

Wide Scope Easy Access to Luminescent Fluorophosphoranes

Jaime Ponce-de-León, Rebeca Infante, and Pablo Espinet*

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
47071-Valladolid (Spain)

*To whom correspondence should be addressed: espinet@qi.uva.es

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Experimental General Section

All the manipulations were performed under N₂ or Ar atmosphere by means of standard Schlenk techniques. Solvents were dried using a solvent purification system SPS PS-MD-5 or distilled from appropriate drying agents,¹ and were sparged with nitrogen gas. CDCl₃ was vacuum-transferred from CaH₂ and degassed using freeze-pump-thaw technique. Solvents for experiments in an inert atmosphere were stored into flame-dried Schlenk flasks over freshly activated 3 or 4 Å molecular sieves. Commercially available chemicals were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Acros Organics and were used without further purification. 2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)diphenylphosphine,² dicyclohexyl(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-il)phosphine, (perfluoro-[1,1'-biphenyl]-2-il)diphenylphosphine, dicyclohexyl(perfluoro-[1,1'-biphenyl]-2-il)phosphine,³ 2-bromo-2'-fluoro-1,1'-biphenyl,⁴ were prepared by reported methods. Flash chromatography was carried out using silica gel (230-240 mesh) and oxygen-free solvents. Chemical yields refer to pure isolated substances.

NMR spectra were recorded with Bruker Avance 400 Ultrashield and Varian 500/54 Premium Shielded instruments equipped with variable-temperature probes. Chemical shifts are reported in ppm referenced to tetramethylsilane (¹H), CCl₃F (¹⁹F), and 85% H₃PO₄ (³¹P), with positive shifts downfield, at 298 K unless otherwise stated. The temperature for the NMR probe was measured with an ethylene glycol standard (high temperature) using standard methods.⁵ In the ¹⁹F and ³¹P NMR spectra registered in non-deuterated solvents, a coaxial tube containing acetone-*d*₆ was used to maintain the ²H lock signal.

IR spectra were obtained on an FT-IR spectrometer equipped with an ATR accessory. Intensities are reported relative to the most intense peak of the spectrum and are defined as follows: w (weak, % T between 0 and 33.3%), medium (m, between 33.3% and 66.6%), and strong (s, between 66.6% and 100%).

HRMS (EI) were performed with a MALDI Bruker Autoflex at the LTI facilities of Valladolid University (Spain). Elemental analysis were carried out with a Carlo Erba 1108 Elemental Analyser at the services of Vigo University (Spain).

Luminescence studies were carried out at the PCT facilities of the University of Burgos. Absorption spectra were recorded in a UV-VIS FLS980 Spectrophotometer (Edinburgh Instruments) equipped with a detector (200-1000 nm) that is allowed for absorbance measurements. Steady-state fluorescence measurements were carried out by using a FLS980 fluorescence spectrometer with a 450W Xe lamp as a light source and double excitation and emission monochromators. Monochromator at 400 nm was used at the excitation and emission arms. A photomultiplier tube detector cooled by a Peltier system was used for detection. To measure the emission lifetimes and photoluminescence quantum yield (QY) the FLS980 fluorescence spectrometer is equipped with an integrating sphere. A rectangular 10 mm cuvette was used for the fluorescence measurements. All data were measured at 25 °C.

Literature Methods for the Synthesis of Biphenyls and Fluorinated Biphenyls.

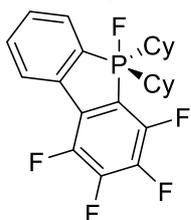
A wide variety of methods with great functional group tolerance have been reported and their references can be found at the end of this document.^{4,6,7,8,9,10,11,12,13,14,15,16} These methodologies can be applied to obtain the desired phosphine precursor.

Synthesis and characterization of compounds

Synthesis of fluorophosphoranes: general procedure

A flame-dried, nitrogen-purged Schlenk flask was charged with the corresponding fluorobiarylphosphine (300 mg) and the minimal amount of solvent (1-3 mL) to dissolve it at room temperature. Then, it was placed in an oil bath at the reaction temperature. The reaction progress was checked by ¹⁹F and ³¹P NMR. Once the starting phosphine was not observed, the Schlenk was cooled down to room temperature and the solvent removed under vacuum. The final product was purified by recrystallization to yield a crystalline solid, which was stored in a vial at -30 °C under N₂ atmosphere.

5,5-dicyclohexyl-1,2,3,4,5-pentafluoro-5H-5λ⁵-benzo[b]phosphindole (5)



This compound was obtained following the general procedure from dicyclohexyl(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phosphine (300 mg, 0.681 mmol) in toluene. It was purified by recrystallization in *n*-hexane at -30 °C to obtain a colourless crystalline solid (246.0 mg, 82.0 % yield).

HRMS (EI) Calculated for C₂₄H₂₆F₄P [M-F]⁺: 421.1703. Experimental [M-F]⁺: 421.1718.

Elemental analysis. C₂₄H₂₆F₅P. Calculated %: C, 65.45; H, 5.95. Experimental %: C, 65.67; H, 5.82.

¹H NMR (499.72 MHz, CDCl₃) δ 8.17 (dd, *J* = 11.6, 7.8 Hz, 1H), 8.09 – 8.03 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.36 (m, 1H), 2.38 – 2.29 (m, 4H), 1.85 – 1.66 (m, 4H), 1.65 – 1.52 (m, 4H), 1.35 – 1.13 (m, 8H), 1.12 – 0.99 (m, 2H).

¹⁹F NMR (470.16 MHz, CDCl₃) -47.59 (d, *J* = 704.2 Hz, 1F), -130.95 – -132.17 (m, 1F), -143.71 (t, *J* = 18.9 Hz, 1F), -154.18 – -155.44 (m, 1F), -156.10 (td, *J* = 19.3, 3.8 Hz, 1F).

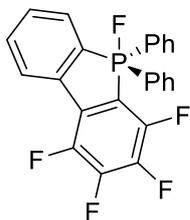
³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -55.9 (dd, *J* = 704.2, 19.2 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, CDCl₃) δ 144.8 (ddd, *J* = 236.3, 9.5, 2.8 Hz, 1C), 144.0 (dd, *J* = 257.2, 10.9 Hz, 1C), 140.7 (dddd, *J* = 250.4, 17.3, 13.2, 3.9 Hz, 1C), 140.1 (br d, *J* = 11.7 Hz, 1C), 140.0 (ddd, *J* = 258.5, 22.2, 13.0 Hz, 1C), 139.3 (dd, *J* = 13.7, 8.7 Hz, 1C), 136.1 – 134.6 (m, 1C), 133.1 (d, *J* = 2.9 Hz, 1C), 131.5 (dd, *J* = 157.2, 40.9 Hz, 1C), 128.6 (d, *J* = 14.3 Hz, 1C), 125.3 (t, *J* = 12.7 Hz, 1C), 122.8 – 121.0 (m, 1C), 46.6 (dd, *J* = 112.2, 34.3 Hz, 2C), 30.4 (br s, 2C), 28.1 (d, *J* = 5.3 Hz, 2C), 27.2 (d, *J* = 18.3 Hz, 2C), 26.8 (d, *J* = 17.2 Hz, 2C), 26.0 (d, *J* = 2.0 Hz, 2C).

IR (ATR, cm⁻¹) 2918 (m), 2852 (m), 1589 (w), 1493 (m), 1480 (m), 1435 (s), 1371 (m), 1267 (m), 1181 (w), 1121 (w), 1084 (m), 1070 (m), 1006 (s), 896 (w), 854 (m), 775 (m), 742

(m), 695 (m), 639 (m), 554 (s), 531 (s), 507 (m), 487 (m), 458 (m), 437 (m), 398 (m), 358 (w), 324 (w), 306 (w).

1,2,3,4,5-pentafluoro-5,5-diphenyl-5H-5 λ^5 -benzo[b]phosphindole (6)



This compound was obtained following the general procedure from (2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)diphenylphosphine (300 mg, 0.700 mmol) in toluene. It was purified by recrystallization from a CH₂Cl₂/*n*-hexane mixture at -30 °C to obtain a colourless crystalline solid (254.7 mg, 84.9 % yield).

X-ray-quality crystals were grown by slow evaporation of a chloroform solution at room temperature.

HRMS (EI) Calculated for C₂₄H₁₄F₄P [M-F]⁺: 409.0764. Experimental [M-F]⁺: 409.0764.

Elemental analysis. C₂₄H₁₄F₅P. Calculated %: C, 67.30; H, 3.29. Experimental %: C, 67.22; H, 3.38.

¹H NMR (499.72 MHz, CDCl₃) δ 8.36 (dd, *J* = 12.8, 7.8 Hz, 1H), 8.25 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.79 – 7.66 (m, 5H), 7.55 – 7.47 (m, 1H), 7.47 – 7.39 (m, 2H), 7.42 – 7.33 (m, 4H).

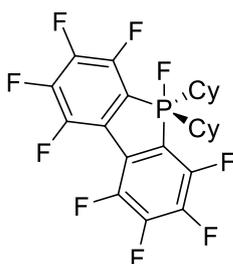
¹⁹F NMR (470.16 MHz, CDCl₃) δ 0.51 (d, *J* = 656.6 Hz, 1F), -129.53 – -132.60 (m, 1F), -143.73 (t, *J* = 17.7 Hz, 1F), -154.11 (dd, *J* = 23.6, 19.9 Hz, 1F), -154.83 (td, *J* = 19.2, 5.0 Hz, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -70.8 (dd, *J* = 657.0, 13.5 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, CDCl₃) δ 144.9 (d, *J* = 243.3 Hz, 1C), 144.0 (dd, *J* = 257.5, 12.0 Hz, 1C), 141.3 (d, *J* = 251.2 Hz, 1C), 140.6 – 140.4 (m, 1C), 140.4 (ddd, *J* = 259.5, 20.6, 12.7 Hz, 1C), 139.7 (d, *J* = 9.9 Hz, 1C), 136.3 (dd, *J* = 159.2, 35.0 Hz, 2C), 135.5 (s, 1C), 134.6 (d, *J* = 3.6 Hz, 1C), 131.9 (dd, *J* = 160.9, 26.3 Hz, 1C), 130.3 (d, *J* = 3.7 Hz, 2C), 129.7 (dd, *J* = 12.1, 1.7 Hz, 4C), 129.3 (d, *J* = 15.0 Hz, 1C), 128.6 (d, *J* = 16.6 Hz, 4C), 126.0 (t, *J* = 13.2 Hz, 1C), 120.8 – 120.2 (m, 1C).

IR (ATR, cm⁻¹) 3059 (w), 1628 (w), 1586 (w), 1492 (m), 1482 (m), 1438 (m), 1373 (m), 1273 (m), 1135 (w), 1119 (m), 1090 (m), 1066 (m), 1011 (s), 962 (w), 884 (w), 857 (m), 777 (w), 761 (w), 737 (s), 726 (s), 691 (s), 640 (m), 618 (w), 564 (s), 542 (s), 524 (s), 508 (s), 501 (s), 478 (s), 436 (m), 401 (w), 376 (w), 355 (m), 305 (w).

5,5-dicyclohexyl-1,2,3,4,5,6,7,8,9-nonafluoro-5H-5 λ^5 -benzo[b]phosphindole (7)



This compound was obtained following the general procedure from dicyclohexyl(perfluoro-[1,1'-biphenyl]-2-yl)phosphine (300 mg, 0.585 mmol) in toluene. It was purified by recrystallization in *n*-hexane at -30 °C to obtain a yellow crystalline solid (234.3 mg, 78.1 % yield).

X-ray-quality crystals were grown by slow evaporation of a chloroform solution at room temperature.

HRMS (EI) Calculated for C₂₄H₂₂F₈P [M-F]⁺: 493.1326. Experimental [M-F]⁺: 493.1343.

Elemental analysis. C₂₄H₂₂F₉P. Calculated %: C, 56.26; H, 4.33. Experimental %: C, 56.50; H, 4.39.

¹H NMR (499.72 MHz, CDCl₃) δ 2.39 – 2.27 (m, 2H), 2.26 – 2.11 (m, 2H), 1.86 – 1.68 (m, 4H), 1.68 – 1.57 (m, 4H), 1.48 – 1.34 (m, 2H), 1.34 – 1.16 (m, 6H), 1.13 – 0.97 (m, 2H).

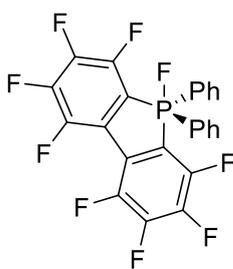
¹⁹F NMR (470.16 MHz, CDCl₃) δ -20.22 (dd, *J* = 763.5, 148.1 Hz, 1F), -120.60 (ddt, *J* = 148.2, 23.9, 12.4 Hz, 1F), -129.78 (dtd, *J* = 167.1, 17.8, 5.4 Hz, 1F), -131.01 – -131.83 (m, 2F), -145.71 – -146.15 (m, 1F), -151.74 (dd, *J* = 26.9, 19.8 Hz, 1F), -152.33 – -152.59 (m, 1F), -153.19 (td, *J* = 19.0, 4.1 Hz, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -46.5 (dd, *J* = 763.9, 12.2 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, CDCl₃) δ 152.5 (dd, *J* = 261.3, 9.2 Hz, 1C), 144.4* (1C), 144.1* (1C), 143.2* (1C), 142.4** (1C), 141.7* (1C), 141.6* (1C), 140.9* (1C), 137.1 – 134.9 (m, 1C), 122.9 (br s, 1C), 115.6 (br s, 1C), 114.8 (ddd, *J* = 159.2, 48.5, 12.4 Hz, 1C), 48.6 (dd, *J* = 111.1, 35.2 Hz, 2C), 30.1 (t, *J* = 5.4 Hz, 2C), 28.2 (d, *J* = 6.4 Hz, 2C), 27.1 (d, *J* = 18.1 Hz, 2C), 26.5 (d, *J* = 17.8 Hz, 2C), 25.8 (d, *J* = 2.3 Hz, 2C). *Determined by ¹³C-¹⁹F HSQC. **Determined by ¹³C-¹⁹F HMBC.

IR (ATR, cm⁻¹) 2933 (m), 2853 (m), 1611 (w), 1498 (s), 1468 (s), 1455 (s), 1378 (m), 1307 (m), 1243 (w), 1179 (w), 1125 (w), 1097 (m), 1070 (s), 1033 (m), 1007 (m), 937 (m), 895 (w), 855 (m), 788 (m), 763 (w), 706 (m), 652 (m), 609 (s), 557 (s), 539 (s), 525 (m), 492 (m), 453 (m), 443 (m), 388 (w), 352 (w), 325 (w).

1,2,3,4,5,6,7,8,9-nonfluoro-5,5-diphenyl-5H-5λ⁵-benzo[b]phosphindole (8)



This compound was obtained following the general procedure from (perfluoro-[1,1'-biphenyl]-2-yl)diphenylphosphine (300 mg, 0.599 mmol) in toluene. It was purified by recrystallization in *n*-hexane at -30 °C to obtain a yellow crystalline solid (225.6 mg, 75.2 % yield).

HRMS (EI) Calculated for C₂₄H₁₀F₉P [M-F]⁺: 481.0387. Experimental [M-F]⁺: 481.0369.

Elemental analysis. C₂₄H₁₀F₉P. Calculated %: C, 57.62; H, 2.01. Experimental %: C, 57.44; H, 1.73.

¹H NMR (499.72 MHz, CDCl₃) δ 7.67 (dd, *J* = 16.5, 7.4 Hz, 4H), 7.51 – 7.43 (m, 2H), 7.44 – 7.36 (m, 4H).

¹⁹F NMR (470.16 MHz, CDCl₃) δ 27.49 (dd, *J* = 726.5, 140.6 Hz, 1F), -119.15 – -119.74 (m, 1F), -129.88 – -130.79 (m, 2F), -130.98 – -131.50 (m, 1F), -143.30 – -143.62 (m, 1F), -151.02 – -151.21 (m, 1F), -151.21 – -151.41 (m, 1F), -151.68 – -151.84 (m, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -66.6 (dt, *J* = 726.5, 11.6 Hz, 1P).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, CDCl_3) δ 152.8 (dd, $J = 264.8, 11.1$ Hz, 1C), 143.6* (1C), 143.2* (1C), 145.5* (1C), 144.3* (1C), 142.5* (1C), 141.8* (1C), 141.3* (1C), 136.1 (d, $J = 24.3$ Hz, 1C), 136.0 (dd, $J = 163.1, 48.1$ Hz, 2C), 131.2 (d, $J = 3.7$ Hz, 2C), 130.5 (dd, $J = 12.4, 3.9$ Hz, 4C), 128.9 (d, $J = 16.7$ Hz, 4C), 123.3 (br s, 1C), 115.7 (ddd, $J = 165.6, 40.4, 11.8$ Hz, 1C), 114.7 (br s, 1C). *Determined by ^{13}C - ^{19}F HSQC.

IR (ATR, cm^{-1}) 3083 (w), 1614 (w), 1497 (m), 1474 (s), 1457 (s), 1439 (s), 1382 (m), 1311 (m), 1293 (m), 1261 (m), 1245 (m), 1106 (s), 1072 (s), 1035 (m), 1000 (m), 938 (m), 840 (w), 789 (m), 741 (s), 716 (m), 709 (m), 688 (s), 651 (m), 631 (s), 612 (s), 558 (s), 524 (s), 506 (s), 482 (m), 467 (m), 373 (w), 346 (w), 322 (w), 307 (w).

5,5-dicyclohexyl-5-fluoro-5H-5 λ^5 -benzo[b]phosphindole (11)



This compound was obtained following the general procedure from dicyclohexyl(2'-fluoro-[1,1'-biphenyl]-2-yl)phosphane (300 mg, 0.814 mmol) in diglyme. It was purified by recrystallization from a $\text{CH}_2\text{Cl}_2/n$ -hexane at -30 °C to obtain a colourless crystalline solid (257.4 mg, 85.8 % yield).

X-ray-quality crystals were grown by slow evaporation of a chloroform solution at room temperature.

HRMS (EI) Calculated for $\text{C}_{24}\text{H}_{30}\text{P}$ $[\text{M}-\text{F}]^+$: 349.2080. Experimental $[\text{M}-\text{F}]^+$: 349.2080.

Elemental analysis. $\text{C}_{24}\text{H}_{30}\text{FP}$. Calculated %: C, 78.23; H, 8.21. Experimental %: C, 78.49; H, 7.95.

^{19}F NMR (376.48 MHz, Toluene- d_8) δ -31.45 (d, $J = 680.3$ Hz, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, Toluene- d_8) δ -59.3 (d, $J = 680.4$ Hz, 1P).

^1H NMR (400.14 MHz, Toluene- d_8 , 232 K) δ 8.67 – 8.49 (m, 1H), 7.42 (d, $J = 30.2$ Hz, 2H), 7.25 – 6.90 (m, 5H), 2.40 (s, 2H), 2.25 (t, $J = 11.7$ Hz, 2H), 2.13 – 1.97 (m, 2H), 1.70 (s, 2H), 1.52 – 1.11 (m, 10H), 1.03 (t, $J = 12.9$ Hz, 2H), 0.73 (t, $J = 12.8$ Hz, 2H).

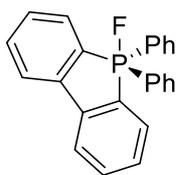
^{19}F NMR (376.48 MHz, Toluene- d_8 , 232 K) δ -32.94 (d, $J = 681.4$ Hz, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, Toluene- d_8 , 232 K) δ -59.6 (d, $J = 681.5$ Hz, 1P).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, Toluene- d_8 , 232 K) 153.0 (d, $J = 56.5$ Hz, 1C), 145.3 (d, $J = 17.7$ Hz, 1C), 140.1 (t, $J = 10.6$ Hz, 1C), 139.3 (d, $J = 12.4$ Hz, 1C), 132.4 (s, 2C), 132.2 (dd, $J = 157.7, 49.2$ Hz, 1C), 128.0* (1C), 128.7* (1C), 120.4 (d, $J = 12.7$ Hz, 1C), 119.3 (s, 2C), 45.6 (dd, $J = 110.0, 37.9$ Hz, 2C), 31.0 (s, 2C), 27.7 (s, 2C), 27.4 – 26.7 (m, 4C), 26.3 (s, 2C). *Determined by ^{13}C - ^1H HMBC.

IR (ATR, cm^{-1}) 3060 (w), 2914 (m), 2845 (m), 1578 (w), 1437 (m), 1257 (m), 1180 (m), 1115 (m), 1075 (m), 1063 (m), 1002 (m), 918 (w), 894 (m), 882 (m), 854 (m), 817 (w), 769 (m), 760 (m), 743 (s), 723 (s), 689 (m), 670 (s), 619 (m), 574 (s), 543 (s), 512 (s), 487 (s), 449 (m), 439 (m), 425 (s), 407 (m), 369 (w), 336 (w).

5-fluoro-5,5-diphenyl-5H-5 λ^5 -benzo[b]phosphindole (13)



This compound was obtained following the general procedure from (2'-fluoro-[1,1'-biphenyl]-2-yl)diphenylphosphane (300 mg, 0.841 mmol) in diglyme. It was purified by recrystallization from a CH₂Cl₂/*n*-hexane at -30 °C to obtain a colourless solid (190.4 mg, 63.4 % yield).

HRMS (EI) Calculated for C₂₄H₁₈P [M-F]⁺: 337.1141. Experimental [M-F]⁺: 337.1144.

Elemental analysis. C₂₄H₁₈FP. Calculated %: C, 80.89; H, 5.09. Experimental %: C, 80.98; H, 5.19.

¹H NMR (499.72 MHz, Toluene-*d*₈, 233 K) δ 8.91 – 8.32 (m, 1H), 7.74 (dd, *J* = 15.4, 7.5 Hz, 4H), 7.60 – 7.49 (m, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.02 (m, 1H), 7.00 – 6.85 (m, 7H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.75 – 6.64 (m, 1H).

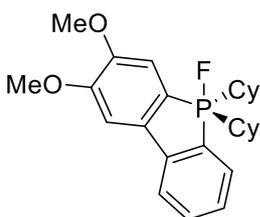
¹⁹F NMR (470.17 MHz, Toluene-*d*₈, 233 K) δ 11.34 (d, *J* = 638.5 Hz, 1F).

³¹P{¹H} NMR (202.29 MHz, Toluene-*d*₈, 233 K) δ -69.3 (d, *J* = 638.3 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, Toluene-*d*₈, 233 K) δ 153.2 (d, *J* = 21.5 Hz, 1C), 152.8 (d, *J* = 21.5 Hz, 1C), 146.0 (dd, *J* = 22.2, 4.1 Hz, 1C), 140.5 (dd, *J* = 11.6, 9.3 Hz, 1C), 139.1 (s, 1C), 138.7 (s, 1C), 138.0 (d, *J* = 15.9 Hz, 1C), 137.9 (s, 1C), 133.9 (d, *J* = 3.0 Hz, 2C), 133.5 (d, *J* = 42.1 Hz, 1C), 132.3 (d, *J* = 41.9 Hz, 1C), 131.5 (dd, *J* = 11.8, 3.4 Hz, 4C), 131.3 (d, *J* = 5.8 Hz, 2C), 129.6 (d, *J* = 3.4 Hz, 4C), 121.4 – 120.8 (m, 1C), 119.4 (d, *J* = 3.9 Hz, 1C).

IR (ATR, cm⁻¹) 1590.79 (w), 1481.13 (w), 1439.55 (w), 1260.55 (w), 1117.17 (w), 1073.78 (w), 769.36 (w), 749.16 (m), 739.32 (m), 732.58 (s), 720.63 (m), 692.3 (m), 680.35 (m), 618.64 (w), 559.75 (s), 550.97 (s), 541.66 (m), 528.14 (s), 514.08 (s), 493.28 (m), 481.62 (m), 450.01 (m), 419.91 (w), 403.16 (w), 369.11 (w), 312.75 (w), 290.07 (w), 268.8 (w).

5,5-dicyclohexyl-5-fluoro-2,3-dimethoxy-5H-5 λ^5 -benzo[b]phosphindole (15)



This compound was obtained following the general procedure from dicyclohexyl(2'-fluoro-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)phosphane (300 mg, 0.700 mmol) in diglyme. It was purified by recrystallization from a CH₂Cl₂/*n*-hexane at -30 °C to obtain a colourless crystalline solid (273.9 mg, 91.3 % yield).

HRMS (EI) Calculated for C₂₆H₃₄O₂P [M-F]⁺: 409.2291. Experimental [M-F]⁺: 409.2301.

Elemental analysis. C₂₆H₃₄FO₂P. Calculated %: C, 72.87; H, 8.00. Experimental %: C, 72.79; H, 7.95.

¹H NMR (499.72 MHz, Toluene-*d*₈, 232 K) δ 8.06 (d, *J* = 11.3 Hz, 1H), 7.40 (d, *J* = 6.6 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.09 (m, 1H), 3.44 (s, 3H), 3.37 (s, 3H), 2.54 – 2.33 (m, 4H), 2.11 (d, *J* = 14.4 Hz, 2H), 1.76 (d, *J* = 12.8 Hz, 2H), 1.60 – 1.33 (m, 8H), 1.26 (q, *J* = 13.1 Hz, 2H), 1.10 (qt, *J* = 13.0, 3.6 Hz, 2H), 0.96 – 0.77 (m, 2H).

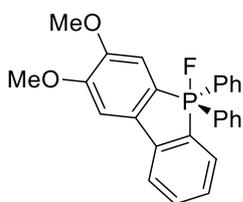
¹⁹F NMR (470.17 MHz, Toluene-*d*₈, 232 K) δ -32.09 (d, *J* = 668.0 Hz, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.29 MHz, Toluene- d_8 , 232 K) δ -58.8 (d, J = 668.4 Hz, 1P).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, Toluene- d_8 , 232 K) δ 153.5 (s, 1C), 153.0 (d, J = 56.0 Hz, 1C), 149.8 (d, J = 17.0 Hz, 1C), 139.9 (d, J = 12.3 Hz, 1C), 139.4 (dd, J = 18.6, 3.8 Hz, 1C), 123.2 (d, J = 49.7 Hz, 1C), 121.9 (d, J = 49.9 Hz, 1C), 120.9 (t, J = 12.4 Hz, 1C), 118.5 (s, 2C), 102.9 (d, J = 16.1 Hz, 1C), 54.8 (s, 1C), 54.8 (s, 1C), 45.5 (dd, J = 110.1, 38.0 Hz, 2C), 31.2 (s, 2C), 27.8 (d, J = 4.3 Hz, 2C), 27.5 (d, J = 17.7 Hz, 2C), 27.2 (d, J = 16.3 Hz, 2C), 26.5 (s, 2C).

IR (ATR, cm^{-1}) 2920.76 (m), 2848.23 (m), 1593.28 (m), 1565.77 (w), 1495.85 (m), 1475.09 (m), 1460.82 (m), 1441.57 (m), 1430.35 (m), 1394.97 (m), 1320.91 (m), 1251.93 (s), 1206.86 (s), 1171.92 (m), 1121.37 (m), 1082.05 (m), 1062.61 (m), 1038.59 (m), 1022.54 (m), 928.01 (m), 895.77 (m), 873.82 (m), 863.47 (m), 853.59 (m), 839.56 (m), 798.35 (m), 768.15 (s), 738.98 (m), 725.13 (m), 680.73 (s), 671.98 (m), 573.3 (s), 562.01 (s), 525.81 (s), 503.98 (s), 490.18 (s), 469.23 (s), 441.47 (m), 416.91 (m), 378.49 (m), 301.69 (m), 264.69 (m).

5-fluoro-2,3-dimethoxy-5,5-diphenyl-5H- λ^5 -benzo[b]phosphindole (17)

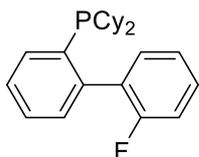


This compound was obtained following the general procedure from (2'-fluoro-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)diphenylphosphane (300 mg, 0.700 mmol) in diglyme. Product was detected by ^{19}F and ^{31}P NMR but any attempt to isolate it was unsuccessful, due to its low conversion (39 %) and some phosphine oxide products formation(22 %).

^{19}F NMR (470.17 MHz, diglyme(acetone- d_6 cap)) δ 11.10 (d, J = 623.0 Hz, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.29 MHz, diglyme(acetone- d_6 cap)) δ -69.6 (d, J = 623.2 Hz, 1P).

Dicyclohexyl(2'-fluoro-[1,1'-biphenyl]-2-yl)phosphane (10)



A flame-dried, nitrogen-purged Schlenk flask was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (600 mg, 2.39 mmol) and 20 mL of Et_2O . It was placed in an *i*-PrOH bath at -78°C and *n*-BuLi (1.5 mL, 2.4 mmol) was added dropwise. The mixture was stirred for one hour keeping the temperature constant. Next, ClPCy_2 (0.60 mL, 2.70 mmol) was added and the temperature was kept at -78°C for one hour. After that, the reaction mixture was allowed to reach room temperature and subsequently was hydrolysed with two drops of water and taken to dryness. A colourless solid was obtained. The title product was purified by chromatography column under air using *n*-hexane; *n*-hexane/DCM (5:1); DCM as eluent. The product was recrystallized from a *n*-hexane/EtOH mixture at -30°C to obtain a colourless crystalline solid (633 mg, 72.0 % yield).

HRMS (EI) Calculated for $\text{C}_{24}\text{H}_{30}\text{FP}$ $[\text{M}+\text{H}]^+$: 369.2142. Experimental $[\text{M}+\text{H}]^+$: 369.2145.

Elemental analysis. $\text{C}_{24}\text{H}_{30}\text{FP}$. Calculated %: C, 78.23; H, 8.21. Experimental %: C, 77.97; H, 8.29.

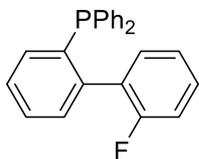
¹H NMR (499.72 MHz, CDCl₃) δ 7.63 – 7.59 (m, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 7.29 – 7.24 (m, 1H), 7.22 – 7.13 (m, 2H), 7.11 – 7.06 (m, 1H), 1.82 (s, 2H), 1.77 – 1.52 (m, 10H), 1.33 – 0.95 (m, 10H).

