

# Characterization of Heavily Contaminated Sites using NMR Spectroscopy

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## Introduction

Groundwater is a vital part of our modern society, supplying a significant amount of water we use in our homes, agricultural fields and industries everyday. Organic contamination at many industrial sites consists of non-aqueous phase liquids (NAPLs) that form in the subsurface above and below the water table (Figure 1). NAPLs act as a partitioning domain for many hydrophobic compounds as well as a point source for groundwater contamination that often confounds remedial efforts.<sup>1</sup>

Characterizing the extent of groundwater contamination is key for developing risk assessments and implementing remedial solutions for contaminated sites. NAPL characterization is challenging due to its high concentrations (% level) and often cannot be determined by traditional environmental analytical methods based on chromatographic separation and mass spectrometric detection. NMR spectroscopy provides a unique analytical approach to present a more complete and unbiased understanding of the composition of NAPLs at many contaminated sites. Furthermore, the use of NMR prediction software allows for a rapid approach to determine the most abundant constituents within the mixture.<sup>2</sup>

## Non-aqueous Phase Liquids (NAPLs) in the Environment

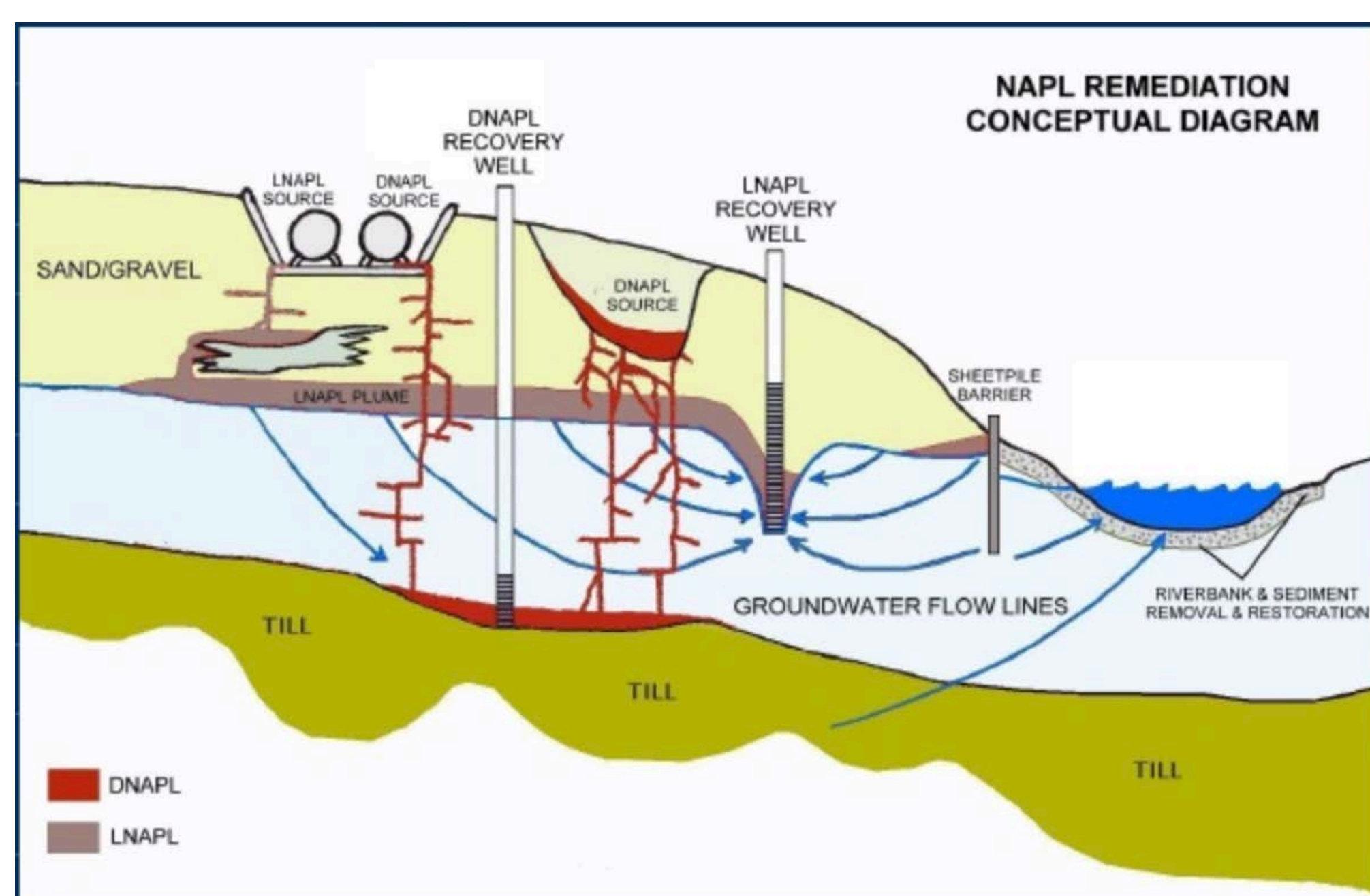


Figure 1. A conceptual diagram of NAPLs in the Environment

## Methods

NMR spectroscopy has been employed to characterize the composition of a NAPL mixture prepared to simulate NAPL samples found at many contaminated sites. All samples were prepared by dissolving 100  $\mu$ L of NAPL into 600  $\mu$ L of DMSO-*d*<sub>6</sub>. NMR experiments were acquired at 400 and 600 MHz as indicated. The ACD/C+H NMR Predictors<sup>3</sup> were used to rapidly screen mixtures to propose the major NAPL constituents present in the mixture.

