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Non covalent interactions in phosphole **8** (calculated structure)

Non covalent interactions in palladium complex **10** (calculated structure)

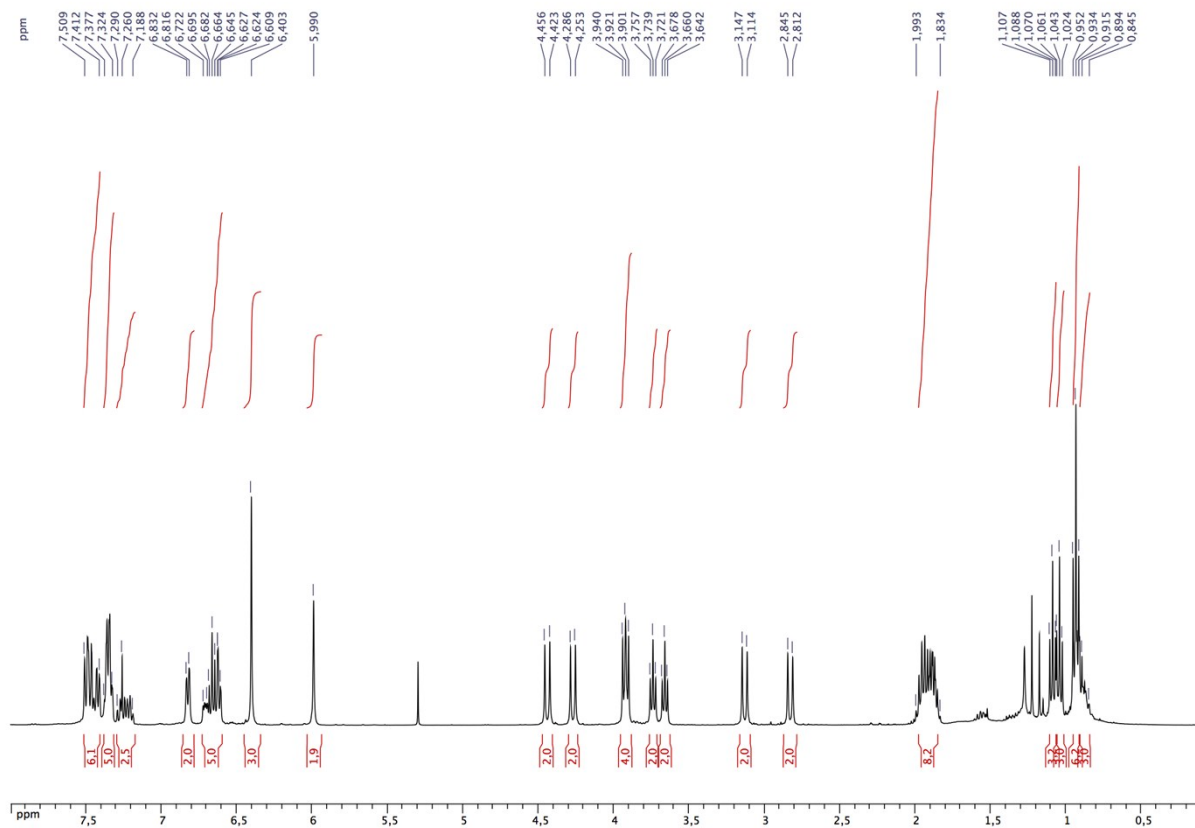
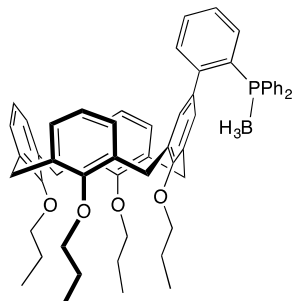
Non covalent interactions in **12** (calculated structure)

UV-vis absorption, excitation, solution fluorescence and thin film fluorescence of **9**

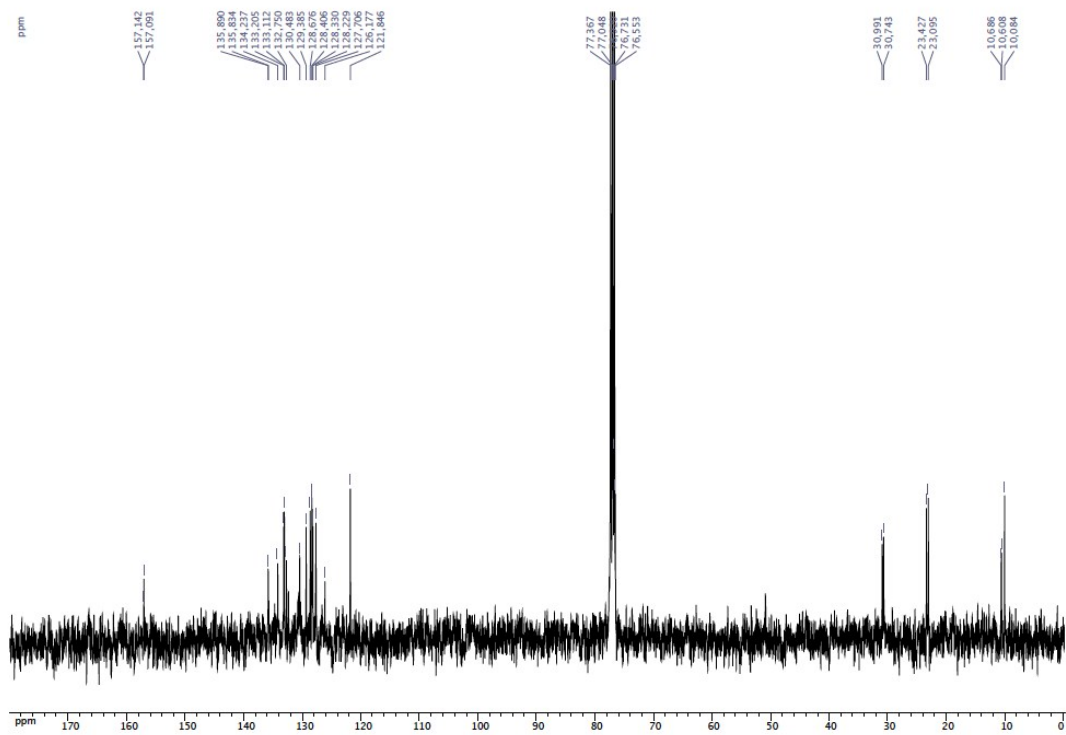
UV-vis absorption, excitation (dashed), solution fluorescence (dashed) of **11**

UV-vis absorption of **4**

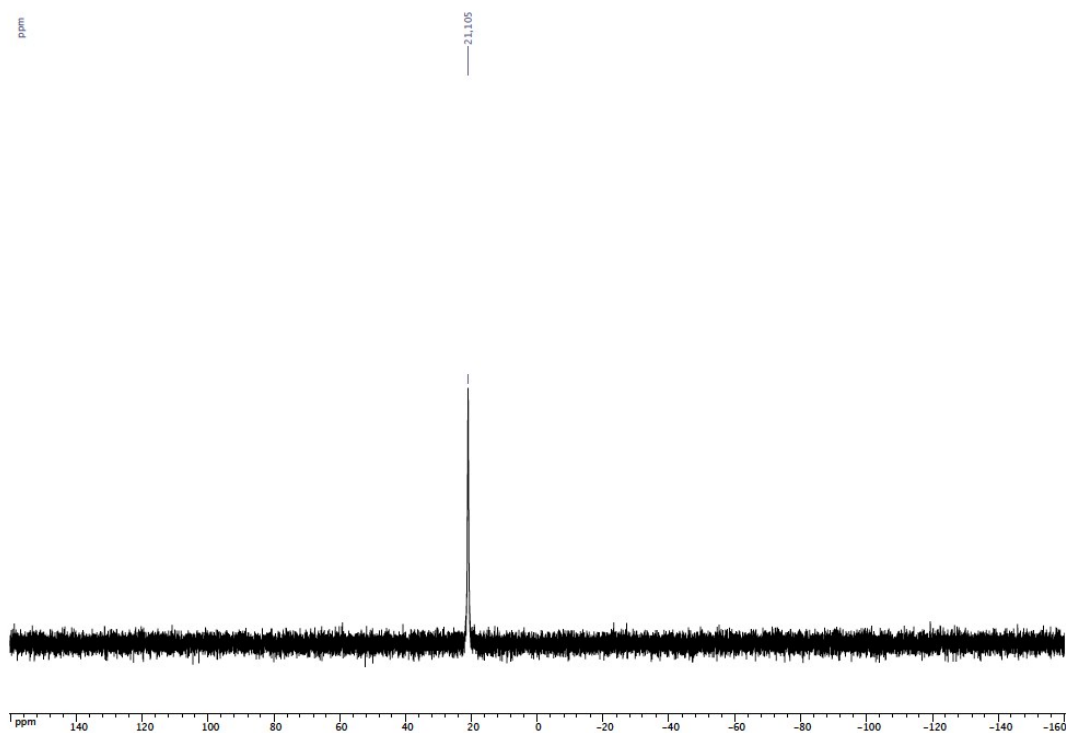
[5-(2-Diphenylphosphanyl-phenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]borane (**2**)



^1H NMR spectrum of **2** (CDCl_3)

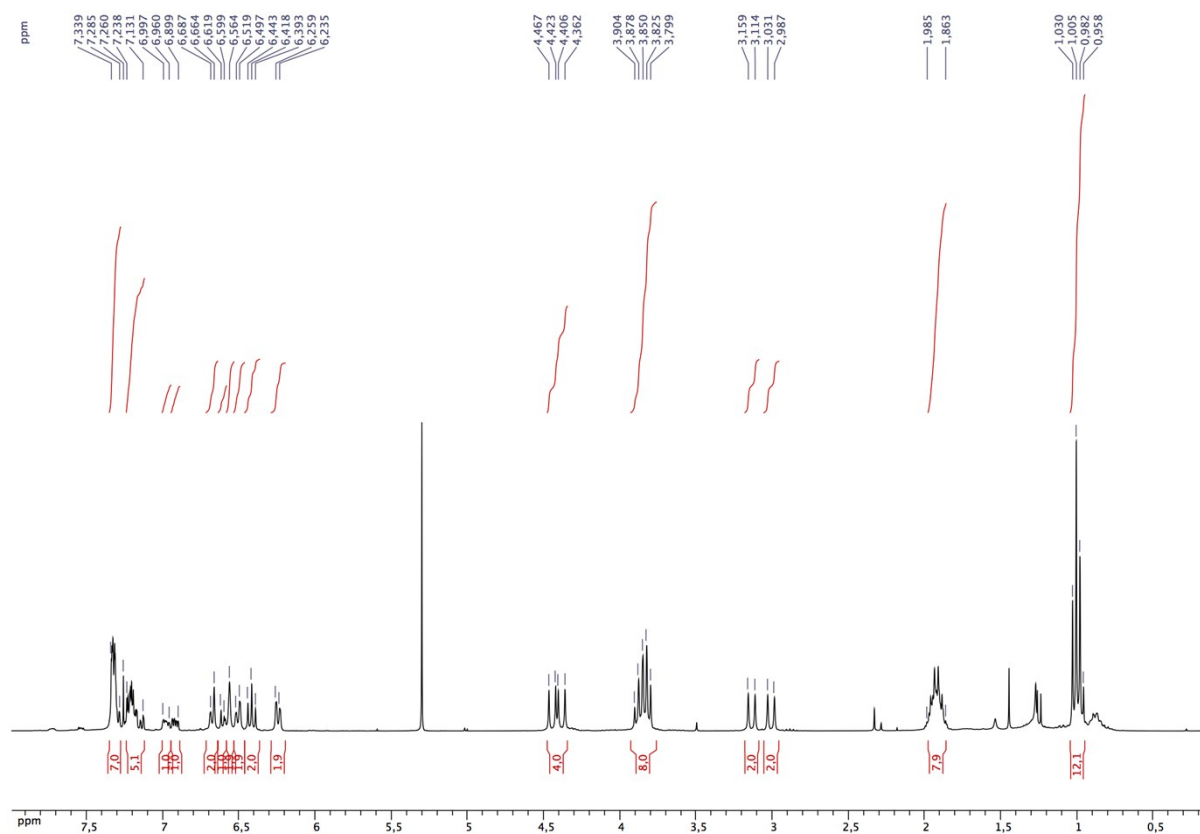
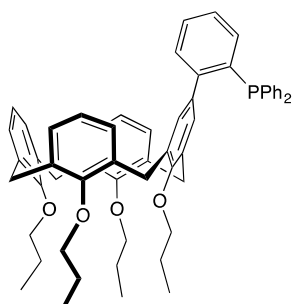


¹³C {¹H} NMR spectrum of **2** (CDCl₃)

