Solvent Suppression

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Why Suppress Solvent Signal?

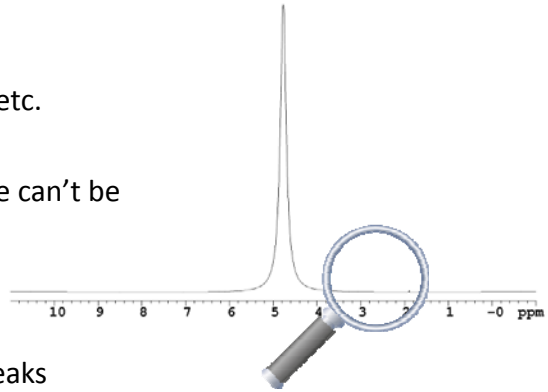
- Dilute samples

  - Biomolecule analysis: proteins etc.

- Where deuterated solvents alone can't be used

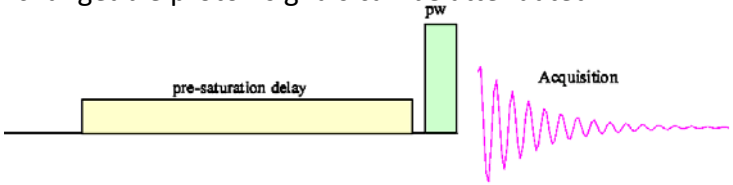
  - Effect on reaction kinetics etc.

- Solvent peak will dwarf solute peaks

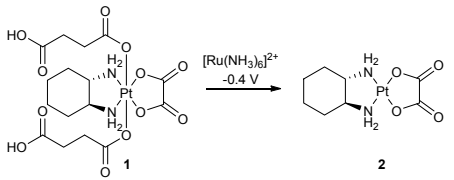


Presaturation - How Does It Work?

- Water (and other solvents) have known resonance frequency
- Long, low-power pulse applied at frequency
- Saturates the resonance -> reducing the intensity
- Exchangeable proton signals can be attenuated



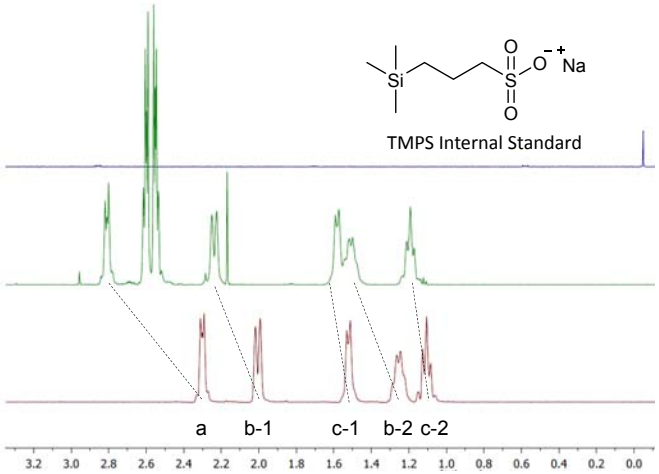
Real-World Example:
Quantification of Pt(II) and (IV) species

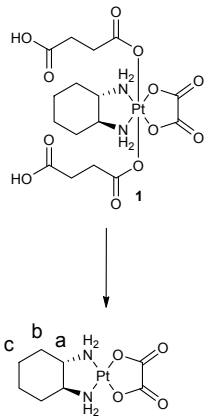


Pt(IV) Pt(II)

- Conversion of inactive prodrug to active drug
- Concentrations used are µM range in aqueous solution

