A Kinetics Study of Copper-Catalysed Click Reactions in Ionic Liquids

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Electronic Supplemental Information

1. Ionic Liquid Cation and Anion Structures and Acronyms

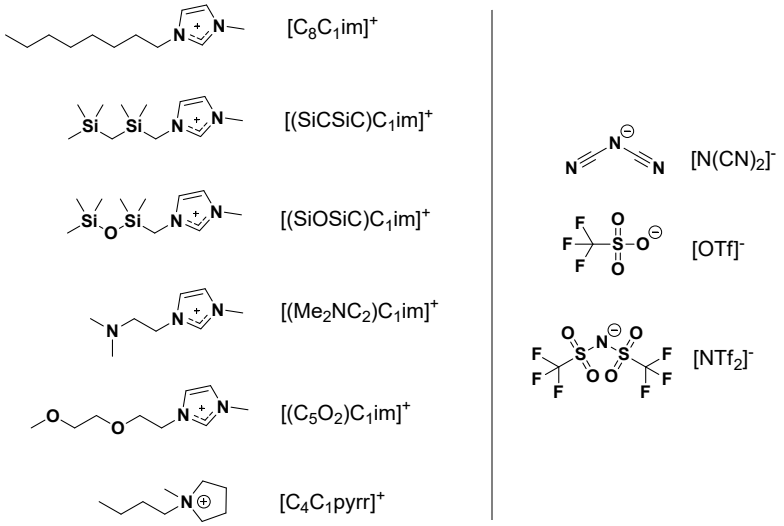

Figure S1. Schematic structures and acronyms for cations and anions studied in this work

2. Synthetic Details

1-Methylimidazole, lithium bis-(trifluoromethanesulfonyl)imide, lithium trifluoromethanesulfonate, chloromethyltrimethylsilane, and phenylacetylene were purchased from *Fluorochem*. 1-Methylimidazole was dried over potassium hydroxide (KOH) pellets for 24h and distilled at reduced pressure, stored under argon. Phenylacetylene was dried over CaH_2, distilled at reduced pressure, passed through a short column of activated alumina and stored under argon. Sodium dicyanamide was purchased from *Merck*. Chloromethyldimethylchlorosilane was purchased from *Gelest*, stored under argon, and used without further purification. Potassium trimethylsilanolate was purchased from *Acros Organics* as a 2M solution in THF under argon and used as received.

All ionic liquid precursors and copper catalysts were synthesized under argon atmosphere using Schlenk techniques, oven-dried glassware, and dry solvents.

3. Analytical Methods for Structure Determination

NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded using *Bruker Fourier-300* spectrometer, chemical shifts were referenced against to the residual NMR solvent signal - ^{1}H: DMSO-d_6, δ = 2.50 ppm; $CDCl_3$, δ = 7.26 ppm; D_2O, δ = 4.79 ppm, ^{13}C: DMSO-d_6, δ = 39.5 ppm; $CDCl_3$, δ = 77.2 ppm

UHPLC–TOF-HRMS system. The chromatography – mass spectrometry system and the method used are described in our previous work.[1]

Elemental analysis. Elemental analyses were conducted on *Carlo Erba CHNSeO EA-1108* apparatus.

4. Synthetic Procedures

Benzyl azide was prepared as described before.[2]

^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.64 – 7.04 (m, 5H), 4.44 (s, 2H) ppm

1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfony)imide was prepared as described before.[3]

^{1}H NMR (300 MHz, DMSO-d_6, δ): 3.57 – 3.22 (m, 6H), 2.98 (s, 3H), 2.19 – 1.99 (m, 4H), 1.77 – 1.59 (m, 2H), 1.42 – 1.21 (m, 2H), 1.00 – 0.85 (m, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 13.4, 19.3, 21.1, 25.0, 47.5, 63.0, 63.4, 119.5 (q, J_{CF} = 321 Hz) ppm

