Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Preparation of carboxylic-trifluoromethylated phosphines by hydrolysis of the trifluoromethyl group

Daniel Herrera, Daniel Peral, J. Carles Bayón*

Department of Chemistry, Universitat Autònoma de Barcelona, Bellaterra, Spain

Experiment 1

[**SP1**] = 0.15 M

[H_3BO_3] = 0.8 M

[SO_3] = 10.5 M

Experiment 2

[**SP1**] = 0.15 M

[H_3BO_3] = 0.8 M

[SO_3] = 12 M

Experiment 3

[**SP1**] = 0.15 M

[H_3BO_3] = 2.0 M

[SO_3] = 12 M

Experiment 4

[**SP1**] = 0.15 M

[H_3BO_3] = 2.4 M

[SO_3] = 10.5 M

Experiment 5

[**SP1**] = 0.10 M

[H_3BO_3] = 1.5 M

[SO_3] = 7 M

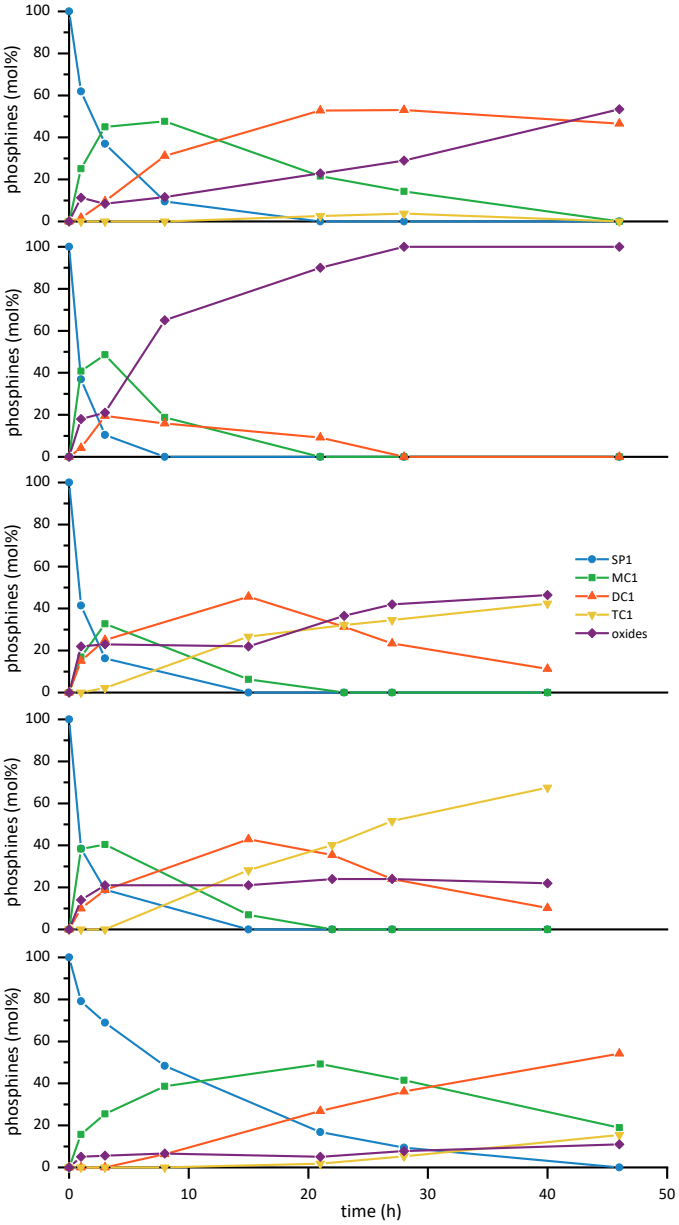


Figure S1. Optimization of reaction conditions for the hydrolysis of phosphine SP1. Products extracted with Et_2O from the aqueous phase after quenching in water. % of compounds correspond to the integration of the phosphorus products in $^{31}P\{^1H\}$ NMR. [SP1] = 0.15 M, [H_3BO_3] = 0.8 M, [SO_3] = 10.5 M was used in the experiments

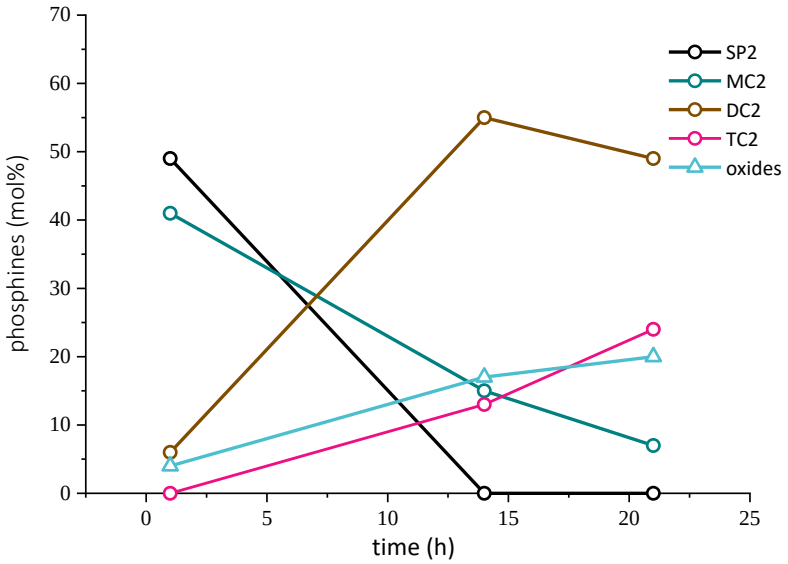


Figure S2. Optimization of reaction conditions for the hydrolysis of phosphine SP2. Products extracted with Et_2O from the aqueous phase after quenching in water. % of compounds correspond to the integration of the phosphorus products in $^{31}P\{^1H\}$ NMR. 0.6 mmol of starting phosphine SP2 were used in the experiments

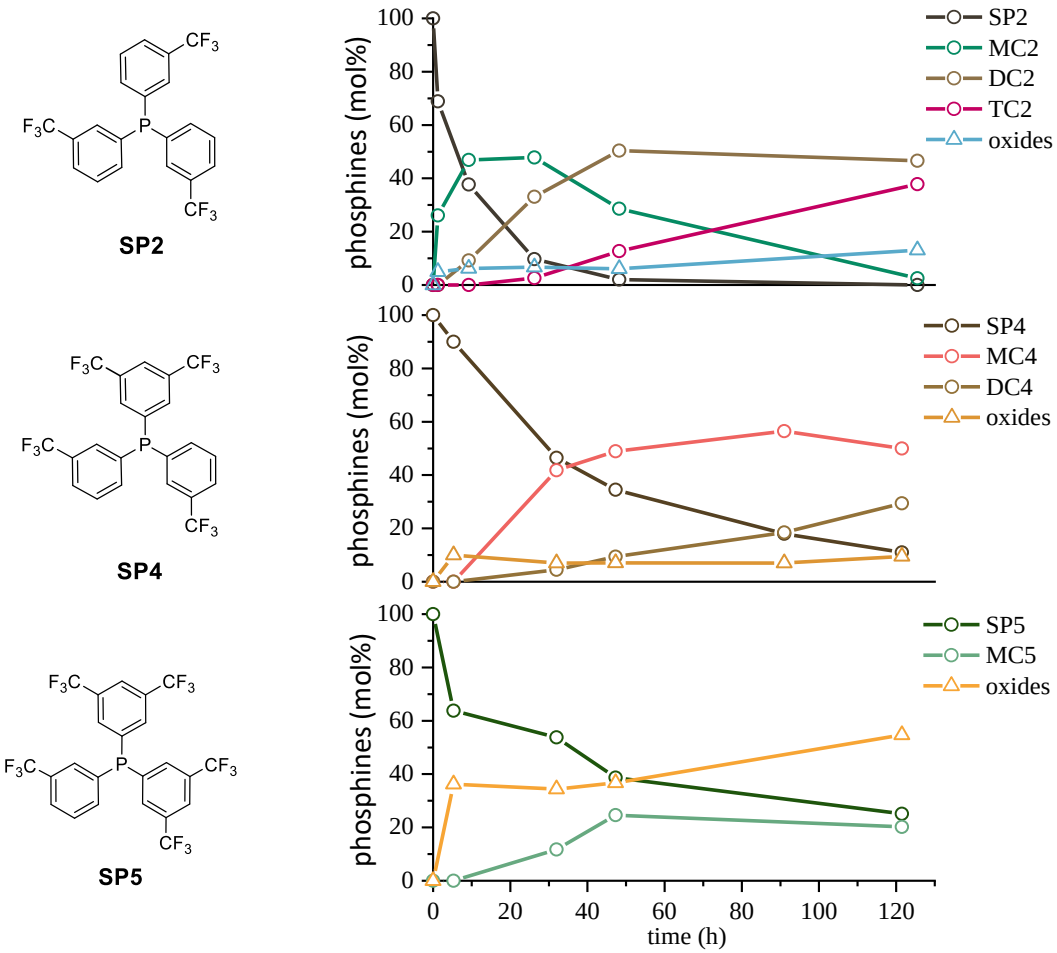


Figure S3. Evolution of the reaction of hydrolysis in phosphines SP2, SP4 and SP5 with time. Products extracted with Et_2O form the aqueous phase after quenching in water. % of compounds correspond to the integration of the phosphorus products in $^{31}P\{^1H\}$ NMR. Reaction conditions:
0.6 mmol of phosphine. [Phosphine] = 0.1 M, [H_3BO_3] = 0.5 M, [SO_3] = 6.7 M.

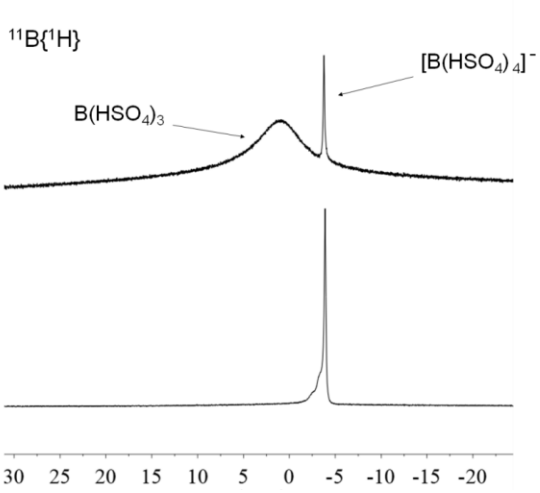


Figure S4. $^{11}B\{^{1}H\}$ NMR (128.38 MHz) of a solution of boric acid in sulfuric acid before (**top**) and after (**bottom**) the addition of oleum. δ in ppm. Signals relative to $BF_3.Et_2O$ (0.0 ppm) used as external standard)

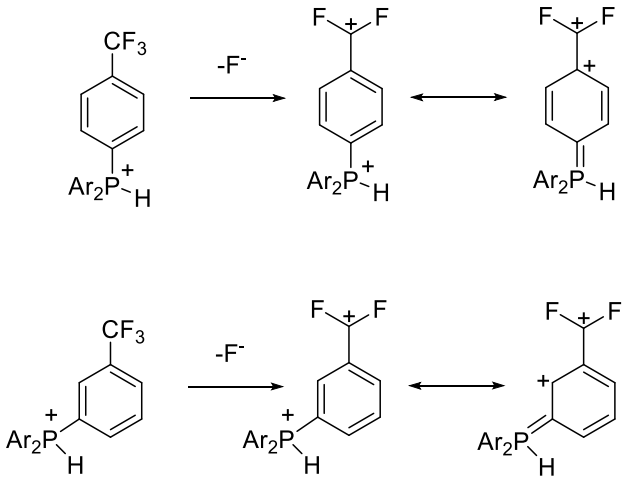


Figure S5. Delocalisation of the phosphonium positive charge.

Table S1. Values of $^{1}J_{PSe}$ for the selenide derivatives of the carboxylic and trifluoromethylated triarylphosphines and selected values from the literature

Phosphine	CF_3 groups	CO_2H groups	CO_2H subst. pattern	$^{1}J_{PSe}$ exp.[a]	$^{1}J_{PSe}$ calc.[b]
PPh_3	0	0	-	731	-
p-DPPBA[c]	0	1	*para*	740[d]	740
DC1	1	2	*para*	761	761
DC2	1	2	*meta*	761	761
MC1	2	1	*para*	764	764
MC2	2	1	*meta*	764	764
DC4	2	2	*meta*	773	773
SP1	3	0	-	766[d]	767
SP2	3	0	-	767[d]	767
MC4	3	1	*meta*	776	776
SP4	4	0	-	780[d]	779
MC5	4	1	*meta*	786	788
SP5	5	0	-	791[d]	791
SP3	6	0	-	800[d]	803

[a] Values obtained from the $^{31}P\{^{1}H\}$ in $CDCl_3$. See text for more details [b] Values estimated from **equation 2**. [c] *p*-(diphenylphosphino)benzoic acid. [d] Values from the literature [i]

General procedure for the synthesis of *trans*-$[PdCl_2L_2]$ of MC1 and MC2 ligands:

In an example reaction, 0.38 mmol of the corresponding carboxylic phosphine were dissolved in a mixture of 3 ml of acetonitrile and 1 ml of CH_2Cl_2. A solution of 0.19 mmol of palladium (II) chloride in 1 ml of acetonitrile was added to the solution of the phosphine and the mixture was stirred at 40 ºC for 1 h. After that time, the palladium complex precipitated as a yellow solid. The solution was cooled down to room temperature and the complex was collected by filtration and washed 3 times with acetonitrile. The MC2 complex showed high solubility in several solvents (CH_2Cl_2, Et_2O, acetone, CH_3CN and ethyl acetate) and could not be precipitated from the reaction mixture. Therefore, the solvent was vacuum evaporated and the yellow solid was recrystallised from CH_2Cl_2/cyclohexane.

Data for ***trans*-$[PdCl_2(MC1)_2]$**

$^{31}P\{^{1}H\}$ NMR (161.98 MHz, acetone- *d6*), δ (ppm): 25.50 (s). **^{1}H NMR** (400.13 MHz, acetone- *d6*), δ (ppm): 8.16 (d, 4H, $H_{C3}\{C_6H_4CO_2H\}$, $^{3}J_{HH}$ = 8.0 Hz); 7.99 (m, 12H, $H_{C2}\{C_6H_4CF_3\}$-$H_{C2}\{C_6H_4CO_2H\}$); 7.88 (d, 8H, $H_{C3}\{C_6H_4CF_3\}$, $^{3}J_{HH}$ = 8.0 Hz). **$^{19}F\{^{1}H\}$ NMR** (376.50 MHz, acetone- *d6*), δ (ppm): -62.54 (s). **HR-MS** (ESI^+ *m/z*) $[M+Na]^+$: calculated for $[C_{42}H_{26}Cl_2F_{12}O_4P_2PdNa]^+$ 1082.9419; found 1082.9386. **Elemental analysis**: calculated for $C_{42}H_{26}Cl_2F_{12}O_4P_2Pd$: C, 47.50; H, 2.47; found: C, 47.04; H, 2.41.

Data for ***trans*-[PdCl$_2$(MC2)$_2$]**

^{31}P{^{1}H} NMR (161.98 MHz, acetone-*d6*), δ (ppm): 26.37 (s). **^{1}H NMR** (400.13 MHz, acetone-*d6*), δ (ppm): 8.43 (m, 2H, $H_{C2}\{C_6H_4CF_3\}$); 8.25 (d, 2H, $H_{C4}\{C_6H_4CO_2H\}$, $^3J_{HH}$ = 7.8 Hz); 8.15 (m, 6H, $H_{C2}\{C_6H_4CF_3\}$-$H_{C6}\{C_6H_4CO_2H\}$); 8.02 (*pseudo*-q, 4H, $H_{C6}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.7, $^3J_{HP}$ = 6.0 Hz); 7.95 (d, 4H, $H_{C4}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.5 Hz); 7.79 (t, 4H, $H_{C5}\{C_6H_4CF_3\}$, $^3J_{HH}$ = 7.5 Hz); 7.73 (t, 2H, $H_{C5}\{C_6H_4CO_2H\}$, $^3J_{HH}$ = 7.8 Hz). **^{19}F{^{1}H} NMR** (376.50 MHz, acetone- *d6*), δ (ppm): -62.26 (s). **HR-MS** (ESI$^+$ *m/z*) [M+Na]$^+$: calculated for $[C_{42}H_{26}Cl_2F_{12}O_4P_2PdNa]^+$ 1082.9419; found 1082.9376. **Elemental analysis**: calculated for $C_{42}H_{26}Cl_2F_{12}O_4P_2Pd$: C, 47.50; H, 2.47; found: C, 47.32; H, 2.81.

Crystallographic data

An empirical absorption correction was applied to the gathered data (SADABS).[ii] The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXL-2013.[iii] Plot of the structures was obtained with ORTEP software included in the WinGX package.[iv]

X-ray diffraction data for ***trans*-[PdCl$_2$(MC1)$_2$]·acetone**

Crystals of good quality for X-ray diffraction were obtained by slow evaporation of a saturated solution of the complex in a mixture of acetone/n-hexane. The structure was solved by Direct methods. All non-hydrogen atoms were refined with anisotropic displacement thermal parameters. All hydrogen atoms were idealised and were positioned geometrically and refined using the riding model with $U_{iso}(H) = 1.2\ U_{eq}(C)$ for those attached to carbon and with $U_{iso}(H) = 1.2\ U_{eq}(O)$ for those of the OH group. The hydrogen atoms of the acetone molecule were also idealised and positioned geometrically but refined using the riding model with $U_{iso}(H) = 1.5\ U_{eq}(C)$. All the CF_3 groups were disordered over two different orientations. The following bond length and angle restrains (DFIX) were applied: C-F distance = 1.33(3); C_{ipso}-F distance = 2.33 (4). Moreover, F-F distances of the disordered F atoms were restrained to be equal within sd of 0.03 (with SADI command) and the Uij were restrained with DELU and SIMU instructions. All disordered atoms were refined anisotropically and the sum of the site occupation factors was restrained to 1.000. CCDC deposition number 2097178

Crystal data ***trans*-[PdCl$_2$(MC1)$_2$]·acetone**

Chemical formula	$C_{45}H_{32}F_{12}O_5P_2Pd$	a	15.3938(7)
Molecular weight	1119.94	b	15.6175(8)
Space group	Monoclinic, P 21/c	c	20.4211(10)
wavelength	0.71073 (Mo Kα)	α	90
Temperature	293(2) K	β	97.1070(10)
Volume	4871.8(4) Å^3	γ	90
Z	4	R[I>2σ(I)]	0.0475
S	1.029	wR2	0.1288

X-ray diffraction data for ***trans*-[$PdCl_2$(MC2)$_2$]**

Crystals of good quality for X-ray diffraction were obtained by slow diffusion of n-hexane into a solution of the complex in CH_2Cl_2. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic displacement thermal parameters. All hydrogen atoms were idealised and were positioned geometrically and refined using the riding model with $U_{iso}(H) = 1.2\ U_{eq}(C)$ for those attached to carbon and with $U_{iso}(H) = 1.2\ U_{eq}(O)$ for those of the OH group. Two of the CF_3 groups were disordered over two different orientations with the F atoms defined anisotropically. The following bond length and angle restrains (DFIX) were applied: C-F distance = 1.33(1); C_{ipso}-F distance = 2.33 (3). Moreover, F-F distances of the disordered F atoms were restrained to be equal within sd of 0.03 (with SADI command) and the sum of the site occupation factors was restrained to 1.000. The Uij were restrained with DELU and SIMU instructions. No restraints were imposed in the non-disordered CF_3 groups. Badly disordered solvent molecules were observed. The SQUEEZE instruction using PLATON[v] was tested with. no significant difference in bond distances and angles. (Parameters after SQUEEZE routine: R = 0.0703, wR2 = 0.1972, S = 0.986). CCDC deposition number 2106238.

