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Practical Applications of Compact High-Resolution 60 MHz Permanent Magnet NMR Systems for Reaction Monitoring and Online Process Control

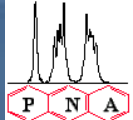
Presented By

John Edwards, Ph.D.

**Process NMR Associates, LLC
Danbury, Connecticut**

March 22, 2011

RSC Reaction Monitoring Symposium, Sandwich, Kent, UK



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300+ Analytical NMR Customers

smiths detection
bringing technology to life



MODCON



ACTIVE SPECTRUMtm

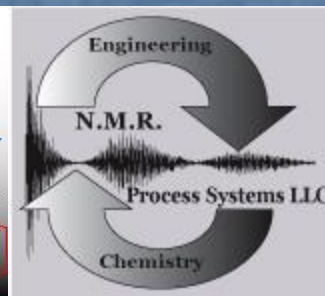
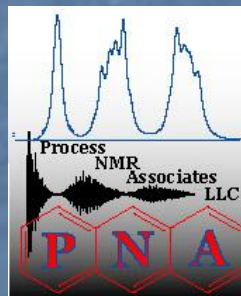


QUALION
NMR ANALYZERS

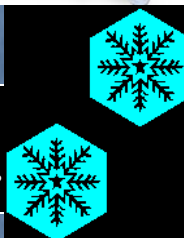


COSA
INSTRUMENT

Swagelok



TTC Labs, Inc.
Process Engineering Excellence

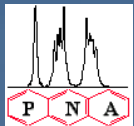


TopNIR Systems



RESONANCE
SYSTEMS

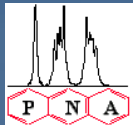




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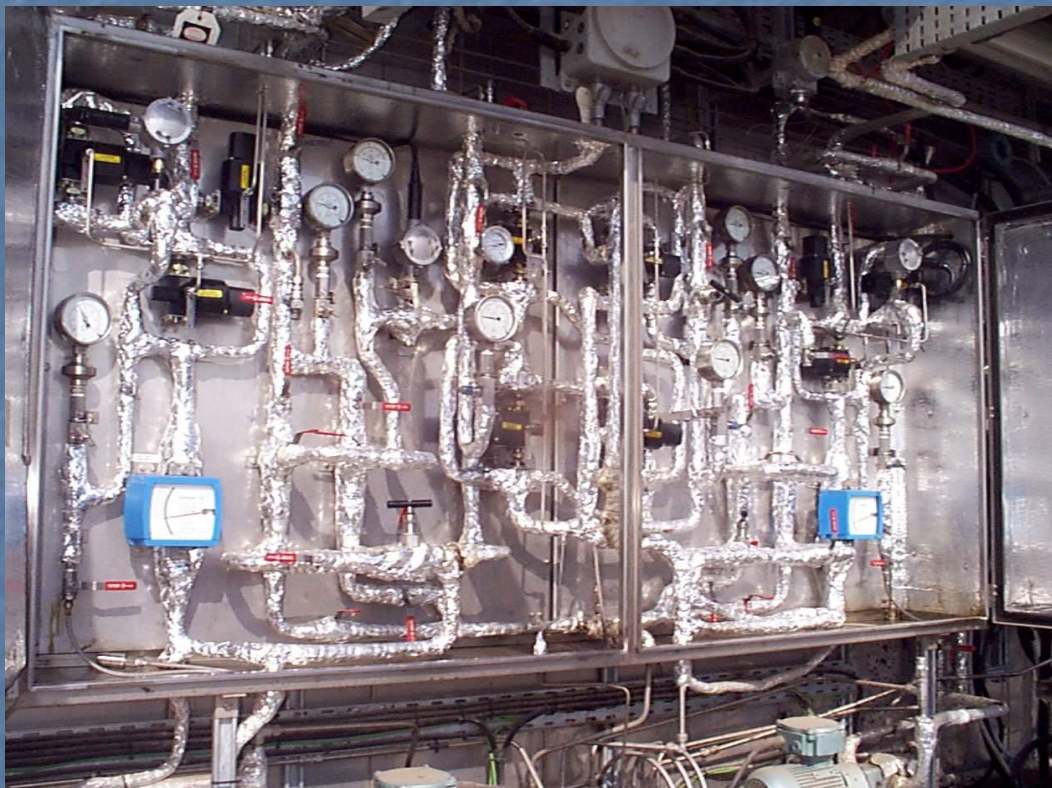
High Resolution FT-NMR – Online / in Process

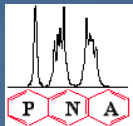




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NMR Sample System and Placement





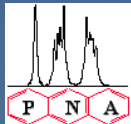
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NMR Lock - External ^7Li Lock @ 22.5 MHz Shim DACs Built into the Magnet Enclosure



Matrix Shimming Performed
by Optimizing FID RMS



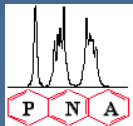


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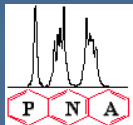
SPECIFICATIONS

Nuclei Observed	H ⁺ (primary)
Operating Frequency	58±1.0 MHz for H ⁺
Sample Tube	Standard laboratory glass tube L: 35.5 cm O.D 8 mm - I.D 7 mm Other size optional
Sample Temperature Heating	Controlled between 30°C – 80°C (86°F to 176°F)
Magnet System	Temperature stabilized, self-condensed field, permanent (neodymium) magnet with integral field gradient (shim) coils and automatic shim control
Field Strength	1.35 Tesla at 45°C
Fringe Field	Less than 1 gauss on external enclosure of magnet
Dimensions	145 cm H x 106 cm W x 65 cm D (57 in H x 42 in W x 26 in D) Add 15 cm (6 in) to height for shipping pallet
Enclosure	Self standing, wheel driven carriage
Weight	400 kg (882 lb) net weight 444 kg (980 lb) gross shipping weight
Power Requirement	220-240 Vac, 3500W maximum 110-120 Vac, 3500W maximum
Other Utilities	Internal Air condition system for higher stability
Operating temperature	Ambient Range: Temperature controlled environment
Relative humidity	Min / Max 30%-50%.
Vibration	Max: 0.3 mm/s ² on the 3 axes
Communication	Local Ethernet Base -10/100. Remote connection via modem.



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New magnet design solves the problem of:

Long term and short term Stability
Temperature sensitivity

New Magnet System

State of the Art electronics:

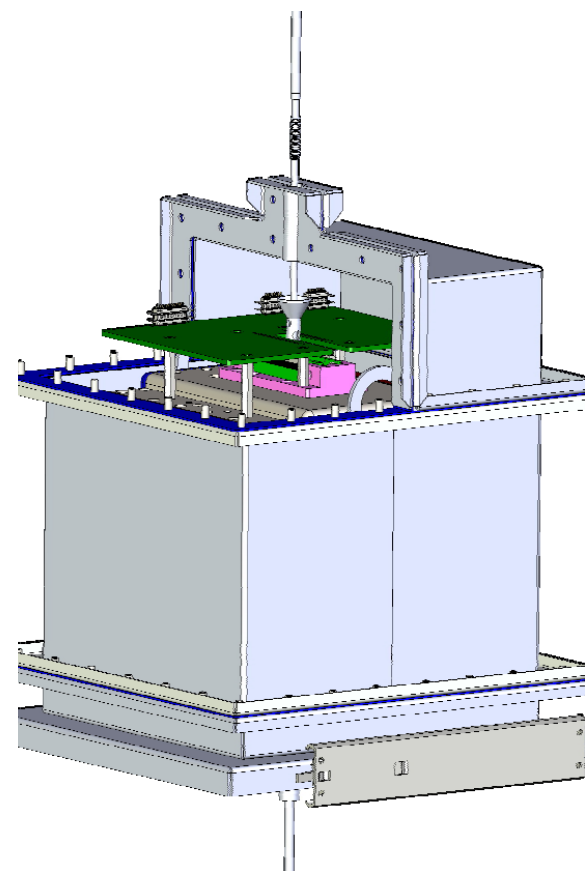
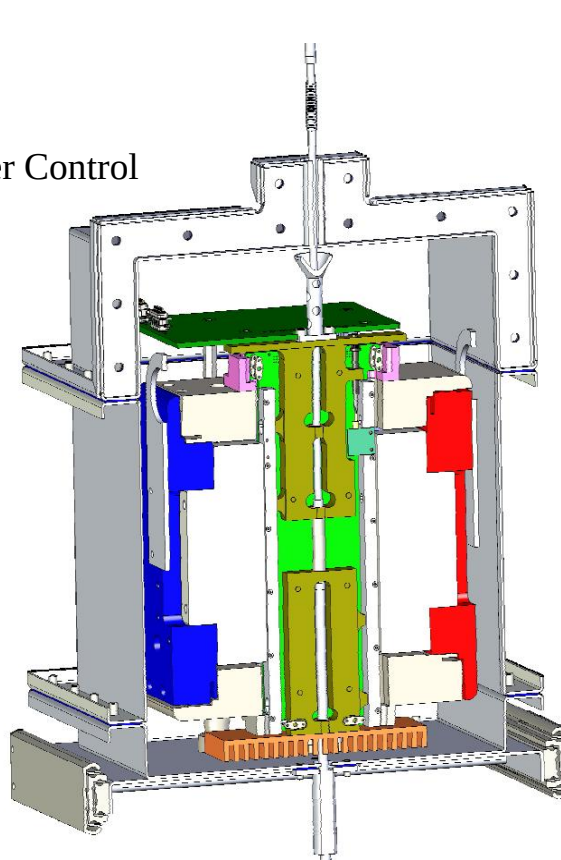
Smaller foot-print
40 Shim coils on 2 single PCB
Integrated PCB for Shim & Heater Control
Digital RF & Acquisition –
improve SNR

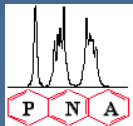
New concept of Process Probe:

Entire sample pipe through
without contact with the system
Much better temperature
insulation
Higher Q (better sensitivity)

New Software:

Includes new algorithm for
standard and global Models
Fully automated process capacity
Extensive remote diagnostic capabilities





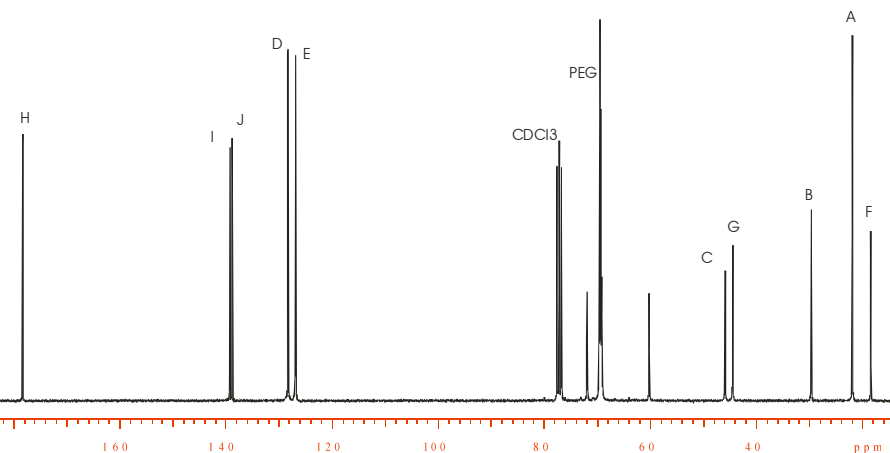
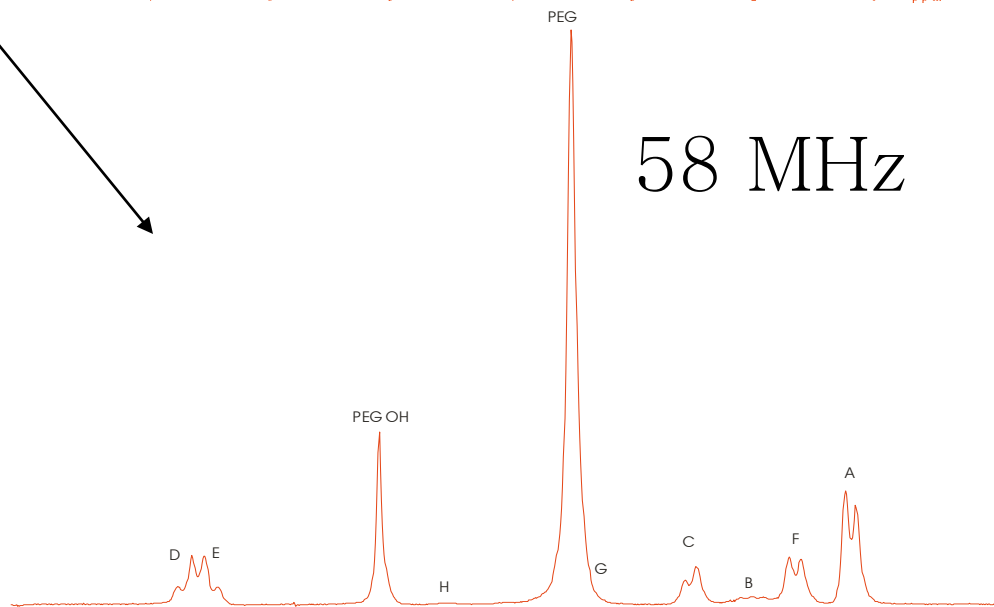
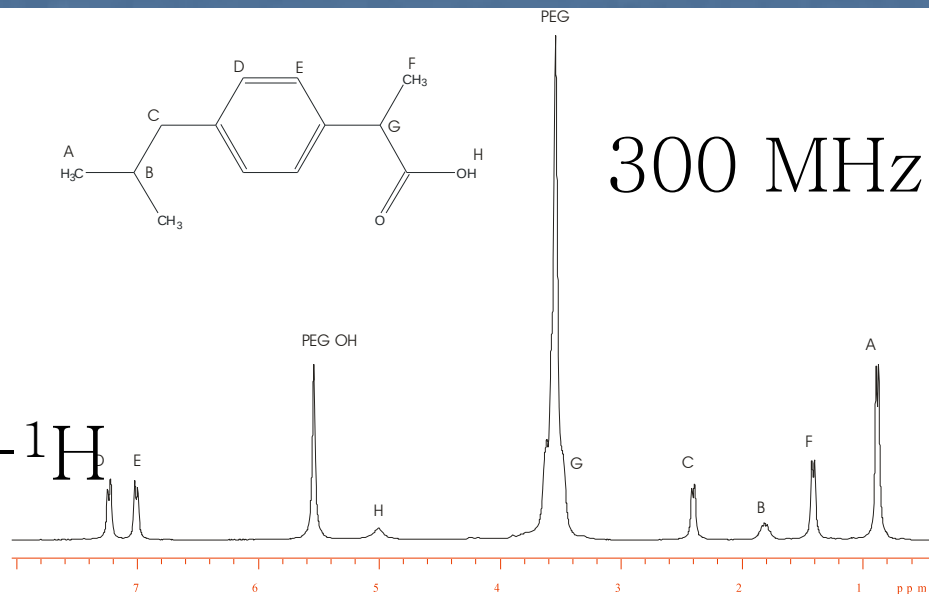
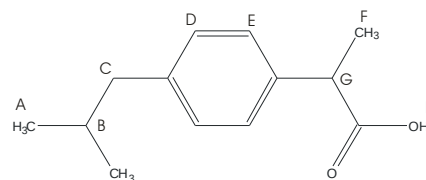
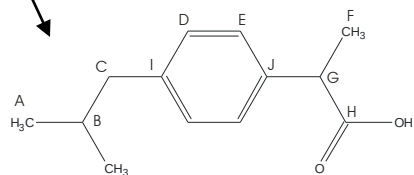
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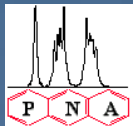
FT- ^{13}C

FT- ^1H

300 MHz

58 MHz





Advantages and Disadvantages of NMR Applied to Process Control

Advantages:

Non-Optical Spectroscopy

No Spectral Temperature Dependence

Minimal Sampling Requirements

Spectral Response to Sample Chemistry is Linear

Chemical Regions of NMR Spectra are Orthogonal

Entire Volume is Sampled by the RF Experiment

Water is in Distinct Region and can be digitally removed

Detailed Hydrocarbon information is readily observed.

