Electronic Supplementary Information

^{1}H, $^{1}H\{^{31}P\}$, $^{31}P\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra of all new compounds reported. Also ^{1}H-$^{31}P\{^{1}H\}$ HMBC and $^{11}B\{^{1}H\}$-$^{11}B\{^{1}H\}$ COSY NMR are included for compounds **1** and **2**. Vertex to centroid distances and "B"-H distances for CH vertices are listed for all compounds **1** to **4**α.

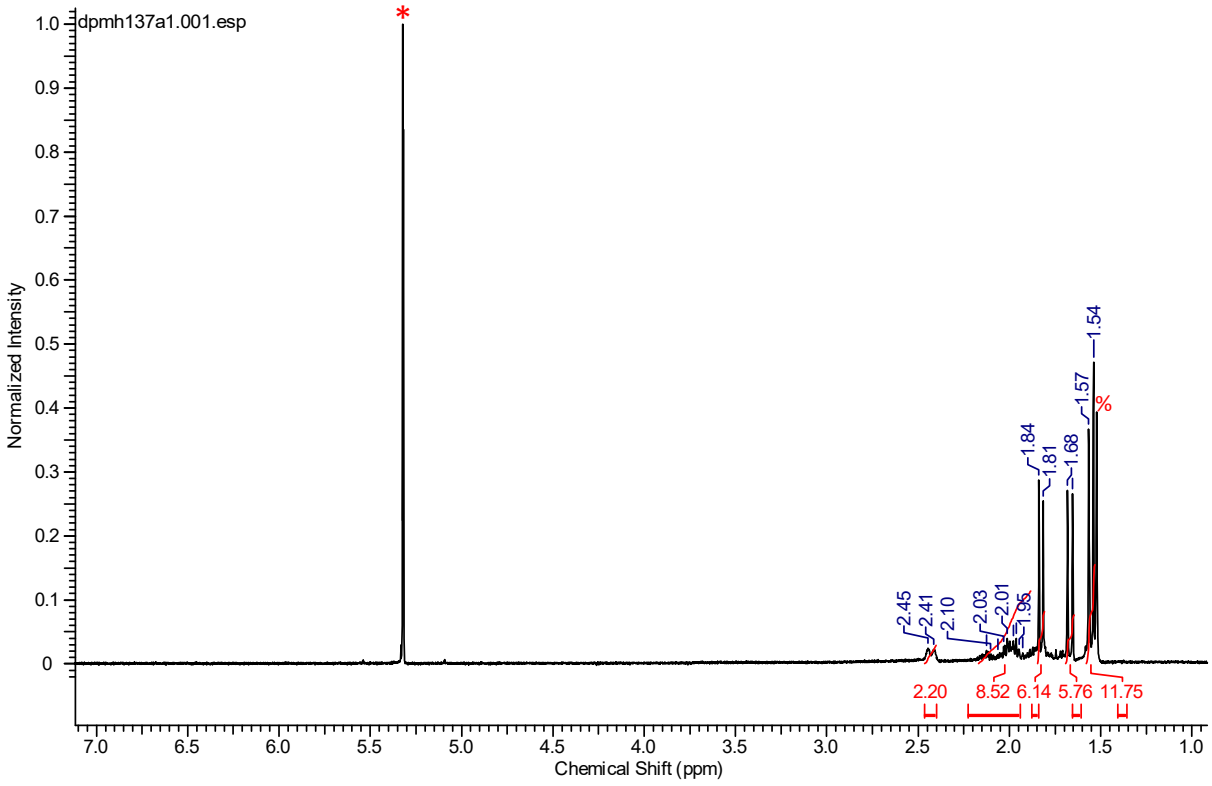
% water

* CD_2Cl_2

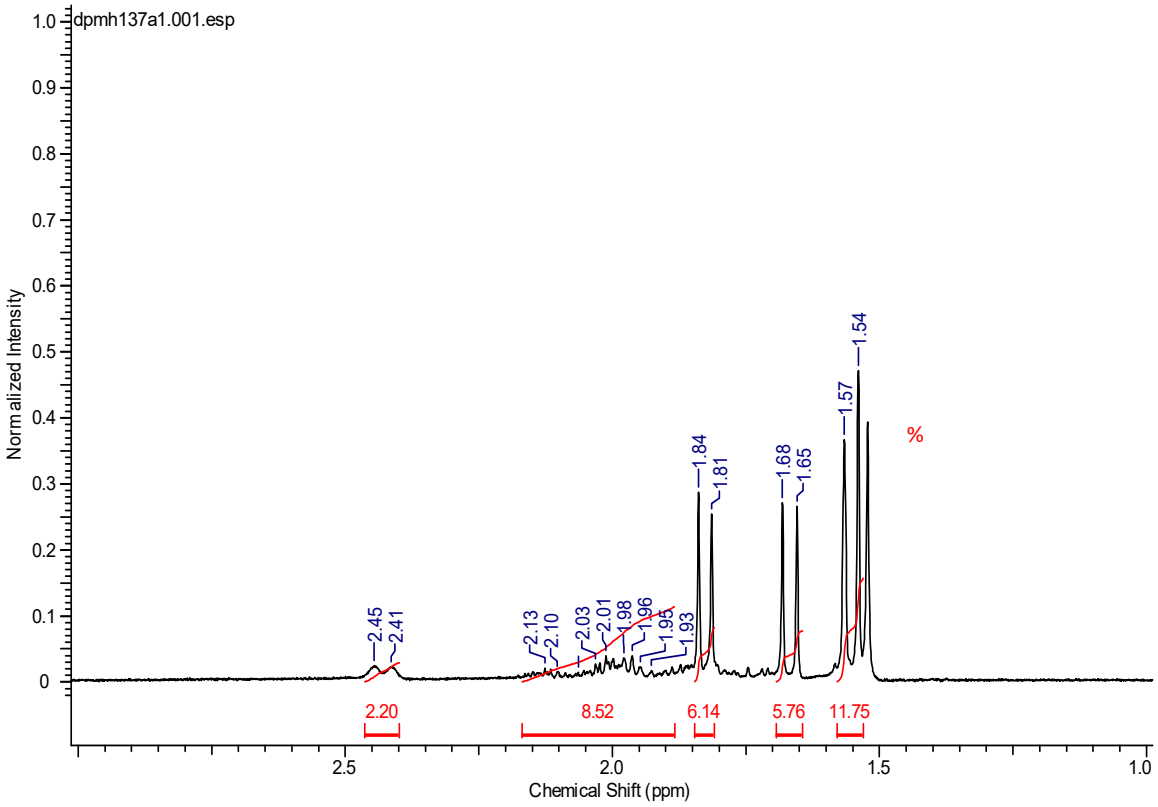
≠ Impurity

Compound **1**: *rac*-[1-(1′-3′-(dmpe)-3′,1′,2′-*closo*-$NiC_2B_9H_{10}$)-3-(dmpe)-3,1,2-*closo*-$NiC_2B_9H_{10}$]

