Universitat Autònoma de Barcelona

SÍNTESI d'ÀCIDS CIANOCARBOXÍLICS: HIDROCARBOXILACIÓ i DEUTERIOCARBOXILACIÓ CATALÍTICA SELECTIVA. DESENVOLUPAMENT de FOSFINES i COMPLEXOS de PAL·LADI i PLATÍ

ANNEX

TESI DOCTORAL

Oriol Vallcorba Valls

2010

Dirigida per:
Juli Real Obradors

Programa de doctorat en Catàlisi Homogènia
Departament de Química
Facultat de Ciències

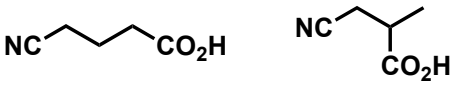
Annex

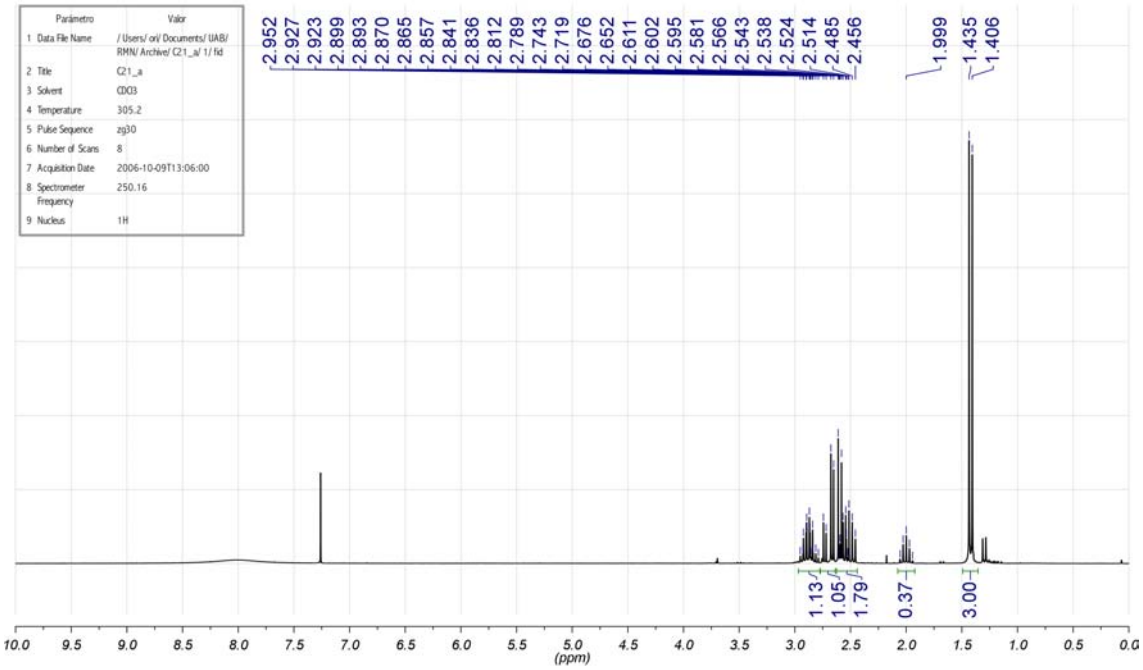
ANNEX

1 Caracterització dels productes d'hidrocarboxilació de substrats nitrogenats

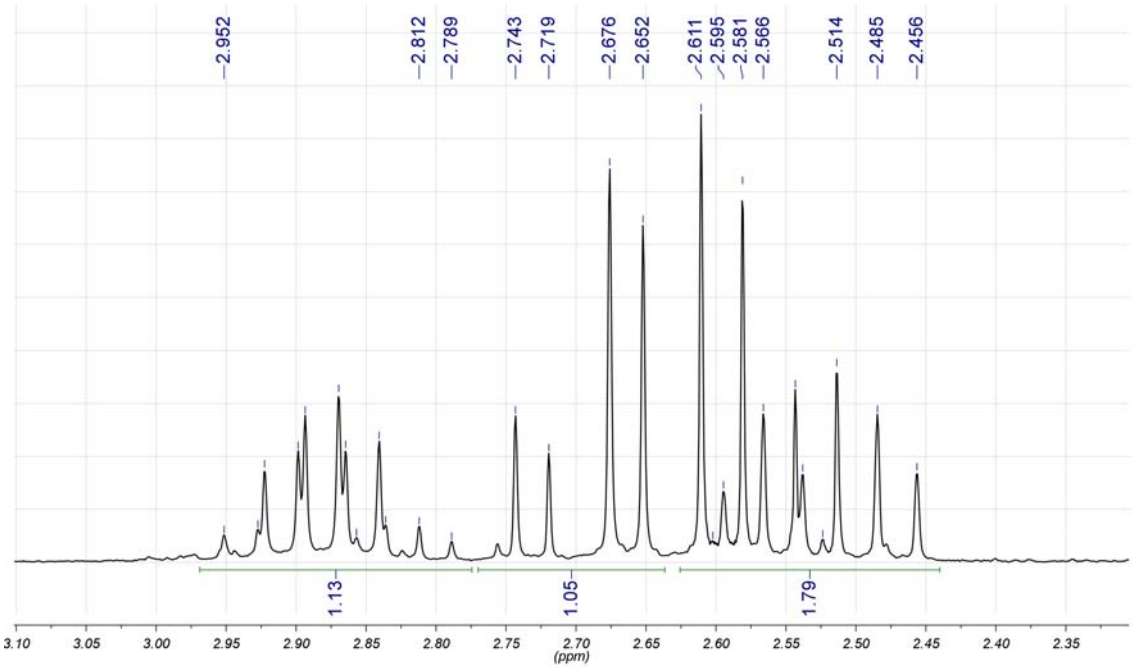
1.1 Àcid 3-ciano-2-metilpropanoic (A2β) i àcid 4-cianobutanoic (A2γ), barreja amb proporció 82:18.

^{1}H-RMN (250 MHz, rt, $CDCl_3$):

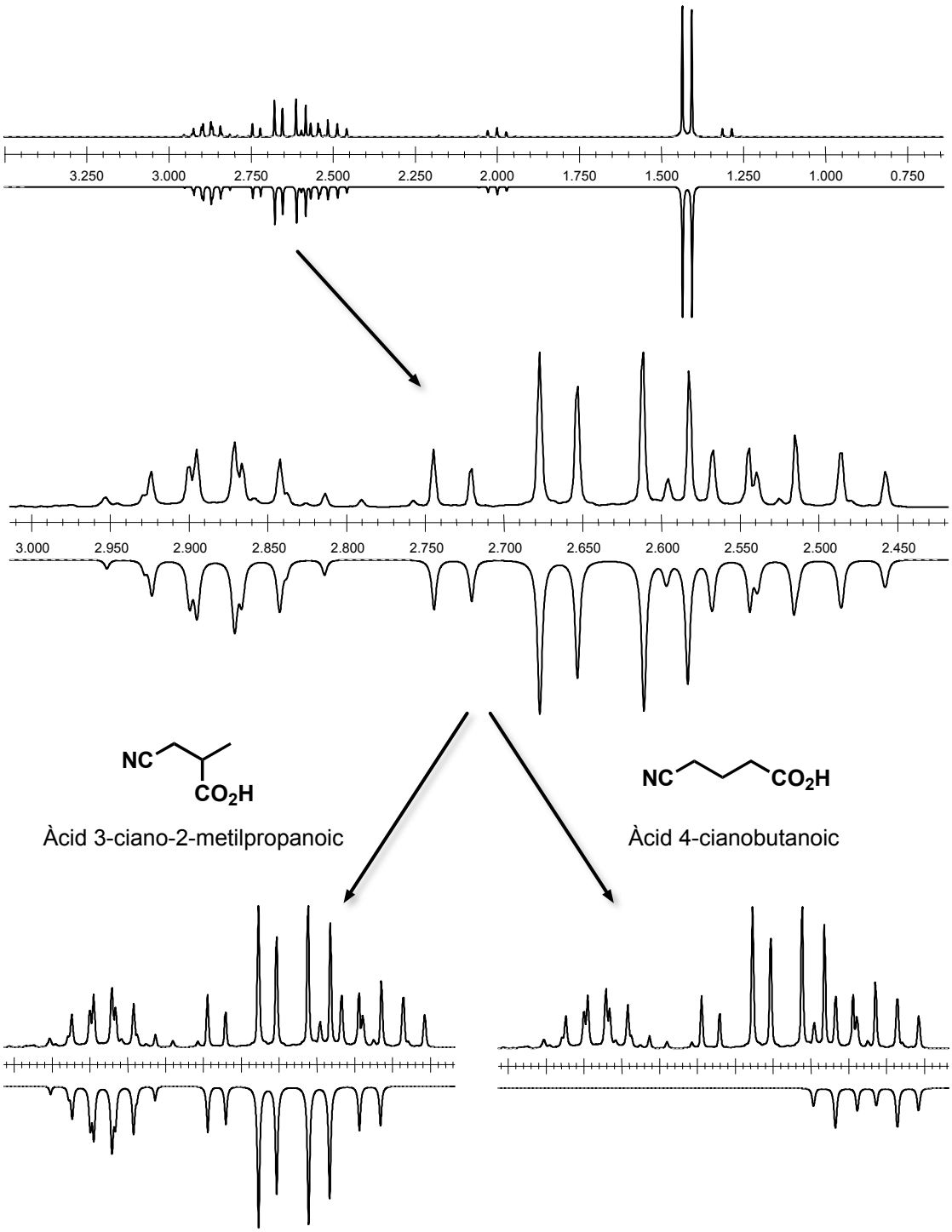




Ampliació de la zona δ 2.30 – 3.10:



Simulació de l'espectre anterior (barreja A1β i A1γ amb proporció 82:18) utilitzant el programa gMNR 4.0:



Acid 3-ciano-2-metilpropanoic:

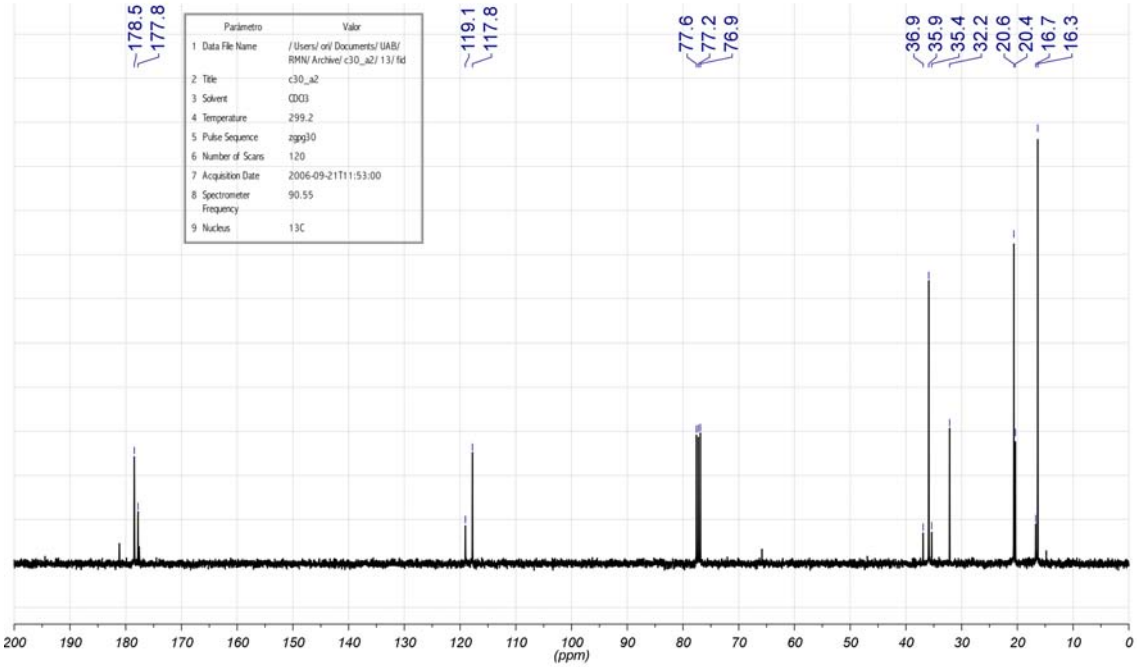
	Nucli	n	δ	J1	J2	J3
1	1H	3	1.421			
			met			

2	1H	1	2.881	7.25		
			c	Jmc		
3	1H	1	2.691	0.00	5.73	
			a	Jam	Jac	
4	1H	1	2.573	0.00	7.25	16.76
			b	Jbm	Jbc	Jba

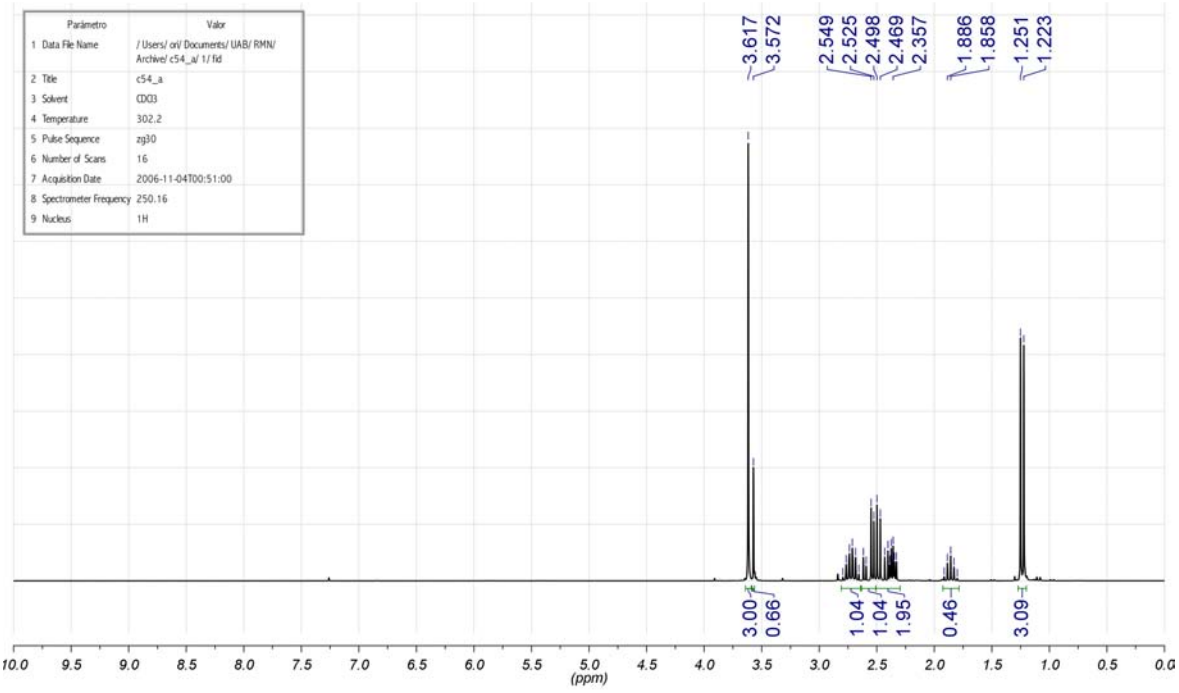
Àcid 4-cianobutanoic:

	Nucli	n	δ	J1	J2
1	1H	2	2.567		
			alfa		
2	1H	2	2.001	7.25	
			beta	Jbeal	
3	1H	2	2.485	0.00	7.00
			gamma	Jgaal	Jgabe

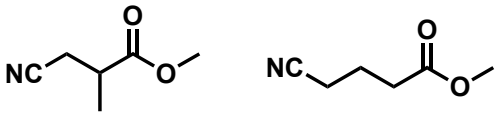
$^{13}C\{^{1}H\}$-RMN (63 MHz, rt, $CDCl_3$):



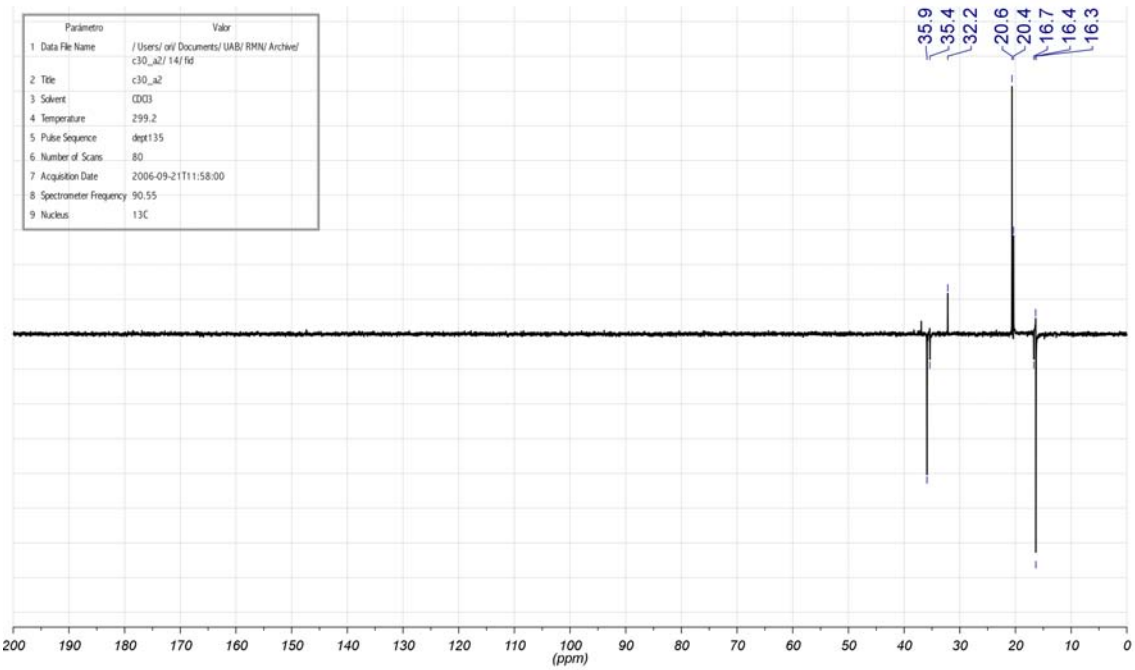
$^{13}C\{^{1}H\}$ RMN DEPT 135 (63 MHz, rt, $CDCl_3$):



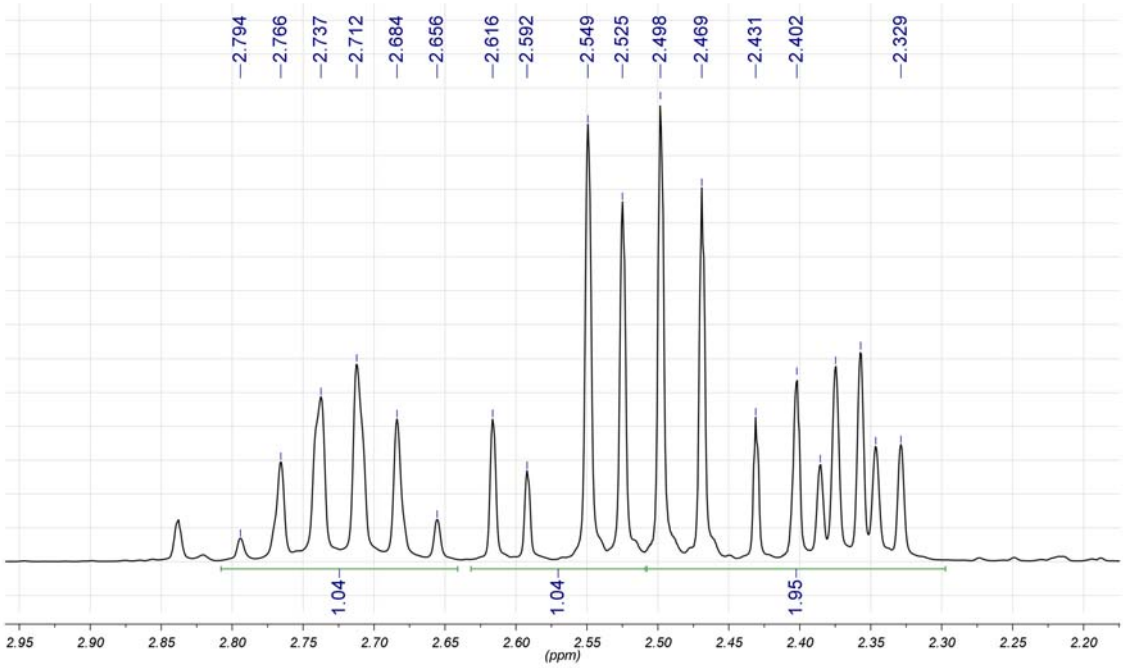
1.2 3-ciano-3-metilpropanoat de metil (A2βMe) i 4-cianobutanoat de metil (A2γMe), barreja amb proporció 82:18.



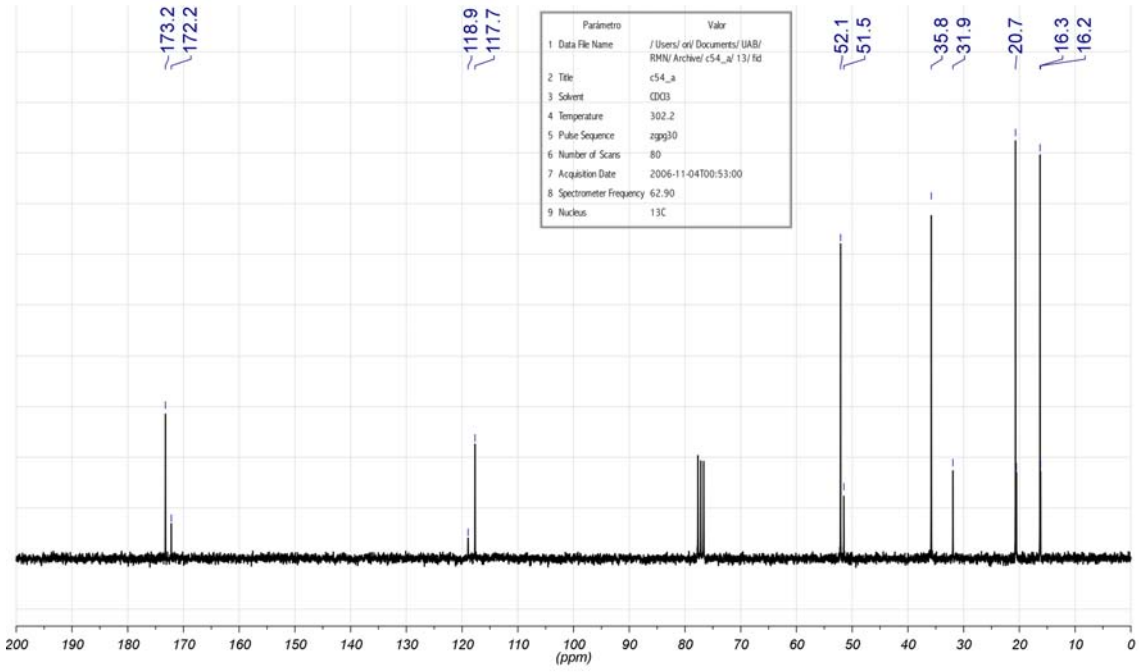
^{1}H RMN (250 MHz, rt, $CDCl_3$):



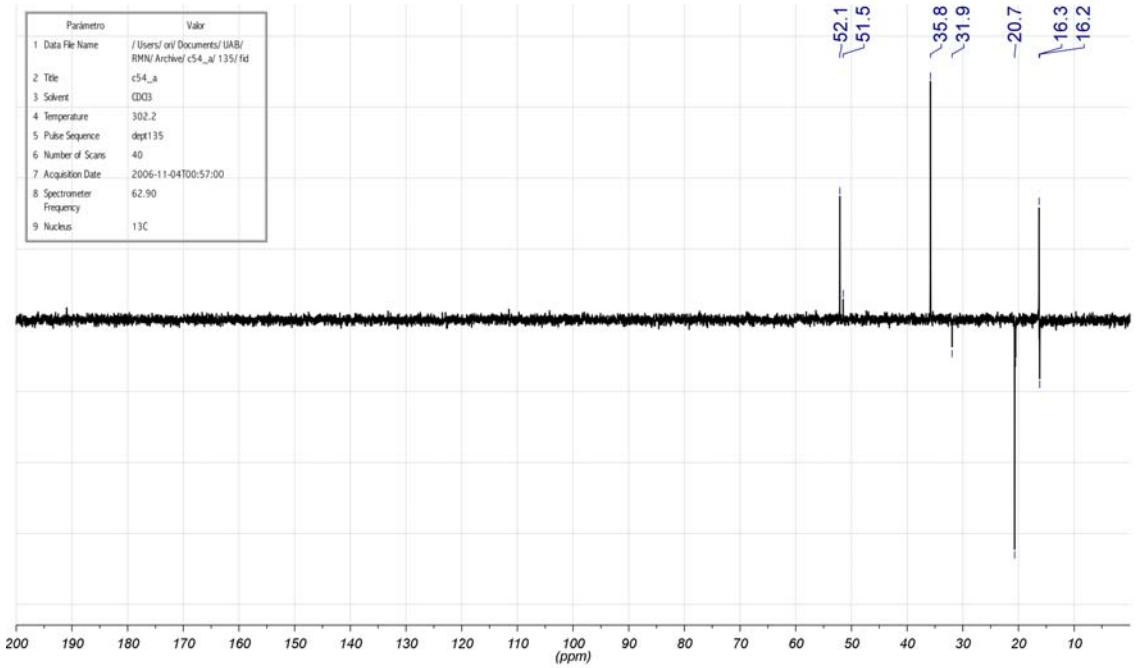
Ampliació de la zona δ 2.15 – 2.95:



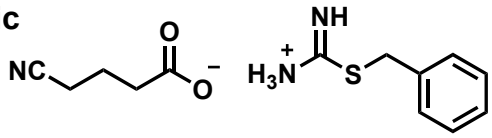
$^{13}C\{^{1}H\}$ RMN (63 MHz, rt, $CDCl_3$):



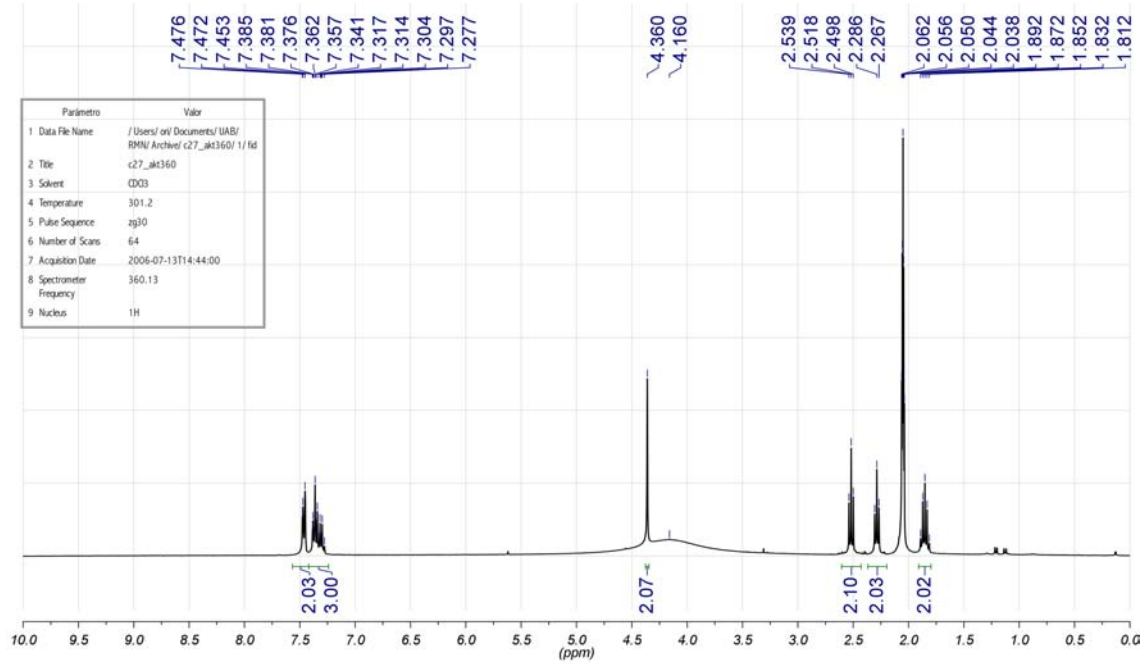
$^{13}C\{^{1}H\}$ RMN DEPT 135 (63 MHz, rt, $CDCl_3$):



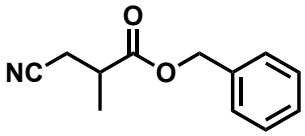
1.3 Sal d'isotiouroni de l'àcid 4-cianobutanoic



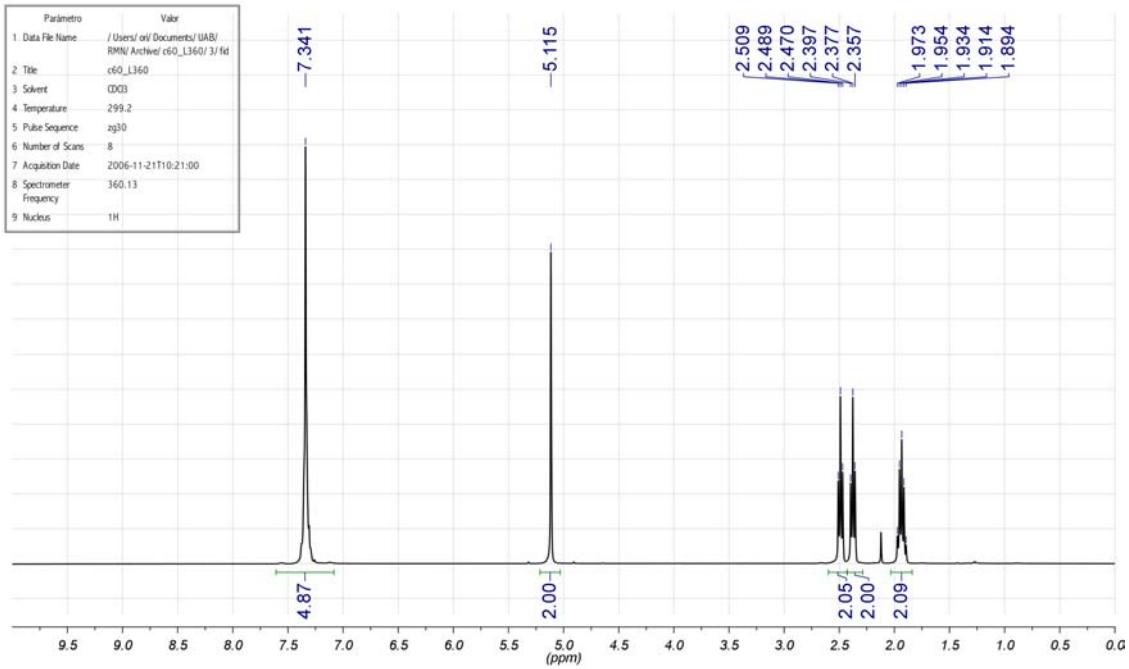
^{1}H RMN (360 Mhz, rt, Acetona-d_6):



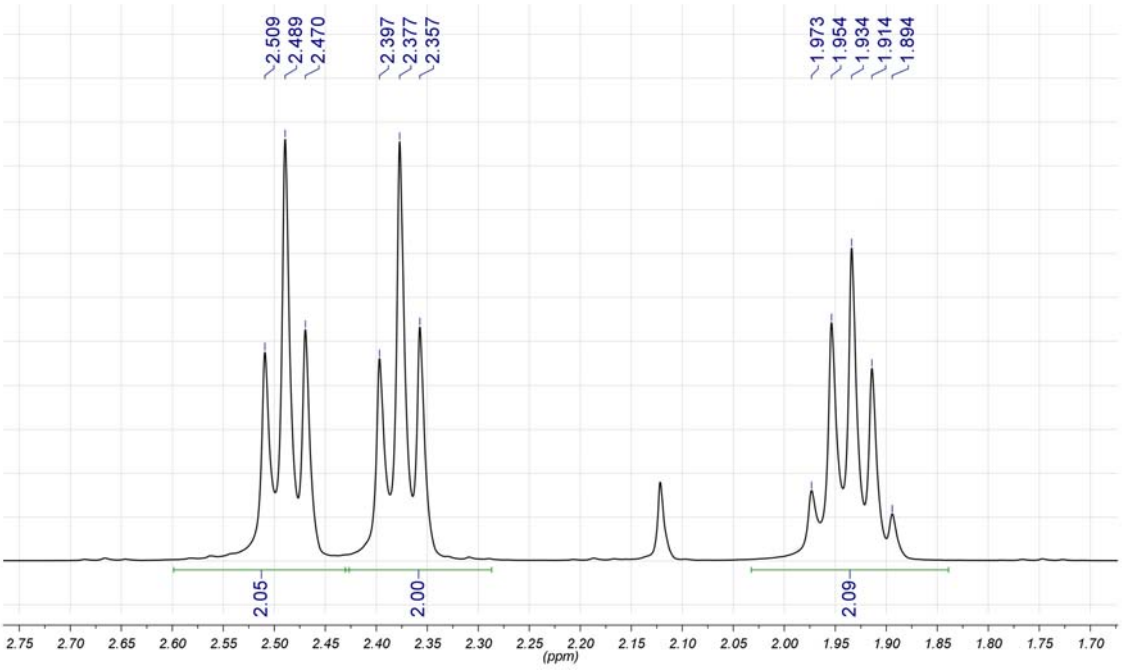
1.4 3-ciano-2-metilpropanoat de benzil (A2βBn)



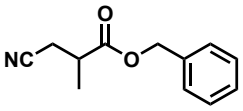
^{1}H RMN (360 Mhz, rt, $CDCl_3$):

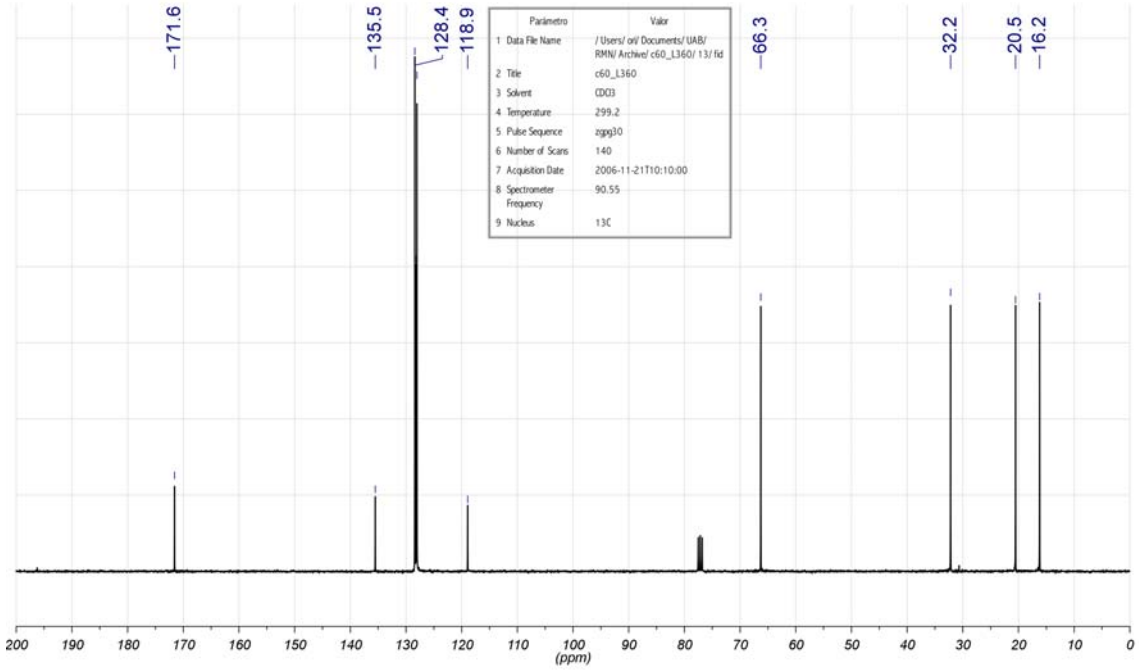


Ampliació de la zona δ 2.35 – 3.05:

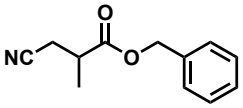


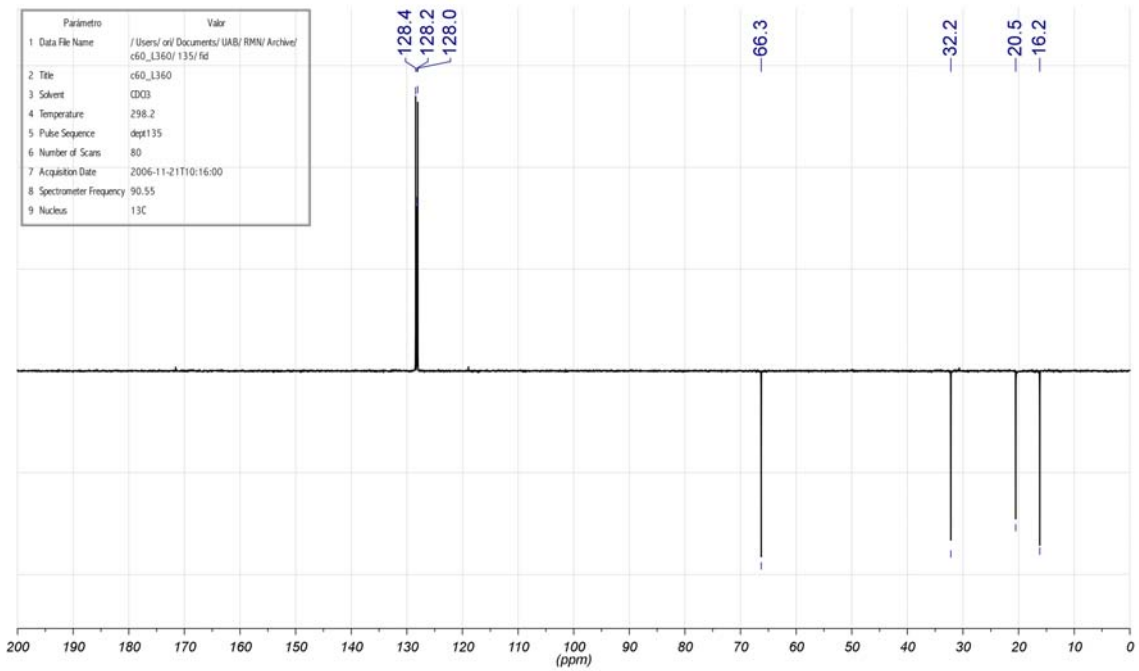
$^{13}C\{^{1}H\}$ RMN (90 MHz, rt, $CDCl_3$):



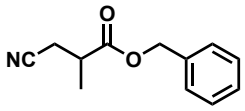


$^{13}C\{^{1}H\}$ RMN DEPT 135 (90 MHz, rt, $CDCl_3$):





HRMS (ESI+):

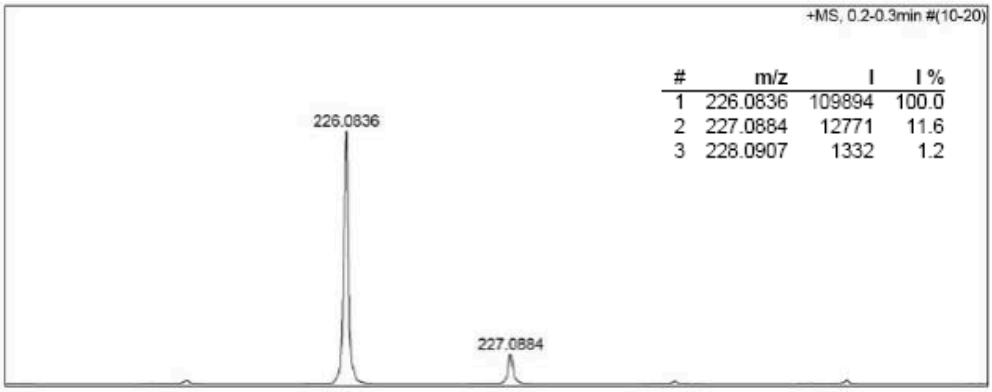


Analysis Info

Analysis Name	D:\temp\29-11-06-000010.D	Acquisition Date	29/11/2006 12:27:36
Method	QTOF-FI2-ESIpos-100-600-focusoff_SAQ.m	Operator	SAQ
Sample Name		Instrument / Ser#	micrOTOF-Q 28
Comment	C56-aR (6EM302-1) // ESI+. Dó ca 2ppm en MeOH. // O. VALLCORBA.		

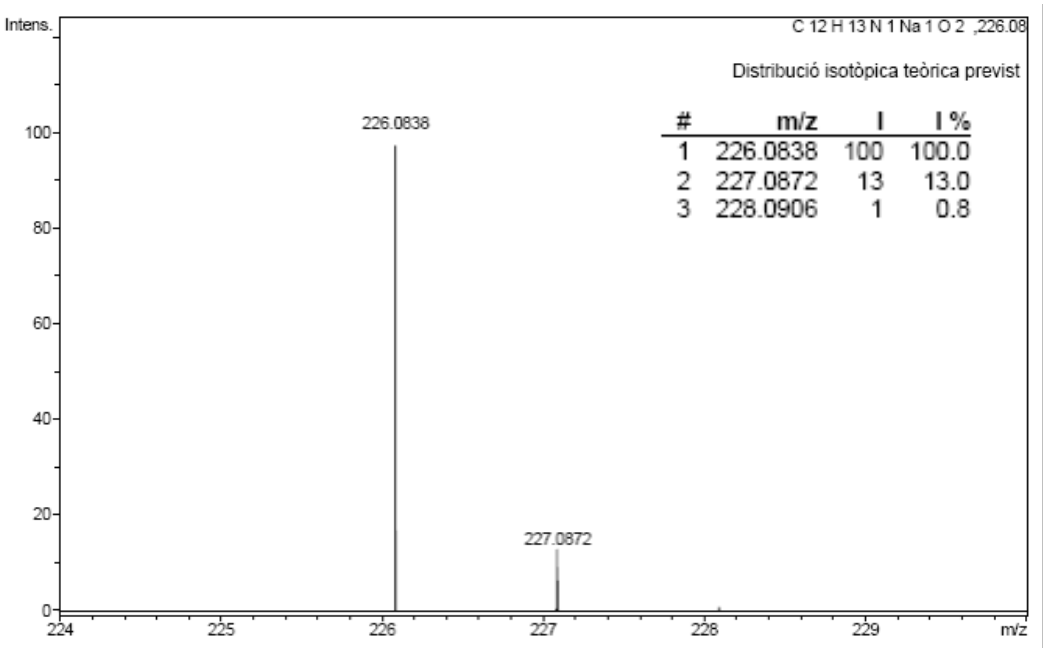
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	900 m/z	Set Collision Cell RF	145.0 Vpp	Set Divert Valve	Waste



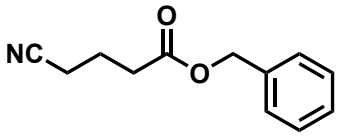
#	m/z	I	I %
1	226.0836	109894	100.0
2	227.0884	12771	11.6
3	228.0907	1332	1.2

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 8 H 9 N 7 Na 1	0.002	226.0812	-10.90	-12.15	-2.46	7.50	ok	even
C 9 H 12 N 3 O 4	0.003	226.0822	-6.17	-7.15	-1.40	5.50	ok	even
C 10 H 8 N 7	0.011	226.0836	-0.26	-1.69	-0.06	10.50	ok	even
C 12 H 13 N 1 Na 1 O 2	0.011	226.0838	0.98	0.14	0.22	6.50	ok	even

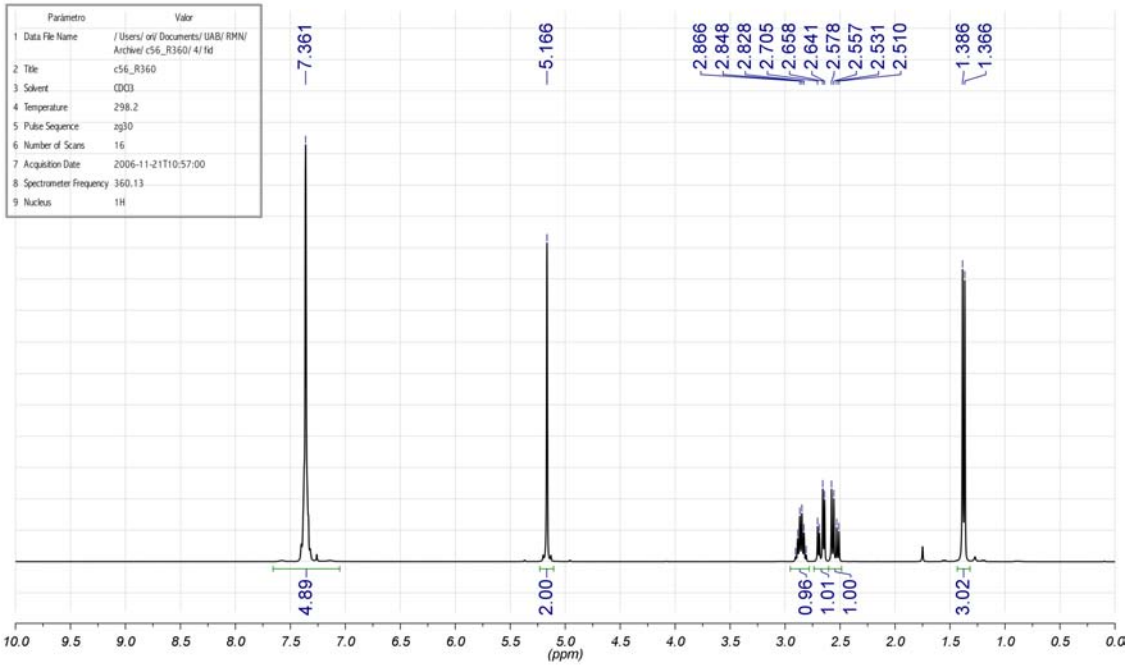


#	m/z	I	I %
1	226.0838	100	100.0
2	227.0872	13	13.0
3	228.0906	1	0.8

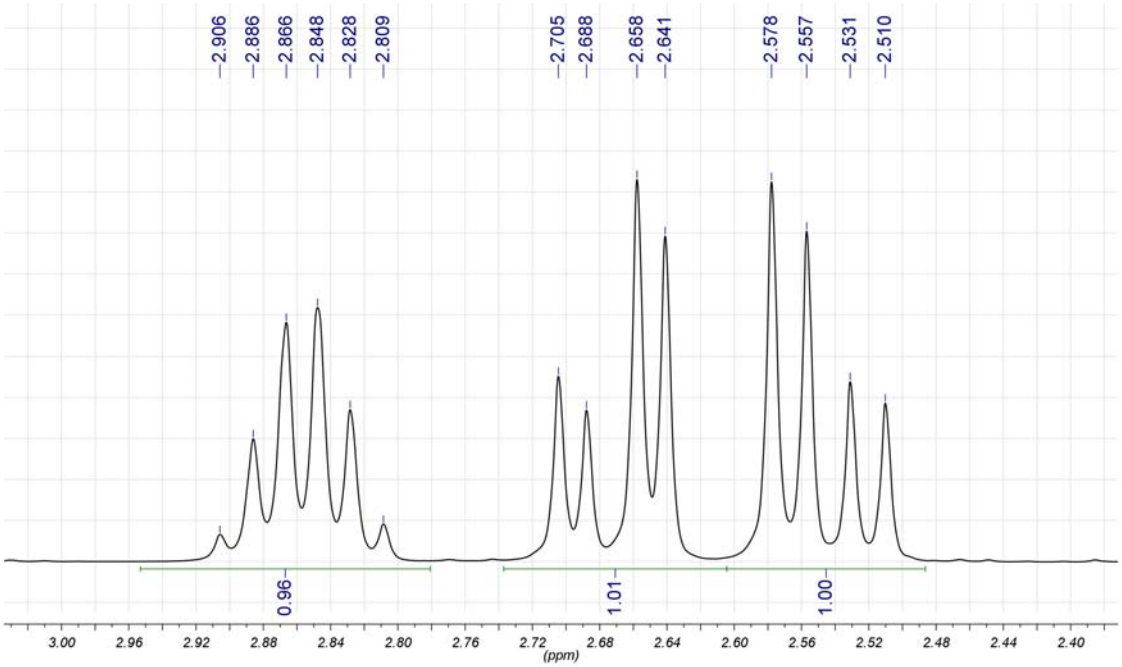
1.6 4-cianobutanoat de benzil (A2γBn)



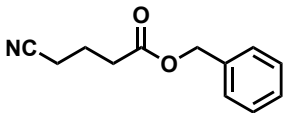
^{1}H RMN (360 MHz, rt, $CDCl_3$):

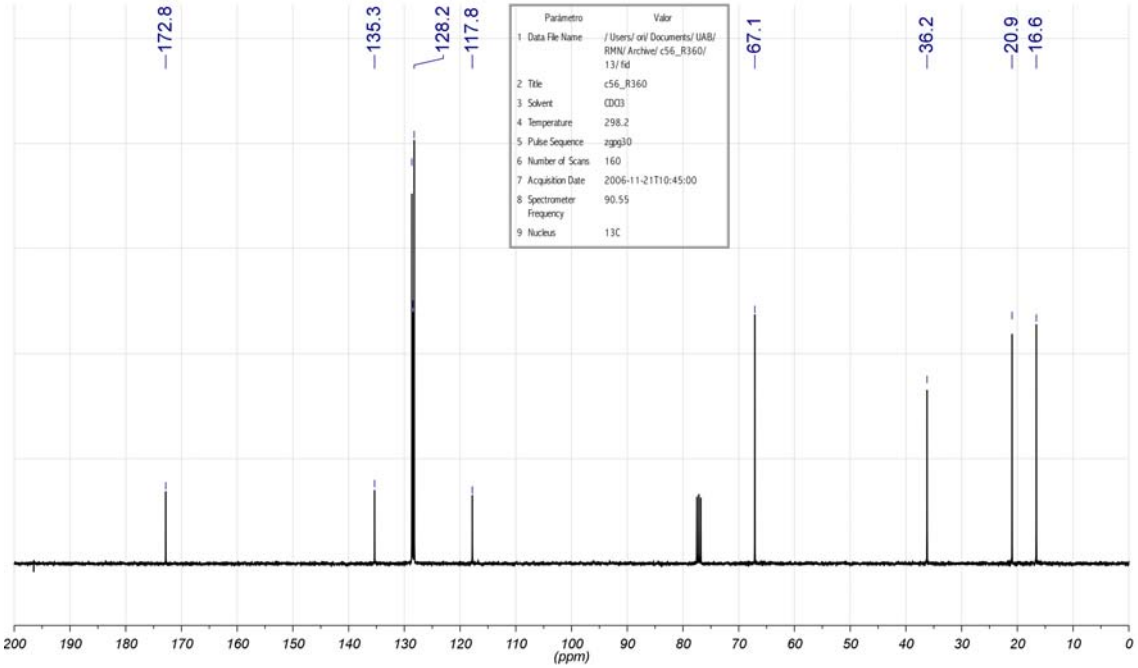


Ampliació de la zona δ 1.70 – 2.75:

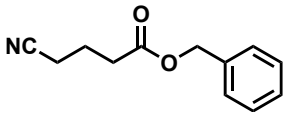


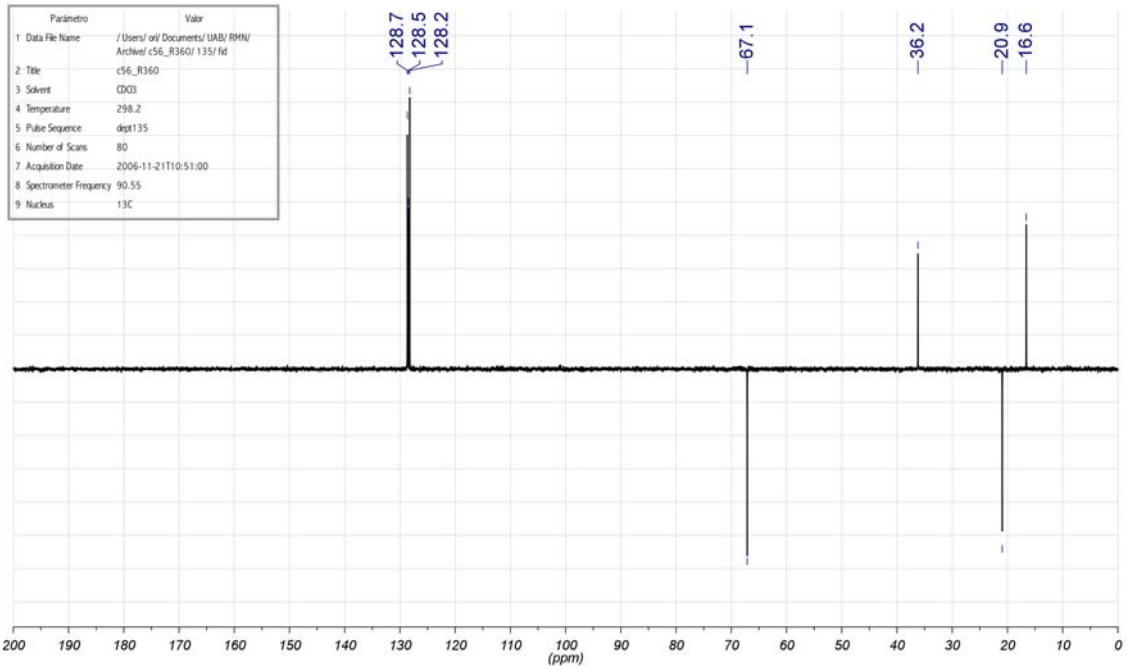
$^{13}C\{^{1}H\}$ RMN (90 MHz, rt, $CDCl_3$):



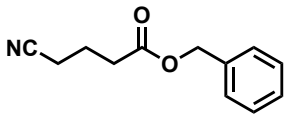


$^{13}C\{^{1}H\}$ RMN DEPT 135 (90 MHz, rt, $CDCl_3$):





HRMS (ESI+):

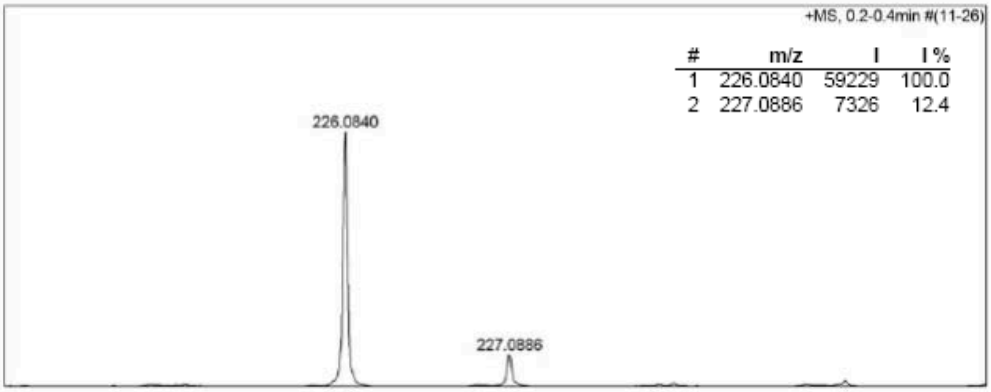


Analysis Info

Analysis Name	D:\temp\29-11-06-000004.D	Acquisition Date	29/11/2006 11:39:08
Method	QTOF-FI2-ESIpos-100-600-focusoff_SAQ.m	Operator	SAQ
Sample Name		Instrument / Ser#	micrOTOF-Q 28
Comment	C60-aL (6EM302-2) // ESI+. Dó ca 2ppm en MeOH. // O. VALLCORBA.		

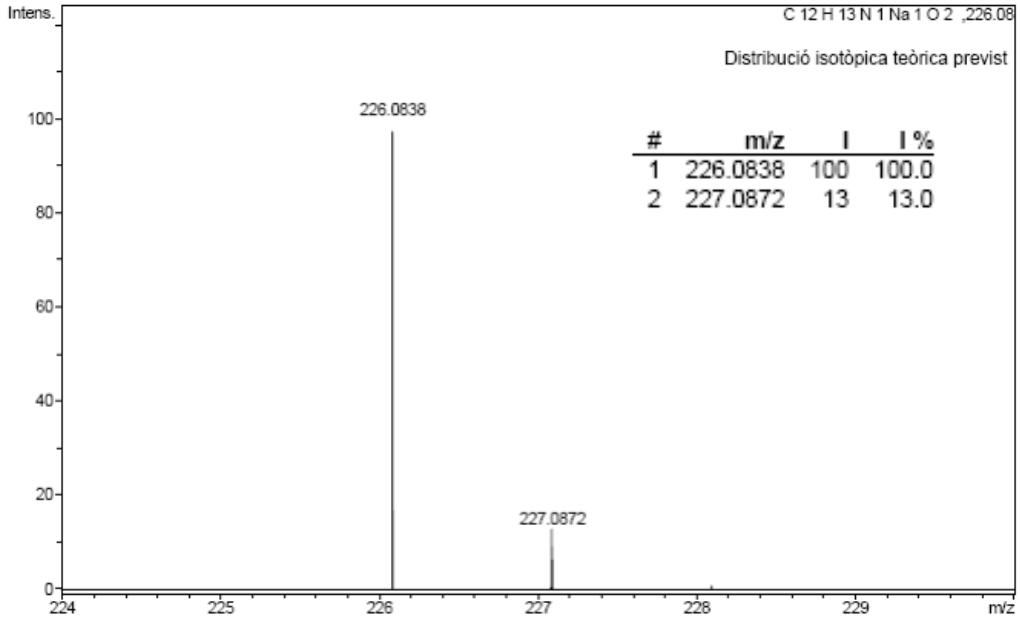
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.0 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	900 m/z	Set Collision Cell RF	145.0 Vpp	Set Divert Valve	Waste



#	m/z	I	I %
1	226.0840	59229	100.0
2	227.0886	7326	12.4

Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e⁻
C 10 H 8 N 7	0.008	226.0836	-1.91	-3.11	-0.43	10.50	ok	even
C 12 H 13 N 1 Na 1 O 2	0.010	226.0838	-0.67	-1.35	-0.15	6.50	ok	even
C 9 H 12 N 3 O 4	0.011	226.0822	-7.82	-8.71	-1.77	5.50	ok	even
C 14 H 12 N 1 O 2	0.021	226.0863	9.97	9.11	2.25	9.50	ok	even



#	m/z	I	I %
1	226.0838	100	100.0
2	227.0872	13	13.0

3 Espectroscòpia de masses (SIM) dels productes A2γBn i A2βBn

A la taula a continuació (taula A-1) es mostren les abundàncies absolutes per pes molecular de cada parella de productes de reacció. Es mostra el número d'experiment (Exp), si es tracta de l'èster ramificat (A2βBn) o el lineal (A2γBn) i l'abundància per cada pic de massa (M(X), on X és el pes molecular). Aquestes dades han estat enregistrades per GC-MS mitjançant la tècnica Single Ion Monitoring (SIM) utilitzant el rang 200 – 210 com a zona d'observació.

Taula A-1. Resultats dels CG-MS SIM pels productes de deuteriocarboxilació del cianur d'al·lil.

Exp	Èster	M(202)	M(203)	M(204)	M(205)	M(206)	M(207)	M(208)
ebzB	**A2βBn**	17	1000	135	12	1	0	0
	A2γBn	7	1000	135	12	1	1	0
11	**A2βBn**	10	582	1000	423	97	13	1
	A2γBn	5	621	1000	463	109	15	2
16	**A2βBn**	5	257	1000	662	218	28	3
	A2γBn	3	283	1000	602	182	23	2
17	**A2βBn**	4	230	1000	310	49	6	1
	A2γBn	2	269	1000	309	47	6	1
24	**A2βBn**	5	297	1000	179	23	3	0
	A2γBn	2	312	1000	168	19	3	1
27	**A2βBn**	3	187	1000	382	85	12	2
	A2γBn	2	220	1000	219	30	4	1
30	**A2βBn**	5	257	1000	150	16	2	0
	A2γBn	2	278	1000	143	15	3	0

3.1 Càlcul del grau d'incorporació de deuteri

Amb aquestes dades s'ha calculat el grau de deuteració per cadascun dels productes. Anomenarem als isotopòmers segons el nombre d'àtoms de deuteri incorporat com a dn, on n indica aquest nombre. El pes molecular dels èsters no deuterats és de M = 203, i aquest pes augmentarà en una unitat per cada deuteri incorporat. No obstant, cal destacar que els pics M+1, M+2, M+n, no provenen únicament degut a la incorporació de deuteri sinó que també afecta la quantitat de ^{13}C natural a la molècula. Als àcids

estudiats, degut a que no tenen un nombre massa elevat de carbonis, l'efecte del 13C natural és despreciable a partir de valors superiors a M+2.

A partir de la mostra no deuterada *ebzB* s'obté la distribució isotòpica natural del producte (presència ^{13}C), i es pot calcular la relació entre un pic M i un pic M+1 i M+2. En aquest estudi, etiquetarem aquestes relacions com a k_1 i k_2, que correspondran a:

$$k_1 = \frac{I(M+1)}{I(M)} = \frac{I(204)}{I(203)} = 0.135 \qquad k_2 = \frac{I(M+2)}{I(M)} = \frac{I(205)}{I(203)} = 0.012$$

Seguidament ja es poden calcular les quantitats de d0, d1 i d2 com:

$$I(M) = Q(d0)$$
$$I(M+1) = I(M) \cdot k_1 + Q(d1)$$
$$I(M+2) = I(M) \cdot k_2 + I(M+1) \cdot k_1 + Q(d2)$$

Així, s'obtenen les quantitats de producte sense incorporació de deuteri (Q(d0)), amb la incorporació d'un sol deuteri (Q(d1)) i amb la incorporació de dos deuteris (Q(d2)), que es poden normalitzar i expressar com un percentatge. La incorporació de dos deuteris és la màxima que s'observa als àcids estudiats però seguiria anàlogament el mateix raonament per calcular productes amb major deuteració. També es pot calcular el grau de deuteració (que expressarem com a $\bar{d}$) com la mesura de mols de deuteri per mol de producte:

$$\bar{d} = \frac{\%d1 + 2 \cdot (\%d2)}{100}$$

Els graus de deuteració obtinguts són:

Exp. 11	**PPh_3, DCl, P/Pd=2, 60 bar CO, 80 ºC (C_A= 96%)**	
	A2βBn (84%)	**A2γBn** (16%)
d0 =	32,62 %	33,43 %
d1 =	51,64 %	49,32 %
d2 =	15,75 %	17,25 %
$\bar{d}$ =	0.83	0.84

Exp. 16	**PPh_3, pTsOD, P/Pd=2, 60 bar CO, 80 ºC (C_A= 95%)**	
	A2βBn (76%)	**A2γBn** (24%)
d0 =	14,72 %	16,57 %
d1 =	55,28 %	56,30 %
d2 =	30,00 %	27,14 %
$\bar{d}$ =	1.15	1.10

Exp. 17	PPh_3, LiCl, P/Pd=2, 60 bar CO, 80 ºC (C_A= 51%)	
	A2βBn (81%)	**A2γBn** (19%)
d0 =	16,77 %	19,17 %
d1 =	70,66 %	68,67 %
d2 =	12,56 %	12,17 %
$\overline{d}$ =	0.96	0.93

Exp. 24	DPEphos, pTsOD, P/Pd=2, 60 bar CO, 100 ºC (C_A= 86%)	
	A2βBn (11%)	**A2γBn** (89%)
d0 =	22,89 %	24,02 %
d1 =	73,99 %	73,73 %
d2 =	3,12 %	2,25 %
$\overline{d}$ =	0.80	0.78

Exp. 27	DPEphos, DCl, P/Pd=2, 60 bar CO, 100 ºC (C_A= 70%)	
	A2βBn (6%)	**A2γBn** (94%)
d0 =	13,30 %	17,30 %
d1 =	69,30 %	76,30 %
d2 =	17,40 %	6,40 %
$\overline{d}$ =	0.95	0.89

Exp. 30	DPEphos, no acid, P/Pd=2, 60 bar CO, 100 ºC (C_A= 68%)	
	A2βBn (26%)	**A2γBn** (74%)
d0 =	20,82 %	22,33 %
d1 =	78,21 %	77,30 %
d2 =	0,97 %	0,37 %
$\overline{d}$ =	0,80	0,78

4 Espectres de ^2H RMN dels productes A2γBn i A2βBn

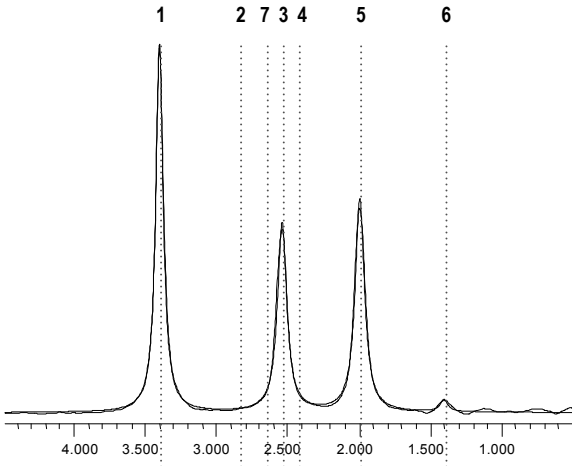
Les quantitats afegides de producte i patró a cada tub de RMN es mostren a la taula a continuació (taula A-2). Les dades més importants que serveixen per la posterior quantificació són els mmol d'acenaftè-d_{10} (a-d_{10}) i els mmol d'èster afegits. Amb aquestes dades i la integral de l'espectre es pot obtenir la relació integral/deuteri i quantificar en valor absolut el nombre de deuteris exactes en cada posició de la molècula. A la taula es mostra l'experiment i producte als quals correspon cada fila i la quantitat de deuteri que conté l'èster afegit, que només s'utilitza per saber la quantitat aproximada d'acenaftè-d_{10} que hem d'afegir per no provocar una gran diferència d'intensitats entre producte i patró en el futur espectre de ressonància. Aquesta quantitat s'ha obtingut multiplicant la quantitat estequiomètrica del patró (considerant els 4 deuteris alquílics) per un factor de 0.8 (es mostren els valors de pes reals, per això la relació no és exacta).

Taula A-2. Quantitats afegides a la preparació dels tubs per ^2H-RMN.

Exp	producte	$\bar{d}$ (MS)	mg èster	mmol èster	mmol "D" èster (MS)	mg a-d_{10}	mmol a-d_{10}	mmol "D" a-d_{10}
11	**A2γBn**	0.839	95.1	0.469	0.373	12.2	0.074	0.297
	A2βBn	0.831	100.8	0.497	0.392	12.9	0.079	0.314
16	**A2γBn**	1.106	94.2	0.464	0.487	15.5	0.094	0.377
	A2βBn	1.153	95.7	0.471	0.516	15.9	0.097	0.387
17	**A2γBn**	0.930	39.0	0.192	0.170	5.6	0.034	0.136
	A2βBn	0.959	99.6	0.491	0.446	14.6	0.089	0.355
24	**A2γBn**	0.782	95.6	0.471	0.350	11.7	0.071	0.285
	A2βBn	0.802	89.5	0.441	0.336	10.8	0.066	0.263
27	**A2γBn**	0.951	96.7	0.476	0.430	13.4	0.082	0.326
	A2βBn	0.891	47.0	0.232	0.196	6.1	0.037	0.149
30	**A2γBn**	0.780	99.9	0.492	0.365	11.9	0.072	0.290
	A2βBn	0.802	99.9	0.492	0.375	12.3	0.075	0.299

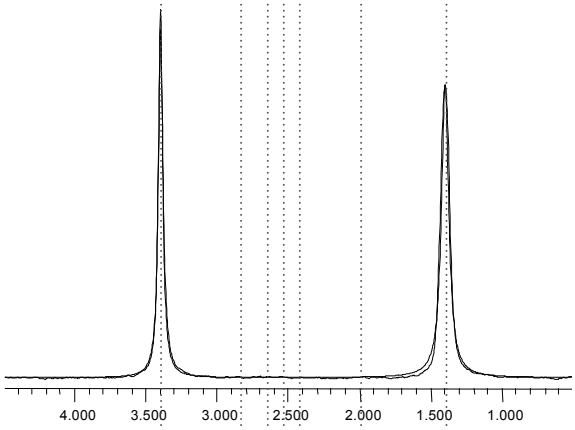
Es mostren els mg d'èster que s'han afegit a cada tub i l'estimació dels mmol de deuteri que conté (a partir del MS-SIM) i així poder afegir una quantitat d'acenaftè que contingui una proporció de deuteri aproximadament 0.8 vegades la del èster.

A continuació es mostren els espectres de ^2H-RMN (registrats a 77 MHz) superposats amb la simulació dels mateixos mitjançant el programa *gNMR v5.0.A2* Es mostren ordenats per reacció catalítica, amb l'espectre de l'èster lineal i del ramificat per cada reacció.



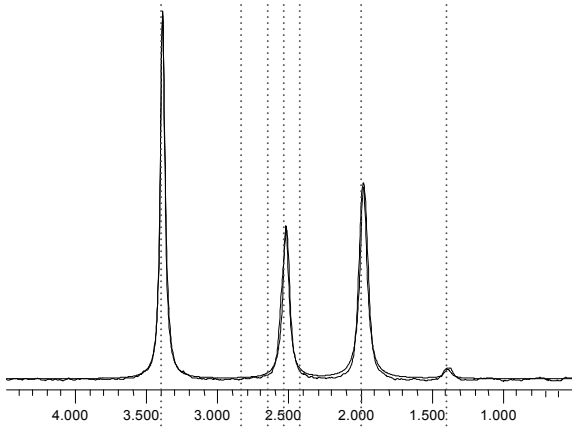
Exp 11 (92.2% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 4.73 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 3
δ= 2.549, w= 5.93 Hz, Integral Simulada = 0.644
Integral Experim. = 0.661
Pic 5
δ= 2.004, w= 5.99 Hz, Integral Simulada = 0.732
Integral Experim. = 0.714
Pic 6
δ= 1.396, w= 4.80 Hz, Integral Simulada = 0.034
Integral Experim. = 0.035



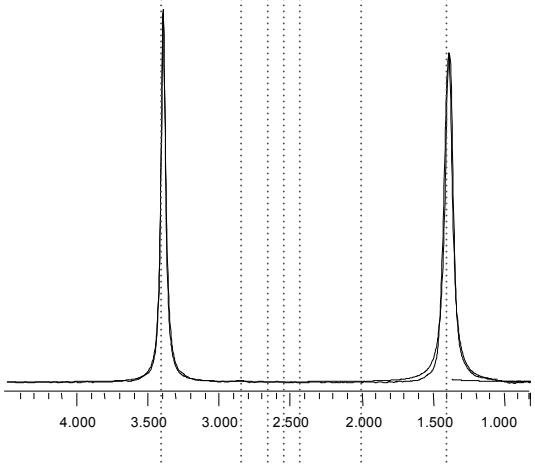
Exp 11 (99.6% de **A2βBn** per GC)

Pic 1
δ= 3.410, w= 2.75 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 6
δ= 1.413, w= 4.60 Hz, Integral Simulada = 1.330
Integral Experim. = 1.324



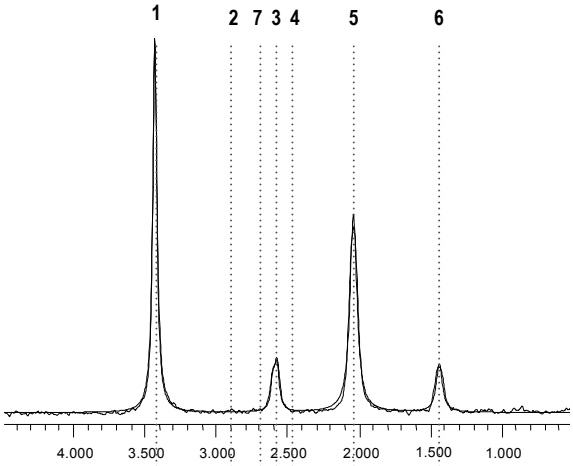
Exp 16 (93.3% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 2.80 Hz, Intensidad per Simulación = 1.000
Intensidad per Integración = 1.000
Pic 3
δ= 2.546, w= 3.92 Hz, Integral Simulada = 0.580
Integral Experim. = 0.587
Pic 5
δ= 2.001, w= 4.50 Hz, Integral Simulada = 0.835
Integral Experim. = 0.816
Pic 6
δ= 1.410, w= 4.80 Hz, Integral Simulada = 0.042
Integral Experim. = 0.046



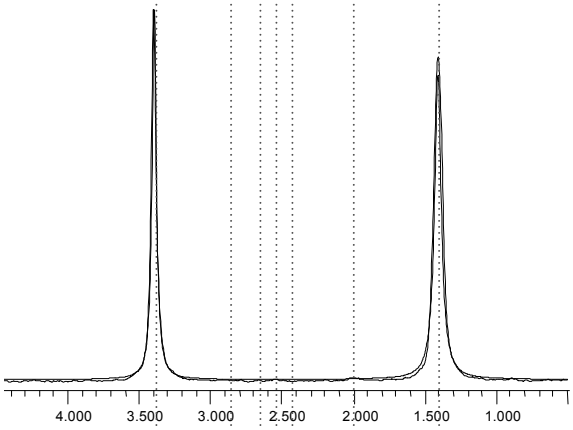
Exp 16 (98.3% de **A2βBn** per GC)

Pic 1
δ= 3.410, w= 2.83 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 6
δ= 1.407, w= 4.60 Hz, Integral Simulada = 1.450
Integral Experim. = 1.412



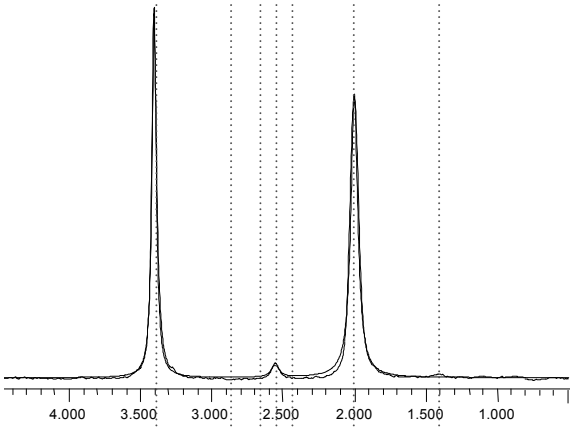
Exp 17 (75.8% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 2.66 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 3
δ= 2.582, w= 2.56 Hz, Integral Simulada = 0.203
Integral Experim. = 0.231
Pic 5
δ= 2.018, w= 4.41 Hz, Integral Simulada = 0.881
Integral Experim. = 0.826
Pic 6
δ= 1.417 , w= 3.93 Hz, Integral Simulada = 0.192
Integral Experim. = 0.202



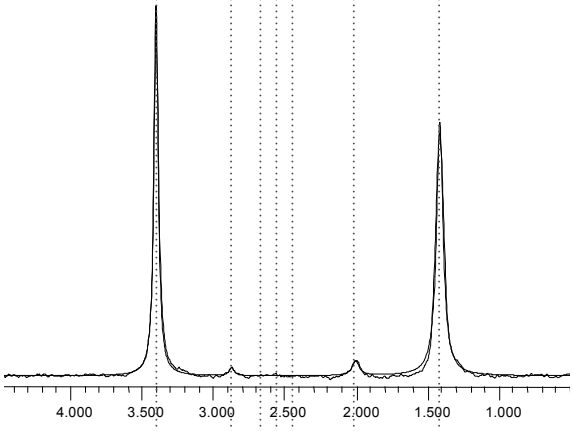
Exp 17 (99.4% de **A2βBn** per GC)

Pic 1
δ= 3.410, w= 2.72 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 6
δ= 1.420, w= 4.30 Hz, Integral Simulada = 1.300
Integral Experim. = 1.381



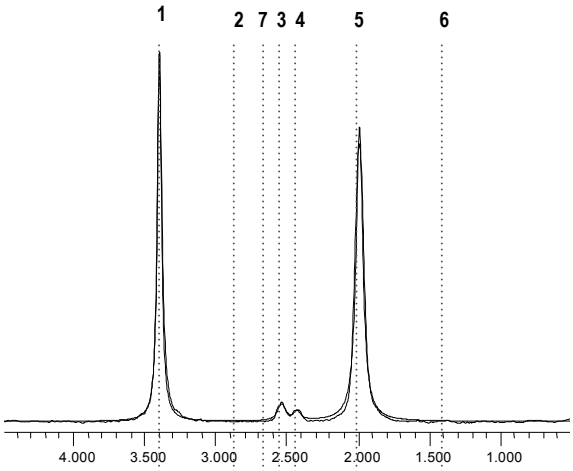
Exp 24 (98.0% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 2.67 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 3
δ= 2.561, w= 4.60 Hz, Integral Simulada = 0.065
Integral Experim. = 0.044
Pic 5
δ= 2.0097, w= 4.26 Hz, Integral Simulada = 1.290
Integral Experim. = 1.228



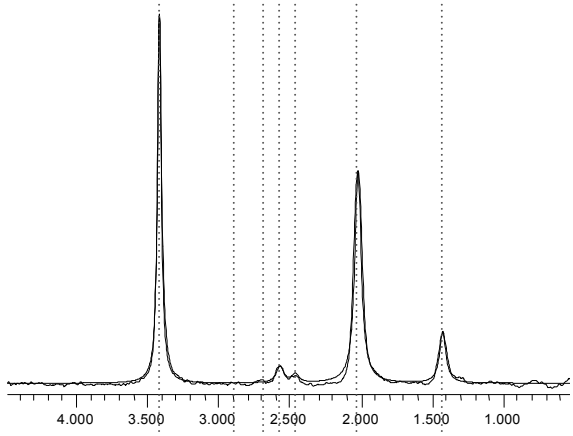
Exp 24 (95.7% de **A2βBn** per GC)

Pic 1
δ= 3.410, w= 2.66 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 2
δ= 2.880, w= 3.00 Hz, Integral Simulada = 0.025
Integral Experim. = 0.018
Pic 5
δ= 2.012, w= 4.50 Hz, Integral Simulada = 0.065
Integral Experim. = 0.047
Pic 6
δ= 1.423 , w= 4.26 Hz, Integral Simulada = 1.100
Integral Experim. = 1.023



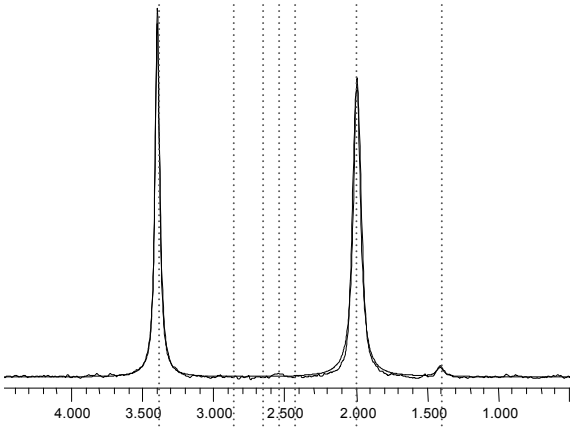
Exp 27 (98.7% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 2.60 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 3
δ= 2.551, w= 4.60 Hz, Integral Simulada = 0.085
Integral Experim. = 0.064
Pic 4
δ= 2.442, w= 4.27 Hz, Integral Simulada = 0.040
Integral Experim. = 0.041
Pic 5
δ= 2.005, w= 4.26 Hz, Integral Simulada = 1.301
Integral Experim. = 1.185



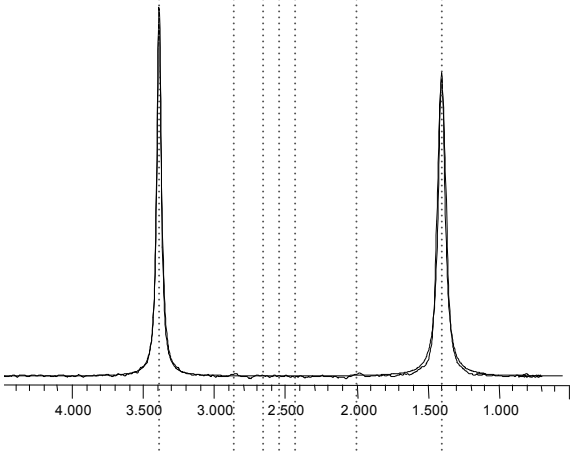
Exp 27 (17.0% de **A2βBn** per GC)

Pic 1
δ= 3.410, w= 2.45 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 3
δ= 2.563, w= 4.60 Hz, Integral Simulada = 0.085
Integral Experim. = 0.068
Pic 4
δ= 2.455, w= 4.27 Hz, Integral Simulada = 0.040
Integral Experim. = 0.026
Pic 5
δ= 2.014, w= 4.11 Hz, Integral Simulada = 0.967
Integral Experim. = 0.971
Pic 6
δ= 1.419 , w= 4.00 Hz, Integral Simulada = 0.228
Integral Experim. = 0.229



Exp 30 (95.6% de **A2γBn** per GC)

Pic 1
δ= 3.410, w= 2.84 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 5
δ= 2.007, w= 4.52 Hz, Integral Simulada = 1.290
Integral Experim. = 1.282
Pic 6
δ= 1.422, w= 4.00 Hz, Integral Simulada = 0.040
Integral Experim. = 0.038

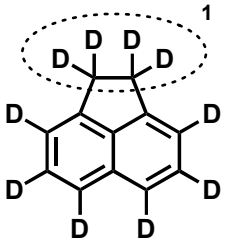


Exp 30 (99.0% de **A2βBn** per GC)

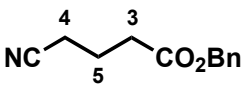
Pic 1
δ= 3.410, w= 2.71 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000
Pic 6
δ= 1.424, w= 4.30 Hz, Integral Simulada = 1.300
Integral Experim. = 1.287

Com es pot observar, de cadascun dels pics es dóna informació del desplaçament químic, de l'amplada del pic (extreta de la simulació) i de la integral experimental mitjançant el programa d'edició d'espectres *TopSpin* de *Bruker*, i l'obtinguda a la simulació mitjançant el programa *gNMR v4.0* (integral simulada).

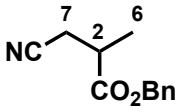
Per l'assignació dels pics observats, el desplaçament químic dels deuteris coincideix amb el desplaçament químic dels protons als espectres ^{1}H-RMN dels productes no deuterats. En conseqüència, l'assignació dels pics 1-7 dels espectres ^{2}H-RMN és la següent:



Acenaftè-d_{10}



4-cianobutanoat de benzil (A2γBn)



3-ciano-2-metilpropanoat de benzil (A2βBn)

Els deuteris aromàtics de l'acenaftè-d_{10} també donen senyal als espectres (3 senyals a δ = 7.681, 7.525 i 7.368) però han quedat fora del rang mostrat als espectres anteriors degut a que no s'han utilitzat per la quantificació.

A continuació s'exposa una taula resum de la deuteració (taula A-3). A la taula es mostra la integració total dels deuteris dels èsters (tant amb les dades experimentals com amb les provinents de les simulacions, expressades com *integral exp* i *integral sim*), que ens permet calcular el grau de deuteració mitjançant RMN ($\bar{d}$ *RMN exp* i $\bar{d}$ *RMN sim*). Si es comparen els valors de $\bar{d}$ obtinguts amb les dades experimentals i simulades ($\Delta\bar{d}$ *RMN sim-exp*) s'observa que no difereixen gaire ja que la integració als espectres experimentals de deuteri era molt neta (sense solapament de pics). Si s'agafa la integració experimental i es compara amb els valors de $\bar{d}$ obtinguts a partir de l'espectroscòpia de masses ($\Delta\bar{d}$ *MS-RMNexp*), s'observa que la diferència és mínima, indicant que ambdós mètodes són quantitatius.

Taula A-3. Resum de la quantificació dels espectres de ^{2}H.

Exp	producte	$\bar{d}$ (MS)	integral exp èster (total)	integral sim èster (total)	$\bar{d}$ (RMN exp)	$\bar{d}$ (RMN sim)	$\Delta\bar{d}$ RMN sim-exp	$\Delta\bar{d}$ MS-RMNexp
11	**A2γBn**	0.8382	1.410	1.410	0.894	0.894	0.000	-0.056
	A2βBn	0.8314	1.324	1.330	0.837	0.841	0.004	-0.006
16	**A2γBn**	1.1058	1.449	1.457	1.178	1.185	0.006	-0.073
	A2βBn	1.1528	1.412	1.450	1.159	1.191	0.031	-0.007
17	**A2γBn**	0.9301	1.259	1.275	0.893	0.905	0.011	0.037
	A2βBn	0.9578	1.381	1.300	1.001	0.942	-0.059	-0.043
24	**A2γBn**	0.7823	1.272	1.355	0.769	0.820	0.050	0.013
	A2βBn	0.8023	1.088	1.190	0.649	0.710	0.061	0.153
27	**A2γBn**	0.951	1.290	1.426	0.884	0.976	0.093	0.067
	A2βBn	0.891	1.294	1.320	0.830	0.846	0.016	0.061
30	**A2γBn**	0.7804	1.320	1.330	0.777	0.783	0.006	0.003
	A2βBn	0.8015	1.287	1.300	0.783	0.791	0.008	0.018

Es mostren les intensitats dels espectres experimentals per integració i la intensitat obtinguda de la simulació, ambdues com la suma dels pics de l'èster. A partir de les intensitats i dels mmol (taula A-2) es calculen els graus de deuteració i les diferències entre els valors obtinguts (integració experimental, intensitat simulada, MS-SIM)

S'observa incorporació significativa de deuteri a la posició 6 de **A2βBn** i a les posicions 3 i 5 de **A2γBn**. A la taula A-4 es presenten els graus de deuteració a aquestes posicions. Al integrar el pic 1 del patró com a valor de referència 1.00, es pot obtenir directament el valor de mmol de D per unitat d'integració a partir dels mmol d'acenaftè-d_{10} considerant que treballem amb els 4 deuteris alquílics. A la taula, els mmol d'èster es refereixen solament al producte d'interès (A2βBn **o** A1γBn) pel que s'estudia la deuteració, per això s'han corregit els mmol totals que hem afegit per pesada al tub segons les pureses determinades per GC.

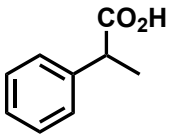
Taula A-4. Graus de deuteració per posició a la molècula.