Real-World Example:
Quantification of Pt(II) and (IV) species





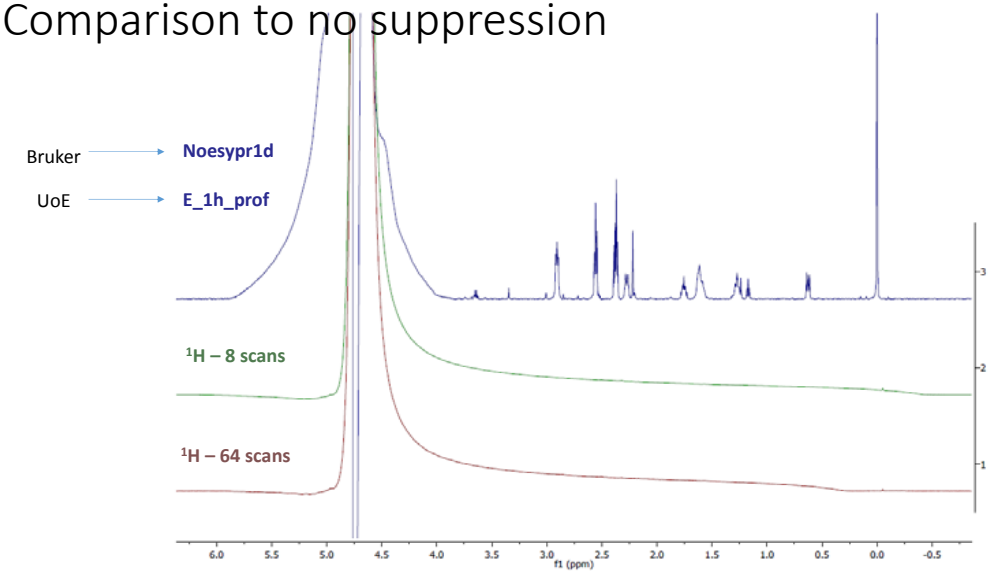
Sample Preparation

Reaction mixture:
- Pt(II)/Pt(IV) species
- H_2O/PBS

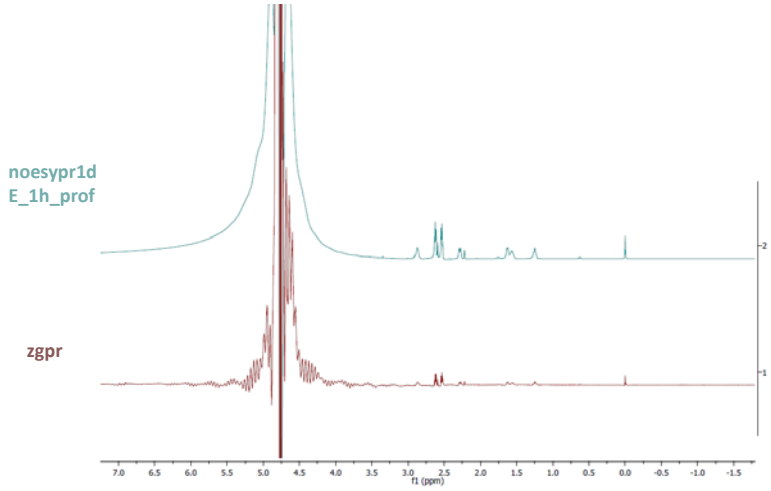
Internal Standard:
- TMPS
- D_2O

NMR Tube:
- Pt species
- TMPS
- 10% D_2O / 90% H_2O

Comparison to no suppression



