Electronic Supplementary Material (ESI) for ChemComm.

Electrochemical Flow-Reactor for Expedient Synthesis of Copper-*N*-Heterocyclic Carbene Complexes

Electronic Supplementary Information (ESI)

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Contents

1. General considerations

Where stated, manipulations were performed under an atmosphere of dry nitrogen by means of standard Schlenk line techniques. Anhydrous solvents were prepared by passing the solvent over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, *via* the Dow-Grubbs solvent system. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX300 spectrometer. The values of chemical shifts are given in ppm and values for coupling constants (*J*) in Hz. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyzer MOD 1106 spectrometer. Imidazolium salts **1**, **5** – **9** were prepared using literature procedures.

2. Synthesis of imidazolium salts

Preparation of 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (1):

A round-bottomed flask equipped with stirrer bar was charged with *N,N'*-dimesityl-1,4-diaza-1,3-butadiene (2.00 g, 6.84 mmol) in ethyl acetate (25 mL) and cooled to 0 ^{o}C. A separate solution of paraformaldehyde (0.27 g, 8.90 mmol) dissolved in hydrochloric acid (2.80 mL, 4M in dioxane) was added dropwise over 10 minutes and the solution allowed to stir at room temperature for 16 hours. After this time, the solid was collected and washed with cold ethyl acetate (3 x 20 mL). Recrystallisation from acetone/pentane delivered the pure title compound as a white microcrystalline solid. Yield: 1.57 g, 4.60 mmol, 67 %; mp decomp. at 351-352 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.07 (br s, 1H, NC*H*N), 7.55 (s, 2H, im*H*), 7.05 (s, 4H, *meta*-C*H*), 2.35 (s, 6H, *para*-C*H*), 2.21 (s, 12H, *ortho*-C*H*) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.1, 139.6, 134.2, 130.5, 129.8, 124.0, 21.1, 17.8 ppm; HR-MS (ESI^{+}): *m/z* 305.2028 $[C_{21}H_{25}N_2]^{+}$, calcd. $[M - Cl]^{+}$ 305.2012. These data are in agreement with those reported in the literature.[1]

Preparation of 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate (5):

Ammonium hexafluorophosphate (1.44 g, 8.81 mmol) and 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (1.00 g, 2.94 mmol) were stirred vigorously in water (50 mL) at room temperature for 2 hours. After this time, a white precipitate formed which was collected *via* vacuum filtration and washed with cold water (3 x 30 mL), followed by recrystallisation from acetone/diethyl ether to yield the title compound as a white crystalline

solid. Yield: 1.21 g, 2.68 mmol, 91 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (s, 1H, NC*H*N), 7.55 (s, 2H, im*H*), 7.07 (s, 4H, mes *meta*-C*H*), 2.37 (s, 6H, mes *para*-CH_3), 2.13 (s, 12H, mes *ortho*-CH_3) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.7, 136.6, 134.1, 130.4, 130.1, 125.4, 21.3, 17.2 ppm; HR-MS (ESI^+): *m/z* 305.1721 $[C_{21}H_{25}N_2]^+$, calcd. $[M - PF_6]^+$ 305.2012. These data are in agreement with those reported in the literature.[2]

Preparation of 1-allyl-3-(2-methylpyridyl)imidazolium bromide (6):

2-Bromomethylpyridine hydrobromide (0.51 g, 2.00 mmol), 1-allylimidazole (0.23 g, 2.1 mmol), potassium carbonate (1.40 g, 10.00 mmol) were charged to a round-bottomed flask and stirred vigorously in acetonitrile (30 mL) at 60 ^{o}C for 18 hours. After this time, the mixture was filtered and solvents removed *in vacuo* to furnish a pale orange oil. Dissolution in acetonitrile (20 mL) followed by reprecipitation with diethyl ether (50 mL) (twice) delivered the pure product as a pale yellow oil. Yield: 0.25 g, 2.00 mmol, quantitative; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.92 (s, 1H, NC*H*N), 8.55 (d, *J* = 4.0 Hz, 1H, im*H*), 7.87 (d, *J* = 8.0 Hz, 1H, *meta*-C*H*), 7.76 (td, *J* = 8.0 Hz, 1H, *para*-C*H*), 7.63 (d, *J* = 4.0 Hz, 1H, im*H*), 7.30 (td, *J* = 8.0 Hz, 1H, *meta'*-C*H*), 7.16 (d, *J* = 8.0 Hz, 1H, *ortho*-C*H*), 6.02 (m, 1H, CH_2=C*H*C), 5.79 (s, 2H, CH_2), 5.49 (d, *J* = 12.0 Hz, 2H, CH_2=CH), 4.92 (d, *J* = 3.0 Hz, 2H, NCH_2) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.5, 150.0, 137.9, 137.6, 129.6, 124.3, 124.2, 123.1, 121.3, 110.1, 54.2, 52.4 ppm; HR-MS (ESI^+): *m/z* 200.1202 $[C_{12}H_{14}N_3]^+$, calcd. $[M - Br]^+$ 200.1182; anal. calcd. (%) for $C_{12}H_{14}N_3Br.(^3/_4H_2O)$: C 49.08, H 5.32, N 14.31; found C 48.70, H 5.10, N 14.90.

Preparation of 1-methyl-3-(*tert*-butylacetate)imidazolium chloride (7):

1-Methylimidazole (1.60 mL, 20.0 mmol) and *tert*-butyl chloroacetate (2.90 mL, 20.0 mmol) were added to a flame-dried Schlenk flask. The mixture was stirred at room temperature for 18 hours, during which the mixture solidified. The title compound was recrystallised from dichloromethane/hexane to afford a white hygroscopic solid, which was subsequently washed repeatedly with cold diethyl ether (3 x 30 mL) and dried *in vacuo*. Yield: 3.59 g, 15.4 mmol, 77 %; ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.31 (s, 1H, NC*H*N), 7.78 (br s, 2H, im*H*), 5.22 (s, 2H, CH_2), 3.91 (s, 3H, CH_3), 1.44 (s, 9H, 3CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, d_6-DMSO): δ 165.8, 137.7, 123.6, 123.1, 82.9, 49.5, 35.7, 27.6 ppm; HR-MS (ESI^+): *m/z* 197.1307 $[C_{10}H_{17}N_2O_2]^+$, calcd. $[M - Cl]^+$ 197.1285. These data are in agreement with those reported in the literature.[3]

Preparation of 1,3-(dibenzyl)imidazolium hexafluorophosphate (8):

1*H*-Imidazole (0.79 g, 11.7 mmol) and potassium carbonate (2.42 g, 17.5 mmol) were stirred vigorously in acetonitrile (60 mL) for 15 minutes at room temperature. Benzyl bromide (2.77 mL, 23.36 mmol) was added in a single portion and stirring continued for a further 48 hours. After this time, the solvent was removed *in vacuo* and water (100 mL) was added. The aqueous phase was extracted with dichloromethane (4 x 40 mL), organic phases combined, dried over anhydrous magnesium sulfate and filtered under vacuum. Following concentration under reduced pressure, the resultant solid was washed repeatedly with cold diethyl ether (3 x 30 mL) and dried *in vacuo* to afford 1,3-(dibenzyl)imidazolium bromide as a white solid. Yield: 3.50 g, 10.62 mmol, 91 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.79 (s, 1H, NC*H*N, 7.49 - 7.45 (m, 4H, 2CH_2), 7.38 – 7.35 (m, 6H, ar*H*), 7.25 (d, *J* = 1.5 Hz, 2H, im*H*), 5.56 (s, 4H, CH_2) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.0, 132.7, 129.5, 129.4, 129.0, 121.8, 53.4 ppm; HR-MS (ESI$^+$): *m/z* 249.1420 $[C_{17}H_{17}N_2]^+$, calcd. $[M - Br]^+$ 249.1386. These data are in agreement with those reported in the literature.[4]

