Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Copper-Catalysed Aromatic-Finkelstein Reactions with Amine-Based Ligand Systems

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1. Experimental

1. 1 General

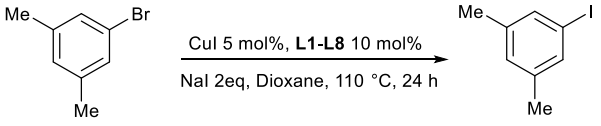
For reactions that required air-free techniques, all glassware was pre-dried at 120 °C overnight and loaded in a glove-box under nitrogen. The experiments were carried out under a protective atmosphere of N_2. For air and moisture stable reactions, the experiments were prepared open to the atmosphere in a fume-hood without any inert atmosphere protection. Anhydrous solvents including MeCN, DMF, acetone, hexane, and toluene were obtained from a solvent tower using the PureSolv solvent purification system, degassed under N_2, and stored over molecular sieves. Anhydrous DMSO and dioxane were purchased in Sure/Seal™ bottles and used directly from the bottle. Deuterated solvents including DMSO-d_6, acetonitrile-d_3, acetone-d_6, benzene-d_6 and chloroform-d were purchased from Sigma-Aldrich or VWR and dried over molecular 4 Å sieves under N_2 before use. Copper(I) iodide (99.999% trace metals basis, powder) and sodium iodide (≥99.5%, powder) were purchased from Sigma-Aldrich and stored in a glove box under N_2. All ligands and aryl halides were purchased from Sigma-Aldrich or VWR and used as received without further purification.

^{1}H and ^{13}C NMR analysis was carried out at room temperature using Bruker AV-400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane and are referenced to the residual protonated solvent and carbon resonances of the solvent in ^{1}H and ^{13}C NMR spectra respectively. Coupling constants (*J*) are *J* coupling constant values are given in Hz units. CHN microanalyses were carried out at the London Metropolitan University, UK. GC analyses were performed using a Hewlett-Packard 5890 Series II GC instrument with an FID detector equipped with a 30 m x 0.25 mm I.D. (5%-phenyl)-methylpolysiloxane stationary phase capillary column. For the analysis of samples from the aromatic Finkelstein reaction, the following GC oven temperature programs was used: (i) 70 °C upon injection, (ii) hold at 70 °C for 2 min, (iii) increase the temperature to 250 °C at a rate of 45 °C per minute, (iv) hold at 250 °C for 5 min. The GC injector and detector

temperatures were both set at 250 °C. GC calibrations against a naphthalene or dodecane internal standard were used to quantify aryl iodides and aryl bromides amounts.

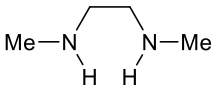
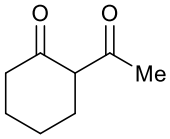
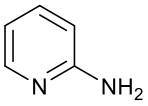
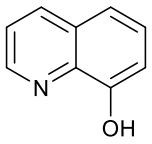
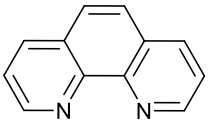
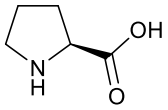
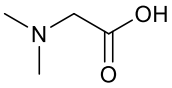
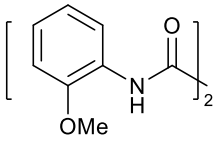
^{1}H and ^{13}C NMR analysis was performed using MESTRELAB MestReNova software; GC data was analysed using DataApex Clarity software.

1. 2 Screening of 'Ullmann Reaction' Ligands in 1,4-Dioxane

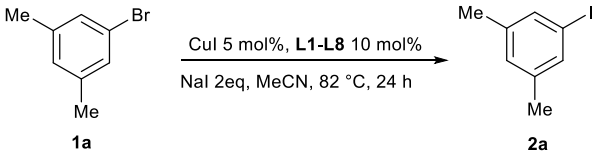


A screw-top vial was charged with CuI (9.6 mg, 5 mol%), ligand **L1**-**L8** (10 mol%, Table S1), NaI (300 mg, 2.0 mmol) and 5-bromo-*meta*-xylene (136 µL, 1.0 mmol) under nitrogen followed by the addition of anhydrous 1,4-dioxane (1.0 mL). The reaction was then heated to 110 °C in an oil bath and stirred for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised Table S1.

Table S1 Ligands studied in dioxane and corresponding yield of 2a

	N,N'-Dimethyl ethylenediamine **L1** Quantity: 10.8 µL Yield: > 99%		2-Acetylcyclohexanone **L2** Quantity: 14 µL Yield: <1%
	2-aminopyridine **L3** Quantity: 9 mg Yield: <1%		8-hydroxyquinoline **L4** Quantity: 15 mg Yield: <1%
	1,10-Phenanthroline **L5** Quantity: 18 mg Yield: 2%		L-Proline **L6** Quantity: 12 mg Yield: <1%
	N,N-Dimethylglycine **L7** Quantity: 10 mg Yield: <1%		Oxalic diamides **L8** Quantity: 30 mg Yield: <1%

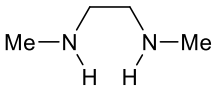
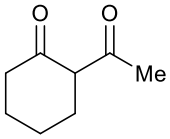
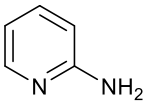
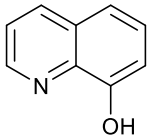
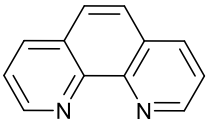
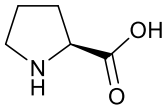
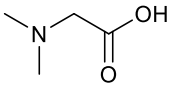
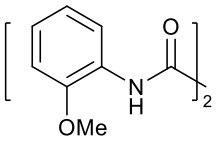
1. 3 Screening of 'Ullmann Reaction' Ligands in MeCN



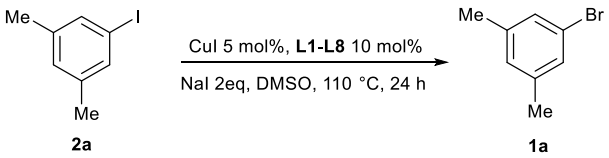
1a **2a**

A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L1**-**L8** (Table S2, 10 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-*meta*-xylene (136 µL, 1.0 mmol) in glove box followed by the addition of anhydrous acetonitrile (1.0 mL). The reaction was then stirred at 82 °C in an oil bath for 24 h. All reactions were carried out under N_2 protection. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised in Table S2.

