Primary alkylphosphine–borane polymers: Synthesis, low glass transition temperature, and a predictive capability thereof

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Supporting Information for “Primary alkyl phosphine-borane polymers: Synthesis, low glass transition temperature, and a predictive capability thereof”

Hamish Cavaye, Francis Clegg, Peter J. Gould, Melissa K. Ladyman, Tracey Temple, Eleftheria Dossi

Table of Contents

Scheme S1 – Synthesis of phosphine-borane monomers and polymers

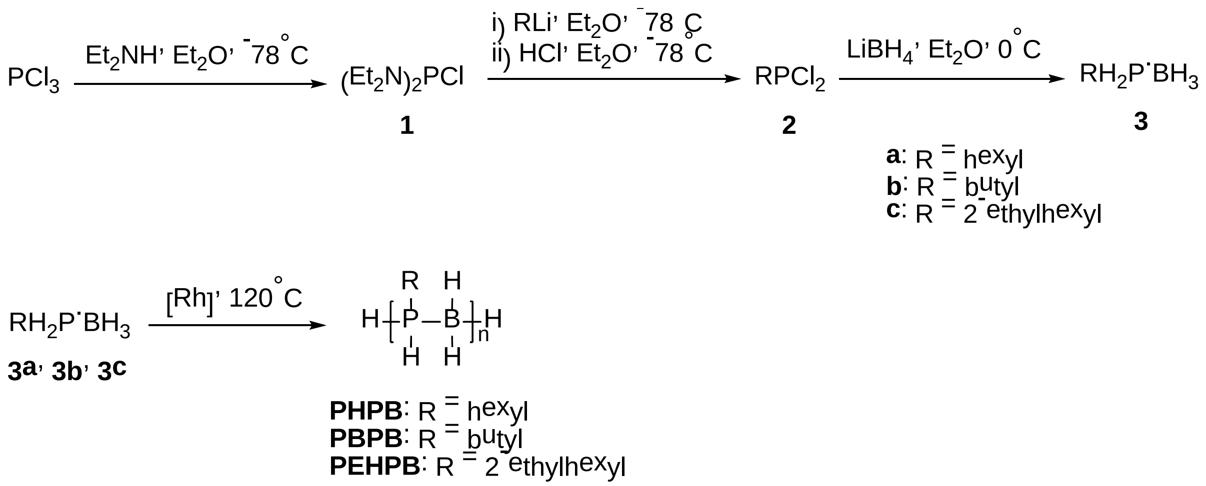

Figure S1 - HexylPCl$_2$ (2a) NMR Spectra

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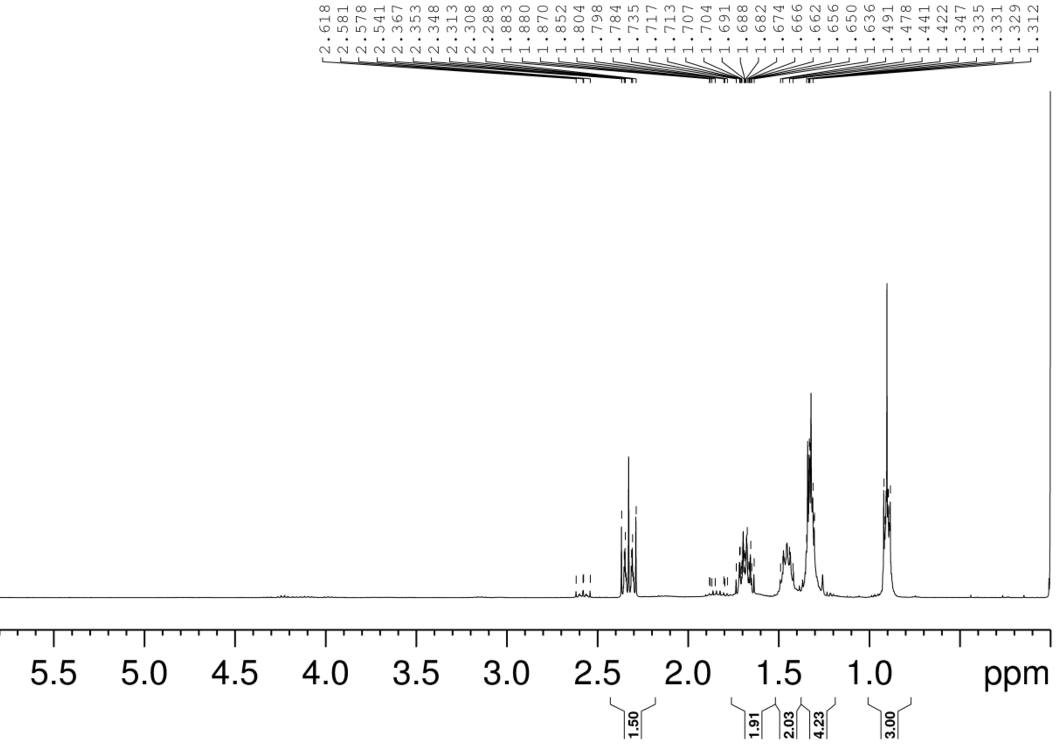

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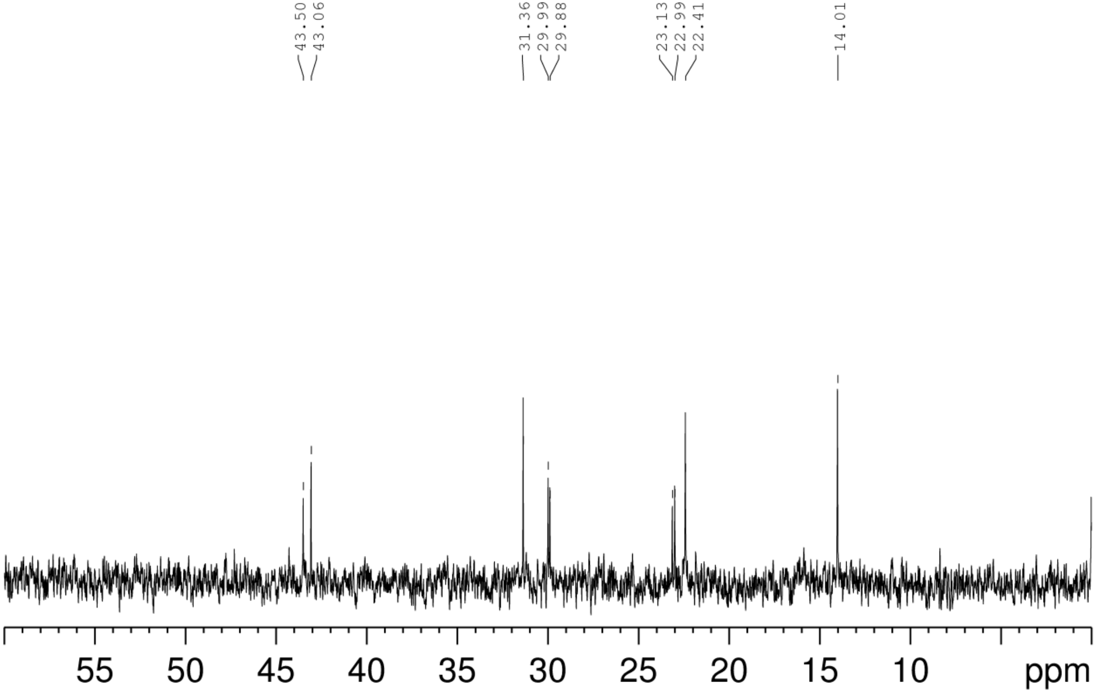

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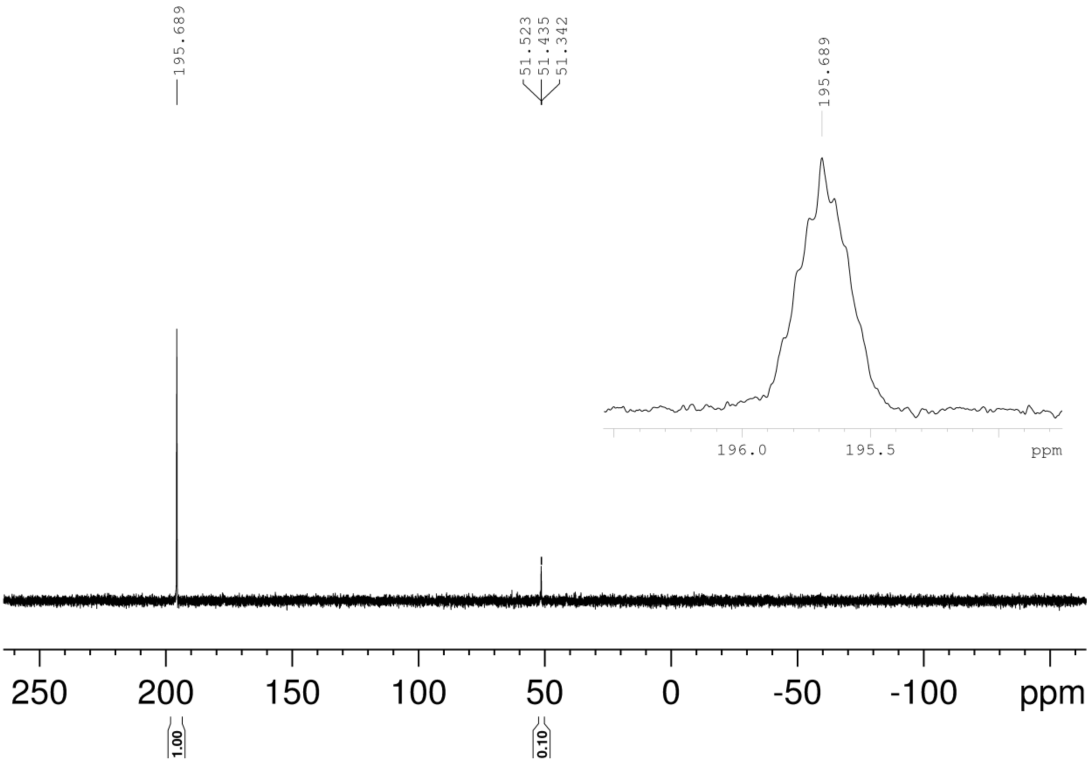
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ppm
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0.10

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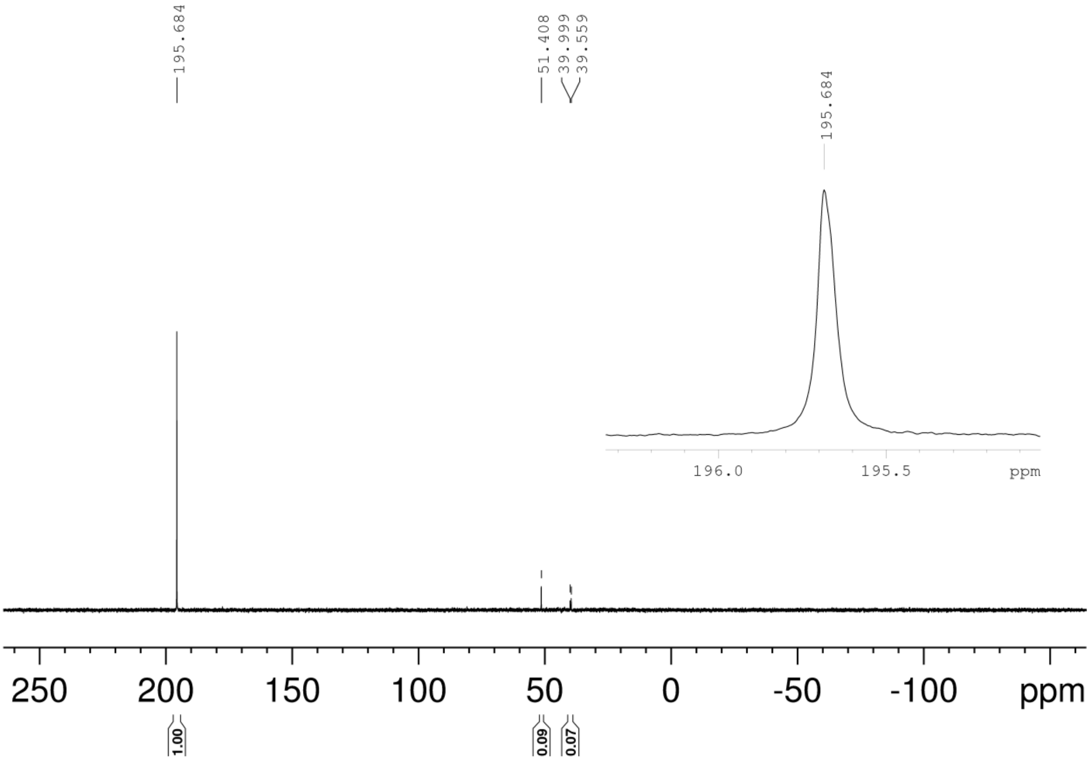
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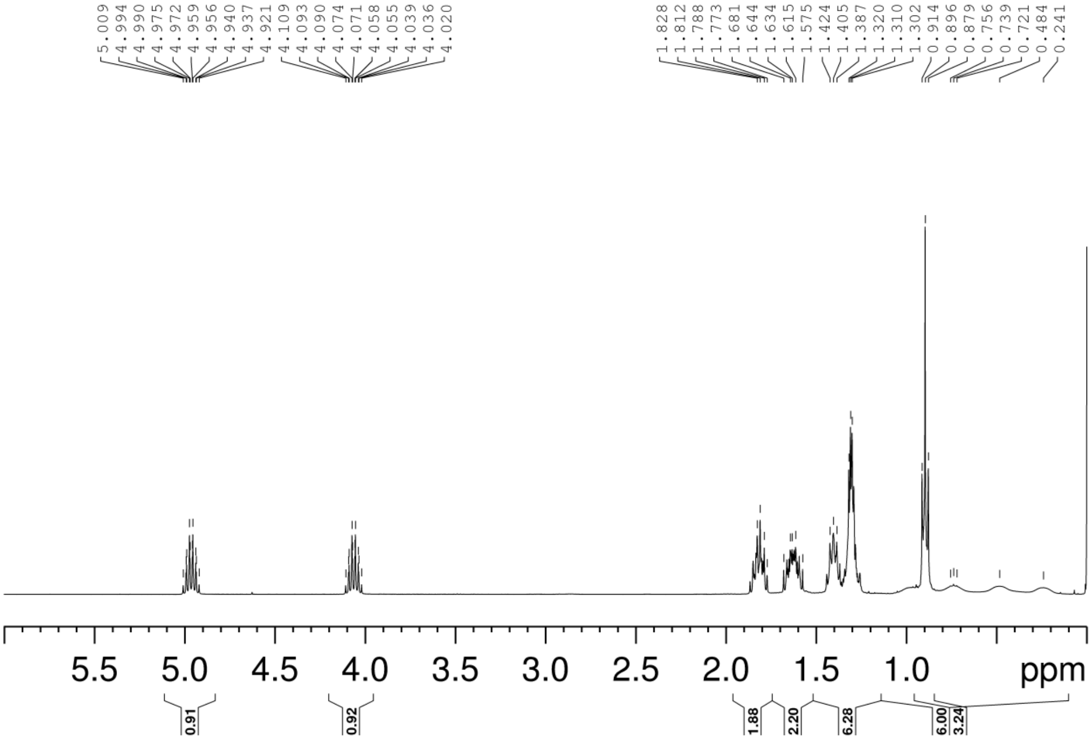
0.07