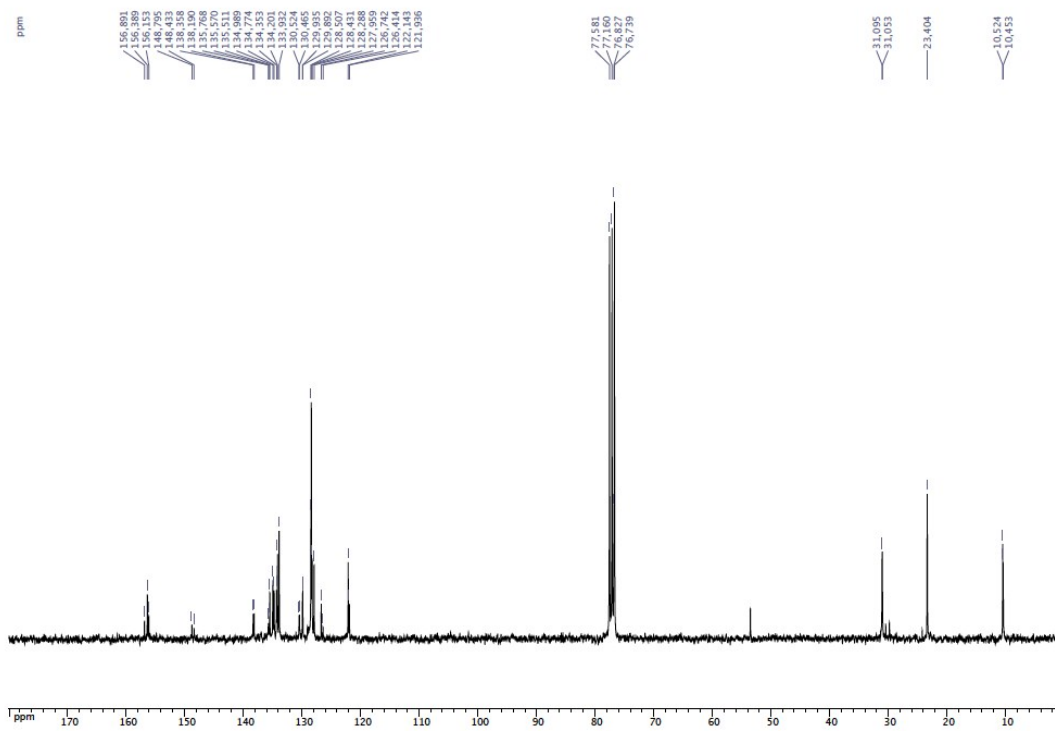


³¹P {¹H} NMR spectrum of **2** (CDCl₃)

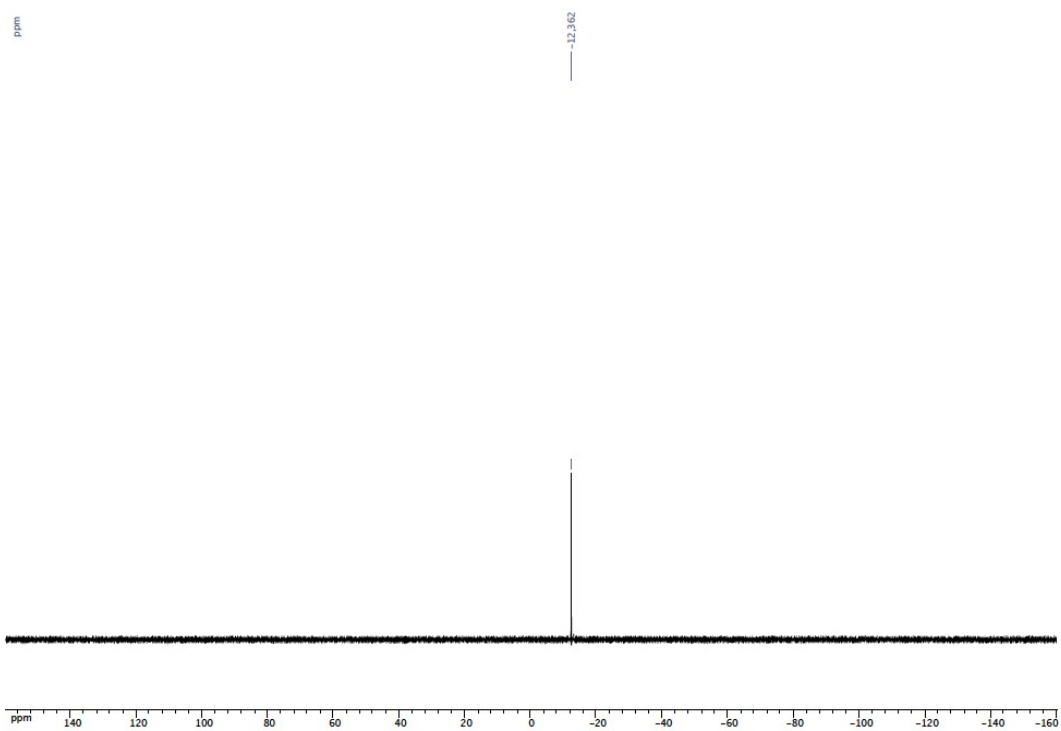
5-(2-Diphenylphosphanyl-phenyl)-25,26,27,28-tetrapropyloxycalix[4]arene (**3**)



^1H NMR spectrum of **3** (CDCl_3)

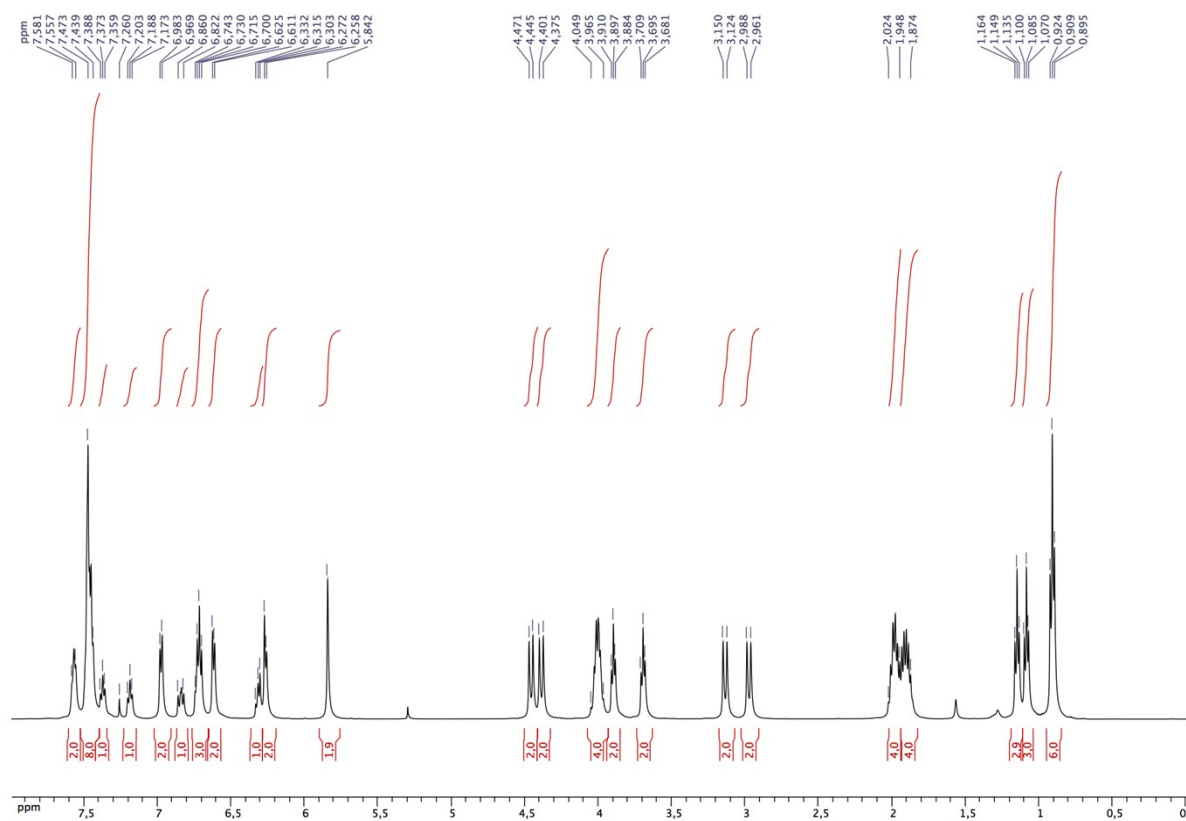
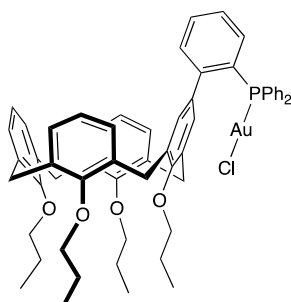


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** (CDCl₃)

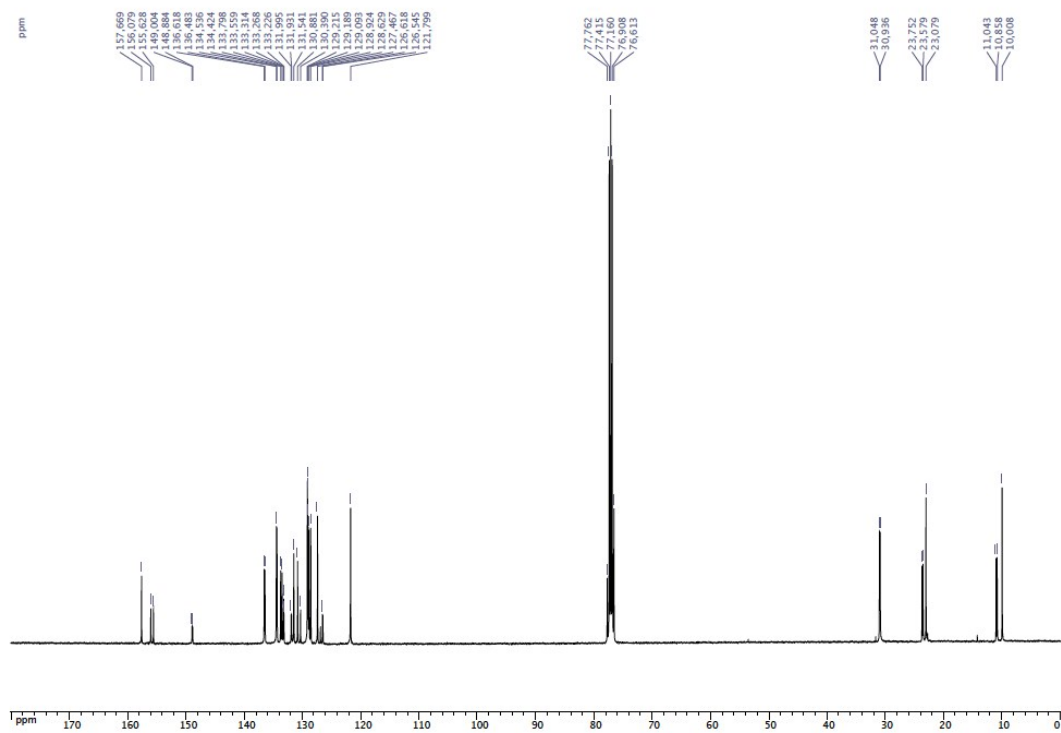


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** (CDCl₃)

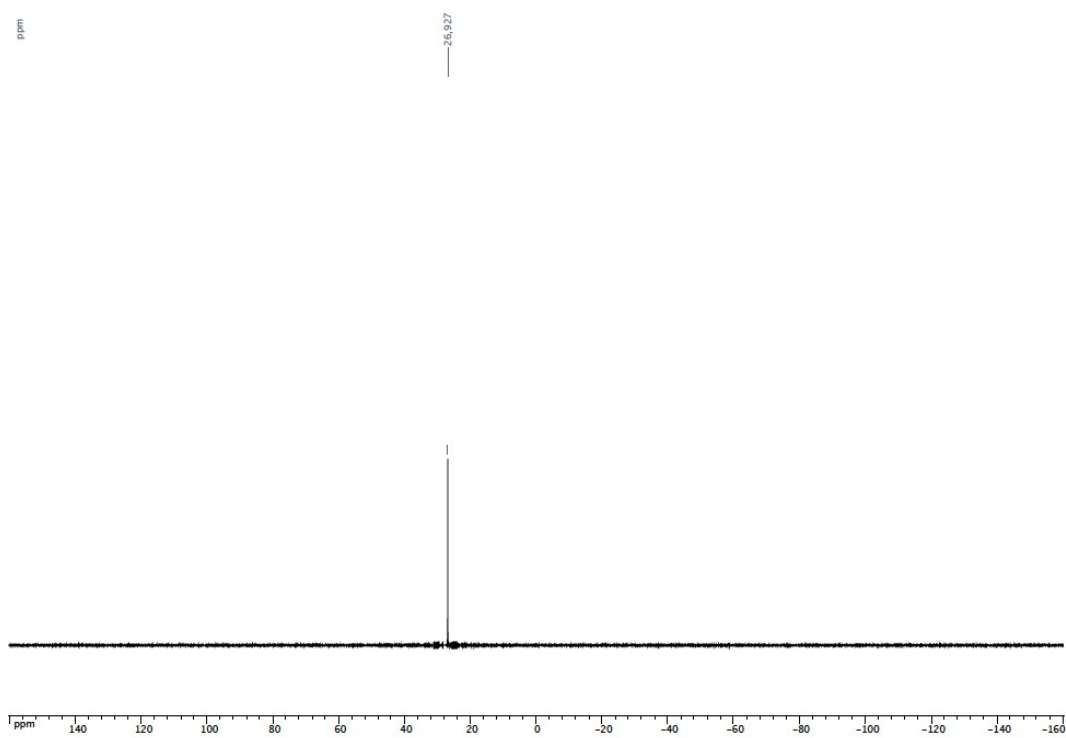
**Chlorido[5-(2-diphenylphosphanyl-phenyl)-25,26,27,28-tetrapropyloxycalix[4]arene]
gold (I) (4)**



^1H NMR spectrum of **4** (CDCl_3)

