Electronic Supporting Information for

"Understanding the effects of solvate ionic liquids as solvents on substitution processes"

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Synthesis of the solvate ionic liquids 1 and 2

Lithium triethylene glycol dimethyl ether *bis*(trifluoromethanesulfonyl)imide ($[Li(G3)][N(SO_2CF_3)_2]$) 1

Triethylene glycol dimethyl ether (50.4g, 0.283 mol) was rinsed into dry lithium *bis*(trifluoromethanesulfonyl)imide (81.1 g, 0.283 mol) with dichloromethane (20 mL). The resulting mixture was stirred under nitrogen for 3 days after which the dichloromethane was removed under reduced pressure. The residual liquid was then further dried under reduced pressure for 24 h to give the product **1** as a clear, colourless liquid (125 g, 0.269 mol, 95%) with a water content of < 200 ppm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.46 (s, 6H $OC\underline{H}_3$), 3.58-3.65 (m, 4H, $C\underline{H}_2OCH_3$), 3.65-3.76 (m, 8H, $C\underline{H}_2OC\underline{H}_2$).[1]

Lithium tetraethylene glycol dimethyl ether *bis*(trifluoromethanesulfonyl)imide ($[Li(G4)][N(SO_2CF_3)_2]$) 2

Tetraethylene glycol dimethyl ether (81.5 g, 0.365 mol) was rinsed into dry lithium *bis*(trifluoromethanesulfonyl)imide (105 g, 0.364 mol) with dichloromethane (20 mL) and the resulting mixture was stirred under nitrogen for 2 days. Excess solvent was removed under reduced pressure and the residue dried for 24 h to give the product **2** as a clear, colourless liquid (186 g, 0.364 mol, 99%) with a water content of < 300 ppm. ^{1}H NMR (400 MHz, $CDCl_3$) δ3.43 (s, 6H $OC\underline{H}_3$), 3.57-3.64 (m, 4H, $C\underline{H}_2OCH_3$), 3.67-3.76 (m, 8H, $C\underline{H}_2OC\underline{H}_2$).[1]

Kinetic analyses

For both of the substitution reactions studied pseudo first order kinetics were observed. The pseudo first order rate constant was obtained from Equation S1 using the LINEST function in Microsoft Excel with the second order rate constant being obtained from Equation S2.

$$\ln [\mathrm{A}] = -k_{obs}t$$

Equation S1: Log form of the integrated first order rate equation; [A] = integral of limiting reagent, k_{obs} = the pseudo first order rate constant and t = time.

$$k_{obs} = k_2[B]$$

Equation S2: Relationship used to convert pseudo first order rate constants into the corresponding bimolecular rate constants; k_2 = the bimolecular rate constant, k_{obs} = the pseudo first order rate constant and [B] = the concentration of the starting material (in excess).

The activation parameters were determined through plotting a function of the rate constant against the inverse of the temperature according to the bimolecular Eyring equation[2] (Equations S3). This was achieved using the LINEST function in Microsoft Excel where the enthalpy of activation was determined from the slope of the graph and the entropy of activation from the intercept.

$$\ln\left(\frac{k_2 h}{k_B R T^2}\right) = \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT}$$

Equation S3: The bimolecular Eyring Equation.

Stock solution composition and rate constant data for the S_N2 reaction

Table S1 Composition of stock solutions (2 mL) by mass, including resultant mole fraction and concentration of the nucleophile [Nu] **4**, for the mole fraction dependent kinetic studies of the reaction between pyridine (Nu) **4** and benzyl bromide **5** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1** and acetonitrile.

Mass salt **1** / g	Mass CH_3CN / g	Mass Nu **4** / g	[Nu] **5** / mol L^{-1}	χ_1
-	1.50	0.089	0.56	0.00
0.704	1.08	0.087	0.55	0.05
1.16	0.851	0.081	0.51	0.10
1.76	0.518	0.080	0.50	0.22
2.21	0.272	0.081	0.51	0.38
2.25	0.190	0.150	0.95	0.42
2.53	0.092	0.092	0.58	0.61
2.70	-	0.091	0.57	0.83

Table S2 Rate constants determined for the mole fraction dependent kinetic studies for the reaction between pyridine **4** and benzyl bromide **5** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1** and acetonitrile at 22.2 ºC. Also included are the corresponding mole fractions of the solvate ionic liquid **1** and concentrations of nucleophile [Nu] **4**. Uncertainties are reported as the standard deviation of at least triplicate results.

χ_1	[Nu] **4** / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.00	0.56	3.46	6.19	6.29 (0.18)
		3.63	6.50	
		3.46	6.18	
0.05	0.55	1.81	3.29	3.51 (0.21)
		1.95	3.53	
		2.05	3.71	
0.10	0.51	1.35	2.64	2.59 (0.04)
		1.32	2.58	
		1.32	2.57	
0.22	0.50	0.735	1.46	1.54 (0.08)
		0.815	1.62	
		0.772	1.53	
0.38	0.51	0.420	0.821	0.87 (0.08)
		0.422	0.825	
		0.390	0.762	
0.42	0.95	0.893	0.942	
		0.851	0.897	
		0.931	0.982	
0.61	0.58	0.286	0.492	0.56 (0.07)
		0.370	0.636	
		0.313	0.537	
0.83	0.57	0.208	0.364	0.36 (0.01)
		0.203	0.356	
		0.203	0.355	

Table S3 Composition of stock solutions (2 mL) by mass, including resultant mole fraction and concentration of the nucleophile [Nu] **4**, for the mole fraction dependent kinetic studies of the reaction between pyridine (Nu) **4** and benzyl bromide **5** in mixtures of $[Li(G4)][N(SO_2CF_3)_2]$ **2** and acetonitrile.

Mass salt **2** / g	Mass CH_3CN / g	Mass Nu **4** / g	[Nu] **4** / mol L^{-1}	χ_2
0.511	1.16	0.107	0.68	0.03
0.855	0.971	0.089	0.56	0.06
0.916	0.945	0.085	0.53	0.07
1.32	0.724	0.083	0.52	0.12
1.81	0.451	0.088	0.55	0.23
2.21	0.210	0.121	0.76	0.39
2.48	0.065	0.119	0.75	0.61
2.65	-	0.086	0.54	0.82

Table S4 Rate constants determined for the mole fraction dependent kinetic studies for the reaction between pyridine **4** and benzyl bromide **5** in mixtures of $[Li(G4)][N(SO_2CF_3)_2]$ **2** and acetonitrile at 22.2 ºC. Also included are the corresponding mole fractions of the solvate ionic liquid **2** and concentrations of nucleophile [Nu] **4**. Uncertainties are reported as the standard deviation of at least triplicate results.

χ_2	[Nu] **4** / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.03	0.68	3.33	4.91	4.75 (0.14)
		3.19	4.70	
		3.15	4.64	
0.06	0.56	2.00	3.57	3.56 (0.07)
		2.00	3.57	
0.07	0.53	1.85	3.46	
		1.94	3.62	
0.12	0.52	1.43	2.74	2.78 (0.03)
		1.46	2.79	
		1.46	2.80	
0.23	0.55	1.04	1.87	1.87 (0.04)
		1.02	1.83	
		1.06	1.91	
0.39	0.76	0.959	1.26	1.26 (0.03)
		0.982	1.29	
		0.943	1.24	
0.61	0.75	0.594	0.790	0.82 (0.08)
		0.684	0.910	
		0.575	0.765	
0.82	0.54	0.339	0.624	0.51 (0.11)
		0.269	0.495	
		0.226	0.415	

Table S5 Composition of stock solutions (2 mL) by mass, including resultant mole fraction and concentration of the nucleophile [Nu] **4**, for the mole fraction dependent kinetic studies of the reaction between pyridine (Nu) **4** and benzyl bromide **5** in mixtures of $Li[N(SO_2CF_3)_2]$and acetonitrile.

Mass salt / g	Mass CH_3CN / g	Mass Nu **4** / g	[Nu] **4** / mol L^{-1}	χ_{salt}
0.196	1.39	0.089	0.56	0.02
0.298	1.38	0.086	0.55	0.03
0.509	1.30	0.081	0.51	0.05
0.831	1.23	0.087	0.55	0.08
1.03	1.08	0.095	0.60	0.11
1.29	0.932	0.088	0.56	0.16
1.56	0.870	0.087	0.55	0.20

Table S6 Rate constants determined for the mole fraction dependent kinetic studies for the reaction between pyridine **4** and benzyl bromide **5** in mixtures of $Li[N(SO_2CF_3)_2]$ and acetonitrile at 22.2 ºC. Also included are the corresponding mole fractions of the salt and concentrations of nucleophile [Nu] **4**. Uncertainties are reported as the standard deviation of triplicate results.

χ_{salt}	[Nu] **4** / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.02	0.56	1.99	3.55	3.56 (0.08)
		1.96	3.49	
		2.05	3.65	
0.03	0.55	1.18	2.16	2.25 (0.14)
		1.19	2.18	
		1.32	2.41	
0.05	0.51	0.803	1.56	1.53 (0.03)
		0.775	1.51	
		0.781	1.52	
0.08	0.55	0.350	0.636	0.64 (0.02)
		0.368	0.668	
		0.346	0.629	
0.11	0.60	0.343	0.572	0.64 (0.06)
		0.393	0.656	
		0.416	0.694	
0.16	0.56	0.198	0.355	0.37 (0.02)
		0.216	0.387	
		0.201	0.361	
0.20	0.55	0.158	0.287	0.29 (0.01)
		0.160	0.291	
		0.156	0.285	

Table S7 Composition of stock solutions (10 mL) by mass, including the resultant mole fractions and concentration of nucleophile [Nu] **4**, for the temperature dependent kinetic studies of the reaction between pyridine (Nu) **4** and benzyl bromide **5** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1**, $[Li(G4)][N(SO_2CF_3)_2]$ **2** and $Li[N(SO_2CF_3)_2]$ in acetonitrile.

Salt	Mass salt/ g	Mass CH_3CN / g	Mass Nu **4** / g	[Nu] **4** / mol L^{-1}	χ_{salt}
$[Li(G3)][N(SO_2CF_3)_2]$ **1**	13.6	-	0.424	0.54	0.83
$[Li(G3)][N(SO_2CF_3)_2]$ **1**[1]	2.69	-	0.103	0.65	0.81
$[Li(G4)][N(SO_2CF_3)_2]$ **2**	13.3	-	0.442	0.56	0.82
$Li[N(SO_2CF_3)_2]$	8.05	4.48	0.424	0.54	0.20

Table S8 Rate constants determined for the temperature dependent kinetic studies of the reaction between pyridine **4** and benzyl bromide **5** in $[Li(G3)][N(SO_2CF_3)_2]$ **1**. Also included are the corresponding mole fractions of the salt **1**, concentrations of nucleophile [Nu] **4** and temperatures used. Uncertainties are reported as the standard deviation of triplicate results.

χ_1	Temp / °C	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.83	42.2	1.11	2.07	2.36 (0.42)
0.83	42.2	1.16	2.16	
0.83	42.3	1.52	2.84	
0.83	52.2	2.48	4.62	5.10 (0.43)
0.83	52.3	2.90	5.43	
0.81	52.3*	3.42	5.25	
0.83	62.2	5.19	9.69	10.3 (0.5)
0.83	62.2	5.58	10.4	
0.83	62.2	5.65	10.6	
0.83	72.1	10.3	19.3	19.7 (0.8)
0.83	72.1	10.0	18.7	
0.83	72.2	11.0	20.5	
0.81	72.2*	13.1	20.1	

Table S9 Rate constants determined for the temperature dependent kinetic studies of the reaction between pyridine **4** and benzyl bromide **5** in $[Li(G4)][N(SO_2CF_3)_2]$ **2**. Also included are the corresponding mole fractions of the salt **2**, concentrations of nucleophile [Nu] **4** and temperatures used. Uncertainties are reported as the standard deviation of triplicate results.