Figure S2 - HexylPH$_2$.BH$_3$ (3a) NMR spectra

^{1}H



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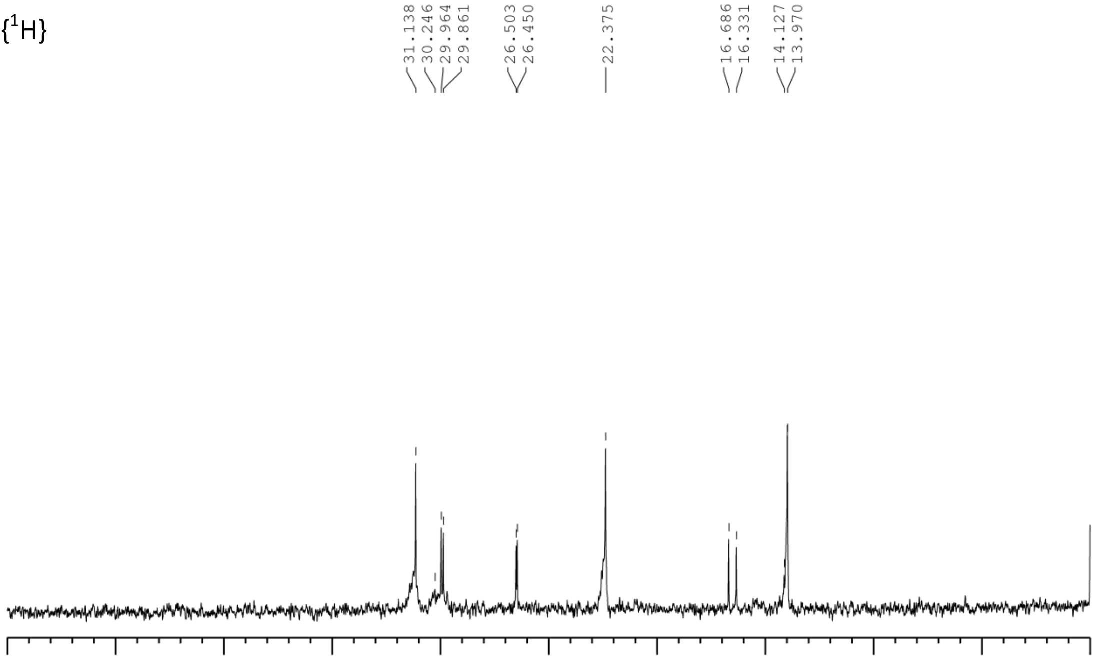

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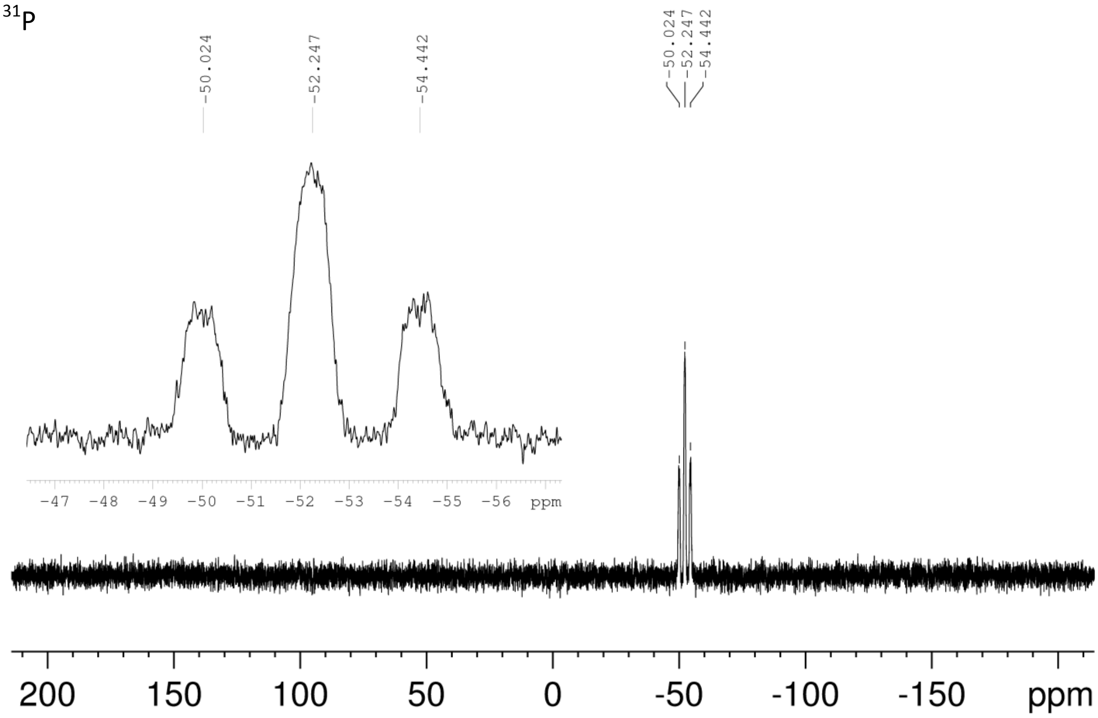
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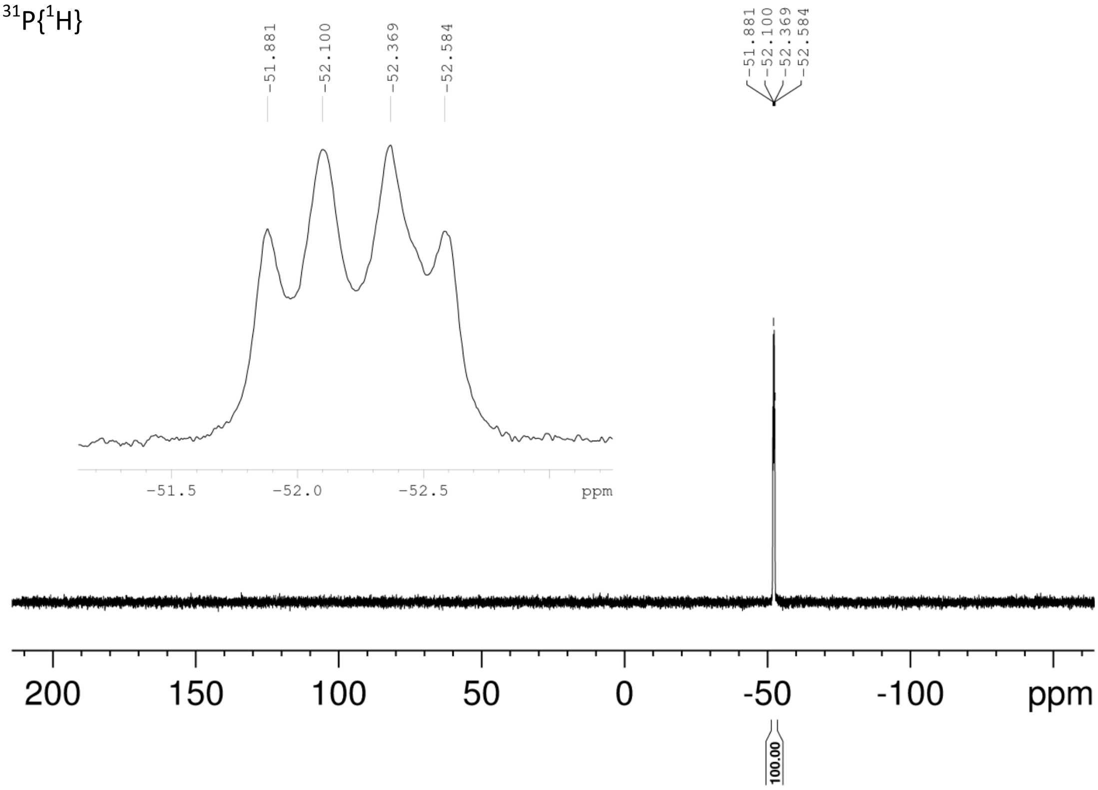
ppm

$^{31}P\{^1H\}$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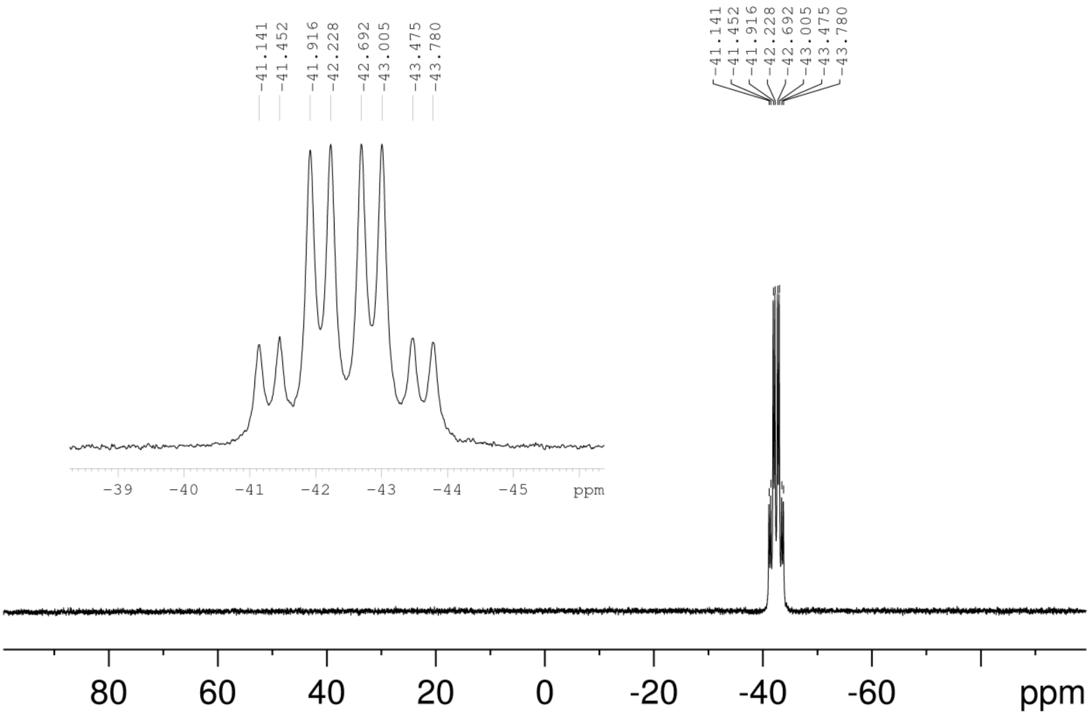
-100
ppm
100.00

^{11}B



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-44
-45
ppm
-41.141
-41.452
-41.916
-42.228
-42.692
-43.005
-43.475
-43.780
80
60
40
20
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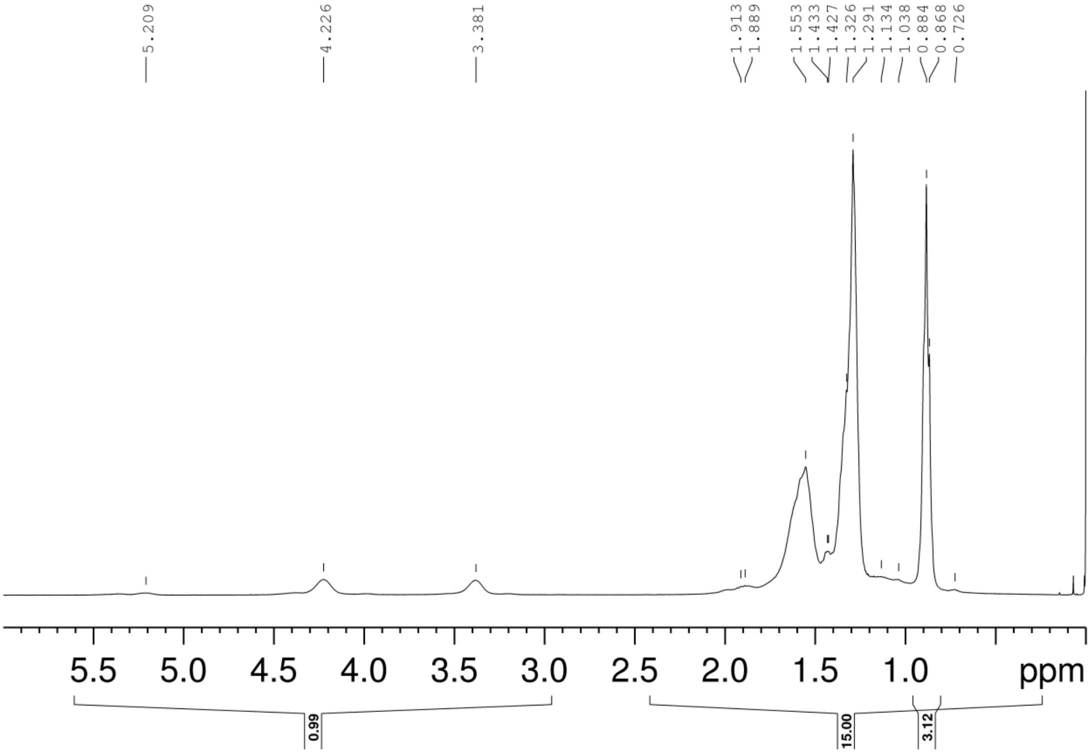
-40
-60
ppm

Figure S3 - Hexyl phosphine-borane polymer (PHPB) NMR spectra

^{1}H



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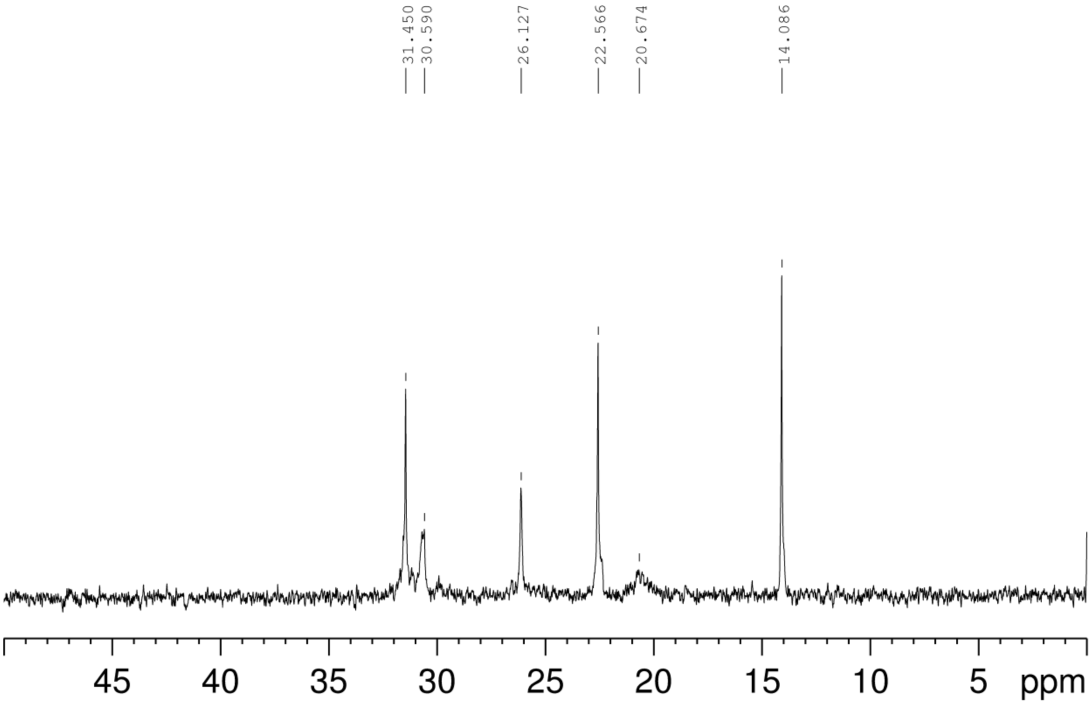

