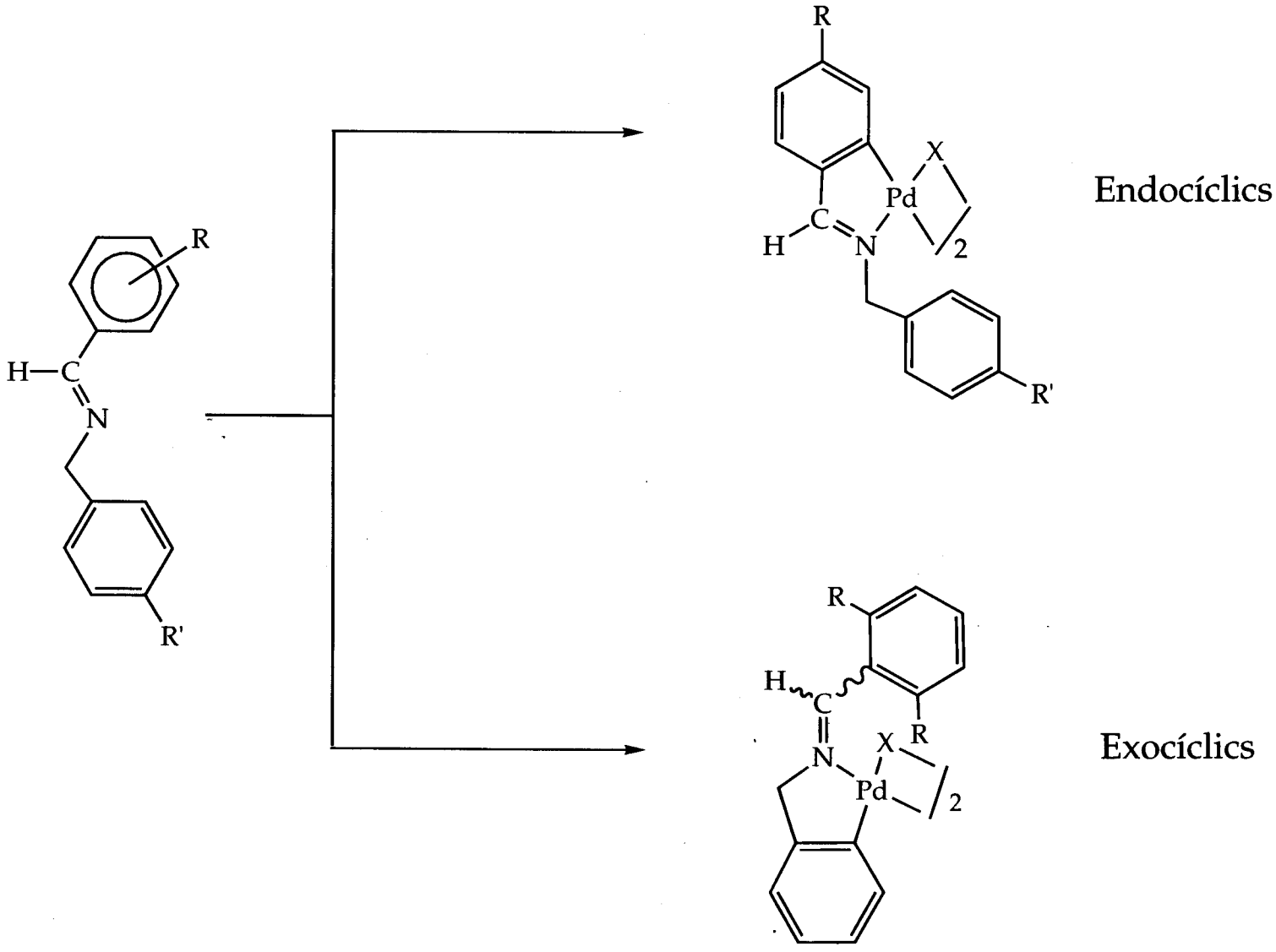
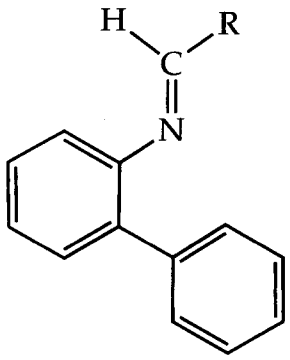
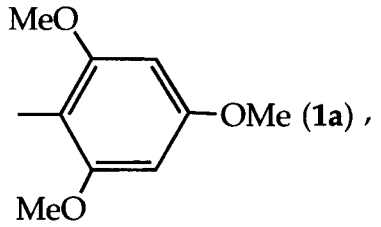
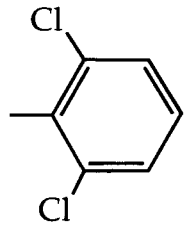
Ciclopal·ladació d'imines aromàtiques. Regioselectivitat.

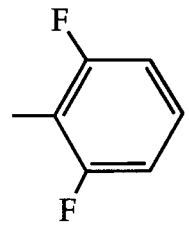


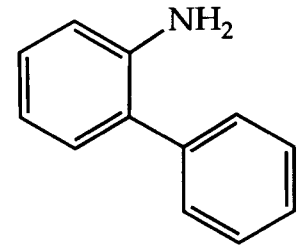
Lligands estudiats a la Memòria.



R = 

(1a) , 

(1b) , 

(1c) ; 

(1d)

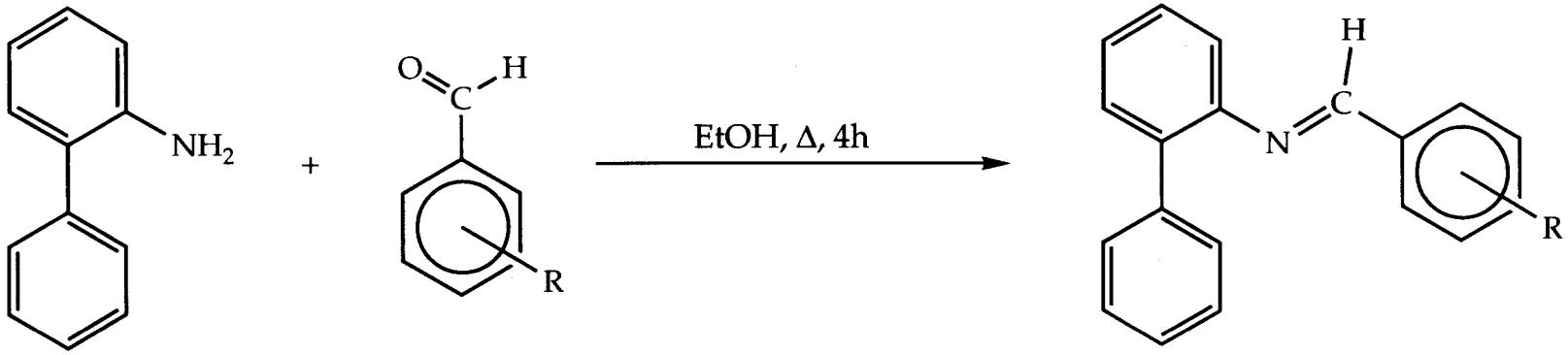
Objectius:

1.- Preparació dels compostos ciclopal·ladats exocíclics de les imines 1a-1c derivades de la 2-fenilanilina,

2.- ciclopal·ladació de la 2-fenilanilina,

3.- reacció de monoinserció de butindioat de dimetil als corresponents compostos ciclopal·ladats.

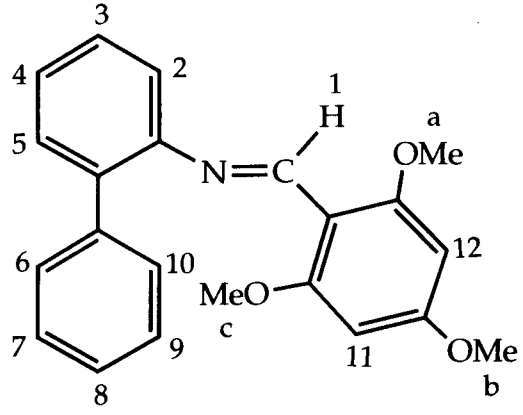
Preparació de les imines.