Comparison of water suppression



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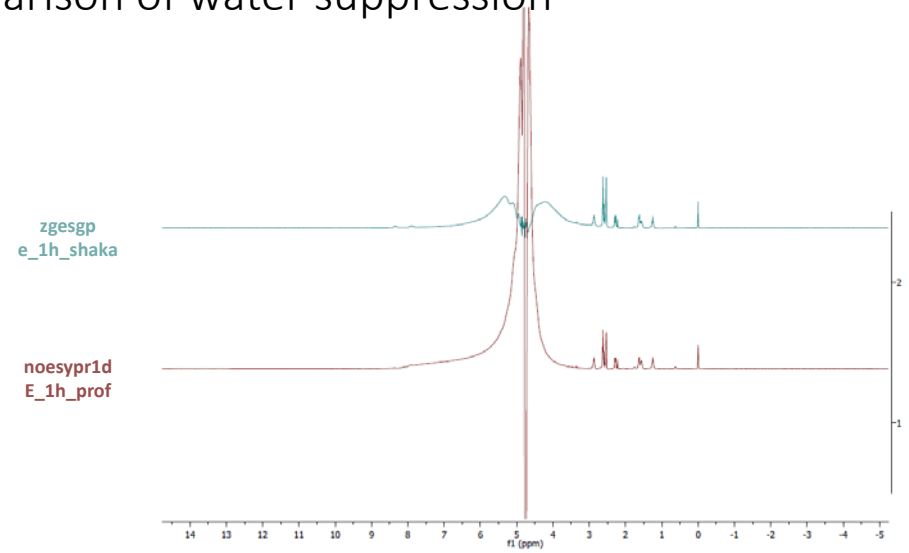
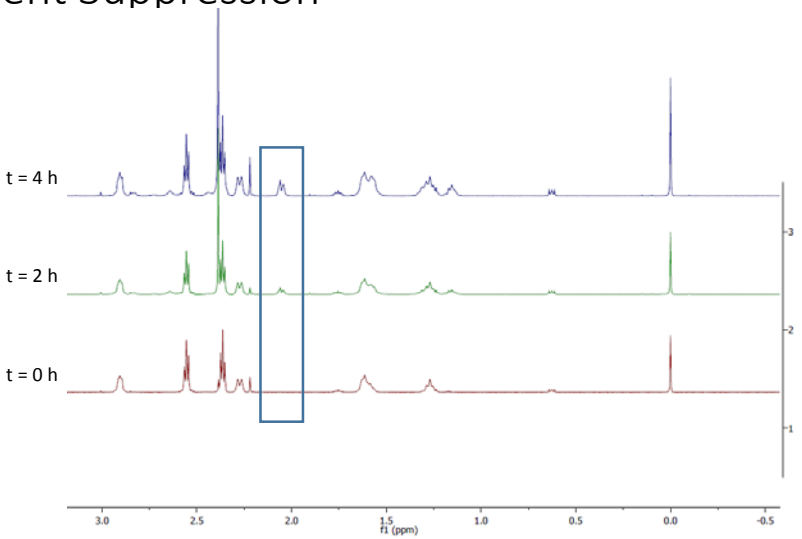


Solvent Suppression



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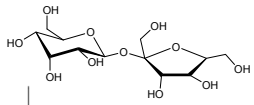
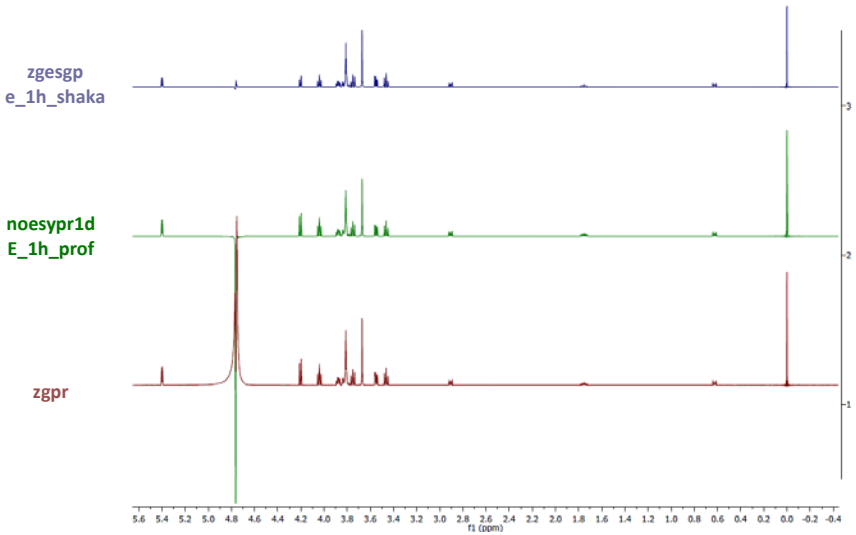
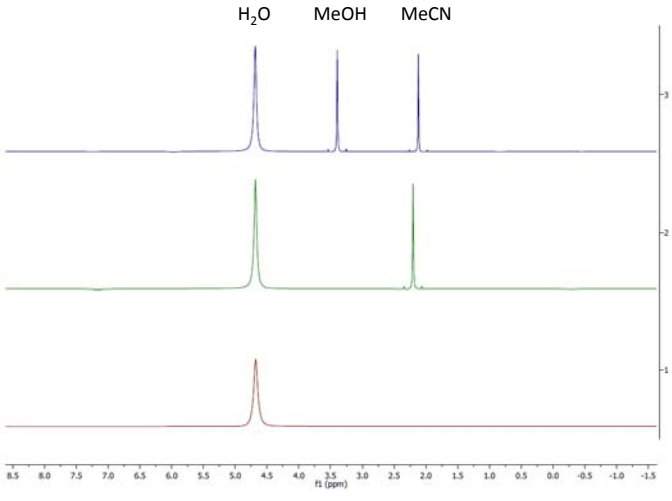