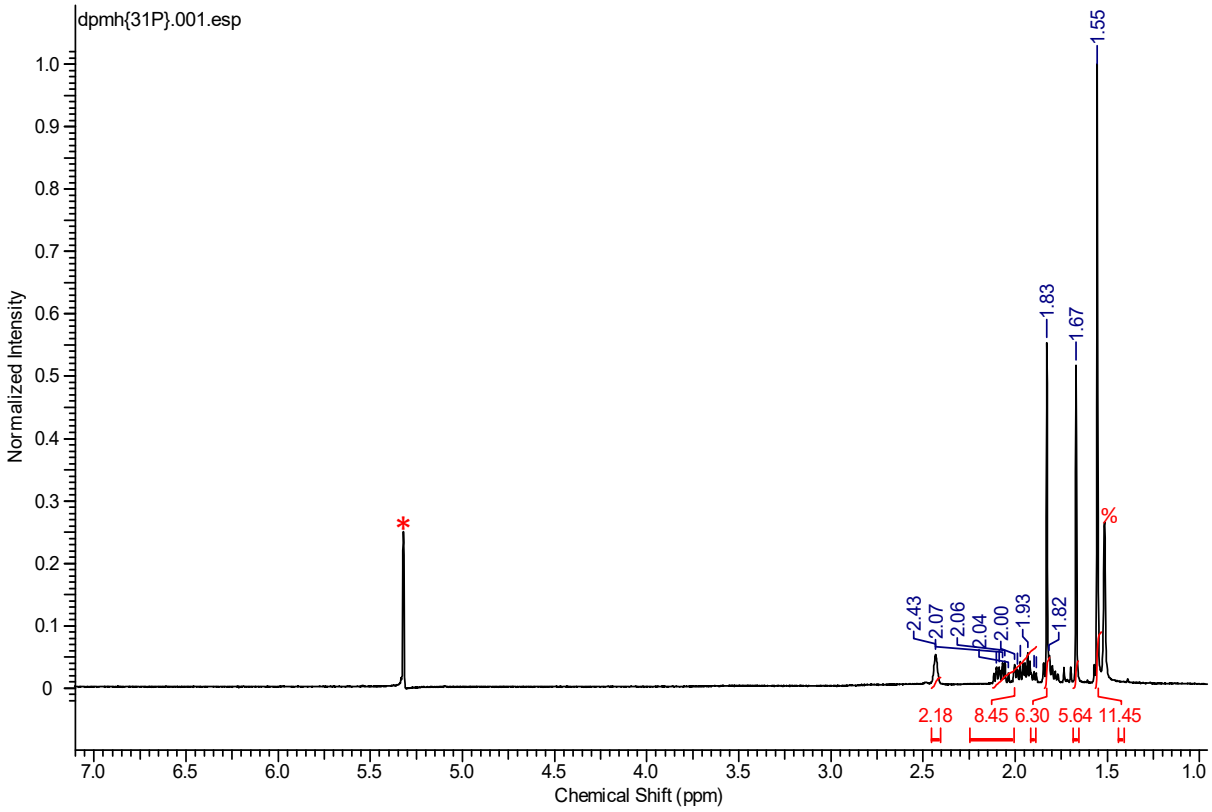
^{1}H NMR



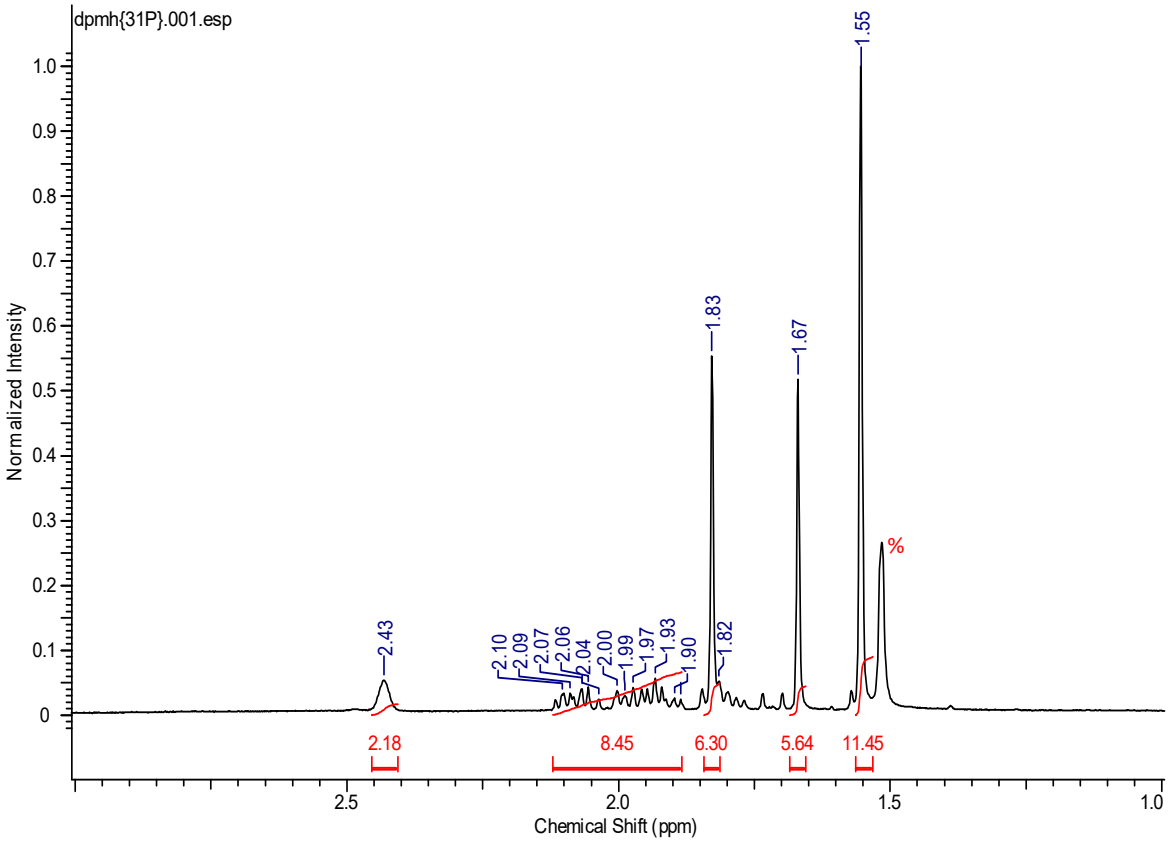
^{1}H NMR (expansion between 1-3 ppm)



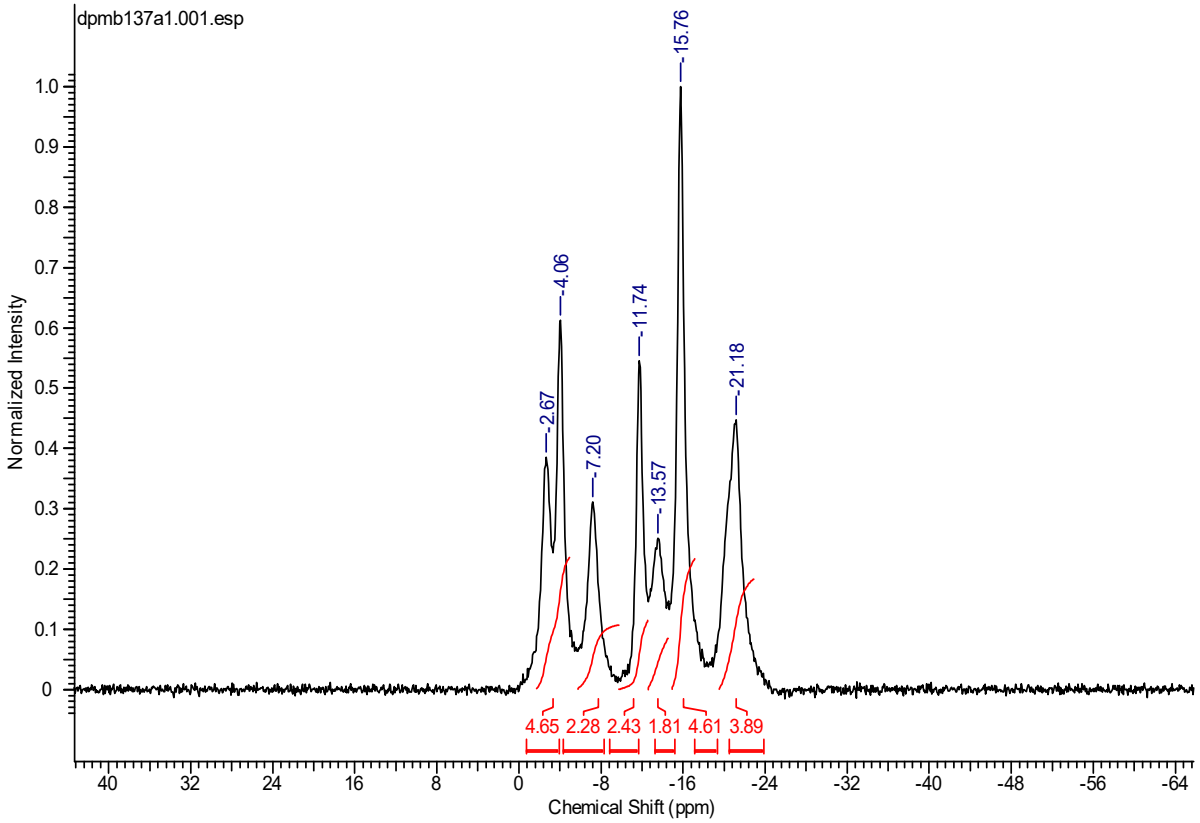
$^{1}H\{^{31}P\}$ NMR



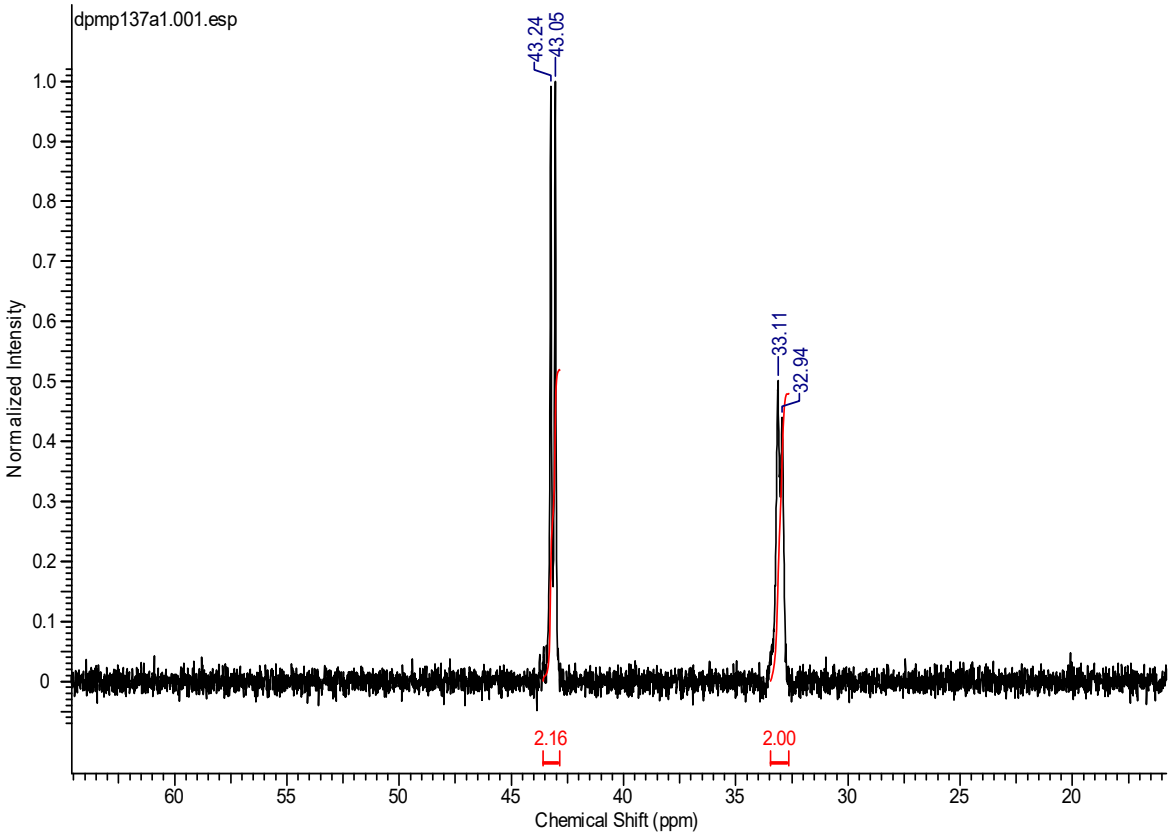
$^{1}H\{^{31}P\}$ NMR (expansion between 1-3 ppm)