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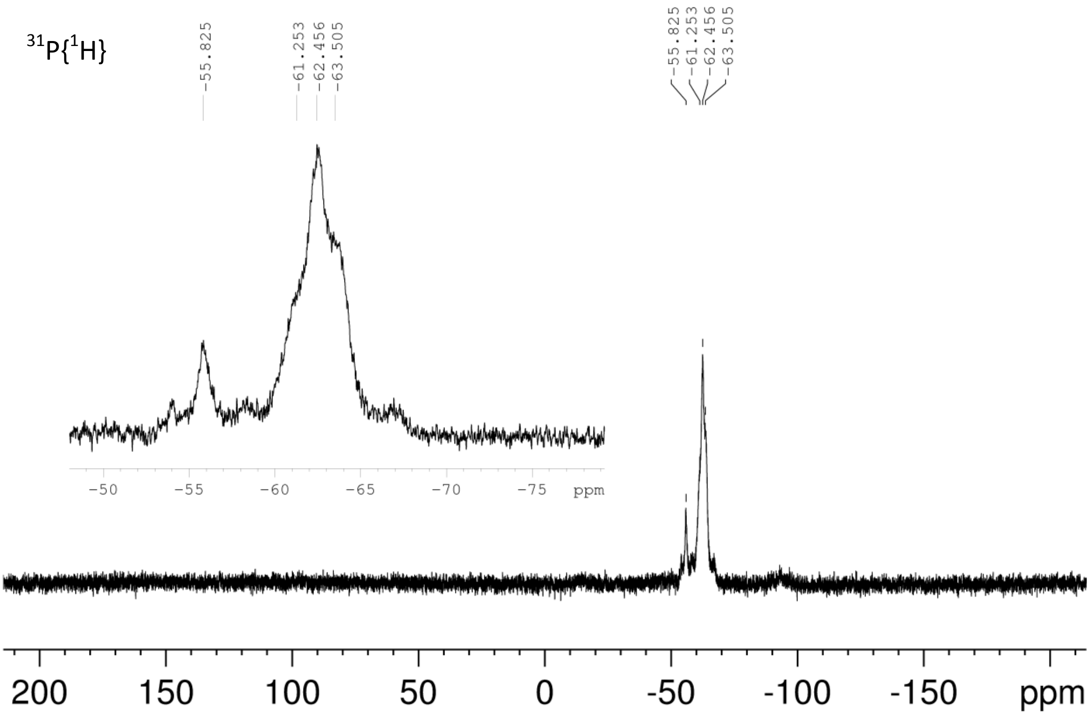
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50
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-50
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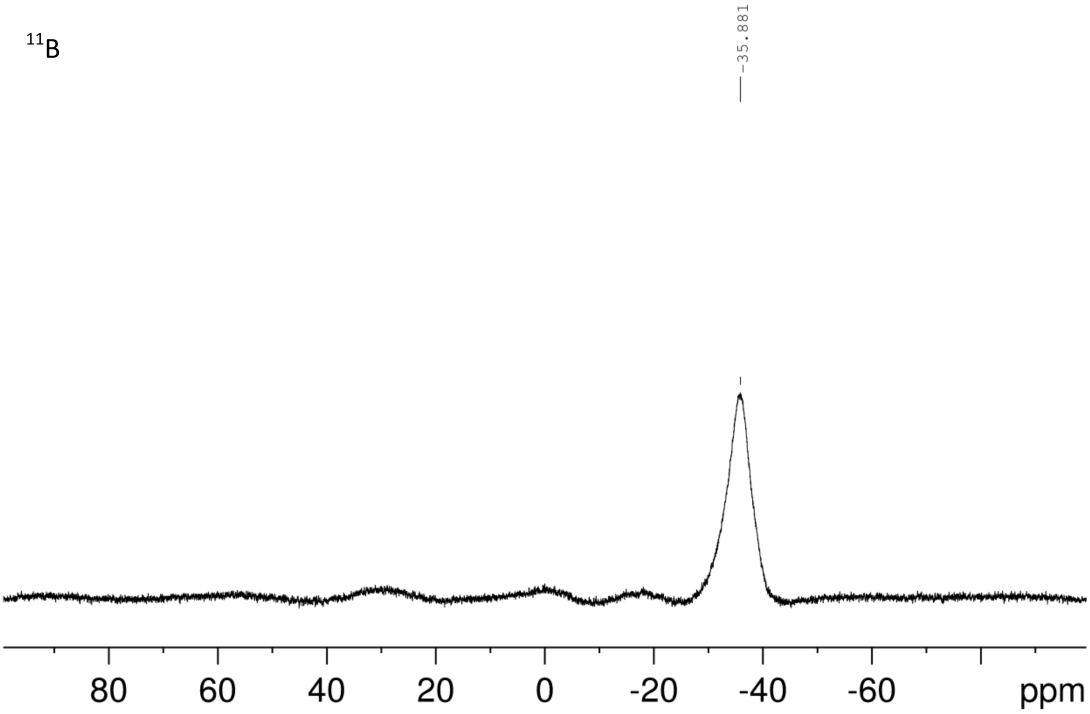
-150
ppm

^{11}B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-60
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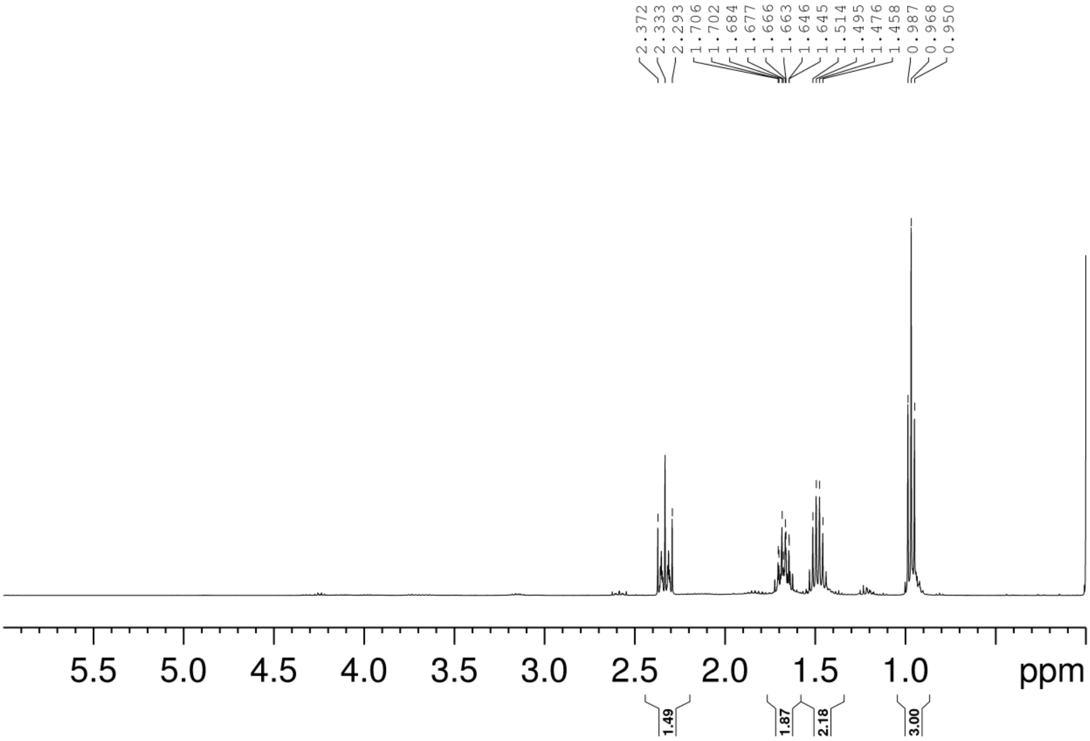
Figure S4 - ButylPCl$_2$ (2b) NMR spectra

^{1}H



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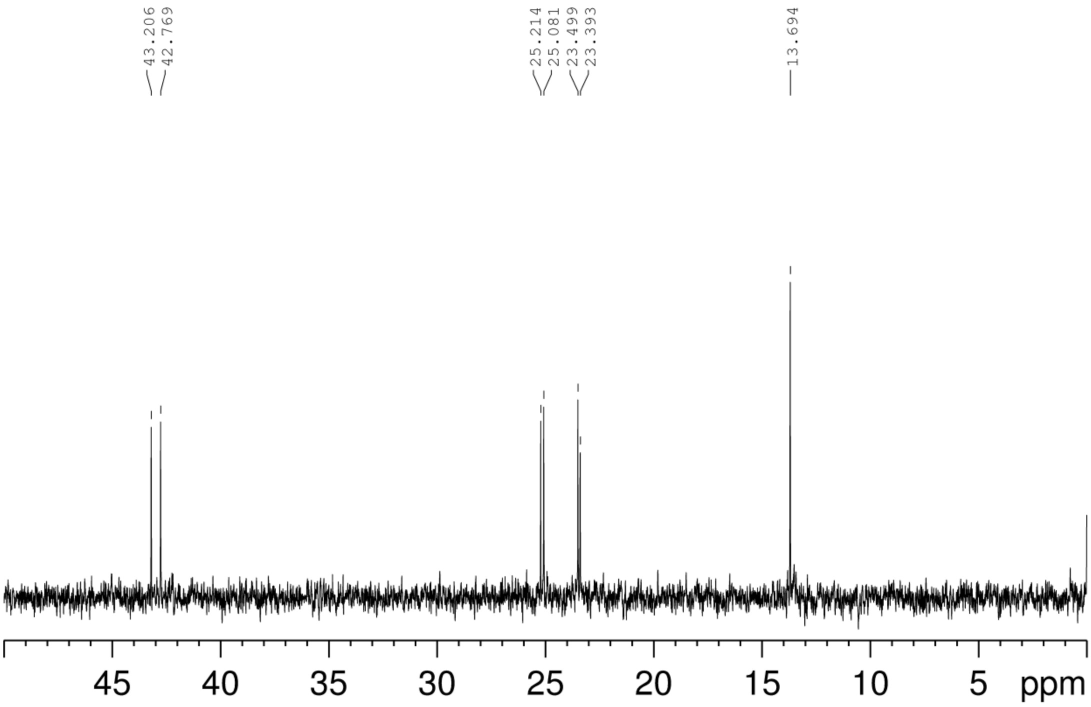

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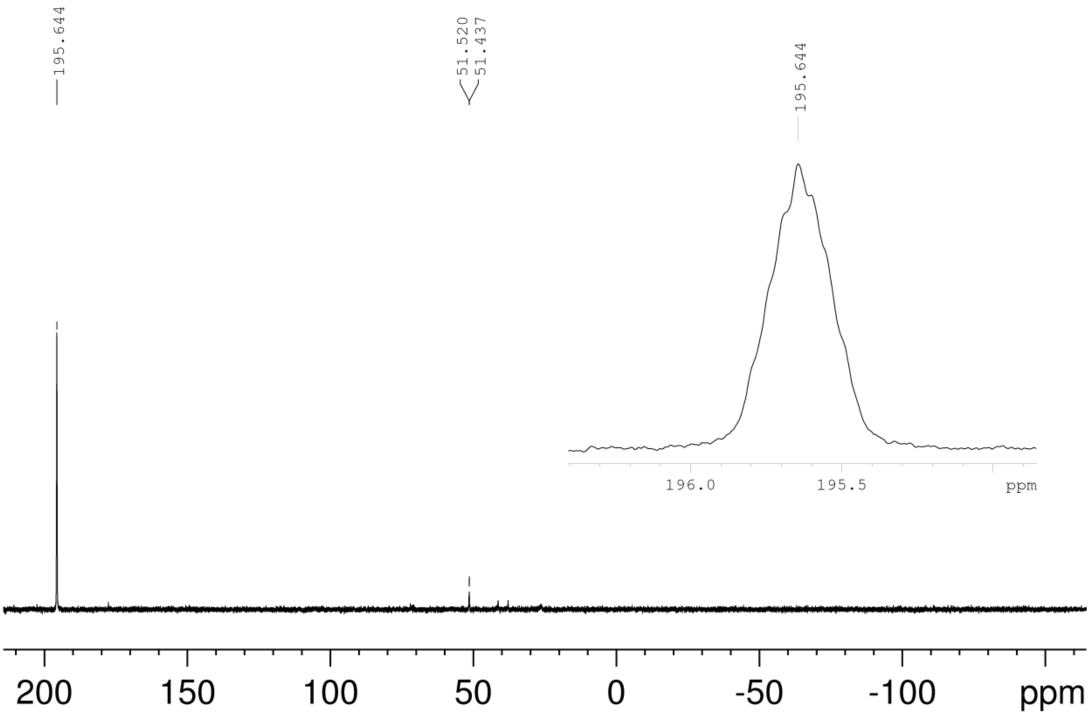
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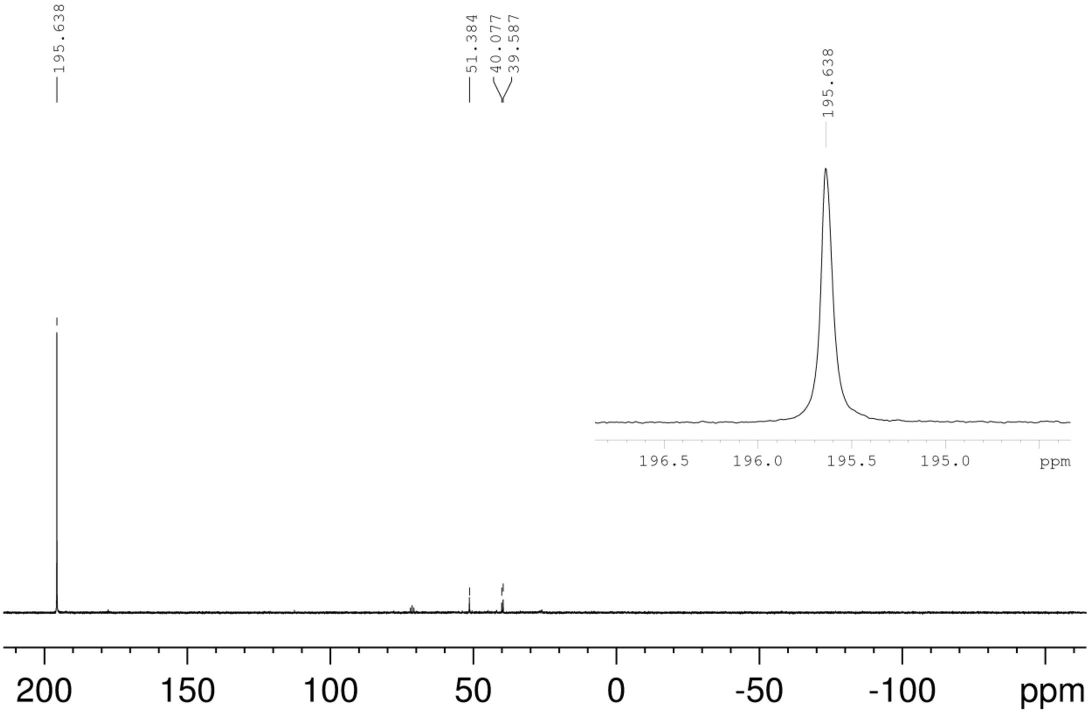
150
100
50
0
-50
-100
ppm

