Electronic Supplementary Information (ESI)

Lineshape analysis of 7k and 7l

Measurements were taken under oxygen-free conditions on a BRUKER DRX 400 using degassed solvent (DMSO-d_6) and solutes. Temperature control (±1 K) was achieved with an BRUKER BVT 3000. Carbon NMR spectra were recorded from 300 K to 370 K with intervals of 10 K and subjected to careful phase and baseline correction. General temperature dependence of line broadening was checked using the solvent and anion signals' linewidths and was found to be insignificant for non-exchanging nuclei (Fig. 1, 4). Lineshape analysis of process (2) was then performed on all splitted signals of the 2-ethylhexyl substituent and the methyl group of **7k** and **7l** using DNMR module of Topspin 3.0 (BRUKER). Each pair of exchanging signals was treated as an isolated spin system and was fitted using simplex iterations on the chemical shifts (δ), intensities (I) and rate constants of the exchange process (k). If possible, multiple adjacent signals were fitted simultaneously. Minor differences in the intensities of exchanging signals were neglected, giving a mutual exchange model. As substantially no exchange effects were observed at 300 K, line broadening due to relaxation was calibrated for each pair of nuclei using the low temperature values obtained from a lorentzian deconvolution. The obtained k values were found to be similar for all probed carbon atoms and were averaged before further analysis. Outliers caused by large experimental errors due to very small line splitting or poor signal-to-noise ratios as well as all insignificant values at the low temperature side (300 K for **7k**, 300 K and 310 K for **7l**, *vide supra*) were rejected (Fig. 2, 5). Activation enthalpy ($\Delta H^{\ddagger}$), activation entropy ($\Delta S^{\ddagger}$) as well as *Gibb*'s free activation enthalpy ($\Delta G^{\ddagger}$) and activation energy (E_A) at 300 K were taken from least-squares linear fits on the corresponding *Eyring* plots (Fig. 3, 6).

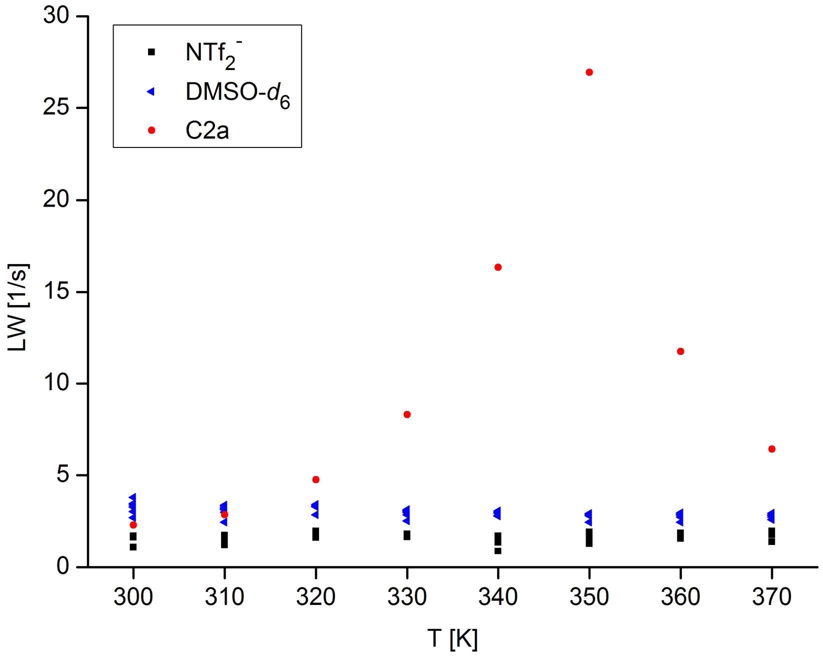

Fig. 1 Linewidths of DMSO-d_6 and Tf_2N^- compared to C2a in measurement of **7k**.

