

# Supplementary Materials: Transition Metal Complexes Coordinated by Water Soluble Phosphane Ligands: How Cyclodextrins can Alter the Coordination Sphere?

Michel Ferreira, Hervé Bricout, Sébastien Tilloy and Eric Monflier

## 1. Platinum Conversion Determination

When RAME- $\beta$ -CD is added to an aqueous solution of the pure  $[\text{PtL}_3\text{Cl}]^+$ ,  $\text{Cl}^-$  organometallic complex, species  $\text{PtCl}_2\text{L}_2$  could be formed according to (L = water-soluble phosphane):



Platinum conversion could be written as follows:

$$\text{conv}_{\text{Pt}} (\%) = \frac{n_{\text{PtCl}_2\text{L}_2}}{n_{[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-} + n_{\text{PtCl}_2\text{L}_2}} \times 100 \quad (2)$$

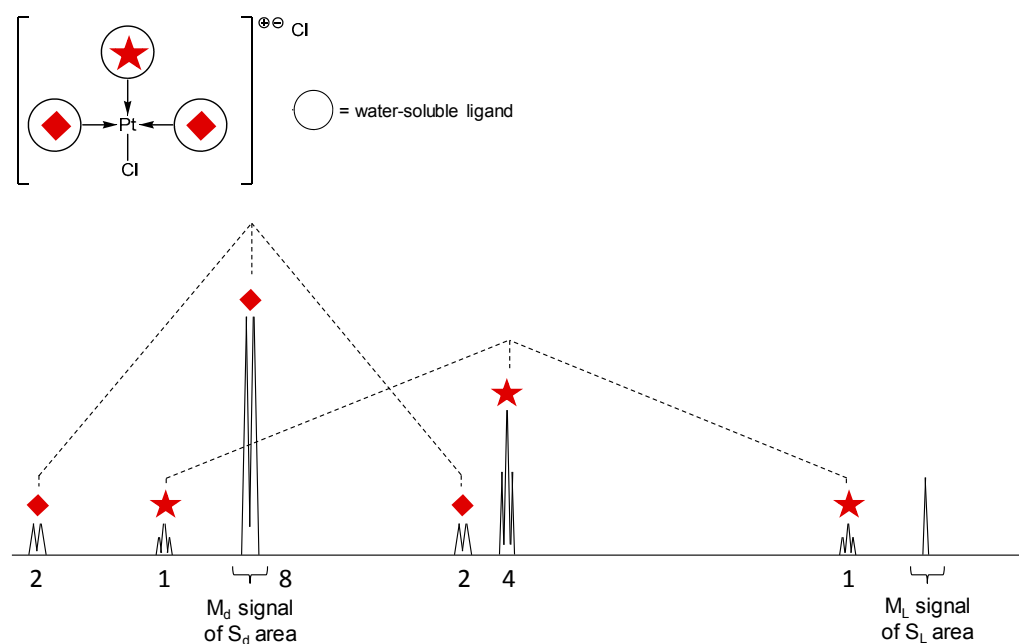
where  $n_x$  = x mole number after RAME- $\beta$ -CD addition.

Taking into account the phosphorus atoms number in the platinum species, Equation (2) becomes:

$$\text{conv}_{\text{Pt}} (\%) = \frac{\frac{S_{\text{PtCl}_2\text{L}_2}}{2}}{\frac{S_{[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-}}{3} + \frac{S_{\text{PtCl}_2\text{L}_2}}{2}} \times 100 \quad (3)$$

where  $S_x = {}^{31}\text{P}\{^1\text{H}\}$  NMR total surface relating to species x.

The fact that  $\text{PtCl}_2\text{L}_2$  species often lead to a large signal difficult to integrate, combined with satellites signals (coming from the platinum coupling) close to the background noise, led us to use the  $M_d$  (doublet) and  $M_L$  (singlet) signals of the  ${}^{31}\text{P}\{^1\text{H}\}$  NMR spectrum represented Figure S1 to calculate the platinum conversion (in order to clarify, the  $\text{PtCl}_2\text{L}_2$  large signals were not represented). The  $M_L$  singlet corresponds to the decoordinated phosphane ligand coming from the cyclodextrin addition.  $S_d$  and  $S_L$  are respectively the surface area of the  $M_d$  and  $M_L$  signals.