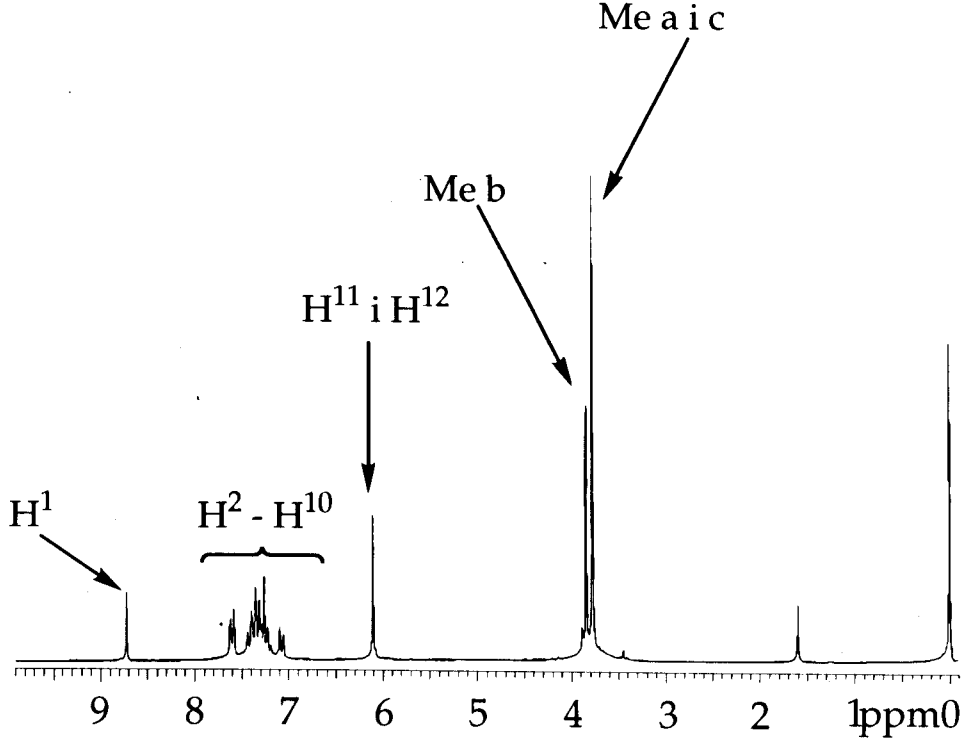
R = 2,4,6-$(OCH_3)_3$ (**1a**)

R = 2,6-Cl_2 (**1b**)

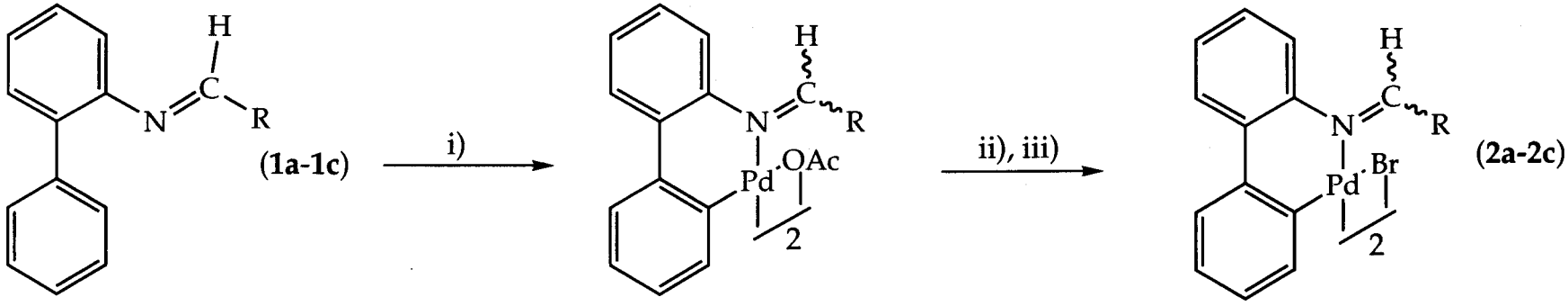
R = 2,6-F_2 (**1c**)



1a



Ciclopal·ladació de les imines.



R = 2,4,6-$(OCH_3)_3C_6H_2$ (**1a**)

R = 2,6-$Cl_2C_6H_3$ (**1b**)

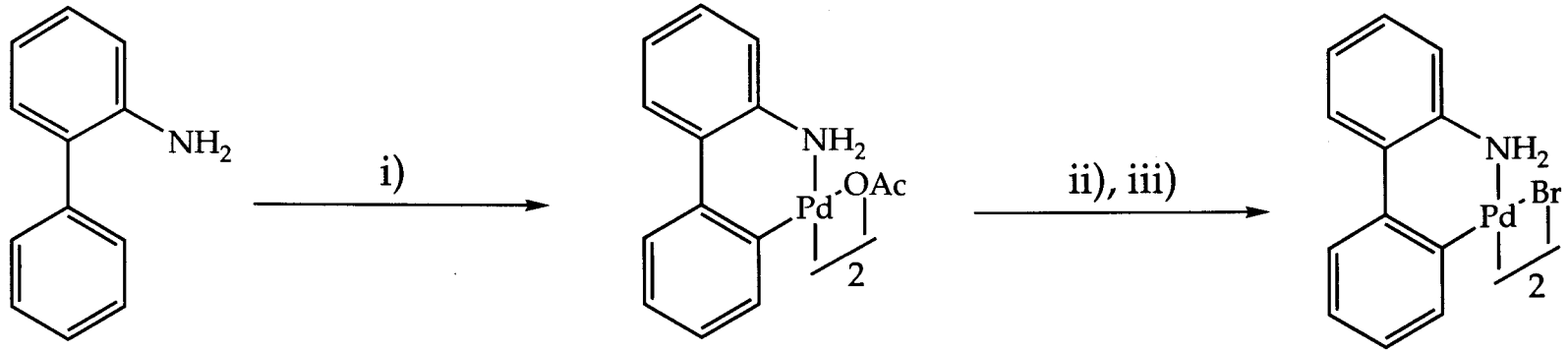
R = 2,6-$F_2C_6H_3$ (**1c**)

i) {
- **1a**: $Pd(AcO)_2$, $CHCl_3$, t.a., 24 h.
- **1b**: $Pd(AcO)_2$, HAcO, 60°C, 2h.
- **1c**: $Pd(AcO)_2$, HAcO, Δ , 45 min.

ii) LiBr, EtOH, t.a., 40 min, agit.

iii) {
- **2a**: SiO_2, $CHCl_3$/MeOH, 100/2
- **2b**, **2c**: SiO_2, $CHCl_3$

Ciclopal·ladació de la 2-fenilanilina.



1d **2d**

i) $Pd(AcO)_2$, toluè, t.a., 24 h.

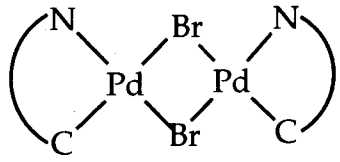
ii) LiBr, EtOH, t.a., 40 min, agit.

iii) SiO_2, $CHCl_3$/MeOH, 100/2

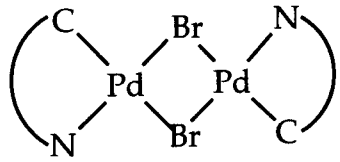
Tipus d'isomeria als dímers.

Isomeria geomètrica:

- *cis-trans*

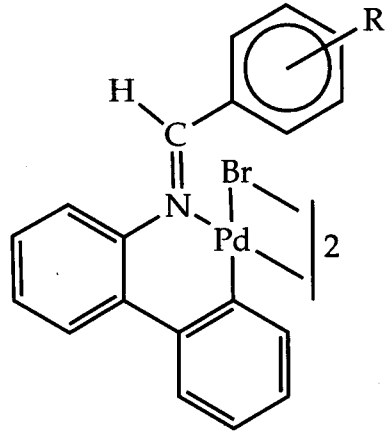


cis

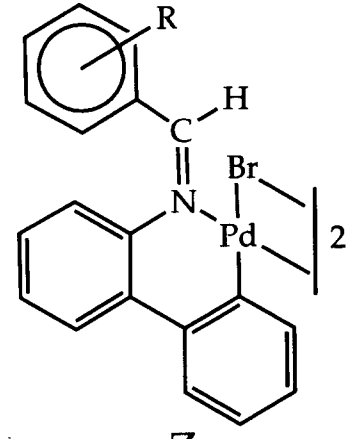


trans

- E-Z



E

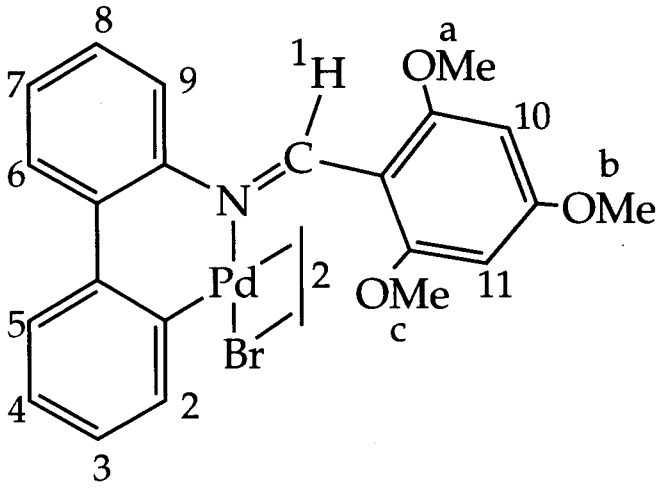


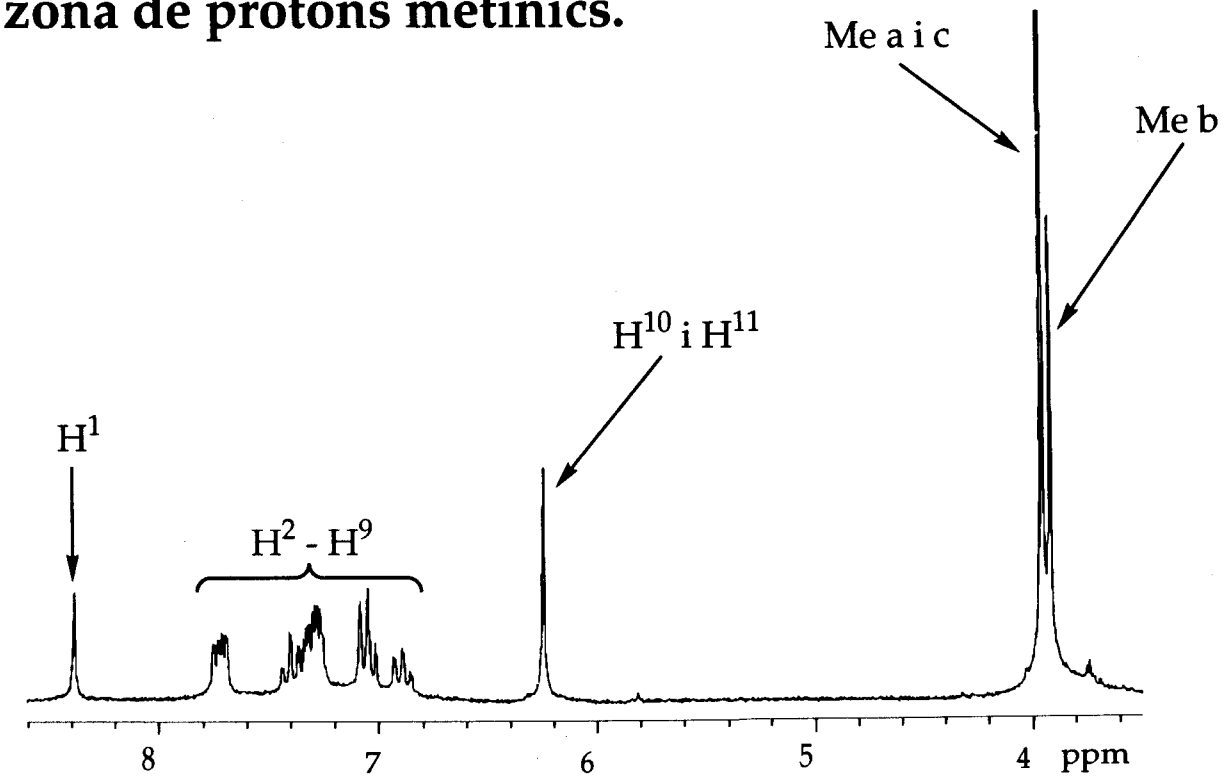
Z

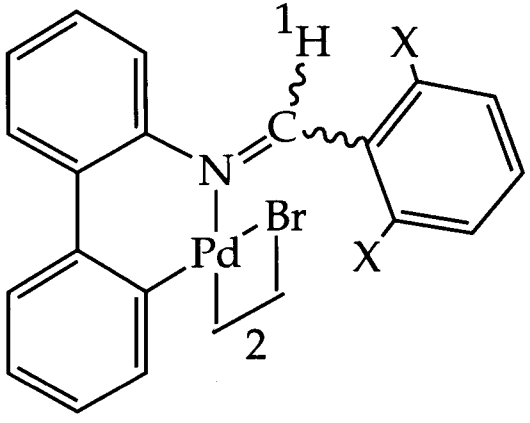
Isomeria conformacional:

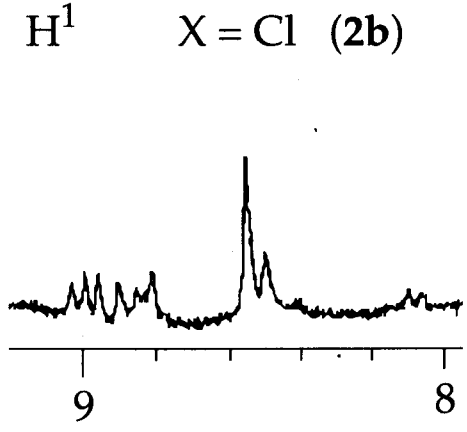
- No planaritat del metal·locicle
- Impediments estèrics del gir al voltant de l'enllaç $C_{imínic}$-$C_{aromàtic}$

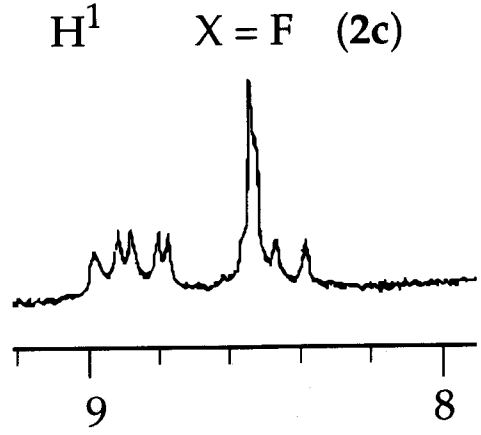
^{1}H RMN de 2a i de 2b i 2c a la zona de protons metínics.