χ_2	Temp / °C	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.82	42.2	2.23	3.99	4.13 (0.13)
	42.2	2.38	4.25	
	42.2	2.32	4.15	
	52.2	4.45	7.98	8.28 (0.71)
	52.2	5.08	9.09	
	52.2	4.34	7.77	
	62.2	9.77	17.5	29.8 (0.3)
	62.2	9.69	17.3	
	62.2	9.43	16.9	
	72.2	19.5	34.9	34.3 (0.6)
	72.2	18.9	33.9	
	72.2	19.0	34.0	

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[1] Stock solution prepared was 2 mL, instead of 10 mL. Rate constant data obtained from this stock solution is highlighted subsequently (*) and does not significantly differ from the results obtain from the 10 mL stock solution.

Table S10 Rate constants determined for the temperature dependent kinetic studies of the reaction between pyridine **4** and benzyl bromide **5** in a mixture of Li[N(SO_2CF_3)$_2$] in acetonitrile. Also included are the corresponding mole fractions of the salt, concentrations of nucleophile [Nu] **4** and temperatures used. Uncertainties are reported as the standard deviation of triplicate results.

χ_{salt}	Temp / °C	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.20	42.2	0.615	1.17	1.20 (0.03)
	42.2	0.647	1.23	
	42.2	0.633	1.20	
	52.2	1.35	2.56	2.41 (0.16)
	52.2	1.28	2.44	
	52.2	1.18	2.24	
	62.2	3.29	6.25	5.93 (0.27)
	62.3	3.04	5.77	
	62.3	3.04	5.78	
	72.2	6.38	12.1	11.3 (0.15)
	72.2	6.42	12.2	
	72.2	5.00	9.49	

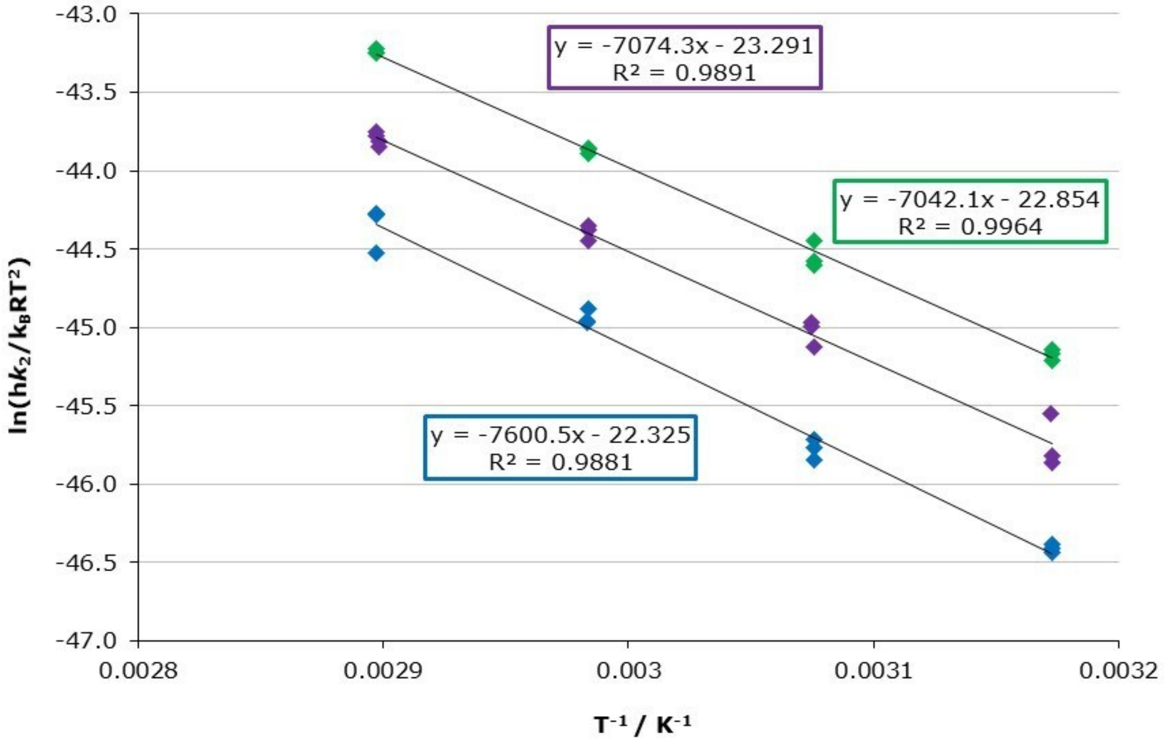

Figure S1 Eyring plots for the reaction between pyridine **4** and benzyl bromide **5** in [Li(G3)][N(SO_2CF_3)$_2$] **1** ($\chi_1 \approx 0.83$, purple), [Li(G4)][N(SO_2CF_3)$_2$] **2** ($\chi_2 \approx 0.82$, green) and Li[N(SO_2CF_3)$_2$] ($\chi_{salt} \approx 0.20$, blue).

Stock solution composition and rate constant data for the S_NAr reaction

Table S11 Composition of stock solutions (2 mL) by mass, including resultant mole fraction and concentration of the nucleophile (ethanol), for the mole fraction dependent kinetic studies of the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1** and ethanol.

Mass salt **1** / g	Mass ethanol / g	Triethylamine / g	χ_1
-	1.50	0.072	0.00
0.588	1.18	0.071	0.05
1.13	0.876	0.071	0.11
1.17	0.857	0.071	0.11
1.61	0.604	0.078	0.20
1.88	0.468	0.071	0.27
2.14	0.321	0.071	0.37

Table S12 Rate constants determined for the mole fraction dependent kinetic studies for the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1** and ethanol at 51.0 ºC, including the resultant mole fractions of the salt **1** in the reaction mixture. Uncertainties are reported as the standard deviation of triplicate results.

χ_1	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.00	1.09	0.0671	0.073 (0.007)
	1.18	0.0726	
	1.31	0.0805	
0.05	11.4	0.890	0.76 (0.11)
	8.88	0.695	
	8.96	0.701	
0.11	15.6	1.64	1.29 (0.26)
	10.1	1.07	
	10.9	1.14	
	12.6	1.33	
0.20	13.5	2.06	1.77 (0.33)
	12.0	1.84	
	9.20	1.40	
0.27	5.50	1.08	1.19 (0.14)
	6.89	1.35	
	5.82	1.14	
0.37	6.45	1.86	1.98 (0.27)
	7.99	2.30	
	6.26	1.80	

Table S13 Composition of stock solutions (2 mL) by mass, including resultant mole fraction and concentration of the nucleophile (ethanol), for the mole fraction dependent kinetic studies of the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in mixtures of [Li(G4)][N($SO_2CF_3)_2$] **2** and ethanol.

Mass salt **2** / g	Mass ethanol / g	Triethylamine / g	χ_2
0.711	1.10	0.071	0.05
1.26	0.796	0.070	0.12
1.66	0.568	0.071	0.20
2.06	0.347	0.070	0.33
2.17	0.282	0.071	0.38

Table S14 Rate constants determined for the mole fraction dependent kinetic studies for the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in mixtures of [Li(G4)][N($SO_2CF_3)_2$] **2** and ethanol at 51.0 ºC, including the resultant mole fractions of the salt **2** in the reaction mixture. Uncertainties are reported as the standard deviation of triplicate results.

χ_2	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.05	9.54	0.798	0.73 (0.06)
	8.10	0.678	
	8.52	0.713	
0.12	9.35	1.08	1.15 (0.06)
	10.1	1.17	
	10.3	1.19	
0.20	7.79	1.26	1.31(0.04)
	8.28	1.34	
	8.14	1.32	
0.33	4.66	1.24	1.18 (0.07)
	4.47	1.19	
	4.13	1.10	
0.38	4.59	1.50	1.37 (0.14)
	4.30	1.41	
	3.73	1.22	

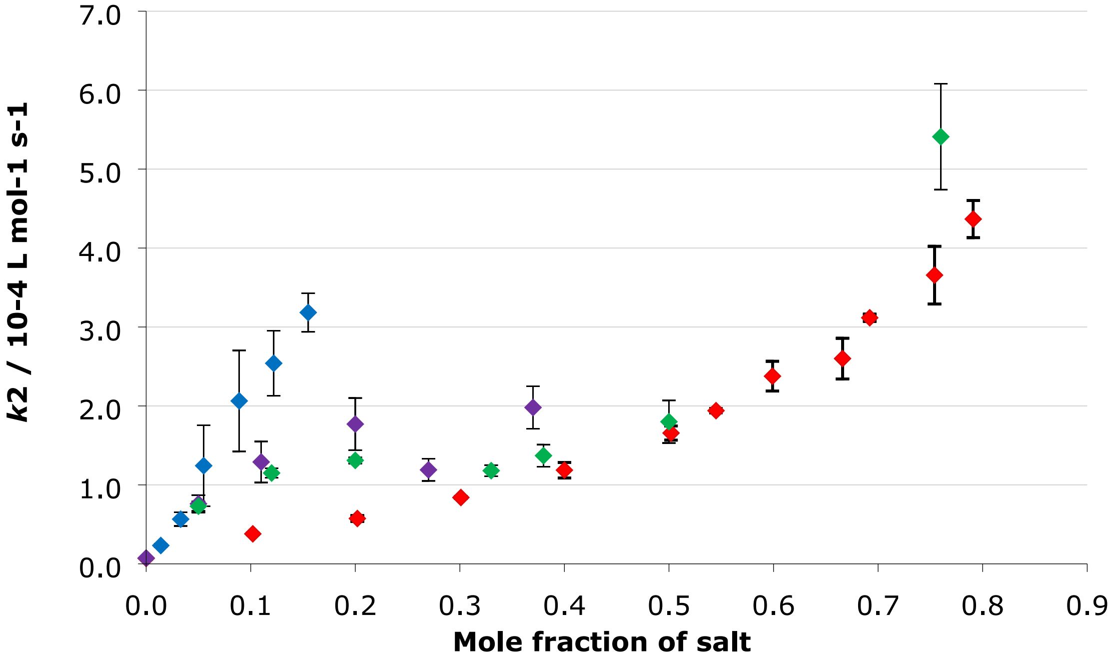

Figure S2 The bimolecular rate constants for the S_NAr reaction between 1-fluoro-2,4-dinitrobenzene **6** and ethanol across a range of different solvent compositions (χ_{salt} 0 – 0.9) of either the ionic liquid [Bmim][N(SO_2CF_3)$_2$] **3** (red),[3] the solvate ionic liquids [Li(G3)][N(SO_2CF_3)$_2$] **1** (purple), [Li(G4)][N(SO_2CF_3)$_2$] **2** (green) or the 'traditional' salt Li[N(SO_2CF_3)$_2$] (blue) in acetonitrile at 51.0 ^{0}C. Uncertainties are the standard deviation of triplicate results, some uncertainties fall with the size of the markers used.

Table S15 Composition of stock solutions (10 mL) by mass, including the resultant mole fractions and concentration of nucleophile (ethanol), for the temperature dependent kinetic studies of the reaction between ethanol and 1-fluoro-2,4-dnitirobenzene **6** in mixtures of $[Li(G3)][N(SO_2CF_3)_2]$ **1** and $[Li(G4)][N(SO_2CF_3)_2]$ **2** in ethanol.