Fundamental Chemical Information Can be Derived Directly from Spectrum.

Colored/Black Samples Readily Observed Without Impact

Disadvantages:

Solids Cannot be Observed in a Liquid Stream

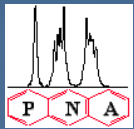
Individual Molecular Component Sensitivity Not Observed Directly in the Spectrum.

Low Sensitivity to Impurities – Quantitative > 500 ppm.

Sensitive to Ferromagnetics.

Sample Viscosity Causes Decrease in Resolution

Non-Hydrogen Containing Species are Not Observed (Exceptions Na, P, F, Al)



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Application: Steam Cracking Optimization Installed 2000

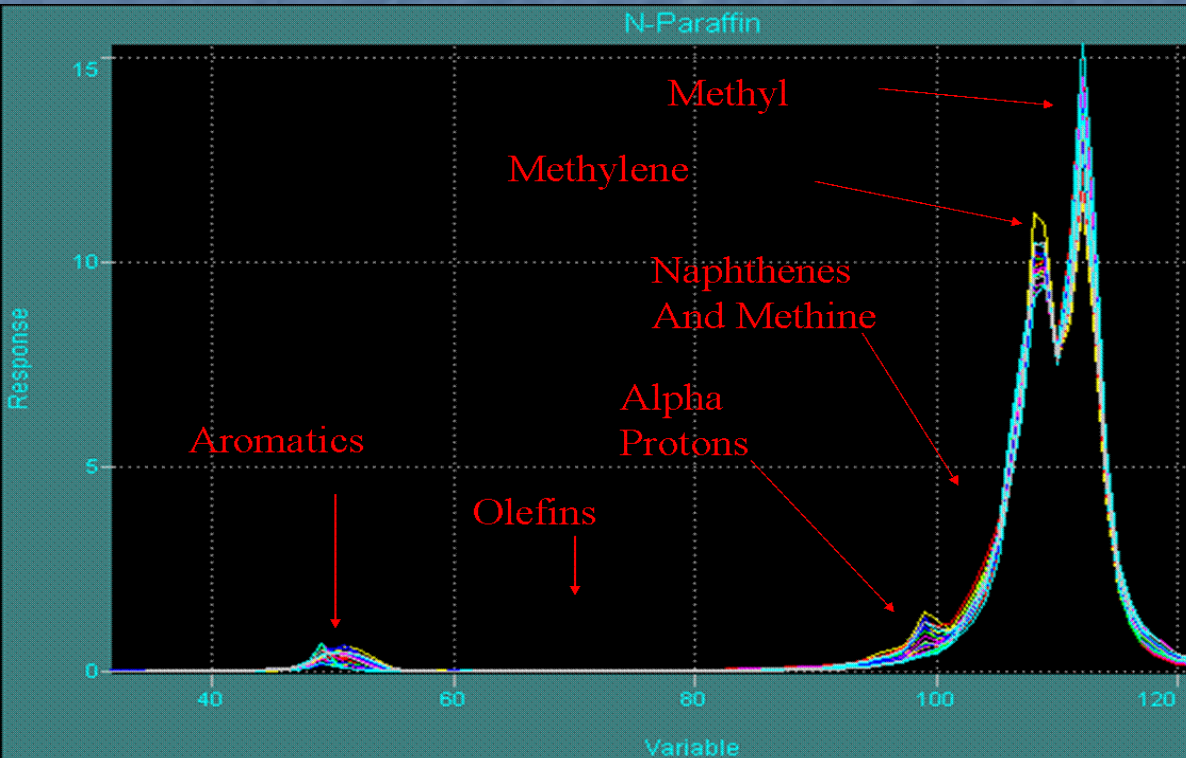
Cracker Facility Capacity: 600,000 Tonnes per Year

Control Strategy: Feed Forward Detailed Hydrocarbon Analysis to SPYRO Optimization

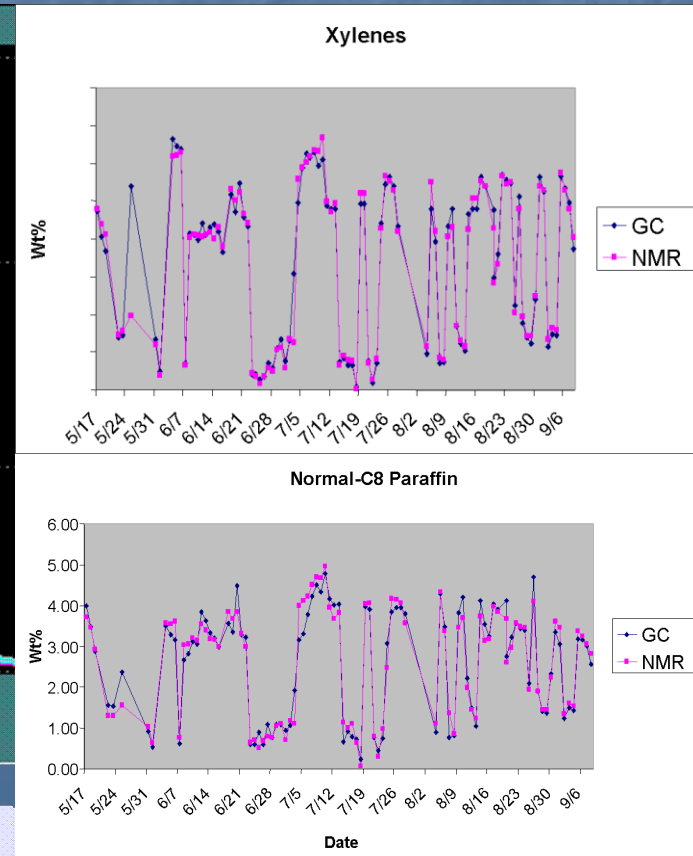
NMR Analysis: 3-4 Minute Cycle (Single Stream)

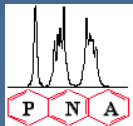
NMR PLS Outputs: Naptha – Detailed PIONA