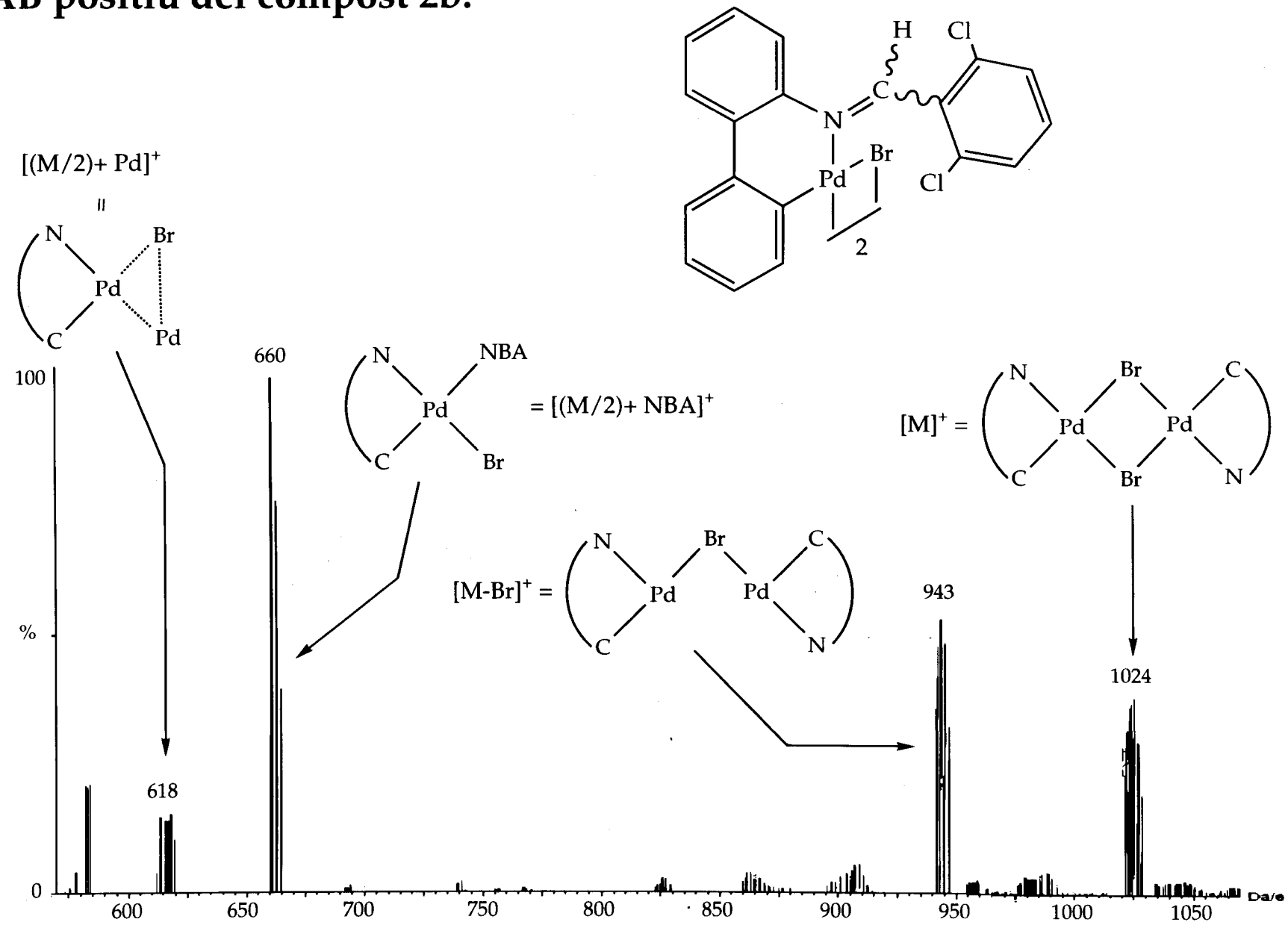




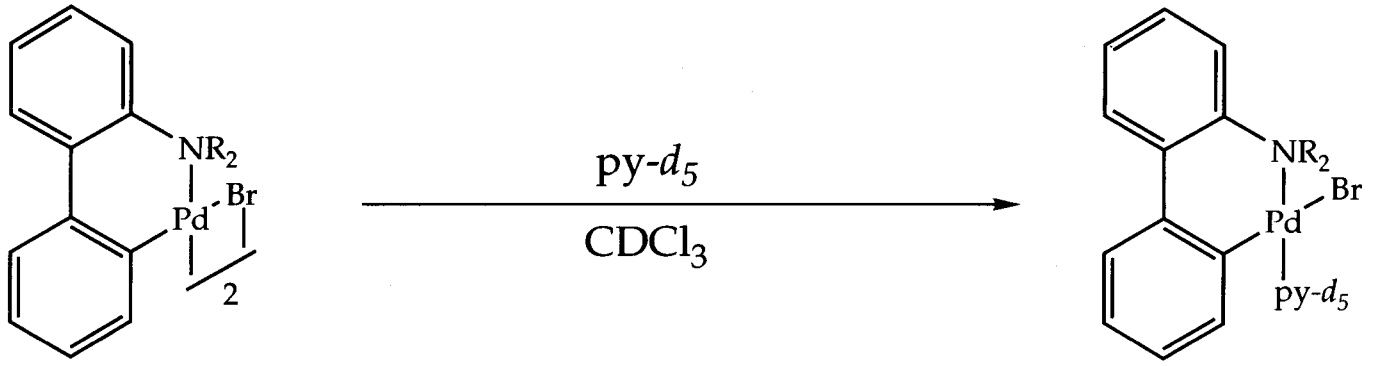




FAB positiu del compost 2b.



Reaccions amb piridina deuterada.



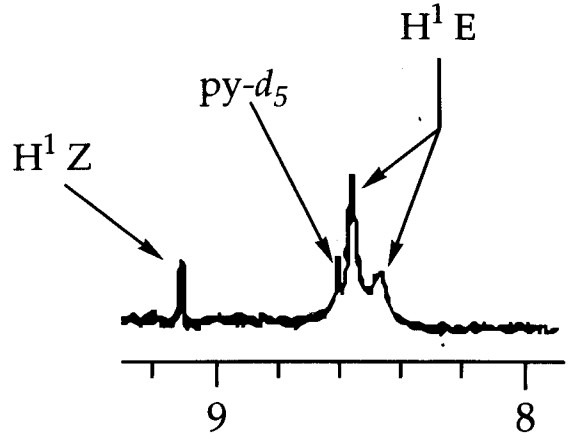
R_2 : =CH-2,4,6-$(OCH_3)_3$-C_6H_2 (**2a**)

R_2 : =CH-2,6-Cl_2-C_6H_3 (**2b**)

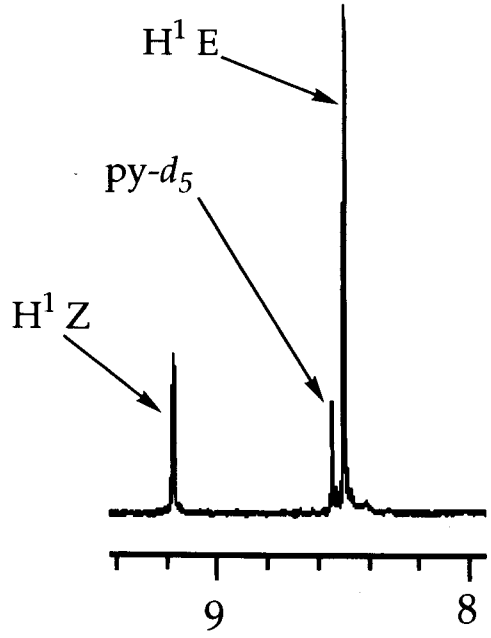
R_2 : =CH-2,6-F_2-C_6H_3 (**2c**)

R : H (**2d**)

