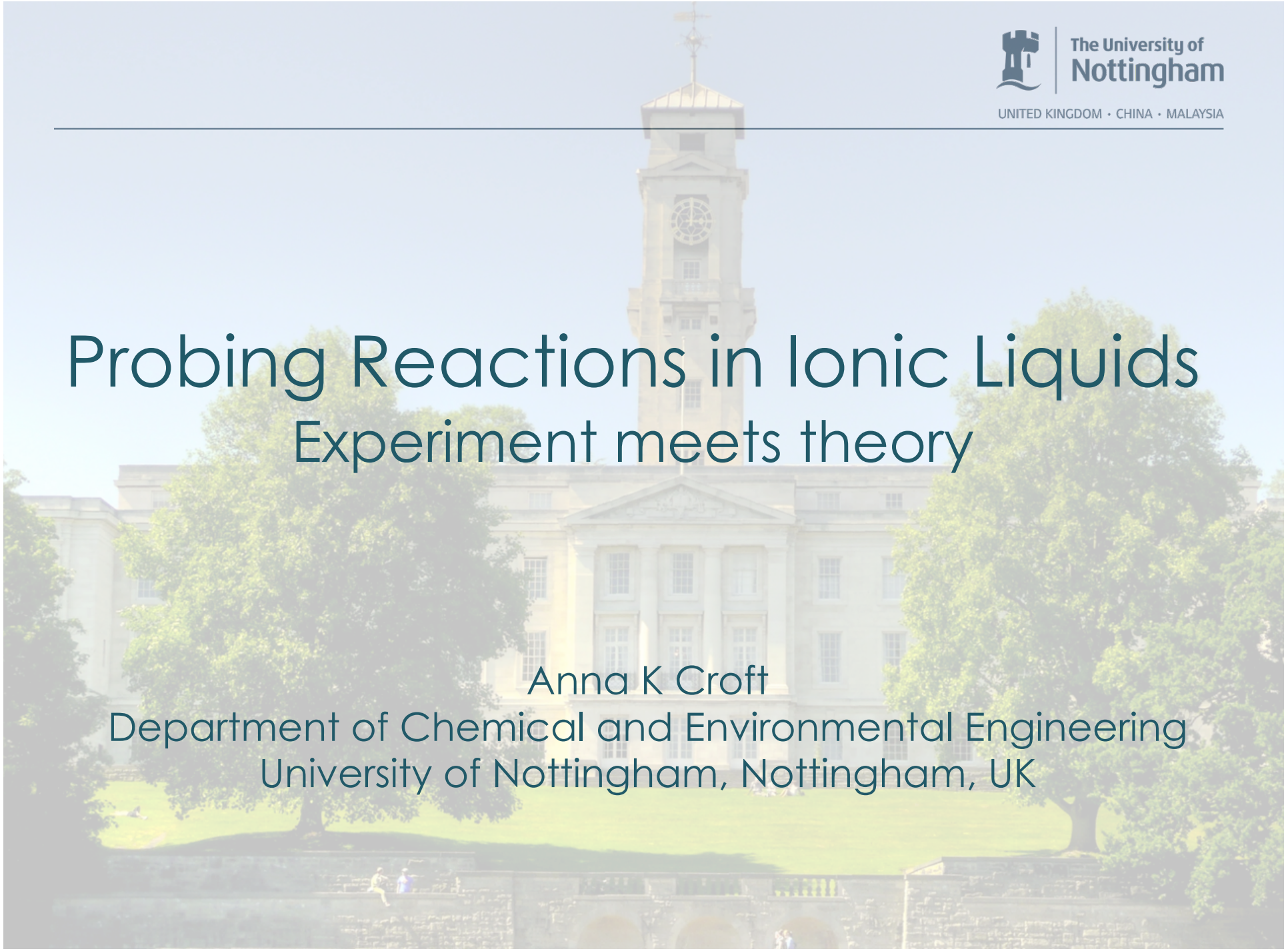

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Probing Reactions in Ionic Liquids

Experiment meets theory

Anna K Croft
Department of Chemical and Environmental Engineering
University of Nottingham, Nottingham, UK

Croft group @ Nottingham

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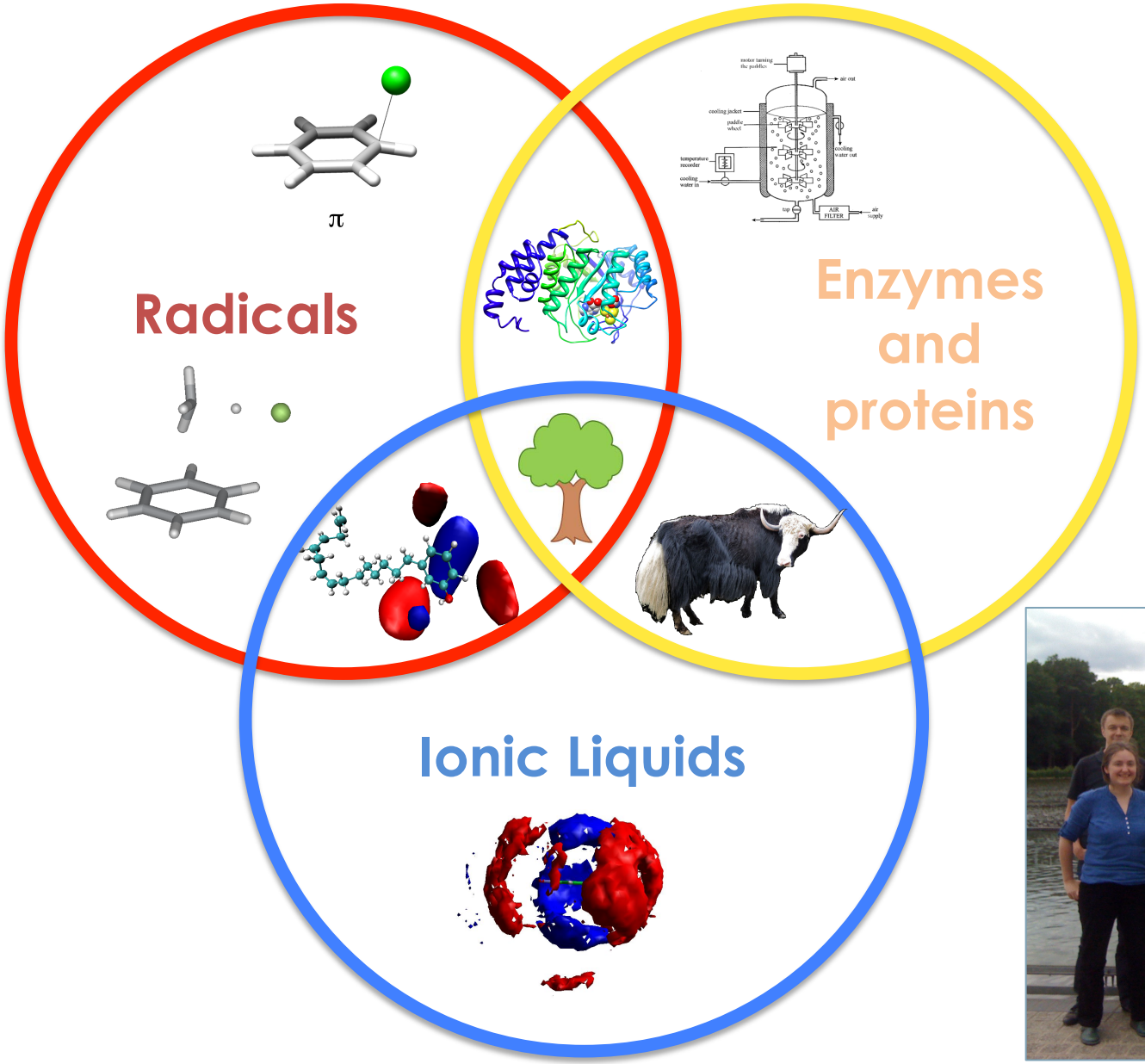
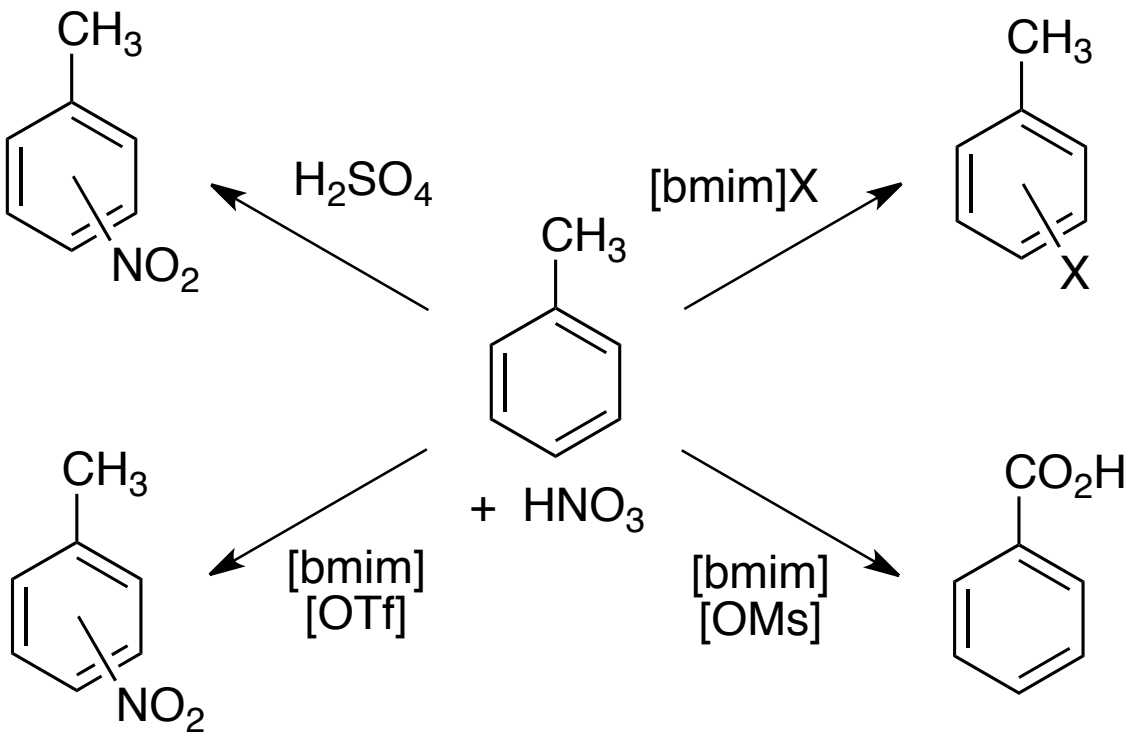
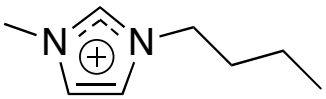