1-(2,2,4,4-Tetramethyl-2,4-disilapentyl)-3-methylimidazolium chloride, 1-(2,2,4,4-tetramethyl-2,4-disilapentyl)-3-methylimidazolium dicyanamide, 1-(2,2,4,4-tetramethyl-2,4-disilapentyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, 1-methyl-3-pentamethyldisiloxymethylimidazolium chloride, 1-methyl-3-pentamethyldisiloxymethylimidazolium dicyanamide, 1-methyl-3-pentamethyldisiloxymethylimidazolium bis(trifluoromethanesulfonyl)imide, 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide were prepared as described previously.[1]

1-Methyl-3-octylimidazolium bromide [C_8C_1im]Br. 1-Bromooctane (67.73 g, 350 mmol, 1.3 eq) was added to a solution of 1-methylimidazole (21.60 g, 263 mmol, 1.0 eq) in dry acetonitrile (100 mL) with stirring. The solution was stirred for 4 days at 50 °C. No residual 1-metlylimidazole could be detected by NMR in the reaction mixture after this time. The reaction mixture was slightly cooled and evaporated *via* rotary evaporation. The resulting viscous substance was purified by washing with petroleum ether (3x100 mL). The solvent was removed in *vacuo* and the liquid was dried at reduced pressure with stirring (50 °C, 0.1 mbar, 4 h) to afford a slightly yellow viscous material (57.96 g, 81%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.29 – 9.37 (m, 1H), 7.90 – 7.82 (m, 1H), 7.81 – 7.72 (m, 1H), 4.18 (t, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.87 – 1.61 (m, 2H), 1.06 – 1.37 (m, 10H), 0.99 – 0.68 (m, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 136.5, 123.5, 122.2, 48.6, 35.7, 31.1, 29.4, 28.5, 28.3, 25.5, 22.0, 13.9 ppm

1-Methyl-3-octylimidazolium dicyanamide [C_8C_1im][$N(CN)_2$]. 1-Methyl-3-octylimidazolium bromide (11.84 g, 43 mmol, 1.0 eq) was dissolved in water (20 mL). To this solution sodium dicyanamide (3.82 g, 43 mmol, 1.0 eq) in water (20 mL) was added. The mixture was extracted with dichloromethane (3x50 mL). the combined organic phases were washed with water (8x10 mL). The organic phase was filtered through the hydrophobic filter paper. The solvent was evaporated *via* rotary evaporation

and remaining ionic liquid was stirred at reduced pressure (60 ˚C, 0.1 mbar, 4h) to afford a viscous colourless liquid (9.68 g, 86%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.09 – 9.17 (m, 1H), 7.74 – 7.79 (m, 1H), 7.65 – 7.71 (m, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.70 – 1.85 (m, 2H), 1.07 – 1.34 (m, 10H), 0.77 – 0.92 (m, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 136.5, 123.6, 122.2, 119.1 ($[N(CN)_2]^-$), 35.7, 31.2, 29.4, 28.4, 25.5, 22.1, 13.9 ppm
HRMS (ESI+) m/z: $[M]^+$ Calcd for $C_{12}H_{23}N_2^+$ 195.1861; Found 195.1863
HRMS (ESI–) m/z: $[M]^-$ Calcd for $C_2N_3^-$ 66.0092; Found 66.0060

1-Methyl-3-octylimidazolium trifluoromethanesulfonate [C_8C_1im][OTf]. 1-Methyl-3-octylimidazolium bromide (3.61 g, 13 mmol, 1.0 eq) was dissolved in water (15 mL). To this solution lithium trifluoromethanesulfonate (2,05 g, 13 mmol, 1.0 eq) in water (15 mL) was added. This mixture was extracted with dichloromethane (3x15 mL). The combined organic phases were washed with water (6x3 mL) until the washing tested negative with 0.1 M $AgNO_3$ solution. The DCM phase was filtered through the hydrophobic filter paper. The solvent was evaporated in *vacuo* and the remaining liquid stirred at reduced pressure (60 ˚C, 0.1 mbar, 4h) to afford a viscous colourless ionic liquid (4.33 g, 96%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.13 – 9.03 (m, 1H), 7.79 – 7.72 (m, 1H), 7.71 – 7.63 (m, 1H), 3.85 (s, 3H), 4.15 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.70 (m, 2H), 1.36 – 1.14 (m, 10H), 0.92 – 0.76 (m, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 136.5, 123.6, 122.3, 120.7 (q, 1C, J_{CF}=324 Hz), 48.8, 35.7, 31.2, 29.4, 28.5, 28.4, 25.5, 22.1, 13.9 ppm
HRMS (ESI+) m/z: $[M]^+$ Calcd for $C_{12}H_{23}N_2^+$ 195.1861; Found 195.1873
HRMS (ESI–) m/z: $[M]^-$ Calcd for $CF_3O_3S^-$ 148.9520; Found 148.9507