Salt	Mass salt/ g	Mass ethanol / g	Mass triethylamine / g	χ_{salt}
$[Li(G3)][N(SO_2CF_3)_2]$ **1**	8.35	2.91	0.355	0.21
$[Li(G4)][N(SO_2CF_3)_2]$ **2**	8.43	2.77	0.351	0.21
$[Li(G4)][N(SO_2CF_3)_2]$ **2**[2]	1.76	0.516	0.071	0.22

Table S16 Rate constants determined for the temperature dependent kinetic studies of the reaction between ethanol and 1-fluoro-2,4-dnitirobenzene **6** in $[Li(G3)][N(SO_2CF_3)_2]$ **1**. Also included are the corresponding mole fractions of the salt **1** and temperatures used. Uncertainties are reported as the standard deviation of triplicate results.

χ_1	Temp / °C	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.21	31.1	2.00	0.316	0.33 (0.02)
	31.0	2.19	0.346	
	31.0	2.13	0.338	
	40.9	4.69	0.742	0.74 (0.04)
	40.9	4.86	0.769	
	41.1	4.38	0.693	
	51.1	9.49	1.50	1.45 (0.06)
	51.1	9.26	1.47	
	51.1	8.70	1.38	
	60.9	19.2	3.04	2.96 (0.44)
	61.1	21.2	3.36	
	60.9	15.7	2.49	

Table S17 Rate constants determined for the temperature dependent kinetic studies of the reaction between ethanol and 1-fluoro-2,4-dnitirobenzene **6** in $[Li(G4)][N(SO_2CF_3)_2]$ **2**. Also included are the corresponding mole fractions of the salt **2** and temperatures used. Uncertainties are reported as the standard deviation of triplicate results.

χ_2	Temp / °C	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0.21	31.1	2.20	0.366	0.43 (0.11)
0.21	31.1	2.44	0.406	
0.21	31.0	3.58	0.594	
0.22**	31.1	2.00	0.357	
0.21	40.9	4.27	0.709	0.68 (0.04)
0.21	41.0	4.17	0.692	
0.21	41.0	3.82	0.635	
0.21	51.1	8.53	1.42	1.42 (0.16)
0.21	51.0	9.50	1.58	
0.21	51.1	7.63	1.27	
0.21	61.1	25.7	4.27	3.22 (0.80)
0.21	61.1	15.8	2.63	

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[2] Stock solution prepared was 2 mL, instead of 10 mL. Rate constant data obtained from this stock solution is highlighted subsequently (**) and does not significantly differ from the results obtain from the 10 mL stock solution.

0.21	61.0	15.4	2.56
0.22**	61.0	19.1	3.42

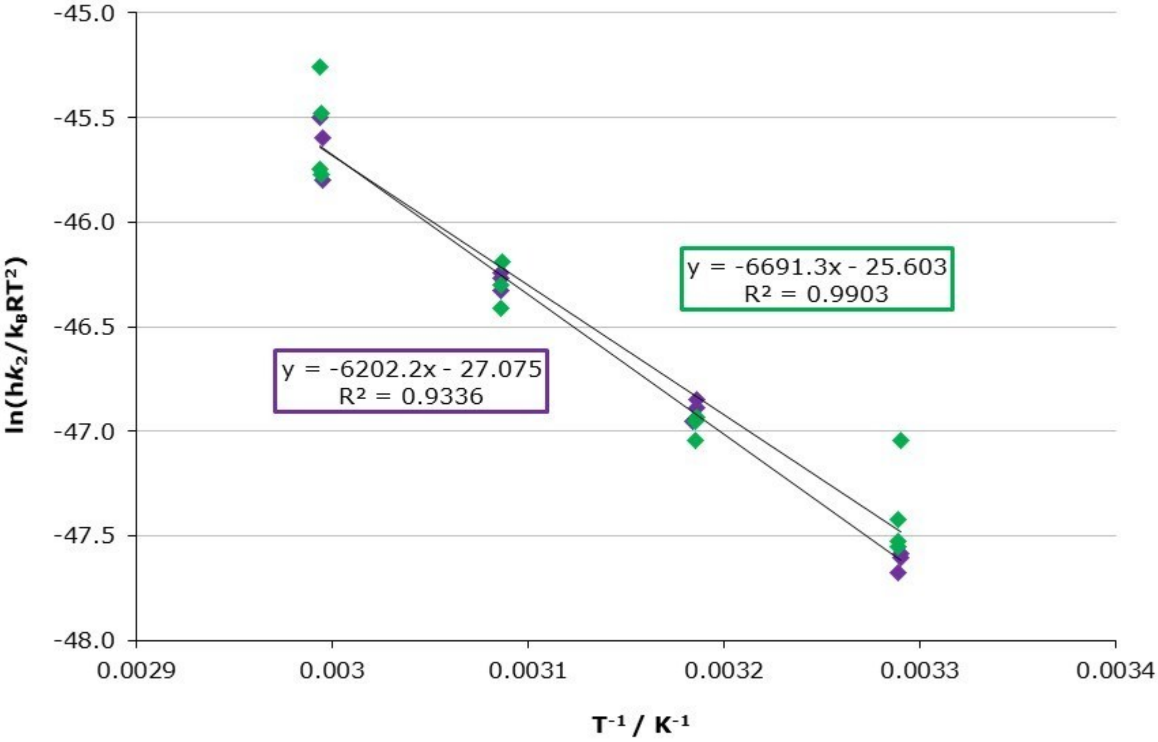

Figure S3 Eyring plots for the reaction between ethanol and 1-fluoro-2,4-dnitirobenzene **6** in [Li(G3)][N(SO_2CF_3)$_2$] **1** ($\chi_1 \approx 0.83$, purple) and [Li(G4)][N(SO_2CF_3)$_2$] **2** ($\chi_2 \approx 0.82$, green).

Determination of the alternate product 9

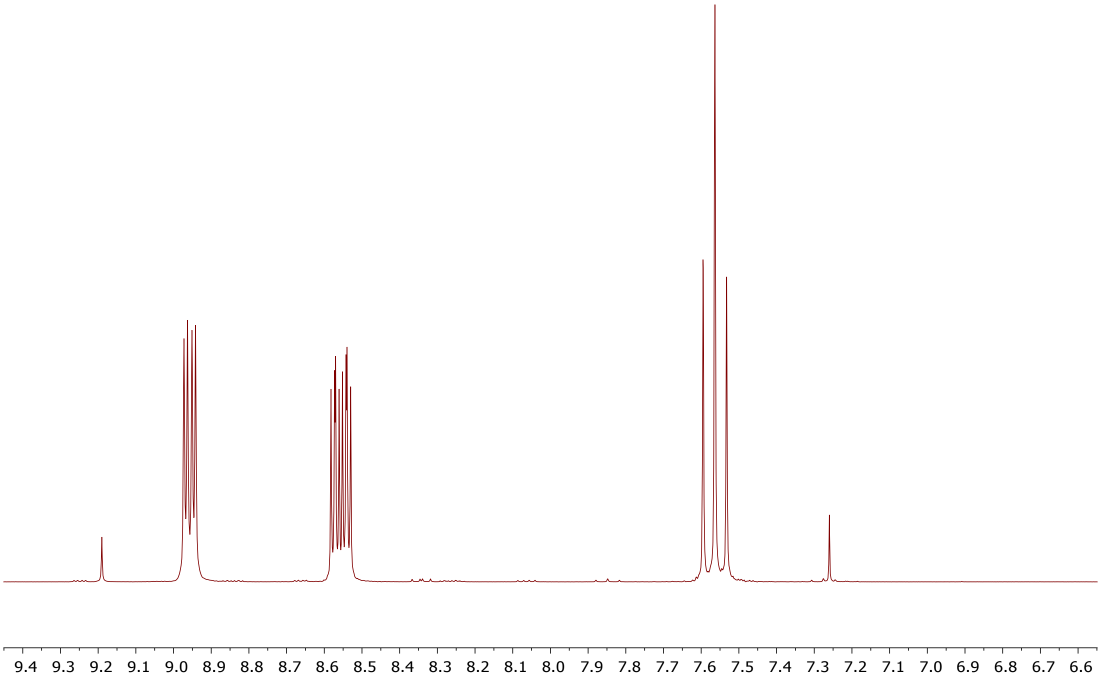

Figure S4 A ^{1}H NMR spectrum of 1-fluoro-2,4-dinitriobenzene **6** in $CDCl_3$.

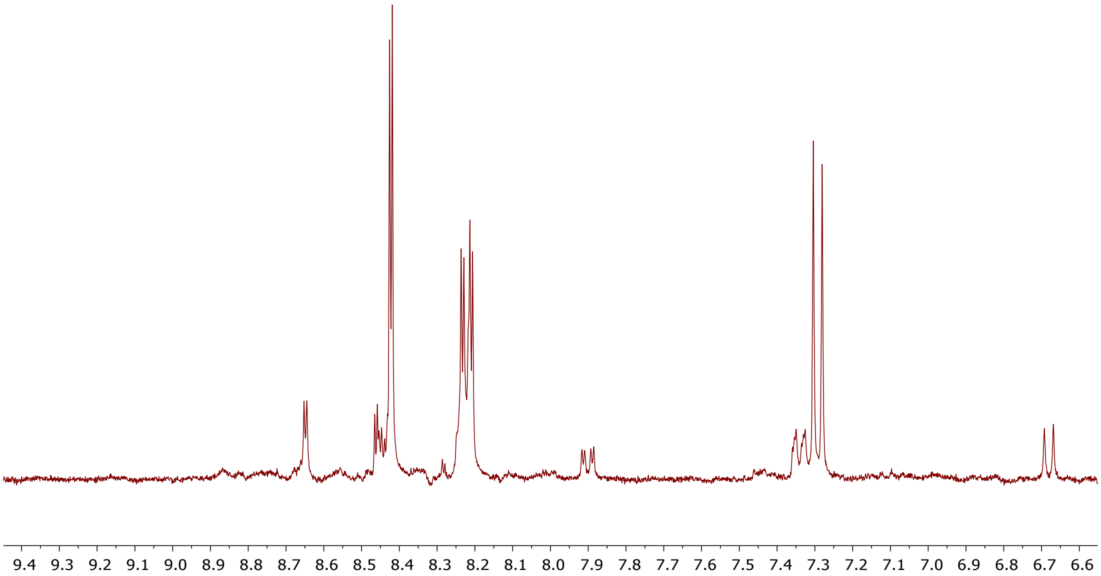

Figure S5. A ^{1}H NMR spectrum of a completed reaction mixture for the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in $[Li(G4)][N(SO_2CF_3)_2]$ **2** ($\chi_2 \approx 0.8$).