¹⁹F NMR (470.16 MHz, CDCl₃) δ -112.89 – -113.03 (m, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -10.5 (d, *J* = 31.5 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, CDCl₃) δ 159.3 (d, *J* = 244.7 Hz, 1C), 144.2 (d, *J* = 31.3 Hz, 1C), 135.4 (d, *J* = 20.7 Hz, 1C), 132.7 (d, *J* = 3.5 Hz, 1C), 132.5 (t, *J* = 3.3 Hz, 1C), 130.6 (dd, *J* = 16.2, 7.2 Hz, 1C), 130.4 (d, *J* = 5.8 Hz, 1C), 129.0 (d, *J* = 8.0 Hz, 1C), 128.4 (s, 1C), 127.1 (s, 1C), 123.1 (d, *J* = 3.7 Hz, 1C), 115.1 (d, *J* = 22.4 Hz, 1C), 34.4 (br d, *J* = 81.2 Hz, 2C), 30.3 (br s, 2C), 29.0 (d, *J* = 8.6 Hz, 2C), 27.3 (d, *J* = 12.2 Hz, 2C), 27.2 (d, *J* = 7.7 Hz, 2C), 26.4 (s, 2C).

(2'-fluoro-[1,1'-biphenyl]-2-yl)diphenylphosphane (12)



A flame-dried, nitrogen-purged Schlenk flask was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (700 mg, 2.78 mmol) and 20 mL of Et₂O. It was placed in an *i*-PrOH bath at -78 °C and *n*-BuLi (1.75 mL, 2.8 mmol) was added dropwise. The mixture was stirred for one hour keeping the

temperature constant. Next, ClPPh₂ (0.57 mL, 3.10 mmol) was added and the temperature was kept at -78 °C for one hour. After that, the reaction mixture was allowed to reach room temperature and subsequently it was hydrolysed with a saturated NH₄Cl solution under air. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 x 30 mL). The combined organic extracts were dried over magnesium sulphate, filtered, and taken to dryness. A colourless oil was obtained. The title product was purified by chromatography column under air using *n*-hexane; *n*-hexane/DCM (5:1); as eluent. The product was recrystallized from a *n*-hexane/EtOH mixture at -30 °C to obtain a colourless crystalline solid (740 mg, 74.7 % yield).

HRMS (EI) Calculated for C₂₄H₁₉FP [M+H]⁺: 357.1208. Experimental [M+H]⁺: 357.1203.

Elemental analysis. C₂₄H₁₈FP. Calculated %: C, 80.89; H, 5.89. Experimental %: C, 81.03; H, 6.01.

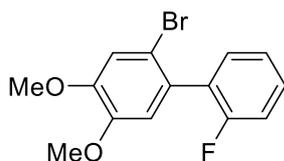
¹H NMR (499.72 MHz, CDCl₃) δ 7.41 (td, *J* = 7.7, 1.4 Hz, 1H), 7.34 – 7.26 (m, 9H), 7.25 – 7.18 (m, 4H), 7.12 – 7.05 (m, 2H), 7.05 – 6.94 (m, 2H).

¹⁹F NMR (470.16 MHz, CDCl₃) δ -113.29 – -113.91 (m, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -12.11 (d, *J* = 24.4 Hz, 1P).

¹³C{¹H} NMR (125.67 MHz, CDCl₃) δ 159.39 (d, *J* = 245.7 Hz, 1C), 141.63 (d, *J* = 30.1 Hz, 1C), 137.36 (d, *J* = 13.4 Hz, 1C), 137.05 (d, *J* = 11.5 Hz, 1C), 133.81 (d, *J* = 20.0 Hz, 2C), 133.77 (s, 1C), 132.03 (t, *J* = 3.6 Hz, 2C), 130.47 (d, *J* = 5.1 Hz, 1C), 129.37 (d, *J* = 7.9 Hz, 1C), 129.22 – 128.88 (m, 1C), 128.56 (d, *J* = 18.0 Hz, 4C), 128.29 (d, *J* = 6.9 Hz, 4C), 128.06 (s, 2C), 123.21 (d, *J* = 3.7 Hz, 1C), 115.32 (d, *J* = 22.4 Hz, 1C).

2-bromo-2'-fluoro-4,5-dimethoxy-1,1'-biphenyl (9-OMe)



A flame-dried, nitrogen-purged Schlenk flask was charged with 1,2-dibromoveratrole (2.30 g, 7.77 mmol), 2-fluorophenylboronic acid (1.15 g, 8.21 mmol), $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ (100 mg, 0.38 mmol) and dppf (223 mg, 0.40 mmol). N_2 spargled DME (8 mL) and water (2 mL) were then added and the mixture was stirred for 5 min at room temperature. Finally, K_2CO_3 (2.69 g, 19.4 mmol) was added and the Schlenk was placed in an oil bath at 80 °C. The mixture was stirred for 5 hours keeping the temperature constant. The reaction mixture was allowed to cool to rt, DME was evaporated, and water (10 mL) and EtOAc (20 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic layers were dried over magnesium sulphate, filtered, and evaporated in vacuo to obtain a yellow oil, which was purified by chromatography column using toluene/*n*-hexane (3:1 to 5:1) as eluent. The product was obtained as a colourless solid (915 mg, 37.8 % yield). Unreacted 1,2-dibromoveratrole and diarylated product 2,2''-difluoro-4',5'-dimethoxy-1,1':2',1''-terphenyl were also recovered.

HRMS (EI) Calculated for $\text{C}_{14}\text{H}_{12}\text{BrFO}_2$ $[\text{M}+\text{Na}]^+$: 332.9902. Experimental $[\text{M}+\text{Na}]^+$: 332.9904.

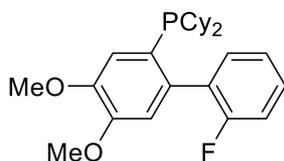
Elemental analysis. $\text{C}_{14}\text{H}_{12}\text{BrFO}_2$. Calculated %: C, 54.04; H, 3.89. Experimental %: C, 54.00; H, 3.91.

^1H NMR (499.72 MHz, CDCl_3) δ 7.40 – 7.33 (m, 1H), 7.30 (td, $J = 7.5, 1.8$ Hz, 1H), 7.20 (td, $J = 7.5, 1.2$ Hz, 1H), 7.17 – 7.10 (m, 2H), 6.82 (s, 1H), 3.91 (s, 3H), 3.86 (s, 3H).

^{19}F NMR (470.16 MHz, CDCl_3) δ -114.06 – -114.22 (m, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, CDCl_3) δ 159.56 (d, $J = 247.0$ Hz, 1C), 149.27 (s, 1C), 148.16 (s, 1C), 131.80 (d, $J = 2.9$ Hz, 1C), 129.66 (d, $J = 8.0$ Hz, 1C), 128.88 (s, 1C), 128.64 (d, $J = 16.0$ Hz, 1C), 123.77 (d, $J = 3.5$ Hz, 1C), 115.68 (d, $J = 22.0$ Hz, 1C), 115.48 (s, 1C), 114.08 (s, 1C), 113.81 (s, 1C), 56.21 (d, $J = 1.6$ Hz, 1C), 56.10 (d, $J = 1.9$ Hz, 1C).

Dicyclohexyl(2'-fluoro-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)phosphane (14)



A flame-dried, nitrogen-purged Schlenk flask was charged with 2-bromo-2'-fluoro-4,5-dimethoxy-1,1'-biphenyl (602 mg, 1.93 mmol) and 20 mL of Et_2O . It was placed in an *i*-PrOH bath at -78 °C and *n*-BuLi (1.2 mL, 1.92 mmol) was added dropwise. The mixture was stirred for one hour keeping the temperature constant. Next, ClPCy_2 (0.50 mL, 2.19 mmol) was added and the temperature was kept at -78 °C for one hour, then the temperature was raised to -50 °C and stirred for one night. After that, the reaction mixture was allowed to reach room temperature and subsequently it was hydrolysed with a saturated NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 30 mL). The combined organic extracts were dried over magnesium sulphate, filtered, and taken to dryness. A yellowish oil was obtained. The title product was purified by chromatography column under air using toluene as eluent.

The product was recrystallized from a Et₂O/EtOH mixture at -30 °C to obtain a colourless crystalline solid (419 mg, 50.7 % yield).

HRMS (EI) Calculated for C₂₆H₃₄FNao₂P [M+Na]⁺: 451.2178. Experimental [M+Na]⁺: 451.2182.

Elemental analysis. C₂₆H₃₄FO₂P. Calculated %: C, 72.87; H, 8.00. Experimental %: C, 72.94; H, 8.09.

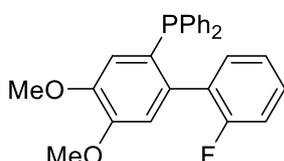
¹H NMR (499.72 MHz, CDCl₃) δ 7.35 – 7.29 (m, 1H), 7.19 (td, *J* = 7.4, 2.0 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.11 – 7.05 (m, 2H), 6.77 (d, *J* = 3.2 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 1.83 – 1.55 (m, 11H), 1.32 – 0.99 (m, 11H).

¹⁹F NMR (470.16 MHz, CDCl₃) δ -112.86 – -113.30 (m, 1F).

³¹P{¹H} NMR (202.30 MHz, CDCl₃) δ -10.55 (d, *J* = 28.3 Hz, 1P).

¹³C{¹H} NMR (100.63 MHz, CDCl₃) δ 159.52 (d, *J* = 244.7 Hz, 1C), 149.21 (s, 1C), 147.89 (s, 1C), 137.61 (d, *J* = 32.9 Hz, 1C), 132.81 (t, *J* = 3.4 Hz, 1C), 130.39 (dd, *J* = 16.2, 7.1 Hz, 1C), 128.89 (d, *J* = 7.9 Hz, 1C), 126.38 (d, *J* = 20.4 Hz, 1C), 123.07 (d, *J* = 3.7 Hz, 1C), 115.47 – 114.57 (m, 2C), 113.23 (d, *J* = 6.9 Hz, 1C), 56.20 (s, 1C), 55.72 (s, 1C), 34.84 (d, *J* = 13.4 Hz, 2C), 30.41 (d, *J* = 17.5 Hz, 2C), 29.06 (d, *J* = 8.2 Hz, 2C), 27.26 (d, *J* = 9.6 Hz, 4C), 26.42 (s, 2C).

(2'-fluoro-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)diphenylphosphane (16)



A flame-dried, nitrogen-purged Schlenk flask was charged with 2-bromo-2'-fluoro-4,5-dimethoxy-1,1'-biphenyl (612.5 mg, 1.97 mmol) and 20 mL of Et₂O. It was placed in an *i*-PrOH bath at -78 °C and *n*-BuLi (1.3 mL, 2.08 mmol) was added dropwise. The mixture was stirred for one hour keeping the temperature constant. Next, ClPPh₂ (0.40 mL, 2.17 mmol) was added and the temperature was kept at -78 °C for one hour, then the temperature was raised to -50 °C and stirred for one night. After that, the reaction mixture was allowed to reach room temperature and subsequently it was hydrolysed with a saturated NH₄Cl solution. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 x 30 mL). The combined organic extracts were dried over magnesium sulphate, filtered, and taken to dryness. A yellowish oil was obtained. The title product was purified by chromatography column under air using toluene as eluent. The product was recrystallized from a Et₂O/EtOH mixture at -30 °C to obtain a colourless crystalline solid (552 mg, 67.3 % yield).

HRMS (EI) Calculated for C₂₆H₂₂FNao₂P [M+Na]⁺: 439.1234. Experimental [M+Na]⁺: 439.1230.

Elemental analysis. C₂₆H₃₄FO₂P. Calculated %: C, 74.99; H, 5.33. Experimental %: C, 75.12; H, 5.29.

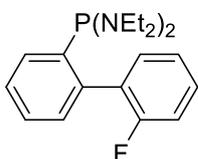
¹H NMR (499.72 MHz, CDCl₃) δ 7.32 – 7.27 (m, 7H), 7.26 – 7.21 (m, 4H), 7.15 – 7.09 (m, 1H), 7.08 – 7.01 (m, 2H), 6.85 (d, *J* = 3.8 Hz, 1H), 6.59 (d, *J* = 3.3 Hz, 1H), 3.89 (s, 3H), 3.59 (s, 3H).

^{19}F NMR (470.16 MHz, CDCl_3) δ -113.45 – -113.68 (m, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.30 MHz, CDCl_3) δ -12.71 (d, J = 23.0 Hz, 1P).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, CDCl_3) δ 159.61 (d, J = 245.4 Hz, 1C), 149.44 (s, 1C), 148.58 (s, 1C), 137.94 (d, J = 12.3 Hz, 1C), 135.27 (d, J = 32.9 Hz, 1C), 133.44 (d, J = 19.4 Hz, 4C), 132.33 (t, J = 3.6 Hz, 1C), 129.29 (d, J = 8.0 Hz, 1C), 129.16 – 128.80 (m, 2C), 128.46 – 128.00 (m, 6C), 127.89 (d, J = 12.7 Hz, 1C), 123.23 (d, J = 3.7 Hz, 1C), 116.66 (s, 1C), 115.37 (d, J = 22.5 Hz, 1C), 113.50 (d, J = 6.6 Hz, 1C), 55.89 (s, 1C), 55.65 (s, 1C).

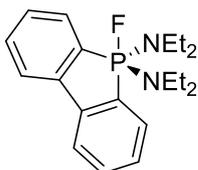
N,N,N',N'-tetraethyl-1-(2'-fluoro-[1,1'-biphenyl]-2-yl)phosphanediamine, N,N,N',N'-tetraethyl-5-fluoro-5H-5 λ^5 -benzo[b]phosphindole-5,5-diamine (18) and 5,5-bis(diethylamino)-5H-benzo[b]phosphindol-5-ium chloride (18-Cl)



Synthesis of the phosphine: A flame-dried, nitrogen-purged Schlenk flask was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (700 mg, 2.78 mmol) and 20 mL of Et_2O . It was placed in an *i*-PrOH bath at -78°C and *n*-BuLi (1.75 mL, 2.8 mmol) was added dropwise. The mixture was stirred for one hour keeping the temperature constant. Next, $\text{ClP}(\text{NEt}_2)_2$ (1.3 eq) was added and the temperature was kept at -78°C for one hour. After that, the reaction mixture was allowed to reach room temperature and the solvent was evaporated under vacuum. The solid obtained was extracted with *n*-hexane and filtered. The colourless solution obtained was taken to dryness to afford a crude yellowish oil which was used for the next step without further purification. The phosphine product was identified by ^{19}F and ^{31}P NMR, but the oil also contained unreacted $\text{ClP}(\text{NEt}_2)_2$, which had been used in excess.

^{19}F NMR (470.16 MHz, *n*-hexane(acetone-d_6)) δ -115.10 – -115.28 (m, 1F).

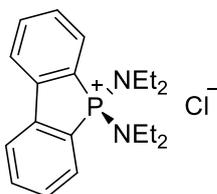
$^{31}\text{P}\{^1\text{H}\}$ NMR (202.30 MHz, *n*-hexane(acetone-d_6)) δ 95.1 (d, J = 22.9 Hz, 1P).



Synthesis of 18 and 18-Cl: the previously obtained oil was dissolved in 5 mL of diglyme and heated in a Schlenk flask at 130°C overnight. A white precipitated was formed in the first 2 hours, the solution turned purple overnight (16 h). The fluorophosphorane (18) was detected in the solution (30 % yield based on NMR) in a mixture of many decomposition byproducts, which prevented its isolation.

^{19}F NMR (376.48 MHz, diglyme(acetone-d_6)) δ -31.15 (d, J = 689.7 Hz, 1F).

$^{31}\text{P}\{^1\text{H}\}$ NMR (161.98 MHz, diglyme(acetone-d_6)) δ -47.9 (d, J = 690.6 Hz, 1P).

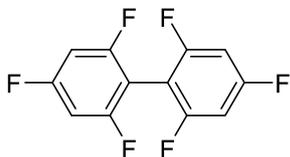


The white solid obtained was filtered and washed with Et_2O (3 x 5 mL), then dried under vacuum. It was identified as a phosphonium chloride (18-Cl). (252.0 mg, 25% yield from starting biaryl), the chloride proceeding from the $\text{ClP}(\text{NEt}_2)_2$ contaminant. Addition of AgClO_4 to an acetone solution of 18-Cl leads to precipitation of AgCl and formation of 18- ClO_4 (not isolated).

$^1\text{H NMR}$ (400.14 MHz, CDCl_3) δ 8.12 (t, $J = 8.7$ Hz, 2H), 8.08 – 8.00 (m, 2H), 7.82 (t, $J = 7.7$ Hz, 2H), 7.71 – 7.59 (m, 2H), 3.37 (dq, $J = 13.9, 7.1$ Hz, 8H), 1.11 (t, $J = 7.1$ Hz, 12H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.30 MHz, CDCl_3) δ 52.7 (s, 1P).

2,4,6,2',4',6'-hexafluorobiphenyl



A flame-dried, nitrogen-purged Schlenk flask was charged with 1-bromo-2,4,6-trifluorobenzene (0.27 mL, 2.3 mmol) and 5 mL of Et_2O . It was placed in an *i*-PrOH bath at -78 °C and *n*-BuLi (1.5 mL, 2.4 mmol) was added dropwise. Reaction was stirred for 1 hour at this temperature and CuCl_2 (162 mg, 1.2 mmol) was added. The reaction was allowed to reach room temperature and it was stirred opened to air for 2 hours. It was hydrolysed with a 2 M HCl solution. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 5 mL). The combined organic extracts were taken to dryness. The title compound was obtained as colourless needles upon recrystallization from hot *n*-hexane (251 mg, 80 % yield).

Elemental analysis. $\text{C}_{12}\text{H}_4\text{F}_6$. Calculated %: C, 54.98; H, 1.54. Experimental %: C, 55.03; H, 1.37.

$^1\text{H NMR}$ (499.72 MHz, CDCl_3). 6.84 – 6.75 (m, 4H).

$^{19}\text{F NMR}$ (470.16 MHz, CDCl_3). δ -105.95 – -106.17 (m, 2F), -107.32 – -107.48 (m, 4F).

The spectroscopic data are in accordance with previously reported data.¹⁷

Photophysical properties

Many dibenzophospholes and their tetrahedral P(V) derivatives (frequently phosphine-oxide derivatives) display interesting optoelectronic behaviour centred in their conjugated organic π -systems. Amongst them, several luminescent systems with fluorinated aryls have been studied. The presence of F substituents stabilizes the LUMO orbitals and moves the electronic transitions to higher wavenumbers in spite of their short conjugation length.¹⁸ However, probably due to the scarcity of stable derivatives as the fluorophosphoranes reported here, five-coordinated P(V) derivatives with bpt geometry have not been studied.

All the fluorophosphoranes display fluorescence in THF solution with photoluminescence quantum yields in the range 37.5–6.4, and also in the solid state (12,8–4.5) (Figure ESI1).

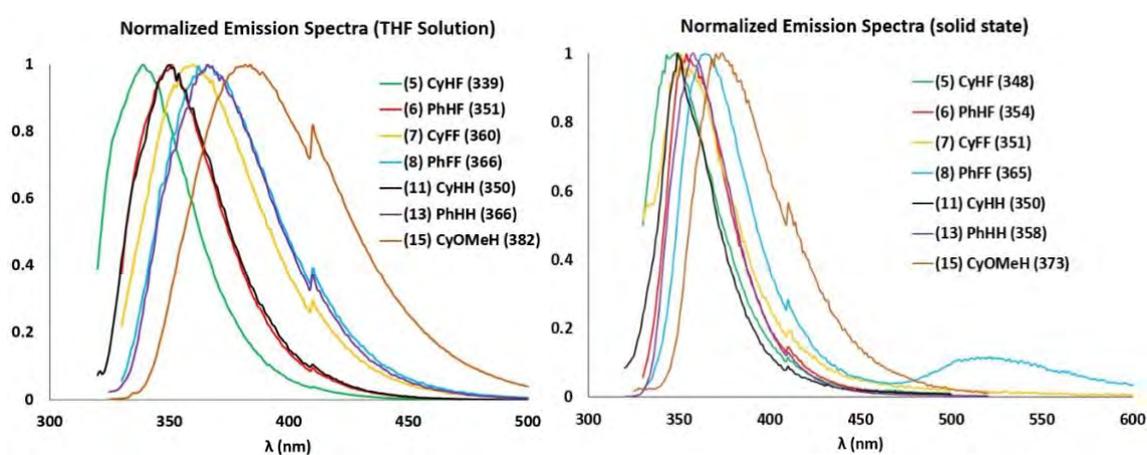


Figure ESI1. Normalized emission spectra in THF solution (left) and in the solid state (right). Maxima emission wavelength in parenthesis.

Evaluation of the photophysical properties of fluorophosphoranes in THF solution ($5 \cdot 10^{-5}$ M) was carried out, and representative data are summarized in Table ESI1. The fluorinated ones (**5–8**) show a maximum absorption peak at 315 nm, and emission bands covering the range 320–450 nm (Figure ESI1, left). The maxima of the emission bands are in the range 339–382 nm, in the blue-UV region for all the compounds (Table ESI1, column 6), and the short average lifetimes support fluorescence processes. The values for compound **8** can be directly compared with those found for the identical phosphine oxide (solution: $\lambda_{\text{abs}} = 325$ nm; $\log \epsilon = 3.6$; $\lambda_{\text{em}} = 365$ nm; $\phi = 18\%$; solid: $\lambda_{\text{em}} = 378$ nm).¹⁹ While the λ_{em} value is almost identical for both compounds, the quantum yield ϕ is only about one third for the bipyramidal fluorophosphorane. For **5–8**, **11** and **13** increasing the donor character of the R substituents at P atom, from Ph to Cy, shifts the maximum to blue (**5** vs **6**, **7** vs **8**). This blue-shift effect is also observed when reducing the fluorine substitution degree at the phosphole core (**5** vs **7**, **6** vs **8**). In addition, a marked increase in the quantum yield is observed (Table ESI1, column 6). The electron rich **15** shows the highest quantum yield (37.5 %) and a maxima emission at 382 nm (blue emission).

Table ESI1. Excitation and emission data in 5·10⁻⁵ M THF solution.

Comp	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon^{\text{a}}/\text{M}^{-1}\text{cm}^{-1}$	$\log \epsilon$	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\phi/\%$	$\tau_{\text{av}}^{\text{b}}/\text{ns}$	$\tau_{\text{n}}^{\text{c}}/\text{ns}; A_{\text{n}}^{\text{d}}$
5	304, 315	1749	3.24	315	339	25.5	3.54	$\tau_1 = 3.54$
6	293, 315	1158	3.06	315	351	30.5	4.40	$\tau_1 = 4.40$
7	315	4305	3.63	315	360	17.6	2.58	$\tau_1 = 2.58$
8	315	3448	3.53	315	366	6.4	3.38	$\tau_1 = 1.03; A_1 = 0.88$ $\tau_2 = 6.23; A_2 = 0.12$
11	294, 321	4853	3.37	294	350	6.7	4.97	$\tau_1 = 1.88, A_1 = 0.87$ $\tau_2 = 9.19, A_2 = 0.13$
13	277, 290	4842	3.69	277	366	13.5	4.56	$\tau_1 = 3.94; A_1 = 0.76$ $\tau_2 = 22.63; A_2 = 0.24$
15	255, 306	7248	3.86	306	382	37.5	7.82	$\tau_1 = 5.70; A_1 = 0.73$ $\tau_2 = 34.95; A_2 = 0.27$
18	289,340	2616	3.42	289	388	0.02	6.01	$\tau_1 = 0.91; A_1 = 0.11$ $\tau_2 = 6.86; A_2 = 0.89$

^a at λ_{exc} . ^b Average lifetime: $\tau_{\text{av}} = (A_1\tau_1^2 + A_2\tau_2^2 + \dots) / (A_1\tau_1 + A_2\tau_2 + \dots)$. ^c Natural lifetime. ^d Intensity coefficients.

All the quantum yields diminish in the solid state (Table ESI2, column 4). Compound **7** is the one less affected, whereas compound **8** shows a new emission maximum at 504 nm (Figure ESI1, right), which might be due to an aggregation induced emission (AIE) phenomenon, possibly due to restriction of intramolecular aryl rotation in the solid state.

Table ESI2. Excitation and emission data in solid state.

Comp	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\phi/\%$	$\tau_{\text{av}}^{\text{a}}/\text{ns}$	$\tau_{\text{n}}^{\text{b}}/\text{ns}; A_{\text{n}}^{\text{c}}$
5	315	348	6.8	5.88	$\tau_1 = 2.69; A_1 = 0.73$ $\tau_2 = 8.58; A_2 = 0.27$
6	315	354	5.6	9.66	$\tau_1 = 3.29; A_1 = 0.94$ $\tau_2 = 23.59; A_2 = 0.06$
7	315	350	12.8	6.80	$\tau_1 = 0.47; A_1 = 0.74$ $\tau_2 = 7.87; A_2 = 0.26$
8	315	365, 504	6.5, 4.5	6.03	$\tau_1 = 0.50; A_1 = 0.79$ $\tau_2 = 2.49; A_2 = 0.14$ $\tau_3 = 10.63; A_3 = 0.07$
11	294	350	5.8	4.03	$\tau_1 = 0.44; A_1 = 0.56$ $\tau_2 = 4.48; A_2 = 0.44$
13	277	358	8.7	3.33	$\tau_1 = 3.77; A_1 = 0.92$ $\tau_2 = 39.85; A_2 = 0.08$
15	306	373	10.3	4.74	$\tau_1 = 5.01; A_1 = 0.81$ $\tau_2 = 27.74; A_2 = 0.19$

^a Average lifetime: $\tau_{\text{av}} = (A_1\tau_1^2 + A_2\tau_2^2 + \dots) / (A_1\tau_1 + A_2\tau_2 + \dots)$. ^b Natural lifetime. ^c Intensity coefficients.

Determination of kinetic constant and activation barrier

Dicyclohexyl(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-2-yl)phosphine (**1**) (10.90 mg, 24.7 μmol) and 2,4,6,2',4',6'-hexafluorobiphenyl (1.91 mg, 7.28 μmol), used as internal standard, were added to a flame-dried NMR tube and set under N_2 atmosphere. A coaxial tube containing $\text{DMSO-}d_6$ was put into the NMR tube. The NMR tube was placed in a $-20\text{ }^\circ\text{C}$ *i*-PrOH bath and 500 μL of toluene were added. The NMR tube was shaken vigorously inside the bath until complete solution of the solids. Once the solution is homogenized, the NMR tube was set into the NMR spectrometer probe, which was already set to the measurement temperature ($60\text{ }^\circ\text{C}$). The initial zero time in Table S1 corresponds to the moment when the tube is taken out of the cooling bath and placed in the probe. ^{19}F NMR spectra were acquired every two minutes to follow the evolution.

In these conditions, concentrations were determined through integration of ^{19}F NMR signals of species versus internal standard. The species concentrations, [Species], were obtained with the following equation:

$$[\text{Species}] = \frac{I_{\text{Species}}}{I_{\text{I.S.}}} \frac{n_{\text{F}}^{\text{I.S.}}}{n_{\text{F}}^{\text{Species}}} \frac{[\text{I.S.}]}{I.R.^{\text{Species}}}$$

where I_{Species} is the ^{19}F NMR integral for a selected fluorine signal, at -132.3 ppm for the fluorophosphorane (**5**) and at -139.3 ppm for the phosphine (**1**); $I_{\text{I.S.}}$ is the ^{19}F NMR integral for 2,4,6,2',4',6'-hexafluorobiphenyl *para* fluorine signal, at -106.4 ppm ; $n_{\text{F}}^{\text{Species}}$ is the number of integrated fluorine atoms for the species: 1 for the fluorophosphorane and 2 for the phosphine; $n_{\text{F}}^{\text{I.S.}}$ is the number of integrated fluorine atoms for internal standard, 2; [I.S.] is the concentration of internal standard; and I.R.^{Species} is the integral relation factor between the species and internal standard in the measurement conditions.

To obtain the kinetic rate constant, the kinetic model was fitted to the measured concentration vs. time experimental data by nonlinear least-squares (NLLS) regression, using the software COPASI.²⁰ Table ESI4 collects the experimental concentration values.

From the rate constant (k), the free activation energy (ΔG^\ddagger) was obtained via Eyring-Polanyi equation, where R is the ideal gases constant, T is the measurement temperature in kelvin degrees, k is the experimental rate constant, h is the Planck constant and k_B is the Boltzmann constant. Table ESI3 shows the experimental kinetic values obtained.

$$k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

$$\text{Then: } \Delta G^\ddagger = -RT \ln \frac{kh}{k_B T}$$

Table ESI3. Experimental kinetic rate and activation energy values for the S_NAr reaction.

[1] ₀ (M)	T (K)	k · 10 ⁴ (s ⁻¹)	ΔG [‡] _{333K} (kcal·mol ⁻¹)
0.050	333	1.367	25.5

Table ESI4. Concentration and time data for the S_NAr reaction kinetic study.