1-Methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide [C_8C_1im][NTf_2]. 1-Methyl-3-octylimidazolium bromide (10.92 g, 40 mmol, 1.0 eq) was dissolved in water (20 mL). To this solution lithium bis(trifluoromethanesulfonyl)imide (11,23 g, 40 mmol, 1.0 eq) dissolved in water (20 mL) was added. The combined solutions were extracted with dichloromethane (3x30 mL). The combined organic phases were washed with water (5x10 mL) until the washing tested negative with 0.1 M $AgNO_3$ solution. The organic phase was filtered through the hydrophobic filter paper. The solvent was evaporated via rotary evaporation. The ionic liquid was further dried by stirring at reduced pressure (60 ˚C, 0.1 mbar, 4h) to afford a viscous colourless liquid (14.64 g, 79%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.07 – 9.11 (m, 1H), 7.64 – 7.68 (m, 1H), 7.71 – 7.75 (m, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 1.70 – 1.87 (m, 2H), 1.16 – 1.36 (m, 10H), 0.80 – 0.92 (m, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 136.9, 124.0, 122.6, 120.0 (q, 2C, J_{CF}=322 Hz), 49.3, 36.0, 32.6, 29.8, 28.9, 28.8, 25.9, 22.5, 24.1 ppm

3-(2-(Dimethylamino)ethyl)-1-methylimidazolium dichloride [$(N(Me)_2C_2)C_1$im]Cl·HCl. 2-Dimethylamino dichloride (9.99 g, 69 mmol, 1.0 eq) was suspended in dry acetonitrile (25 mL), stirred at 50 °C for 1h. To the obtained

suspension 1-methylimidazole (5,70 g, 69 mmol, 1.0 eq) dissolved in dry MeCN (10 mL) was added. The reaction mixture was refluxed for 72 h. The resulting solid was filtered and recrystalized from ethanol-water. White crystals were obtained (3.12 g, 16%, m.p. 215-217 °C)

^{1}H NMR (300 MHz, D_2O, δ): 8.97 – 8.90 (m, 1H), 7.67 – 7.60 (m, 1H), 7.58 – 7.51 (m, 1H), 4.73 (t, *J* = 6.8 Hz, 2H), 3.93 (s, 3H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.00 (s, 6H) ppm
^{13}C NMR (75 MHz, D_2O, δ): 136.9, 124.5, 122.2, 55.6, 43.8, 43.2, 36.0 ppm

3-(2-(Dimethylamino)ethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide [$(N(Me)_2C_2)C_1$im][NTf_2].
3-(2-(Dimethylamino)ethyl-1-methylimidazolium chloride (3.00 g, 13 mmol, 1.0 eq), K_2CO_3 (2.20 g, 16 mmol, 1.2 eq) and lithium bis(trifluoromethanesulfonyl)imide (2.48 g, 13 mmol, 1.0 eq) were dissolved in water (15 mL) and stirred for 2h. The aqueous phase was extracted with dichloromethane (3x15 mL). The combined organic phases were washed with water (6x2 mL) until the washings tested negative with 0.1M $AgNO_3$. The organic phase was filtered through the hydrophobic filter paper. The solvent was removed in *vacuo* and the remaining liquid stirred at reduced pressure (60 ˚C, 0.1 mbar, 24h) to afford a viscous colourless ionic liquid (2.79 g, 48%).

