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Supporting Information for:

# Synthesis of an Oxygen-bridged P/B Frustrated Lewis Pair and Its Reactivity Against Small Molecules

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## General Experimental methods

Solvents were dried by reflux under $N_2$ over sodium or $CaH_2$ and freshly distilled prior to use. Air-sensitive compounds were handled under a $N_2$ atmosphere using standard Schlenk and glovebox techniques. NMR spectra were recorded on Bruker SPECT NMR (400 MHz for $^{1}H$, 376 MHz for $^{19}F$, 100 MHz for $^{13}C$) and Bruker DMX500 NMR (500 MHz for $^{1}H$, 160 MHz for $^{11}B$) spectrometers. Most assignments were based on a series of 2D NMR experiments. HRMS analyses were performed at Bruker micrOTOF II. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC 1843771-1843777 (compound **2-8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. $Mes_2P(O)H$ (Mes = 2,4,6-trimethylphenyl),[1] $ClB(C_6F_5)_2$[2] and $HB(C_6F_5)_2$[2] were prepared as reported.

## NMR spectra

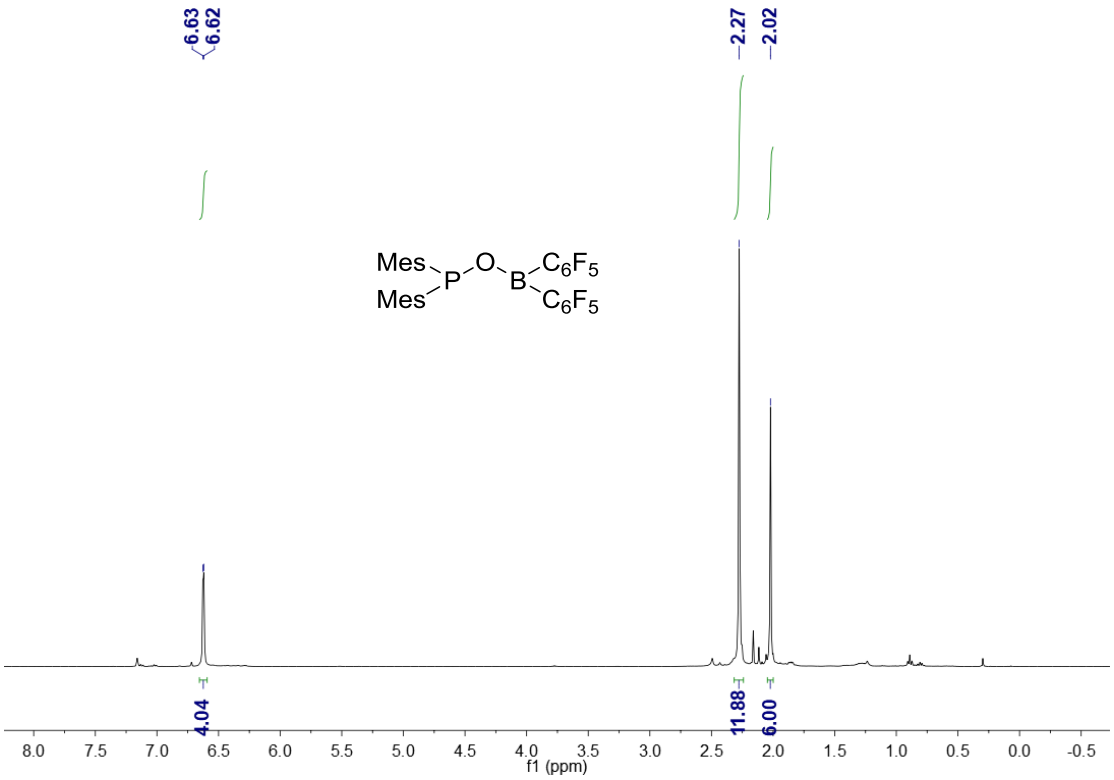


Figure S1. $^{1}$H NMR spectrum of **1** in $C_6D_6$

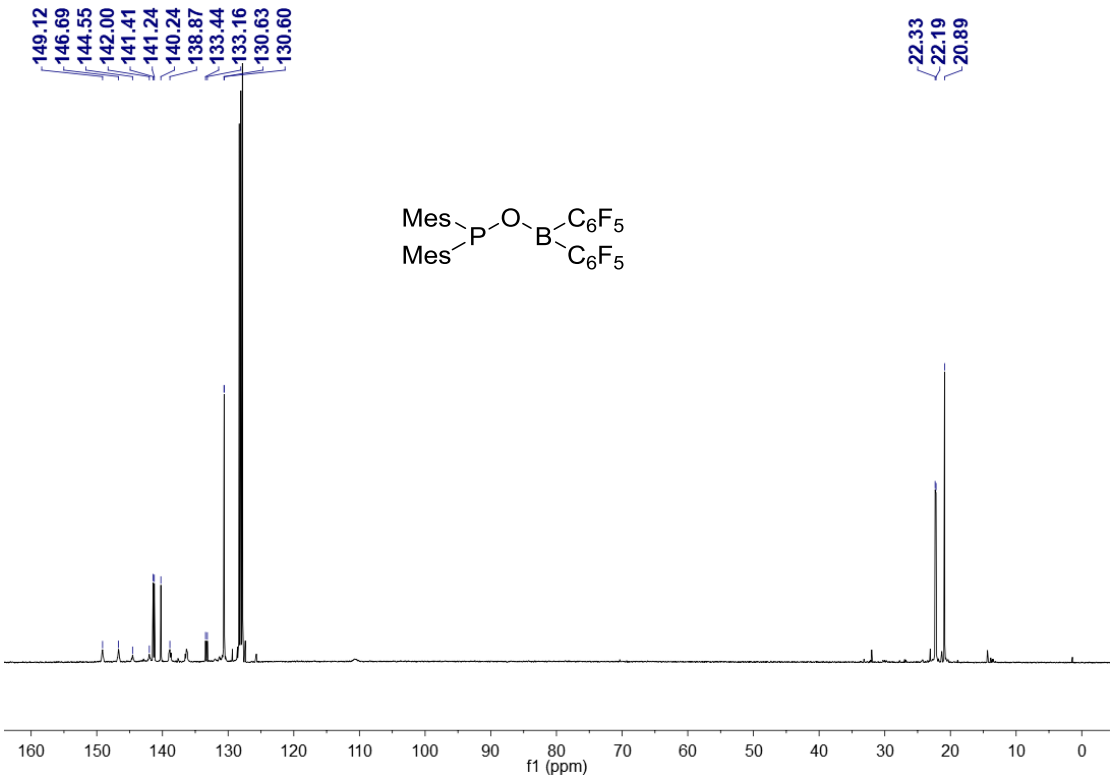


Figure S2. $^{13}$C NMR spectrum of **1** in $C_6D_6$

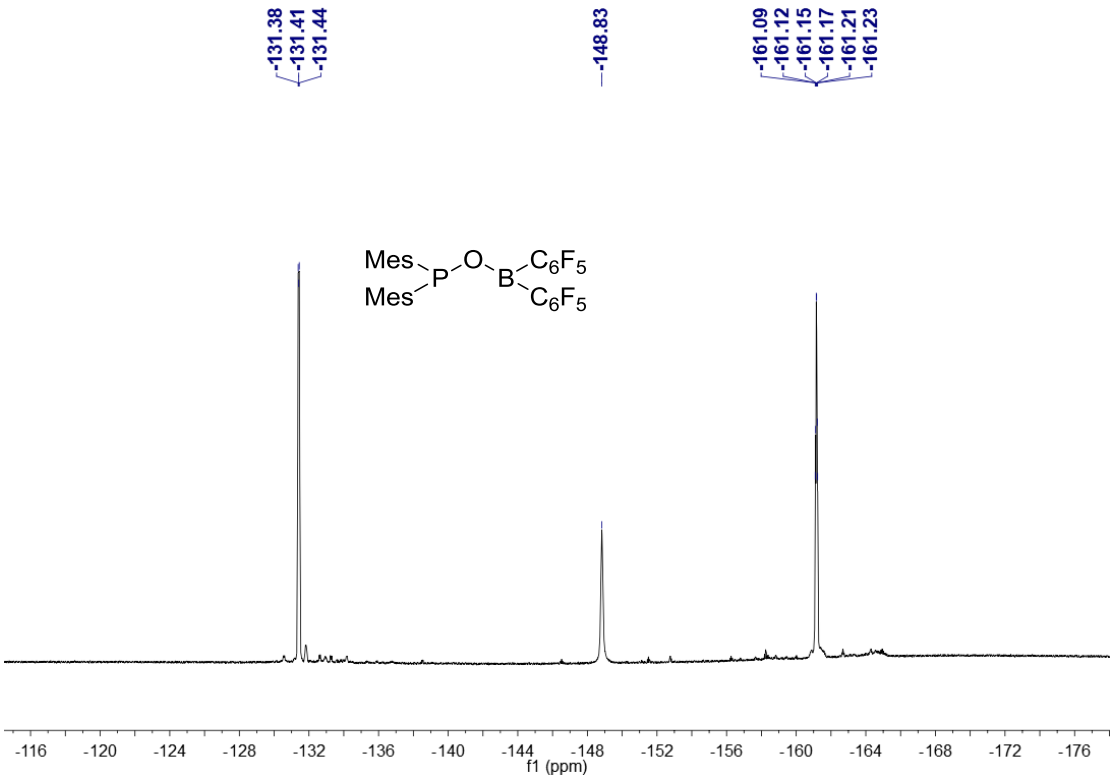


Figure S3. $^{19}F$ NMR spectrum of **1** in $C_6D_6$

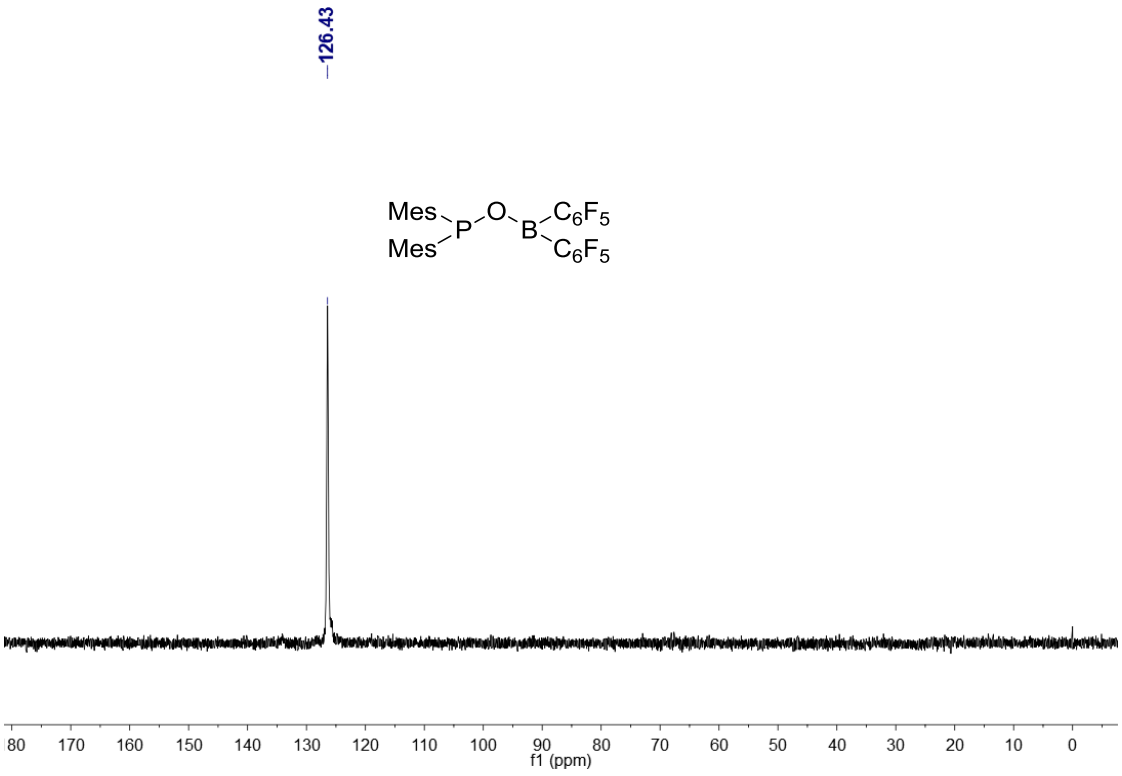


Figure S4. $^{31}P$ NMR spectrum of **1** in $C_6D_6$

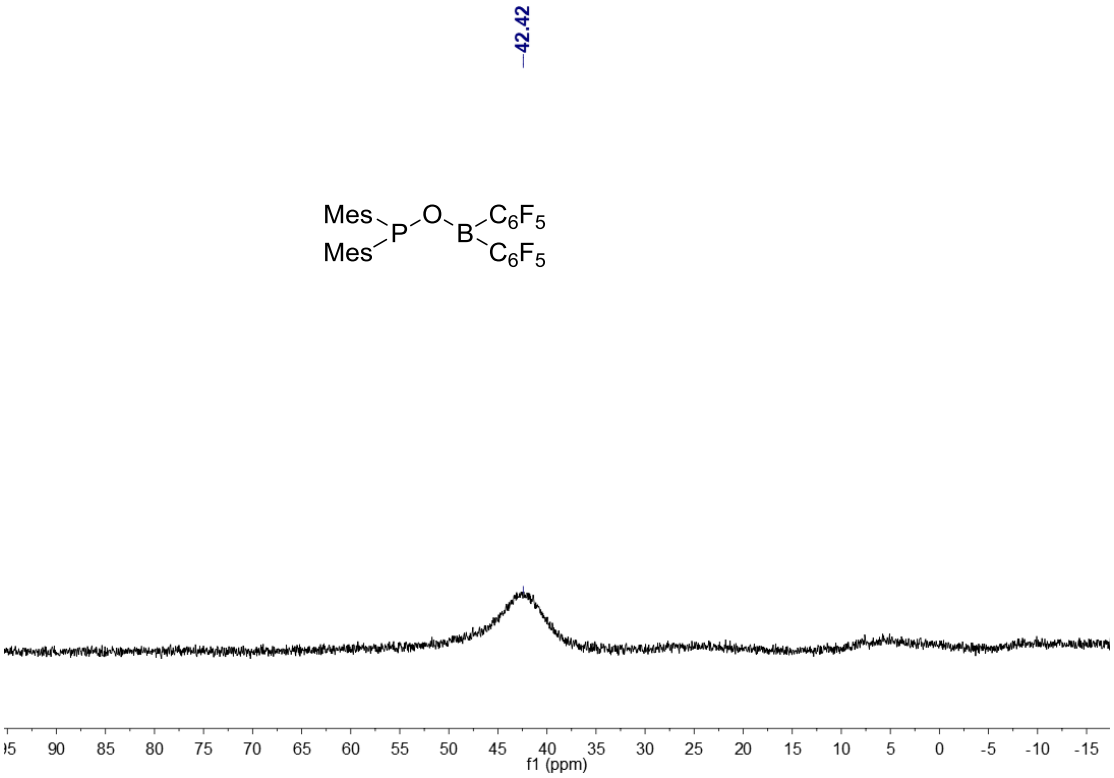