Reactions in Ionic Liquids



bmim = 

M. J. Earle, S. P. Katdare and K. R. Seddon, *Org. Lett.* **2004**, *6*, 707.

Understanding molecular drivers

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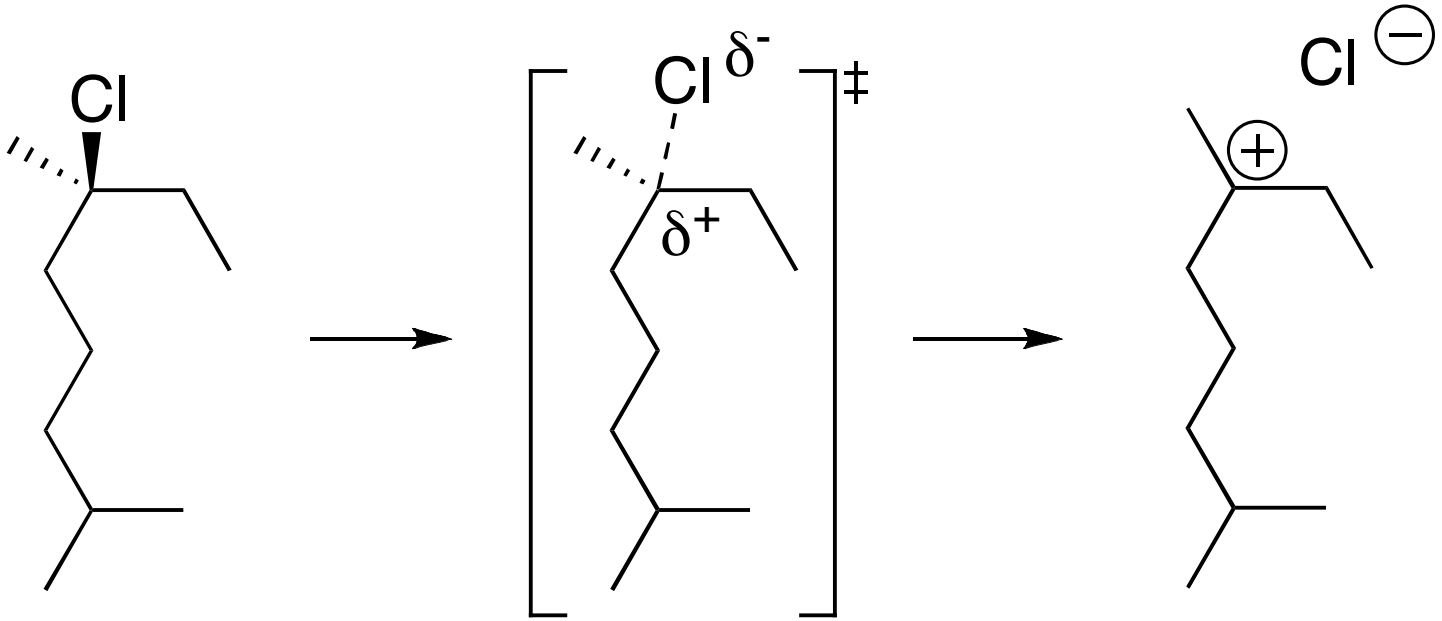
S_N1
S_NAr
S_N2



Eyring equation

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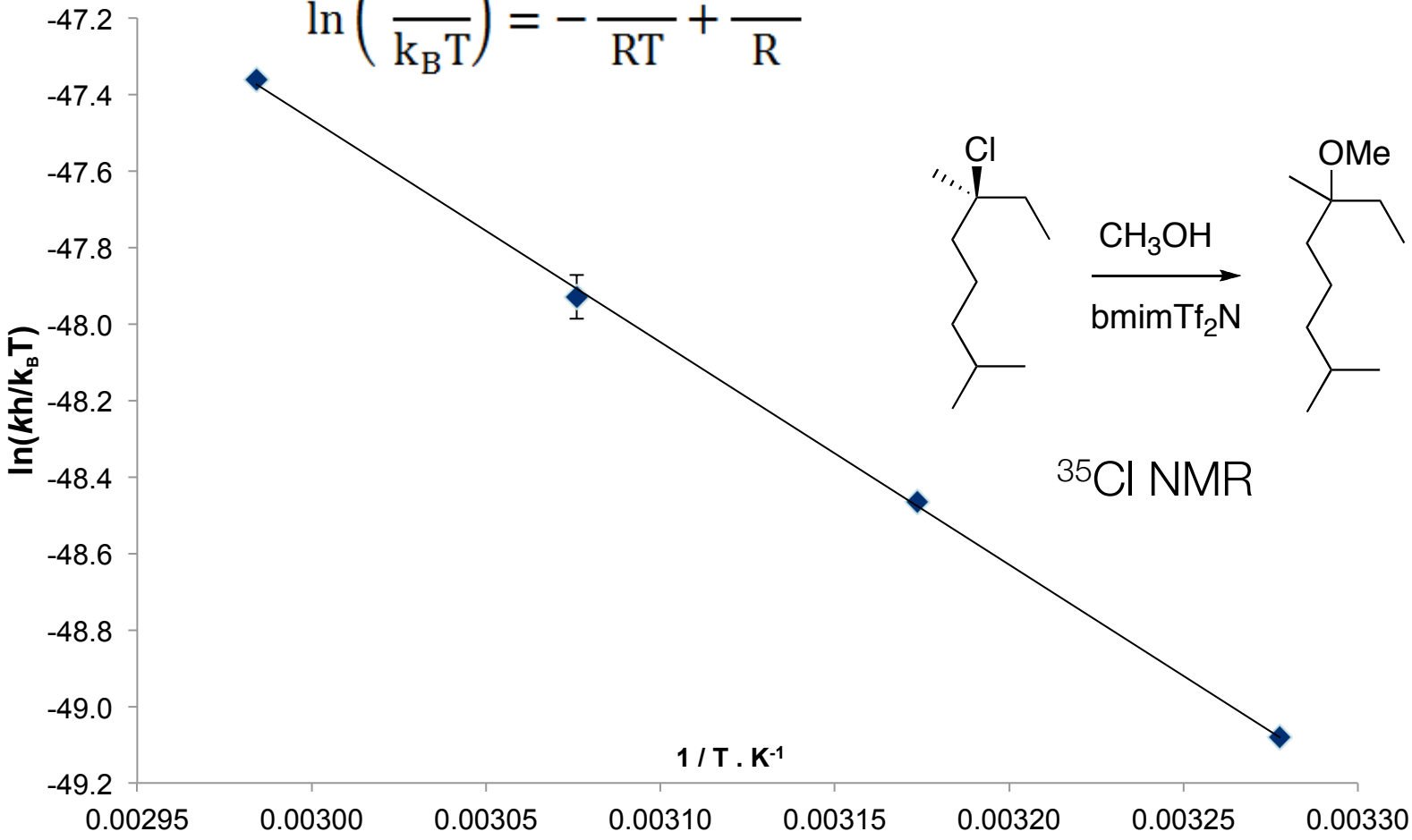
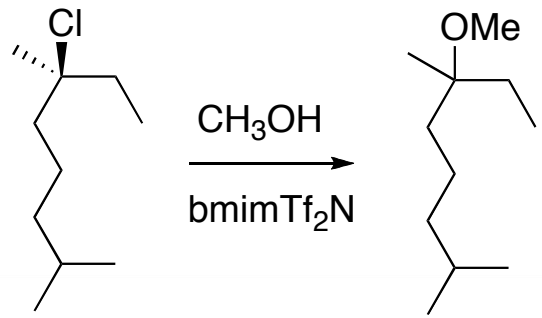
S_N1
S_NAr
S_N2