1,3-(Dibenzyl)imidazolium bromide (1.00 g, 3.04 mmol) and ammonium hexafluorophosphate (2.48 g, 15.2 mmol) were stirred vigorously in water (50 mL) at room temperature for 2 hours. After this time, a white precipitate formed which was collected *via* vacuum filtration and washed with cold water (3 x 30 mL), followed by recrystallisation from acetone/diethyl ether to yield the title compound as a white crystalline solid. Yield: 1.14 g, 2.89 mmol, 95 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.63 (s, 1H, NC*H*N), 7.30 – 7.40 (m, 10H, ar*H*), 7.24 (m, 2H, im*H*), 5.23 (s, 4H, NCH_2) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.2, 132.5, 129.3, 129.1, 128.6, 121.4, 53.2 ppm; HR-MS (ESI$^+$): *m/z* 249.1391 $[C_{17}H_{17}N_2]^+$, calcd. $[M - PF_6]^+$ 249.1386. These data are in agreement with those reported in the literature.[5]

Preparation of diimidazolium cyclophane hexafluorophosphate (9):

1,3-*Bis*(bromomethyl)benzene (2.50 g, 9.41 mmol) was dissolved in anhydrous acetone (100 mL). A solution of 1,3-*bis*(imidazole-1-ylmethyl)benzene (2.30 g, 9.41 mmol) in anhydrous acetone (100 mL) was added dropwise over 4 hours at room temperature. The mixture was further stirred for 18 hours, upon which a white precipitate had formed, which was collected *via* vacuum filtration and washed repeatedly with cold acetone (2 x 40 mL) and diethyl ether (2 x 40 mL) to deliver the diimidazolium bromide as a microcrystalline white solid. Yield: 2.70 g, 5.41 mmol, 57 %; ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.50 (s, 2H, NC*H*N), 7.86 (s,

4H, im*H*), 7.60 (d, *J* = 7.4 Hz, 4H, ar*H*), 7.54 – 7.45 (m, 2H, ar*H*), 7.17 (s, 2H, ar*H*), 5.46 (s, 8H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, d_6-DMSO): δ 136.3, 136.0, 129.4, 129.1, 126.0, 123.1, 51.7 ppm; HR-MS (ESI^+): *m/z* 421.1041 $[C_{22}H_{22}N_4Br]^+$, calcd. $[M - Br]^+$ 421.1028.

To a methanolic solution of diimidazolium bromide (1.20 g, 2.40 mmol), ammonium hexafluorophosphate (3.90 g, 24.1 mmol) in methanol was added in a single portion and allowed to stir for 2 hours. The resultant white precipitate was collected *via* vacuum filtration and washed repeatedly with cold methanol (3 x 30 mL) followed by diethyl ether (3 x 30 mL) and dried *in vacuo* to give the pure product as a white solid. Yield: 1.30 g, 2.00 mmol, 84 %; ^1H NMR (500 MHz, d_6-DMSO): δ 9.22 (s, 2H, NC*H*N), 7.81 (d, *J* = 1.4 Hz, 4H, im*H*), 7.58 (d, *J* = 6.4 Hz, 4H, ar*H*), 7.56 – 7.50 (m, 2H, ar*H*), 6.94 (s, 2H, ar*H*), 5.43 (s, 8H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, d_6-DMSO): δ 136.2, 136.1, 129.5, 129.1, 125.5, 123.2, 51.8 ppm. These data are in agreement with those reported in the literature.[6]

3. Cyclic voltammetry of [IMesH]Cl (1)

Electrochemical measurements were conducted using an Autolab PGSTAT20 voltammetric analyser under an argon atmosphere, solvated in pre-dried CH_3CN containing 0.10 M $[^nBu_4N]BF_4$ as supporting electrolyte. Voltammetric experiments utilised a Pt disk working electrode, a Pt rod auxiliary electrode and an Ag/AgCl reference electrode. All potentials quoted are referenced to an internal ferrocene/ferrocenium standard and were obtained at a scan rate (v) of 300 mVs^{-1}. The ferrocene/ferrocenium couple under these conditions was observed at $+ 0.44 \leq E_{1/2} \leq 0.58$ V vs Ag/AgCl, providing an observed reduction potential of **1** at – 2.32 V (*vs* Fc/Fc^+).

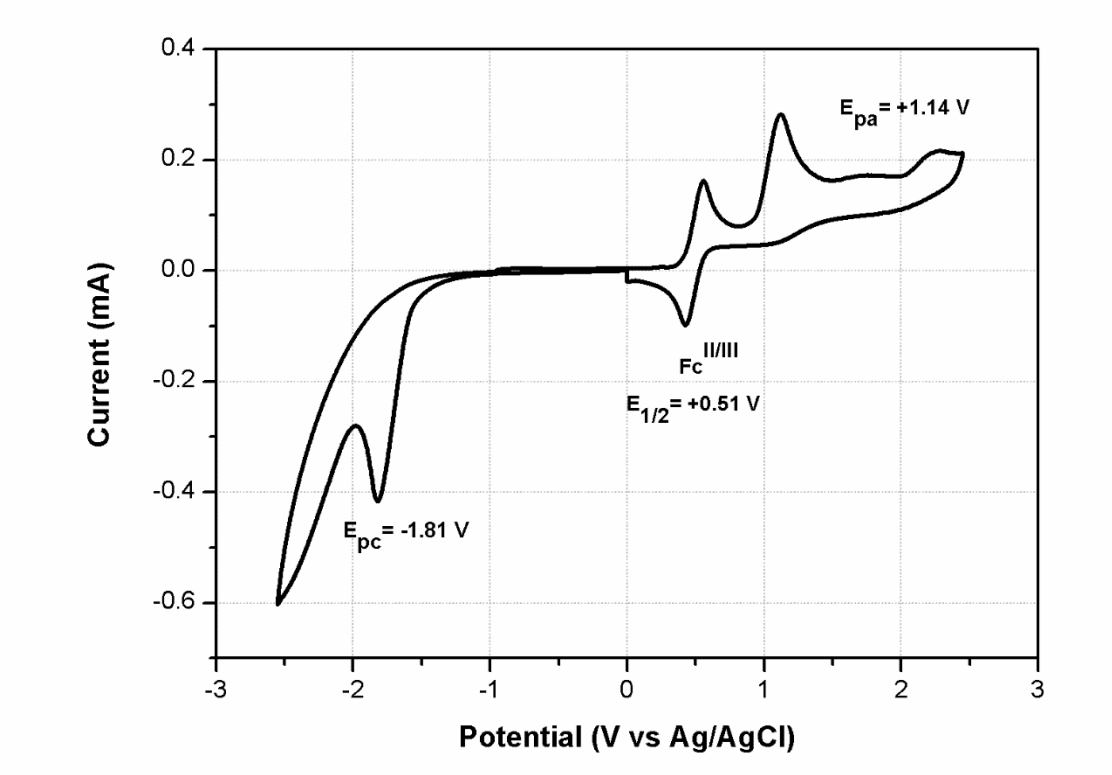
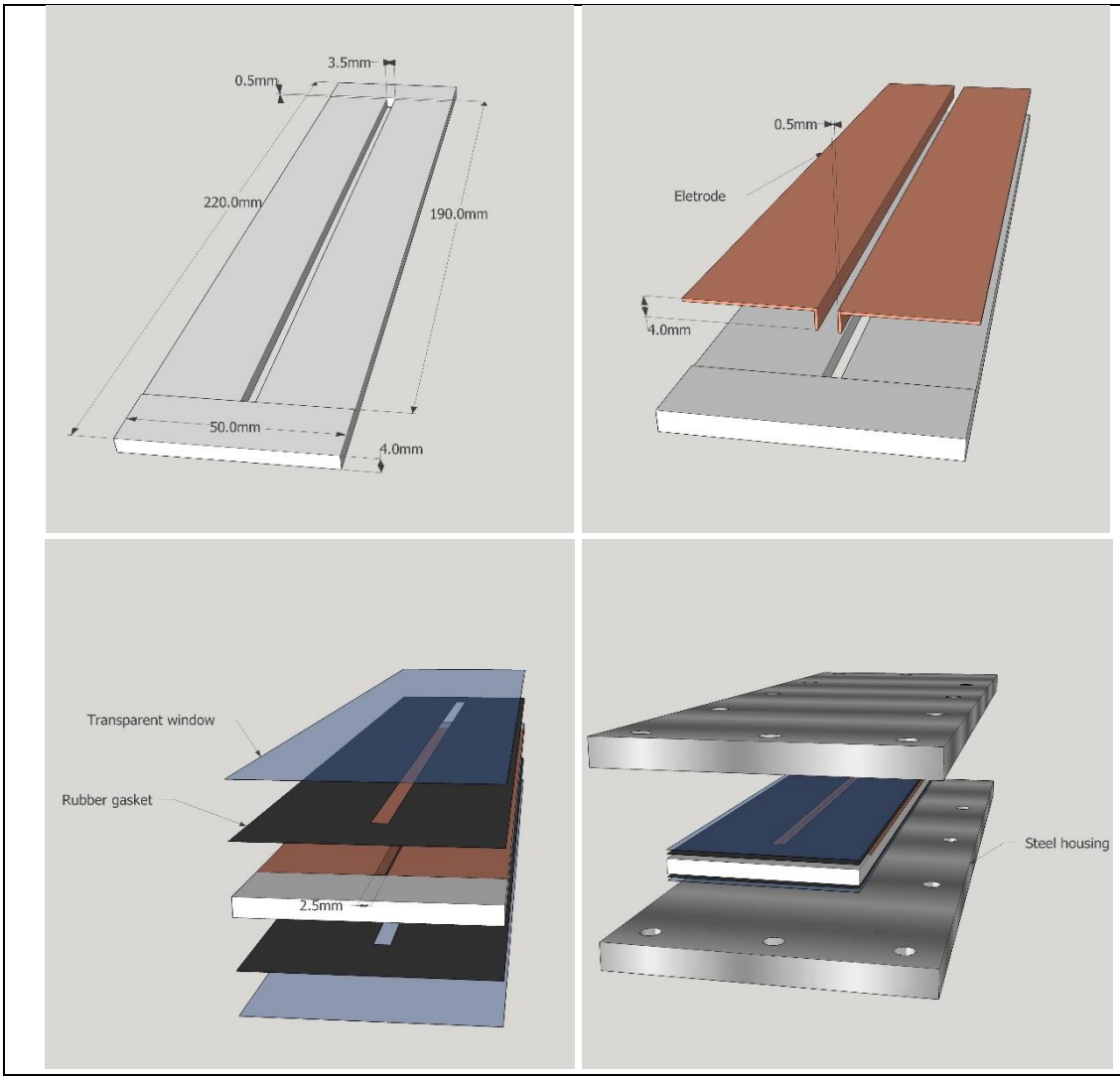