Time (s)	[5] (M)	[1] (M)	Time (s)	[5] (M)	[1] (M)
105	0.00014068	0.05136845	5505	0.02653517	0.02349420
225	0.00119180	0.05028676	5625	0.02695277	0.02313983
345	0.00199565	0.04940140	5745	0.02724647	0.02266154
465	0.00285470	0.04841607	5865	0.02785248	0.02220650
585	0.00351328	0.04772683	5985	0.02812661	0.02182314
705	0.00430593	0.04688463	6105	0.02847452	0.02133981
825	0.00504567	0.04600684	6225	0.02862174	0.02098569
945	0.00584979	0.04519062	6345	0.02895623	0.02065755
1065	0.00662967	0.04448041	6465	0.02943424	0.02030768
1185	0.00739047	0.04367266	6585	0.02974663	0.01990228
1305	0.00795917	0.04304342	6705	0.03014336	0.01968146
1425	0.00877574	0.04227787	6825	0.03038166	0.01943722
1545	0.00934637	0.04164698	6945	0.03070508	0.01892385
1665	0.01012055	0.04092458	7065	0.03114831	0.01875206
1785	0.01080822	0.04021375	7185	0.03137387	0.01840406
1905	0.01152135	0.03958713	7305	0.03144333	0.01804154
2025	0.01205201	0.03895512	7425	0.03186550	0.01771472
2145	0.01259616	0.03827406	7545	0.03212416	0.01737184
2265	0.01331173	0.03765380	7665	0.03242073	0.01717885
2385	0.01388585	0.03703204	7785	0.03264655	0.01698484
2505	0.01438152	0.03637587	7905	0.03298988	0.01656533
2625	0.01503310	0.03571825	8025	0.03326969	0.01628559
2745	0.01569647	0.03507391	8145	0.03353208	0.01601039
2865	0.01627767	0.03452241	8265	0.03357491	0.01577427
2985	0.01673067	0.03402051	8385	0.03406766	0.01543846
3105	0.01736840	0.03342250	8505	0.03405764	0.01508152
3225	0.01783945	0.03282471	8625	0.03433921	0.01494300
3345	0.01819511	0.03209138	8745	0.03465143	0.01470411
3465	0.01896464	0.03162421	8865	0.03483027	0.01437451
3585	0.01939923	0.03116370	8985	0.03504717	0.01424473
3705	0.01997181	0.03059344	9105	0.03525570	0.01394009
3825	0.02045989	0.03007389	9225	0.03561285	0.01367358
3945	0.02104059	0.02955283	9345	0.03561198	0.01341318
4065	0.02146972	0.02904828	9465	0.03589349	0.01317977
4185	0.02191988	0.02857468	9585	0.03617590	0.01311261
4305	0.02244524	0.02808362	9705	0.03611744	0.01272603
4425	0.02280011	0.02763354	9825	0.03631635	0.01253817
4545	0.02325734	0.02700490	9945	0.03687339	0.01233082

4665	0.02366895	0.02652499	10065	0.03699000	0.01219491
4785	0.02406600	0.02608765	10185	0.03688254	0.01186901
4905	0.02455846	0.02569934	10305	0.03725241	0.01171697
5025	0.02492110	0.02511811	10425	0.03732469	0.01159650
5145	0.02545390	0.02471289	10545	0.03753215	0.01139683
5265	0.02575947	0.02441664	10665	0.03783265	0.01111342
5385	0.02623195	0.02390374	10785	0.03775275	0.01089370

Computational General Section

Density Functional Theory (DFT) calculations reported in this work were carried out using the dispersion corrected hybrid functional ω B97X-D developed by Head-Gordon and Chai,²¹ implemented in the Gaussian16 program.²² The choice of this level of theory is based on the satisfactory results obtained in previous theoretical studies on S_NAr processes.²³ C, H, F and P atoms were described using the double- ζ 6-31+G(d,p) basis set.

Geometry optimizations were performed in toluene (SMD solvation model, $\epsilon = 2.3741$)²⁴ without imposing any constraint, and the nature of all the stationary points was further verified through vibrational frequency analysis.

Table ES15 collects all the energy data that support the discussion made in the text about the thermodynamics of the reaction. The Cartesian coordinates of all the computed structures are collected below.

Table ES15. DFT energy data.

Species	G (hartrees)	G (kcal mol ⁻¹)	relative G (kcal mol ⁻¹)
1	-1770.02608	-1110707.99	0.0
TS1	-1769.98381	-1110681.46	26.5
I1	-1770.01990	-1110704.11	3.9
I2	-1770.03391	-1110712.90	-4.9
5	-1770.06120	-1110730.02	-22.0

Cartesian coordinates of all the calculated species

1 (Phosphine)

15	-0.91645900	-0.16251700	-0.33358200	6	-5.08395900	-1.55172500	-1.97345100
6	-0.75164200	1.64835100	0.13731300	1	-5.22116700	0.48210200	-2.71780800
6	-0.51401400	2.54035500	-1.09254700	1	-5.38383100	0.33529200	-0.96975900
6	-1.85133300	2.21977700	1.04128700	1	-4.61928400	-3.39472700	-0.92612700
1	0.18066000	1.66157800	0.71967700	1	-5.01457900	-2.04014900	0.12890000
6	-0.20133700	3.98079200	-0.67308700	1	-6.15889200	-1.75202700	-2.04904500
1	-1.40272400	2.53839300	-1.73719500	1	-4.62679500	-1.91244100	-2.90548000
1	0.30861800	2.13371300	-1.69252800	6	-0.47956400	-0.90145400	1.31133300
6	-1.53084500	3.66182200	1.45222300	6	0.87937000	-1.14781600	1.58753500
1	-2.81282200	2.20768800	0.51076400	6	-1.41023900	-1.20212800	2.31277200
1	-1.96928600	1.59480000	1.93404600	6	1.27760100	-1.66414500	2.82199500
6	-1.29824800	4.55297300	0.22904300	6	1.92657000	-0.84539900	0.56641400
1	-0.07254000	4.60881300	-1.56214100	6	-1.01461400	-1.72674100	3.54094600
1	0.75535800	3.99614200	-0.13193900	1	-2.46702000	-1.02552300	2.14063500
1	-2.34475100	4.06358600	2.06702200	6	0.33310900	-1.95783600	3.80031000
1	-0.62808200	3.66391800	2.07878800	1	2.33271200	-1.84029200	3.01046100
1	-1.03692000	5.56939500	0.54498500	6	2.69260700	0.31465400	0.62956900
1	-2.23326100	4.62974500	-0.34440700	1	-1.76232700	-1.94959000	4.29624400
6	-2.74604500	-0.49024200	-0.46578000	1	0.64899400	-2.36442400	4.75582300

6	-3.34299200	0.26586200	-1.66654600	6	3.10962400	-1.41003400	-1.48361900
6	-2.99146600	-2.00207600	-0.62554500	6	3.63809400	0.63265200	-0.33630300
1	-3.26381900	-0.13970100	0.43785400	6	3.84602000	-0.23548400	-1.39832800
6	-4.83312600	-0.04815000	-1.84054400	9	2.51302200	1.18020500	1.63625000
1	-2.79965000	-0.01716600	-2.57927700	9	4.34487200	1.76164600	-0.24945500
1	-3.21371500	1.34594500	-1.54474200	9	4.75278200	0.05347300	-2.33001800
6	-4.48140100	-2.31572200	-0.79230800	9	3.31150200	-2.24655300	-2.50317000
1	-2.44471000	-2.35762800	-1.51026600	6	2.16904500	-1.70005200	-0.50651200
1	-2.58863300	-2.55367900	0.23046400	9	1.47094200	-2.83270500	-0.62452400

TS1

15	0.73879800	0.09993700	-0.02571700	6	5.03514700	-0.18074000	-1.88640600
6	0.21133400	-1.12690200	1.25110600	1	4.92385900	-2.26541400	-1.29104600
6	-0.01998500	-2.53698400	0.67919400	1	5.08732000	-1.13408700	0.04901200
6	1.12213000	-1.16111700	2.48758500	1	4.80370000	1.96218000	-2.14134500
1	-0.76878800	-0.73238500	1.55986700	1	5.00489300	1.44887500	-0.46809700
6	-0.59321000	-3.46109300	1.75857800	1	6.12698700	-0.16914900	-1.97688200
1	0.92470700	-2.95566400	0.31282000	1	4.63440100	-0.39296600	-2.88706800
1	-0.70079000	-2.49576000	-0.17622400	6	0.34232000	1.71558200	0.72265200
6	0.55091300	-2.10016200	3.55586300	6	-0.94086600	2.18615600	0.37167600
1	2.12059600	-1.51415500	2.19519400	6	1.15709800	2.46095900	1.56698700
1	1.24118300	-0.15323600	2.90098600	6	-1.37949500	3.41296700	0.86327000
6	0.30650800	-3.50412000	2.99637200	6	-1.72520000	1.25116300	-0.46798300
1	-0.72524300	-4.46756500	1.34698900	6	0.71053200	3.69093300	2.05629300
1	-1.59124900	-3.10190300	2.04523900	1	2.14454100	2.10016200	1.84230600
1	1.23455500	-2.14334400	4.41110500	6	-0.55100900	4.16010700	1.70270700
1	-0.39651700	-1.68587900	3.92651400	1	-2.35782100	3.79009100	0.58616800
1	-0.13963700	-4.14372400	3.76587400	6	-3.02582900	0.86075300	-0.16962700
1	1.27042700	-3.95845400	2.72634300	1	1.35128200	4.28045700	2.70445200
6	2.57328900	0.07679300	-0.25892600	1	-0.89586400	5.11935200	2.07649200
6	3.07881700	-1.29955800	-0.72075100	6	-1.58872400	-0.67042200	-1.95146900
6	3.00467400	1.18030300	-1.24170200	6	-3.62816100	-0.24950200	-0.73733100
1	3.00889600	0.29344300	0.72884100	6	-2.87735000	-1.02425100	-1.62088000
6	4.59801500	-1.28619000	-0.92344200	9	-3.73720000	1.56020000	0.73425500
1	2.58156400	-1.57054000	-1.66197700	9	-4.90731500	-0.57165100	-0.46603200
1	2.81917500	-2.06867900	0.01286000	9	-3.42837000	-2.11215600	-2.17132200
6	4.52530900	1.18495400	-1.42134500	9	-0.86190000	-1.47286700	-2.75903000
1	2.52470500	1.00264600	-2.21161600	6	-0.94645100	0.44900900	-1.36790700
1	2.66198600	2.16023200	-0.89435200	9	-0.13295600	1.16587000	-2.28940200

I1

15	-0.71046900	0.40533000	0.05420700	6	-1.38535300	-2.50125500	3.63942500
6	-1.95008200	0.60671800	-1.28580400	1	-2.66964200	-3.57036100	2.25720200
6	-2.01019100	-0.56116600	-2.28500300	1	-3.30482500	-2.00467000	2.76674100
6	-3.33656700	0.92195200	-0.69154800	1	-0.16690200	-1.06873300	4.71662300
1	-1.58584900	1.49545200	-1.82058500	1	-1.77011400	-0.47124700	4.28542000

6	-3.03635400	-0.26220800	-3.38308800	1	-1.83455500	-2.93812300	4.53874500
1	-2.28527800	-1.48666300	-1.76760800	1	-0.51363800	-3.10973000	3.37224900
1	-1.02683400	-0.72349700	-2.73420500	6	-0.06910900	2.02339200	0.51451200
6	-4.34587500	1.20906100	-1.80741600	6	1.31644600	2.08356800	0.27940400
1	-3.68484500	0.06143100	-0.10672600	6	-0.76658600	3.09863200	1.04950200
1	-3.28205400	1.77817900	-0.00933700	6	2.00487100	3.25717500	0.58382000
6	-4.41722200	0.04996400	-2.80336400	6	1.86405800	0.82730800	-0.27741600
1	-3.09086400	-1.11847600	-4.06307900	6	-0.06886600	4.26850500	1.34833300
1	-2.68940900	0.59398300	-3.97790500	1	-1.83287400	3.03334600	1.24159700
1	-5.32945900	1.39562300	-1.36368700	6	1.30350200	4.34007700	1.11414800
1	-4.05314900	2.12761000	-2.33376700	1	3.07205000	3.33268700	0.41688900
1	-5.11942100	0.28872200	-3.60903500	6	3.18258900	0.53061900	-0.56333000
1	-4.80783500	-0.84191900	-2.29450900	1	-0.59468900	5.11962600	1.76814300
6	-1.35193600	-0.45806900	1.52651600	1	1.84127100	5.25235100	1.35217200
6	-1.79038600	-1.90120000	1.21965700	6	1.24043200	-1.41701200	-0.98968800
6	-0.32180800	-0.42034500	2.67109500	6	3.53398700	-0.72087100	-1.07075700
1	-2.23189400	0.14656300	1.80122300	6	2.57211100	-1.68748900	-1.29734100
6	-2.38475900	-2.53678100	2.48098200	9	4.16659200	1.42282400	-0.37103000
1	-0.89779000	-2.46443700	0.92011300	9	4.80899100	-0.98078500	-1.34854700
1	-2.52429300	-1.92367500	0.40639700	9	2.92181500	-2.86996000	-1.79131900
6	-0.92111400	-1.07065500	3.92257900	9	0.32409800	-2.33066700	-1.28590000
1	0.55522200	-0.99988300	2.34512100	6	0.88993800	-0.16867100	-0.51572200
1	-0.02374300	0.61098900	2.89098600	9	1.33384700	-2.53725800	1.23132200

12

15	0.57050200	0.14991400	-0.36110900	6	4.62945300	-1.45143300	-2.17430800
6	0.72313800	0.36854300	1.53425400	1	3.70271100	-3.40855900	-2.03549400
6	0.79747700	-0.95171400	2.32120000	1	4.09119200	-2.67895800	-0.48038800
6	1.87531500	1.30358600	1.94597300	1	5.22622500	0.62740500	-1.98076600
1	-0.21290200	0.86651500	1.82797200	1	5.02895500	-0.21853700	-0.44800500
6	0.82126200	-0.70422600	3.83458200	1	5.65469200	-1.83663800	-2.21206000
1	1.69949200	-1.51332900	2.04115500	1	4.30094800	-1.31305600	-3.21336200
1	-0.05553600	-1.59375900	2.08093800	6	-0.06013600	1.83322300	-0.65599900
6	1.88484100	1.54980700	3.45908100	6	-1.46951700	1.81604000	-0.59889400
1	2.84137200	0.86431200	1.66160400	6	0.62666100	3.01693400	-0.88367800
1	1.79533900	2.26320900	1.42433000	6	-2.17412900	3.01186500	-0.75308300
6	1.95948700	0.23494000	4.23713800	6	-2.05060300	0.46962300	-0.39285500
1	0.90964300	-1.66040400	4.36291300	6	-0.08875900	4.20371900	-1.04732500
1	-0.13723700	-0.26112800	4.13883400	1	1.70906000	3.02761200	-0.94901500
1	2.72841500	2.19816500	3.72278900	6	-1.47909100	4.19900600	-0.97586100
1	0.96962300	2.08841800	3.74113800	1	-3.25583800	3.02505200	-0.71012800
1	1.92900300	0.42823400	5.31540900	6	-3.39706300	0.13476300	-0.32216000
1	2.92243400	-0.25343900	4.02964100	1	0.44398300	5.13108800	-1.23324000
6	2.25987000	-0.58380100	-0.64416000	1	-2.03176100	5.12468500	-1.10141700
6	2.27251300	-1.92933800	-1.38627600	6	-1.51105300	-1.87796800	-0.13034200
6	3.17482000	0.44733000	-1.33354000	6	-3.80450700	-1.18612600	-0.16508900

1	2.66094300	-0.75735600	0.35890100	6	-2.86347500	-2.19873900	-0.07176600
6	3.70659800	-2.46021700	-1.48690300	9	-4.36163100	1.06346900	-0.40736500
1	1.85278700	-1.79345800	-2.38603200	9	-5.10405000	-1.48177600	-0.10664800
1	1.64313200	-2.65610400	-0.86513500	9	-3.25672300	-3.46468100	0.07333900
6	4.60082500	-0.10190800	-1.45383400	9	-0.62422500	-2.88129500	-0.03504500
1	2.77476600	0.67754400	-2.32657000	6	-1.10500500	-0.57287200	-0.28223700
1	3.19843600	1.38151200	-0.76039700	9	0.35541400	-0.06171200	-2.19433600

5 (Fluorophosphorane)

15	0.91783300	-0.17011400	0.58717600	6	1.61768000	4.52406600	0.85977100
6	1.63623600	-1.09663800	-0.87115700	1	3.56376500	4.02491400	0.03878900
6	3.16208300	-1.23478600	-0.95315800	1	3.29949500	3.45252700	1.68372700
6	0.97186400	-2.48764100	-0.94343000	1	-0.34131400	4.55698000	1.79390300
1	1.31026000	-0.52599700	-1.74659700	1	0.90275100	3.75367400	2.74940600
6	3.55388000	-1.94044300	-2.25731500	1	1.94049500	5.47822600	1.29123300
1	3.52765600	-1.81041900	-0.09832100	1	1.20263900	4.74793200	-0.13292900
1	3.64130800	-0.25340600	-0.90545000	6	-0.13235800	-1.06183300	1.80101800
6	1.37506500	-3.21330300	-2.23113900	6	-1.50686400	-1.07089800	1.50783600
1	1.28599900	-3.07822100	-0.07288700	6	0.33733500	-1.68494600	2.95555800
1	-0.11929000	-2.40478000	-0.89880000	6	-2.40142300	-1.70391200	2.37299400
6	2.89538100	-3.31734000	-2.36911700	6	-1.84426400	-0.37217100	0.25174500
1	4.64448600	-2.03632900	-2.30502900	6	-0.55921000	-2.31664000	3.81648500
1	3.25304400	-1.32159900	-3.11458700	1	1.39734000	-1.67585900	3.17335300
1	0.92037100	-4.21024700	-2.24602300	6	-1.92071800	-2.32398100	3.52432800
1	0.96751500	-2.66523300	-3.09213300	1	-3.46243000	-1.71690600	2.15813800
1	3.15696900	-3.78956700	-3.32287000	6	-0.72032900	0.17514000	-0.38421100
1	3.28551400	-3.96773700	-1.57389800	6	-3.10171900	-0.22686100	-0.32132700
6	1.29621400	1.59753400	1.04897800	1	-0.19119500	-2.80297700	4.71446100
6	2.40248300	2.20701000	0.17087600	1	-2.61803900	-2.81568300	4.19579000
6	0.08885200	2.53793700	1.15440000	6	-0.89944900	0.84941500	-1.57315800
1	1.70793600	1.47189200	2.05618200	6	-3.26024900	0.45520500	-1.52167900
6	2.81514400	3.58363300	0.70632600	6	-2.15346500	0.99852300	-2.15508400
1	2.04487200	2.30569200	-0.86143800	9	2.35600600	-0.61602200	1.53420100
1	3.27488500	1.54846100	0.15722800	9	-4.20983600	-0.73301300	0.24680700
6	0.52618100	3.89111300	1.72644900	9	-4.47200400	0.58910000	-2.06619800
1	-0.35238800	2.71040800	0.16701000	9	-2.30329500	1.66031600	-3.30571200
1	-0.69041600	2.09329700	1.78404300	9	0.14137100	1.41890500	-2.21974900

X-ray Crystallography Data

A crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector (Valladolid University facilities). The crystal was kept at constant temperature during data collection. Data collection was performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data integration, scaling and empirical absorption correction were carried out using the CrysAlisPro program package.²⁵ Using Olex2,²⁶ the structure was solved with the olex2.solve²⁷ structure solution program and

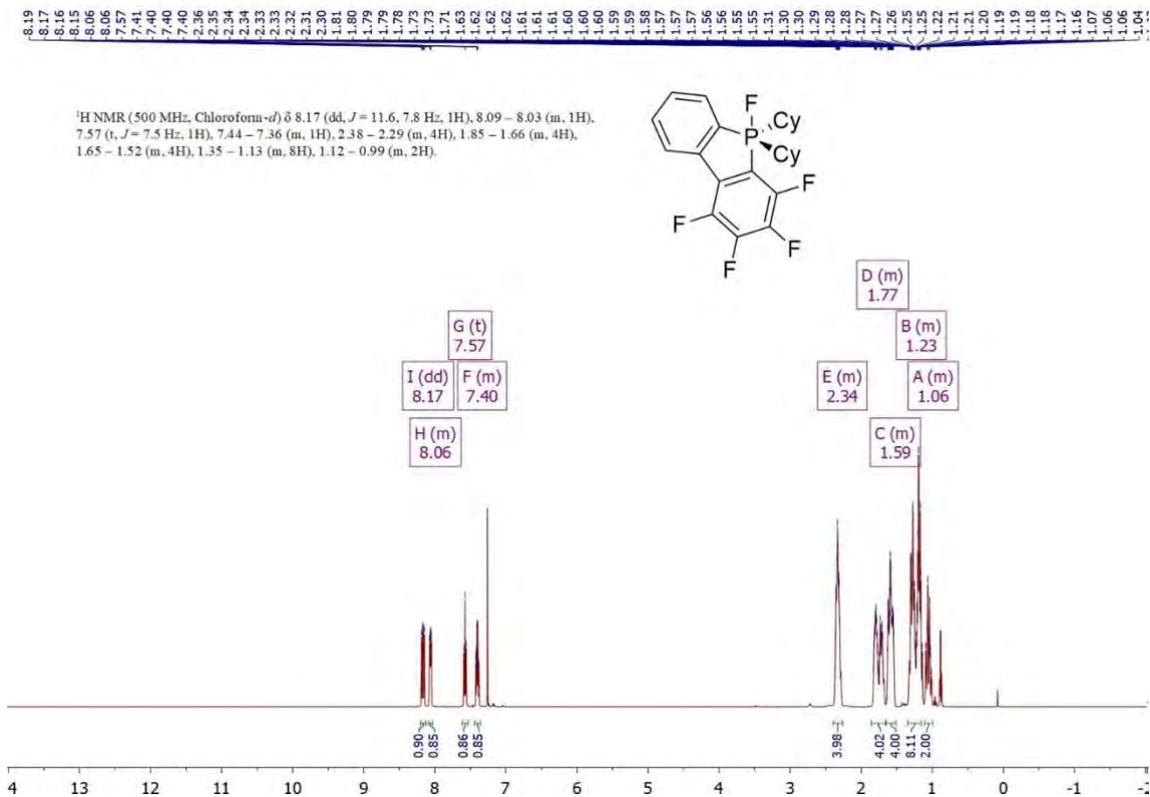
refined with ShelX program.²⁸ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Tables ESI6. CCDC contains the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table ESI6. Crystal data and structure refinements for complexes **6**, **7**, **11**.

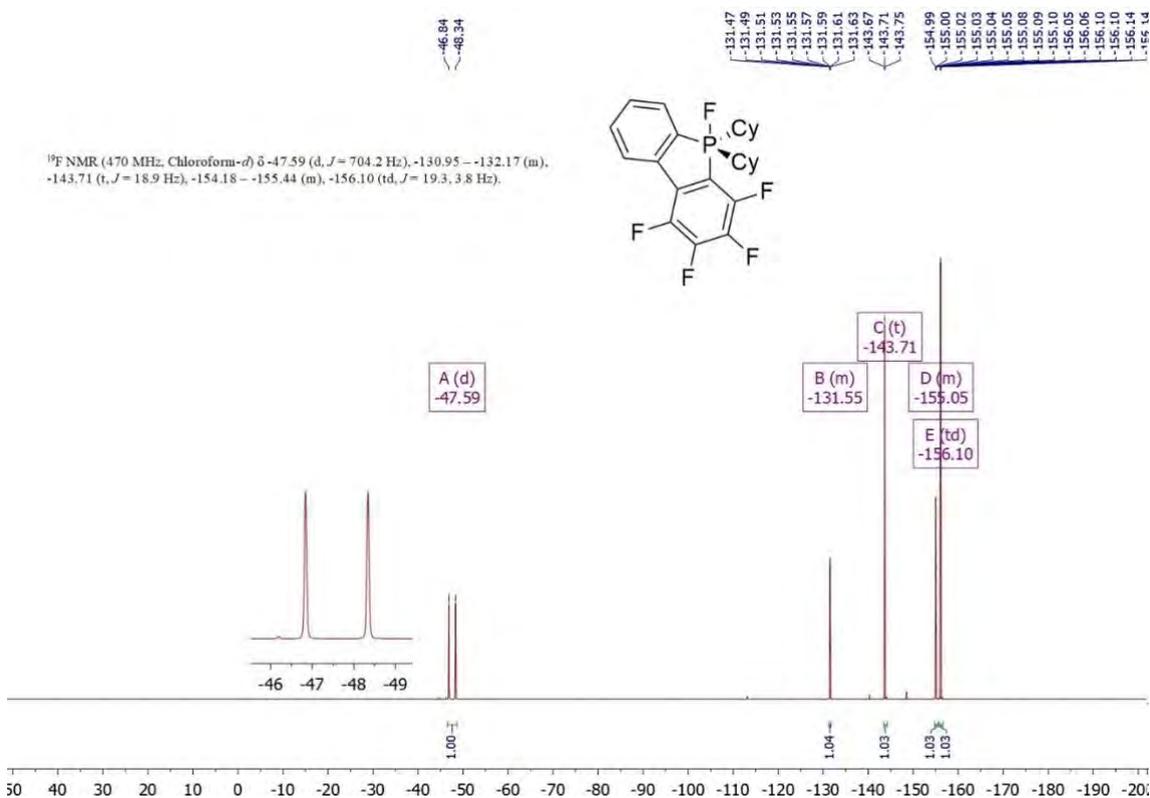
Identification code	6	7	11
CCDC deposition N°	2058334	2058335	2058336
Empirical formula	C ₂₄ H ₁₄ F ₅ P	C ₂₄ H ₂₂ F ₉ P	C ₂₄ H ₃₀ FP
Formula weight	428.32	512.38	368.45
Temperature/K	297.5(7)	219.9(4)	294
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	Pbca	P2 ₁ /n
a/Å	9.4654(5)	8.5949(5)	9.4899(4)
b/Å	11.0784(6)	17.1989(10)	11.6773(4)
c/Å	18.2148(10)	29.961(2)	18.4024(6)
α/°	90	90	90
β/°	90	90	102.701(4)
γ/°	90	90	90
Volume/Å ³	1910.03(18)	4428.9(5)	1989.39(13)
Z	4	8	4
ρ _{calc} /cm ³	1.489	1.537	1.23
μ/mm ⁻¹	0.199	0.21	0.152
F(000)	872	2096	792
Crystal size/mm ³	0.323 × 0.159 × 0.132	0.356 × 0.247 × 0.066	0.426 × 0.301 × 0.157
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	7.216 to 59.318	6.688 to 59.428	6.978 to 59.19
Index ranges	-9 ≤ h ≤ 12, -11 ≤ k ≤ 14, -25 ≤ l ≤ 25	-10 ≤ h ≤ 11, -22 ≤ k ≤ 23, -25 ≤ l ≤ 39	-12 ≤ h ≤ 13, -13 ≤ k ≤ 15, -18 ≤ l ≤ 25
Reflections collected	7141	12364	8723
Independent reflections	4039 [R _{int} = 0.0275, R _{sigma} = 0.0491]	5253 [R _{int} = 0.0410, R _{sigma} = 0.0588]	4641 [R _{int} = 0.0275, R _{sigma} = 0.0538]
Data/restraints/parameters	4039/0/271	5253/0/325	4641/0/235
Goodness-of-fit on F ²	1.058	1.041	1.046
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0442, wR ₂ = 0.0825	R ₁ = 0.0710, wR ₂ = 0.1862	R ₁ = 0.0561, wR ₂ = 0.1174
Final R indexes [all data]	R ₁ = 0.0703, wR ₂ = 0.0985	R ₁ = 0.1505, wR ₂ = 0.2309	R ₁ = 0.0993, wR ₂ = 0.1469
Largest diff. peak/hole / e Å ⁻³	0.24/-0.21	0.32/-0.35	0.31/-0.30

NMR Spectra

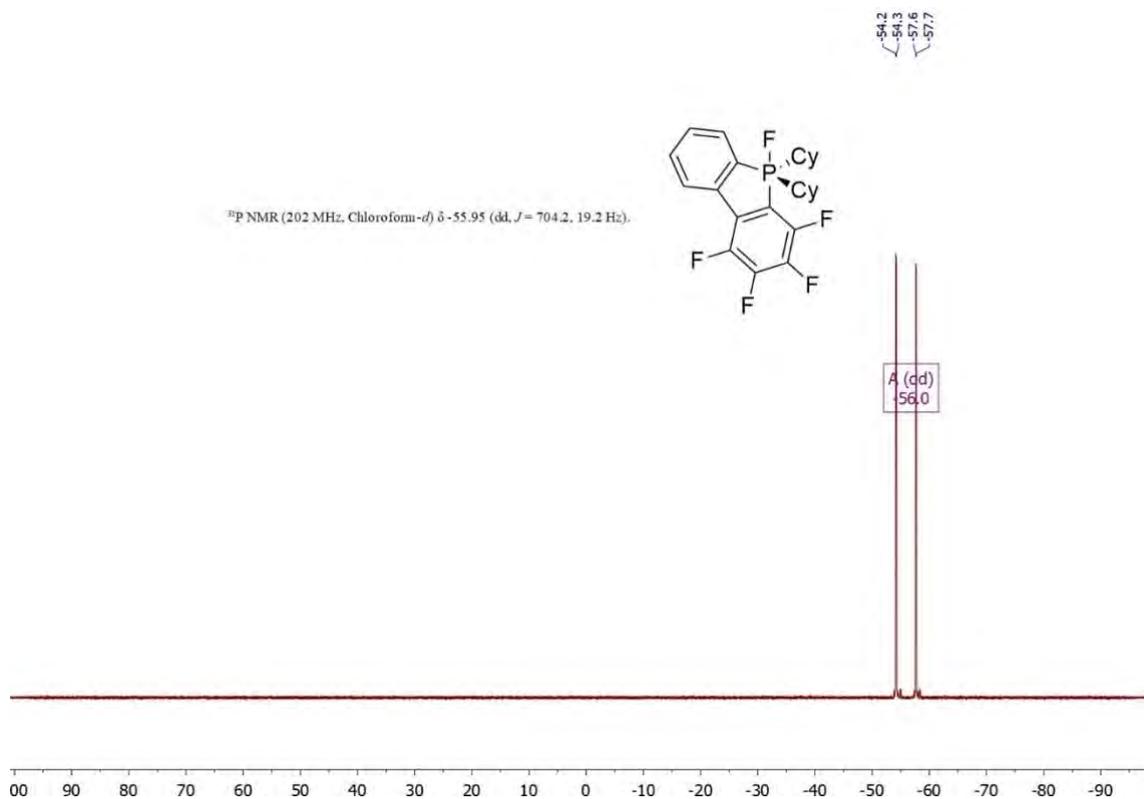
¹H NMR Spectra of FPCy₂C₆H₄C₆F₄ (**5**) in CDCl₃.