^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.98 – 9.12 (m, 1H), 7.69 –7.75 (m, 1H), 7.62 – 7.67 (m, 1H), 4.17 – 4.30 (m, 2H), 3.86 (s, 3H), 2.57 – 2.67 (m, 2H), 2.17 (s, 6H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 137.1, 123.7, 123.0, 119.9 (q, 2C, J_{CF}=322 Hz), 58.1, 46.9, 45.2, 36.1 ppm
HRMS (ESI+) m/z: $[M]^+$ Calcd for $C_8H_{16}N_3^+$ 154.1344; Found 154.1360
HRMS (ESI–) m/z: $[M]^-$ Calcd for $C_2F_6NO_4S_2^-$ 279.9173; Found 279.9172

1-(2-(2-Methoxyethoxy)ethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [$(C_5O_2)C_1$im][NTf_2] was prepared as described before.[4]

^{1}H NMR (300 MHz, DMSO-d_6, δ): 9.08 – 9.01 (m, 1H), 7.75 – 7.65 (m, 2H), 4.37 – 4.28 (m, 2H), 3.86 (s, 3H), 3.81 – 3.71 (m, 2H), 3.59 – 3.50 (m, 2H), 3.45 – 3.39 (m, 2H), 3.22 (s, 3H) ppm
^{13}C NMR (75 MHz, DMSO-d_6, δ): 35.7, 48.8, 58.0, 68.2, 69.4, 71.1, 119.6 (q, 2C, J_{CF}=322 Hz), 123.4, 136.9 ppm

Bis[(tetrabutylammonium)di-μ-iodo-diiododicuprate(I)] [$(nBu_4N)_2$][Cu_2I_4] was prepared as described before.[5]

^{1}H NMR (300 MHz, DMSO-d_6, δ): 1.00 (t, *J* = 7.3 Hz, 24H), 1.39 – 1.57 (m, 16H), 1.60 – 1.77 (m, 16H), 3.18 – 3.42 (m, 16H) ppm
Elemental analysis (expected for $C_{32}H_{72}Cu_2I_4N_2$): C, 33.91 (34.33); H, 6.30 (6.48); N, 2.46 (2.50)%

Bis[(tetrabutylammonium)di-μ-iodo-dibromodicuprate(I)] [$(nBu_4N)_2$][Cu_2Br_4].
Freshly prepared CuBr[6] (0.25 g, 17.4 mmol, 1.0 eq) and tetrabutylammonium bromide (0.56 g, 17.4 mmol, 1.0 eq) were dissolved in dry THF (2.5 mL) in an atmosphere of argon and stirred at 50 °C until a homogeneous solution was obtained. The reaction mixture was cooled to room temperature and further to 6 °C in an ice bath. To the stirred

reaction mixture, degassed ^{t}BuOMe (4 mL) was added. After addition, the mixture was stirred at 6 °C for 1 h. The resulting solid was filtered and washed with degassed ^{t}BuOMe and dried *in vacuo* at 50 °C. A white powder (1.28 g, 79%) was obtained.

^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.93 (t, J = 7.3 Hz, 24H), 1.40 – 1.22 (m, 16H), 1.65 – 1.48 (m, 16H), 3.22 – 3.10 (m, 16H) ppm
Elemental analysis for $C_{32}H_{72}Cu_2Br_4N_2$: Calculated: C, 41.25; H, 7.79; N, 3.01. Experimental: C, 41.40; H, 7.81; N, 2.98.

5. Methods for Obtaining and Analysing Kinetic Data

For sample preparation and acquisition details, refer to the main text.

NMR spectra were analysed using *MestReNova v14.2.0-26256* software. After spectra acquisition, the phase and baseline were corrected using the automated tools *Phase Correction Automatic* and *Baseline Correction – Whittaker Smoother*. For each of the ionic liquid solvents, suitable integration regions were chosen and saved as *predefined integrals* to ensure a constant integration region in different experiments where the same ionic liquid was used.

It was important to choose peaks that do not overlap with other peaks. To plot the kinetic curves, protons from the product and ionic liquid were used: (**A**, 1-4-triazole; **B**, benzyl azide; **C**, imidazolium ionic liquid; **D**, pyrrolidinium ionic liquid; Fig. S2) as no other peaks interfered with the determination of integral values. The target value to obtain was the amount of product in moles, so that the conversion in time could be calculated.