## 1D NMR and Diffusion Ordered Spectroscopy (DOSY) of NAPLs

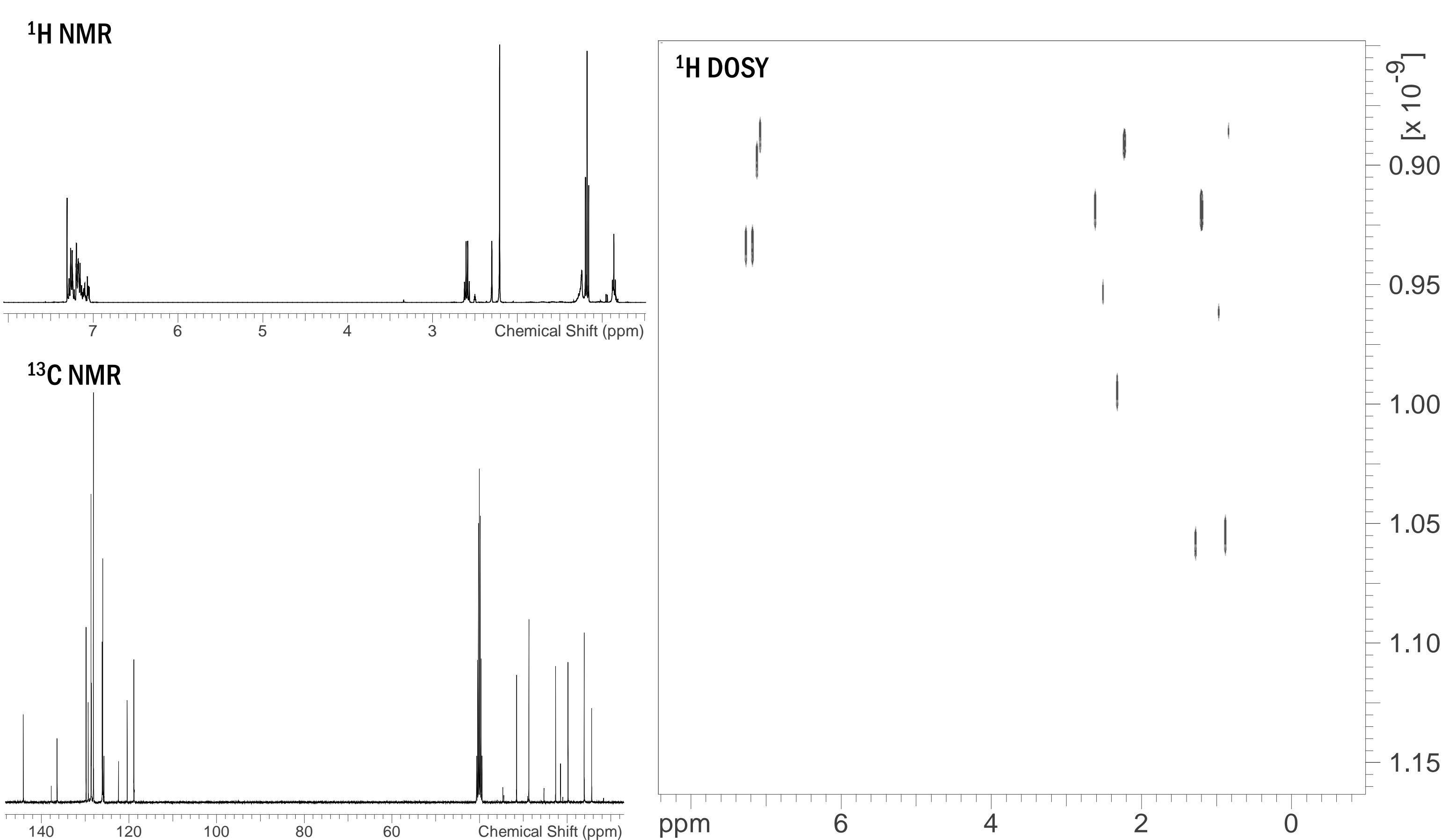


Figure 2. NMR Spectra of a NAPL mixture to highlight the overall composition. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were acquired with a 5 mm BB-1H/19F/D/Z-GRD probe on a 400 MHz Bruker Avance Spectrometer. These spectra highlight that the mixture is mainly composed of aromatic and aliphatic (likely short chain) constituents. Characteristic chemical shifts of halogenated species are clearly observed. The <sup>1</sup>H DOSY spectrum was acquired with a 5 mm BB-1H/19F/D/Z-GRD probe on a 600 MHz Bruker Avance Spectrometer with  $\Delta$  (100 ms) &  $\delta$  (2.4 ms). Prior to the DOSY transformation, the signals were peak fitted using a 50/50 Gauss/Lorentz function for the entire series, and each signal grouped to a single peak. The pseudo-2D DOSY plot clearly suggests that NAPLs are composed of small molecules, mostly aromatic and short chain alkanes/alkenes.