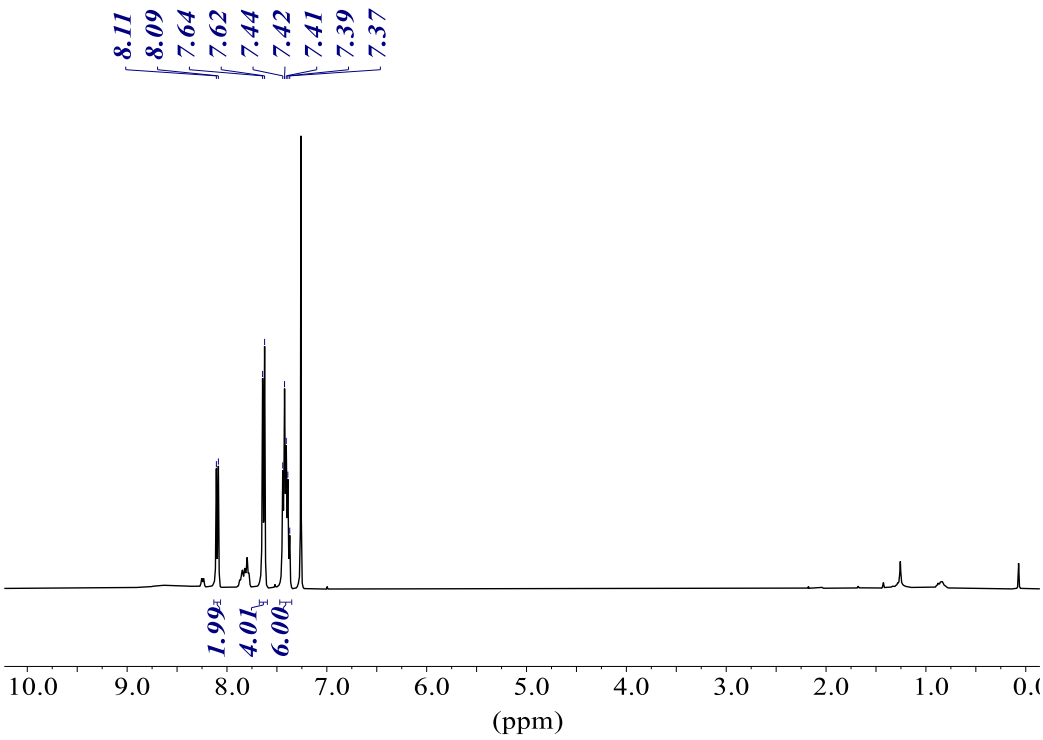
Crystal data ***trans*-[$PdCl_2$(MC2)$_2$]**

Chemical formula	$C_{42}H_{26}F_{12}O_4P_2Pd$	a	10.1026(5)
Molecular weight	1061.87	b	27.1594(13)
Space group	Orthorhombic, P bca	c	36.7299(17)
wavelength	0.71073 (Mo Kα)	α	90
Temperature	293(2) K	β	90
Volume	10078.0(8) Å^3	γ	90
Z	8	R[I>2σ(I)]	0.0832
S	1.028	wR2	0.2908

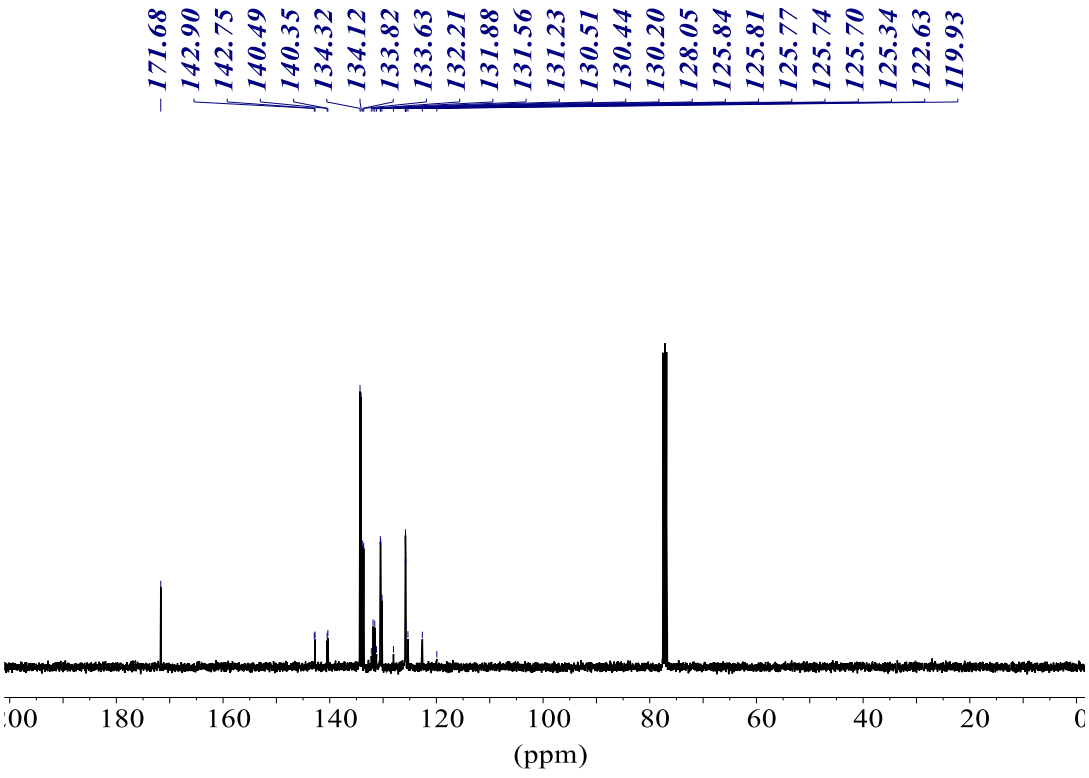
NMR spectra of phosphine compounds and derivatives

MC1

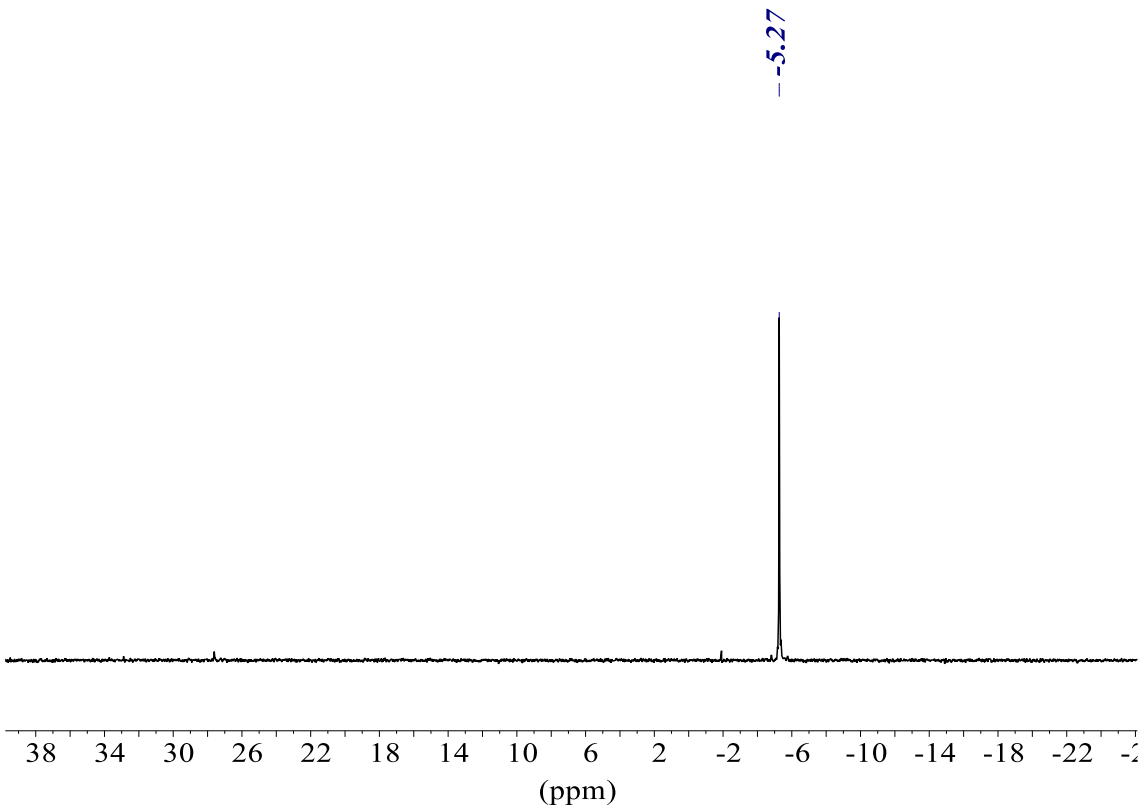
^{1}H (400.13 MHz, $CDCl_3$)



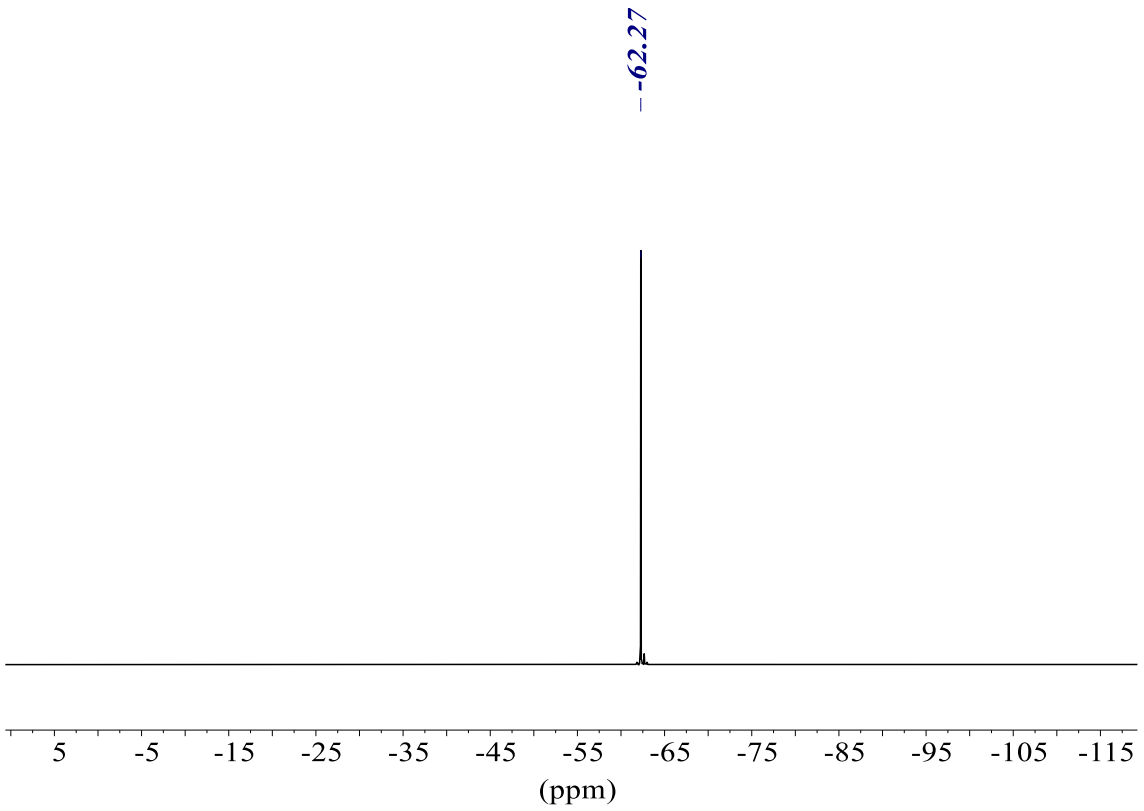
^{13}C{^{1}H} (100.61 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ (101.27 MHz, $CDCl_3$)

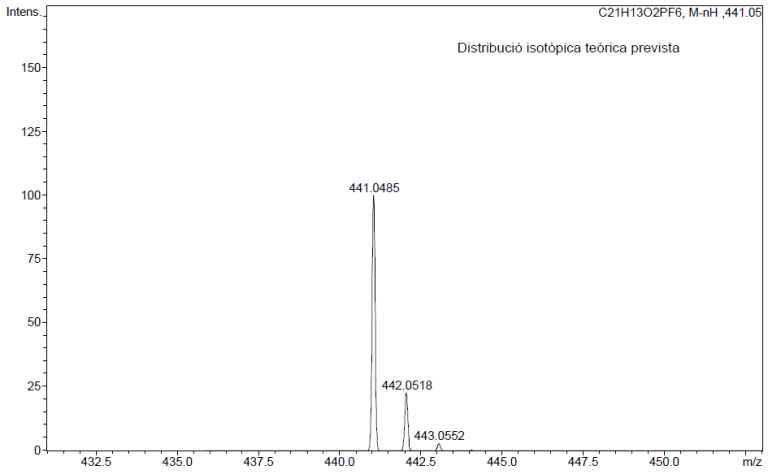


$^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$)



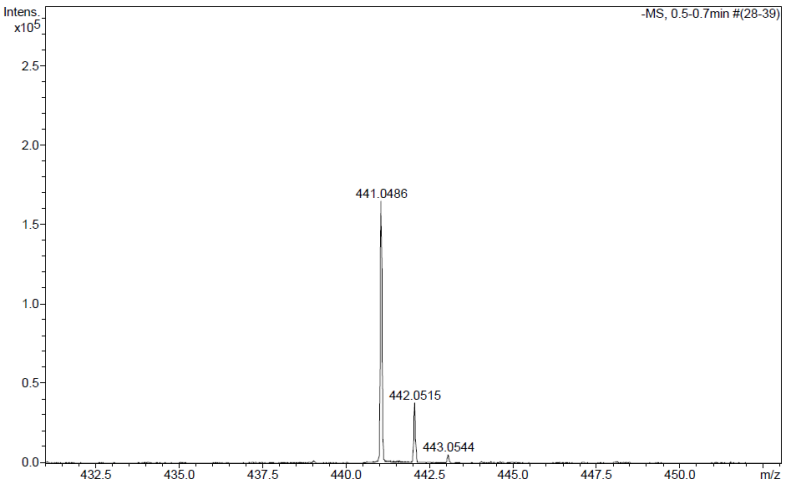
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{21}H_{12}F_6O_2P]^-$



#	m/z	I	I %
1	441.0485	100	100.0
2	442.0518	23	22.9
3	443.0552	3	2.9

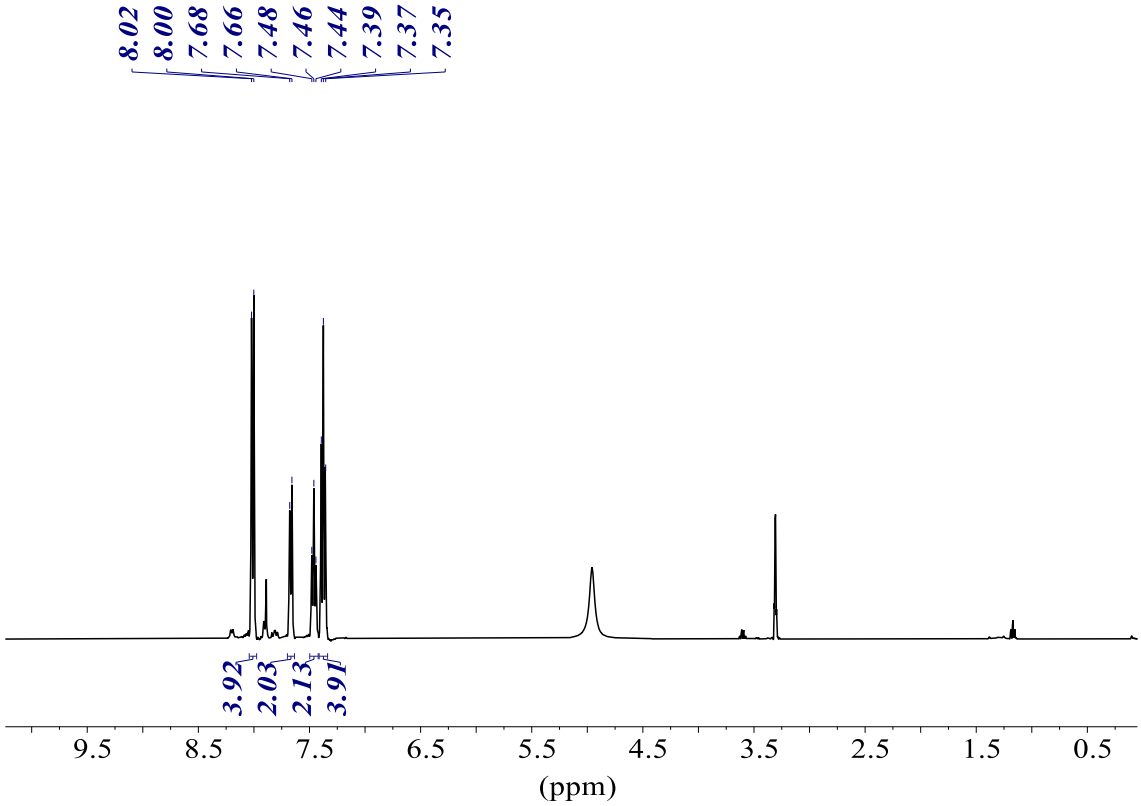
found



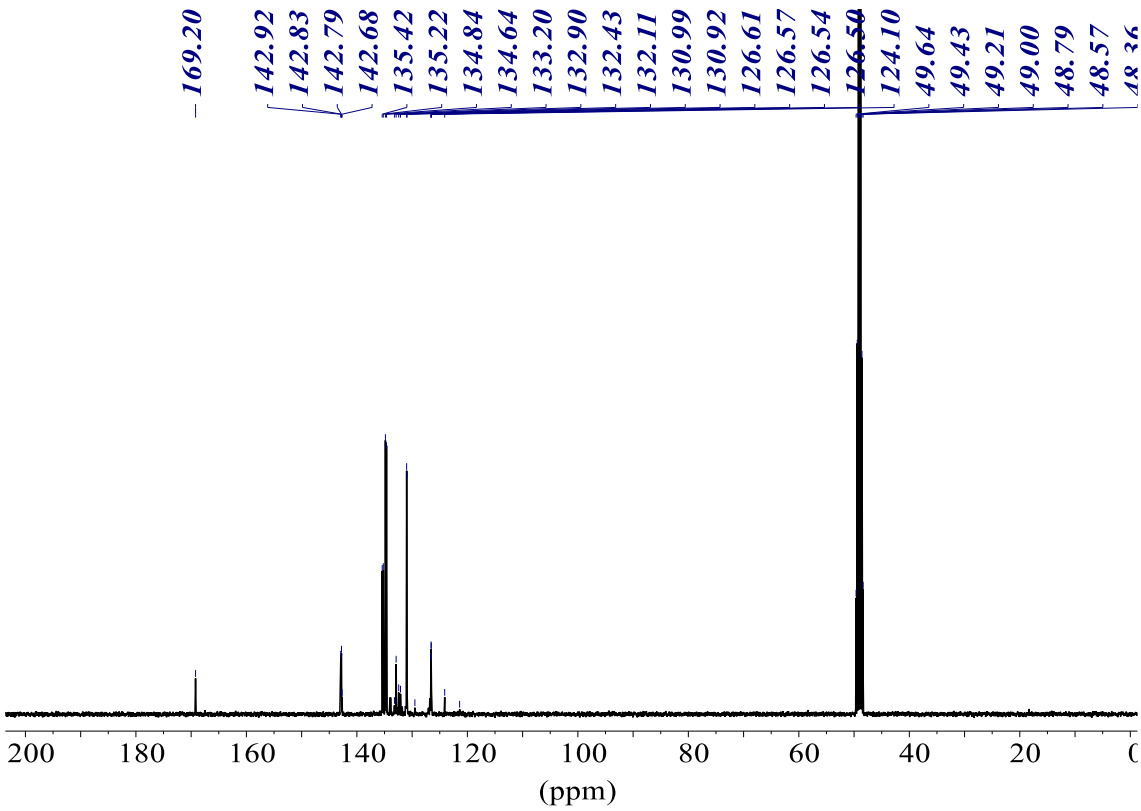
#	m/z	I	I %
1	441.0486	164644	100.0
2	442.0515	37951	23.1
3	443.0544	5198	3.2