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

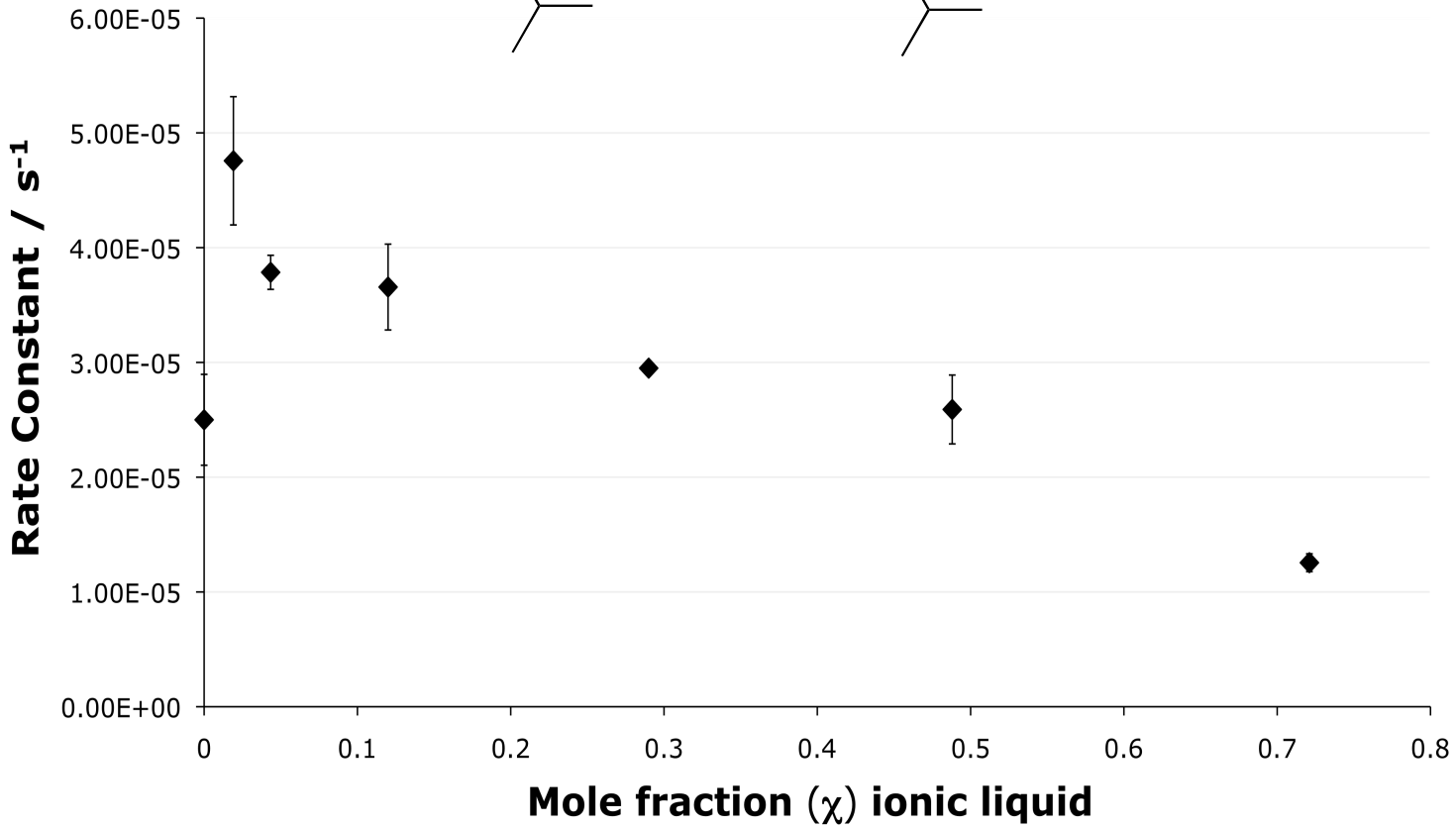


^{35}Cl NMR

Enthalpy/Entropy change



S_N1
S_NAr
S_N2



B. Y. W. Man, J. M. Hook, J. B. Harper,
Tetrahedron Lett. 7641, **46**, 2005

Enthalpy/Entropy change

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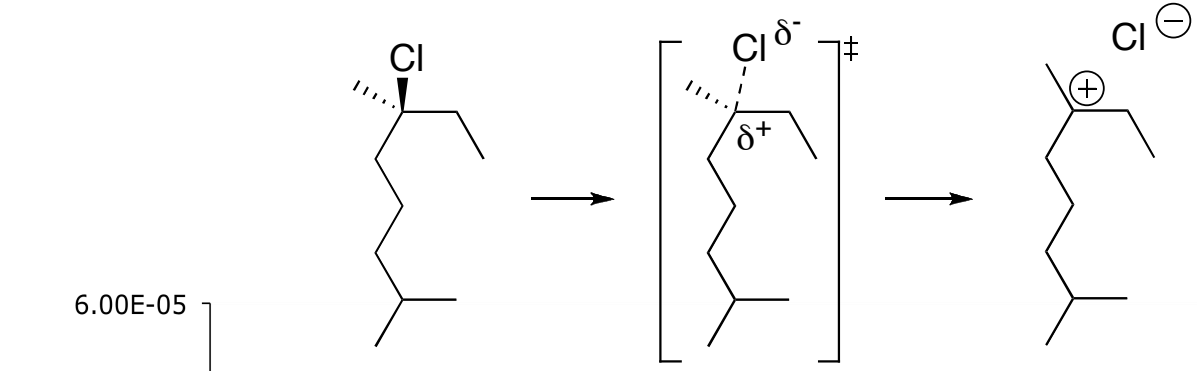
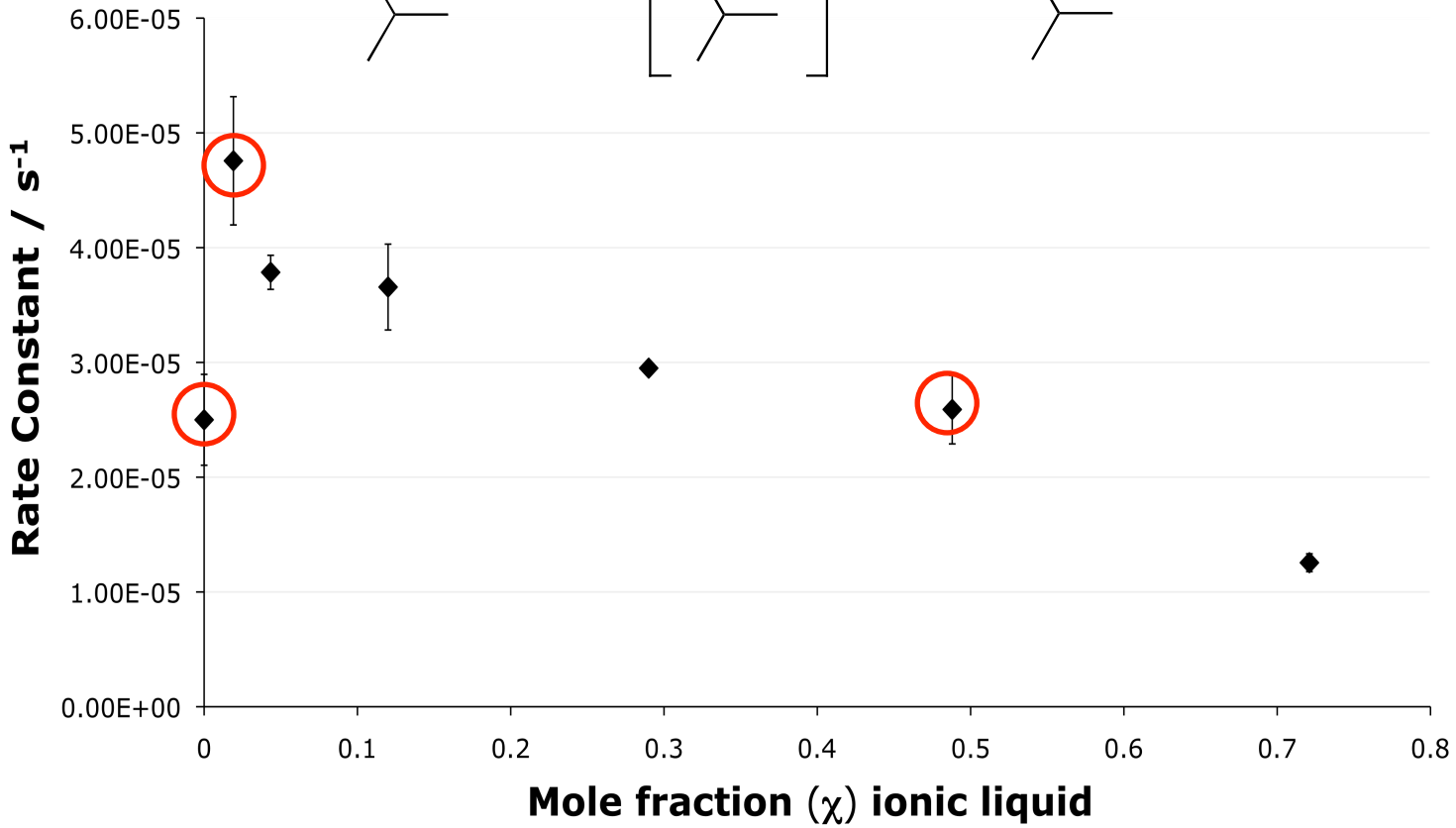


S_N1
S_NAr
S_N2



B. Y. W. Man, J. M. Hook, J. B. Harper,
Tetrahedron Lett. 7641, **46**, 2005

Enthalpy/Entropy change

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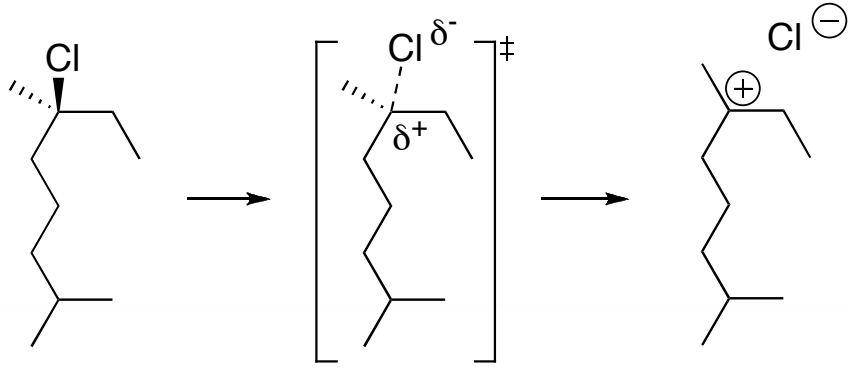
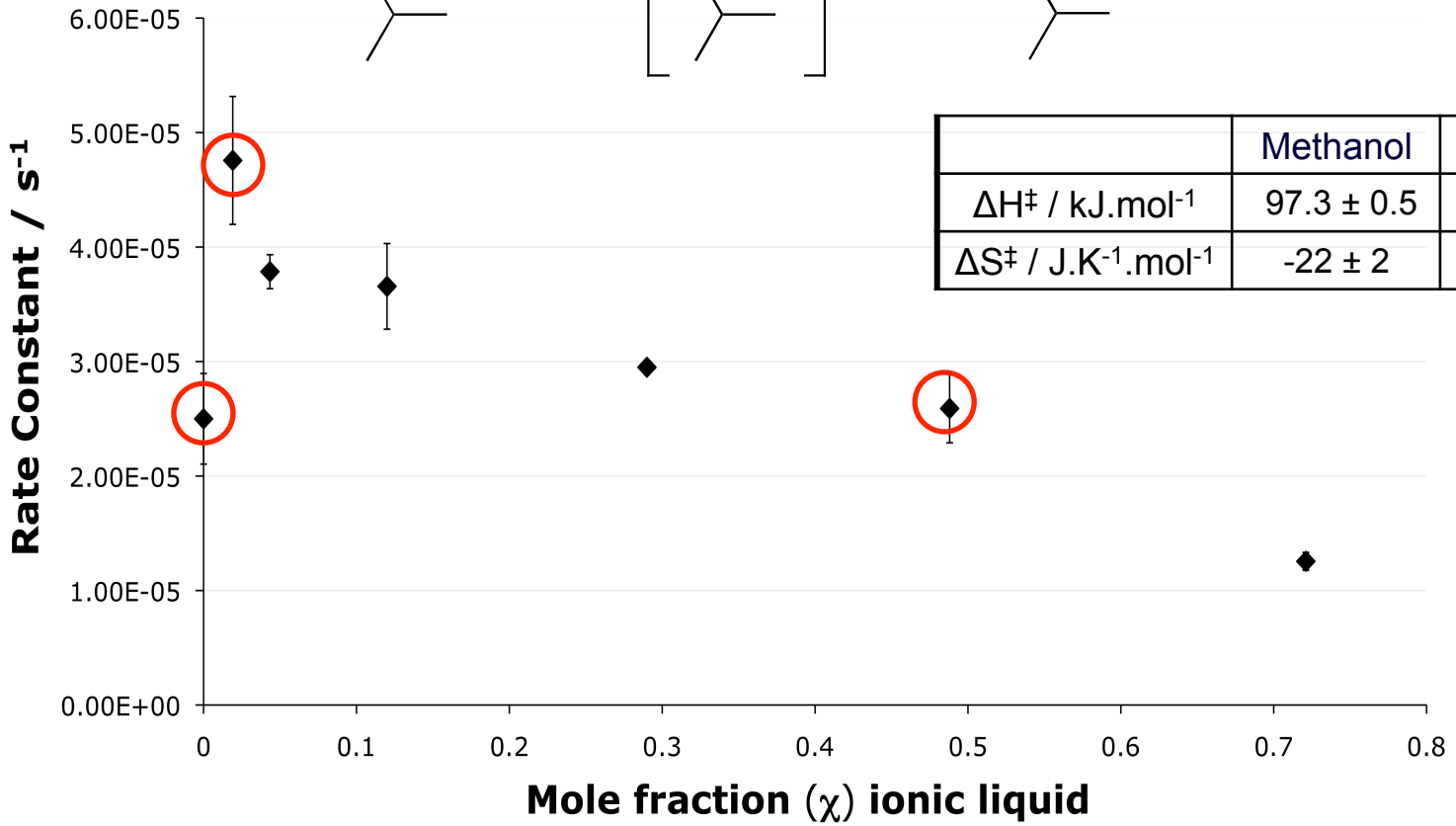


S_N1
S_NAr
S_N2



	Methanol	Ionic liquid
$\Delta H^{\ddagger}$ / kJ.mol^{-1}	97.3 ± 0.5	43.2 ± 5.9
$\Delta S^{\ddagger}$ / J.K^{-1}.mol^{-1}	-22 ± 2	-195 ± 18

B. Y. W. Man, J. M. Hook, J. B. Harper,
Tetrahedron Lett. 7641, **46**, 2005

Enthalpy/Entropy change

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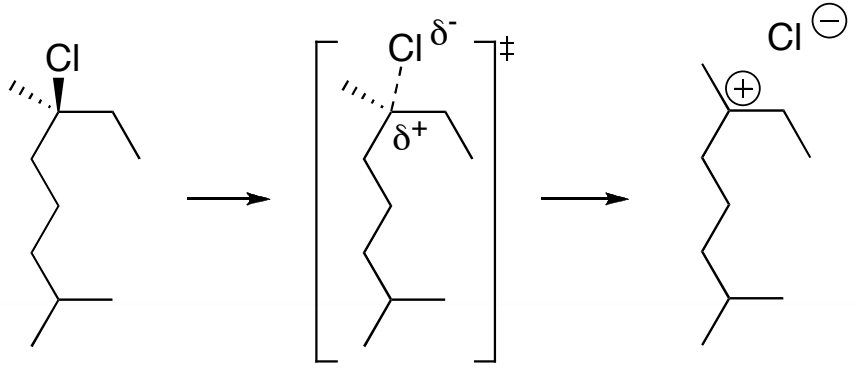
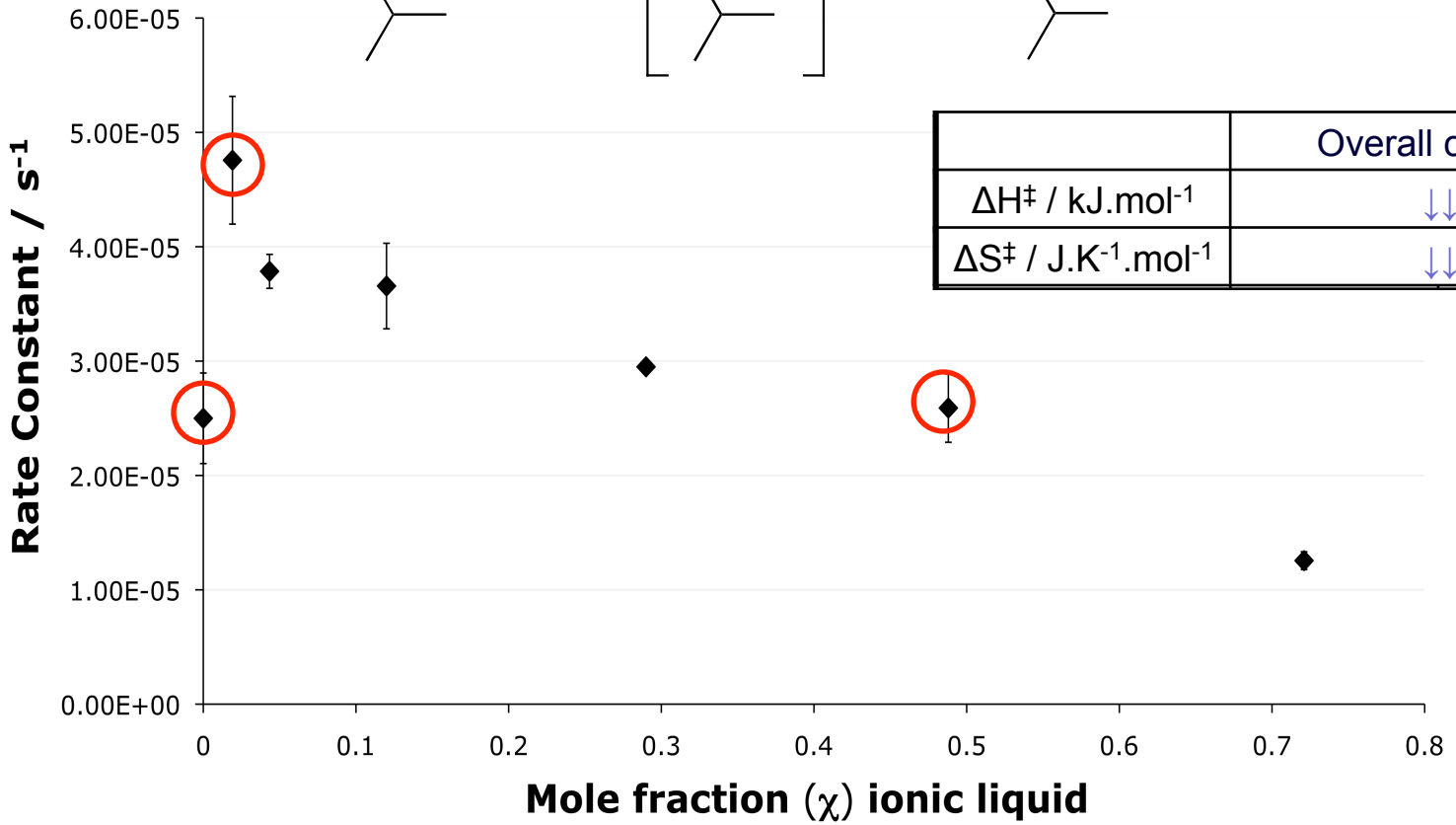