Exp	producte	mmol èster	mmol D pic 1	$\bar{d}$ pic 2	$\bar{d}$ pic 3	$\bar{d}$ pic 4	$\bar{d}$ pic 5	$\bar{d}$ pic 6	$\bar{d}$ pic 7
11	**A1γBn**	0.432	0,297	-	0.454	-	0.491	-	-
	A1βBn	0.495	0,314	-	-	-	-	0.839	-
16	**A1γBn**	0.439	0,377	-	0.516	-	0.720	-	-
	A1βBn	0.463	0,387	-	-	-	-	1.179	-
17	**A1γBn**	0.146	0,136	-	0.215	-	0.769	-	-
	A1βBn	0.488	0,355	-	-	-	-	1.004	-
24	**A1γBn**	0.462	0,285	-	0.028	-	0.757	-	-
	A1βBn	0.430	0,263	0.011	-	-	-	0.626	-
27	**A1γBn**	0.470	0,326	-	0.045	0.028	0.822	-	-
	A1βBn	0.039	0,149	-	-	-	-	0.875	-
30	**A1γBn**	0.470	0,290	-	-	-	0.791	-	-
	A1βBn	0.442	0,299	-	-	-	-	0.870	-

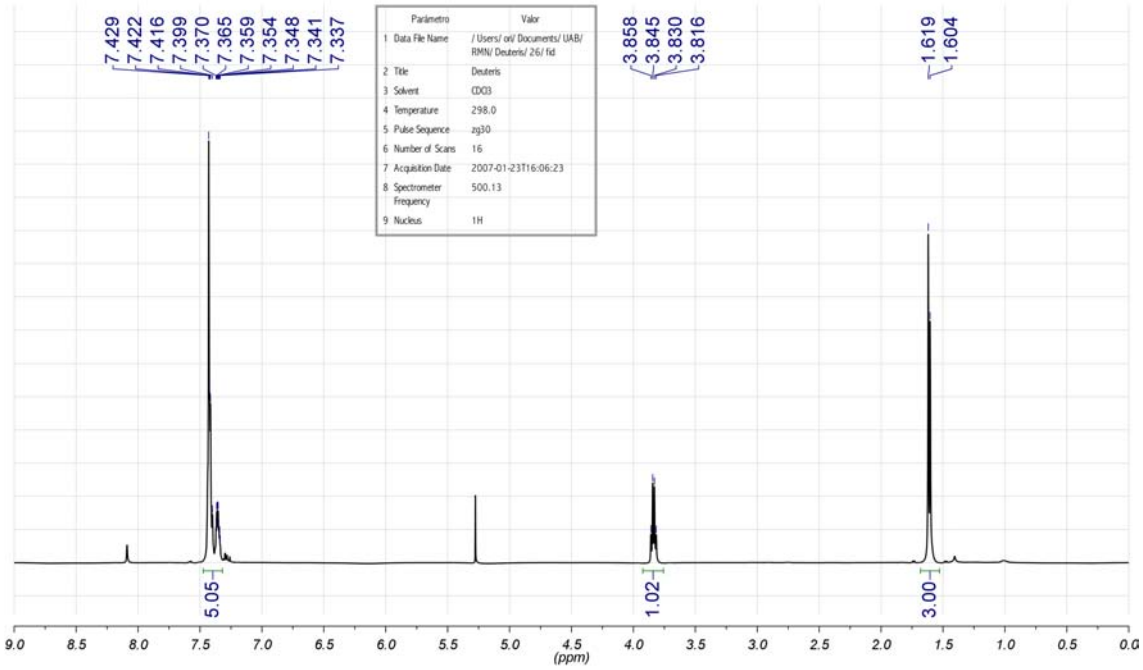
$\bar{d}$ posició calculada com: $\frac{\textbf{Integral experimental del pic} \cdot \textbf{mmol D pic 1}}{\textbf{mmol èster}}$

5 Caracterització dels productes d'hidrocarboxilació de substrats vinilarènics i propenilarènics

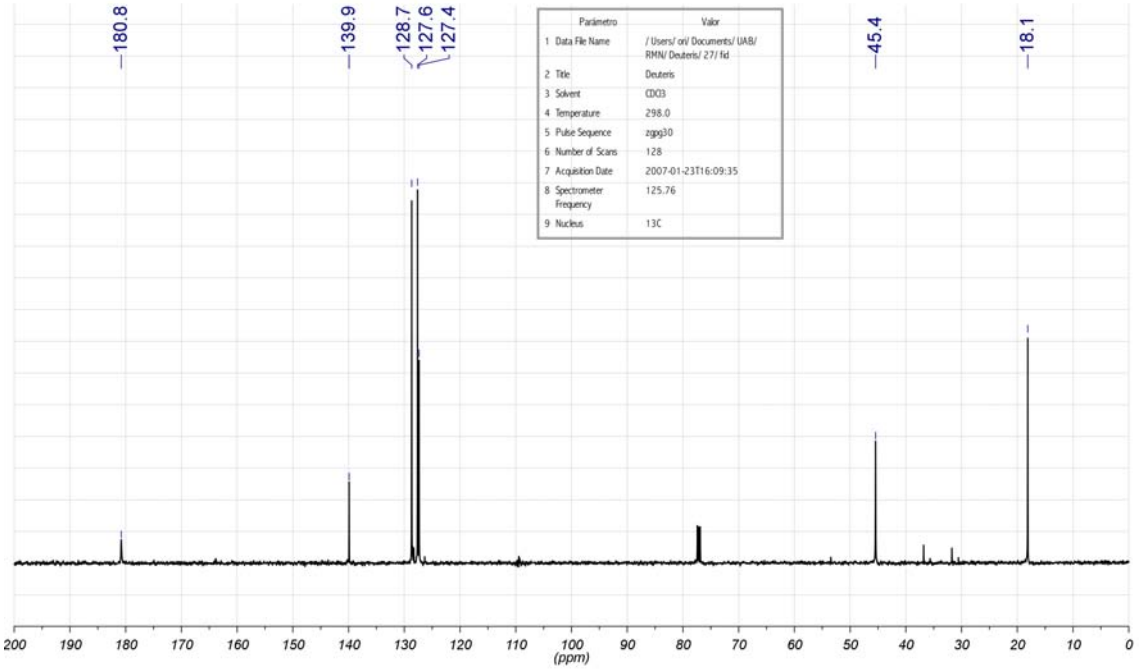
5.1 Àcid 2-fenilpropionic (A1α)



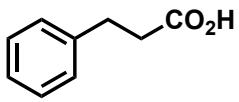
^{1}H-RMN (500 MHz, rt, $CDCl_3$):



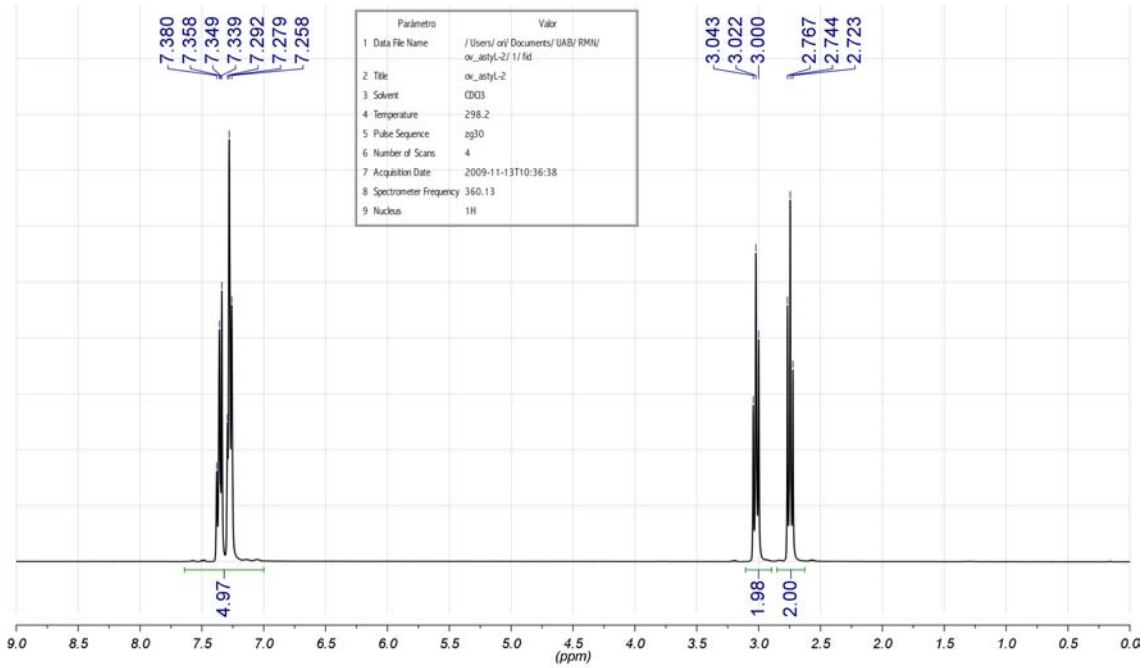
^{13}C{^{1}H}-RMN (126 MHz, rt, $CDCl_3$):



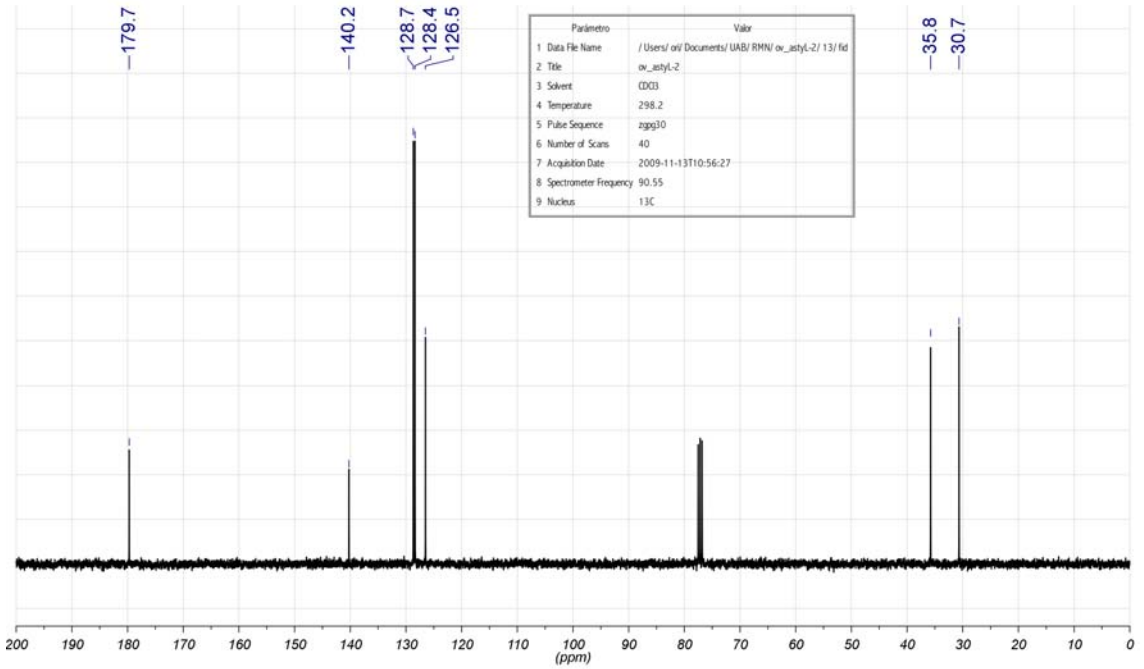
5.2 Àcid 3-fenilpropionic (A7β)



^{1}H-RMN (360 MHz, rt, $CDCl_3$):



^{13}C{^{1}H}-RMN (91 MHz, rt, $CDCl_3$):



6 Espectroscòpia de masses (SIM) dels àcids A1α i A1β.

A les taules a continuació es mostren les abundàncies absolutes per pes molecular tant pels productes d'hidrocarboxilació de l'estirè (taula A-5), com per l'estirè sobrant a les reaccions de baixa conversió (taula A-6). Es mostra el número d'experiment (Exp), de quin producte es tracta, i l'abundància per cada pic de massa (M(X), on X és el pes molecular). Aquestes dades han estat enregistrades per GC-MS mitjançant la tècnica Single Ion Monitoring (SIM) utilitzant el rang 90 – 120 com a zona d'observació per l'estirè i 140 – 164 per als productes de deuteriocarboxilació.

Taula A-5. Resultats dels CG-MS SIM pels productes de deuteriocarboxilació de l'estirè

Exp	Prod.	M(150)	M(151)	M(152)	M(153)	M(154)
31	**A1α**	709	1000	366	108	14
	A1β	559	1000	341	83	10
39	**A1α**	267	1000	775	103	15
40	**A1α**	421	1000	476	88	14
41	**A1α**	199	1000	635	81	10
*42**	**A1α**	1000	109	12	0	0

* Experiment no deuterat

Taula A-6. Resultats dels CG-MS SIM per l'estire sobrant a les reaccions de baixa conversió

Exp	M(101)	M(102)	M(103)	M(104)	M(105)	M(106)
39	9	80	476	1000	110	6
40	8	78	468	1000	163	15
*42**	8	77	466	1000	89	3

* Experiment no deuterat

6.1 Càlcul del grau d'incorporació de deuteri

S'ha seguit exactament el mateix procediment de càlcul pel grau d'incorporació de deuteri en aquests productes que el seguit pel cas del cianur d'al·lil (apartat 3.1 d'aquest annex). La nomenclatura pels isotopòmers també és equivalent, del tipus **dn**, on n és el nombre de deuteris incorporats per la molècula.

A partir de la mostra no deuterada (exp. *42*) s'obté la distribució isotòpica natural (presència ^{13}C) dels àcids productes i de l'estirè, i aleshores es calcula la relació entre el

pic M i un pic M+1 i M+2. Etiquetarem aquestes relacions com a k_1 i k_2, que correspondran a:

Àcids **A1α** i **A1β**: $k_1 = \frac{I(M+1)}{I(M)} = \frac{I(151)}{I(150)} = 0.109$ $\quad k_2 = \frac{I(M+2)}{I(M)} = \frac{I(152)}{I(150)} = 0.012$

Estirè: $k_1 = \frac{I(M+1)}{I(M)} = \frac{I(105)}{I(104)} = 0.089$ $\quad k_2 = \frac{I(M+2)}{I(M)} = \frac{I(152)}{I(150)} = 0.003$

Aleshores ja es poden calcular les quantitats de d0, d1 i d2 com:

$$I(M) = Q(d0)$$
$$I(M+1) = I(M) \cdot k_1 + Q(d1)$$
$$I(M+2) = I(M) \cdot k_2 + I(M+1) \cdot k_1 + Q(d2)$$

D'aquesta forma s'obtenen les quantitats de producte sense incorporació de deuteri (Q (d0)), amb la incorporació d'un sol deuteri (Q(d1)) i amb la incorporació de dos deuteris (Q(d2)), que es poden normalitzar i expressar com a percentatge. La incorporació de dos deuteris és la màxima que s'observa als àcids estudiats però es seguiria anàlogament el mateix raonament per calcular productes amb major deuteració. També es pot calcular el grau de deuteració ($\bar{d}$) com la mesura de mols de deuteri per mol de producte:

$$\bar{d} = \frac{\%d1 + 2 \cdot (\%d2)}{100}$$

Graus de deuteració obtinguts:

Exp. 31	**L=(S)-(-)-BINPO, [P]/[Pd]= 3, P_{CO}= 60 bar, T= 100 ºC (C_A= 76%)**		
	A1α (69%)	**A1β** (31%)	**Estirè sobrant**
d0	37.71 %	32.44 %	-
d1	49.08 %	54.49 %	-
d2	13.22 %	13.07 %	-
$\bar{d}$	0.75	0.80	-

Exp. 39	L=(S)-(-)-BINPO, [P]/[Pd]= 3, P_{CO}= 60 bar, T= 50 ºC (C_A= 2%)		
	A1α (100%)	**A1β** (0%)	**Estirè sobrant**
d0	14.05 %	-	97.95 %
d1	51.08 %	-	2.05 %
d2	34.87 %	-	-
$\bar{d}$	1.20	-	0.02

Exp. 40	L=(S)-(-)-BINPO, [P]/[Pd]= 3, P_{CO}= 15 bar, T= 50 ºC (C_A= 5%)		
	A1α (98%)	**A1β** (2%)	**Estirè sobrant**
d0	24.24 %	-	93.1 %
d1	59.93 %	-	6.90 %
d2	20.84 %	-	-
$\bar{d}$	0.97	-	0.07

Exp. 41	L=(S)-(-)-BINPO, [P]/[Pd]= 3, P_{CO}= 60 bar, T= 80 ºC (C_A= 41%)		
	A1α (99%)	**A1β** (1%)	**Estirè sobrant**
d0	11.70 %	-	-
d1	57.52 %	-	-
d2	30.78 %	-	-
$\bar{d}$	1.18	-	-

7 Espectres de ^{2}H-RMN dels productes d'hidrocarboxilació A1α i A1β

Les quantitats afegides de producte i patró a cada tub de RMN es mostren a la taula a continuació (taula A-7). Les dades més importants que serveixen per la posterior quantificació són els mmol d'acenaftè-d_{10} (a-d_{10}) i els mmol d'àcid afegits. Amb aquestes dades i la integral de l'espectre es pot obtenir la relació integral/deuteri i quantificar en valor absolut el nombre de deuteris exactes en cada posició de la molècula. A la taula es mostra l'experiment i producte als quals correspon cada fila i la quantitat de deuteri que conté l'èster afegit, que només s'utilitza per saber la quantitat aproximada d'acenaftè-d_{10} que hem d'afegir per no provocar una gran diferència d'intensitats entre producte i patró en el futur espectre de ressonància. Aquesta quantitat s'ha obtingut multiplicant la quantitat estequiomètrica del patró (considerant els 4 deuteris alquílics) per un factor de 0.8 (es mostren els valors de pes reals, per això la relació no és exacta).

Taula A-7. Quantitats de producte i patró afegides a la preparació dels tubs de ^{2}H-RMN.

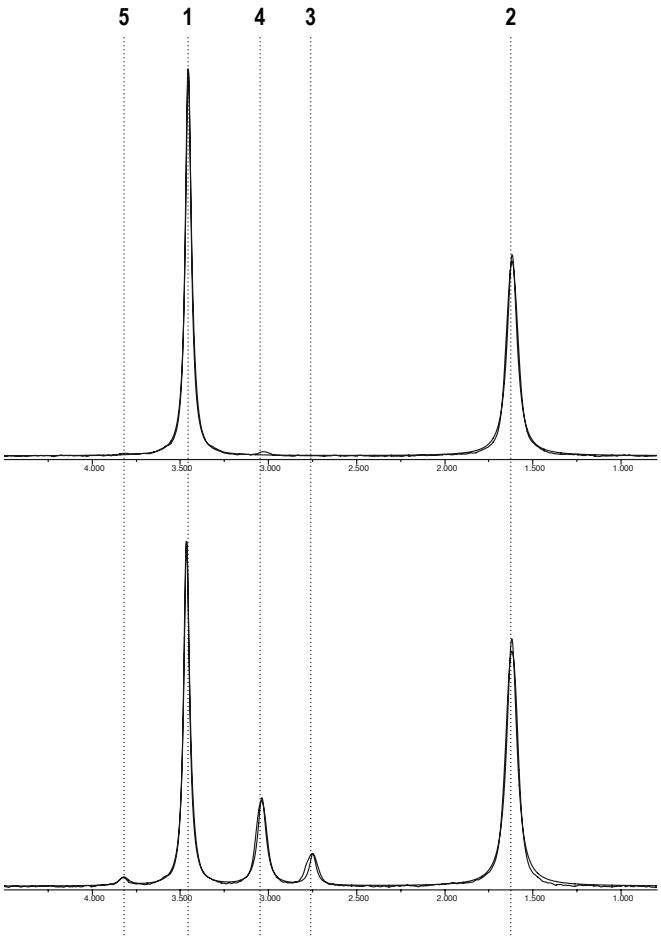
Exp	prod.	$\bar{d}$ (MS)	mg acid	mmol acid	mmol "D" acid (MS)	mg a-d_{10}	mmol a-d_{10}	mmol "D" a-d_{10}
41	**A1α**	1.18	107.9	0.718	0.848	30.4	0.185	0.740
31 [a]	**A1α**	0.75	110.1	0.506	0.379	16.8	0.102	0.409
	A1β	0.80		0.227	0.162			

Es mostren els mg d'àcid que s'han afegit a cada tub i l'estimació dels mmol de deuteri que conté (a partir del MS-SIM) i així poder afegir una quantitat d'acenaftè que contingui una proporció de deuteri aproximadament 0.8 vegades la del èster.

[a] Per calcular els mmol de cada àcid a aquest experiment s'ha fet a partir de la regioselectivitat de la reacció, ja que es tracta de la mescla d'àcids.

A la pàgina següent es mostren els espectres de ^{2}H-RMN (registrats a 77 MHz) de les dues reaccions, superposats amb la simulació dels mateixos mitjançant el programa *gNMR v4.0*.

Com es pot observar, de cadascun dels pics es dóna informació del desplaçament químic, de l'amplada del pic (extreta de la simulació) i de la integral experimental mitjançant el programa d'edició d'espectres *TopSpin* de *Bruker*, i l'obtinguda a la simulació mitjançant el programa *gNMR v5.0.6* (integral simulada).



Exp.41 (Estirè/BINPO P60, T80)

Pic 1:
δ= 3.455, w= 3.01 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000

Pic 2:
δ= 1.618, w= 5.11 Hz, Integral Simulada = 0.884
Integral Experim. = 0.874

Exp. 31 (Estirè/BINPO P60, T100)

Pic 1:
δ= 3.465, w= 2.92 Hz, Integral Simulada = 1.000
Integral Experim. = 1.000

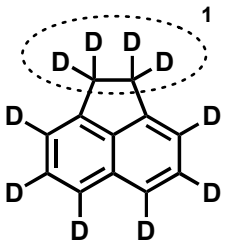
Pic 2:
δ= 1.620, w= 5.29 Hz, Integral Simulada = 1.298
Integral Experim. = 1.191

Pic 3:
δ= 2.749, w= 3.60 Hz, Integral Simulada = 0.111
Integral Experim. = 0.147

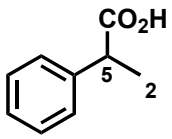
Pic 4:
δ= 3.038, w= 4.33 Hz, Integral Simulada = 0.375
Integral Experim. = 0.390

Pic 5:
δ= 3.820, w= 5.00 Hz, Integral Simulada = 0.038
Integral Experim. = 0.022

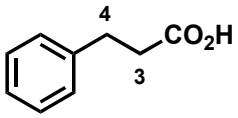
Per l'assignació dels pics observats, el desplaçament químic dels deuteris coincideix amb el desplaçament químic dels protons als espectres ^{1}H-RMN dels productes no deuterats. En conseqüència, l'assignació dels pics 1-5 dels espectres ^{2}H-RMN és la següent:



Acenaftè-d_{10}



Àcid 2-fenilpropiònic (A1α)



Àcid 3-fenilpropiònic (A1β)

Els deuteris aromàtics de l'acenaftè-d_{10} també donen senyal als espectres (3 senyals a δ = 7.681, 7.525 i 7.368) però han quedat fora del rang mostrat als espectres anteriors degut a que no s'han utilitzat per la quantificació.

A continuació s'exposa una taula resum de la deuteració (taula A-8). A la taula es mostra la integració total dels deuteris dels àcids (tant amb les dades experimentals com amb les provinents de les simulacions, expressades com *integral exp* i *integral sim*), que ens permet calcular el grau de deuteració mitjançant RMN ($\bar{d}$ *RMN exp* i $\bar{d}$ *RMN sim*). Si es comparen els valors de $\bar{d}$ obtinguts amb les dades experimentals i simulades ($\Delta\bar{d}$ *RMN sim-exp*) s'observa que són gaire diferents, indicant que la integració experimental és prou bona (no hi ha solapaments de pics). Si s'agafa la integració experimental i es compara amb els valors de $\bar{d}$ obtinguts a partir de l'espectroscòpia de masses ($\Delta\bar{d}$ *MS-RMNexp*), la diferència és una mica superior.

Taula A-8. Resum de la quantificació dels espectres de ^{2}H-RMN.

Exp	prod.	$\bar{d}$ (MS)	Int. exp. acid (total)	Int. sim. acid (total)	$\bar{d}$ (RMN exp.)	$\bar{d}$ (RMN sim.)	$\Delta\bar{d}$ RMN sim-exp	$\Delta\bar{d}$ MS-RMN$_{exp}$
41	**A1α**	1.18	0.874	0.884	0.900	0.911	0.010	0.280
31 [a]	**A1α**	0.75	1.213	1.336	1.022	1.080	0.058	-0.272
	A1β	0.80	0.537	0.486	0.967	0.875	-0.092	-0.167

Es mostren les intensitats dels espectres experimentals per integració i la intensitat obtinguda de la simulació, ambdues com la suma dels pics de l'àcid en qüestió. A partir de les intensitats i dels mmol (taula A-7) es calculen els graus de deuteració i les diferències entre els valors obtinguts (integració experimental, intensitat simulada, MS-SIM)

[a] A l'experiment 31 els càlculs per els dos àcids es fan a partir de la regioselectivitat de la reacció.

Als espectres de ^{2}H-RMN es pot observar que la incorporació a l'àcid ramificat **A1α** es troba principalment al metil (pic 2) mentre que per l'àcid lineal **A1β** s'observa incorporació als dos metilens (pics 3 i 4), essent una mica superior al metilè en α al fenil. A la taula A-9 es presenten els graus de deuteració per posició. Al integrar el pic 1 del patró com a valor de referència 1.00, es pot obtenir directament el valor de mmol de D per unitat d'integració a partir dels mmol d'acenaftè-d_{10} considerant que treballem amb els 4 deuteris alquílics.

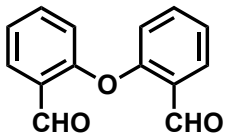
Taula A-9. Graus de deuteració per posició als productes.

Exp	producte	mmol àcid	mmol D pic 1	$\bar{d}$ pic 2	$\bar{d}$ pic 3	$\bar{d}$ pic 4	$\bar{d}$ pic 5
31	**A1α**	0.718	0.740	0.900	-	-	-
41	**A1α**	0.506	0.409	0.963	-	-	0.040
	A1β	0.227		-	0.265	0.702	-

$\bar{d}$ a la posició calculada com: $\frac{\textbf{Integral experimental del pic} \cdot \textbf{mmol D pic 1}}{\textbf{mmol àcid}}$

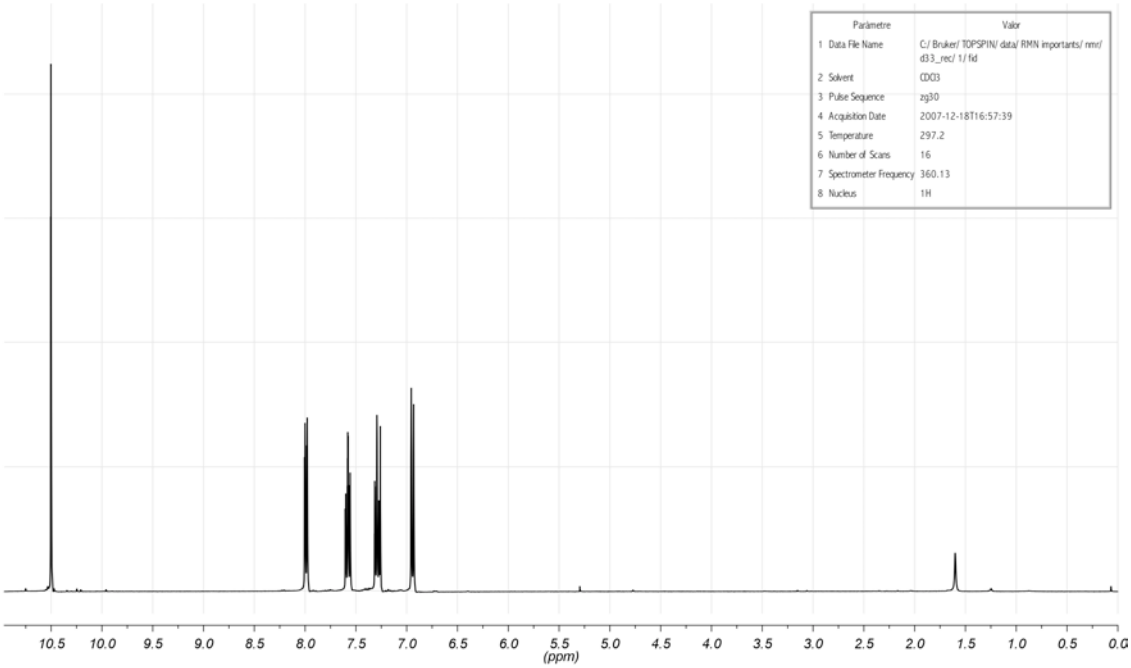
8 Caracterització d'intermedis i productes a la síntesi de difosfines benzíliques

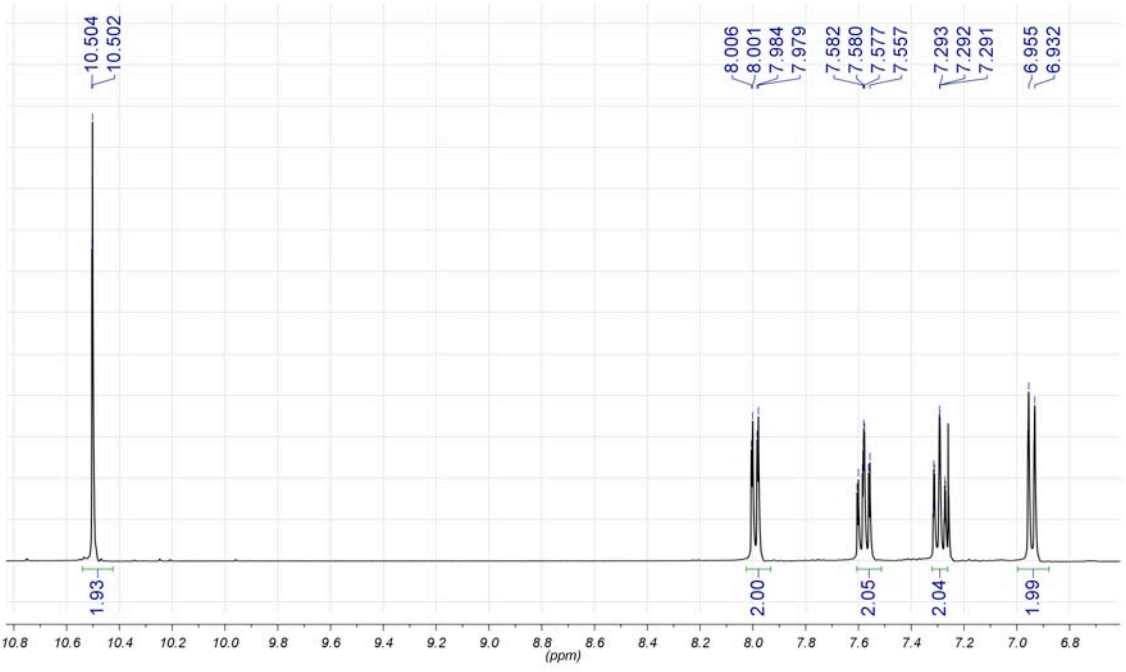
8.1 Síntesi de la DPEMephos (L33)



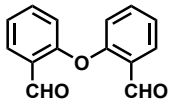
2-(2-formilfenoxi)benzaldehid (I11)

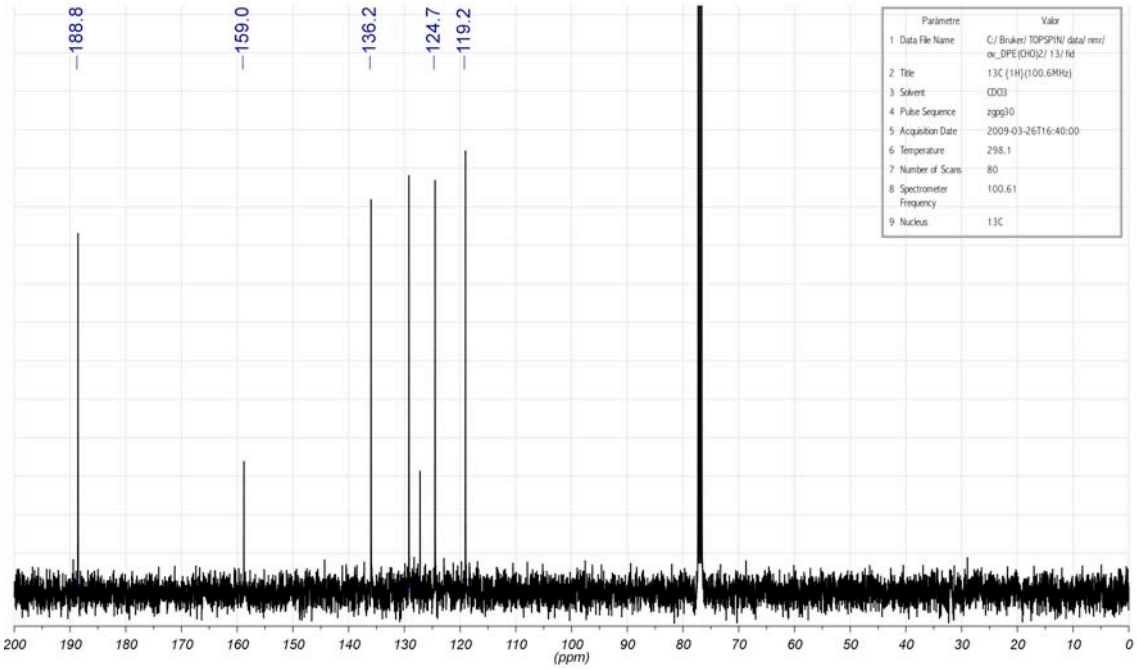
^{1}H RMN (360 MHz, rt, $CDCl_3$):



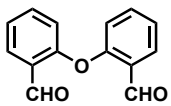


$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):



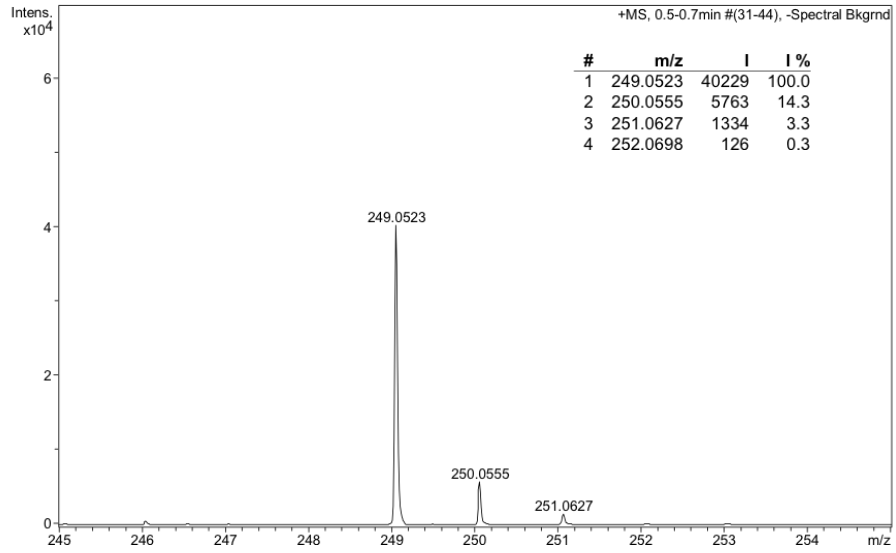


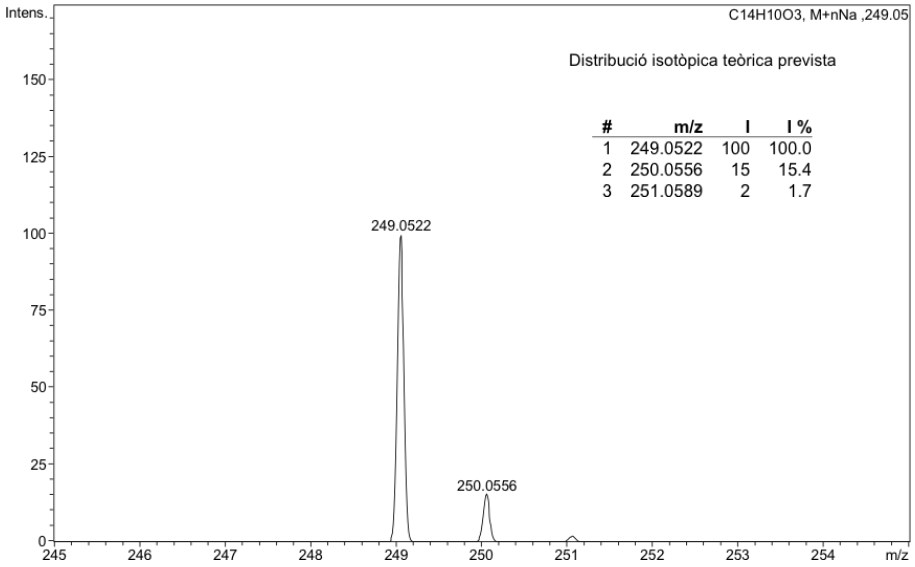
HRMS (ESI+):



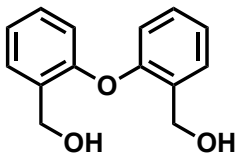
Analysis Info

Analysis Name	OV-DPE1(09EM117)_1-C,5_01_1889.d	Acquisition Date	18/03/2009 12:18:45
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-DPE1(09EM117)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

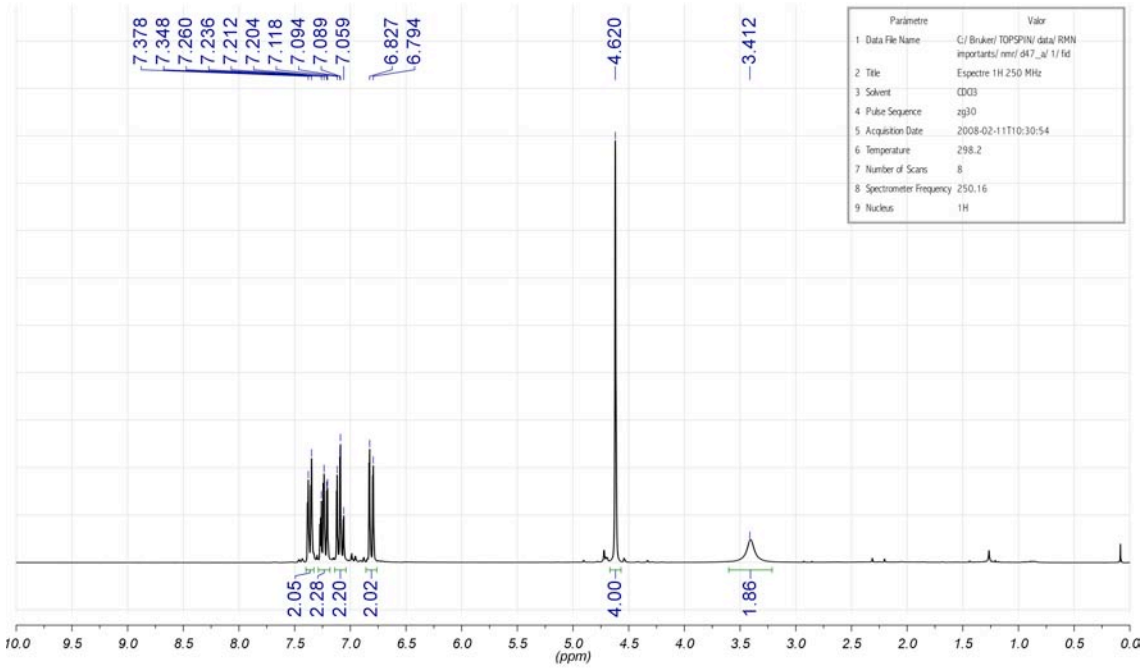


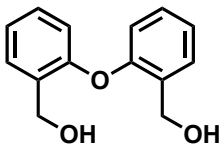


{2-[2-(hidroximetil)fenoxi]fenil}metanol (I12)

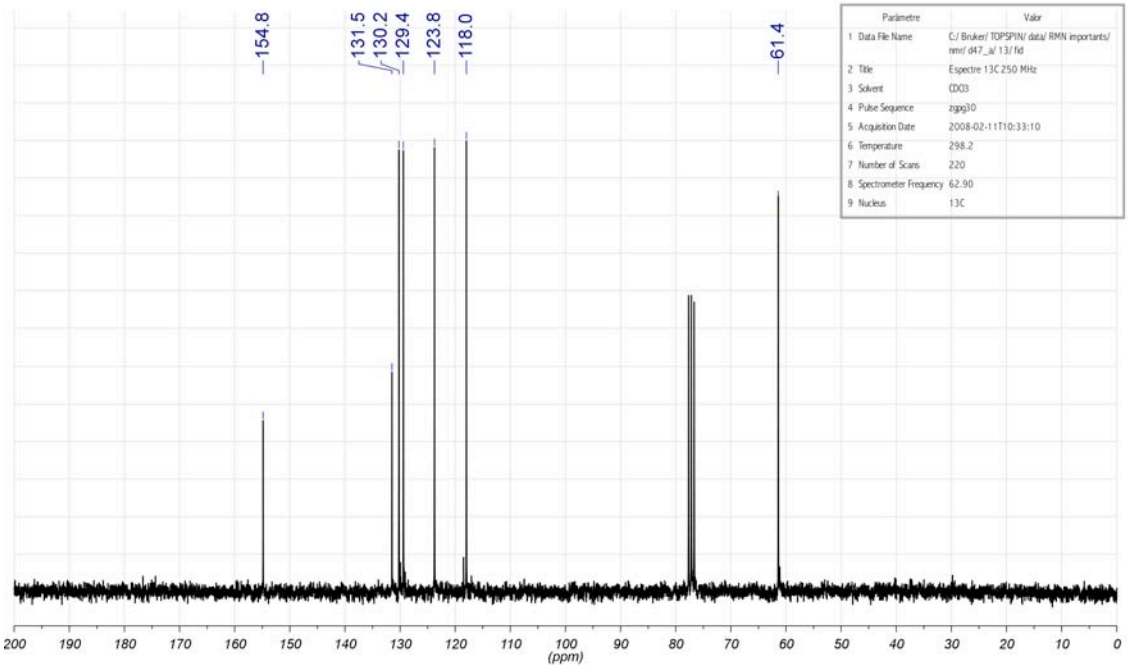


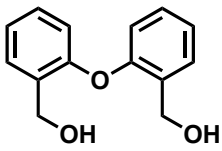
^{1}H RMN (250 MHz, rt, $CDCl_3$):





$^{13}C\{^{1}H\}$ RMN (63 MHz, rt, $CDCl_3$):

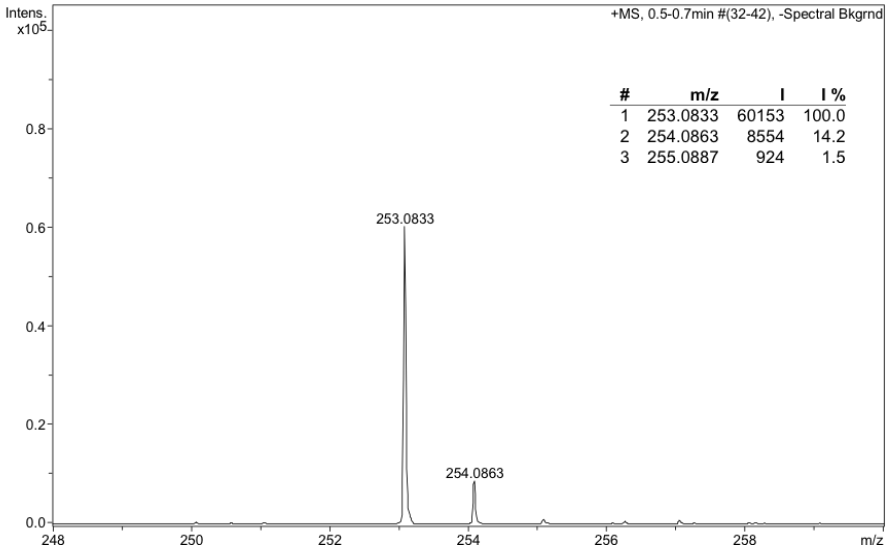


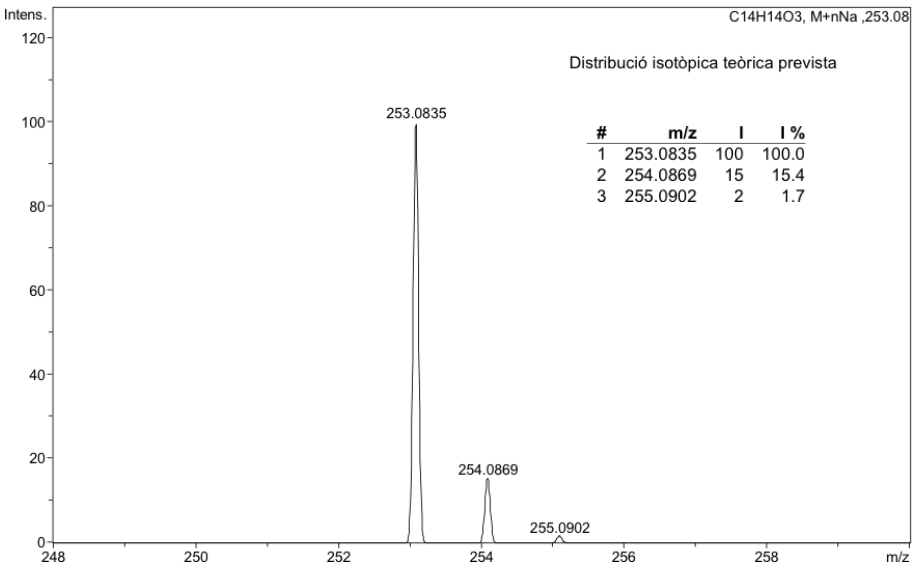


HRMS (ESI+):

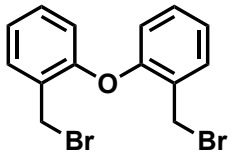
Analysis Info

Analysis Name	OV-DPE2(09EM118)_1-C,6_01_1890.d	Acquisition Date	18/03/2009 12:25:29
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-DPE2(09EM118)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

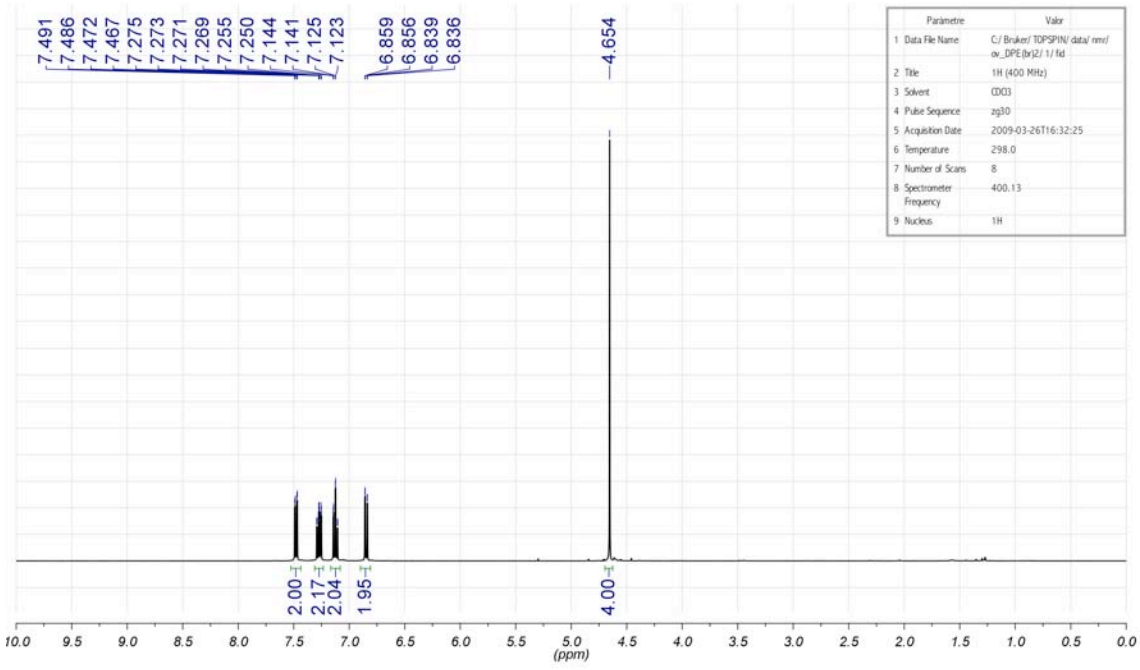


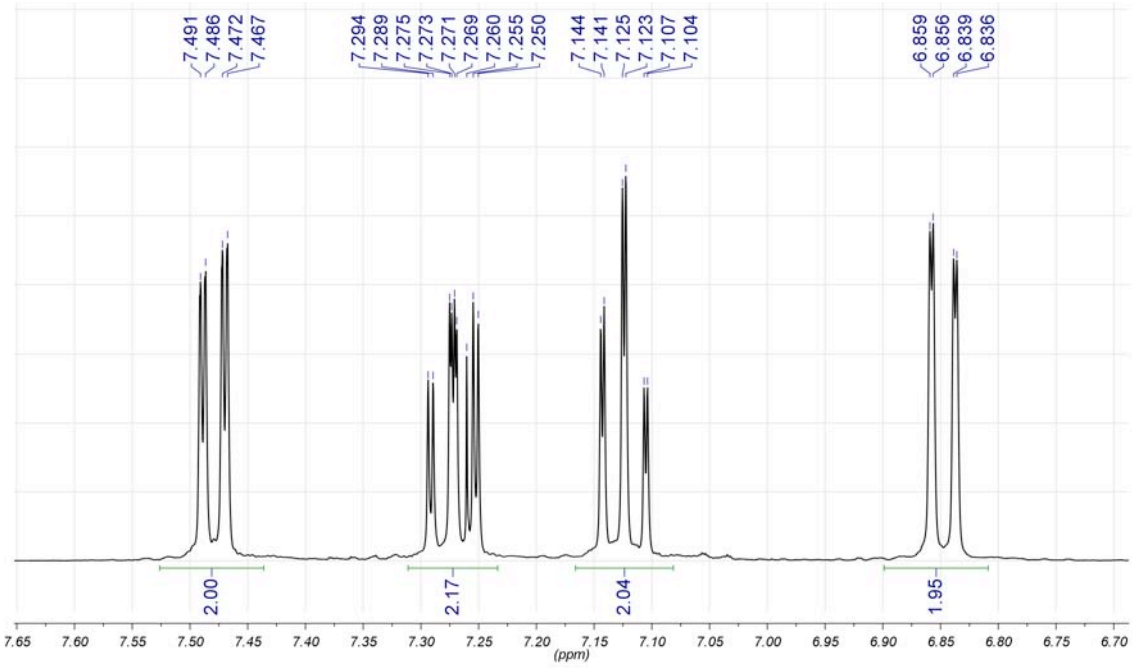


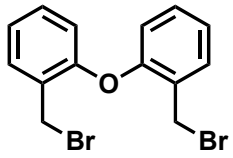
1-(bromometil)-2-[2-(bromometil)fenoxi]benzè (I10)



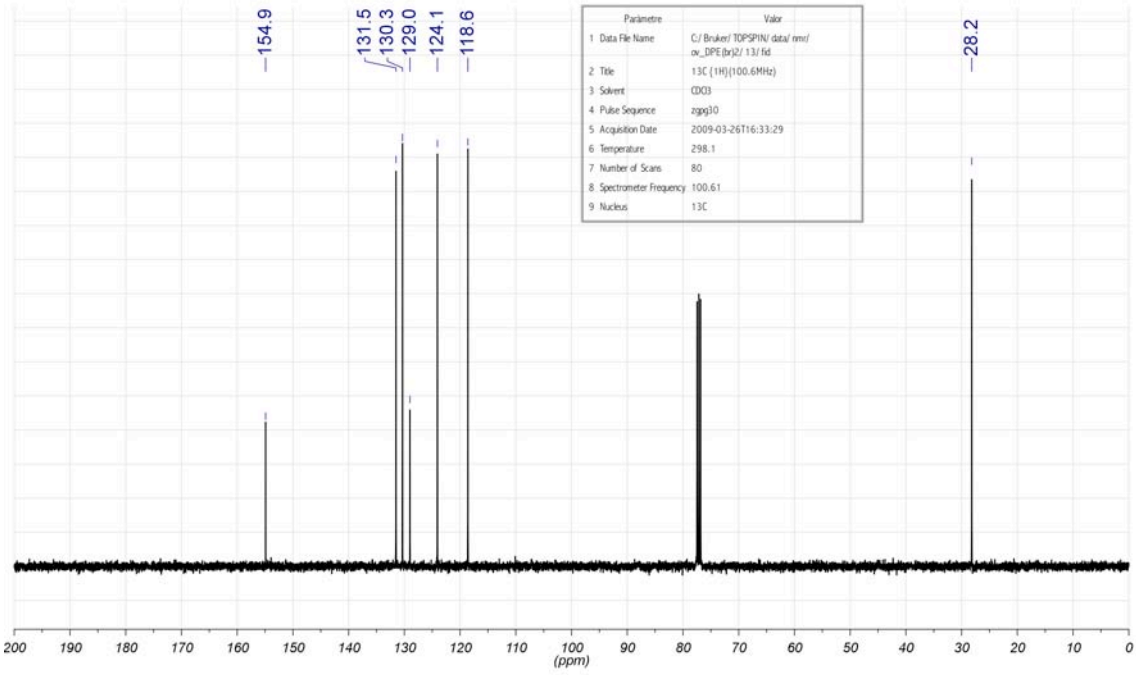
^{1}H RMN (400 MHz, rt, $CDCl_3$):



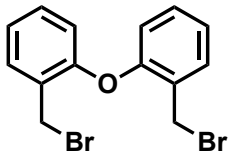




$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

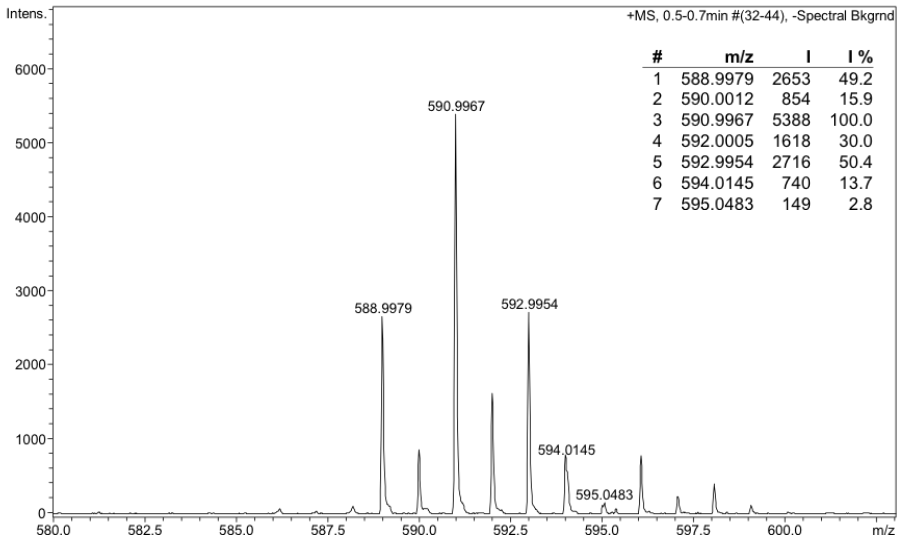


HRMS (ESI+):

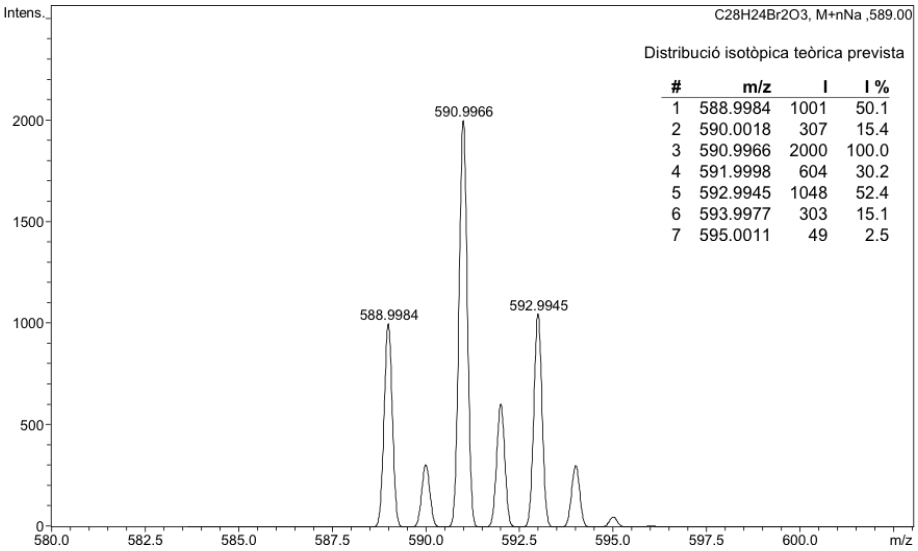


Analysis Info

Analysis Name	OV-DPE3(09EM119)_1-E,6_01_1908.d	Acquisition Date	18/03/2009 17:45:13
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-DPE3(09EM119)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 10 ppm en Acetona:MeOH (1:1). // O. VALLCORBA		

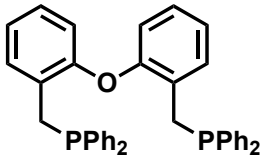


#	m/z	I	I %
1	588.9979	2653	49.2
2	590.0012	854	15.9
3	590.9967	5388	100.0
4	592.0005	1618	30.0
5	592.9954	2716	50.4
6	594.0145	740	13.7
7	595.0483	149	2.8

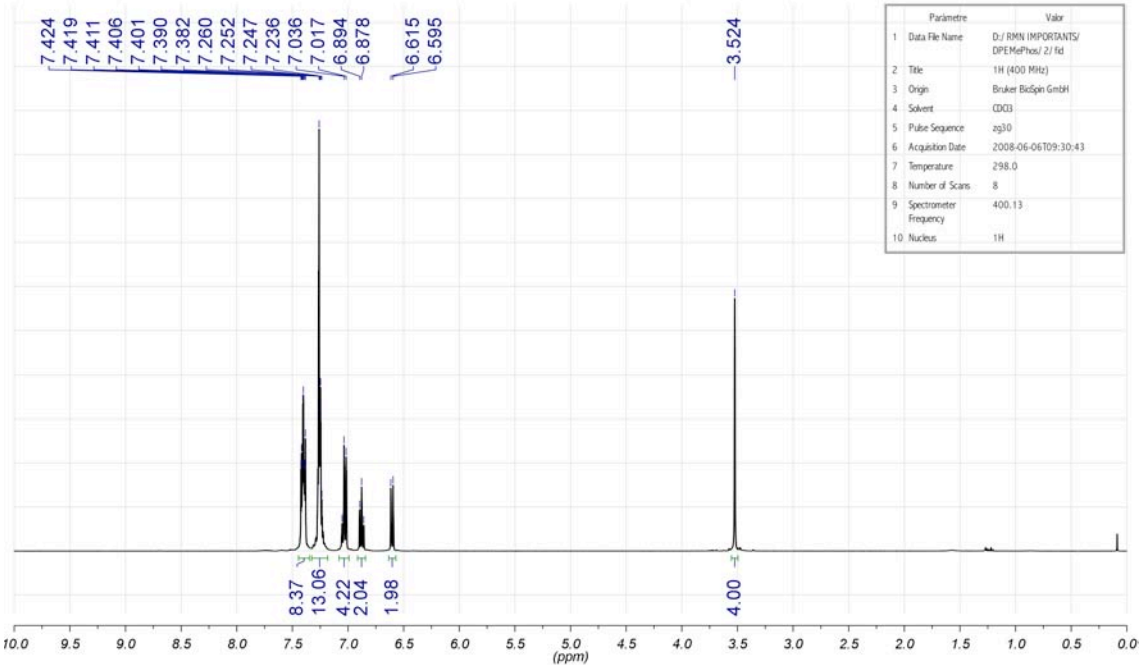


#	m/z	I	I %
1	588.9984	1001	50.1
2	590.0018	307	15.4
3	590.9966	2000	100.0
4	591.9998	604	30.2
5	592.9945	1048	52.4
6	593.9977	303	15.1
7	595.0011	49	2.5

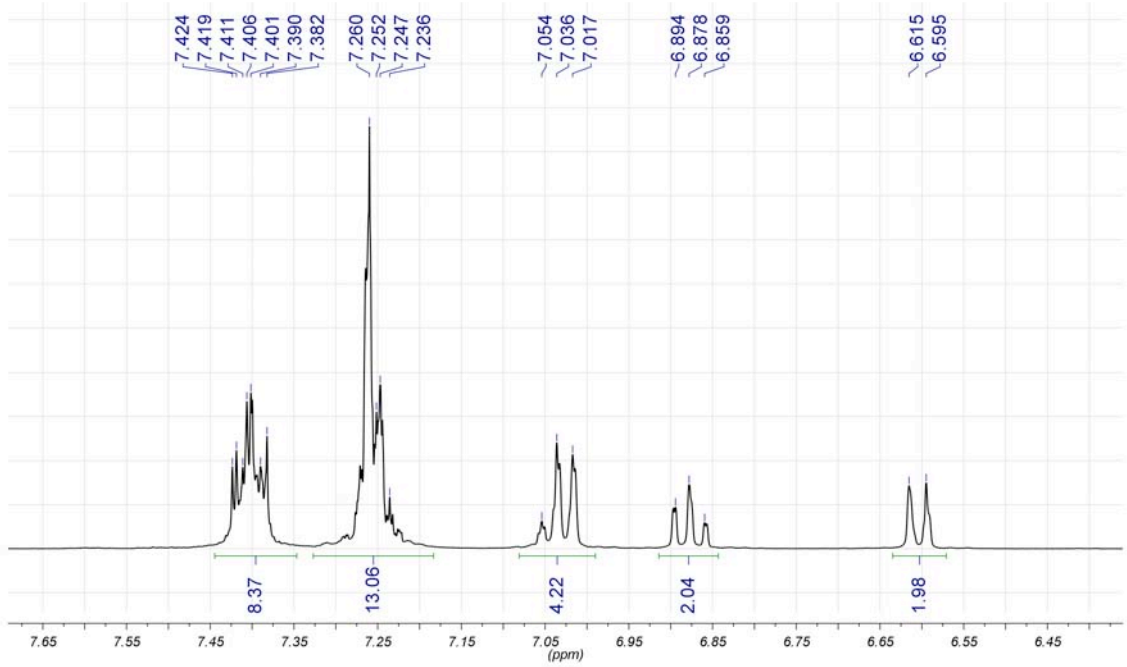
(2-[2-{1,1-difenilfosfinometil}fenoxi]benzil)difenilfosfina (DPEMephos, L33)

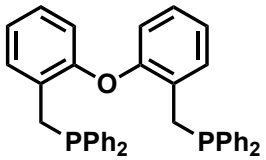


^{1}H RMN (400 MHz, rt, $CDCl_3$):

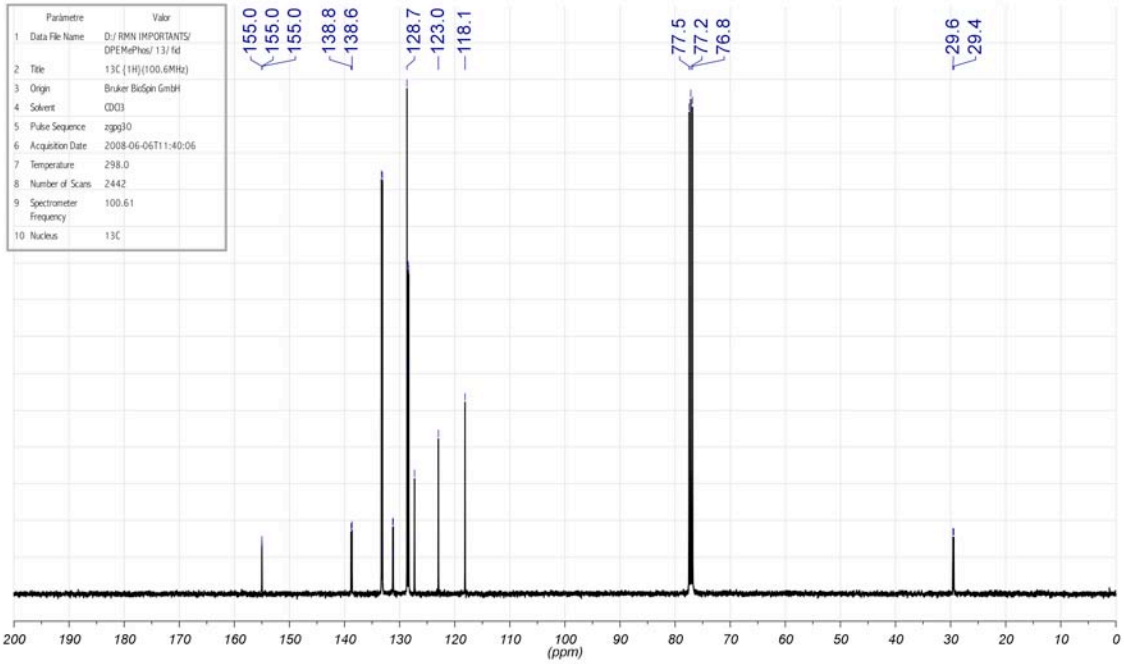


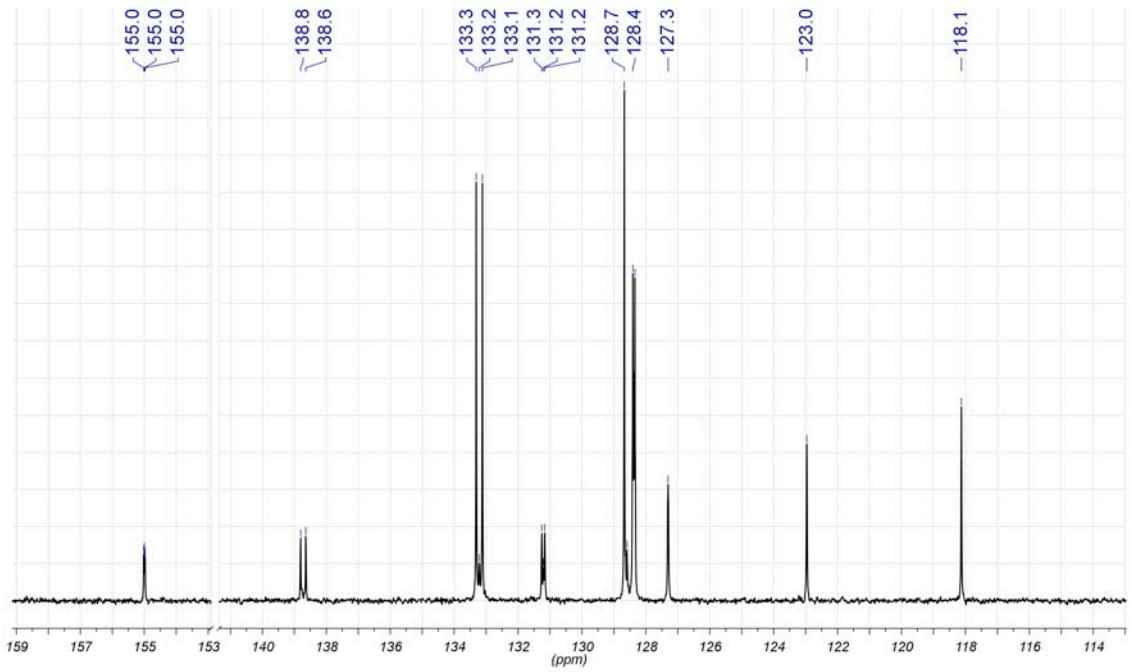
	Parámetro	Valor
1	Data File Name	D:/ RMN IMPORTANTS/ DPEMePhos/ 2/ fid
2	Title	1H (400 MHz)
3	Origin	Bruker BioSpin GmbH
4	Solvent	CDCl3
5	Pulse Sequence	zg30
6	Acquisition Date	2008-06-06T09:30:43
7	Temperature	298.0
8	Number of Scans	8
9	Spectrometer Frequency	400.13
10	Nucleus	1H

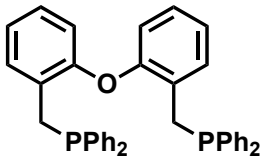




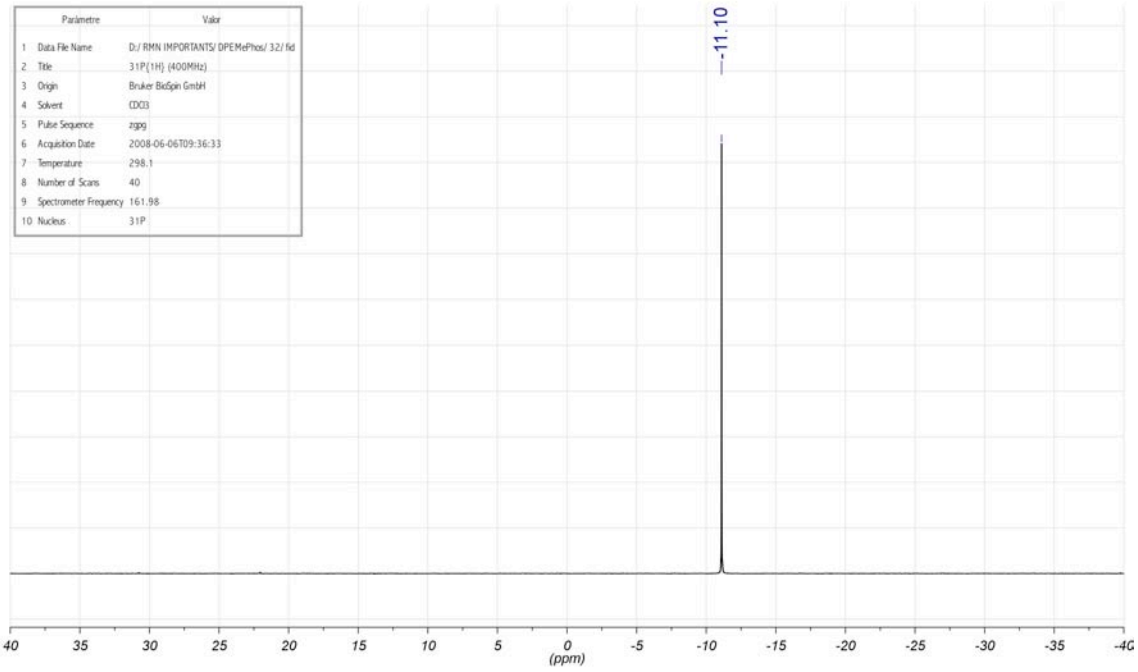
$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):



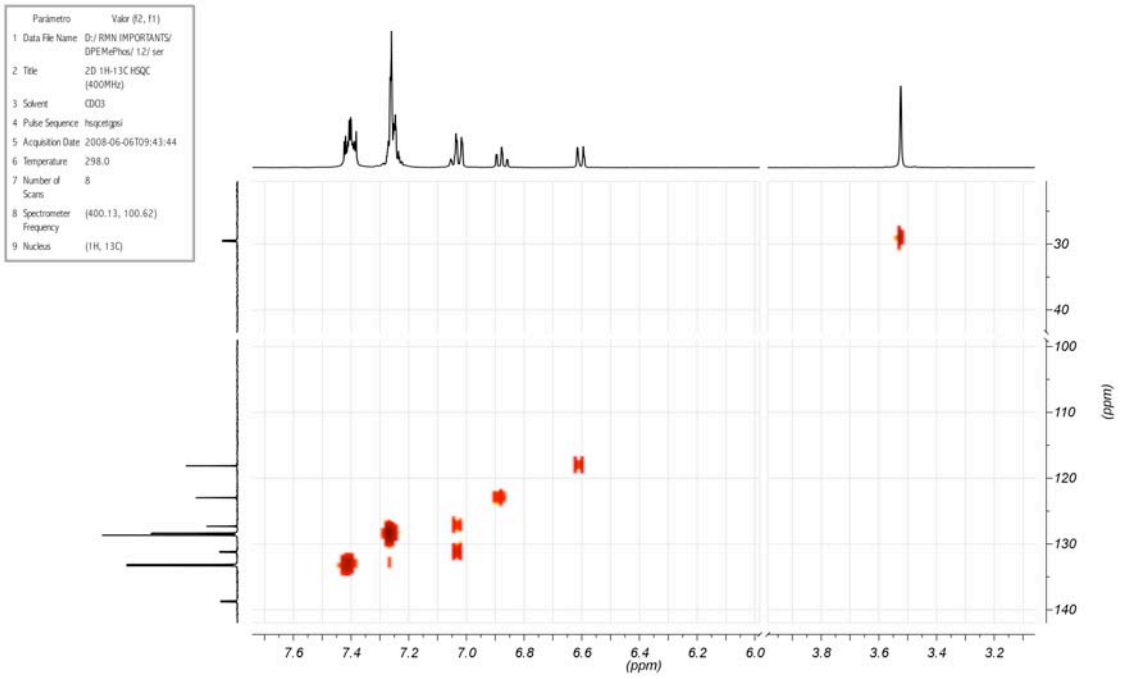




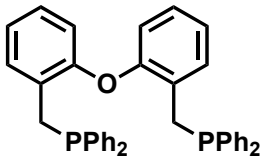
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



Espectre de correlació ^{1}H-^{13}C (HSQC):

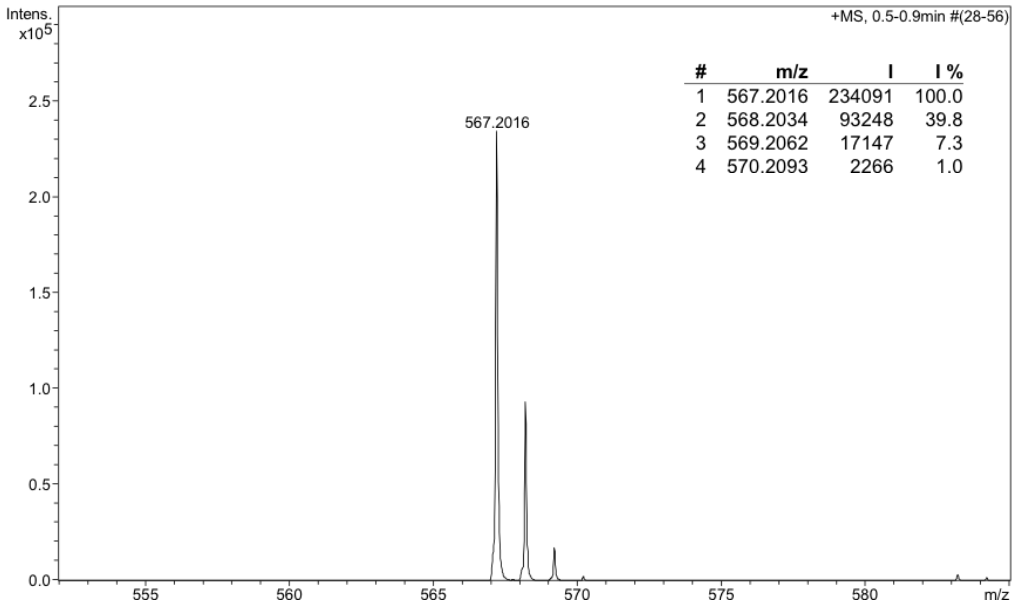


HRMS (ESI+):

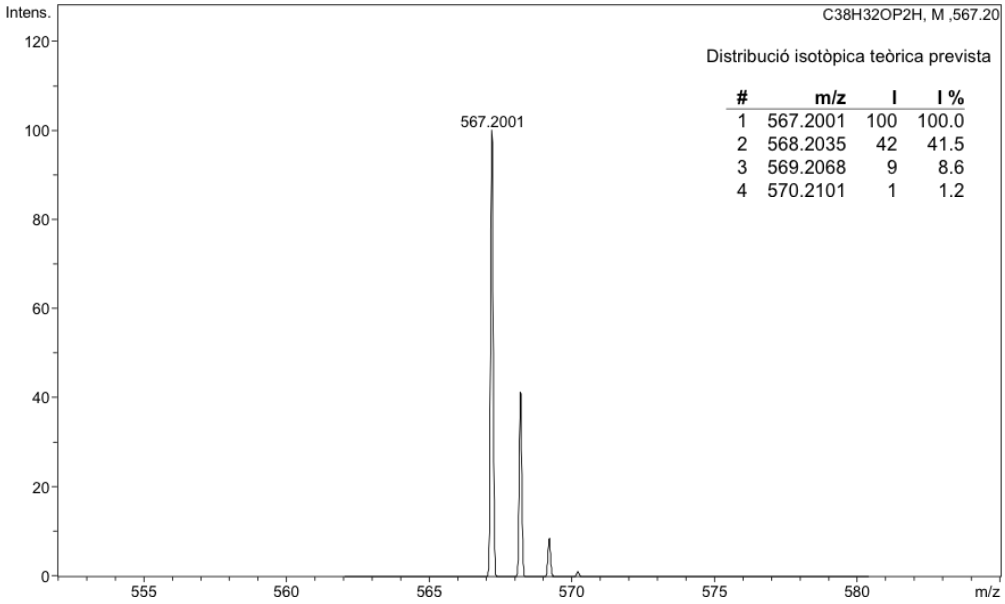


Analysis Info

Analysis Name	ds6 (8EM-144)_1-B,8_01_132.d	Acquisition Date	09/05/2008 12:36:52
Method	ESIpos100-600_FI-HS_MeOH_29-4-08.m	Operator	SAQ
Sample Name	ds6 (8EM-144)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2ppm en MeOH. // O. VALLCORBA		



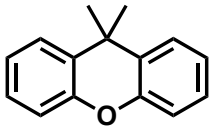
#	m/z	I	I %
1	567.2016	234091	100.0
2	568.2034	93248	39.8
3	569.2062	17147	7.3
4	570.2093	2266	1.0



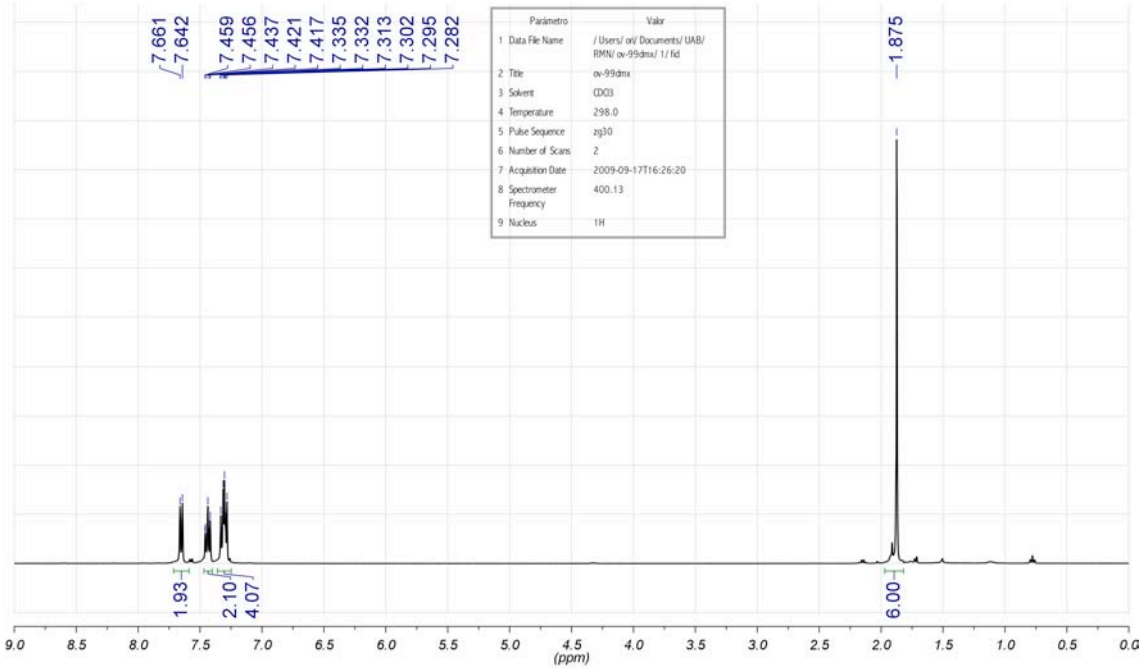
#	m/z	I	I %
1	567.2001	100	100.0
2	568.2035	42	41.5
3	569.2068	9	8.6
4	570.2101	1	1.2

8.2 Síntesi de la XantMephos (L34)

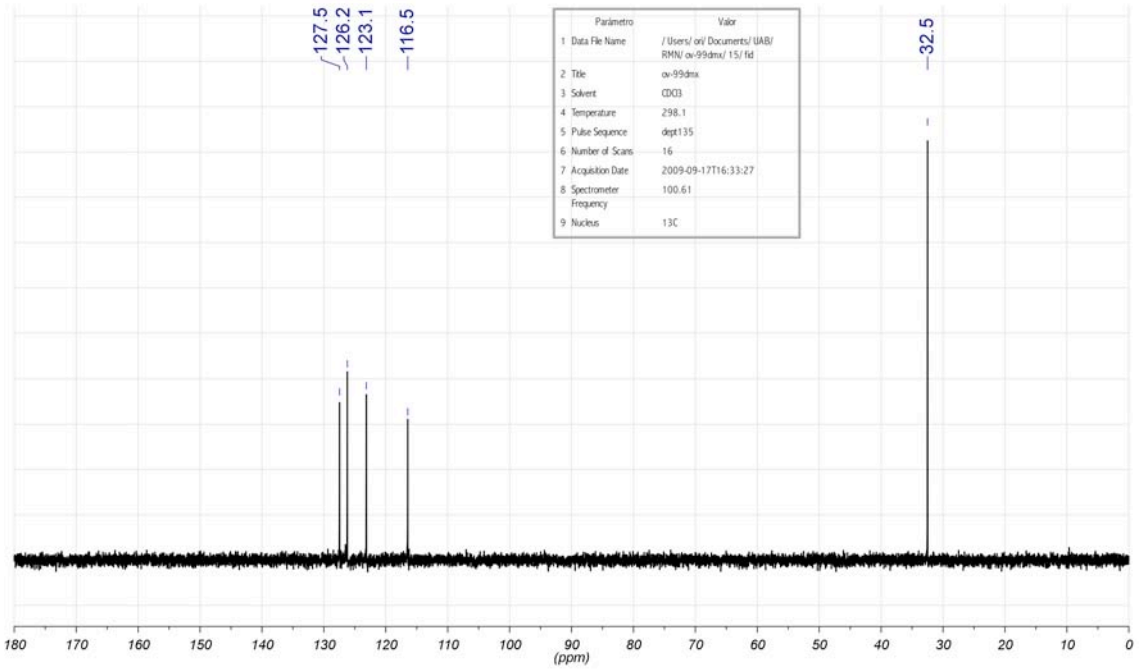
9,9-dimetil-9H-xantè (I13)



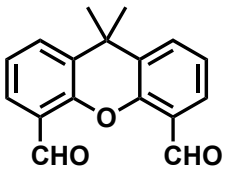
^{1}H RMN (400 MHz, rt, $CDCl_3$):



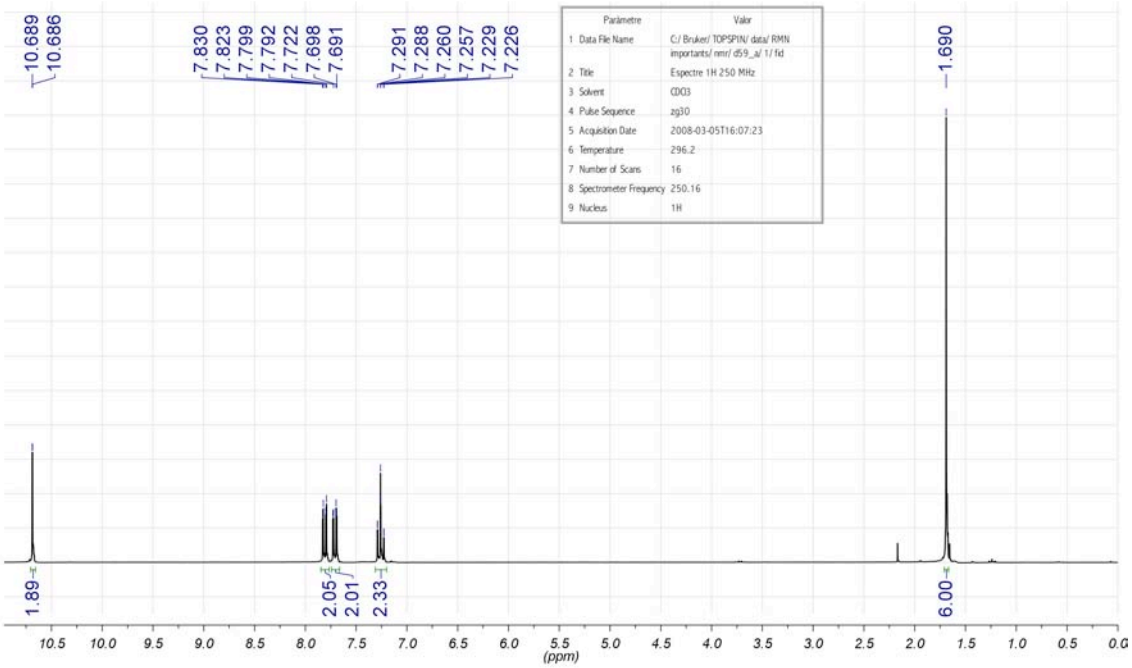
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):



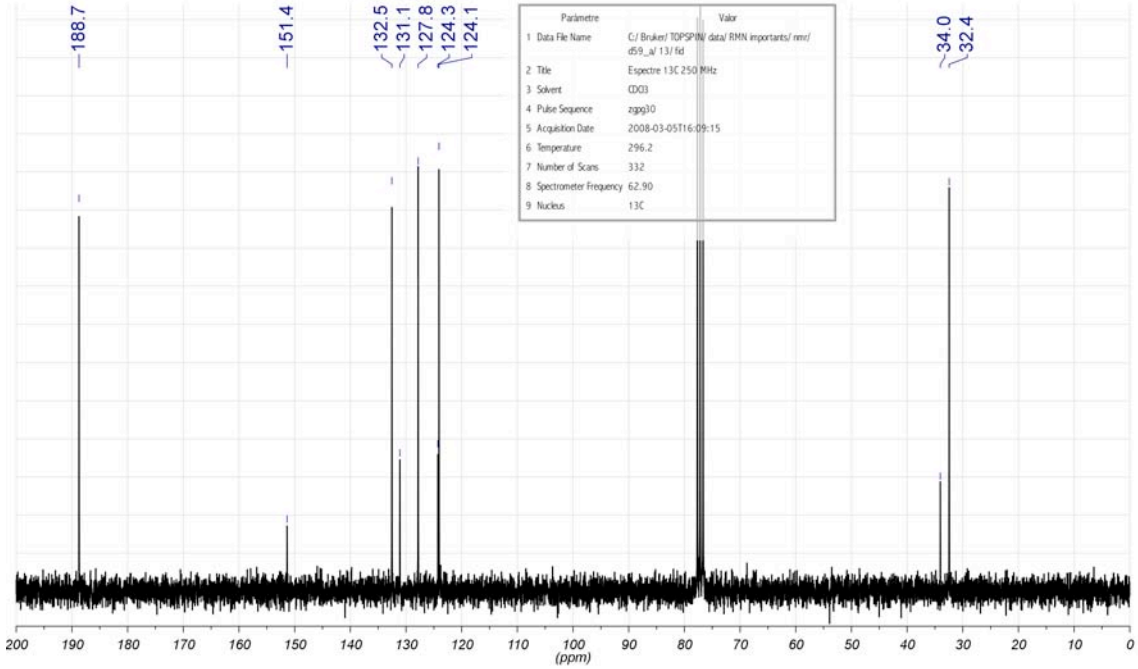
9,9-dimetil-9H-xantè-4,5-dicarbaldehid (I14)



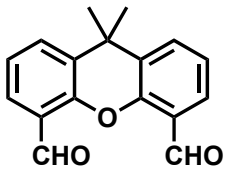
^{1}H RMN (250 MHz, rt, $CDCl_3$):



^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):

