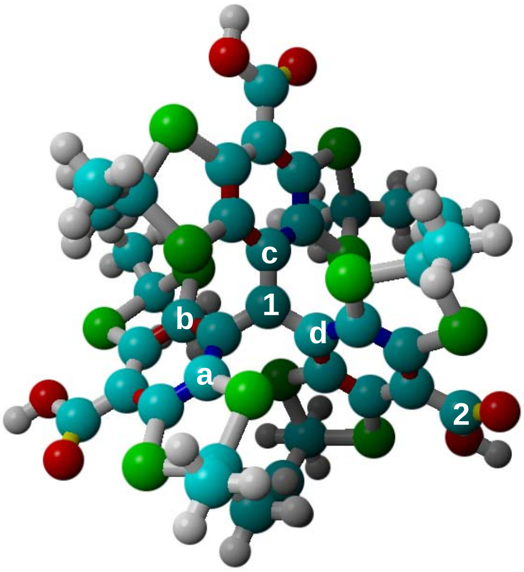
Macholl et al., Trityl biradicals and ^{13}C Dynamic Nuclear Polarization, PCCP 2010

Supplementary Material

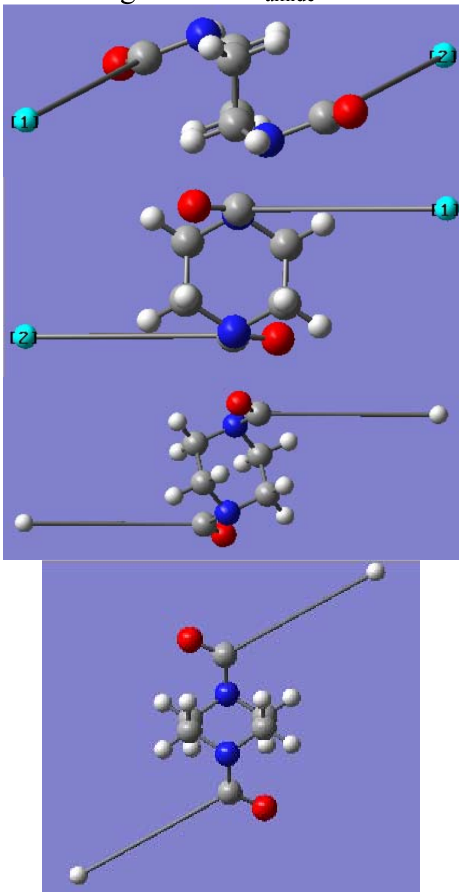
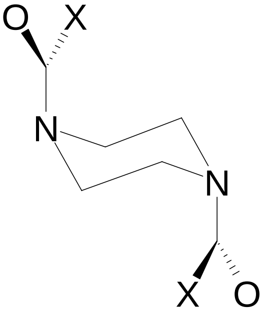
1. 3-dimensional structure of the trityl monoradical

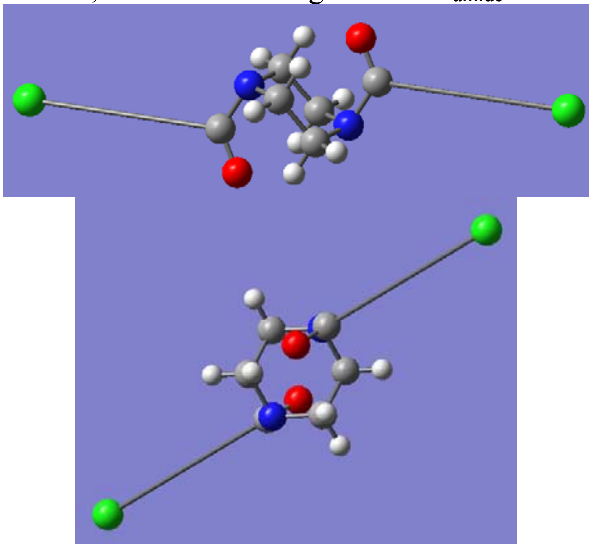
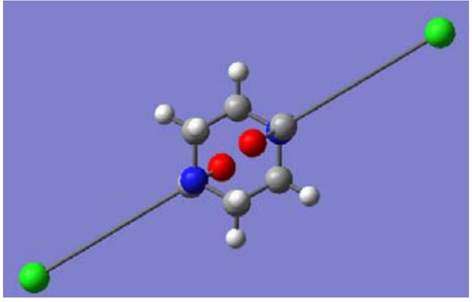
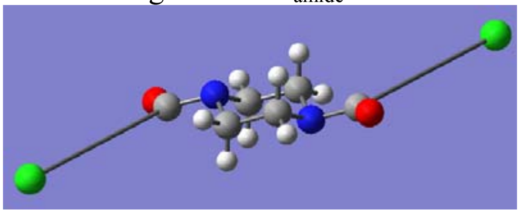