S_N1
S_NAr
S_N2



	Overall change
$\Delta H^{\ddagger}$ / kJ.mol^{-1}	↓↓
$\Delta S^{\ddagger}$ / J.K^{-1}.mol^{-1}	↓↓

B. Y. W. Man, J. M. Hook, J. B. Harper,
Tetrahedron Lett. 7641, **46**, 2005

Visualising organisation

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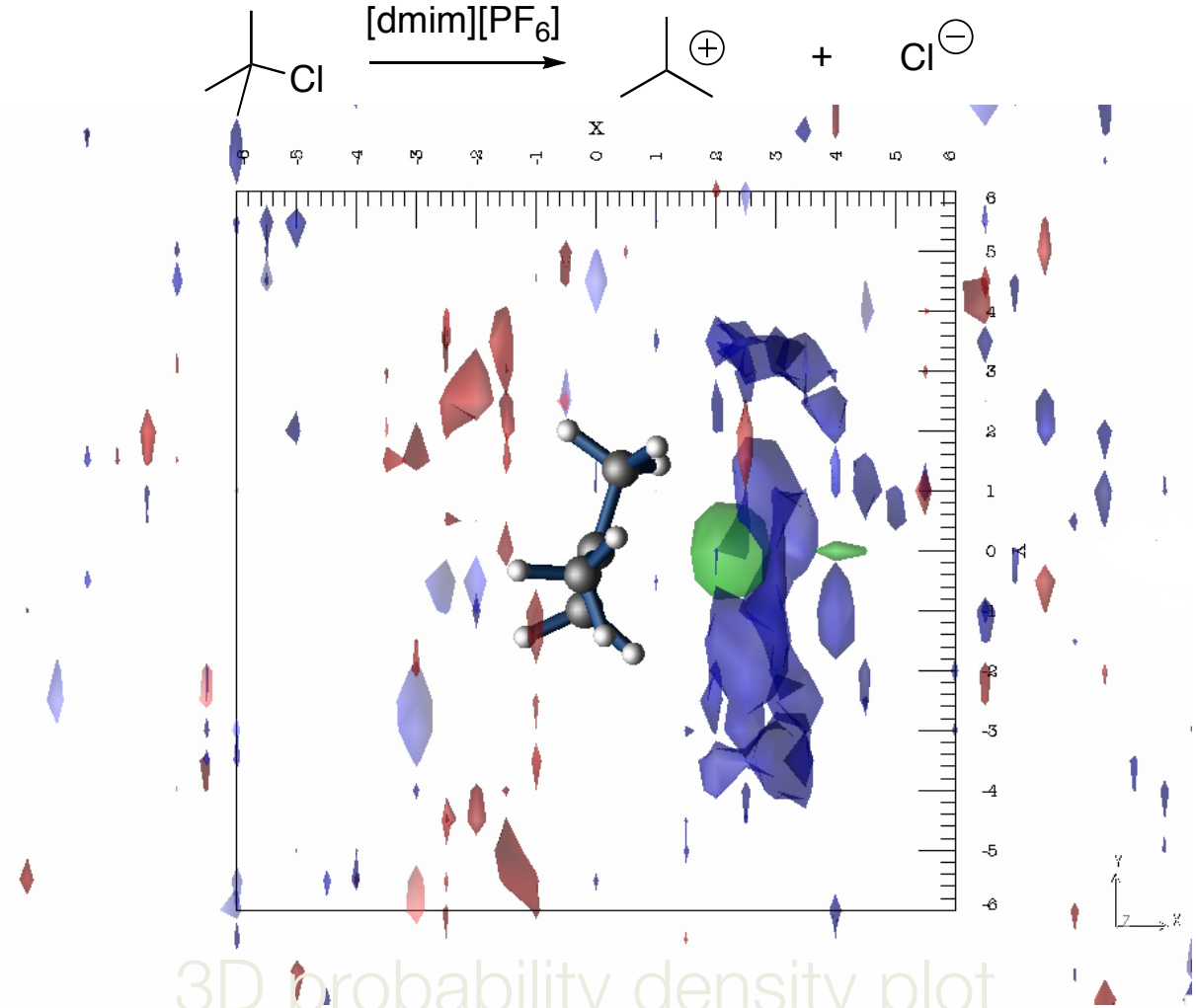


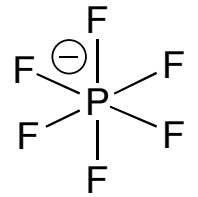
S_N1

S_NAr

S_N2

Cation – dmim$^+$

Anion – PF_6^-



Cl^-

H. M. Yau, S. A. Barnes, J. M. Hook, T. G. A. Youngs, A. K. Croft, and J. B. Harper, *Chem. Commun.*, 3576, 2008

Aromatic substitutions

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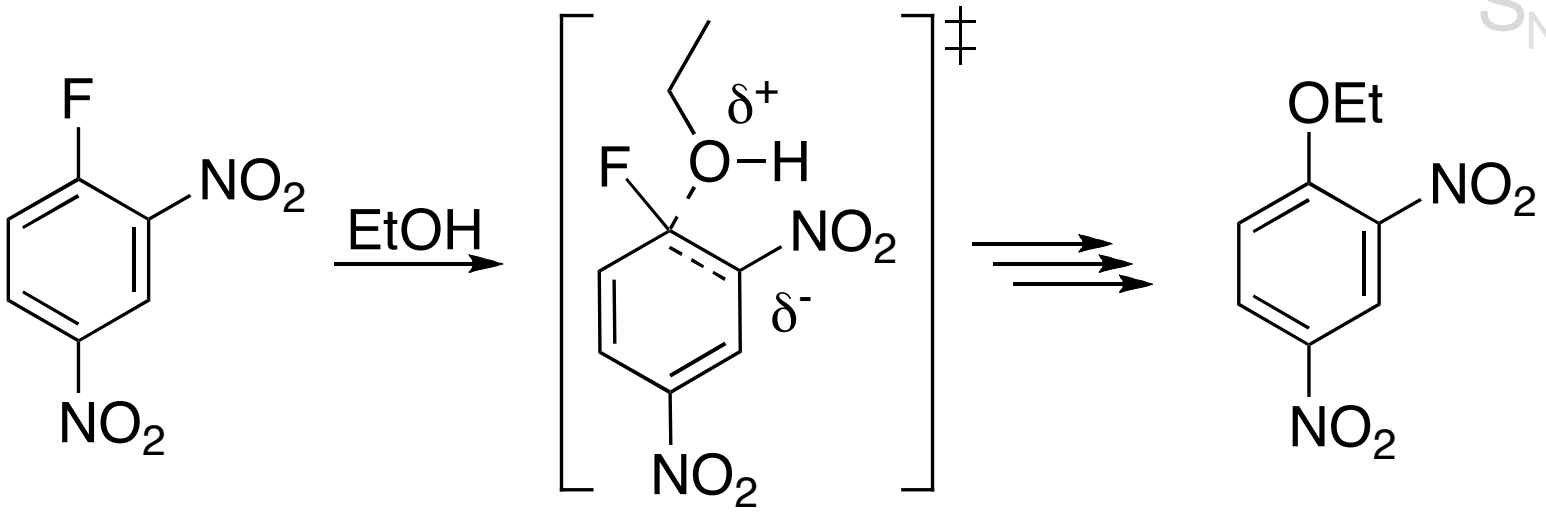
S_N1
S_NAr
S_N2



S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft,
Phys. Chem. Chem. Phys., 1873-1878, **12**(8), 2010

Activation entropy the driver

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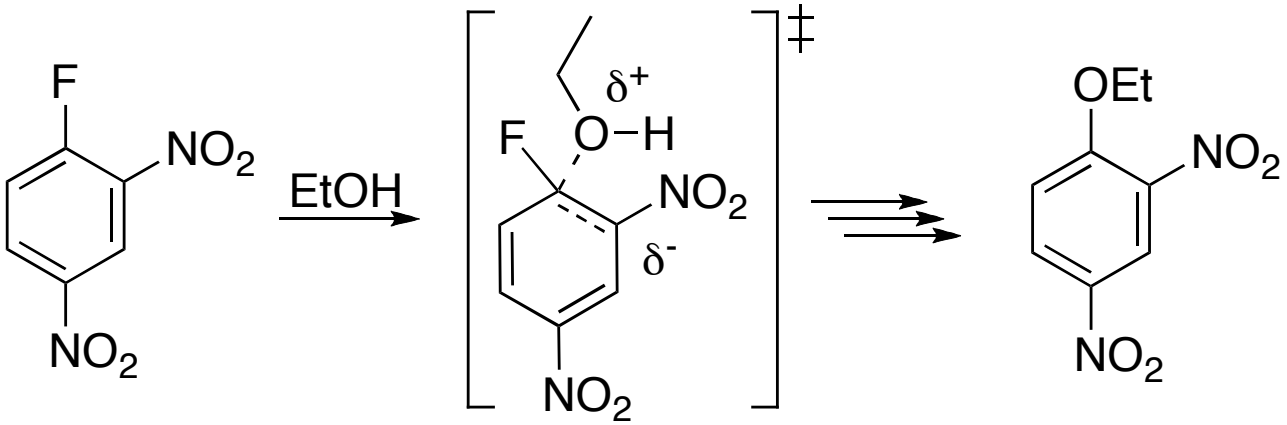
S_N1
S_NAr
S_N2



	Ethanol	Ionic liquid
$\Delta H^{\ddagger}$ / kJ.mol^{-1}	48.3 ± 1.4	49.6 ± 0.6
$\Delta S^{\ddagger}$ / J.K^{-1}.mol^{-1}	-252 ± 4	-229 ± 2

S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft,
Phys. Chem. Chem. Phys., 1873-1878, **12**(8), 2010

Activation entropy the driver

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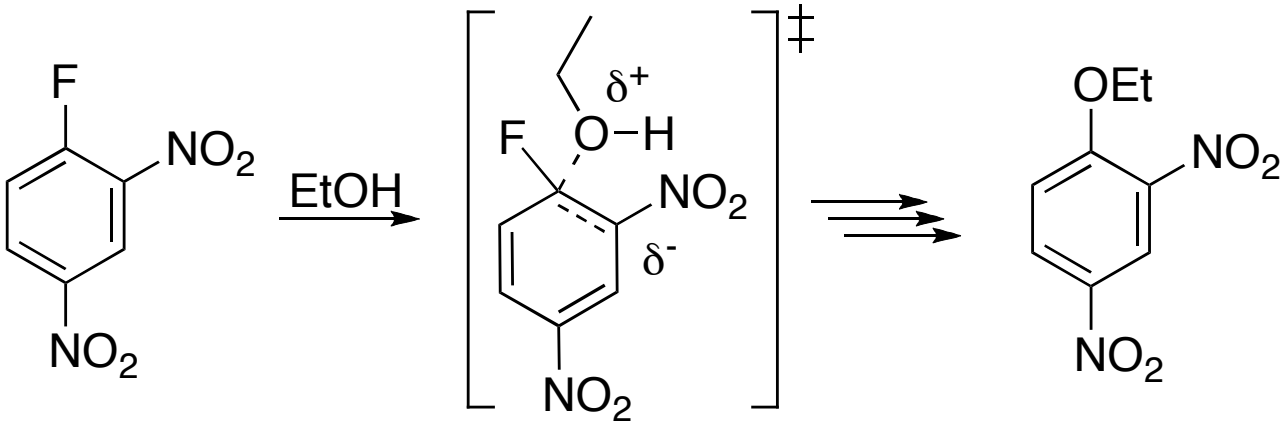
S_N1
S_NAr
S_N2