**Figure S1.** Theoretical  ${}^{31}\text{P}\{^1\text{H}\}$  spectrum of  $[\text{PtL}_3\text{Cl}]^+$ ,  $\text{Cl}^-$  and free ligand signal (L).

As only one third of the platinum ( $^{195}\text{Pt}$ ) has a spin of 1/2, doublets and triplets of the  $[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-$  species appear, from downfield to upfield, in relative ratios 2:1:8:2:4:1, representing a total area of 18. So:

$$S_d = \frac{8}{18} \times S_{[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-} = \frac{4}{9} \times S_{[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-} \quad (1)$$

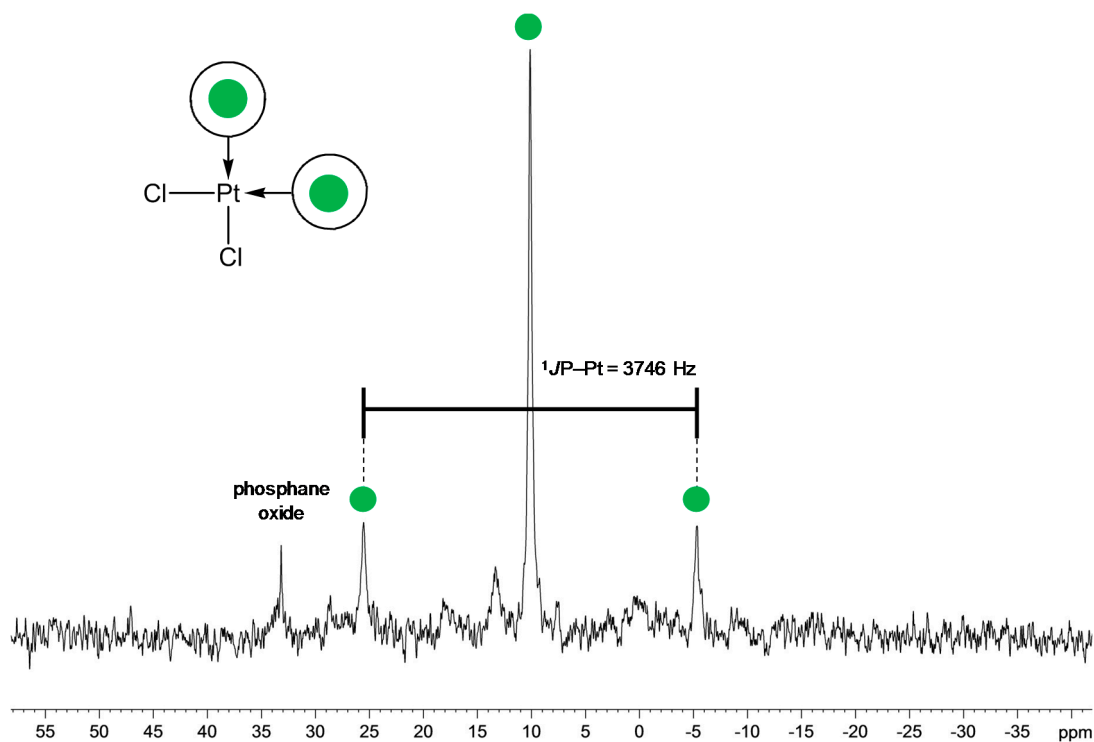
Moreover, given that every ligand decoordination from the  $[\text{PtL}_3\text{Cl}]^+, \text{Cl}^-$  complex leads to formation of 1 equiv of  $\text{PtCl}_2\text{L}_2$ :

$$S_L = \frac{S_{\text{Cl}_2\text{PtL}_2}}{2} \quad (2)$$

By combining Equations (4) and (5) with (3):

$$\text{conv}_{\text{Pt}} (\%) = \frac{S_L}{\frac{3 S_d}{4} + S_L} \times 100 \quad (3)$$

## 2. Complexes formed by Mixing $\text{K}_2\text{PtCl}_4$ Platinum Aqueous Solution with 2 Equiv. of *Para*-Substituted Phosphane



**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of  $\text{cis-PtCl}_2(\text{tris}(p\text{-Me})\text{TPPTS})_2$  at  $25^\circ\text{C}$ .