C4-C10 normal-paraffin, iso-paraffin, aromatics, naphthenes

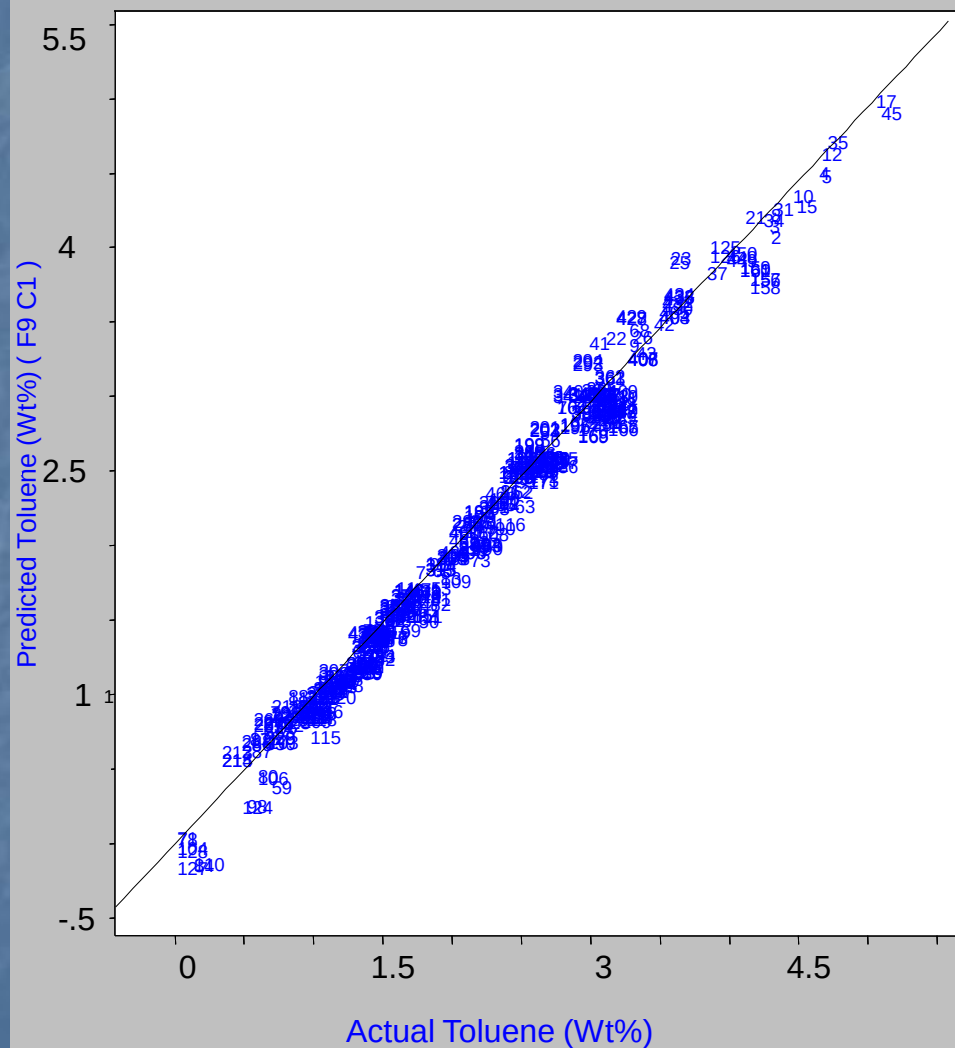


Spectral Variability Observed in Naptha Samples

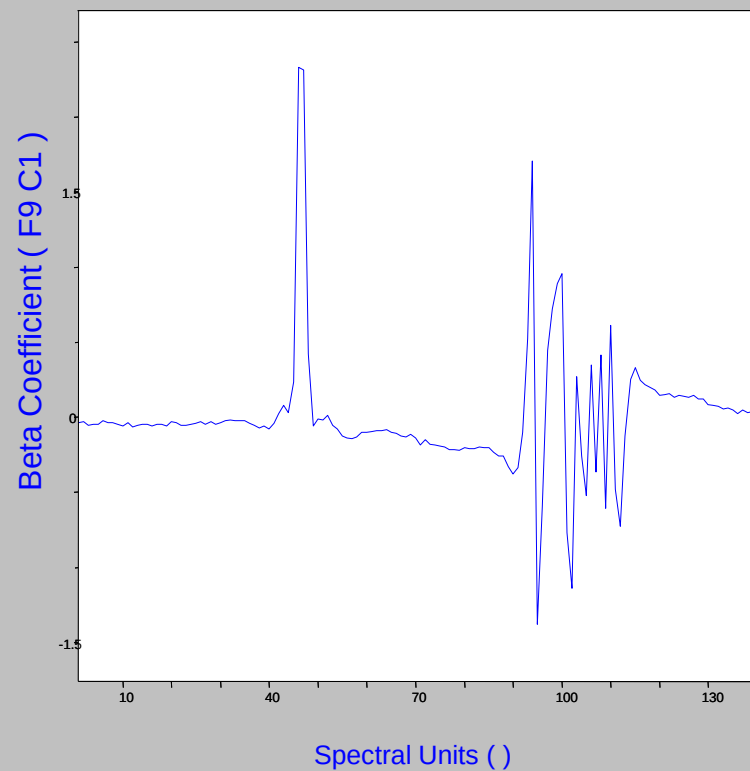


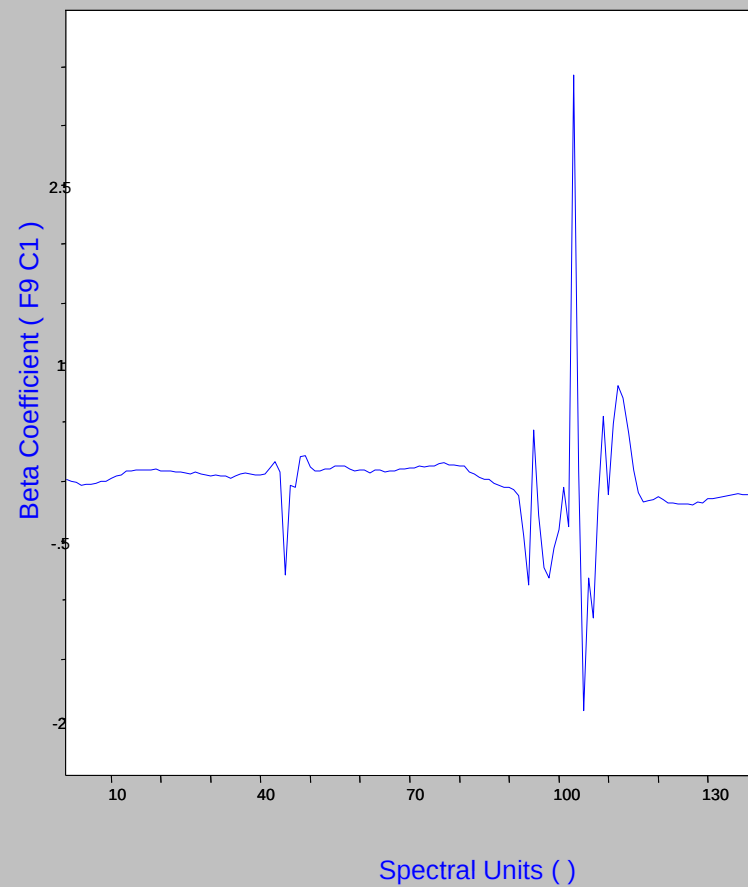


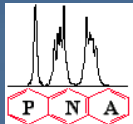
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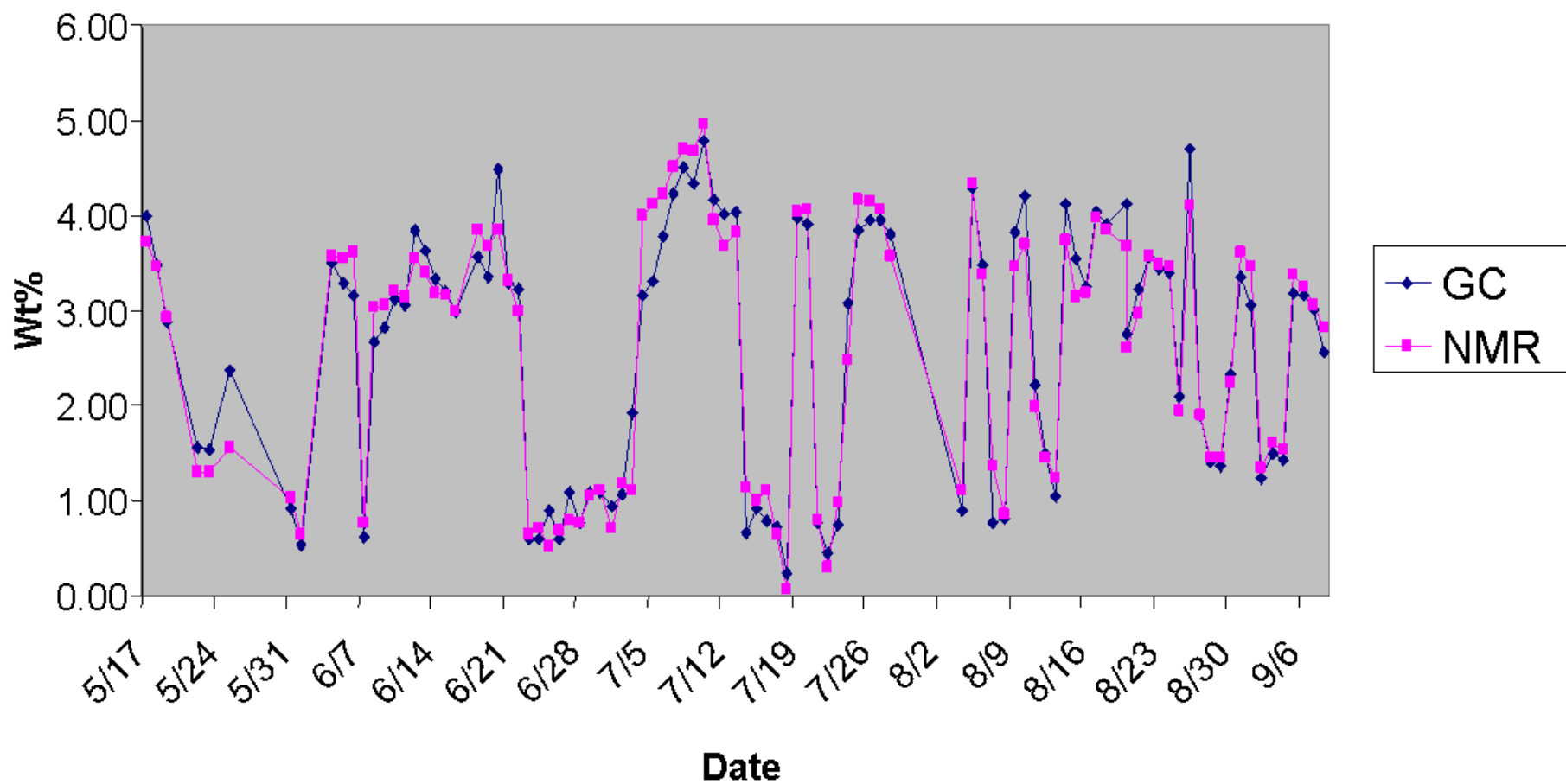
Toluene

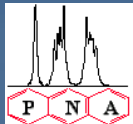




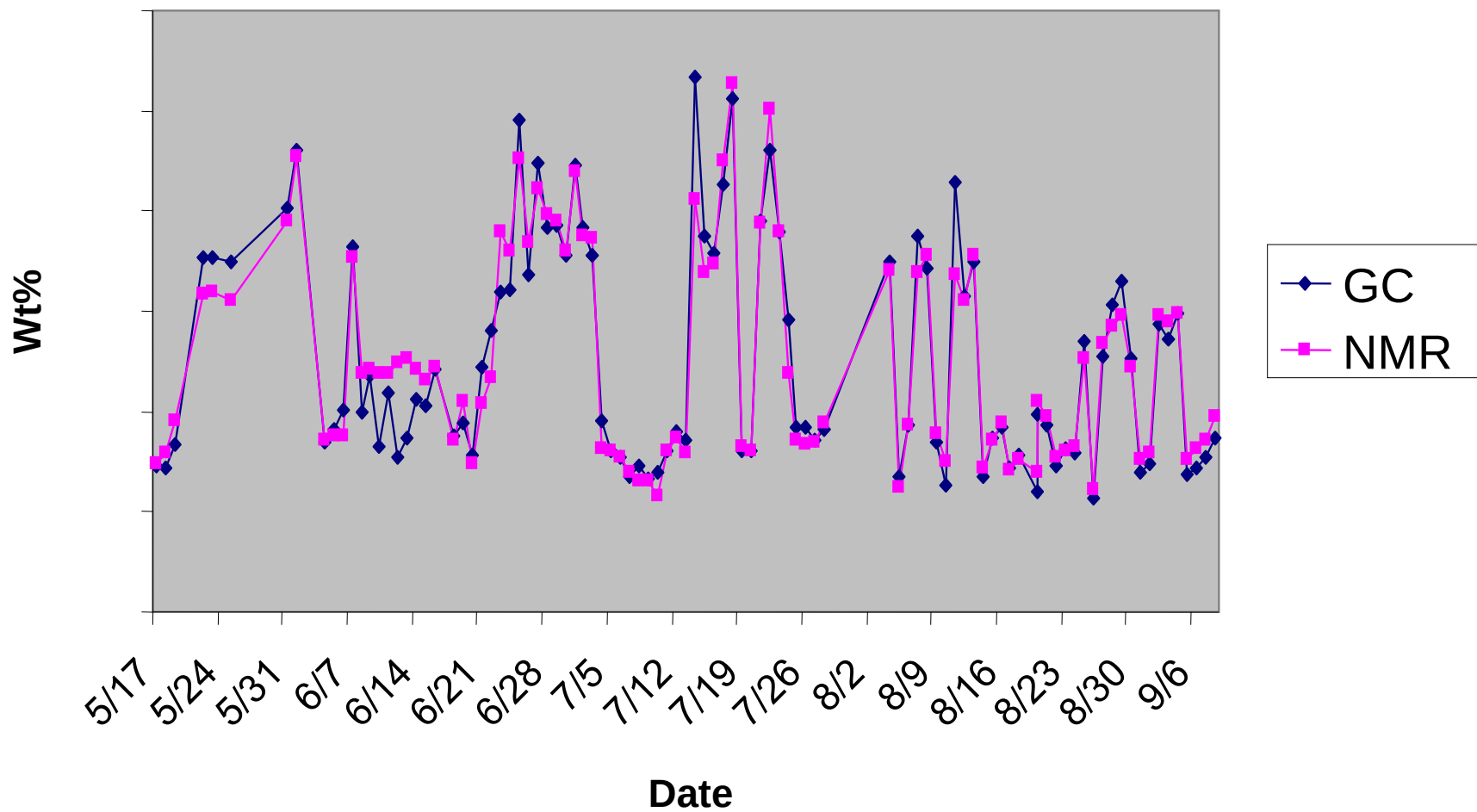


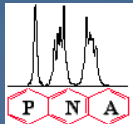
Normal-C8 Paraffin





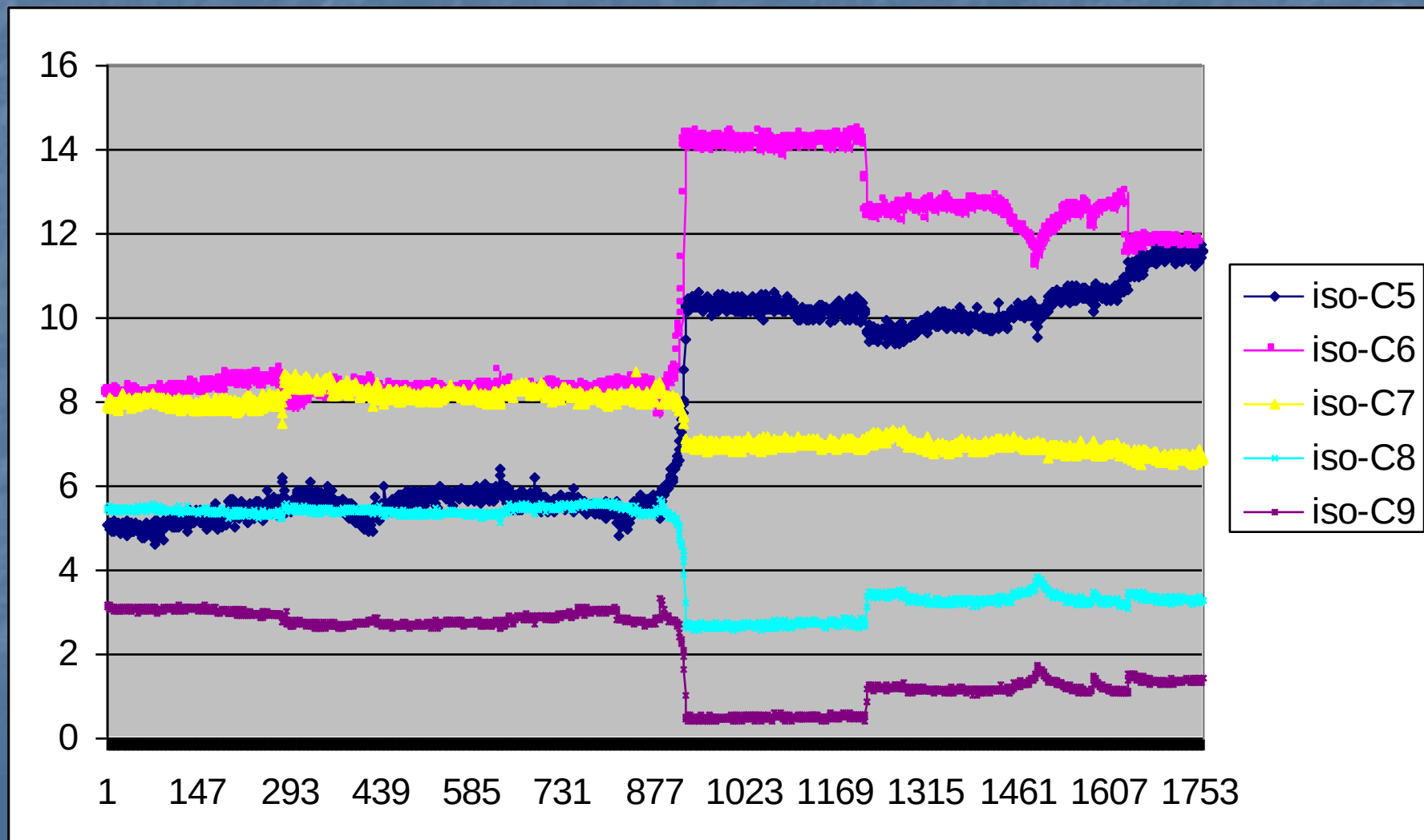
Cyclopentane

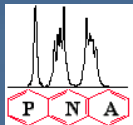




PROCESS NMR ASSOCIATES

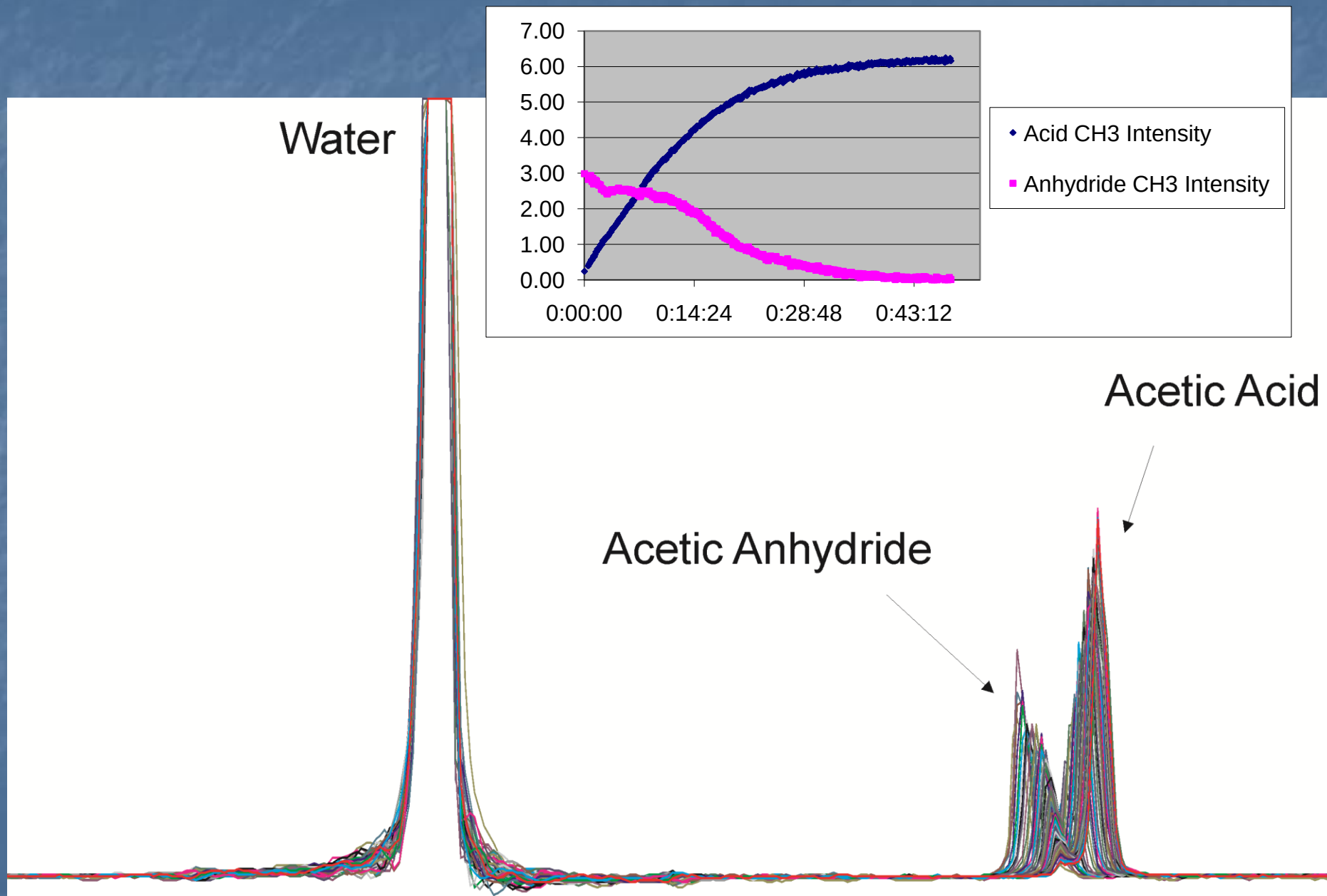
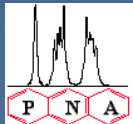
96 Hours of NMR Process Output – iso-Paraffin Components