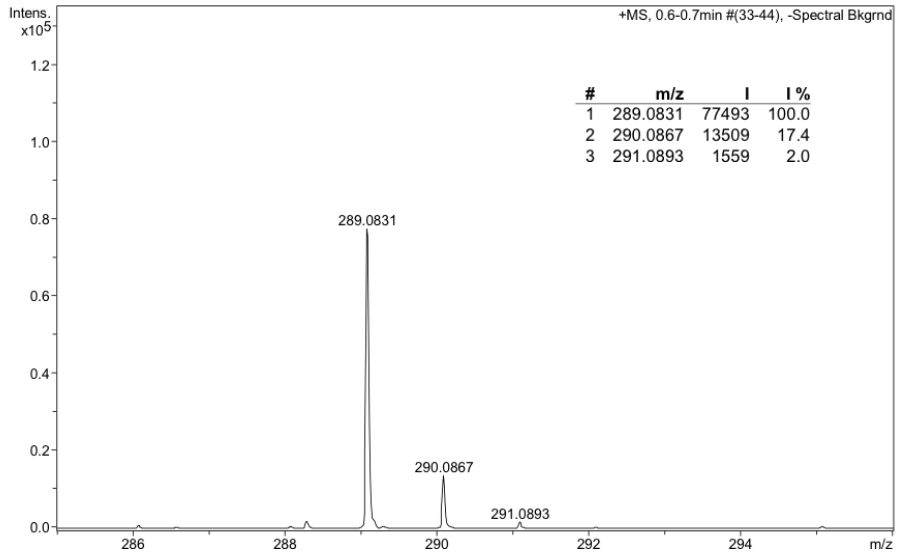


HRMS (ESI+):

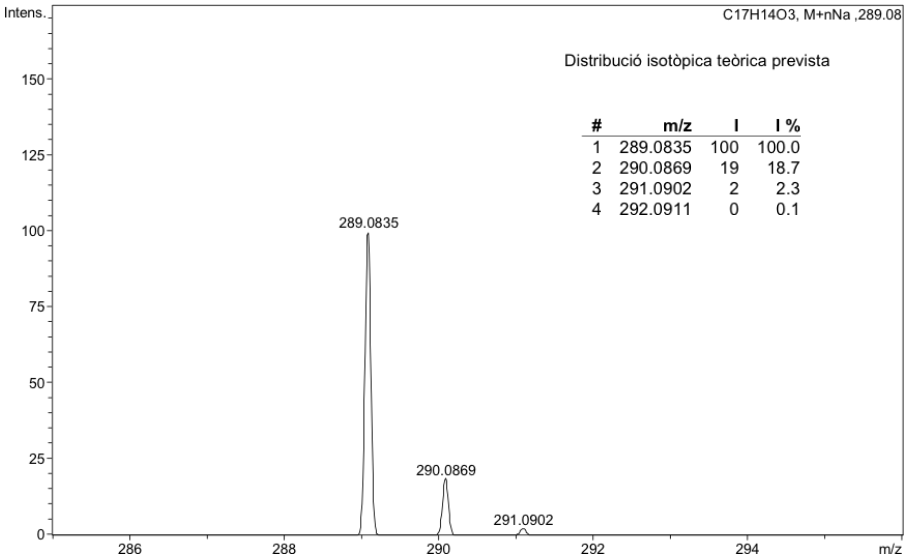


Analysis Info

Analysis Name	OV-XANT1(09EM116)_1-C,4_01_1888.d	Acquisition Date	18/03/2009 12:12:02
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-XANT1(09EM116)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

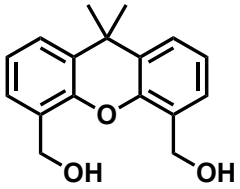


#	m/z	I	I %
1	289.0831	77493	100.0
2	290.0867	13509	17.4
3	291.0893	1559	2.0

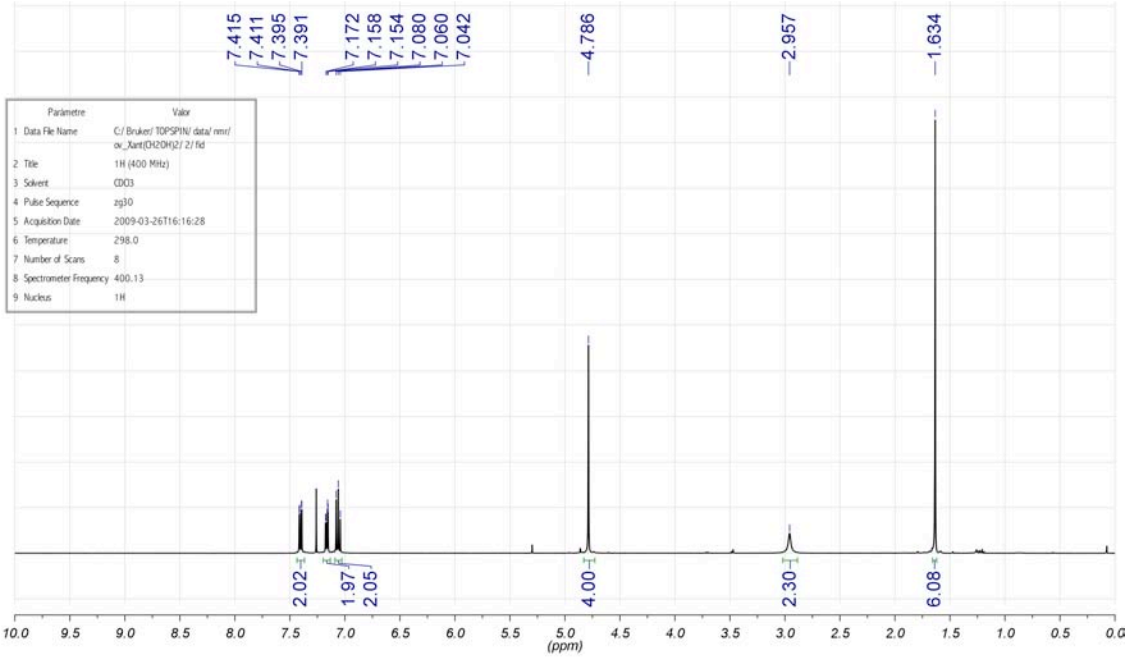


#	m/z	I	I %
1	289.0835	100	100.0
2	290.0869	19	18.7
3	291.0902	2	2.3
4	292.0911	0	0.1

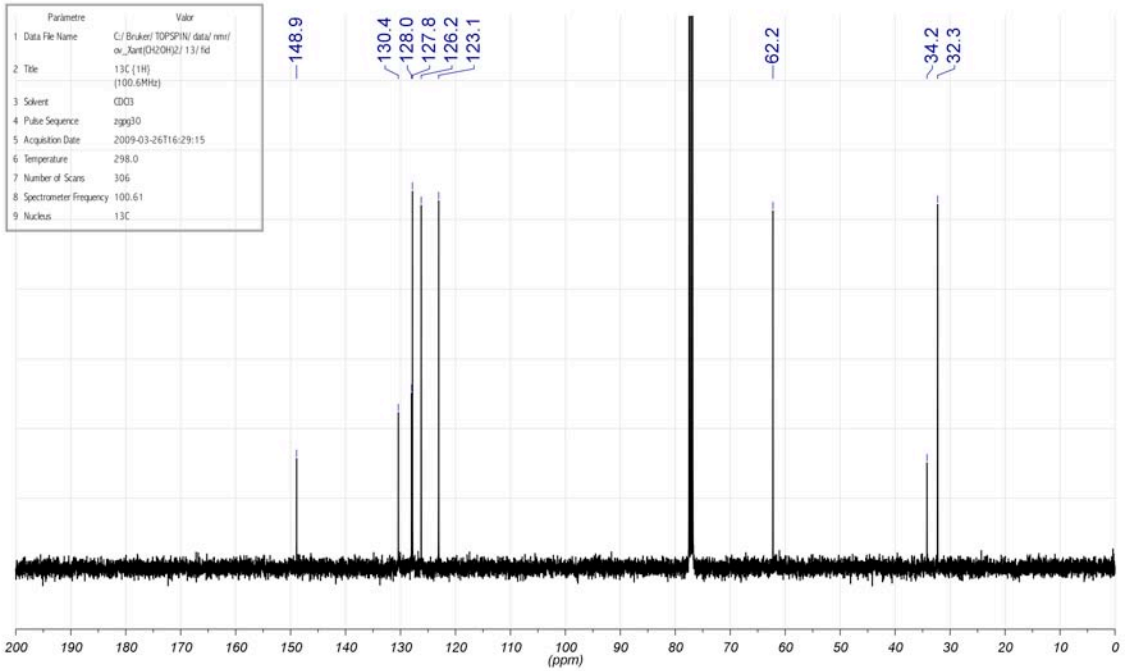
[5-(hidroximetil)-9,9-dimetil-9H-4-xantenil]metanol (I15)



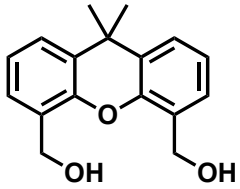
^{1}H RMN (400 MHz, rt, $CDCl_3$):



^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

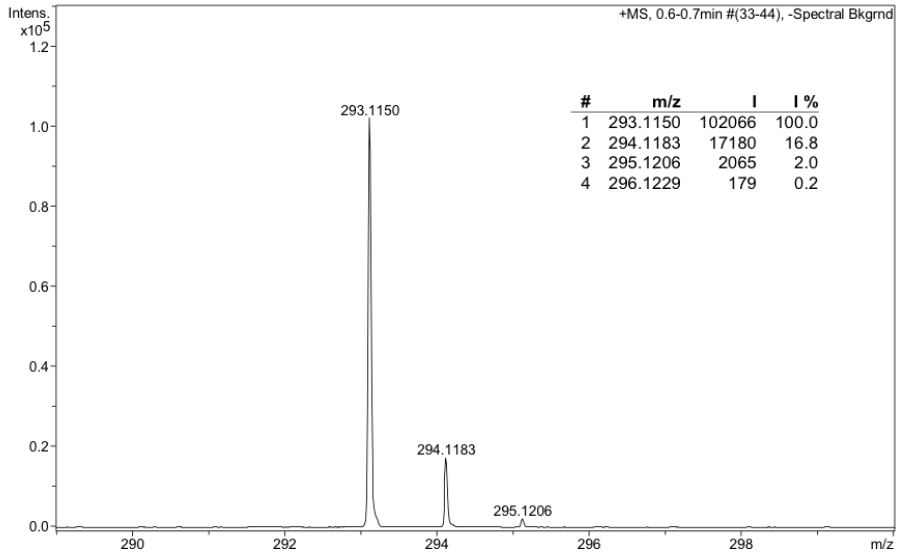


HRMS (ESI+):

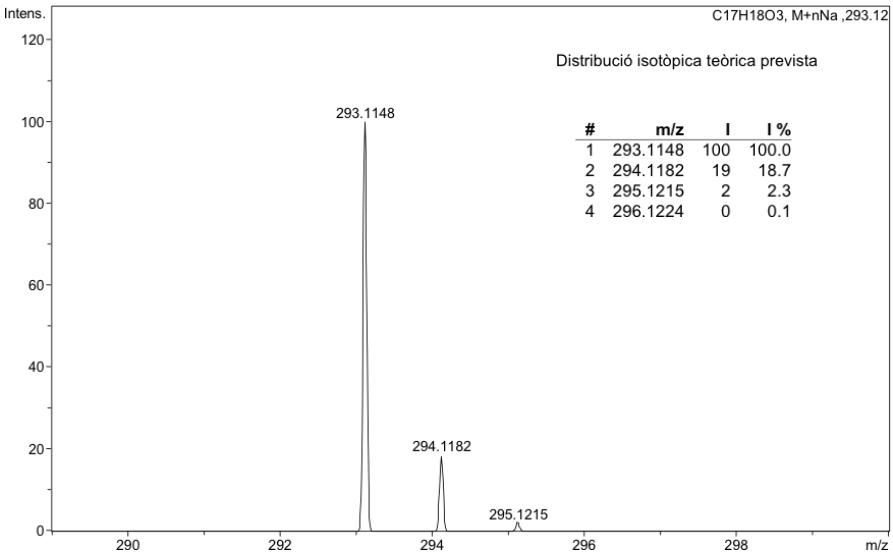


Analysis Info

Analysis Name	OV-XANT2(09EM114)_1-B,8_01_1883.d	Acquisition Date	18/03/2009 11:38:22
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-XANT2(09EM114)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

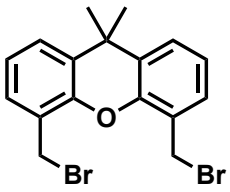


#	m/z	I	I %
1	293.1150	102066	100.0
2	294.1183	17180	16.8
3	295.1206	2065	2.0
4	296.1229	179	0.2

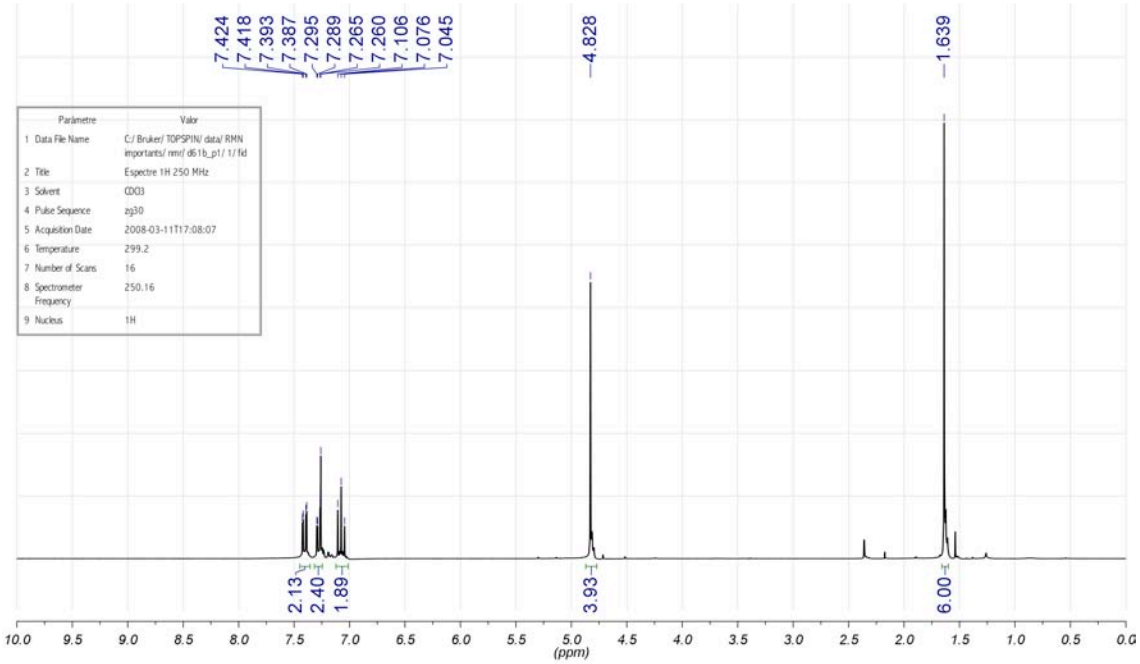


#	m/z	I	I %
1	293.1148	100	100.0
2	294.1182	19	18.7
3	295.1215	2	2.3
4	296.1224	0	0.1

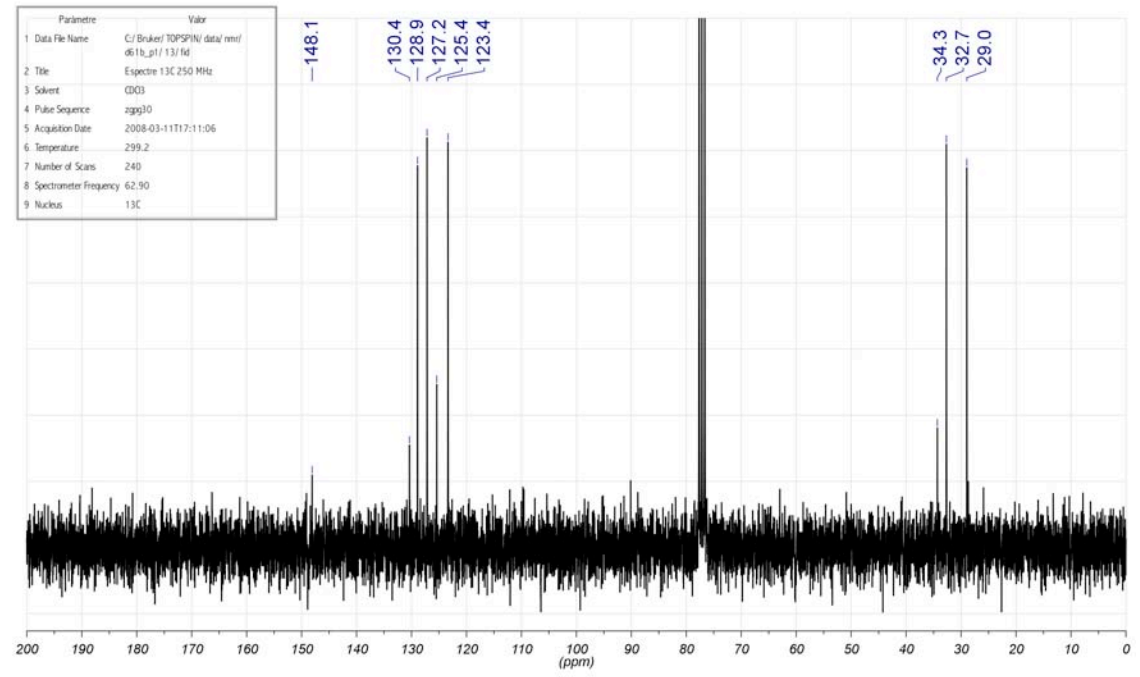
4,5-di(bromometil)-9,9-dimetil-9H-xantè (I16)



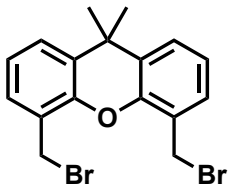
^{1}H RMN (250 MHz, rt, $CDCl_3$):



^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):

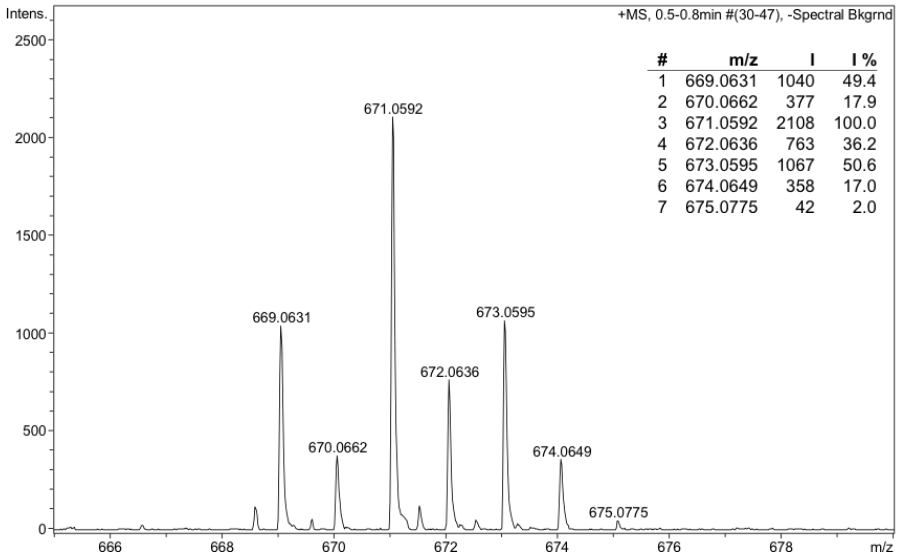


HRMS (ESI+):

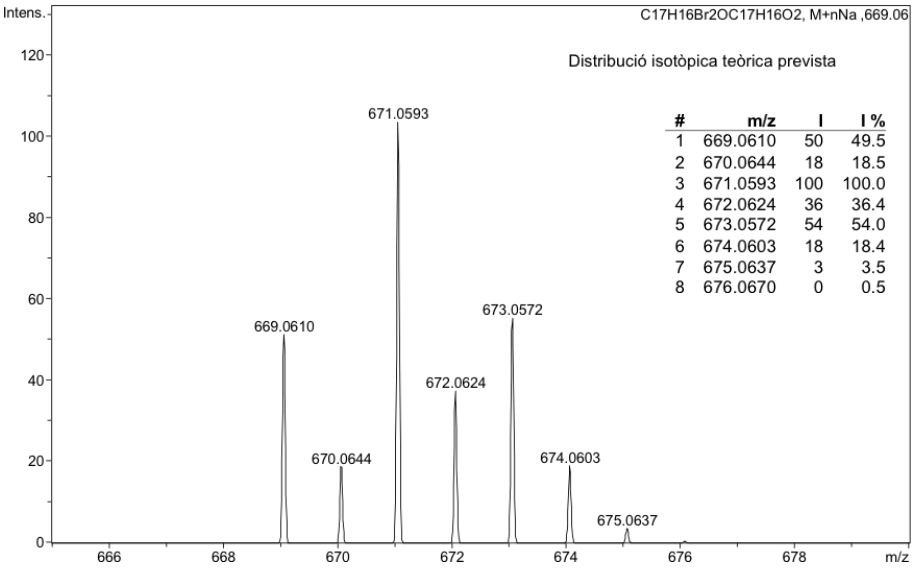


Analysis Info

Analysis Name	OV-XANT3(09EM115)_1-E,5_01_1907.d	Acquisition Date	18/03/2009 17:38:29
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-XANT3(09EM115)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 10 ppm en Acetona:MeOH (1:1)// O. VALLCORBA		

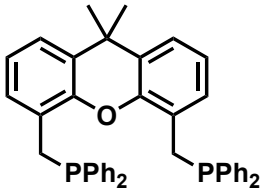


#	m/z	I	I %
1	669.0631	1040	49.4
2	670.0662	377	17.9
3	671.0592	2108	100.0
4	672.0636	763	36.2
5	673.0595	1067	50.6
6	674.0649	358	17.0
7	675.0775	42	2.0

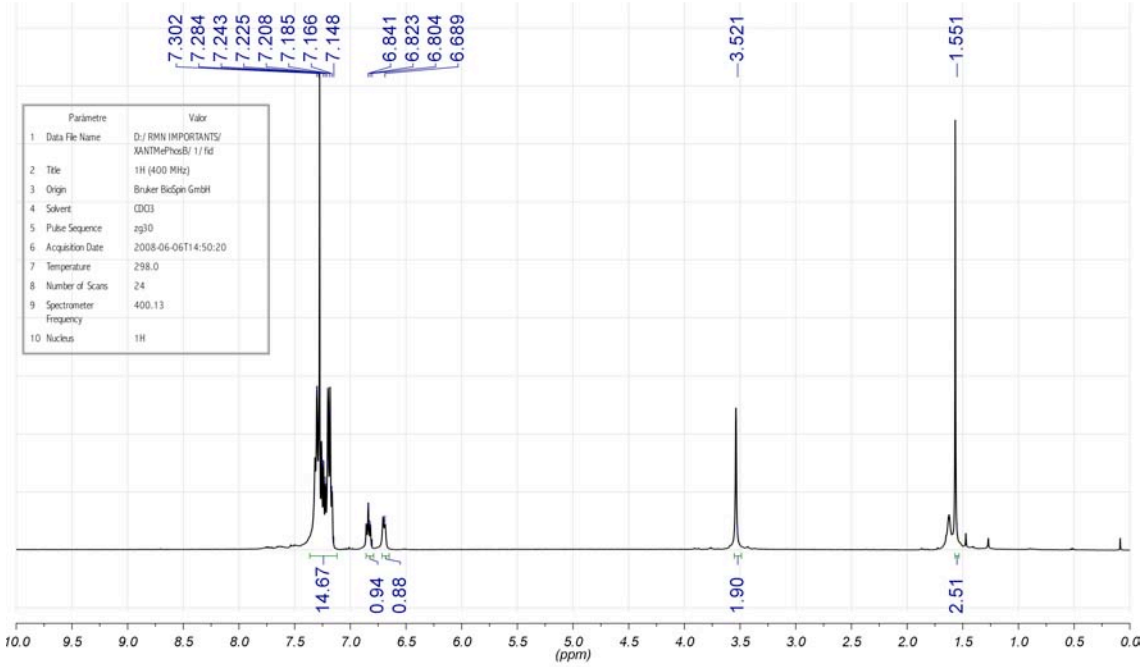


#	m/z	I	I %
1	669.0610	50	49.5
2	670.0644	18	18.5
3	671.0593	100	100.0
4	672.0624	36	36.4
5	673.0572	54	54.0
6	674.0603	18	18.4
7	675.0637	3	3.5
8	676.0670	0	0.5

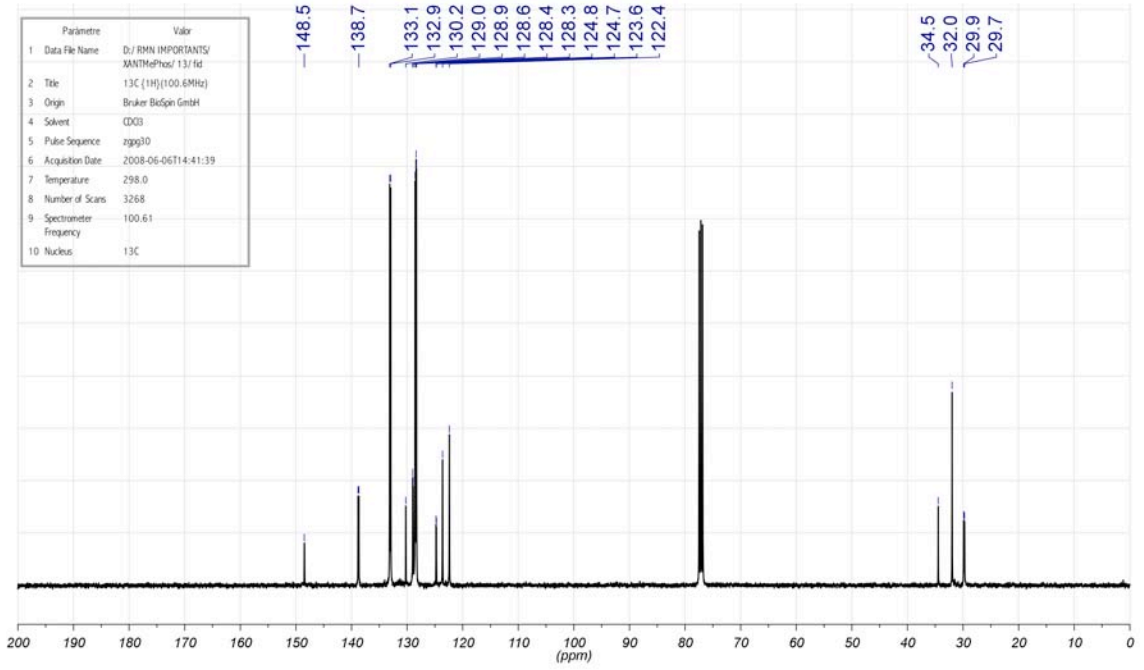
([5-{1,1-difenilfosfinometil}-9,9-dimetil-9H-4-xantenil]metil)difenilfosfina (XantMephos, L34)

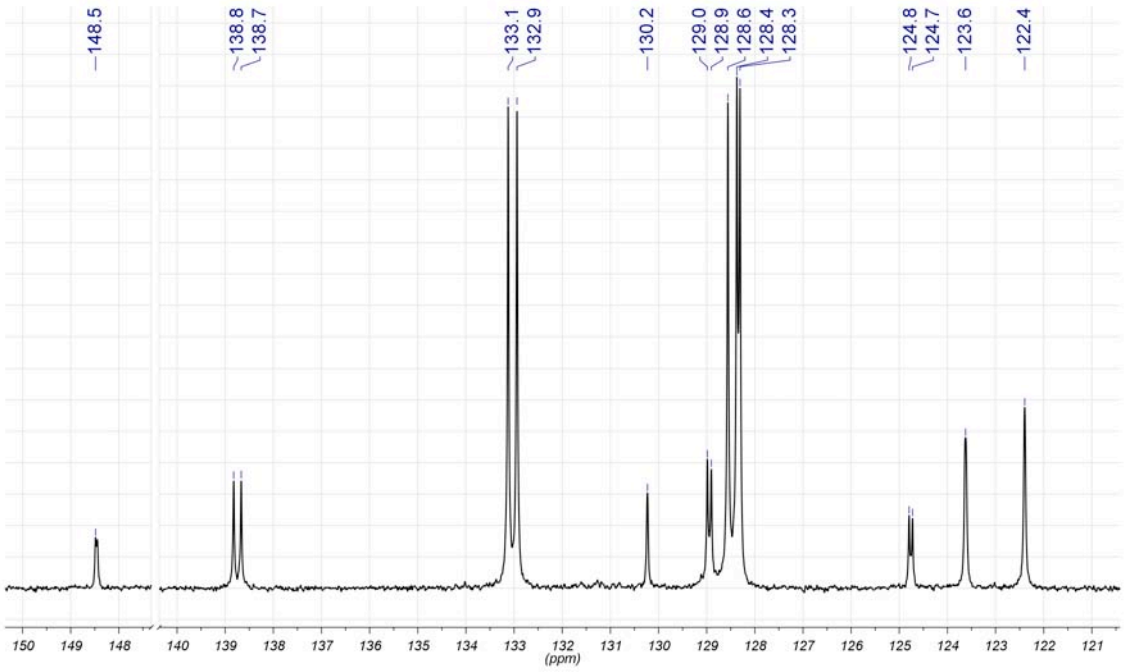


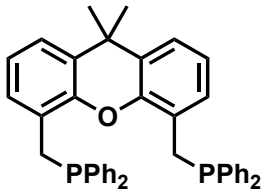
^{1}H RMN (400 MHz, rt, $CDCl_3$):



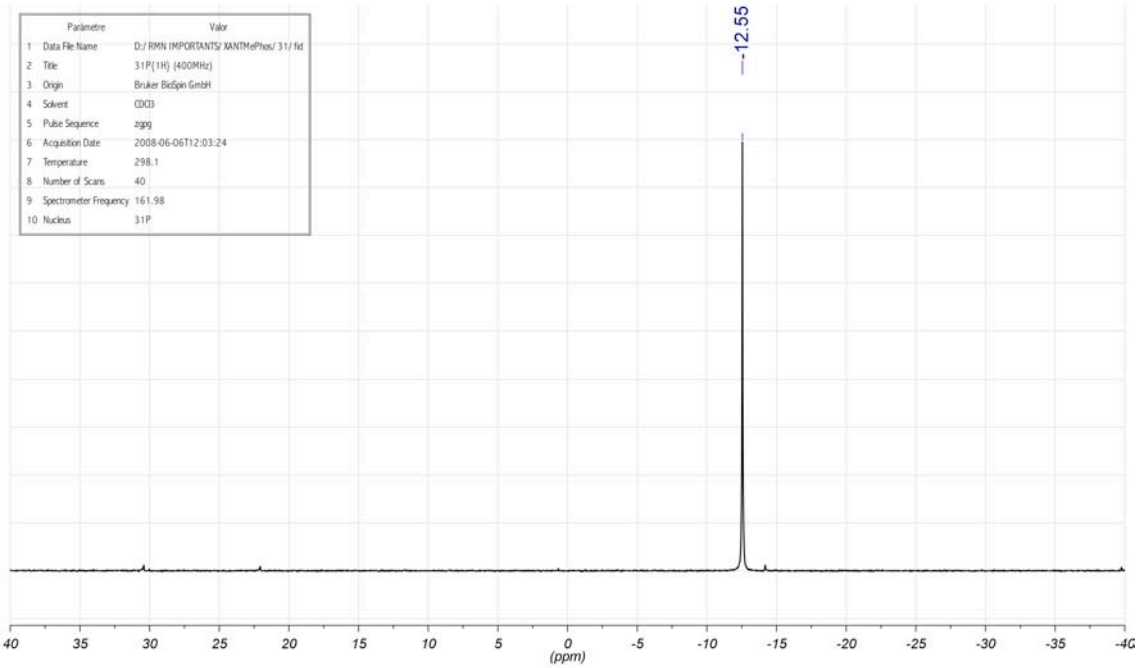
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):



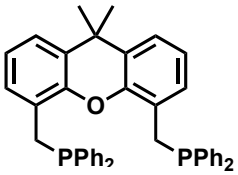


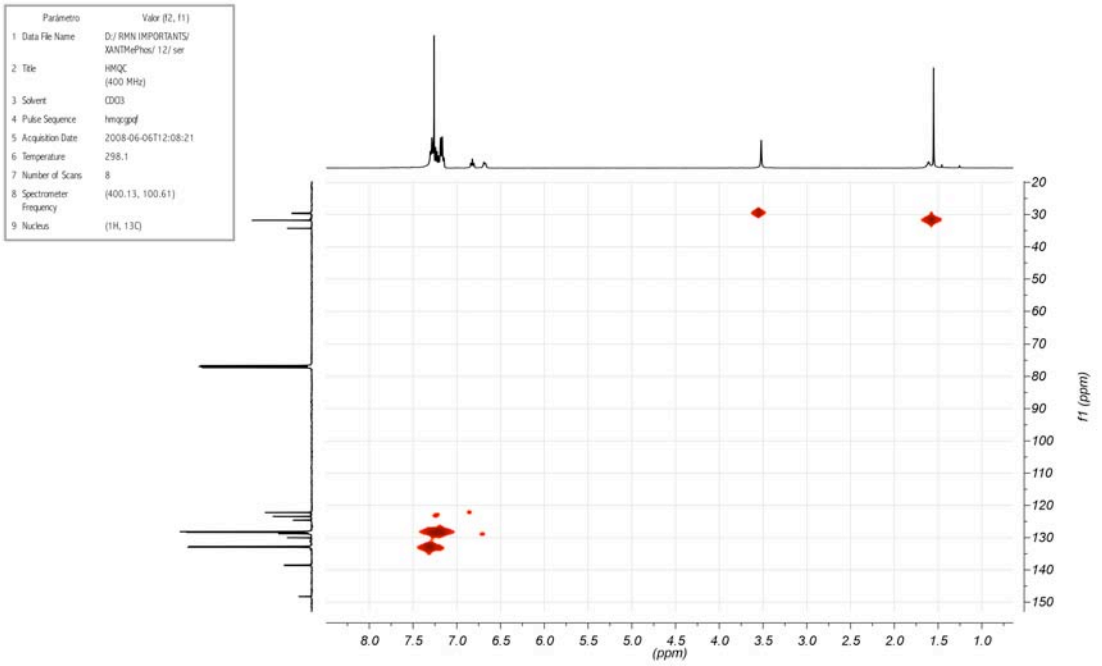


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

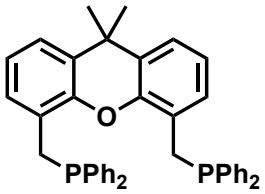


Espectre de correlació ^{1}H-^{13}C (HMQC):



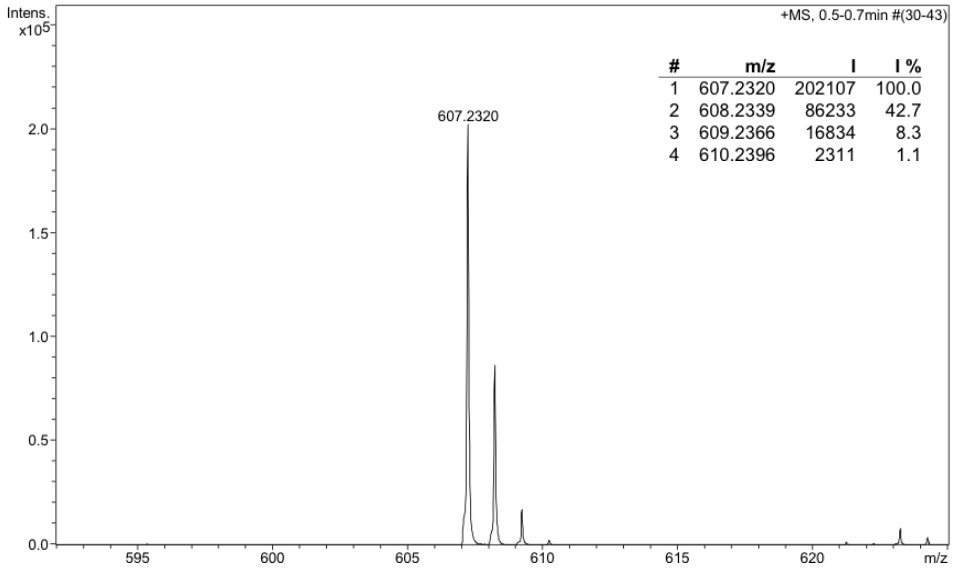


HRMS (ESI+):

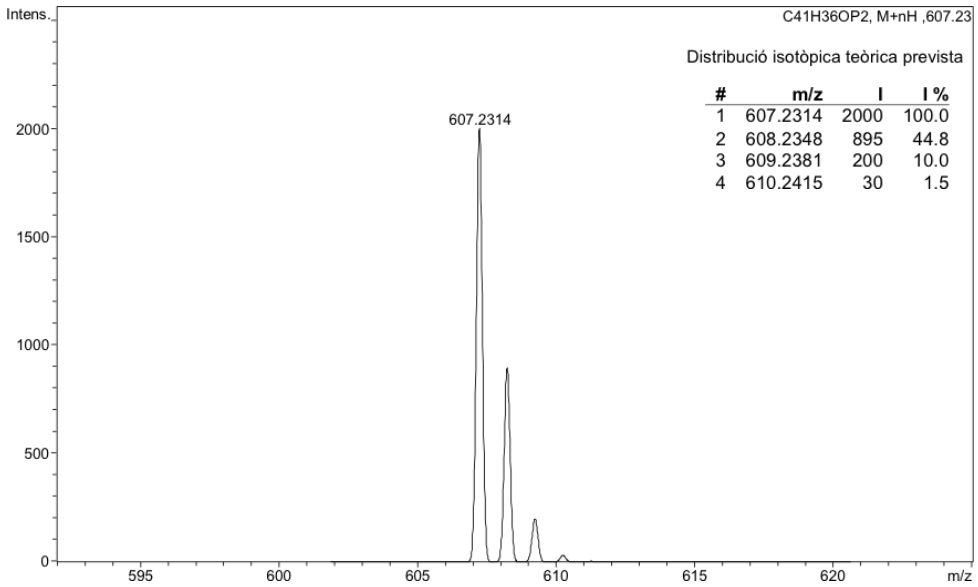


Analysis Info

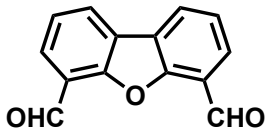
Analysis Name	d63 (8EM-145)_1-d,4_01_148.d	Acquisition Date	09/05/2008 16:08:10
Method	ESIpos100-600_FI-HS_MeOH_29-4-08.m	Operator	SAQ
Sample Name	d63 (8EM-145)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2ppm en MeOH. // O. VALLCORBA		



#	m/z	I	I %
1	607.2320	202107	100.0
2	608.2339	86233	42.7
3	609.2366	16834	8.3
4	610.2396	2311	1.1

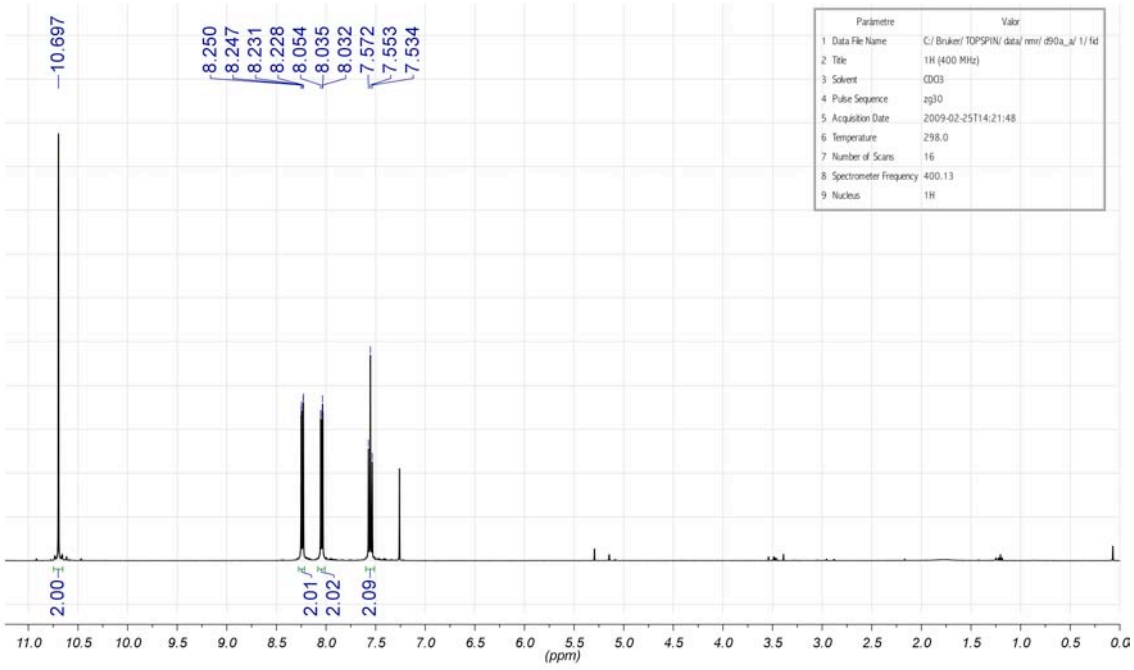


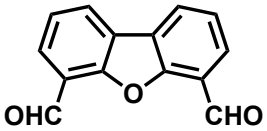
8.3 Síntesi de la DBFMephos (L35)



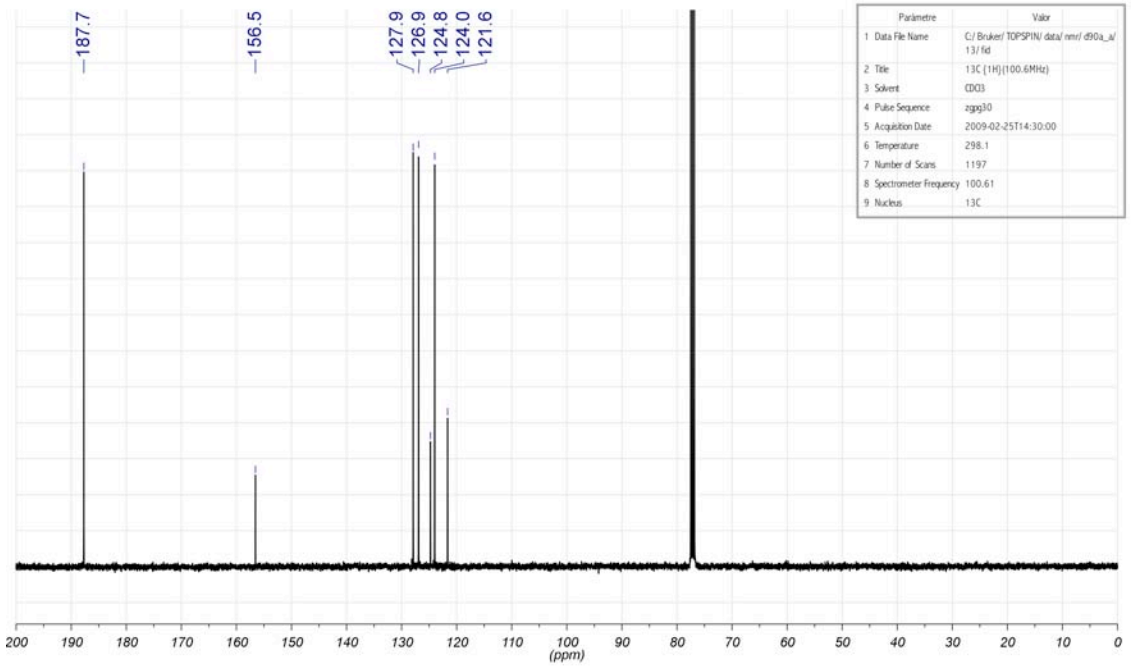
Dibenzo[b,d]furan-4,6-dicarbaldeid (I18)

^{1}H RMN (400 MHz, rt, $CDCl_3$):

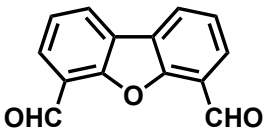




$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

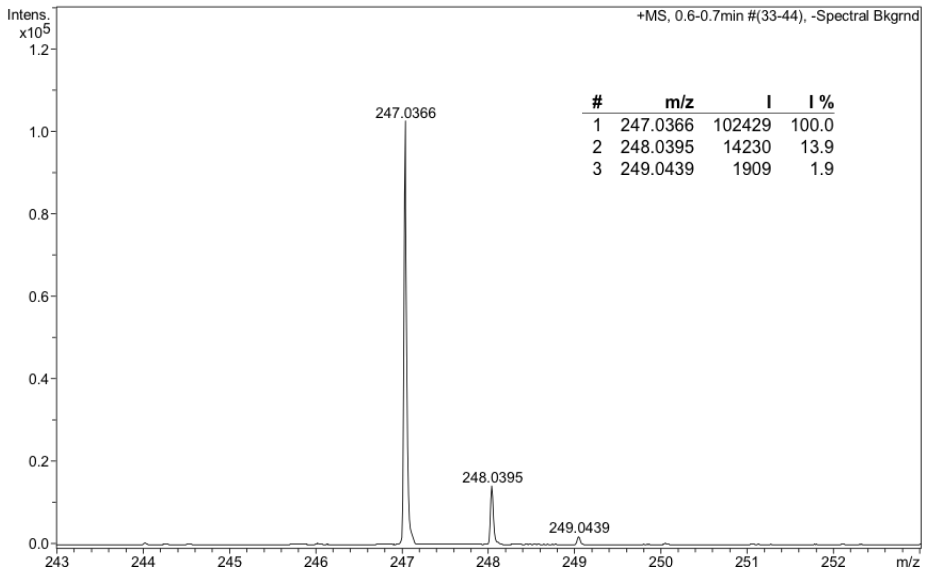


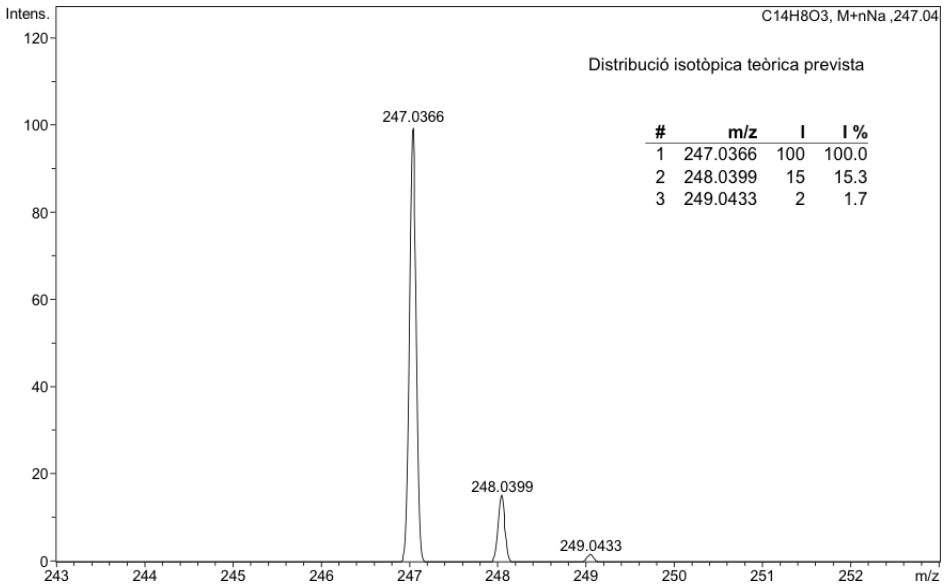
HRMS (ESI+):



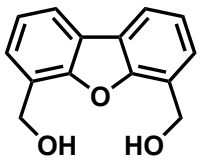
Analysis Info

Analysis Name	OV-DBF1(09EM120)_1-D,8_01_1901.d	Acquisition Date	18/03/2009 13:39:35
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-DBF1(09EM120)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

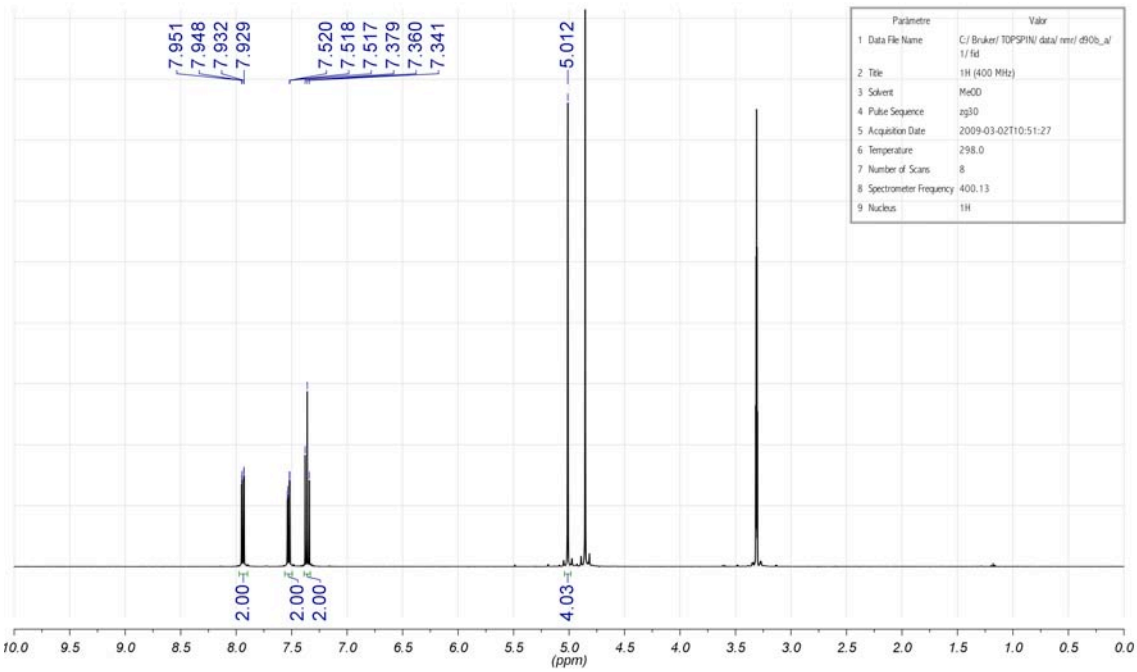


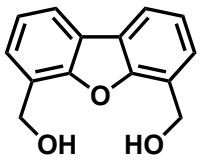


6-hidroximetildibenzo[b,d]furan-4-ilmetanol (**I19**)

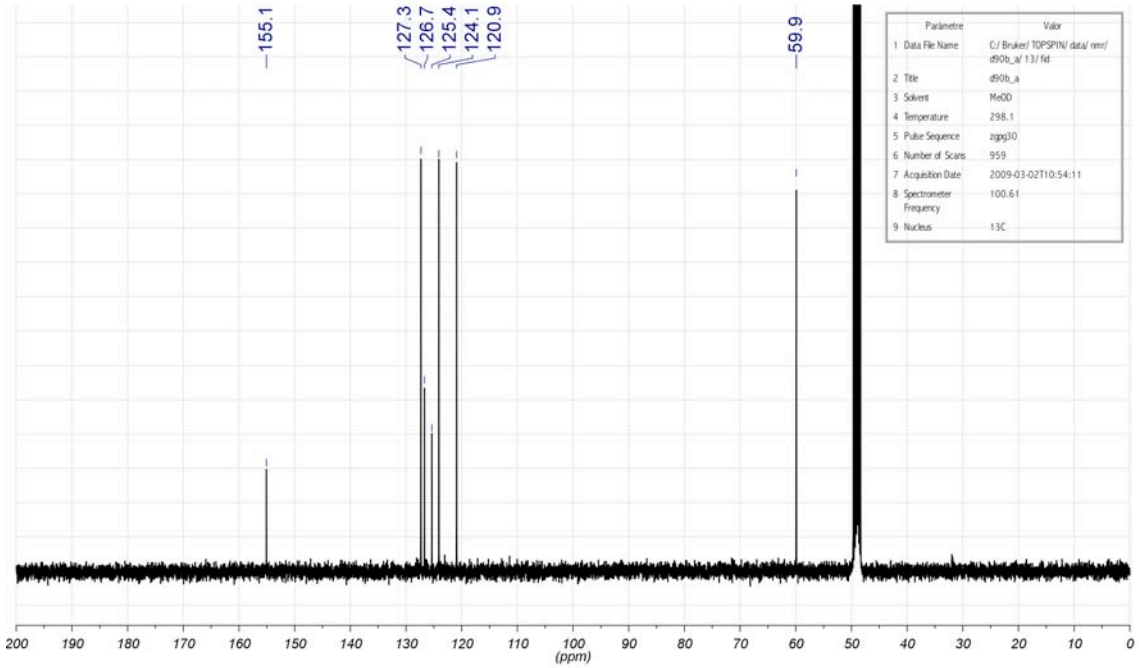


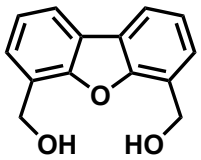
^{1}H RMN (400 MHz, rt, CH_3OD):





$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, CH_3OD):

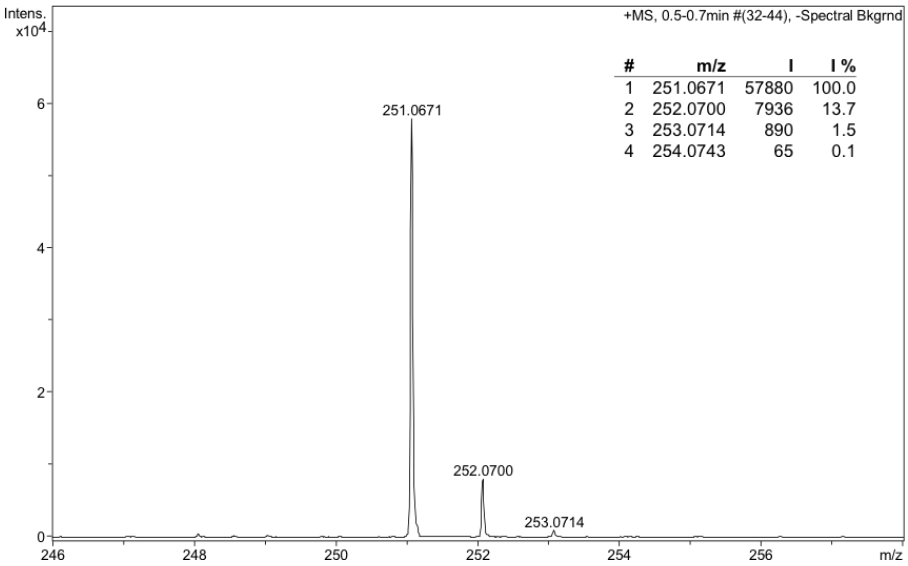


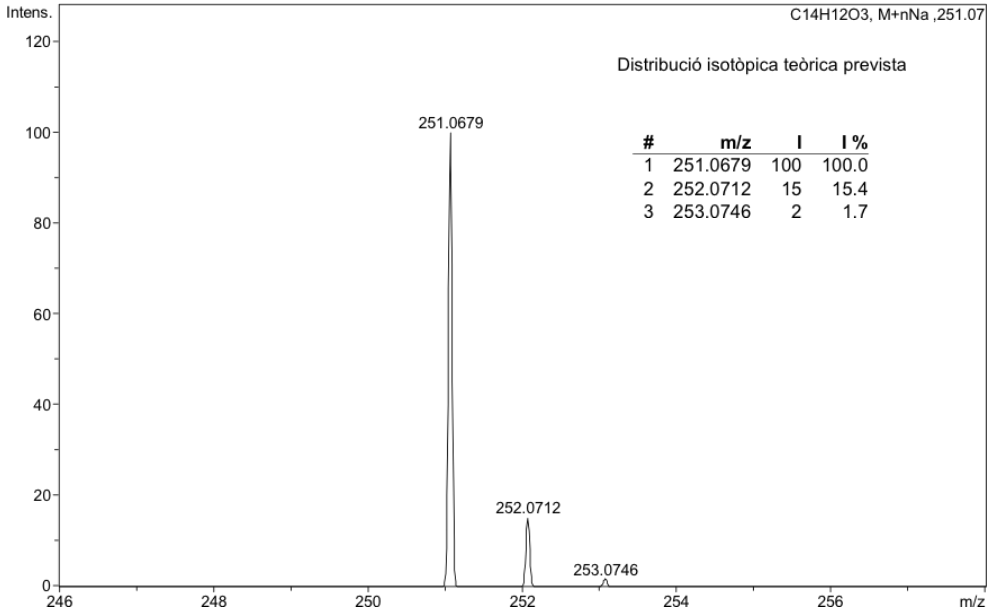


HRMS (ESI+):

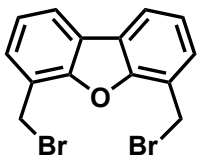
Analysis Info

Analysis Name	OV-DPF2(09EM121)_1-C,8_01_1892.d	Acquisition Date	18/03/2009 12:38:58
Method	esipos100-600_fi_02-02-09.m	Operator	SAQ
Sample Name	OV-DPF2(09EM121)	Instrument	micrOTOF-Q
Comment	AER. ESI+. Dó ca 2 ppm en MeOH // O. VALLCORBA		

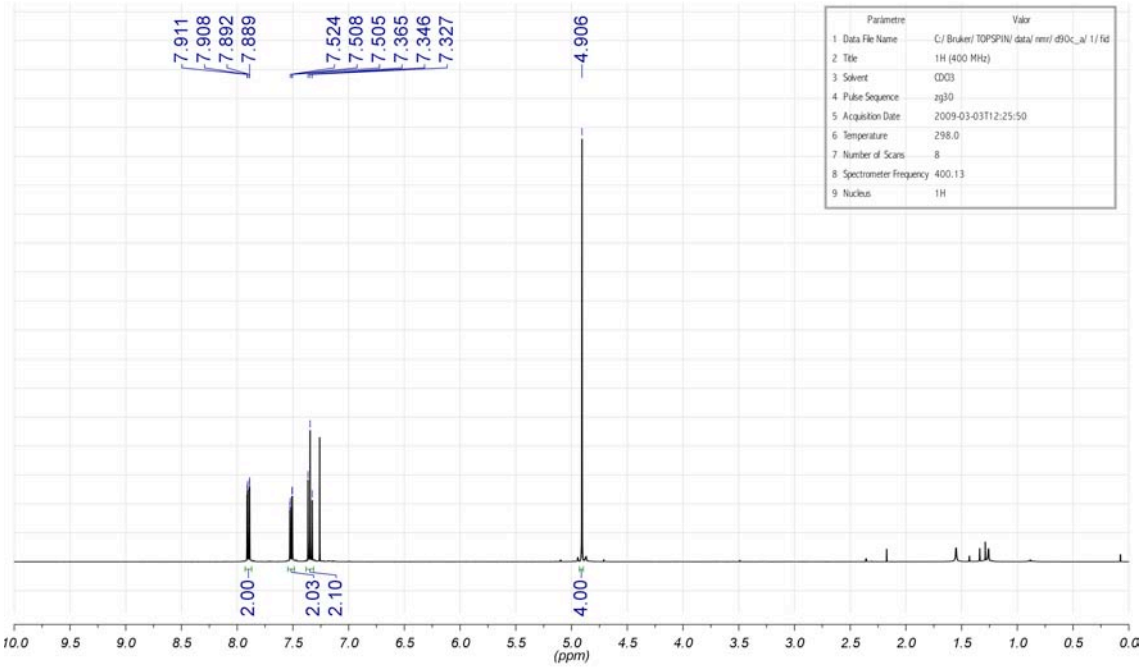


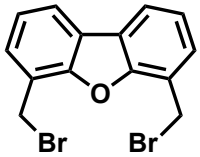


4,6-di(bromometil)dibenzo[b,d]furà (**I20**)

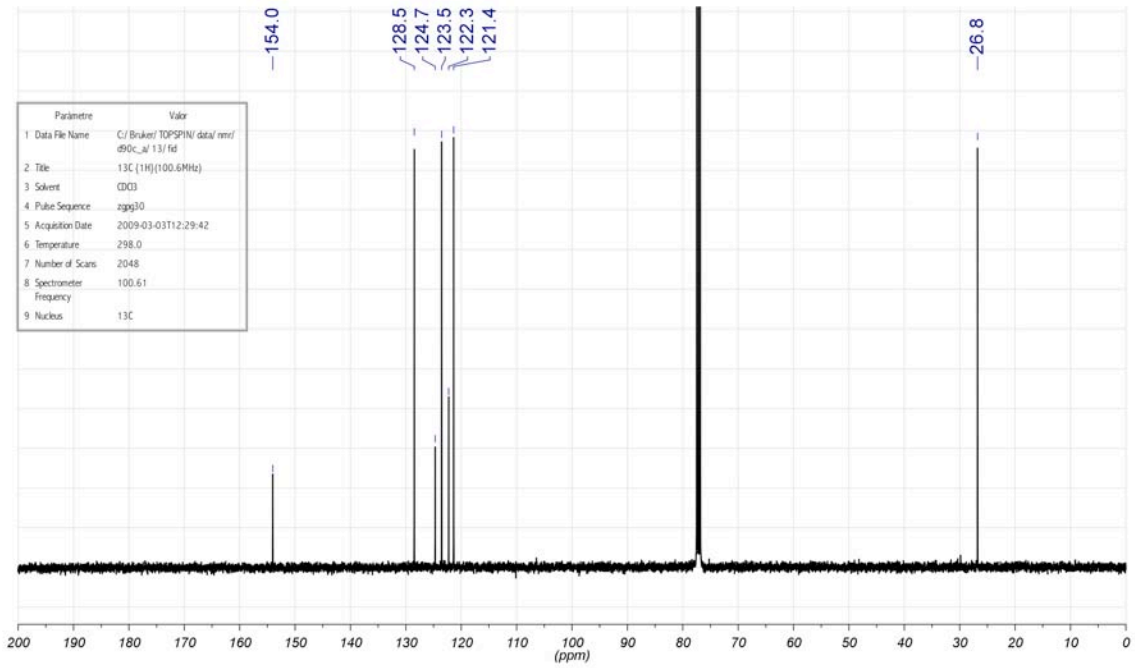


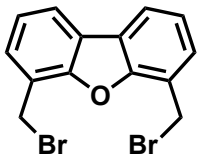
^{1}H RMN (400 MHz, rt, $CDCl_3$):



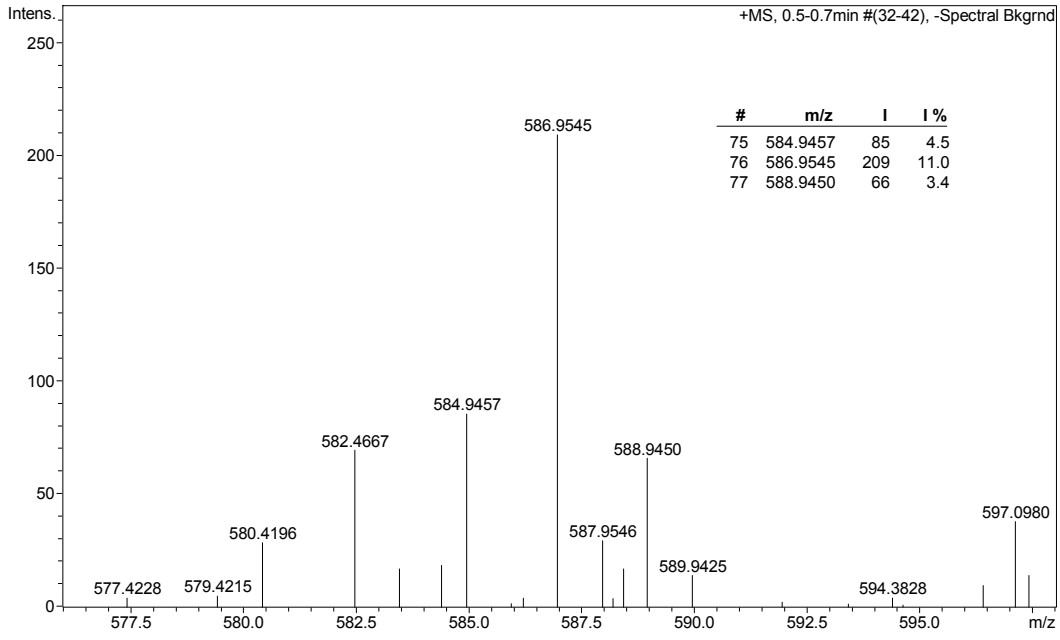


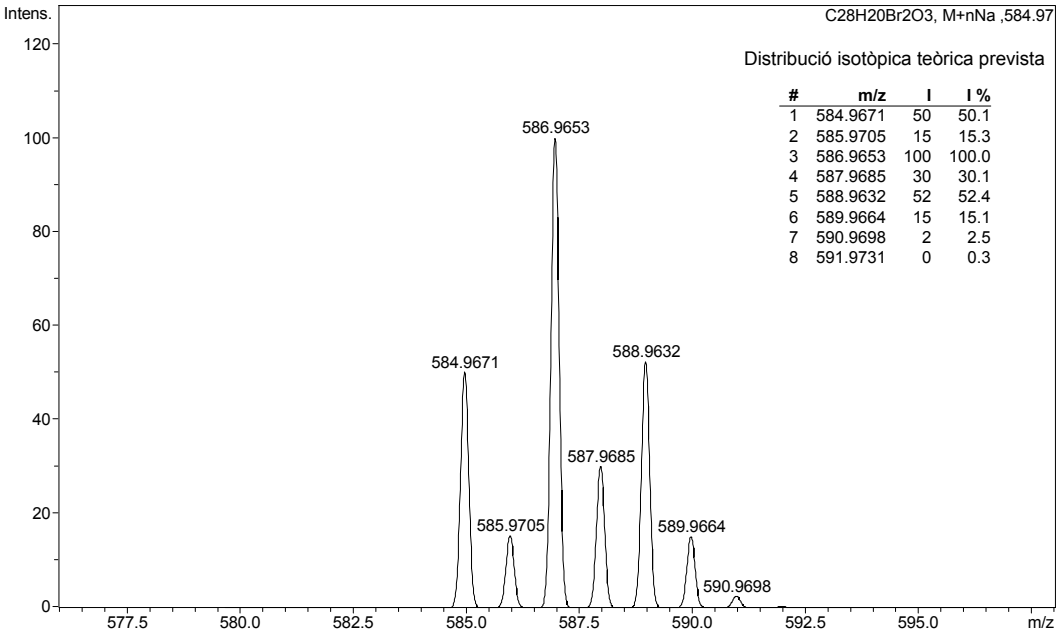
$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):



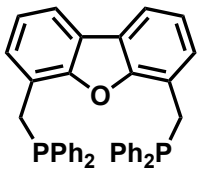


HRMS (ESI+):

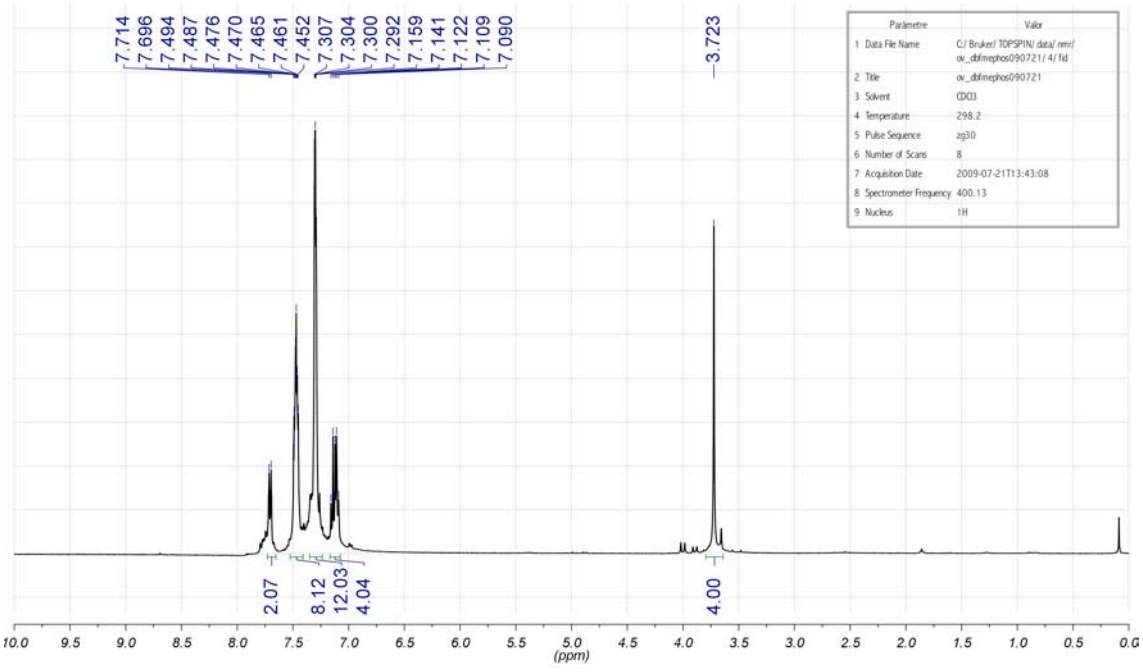


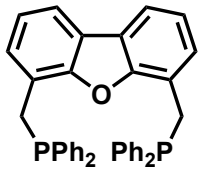


4,6-bis((diphenylphosphino)methyl)dibenzo[b,d]furan (DBFMephos, L35)

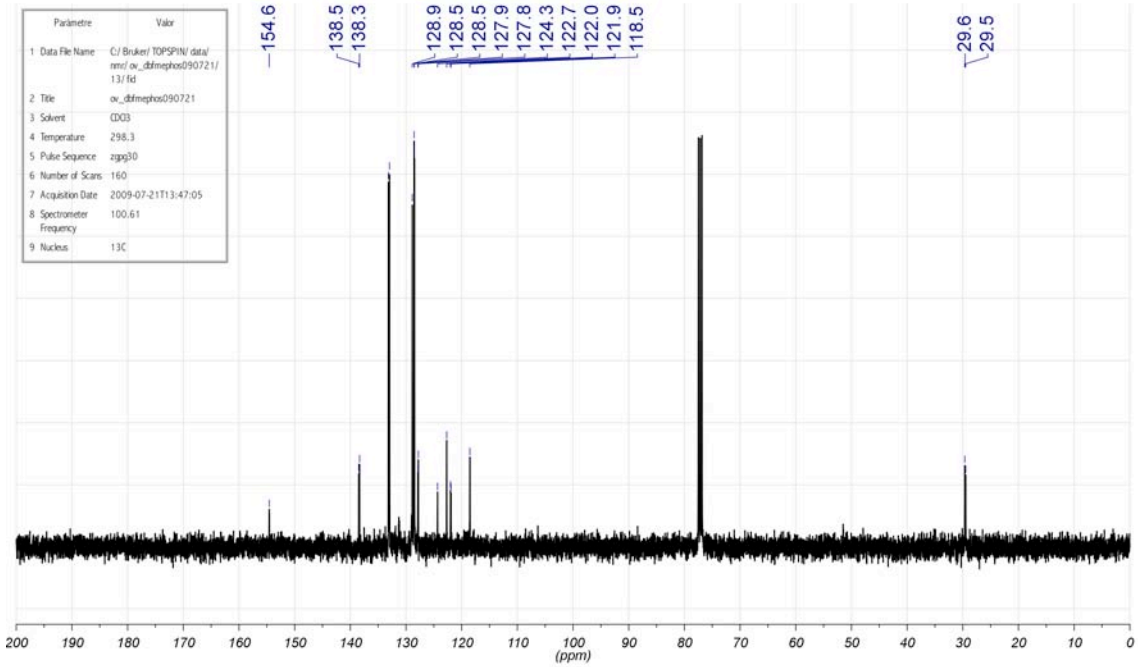


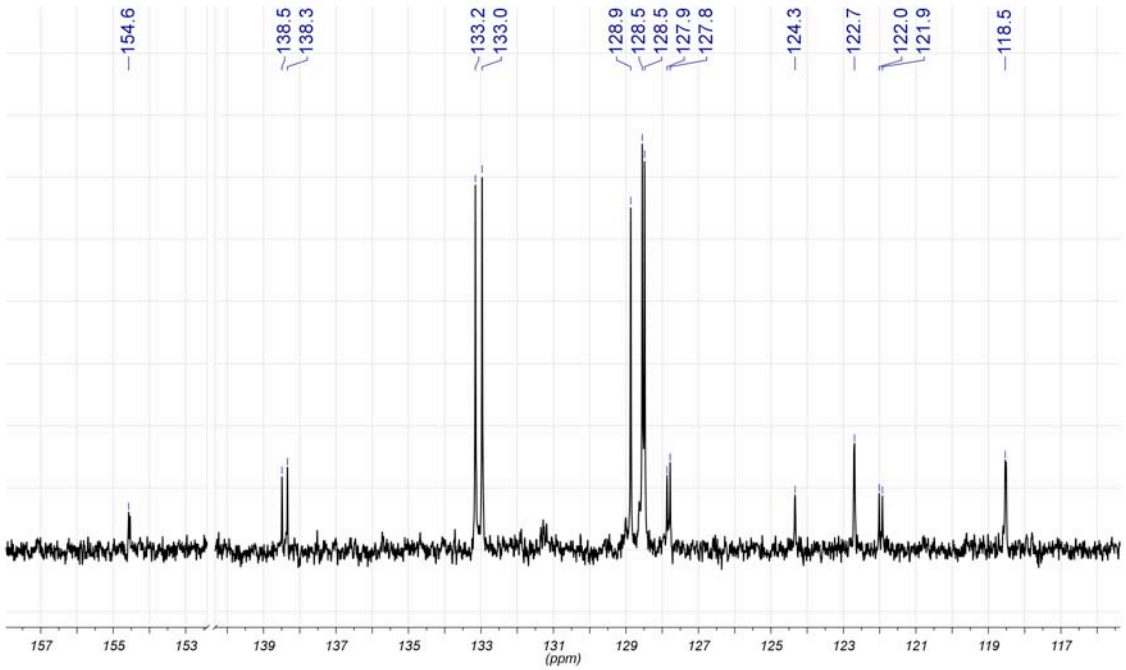
^{1}H RMN (400 MHz, rt, $CDCl_3$):

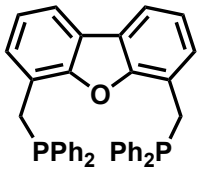




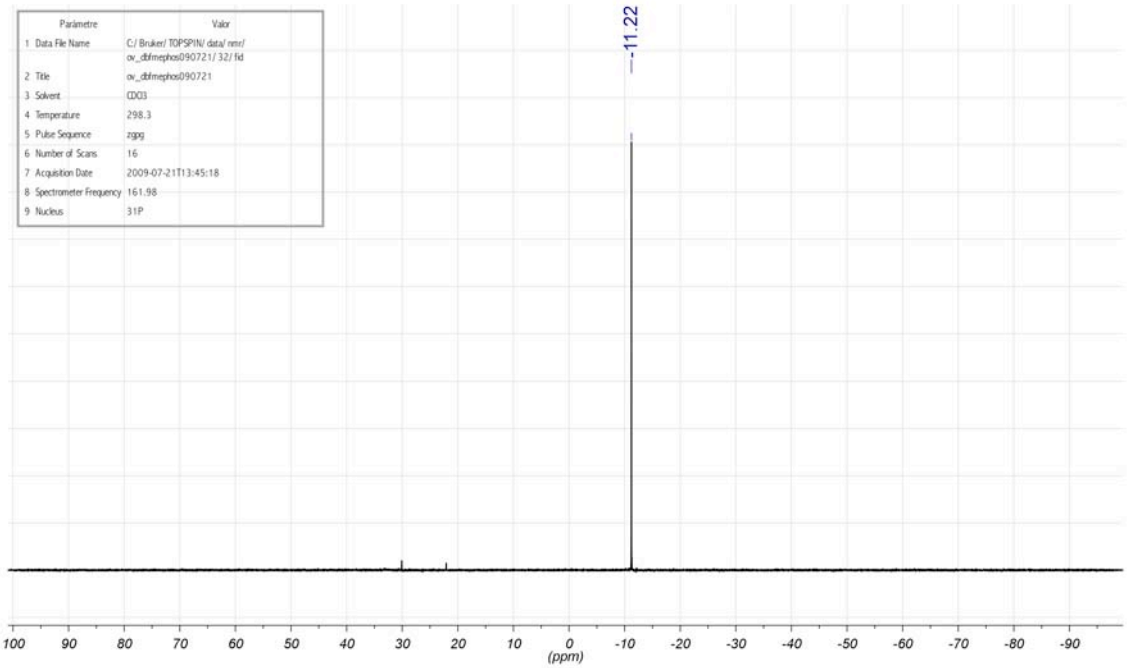
$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

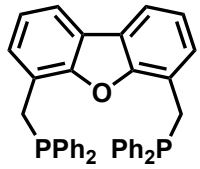




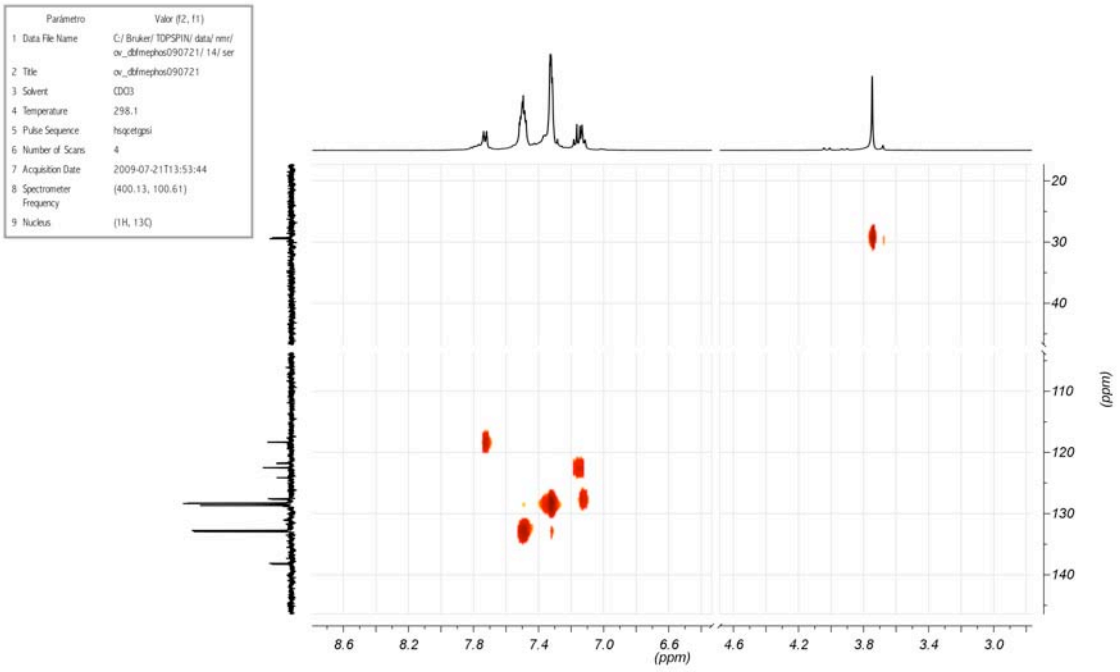


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

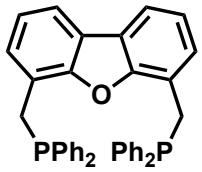




Espectre de correlació ^{1}H-^{13}C (HMQC):

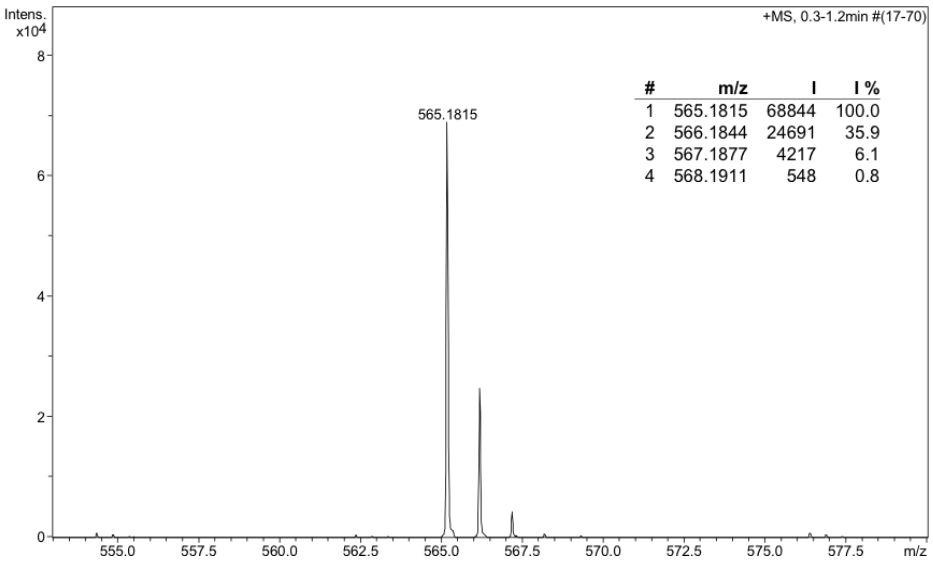


HRMS (ESI+):

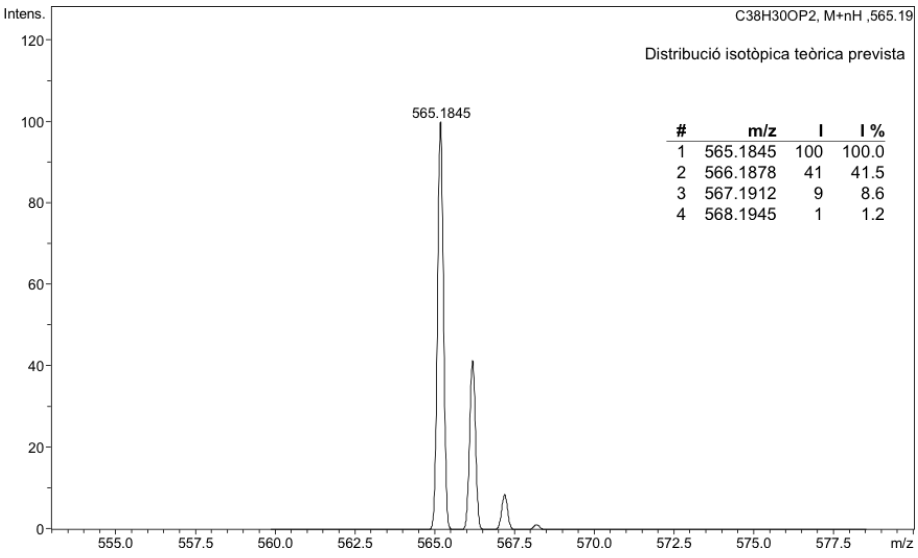


Analysis Info

Analysis Name	09EM421-QTOF-pos1-1.d	Acquisition Date	17/09/2009 12:38:34
Method	09EM421-QTOF-pos1.m	Operator	SAQ
Sample Name	OVDB F Me	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 5 ppm en MeOH. O. VALLCORBA		



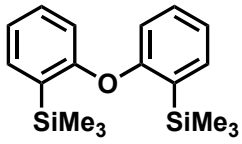
#	m/z	I	I %
1	565.1815	68844	100.0
2	566.1844	24691	35.9
3	567.1877	4217	6.1
4	568.1911	548	0.8



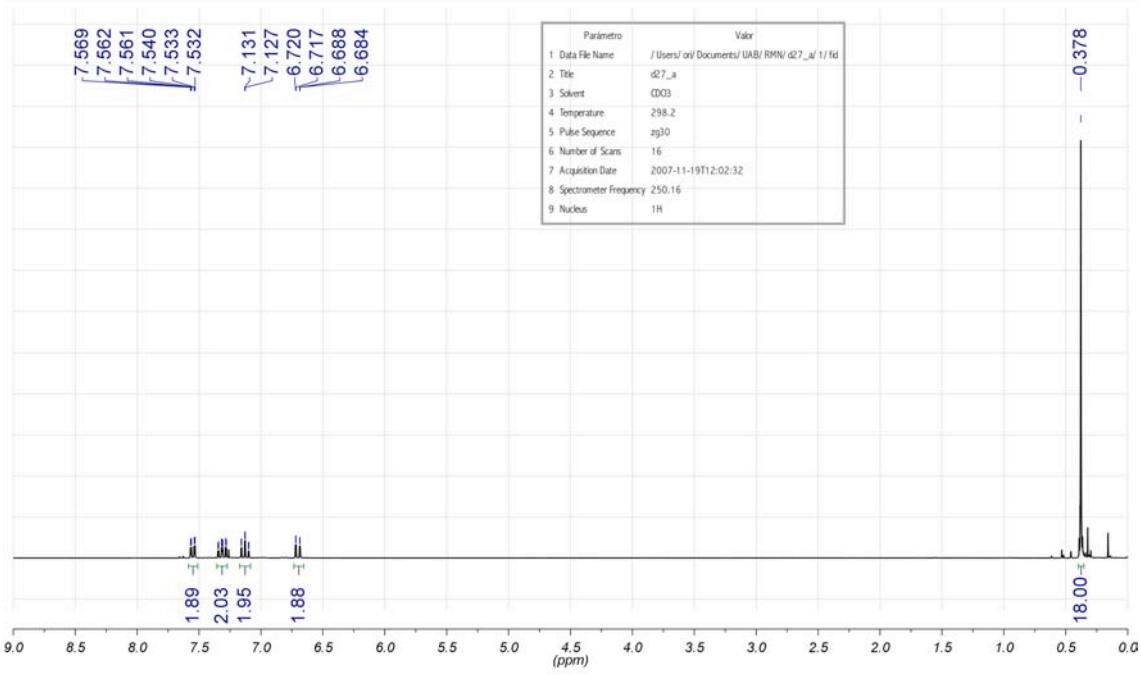
#	m/z	I	I %
1	565.1845	100	100.0
2	566.1878	41	41.5
3	567.1912	9	8.6
4	568.1945	1	1.2

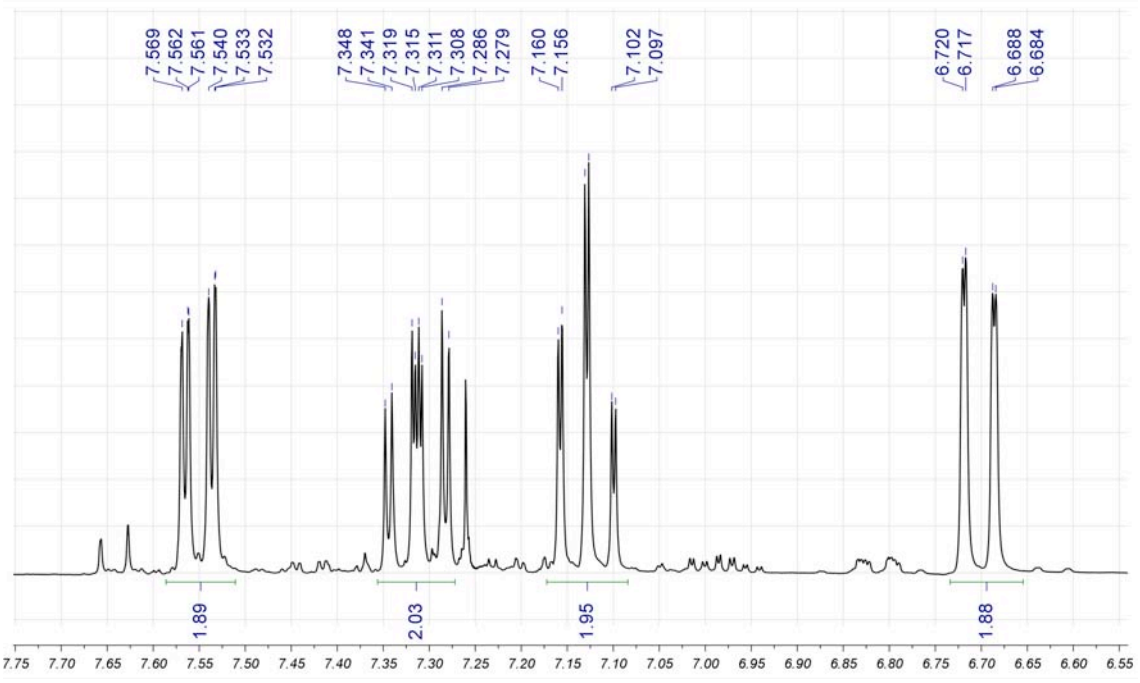
8.4 Altres intermedis en la modificació de la DPEphos

