NMR of X-nuclei

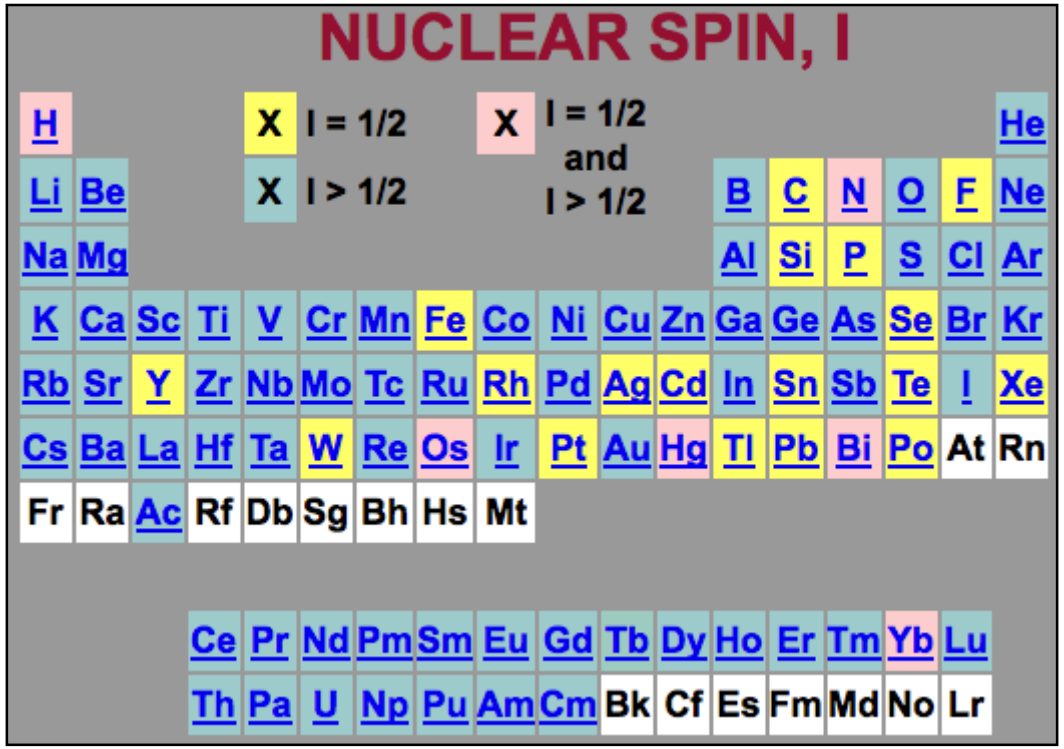
Daniel De Rosa

2017 Postgraduate Course in Liquid State NMR Spectroscopy

6th December 2017

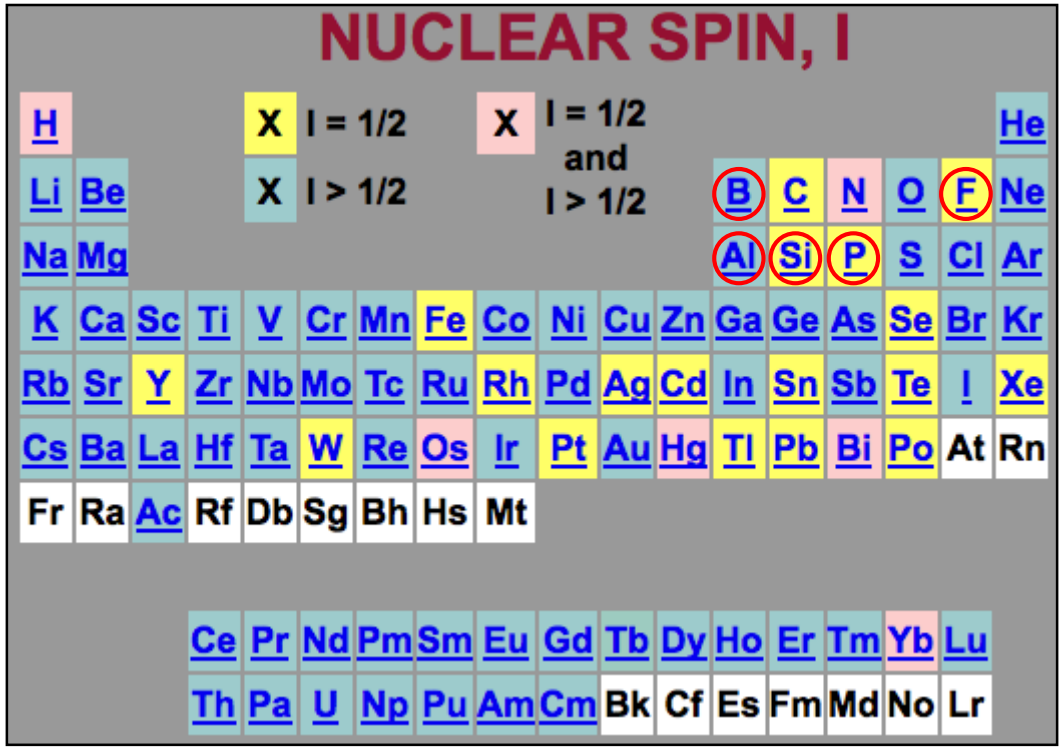
What X-nuclei can be used?

^{1}H and ^{13}C are the most commonly used NMR nuclei, however, any nucleus with a non zero spin is NMR active.



What X-nuclei can be used?

^{1}H and ^{13}C are the most commonly used NMR nuclei, however, any nucleus with a non zero spin is NMR active.



Properties of X-nuclei NMR

Advantages:

- Can directly observe nuclei of interest in your target compounds.
- Able to run NMR spectra in protonated solvent (lock and shim off).
  - Allows monitoring of reactions by aliquot.
- Makes analysing products with complicated ^{1}H and ^{13}C NMR easier.
- Can run ^{1}H coupled and ^{1}H decoupled spectra.

Properties of X-nuclei NMR

Disadvantages:

- May require large amounts of sample due to:
  - Low isotopic abundances.
  - Low sensitivity.
  - Quadrupolar effects.

- Acquiring quantitative spectra might require long experiment times due to slow nuclear relaxation.