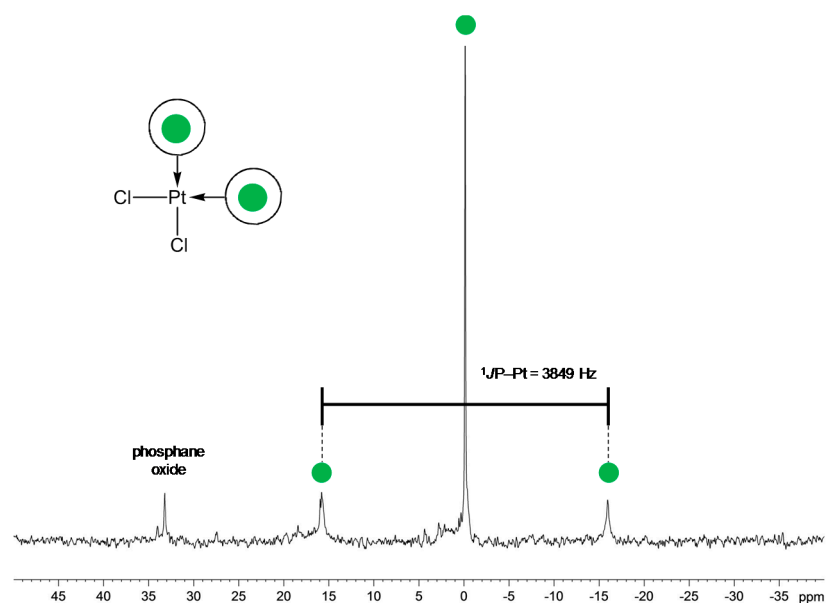


Figure S3.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of *cis*- $\text{PtCl}_2(\text{tris}(p\text{-OMe})\text{TPPTS})_2$  at 25 °C.

### 3. RAME- $\beta$ -CD Influence on $[\text{PtL}_3\text{Cl}]\text{Cl}$ Complexes with $\text{L} = \text{tris}(p\text{-Me})\text{TPPTS}$ and $\text{L} = \text{tris}(p\text{-OMe})\text{TPPTS}$

