SUPLEMENTARY INFORMATION

Selective Deuteration of Phosphorus Ligands using Ruthenium Nanoparticles. A Procedure for Obtaining Information about Ligand Coordination to the Nanoparticle Surface

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Table of contents:

S1. Reagents and General Procedures

Ru@PVP nanoparticles were synthesized following a reported method [1] and stored in a glove box under argon atmosphere. The synthesis of the nanoparticles and the catalysis was carried out in a Fischer-Porter glassware under argon. The chemicals were purchased from Aldrich Chemical and used without further purification. The precursor [Ru(COD)(COT)] was purchased from Nanomeps. THF was dried over sodium and benzophenone, distilled and then thoroughly degassed before use.

^{1}H, ^{13}C and ^{31}P spectra were recorded on a Varian® Mercury VX 400 (400 MHz, 100.6 MHz, 162 MHz respectively). Chemical shift values for ^{1}H and ^{13}C were referred to internal $SiMe_4$ (0.0 ppm) and for ^{31}P was referred to H_3PO_4 (85% solution in D_2O, 0 ppm). Chemical shifts are reported in parts per million (ppm) and coupling constants are reported in Hertz (Hz).

Mass spectra was recorded on a Finnigan MAT 900S (EB-Trap-Geometry) Syringes pump Model 22.

The isotopic labelling was quantified by ^{31}P spectroscopy.

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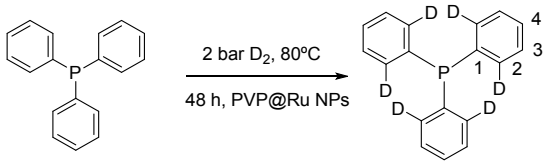
S3. General Procedure for H/D exchanges [2]:

A 100 ml Fischer-porter glassware was charged in a dry-box with RuNPs@PVP (8mg, 3.3%) and a magnetic stirrer. The Fischer-Porter was left under vacuum for 5 minutes and then it was pressurized under 3 bar of D_2 gas during 2 hours. Next a solution of the substrate (0.15 mmol) in degassed THF (1 ml) was added under argon. The reaction was stirred under 2 bar of D_2 under the required temperatures and time. Then the solution was cooled down to room temperature, filtered on a small neutral alumina pad and evaporated to dryness.

S4. Synthesis and Characterization

Synthesis of hexadeuterated tri-phenylphosphine $P(C_6H_3D_2)_3$ (2f).

Following the general procedure triphenylphosphine was heated for 48h at 80ºC for providing the hexadeuterated phosphine (**2f**).



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.26 (bs). **^{13}C NMR** (100.6 MHz, $CDCl_3$, δ in ppm): 137.3 (d, C1, *J*= 12.0 Hz), 133.8 (dt, C2, *J*= 19.0, 24.0 Hz), 129.0 (s, C4), 128.7 (d, C3, *J*= 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$, δ in ppm): -6.2. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.58 (bs).

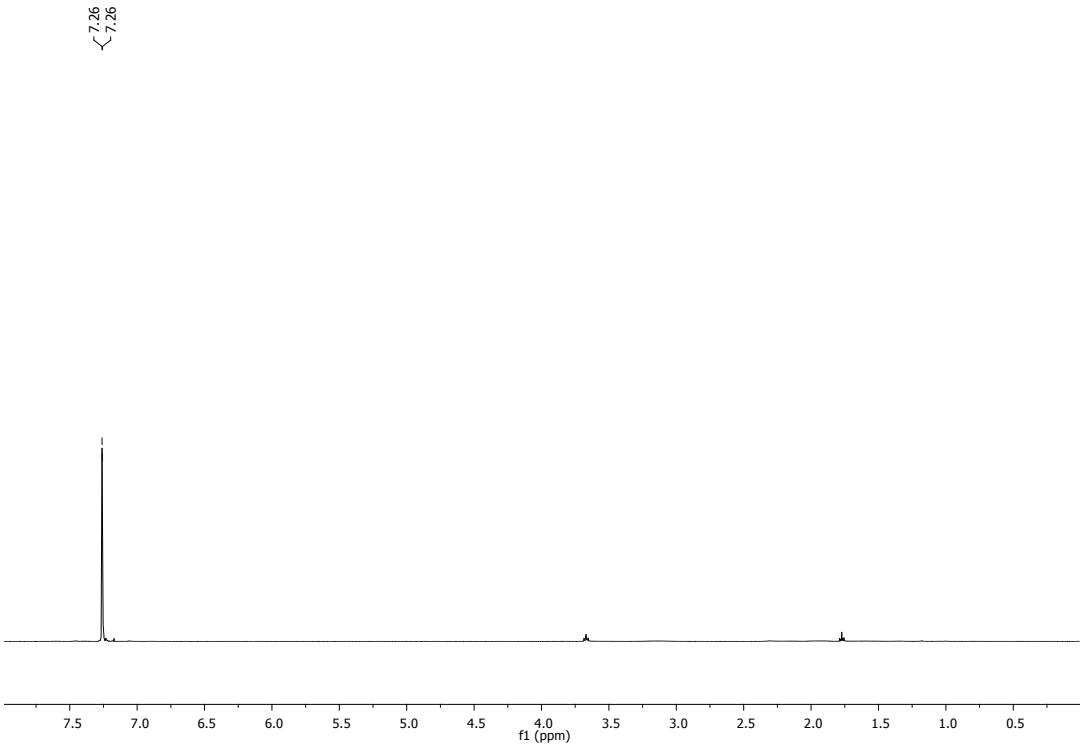


Figure 1. ^{1}H-NMR of hexadeuterated PPh_3 (**2f**).

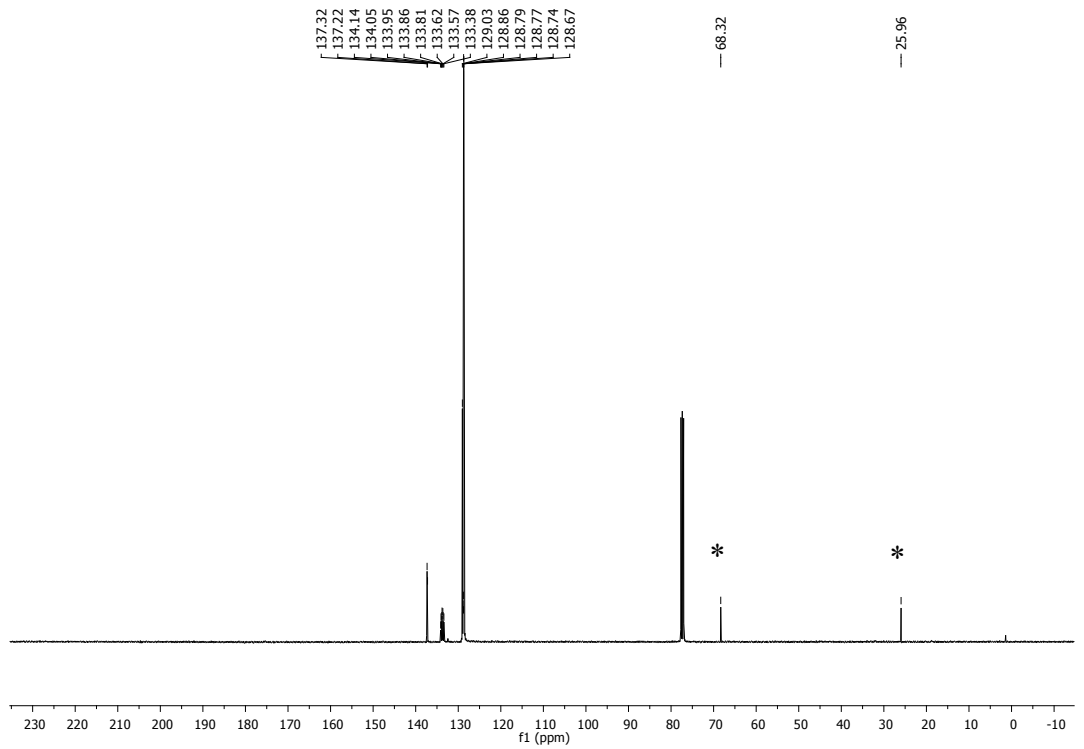


Figure 2. ^{13}C-NMR of hexadeuterated PPh_3 (**2f**).

*The signals at 68 and 26 ppm correspond to residual THF.

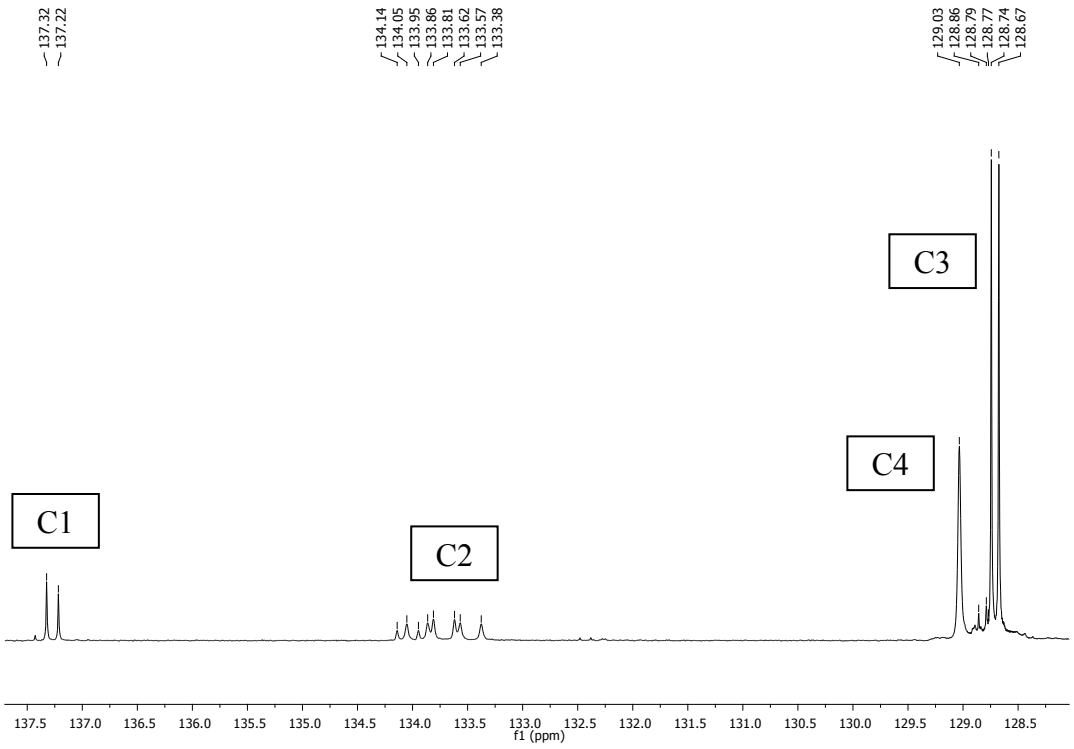


Figure 3. ^{13}C-NMR of hexadeuterated PPh_3 (**2f**).

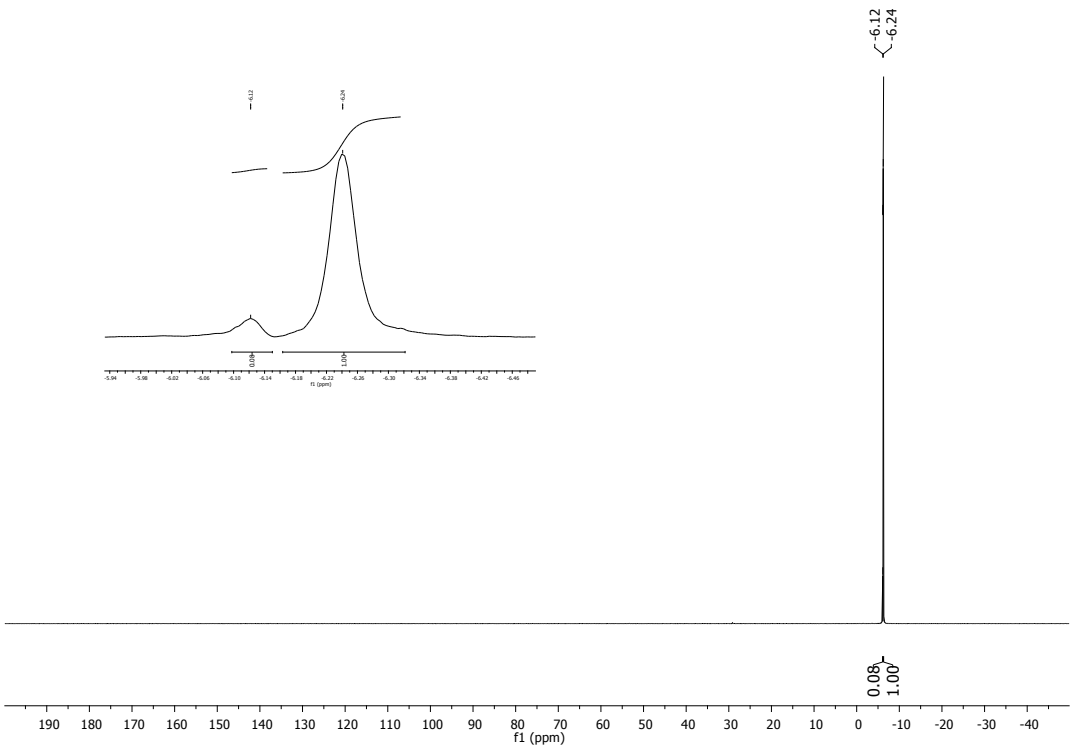


Figure 4. ^{31}P-NMR of hexadeuterated PPh_3 (**2f**).

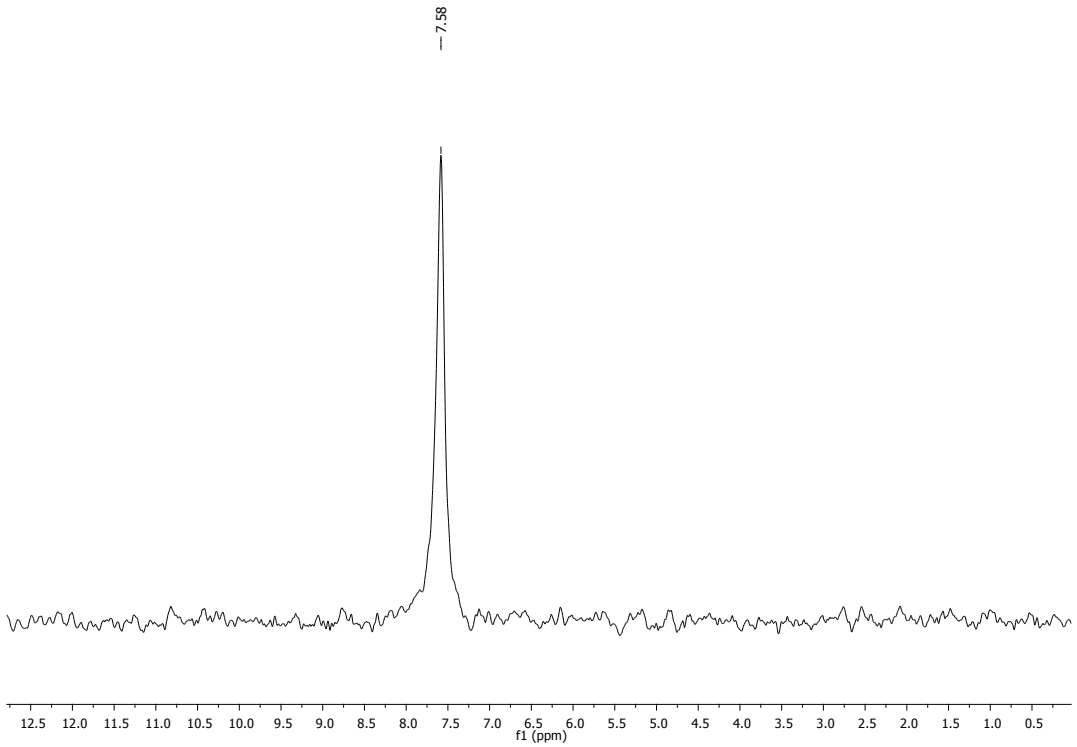


Figure 5. ^{2}H-NMR of hexadeuterated PPh_3 (**2f**) at 2 bar of D_2 and 80°C for 48 hours.