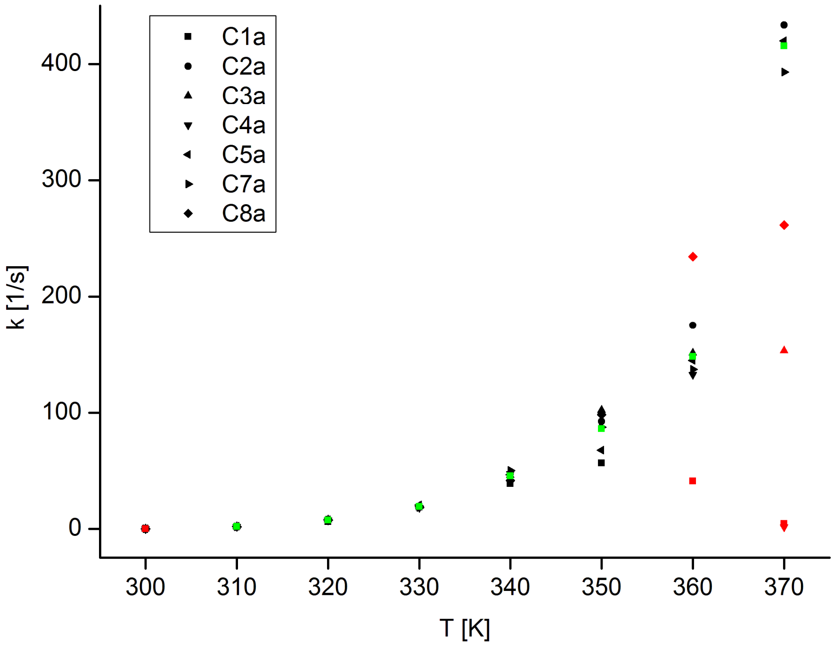

Fig. 2 Rate constants k for different carbon atoms (black), averaged values (green) and rejected data points (red) for **7k**.

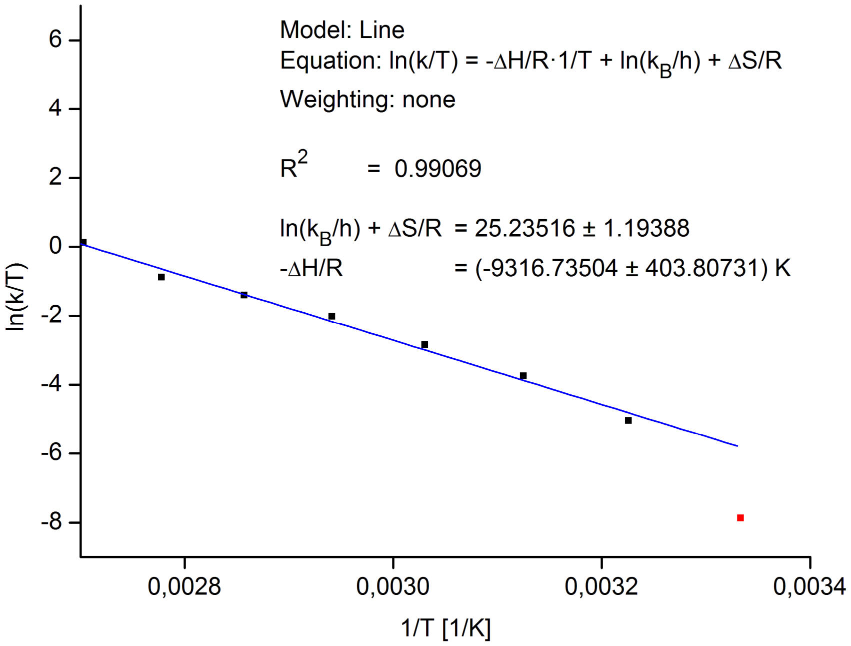

Fig. 3 *Eyring* plot for **7k**.

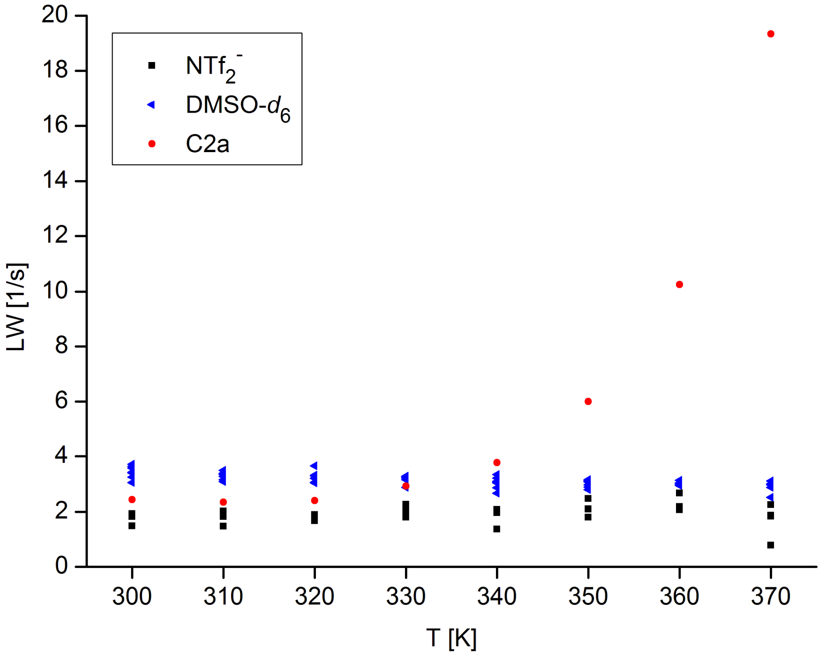

Fig. 1 Linewidths of DMSO-d_6 and Tf_2N^- compared to C2a in measurement of **7l**.