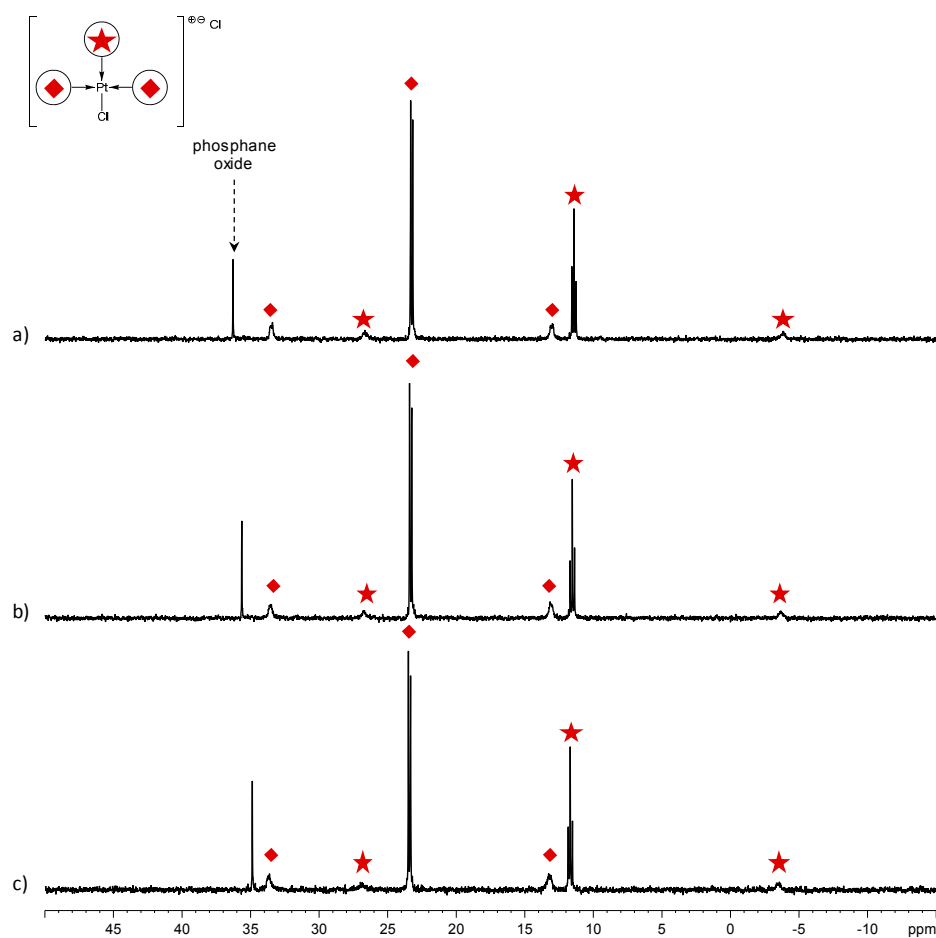
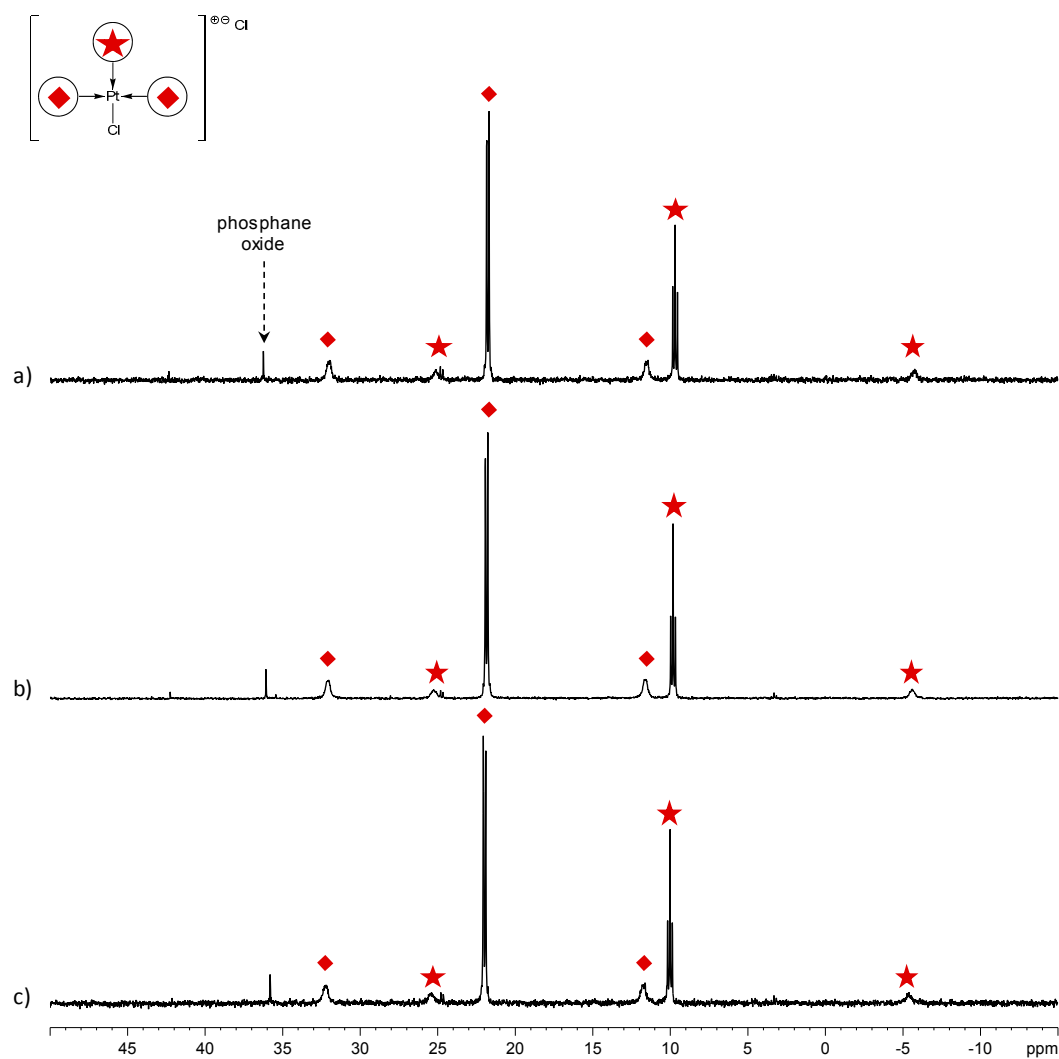
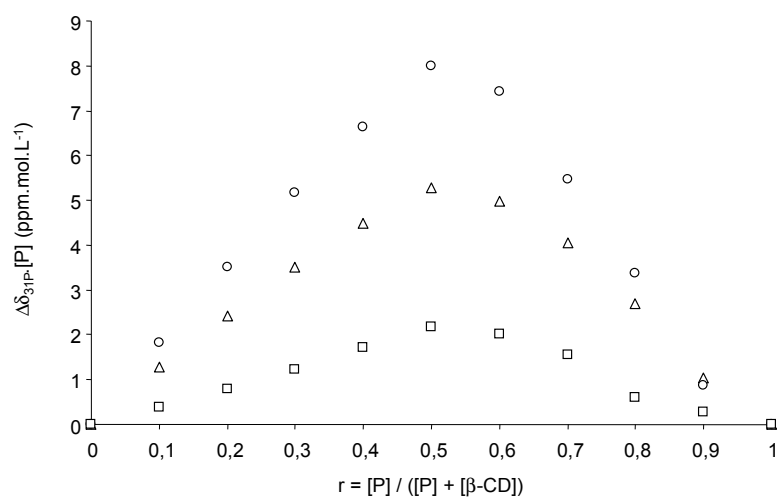


