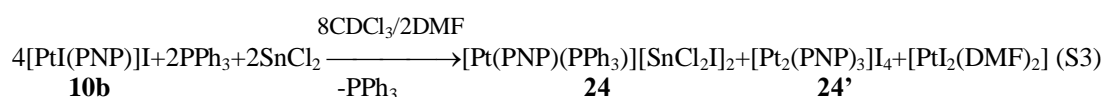
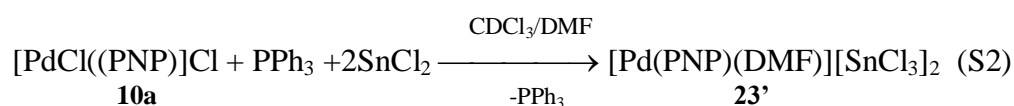
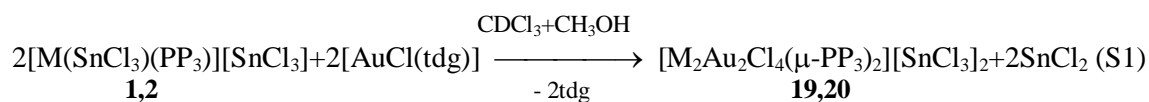


Equations Supplementary Information



Scheme and Figure Captions. Supplementary Information

Scheme S1. Labelled atoms for **9***, **9'***, **13a** and **19-22**.

Scheme S2. Proposed development of a five coordinate intermediate with M-SnX₃ bonds in the formation of (**4**, **6**: X=Br) and (**9**, **10**: X=I).

Scheme S3. Formation of ionic distorted square-planar complexes with M-SnX₃ bonds *via* trigonal bipyramidal species, starting from **14a-15a** / **16a-18a** with X₂MP₂/ XMP₃ arrangements and P-Au-X dangling arms.

Figure S1. Crystal structure for **6a'**-cation (top) and comparative crystal packing for **6a'** (middle) and **4a** (bottom).

Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR (r.t.) for **2** (bottom) and **2+ 1 eq [AuCl(tdg)]** (top) in $\text{CDCl}_3+\text{CH}_3\text{OH}$.

Figure S3. Titration (r.t.) of $[\text{PtCl}(\text{PP}_2\text{PO})]\text{Cl}$ (**11a**) with SnCl_2 in $\text{CDCl}_3 + \text{CD}_3\text{OD}$ followed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

Figure S4. Titration (r.t.) of $[\text{PtCl}(\text{PP}_2\text{PO})]\text{Cl}$ (**11a**) with SnPh_2Cl_2 in $\text{CDCl}_3 + \text{CD}_3\text{OD}$ followed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

Figure S5.Crystal packing for **13a**· $(\text{CH}_3)_2\text{SO}$ · $5.5\text{H}_2\text{O}$ (top) and $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum (r.t.) for **13a**· $3\text{CH}_2\text{Cl}_2$ in DMSO-d_6 (bottom).

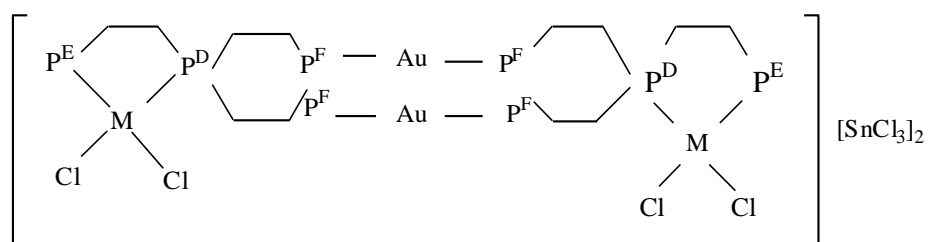
Figure S6. $^{31}\text{P}\{^1\text{H}\}$ NMR (r.t.) for **9a** (bottom) and **9a+2PPh₃+4SnI₂+O₂** (top) in CDCl_3 .

Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR (r.t.) for **15a+PPh₃+3SnBr₂** in CDCl_3 giving **15+15***

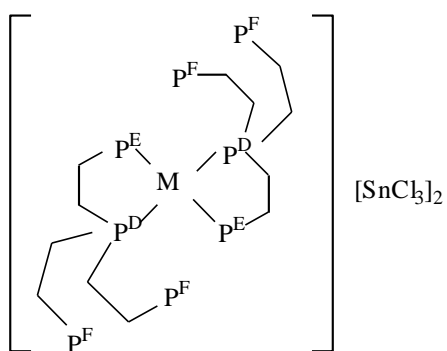
Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR (r.t.) for **10a+PPh₃+2SnCl₂** in CDCl_3 giving **23** in coexistence with free PPh_3 .

Figure S9. $^{31}\text{P}\{^1\text{H}\}$ NMR (r.t.) for **10a+PPh₃+2SnCl₂** (top) and **10b+PPh₃+2SnCl₂** (bottom) in CDCl_3+DMF giving **23'** and (**24** [$\text{P}^{\text{A}}(\cdot)$ and $\text{P}^{\text{G}}(\text{x})$] +**24'** [$\text{P}^{\text{A}}(*)$ and $\text{P}^{\text{B}}(+)$]), respectively, coexisting with free PPh_3 .