	Ethanol	Ionic liquid
$\Delta(\Delta H^{\ddagger})$ / kJ.mol^{-1}	↑	
$\Delta(\Delta S^{\ddagger})$ / J.K^{-1}.mol^{-1}	↑	

S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft,
Phys. Chem. Chem. Phys., 1873-1878, **12**(8), 2010

An anion-π interaction

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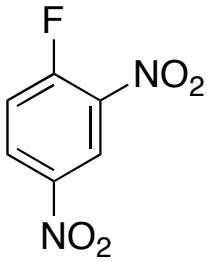
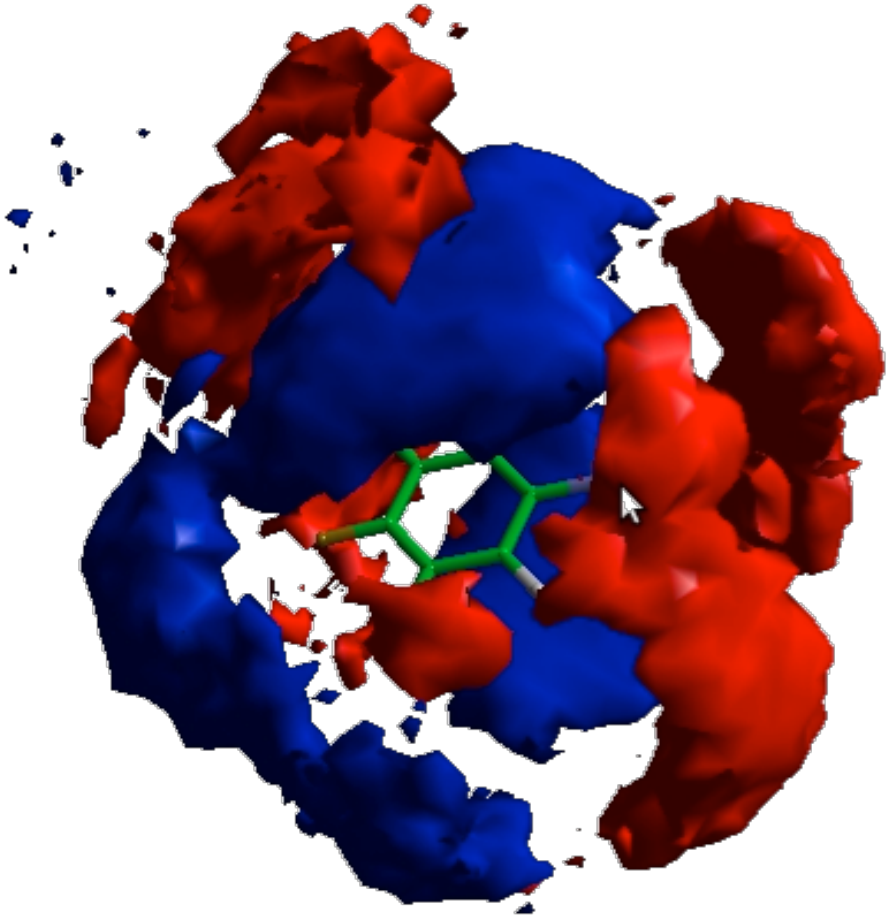
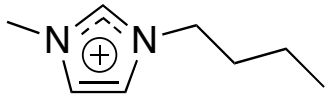
S_N1
S_NAr
S_N2

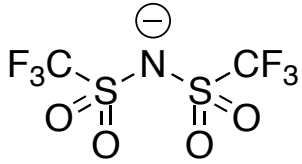




Cation – $bmim^+$



Anion – NTf_2^-



S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft,
Phys. Chem. Chem. Phys., 1873-1878, **12**(8), 2010

An anion-π interaction

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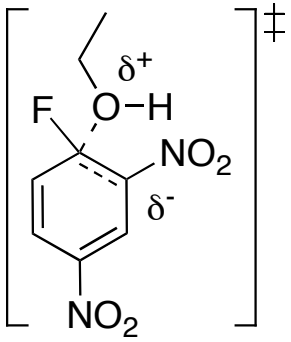
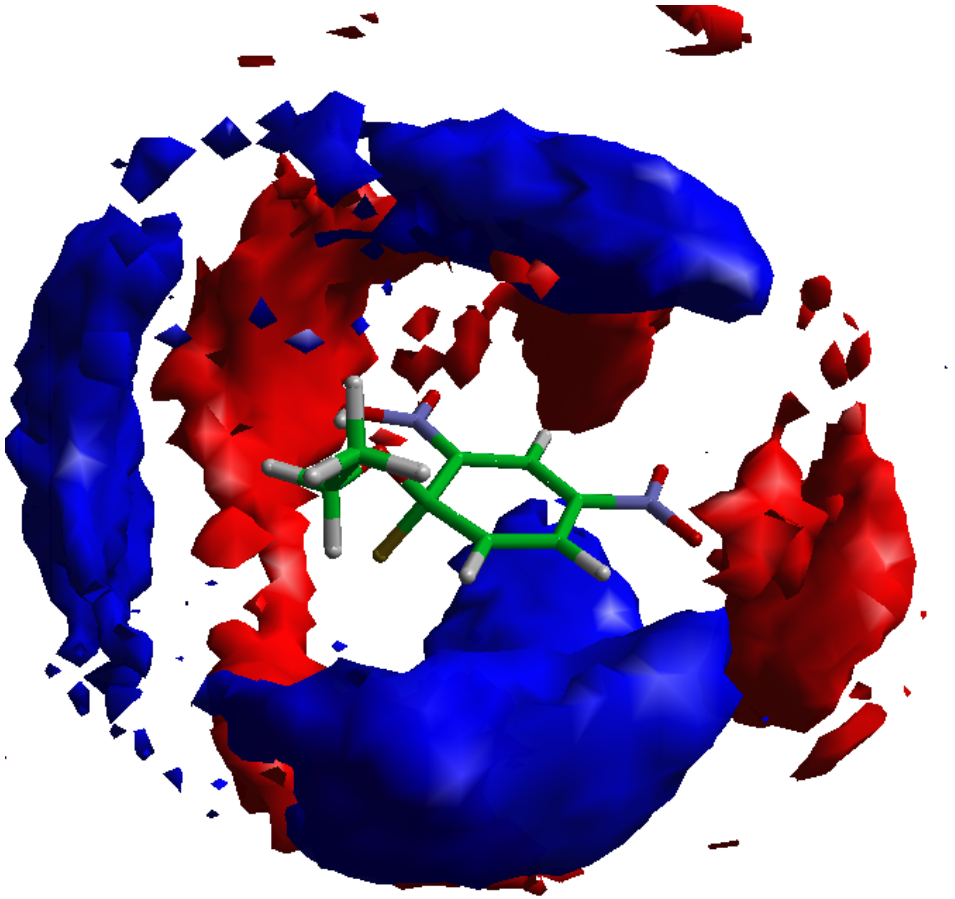
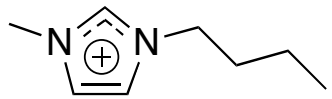
S_N1
S_NAr
S_N2

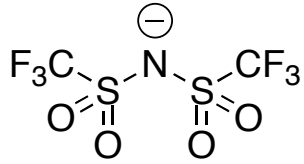




Cation – bmim$^+$



Anion – NTf_2^-



S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft,
Phys. Chem. Chem. Phys., 1873-1878, **12**(8), 2010

Organisation relative to ethanol

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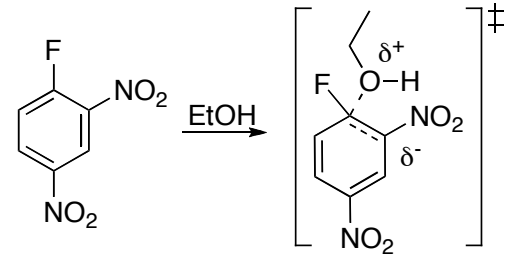
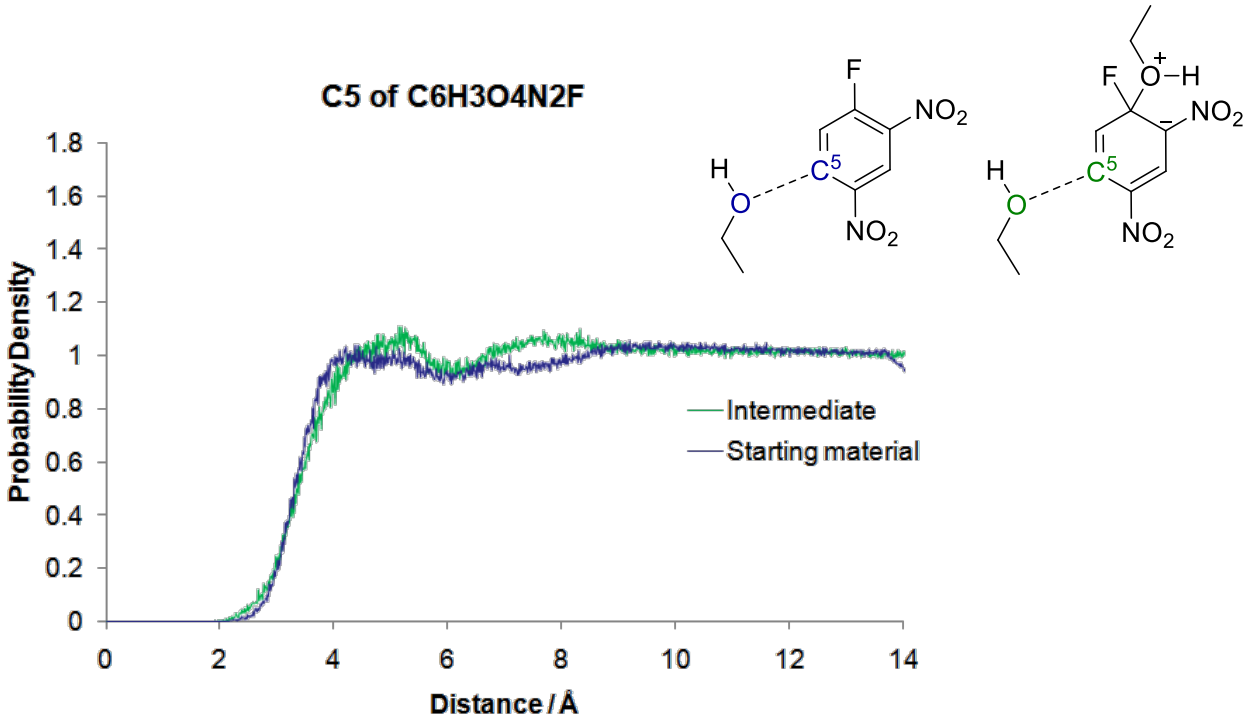
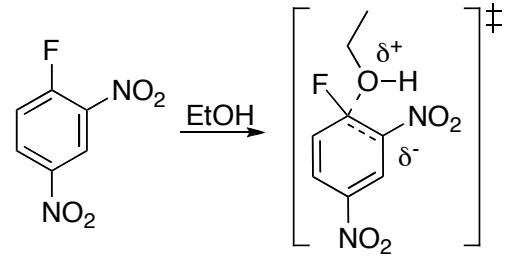