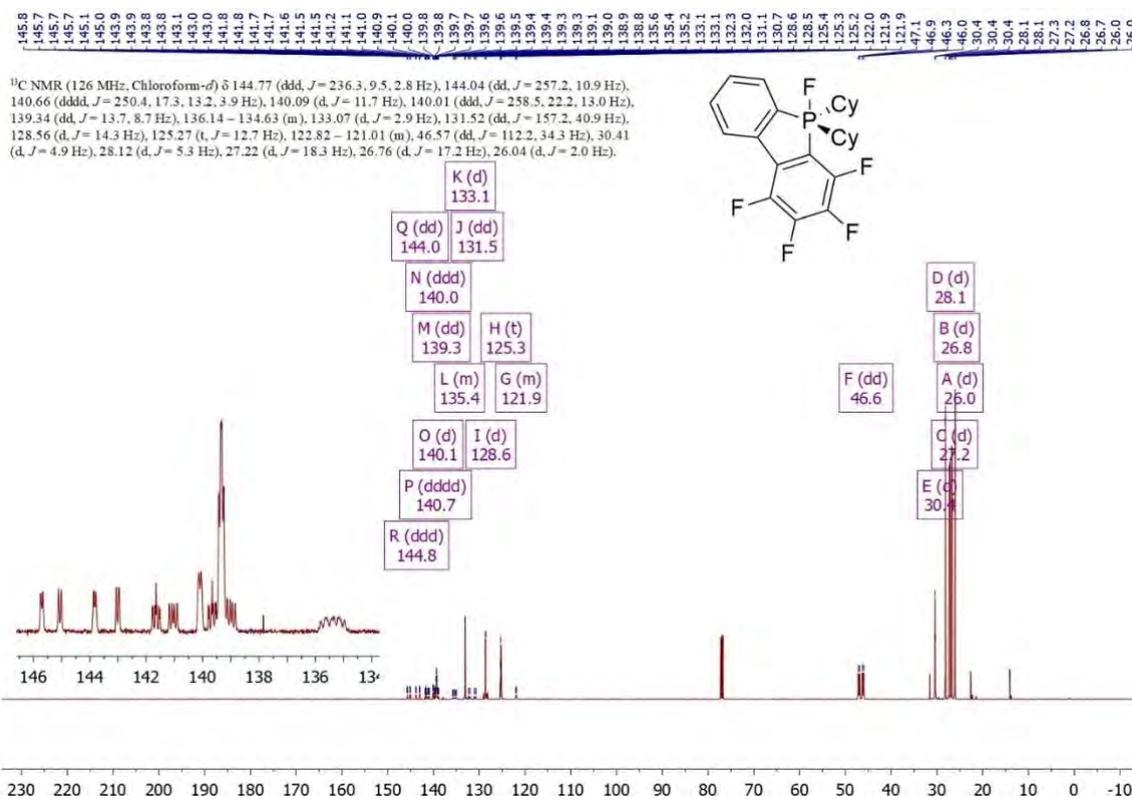
¹⁹F NMR Spectra of FPCy₂C₆H₄C₆F₄ (**5**) in CDCl₃.



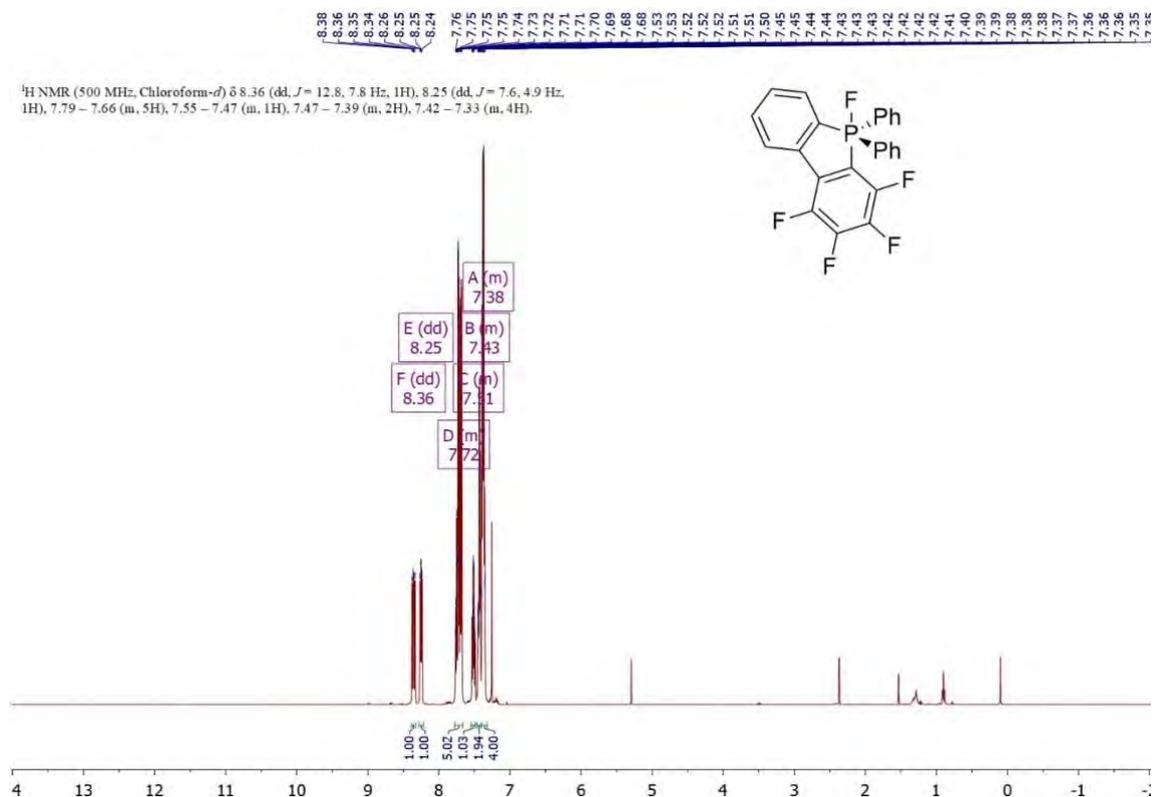
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**5**) in CDCl_3 .



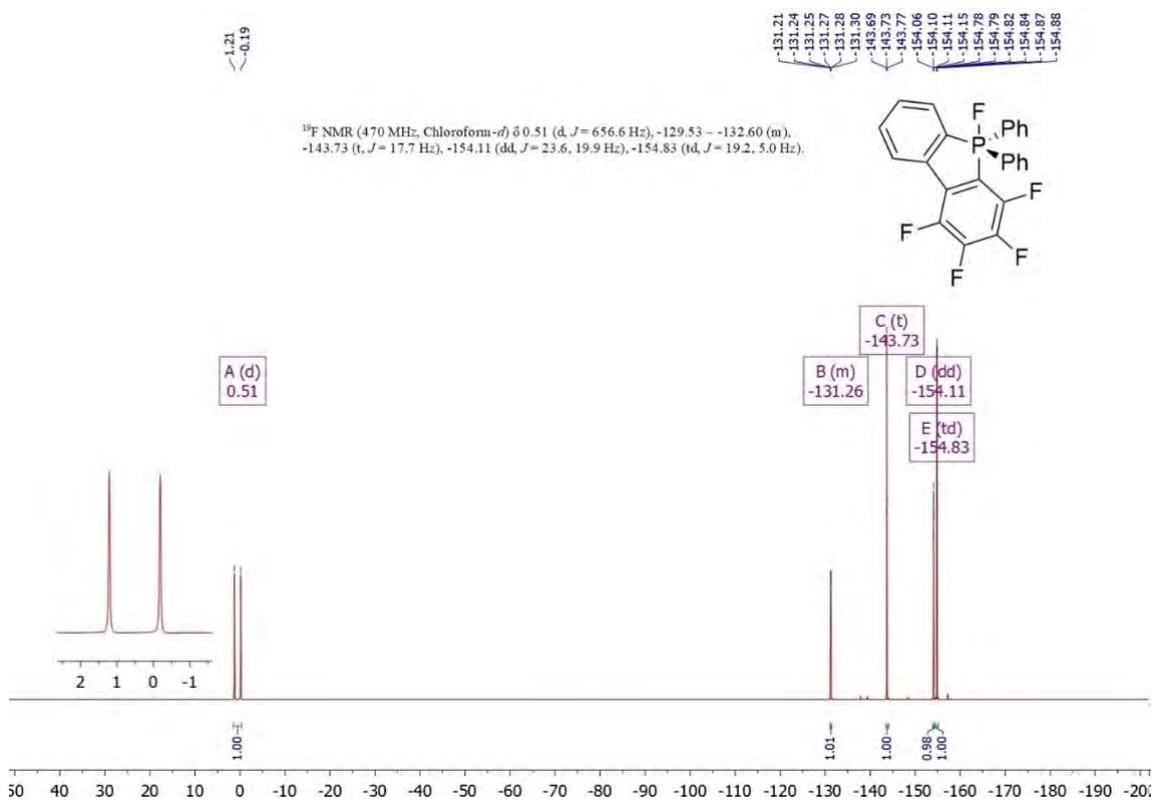
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**5**) in CDCl_3 .



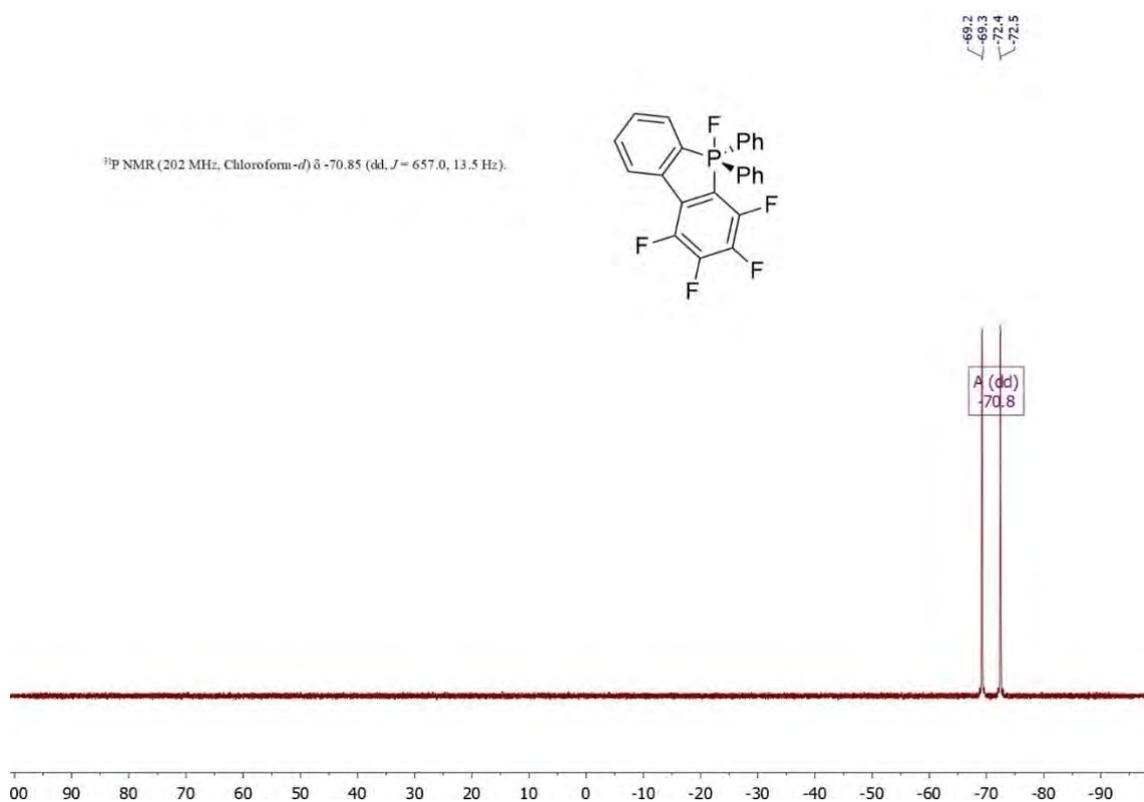
^1H NMR Spectra of $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**6**) in CDCl_3 .



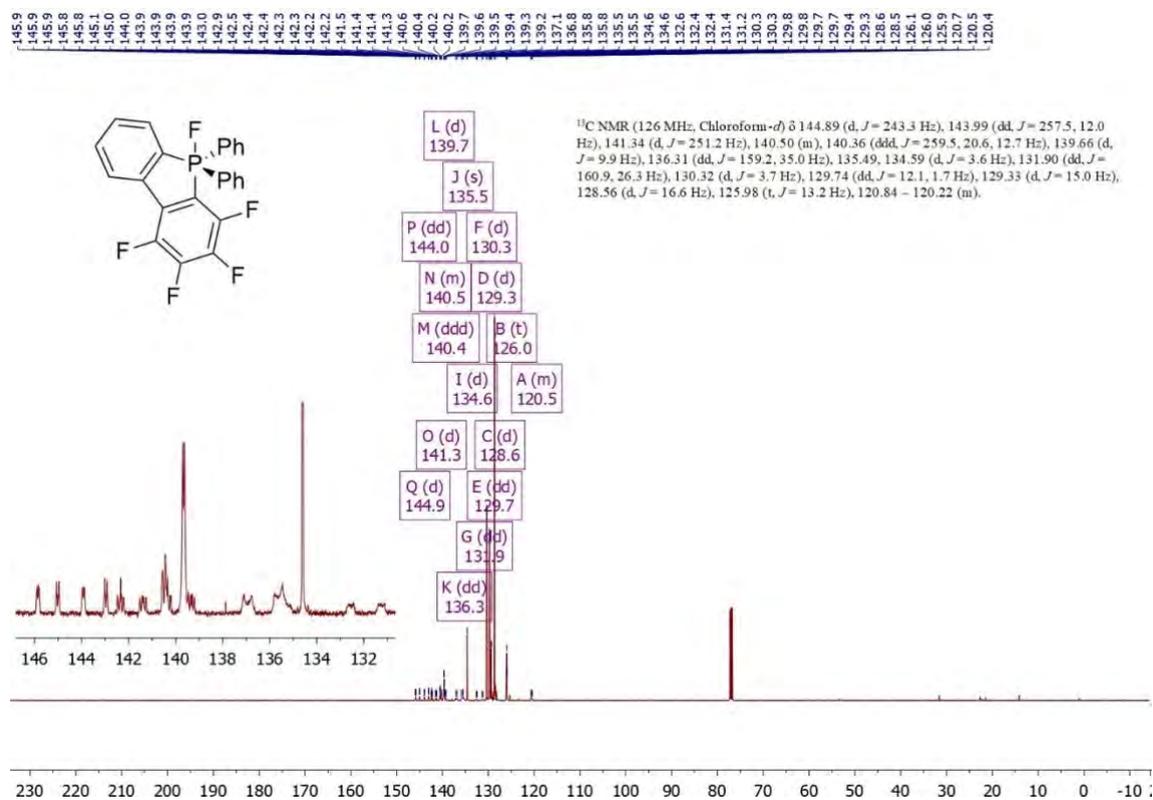
^{19}F NMR Spectra of $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**6**) in CDCl_3 .



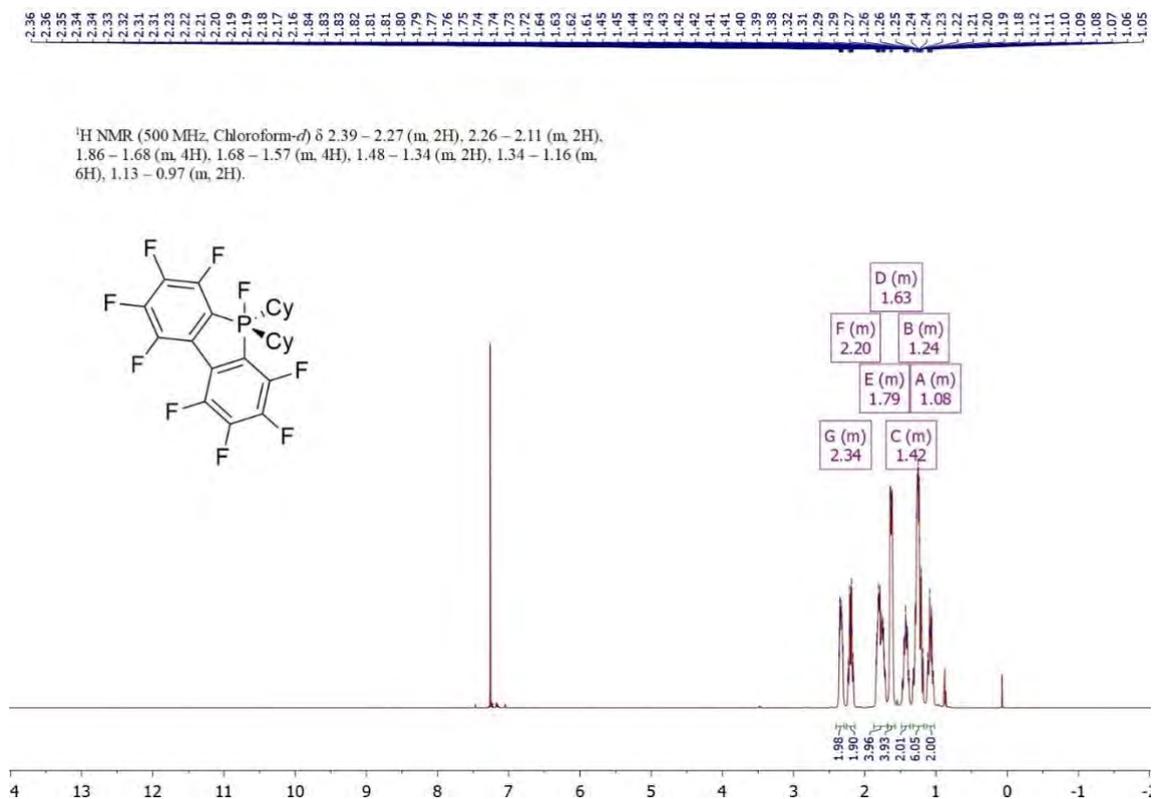
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPPh}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**6**) in CDCl_3 .



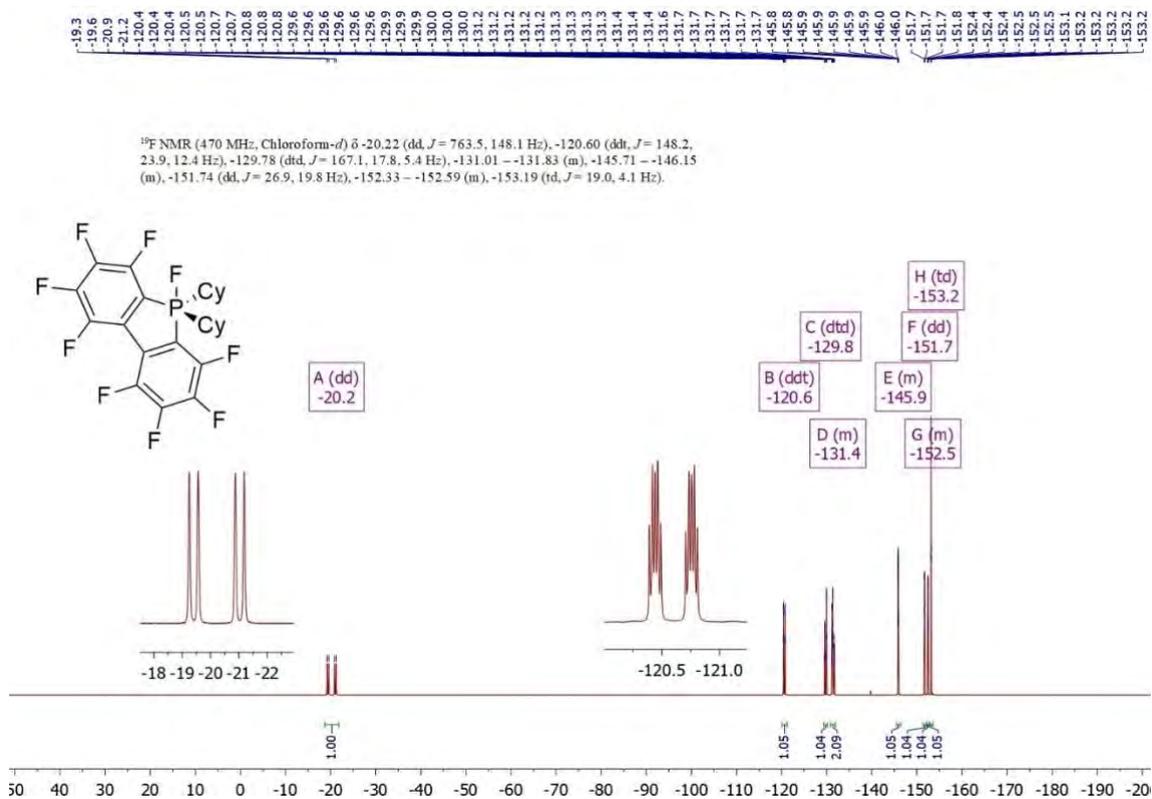
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{FPPh}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_4$ (**6**) in CDCl_3 .



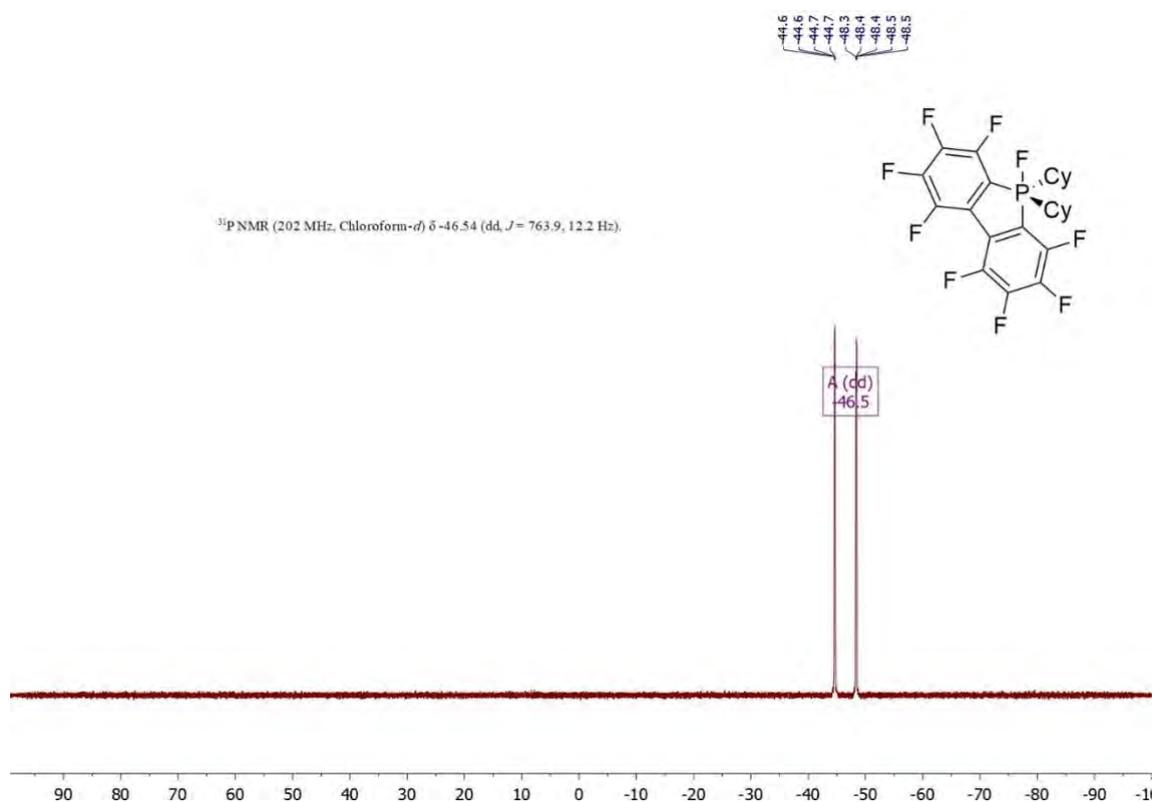
^1H NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 .



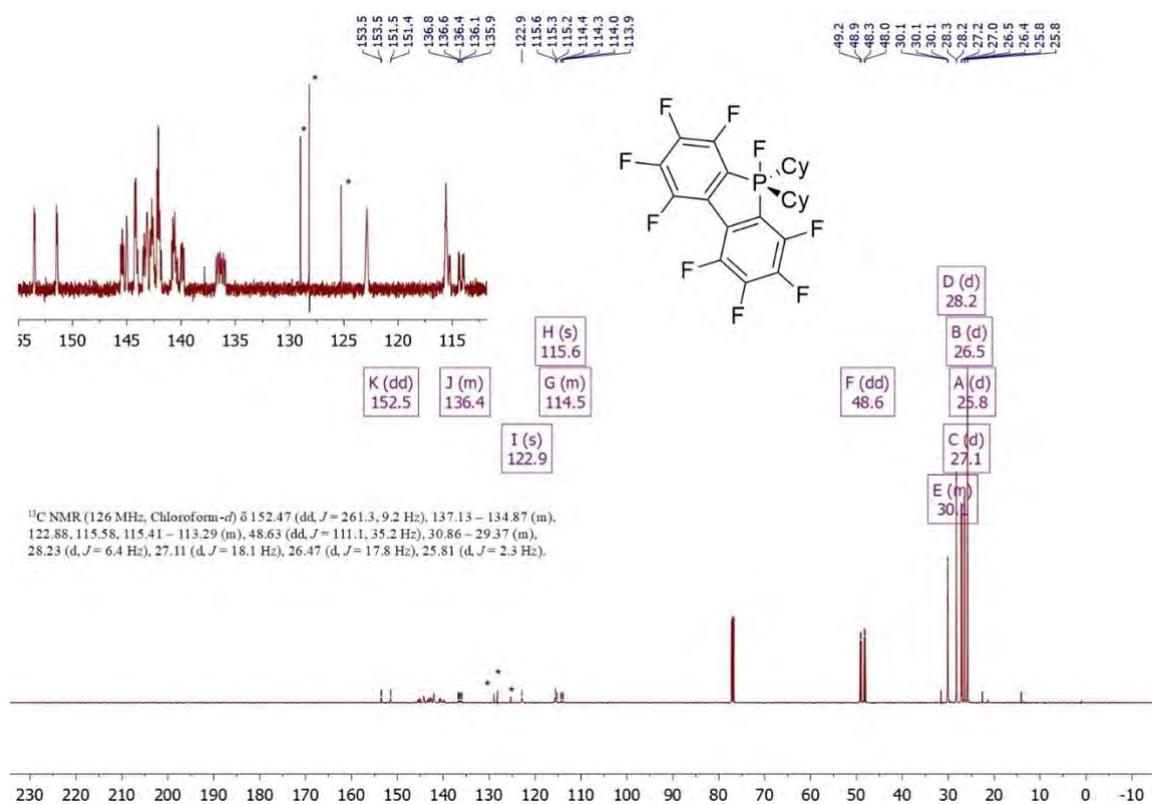
^{19}F NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 .



$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 .



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 . * Residual toluene signals.



^{13}C - ^{19}F HSQC NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 .

^{13}C NMR (126 MHz, cdcl_3) δ 152.47, 143.19, 144.07, 144.38, 140.93, 141.58, 141.72

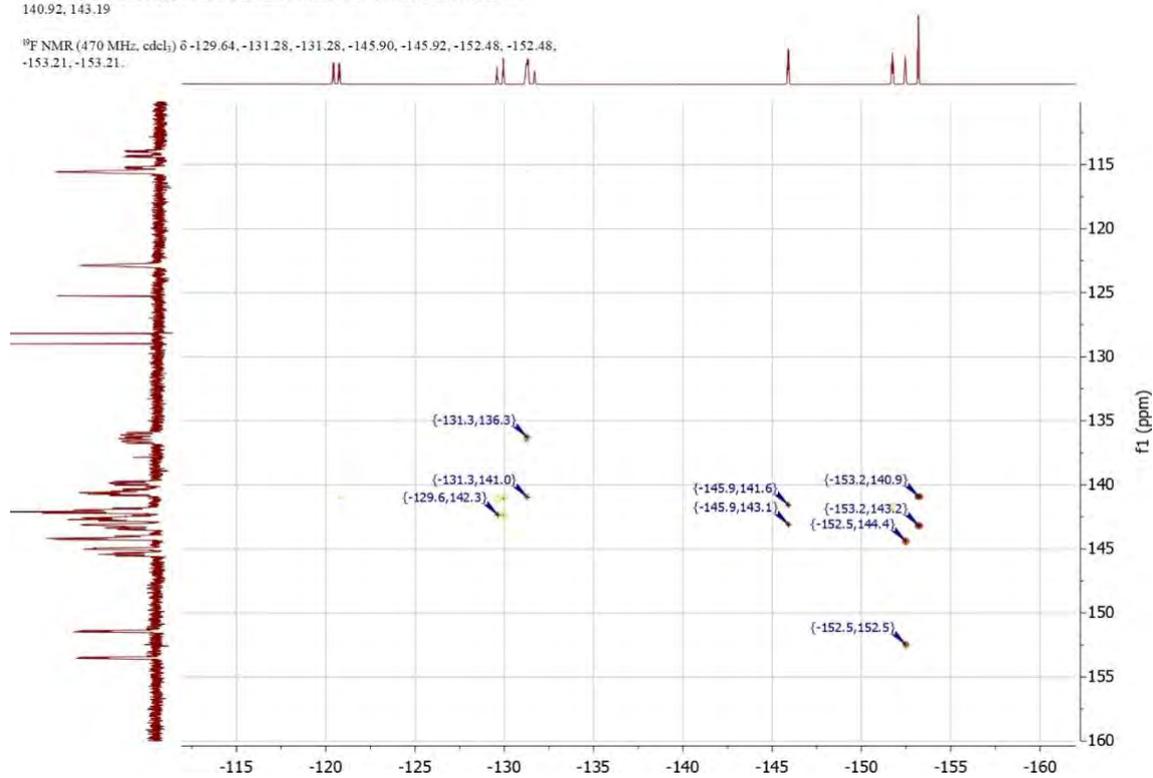
^{19}F NMR (470 MHz, cdcl_3) δ -120.52, -129.96, -131.40, -146.05, -151.91, -152.62, -153.14.