Experiments to determine the presence of a lithiated complex by dilution of the reaction mixture with ethanol

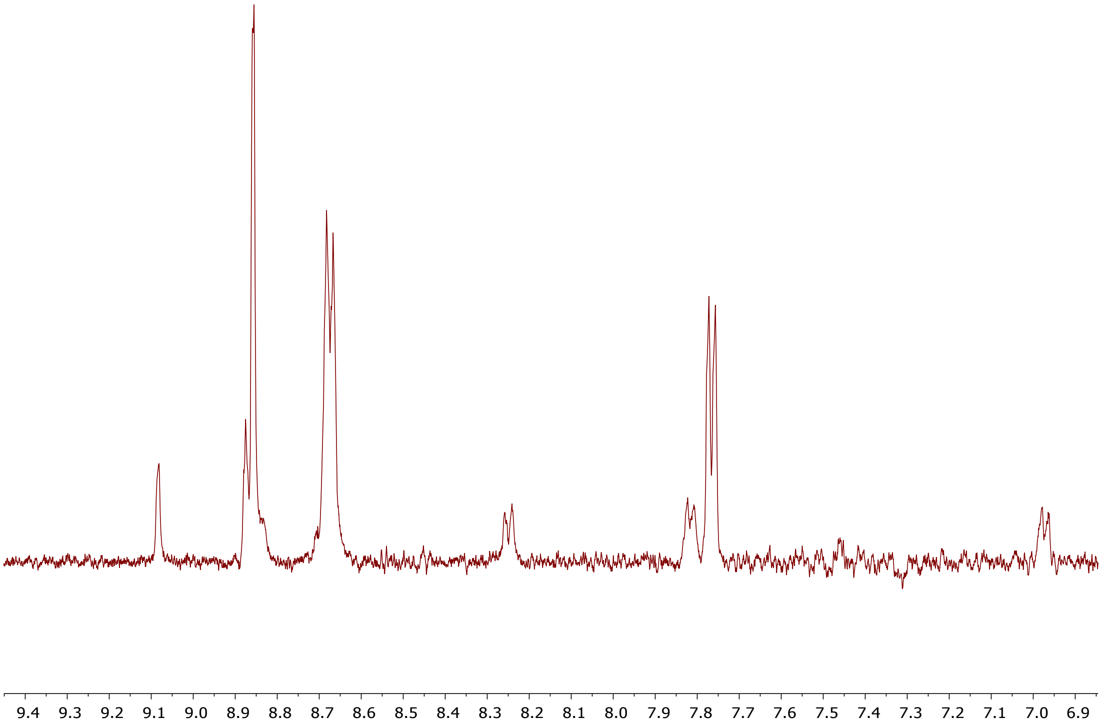

Figure S6. A ^{1}H NMR spectrum of a completed reaction mixture for the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in $[Li(G4)][N(SO_2CF_3)_2]$ **2** ($\chi_2 \approx 0.8$) diluted with ~ 0.5 mL of ethanol.

Experiments to determine the presence of 2,4-dinitrophenol in the reaction mixture

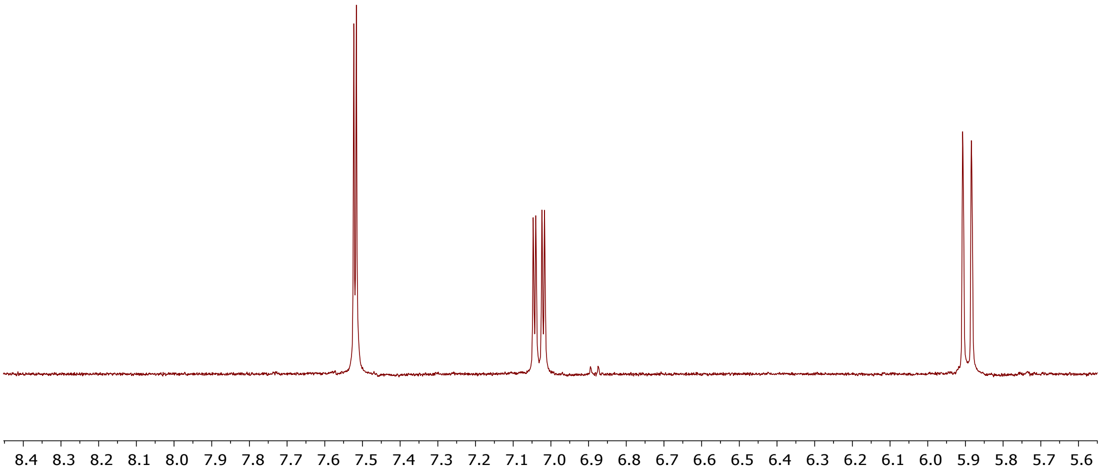

Figure S7 A ^{1}H NMR spectrum of 2,4-dinitrophenol in CD_3CN.

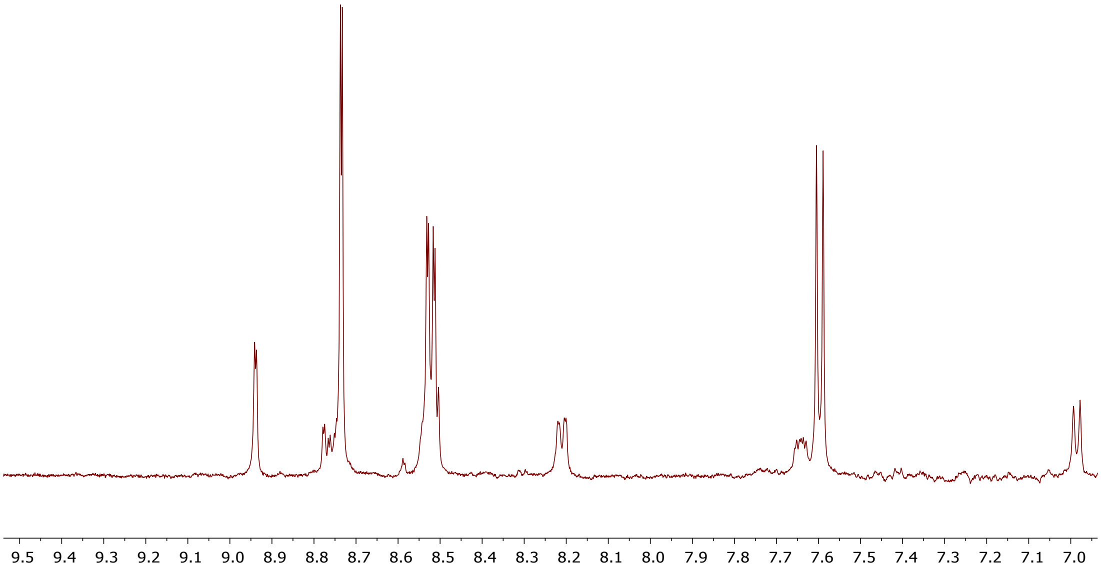

Figure S8. A ^{1}H NMR spectrum of a completed reaction mixture for the reaction between ethanol and 1-fluoro-2,4-dinitrobenzene **6** in $[Li(G4)][N(SO_2CF_3)_2]$ **2** ($\chi_2 \approx 0.8$) 'spiked' with 2,4-dinitrophenol.

Experiments to determine the presence of a 2,4-dinitroaniline in the reaction mixture

1-Fluoro-2,4-dinitrobenzene **6** (0.264 g, 1.42 mmol) and triethylamine (0.323 g, 3.19 mmol) were dissolved in acetonitrile (3 mL) and the reaction mixture was stirred at room temperature overnight followed by heating at 55 ^{0}C for 4 h. A ^{1}H NMR spectrum was taken after this time shown in Figure S9 below. The reaction mixture was then stirred at room temperature for a further 48 h after which time another ^{1}H NMR spectrum (CD_3CN) as well as an ESI$^+$ high resolution mass spectrum was acquired (Figures S10 and S11-12, respectively). In the ^{1}H NMR spectrum signals corresponding to the aromatic protons of a 2,4-dinitroaniline product were observed; δ *ca.* 6.5 (d, J = 9.7 Hz, 1H, $C\underline{H}CN(CH_2CH_3)_2$), 7.9 (dd, J = 9.7, 3.2 Hz, 1H, $C\underline{H}CHCN(CH_2CH_3)_2$), 8.7 (d, J = 3.2 Hz, 1H, $NO_2C\underline{H}NO_2$). The predominate signal in the ESI$^+$ mass spectrum at *m*/*z* 262.0795 corresponds to an elemental composition of $C_{10}H_{13}N_3O_4Na$; the sodiated form of *N*,*N*-diethyl-2,4-dinitroaniline.

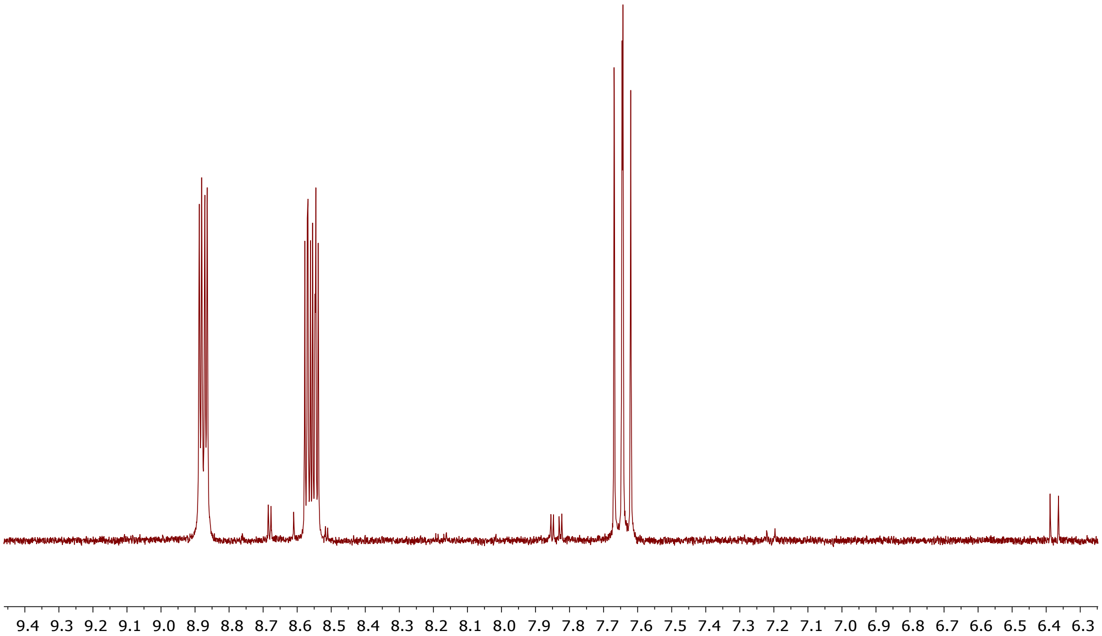

Figure S9. A ^{1}H NMR spectrum of a reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6** and triethylamine in acetonitrile after stirring at room temperature overnight, followed by heating at 55 ^{0}C for 4 h.

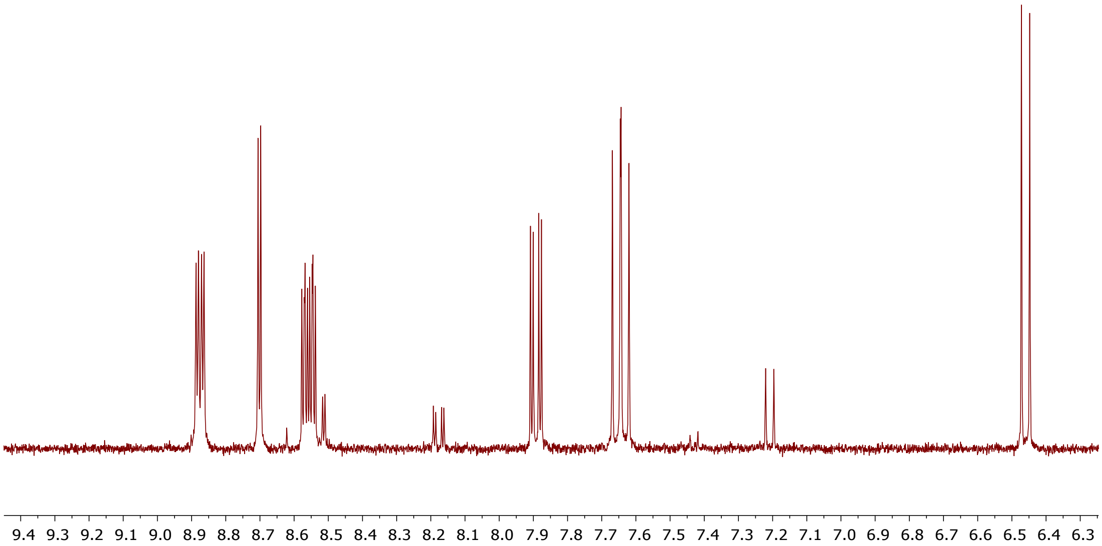

Figure S10. A ^{1}H NMR spectrum of a reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6** and triethylamine in acetonitrile after stirring at room temperature for a further 48 h.

