

Electronic Supplementary Information for:

Rhodium and Ruthenium Complexes of Methylene-Bridged, *P*-Stereogenic, Unsymmetrical Diphosphanes

Javier Eusamio,^{a,b} Yaiza M. Medina,^{a,b} Javier C. Córdoba,^a Anton Vidal-Ferran,^{a,b,c}
Daniel Sainz,^{a,b} Albert Gutiérrez,^{a,b} Mercè Font-Bardía,^d and Arnald Grabulosa^{a,b,*}

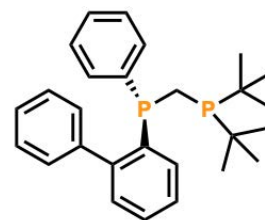
^aDepartament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès, 1-11, E-08028, Barcelona, Spain. ^bInstitut de Nanociència i Nanotecnologia (IN2UB), Universitat de Barcelona, E-08028, Barcelona, Spain. ^cInstitució Catalana de Recerca i Estudis Avançats (ICREA), Passeig Lluís Companys 23, E-08010, Barcelona, Spain. ^dUnitat de Difracció de Raigs X, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Solé i Sabarís 1-3, E-08028, Barcelona, Spain

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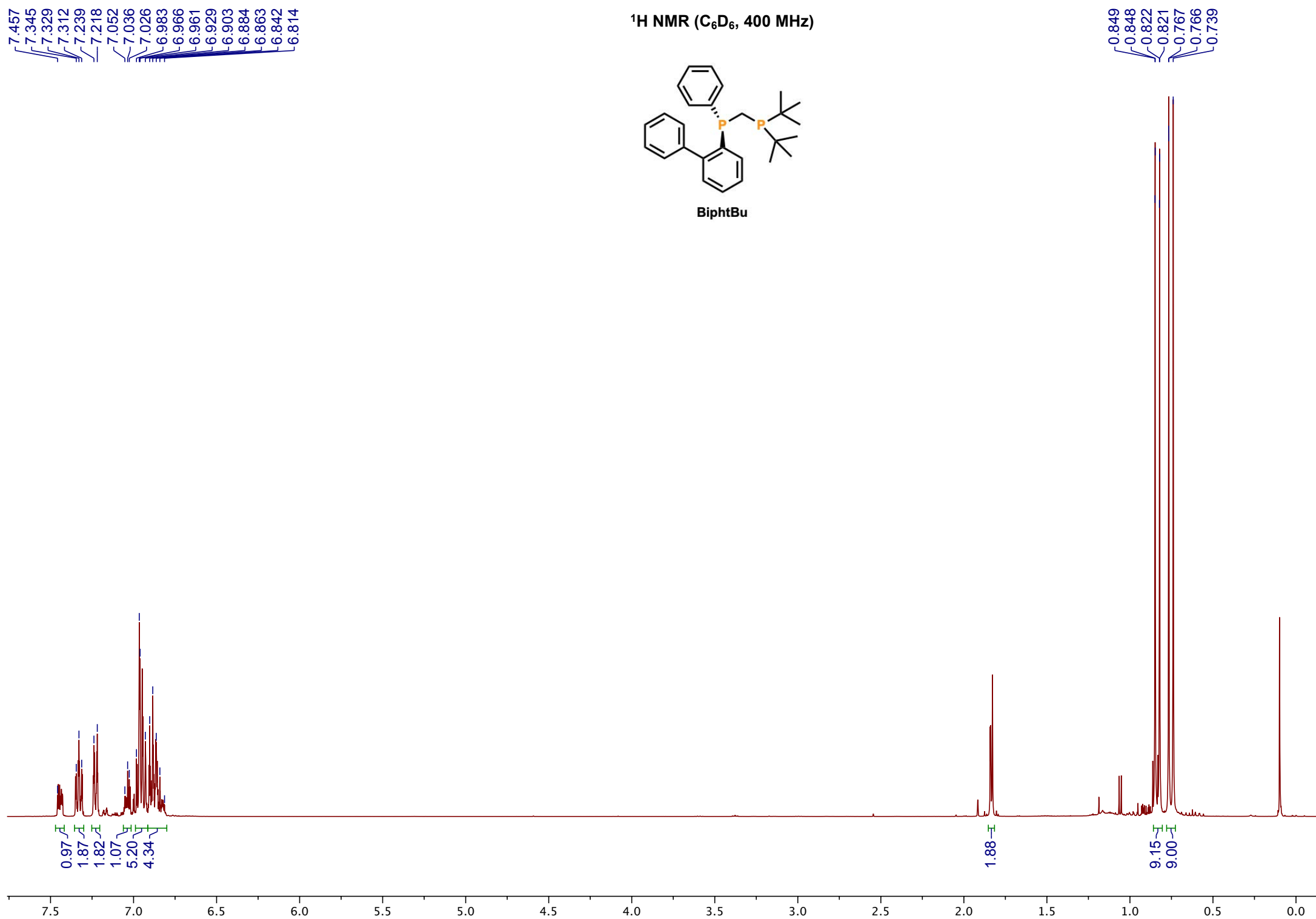
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S1

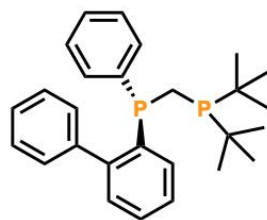
¹H NMR (C₆D₆, 400 MHz)

BiphtBu



S2

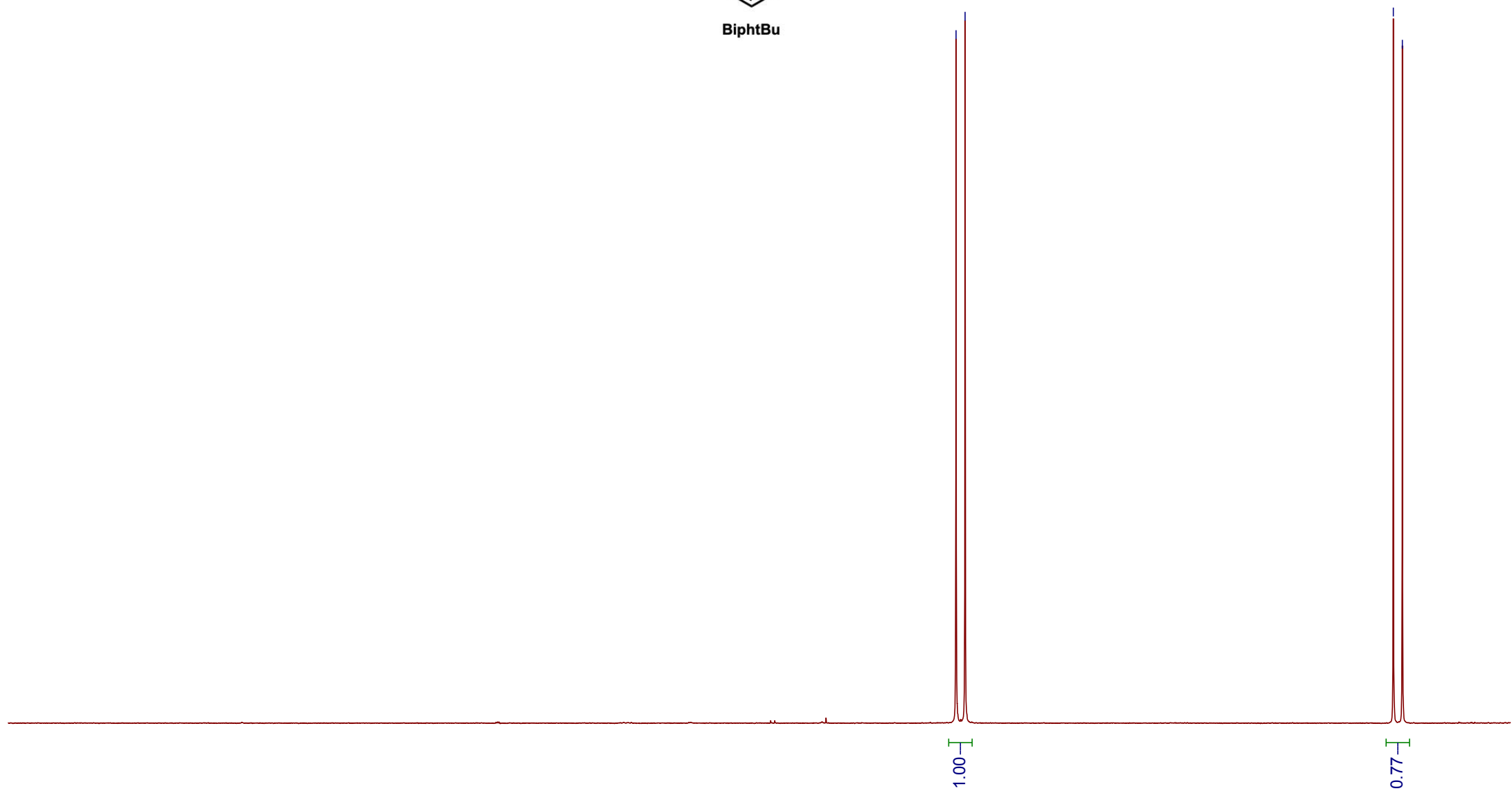
$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz)



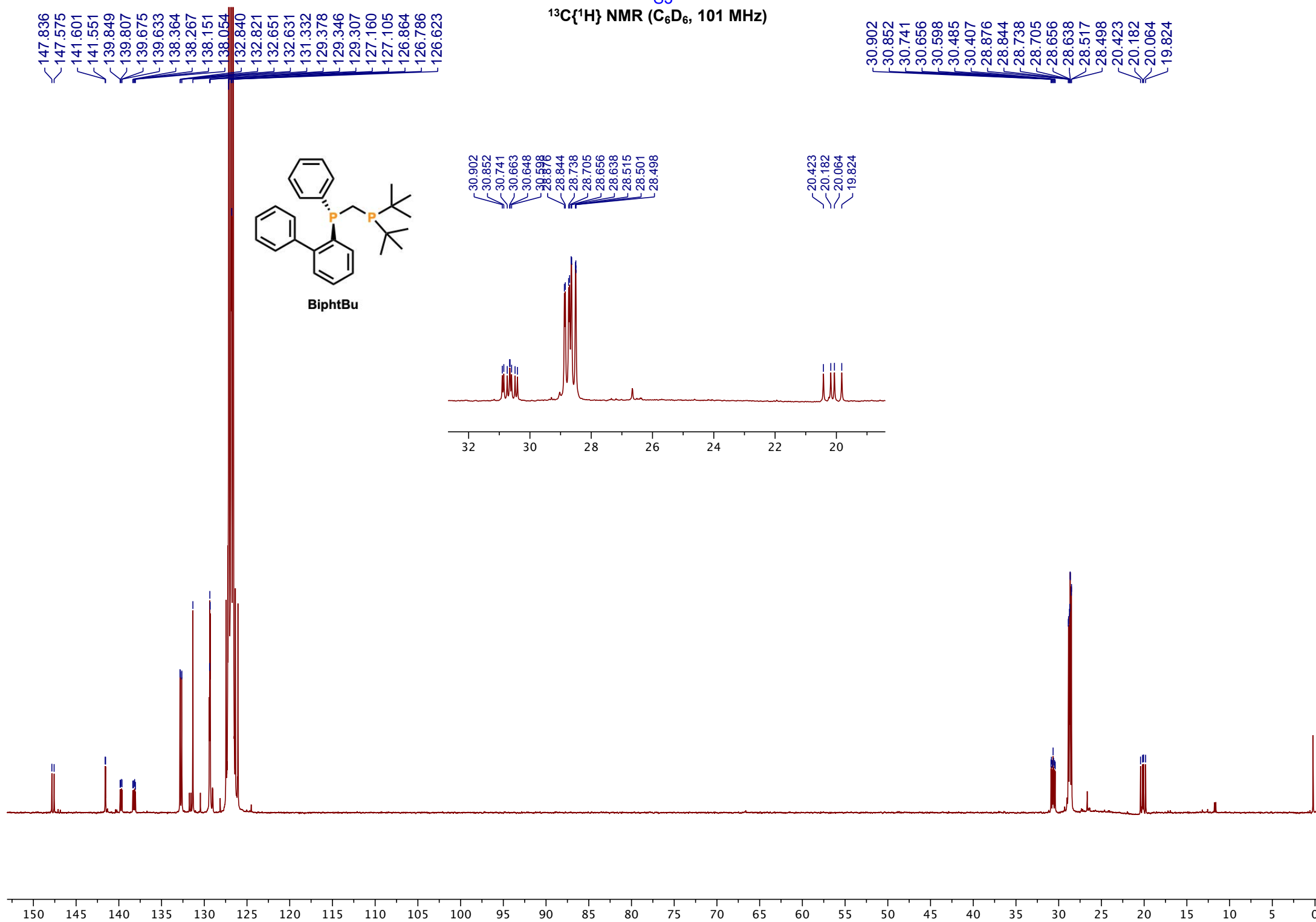
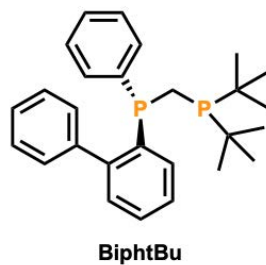
BiphtBu

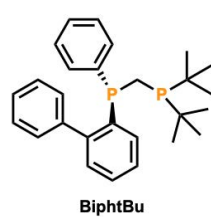
~14.150
~13.349

~24.650
~25.452



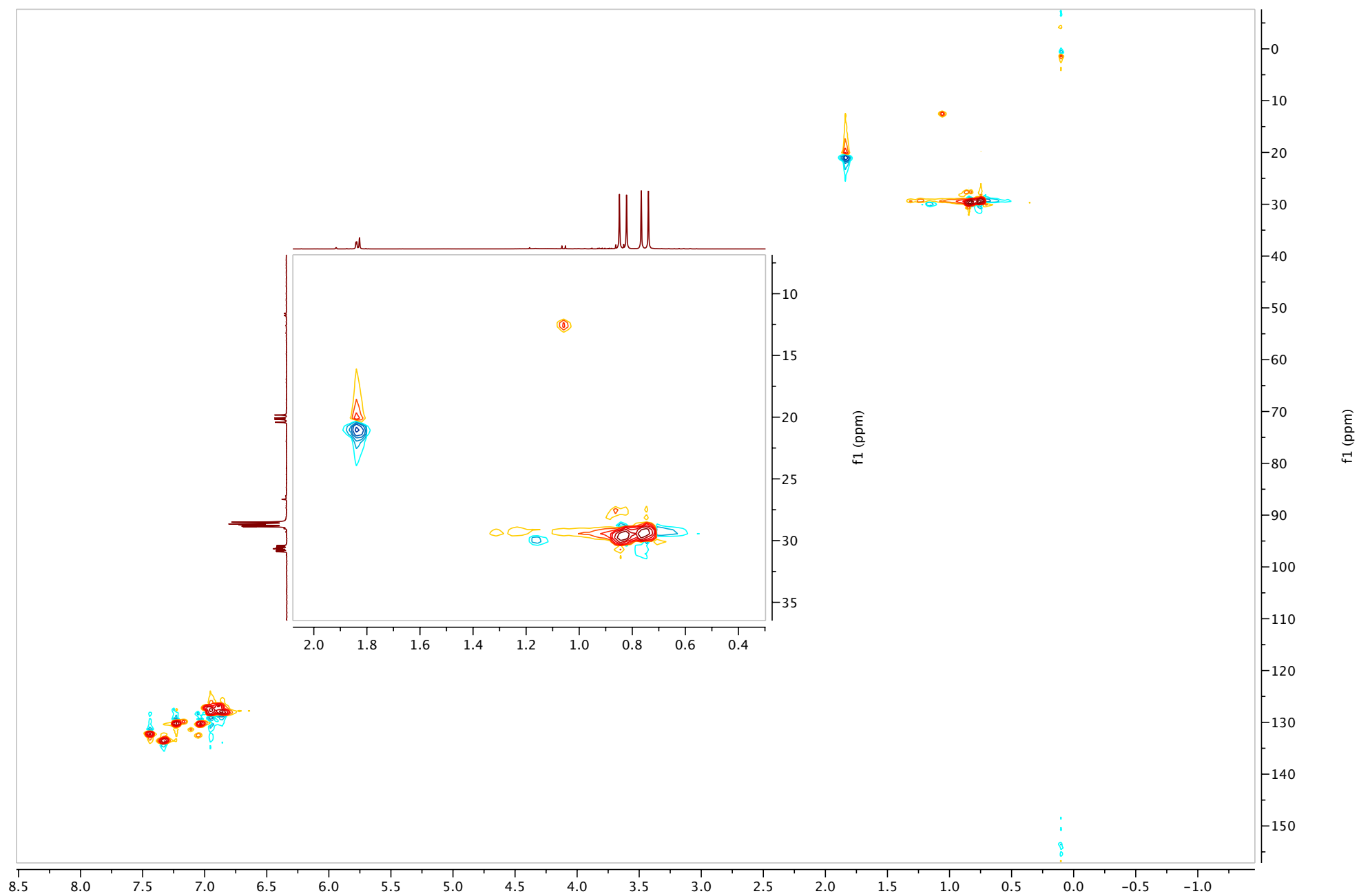
S3
 $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 101 MHz)





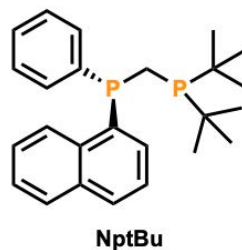
^1H - ^{13}C HSQC NMR (C_6D_6)

S4



8.659
8.655
8.652
8.648
8.643
8.641
8.636
8.634
8.632
8.628
8.625
8.623
7.469
7.452
7.448
7.445
7.400
7.162
7.145
7.141
7.124
7.009
6.991
6.966
6.963
6.960
6.936
6.850
6.809
6.791

¹H NMR (C₆D₆, 400 MHz)

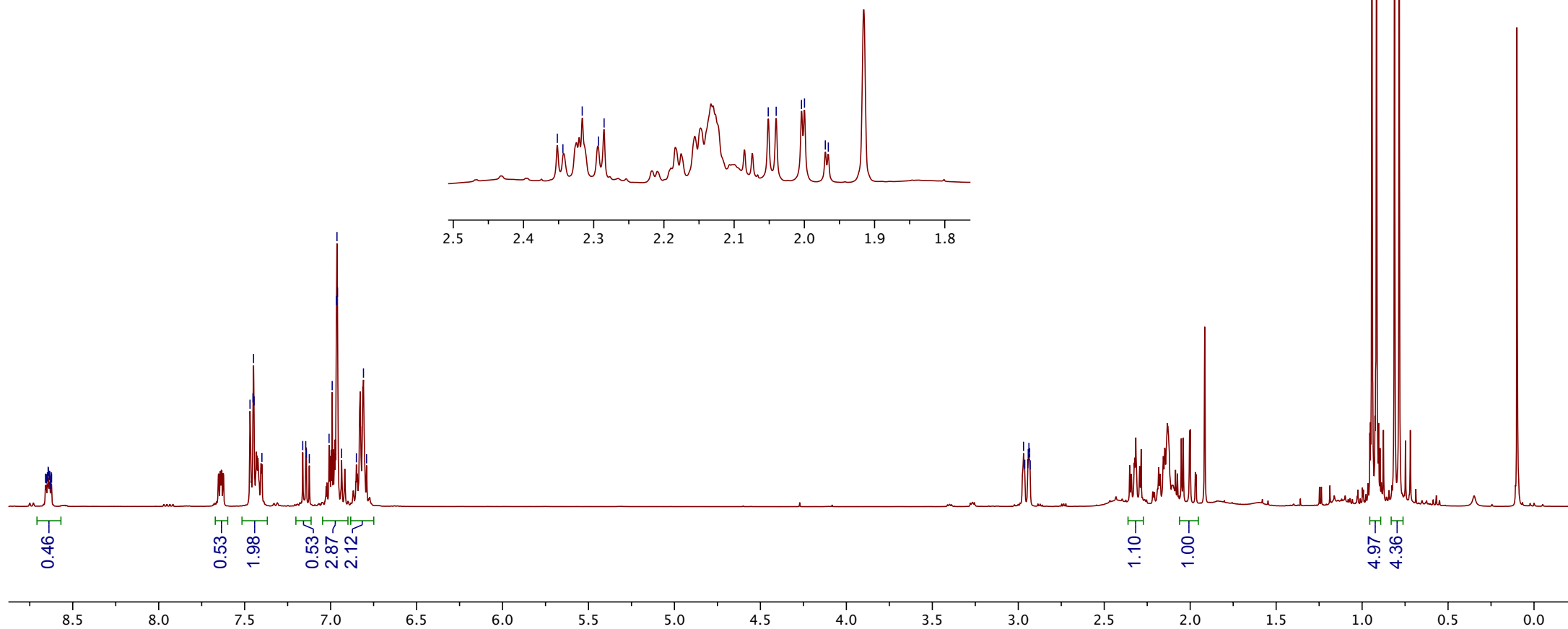


2.969
2.962
2.945
2.942
2.938
2.934
2.931

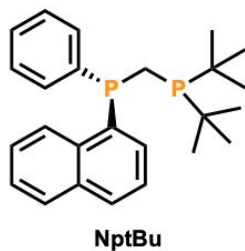
0.943
0.916
0.811
0.784

2.352
2.344
2.316
2.293
2.285

2.051
2.040
2.004
2.000
1.970
1.966



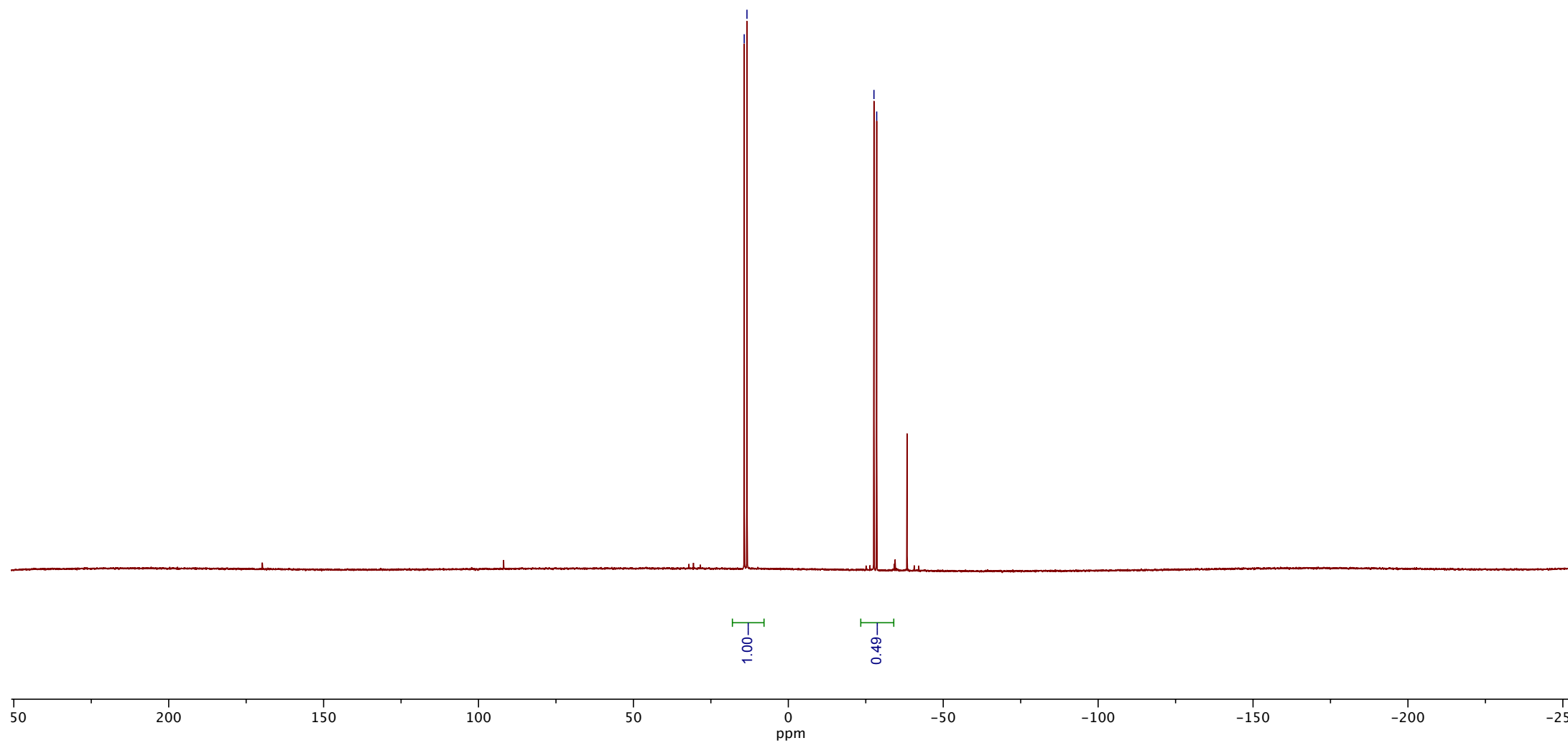
$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz)



14.241
13.352

S6

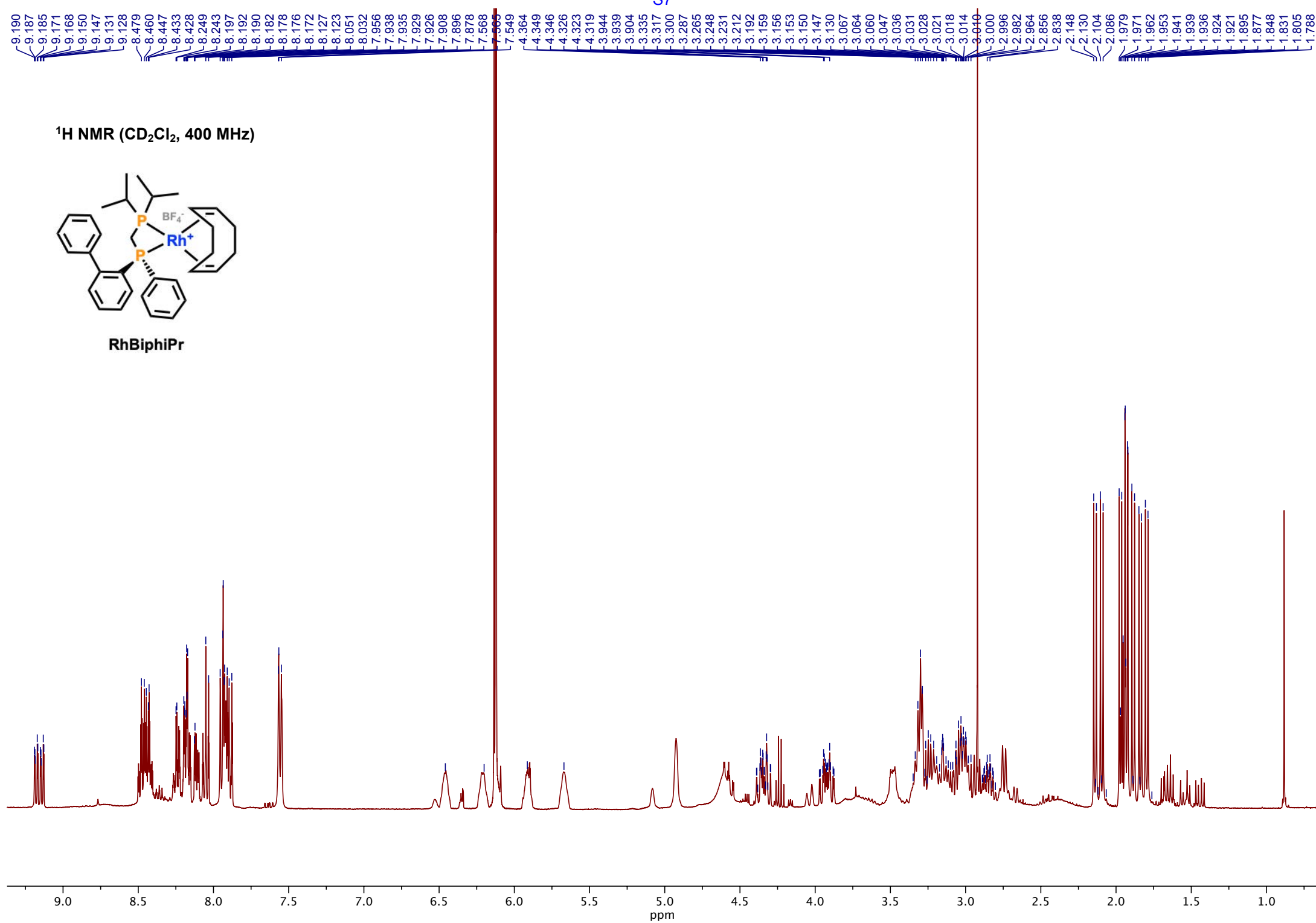
-27.642
-28.531



¹H NMR (CD₂Cl₂, 400 MHz)



RhBiphiPr



S8

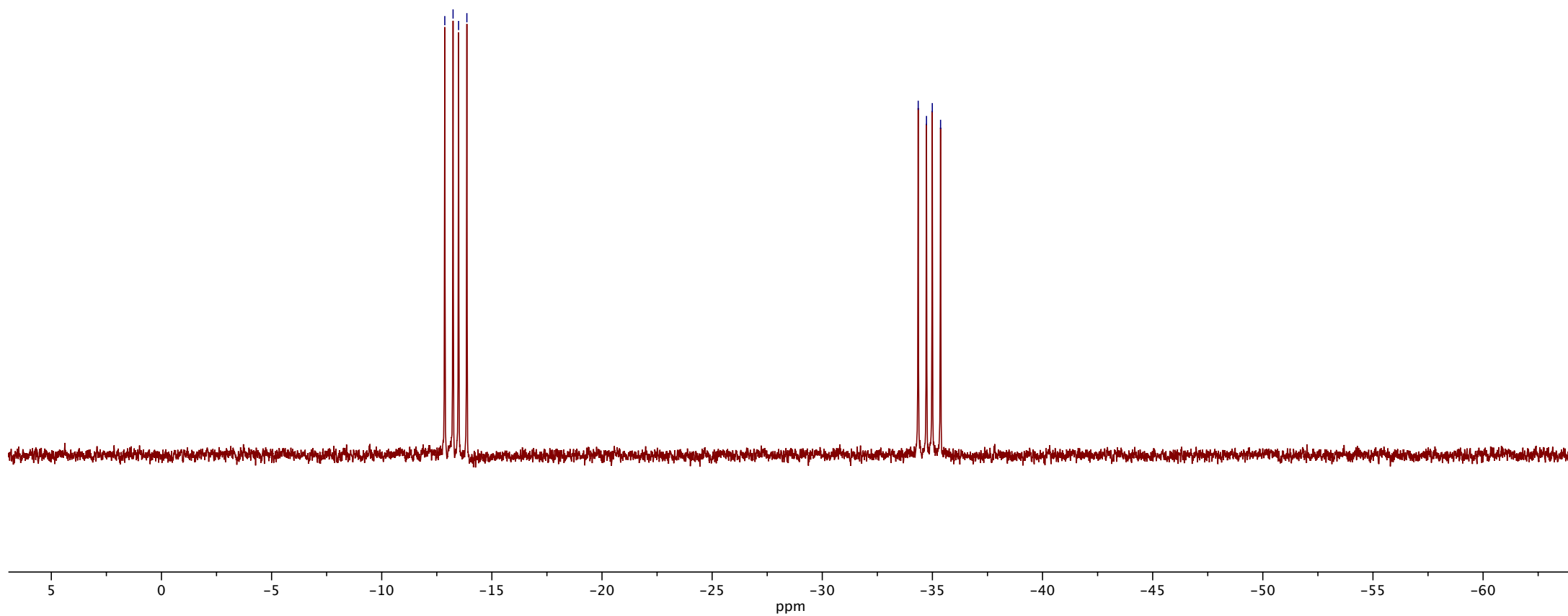
-12.863
-13.239
-13.490
-13.866

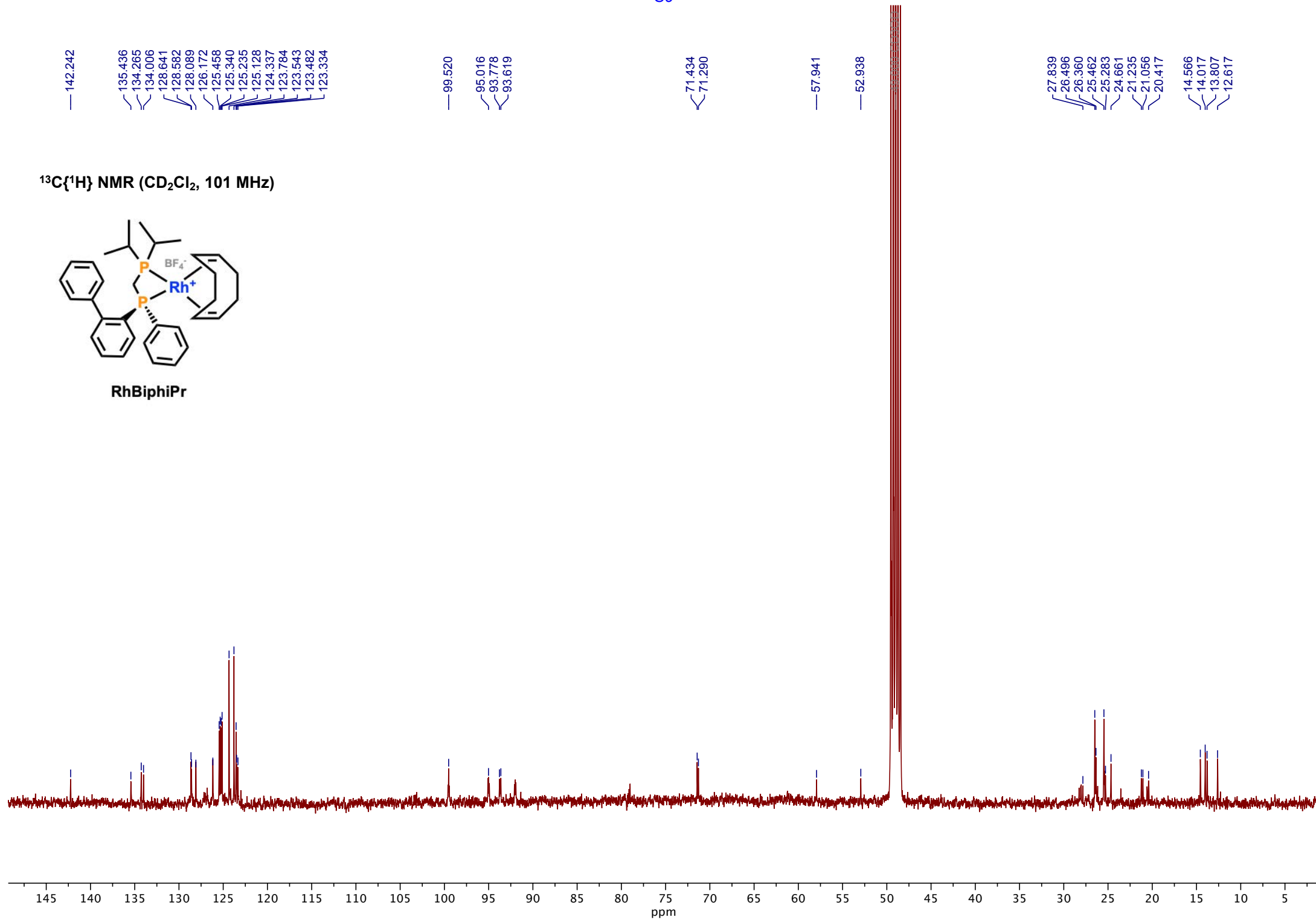
-34.355
-34.731
-34.995
-35.371

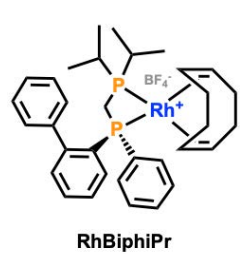
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz)