Figure S4.  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of (a)  $[\text{Pt}(\text{tris}(p\text{-Me})\text{TPPTS})_3\text{Cl}]\text{Cl}$  at 25 °C, with addition of (b) 3 equiv. or (c) 9 equiv. of RAME- $\beta$ -CD.

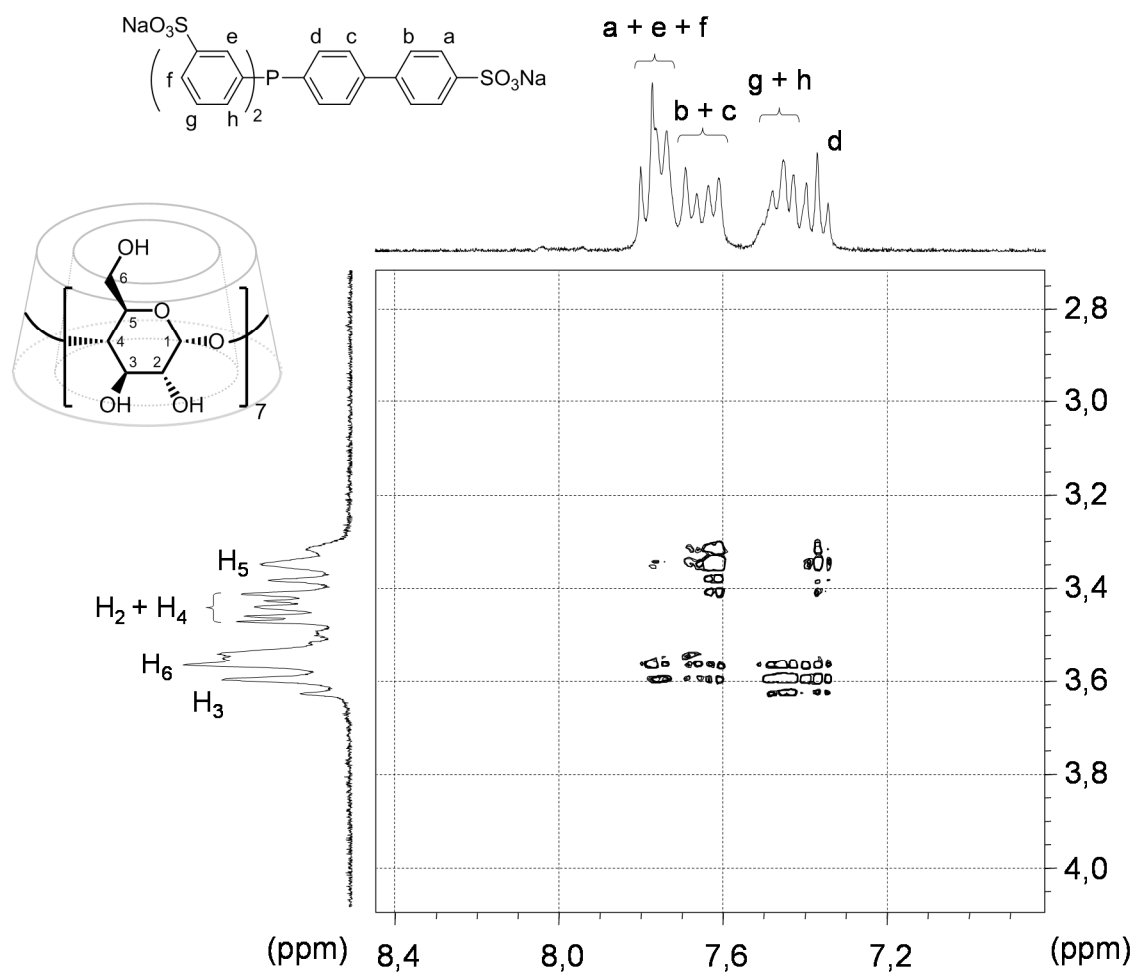


**Figure S5.**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of (a)  $[\text{Pt}(\text{tris}(p\text{-OMe})\text{TPPTS})_3\text{Cl}]\text{Cl}$  at 25 °C, with addition of (b) 3 equiv. or (c) 9equiv. of RAME- $\beta$ -CD.