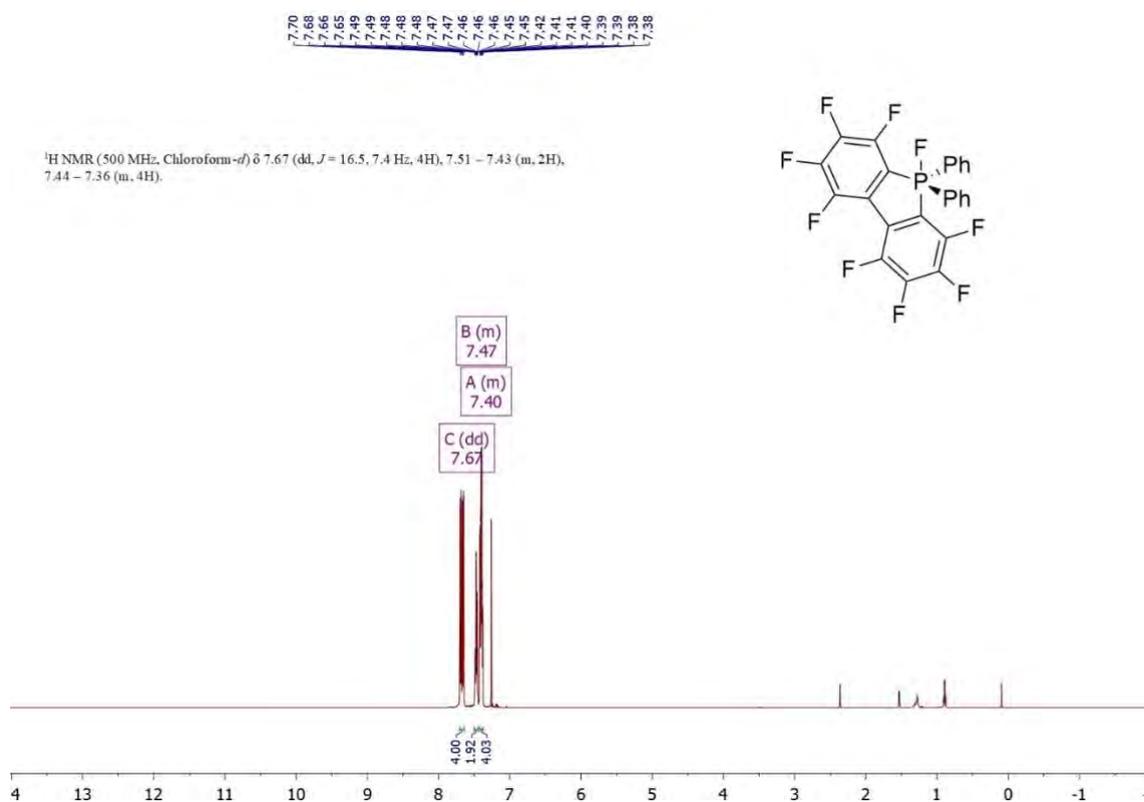
^{13}C - ^{19}F HMBC NMR Spectra of $\text{FPCy}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**7**) in CDCl_3 .

^{13}C NMR (126 MHz, cdcl_3) δ 142.34, 136.28, 140.96, 141.57, 143.10, 144.40, 152.48, 140.92, 143.19

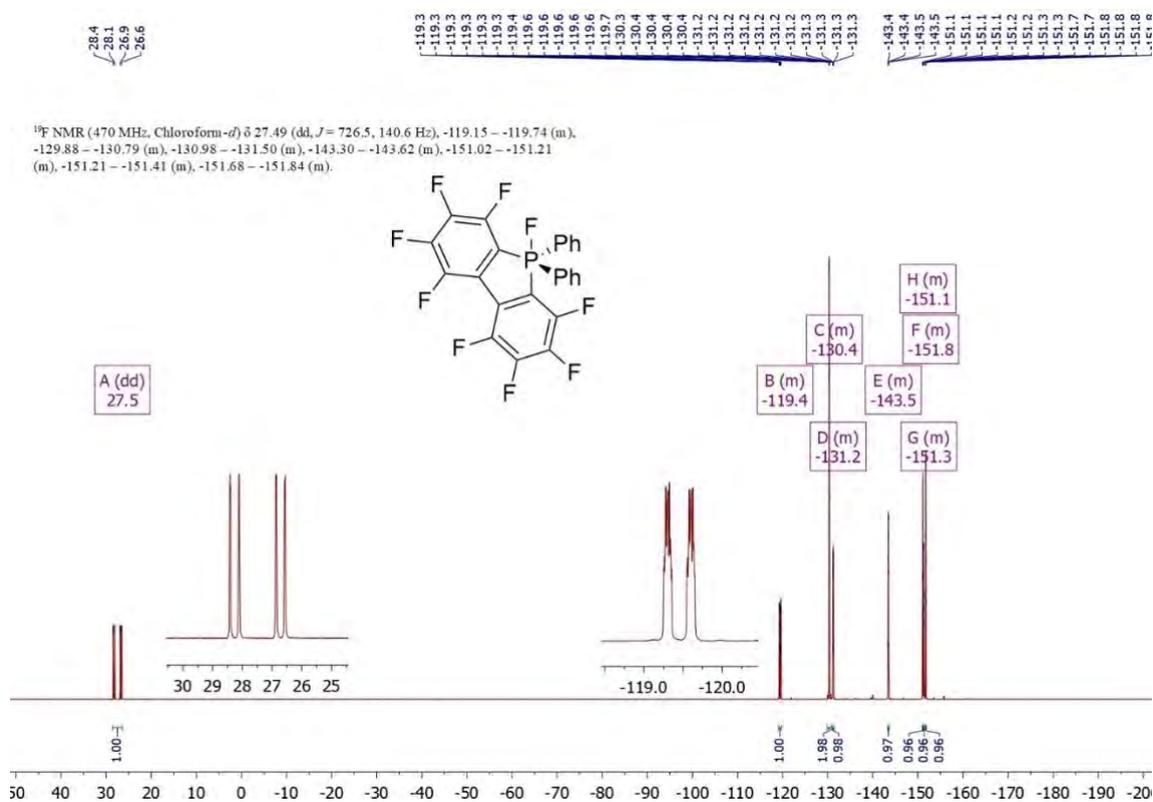
^{19}F NMR (470 MHz, cdcl_3) δ -129.64, -131.28, -131.28, -145.90, -145.92, -152.48, -152.48, -153.21, -153.21.



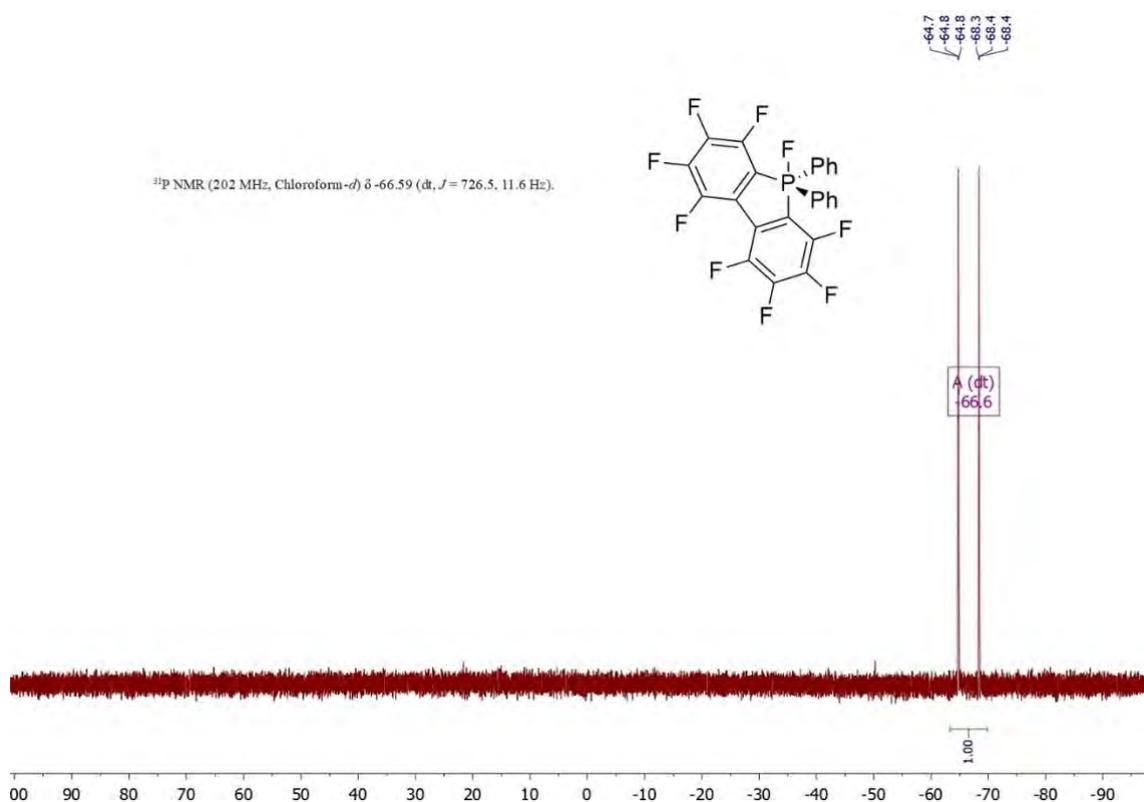
^1H NMR Spectra of $\text{FPh}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**8**) in CDCl_3 .



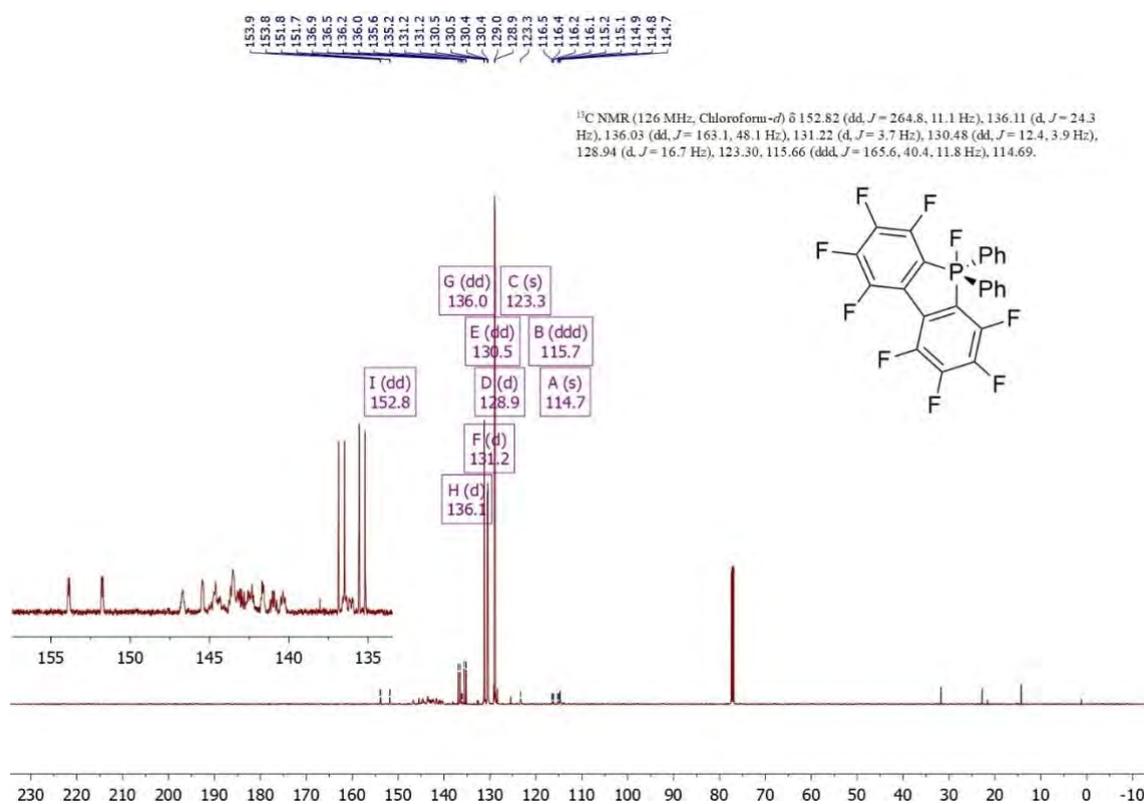
^{19}F NMR Spectra of $\text{FPh}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**8**) in CDCl_3 .



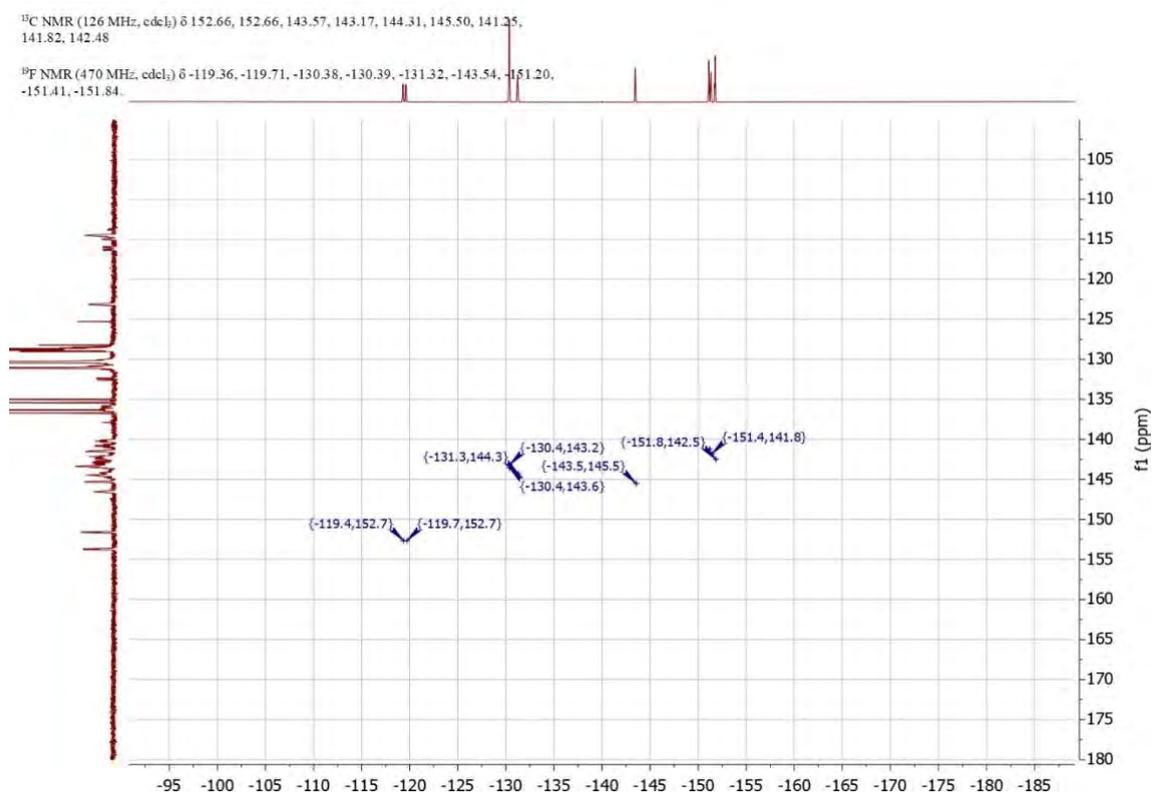
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPPh}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**8**) in CDCl_3 .



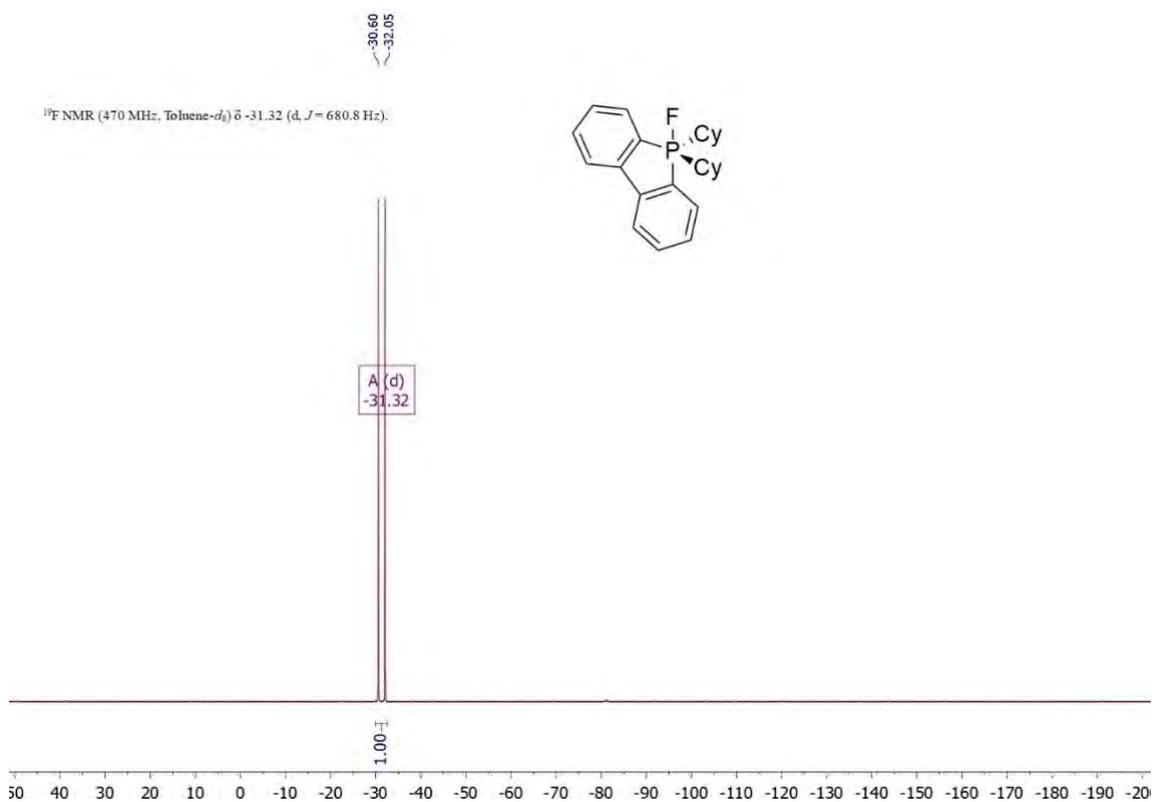
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{FPPh}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**8**) in CDCl_3 .



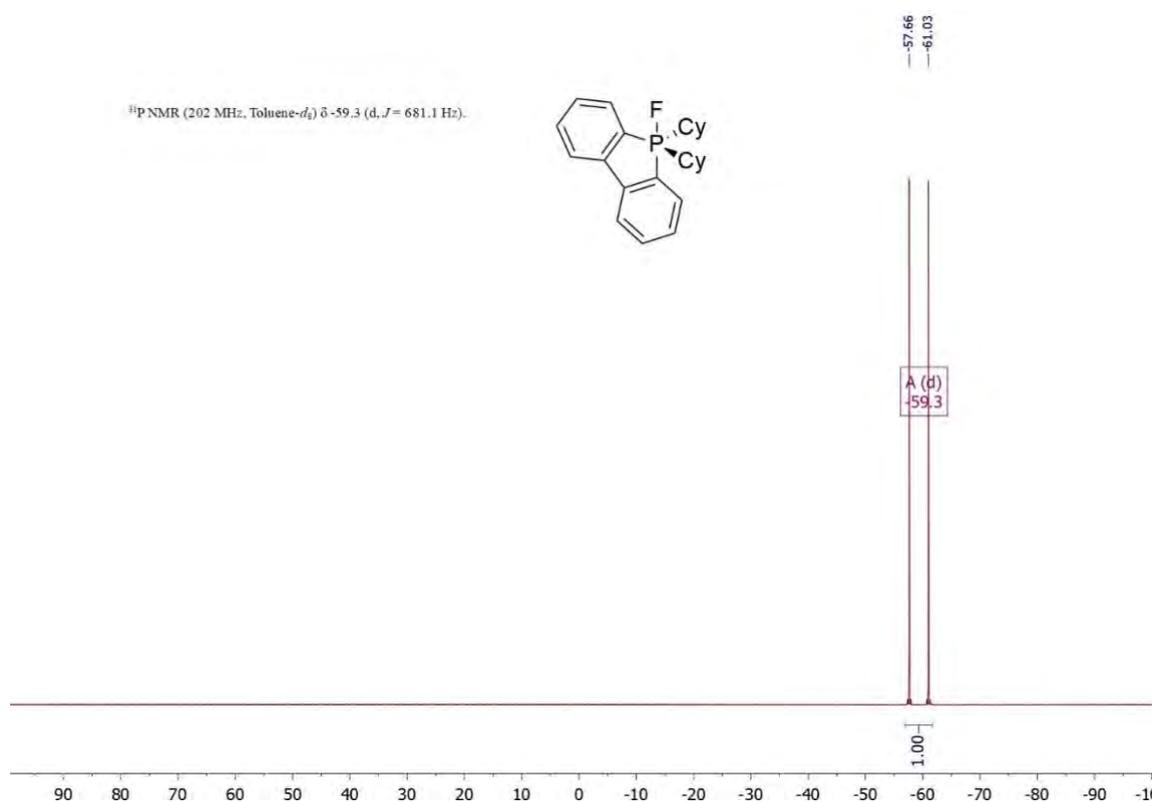
^{13}C - ^{19}F HSQC NMR Spectra of $\text{FPh}_2\text{C}_6\text{F}_4\text{C}_6\text{F}_4$ (**8**) in CDCl_3 .



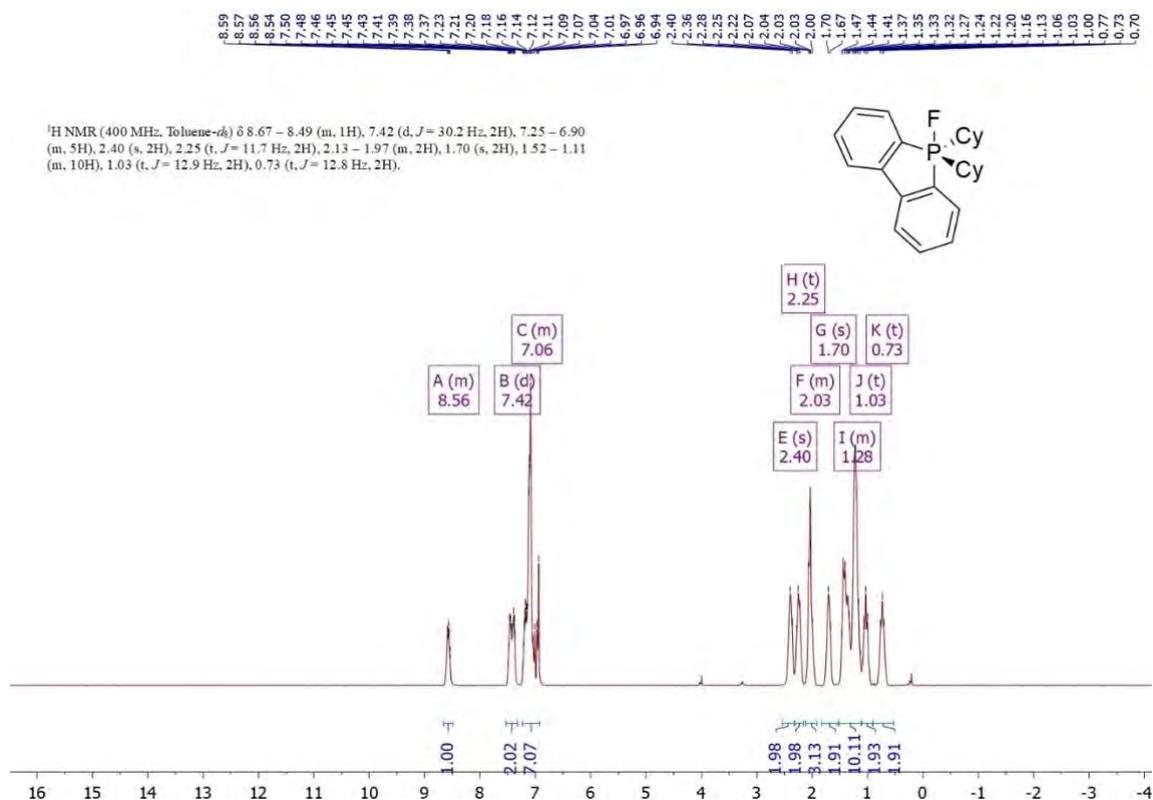
^{19}F NMR Spectra of $\text{FCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 .



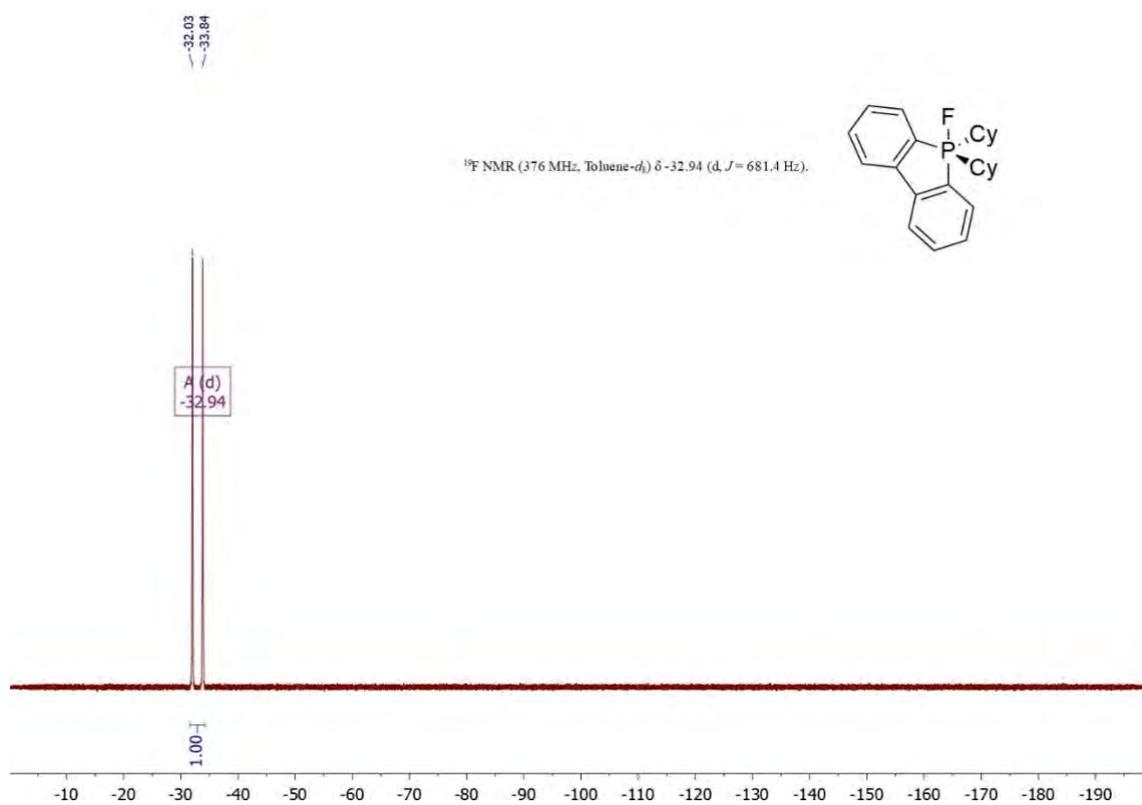
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 .



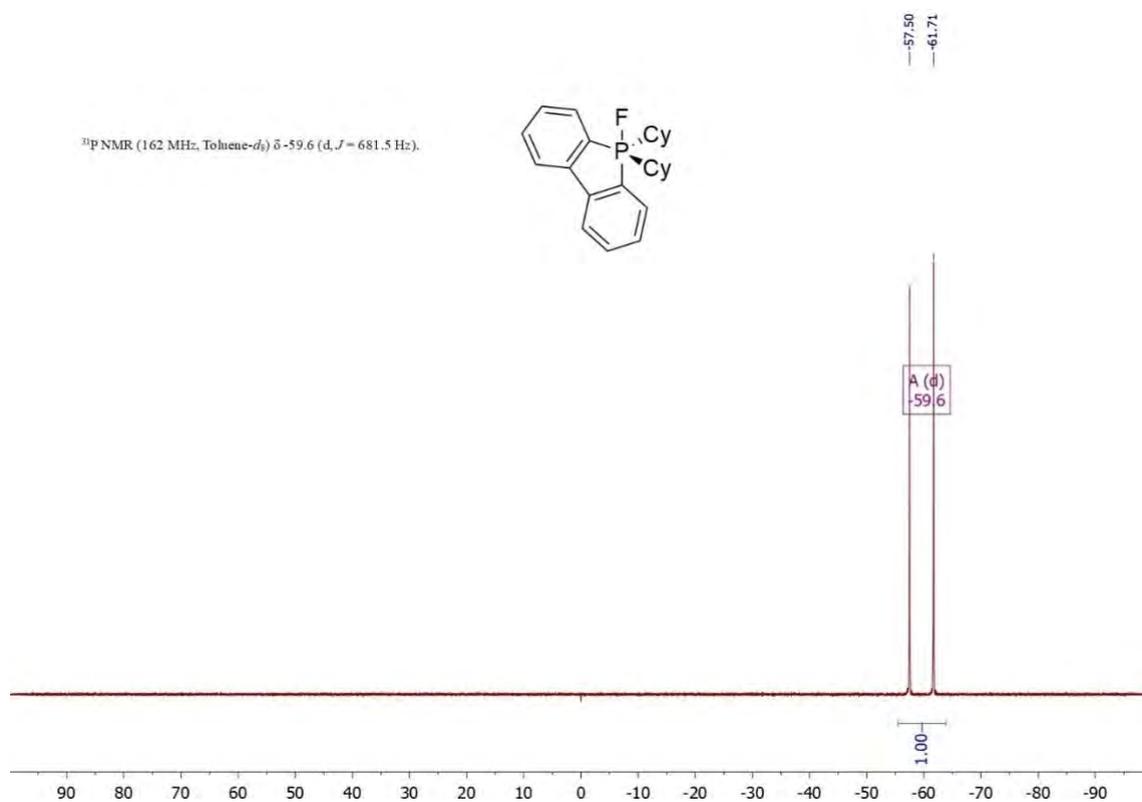
^1H NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 at 233 K.



