Supporting Information

On the Mechanism of Benzimidazole Synthesis via Copper-Catalyzed Intramolecular N-Arylation

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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. 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) was 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. Reaction calorimetry was performed using an Omnical SuperCRC reaction calorimeter, which is a differential

scanning calorimeter (DSC) that compares the heat released or absorbed between a sample vial and reference vial. The calorimetry heat flow was measured every three seconds. The heat of mixing associated with the addition of the final reactant was subtracted from the tau-corrected heat flow experimental data. 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 catalytic reactions that did not use ligand **L**, 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. For samples from catalytic reactions that used **L**, the rate for the oven temperature increase was changed from 45 °C per minute to 10 °C per minute. GC calibrations against a naphthalene internal standard were used to quantify products and aryl halides amounts. GC-MS analysis was performed on a Micromass Autospec Premier / Agilent HP6890 GC.

^{1}H and ^{13}C NMR analysis was performed using MESTRELAB MestReNova software; GC data was analysed using DataApex Clarity software; and reaction calorimetry data was captured using WinCRC and processed in Microsoft Excel.

1.2 Synthesis of *N'*-(2-Halogenphenyl)-*N*-Methylethanimidamide[1]

N-methylacetamide (4.58 mL, 60 mmol) was dissolved in anhydrous toluene (150 mL) in a round bottom flask at 0 °C followed by dropwise addition of $POCl_3$ (2.80 mL, 30 mmol). The mixture was stirred at 0 °C for 2 h before addition of 2-halogenaniline (30mmol). The mixture was heated and stirred under reflux for 4 h. The solid crude product was collected and dissolved in 100 mL distilled water. Charcoal (active, decolorising powder) was added into the solution and stirred for 1 h at room temperature. Aqueous sodium hydroxide solution (5 M) was slowly added to the solution to adjust the pH value to 10. The solution was left at rt for 1-2 h. The product was collected by filtration and then redissolved in ethyl acetate (50 mL). The organic layer was separated and dried over $MgSO_4$. The pure product was collected by vacuum evaporation of the solvent.

N'-(2-iodophenyl)-*N*-methylethanimidamide (**1a**): Light yellow solid (6.94 g, 84 %); Melting point: 96.4 – 97.3°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.8Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 4.47 (s, 1H), 2.96 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.37, 153.67, 153.7, 127.7, 123.7, 122.92, 116.57, 28.32, 17.73; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (1 H, dd, *J* = 7.7, 1.5 Hz), 7.23 (1 H, td, *J* = 7.5, 1.5 Hz), 6.86 (1 H, s), 6.72 (1H, dd, *J* = 7.7 Hz, 1.6 Hz), 6.65 (1 H, td, *J* = 7.6, 1.5 Hz), 2.74 (3 H, d, *J* = 4.6 Hz), 1.61 (3 H, s); IR (ATR) ν_{max}/cm^{-1}: 3244 (N-H str), 1623 (C=N), 1547 (N-H b), 1464 (methyl

C-H), 1232 (C-N); MS (CI) m/z = 275 $[M+H]^+$; Elemental analysis: $C_9H_{11}I_1N_2$, C 39.55%; H 3.99%; N 10.09% (calc. C 39.44%; H 4.04%; N 10.22%).

N'-(2-bromophenyl)-*N*-methylethanimidamide (**1b**)[1]: Light yellow solid, yield: 6.13 g (90 %); Melting point: 35.4 – 36.2°C (lit. 35 – 37 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 6.89 – 6.77 (m, 2 H), 4.58 (s, 1 H), 2.93 (d, *J* = 4.1 Hz, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.3, 150.1, 132.7, 127.7, 123.7, 123.2, 117.4, 28.5, 17.7; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H),6.87 (br, 1H) 6.86 – 6.73 (t, *J* = 7.8 Hz, 2H), 2.75 (d, *J* = 4.6 Hz, 3H), 1.63 (s, 3H); IR (ATR) νmax/cm^{-1}: 3243 (N-H str), 1620 (C=N), 1547 (N-H b), 1465 (methyl C-H), 1232 (C-N); MS (CI) m/z = 227 $[M+H]^+$

N'-(2-chlorophenyl)-*N*-methylethanimidamide (**1c**): Yellow solid, yield: 4.90 g (90 %); Melting point: 43.5 – 44.1°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.94 – 6.79 (m, 2H), 4.53 (s, 1H), 2.93 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.19, 148.82, 129.52, 127.17, 126.71, 123.93, 122.84, 28.48, 17.95; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.15 (td, *J* = 7.6, 1.5 Hz, 1H), 6.94 – 6.81 (m, 2H), 6.76 (dd, *J* = 7.8, 1.8 Hz, 1H), 2.72 (d, *J* = 4.8 Hz, 3H), 1.62 (s, 3H); IR (ATR) νmax/cm^{-1}: 3256 (N-H str) 1623 (C=N), 1547 (N-H b), 1467 (methyl C-H), 1232 (C-N); MS (CI) m/z = 182 $[M+H]^+$; Elemental analysis: $C_9H_{11}Cl_1N_2$, C 59.08%; H 5.99%; N 15.29% (calc. C 59.18%; H 6.07%; N 15.34%).

