

Supplementary Material

Electrochemical Properties of a Verdazyl Radical in Room Temperature Ionic Liquids

Junqiao Lee,^A Chiara Caporale,^A Allan J. McKinley,^B Rebecca O. Fuller,^{A,C} and Debbie S. Silvester^{A,D}

^ACurtin Institute for Functional Molecules and Interfaces, School of Molecular and Life Sciences, Curtin University, GPO Box U1987, Perth, WA 6845, Australia.

^BChemistry, School of Molecular Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia.

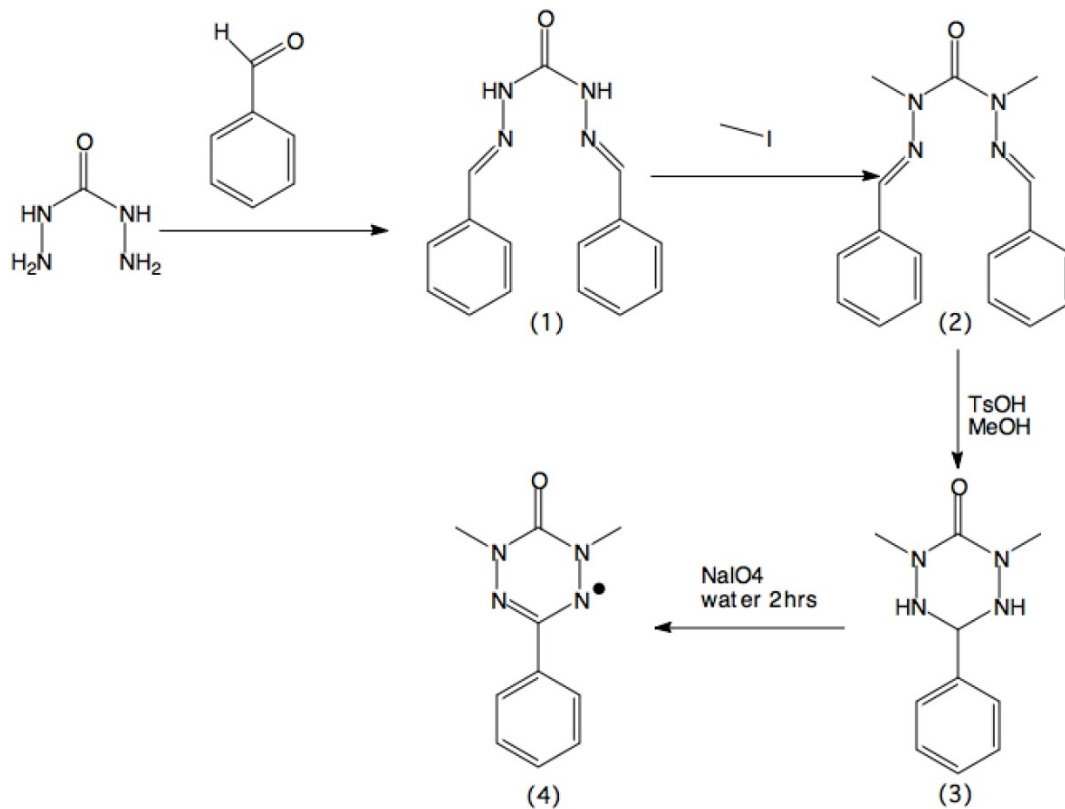
^CCurrent address: School of Natural Sciences-Chemistry, University of Tasmania, Hobart, Tas. 7001, Australia.

^DCorresponding author. Email: d.silvester-dean@curtin.edu.au

Synthesis of the verdazyl radical

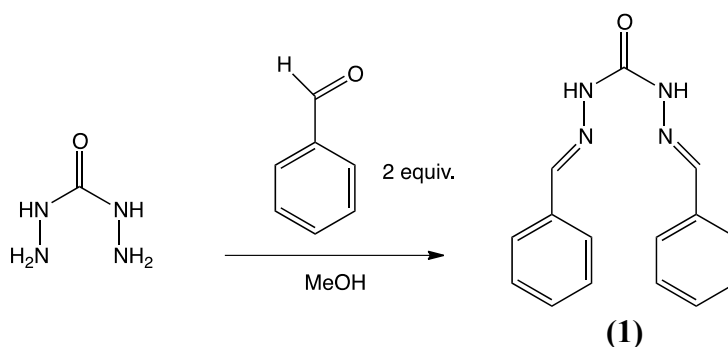
The synthesis of 1,5-dimethyl-3-phenyl-6-oxoverdazyl (MPV) followed a previously reported method [1] with the final product being oxidised to the radical (**4**) in *Scheme S1*.

[1] M. Bancercz, B. Yuon, M. V. DaCosta and M. K. Georges, *J. Org. Chem.*, 2012, **77**, 2415-2421.



Scheme S1: Synthesis of the verdazyl radical (4)

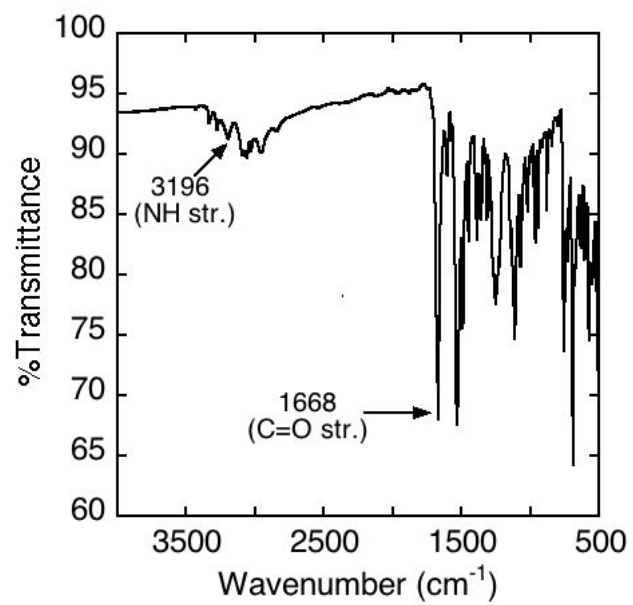
Synthesis of Carbo-di-N-benzylhydrazone (1)