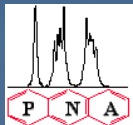




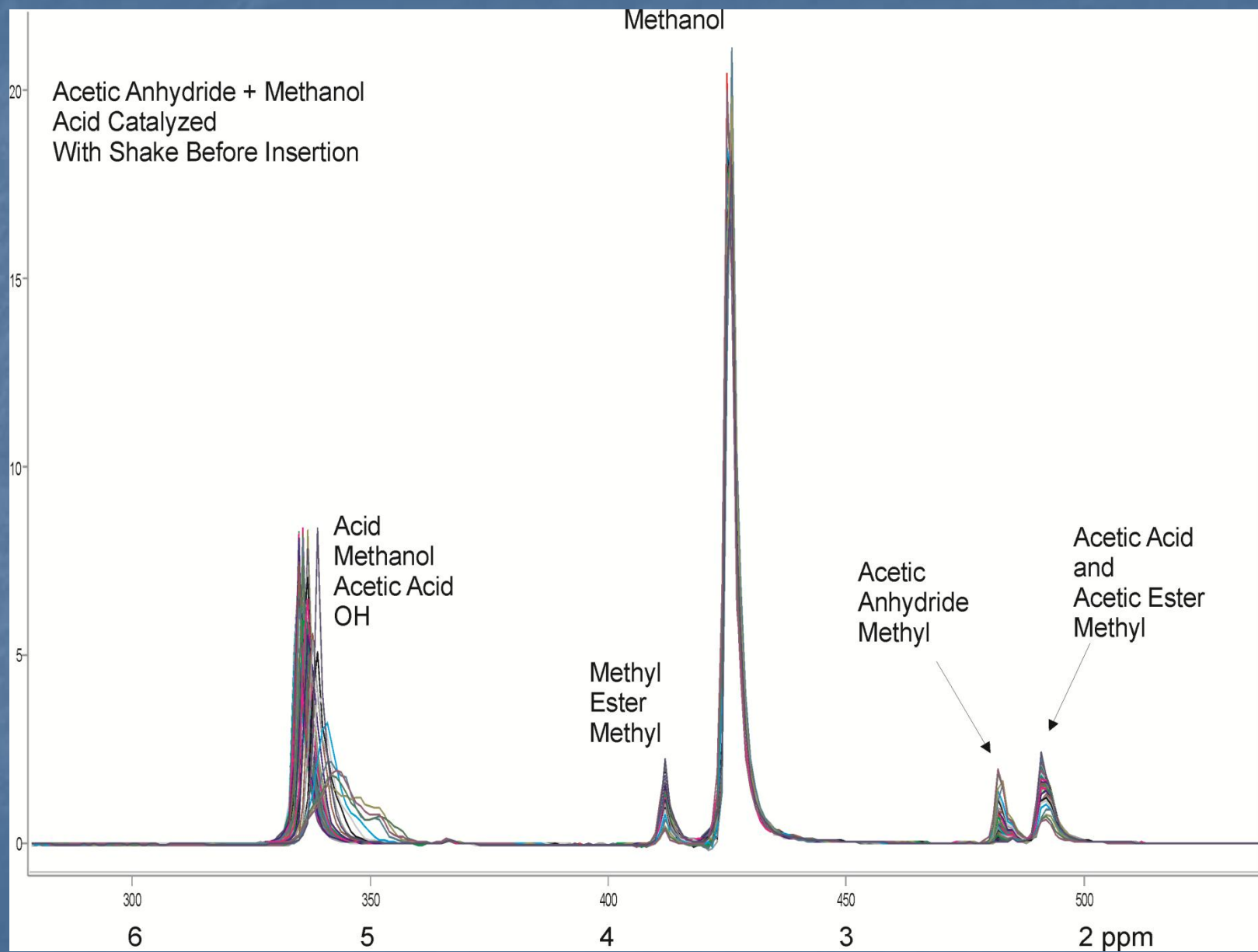
Online NMR Applications Timeline

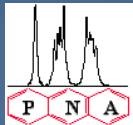
- 1993 - Development of Laboratory Based process NMR Methodologies
- 1995 - BTU Analysis of Refinery Fuel Gas
- 1995 - Sulfuric Acid Strength in Emulsion Zone of Stratco Acid Alkylation Unit
- 1999 - Diesel Blending System
- 1999 - Reformer Control System
- 2000 - Naphtha Cracker Feed Analyzer – Full GC PIONA
- 2000 - Crude Unit Analyzer
- 2000 - Crude Blending System
- 2001 - Gasoline Blending System,
- 2001 - Base Oil Manufacturing Analyzer
- 2002 - FCC Unit Analyzer



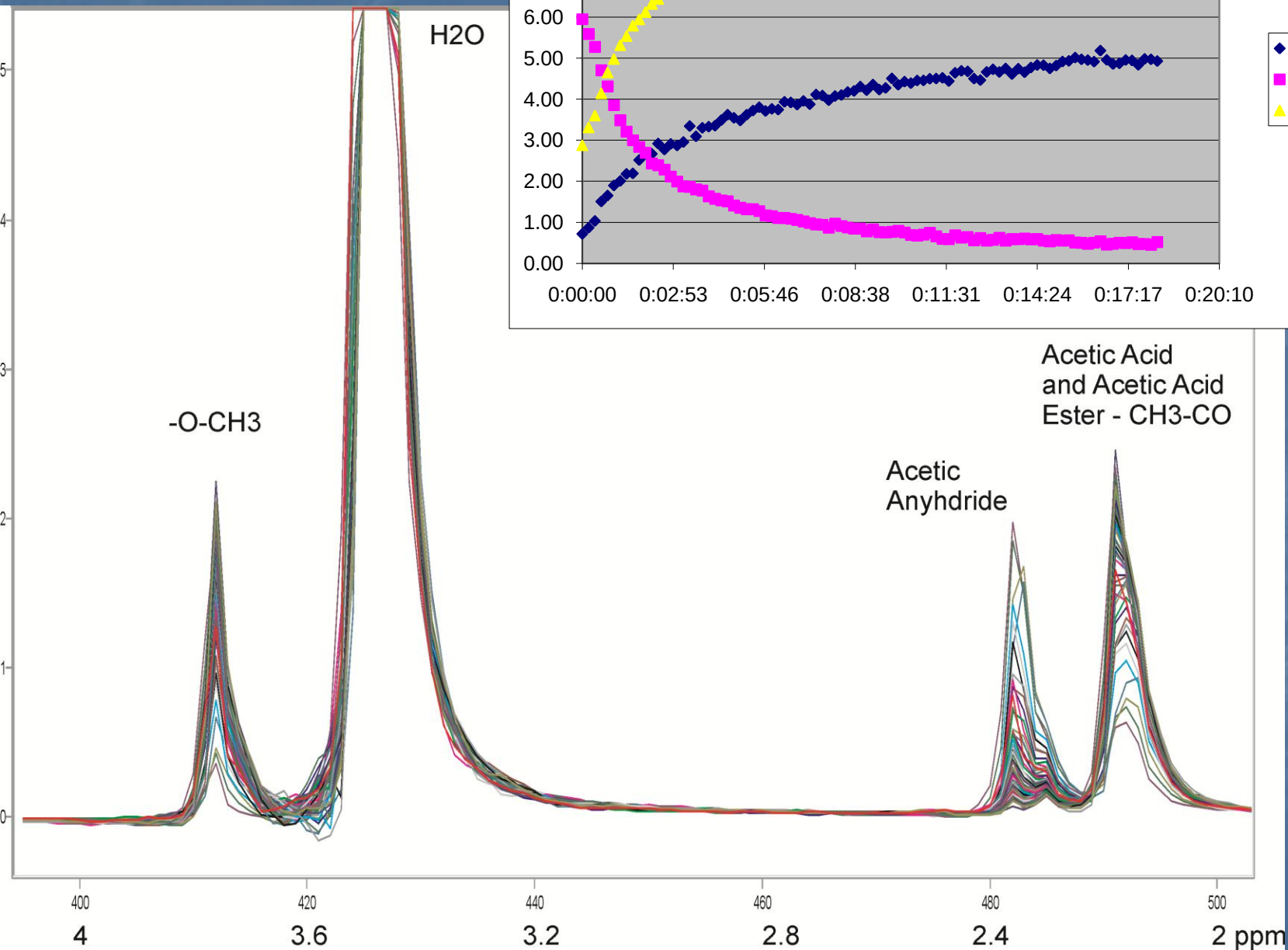


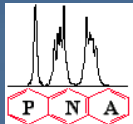
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PROCESS NMR ASSO

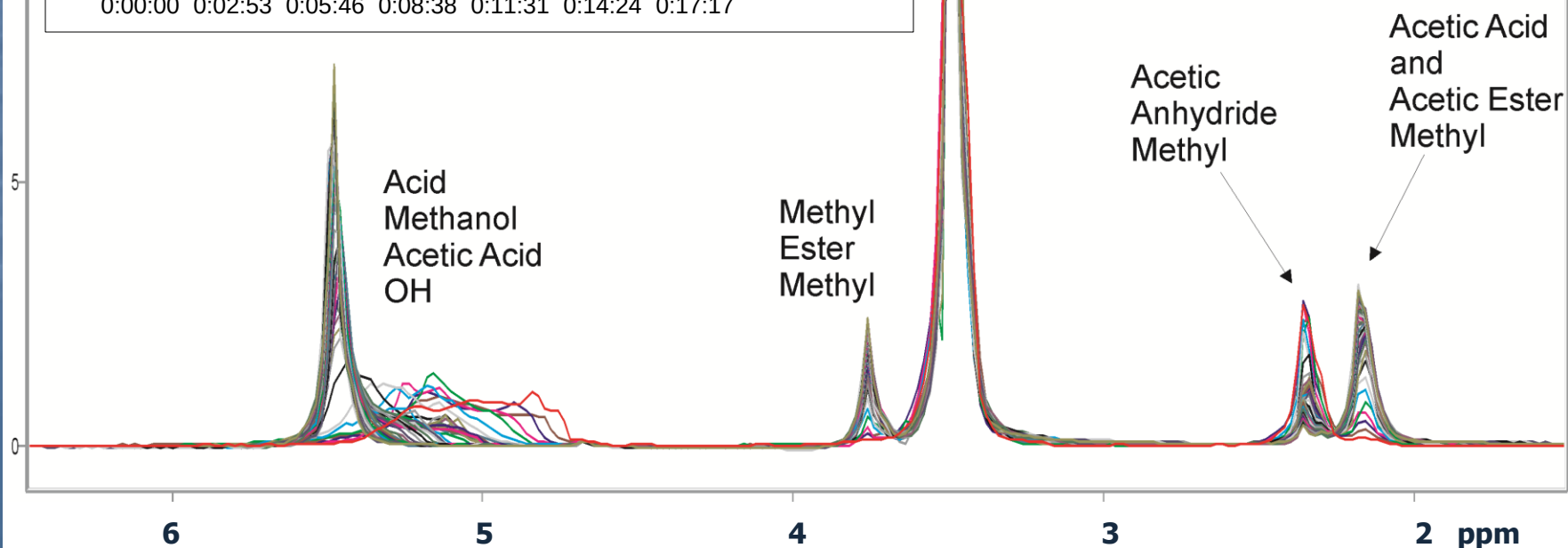
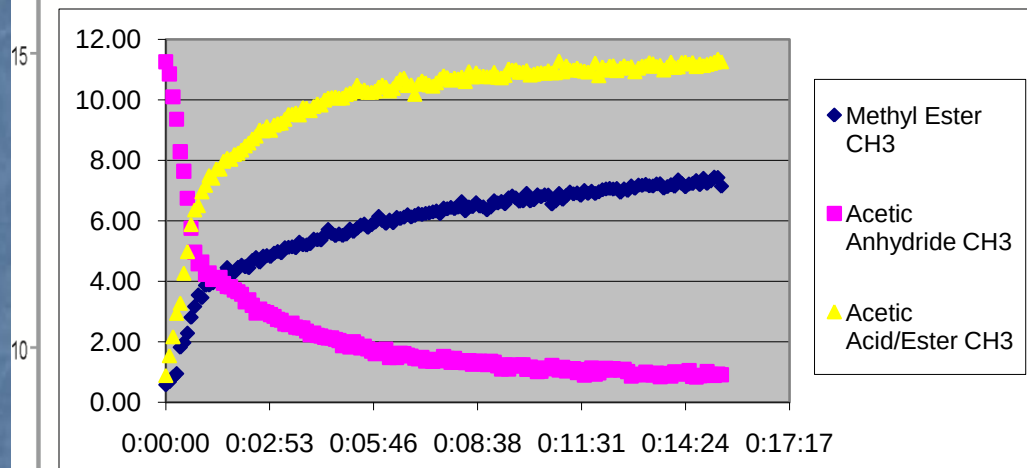


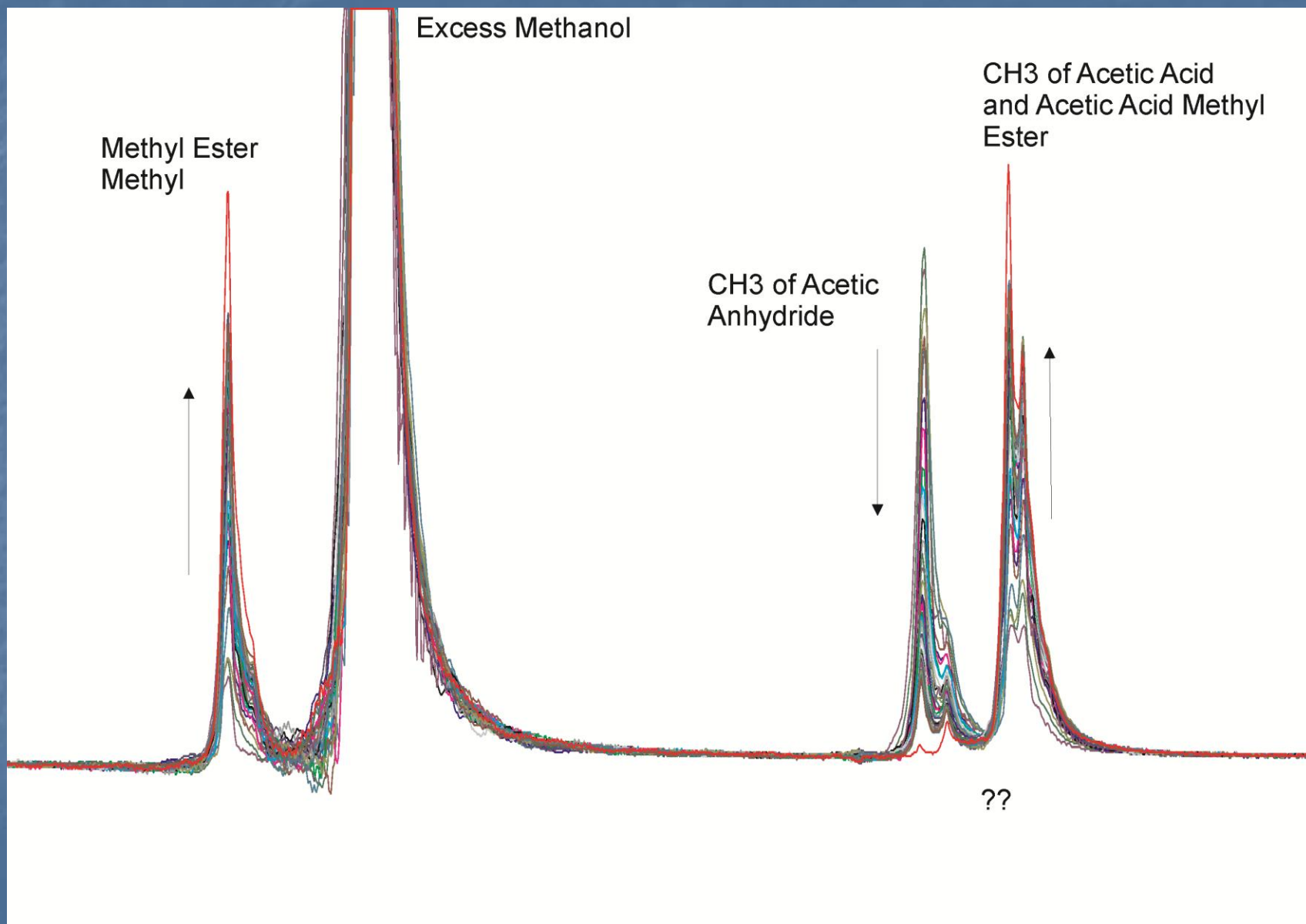
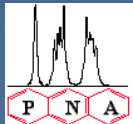


