

Supporting informations

Surface-active ionic liquids in micellar catalysis: Impact of anion selection on reaction rates in nucleophilic substitutions

Alice Cognigni,^a Peter Gaertner,^a Ronald Zirbs,^b Herwig Peterlik,^c Katharina Prochazka,^c Christian Schröder,^d and Katharina Bica^{*,a}

^aInstitute of Applied Synthetic Chemistry, Vienna University of Technology, Getreidemarkt 9/163, 1060 Vienna, Austria.

^bGroup for Biologically Inspired Materials, Institute of Nanobiotechnology (DNBT), University of Natural Resources and Life Sciences, Muthgasse 11, 1190 Vienna, Austria.

^cDynamics of Condensed Systems, University of Vienna, Boltzmanngasse 5, 1090 Vienna, Austria.

^dInstitute of Computational Biological Chemistry, University of Vienna, Währingerstrasse 17, 1090 Vienna, Austria

*Corresponding author Katharina Schröder (née Katharina Bica). Email: katharina.schroeder@tuwien.ac.at

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1. CMC determination and aggregation parameters calculation

For all the techniques implied the CMC was determined at the break point, i.e. the intersection of the two linear fittings of data points.

Surface tension

Π_{CMC} is the effectiveness of the surface tension reduction, it is defined according to the following equation¹ (1):

$$\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}, \quad (1)$$

where γ_0 is the surface tension of water, and γ_{CMC} is the surface tension of the solution at the CMC.

The Gibbs adsorption isotherm equation can be used to estimate the average area per molecule residing at the surface (A_{min}), assuming that the structure pattern corresponds to a monolayer, it is defined according to the following equations² (2-3):

$$A_{\text{min}} = 10^{21} / N\Gamma \text{ [nm}^2\text{]} \quad (2)$$

where N = Avogadro's number, and Γ = surface excess concentration [mol/1000 m²]

$$\Gamma = - \frac{1}{4.606 RT} \left(\frac{d\gamma}{d \log C_1} \right)^T \quad (3)$$

where $\frac{d\gamma}{d \log C_1}$ is the slope of the curve surface tension vs logC before the CMC, and the concentration is expressed in mol/L, and $R=8.31 \text{ J/mol K}$.

The packing parameter³ (P) which includes the volume (v) of the hydrocarbon chain imbedded in the hydrocarbon core of the aggregate and the maximum effective length (l_c) that the chain can assume, calculated according to Tanford equation (6-7)³⁷:

$$v = (27.4 + 26.9 * n) * 10^{-3} \text{ nm}^3 \quad (6)$$

$$l_c = (0.154 + 0.1265 * n) \text{ nm} \quad (7)$$

n equals the actual number of atom in the hydrophobic core of the micelle, so generally one is left out.

The packing parameter is then defined as $P=v/a_0l_c$, where a_0 is the cross-sectional area occupied by the hydrophilic group at the micelle-solution interface, it is in our case approximated with A_{min} . A value of $P < 0.33$ corresponds to spherical micelles, and intermediate value $0.33 < P < 0.5$ corresponds

¹Blesic, M.; Swadźba-Kwaśny, M.; Holbrey, J. D.; Canongia Lopes, J. N.; Seddon, K. R.; Rebelo, L. P. N. *Physical Chemistry Chemical Physics* 2009, **11**, 4260.

² Milton J. Rosen and Joy T. Kunjappu, *Surfactants and interfacial phenomena*, John Wiley & Sons, 4th end., 2012.

³ J. N. Israelachvili, in *Intermolecular and Surface Forces*, Elsevier, 2011, pp. 535–576.

to non-spherical, ellipsoidal micelles, while higher values correspond to rod-like micelles and various interconnected structures.³⁶

Conductivity

The degree of counterion binding (β) can be estimated from the conductivity data, based on the ratio of the slopes above (S_2) and below (S_1) the cmc⁴ (4):

$$\beta = (1 - S_2/S_1) \quad (4)$$

The Gibbs energy of micellization (ΔG^0_{mic}) was calculated from the conductivity data according to the following equation⁵ (5):

$$\Delta G^0_{mic} = (1 + \beta) RT \ln (CMC/W) \quad (5)$$

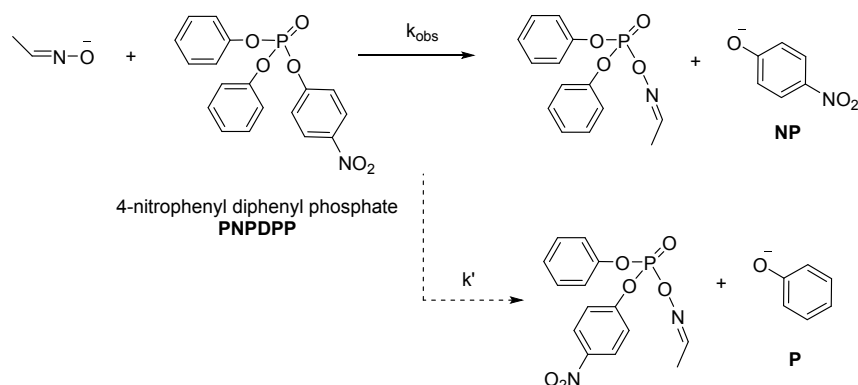
Where the argument of the logarithms is the molar fraction of the surfactant, and water concentration is taken as $W=55.4$ mol/L.

⁴ Ao, M.; Kim, D. *Journal of Chemical & Engineering Data* 2013, **58**, 1529.

⁵ R. Zana, *Langmuir*, 1996, **12**, 1208.

2. Kinetic constants fitting

The investigated reaction between 4-nitrophenyl diphenyl phosphate (**PNPDPP**) and acetaldoxime follows a $S_N2(P)$ mechanism via the attack of the nucleophile acetaldoxime at the phosphorous centre. Two leaving groups are possible, either the favoured *p*-nitrophenolate (**NP**), whose formation can be followed at 402.5 nm or phenolate (**P**) as a by-product.