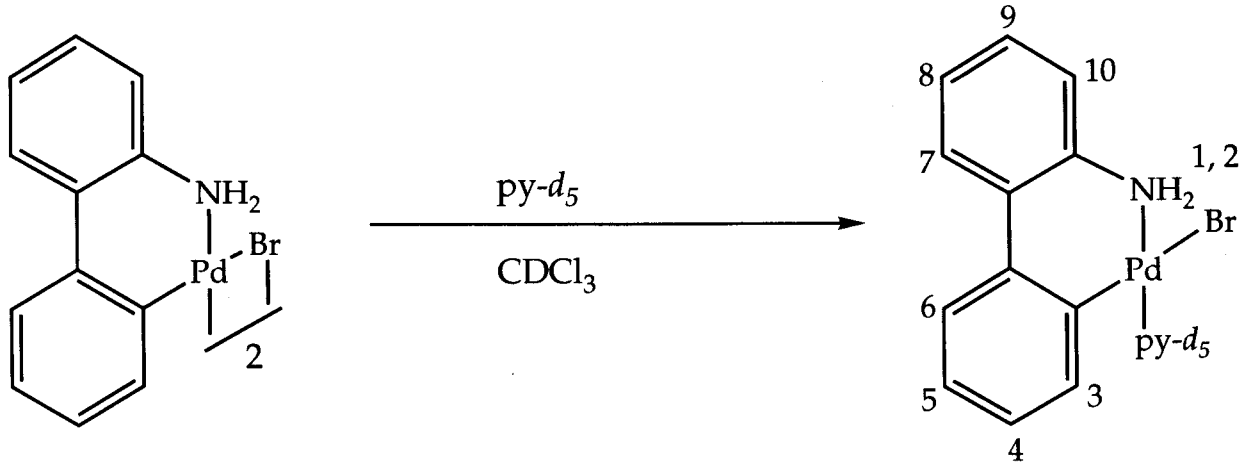
2a+py-d_5

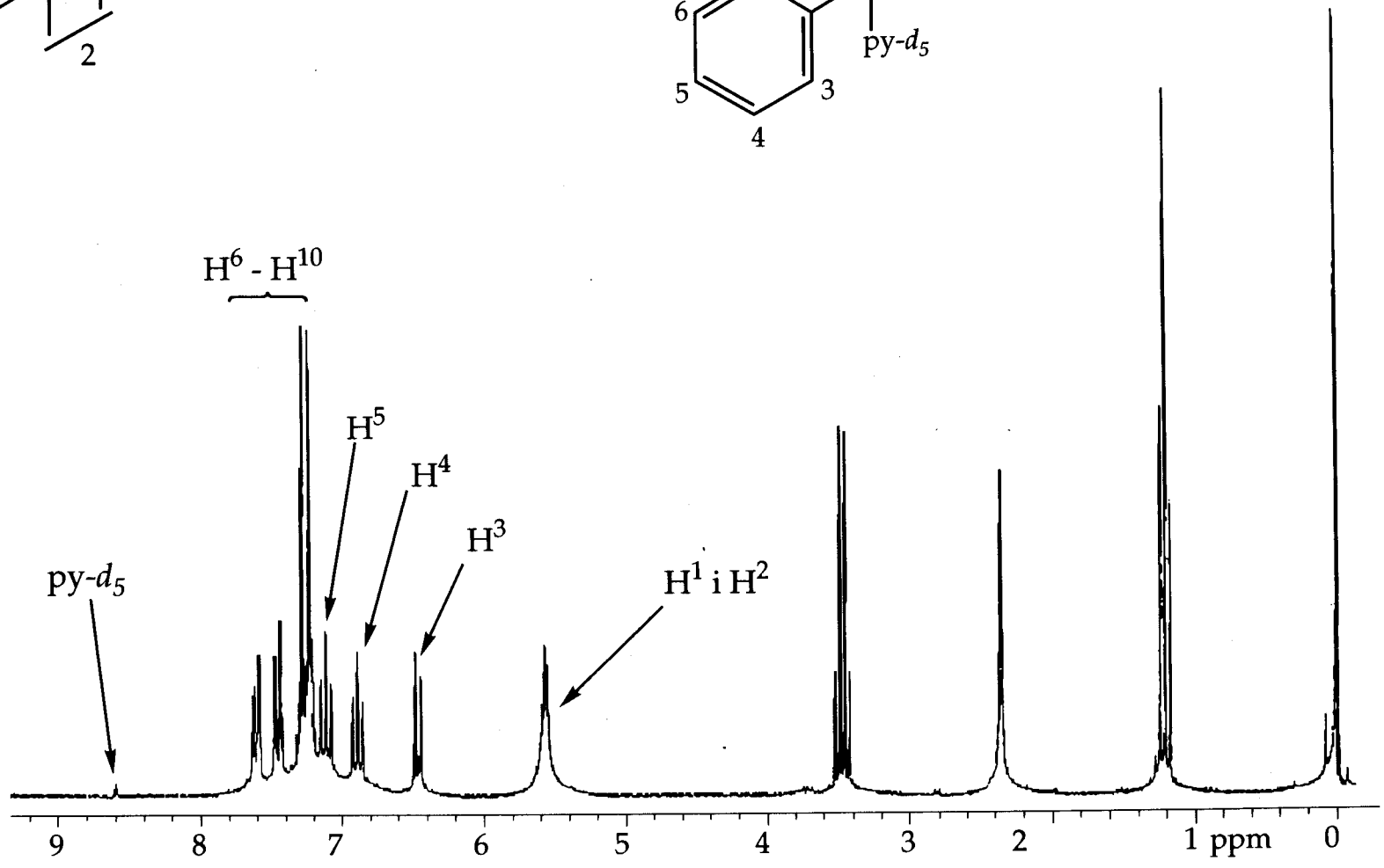


2c+py-d_5

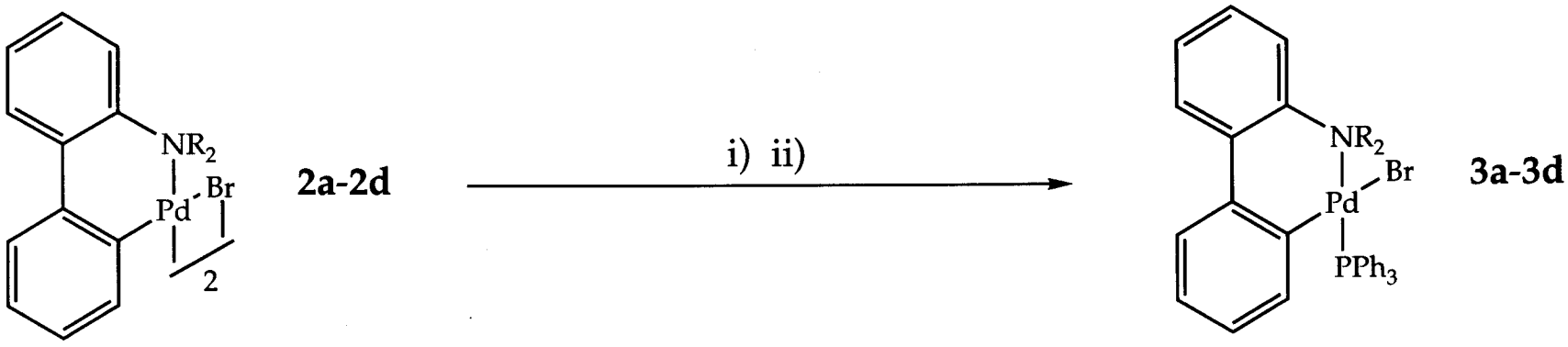


Reacció de 2d amb piridina deuterada.





Reaccions amb trifenilfosfina.



R_2 : =CH-2,4,6-$(CH_3O)_3C_6H_2$ (**2a**)

R_2 : =CH-2,6-$Cl_2C_6H_3$ (**2b**)

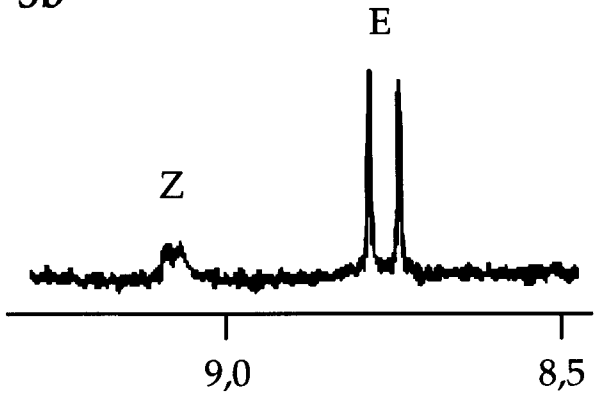
R_2 : =CH-2,6-$F_2C_6H_3$ (**2c**)

R : H (**2d**)

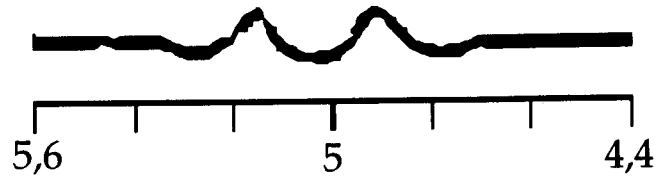
i) 2 PPh_3, acetona, t.a., 30 min.

ii)
- **3a**: SiO_2, $CHCl_3$/MeOH 100/2
- **3b**, **3c**: SiO_2, $CHCl_3$
- **3d**: SiO_2, $CHCl_3$/MeOH 100/1