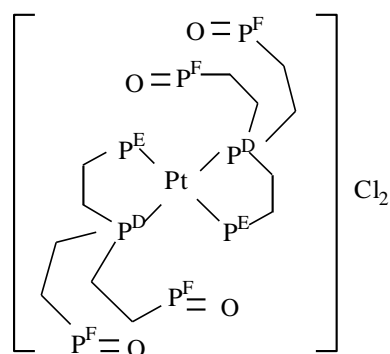
Scheme S1



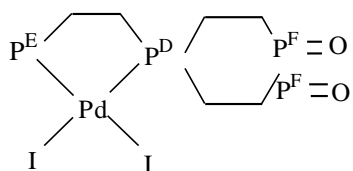
19, 20



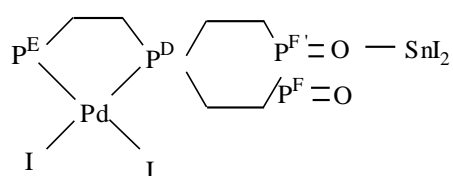
21, 22



13a

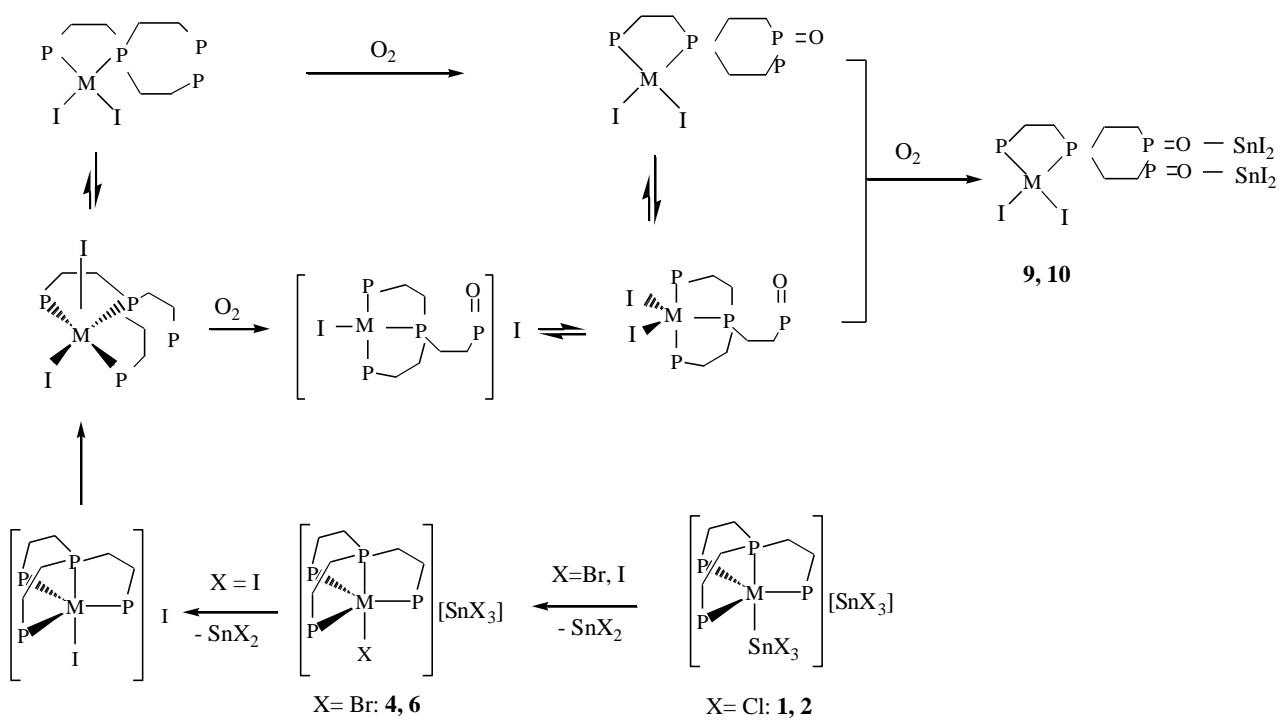


