

Double deboronation and homometalation of 1,1'-bis(*ortho*-carborane)

Gobika Thiripuranathar, Antony P. Y. Chan, Dipendu Mandal, Wing Y. Man, Mario Argentari, Georgina M. Rosair and Alan J. Welch

Electronic Supplementary Information

A. ^1H and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of all new compounds reported.

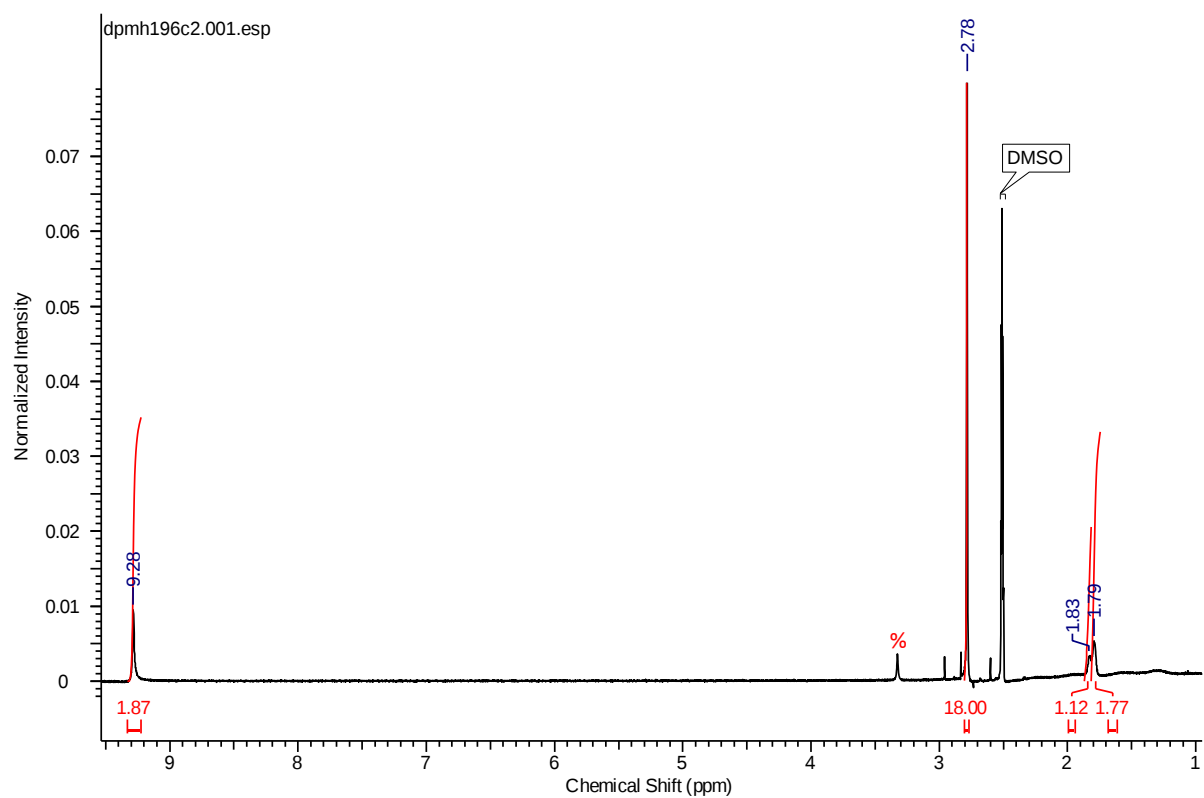
% water

* CHCl_3

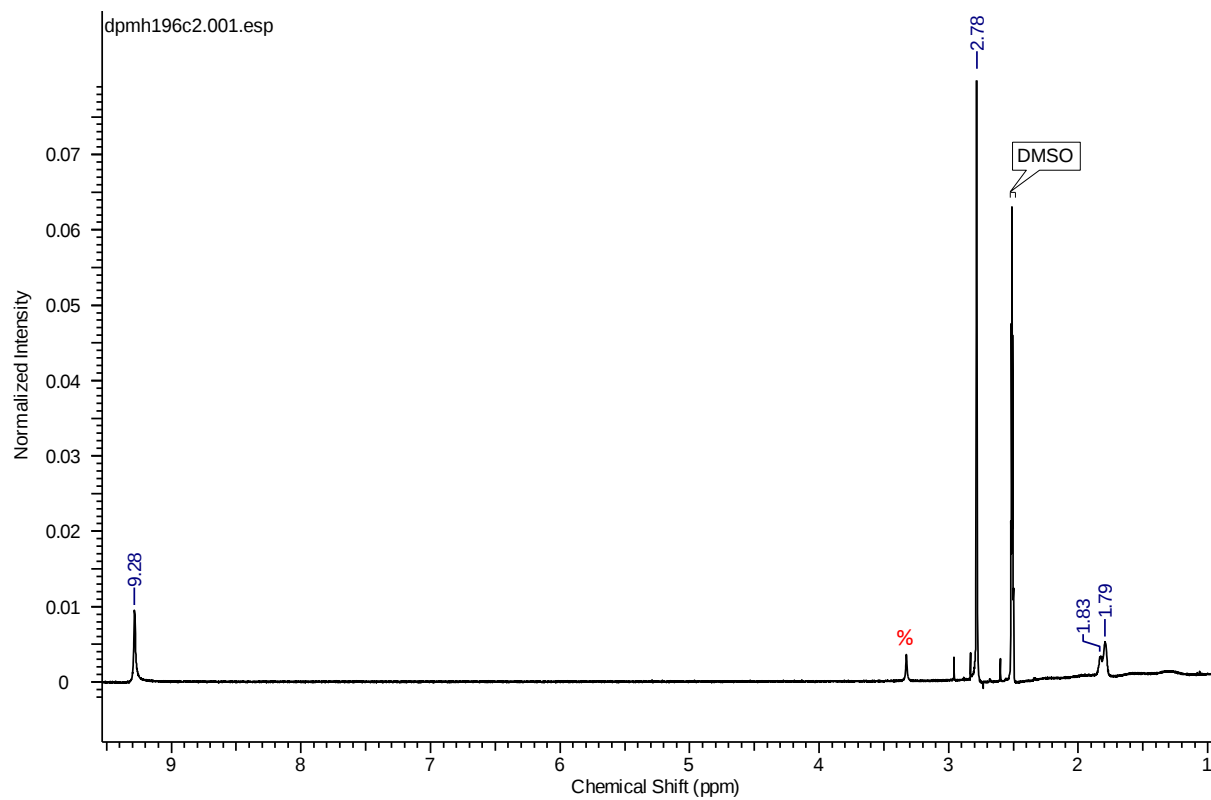
CH_2Cl_2

≠ unknown impurity (compound 3α and 3β)