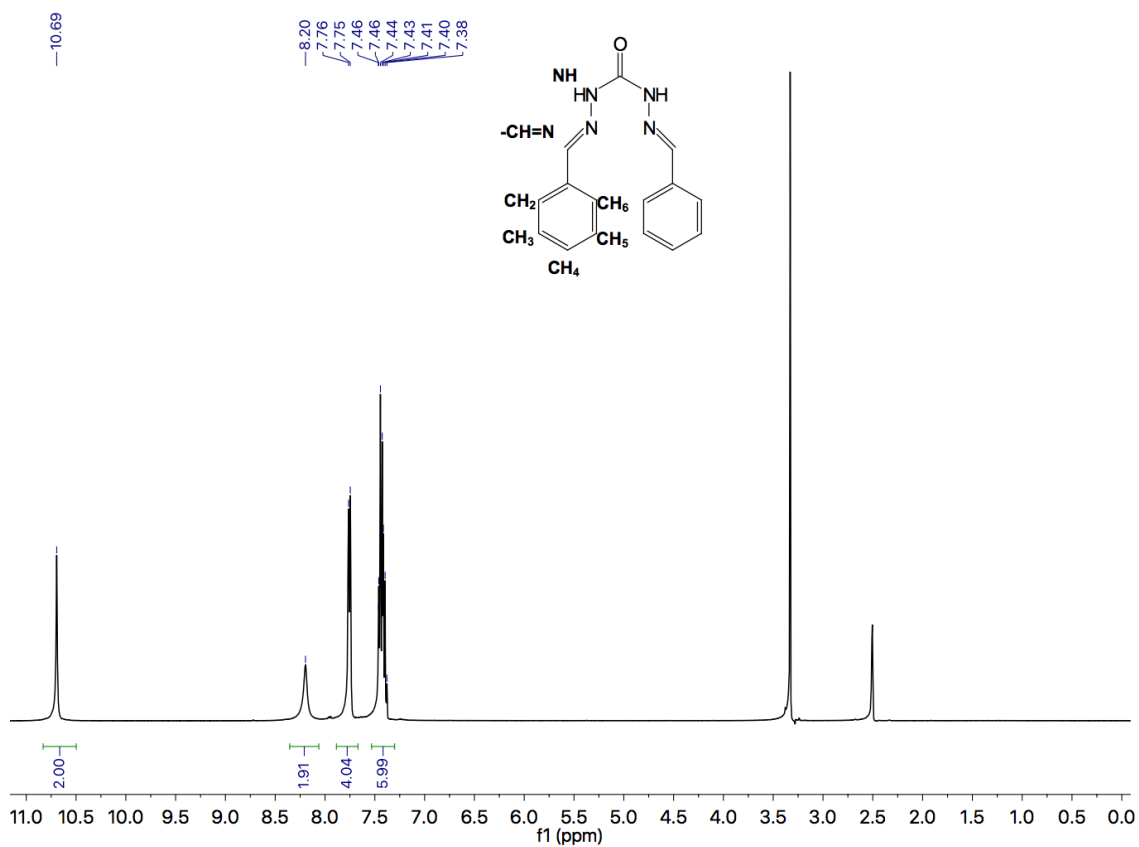
Carbohydrazide (0.9 g, 0.01 mol) was added to 55 mL of methanol. Benzaldehyde (2.1 ml, 0.02 mol) was added dropwise to the solution. The mixture was heated to reflux for 1.5 hours. The mixture was cooled and the crude product collected then recrystallised from 3:1 v/v hot ethanol in water (1.385 g). Yield 52.1 %. MP: 211-212°C. The spectroscopic data for compound **2** matched that reported previously in the literature. [2] IR (ν / cm^{-1}): 3195 (N-H stretch), 3059 (Ar)1668 (C=O stretch). ^1H NMR (δ / ppm , $\text{DMSO-}d_6$): 10.70 (s, 2H, **2NH**), 8.20 (s, 2H, **2-CH=N**), 7.75 (d, 4H, **2CH₂**, **2CH₆**, $J = 7.20$ Hz), 7.46 – 7.38 (m, 6H, **2CH₃**, **2CH₄**, **2CH₅**). ^{13}C NMR (δ / ppm , $\text{DMSO-}d_6$): 152.4 (CO), 143.5 (**2-CH=N**), 135.0 (**2C₁**), 129.9 (**2CH₂** or **2CH₆**), 129.1 (**2CH₃**, **2CH₄**, **2CH₅**), 127.2 (**2CH₂** or **2CH₆**). Anal. calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}$: C, 67.65; H, 5.30; N, 21.04. Found C, 67.68; H, 5.39; N, 20.92.

[2] Z. Li, W. Zhu, J. Yu, X. Ma, Z. Lu and S. Xiao, *Synthetic Communications*, 2006, **36(18)** 2623-2619.

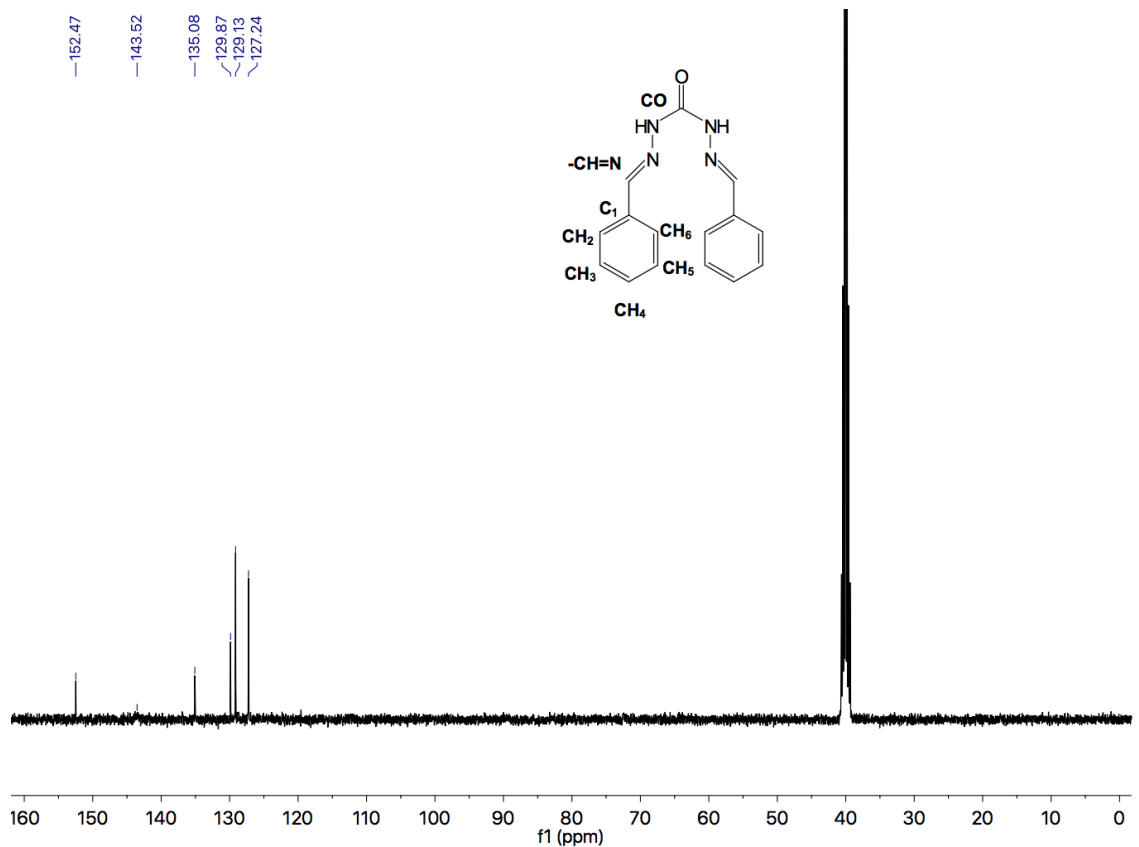
IR Spectroscopy of (1):



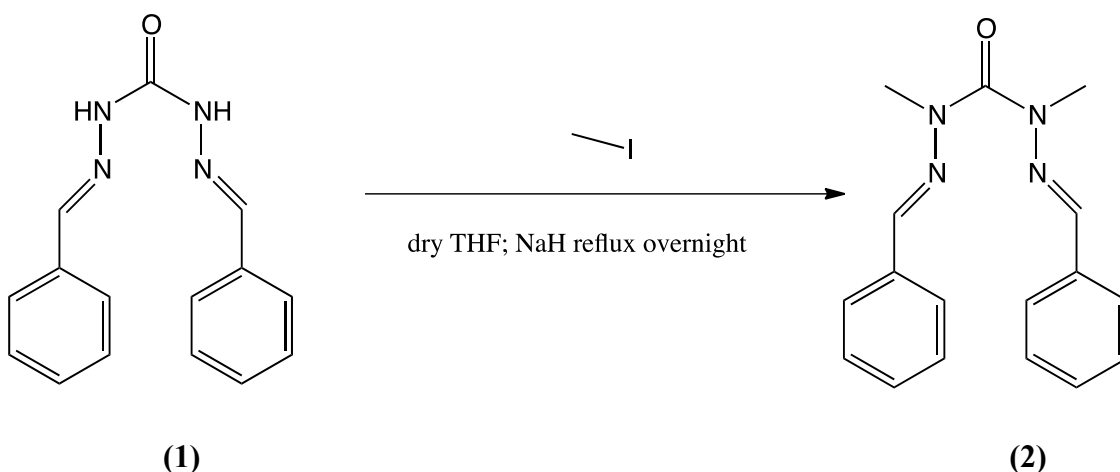
¹H NMR of (1)



¹³C NMR of (1)