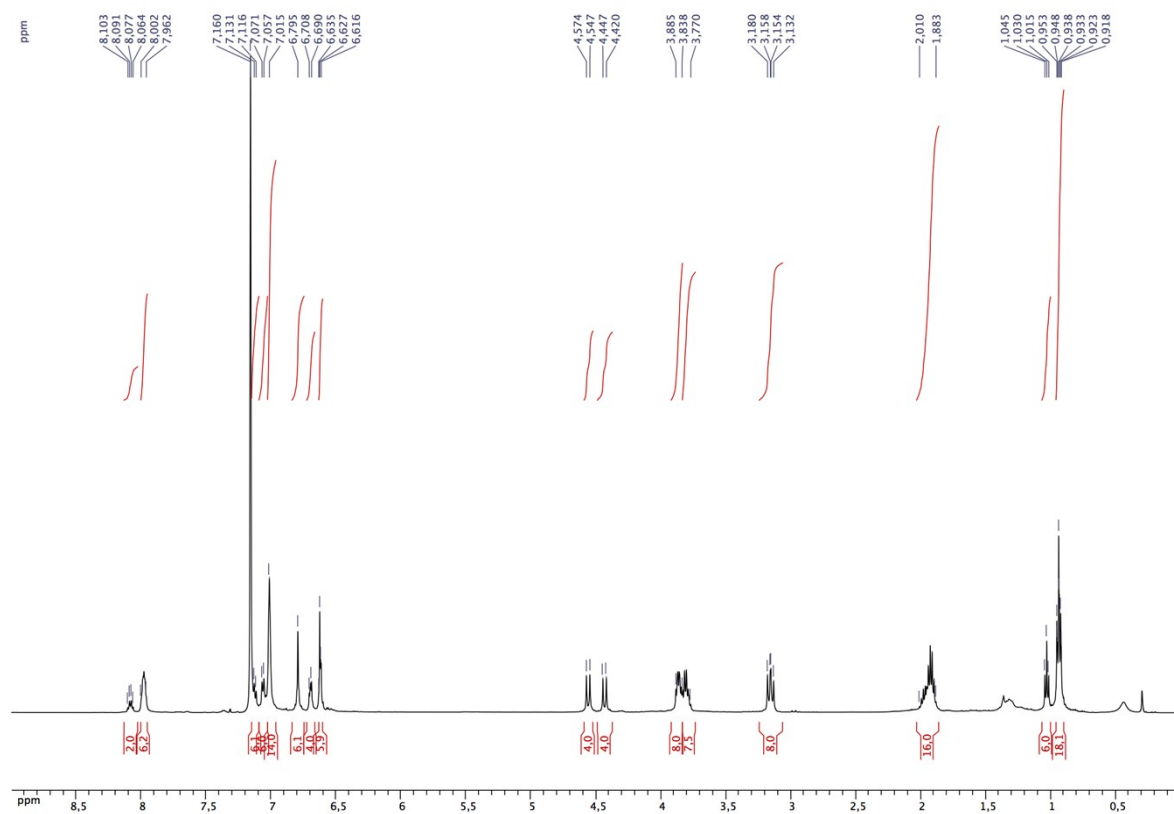
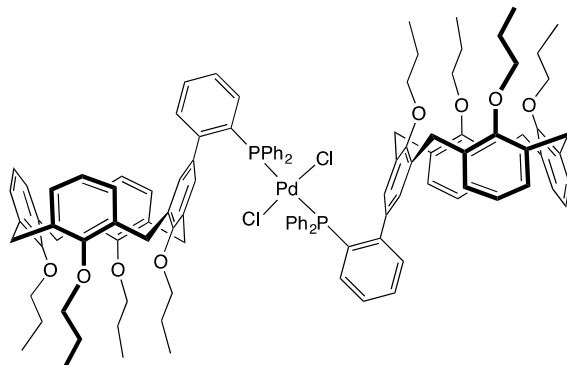


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (CDCl_3)

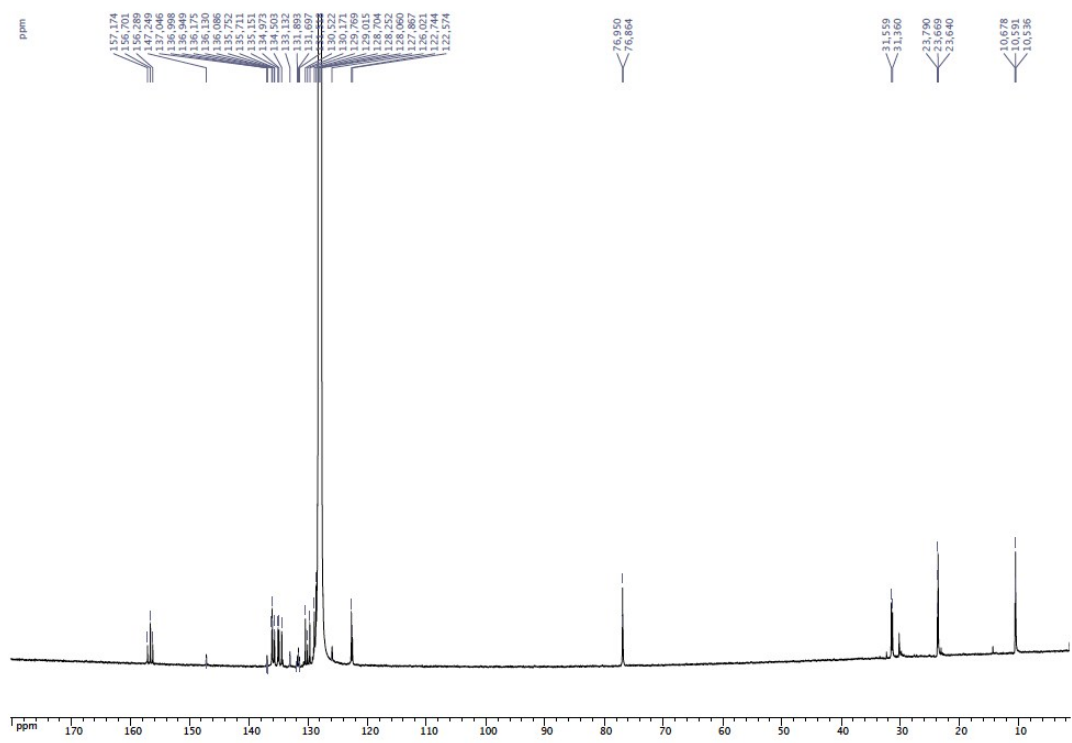


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** (CDCl_3)

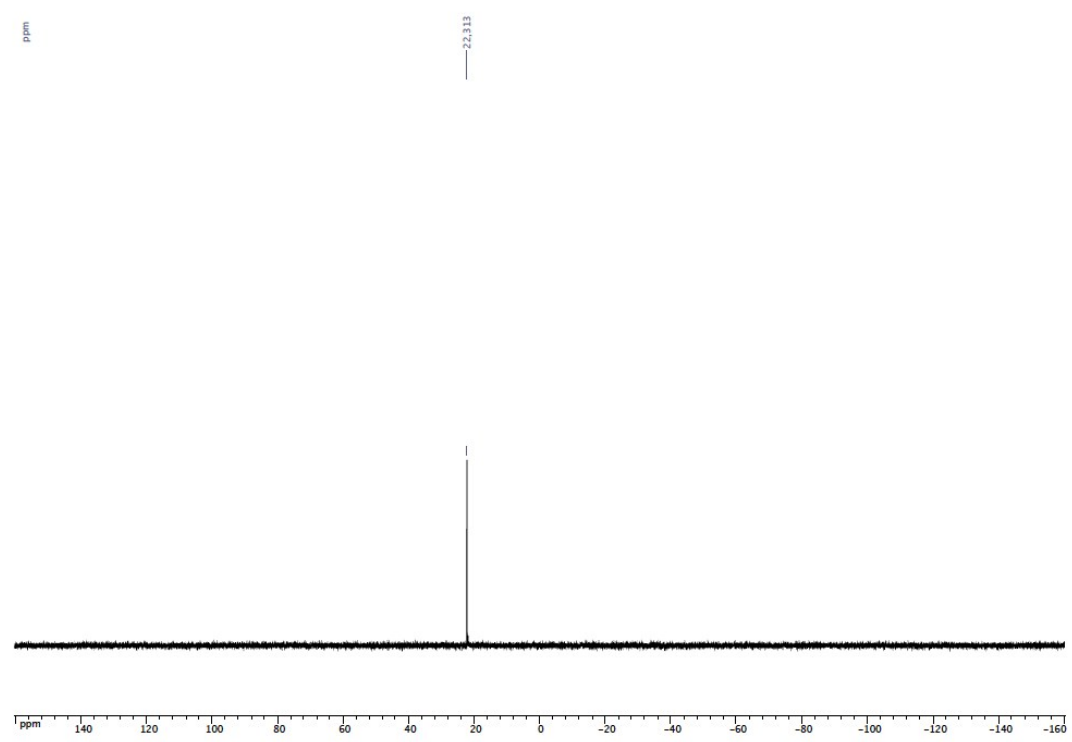
***trans-P,P*-Dichloridobis[5-(2-diphenylphosphanyl-phenyl)-25,26,27,28-tetrapropoxy-calix[4]arene]palladium (II) (**5**)**



^1H NMR spectrum of **5** (C_6D_6)

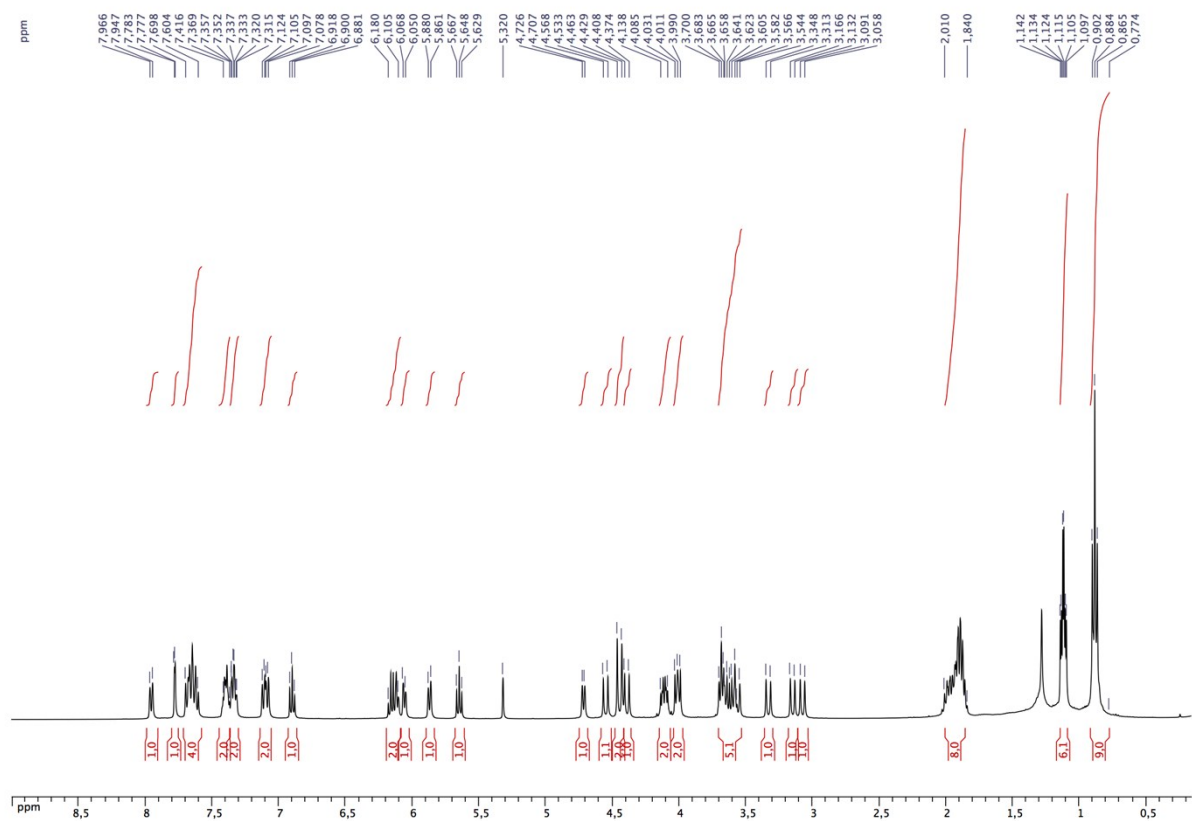
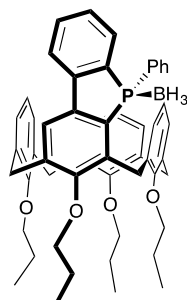


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (C_6D_6)

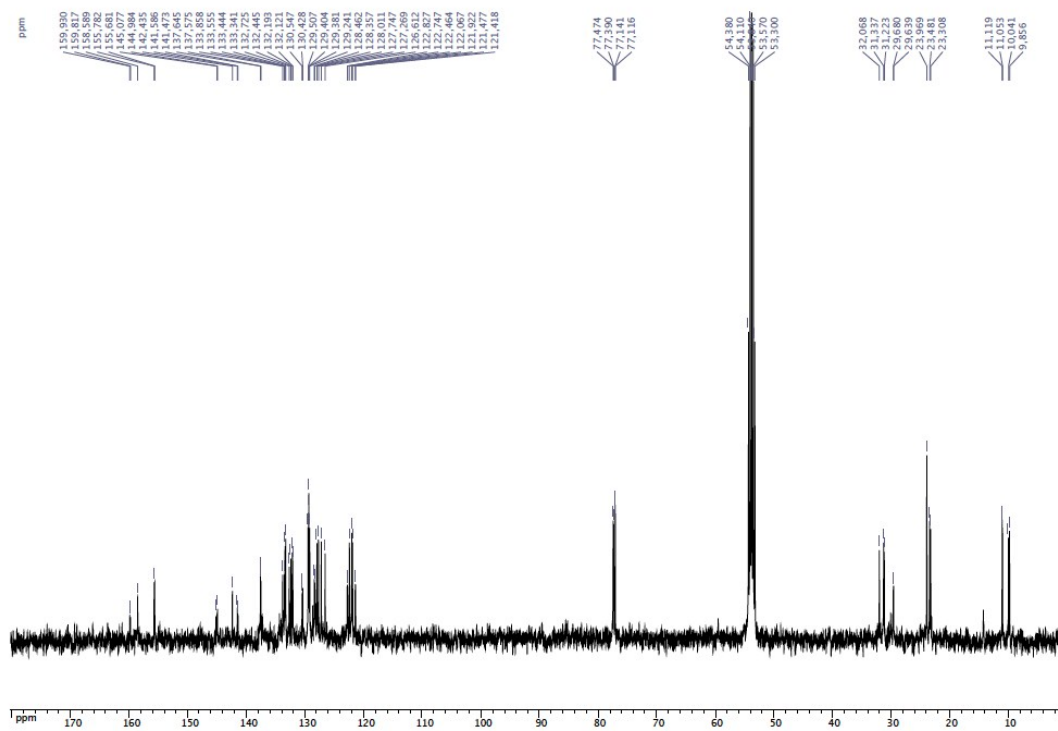


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** (C_6D_6)