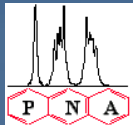
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Acetic Anhydride + Methanol
Acid Catalyzed
No Shaking

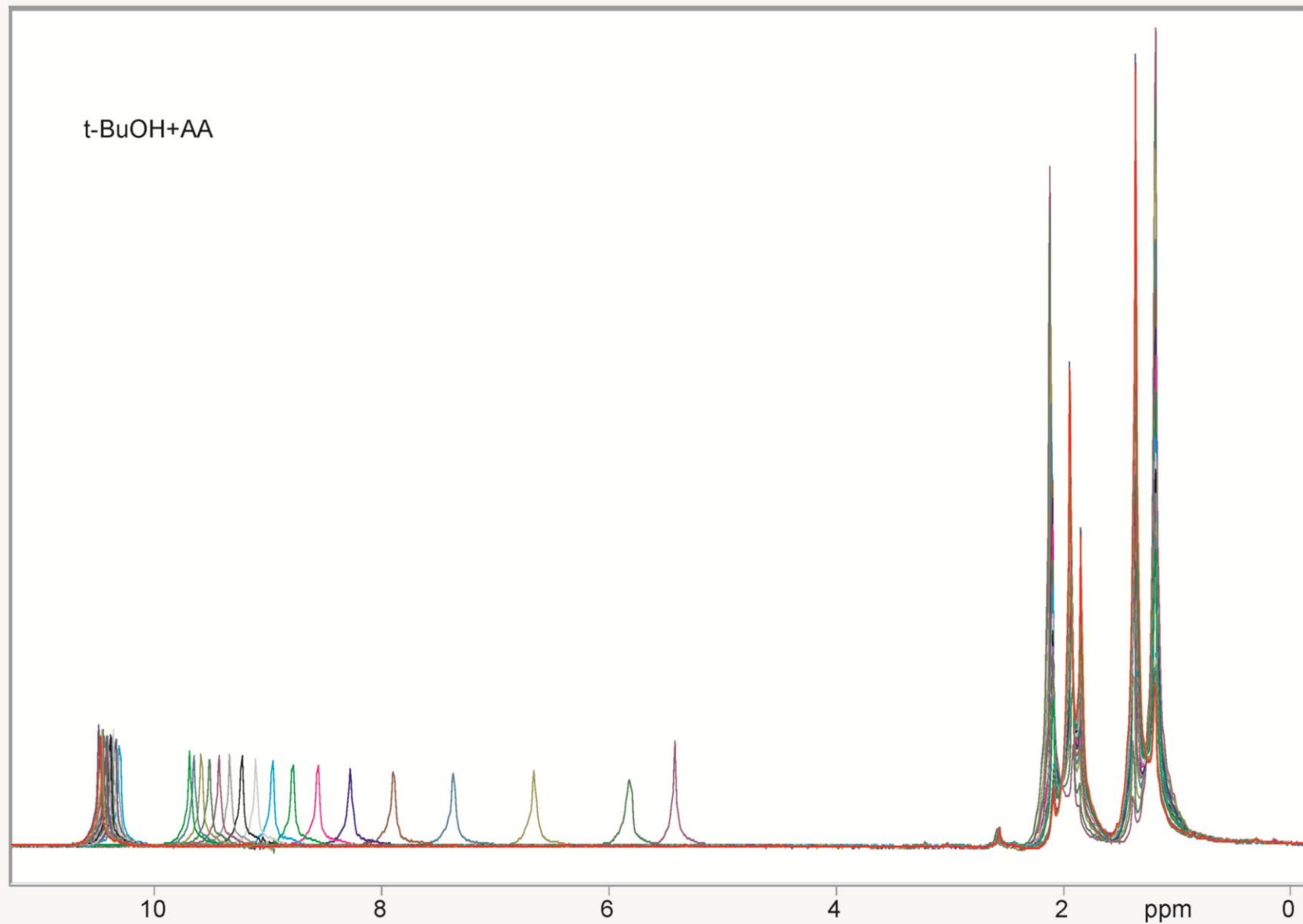
Methanol



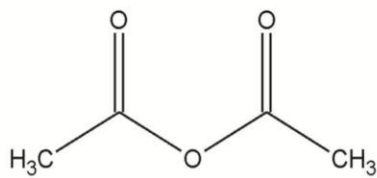




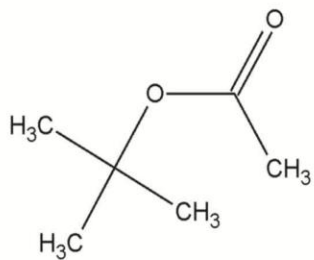
t-BuOH+AA



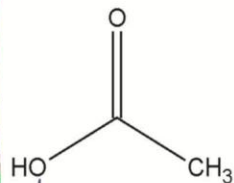
t-BuOH + AA



AA



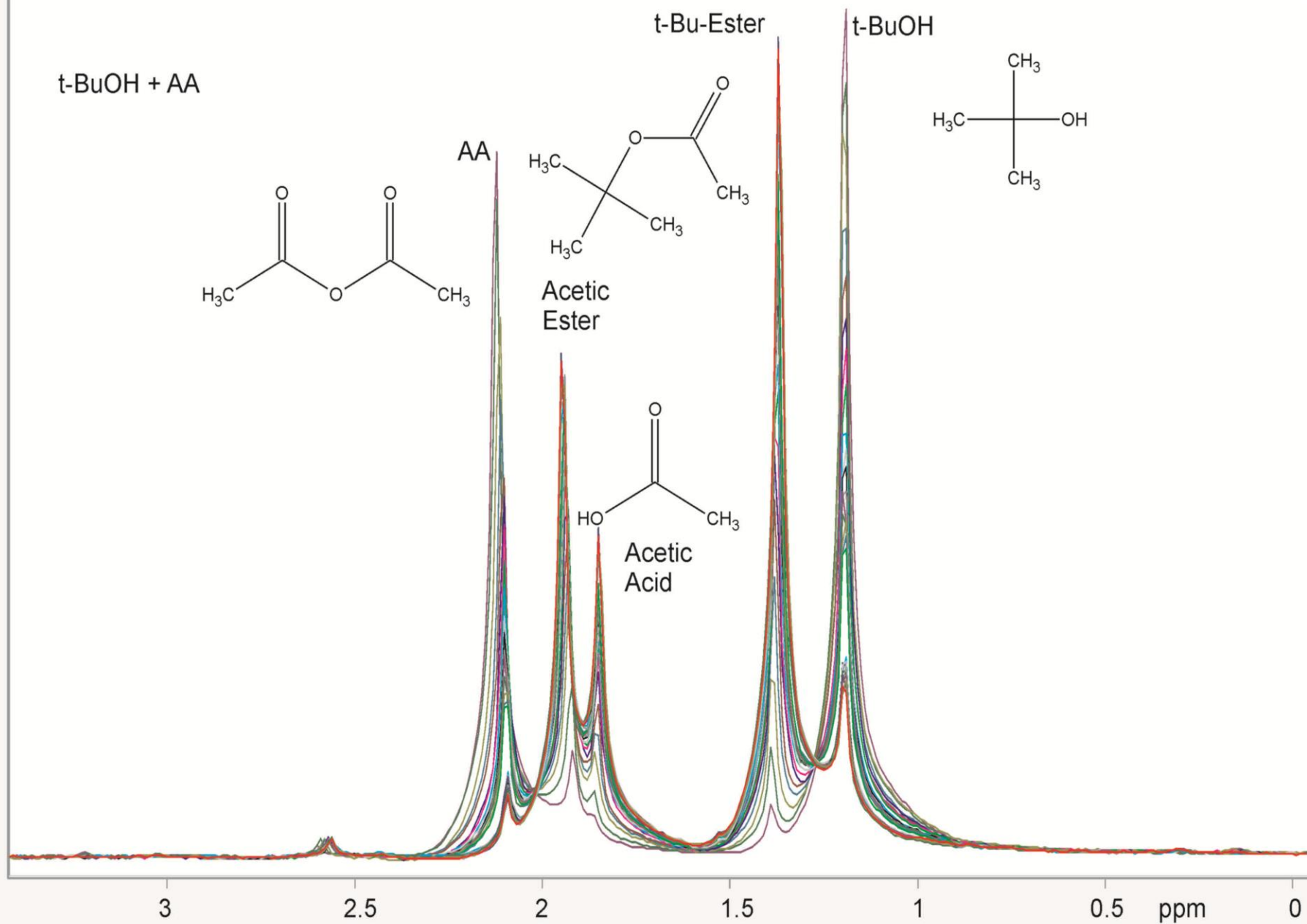
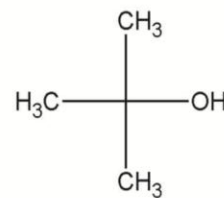
Acetic Ester