Figure S5. $^{11}B$ NMR spectrum of **1** in $C_6D_6$

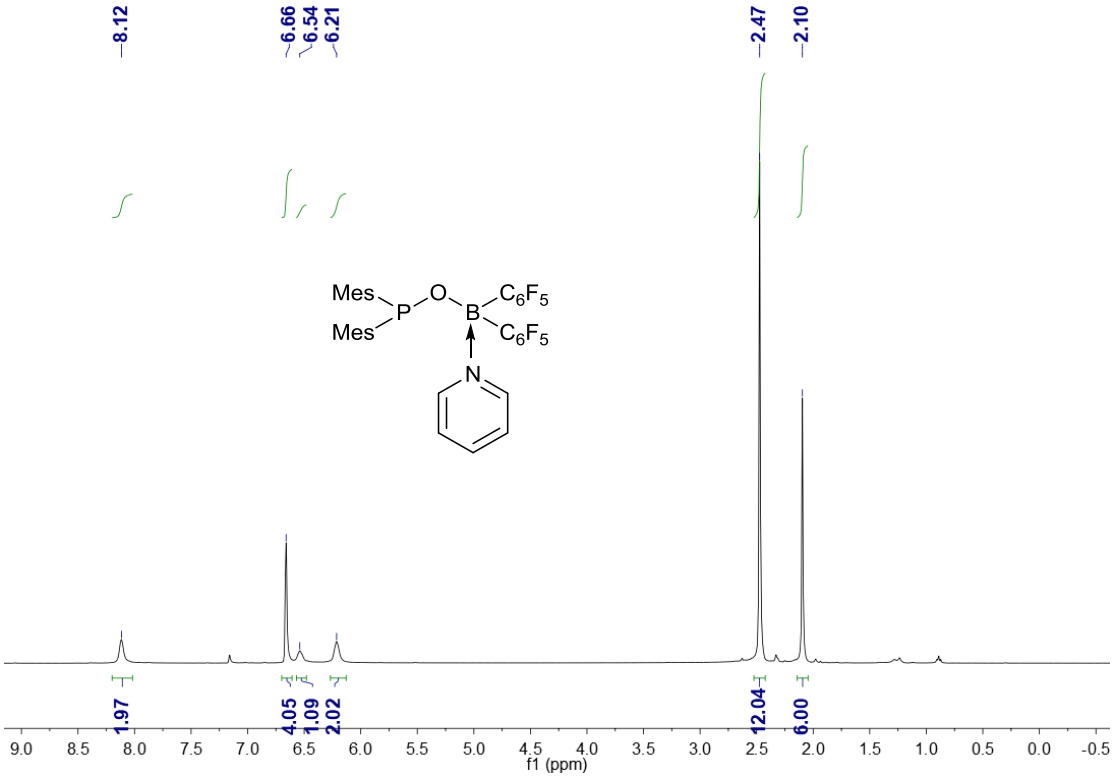


Figure S6. $^{1}H$ NMR spectrum of **2** in $C_6D_6$

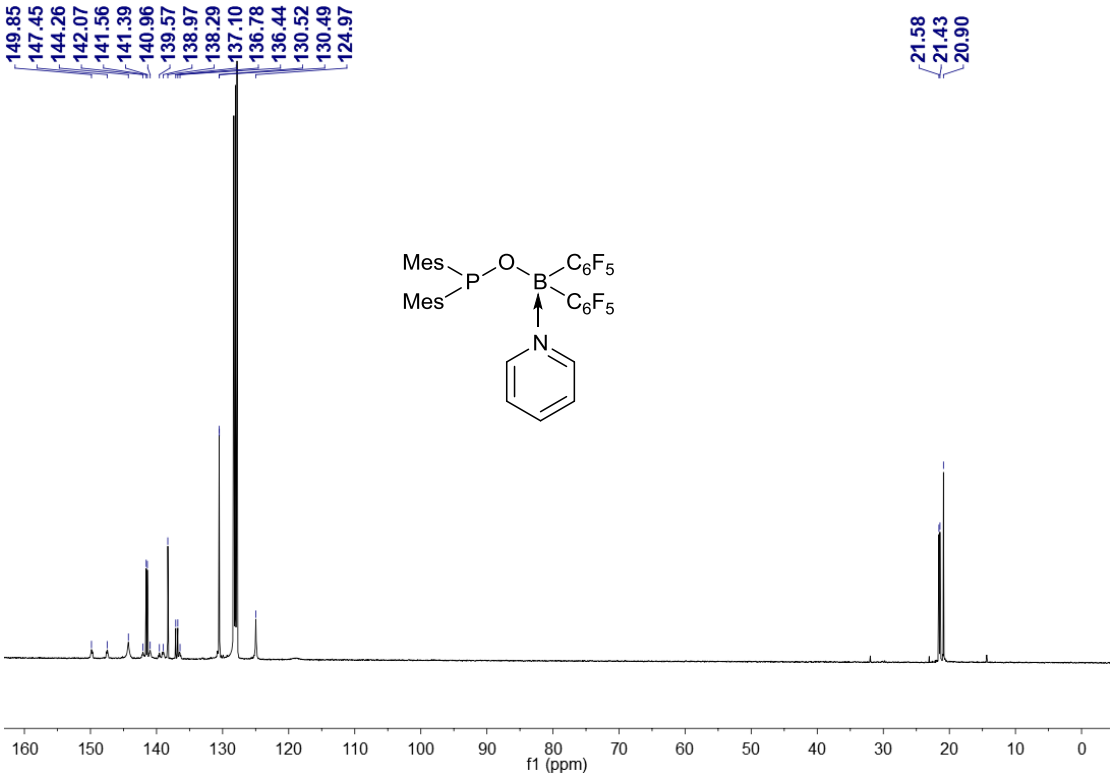


Figure S7. $^{13}C$ NMR spectrum of **2** in $C_6D_6$

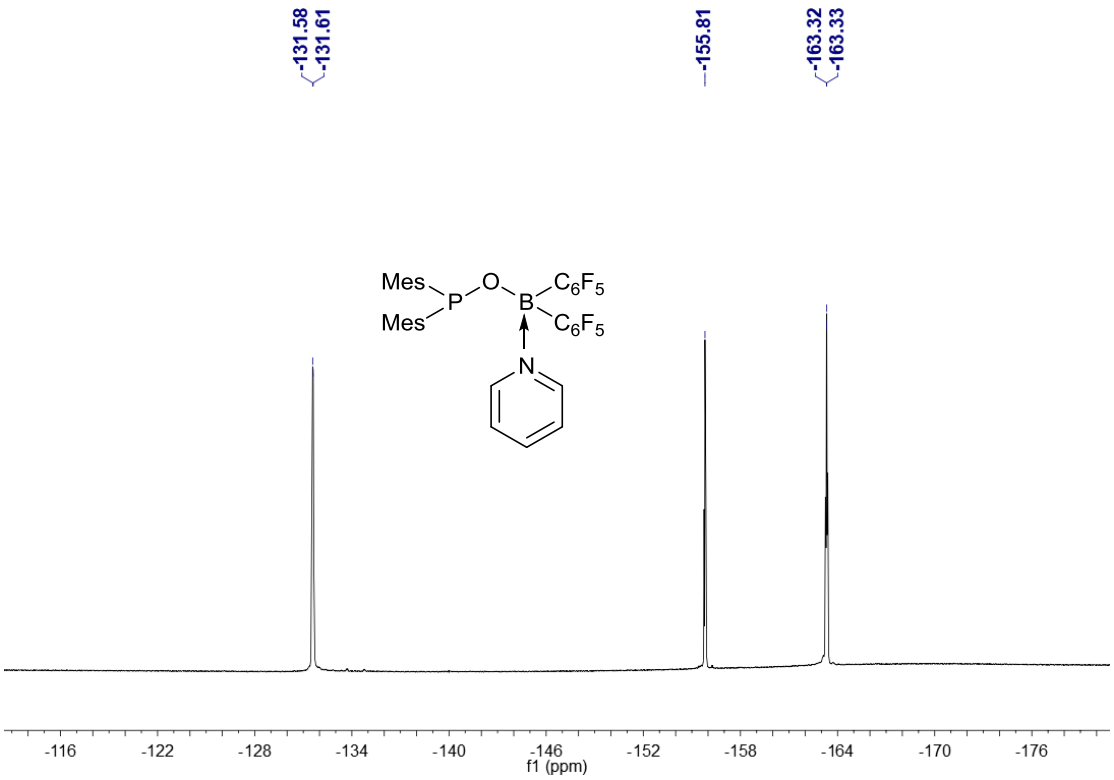


Figure S8. $^{19}F$ NMR spectrum of **2** in $C_6D_6$

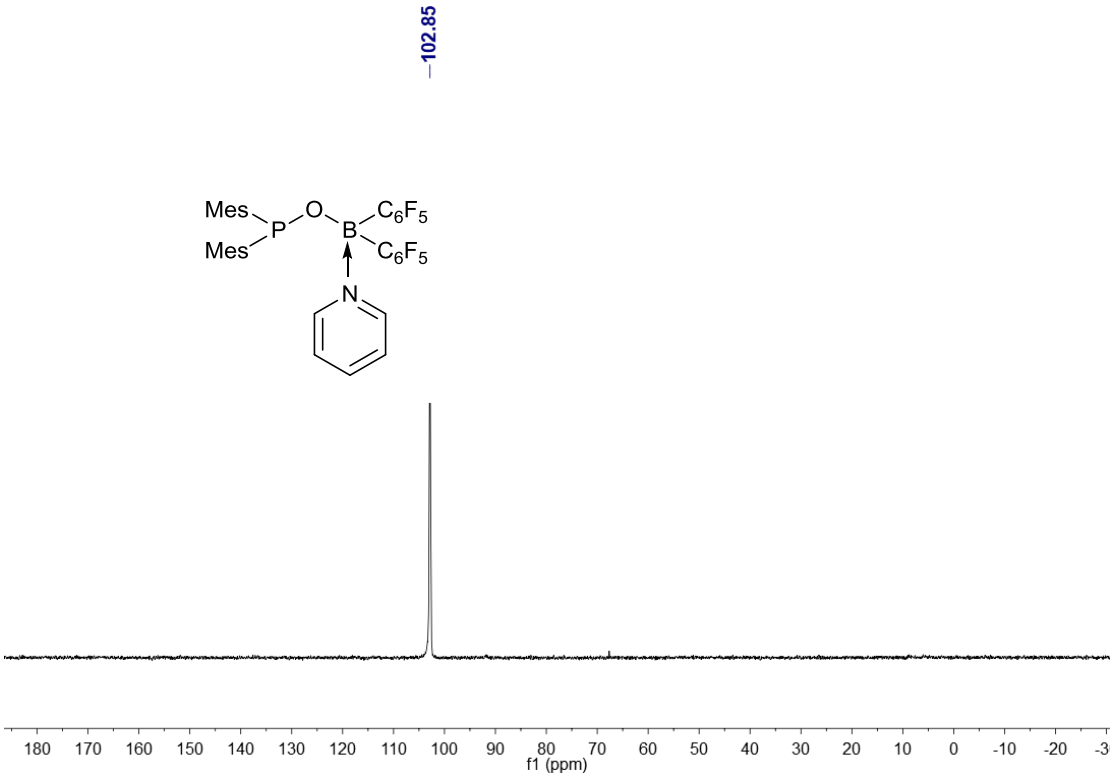


Figure S9. $^{31}P$ NMR spectrum of **2** in $C_6D_6$

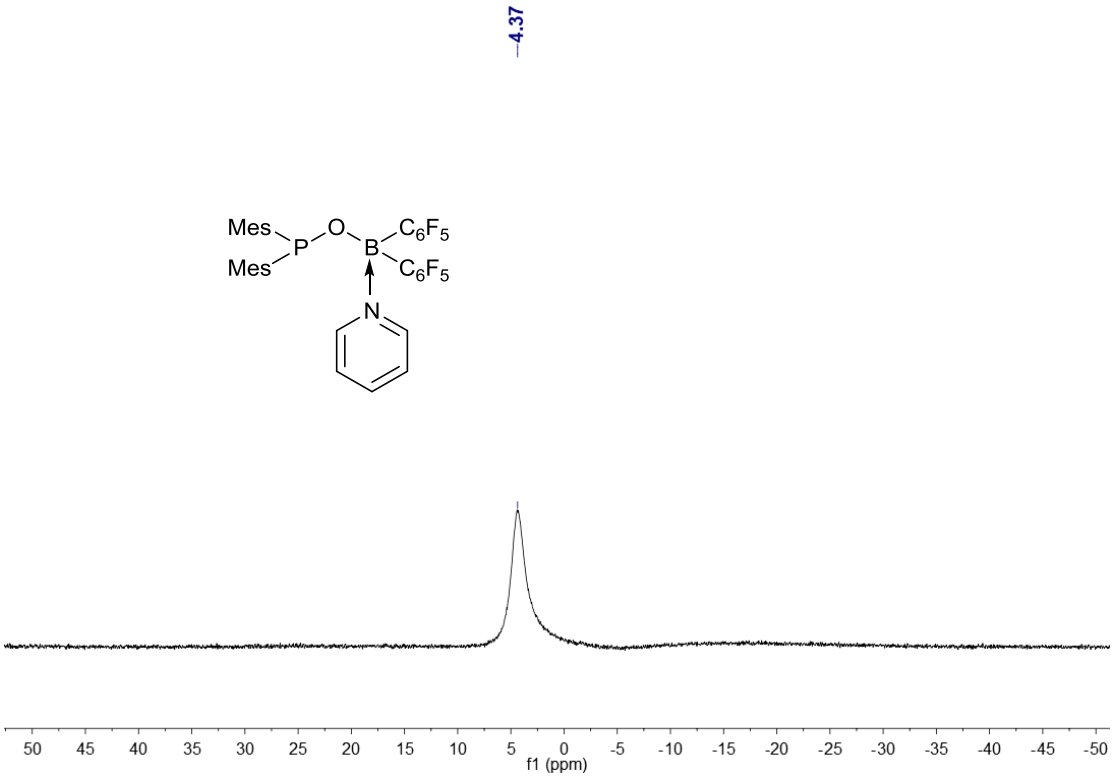