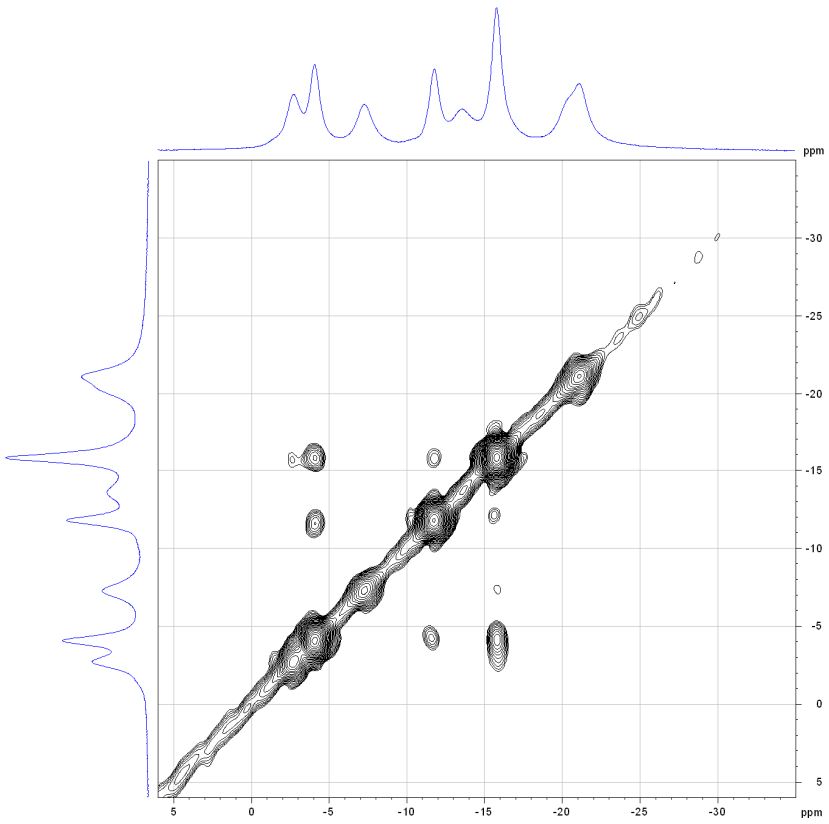
$^{11}B\{^{1}H\}$ NMR



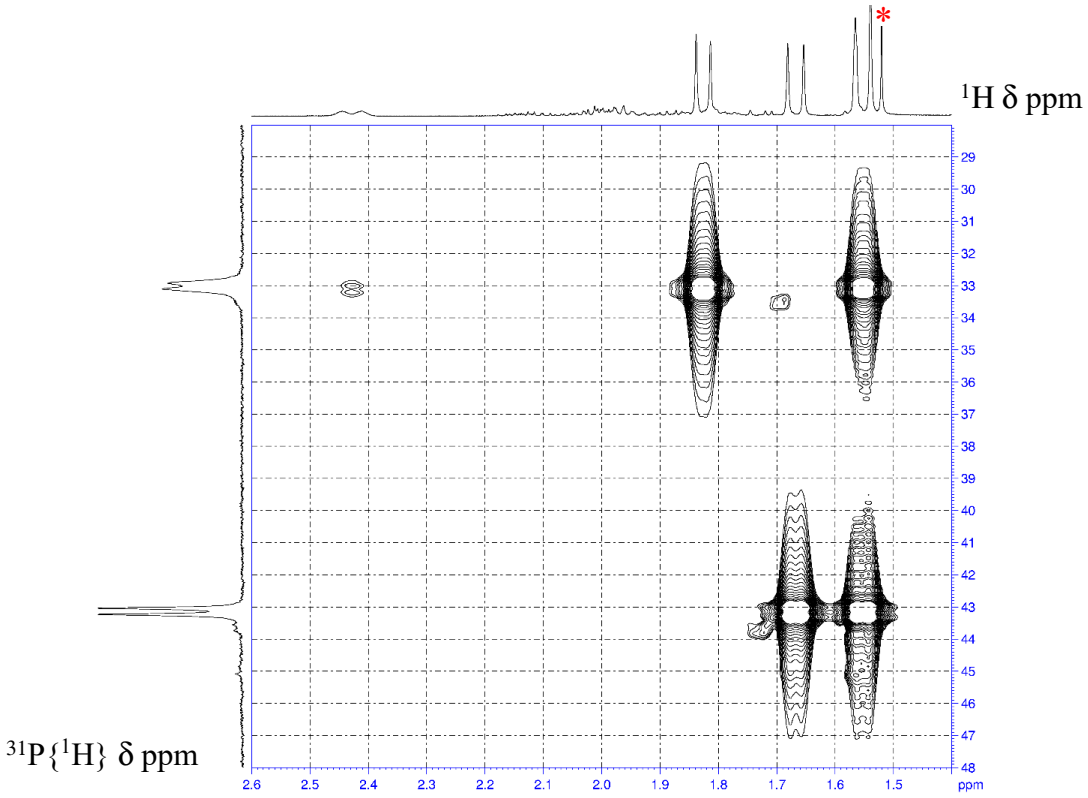
$^{31}P\{^{1}H\}$ NMR



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

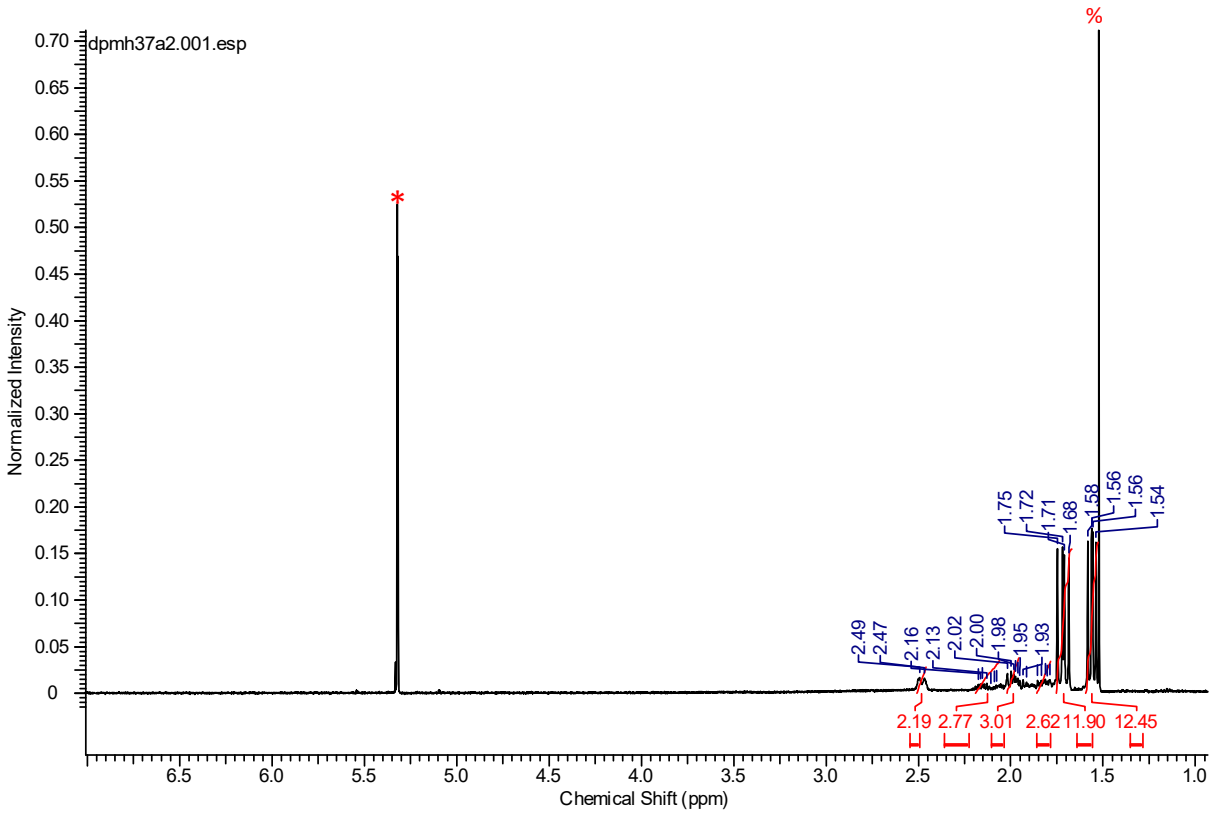


^{1}H-$^{31}P\{^{1}H\}$ NMR

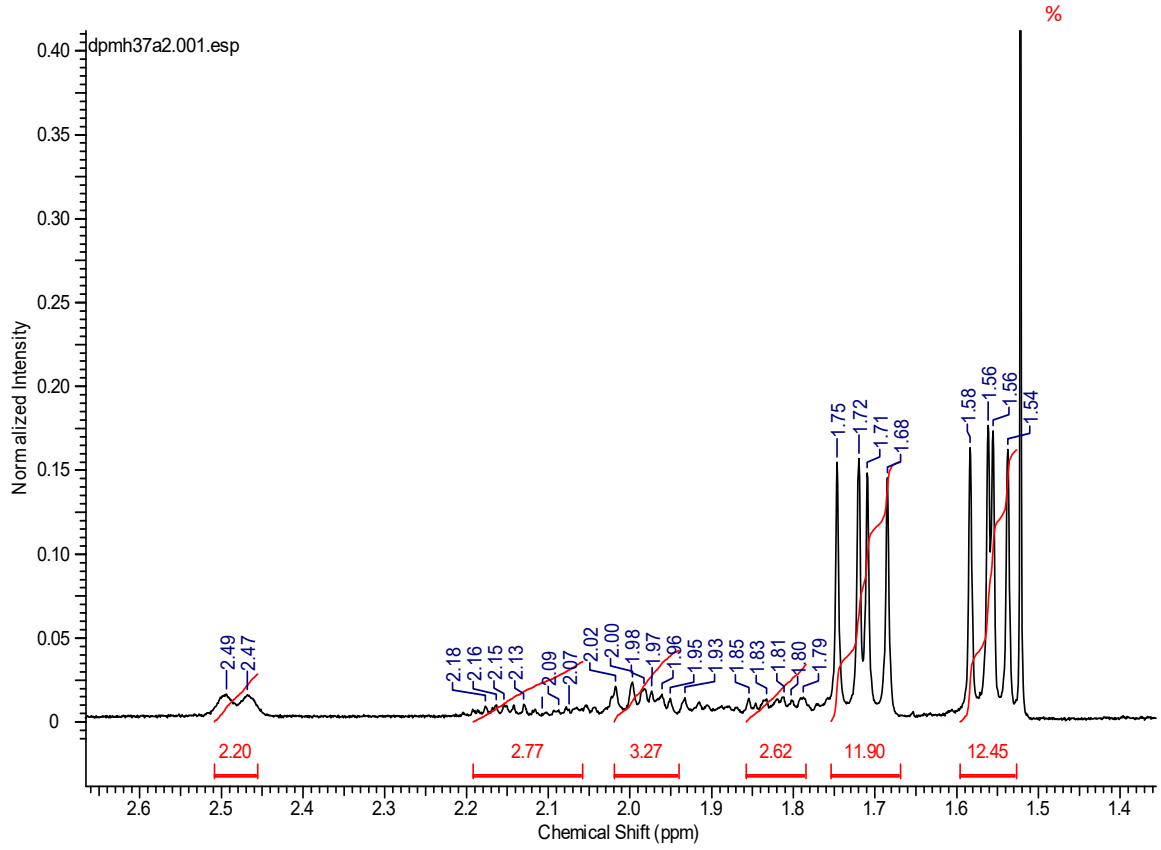

*
^{1}H δ ppm