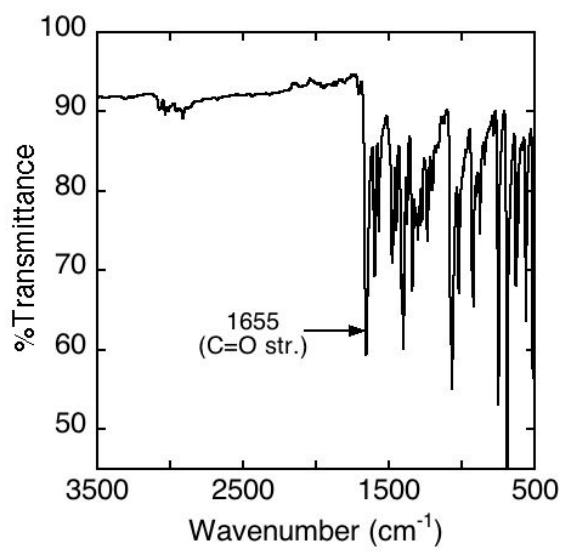
Synthesis of Carbo-di(N'-benzylidene-N-methylhydrazide) (2)



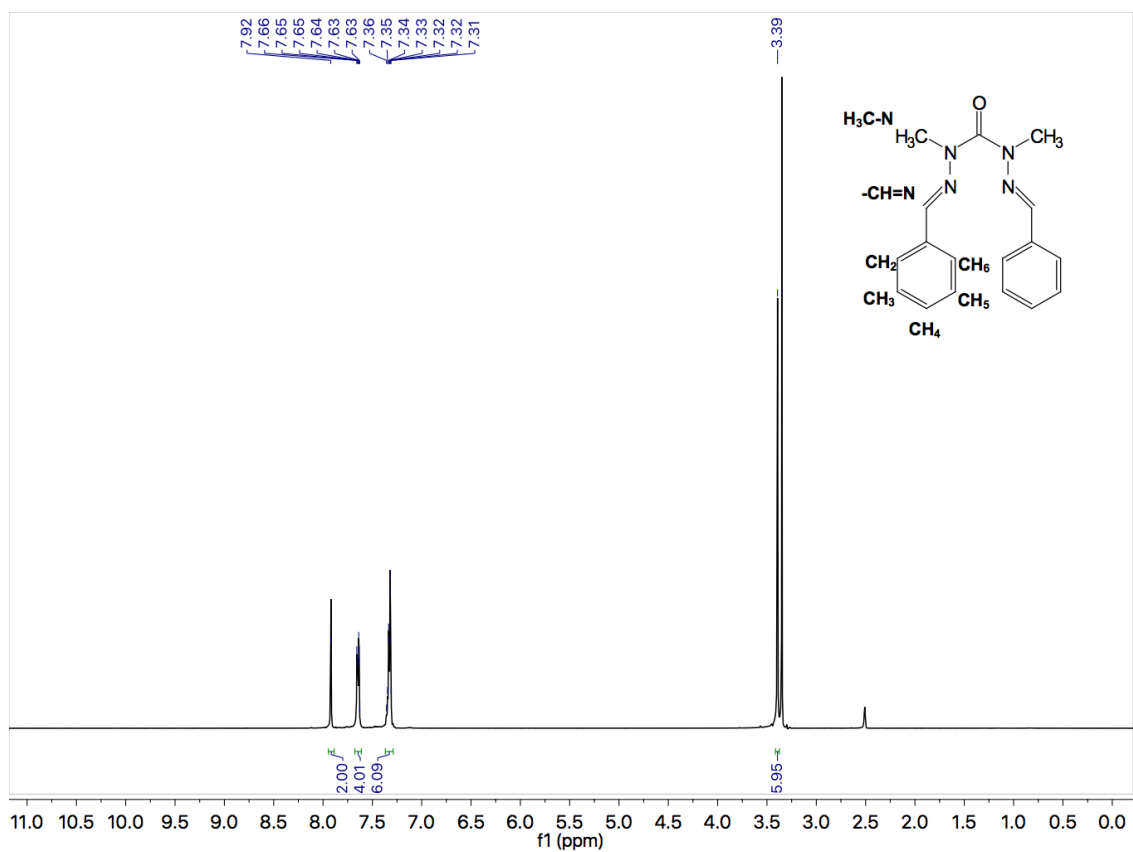
2 was prepared using a modified literature procedure [1]. **1** (5.00 g, 0.0187 mol) was added to a 500 mL round bottom flask and dissolved in dry THF (200 mL) with stirring. Methyl iodide (6.99 mL, 0.112 mol) was added to the solution, followed by the slow addition of sodium hydride (2.27 g dispersed in oil 60 %, 0.0946 mol). A reflux condenser fitted with a drying tube (CaCl₂) was mounted on the flask and the solution then heated to reflux overnight. After cooling, methanol (~10 mL) was slowly added (to quench any unreacted methyl iodide) until effervescence ceased. The precipitate was filtered out and discarded, while the filtrate was evaporated under reduced pressure. Ether (20 mL) was added and then evaporated under vacuum (3 times) to remove any unreacted methyl iodide. The crude product was filtered through a short silica gel column using a dichloromethane in acetone (80:20 v/v) as eluent mixture. The product was collected as the final fraction. The target compound was collected as an off white solid (3.74 g). Yield 67.4 %. MP: 132-133°C. The spectroscopic data for compound **2** matched that reported previously in the literature. [1] IR (ν / cm⁻¹): 3074 (Ar), 1655 (C=O stretch). ¹H NMR (δ / ppm, DMSO-*d*₆): 7.92 (s, 2H -CH=N), 7.66-7.63 (m, 4H, **2CH**₂, **2CH**₆), 7.36-7.31 (m, 6H, **2CH**₃, **2CH**₄, **2CH**₅), 3.39 (s, 6H **2H**₃C-N); ¹³C NMR (δ / ppm, DMSO-*d*₆): 152.0 (CO), 138.5(**2** -CH=N), 135.8 (**2C**₁), 129.4 (**2CH**₂ or **2CH**₆), 129.0 (**2CH**₃, **2CH**₄, **2CH**₅), 127.1 (**2CH**₂ or **2CH**₆) 33.5 (**2** H₃C-N). Anal. calcd. for C₁₇H₁₈N₄O: C, 69.37; H, 6.16; N, 19.03. Found C, 69.46; H, 6.70; N, 19.46.

[1] M. Bancercz, B. Yuon, M. V. DaCosta and M. K. Georges, *J. Org. Chem.*, 2012, **77**, 2415-2421.

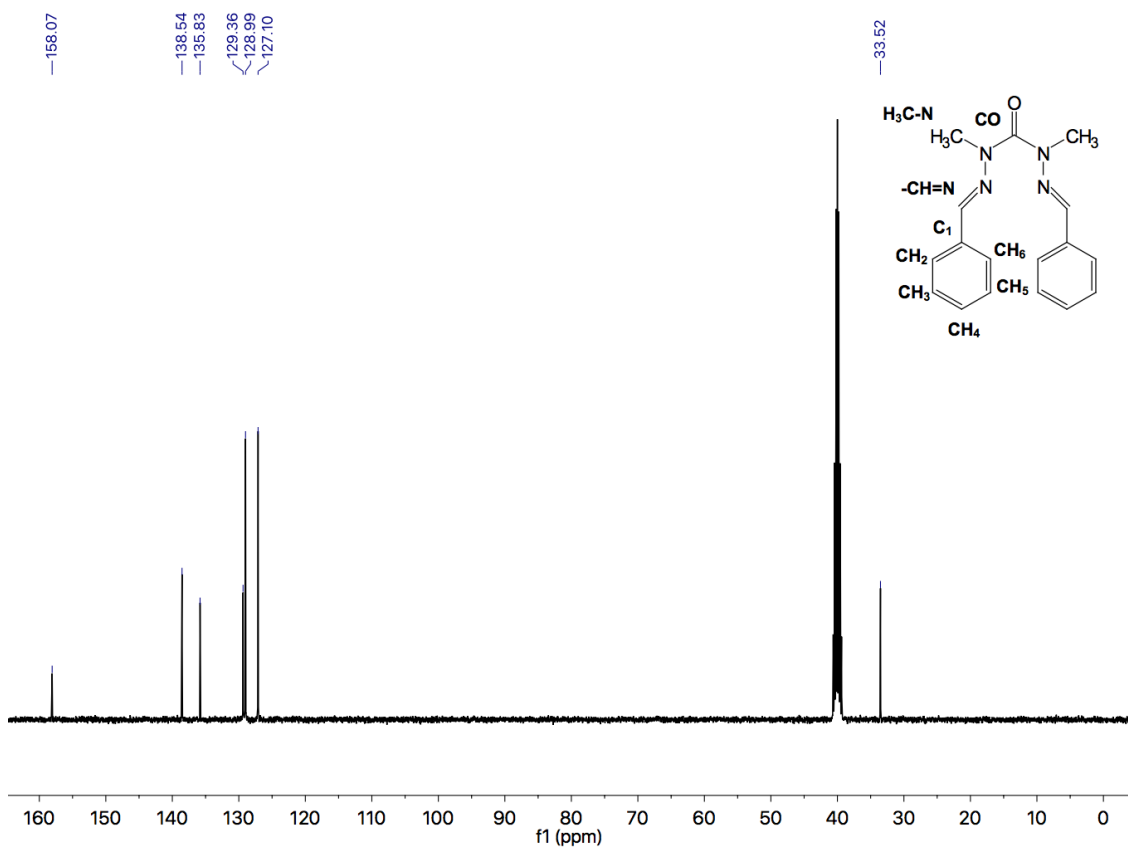
IR Spectroscopy of (2):