RhBiphiPr

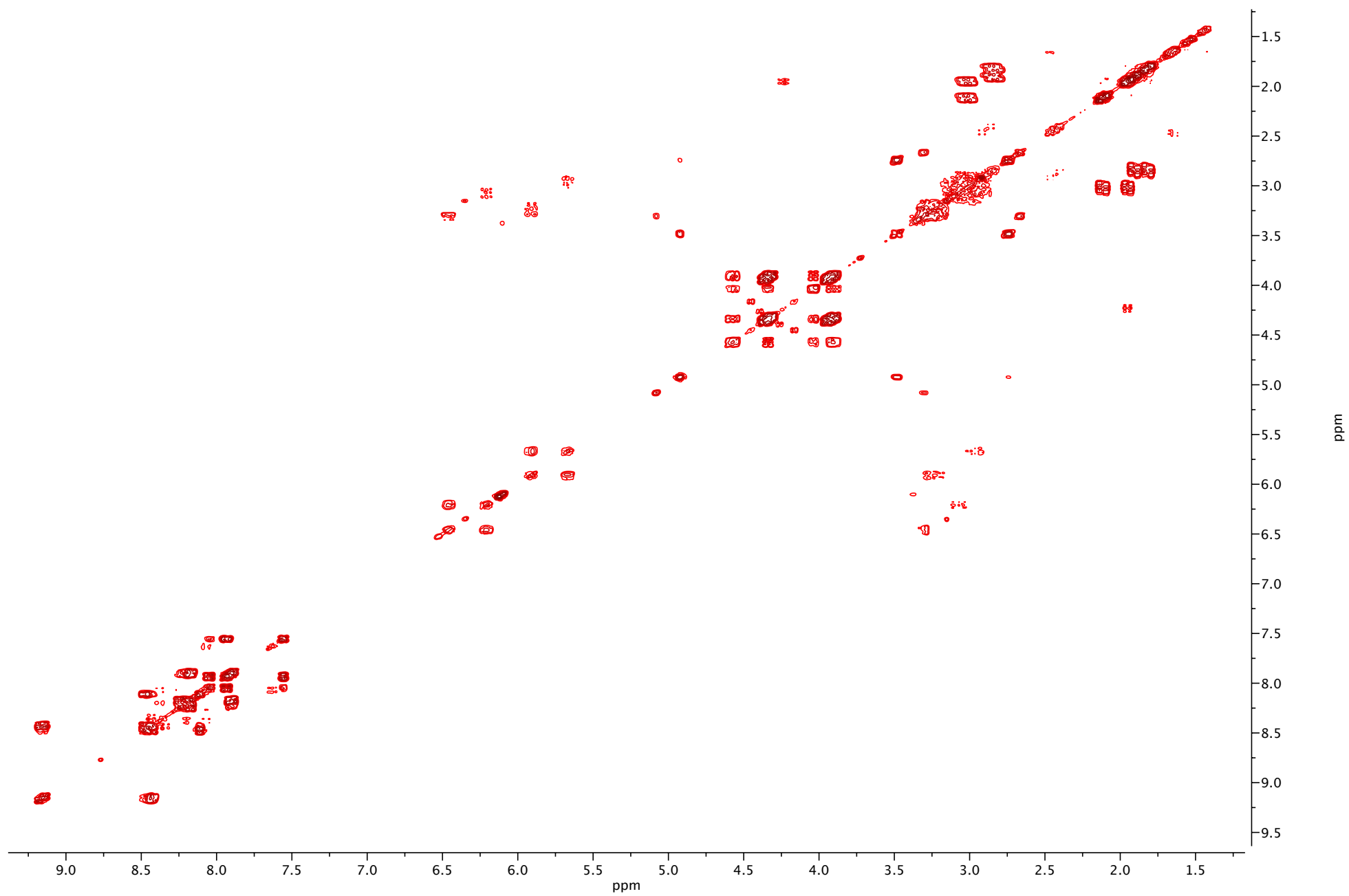


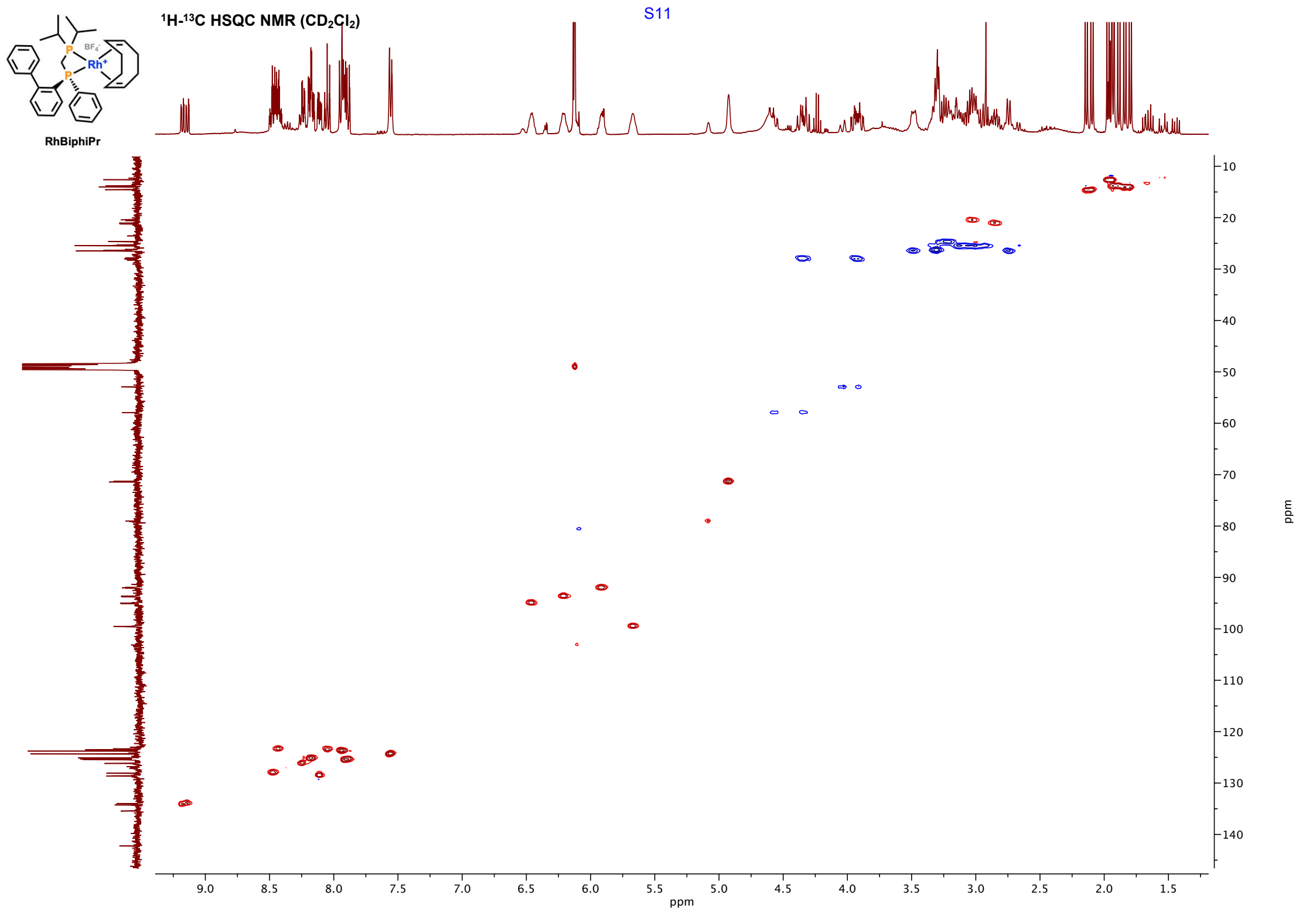


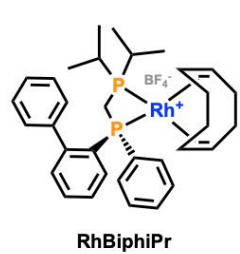


^1H - ^1H COSY NMR (CD_2Cl_2 , 400 MHz)

S10

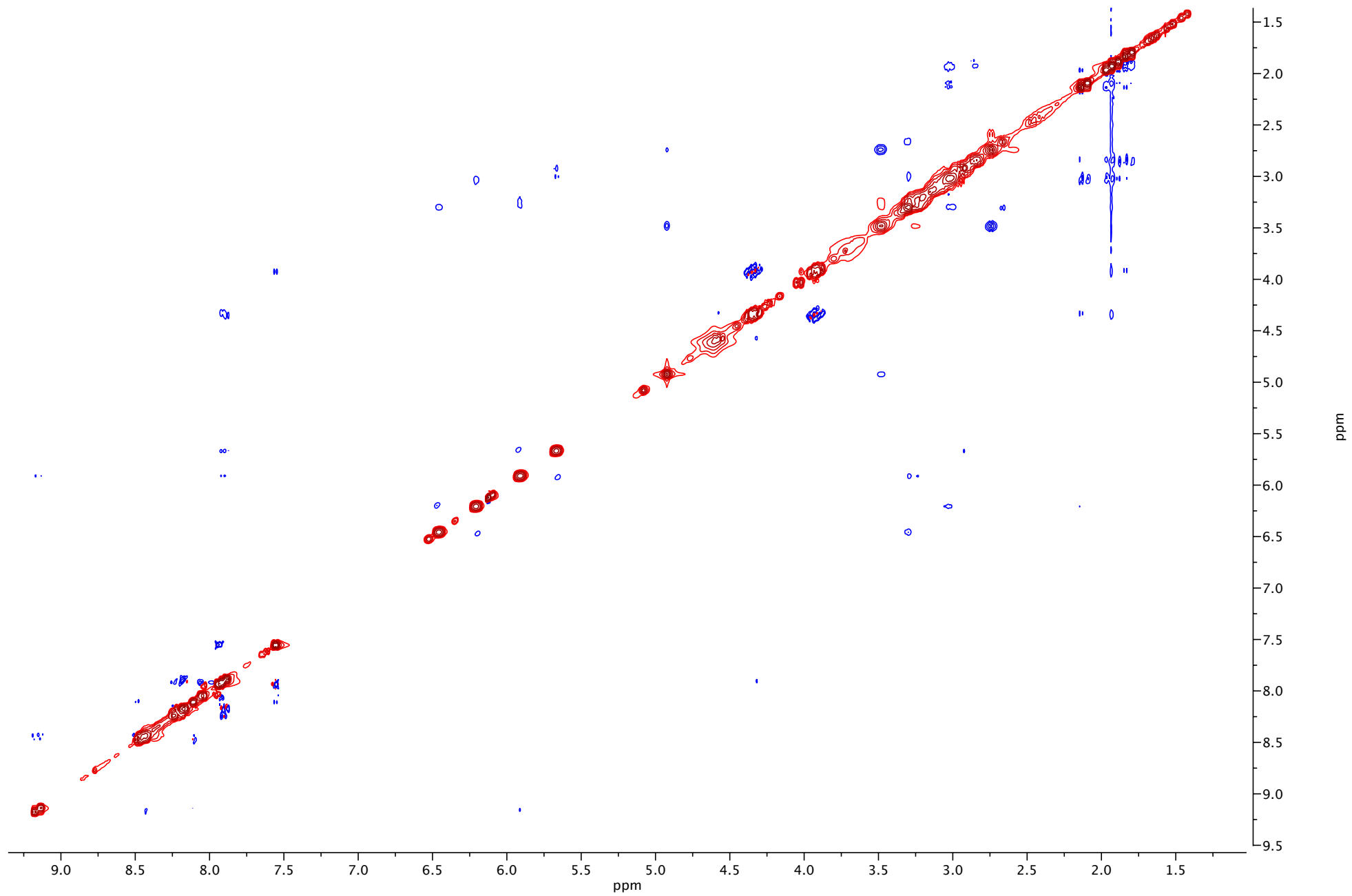


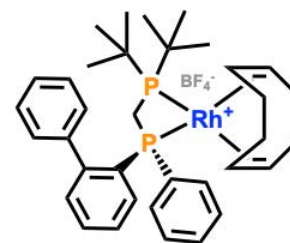




¹H-¹H NOESY NMR (CD₂Cl₂, 400 MHz)

S12



¹H NMR (CD₂Cl₂, 400 MHz)

RhBiphtBu

7.347
7.342
7.328
7.323
7.291
7.286
7.284
7.276
7.272
7.269
7.265
7.221
7.213
7.205
7.158
7.139
7.049
7.031
7.029
6.956
6.953
6.936
6.932
6.926
6.923
6.906

— 5.906

— 5.501

— 4.872

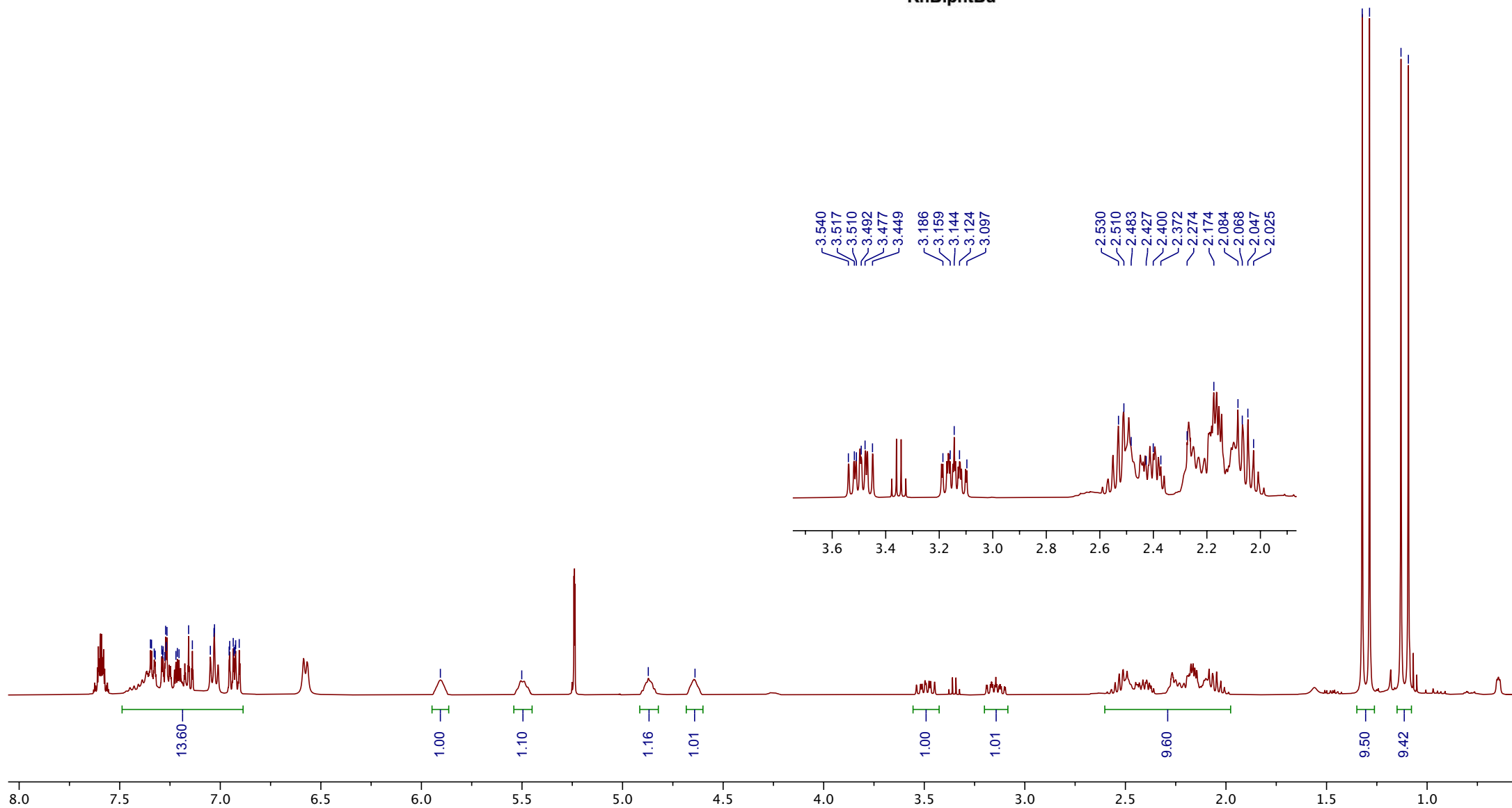
— 4.640

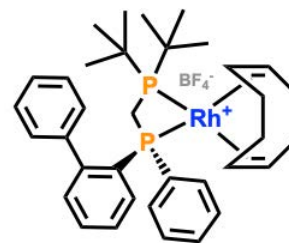
— 1.322

— 1.286

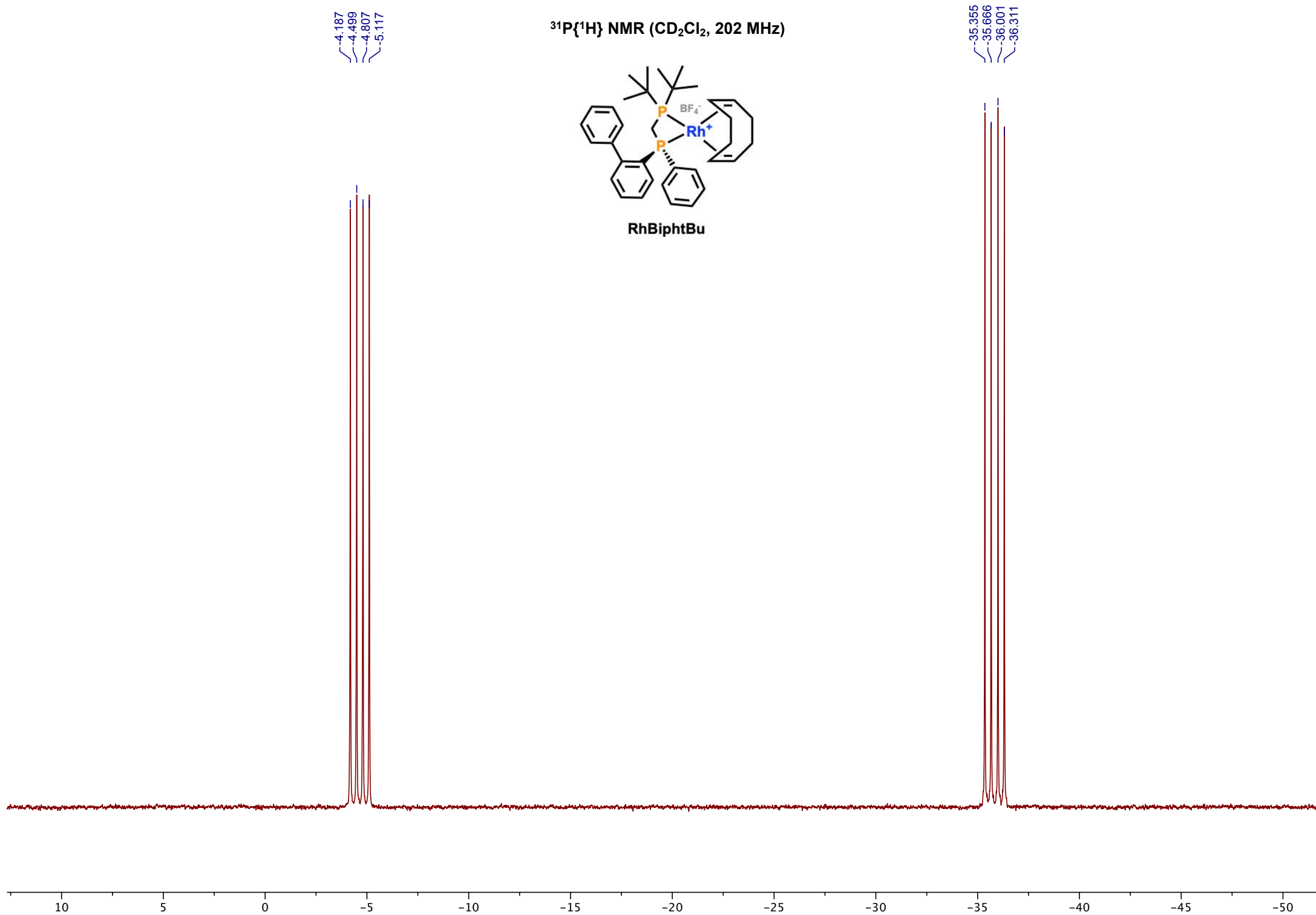
— 1.130

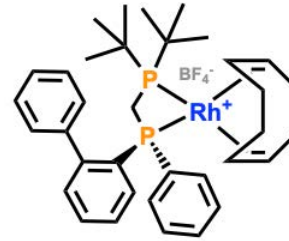
— 1.093



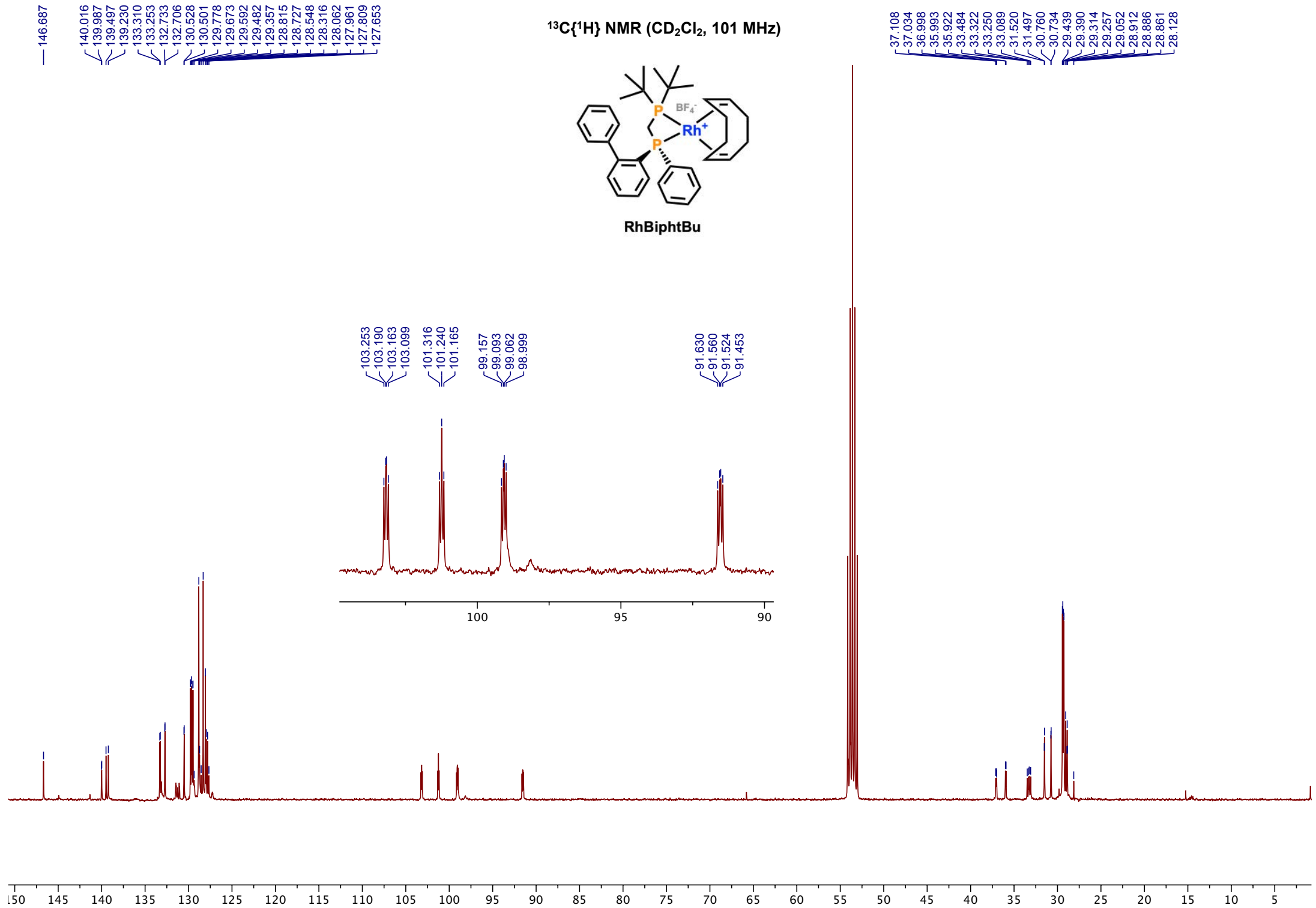
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz)

RhBiphtBu



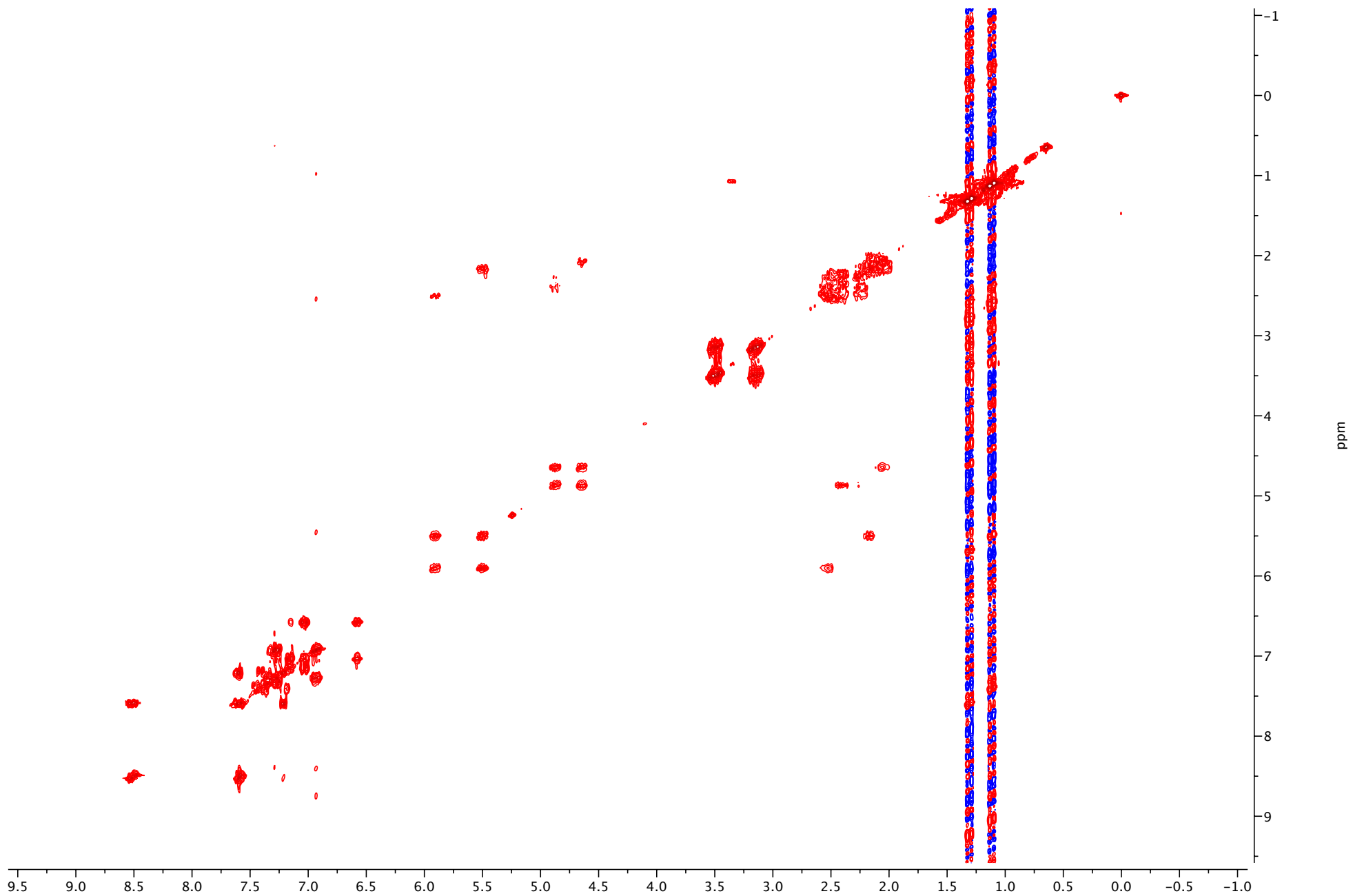
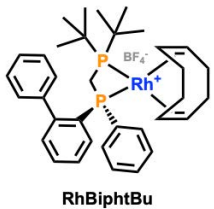
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz)

RhBiphtBu



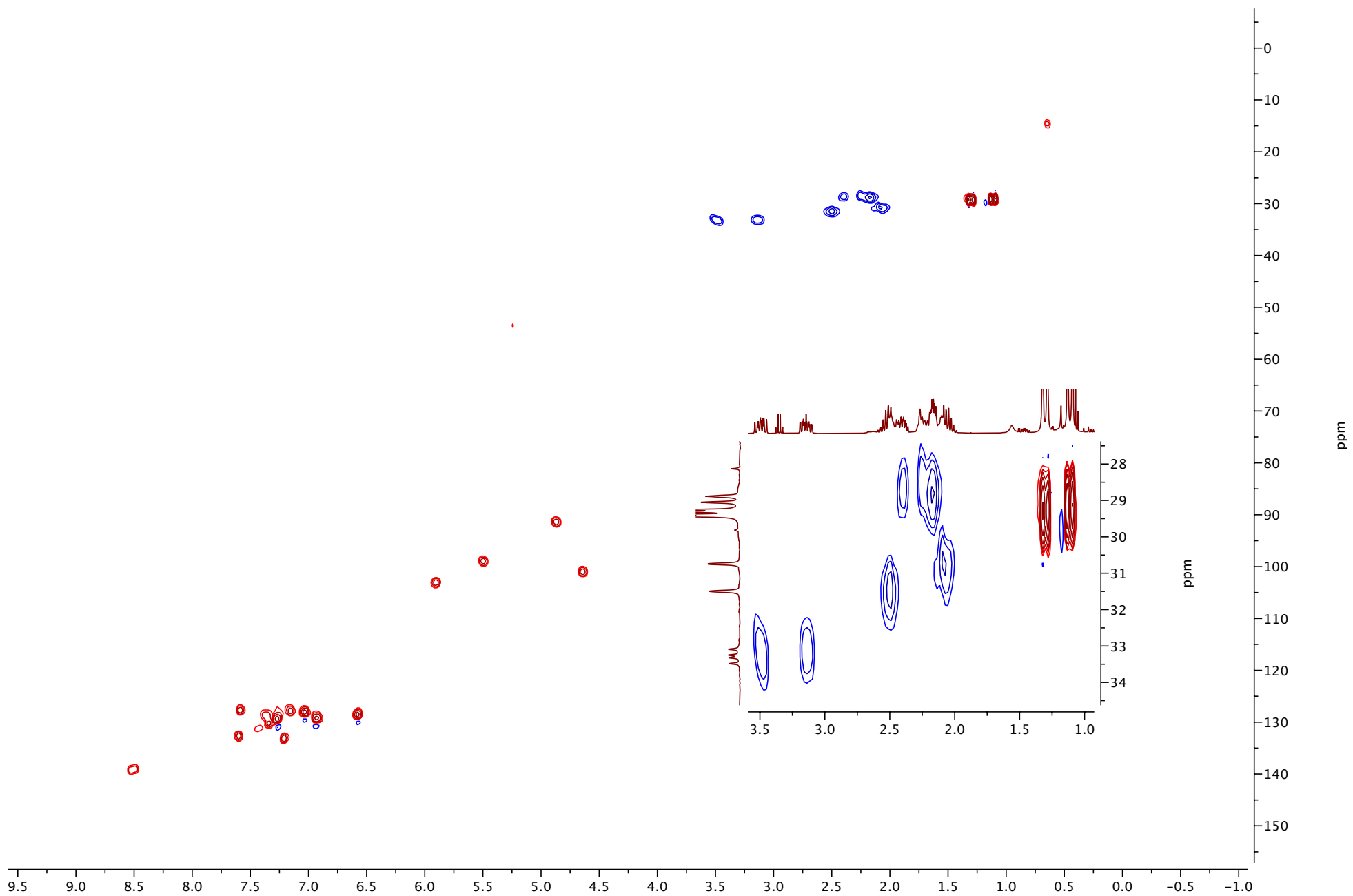
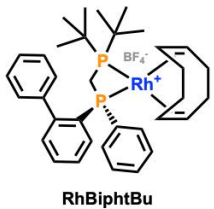
¹H-¹H COSY NMR (CD₂Cl₂, 400 MHz)

S16



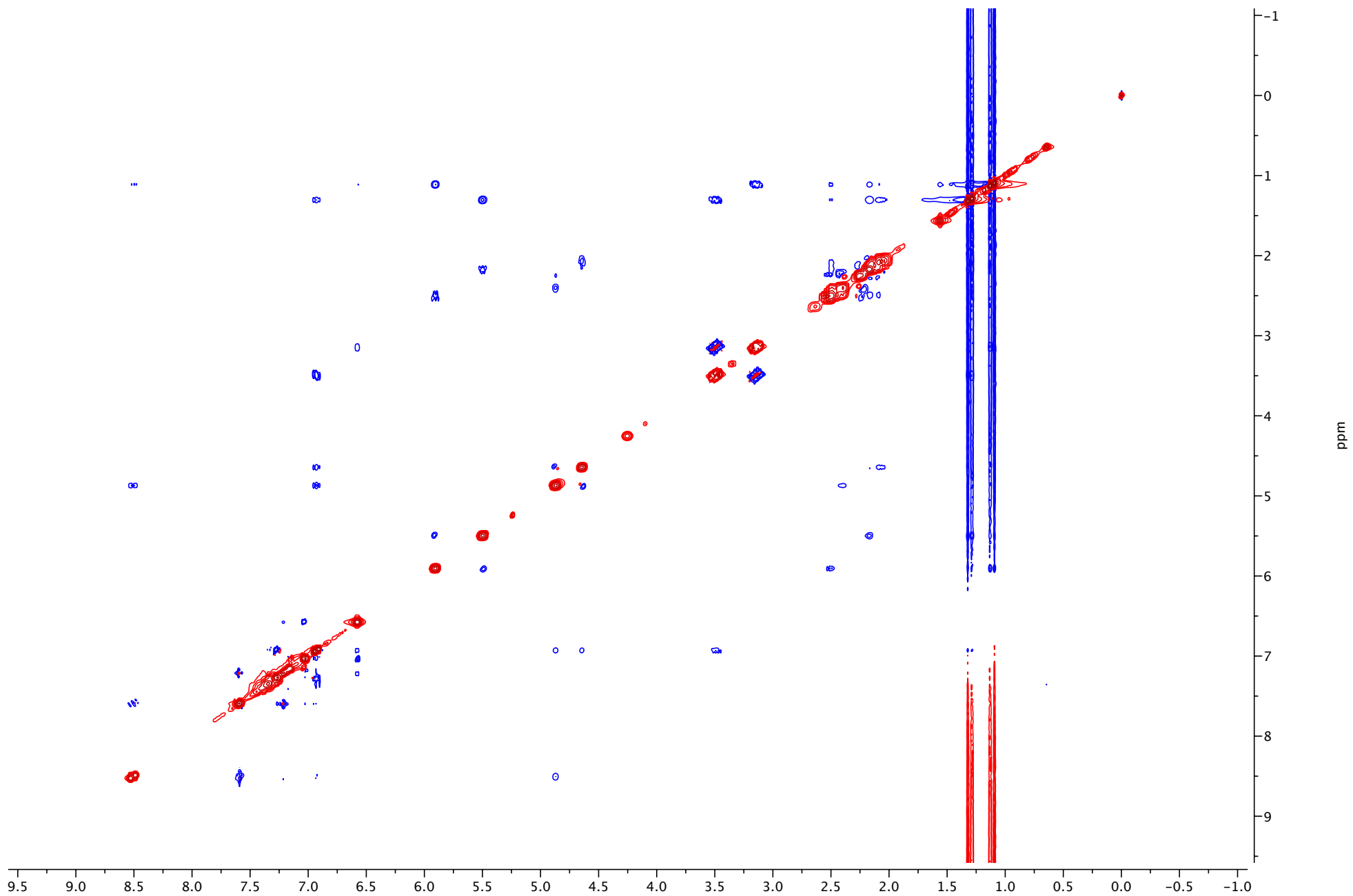
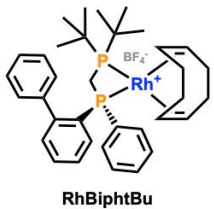
¹H-¹³C HSQC NMR (CD₂Cl₂)

S17

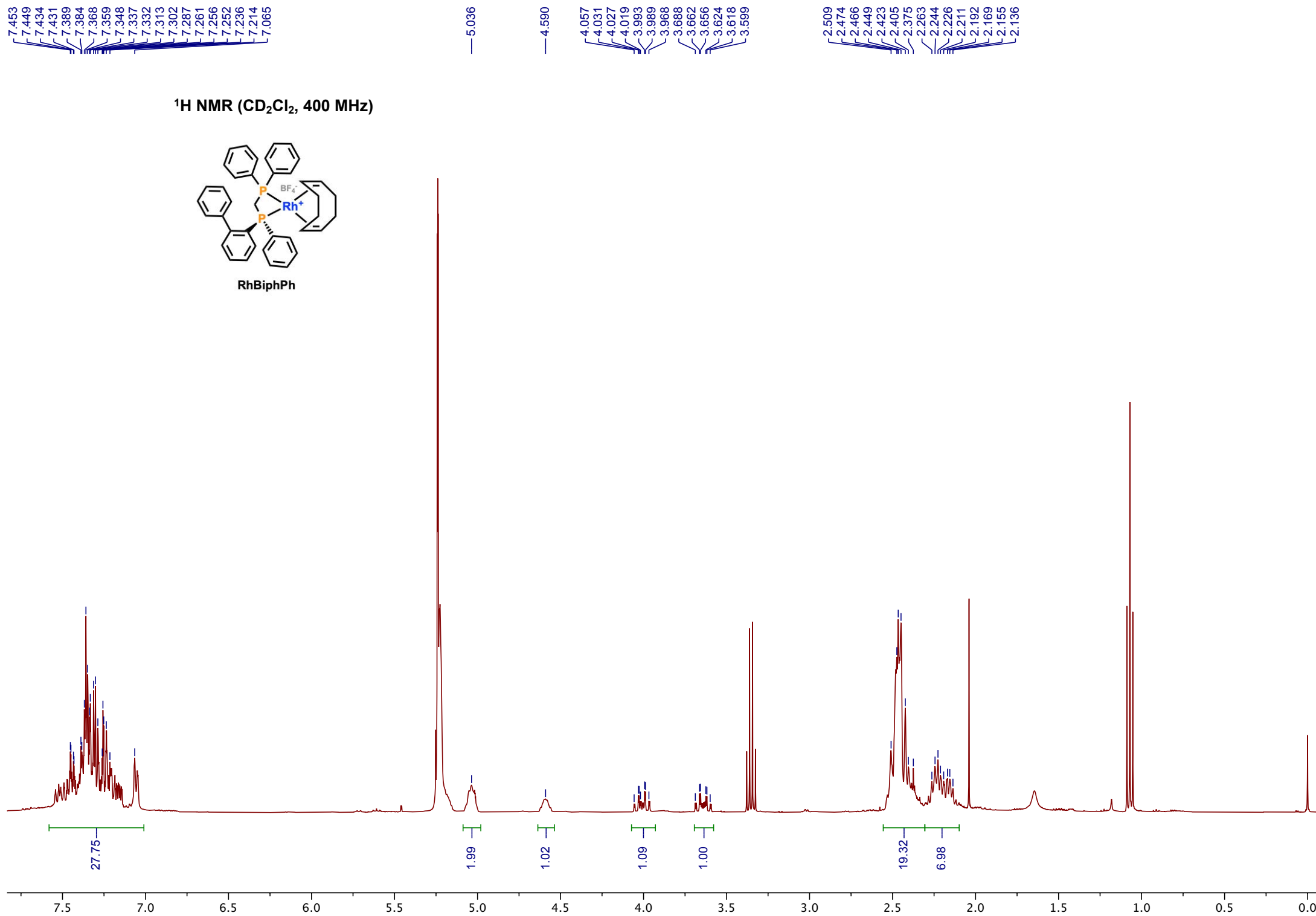
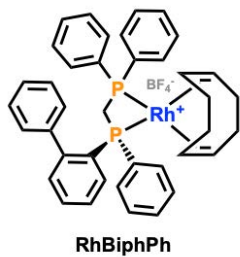


¹H-¹H NOESY NMR (CD₂Cl₂, 400 MHz)

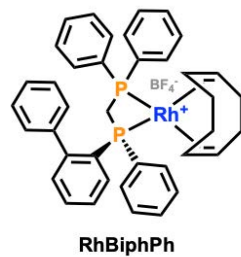
S18



¹H NMR (CD₂Cl₂, 400 MHz)



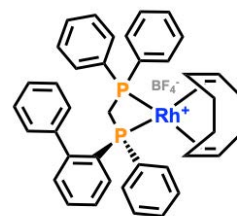
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz)



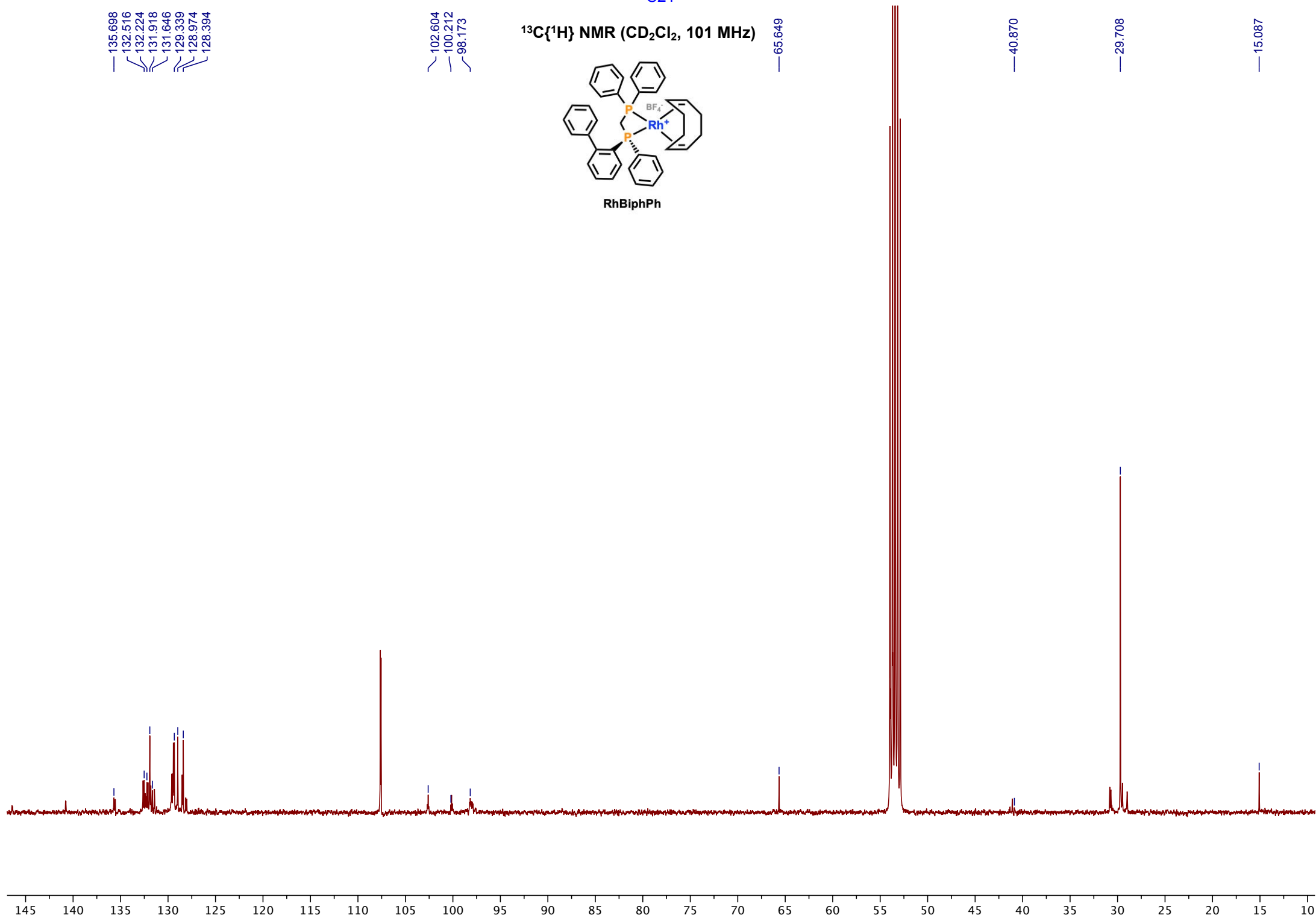
S20
-28.449
-28.916
-29.225
-29.705
-30.029
-30.496