Figure S10. $^{11}B$ NMR spectrum of **2** in $C_6D_6$

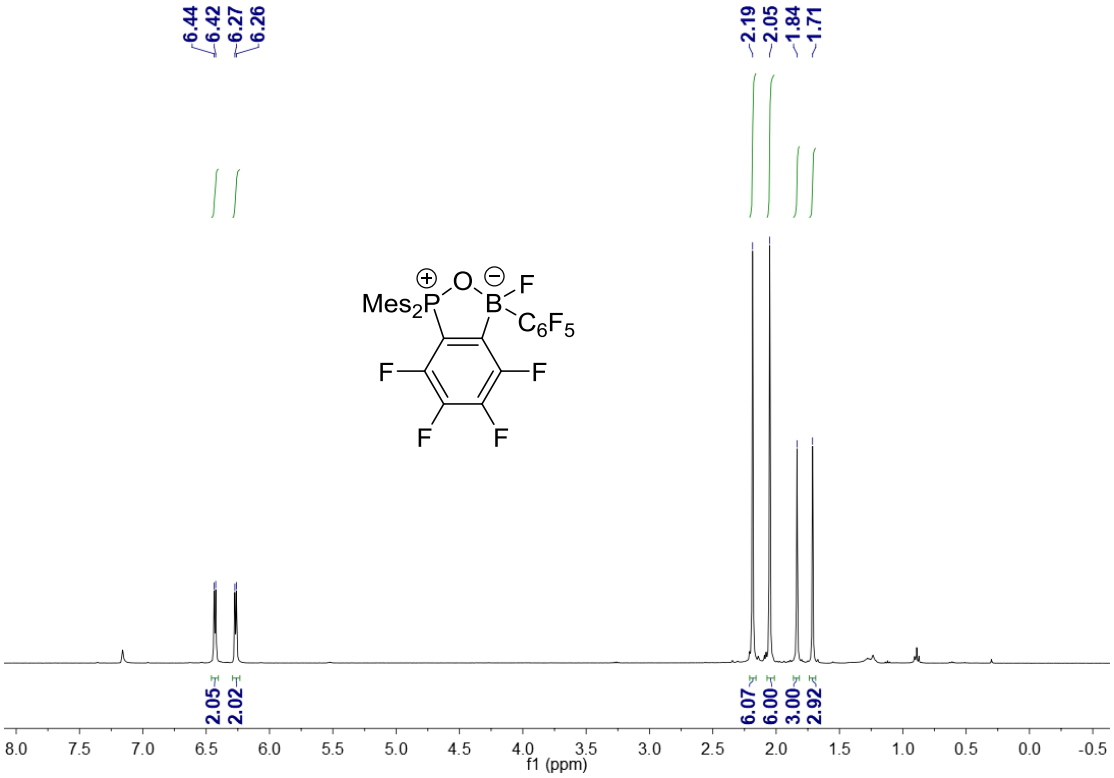


Figure S11. $^{1}$H NMR spectrum of **3** in $C_6D_6$

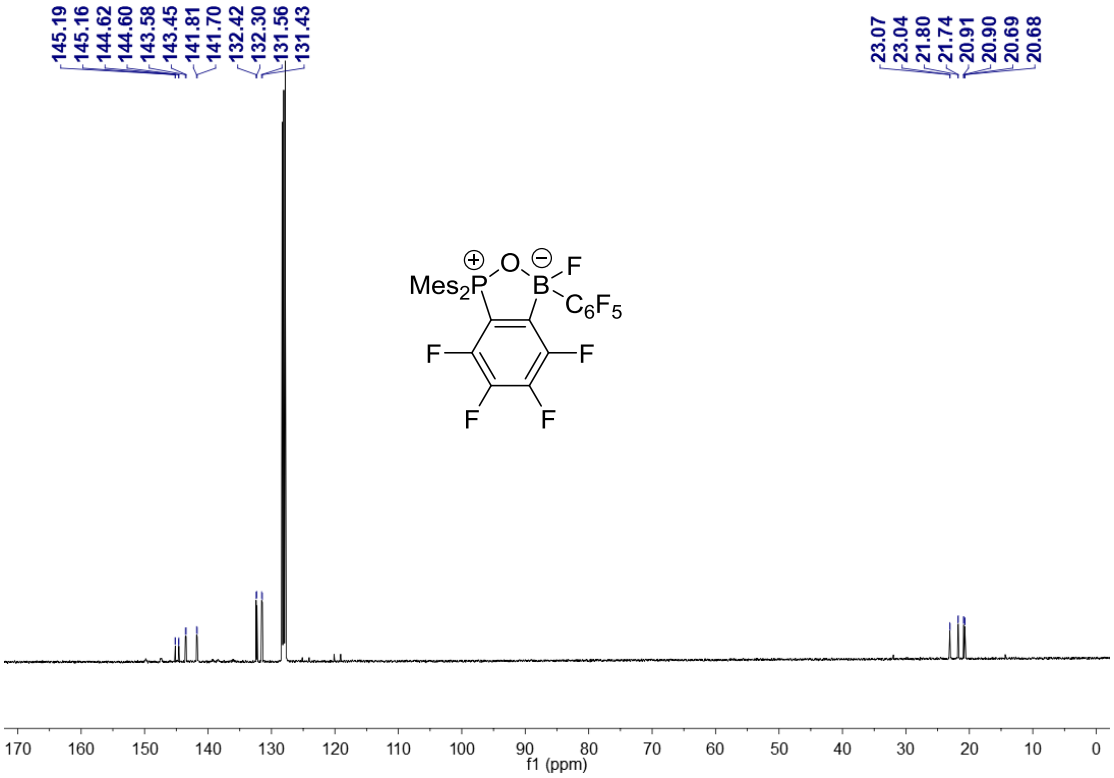


Figure S12. $^{13}$C NMR spectrum of **3** in $C_6D_6$

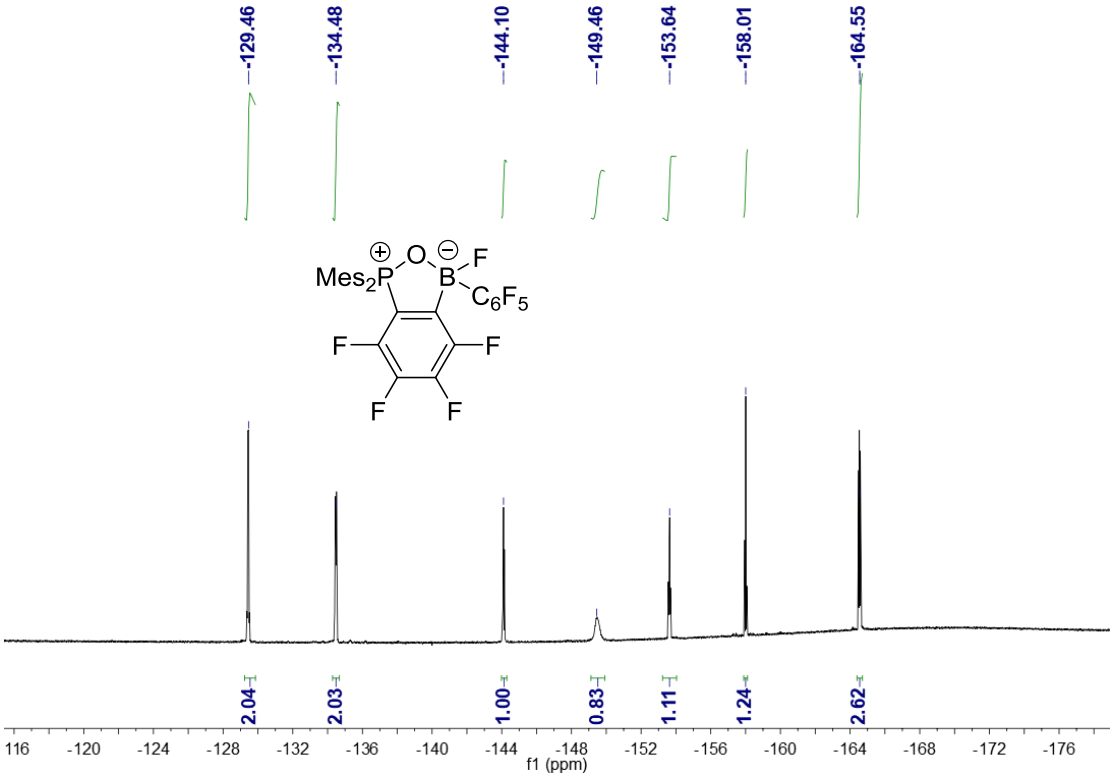


Figure S13. $^{19}F$ NMR spectrum of **3** in $C_6D_6$

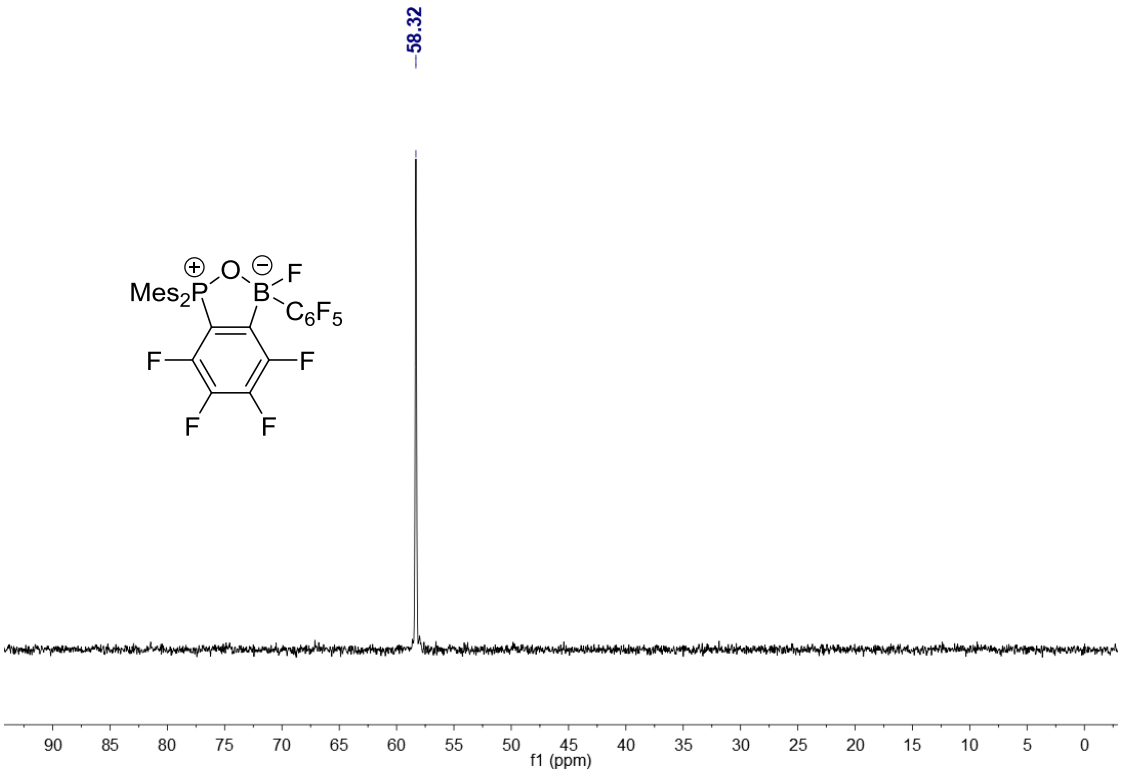


Figure S14. $^{31}P$ NMR spectrum of **3** in $C_6D_6$

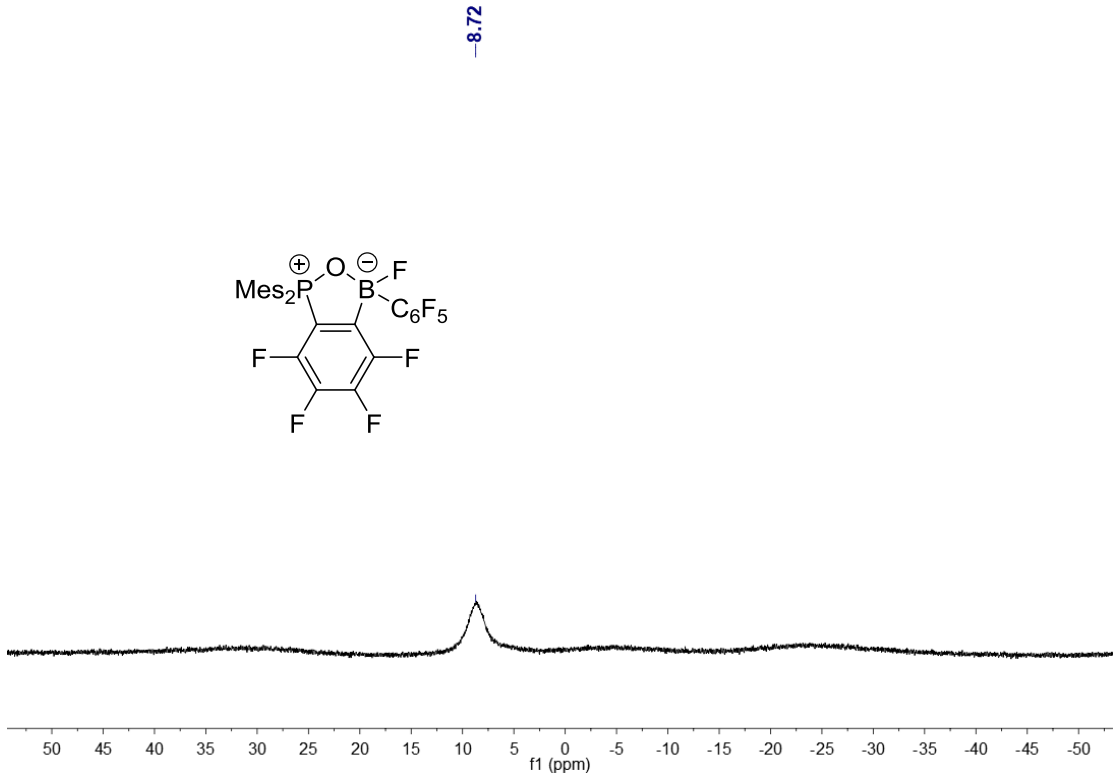


Figure S15. $^{11}$B NMR spectrum of **3** in $C_6D_6$