$^{31}P\{^{1}H\}$ δ ppm
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
ppm

Compound **2**: *meso*-[1-(1′-3′-(dmpe)-3′,1′,2′-*closo*-$NiC_2B_9H_{10}$)-3-(dmpe)-3,1,2-*closo*-$NiC_2B_9H_{10}$]

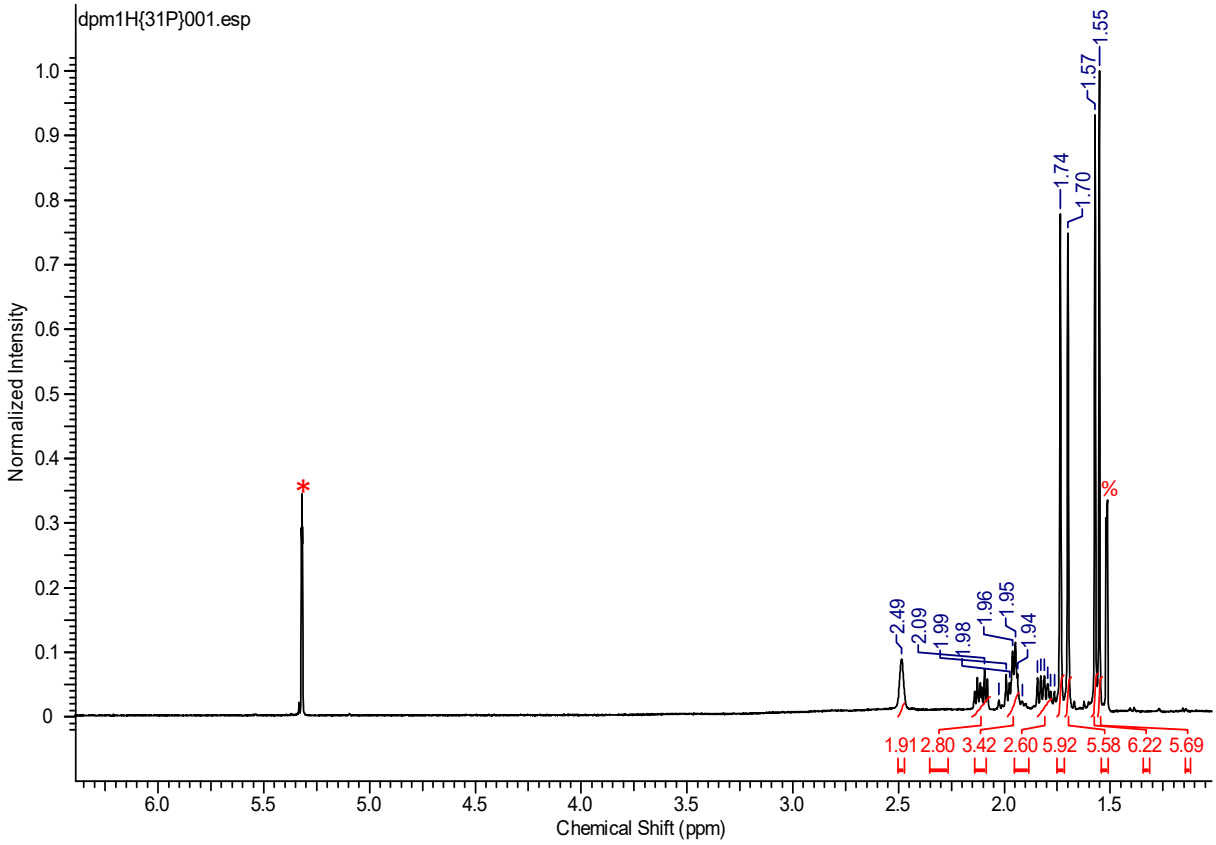
^1H NMR



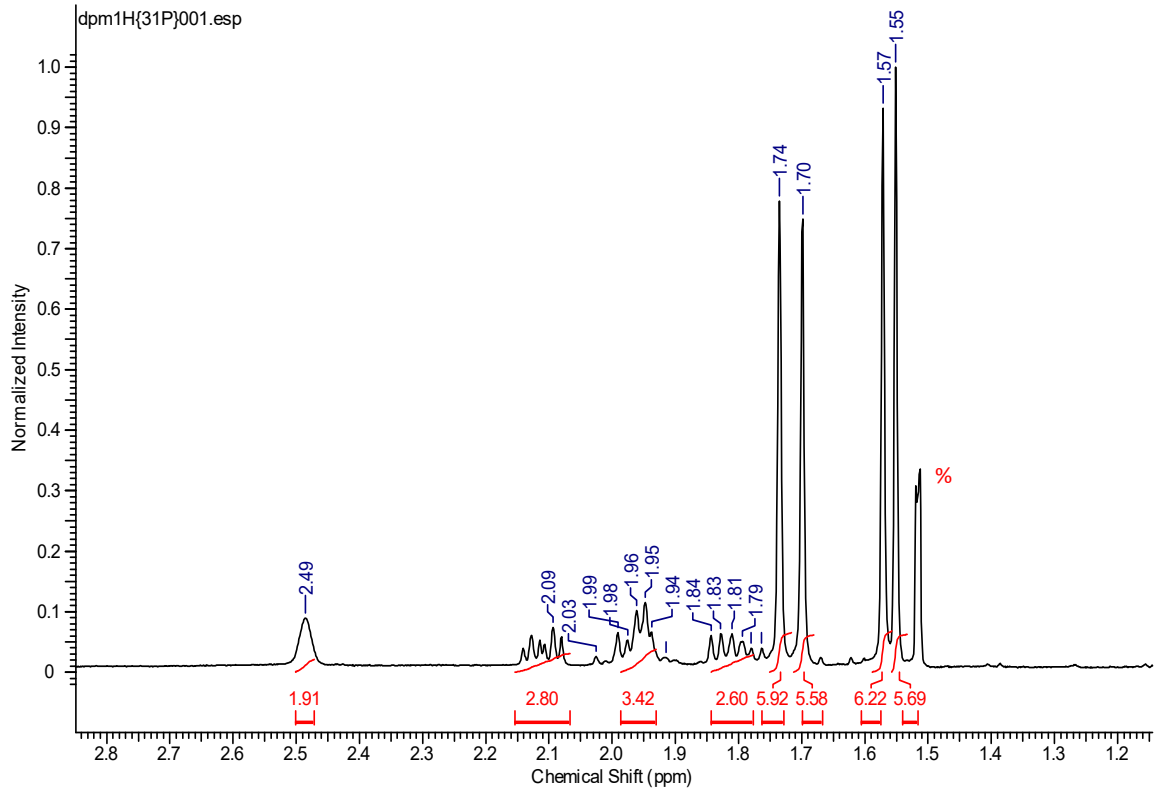
^1H NMR (expansion between 1-3 ppm)