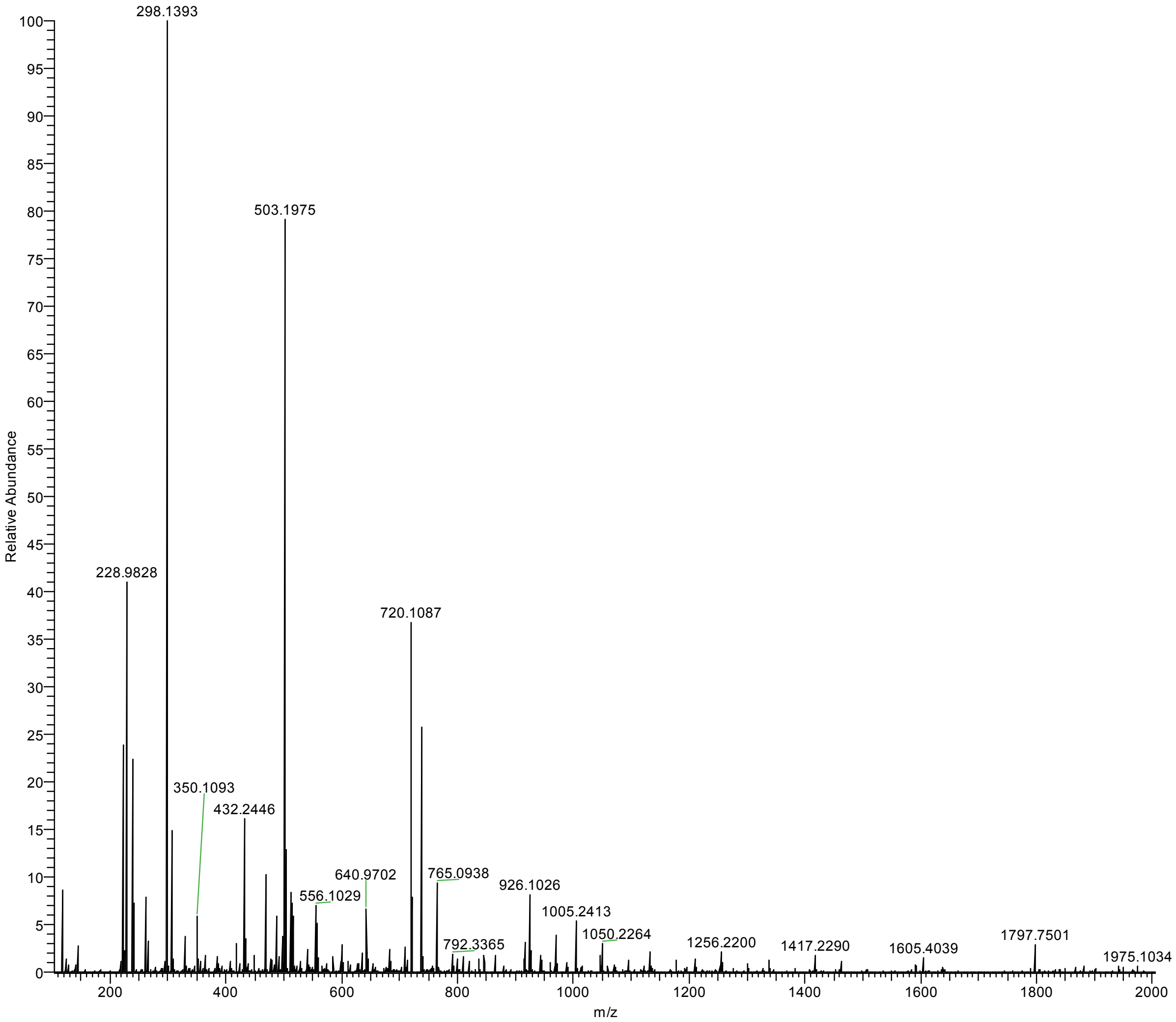

Figure S11. The high resolution mass spectrum of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6** and triethylamine in acetonitrile.

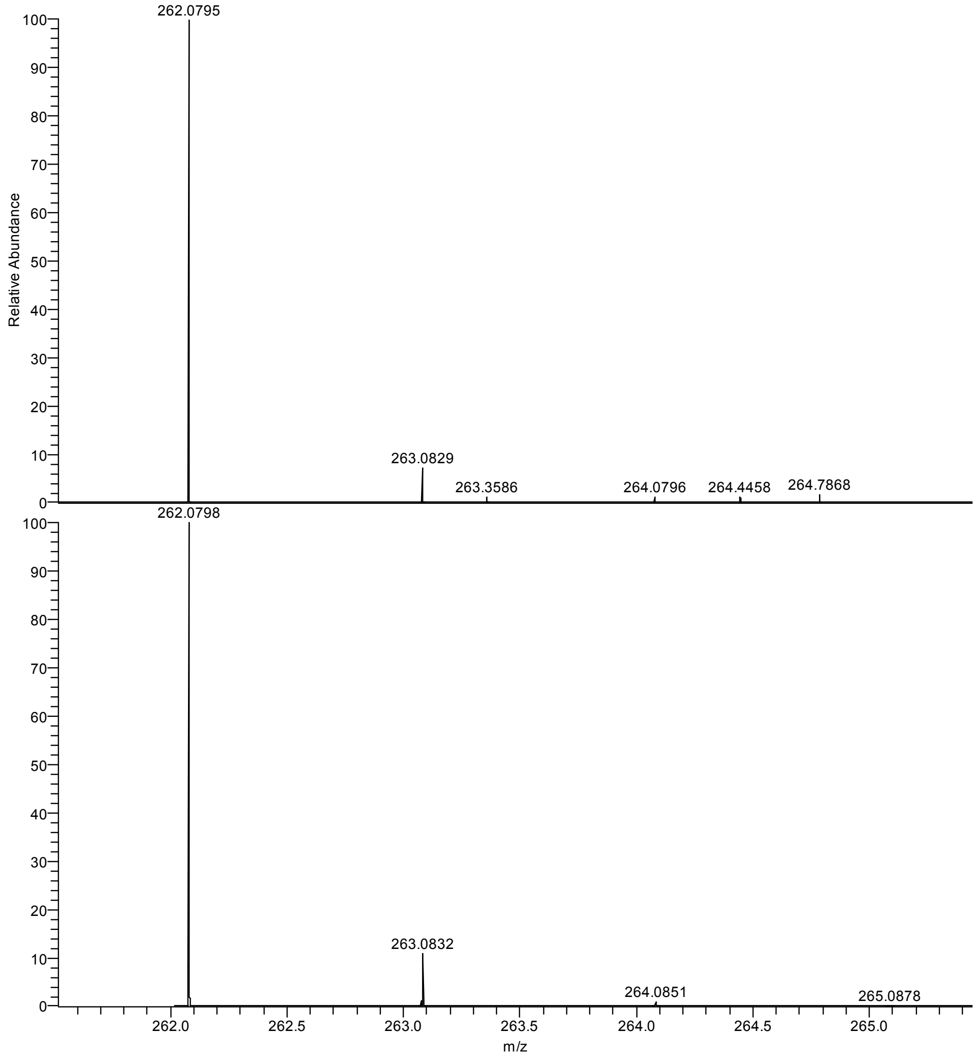

Figure S12. A zoomed in version of the high resolution mass spectrum presented above in Figure S11 of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6** and triethylamine in acetonitrile. The predominate signal at *m*/*z* 262.0795 corresponds to an elemental composition of $C_{10}H_{13}N_3O_4Na$; the sodiated form of *N*,*N*-diethyl-2,4-dinitroaniline.

Experiments to determine the presence of tetraglyme substituted benzene

1-Fluoro-2,4-dinitrobenzene **6** (0.0050 g, 0.029 mmol) and triethylamine (0.0688 g, 0.680 mmol) were dissolved in the tetraglyme (1.52 g, 6.83 mmol). The reaction mixture was stirred at room temperature overnight followed by heating at 55 ^{0}C for 4 h. A ^{1}H NMR spectrum (Figure S13) showed only signals corresponding to the starting materials and an ESI$^+$ mass spectrum (Figure S14-15) had a predominate signal at *m*/*z* 245.1359 corresponding to an elemental composition of $C_{10}H_{22}O_5Na$; the sodiated form of the tetraglyme starting material.

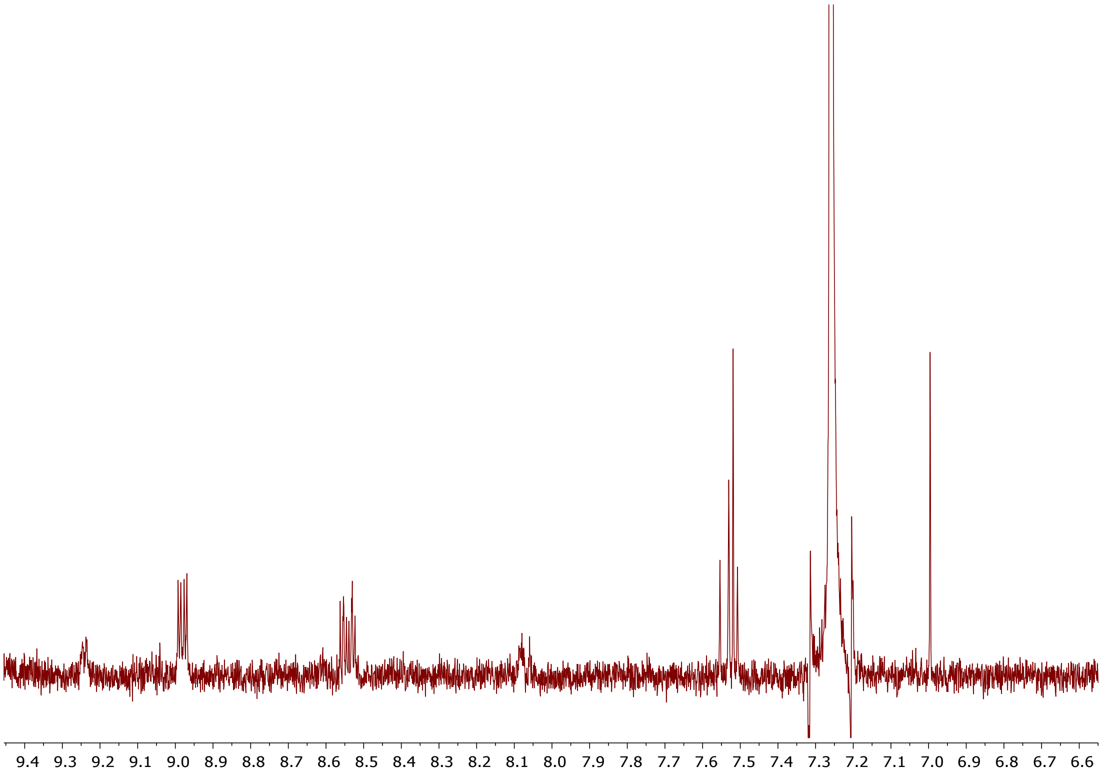

Figure S13. A ^{1}H NMR spectrum of a reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and tetraglyme in acetonitrile after stirring at room temperature overnight, followed by heating at 55 ^{0}C for 4 h. Residual solvent signal at 7.26 ppm due to $CDCl_3$.

