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SUPPORTING INFORMATION

Electrophilic Phosphonium Cations (EPCs) with Perchlorinated-Aryl Substituents: Towards Air Stable Phosphorus-based Lewis Acid Catalysts

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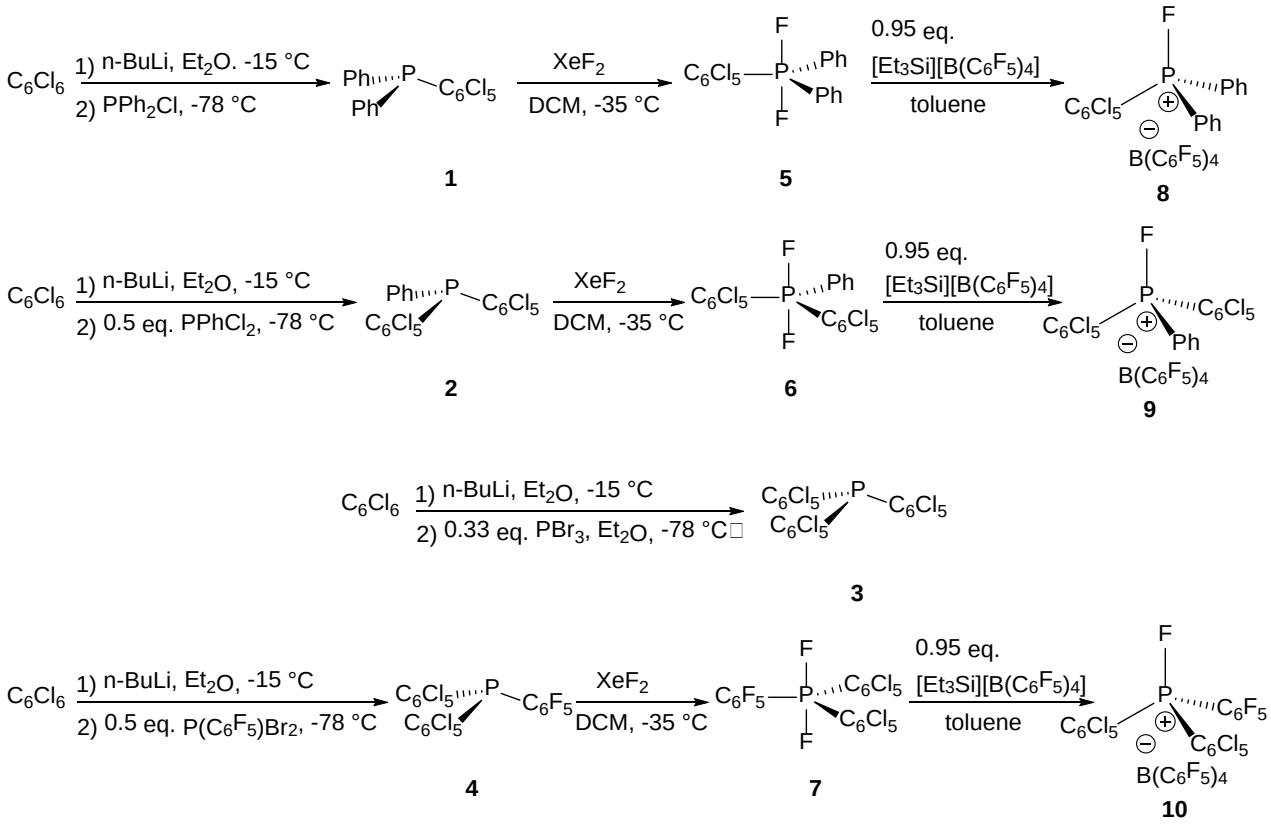
General Procedures:

All manipulations were performed in a Glove box MB Unilab produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N_2. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (CH_2Cl_2, Et_2O, toluene and *n*-pentane) were prepared using an Innovative Technologies solvent purification system. CD_2Cl_2 and CD_3CN (Aldrich) were deoxygenated, distilled over CaH_2, then stored over 4 Å molecular sieves before use. C_6D_6 and C_6D_5Br (Aldrich) were deoxygenated and stored over 4 Å molecular sieves before use. Commercial reagents were purchased from Sigma-Aldrich, Strem Chemicals, Apollo Scientific, TCI Chemicals or Alfa Aesar, and were used without further purification unless indicated otherwise. $[Et_3Si][B(C_6F_5)_4]\cdot(C_7H_8)$ was prepared by the reported procedure.[34] NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer, Varian NMR system 400 MHz spectrometer, Agilent DD2-500 MHz spectrometer, or Agilent DD2-600 MHz spectrometer. ^{1}H NMR data, referenced to external Me_4Si, are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), normalized integrals. $^{13}C\{^1H\}$ NMR chemical shifts (δ) are referenced to external Me_4Si. Assignments of individual resonances were done using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JEOL AccuTOF (DART) mass spectrometer. Elemental analyses were performed at the University of Toronto employing a Perkin Elmer 2400 Series II CHNS Analyser. Crystals were coated in paratone oil and mounted in a cryo-loop. Data were collected on a Bruker APEX2 X-ray diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å). The temperature was maintained at 150(2) K using an Oxford cryo-stream cooler for both, initial indexing and full data collection. Data were collected using Bruker APEX-2 software and processed using SHELX and Olex2 an absorption correction applied using multi-scan within the APEX-2 program. All structures were solved by direct methods within the SHELXTL package and refined with Olex2.

Synthesis of phosphines, phosphoranes, and phosphoniums:



Scheme 1. Synthesis of phosphines, phosphoranes, and phosphinums

Synthesis of phosphines:

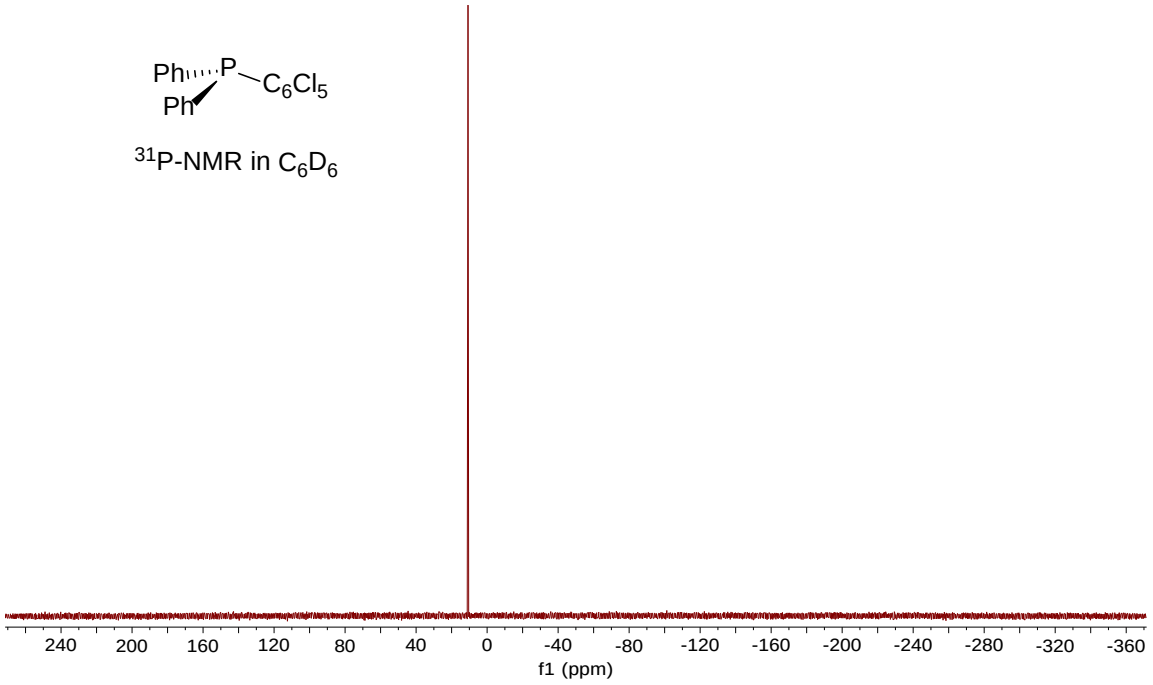
Perchlororophenyl(diphenyl) phosphine (1). A 100 mL Schlenk flask was charged with C_6Cl_6 (318 mg, 1.12 mmol), a large magnetic stir-bar and anhydrous Et_2O (30 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M *n*-BuLi (0.44 mL, 1.12 mmol) was added dropwise to the stirring solution under an atmosphere of N_2; slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of PPh_2Cl (247 mg, 1.12 mmol) in anhydrous Et_2O (3 mL) was added dropwise by syringe over 5 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed *in vacuo* and the solid extracted with anhydrous CH_2Cl_2 (6 mL) before being filtered over Celite. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The filtrate was then washed with *n*-pentane (2 x 2 mL) before removing the solvent *in vacuo*, producing a white solid (340 mg, 70% yield). Vapour diffusion of *n*-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for $PC_{18}H_{10}Cl_5$: C: 49.76, H: 2.32. Found: C: 49.82%, H: 1.99%.

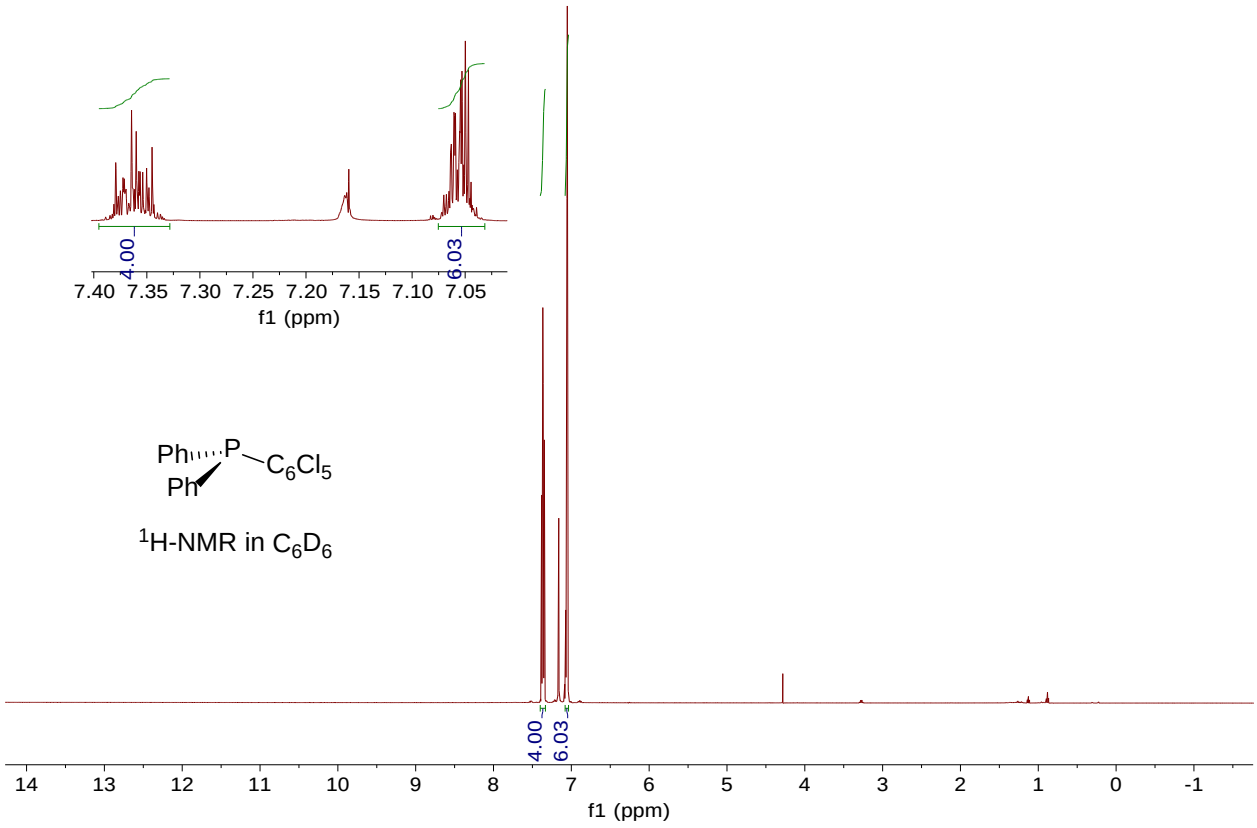
$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 10.68 (s) ppm.

^1H NMR (500 MHz, C_6D_6): δ 7.33 – 7.39 (m, 4H, *m*-C6H5), 7.08 – 7.03 (m, 6H, *o*-, *p*-C_6H_5) ppm.

^{13}C NMR (125 MHz, C_6D_6): δ 139.70 (d, $^2J_{PC}$ = 17.7 Hz, *o*-C_6Cl_5), 136.37 (s, *p*-C_6Cl_5), 135.97 (d, $^1J_{PC}$ = 24.2 Hz, *i*-C_6Cl_5), 134.26 (d, $^1J_{PC}$ = 15.4 Hz, *i*-C_6H_5), 133.28 (s, *m*-C_6Cl_5), 132.92 (d, $^2J_{PC}$ = 20.7 Hz, *o*-C_6H_5), 129.14 (s, *p*-C_6H_5), 128.98 (d, $^3J_{PC}$ = 6.3 Hz, *m*-C_6H_5) ppm.

HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd for $C_{18}H_{10}Cl_5P$: 432.90410, Found: 432.90360.


Ph
P
C6Cl5
Ph
31P-NMR in C6D6
240 200 160 120 80 40 0 -40 -80 -120 -160 -200 -240 -280 -320 -360
f1 (ppm)


4.00
6.03
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
Ph
P
C6Cl5
Ph
1H-NMR in C6D6
4.00
6.03
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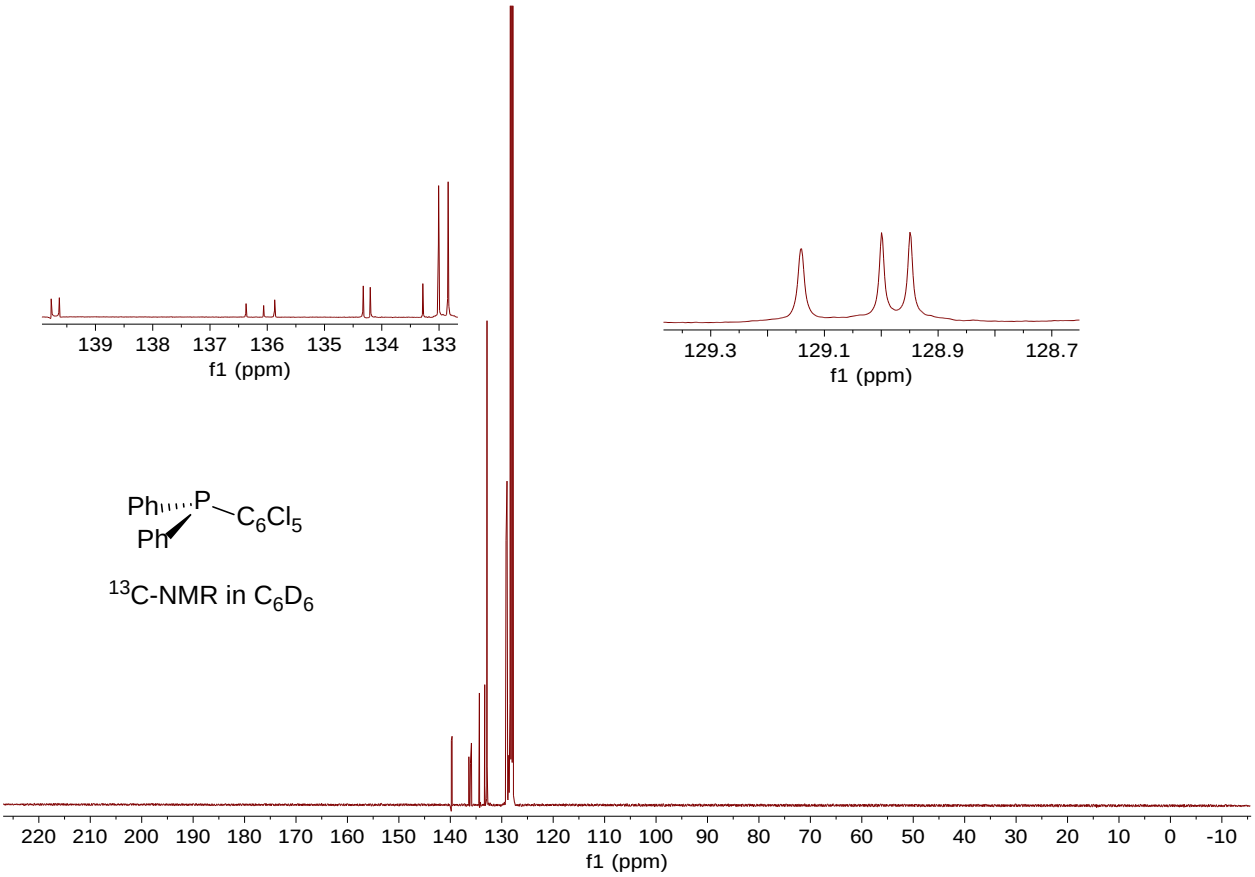
f1 (ppm)


139 138 137 136 135 134 133
f1 (ppm)
129.3 129.1 128.9 128.7
f1 (ppm)
Ph
P
C6Cl5
Ph
13C-NMR in C6D6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