For the determination of the rate constants for both, the desired reaction (k_{obs}) and the by-product formation (k'), a competitive reaction scheme (see figure above) is assumed which leads to a system of coupled differential equations:

$$\frac{d\vec{c}(t)}{dt} = \mathbf{R} \cdot \vec{c}(t) \quad (1)$$

where the vector $\vec{c}(t)$ represents the concentration of PNPDP, NP and P at time t

$$\vec{c}(t) = \begin{pmatrix} [\text{PNPDPP}](t) \\ [\text{NP}](t) \\ [\text{P}](t) \end{pmatrix} \quad (2)$$

and the reaction matrix \mathbf{R} looks like

$$\mathbf{R} = \begin{pmatrix} -k_{obs} - k' & 0 & 0 \\ k_{obs} & 0 & 0 \\ k' & 0 & 0 \end{pmatrix} \quad (3)$$

The general solution of the coupled differential equations in Eq. (1) depends on the Eigenvalues $\lambda_1=0$, $\lambda_2=0$ and $\lambda_3=-(k_{obs} + k')$ and the corresponding Eigenvectors

$$\vec{e}_1 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad \vec{e}_2 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad \vec{e}_3 = \frac{1}{k'} \begin{pmatrix} -(k_{obs} + k') \\ k_{obs} \\ k' \end{pmatrix}$$

of the reaction matrix \mathbf{R} :

$$\vec{c}(t) = \sum_{i=1}^3 \alpha_i \vec{e}_i e^{\lambda_i t} \quad (4)$$

At time $t=0$, $\vec{c}(0) = ([\text{PNPDPP}]_0, 0, 0)$ since only the reactant is present. Using this initial condition, the α -coefficients can be determined:

$$\alpha_3 = -[\text{PNPDPP}]_0 \frac{k'}{k_{obs} + k'}$$

$$\alpha_2 = [\text{PNPDPP}]_0 \frac{k_{obs}}{k_{obs} + k'}$$

$$\alpha_1 = [\text{PNPDPP}]_0 \frac{k'}{k_{obs} + k'} = -\alpha_3$$

As a result, the time-dependent concentration of NP yields

$$[\text{NP}](t) = [\text{PNPDPP}]_0 \frac{k_{obs}}{k_{obs} + k'} \left(1 - e^{-(k_{obs} + k')t} \right) \quad (5)$$

In a least-square fit of the spectroscopic data to Eq. (5) using gnuplot, the sum of the two rate constants $k_{obs} + k'$ can be determined. The individual values of k_{obs} and k' are evaluated from the ratio of the initial concentration of the reactant $[\text{PNPDPP}]_0$ and the final concentration of the product NP which also equals $k_{obs} / (k_{obs} + k')$.

3. Additional SAXS data

The scaled medium contrast is obtained by the ratio of the electron densities (ref. 35 of the paper, P. Bartlett and R.H. Ottewill, *J. Chem. Phys.*, 1992, **96**, 3306)

$$\gamma = \frac{\rho_m - \rho_s}{\rho_c - \rho_s}$$

where the subscript denotes (surrounding) **m**atrix, **s**hell and **c**ore, respectively. $\gamma = 0$ means that density of core and medium are identical, $\rho_m = \rho_s$, and only the core scatters. For $\gamma = 1$, $\rho_m = \rho_c$ and only the shell contributes to scattering.

The following Figures S1a to S1c show the shift towards a more uniform distribution of the radius of the core for higher concentrations. It may be not the case for Cl (as these data are difficult to evaluate due to the weakly pronounced maximum in the scattering intensities), but clearly visible for Br and OTS.

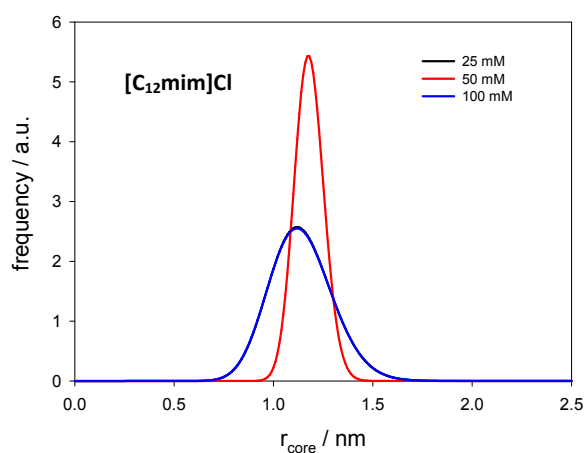


Fig. S1a: Size distribution of core radius for different concentrations of [C₁₂mim]Cl.

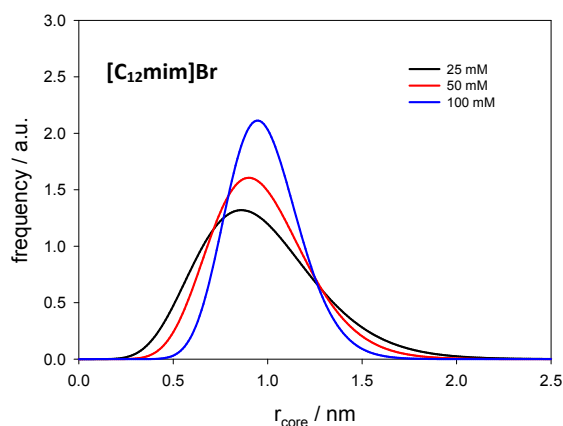


Fig. S1b: Size distribution of core radius for different concentrations of [C₁₂mim]Br.