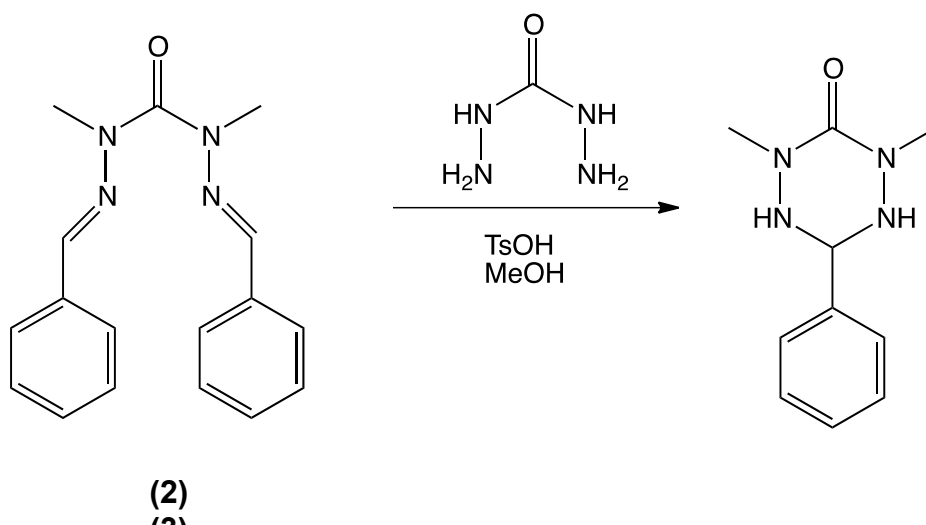
¹H NMR of (2)



¹³C NMR of (2)



Synthesis of 1,5-dimethyl-3-phenyl-1,2,4,5-tetrazian-6-one (3)

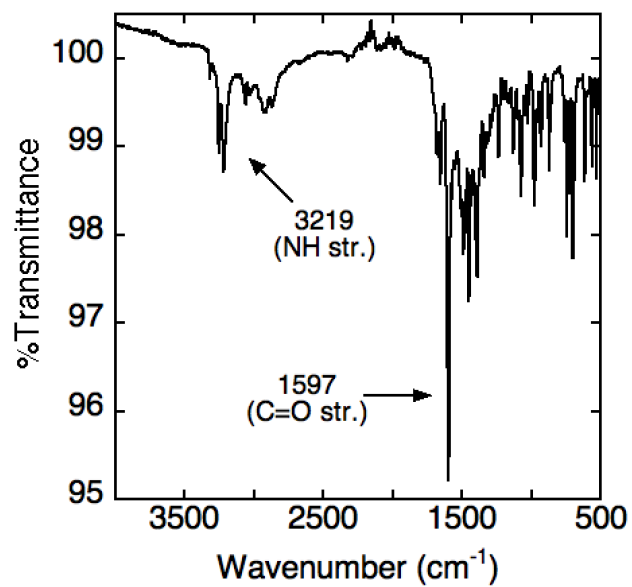


Compound **3** was prepared using a modified literature procedure [1]. Compound **2** (1.00 g, 3.4 mmol) was dissolved in 40 mL of methanol. *p*-Toluenesulfonic acid (0.97 g, 5.1 mmol) and carbohydrazide (0.46 g, 5.1 mmol) were added to the solution, and the reaction was allowed to stir for 1.5 hours at room temperature. TLC was used to check if reaction was complete. Sodium ethoxide was added slowly until the solution reached pH~11. The solution was evaporated under reduced pressure and the crude product was purified by a short silica gel column using 1:19 v/v methanol : ethyl acetate solvent mixture. The product was collected as fourth fraction and then recrystallised from 1:2 v/v ethyl acetate : hexanes solvent mixture. The product was collected as a white solid (0.47 g). Yield: 67.6 %. MP: 128 – 129°C. The spectroscopic data for compound **3** matched that reported previously in the literature. [1,3] IR (ν / cm^{-1}): 3219 m (N-H stretch), 1597 s (C=O stretch). ^1H NMR (δ / ppm , DMSO- d_6): 7.53 (d, 2H, CH_2 , CH_6 , $J = 7.3$ Hz), 7.42 – 7.27 (m, 3H, CH_3 , CH_4 , CH_5), 5.69 (d, 2H, 2NH $J = 8.0$ Hz), 4.91 (t, 1H, CH-N_2 , $J = 8.0$ Hz), 2.95 (s, 6H, 2 $\text{H}_3\text{C-N}$). ^{13}C NMR (δ / ppm , DMSO- d_6): 154.5 (CO), 136.6 (C_1), 128.19 (CH_2 , CH_6), 127.9 (CH_4), 127.02 (CH_3 , CH_5), 68.63 (CH-N_2) 37.7 (2 $\text{H}_3\text{C-N}$). Anal. calcd. for $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}$: C, 58.24; H, 6.84; N, 27.17. Found C, 58.45; H, 6.85; N, 26.75.