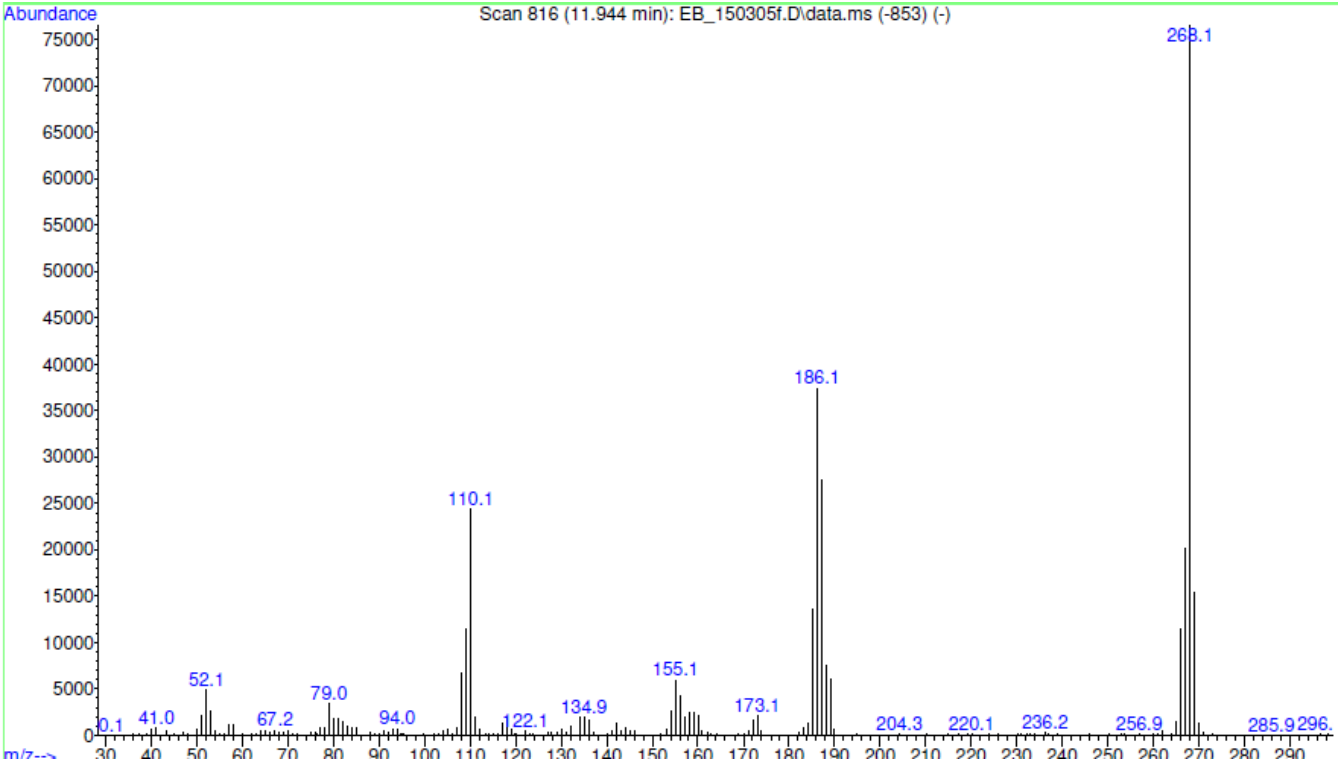
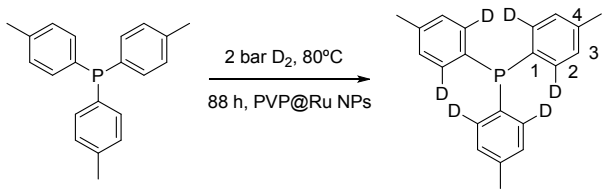


Figure 6. Mas spectrum (electronic impact) of hexadeuterated PPh_3 (**2f**).

Synthesis of hexadeuterated tri-*p*-tolylphosphine $P(C_7H_6D_2)_3$ (7).

Following the general procedure tri(*para*-tolyl)phosphine was heated for 88h at 80ºC for providing hexadeuterated tri(*p*-tolyl)phosphine (**7**).



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.06 (s), 2.26 (s, CH_3). **^{13}C NMR** (100.6 MHz, $CDCl_3$, δ in ppm): 138.8 (s, C4), 134.2 (d, C1, *J*= 9.0 Hz), 133.4 (dt, C2, *J*= 19.0, 26.0 Hz), 129.1 (d, C3, *J*= 8.0 Hz), 21.7 (s, CH_3). **^{31}P NMR** (162 MHz, $CDCl_3$, δ in ppm): -8.8. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.45 (bs).

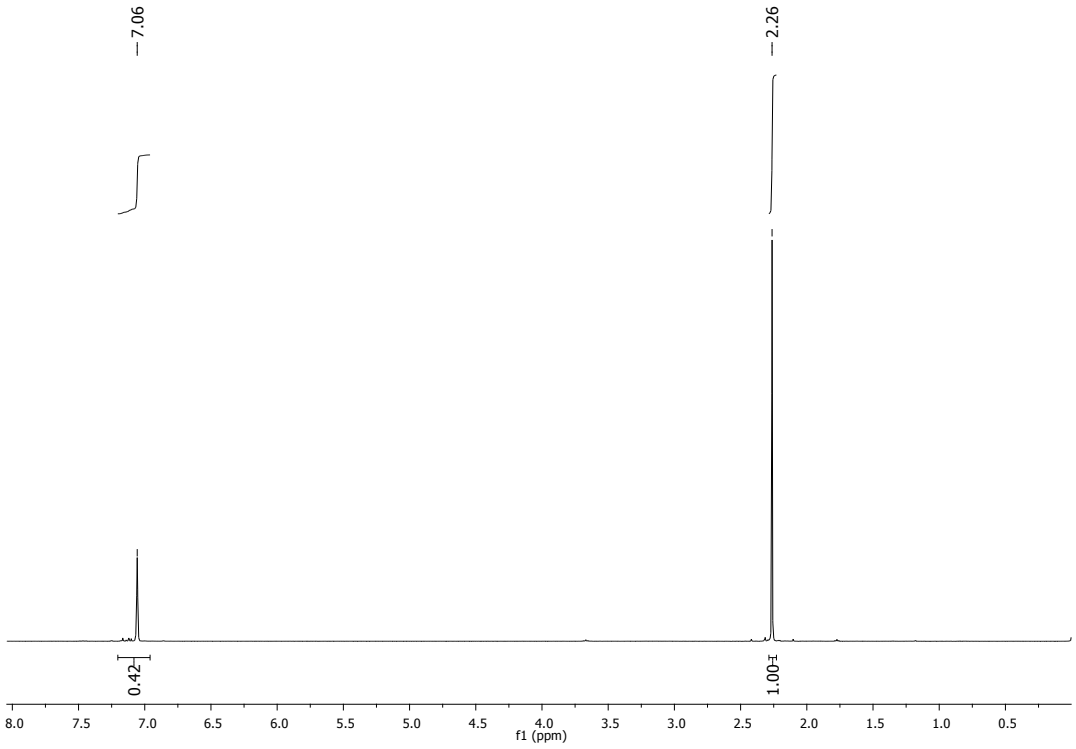


Figure 7. ^{1}H-NMR of hexadeuterated tri-*p*-tolylphosphine (**7**).

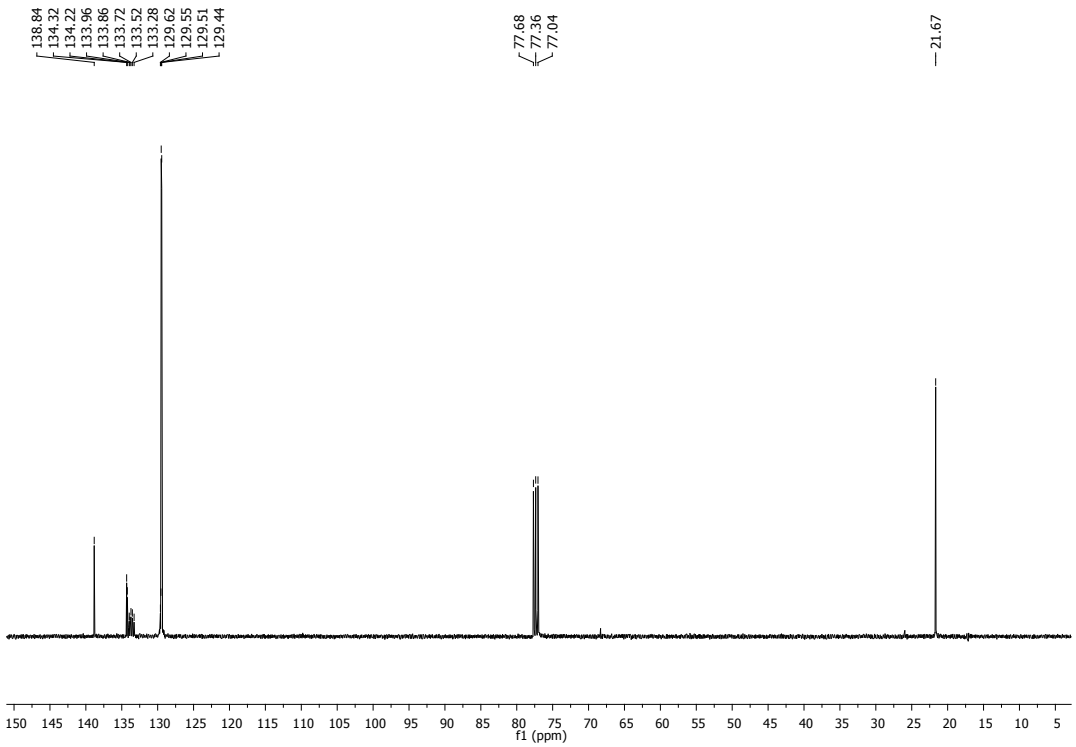


Figure 8. ^{13}C-NMR of hexadeuterated tri-*p*-tolylphosphine (**7**).

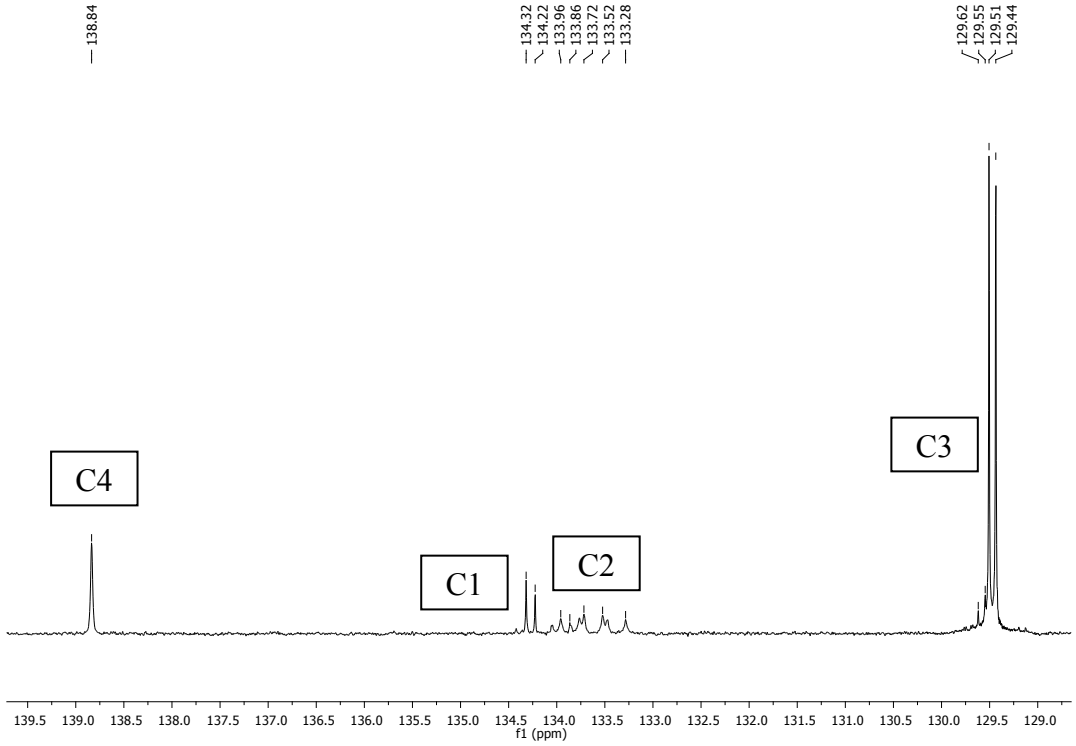


Figure 9. ^{13}C-NMR of hexadeuterated tri-*p*-tolylphosphine (**7**), aromatic zone.

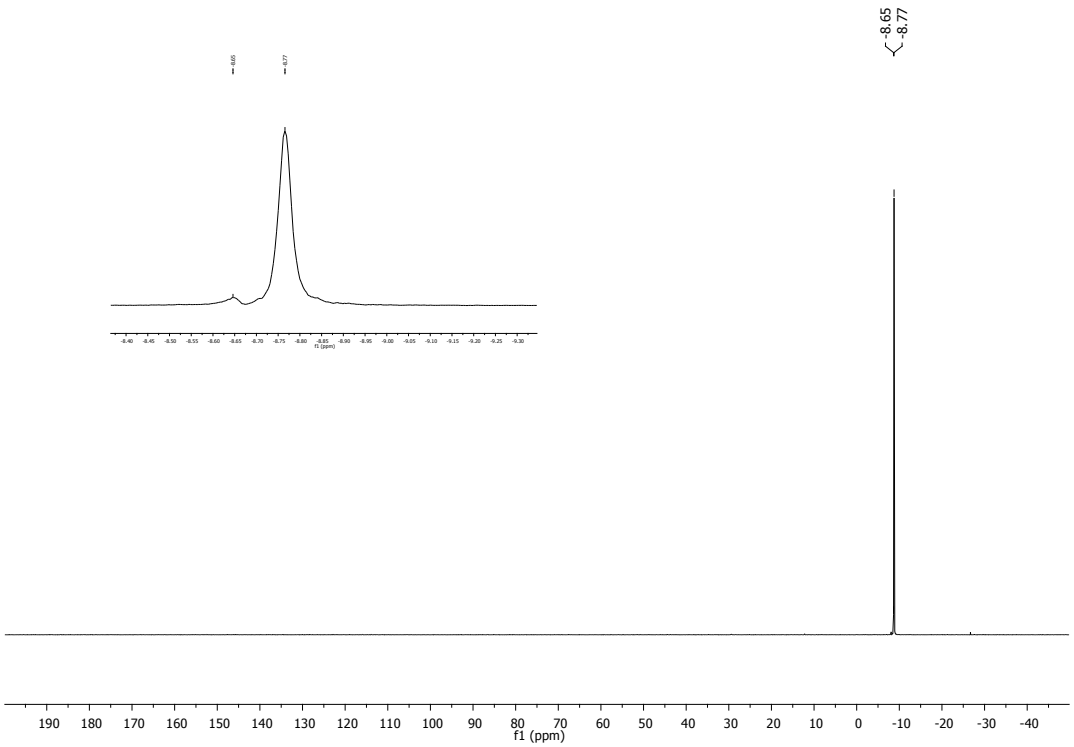


Figure 10. ^{31}P-NMR of hexadeuterated tri-*p*-tolylphosphine (**7**).

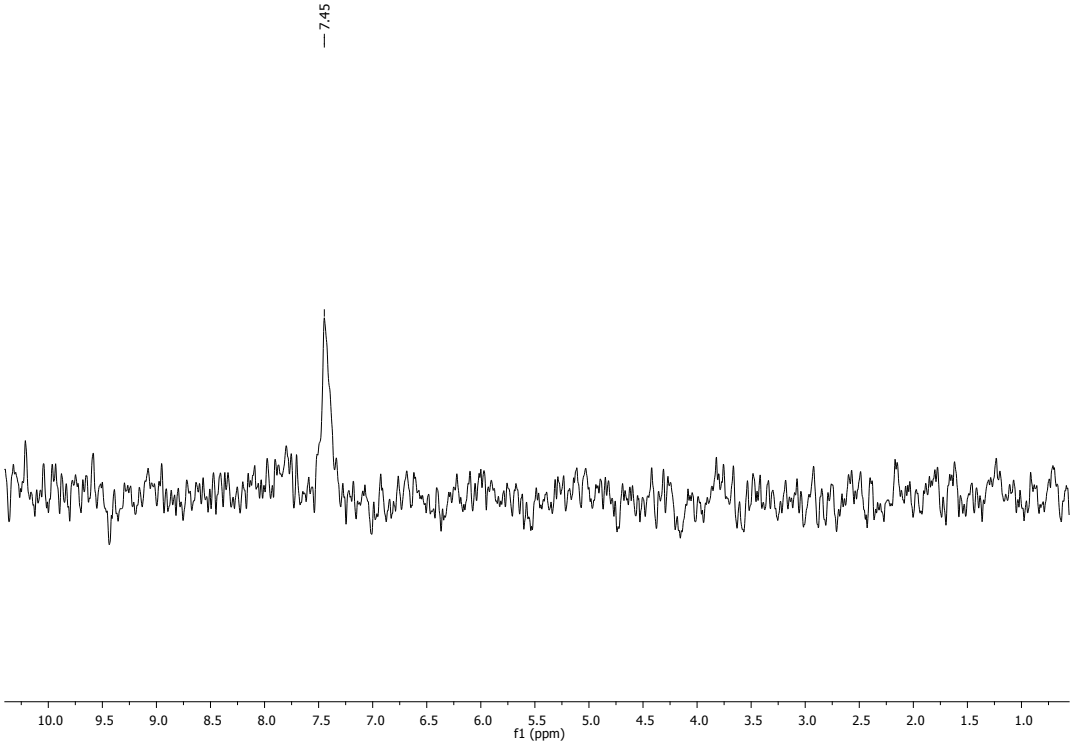


Figure 11. ^{2}H-NMR of hexadeuterated tri-*p*-tolylphosphine (**7**).