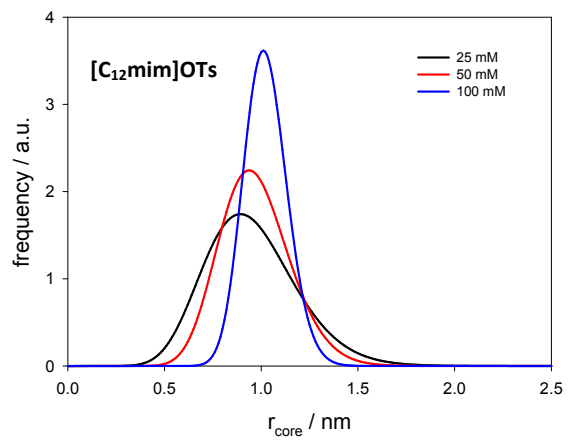
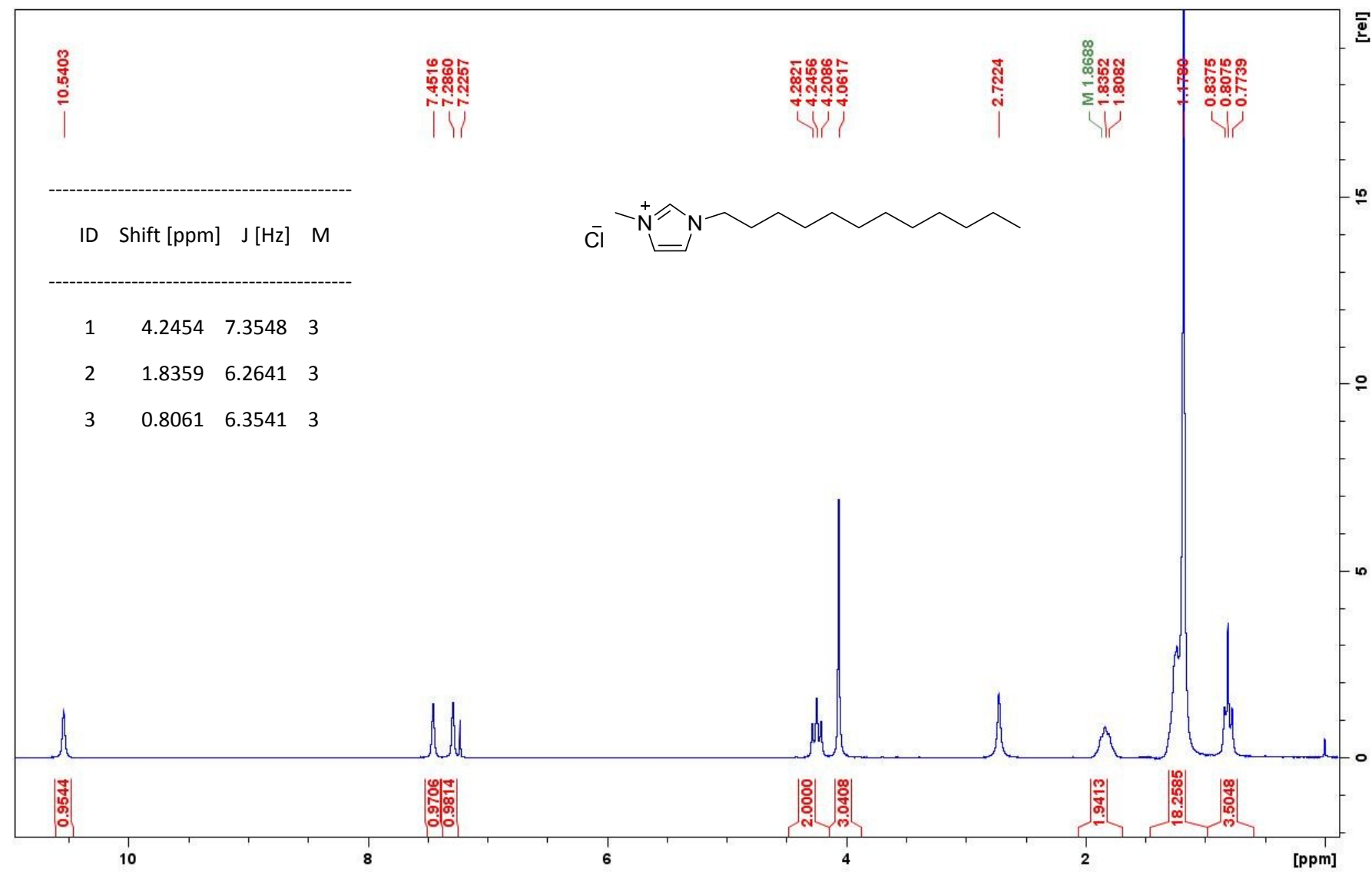