Figure S1. Cyclic voltammogram of [IMesH]Cl (**1**) (1.0 mM) in non-aqueous media ($CH_3CN/[^nBu_4N]BF_4$ 0.10 M), v = 300 mVs^{-1}, T = 298 K, [Fc] = 1.0 mM; E_{pa} ascribed to counterion oxidation band.

4. Design of first electrochemical flow-cell



Flow channel	
Channel length	190 mm
Channel depth	4.0 mm
Distance between electrodes	2.5 mm
Width of electrodes	4.0 mm
Volume	1.9 cm^3
Surface area of each electrode	7.6 cm^2
Window (PMMA) thickness	2.0 mm
Inlet/outlet tube	
O.D.	$^1/_{16}$ inch
Length	5 cm
Volume	24 mm^3

Figure S2. Simulated design images of flow-cell comprising a PTFE flow channel (top left), two copper electrodes (top right), rubber gaskets (bottom left) and steel encasement (bottom right).

The volume of the flow channel, after packing with soda-lime glass beads (dia. 2 mm, Smith Scientific Ltd.) was determined indirectly by subtracting the volume of the glass beads.

The effective channel volume was therefore calculated by measuring the increase in volume of a quantity of water (3.0 mL) upon the addition of the glass beads (measured to be 0.85 mL). An alternative method involved measuring the weight of the glass beads (2.155 g, using d = 2.52 g/mL, volume = 2.155/2.52 = 0.855 mL). Both methods provided strong agreement, therefore the average value for volume of glass beads was taken to be 0.85 mL.

Flow channel volume (with glass beads) = 1.9 mL - 0.85 mL = 1.05 mL.

5. Optimisation of first electrochemical flow-cell

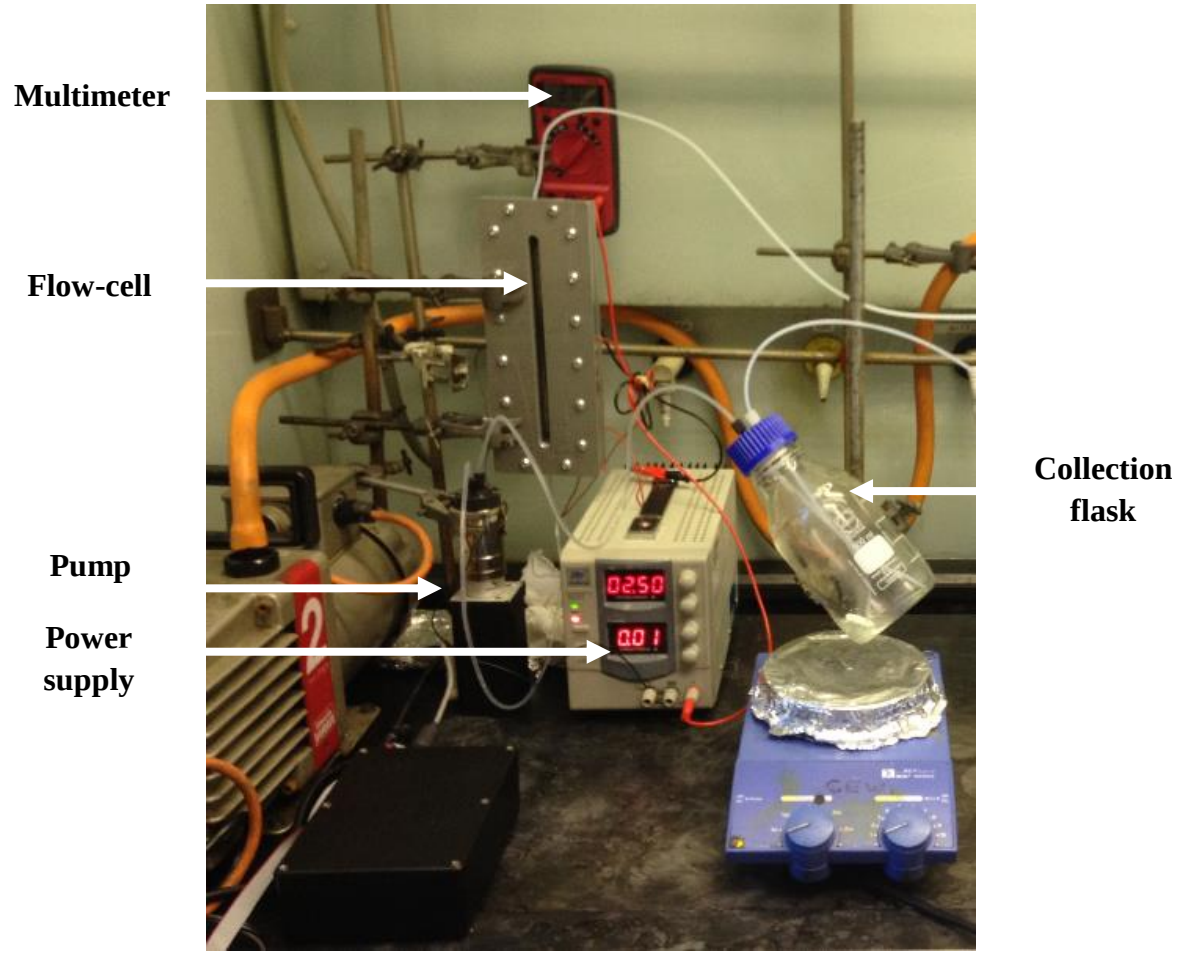


Figure S3. Laboratory experimental configuration.