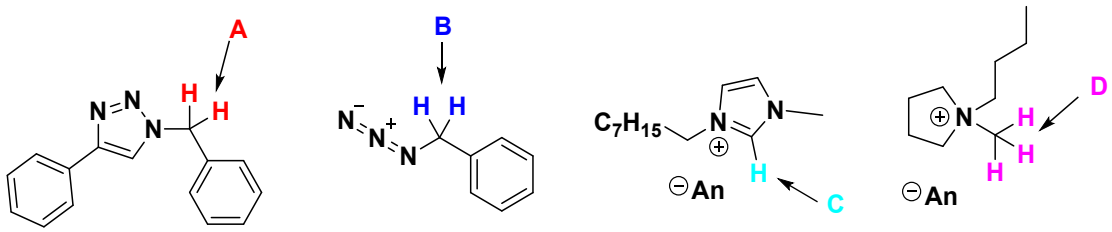

Figure S2.

The relation between NMR integral value, number of protons, and amount of substance is provided in equation S1:

$$\frac{I_p \cdot nH_p^{-1}}{I_{IL} \cdot nH_{IL}^{-1}} = \frac{n_p,mol}{n_{IL},mol} \qquad \text{(eq.S1)}$$

where I_p and I_{IL} are integrals of product protons (Fig. S2, **A**) and IL proton(s) (Fig. S2 **C** or **D**). nH_p and nH_{IL} are the number of protons in the product and IL, respectively, n_p and n_{IL} are the amounts in moles. The amounts of benzylazide (n_b, mol) and phenylacetylene (n_{ph}, mol) can be obtained in a similar fashion.

An example of obtaining a kinetic curve for copper(I) iodide catalysed benzyl azide-phenylacetylene cycloaddition in $[C_8C_1im][N(CN)_2]$ medium is provided. Using Equation S1, the amount of benzyl azide and the product (n_b and n_p, mol) were

calculated and these values were used in Equation S2 to calculate the conversion (C, %) in a given time period.

$$C\ (\%) = \frac{n_p\ mmol}{0{,}500\ mmol} * 100 \qquad \text{(eq.S2)}$$

The calculated benzyl azide and product conversion / residual values in different time stamps are shown in Table S1. Using this data set, a kinetic curve was plotted that illustrates the copper(I) iodide-catalysed benzyl azide-phenylacetylene cycloaddition reaction was plotted (fig. S4). Reasons for ($\mathbf{C_b}$ + $\mathbf{C_p}$) exceeding 100% could be associated with variations in IL and reagent purity (assay) and/or the experimental error associated with integration of low intensity signals with respect to larger intensity reference (IL) signals.[7]

Table S1. Integral values of benzylazide (I_b), product (I_p) and calculated conversions

t, min	I_b	I_p	I_{IL}	C_b, %	C_p, %
35	0.4162	0.0171	1.000	101.5619	4.1728
95	0.3997	0.0465	1.000	97.5356	11.3470
160	0.3477	0.0845	1.000	84.8464	20.6199
223	0.3015	0.1200	1.000	73.5726	29.2826
284	0.2667	0.1597	1.000	65.0806	38.9703
1337	0.0501	0.3882	1.000	12.2255	94.7293

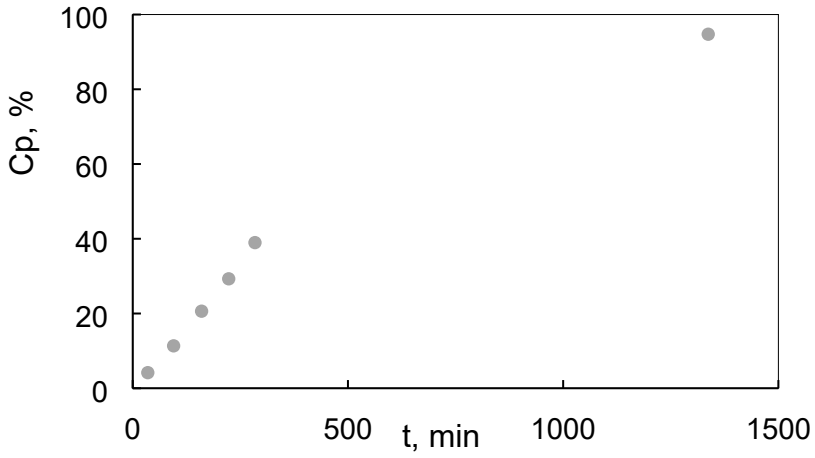

Figure S3. Copper(I) iodide catalysed benzy lazide-phenylacetylene cycloaddition reaction in $[C_8C_1im][N(CN)_2]$. Conversion of reaction products (C_p,%) over time (t, min).