3b

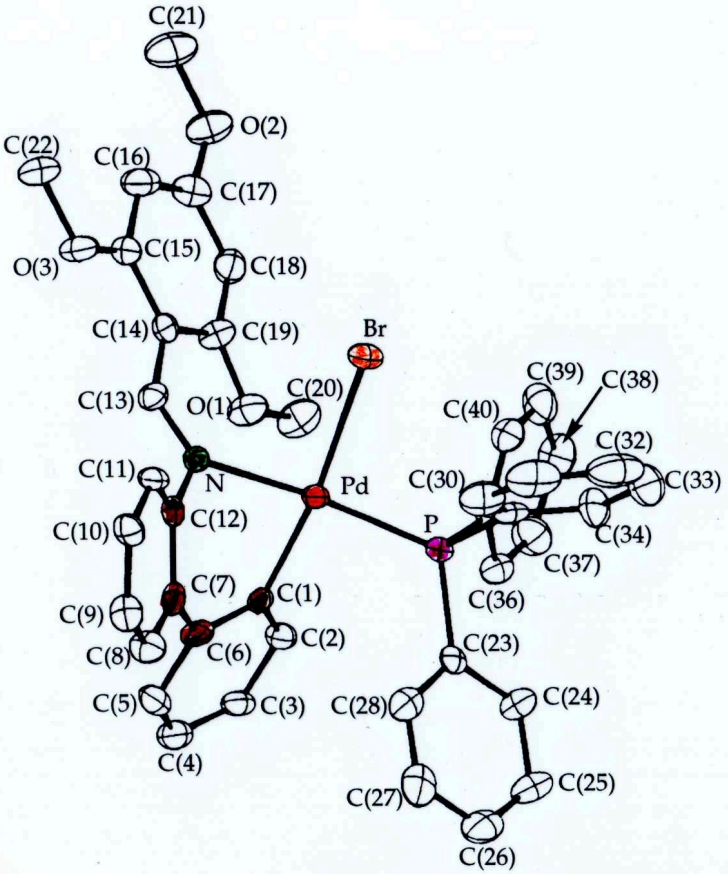


3d

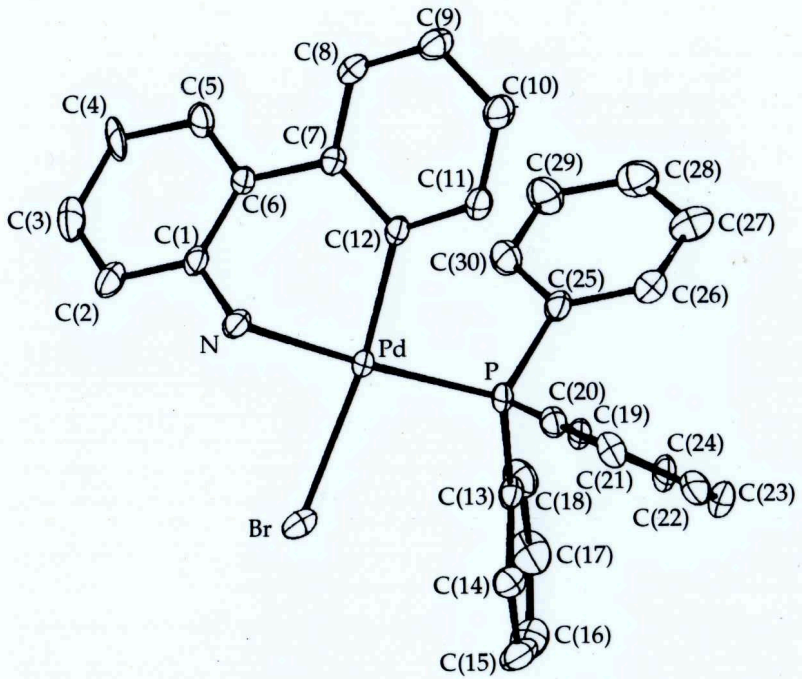


Estructures cristal·lines dels compostos 3a i 3d.

3a



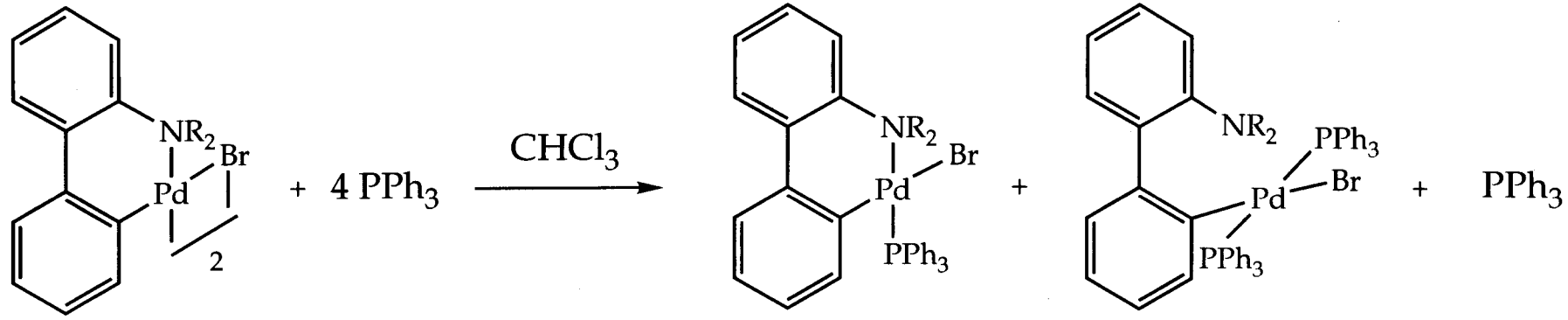
3d



Desviacions respecte el pla de coordinació del pal·ladi (Å):

Pd = -0,042	Pd = -0,005
Br = -0,096	Br = 0,013
P = 0,120	P = -0,011
N = 0,144	N= -0,014
C(1) = -0,127	C(12) = 0,017

Reaccions amb trifenilfosfina en relació 1 a 4.



R_2 : =CH-2,4,6-$(OCH_3)_3$-C_6H_2 (**2a**)

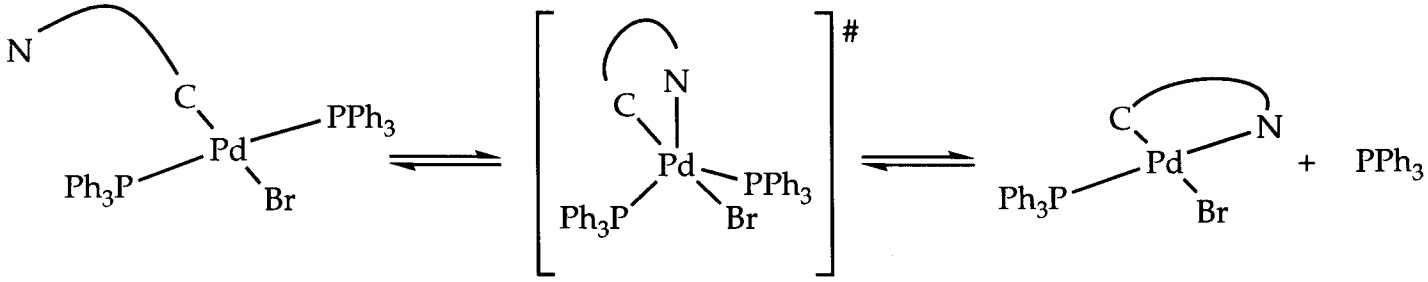
R_2 : =CH-2,6-Cl_2-C_6H_3 (**2b**)

R_2 : =CH-2,6-F_2-C_6H_3 (**2c**)

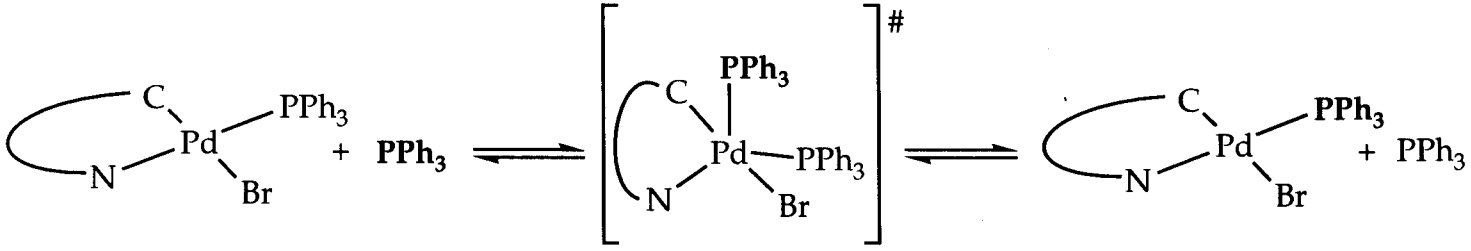
R : H (**2d**)

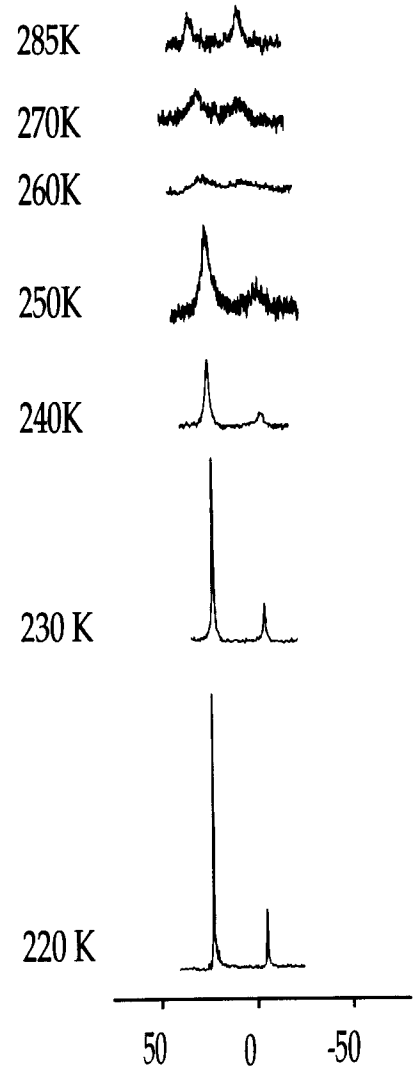
$^{31}P\ \{^{1}H\}$ RMN a temperatura variable de la reacció: 2d + 4,5 PPh_3