9*

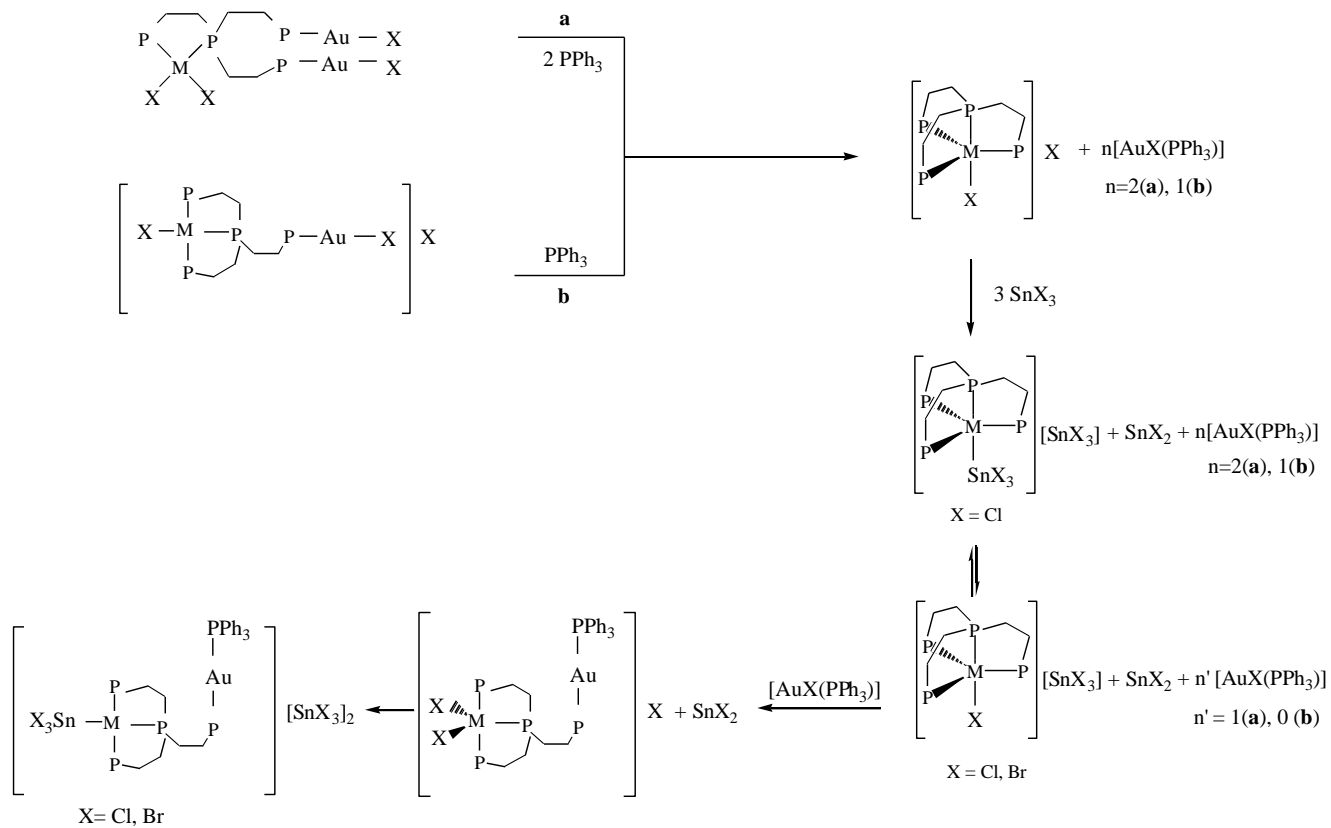


9'*

Scheme S2



Scheme S3



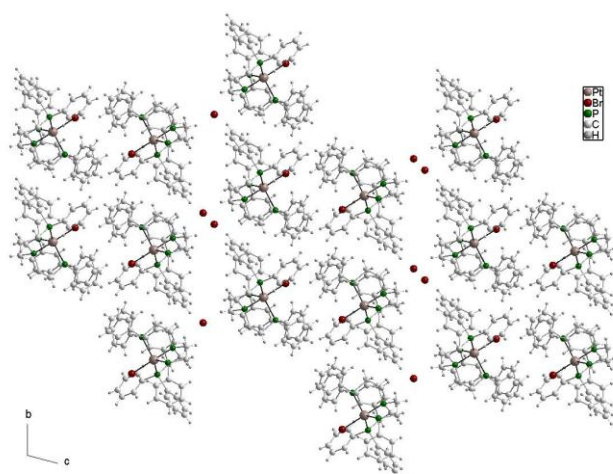
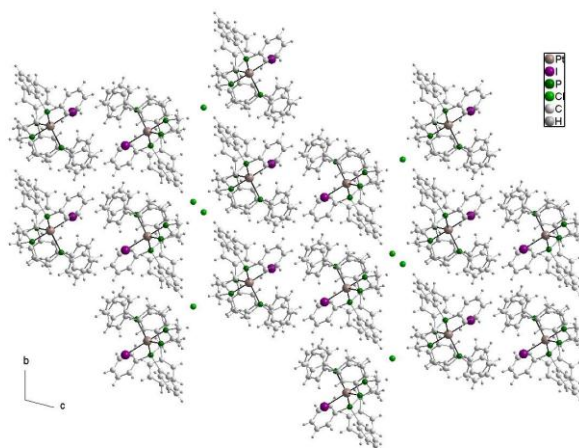
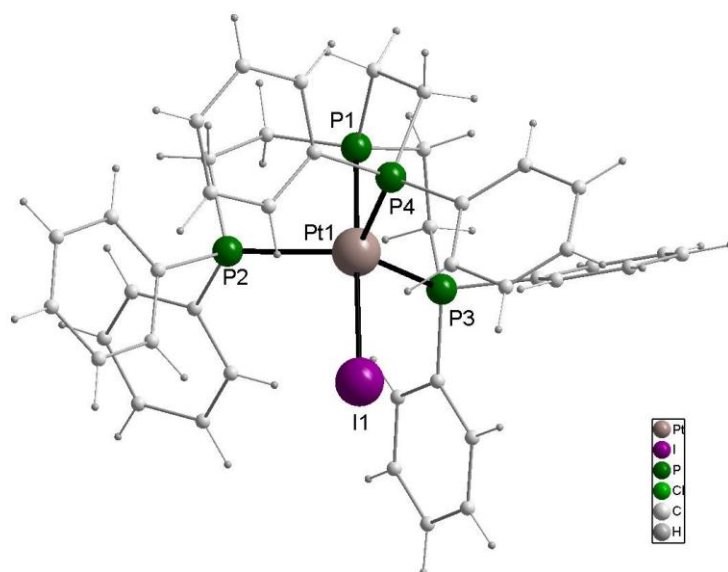