A 6.6 mM solution of imidazolium **1** in anhydrous acetonitrile was prepared and pumped through the primary flow-cell in a single-pass at a range of flow rates, whilst subject to

varying applied potential. The resulting output for each condition were collected and solvents removed *in vacuo* to deliver crude reaction mixtures, which were analysed *via* ^{1}H NMR spectroscopy (Table S1).

Table S1. Ratio of **1** : **2** : **3** in single-pass mode from the first flow-cell using [**1**] = 6.6 mM; [a] registered at steady-state; [b] determined by ^{1}H NMR spectroscopy; τ_R = residence time.

Entry	F ($mLmin^{-1}$)	τ_R (min)	E_{appl} (V)	Current (mA)[a]	Conversion Ratio[b]
1	0.50	2.10	1.50	0.82	82:18:0
2	0.50	2.10	2.00	1.27	70:30:0
3	0.50	2.10	2.50	2.70	64:36:0
4	0.75	1.40	1.50	0.92	90:10:0
5	0.75	1.40	2.00	1.31	77:23:0
6	0.75	1.40	2.50	2.81	70:30:0
7	1.00	1.05	1.50	1.01	93:7:0
8	1.00	1.05	2.00	1.47	79:21:0
9	1.00	1.05	2.50	2.90	73:27:0

Of the conditions outlined, a residence time of 2.10 minutes and applied potential of 2.50 V (Table S1, Entry 3) delivered highest conversion in a single-pass (36 %). It was found that applying a cell potential greater than 2.50 V generated insoluble salt deposits which caused salt-bridging and/or reactor blockage. A minimal flow rate of 0.50 $mLmin^{-1}$ was adopted to avoid side reactions.

Table S2. Ratio of **1** : **2** : **3** in single-pass mode from the first flow-cell using [**1**] = 33.0 mM; [a] registered at steady-state; [b] determined by ^{1}H NMR spectroscopy; τ_R = residence time.

Entry	F ($mLmin^{-1}$)	τ_R (min)	E_{appl} (V)	Current (mA)[a]	Conversion Ratio[b]
1	0.50	2.10	1.50	0.87	95:5:0
2	0.50	2.10	2.00	1.47	81:19:0
3	0.50	2.10	2.50	7.15	75:25:0
4	0.75	1.40	1.50	1.01	96:4:0

5	0.75	1.40	2.00	5.15	83:17:0
6	0.75	1.40	2.50	8.45	72:28:0
7	1.00	1.05	1.50	1.20	96:4:0
8	1.00	1.05	2.00	6.45	84:16:0
9	1.00	1.05	2.50	9.15	74:26:0

Experiments at ≥ 3.0 V rapidly resulted in precipitation of a green solid which caused reactor blockage.

6. Recirculation experiment

A circulatory configuration was employed whereby the resultant reactor output phase containing [IMesH]Cl **1** and IMesCuCl **2** was recirculated through the electrochemical flow reactor, allowing further imidazolium consumption over time. Samples of 0.5mL were flowed into a round-bottomed flask at certain time intervals, the solvent removed *in vacuo*, and conversion obtained using ^{1}H NMR spectroscopy in CD_3CN. Electrolytic recirculation of a 6.6 mM (20 cm^3, 0.132 mmol) solution of **1** in anhydrous acetonitrile allowed full conversion to give complex **2** in 92 % yield after 80 minutes (Figure S4).

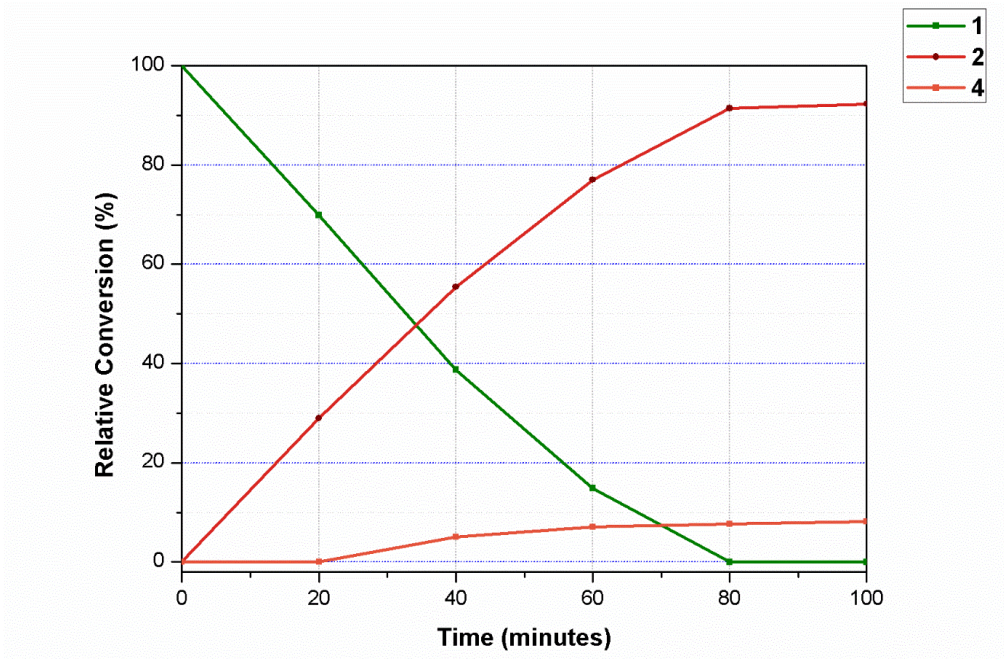
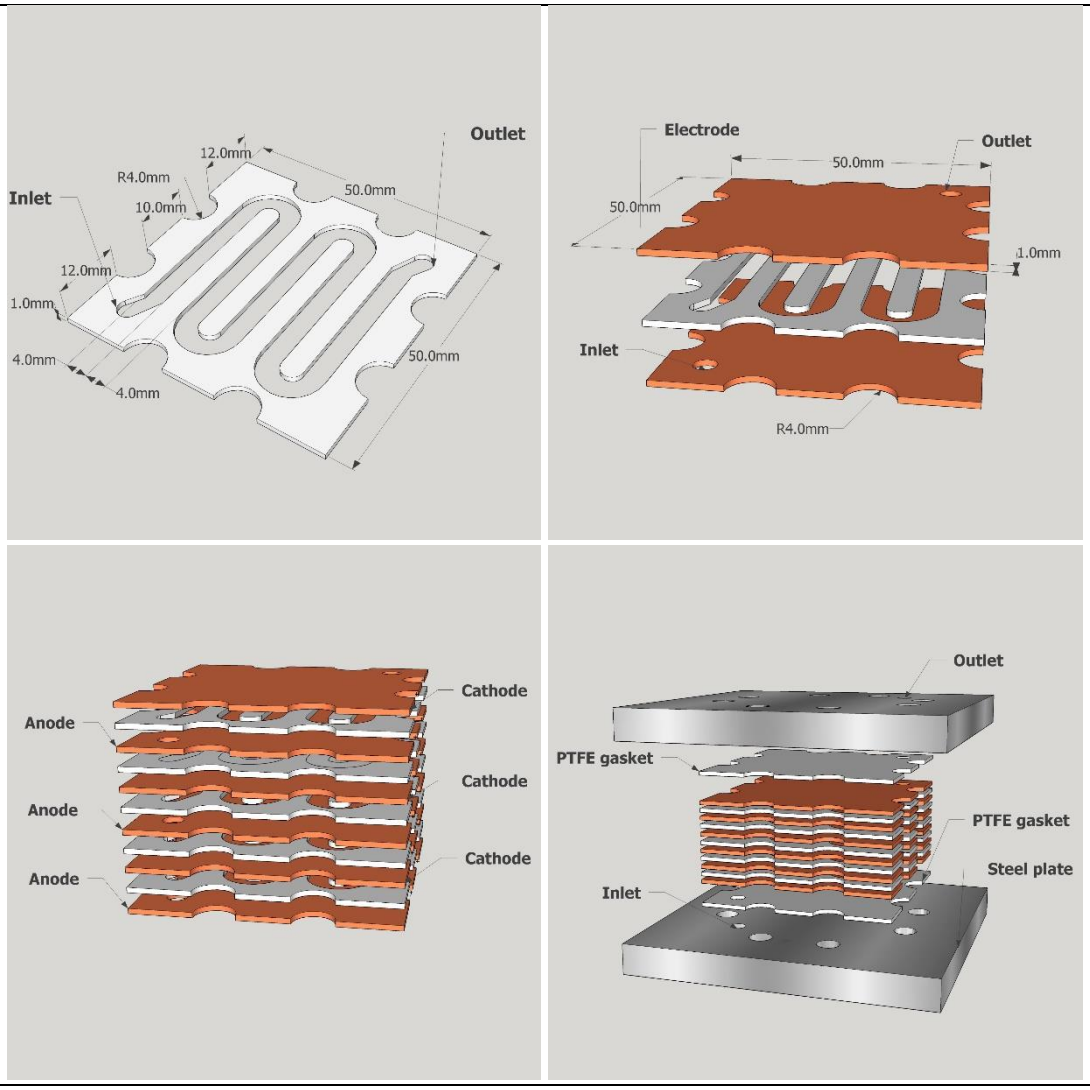