N'-(2-fluorophenyl)-*N*-methylethanimidamide (**1d**): Orange oil, yield: 4.08 g (81 %); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 – 6.93 (m, 2H), 6.93 – 6.77 (m, 2H), 4.92 (s, 1H), 2.86 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.32, 155.8, 129.49, 125.16, 124.15, 122.72, 115.68, 28.30, 17.72; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.12 – 6.96 (m, 2H), 6.93 – 6.82 (m, 2H), 6.77 (m, 1H), 2.70 (d, *J* = 4.6 Hz, 3H), 1.65 (s, 3H); ^{19}F NMR (377 MHz, DMSO-d_6) δ -127.20; IR (ATR) νmax/cm^{-1}: 3260 (N-H str) 1620 (C=N), 1547 (N-H b), 1466 (methyl C-H), 1244 (C-N); MS (CI) m/z = 167 $[M+H]^+$; Elemental analysis: $C_9H_{11}F_1N_2$, C 64.91%; H 6.45%; N 16.66% (calc. C 65.04%; H 6.67%; N 16.86%,).

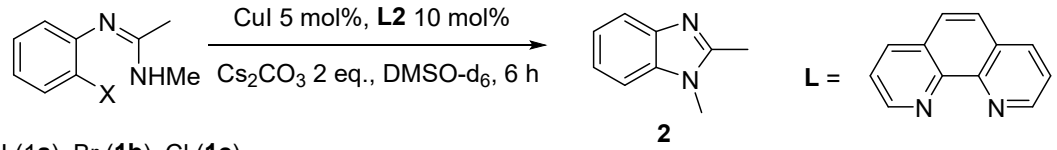
1.3 Synthesis of *Bis*(tetra-(*n*-Butyl)Phosphonium) Malonate (TBPM)[2]

Malonic acid (5.20 g, 50.0 mmol) was dissolved in tetra-*n*-butylphosphonium hydroxide solution (66.9 mL, 40.0 wt.% in water, 100 mmol). The mixture was stirred at rt for 4 h. The water was removed by rotary evaporation until light yellow viscous oil was obtained. The oil was further dried with stirring at 60 °C under high vacuum for another 48 h to obtain a white powder. The mixture was redissolved in acetonitrile (100 mL) to give a colourless solution with some suspended insoluble white solid, which was removed by filtration. The majority of the solvent was removed by rotary evaporation from the filtrate. The light yellow viscous liquid was vigorously dried with stirring at 60 °C under high vacuum for another 48 h. The viscous liquid was stored in an N_2 filled glovebox at the end of the drying and the liquid solidified to a waxy, white solid to give

the pure product. TBPM (29.2 g, 94% yield), ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.91 (t, J = 7.0 Hz, 24H), 1.32 – 1.52 (m, 32H), 2.16 – 2.32 (m, 16H), 2.44 (br, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.5, 50.1, 23.2, 22.7, 17.2, 13.1. The NMR is in agreement with the literature.[3]

1.4 General 1,2-Dimethylbenzimidazole Synthesis Procedure using Cs_2CO_3

A sample vial was charged with Cs_2CO_3 (65 mg, 0.2 mmol) and **1b** (100 µL, 1 M in DMSO-d_6, 0.1 mmol) followed by addition of CuI solution (50 µL, 0.1 M in DMSO-d_6, 5 mol %), 1,10-phenantroline (100 µL, 0.1 M in DMSO-d_6, 10 mol %) and internal standard naphthalene (100 µL, 0.5 M in DMSO-d_6, 0.05 mmol). Another 650 µL of DMSO-d_6 was added to make up the total volume to 1 mL. The reaction was then stirred at 80 °C for 6 h. The mixture was cooled to room temperature and the clear organic layer was transferred into Young's type NMR tube under an N_2 atmosphere. The conversion and yield were determined by ^{1}H NMR. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 – 7.43 (m, 2H), 7.16 (dtd, J = 19.3, 7.3, 1.2 Hz, 2H), 3.72 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.1, 142.3, 135.8, 121.3, 121.0, 118.1, 109.6, 29.6, 13.4. The NMR is in agreement with literature.[4]