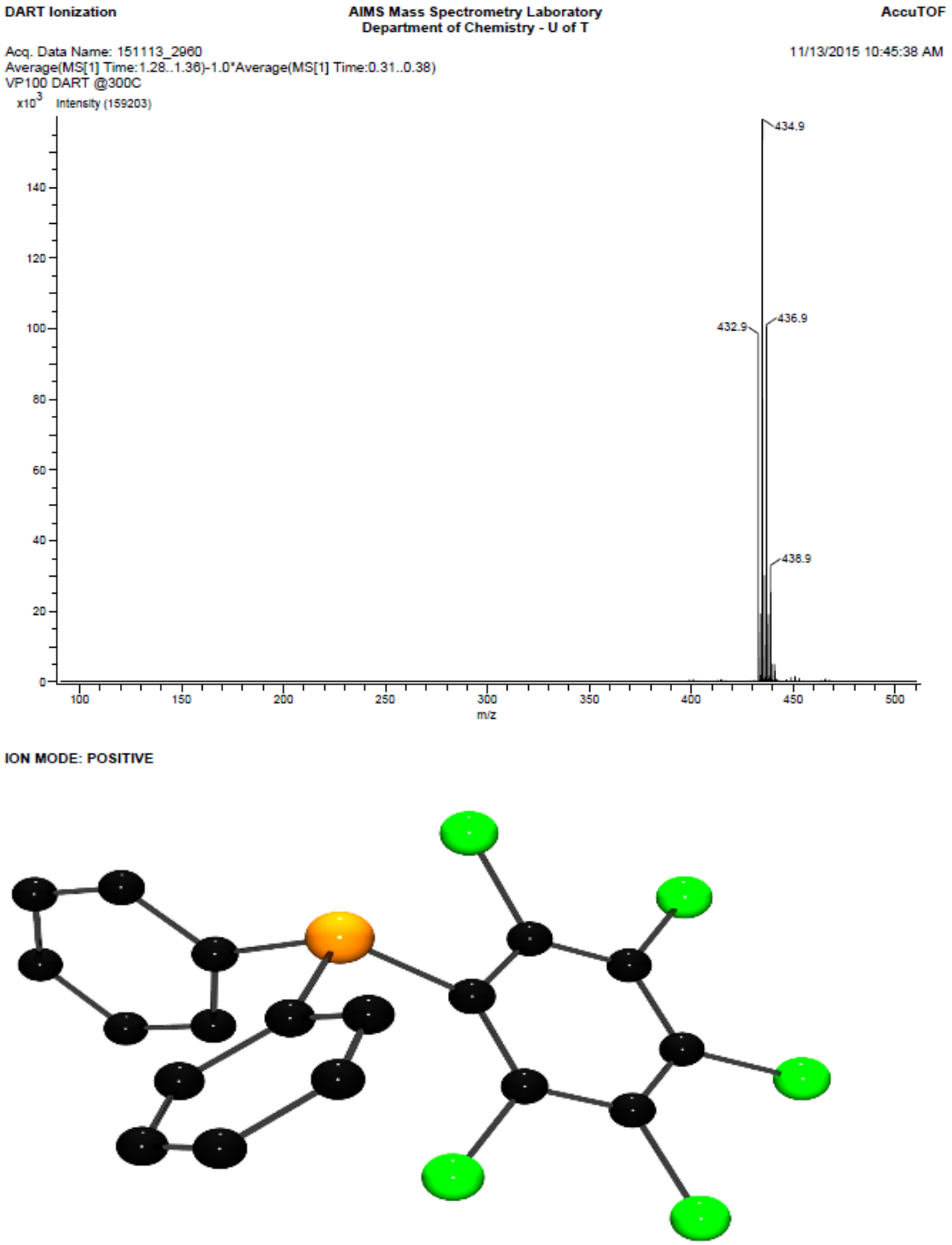


Figure 1. POV–Ray depiction of **1**. P: yellow, Cl: green, C: Black.

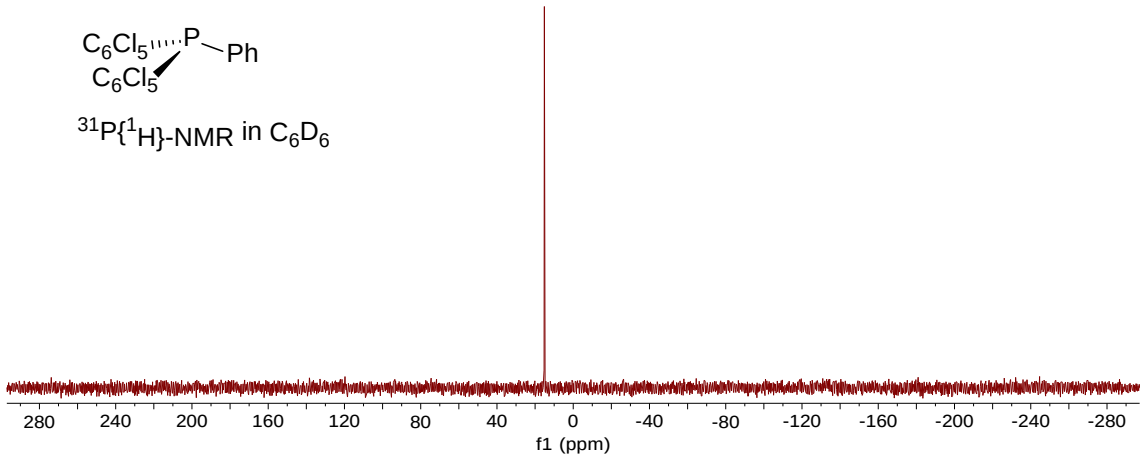
Bis(perchlorophenyl)phenyl phosphine (2). A 100 mL Schlenk flask was charged with C_6Cl_6 (597 mg, 2.10 mmol), a large magnetic stir-bar and anhydrous Et_2O (30 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M *n*-BuLi (0.84 mL, 2.10 mmol) was added dropwise to the stirring solution under an atmosphere of N_2; slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of $PPhCl_2$ (188 mg, 1.05 mmol) in anhydrous Et_2O (4 mL) was added dropwise by syringe over 6 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed *in vacuo* and the solid extracted with anhydrous CH_2Cl_2 (6 mL) before being filtered over Celite. The solvent was reduced and the solution cooled to -35 °C to produce an off-white precipitate, which was collected by filtration. The filtrate was then washed with *n*-pentane (3 x 3 mL) before removing the solvent *in vacuo*, producing an off-white solid (231 mg, 36% yield). Anal. Calcd. for $PC_{18}H_5Cl_{10}$: C: 35.63, H: 0.83. Found: C: 35.29%, H: 0.92%.

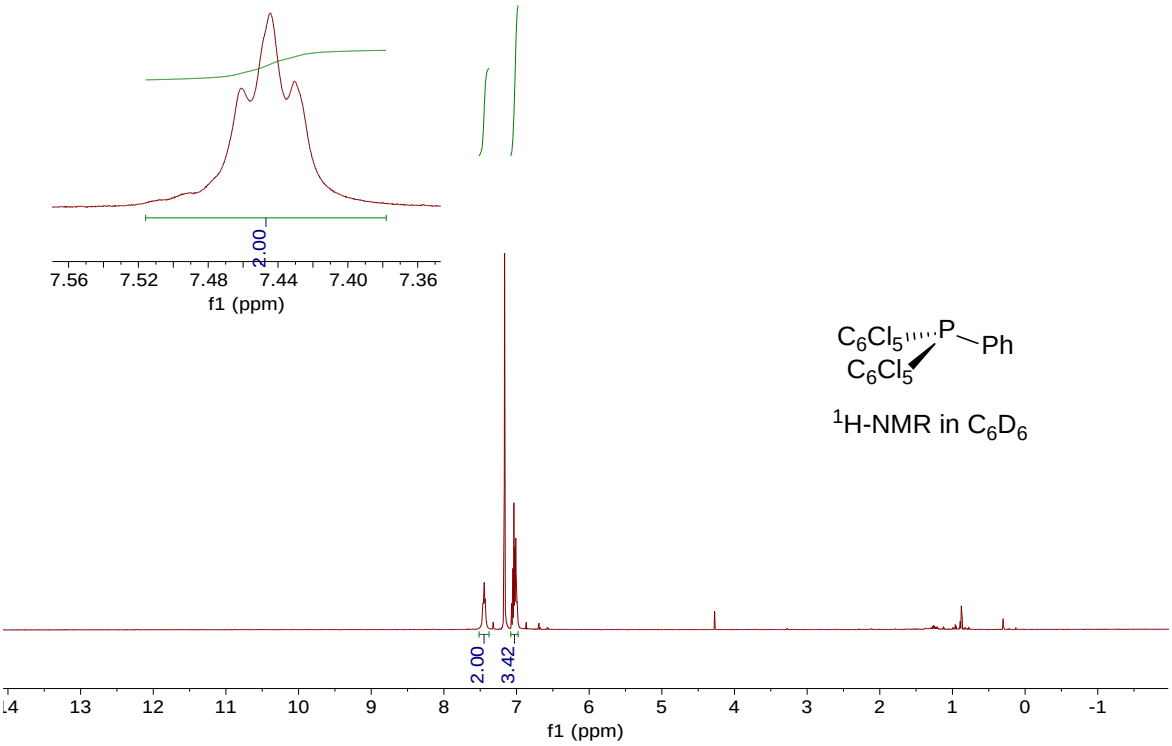
$^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6): δ 15.14 (s) ppm.

^1H NMR (500 MHz, C_6D_6): δ 7.44 (apparent triplet, $^3J_{PH}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, *m*-C_6H_5), 6.98 – 7.07 (m, 4H, *o*-, *p*-C_6H_5) ppm.

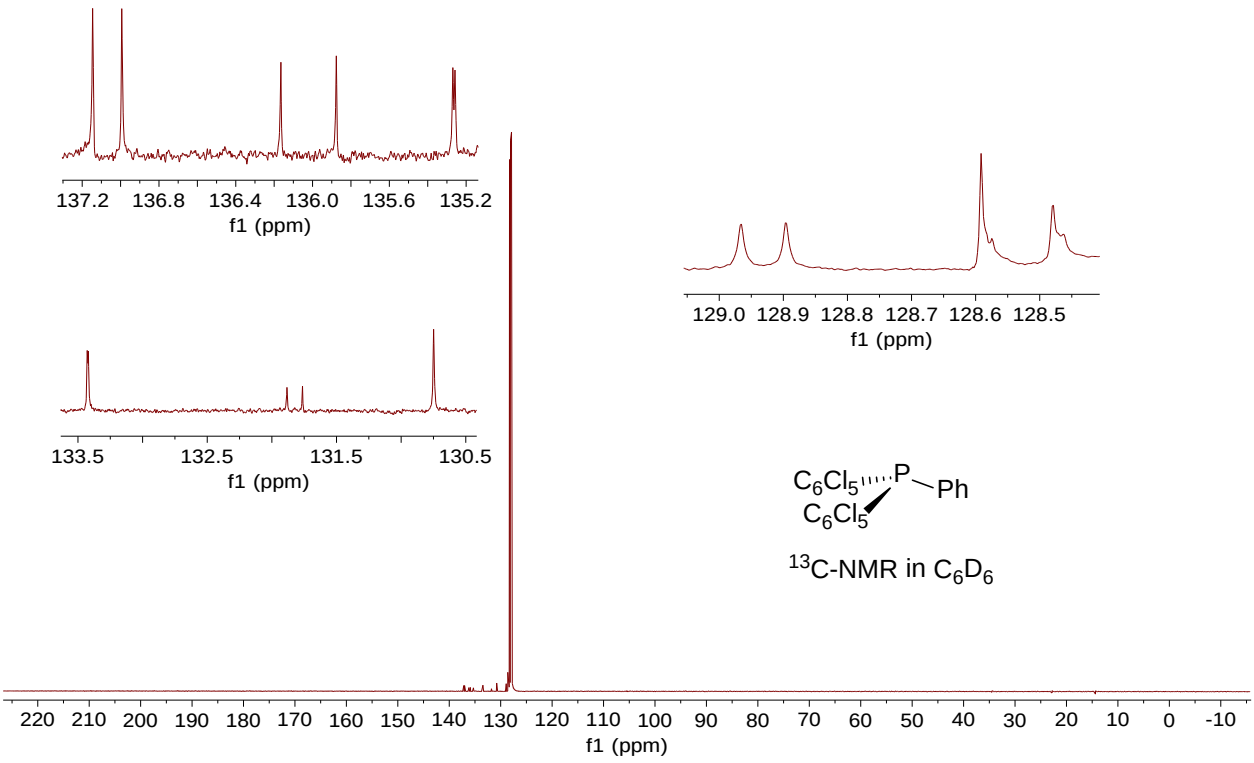
^{13}C NMR (125 MHz, C_6D_6): δ 137.07 (d, $^2J_{PC}$ = 19.0 Hz, *o*-C_6Cl_5), 136.02 (d, $^1J_{PC}$ = 36.3 Hz, *i*-C_6Cl_5), 135.26 (d, $^4J_{PC}$ = 1.4 Hz, *p*-C_6Cl_5), 133.42 (d, $^3J_{PC}$ = 1.2 Hz, *m*-C_6H_5), 131.82 (d, $^1J_{PC}$ = 14.8 Hz, *i*-C_6H_5), 130.75 (s, *p*-C_6H_5), 128.94 (d, $^2J_{PC}$ = 8.6 Hz, *o*-C_6H_5), 128.54 (d, $^3J_{PC}$ = 14.2 Hz, *m*-C_6H_5) ppm.

HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd. for $C_{18}H_5Cl_{10}P$: 602.70924, Found: 602.70831.


C6Cl5
P
Ph
C6Cl5
31P{1H}-NMR in C6D6
280
240
200
160
120
80
40
0
-40
-80
-120
-160
-200
-240
-280
f1 (ppm)



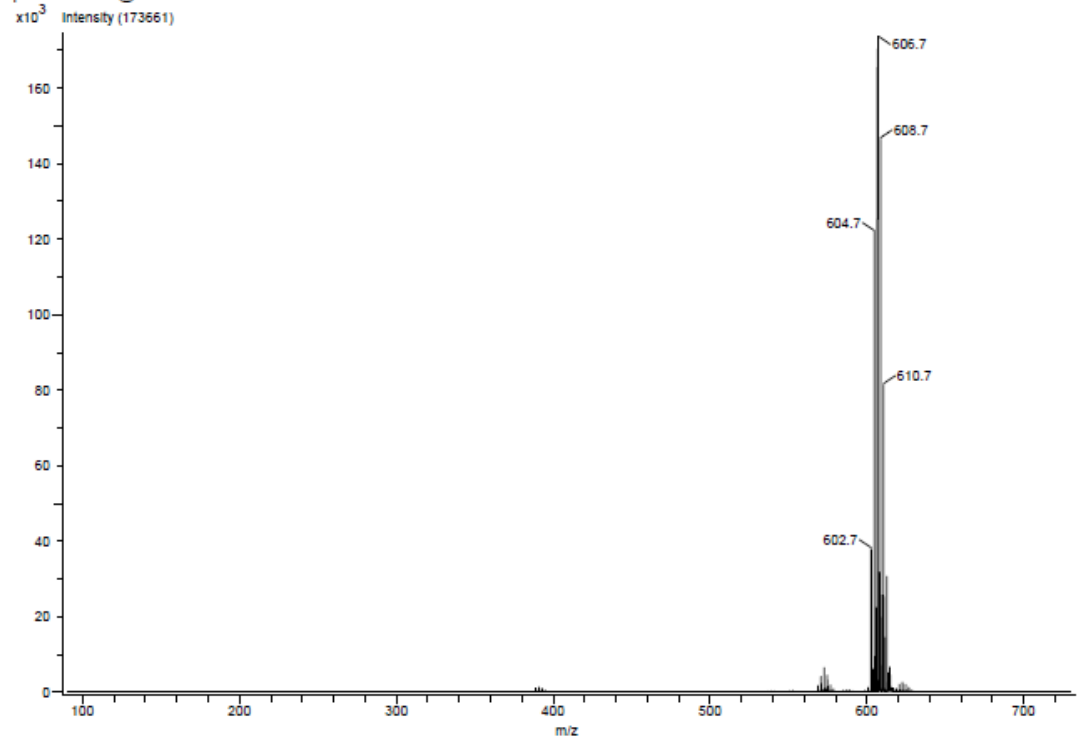
^{1}H-NMR in C_6D_6



^{13}C-NMR in C_6D_6

DART Ionization | **AIMS Mass Spectrometry Laboratory**
Department of Chemistry - U of T | **AccuTOF**

Acq. Data Name: 160322_4796 | 3/22/2016 2:48:38 PM
Average(MS[1] Time:0.99..1.04)-1.0*Average(MS[1] Time:0.05..0.09)
Vp 112 DART @350C

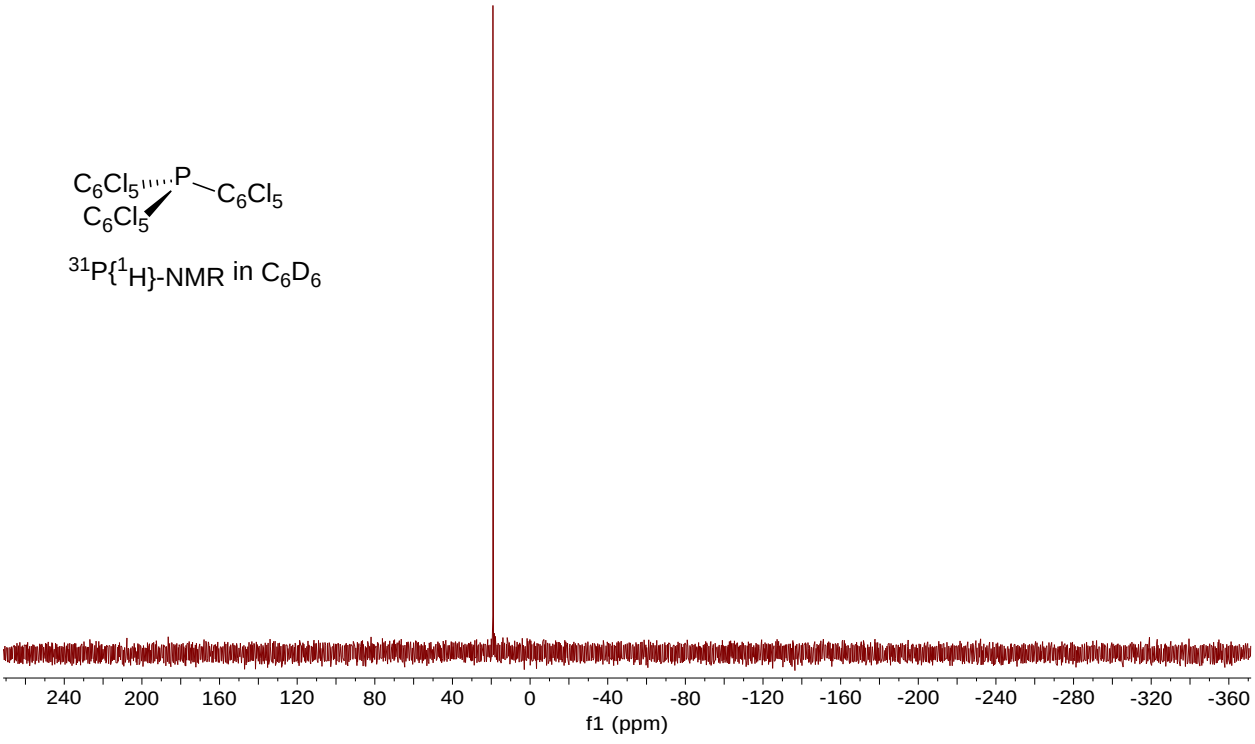


ION MODE: POSITIVE

Tris(perchlorophenyl) phosphine (3). A 250 mL Schlenk flask was charged with C_6Cl_6 (1053 mg, 3.70 mmol), a large magnetic stir-bar and anhydrous Et_2O (60 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M *n*-BuLi (1.47 mL, 3.70 mmol) was added dropwise to the stirring solution under an atmosphere of N_2; slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of PBr_3 (333 mg, 1.23 mmol) in anhydrous Et_2O (4 mL) was added dropwise by syringe over 5 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed *in vacuo* and the solid extracted with anhydrous CH_2Cl_2 (2 x 6 mL) before being filtered over Celite. The solvent was reduced and the solution cooled to -35 °C to produce an off-white precipitate, which was collected by filtration. The filtrate was then washed with *n*-pentane (2 x 3 mL) before removing the solvent *in vacuo*, producing an off-white solid (199 mg, 21% yield). Anal. Calcd. for $PC_{18}Cl_{18}$: C: 27.76. Found: C: % 25.87.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 19.07 (s) ppm.