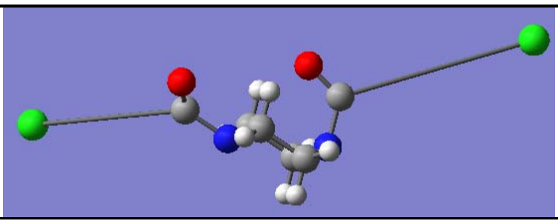
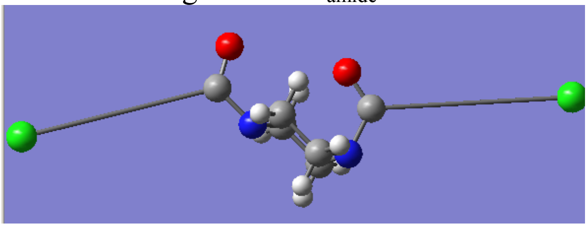
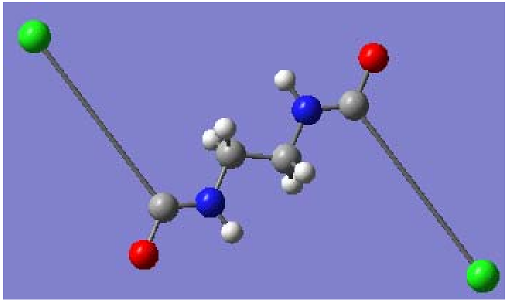
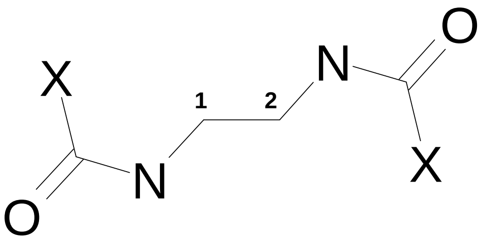
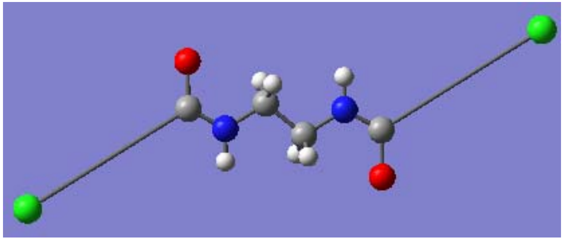
Gaussian98 calculated[1] molecular structure of the Finland trityl radical (similar to **M** but with methyl instead of (2-methoxy)ethyl groups) visualised with Yasara (www.yasara.org). The distance between central carbon (1) and a carboxyl carbon (2) is 5.8 Å. The trityl core of central carbon and its three neighbour atoms are in a plane perpendicular to the pseudo-C_3 symmetry axis. The dihedral angle between each benzene ring (e.g. atoms a, b) and the trityl core (e.g. atoms c, d) is 45(4) °.

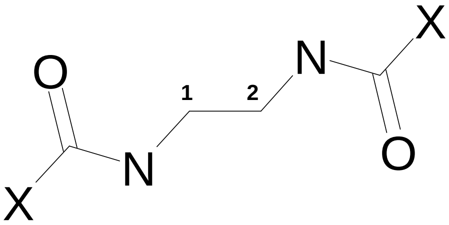
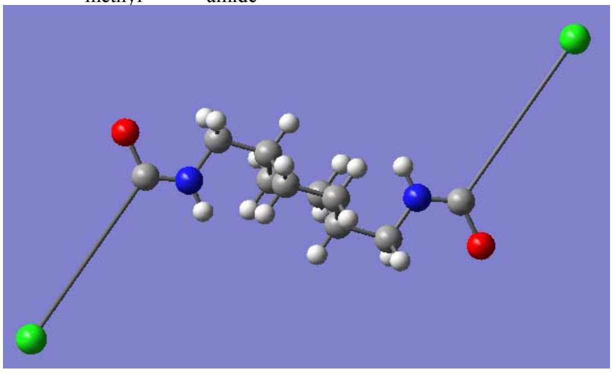
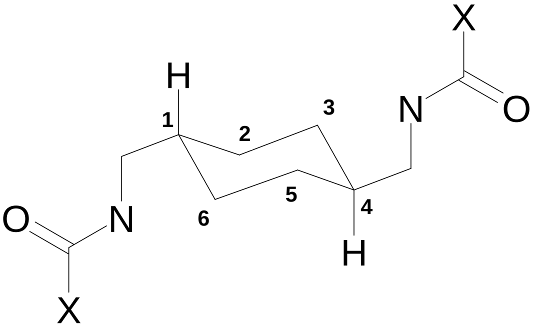
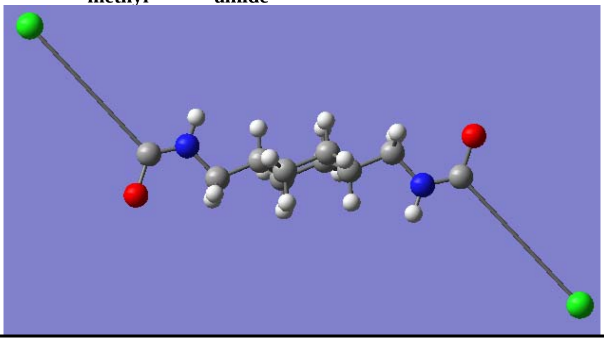
2. Molecular substructures of biradicals