X = I (1**a**), Br (**1b**), Cl (**1c**)

Entry	Substrate	CuI	Ligand	Temp.(°C)	Yield (%)
1	**1a**	-	-	80	68
2	**1a**	5 %	-	80	>99
3	**1b**	-	-	80	6
4	**1b**	5 %	-	80	81
5	**1b**	5%	**L**	30	>99
6	**1b**	5%	**-**	30	20
7[b]	**1b**	5%	**L**	30	32
8[b]	**1b**	5%	**L**	80	>99
9	**1c**	5%	**L**	130	85%

[a] Reaction yield was measured by ^{1}H-NMR using naphthalene as internal standard. [b] K_3PO_4 was used as base.

1.5 General 1,2-Dimethylbenzimidazole Synthesis Procedure using TBPM

A sample vial was charged with TBPM (400 µL, 0.5M, 0.2 mmol) and **1b** (100 µL, 1 M in DMSO-d_6, 0.1 mmol) followed by addition of CuI solution (50 µL, 0.1 M in DMSO-d_6, 10 mol %), ligand (100 µL, 0.1 M in DMSO-d_6, 10 mol %) and internal standard naphthalene (100 µL, 0.5 M in DMSO-d_6, 0.05 mmol). Another 250 µL of DMSO-d_6 was added to make up the total volume to 1 mL. The reaction was then stirred at rt for 6 h. The mixture was cooled to room temperature and the clear organic layer was transferred into Young's type NMR tube under an N_2 atmosphere. The conversion and yield were determined by ^{1}H NMR.

1.6 General 1,2-Dimethylbenzimidazole Synthesis Procedure by 1c Activation

A sample vial was charged with base (Cs_2CO_3, 65 mg, 0.2 mmol or TBPM, 400 µL, 0.5M in DMSO-d_6, 0.2 mmol) and **1c** (100 µL, 1 M in DMSO-d_6, 0.1 mmol) followed by addition of CuI solution (50 µL, 0.1 M in DMSO-d_6, 5 mol %), ligand (100 µL, 0.1 M in DMSO-d_6, 10 mol %) and internal standard naphthalene (100 µL, 0.5 M in DMSO-d_6, 0.05 mmol). DMSO-d_6 was added to make up the total volume to 1 mL. The reaction was then stirred at 130 ºC for 24 h. The mixture was cooled to room temperature and the clear organic layer was transferred into Young's type NMR tube under an N_2 atmosphere. The conversion and yield were determined by ^{1}H NMR.

1.7 Synthesis of Mesitylcopper(I)[5]

Magnesium turnings (2.48g, 100 mmol) were dried using a heat gun under vacuum in a Schlenk round bottom flask for at least 20 minutes with stirring. The flask was then filled with N_2 and cooled down to rt followed by addition of 100 mL pre-dried and degassed THF. 2-Bromomesitylene (15.30 mL, 100 mmol) was added slowly into the magnesium suspension solution at rt. Afterward, the mixture was stirring at 0 °C for 2 h to give a grey solution of MgMesBr. Another Schlenk round bottom flask was charged with Cu(I)Cl (10.90 g, 100 mmol) under N_2 atmosphere and dissolved in 50 mL THF. The CuCl solution was cooled down to –78 °C whilst stirring before MgMesBr solution was transferred into it *via* a PTFE cannula. The obtained green mixture was kept stirring overnight under N_2 atmosphere. Afterward, 60 mL anhydrous dioxane was

added to the suspension and allowed to stir for another 30 minutes. A Schlenk tube equipped with a filter stick and a 3 cm layer of pre-dried Celite was flushed with N_2. The suspension was transferred into the filter stick by PTFE cannula (the end on reaction mixture side was equipped with filter paper to avoid the solid blocking the filter stick). The bright yellow filtrate was collected into the Schlenk tube at the end of the filtration. The solvent was evaporated under vacuum to obtain yellow solid which was then redissolved in 50 mL anhydrous toluene. The insoluble impurities were filtered by cannula to obtain bright yellow clear solution which was further concentrated and then placed in the freezer overnight. The pale yellow crystal was collected by PTFE cannula and dried under vacuum to give the pure product. The filtrate was concentrated again and placed in the freezer again overnight to give the product. Pale yellow solid (8.79 g yield: 48%), ^{1}H NMR (400 MHz, benzene-d_6) δ 6.67 (2 H, s), 6.59 (2 H, s), 2.92 (6 H, s), 2.93 (6 H, s) 2.02 (3 H, s), 1.90 (3 H, s). ^{13}C NMR (101 MHz, benzene-d_6) δ 154.31, 152.50, 141.19, 140.52, 128.96, 126.65, 29.01, 28.77, 20.96, 20.81. The NMR is in agreement with literature and reflects the presence of two different aggregation states in benzene.[6]