HRMS (EI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{18}HCl_{15}P$: 778.50553, Found: 778.50594.



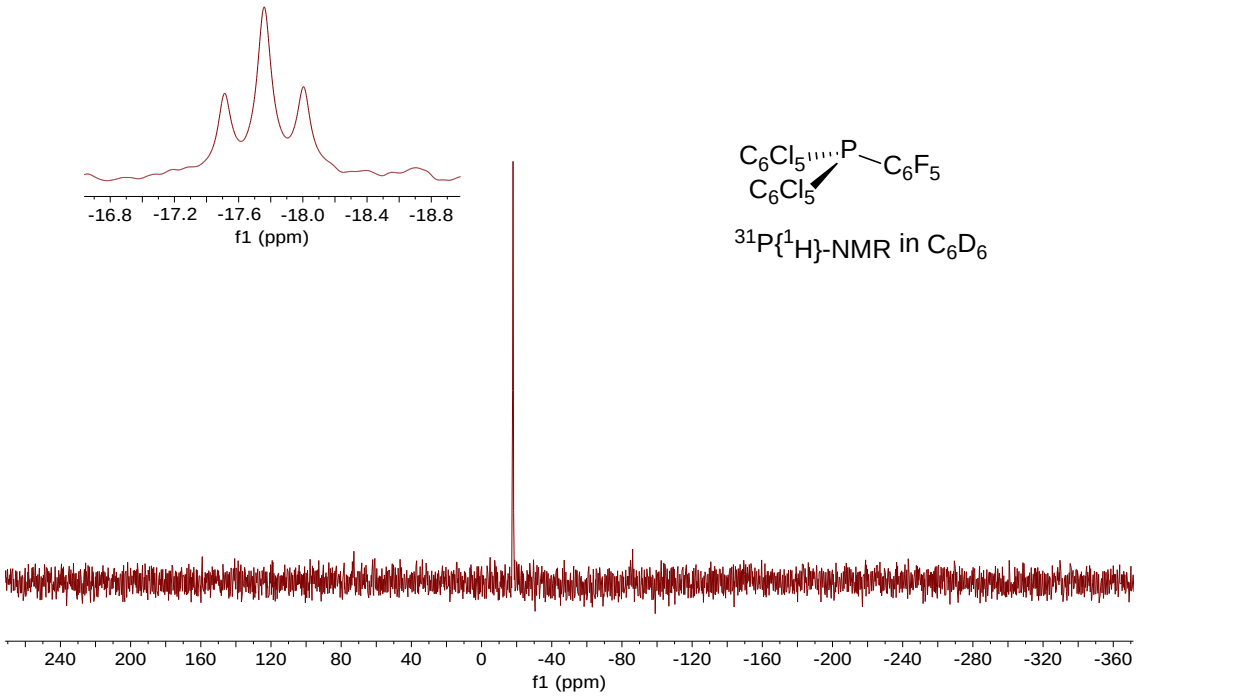
bis(perchlorophenyl)(perfluorophenyl) phosphine (4). A 250 mL Schlenk flask was charged with C_6Cl_6 (513 mg, 1.80 mmol), a large magnetic stir-bar and anhydrous Et_2O (40 mL), generating a white slurry. The reaction flask was cooled to -15 °C using a dry ice/acetone bath. A hexane solution of 2.5 M *n*-BuLi (0.72 mL, 1.80 mmol) was added dropwise to the stirring solution under an atmosphere of N_2; slowly turning the slurry to a clear light yellow solution. The solution was cooled to -78 °C and a solution of $P(C_6F_5)Br_2$ (323 mg, 0.90 mmol) in anhydrous Et_2O (3 mL) was added dropwise by syringe over 4 minutes. The stirring solution was left to warm to room temperature overnight. The solvent was removed *in vacuo* and the solid extracted with anhydrous CH_2Cl_2 (6 mL) before being filtered over Celite. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The white filtrate was then washed with *n*-pentane (2 x 2 mL) before removing the solvent *in vacuo*, producing a white solid (261 mg, 42% yield). Vapour diffusion of *n*-pentane into a solution of the compound in dichloromethane yielded X-Ray quality crystals. Anal. Calcd. for $PC_{18}F_5Cl_{10}$: C: 31.03. Found: C: 31.19%.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ -17.76 (t, $^3J_{PF}$ = 40.0 Hz) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ -129.20 to -129.61 (m, 2F, *o*-C_6F_5), -147.50 (tt, $^3J_{FF}$ = 21.8 Hz, $^5J_{FF}$ = 4.7 Hz, 1F, *p*-C_6F_5), -159.63 to -159.88 (m, 2F, *m*-C_6F_5) ppm.

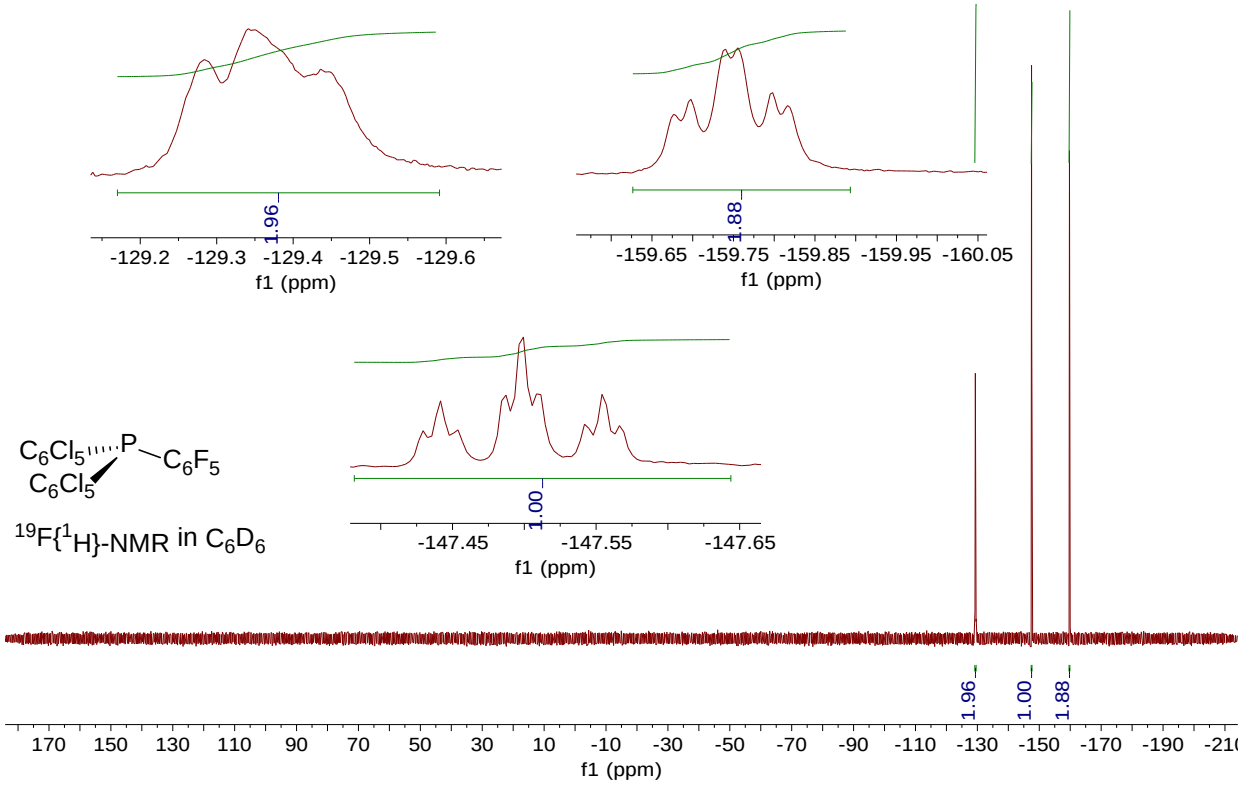
^{13}C NMR (125 MHz, C_6D_6): δ 147.92 (br d, $^1J_{FC}$ = 244.8 Hz, *o*-C_6F_5), 143.17 (br d, $^1J_{FC}$ = 258.0 Hz, *p*-C_6F_5), 137.90 (br d, $^1J_{FC}$ = 247.5 Hz, *m*-C_6F_5), 137.12 (d, $^2J_{PC}$ = 20.7 Hz, *o*-C_6Cl_5), 136.43 (s, *p*-C_6Cl_5), 133.59 (s, *m*-C_6Cl_5), 132.39 (d, $^1J_{PC}$ = 34.2 Hz, *i*-C_6Cl_5), 108.64 (br s, *i*-C_6F_5) ppm.

HRMS (DART Ionization) m/z: $[M+H]^+$ Calcd. for $C_{18}F_5Cl_{10}P$: 692.66213, Found: 692.66280.



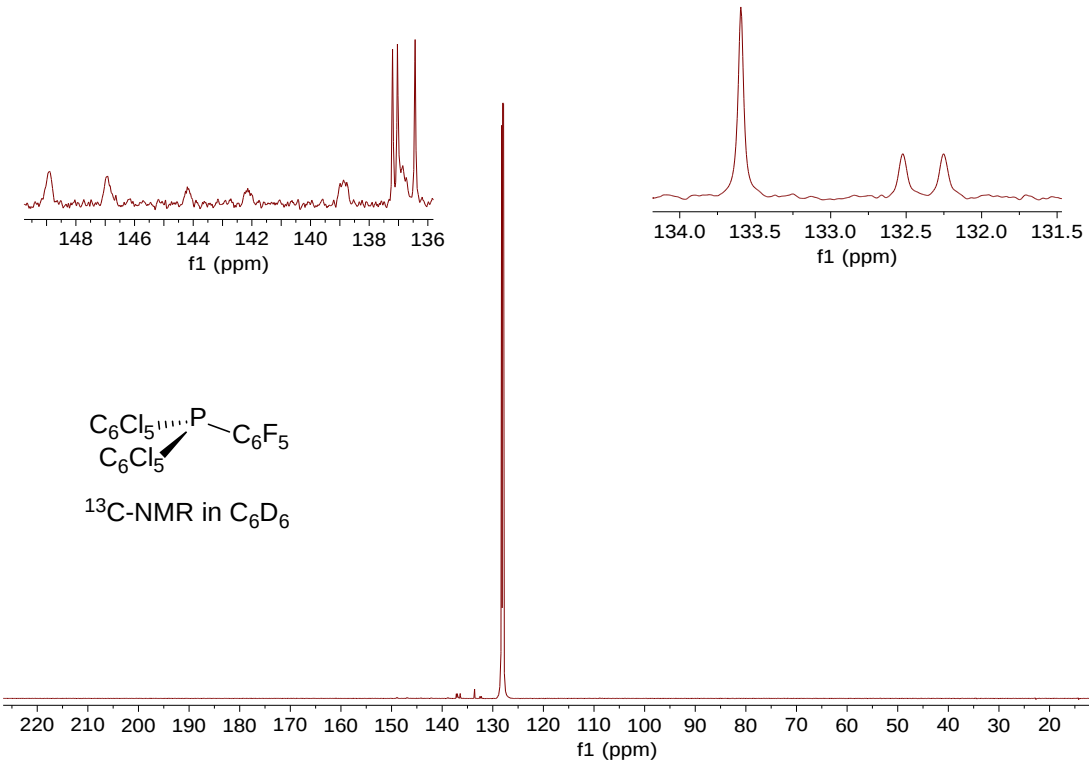
C_6Cl_5 C_6Cl_5 P C_6F_5

$^{31}P\{^1H\}$-NMR in C_6D_6



C_6Cl_5 C_6Cl_5 P C_6F_5

$^{19}F\{^1H\}$-NMR in C_6D_6


148 146 144 142 140 138 136
f1 (ppm)
134.0 133.5 133.0 132.5 132.0 131.5
f1 (ppm)
C6Cl5
P
C6F5
C6Cl5
13C-NMR in C6D6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

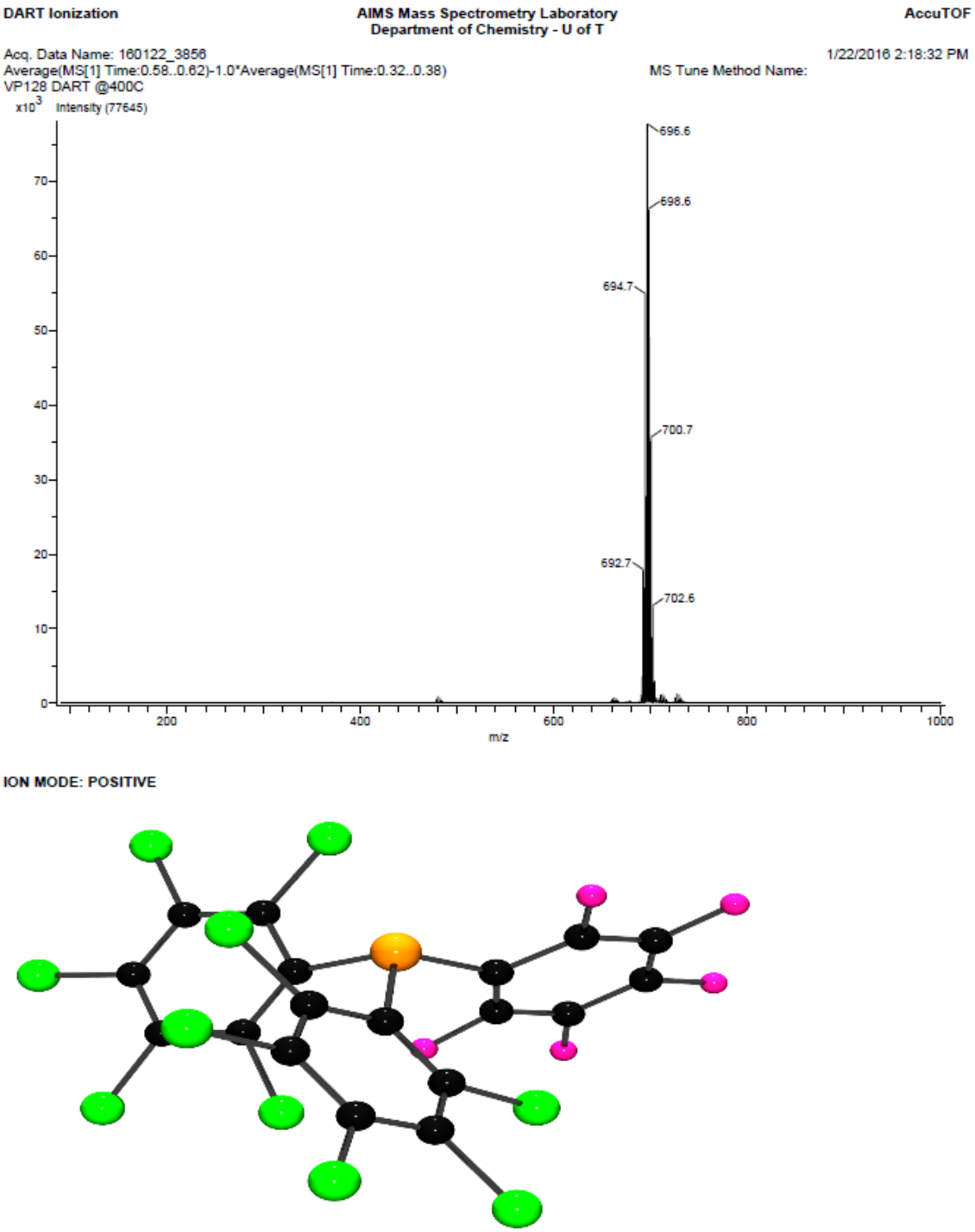


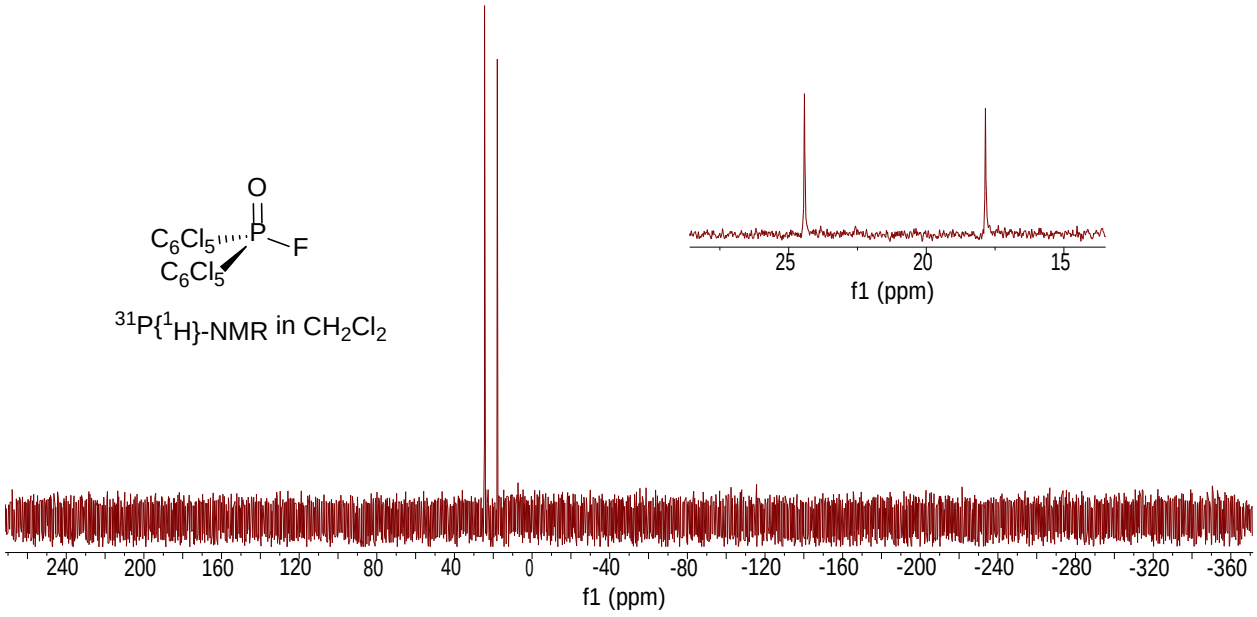
Figure 2. POV–Ray depiction of **4**. P: orange, Cl: green, C: black, F: pink.