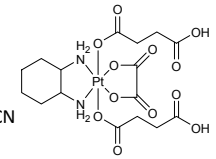
Multiple Solvent Suppression

- Solvent signals of multiple solvents
- More complex splitting of signals than just water's singlet
- S/D/Tpresat

  -> Integration to find peak with highest intensity



Multiple Solvent Suppression

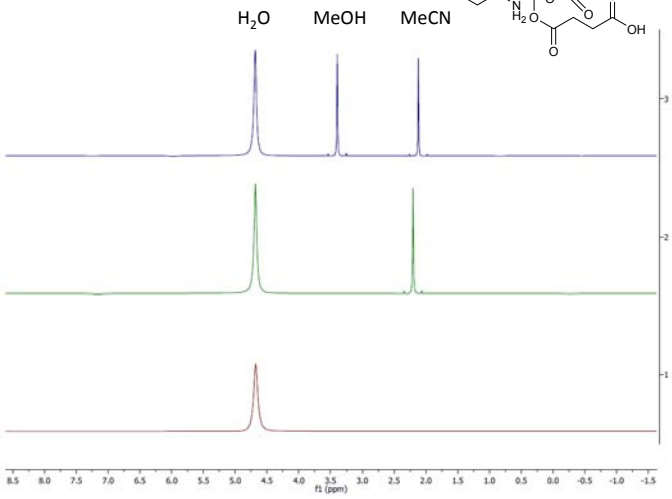


Composition:

H_2O:MeOH:MeCN:D_2O
5:2:2:1

H_2O:MeCN:D_2O
6:3:1

H_2O:D_2O
9:1



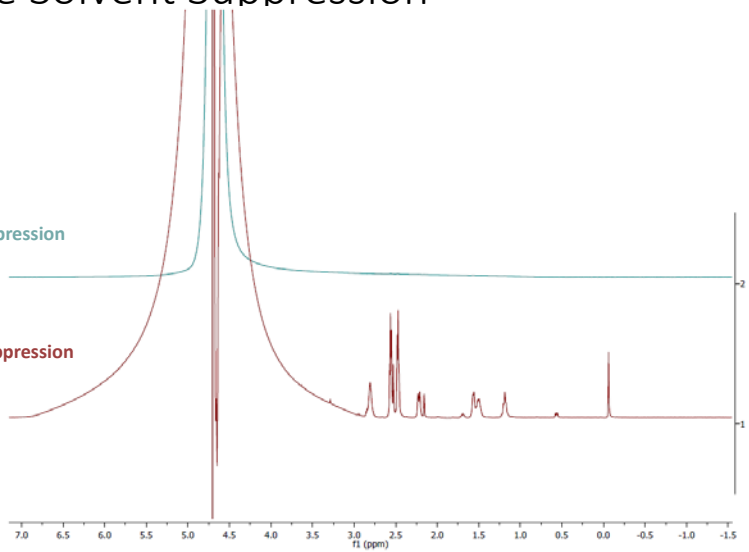
Multiple Solvent Suppression

SPresat

H_2O:D_2O
9:1

No suppression

With suppression



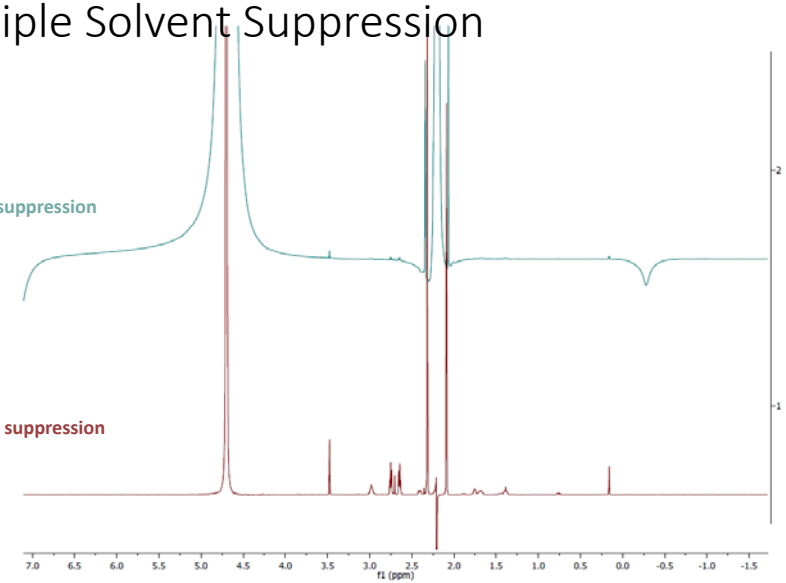
Multiple Solvent Suppression

DPresat

H_2O:MeCN:D_2O
6:3:1

No suppression

With suppression



Multiple Solvent Suppression

TPresat

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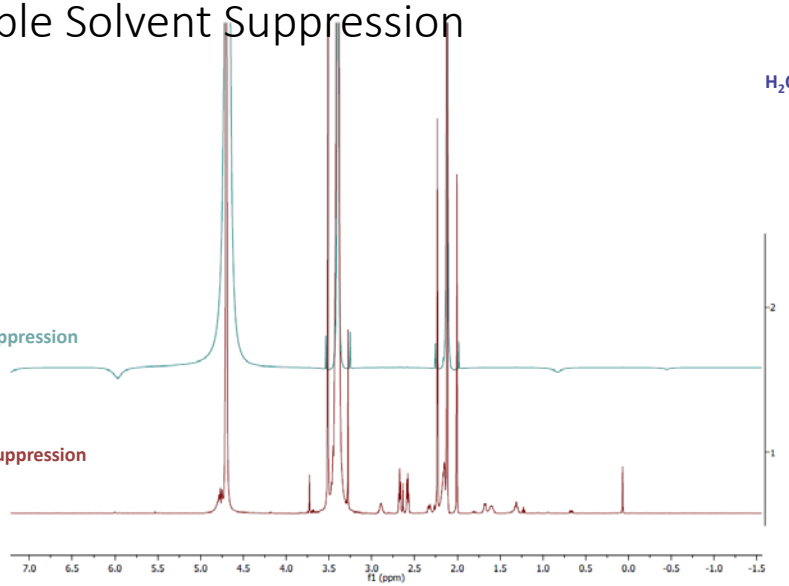
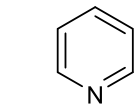
With suppression