## NAPL Composition Proposed by ACD/C+H NMR Predictors

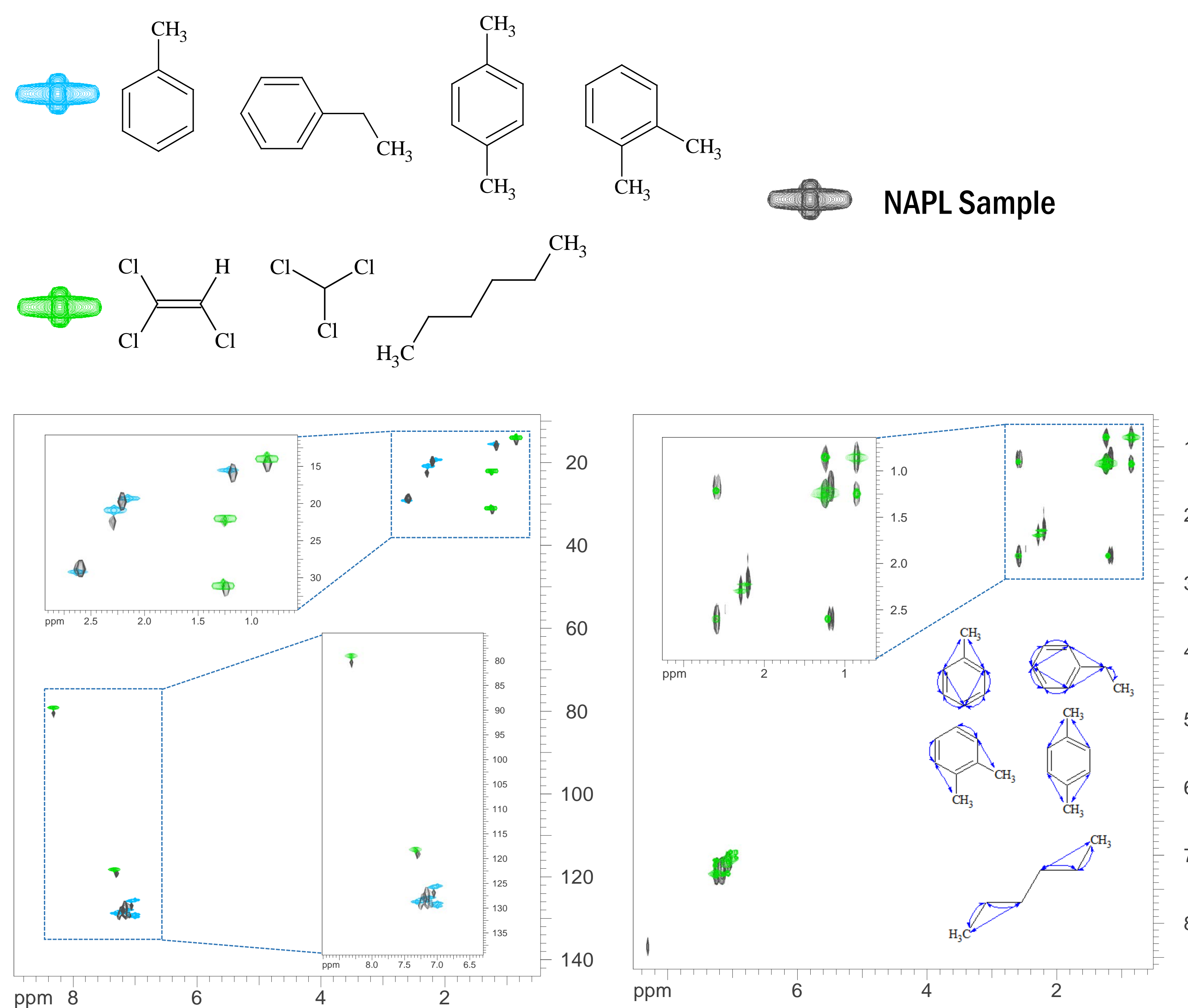


Figure 3. <sup>1</sup>H-<sup>13</sup>C HSQC and <sup>1</sup>H-<sup>1</sup>H TOCSY of the NAPL mixture acquired with a 5 mm BB-1H/19F/D/Z-GRD probe on a 400 MHz Bruker Avance spectrometer (black contours). Spectral overlays of aromatic compounds (blue contours) and chlorinated solvents & hexane (green contours) on the HSQC from ACD/C+H NMR Predictors clearly overlay with the NAPL (black contours) solution, suggesting that they are the main constituents. The Spectral overlays of the relevant compounds (green contours) on the TOCSY from ACD/C+H NMR Predictors show the major <sup>1</sup>H-<sup>1</sup>H spin systems (inset molecules) are consistent with the NAPL mixture (black contours). This is in conjunction with the overlays from <sup>1</sup>H and <sup>13</sup>C NMR (data not shown) and suggests that the major constituents present have been identified.