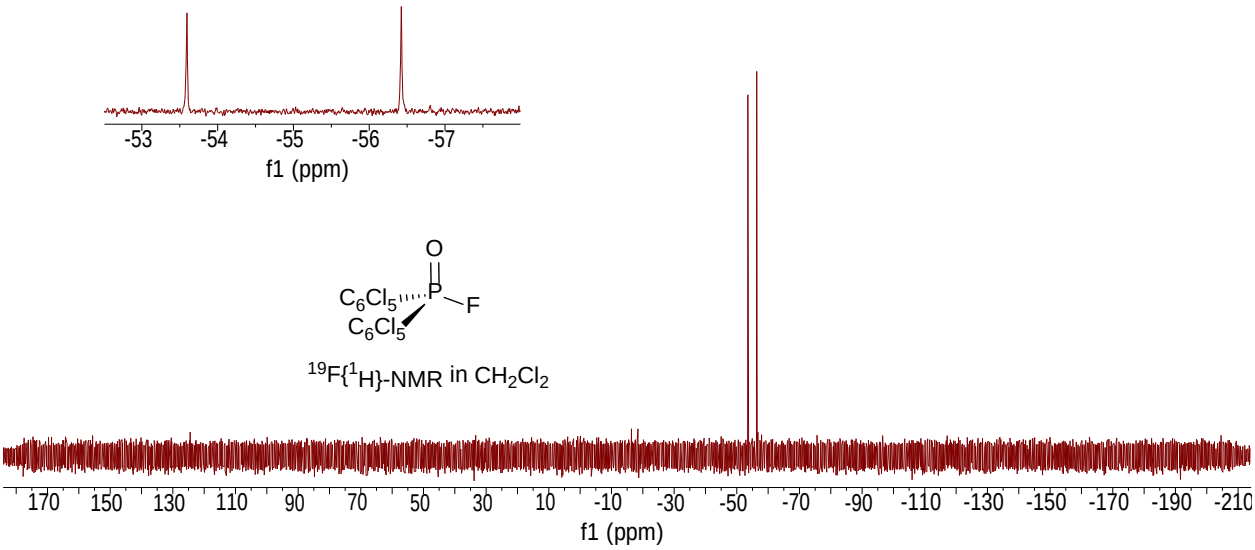
fluorobis(perchlorophenyl) phosphineoxide (11). A 20 mL vial was charged with $P(C_6Cl_5)_3$ (78 mg, 0.10 mmol), MeCN (3 mL), and a magnetic stir bar. A solution of 1-chloromethyl-4-fluoro-1,4-diazonia-bicyclo-[2.2.2]octane bis(tetrafluoroborate) {Selectfluor} in MeCN was added. The solution briefly turns dark purple as a black precipitate is formed before returning to a pale green colour. The supernatant is decanted off and the solvent is removed *in vacuo* resulting in a yellow solid (24 mg, 43 %).

$^{31}P\{^1H\}$ NMR (162 MHz, CH_2Cl_2): δ 21.15 (d, $^1J_{PF}$ = 1065.8 Hz) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, CH_2Cl_2): δ –54.30 (d, $^1J_{PF}$ = 1063.8 Hz) ppm.

HRMS (EI-TOF) m/z: $[M]^+$ Calcd. for $C_{12}Cl_{10}FPO$: 564.65753, Found: 564.65713.




-53
-54
-55
-56
-57
f1 (ppm)
O
P
F
C_6Cl_5
C_6Cl_5
$^{19}F\{^1H\}$-NMR in CH_2Cl_2
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Synthesis of phosphoranes:

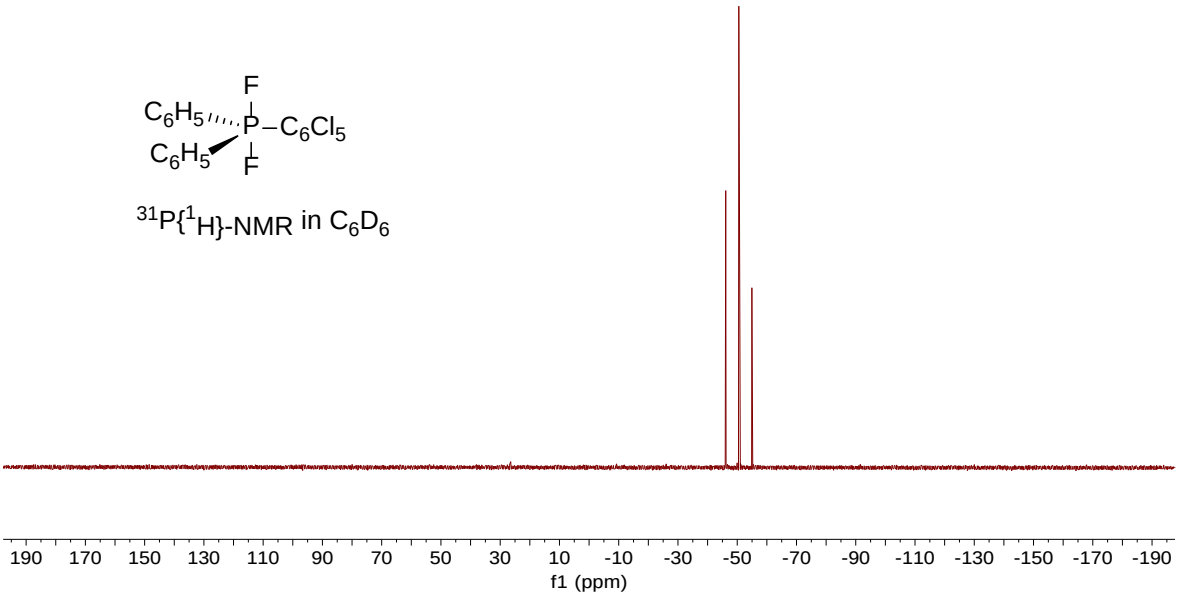
Difluoro perchlorophenyl(diphenyl) phosphorane (5). In a cold well, a 20 mL vial was charged with $Ph_2P(C_6Cl_5)$ (257 mg, 0.59 mmol), CH_2Cl_2 (4 mL), and a magnetic stir bar, forming a light yellow solution. XeF_2 (100 mg, 0.59 mmol) was quickly added to the stirring solution. The solution gradually lightens as it was left to stir and warm up to room temperature for 2 hours. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The white filtrate was then washed with *n*-pentane (2 x 2 mL) before removing the solvent *in vacuo*, producing a white solid (230 mg, 83% yield). X-Ray quality crystals were obtained from CH_2Cl_2 in glovebox freezer. Anal. Calcd. for $PC_{18}H_{10}Cl_5F_2$: C: 45.76, H: 2.13. Found: C: 45.24%, H: 2.00%.

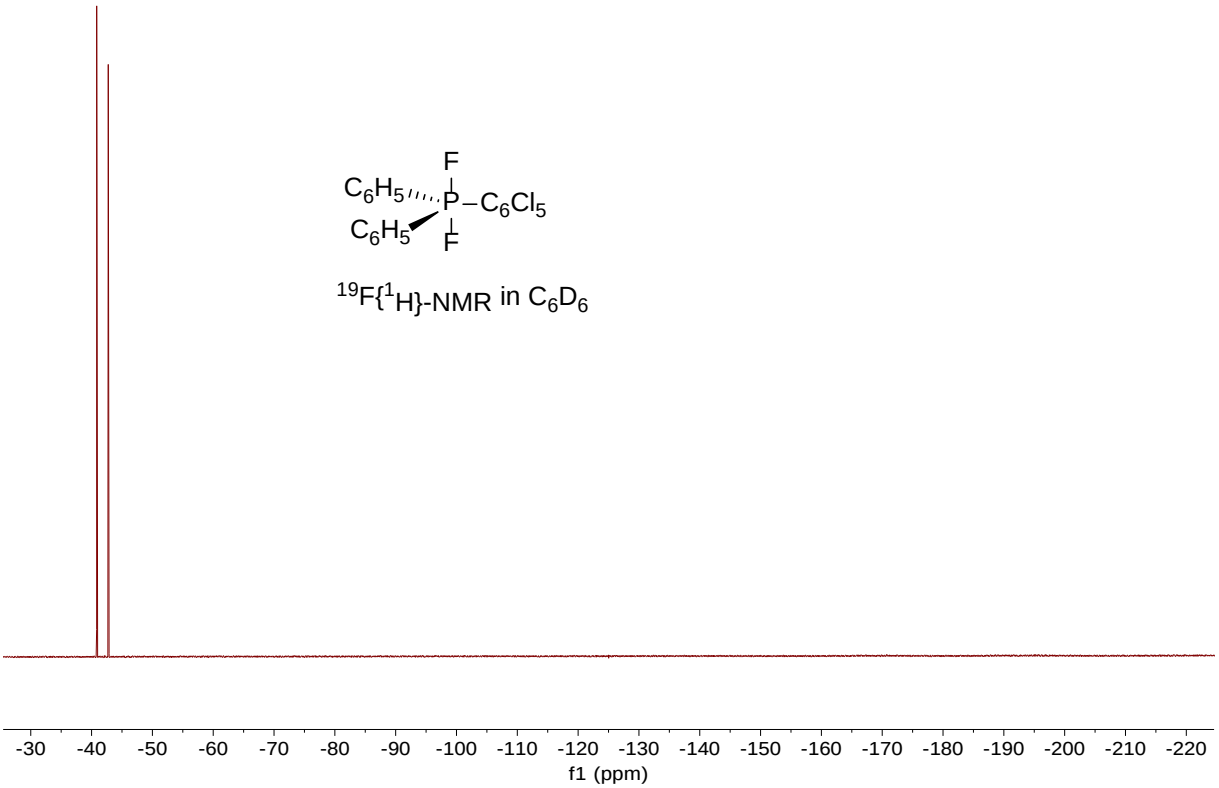
$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ -50.69 (t, $^1J_{PF}$ = 715.3 Hz) ppm.

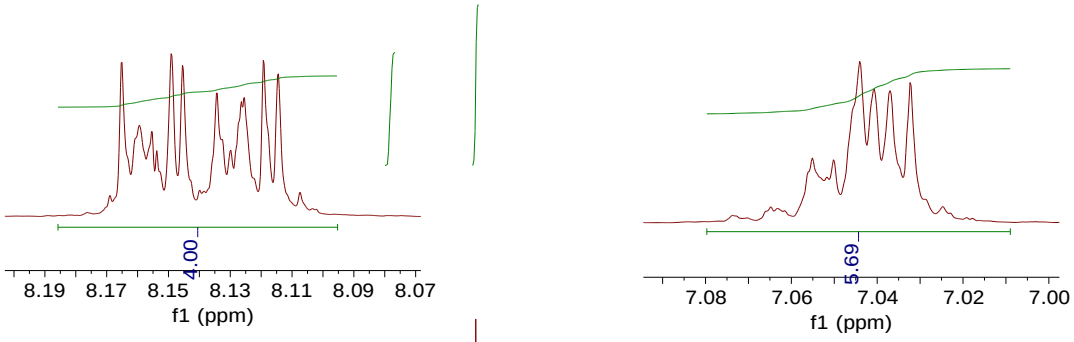
$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): δ -41.79 (d, $^1J_{PF}$ = 715.7 Hz, PF_2) ppm.

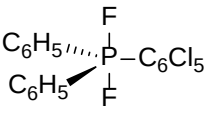
^1H NMR (500 MHz, C_6D_6): δ 8.17 – 8.10 (m, 4H, *m*-C_6H_5), 7.08 – 7.01 (m, 6H, *o*-, *p*-C_6H_5) ppm.

^{13}C NMR (125 MHz, C_6D_6): δ 140.11 (dt, $^1J_{PC}$ = 217.3 Hz, $^2J_{FC}$ = 42.3 Hz, *i*-C_6Cl_5), 137.54 (dt, $^1J_{PC}$ = 180.8 Hz, $^2J_{FC}$ = 23.7 Hz, *i*-C_6H_5), 134.98 (dt, $^2J_{PC}$ = 13.1 Hz, $^3J_{FC}$ = 10.2 Hz, *o*-C_6H_5), 134.53 (dt, $^2J_{PC}$ = 3.4 Hz, $^3J_{FC}$ = 1.8 Hz, *o*-C_6Cl_5), 133.50 (d, $^4J_{PC}$ = 16.6 Hz, *p*-C_6Cl_5), 132.58 (dt, $^3J_{PC}$ = 3.0 Hz, $^4J_{FC}$ = 2.8 Hz, *m*-C_6Cl_5), 131.72 (dt, $^4J_{PC}$ = 3.8 Hz, $^5J_{FC}$ = 1.2 Hz, *p*-C_6H_5), 128.57 (dt, $^3J_{PC}$ = 13.1 Hz, $^4J_{PC}$ = 10.2 Hz, *m*-C_6H_5) ppm.

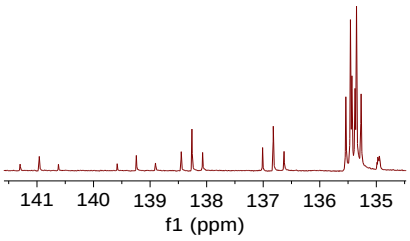


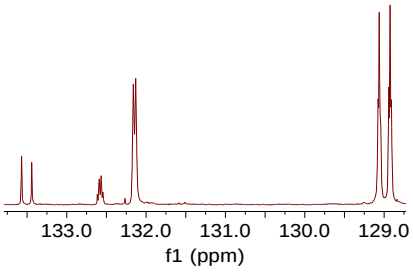

F
C6H5
P
C6Cl5
C6H5
F
19F{1H}-NMR in C6D6
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

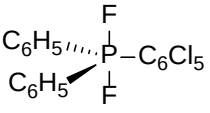




^{1}H-NMR in C_6D_6







^{13}C-NMR in C_6D_6

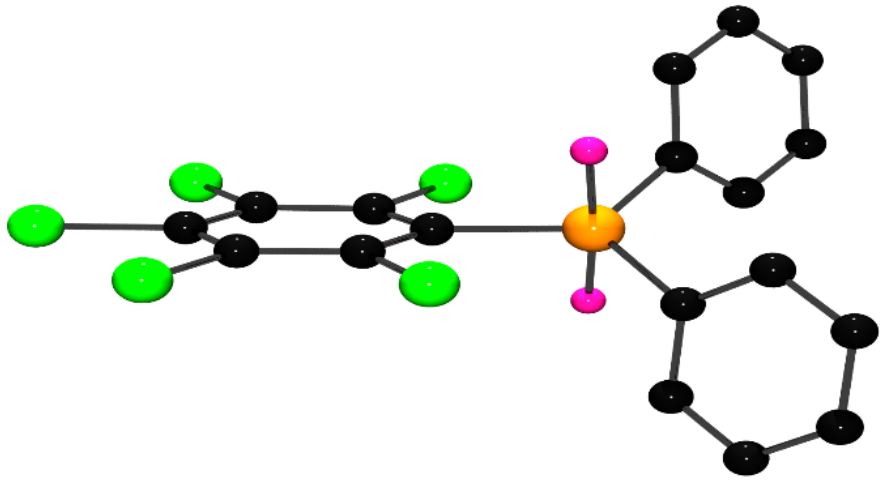


Figure 3. POV–Ray depiction of **5**. P: orange, Cl: green, C: black, F: pink.