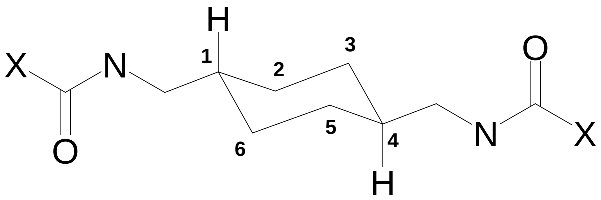
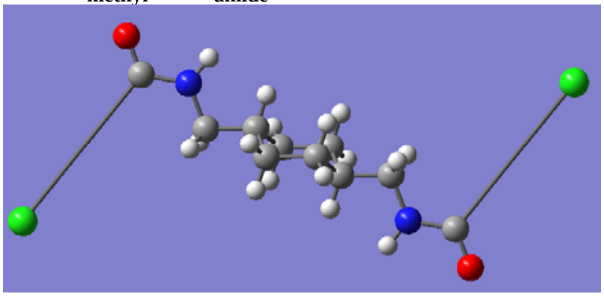
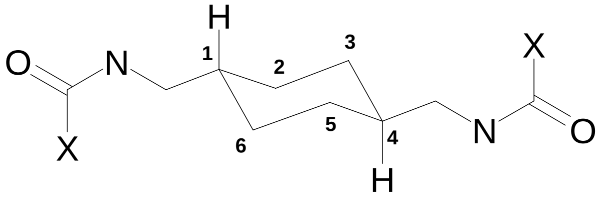
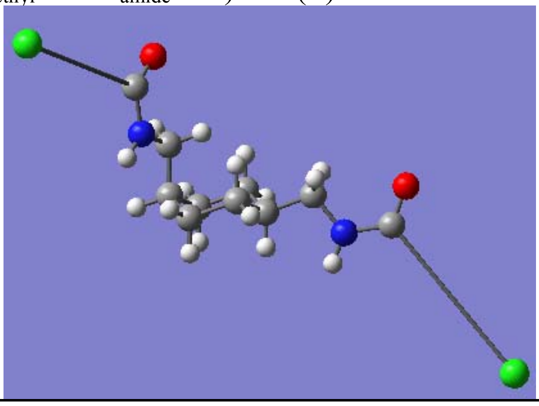
Different potential and plausible conformations and configurations are shown. The trityl moiety is condensed to a single green ball with a distance of 5.8 Å between trityl centre and trityl carboxyl carbon. All simplified structures shown below are chosen to be symmetric about the molecule centre.