$^{31}P\{^1H\}$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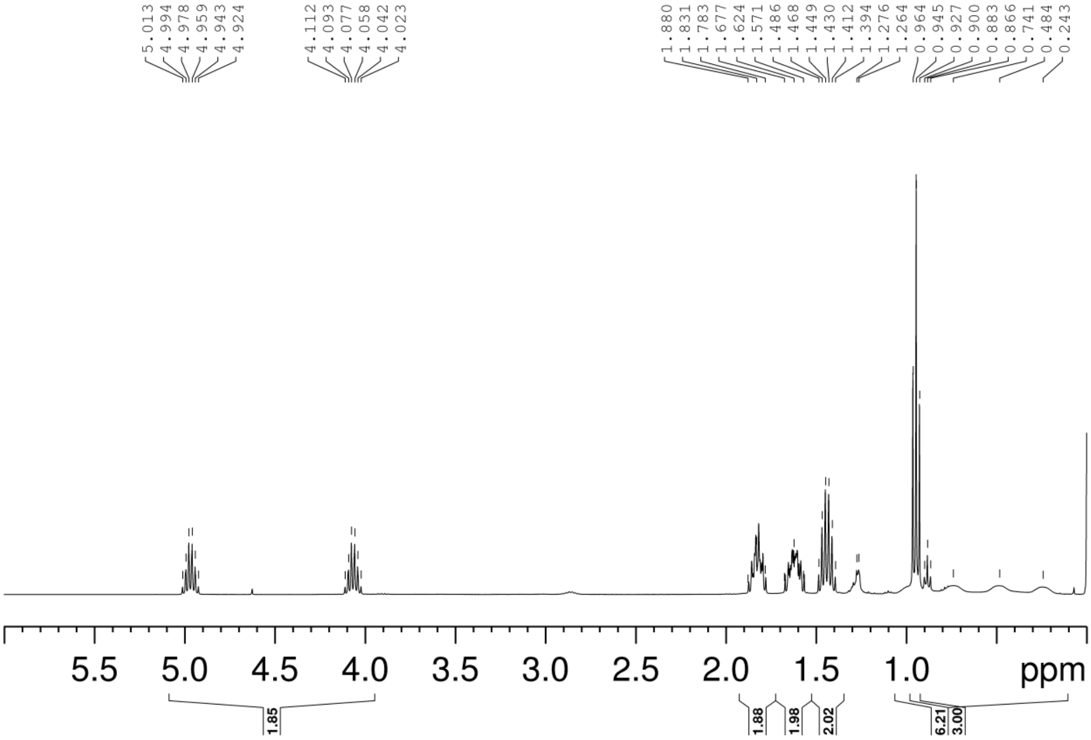
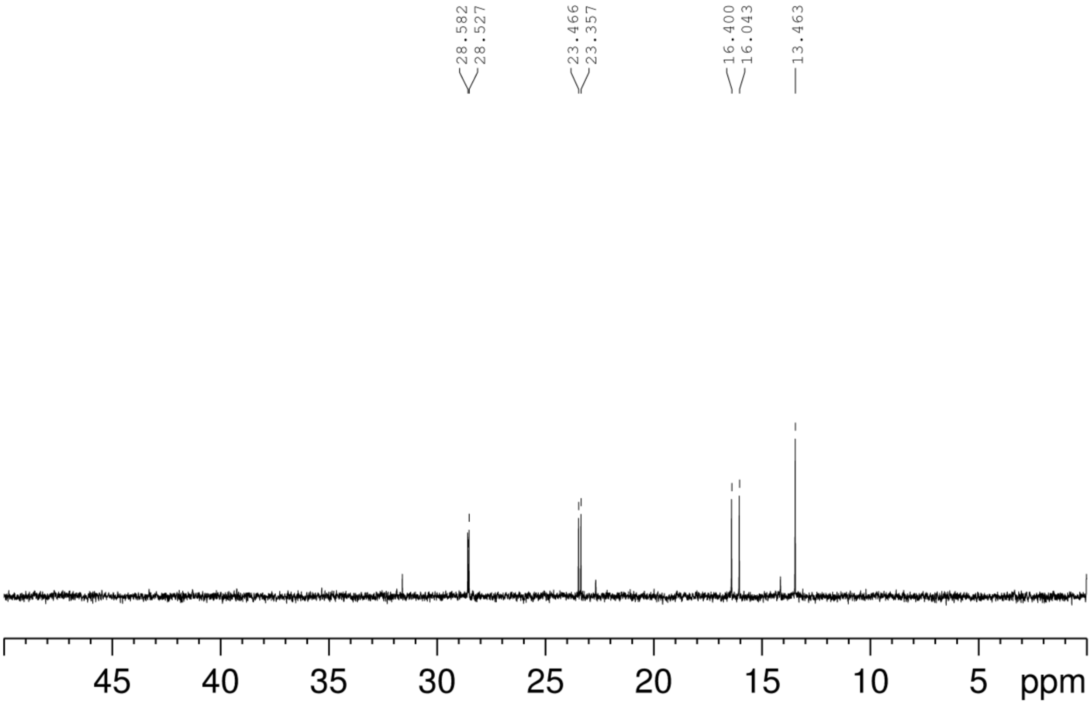
-50
-100
ppm

Figure S5 - ButylPH$_2$.BH$_3$ (3b) NMR spectra

^{1}H



^{13}C{^{1}H}



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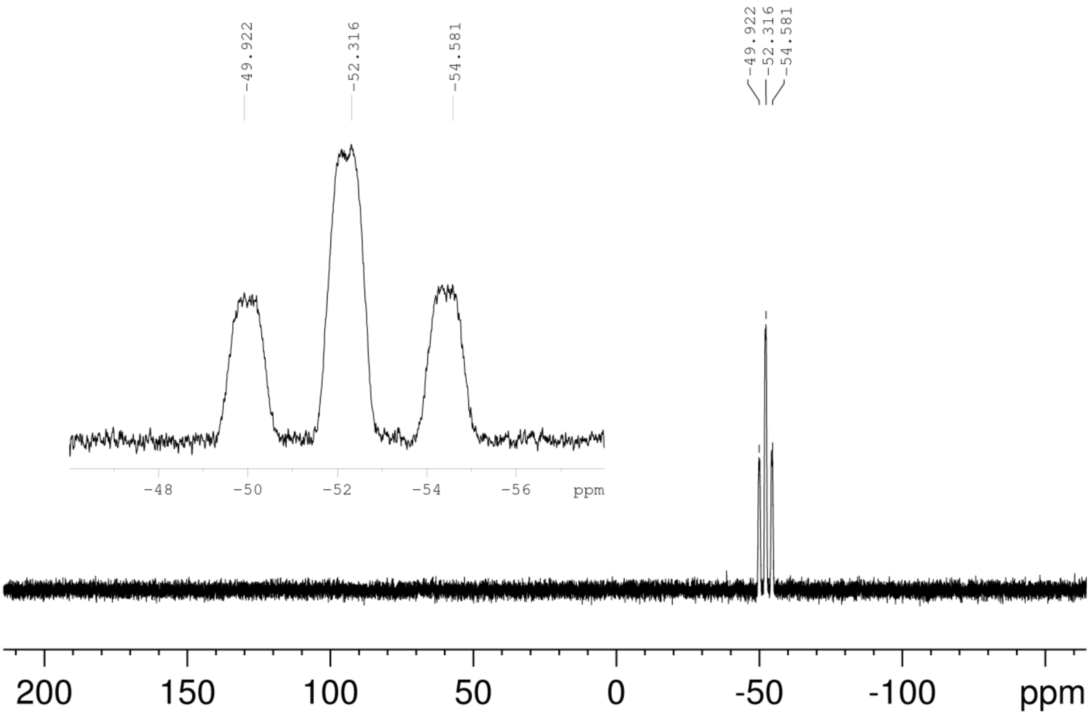
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-54
-56
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-54.581
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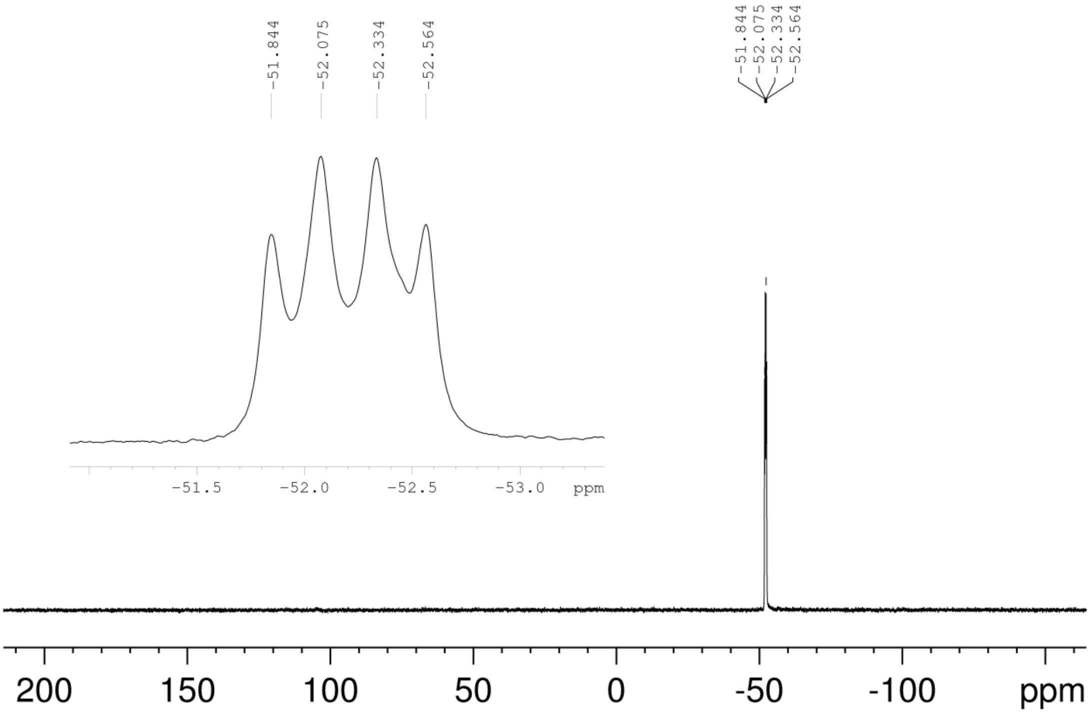
150
100
50
0
-50
-100
ppm

$^{31}P\{^{1}H\}$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-53.0
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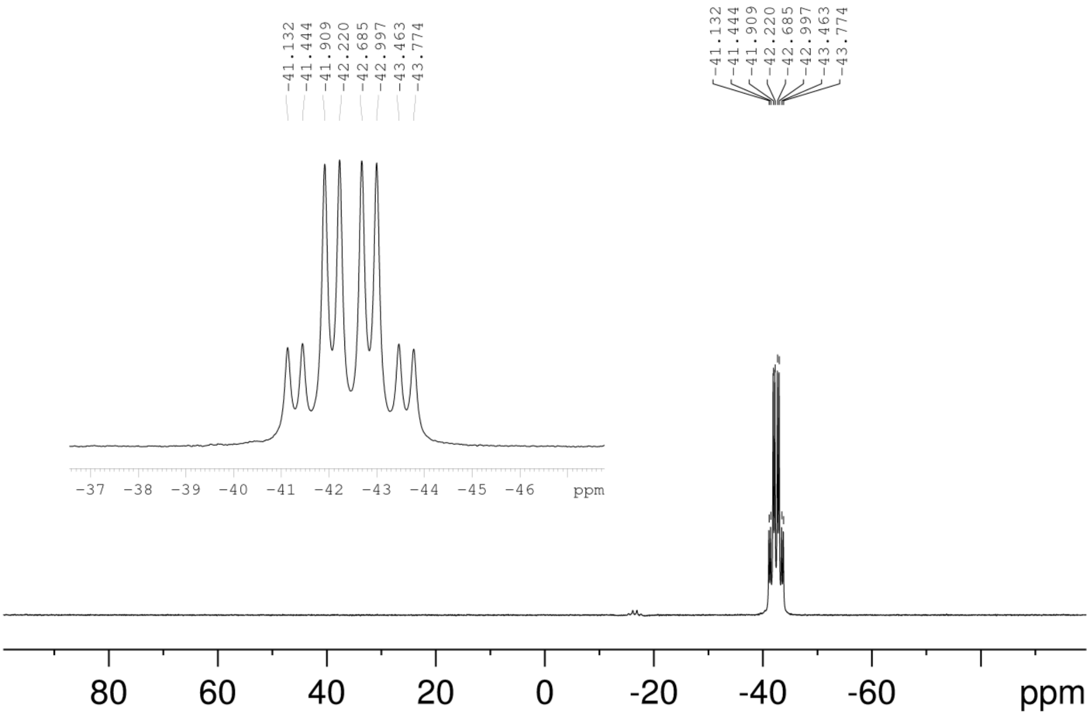
50
0
-50
-100
ppm

^{11}B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-41.132
-41.444
-41.909
-42.220
-42.685
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-43.463
-43.774
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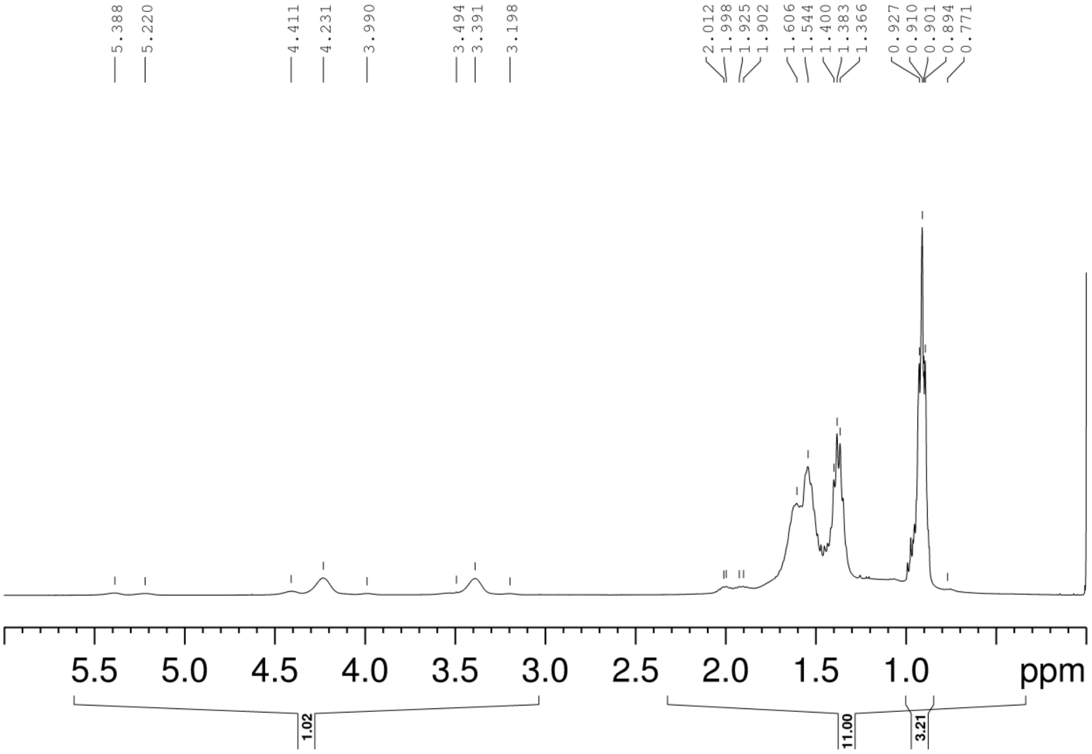
Figure S6 - Butyl phosphine-borane polymer (PBPB) NMR spectra