S_N1
S_NAr
S_N2

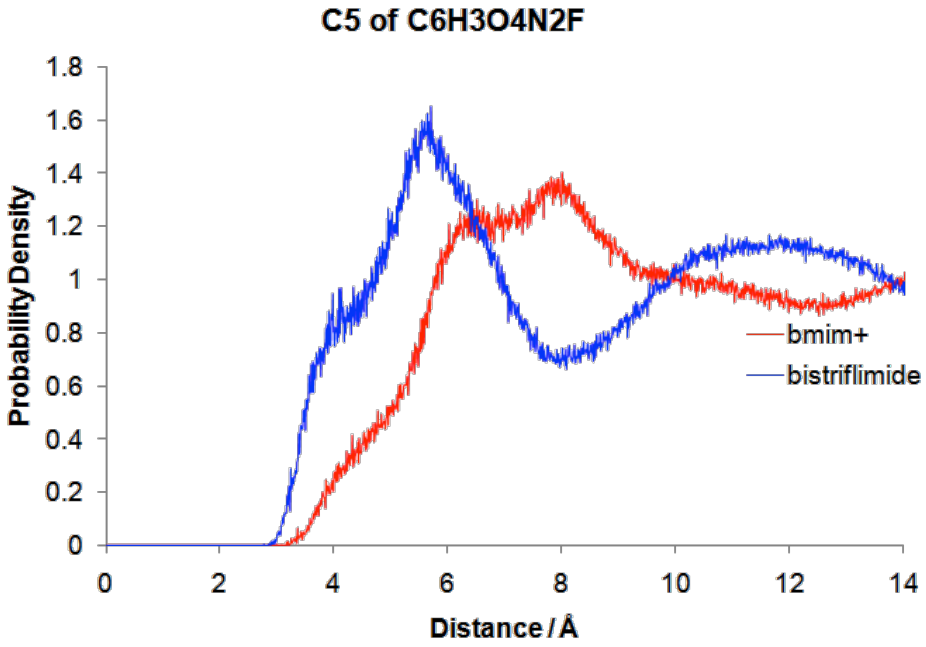


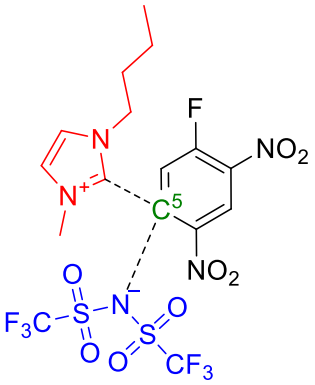
S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft, *Phys. Chem. Chem. Phys.*, 1873-1878, **12**(8), 2010

Organisation relative to ethanol



S_N1
S_NAr
S_N2





S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft, *Phys. Chem. Chem. Phys.*, 1873-1878, **12**(8), 2010

Organisation relative to ethanol

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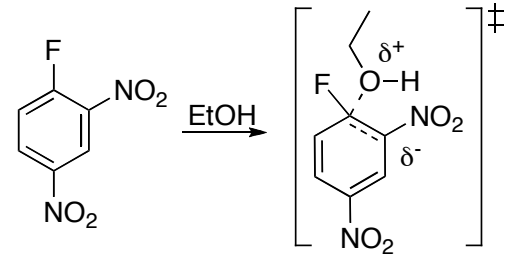
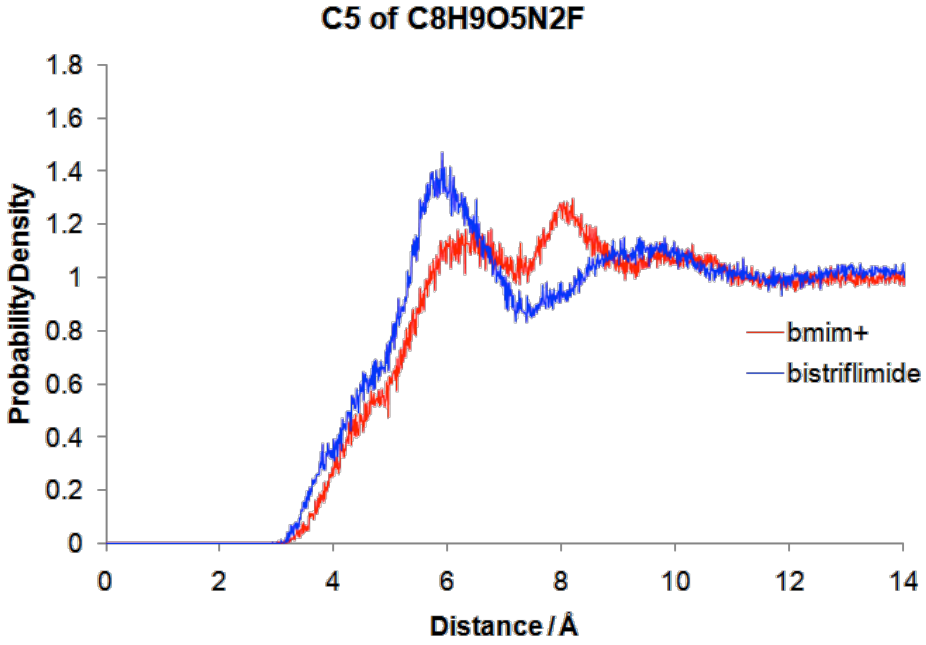
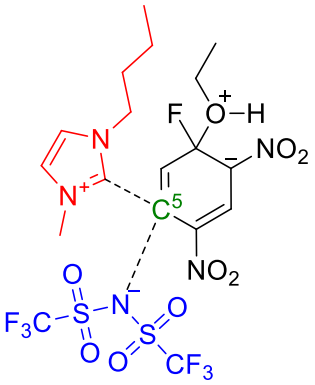


S_N1
S_NAr
S_N2





S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft, *Phys. Chem. Chem. Phys.*, 1873-1878, **12**(8), 2010

Anion-dominated changes

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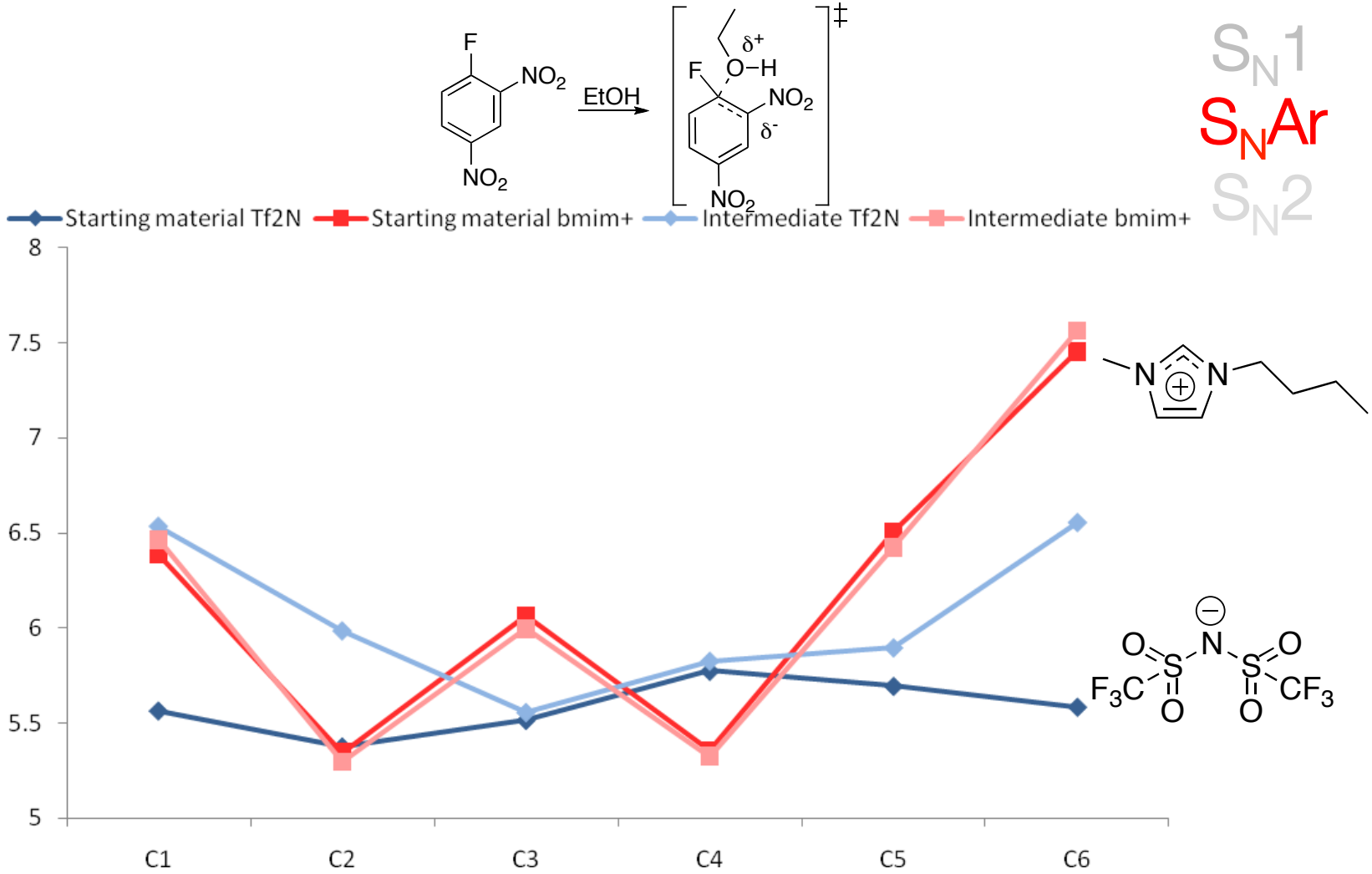
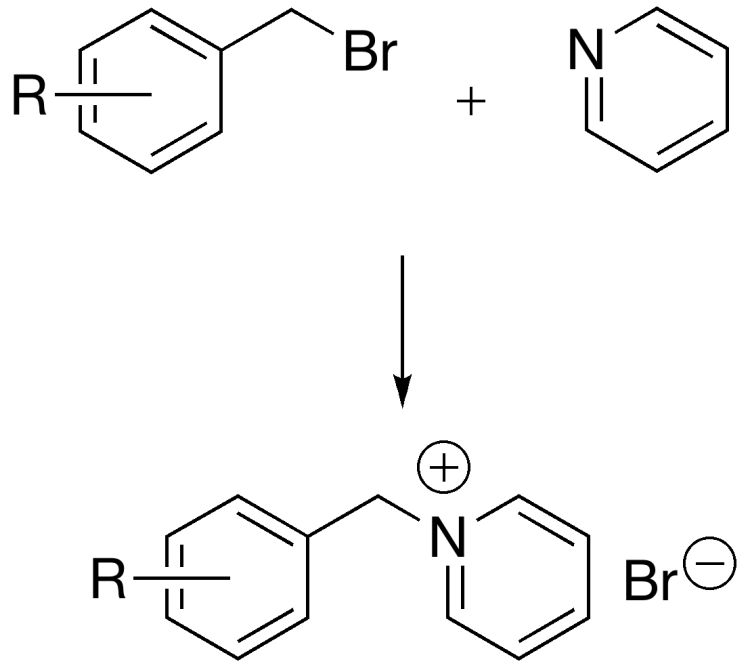


S. G. Jones, H. M. Yau, E. Davies, T. G. A. Youngs, J. B. Harper and A. K. Croft, *Phys. Chem. Chem. Phys.*, 1873-1878, **12**(8), 2010