Figure S1

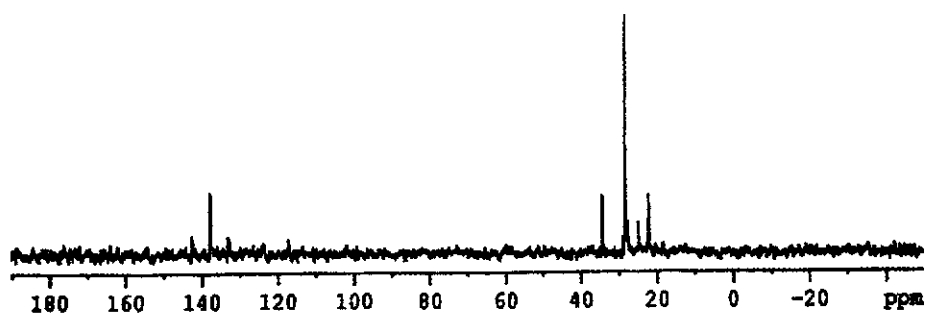
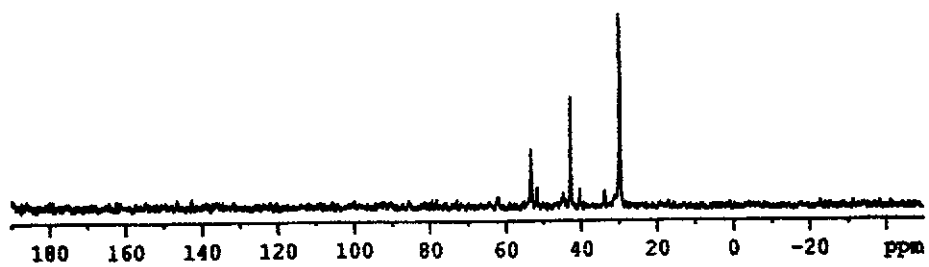
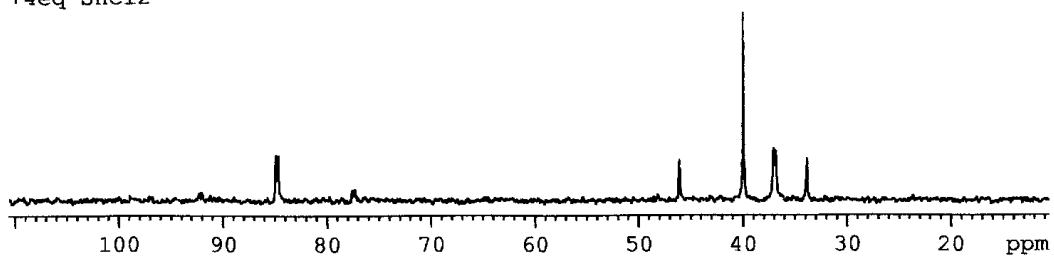
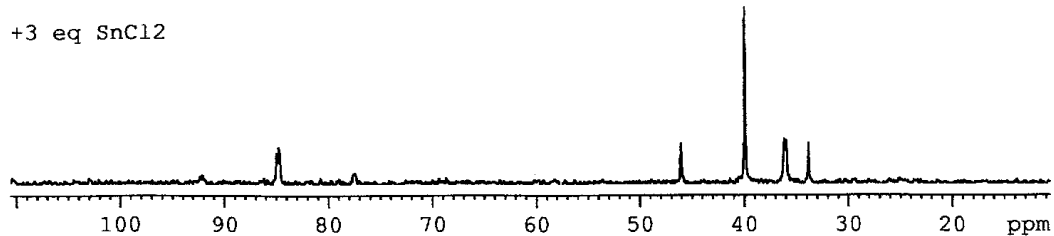


Figure S2

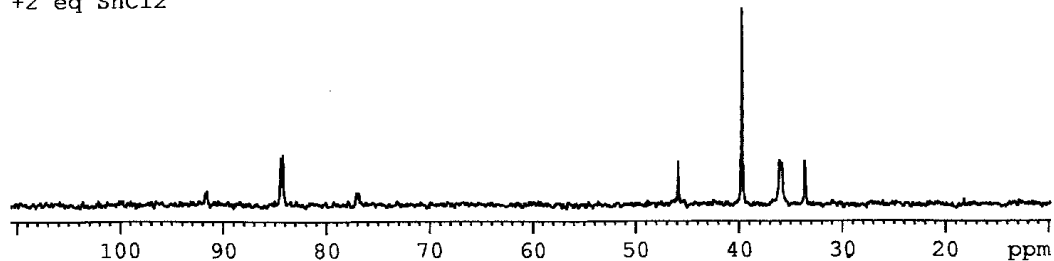
+4eq SnCl₂



+3 eq SnCl₂



+2 eq SnCl₂



+1eq SnCl₂

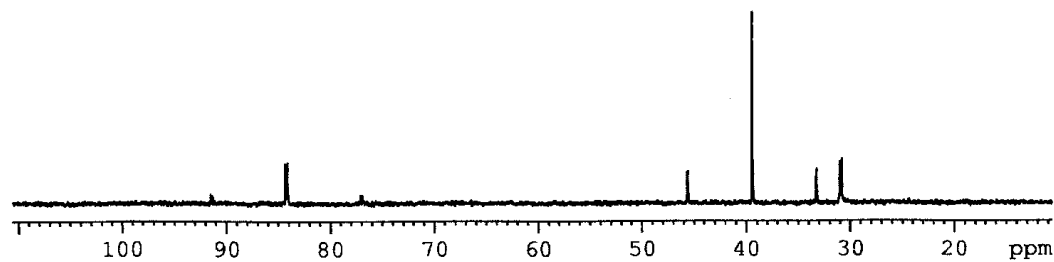
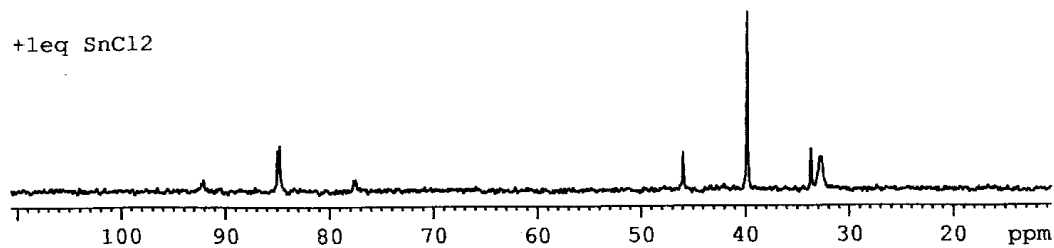