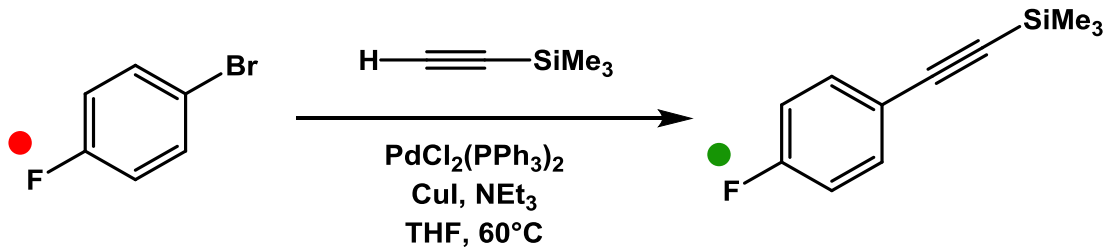
^{19}F NMR

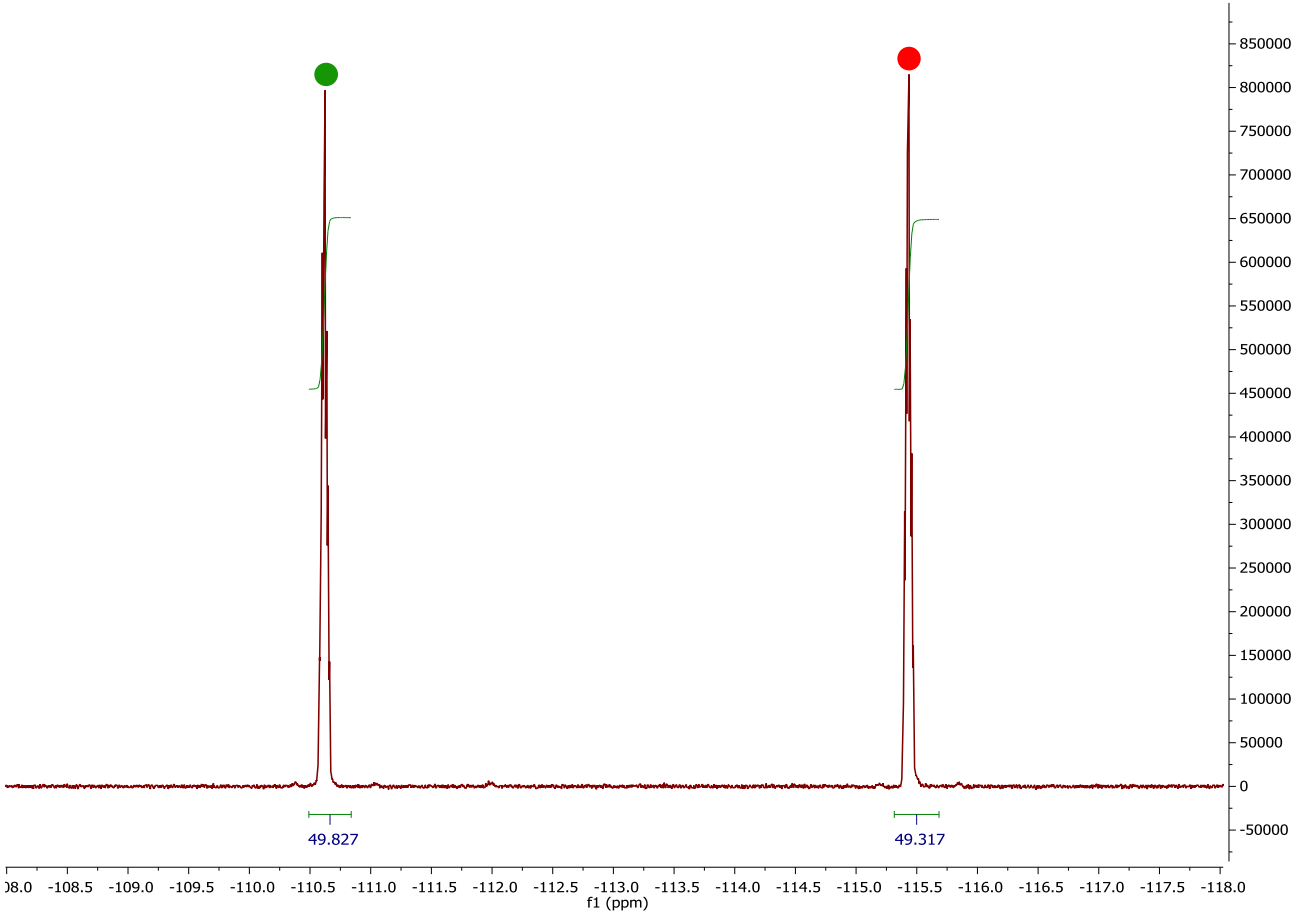
- ^{19}F is spin $^{1}/_{2}$, 100% isotopic abundance, and high sensitivity making its NMR properties very similar to ^{1}H.

- With the correct parameters quantitative spectra can be taken with short experiment time.

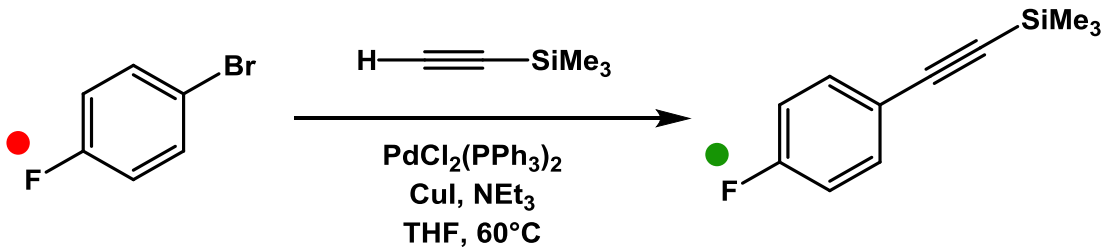
- Useful as an NMR handle in organic reactions.