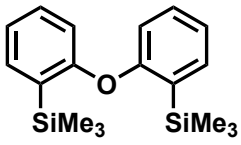
(oxibis(2,1-fenilè))bis(trimetilsilà) (I8)



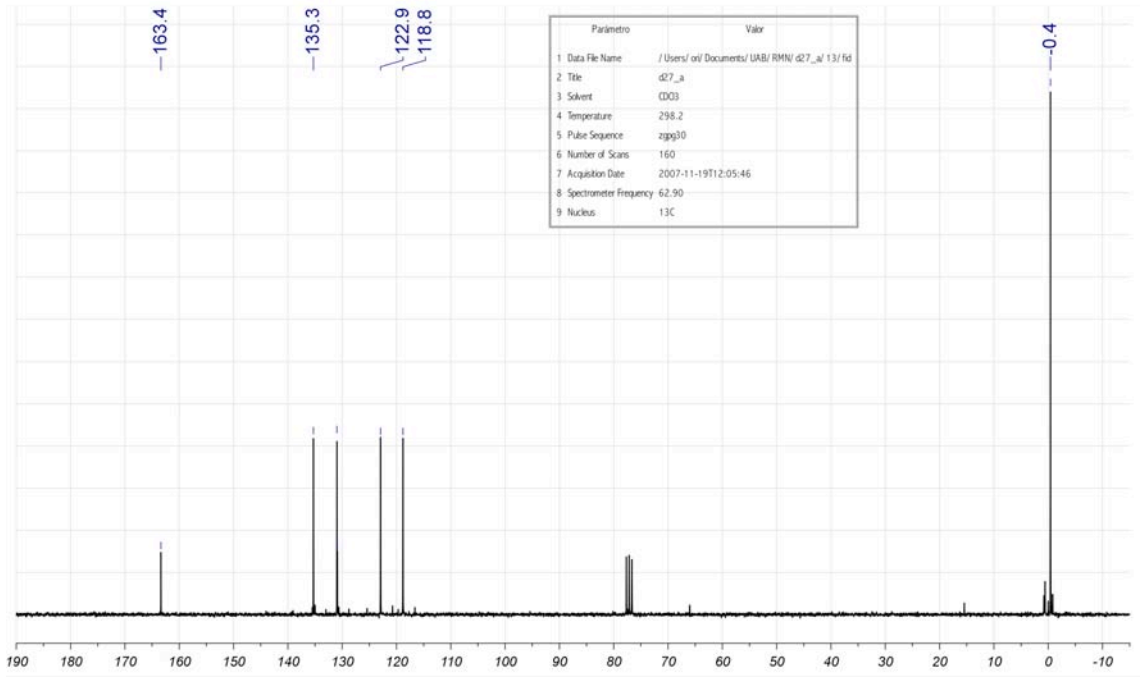
^{1}H RMN (400 MHz, rt, $CDCl_3$):







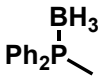
$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):



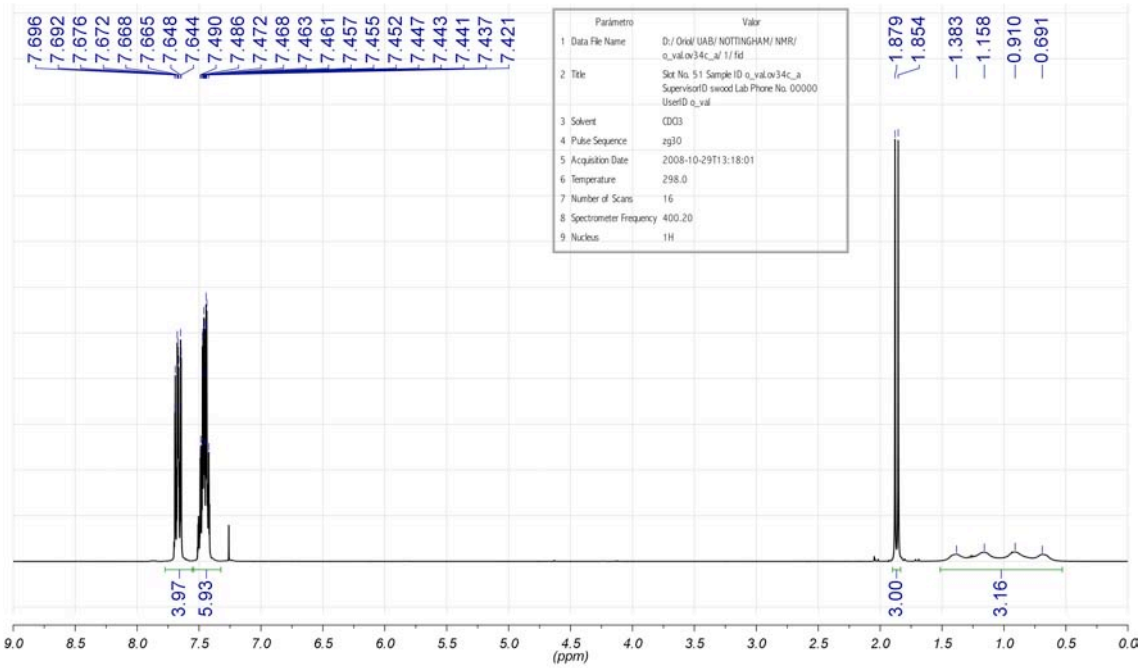
9 Caracterització d'intermedis i productes a la síntesi de monofosfines benzíliques

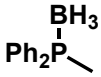
9.1 Intermedis

Difenilmetilfosfina-P-borà (L42b)

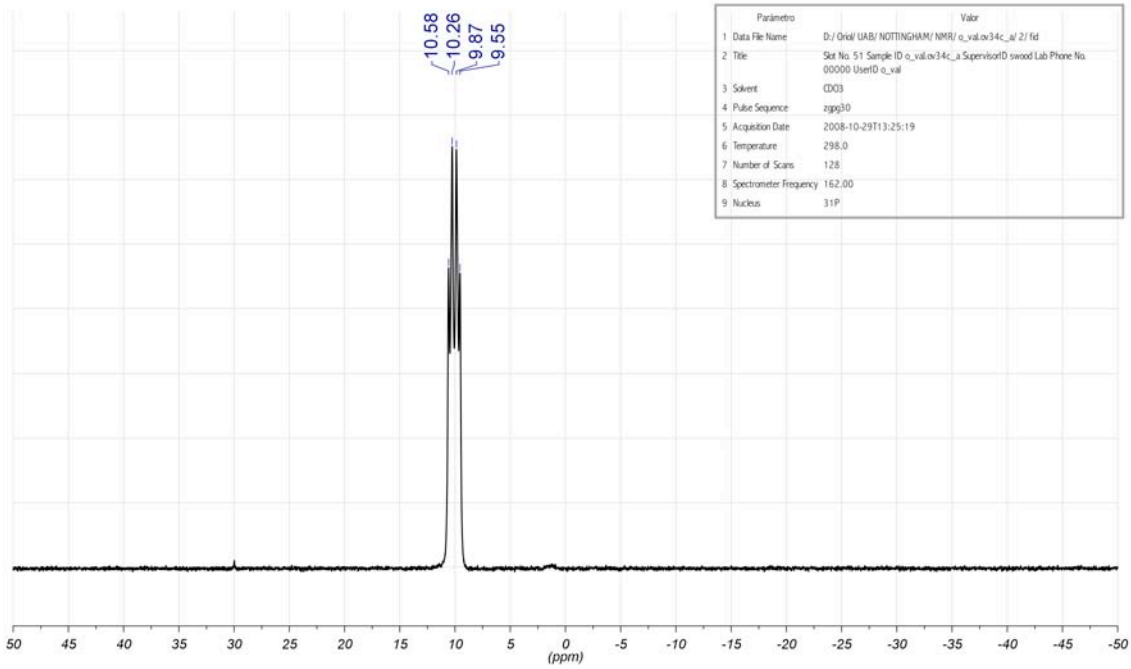


^{1}H RMN (400 MHz, rt, $CDCl_3$):

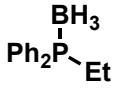




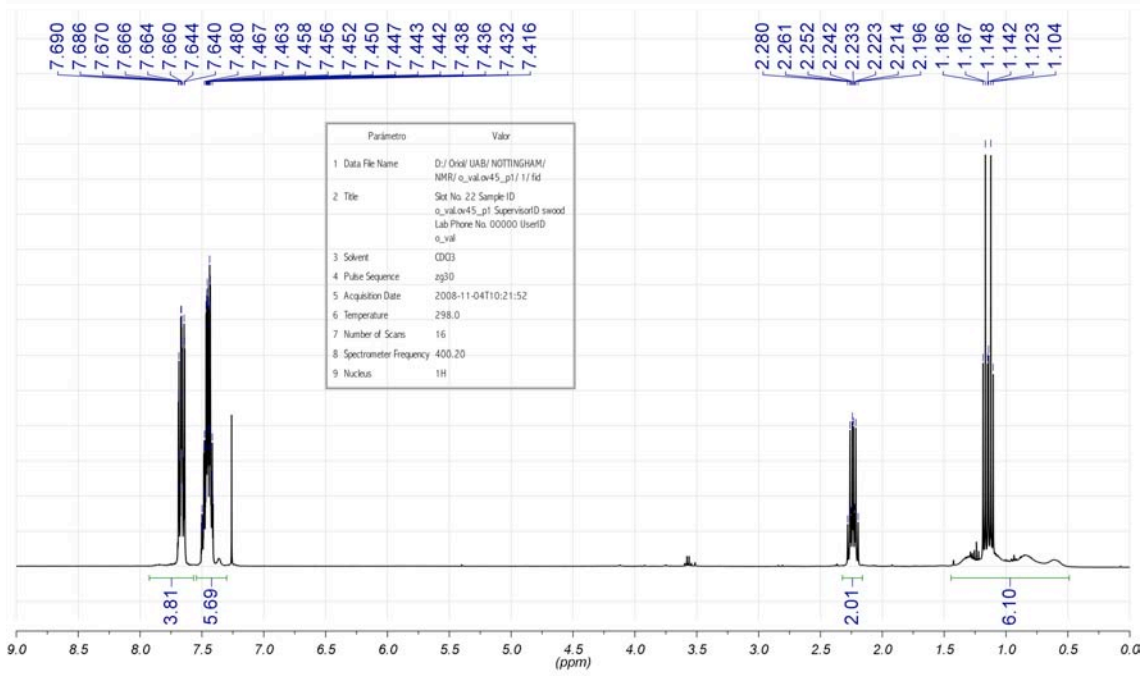
^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

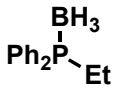


Etildifenilfosfina-P-borà (L53b)

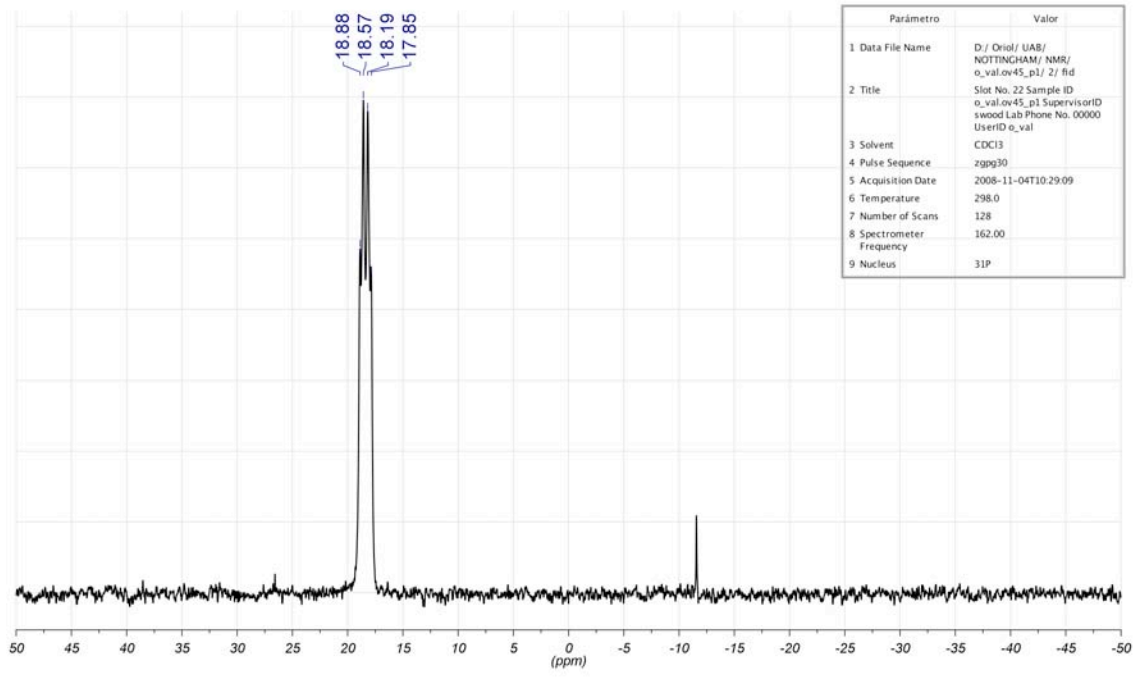


^{1}H RMN (400 MHz, rt, $CDCl_3$):

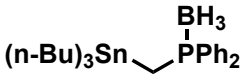




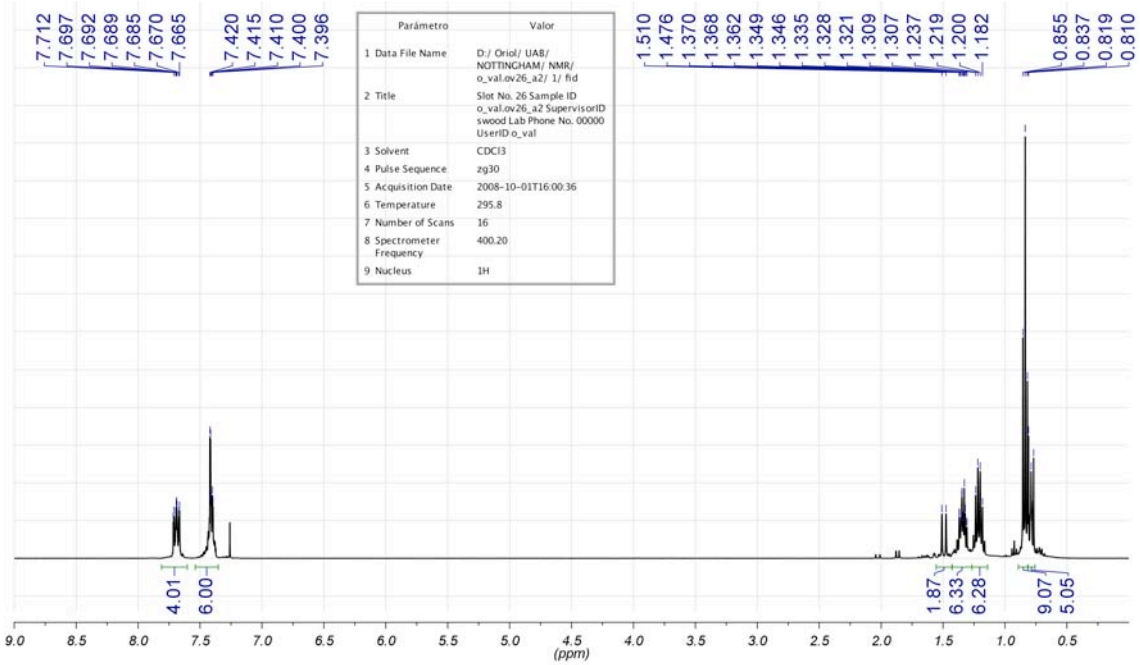
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

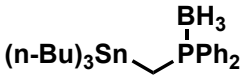


Difenil[(1,1,1-tributilestannil)metil]fosfina-P-borà **(L42b-Sn)**

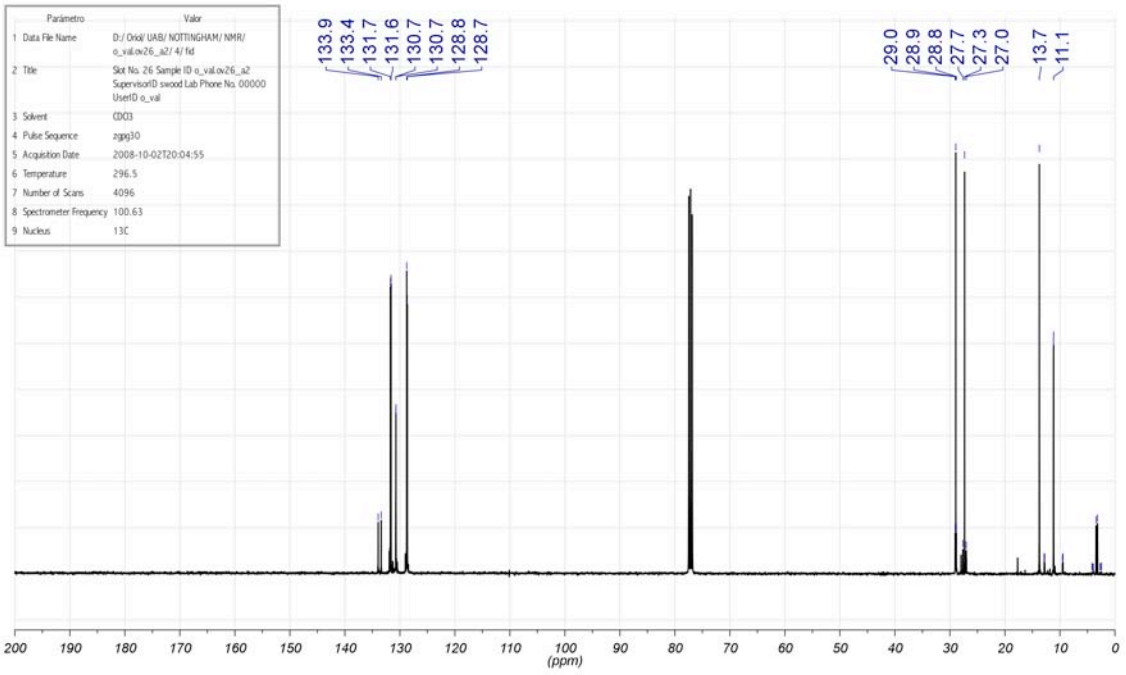


^{1}H RMN (400 MHz, rt, $CDCl_3$):

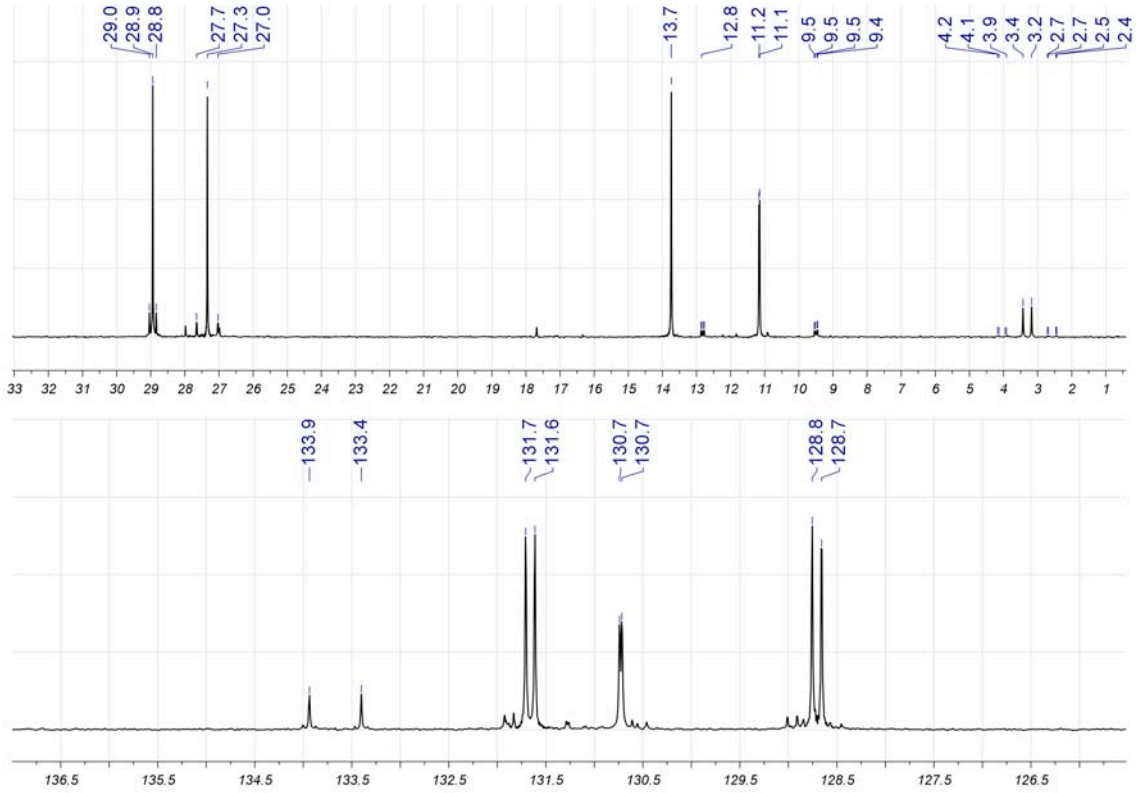




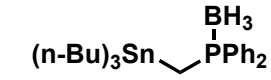
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

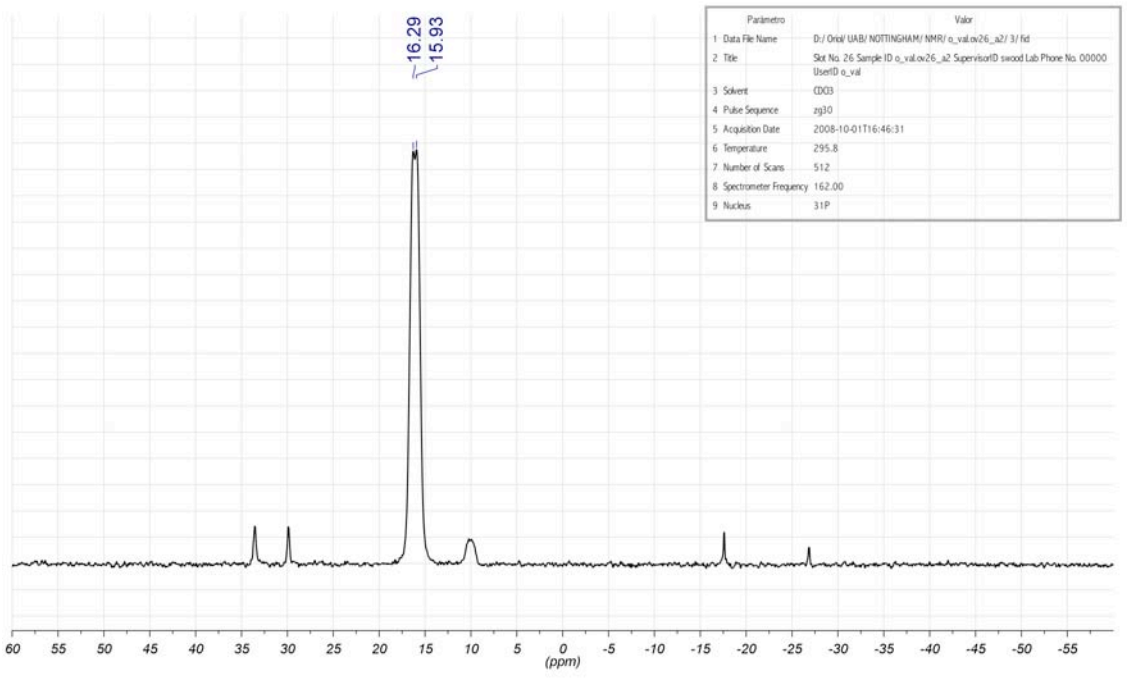


Ampliacions de l'espectre ^{13}C per veure els acoblaments amb l'Sn:



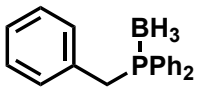
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



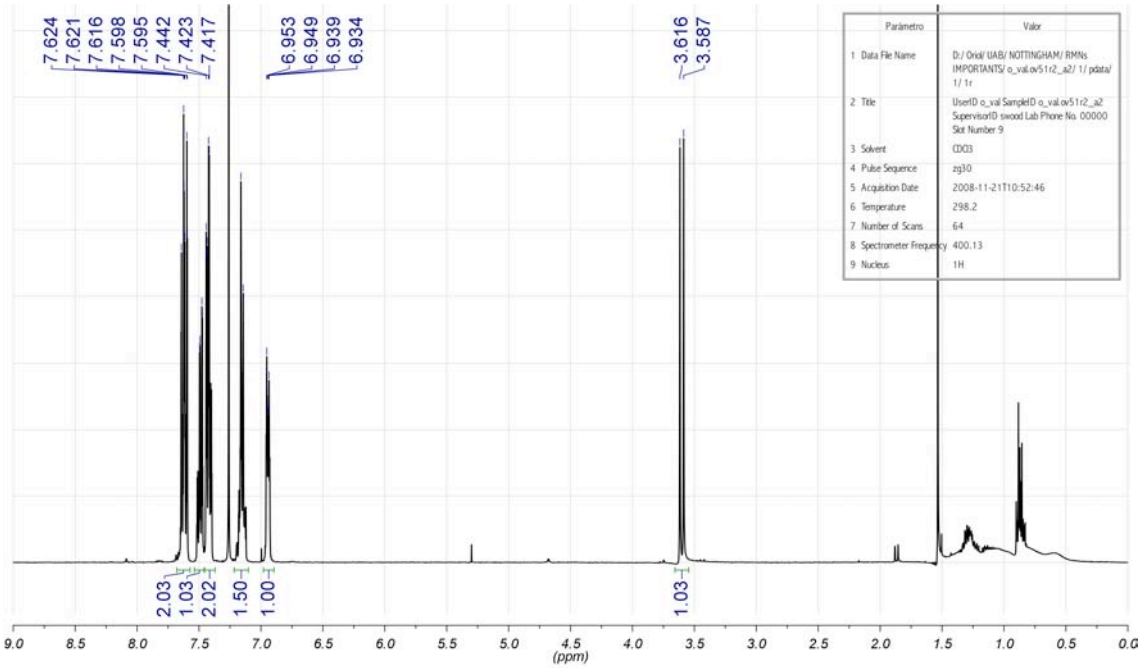


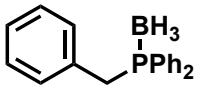
9.2 Productes

Benzildifenilfosfina-P-bora (L43b)

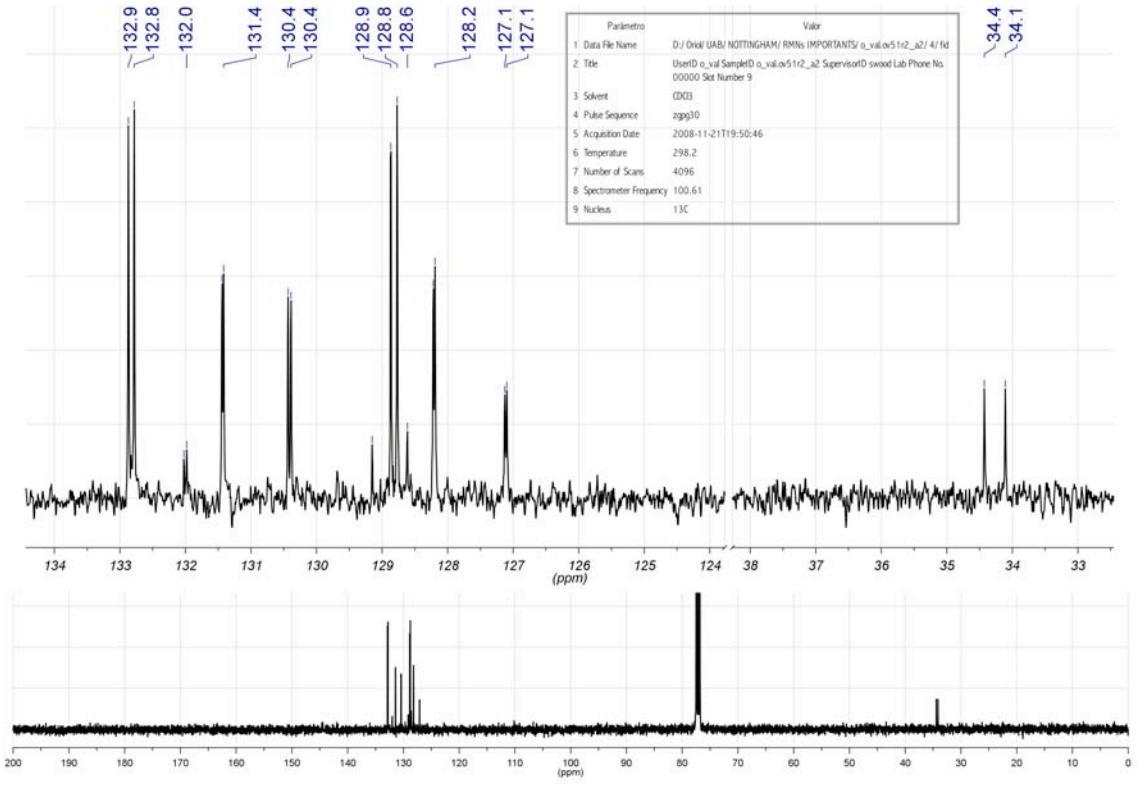


^{1}H RMN (400 MHz, rt, $CDCl_3$):

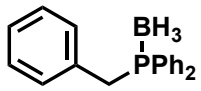


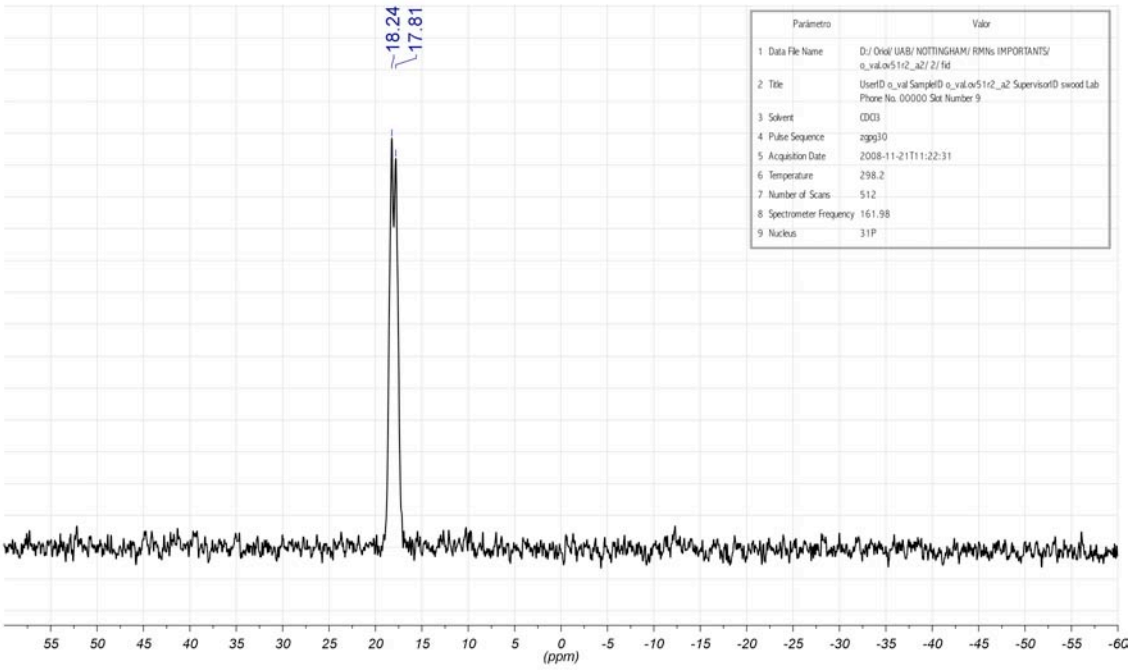


^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

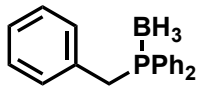


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):





HRMS (ESI+):



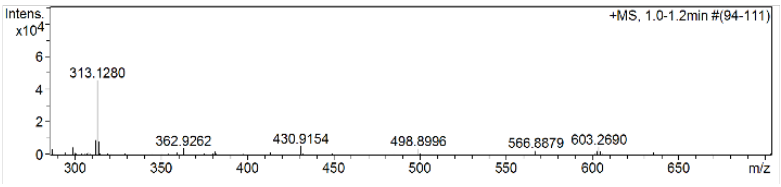
Sample-ID o_val_ov51r2_a2_383150 Lab C29

Submitter Supervisor

Analysis Name o_val_ov51r2_a2_383150_5_01_31932.d Acquisition Date 11/25/2008 11:18:10 AM

Ionisation Mode ESI Positive

+MS, 1.0-1.2min #(94-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

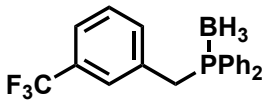
Expected Formula C19 H20 B1 P1 **Adduct(s):** H, Na, NH4, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	313.1280	313.1288	2.40	0.0245	C19H20BNaP	M+Na	22.9898
1	308.1733	308.1734	0.40	0.0444	C19H24BNP	M+H4N	18.0344

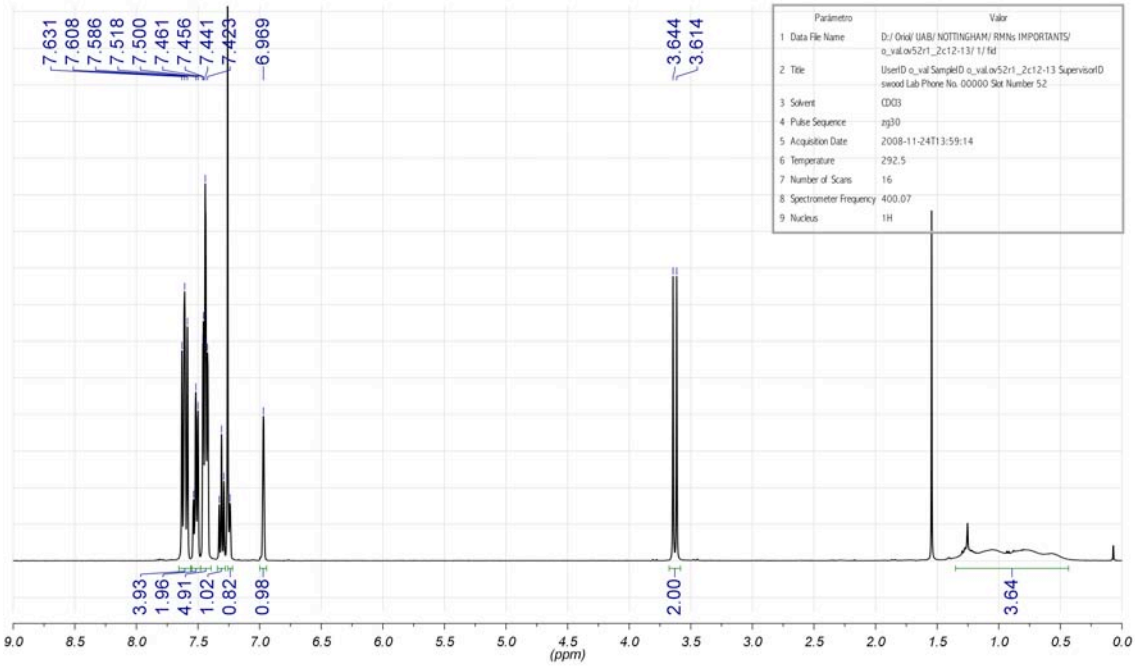
Note: Sigma fits < 0.05 indicates high probability of correct MF

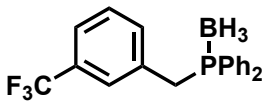
#	m/z	I %
1	286.1200	1.8
2	287.1162	6.8
3	294.9390	3.3
4	299.0956	9.0
5	300.0994	1.8
6	308.1733	3.0
7	312.1318	19.7
8	313.1280	100.0
9	314.1320	17.4
10	359.2402	2.9
11	362.9262	8.2
12	381.1179	3.2
13	413.2651	2.1
14	430.9154	11.0
15	498.8996	7.3
16	566.8879	4.9
17	602.2714	4.4
18	603.2690	9.9
19	604.2713	3.8
20	634.8764	2.5

Difenil[3-(trifluorometil)benzil]fosfina-P-borà (L44b)

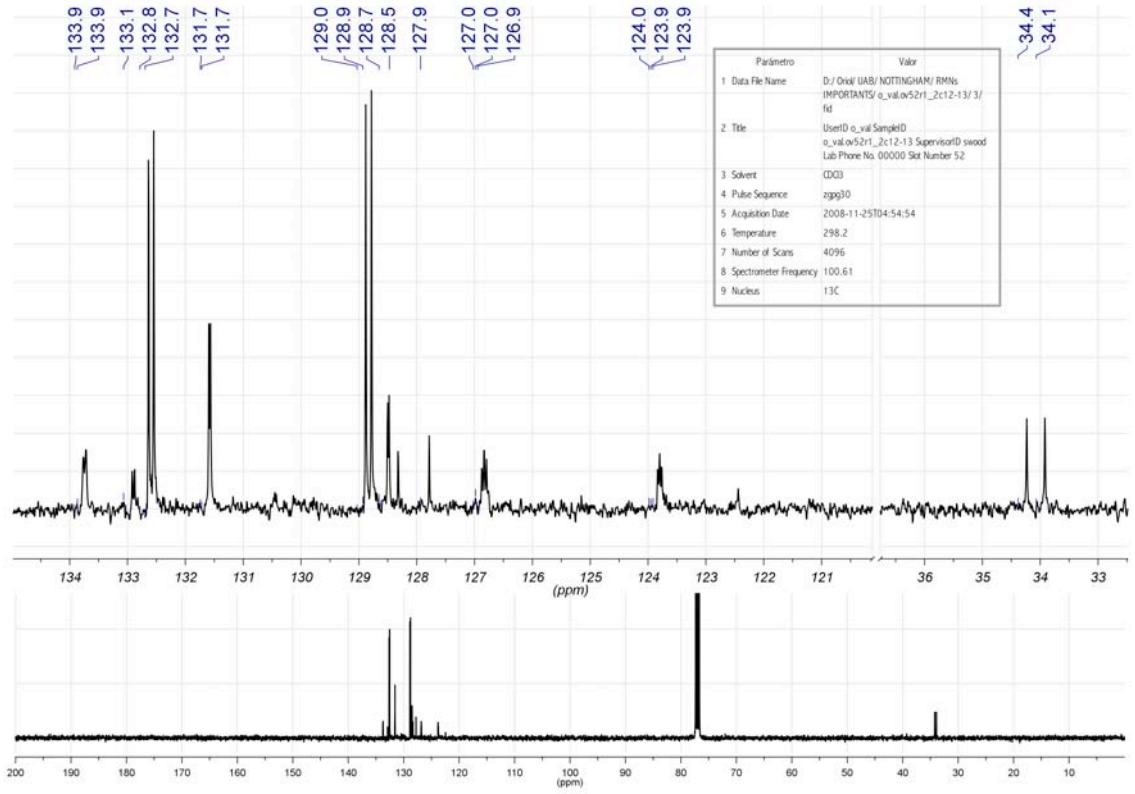


^{1}H RMN (400 MHz, rt, $CDCl_3$):

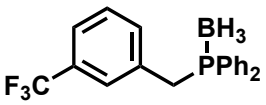


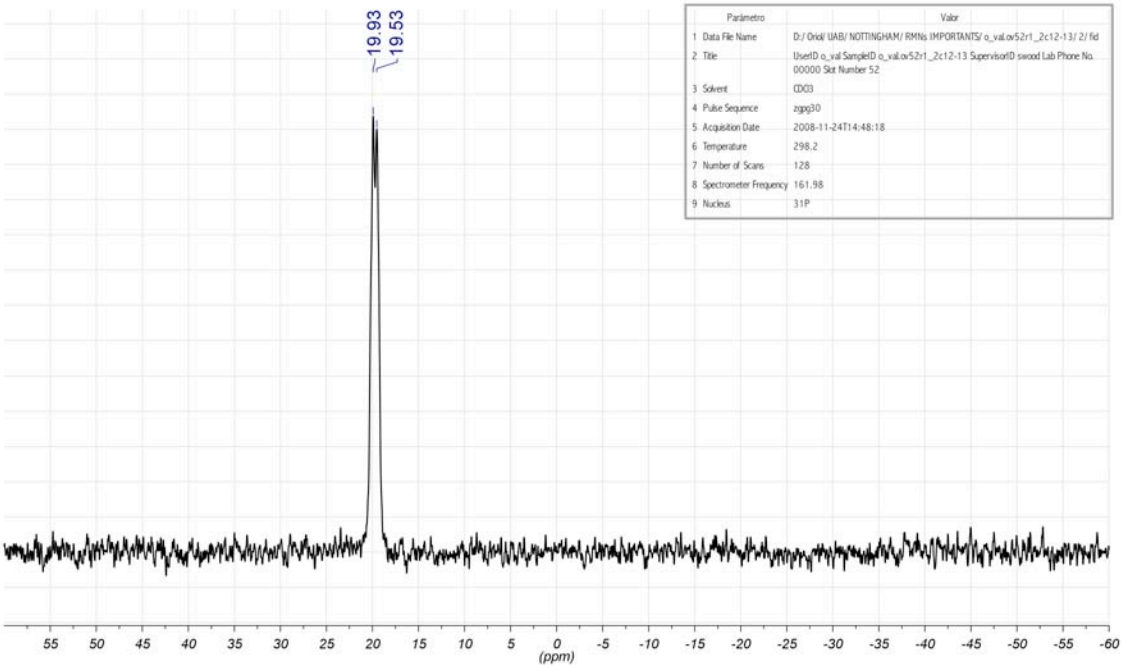


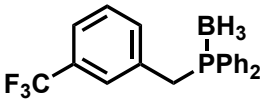
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):



$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):







HRMS (ESI+):

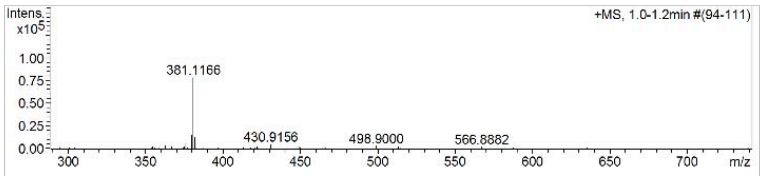
Sample-ID o_val_ov52r1_c12-13_383151 Lab C29

Submitter Supervisor

Analysis Name o_val_ov52r1_c12-13_383151_4_01_31931.d Acquisition Date 11/25/2008 11:14:25 AM

Ionisation Mode ESI Positive

+MS, 1.0-1.2min #(94-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

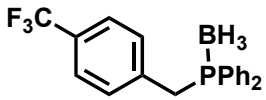
Expected Formula C20 H19 B1 F3 P1 **Adduct(s):** H, Na, NH4, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	381.1166	381.1162	1.00	0.0338	C20H19BF3NaP	M+Na	22.9898

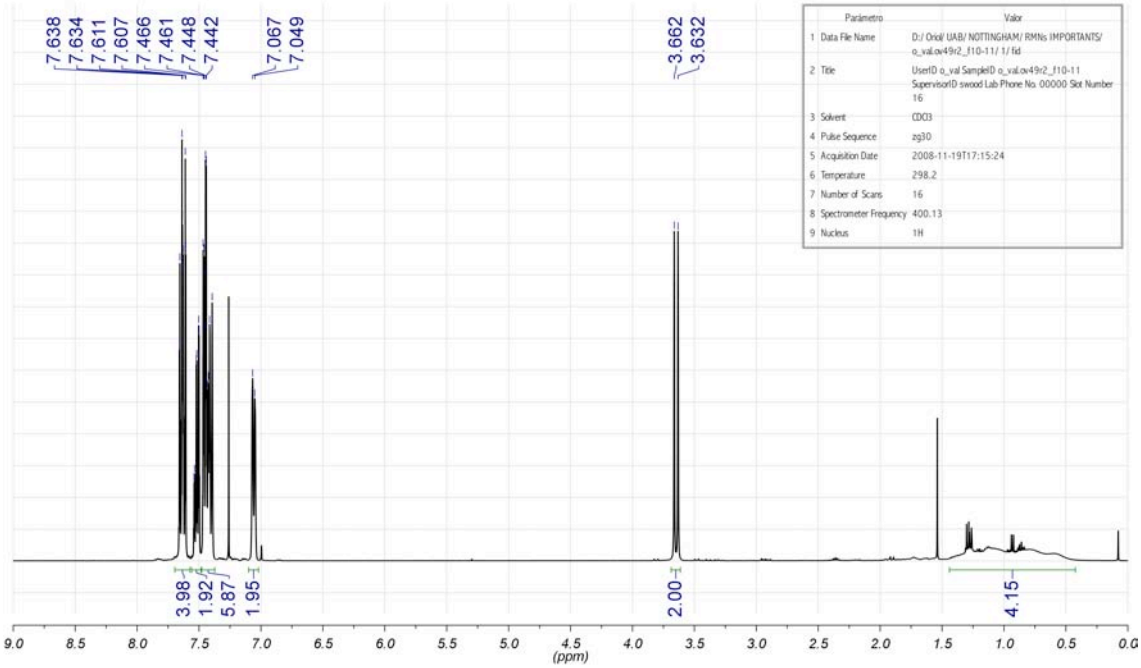
Note: Sigma fits < 0.05 indicates high probability of correct MF

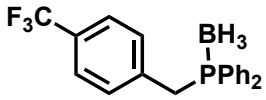
#	m/z	I %
1	294.9392	1.7
2	355.1021	3.5
3	362.9256	4.2
4	367.0838	2.1
5	375.1595	3.1
6	376.1602	7.0
7	377.1659	1.4
8	380.1191	19.0
9	381.1166	100.0
10	382.1194	16.4
11	383.1163	1.5
12	413.1423	2.0
13	413.2647	1.4
14	422.1437	2.2
15	430.9156	5.7
16	449.1048	2.1
17	465.1685	2.7
18	498.9000	3.7
19	513.3786	2.1
20	566.8882	2.4

Difenil[4-(trifluorometil)benzil]fosfina-P-borà (L45b)

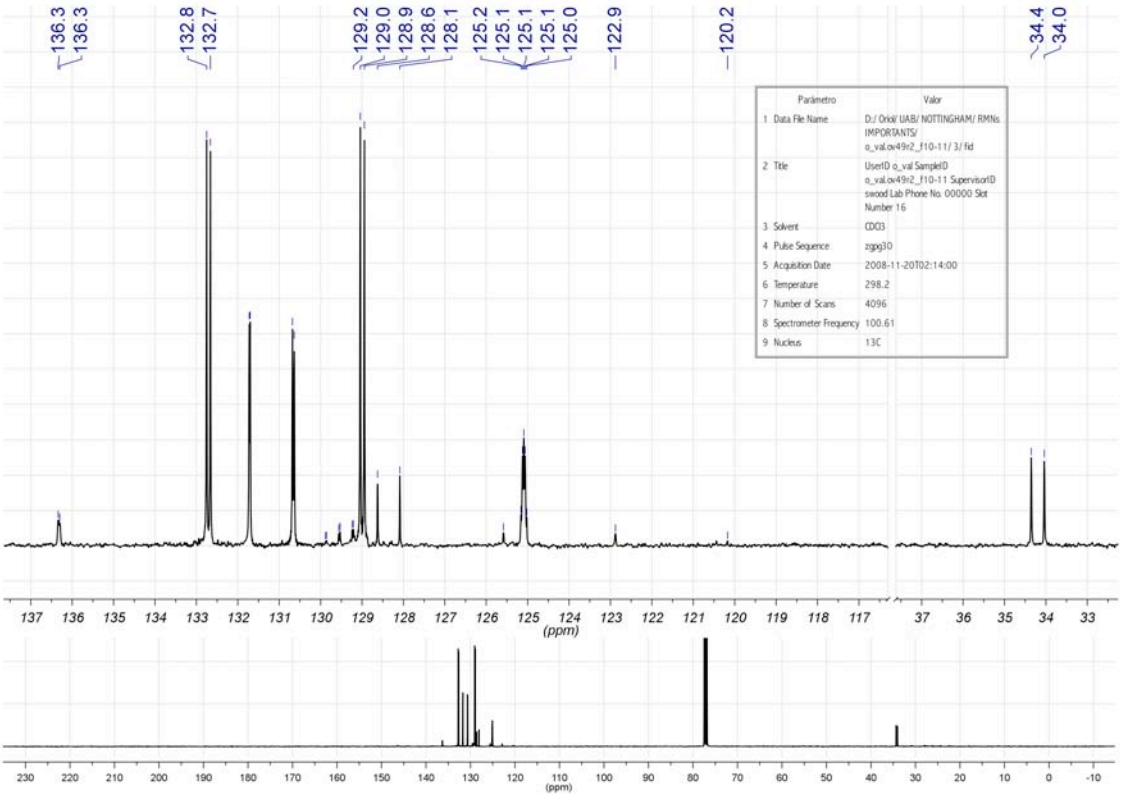


^{1}H RMN (400 MHz, rt, $CDCl_3$):

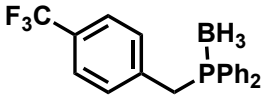


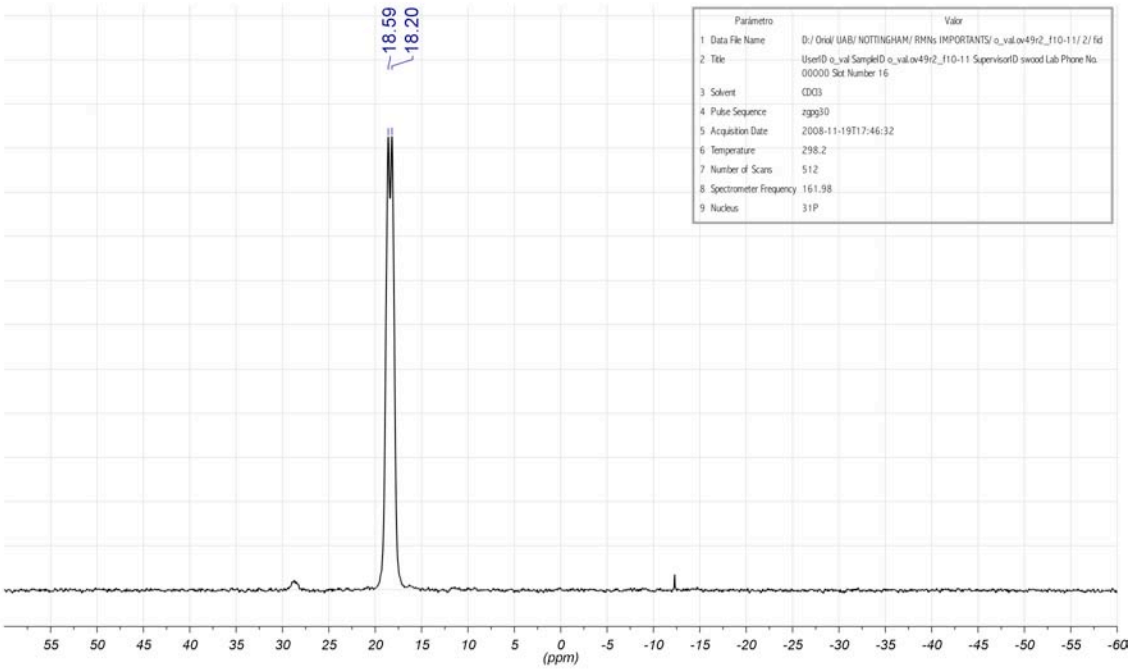


$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

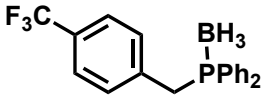


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



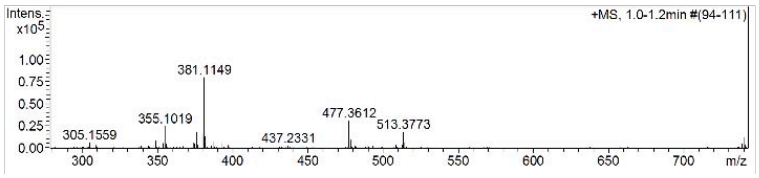


HRMS (ESI+):



Sample-ID	o_val_49r2_f10-11_382949	Lab	C29
Submitter		Supervisor	
Analysis Name	o_val_49r2_f10-11_382949_19_01_31696.d	Acquisition Date	11/20/2008 11:51:37 AM
Ionisation Mode	ESI Positive		

+MS, 1.0-1.2min #(94-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

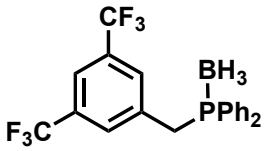
Expected Formula C20 H19 B1 F3 P1 **Adduct(s):** H, Na, NH4, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	381.1149	381.1162	3.20	0.0388	C20H19BF3NaP	M+Na	22.9898
1	376.1599	376.1608	2.50	0.0110	C20H23BF3NP	M+H4N	18.0344

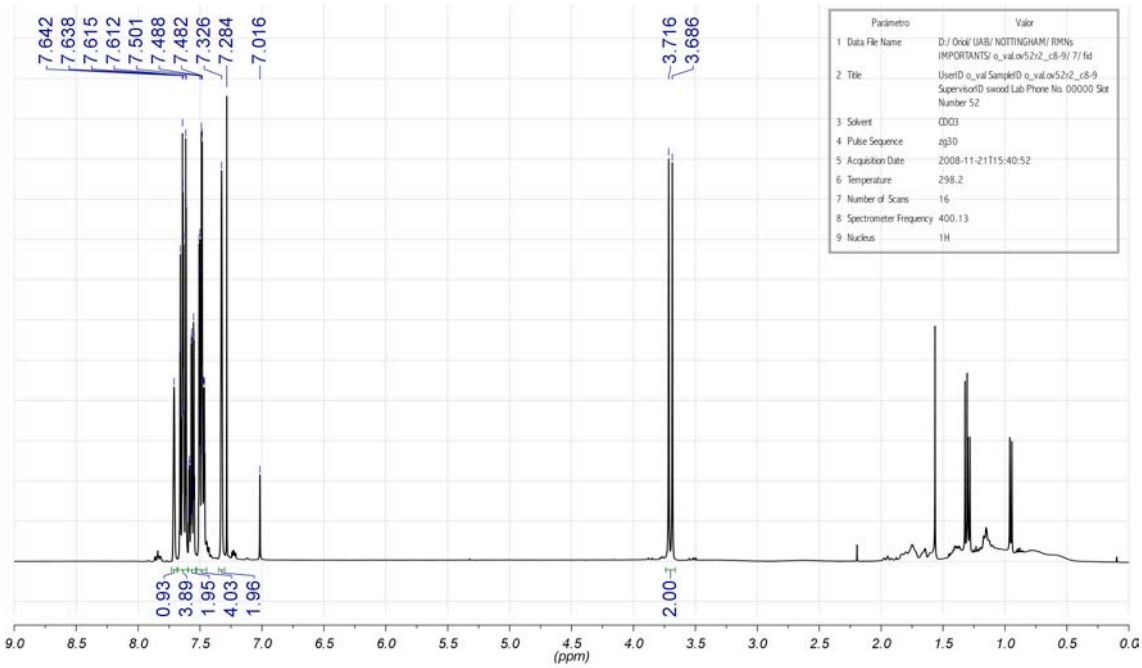
Note: Sigma fits < 0.05 indicates high probability of correct MF

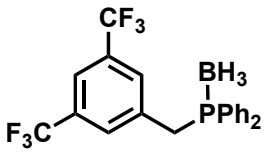
#	m/z	I %
1	305.1559	7.9
2	349.1829	10.6
3	354.1056	6.5
4	355.1019	30.3
5	356.1060	5.8
6	374.1440	6.9
7	375.1598	5.8
8	376.1599	22.7
9	380.1185	18.1
10	381.1149	100.0
11	382.1184	15.8
12	387.1277	9.3
13	393.2079	6.3
14	477.3612	38.5
15	478.3653	11.1
16	489.3787	5.4
17	513.3773	22.5
18	514.3808	6.8
19	738.2433	5.7
20	739.2391	15.6

*[3,5-bis(trifluorometil)benzil]difenilfosfina-P-borà (*L46b)

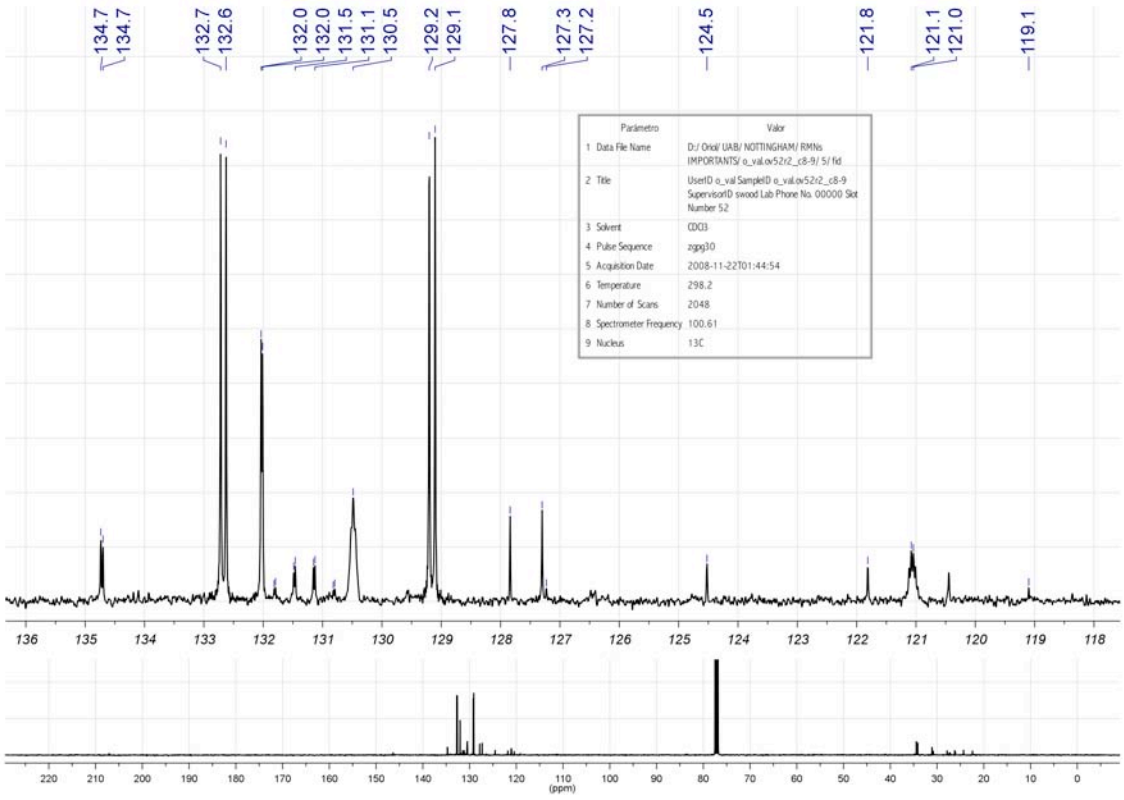


^{1}H RMN (400 MHz, rt, $CDCl_3$):

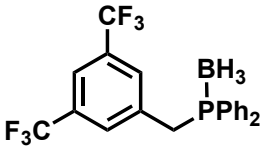


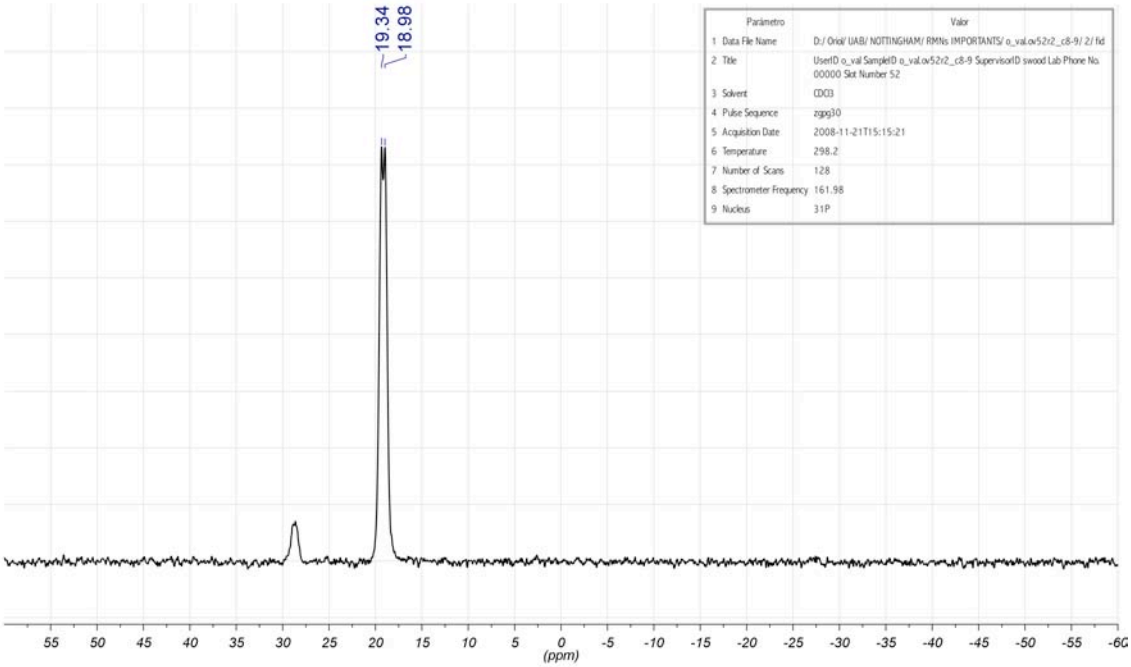


^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

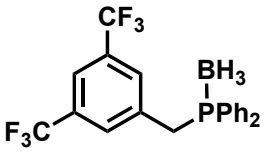


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



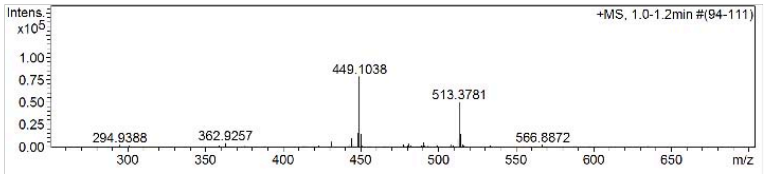


HRMS (ESI+):



Sample-ID	o_val_ov52r2_c8-9_383152	Lab	C29
Submitter		Supervisor	
Analysis Name	o_val_ov52r2_c8-9_383152_3_01_31930.d	Acquisition Date	11/25/2008 11:10:40 AM
Ionisation Mode	ESI Positive		

+MS, 1.0-1.2min #(94-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

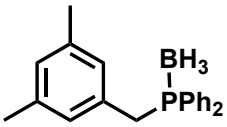
Expected Formula C21 H18 B1 F6 P1 **Adduct(s):** H, Na, NH4, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	449.1038	449.1036	0.60	0.0304	C21H18BF6NaP	M+Na	22.9898
1	444.1489	444.1482	1.60	0.0242	C21H22BF6NP	M+H4N	18.0344

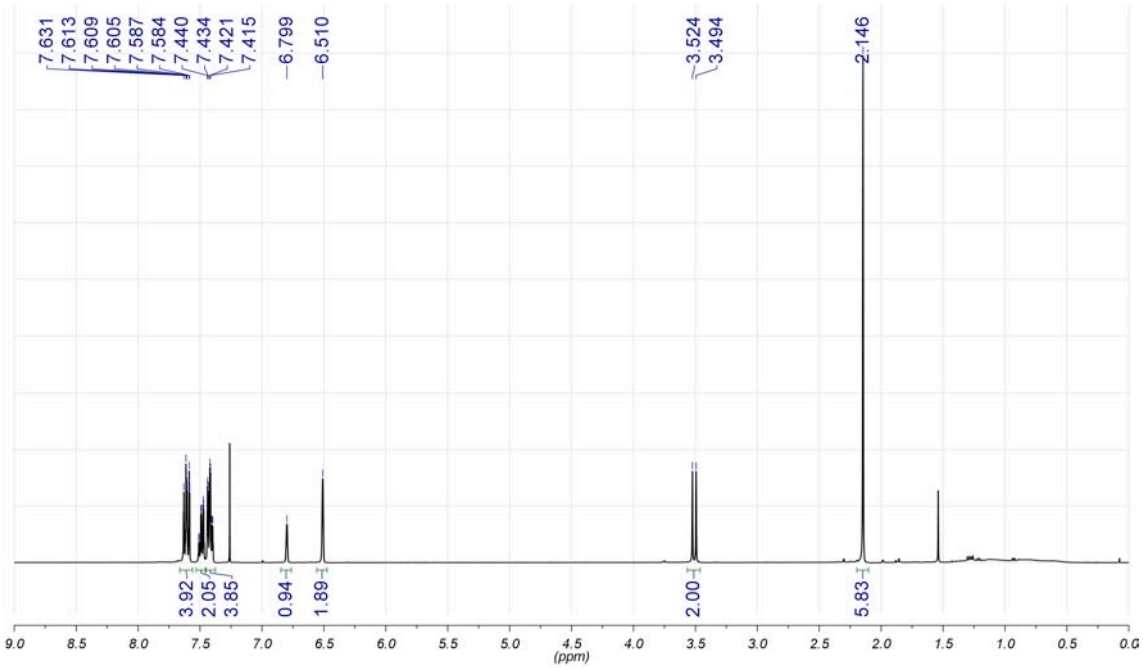
Note: Sigma fits < 0.05 indicates high probability of correct MF

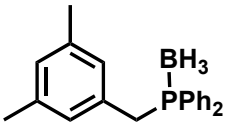
#	m/z	I %
1	294.9388	2.3
2	362.9257	5.4
3	430.9153	7.2
4	443.1514	2.6
5	444.1489	12.2
6	445.1528	2.4
7	448.1077	19.2
8	449.1038	100.0
9	450.1069	18.0
10	477.3642	3.0
11	481.1308	3.9
12	489.3808	2.4
13	490.1303	6.3
14	498.8993	4.5
15	508.4238	3.4
16	512.3818	11.1
17	513.3781	63.2
18	514.3821	18.2
19	515.3607	3.6
20	566.8872	2.9

(3,5-dimetilbenzil)difenilfosfina-P-borà (L47b)

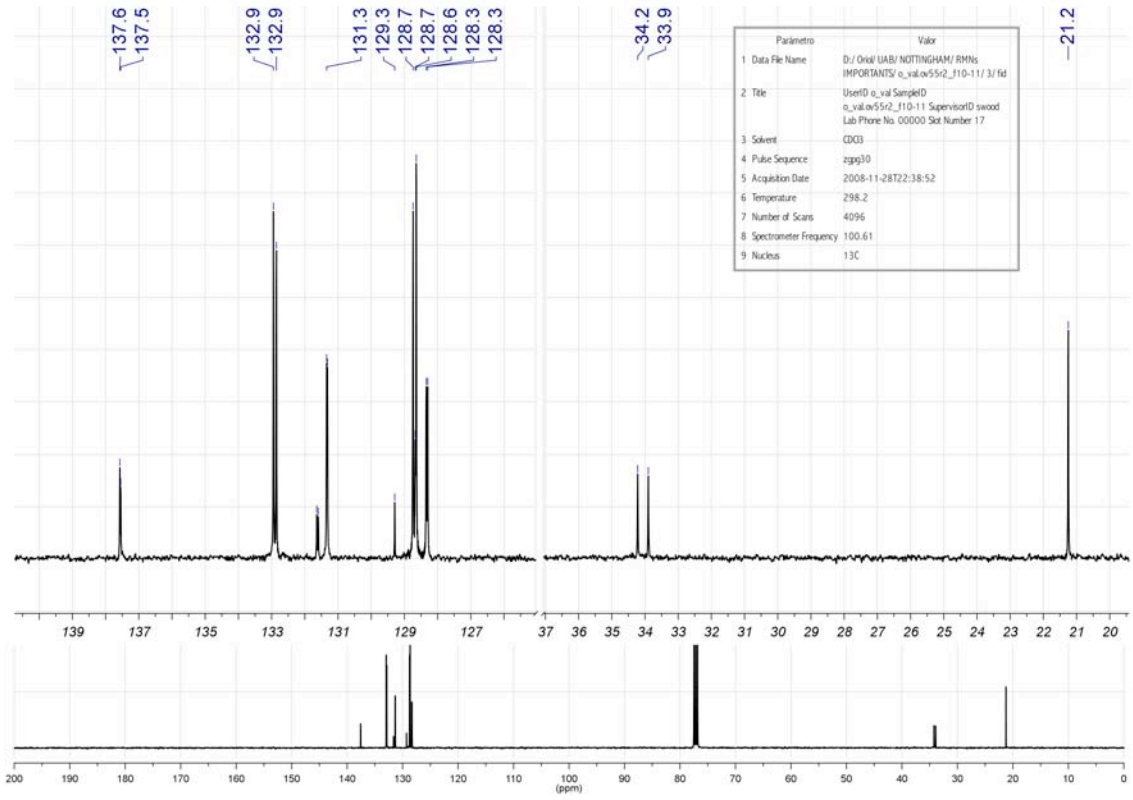


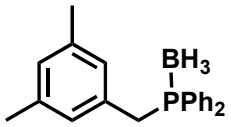
^{1}H RMN (400 MHz, rt, $CDCl_3$):



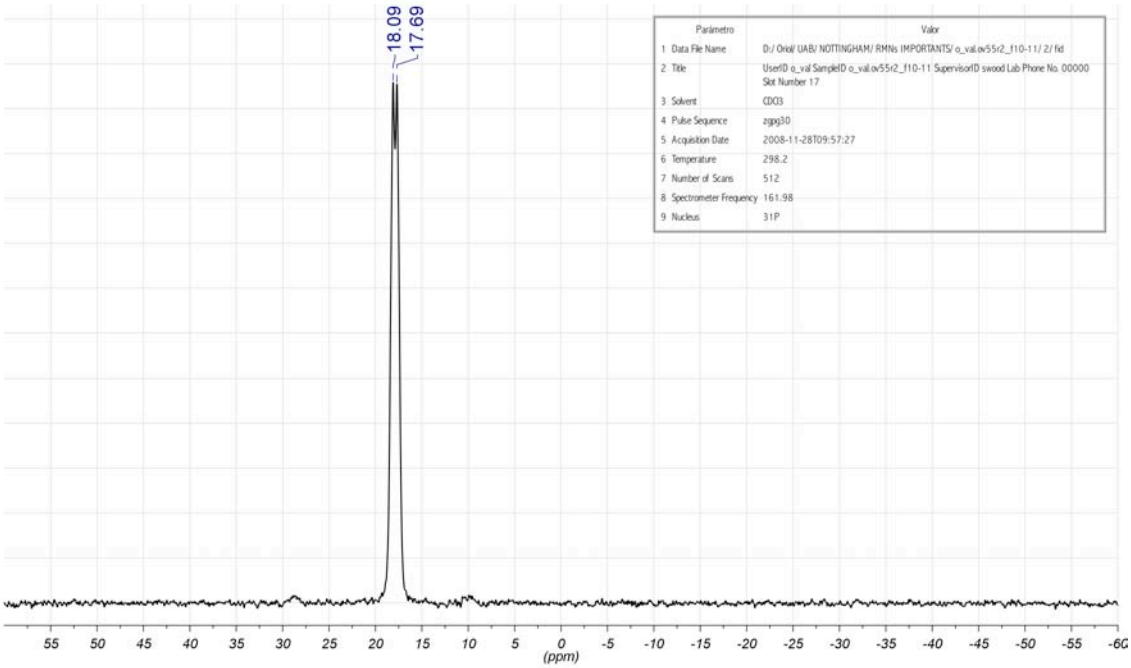


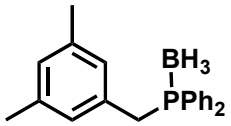
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):





$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

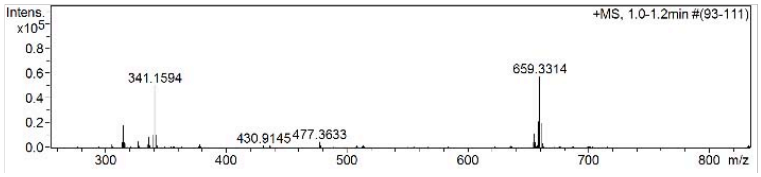




HRMS (ESI+):

Sample-ID	o_val_ov55r2_f10-11_383328	Lab	C29
Submitter		Supervisor	
Analysis Name	o_val_ov55r2_f10-11_383328_19_01_32127.d	Acquisition Date	11/28/2008 10:59:48 AM
Ionisation Mode	ESI Positive		

+MS, 1.0-1.2min #(93-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

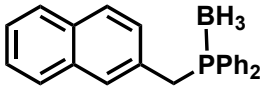
Expected Formula C21 H24 B1 P1 **Adduct(s):** H, Na, NH4, radical

#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	341.1594	341.1601	2.00	0.0261	C21H24BNaP	M+Na	22.9898
1	336.2042	336.2047	1.50	0.0203	C21H28BNP	M+H4N	18.0344

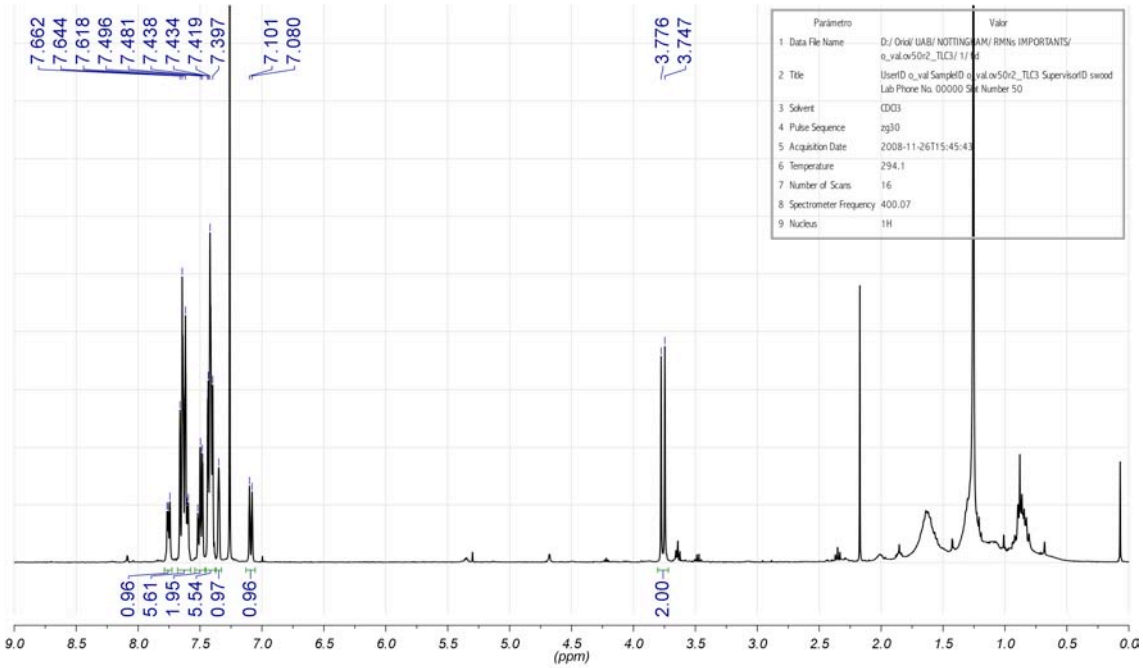
Note: Sigma fits < 0.05 indicates high probability of correct MF

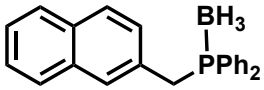
#	m/z	I %
1	305.1462	3.8
2	314.1494	6.9
3	315.1460	31.0
4	316.1522	6.5
5	317.1614	4.7
6	327.1264	8.3
7	335.2036	3.6
8	336.2042	13.7
9	340.1627	17.0
10	341.1594	87.3
11	342.1629	16.7
12	378.2511	4.3
13	477.3633	7.6
14	653.3790	6.6
15	654.3760	18.5
16	655.3785	6.4
17	658.3336	36.3
18	659.3314	100.0
19	660.3335	33.4
20	661.3325	5.7

(naftalen-2-ilmetil)difenilfosfina-P-borà **(L48b)**

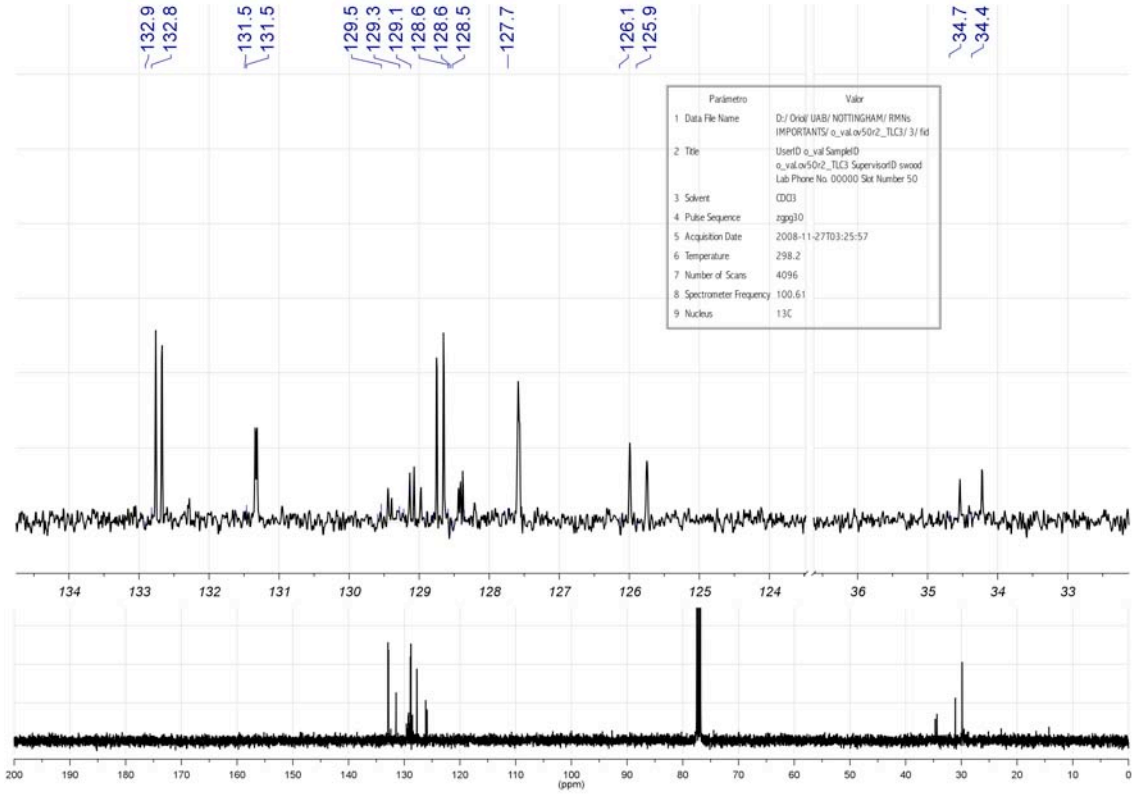


^{1}H RMN (400 MHz, rt, $CDCl_3$):

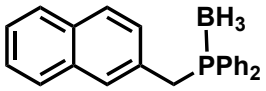


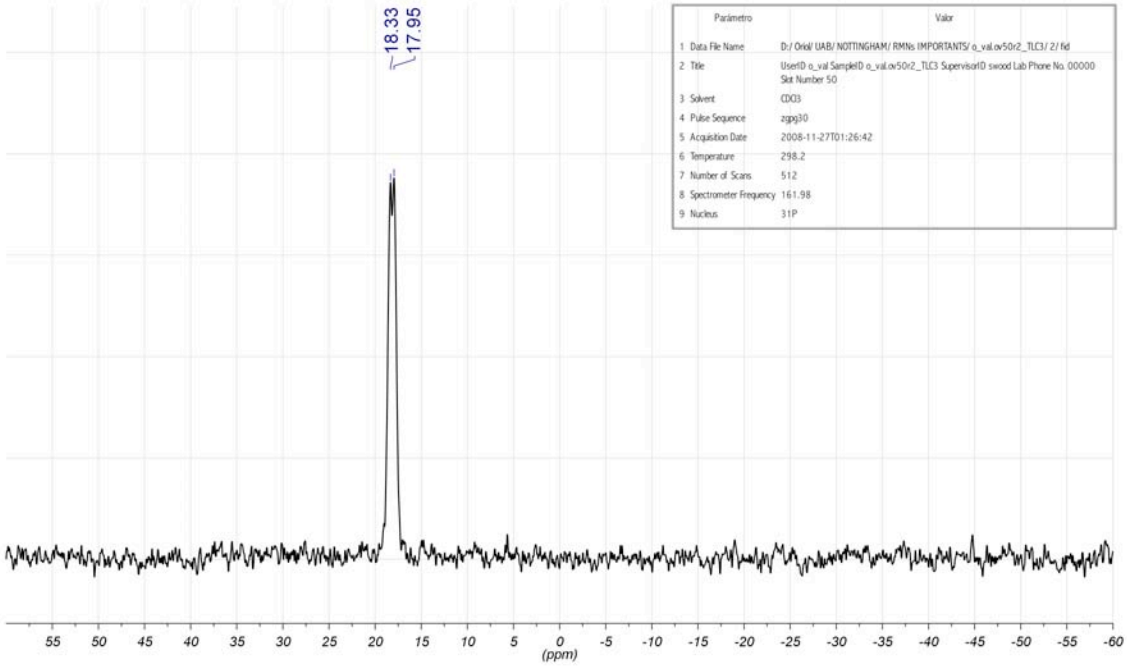


^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

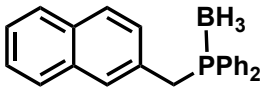


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



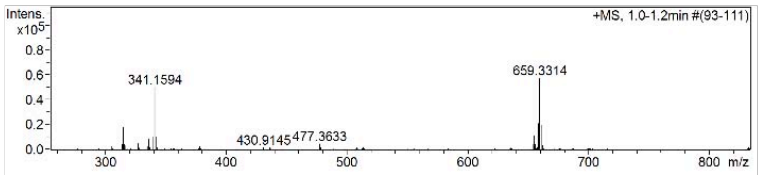


HRMS (ESI+):



Sample-ID	o_val_ov55r2_f10-11_383328	Lab	C29
Submitter		Supervisor	
Analysis Name	o_val_ov55r2_f10-11_383328_19_01_32127.d	Acquisition Date	11/28/2008 10:59:48 AM
Ionisation Mode	ESI Positive		

+MS, 1.0-1.2min #(93-111)



Generate Molecular Formula Parameters Source Type ESI

Charge	Tolerance	sigma limit	H/C Ratio	Electron Conf.	Nitrogen Rule	Chrom.BackGround	Calibration
+1	6 ppm	0.08	3 - 0	both	false	false	TRUE

Expected Formula C21 H24 B1 P1 **Adduct(s):** H, Na, NH4, radical

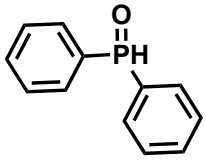
#	meas. m/z	theo. m/z	|Err|[ppm]	Sigma	Formula	Adduct	Adduct Mass
1	341.1594	341.1601	2.00	0.0261	C21H24BNaP	M+Na	22.9898
1	336.2042	336.2047	1.50	0.0203	C21H28BNP	M+H4N	18.0344

Note: Sigma fits < 0.05 indicates high probability of correct MF

#	m/z	I %
1	305.1462	3.8
2	314.1494	6.9
3	315.1460	31.0
4	316.1522	6.5
5	317.1614	4.7
6	327.1264	8.3
7	335.2036	3.6
8	336.2042	13.7
9	340.1627	17.0
10	341.1594	87.3
11	342.1629	16.7
12	378.2511	4.3
13	477.3633	7.6
14	653.3790	6.6
15	654.3760	18.5
16	655.3785	6.4
17	658.3336	36.3
18	659.3314	100.0
19	660.3335	33.4
20	661.3325	5.7

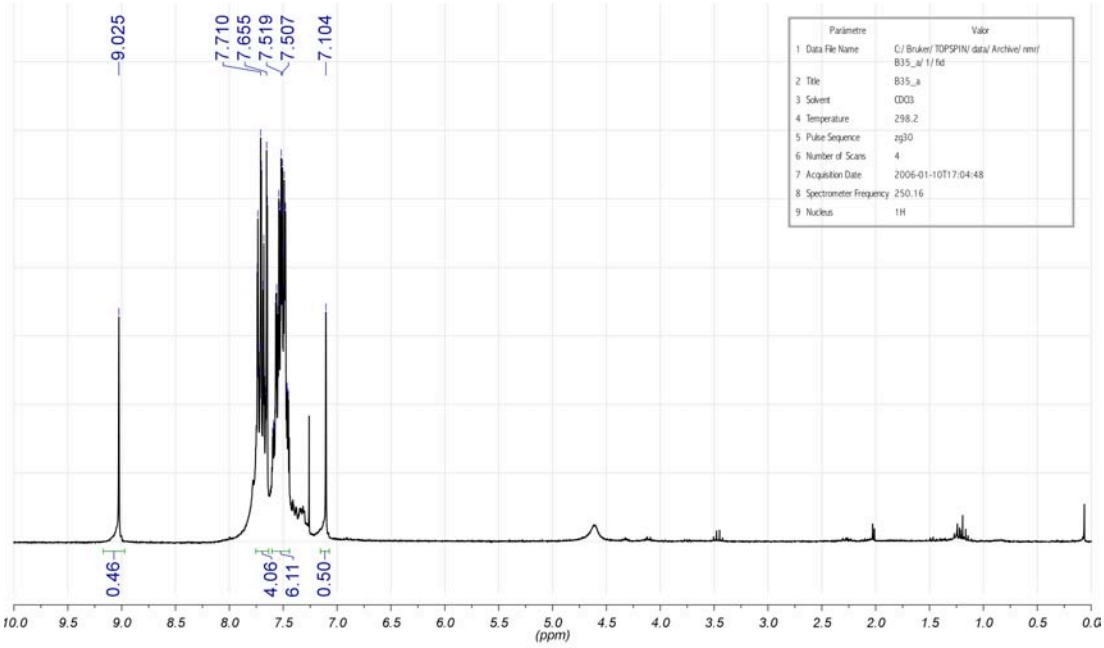
10 Caracterització d'intermedis i productes a la síntesi de monofosfines quirals