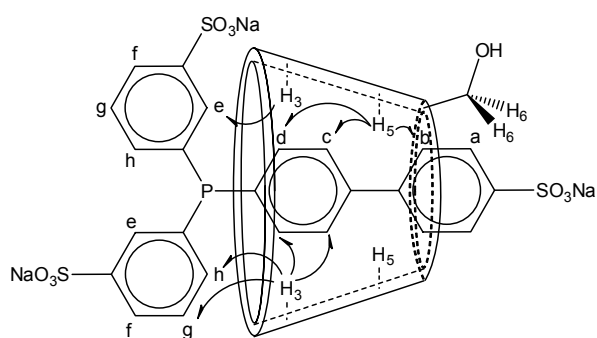
#### 4. Interaction Study $\beta$ -CD/Biphenylphosphanes



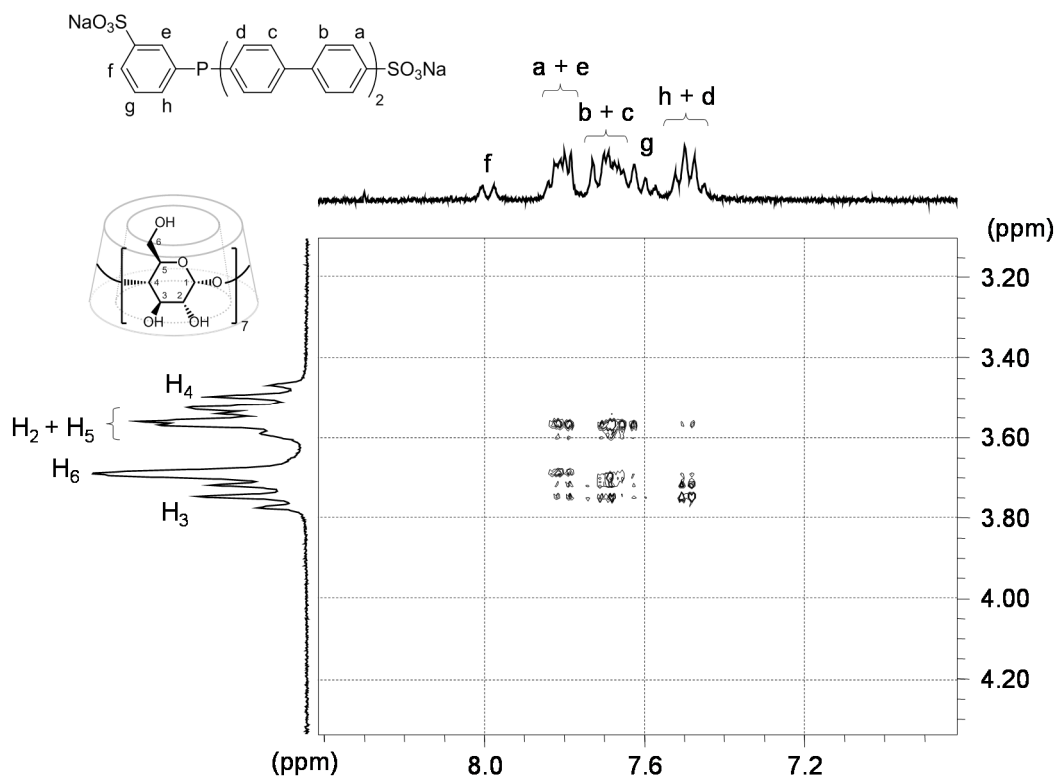
**Figure S6.** Job plots for inclusion complexes  $\beta$ -CD/biphenyl phosphane at 25 °C in  $\text{D}_2\text{O}$ .  $\text{P}(\text{Biph})_2\text{PhTS}$ :  $\circ$ ; de la  $\text{P}(\text{Biph})\text{Ph}_2\text{TS}$ :  $\Delta$ ; de la  $\text{P}(\text{Biph})_3\text{TS}$ :  $\square$ .