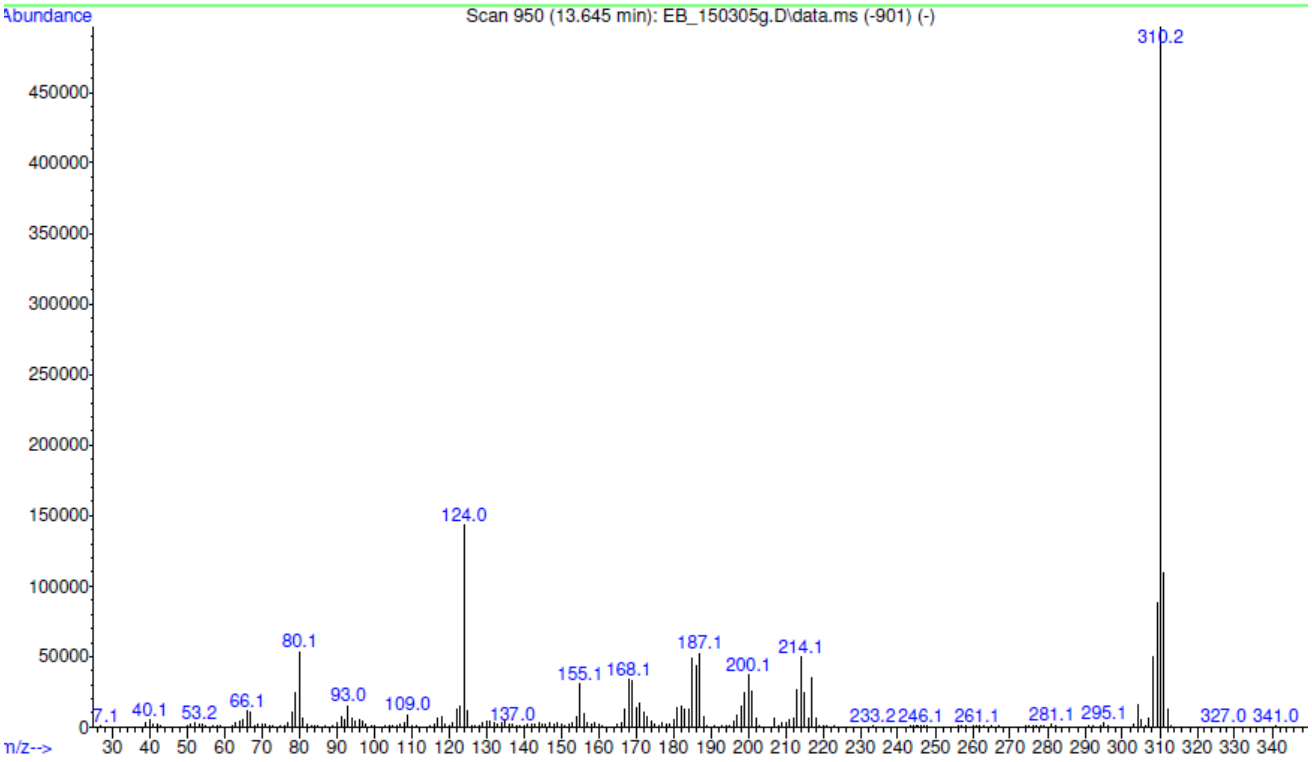
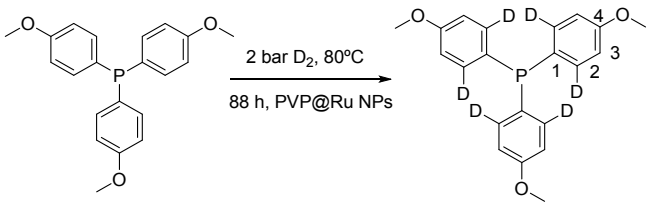


Figure 12. Mas spectrum (electronic impact) of $P(C_7H_6D_2)_3$ (**7**).

Synthesis of hexadeuterated tris(4-methoxyphenyl)phosphine $P(C_7H_5OD_2)_3$ (8).

Following the general procedure tris(4-methoxyphenyl)phosphine was heated for 88h at 80ºC for providing the hexadeuterated phosphine (**8**).



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 6.79 (bs), 3.71 (s, CH_3). **^{13}C NMR** (100.6MHz, $CDCl_3$, δ in ppm): 160.4 (s, C4), 134.9 (dt, C2, *J*= 21.0, 26.0 Hz), 129.0 (d, C1, *J*= 9.0 Hz), 114.3 (d, C3, *J*= 8.0 Hz), 55.5 (s, CH_3). **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): -11.1. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.42 (bs).

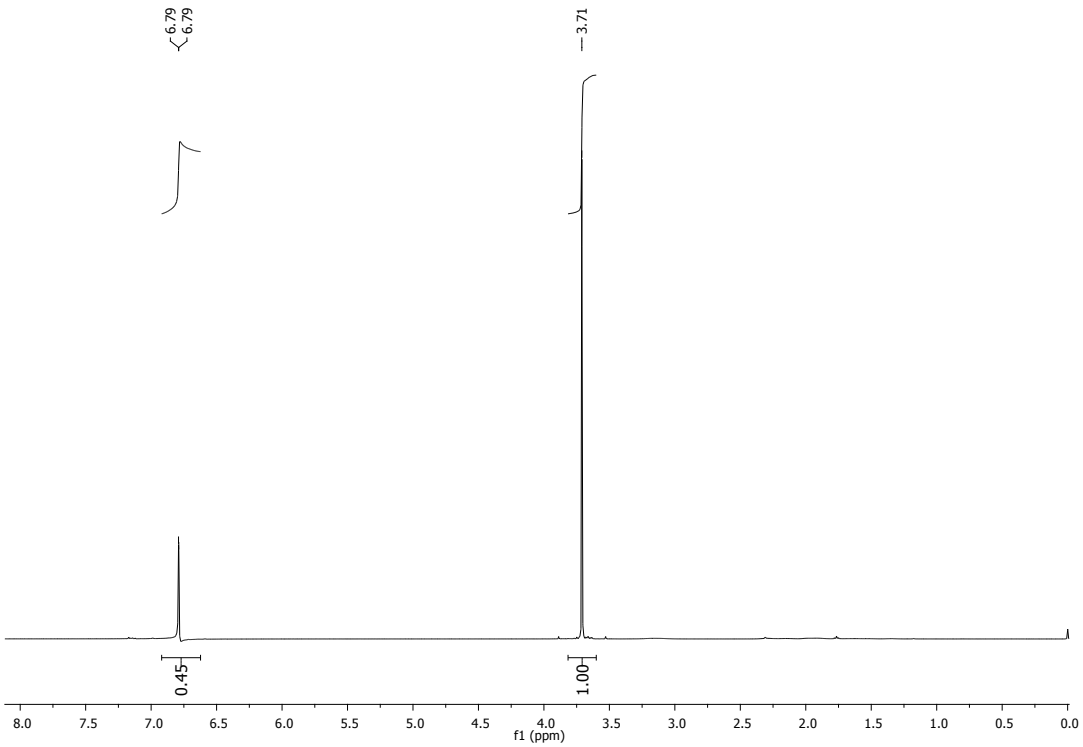


Figure 13. ^{1}H-NMR of hexadeuterated tris(4-methoxyphenyl)phosphine (**8**).

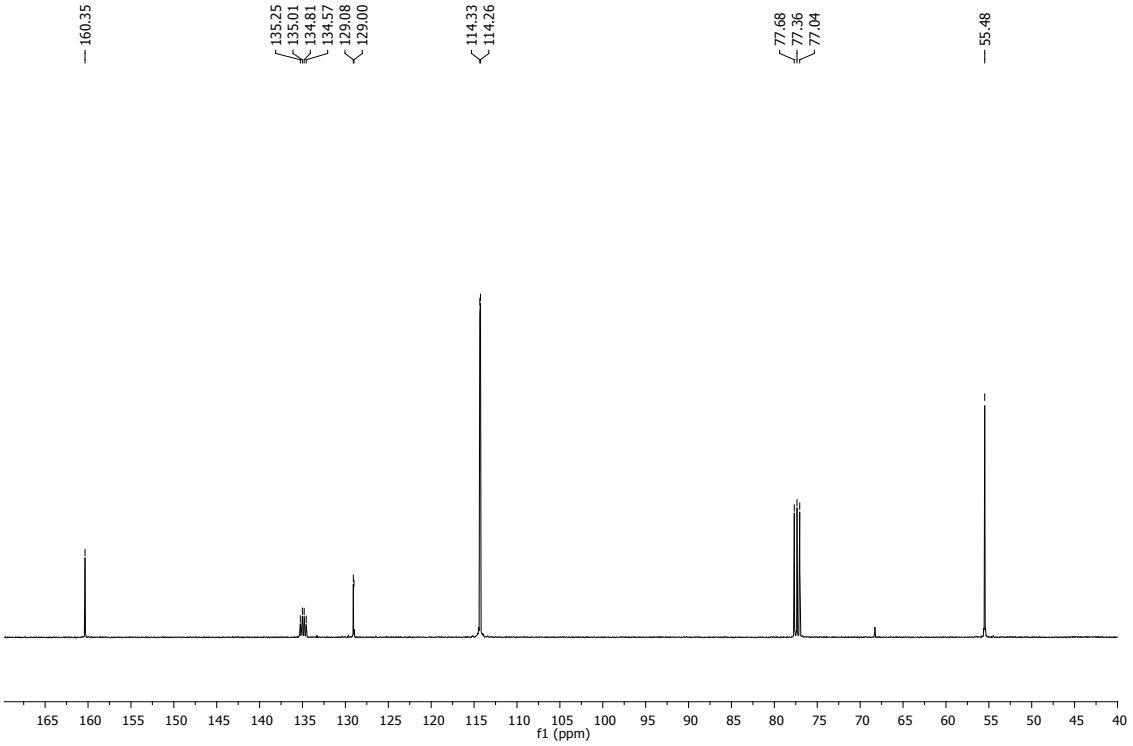


Figure 14. ^{13}C-NMR of hexadeuterated tris(4-methoxyphenyl)phosphine (**8**).

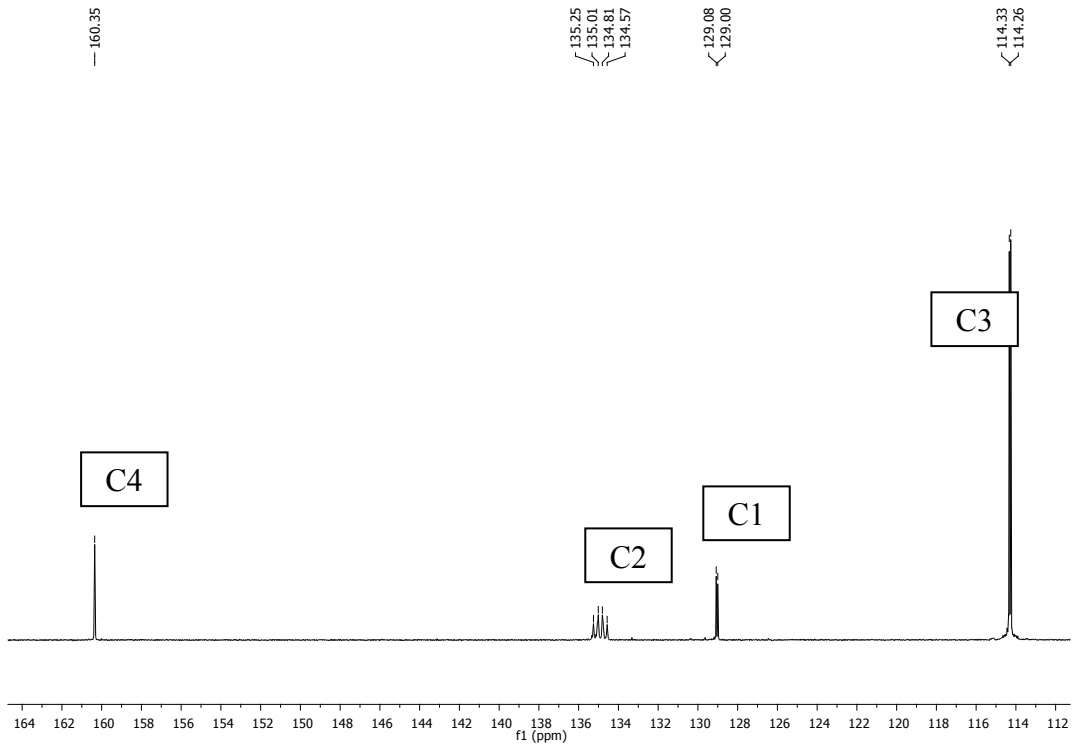


Figure 15. ^{13}C-NMR of hexadeuterated tris(4-methoxyphenyl)phosphine (**8**).

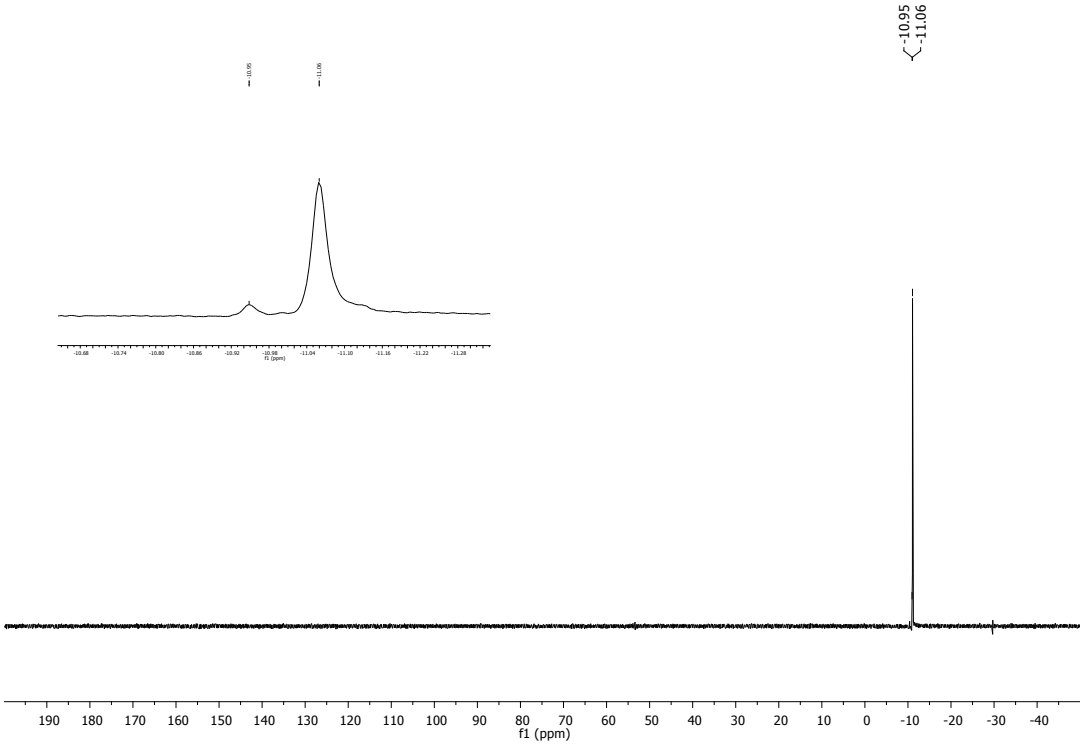


Figure 16. ^{31}P-NMR of hexadeuterated tris(4-methoxyphenyl)phosphine (**8**).

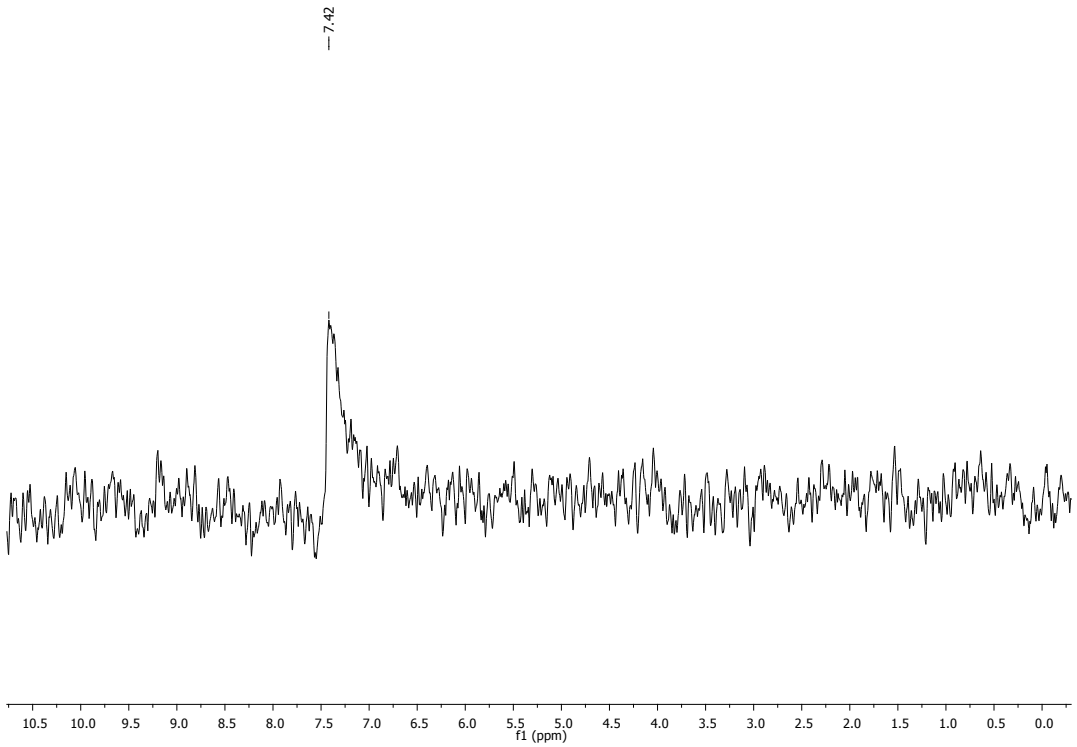


Figure 17. ^{2}H-NMR of hexadeuterated tris(4-methoxyphenyl)phosphine (**8**).