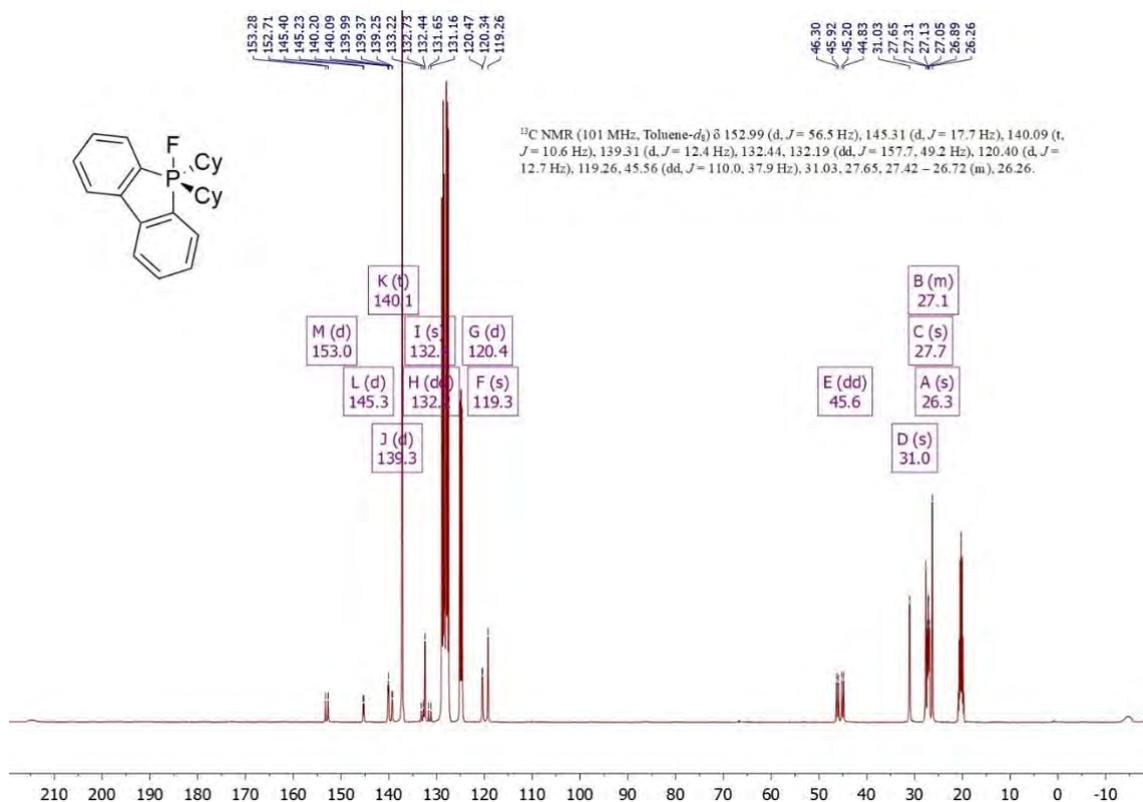
^{19}F NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 at 233 K.



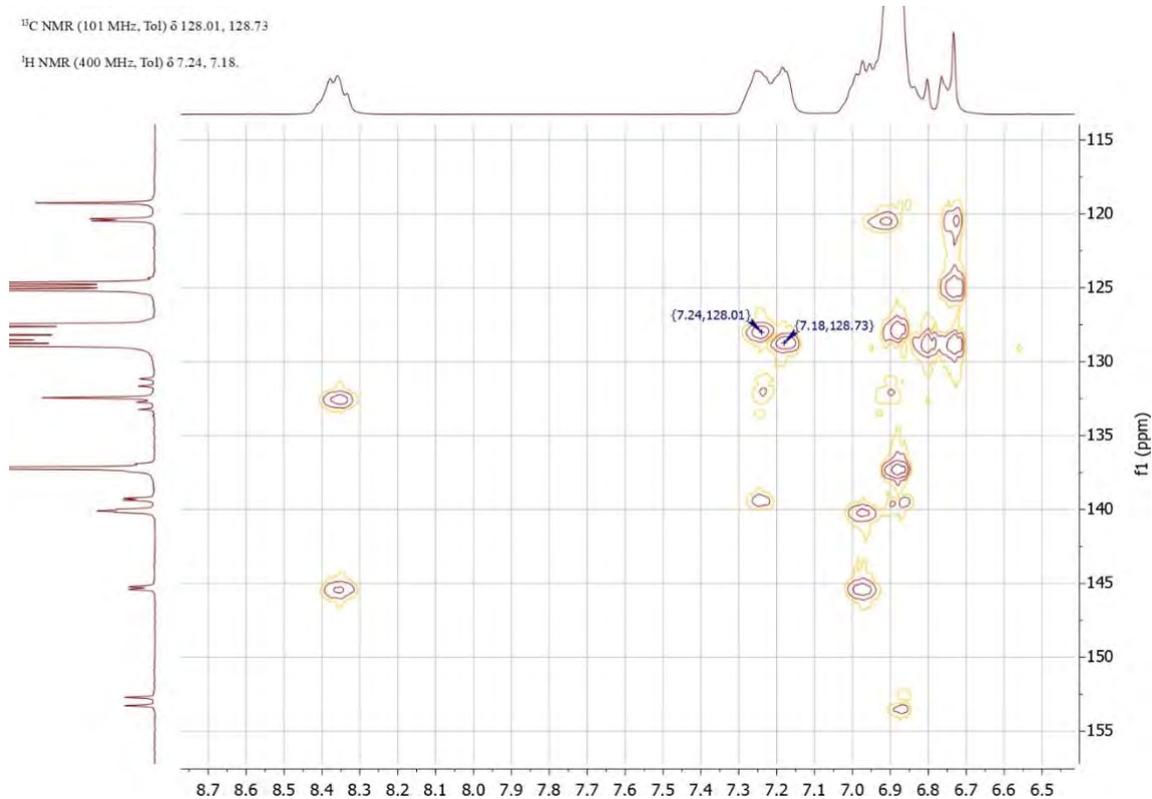
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 at 233 K.



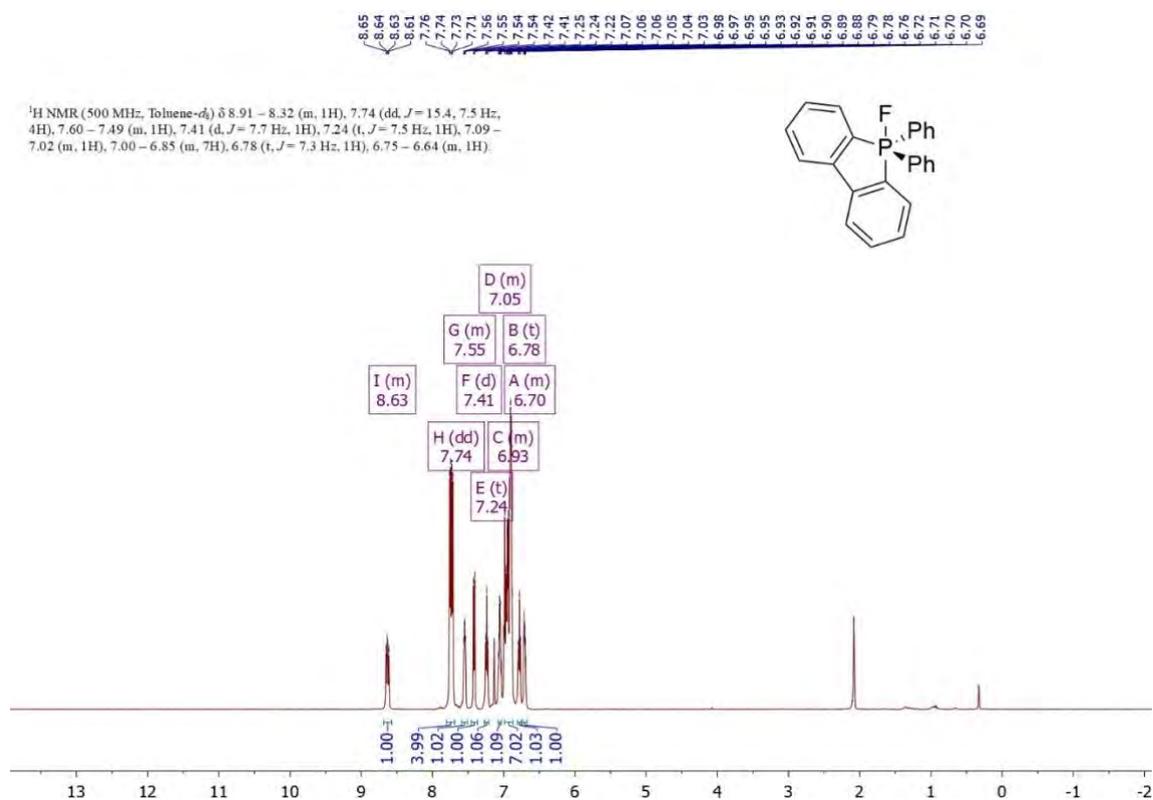
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 at 233 K.



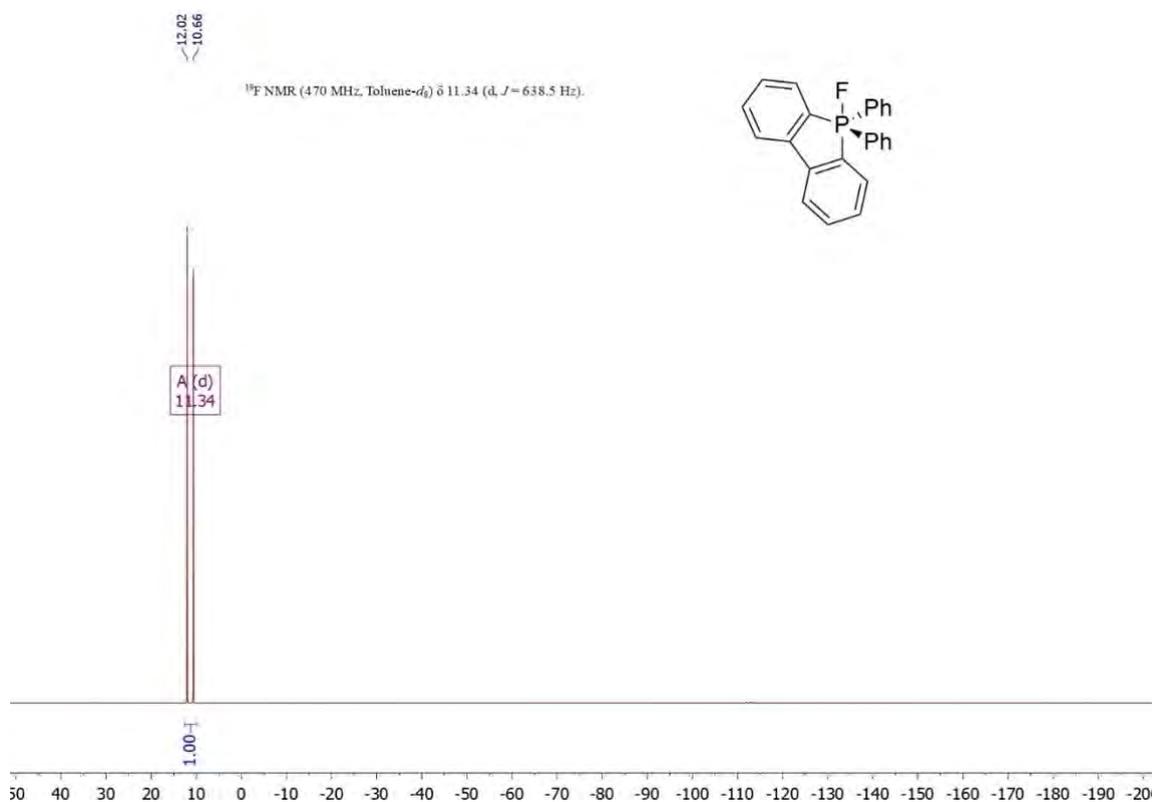
^1H - ^{13}C HSQC NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**11**) in toluene- d_8 at 233 K.



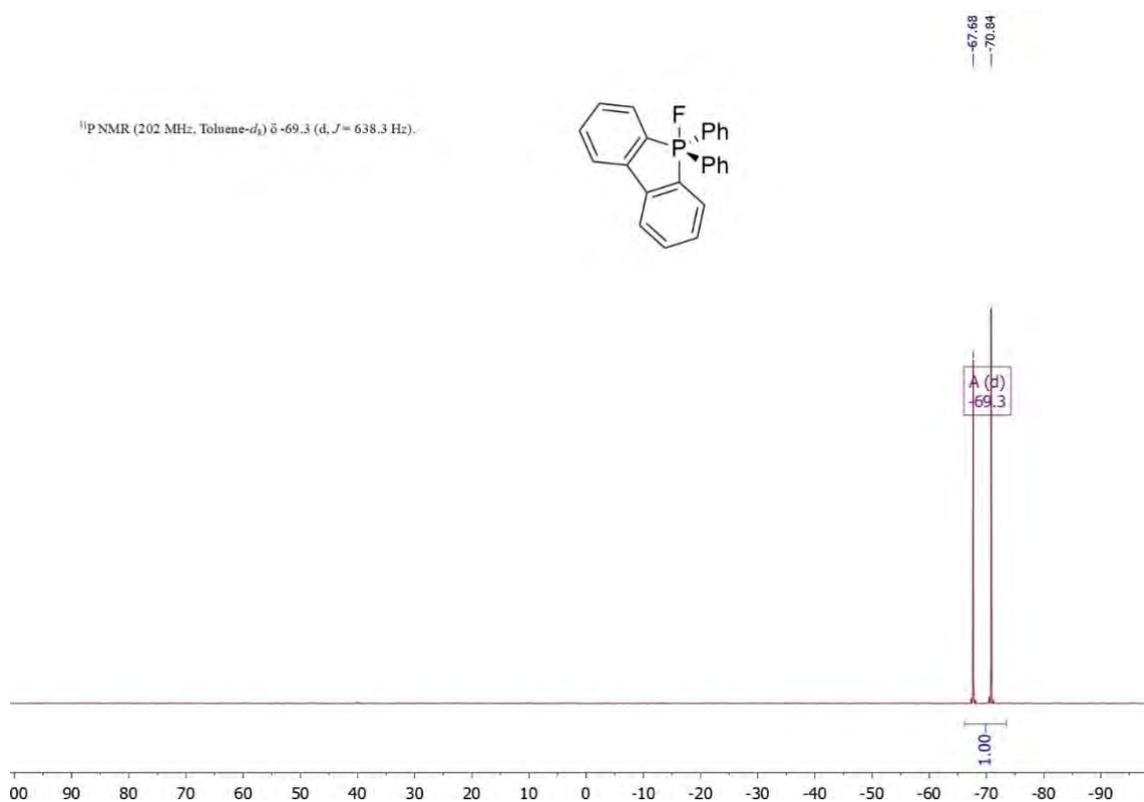
^1H NMR Spectra of $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**13**) in toluene- d_8 at 233 K.



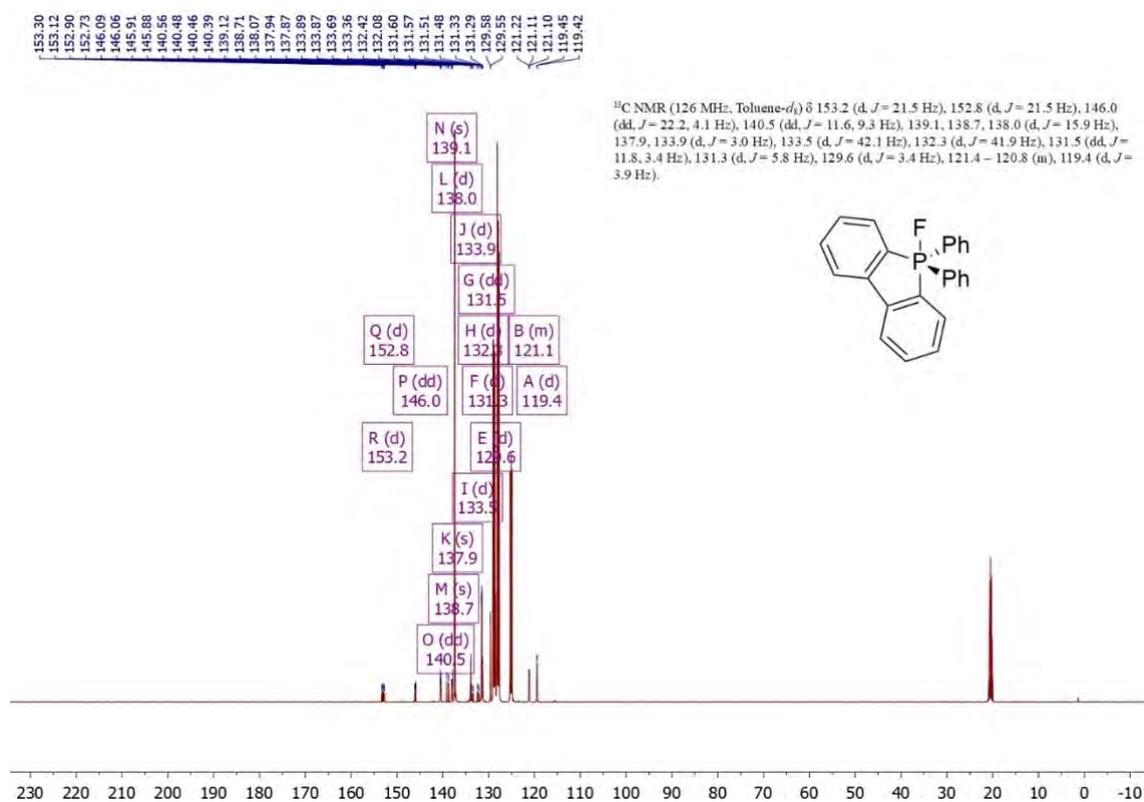
^{19}F NMR Spectra of $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**13**) in toluene- d_8 at 233 K.



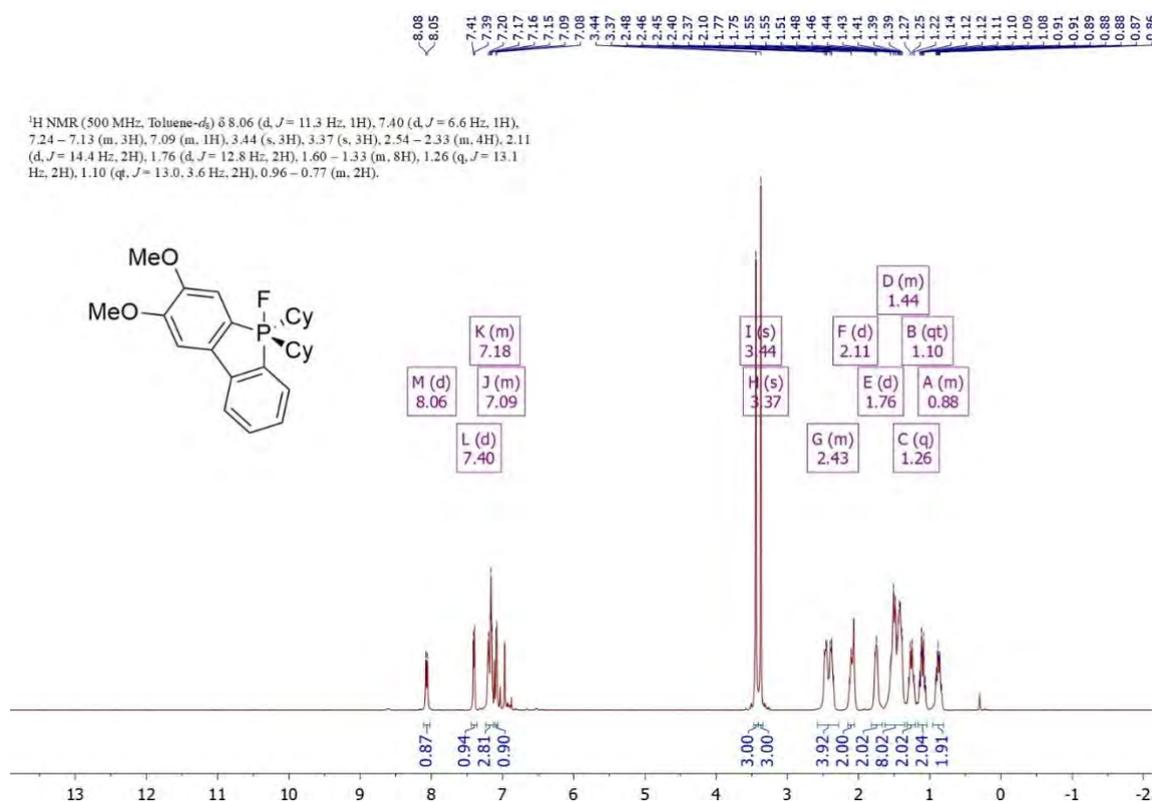
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**13**) in toluene- d_8 at 233 K.



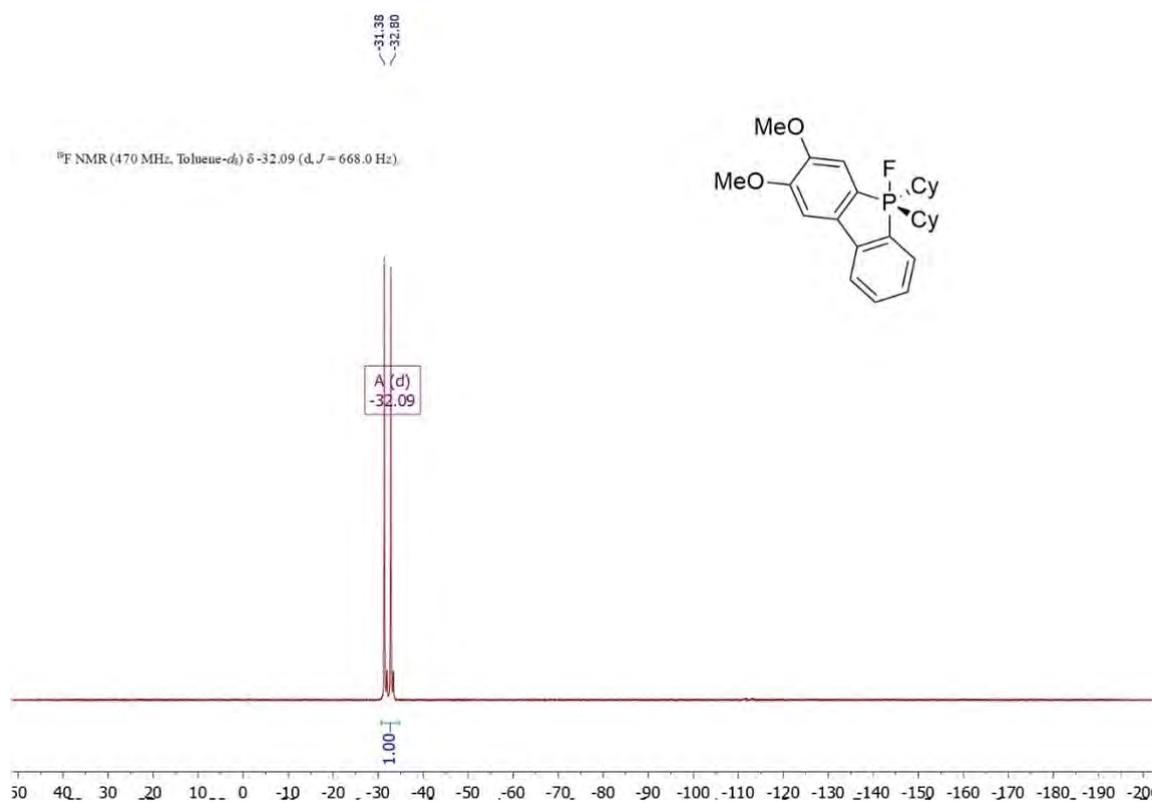
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra $\text{FPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4$ (**13**) in toluene- d_8 at 233 K.



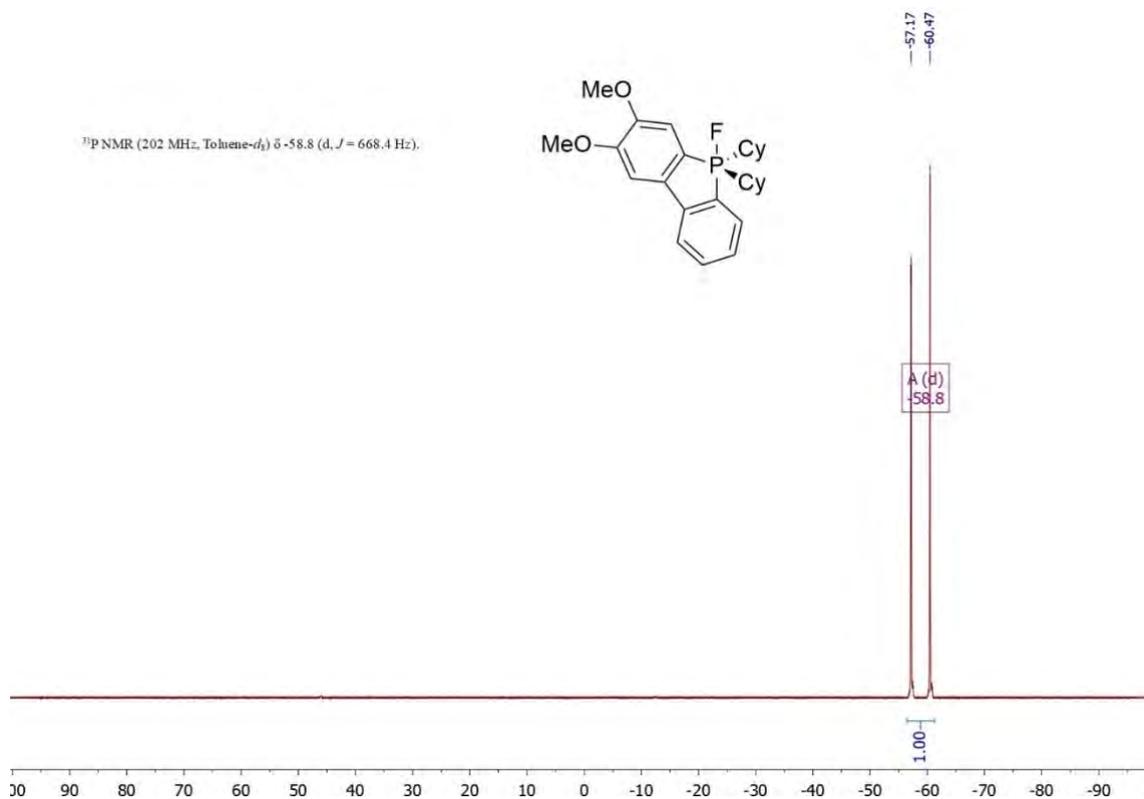
¹H NMR Spectra of FPCy₂C₆H₂(OMe)₂C₆H₄ (**15**) in toluene-d₈ at 233 K.



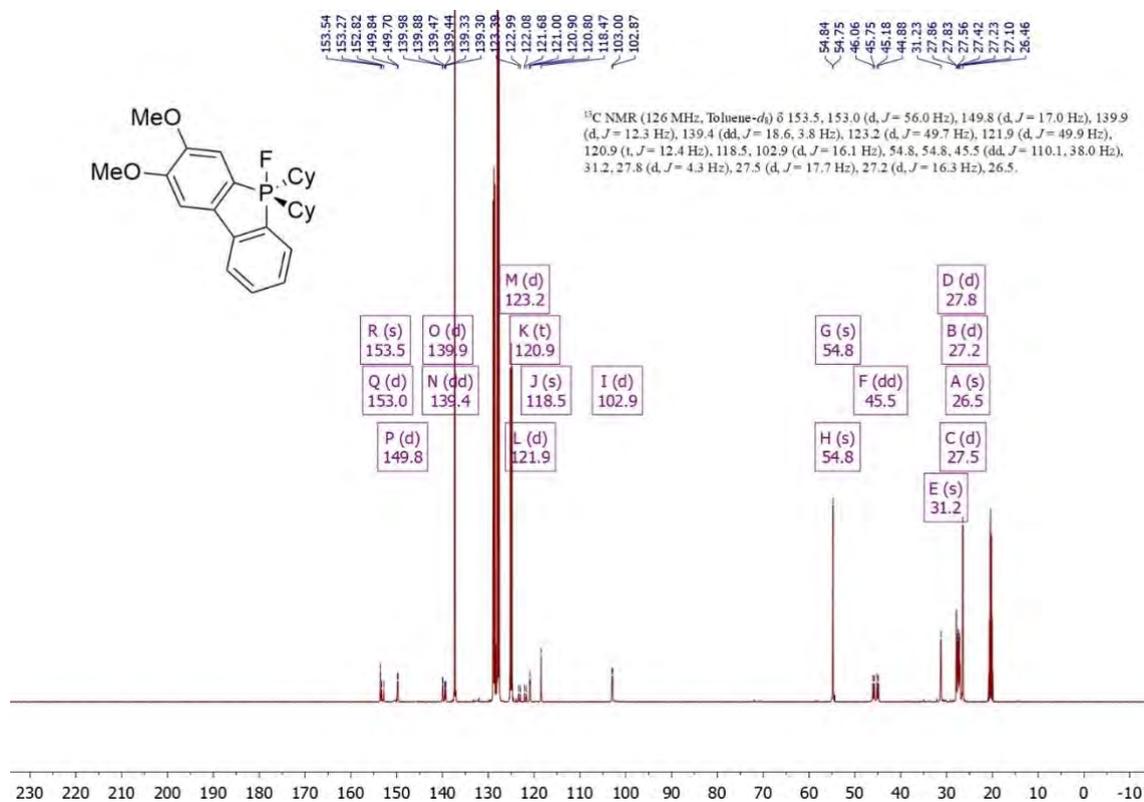
¹⁹F NMR Spectra of FPCy₂C₆H₂(OMe)₂C₆H₄ (**15**) in toluene-d₈ at 233 K.