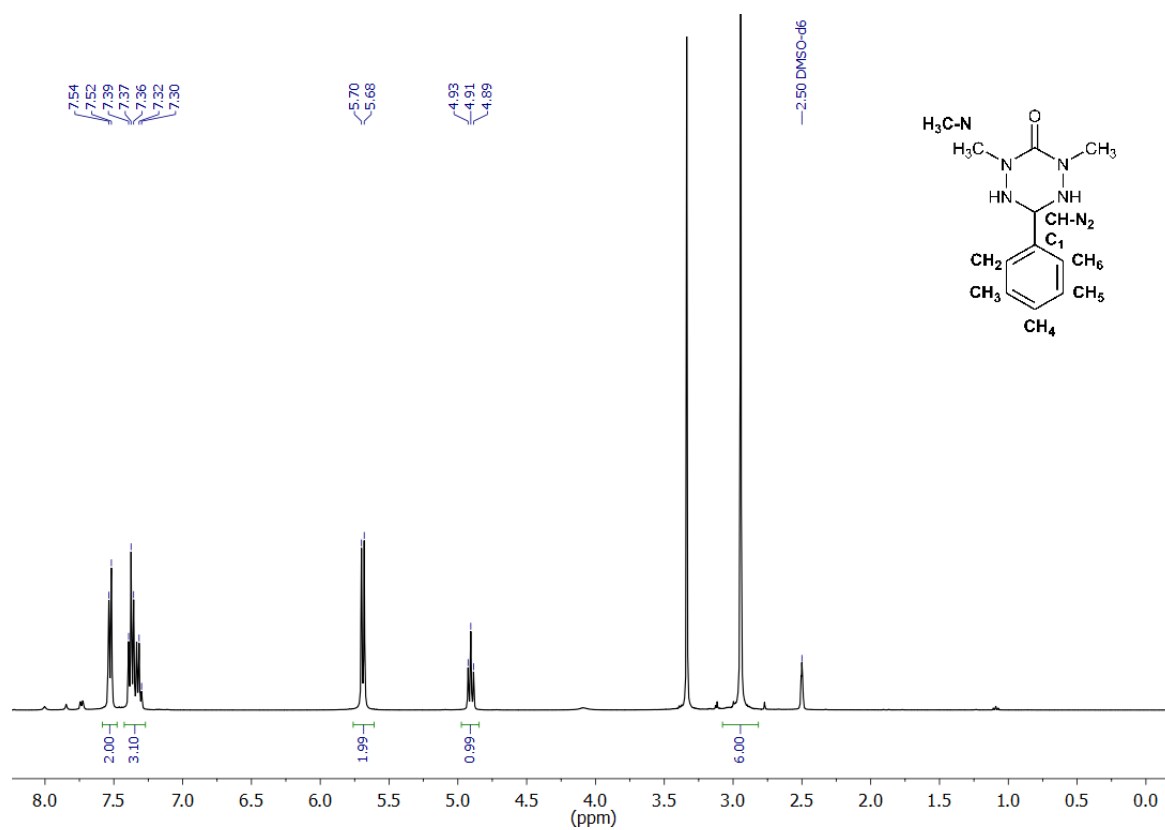
[1] M. Bancercz, B. Yuon, M. V. DaCosta and M. K. Georges, *J. Org. Chem.*, 2012, **77**, 2415-2421.

[3] G. Rayner, T. Smith, W. Barton, M. Newton, R. J. Deeth, I. Prokes, G. J. Clarkson and D. M. Haddleton *Polym. Chem.*, 2012, **3**, 2254

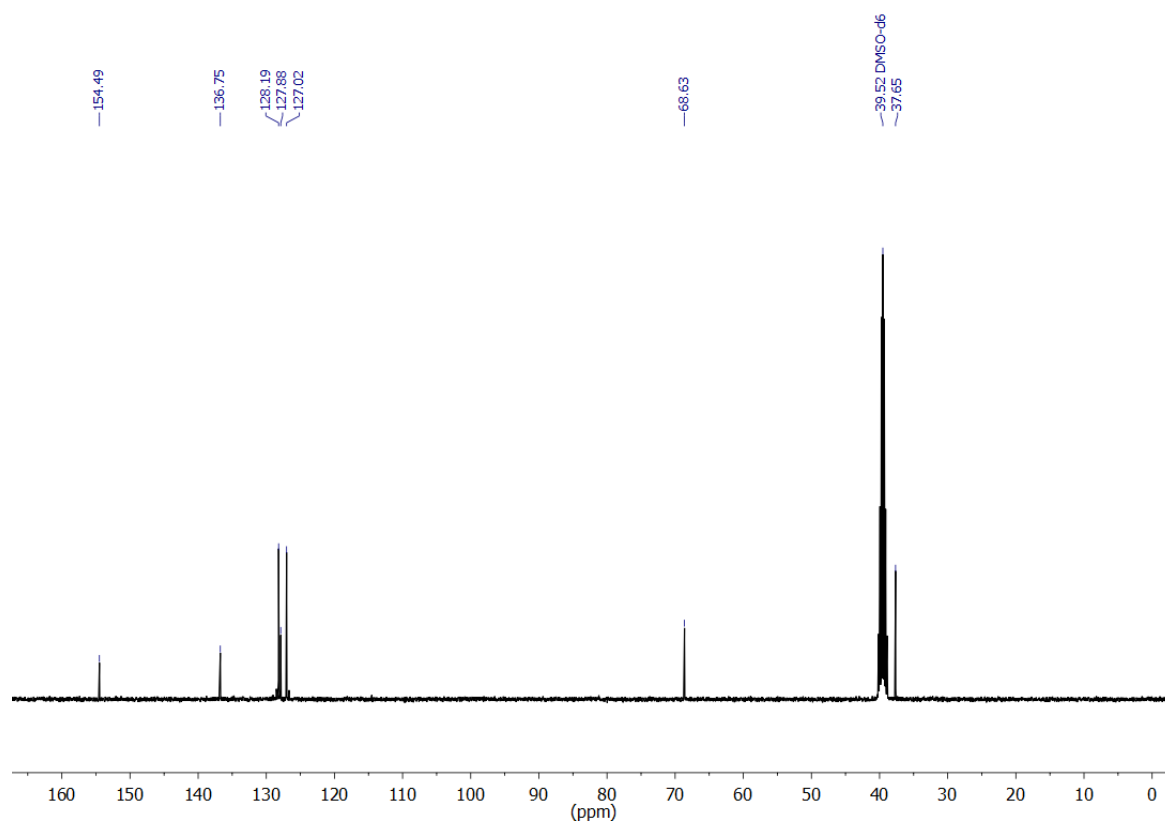
IR Spectroscopy of (3):



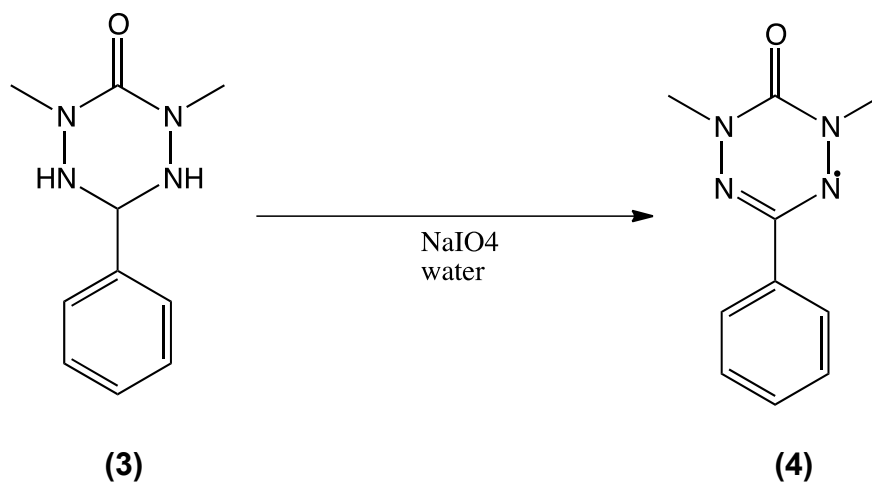
¹H NMR of (3)



¹³C NMR of (3)



1,5-dimethyl-3-phenyl-6-oxoverdazyl (4)

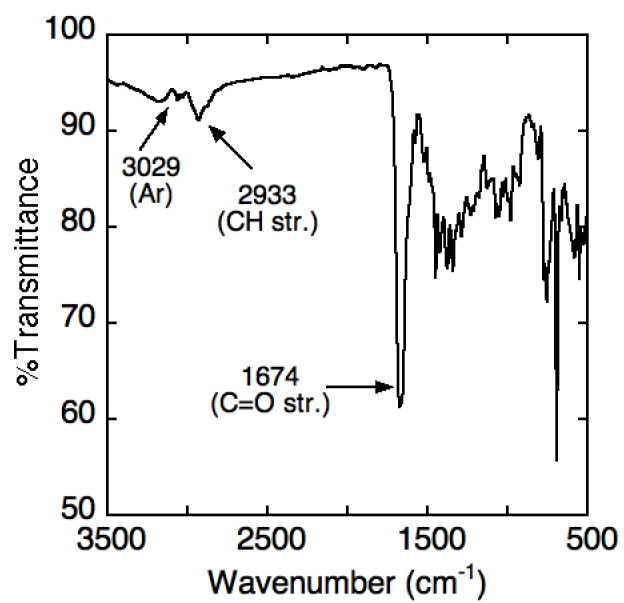


1,5-dimethyl-3-phenyl-1,2,4,5-tetrazian-6-one (**3**) (0.075 g, 0.36 mmol) and NaIO₄ (0.132 g, 0.62 mmol) were stirred in water (~25 mL) for two hours. The crude product was then extracted with CH₂Cl₂ (3 x 15mL). The organic layers (red) were combined and dried with anhydrous MgSO₄. The filtrate was collected and evaporated under reduced pressure to yield the title compound as an orange/red solid (0.063 g). Yield: 85.2%. MP: 67-68 °C. The spectroscopic data for compound **4** matched that reported previously in the literature. [3-4] IR (ν / cm⁻¹): 3028 w (Ar), 2933 w (CH stretch), 1674 s (C=O stretch). Anal. calcd. for C₁₀H₁₁N₄O: C, 59.10; H, 5.45; N, 27.56. Found C, 58.77; H, 5.27; N, 27.34. ESR(CHCl₃ 298 K): 13 line group $a(N_{2,4}) = 6.50$ G; $a(N_{1,5}) = 5.30$ G; $a(H_{CH}) = 5.30$ G (6H); $g = 2.0048$.