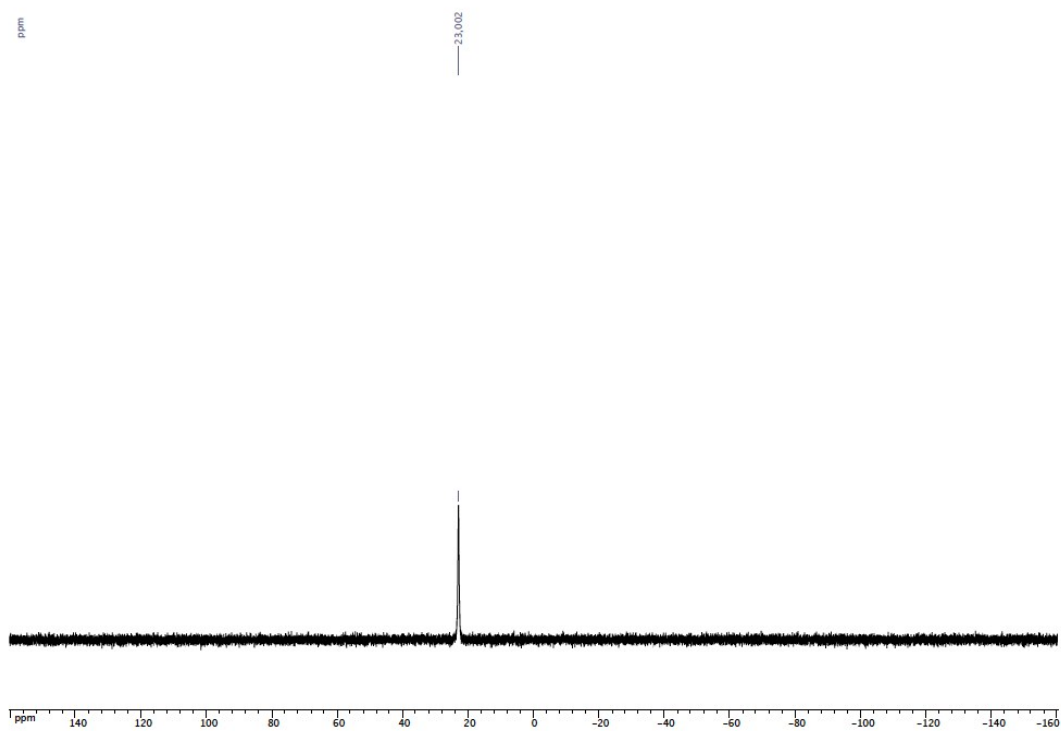
exo-benzophosphole borane **6**



¹H NMR spectrum of **6** (CD₂Cl₂)

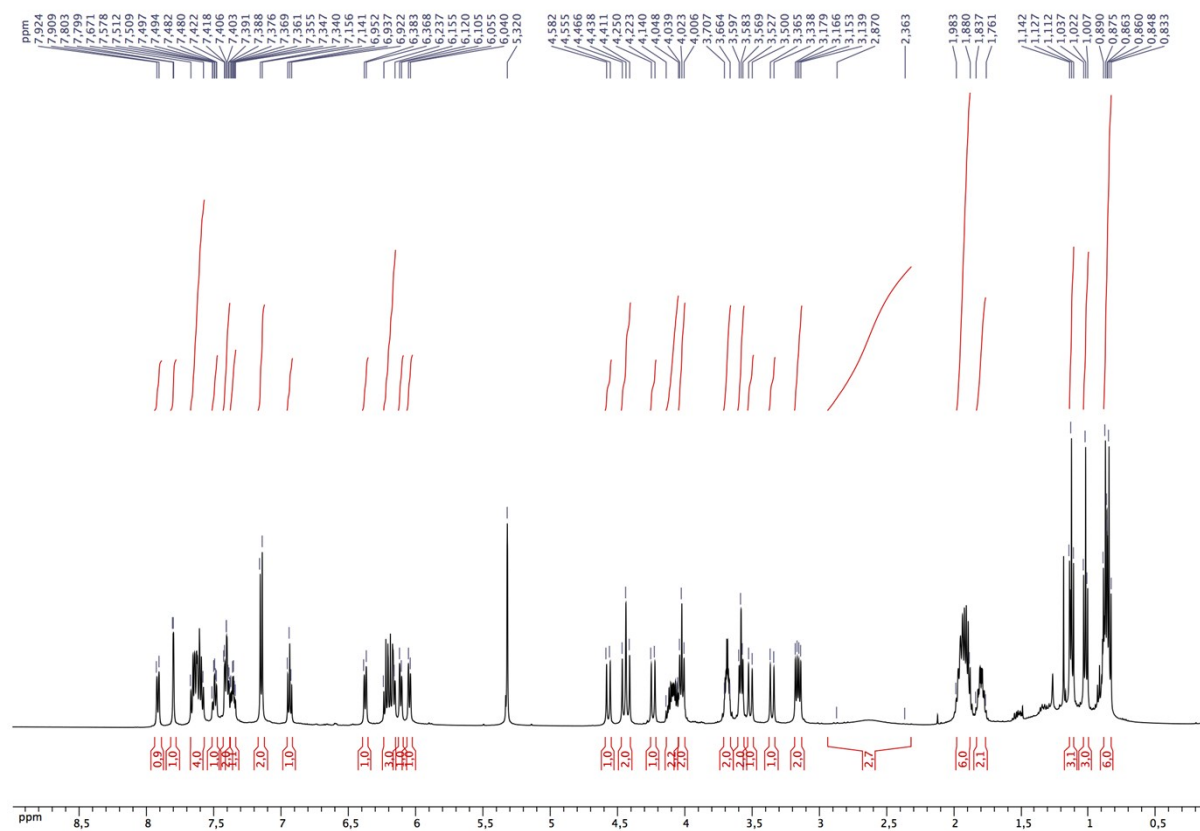
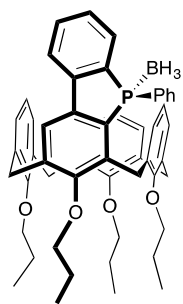


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** (CD_2Cl_2)

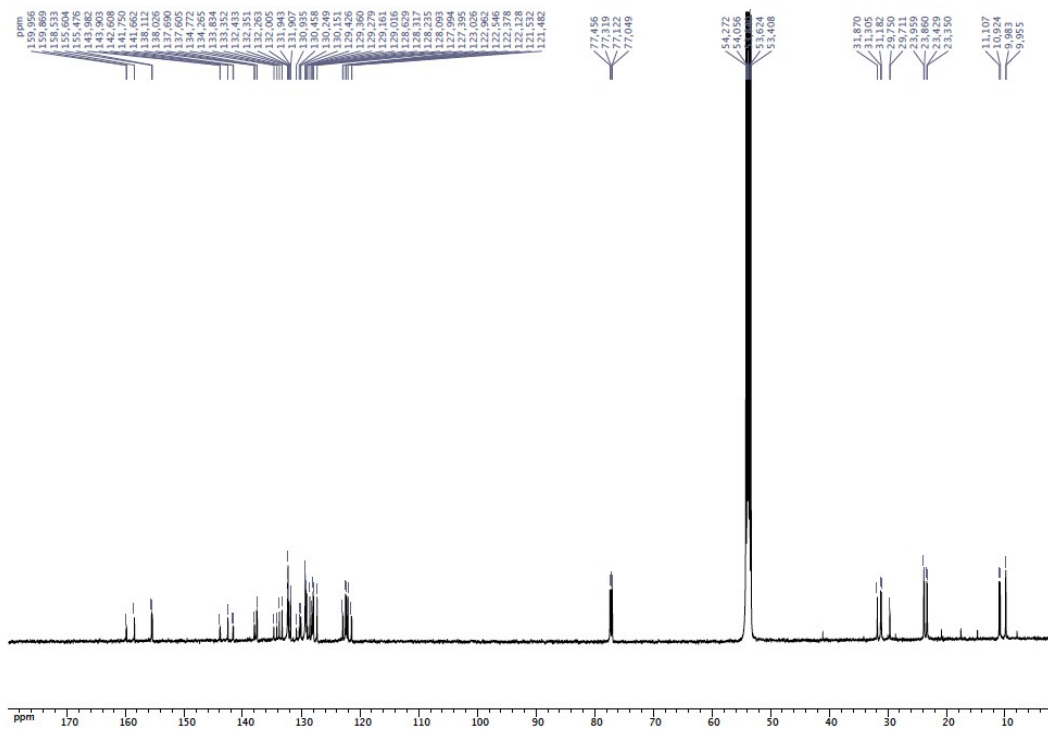


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** (CD_2Cl_2)

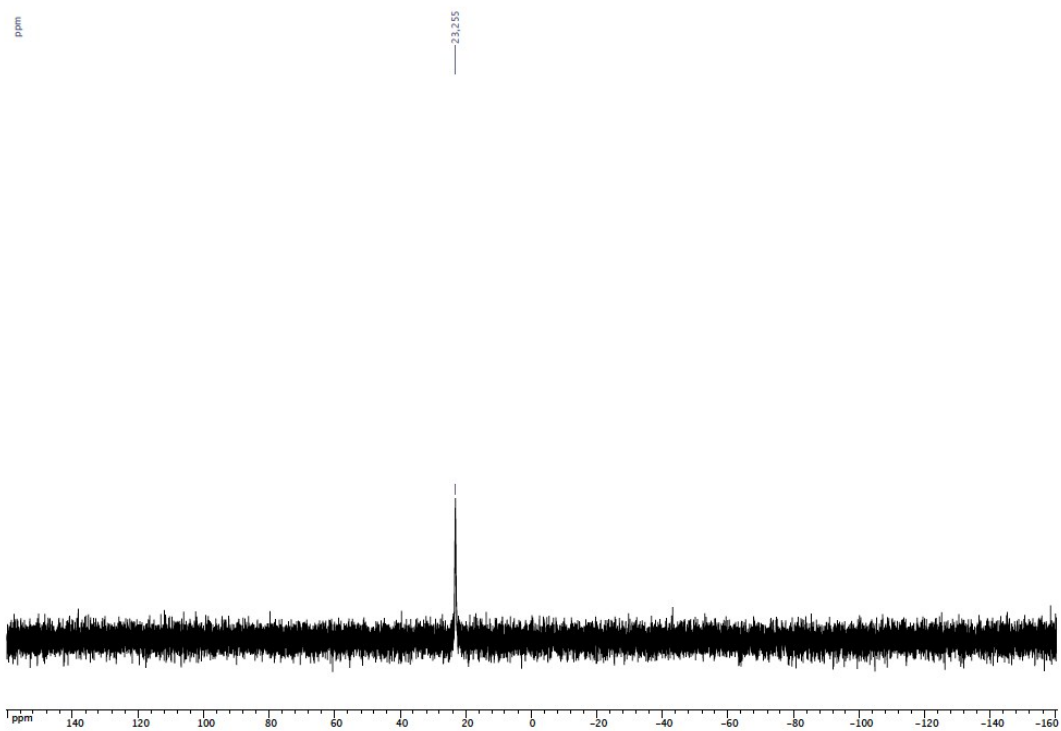
endo-benzophosphole borane **7**



^1H NMR spectrum of **7** (CD_2Cl_2)

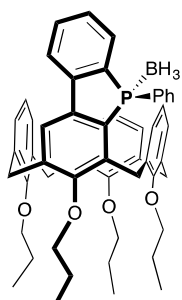


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7** (CD_2Cl_2)



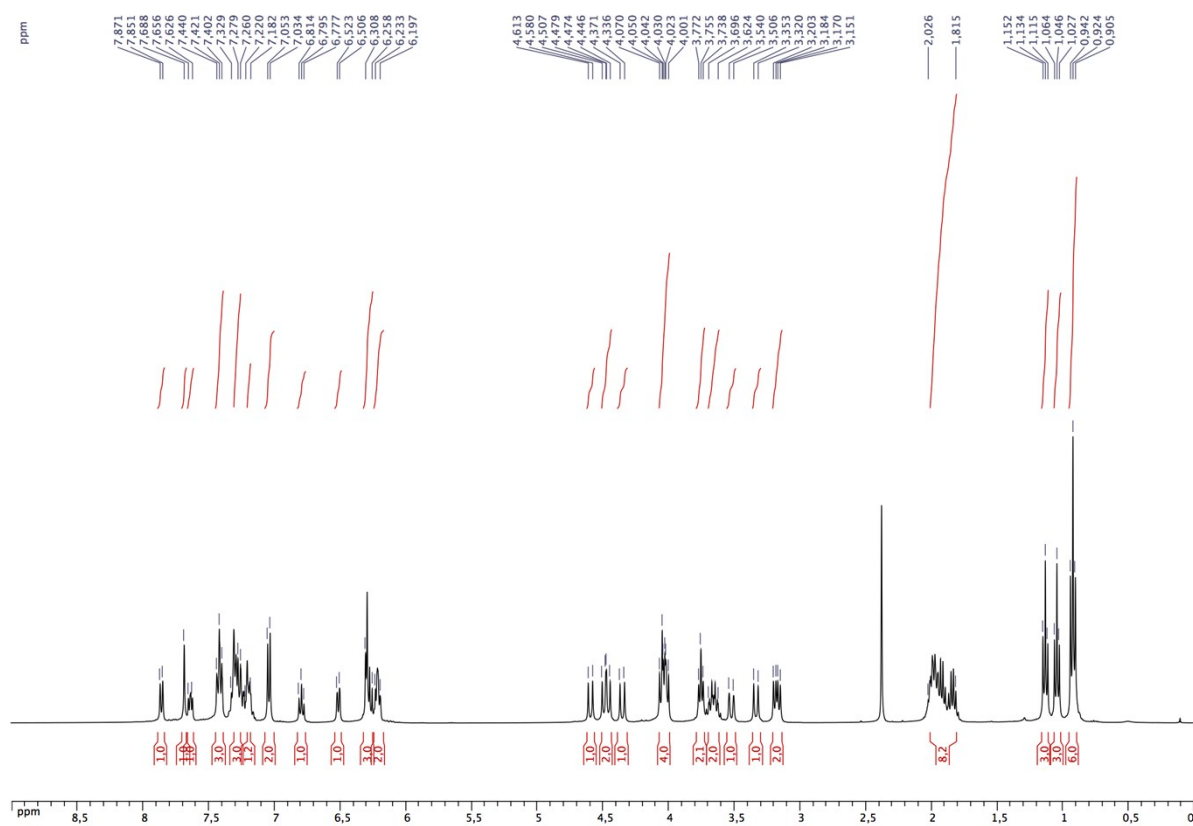
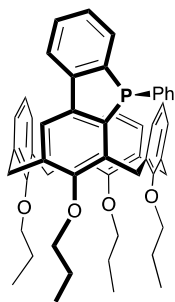
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7** (CD_2Cl_2)

endo-benzophosphole borane **7** in CH_2Cl_2 under uv lamp (365 nm)