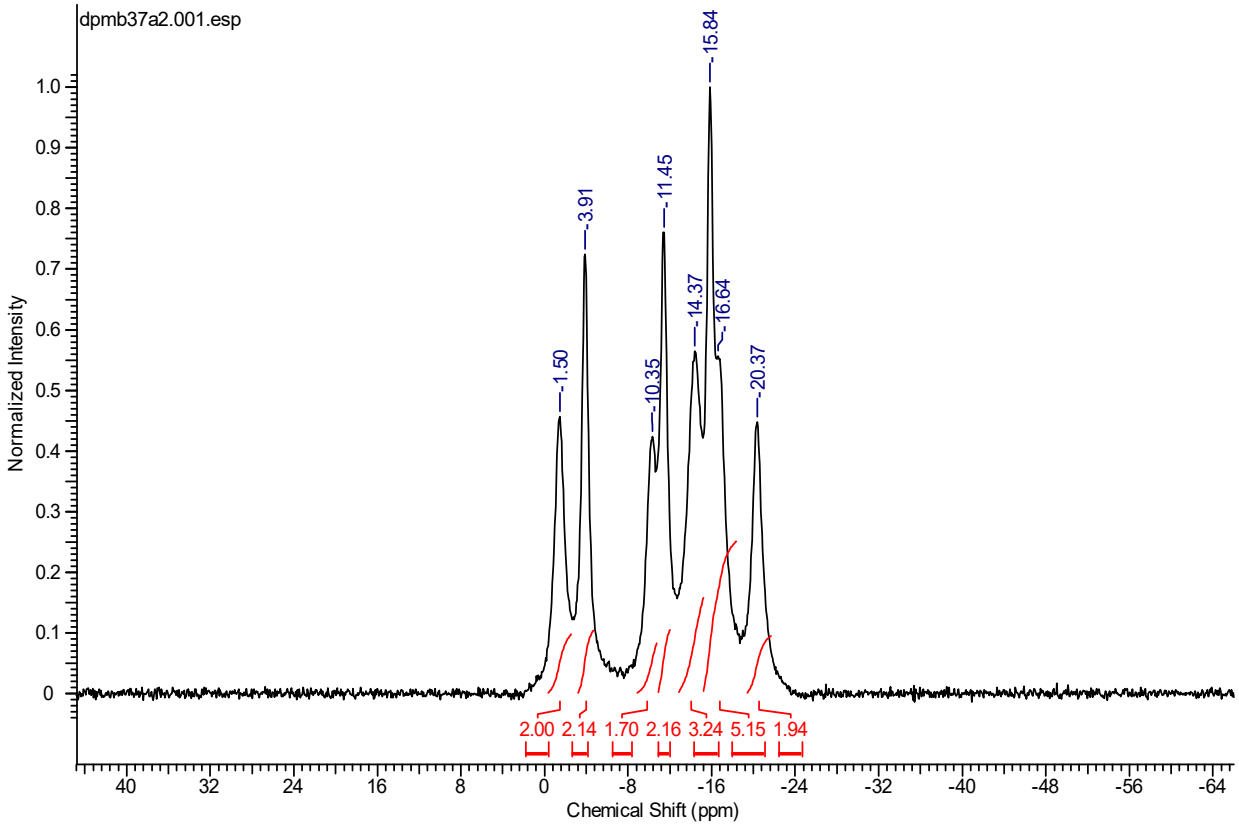
$^{1}H\{^{31}P\}$ NMR



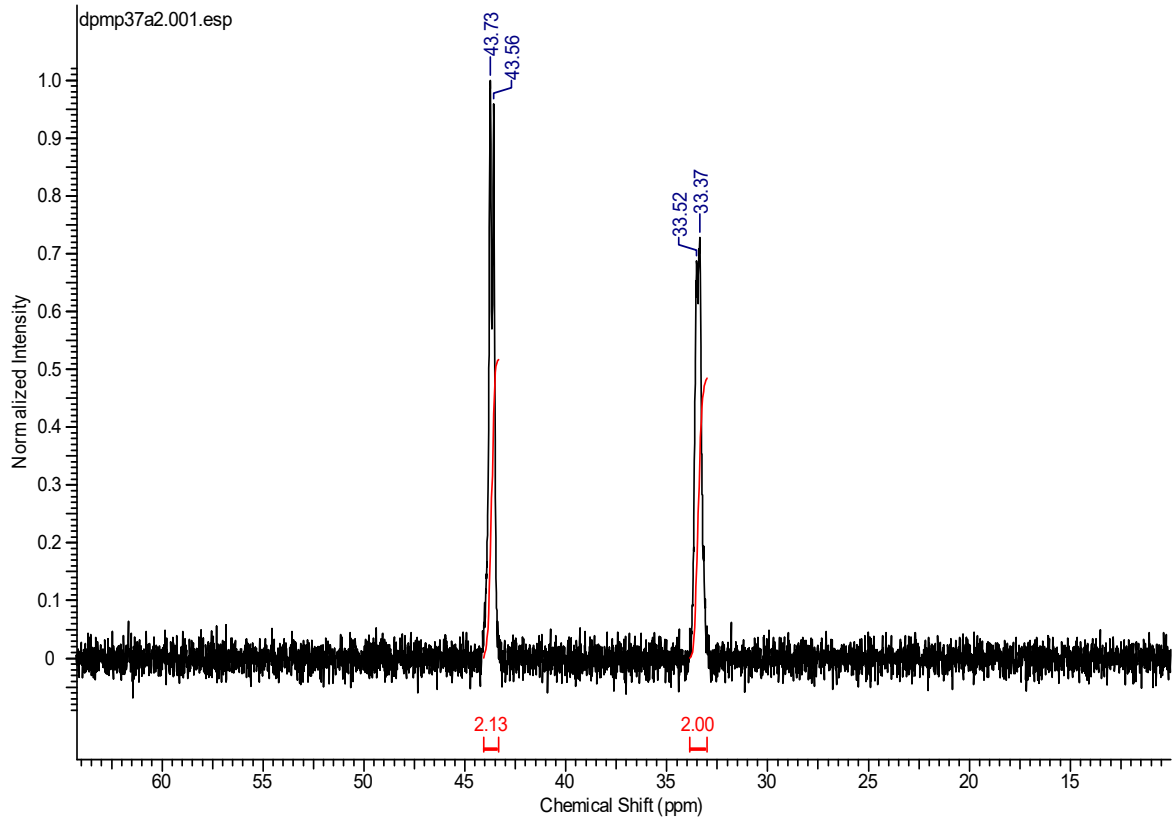
$^{1}H\{^{31}P\}$ NMR (expansion between 1-3 ppm)