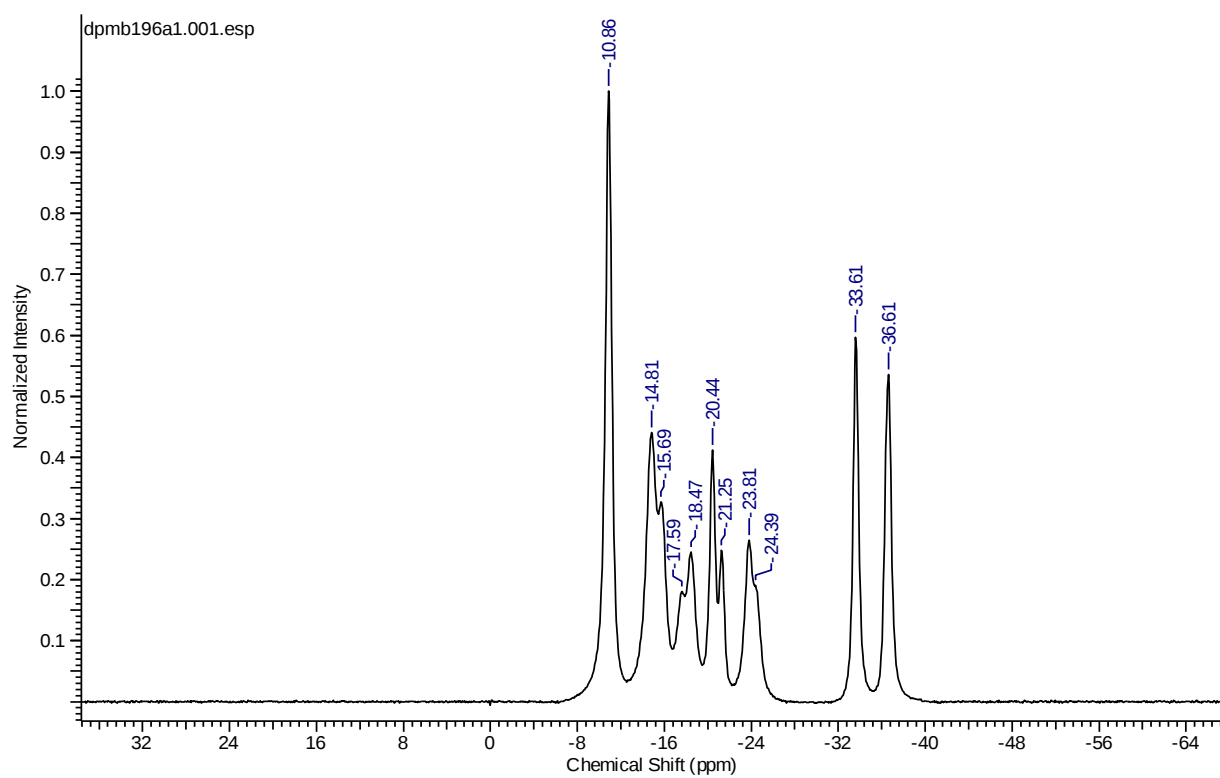
[HNMe₃]₂**1**: [HNMe₃]₂[7-(7'-7',8'-nido-C₂B₉H₁₁)-7,8-nido-C₂B₉H₁₁]
¹H NMR (with integration)



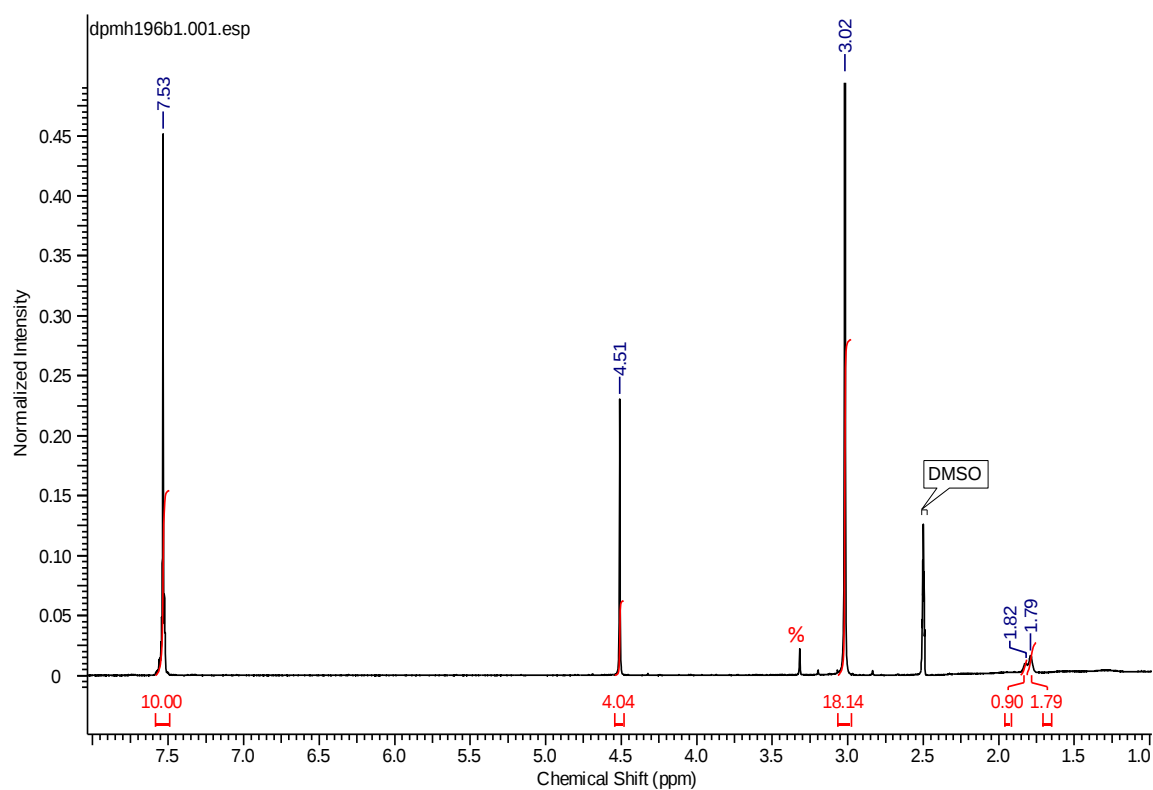
¹H NMR (without integration)