1.8 Synthesis of Cu_4I_4**2**$_4$

A 4mL vial was charged with mesitylcopper(I) (18 mg, 0.1 mmol) and **1a** (27 mg, 0.1 mmol) fully dissolved in anhydrous toluene (1.0 mL). The vial was placed inside a larger vial (20 mL) containing anhydrous hexane (500 µL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after

72 h. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.32 – 7.19 (m, 2H), 3.80 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 134.93, 129,37, 123.15, 122.75, 118.41, 110.85, 65.38, 30.75, 14.53; Anal. Calcd for $C_{39}H_{40}I_4N_8$: C 32.11; H 2.99; N 8.32%. Found C 32.19; H 2.87; N 8.22%.

1.9 Synthesis of $CuBr2_2$

A 4mL vial was charged with mesitylcopper(I) (18 mg, 0.1 mmol) and **1b** (23 mg, 0.1 mmol) fully dissolved in anhydrous toluene (1.0 mL). The vial was placed inside a larger vial (20 mL) containing anhydrous hexane (500 µL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after 72 h. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.39 – 7.19 (m, 2H), 3.83 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.38, 129,35, 123.28, 122.96, 118.27, 111.85, 65.18, 32.34, 15.42; Anal. Calcd for $C_{18}H_{20}BrCuN_4$: C 49.61; H 4.63; N 12.86%. Found C 49.87; H 4.77; N 12.75%.

1.10 Synthesis of $Cu_21c'_2$

A 4mL vial was charged with mesitylcopper(I) (18 mg, 0.1 mmol) and **1c** (18 mg, 0.1 mmol) fully dissolved in anhydrous toluene (1.0 mL). The vial was placed inside a larger vial (20 mL) containing anhydrous hexane (500 µL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after 72 h. IR (ATR) vmax/cm-1: 2924 2868 (C-H str), 1623 (C=N), 1458 (methyl C-H), 1245 (C-N); Anal. Calculated for $C_{18}H_{20}Cl_2Cu_2N_4$: C 44.09; H 4.11; N 11.43%. Found C 44.10; H 4.03; N 11.41%.

1.11 Synthesis of $Cu_4$1d'$_4$

A 4mL vial was charged with mesitylcopper(I) (18 mg, 0.1 mmol) and **1d** (17 mg, 0.1 mmol) fully dissolved in anhydrous toluene (1.0 mL). The vial was placed inside a larger vial (20 mL) containing anhydrous hexane (500 µL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after 72 h. IR (ATR) vmax/cm-1: 2926 2864 (C-H str), 1679 (C=N), 1457 (methyl C-H), 1228 (C-N); Anal. Calculated for $C_{36}H_{40}F_4Cu_4N_8$: C 47.26; H 4.41; N 12.25%. Found C 47.07; H 4.56; N 11.99%.

1.12 Synthesis of Cu_2(1d')$_2$(L1)

The crystal was formed by vapour diffusion method. The crystallisation experimental setup consist two containers. The inner vial (4 mL) was charged with clear dark red solution which was obtained by filtration of mesitylcopper(I) (18 mg, 0.1 mmol), *N'*-(2-fluoro-phenyl)-*N*-methylethanimidamide (**1d**) (18 mg, 0.1 mmol) and 1,10-phenanthroline (18 mg, 0.1 mmol) solution in anhydrous toluene (1.0 mL). The outer vial (20 mL) was charged with anhydrous hexane (100 µL). The brown needle crystal was isolated and characterized after 72 h. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (dd, *J* = 4.5, 1.6 Hz, 2H), 8.81 – 8.59 (m, 2H), 8.15 (s, 2H), 7.90 (dd, *J* = 8.1, 4.5 Hz, 2H), 7.15 – 6.75 (m, 8H), 2.95 (s, 2H), 2.72 (s, 4H), 1.65 (m, 6H). Anal. Calculated for $C_{30}H_{28}F_2Cu_2N_6$: C 56.51; H 4.43; N 13.18%. Found C 56.77; H 4.43; N 13.11%.

1.13 General Procedure for the Kinetic Studies using Reaction Calorimetry[3]

The reaction was carried out in a 14 mL screw top vial (12mm O.D. x 70mm h x 21mm I.D.) supplied with rubber septum. The reference vial was charged with anhydrous DMSO (10 mL) for comparison. The reaction was initialised by addition of catalyst (CuI solution) by a gas-tight syringe (1000 μL). The reaction temperature was set at 30 °C controlled by a cooling / heating circulator. The real-time data was collected every three seconds by Omnical SuperCRC reaction calorimetry to produce the raw heat flow graph.