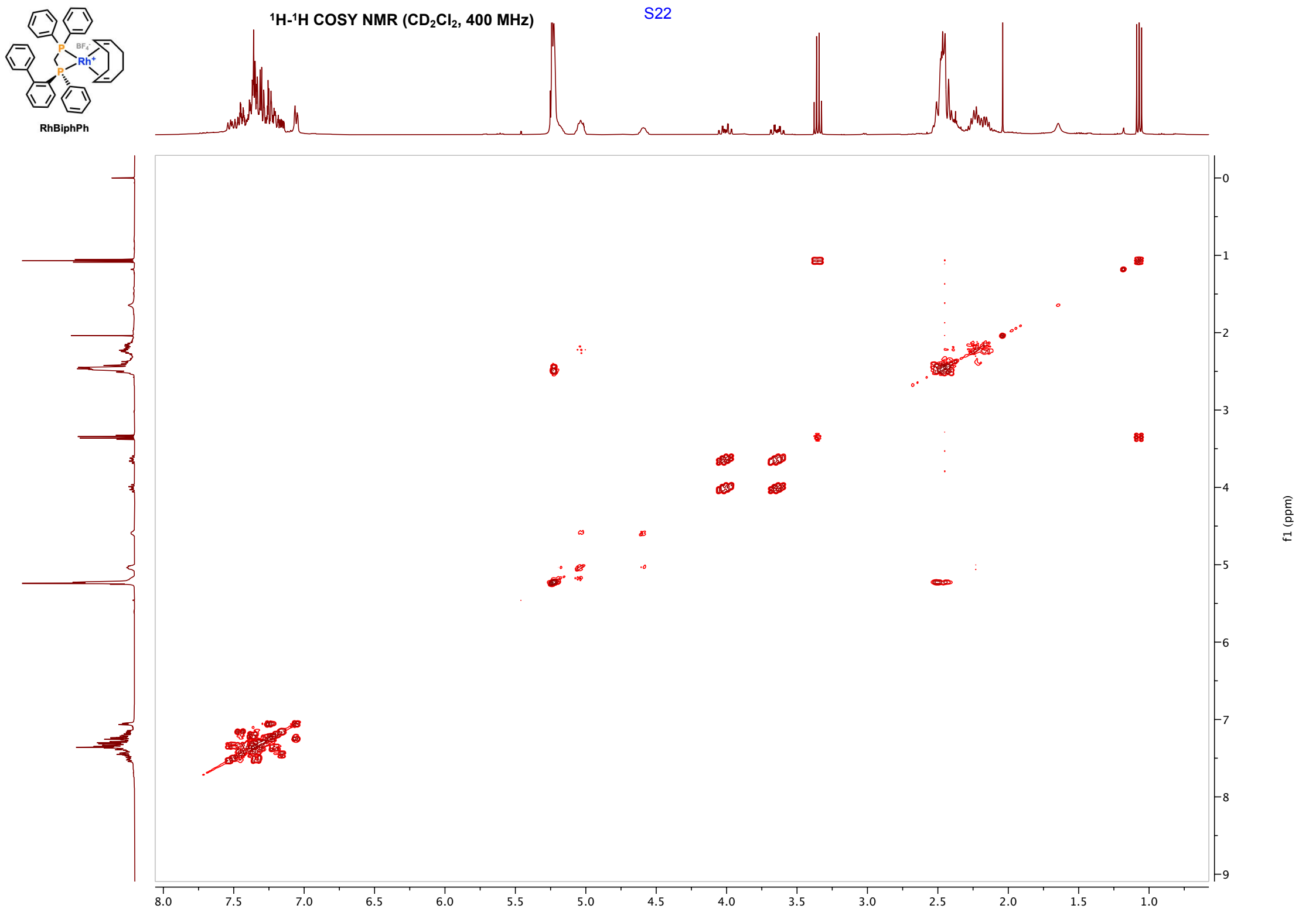
25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85

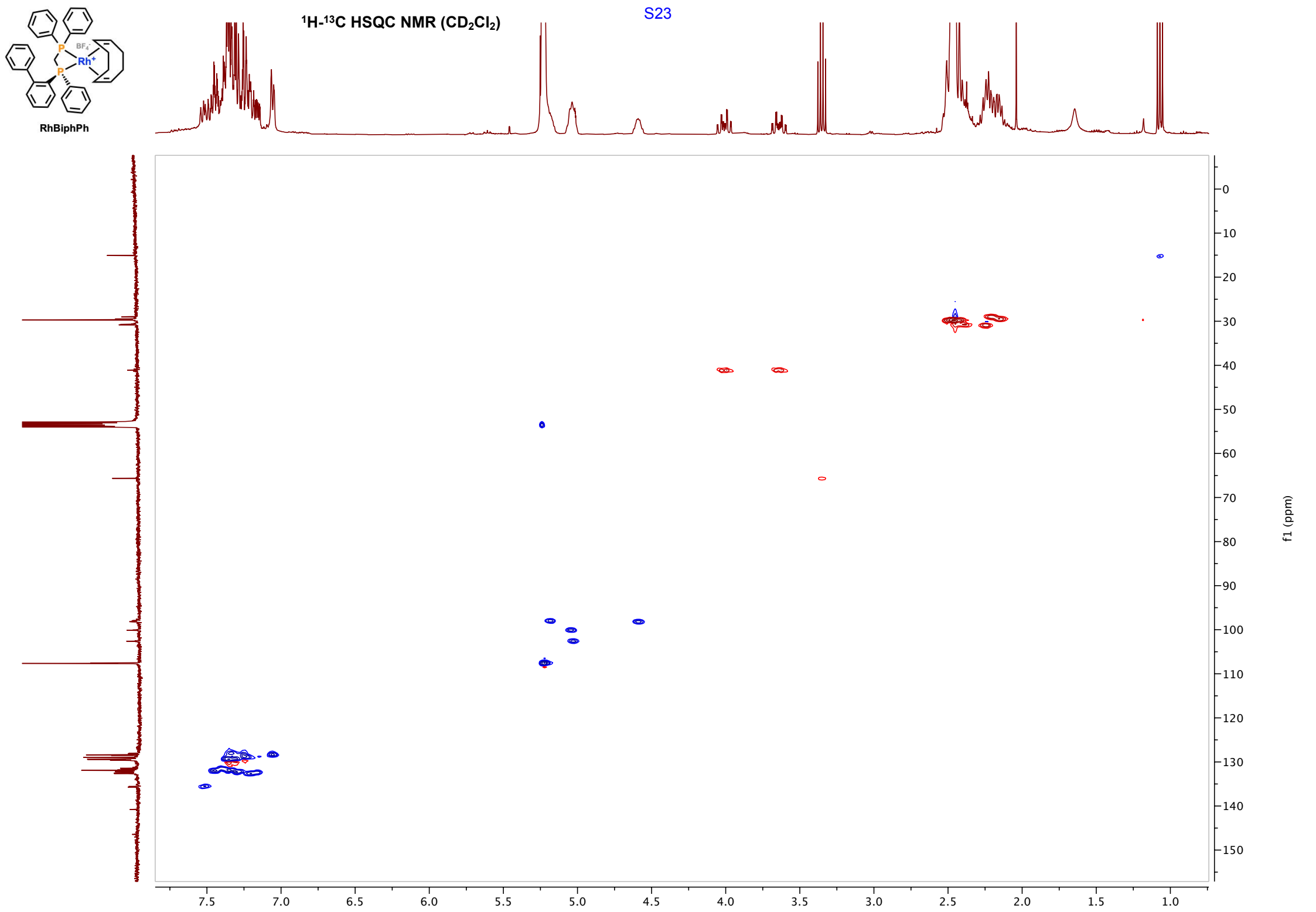
S21

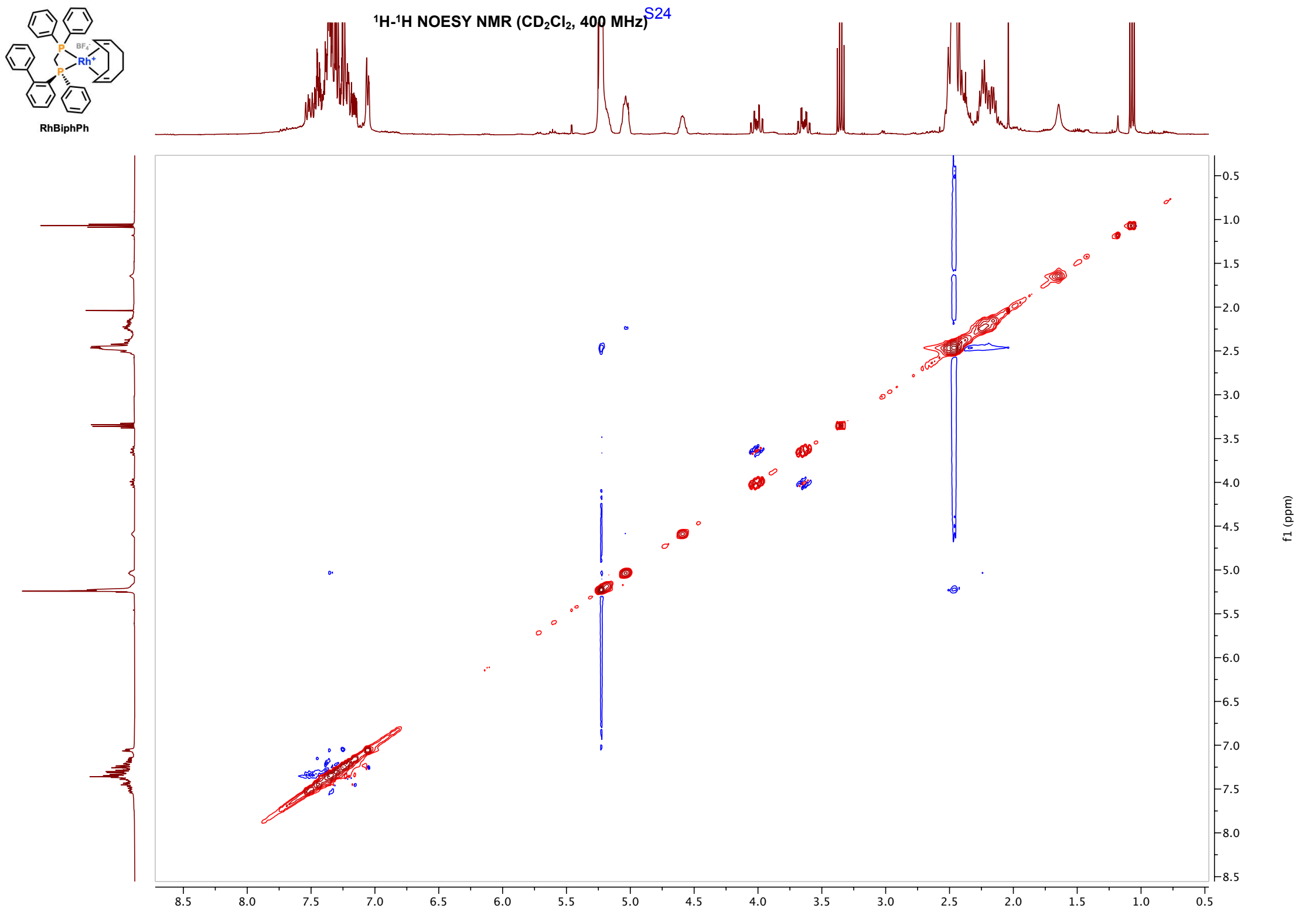
 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 101 MHz)

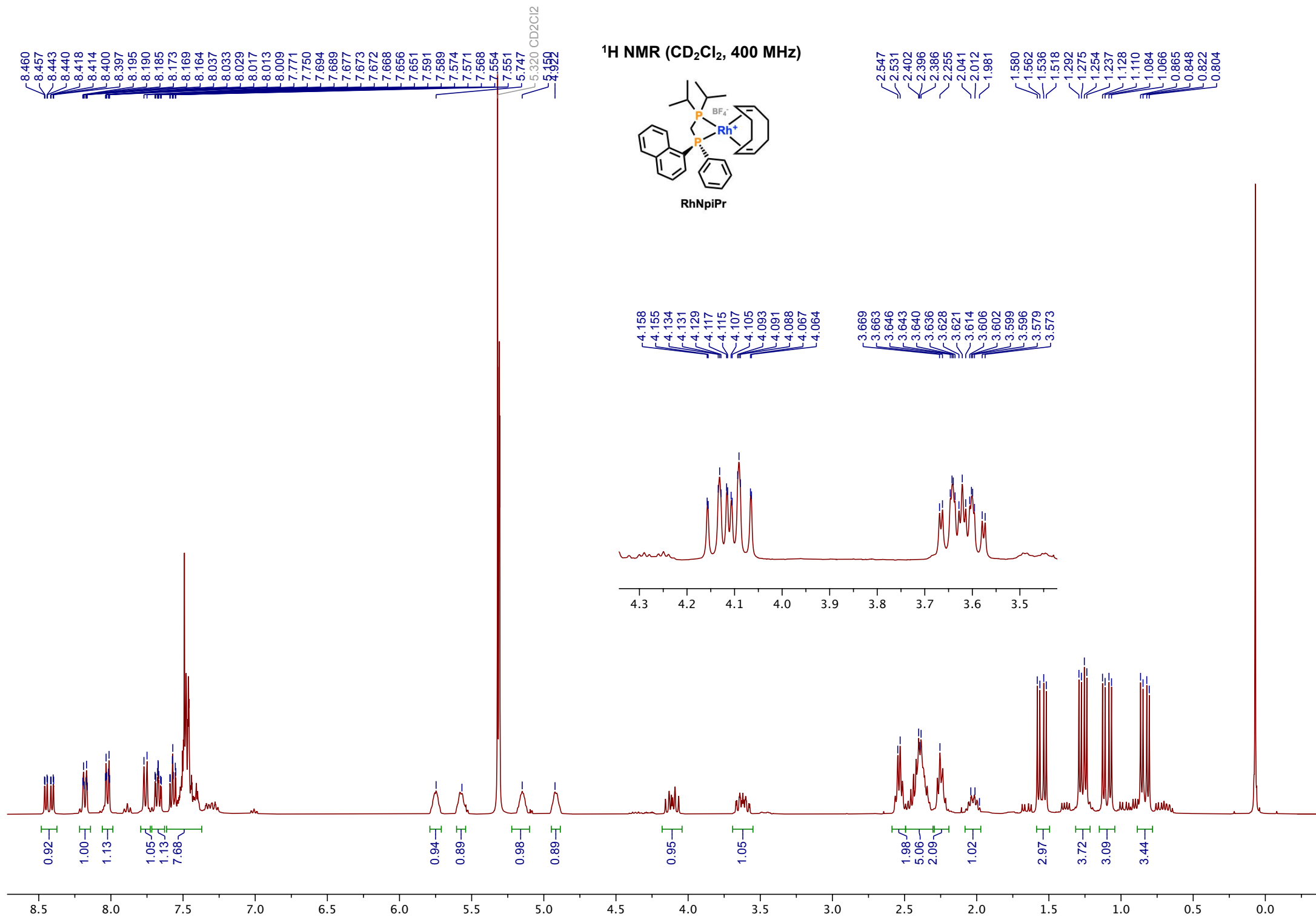
RhBiphPh

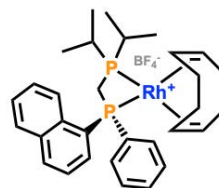








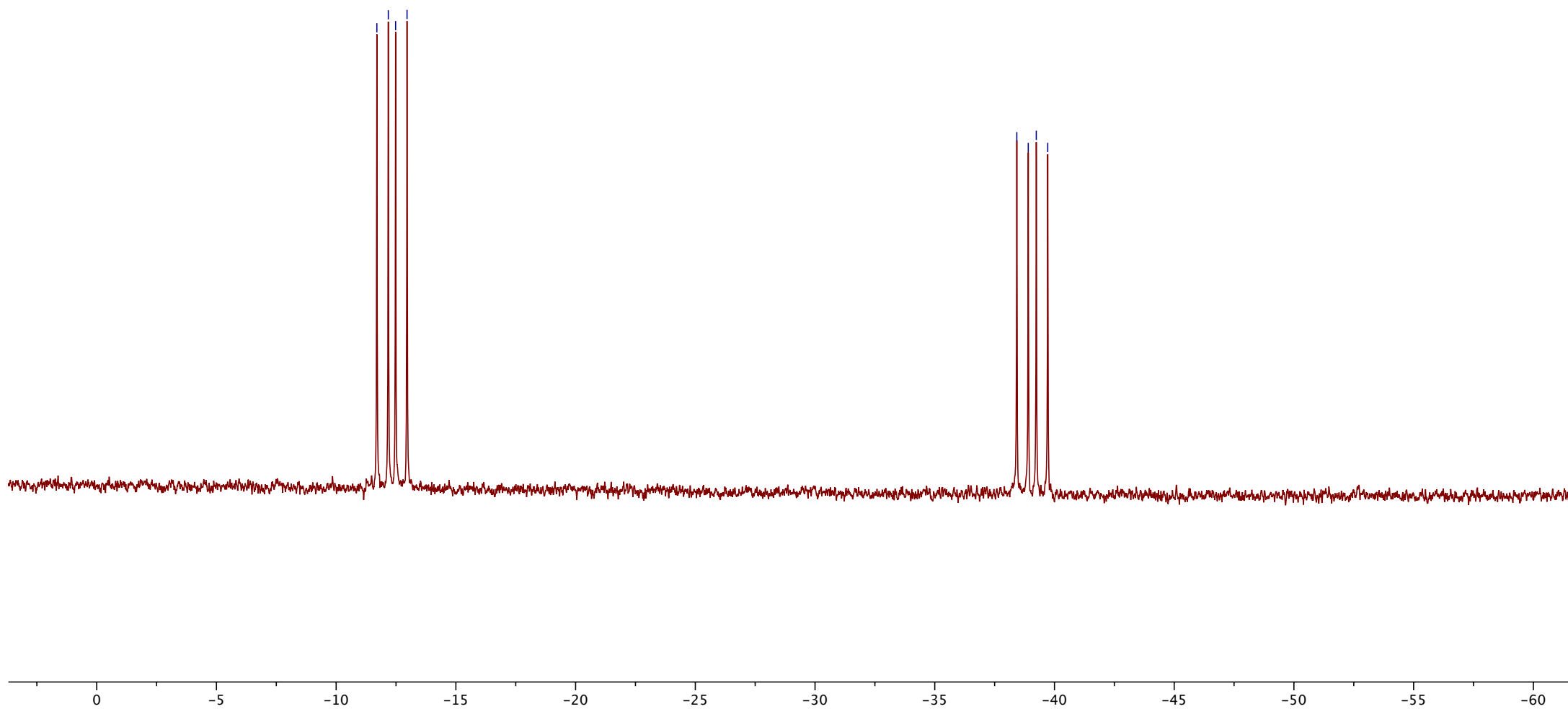


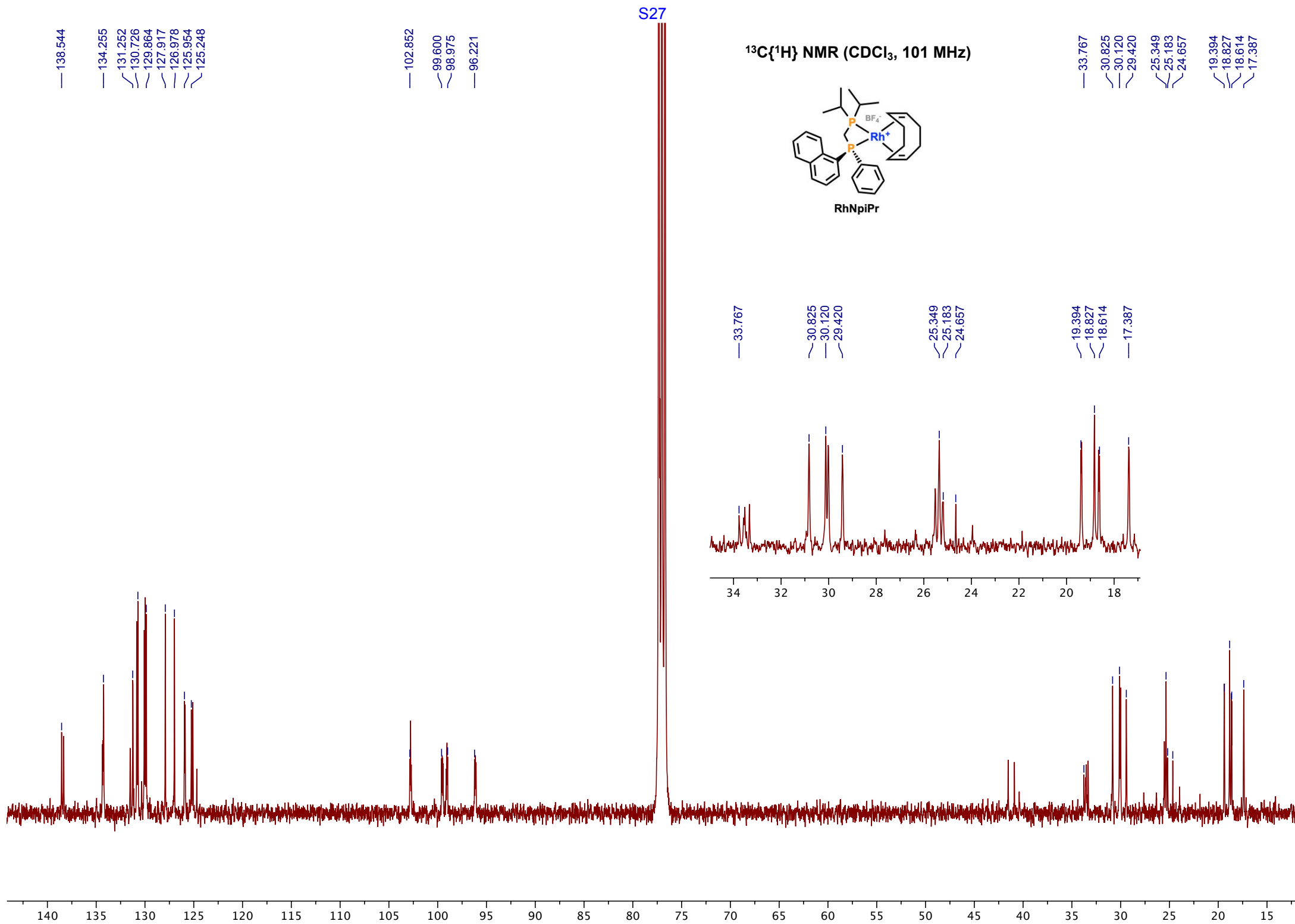
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz)

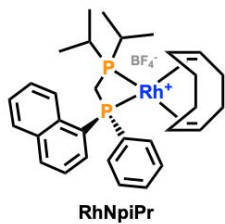
RhNpiPr

-11.700
-12.178
-12.482
-12.960

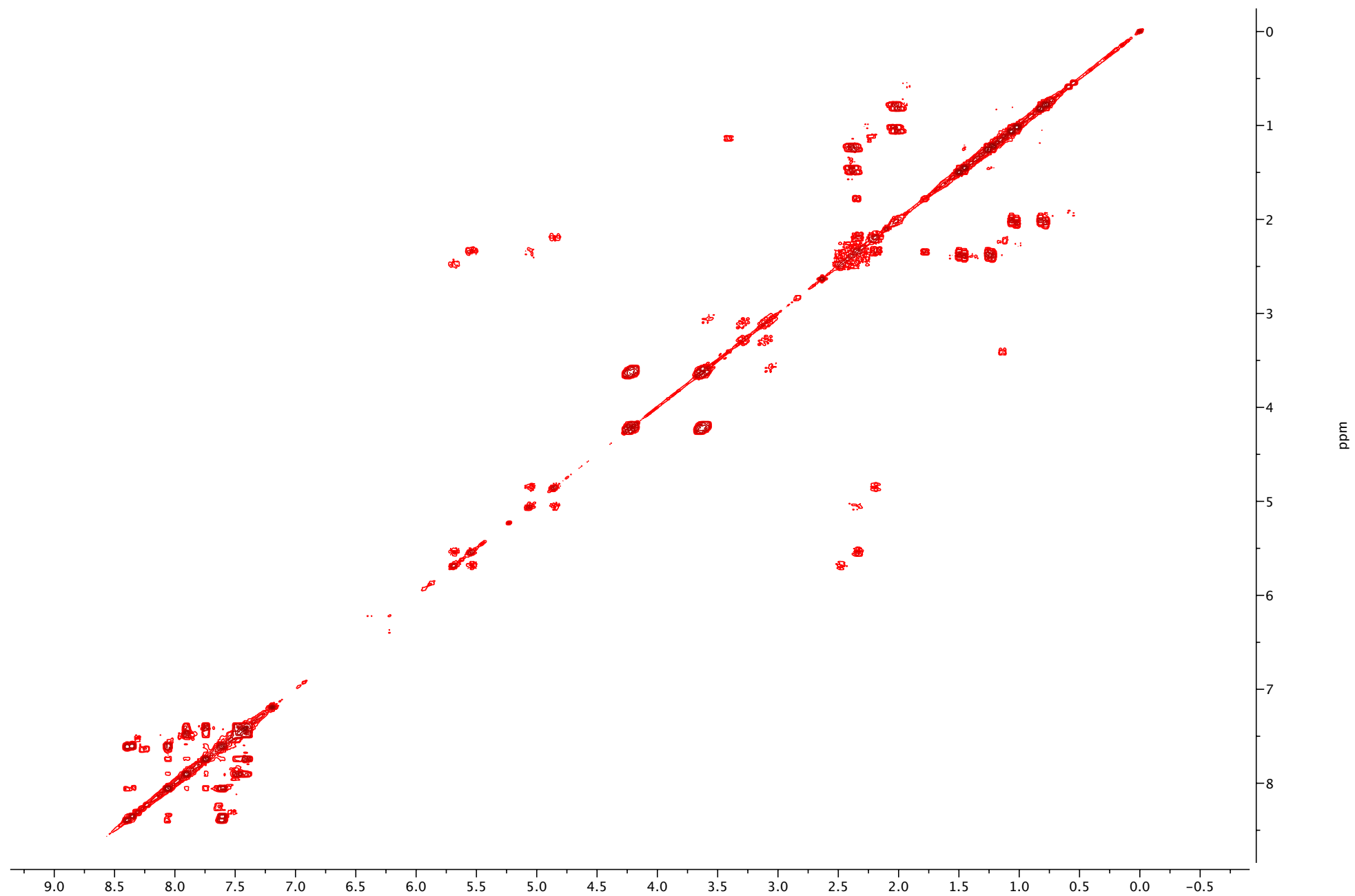
-38.428
-38.905
-39.240
-39.718

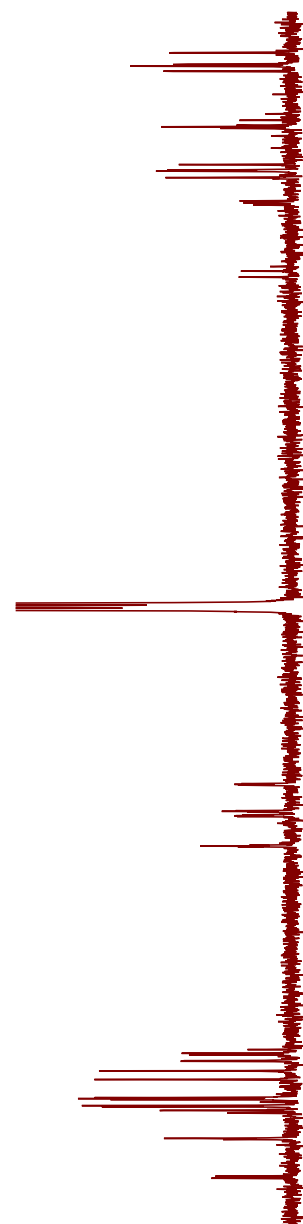




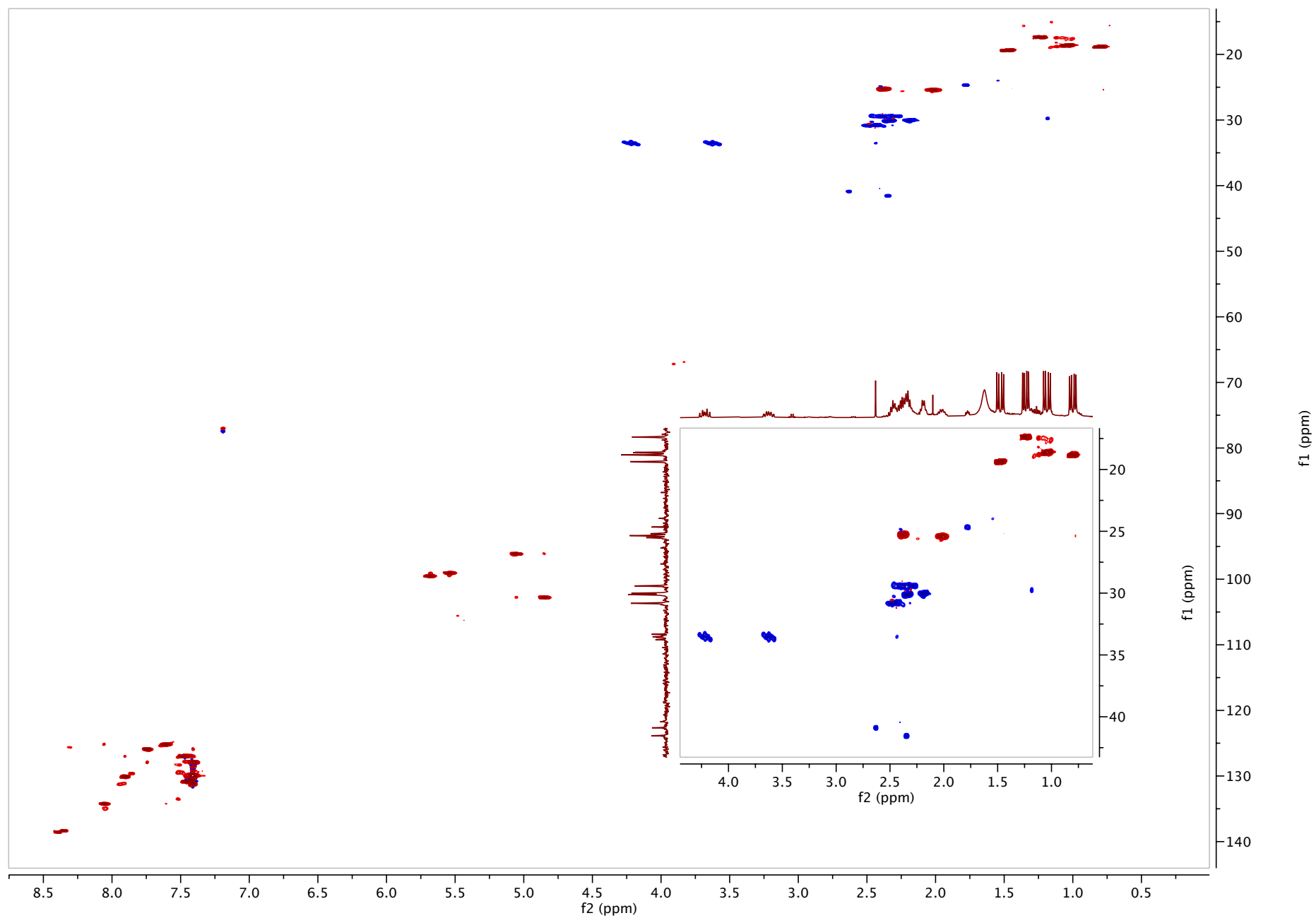


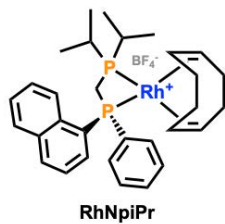
¹H-¹H COSY NMR (CDCl₃, 400 MHz)





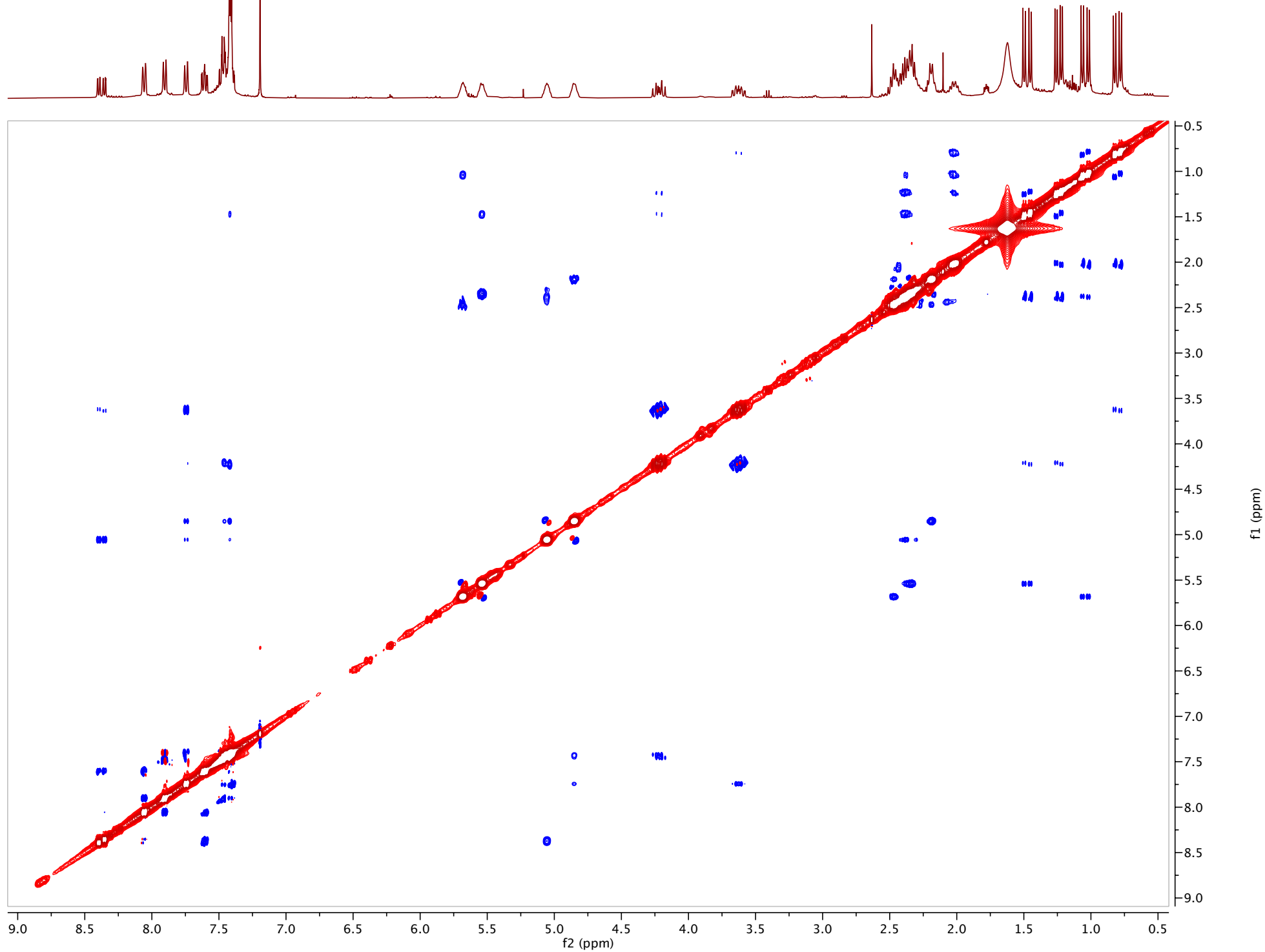
S29



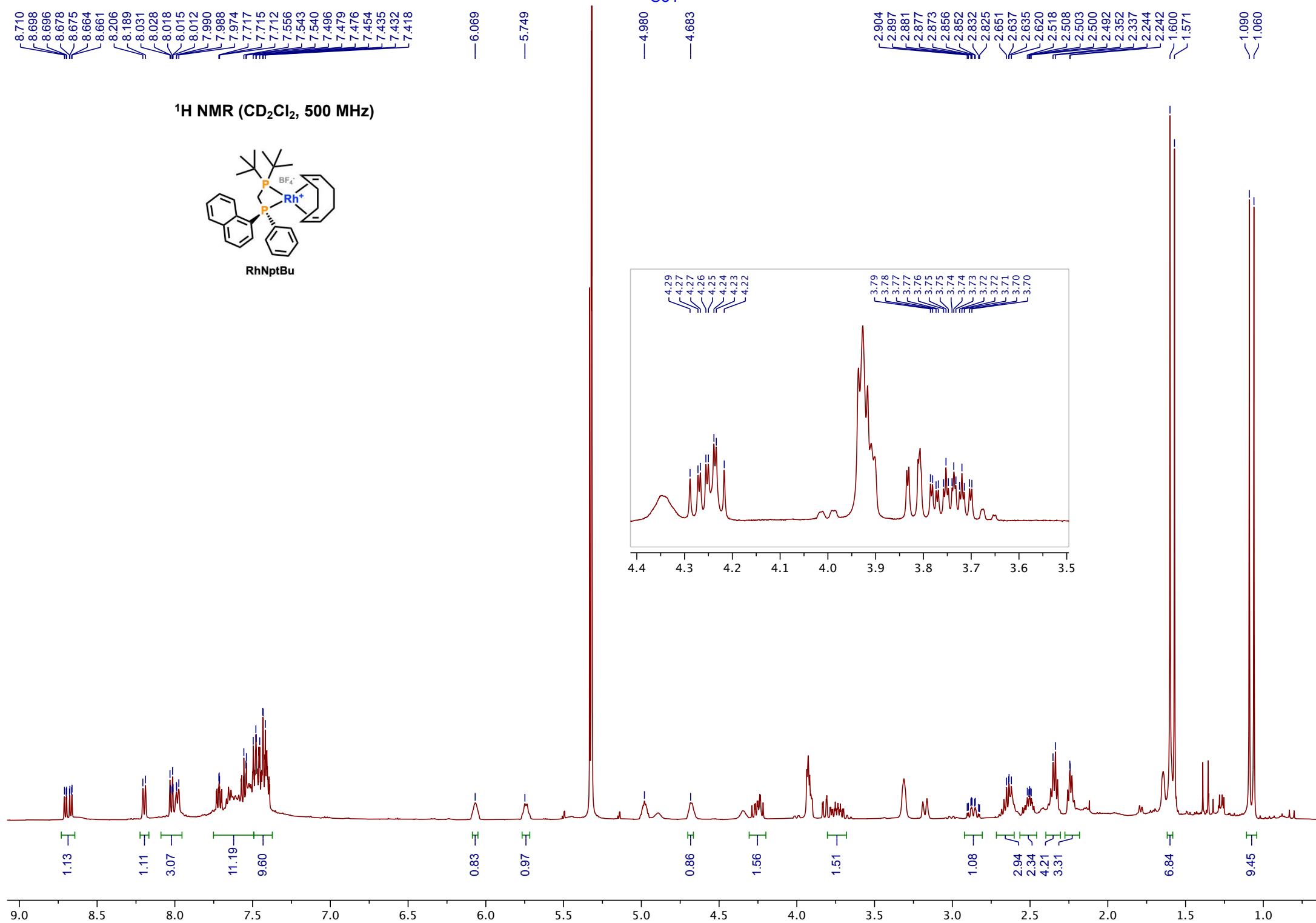
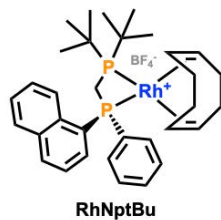