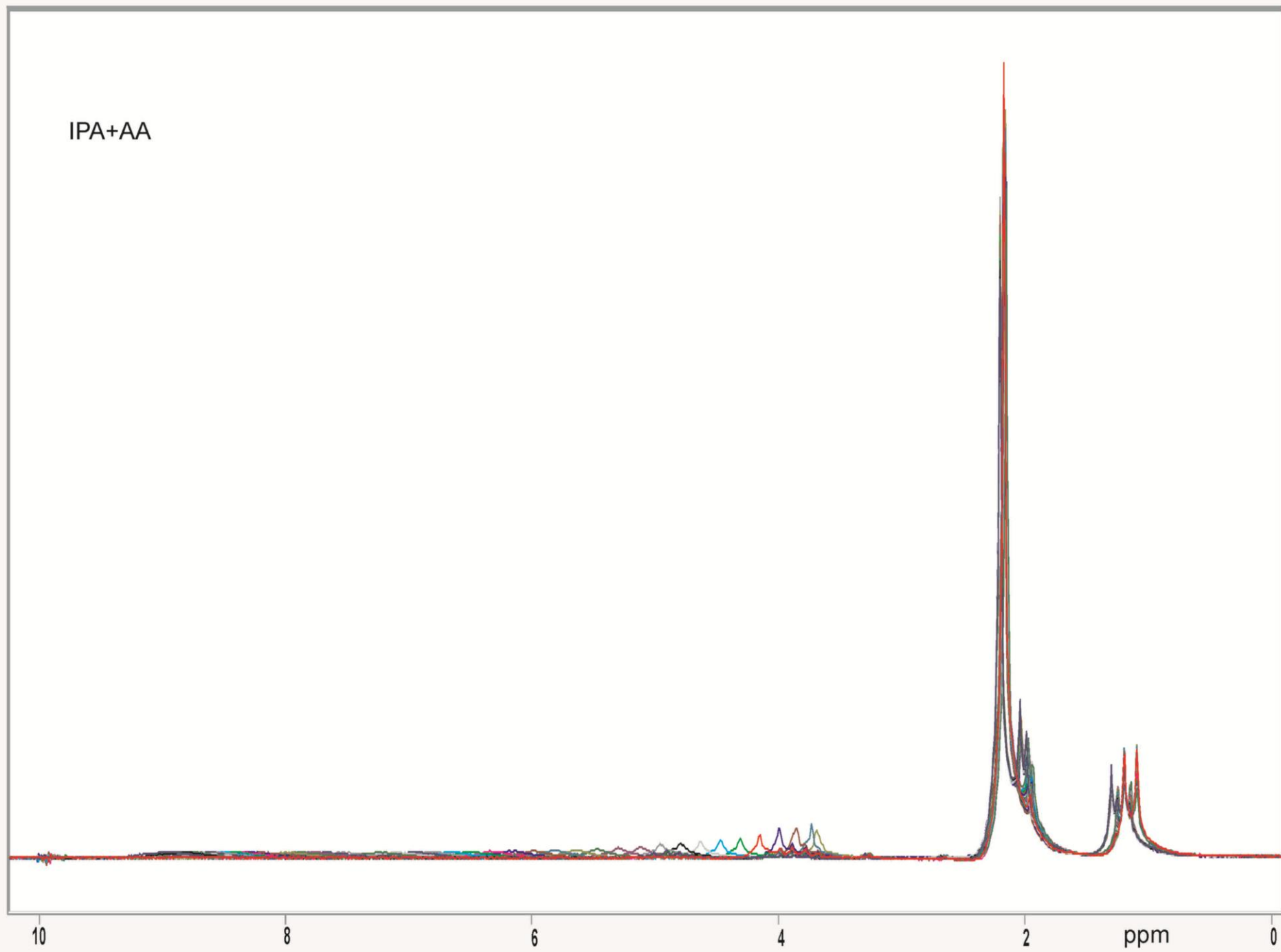
Acetic Acid

t-Bu-Ester

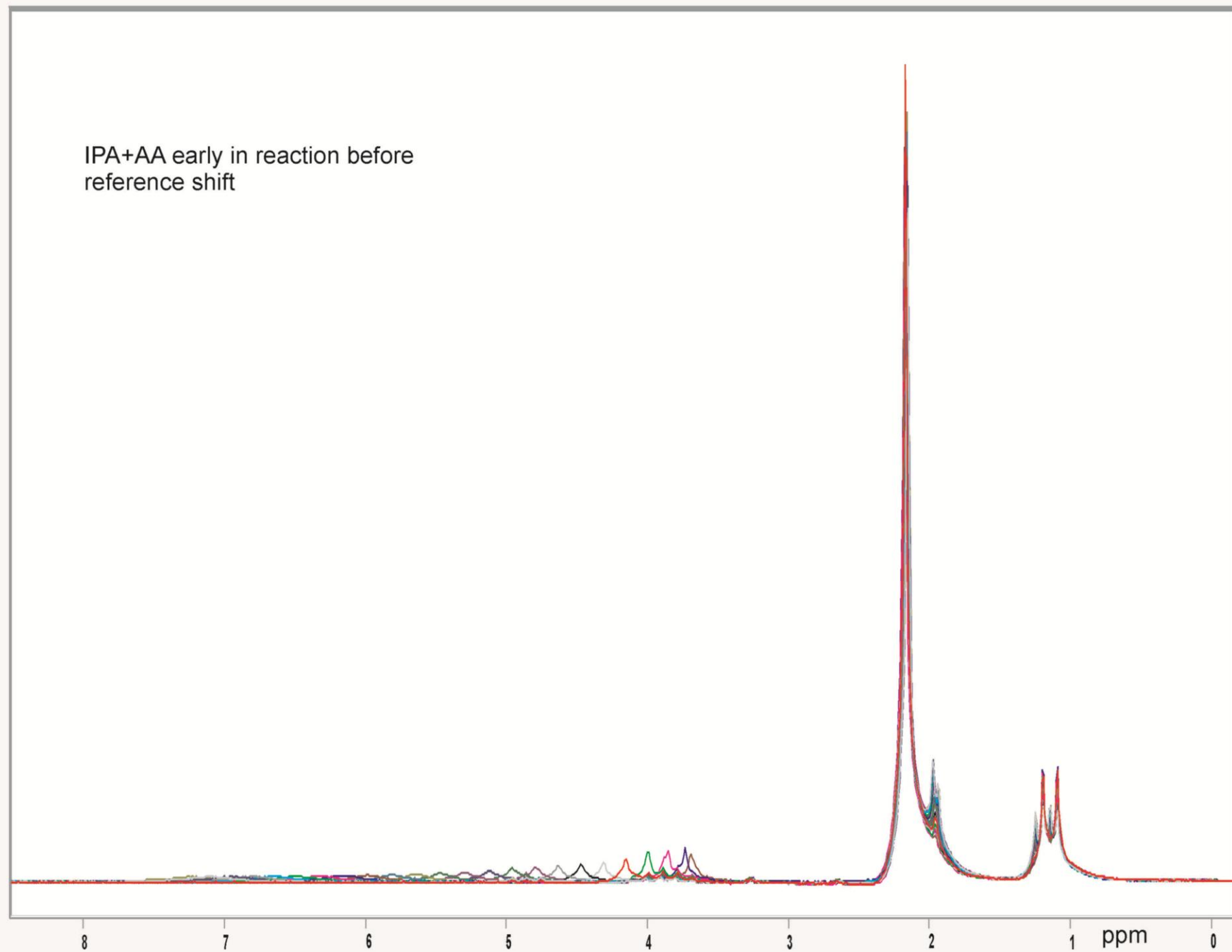
t-BuOH

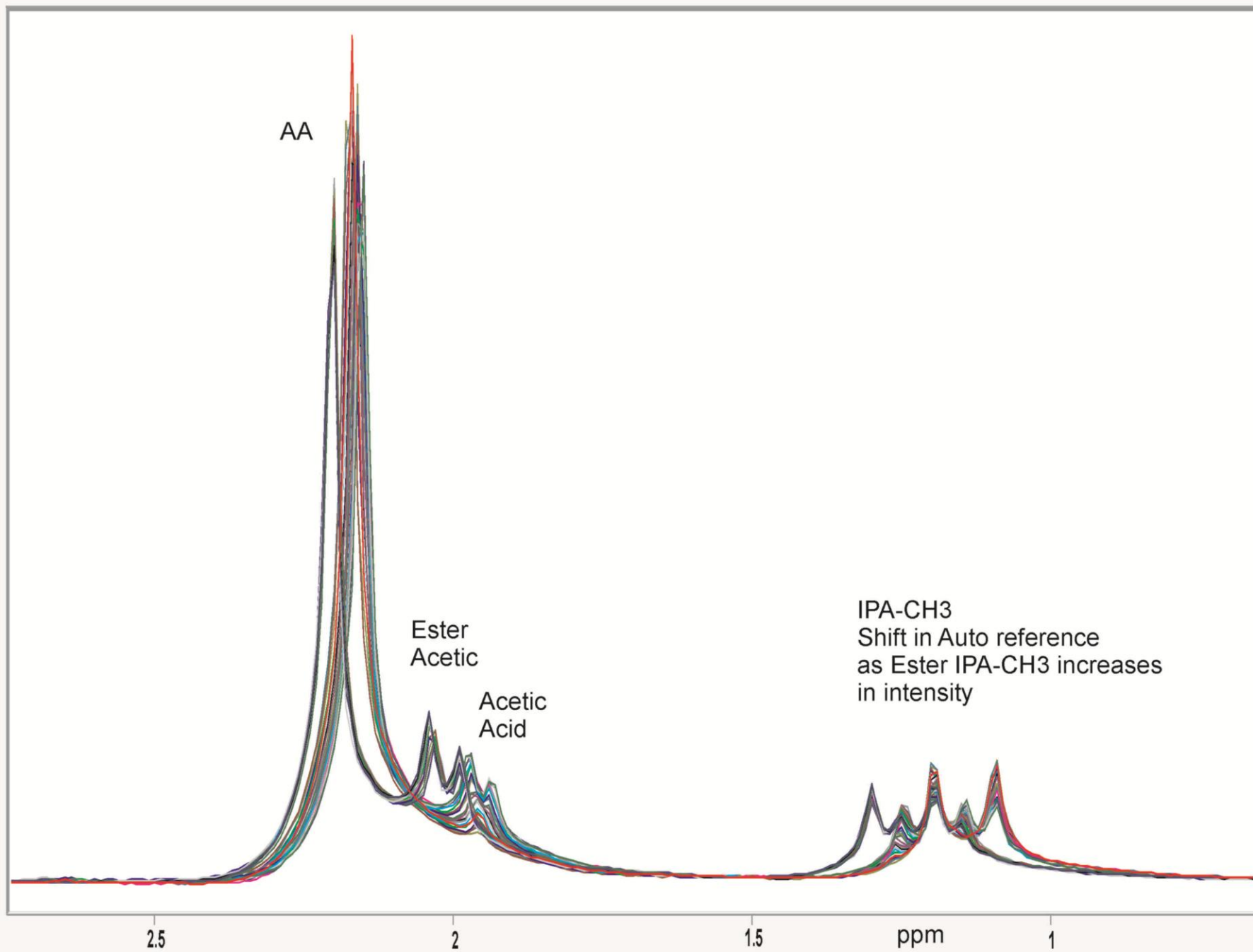


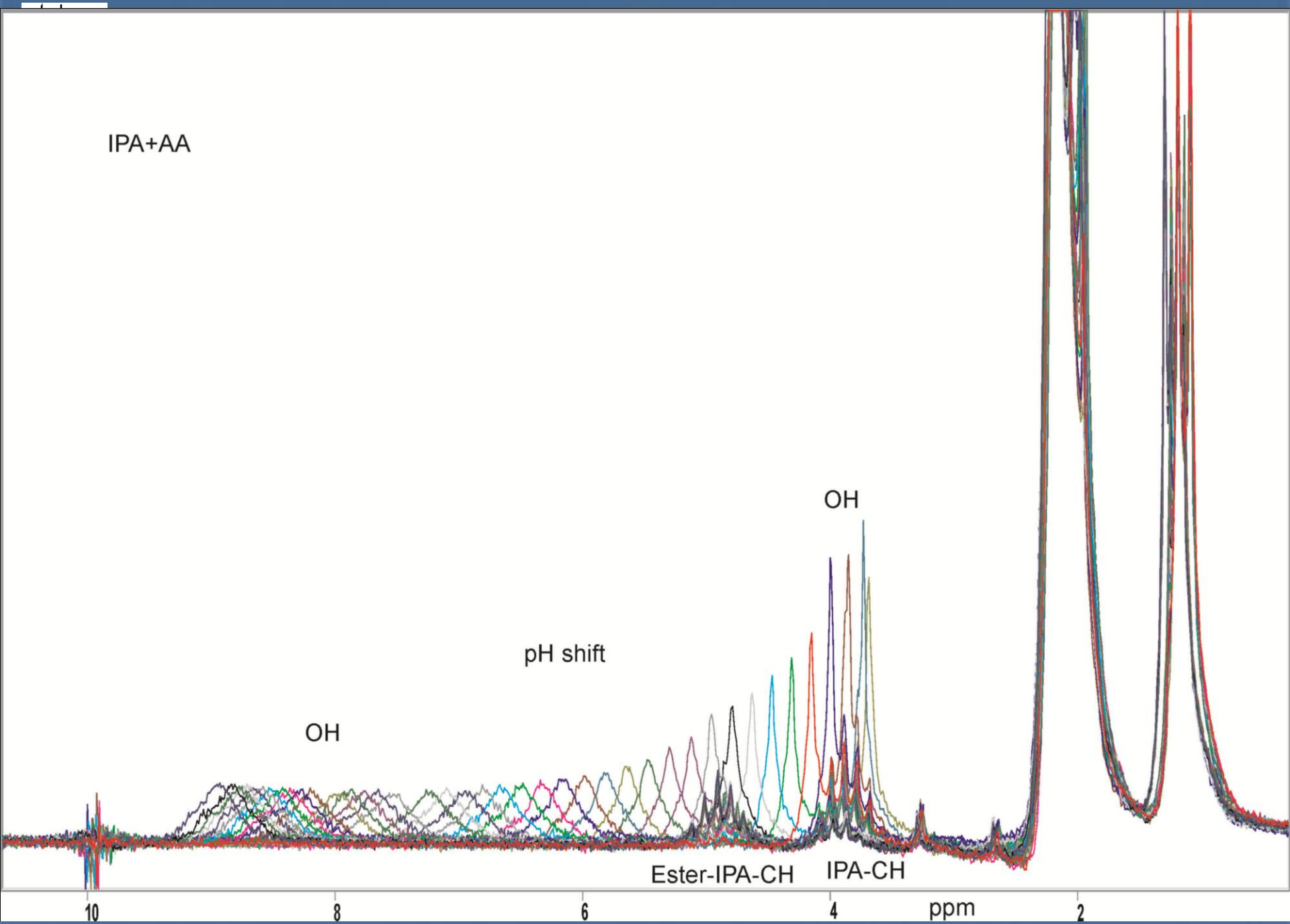
IPA+AA

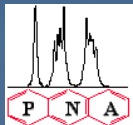


IPA+AA early in reaction before
reference shift





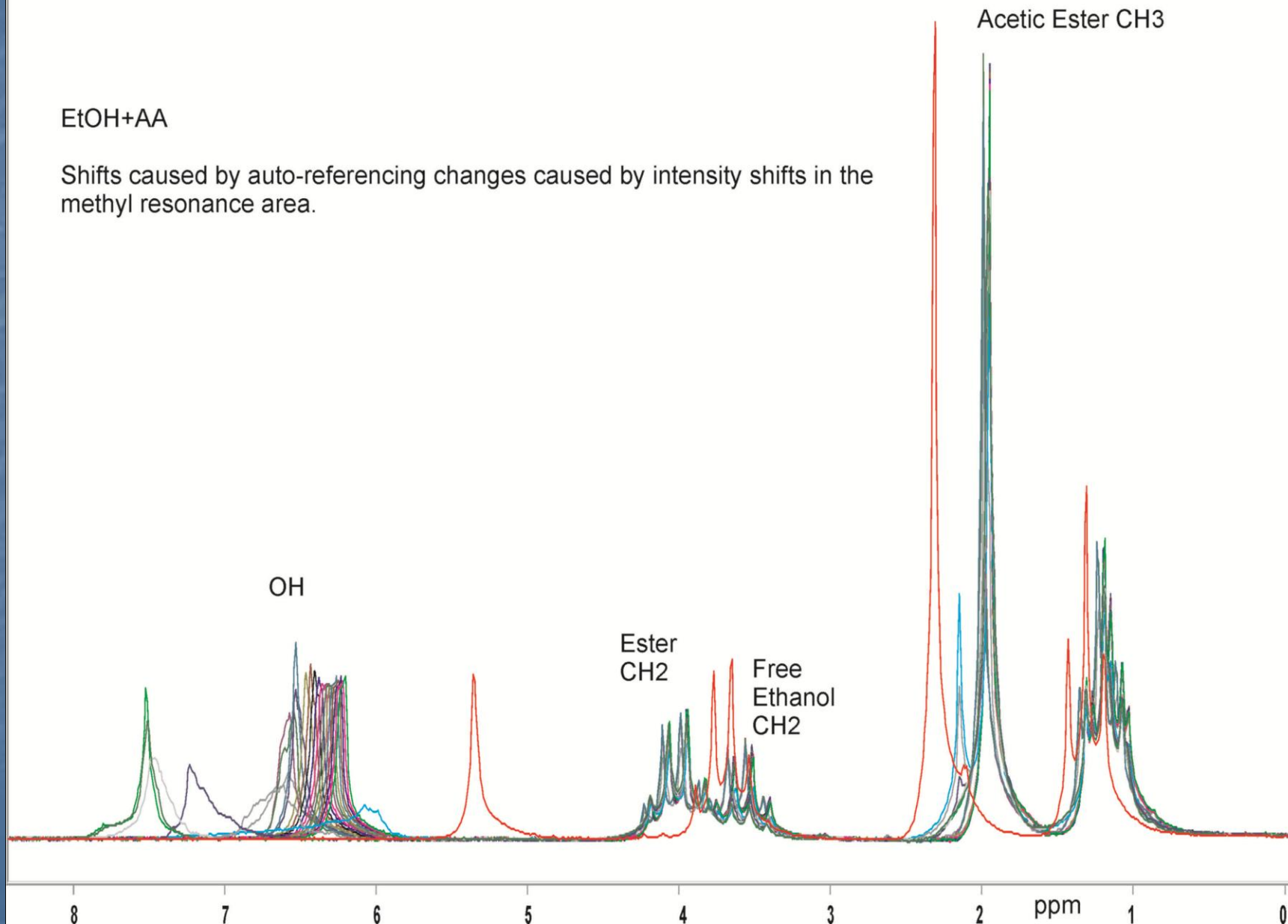


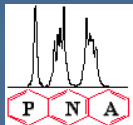


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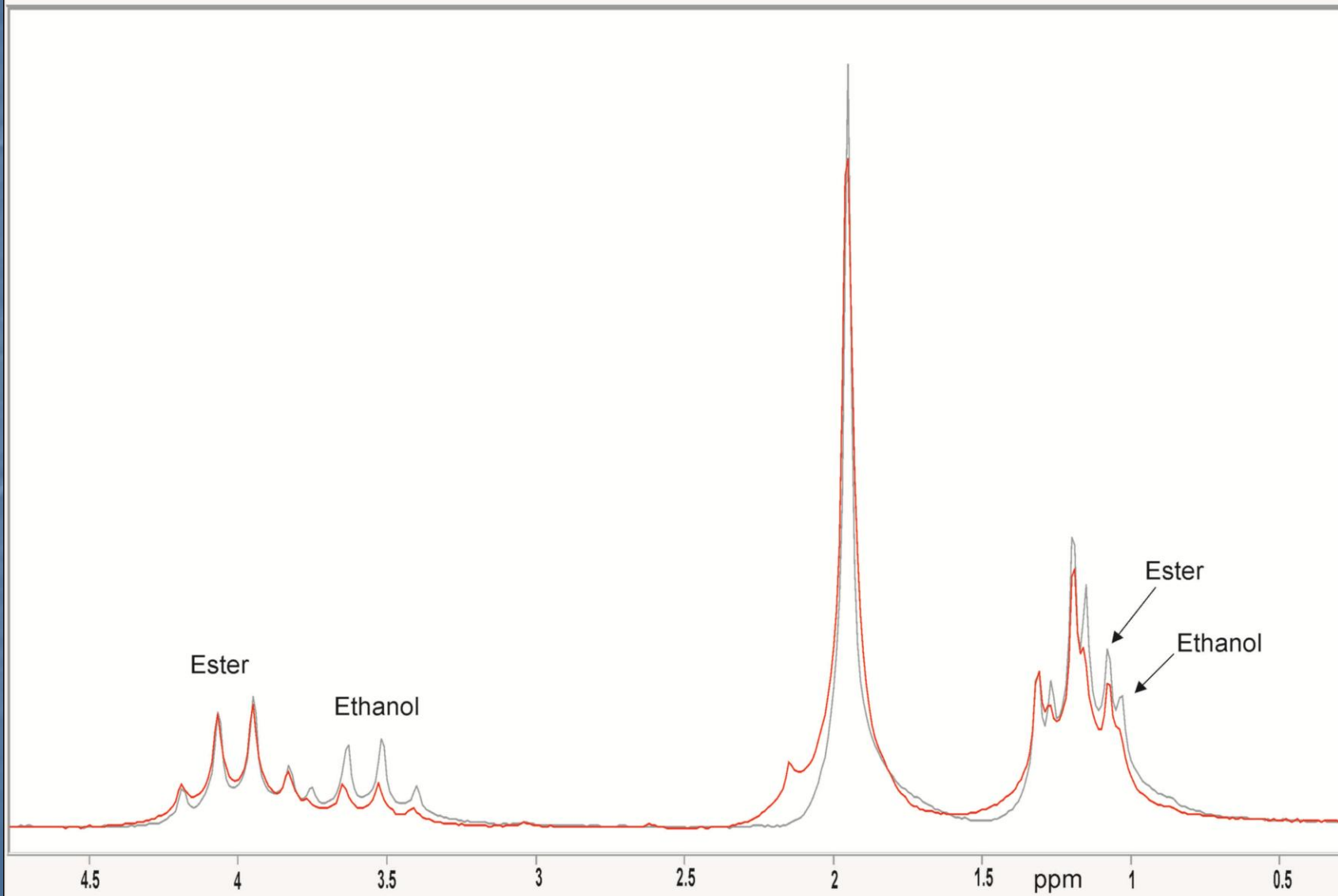
EtOH+AA