Figure S4. Product distribution during recirculation mode determined by ^{1}H NMR spectroscopy.

7. Design of second electrochemical flow-cell



Flow channel	
Channel length (each)	200 mm
Channel width	4.0 mm
Distance between electrodes	1.0 mm
Thickness of electrodes	1.0 mm
Volume	4.0 mL
Surface area of each electrodes	40 cm^2
Inlet/outlet tube	
O.D.	$^1/_8$ inch
Length	10.0 cm
Volume	0.20 cm^3

Figure S5. Simulated design images of flow-cell comprising a PTFE flow channel/spacer (top left), cathode-spacer-anode sequence (top right), extended stacked-disk arrangement (bottom left) and steel encasement (bottom right).

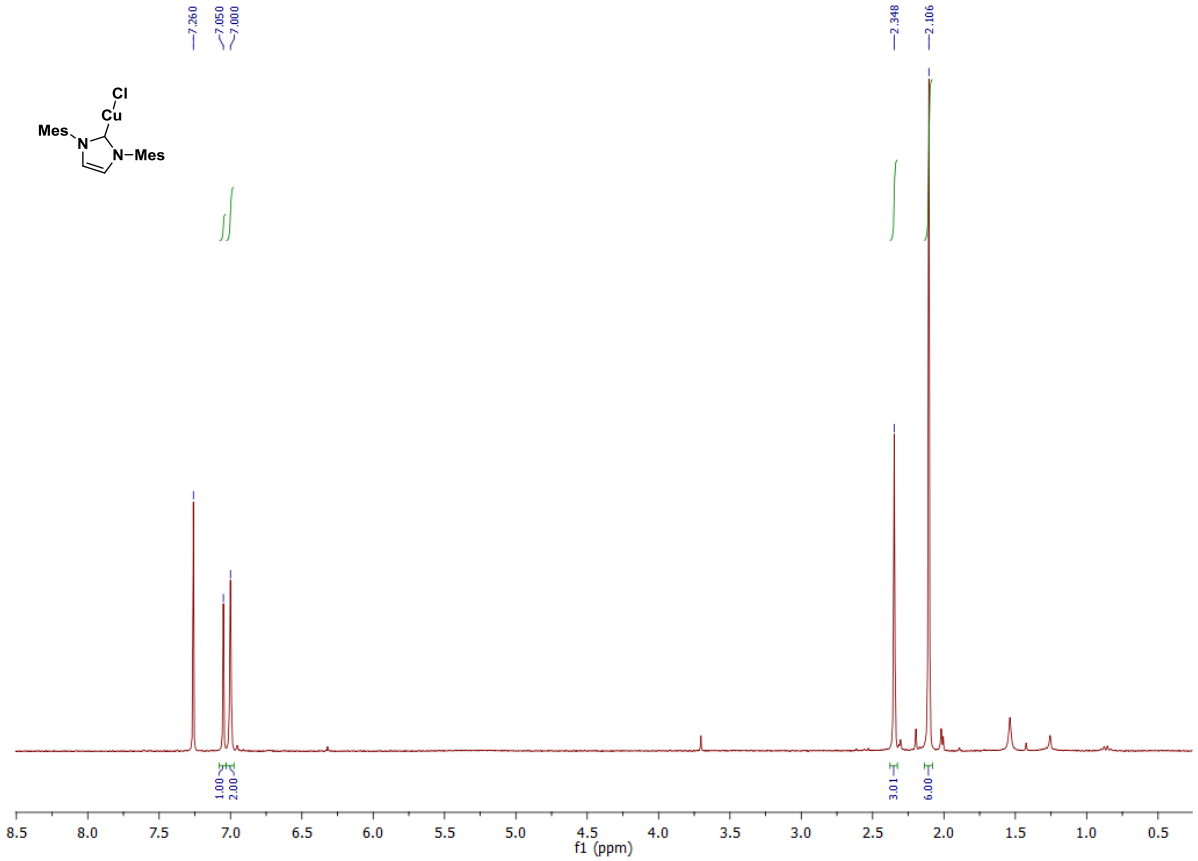
8. Optimisation of second electrochemical flow-cell