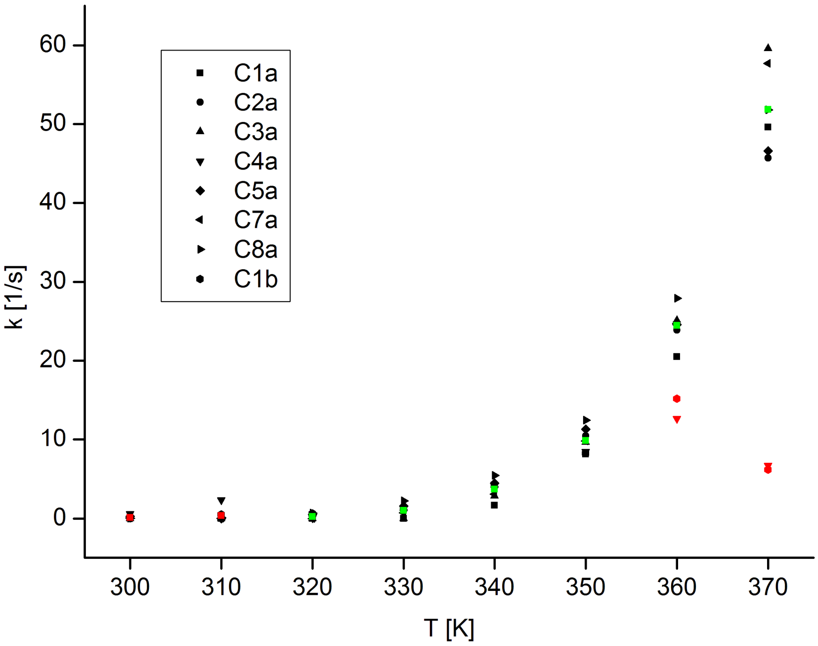

Fig. 4 Rate constants k for different carbon atoms (black), averaged values (green) and rejected data points (red) for **7l**.

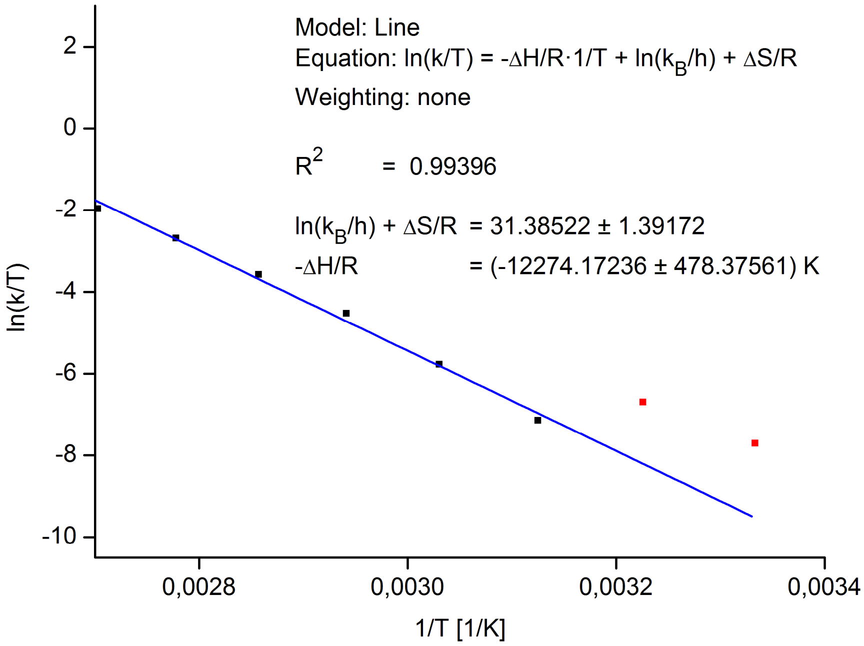

Fig. 5 *Eyring* plot for **7l**.

Crystal structure determination of 10

Table 1 Crystal data and structure refinement.