^{1}H



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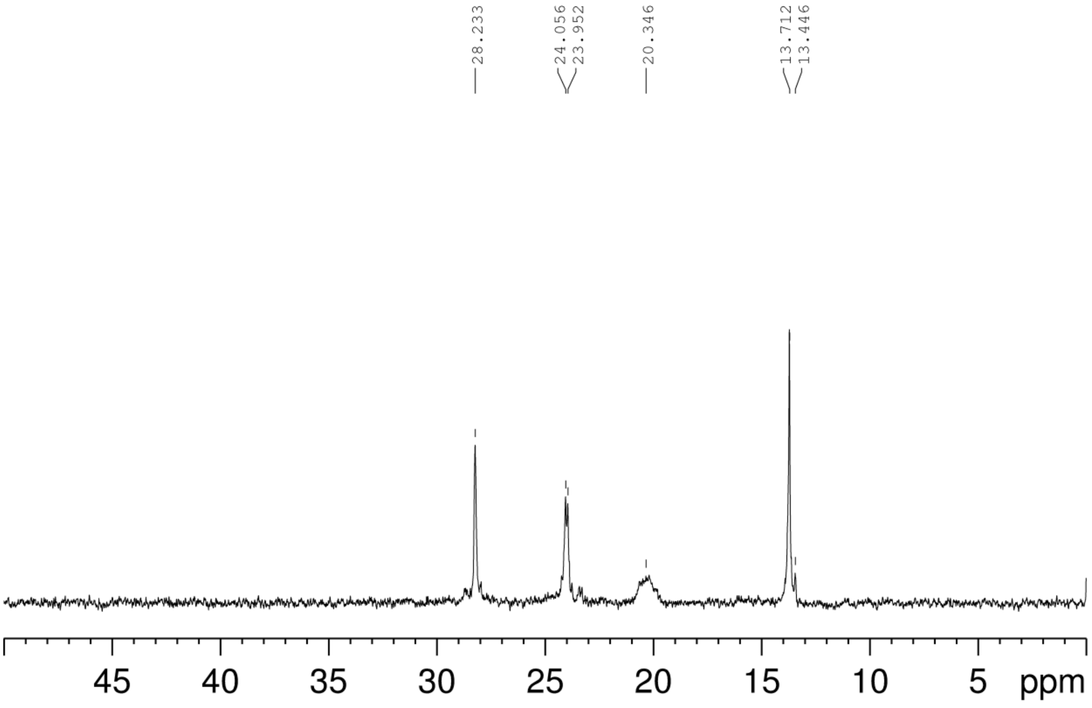

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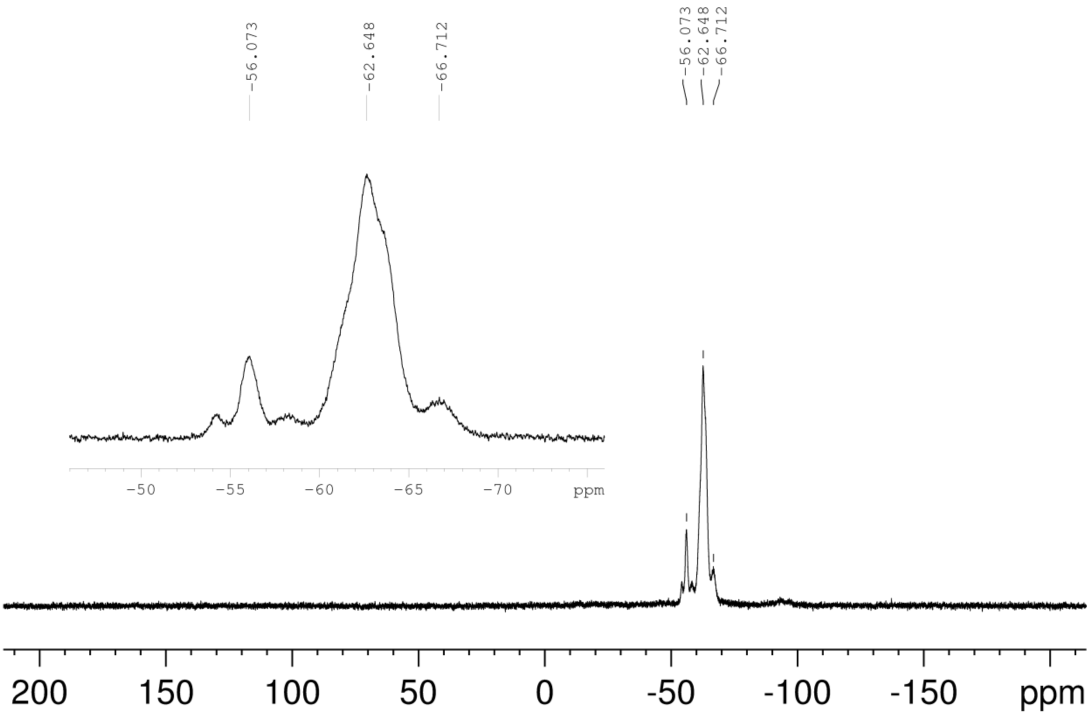
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-66.712
-50
-55
-60
-65
-70
ppm
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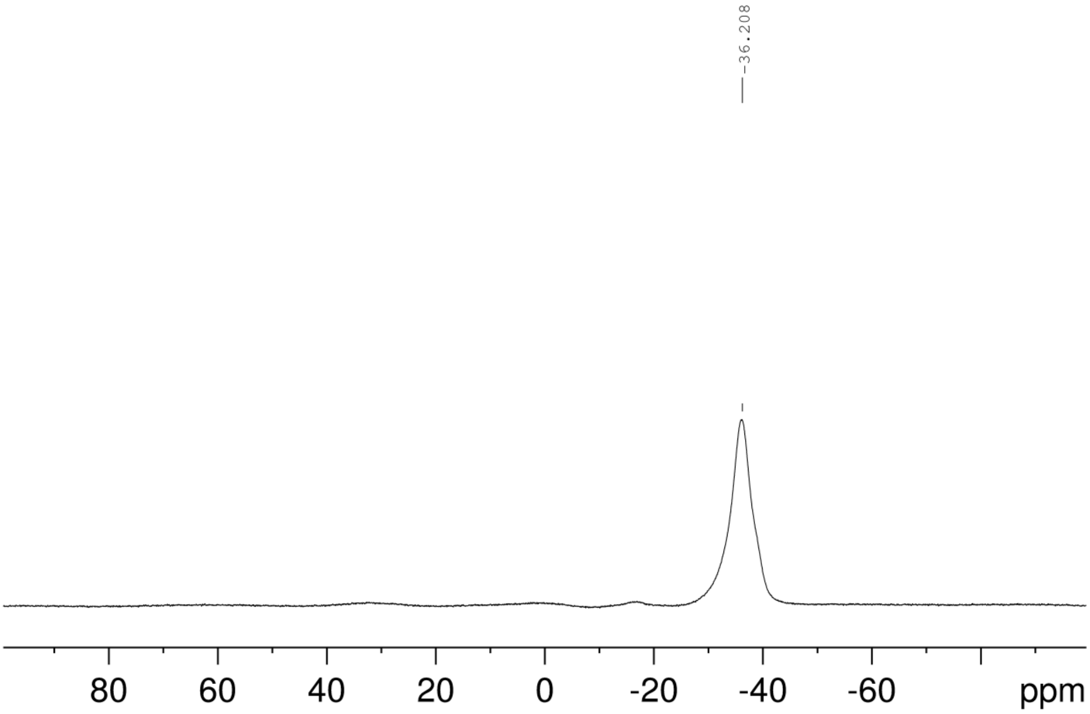
-62.648
-66.712
200
150
100
50
0
-50
-100
-150
ppm

^{11}B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20
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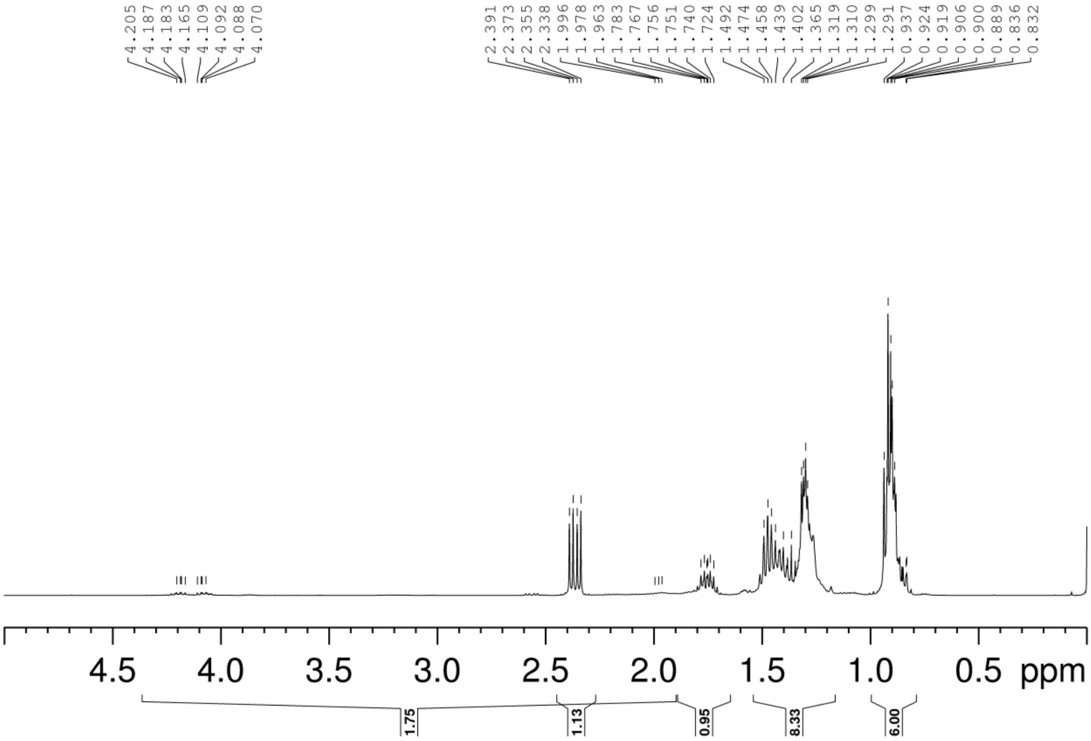
-20
-40
-60
ppm

Figure S7 - 2-(Ethylhexyl)PCl_2 (2c) NMR spectra

^1H



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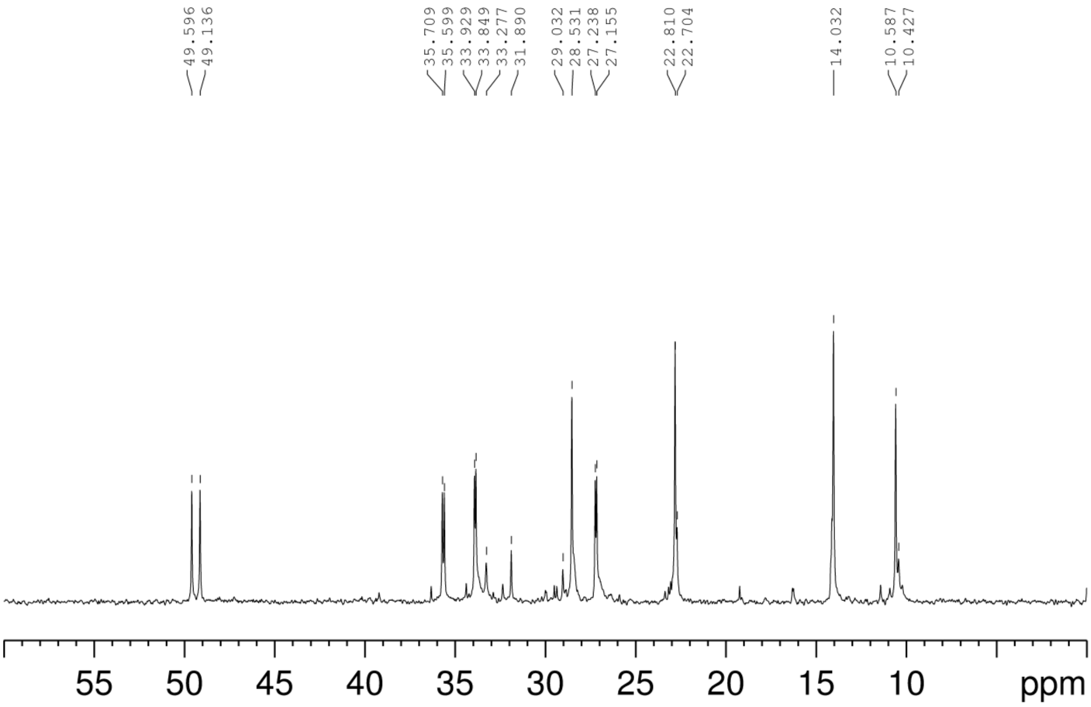
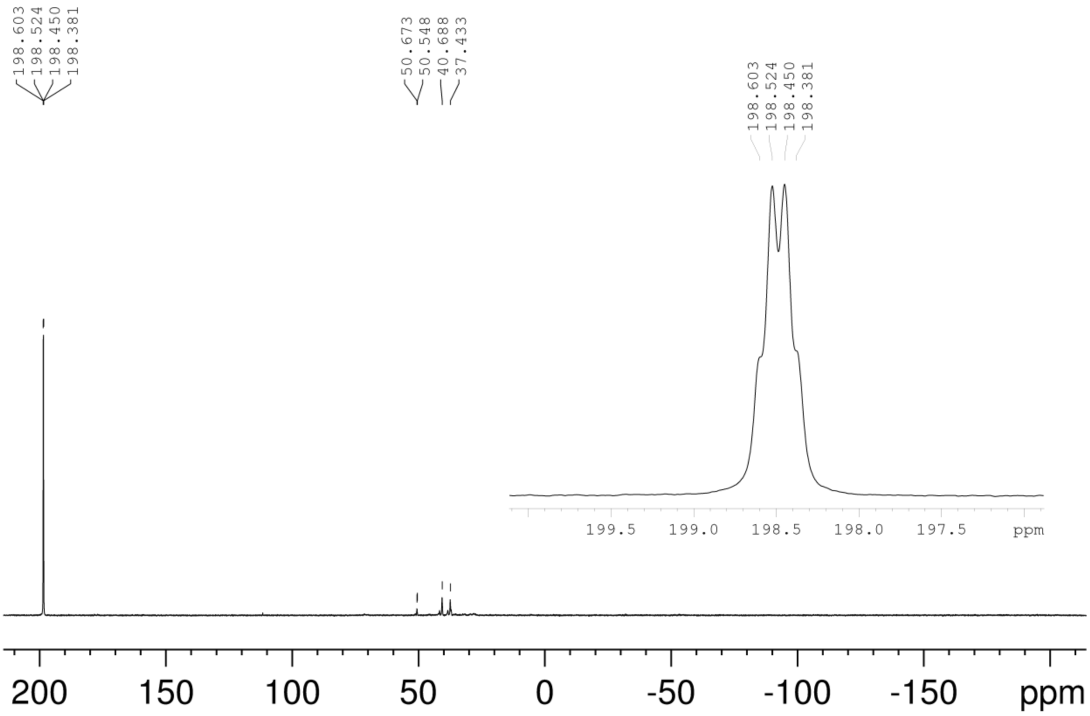