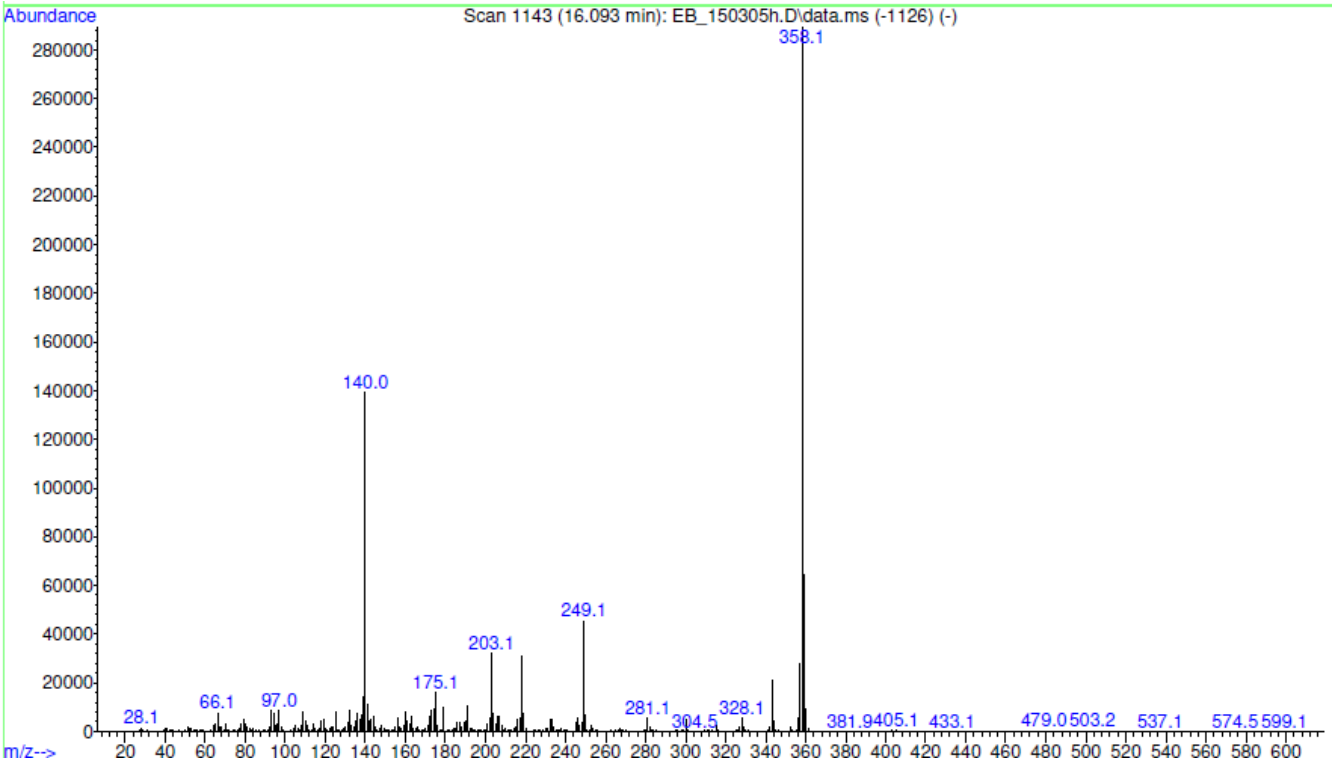
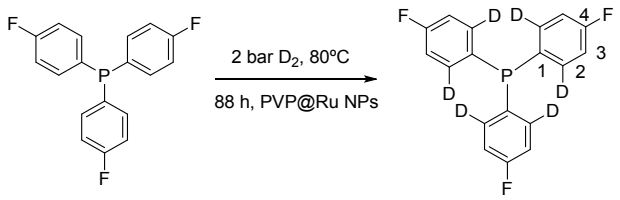


Figure 18. Mas spectrum (electronic impact) of $P(C_7H_5OD_2)_3$ (**8**).

Synthesis of deuterated tris(4-(fluorophenyl)phosphine $P(C_6H_2FD_2)_3$ (9).

Following the general procedure tris(4-fluorophenyl)phosphine was heated for 88h at 80ºC for providing the deuterated phosphine **9** as major isomer. Labelling 72% .



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm):7.72-7.57 (m), 7.27-7.22 (m), 7.21-7.15 (m), 7.08-7.03 (m). **^{13}C NMR** (100.6MHz, $CDCl_3$, δ in ppm): 165.0, 162.5, 134.7-135.8 (m), 132.5-132.6 (dd, J= 11.0, 4.0 Hz), 116.6-116.0 (m). **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): - 9.92. **^{19}F NMR** (376 MHz,$CDCl_3$, δ in ppm): **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.46 (td, 7.2, 3.8 Hz).

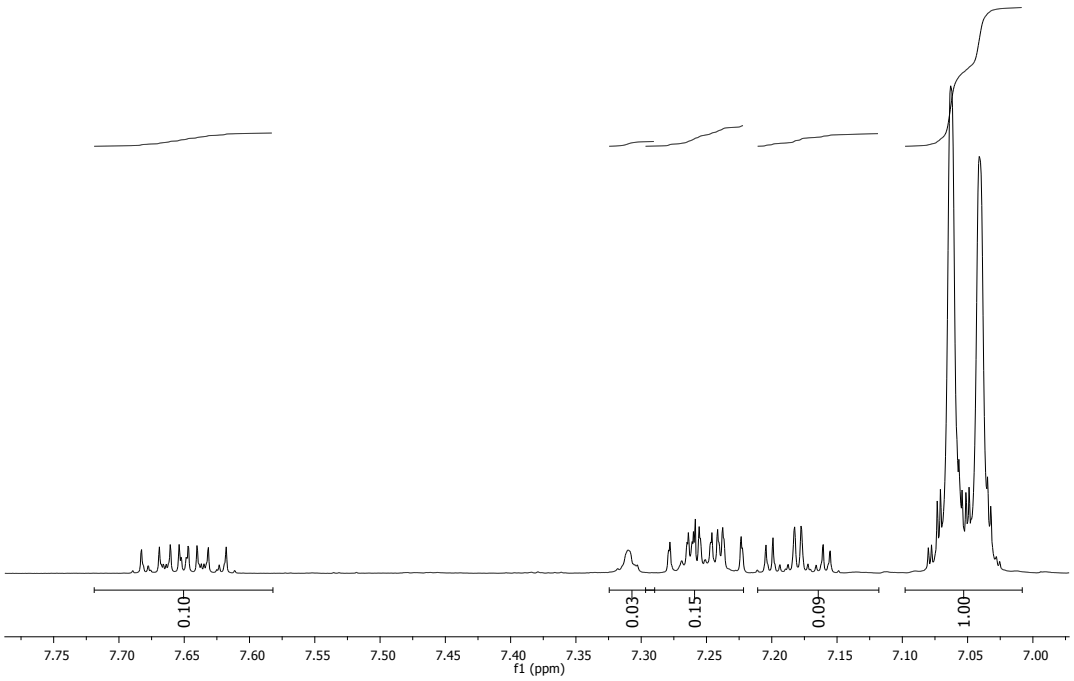


Figure 19. ^{1}H-NMR of partially deuterated tris(4-fluoromethylphenyl)phosphine.

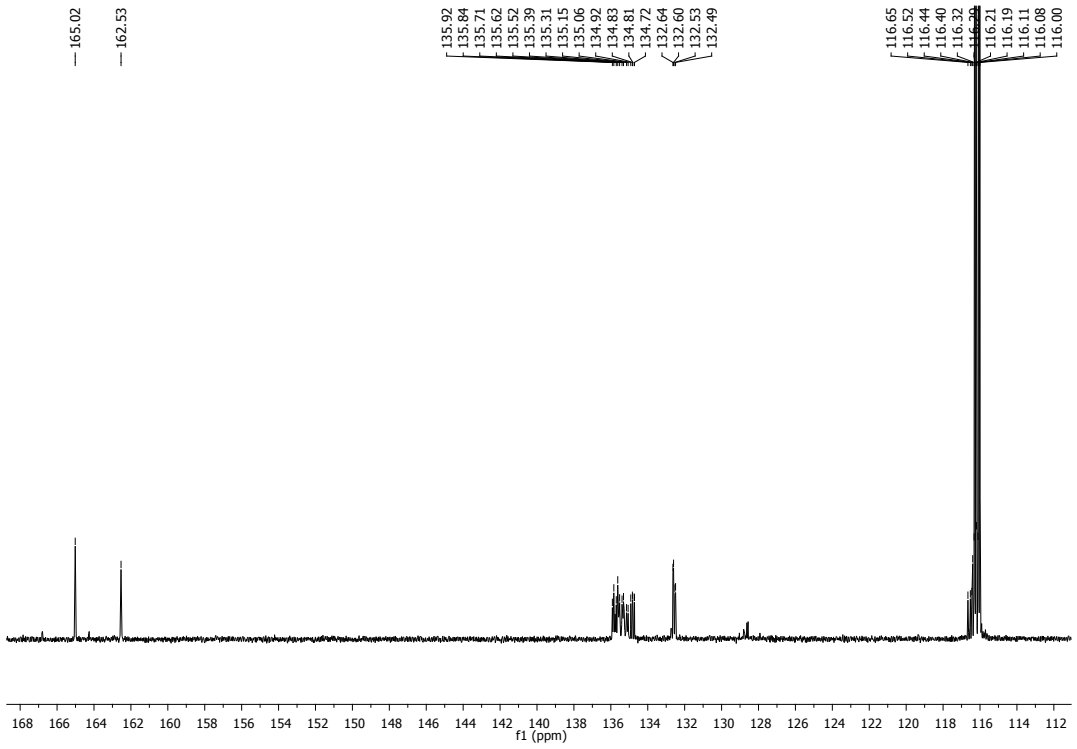


Figure 20. ^{13}C-NMR of partially deuterated tris(4-fluorophenyl)phosphine.

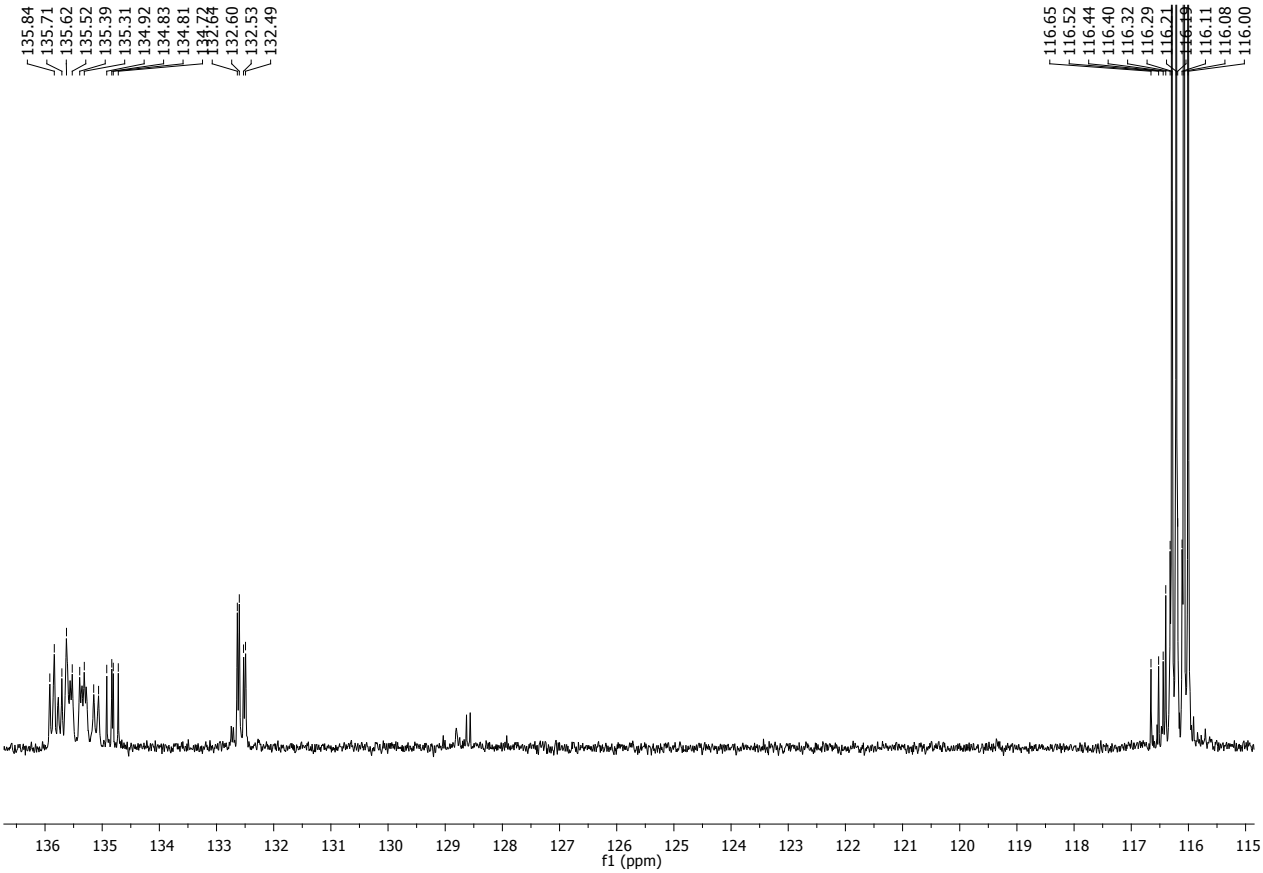


Figure 21. ^{13}C-NMR of partially deuterated tris(4-fluorophenyl)phosphine, enlargement.

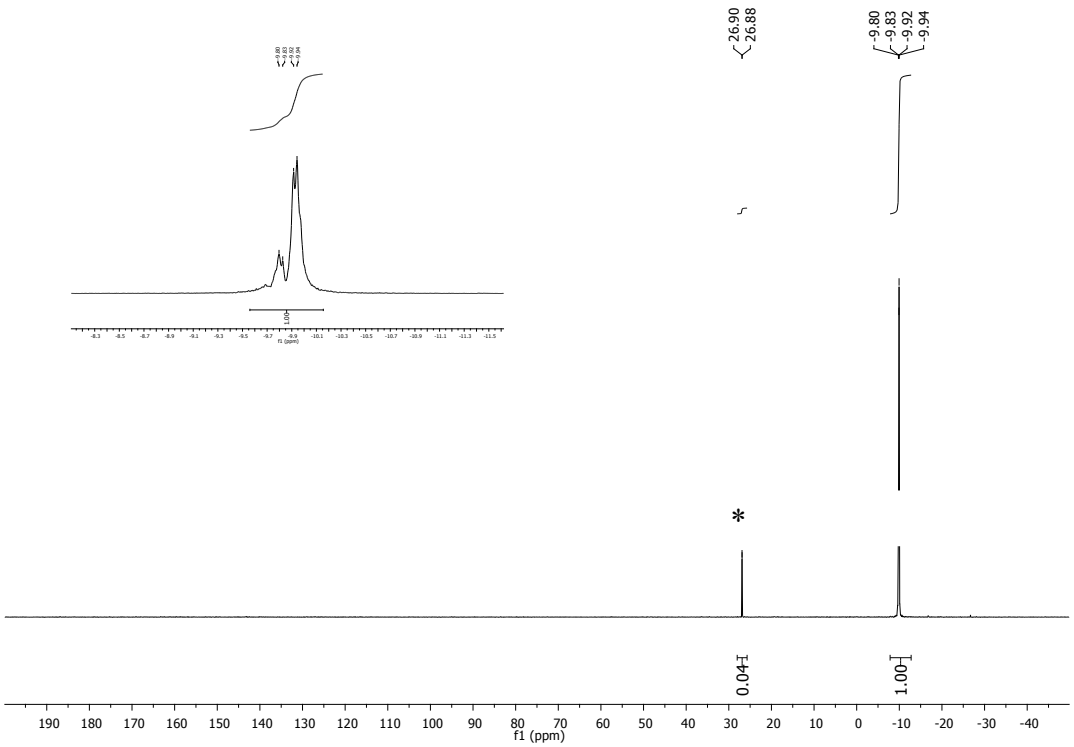


Figure 22. ^{31}P-NMR of partially deuterated tris(4-fluorophenyl)phosphine.

*The signal at 26.90 ppm corresponds to the 4% of oxide.

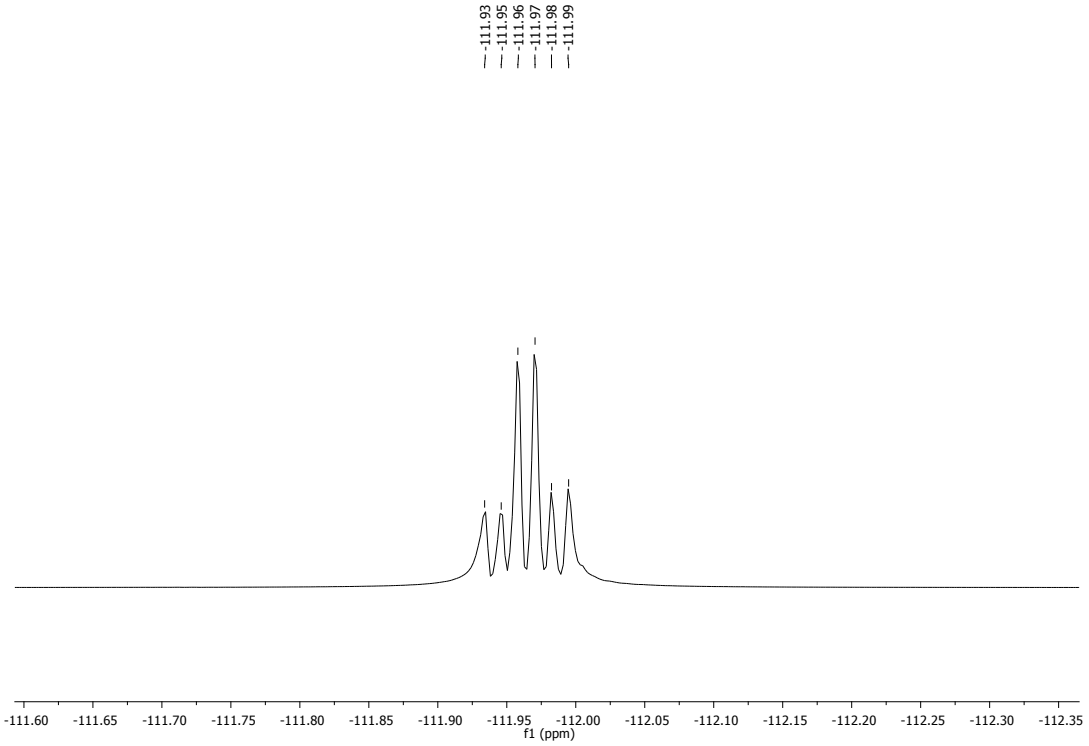


Figure 23. ^{19}F-NMR of partially deuterated tris(4-fluorophenyl)phosphine.