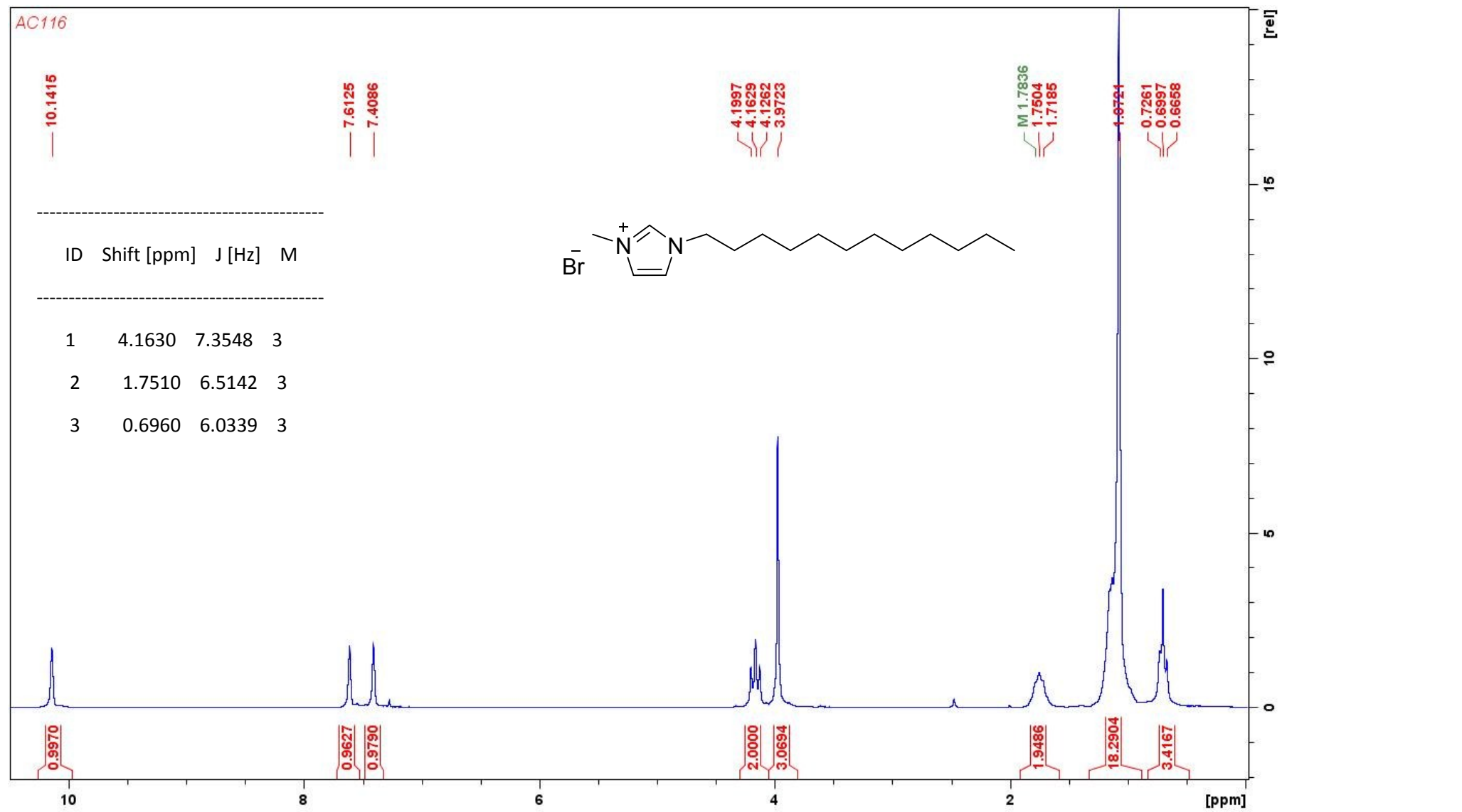
Fig. S1c: Size distribution of core radius for different concentrations of [C₁₂mim]OTs.

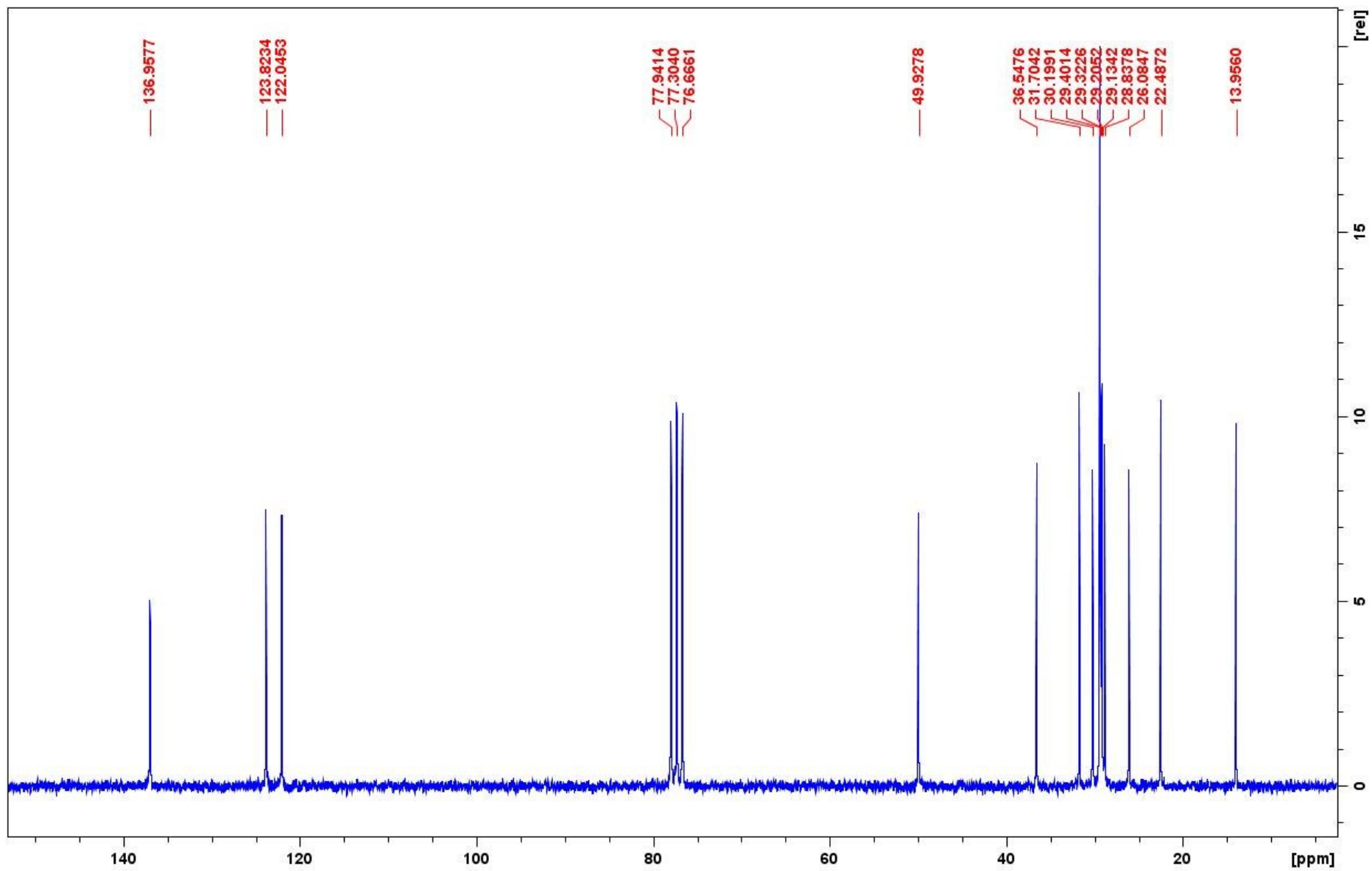
4. ¹H and ¹³C NMR spectra of the surface active ILs