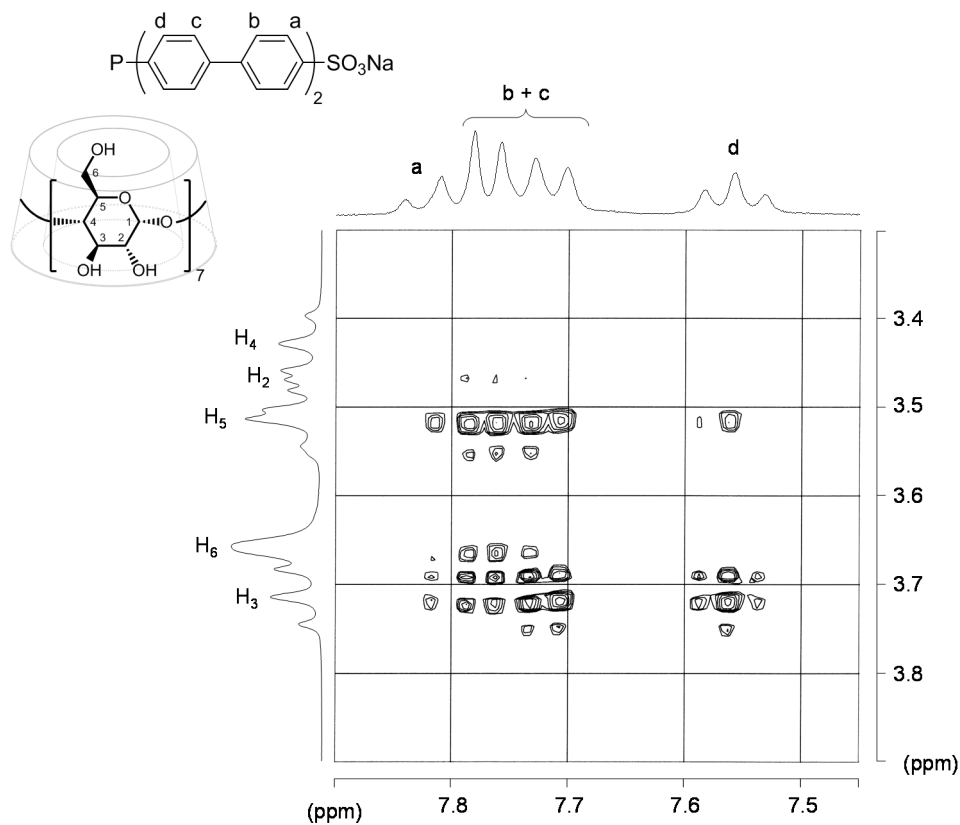
**Figure S7.** 2D T-ROESY spectrum of a solution containing [β-CD] (1 mM) and [P(Biph)Ph<sub>2</sub>TS] (4 mM) at 25 °C in D<sub>2</sub>O.



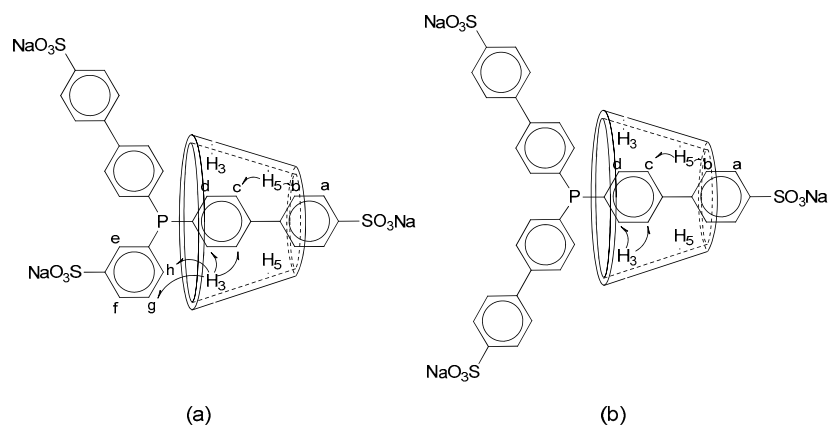
**Figure S8.** Proposed structure of the inclusion complex between β-CD and P(Biph)Ph<sub>2</sub>TS.