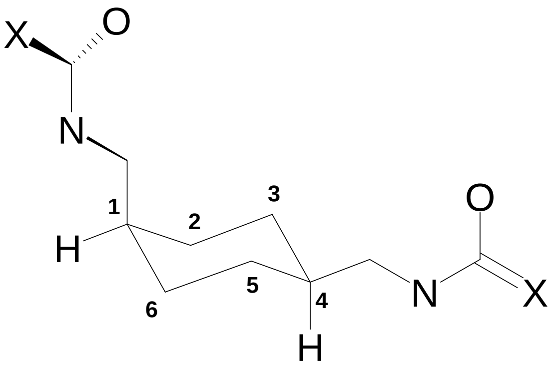
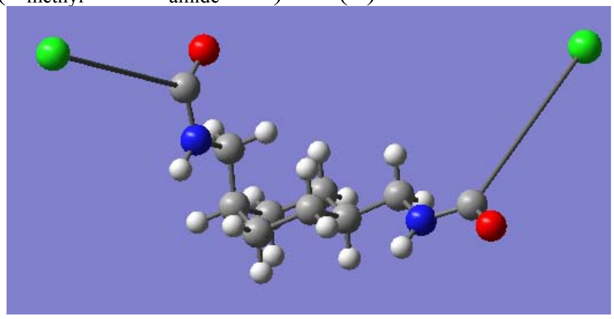
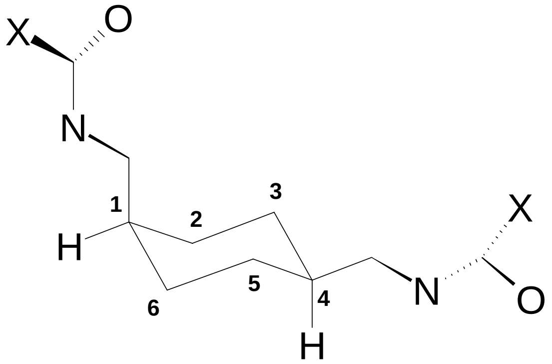
name	description	structure	intramolecular e^{-}-e^{-} distance [Å]
A1	piperazine in chair conformation, *trans*-1,4 isomer in (a,a) conformation with respect to substituents at N,N', Z form with respect to radical,radical' substituents: dihedral angle (O-C_{amide}-C_{amide}-O)=180 °	isomer 1 from different perspectives, both dihedral angles N-N-C_{amide}-O: 90 °  	13.9

		isomer 2, both dihedral angles N-N-C_{amide}-O: 30 ° 	15.6
		isomer 3, both dihedral angles N-N-C_{amide}-O: 0 ° (bisecting conformation of C=O with respect to $N(CH_2)_2$) 	15.8
A2	piperazine in chair conformation, *trans*-1,4 isomer in (e,e) conformation with respect to substituents at N,N', Z form with respect to radical,radical' substituents: dihedral angle (O-C_{amide}-C_{amide}-O)=180 °	both dihedral angles N-N-C_{amide}-O: 90 ° 	15.2
A3	piperazine (chair conformation, *cis*-1,4 isomer in (e,a) conformation with respect to substituents at N,N', dihedral angle(O-	dihedral angles N-N-C_{amide}-O: 0 ° and -60 °	14.6

	C_{amide}-C_{amide}-O)=-51 °		
A4	piperazine (chair conformation, *cis*-1,4 isomer in (e,a) conformation with respect to substituents at N,N', dihedral angle(O-C_{amide}-C_{amide}-O)=0 °	both dihedral angles N-N-C_{amide}-O: 0 ° 	15.9
B1	*trans*-1,2-diamino ethane *trans* for C_2-C_1-N-C_{amide}	dihedral angle: **E for C_1-N-C_{amide}-O**   	13.8
B2	*trans*-1,2-diamino ethane *trans* for C_2-C_1-N-C_{amide}	dihedral angle: **Z for C_1-N-C_{amide}-O** 	16.8

			
C1	1,4-(e,e)-bis(aminomethyl) cyclohexane in chair conformation	dihedral angles: **E for H_1-C_1-C_{methyl}-N** E for C_1-C_{methyl}-N-C_{amide} Z for C_{methyl}-N-C_{amide}-O  	18.2
C2	1,4-(e,e)-bis(aminomethyl) cyclohexane in chair conformation	dihedral angles: **Z for H_1-C_1-C_{methyl}-N** E for C_1-C_{methyl}-N-C_{amide} **Z for C_{methyl}-N-C_{amide}-O** 	20.4

			
C3	1,4-(e,e)-bis(aminomethyl) cyclohexane in chair conformation	dihedral angles: **Z for H_1-C_1-C_{methyl}-N** E for C_1-C_{methyl}-N-C_{amide} **E for C_{methyl}-N-C_{amide}-O**  	17.5
C4	1,4-(a,e)-bis(aminomethyl) cyclohexane in chair conformation	dihedral angles: (H_1-C_1-C_{methyl}-N)=+60 ° (C_1-C_{methyl}-N-C_{amide})=180 ° (E) (C_{methyl}-N-C_{amide}-O)=0 ° (Z) (H_2-C_2-C_{methyl}'-N')=0 ° (C_2-C_{methyl}'-N'-C_{amide}')=180 ° (E) C_{methyl}'-N'-C_{amide}'-O')=0 ° (Z) 	18.7