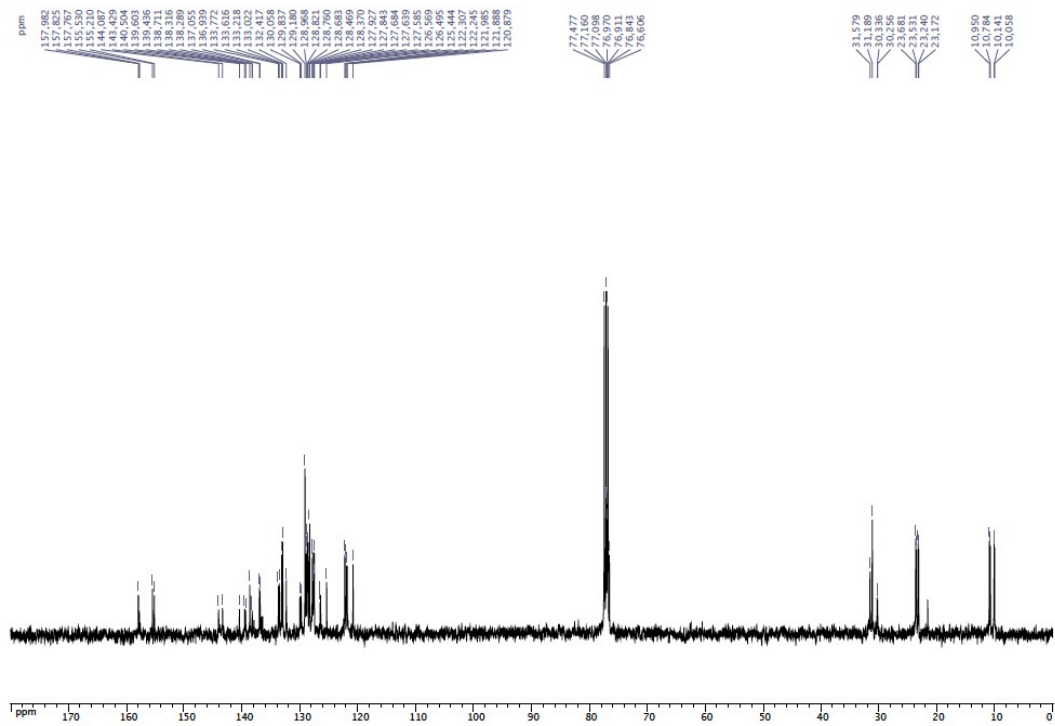


left sample: **7** in CH_2Cl_2 ; right sample: pure CH_2Cl_2

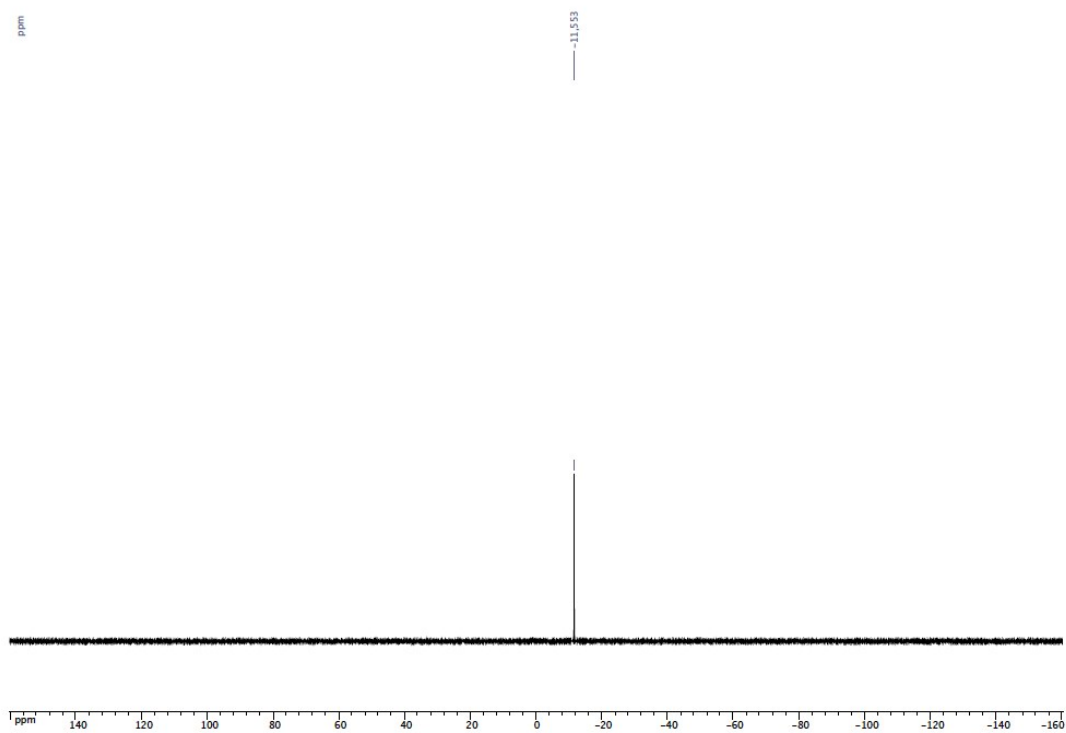
benzophosphole **8**



^1H NMR spectrum of **8** (CDCl_3)

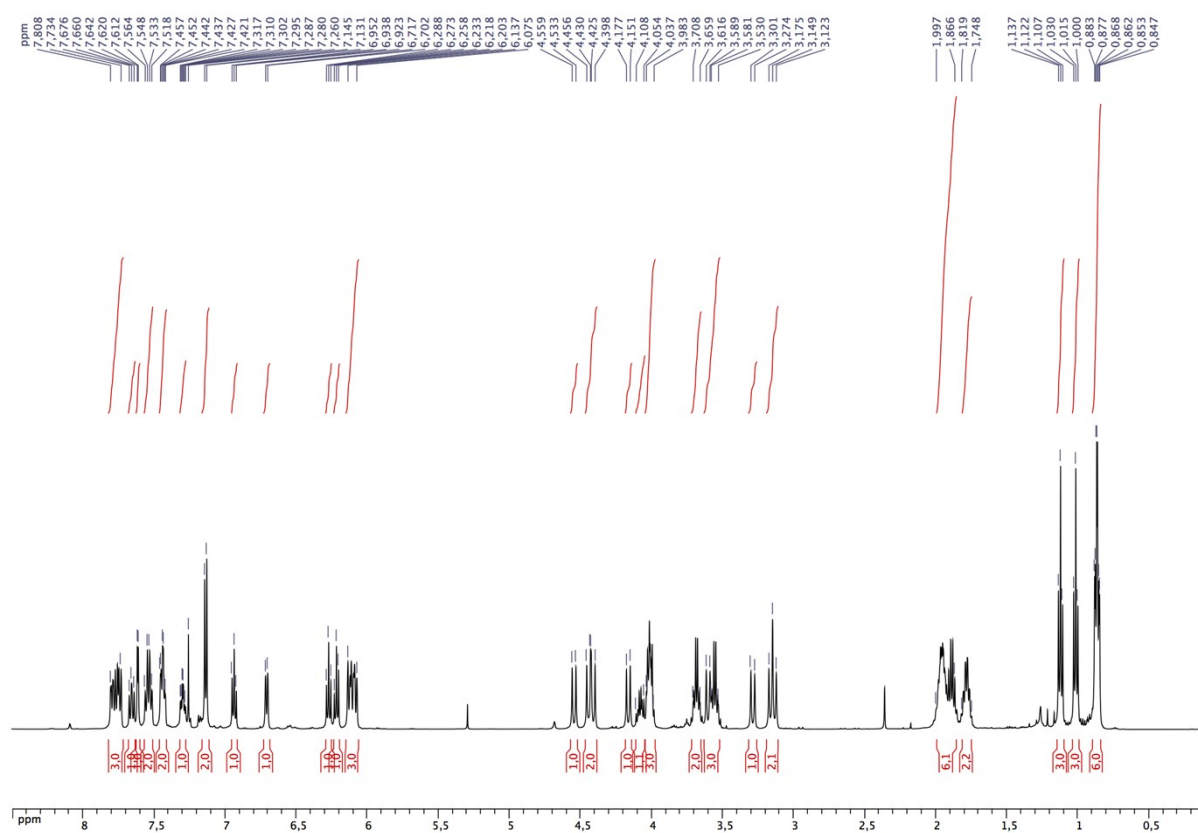
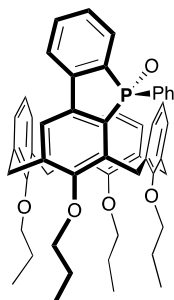


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8** (CDCl_3)

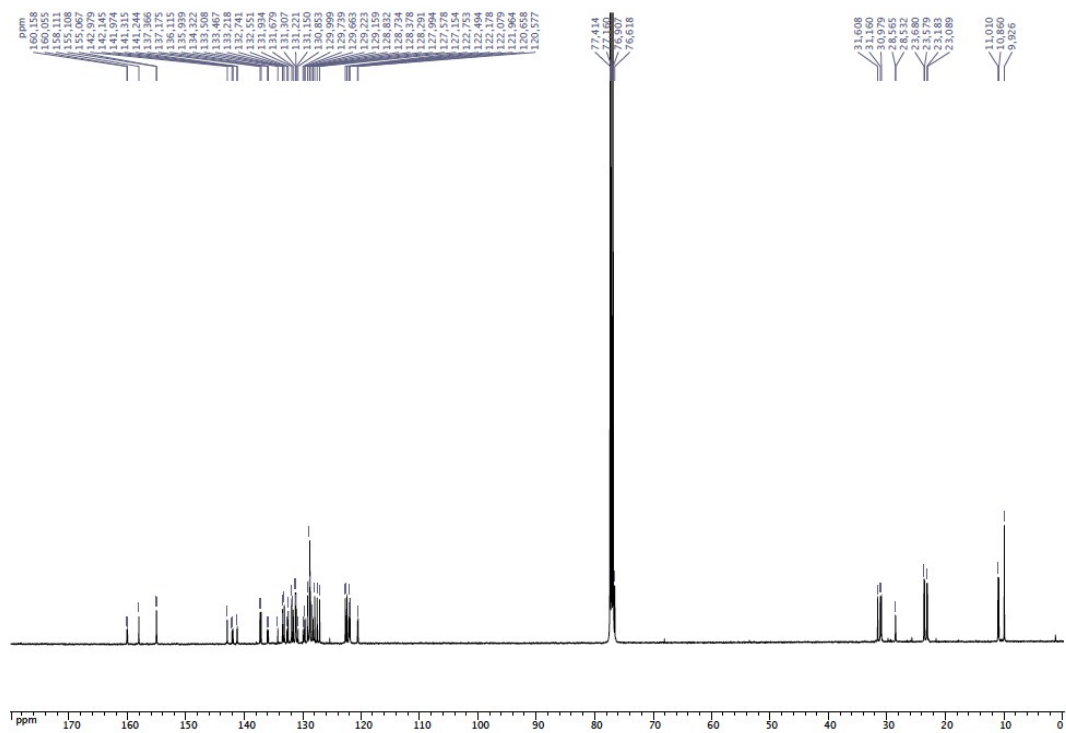


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** (CDCl_3)

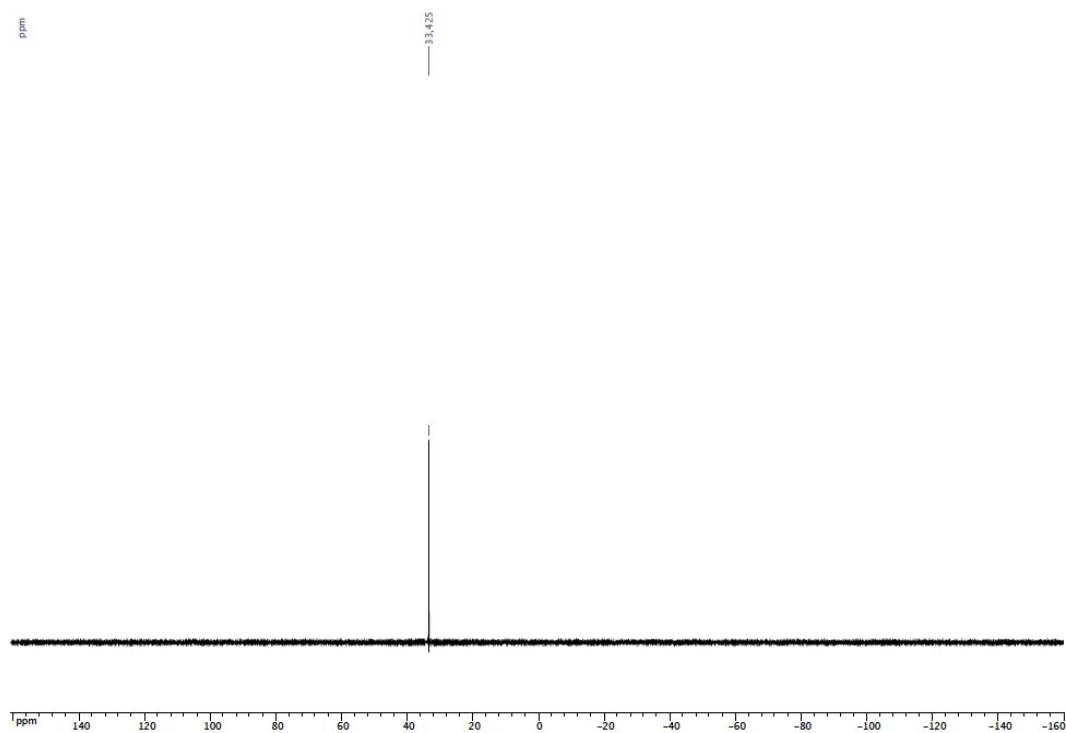
benzophosphole oxide **9**



¹H NMR spectrum of **9** (CDCl₃)