^{31}P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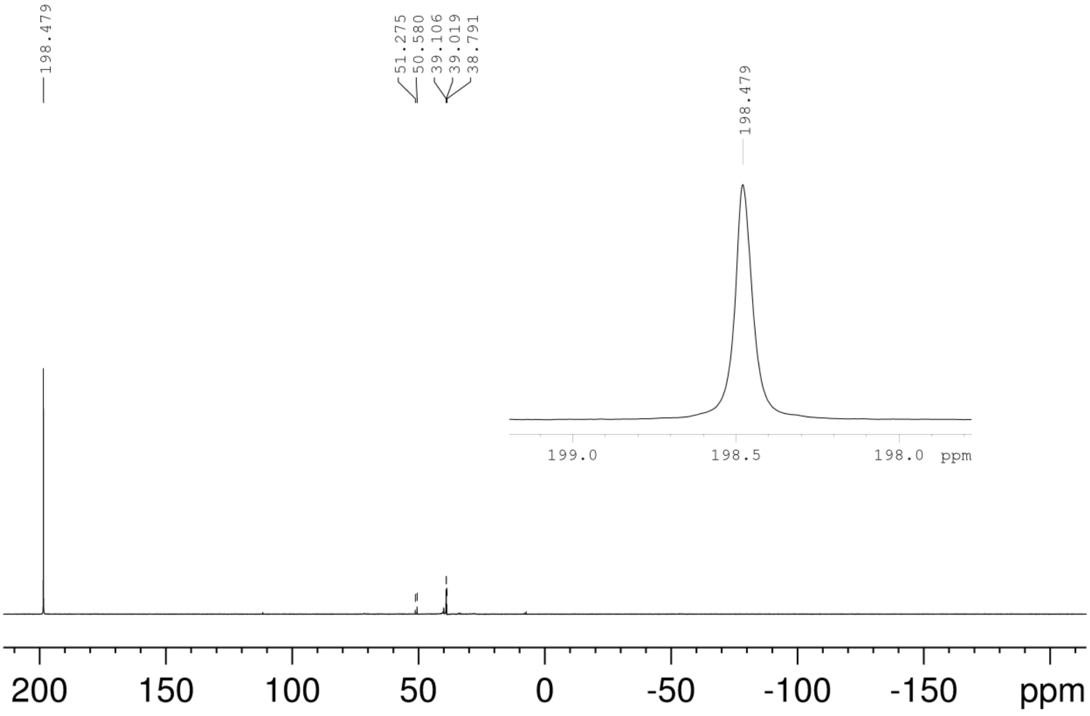
199.5
199.0
198.5
198.0
197.5
ppm
200
150
100
50
0
-50
-100
-150
ppm

$^{31}P\{^1H\}$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198.5
198.0
ppm
200
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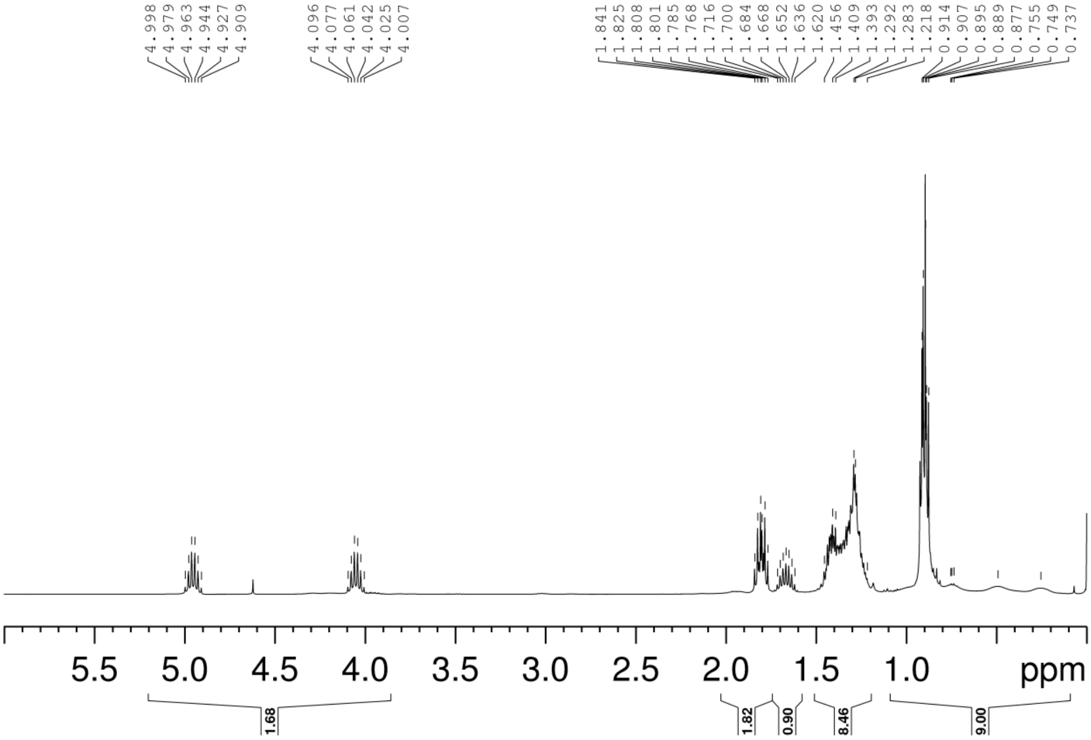
0
-50
-100
-150
ppm

Figure S8 - 2-(Ethylhexyl)$PH_2.BH_3$ (3c) NMR spectra

^1H



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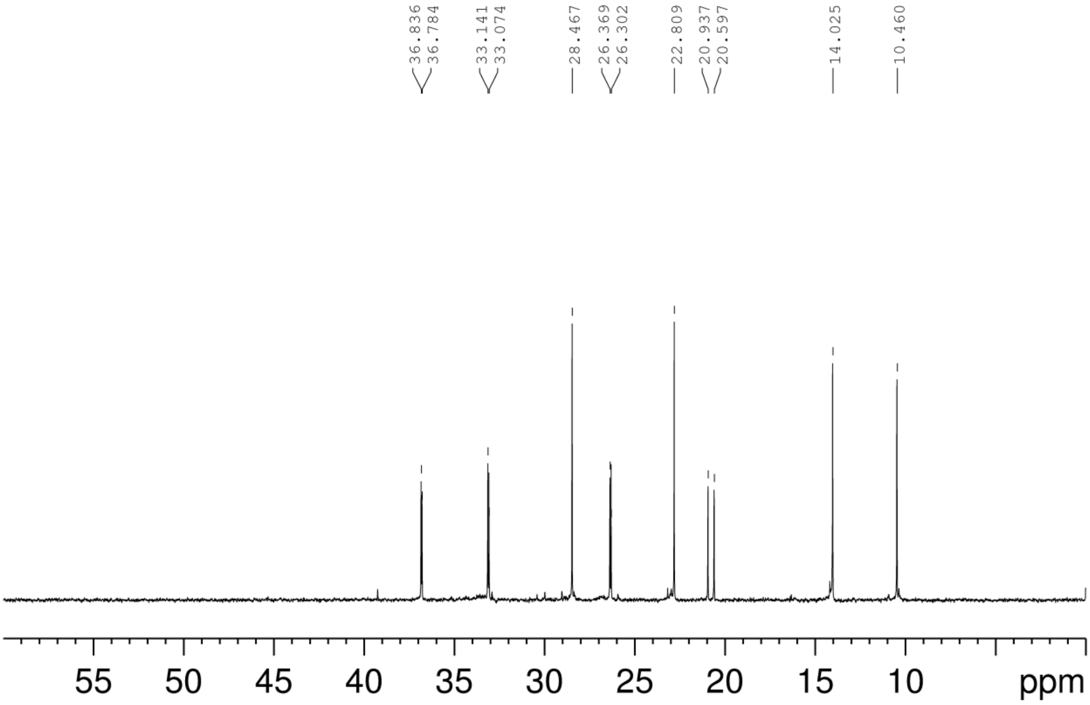

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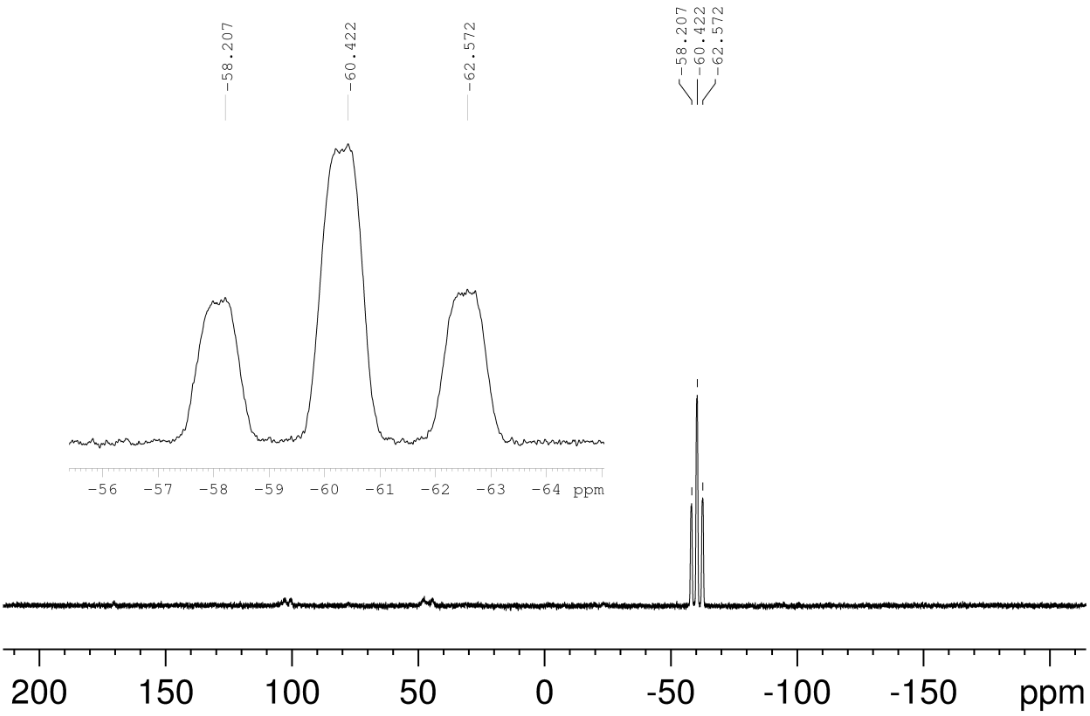

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-58
-59
-60
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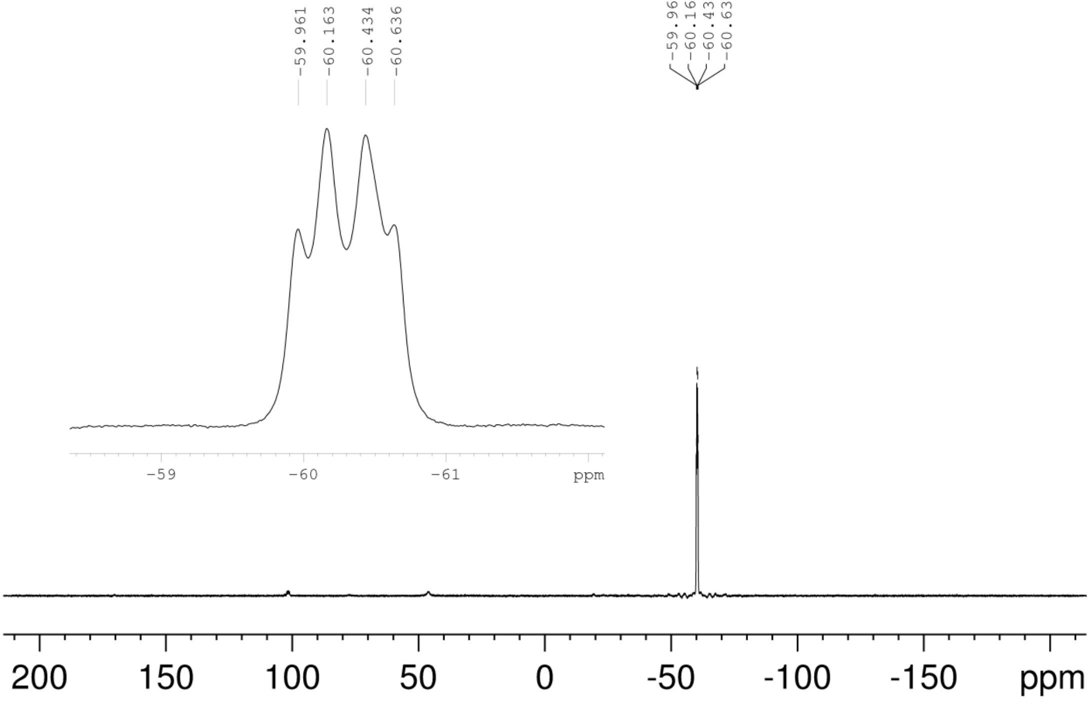
-150
ppm

$^{31}P\{^1H\}$



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-61
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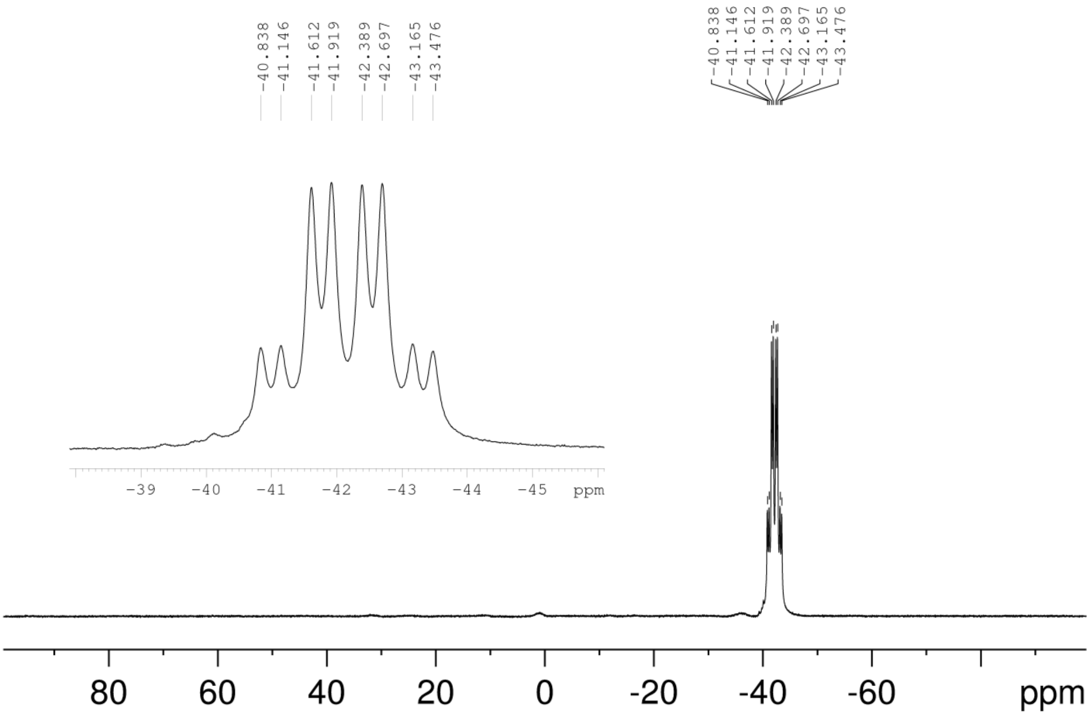
ppm