¹H-¹H NOESY NMR (CDCl₃, 400 MHz)

S30

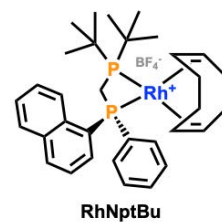


¹H NMR (CD₂Cl₂, 500 MHz)



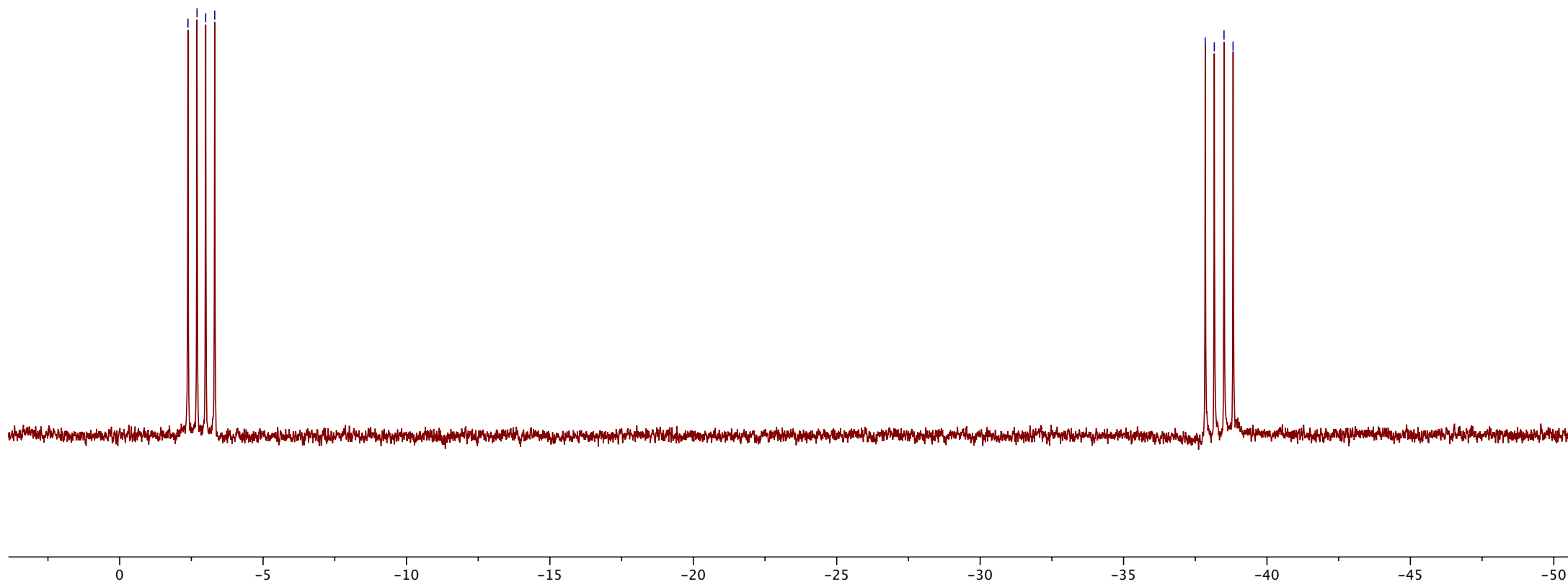
S32

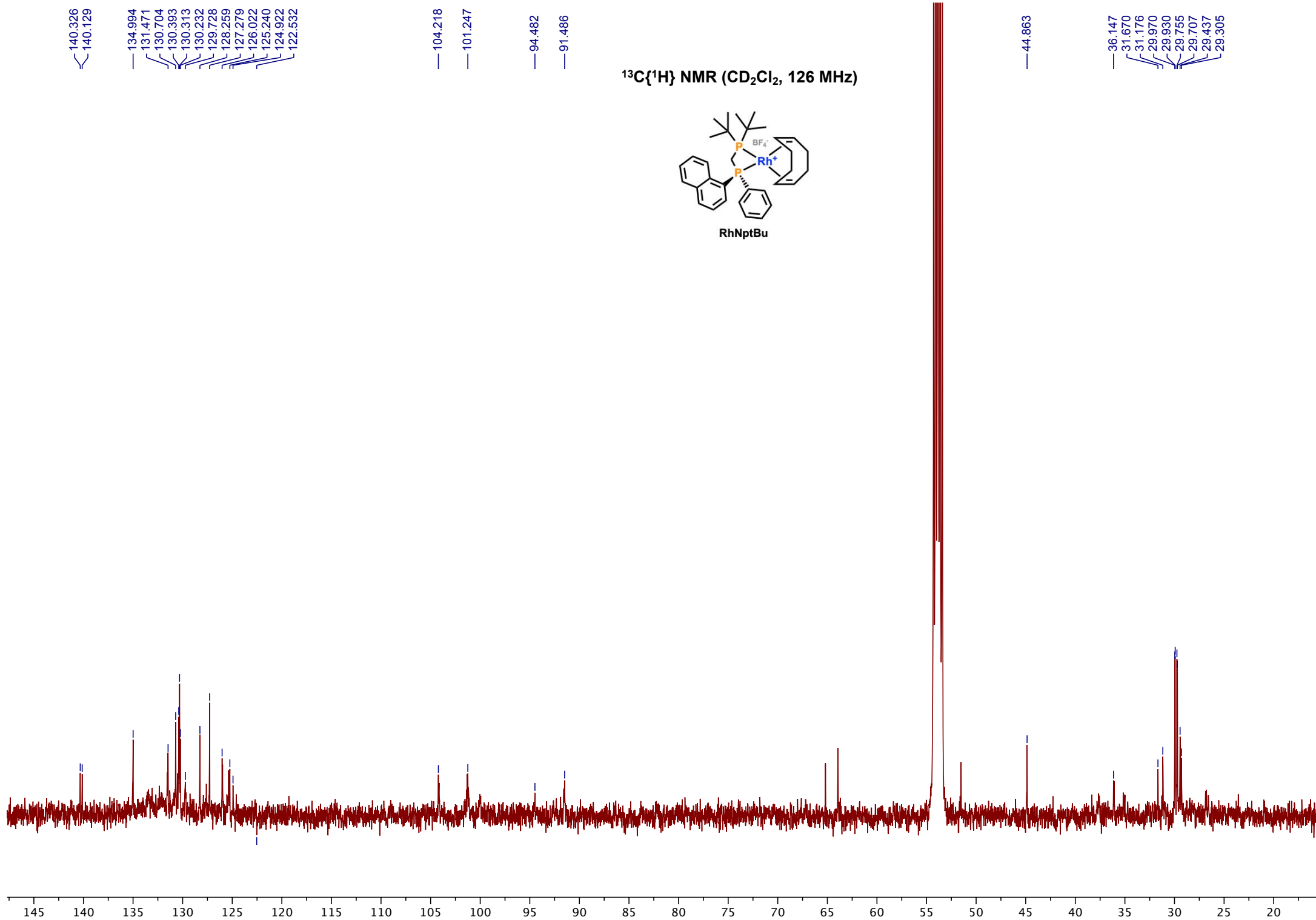
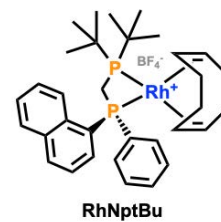
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202 MHz)



-2.382
-2.697
-2.999
-3.314

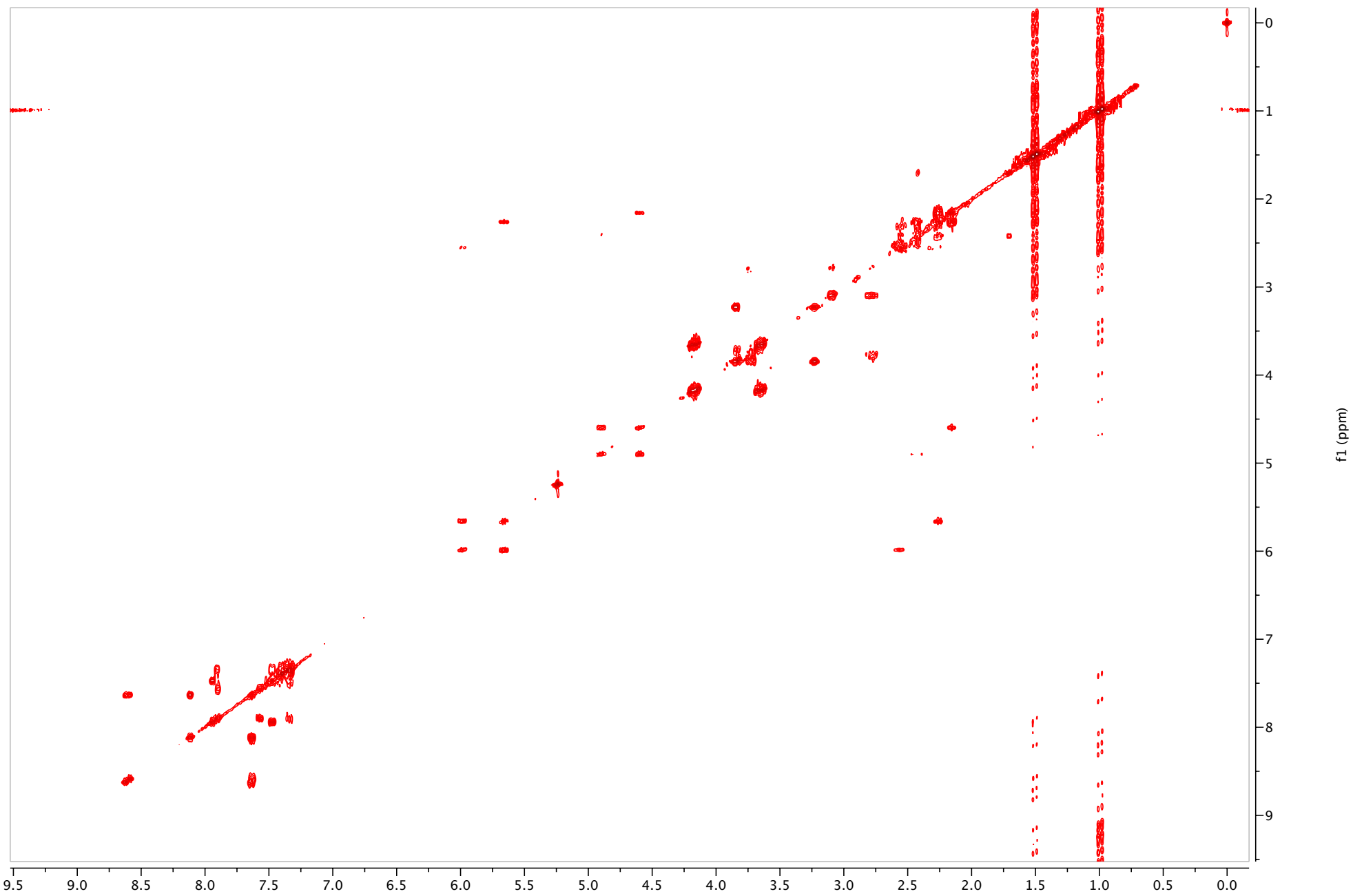
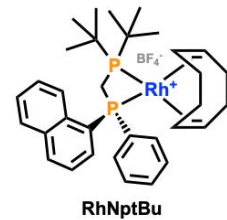
-37.846
-38.163
-38.503
-38.818

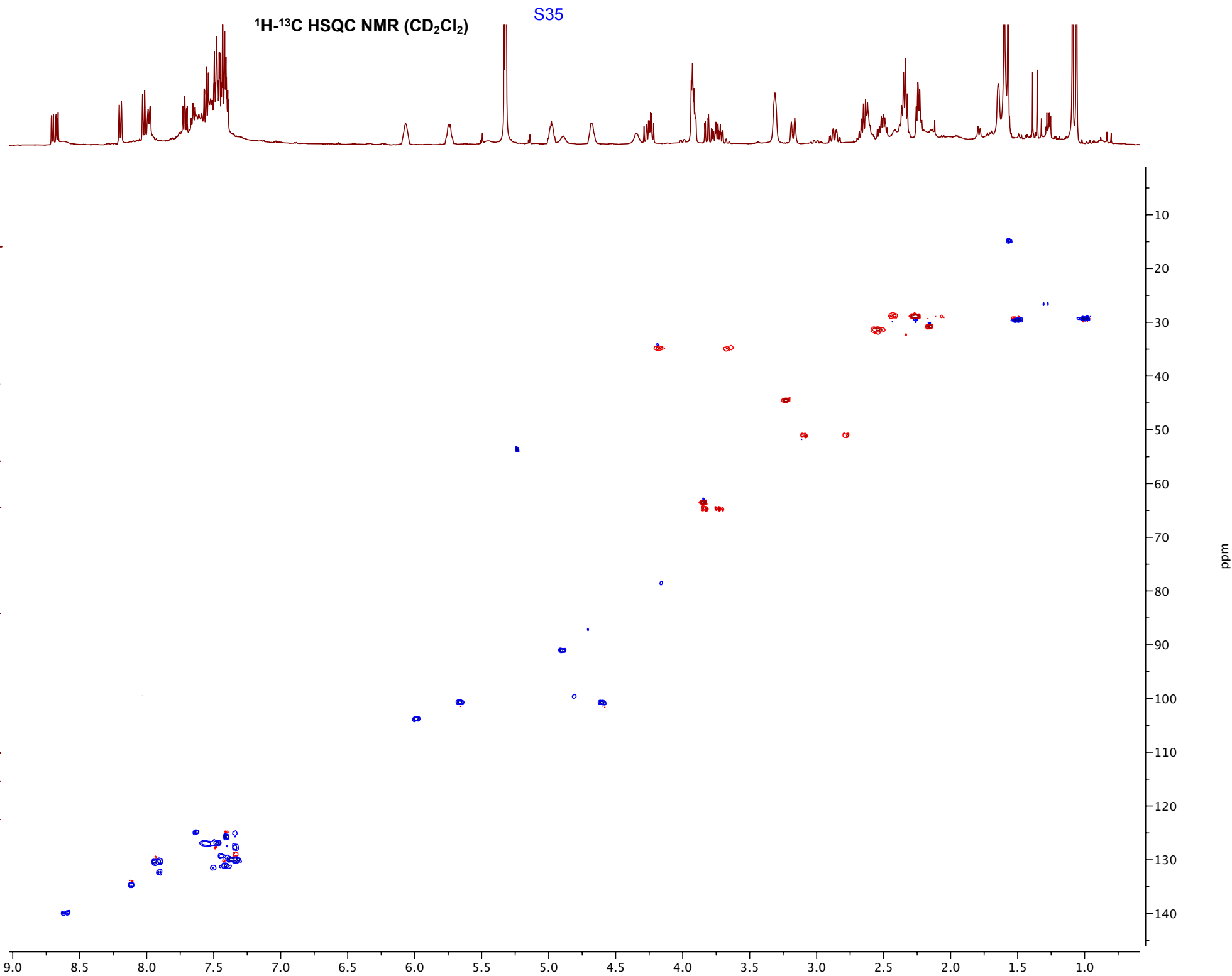


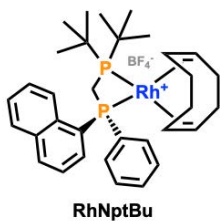
$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz)

^1H - ^1H COSY NMR (CD_2Cl_2 , 500 MHz)

S34

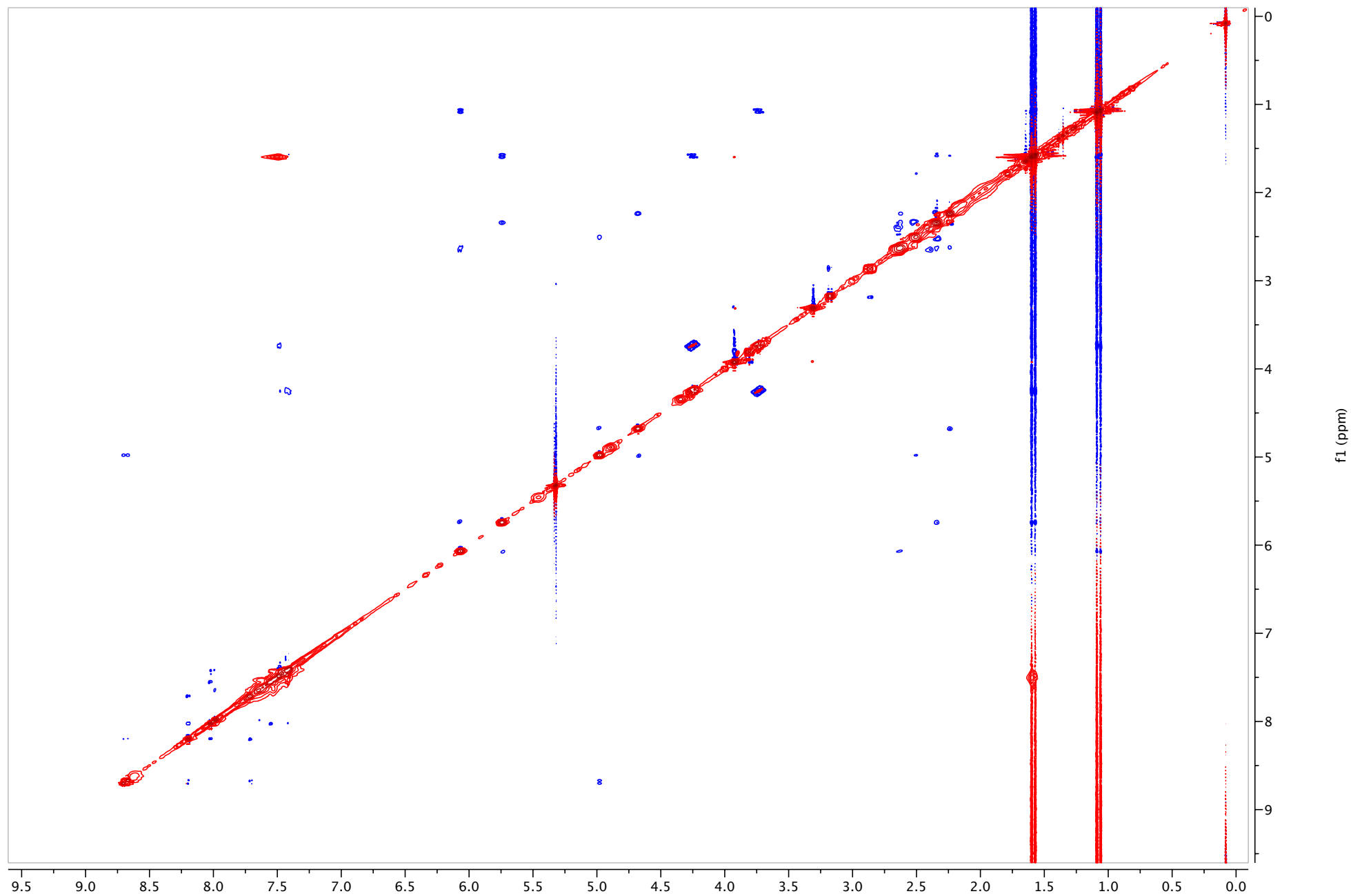




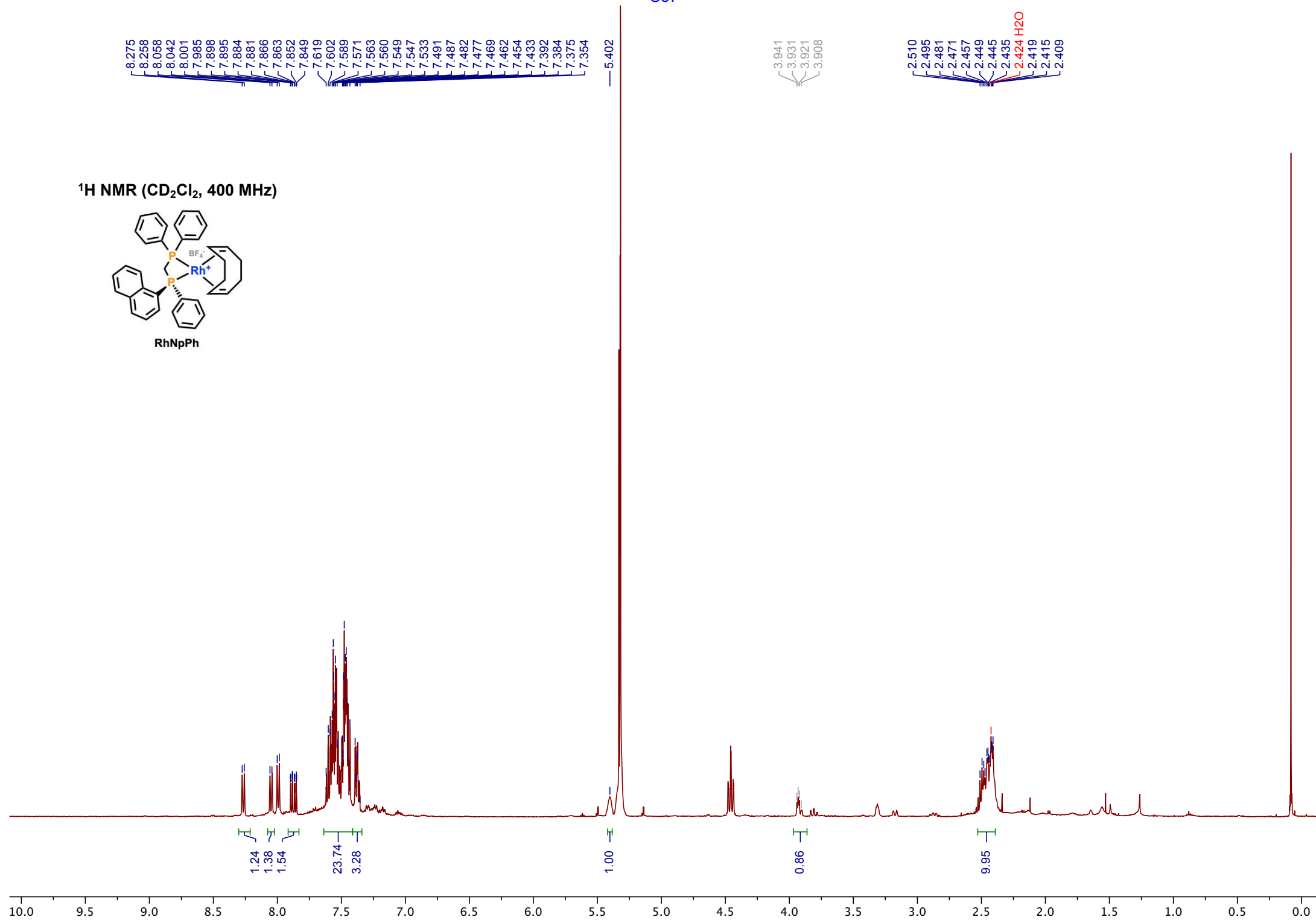
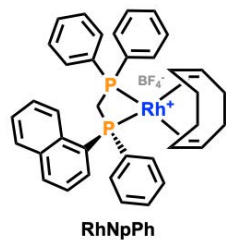


¹H-¹H NOESY NMR (CD₂Cl₂, 500 MHz)

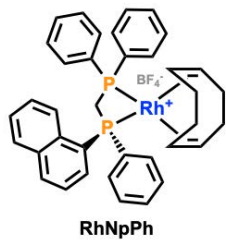
S36



¹H NMR (CD₂Cl₂, 400 MHz)



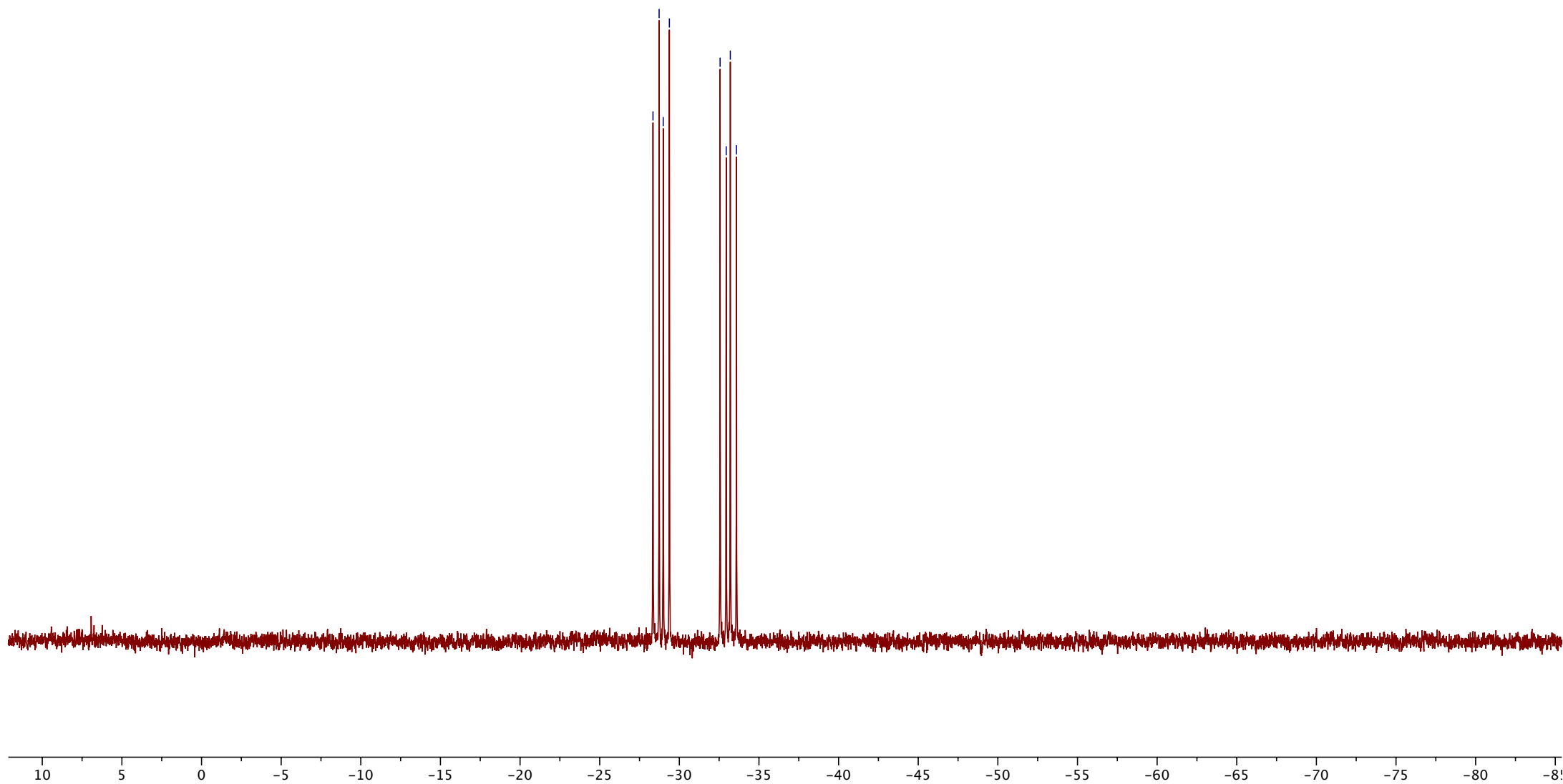
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz)



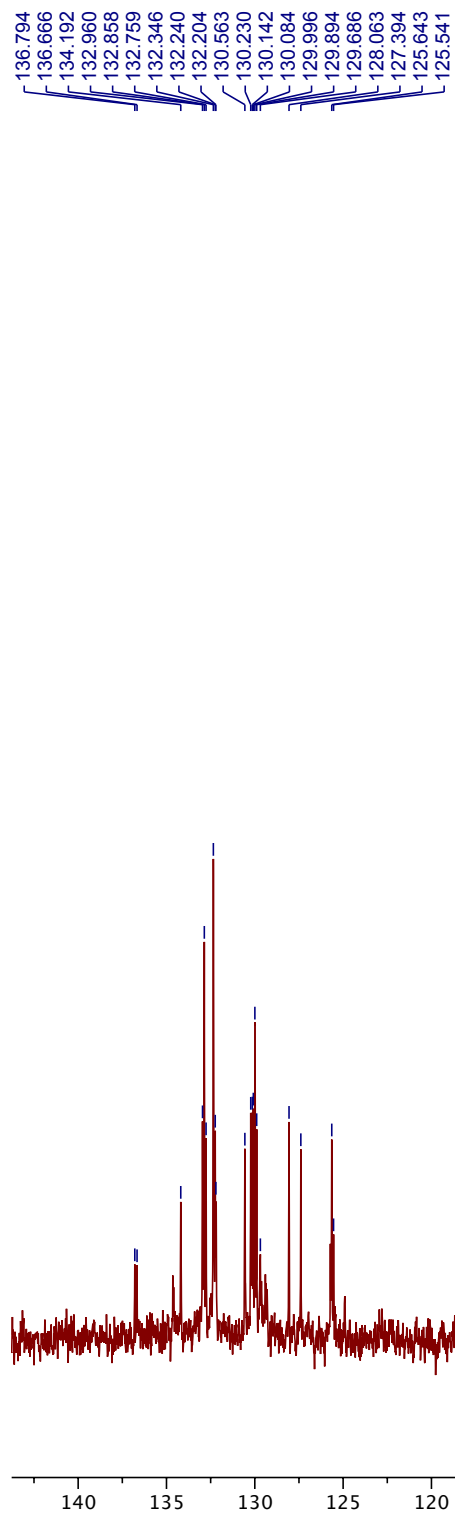
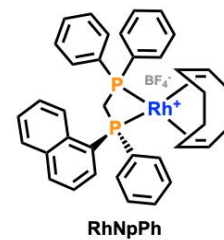
S38

Chemical shift values (ppm):

- 28.347
- 28.731
- 28.989
- 29.375
- 32.560
- 32.944
- 33.202
- 33.587



S39

 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 126 MHz)

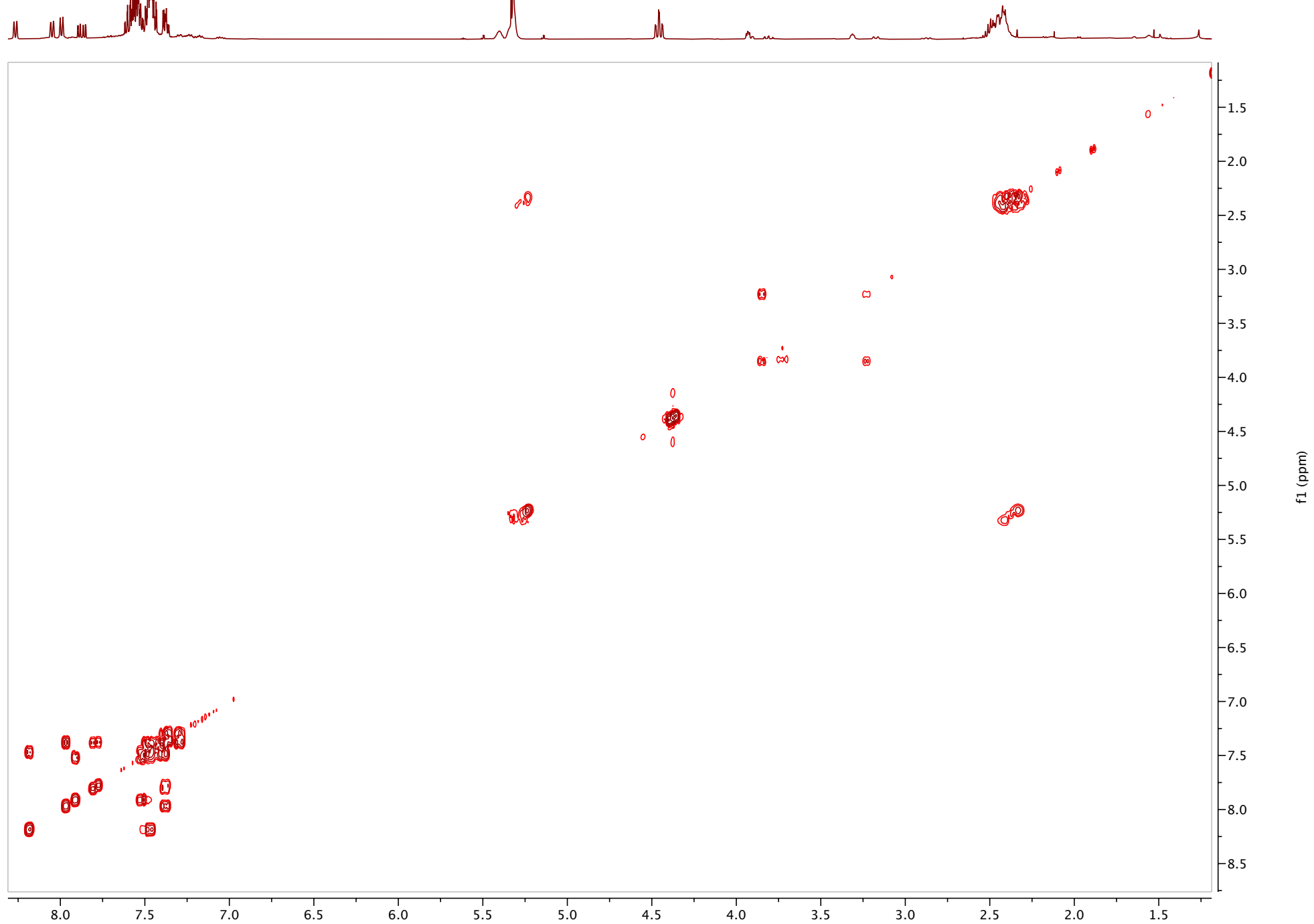
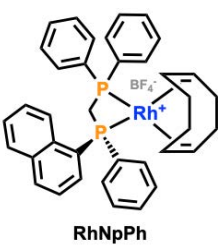
103.719
101.121
101.055
100.141

42.613
42.438

30.597
30.348

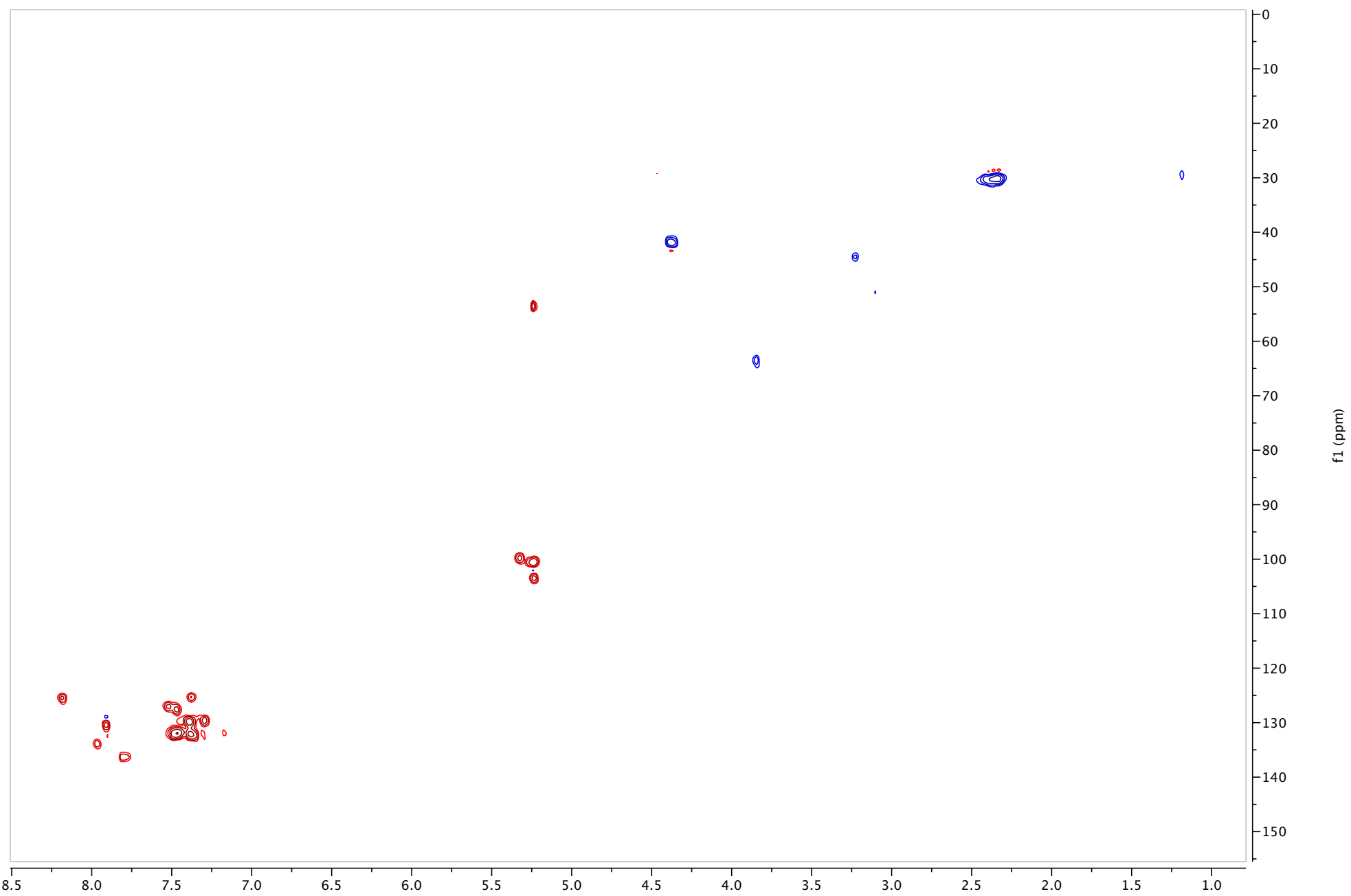
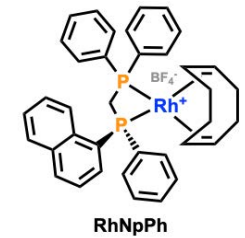
^1H - ^1H COSY NMR (CD_2Cl_2 , 400 MHz)

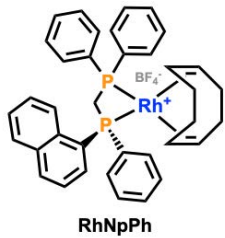
S40



^1H - ^{13}C HSQC NMR (CD_2Cl_2)