10.1 Síntesi de l'(R)-(+)-BINPO (L28)

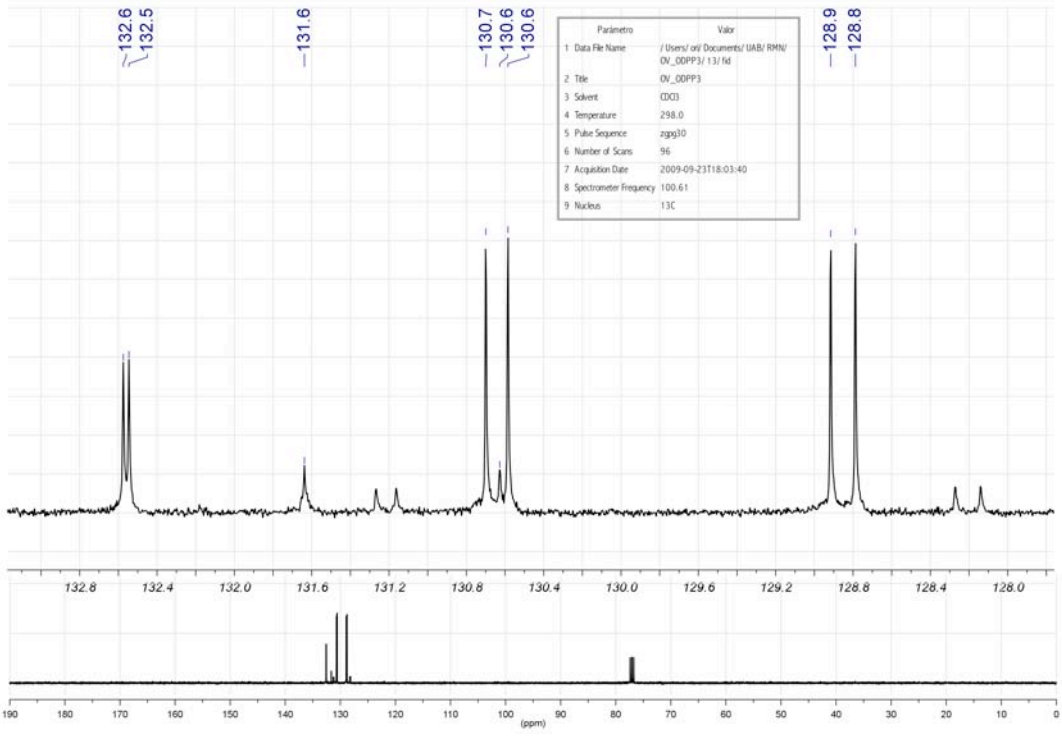


Òxid de difenilfosfina (L19(O))

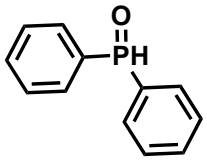
^{1}H RMN (250 MHz, rt, $CDCl_3$):

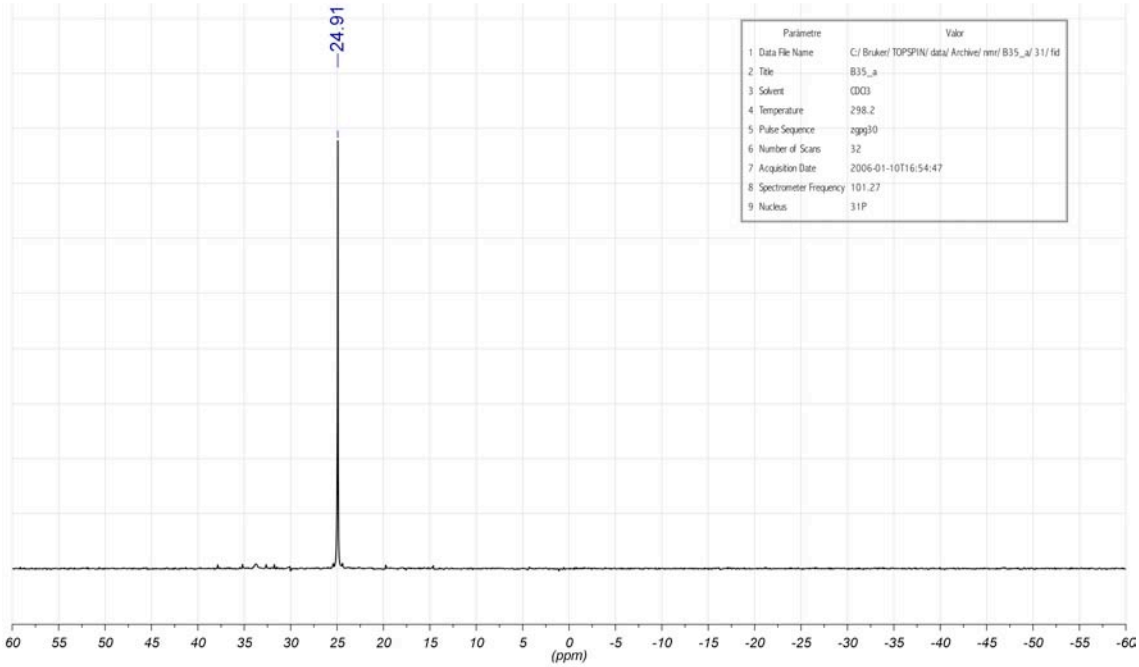


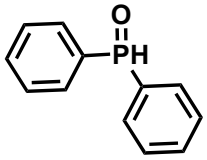
^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):



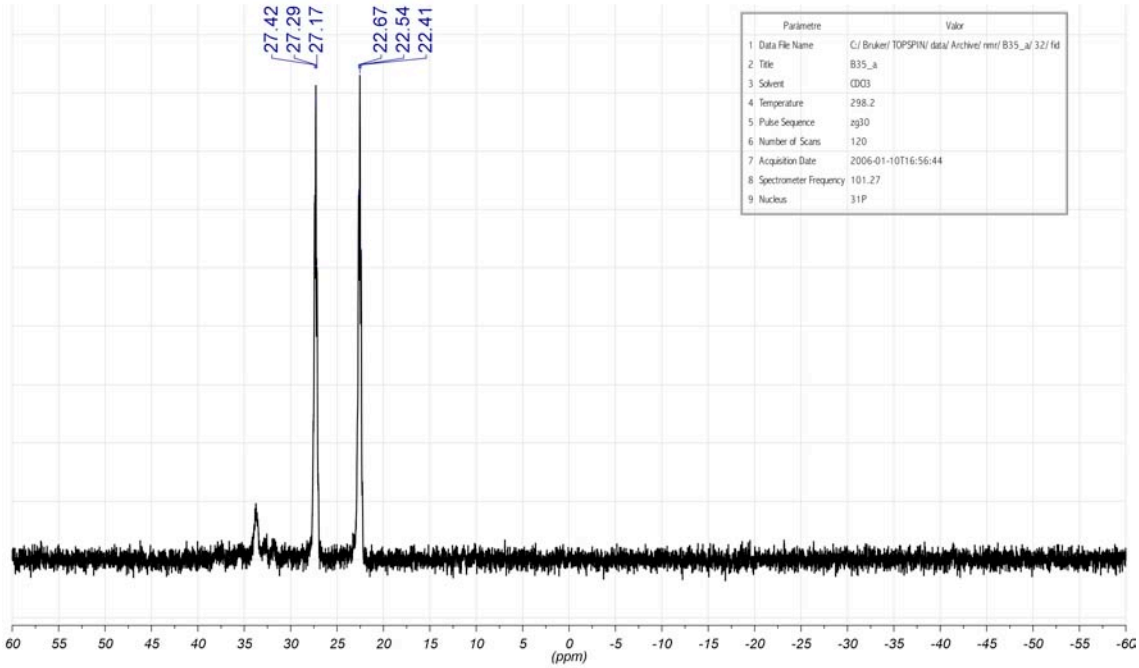
$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):



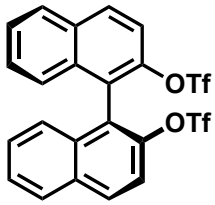




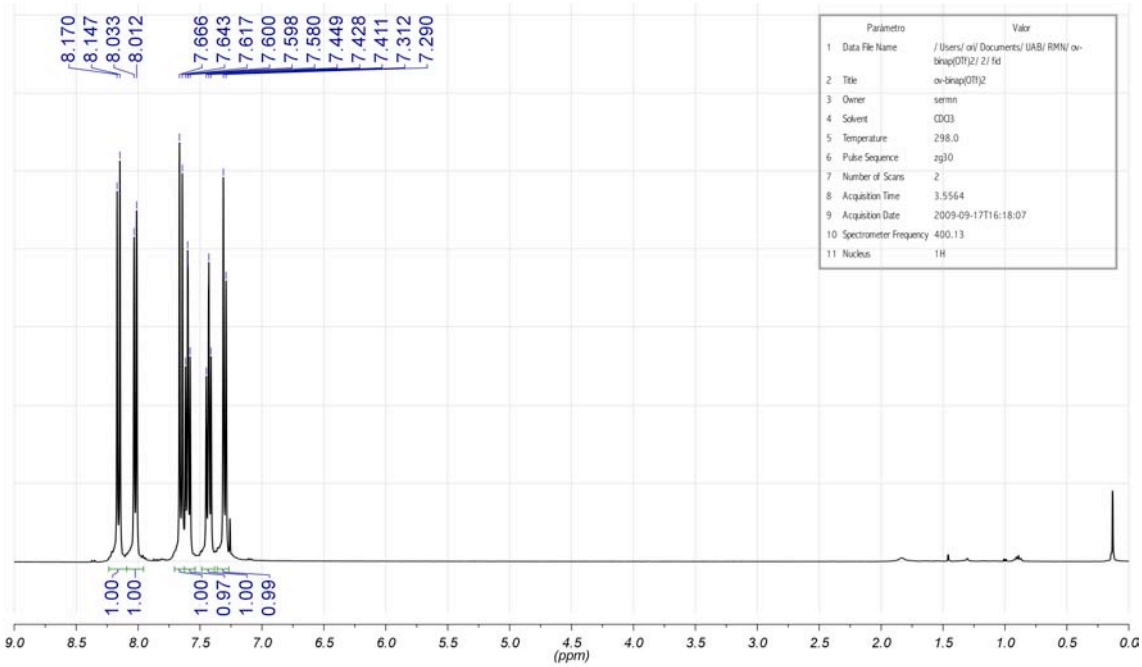
^{31}P RMN (101 MHz, rt, $CDCl_3$)



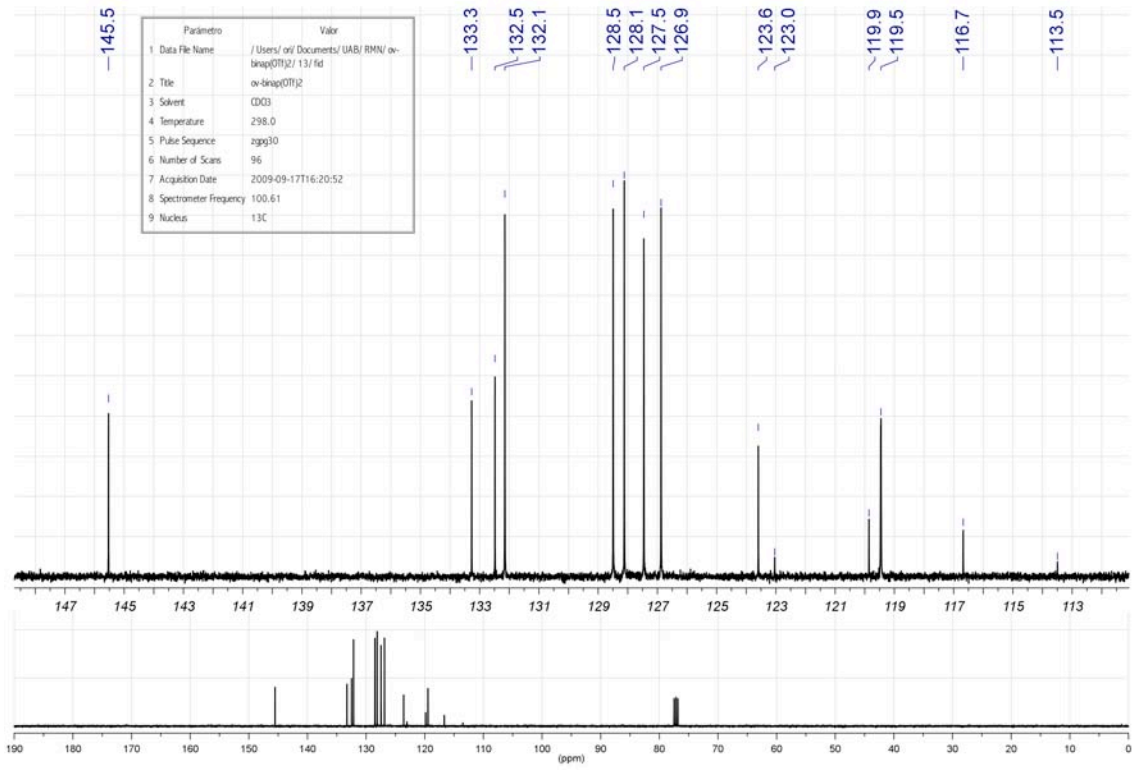
(S)-(-)-2,2'-bis(trifluorometansulfoniloxi)-1,1'-binaftil (**I36**)



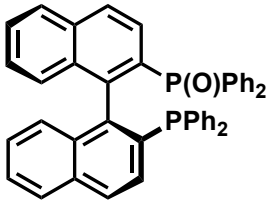
^{1}H RMN (400 MHz, rt, $CDCl_3$):



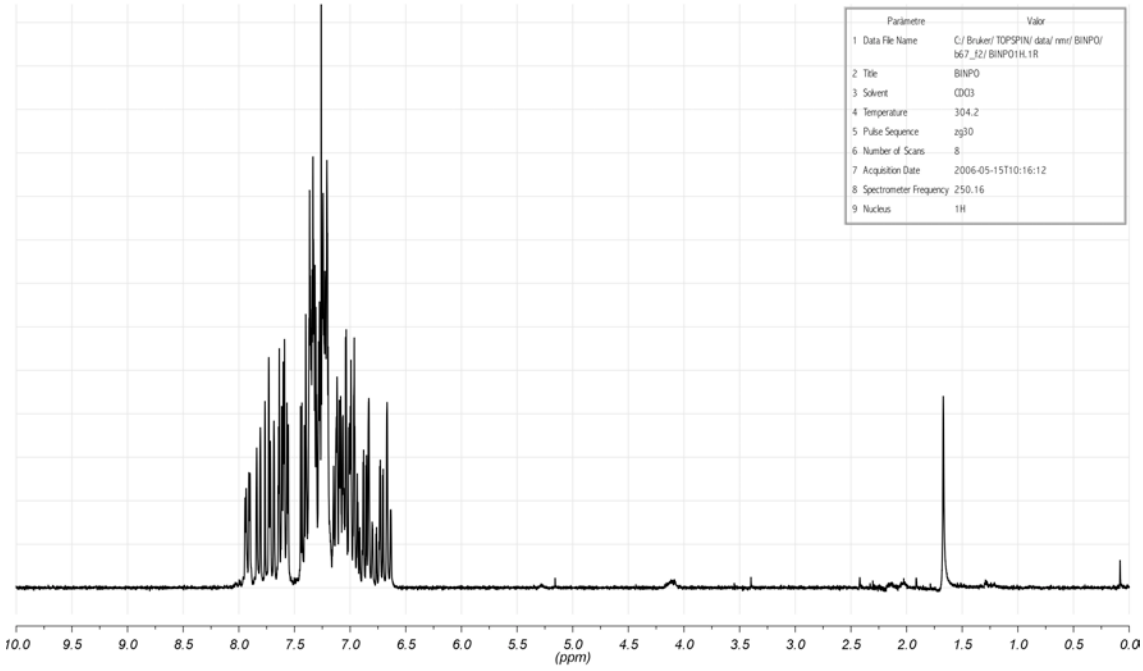
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

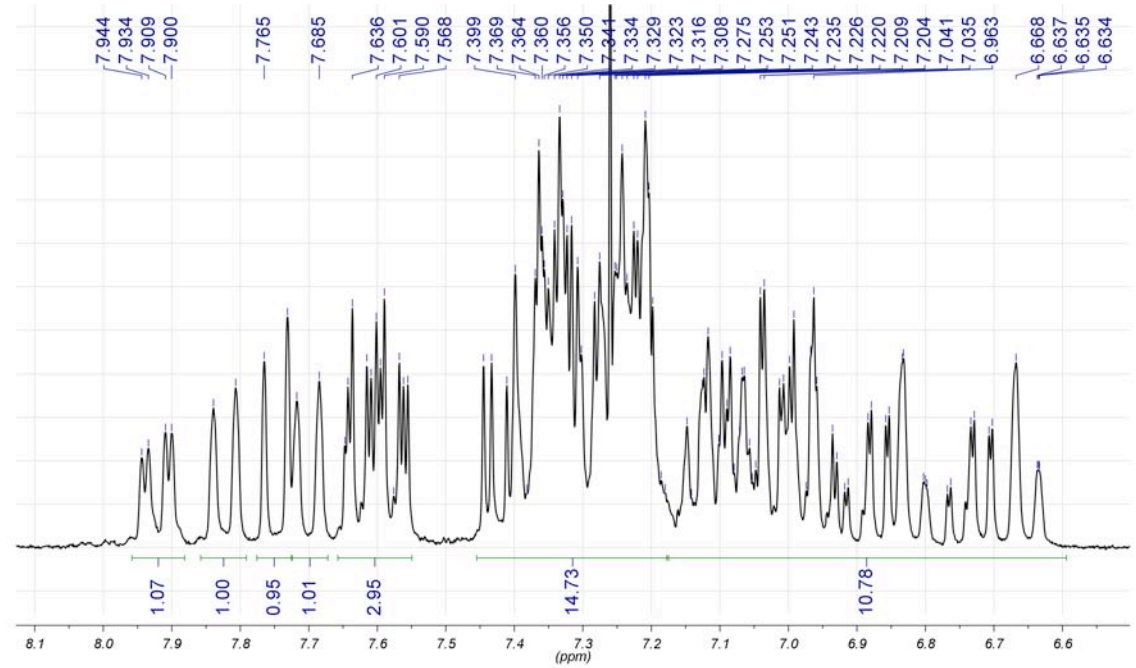


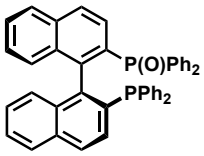
***Òxid de (S)-(-)-2-difenilfosfino-2'-difenilfosfinil-1,1'binaftalè* (BINPO, L28)**



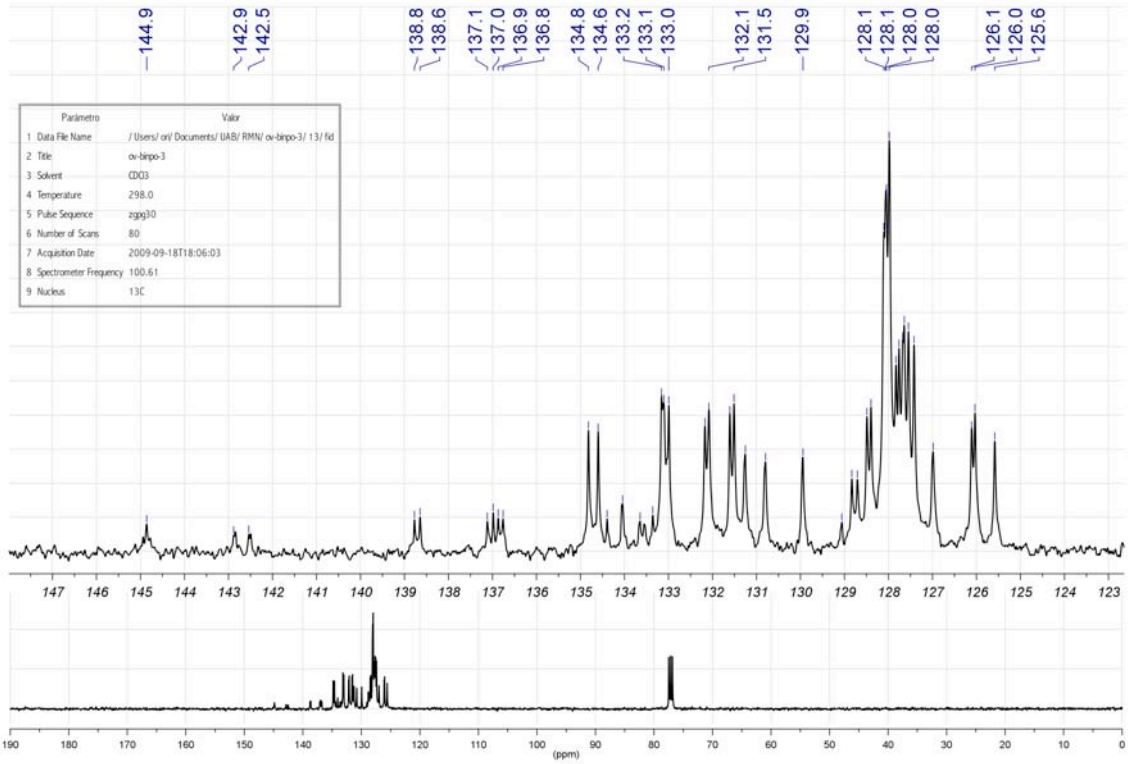
^{1}H RMN (250 MHz, rt, $CDCl_3$):

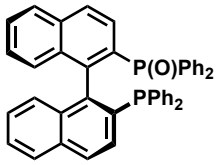




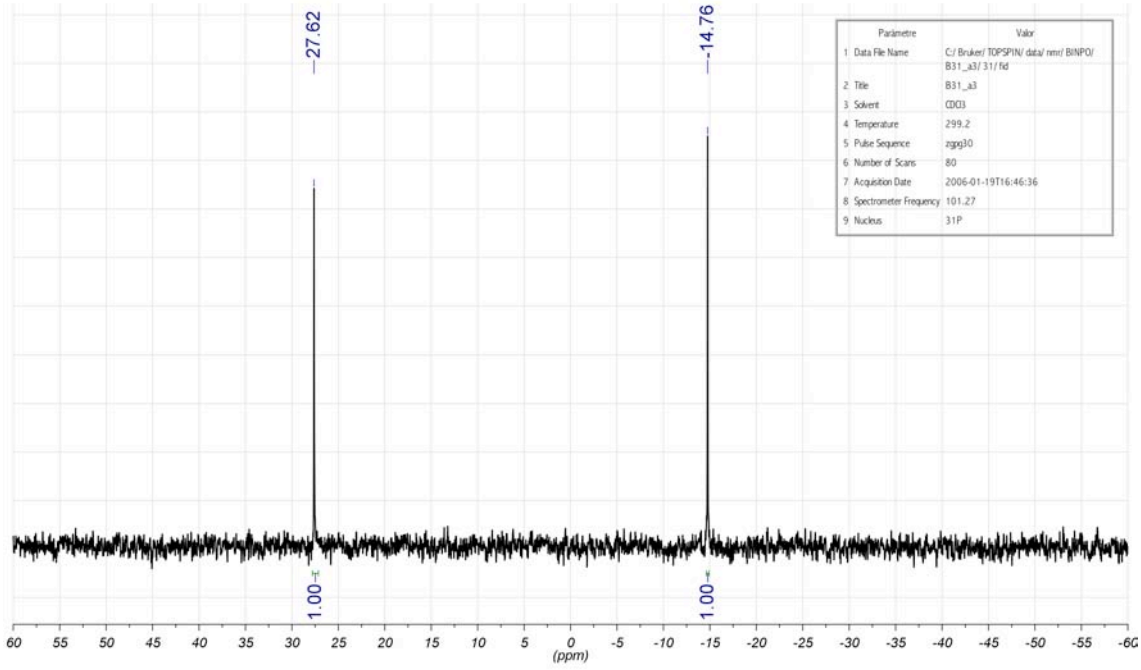


$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

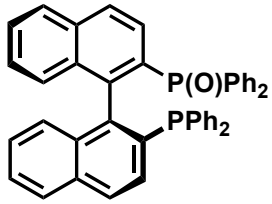




$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

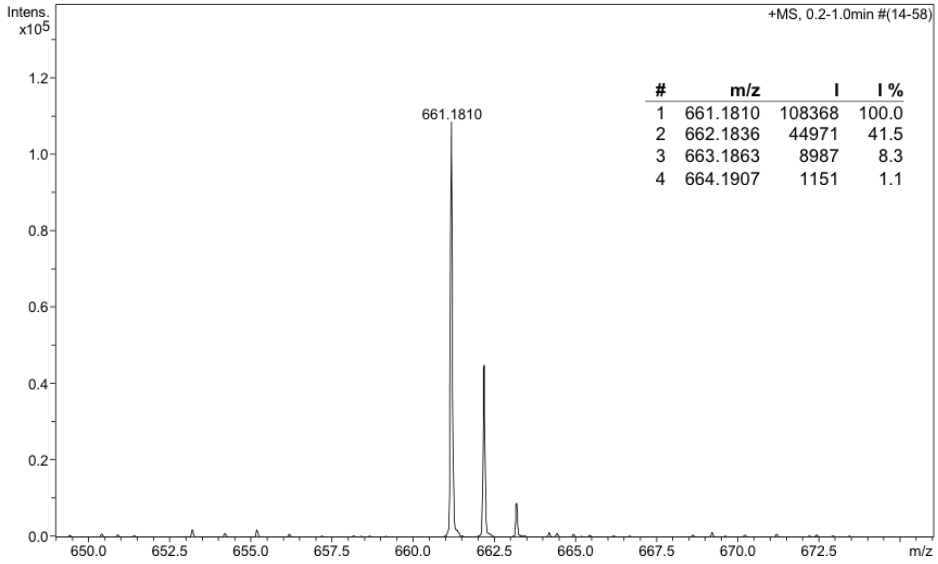


HRMS (ESI+):

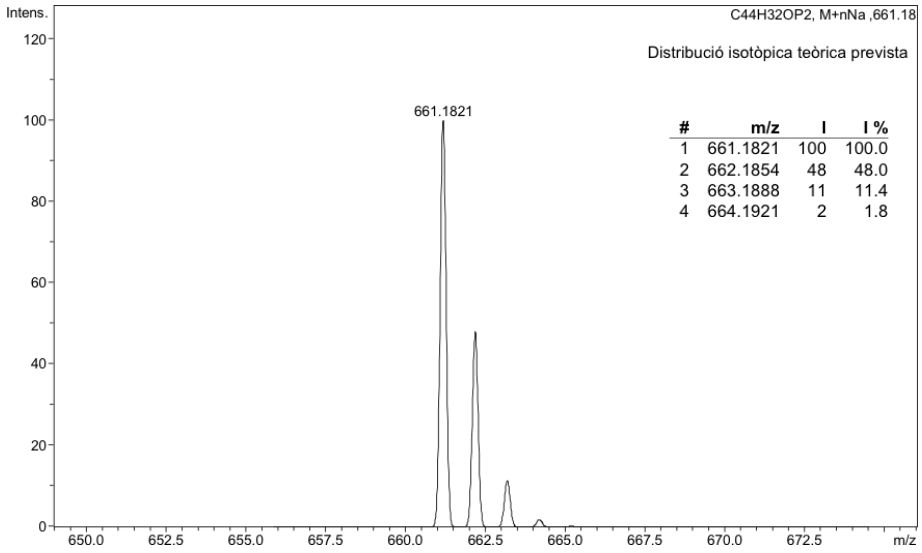


Analysis Info

Analysis Name	09EM422-QTOF-pos1-1.d	Acquisition Date	17/09/2009 12:08:34
Method	09EM422-QTOF-pos1.m	Operator	SAQ
Sample Name	BINPO	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 5 ppm en MeOH. O. VALLCORBA		

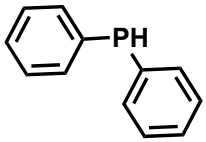


#	m/z	I	I %
1	661.1810	108368	100.0
2	662.1836	44971	41.5
3	663.1863	8987	8.3
4	664.1907	1151	1.1



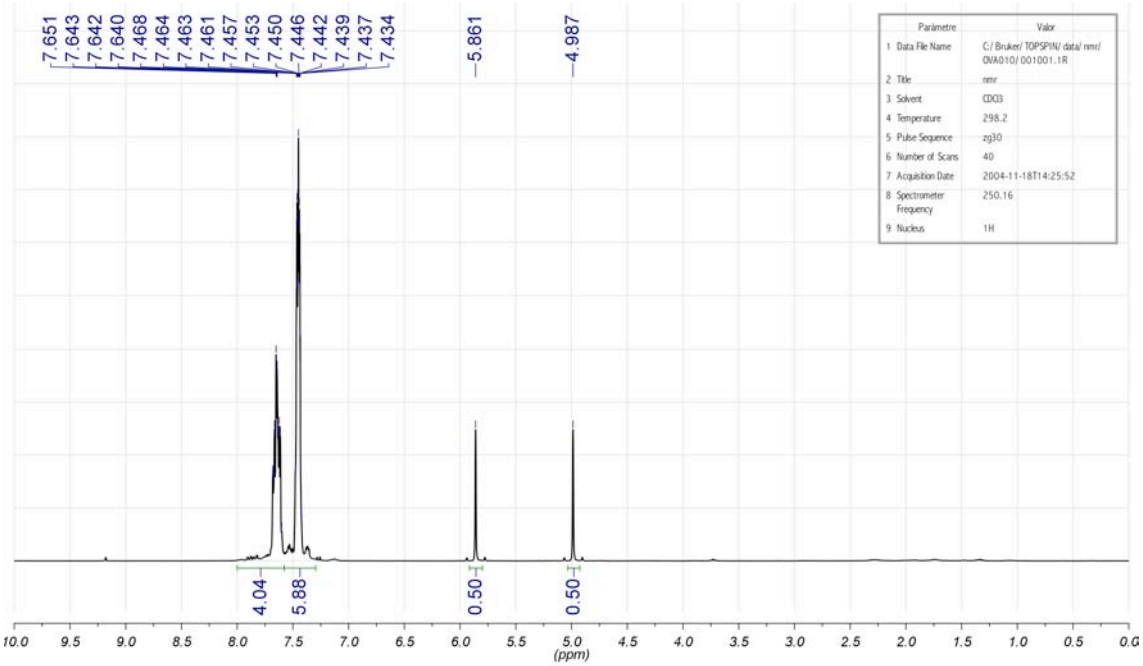
#	m/z	I	I %
1	661.1821	100	100.0
2	662.1854	48	48.0
3	663.1888	11	11.4
4	664.1921	2	1.8

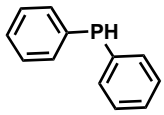
10.2 Síntesi de l'(R)-(+)-Metilbinap (BINAP(Me), L29)



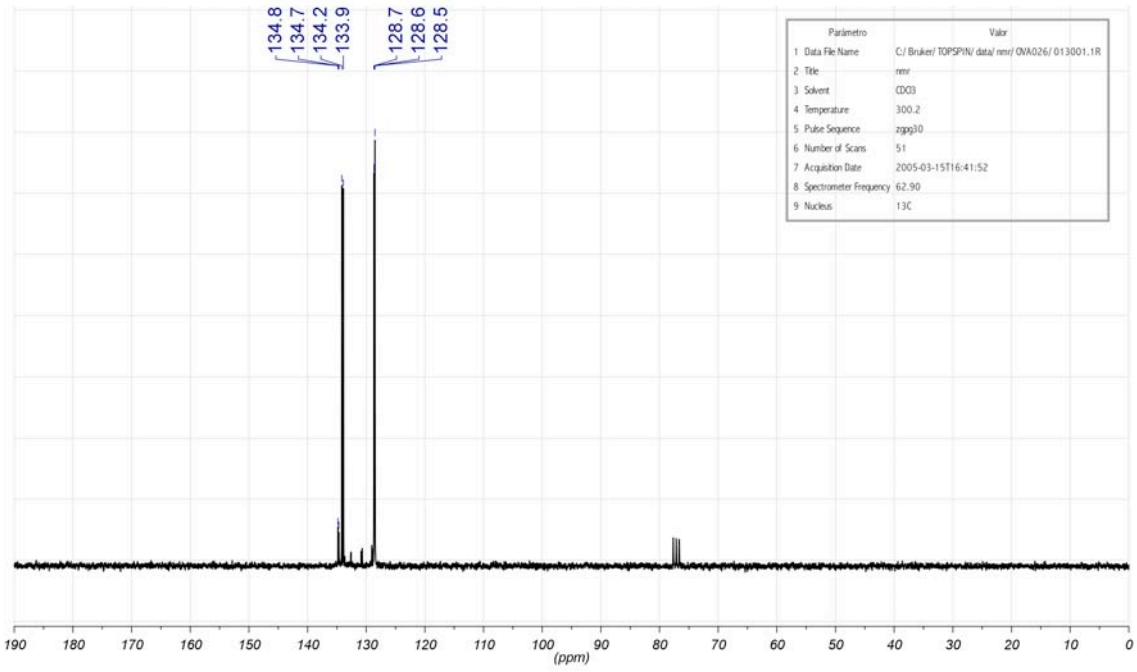
Difenilfosfina (L19)

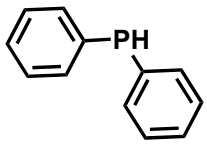
^{1}H RMN (250 MHz, rt, $CDCl_3$):



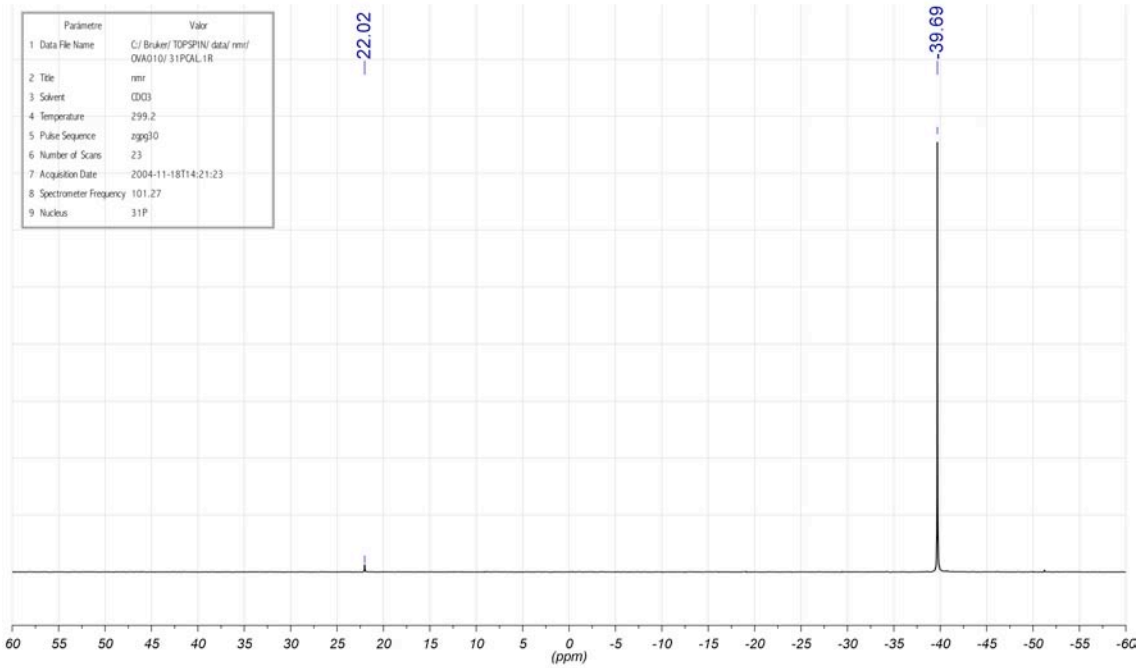


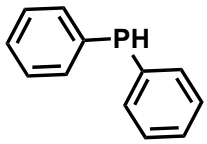
$^{13}C\{^{1}H\}$ RMN (63 MHz, rt, $CDCl_3$):



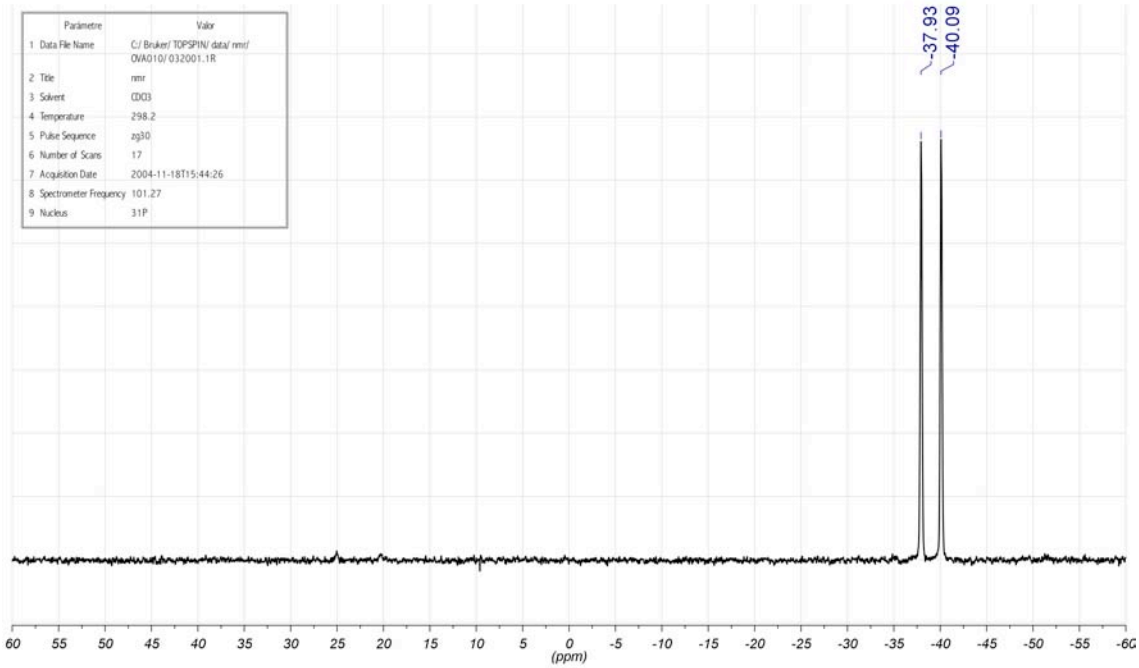


$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

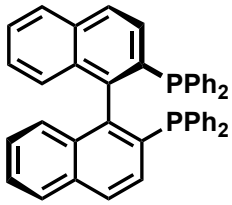




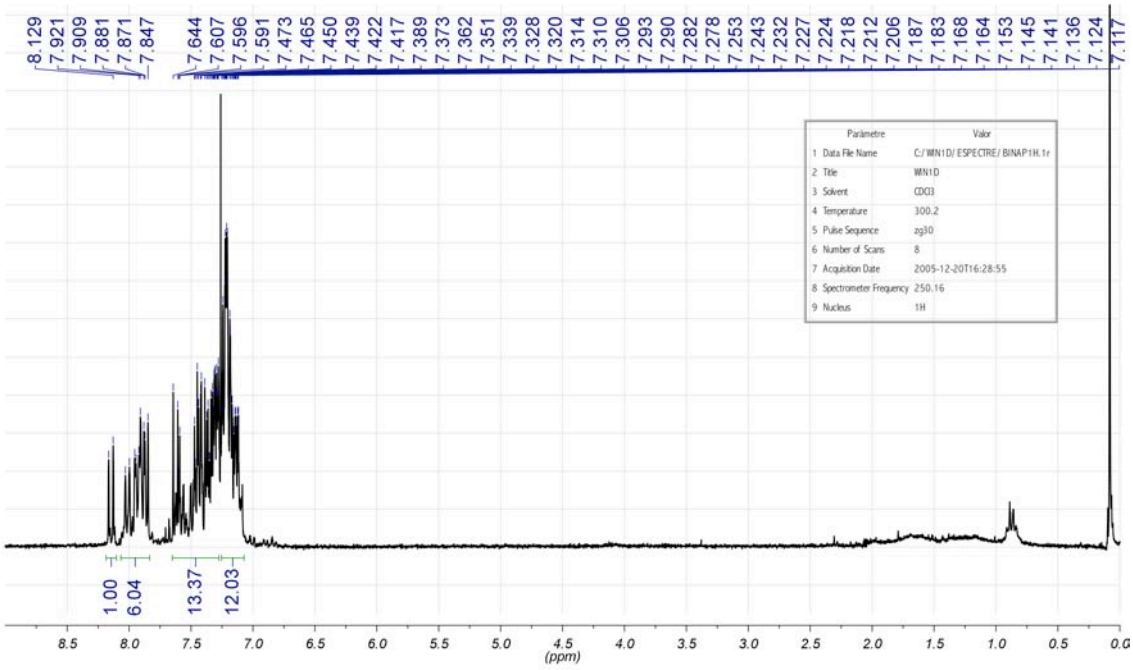
^{31}P RMN (101 MHz, rt, $CDCl_3$):



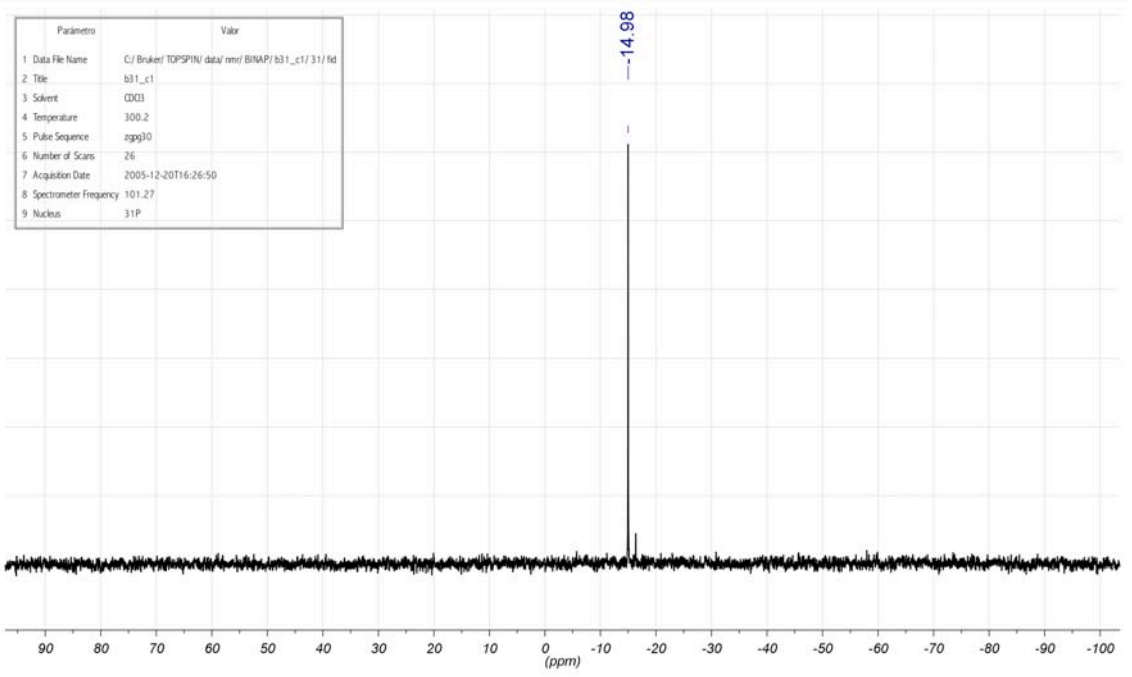
(R)-(+)-2,2'-bis(difenilfosfino)-1,1'-binaftil (BINAP, L18)



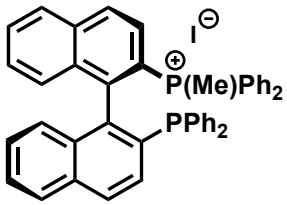
^{1}H RMN (250 MHz, rt, $CDCl_3$):



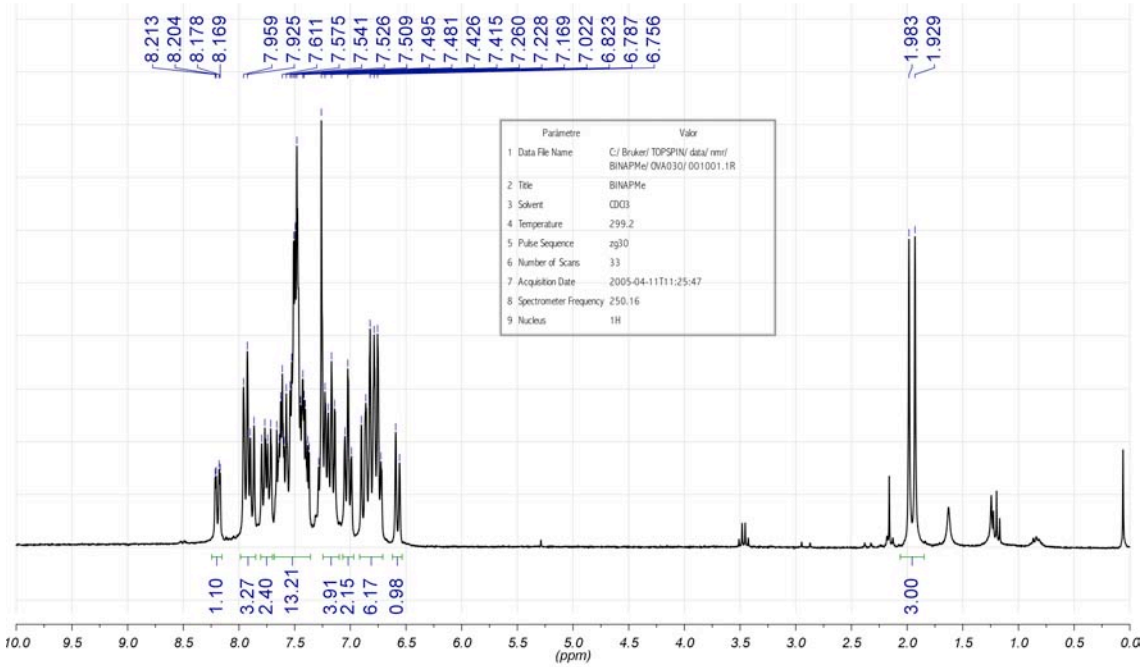
^{31}P{^{1}H} RMN (101 MHz, rt, $CDCl_3$):



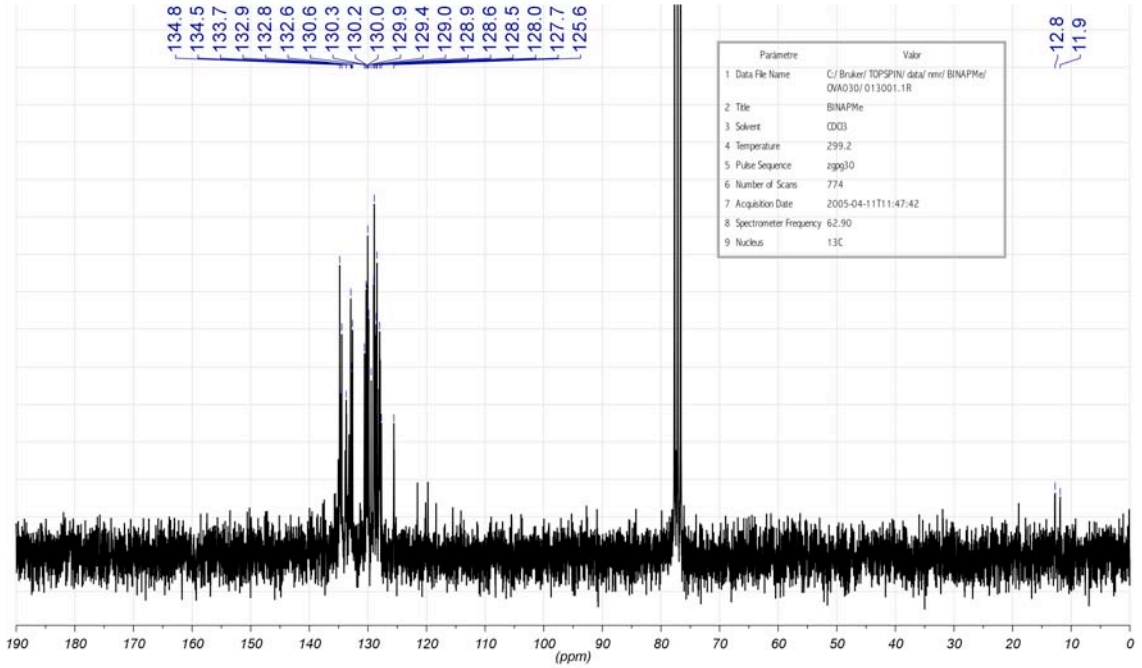
Iodur de (R)-(+)-Metilbinap **(BINAP(Me)I, L29a)**

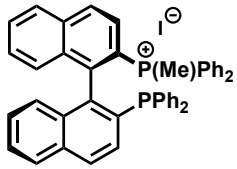


^{1}H RMN (250 MHz, rt, $CDCl_3$):

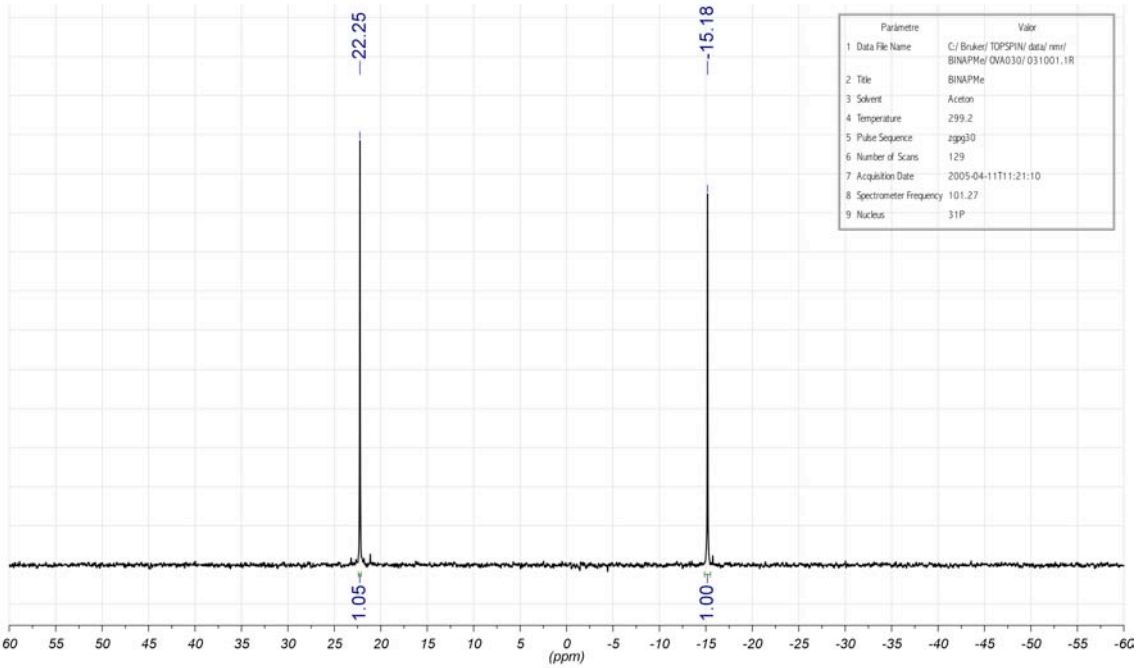


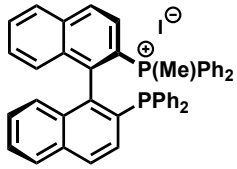
^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):



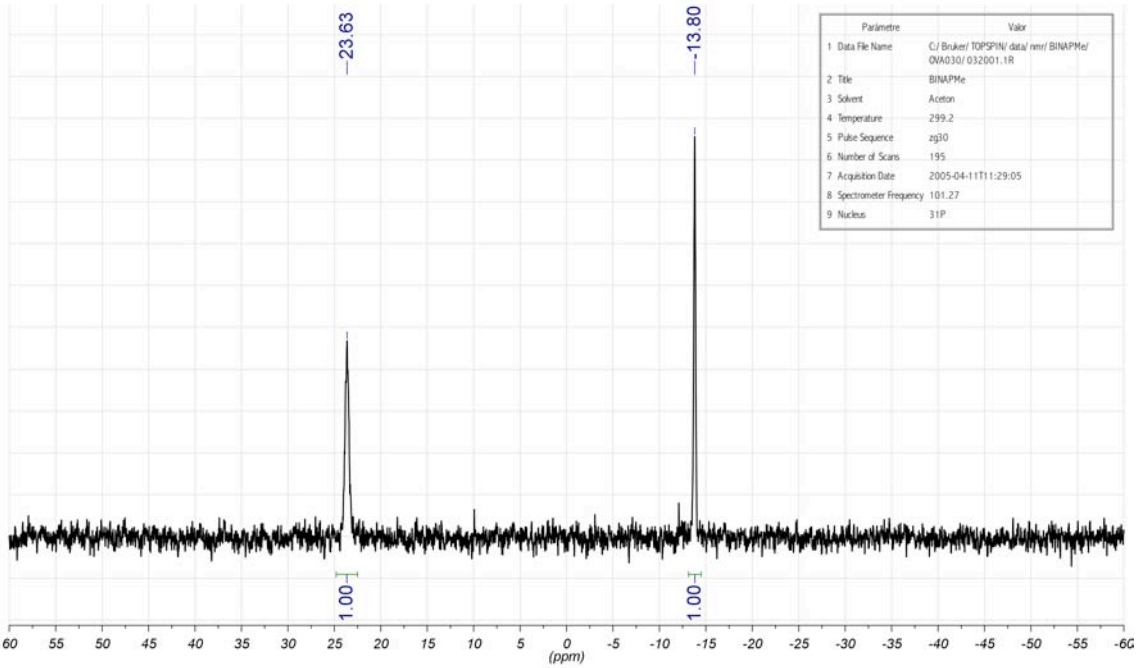


$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

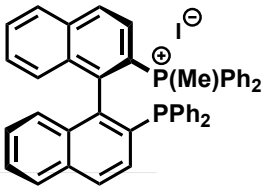




^{31}P RMN (101 MHz, rt, $CDCl_3$):

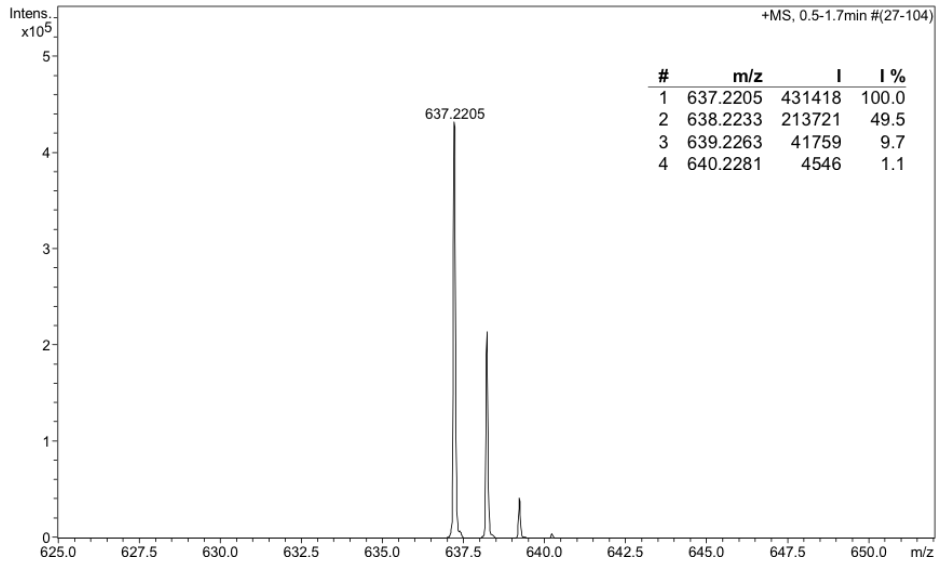


HRMS (ESI+):

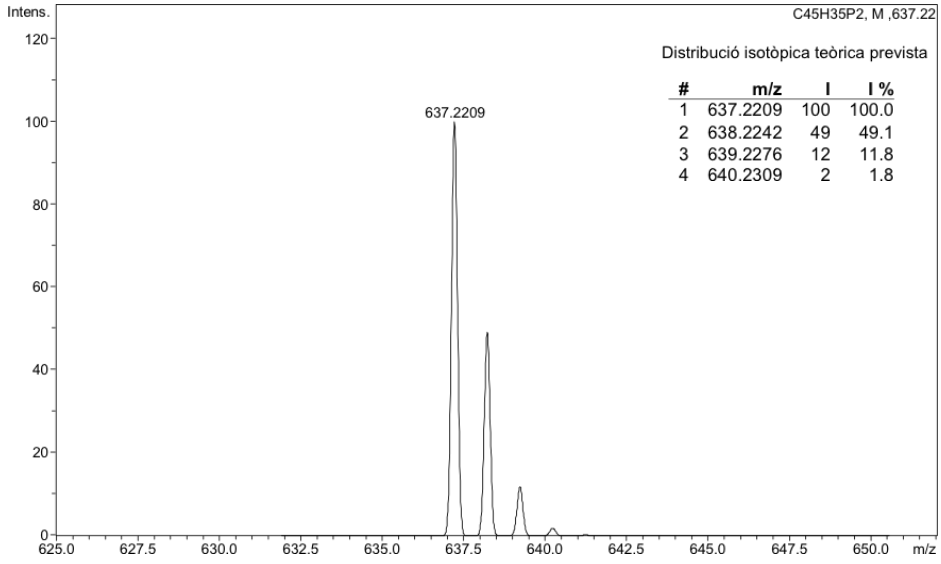


Analysis Info

Analysis Name	09EM424-QTOF-pos1-1.d	Acquisition Date	17/09/2009 11:50:44
Method	09EM424-QTOF-pos1.m	Operator	SAQ
Sample Name	BINAP Me I	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 5 ppm en MeOH. O. VALLCORBA		



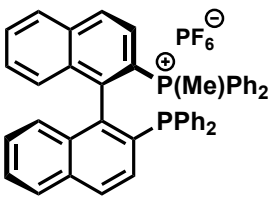
#	m/z	I	I %
1	637.2205	431418	100.0
2	638.2233	213721	49.5
3	639.2263	41759	9.7
4	640.2281	4546	1.1



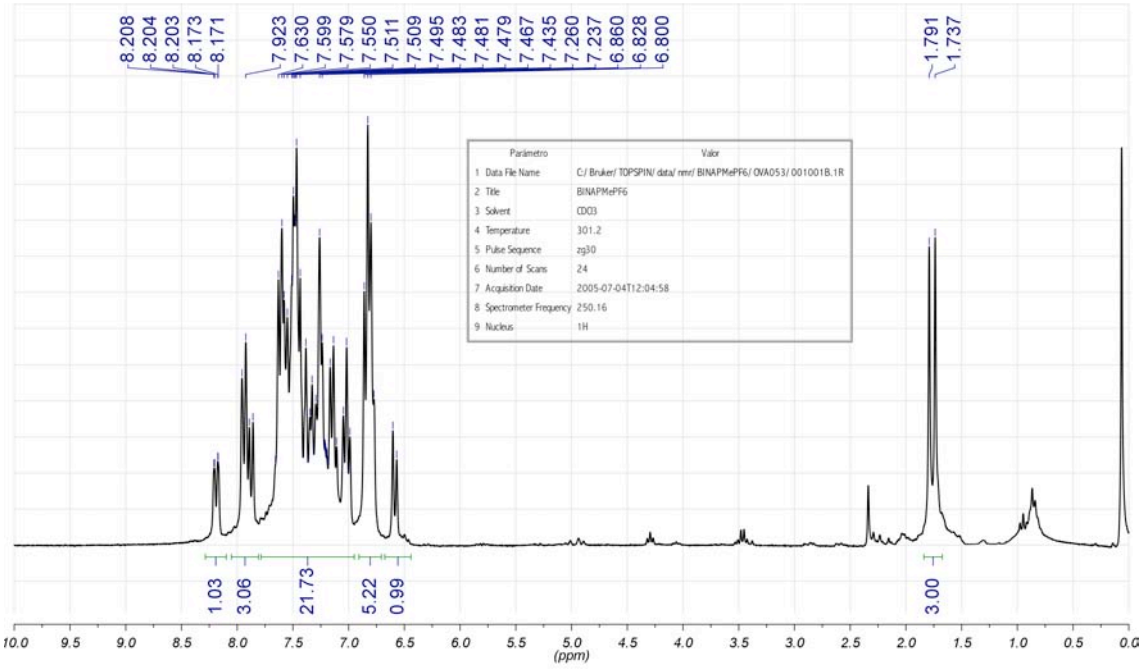
Distribució isotòpica teòrica prevista

#	m/z	I	I %
1	637.2209	100	100.0
2	638.2242	49	49.1
3	639.2276	12	11.8
4	640.2309	2	1.8

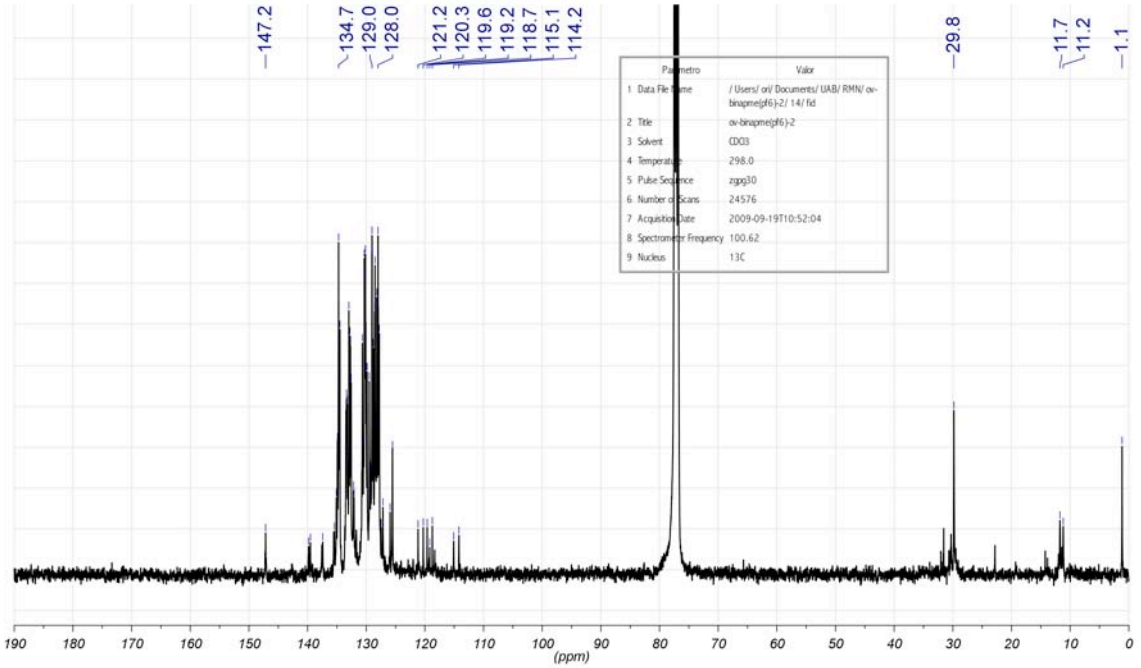
Hexafluorofosfat de (R)-(+)-Metilbinap **(BINAP(Me)PF_6, L29b)**

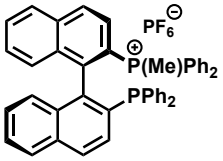


^{1}H RMN (250 MHz, rt, $CDCl_3$):

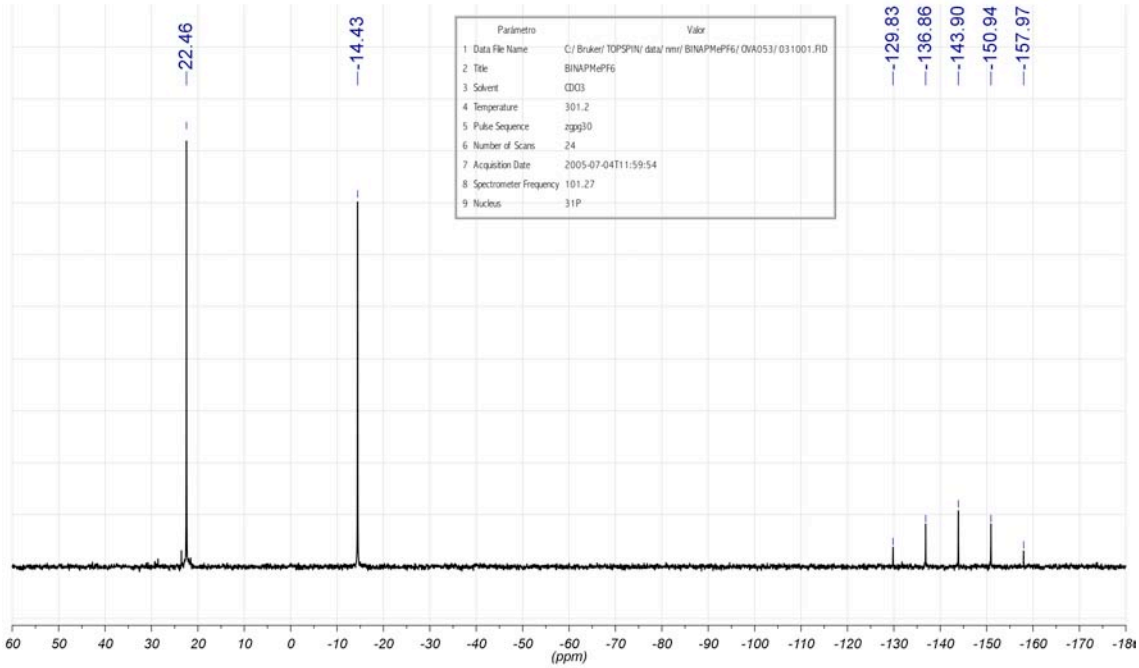


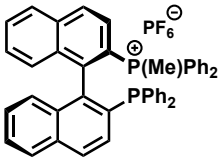
^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):



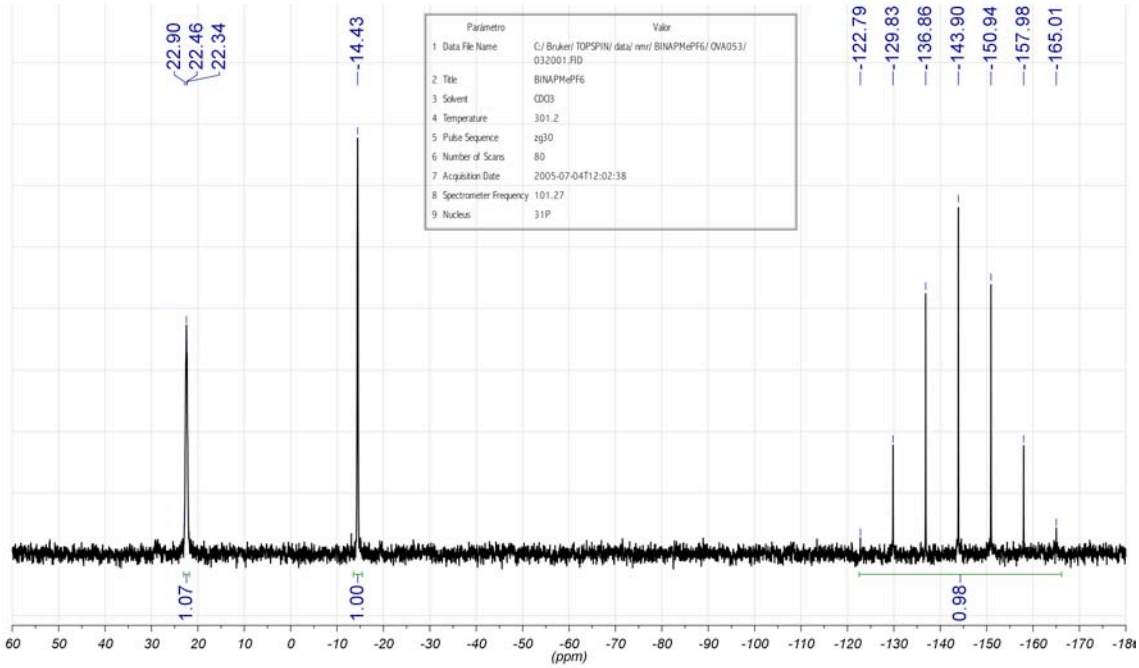


$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

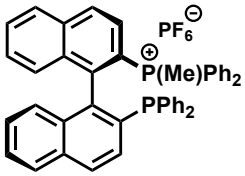




^{31}P RMN (101 MHz, rt, $CDCl_3$):

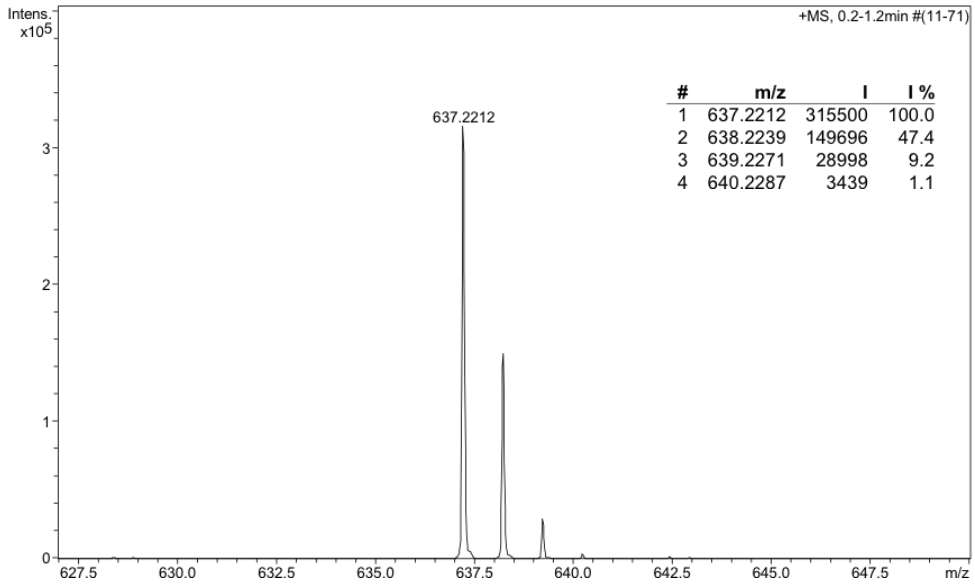


HRMS (ESI+):

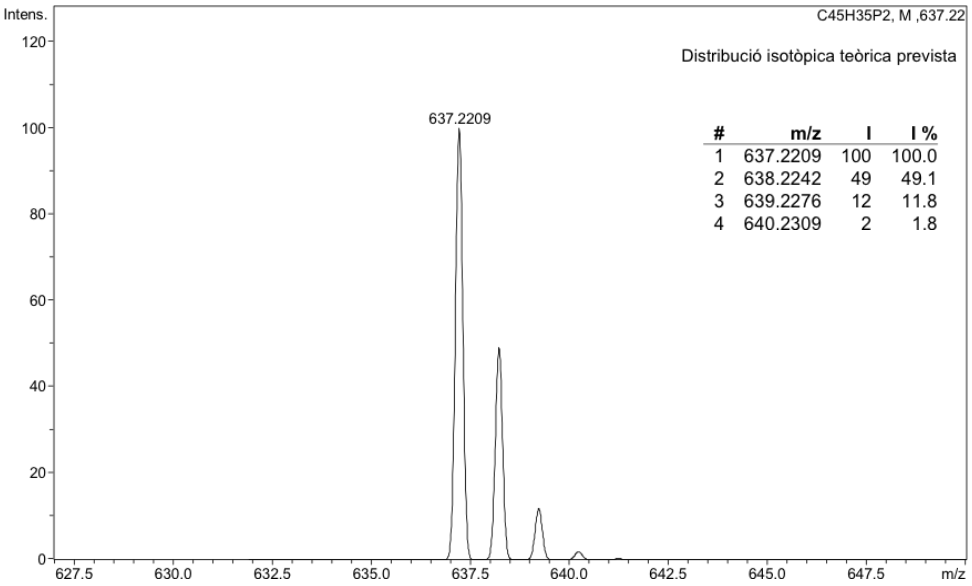


Analysis Info

Analysis Name	09EM423-QTOF-pos1-1.d	Acquisition Date	17/09/2009 12:23:20
Method	09EM423-QTOF-pos1.m	Operator	SAQ
Sample Name	BINAP Me PF	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 5 ppm en MeOH. O. VALLCORBA		



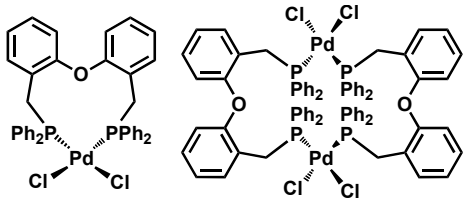
#	m/z	I	I %
1	637.2212	315500	100.0
2	638.2239	149696	47.4
3	639.2271	28998	9.2
4	640.2287	3439	1.1



#	m/z	I	I %
1	637.2209	100	100.0
2	638.2242	49	49.1
3	639.2276	12	11.8
4	640.2309	2	1.8

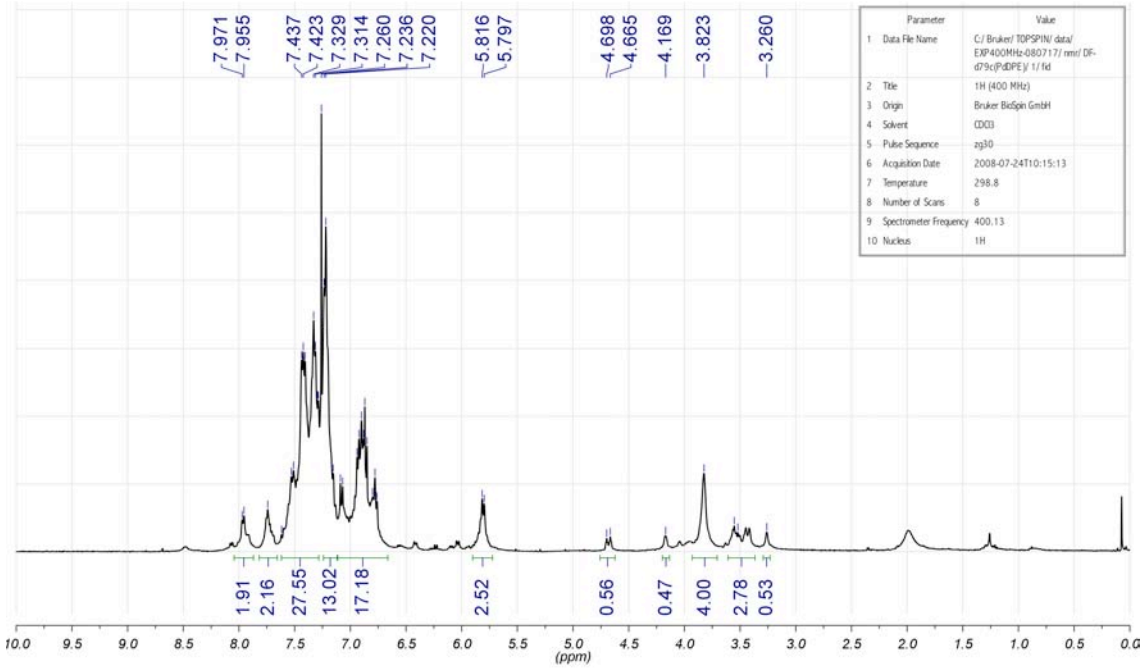
11 Caracterització dels complexos metàl·lics

11.1 DPEMephos amb Pd i Pt

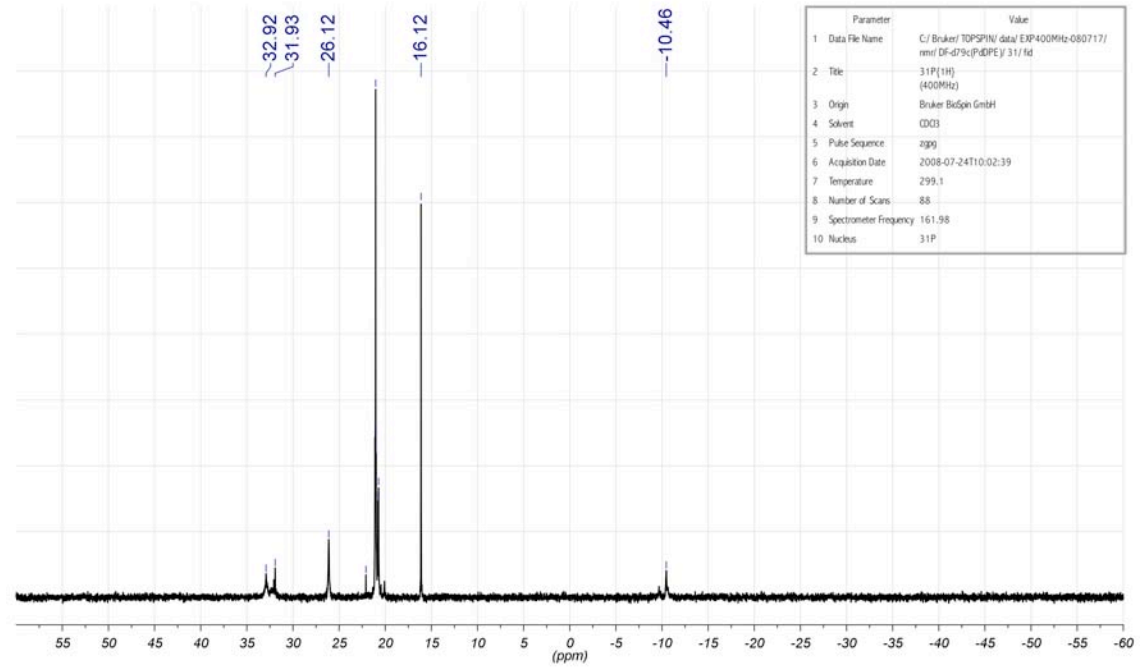


[PdCl$_2$(DPEMephos)] (C32)

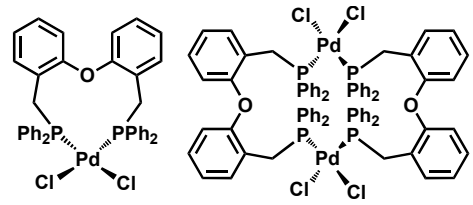
^{1}H RMN (400 MHz, rt, $CDCl_3$):

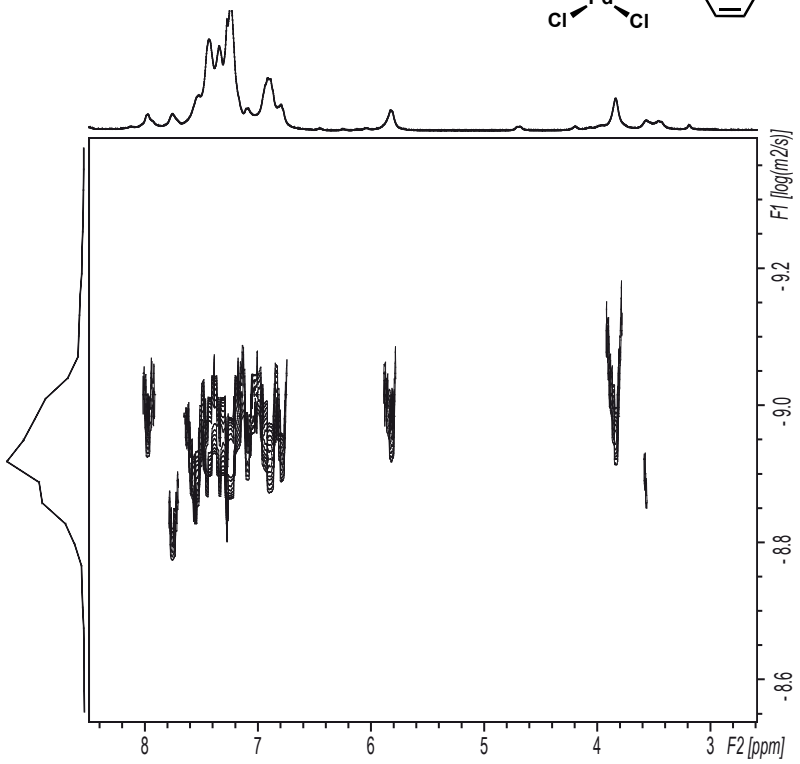


^{31}P{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

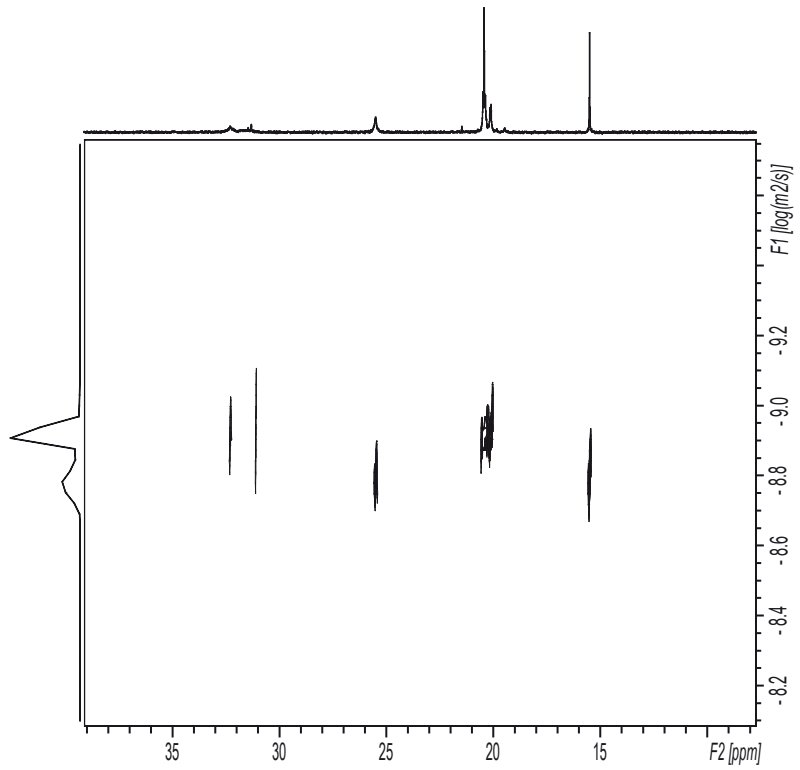


^{1}H DOSY PFG-RMN (400 MHz, rt, $CDCl_3$):

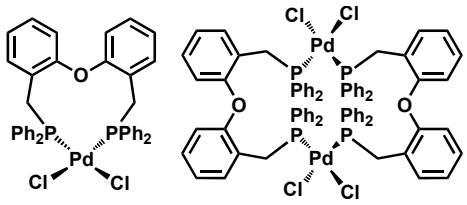




^{31}P{^{1}H} DOSY PFG-RMN (101 MHz, rt, $CDCl_3$):

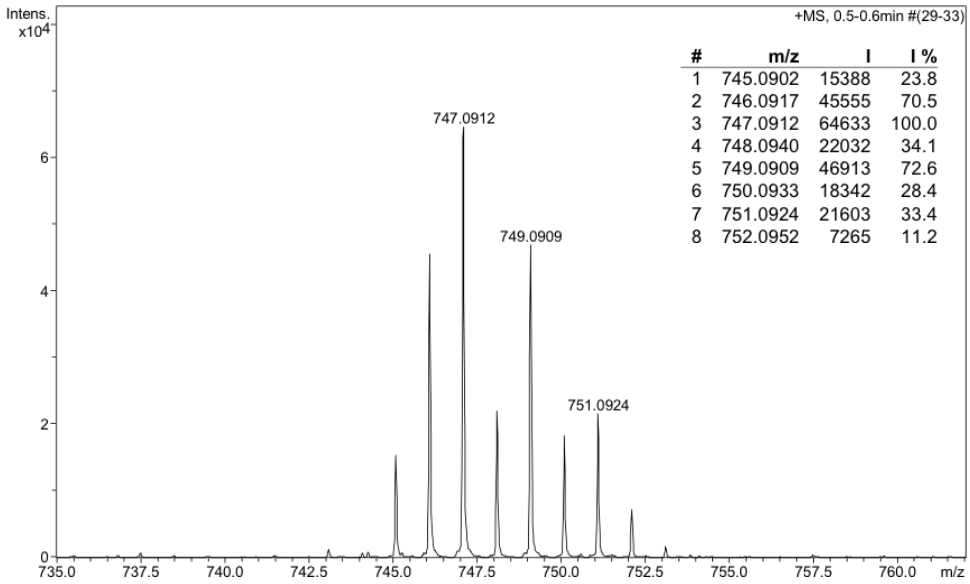


HRMS (ESI+):

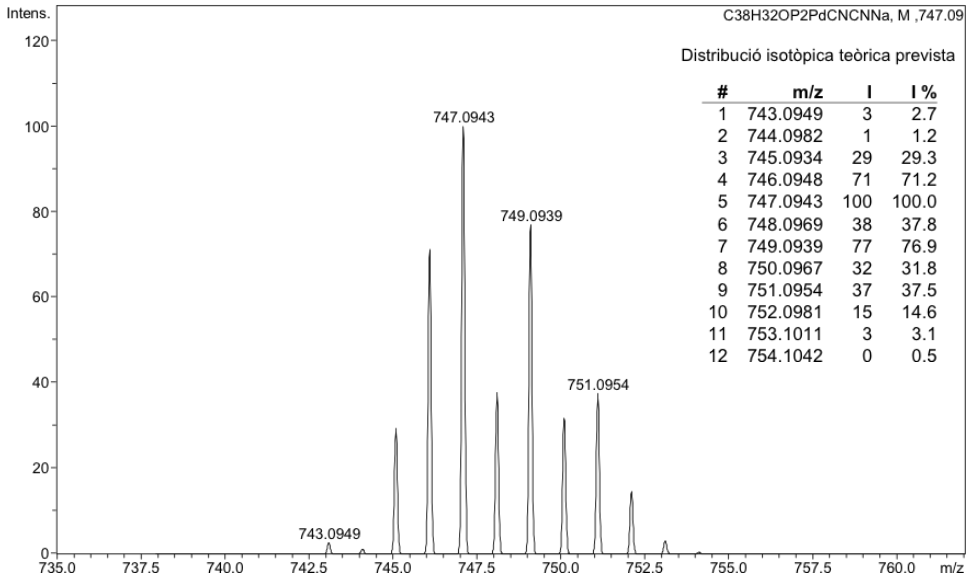


Analysis Info

Analysis Name	d57aPd (8EM-147)_1-B,1_01_250.d	Acquisition Date	27/05/2008 10:51:41
Method	ESIpos250-1300_FI-HS_MeCN_27-5-08.m	Operator	SAQ
Sample Name	d57aPd (8EM-147)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2 ppm en MeCN. // O. VALLCORBA.		