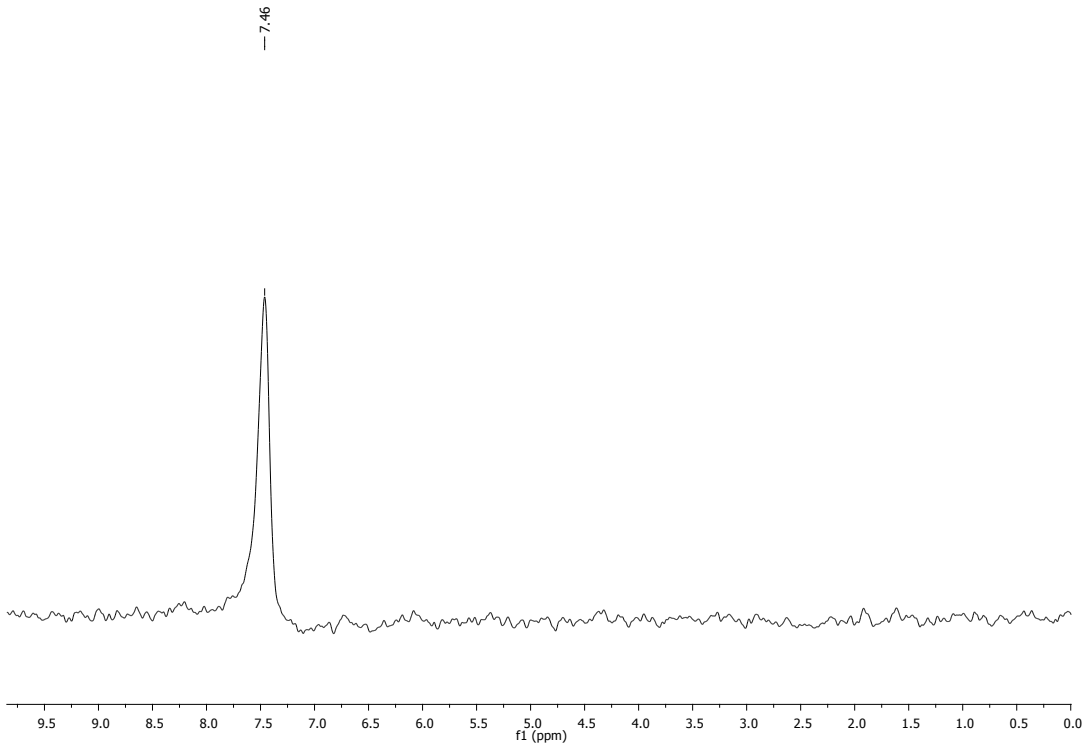


Figure 24. ^{2}H-NMR of partially deuterated tris(4-fluorophenyl)phosphine.

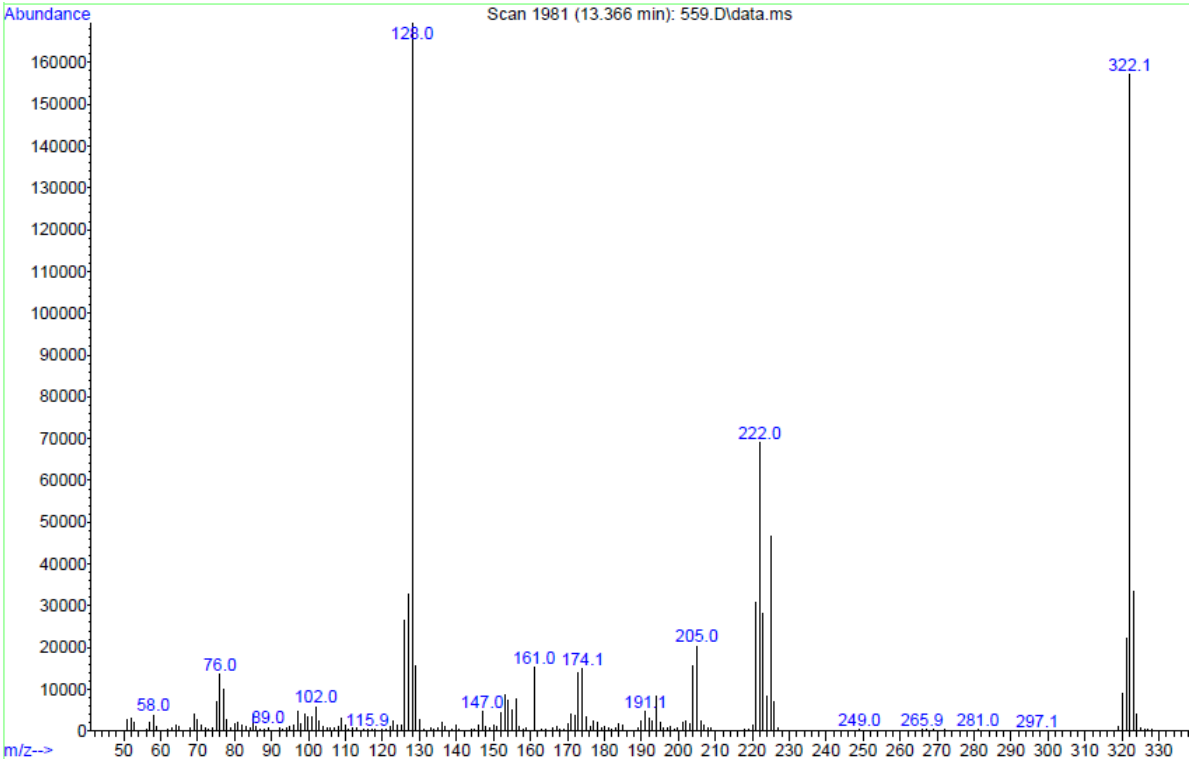
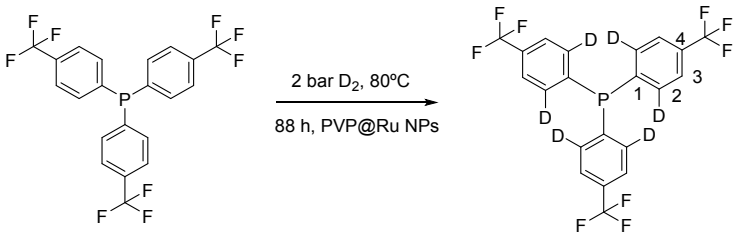


Figure 25. Mas spectrum of $P(C_6H_2FD_2)_3$ (**9**).

Synthesis of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine $P(C_7H_2F_3D_2)_3$ (10).

Following the general procedure tris(4-(trifluoromethyl)phenyl)phosphine was heated for 88h at 80ºC for providing the hexadeuterated phosphine (**10**).



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.56 (bs). **^{13}C NMR** (100.6MHz, $CDCl_3$, δ in ppm): 140.3 (d, C1, *J*= 14 Hz), 133.9 (td, C2, *J*= 19, 25 Hz), 131.7 (q, C4, *J*= 31, 63 Hz), 125.9 (m, C3), 124.2 (q, CF_3, *J*= 269,0 Hz). **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): - 6.93. **^{19}F NMR** (376 MHz,$CDCl_3$, δ in ppm): -62.98. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.61.

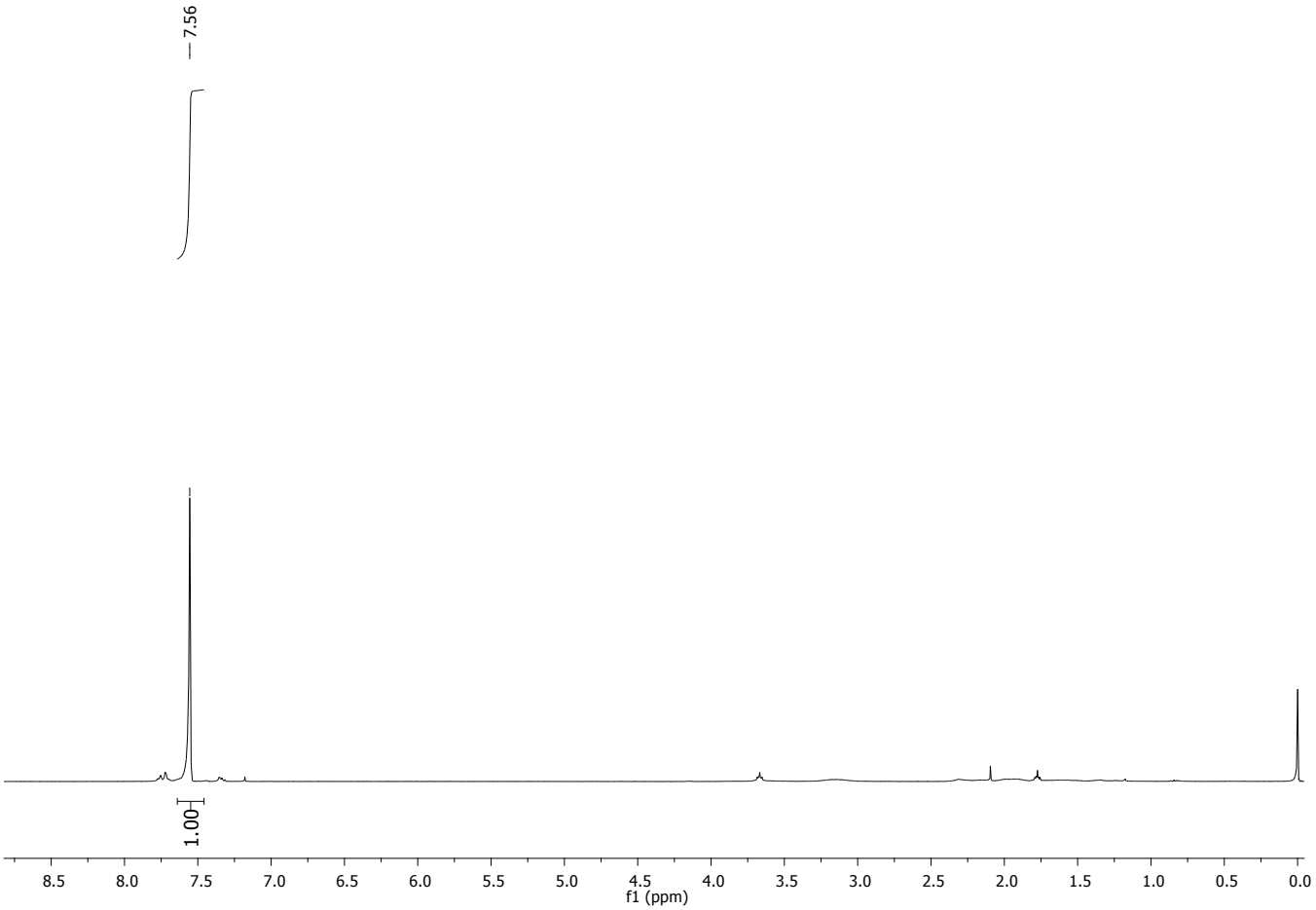


Figure 26. ^{1}H-NMR of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine (**10**).

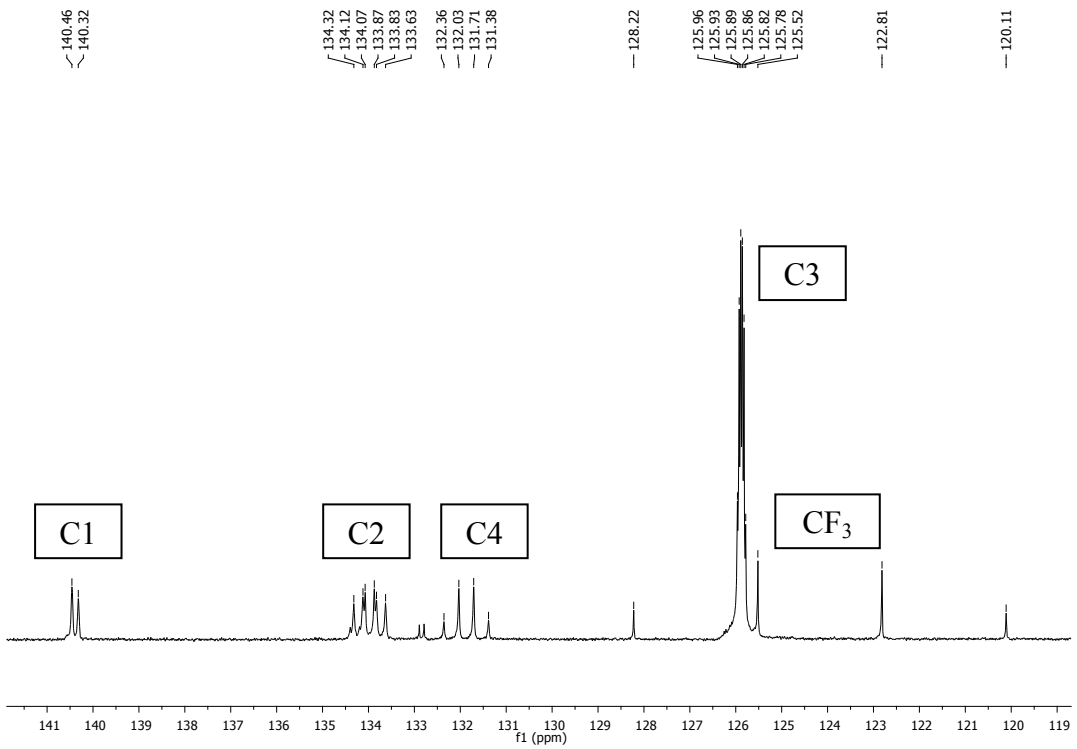


Figure 27. ^{13}C-NMR of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine (**10**).

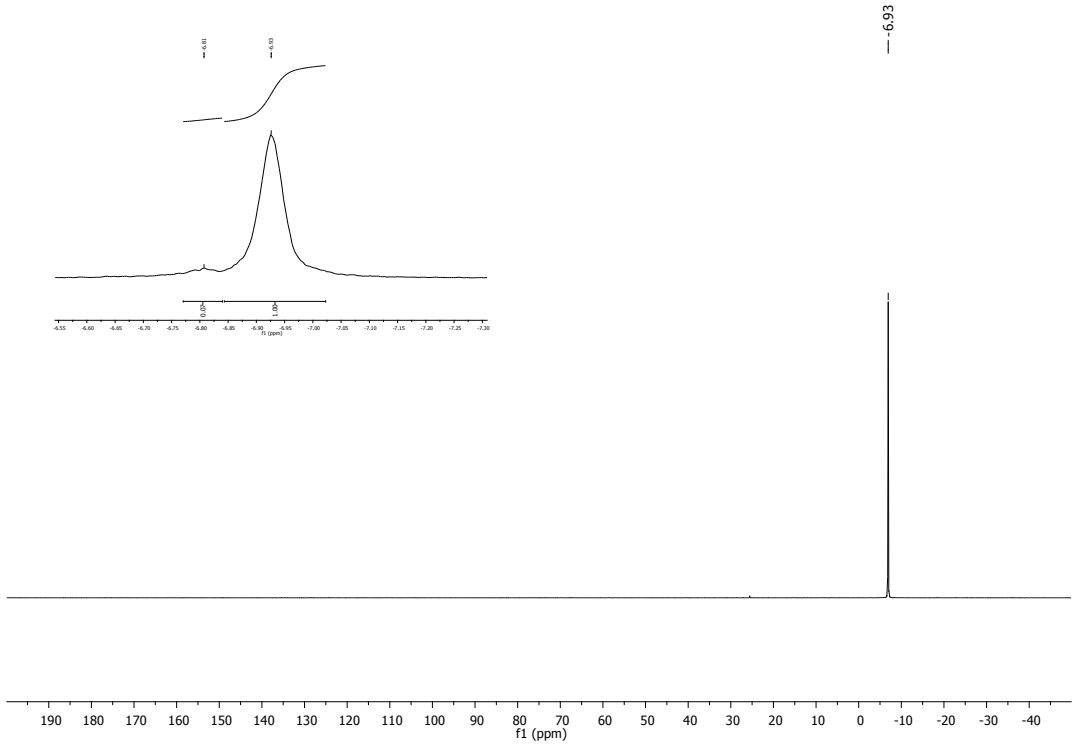


Figure 28. ^{31}P-NMR of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine (**10**).