Equilibri 1

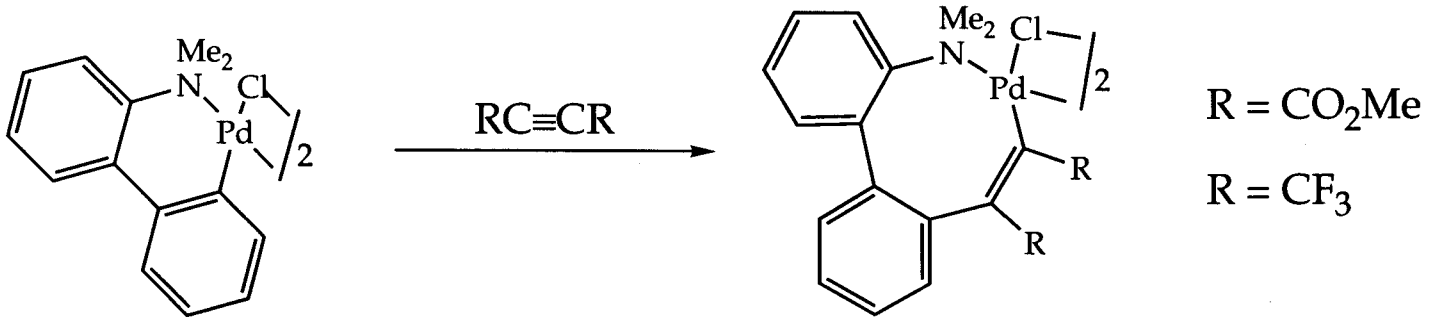


Equilibri 2



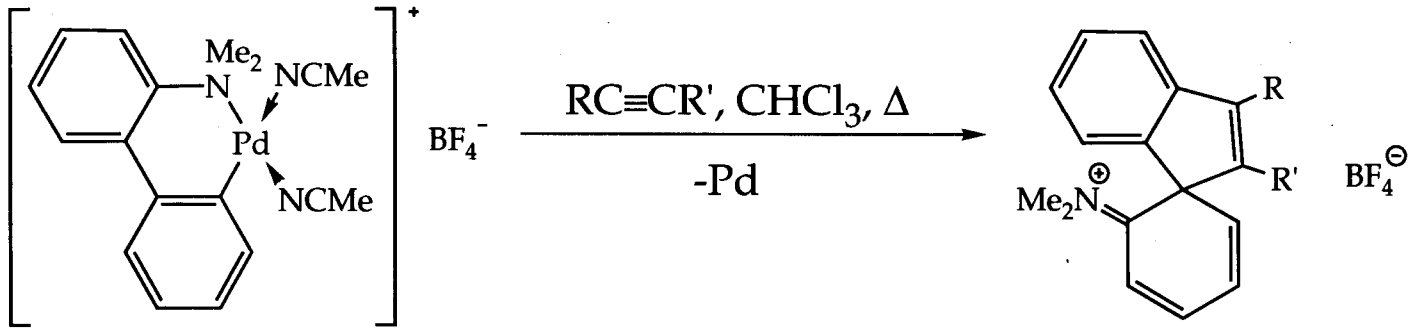


Reactivitat del dímer ciclopal·ladat de la N,N-dimetil-2-fenilanilina amb alquins.



R = CO_2Me

R = CF_3



R, R' = ^tBu, Me

R = R' = CO_2Me

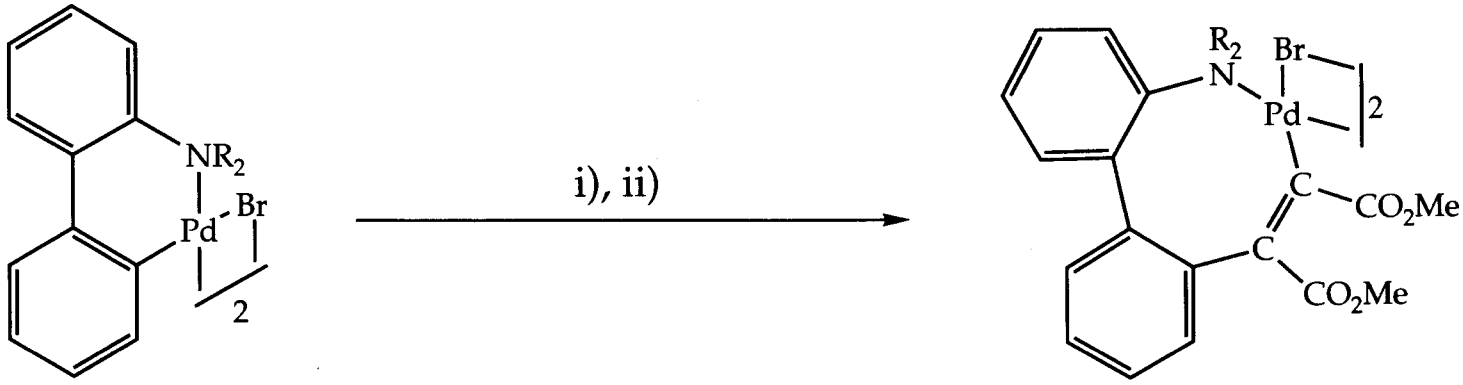
R, R' = Ph, $CH(OEt)_2$

R = R' = Ph

R, R' =Ph, CO_2Et

R, R' = Ph, CHO

Reacció de monoinserció de butindioat de dimetil.



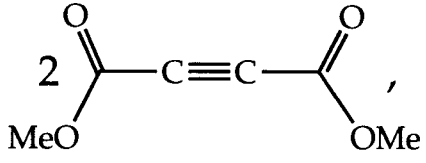
4a-4d

R_2: =CH-2,4,6-$(OCH_3)_3$-C_6H_2 (**2a**)

R_2: =CH-2,6-Cl_2-C_6H_3 (**2b**)

R_2: =CH-2,6-F_2-C_6H_3 (**2c**)

R: H (**2d**)

i) 2  , $CHCl_3$

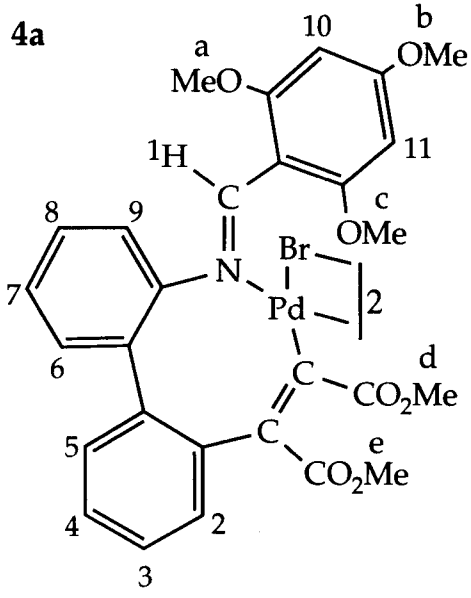
- **2a**: reflux, 24h.
- **2b**: 0°C, 72 h.
- **2c**: 0°C, 48 h.
- **2d**: 0°C, 24 h.