Figure S3

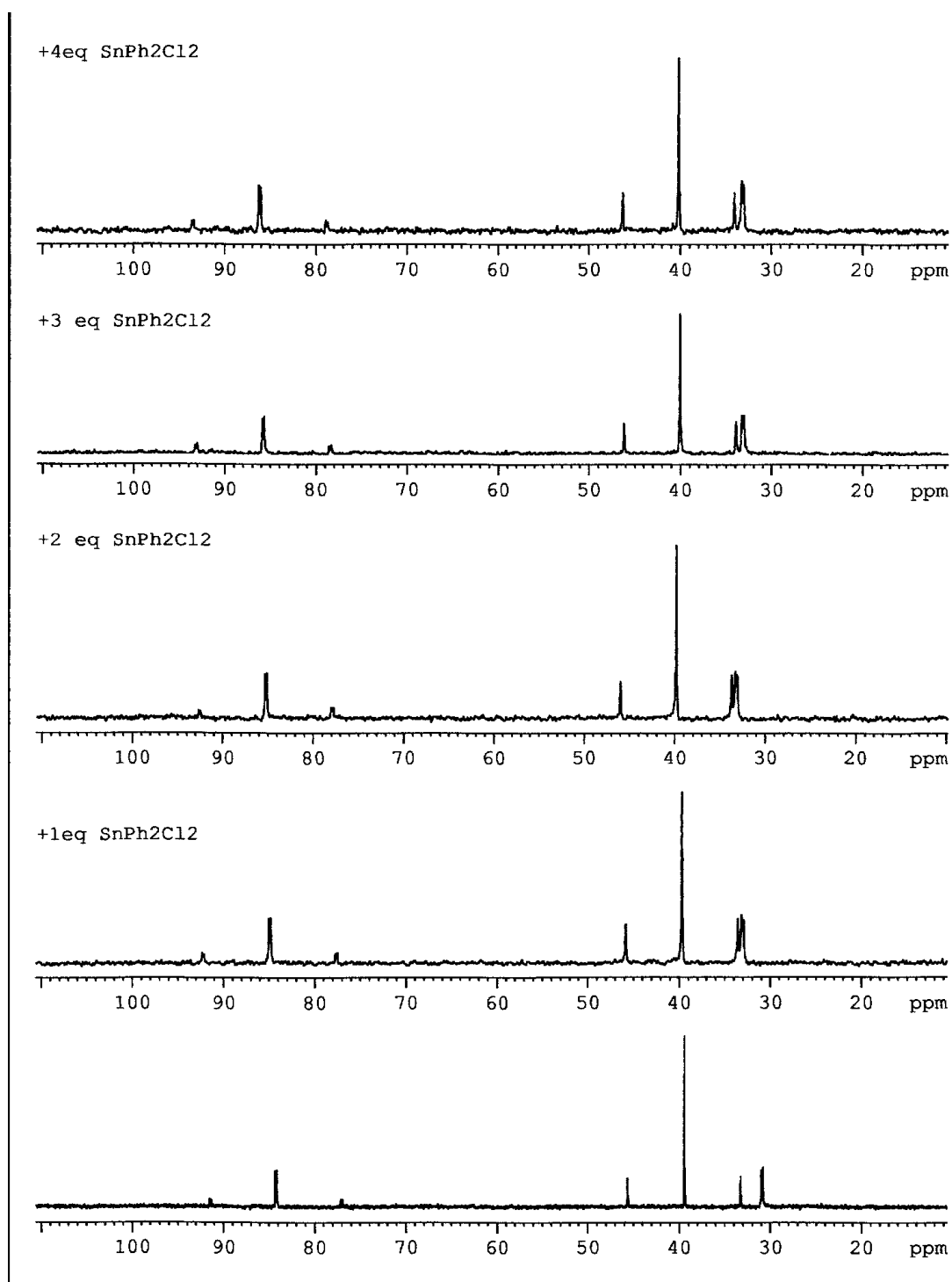


Figure S4

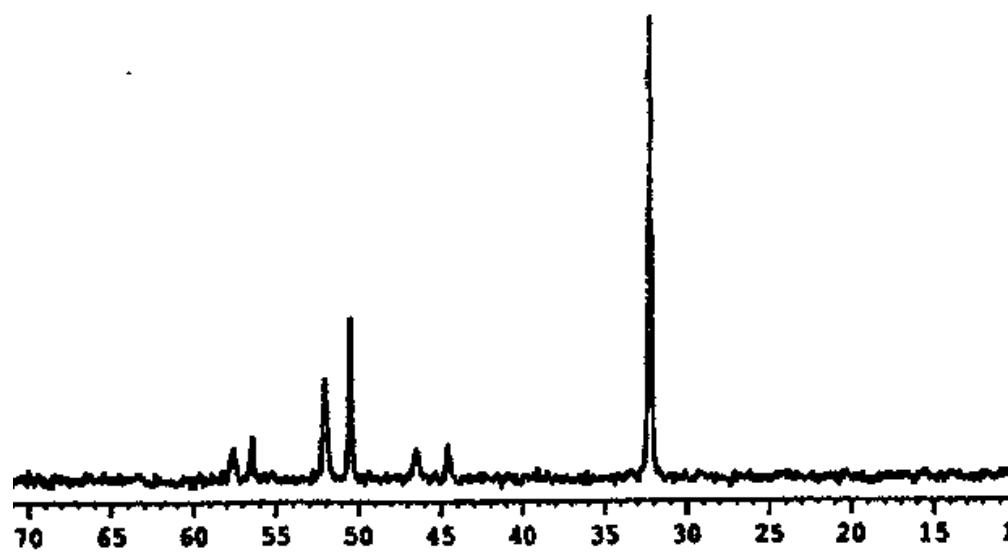