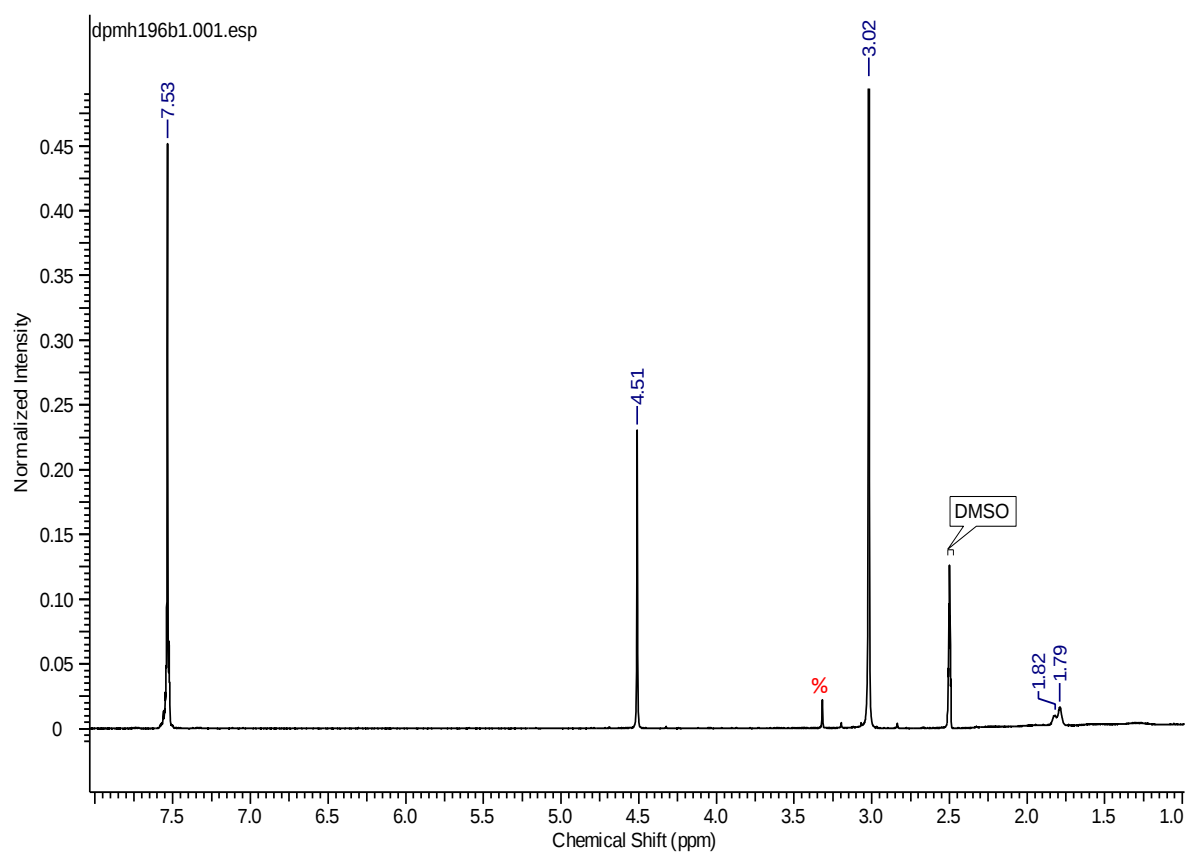
$^{11}\text{B}\{^1\text{H}\}$ NMR



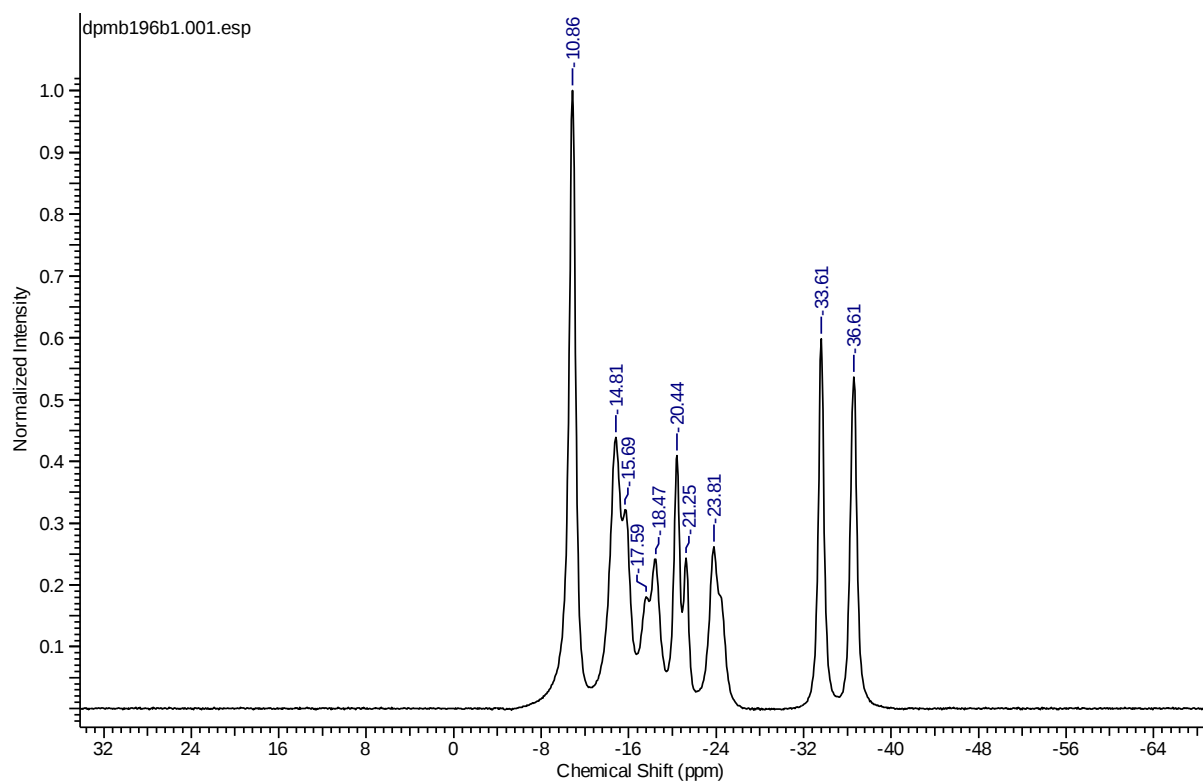
[BTMA]₂1: [BTMA]₂[7-(7'-7',8'-nido-C₂B₉H₁₁)-7,8-nido-C₂B₉H₁₁]
¹H NMR (with integration)



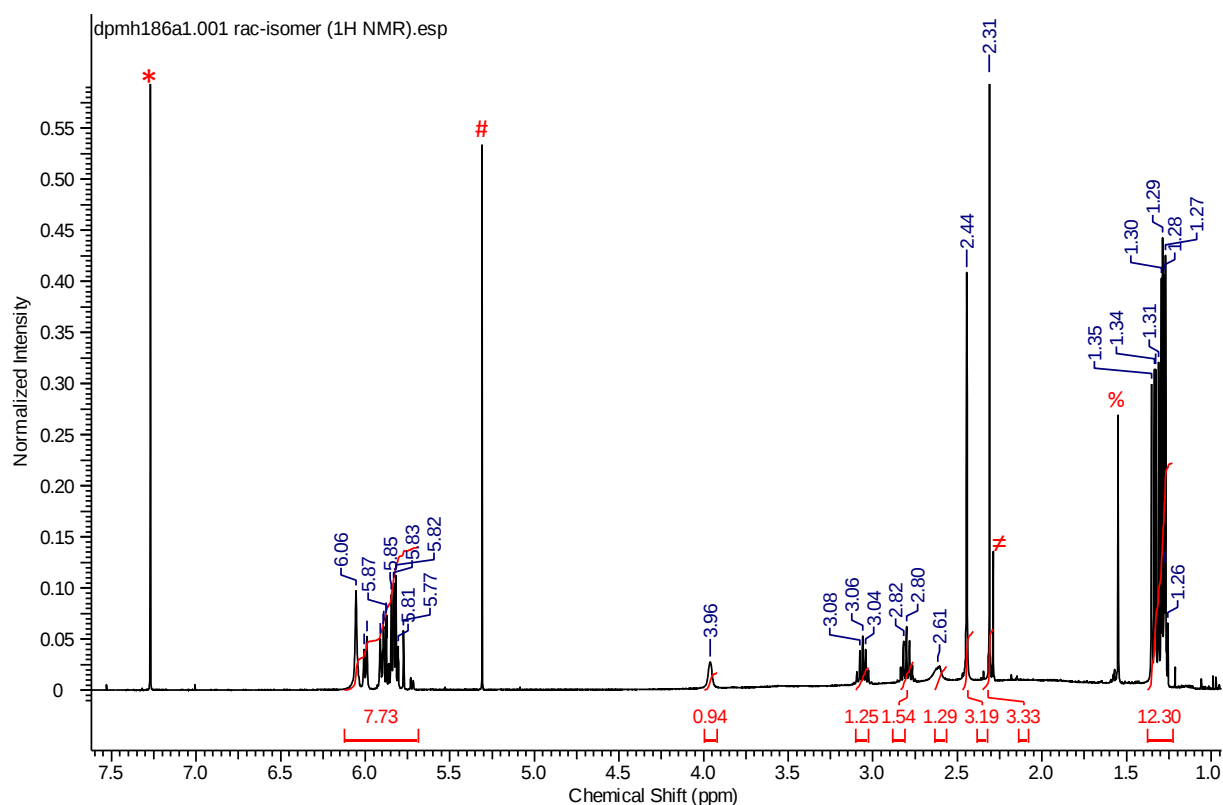
¹H NMR (without integration)