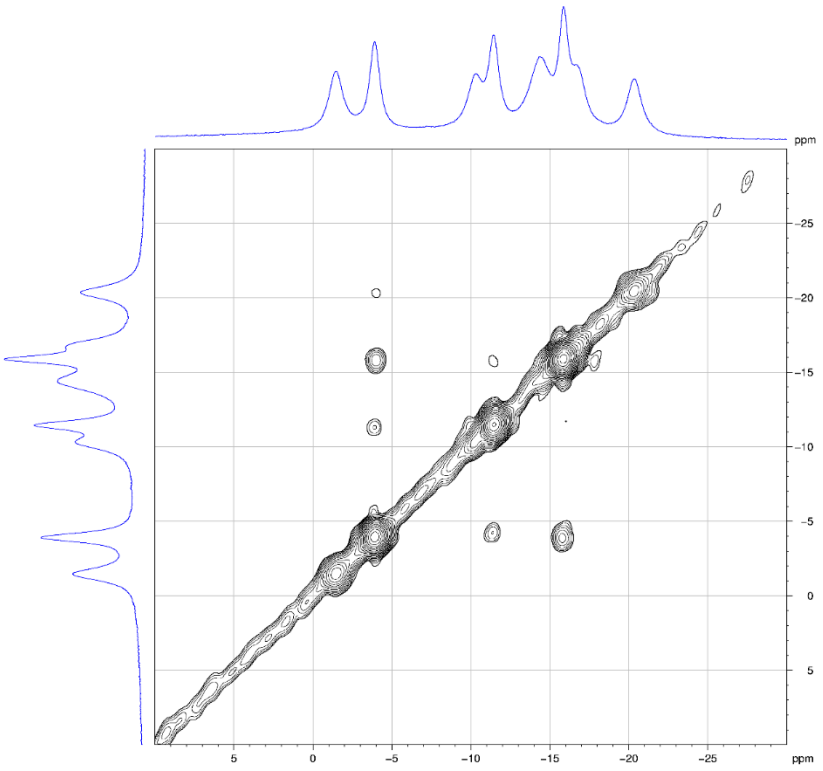
$^{11}B\{^{1}H\}$ NMR



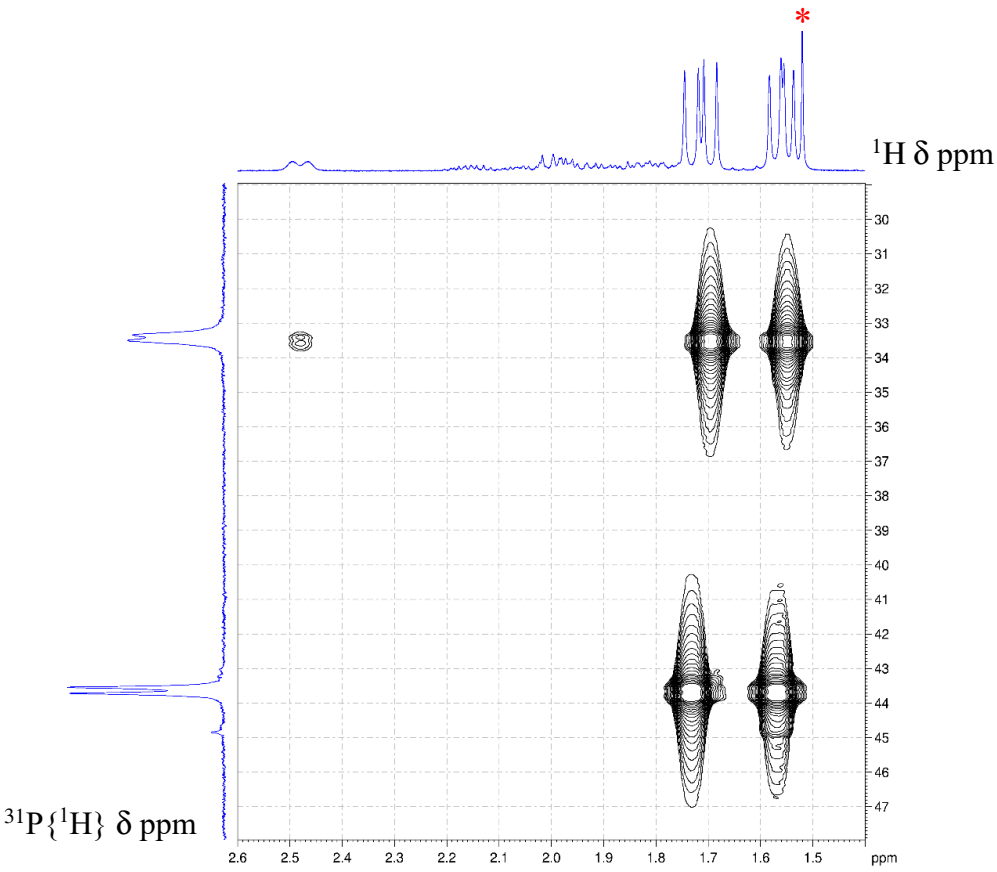
$^{31}P\{^{1}H\}$ NMR



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

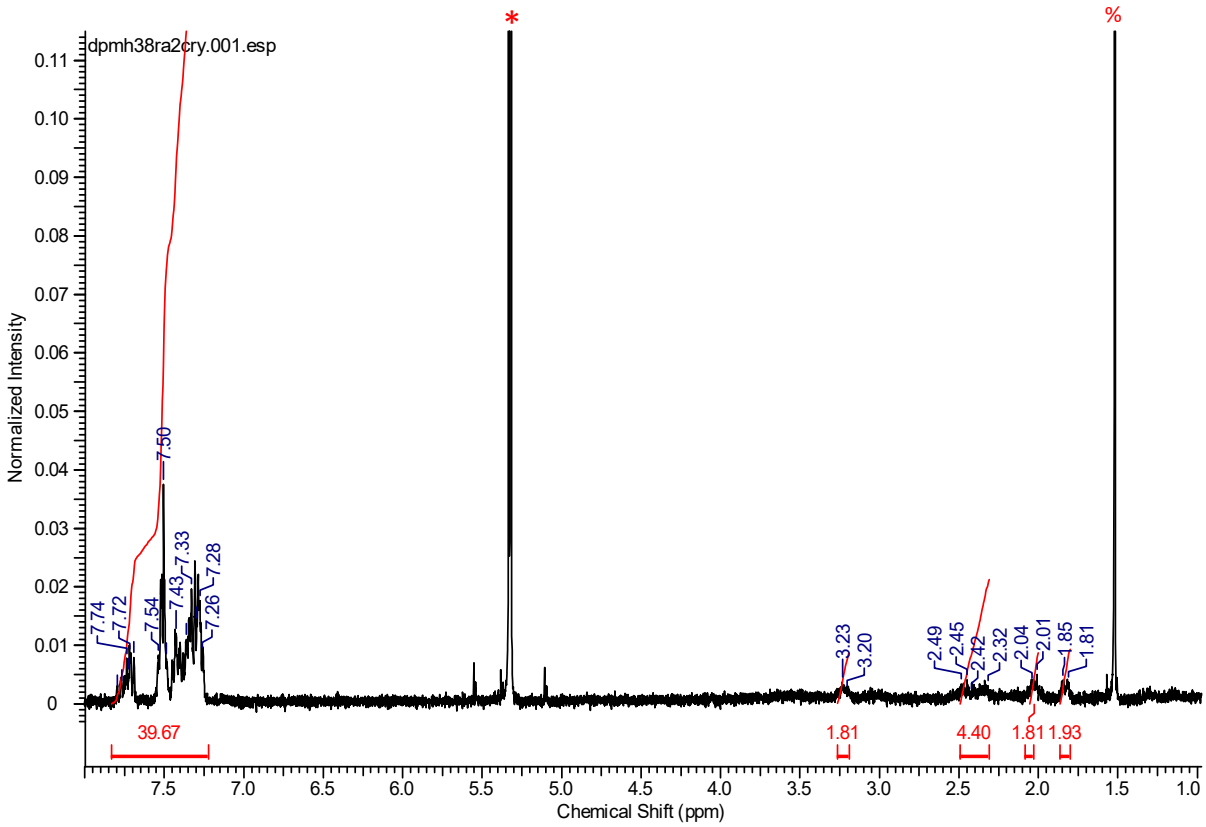


^{1}H-$^{31}P\{^{1}H\}$ NMR

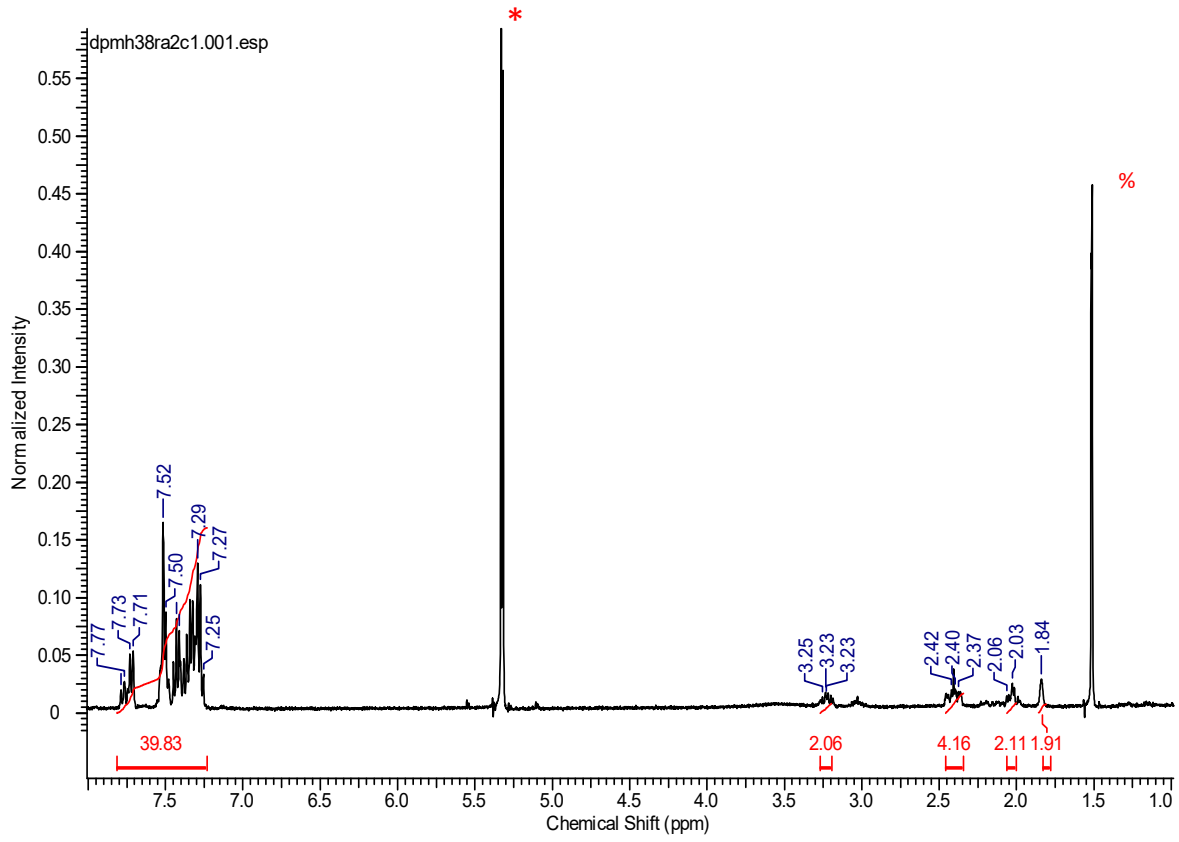


Compound **3**: *rac*-[1-(1′-3′-(dppe)-3′,1′,2′-*closo*-$NiC_2B_9H_{10}$)-3-(dppe)-3,1,2-*closo*-$NiC_2B_9H_{10}$]