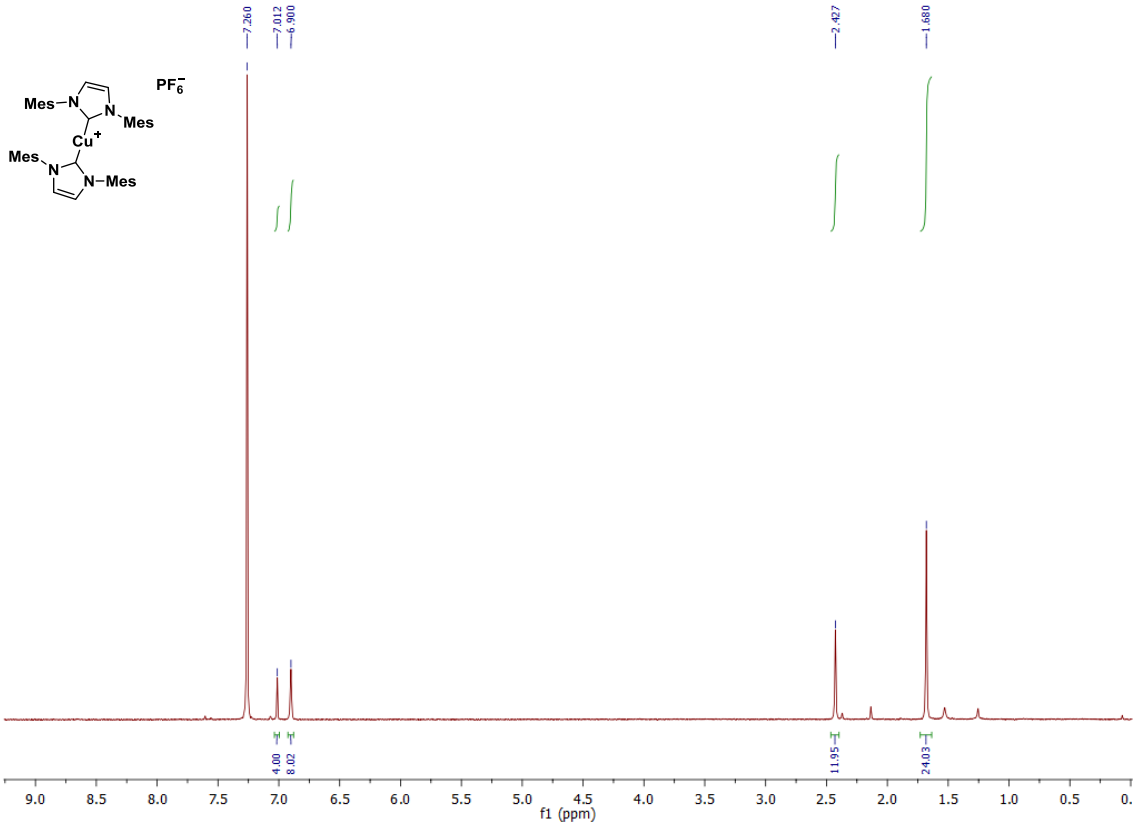
A 6.6 mM solution of [IMesH]Cl **1** was passed through the second cell at varying flow rates whilst applying a range of cell potentials (Table S3).

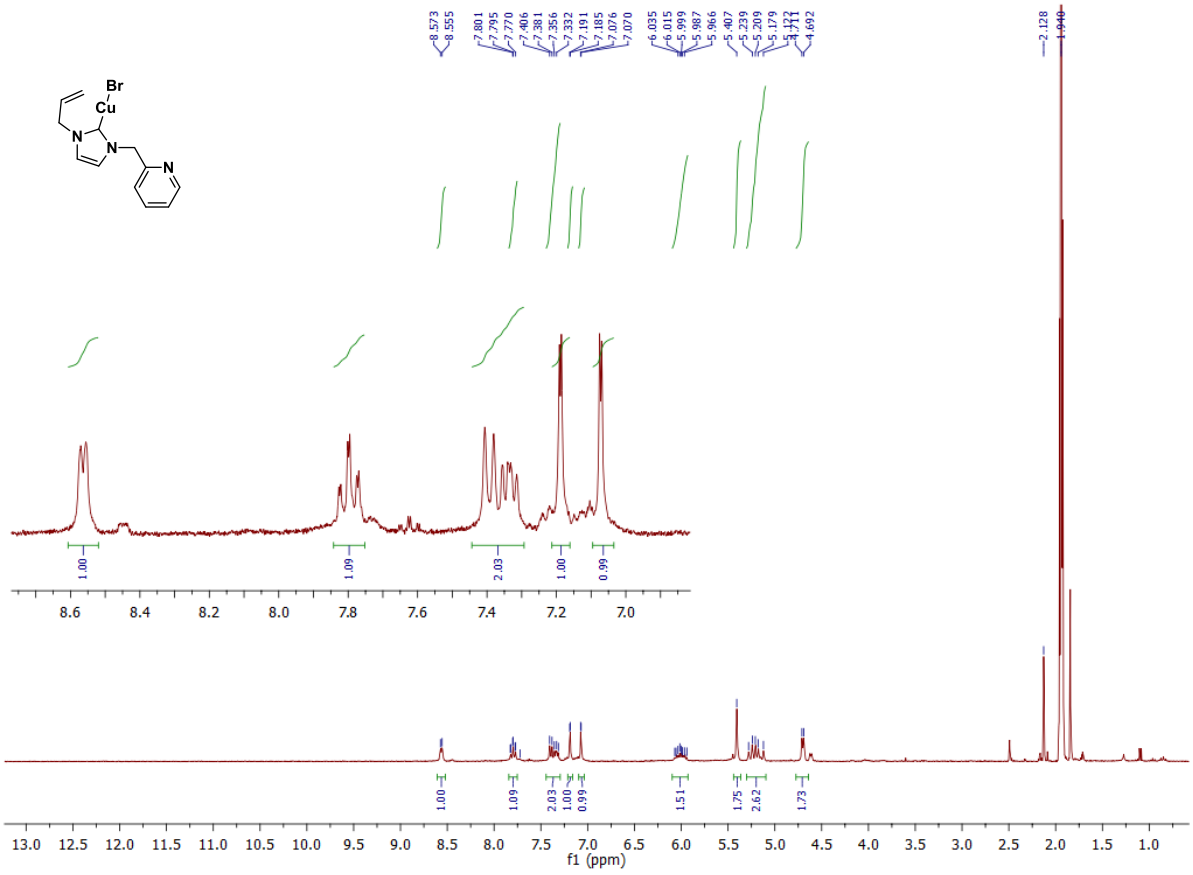
Table S3. Ratio of **1** : **2** : **3** in single-pass mode from the second flow-cell using [**1**] = 6.6 mM; [a] registered at steady-state; [b] determined by ^{1}H NMR spectroscopy; τ_R = residence time.

Entry	F ($mLmin^{-1}$)	τ_R (min)	E_{appl} (V)	Current (mA)[a]	Conversion Ratio[b]
1	0.67	6.0	1.37	1.79	80:20
2	0.67	6.0	1.45	2.78	69:31
3	0.67	6.0	1.70	5.89	37:63
4	0.67	6.0	1.94	10.00	3:97
5	1.00	4.0	1.16	2.01	84:16
6	1.00	4.0	1.30	2.88	74:26
7	1.00	4.0	1.59	6.13	51:49
8	1.00	4.0	1.88	10.00	23:77
9	1.33	3.0	1.10	2.20	85:15
10	1.33	3.0	1.24	3.21	78:22
11	1.33	3.0	1.41	6.33	59:41