DC1

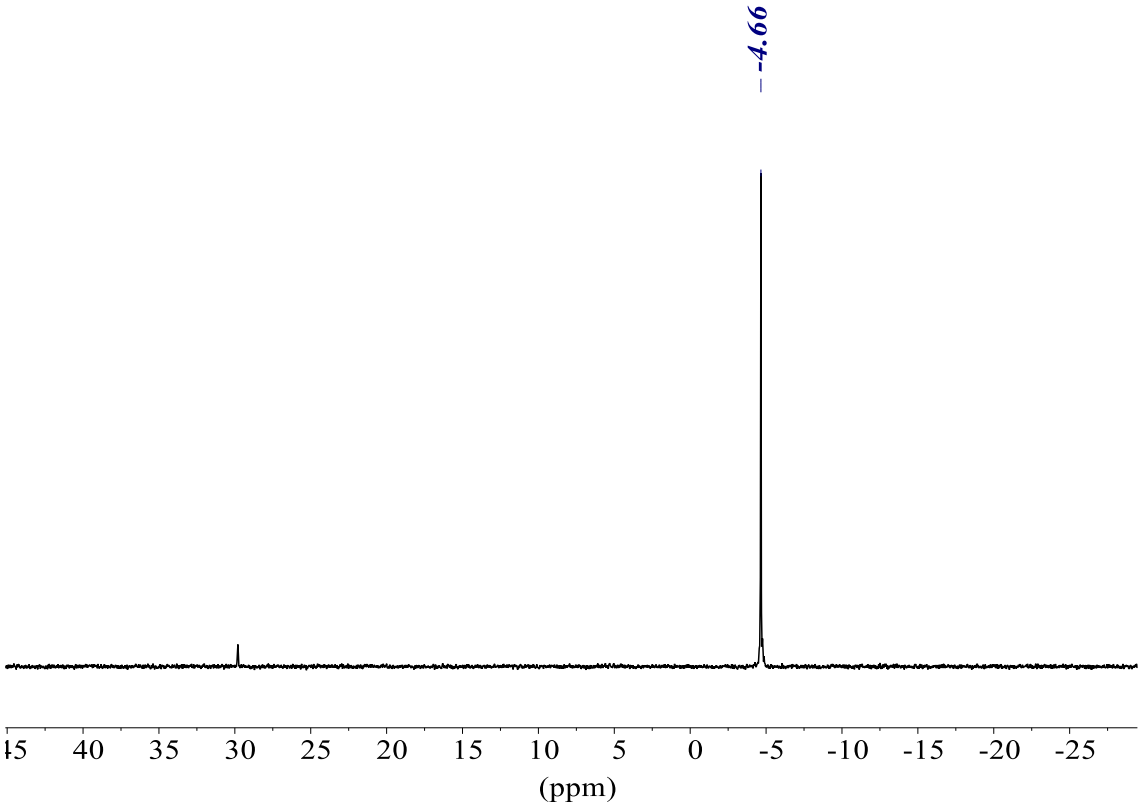
^{1}H (400.13 MHz, CD_3OD)



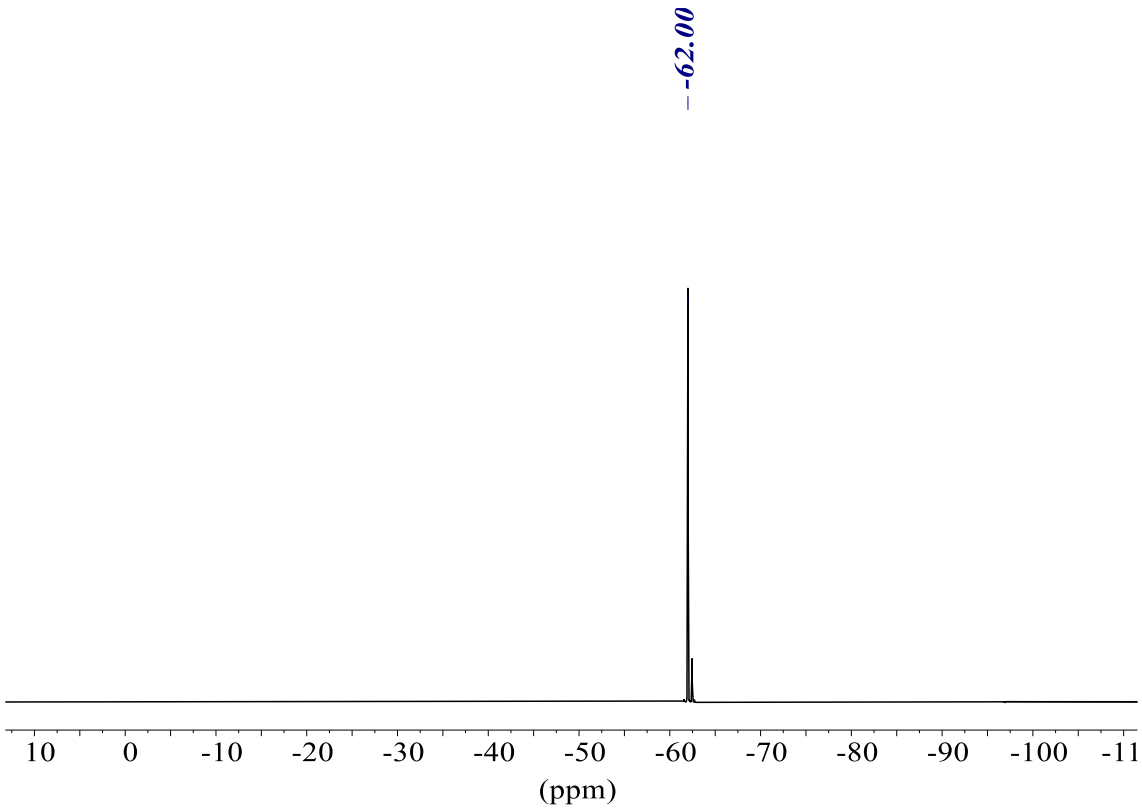
^{13}C{^{1}H} (100.61 MHz, CD_3OD)



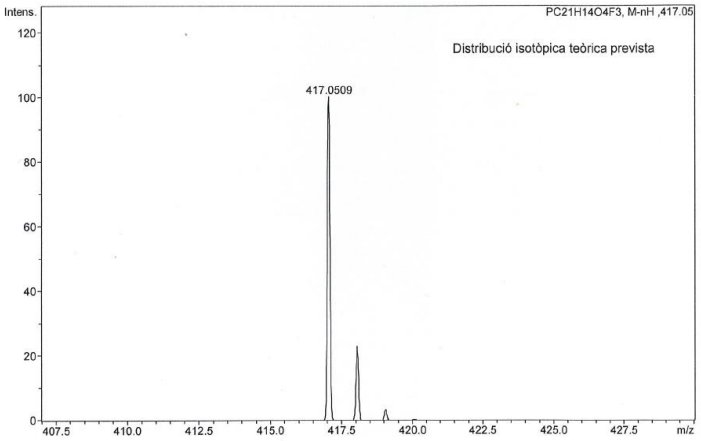
$^{31}P\{^{1}H\}$(101.27 MHz, CD_3OD)



$^{19}F\{^{1}H\}$ (235.39 MHz, CD_3OD)

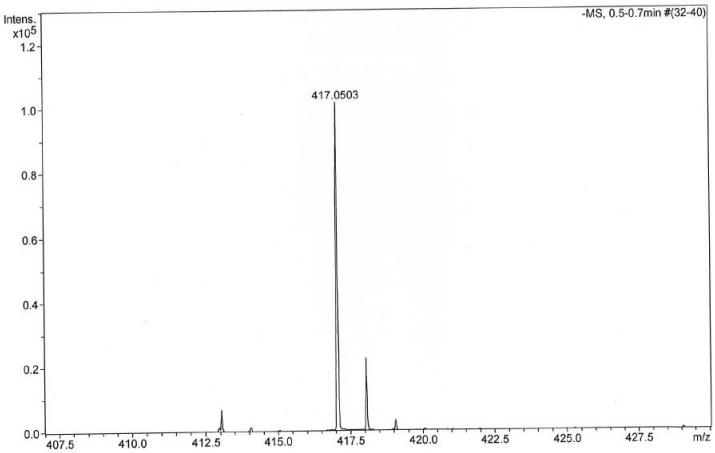


HR-MS (ESI$^-$ *m/z*) [M-H]$^-$



#	m/z	I	I %
1	417.0509	100	100.0
2	418.0543	23	23.0
3	419.0576	3	3.3

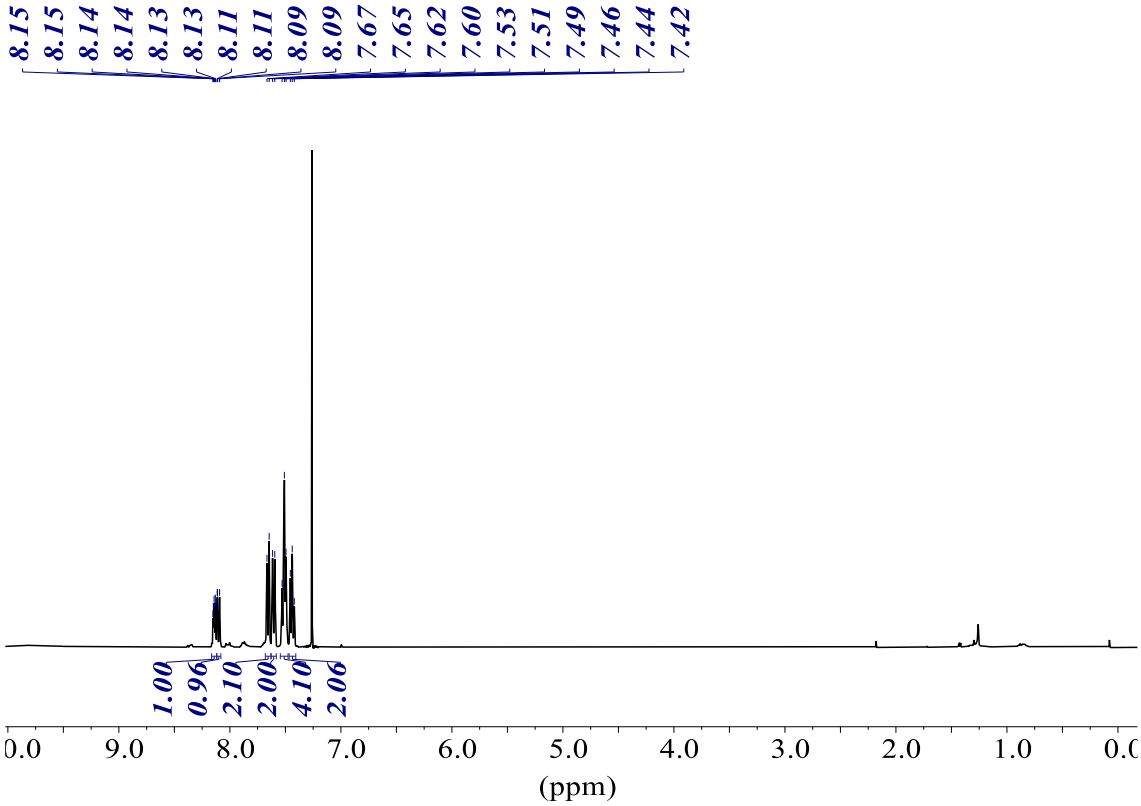
found



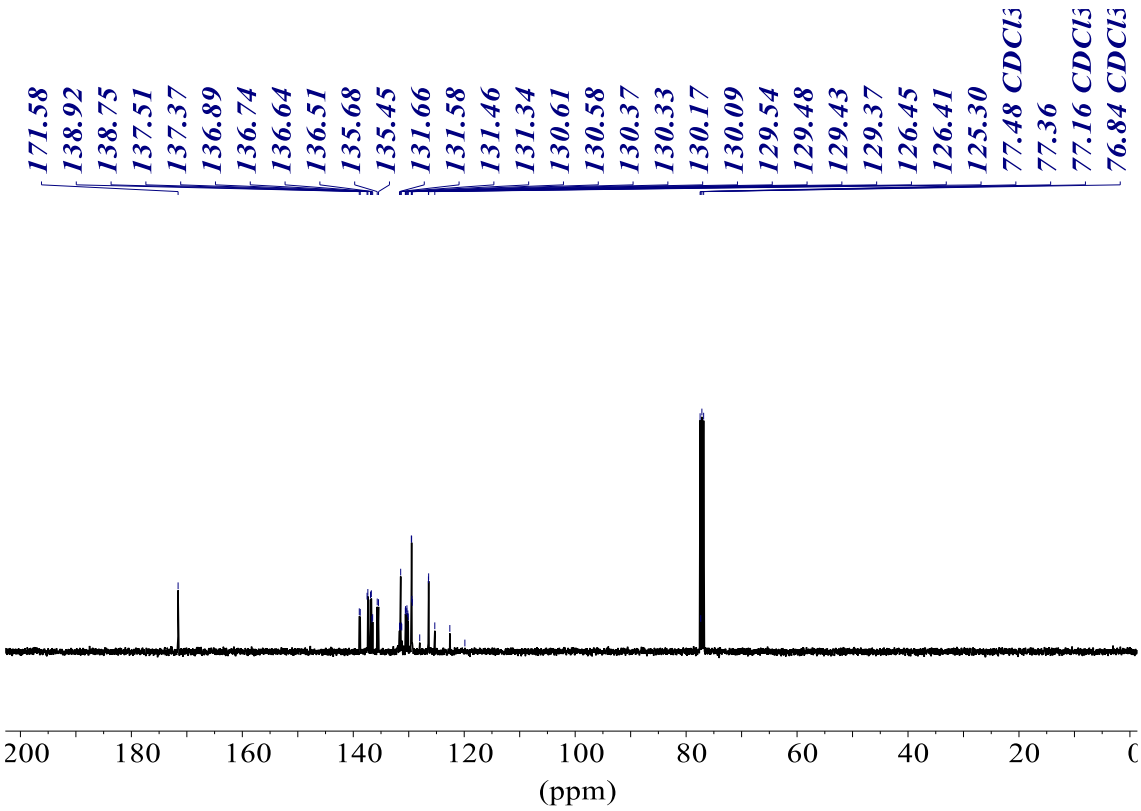
#	m/z	I	I %
1	417.0503	101686	100.0
2	418.0529	22379	22.0
3	419.0556	3231	3.2

MC2

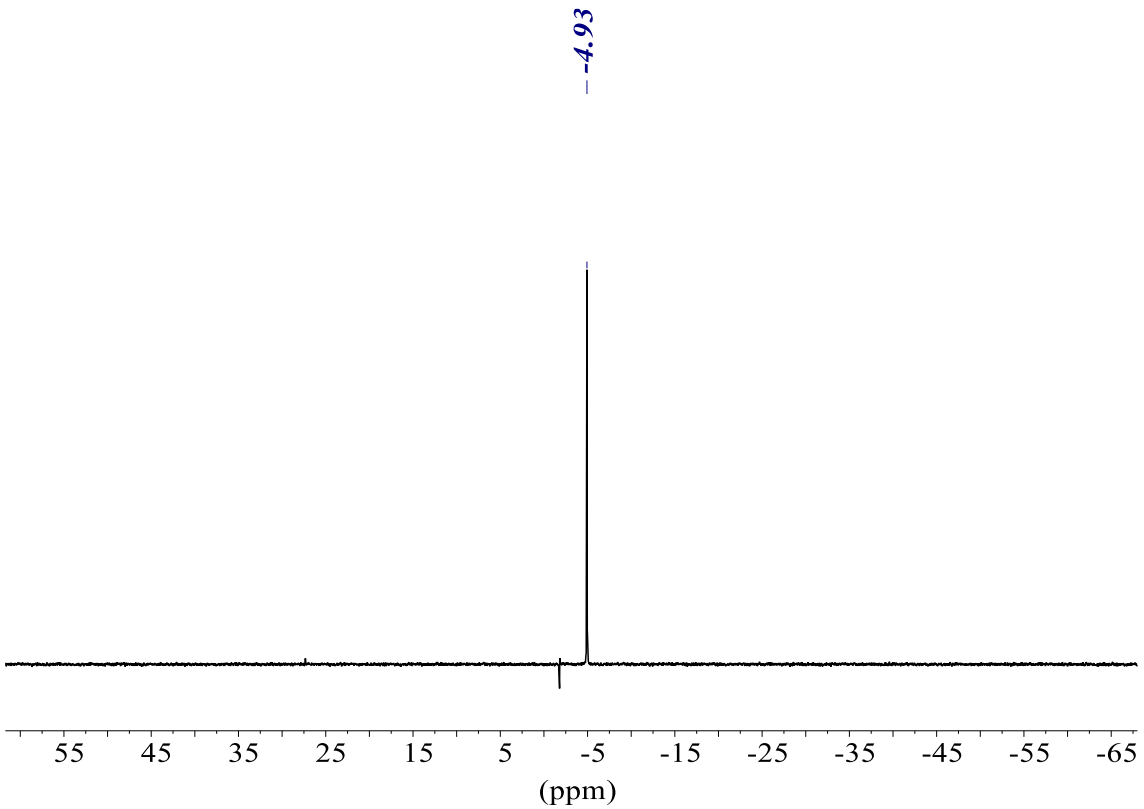
^{1}H (400.13 MHz, $CDCl_3$)