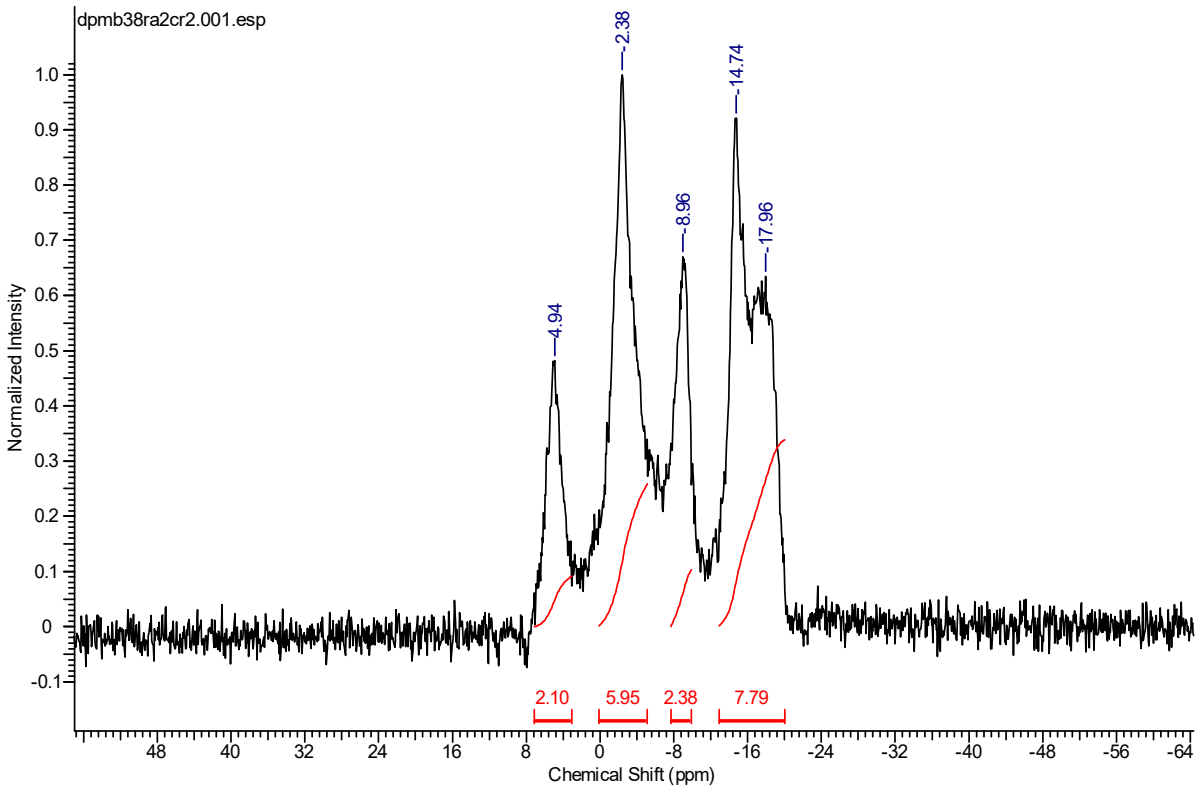
^1H NMR



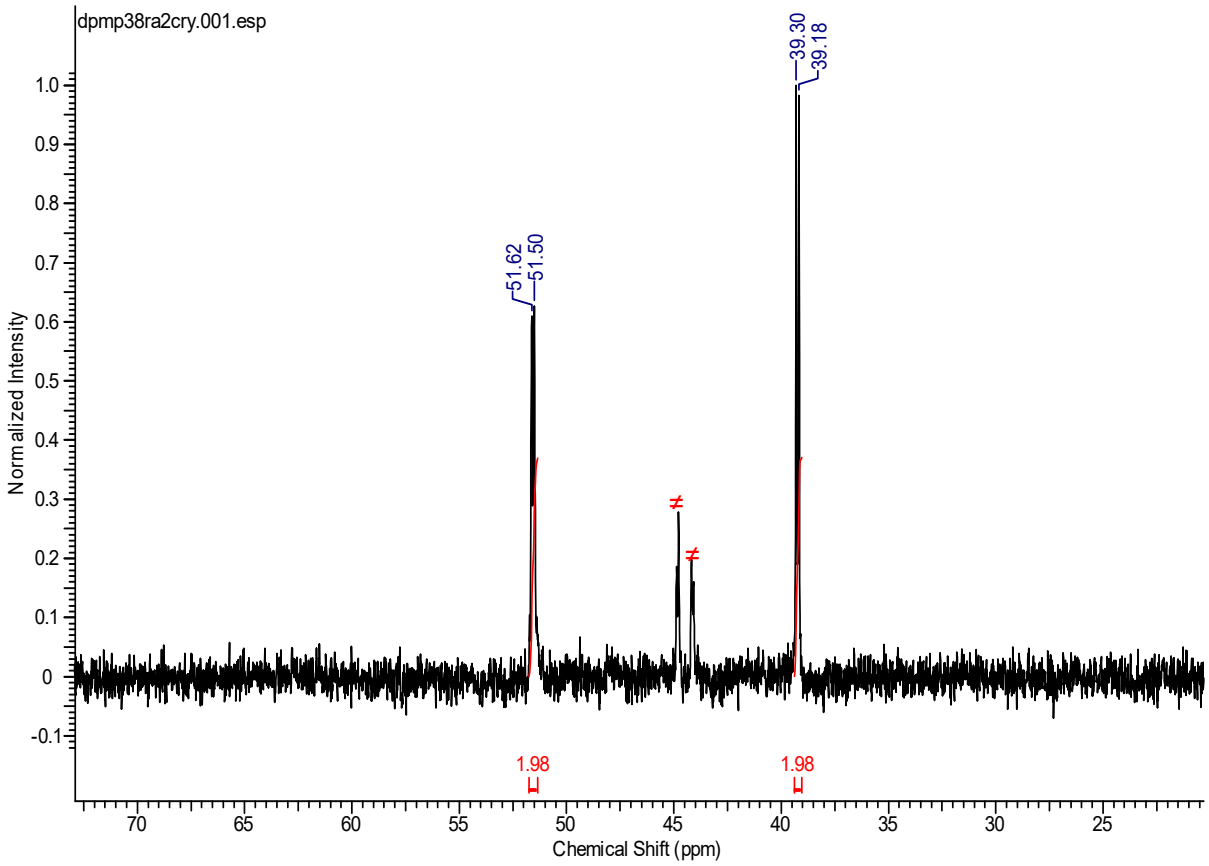
$^1H\{^{31}P\}$ NMR



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

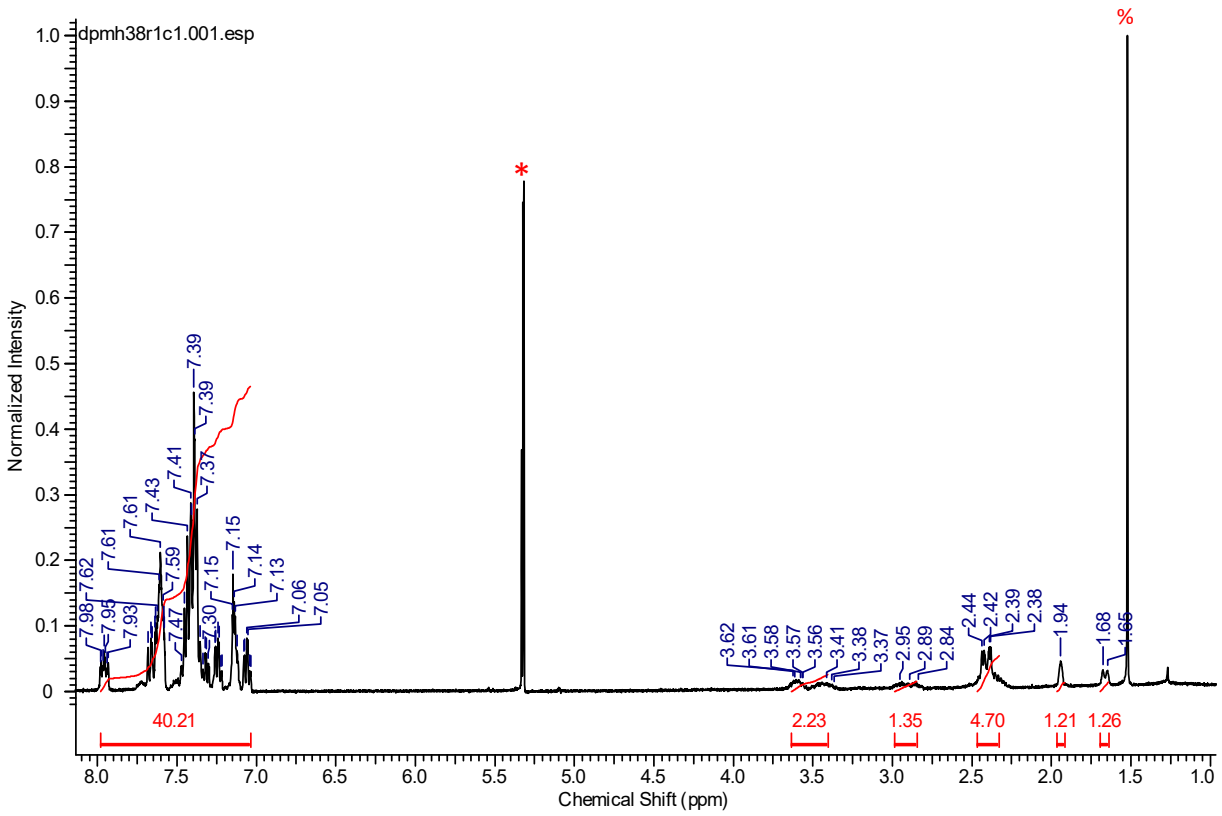


$^{31}P\{^{1}H\}$ NMR

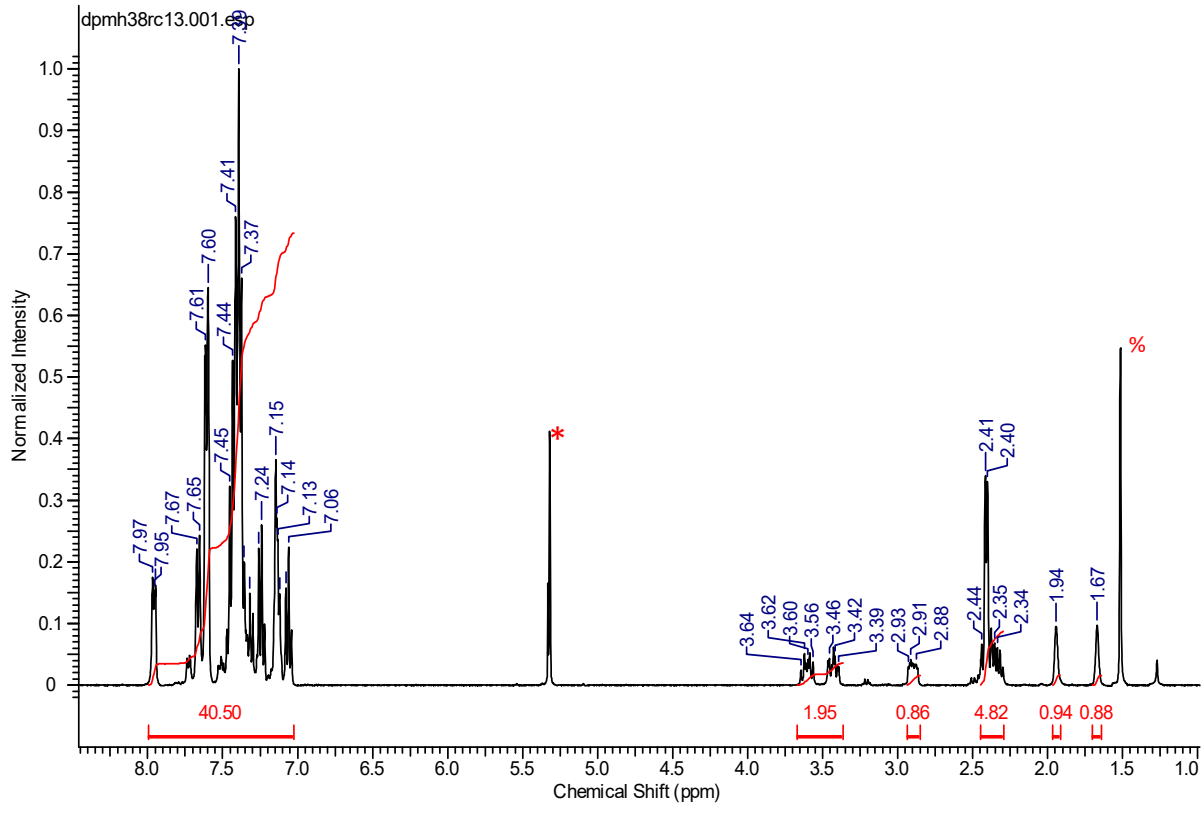


Compound **4α**: [1-(2′-4′-(dppe)-4′,1′,2′-*closo*-$NiC_2B_9H_{10}$)-3-(dppe)-3,1,2-*closo*-$NiC_2B_9H_{10}$]

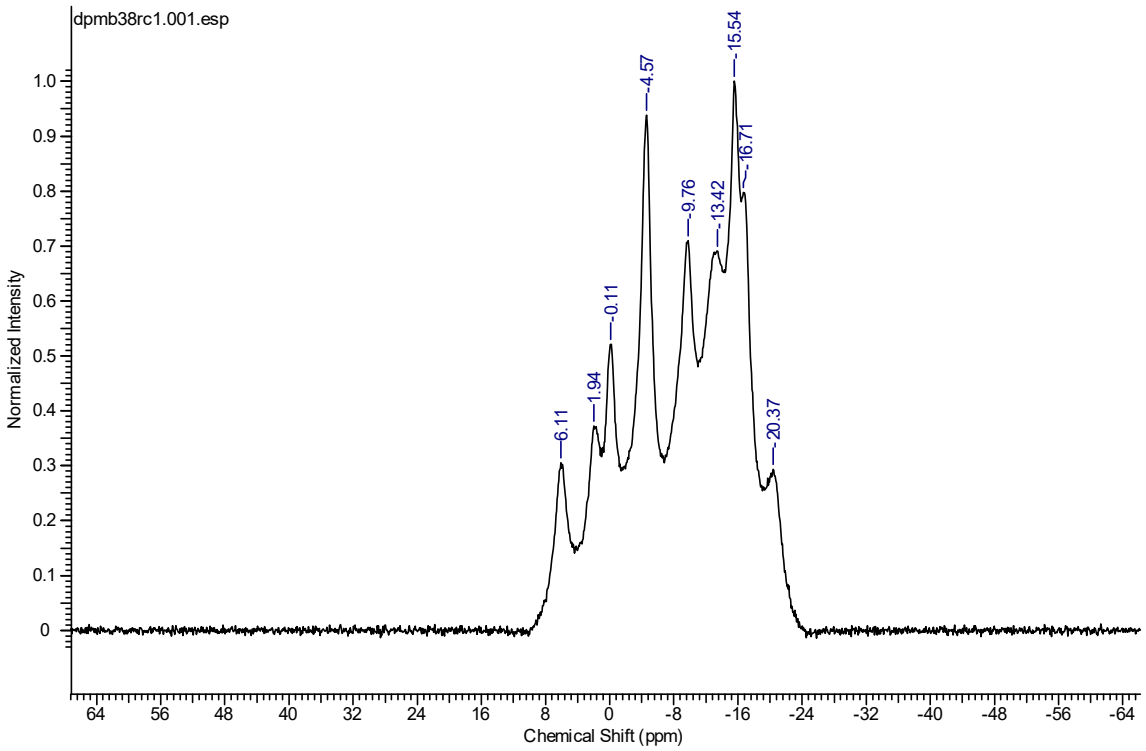
^1H NMR



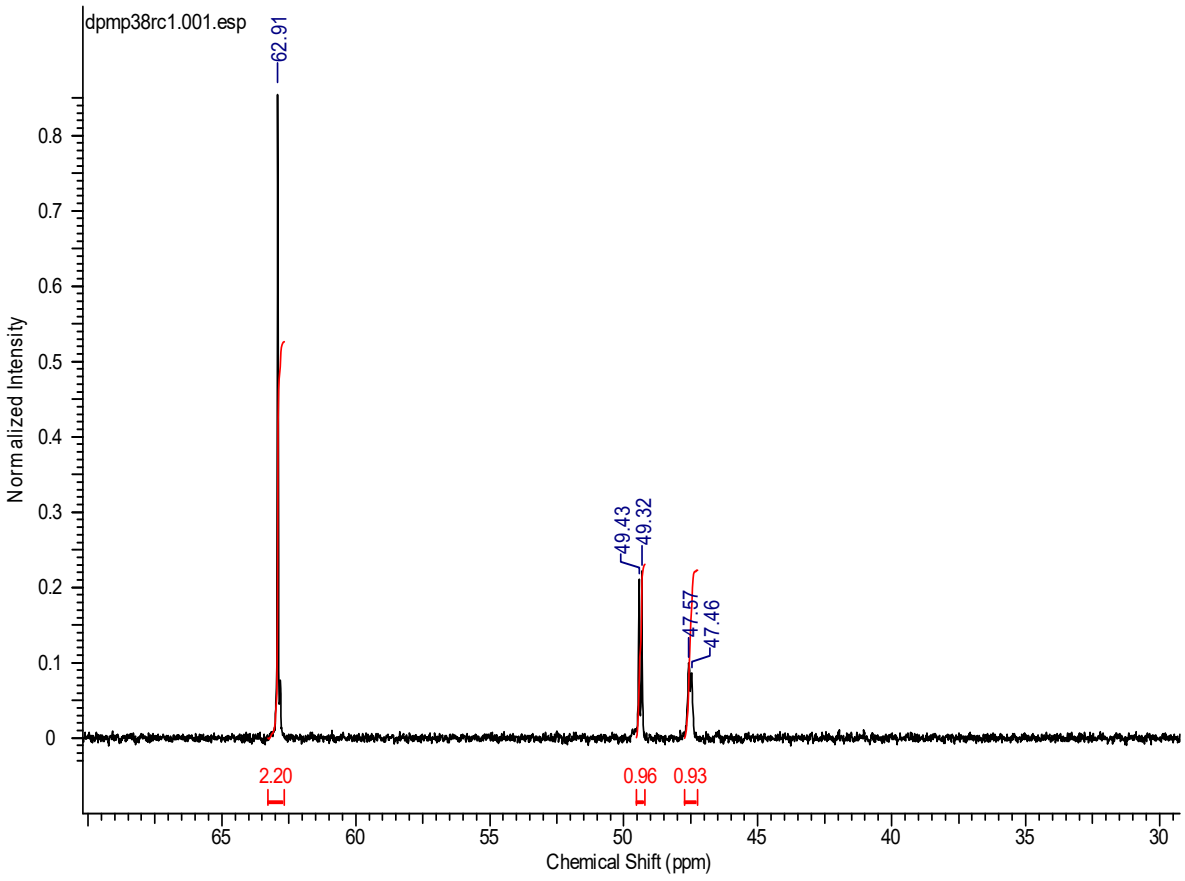
$^1H\{^{31}P\}$ NMR



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



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



Vertex to centroid distances (VCD) (Å) and "B"-H distance (BHD) (Å) for CH vertices.

Shortest distances show vertex is a C and not B atom.