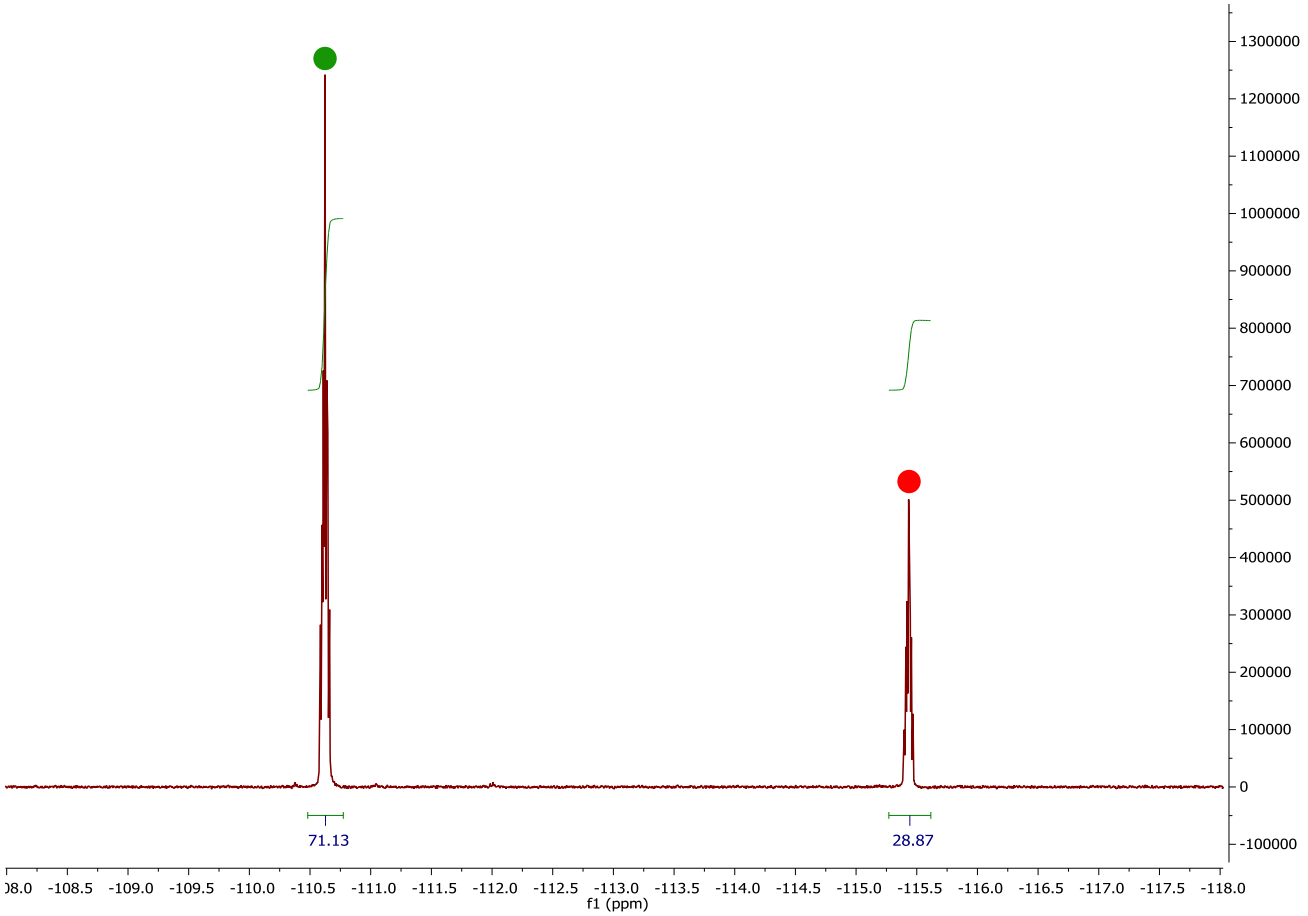
^{19}F NMR


Br
F
H
SiMe3
PdCl2(PPh3)2
CuI, NEt3
THF, 60°C
SiMe3
F

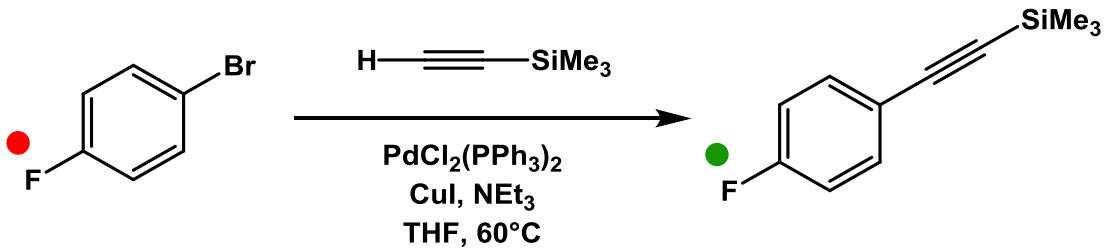

850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
49.827
49.317
-108.5 -109.0 -109.5 -110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0
f1 (ppm)

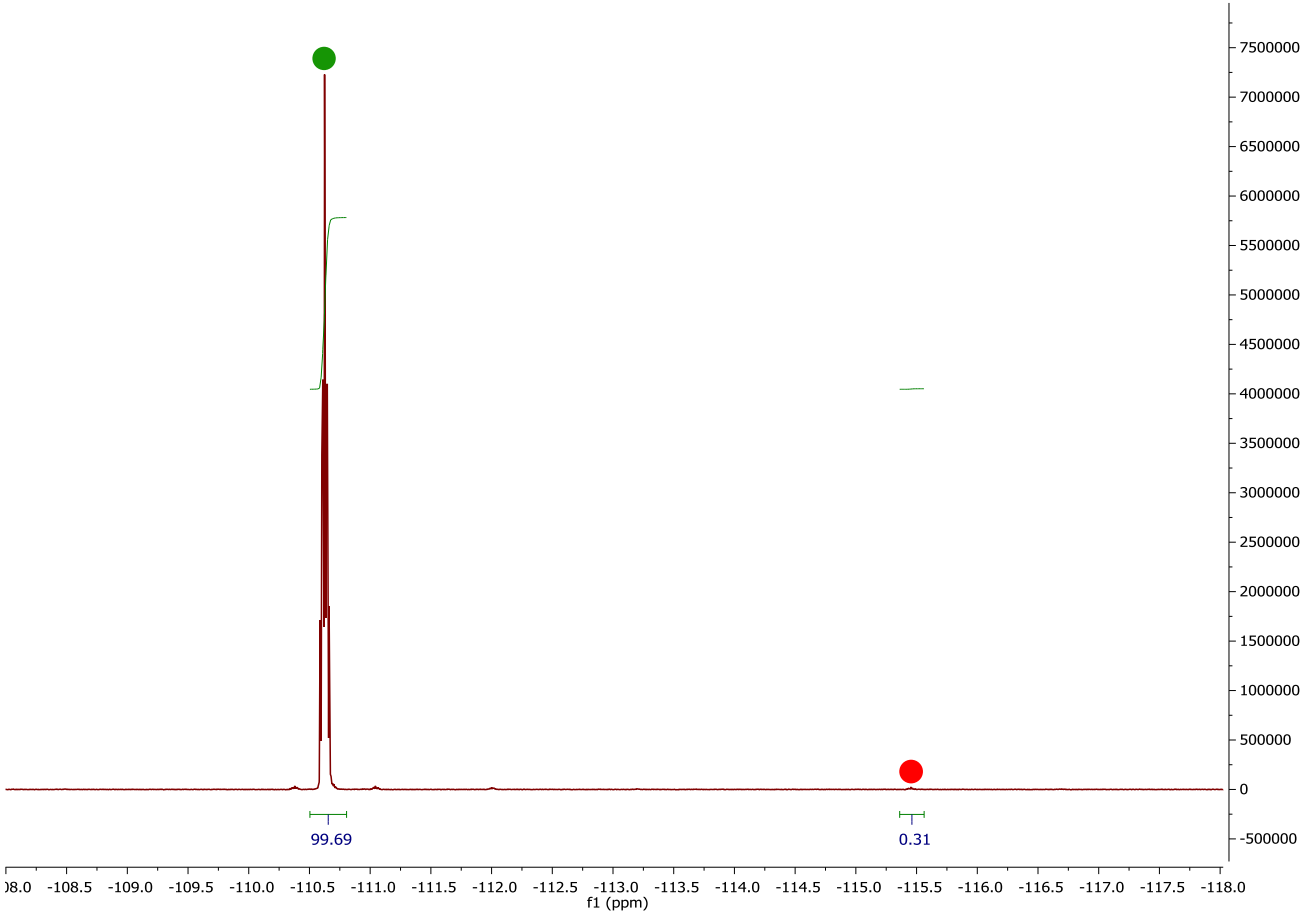
^{19}F NMR


Br
F
H
SiMe3
PdCl2(PPh3)2
CuI, NEt3
THF, 60°C
SiMe3
F


1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
71.13
28.87
-108.5 -109.0 -109.5 -110.0 -110.5 -111.0 -111.5 -112.0 -112.5 -113.0 -113.5 -114.0 -114.5 -115.0 -115.5 -116.0 -116.5 -117.0 -117.5 -118.0
f1 (ppm)

^{19}F NMR


Br
F
H
SiMe3
PdCl2(PPh3)2
CuI, NEt3
THF, 60°C
SiMe3
F


99.69
0.31
f1 (ppm)