In a nitrogen-filled glovebox, the stock solutions were prepared by using a volumetric flask: **1b** (1.136 g in 5 mL DMSO, 1.00 M), TBPM (3.105 g in 10 mL DMSO, 0.50 M), naphthalene (641 mg in 10 mL DMSO, 0.50 M) and CuI (95 mg in 5 mL DMSO, 0.10 M, stored in dark). The standard reaction was prepared following the instruction here: The reaction vial was charged with **1b** (1000 μL, 1.00 M, 1.00 mmol), TBPM (3000 μL, 0.50 M, 1.50 mmol), naphthalene (1000 μL, 0.50 M, 0.50 mmol) and DMSO (4500 μL; make up to 10.000 mL total liquid). A gas-tight syringe charged with CuI solution (500 μL, 0.10 M, 0.05 mmol) was sealed at the tip of the needle using soft PTFE plugs. The reaction vial and syringe were then taken out of the glovebox. The reaction vial was placed into the calorimetry holder under stirring at 30 °C and the gas-tight syringe loaded with catalyst solution was placed instantaneously in the sample injection port on the top of the reaction vial. The reaction vial was allowed to stabilise at 30 °C for at least 1 h to reach the thermal equilibrium which was observed by

Omnical SuperCRC software (flat baseline). Afterward, the CuI solution was injected into the reaction vial and the syringe was removed immediately from the calorimetry. The monitoring stopped when the heat flow became a flat line again followed by the "tau"-correction experiment on the same reaction vial. When the "tau"-correction was accomplished, the reaction vial was taken out of the calorimetry and a 1000 µL of the reaction solution was taken and dissolved in 1000 µL $CDCl_3$. The mixture was washed with distilled water (1 mL) and twice with brine (2 mL in total). The organic layer was dried over $MgSO_4$ and the conversion and yield were determined by ^1H NMR analysis against an internal standard of naphthalene (all 100%).

1.14 Procedure for validating the calorimetry data using ^1H NMR

The reaction vial was charged with **1b** (1000 µL, 1.00 M, 1.00 mmol), TBPM (3000 µL, 0.50 M, 1.50 mmol), naphthalene (1000 µL, 0.50 M, 0.50 mmol) and DMSO (4500 µL; make up to 10.000 mL total liquid). A gas-tight syringe charged with CuI solution (500 µL, 0.10 M, 0.05 mmol) was sealed at the tip of the needle using soft PTFE plugs. The reaction vial and syringe were then taken out of the glovebox. The reaction vial was heated at 30 °C under stirring for 1 h followed by injection of CuI solution. ^1H NMR samples were prepared by drawing 200 µL solution out of the reaction vial at 10, 20, 30, 40, 60, 80 and 100 min which were then dissolved individually in 1000 µL $CDCl_3$. Each mixture was washed with distilled water (1 mL) and twice with brine (2 mL in total). The organic layer was dried over $MgSO_4$ and the conversion and yield were determined by ^1H NMR analysis against an internal standard of naphthalene.

1.15 Procedure for Catalyst Dependence Experiment

The reaction was carried out following the general procedure with different concentration of CuI (details see Table 1).

Table 1 Catalyst dependence experiment

Entry	CuI solution	DMSO
1	500 μL, 0.100 M, 0.050 mmol	4500 μL
2	250 μL, 0.100 M, 0.025 mmol	4750 μL
3	500 μL, 0.200 M, 0.100 mmol	4500 μL

1.16 Procedure for "Same Excess" Experiment

The reaction was carried out following the general procedure with different concentration of **1b** and TBPM ([*e*] = 0.50 M) (details see Table 2).

Table 2"Same excess" experiment

Entry	**1b**	TBPM	DMSO
1	1000 μL, 1.00 M, 1.00 mmol	3000 μL, 0.50 M, 1.50 mmol	4500 μL
2	750 μL, 1.00 M, 0.75 mmol	2750 μL, 0.50 M, 1.25 mmol	5000 μL
3	500 μL, 1.00 M, 0.50 mmol	2500 μL, 0.50 M, 1.00 mmol	5500 μL

1.17 Procedure for Catalyst Deactivation Experiment

The “same excess” experiment was repeated with addition of 1,2-dimethylbenzimidazole (**2**), mono tetrabutylphosphonium malonate (MalH), tetrabutylphosphonium bromide (TBPB) (details see Table 3).