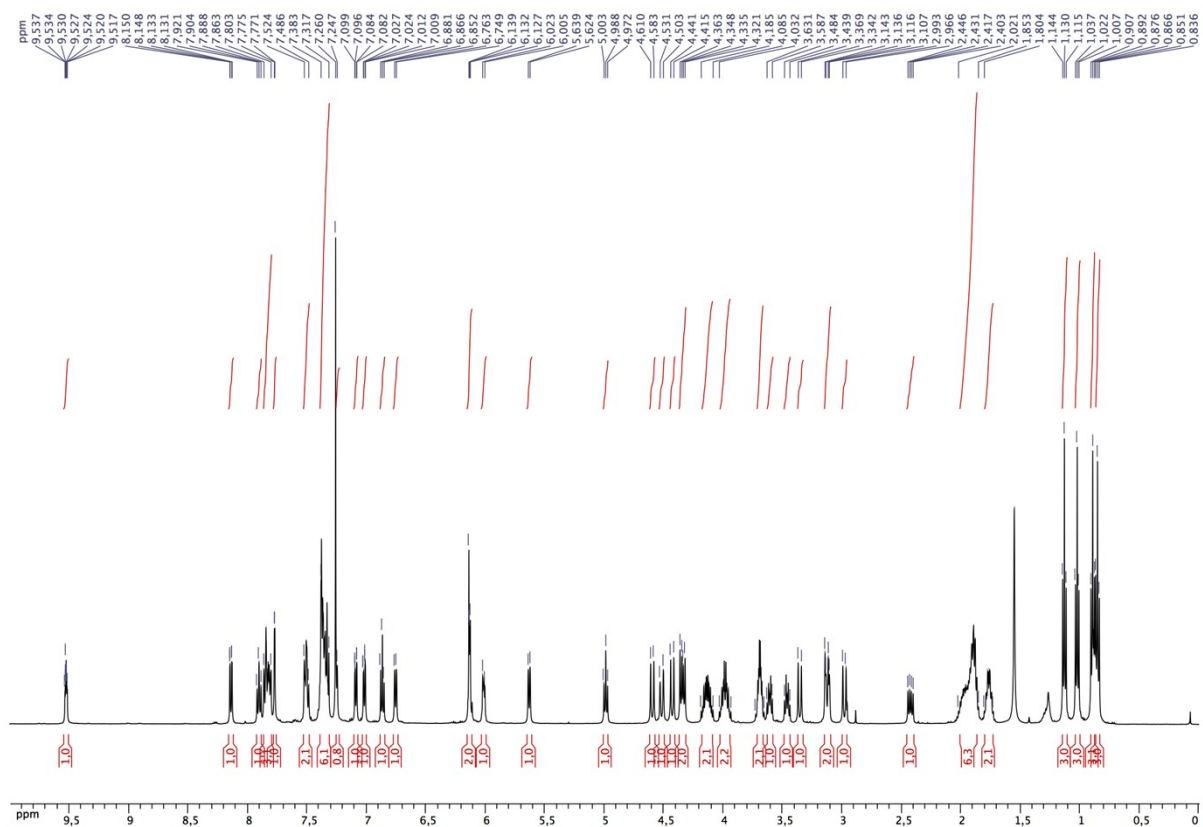
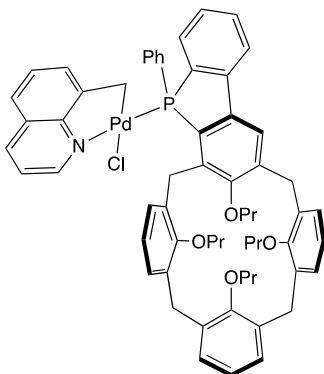


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9** (CDCl_3)

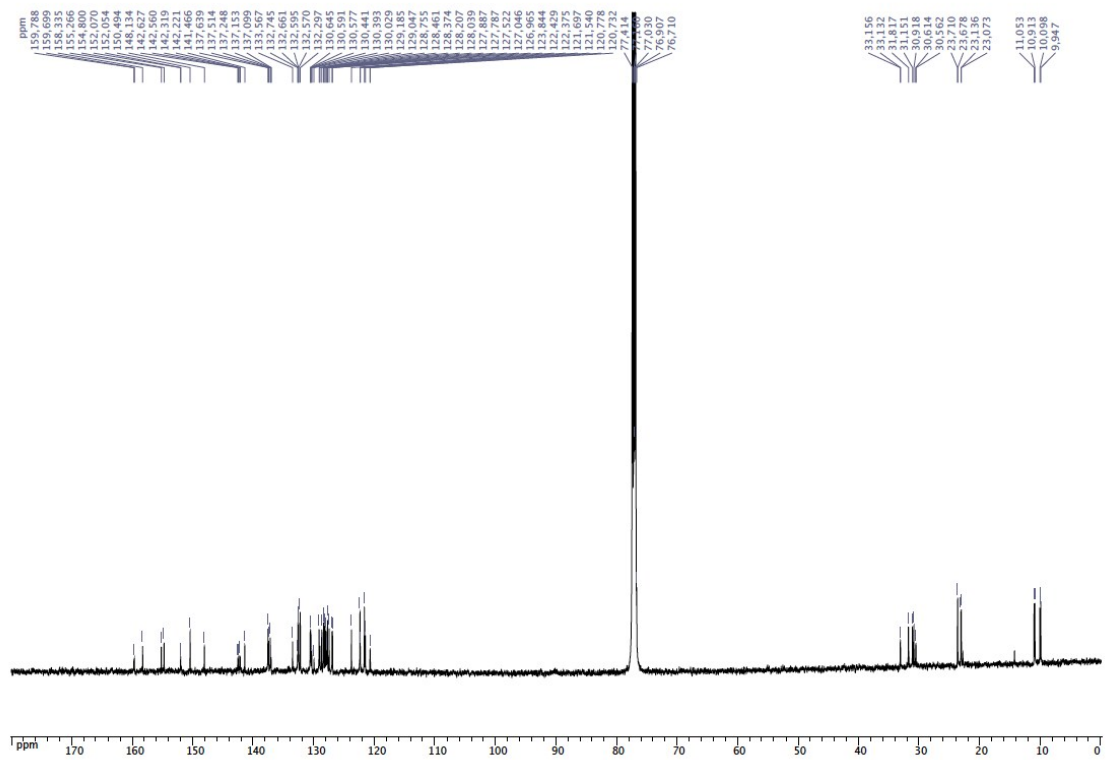


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9** (CDCl_3)

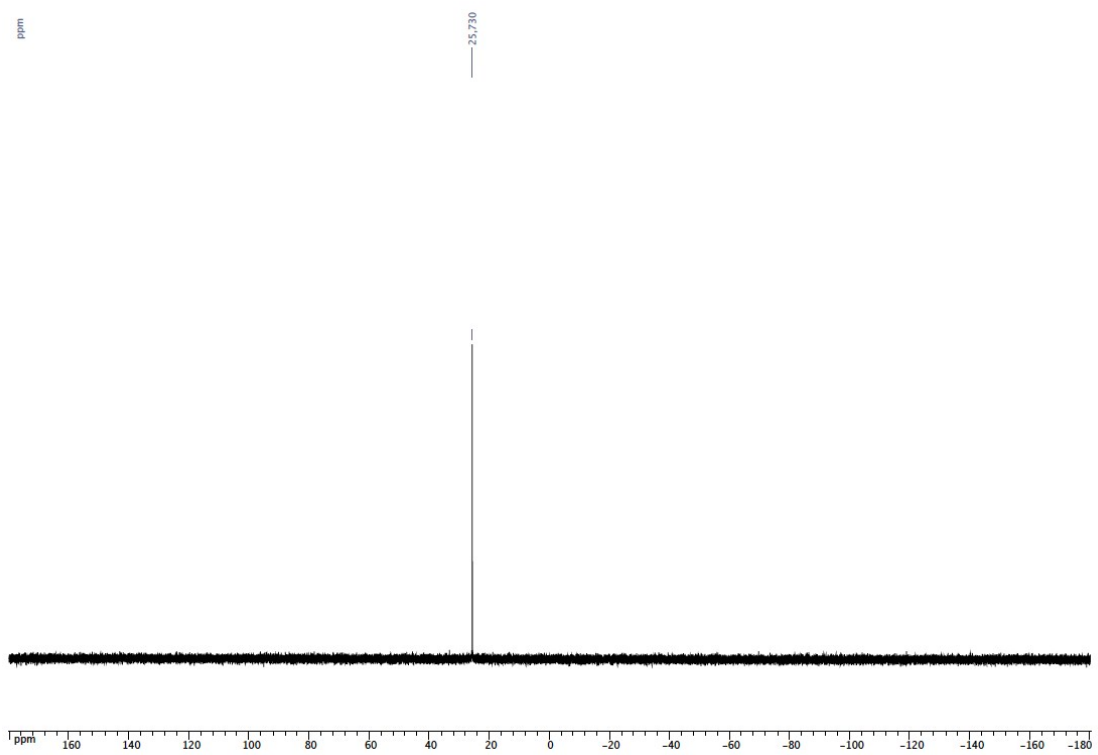
Palladium complex **10**



^1H NMR spectrum of **10** (CDCl_3)

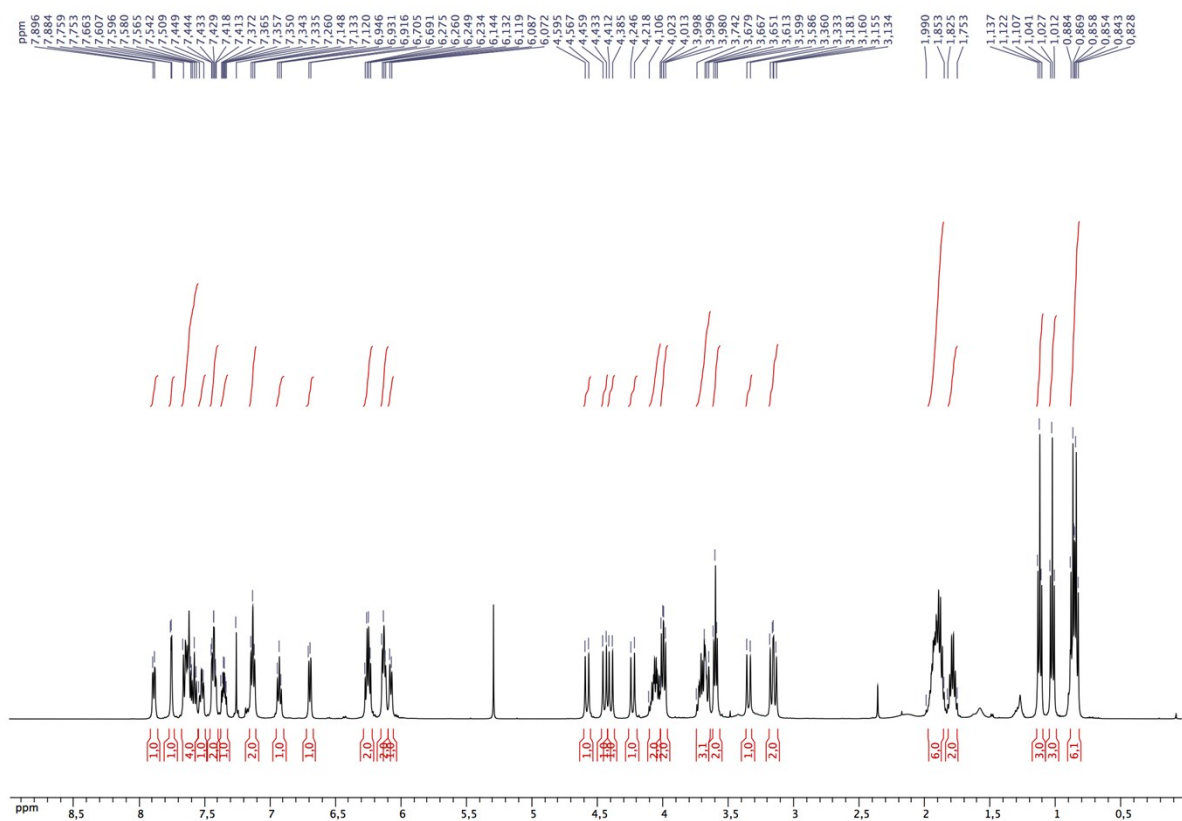
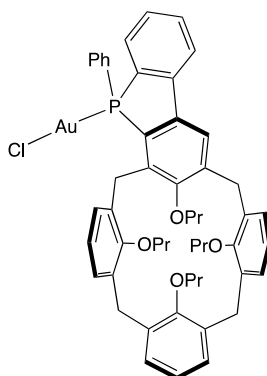