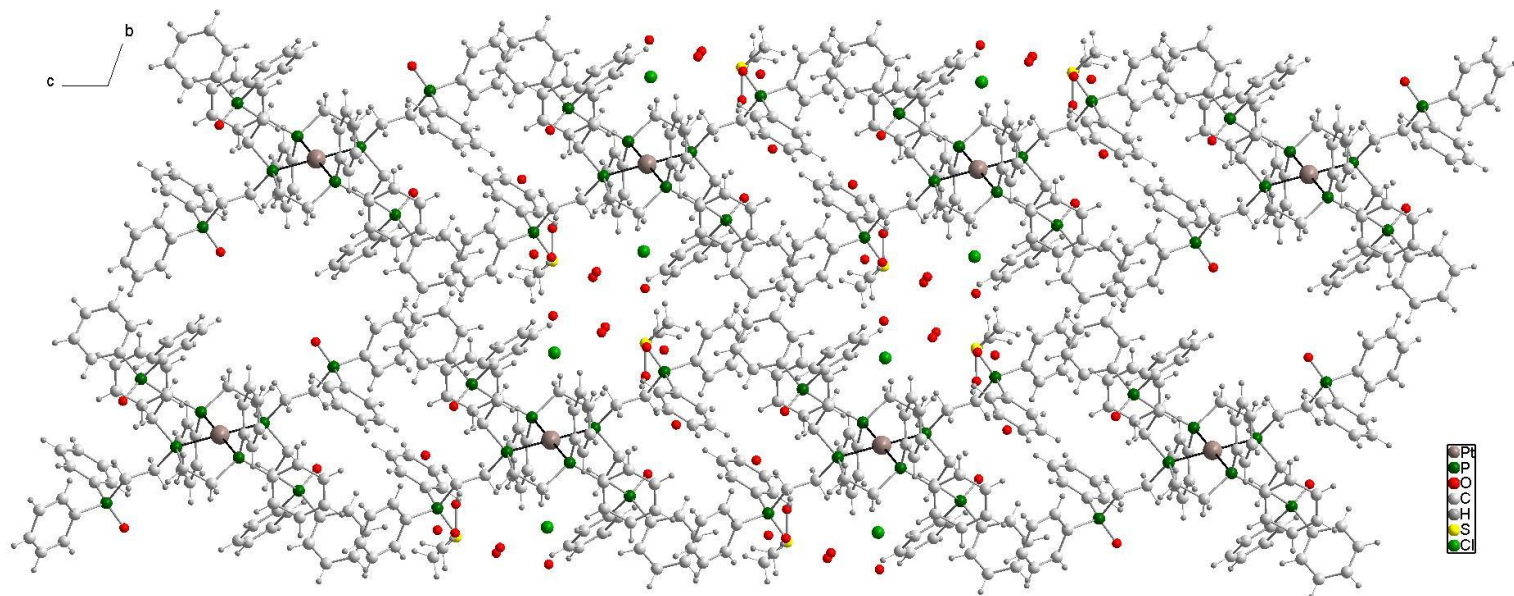


Figure S5

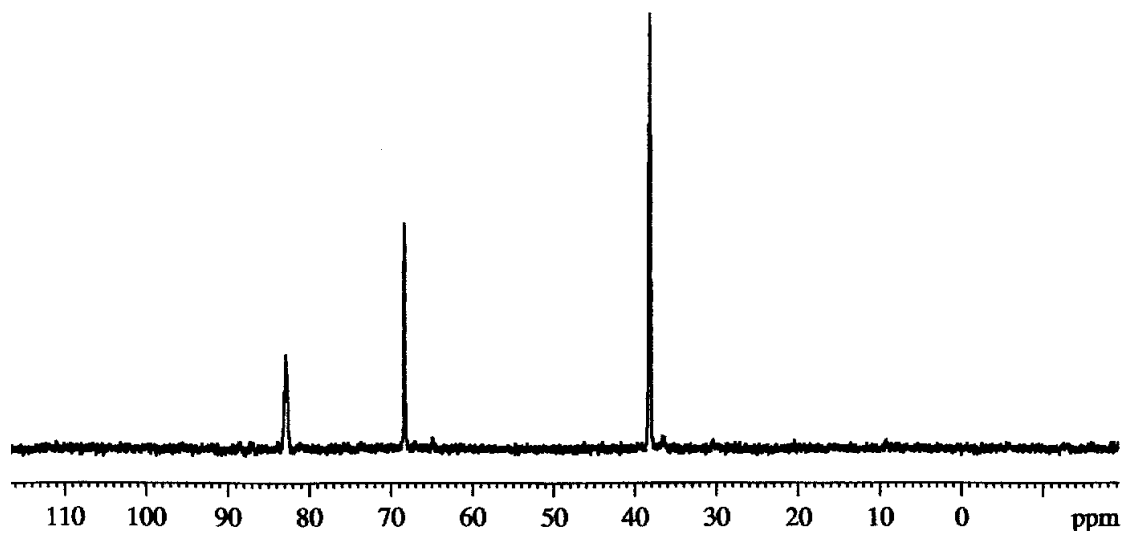
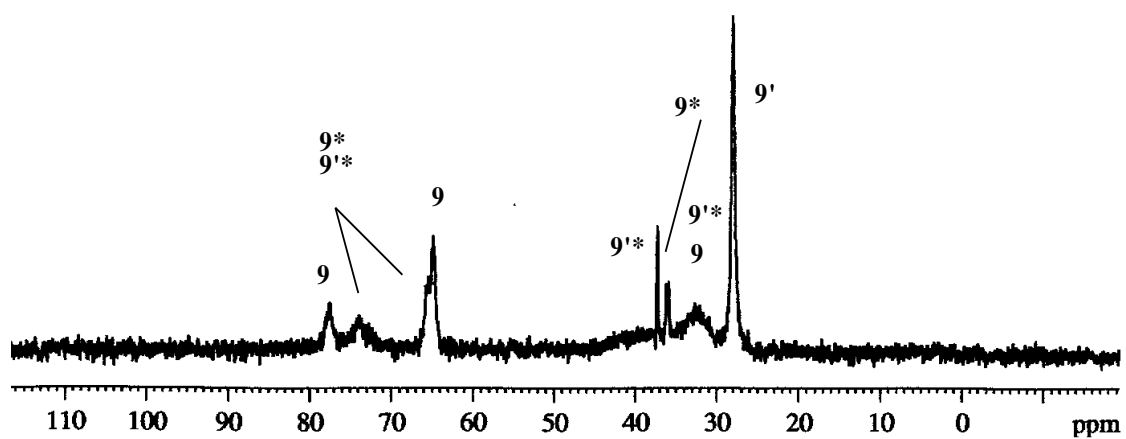