Table S2 Ligands studied in MeCN and corresponding yield of 2a

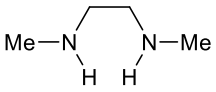
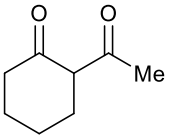
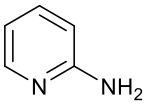
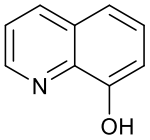
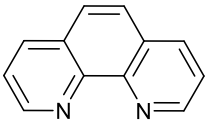
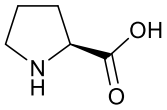
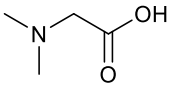
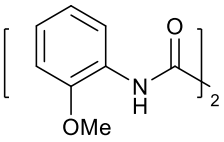
	N,N'-Dimethyl ethylenediamine **L1** Quantity: 10.8 µL Yield: 98%		2-Acetylcyclohexanone **L2** Quantity: 14 µL Yield: <1%
	2-aminopyridine **L3** Quantity: 9 mg Yield: 1%		8-hydroxyquinoline **L4** Quantity: 15 mg Yield: 2%
	1,10-Phenanthroline **L5** Quantity: 18 mg Yield: <1%		L-Proline **L6** Quantity: 12 mg Yield: <1%
	N,N-Dimethylglycine **L7** Quantity: 10 mg Yield: <1%		Oxalic diamides **L8** Quantity: 30 mg Yield: <1%

1. 4 Reverse Aryl-Iodide to Bromide Exchange Reaction

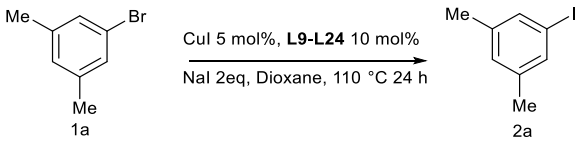


A sample vial was charged with CuI (9.6 mg, 5 mol %), ligand **L1**-**L8** (10 mol%, Table S3), NaBr (206 mg, 2.0 mmol) and 5-iodo-*m*eta-xylene (144 µL, 1.0 mmol) in glove box followed by the addition of anhydrous DMSO (1.0 mL). The reaction was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised in Table S3.

Table S3 Ligands studied in 'reverse' halogen exchange reaction and corresponding yield of 1a

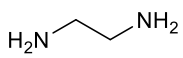
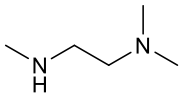
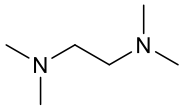
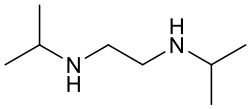
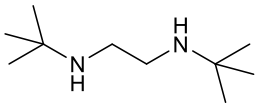
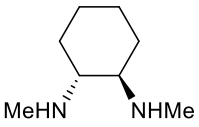
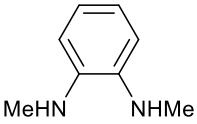
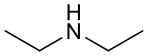
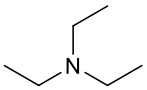
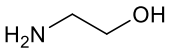
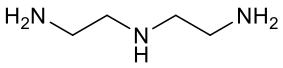
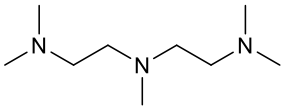
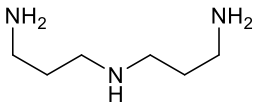
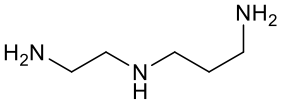
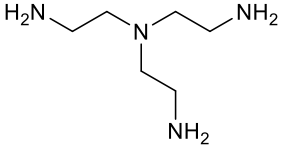
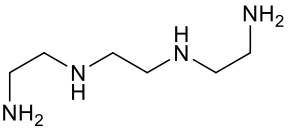
	N,N'-Dimethyl ethylenediamine **L1** Quantity: 10.8 µL Yield: 74%		2-Acetylcyclohexanone **L2** Quantity: 14 µL Yield: <1%
	2-aminopyridine **L3** Quantity: 9 mg Yield: 2%		8-hydroxyquinoline **L4** Quantity: 15 mg Yield: <1%
	1,10-Phenanthroline **L5** Quantity: 18 mg Yield: <1%		L-Proline **L6** Quantity: 12 mg Yield: <1%
	N,N-Dimethylglycine **L7** Quantity: 10 mg Yield: <1%		Oxalic diamides **L8** Quantity: 30 mg Yield: 1%

1. 5 Screening of Amine-based Ligands in 1,4-Dioxane

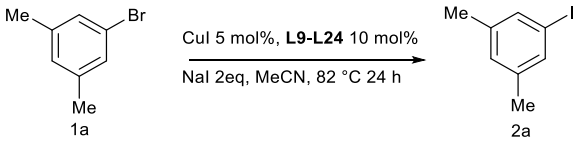


A sample vial was charged with CuI (9.6 mg, 5 mol %), ligand **L9**-**L24** (10 mol%, Table S4), NaI (300mg, 2.0 mmol) and 5-bromo-m-xylene (136 µL, 1.0 mmol) in glove box followed by the addition of anhydrous 1,4-dioxane (1.0 mL). The reaction was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised in Table S4.