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** (CDCl_3)

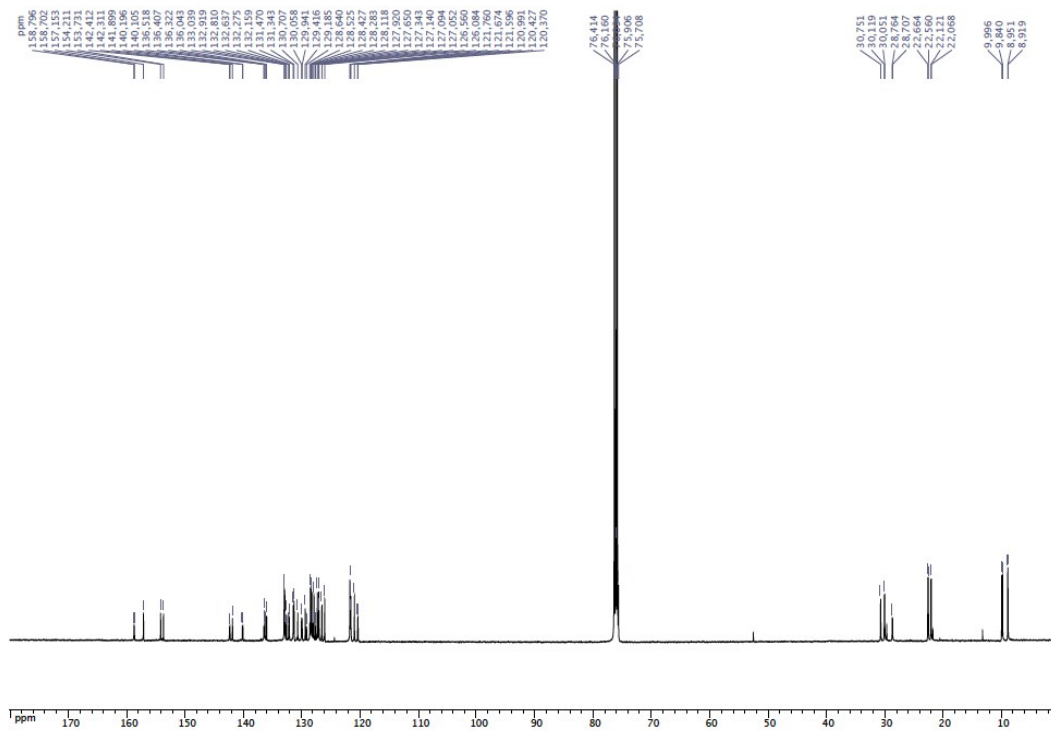


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10** (CDCl_3)

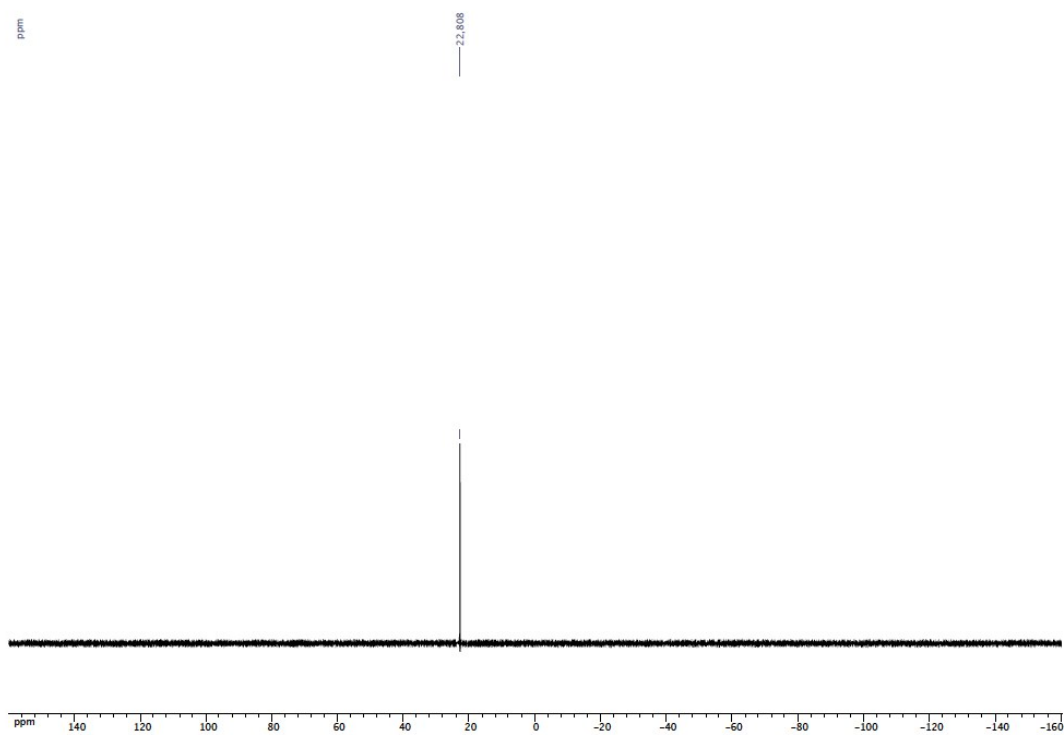
Gold complex **11**



¹H NMR spectrum of **11** (CDCl₃)

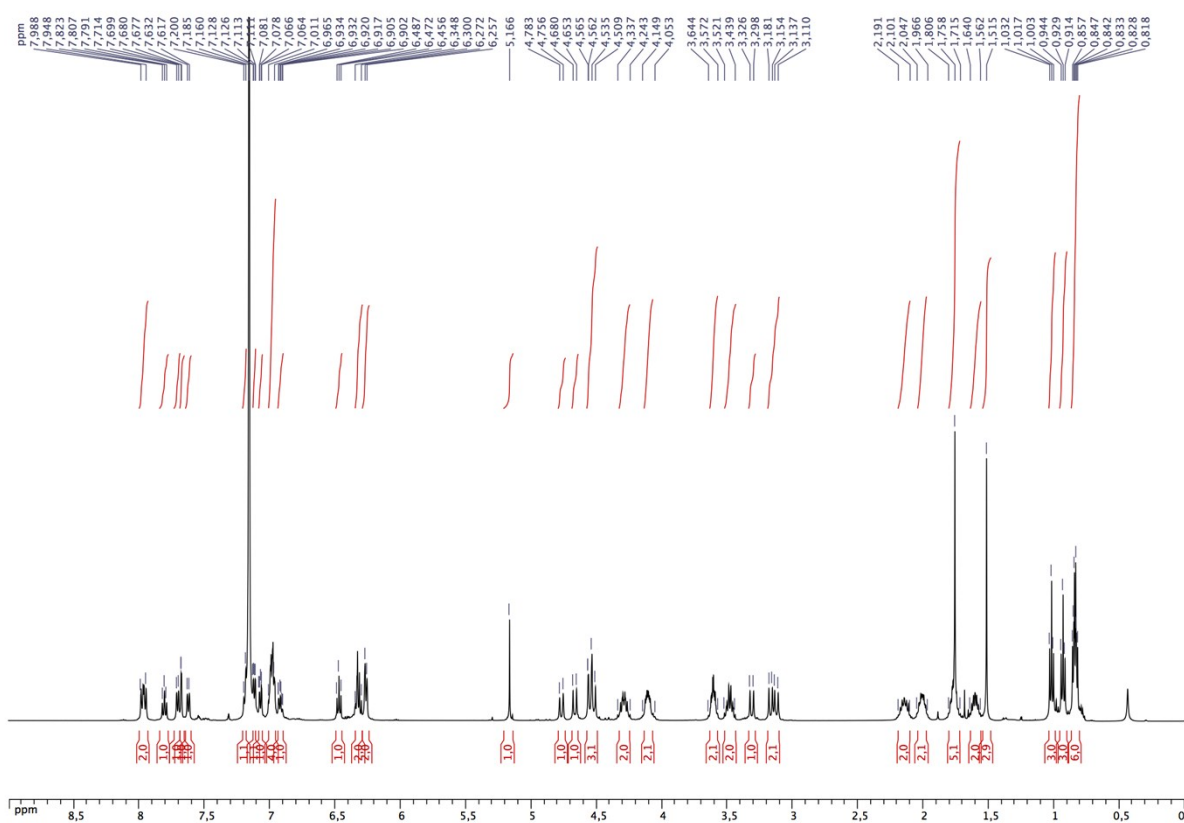
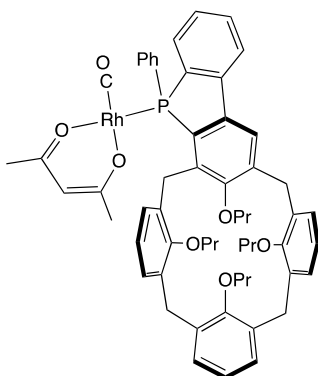


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11** (CDCl_3)

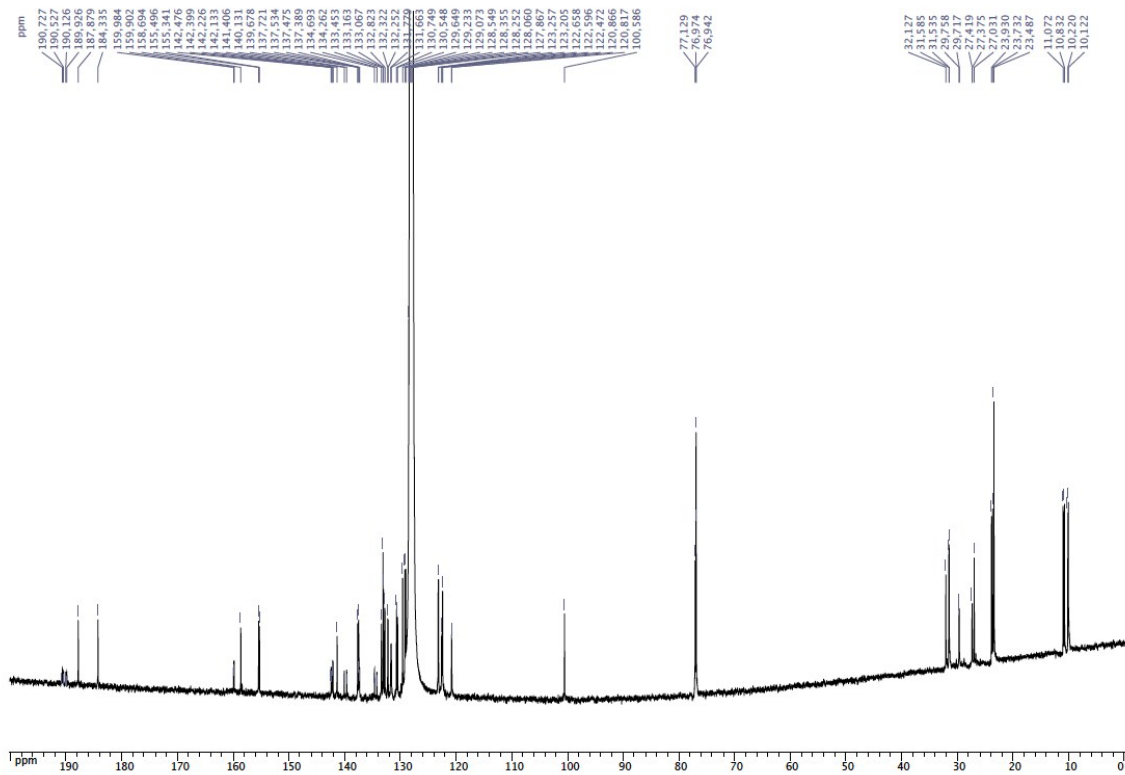


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** (CDCl_3)