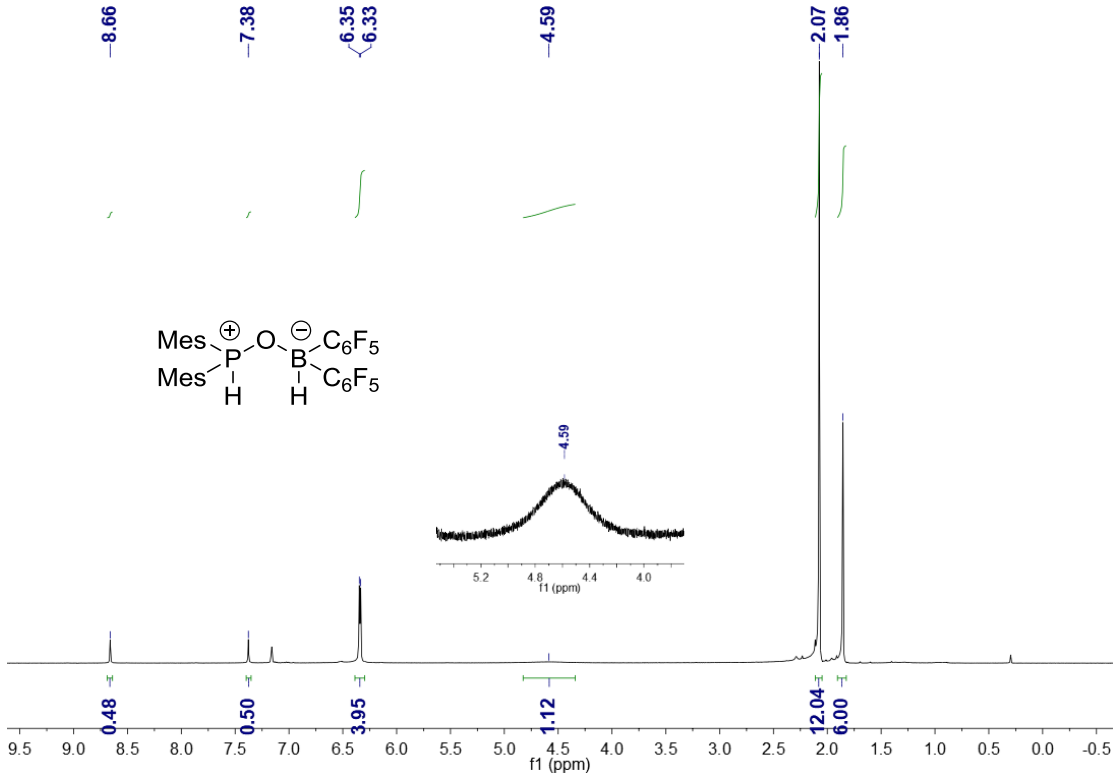


Figure S16. $^{1}$H NMR spectrum of **4** in $C_6D_6$

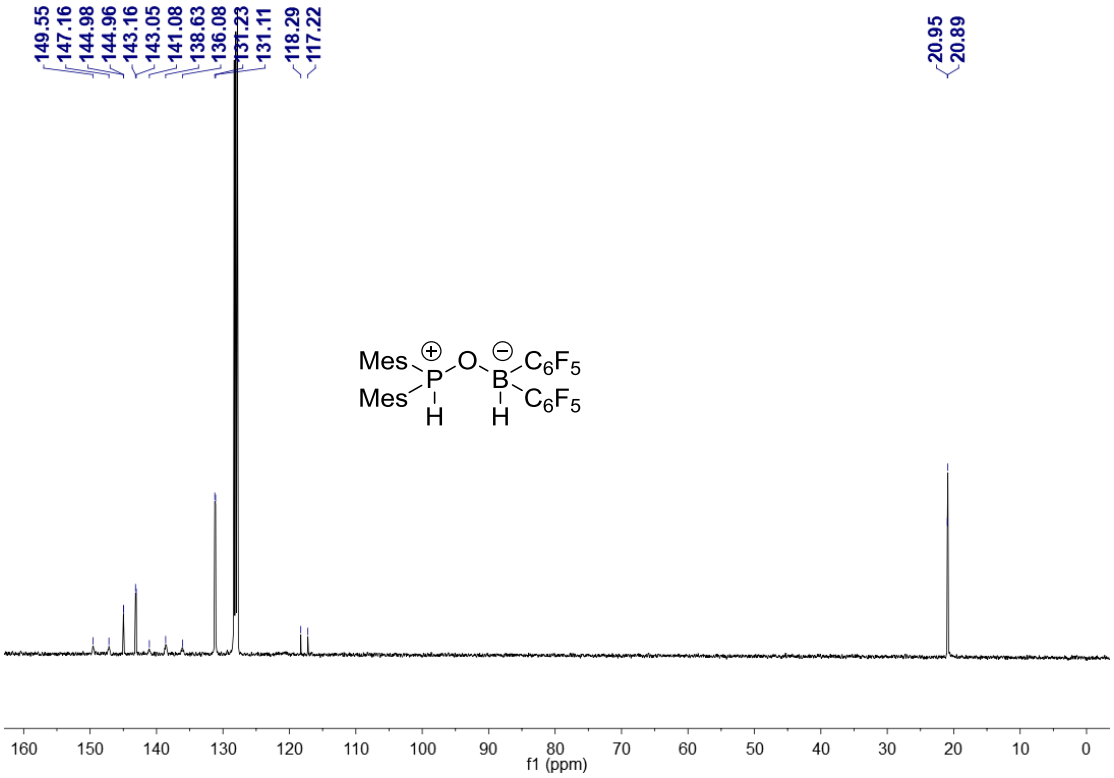


Figure S17. $^{13}C$ NMR spectrum of **4** in $C_6D_6$

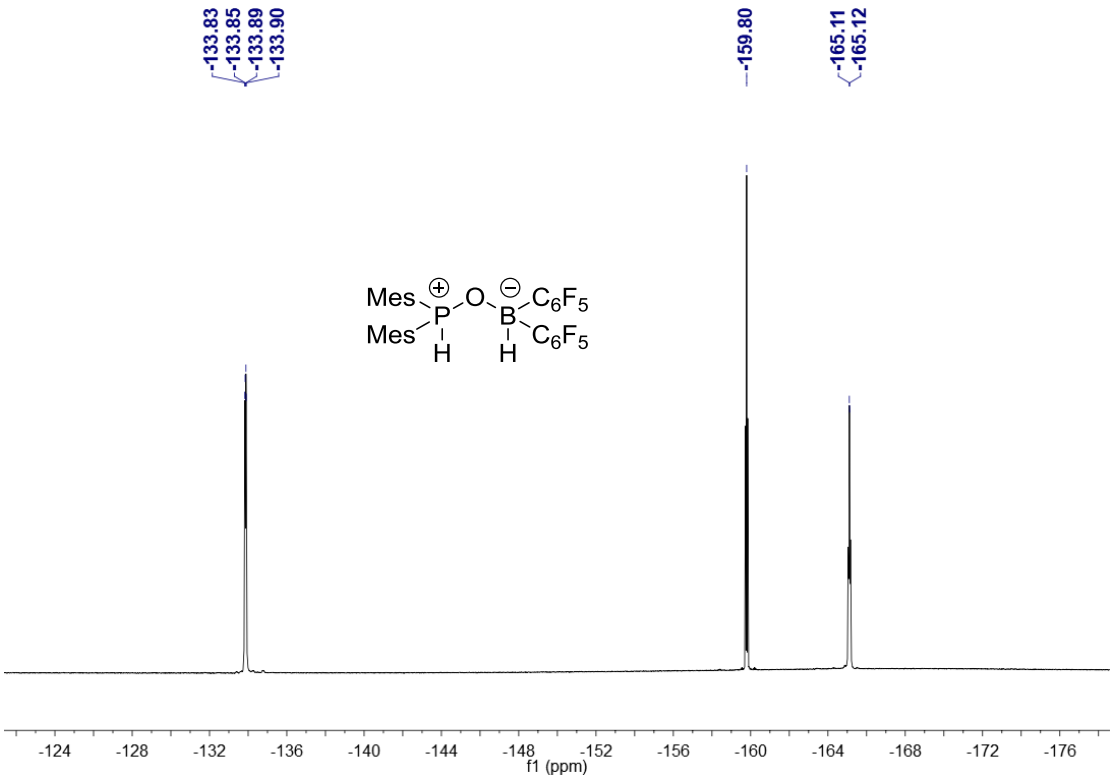


Figure S18. $^{19}F$ NMR spectrum of **4** in $C_6D_6$

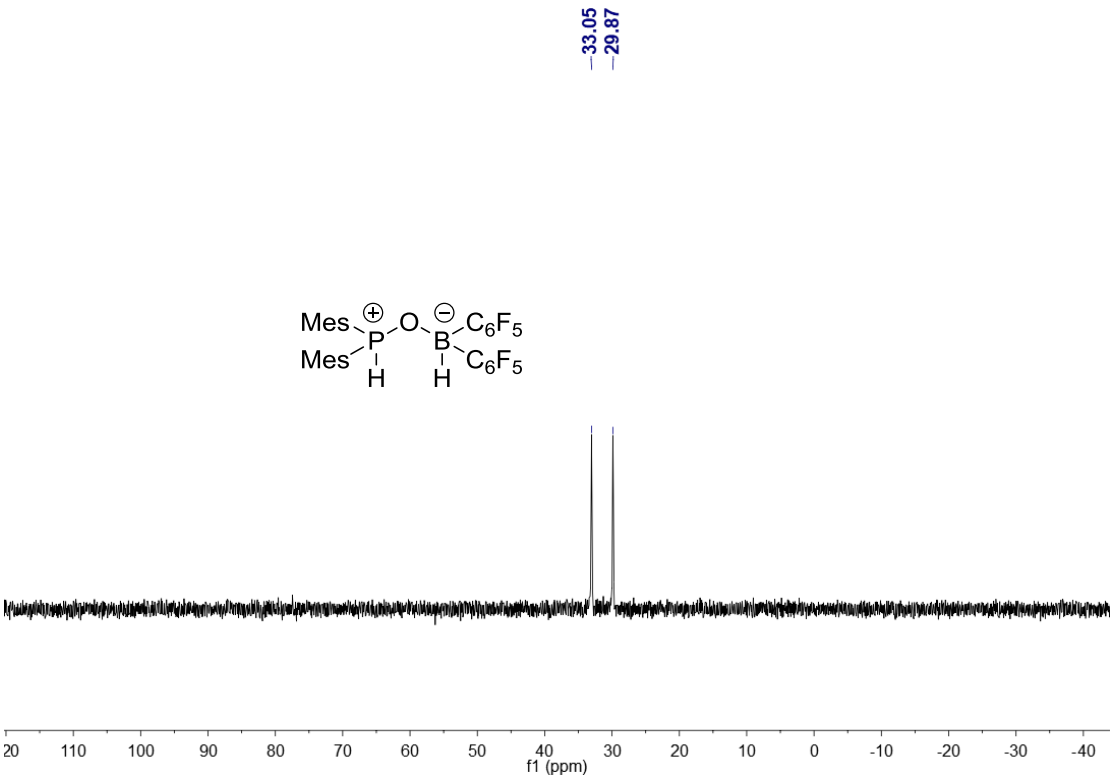


Figure S19. $^{31}P$ NMR spectrum of **4** in $C_6D_6$

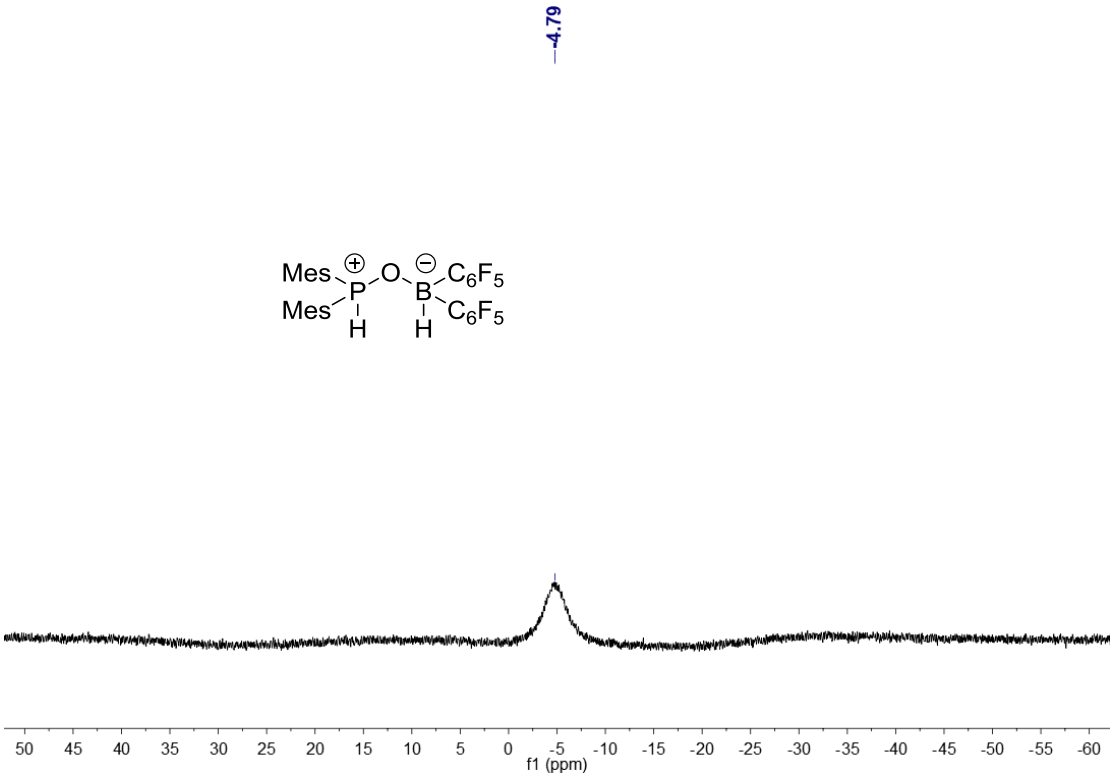


Figure S20. $^{11}B$ NMR spectrum of **4** in $C_6D_6$