Shifts caused by auto-referencing changes caused by intensity shifts in the methyl resonance area.

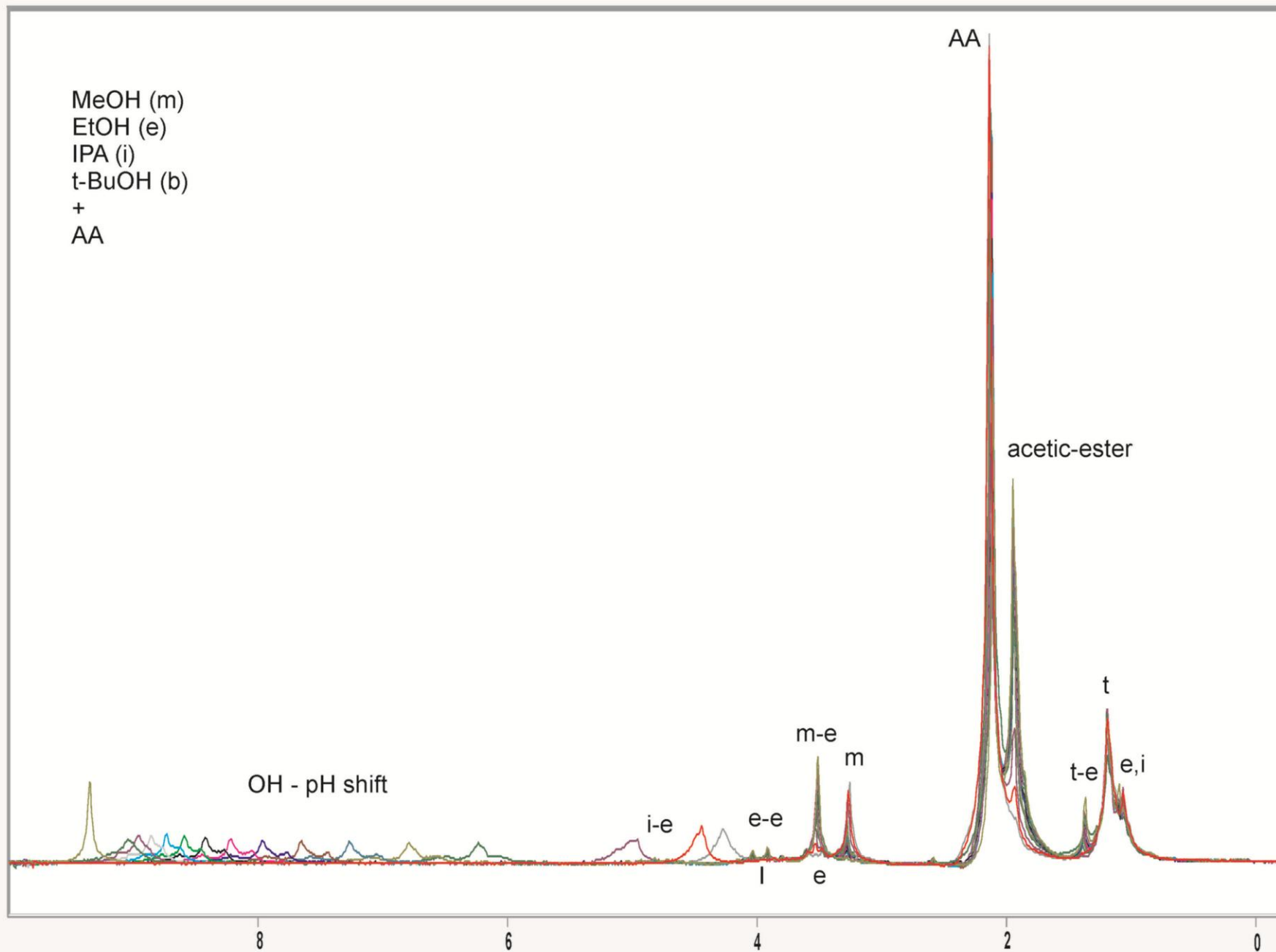




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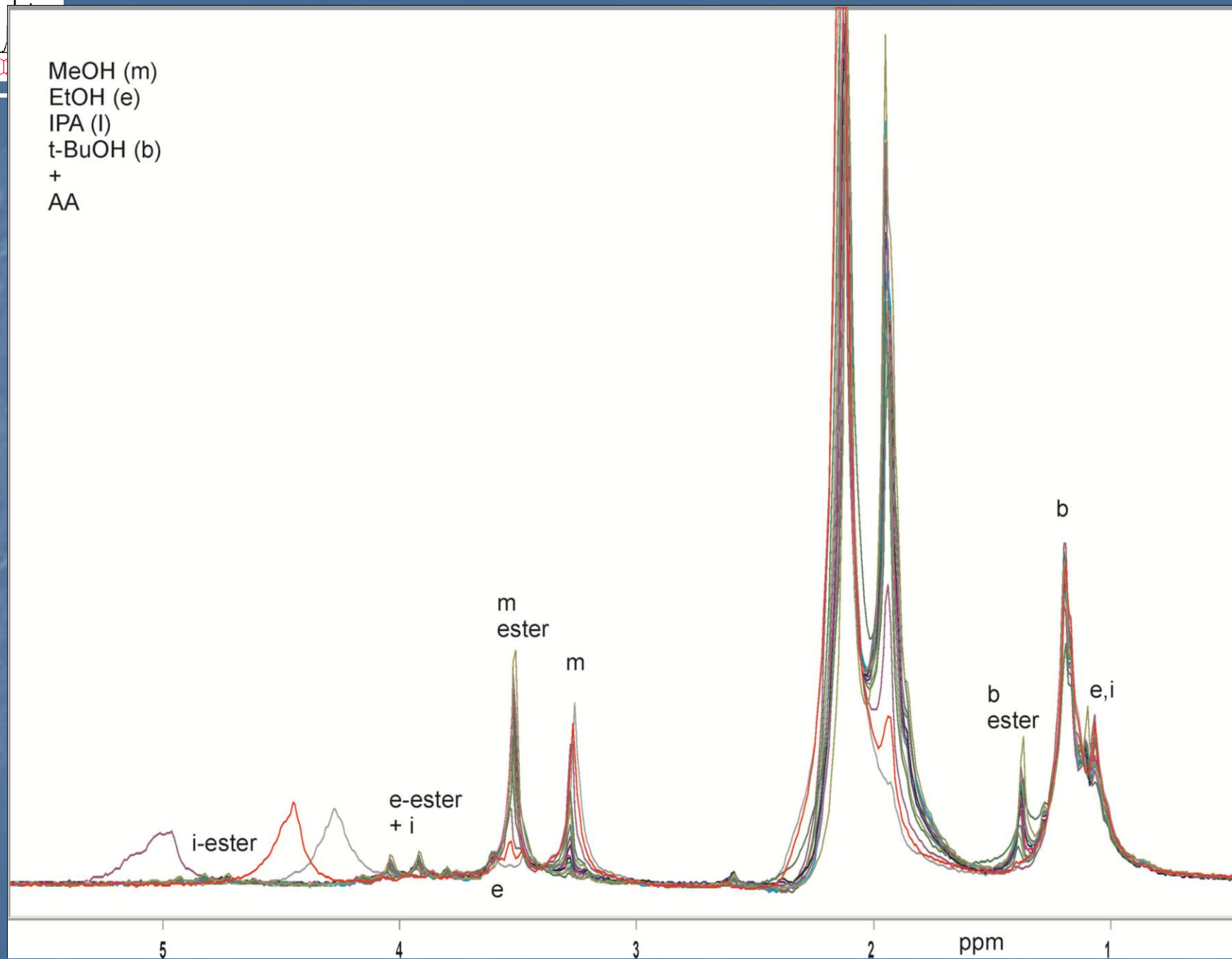


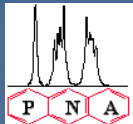
MeOH (m)
EtOH (e)
IPA (i)
t-BuOH (b)
+
AA



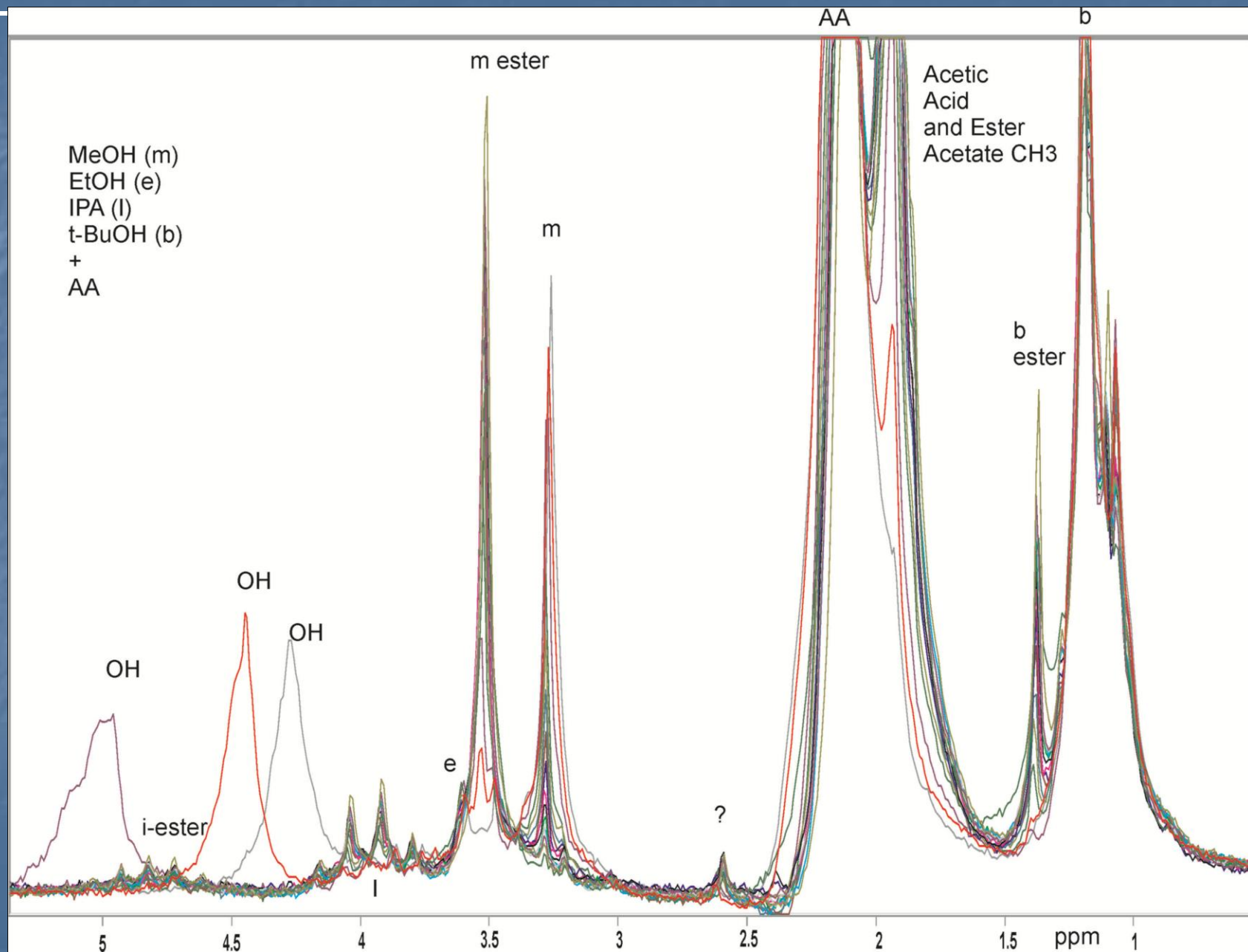


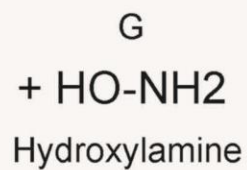
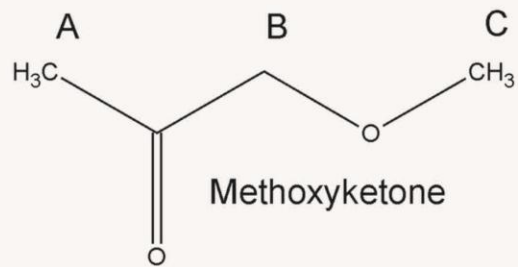
MeOH (m)
EtOH (e)
IPA (l)
t-BuOH (b)
+
AA