			
C5	1,4-(a,e)-bis(aminomethyl) cyclohexane in chair conformation	dihedral angles: (H$_1$-C$_1$-C$_{methyl}$-N)=+60 ° (C$_1$-C$_{methyl}$-N-C$_{amide}$=180 ° (E) (C$_{methyl}$-N-C$_{amide}$-O)=0 ° (Z) (H$_2$-C$_2$-C$_{methyl}$'-N')=+60 ° (C$_2$-C$_{methyl}$'-N'-C$_{amide}$')=0 °(E) (C$_{methyl}$'-N'-C$_{amide}$'-O')=0 °(E)  	15.6

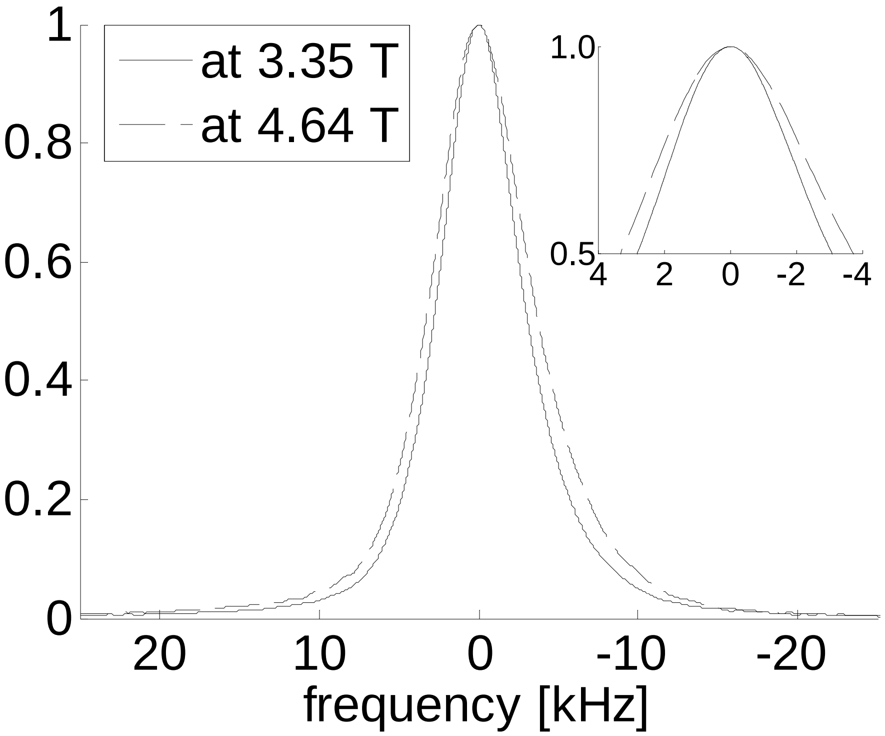
3. Further information on “Simulation of EPR spectra”

Calculation of g_{iso} at W-band: For the calculation of g_{iso}, the EPR spectrum at W-band (94.90 GHz) is referenced to the DNP curve zero-crossing frequency (acquired at a *ca.* 1 % lower field due to technical reasons) which coincides with the EPR resonance.[2] The [1-^{13}C]pyruvic acid NMR resonance from a DNP curve NMR spectrum gives the B_0 field strength taking into account the chemical shift of 157 ppm (see section on [1-^{13}C]pyruvic acid line shape) and using $\gamma(^{13}\mathrm{C})=6.728284\cdot10^7/(2\pi)$ rad T^{-1} s^{-1} for tetramethylsilane. The estimated error is 70 µT or 20 ppm due to the polarization dependent M_1 contribution and the overall FWHM of *ca.* 200 ppm. This value for B_0 allows calculating g_{iso} for the DNP curve zero-crossing frequency, and the W-band spectrum is shifted accordingly on the B axis in Fig. 3. Main experimental errors for the DNP curve zero-crossing frequency and the MW frequency accuracy are estimated as 15 MHz or 150 ppm.