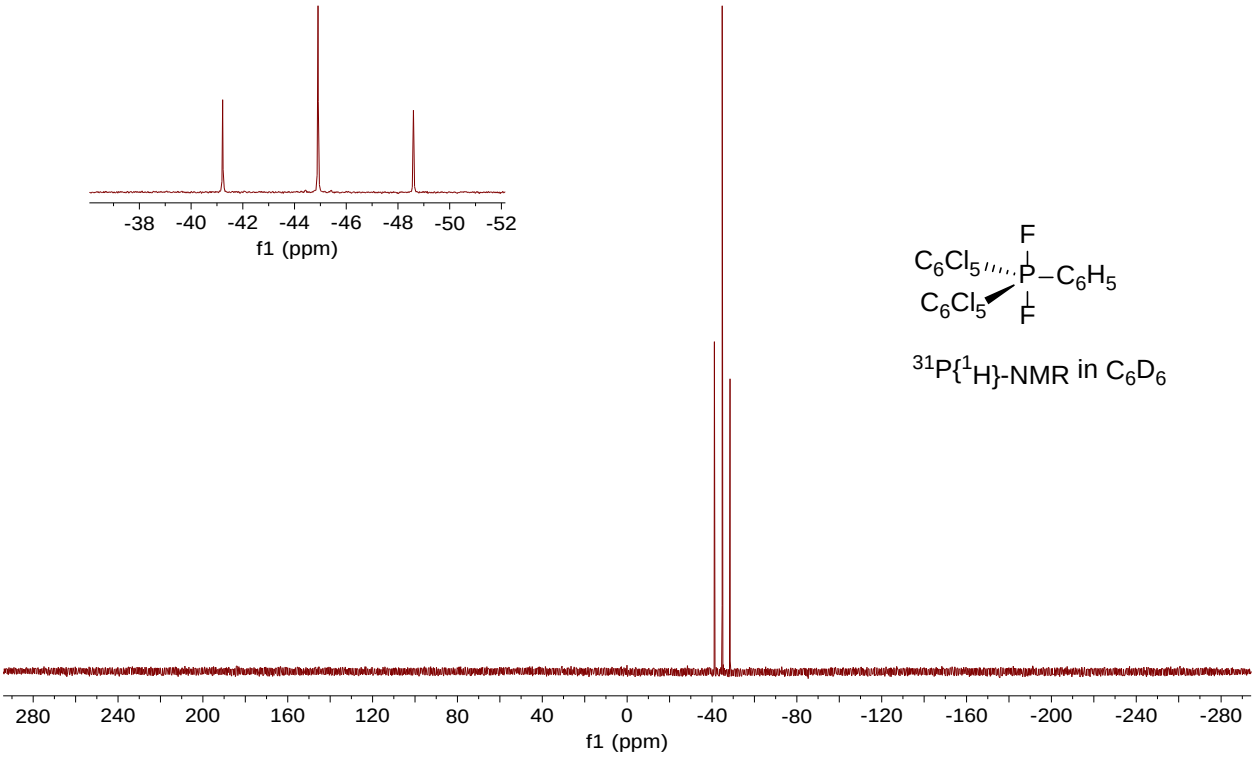
Difluoro bis(perchlorophenyl)(phenyl) phosphorane (6). In a cold well, a 20 mL vial was charged with $PhP(C_6Cl_5)_2$ (153 mg, 0.25 mmol), CH_2Cl_2 (6 mL), and a magnetic stir bar, forming a yellow solution. XeF_2 (43 mg, 0.25 mmol) was quickly added to the stirring solution. The solution gradually lightens as it was left to stir and warm up to room temperature for 1.5 hours. The solvent was reduced and the solution cooled to -35 °C to produce an off-white precipitate, which was collected by filtration. The filtrate was then washed with *n*-pentane (3 x 2 mL) before removing the solvent *in vacuo*, producing an off-white solid. (123 mg, 76% yield). Anal. Calcd. for $PC_{18}H_5Cl_{10}F_2$: C: 33.53, H: 0.78. Found: C: 34.16%, H: 0.86%.

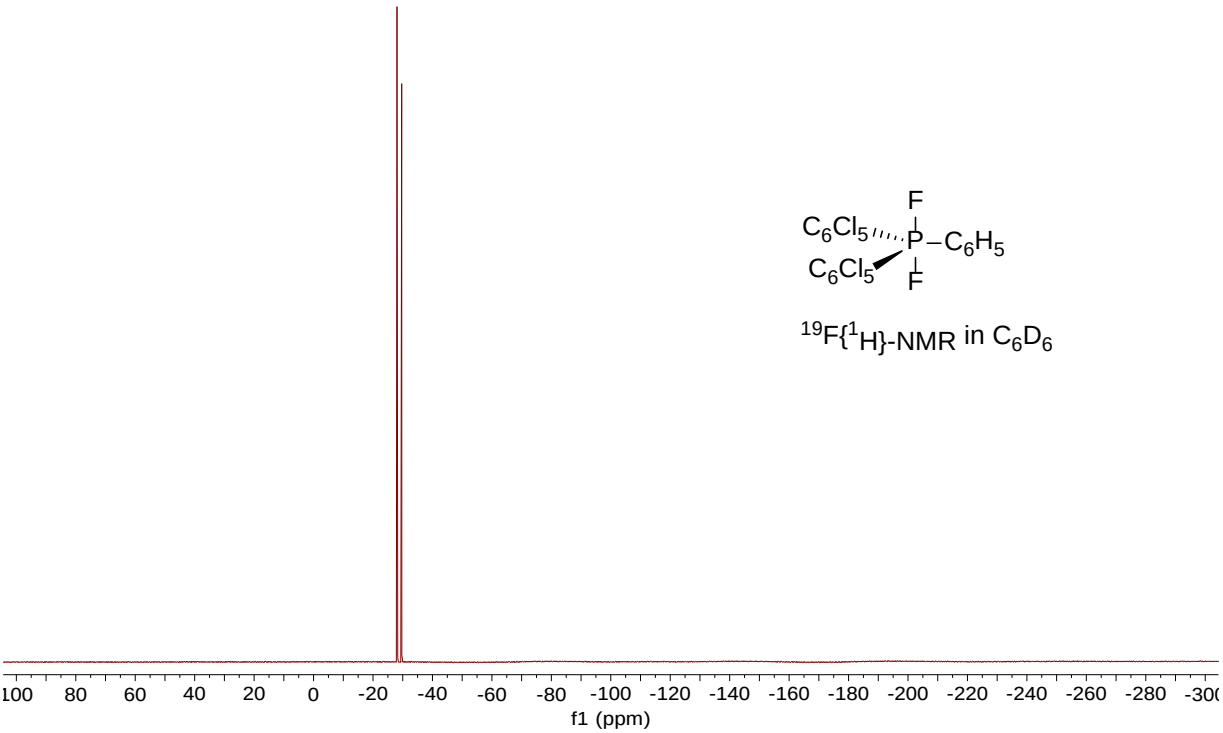
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ -44.91 (t, $^1J_{PF}$ = 746.5 Hz) ppm.

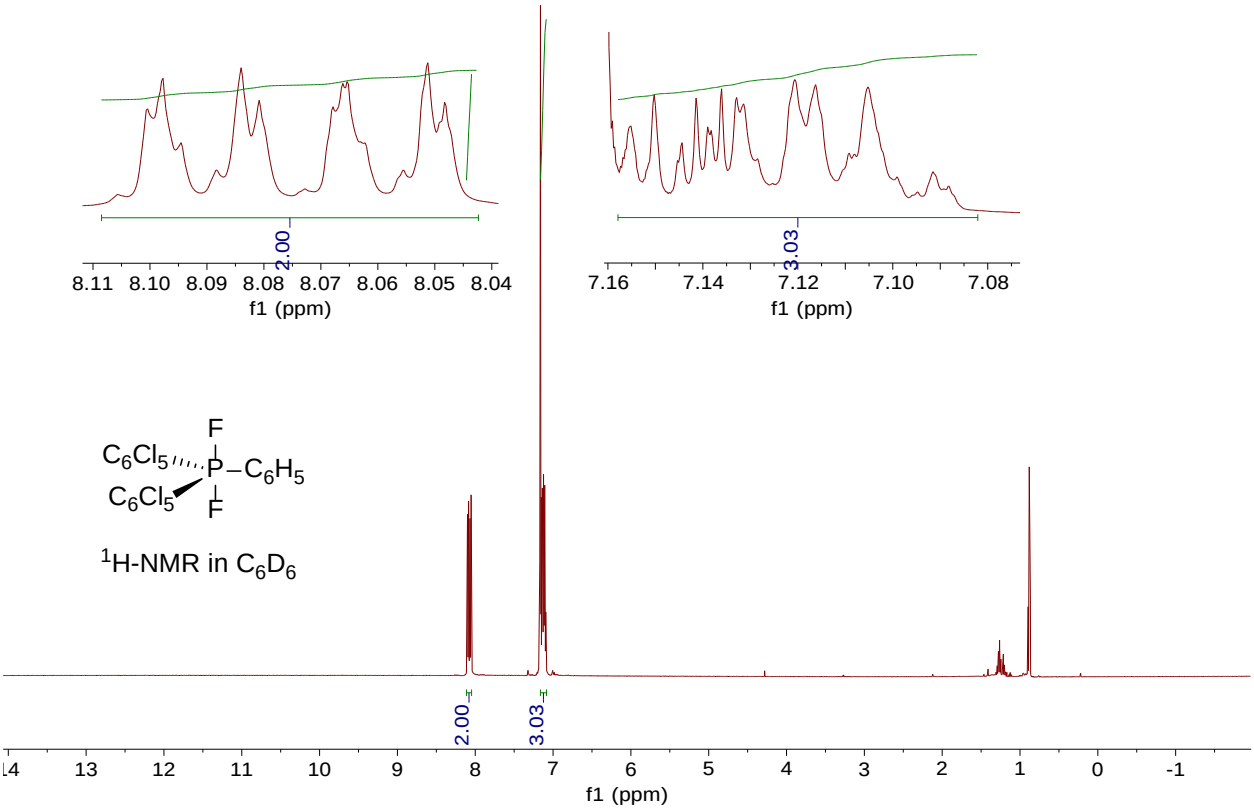
$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6): δ -28.9 (d, $^1J_{PF}$ = 746.5 Hz, PF_2) ppm.

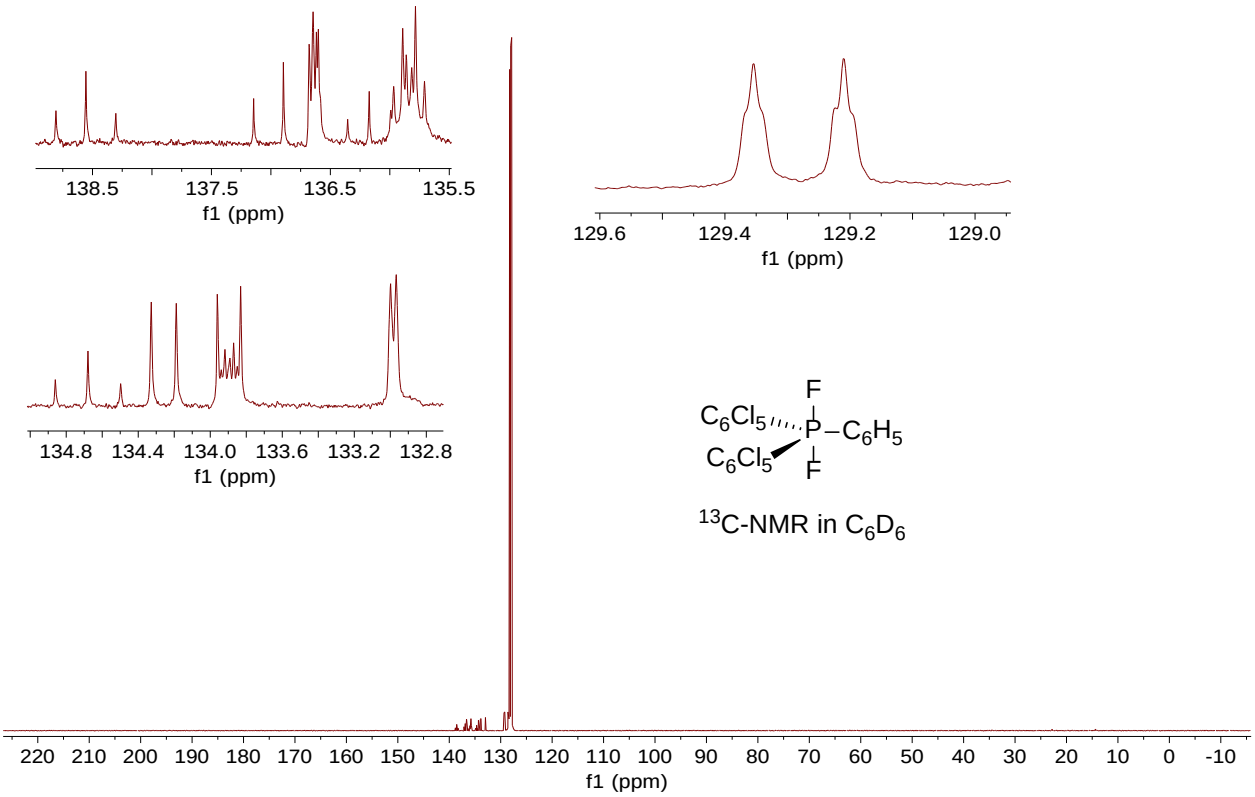
^1H NMR (500 MHz, C_6D_6): δ 8.11 – 8.04 (m, 2H, *m*-C_6H_5), 7.16 – 7.08 (m, 3H, *o*-, *p*-C_6H_5) ppm.

^{13}C NMR (125 MHz, C_6D_6): δ 137.73 (dt, $^1J_{PC}$ = 209.6 Hz, $^2J_{FC}$ = 31.5 Hz, *i*-C_6Cl_5), 136.70 – 136.55 (m, *o*-C_6Cl_5), 135.84 (dt, $^2J_{PC}$ = 13.6 Hz, $^3J_{FC}$ = 9.7 Hz, *o*-C_6H_5), 135.43 (dt, $^1J_{PC}$ = 187.3 Hz, $^2J_{FC}$ = 22.8 Hz, *i*-C_6H_5), 134.26 (d, $^4J_{PC}$ = 17.5 Hz, *p*-C_6Cl_5), 133.98 – 133.81 (m, *m*-C_6Cl_5), 132.98 (br d, $^4J_{PC}$ = 4.1 Hz, *p*-C_6H_5), 129.28 (dm, $^3J_{PC}$ = 18.1 Hz, *m*-C_6H_5) ppm.




F
C6Cl5
P
C6H5
C6Cl5
F
19F{1H}-NMR in C6D6
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)


2.00
8.11 8.10 8.09 8.08 8.07 8.06 8.05 8.04
f1 (ppm)
3.03
7.16 7.14 7.12 7.10 7.08
f1 (ppm)
F
C6Cl5
P
C6H5
C6Cl5
F
1H-NMR in C6D6
2.00
3.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

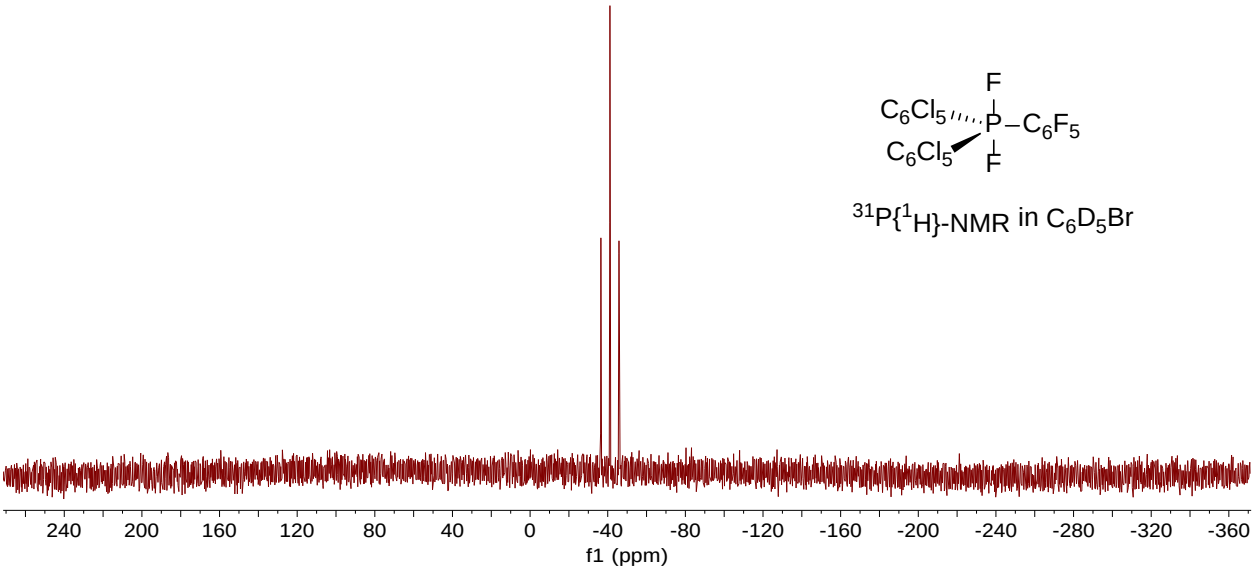

138.5
137.5
136.5
135.5
f1 (ppm)
134.8
134.4
134.0
133.6
133.2
132.8
f1 (ppm)
129.6
129.4
129.2
129.0
f1 (ppm)
F
C6Cl5
P–C6H5
C6Cl5
F
13C-NMR in C6D6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

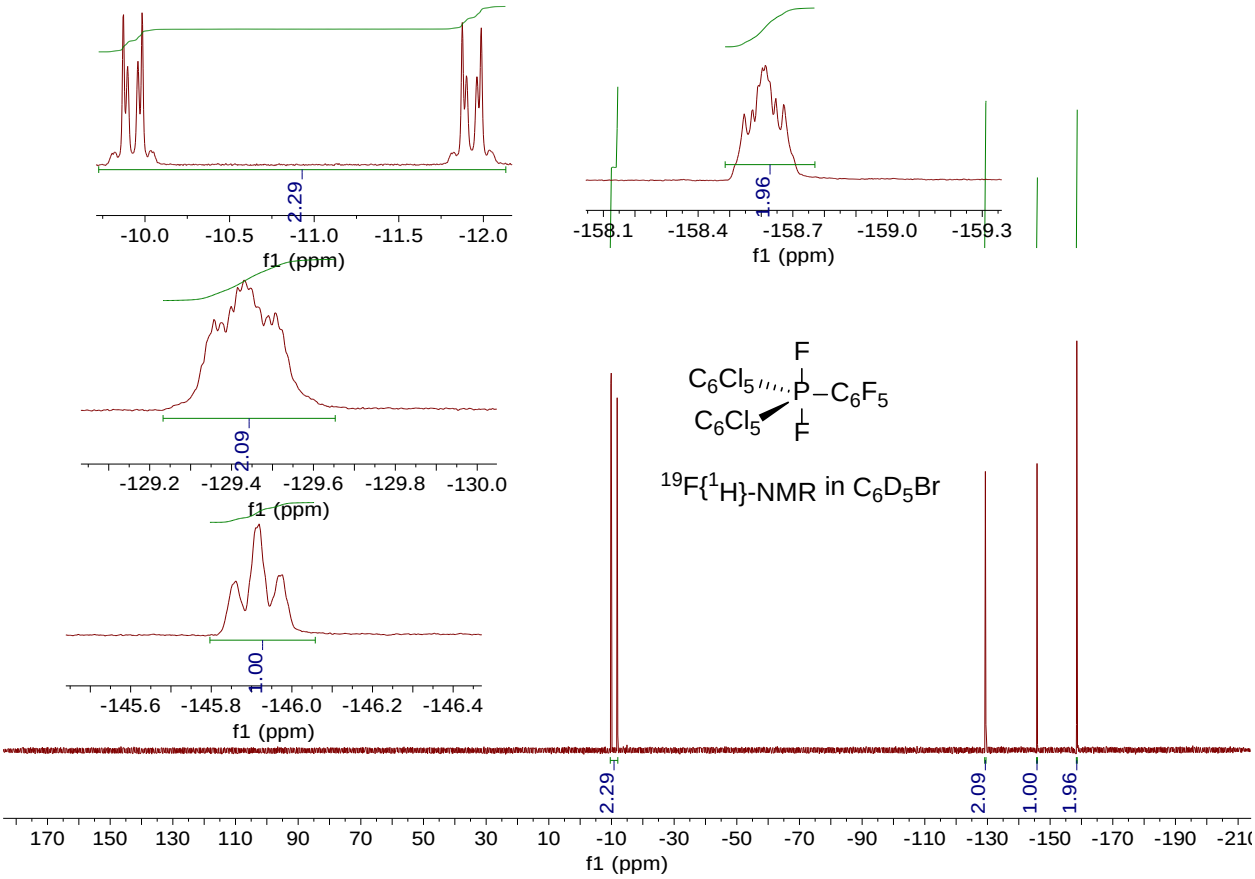
Difluoro bis(perchlorophenyl)(perfluorophenyl) phosphorane (7). In a cold well, a 20 mL vial was charged with $(C_6F_5)P(C_6Cl_5)_2$ (228 mg, 0.33 mmol), CH_2Cl_2 (5 mL), and a magnetic stir bar, forming a light yellow solution. XeF_2 (56 mg, 0.33 mmol) was quickly added to the stirring solution. The solution gradually lightens as it was left to stir and warm up to room temperature for 2 hours. The solvent was reduced and the solution cooled to -35 °C to produce a white precipitate, which was collected by filtration. The filtrate was then washed with *n*-pentane (2 x 3 mL) before removing the solvent *in vacuo*, producing a white solid (192 mg, 80% yield). Anal. Calcd. for $PC_{18}Cl_{10}F_7$: C: 29.43. Found: C: 28.52%.