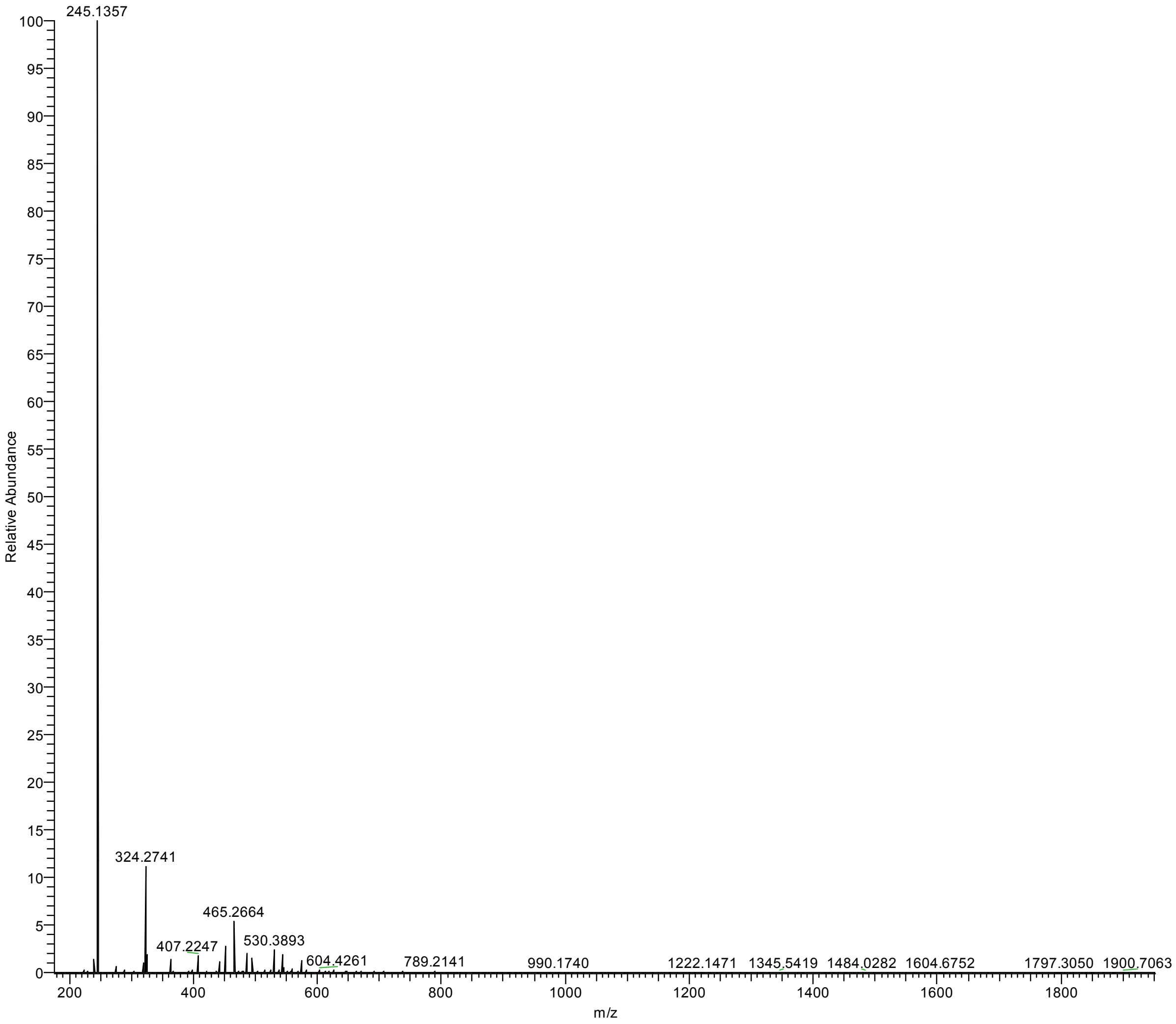

Figure S14. The high resolution mass spectrum of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and tetraglyme.

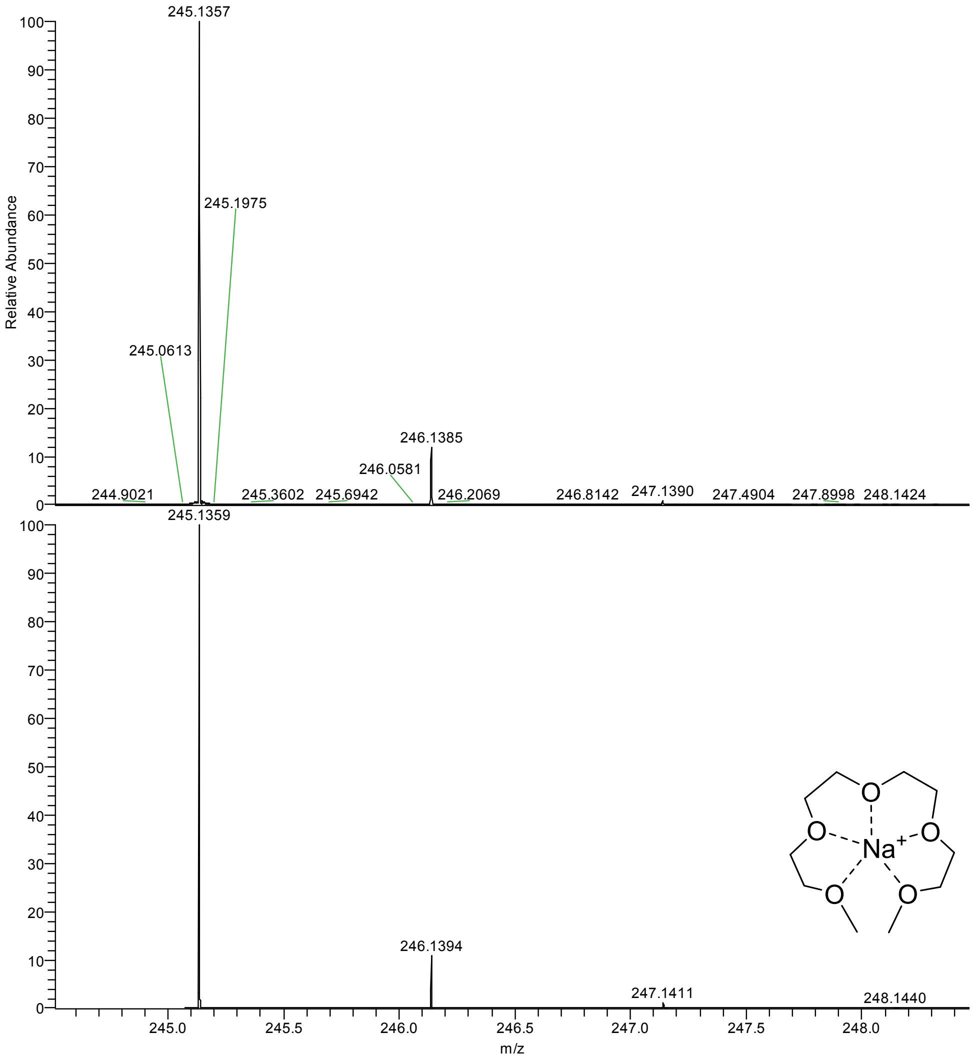

Figure S15. A zoomed in version of the high resolution mass spectrum shown in Figure S14 above of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and tetraglyme. The predominate signal shown at *m*/*z* 245.1359 corresponds to an elemental composition of $C_{10}H_{22}O_5Na$; the sodiated form of the tetraglyme starting material.

Experiments to determine whether reaction of [Li(G4)][N(SO_2CF_3)$_2$] ***2*** *has occurred*

1-Fluoro-2,4-dinitrobenzene **6** (0.0087 g, 0.051 mmol) and triethylamine (0.0716 g, 0.708 mmol) were dissolved in [Li(G4)][N(SO_2CF_3)$_2$] **2**. The reaction mixture was then stirred at room temperature overnight followed by heating at 55 ^{0}C for 4 hours. A ^{1}H NMR spectrum (Figure S17) was taken of the reaction mixture and new signals at *δ ca.* 7.5 and 8.5 were noted, consistent with the alternate product signals observed in Figure S5 above. An ESI$^+$ mass spectrum of the reaction mixture was also acquired noting in particular the signal at *m*/*z* 381.1473 which corresponded to an elemental composition of $C_{15}H_{22}Li_1N_2O_9$. This formula is consistent with the lithiated form of the glyme substituted benzene **9**.

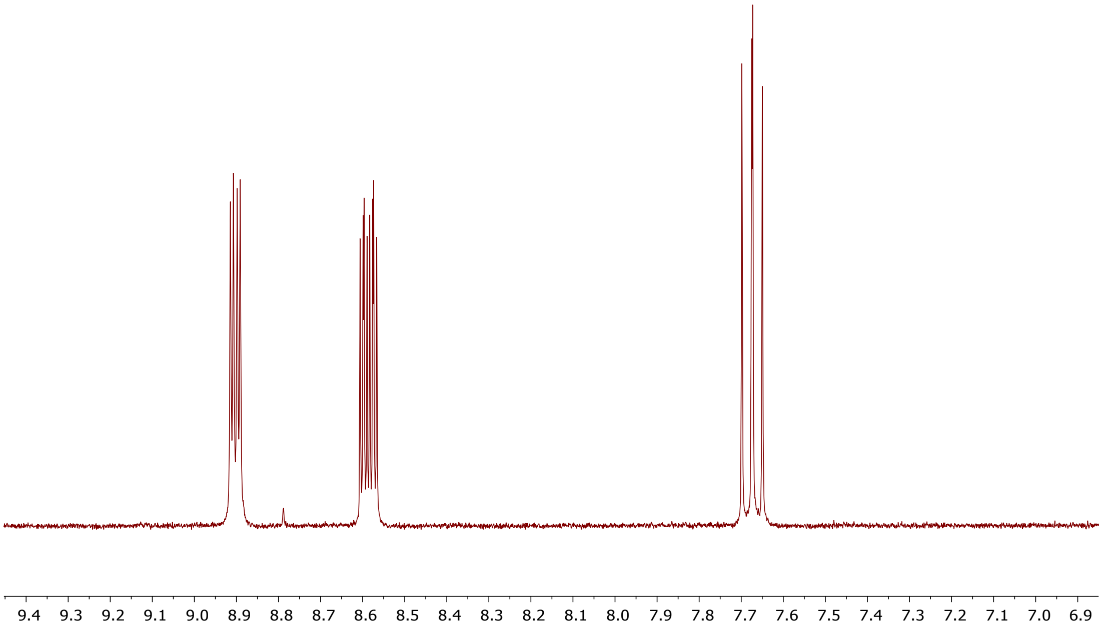

Figure S16. A section of the ^{1}H NMR spectrum of a reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6** and [Li(G4)][N(SO_2CF_3)$_2$] **2** after stirring at room temperature overnight, followed by heating at 55 ^{0}C for 4 h.