Table S4 Amine ligands studied in dioxane and corresponding yield of 2a

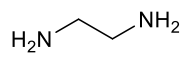
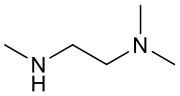
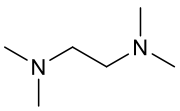
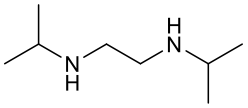
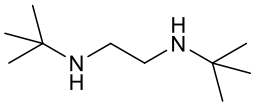
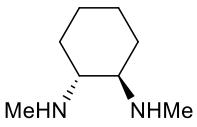
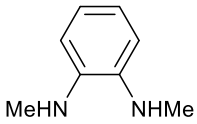
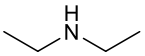
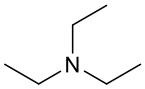
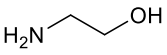
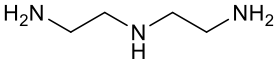
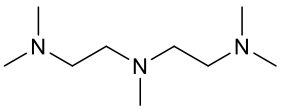
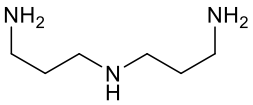
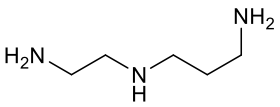
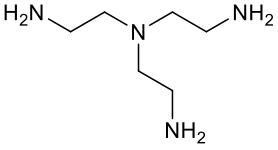
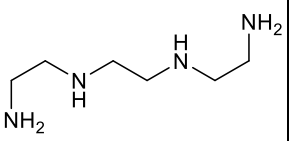
	Ethylenediamine **L9** Quantity: 6.7 μL Yield: 52%		N,N,N'-Trimethyl ethylenediamine **L10** Quantity: 13 μL Yield: 20%
	N,N,N',N'-Tetramethyl ethylenediamine **L11** Quantity: 15 μL Yield: <1%		N,N'-Diisopropyl ethylenediamine **L12** Quantity: 18 μL Yield: <1%
	N,N'-Di-tert-butyl ethylenediamine **L13** Quantity: 22 μL Yield: <1%		trans-N,N'-Dimethyl cyclohexane-1,2-diamine **L14** Quantity: 16 μL Yield: 99%
	N,N'-Dimethyl-1,2-phenylenediamine **L15** Quantity: 14 mg Yield: <1%		Diethylamine **L16** Quantity: 10.3 μL Yield: <1%
	Triethylamine **L17** Quantity: 14 μL Yield: <1%		Ethanolamine **L18** Quantity: 6.0 μL Yield: <1%
	Diethylenetriamine **L19** Quantity: 10.8 μL Yield: 42%		N,N,N',N'',N''-Pentamethyl diethylenetriamine **L20** Quantity: 21 μL Yield: <1%
	Bis(3-aminopropyl)amine **L21** Quantity: 14 μL Yield: 76%		N-(2-Aminoethyl)-1,3-propanediamine **L22** Quantity: 13 μL Yield: 50%
	Tris(2-aminoethyl)amine **L23** Quantity: 15 μL Yield: 3%		Triethylenetetramine **L24** Quantity: 15 μL Yield: 28%

1. 6 Screening of Amine-based Ligands in MeCN

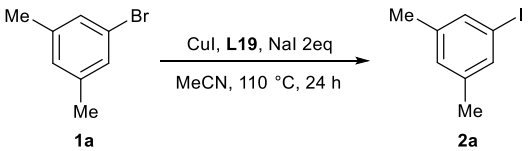


A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L9**-**L24** (Table S5, 10 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-m-xylene (136 µL, 1.0 mmol) in glove box. followed by the addition of anhydrous acetonitrile (1.0 mL). The reaction was then stirred at 82 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised in Table S5.

Table S5 Amine ligands studied in MeCN and corresponding yield of 2a

	Ethylenediamine **L9** Quantity: 6.7 µL Yield: 53%		N,N,N'-Trimethyl ethylenediamine **L10** Quantity: 13 µL Yield: 12%
	N,N,N',N'-Tetramethyl ethylenediamine **L11** Quantity: 15 µL Yield: <1%		N,N'-Diisopropyl ethylenediamine **L12** Quantity: 18 µL Yield: <1%
	N,N'-Di-tert-butyl ethylenediamine **L13** Quantity: 22 µL Yield: <1%		trans-N,N'-Dimethyl cyclohexane-1,2-diamine **L14** Quantity: 16 µL Yield: 97%
	N,N'-Dimethyl-1,2-phenylenediamine **L15** Quantity: 14 mg Yield: <1%		Diethylamine **L16** Quantity: 10.3 µL Yield: <1%
	Triethylamine **L17** Quantity: 14 µL Yield: <1%		Ethanolamine **L18** Quantity: 6.0 µL Yield: <1%
	Diethylenetriamine **L19** Quantity: 10.8 µL Yield: 84%		N,N,N',N'',N''-Pentamethyl diethylenetriamine **L20** Quantity: 21 µL Yield: <1%
	Bis(3-aminopropyl)amine **L21** Quantity: 14 µL Yield: 72%		N-(2-Aminoethyl)-1,3-propanediamine **L22** Quantity: 13 µL Yield: 64%
	Tris(2-aminoethyl)amine **L23** Quantity: 15 µL Yield: 12%		Triethylenetetramine **L24** Quantity: 15 µL Yield: 43%

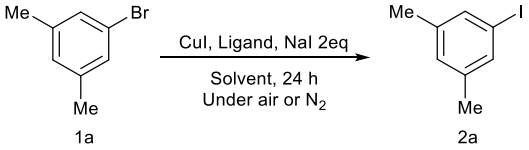
1. 7 Optimisation of the Reaction with Diethylenetriamine (L19)



A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L19** (10.8 µL, 10 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-m-xylene (136 µL, 1.0 mmol) in glove box followed by the

addition of anhydrous acetonitrile (1.0 mL). The blue solution was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of organic layer was extracted, diluted with ethyl acetate (1 mL) and analysed by GC (Yield of **2a**: 99%).

1. 8 Air and Moisture Sensitivity for L1, L14 and L19

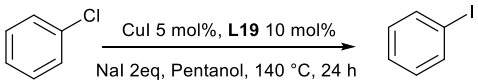


A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand (**L1** or **L19** 10 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-m-xylene (136 µL, 1.0 mmol) and HPLC grade acetonitrile (1.0 mL). The reaction was allowed to stir under air for at least 10 min (extra 11.6 µL distilled water was added for an independent reaction to test the water tolerance). The solution turned immediately to dark green colour (solution turned blue when 11.6 µL distilled water was added). The sample vial was then sealed and heated to 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The reaction exposed to air gave yields of **2a** of 85%, 93% and 99% using ligands **L1**, **L14** and **L19** respectively. The reaction with the extra addition of 11.6 µL distilled water gave yields of 70%, 88% and 96% using ligands **L1**, **L14** and **L19** respectively.