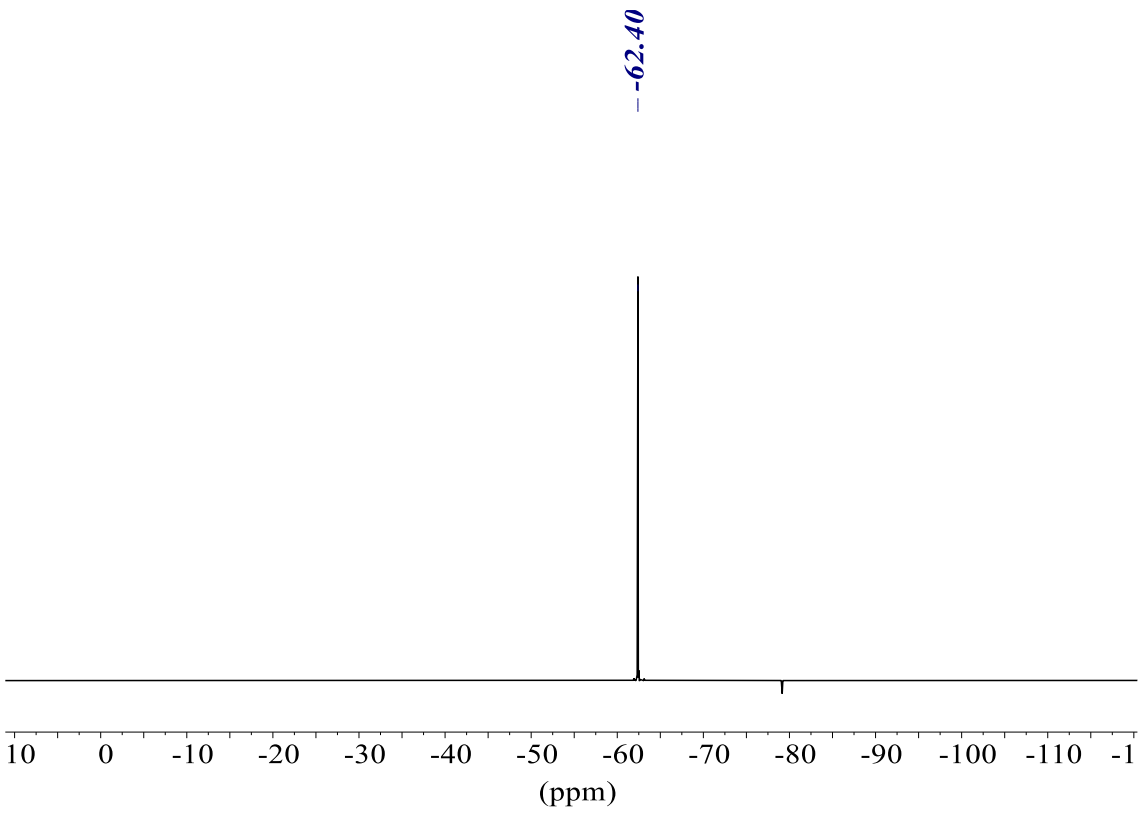
^{13}C{^{1}H} (100.61 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$(101.27 MHz, $CDCl_3$)

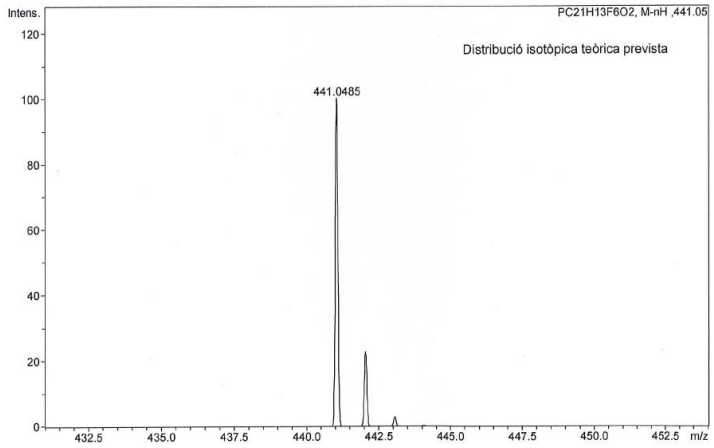


$^{19}F\{^{1}H\}$ (235.39 MHz, $CDCl_3$)



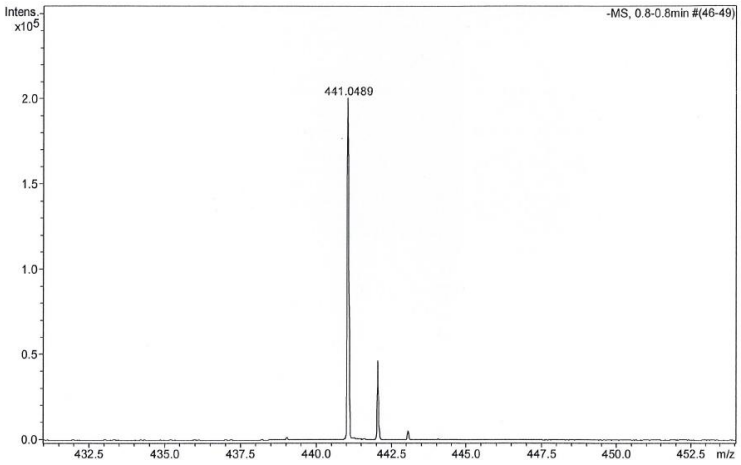
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{21}H_{12}F_6O_2P]^-$



#	m/z	I	I %
1	441.0485	100	100.0
2	442.0518	23	22.9
3	443.0552	3	2.9

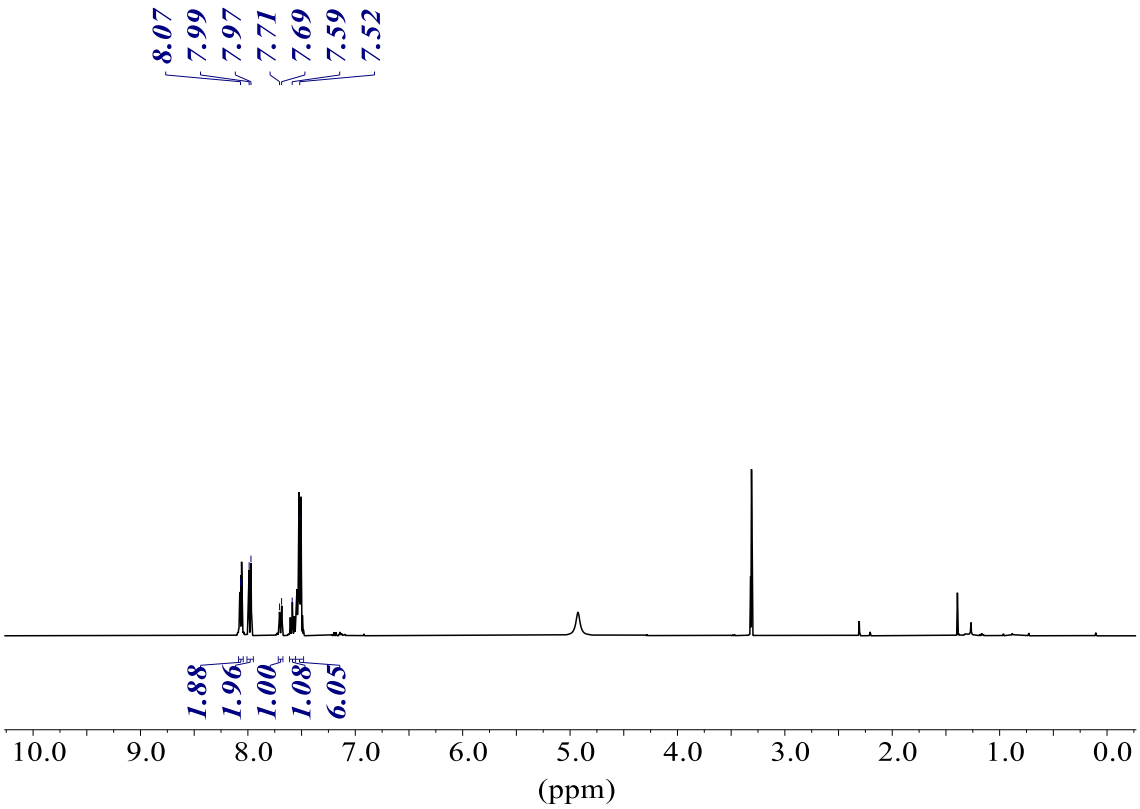
found



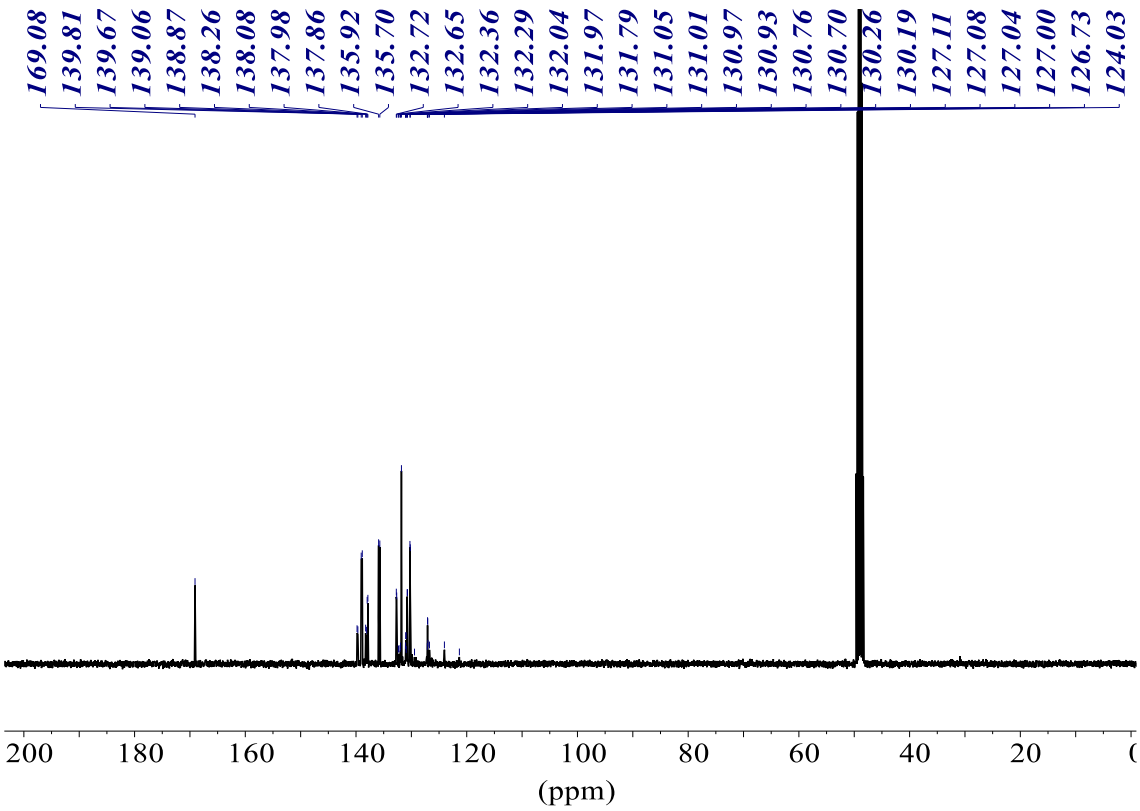
#	m/z	I	I %
1	441.0489	200125	100.0
2	442.0512	46380	23.2
3	443.0547	5585	2.8

DC2

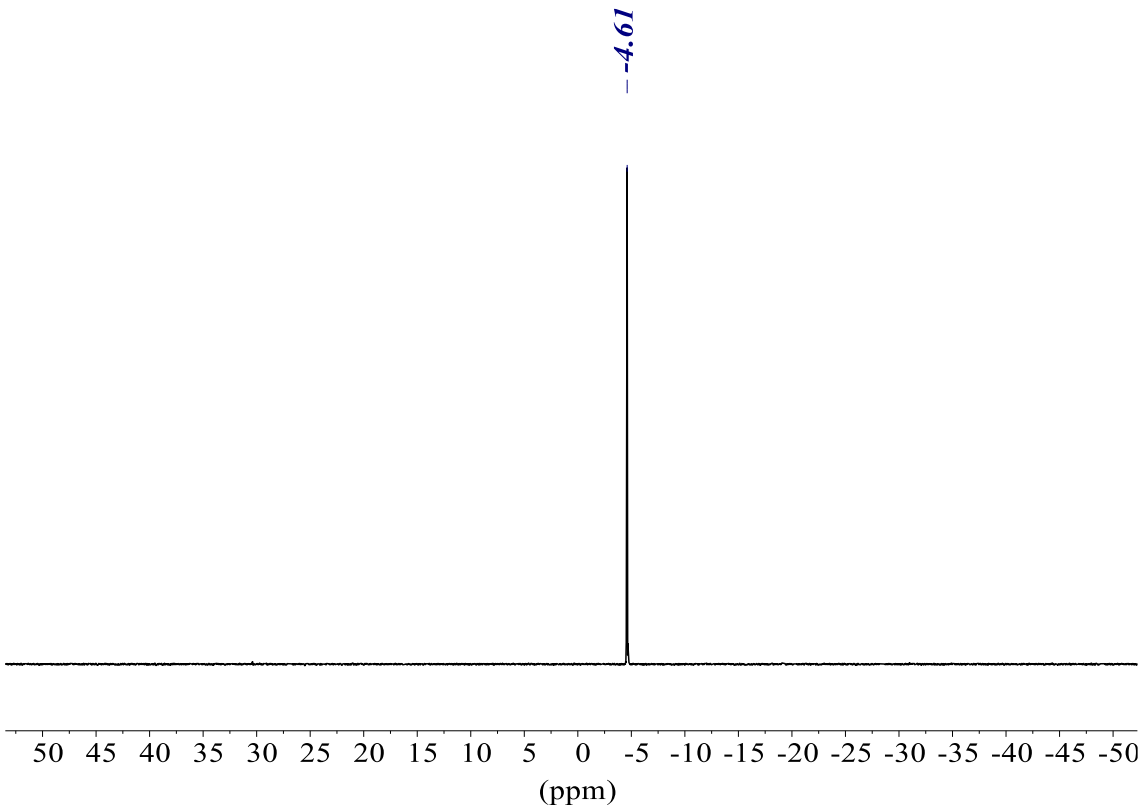
^{1}H (400.13 MHz, CD_3OD)



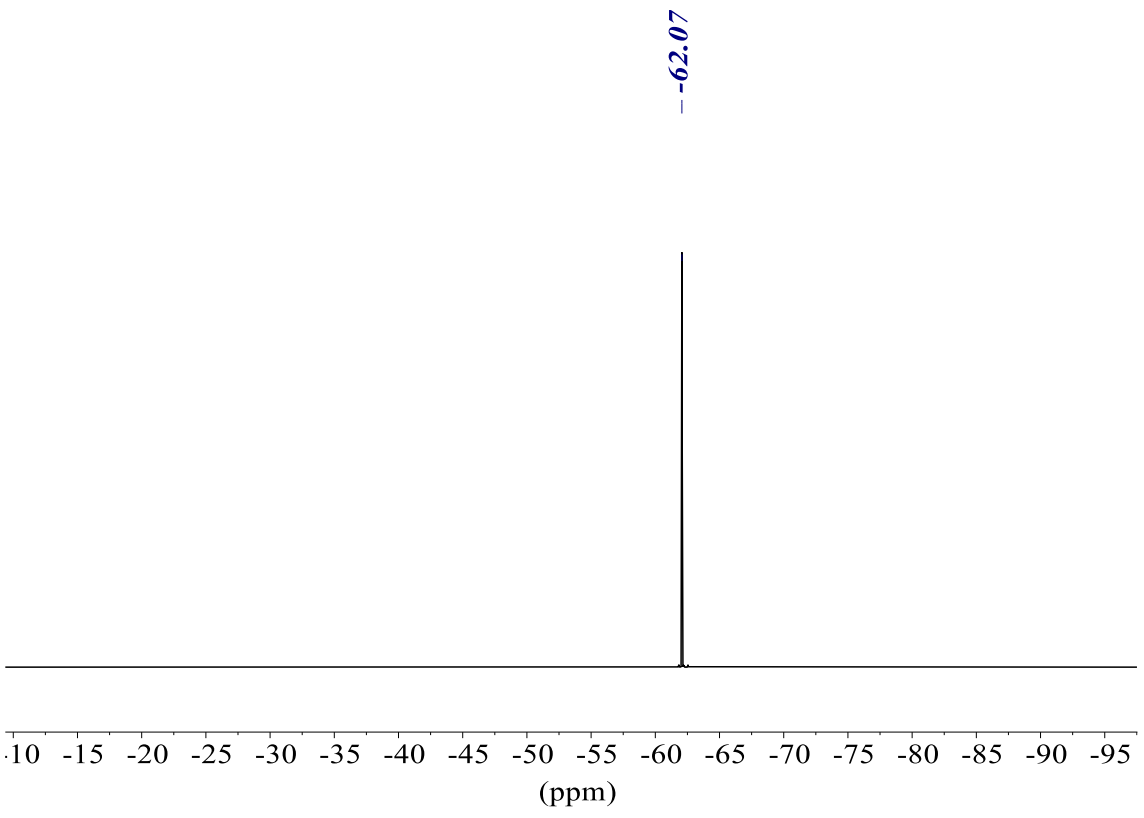
^{13}C{^{1}H} (100.61 MHz, CD_3OD)



$^{31}P\{^{1}H\}$ (161.98 MHz CD_3OD)

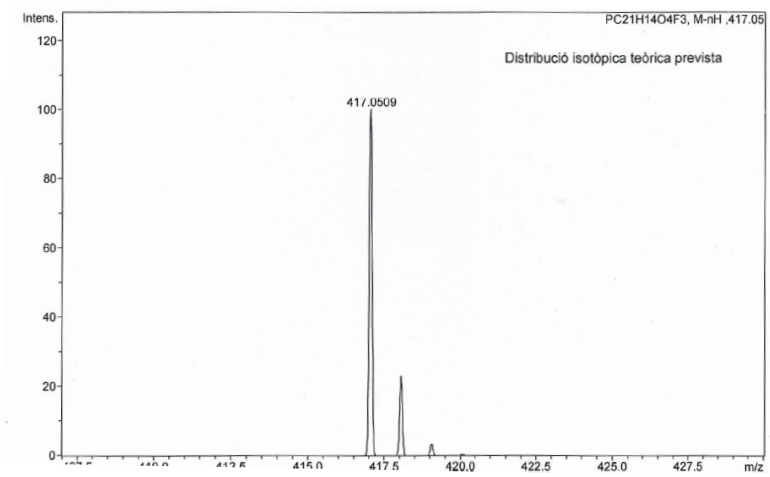


$^{19}F\{^{1}H\}$ (376.50 MHz, CD_3OD)



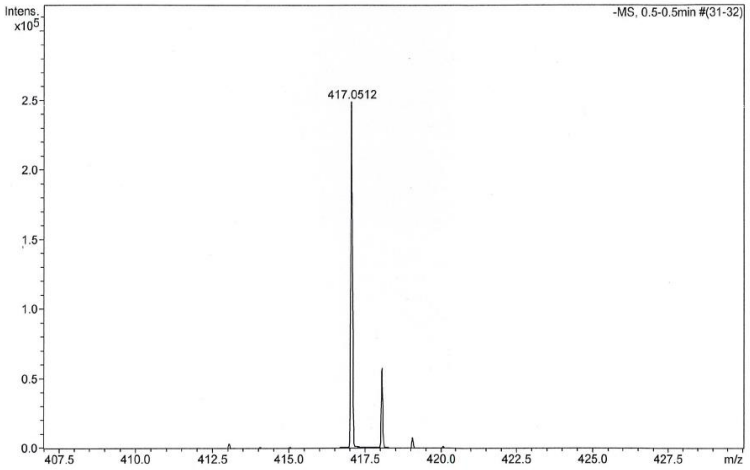
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{21}H_{13}F_3O_4P]^-$