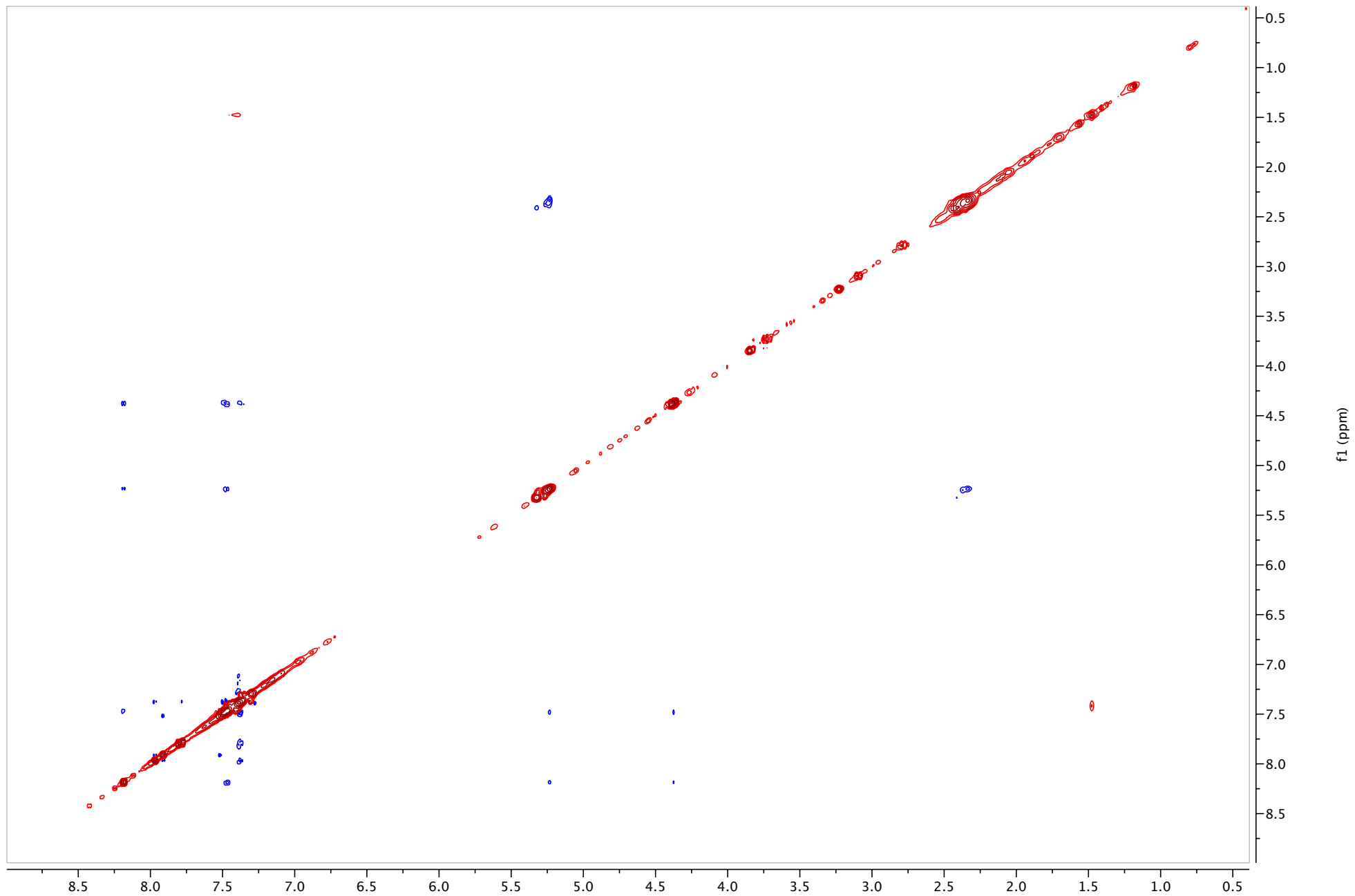
S41





^1H - ^1H NOESY NMR (CD_2Cl_2 , 400 MHz)

S42

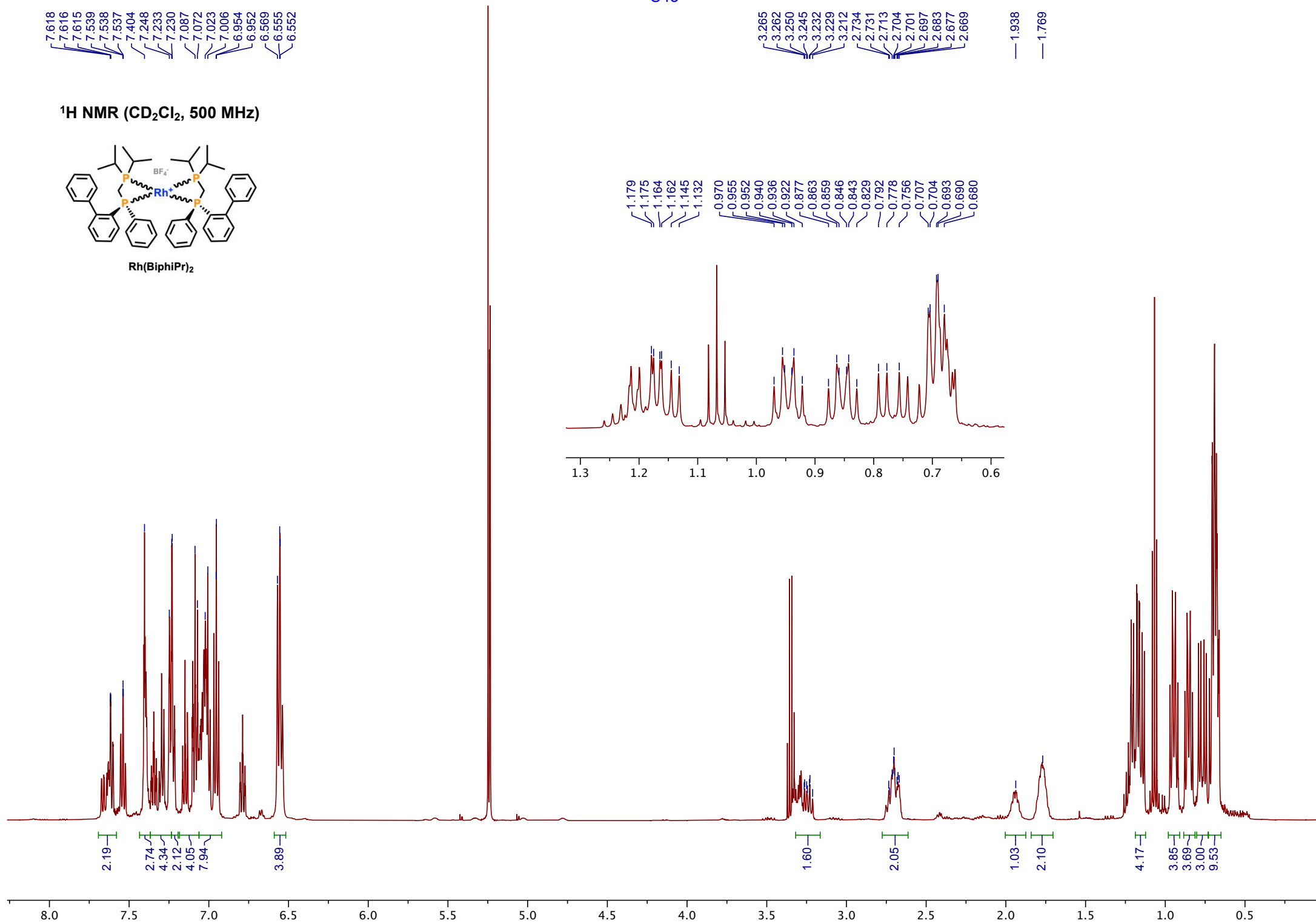


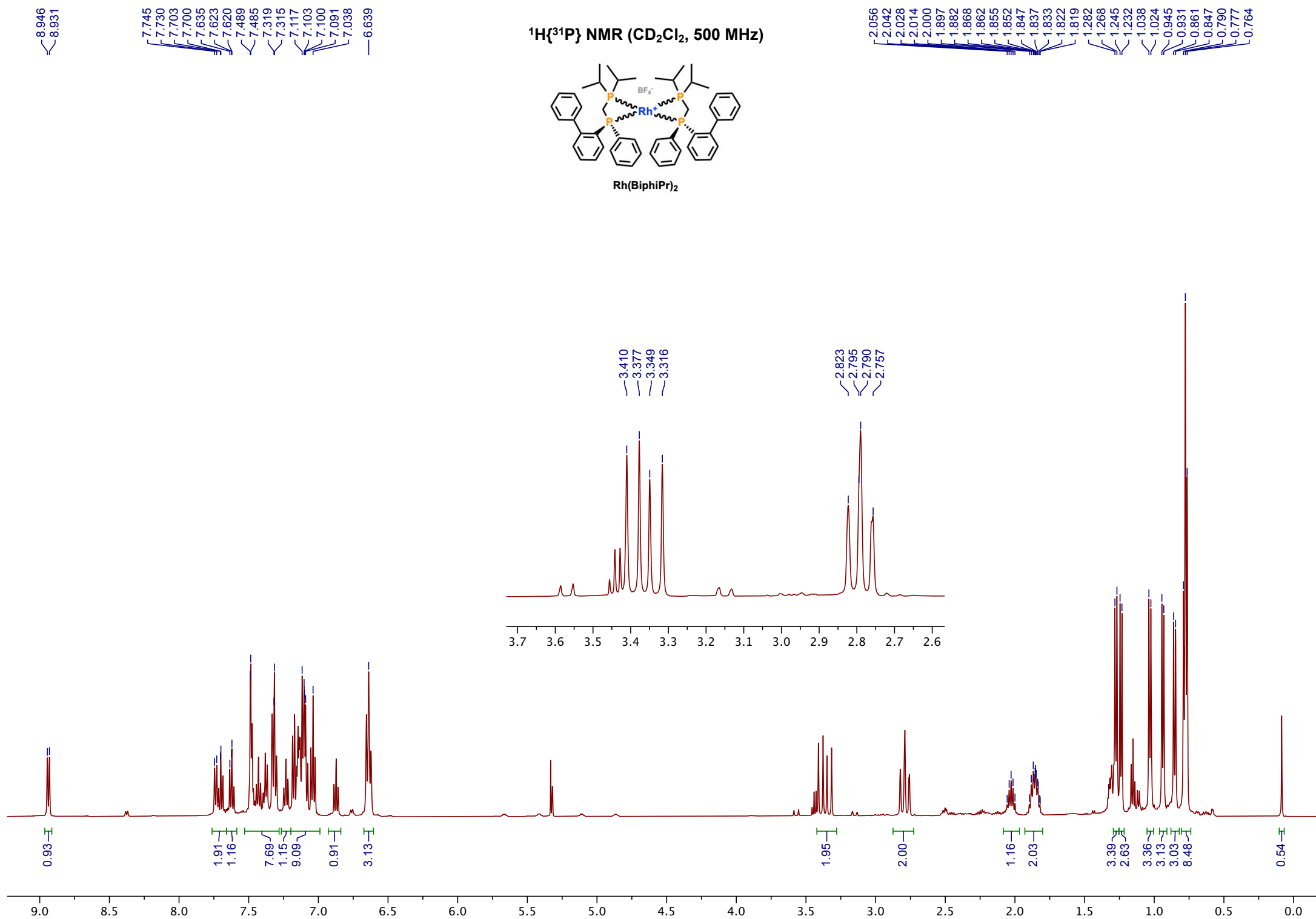
S43

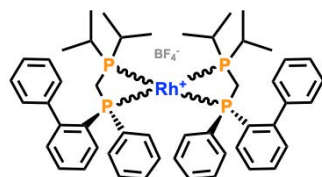
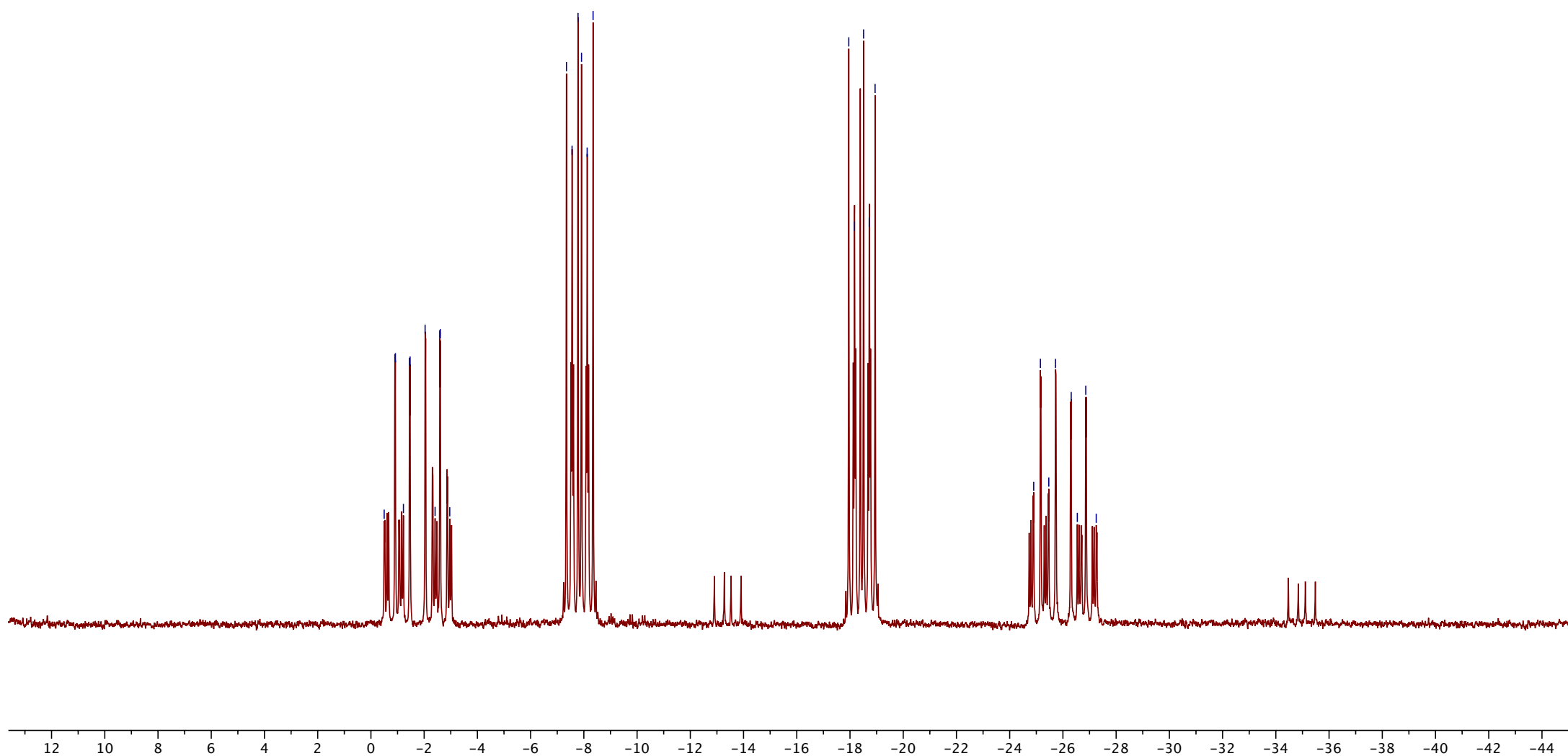
¹H NMR (CD₂Cl₂, 500 MHz)

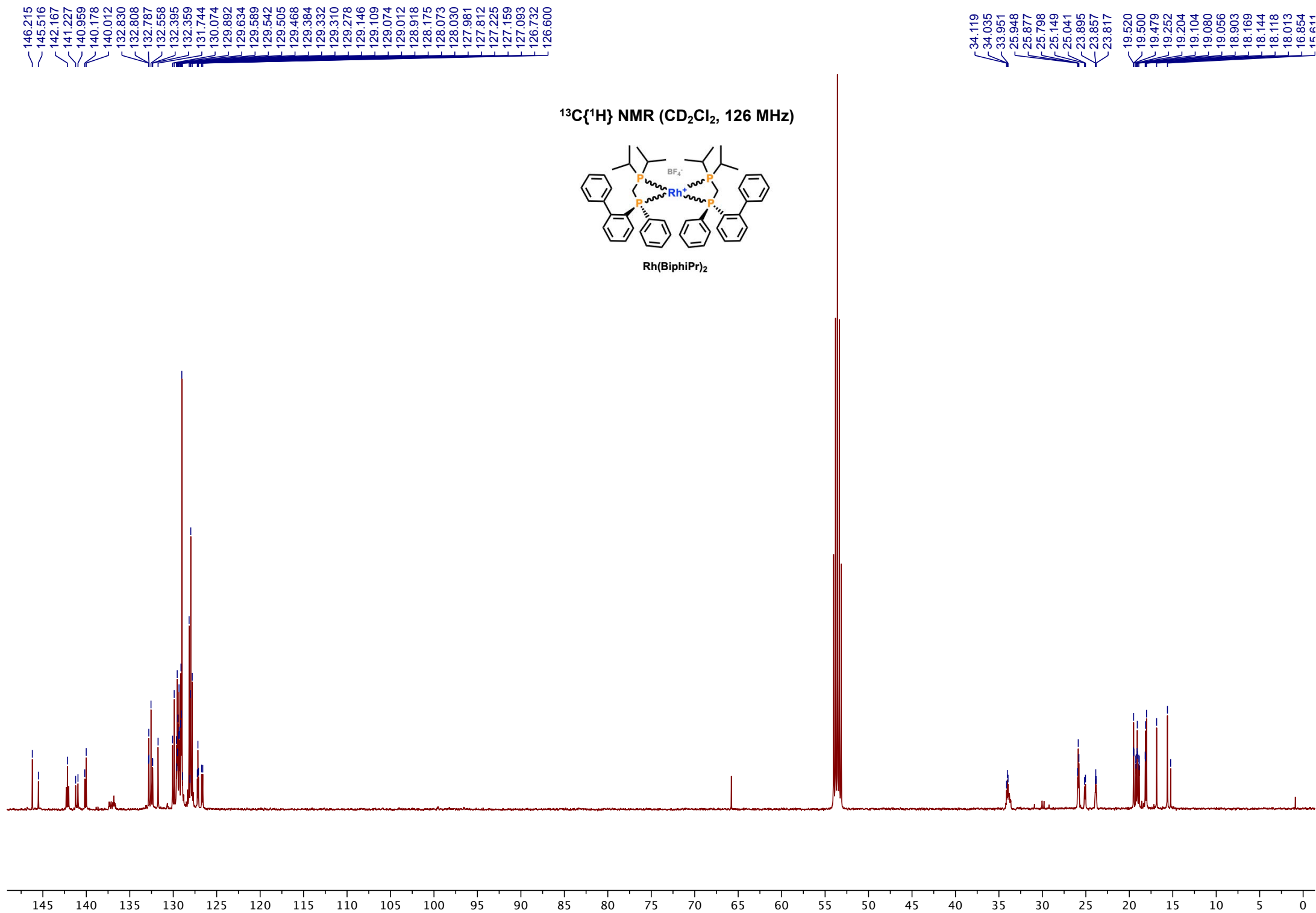


Rh(BiphiPr)₂

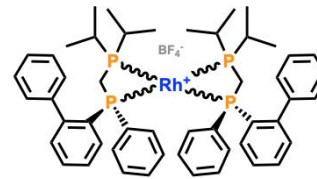
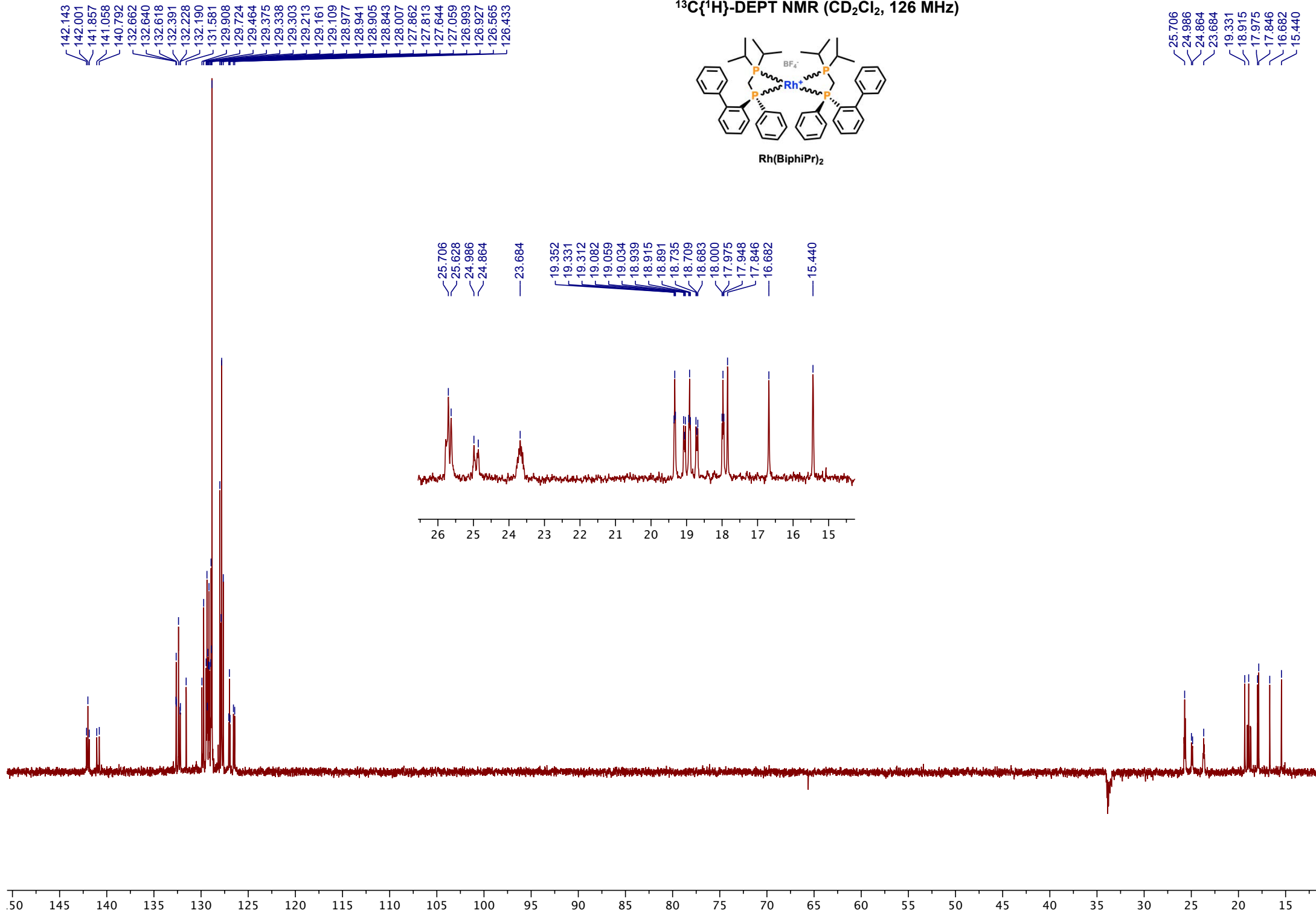


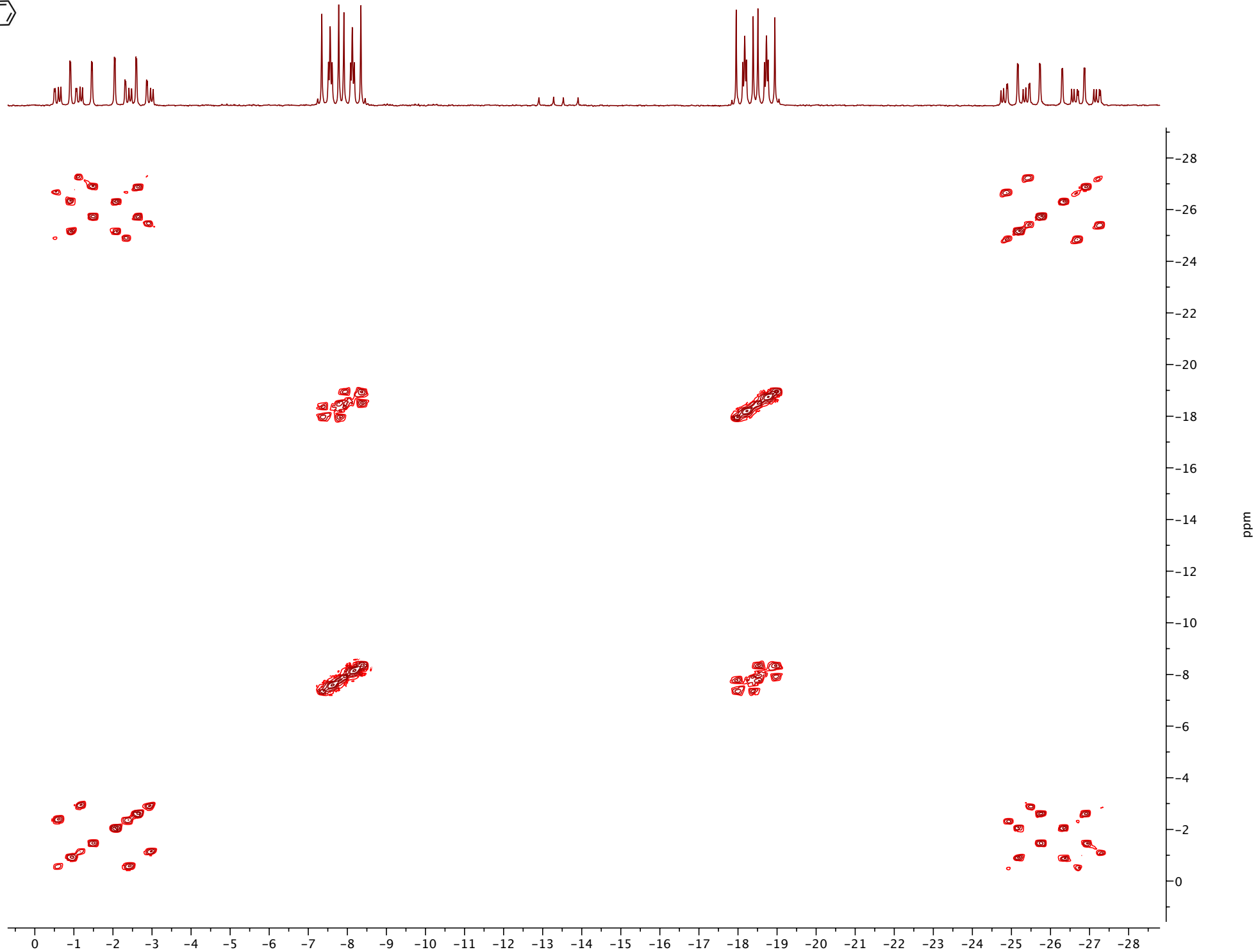
$^1\text{H}\{^{31}\text{P}\}$ NMR (CD_2Cl_2 , 500 MHz) $\text{Rh}(\text{BiphiPr})_2$ 

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162 MHz)Rh(BiphiPr)₂

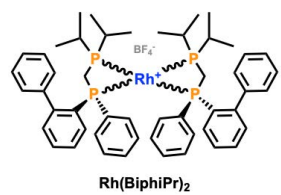


S47

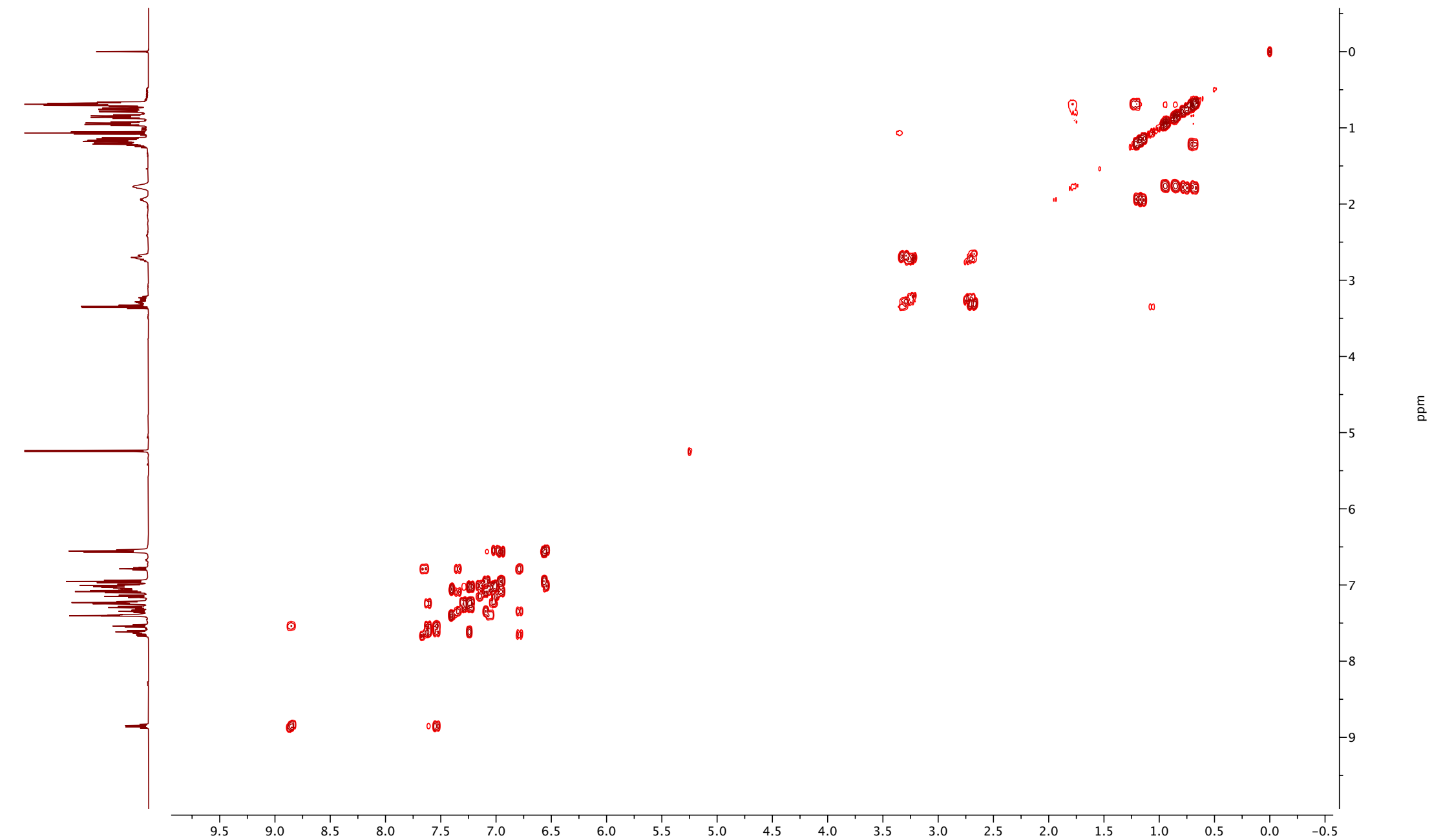
 $^{13}\text{C}\{^1\text{H}\}$ -DEPT NMR (CD_2Cl_2 , 126 MHz)Rh(BiphiPr)₂

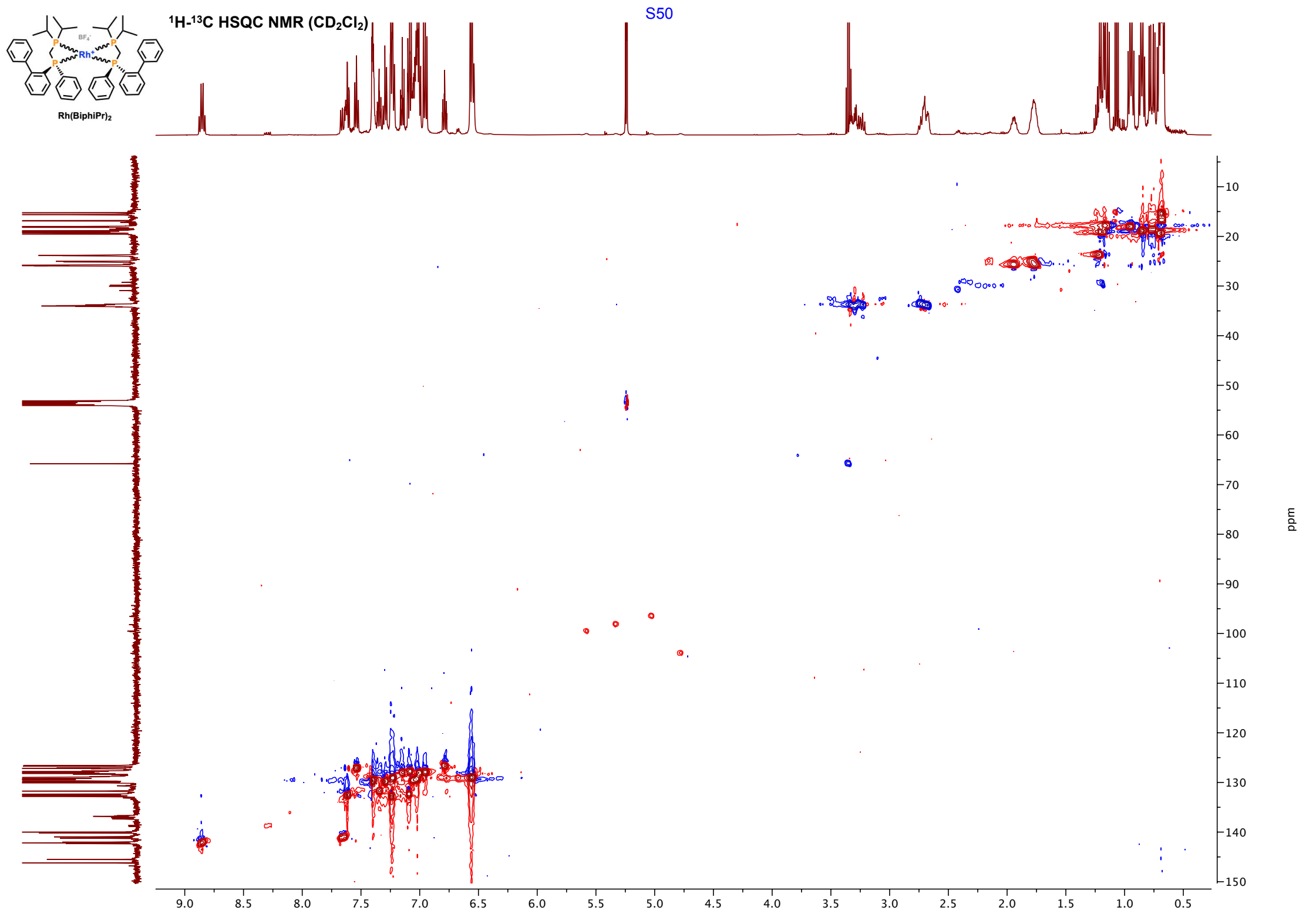


¹H-¹H COSY NMR (CD₂Cl₂, 500 MHz)

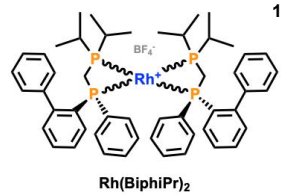


S49

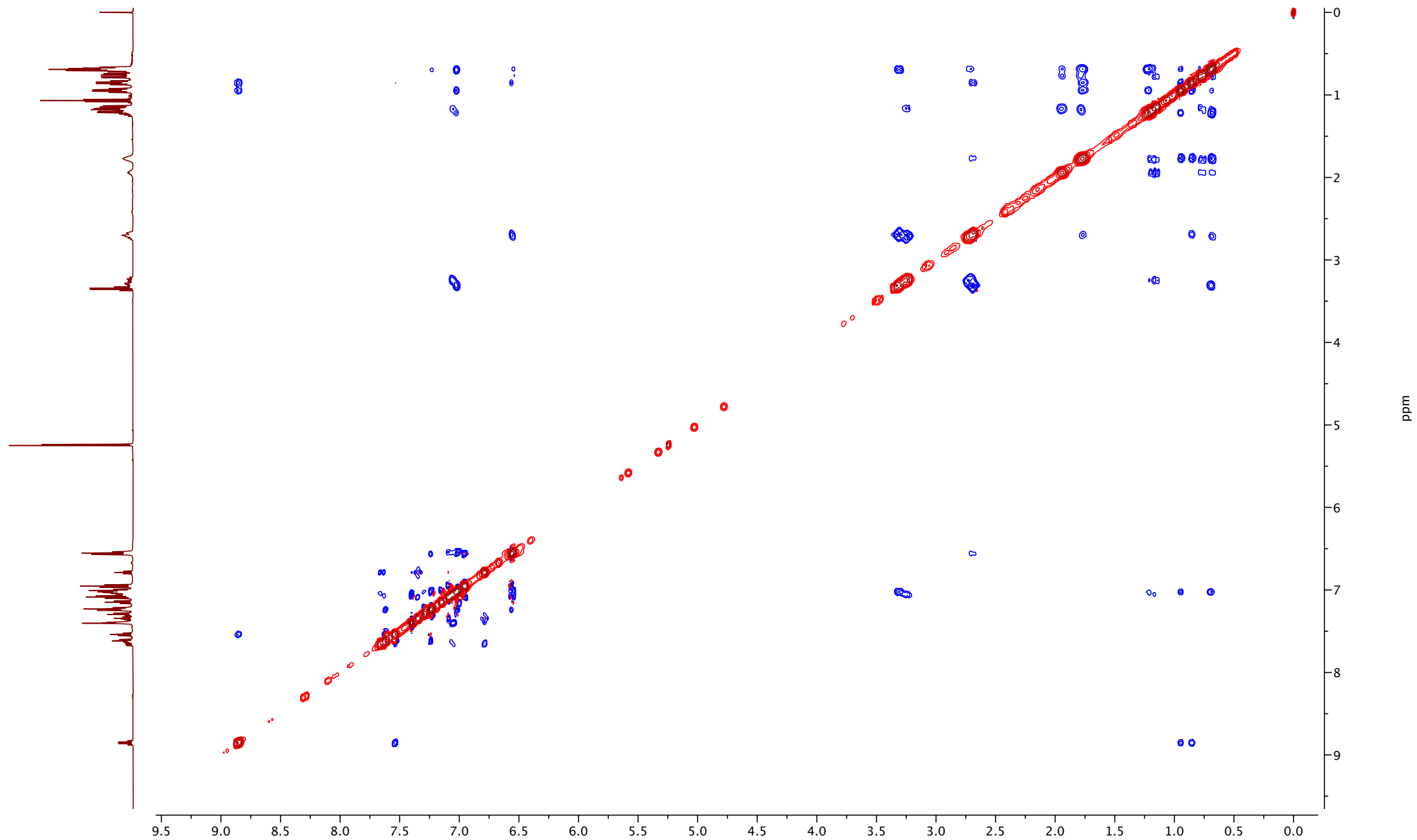


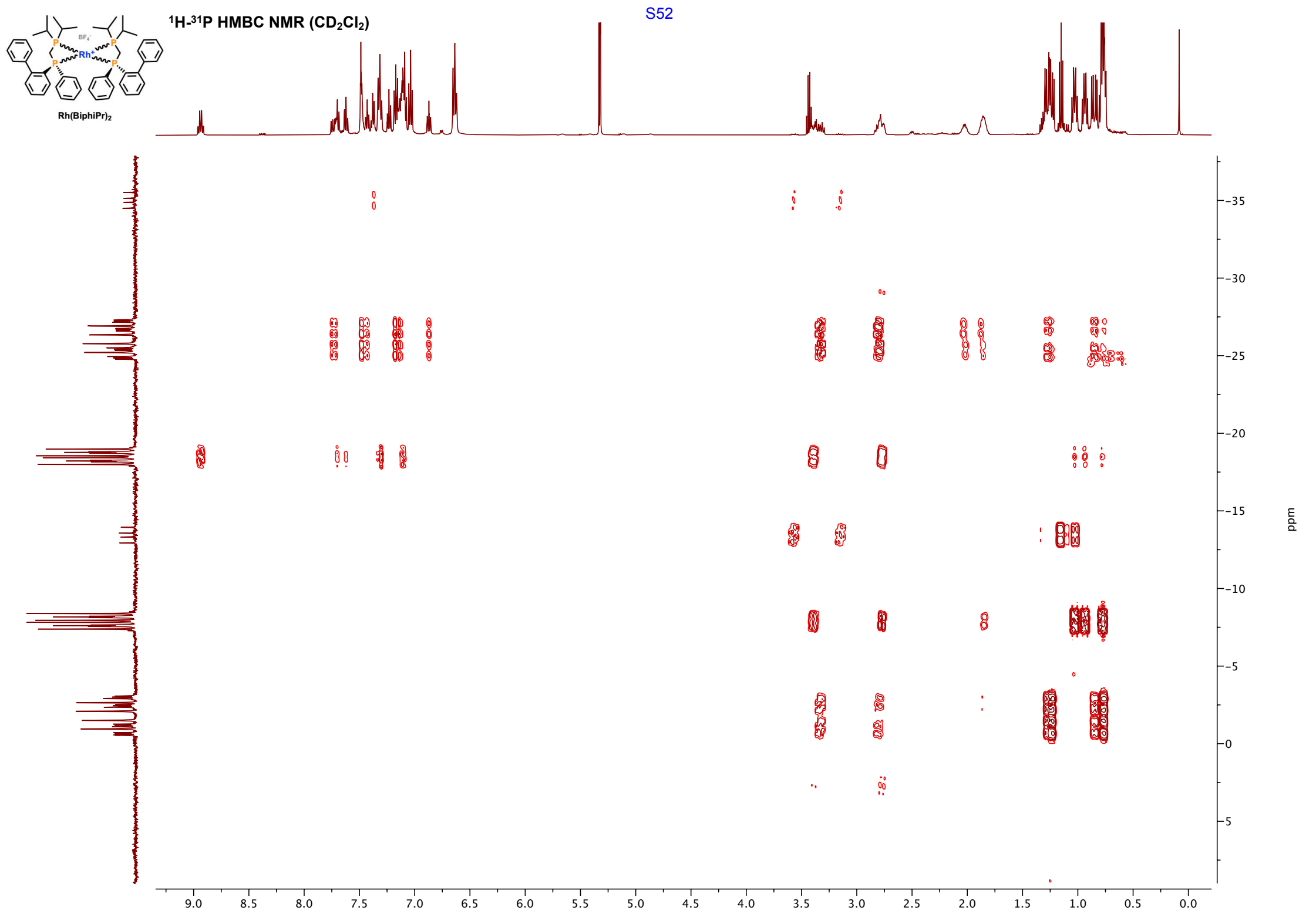


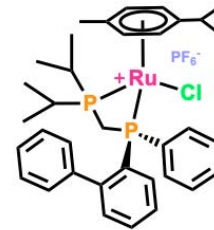
¹H-¹H NOESY NMR (CD₂Cl₂, 500 MHz)