Table 3 Catalyst deactivation experiment

	1b	TBPM	**2**	MalH	TBPB	DMSO
1	1000 μL, 1.00 M, 0.50 mmol	3000 μL, 0.50 M, 1.50 mmol	-	-	-	4500 μL
2	750 μL, 1.00 M, 0.75 mmol	2750 μL, 0.50 M, 1.25 mmol	500 μL, 0.50 M, 0.25 mmol	500 μL, 0.50 M, 0.25 mmol	500 μL, 0.50 M, 0.25 mmol	3500 μL
3	500 μL, 1.00 M, 0.50 mmol	2500 μL, 0.50 M, 1.50 mmol	1000 μL, 0.50 M, 0.50 mmol	1000 μL, 0.50 M, 0.50 mmol	1000 μL, 0.50 M, 0.50 mmol	2500 μL

1.18 Procedure for Product Inhibition Experiment

The reaction was carried out following the general procedure with extra addition of 1,2-dimethylbenzimidazole (**2**) (details see Table 4).

Table 4 Product inhibition experiment

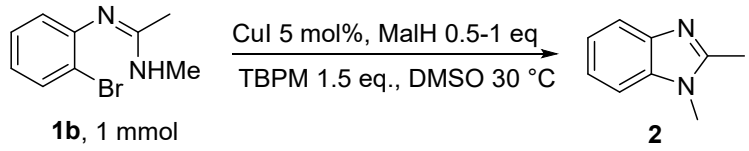
Entry	**2**	DMSO
1	1000 μL, 0.50 M, 0.50 mmol	3500 μL
2	2000 μL, 0.50 M, 1.00 mmol	2500 μL

1.19 Procedure for MalH Inhibition Experiment

The reaction was carried out following the general procedure with extra addition of MalH (TBPM : Malonic acid = 1 : 1, details see Table 5).

Table 5 MalH inhibition experiment

Entry	MalH	DMSO
1	1000 μL, 0.50 M, 0.50 mmol	3500 μL
2	2000 μL, 0.50 M, 1.00 mmol	2500 μL



1b, 1 mmol **2**

Symbol	$[\mathbf{1b}]_0$ (M)	$[TBPM]_0$ (M)	[*e*] (M)	$[MalH]_0$ (M)
●	0.1000	0.1500	0.0500	0
●	0.1000	0.1500	0.0500	0.0500
●	0.1000	0.1500	0.0500	0.1000

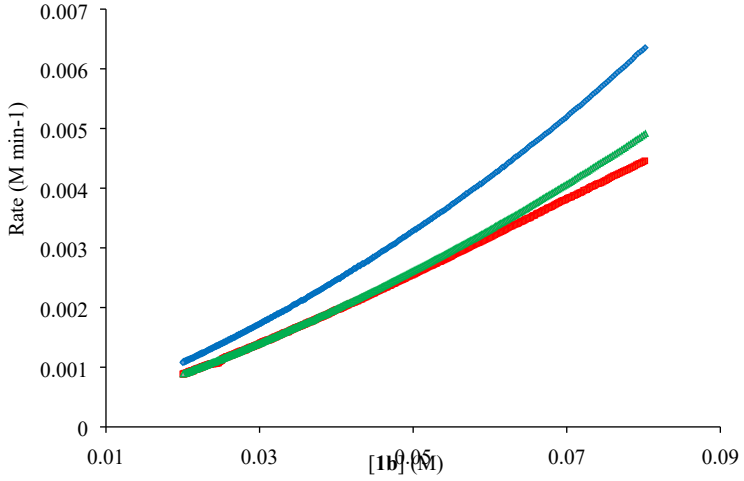


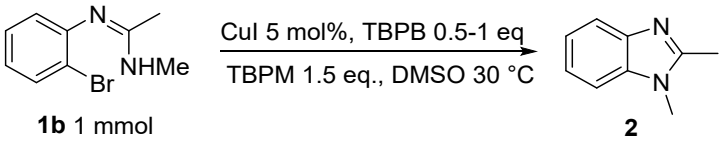
Figure 1. Catalyst inhibition experiment: Graphical rate against [**1b**] with addition of MalH.

1.20 Procedure for $^{n}Bu_4PBr$ Inhibition Experiment

The reaction was carried out following the general procedure with extra addition of $^{n}Bu_4PBr$ (TBPB, details see Table 6).