[C₁₂mim]Cl

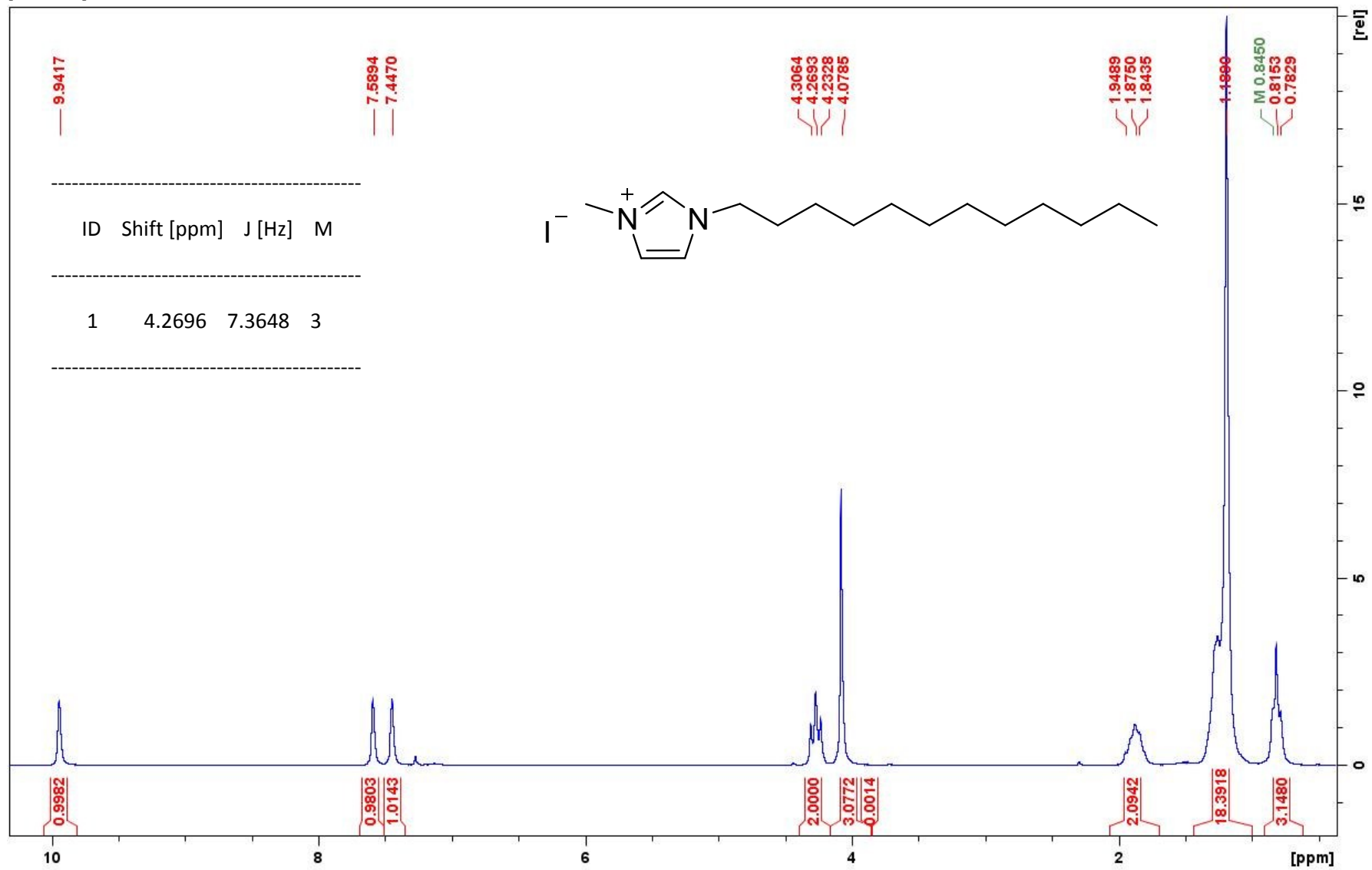


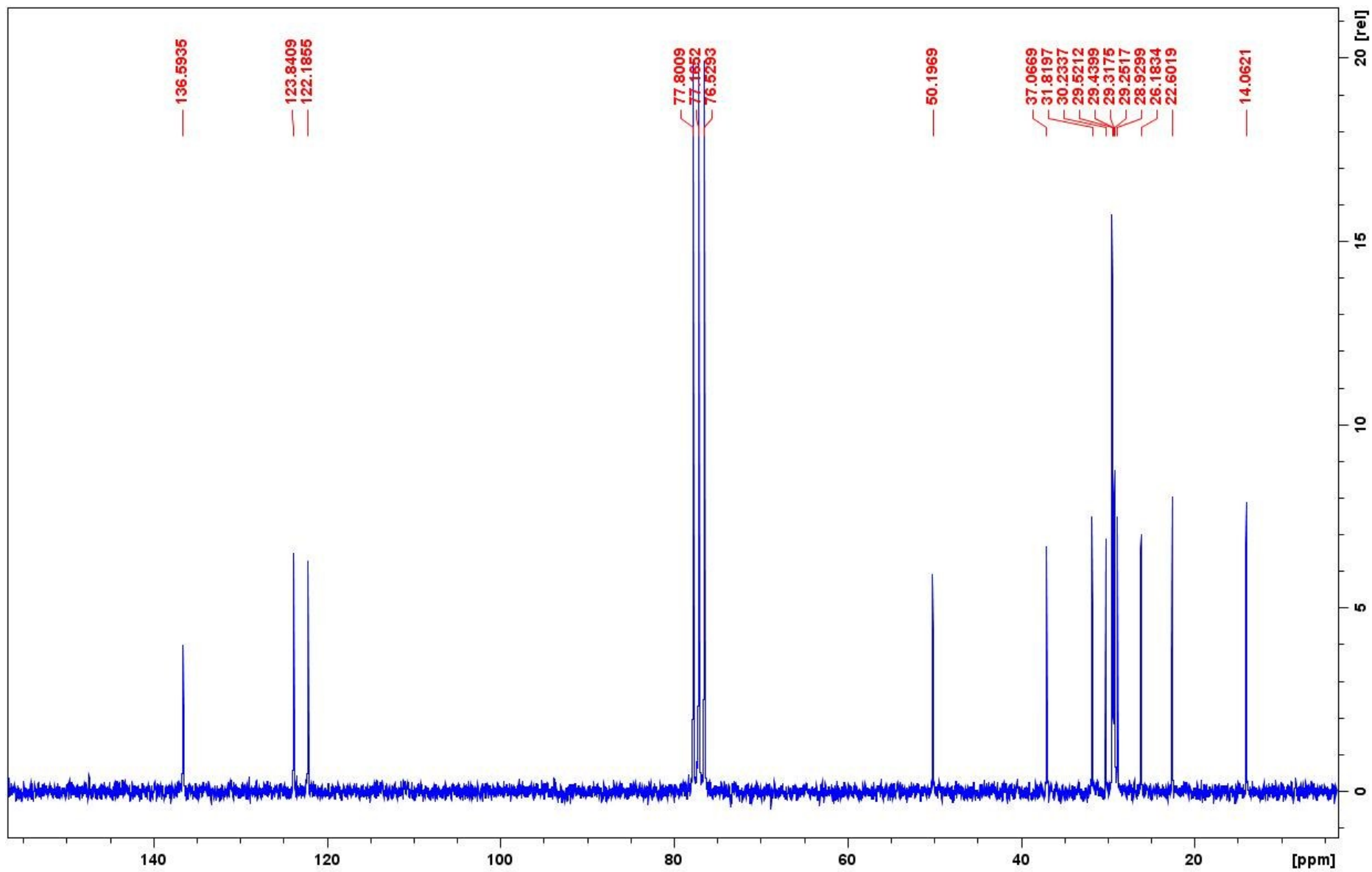