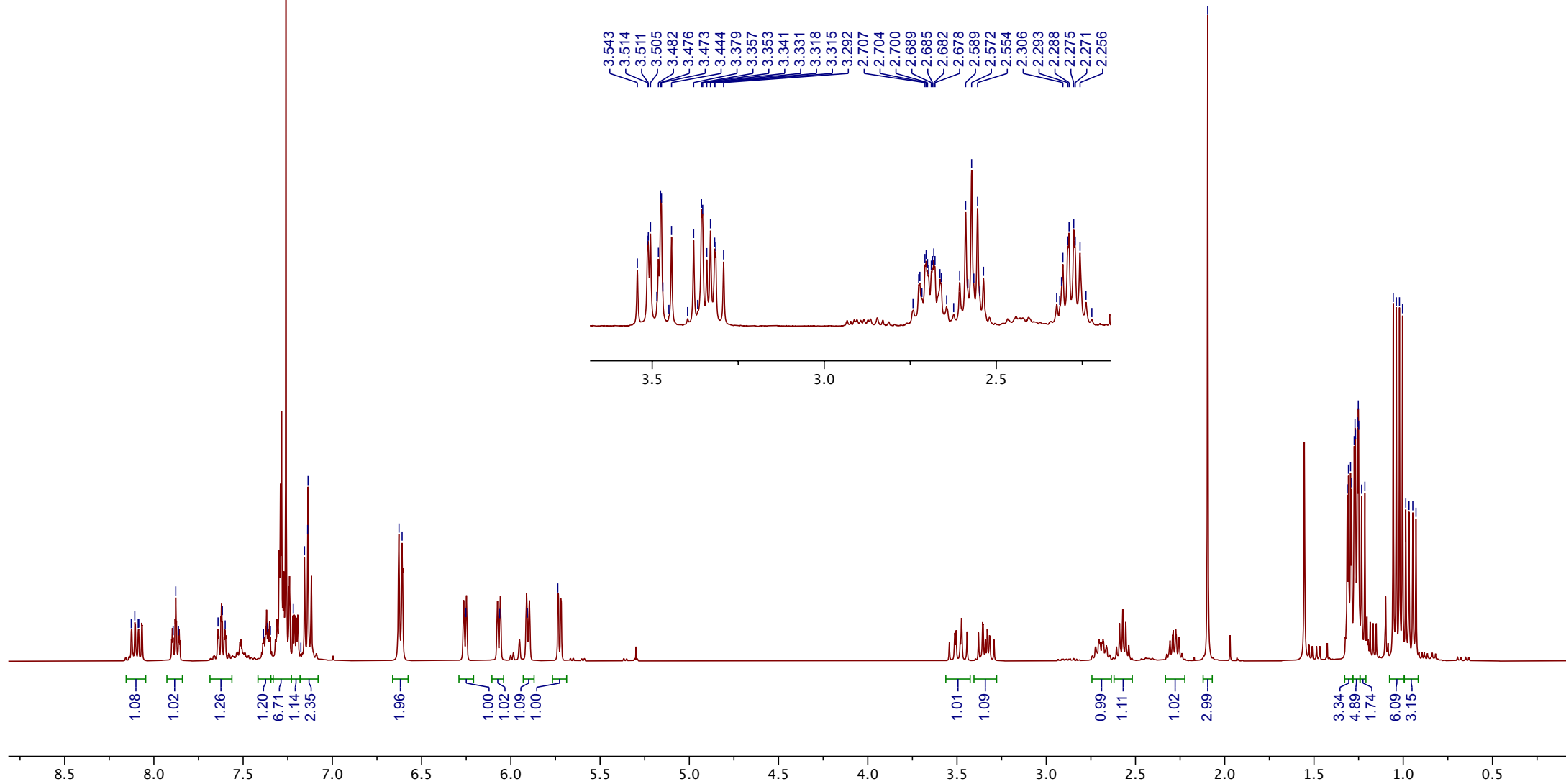
S51

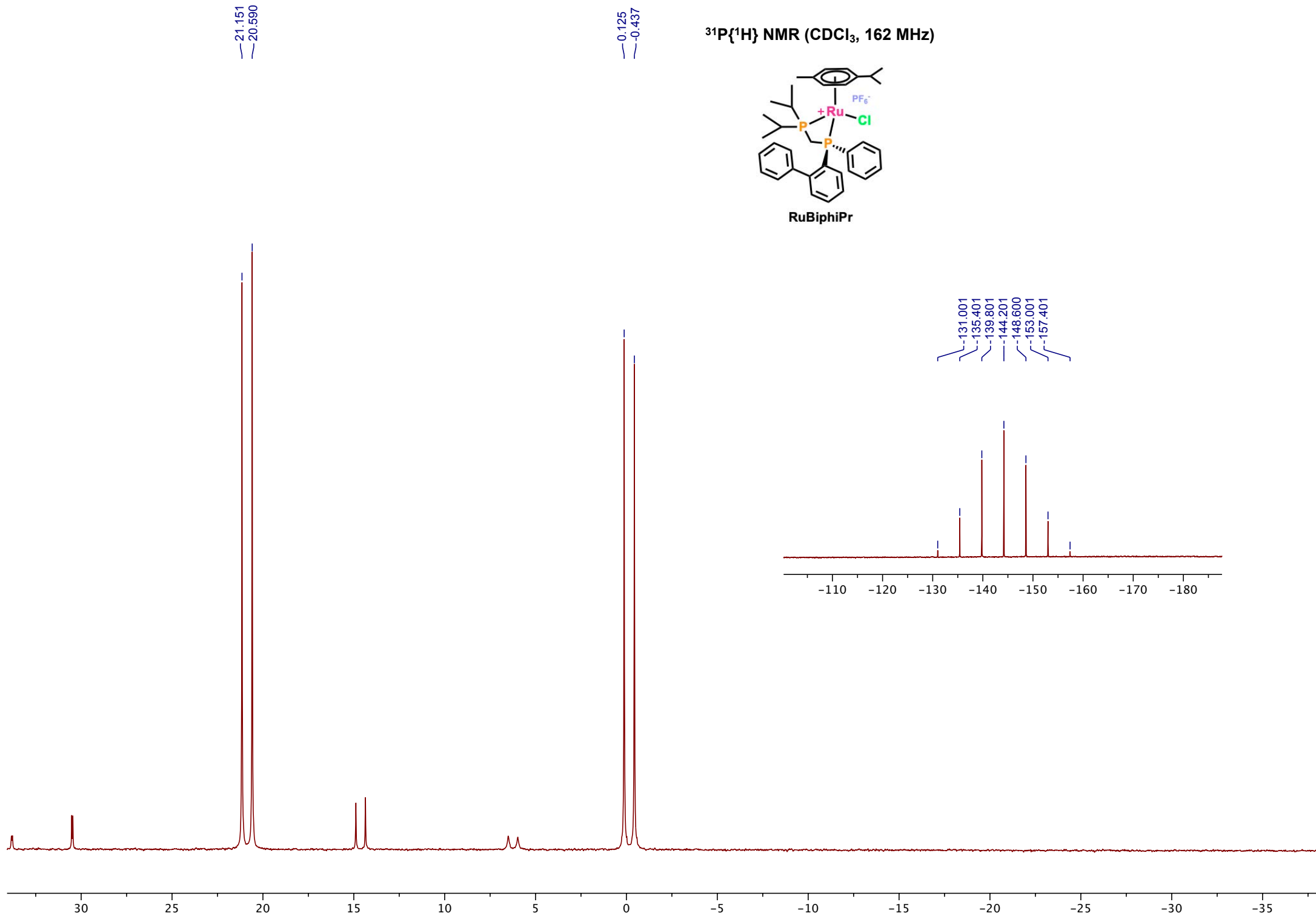




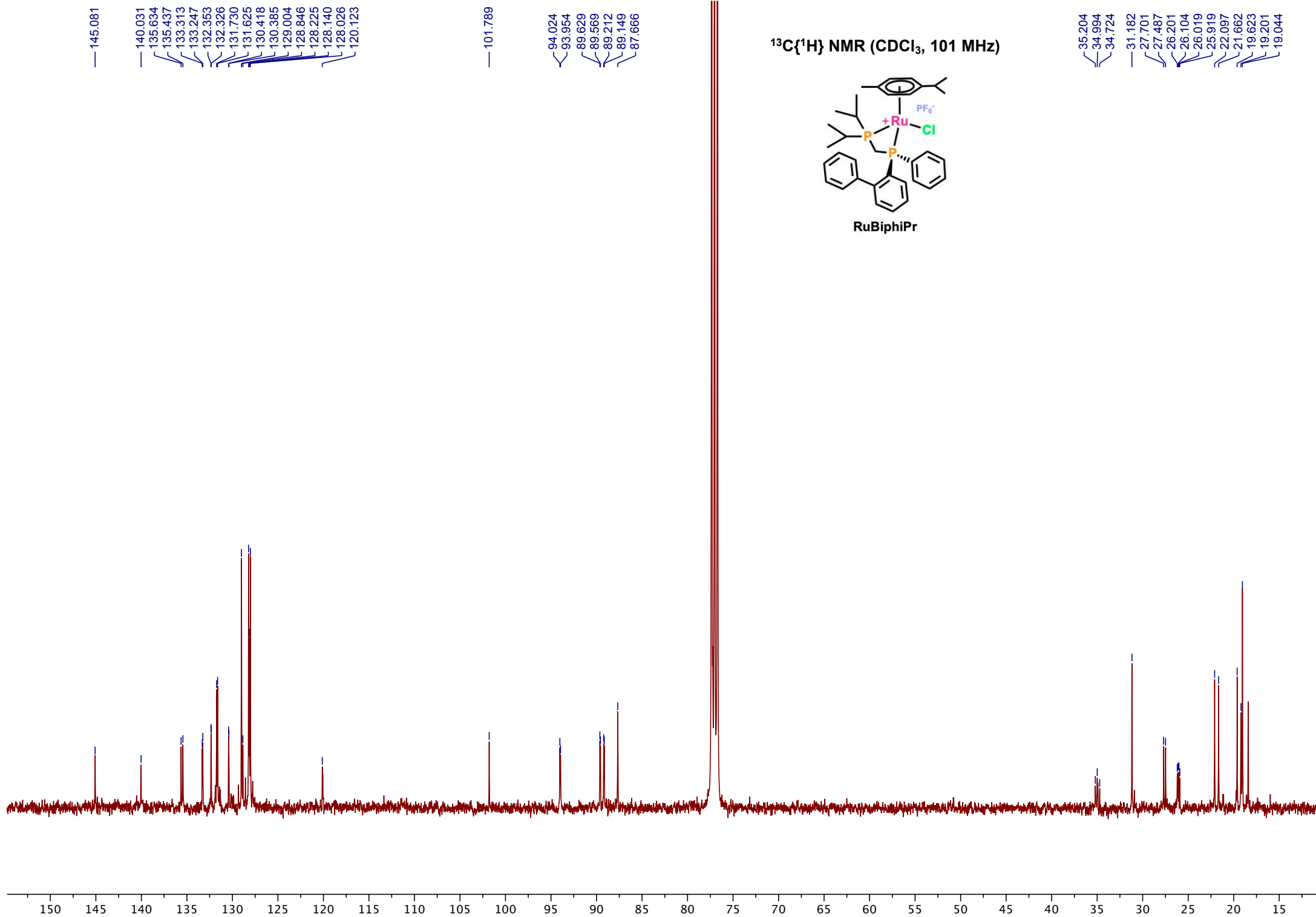
¹H NMR (CDCl₃, 400 MHz)

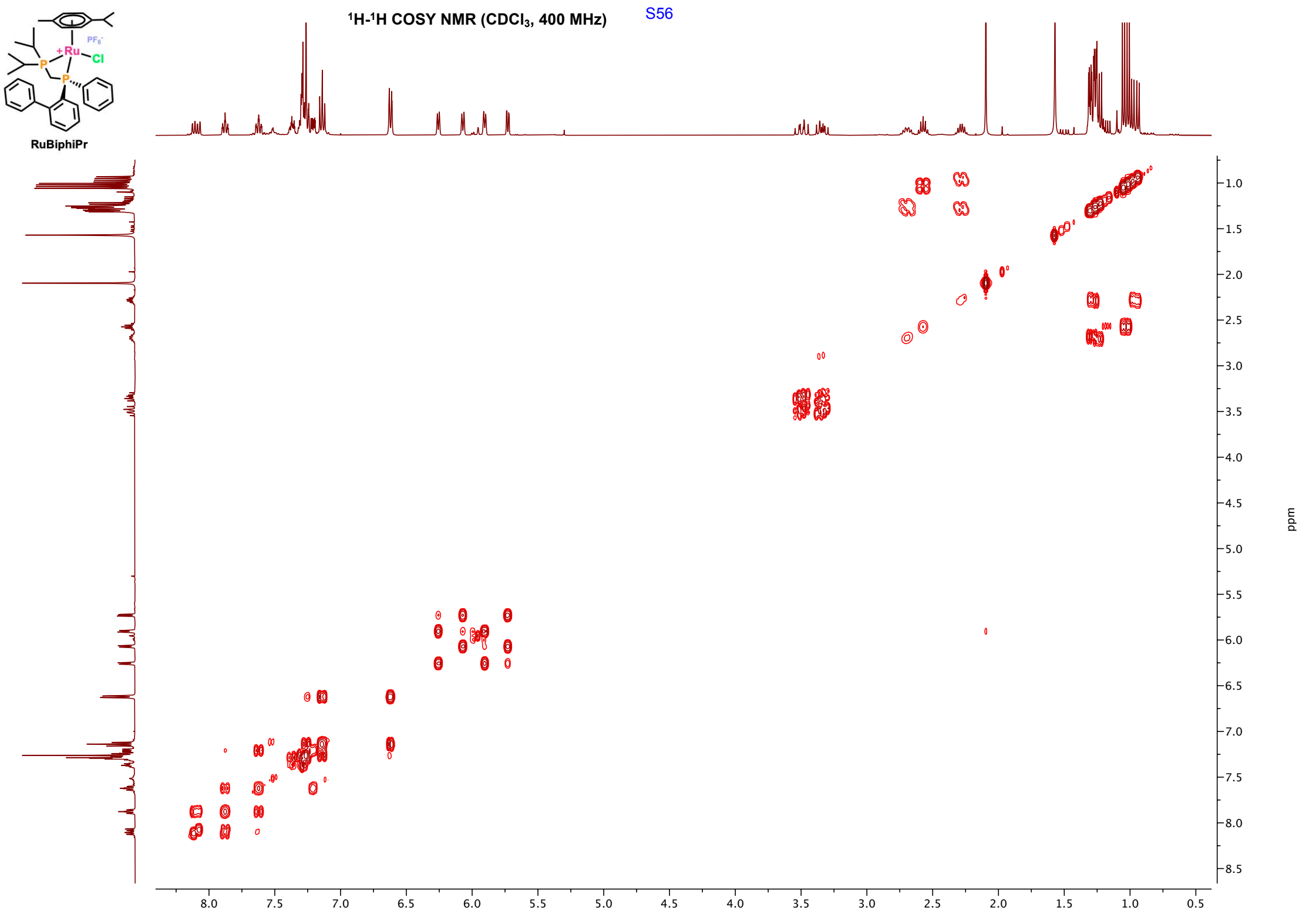
RuBiphiPr



$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

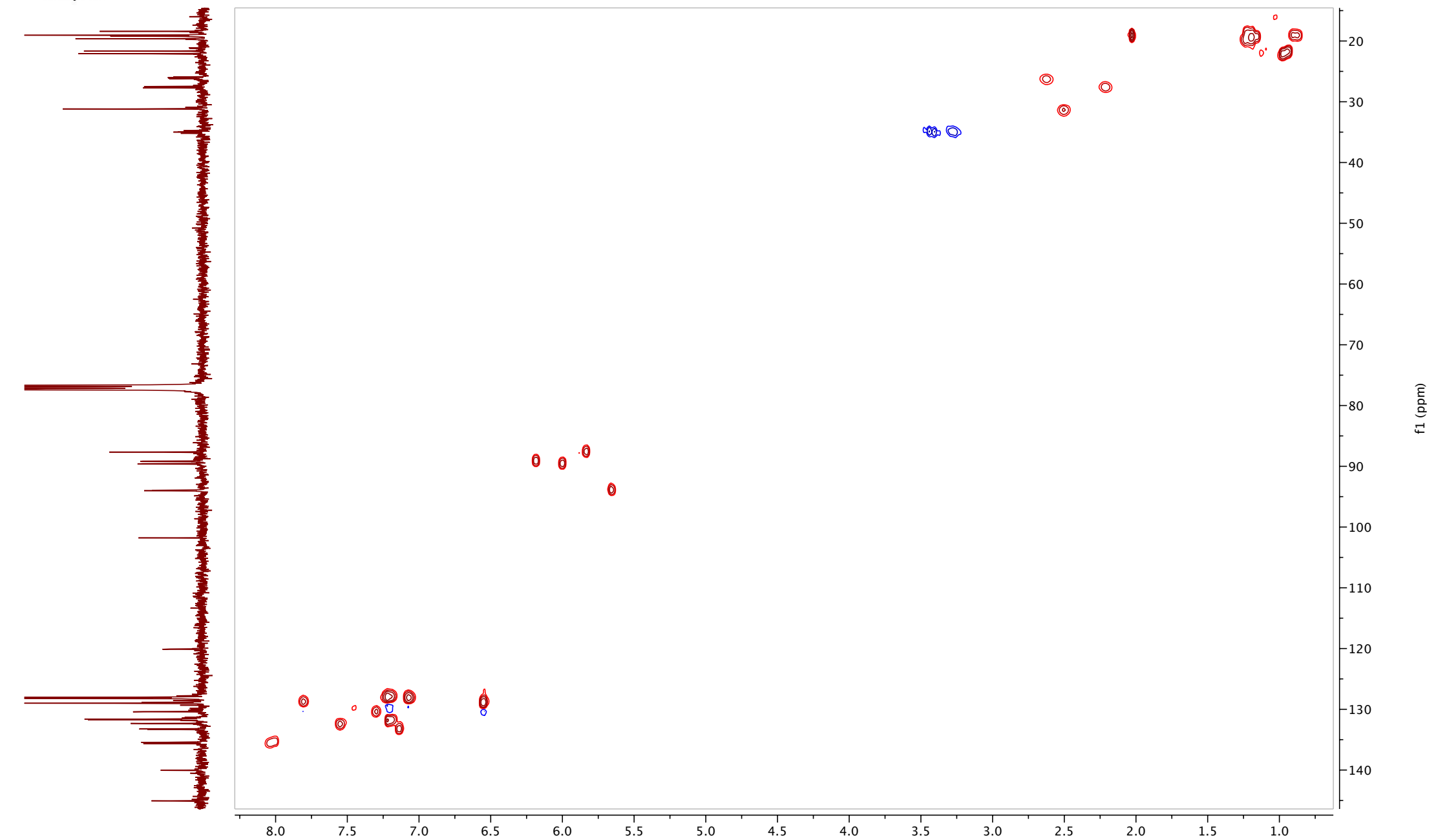
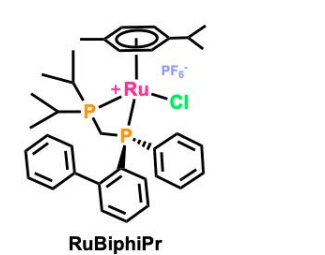
S55

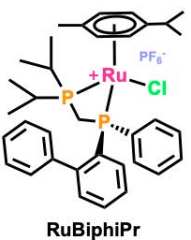
 $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)



¹H-¹³C HSQC NMR (CDCl₃)

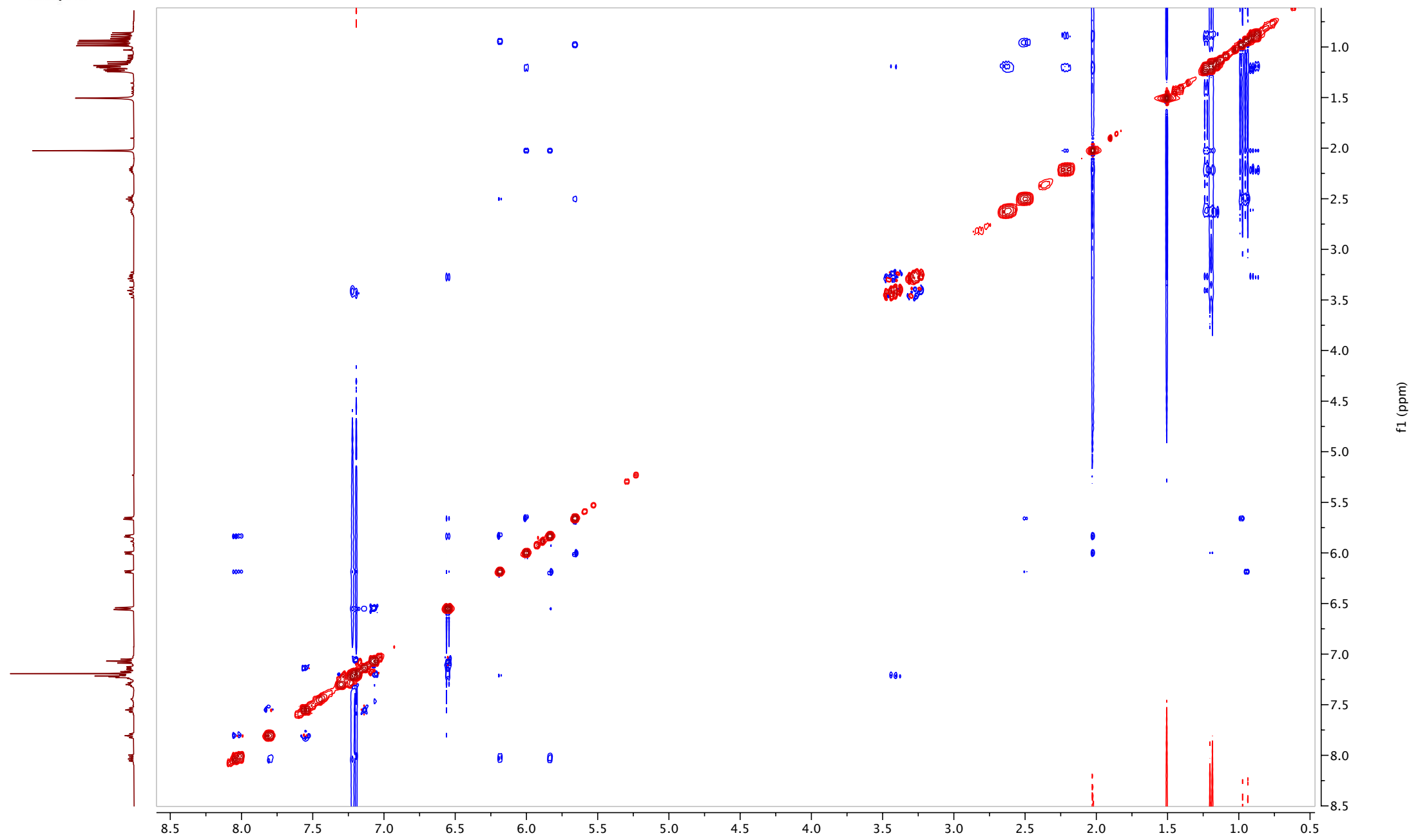
S57

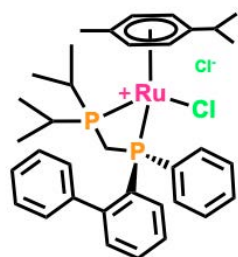




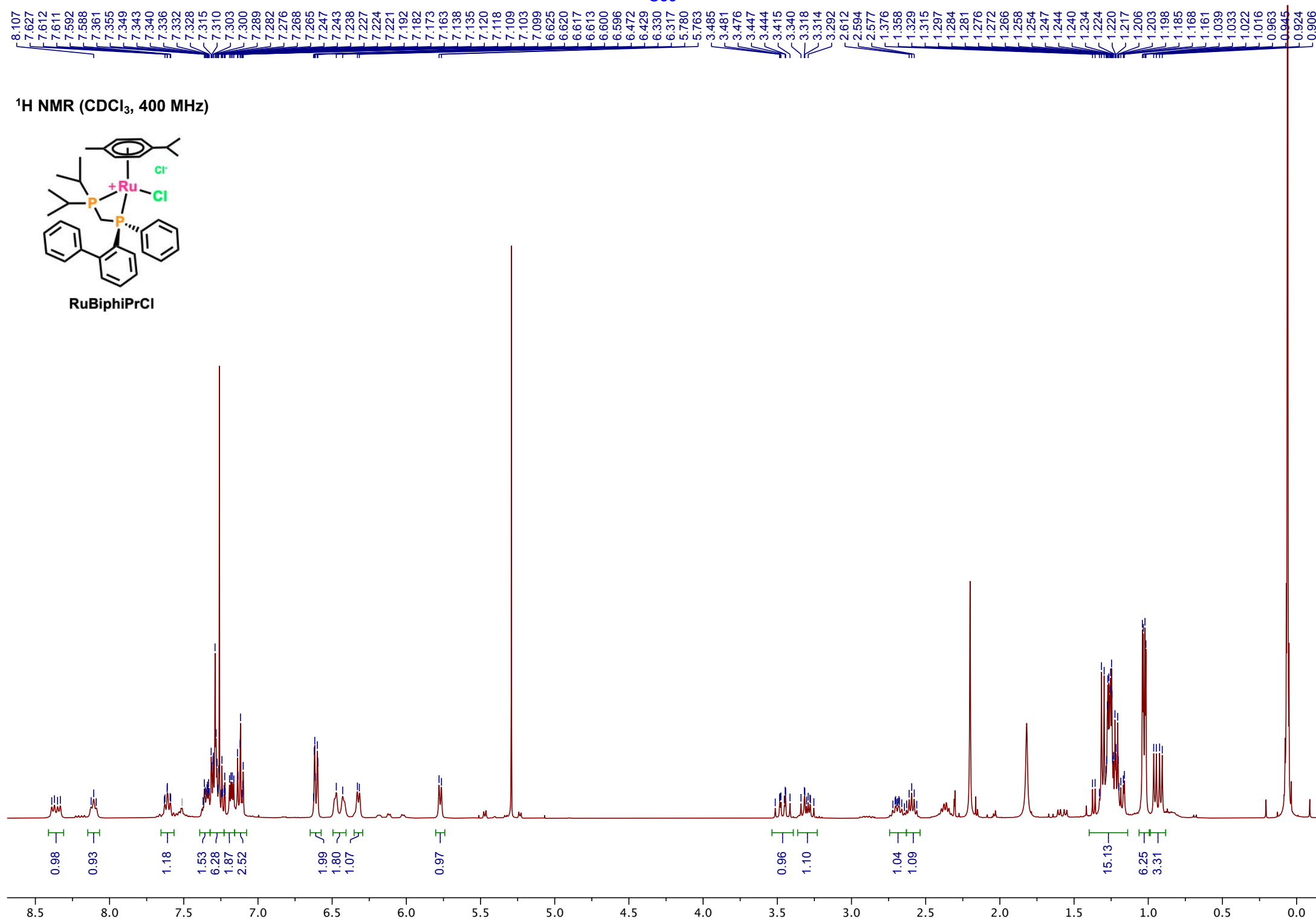
¹H-¹H NOESY NMR (CDCl₃, 400 MHz)

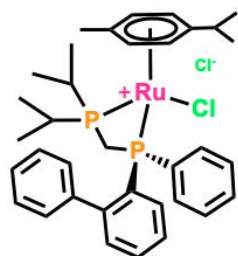
S58



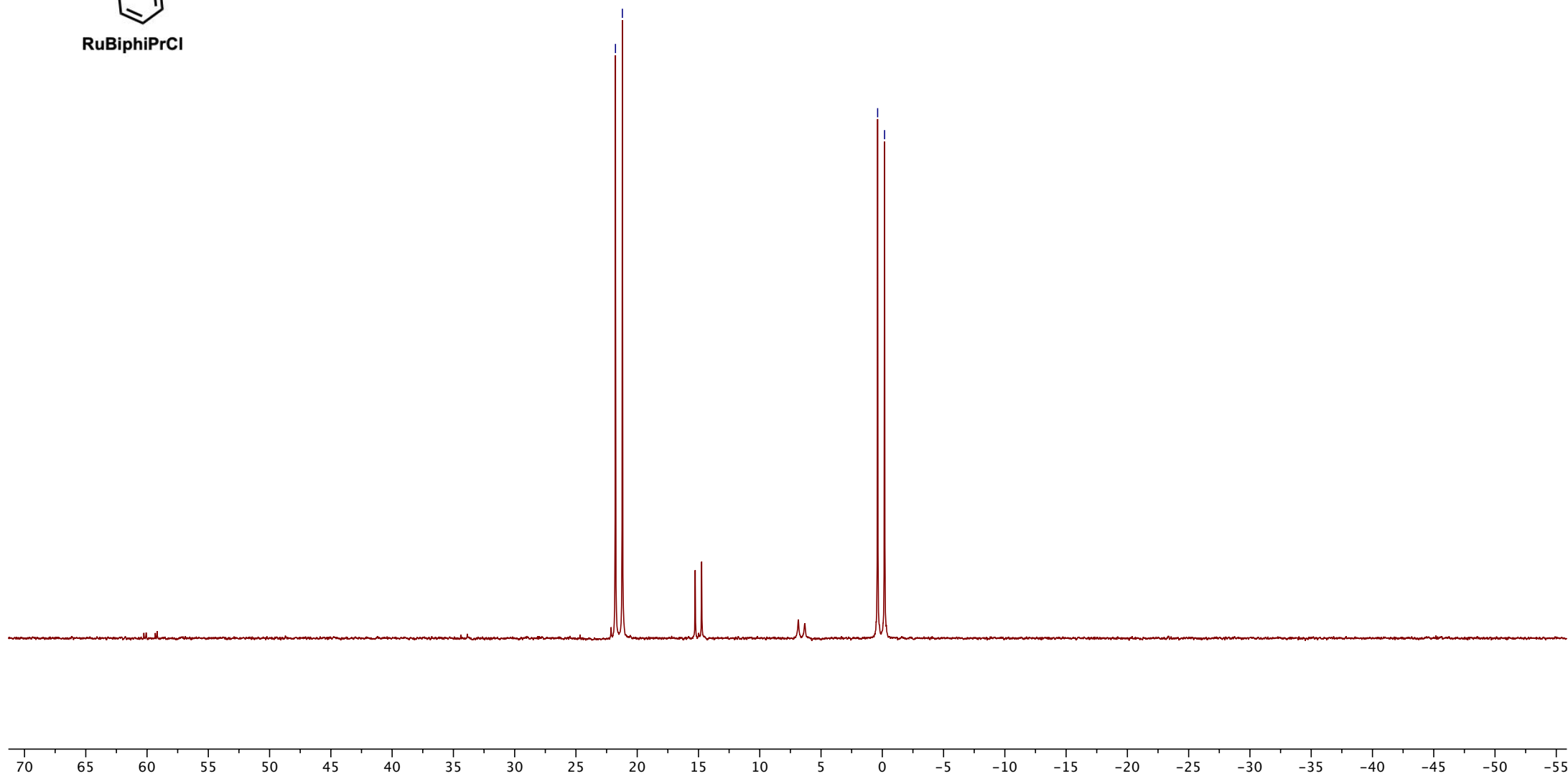
^1H NMR (CDCl_3 , 400 MHz)

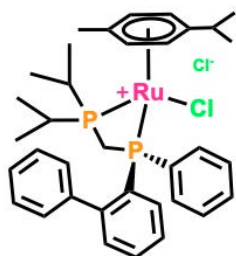
RuBiphiPrCl



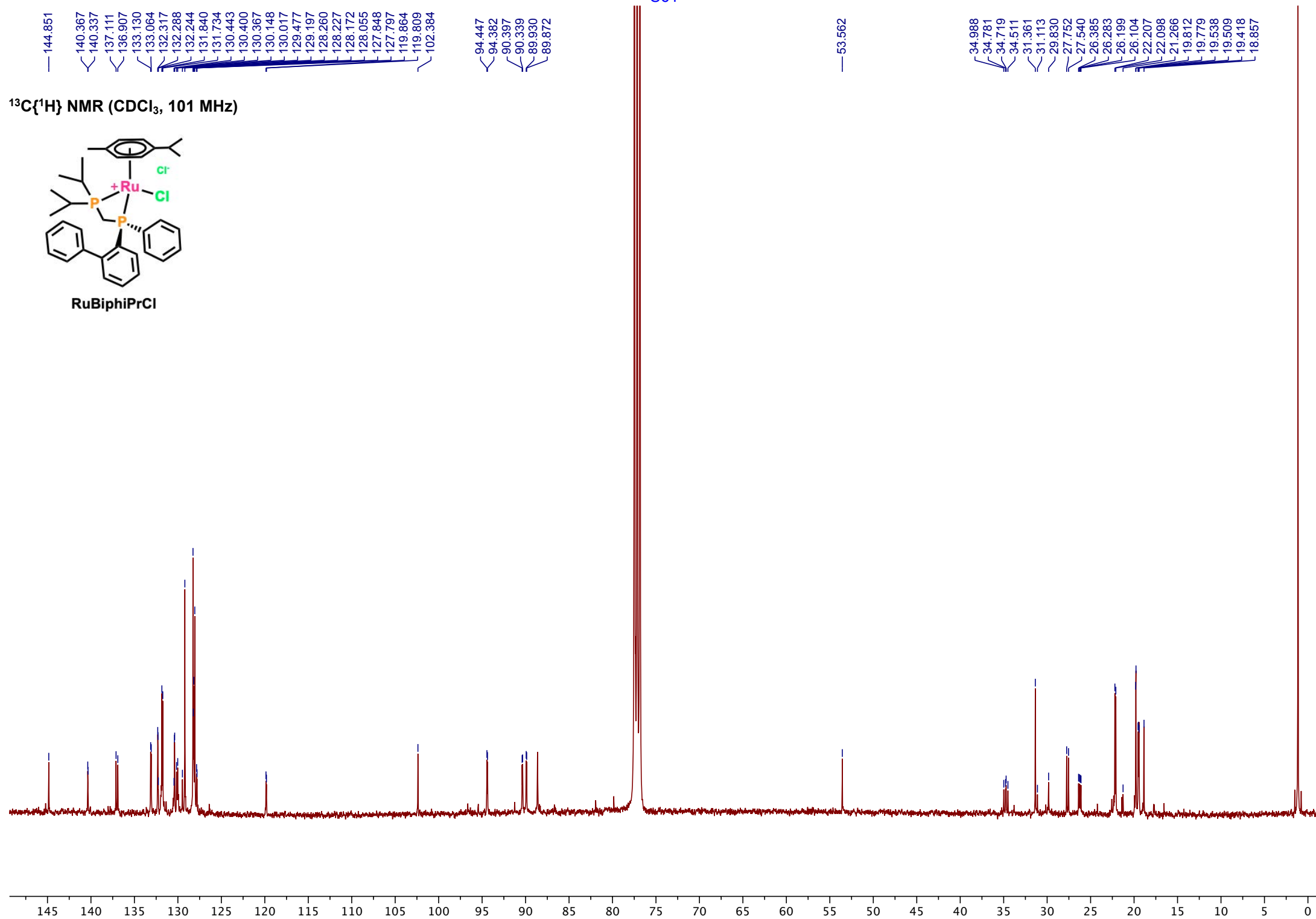
21.775
21.2110.380
-0.184 $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

RuBiphiPrCl



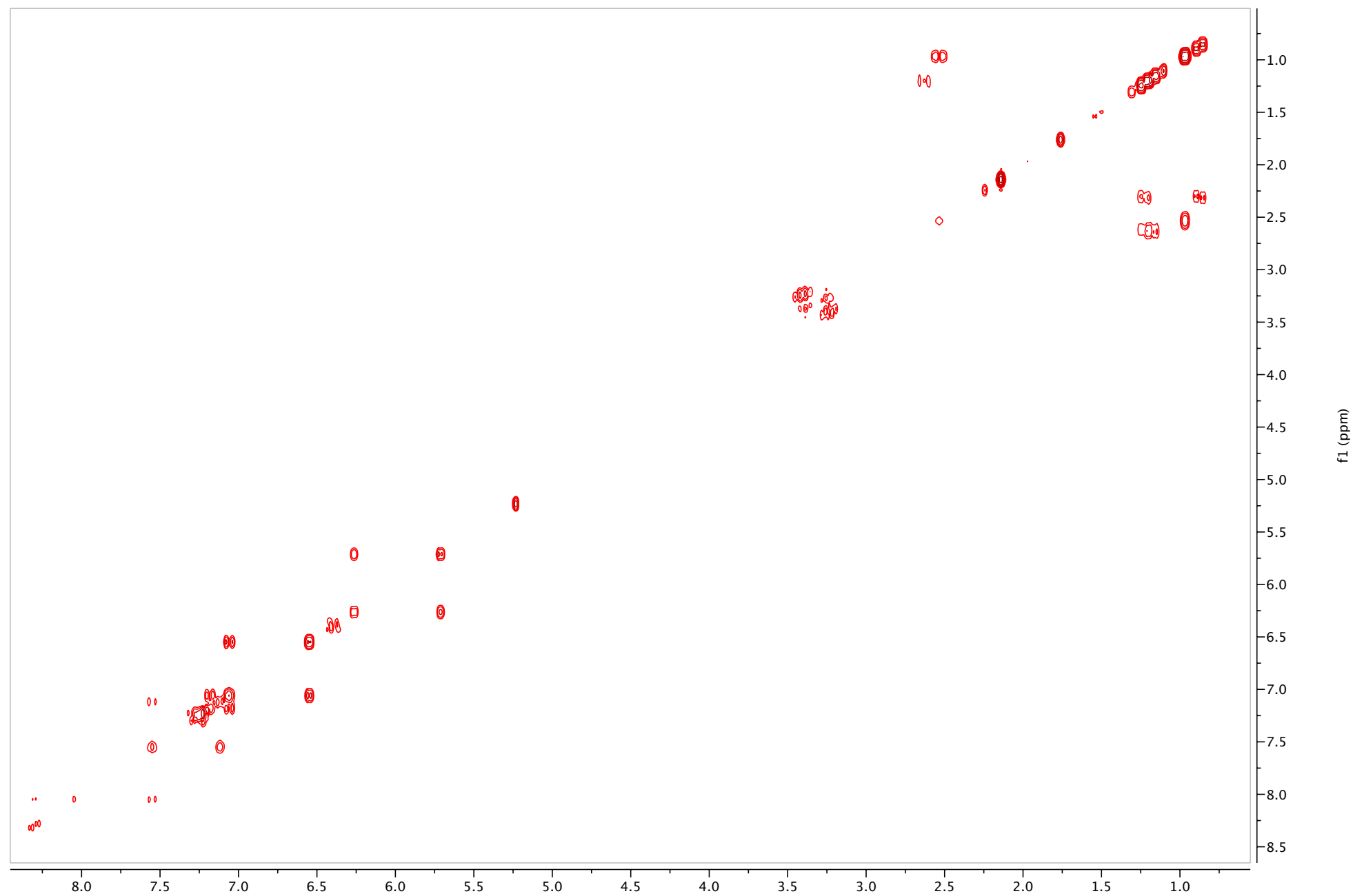
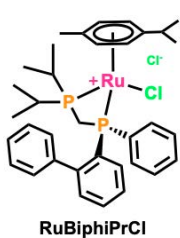
$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