**Figure S9.** 2D T-ROESY spectrum of a solution containing  $[\beta\text{-CD}]$  (7 mM) and  $[\text{P(Biph)}_2\text{PhTS}]$  (3 mM) at 25 °C in  $\text{D}_2\text{O}$ .

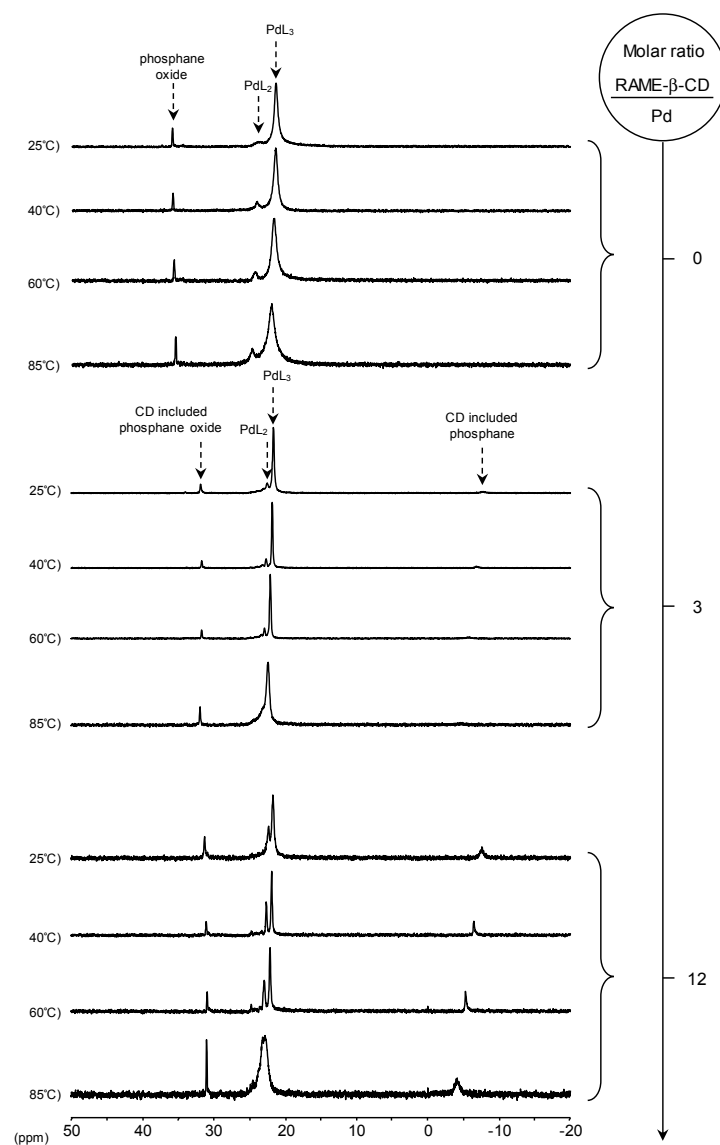


**Figure S10.** 2D T-ROESY spectrum of a solution containing  $[\beta\text{-CD}]$  (7 mM) and  $[\text{P(Biph)}_3\text{TS}]$  (3 mM) at 25 °C in  $\text{D}_2\text{O}$ .



**Figure S11.** Proposed structure of the inclusion complex between  $\beta$ -CD and (a)  $P(\text{Biph})_2\text{PhTS}$  or (b)  $P(\text{Biph})_3\text{TS}$ .

### 5. RAME- $\beta$ -CD Influence on $\text{PdL}_3$ Complex with $L = P(\text{Biph})\text{Ph}_2\text{TS}$



**Figure S12.**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of  $\text{Pd}(\text{P}(\text{Biph})\text{Ph}_2\text{TS})_3$  depending on both temperature and RAME- $\beta$ -CD quantity in  $\text{D}_2\text{O}$  with a ligand concentration of 66 mM.