^{11}B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-44
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-42.389
-42.697
-43.165
-43.476
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40
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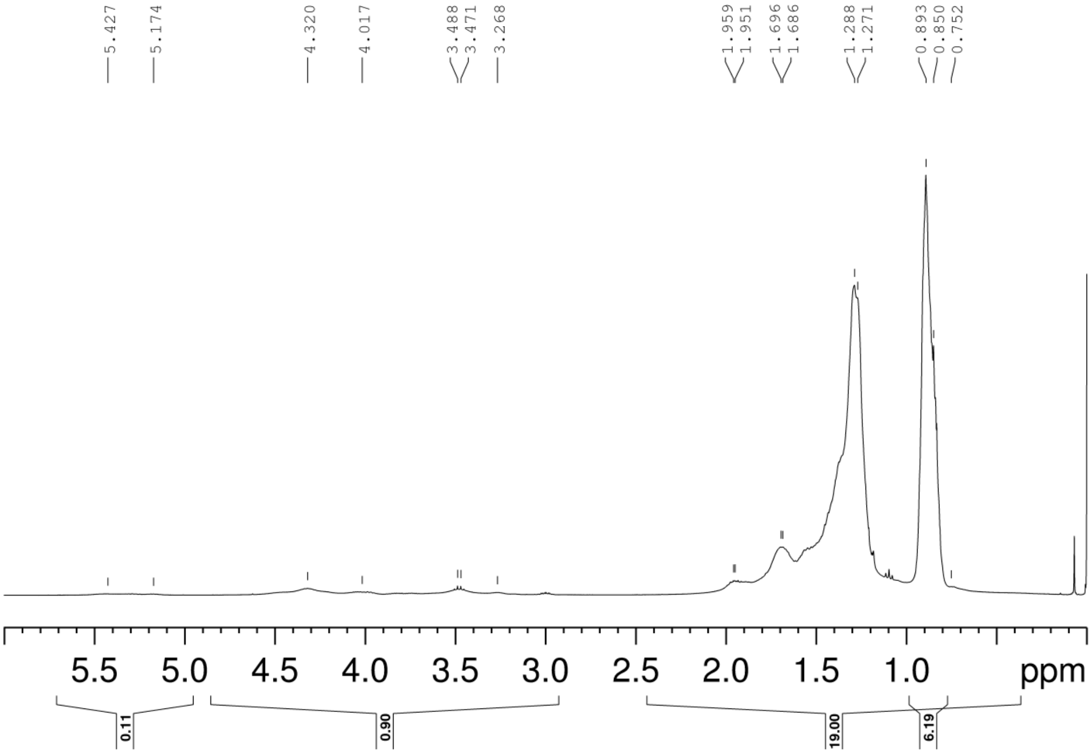
-60
ppm

Figure S9 - 2-(Ethylhexyl) phosphine-borane polymer (PEHPB) NMR spectra

^{1}H



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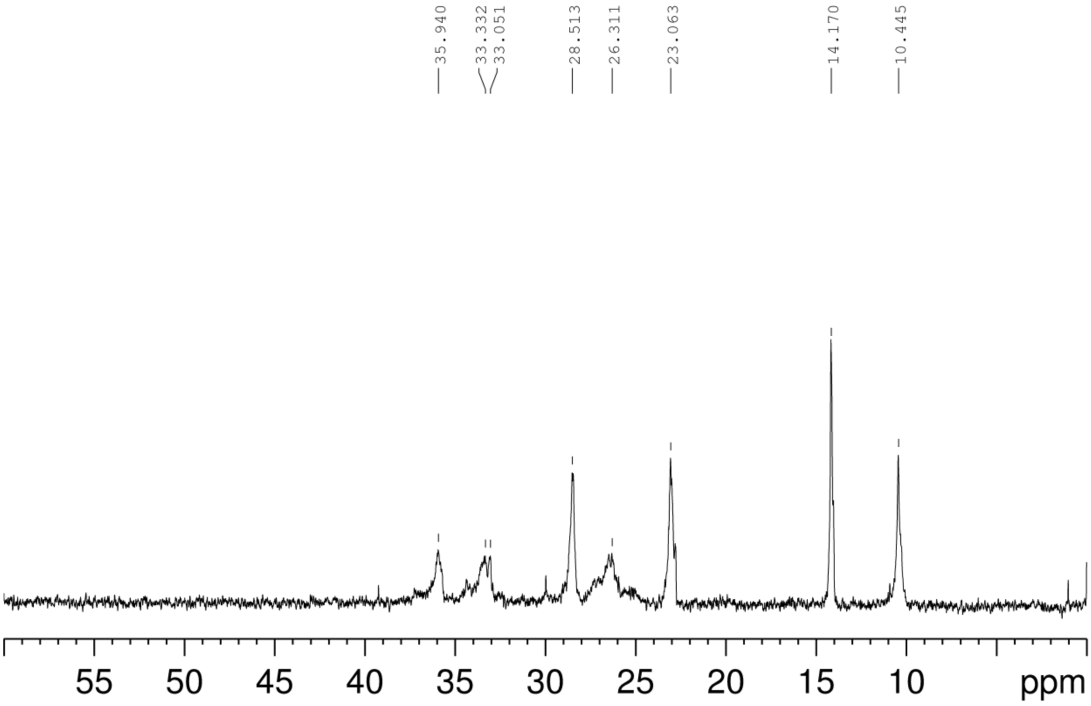

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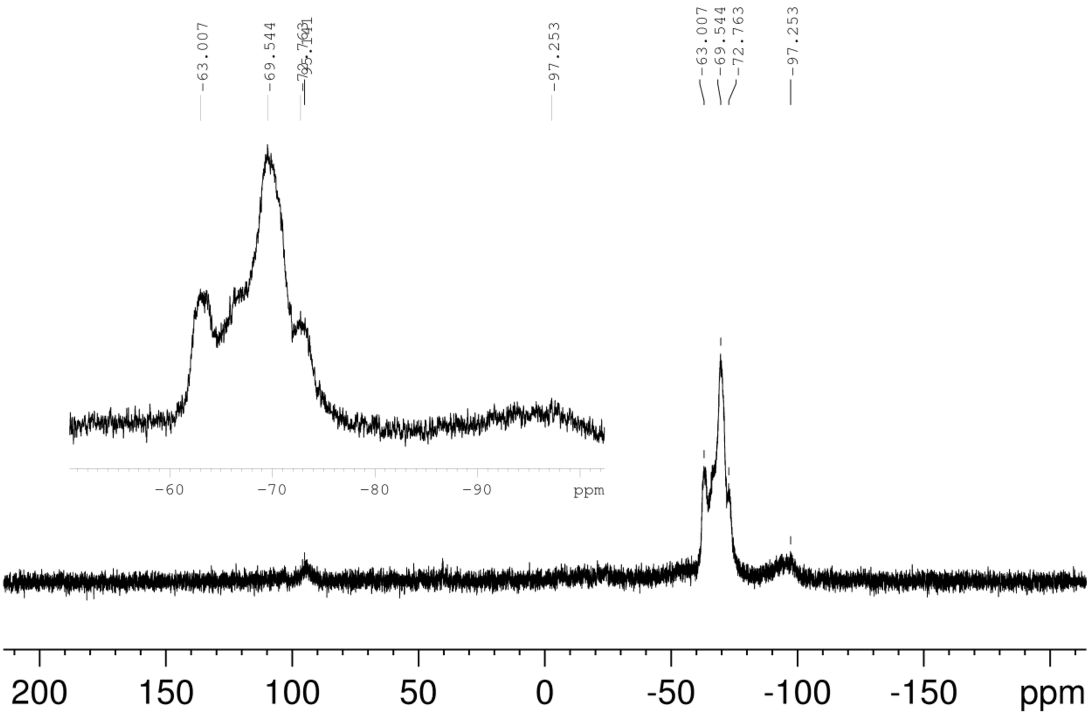
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-72.763
-95.141
-97.253
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-69.544
-72.763
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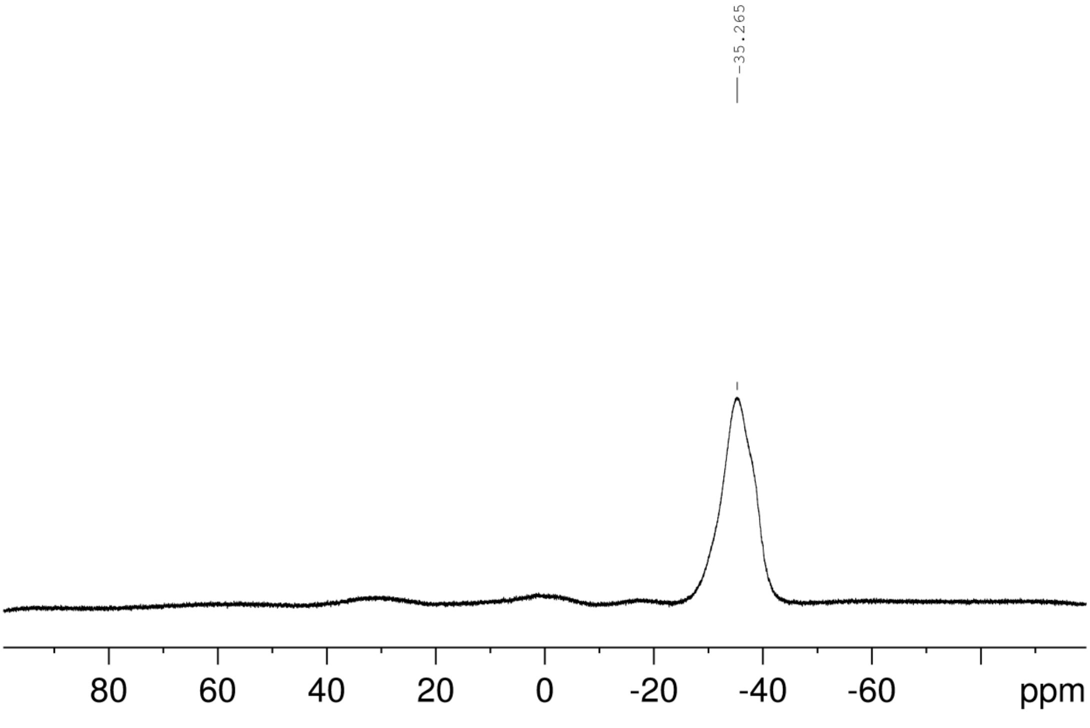
-70
-80
-90
ppm
200
150
100
50
0
-50
-100
-150
ppm

^{11}B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20
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-20
-40
-60
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Figure S10 - Rotational rheology of PHPB formed with 2 mol% catalyst loading at 25 °C

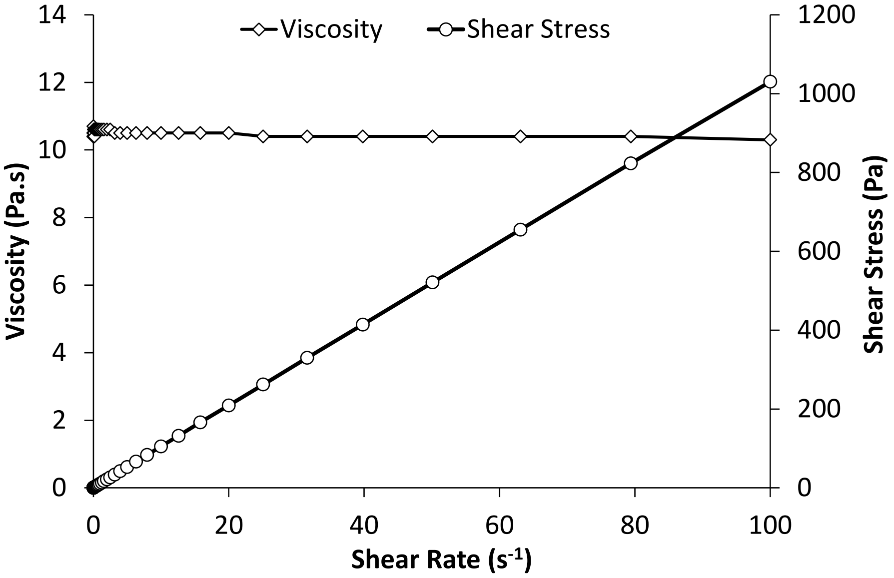


Figure S11 - DSC showing T_g curves for PHPB (solid line), PBPB (dashed line), and PEHPB (dotted line) samples from polymerisations using 2 mol% catalyst loading.

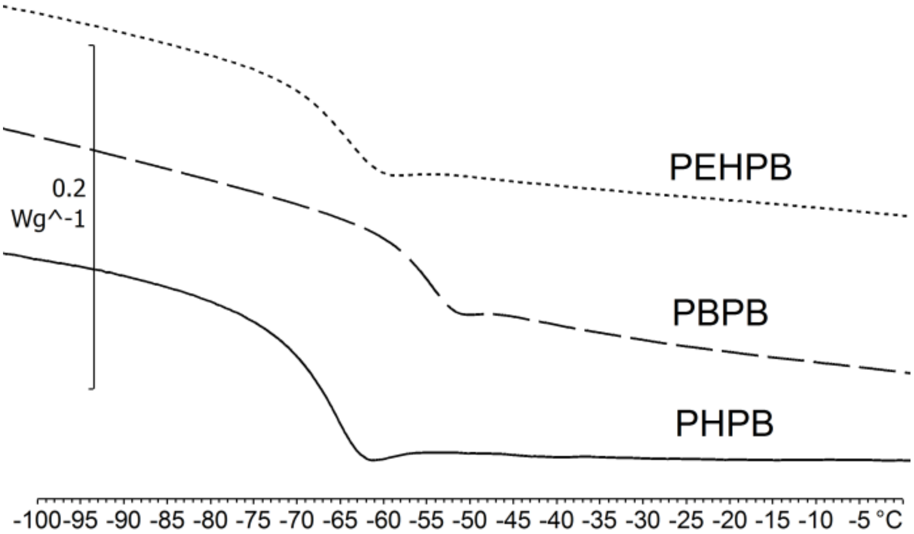


Figure S12 – GPC chromatogram (MV vs min) of sample PHPB from polymerisations using 0.5 mol% catalyst loading.

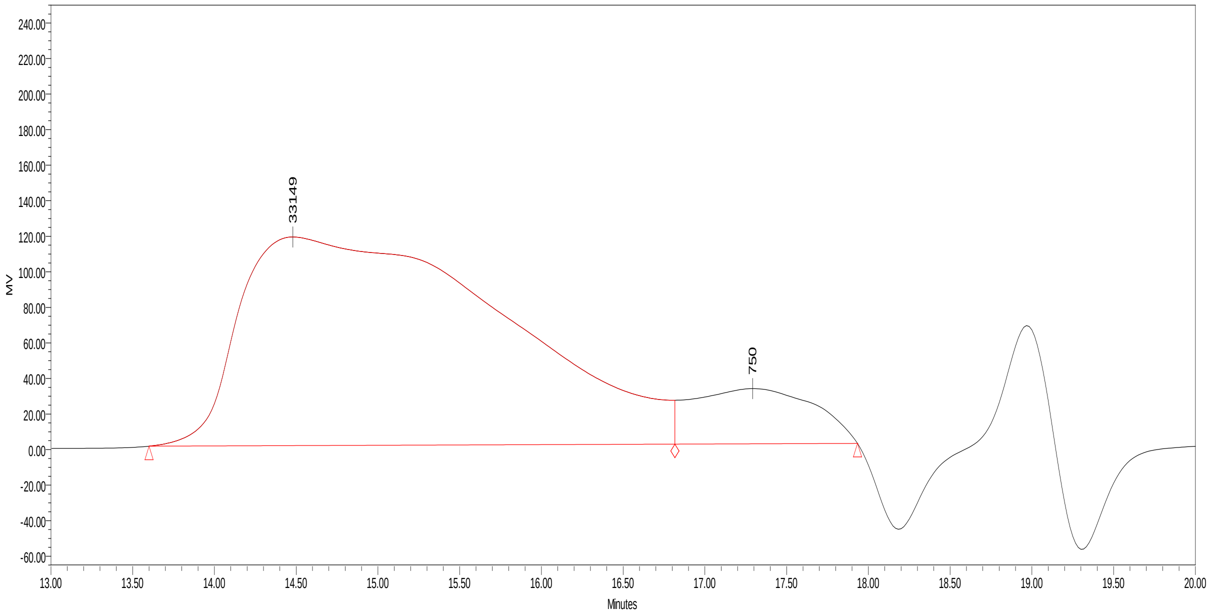


Figure S13 – GPC chromatogram (MV vs min) of sample PHPB from polymerisations using 2 mol% catalyst loading.