[C₁₂mim]Br



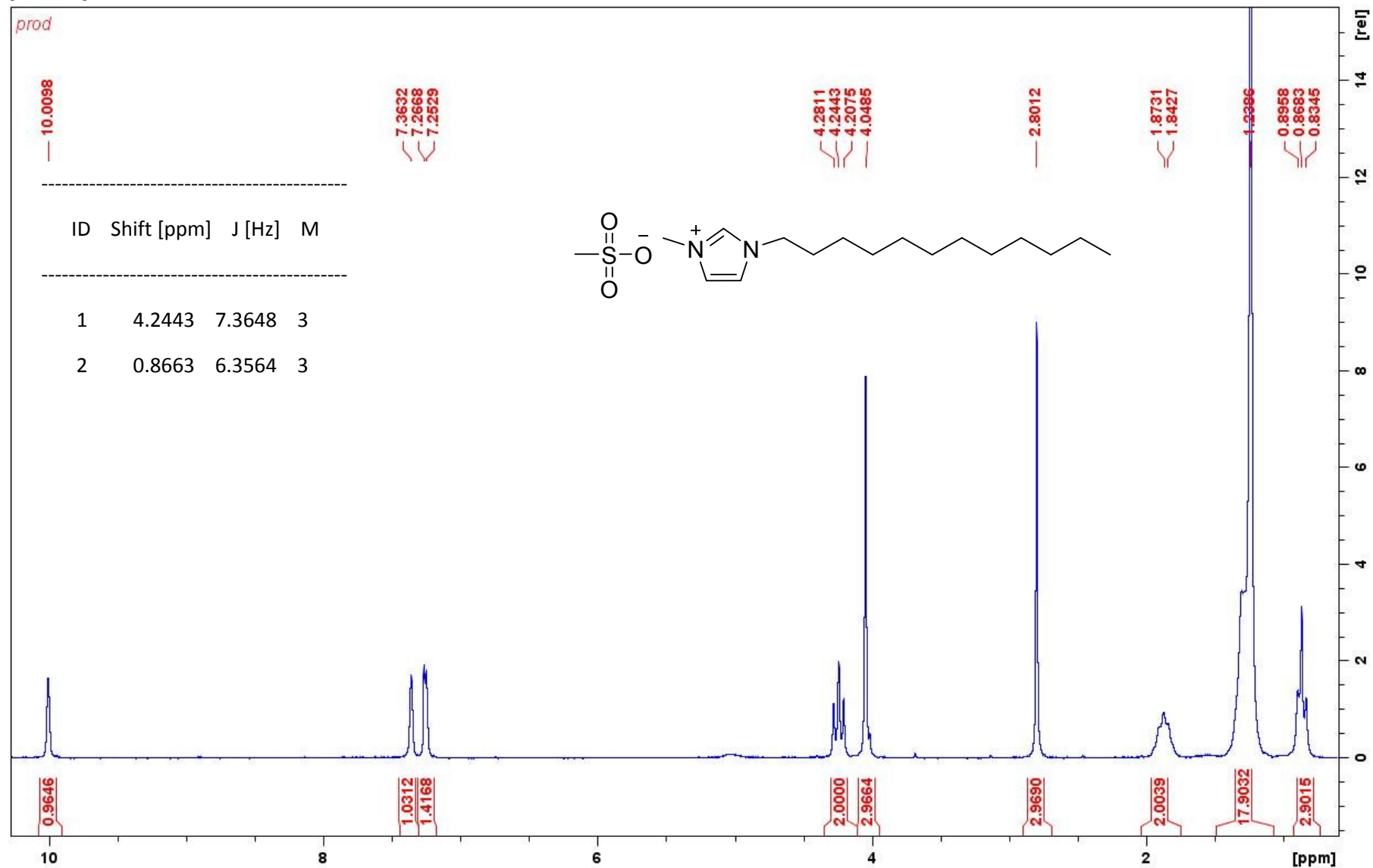