9. ^{1}H NMR spectra of Cu-NHCs



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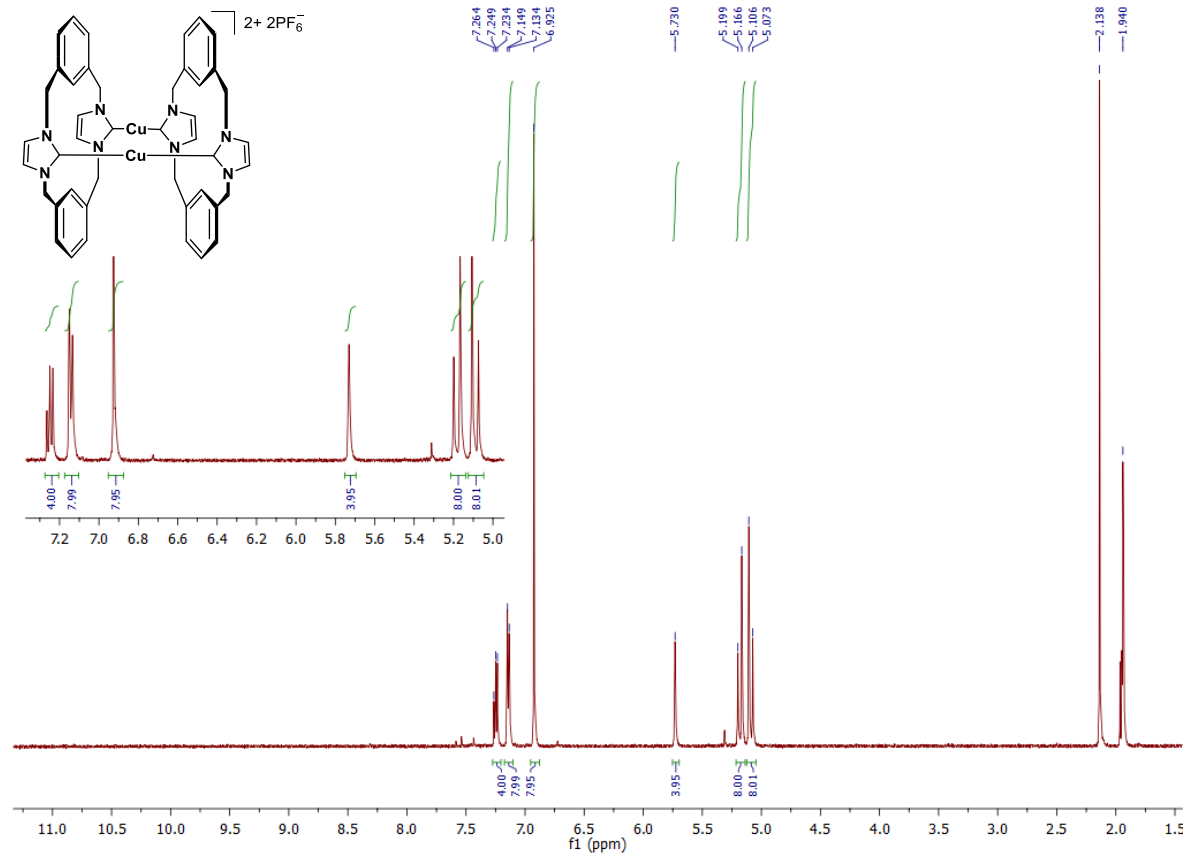
f1 (ppm)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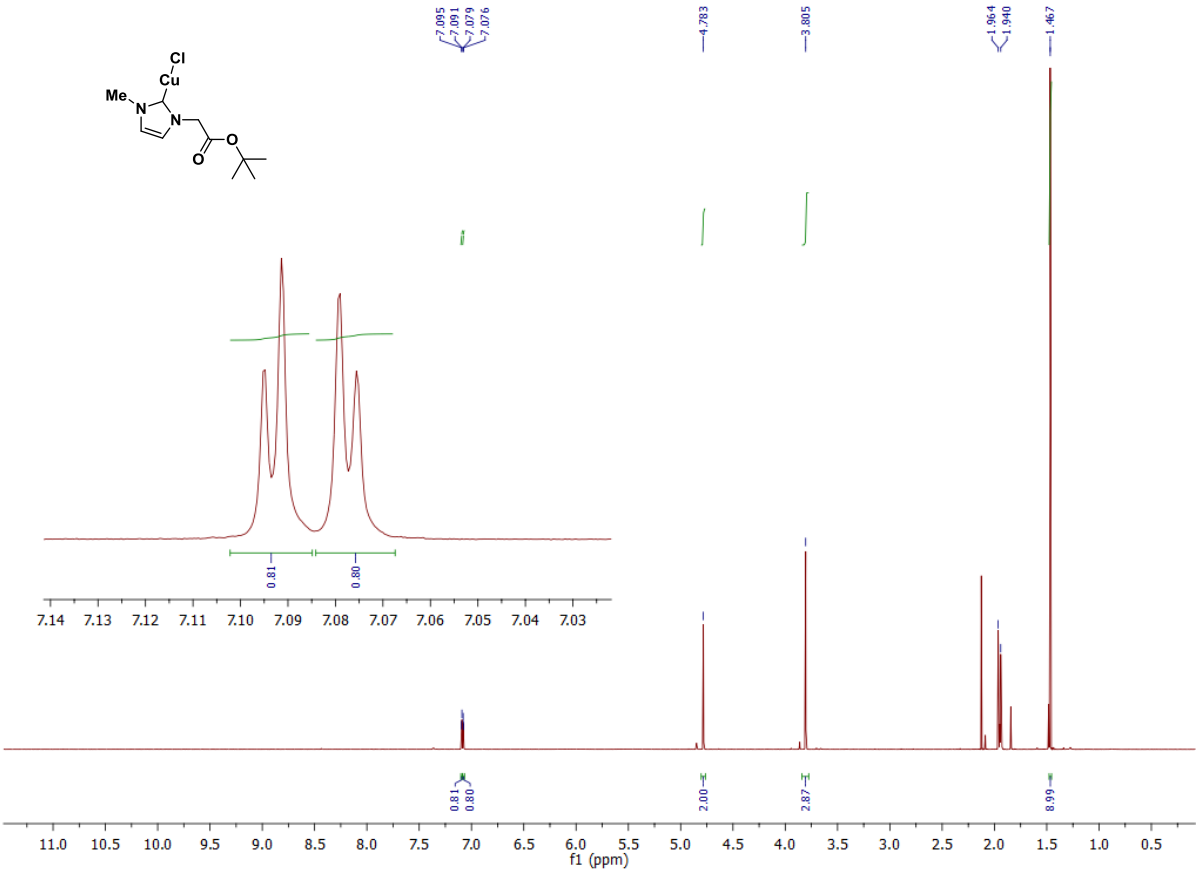
f1 (ppm)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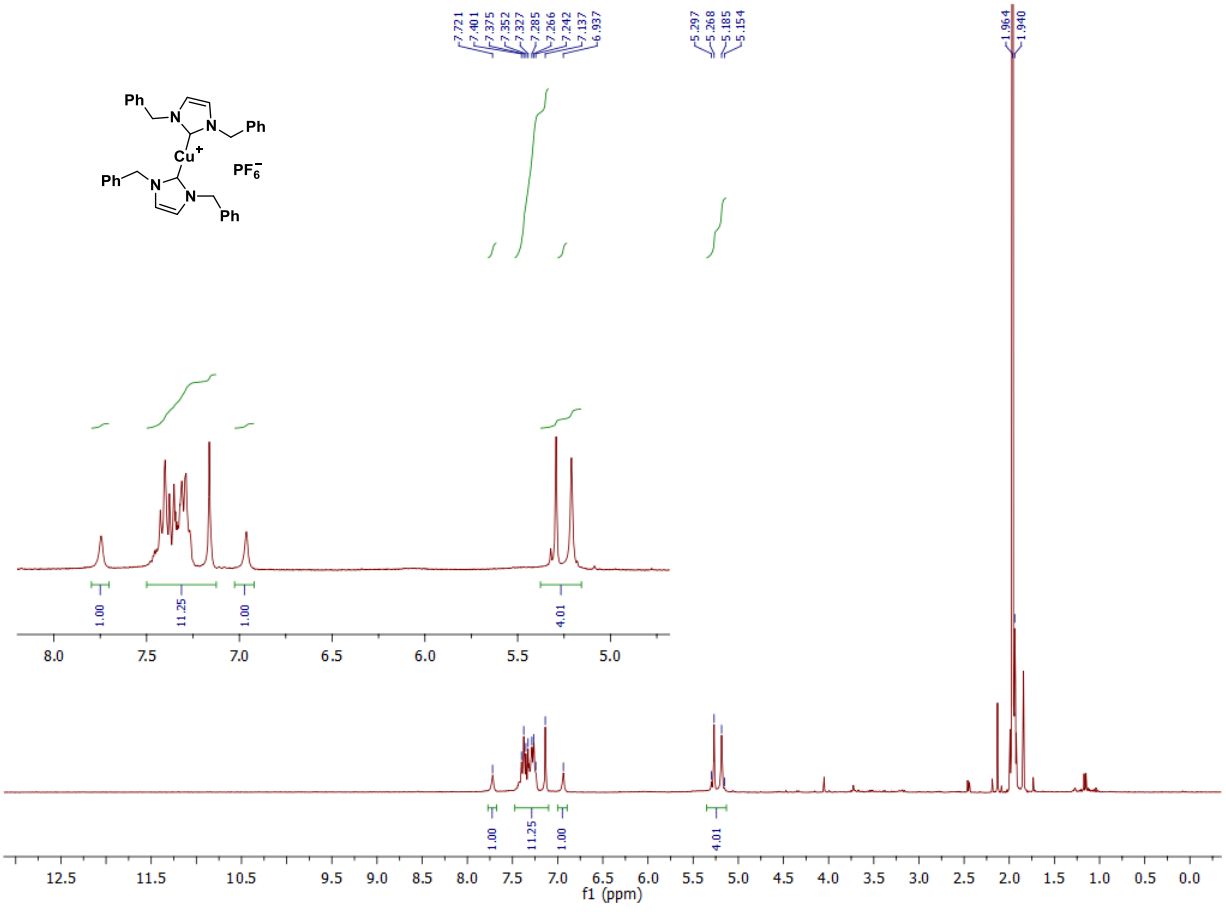
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7.137
6.937
5.297
5.268
5.185
5.154
1.964
1.940
1.00
11.25
1.00
4.01
f1 (ppm)