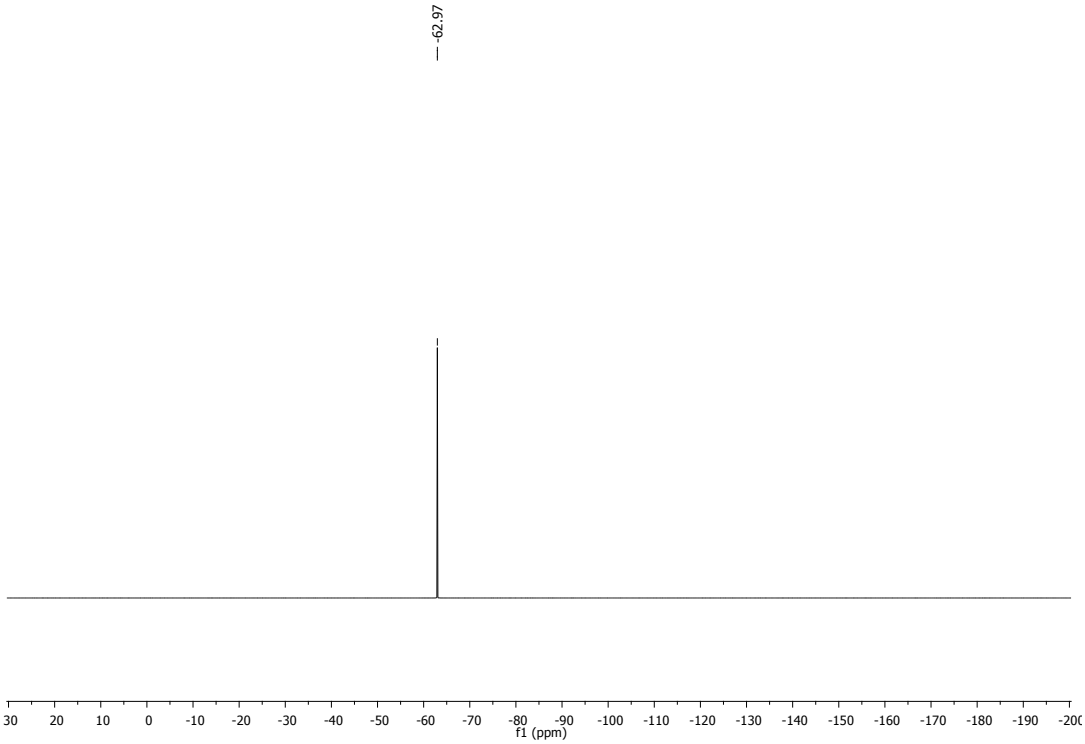


Figure 29. ^{19}F-NMR of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine (**10**).

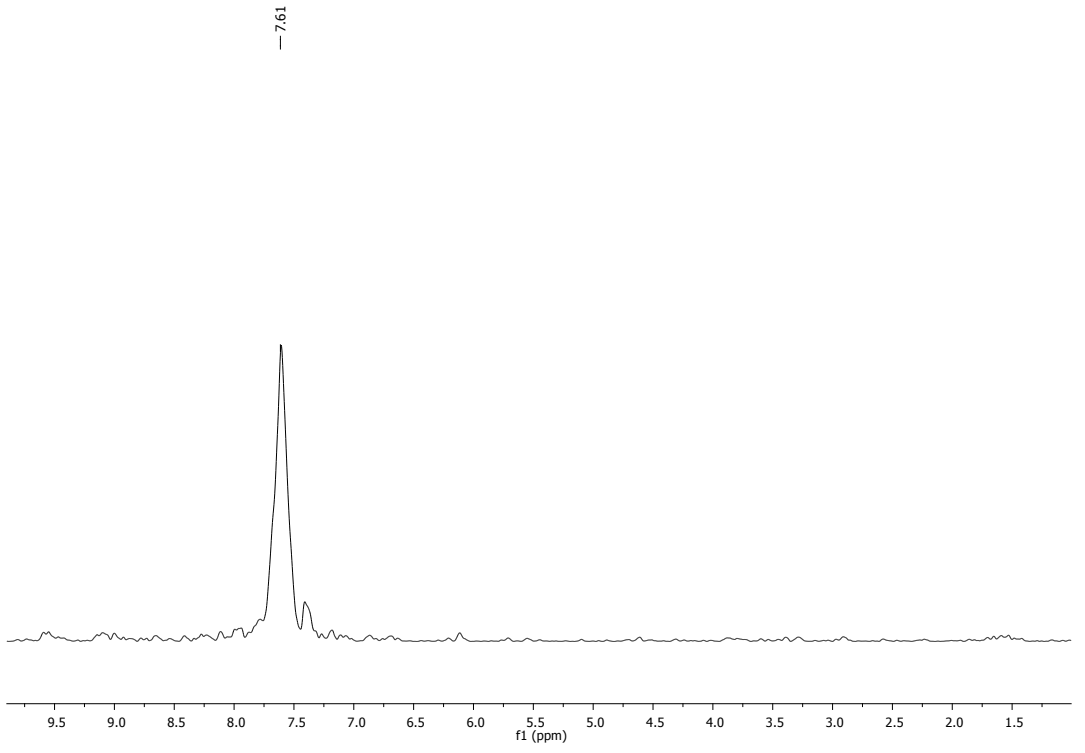


Figure 30. ^{2}H-NMR of hexadeuterated tris(4-(trifluoromethyl)phenyl)phosphine (**11**)

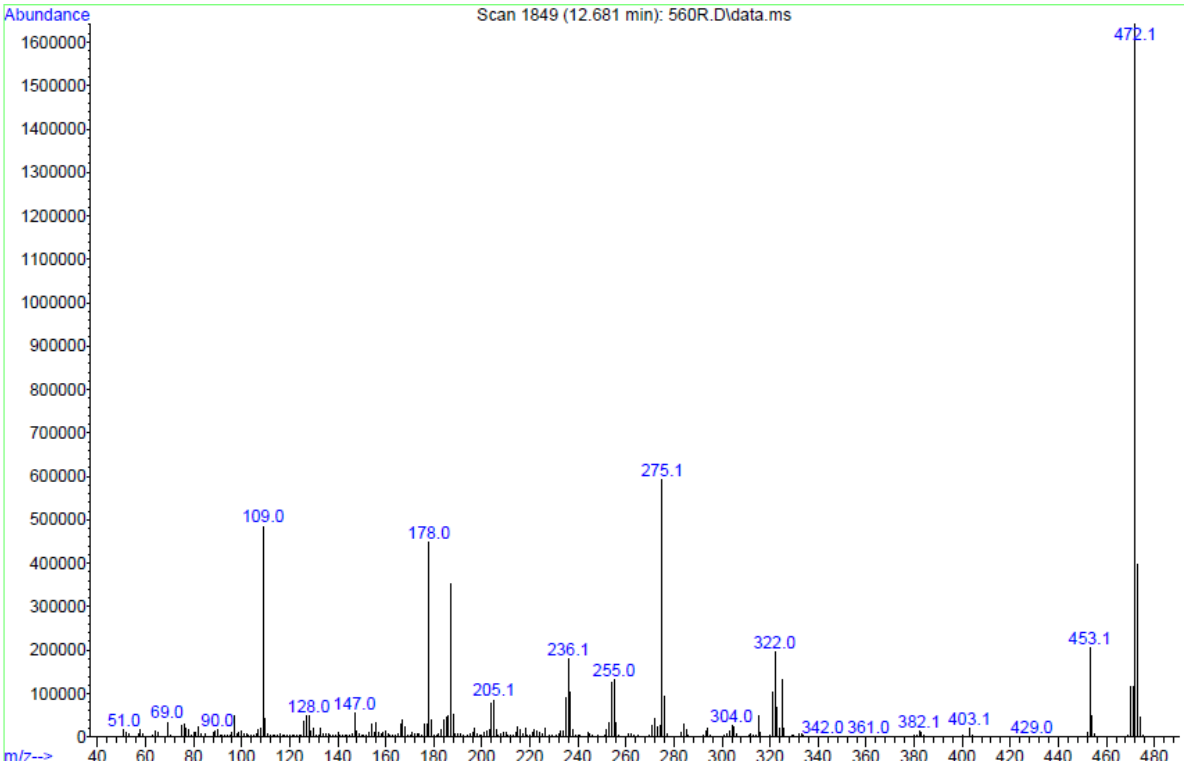
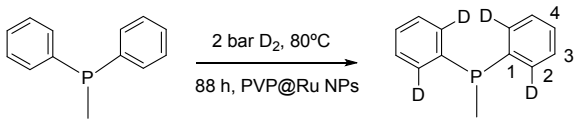


Figure 31. Mas spectrum of $P(C_7H_2F_3D_2)_3$ (**10**)

Synthesis of tetradeuterated methyldiphenylphosphine $PC_{13}H_9D_4$ (12).

Following the general procedure methyldiphenylphosphine was heated for 88h at 80ºC for providing the hexadeuterated phosphine (**12**).



^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.28-7.76 (bs), 1.62 (d, CH_3, *J*=3.0 Hz). **^{13}C NMR** (100.6MHz, $CDCl_3$, δ in ppm): 140.2 (d, C1, *J*= 13.0 Hz), 133.9 (td, C2, *J*= 20.0, 25.0 Hz), 128.7 (s, C4), 128.6 (d, C3, *J*= 8.0 Hz), 12.8 (d, CH_3, *J*= 14.0 Hz). **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): -27.41. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.52.

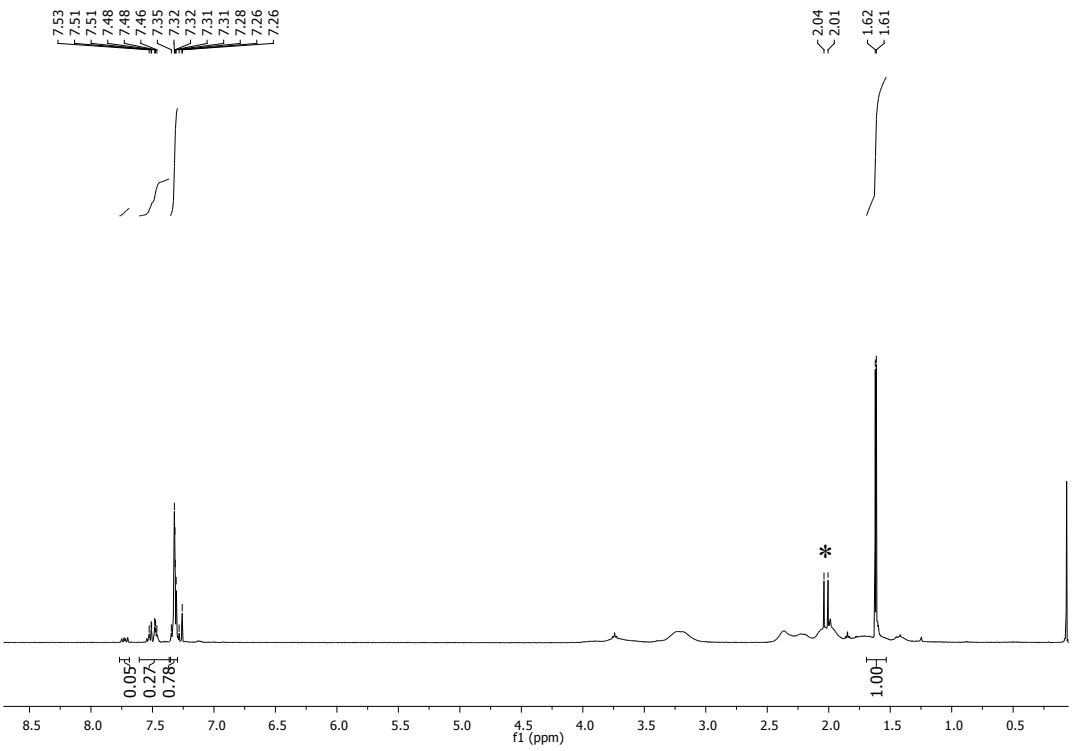


Figure 32. ^{1}H-NMR of tetradeuterated methyldiphenylphosphine (**12**)

*Signal corresponding to methyldiphenylphsphine oxide.

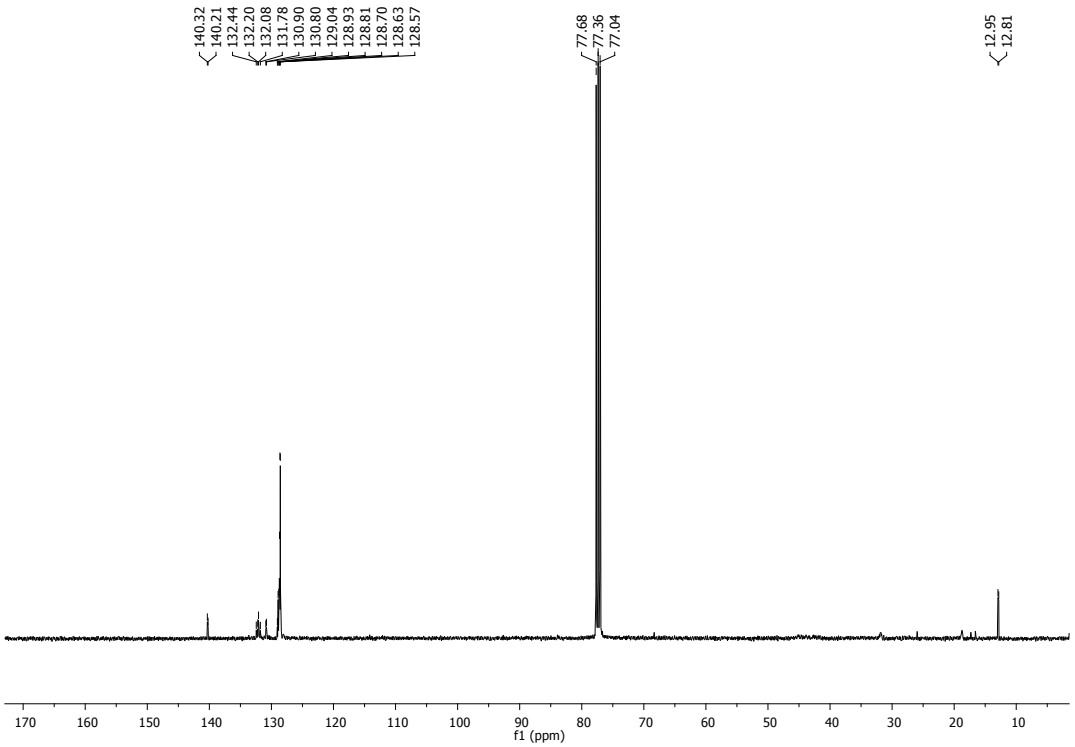


Figure 33. ^{13}C-NMR of tetradeuterated methyldiphenylphosphine (**12**).

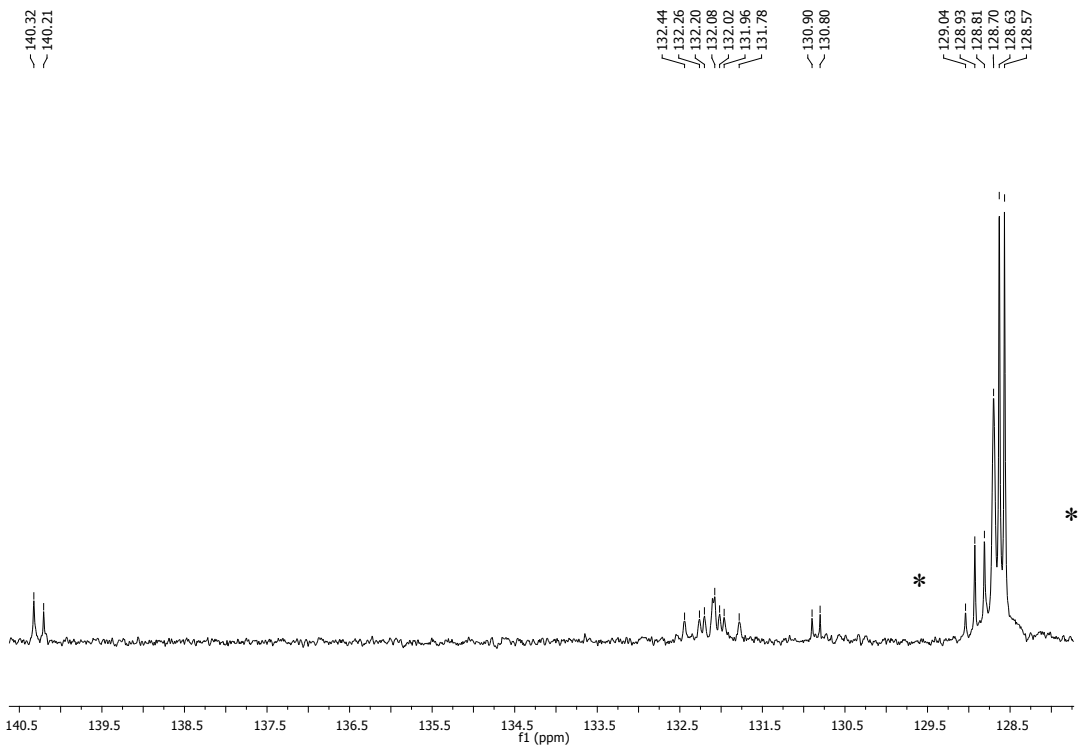


Figure 34. ^{13}C-NMR of tetradeuterated methyldiphenylphosphine (**12**).