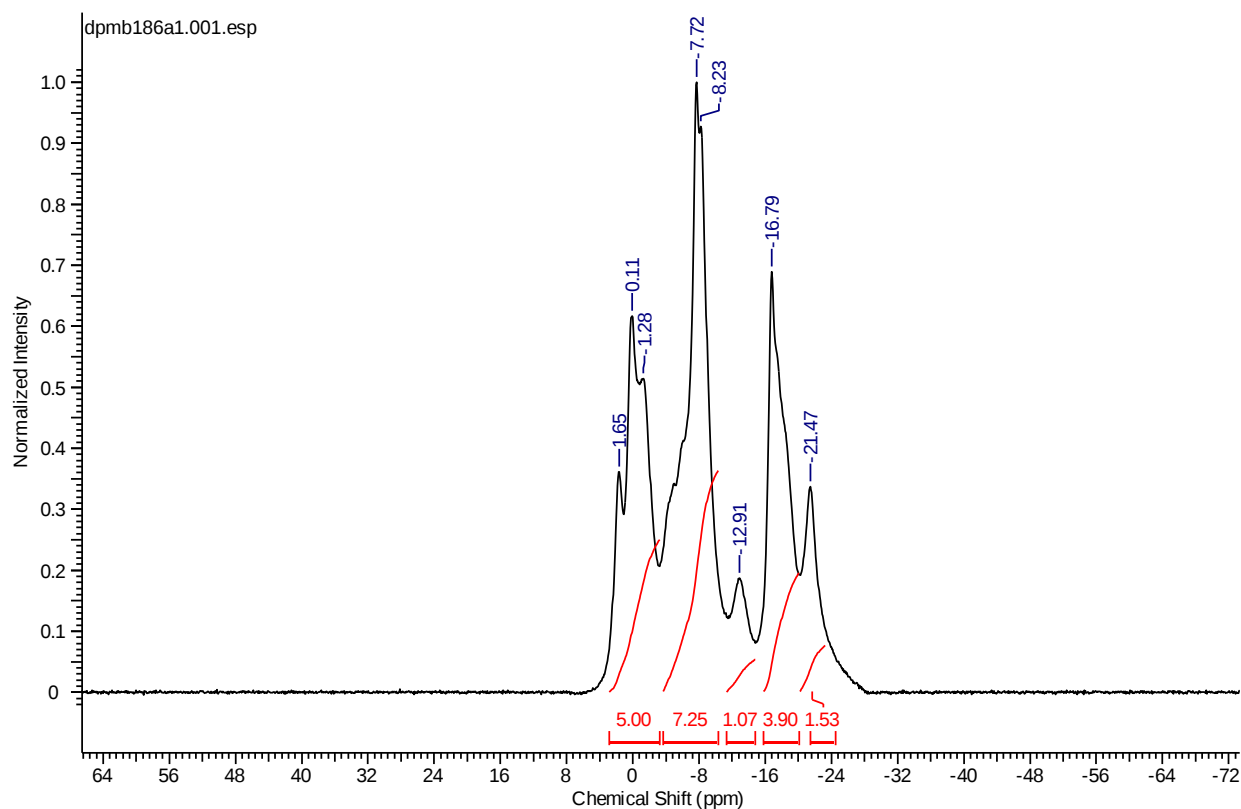
$^{11}\text{B}\{^1\text{H}\}$ NMR



Compound **3α**: α -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC₂B₉H₁₀)-3-(*p*-cymene)-*closo*-3,1,2-RuC₂B₉H₁₀]
¹H NMR