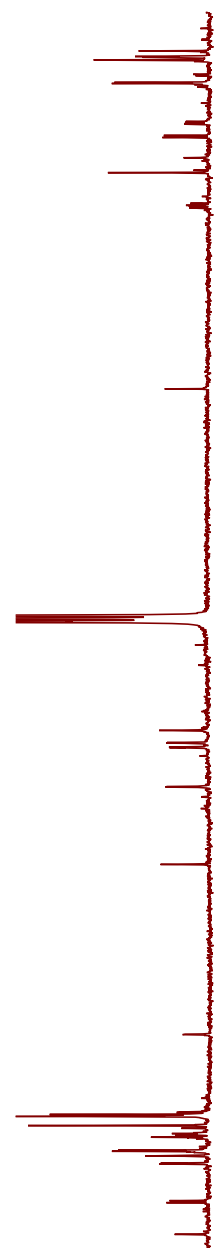
RuBiphiPrCl



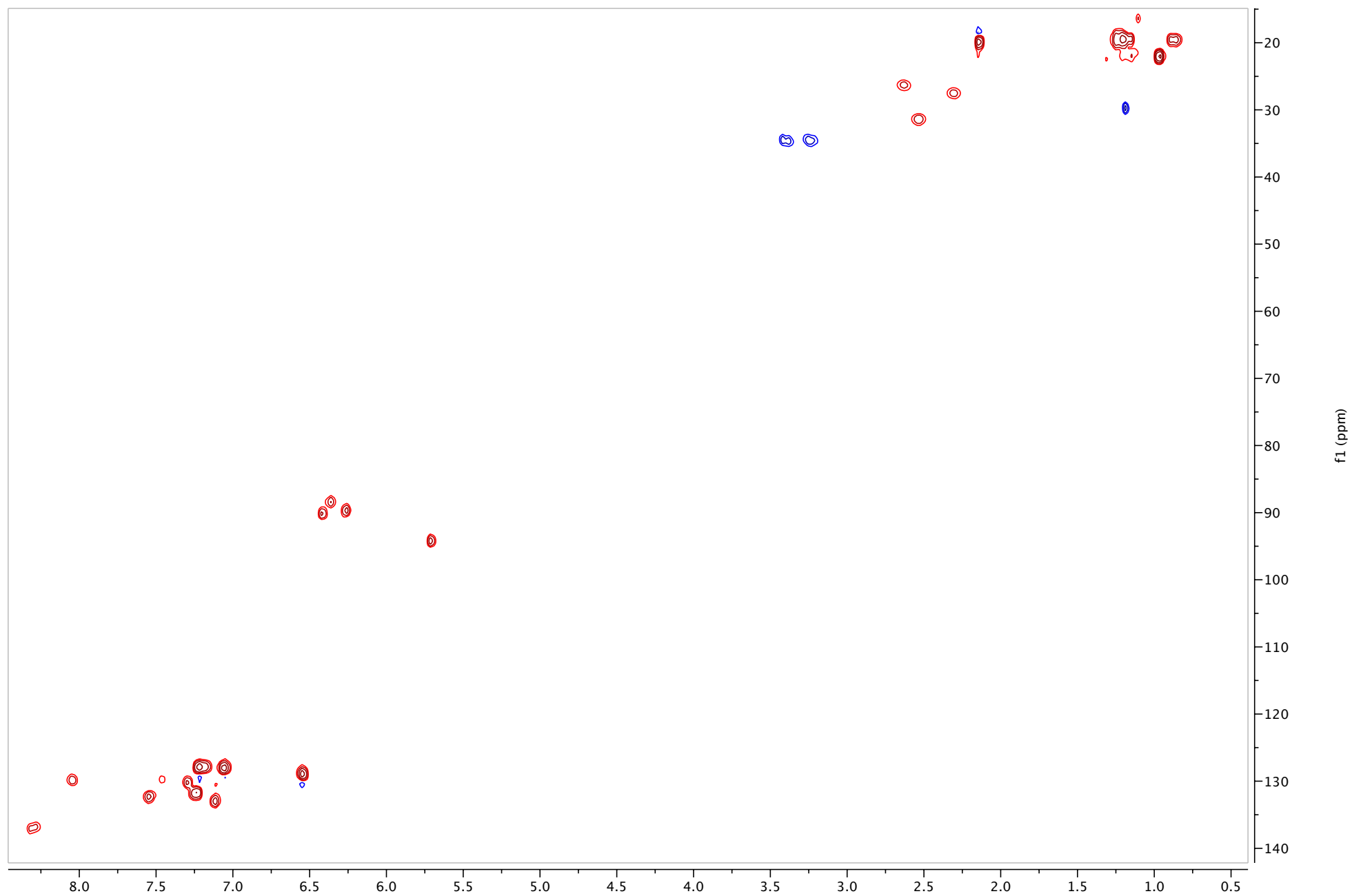
¹H-¹H COSY NMR (CDCl₃, 400 MHz)

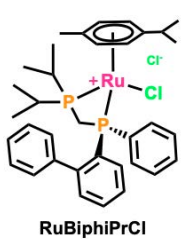
S62



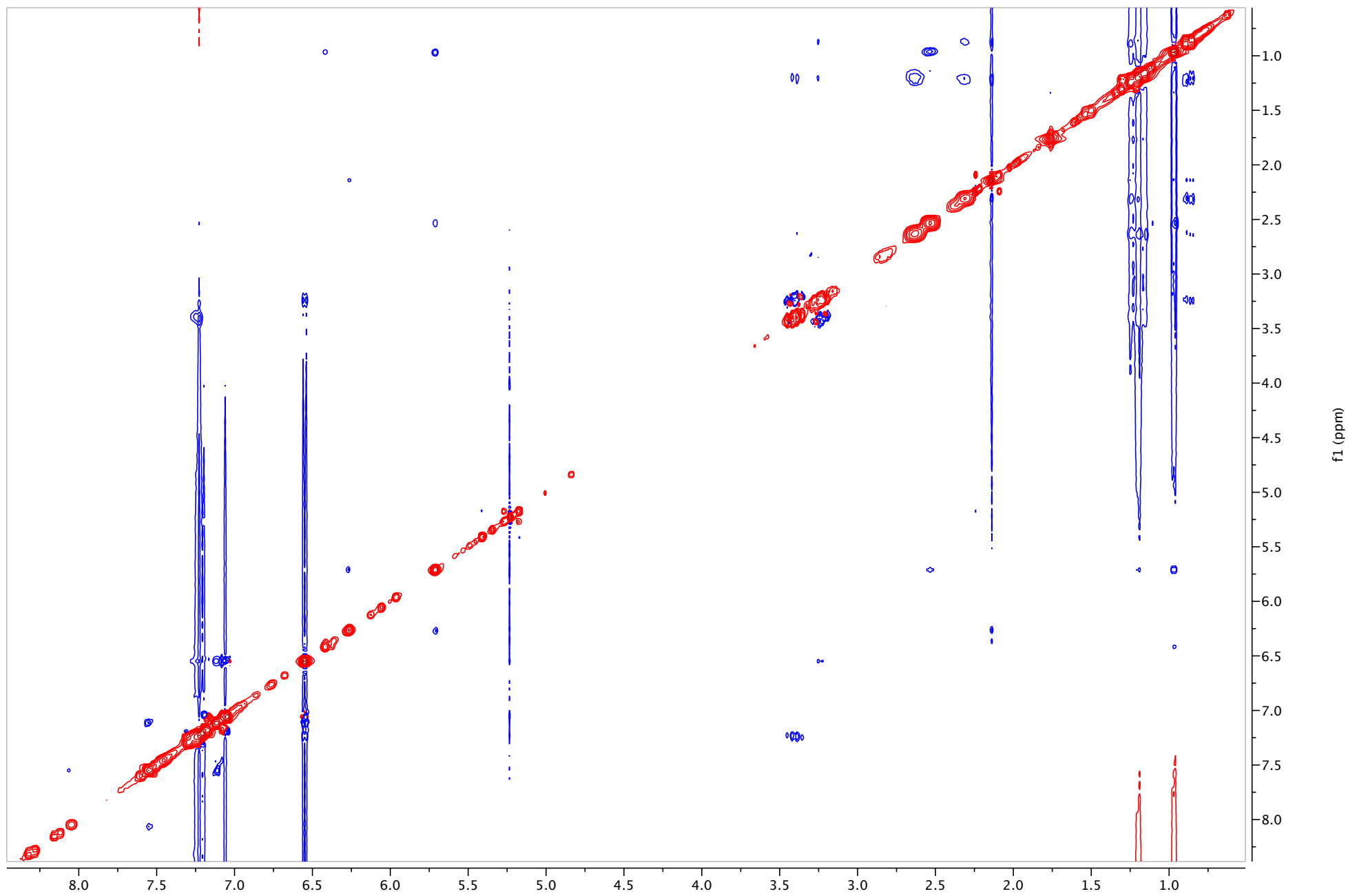


S63



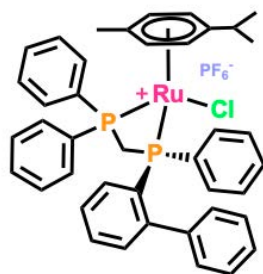


^1H - ^1H NOESY NMR (CDCl_3 , 400 MHz) S64

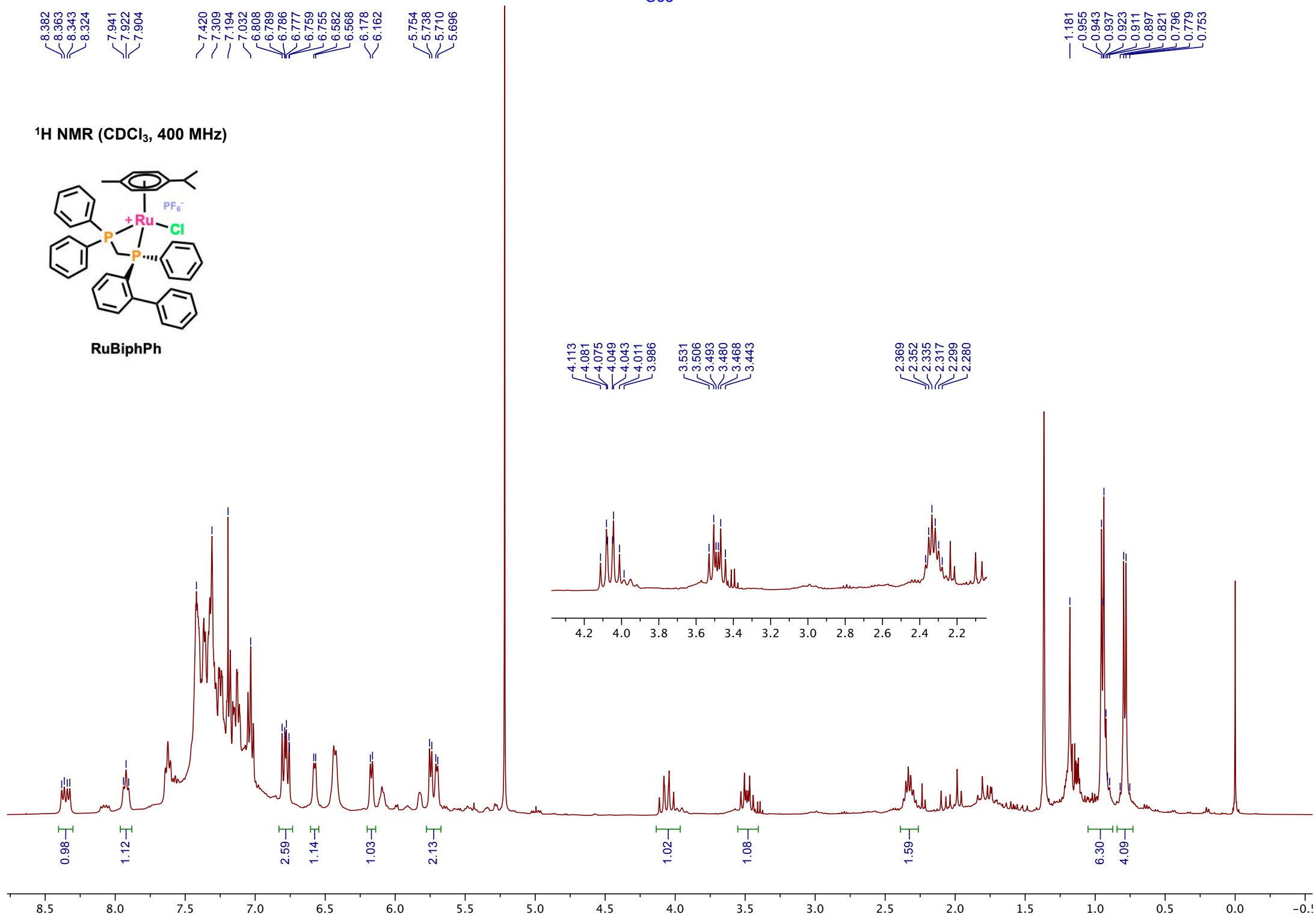


S65

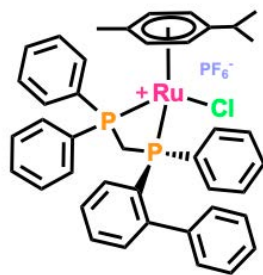
^1H NMR (CDCl_3 , 400 MHz)



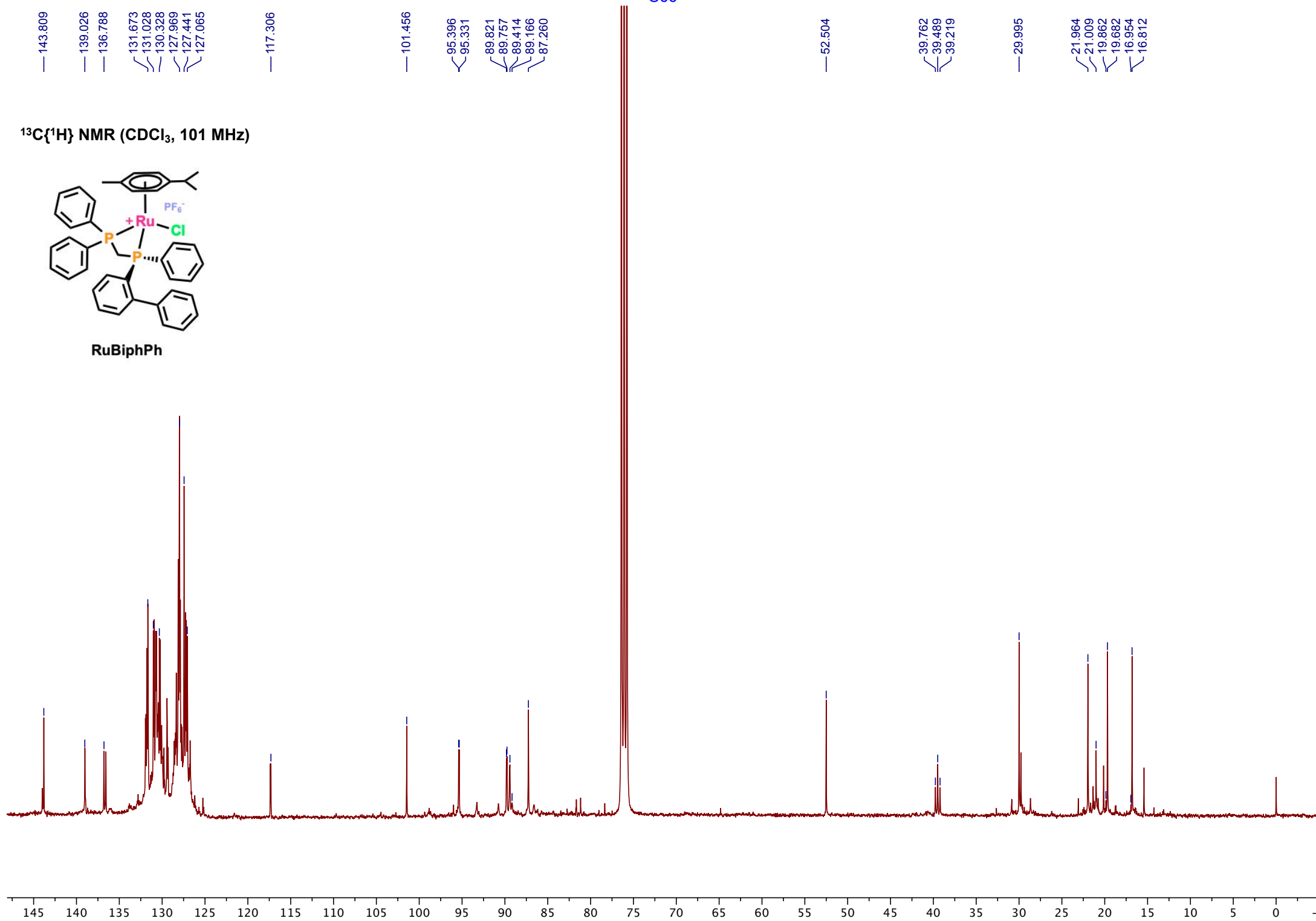
RuBiphPh



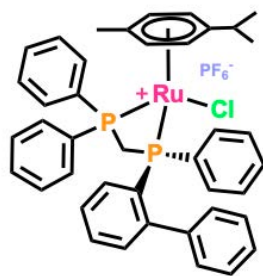
S66

 $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 101 MHz)

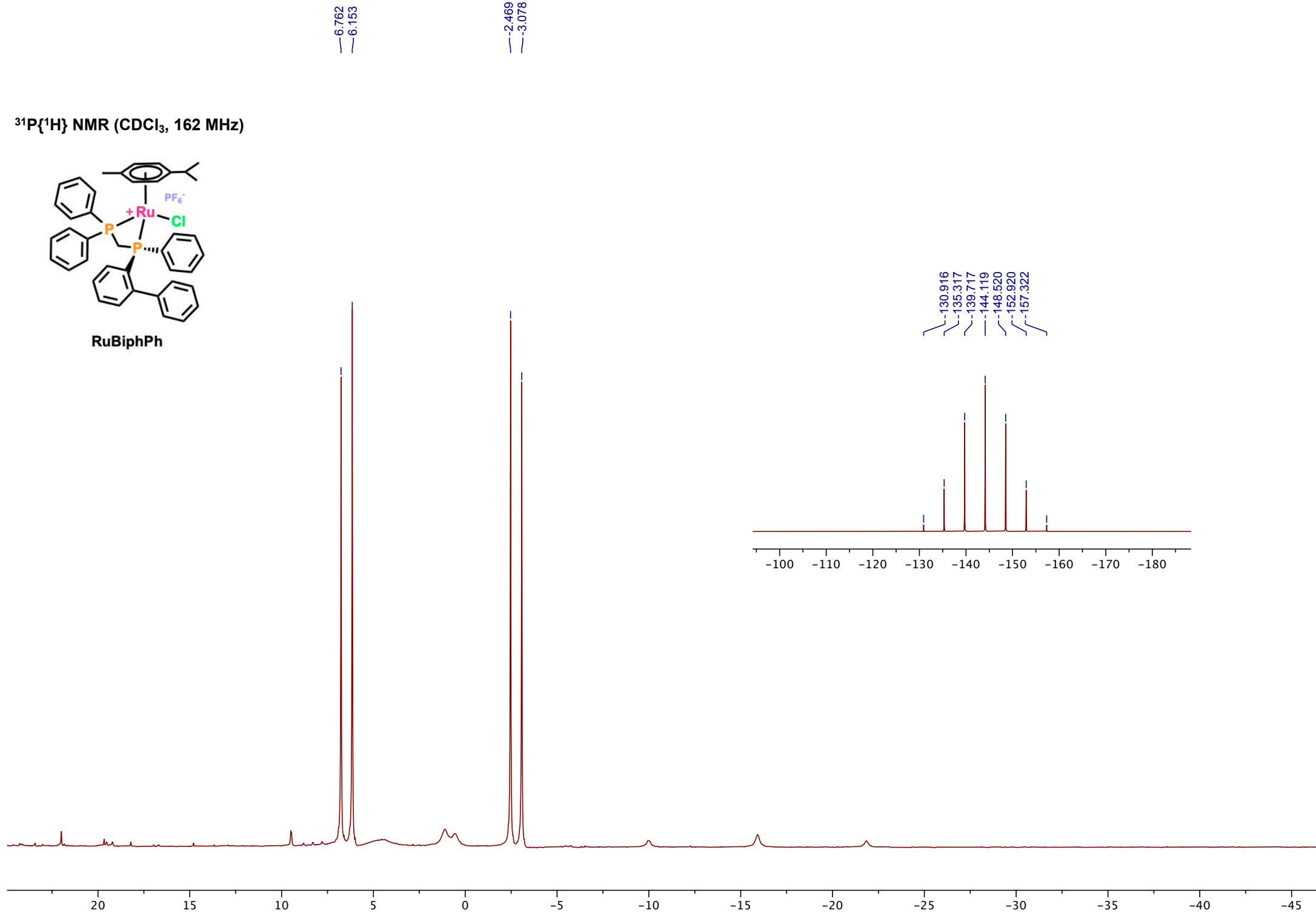
RuBiphPh



$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)

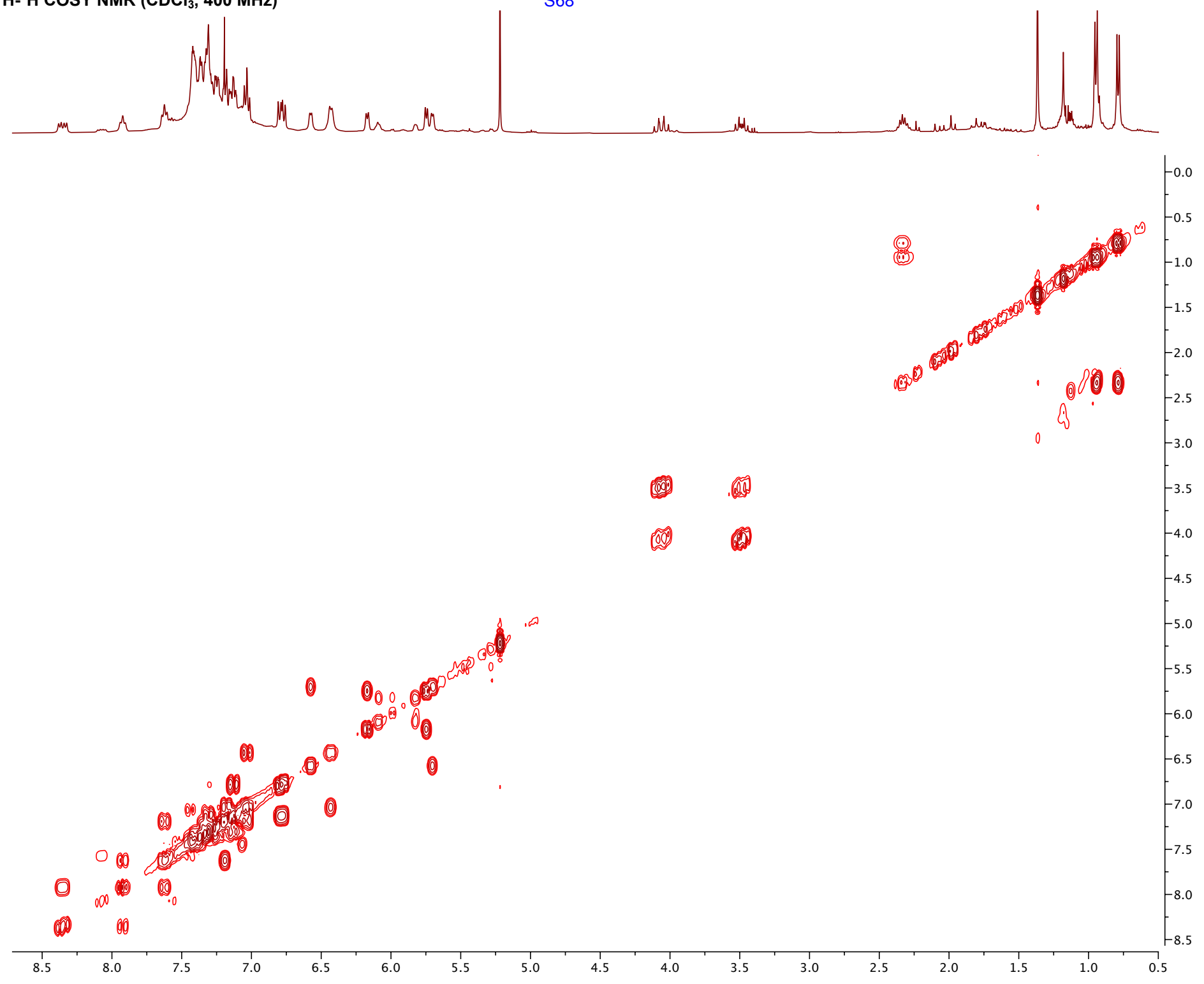
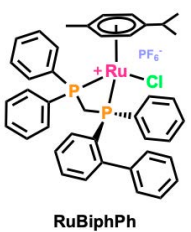


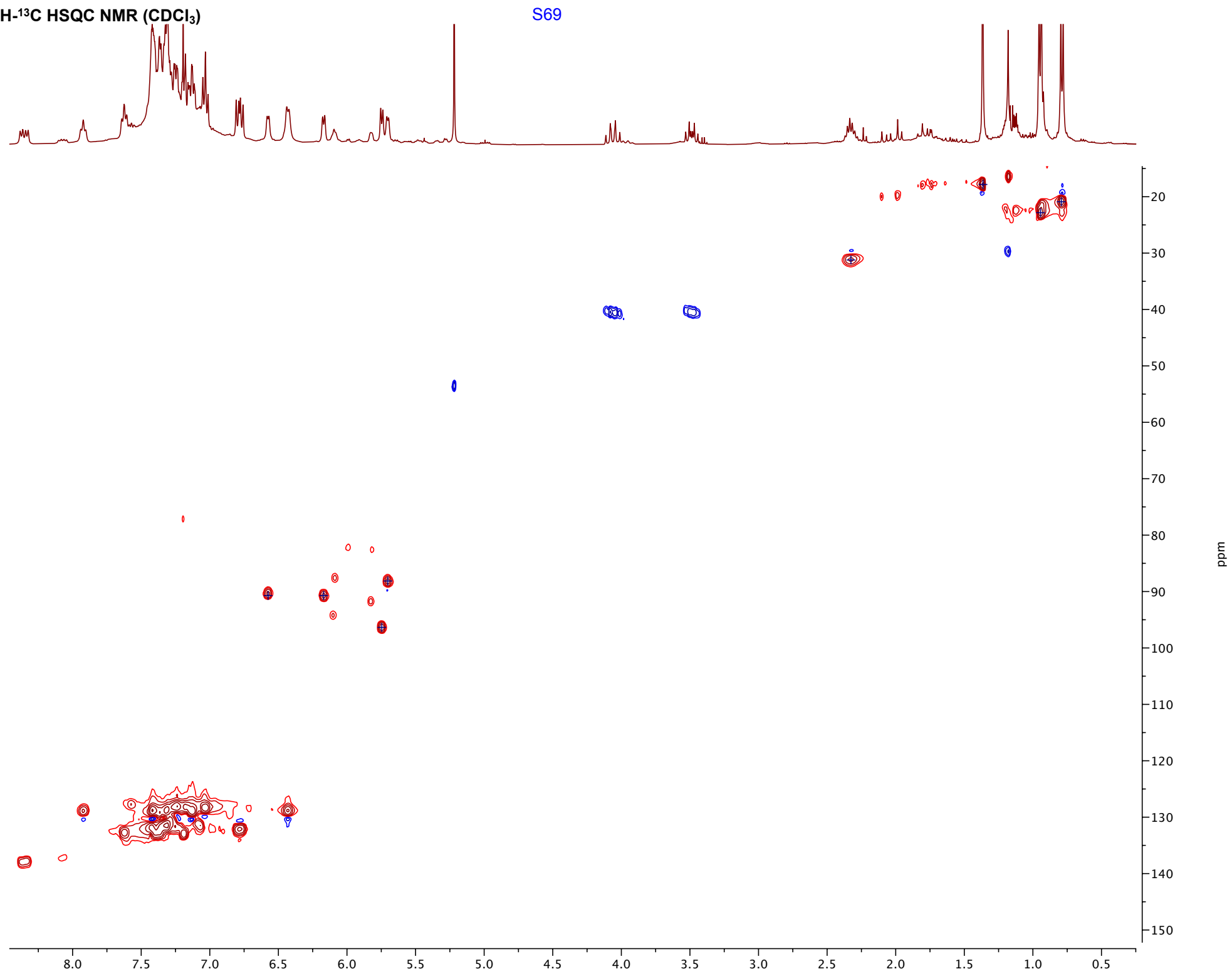
RuBiphPh



¹H-¹H COSY NMR (CDCl₃, 400 MHz)

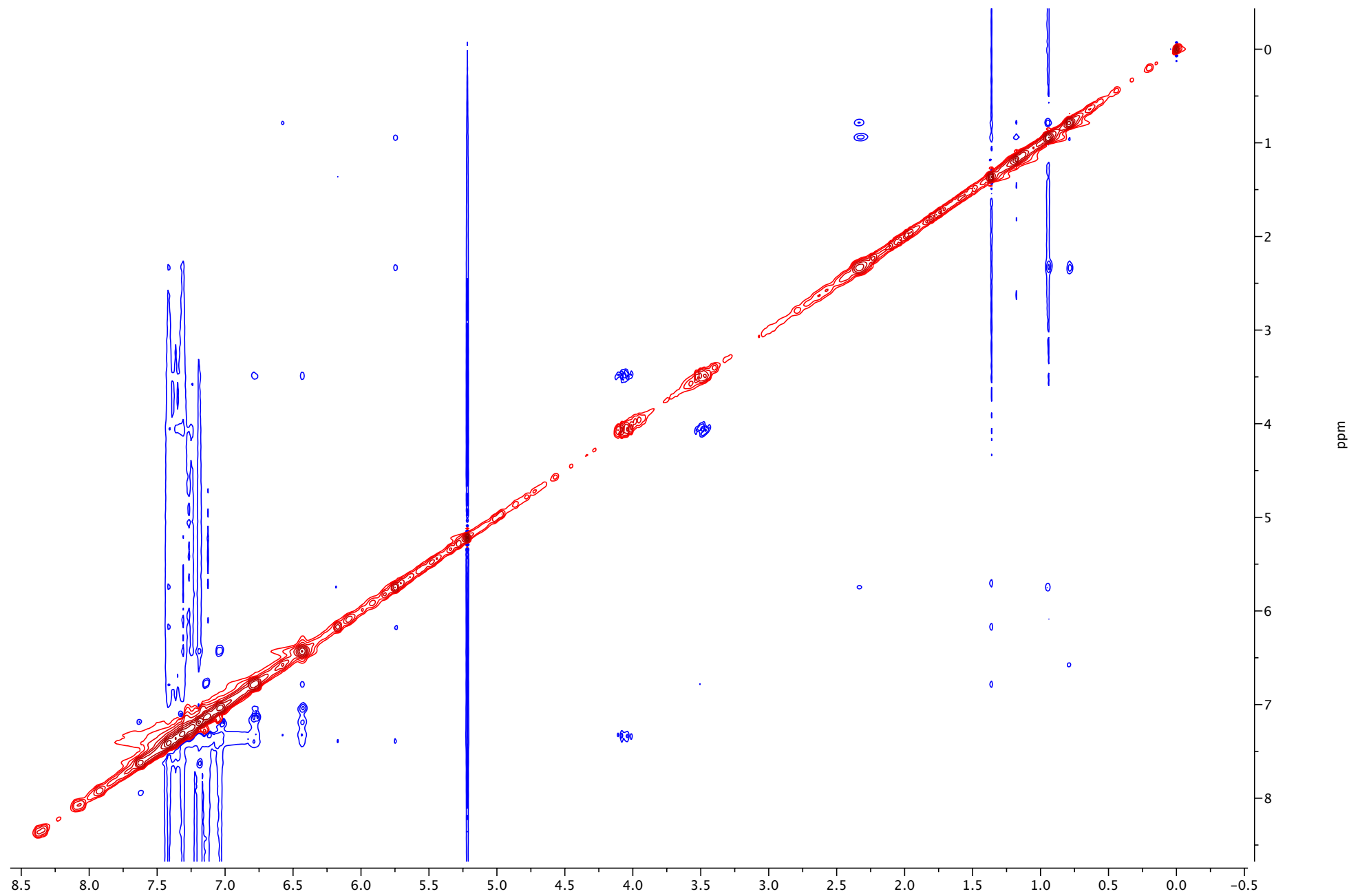
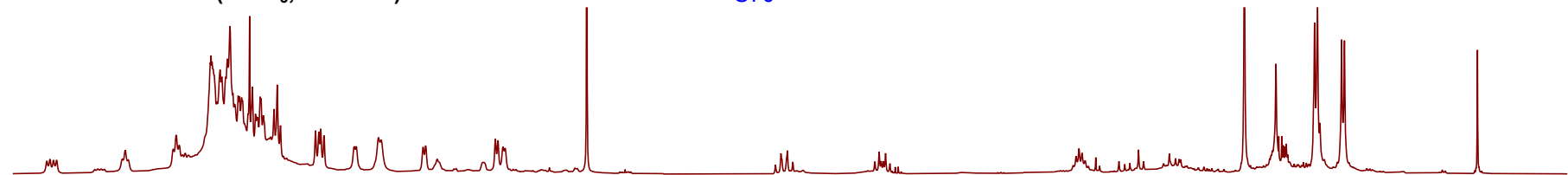
S68



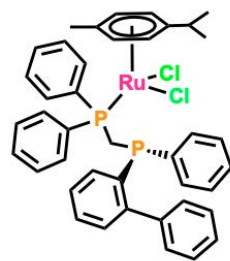


^1H - ^1H NOESY NMR (CDCl_3 , 400 MHz)

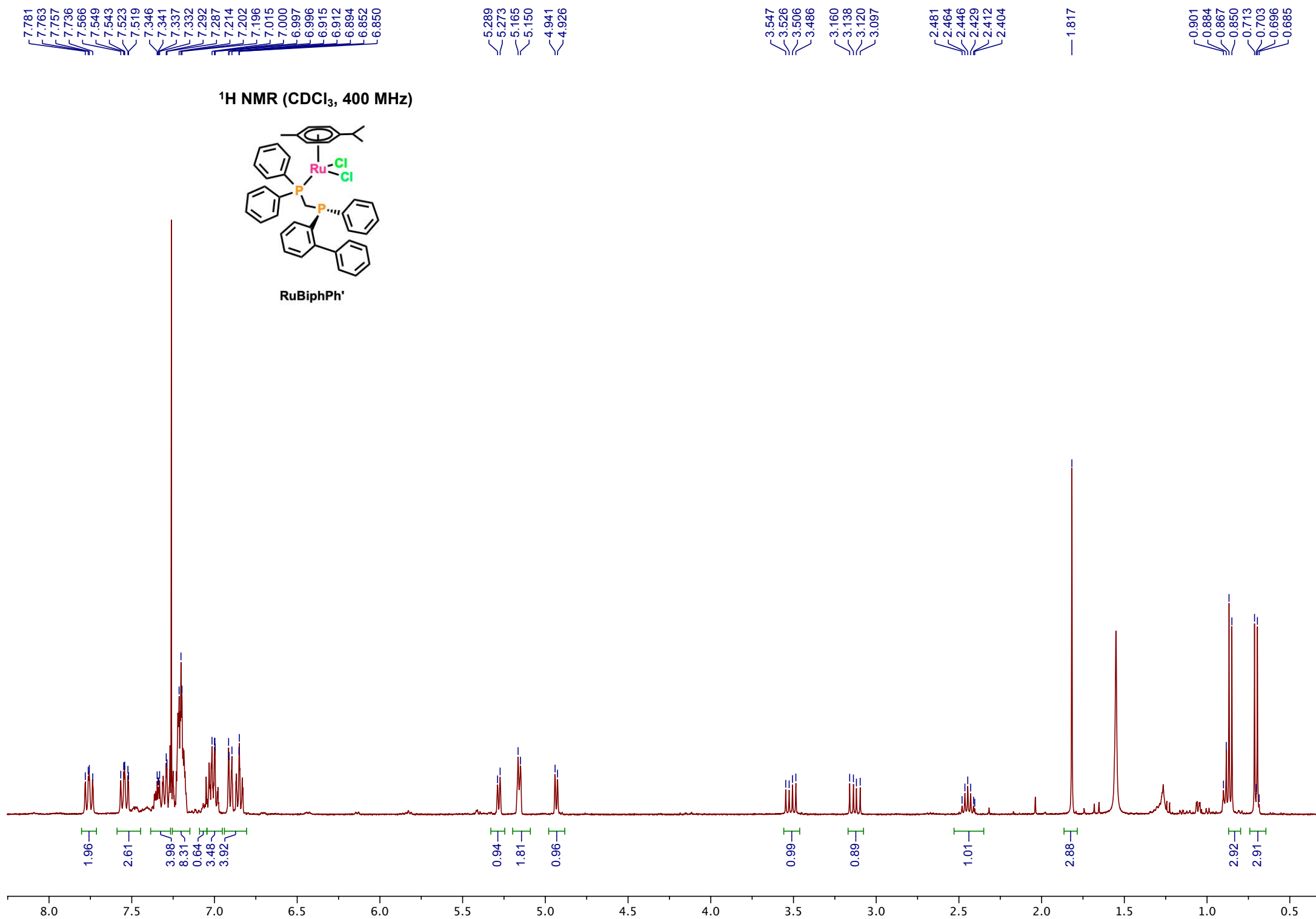
S70



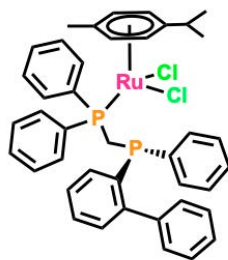
S71

¹H NMR (CDCl₃, 400 MHz)

RuBiphPh'