10. Catalytic hydrosilylation reactions

Hydrosilylation Procedure of Functionalised Ketones *via* Pre-Defined Catalyst:

Bis[1,3-*bis*(2,4,6-trimethylphenyl)imidazol-2-ylidene]copper(I) chloride (31.2 mg, 0.0772 mmol) and sodium *tert*-butoxide (50.0 mg, 0.520 mmol) were stirred vigorously in anhydrous toluene (10 mL) for 10 minutes. To this solution, triethylsilane (2.05 mL, 12.9 mmol) was added dropwise *via* syringe and the solution stirred for a further 10 minutes, upon which ketone susbtrate (2.57 mmol) was added and the mixture heated to 80 ^{o}C for 2 hours under an inert atmosphere. After this time, the mixture was filtered through a celite plug and rinsed with a portion of ethyl acetate (10 mL) which was concentrated under reduced pressure to afford spectroscopically pure title compound as a colourless oil. Yield: 94 % or above.[7]

Hydrosilylation Procedure of Functionalised Ketones *via* Electrogenerated Catalyst:

A freshly prepared anhydrous solution of 1,3-*bis*(2,4,6-trimethylphenyl)imidazolium chloride (45 mg, 0.13 mmol) in acetonitrile (20 mL) was recirculated through a continuous electrochemical flow reactor at 0.50 mLmin^{-1} under a fixed applied potential of 2.50 V ($i_{init.}$ = 3.00 mA) at room temperature for 80 minutes. After this time (t_{80}), the solution (5.0 mL, 0.03 mmol) was flowed directly into a flame-dried Schlenk flask charged with sodium *tert*-butoxide (19.0 mg, 0.20 mmol) in anhydrous toluene (10 mL) and stirred vigorously at room temperature under an inert atmosphere for 10 minutes. To this solution, triethylsilane (0.81 mL, 5.07 mmol) was added dropwise *via* syringe and the solution stirred for a further 10 minutes at 80 ˚C, upon which ketone substrate (1.00 mmol) was added and the mixture stirred at 80 ^{o}C for 2 – 6.5 hours under an inert atmosphere. After this time, the mixture was filtered through a celite plug and rinsed with a portion of ethyl acetate (10 mL) which was concentrated under reduced pressure to afford spectroscopically pure title compound as a colourless oil. Yield: 94 % or above.

Preparation of (dicyclohexylmethoxy)triethylsilane:

Title compound isolated as a pale yellow oil. Yield: 0.78 g, 2.50 mmol, 97 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.14 (t, *J* = 6.0 Hz, 1H, H_{α}OSi), 1.85 – 1.70 (m, 6H, Cy*H*), 1.70 – 1.59 (m, 2H, Cy*H*), 1.59 – 1.48 (m, 2H, Cy*H*), 1.47 – 1.33 (m, 2H, Cy*H*), 1.28 – 0.93 (m) and 0.97 (t, *J* = 8.1 Hz, 19H, SiCH_2), 0.61 (q, *J* = 8.1 Hz, 6H, CH_2CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 81.9, 41.1, 30.7, 28.1, 26.7, 7.2, 5.6 ppm.

Preparation of [1-(furanyl-2yl)ethoxy]triethylsilane:

Title compound isolated as a pale yellow oil. Yield: 0.55 g, 2.44 mmol, 95 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 (d, *J* = 2.6 Hz, 1H, fur*H*), 6.34 – 6.24 (m, 1H, fur*H*), 6.18 (d, *J* = 2.6 Hz, 1H, fur*H*), 4.88 (q, *J* = 6.4 Hz, 1H, H_αOSi), 1.50 (d, *J* = 6.4 Hz, 3H, CH_3), 0.94 (t, *J* = 8.0 Hz, 9H, CH_2CH_3), 0.61 (q, *J* = 8.0 Hz, 6H, CH_2CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 158.2, 141.2, 109.9, 104.7, 64.1, 22.9, 6.6, 4.6 ppm.

Preparation of [1-(thien-2-yl)ethoxy]triethylsilane:

Title compound isolated as a pale yellow oil. Yield: 0.60 g, 2.50 mmol, 97 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (d, *J* = 3.6 Hz, 1H, thio*H*), 6.95- 6.87 (m, 1H, thio*H*), 6.88 (d, *J* = 3.6 Hz, 1H, thio*H*), 5.14 (q, *J* = 6.4 Hz, 1H, H_αOSi), 1.55 (d, *J* = 6.4 Hz, 3H, CH_3), 0.96 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 0.63 (q, *J* = 7.9 Hz, 6H, CH_2CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 151.5, 126.3, 123.6, 122.0, 66.9, 27.1, 6.8, 4.7 ppm.

Preparation of [1-pyridin-2-yl)ethoxy]triethylsilane:

Title compound isolated as a pale yellow oil. Yield: 0.57 g, 2.40 mmol, 94 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J* = 4.0 Hz, 1H, pyr*H*), 7.72 – 7.63 (m, 1H, pyr*H*), 7.51 (d, *J* = 4.0 Hz, 1H, pyr*H*), 7.17 – 7.06 (m, 1H, pyr*H*), 4.92 (q, *J* = 6.4 Hz, 1H, H_αOSi), 1.44 (d, *J* = 6.4 Hz, 3H, CH_3), 0.89 (t, *J* = 8.0 Hz, 9H, CH_2CH_3), 0.51 (q, *J* = 8.0 Hz, 6H, CH_2CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 165.8, 148.3, 136.5, 121.6, 119.2, 71.8, 25.5, 6.7, 4.7 ppm.

Preparation of [1-(2-chlorophenyl)ethoxy]triethylsilane:

Title compound isolated as a pale yellow oil. Yield: 0.15 g, 0.98 mmol, 97 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, *J* = 6.0 Hz, 1H, aryl*H*), 7.26 (d, *J* = 6.0 Hz, 1H, aryl*H*), 7.14 (t, *J* = 6.0 Hz, 2H, aryl*H*), 5.22 (q, *J* = 6.4 Hz, 1H, H_αOSi), 1.40 (d, *J* = 6.4 Hz, 3H, CH_3), 0.90 (t, *J* = 6.0 Hz, 9H, CH_2CH_3), 0.51 (q, *J* = 6.0 Hz, 6H, CH_2CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 144.4, 130.6, 128.9, 127.8, 127.0, 126.9, 67.0, 25.2, 6.7, 4.4 ppm.

All above data are in agreement with those reported in the literature.[7]

11. References

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