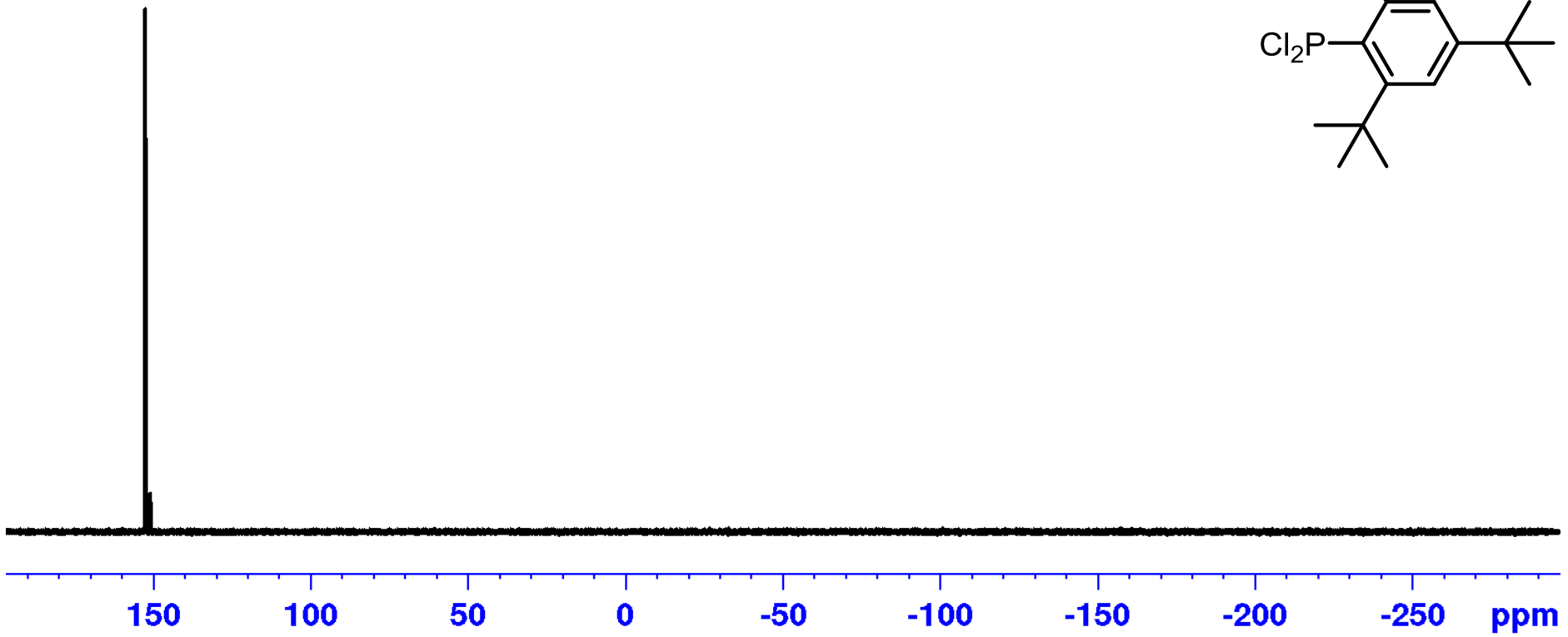
^{31}P NMR

- ^{31}P is spin $^{1}/_{2}$ and 100% isotopic abundance, but with lower sensitivity than that of ^{1}H or ^{19}F.

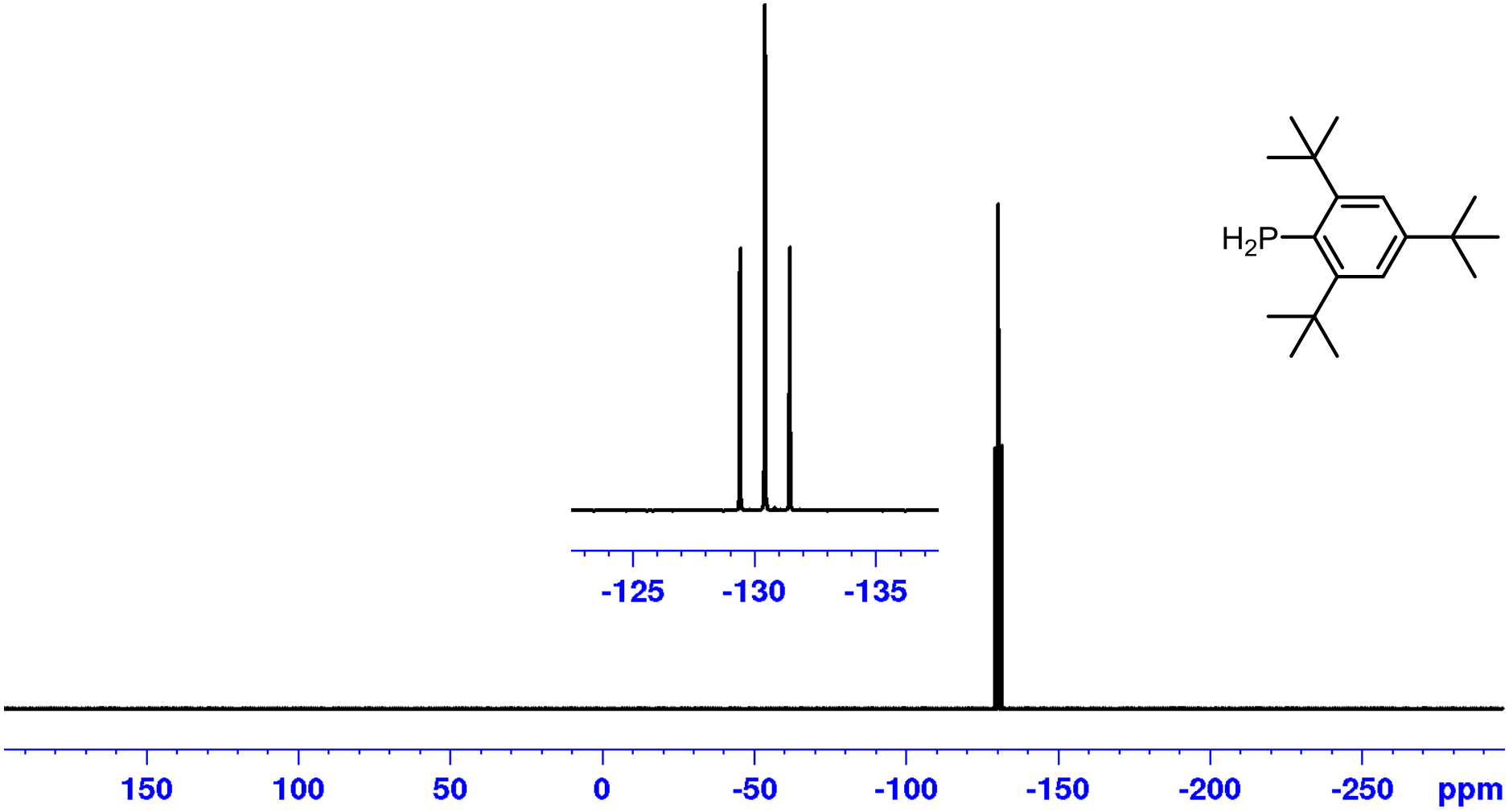
- Phosphorus compounds tend to have longer relaxation times making quantitative NMR experiments longer to run.

- Can help identify changes in oxidation state from P(III) to P(V) due to large changes in chemical shift. Distinctive coupling values for P-H, P-F etc, give good information on what is coordinated to the phosphorus.

^{31}P NMR



^{31}P NMR



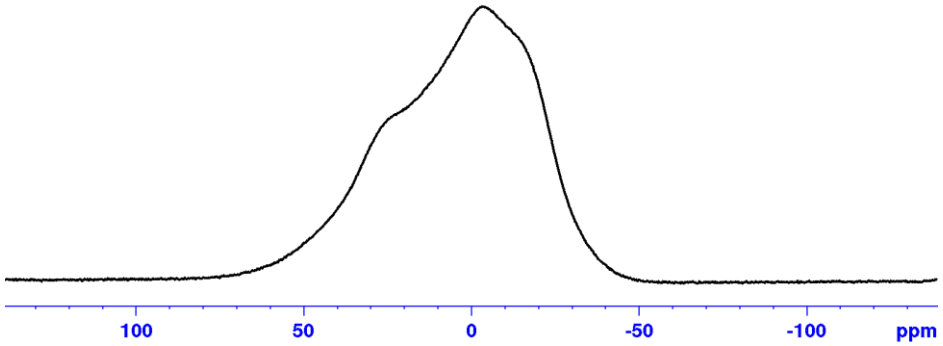
Glass Peaks - $^{10}B/^{11}B$, ^{27}Al, ^{29}Si NMR

- Borosilicate glass contains the above elements.
  - Therefore signals from your NMR tube are observed in the NMR spectra.
  - The NMR probe also contains glass so signals from this are also present.