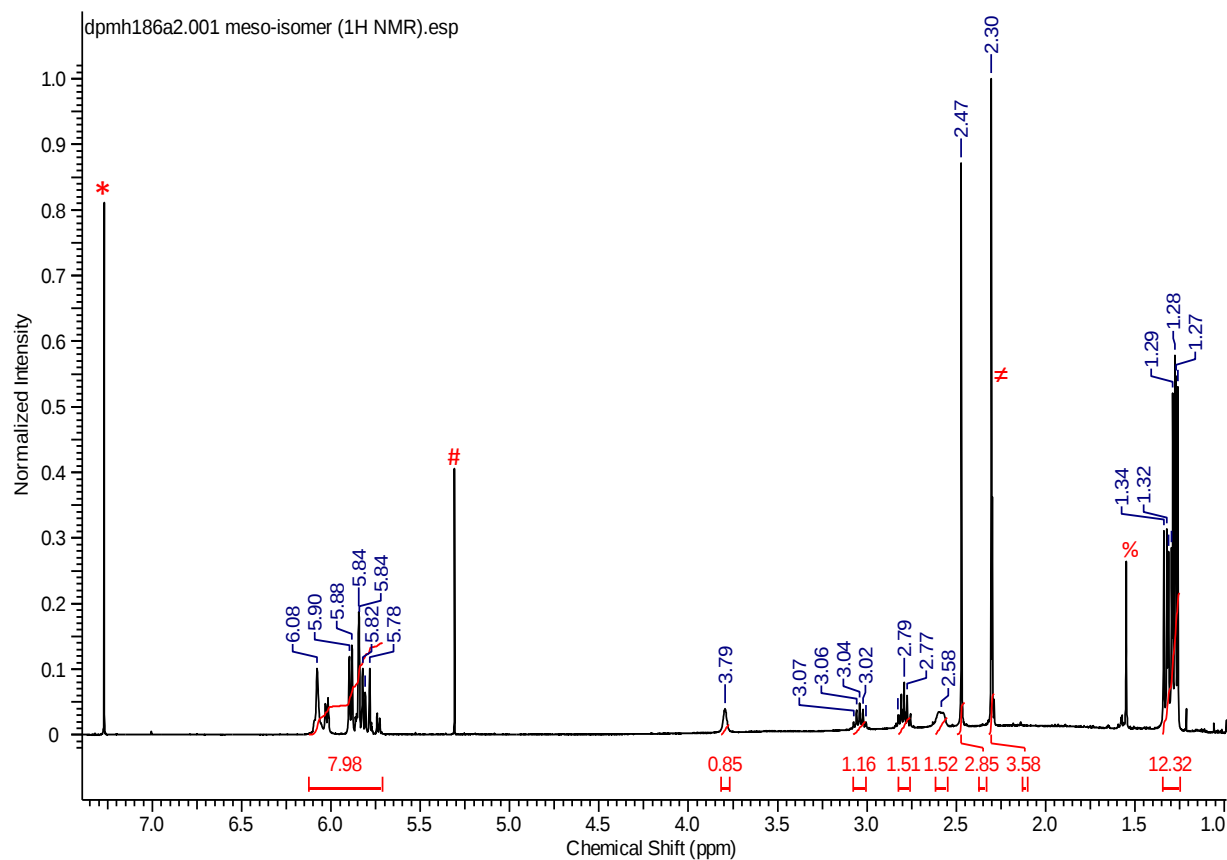


¹¹B{¹H} NMR

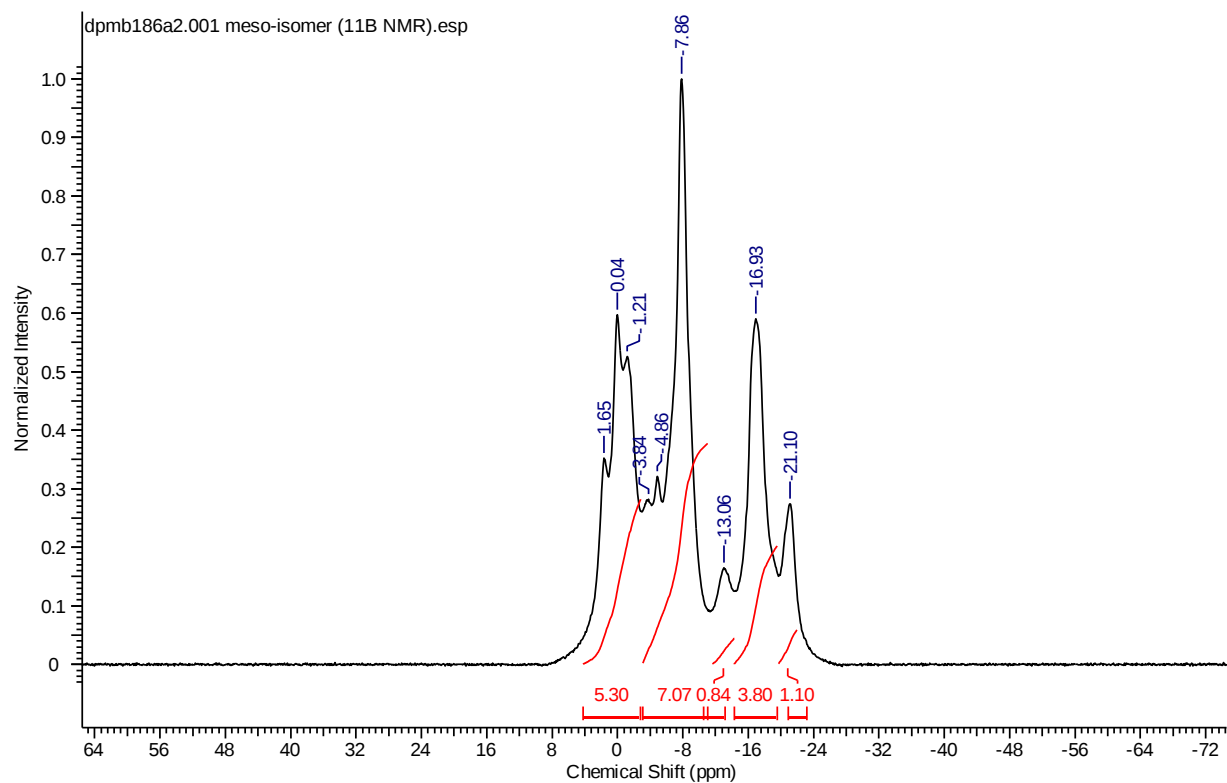


Compound **3 β** : β -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC₂B₉H₁₀)-3-(*p*-cymene)-*closo*-3,1,2-RuC₂B₉H₁₀]

¹H NMR

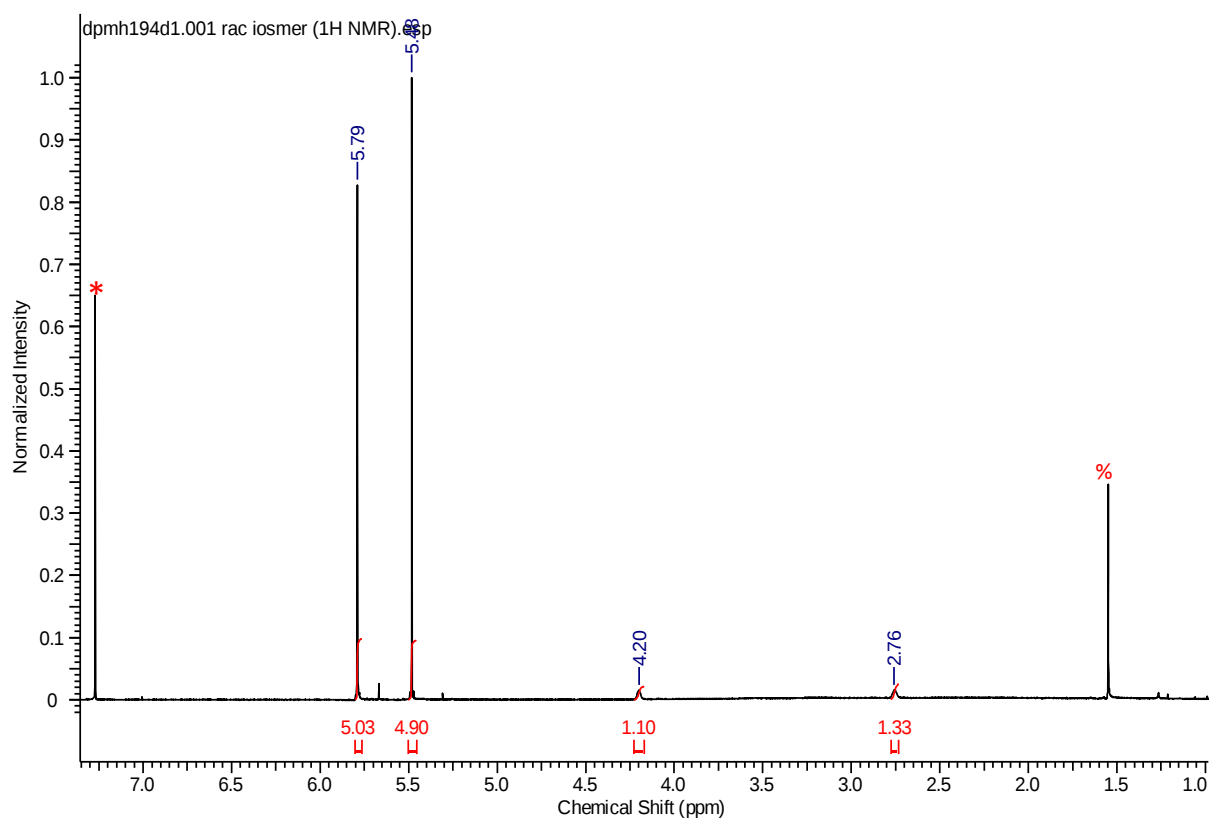


¹¹B{¹H} NMR

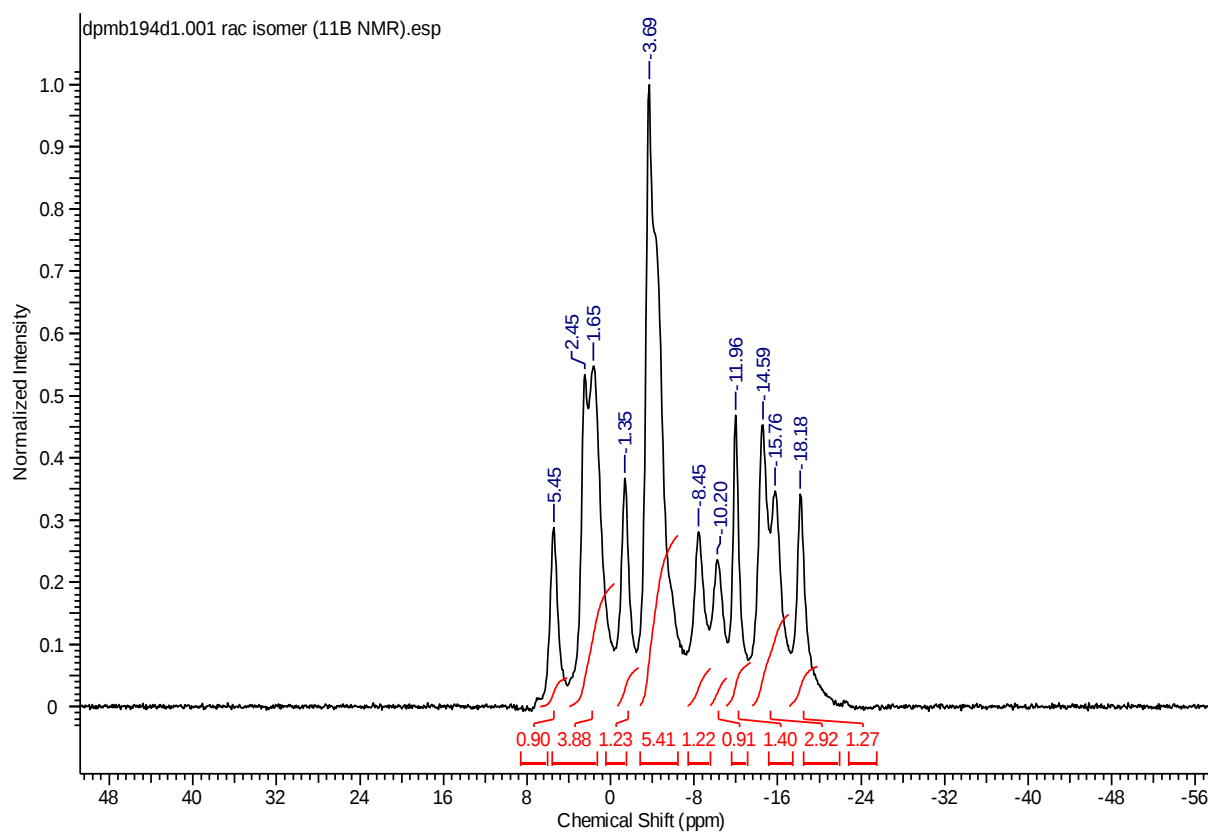


Compound **4a**: α -[1-(8'-2'-Cp-2',1',8'-closo-CoC₂B₉H₁₀)-3-Cp-3,1,2-closo-CoC₂B₉H₁₀]