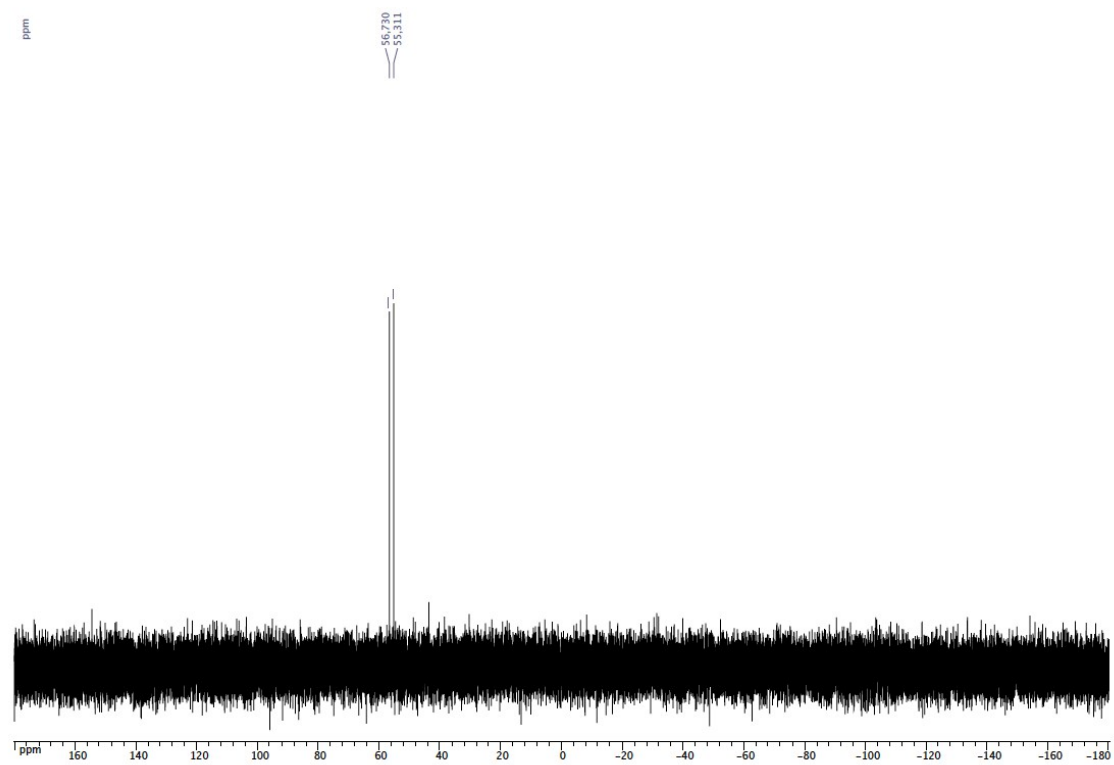
Rhodium complex **12**



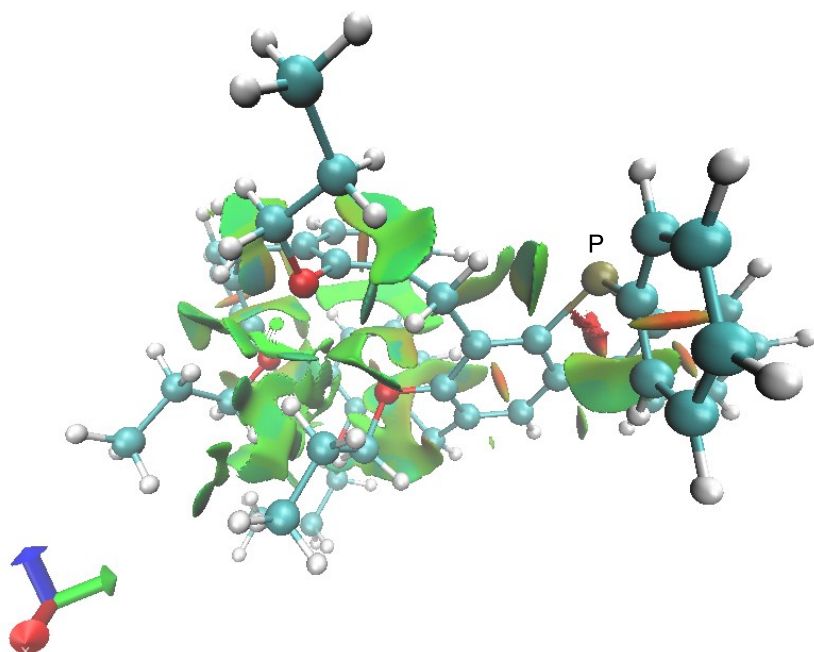
^1H NMR spectrum of **12** (C_6D_6)



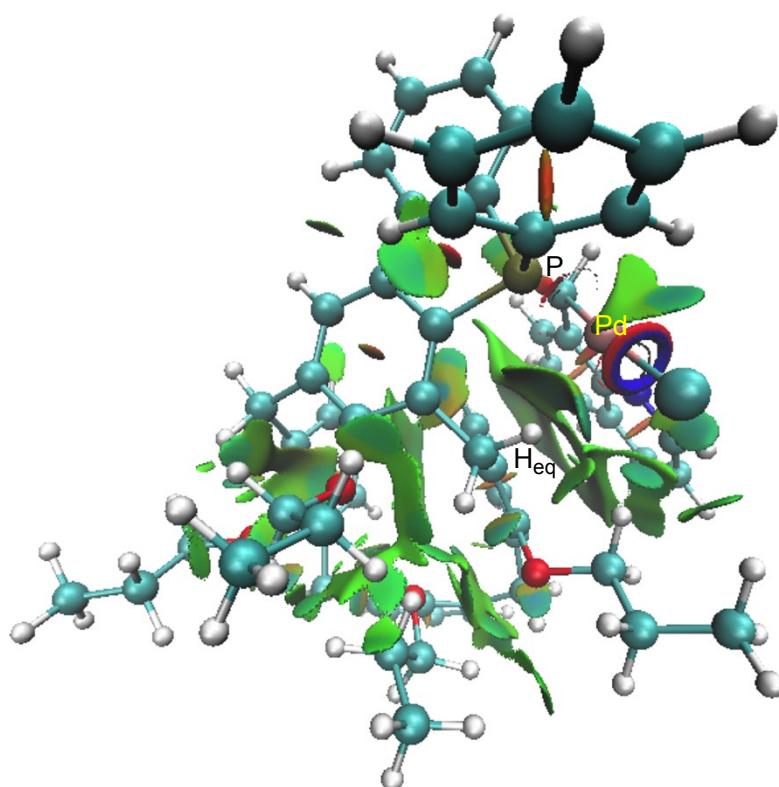
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **12** (C_6D_6)



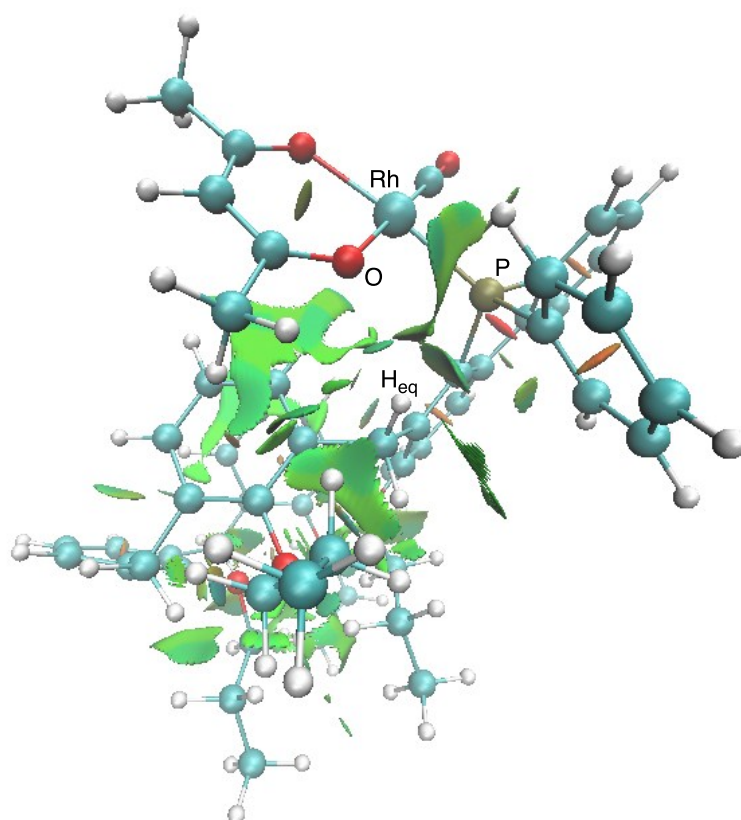
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **12** (C_6D_6)



Non covalent interactions in phosphole **8** (calculated structure)



Non covalent interactions in palladium complex **10** (calculated structure)



Non covalent interactions in rhodium complex **12** (calculated structure)

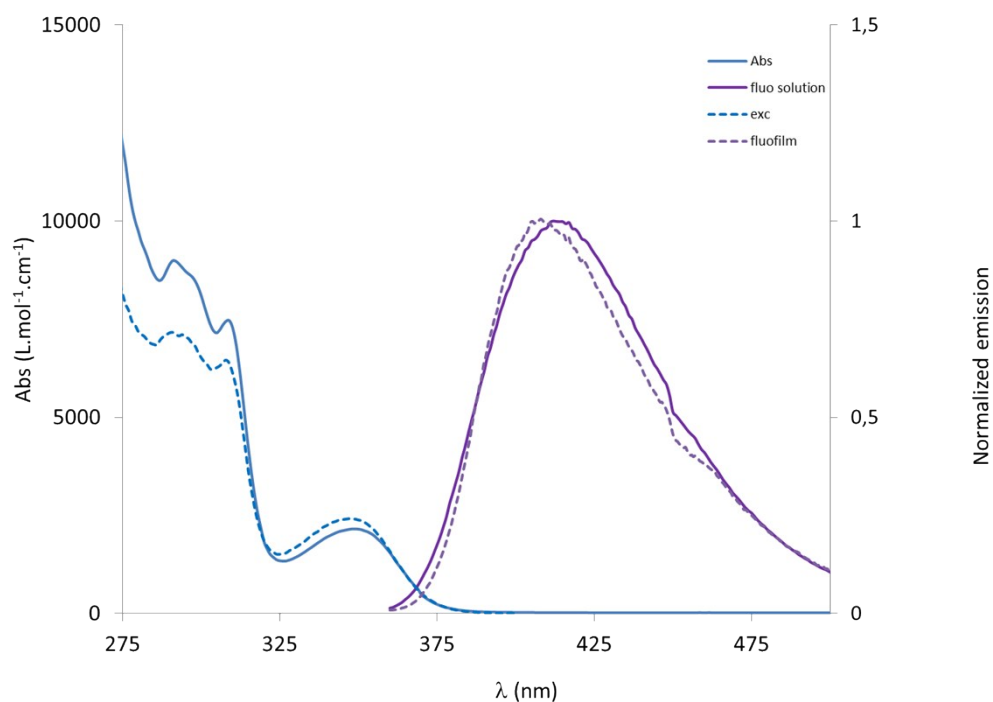


Fig S1: UV-vis absorption, excitation (dashed), solution fluorescence (in diluted DCM solution) and thin film fluorescence (dashed) of **9** in diluted DCM solution.

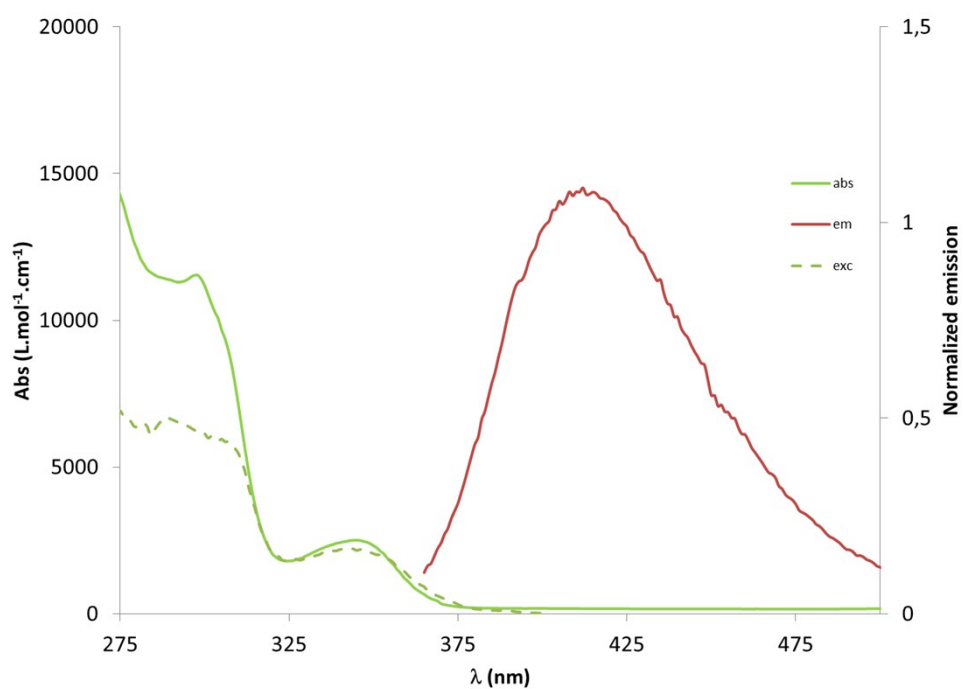


Fig S2: UV-vis absorption, excitation (dashed), solution fluorescence (dashed) of **11** (in diluted DCM solution)

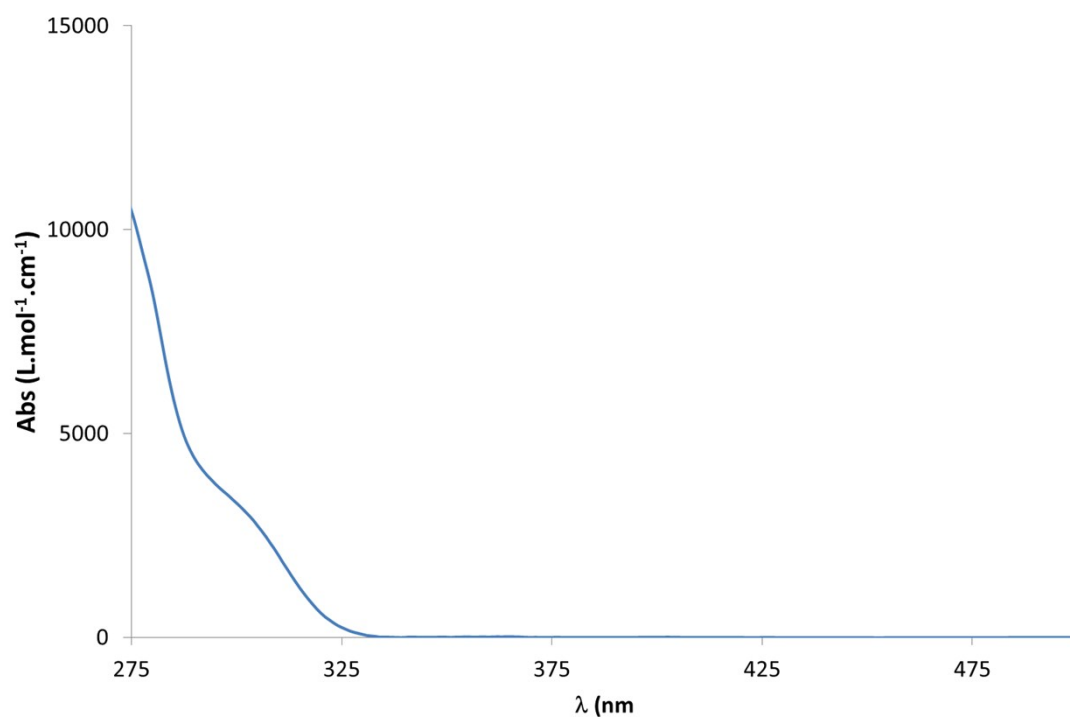


Fig S3: UV-vis absorption of **4** (in diluted DCM solution).