ii) SiO_2 flash, $CHCl_3$/MeOH

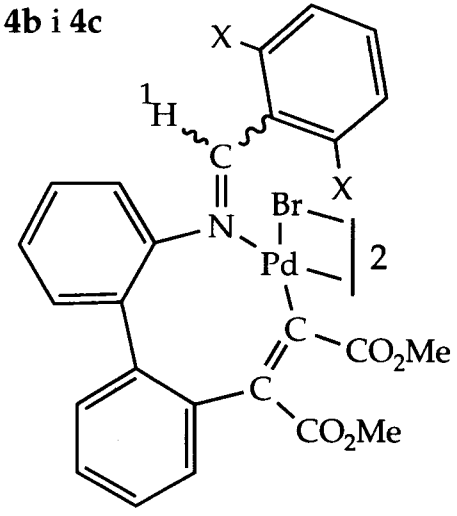
- **4a-4c**: 100/2
- **4d**: 100/4

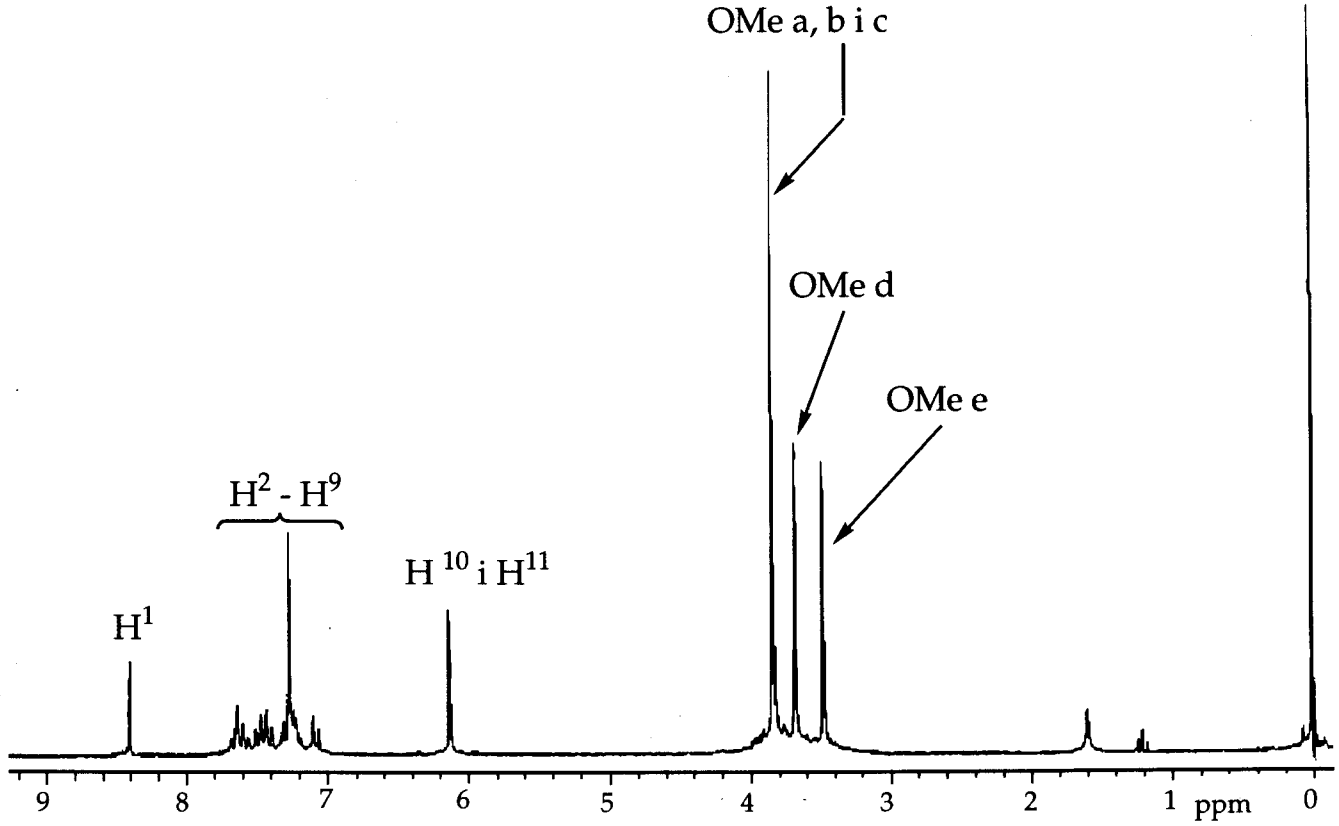
^{1}H RMN de 4a; i de 4b i 4c a la zona de protons metínics.

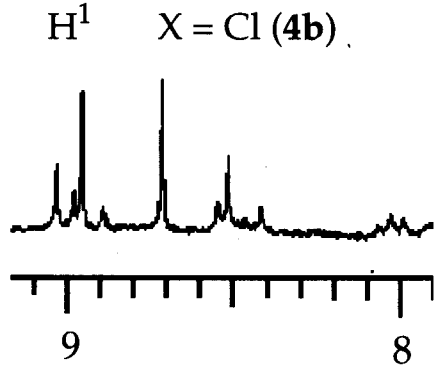
4a

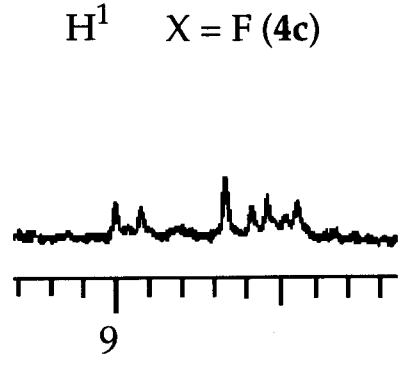


4b i 4c

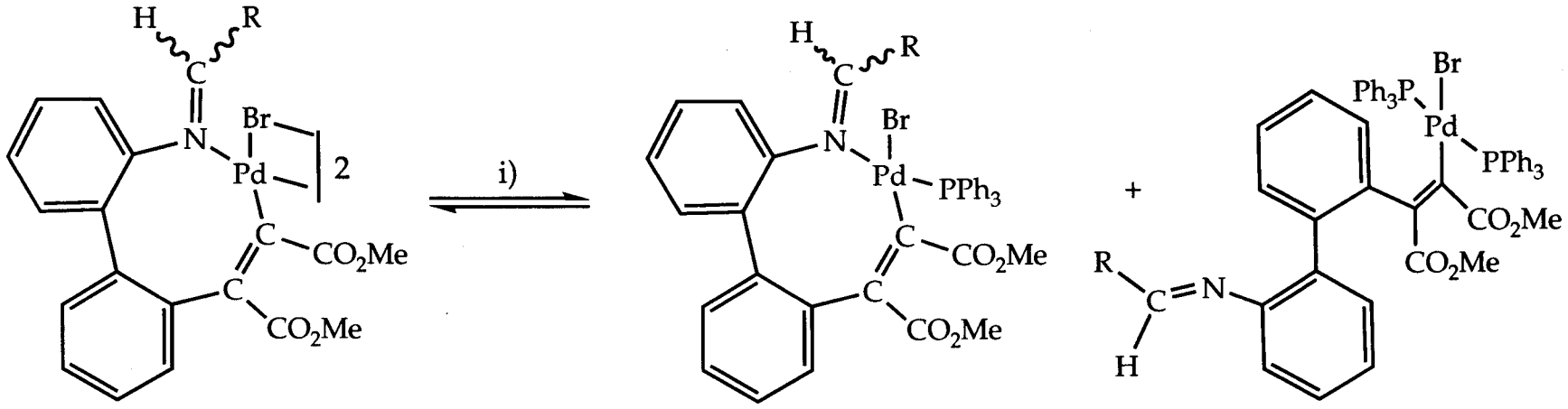








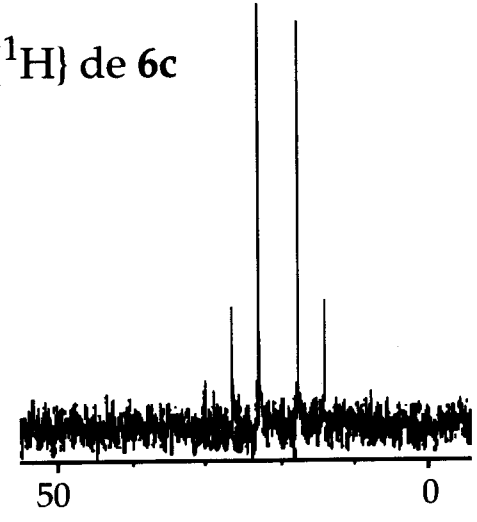
Reaccions dels dímers insertats 4a-c amb excés de PPh_3.



R = 2,4,6-$(CH_3O)_3C_6H_2$ (**4a**)	**5a**	1 : 2	**6a**
R = 2,6-$Cl_2C_6H_3$ (**4b**)	**5b**	1 : 12	**6b**
R = 2,6-$F_2C_6H_3$ (**4c**)			**6c**

i) 4 PPh_3, THF, 0°C { **4a**: 24 h. / **4b**, **4c**: 6h.

RMN $^{31}P\{^1H\}$ de **6c**



Estructura proposada per a 6c i ROESY ^{1}H-^{1}H.