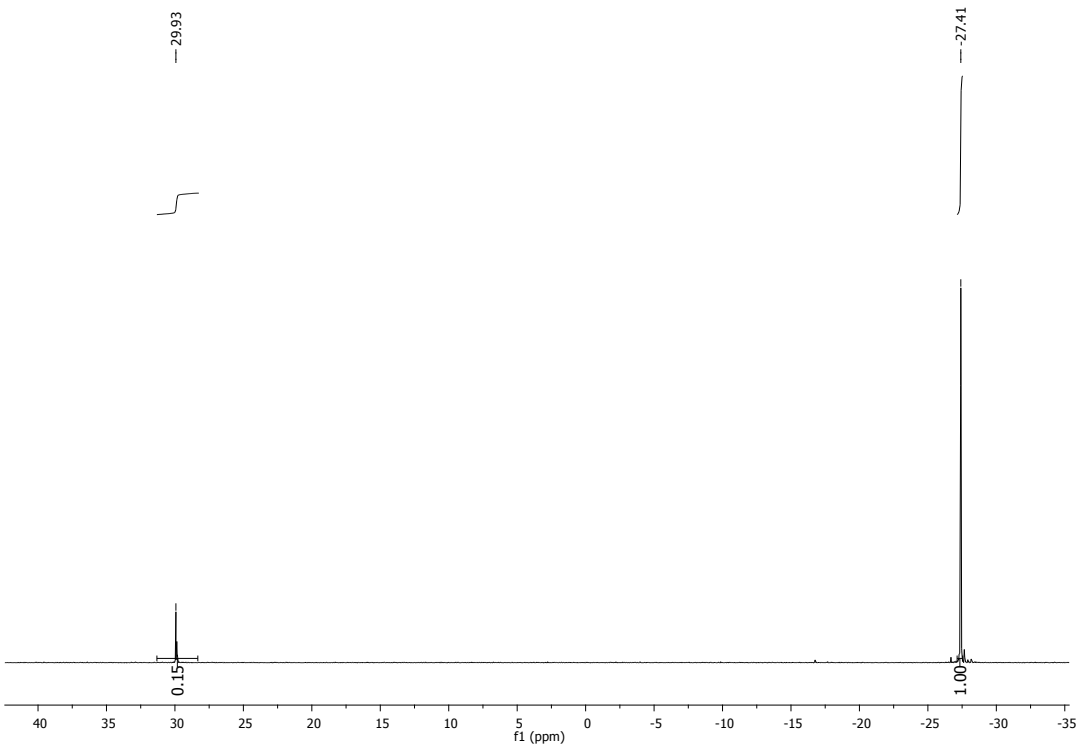


Figure 35. ^{31}P-NMR of h tetradeuterated methyldiphenylphosphine (**12**).

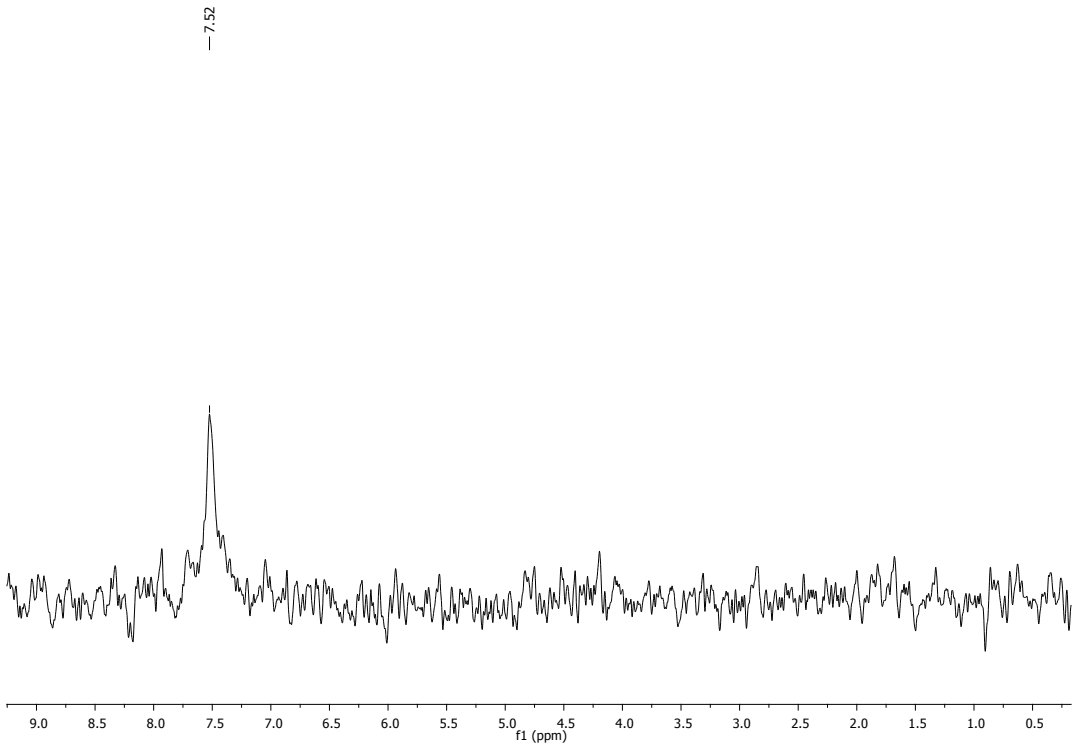


Figure 36. ^{2}H-NMR of tetradeuterated methyldiphenylphosphine (**12**).

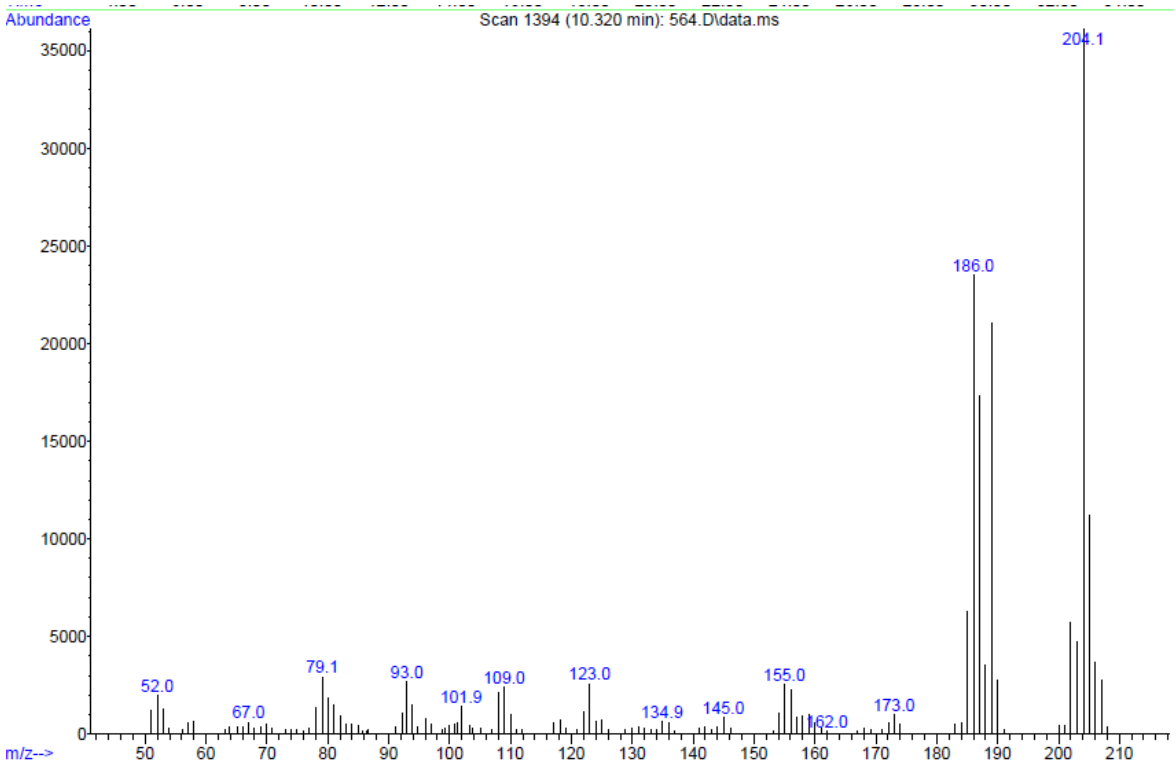
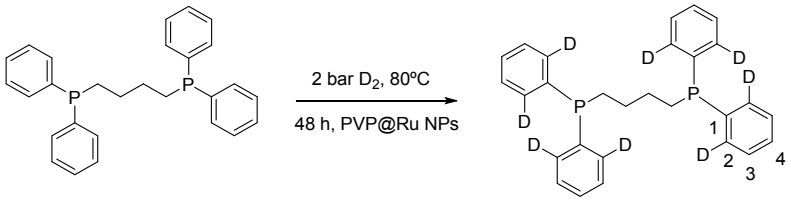


Figure 37. Mas spectrum of tetradeuterated methyldiphenylphosphine (**12**) $PC_{13}H_9D_4$.

Synthesi of octadeuterated 1,4-bis(diphenylphosphino)butane $P_2C_{28}H_{20}D_8$ (14).

Following the general procedure 1,4-bis(diphenylphosphino)butane was heated for 48h at 80ºC for providing the octadeuterated phosphine (**14**).



H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.22 (s), 1.93 (m, CH_2),1.46 (m, CH_2). **^{13}C NMR** (100.6MHz, $CDCl_3$, δ in ppm): 138.8 (d, C1, *J*= 15.0 Hz), 132.7 (td, C2, *J*= 18.0, 25.0 Hz), 128.8 (s, C4), 128.6 (d, C3, *J*= 6.0 Hz), 28.0 (m, CH_2). **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): -16.74. **^{2}H NMR** (400 MHz, $CDCl_3$, δ in ppm): 7.60.

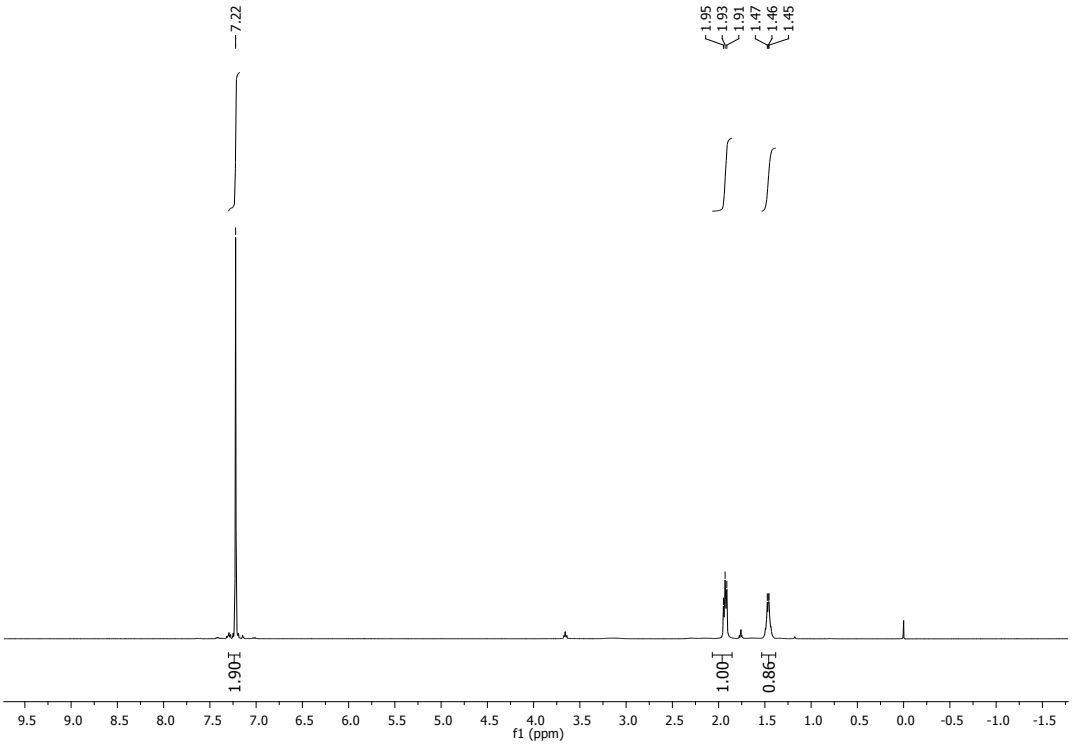


Figure 38. ^{1}H-NMR octadeuterated 1,4-bis(diphenylphosphino)butane (**14**).

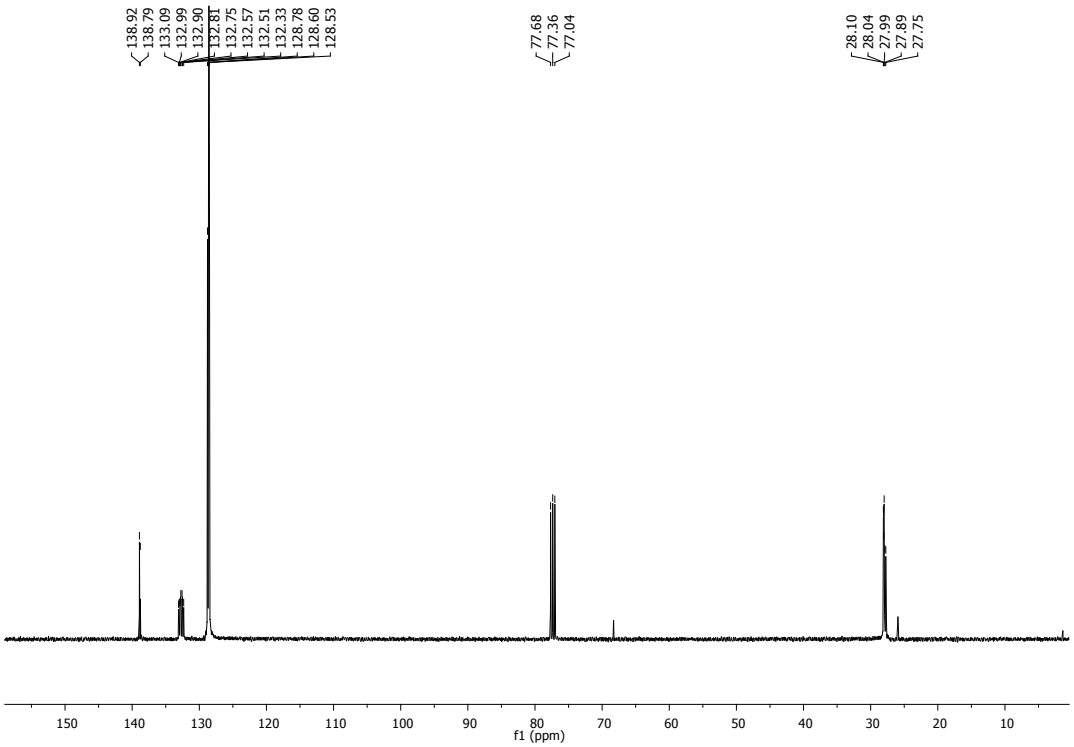


Figure 39. ^{13}C-NMR octadeuterated 1,4-bis(diphenylphosphino)butane (**14**).

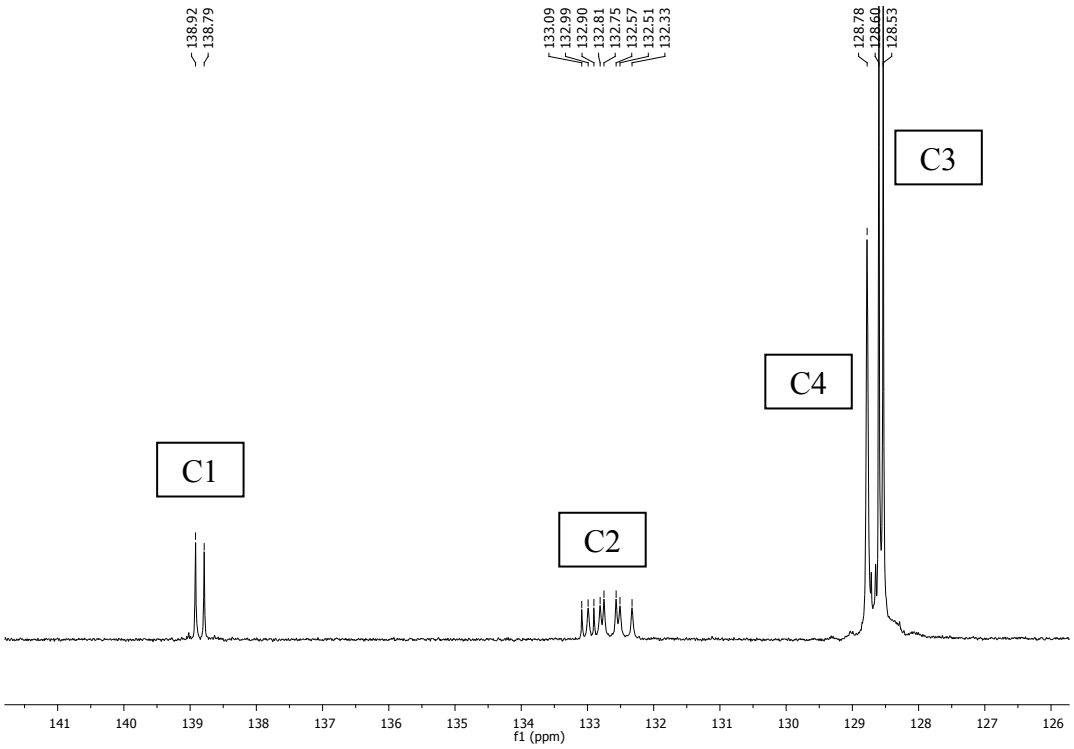


Figure 40. ^{13}C-NMR octadeuterated 1,4-bis(diphenylphosphino)butane (**14**) (aromatic zone).