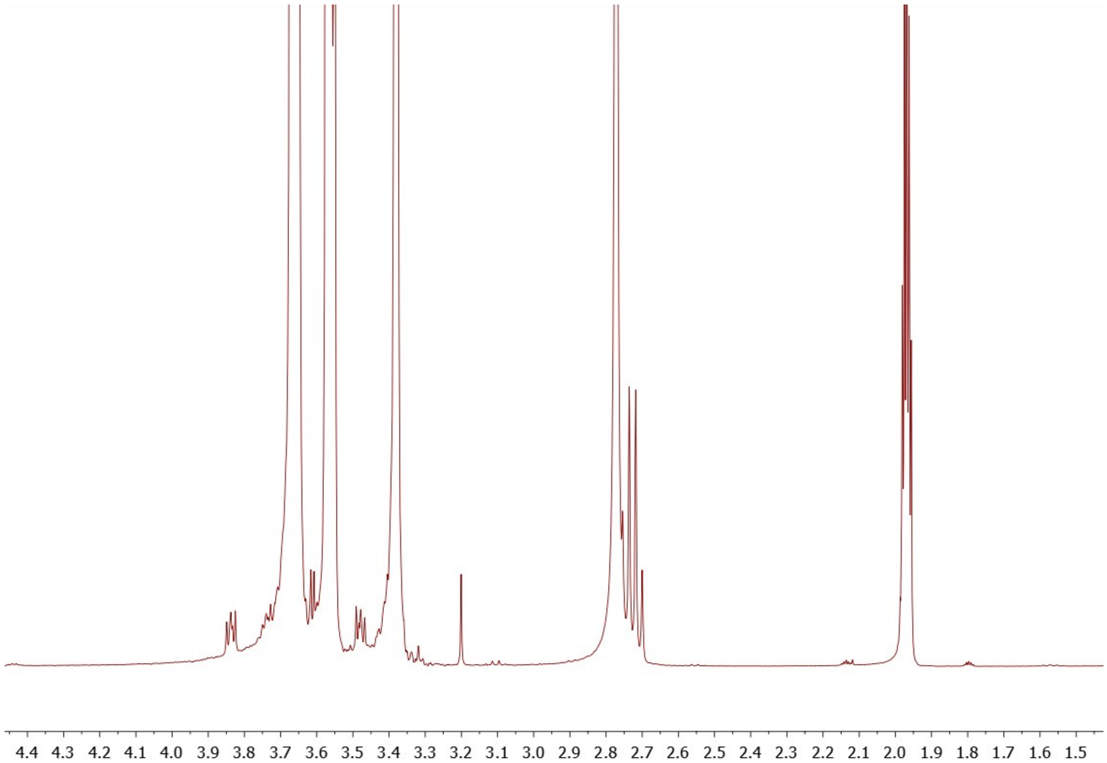

Figure S17. A section of the ^1H NMR spectrum of a reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and $[Li(G4)][N(SO_2CF_3)_2]$ **2** after stirring at room temperature overnight, followed by heating at 55 ^0C for 4 h. Note that no additional signals due to product **9** are visible in this region.

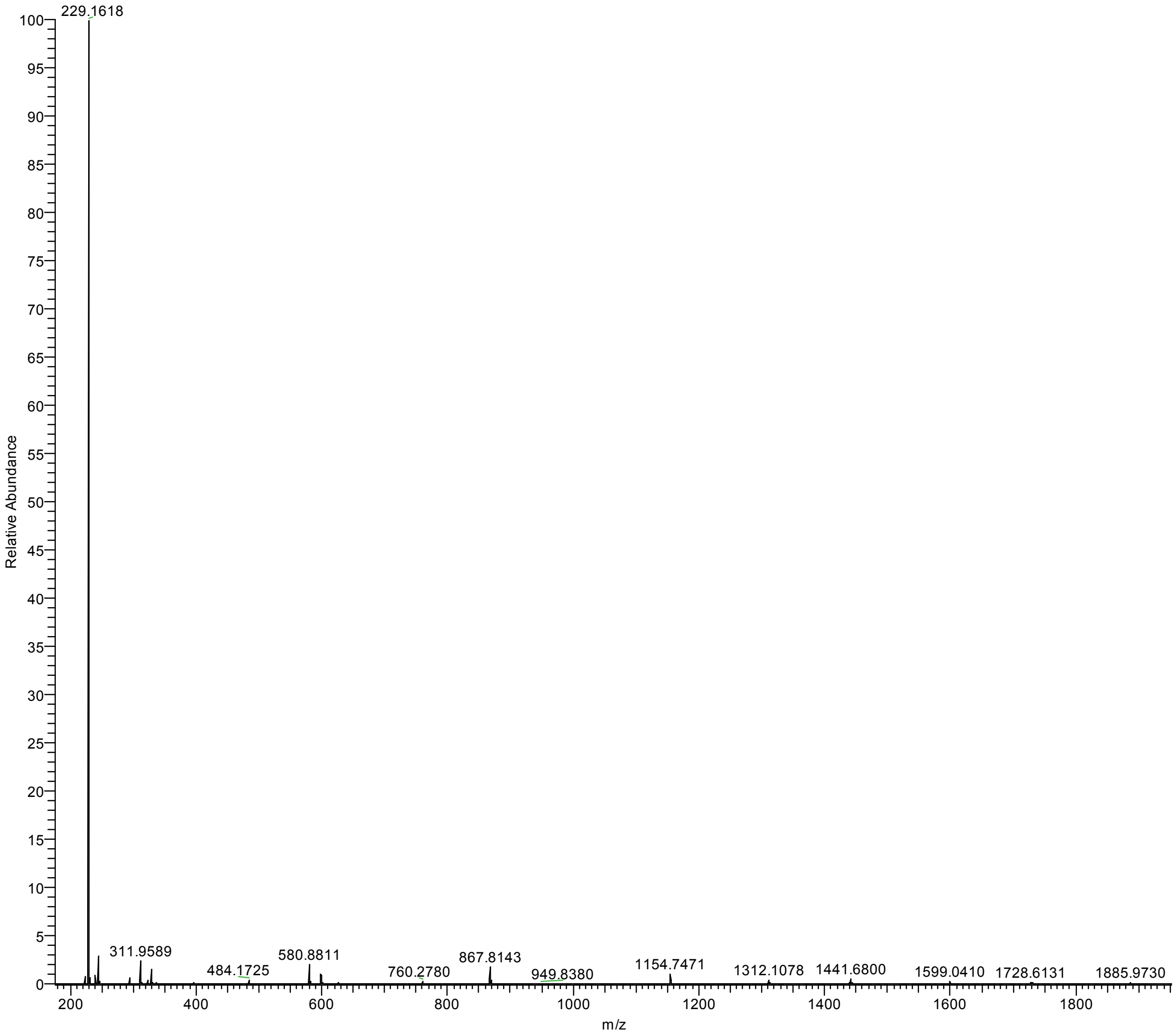

Figure S18. The high resolution mass spectrum of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and $[Li(G4)][N(SO_2CF_3)_2]$ **2**.

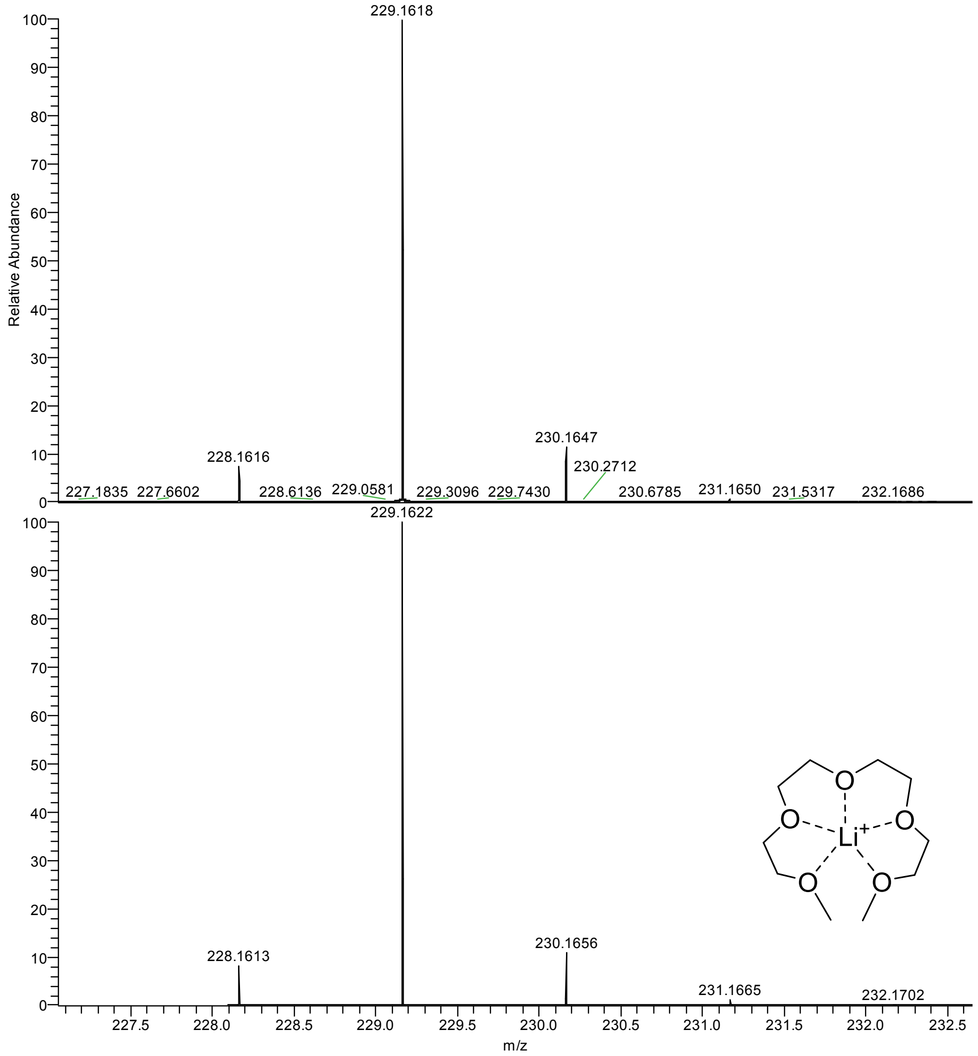

Figure S19. A zoomed in version of the high resolution mass spectrum shown in Figure S18 above of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and [Li(G4)][N(SO_2CF_3)$_2$] **2**. The predominate signal shown at *m*/*z* 229.1622 corresponds to an elemental composition of $C_{10}H_{22}Li_1O_5$; the cation of the solvate ionic liquid **2**, [Li(G4)]$^+$.