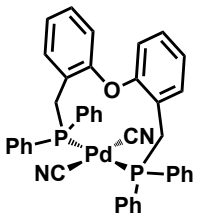
#	m/z	I	I %
1	745.0902	15388	23.8
2	746.0917	45555	70.5
3	747.0912	64633	100.0
4	748.0940	22032	34.1
5	749.0909	46913	72.6
6	750.0933	18342	28.4
7	751.0924	21603	33.4
8	752.0952	7265	11.2



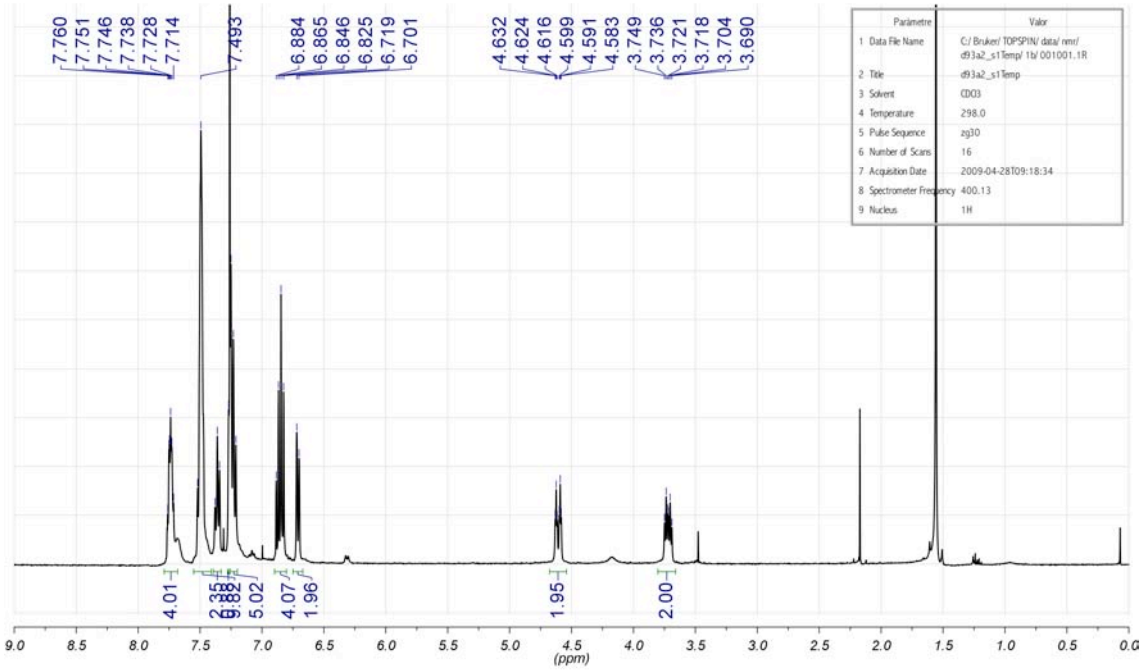
Distribució isotòpica teòrica prevista

#	m/z	I	I %
1	743.0949	3	2.7
2	744.0982	1	1.2
3	745.0934	29	29.3
4	746.0948	71	71.2
5	747.0943	100	100.0
6	748.0969	38	37.8
7	749.0939	77	76.9
8	750.0967	32	31.8
9	751.0954	37	37.5
10	752.0981	15	14.6
11	753.1011	3	3.1
12	754.1042	0	0.5

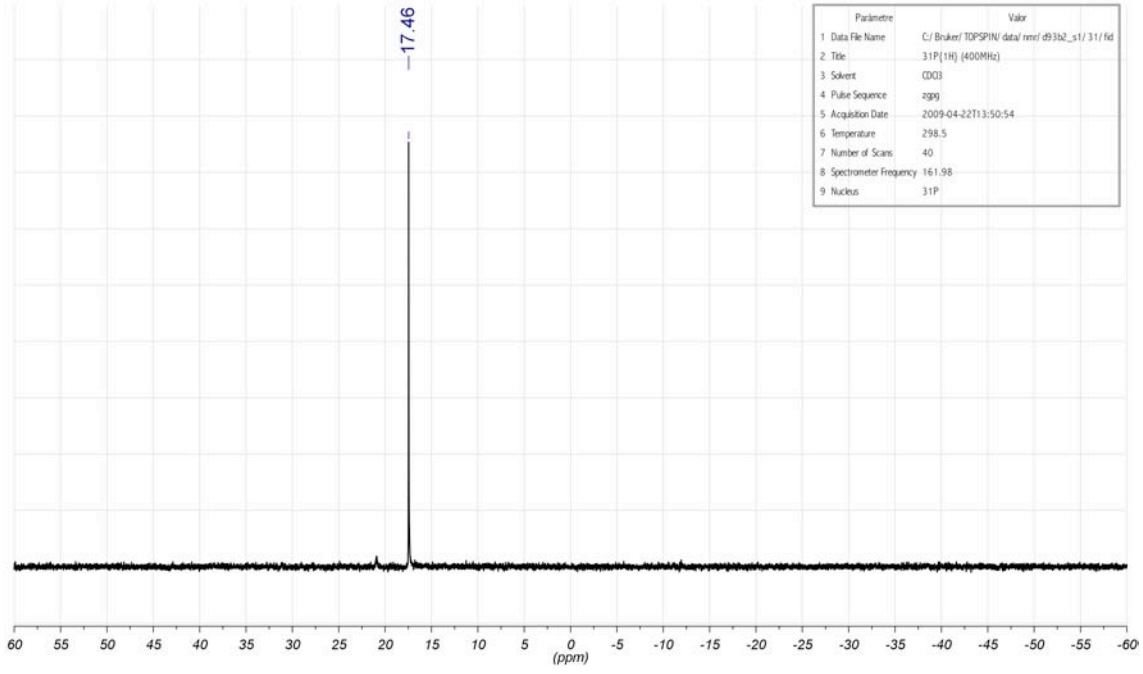
[Pd(CN)$_2$(DPEMephos)] (C34)



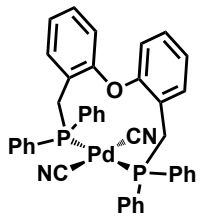
^{1}H RMN (400 MHz, rt, $CDCl_3$):

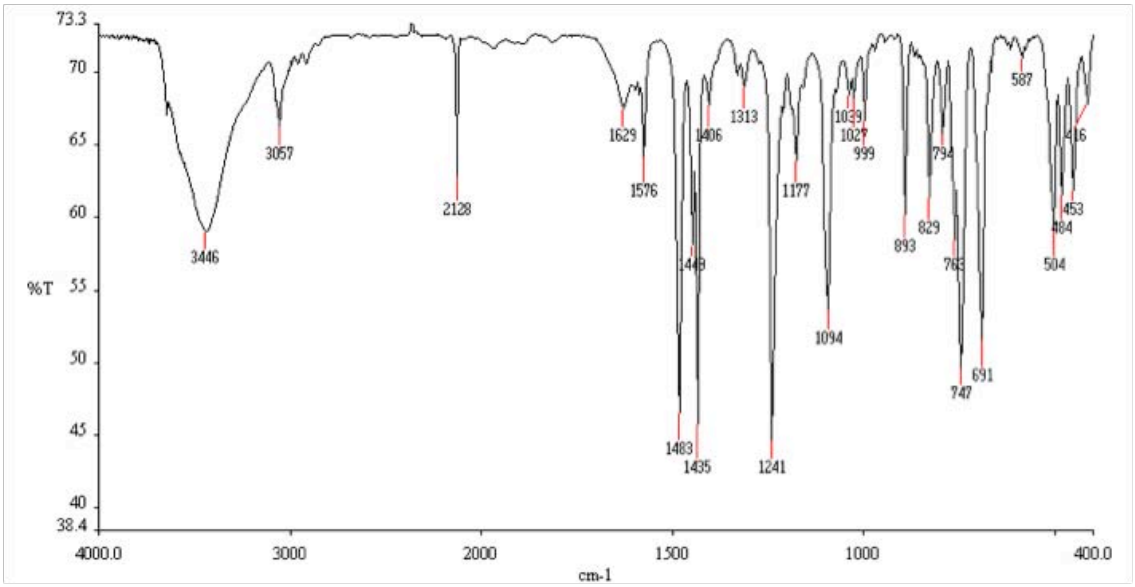


^{31}P{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

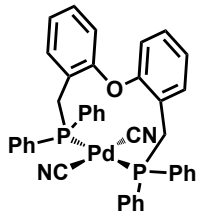


IR (KBr):



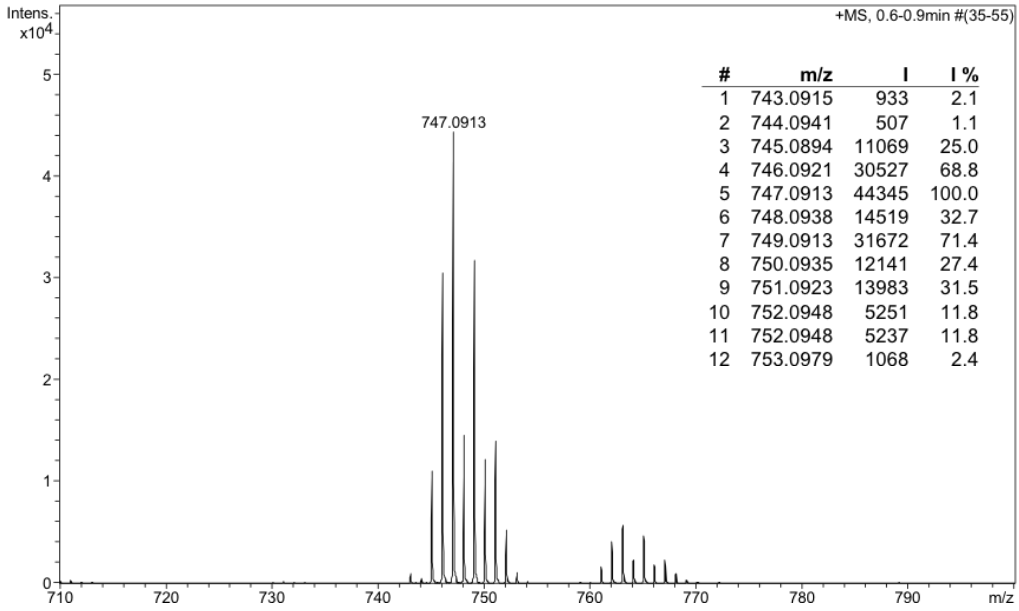


HRMS (ESI+):

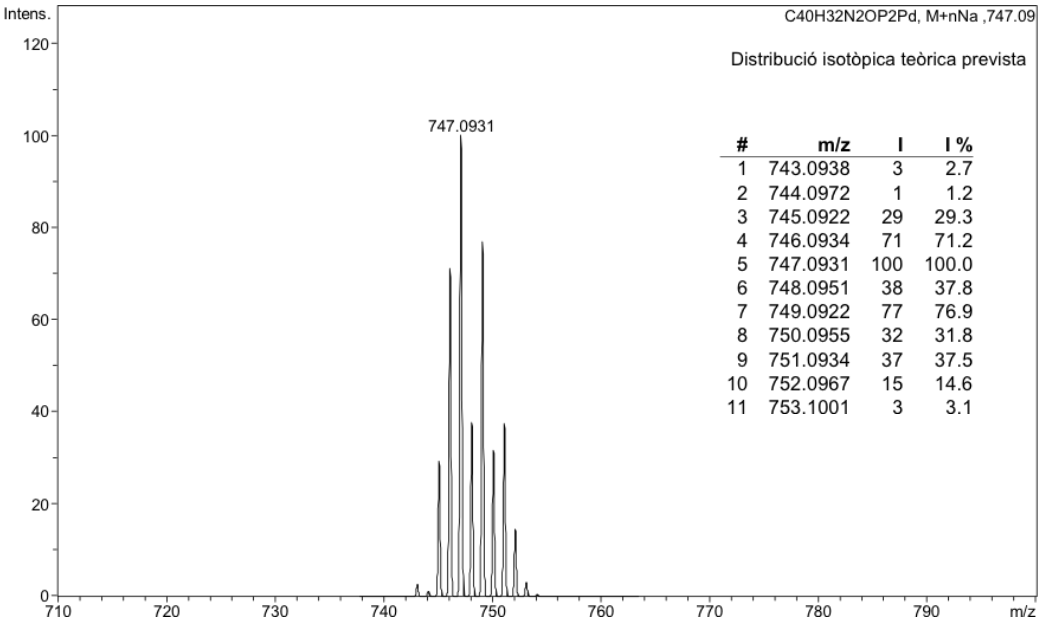


Analysis Info

Analysis Name	09EM211-QTOF-pos1-1.d	Acquisition Date	08/05/2009 12:50:43
Method	09EM211-QTOF-pos1.m	Operator	SAQ
Sample Name	d93b2	Instrument	micrOTOF-Q
Comment	MIE // ESI+ // Dó en CH2Cl2:MeOH (1:5) // ORIOL VALLCORBA		

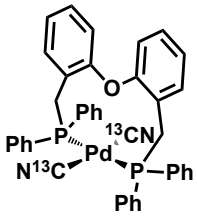


#	m/z	I	I %
1	743.0915	933	2.1
2	744.0941	507	1.1
3	745.0894	11069	25.0
4	746.0921	30527	68.8
5	747.0913	44345	100.0
6	748.0938	14519	32.7
7	749.0913	31672	71.4
8	750.0935	12141	27.4
9	751.0923	13983	31.5
10	752.0948	5251	11.8
11	752.0948	5237	11.8
12	753.0979	1068	2.4

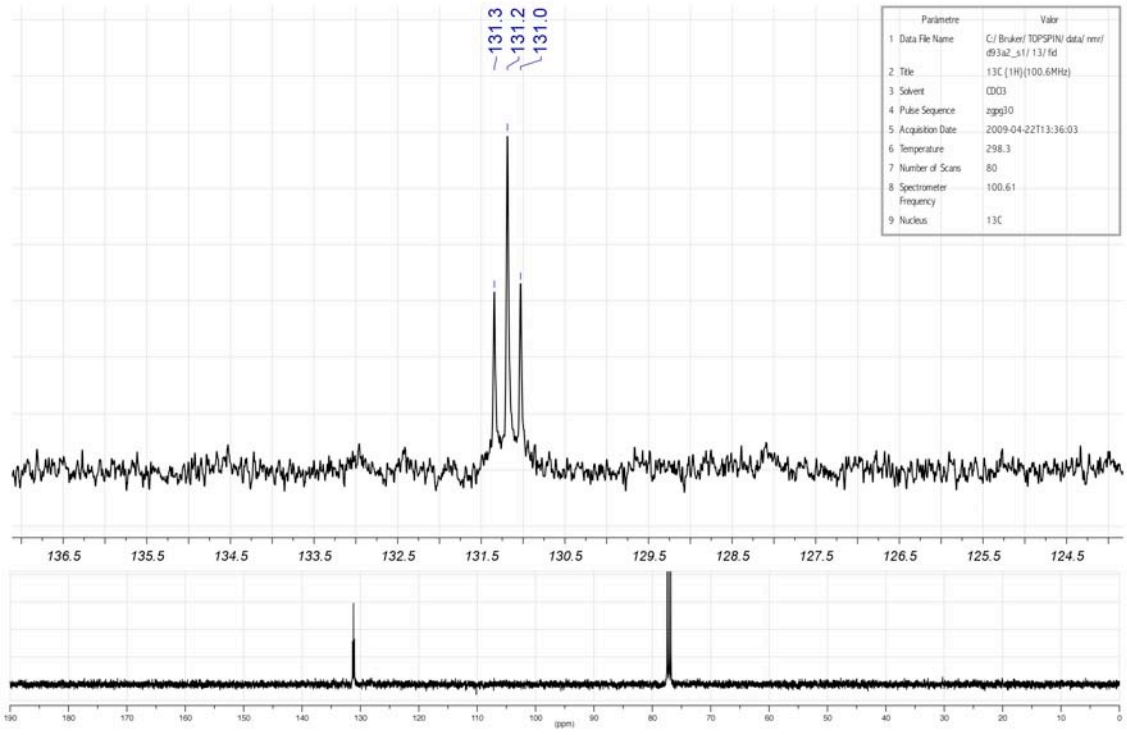


#	m/z	I	I %
1	743.0938	3	2.7
2	744.0972	1	1.2
3	745.0922	29	29.3
4	746.0934	71	71.2
5	747.0931	100	100.0
6	748.0951	38	37.8
7	749.0922	77	76.9
8	750.0955	32	31.8
9	751.0934	37	37.5
10	752.0967	15	14.6
11	753.1001	3	3.1

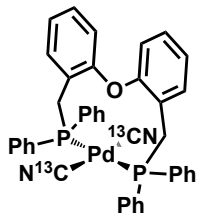
[Pd(^{13}CN)$_2$(DPEMephos)] (C34m)

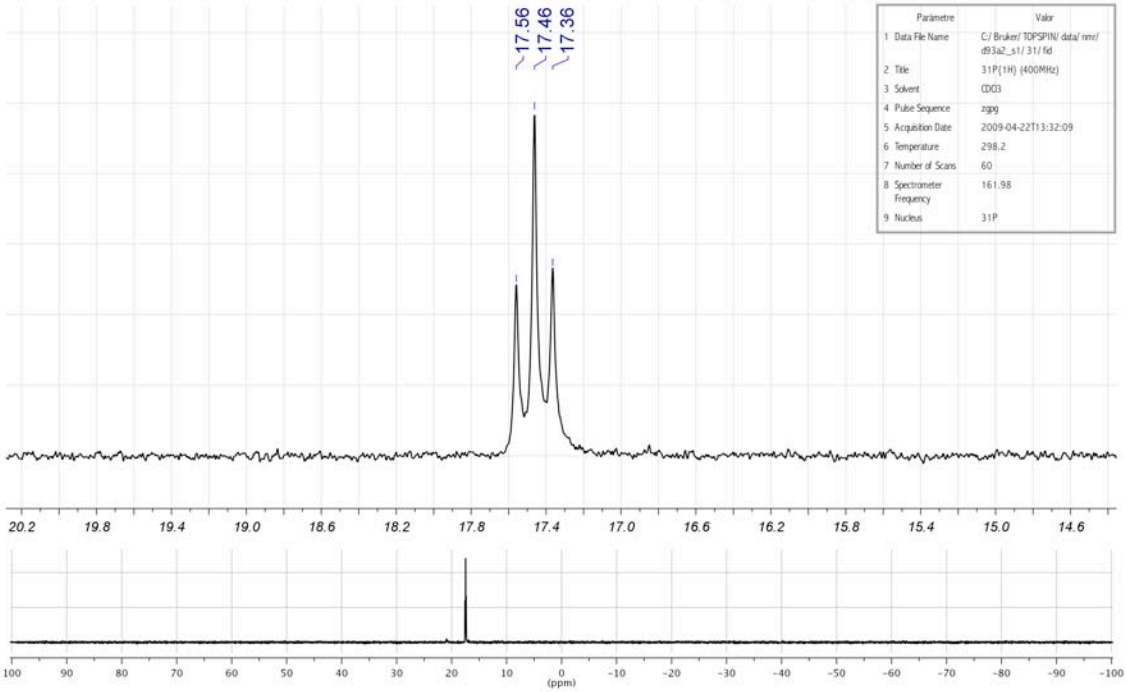


^{13}C{^{1}H} RMN (63 MHz, rt, $CDCl_3$):

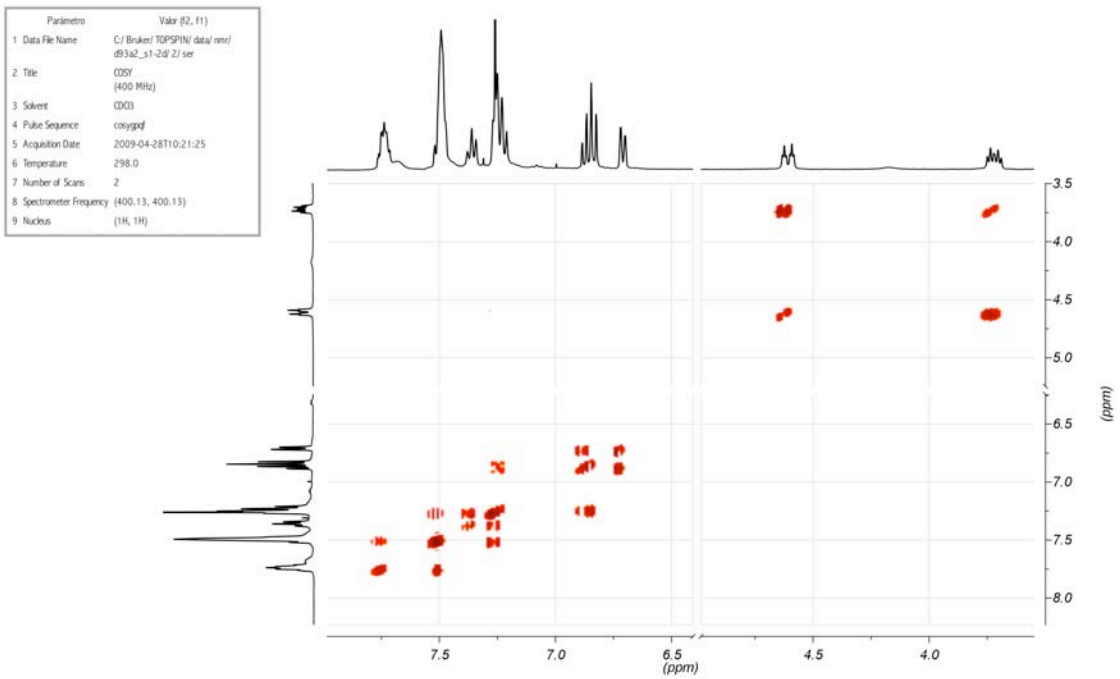


$^{31}P\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

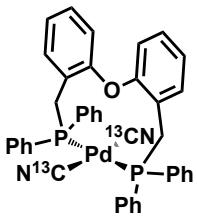




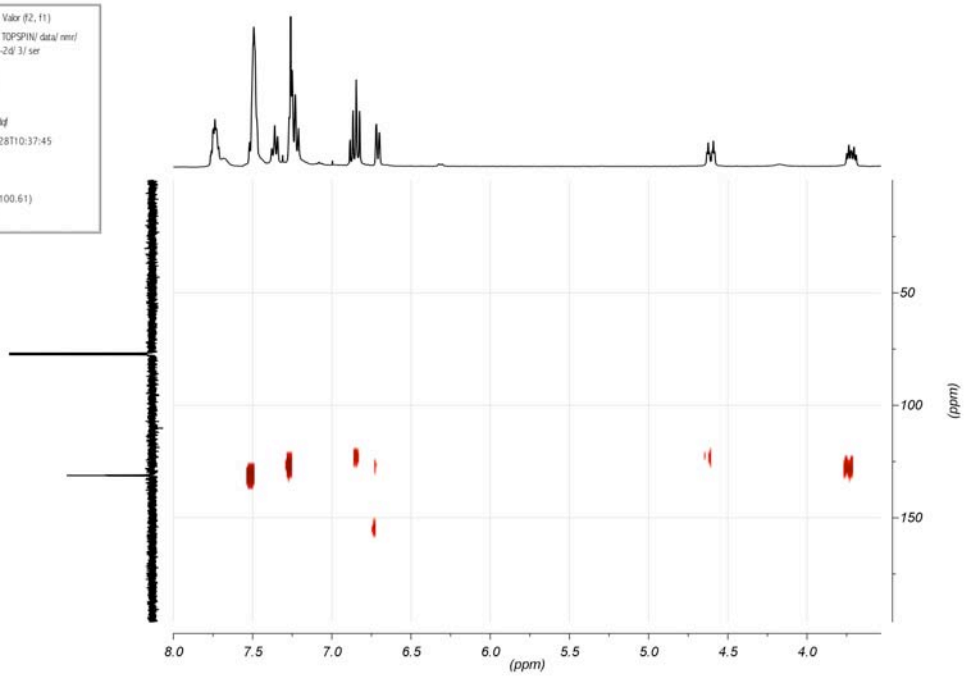
Espectre de correlació ^{1}H-^{1}H (COSY):



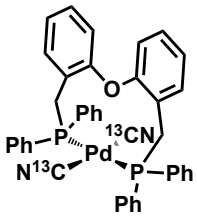
Espectre de correlació ^{1}H-^{13}C (HMBC):



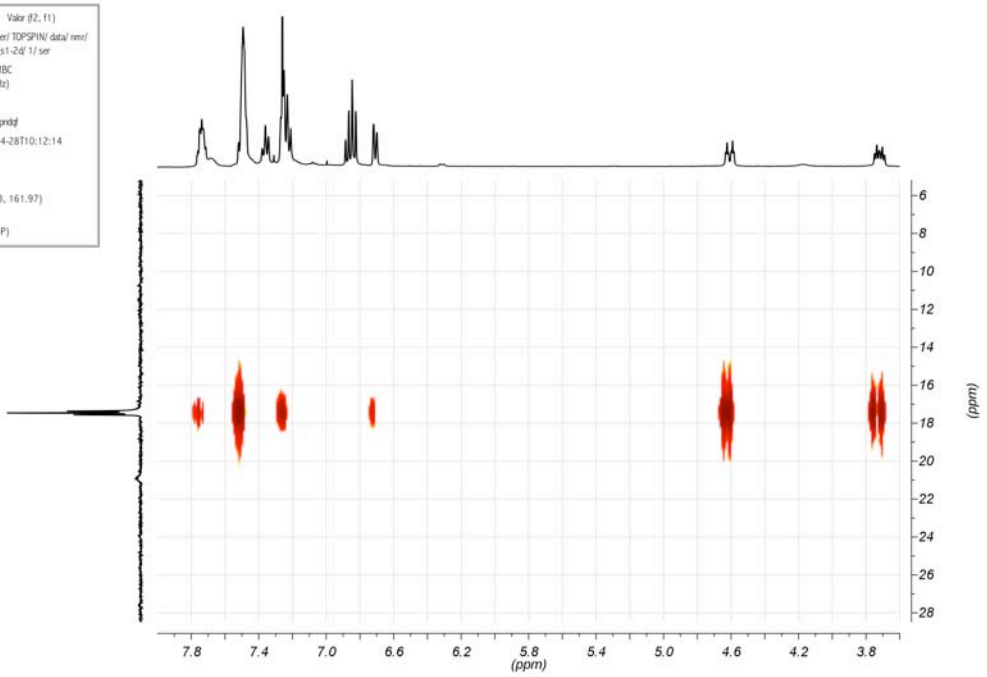
Parámetro	Valor (f2, f1)
1 Data File Name	C:/ Bruker/ TOPSPIN/ data/ nmr/ d93a2_s1-2d/ 3/ ser
2 Title	HMBC (400MHz)
3 Solvent	CDCl3
4 Pulse Sequence	hmbcgplpndqf
5 Acquisition Date	2009-04-28T10:37:45
6 Temperature	298.0
7 Number of Scans	4
8 Spectrometer Frequency	(400.13, 100.61)
9 Nucleus	(1H, 1H)



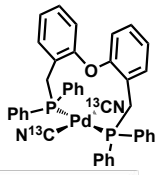
Espectre de correlació ^{1}H-^{31}P (HMBC):

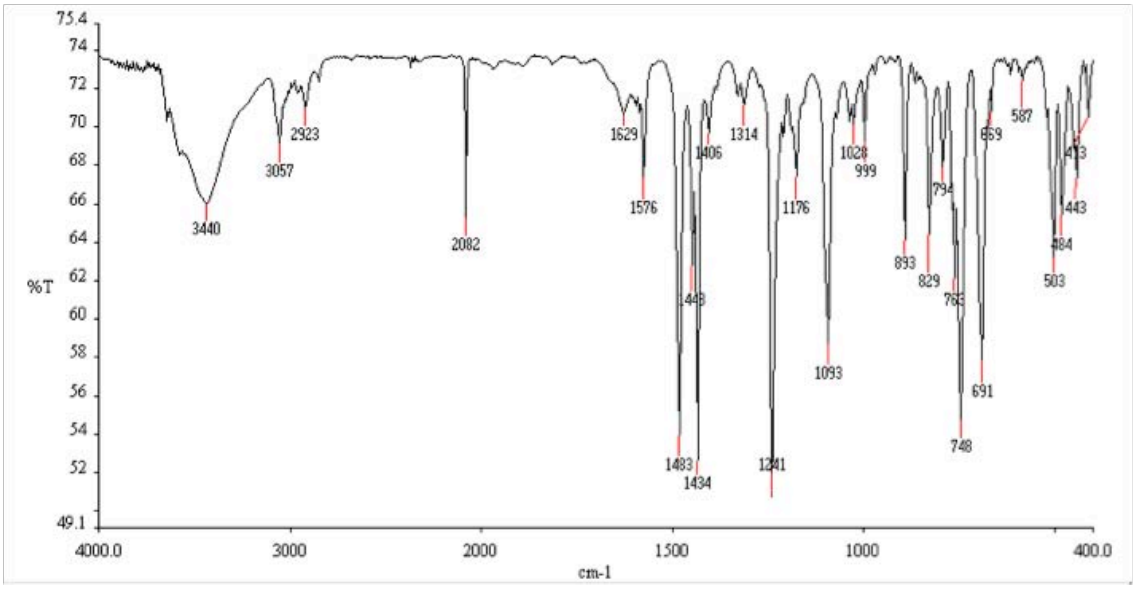


Parámetro	Valor (f2, f1)
1 Data File Name	C:/ Bruker/ TOPSPIN/ data/ nmr/ d93a2_s1-2d/ 1/ ser
2 Title	31P HMBC (400MHz)
3 Solvent	CDCl3
4 Pulse Sequence	hmbcgplpndqf
5 Acquisition Date	2009-04-28T10:12:14
6 Temperature	297.9
7 Number of Scans	4
8 Spectrometer Frequency	(400.13, 161.97)
9 Nucleus	(1H, 31P)

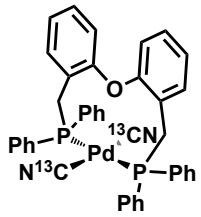


IR (KBr):





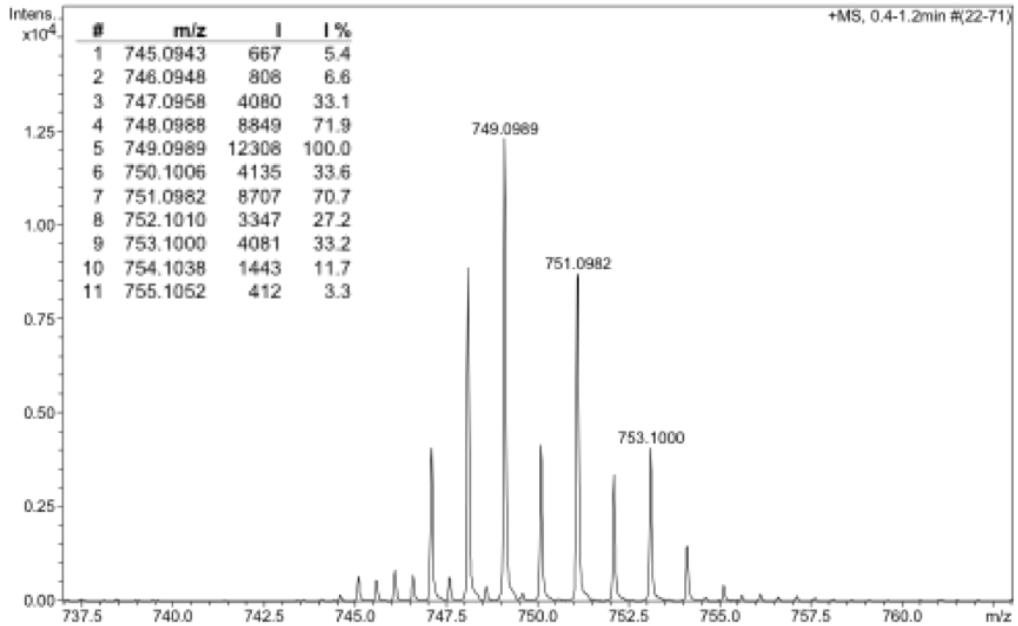
HRMS (ESI+):

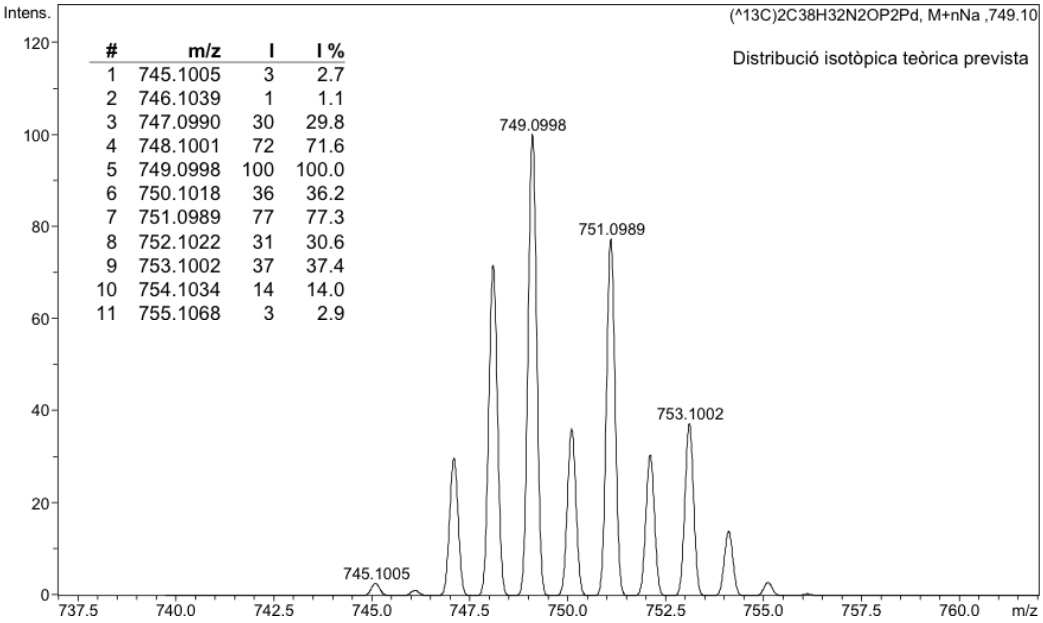


Analysis Info

Analysis Name	09EM210-QTOF-pos1-1.d	Acquisition Date	08/05/2009 12:42:13
Method	09EM210-QTOF-pos1.m	Operator	SAQ
Sample Name	d93a2	Instrument	micrOTOF-Q
Comment	MIE // ESI+ // Dó ca. 15 ppm en CH2Cl2:MeOH (1:5) // ORIOL VALLCORBA		

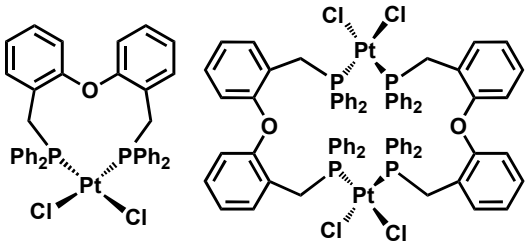
#	m/z	I	I %
1	745.0943	667	5.4
2	746.0948	808	6.6
3	747.0958	4080	33.1
4	748.0988	8849	71.9
5	749.0989	12308	100.0
6	750.1006	4135	33.6
7	751.0982	8707	70.7
8	752.1010	3347	27.2
9	753.1000	4081	33.2
10	754.1038	1443	11.7
11	755.1052	412	3.3



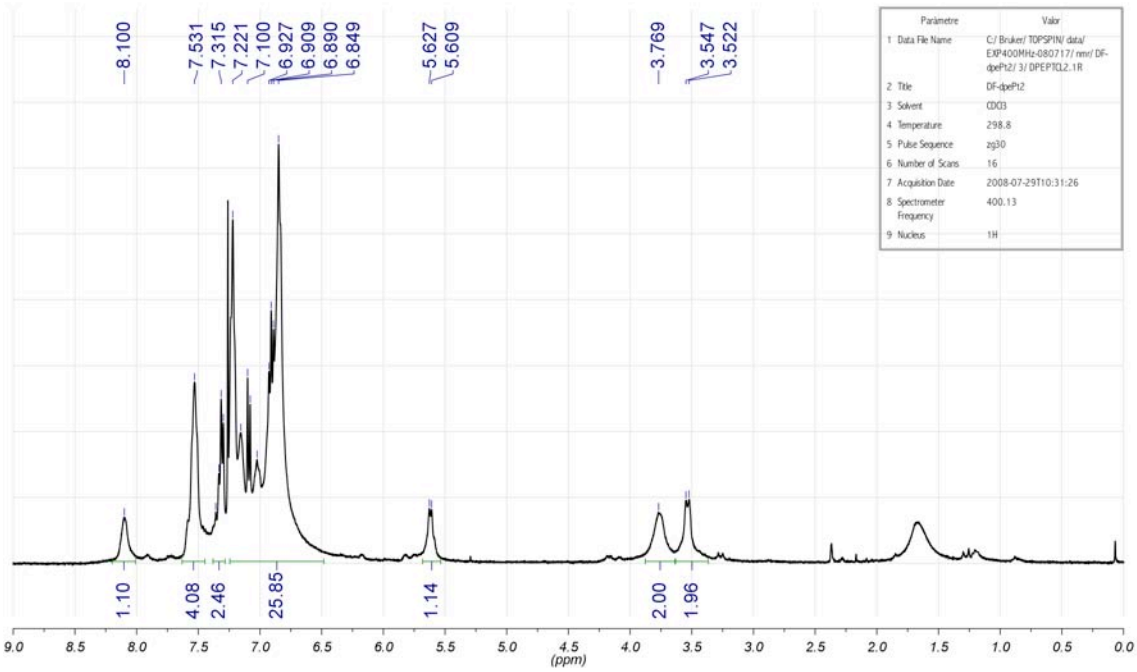


#	m/z	I	I %
1	745.1005	3	2.7
2	746.1039	1	1.1
3	747.0990	30	29.8
4	748.1001	72	71.6
5	749.0998	100	100.0
6	750.1018	36	36.2
7	751.0989	77	77.3
8	752.1022	31	30.6
9	753.1002	37	37.4
10	754.1034	14	14.0
11	755.1068	3	2.9

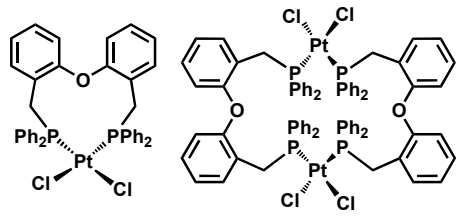
[$PtCl_2$(DPEMephos)] (C33)

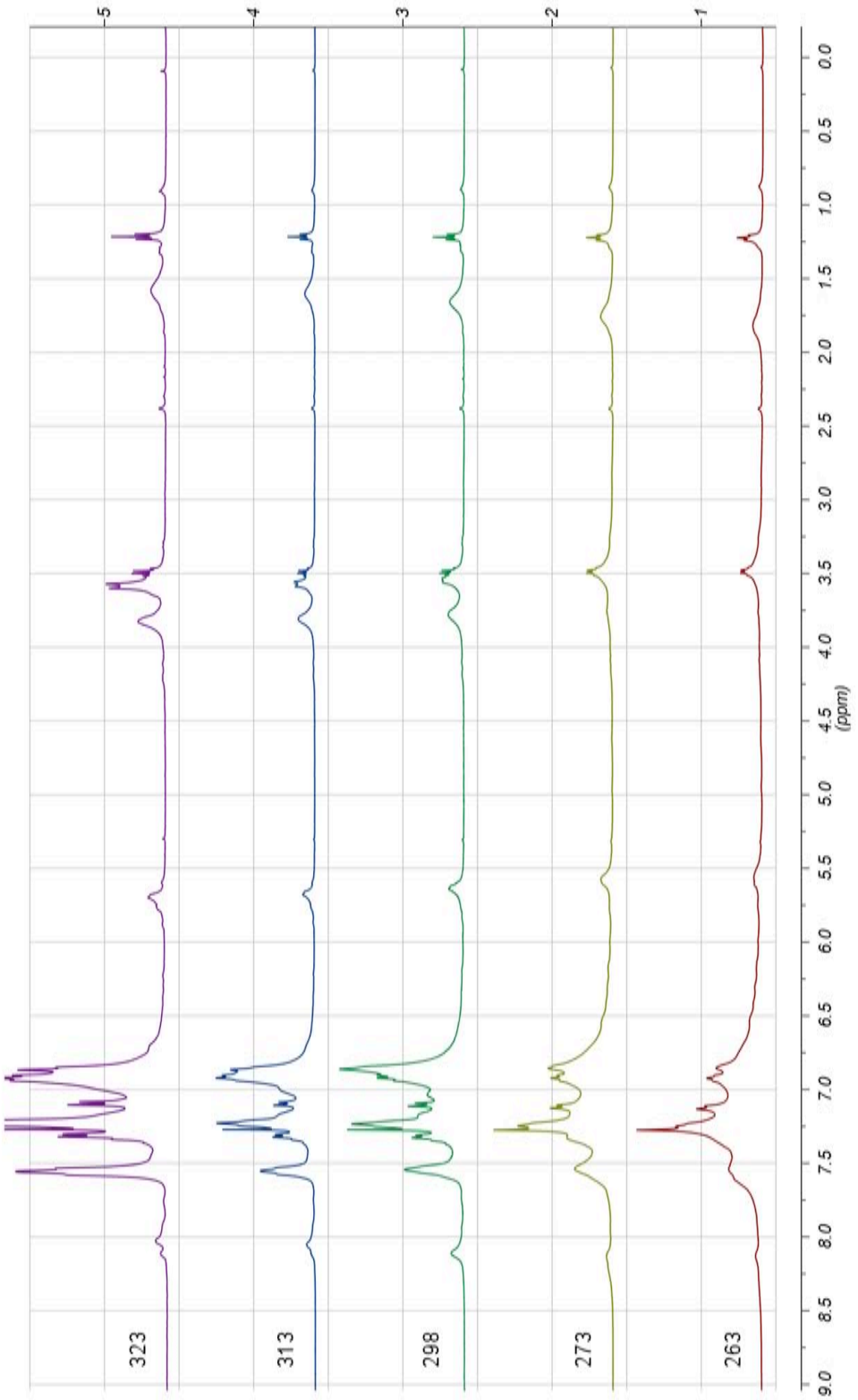


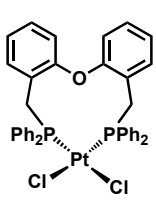
^{1}H RMN (400 MHz, rt, $CDCl_3$):

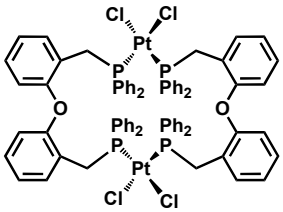


^{1}H RMN (400 MHz, temperatura variable, $CDCl_3$):

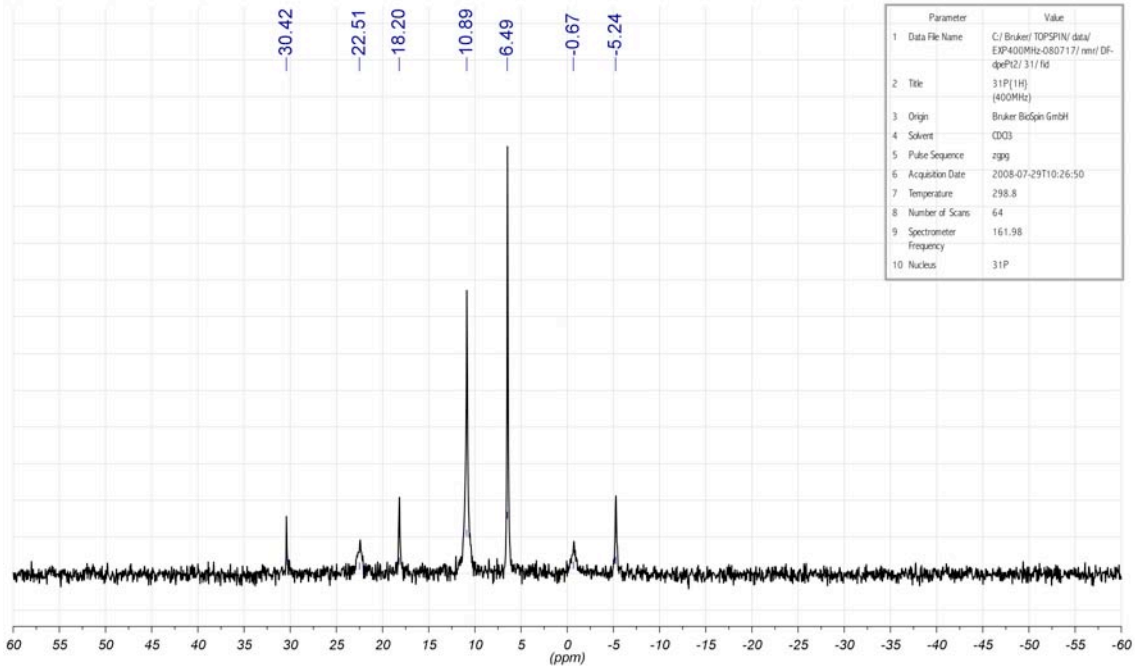


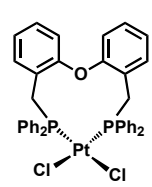


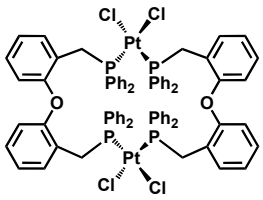




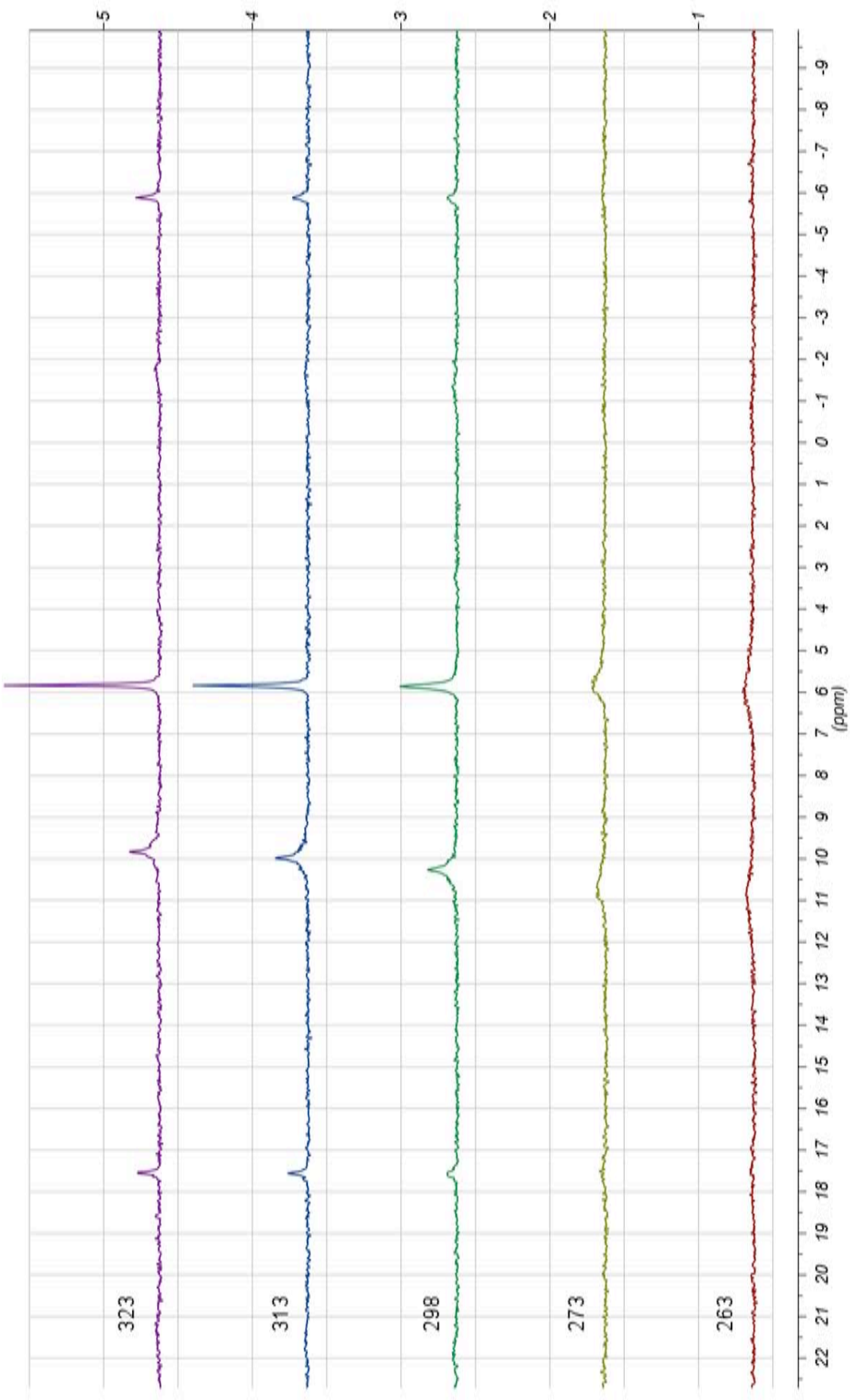
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



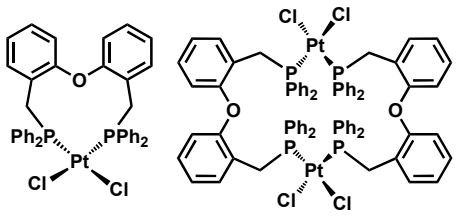


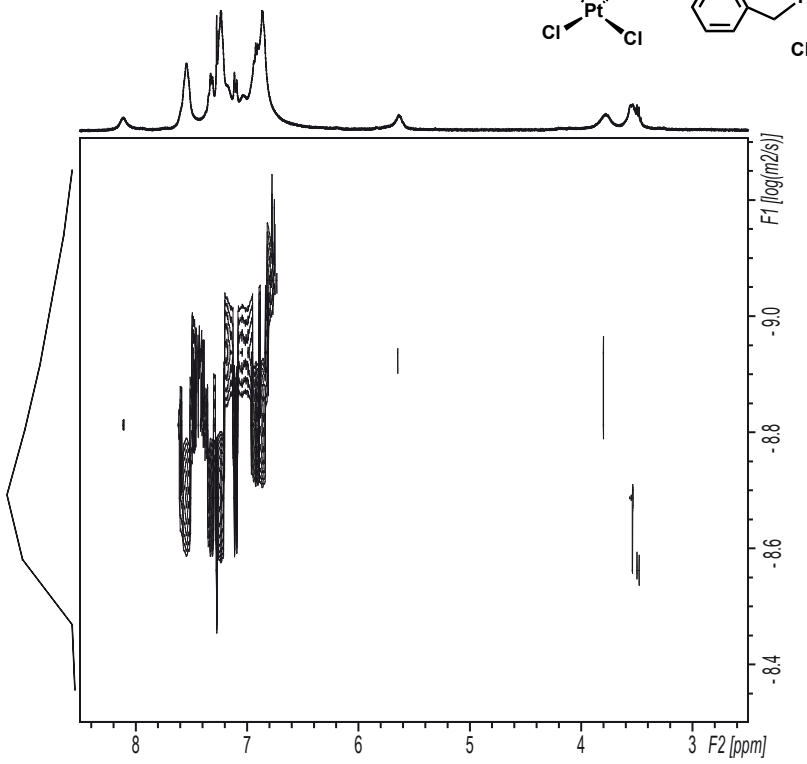


$^{31}P\{^{1}H\}$ RMN (162 MHz, temperatura variable, $CDCl_3$):

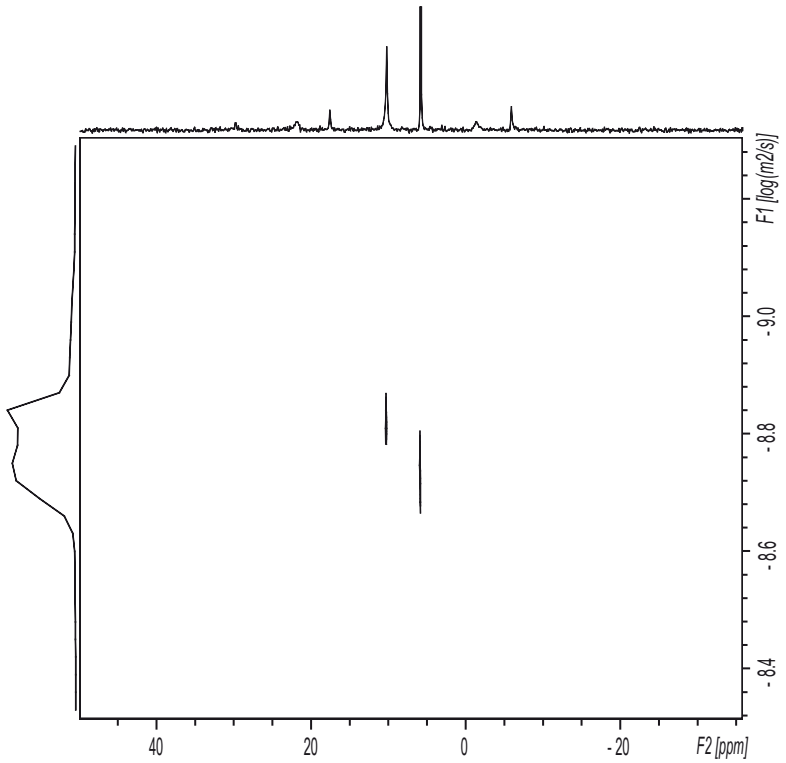


^{1}H DOSY PFG-RMN (400 MHz, rt, $CDCl_3$):

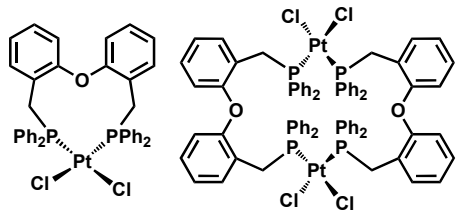




^{31}P{^{1}H} DOSY PFG-RMN (101 MHz, rt, $CDCl_3$):

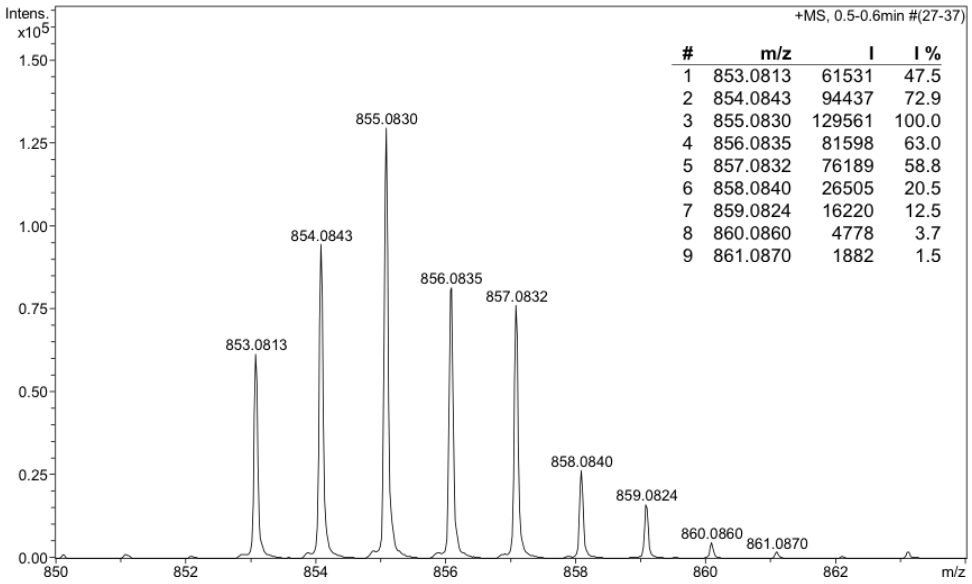


HRMS (ESI+):

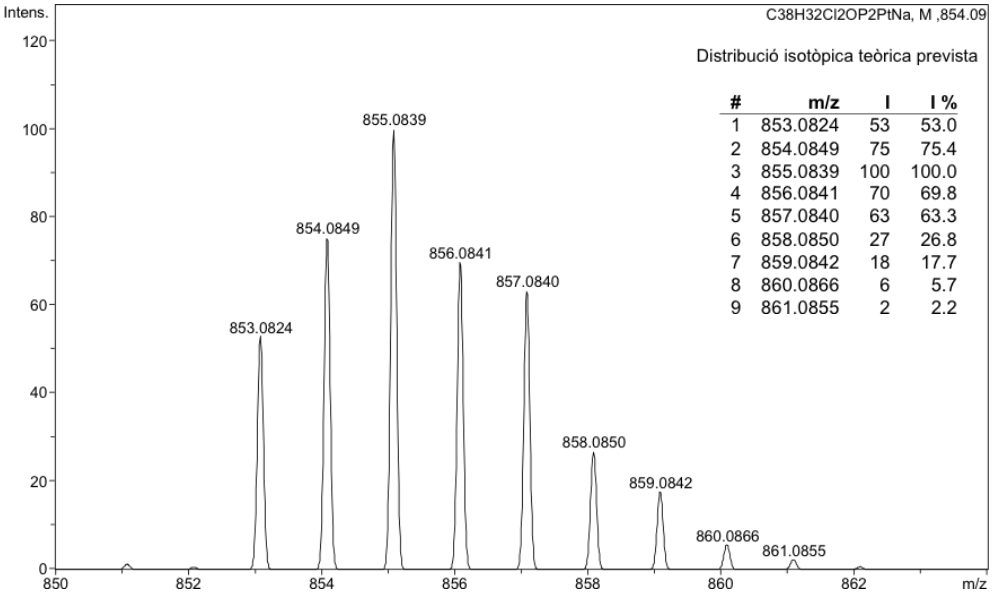


Analysis Info

Analysis Name	d57bPt (8EM-148)_1-B,2_01_251.d	Acquisition Date	27/05/2008 10:58:29
Method	ESIpos250-1300_FI-HS_MeCN_27-5-08.m	Operator	SAQ
Sample Name	d57bPt (8EM-148)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2 ppm en MeCN. // O. VALLCORBA.		

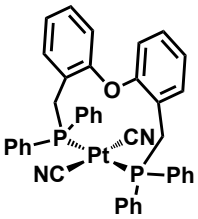


#	m/z	I	I %
1	853.0813	61531	47.5
2	854.0843	94437	72.9
3	855.0830	129561	100.0
4	856.0835	81598	63.0
5	857.0832	76189	58.8
6	858.0840	26505	20.5
7	859.0824	16220	12.5
8	860.0860	4778	3.7
9	861.0870	1882	1.5

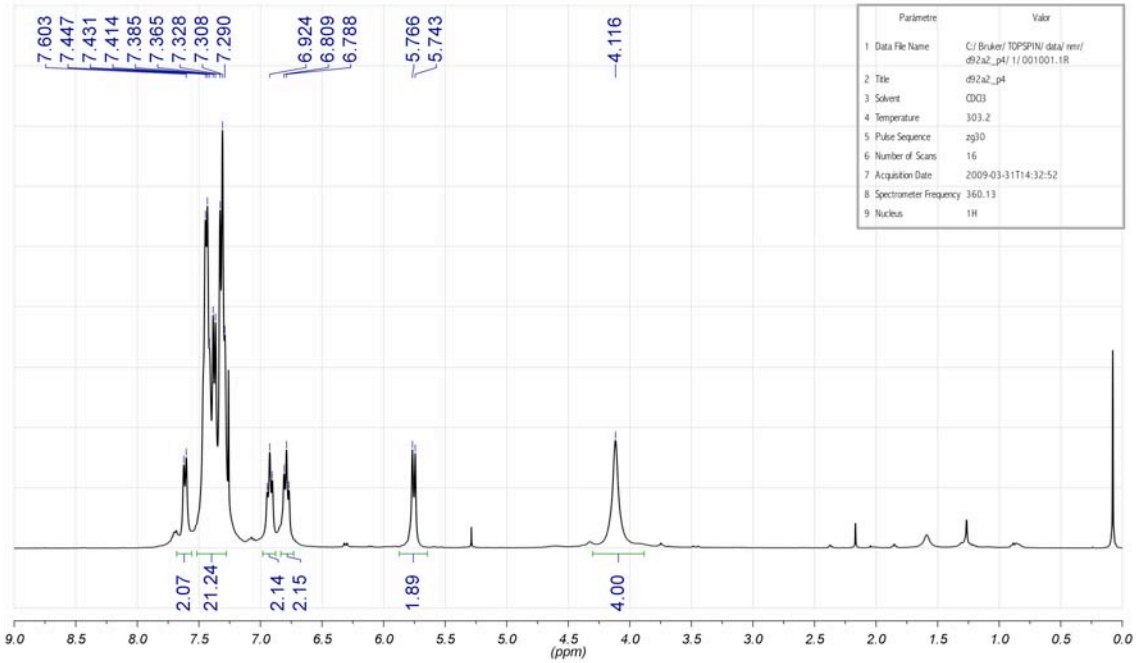


#	m/z	I	I %
1	853.0824	53	53.0
2	854.0849	75	75.4
3	855.0839	100	100.0
4	856.0841	70	69.8
5	857.0840	63	63.3
6	858.0850	27	26.8
7	859.0842	18	17.7
8	860.0866	6	5.7
9	861.0855	2	2.2

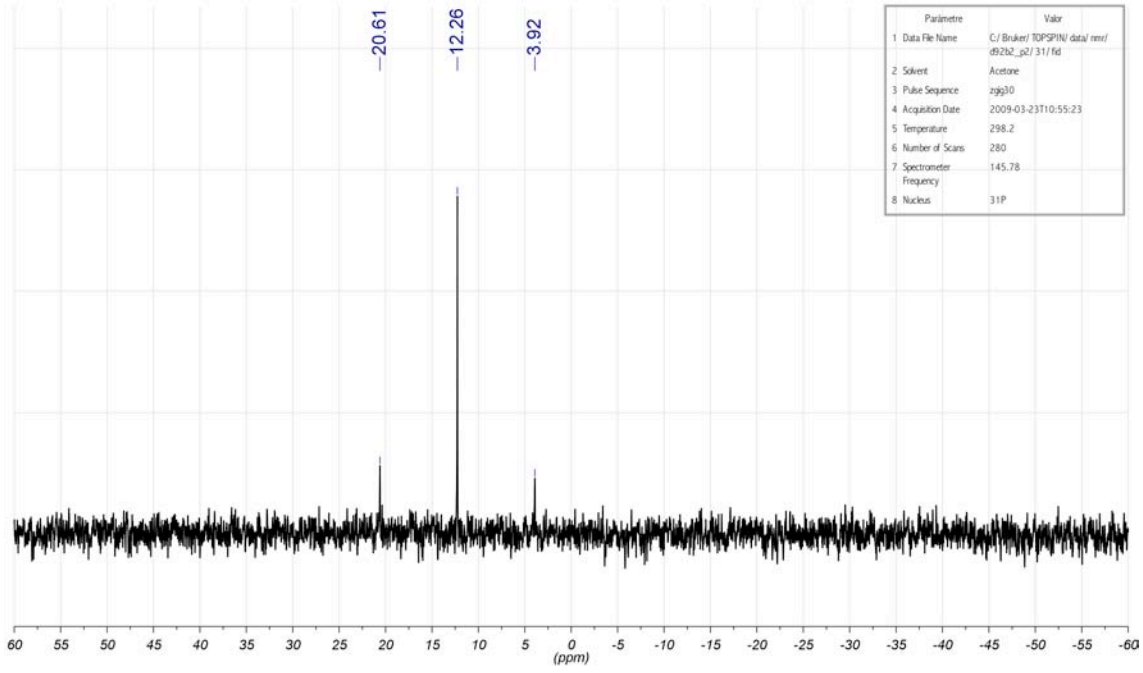
[Pt(CN)$_2$(DPEMephos)] (C35)



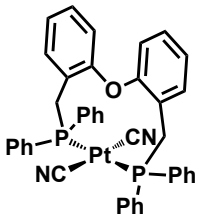
^{1}H RMN (400 MHz, rt, $CDCl_3$):

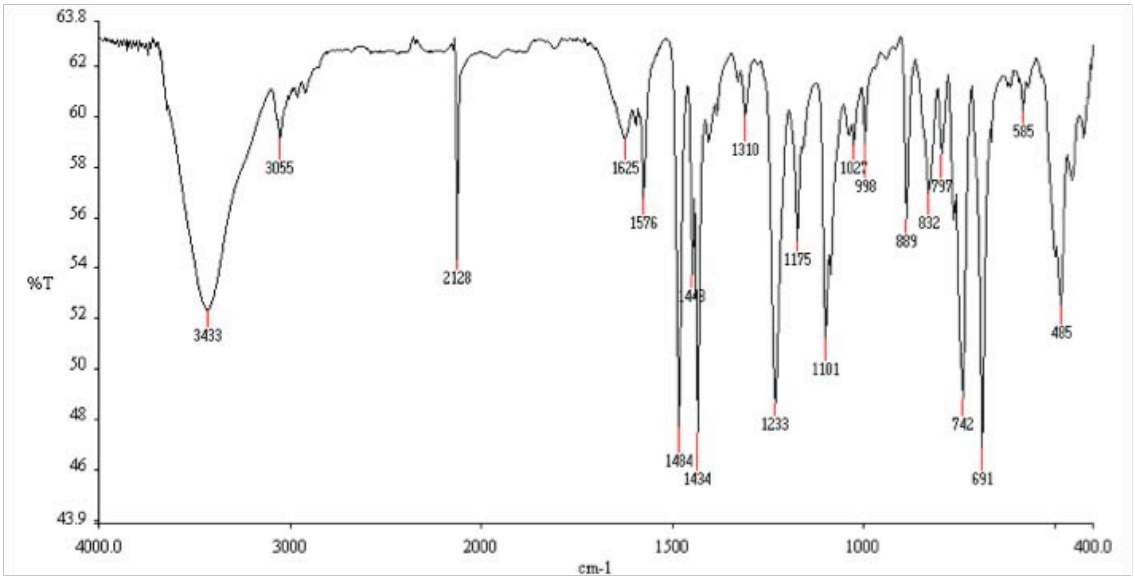


^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

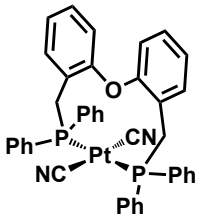


IR (KBr):



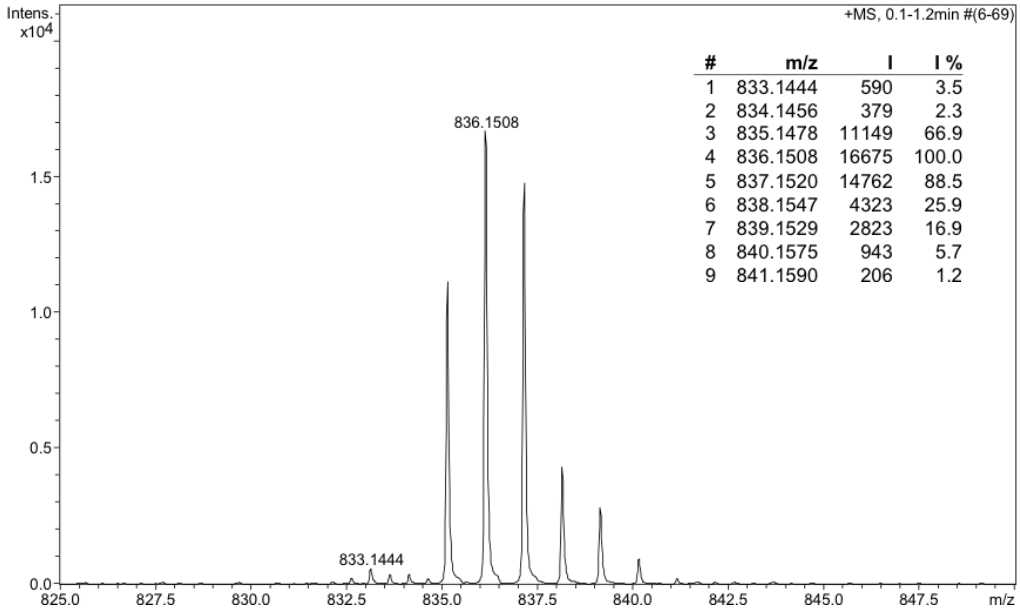


HRMS (ESI+):

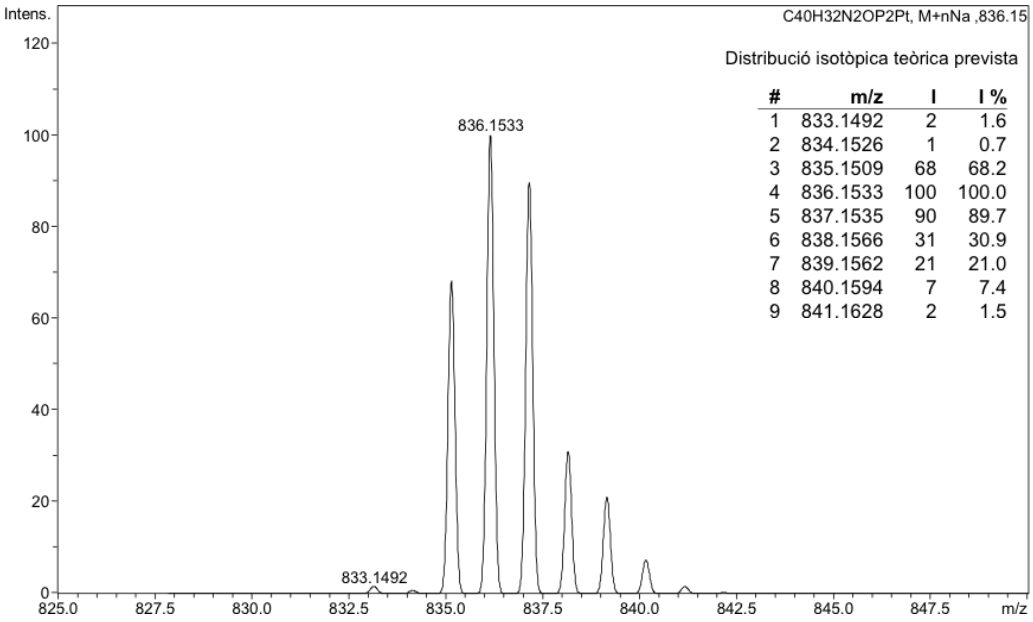


Analysis Info

Analysis Name	09EM208-QTOF-pos1-1.d	Acquisition Date	08/05/2009 11:42:58
Method	09EM208-QTOF-pos1.m	Operator	SAQ
Sample Name	d92b2	Instrument	micrOTOF-Q
Comment	MIE // ESI+ // Dó ca. 15 ppm en CH2Cl2:MeOH (1:5) // ORIOL VALLCORBA		

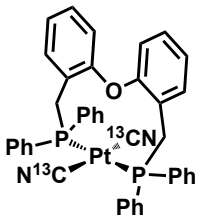


#	m/z	I	I %
1	833.1444	590	3.5
2	834.1456	379	2.3
3	835.1478	11149	66.9
4	836.1508	16675	100.0
5	837.1520	14762	88.5
6	838.1547	4323	25.9
7	839.1529	2823	16.9
8	840.1575	943	5.7
9	841.1590	206	1.2

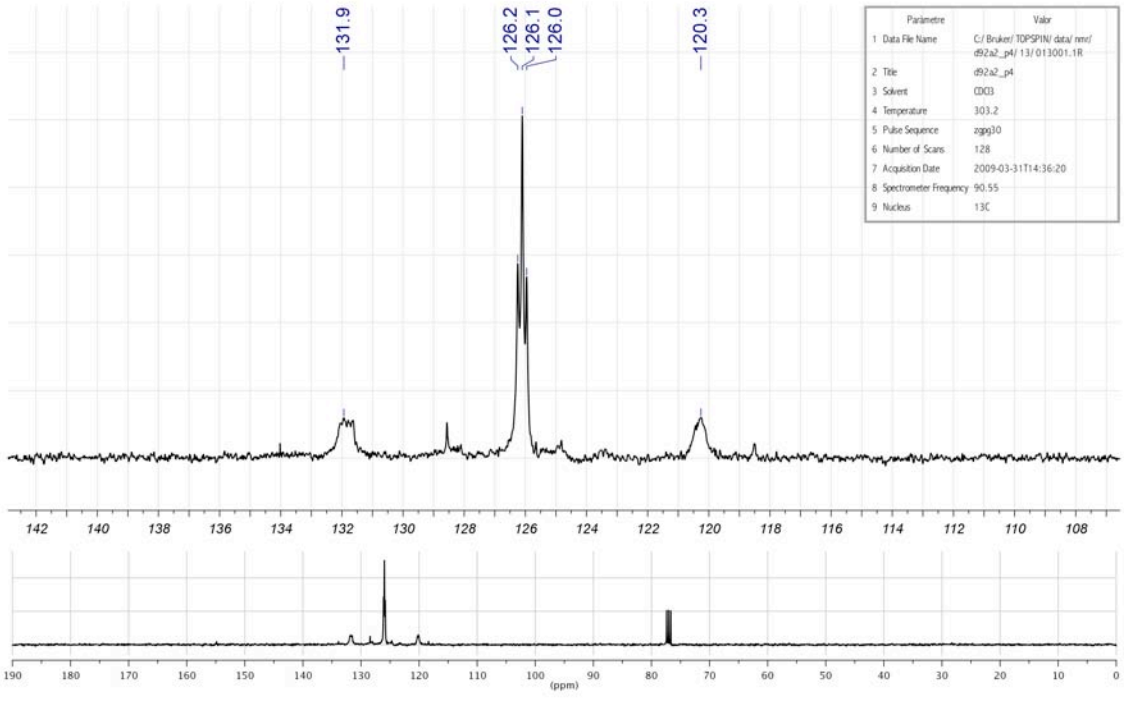


#	m/z	I	I %
1	833.1492	2	1.6
2	834.1526	1	0.7
3	835.1509	68	68.2
4	836.1533	100	100.0
5	837.1535	90	89.7
6	838.1566	31	30.9
7	839.1562	21	21.0
8	840.1594	7	7.4
9	841.1628	2	1.5

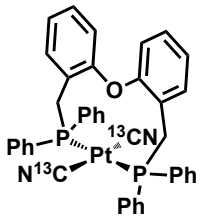
[Pt(^{13}CN)$_2$(DPEMephos)] (C35m)

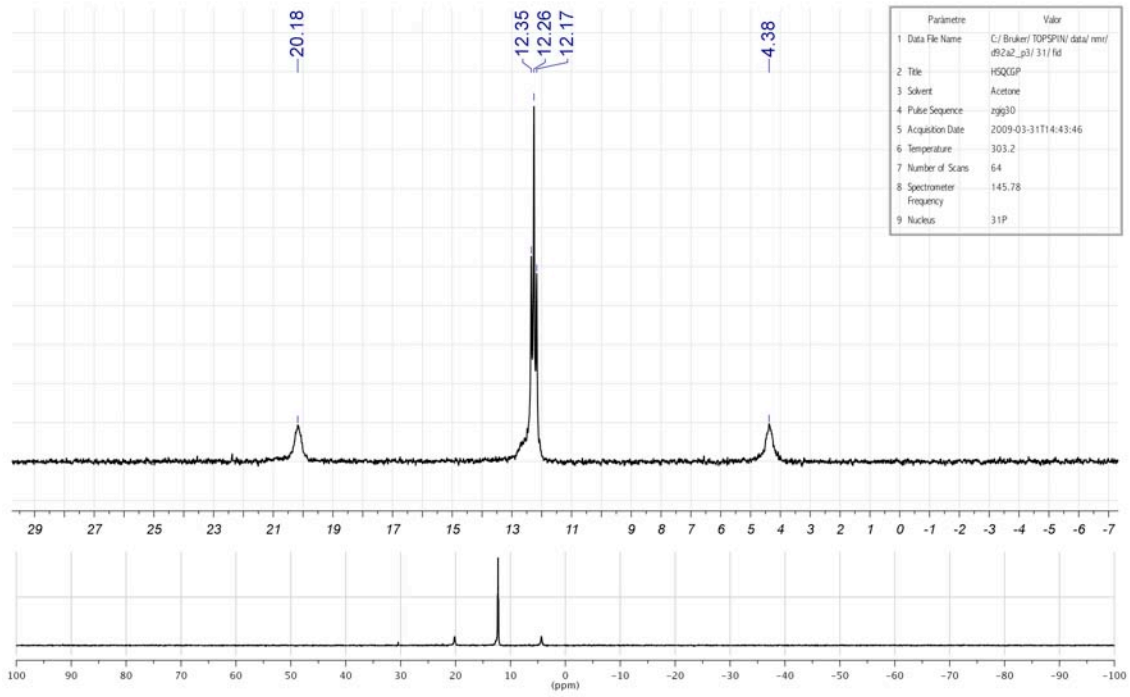


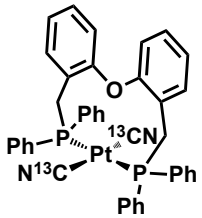
^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):



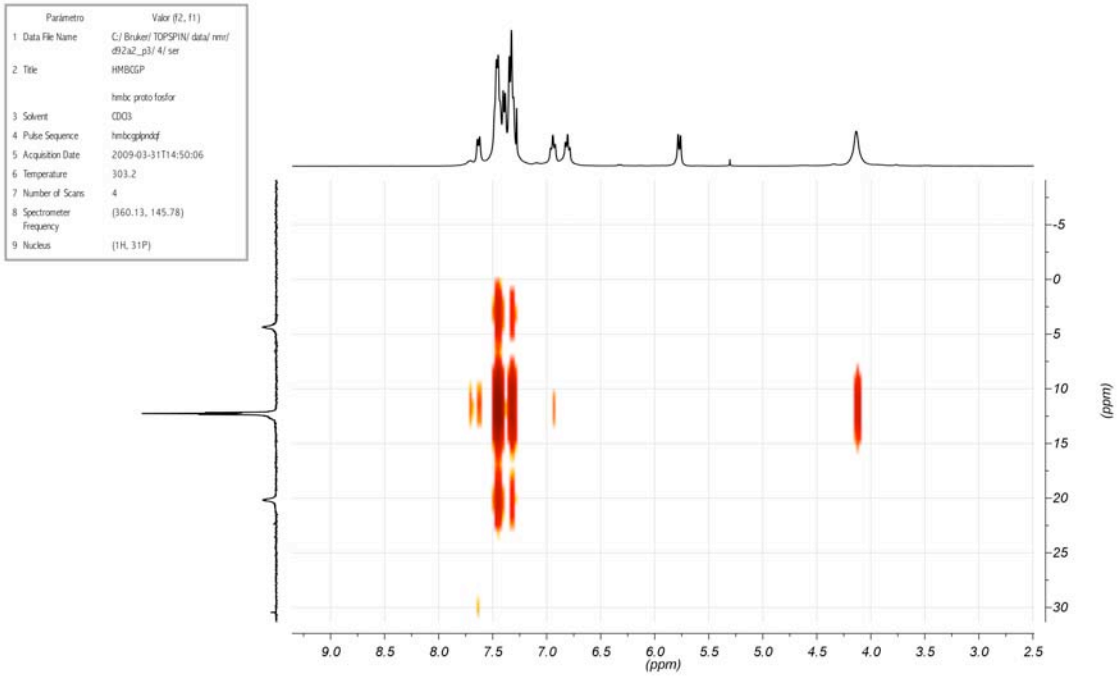
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):



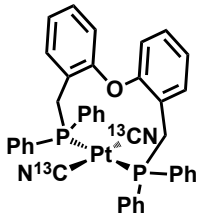


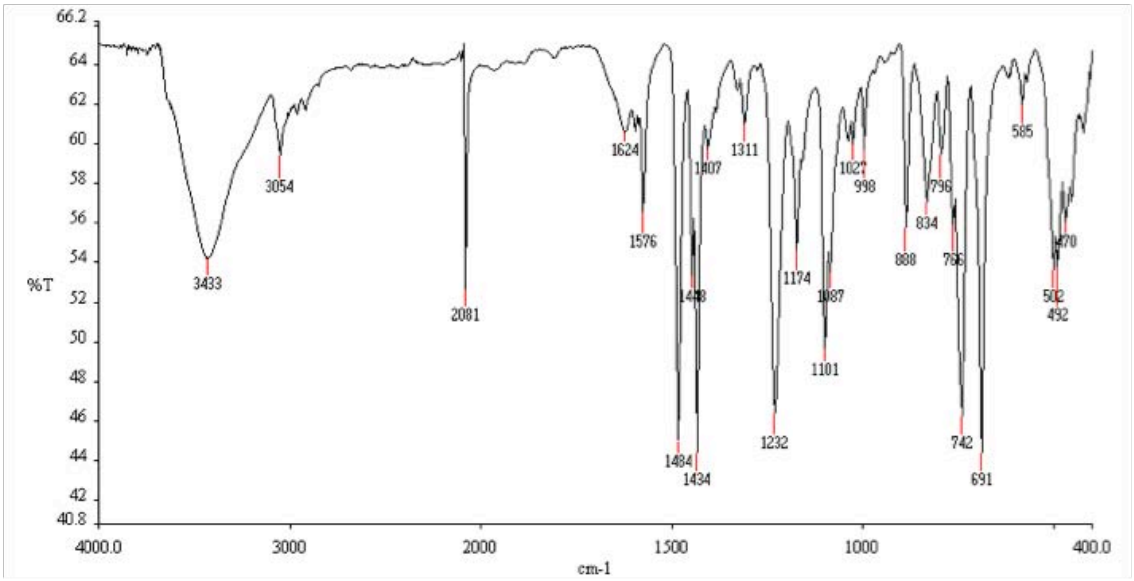


Espectre de correlació ^{1}H-^{31}P (HMBC):

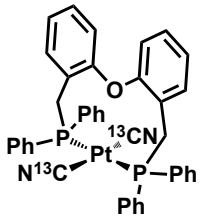


IR (KBr):



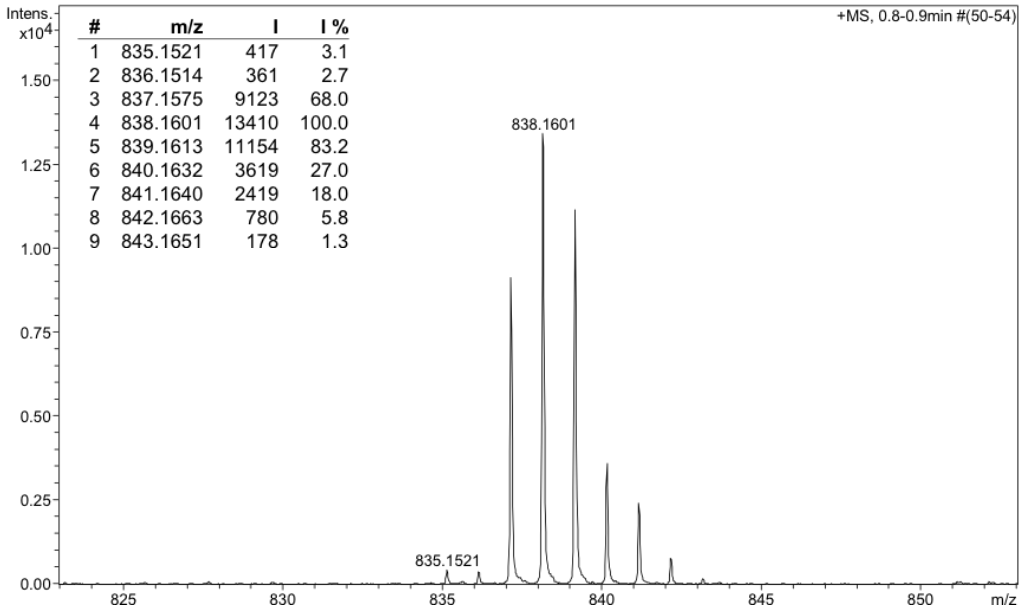


HRMS (ESI+):

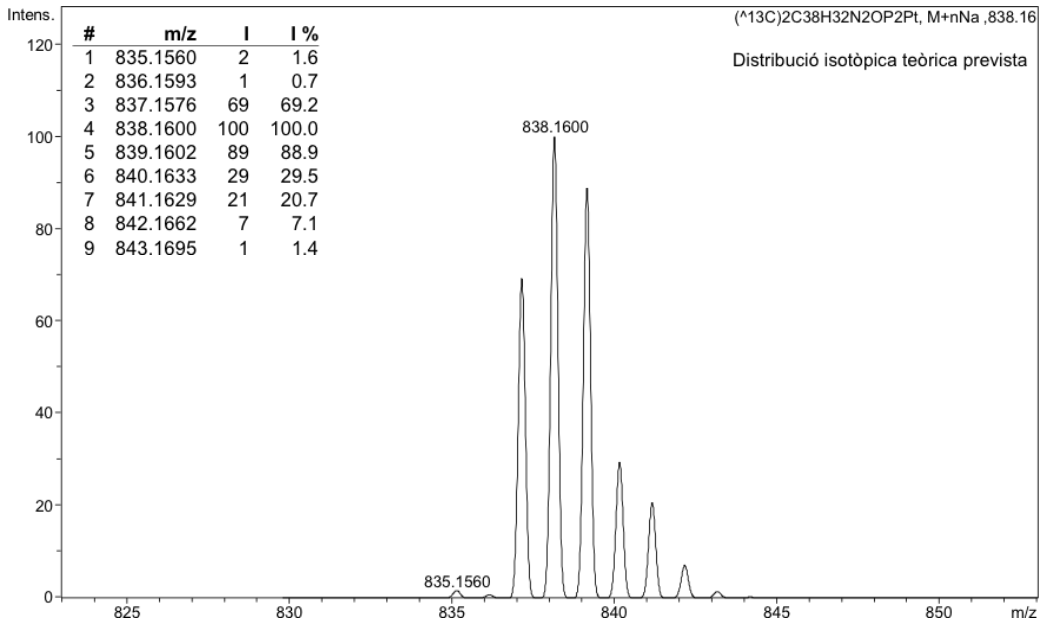


Analysis Info

Analysis Name	09EM209-QTOF-pos1-1.d	Acquisition Date	08/05/2009 12:31:43
Method	09EM209-QTOF-pos1.m	Operator	SAQ
Sample Name	d92a2	Instrument	micrOTOF-Q
Comment	MIE // ESI+ // Dó ca. 15 ppm en CH2Cl2:MeOH (1:5) // ORIOL VALLCORBA		

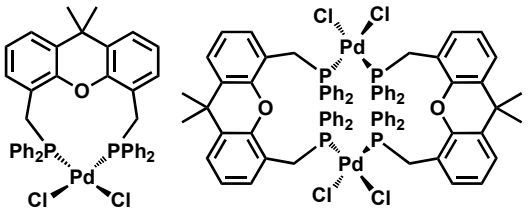


#	m/z	I	I %
1	835.1521	417	3.1
2	836.1514	361	2.7
3	837.1575	9123	68.0
4	838.1601	13410	100.0
5	839.1613	11154	83.2
6	840.1632	3619	27.0
7	841.1640	2419	18.0
8	842.1663	780	5.8
9	843.1651	178	1.3



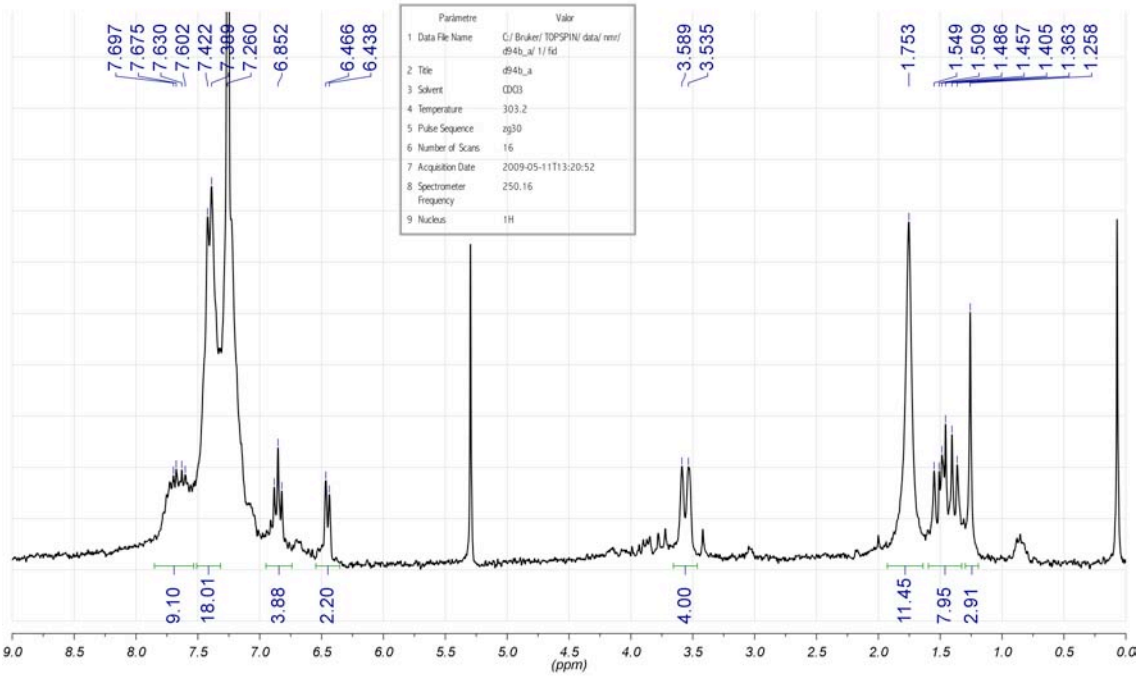
#	m/z	I	I %
1	835.1560	2	1.6
2	836.1593	1	0.7
3	837.1576	69	69.2
4	838.1600	100	100.0
5	839.1602	89	88.9
6	840.1633	29	29.5
7	841.1629	21	20.7
8	842.1662	7	7.1
9	843.1695	1	1.4