[3] G. Rayner, T. Smith, W. Barton, M. Newton, R. J. Deeth, I. Prokes, G. J. Clarkson and D. M. Haddleton, *Polym. Chem.*, 2012, 3, 2254

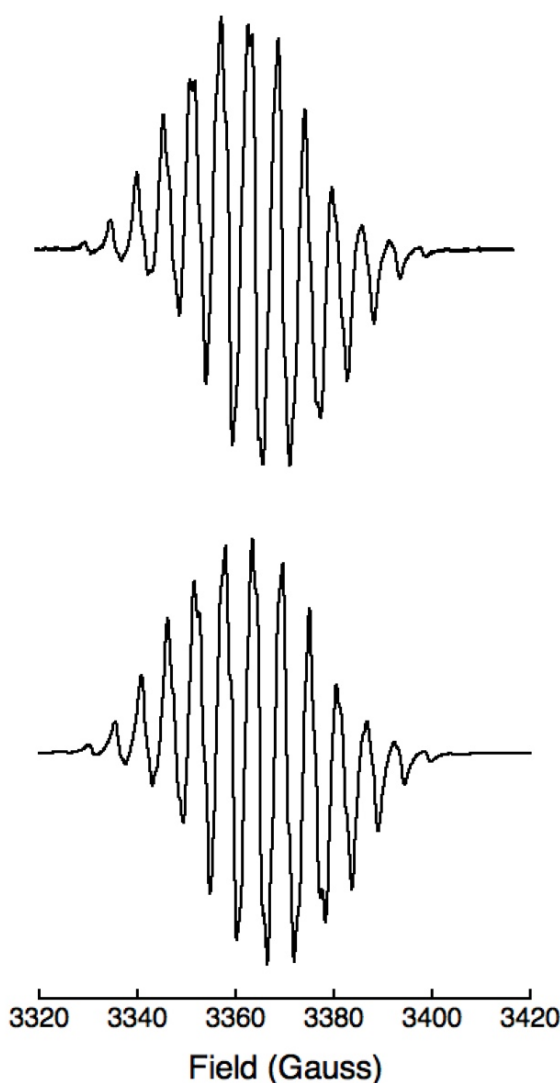
[4] F. A. Neugebauer, H. Fischee and R. Siegel *Chem. Ber.* 121 815-822 1988

IR Spectroscopy of (4):



ESR of (4): The first derivative X-band ESR spectrum ($\nu=9.442$ GHz) of (4) in degassed chloroform at 298 K (top) together with simulation (bottom).

A 13 line group $a(N_{2,4}) = 6.50$ G; $a(N_{1,5}) = 5.30$ G; $a(H_{CH}) = 5.3$ G; $g = 2.0048$. 11 lines (plus 2 very weak lines) from the hyperfine coupling of the unpaired electron with four nitrogen atoms of the verdazyl ring (^{14}N , $I=1$ abundance 99.6 %) with six hydrogen atoms (^1H , $I=1/2$, natural abundance=99.98 %) on the methyl groups. The position, shape and intensity of peaks a result of the hyperfine coupling of two groups of equivalent nitrogens (N1, N5) and (N2, N4) plus coupling with the six hydrogen atoms of the methyl groups. Previous ESR studies have shown that the hyperfine coupling constants of the alkyl groups are identical to the nitrogen (N1, N5) to which they are bonded (approximately 5.3) with the other hyperfine constant is usually around 6.3-6.5 G.[5] The simulation used the EasySpin software package.[6]

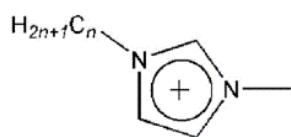


[5] G. N. Lipunova, T.G. Fedorchenko and O. N. Chupakhin, *Russ. Chem. Rev.* 2013, 82, 701-734.

[6] S. Stoll and A. Schweiger, *J. Magn. Reson.* 2006, 178 42-55.

Chemical structures and abbreviations of the RTIL anions and cations used in this work:

Cations

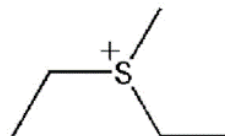


$[C_n\text{mim}]^+$

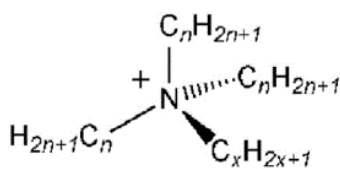
$n, x = 2-14$



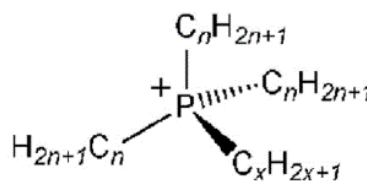
$[C_4\text{mpyr}]^+$



$[S_{2,2,1}]^+$

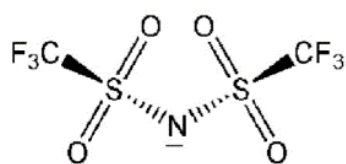


$[N_{x,n,n,n}]^+$



$[P_{x,n,n,n}]^+$

Anions



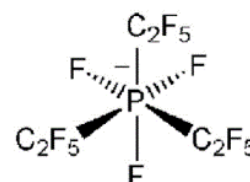
$[NTf_2]^-$



$[PF_6]^-$



$[BF_4]^-$



$[FAP]^-$

Photos of the synthesised 1,5-dimethyl-3-phenyl-6-oxoverdazyl 'dry' powder, and the powder dissolved in two room-temperature ionic liquids.



Electrochemistry experiments (referenced in the main text)