¹H NMR

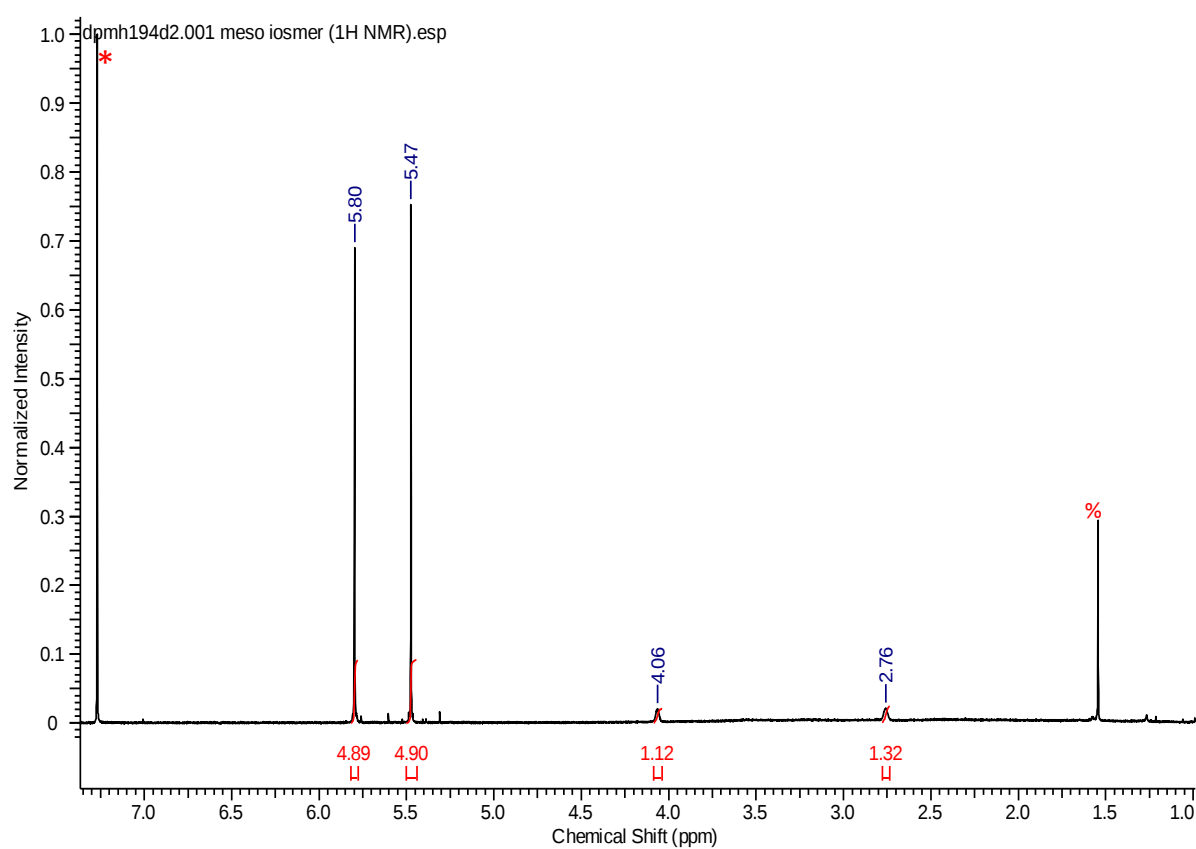


¹¹B{¹H} NMR

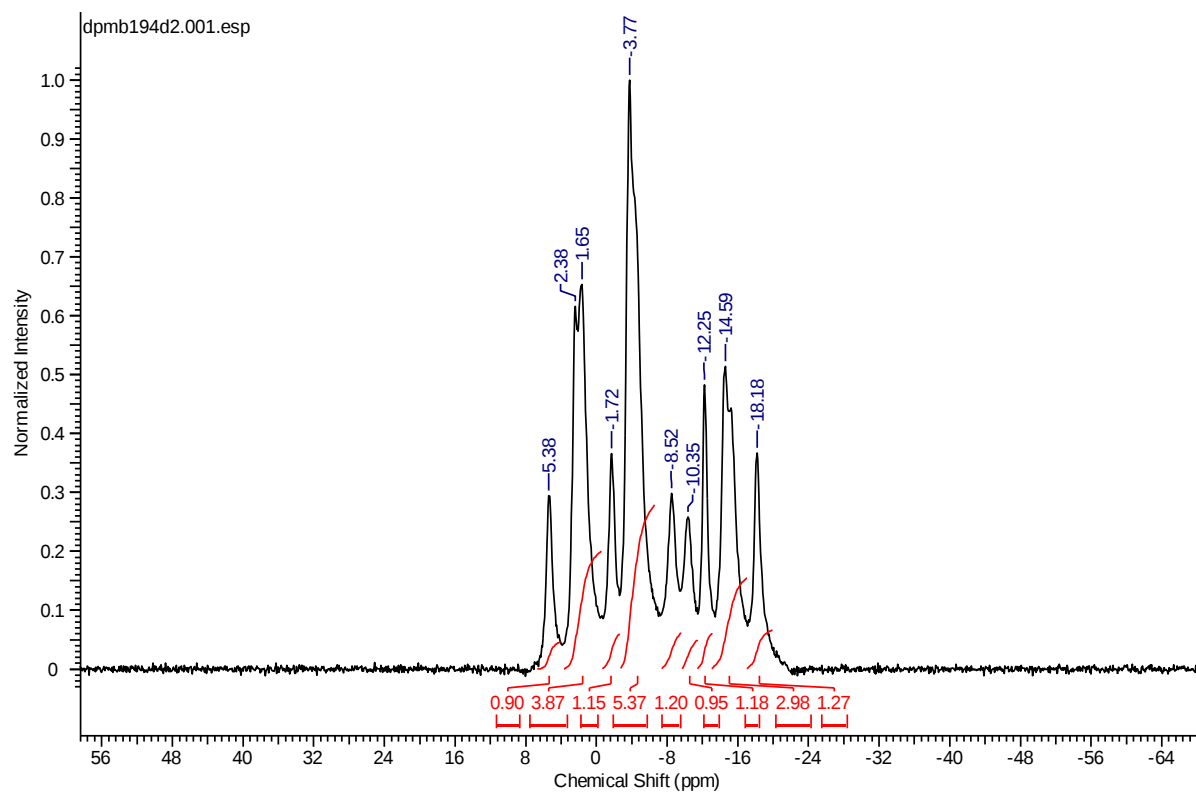


Compound **4 β** : β -[1-(8'-2'-Cp-2',1',8'-*closo*-CoC₂B₉H₁₀)-3-Cp-3,1,2-*closo*-CoC₂B₉H₁₀]