11.2 XantMephos amb Pd i Pt

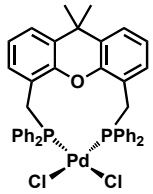


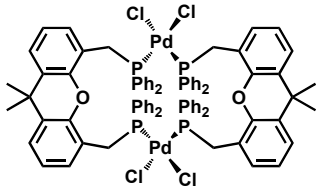
[PdCl₂(XantMephos)] (C36)

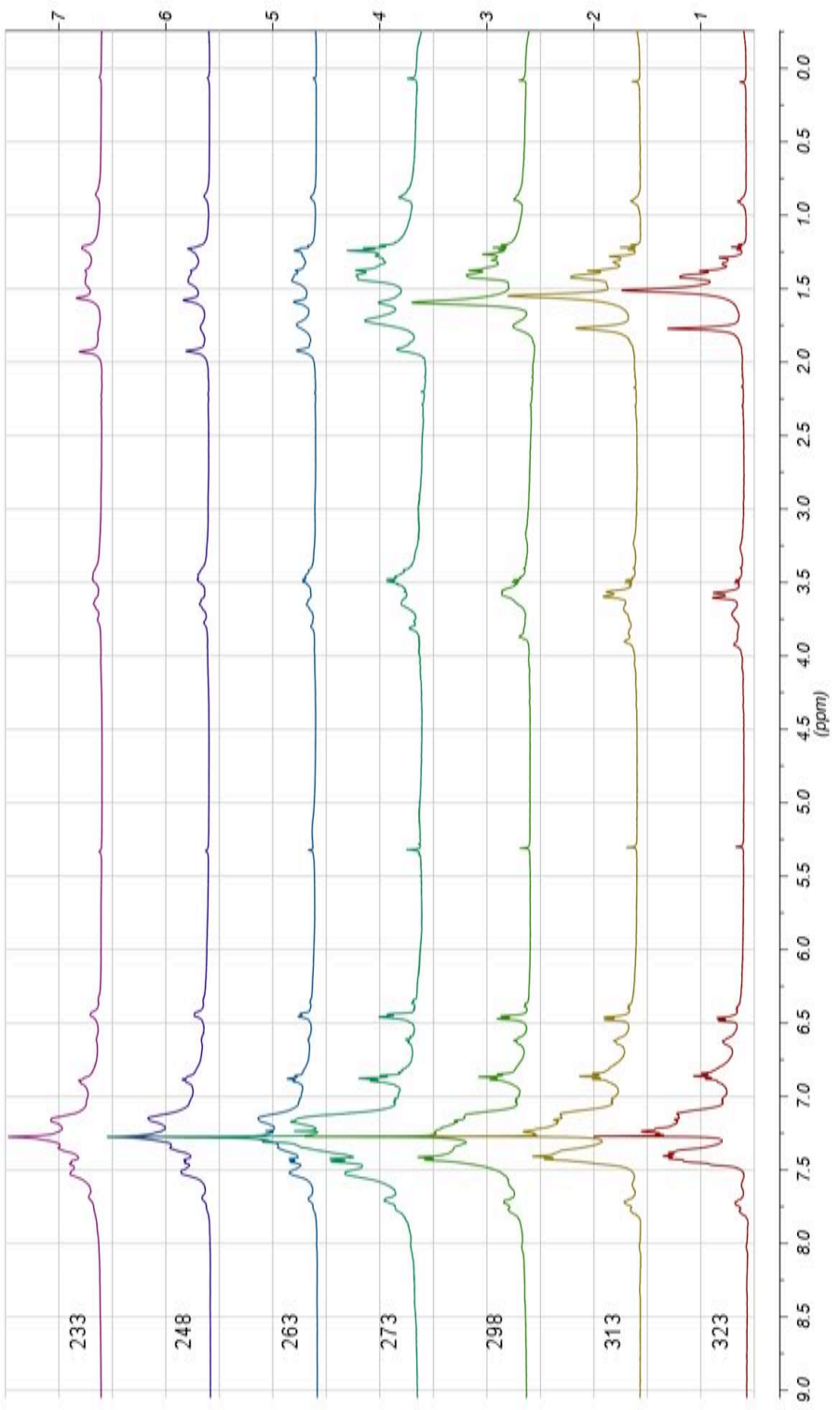
^{1}H RMN (400 MHz, rt, $CDCl_3$):



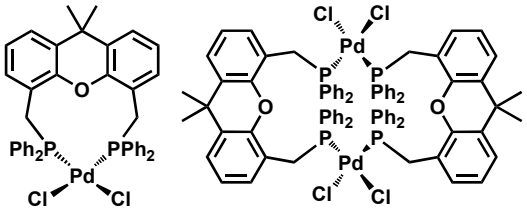
^{1}H RMN (400 MHz, temperatura variable, $CDCl_3$):

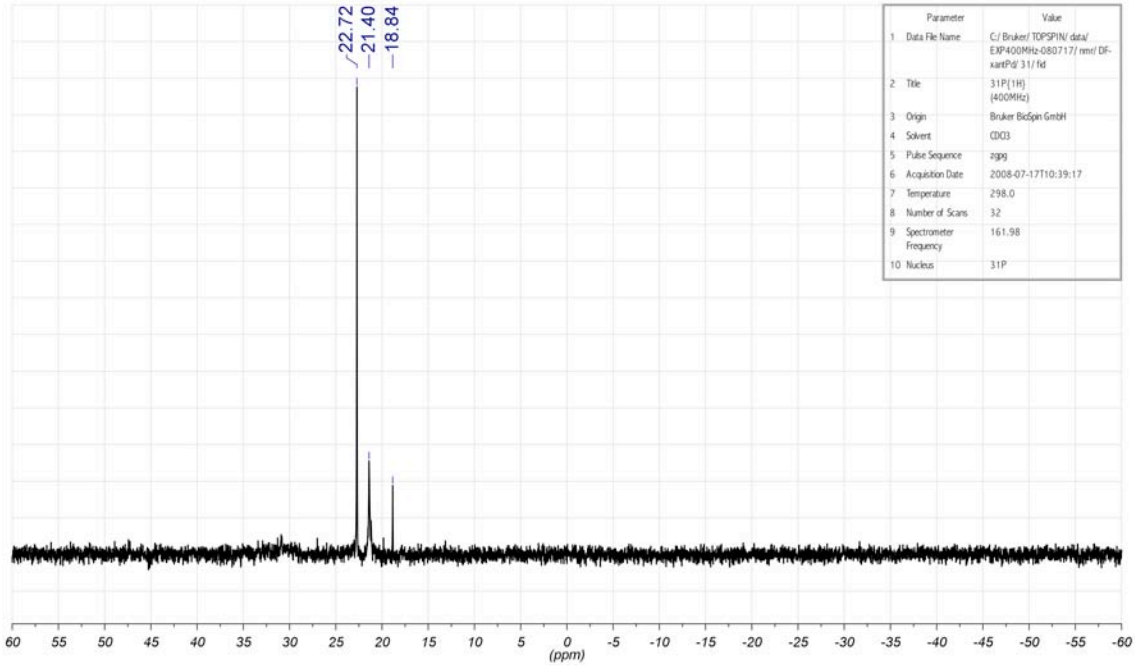




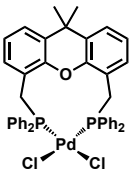


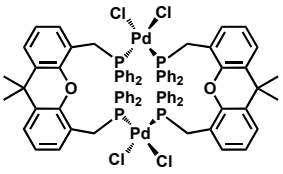
$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

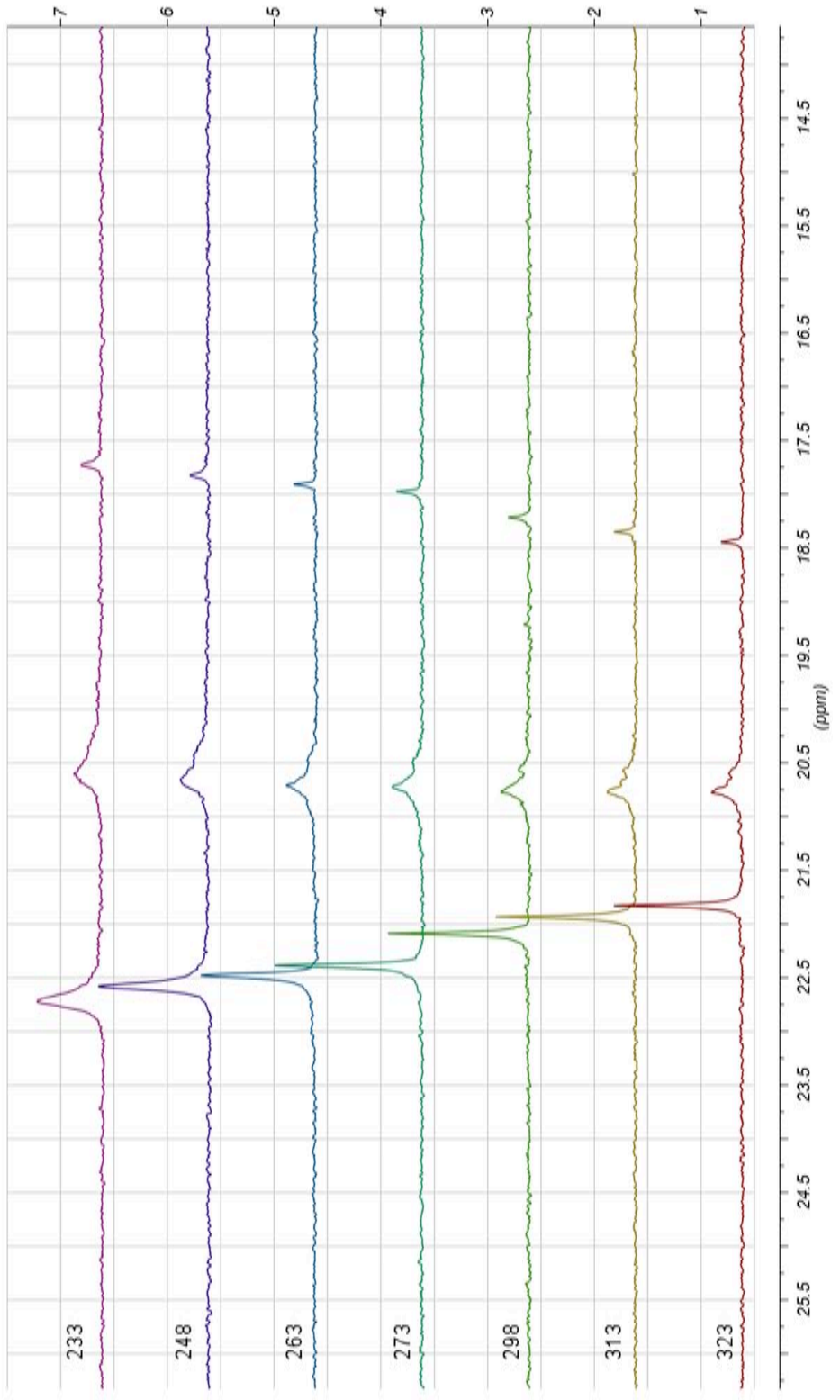




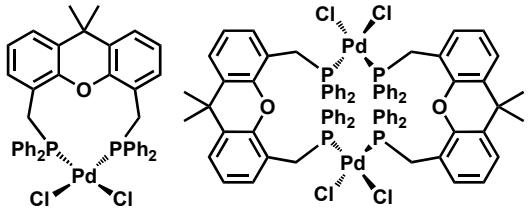
$^{31}P\{^{1}H\}$ RMN (162 MHz, temperatura variable, $CDCl_3$):





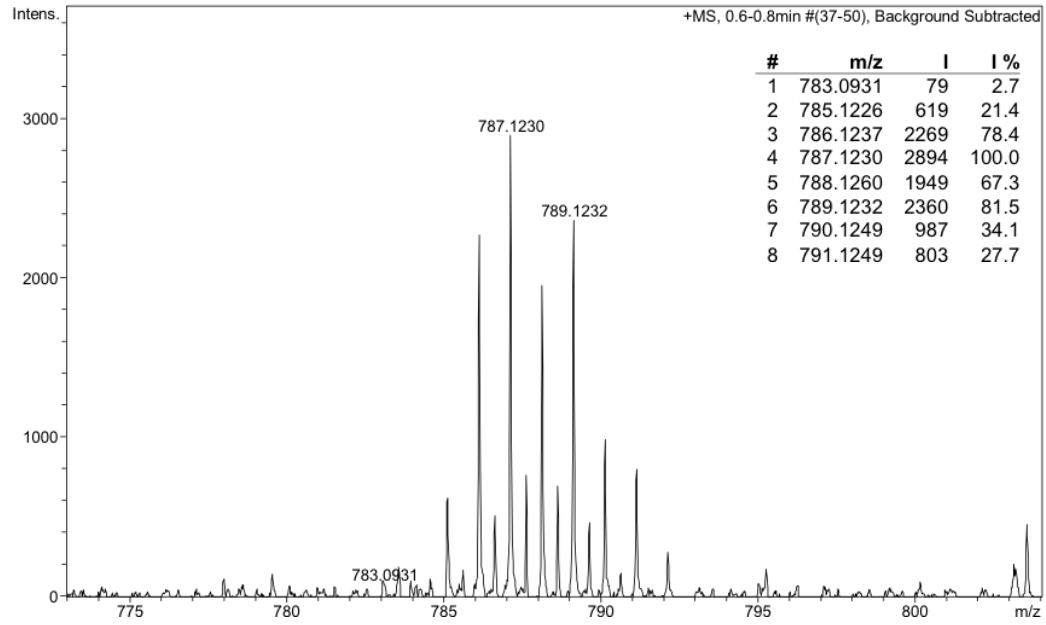


HRMS (ESI+):

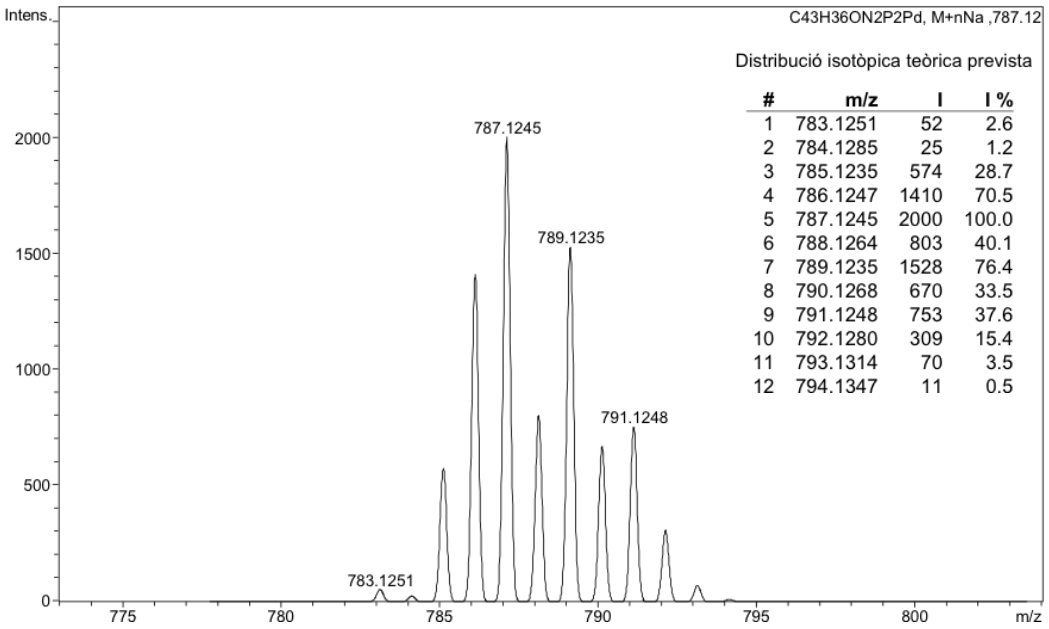


Analysis Info

Analysis Name	d65aPd (8EM-149)_1-B,3_01_252.d	Acquisition Date	27/05/2008 11:05:17
Method	ESIpos250-1300_FI-HS_MeCN_27-5-08.m	Operator	SAQ
Sample Name	d65aPd (8EM-149)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2 ppm en MeCN. // O. VALLCORBA.		



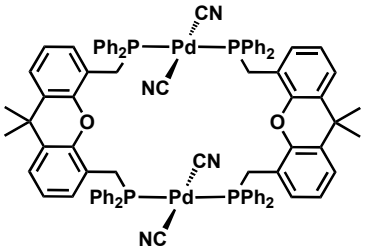
#	m/z	I	I %
1	783.0931	79	2.7
2	785.1226	619	21.4
3	786.1237	2269	78.4
4	787.1230	2894	100.0
5	788.1260	1949	67.3
6	789.1232	2360	81.5
7	790.1249	987	34.1
8	791.1249	803	27.7



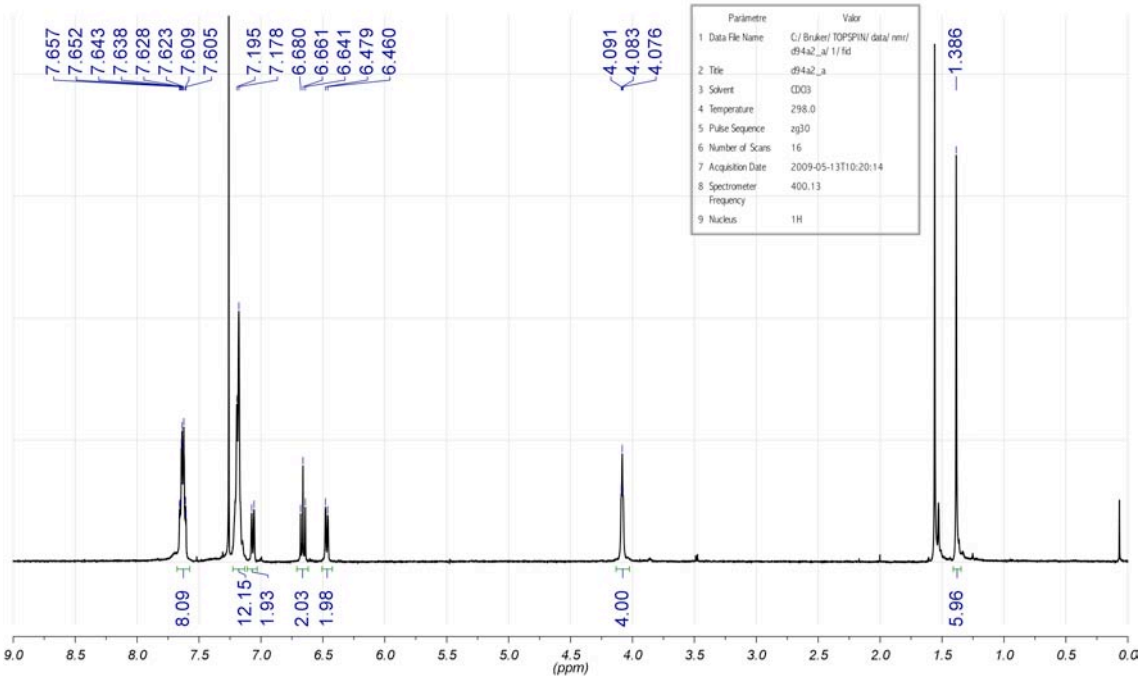
Distribució isotòpica teòrica prevista

#	m/z	I	I %
1	783.1251	52	2.6
2	784.1285	25	1.2
3	785.1235	574	28.7
4	786.1247	1410	70.5
5	787.1245	2000	100.0
6	788.1264	803	40.1
7	789.1235	1528	76.4
8	790.1268	670	33.5
9	791.1248	753	37.6
10	792.1280	309	15.4
11	793.1314	70	3.5
12	794.1347	11	0.5

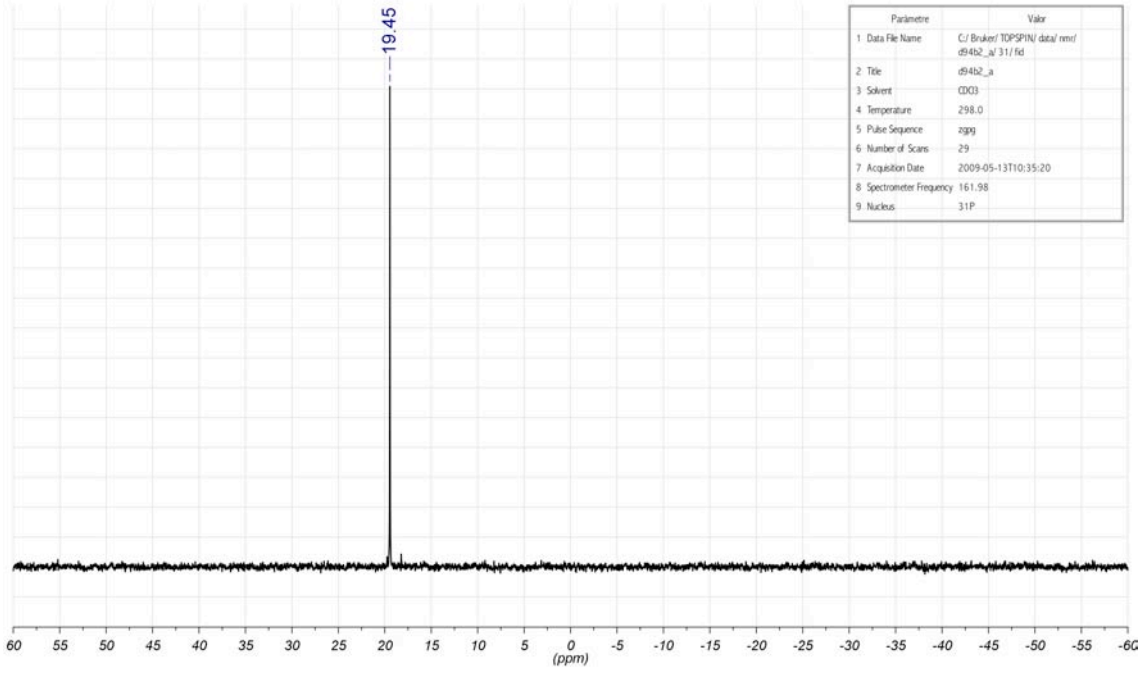
[Pd(CN)$_2$(XantMephos)] (C38)



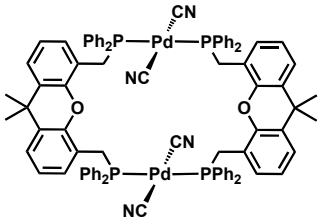
^{1}H RMN (400 MHz, rt, $CDCl_3$):

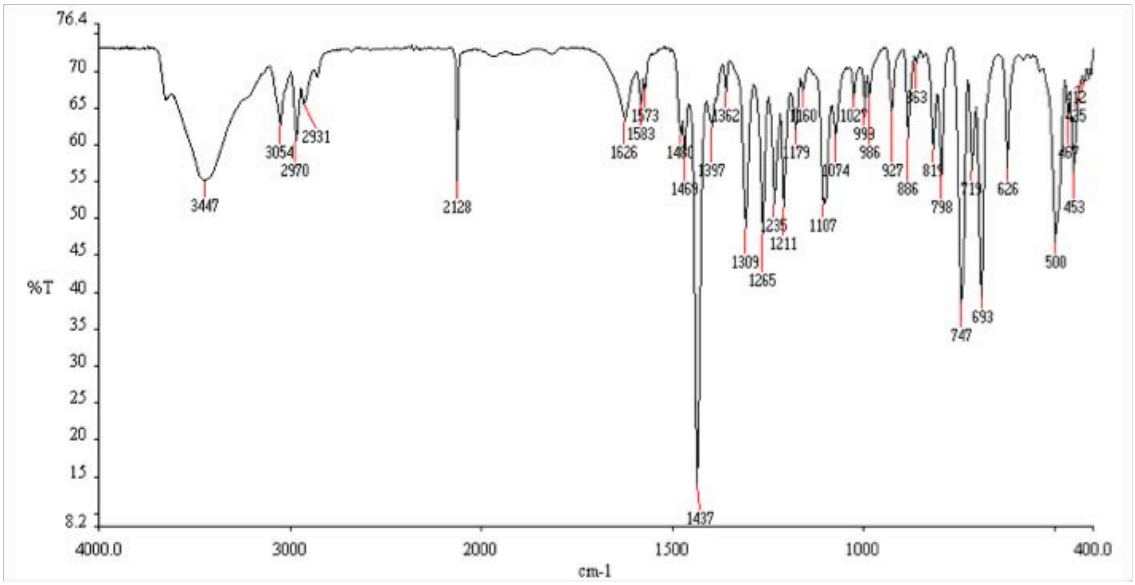


^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

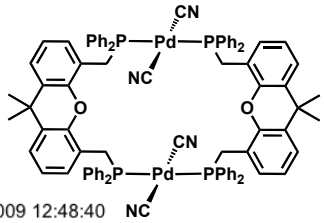


IR (KBr):



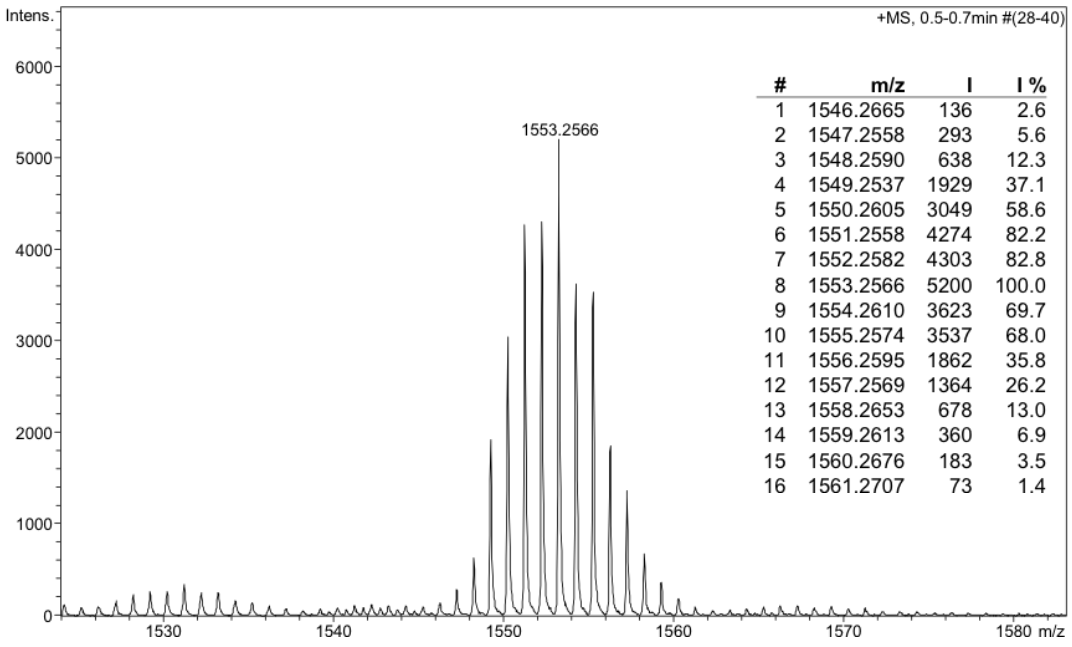


HRMS (ESI+):

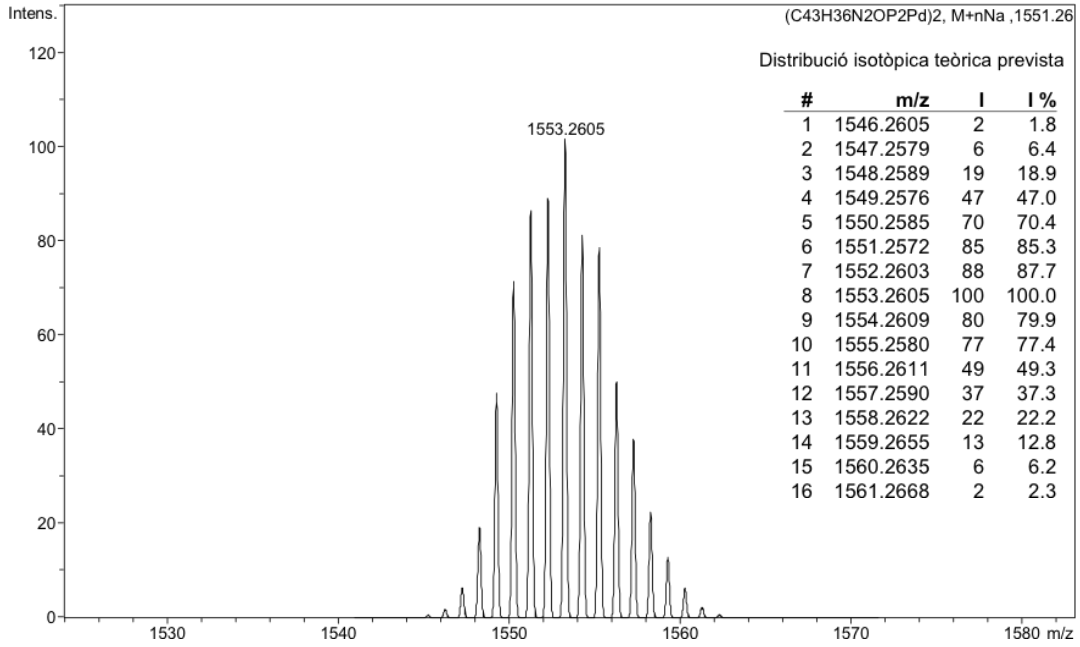


Analysis Info

Analysis Name	09EM343 (d94b)_1-c,2_01_3275.d	Acquisition Date	29/07/2009 12:48:40
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM343 (d94b)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca. 10 ppm en CH2Cl2:MeOH (1:3) ORIOL VALLCORBA		

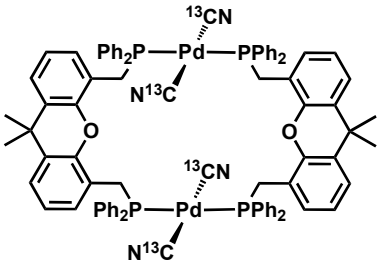


#	m/z	I	I %
1	1546.2665	136	2.6
2	1547.2558	293	5.6
3	1548.2590	638	12.3
4	1549.2537	1929	37.1
5	1550.2605	3049	58.6
6	1551.2558	4274	82.2
7	1552.2582	4303	82.8
8	1553.2566	5200	100.0
9	1554.2610	3623	69.7
10	1555.2574	3537	68.0
11	1556.2595	1862	35.8
12	1557.2569	1364	26.2
13	1558.2653	678	13.0
14	1559.2613	360	6.9
15	1560.2676	183	3.5
16	1561.2707	73	1.4

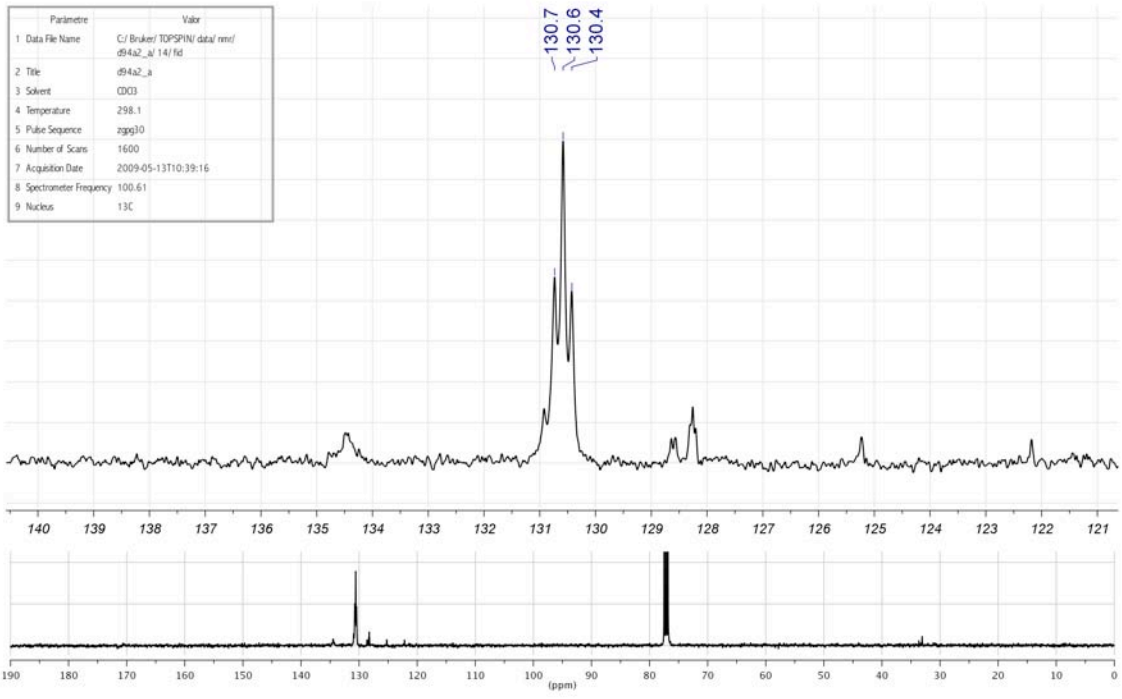


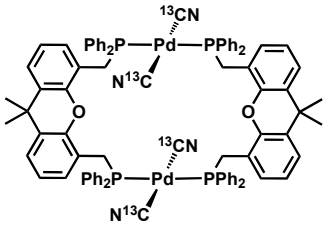
#	m/z	I	I %
1	1546.2605	2	1.8
2	1547.2579	6	6.4
3	1548.2589	19	18.9
4	1549.2576	47	47.0
5	1550.2585	70	70.4
6	1551.2572	85	85.3
7	1552.2603	88	87.7
8	1553.2605	100	100.0
9	1554.2609	80	79.9
10	1555.2580	77	77.4
11	1556.2611	49	49.3
12	1557.2590	37	37.3
13	1558.2622	22	22.2
14	1559.2655	13	12.8
15	1560.2635	6	6.2
16	1561.2668	2	2.3

[Pd(^{13}CN)$_2$(XantMephos)] **(C38m)**

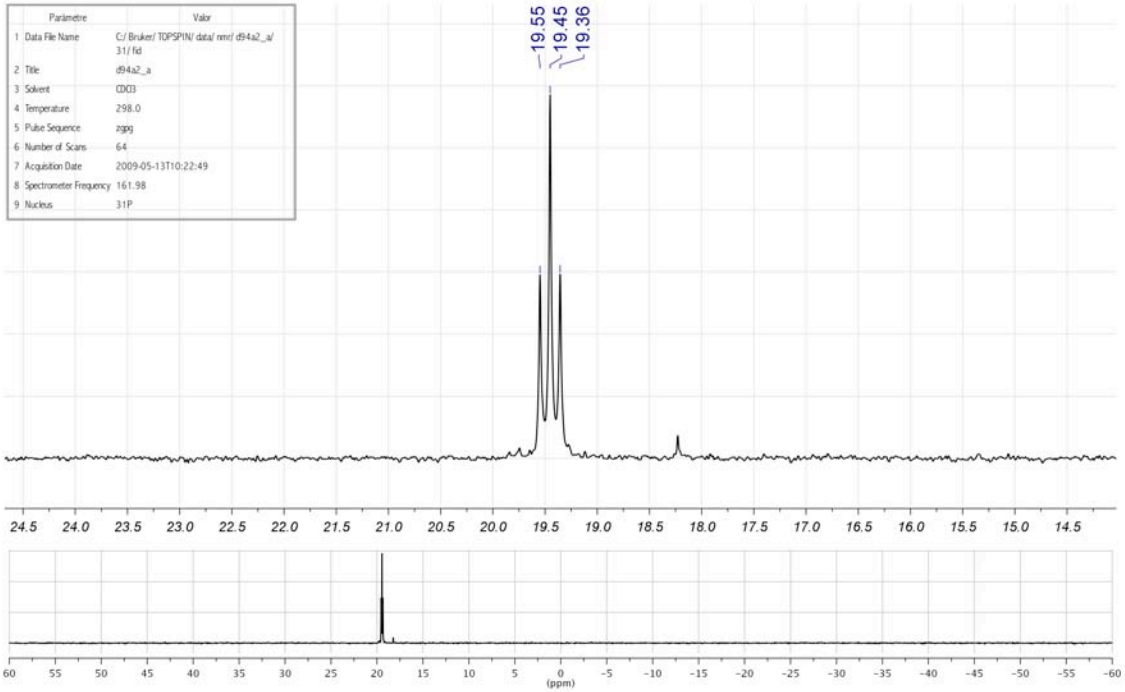


$^{13}C\{^{1}H\}$ RMN (101 MHz, rt, $CDCl_3$):

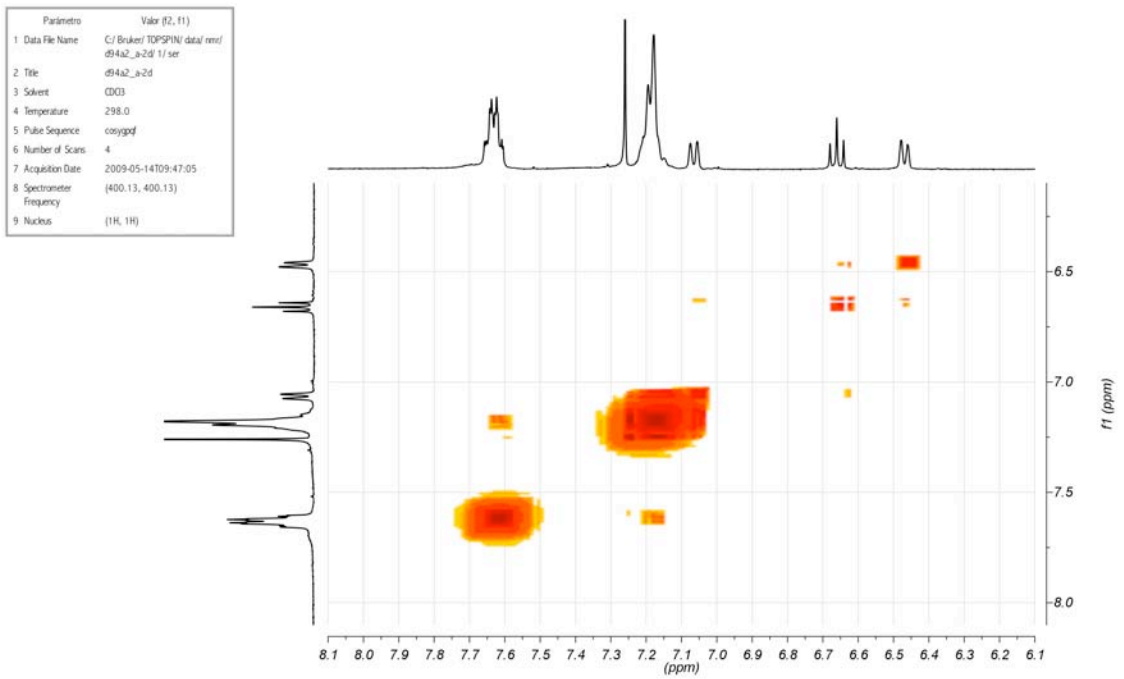


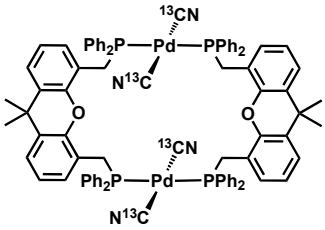


$^{31}P\{^{1}H\}$ RMN (162 MHz, rt, $CDCl_3$):

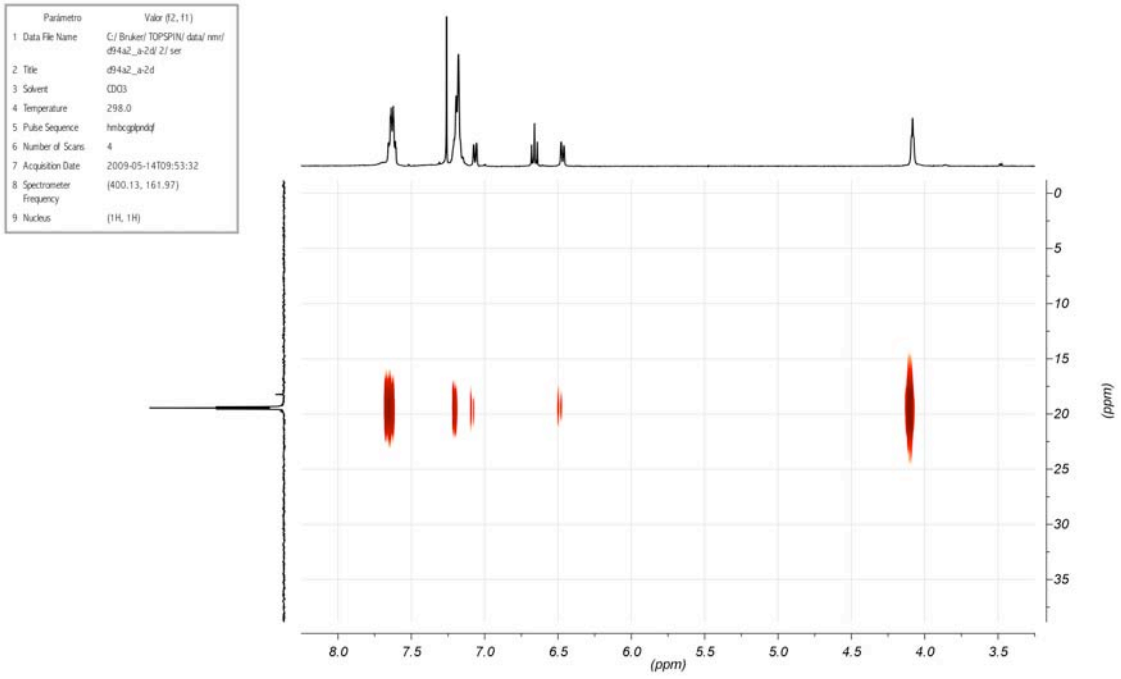


Espectre de correlació ^{1}H-^{1}H (COSY):

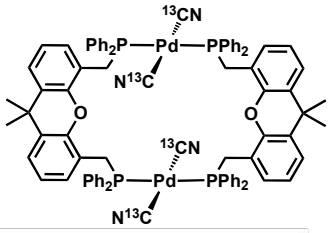


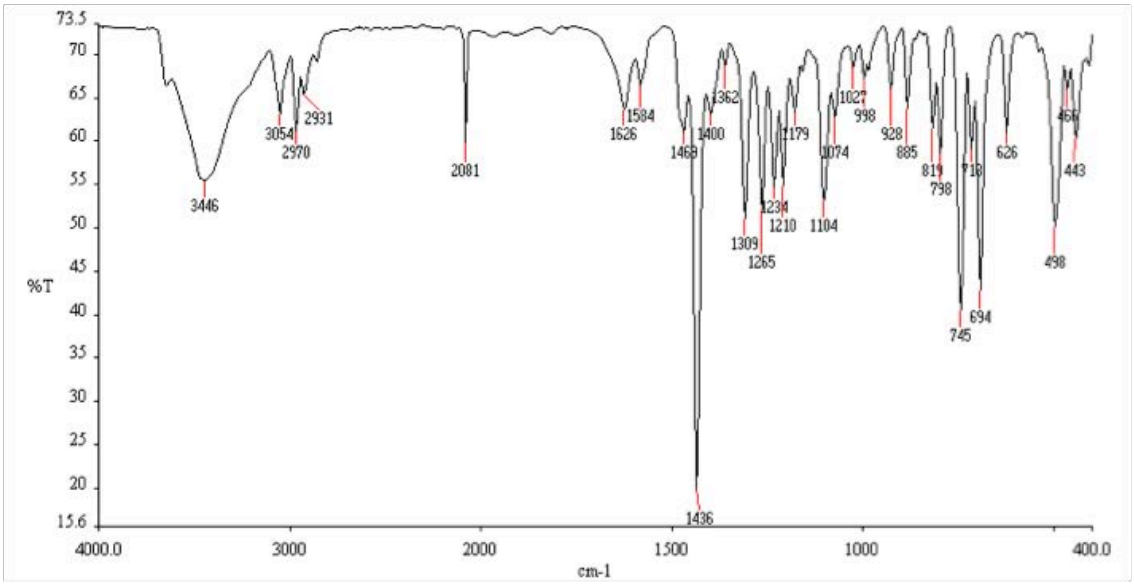


Espectre de correlació ^{1}H-^{31}P (HMBC):

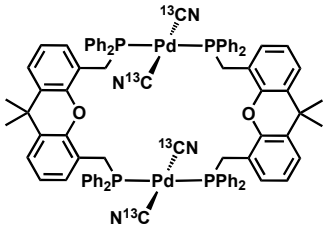


IR (KBr):



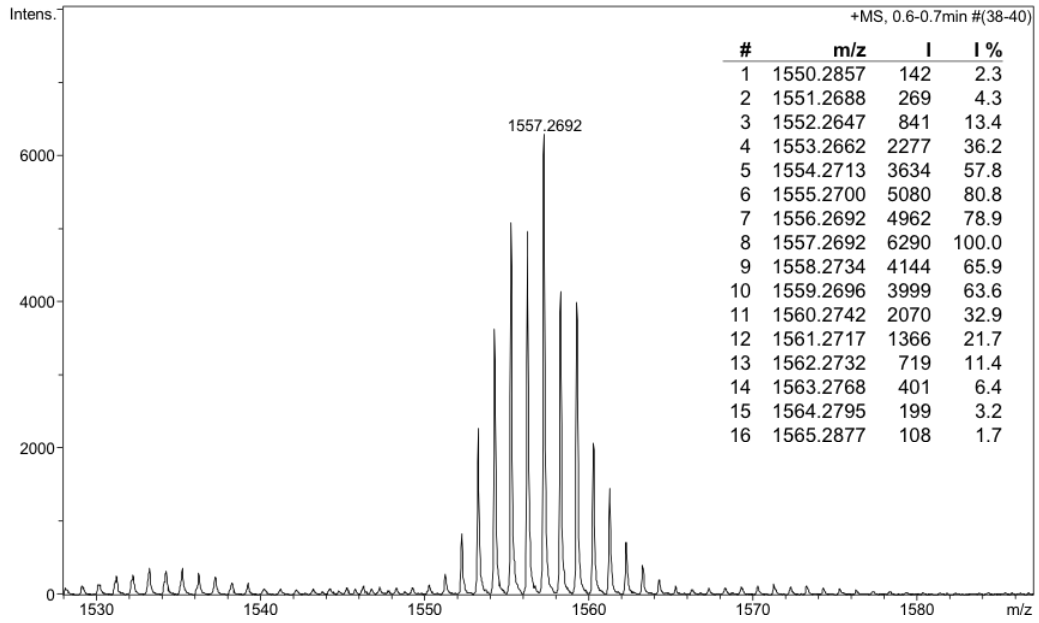


HRMS (ESI+):

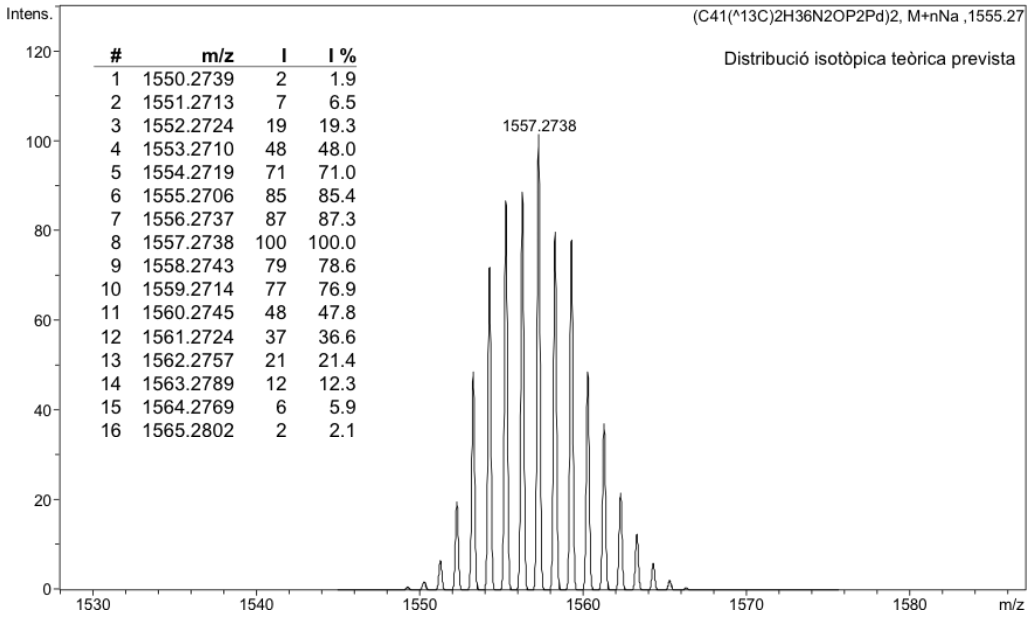


Analysis Info

Analysis Name	09EM342 (d94a)_1-c,1_01_3274.d	Acquisition Date	29/07/2009 12:41:56
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM342 (d94a)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca. 10 ppm en CH2Cl2:MeOH (1:9) ORIOL VALLCORBA		

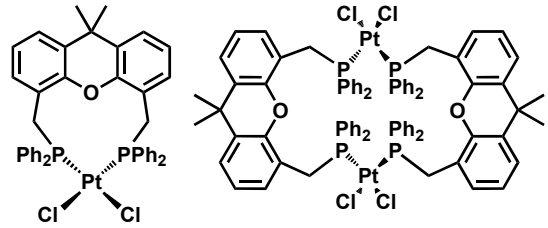


#	m/z	I	I %
1	1550.2857	142	2.3
2	1551.2688	269	4.3
3	1552.2647	841	13.4
4	1553.2662	2277	36.2
5	1554.2713	3634	57.8
6	1555.2700	5080	80.8
7	1556.2692	4962	78.9
8	1557.2692	6290	100.0
9	1558.2734	4144	65.9
10	1559.2696	3999	63.6
11	1560.2742	2070	32.9
12	1561.2717	1366	21.7
13	1562.2732	719	11.4
14	1563.2768	401	6.4
15	1564.2795	199	3.2
16	1565.2877	108	1.7

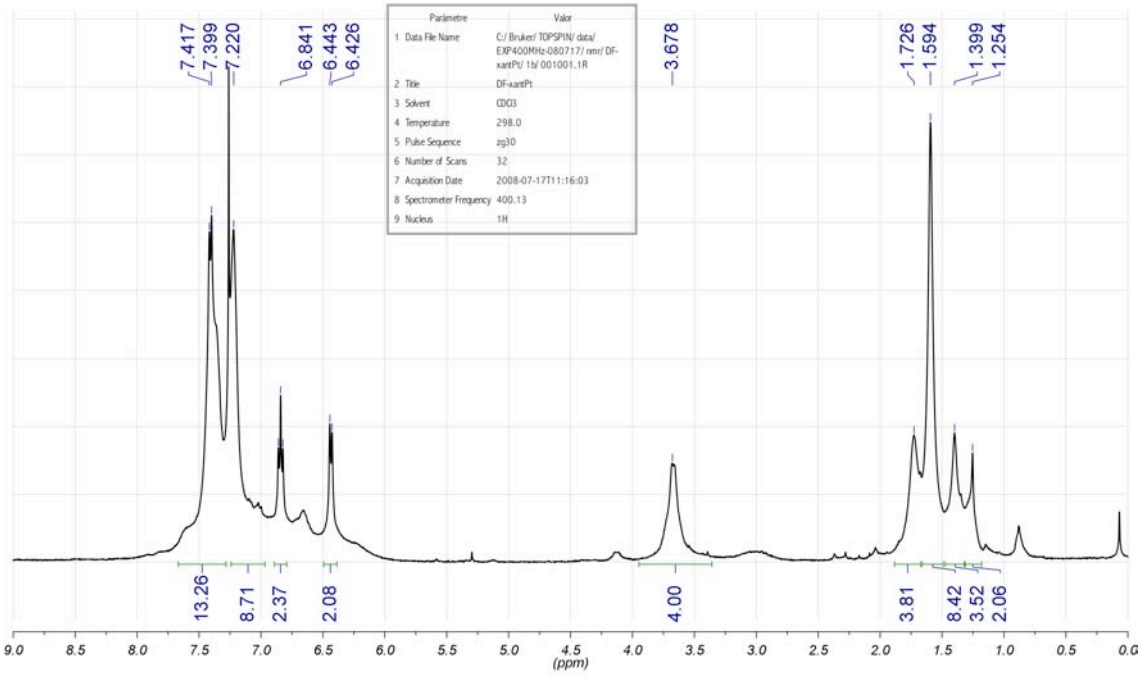


#	m/z	I	I %
1	1550.2739	2	1.9
2	1551.2713	7	6.5
3	1552.2724	19	19.3
4	1553.2710	48	48.0
5	1554.2719	71	71.0
6	1555.2706	85	85.4
7	1556.2737	87	87.3
8	1557.2738	100	100.0
9	1558.2743	79	78.6
10	1559.2714	77	76.9
11	1560.2745	48	47.8
12	1561.2724	37	36.6
13	1562.2757	21	21.4
14	1563.2789	12	12.3
15	1564.2769	6	5.9
16	1565.2802	2	2.1

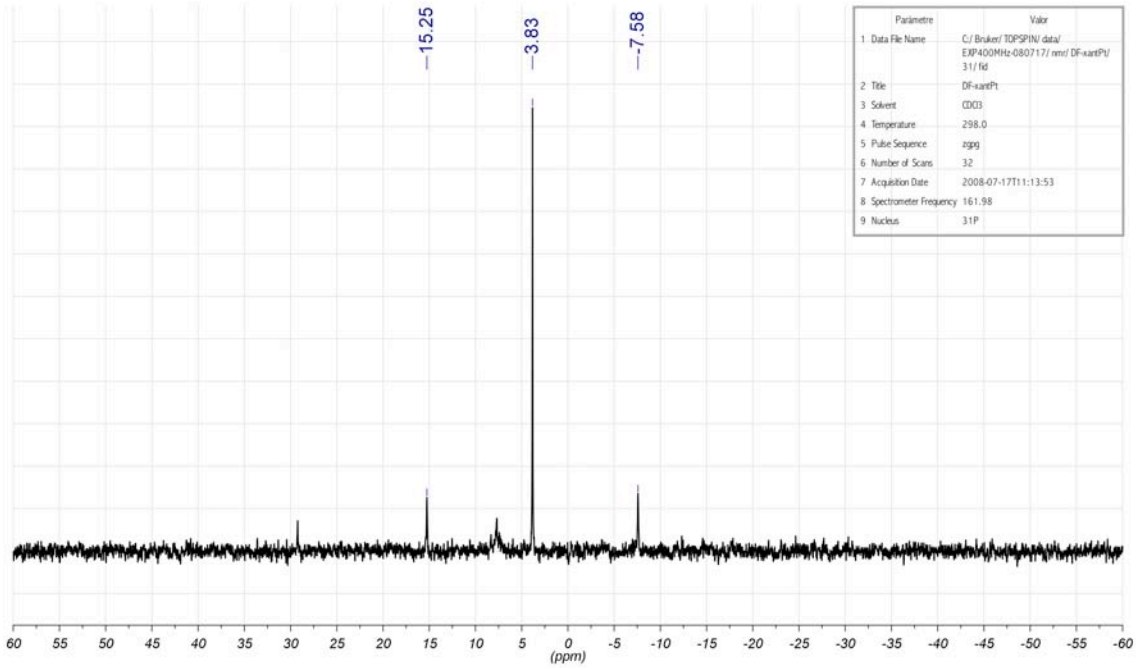
[PtCl$_2$(XantMephos)] (C37)



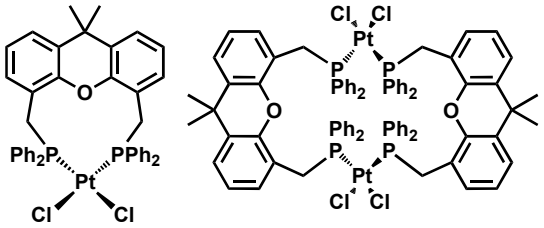
^{1}H RMN (400 MHz, rt, $CDCl_3$):



^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

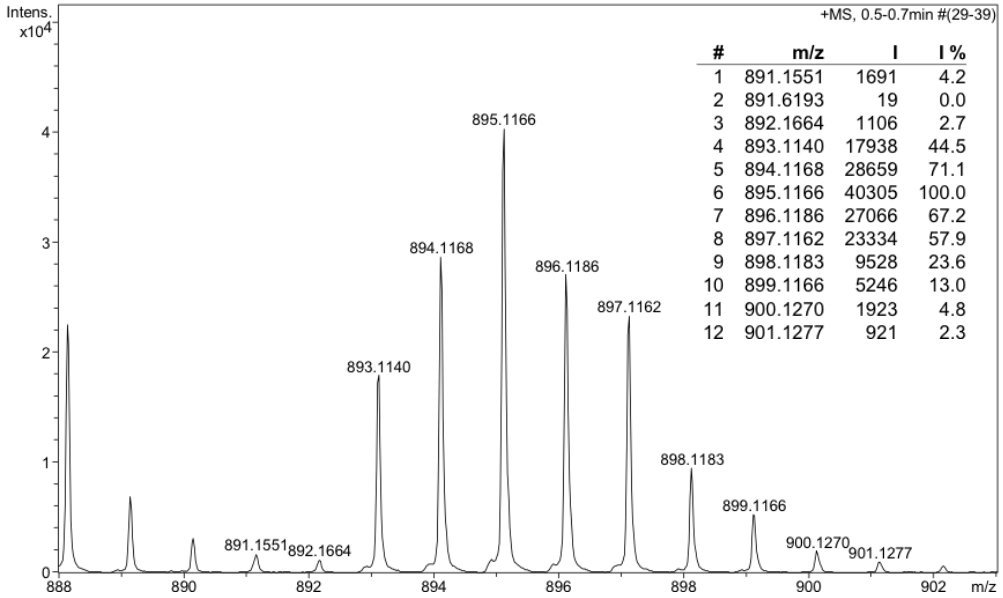


HRMS (ESI+):

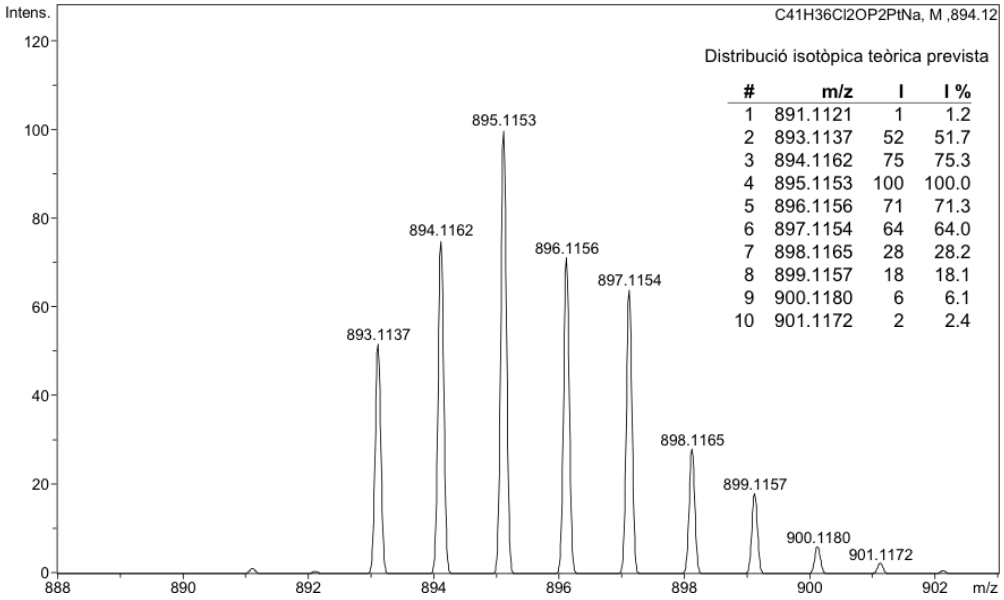


Analysis Info

Analysis Name	d65bPt (8EM-150)_1-B,4_01_253.d	Acquisition Date	27/05/2008 11:12:06
Method	ESIpos250-1300_FI-HS_MeCN_27-5-08.m	Operator	SAQ
Sample Name	d65bPt (8EM-150)	Instrument	micrOTOF-Q
Comment	ESI+. AER. Dó ca 2 ppm en MeCN. // O. VALLCORBA.		

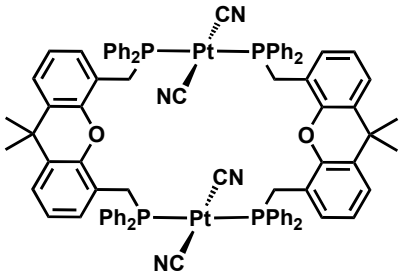


#	m/z	I	I %
1	891.1551	1691	4.2
2	891.6193	19	0.0
3	892.1664	1106	2.7
4	893.1140	17938	44.5
5	894.1168	28659	71.1
6	895.1166	40305	100.0
7	896.1186	27066	67.2
8	897.1162	23334	57.9
9	898.1183	9528	23.6
10	899.1166	5246	13.0
11	900.1270	1923	4.8
12	901.1277	921	2.3

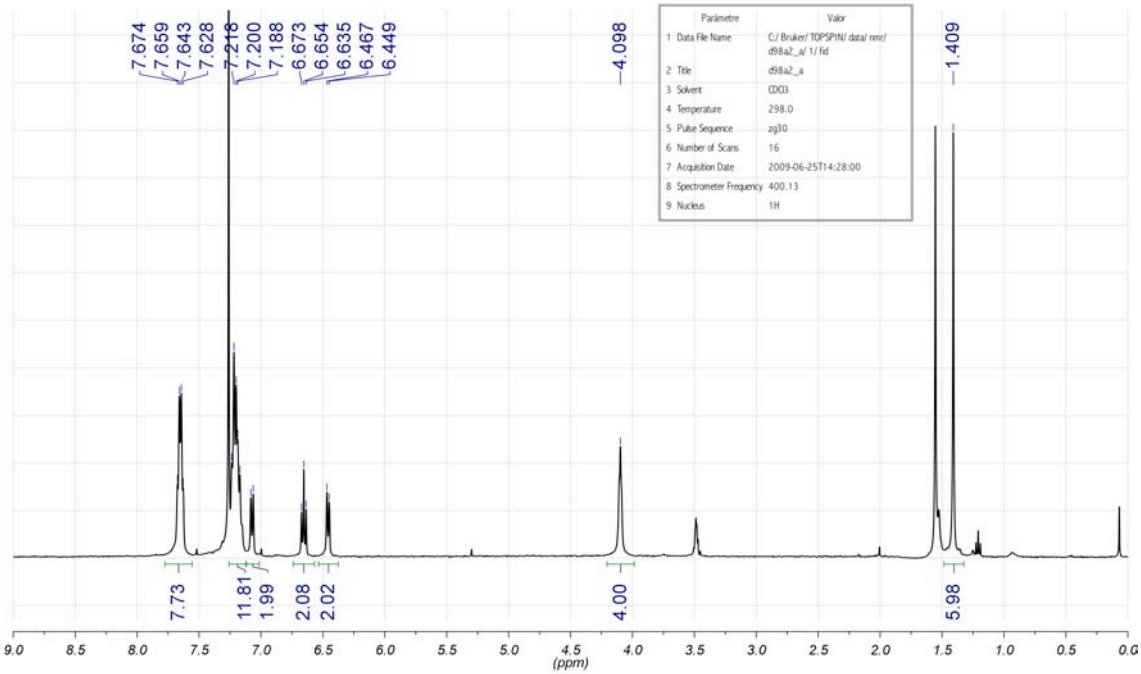


#	m/z	I	I %
1	891.1121	1	1.2
2	893.1137	52	51.7
3	894.1162	75	75.3
4	895.1153	100	100.0
5	896.1156	71	71.3
6	897.1154	64	64.0
7	898.1165	28	28.2
8	899.1157	18	18.1
9	900.1180	6	6.1
10	901.1172	2	2.4

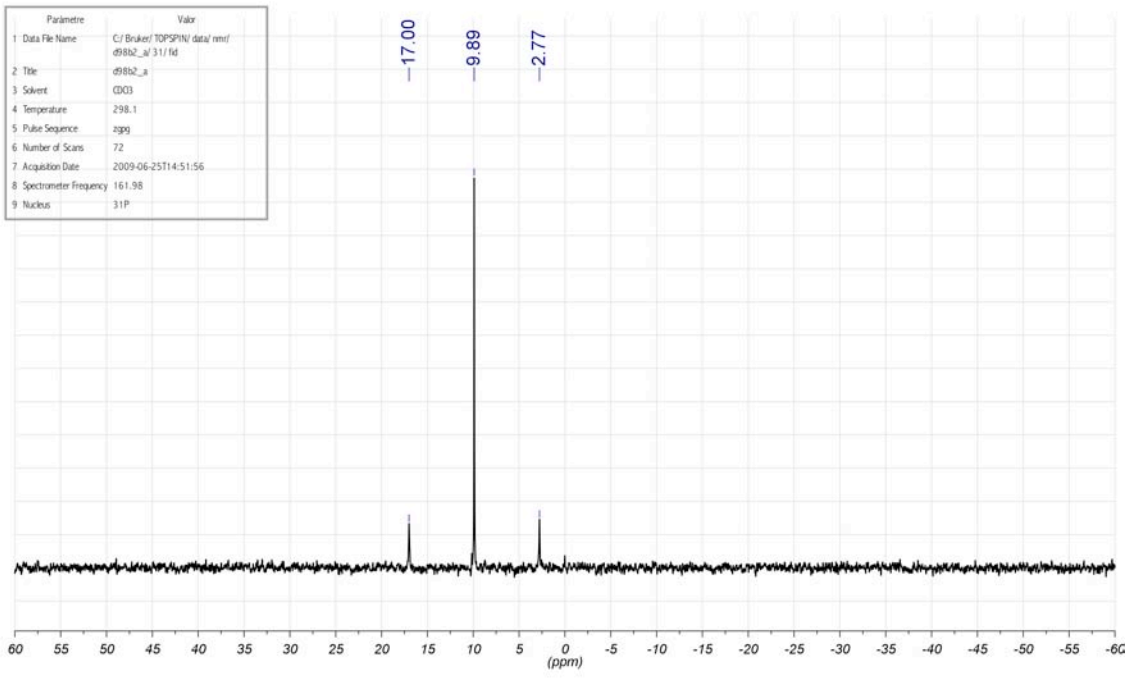
[Pt(CN)$_2$(XantMephos)] (C39)

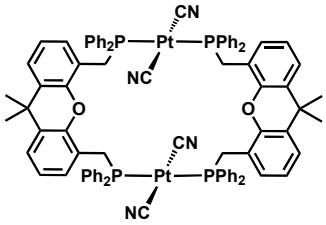


^{1}H RMN (400 MHz, rt, $CDCl_3$):

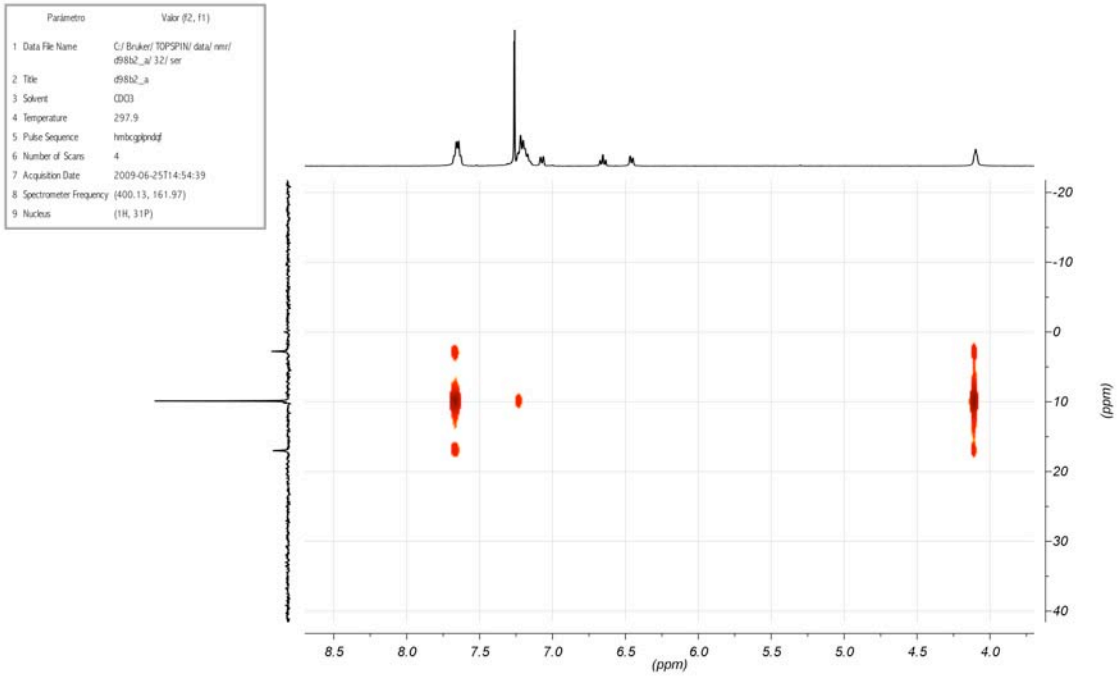


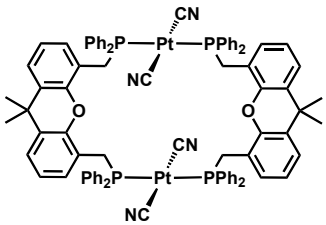
^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):



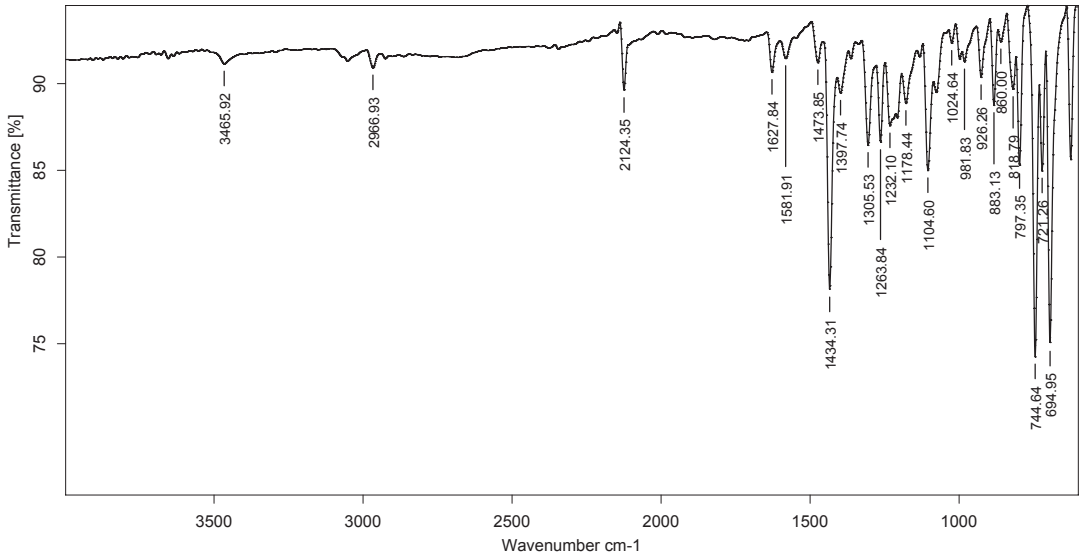


Espectre de correlació ^{1}H-^{31}P (HMBC):



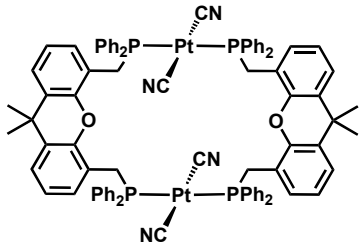


IR (ATR):



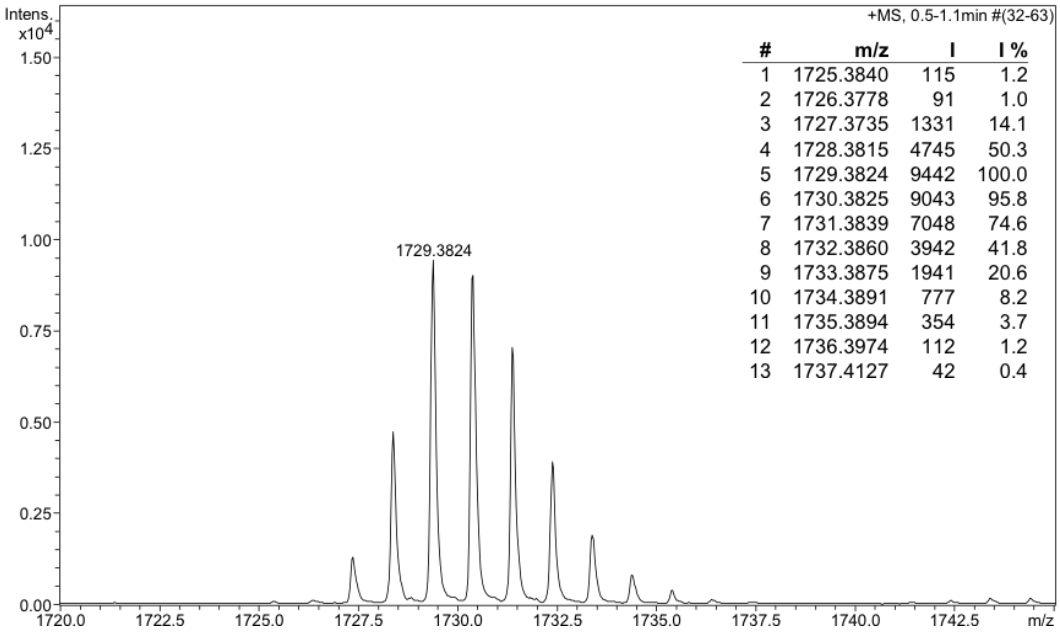
d98b2_a ; C:\MEAS\USUARIS_IR\ORIOL_V\d98b2_a.0 ; 29/06/2009 ; MKII Golden Gate

HRMS (ESI+):

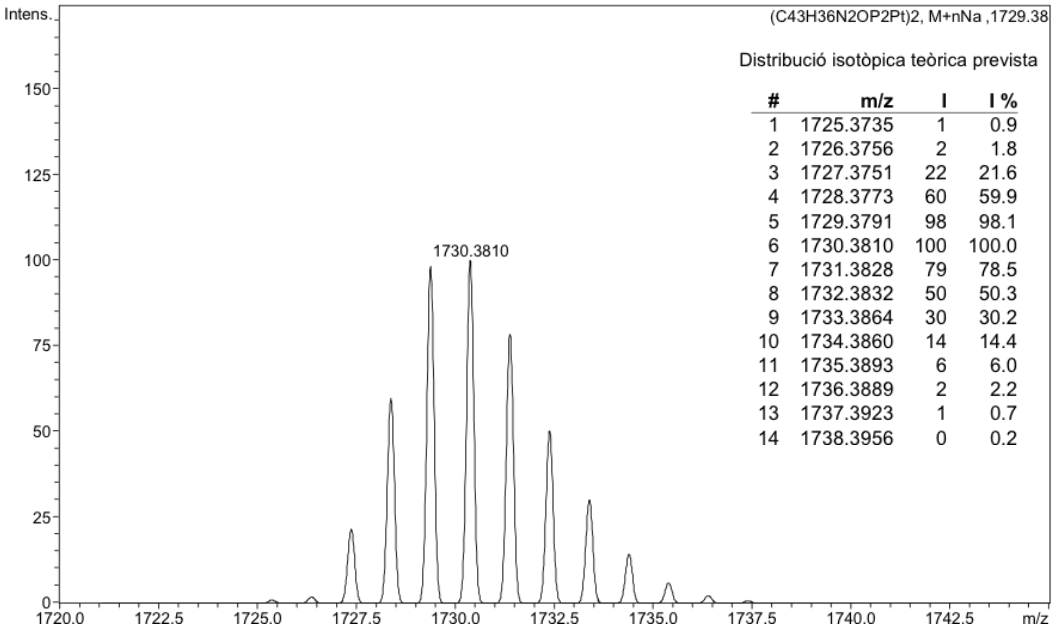


Analysis Info

Analysis Name	09EM345 (d98b)_1-d,4_01_2874.d	Acquisition Date	15/07/2009 14:03:52
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM345 (d98b)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 20 ppm CH2Cl2:MeOH (1:3)+ NaOH ORIOL VALLCORBA		



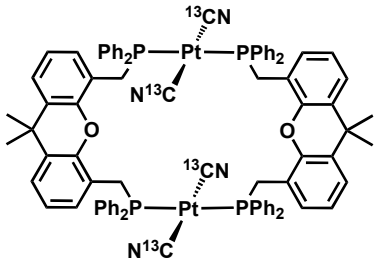
#	m/z	I	I %
1	1725.3840	115	1.2
2	1726.3778	91	1.0
3	1727.3735	1331	14.1
4	1728.3815	4745	50.3
5	1729.3824	9442	100.0
6	1730.3825	9043	95.8
7	1731.3839	7048	74.6
8	1732.3860	3942	41.8
9	1733.3875	1941	20.6
10	1734.3891	777	8.2
11	1735.3894	354	3.7
12	1736.3974	112	1.2
13	1737.4127	42	0.4



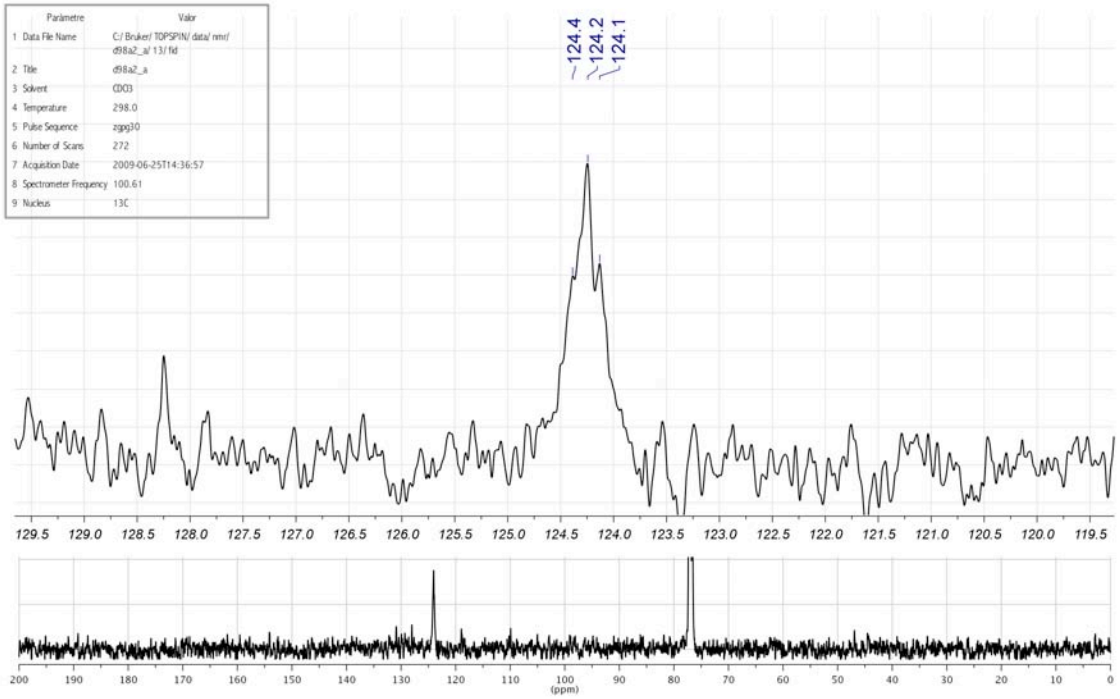
Distribució isotòpica teòrica prevista

#	m/z	I	I %
1	1725.3735	1	0.9
2	1726.3756	2	1.8
3	1727.3751	22	21.6
4	1728.3773	60	59.9
5	1729.3791	98	98.1
6	1730.3810	100	100.0
7	1731.3828	79	78.5
8	1732.3832	50	50.3
9	1733.3864	30	30.2
10	1734.3860	14	14.4
11	1735.3893	6	6.0
12	1736.3889	2	2.2
13	1737.3923	1	0.7
14	1738.3956	0	0.2

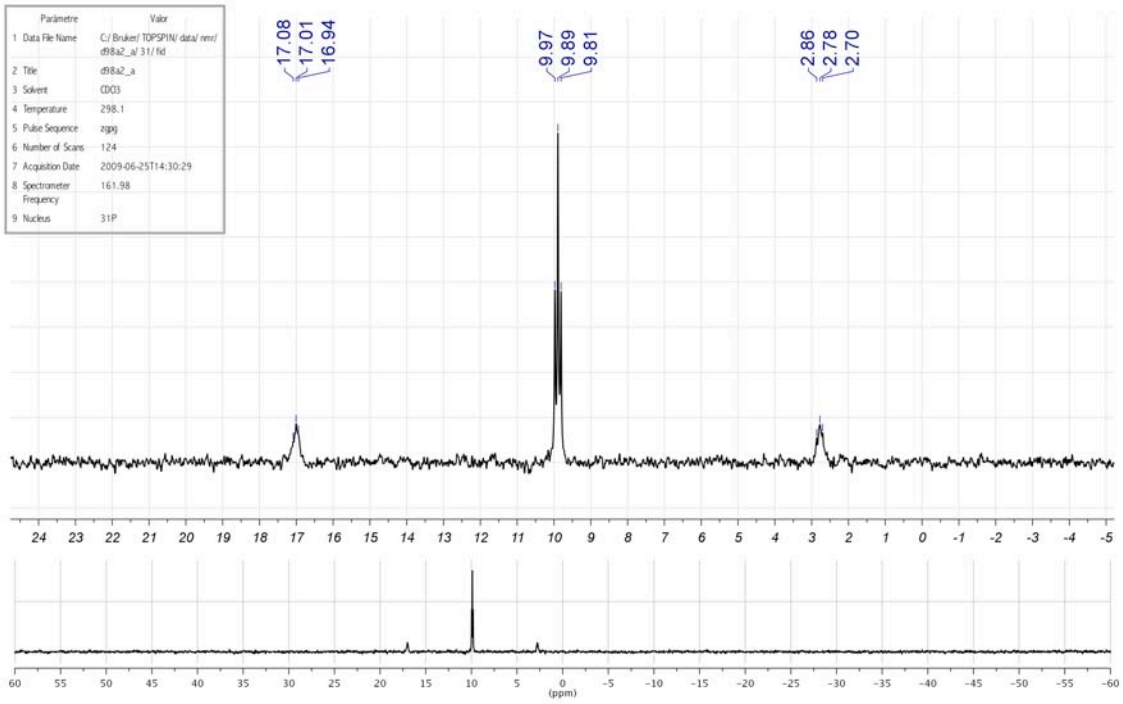
[Pt(^{13}CN)$_2$(XantMephos)] (C39m)

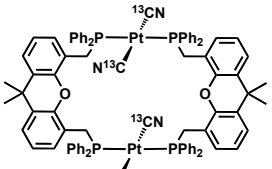


^{13}C{^{1}H} RMN (101 MHz, rt, $CDCl_3$):

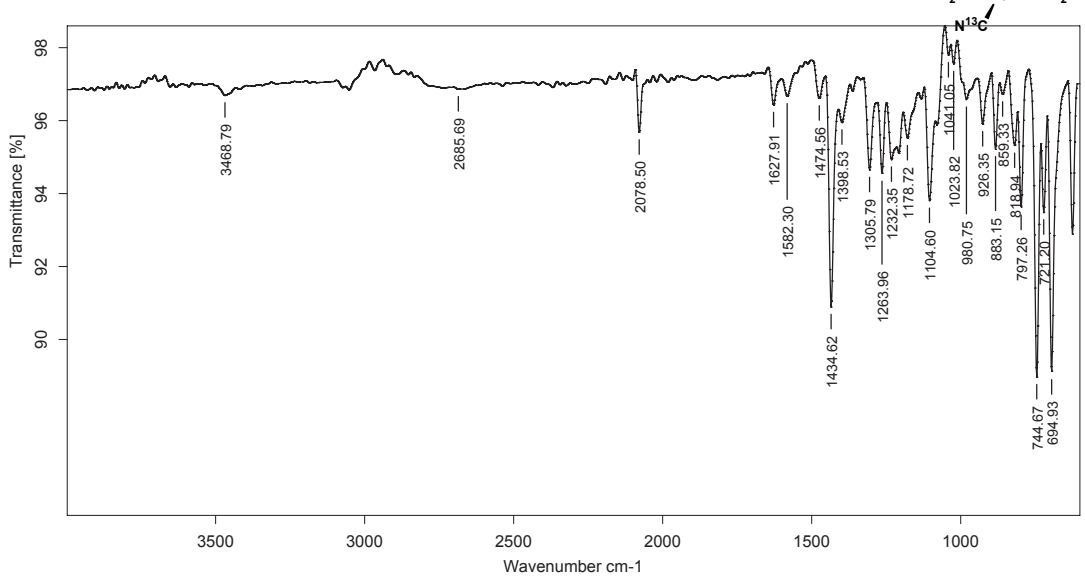


^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

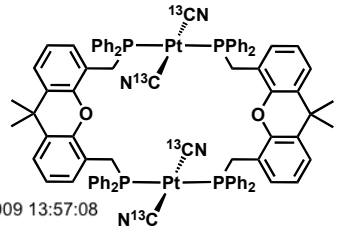




IR (ATR):