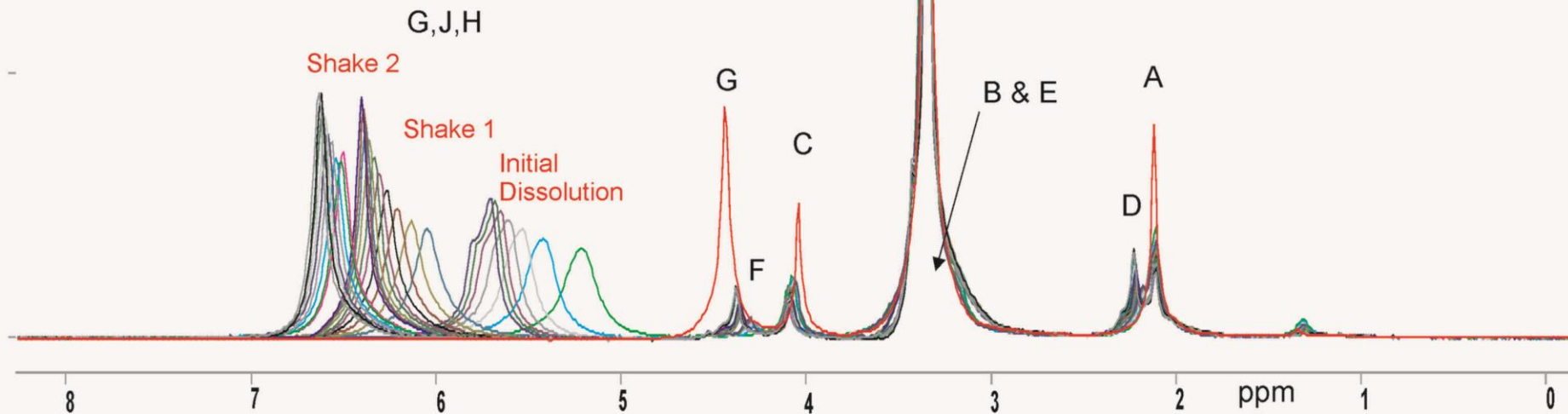
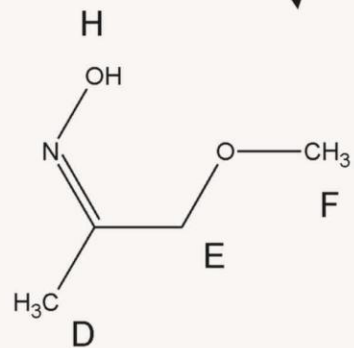


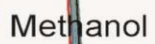
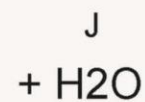
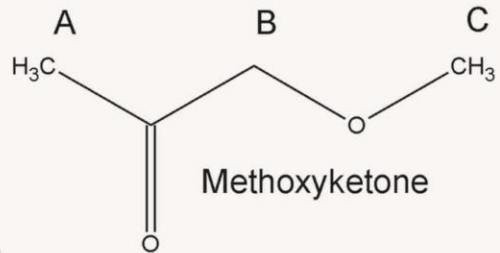
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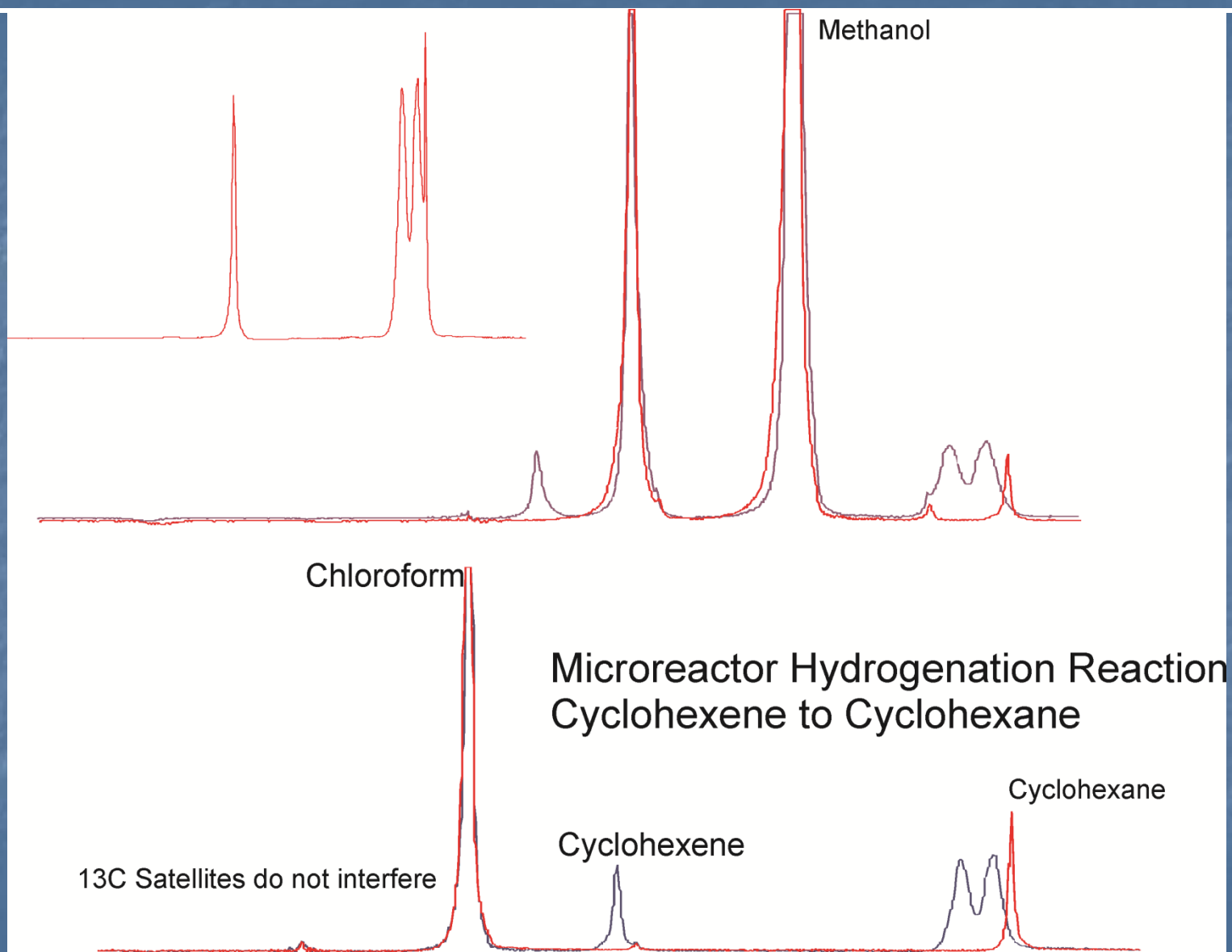
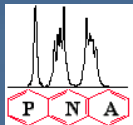


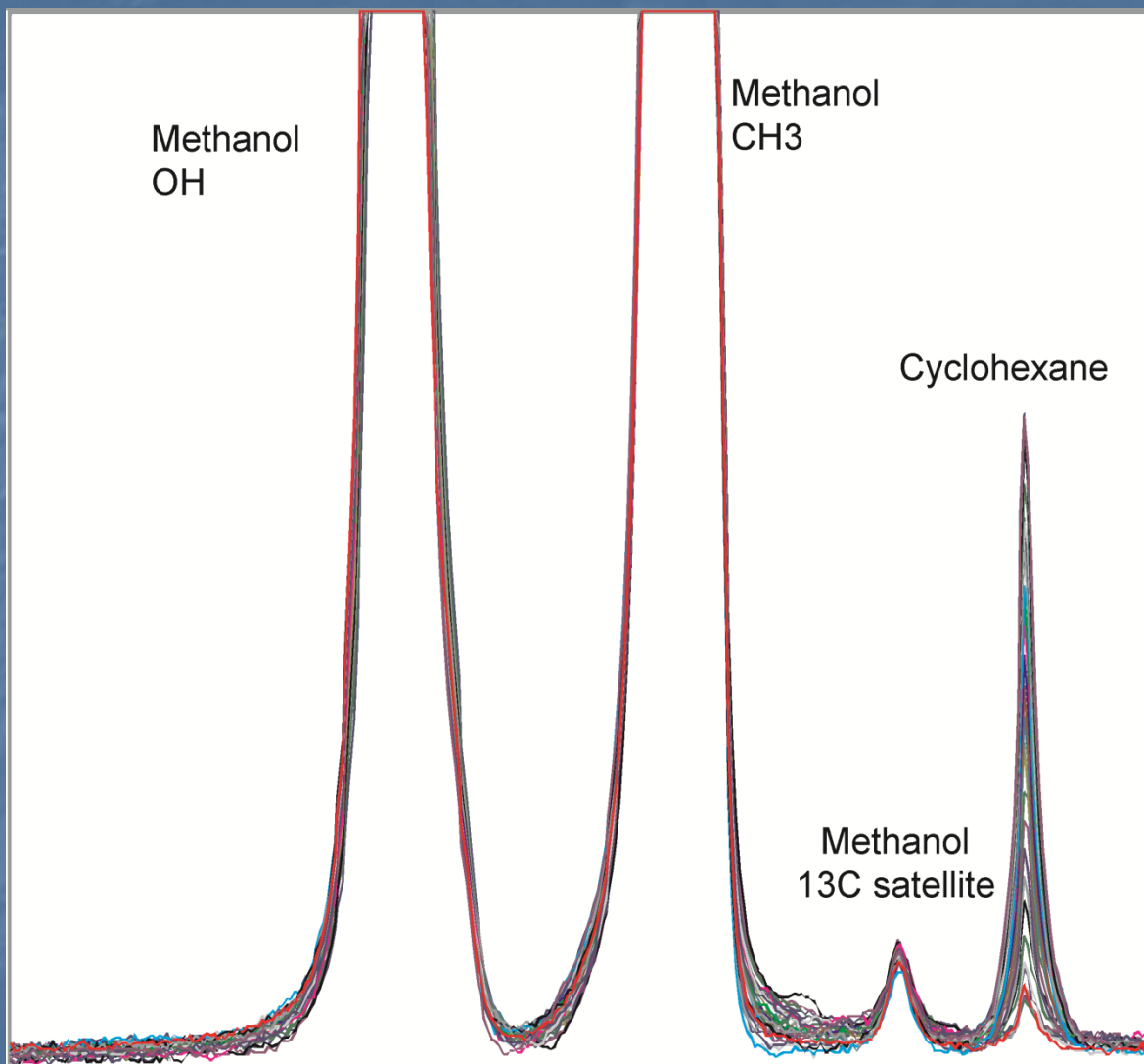
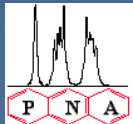
Methanol





B & E





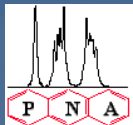
Continuous Flow (10 ml/min).

Starting Cyclohexane concentration 0.08 gm/18 ml MeOH.

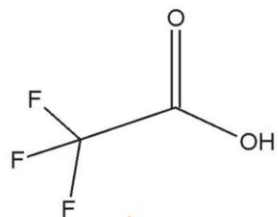
Final Cyclohexane concentration 0.4 gm in 18 ml MeOH.

Cyclohexane was added in 0.01 gm increments every 12 seconds with no mixing.

Total run time: 9 minutes.

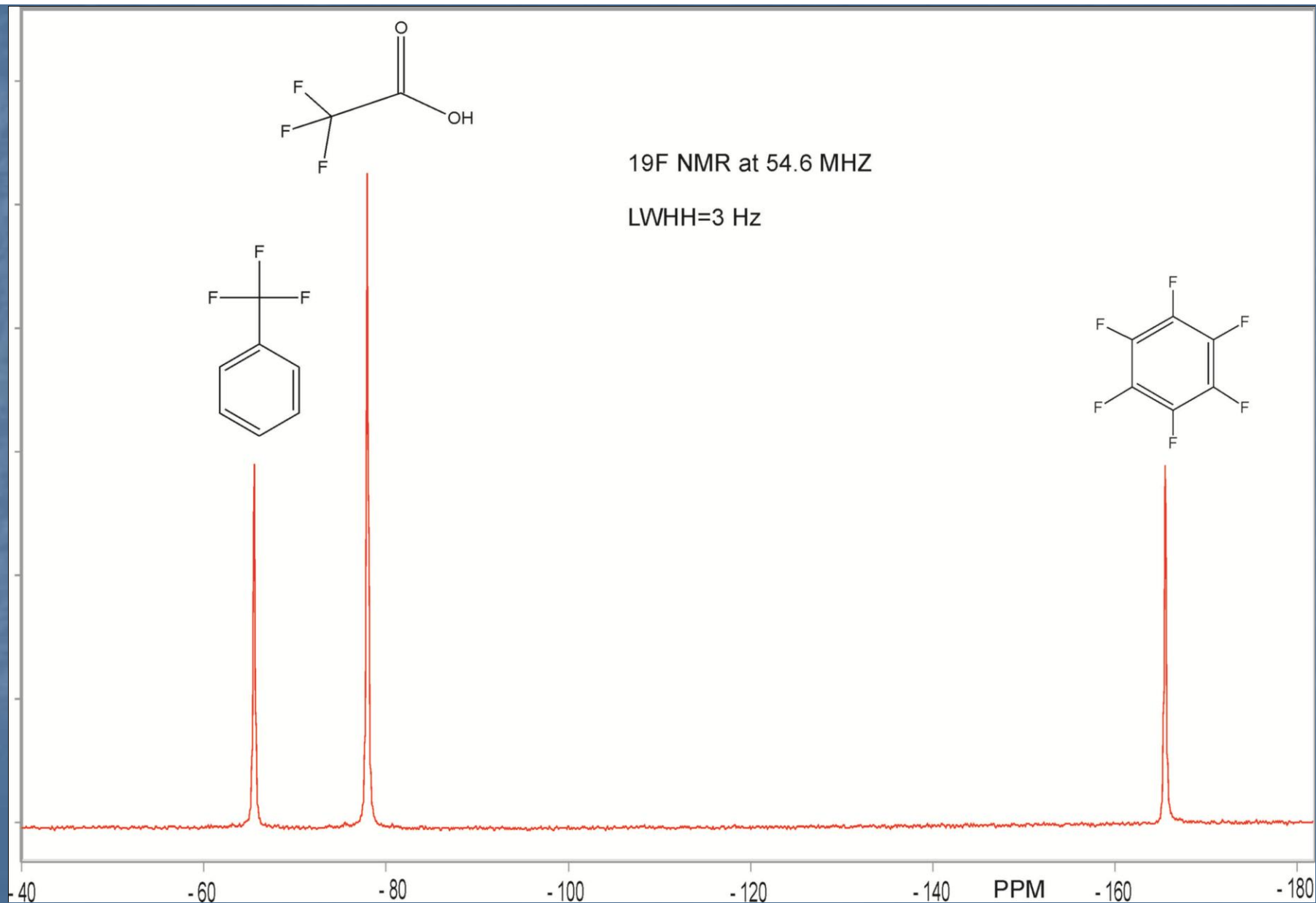
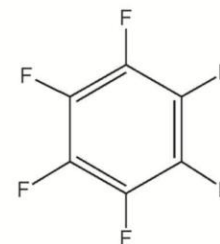
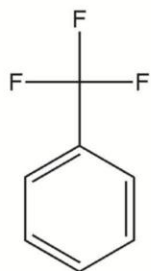


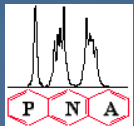
PROCESS NMR ASSOCIATES



^{19}F NMR at 54.6 MHz

LWHH=3 Hz





PROCESS NMR ASSOCIATES

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