The **L1** and **L14** promoted aryl halide exchange reaction was also carried out in dioxane using the conditions as first set out by Klapers and Buchwald.[1] On exposure to air the yield of **2a** dropped to 65% and 79% using ligands **L1** and **L14** respectively. The reaction with the extra

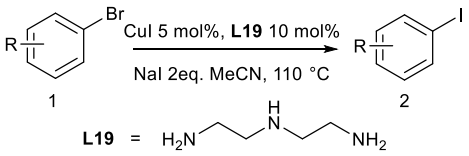
addition of 11.6 µL distilled water gave yields of 32% and 42% using ligands **L1** and **L14** respectively.

1. 9 Aryl Chloride Activation with Diethylenetriamine (L19)



A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L19** (10.8 µL, 10 mol%), NaI (300 mg, 2.0 mmol) and chlorobenzene (101 µL, 1.0 mmol) in glove box followed by the addition of anhydrous pentanol (1.0 mL). The solution was then stirred at 140 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of organic layer was extracted, diluted with ethyl acetate (1 mL) and analysed by GC (Yield of iodobenzene: 8%).

1. 10 Reaction Scope using Diethylenetriamine L19



Procedure (A): Under nitrogen

A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L19** (10.8 µL, 10 mol%), NaI (300 mg, 2.0 mmol), aryl bromide (1.0 mmol) and anhydrous acetonitrile (1.0 mL) in a glove box followed. The mixture was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of water (2 mL) and ethyl acetate (2 mL). Yields of the aryl-iodide product were determined by GC. The pure product was obtained using flash chromatography and all NMR data was in agreement with previously published data (see below).

Procedure (B): In air

A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L19** (10.8 µL, 10 mol%), NaI (300 mg, 2.0 mmol), aryl bromide (1.0 mmol) and acetonitrile (1.0 mL). The mixture was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of water (2 mL) and ethyl acetate (2 mL). The pure product was obtained using flash chromatography and all NMR data was in agreement with previously published data (see below).

2-iodo-pyridine (2b)[2]

Yield: 99% (procedure A), 95% (procedure B), light red oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, J = 2.0 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.30 – 7.26 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ150.6, 137.4, 134.8, 122.8, 118.0.

β-iodostyrene (E) (2c)[3]

Yield: >99% (procedure A), >99% (procedure B) yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 15.0 Hz, 1H), 7.37 – 7.27 (m, 5H), 6.84 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.0, 137.7, 128.73, 128.38, 126.02, 76.68.

Iodobenzene (2d)[2]

Yield: 99% (procedure A), 98% (procedure B), light yellow oil.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.50, 130.26, 127.48, 94.42.

4-iodobiphenyl (2e)[4]

Yield: >99% (procedure A), 95% (procedure B), white solid. Melting Point: 110-111 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.45 (t, *J* =

7.6 Hz, 2H), 7.34 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.74, 140.07, 137.85, 129.02, 128.91, 127.70, 126.91, 93.03.

3-iodoanisole (2f)[5]

Yield: 95% (procedure A), 92% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.22 (m, 2H), 7.01 (dd, *J* = 8.3, 7.7 Hz, 1H), 6.88 (ddd, *J* = 8.4, 2.5, 0.9 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.14, 130.76, 129.83, 123.03, 113.79, 94.37, 55.39.

4-iodoanisole (2g)[3]

Yield: 92% (procedure A), 88% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.50 (m, 2H), 6.77 – 6.64 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.45, 138.19, 116.36, 82.69, 55.33.

2-iodoaniline (2h)[6]

Yield: 90% (procedure A), 92% (procedure B), off-white solid. Melting Point: 55-56 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.14 (ddd, *J* = 8.0, 7.2, 1.4 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.48 (ddd, *J* = 7.9, 7.3, 1.5 Hz, 1H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.52, 133.18, 118.23, 111.76, 100.32.

4-iodobenzonitrile (2i)[2]

Yield: 90% (procedure A), 91% (procedure B), white solid. Melting Point: 125-126 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 1H), 7.41 – 7.32 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.53, 133.16, 118.21, 111.78, 100.29.

2-iodoanisole (2j)[5]

Yield: 88% (procedure A), 88% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.31 (t, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.71 (td, *J* = 7.6, 1.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.1, 139.5, 129.5, 122.5, 111.0, 86.0, 56.3.

1,4-diiodobenzene (2k)[3]

Yield: 77% (procedure A), 55% (procedure B), white solid. Melting Point: 133-134 °C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (s, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.34, 93.38.

Ethyl 4-iodobenzonate (2l)[5]

Yield: 70% (procedure A), 38% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.65 (m, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.10, 137.66, 131.01, 129.98, 100.55, 61.23, 14.30.

1-iodo-4-nitrobenzene (2m)[2]

Yield: 60% (procedure A), 67% (procedure B), yellow solid. Melting Point: 174-175 °C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.86 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.67, 124.85.

1-iodonaphthalene (2n)[3]

Yield: 54% (procedure A), 49% (procedure B), brown oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 3.2 Hz, 1H), 8.09 (d, *J* = 0.8 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz ,1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.51 (m, 1H), 7.21 – 7.17 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.45, 134.39, 134.16, 132.15, 129.01, 128.57, 127.73, 126.87, 126.74, 99.58.

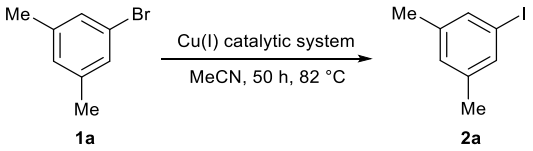
2-iodothioanisole (2o)[7]

Yield: 52% (procedure A), 50% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.40 – 7.32 (m, 1H), 7.10 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90 – 6.79 (td, *J* = 7.8, 1.4 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.3, 139.5, 128.9, 126.2, 125.1, 97.6, 17.2.