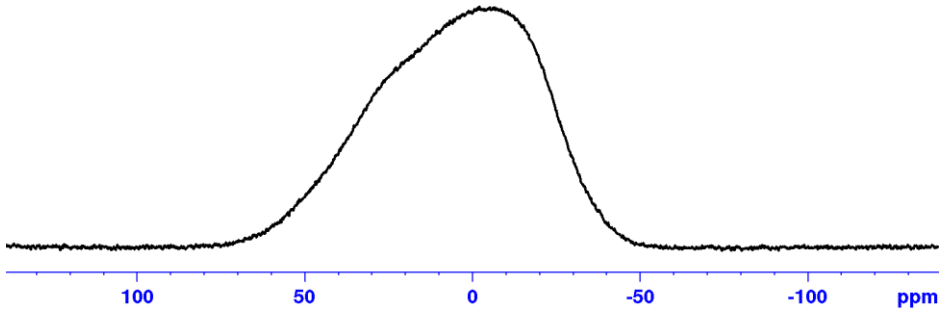
Glass Peaks - $^{10}B/^{11}B$, ^{27}Al, ^{29}Si NMR

- Borosilicate glass contains the above elements.
  - Therefore signals from your NMR tube are observed in the NMR spectra.
  - The NMR probe also contains glass so signals from this are also present.

- The signal from the tube can be eliminated by using a different tube eg. Quartz tube will eliminate B/Al signals.



^{11}B NMR background with normal NMR tube



^{11}B NMR background with quartz NMR tube

Glass Peaks - $^{10}B/^{11}B$, ^{27}Al, ^{29}Si NMR

- Borosilicate glass contains the above elements.
  - Therefore signals from your NMR tube are observed in the NMR spectra.
  - The NMR probe also contains glass so signals from this are also present.

- The signal from the tube can be eliminated by using a different tube eg. Quartz tube will eliminate B/Al signals.

- If this is not sufficient, there are many different pre- and post-acquisition techniques that can reduce or eliminate these background signals, however, this causes integration to become unreliable.

^{29}Si NMR

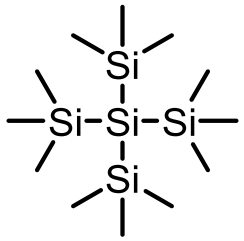
- ^{29}Si is a spin $^{1}/_{2}$ nucleus, but has poor sensitivity and an isotopic abundance of 4.7%.

- Collection of ^{29}Si spectra requires very long experiment time.

- Si INEPT and Si HMBC experiments can give information on the Si environments while being much shorter experiments based on ^{1}H polarisation. Requires protons close to silicon to be used.

^{29}Si NMR

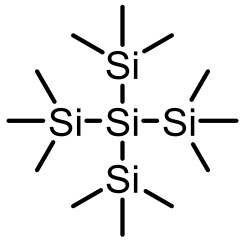
- ^{29}Si IG spectrum



Runtime:
60 mins

^{29}Si NMR

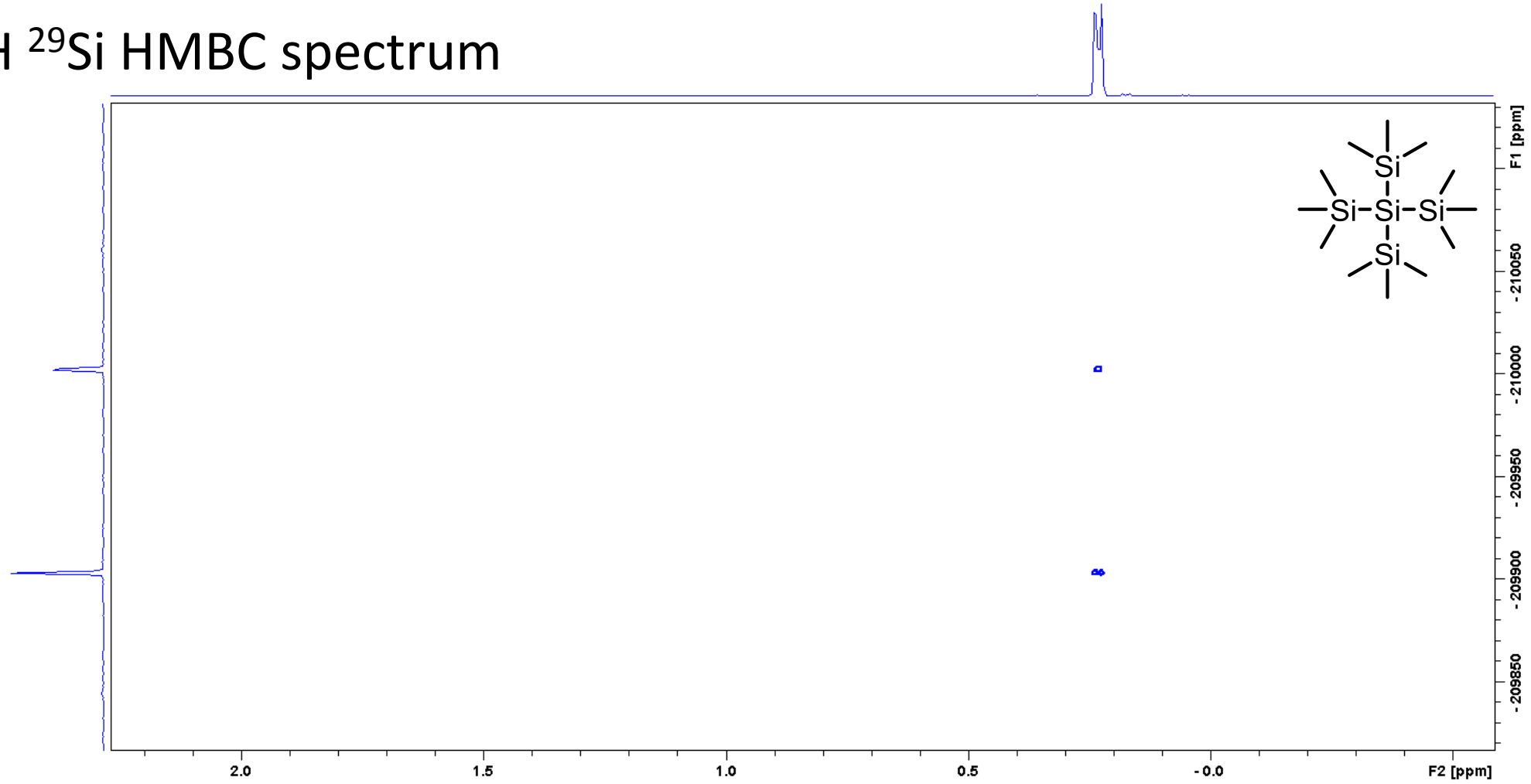
- ^{29}Si INEPT spectrum



Runtime:
5 mins

^{29}Si NMR

- ^{1}H ^{29}Si HMBC spectrum



Runtime:
5 mins

NMR of quadrupolar X-nuclei

- Quadrupolar nuclei are those with spin greater than $^1/_2$.

- These nuclei relax much faster than spin $^1/_2$ nuclei, and so signals in spectra tend to be broad (higher symmetry environments have sharper signals).

- Also be aware that quadrupolar nuclei will cause broadening of the signals of other nuclei coupled to them.

$^{10}B/^{11}B$ NMR

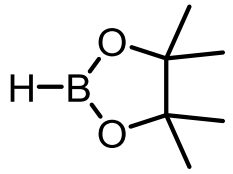
- ^{10}B and ^{11}B are both quadrupolar nuclei with spins of 3 and $^{3}/_{2}$ respectively.