1		**2**				**3**		**4α**			
vertex	VCD (Å)	vertex	VCD (Å)	vertex	VCD (Å)	vertex	VCD (Å)	vertex	VCD (Å)	vertex	VCD (Å)
B2	1.52	B2	1.53	B2'	1.54	B2	1.52	B2	1.53	C2'	1.60
C1	1.65	B9	1.64	B4'	1.63	C1	1.64	C1	1.62	B1'	1.60
B9	1.65	C1	1.65	C1'	1.65	B7	1.65	B9	1.66	B7'	1.65
B4	1.66	B4	1.65	B9'	1.65	B10	1.66	B4	1.66	B5'	1.65
B11	1.67	B11	1.66	B11'	1.66	B4	1.67	B11	1.68	B10	1.65
B5	1.68	B12	1.68	B12'	1.68	B5	1.68	B12	1.68	B11	1.66
B12	1.69	B5	1.68	B5'	1.69	B12	1.68	B5	1.68	B3'	1.68
B10	1.70	B10	1.69	B10'	1.69	B11	1.69	B7	1.68	B12	1.69
B7	1.71	B6	1.70	B6'	1.70	B9	1.70	B10	1.69	B9'	1.71
B6	1.72	B7	1.71	B7'	1.70	B6	1.72	B6	1.72	B8'	1.72
B8	1.73	B8	1.72	B8'	1.72	B8	1.73	B8	1.73	B6'	1.73
BHD											
B2H2	0.46(2)	B2H2	0.49(4)	B2'H2′	0.58(4)	B2H2	0.39(2)		n/a		n/a