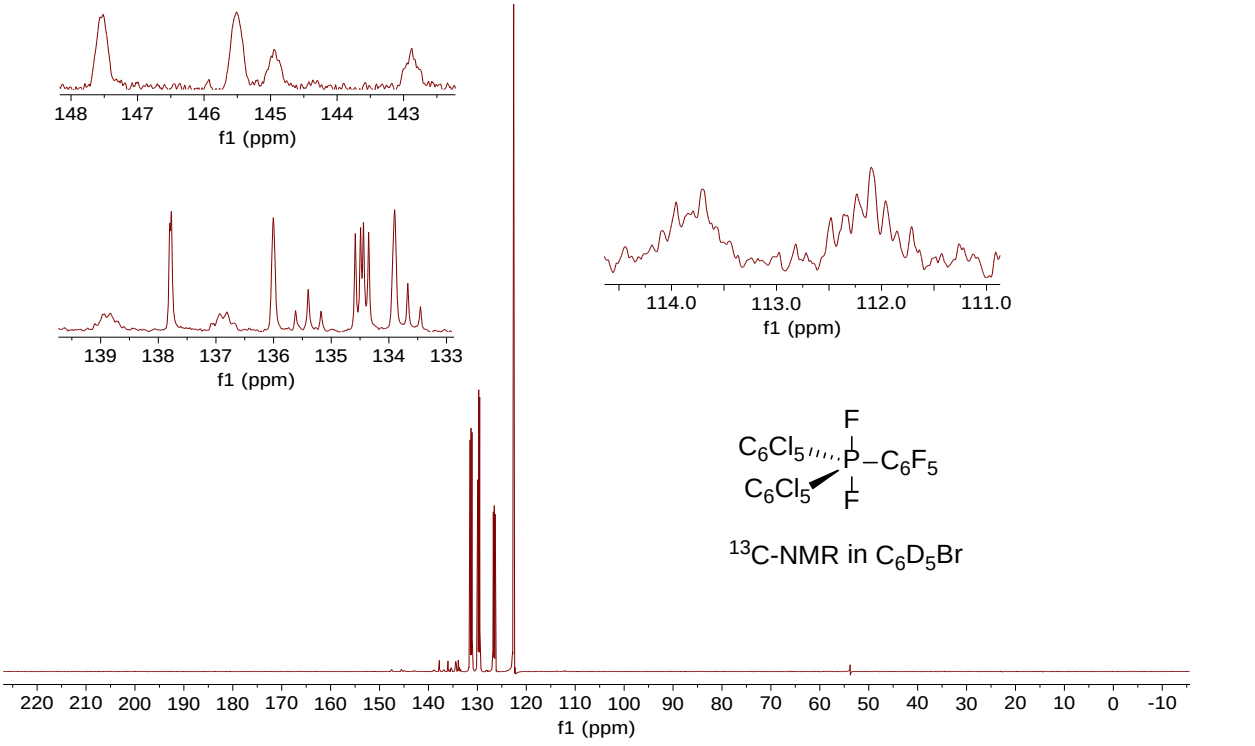
$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_5Br): δ -41.22 (t, $^1J_{PF}$ = 756.6 Hz) ppm.

$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_5Br): δ -10.92 (dm, $^1J_{PF}$ = 756.4 Hz, PF_2), -129.24 to -129.64 (m, 2F, *o*-C_6F_5), -145.91 (t, $^3J_{FF}$ = 21.7 Hz, 1F, *p*-C_6F_5), -158.50 to -158.72 (m, 2F, *m*-C_6F_5) ppm.

^{13}C NMR (125 MHz, C_6D_5Br): δ 146.53 (br d, $^1J_{FC}$ = 254.4 Hz, *o*-C_6F_5), 143.91 (br d, $^1J_{FC}$ = 259.1 Hz, *p*-C_6F_5), 137.89 (br dm, $^1J_{FC}$ = 255.1 Hz, *m*-C_6F_5), 136.91 (d, $^4J_{PC}$ = 3.7 Hz, *p*-C_6Cl_5), 134.96 (br d, $^2J_{PC}$ = 264.0 Hz, *o*-C_6Cl_5), 134.53 (dt, $^1J_{PC}$ = 217.0 Hz, $^2J_{FC}$ = 28.7 Hz, *i*-C_6Cl_5), 134.46 (dm, $^3J_{PC}$ = 17.8 Hz, *m*-C_6Cl_5), 112.95 (br dm, $^1J_{PC}$ = 200.8 Hz, *i*-C_6F_5) ppm.




2.29
-10.0 -10.5 -11.0 -11.5 -12.0
f1 (ppm)
1.96
-158.1 -158.4 -158.7 -159.0 -159.3
f1 (ppm)
2.09
-129.2 -129.4 -129.6 -129.8 -130.0
f1 (ppm)
1.00
-145.6 -145.8 -146.0 -146.2 -146.4
f1 (ppm)
F
C6Cl5
P
C6F5
C6Cl5
F
19F{1H}-NMR in C6D5Br
2.29
2.09
1.00
1.96
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -21(
f1 (ppm)


148 147 146 145 144 143
f1 (ppm)
139 138 137 136 135 134 133
f1 (ppm)
114.0 113.0 112.0 111.0
f1 (ppm)
F
C6Cl5
P
C6F5
C6Cl5
F
13C-NMR in C6D5Br
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Synthesis of phosphoniums:

Fluoro bis(perchlorophenyl)(diphenyl)phosphonium tetrakis(perfluorophenyl)borate (8). A 20 mL vial was charged with $(C_6Cl_5)PF_2Ph_2$ (382 mg, 0.81 mmol), toluene (3 mL), and a magnetic stir bar. To the stirring solution, $[Et_3Si][B(C_6F_5)_4]$ (682 mg, 0.77 mmol) was added as a solid. The dark orange solution was stirred for an hour, before allowing it to settle. Upon settling, a dark orange oil collected at the bottom of the vial, leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 3 mL) was used to wash the oil before being decanted off. The oil was subsequently washed with *n*-pentane (3 x 4 mL) before removing the solvent *in vacuo* resulting in a fluffy white solid (697 mg, 80% yield) upon trituration. Anal. Calcd. for $PC_{42}H_{10}Cl_5F_{21}B$: C: 44.54, H: 0.89. Found: C: 45.15%, H: 0.94%.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_5Br): δ 89.50 (d, $^1J_{PF}$ = 1008.5 Hz) ppm.

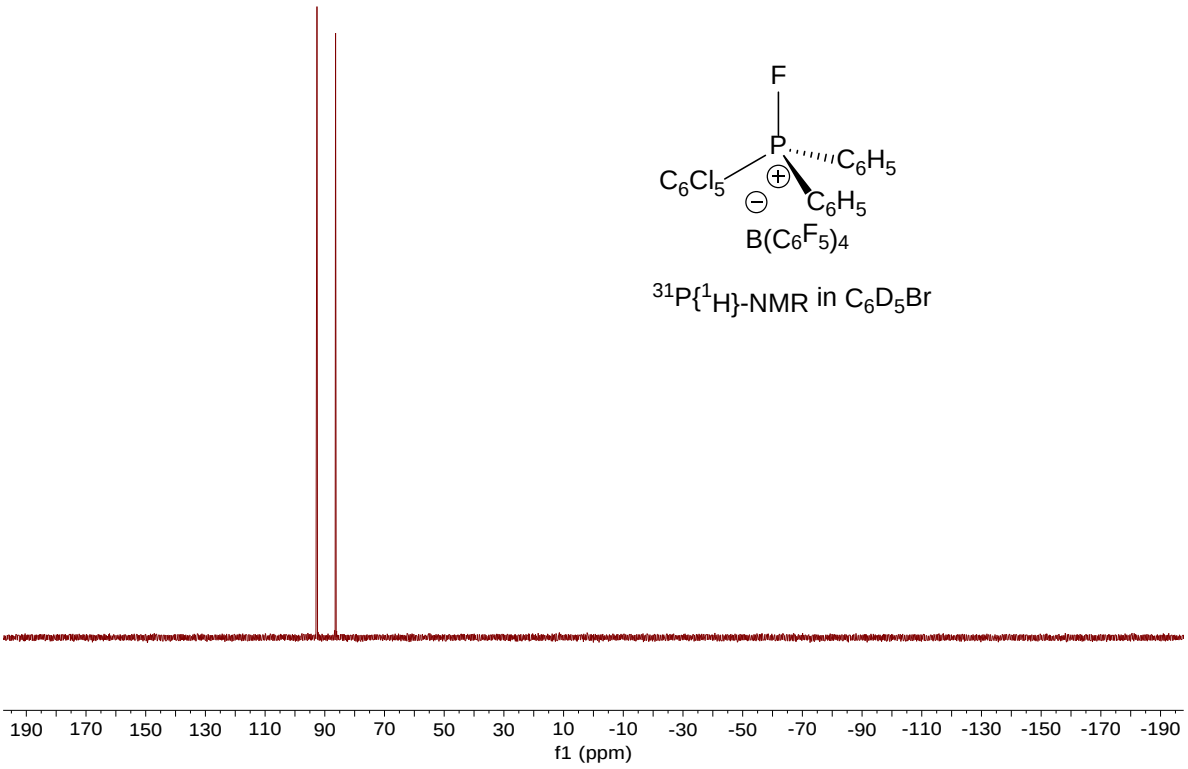
$^{19}F\{^1H\}$ NMR (376 MHz, C_6D_5Br): δ -116.01 (d, $^1J_{PF}$ = 1009.8 Hz, PF_2), -131.98 (m/br, 8F, B(*o*-C_6F_5)), -162.30 (t, $^3J_{FF}$ = 21.0 Hz, 4F, B(*p*-C_6F_5)), -166.18 (m/br, 8F, B(*m*-C_6F_5)) ppm.

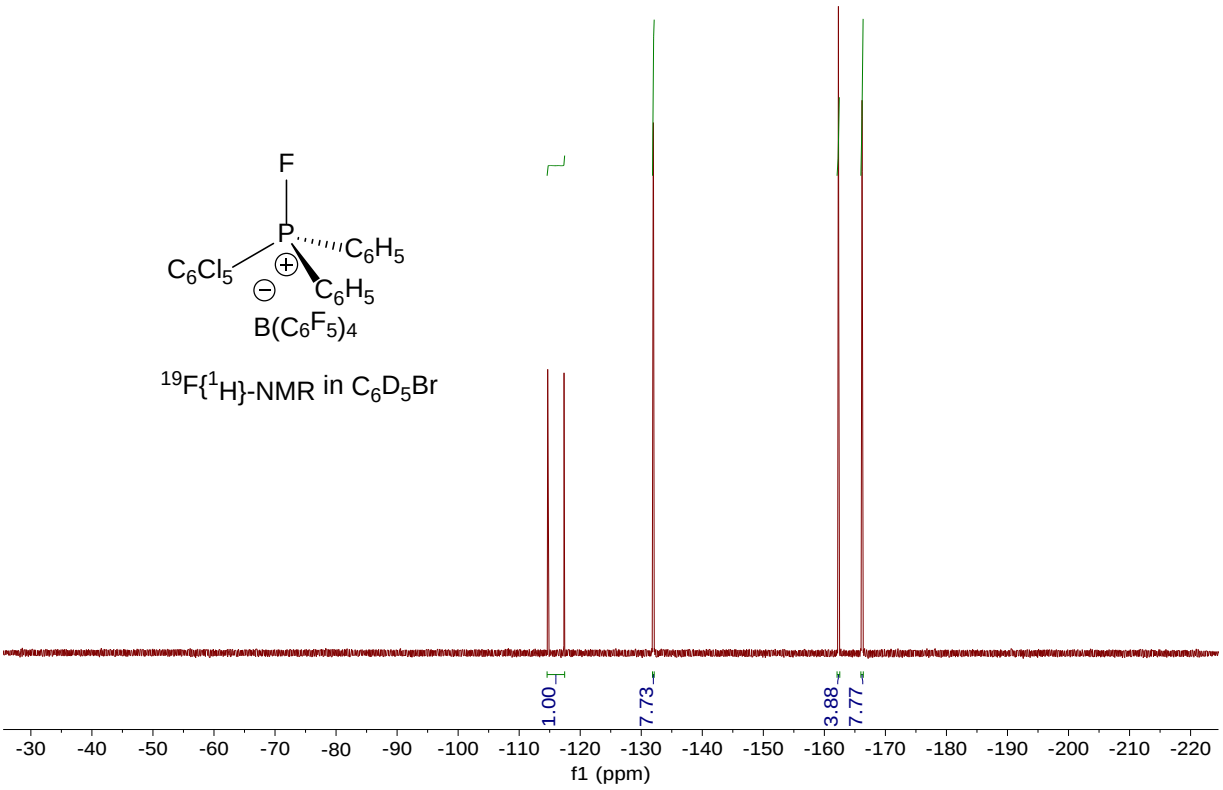
^{11}B NMR (128 MHz, C_6D_5Br): -16.52 (s) ppm.

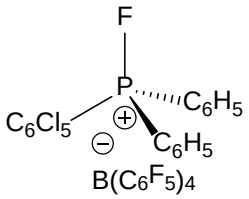
^1H NMR (500 MHz, $CDCl_3$): δ 8.09 – 8.04 (m, 1H, *p*-C_6H_5), 7.88 – 7.78 (m, 4H, *o*-, *m*-C_6H_5) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.25 (br d, $^1J_{FC}$ = 241.4 Hz, B(*o*-C_6F_5)), 145.26 (d, $^4J_{PC}$ = 3.2 Hz, P(*p*-C_6Cl_5)), 139.48 (dd, $^4J_{PC}$ = 2.4 Hz, $^5J_{FC}$ = 2.4 Hz, P(*p*-C_6H_5)), 138.25 (br d, $^1J_{FC}$ = 238.0 Hz, B(*p*-C_6F_5)), 137.74 (dd, $^2J_{PC}$ = 6.2 Hz, $^3J_{FC}$ = 1.0 Hz, P(*o*-C_6Cl_5)), 137.06 (d, $^3J_{PC}$ = 12.3 Hz, P(*m*-C_6Cl_5)), 136.26 (br d, $^1J_{FC}$ = 234.6 Hz, B(*m*-C_6F_5)), 133.53 (dd, $^2J_{PC}$ = 13.8 Hz, $^3J_{FC}$ = 1.3 Hz, P(*o*-C_6H_5)), 131.48 (d, $^3J_{PC}$ = 15.4 Hz, P(*m*-C_6H_5)), 123.80 (br s, B(*i*-C_6F_5)), 116.12 (dd, $^1J_{PC}$ = 112.0 Hz, $^2J_{FC}$ = 14.0 Hz, P(*i*-C_6H_5)), 115.91 (dd, $^1J_{PC}$ = 121.1 Hz, $^2J_{FC}$ = 11.1 Hz, P(*i*-C_6Cl_5)) ppm.

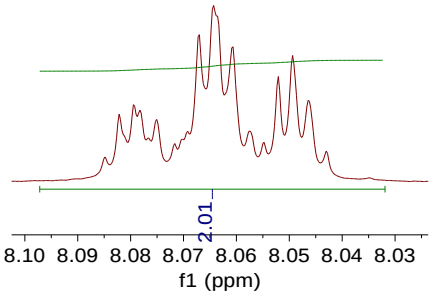
HRMS (DART Ionization) m/z: $[M]^+$ Calcd. for $C_{18}H_{10}Cl_5PF$: 450.89468, Found 450.89445.