Table 6 $^{n}Bu_4PBr$ inhibition experiment

Entry	TBPB	DMSO
1	1000 μL, 0.50 M, 0.50 mmol	3500 μL
2	2000 μL, 0.50 M, 1.00 mmol	2500 μL



1b 1 mmol **2**

Symbol	$[\mathbf{1b}]_0$ (M)	$[TBPM]_0$ (M)	[*e*] (M)	$[TBPB]_0$ (M)
■	0.1000	0.1500	0.0500	0
■	0.1000	0.1500	0.0500	0.0500
■	0.1000	0.1500	0.0500	0.1000

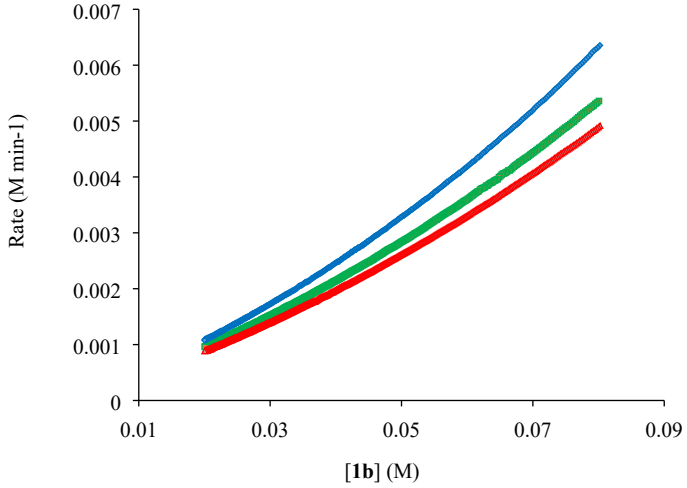


Figure 2. Catalyst inhibition experiment: Graphical rate against [**1b**] with addition of TBPB.

1.21 Procedure for "Different Excess" Experiment

The reaction was carried out following the general procedure with different concentration of **1b** ([*e*] = 1.00 and 1.50 M) or TBPM ([*e*] = 0.75 and 1.00 M) (details see Table 7).

Table 7 "Different excess" experiment

Entry	**1b**	TBPM	DMSO
1	1000 µL, 1.00 M, 1.00 mmol	4000 µL, 0.50 M, 2.00 mmol	3500 µL
2	1000 µL, 1.00 M, 1.00 mmol	5000 µL, 0.50 M, 2.50 mmol	2500 µL
3	750 µL, 1.00 M, 0.75 mmol	3000 µL, 0.50 M, 1.50 mmol	4750 µL
4	500 µL, 1.00 M, 0.50 mmol	3000 µL, 0.50 M, 1.50 mmol	5000 µL

1.22 General 1,2-Dimethylbenzimidazole Synthesis Procedure Using Sub-Mol% Catalyst Loading

A sample vial was charged with TBPM (400 µL, 0.5M, 0.2 mmol) and **1b** (100 µL, 1 M in DMSO-d_6, 0.1 mmol) followed by addition of CuI solution (50 µL, 0.1 M in DMSO-d_6, 0.1 mol %) and internal standard naphthalene (100 µL, 0.5 M in DMSO-d_6, 0.05 mmol). DMSO-d_6 was added to make up the total volume to 1 mL. The reaction was then stirred at rt for 72 h. The mixture was cooled to room temperature and the clear organic layer was transferred into Young's type NMR tube under an N_2 atmosphere. The conversion and yield were determined by ^{1}H NMR (91%).

2 X-ray Crystallographic Data

Table S1. Crystal Data, Data Collection and Refinement Parameters for the structures of **1a**, **1a·tol**, **1b**, **1c**, **1d** and **1d+phen**.

data	1a	1a·tol	1b	1c
formula	$C_{36}H_{40}Cu_4I_4N_8$	$C_{36}H_{40}Cu_4I_4N_8$	$C_{18}H_{20}BrCuN_4$	$C_{18}H_{20}Cl_2Cu_2N_4$
solvent	—	C_7H_8	—	—
formula weight	1346.52	1438.65	435.83	490.36
colour, habit	colourless	colourless	pale brown	colourless
temperature / K	173	173	173	173
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	*Pnna* (no. 52)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
***a* / Å**	9.52910(20)	20.0759(2)	15.1457(4)	10.4396(5)
***b* / Å**	22.9164(5)	16.97565(17)	8.88279(16)	13.5659(10)
***c* / Å**	9.8700(2)	14.15214(16)	14.4845(4)	14.4025(11)
α / deg	90	90	90	74.007(7)
β / deg	102.612(2)	90	110.461(3)	89.553(5)
γ / deg	90	90	90	79.913(5)
***V* / Å^3**	2103.34(8)	4823.06(9)	1825.75(8)	1928.7(2)
Z	2 [c]	4 [d]	4	4 [e]
***D*$_c$ / g cm^{-3}**	2.126	1.981	1.586	1.689
radiation used	Cu-Kα	Cu-Kα	Cu-Kα	Mo-Kα
μ / mm^{-1}	25.609	22.389	4.293	2.492
no. of unique reflns				
measured (*R*$_{int}$)	4018 (0.0377)	4704 (0.0199)	3510 (0.0249)	9964 (0.0333)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	3686	4248	3090	6516
completeness (%) [a]	98.4	99.2	98.6	98.0
no. of variables	240	275	221	479
***R*$_1$(obs), *wR*$_2$(all)** [b]	0.0320, 0.0791	0.0261, 0.0662	0.0288, 0.0726	0.0329, 0.0652
CCDC code	2263362	2263363	2263364	2263365