Mentschukin reaction

S_N1
S_NAr
S_N2



Hammett data

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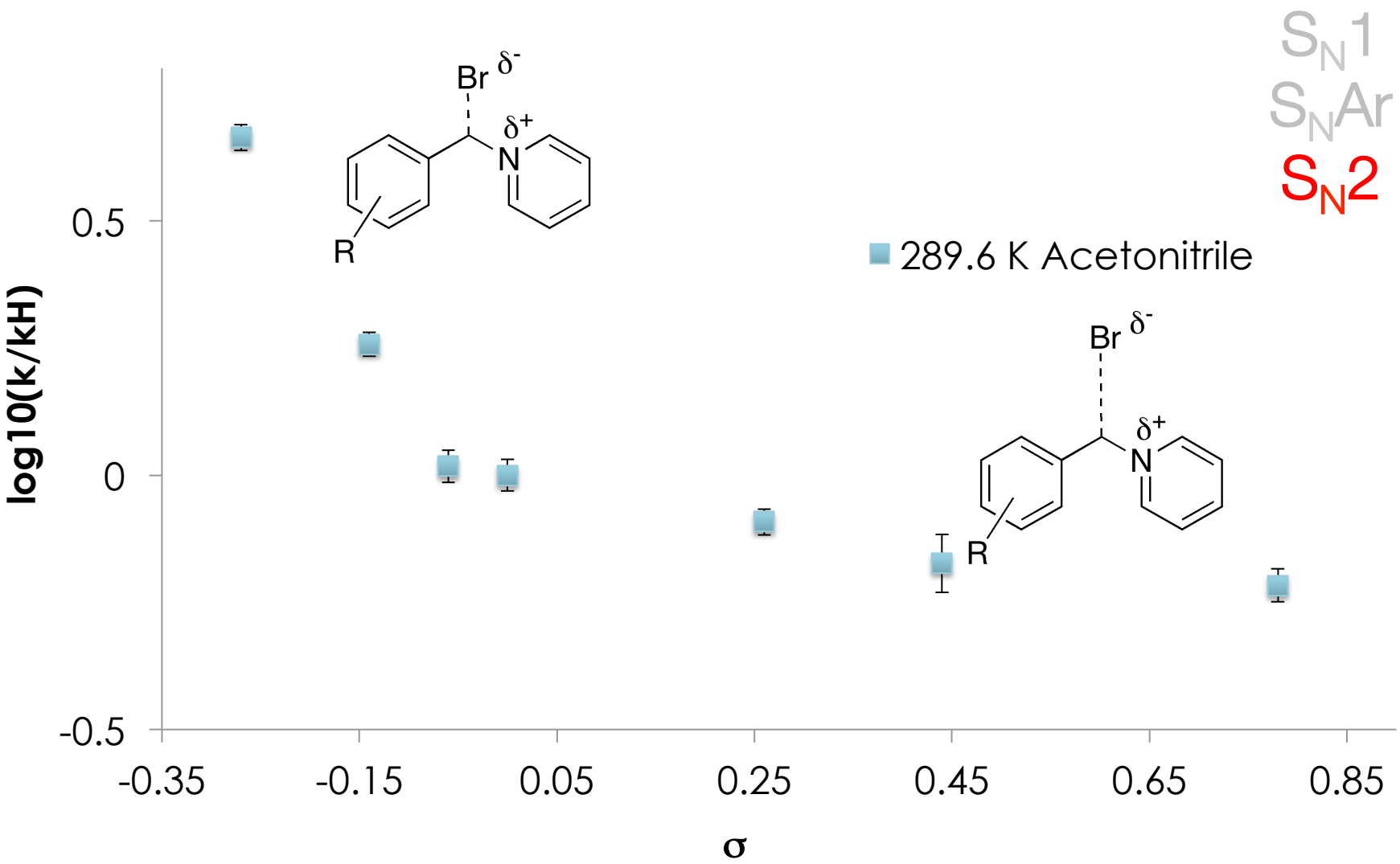
S_N1
S_NAr
S_N2



H. M. Yau, A. G. Howe, J. M. Hook, A. K. Croft, J. B. Harper, *Org. Biomol. Chem.*, 3572-3575, **7,** 2009.

Hammett data

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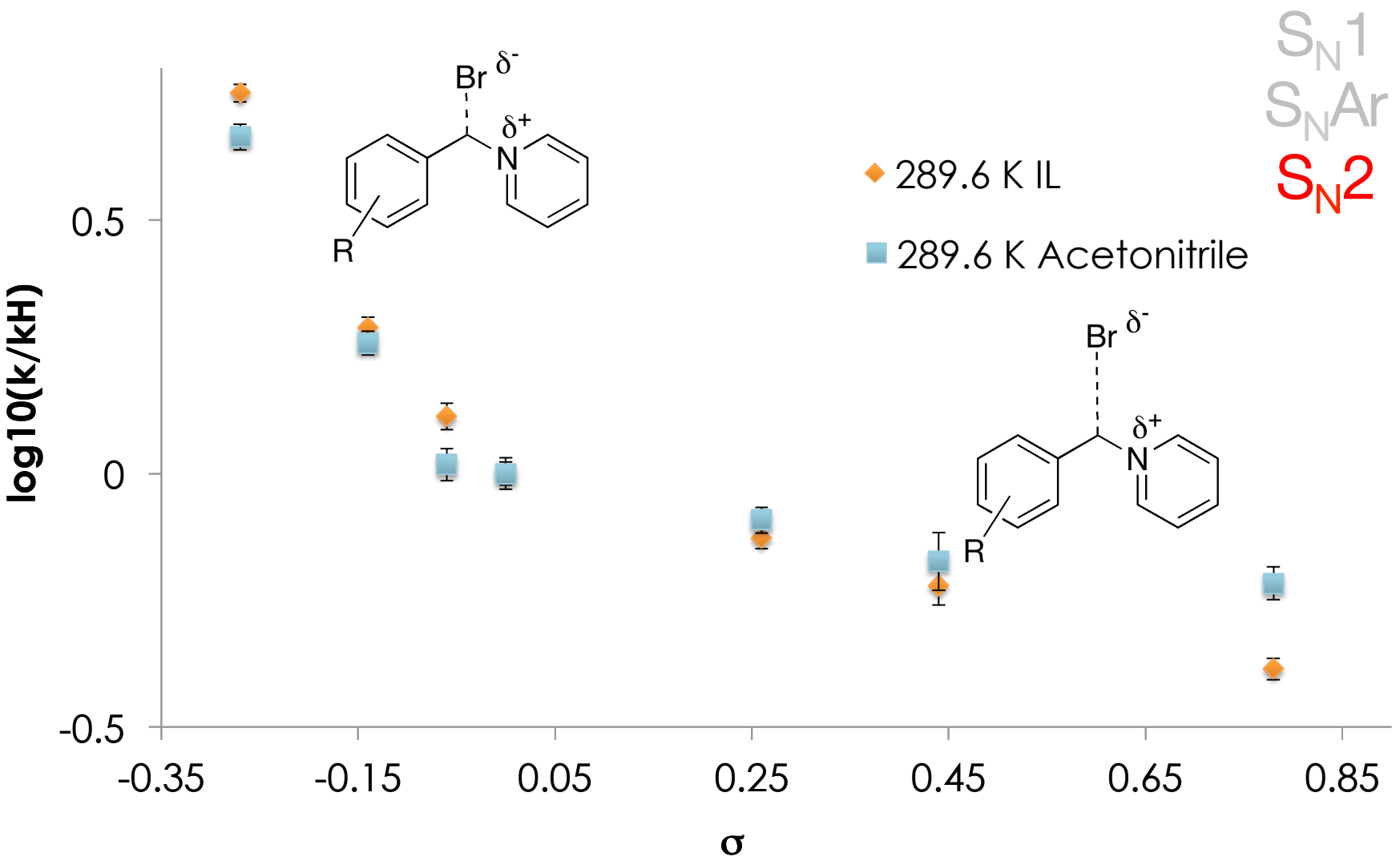

H. M. Yau, A. G. Howe, J. M. Hook, A. K. Croft, J. B. Harper, *Org. Biomol. Chem.*, 3572-3575, **7,** 2009.

Complex data

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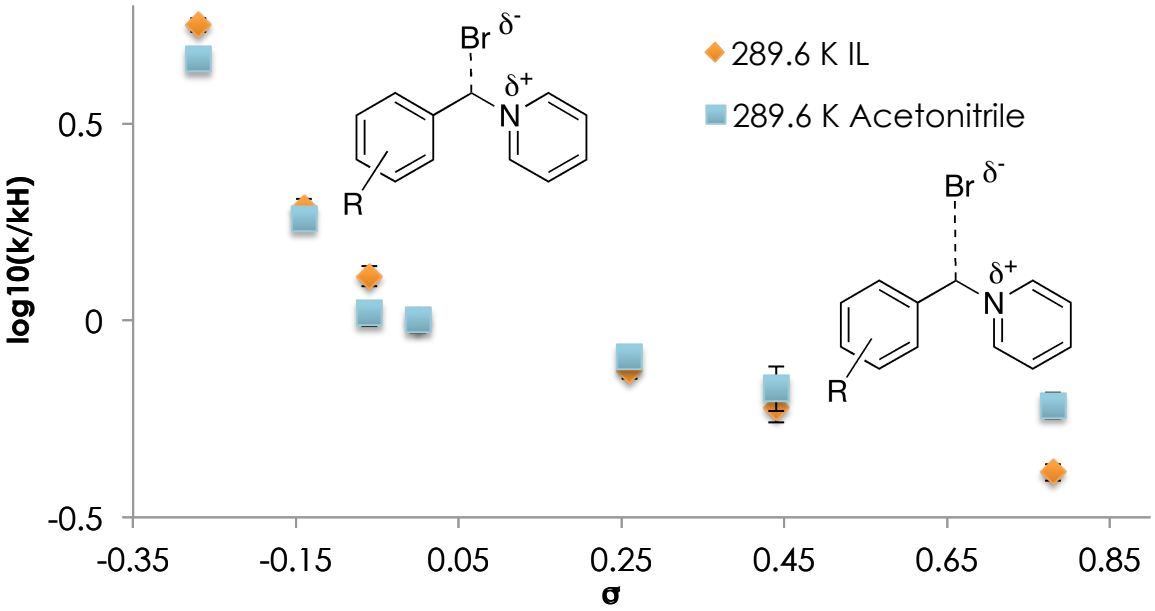
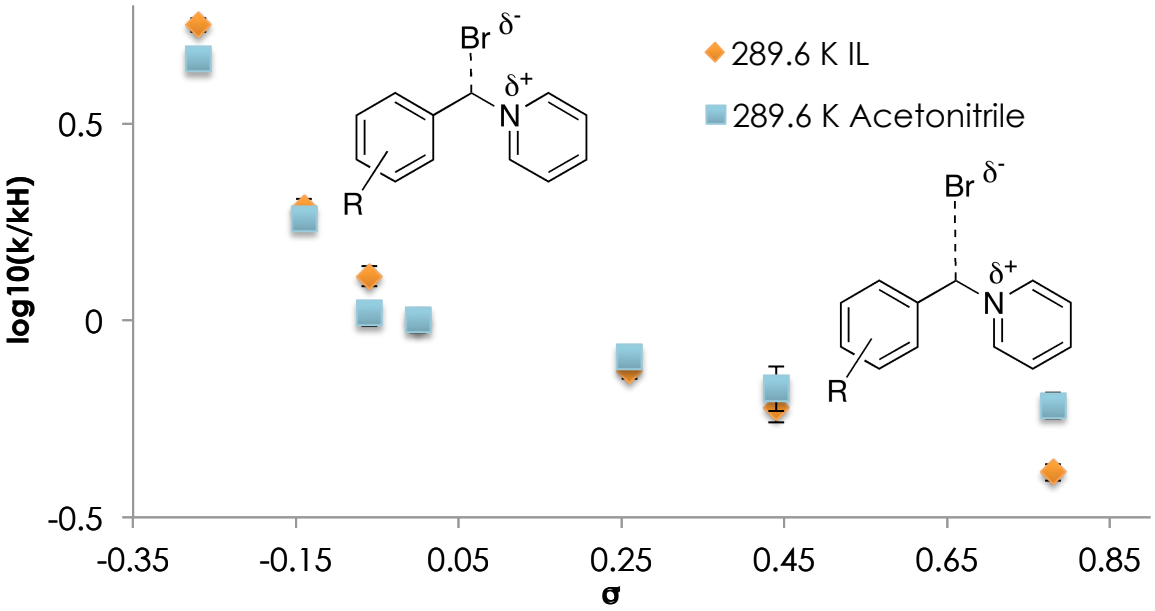


S_N1
S_NAr
S_N2

	$\Delta H^{\ddagger}$ / kJ.mol^{-1}		$\Delta S^{\ddagger}$ / J.K^{-1}.mol^{-1}	
Substituent	Acetonitrile	Ionic liquid	Acetonitrile	Ionic liquid
R = OCH_3	40.9 ± 1.2	47.7 ± 1.1	-220 ± 4	-188 ± 4
R = *p*-CH_3	43.2 ± 1.1	48.8 ± 0.9	-219 ± 4	-193 ± 3
R = *o*-CH_3	42.6 ± 1.3	53.5 ± 2.0	-226 ± 4	-181 ± 7
R = H	43.4 ± 0.8	49.9 ± 0.8	-224 ± 3	-195 ± 3
R = Br	47.7 ± 1.0	51.5 ± 1.2	-210 ± 3	-191 ± 4
R = $COOCH_3$	50.0 ± 2.8	53.1 ± 2.1	-205 ± 9	-187 ± 4
R = NO_2	44.2 ± 1.0	48.7 ± 0.7	-225 ± 3	-207 ± 2