Figure S6

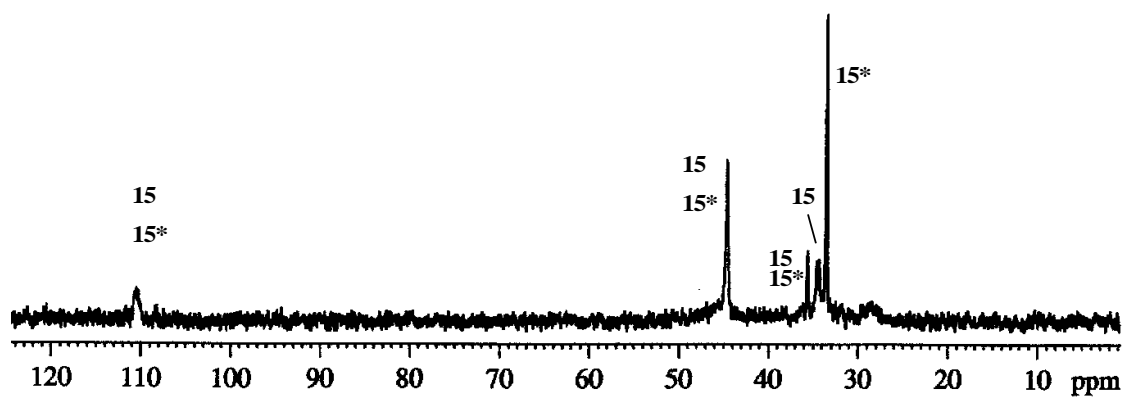


Figure S7

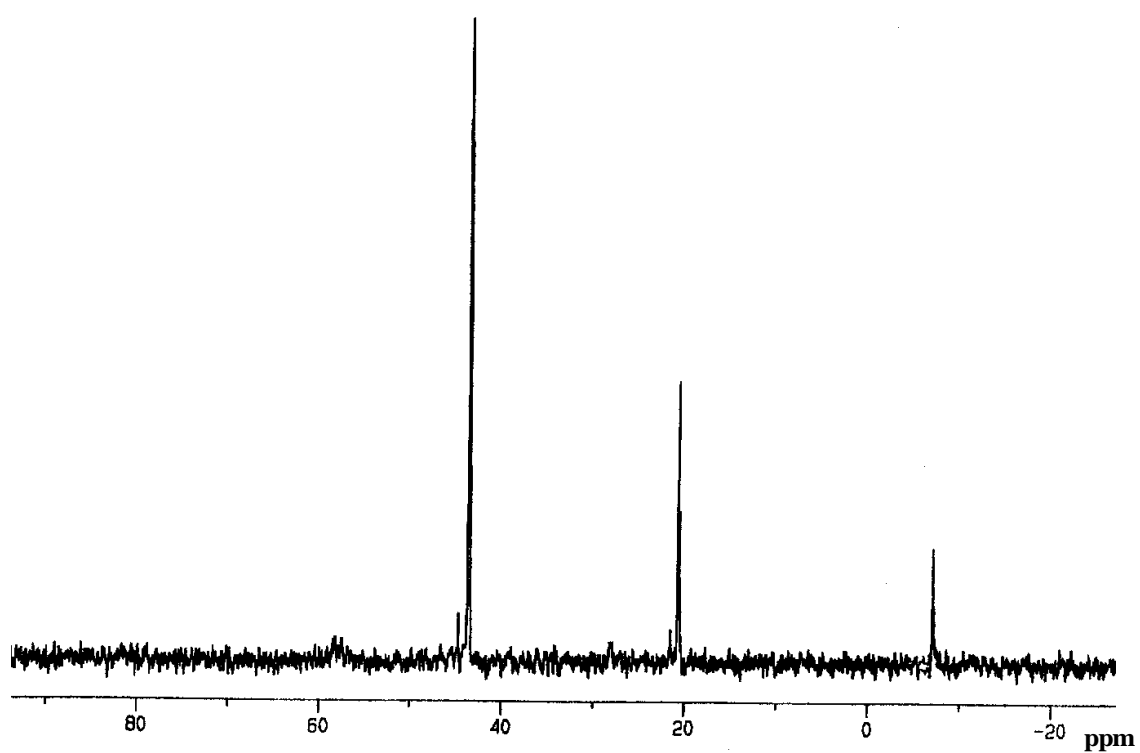


Figure S8

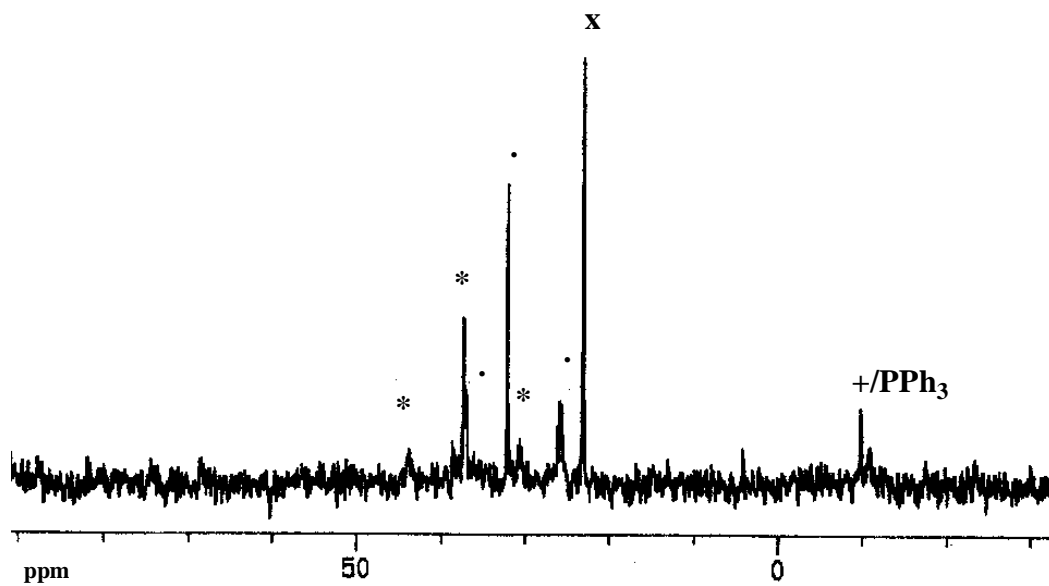
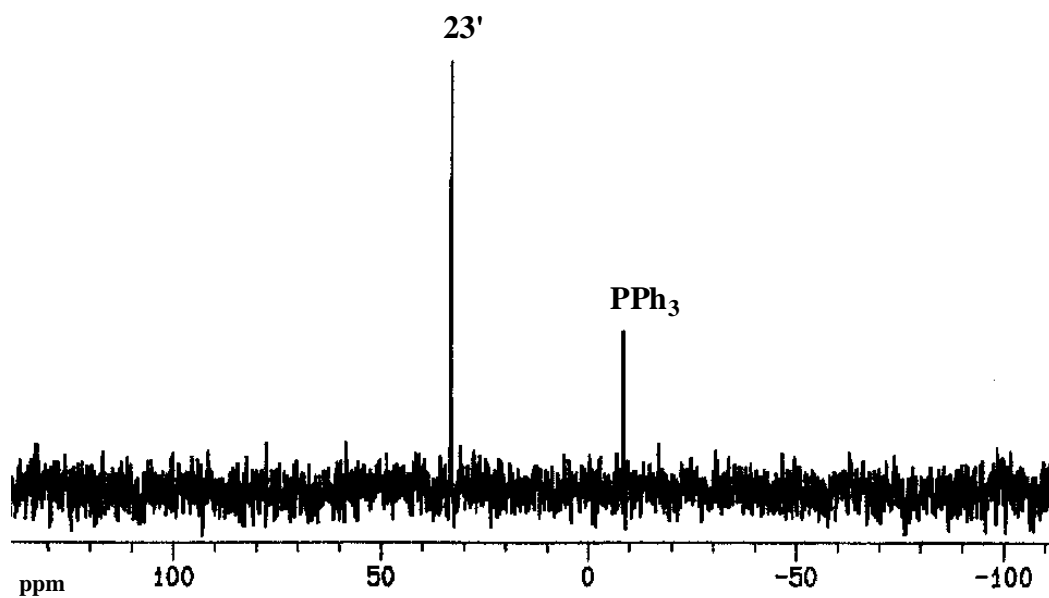


Figure S9

Crystallographic Information Files Comments

Data were not correct with SQUEEZE/PLATON programs. The **4a** and **6a'** structures contain voids of 154 Å³ and 142 Å³, respectively, but the corresponding Fourier map present residuals < 1 e.Å³. Thus, we have discarded the presence of solvents and think that the voids are generate in the crystal packing of the molecules (Figure S1). Since the crystal dimensions of **4a** are reported to be rather similar, absorption is unlikely to have much of an effect on this structure. Consequently, no absorption correction applied. The highest peak in the final difference Fourier map for **6a'** had a height of 2.1(2) e·ångstrom's⁻³, and the minimum negative peak had a depth of -1.1(2) e·ångstrom's⁻³, both near the Pt atom. X-H bond distances and X-Y-H and H-Y-H angles for **4a** and **6a'** are included in the cifs.

C33 and C41 atoms and some C atoms of phenyl groups for **13a** are affected with a considerable disorder degree as shown by its high anisotropic and thermal displacement parameters and it was not possible in the phenyl groups to localize these atoms better. The H atoms of four water molecules, O1W to O4W, cannot be located and their positions cannot otherwise be calculated or predicted from geometrical considerations. There is a disordered region in the cell with solvent molecules (DMSO and four water). Despite large correlation coefficients between the parameters of the atoms, this model appeared to be the best possible and no further attempt was made to improve it. The problem of disorder around the some C and solvent site gave rise to rather elongated ellipsoids. Final refinement included the bond-length restrains SADI for S1S-C1S and S1S-C2S to force these bonds to be equal distances.