6. Molar Ratios of Copper(I) Sources in Ionic Liquids

Table S2. Molar ratios *n*(catalyst) to *n*(IL) in solutions used for obtaining kinetic profiles

Solvent	*n*($Cu^{(I)}$ source) / *n*(IL)			
	CuI	$[Cu_2I_4]^{2-}$ [b]	$[Cu_2Br_4]^{2-}$ [b]	$[Cu(MeCN)_4]^{+}$ [c]
$[C_8C_1im][NTf_2]$	[a]	0.0104	0.0106	0.0207
$[C_8C_1im][N(CN)_2]$	0.0148	0.0070		0.0147
$[C_8C_1im][OTf]$	[a]	0.0087		
$[(C_5O_2)C_1im][NTf_2]$	[a]	0.0097		
$[(SiCSiC)C_1im][NTf_2]$	[a]	0.0136		
$[(SiCSiC)C_1im][N(CN)_2]$	0.0178	0.0088		
$[(SiOSiC)C_1im][NTf_2]$	[a]	0.0120		
$[(SiOSiC)C_1im][N(CN)_2]$	0.0173	0.0084		
$[C_4C_1pyrr][NTf_2]$	[a]	0.0089		

[a] solubilisation could not be achieved at any composition that would be visually detectable
[b] tetrabutylammonium salt
[c] tetrafluoroborate salt

7. Testing for Reaction Autocatalysis

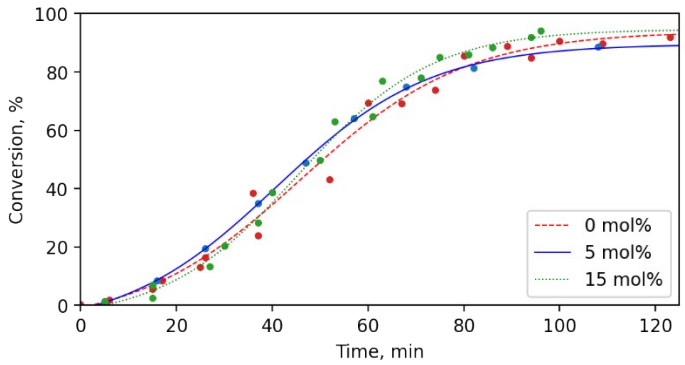

Figure S4. Kinetic profiles at 75 °C for the CuAAC reaction in $[C_8C_1im][NTf_2]$ comparing the effect of initially adding 0, 5 or 15 mol% of the 1,4-triazole product. Catalyst $[Cu_2I_4]^{2-}$

8. Reproducibility and uncertainty analysis for the CuAAC reaction in $[C_8C_1im][NTf_2]$

Table S3. Fitting parameters and their uncertainties for the dataset of 3 combined kinetics experiments

	Parameters for the sigmoid fit	Parameter uncertainty, ±	Fit equation. Conversion *c* (%), time *t* (min)
L (%):	97.0560	5.3089	$c = b + \frac{L}{e^{k(t_0 - t)} + 1}$
t0 (s):	41.6390	1.7151	
k (1/s):	0.074878	0.009451	
b (%):	-4.6972	3.8983	

Table S4. Calculated and experimental conversions and their absolute deviations for the dataset of 3 combined kinetics experiments

Time (min)	Conversion (%) calculated from the fit	Conversion (%), experimental	Absolute deviation (%)
0	-0.58	0.41	1.00
5	1.17	1.76	0.59
5	1.17	1.35	0.18
6	1.60	1.42	0.18
15	6.93	8.58	1.65
15	6.93	5.53	1.39
17	8.55	6.15	2.40
25	16.99	13.08	3.91
26	18.27	23.90	5.63
28	21.00	16.51	4.49
36	33.74	43.08	9.34
40	40.86	38.69	2.17
43	46.30	38.48	7.83
52	61.76	69.33	7.56
60	72.77	73.94	1.17
63	76.05	69.25	6.80
74	84.46	85.61	1.15
80	87.16	89.72	2.56
83	88.16	84.88	3.29
89	89.64	88.76	0.88
100	91.15	94.80	3.65
106	91.58	91.99	0.41
131	92.24	90.66	1.58
		Max, %	9.34
		Average, %	3.32
		Standard deviation	2.70