#	m/z	I	I %
1	417.0509	100	100.0
2	418.0543	23	23.0
3	419.0576	3	3.3

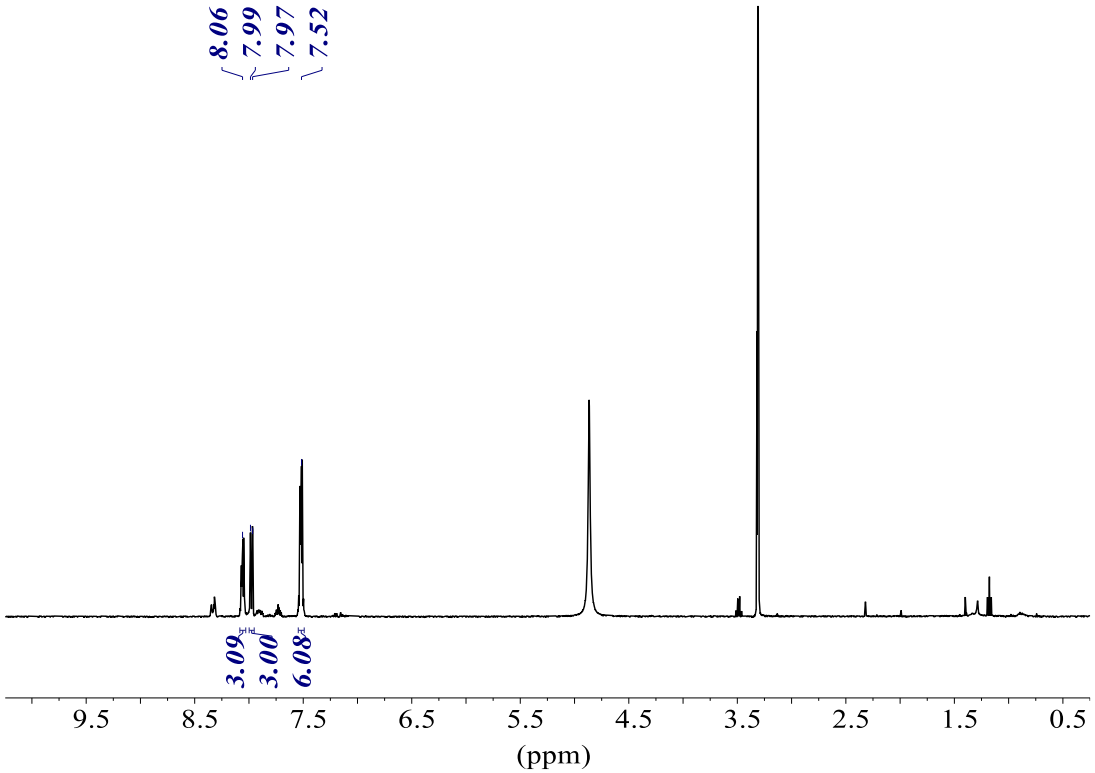
found



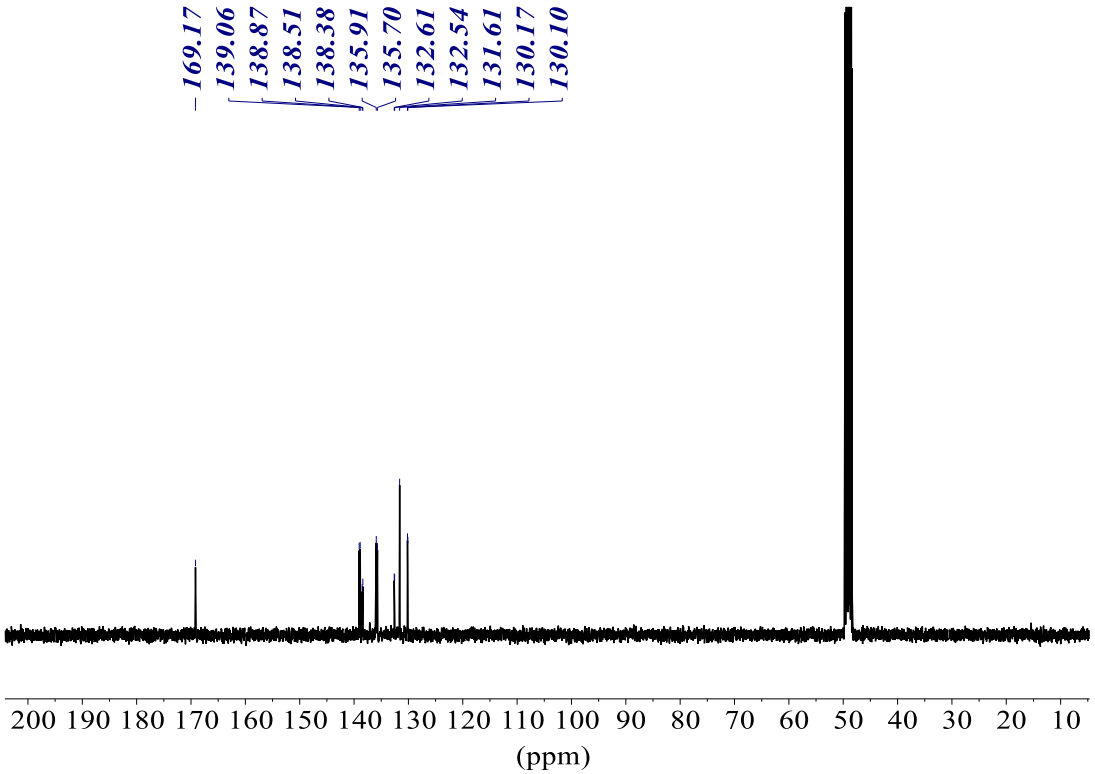
#	m/z	I	I %
1	417.0512	248910	100.0
2	418.0537	57557	23.1
3	419.0555	7600	3.1

TC2

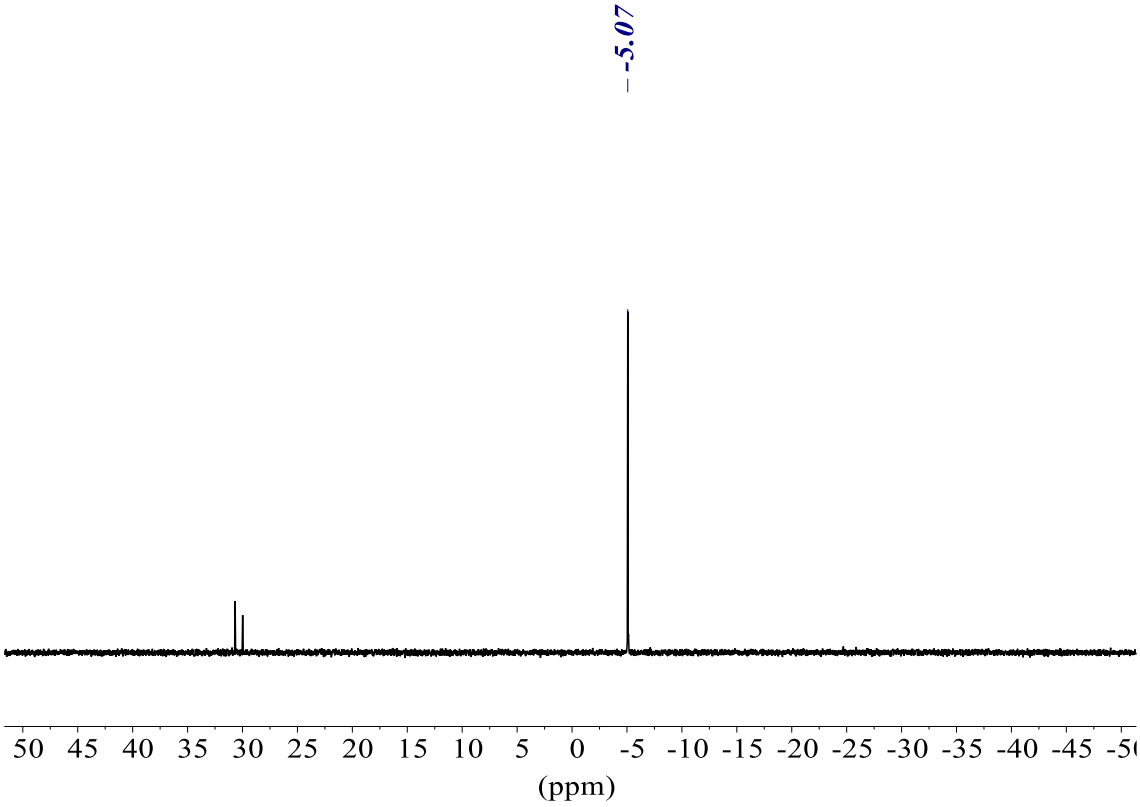
^{1}H (400.13 MHz, CD_3OD)



^{13}C{^{1}H} (100.61 MHz, CD_3OD)

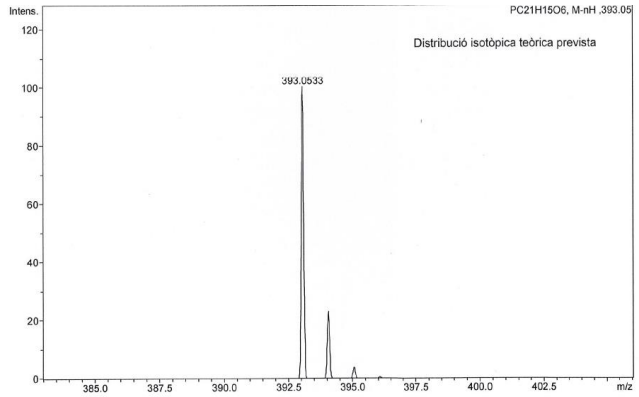


$^{31}P\{^{1}H\}$ (101.27 MHz CD_3OD)



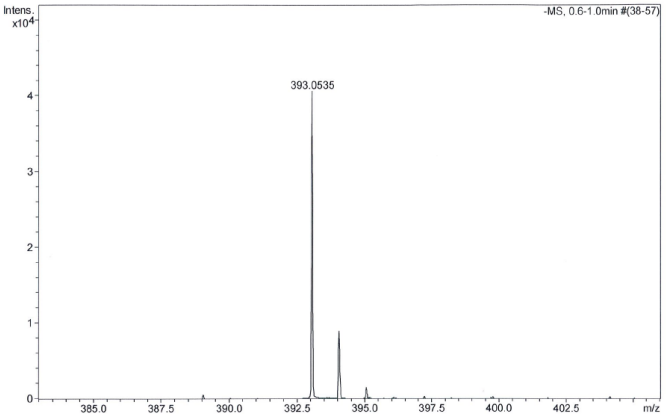
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{21}H_{14}O_6P]^-$



#	m/z	I	I %
1	393.0533	100	100.0
2	394.0567	23	23.1
3	395.0600	4	3.8

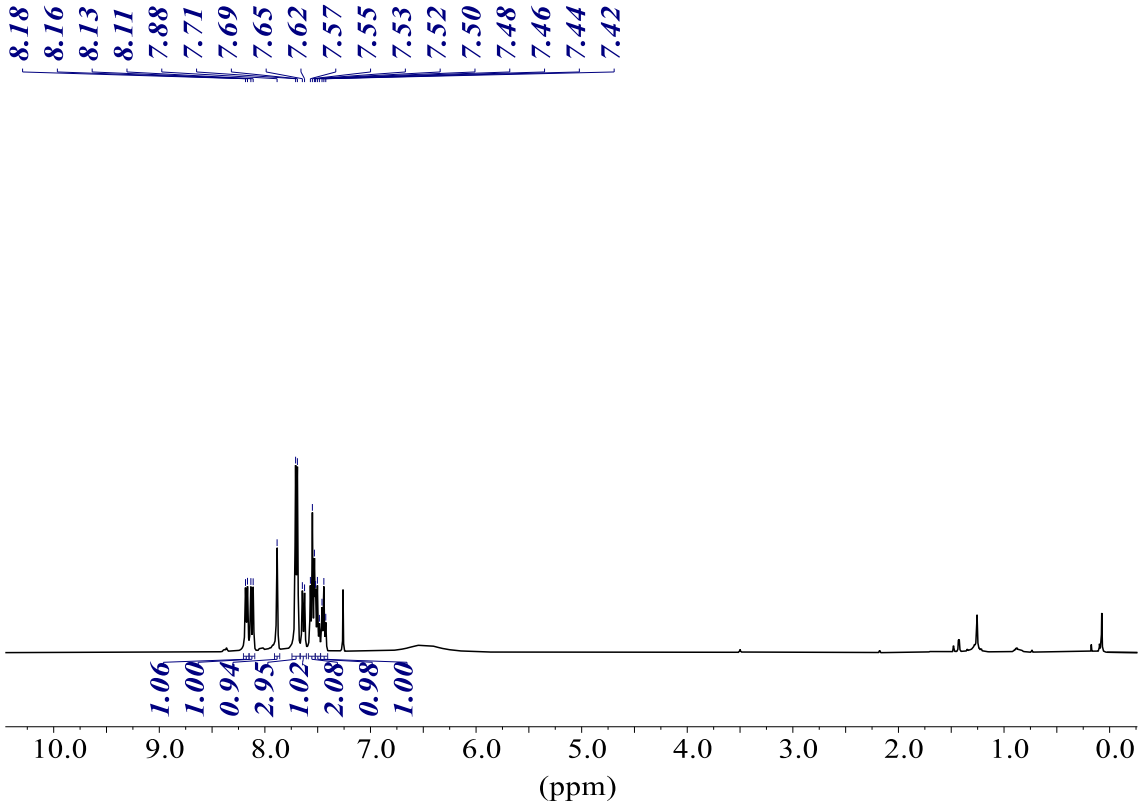
found



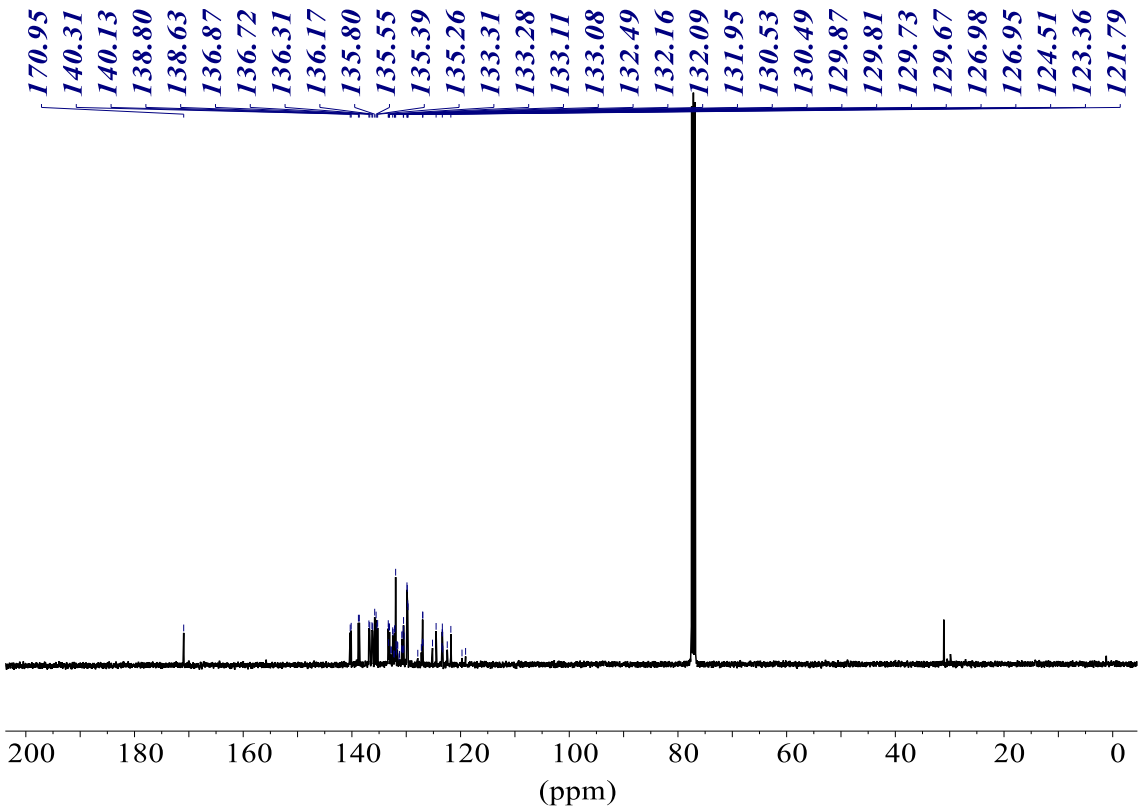
#	m/z	I	I %
1	393.0535	40578	100.0
2	394.0559	8988	22.2
3	395.0589	1474	3.6

MC4

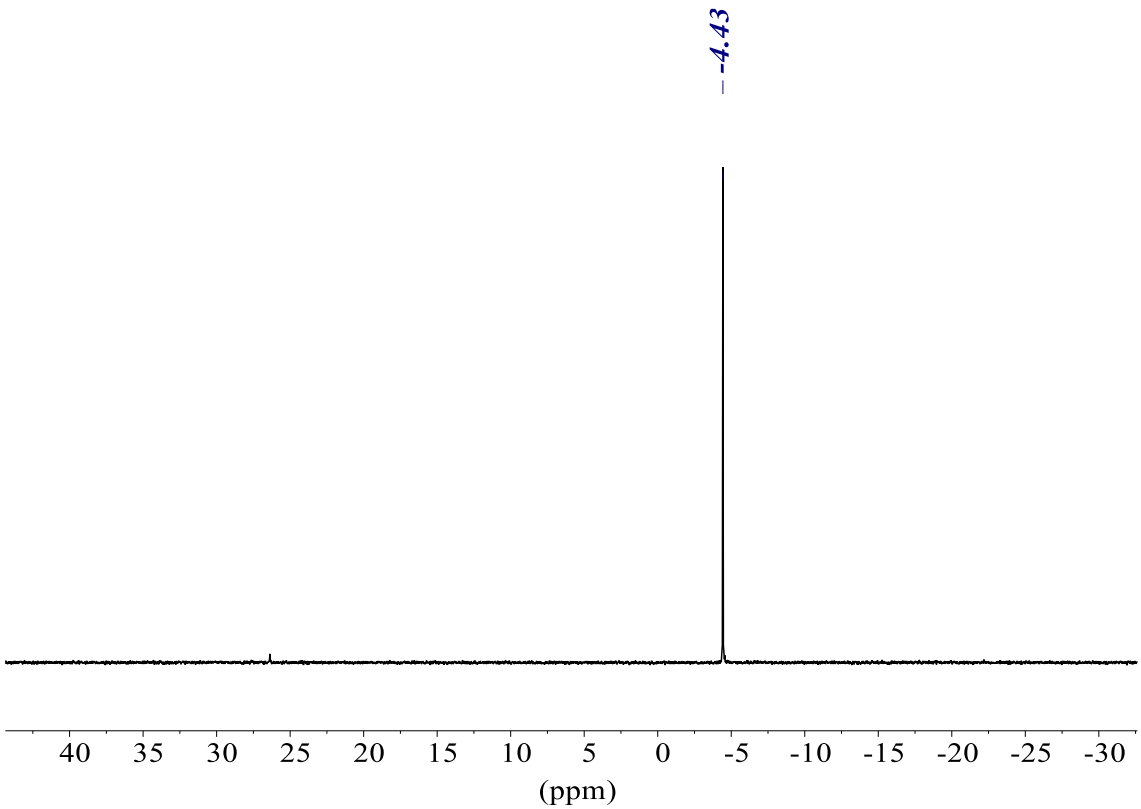
^{1}H (400.13 MHz, $CDCl_3$)