Multiple Solvent Suppression – Organic Solvents

TPresat



Multiple Solvent Suppression - Whisky

- ~40% ethanol in aqueous solution
- Flavour molecules in low concentration

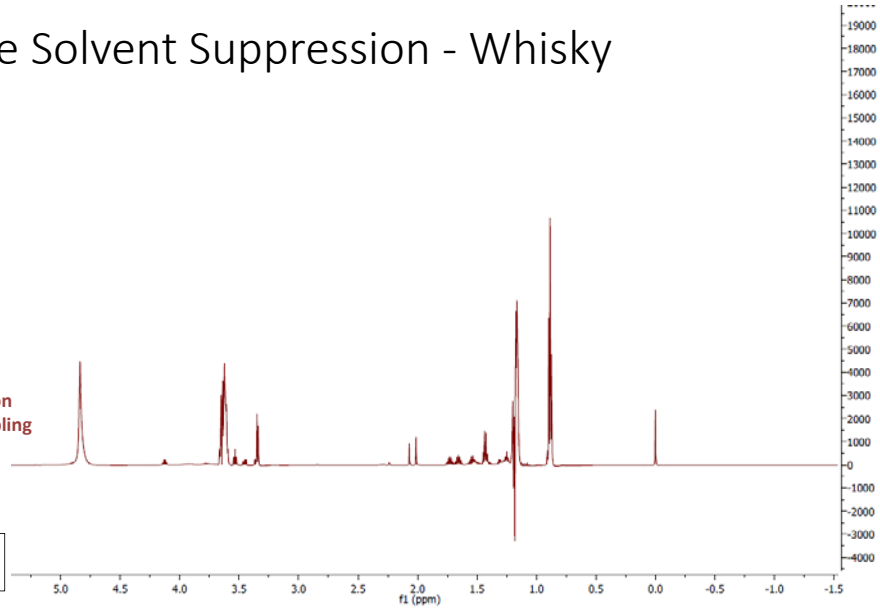
zgpr

Data from Will Kew

Multiple Solvent Suppression - Whisky

With suppression and 13C-decoupling

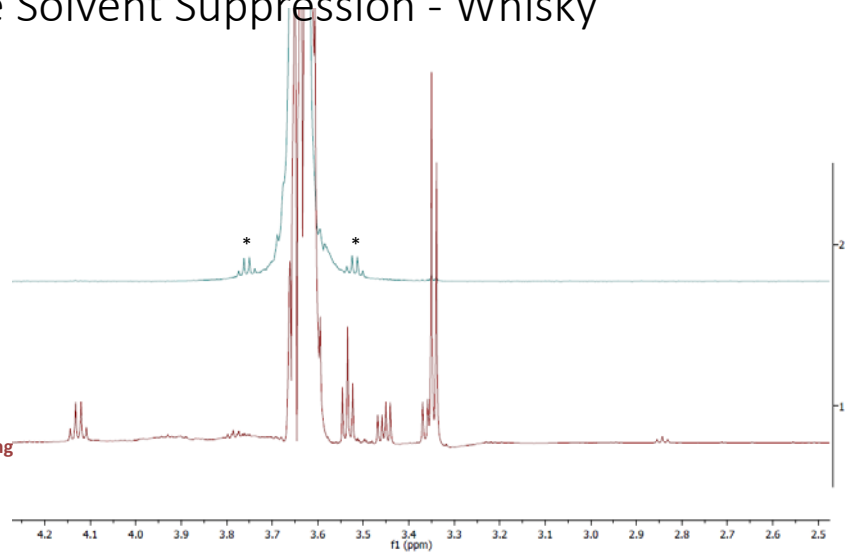
Data from Will Kew



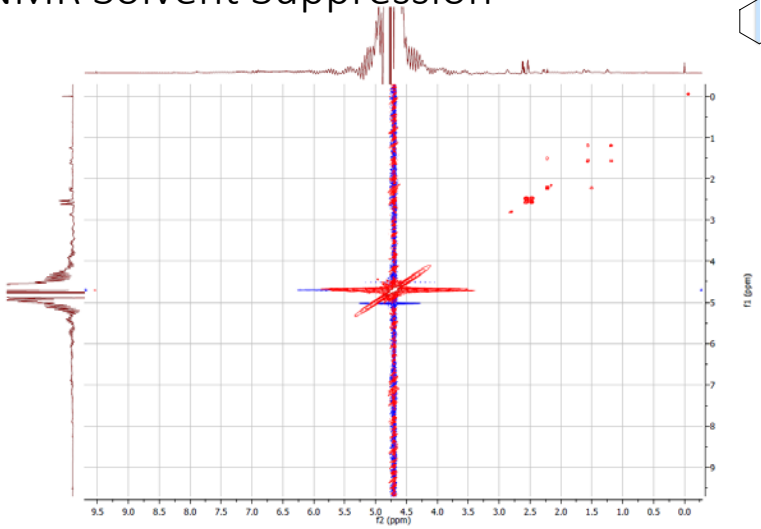
Multiple Solvent Suppression - Whisky