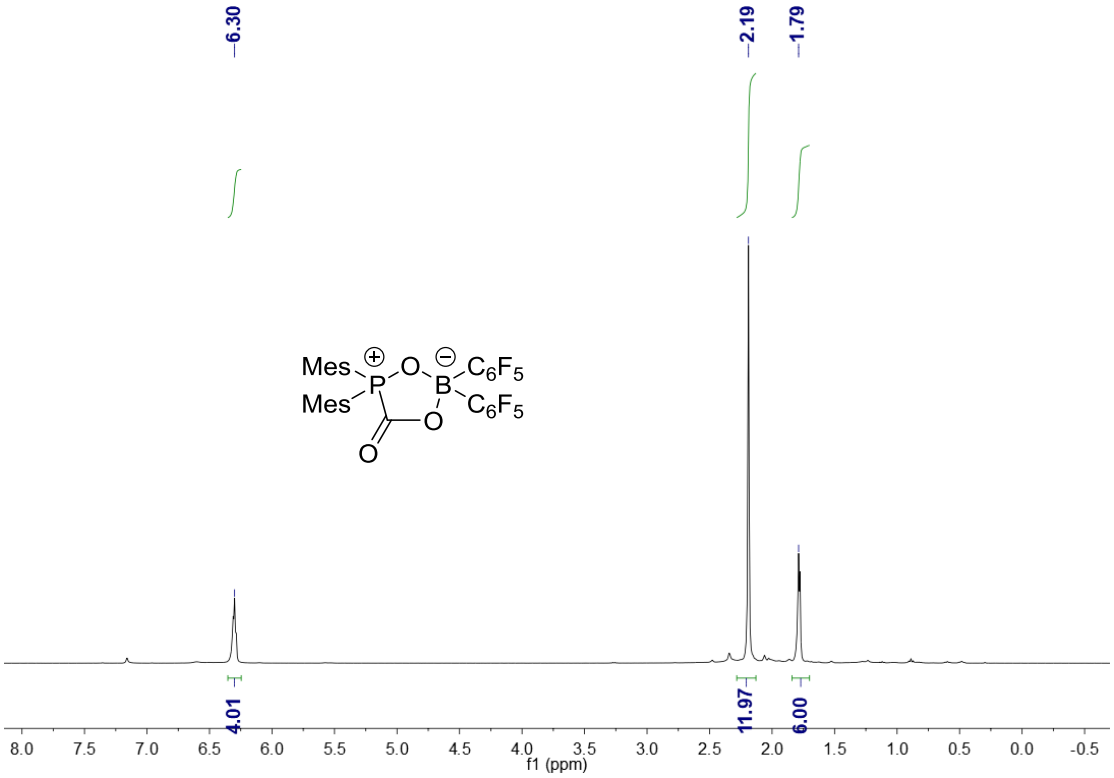


Figure S21. $^{1}$H NMR spectrum of **5** in $C_6D_6$

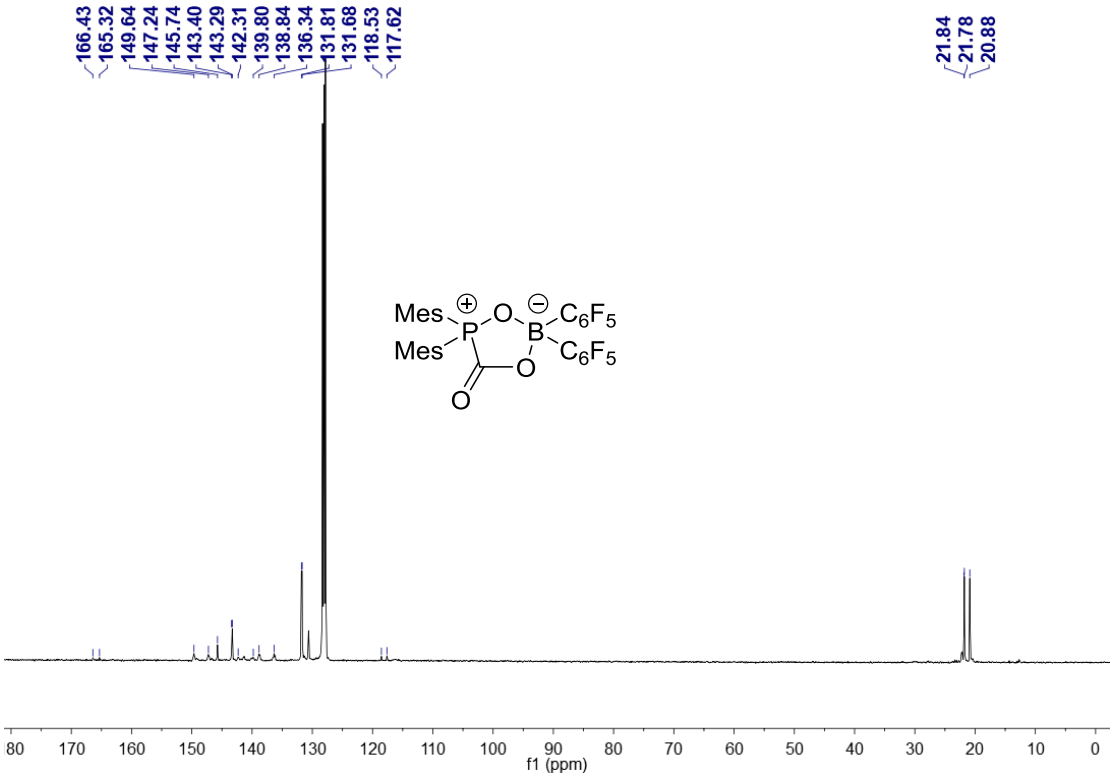


Figure S22. $^{13}$C NMR spectrum of **5** in $C_6D_6$

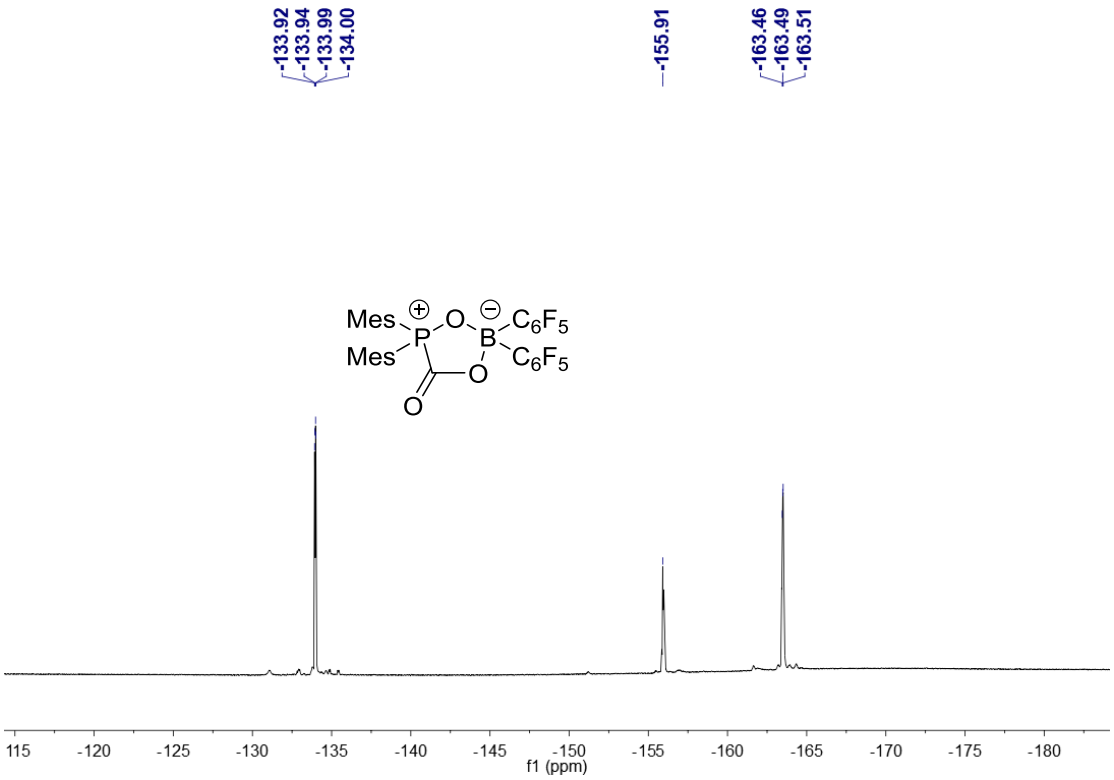


Figure S23. $^{19}F$ NMR spectrum of **5** in $C_6D_6$

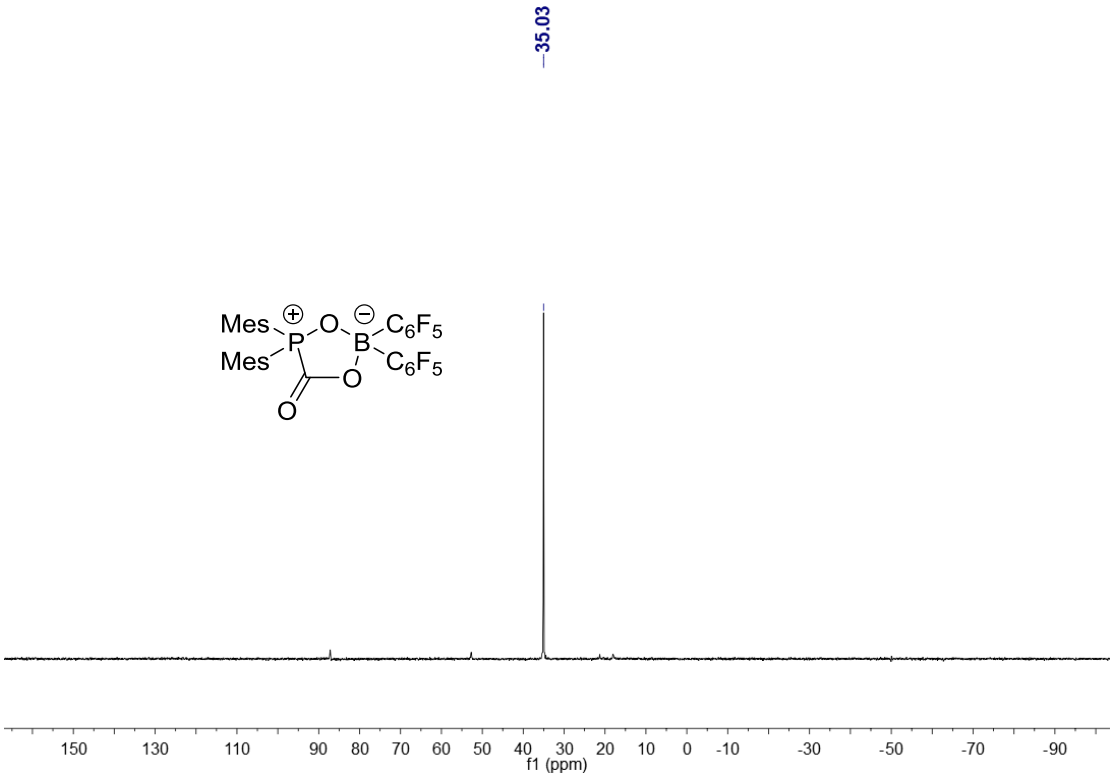


Figure S24. $^{31}P$ NMR spectrum of **5** in $C_6D_6$

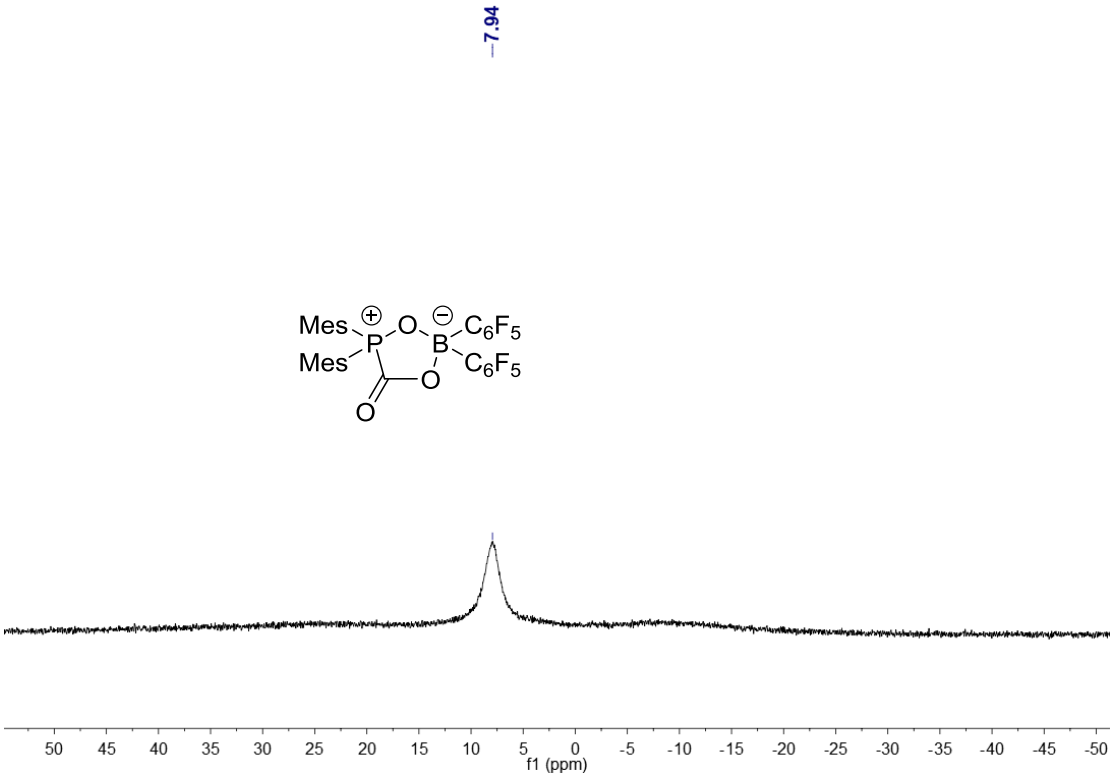


Figure S25. $^{11}B$ NMR spectrum of **5** in $C_6D_6$