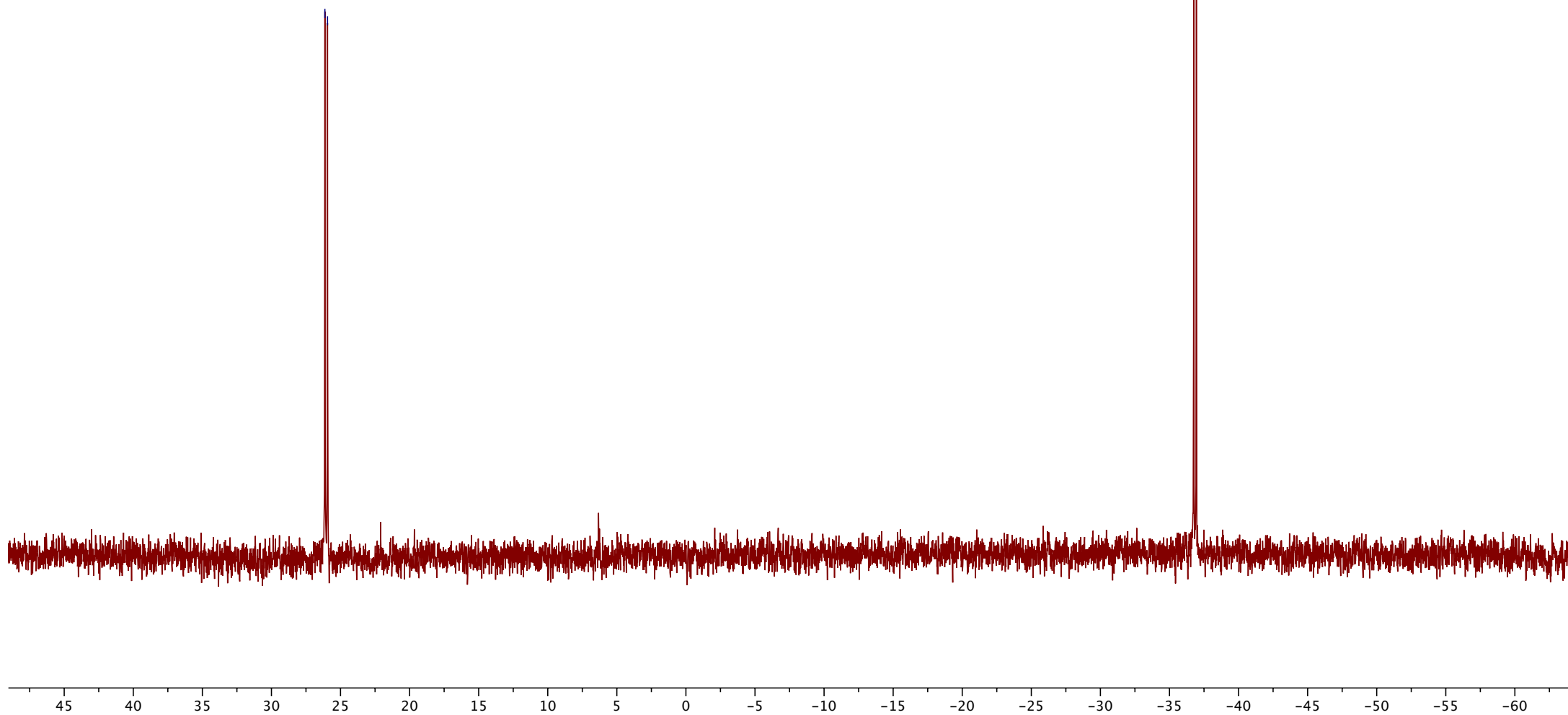
$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz)



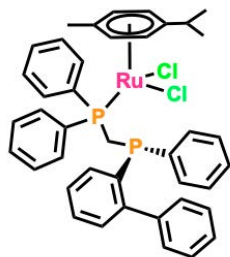
RuBiphPh'

26.132
25.941

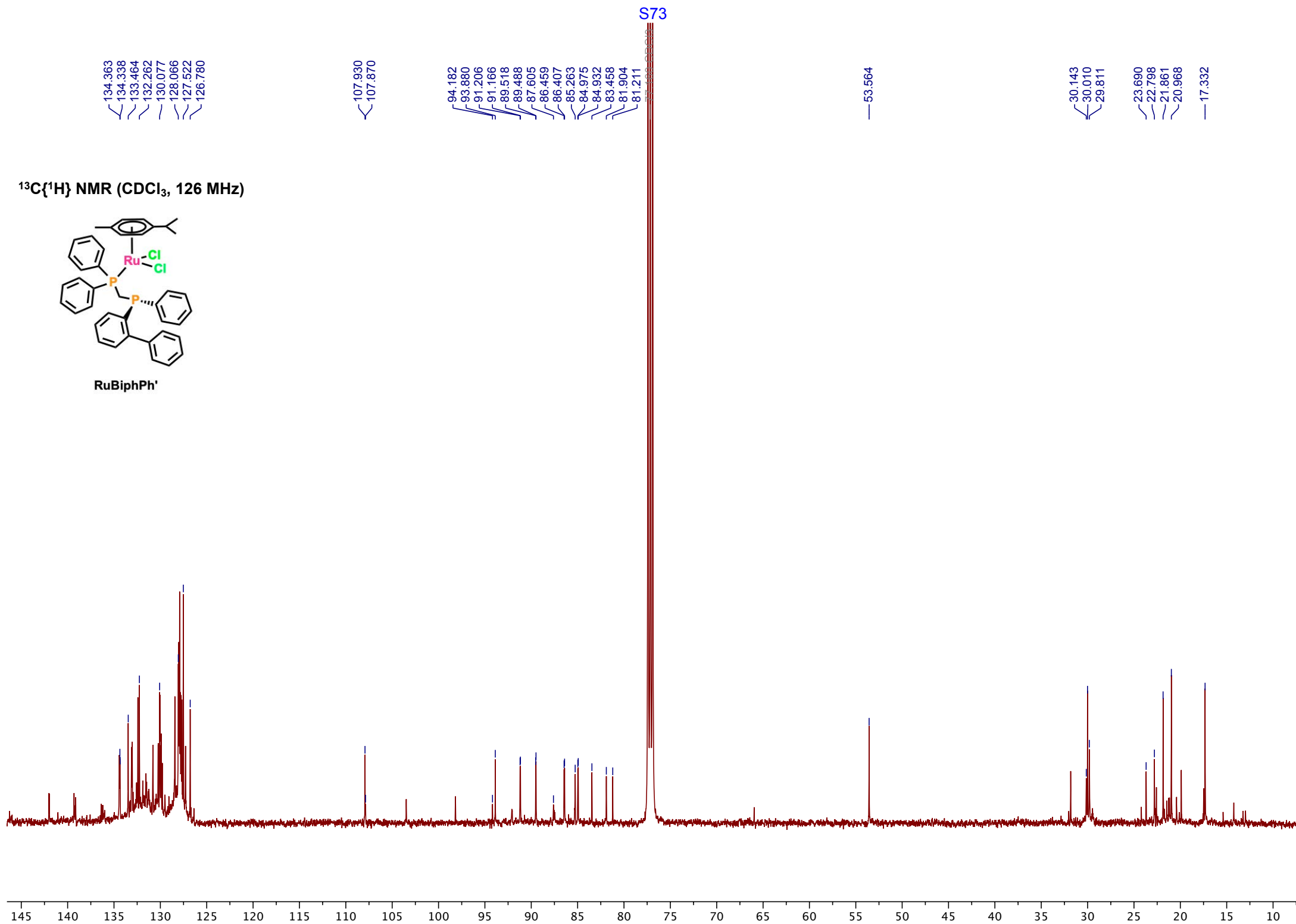
36.757
36.948



$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 126 MHz)

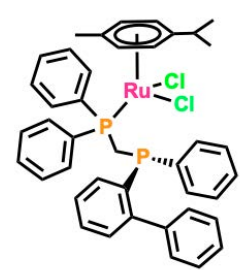


RuBiphPh'

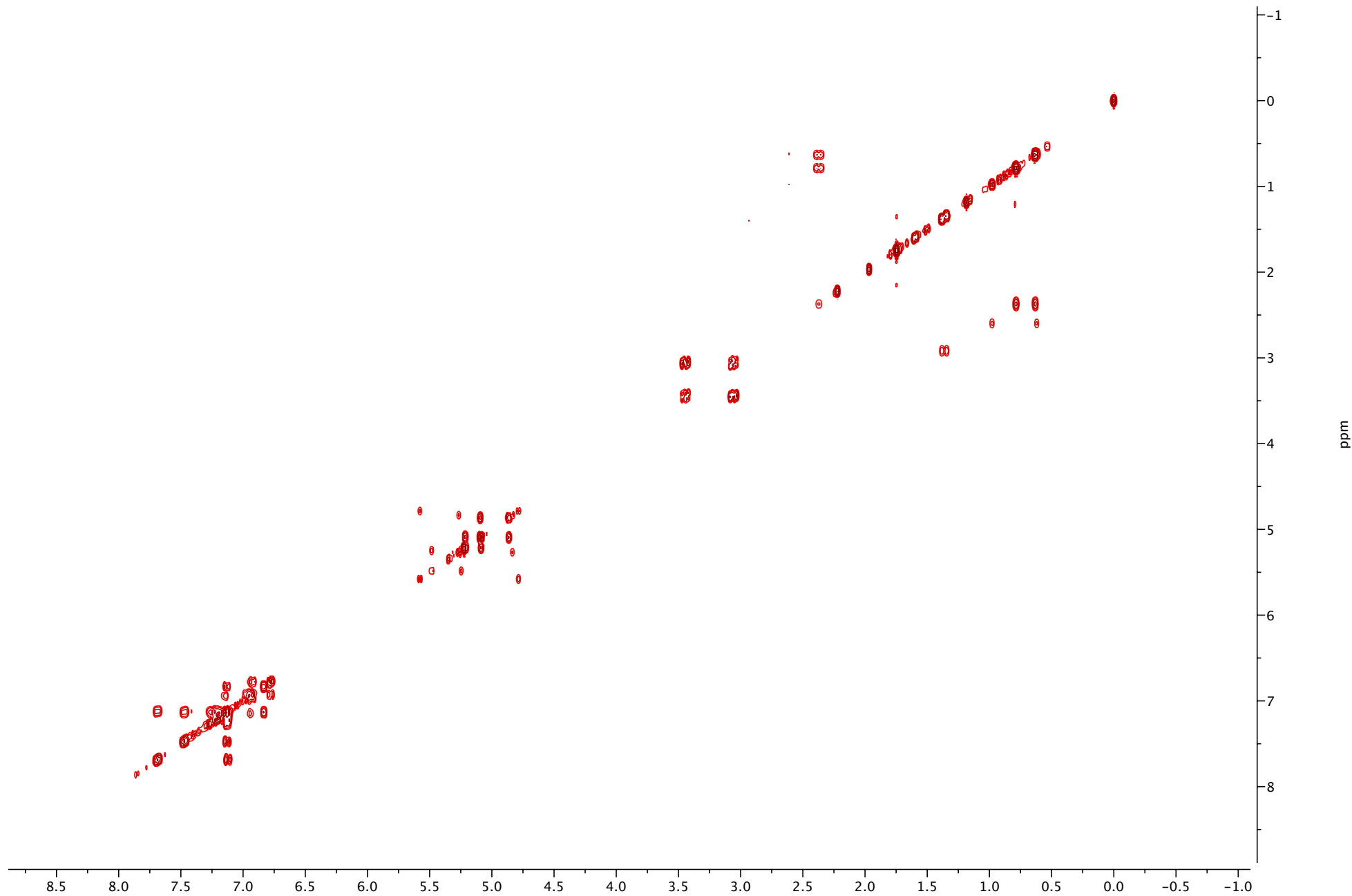


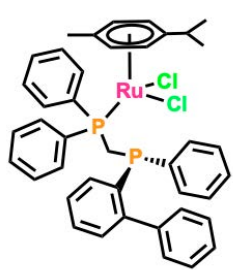
¹H-¹H COSY NMR (CDCl₃, 500 MHz)

S74

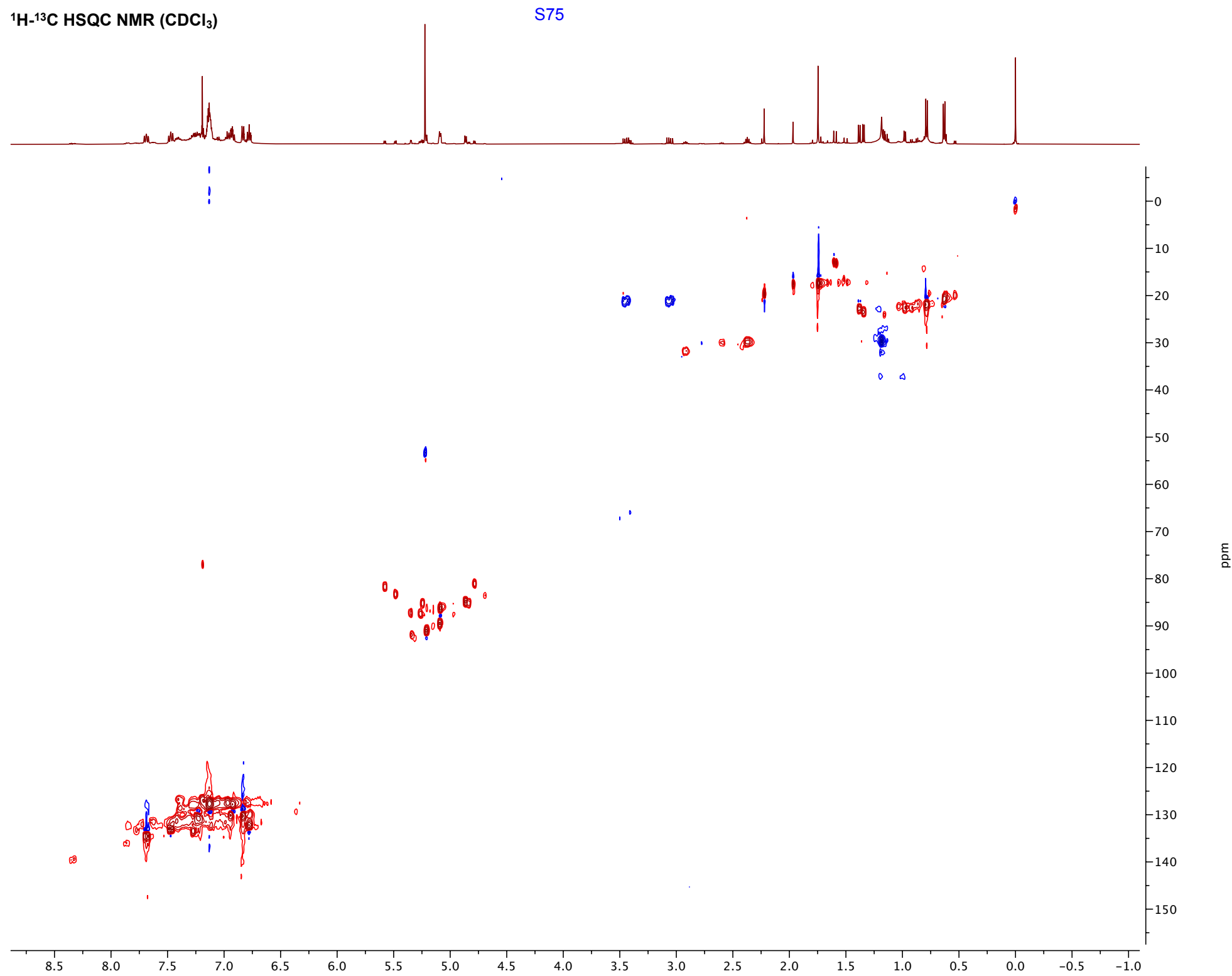


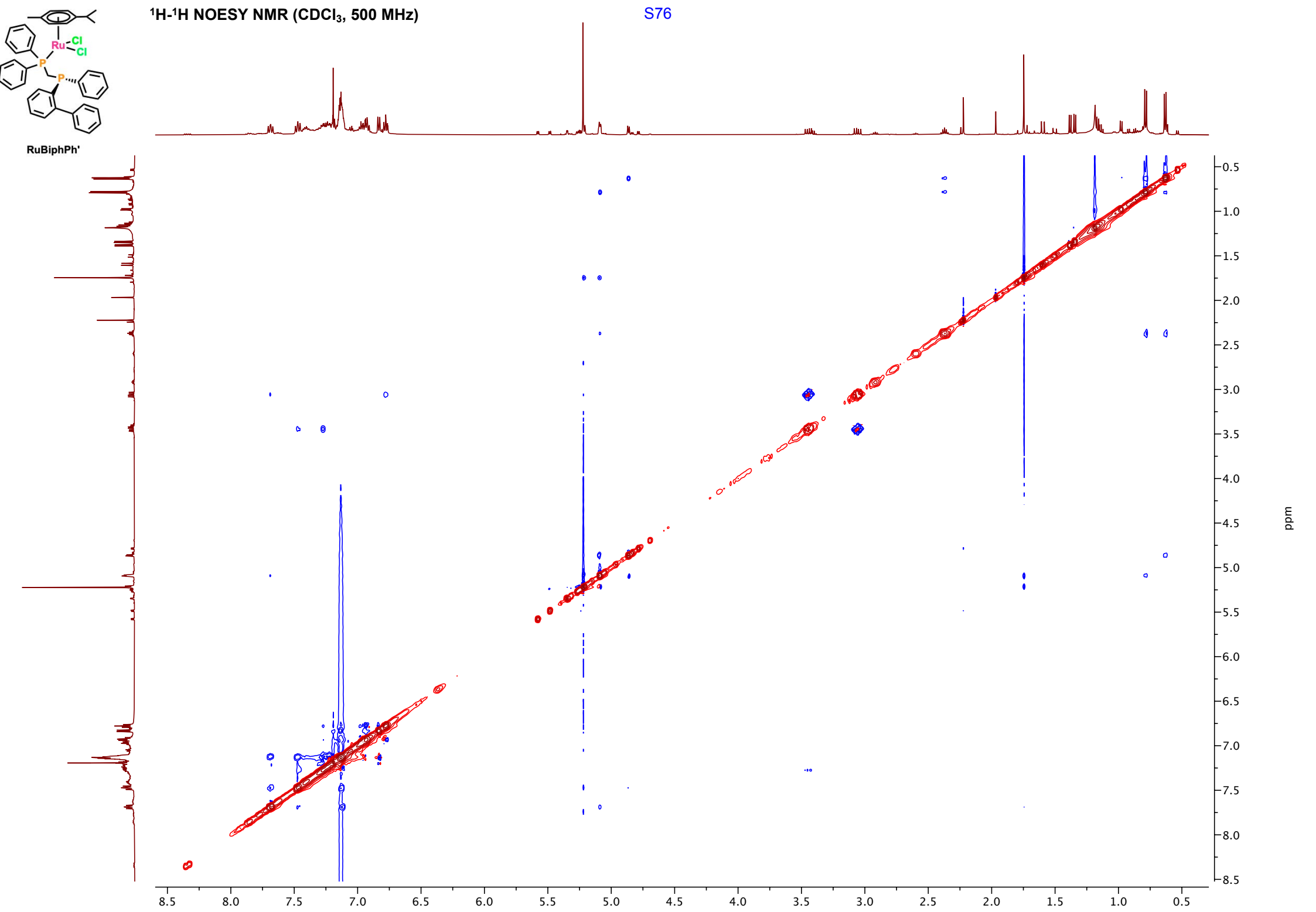
RuBiphPh'





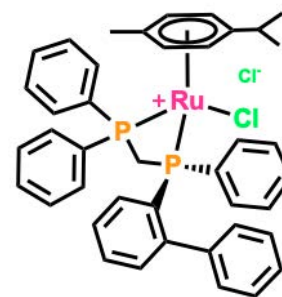
RuBiphPh'



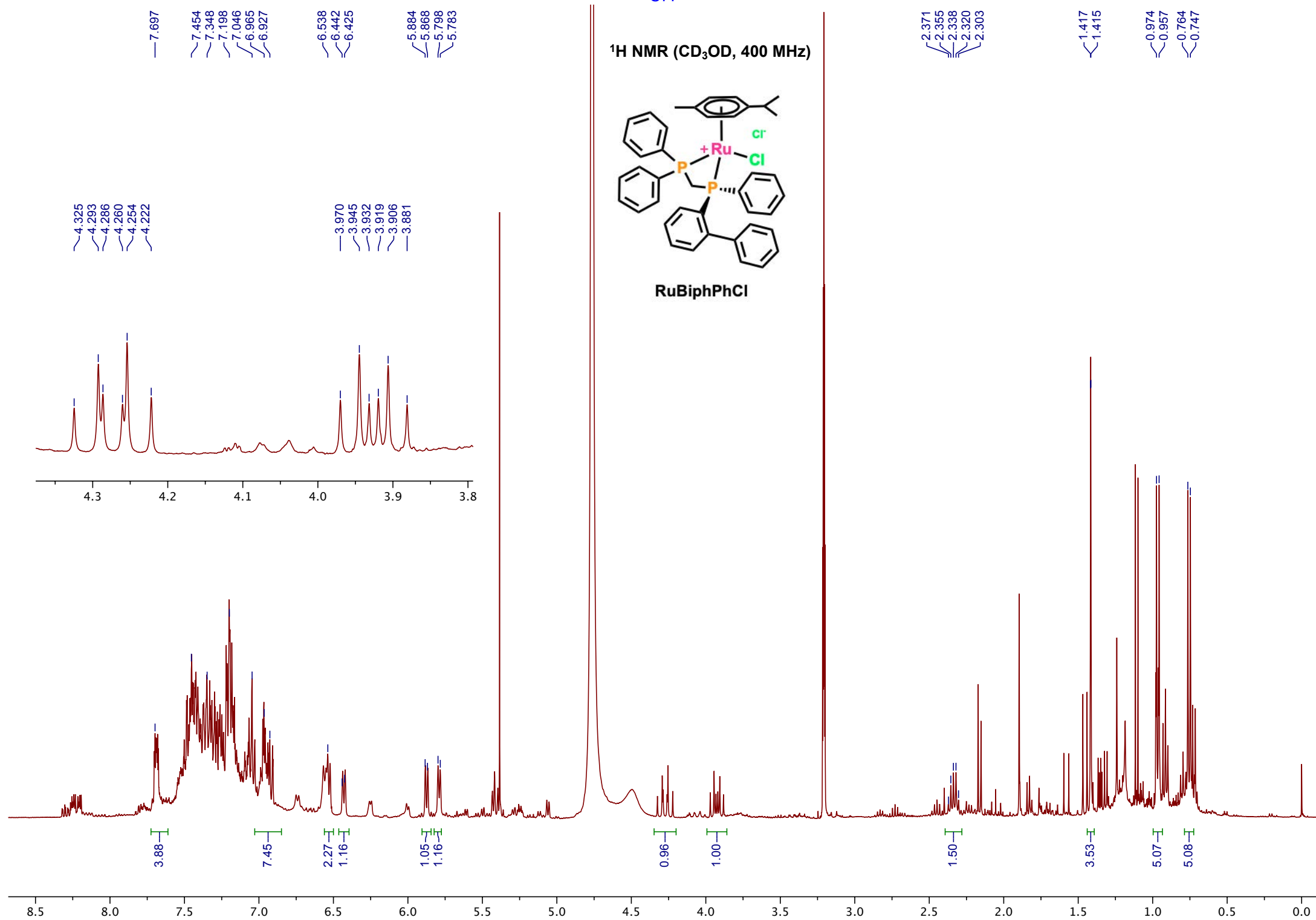


S77

¹H NMR (CD₃OD, 400 MHz)

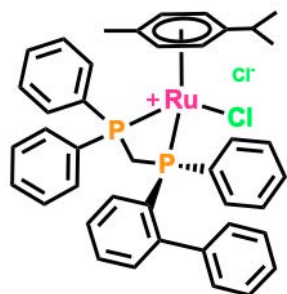


RuBiphPhCl

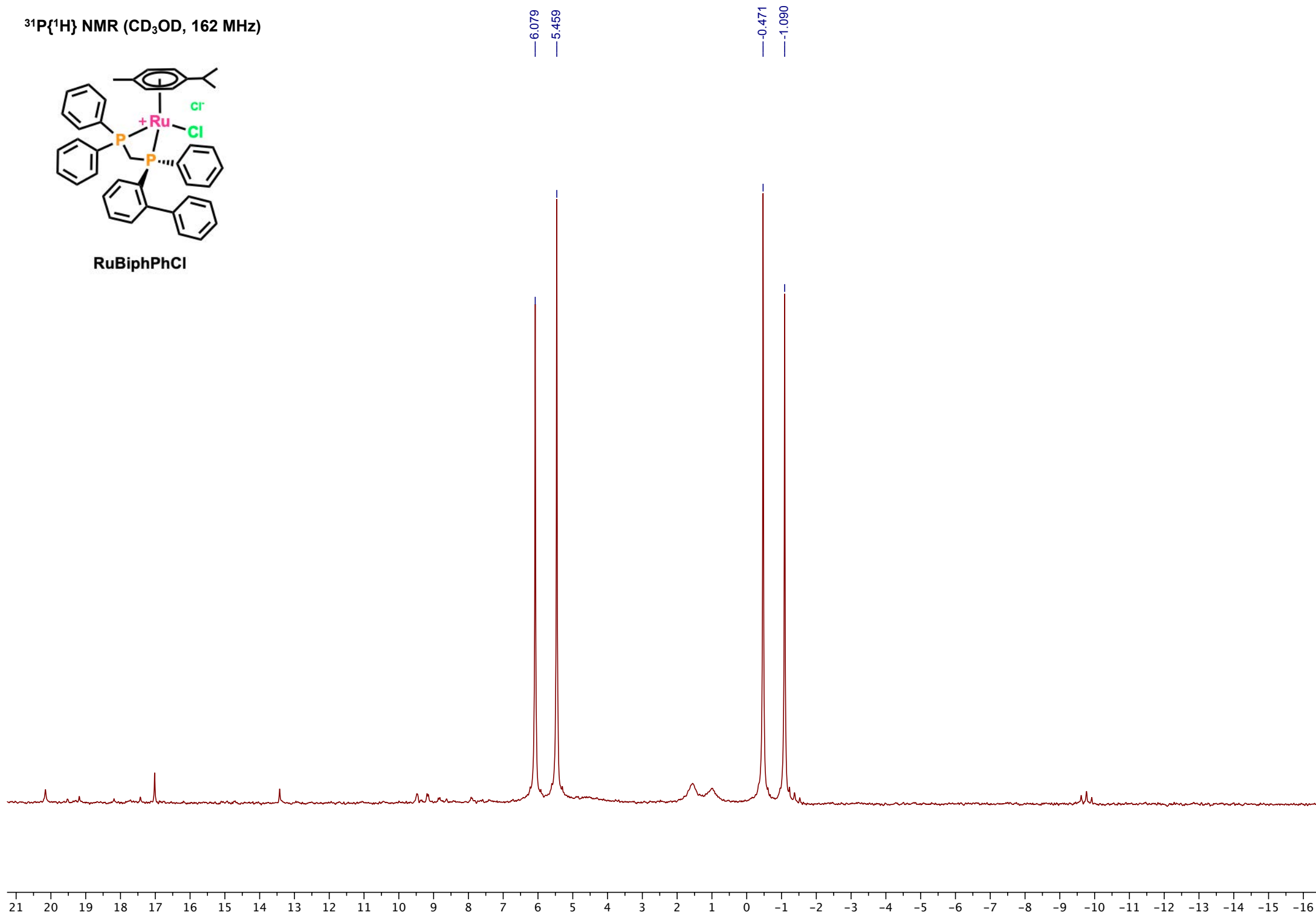


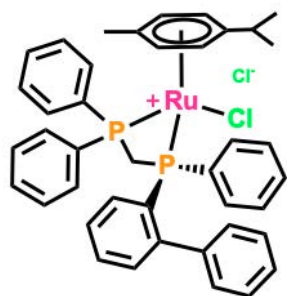
$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3OD , 162 MHz)

S78

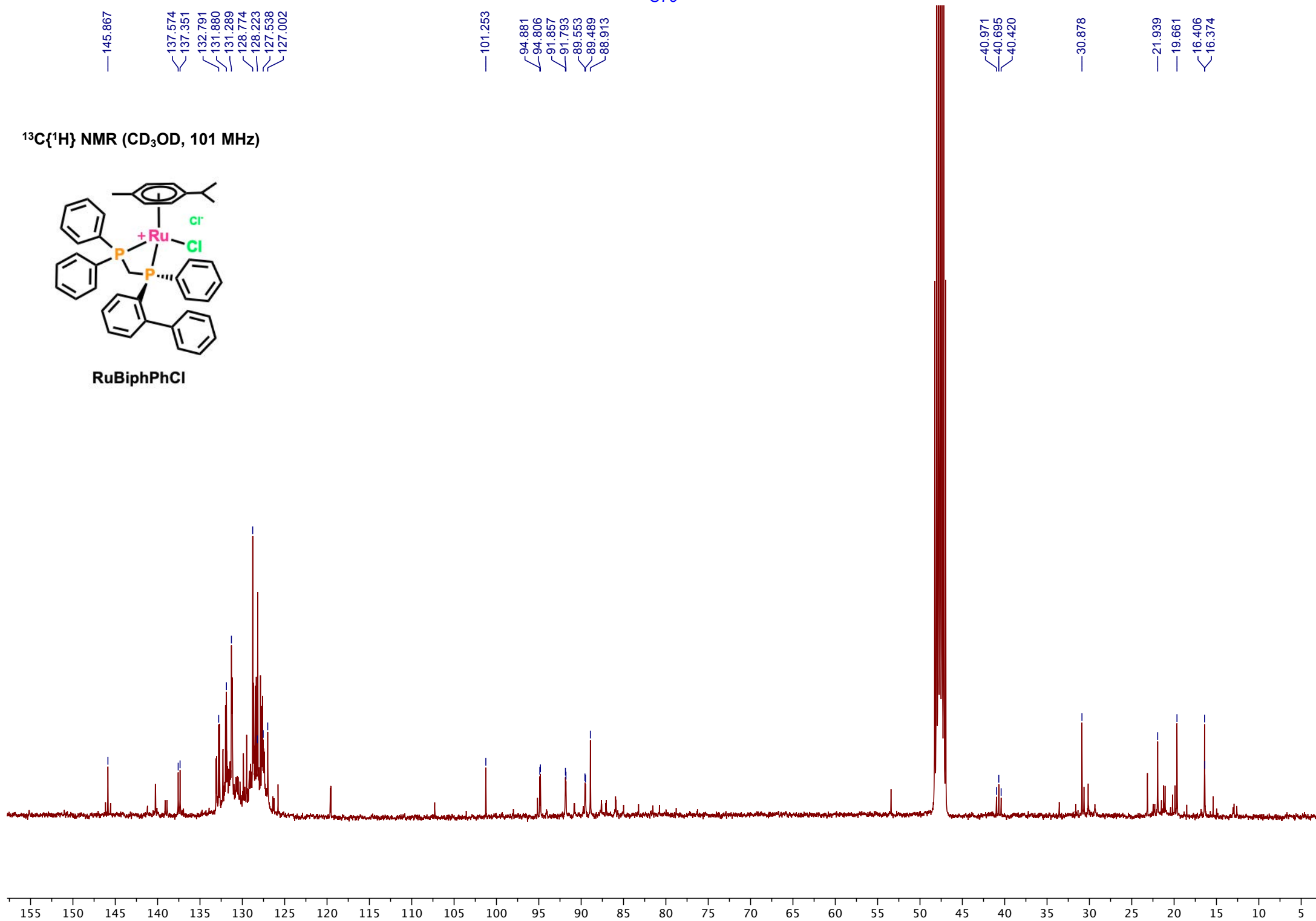


RuBiphPhCl

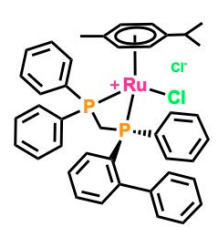


$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , 101 MHz)

RuBiphPhCl

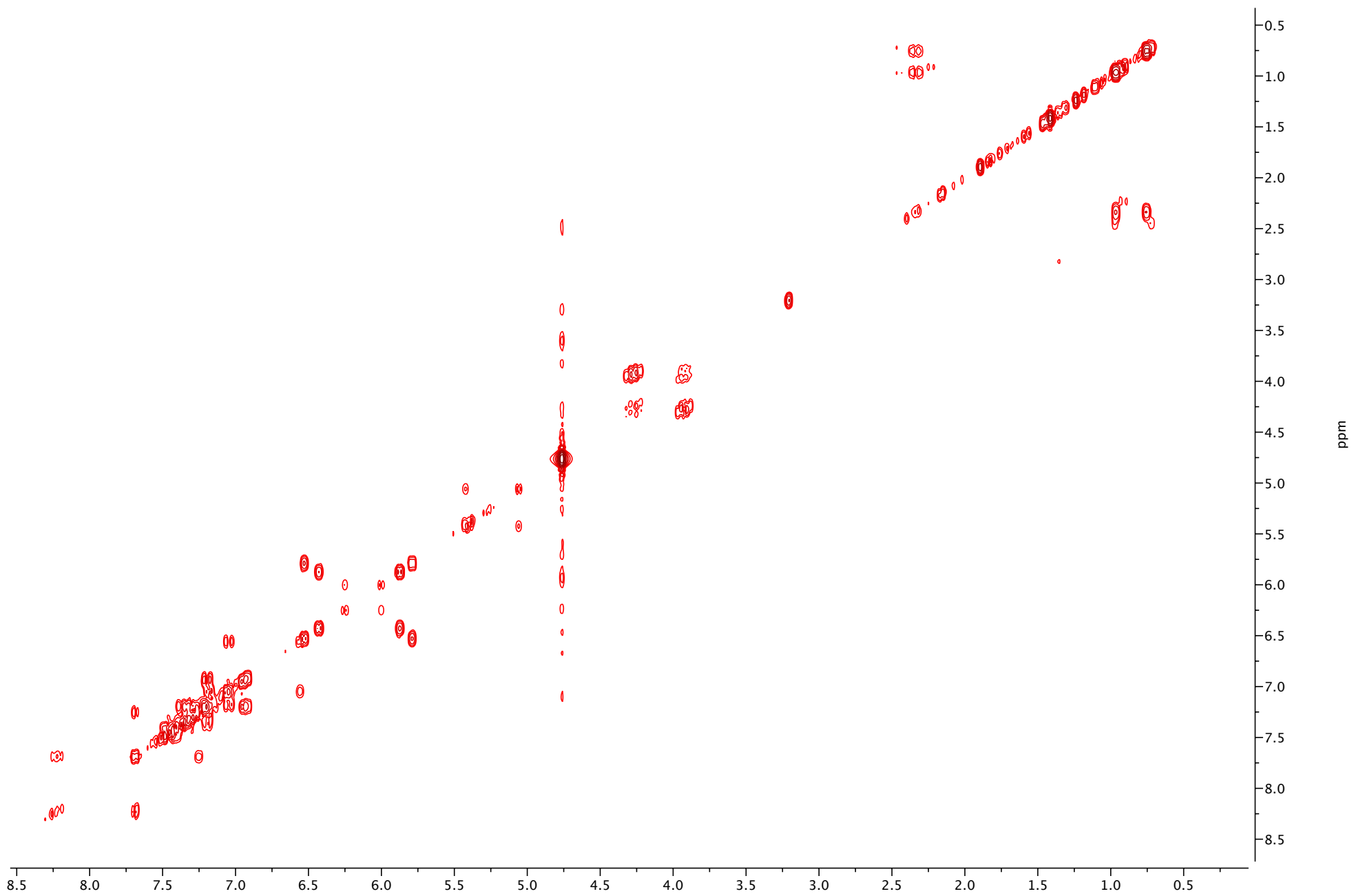


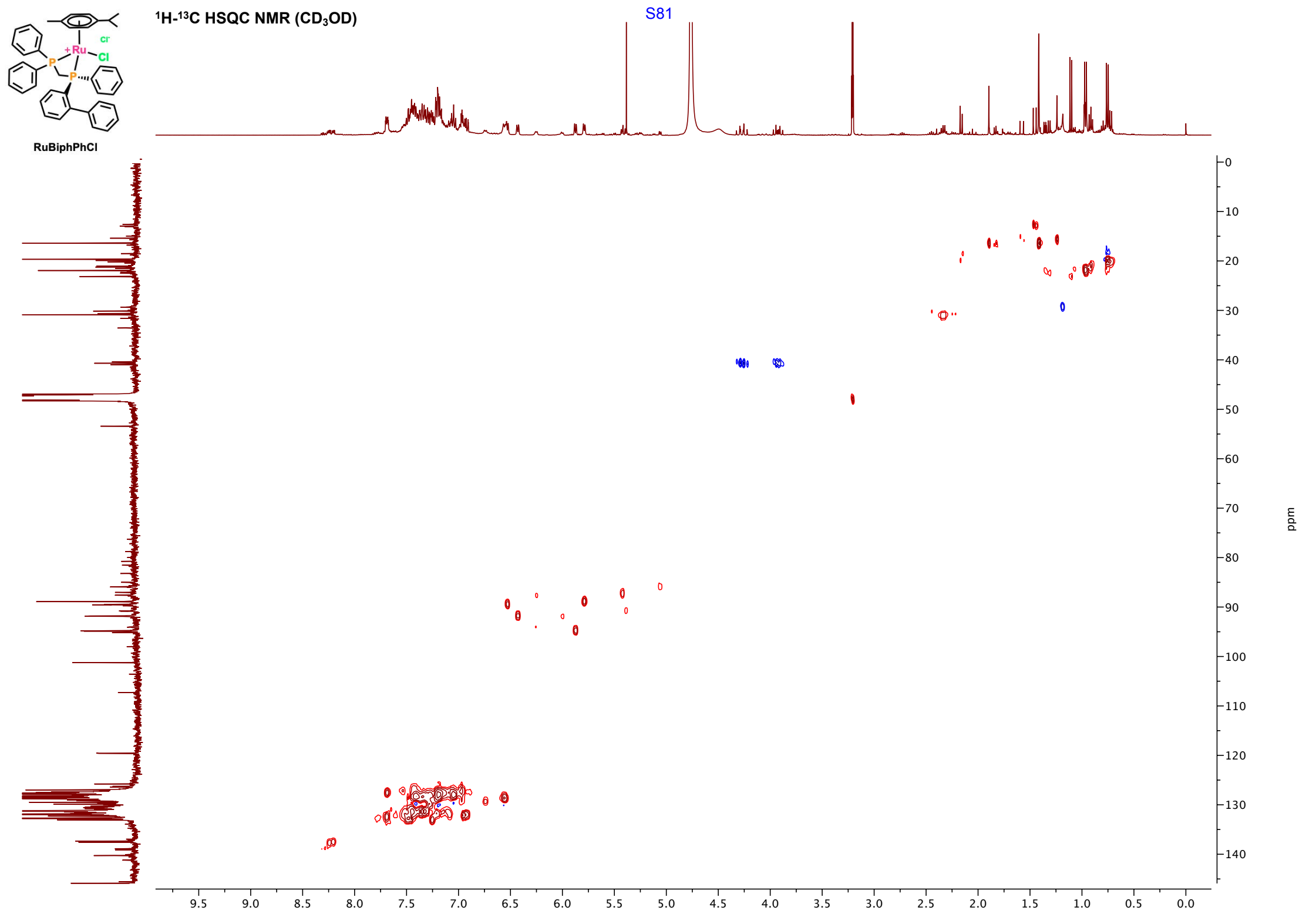
^1H - ^1H COSY NMR (CD_3OD , 400 MHz)



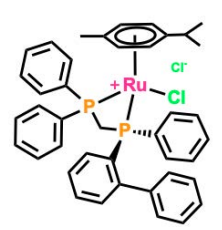
RuBiphPhCl

S80





^1H - ^1H NOESY NMR (CD_3OD , 400 MHz)



RuBiphPhCl