2-fluoroiodobenzene (2p)[8,9]

Yield: 49% (procedure A), 52% (procedure B), light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (ddd, *J* = 7.9, 6.4, 1.6 Hz, 1H), 7.38 – 7.28 (m, 1H), 7.07 (td, *J* = 8.2, 1.4 Hz, 1H), 6.90 (td, *J* = 7.7, 1.5 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 139.4, 130.0, 125.8, 115.6, 81.2.

1. 11 General Method for Kinetic Studies using L1



1a **2a**

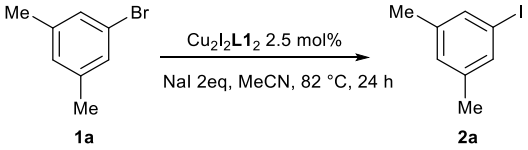
A screw-top vial (8 mL) sealed with a septum was charged with CuI (28.8 mg, 5 mol%), N,N'-dimethylenediamine **L1** (8.1 – 32.4 µL, 2.5 - 10 mol%), NaI (900 mg, 6.0 mmol) and 5-bromo-m-xylene (408 µL, 3.0 mmol) in glove box followed by addition of anhydrous acetonitrile (2.7 mL) and an internal standard for GC (300 µL 0.5 M Naphthalene solution in MeCN). The reaction was then stirred at 110 °C in an oil bath. 25 µL of solution was extracted at 0.5h – 2h intervals using pre-dried and degassed air-tight syringe (100 µL) followed by dilution with ethyl acetate (1 mL). The conversion and yield were obtained by GC against the internal standard.

1. 12 $Cu_2I_2L1_2$ Synthesis

A 4mL vial was charged with CuI (19.2 mg, 0.1 mmol) and N,N'-dimethylenediamine **L1** (21.6 µL, 0.2 mmol) in dry 1,4-dioxane (250 µL). The vial was placed inside a larger vial (20 mL)

containing dry hexane (2 mL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after 72 h to give 19 mg of Cu_2I_2**L1**$_2$ (68 % yield). Mp: 263 °C. ^{1}H NMR (400MHz, DMSO-*d6*,) δ 2.38 (d, *J* = 6.0 Hz, 3H), 2.54 (dd, *J* = 4.4, 2.1 Hz, 2 H), 3.55 (dt, *J* = 12.1, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 38.09, 51.04. Elemental analysis: C 17.42%, H 4.34%, N 9.74% (calc. C 17.24%, H 4.34%, N 10.06%).

1. 13 Aryl Halide Exchange Reaction using $Cu_2I_2L1_2$ as Catalyst

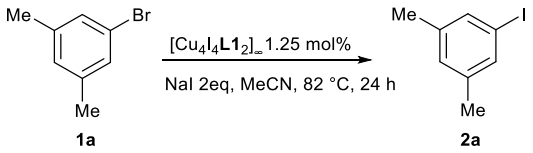


A reaction vial was charged with Cu_2I_2**L1**$_2$ (14 mg, 2.5 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-*meta*-xylene (136 µL, 1.0 mmol) in a glove box followed by the addition of 1,4-dioxane (850 µL) and an internal standard for GC (150 µL dodecane). The reaction was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. Yields of the aryl-iodide product were determined by GC. (Yield of **2a**: 89%).

1. 14 $Cu_4I_4L1_2$ Synthesis

A reaction vial (4 mL) was charged with CuI (18.2 mg, 0.1 mmol) and NaI (15 mg, 0.1 mmol) in dry acetone (250 µL) followed by addition of N,N'-dimethylenediamine **L1** (21.6 µL, 0.2 mmol). Colourless crystals started to form after 10 minutes at 0 °C and were isolated after 18 h (38% yield). Mp: 261 °C ^{1}H NMR (400MHz, DMSO-*d6*,) δ 0.87 (s, 3H), 2.17 (s, 3H), 2.64 (s, 2H), 3.34 (s, 2H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 18.95, 35.93, 50.78. Elemental analysis: C 10.12%, H 2.51%, N 5.95% (calc. C 10.24%, H 2.58%, N 5.97%).

1. 15 Aryl Halide Exchange Reaction using $[Cu_4I_4L1_2]_\infty$ as Catalyst



A reaction vial was charged with $[Cu_4I_4\mathbf{L1}_2]_\infty$ (12 mg, 1.25 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-*meta*-xylene (136 µL, 1.0 mmol) in glove box followed by the addition of 1,4-dioxane (850 µL) and an internal standard for GC (150 µL dodecane). The reaction was then stirred at 110 °C in an oil bath. The mixture was cooled to room temperature followed by addition of water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was then extracted, diluted with ethyl acetate (1 mL) and analysed by GC. Yields of the aryl-iodide product were determined by GC. (Yield of **2a:** 73%).

The kinetic studies method followed the same procedure as detailed in Section 1.9. The catalytic system (CuI/Ligand) was replaced by the corresponding crystals. The reaction temperature was increased to 110 °C in order to obtain complete conversion. All other parameters remained unchanged.

1. 16 ^{1}H-NMR Studies on NaI Coordination to L1

The NaI (15 mg, 0.1 mmol or 30 mg, 0.2 mmol) and **L1** (10.8 µL, 0.1mmol) were mixed together in acetonitrile-d_3 (1 mL) in a Young's NMR tube and analysed by ^{1}H NMR spectroscopy. The CH_2 and CH_3 ligand protons shifted slightly upfield shift with the increasing addition of NaI whereas the NH proton showed a downfield shift.

L1 ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 2.59 (s, 2H) 2.35 (s, 3H), 1.09 (s, 1H).

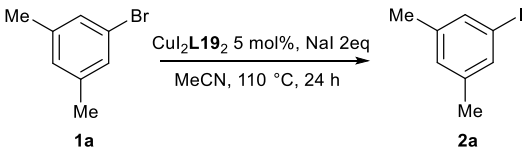
NaI:**L1** = 1:1, ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 2.56 (s, 2H) 2.31 (s, 3H), 1.24 (s, 1H).

NaI:**L1** = 2:1, ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 2.54 (s, 2H) 2.29 (s, 3H), 1.29 (s, 1H).