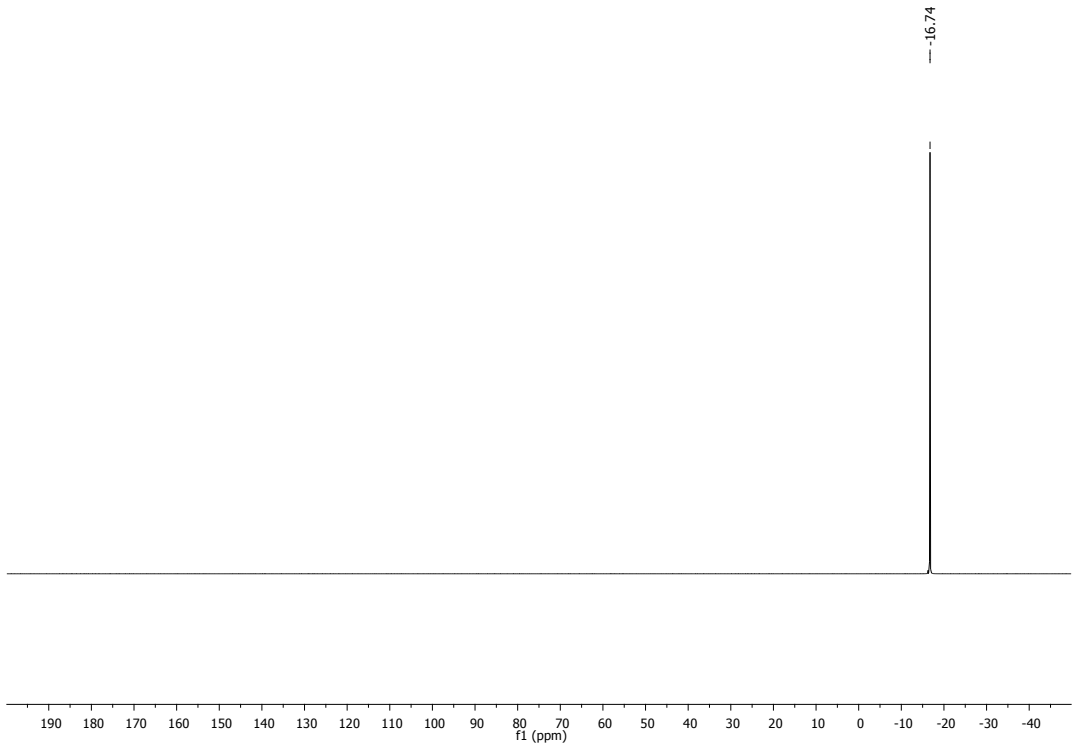


Figure 41. ^{31}P-NMR of octadeuterated 1,4-bis(diphenylphosphino)butane (**14**).

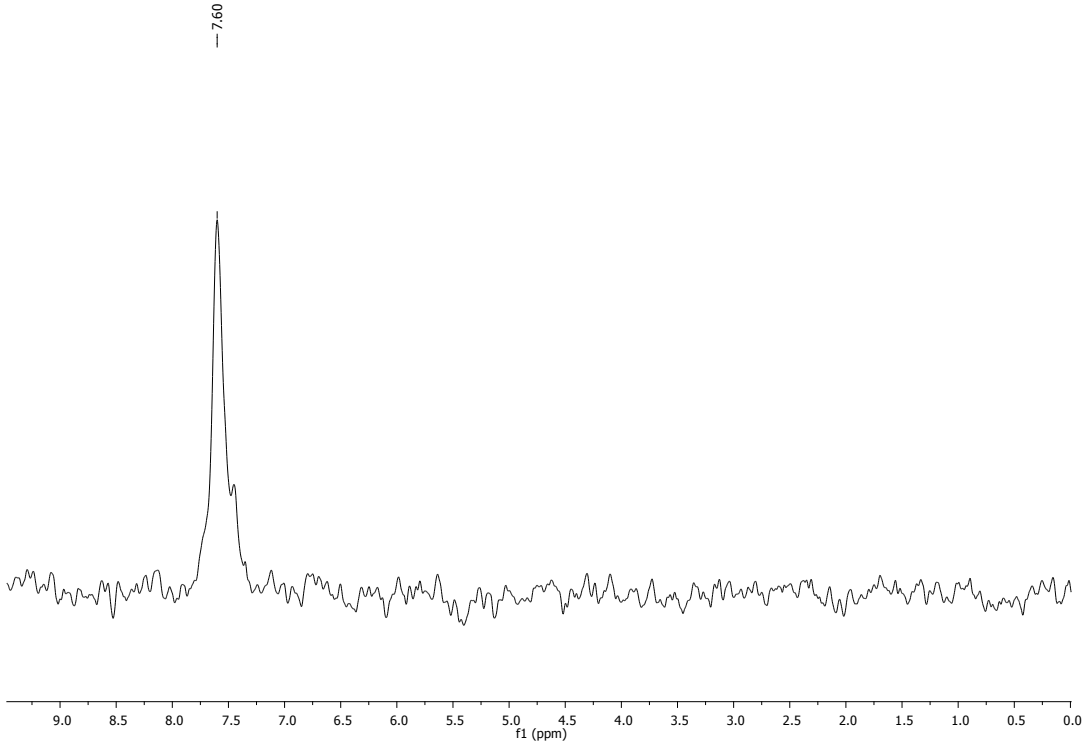
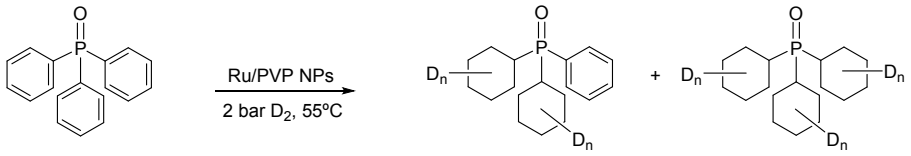


Figure 42. ^{2}H-NMR of octadeuterated 1,4-bis(diphenylphosphino)butane (**14**).

Deuteration of triphenylphosphine oxide at 55ºC for 36 h. Synthesis of 17-18.

Following the general procedure triphenylphosphine oxide was heated at 55ºC for 36h providing a mixture of reduced products **17-18**.



15 **17** **18**

Dicyclohexyl(phenyl)phosphine oxide (**17**) [4], **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): 45.95.
Tricyclohexylphosphine oxide (**18**) [5], **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): 51.40.

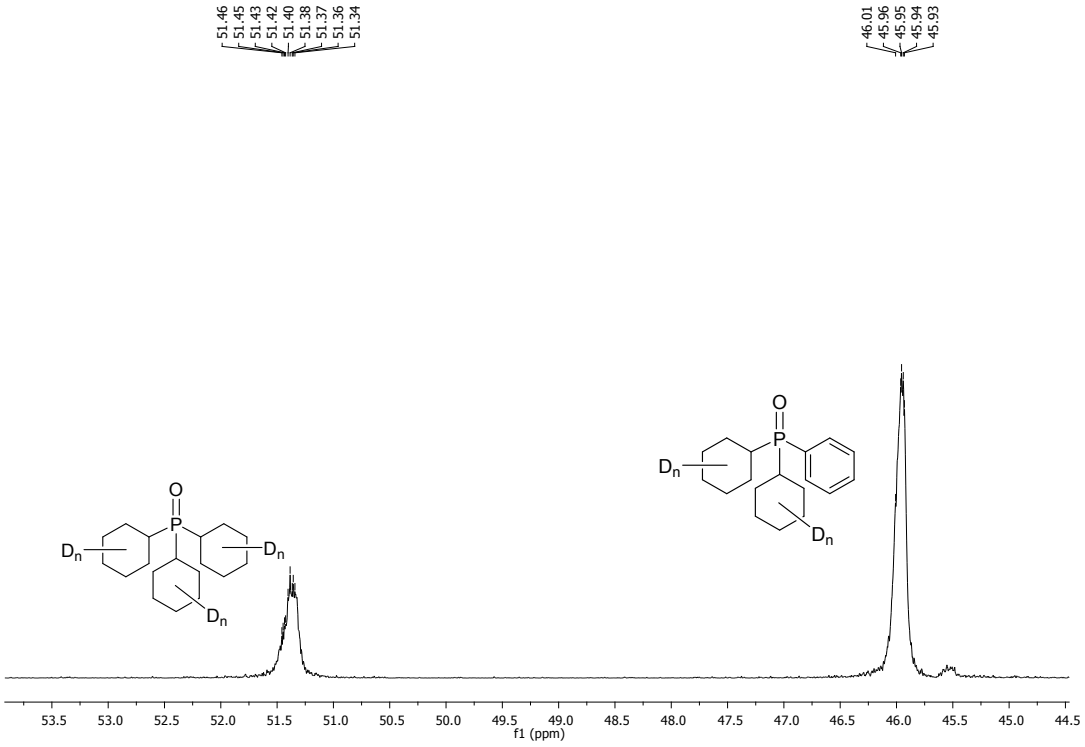


Figure 43. ^{31}P-NMR of the mixture of compounds **17** and **18** obtained by deuteration at 55°C for 36 hours.

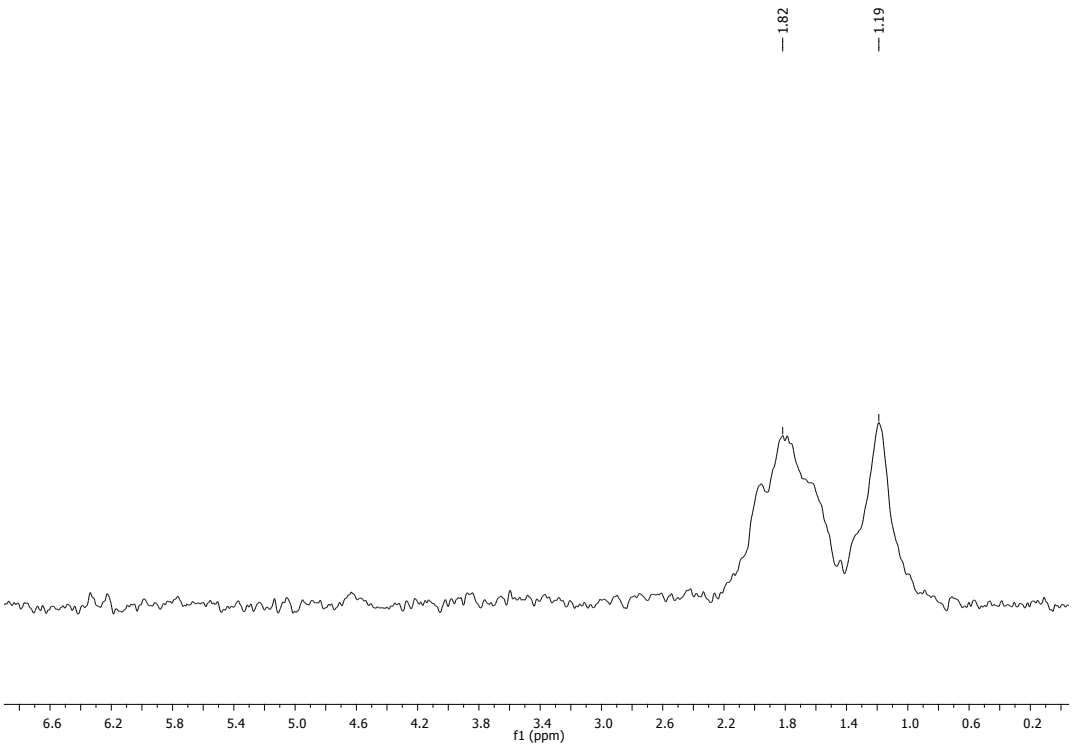
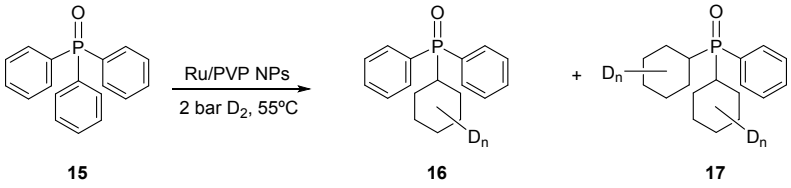


Figure 44. ^{2}H-NMR of the mixture of compounds **17** and **18**.

Deuteration of triphenylphosphine oxide at 55ºC for 16 h. Synthesis of 16-17.

Following the general procedure triphenylphosphine oxide was heated for 16h at 55ºC providing a mixture of products (**15, 16**).



Cyclohexyldiphenylphosphine oxide (**16**) [3], **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): 34.41.
Dicyclohexyl(phenyl)phosphine oxide [4], **^{31}P NMR** (162MHz, $CDCl_3$, δ in ppm): 45.18.

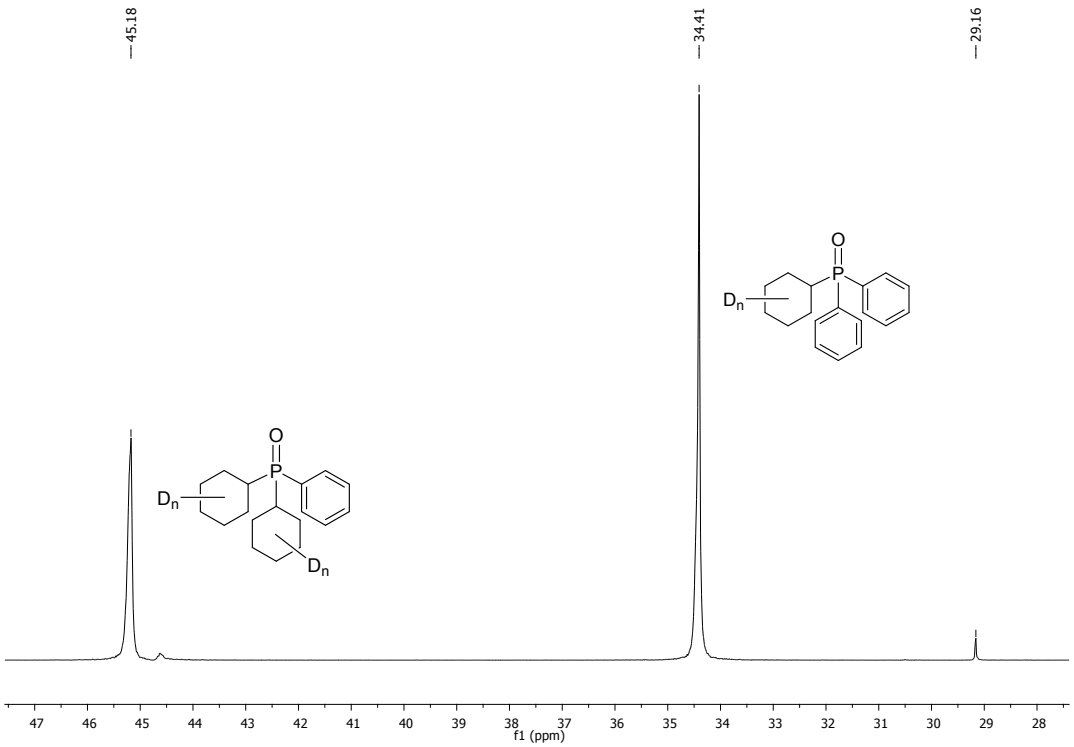


Figure 45. ^{31}P-NMR of the mixture of compounds **16** and **17** obtained by deuteration at 55°C for 36 hours.

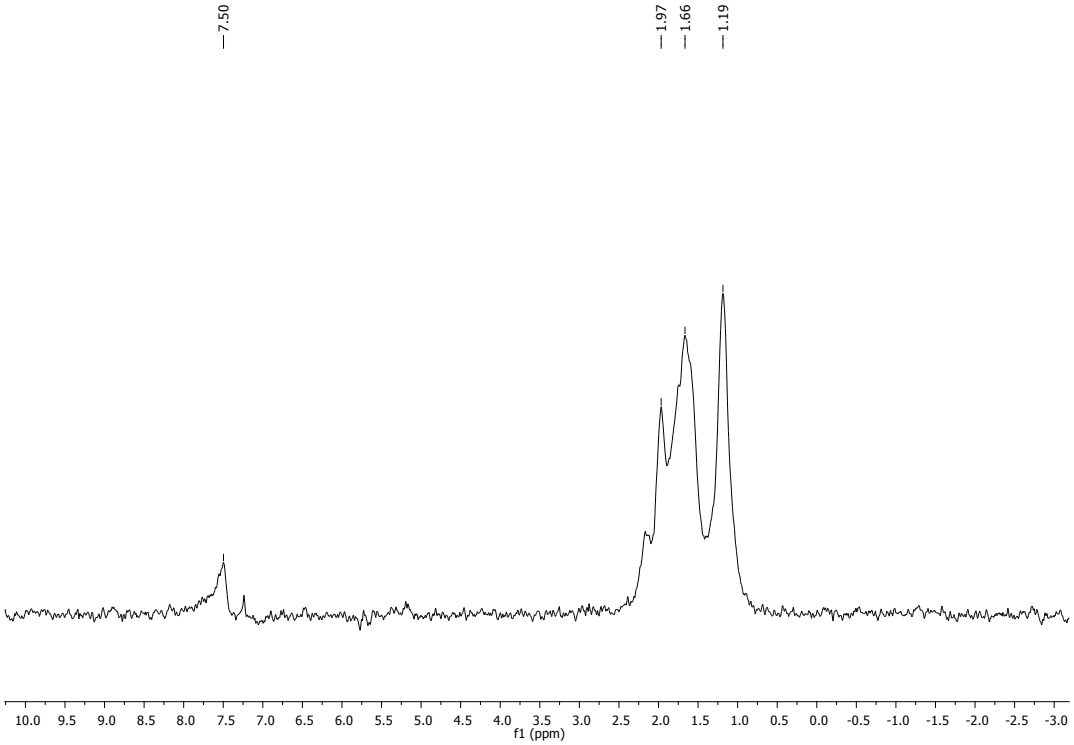


Figure 46. ^{2}H-NMR of the mixture of compounds **16** and **17** obtained by deuteration at 55°C for 36 hours.

S5. References

[1] F. Novio, K. Philippot, B. Chaudret*Cat. Lett.* 2010, **140**, 1–7.

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