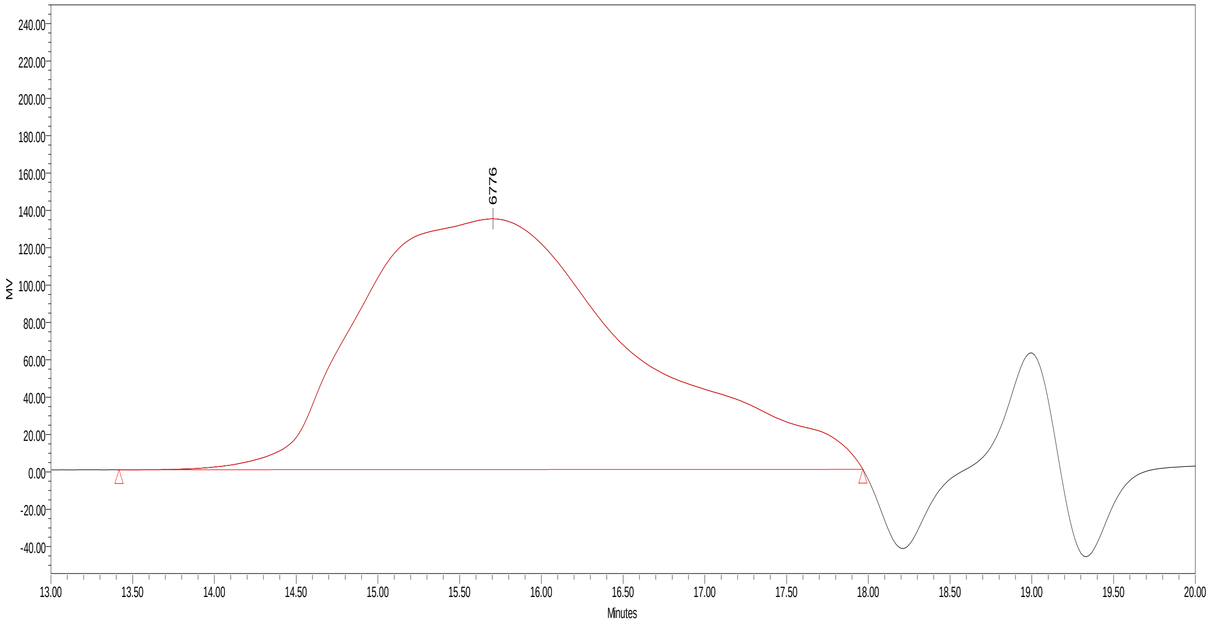


Figure S14 – GPC chromatogram (MV vs min) of sample PHPB from polymerisations using 5 mol% catalyst loading.

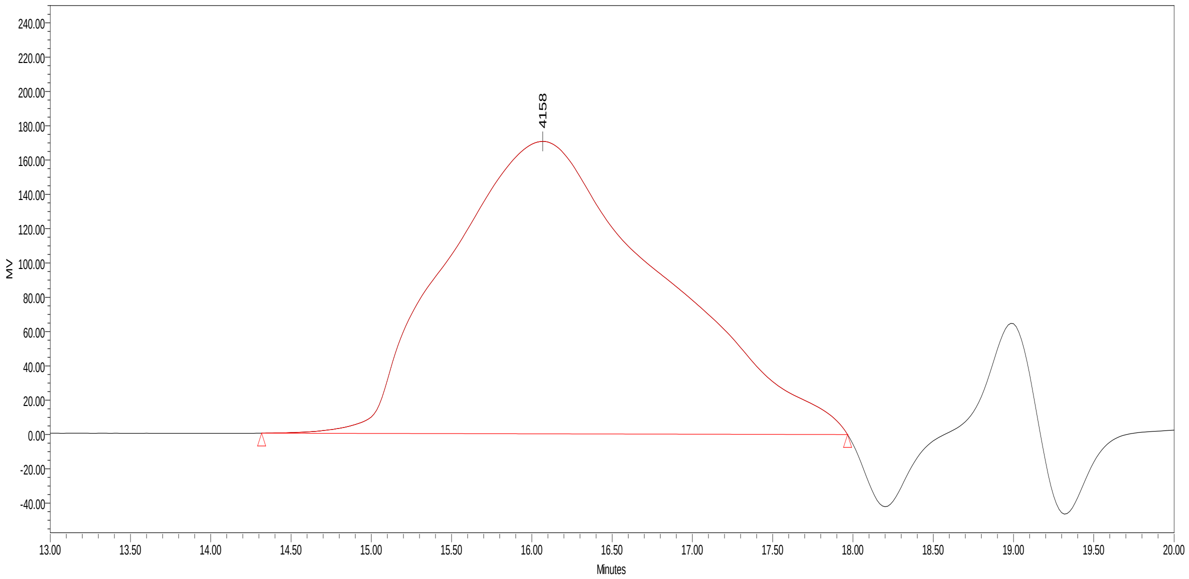


Figure S15 – GPC chromatogram (MV vs min) of sample PBPB from polymerisations using 2 mol% catalyst loading.

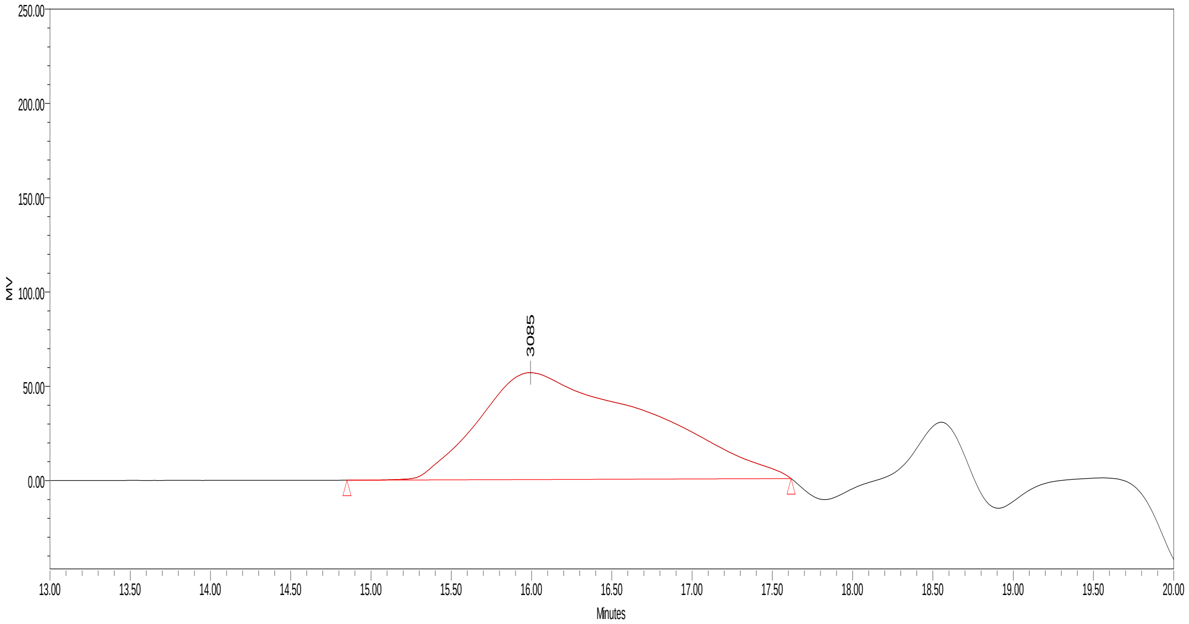


Figure S16 – GPC chromatogram (MV vs min) of sample PEHPB from polymerisations using 2 mol% catalyst loading.

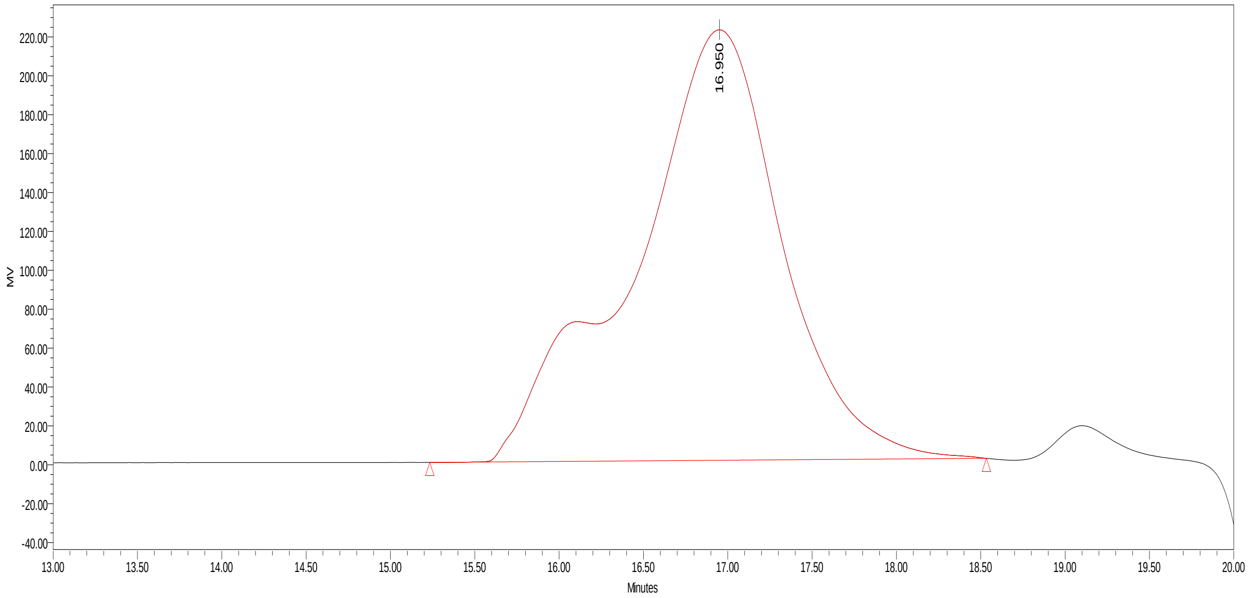
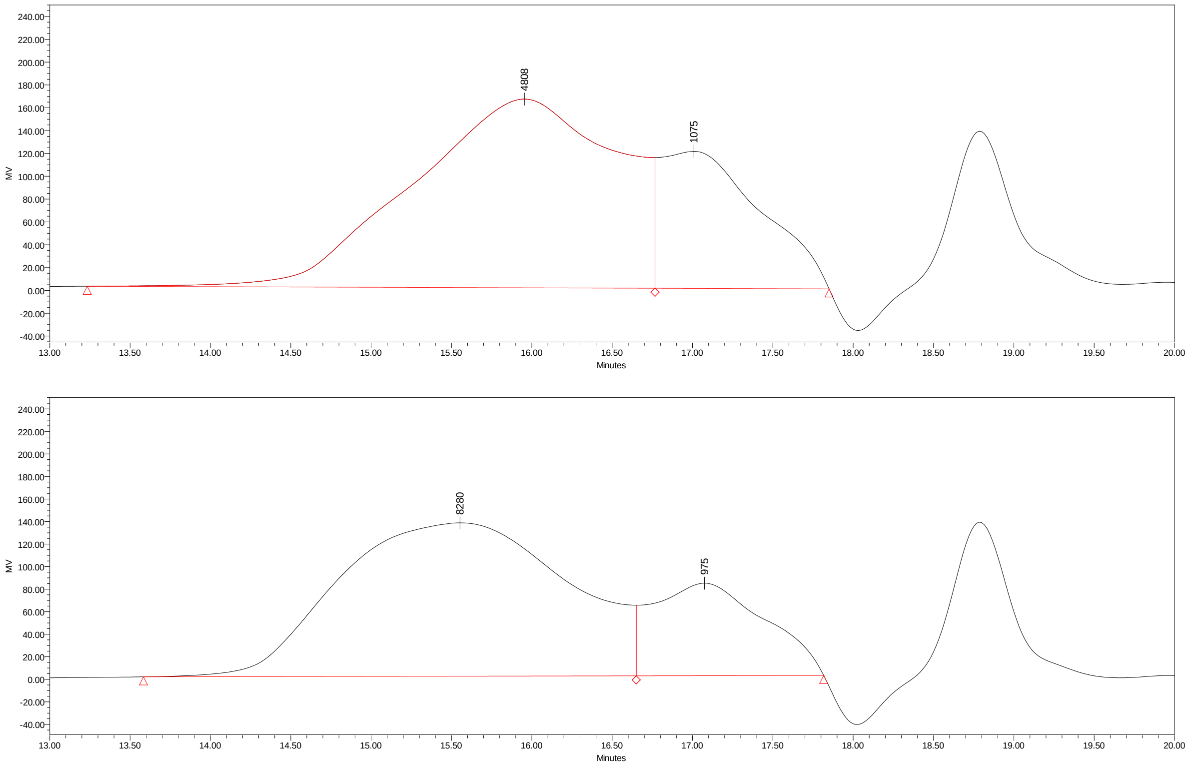


Figure S17 – GPC chromatograms (MV vs min) of PHPB sample before (top) and after heating (bottom) at 100 °C for 24 hours.



Group Interaction modelling (GIM)

GIM defines the glass transition temperature, T_g, as the temperature at 1Hz measurement rate and zero pressure of the peak in the loss tangent associated with the specific interaction. For a homopolymer this corresponds to the only alpha peak measured in a Dynamic Mechanical Analysis test. The peak appears because the number of skeletal degrees of freedom for the polymer increases by a factor 3/2 as the chains gain extra mobility through the glass transition; as well as being able to vibrate normal to the chain axis the polymer chains can start to move translationally relative to each other. The glass transition temperature is predicted using the following equation:

$$T_g = 0.224\,\theta_1 + 0.0513\,\frac{E_{coh}}{N}1 \tag{1}$$

where θ_1 is the 1-D Debye temperature of skeletal chain vibrations, E_{coh} is the cohesive energy of the polymer and N is the number of skeletal chain vibrations.

The 1-D Debye temperature is a measure of the characteristic timescale for vibrations in the polymer backbone. For –C-C- chains this is well established and, for trans conformers, is well predicted based upon the mass of the mer unit relative to polymethylene. If M_{av} is taken to be the mass of the mer unit, M, divided by the number of backbone atoms then:

$$\theta_1 = 550\,\sqrt{\frac{14}{M_{av}}}\,Kelvin \tag{2}$$

Such a relation is not available for phosphine-borane chains but it will be presumed to follow equation 2 with the 14 Daltons for polymethylene being replaced with 42 Daltons for P+B and M_{av} being replaced by M (the mers of the current compounds are all two chain units long). Actual values could be calculated by molecular mechanics methods or measured experimentally and this is recommended.

Cohesive energy is calculated by group contribution methods.

Group contribution values used in predictions of cohesive energy

Group	E_{coh} (J/mol)
$-CH_n-$	4500
P	9500
B	14000

The number of skeletal degrees of freedom for a mer unit in GIM is also calculated by a group contribution method but following selection rules:

- Main chain atoms have N=2
  - Unless they are phenyl groups which have N=5 for para-rings and N=6 for meta-rings
- Side chain atoms have N=1
  - Unless it is a phenyl group which acts as a unit with N=2
  - The group at the end of the side chain has N=2
- H atoms do not contribute to degrees of freedom

These are simple rules and do not take into account the complex interactions that are found in some polymers where hindrance or pinning by other groups can reduce the available degrees of freedom or where extra degrees of freedom due to crankshaft modes become available.