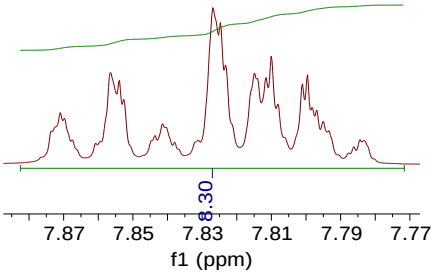

F
P
C6H5
C6Cl5
C6H5
B(C6F5)4
31P{1H}-NMR in C6D5Br
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)

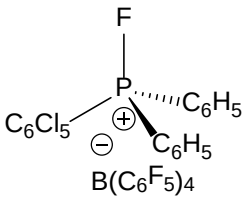

F
P
C6H5
C6Cl5
C6H5
B(C6F5)4
19F{1H}-NMR in C6D5Br
1.00
7.73
3.88
7.77
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)



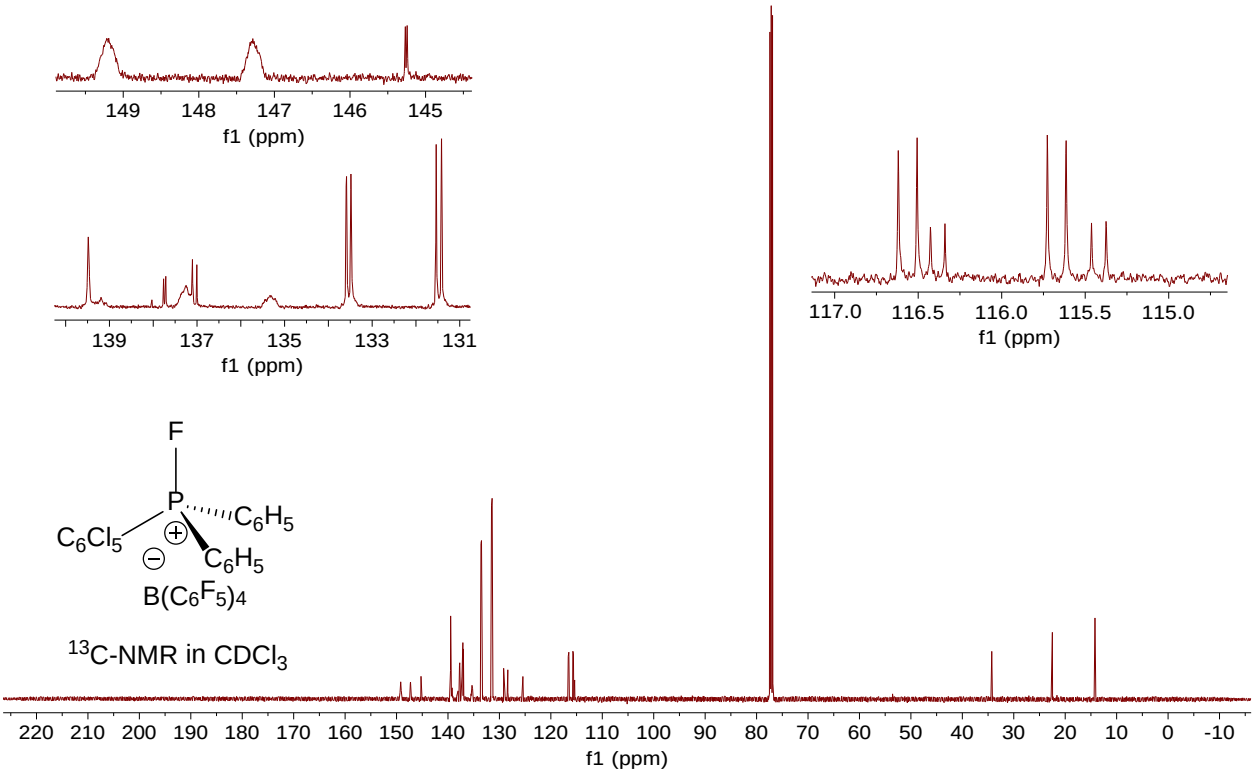
^{11}B-NMR in C_6D_5Br





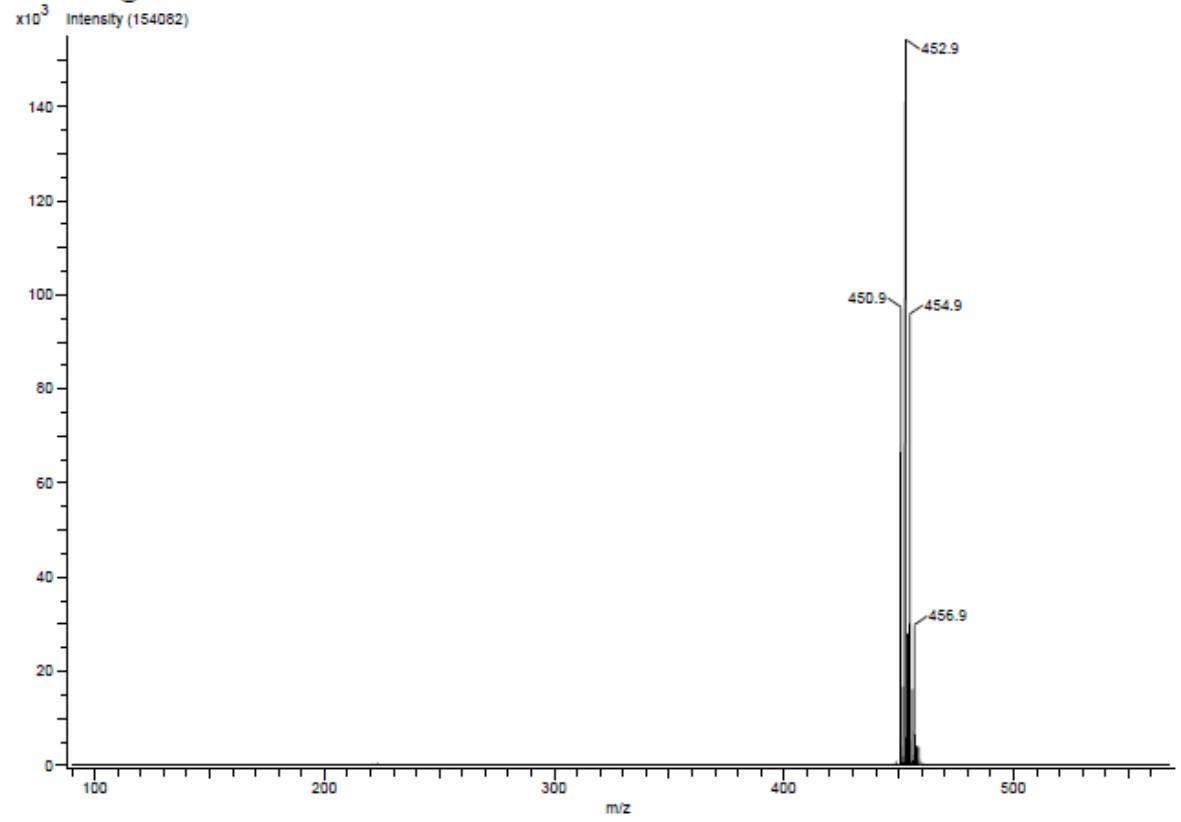


^{1}H-NMR in $CDCl_3$


149 148 147 146 145
f1 (ppm)
139 137 135 133 131
f1 (ppm)
117.0 116.5 116.0 115.5 115.0
f1 (ppm)
F
P
C6H5
C6Cl5
C6H5
B(C6F5)4
13C-NMR in CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

DART Ionization | **AIMS Mass Spectrometry Laboratory**
Department of Chemistry - U of T | **AccuTOF**

Acq. Data Name: 151211_3411 12/11/2015 10:38:08 AM
Average(MS[1] Time:0.58..0.60)-1.0*Average(MS[1] Time:0.05..0.08)
VP107 DART @350C



ION MODE: POSITIVE

Fluoro bis(perchlorophenyl)(phenyl)phosphonium tetrakis(perfluorophenyl)borate (9). A 20 mL vial was charged with $(C_6Cl_5)_2PF_2Ph$ (186 mg, 0.29 mmol), toluene (5 mL), and a magnetic stir bar. To the stirring solution, $[Et_3Si][B(C_6F_5)_4]$ (243 mg, 0.28 mmol) was added as a solid. The dark orange solution was stirred for an hour, before allowing it to settle. Upon settling, a dark orange oil collected at the bottom of the vial, leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 3 mL) was used to wash the oil before being decanted off. The oil was triturated in *n*-pentane (4 mL) until an off-white solid was formed. The solid was subsequently washed with *n*-pentane (2 x 4 mL) before removing the solvent *in vacuo* yielding an off-white solid (320 mg, 90% yield). X-Ray quality crystals were obtained from CH_2Cl_2 in glovebox freezer. Anal. Calcd. for $PC_{42}H_5Cl_{10}F_{21}B$: C: 38.66. H: 0.39. Found: C: 42.17%, H: 0.87%.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2): δ 84.38 (d, $^1J_{PF}$ = 1009.0 Hz) ppm.

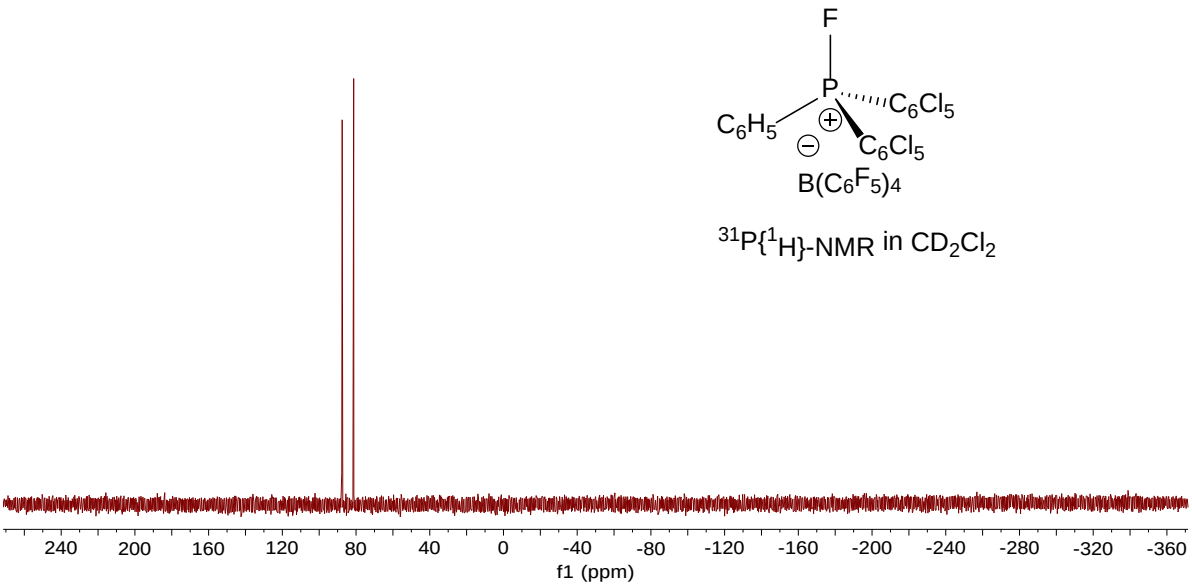
$^{19}F\{^1H\}$ NMR (470 MHz, C_6H_5Br): δ -125.64 (d, $^1J_{PF}$ = 1010.7 Hz, PF_2), -138.89 (m/br, 8F, B(*o*-C_6F_5)), -169.24 (m/br, 4F, B(*p*-C_6F_5)), -173.12 (m/br, 8F, B(*m*-C_6F_5)) ppm.

^{11}B NMR (128 MHz, CD_2Cl_2): -16.66 (s) ppm.

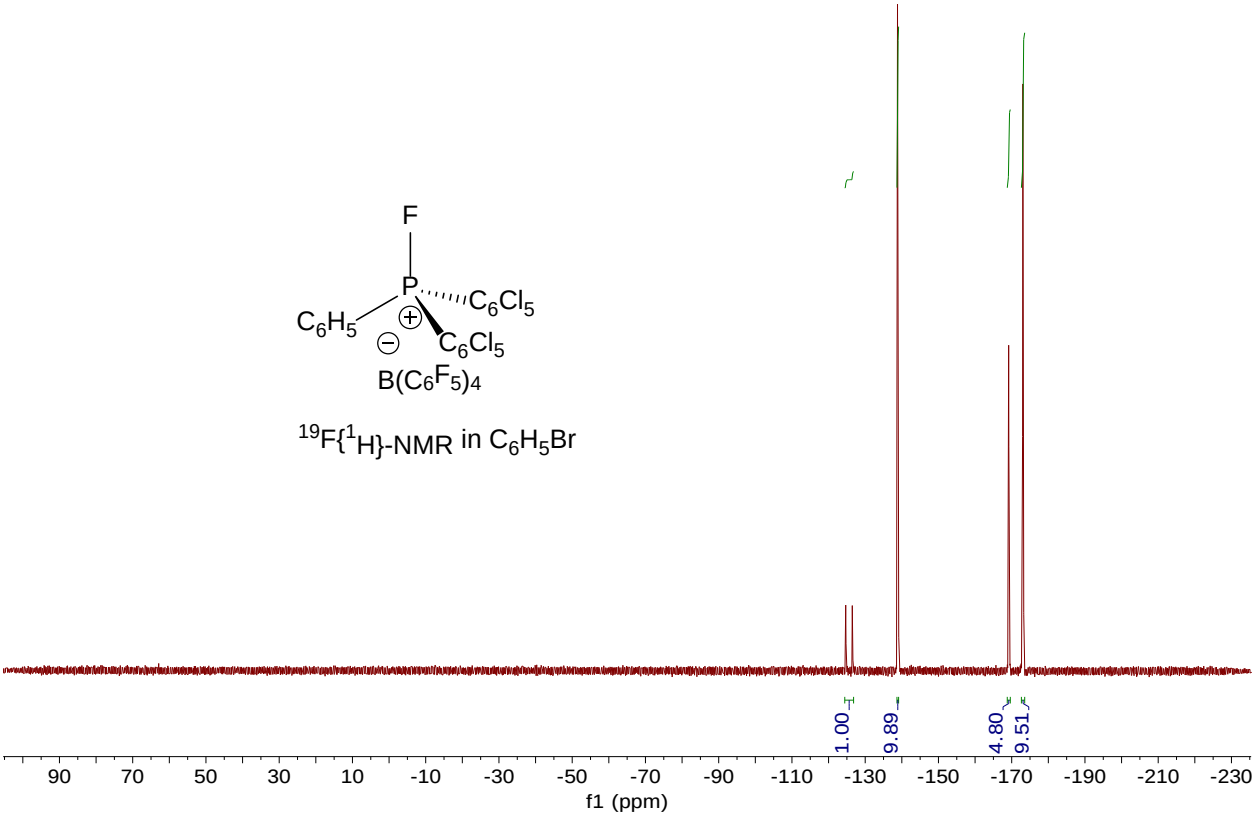
^1H NMR (500 MHz, $CDCl_3$): δ 8.13 – 8.08 (m, 1H, *p*-C_6H_5), 7.98 – 7.76 (m, 4H, *o*-, *m*-C_6H_5) ppm.

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.28 (br d, $^1J_{FC}$ = 240.3 Hz, B(*o*-C_6F_5)), 145.51 (dm, $^4J_{PC}$ = 3.2 Hz, P(*p*-C_6Cl_5)), 140.54 (m, P(*p*-C_6H_5)), 138.25 (br d, $^1J_{FC}$ = 239.2 Hz, B(*p*-C_6F_5)), 137.20 (d, $^3J_{PC}$ = 13.3 Hz, P(*m*-C_6Cl_5)), 136.65 (d, $^2J_{PC}$ = 6.2 Hz, P(*o*-C_6Cl_5)), 136.33 (br d, $^1J_{FC}$ = 239.0 Hz, B(*m*-C_6F_5)), 133.12 (d, $^2J_{PC}$ = 13.5 Hz, P(*o*-C_6H_5)), 132.15 (d, $^3J_{PC}$ = 16.6 Hz, P(*m*-C_6H_5)), 124.12 (br s, B(*i*-C_6F_5)), 118.30 (dd, $^1J_{PC}$ = 130.7 Hz, $^2J_{FC}$ = 10.8 Hz, P(*i*-C_6H_5)), 115.99 (dd, $^1J_{PC}$ = 113.9 Hz, $^2J_{FC}$ = 12.5 Hz, P(*i*-C_6Cl_5)) ppm.

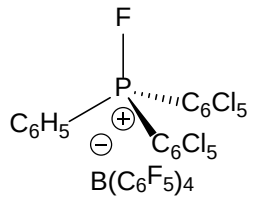
HRMS (DART Ionization) m/z: $[M]^+$ Calcd. for $C_{18}H_5Cl_{10}PF$: 620.69982, Found 620.69896.