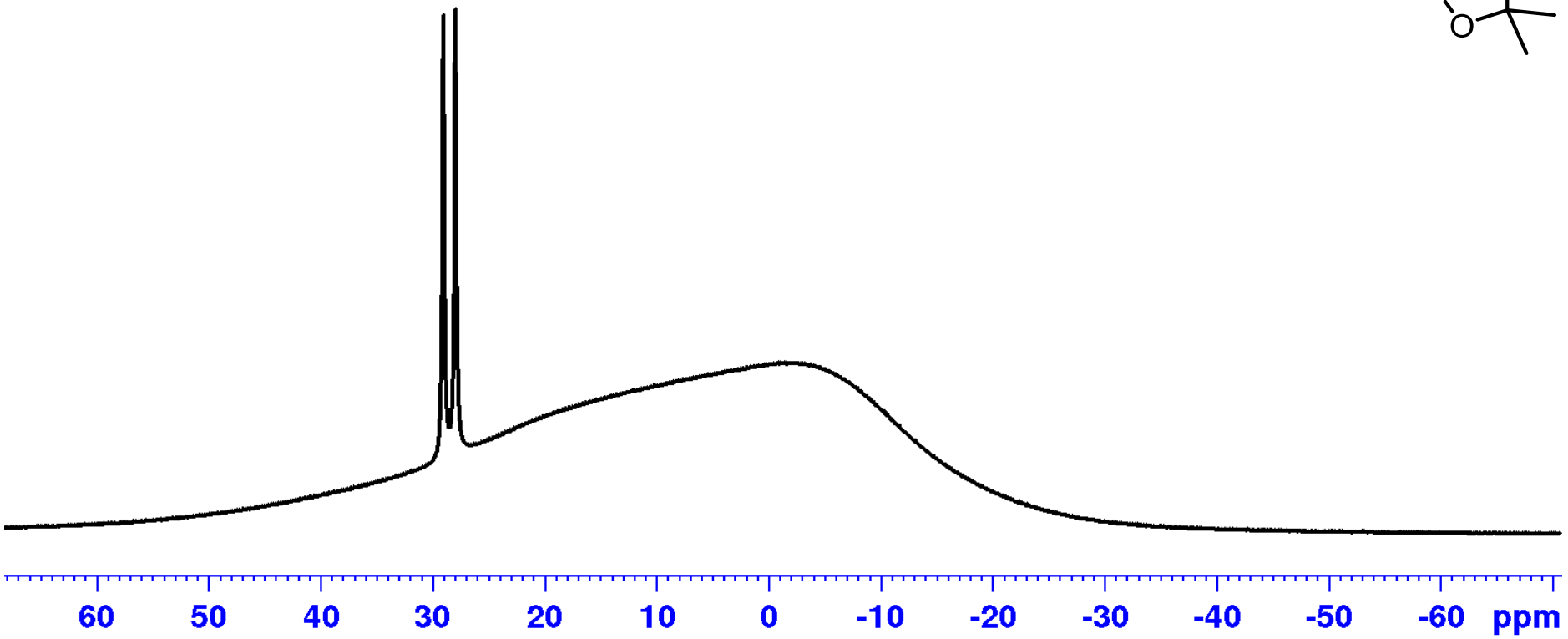
- ^{11}B NMR is more commonly used due to it's higher natural abundance of 80.1%, and higher sensitivity.

- Diagnostic regions for 3 and 4 co-ordinate boron species, and distinctive couplings for B-H, B-F etc, giving information on bonding around the boron centre.