¹H NMR

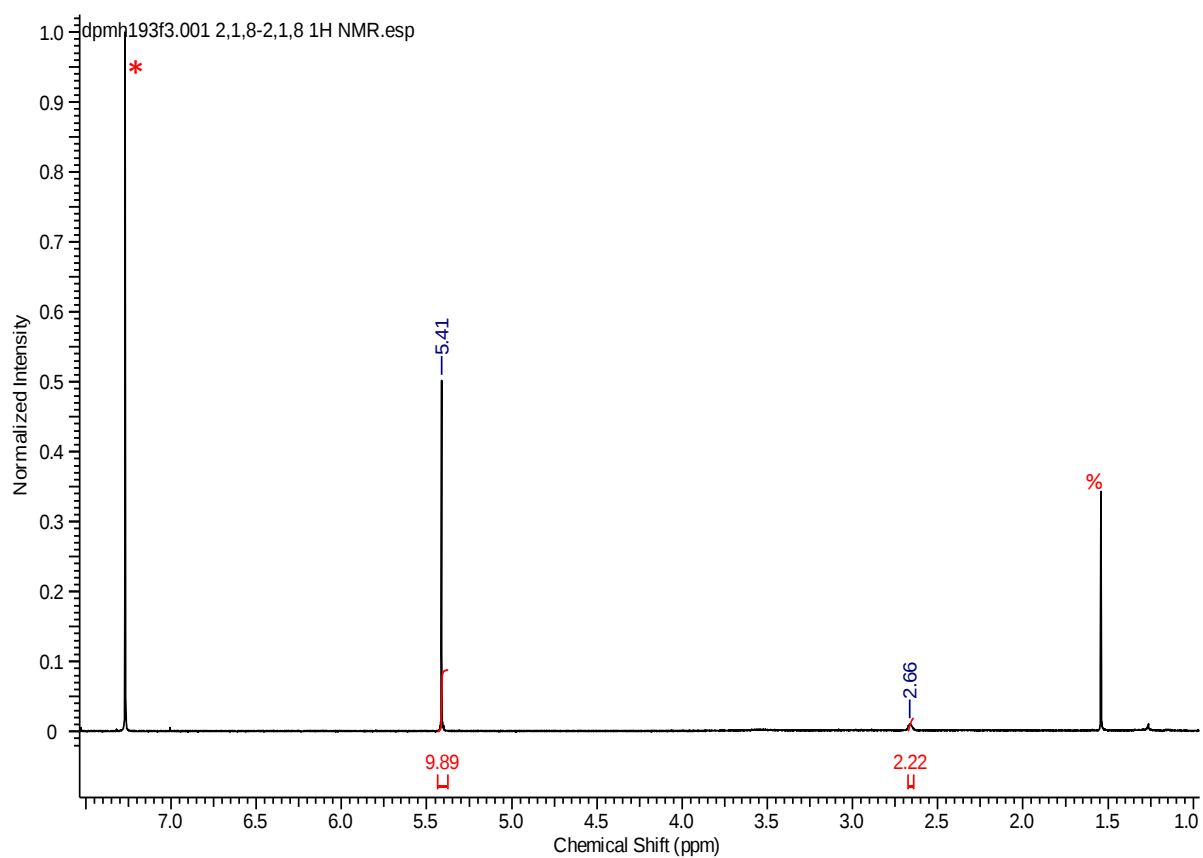


¹¹B{¹H} NMR

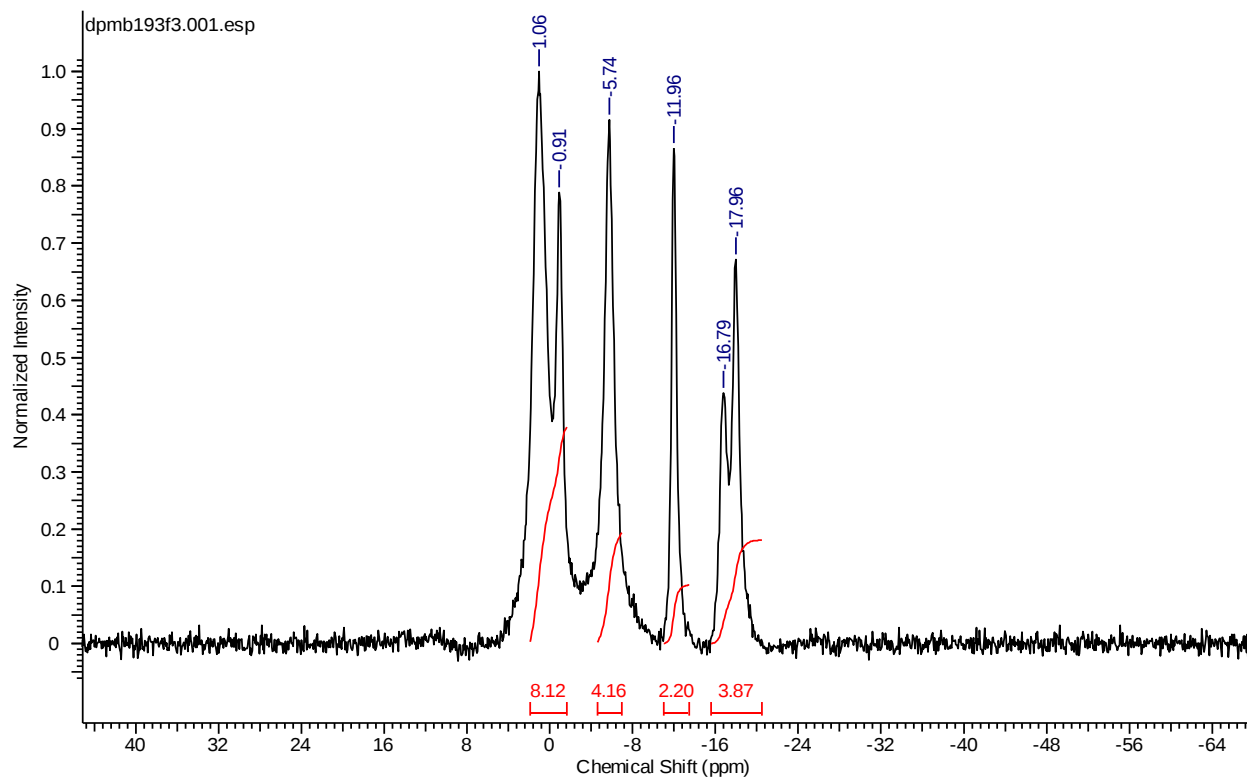


Compound 5: [8-(8'-2'-Cp-2',1',8'-*closo*-CoC₂B₉H₁₀)-2-Cp-2,1,8-*closo*-CoC₂B₉H₁₀]