1. 17 CuI_2L19_2 Synthesis

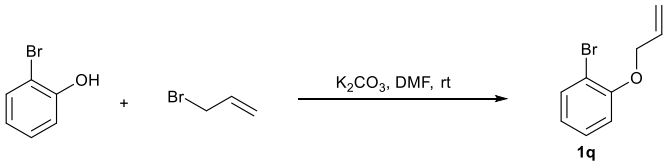
A mixture of CuI (19.2 mg, 0.1 mmol) and **L19** (21.6 µL, 0.2 mmol) in dry MeCN (500 µL) was stirred at room temperature for 10 min. This mixture was then filtered into a 4mL vial to give a clear blue solution. The vial was placed inside a larger vial (20 mL) containing dry hexane (500 µL) and left at room temperature. Blue crystals started to form after 10 min and were isolated after 24 h to give 19 mg of CuI_2**L19**$_2$ (28 % yield). Elemental analysis: C 18.80%, H 5.39%, N 15.59% (calc. C 18.35%, H 5.00%, N 16.05%). We were unable to obtain satisfactory ^{1}H NMR data due to the paramagnetic nature of the complex.

1. 18 Aryl Halides Exchange Reaction using CuI_2L19_2 as Catalyst



A reaction vial was charged with CuI_2**L19**$_2$ (29 mg, 5 mol%), NaI (300 mg, 2.0 mmol) and 5-bromo-m-xylene (136 µL, 1.0 mmol) in the glove box. The starting materials were dissolved in anhydrous acetonitrile (1.0 mL) followed by addition of an internal standard for GC (100 µL 0.5 M Naphthalene solution in MeCN). The reaction was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of water (2 mL) and ethyl acetate (2 mL). A 50 µL extract from the organic layer was diluted with ethyl acetate (1 mL) and analysed by GC. Yields of the aryl-iodide product were determined by GC (yield of **2a:** 99%).

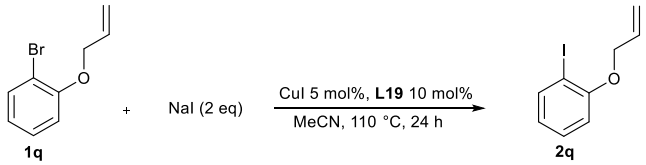
1. 19 Synthesis of 2-(allyloxy) bromobenzene 1q[10]



2-bromophenol (1.74 mL,15 mmol) was added to a suspension of K_2CO_3 (6.20 g, 45 mmol) in DMF (50 mL) under N_2 followed by a slow addition of allyl bromide (1.56 mL, 18 mmol). The mixture was allowed to stir at room temperature overnight before addition of 100 mL distilled water. The organic layer was extracted by ethyl acetate (3 x 50 mL) and the combined organic layer was washed with brine (3 x 50 mL), dried over $MgSO_4$ and the solvent removed under vacuum. A pure light yellow oil product was obtained (97% yield). The NMR data was in agreement with previously published data.[10]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.27 (ddd, *J* = 8.3, 7.4, 1.6 Hz, 1H), 6.80 – 7.00 (2 H, m), 6.10 (ddt, *J* = 17.2, 10.4, 5.0 Hz, 1H), 5.52 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.34 (dq, *J* = 10.7, 1.5 Hz, 1H), 4.64 (dt, *J* = 5.0, 1.6 Hz, 1H).

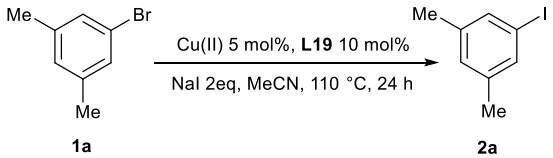
1. 20 Aryl Halides Exchange Reaction using 1q as Substrate



A sample vial was charged with CuI (9.6 mg, 5 mol%), ligand **L19** (10.8 µL, 10 mol%), NaI (300 mg, 2.0 mmol), **1q** (213 mg, 1.0 mmol) and anhydrous acetonitrile (1.0 mL) in the glove box. The resultant blue solution was stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of water (10 mL) and ethyl acetate (10 mL). The organic layer was separated and washed with brine (3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed under vacuum. A light yellow oil was obtained (75% conversion and yield). The NMR data was in agreement with previously published data.[11]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.32-7.27 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.73 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.11-6.01 (m, 1H), 5.58-5.52 (m, 1H), 5.35-5.31 (m, 1H), 4.61-4.59 (m, 2H).

1. 21 Catalytic Activity of Copper(II) Salts with L19



A sample vial was charged with a Cu(II) salt (5 mol%, Table S6), **L19** (10 mol%), NaI (300 mg, 2.0 mmol), 5-bromo-*meta*-xylene (136 µL, 1.0 mmol) and anhydrous acetonitrile (1.0 mL) in a glove box. The reaction was then stirred at 110 °C in an oil bath for 24 h. The mixture was cooled to room temperature followed by addition of an internal standard for GC (150 µL dodecane for reaction in dioxane, or 100 µL 0.5 M naphthalene solution in MeCN), water (2 mL) and ethyl acetate (2 mL). A 50 µL sample of the organic layer was extracted, diluted with ethyl acetate (1 mL) and analysed by GC. The yields reported are an average of two independent runs (<5% difference) and are summarised in Table S6.

Table S6 Copper(II) salt and corresponding yield of 2a

Entry	Copper salt	Amount	Yield (%)
1	$Cu(acetate)_2$	9 mg	76
2	$CuCl_2$	7 mg	70
3	$CuBr_2$	11 mg	62
4	$Cu(CF_3SO_3)_2$	18 mg	58
5	$Cu(NO_3)_2 \cdot 3H_2O$	12 mg	43

2. X-ray Crystallographic Data

The X-ray crystal structure of Cu_2I_2**L1**$_2$

Crystal data for Cu_2I_2**L1**$_2$: $C_8H_{24}Cu_2I_2N_4$, M = 557.19, monoclinic, $P2_1/c$ (no. 14), a = 13.3569(10), b = 11.5554(8), c = 11.4189(9) Å, β = 95.026(7)°, V = 1755.7(2) Å^3, Z = 4 [two independent C_i symmetric molecules], D_c = 2.108 g cm^{-3}, µ(Mo-Kα) = 5.925 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 6270 independent measured reflections (R_{int} = 0.0501), F^2 refinement,[12,13] R_1(obs) = 0.0436, wR_2(all) = 0.1608, 4326 independent

observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 56°$], 147 parameters. CCDC 1538590.