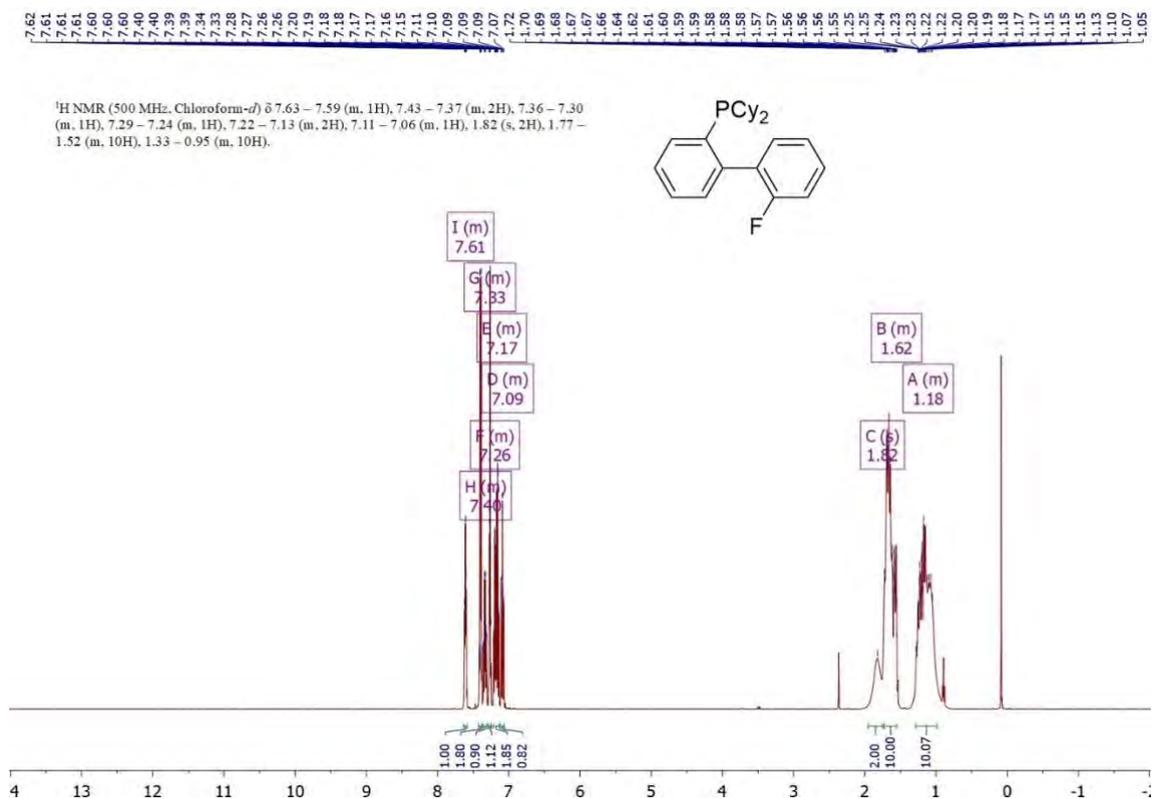
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{FPCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4$ (**15**) in toluene- d_8 at 233 K.



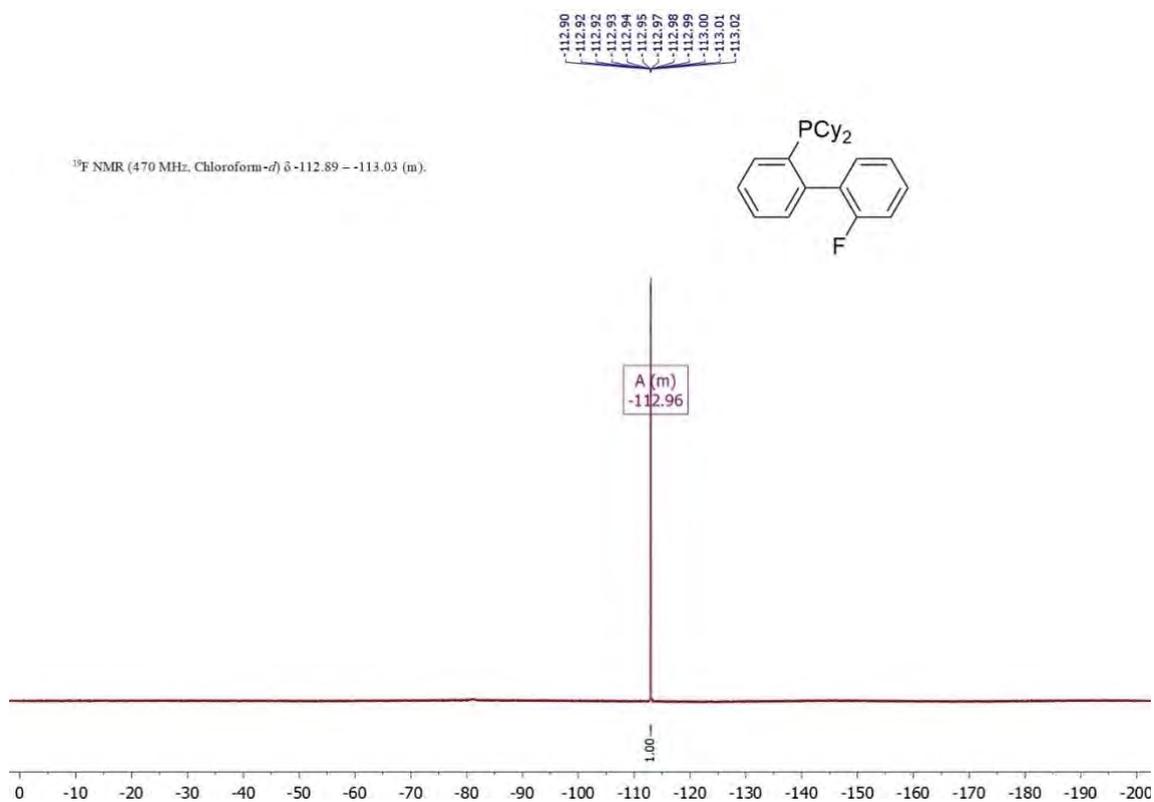
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra $\text{FPCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4$ (**15**) in toluene- d_8 at 233 K.



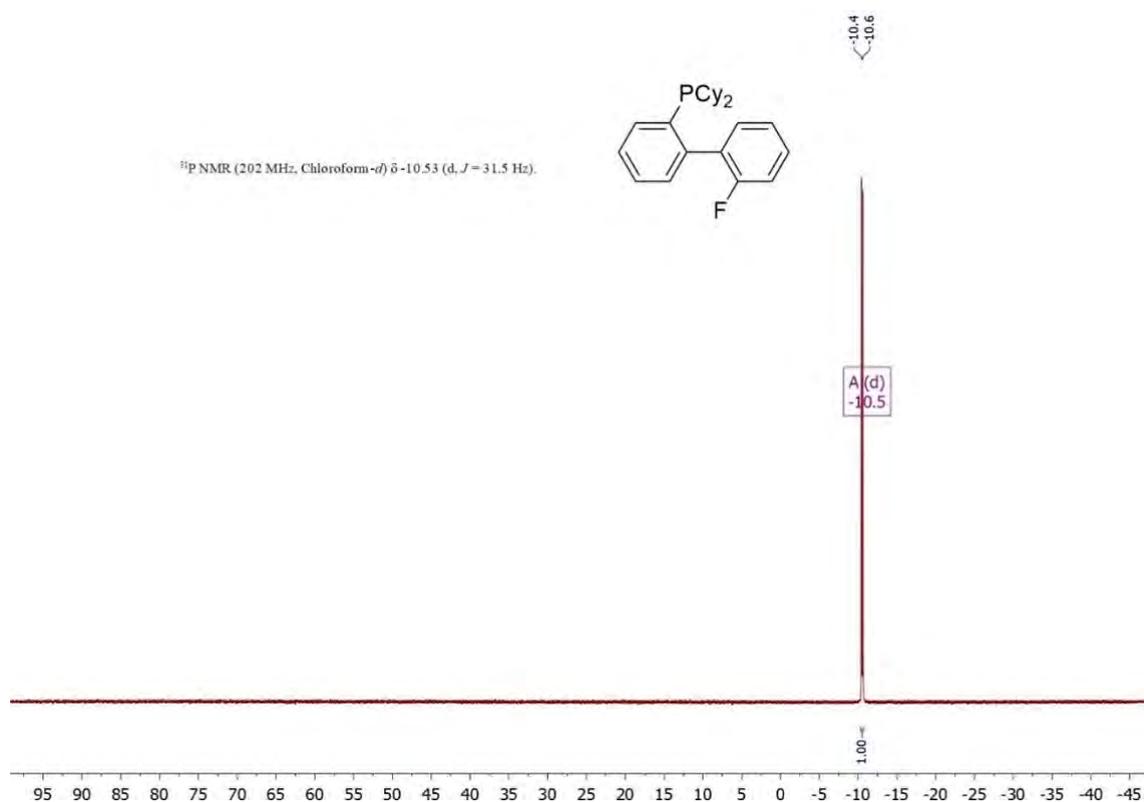
¹H NMR Spectra of PCy₂C₆H₄C₆H₄F (**10**) in CDCl₃.



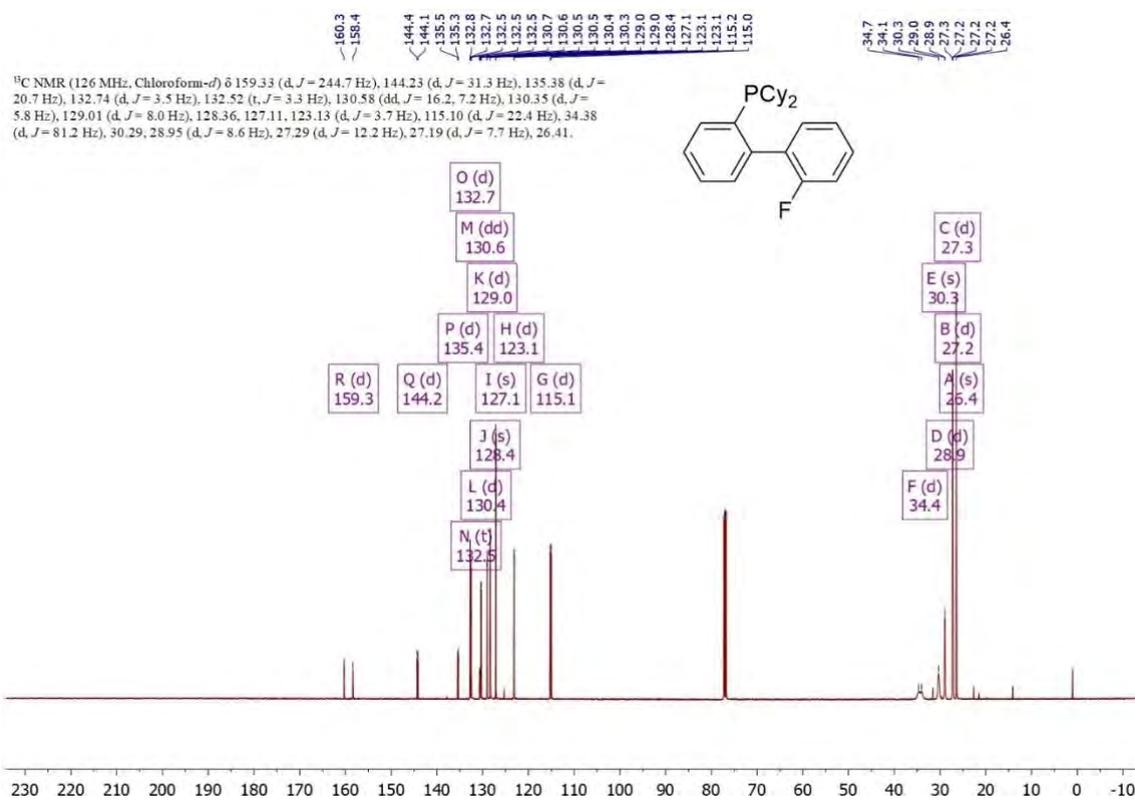
¹⁹F NMR Spectra of PCy₂C₆H₄C₆H₄F (**10**) in CDCl₃.



$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{F}$ (**10**) in CDCl_3 .



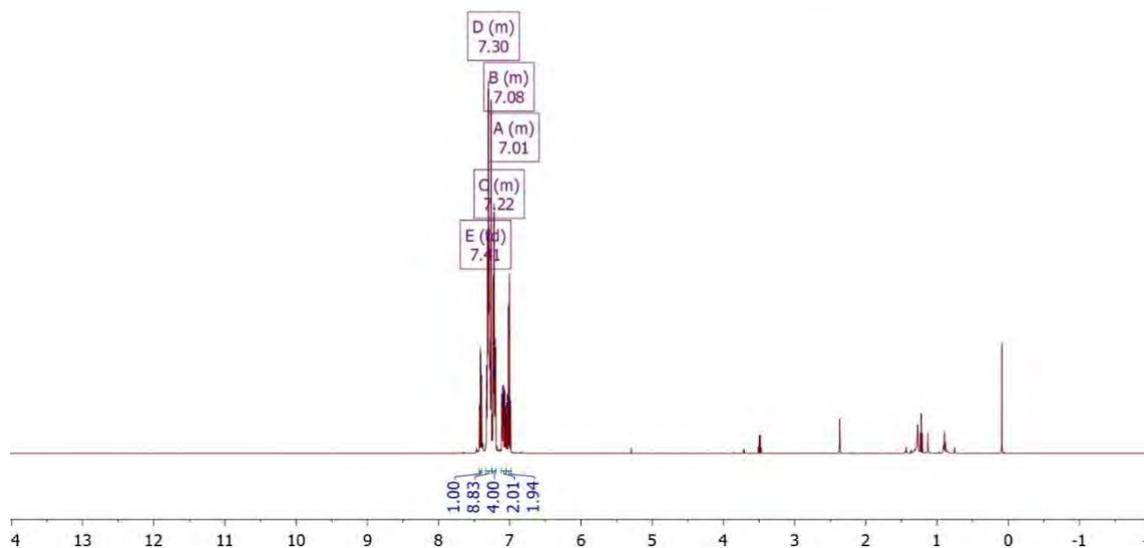
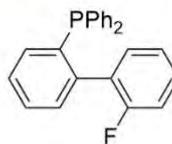
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{F}$ (**10**) in CDCl_3 .



^1H NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{F}$ (**12**) in CDCl_3 .

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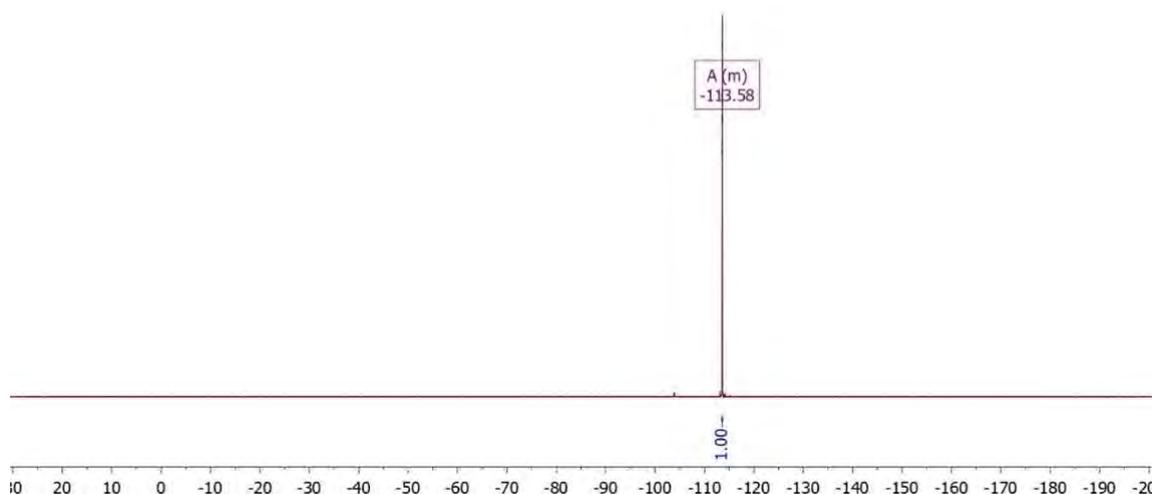
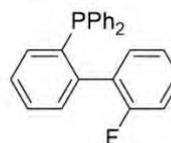
^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 (td, $J = 7.7, 1.4$ Hz, 1H), 7.34 – 7.26 (m, 9H), 7.25 – 7.18 (m, 4H), 7.12 – 7.05 (m, 2H), 7.05 – 6.94 (m, 2H).



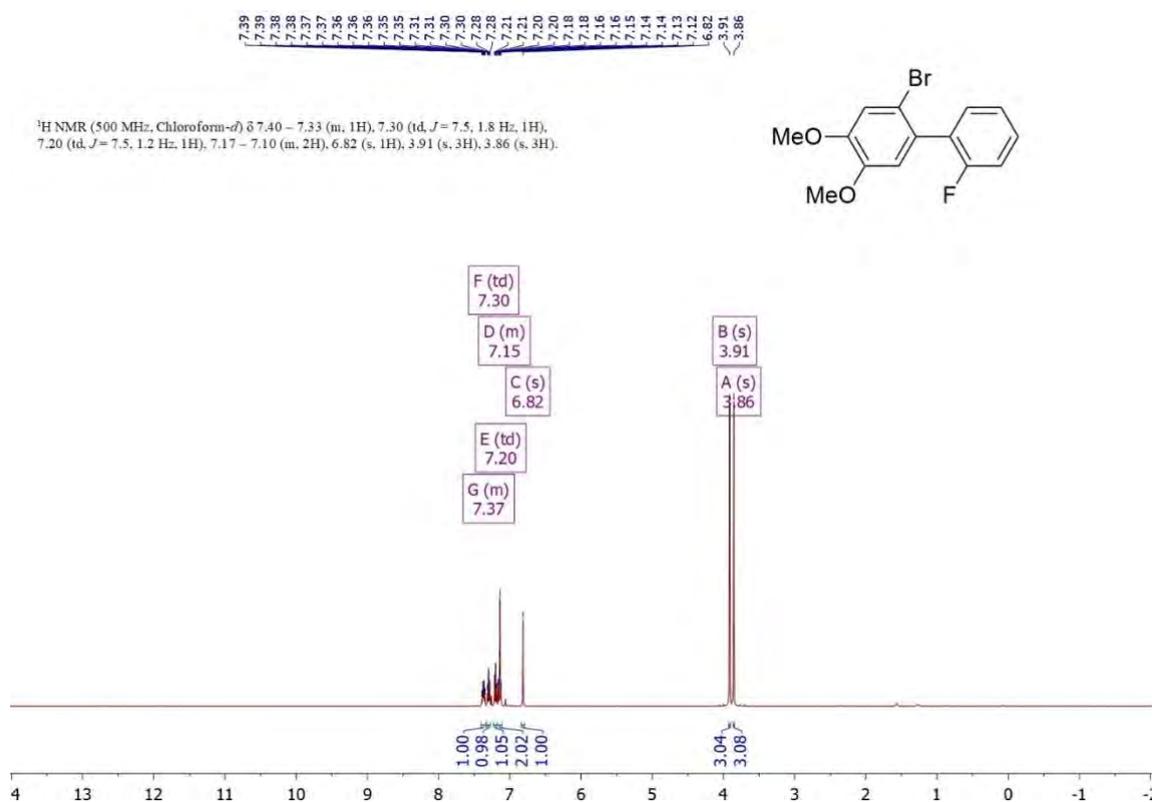
^{19}F NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{F}$ (**12**) in CDCl_3 .

^{19}F NMR (470 MHz, Chloroform-*d*) δ -113.29 – -113.91 (m).

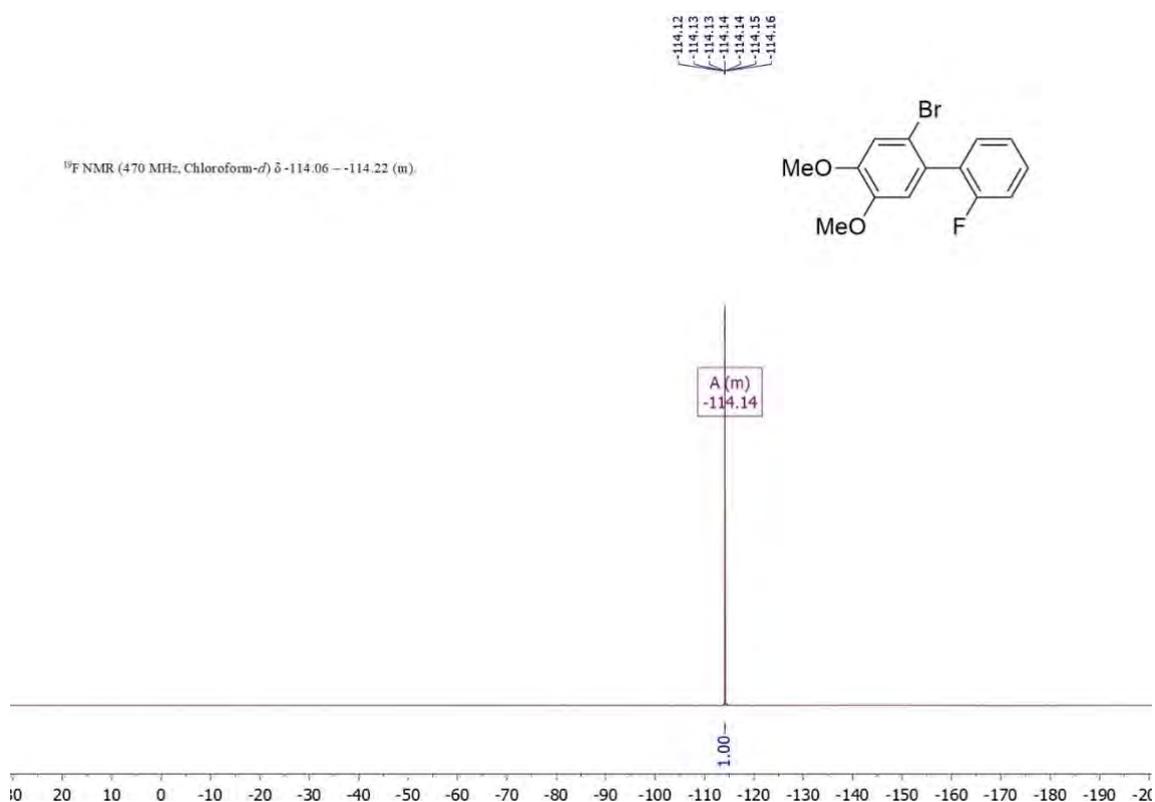
-113.54
-113.55
-113.55
-113.56
-113.57
-113.58
-113.60
-113.61
-113.62
-113.63



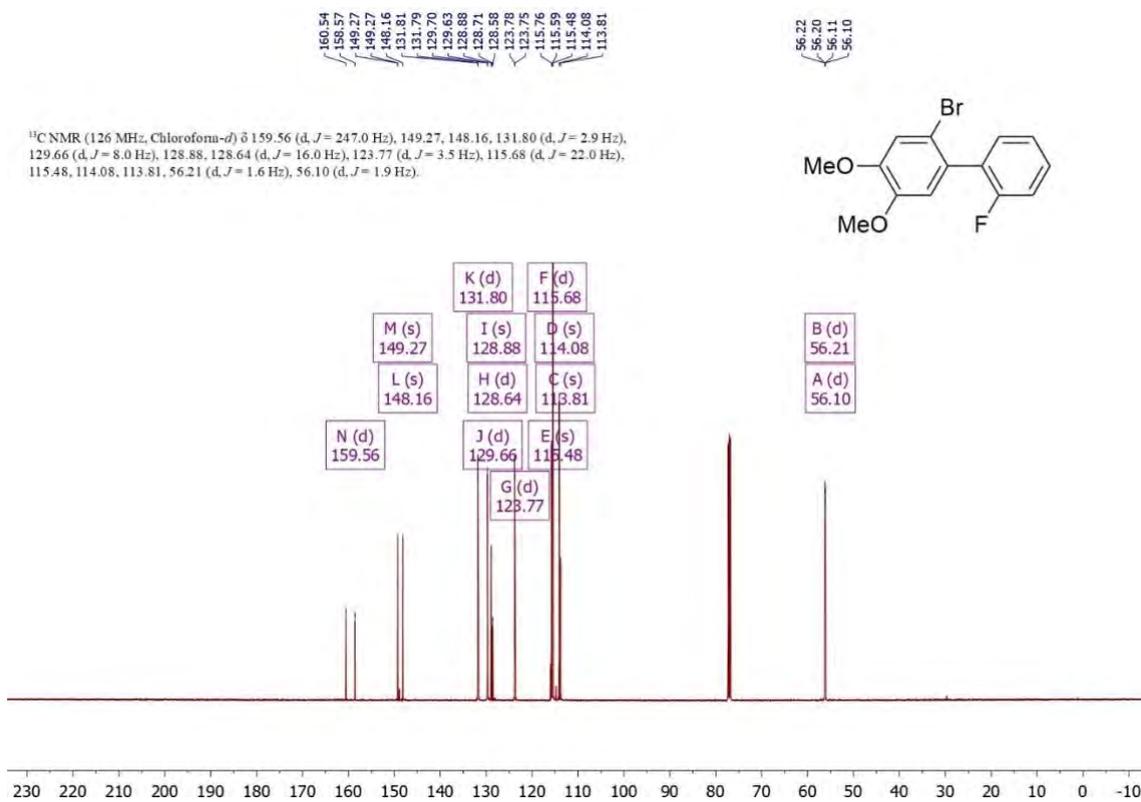
^1H NMR Spectra of $\text{C}_6\text{H}_2\text{Br}(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**9-OMe**) in CDCl_3 .



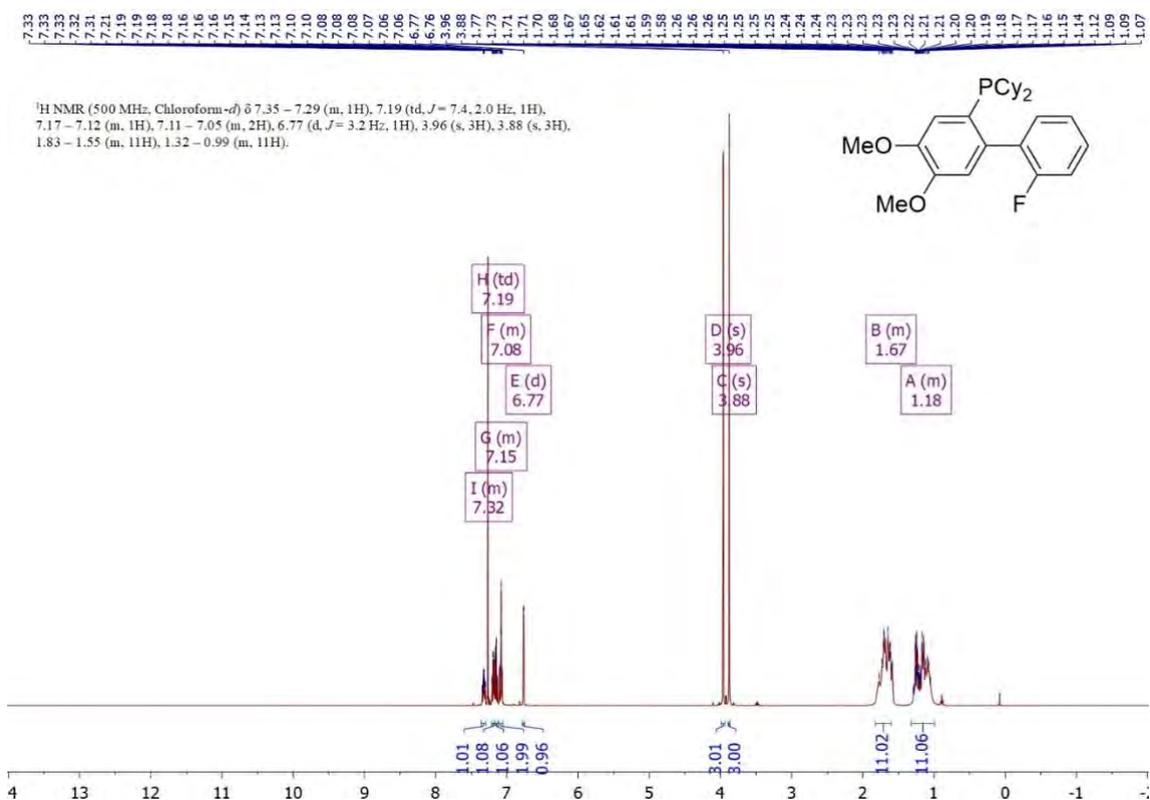
^{19}F NMR Spectra of $\text{C}_6\text{H}_2\text{Br}(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**9-OMe**) in CDCl_3 .



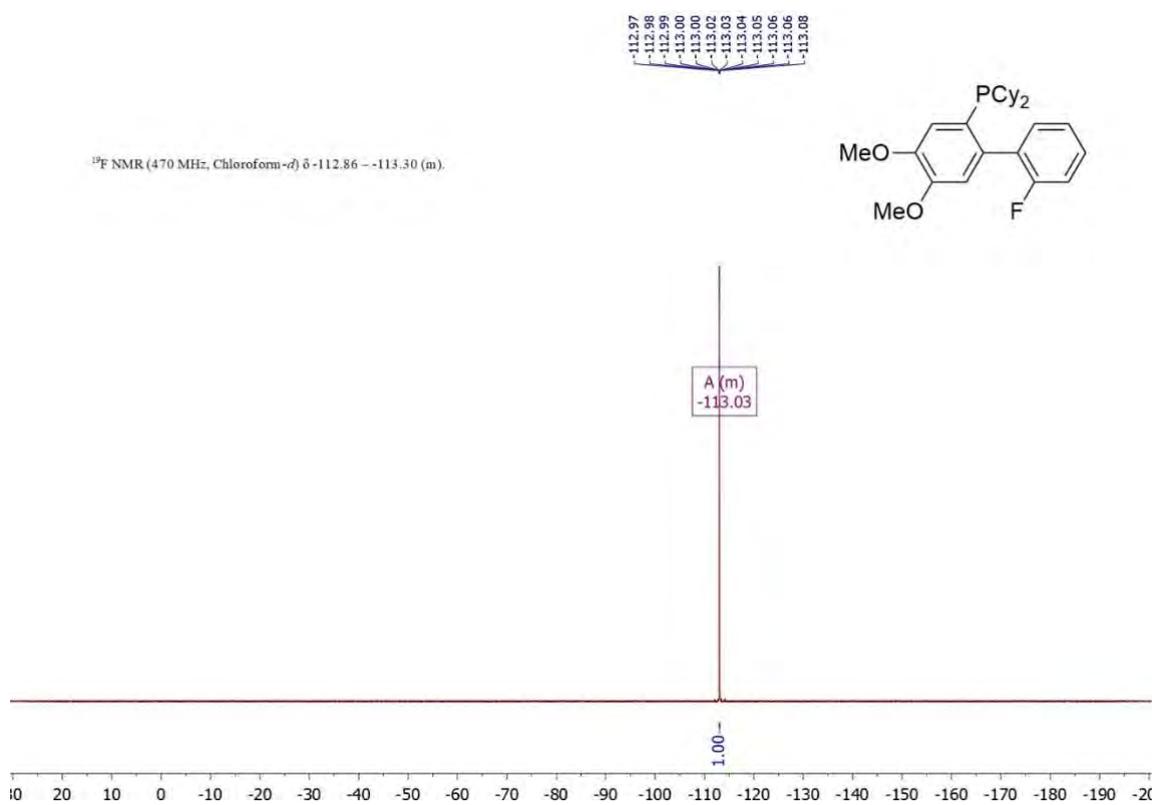
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{C}_6\text{H}_2\text{Br}(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**9-OMe**) in CDCl_3 .