## ACD/C+H NMR Predictors Suggest Absence of Nitro-benzenes

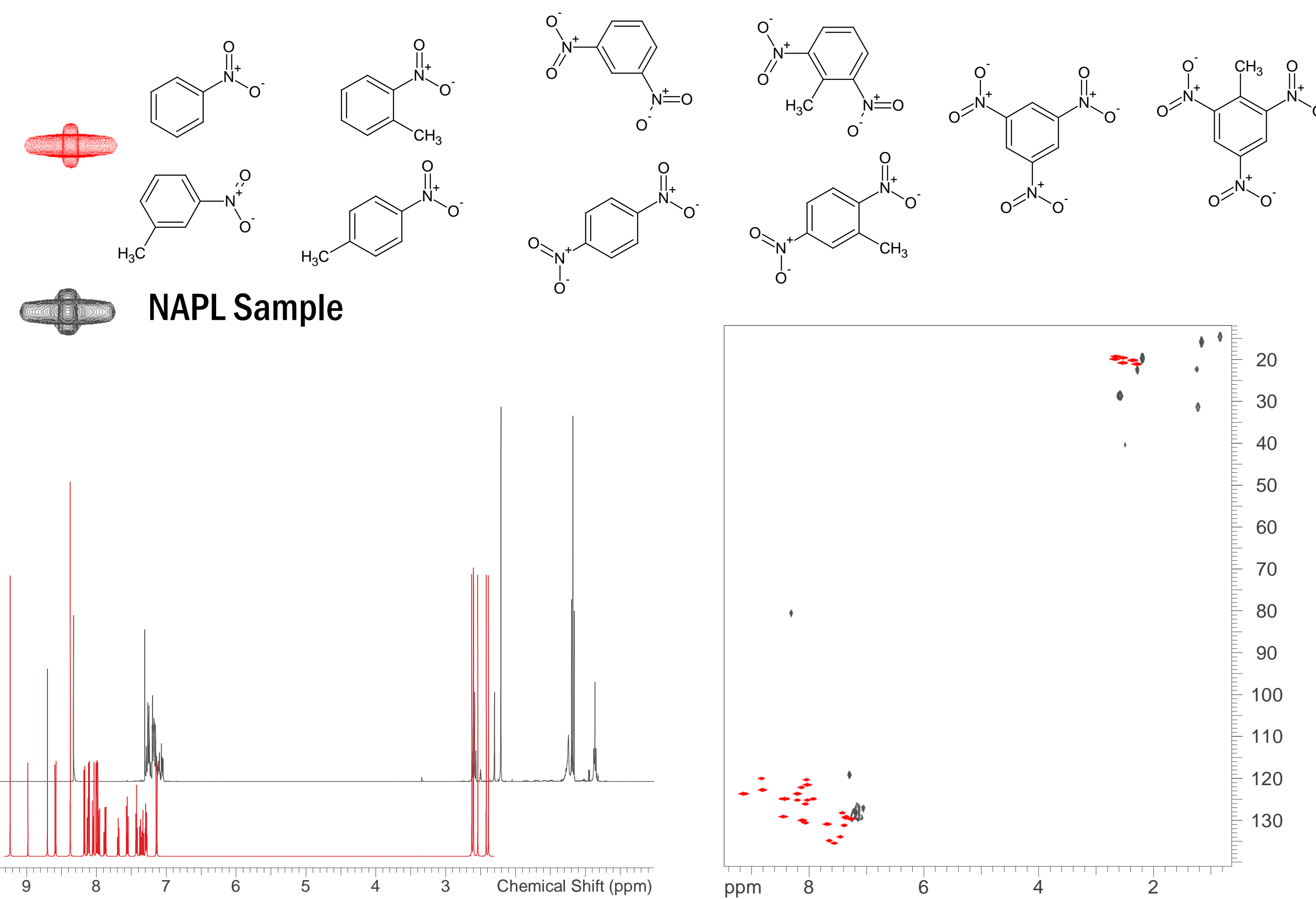


Figure 4. Nitro-benzenes and toluenes present in NAPLs is a major environmental and safety concern, drastically increasing remediation costs.<sup>1</sup> A quick survey of these compounds using ACD/C+H NMR Predictors (red) and overlay of with the NAPL mixture (black) suggests that these constituents are likely absent or below the detection limits.

## Conclusions

NMR spectroscopy when combined with ACD/C+H NMR Predictors is shown to be useful in the rapid identification of the constituents present/absent in a complex NAPL mixture. The analysis of NAPLs by NMR may be used to improve the characterization of many contaminated sites undergoing risk assessment and remedial activity.

### Acknowledgements

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References [1] Pankow & Cherry, 1996, Dense Chlorinated Solvents and other DNAPLs in Groundwater. Waterloo Press. [2] Simpson *et al.*, *Magn. Reson. Chem.* 2004, 42, 14. [3] ACD/C+H NMR Predictors, 2016, [www.acdlabs.com/products/adh/nmr/nmr\\_pred/](http://www.acdlabs.com/products/adh/nmr/nmr_pred/)