4. [1-^{13}C]pyruvic acid line shape

The molecule orientations in the glass are assumed to be uniformly distributed. Then the the ^{13}C solid state NMR signal is dominated by the Chemical Shift Anisotropy (CSA) and the direct magnetic dipolar interaction (DD) between pairs of ^{13}C and ^{1}H nuclei while the interactions to dilute electron spins (first moment shifts and second moment broadening discussed in the paper) and between ^{13}C spin pairs can be ignored. The major DD contribution to the ^{13}C NMR line width from the intramolecular acidic ^{1}H nucleus is calculated as $D(^{13}\mathrm{C},^{1}\mathrm{H}) \approx 4.7$ kHz, but an expected dispersion of the acidic proton position (e.g. tunneling in hydrogen bonds with double well potential) is expected to result in a slight decrease of the average value. The chemical shift tensor of the pyruvic acid carboxyl carbon was measured via MAS (1.5 and 7.5 kHz; 7 T; 173 K) and confirmed by static spectra with ^{1}H decoupling. Both types of spectra were acquired with and without CP which gave slight differences in the intensity pattern as expected, but the same chemical shift tensor eigenvalues were obtained. Data were fitted with SIMPSON[3] (gcompute method; Zaremba, Conroy, Wolfsberg set of up to 4180 angles) with the following results: isotropic chemical shift $\delta_{\mathrm{iso}}=157.0(5)$ ppm [external reference TMS], anisotropy $\zeta=-86(4)$ ppm and asymmetry $\eta=0.21(4)$. Anisotropy ζ and asymmetry η are given according to the Haeberlen convention.[4] The isotropic chemical shift is referenced to TMS in 2 steps. First the methyl carbon resonance of the same neat pyruvic acid sample was measured in the same spectrometer in the solid and the liquid state (room temperature). Then the chemical shift of the liquid was measured again with a liquid state NMR spectrometer at 293 K and referenced to an external sample of TMS in $CHCl_3$ yielding 25.45 ppm [TMS] for the methyl carbon of pyruvic acid. A small spectral contribution from pyruvic acid hydrate[5] could be resolved in the MAS spectra ($\delta_{\mathrm{iso}}=165.5(5)$ ppm, $\zeta=-100(20)$ ppm, $\eta=0.2(2)$). The measured anisotropies for pyruvic acid and its hydrate are well in the expected range from 70 ppm to 110 ppm typical for amino acids, amides and imides.[6, 7] Also $\delta=70$ ppm ($\eta=0.8$) has been reported for phosphoenolpyruvate.[8]

The measured chemical shift tensor of pyruvic acid corresponds to the span $\Delta=\delta(3+\eta)/2=4.9$ kHz at 3.35 T and 6.9 kHz at 4.64 T. The FWHM and the overall asymmetry of the signal line shape depends largely on the orientation of the dipole tensor with respect to the CSA Principal Axis System and the polarization levels of all relevant spins. The experimental FWHM of the ^{13}C NMR line is 5.9 kHz at 3.35 T and 7.0 kHz at 4.64 T (without apodization), both measured at a ^{13}C polarization of ca. 25 % and with ca. 60 % electron spin saturation (at $\nu_{\mathrm{MW,opt}}$). The figure shows corresponding spectra of sample composition **M15**, each with the centre of gravity (first moment) shifted to 0 kHz. The asymmetry due to the CS tensor is visible as shoulder to the highfield side after careful phase correction of 0th order, see inset. However, the signal is narrower than expected from the measured CS tensor values and additional ^{13}C, ^{1}H dipolar broadening, in particular at higher field and since ^{1}H polarization is expected to be <10 %. A more detailed analysis of the line shape via a multi spin system simulation is out of the scope of this paper.



5. References

1 G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, Gaussian, Inc., Pittsburgh, PA, Revision A.11 edn., 1998.

2 S. T. Goertz, *Nucl. Instrum. Meth. A*, 2004, **526**, 28-42.

3 M. Bak, J. T. Rasmussen and N. C. Nielsen, *J. Magn. Reson.*, 2000, **147**, 296-330.

4 R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, P. Granger, R. E. Hoffman and K. W. Zilm, *Solid State Nucl. Magn. Reson.*, 2008, **33**, 41-56.

5 S. A. Margolis and B. Coxon, *Anal. Chem.*, 1986, **58**, 2504-2510.

6 S. Macholl, F. Börner and G. Buntkowsky, *Z. Phys. Chem.*, 2003, **217**, 1473-1505.

7 C. Ye, R. Fu, J. Hu, L. Hou and S. Ding, *Magn. Reson. Chem.*, 1993, **31**, 699-704.

8 M. Bechmann, S. Dusold, A. Sebald, W. A. Shuttleworth, D. L. Jakeman, D. J. Mitchell and J. N. S. Evans, *Solid State Sci.*, 2004, **6**, 1097-1105.