[a] Completeness to 0.84 Å resolution. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [c] The complex has crystallographic C_i symmetry. [d] The complex has crystallographic C_2 symmetry. [e] There are two independent complexes. [f] The complex has crystallographic C_S symmetry.

Table S1. …part 2

data	1d	1d+phen
formula	$C_{36}H_{40}Cu_4F_4N_8$	$C_{30}H_{28}Cu_2F_2N_6$
solvent	—	—
formula weight	914.92	637.66
colour, habit	colourless	red needles
temperature / K	173	173
crystal system	triclinic	orthorhombic
space group	*P*-1 (no. 2)	*Pnma* (no. 62)
***a* / Å**	9.6197(5)	17.3777(6)
***b* / Å**	14.6022(6)	14.5390(5)
***c* / Å**	15.2132(8)	10.7488(4)
α / deg	116.031(5)	90
β / deg	98.314(4)	90
γ / deg	100.323(4)	90
***V* / Å^3**	1827.90(17)	2715.71(17)
Z	2	4 [f]
***D*$_c$ / g cm^{-3}**	1.662	1.560
radiation used	Mo-Kα	Mo-Kα
μ / mm^{-1}	2.355	1.612
no. of unique reflns		
measured (*R*$_{int}$)	12266	2815 (0.0301)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	7363	2262
completeness (%) [a]	98.4	98.7
no. of variables	488	212
***R*$_1$(obs), *wR*$_2$(all)** [b]	0.0341, 0.0803	0.0412, 0.1050
CCDC code	2263366	2263367

Table S1 provides a summary of the crystallographic data for the structures of **1a**, **1a·tol**, **1b**, **1c**, **1d** and **1d+phen**. Data were collected using Agilent Xcalibur PX Ultra A (**1a**, **1a·tol** and **1b**) and Agilent Xcalibur 3 E (**1c**, **1d** and **1d+phen**) diffractometers, and the structures were solved and refined using the OLEX2,[7] SHELXTL[8] and SHELX-2013[9] program systems. CCDC 2263362 to 2263367.

The X-ray crystal structures of 1a, 1a·tol, 1b, 1c, 1d and 1d+phen.

The structure of **1a** was found to sit across a centre of symmetry at the middle of the central Cu_2I_2 ring. The structure of **1a·tol**, the toluene solvate of the same complex seen in the structure of **1a**, was found to sit across a C_2 axis that bisects the N(3)···N(3A) and N(23)···N(23A) vectors. The C40-based included toluene solvent molecule was found to be disordered across a C_2 axis, and two unique orientations were identified of *ca*. 29 and 21% occupancy (with two further orientations of the same occupancies being generated by operation of the C_2 axis). The geometries of the two unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically. The crystal of **1c** that was studied was found to be a two component twin in a *ca*. 52:48 ratio, with the two lattices related by the approximate twin law [–1.00 0.00 0.00 –0.45 1.00 –0.52 0.00 0.00 –1.00]. The structure was found to contain two crystallographically independent complexes (**1c-A** and **1c-B**) in the asymmetric unit. The crystal of **1d** that was studied was found to be a two component twin in a *ca*. 63:37 ratio, with the two lattices related by the approximate twin law [0.93 –0.14 0.12 –0.96 –0.93 –0.06 –0.01 0.00 –1.00]. The fluorine atoms of the C6- and C26-based C_6H_5F rings were found to be disordered across the two *ortho*- sites in *ca*. 84:16 and 55:45 ratios respectively. In both cases the thermal parameters of the two partial-occupancy fluorine atoms were restrained to be similar, and only the major occupancy fluorine atoms were refined anisotropically (the minor occupancy fluorine atoms were refined isotropically). The

structure of **1d+phen** was found to sit across a mirror plane that passes through Cu1, Cu2 and the whole of the N21 to C34 phenanthroline unit. The fluorine atom of the C6-based C_6H_5F ring was found to be disordered across the two *ortho*- sites in a *ca*. 57:43 ratio. The thermal parameters of the two partial-occupancy fluorine atoms were restrained to be similar, and only the major occupancy fluorine atom was refined anisotropically (the minor occupancy fluorine atom was refined isotropically).

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