^{11}B NMR

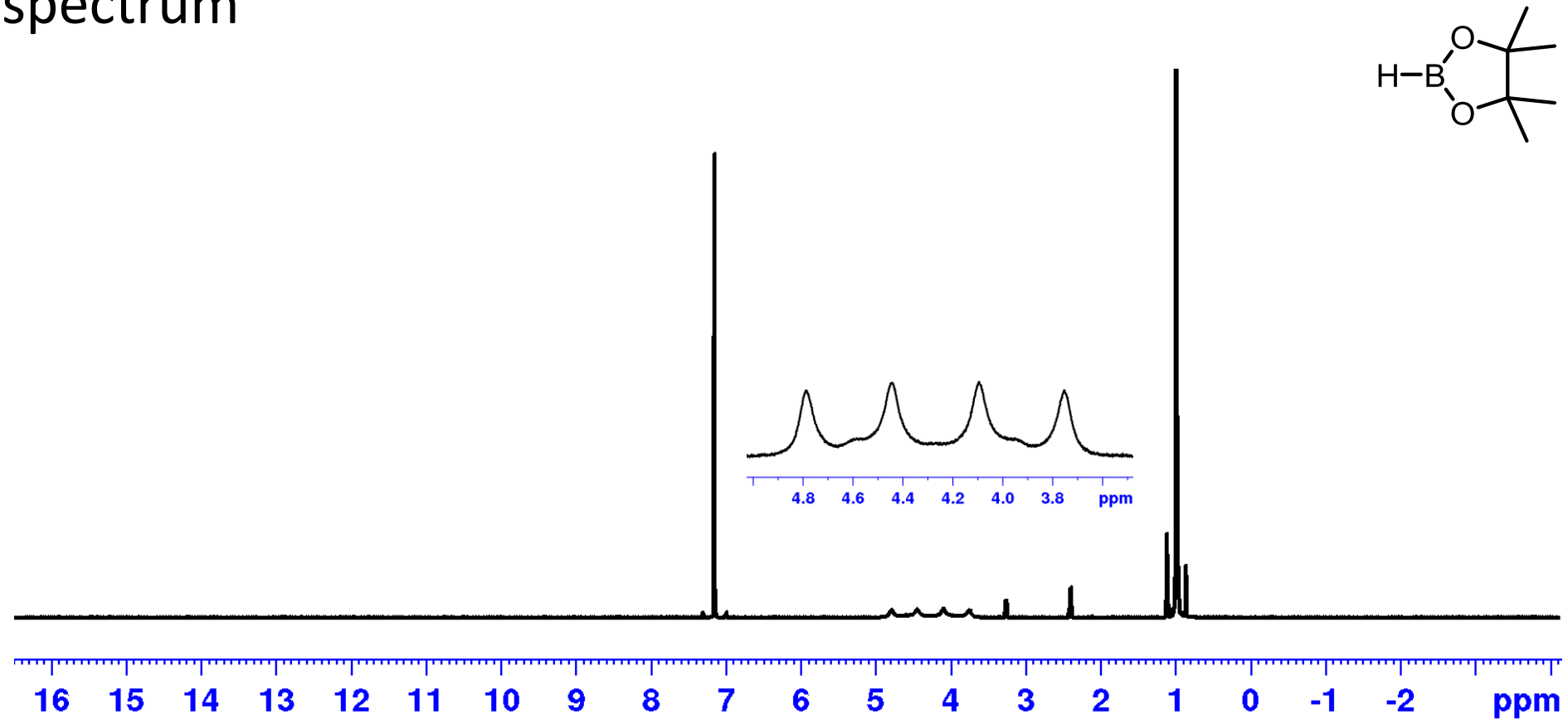
- ^{11}B spectrum



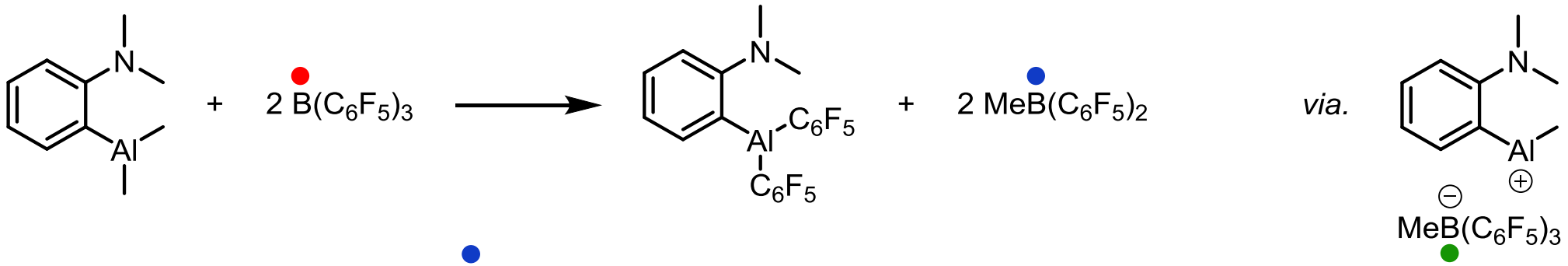


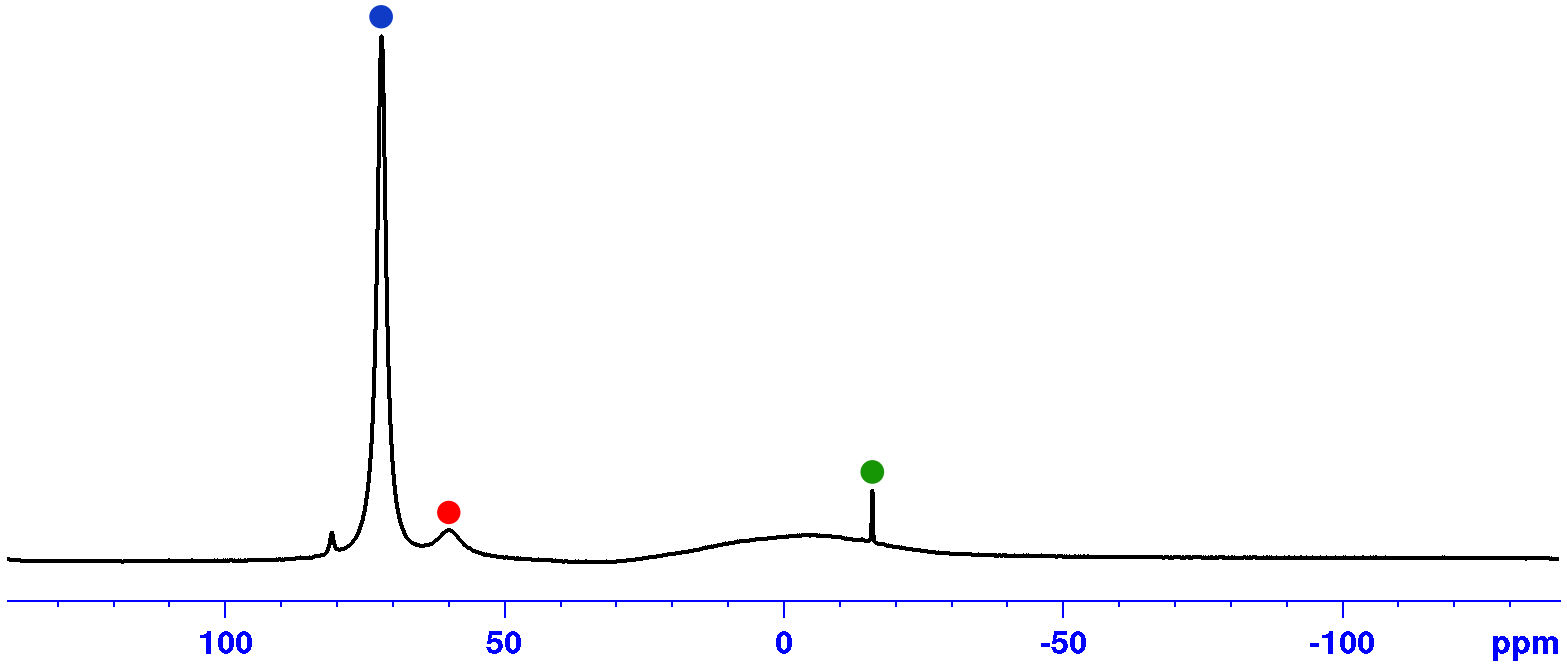
^{11}B NMR

- ^{1}H spectrum



^{11}B NMR


N
Al
+
2 B(C6F5)3
C6F5
C6F5
+
2 MeB(C6F5)2
via.
MeB(C6F5)3


100
50
0
-50
-100
ppm

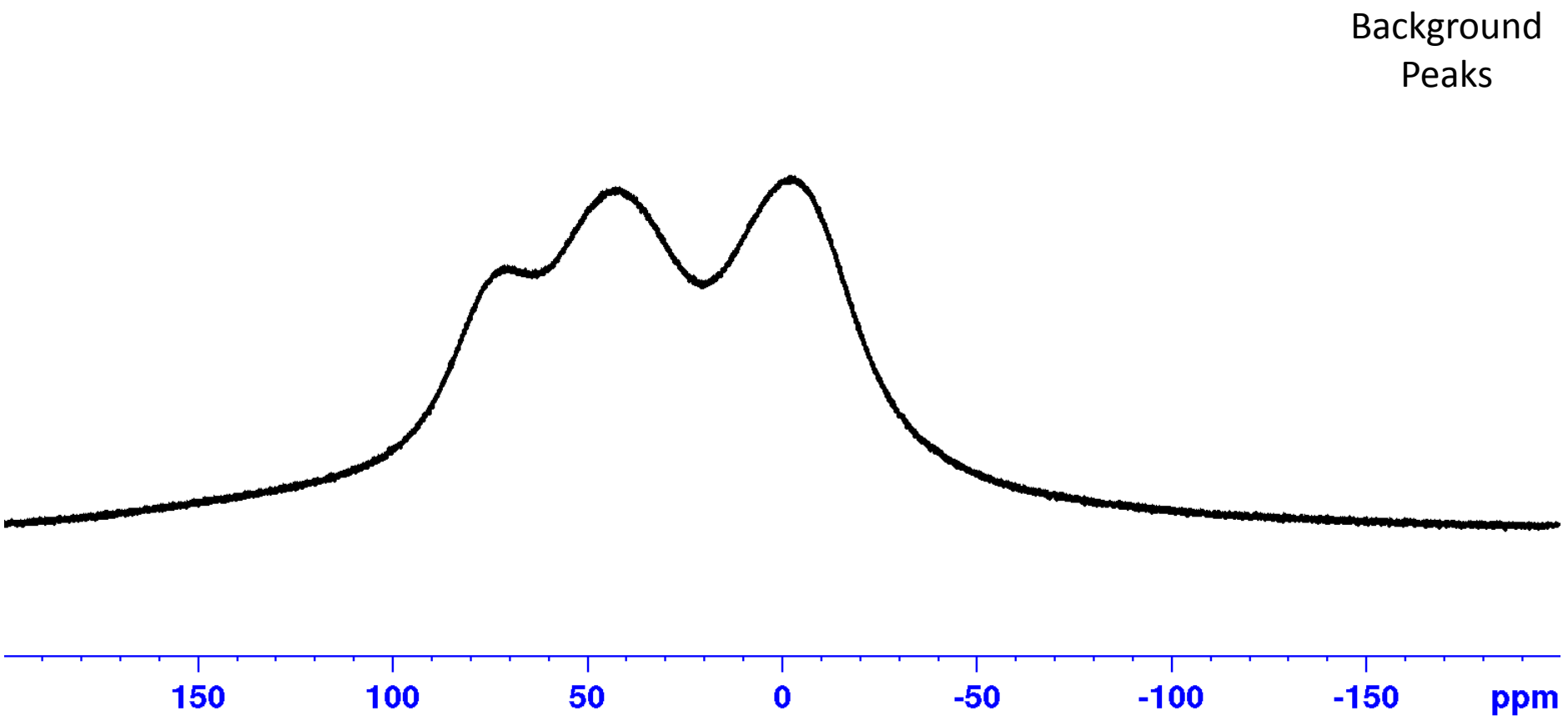
^{27}Al NMR

- ^{27}Al is quadrupolar with a nuclear spin of $^{5}/_{2}$, has 100% isotopic abundance, and good sensitivity.