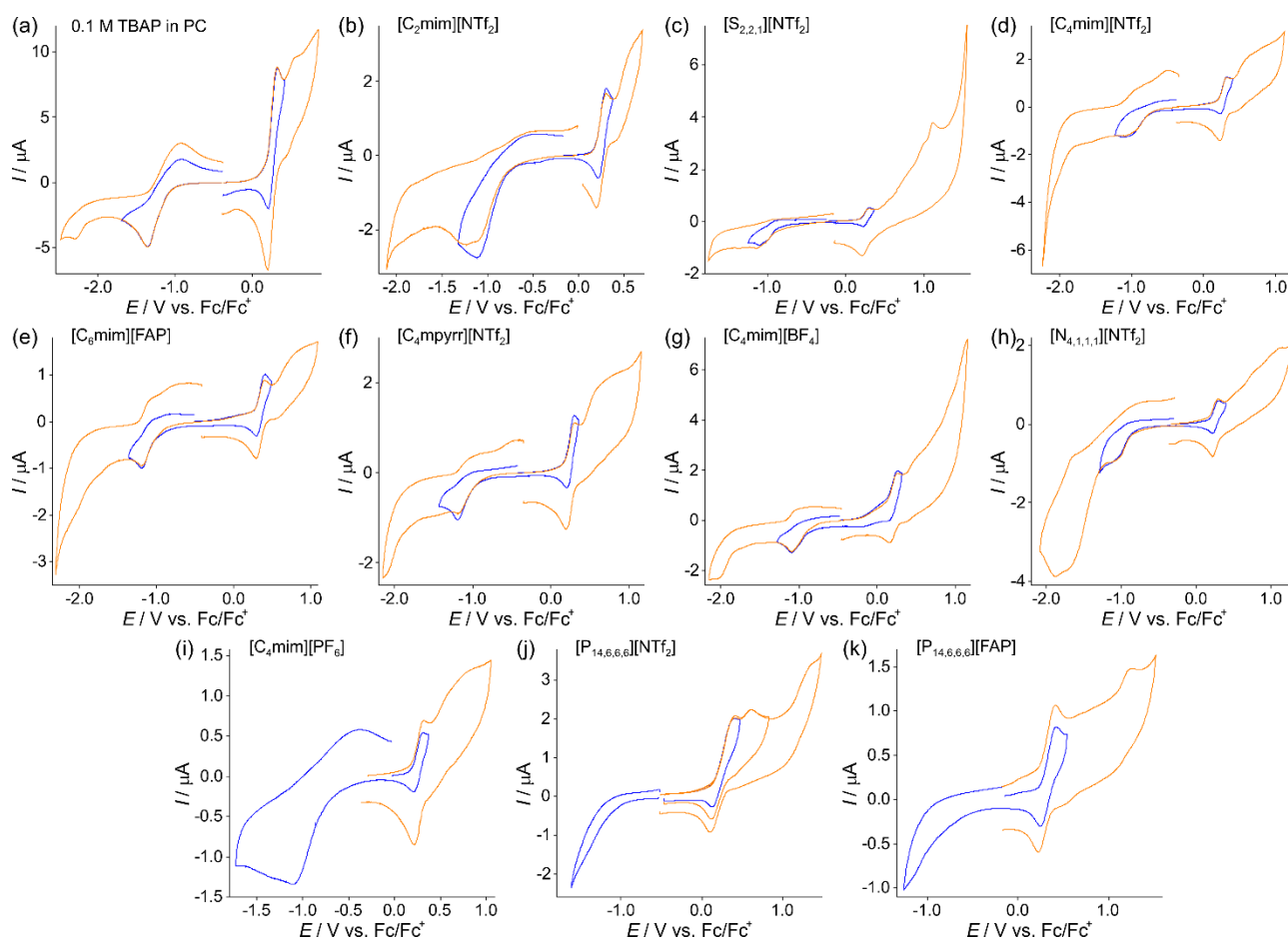


Fig. S1 Cyclic voltammograms of ~ 10 mM 1,5-dimethyl-3-phenyl-6-oxoverdazyl in different solvents/ILs at 2000 mV s^{-1} on Pt-TFEs, including the phosphonium RTILs. The potentials were shifted so that the mid-point of ferrocene/ferrocenium (Fc/Fc^+) redox couple was at 0 V. The blue curves show the voltammetry when the potential range is limited potential to the first oxidation and first reduction peaks only, and the orange curves show the wider potential range scans revealing additional oxidation and reduction features.

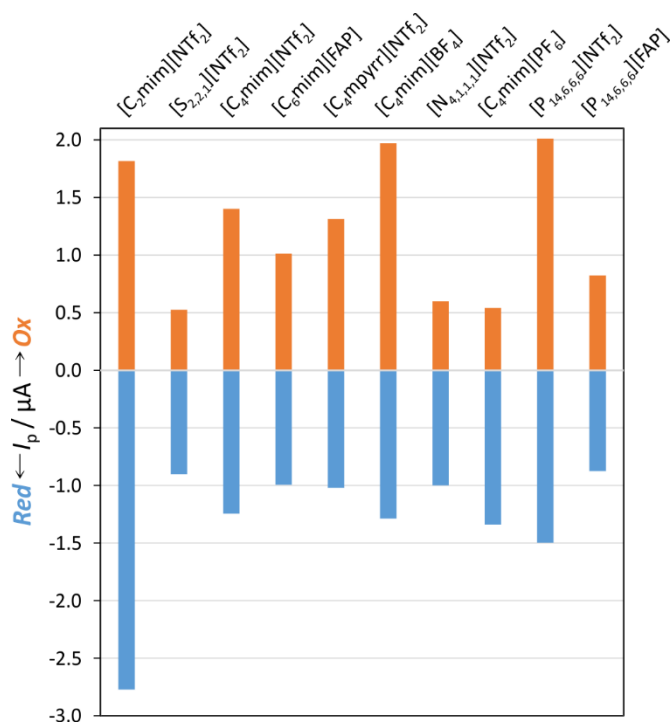


Fig. S2 Comparison of CV peak currents (I_p) for the first oxidation peak (Ox, orange) and first reduction peak (Red, blue) of ~ 10 mM 1,5-dimethyl-3-phenyl-6-oxoverdazyl at 2000 mV s^{-1} on a Pt-TFE, arranged (left to right) in order of increasing viscosity.

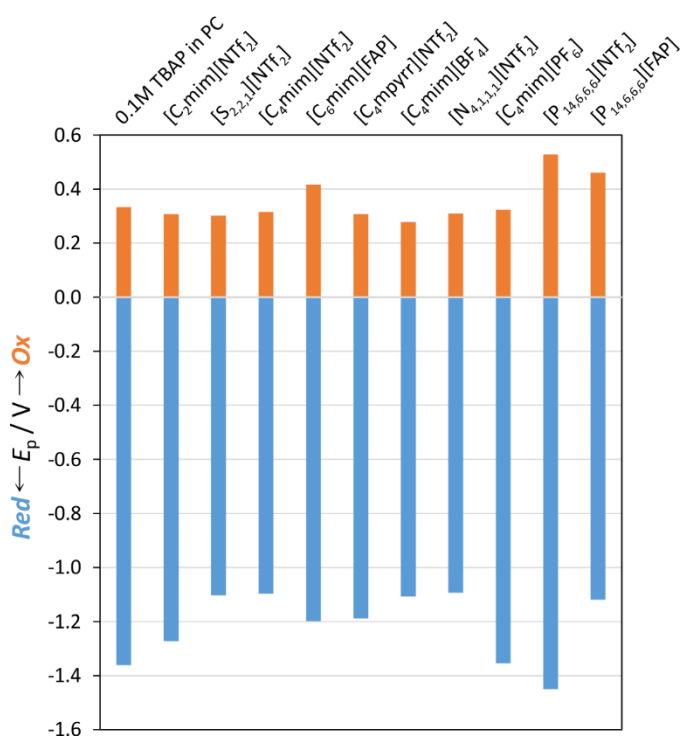


Fig. S3 Comparison of CV peak potentials (E_p vs. Fc/Fc^+) for the first oxidation peak (Ox, orange) and the first reduction peak (Red, blue) of ~ 10 mM 1,5-dimethyl-3-phenyl-6-oxoverdazyl at 2000 mV s^{-1} on Pt-TFE, arranged (left to right) in order of increasing viscosity.