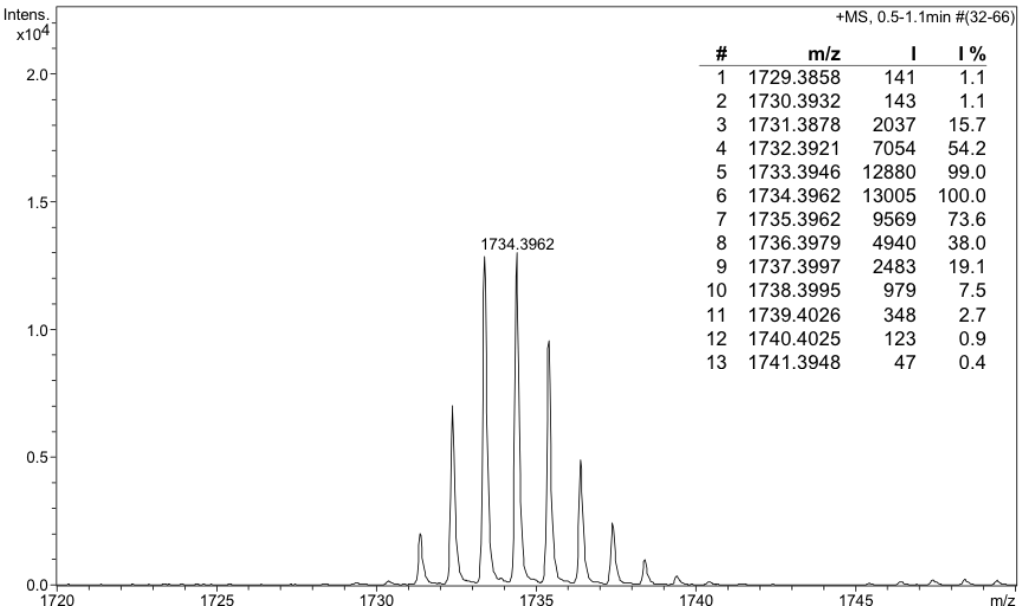
d98a2_a ; C:\MEAS\USUARIS_IR\ORIOL_V\d98a2_a.0 ; 29/06/2009 ; MKII Golden Gate



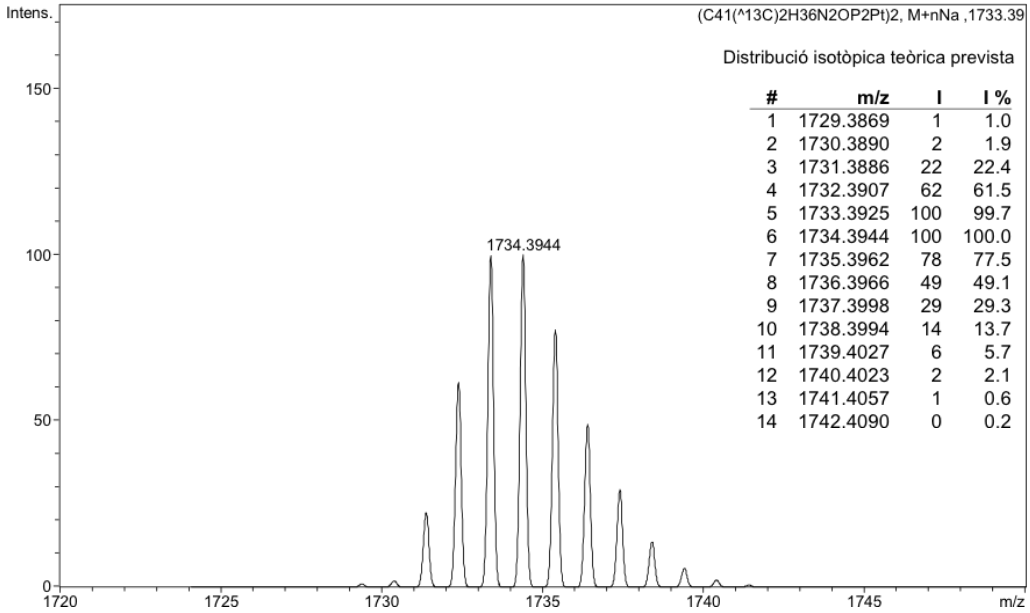
HRMS (ESI+):

Analysis Info

Analysis Name	09EM344 (d98a)_1-d,3_01_2873.d	Acquisition Date	15/07/2009 13:57:08
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM344 (d98a)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 20 ppm CH2Cl2:MeOH (1:5) + NaOH ORIOL VALLCORBA		

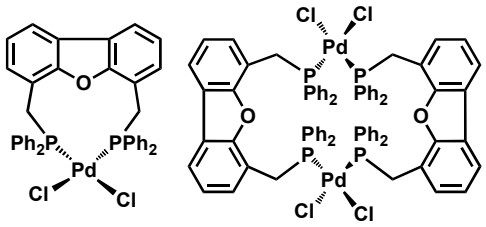


#	m/z	I	I %
1	1729.3858	141	1.1
2	1730.3932	143	1.1
3	1731.3878	2037	15.7
4	1732.3921	7054	54.2
5	1733.3946	12880	99.0
6	1734.3962	13005	100.0
7	1735.3962	9569	73.6
8	1736.3979	4940	38.0
9	1737.3997	2483	19.1
10	1738.3995	979	7.5
11	1739.4026	348	2.7
12	1740.4025	123	0.9
13	1741.3948	47	0.4

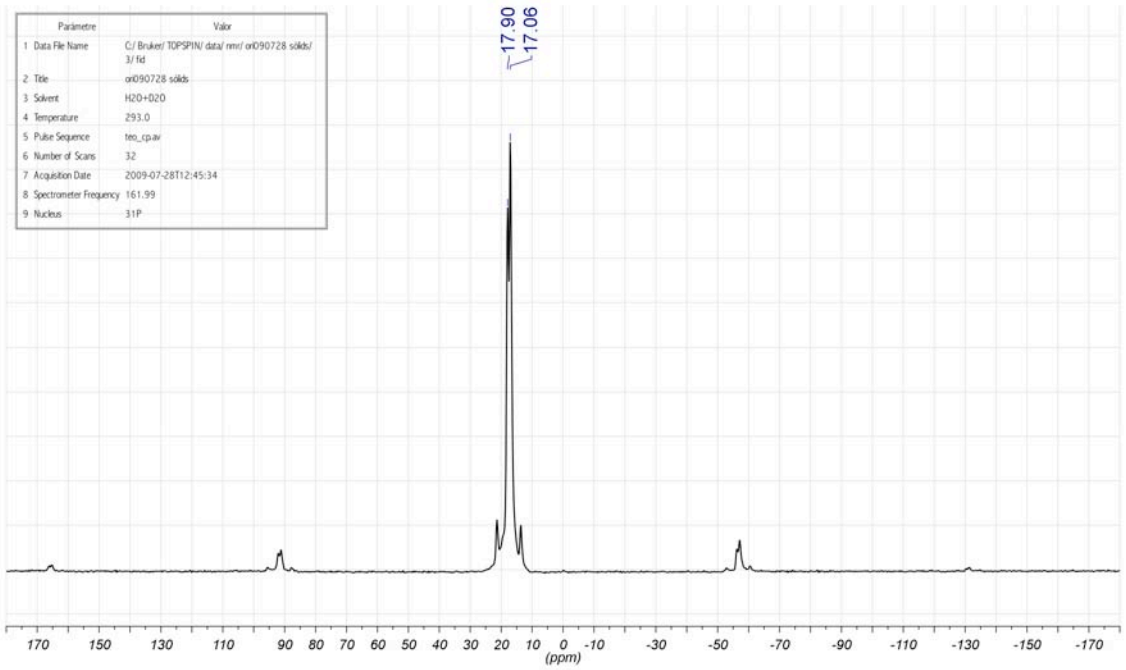


11.3 DBFMephos amb Pd i Pt

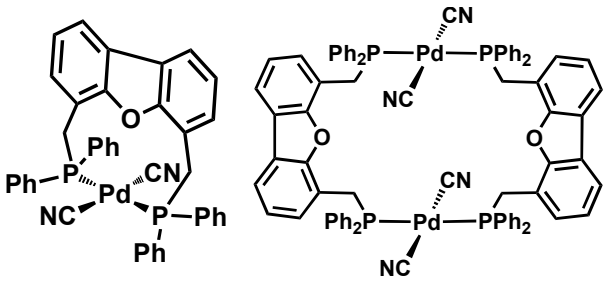
[PdCl$_2$(DBFMephos)] (C40)



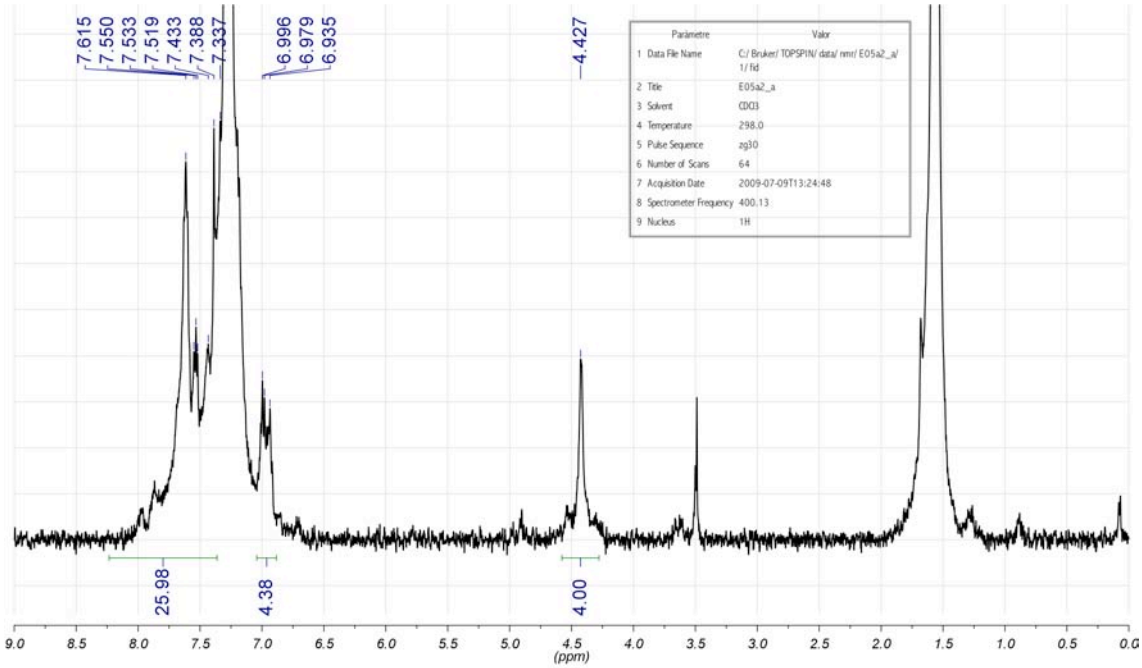
$^{31}P\{^{1}H\}$ RMN CP-MAS (162 MHz, rt, sòlid):



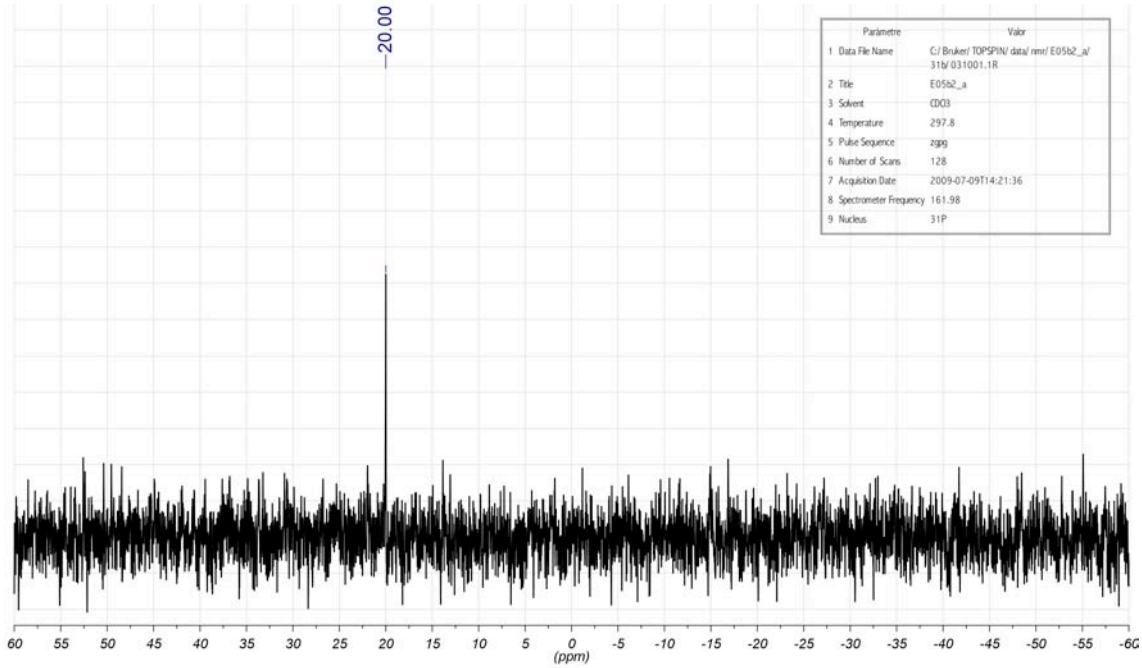
[Pd(CN)$_2$(DBFMephos)] **(C42)**



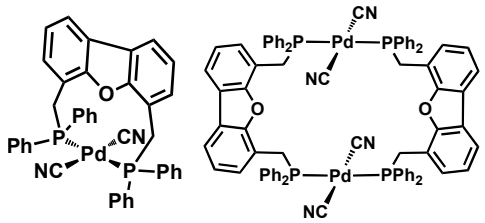
^{1}H RMN (400 MHz, rt, $CDCl_3$):

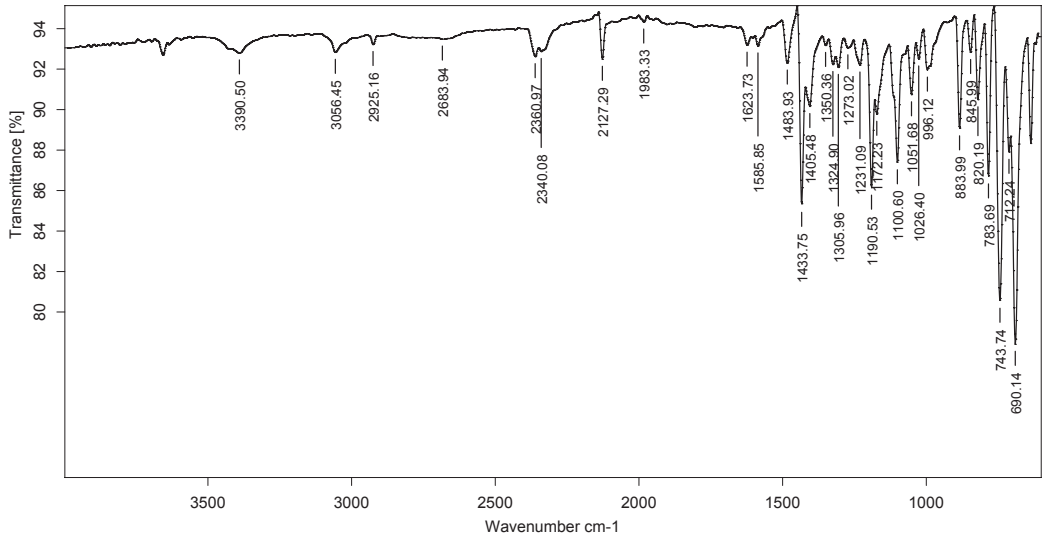


^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):



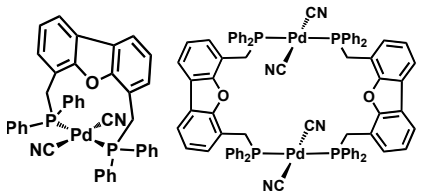
IR (ATR):





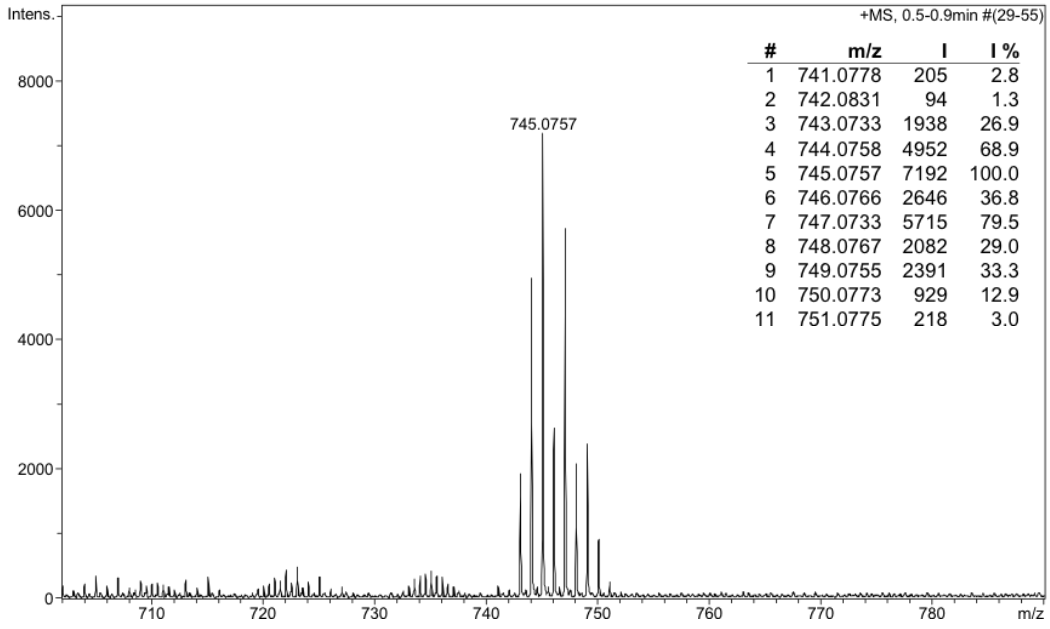
E05a2_a ; C:\MEAS\USUARIS_IR\ORIOL_V\E05a2_a.0 ; 09/07/2009 ; MKII Golden Gate

HRMS (ESI+):

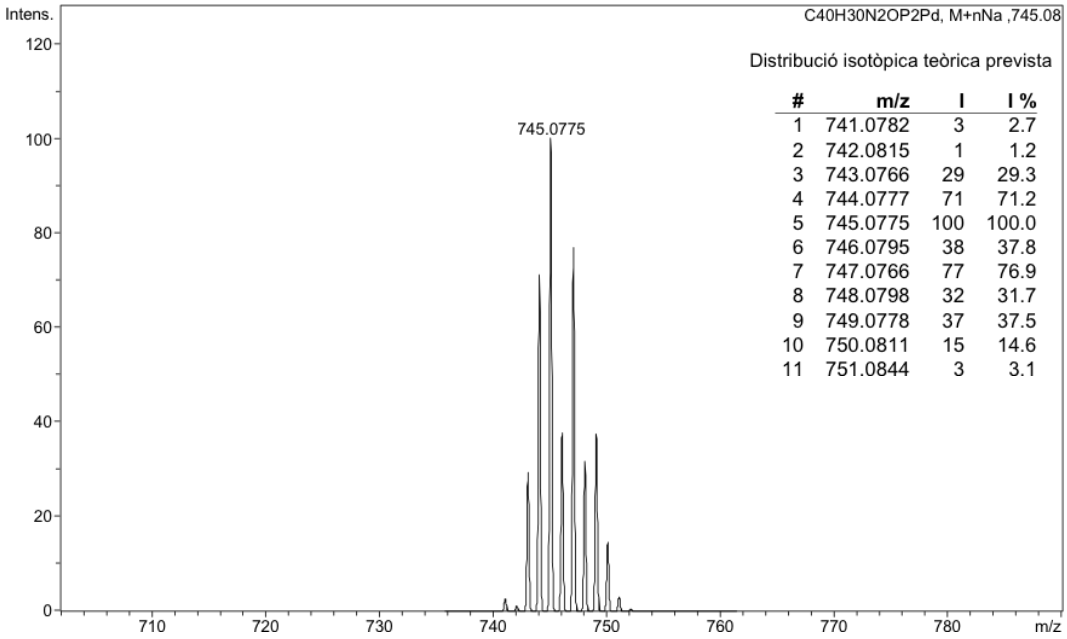


Analysis Info

Analysis Name	09EM362(E05 b)_1-C,7_01_2869.d	Acquisition Date	15/07/2009 13:08:12
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM362(E05 b)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca. 18 ppm en CH2Cl2:MeOH (1:4) ORIOL VALLCORBA		



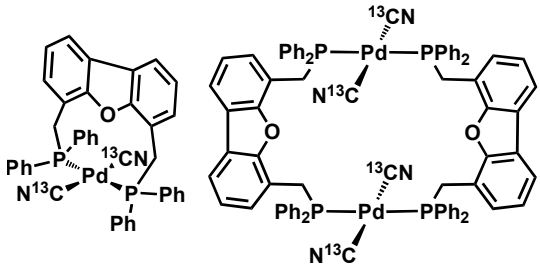
#	m/z	I	I %
1	741.0778	205	2.8
2	742.0831	94	1.3
3	743.0733	1938	26.9
4	744.0758	4952	68.9
5	745.0757	7192	100.0
6	746.0766	2646	36.8
7	747.0733	5715	79.5
8	748.0767	2082	29.0
9	749.0755	2391	33.3
10	750.0773	929	12.9
11	751.0775	218	3.0



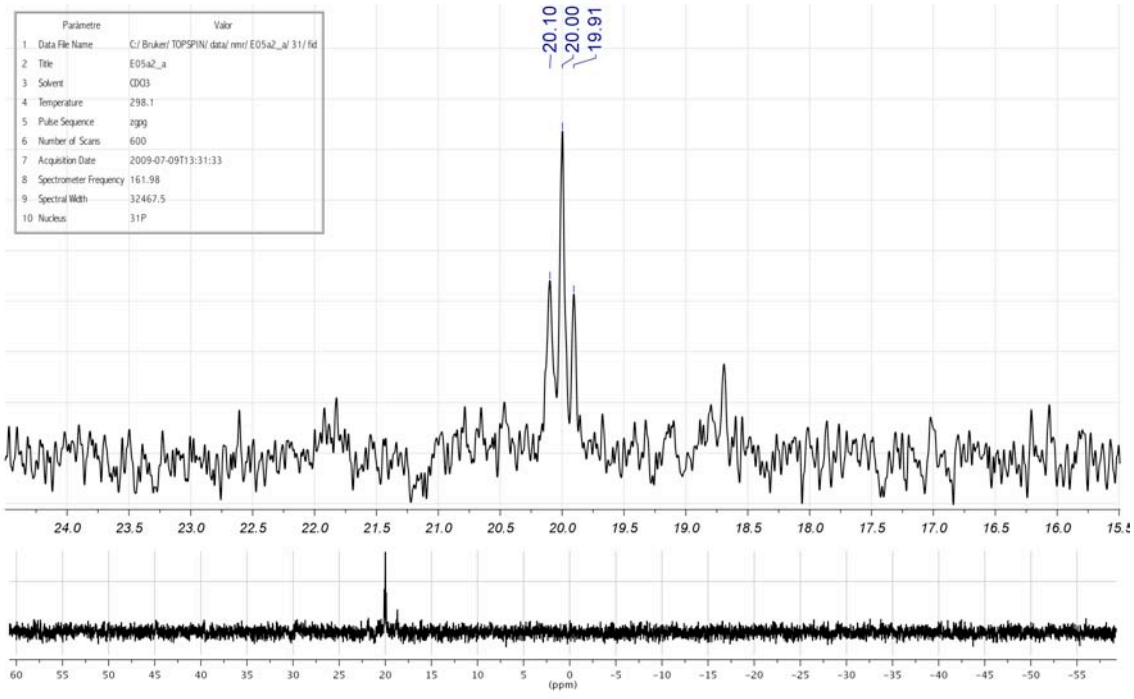
Distribució isotòpica teòrica prevista

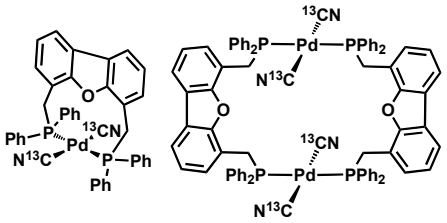
#	m/z	I	I %
1	741.0782	3	2.7
2	742.0815	1	1.2
3	743.0766	29	29.3
4	744.0777	71	71.2
5	745.0775	100	100.0
6	746.0795	38	37.8
7	747.0766	77	76.9
8	748.0798	32	31.7
9	749.0778	37	37.5
10	750.0811	15	14.6
11	751.0844	3	3.1

[Pd(^{13}CN)$_2$(DBFMephos)] **(C42m)**

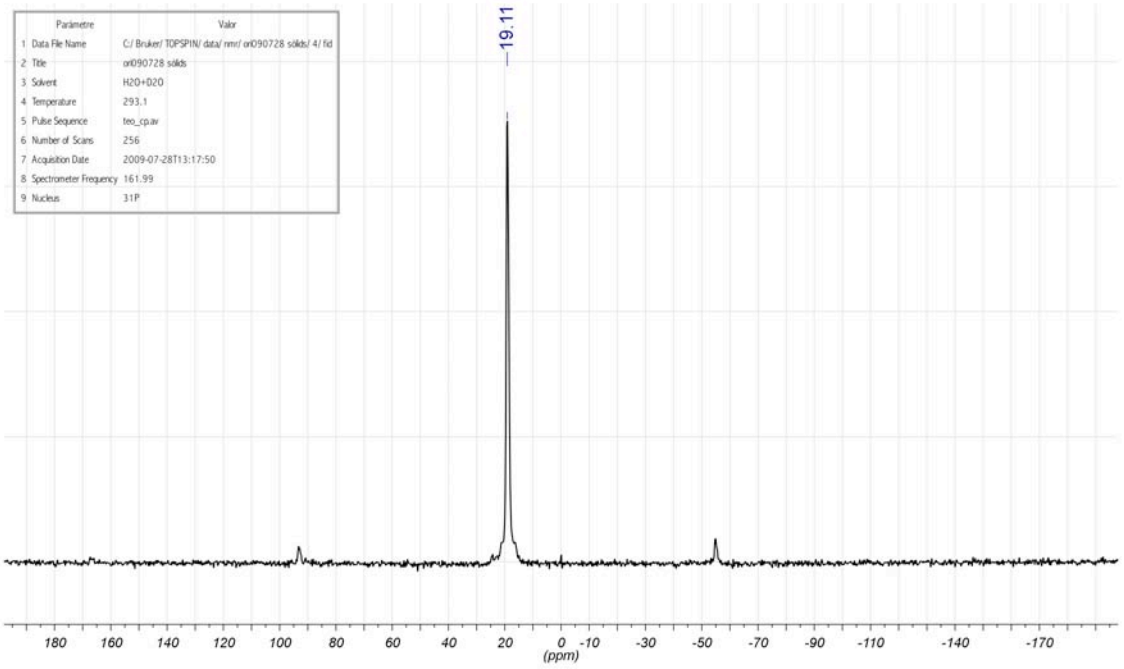


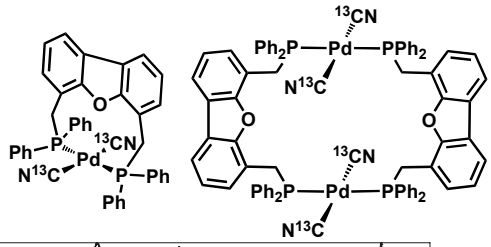
^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):



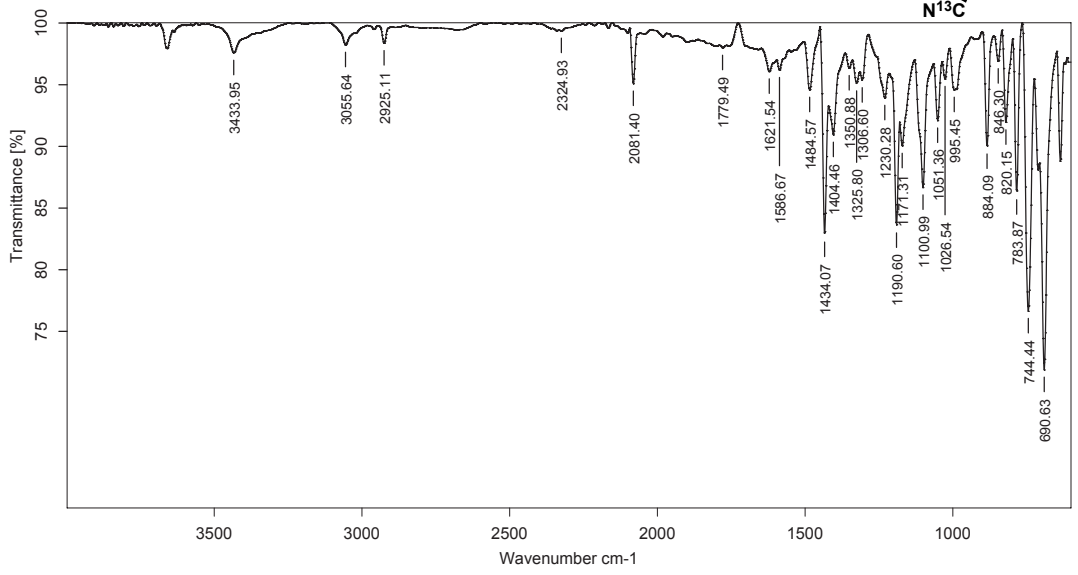


$^{31}P\{^{1}H\}$ RMN CP-MAS (162 MHz, rt, sòlid):



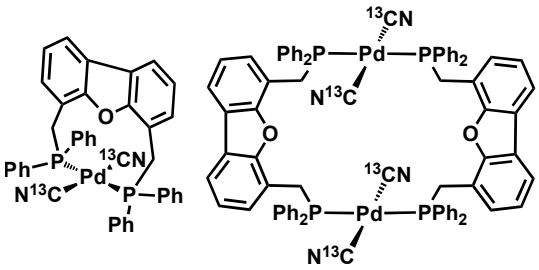


IR (ATR):



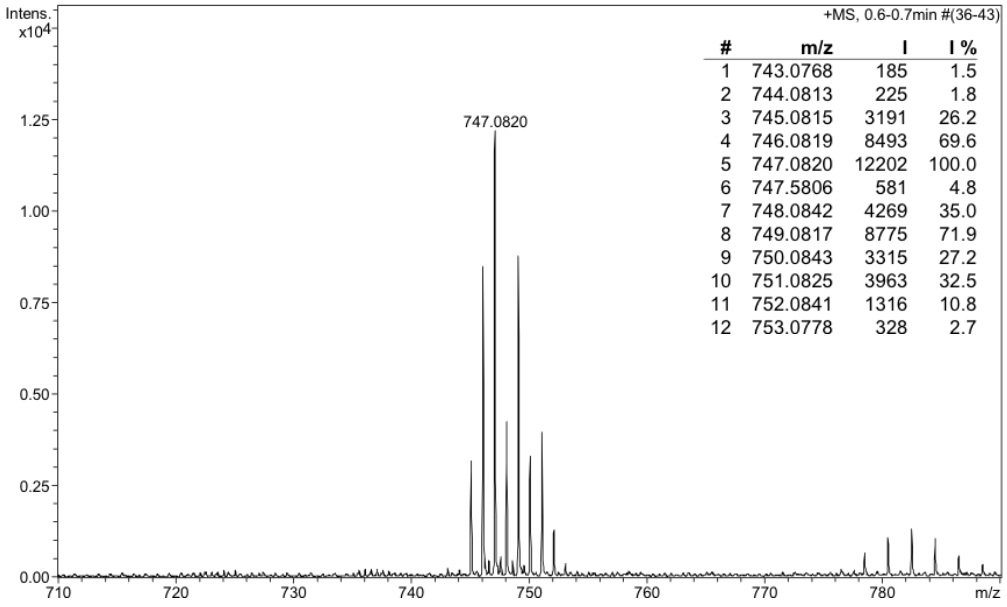
E05b2_a ; C:\MEAS\USUARIS_IR\ORIOL_V\E05b2_a.0 ; 09/07/2009 ; MKII Golden Gate

HRMS (ESI+):

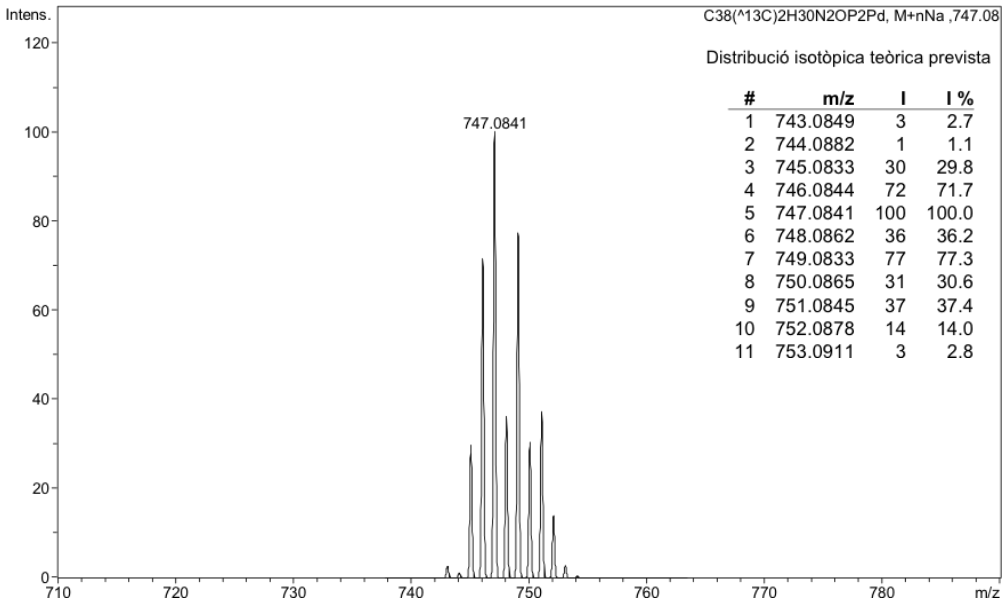


Analysis Info

Analysis Name	09EM361 (E05 a)_1-C,6_01_2870.d	Acquisition Date	15/07/2009 13:14:56
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM361 (E05 a)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca 12 ppm en CH2Cl2:MeOH (1:4) ORIOL VALLCORBA		

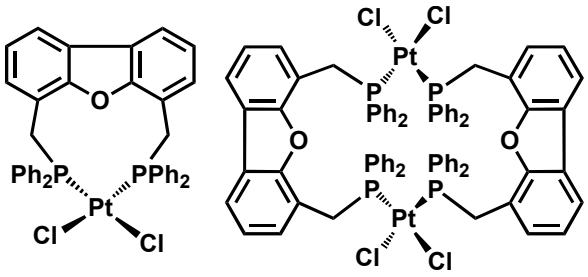


#	m/z	I	I %
1	743.0768	185	1.5
2	744.0813	225	1.8
3	745.0815	3191	26.2
4	746.0819	8493	69.6
5	747.0820	12202	100.0
6	747.5806	581	4.8
7	748.0842	4269	35.0
8	749.0817	8775	71.9
9	750.0843	3315	27.2
10	751.0825	3963	32.5
11	752.0841	1316	10.8
12	753.0778	328	2.7

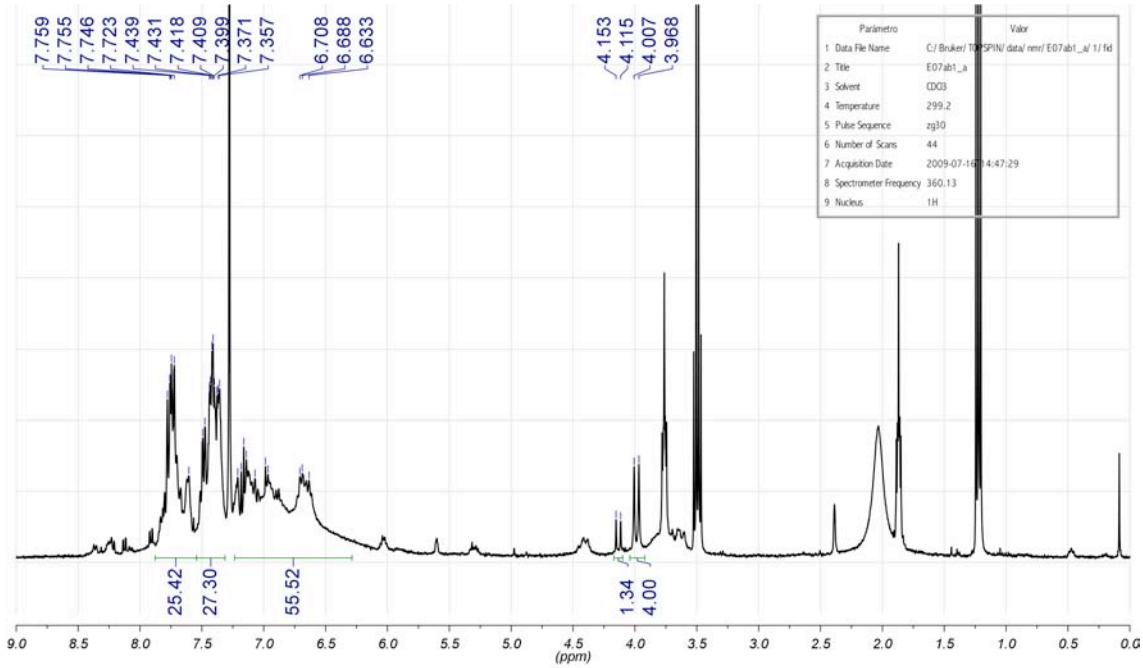


#	m/z	I	I %
1	743.0849	3	2.7
2	744.0882	1	1.1
3	745.0833	30	29.8
4	746.0844	72	71.7
5	747.0841	100	100.0
6	748.0862	36	36.2
7	749.0833	77	77.3
8	750.0865	31	30.6
9	751.0845	37	37.4
10	752.0878	14	14.0
11	753.0911	3	2.8

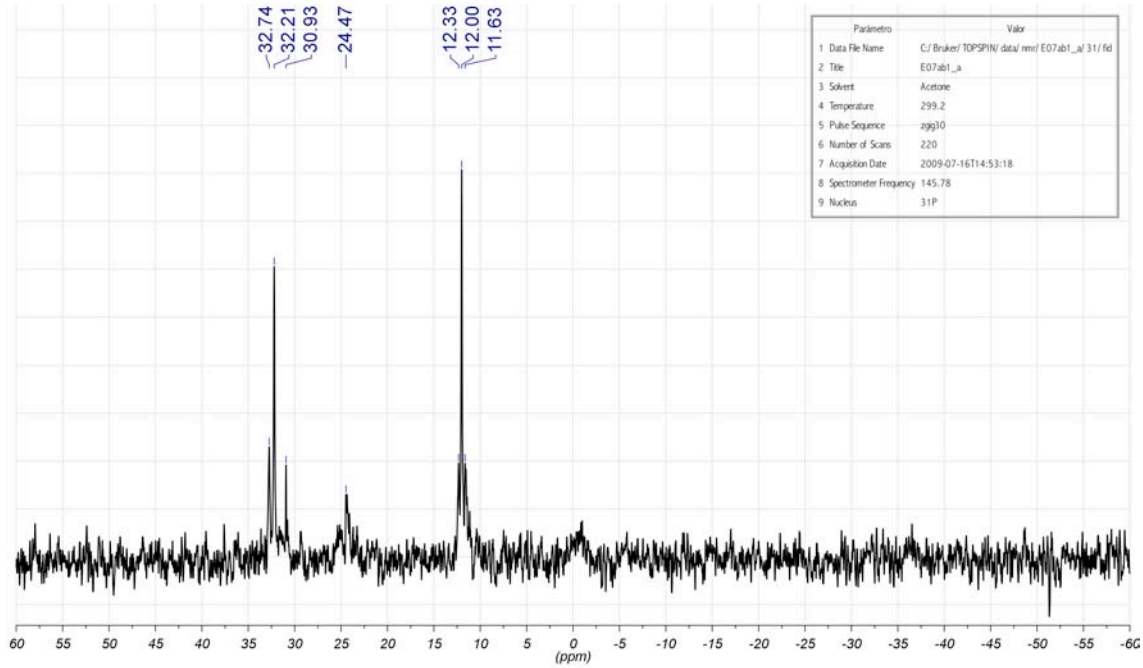
[$PtCl_2$(DBFMephos)] (C41)



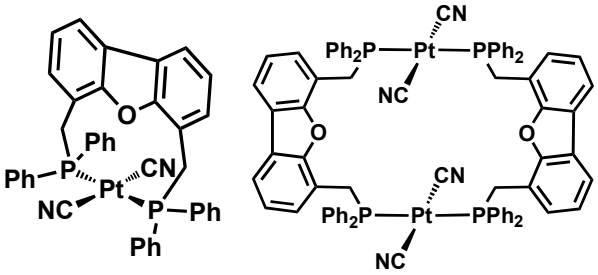
^{1}H RMN (400 MHz, rt, $CDCl_3$):



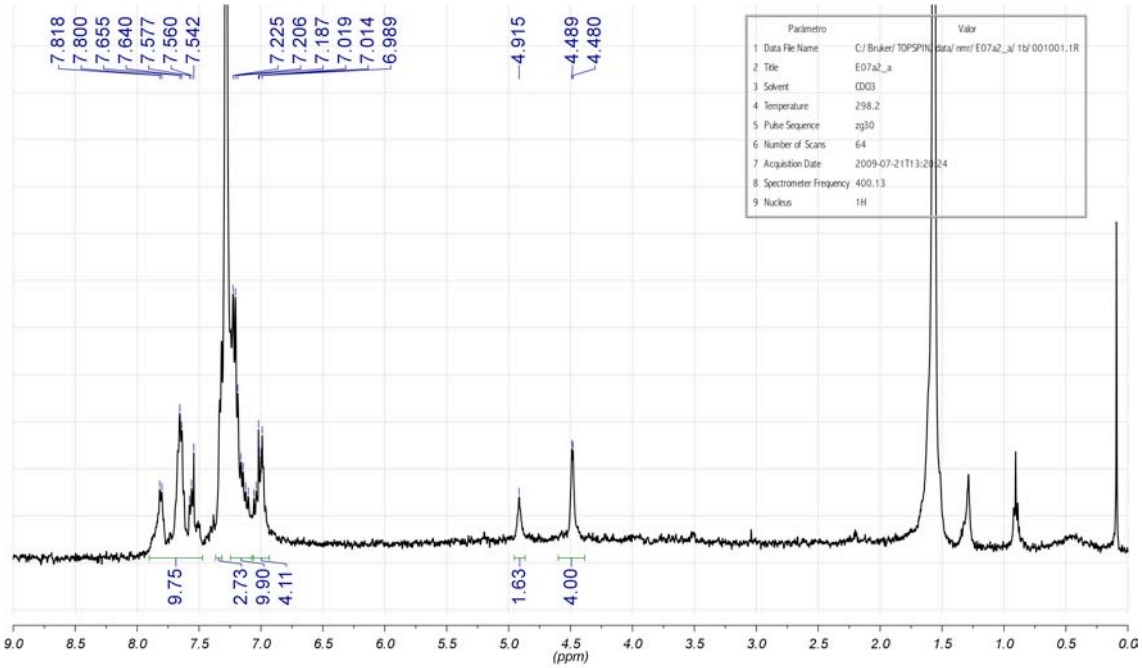
^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

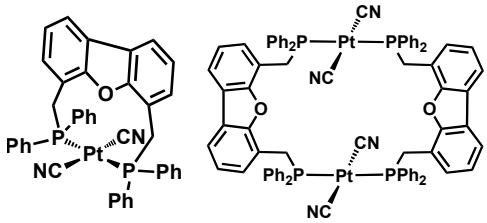


[Pt(CN)$_2$(DBFMephos)] (C43)

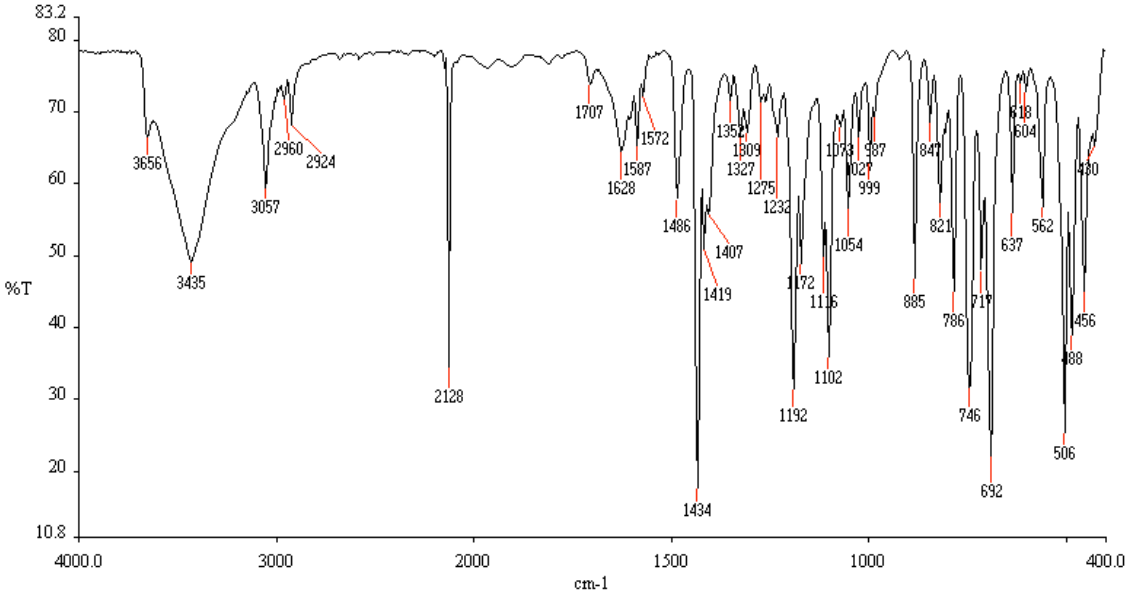


^{1}H RMN (400 MHz, rt, $CDCl_3$):

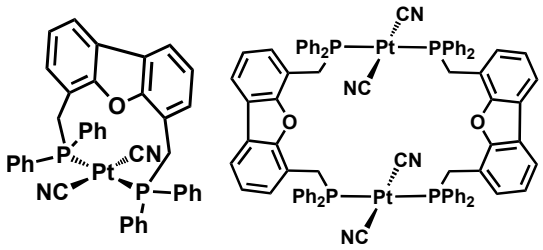




IR (KBr):

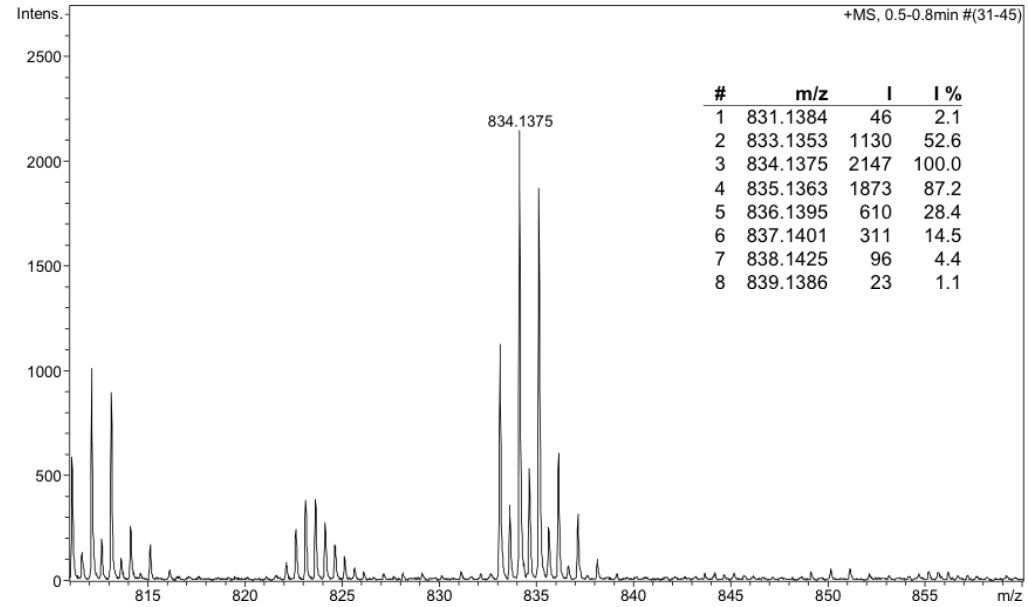


HRMS (ESI+):

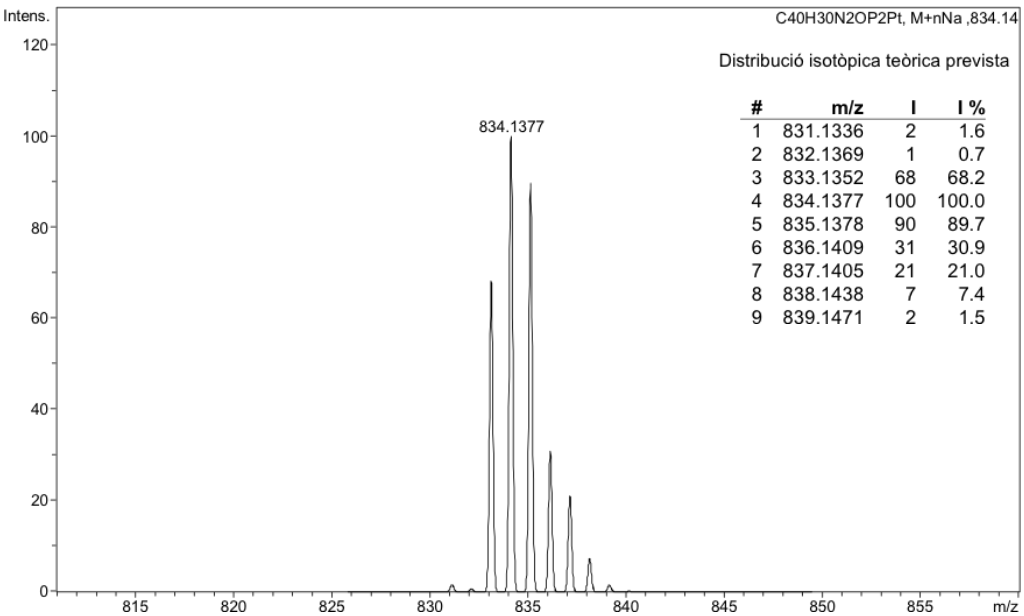


Analysis Info

Analysis Name	09EM376 (E07 b)_1-c,3_01_3276.d	Acquisition Date	29/07/2009 12:55:24
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM376 (E07 b)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca. 10 ppm en CH2Cl2:MeOH (1:1) ORIOL VALLCORBA		

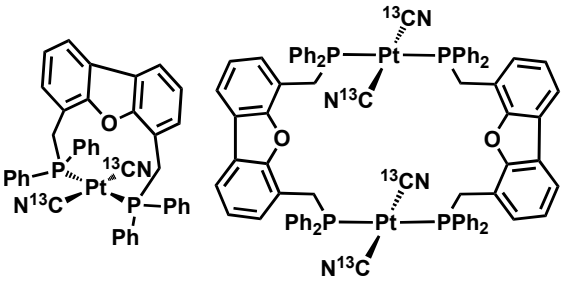


#	m/z	I	I %
1	831.1384	46	2.1
2	833.1353	1130	52.6
3	834.1375	2147	100.0
4	835.1363	1873	87.2
5	836.1395	610	28.4
6	837.1401	311	14.5
7	838.1425	96	4.4
8	839.1386	23	1.1

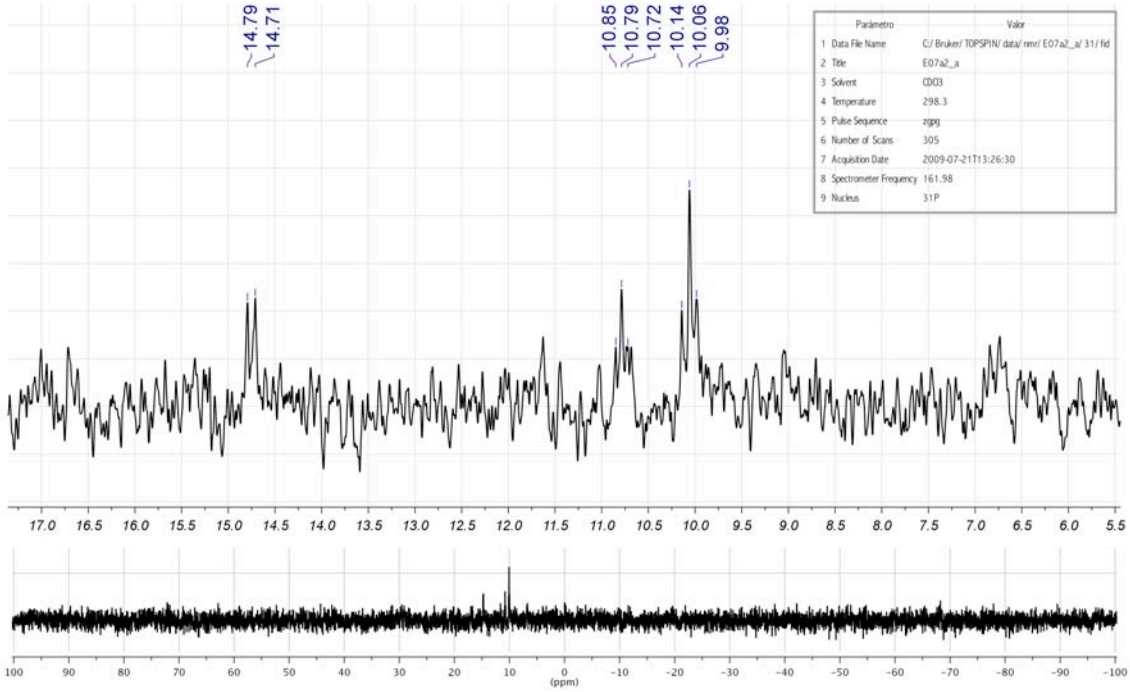


#	m/z	I	I %
1	831.1336	2	1.6
2	832.1369	1	0.7
3	833.1352	68	68.2
4	834.1377	100	100.0
5	835.1378	90	89.7
6	836.1409	31	30.9
7	837.1405	21	21.0
8	838.1438	7	7.4
9	839.1471	2	1.5

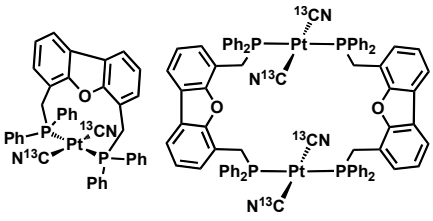
[Pt(^{13}CN)$_2$(DBFMephos)] (C43m)

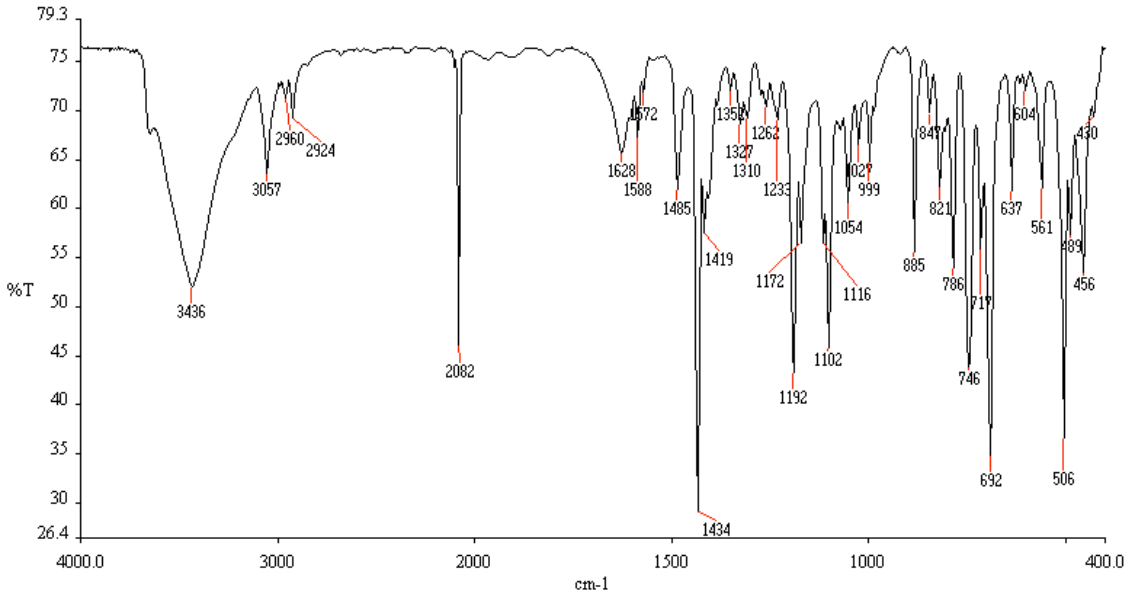


^{31}P{^{1}H} RMN (162 MHz, rt, $CDCl_3$):

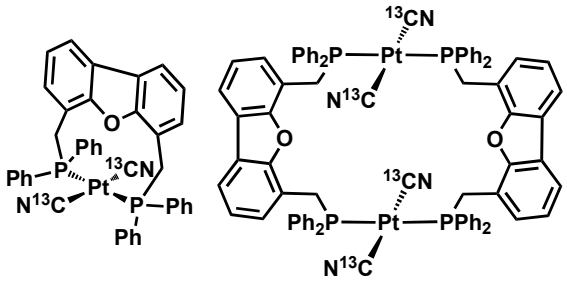


IR (KBr):



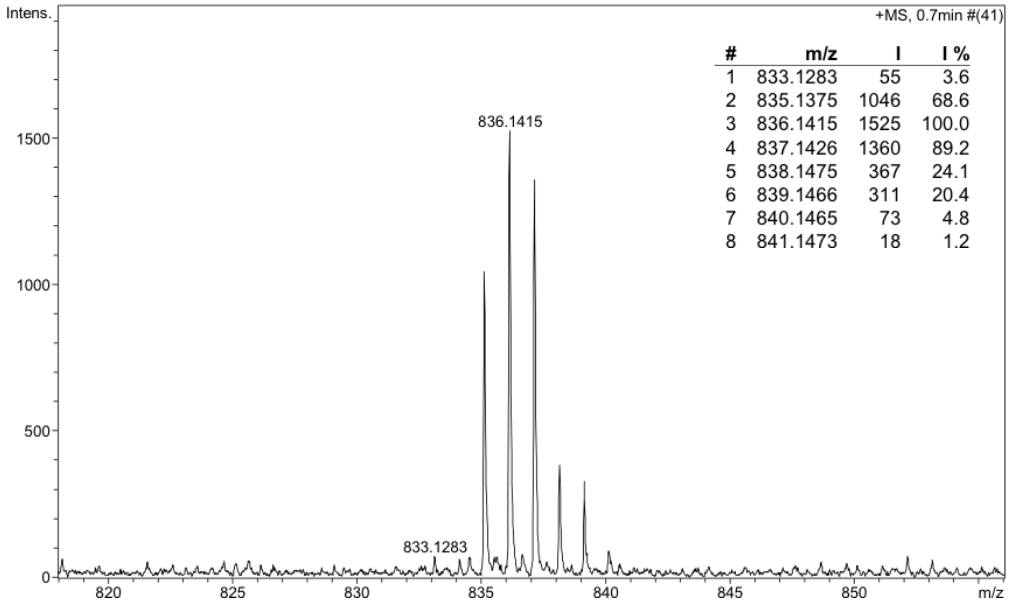


HRMS (ESI+):

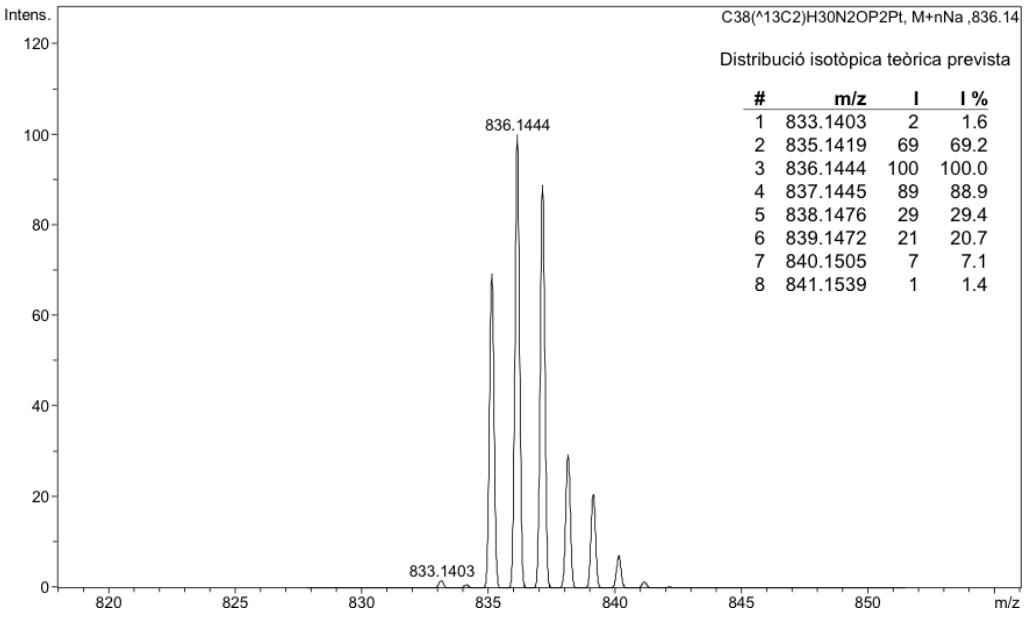


Analysis Info

Analysis Name	09EM377 (E07 a)_1-d,6_01_3289.d	Acquisition Date	29/07/2009 14:22:52
Method	esipos622-2722_fi_11-02-09.m	Operator	SAQ
Sample Name	09EM377 (E07 a)	Instrument	micrOTOF-Q
Comment	MIE. ESI+. Dó ca. 20 ppm en CH2Cl2:MeOH (1:8) ORIOL VALLCORBA		



#	m/z	I	I %
1	833.1283	55	3.6
2	835.1375	1046	68.6
3	836.1415	1525	100.0
4	837.1426	1360	89.2
5	838.1475	367	24.1
6	839.1466	311	20.4
7	840.1465	73	4.8
8	841.1473	18	1.2



#	m/z	I	I %
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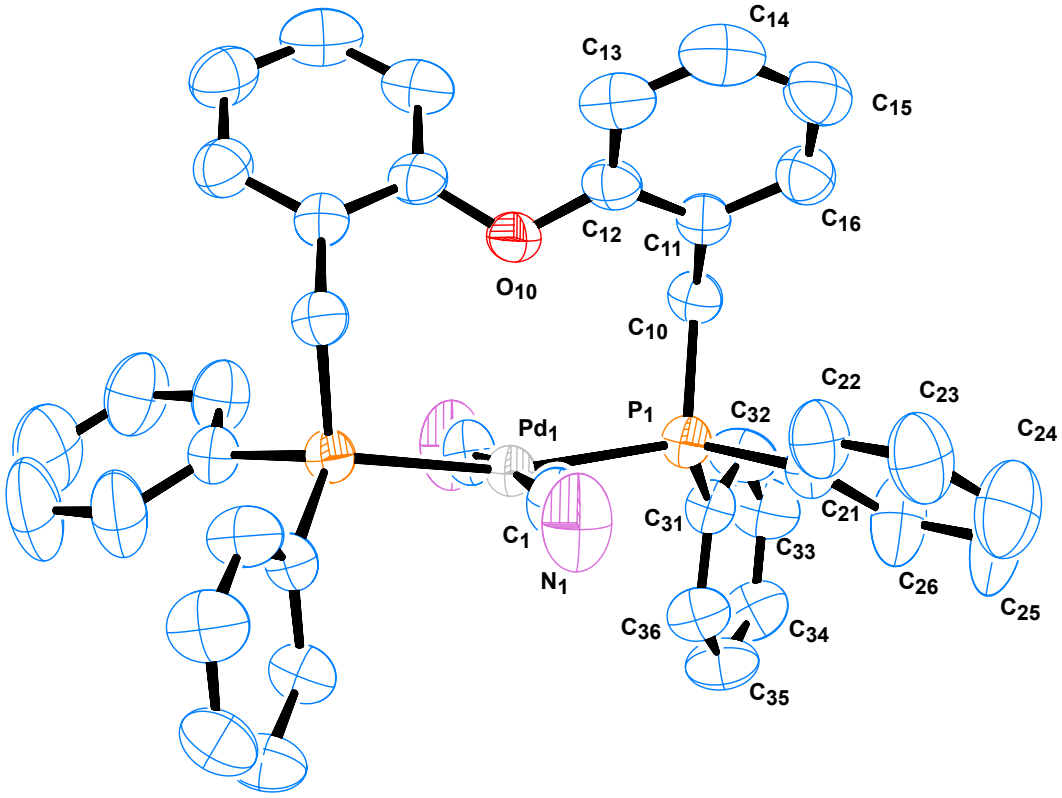
2	835.1419	69	69.2
3	836.1444	100	100.0
4	837.1445	89	88.9
5	838.1476	29	29.4
6	839.1472	21	20.7
7	840.1505	7	7.1
8	841.1539	1	1.4

12 Dades cristal·logràfiques

12.1 CIF de la estructura cristal·lina de [(DPEMephos)Pd(CN)$_2$] (C34)

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 'H'  'H'   0.0000   0.0000
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 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'P'  'P'   0.1023   0.0942
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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 'Pd'  'Pd'  -0.9988   1.0072
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_cell_length_c                    19.0002(13)
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_cell_volume                      3812.1(5)
_cell_formula_units_Z             4
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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_refine_ls_extinction_coef        ?
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P1 P 0.42370(4) 0.10328(10) 0.14934(4) 0.0382(2) Uani 1 1 d . . .
C21 C 0.35011(15) 0.1222(4) 0.1553(2) 0.0473(8) Uani 1 1 d . . .
C1 C 0.45313(16) 0.1430(4) 0.3228(2) 0.0532(9) Uani 1 1 d . . .
C36 C 0.43082(17) 0.3871(4) 0.08340(19) 0.0515(9) Uani 1 1 d . . .
H36 H 0.4333 0.4283 0.1295 0.062 Uiso 1 1 calc R . .
C10 C 0.42788(15) -0.1011(4) 0.11826(18) 0.0437(7) Uani 1 1 d . . .
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H10A H 0.4033 -0.1110 0.0700 0.052 Uiso 1 1 calc R . .
H10B H 0.4662 -0.1207 0.1144 0.052 Uiso 1 1 calc R . .
N1 N 0.42845(16) 0.1512(5) 0.3658(2) 0.0837(13) Uani 1 1 d . . .
C33 C 0.42490(19) 0.2686(5) -0.0532(2) 0.0677(11) Uani 1 1 d . . .
H33 H 0.4234 0.2284 -0.0991 0.081 Uiso 1 1 calc R . .
C32 C 0.42515(19) 0.1681(4) 0.0036(2) 0.0601(10) Uani 1 1 d . . .
H32 H 0.4236 0.0598 -0.0043 0.072 Uiso 1 1 calc R . .
C31 C 0.42774(13) 0.2265(4) 0.07220(16) 0.0410(7) Uani 1 1 d . . .
O10 O 0.5000 -0.2027(4) 0.2500 0.0620(10) Uani 1 2 d S . .
C11 C 0.41212(13) -0.2274(4) 0.16557(17) 0.0406(7) Uani 1 1 d . . .
C12 C 0.44945(15) -0.2823(4) 0.22726(17) 0.0459(8) Uani 1 1 d . . .
C16 C 0.35886(16) -0.2965(4) 0.1462(2) 0.0554(9) Uani 1 1 d . . .
H16 H 0.3325 -0.2597 0.1055 0.066 Uiso 1 1 calc R . .
C34 C 0.42688(19) 0.4290(5) -0.0418(2) 0.0642(11) Uani 1 1 d . . .
H34 H 0.4260 0.4974 -0.0803 0.077 Uiso 1 1 calc R . .
C35 C 0.43014(19) 0.4870(5) 0.0252(2) 0.0640(11) Uani 1 1 d . . .
H35 H 0.4319 0.5955 0.0326 0.077 Uiso 1 1 calc R . .
C22 C 0.33314(17) 0.0577(6) 0.2126(2) 0.0653(11) Uani 1 1 d . . .
H22 H 0.3594 0.0060 0.2490 0.078 Uiso 1 1 calc R . .
C26 C 0.31090(18) 0.2026(7) 0.1032(3) 0.0836(14) Uani 1 1 d . . .
H26 H 0.3217 0.2496 0.0644 0.100 Uiso 1 1 calc R . .
C24 C 0.2392(2) 0.1460(7) 0.1659(4) 0.100(2) Uani 1 1 d . . .
H24 H 0.2019 0.1540 0.1693 0.120 Uiso 1 1 calc R . .
C23 C 0.27688(19) 0.0684(7) 0.2172(3) 0.0826(14) Uani 1 1 d . . .
H23 H 0.2657 0.0217 0.2558 0.099 Uiso 1 1 calc R . .
C25 C 0.2548(2) 0.2135(9) 0.1086(4) 0.117(2) Uani 1 1 d . . .
H25 H 0.2282 0.2666 0.0731 0.141 Uiso 1 1 calc R . .
C13 C 0.4361(2) -0.4072(4) 0.2674(2) 0.0582(10) Uani 1 1 d . . .
H13 H 0.4625 -0.4444 0.3079 0.070 Uiso 1 1 calc R . .
C15 C 0.34420(19) -0.4195(5) 0.1864(3) 0.0661(11) Uani 1 1 d . . .
H15 H 0.3083 -0.4640 0.1729 0.079 Uiso 1 1 calc R . .
C14 C 0.3834(2) -0.4754(5) 0.2467(2) 0.0678(12) Uani 1 1 d . . .
H14 H 0.3741 -0.5591 0.2732 0.081 Uiso 1 1 calc R . .
C2A C 0.3022(8) 0.241(2) 0.4182(13) 0.072(5) Uiso 0.30 1 d PD A 1
H2A1 H 0.3280 0.3273 0.4335 0.107 Uiso 0.30 1 calc PR A 1
H2A2 H 0.2733 0.2441 0.4446 0.107 Uiso 0.30 1 calc PR A 1
H2A3 H 0.2852 0.2506 0.3672 0.107 Uiso 0.30 1 calc PR A 1
O2A O 0.3309(6) 0.1016(14) 0.4315(7) 0.078(3) Uiso 0.30 1 d PD A 1
O2B O 0.2973(16) 0.109(4) 0.4371(18) 0.071(8) Uiso 0.10 1 d PD B 2
C2B C 0.317(6) 0.081(16) 0.375(5) 0.22(5) Uiso 0.10 1 d PD B 2
C2C C 0.3064(6) 0.281(2) 0.4181(11) 0.155(7) Uiso 0.60 1 d PD C 3
H2C1 H 0.3017 0.3612 0.4519 0.232 Uiso 0.60 1 calc PR C 3
H2C2 H 0.2719 0.2226 0.4025 0.232 Uiso 0.60 1 calc PR C 3
H2C3 H 0.3157 0.3296 0.3768 0.232 Uiso 0.60 1 calc PR C 3
O2C O 0.3498(2) 0.1794(7) 0.4516(3) 0.0792(15) Uiso 0.60 1 d PD C 3

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C1 0.047(2) 0.071(2) 0.0412(19) -0.0033(17) 0.0112(16) 0.0060(18)
C36 0.069(2) 0.052(2) 0.0371(18) 0.0005(14) 0.0207(17) 0.0070(17)
C10 0.0511(19) 0.0450(17) 0.0351(17) -0.0017(13) 0.0107(15) -0.0016(14)
N1 0.064(2) 0.142(4) 0.051(2) -0.008(2) 0.0256(19) 0.004(2)
C33 0.102(3) 0.072(3) 0.0341(19) -0.0024(18) 0.026(2) -0.006(2)
C32 0.091(3) 0.052(2) 0.0394(19) -0.0032(15) 0.020(2) -0.006(2)
C31 0.0424(17) 0.0502(18) 0.0319(16) 0.0032(13) 0.0122(13) 0.0021(14)
O10 0.064(2) 0.0376(17) 0.068(2) 0.000 -0.0161(19) 0.000
C11 0.0453(18) 0.0432(17) 0.0354(16) -0.0050(13) 0.0140(14) 0.0013(14)
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C16 0.054(2) 0.054(2) 0.058(2) -0.0043(18) 0.0140(18) -0.0013(18)
C34 0.085(3) 0.066(2) 0.046(2) 0.0165(19) 0.026(2) 0.013(2)
C35 0.095(3) 0.048(2) 0.056(2) 0.0055(17) 0.032(2) 0.008(2)
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C22 0.052(2) 0.092(3) 0.054(2) -0.002(2) 0.0182(19) -0.006(2)
C26 0.049(2) 0.130(4) 0.068(3) 0.029(3) 0.008(2) 0.000(3)
C24 0.052(3) 0.140(5) 0.118(5) 0.010(4) 0.037(3) 0.003(3)
C23 0.055(3) 0.120(4) 0.080(3) -0.005(3) 0.030(2) -0.014(3)
C25 0.044(3) 0.185(7) 0.115(5) 0.044(5) 0.004(3) 0.017(3)
C13 0.092(3) 0.0473(19) 0.0390(19) 0.0013(15) 0.022(2) 0.006(2)
C15 0.058(3) 0.060(2) 0.088(3) -0.007(2) 0.035(2) -0.010(2)
C14 0.097(3) 0.054(2) 0.069(3) 0.002(2) 0.052(3) -0.005(2)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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Pd1 P1 2.3372(8) . ?
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P1 C31 1.822(3) . ?
P1 C21 1.834(4) . ?
P1 C10 1.842(3) . ?
C21 C26 1.378(6) . ?
C21 C22 1.369(5) . ?
C1 N1 1.129(5) . ?
C36 C31 1.378(4) . ?
C36 C35 1.389(5) . ?
C10 C11 1.507(4) . ?
C33 C32 1.373(5) . ?
C33 C34 1.375(6) . ?
C32 C31 1.381(5) . ?
O10 C12 1.380(4) . ?
O10 C12 1.380(4) 6_656 ?
C11 C12 1.378(5) . ?
C11 C16 1.391(5) . ?
C12 C13 1.389(5) . ?
C16 C15 1.391(6) . ?
C34 C35 1.349(5) . ?
C22 C23 1.400(6) . ?
C26 C25 1.400(6) . ?
C24 C23 1.339(8) . ?
C24 C25 1.364(8) . ?
C13 C14 1.378(6) . ?
C15 C14 1.384(6) . ?
C2A O2A 1.368(9) . ?
O2B C2B 1.403(12) . ?
C2C O2C 1.393(9) . ?

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C1 Pd1 P1 95.39(11) 6_656 6_656 ?
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C31 P1 Pd1 113.79(11) . . ?
C21 P1 Pd1 122.41(12) . . ?
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C26 C21 P1 121.2(3) . . ?
C22 C21 P1 120.3(3) . . ?
N1 C1 Pd1 177.0(4) . . ?
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C11 C10 P1 115.8(2) . . ?
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C33 C32 C31 120.6(4) . . ?
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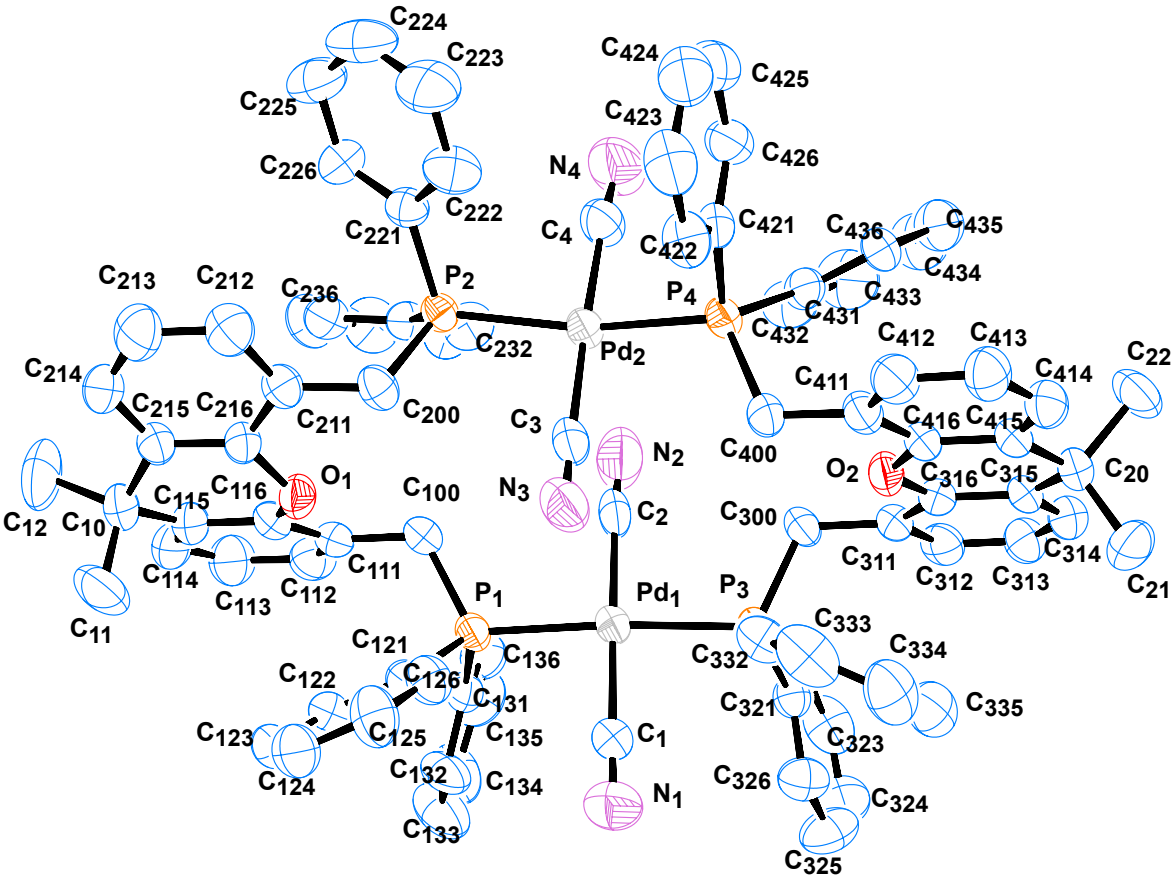
12.2 CIF de la estructura cristal·lina de [(XantMephos)Pd(CN)$_2$]$_2$ (C38)

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 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
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C112 0.059(5) 0.059(4) 0.064(4) 0.013(3) 0.023(4) 0.013(3)
C113 0.072(5) 0.068(5) 0.073(5) 0.022(4) 0.026(4) 0.029(4)
C114 0.054(4) 0.061(4) 0.072(5) 0.016(3) 0.023(4) 0.027(3)
C115 0.050(4) 0.044(3) 0.069(4) 0.009(3) 0.027(3) 0.018(3)
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C124 0.076(5) 0.071(5) 0.063(5) -0.011(4) 0.038(4) 0.016(4)
C125 0.099(6) 0.070(5) 0.062(5) 0.010(4) 0.048(5) 0.032(4)
C126 0.068(5) 0.051(4) 0.055(4) 0.010(3) 0.030(3) 0.017(3)
C131 0.051(4) 0.044(3) 0.060(4) 0.008(3) 0.031(3) 0.014(3)
C132 0.089(6) 0.047(4) 0.098(6) -0.005(4) 0.068(5) -0.006(4)
C133 0.151(10) 0.058(5) 0.133(9) 0.005(5) 0.111(8) 0.002(5)
C134 0.145(9) 0.069(5) 0.110(7) 0.026(5) 0.101(7) 0.030(6)
C135 0.096(7) 0.116(8) 0.075(6) 0.026(5) 0.058(5) 0.034(6)
C136 0.067(5) 0.073(5) 0.064(5) 0.009(4) 0.037(4) 0.017(4)
C2 0.063(5) 0.049(4) 0.085(5) -0.006(4) 0.027(4) 0.029(4)
C20 0.050(4) 0.035(3) 0.076(4) 0.008(3) 0.029(3) 0.016(3)
C200 0.054(4) 0.039(3) 0.040(3) 0.005(2) 0.014(3) 0.015(3)
C21 0.047(4) 0.074(5) 0.097(6) 0.027(4) 0.023(4) 0.024(4)
C211 0.052(4) 0.045(3) 0.038(3) 0.000(2) 0.020(3) 0.012(3)
C212 0.076(5) 0.063(4) 0.055(4) 0.008(3) 0.039(4) 0.018(4)
C213 0.087(6) 0.074(5) 0.080(6) 0.004(4) 0.055(5) 0.024(4)
C214 0.063(5) 0.060(4) 0.074(5) -0.004(3) 0.041(4) 0.017(3)
C215 0.046(3) 0.043(3) 0.054(4) -0.003(3) 0.019(3) 0.013(3)
C216 0.043(3) 0.043(3) 0.051(3) -0.002(2) 0.020(3) 0.013(3)
C22 0.096(6) 0.034(3) 0.118(7) -0.003(4) 0.070(6) 0.009(4)
C221 0.046(3) 0.043(3) 0.041(3) 0.002(2) 0.019(3) 0.006(2)
C222 0.072(5) 0.063(4) 0.055(4) 0.019(3) 0.029(4) 0.008(4)
C223 0.093(7) 0.081(6) 0.086(6) 0.025(5) 0.054(6) 0.010(5)
C224 0.075(6) 0.091(6) 0.074(5) -0.002(4) 0.042(5) -0.020(5)
C225 0.061(5) 0.089(6) 0.080(6) 0.003(4) 0.041(4) 0.000(4)
C226 0.048(4) 0.065(4) 0.072(5) 0.007(3) 0.031(4) 0.013(3)
C231 0.040(3) 0.044(3) 0.037(3) 0.011(2) 0.012(2) 0.010(2)
C232 0.066(5) 0.075(5) 0.043(4) 0.013(3) 0.027(3) 0.017(4)
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C233 0.088(6) 0.104(6) 0.045(4) 0.022(4) 0.030(4) 0.040(5)
C234 0.093(7) 0.088(6) 0.048(4) 0.027(4) 0.022(4) 0.029(5)
C235 0.088(6) 0.063(4) 0.058(4) 0.022(3) 0.025(4) 0.029(4)
C236 0.048(4) 0.054(4) 0.046(3) 0.010(3) 0.010(3) 0.014(3)
C3 0.055(4) 0.040(3) 0.075(5) 0.001(3) 0.020(4) 0.021(3)
C30 0.070(7) 0.113(9) 0.166(13) 0.055(9) 0.041(8) 0.015(6)
C300 0.051(4) 0.031(3) 0.058(4) 0.004(2) 0.019(3) 0.011(2)
C311 0.041(3) 0.035(3) 0.053(3) -0.001(2) 0.016(3) 0.008(2)
C312 0.058(4) 0.049(3) 0.049(4) -0.007(3) 0.022(3) 0.008(3)
C313 0.062(4) 0.054(4) 0.062(4) -0.001(3) 0.027(4) 0.016(3)
C314 0.053(4) 0.048(3) 0.072(5) -0.002(3) 0.027(3) 0.015(3)
C315 0.043(3) 0.030(3) 0.065(4) -0.003(2) 0.022(3) 0.008(2)
C316 0.038(3) 0.037(3) 0.051(3) 0.001(2) 0.016(3) 0.008(2)
C321 0.050(4) 0.042(3) 0.044(3) 0.010(2) 0.022(3) 0.015(3)
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C323 0.127(8) 0.071(5) 0.070(5) 0.020(4) 0.064(6) 0.030(5)
C324 0.085(7) 0.086(6) 0.096(7) 0.021(5) 0.057(6) 0.014(5)
C325 0.059(5) 0.099(6) 0.092(7) 0.026(5) 0.039(5) 0.007(5)
C326 0.062(5) 0.062(4) 0.063(4) 0.010(3) 0.025(4) 0.006(3)
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C335 0.074(5) 0.064(5) 0.063(5) 0.013(4) 0.009(4) 0.025(4)
C336 0.060(4) 0.053(4) 0.054(4) 0.003(3) 0.014(3) 0.022(3)
C4 0.057(4) 0.050(4) 0.059(4) 0.003(3) 0.011(3) 0.016(3)
C40 0.39(3) 0.069(10) 0.23(2) 0.042(13) 0.04(2) 0.009(13)
C400 0.045(3) 0.039(3) 0.053(3) -0.002(2) 0.019(3) 0.014(3)
C411 0.047(3) 0.036(3) 0.047(3) 0.005(2) 0.015(3) 0.012(2)
C412 0.055(4) 0.053(4) 0.050(4) 0.007(3) 0.013(3) 0.015(3)
C413 0.061(4) 0.058(4) 0.055(4) 0.010(3) 0.018(3) 0.023(3)
C414 0.051(4) 0.048(3) 0.060(4) 0.011(3) 0.016(3) 0.018(3)
C415 0.041(3) 0.031(3) 0.064(4) 0.001(2) 0.017(3) 0.008(2)
C416 0.041(3) 0.031(3) 0.054(3) 0.003(2) 0.017(3) 0.009(2)
C421 0.052(4) 0.041(3) 0.045(3) 0.011(2) 0.027(3) 0.020(3)
C422 0.074(5) 0.060(4) 0.046(4) 0.007(3) 0.029(3) 0.024(4)
C423 0.108(7) 0.071(5) 0.068(5) 0.024(4) 0.056(5) 0.038(5)
C424 0.100(7) 0.073(5) 0.101(7) 0.031(5) 0.072(6) 0.031(5)
C425 0.085(6) 0.057(4) 0.099(6) 0.011(4) 0.058(5) 0.012(4)
C426 0.061(4) 0.048(4) 0.067(4) 0.001(3) 0.032(4) 0.007(3)
C431 0.045(3) 0.048(3) 0.048(3) -0.006(2) 0.023(3) 0.010(3)
C432 0.073(5) 0.076(5) 0.054(4) -0.001(3) 0.037(4) 0.007(4)
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C434 0.110(8) 0.088(7) 0.121(9) -0.035(6) 0.074(7) 0.010(6)
C435 0.080(6) 0.065(5) 0.111(7) -0.030(5) 0.056(5) 0.010(4)
C436 0.057(4) 0.037(3) 0.093(5) -0.012(3) 0.034(4) 0.009(3)
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N4 0.079(5) 0.077(5) 0.101(6) -0.018(4) 0.000(5) 0.014(4)
O1 0.053(3) 0.044(2) 0.071(3) 0.017(2) 0.035(2) 0.022(2)
O2 0.053(3) 0.038(2) 0.063(3) 0.0137(18) 0.032(2) 0.0199(18)
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O4 0.37(2) 0.47(2) 0.172(15) -0.001(15) -0.016(18) 0.086(18)
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P4 0.0450(8) 0.0331(7) 0.0392(7) 0.0014(5) 0.0164(6) 0.0115(6)
Pd1 0.0455(3) 0.0347(2) 0.0449(3) 0.00268(17) 0.0198(2) 0.01174(18)
Pd2 0.0431(3) 0.0352(2) 0.0382(2) 0.00282(16) 0.01309(19) 0.01209(18)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
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C20 C21 1.534(10) . ?
C20 C315 1.524(9) . ?
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P1 Pd1 2.3415(15) . ?
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C431 P4 Pd2 118.2(2) . . ?
C421 P4 Pd2 101.88(19) . . ?
C400 P4 Pd2 115.51(19) . . ?
C1 Pd1 C2 177.2(3) . . ?
C1 Pd1 P3 88.7(2) . . ?
C2 Pd1 P3 90.65(19) . . ?
C1 Pd1 P1 90.3(2) . . ?
C2 Pd1 P1 89.89(19) . . ?
P3 Pd1 P1 172.04(6) . . ?
C4 Pd2 C3 177.0(3) . . ?
C4 Pd2 P4 89.6(2) . . ?
C3 Pd2 P4 89.27(19) . . ?
C4 Pd2 P2 88.9(2) . . ?
C3 Pd2 P2 93.07(19) . . ?
P4 Pd2 P2 163.28(6) . . ?

_diffrn_measured_fraction_theta_max    0.826
_diffrn_reflns_theta_full              29.49
_diffrn_measured_fraction_theta_full   0.826
_refine_diff_density_max    1.876
_refine_diff_density_min   -0.998
_refine_diff_density_rms    0.155
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