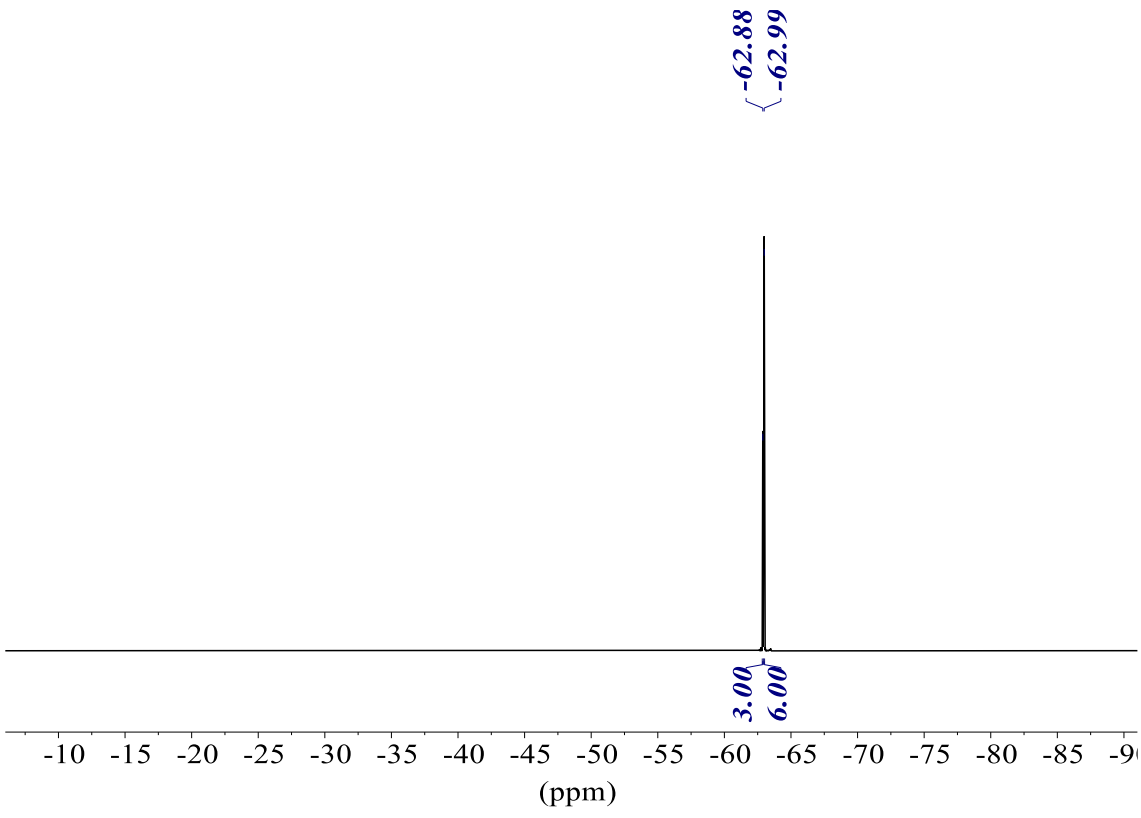
^{13}C{^{1}H} (100.61 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ (161.98 MHz, $CDCl_3$)

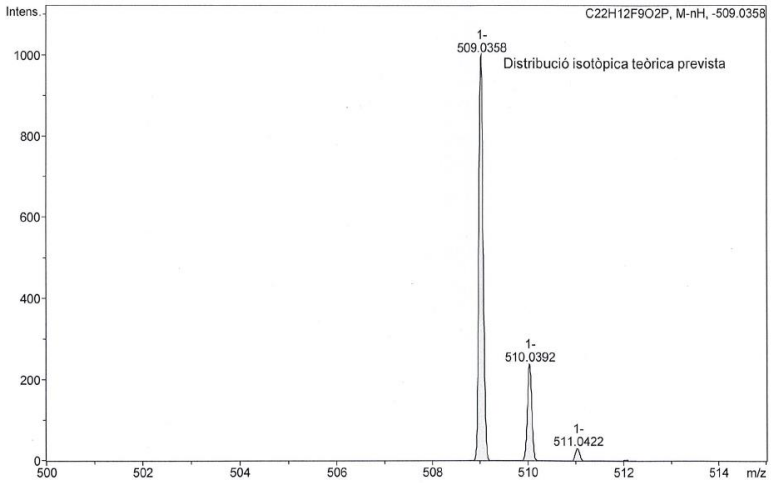


$^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$)



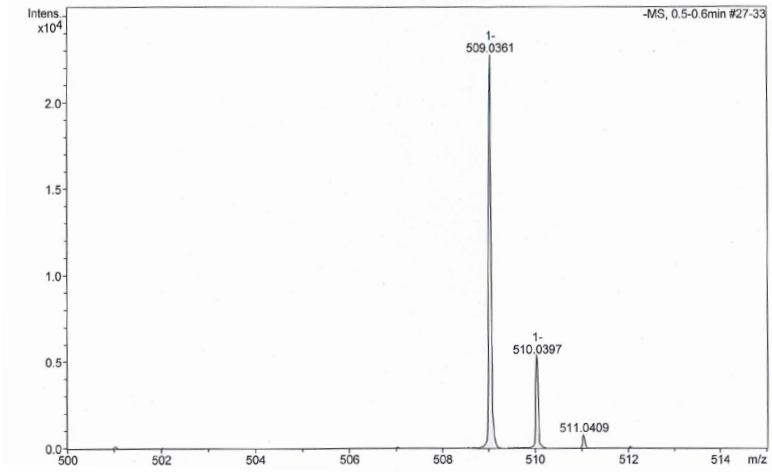
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{22}H_{11}F_9O_2P]^-$



#	m/z	I	I %
1	509.0358	1000	100.0
2	510.0392	239	23.9
3	511.0422	31	3.1

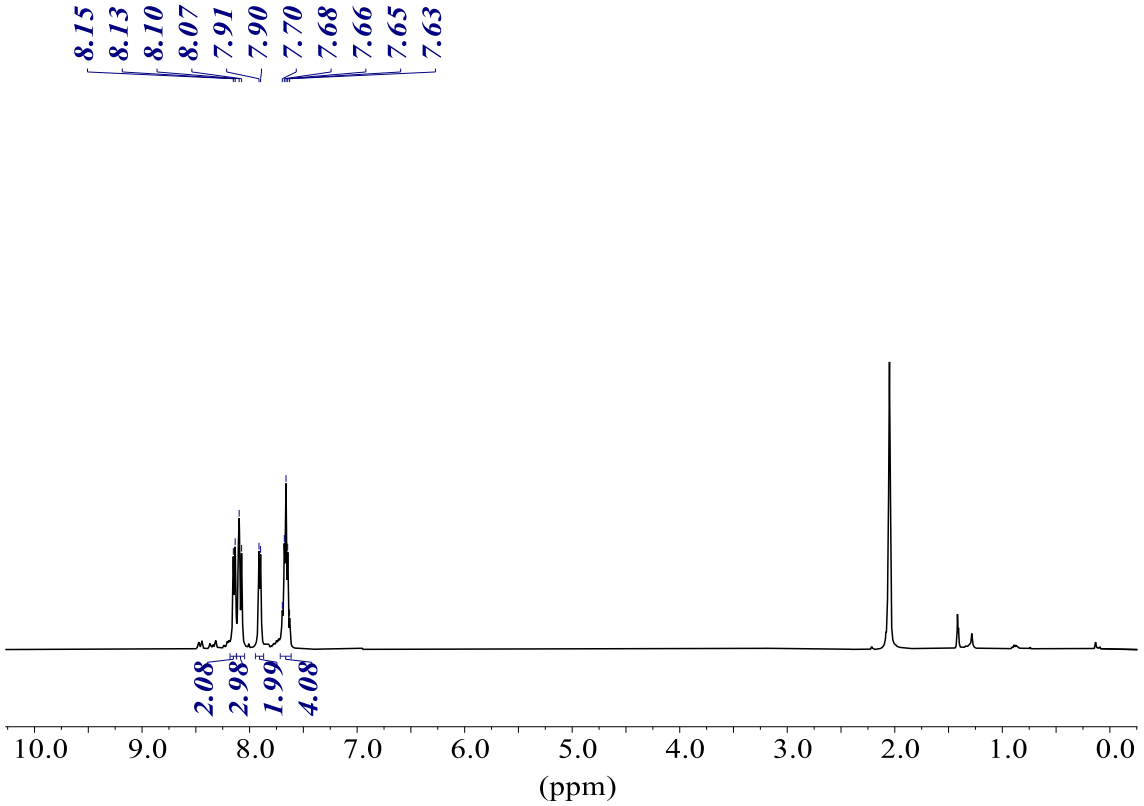
found



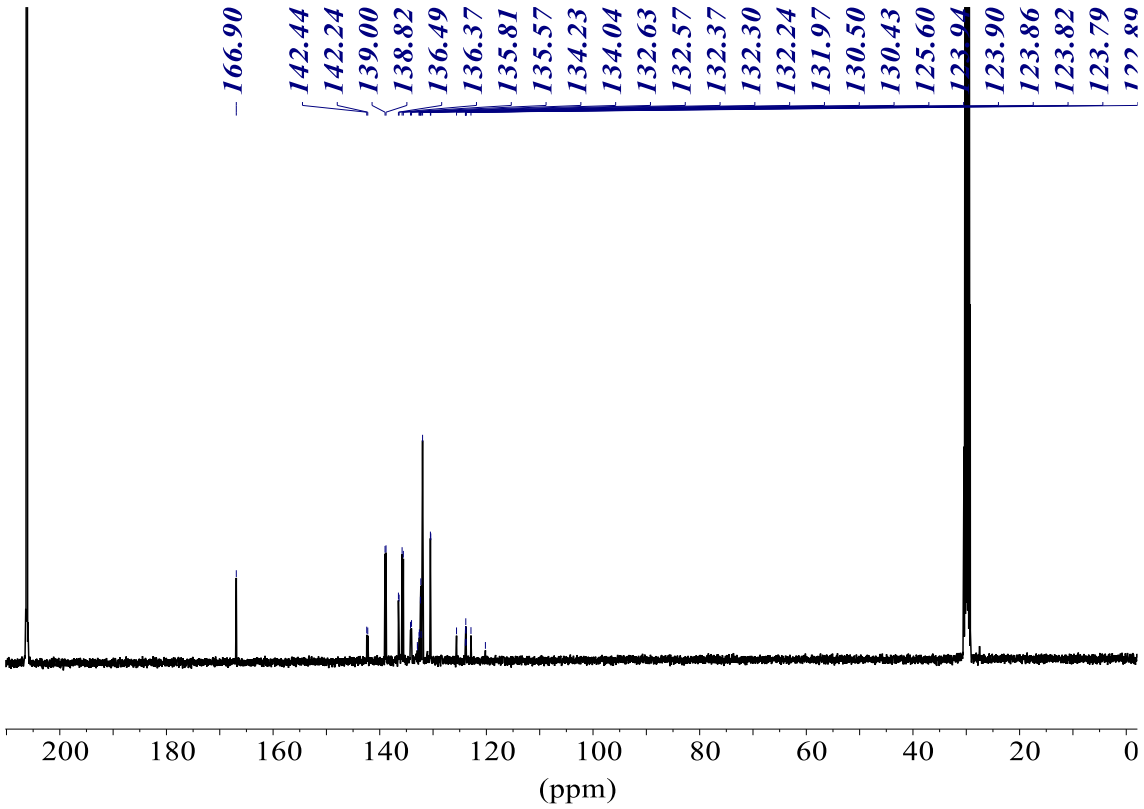
#	m/z	I	I %
1	509.0361	22740	100.0
2	510.0397	5340	23.5
3	511.0409	805	3.5

DC4

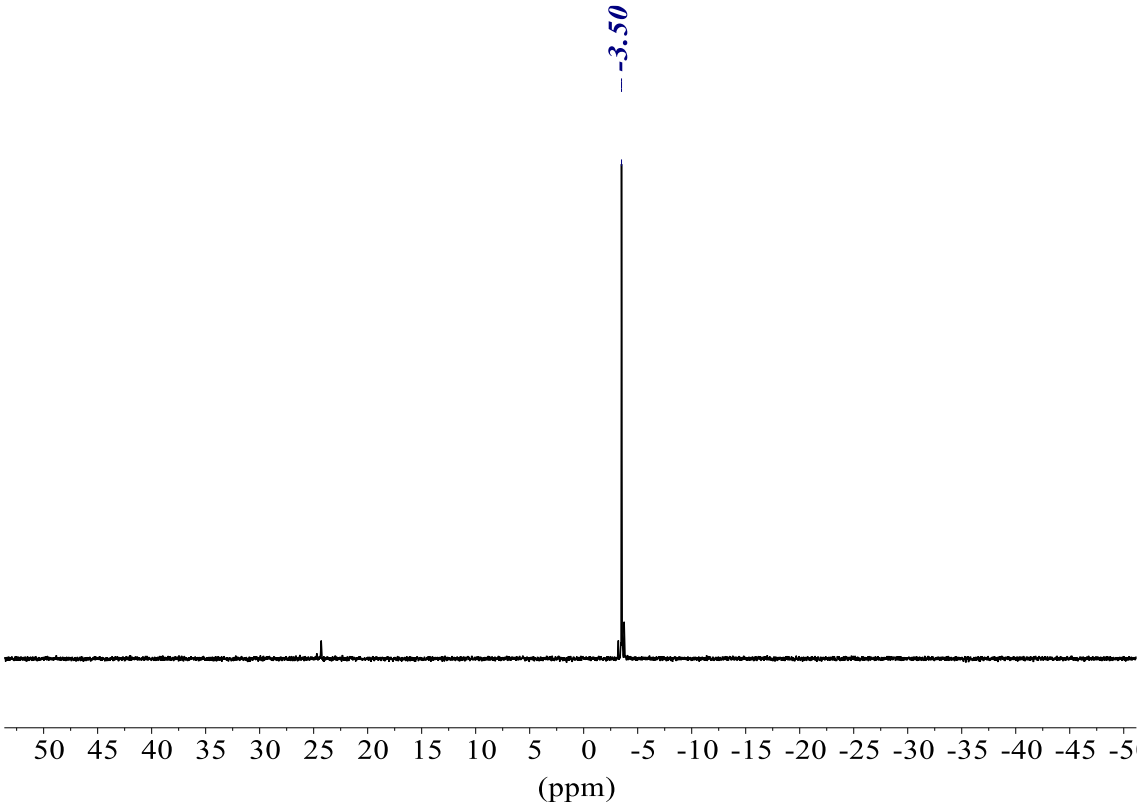
^{1}H (400.13 MHz, acetone-*d6*)



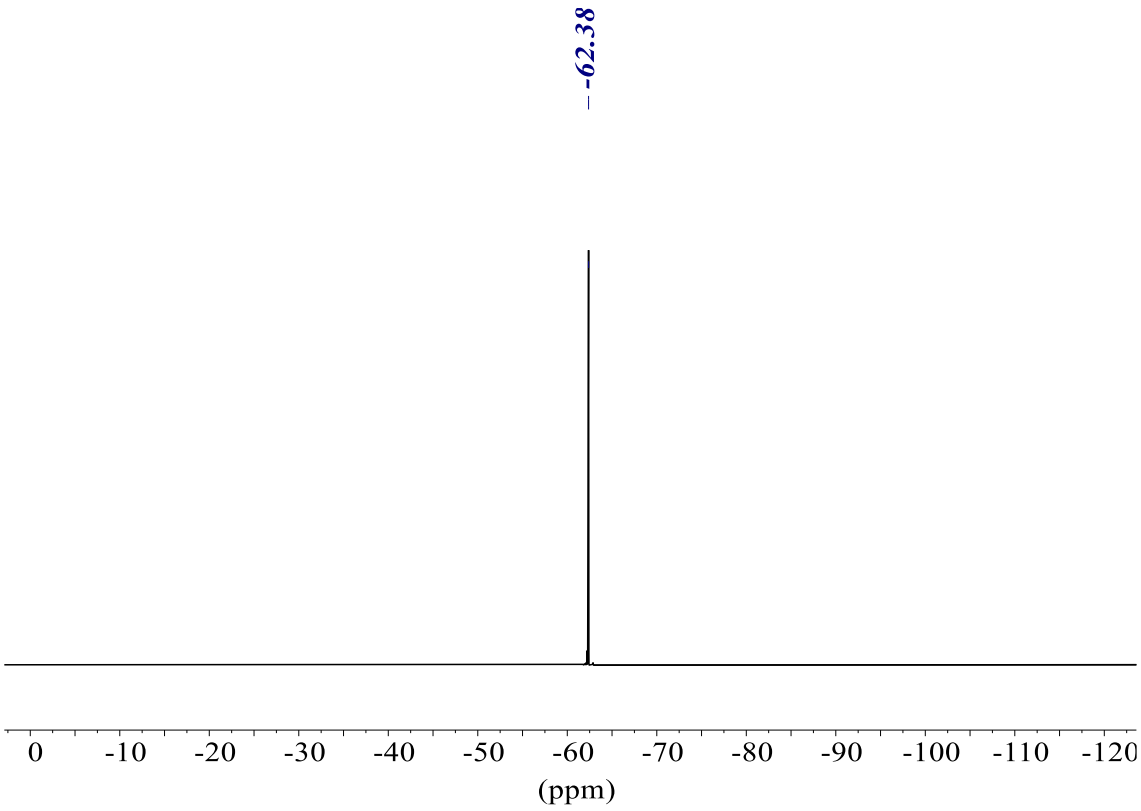
^{13}C{^{1}H} (100.61 MHz, acetone-*d6*)



$^{31}P\{^{1}H\}$(161.98 MHz, acetone-*d6*)

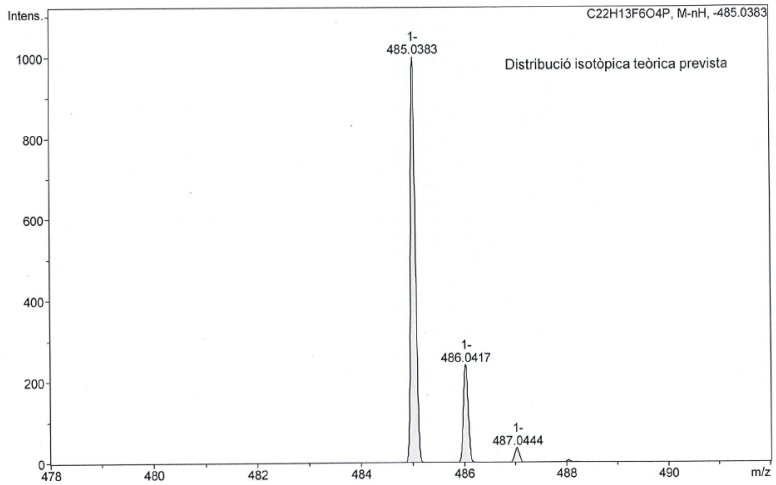


$^{19}F\{^{1}H\}$ (376.50 MHz, acetone-*d6*)



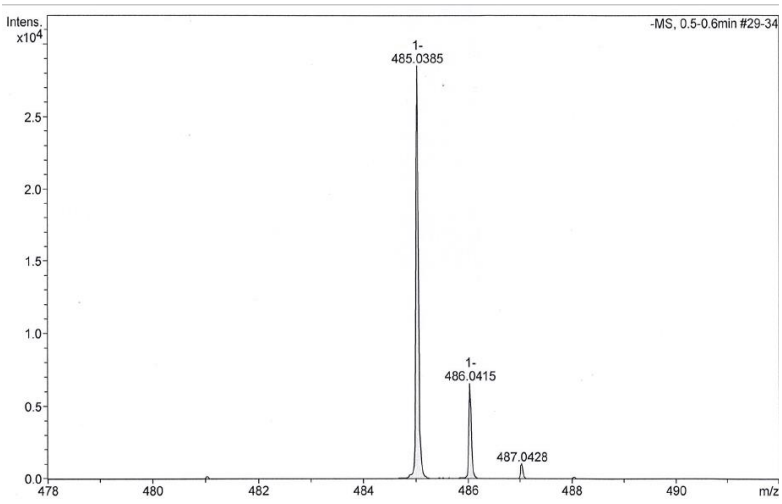
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{22}H_{12}F_6O_4P]^-$