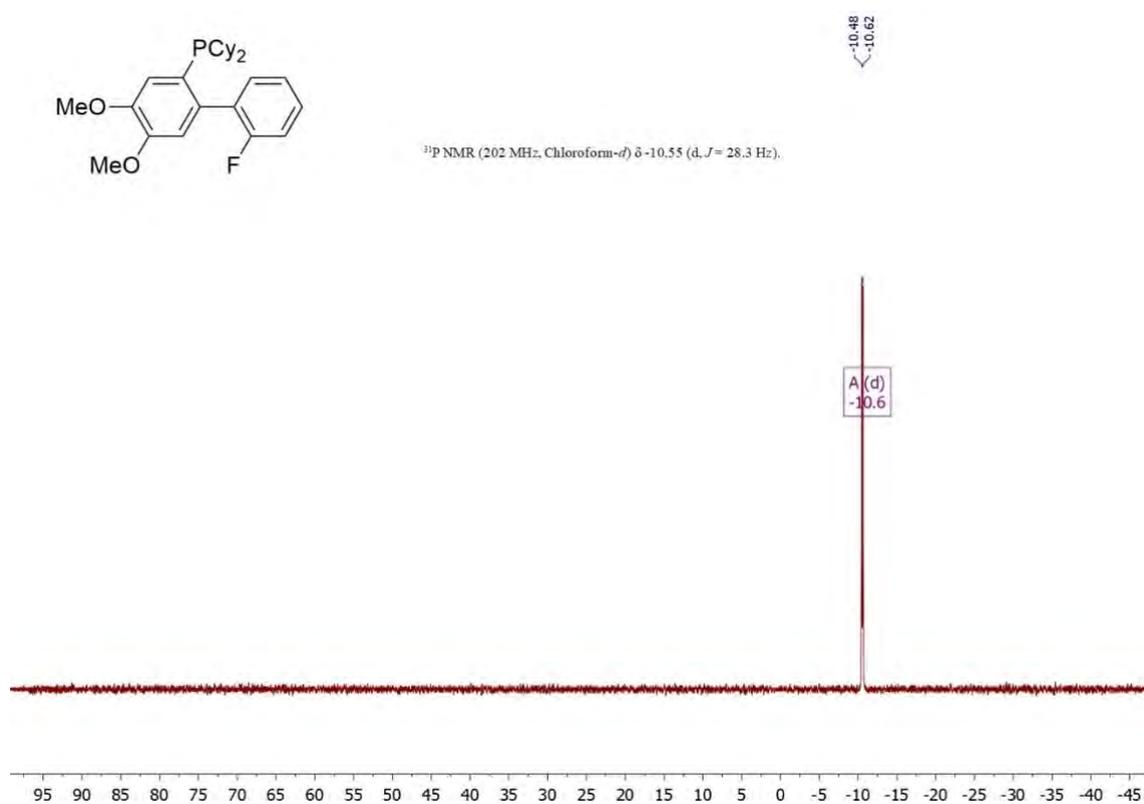
^1H NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**14**) in CDCl_3 .



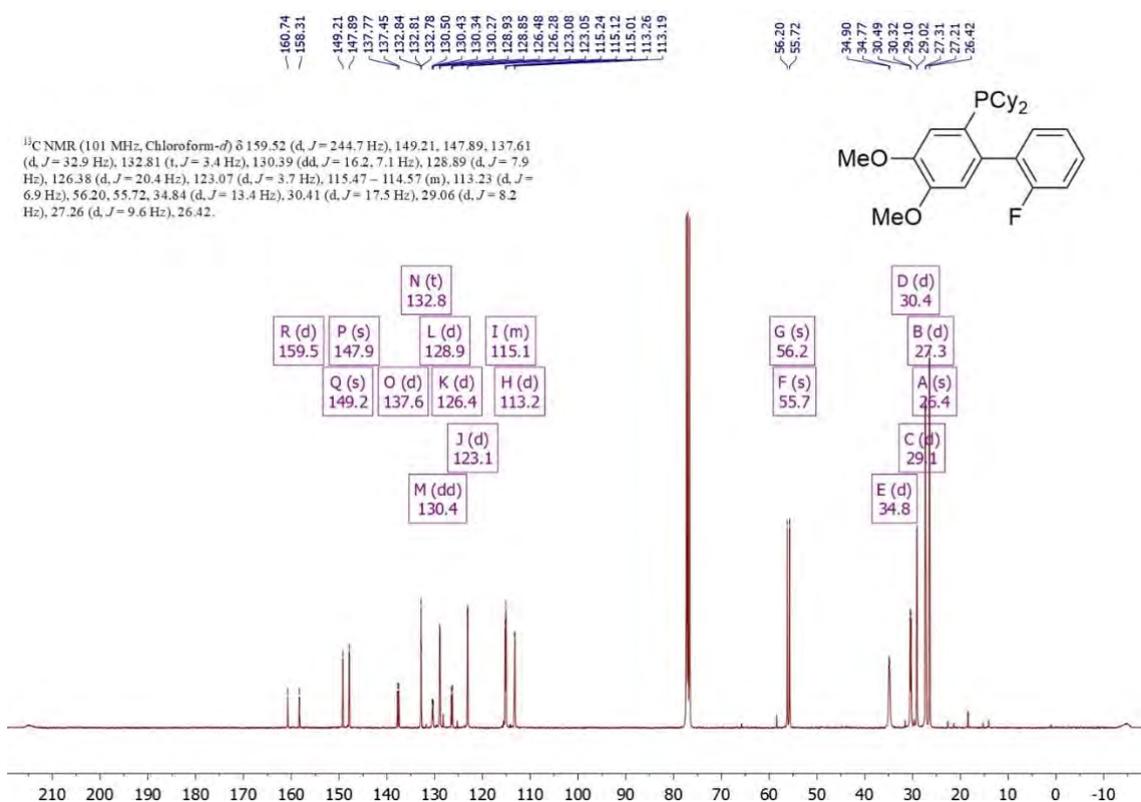
^{19}F NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**14**) in CDCl_3 .



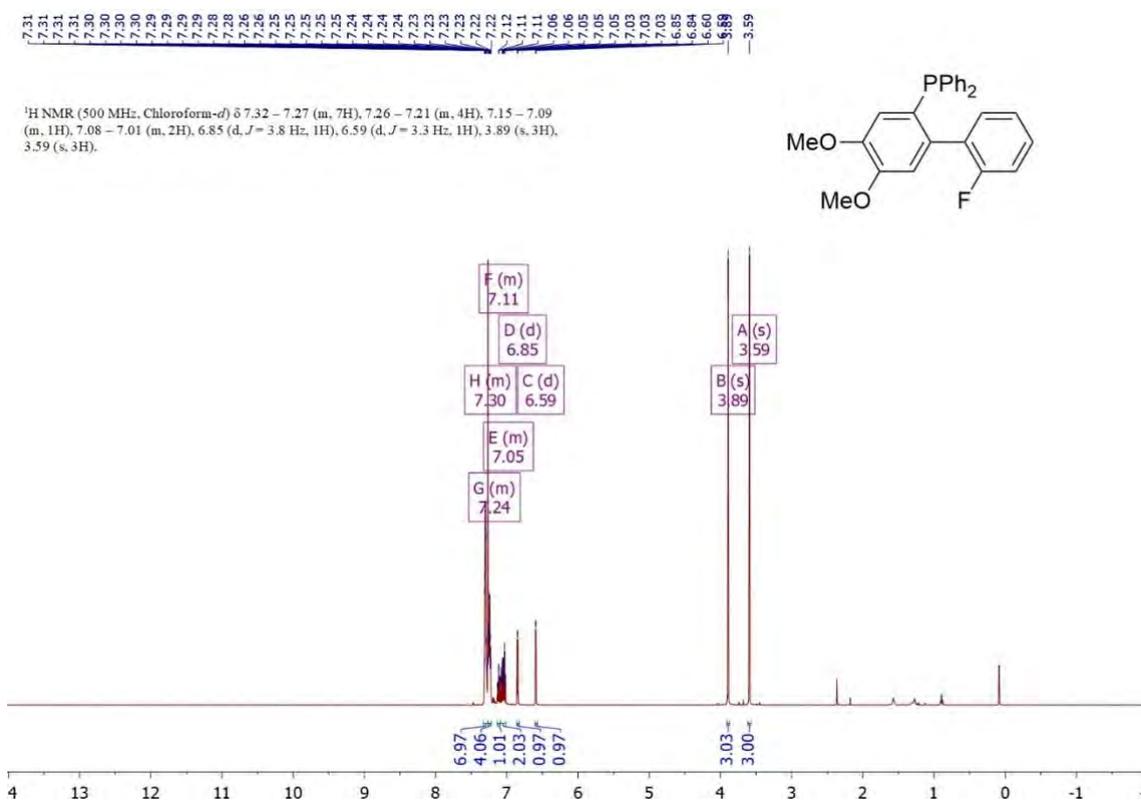
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**14**) in CDCl_3 .



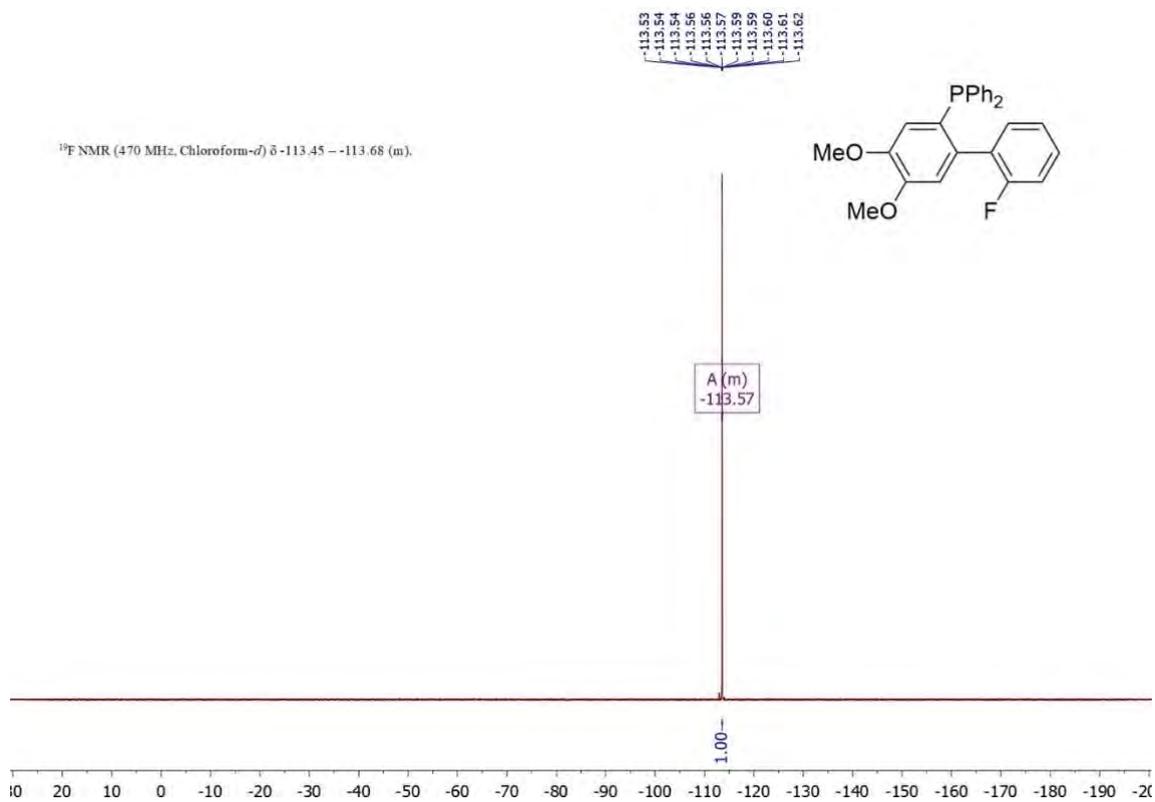
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{PCy}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**14**) in CDCl_3 .



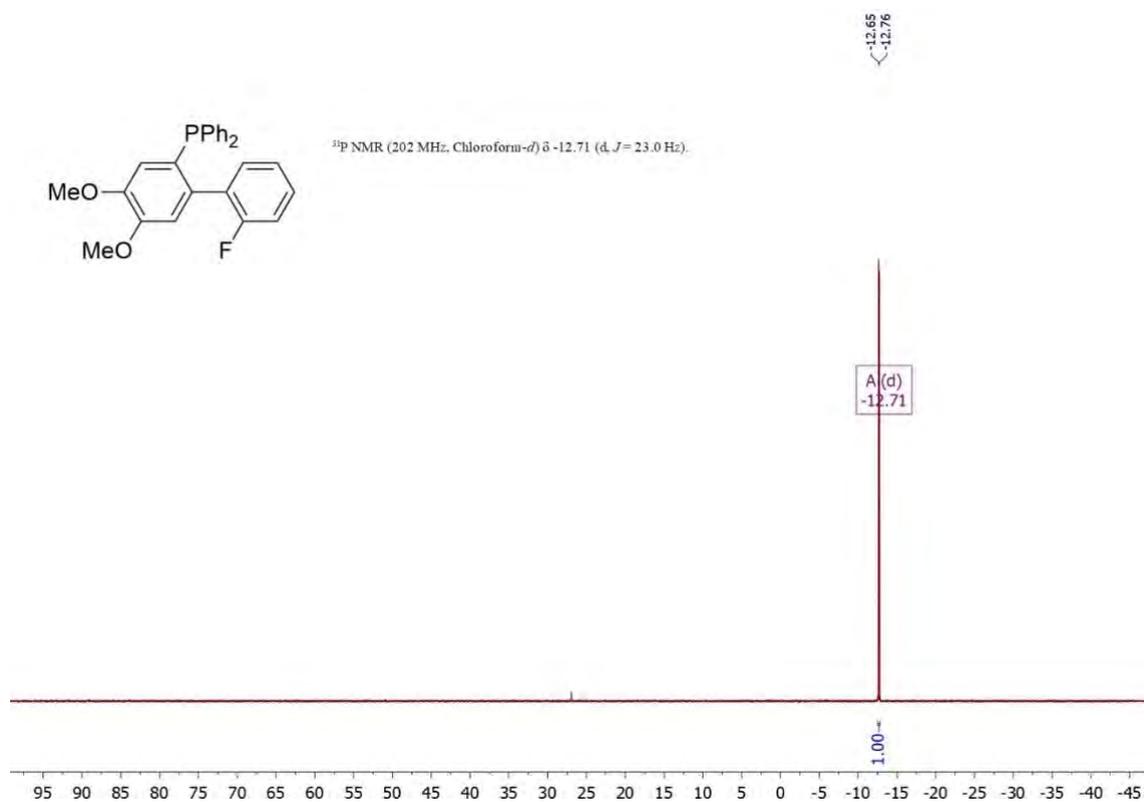
^1H NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**16**) in CDCl_3 .



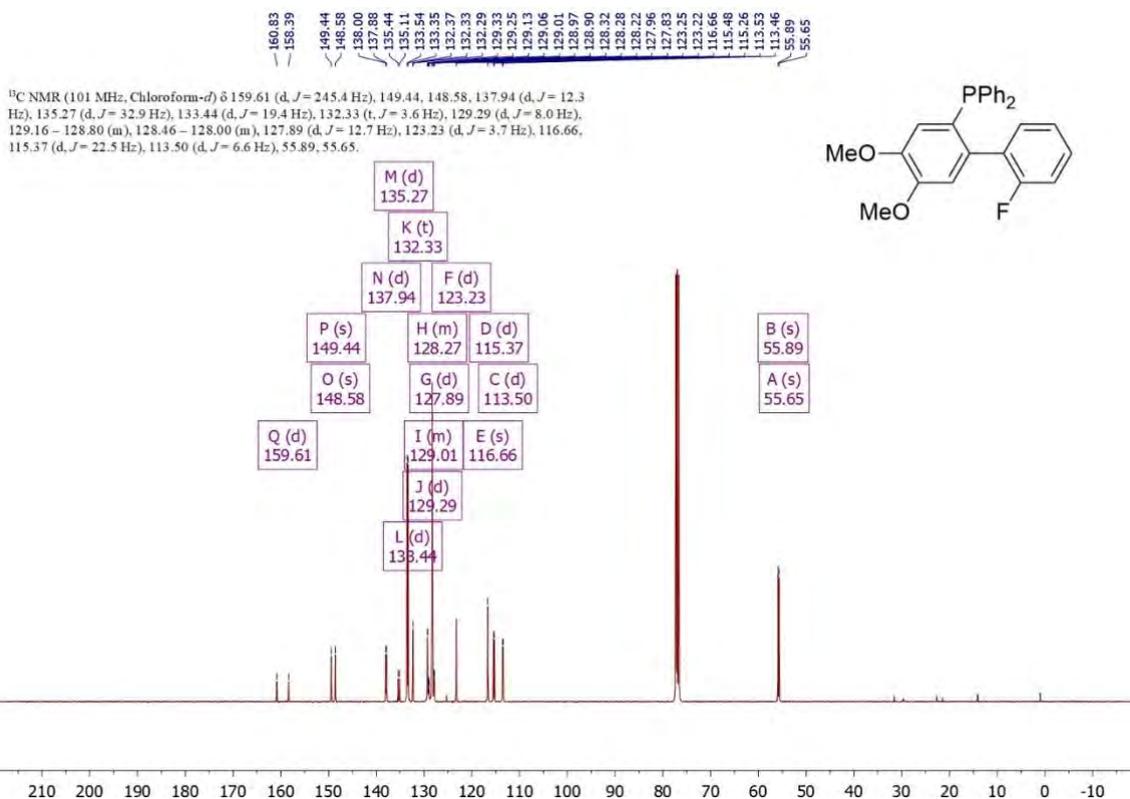
^{19}F NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**16**) in CDCl_3 .



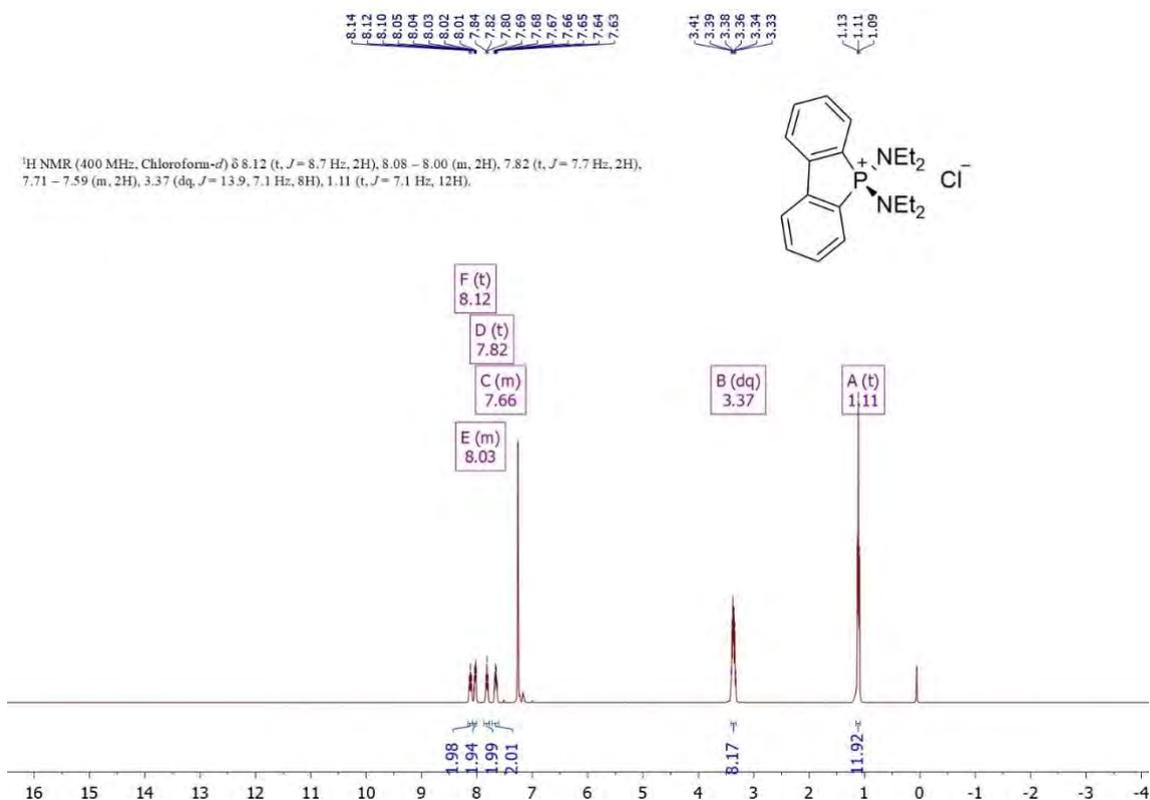
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**16**) in CDCl_3 .



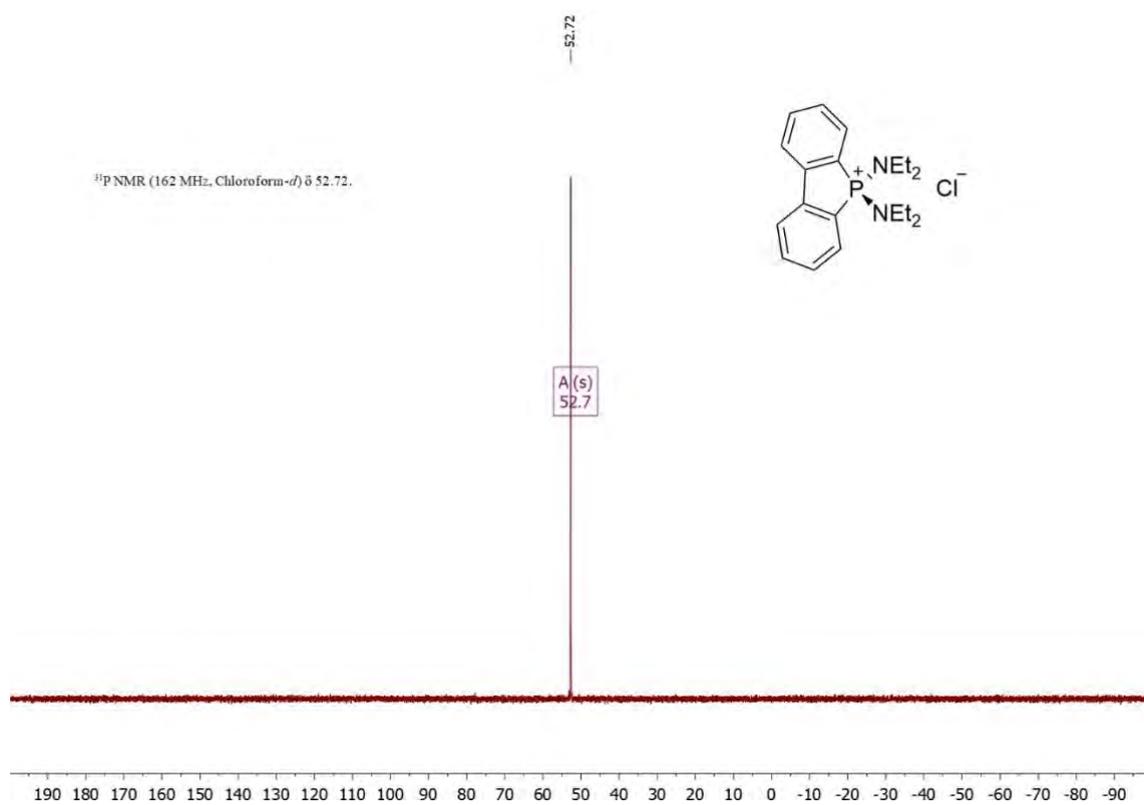
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectra of $\text{PPh}_2\text{C}_6\text{H}_2(\text{OMe})_2\text{C}_6\text{H}_4\text{F}$ (**16**) in CDCl_3 .



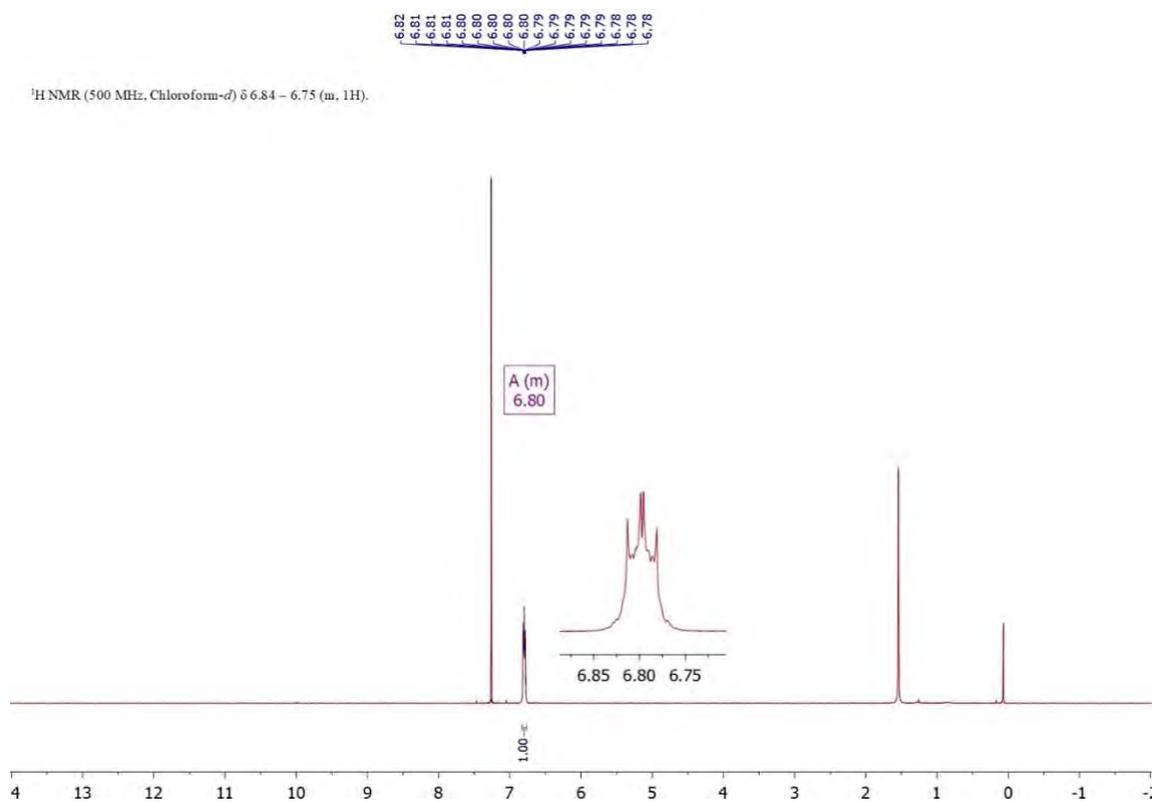
^1H NMR Spectra of $[\text{P}(\text{NEt}_2)_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4]\text{Cl}$ (**18-Cl**) in CDCl_3 .



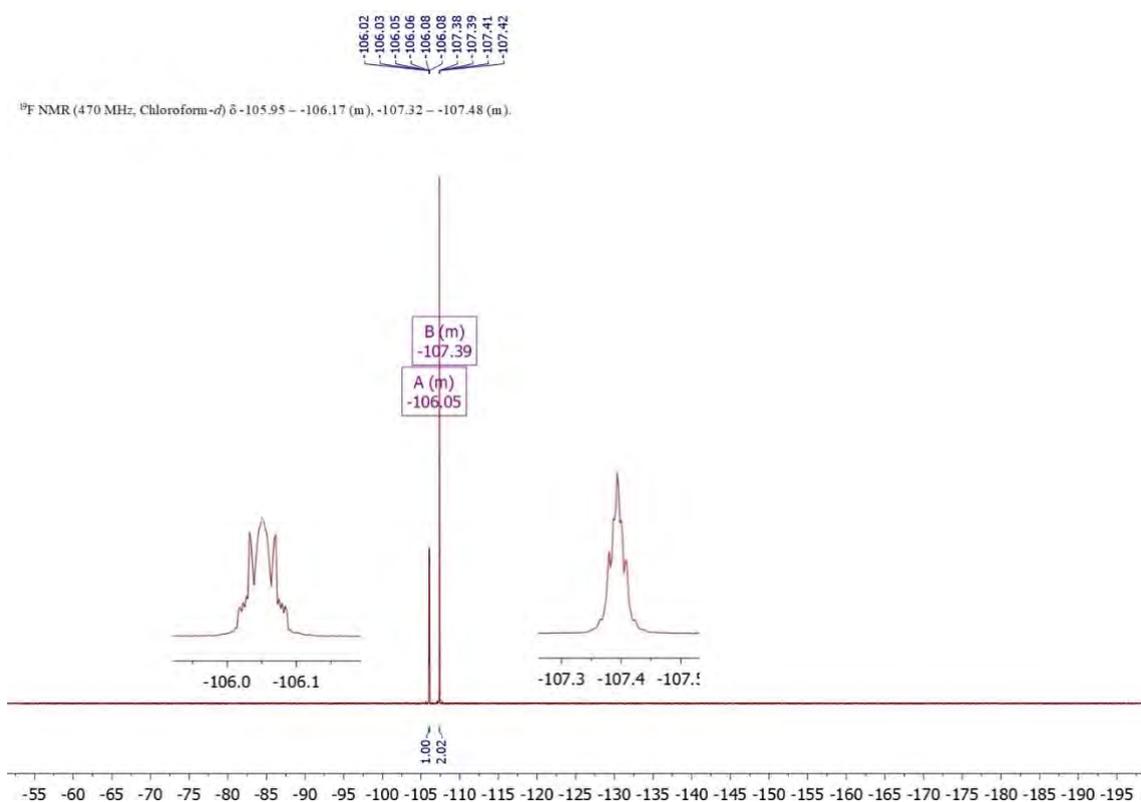
$^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of $[\text{P}(\text{NEt}_2)_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4]\text{Cl}$ (**18-Cl**) in CDCl_3 .



^1H NMR Spectra of 2,4,6,2',4',6'-hexafluorobiphenyl in CDCl_3 .



^{19}F NMR Spectra of 2,4,6,2',4',6'-hexafluorobiphenyl in CDCl_3 .



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