The crystal of Cu_2I_2**L1**$_2$ that was studied was found to be a two component twin in a *ca*. 79:21 ratio, with the two lattices related by the approximate twin law [–0.01 0.99 –0.08 –1.01 –0.01 –0.08 0.00 0.00 1.00]. The N–H hydrogen atoms on N1A, N4A, N1A and N4A were not located from Δ*F* maps, and so were instead added in idealised positions at a distance of 0.90 Å from their parent nitrogen.

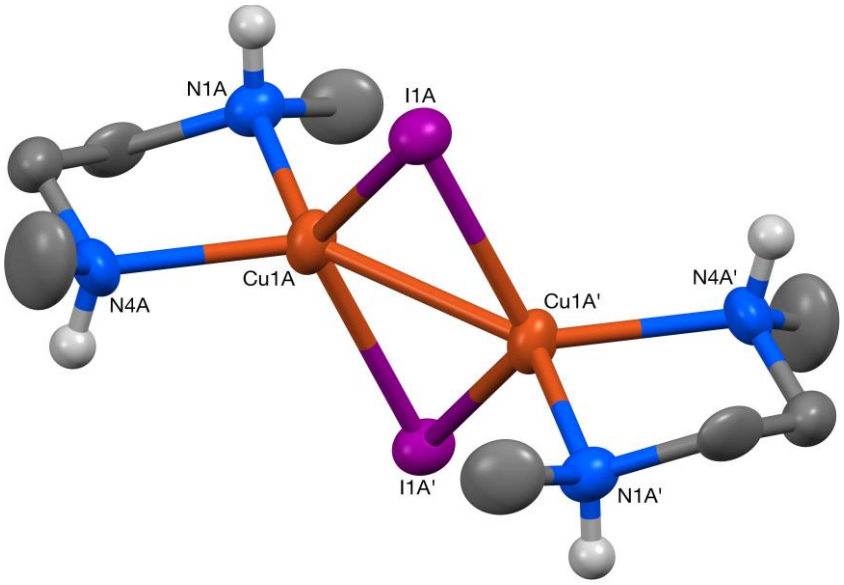


Fig. S1 The structure of one (**A**) of the two independent C_i-symmetric complexes present in the crystal of Cu_2I_2**L1**$_2$ (50% probability ellipsoids).

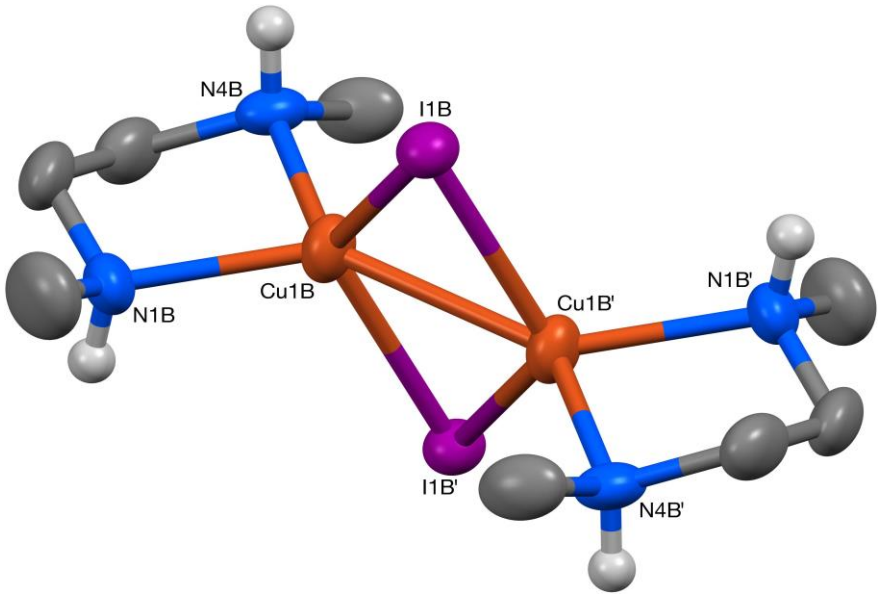


Fig. S2 The structure of one (**B**) of the two independent C_i-symmetric complexes present in the crystal of Cu_2I_2**L1**$_2$ (50% probability ellipsoids).

The X-ray crystal structure of $[Cu_4I_4$**L1**$_2]_\infty$

Crystal data for $[Cu_4I_4$**L1**$_2]_\infty$: $C_4H_{12}Cu_2I_2N_2$, M = 469.04, tetragonal, $P4_2/n$ (no. 86), a = b = 11.7663(3), c = 7.5184(3) Å, V = 1040.90(7) Å^3, Z = 4 [the Cu_4 node sits across a –4 position], D_c = 2.993 g cm^{-3}, μ(Mo-Kα) = 9.958 mm^{-1}, T = 173 K, colourless blocks, Agilent Xcalibur 3 E diffractometer; 1049 independent measured reflections (R_{int} = 0.0244), F^2 refinement,[12,13] R_1(obs) = 0.0263, wR_2(all) = 0.0469, 912 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 52 parameters. CCDC 1538591.

The Cu_4 node in the structure of $[Cu_4I_4$**L1**$_2]_\infty$ sits across a –4 position. The N1–H hydrogen atom was located from a ΔF map and refined freely subject to an N–H distance constraint of 0.90 Å.