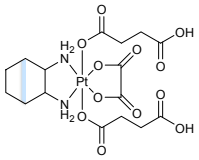
No suppression

With suppression and 13C-decoupling



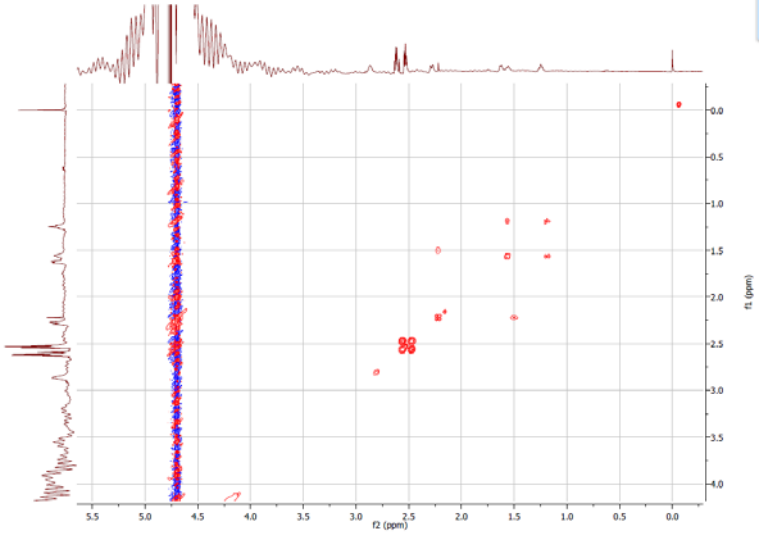
2D-NMR Solvent Suppression



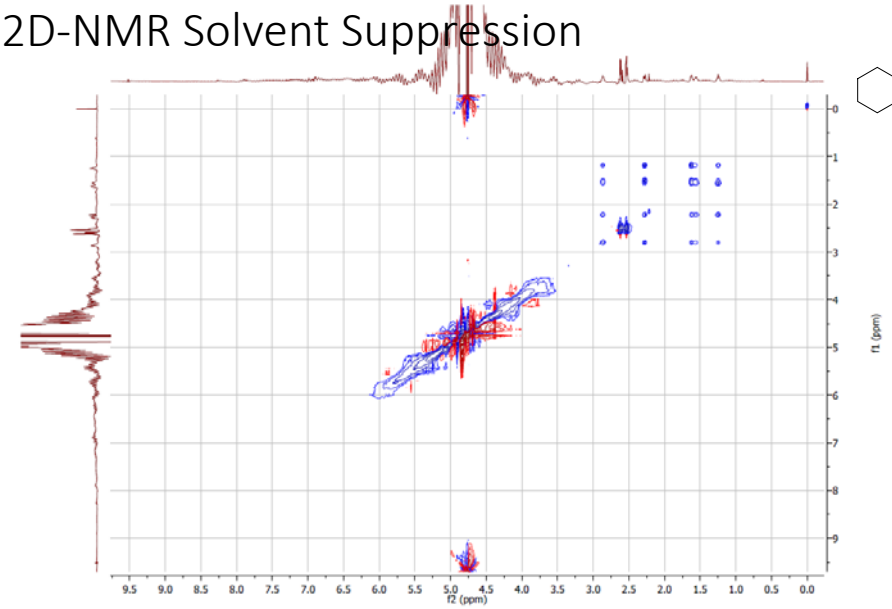


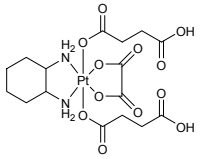
^{1}H-^{1}H COSY

2D-NMR Solvent Suppression



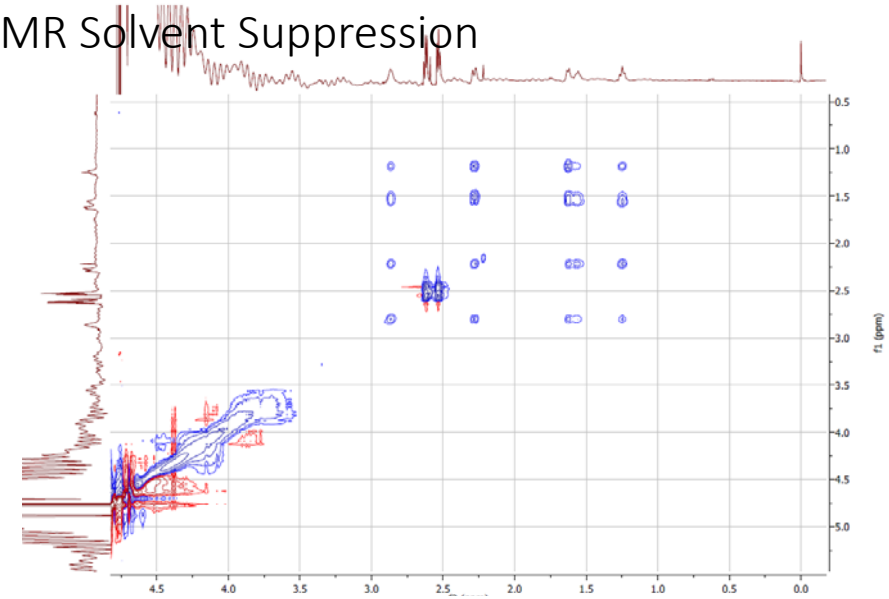
2D-NMR Solvent Suppression





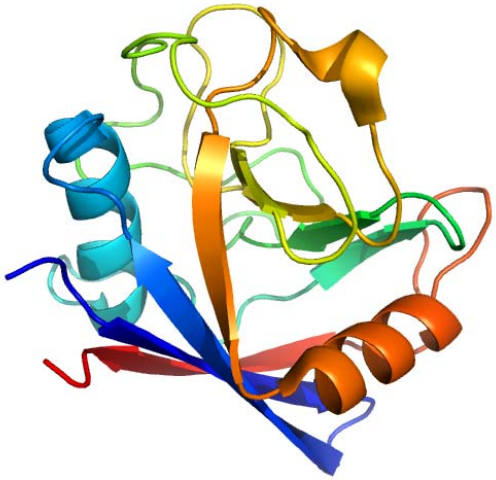
^{1}H-^{1}H TOCSY

2D-NMR Solvent Suppression