#	m/z	I	I %
1	485.0383	1000	100.0
2	486.0417	241	24.1
3	487.0444	36	3.6

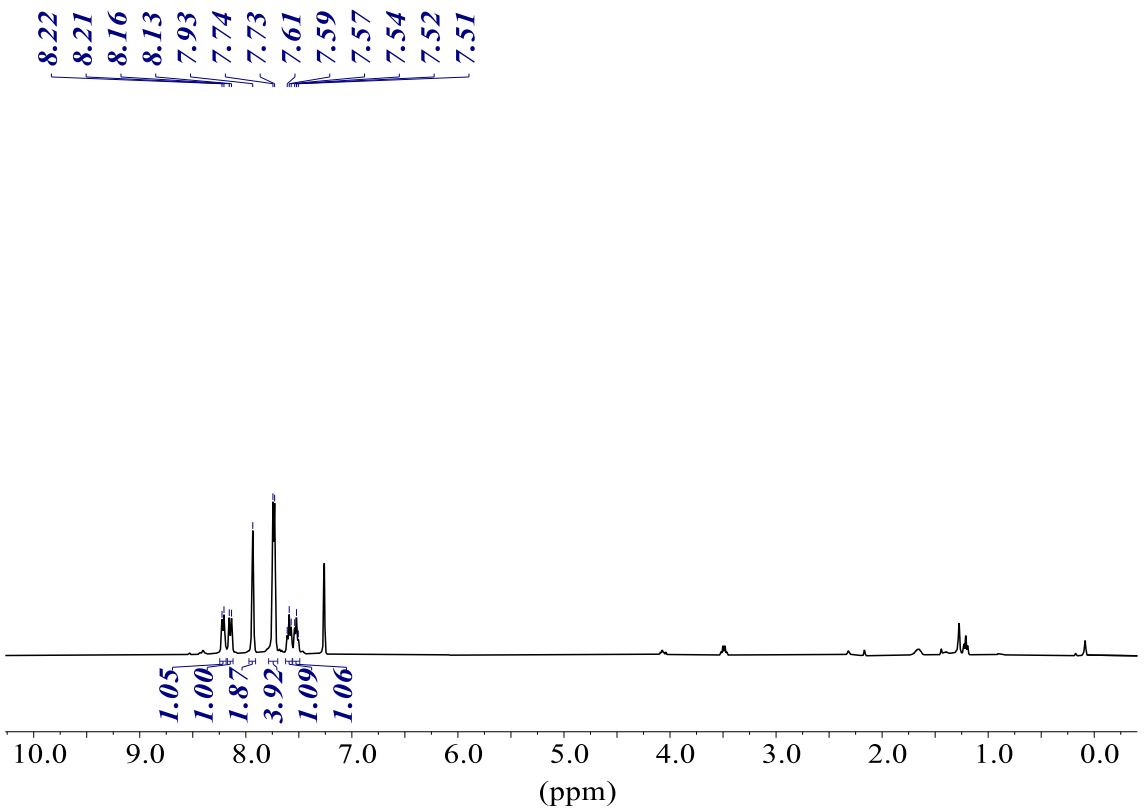
found



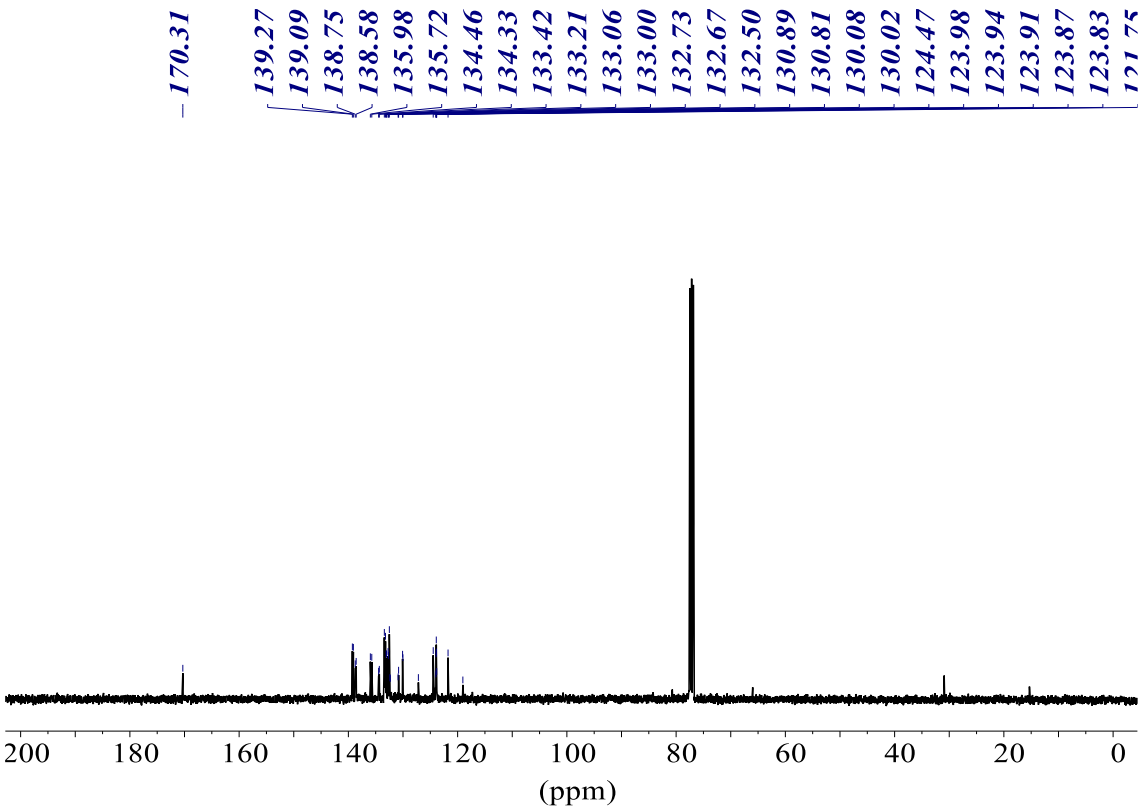
#	m/z	I	I %
1	485.0385	28499	100.0
2	486.0415	6598	23.2
3	487.0428	1028	3.6

MC5

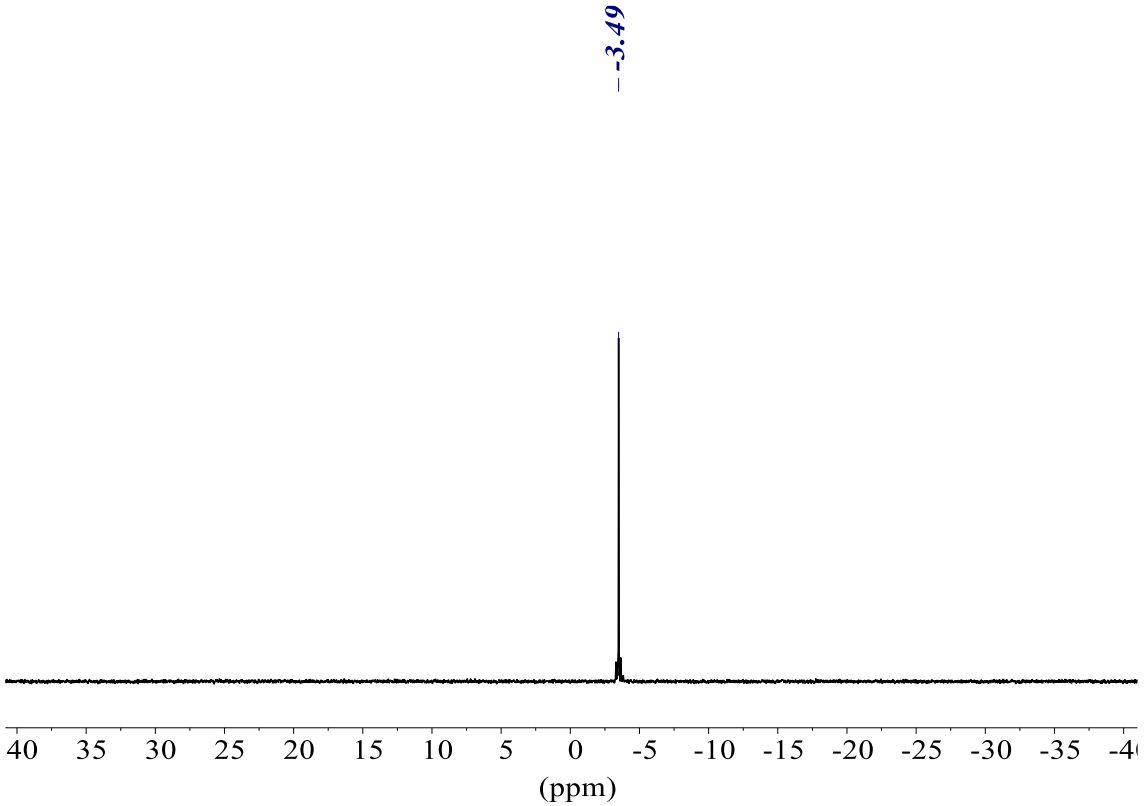
^{1}H (400.13 MHz, $CDCl_3$)



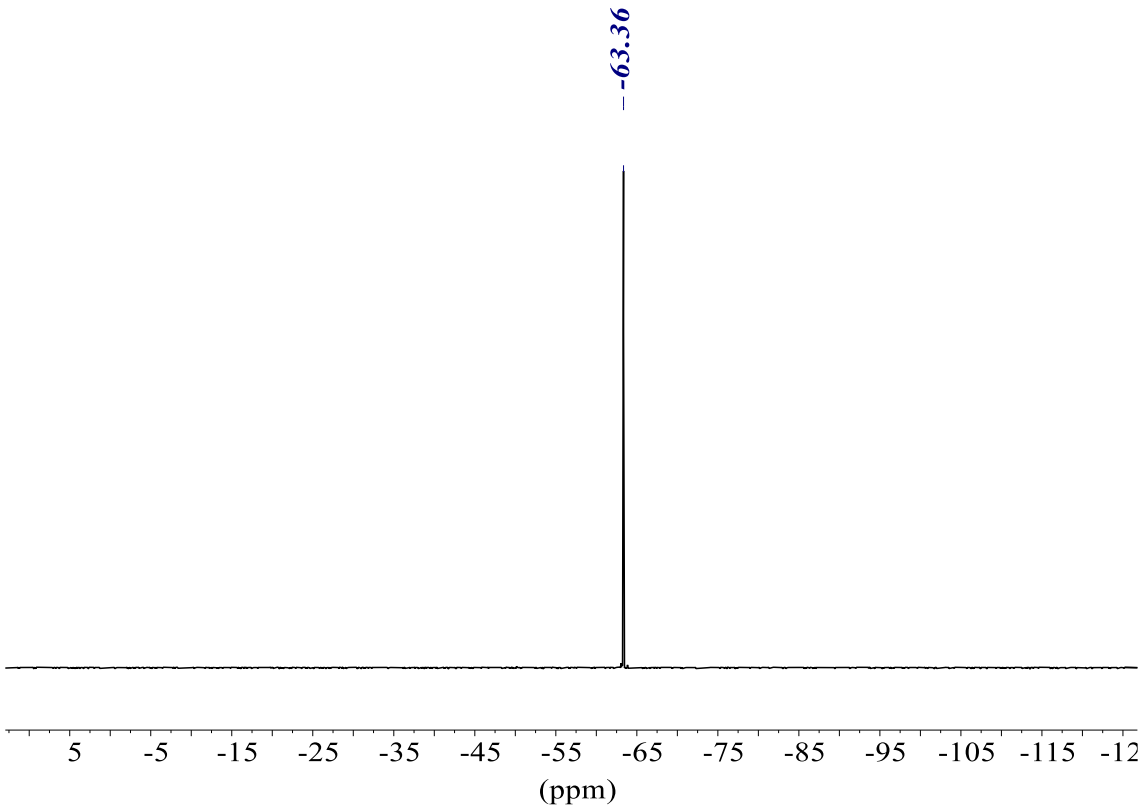
^{13}C{^{1}H} (100.61 MHz, $CDCl_3$)



$^{31}P\{^{1}H\}$ (161.98 MHz, $CDCl_3$)

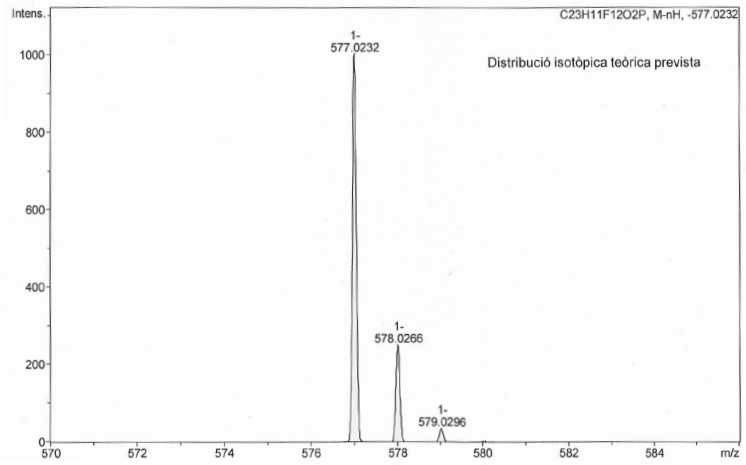


$^{19}F\{^{1}H\}$ (376.50 MHz, $CDCl_3$)



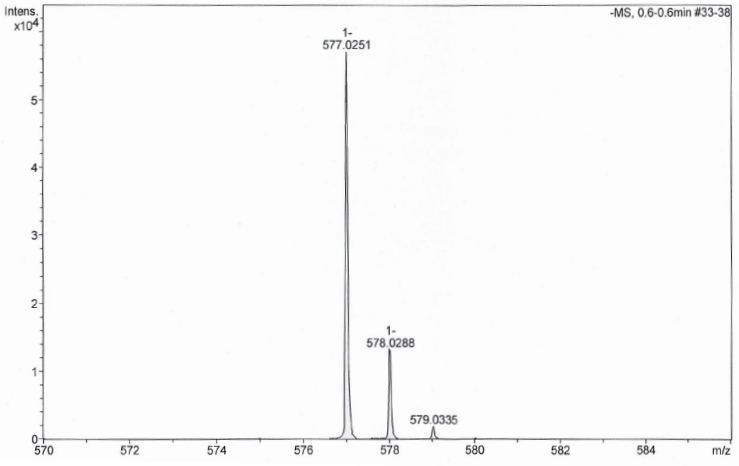
HR-MS (ESI$^-$ *m/z*) $[M-H]^-$

calculated for $[C_{23}H_{10}F_{12}O_2P]^-$



#	m/z	I	I %
1	577.0232	1000	100.0
2	578.0266	250	25.0
3	579.0296	34	3.4

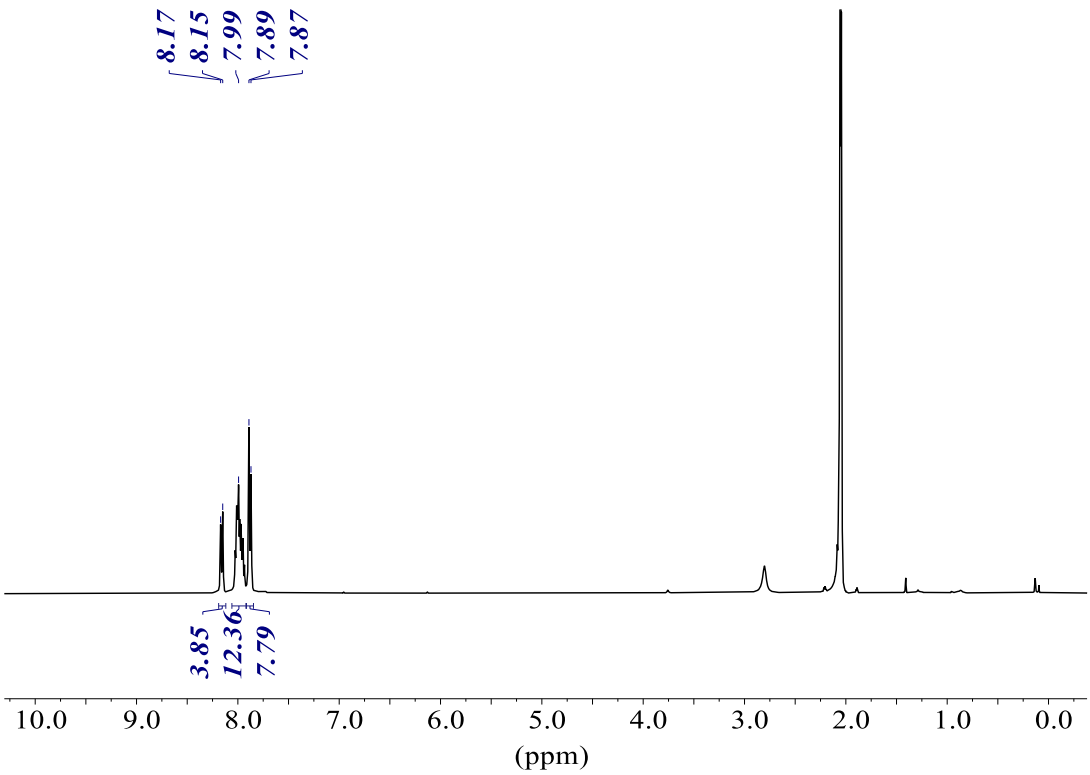
found



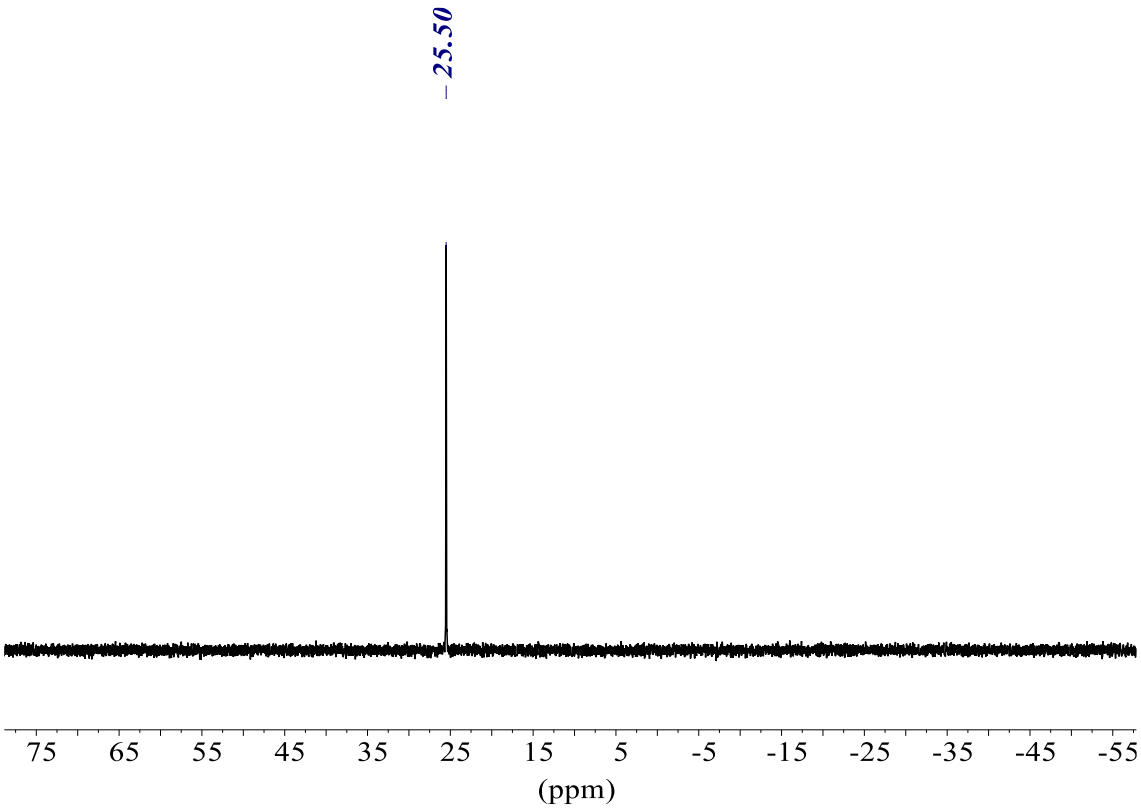
#	m/z	I	I %
1	577.0251	57043	100.0
2	578.0288	13250	23.2
3	579.0335	1891	3.3