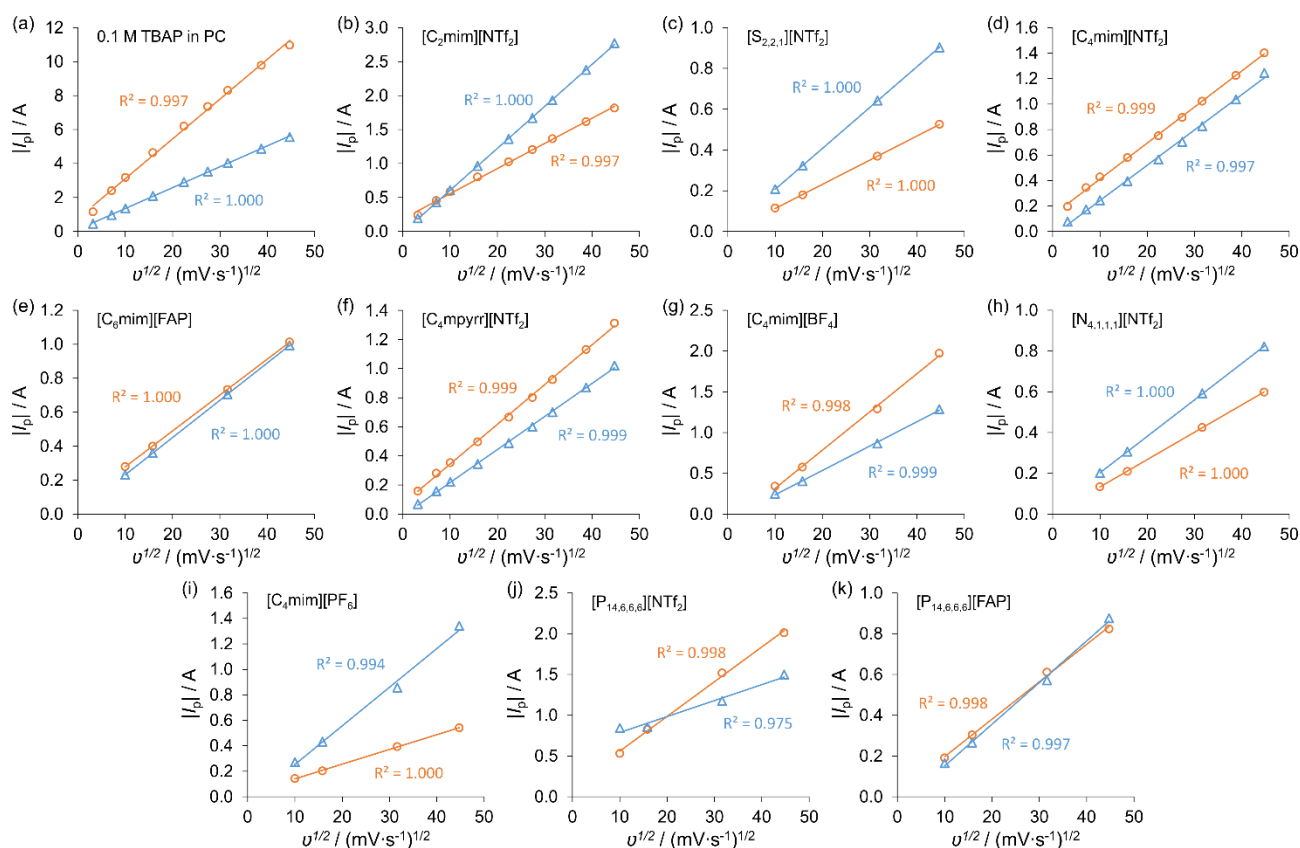


Fig. S4 Plots of peak current vs. scan rate for ~ 10 mM 1,5-dimethyl-3-phenyl-6-oxoverdazyl in different solvents on Pt-TFEs. The oxidation currents are in orange, and the reduction currents are in blue. 0.1 M TBAP in PC, $[C_2mim][NTf_2]$, $[C_4mim][NTf_2]$, and $[C_4mpyrr][NTf_2]$ were carried out at 2000, 1500, 1000, 750, 500, 250, 100, 50, 10 mVs^{-1} , while the rest of the RTILs were carried out at only 2000, 1000, 250, 100 mVs^{-1} . The R^2 value of the linear fits are shown.

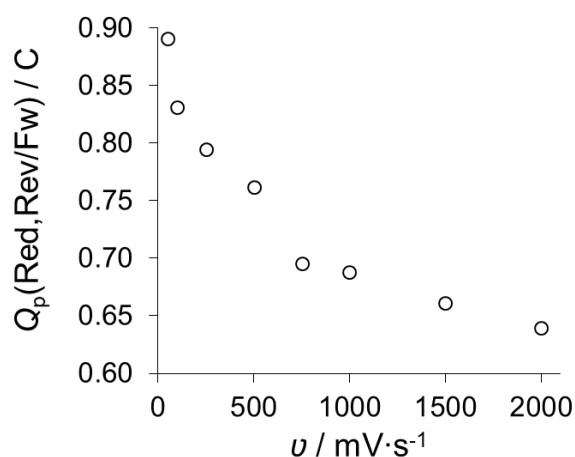


Fig. S5 Plot of the integrated charge of the reverse peak divided by the charge of the forward peak, Q_p , for the reduction of ~ 10 mM 1,5-dimethyl-3-phenyl-6-oxoverdazyl at different scan rates (Fig. S4) on Pt-TFE in PC (+0.1 M TBAP).

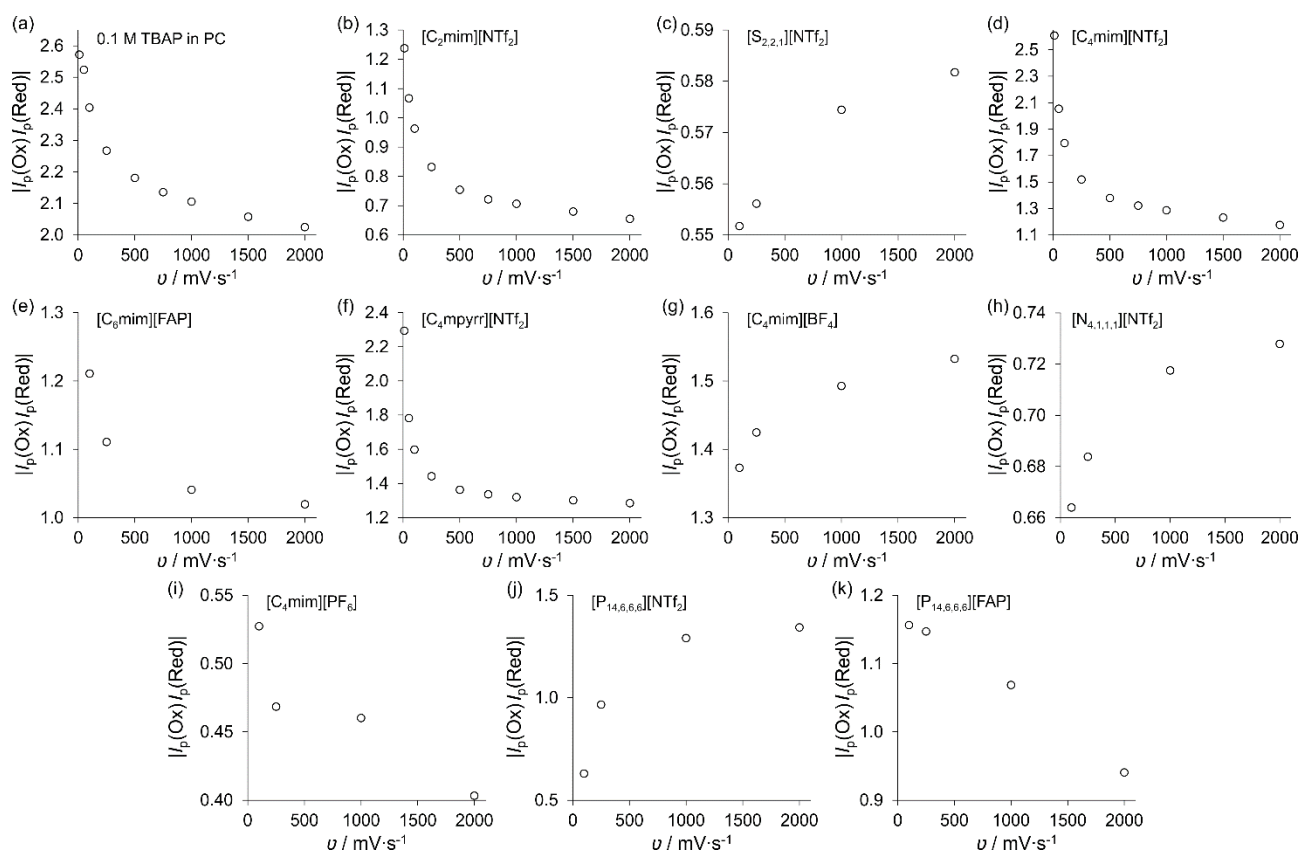


Fig. S6 Plots of $I_p(\text{Ox})$ divided by $I_p(\text{Red})$ vs. scan rate for $\sim 10 \text{ mM}$ 1,5-dimethyl-3-phenyl-6-oxoverdazyl in different solvents.