Empirical formula	$C_7 H_{18} Cl N_3$	
Formula weight	179.69 g/mol	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/m	
Unit cell dimensions	a = 13.622(3) Å	α = 90°.
	b = 7.8211(11) Å	β = 104.10(2)°.
	c = 9.8987(17) Å	γ = 90°.
Volume	1022.9(3) $Å^3$	
Z	4	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.324 mm^{-1}	
F(000)	392	
Crystal size	0.36 x 0.27 x 0.09 mm^3	
Theta range for data collection	2.12 to 25.96°.	
Index ranges	-16<=h<=16, -9<=k<=9, -12<=l<=12	
Reflections collected	4051	
Independent reflections	1080 [R(int) = 0.0638]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Treatment of hydrogens	Constrained (riding model)	
Data / restraints / parameters	1080 / 0 / 77	
Goodness-of-fit on F^2	1.257	
Final R indices [I>2sigma(I)]	R_1 = 0.0701, wR_2 = 0.2253	
R indices (all data)	R_1 = 0.0933, wR_2 = 0.2320	
Largest diff. peak and hole	0.466 and -0.280 e.$Å^{-3}$	

Table 2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5000	0	0	37(2)
C(2)	3969(4)	-2607(6)	-474(5)	56(1)
C(3)	3596(5)	0	1137(6)	69(2)
C(11)	0	5000	5000	30(2)
C(12)	646(4)	7627(6)	4177(5)	60(1)
C(13)	1854(4)	5000	5504(6)	70(2)
N(1)	5000	-1603(12)	0	40(2)
N(2)	4213(4)	-978(8)	238(6)	35(1)
N(11)	0	6666(11)	5000	35(2)
N(12)	829(4)	5896(8)	4892(6)	35(1)
Cl(1)	1819(1)	0	7489(2)	59(1)

Table 3 Bond lengths [Å] and angles [°].

C(1)-N(1)	1.254(10)	N(1)-C(1)-N(2)#1	123.6(3)
C(1)-N(2)	1.384(6)	N(1)-C(1)-N(2)	56.4(3)
C(2)-N(1)	1.578(6)	N(2)-C(1)-N(2)#2	112.9(5)
C(3)-N(2)	1.564(7)	N(2)-C(1)-N(2)#3	67.1(5)
C(11)-N(11)	1.303(9)	N(11)-C(11)-N(12)#4	121.1(3)
C(11)-N(12)	1.355(6)	N(11)-C(11)-N(12)	58.9(3)
C(12)-N(11)	1.534(6)	N(12)#5-C(11)-N(12)	117.7(6)
C(13)-N(12)	1.548(8)	N(12)-C(11)-N(12)#6	62.3(6)
N(1)-C(2)#2	1.578(6)	C(1)-N(1)-C(2)	119.8(3)
N(11)-C(12)#5	1.534(6)	C(2)-N(1)-C(2)#2	120.3(7)
		C(1)-N(2)-C(3)	111.9(4)
		C(11)-N(11)-C(12)	119.3(4)
		C(12)#5-N(11)-C(12)	121.3(7)
		C(11)-N(12)-C(13)	115.2(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z #2 -x+1,y,-z #3 x,-y,z #4 -x,-y+1,-z+1 #5 -x,y,-z+1 #6 x,-y+1,z

Table 4 Anisotropic displacement parameters (Å^{2}x 10^3). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	32(4)	55(6)	24(3)	0	8(3)	0
C(2)	74(3)	43(3)	47(2)	-5(2)	9(2)	-13(2)
C(3)	43(3)	132(7)	37(3)	0	23(3)	0
C(11)	27(3)	40(5)	21(3)	0	5(3)	0
C(12)	86(3)	47(3)	46(2)	9(2)	17(2)	-20(2)
C(13)	24(3)	149(8)	37(3)	0	8(2)	0
N(1)	43(5)	31(6)	44(5)	0	8(4)	0
N(2)	34(3)	42(4)	32(3)	-4(3)	15(2)	-5(3)
N(11)	36(4)	35(6)	38(4)	0	16(4)	0
N(12)	29(3)	44(3)	33(3)	4(3)	9(2)	-8(3)
Cl(1)	48(1)	90(1)	34(1)	0	4(1)	0

Table 5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3).

	x	y	z	U(eq)
H(2A)	3828	-3209	327	83
H(2B)	4017	-3437	-1196	83
H(2C)	3420	-1799	-847	83
H(3A)	3534	-718	1923	103
H(3B)	2920	268	562	103
H(3C)	3947	1063	1488	103
H(12A)	977	6803	3688	89
H(12B)	1161	8305	4820	89
H(12C)	213	8388	3499	89
H(13A)	1740	3951	5985	105
H(13B)	2296	5768	6166	105
H(13C)	2176	4714	4749	105