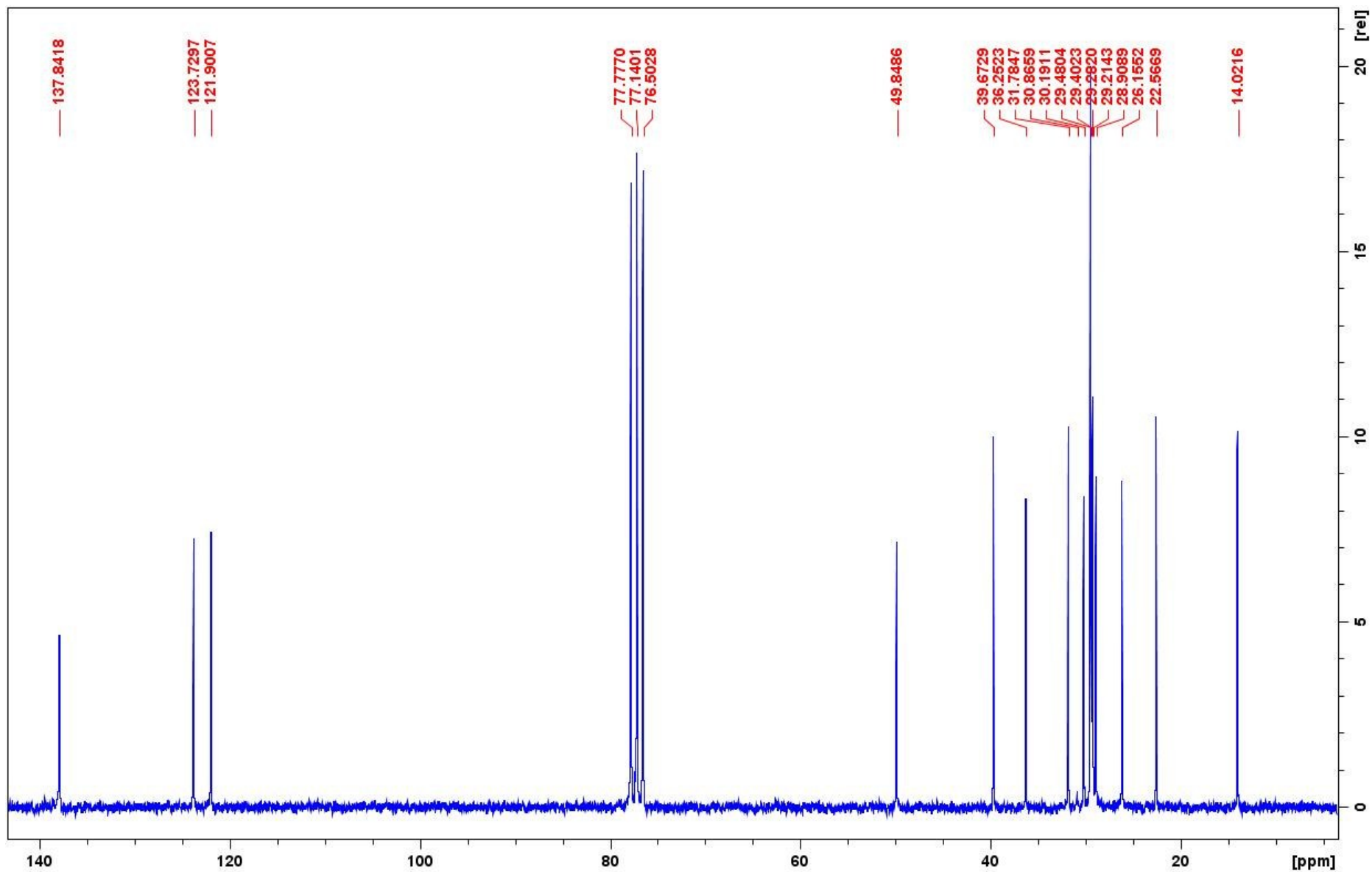
[C₁₂mim]⁺I⁻



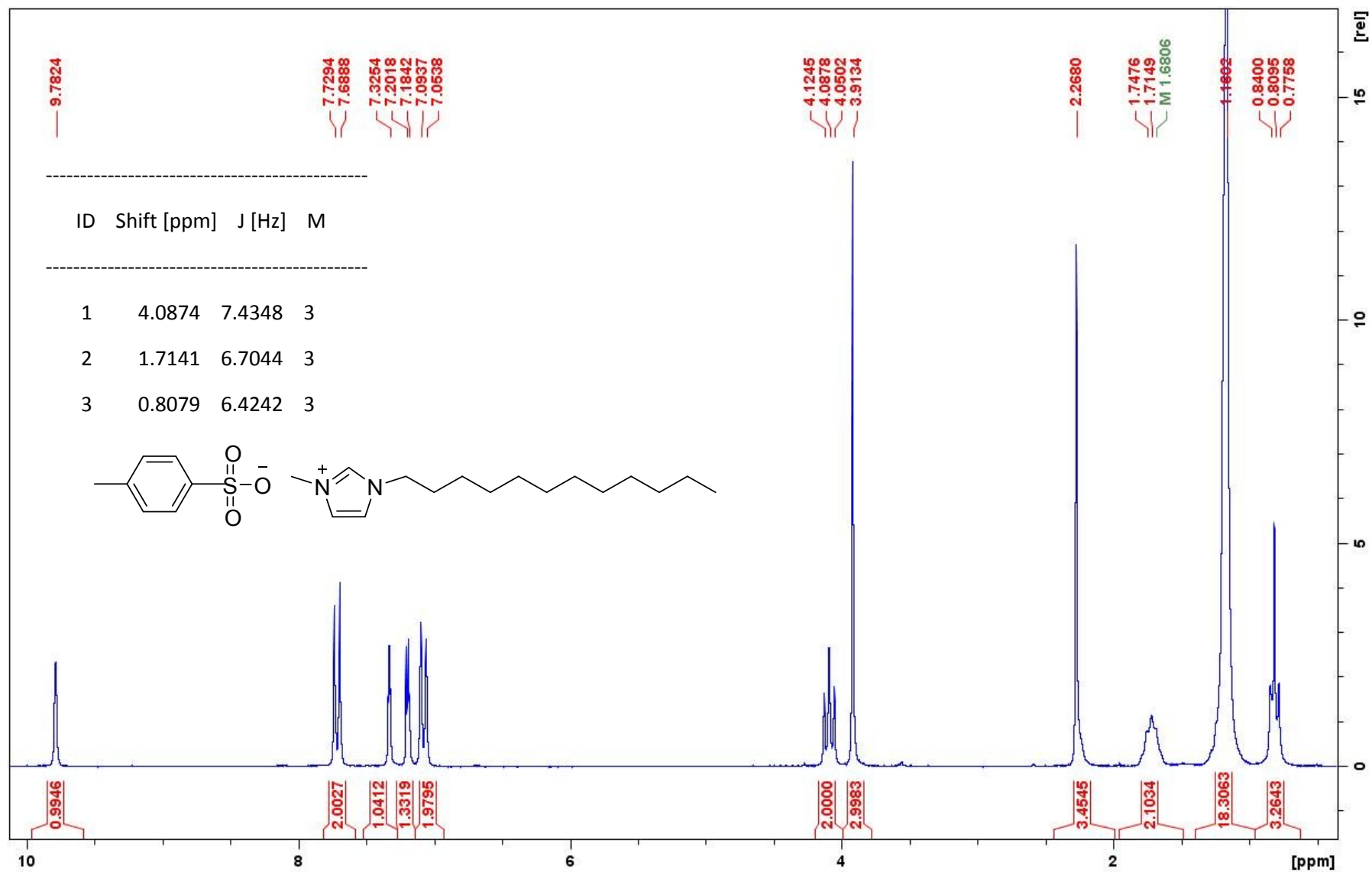