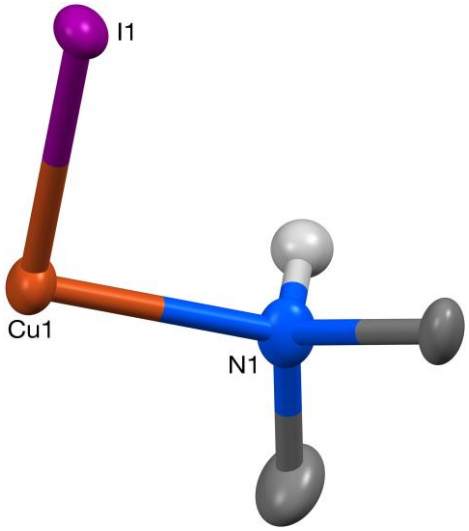


Fig. S3 The contents of the asymmetric unit in the crystal structure of $[Cu_4I_4\mathbf{L1}_2]_\infty$ (50% probability ellipsoids).

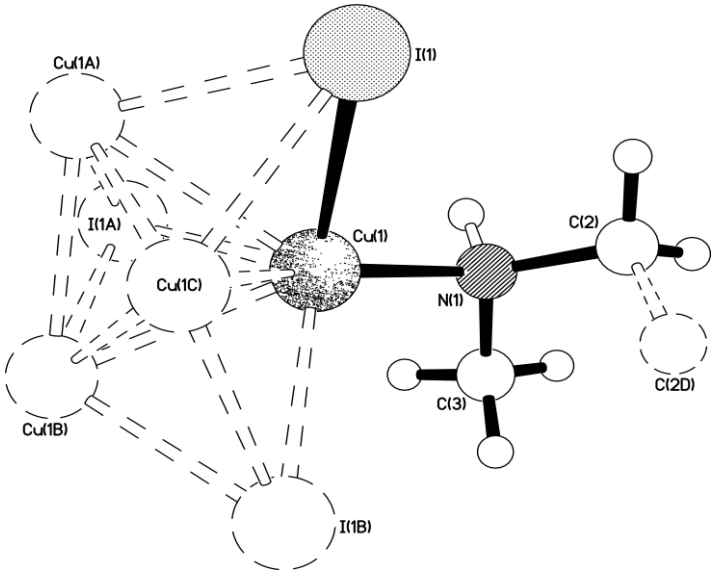


Fig. S4 The contents of the asymmetric unit in the crystal structure of $[Cu_4I_4\mathbf{L1}_2]_\infty$ showing how the unique atoms link to their symmetry related counterparts.

The X-ray crystal structure of $[Cu\mathbf{L19}_2]I_2$

Crystal data for $[Cu\mathbf{L19}_2]I_2$: $2\{[C_8H_{26}CuN_6]I_2\}\cdot C_4H_{13}N_3$, M = 1150.55, orthorhombic, $P2_12_12_1$ (no. 19), a = 9.18796(19), b = 12.5494(3), c = 35.7355(7) Å, V = 4120.43(14) Å^3, Z = 4, D_c = 1.855 g cm^{-3}, μ(Mo-Kα) = 4.062 mm^{-1}, T = 173 K, blue plates, Agilent Xcalibur 3 E diffractometer; 7172 independent measured reflections (R_{int} = 0.0179), F^2 refinement,[12,13] R_1(obs) = 0.0296, wR_2(all) = 0.0441, 6516 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 57°], 383 parameters. CCDC 1538592.

The structure of [Cu**L19**$_2$]I_2 was found to contain two independent Cu**L19**$_2$ complexes, four iodide anions and one non-coordinated **L19** molecule. The C45 to N47 portion of the non-coordinated **L19** molecule was found to be disordered. Two orientations were identified of *ca*. 54 and 46% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). None of the presumed 25 N–H hydrogen atoms were reliably located from Δ*F* maps, and so they were all added in idealised positions (at a distance of 0.90 Å from their parent nitrogen) based on each of the five **L19** units having NH_2 termini and a central NH group. For the N37, N41 and N47 NH_2 groups (which each make only one bond to a non-hydrogen atom), vectors to either the adjacent Cu2 copper centre (in the N37 case) or to the hydrogen bond donors on N14 (for the N41 group) and N34 (for the N47 group) were considered when calculating the positions of the NH_2 hydrogen atoms. For the N44 NH group (which makes two bonds to non-hydrogen atoms) both of the two possible tetrahedral sites for the hydrogen atom were considered, with preference given to the site that approaches the I3 iodine atom.

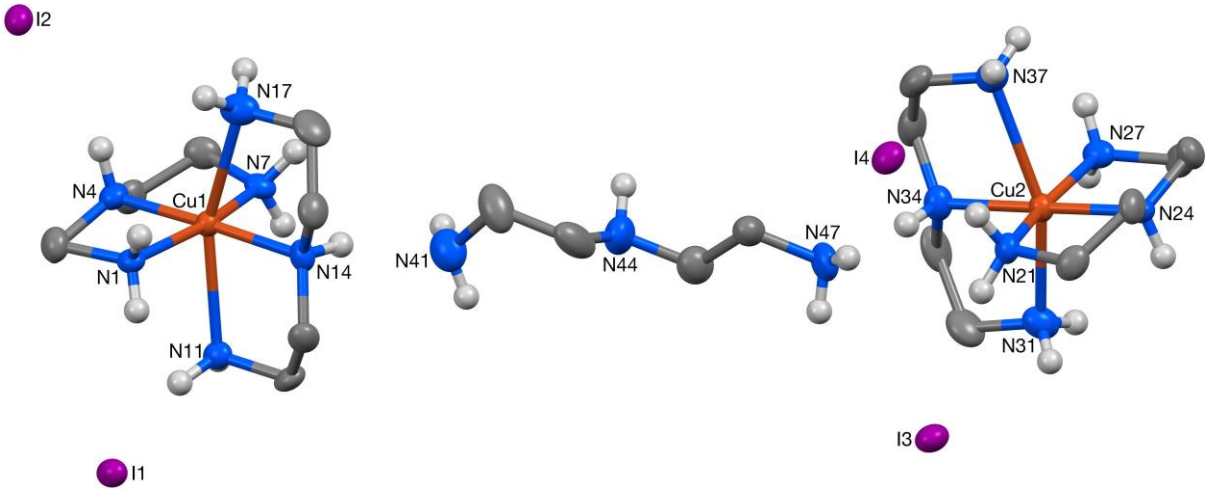


Fig. S5 The crystal structure of [Cu**L19**$_2$]I_2 (50% probability ellipsoids).

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