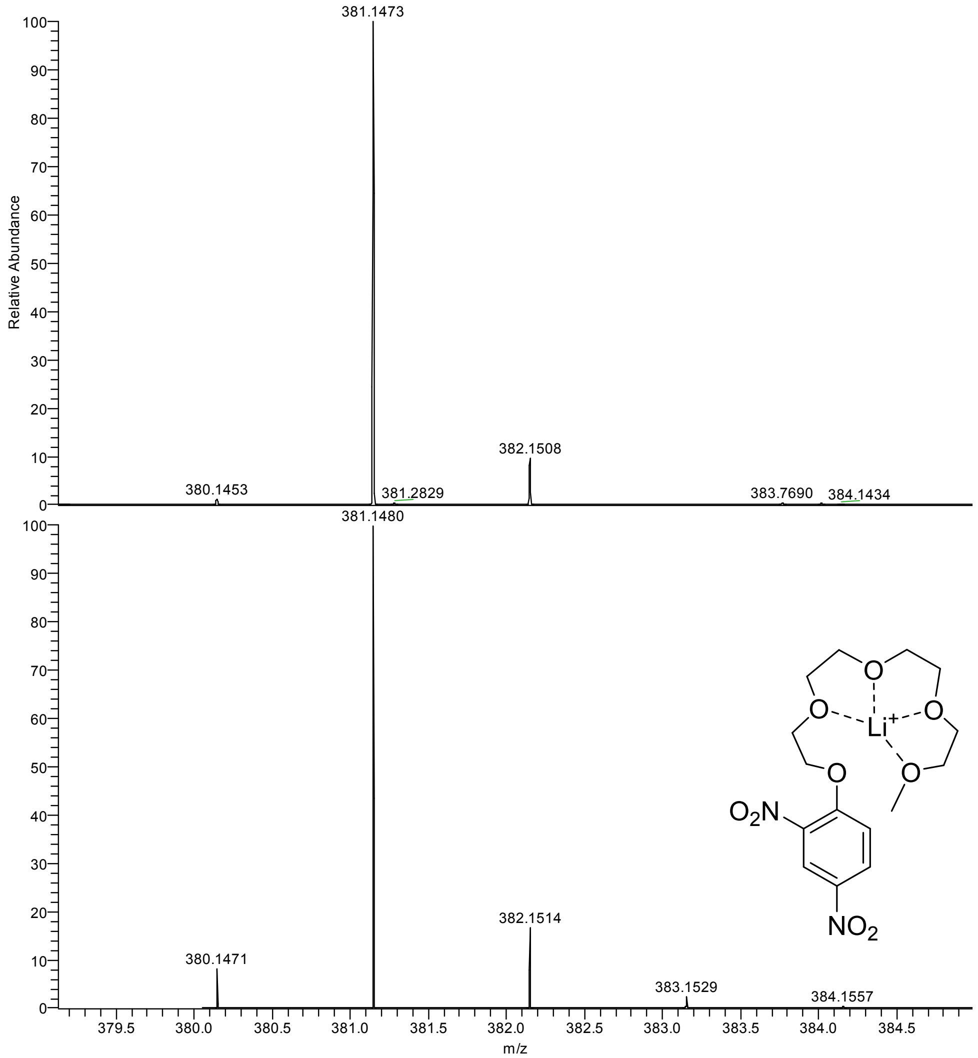

Figure S20. A zoomed in version of the high resolution mass spectrum shown in Figure S18 above of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and $[Li(G4)][N(SO_2CF_3)_2]$ **2**. The predominate signal shown at *m*/*z* 381.1480 corresponds to an elemental composition of $C_{15}H_{22}Li_1N_2O_9$ corresponding to the lithiated form of the tetraglyme substituted benzene **9**.

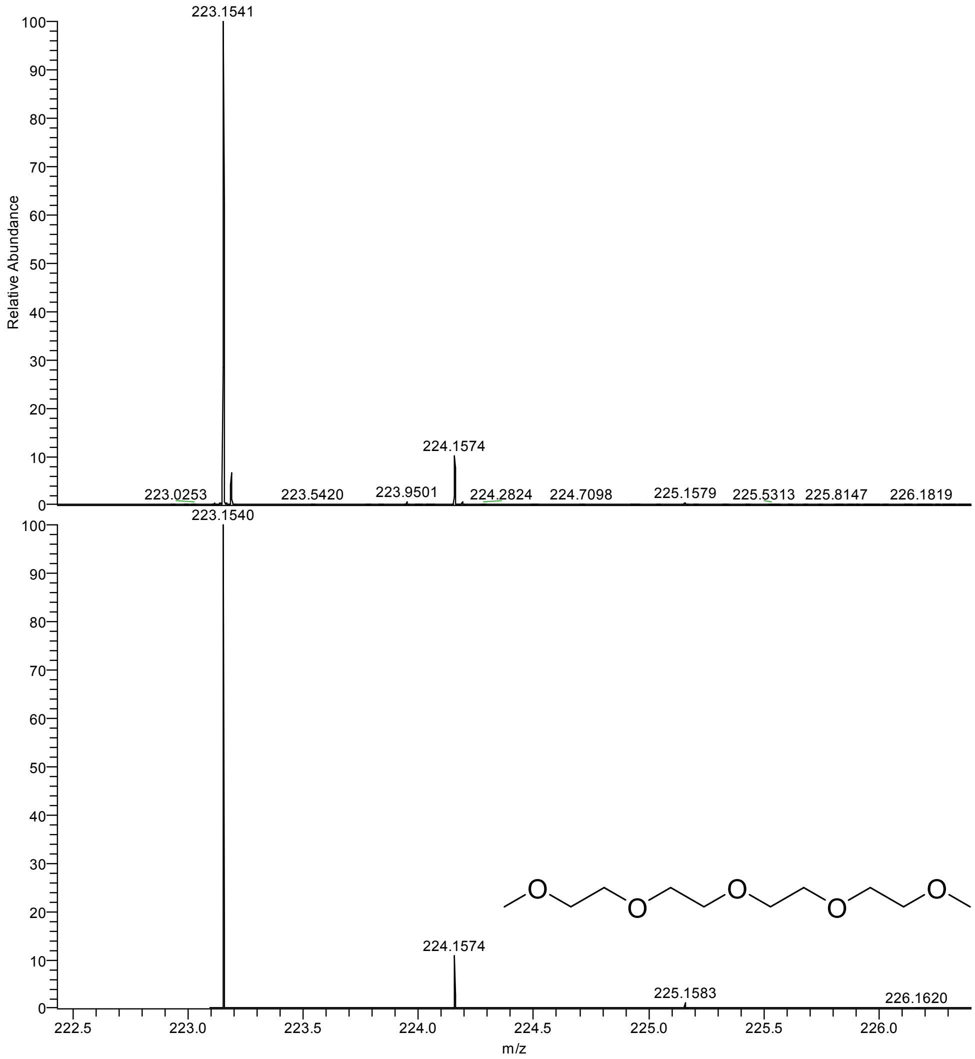

Figure S21. A zoomed in version of the high resolution mass spectrum shown in Figure S18 above of the reaction mixture from the reaction between 1-fluoro-2,4-dinitrobenzene **6**, triethylamine and [Li(G4)][N(SO_2CF_3)$_2$] **2**. The predominate signal shown at *m*/*z* 223.1540 corresponds to an elemental composition of $C_{10}H_{23}O_5$ corresponding to the protonated form of the tetraglyme.

Experiments to determine the importance of fluoride in the formation of species ***9*** *– 1*

A fluoride scavenger

A reaction mixture containing 1-fluoro-2,4-dinitrobenzene **6** (0.0085 g, 0.046 mmol), triethylamine (0.075 g, 0.74 mmol), ethanol (0.0729 g, 1.58 mmol) and methoxytrimethylsilane (0.109 g, 1.05 mmol) in the solvate ionic liquid **2** (2 mL) was heated at 55 ^{0}C for 16 h. A ^{1}H NMR spectrum was taken after this time (shown in Figure S22 below). In the ^{1}H NMR spectrum, no new signals corresponding to the additional product at *δ ca.* 7.5 and 8.5 were noted. Formation of 1-methoxy-2,4-dinitrobenzene was observed in the ^{1}H NMR spectrum and is likely due to the methanol formed in reaction of methoxytrimethylsilane with fluoride; its identity is supported by an additional signal (relative integration 3H) at *δ ca.* 4.1.

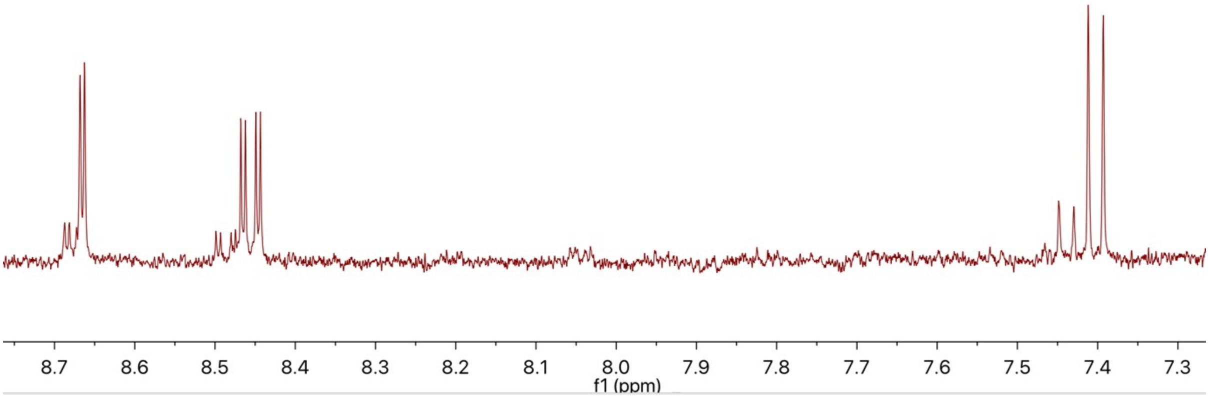

Figure S22. A section of the ^{1}H NMR spectrum of a reaction mixture typical of a kinetic run in $[Li(G4)][N(SO_2CF_3)_2]$ **2** (χ_{IL} *ca.* 0.8) after heating at 55 ^{0}C for 16 h except that the fluoride scavenger methoxytrimethylsilane had been added. The smaller signals downfield from each signal representing the expected product, 2,4-dinitrophenetole **8**, are those of 1-methoxy-2,4-dinitrobenzene.

Experiments to determine the importance of fluoride in the formation of species ***9*** *– 2*

A fluoride source

Tetrabutylammonium fluoride (0.397 g, 1.52 mmol), 1-fluoro-2,4-dinitrobenzene **6** (0.0095 g, 0.051 mmol), ethanol (0.104 g, 2.26 mmol) and triethylamine (0.0768 g, 0.759 mmol) were dissolved in the solvate ionic liquid **2** (2 mL) and the reaction mixture was heated at 55 ^{0}C for 24 h. A ^{1}H NMR spectrum was taken after this time (shown in Figure S23 below). In the ^{1}H NMR spectrum, new signals at δ *ca.* 7.5 and 8.5 were noted, consistent with the alternate product signals observed in Figure S5 above.

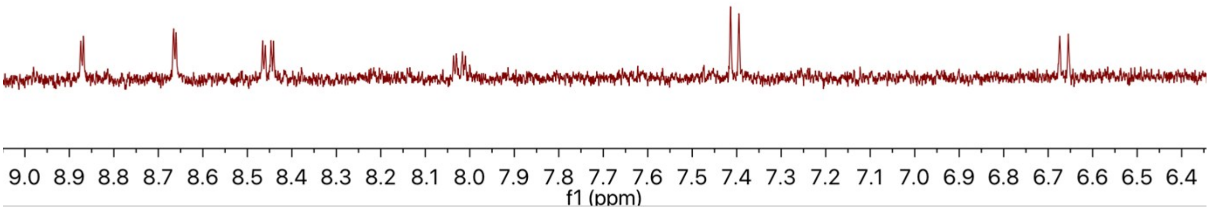

Figure S23. A section of the ^{1}H NMR spectrum of a reaction mixture of [Li(G4)][N(SO$_2$CF$_3$)$_2$] **2**, tetrabutylammonium fluoride, 1-fluoro-2,4-dinitrobenzene **6**, ethanol and triethylamine after heating at 55 ^{0}C for 24 h.

References

1. K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko and M. Watanabe, *J. Phys. Chem. B*, 2012, **116**, 11323-11331.
2. H. Eyring, *J. Chem. Phys.*, 1935, **3**, 107-115.
3. R. R. Hawker, M. J. Wong, R. S. Haines and J. B. Harper, *Org. Biomol. Chem.*, 2017, **15**, 6433-6440.