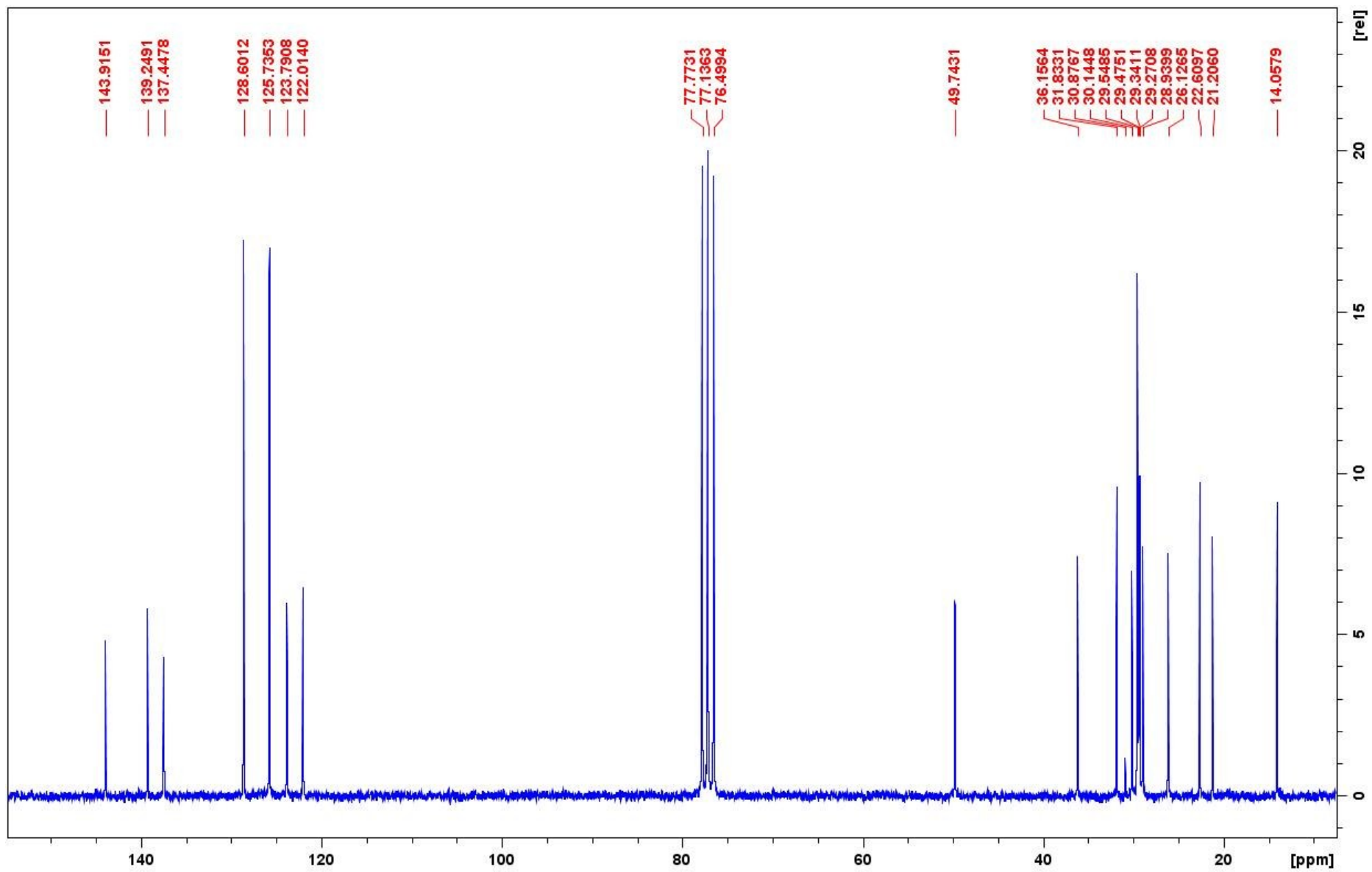
[C₁₂mim]OMs





[C₁₂mim]OTs





[C₁₂mim]OTf