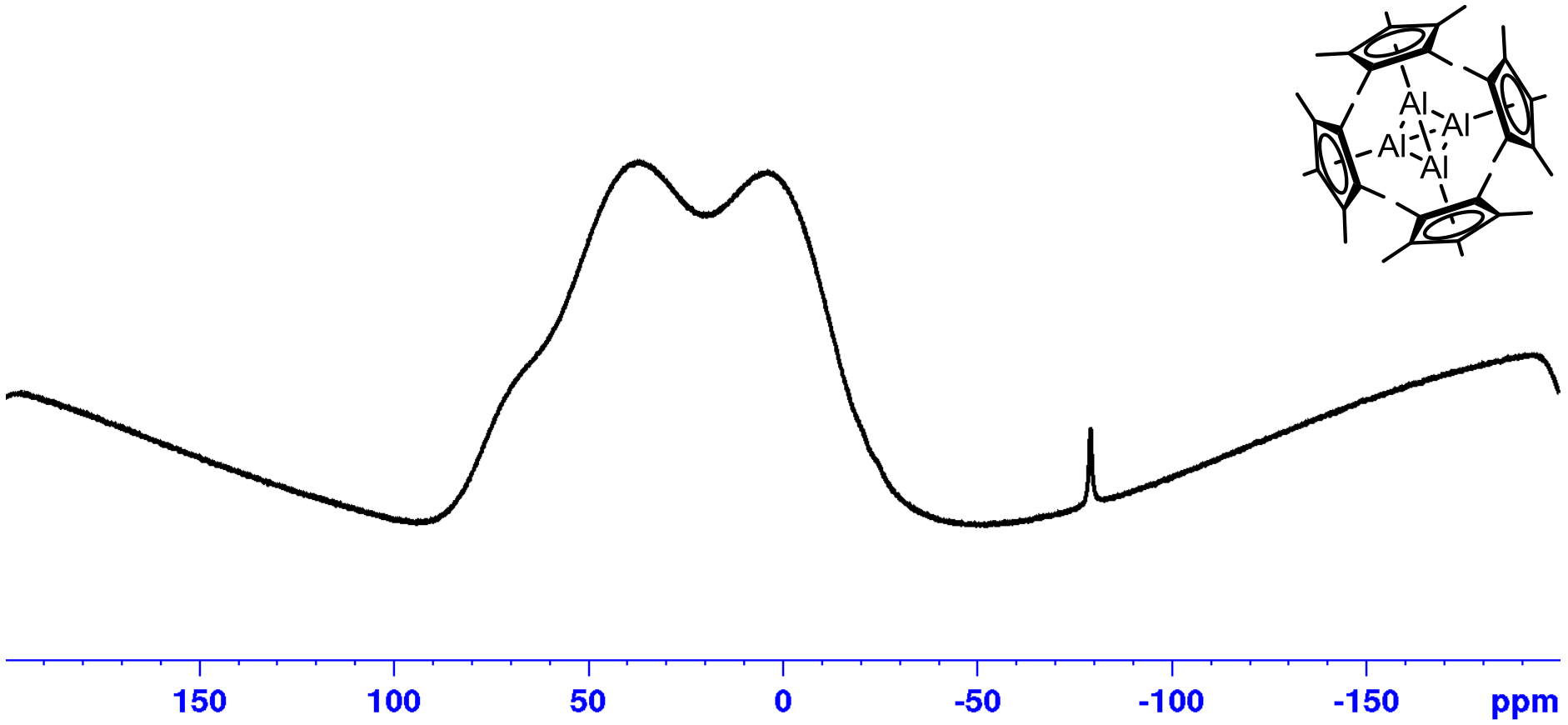
- However, despite the abundance and sensitivity, many of the signals observed are very broad due to fast relaxation time.

- Only for highly symmetric species are sharp signals observed, and even then in relatively low intensity.

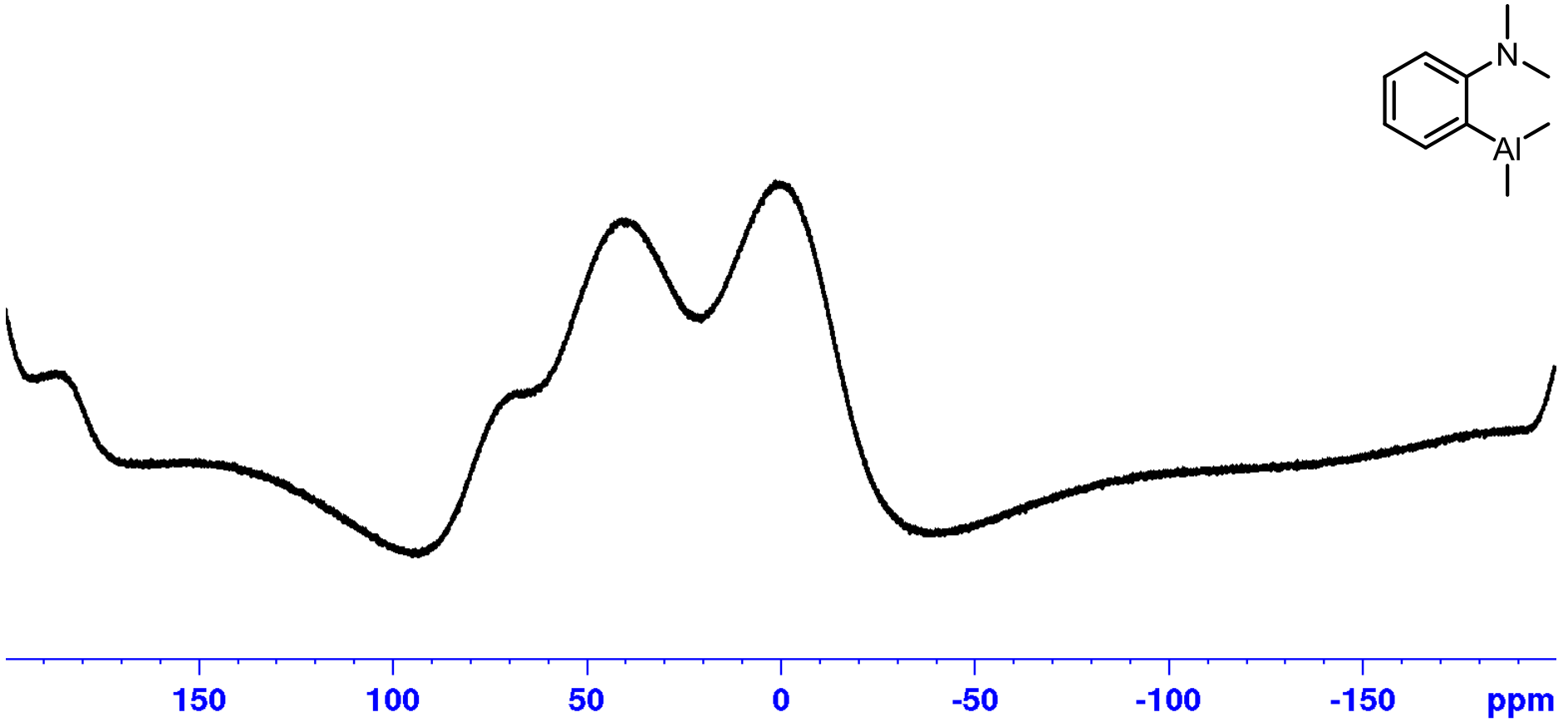
^{27}Al NMR



^{27}Al NMR



^{27}Al NMR



X-nuclei available at Edinburgh

Available in automation

^{2}H	^{31}P
^{7}Li	^{51}V
$^{10}B/^{11}B$	^{59}Co
^{15}N	^{71}Ga
^{19}F	^{77}Se
^{23}Na	^{113}Cd
^{27}Al	^{119}Sn
^{29}Si	^{195}Pt

For any other X-nuclei needs speak to Lorna or Juraj to arrange them.

Any questions?