Complex data



S_N1
S_NAr
S_N2

	$\Delta H^{\ddagger}$ / kJ.mol^{-1}		$\Delta S^{\ddagger}$ / J.K^{-1}.mol^{-1}	
Substituent	Acetonitrile	Ionic liquid	Acetonitrile	Ionic liquid
R = OCH_3	40.9 ± 1.2	47.7 ± 1.1	-220 ± 4	-188 ± 4
R = *p*-CH_3	43.2 ± 1.1	48.8 ± 0.9	-219 ± 4	-193 ± 3
R = *o*-CH_3	42.6 ± 1.3	53.5 ± 2.0	-226 ± 4	-181 ± 7
R = H	43.4 ± 0.8	49.9 ± 0.8	-224 ± 3	-195 ± 3
R = Br	47.7 ± 1.0	51.5 ± 1.2	-210 ± 3	-191 ± 4
R = $COOCH_3$	50.0 ± 2.8	53.1 ± 2.1	-205 ± 9	-187 ± 4
R = NO_2	44.2 ± 1.0	48.7 ± 0.7	-225 ± 3	-207 ± 2

Understanding molecular drivers

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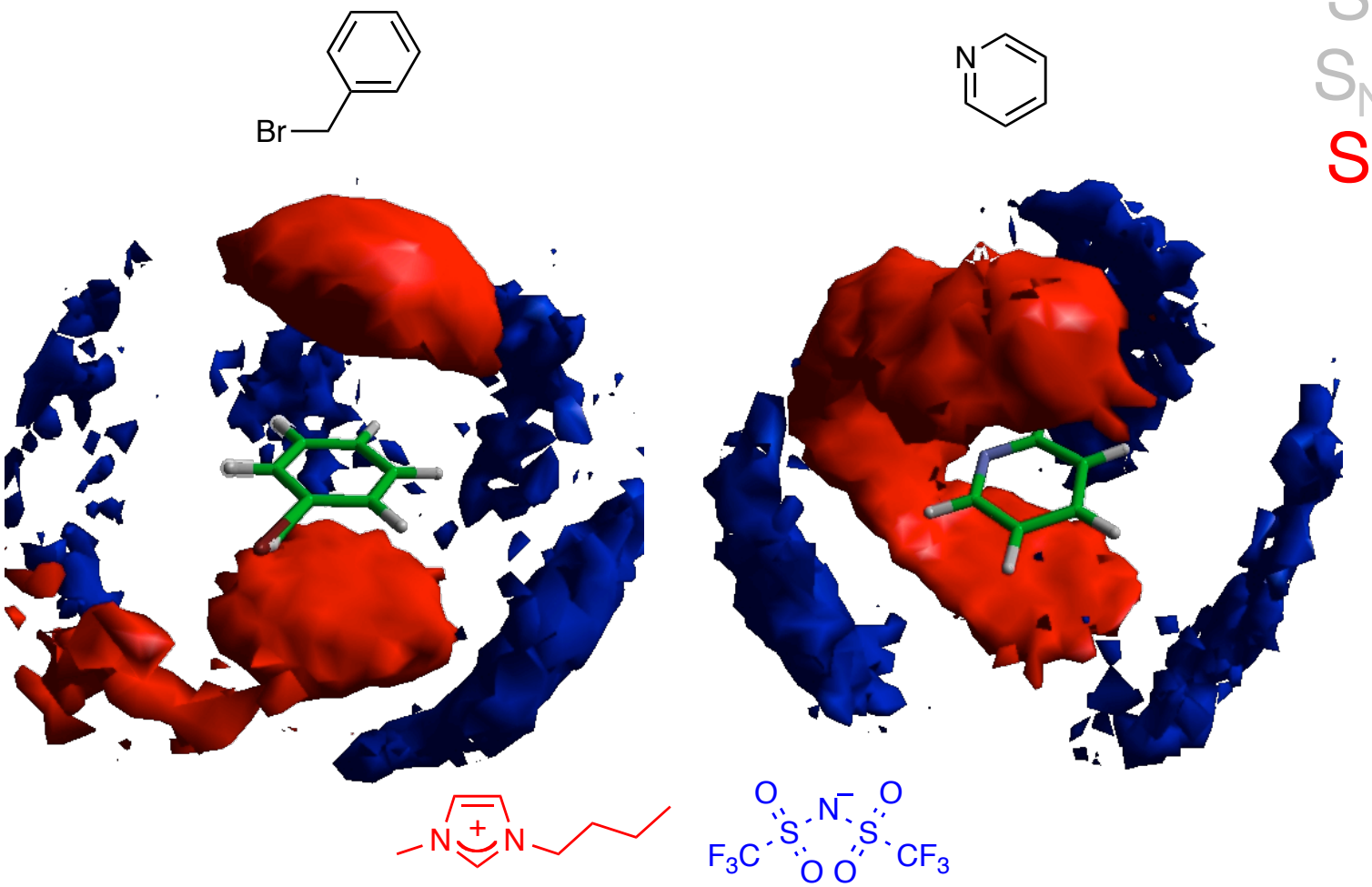
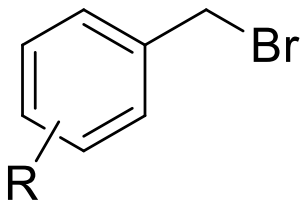
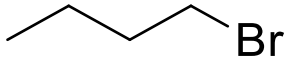
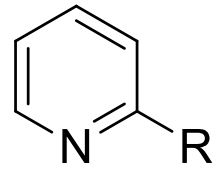
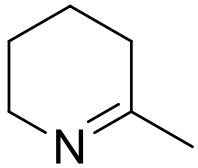
S_N1
S_NAr
S_N2

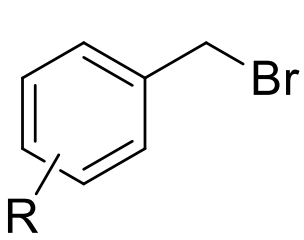
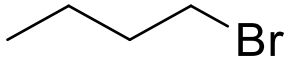
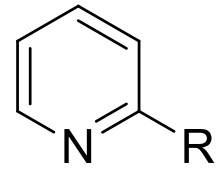
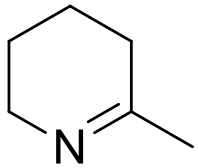


H. M. Yau, A. K. Croft and J. B. Harper, *Faraday Discuss.* **2012**, *154*, 365.
H. M. Yau, S. Keaveney, B. Butler, E. Tanner, M. Guerry, S. George, M. Dunn, A. K. Croft and J. B. Harper, *Pure Appl. Chem.*, **2013**, *85*, 1979.

S_N1
S_NAr
S_N2

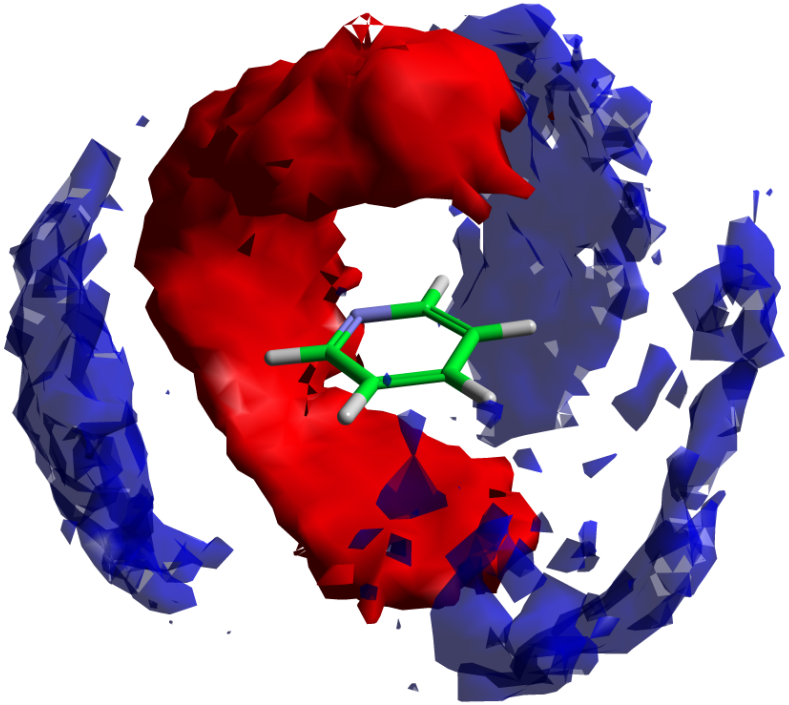
		
 R=H or CH_3	Aromatic	Non-Aromatic
	Aromatic	Aromatic
	Aromatic	Non-aromatic
	Non-aromatic	Non-aromatic

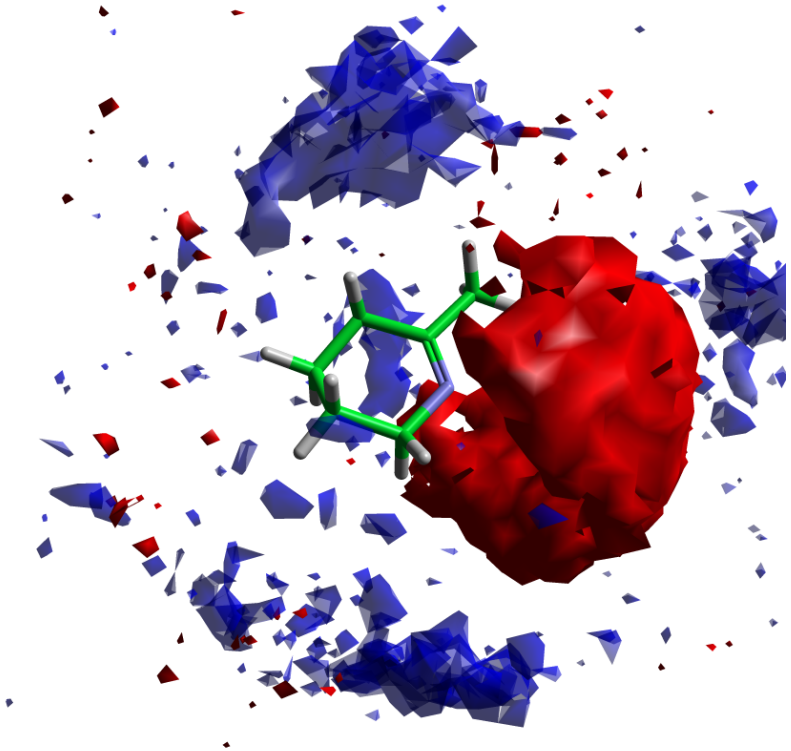
S_N1
S_NAr
S_N2

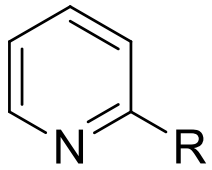
		
 R=H or CH_3	Aromatic	Non-Aromatic
	Aromatic	Aromatic
	Aromatic	Non-aromatic
	Non-aromatic	Non-aromatic

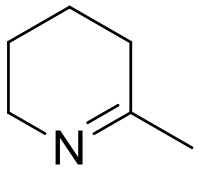
$\Delta H^{\ddagger}$ & $\Delta S^{\ddagger}$

Organisation around Nitrogen key









Take home messages …

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- Ionic liquids are not the same as molecular solvents.
  - Being mixtures of ions introduces more significant interactions than in molecular solvents.
  - Considering them in terms developed for molecular solvents does not work.
- Electrostatic interactions with (incipient) charges aren't as important as is often touted – it is all about the entropy.
  - Organisation about both starting material and transition state must be considered, in all forms.
- **There is the potential to exploit these effects in controlling reaction outcome**

Where to next

- Upgrade calculations to ensure effects are taken into account
  - Switch from DL_POLY to Amber
  - Start incorporating polarisation

Acknowledgements

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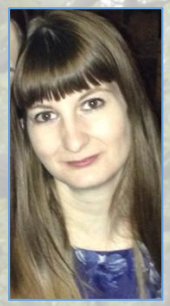
NGS



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