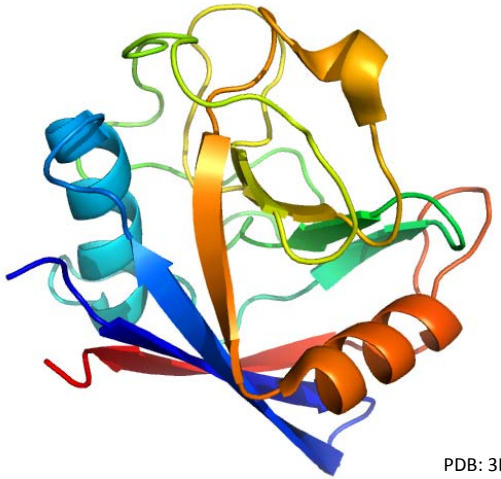
Solvent Suppression for Protein NMR

- Precious samples
  -> dilute aqueous
- Exchangeable protons analysis
  e.g. 90% H_2O 10% D2O
  -> amide backbone



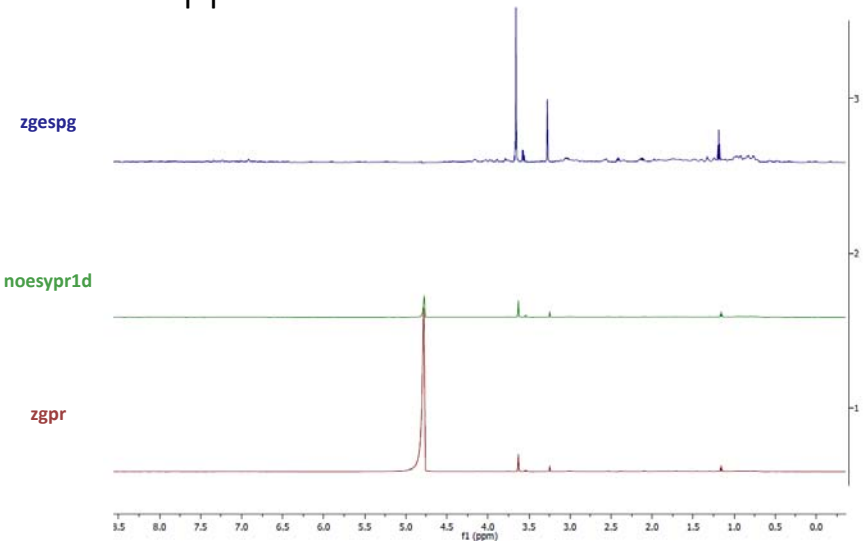
Solvent Suppression for Protein NMR

- Cyclophilin D
  -> £4215/mg
  -> 42.9 kDa
- Involved in mitochondrial processes and immunosuppression



PDB: 3R56

Solvent Suppression for Protein NMR



Solvent Suppression for Protein NMR