¹H NMR

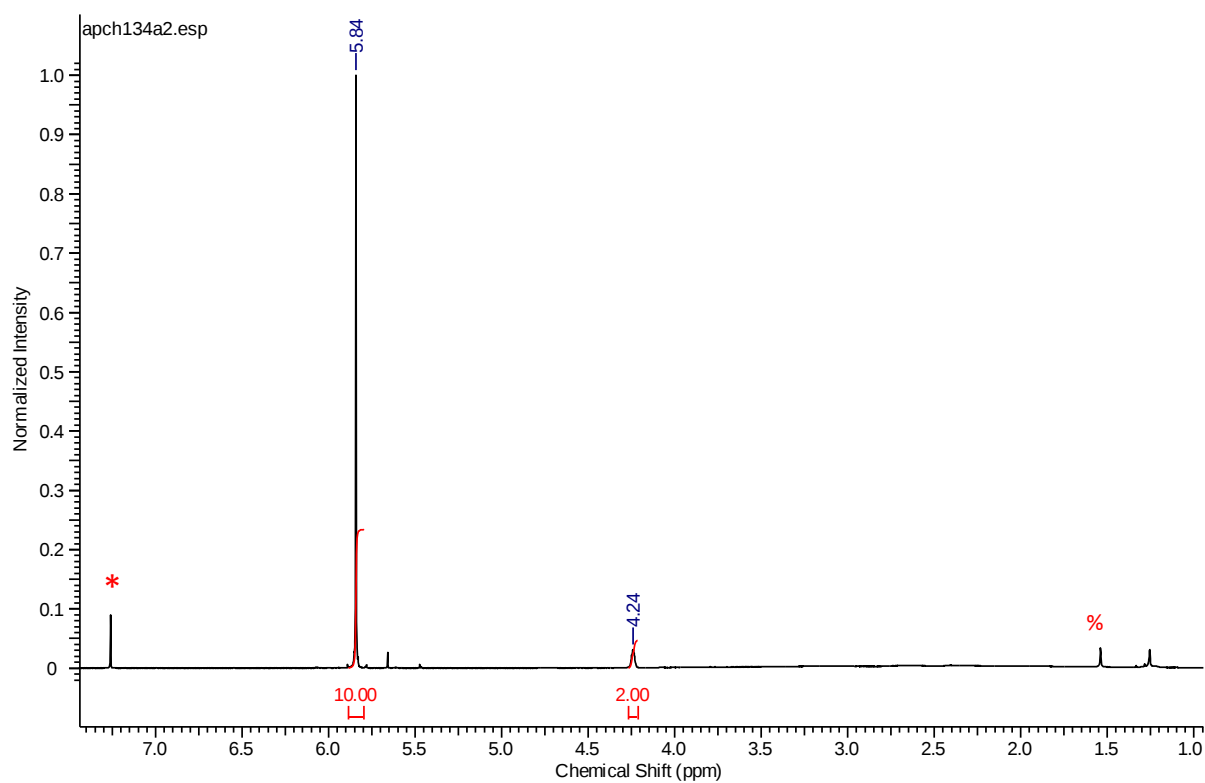


¹¹B{¹H} NMR

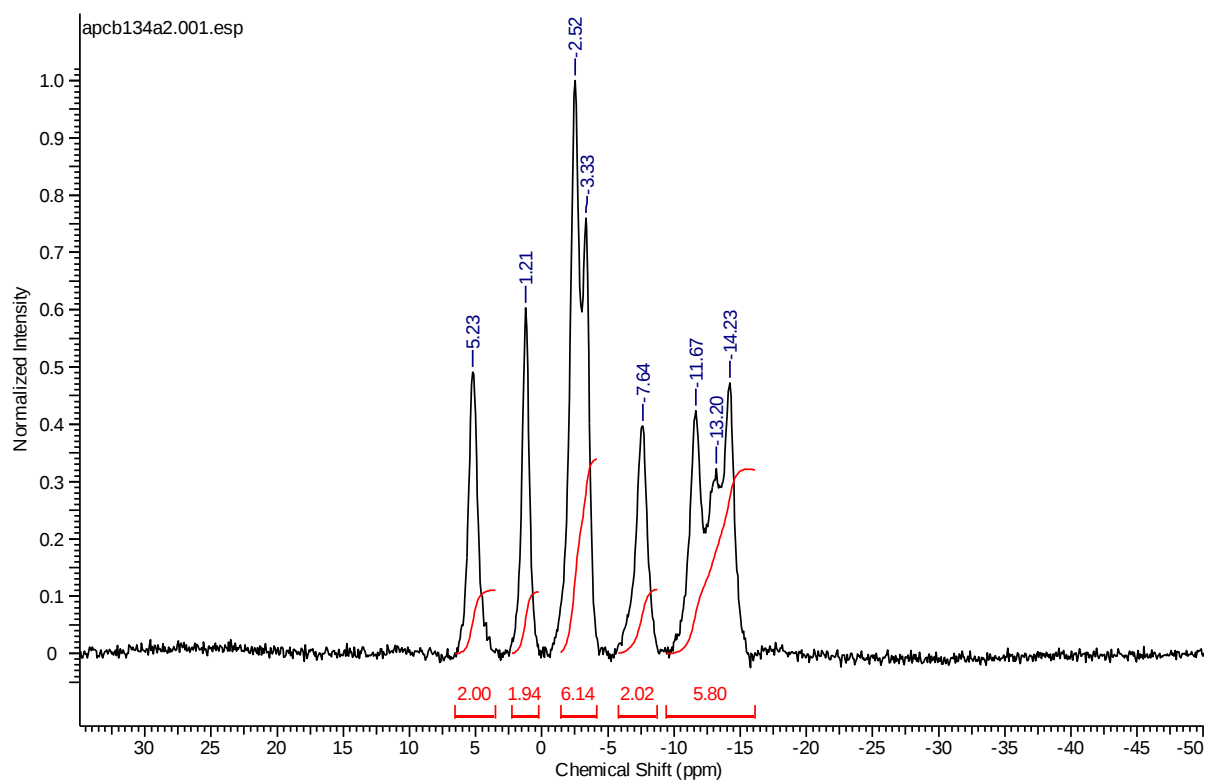


Compound 6: [1-(1'-3'-Cp-3',1',2'-closo-CoC₂B₉H₁₀)-3-Cp-3,1,2-closo-CoC₂B₉H₁₀]

¹H NMR

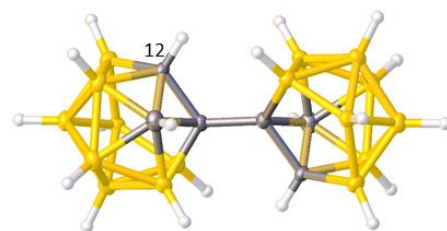
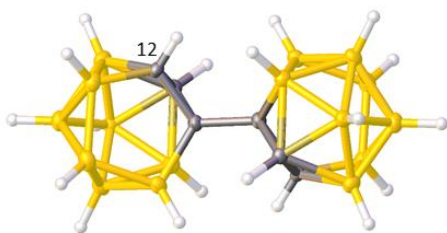
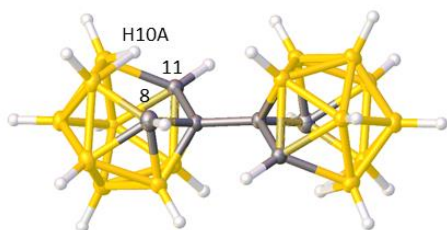


¹¹B{¹H} NMR



B. Crystallographic disorder in [BTMA]₂[1]

The disorder is best described as a superposition of three views of the anion (in these please ignore the C or B occupation of vertices that the colour coding implies). In the top view (representing 60% of



the structure) there is no occupation of vertex 12 and the bridging H atom, H10A, lies on the B9-B10 connectivity. However, in this view there is C/B disorder between vertices 8 and 11 which means, given that there is an inversion centre at the mid-point of the C7–C7' bond, that the overall structure cannot be described as simply racemic or meso.

In the middle view vertex 8 is unoccupied and in the bottom view vertex 11 is unoccupied. Both these forms involve occupation of vertex 12, the “ghost” vertex. The combined occupation of these forms is 40%.

Overall, the best fit of occupation to vertices is:

Vertex 8	51%C	15%B
Vertex 11	21%C	65%B
Vertex 12	20%C	20%B

This gives the correct overall C and B count.

In this combined model of the disorder the SOF of H10A is only 0.60. The remaining 0.4 of this bridging H atom is disordered over two different B–B connectivities (middle and bottom views). Although these partial H atoms are not included in the model their contribution to the scattering is minimal.