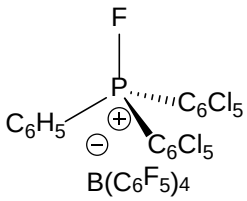
$^{31}P\{^{1}H\}$-NMR in CD_2Cl_2



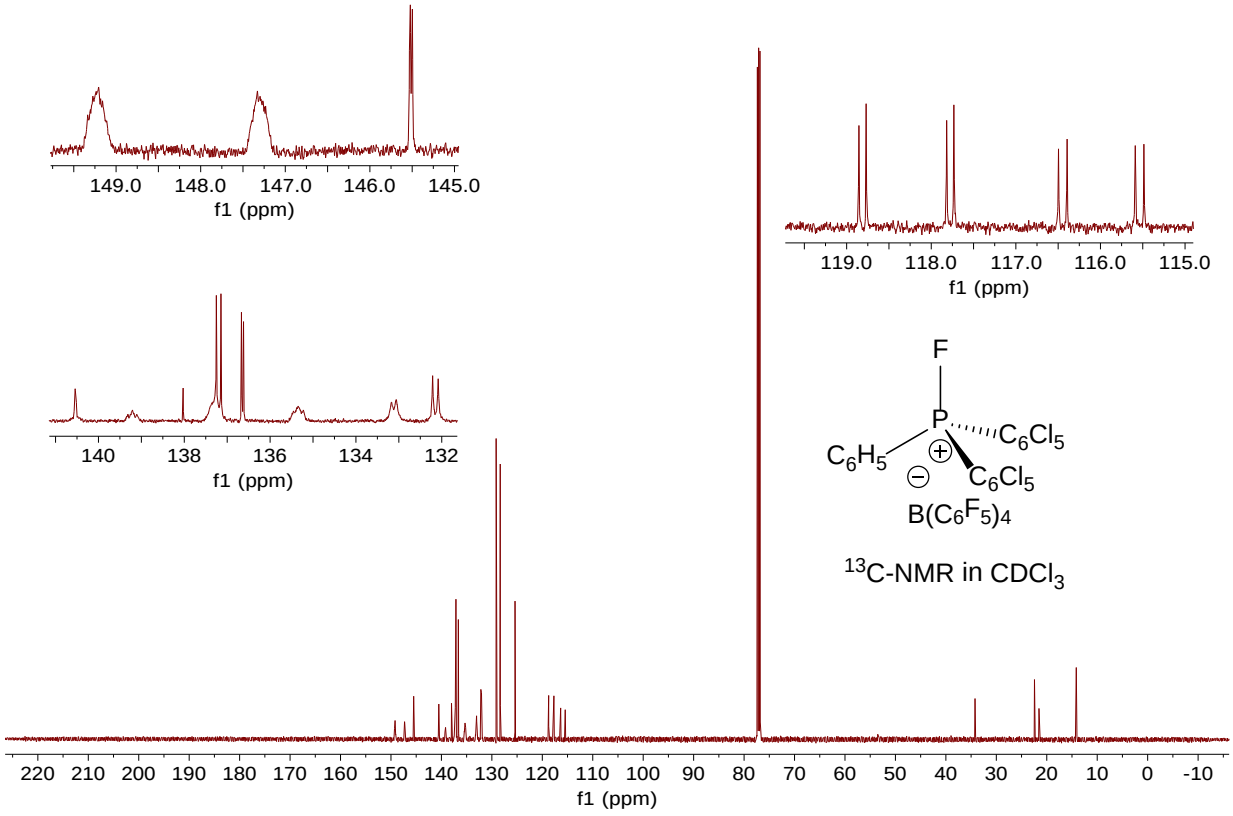
$^{19}F\{^{1}H\}$-NMR in C_6H_5Br

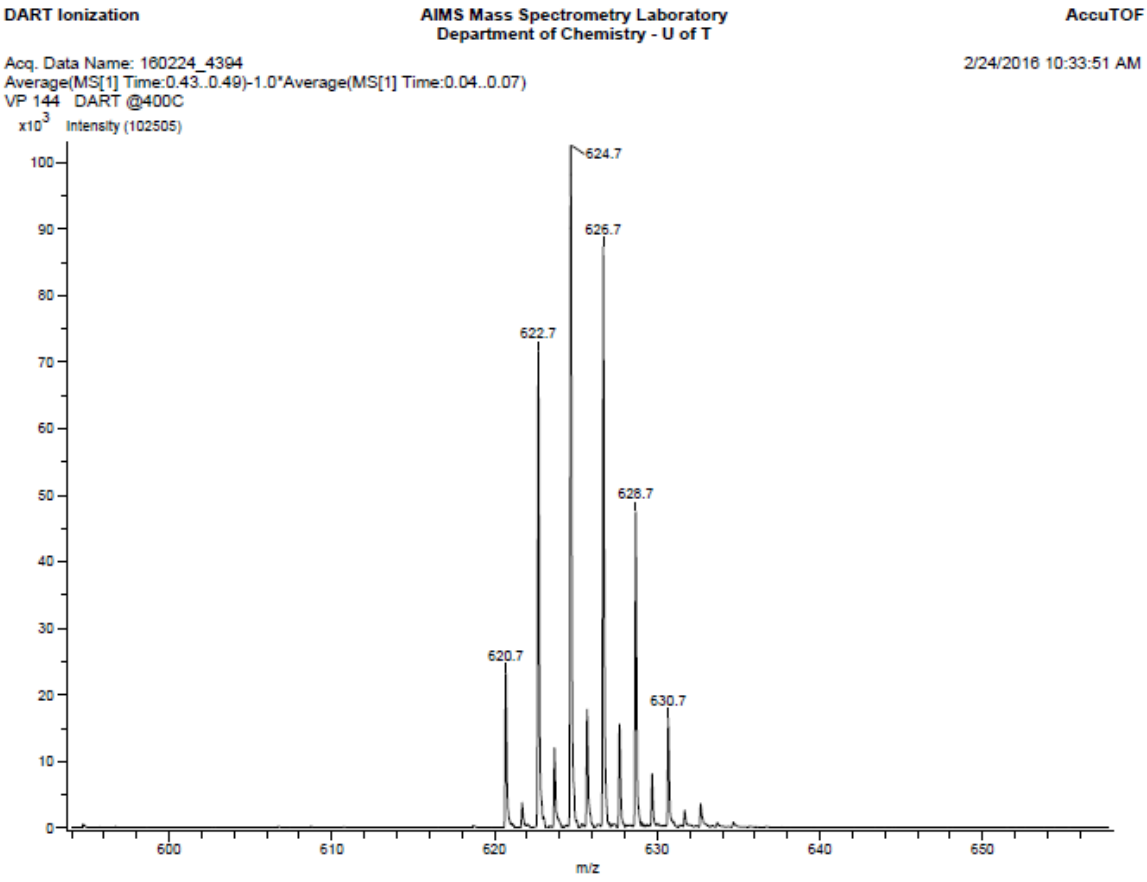


^{11}B-NMR in CD_2Cl_2



^{1}H-NMR in $CDCl_3$


149.0 148.0 147.0 146.0 145.0
f1 (ppm)
119.0 118.0 117.0 116.0 115.0
f1 (ppm)
140 138 136 134 132
f1 (ppm)
F
P
C6Cl5
C6H5
C6Cl5
B(C6F5)4
13C-NMR in CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



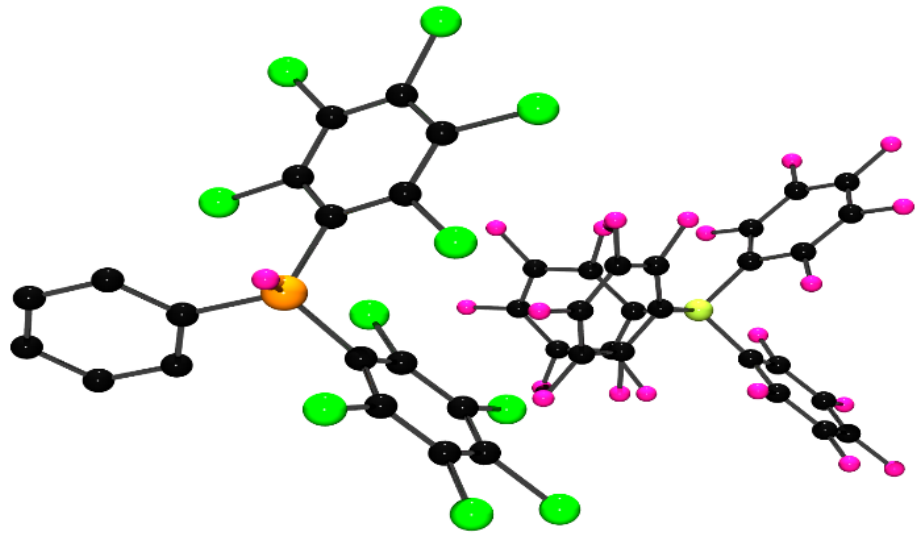


Figure 4. POV–Ray depiction of **9**. P: orange, Cl: green, C: black, F: pink.

Fluoro bis(perchlorophenyl)(perfluorophenyl)phosphonium tetrakis(perfluorophenyl) borate (10). A 20 mL vial was charged with $(C_6Cl_5)_2PF_2(C_6F_5)$ (172 mg, 0.23 mmol), toluene (5 mL), and a magnetic stir bar. To the stirring solution, $[Et_3Si][B(C_6F_5)_4]$ (197 mg, 0.22 mmol) was added as a solid. The clear solution was stirred for an hour, before allowing it to settle. Upon settling, a brown oil collected at the bottom of the vial, leaving a clear supernatant. After decanting the toluene from the oil, additional toluene (2 x 3 mL) was used to wash the oil before being decanted off. The oil was triturated in *n*-pentane (4 mL) until an off-white solid was formed. The solid was subsequently washed with *n*-pentane (2 x 4 mL) before removing the solvent *in vacuo* resulting in an off-white solid (229 mg, 74% yield). Anal. Calcd. for $PC_{42}Cl_{10}F_{26}B$: C: 36.17. Found: C: 37.21%

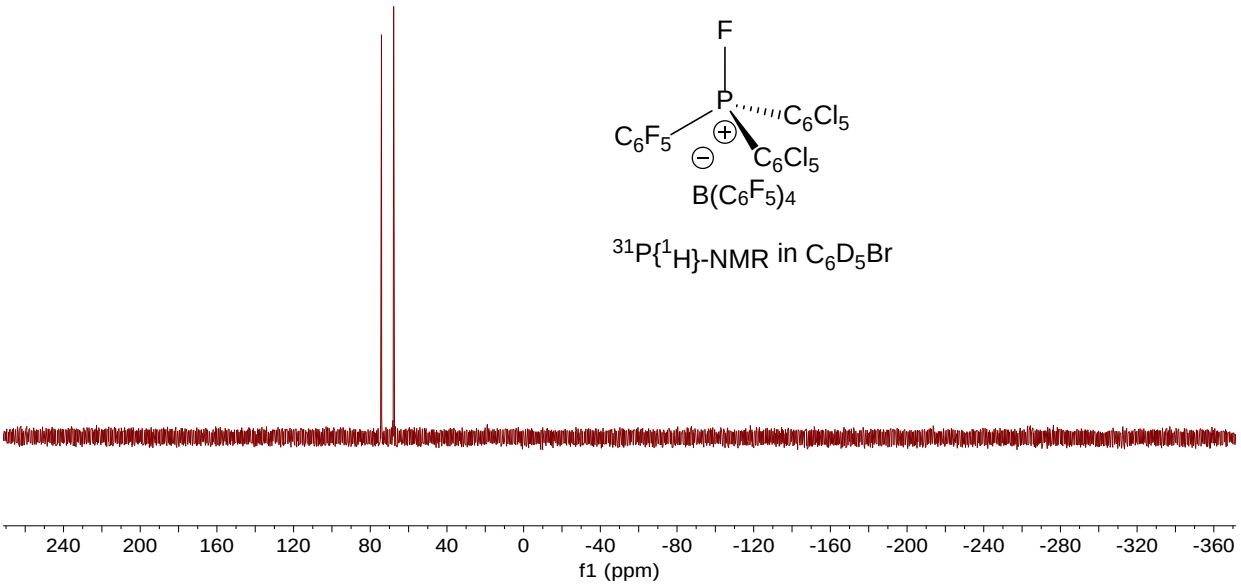
$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_5Br): δ 71.02 (d, $^1J_{PF}$ = 1030.8 Hz) ppm.

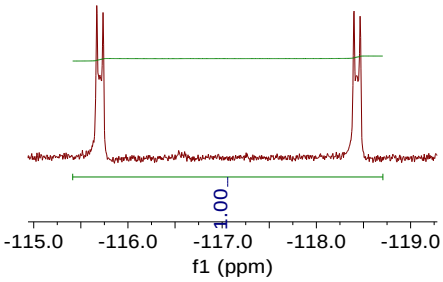
$^{19}F\{^1H\}$ NMR (470 MHz, C_6H_5Br): δ -117.04 (dd, $^1J_{PF}$ = 1030.3 Hz, $^3J_{FF}$ = 25.5 Hz, 1F, PF), -123.43 (br s, P(*o*-C_6F_5)), -124.73 (m, 1F, P(*p*-C_6F_5)), -126.84 (m, 1F, P(*o*-C_6F_5)), -132.24 (m/br, 8F, B(*o*-C_6F_5)), -150.35 (br s, P(*m*-C_6F_5)), -162.36 (t, $^3J_{FF}$ = 20.8 Hz, 4F, B(*p*-C_6F_5)), -166.43 (m/br, 8F, B(*p*-C_6F_5)) ppm.

^{11}B NMR (128 MHz, CD_2Cl_2): -16.59 (s) ppm.

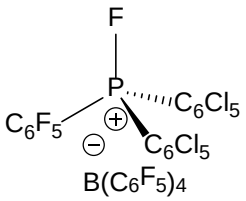
^{13}C NMR (125 MHz, $CDCl_3$): δ 150.58 (br d, $^1J_{FC}$ = 276.5 Hz, P(*o*-C_6F_5)), 148.28 (br d, $^1J_{FC}$ = 241.2 Hz, B(*o*-C_6F_5)), 147.07 (d, $^4J_{PC}$ = 3.2 Hz, P(*p*-C_6Cl_5)), 139.38 (br d, $^1J_{FC}$ = 269.2 Hz, P(*p*-C_6F_5)), 138.27 (br d, $^1J_{FC}$ = 241.2 Hz, B(*p*-C_6F_5)), 137.69 (d, $^3J_{PC}$ = 15.3 Hz, P(*m*-C_6Cl_5)), 136.69 (d, $^2J_{PC}$ = 6.1 Hz, P(*o*-C_6Cl_5)), 136.38 (br d, $^1J_{FC}$ = 234.7 Hz, B(*m*-C_6F_5)), 134.90 (br d, $^1J_{FC}$ = 259.8 Hz, P(*m*-C_6F_5)), 124.01 (br s, B(*i*-C_6F_5)), 116.32 (dd, $^1J_{PC}$ = 143.6 Hz, $^2J_{FC}$ = 9.9 Hz, P(*i*-C_6Cl_5)), 95.79 (br d, $^1J_{PC}$ = 136.8 Hz, P(*i*-C_6F_5)) ppm.

HRMS (DART Ionization) *m/z*: $[M]^+$ Calcd. for $C_{18}F_6Cl_{10}P$: 710.65271, Found 710.65339.

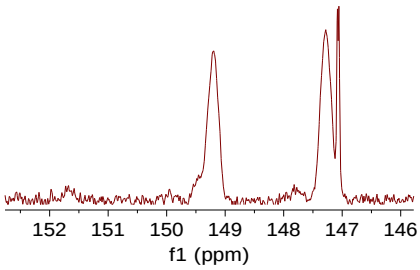

F
P
C6Cl5
C6F5
C6Cl5
B(C6F5)4
31P{1H}-NMR in C6D5Br
240 200 160 120 80 40 0 -40 -80 -120 -160 -200 -240 -280 -320 -360
f1 (ppm)

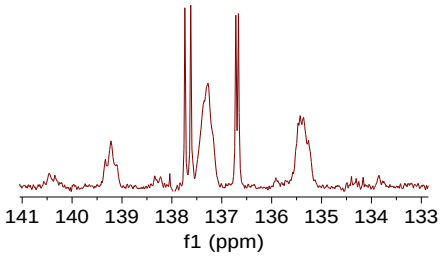

1.00
-115.0 -116.0 -117.0 -118.0 -119.0
f1 (ppm)

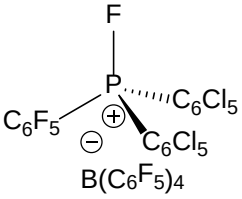
F
P
C6Cl5
C6F5
C6Cl5
B(C6F5)4
19F{1H}-NMR in C6D5Br
1.00 0.86 0.94 0.86 8.78 1.91 4.18 8.30
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)



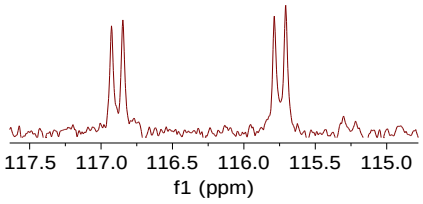
^{11}B-NMR in C_6D_5Br

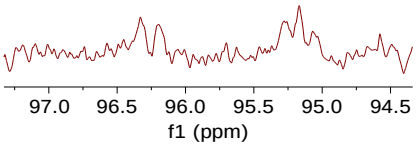






^{13}C-NMR in $CDCl_3$





DART Ionization

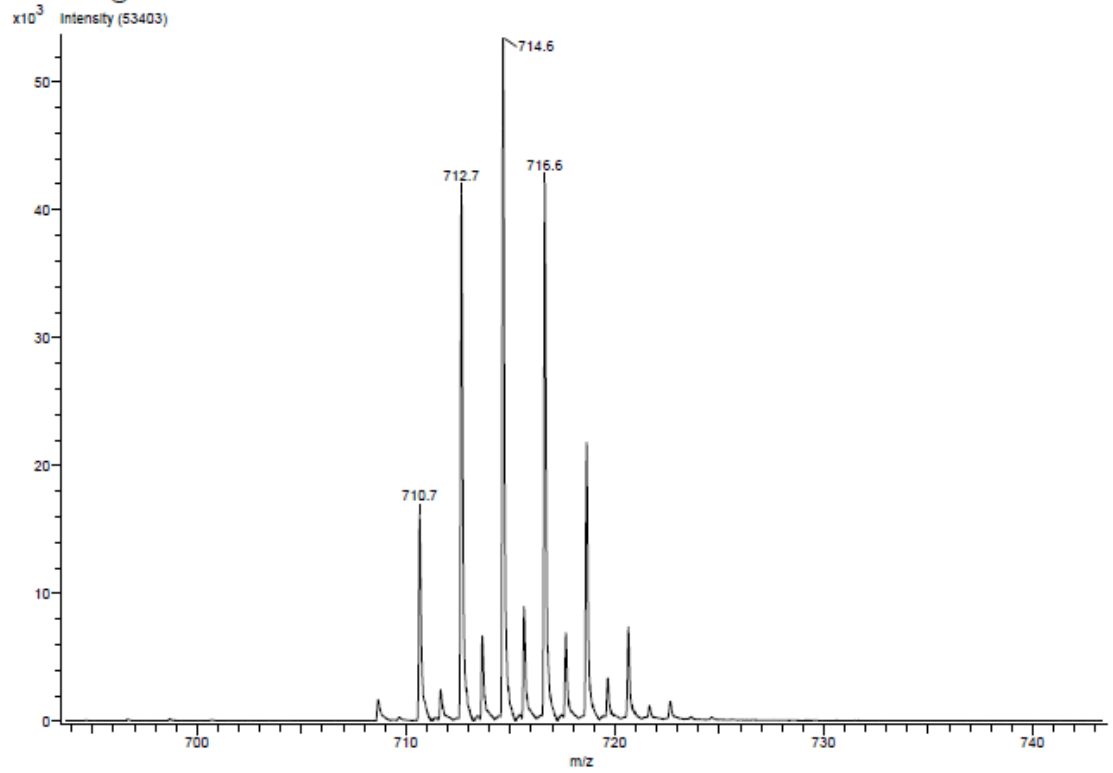
AIMS Mass Spectrometry Laboratory
Department of Chemistry - U of T

AccuTOF

Acq. Data Name: 160128_3944

1/28/2016 2:45:05 PM

Average(MS[1] Time:0.77..0.83)-1.0*Average(MS[1] Time:0.62..0.68)
VP 130 DART @350C



ION MODE: POSITIVE