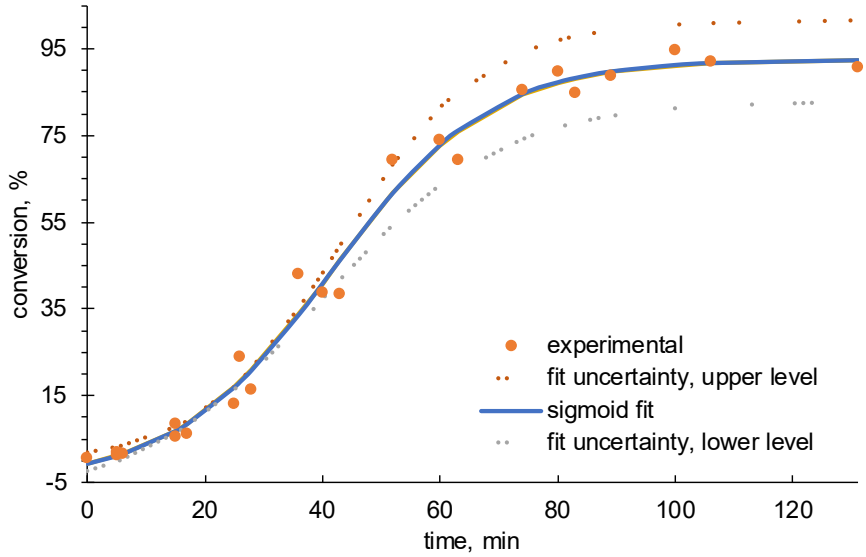

Figure S5. Fitting for the combined dataset of 3 kinetics experiments and estimated fit uncertainties

Table S5. Raw data - calculated and experimental conversions and their standard deviations (for datapoints sampled within ±3 min) for 3 replicated kinetics experiments

Experiment 1		Experiment 2		Experiment 3		c_{AVG} (%)	STDEV
time (min)	conversion *c*, (%)	time (min)	conversion *c*, (%)	time (min)	conversion *c*, (%)		
0	0,41						
5	1.76	**5**	1.35	**6**	1.42	1.51	0.22
15	8.58	**15**	5.53	**17**	6.15	6.75	1.61
26	23.90	**25**	13.08	**28**	16.51	17.83	5.53
36	43.08	40	38.69	43	38.48		
52	69.33	60	73.94	63	69.25		
74	85.61	80	89.72	83	84.88		
89	88.76	100	94.80	106	91.99		
131	90.66						
						Max:	5.53
						Average:	2.45

9. References

1 E. Bakis, K. Goloviznina, I. C. M. Vaz, D. Sloboda, D. Hazens, V. Valkovska, I. Klimenkovs, A. Padua and M. Costa Gomes, *Chem. Sci.*, 2022, **13**, 9062–9073.

2 S. G. Alvarez and M. T. Alvarez, *Synthesis (Stuttg).*, 1997, **1997**, 413–414.

3 N. L. Lancaster, P. A. Salter, T. Welton and G. B. Young, *J. Org. Chem.*, 2002, **67**, 8855–8861.

4 E. Bakis, A. van den Bruinhorst, L. Pison, I. Palazzo, T. Chang, M. Kjellberg, C. C. Weber, M. Costa Gomes and T. Welton, *Phys. Chem. Chem. Phys.*, 2021, **23**, 4624–4635.

5 S. Nekkanti, K. Veeramani, N. Praveen Kumar and N. Shankaraiah, *Green Chem.*, 2016, **18**, 3439–3447.

6 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, Eds., *Vogel's Textbook of Practical Organic Chemistry*, Longmans, London, 1989.

7 B. J. Butler, D. S. Thomas, J. M. Hook and J. B. Harper, *Magn. Reson. Chem.*, 2016, **54**, 423–428.