Pd-complex MC1

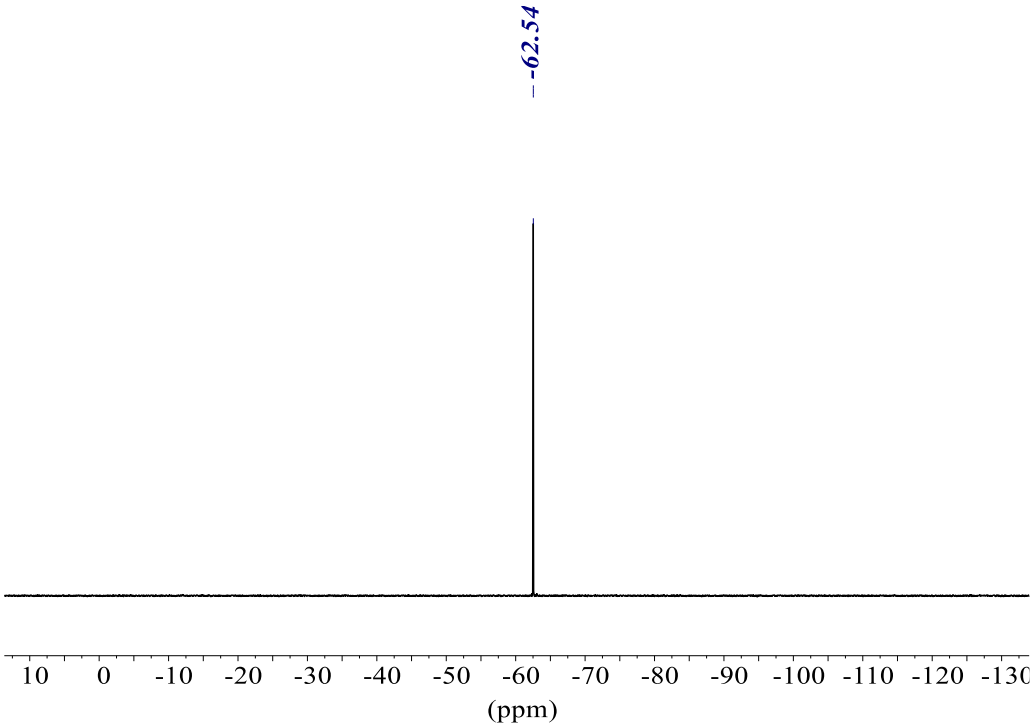
^{1}H (400.13 MHz, acetone-*d6*)



^{31}P{^{1}H}(161.98 MHz, acetone-*d6*)

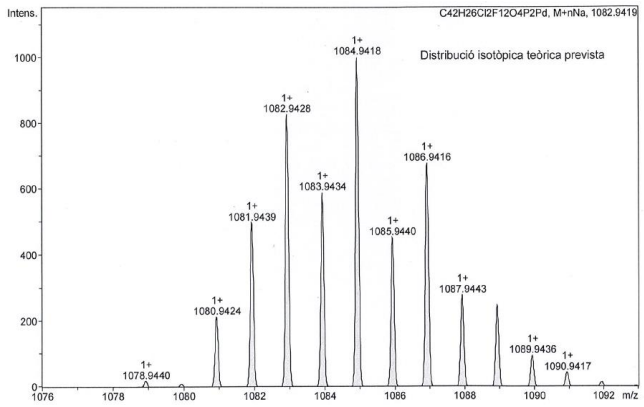


$^{19}F\{^{1}H\}$ (376.50 MHz, acetone-*d6*)



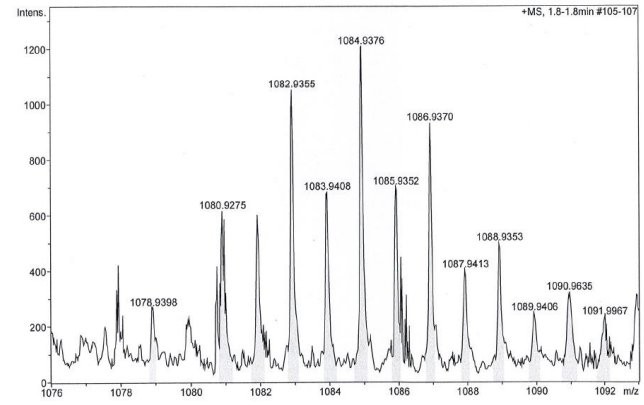
HR-MS (ESI^+ *m/z*) $[M+Na]^+$

calculated for $[C_{42}H_{26}Cl_2F_{12}O_4P_2PdNa]^+$



#	m/z	I	I %
1	1078.9440	18	1.8
2	1080.9424	213	21.3
3	1081.9439	496	49.6
4	1082.9428	825	82.5
5	1083.9434	587	58.7
6	1084.9418	1000	100.0
7	1085.9440	452	45.2
8	1086.9416	677	67.7
9	1087.9443	278	27.8
10	1088.9415	248	24.8
11	1089.9436	94	9.4
12	1090.9417	43	4.3
13	1091.9430	13	1.3

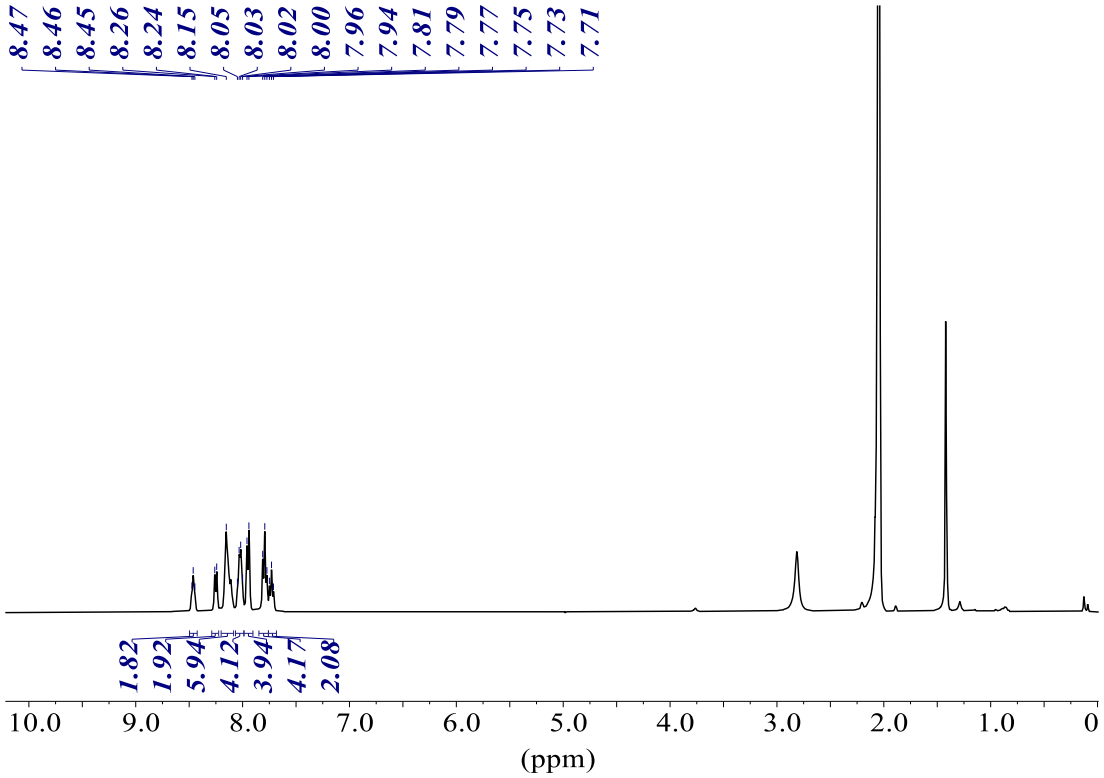
found



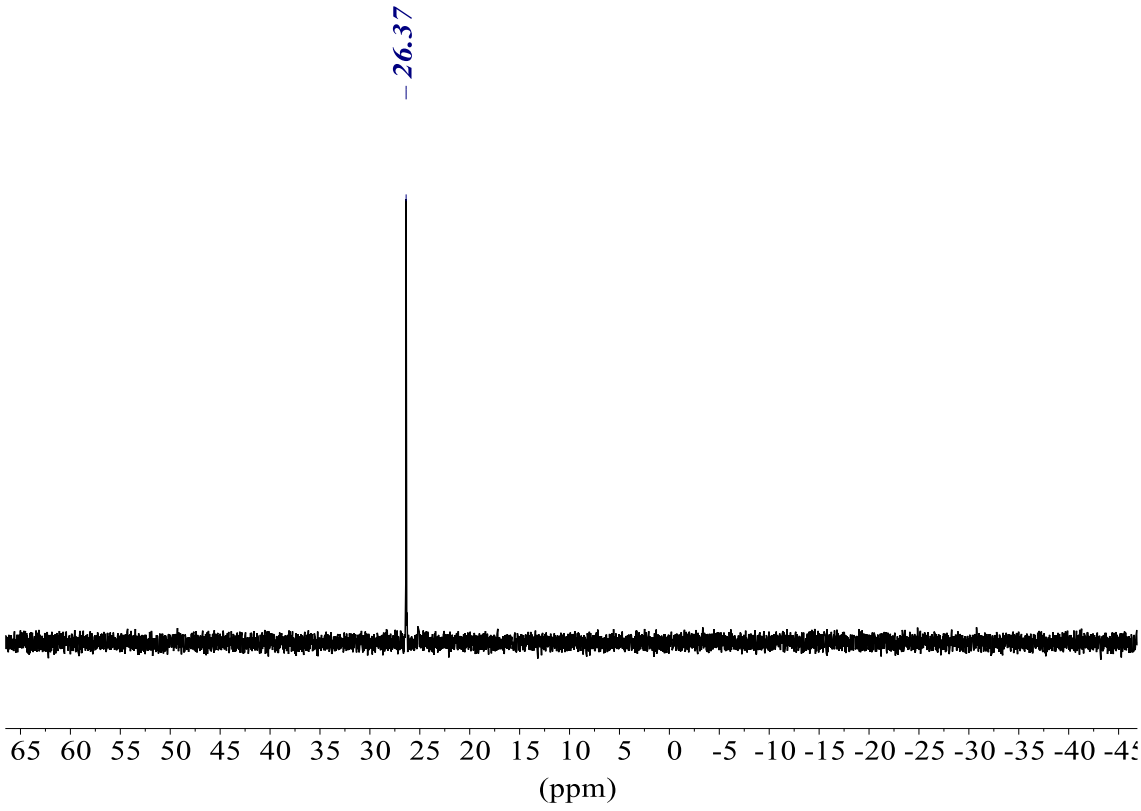
#	m/z	I	I %
1	1078.9398	269	22.3
2	1080.9275	617	51.1
3	1081.9453	604	50.0
4	1082.9355	1053	87.2
5	1083.9408	683	56.6
6	1084.9376	1207	100.0
7	1085.9352	702	58.2
8	1086.9370	932	77.2
9	1087.9413	403	33.4
10	1088.9353	501	41.5
11	1089.9406	249	20.6
12	1090.9635	324	26.8
13	1091.9967	235	19.4

Pd-complex MC2

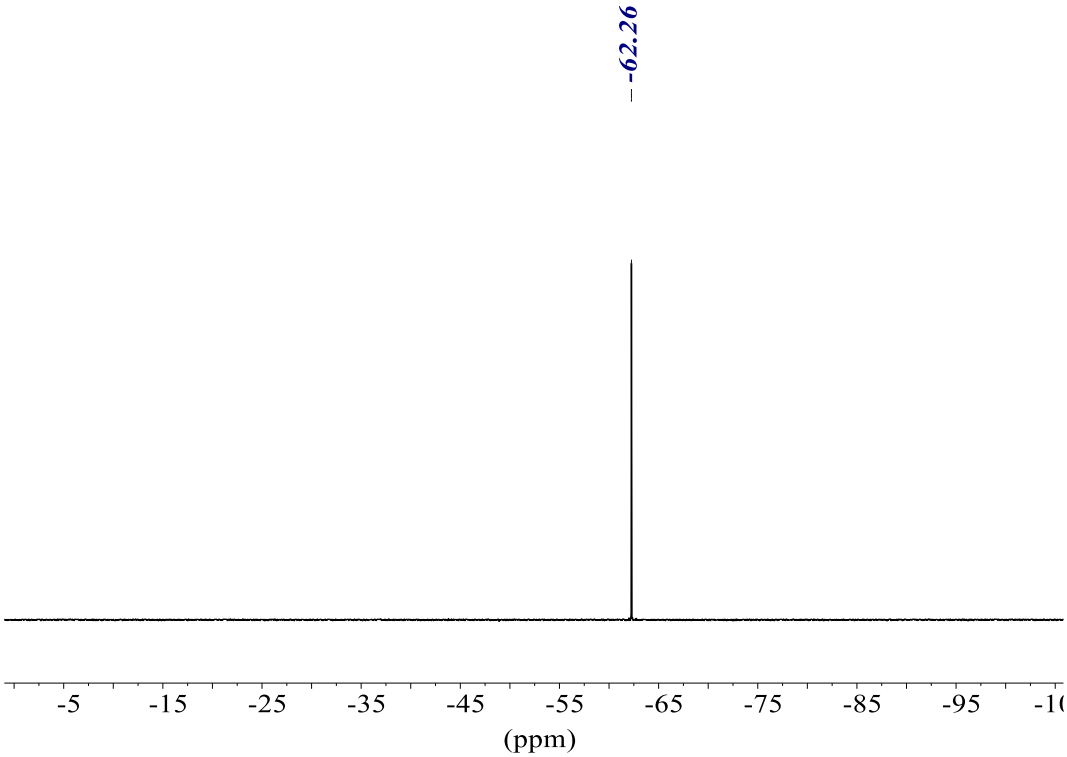
^{1}H (400.13 MHz, acetone-*d6*)



^{31}P{^{1}H}(161.98 MHz, acetone-*d6*)

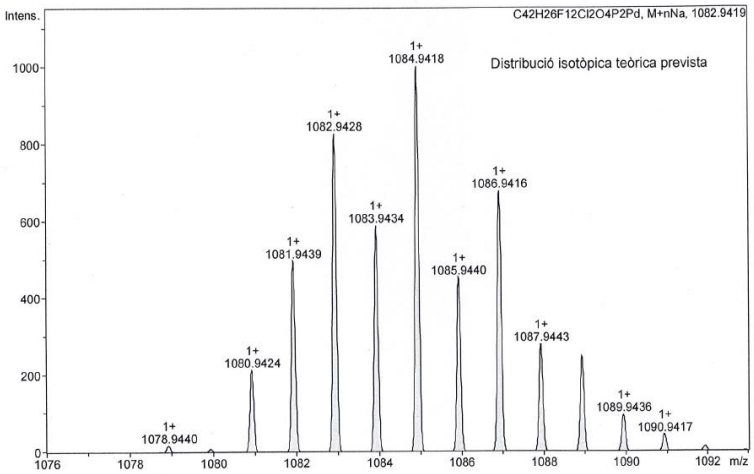


$^{19}F\{^{1}H\}$ (376.50 MHz, acetone-*d6*)



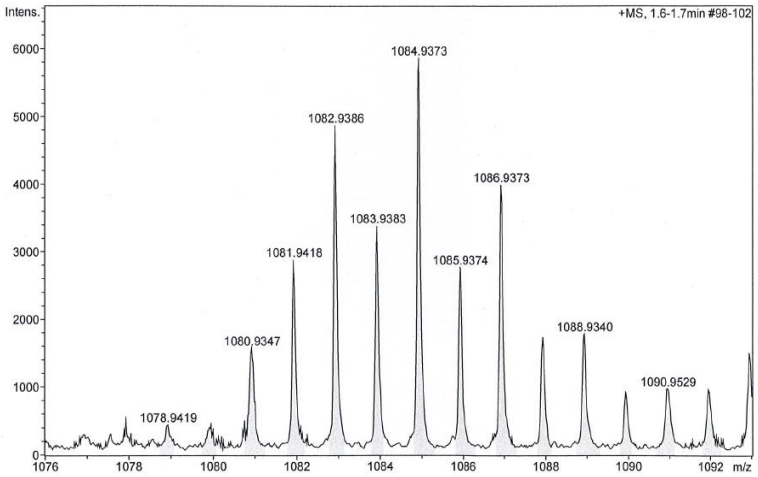
HR-MS (ESI^{+} *m/z*) $[M+Na]^{+}$

calculated for $[C_{42}H_{26}Cl_2F_{12}O_4P_2PdNa]^{+}$



#	m/z	I	I %
1	1078.9440	18	1.8
2	1079.9474	8	0.8
3	1080.9424	213	21.3
4	1081.9439	496	49.6
5	1082.9428	825	82.5
6	1083.9434	587	58.7
7	1084.9418	1000	100.0
8	1085.9440	452	45.2
9	1086.9416	677	67.7
10	1087.9443	278	27.8
11	1088.9415	248	24.8
12	1089.9436	94	9.4
13	1090.9417	43	4.3
14	1091.9430	13	1.3

found



#	m/z	I	I %
1	1078.9419	451	7.7
2	1079.9383	418	7.1
3	1080.9347	1579	27.0
4	1081.9418	2887	49.3
5	1082.9386	4870	83.1
6	1083.9383	3384	57.8
7	1084.9373	5857	100.0
8	1085.9374	2776	47.4
9	1086.9373	3993	68.2
10	1087.9398	1739	29.7
11	1088.9340	1789	30.5
12	1089.9376	923	15.8
13	1090.9529	978	16.7

[i] D. Herrera, D. Peral, M. Cordón, J.C. Bayón, *Eur. J. Inorg. Chem.*, 2021, 354–363

[ii] Bruker, SADABS, Bruker Analytical X-Ray Division, Madison 2001

[iii] G. M Sheldrick,. *Acta Cryst.. Sect. A Found. Crystallogr.* 2008, **64**, 112–122.

[iv] L. J. Farrugia,. *J. Appl. Crystallogr.* 1999, **32**, 837–838.

[v] a) A. L. Spek, *Acta Crystallogr.* 2009, D65, 148-155; b) A. L. Spek, *Acta Crystallogr. C Struct. Chem*. 2005, **71**, 9-18