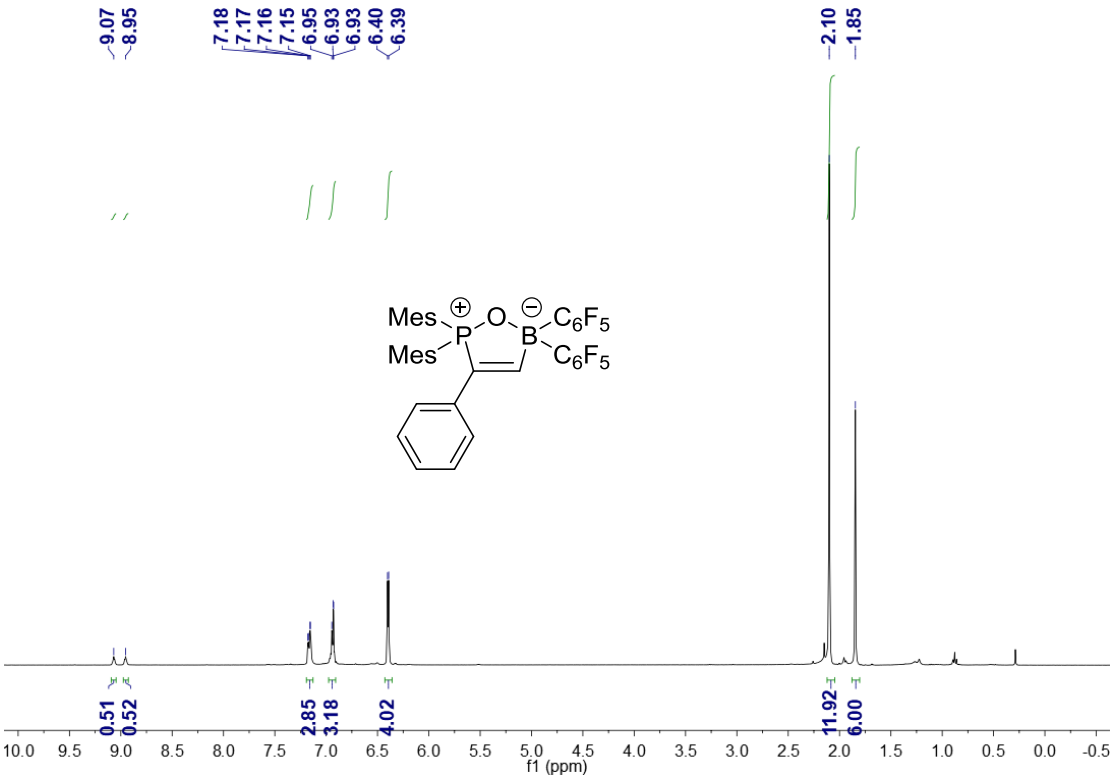


Figure S26. $^{1}H$ NMR spectrum of **6** in $C_6D_6$

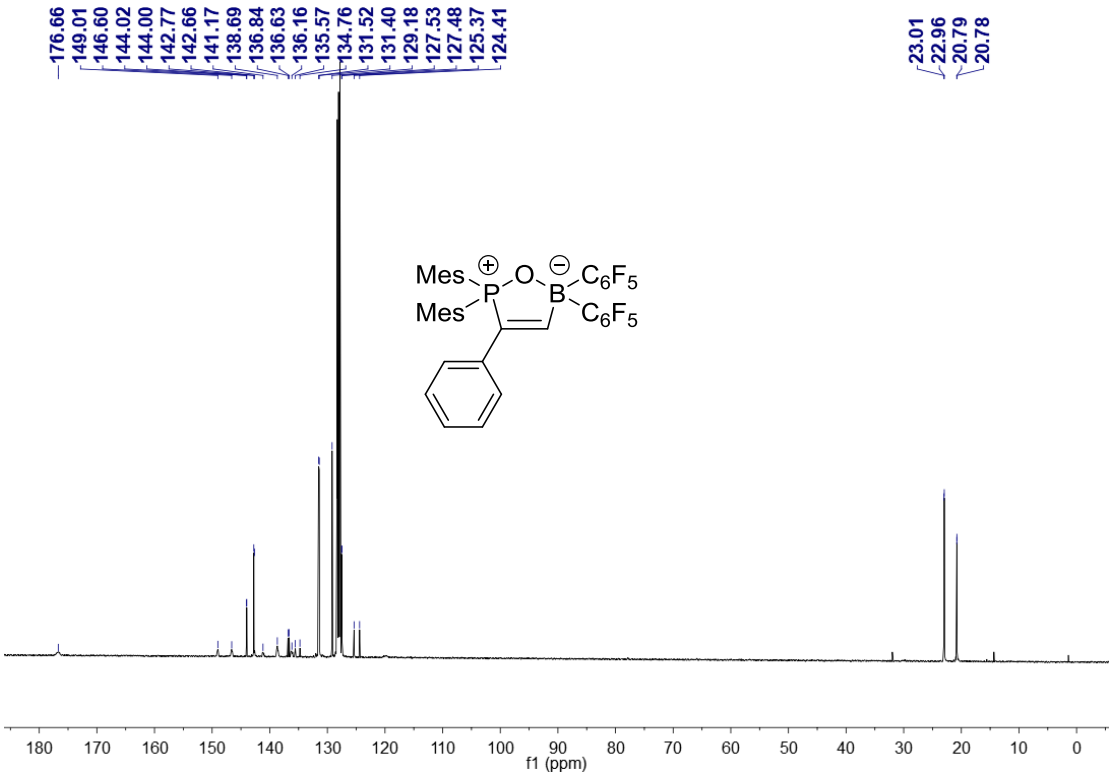


Figure S27. $^{13}C$ NMR spectrum of **6** in $C_6D_6$

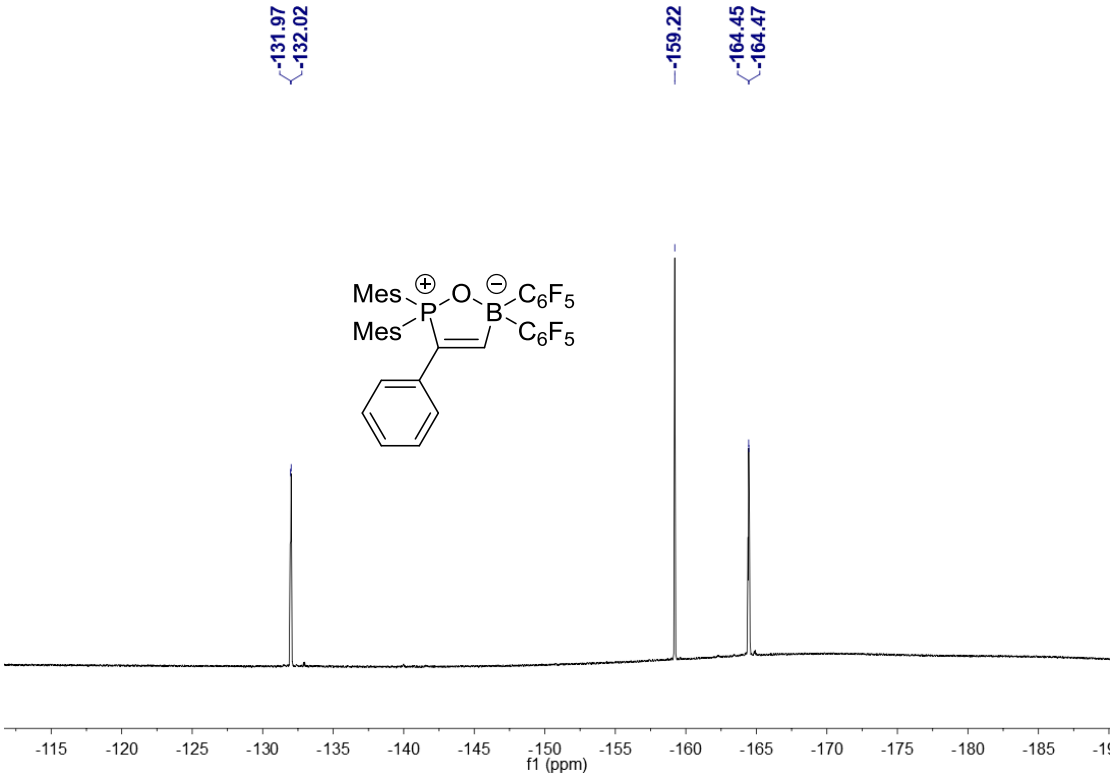


Figure S28. $^{19}F$ NMR spectrum of **6** in $C_6D_6$

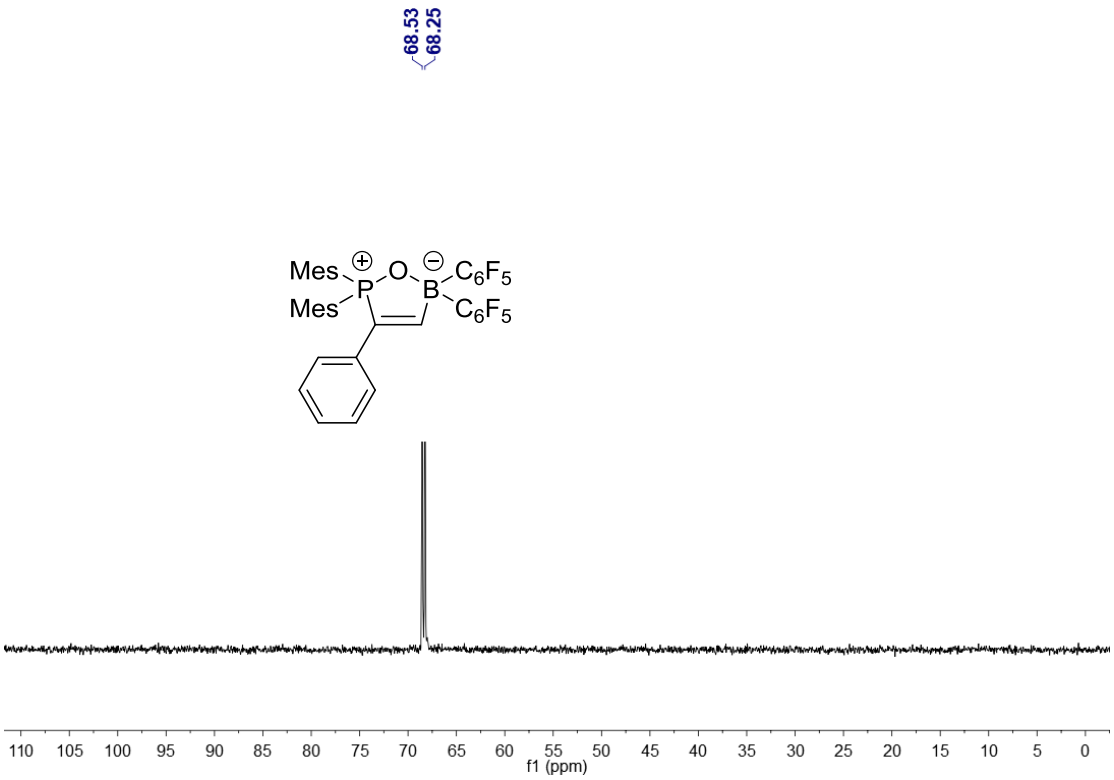


Figure S29. $^{31}P$ NMR spectrum of **6** in $C_6D_6$

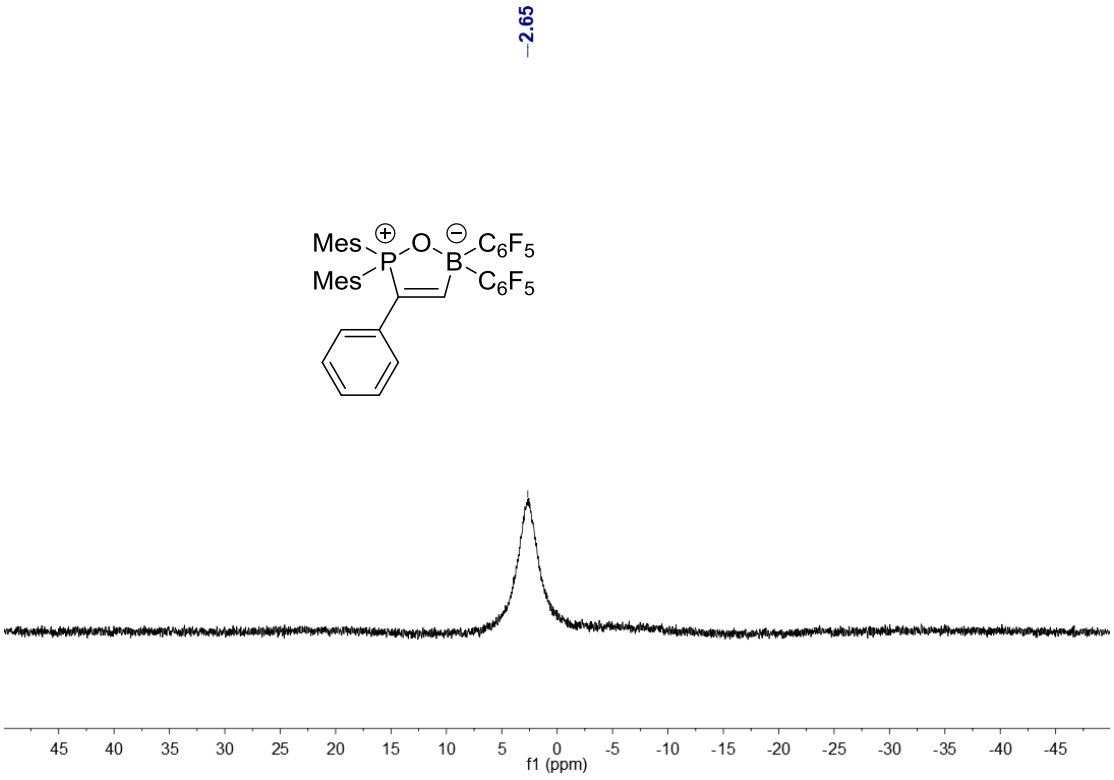


Figure S30. $^{11}B$ NMR spectrum of **6** in $C_6D_6$

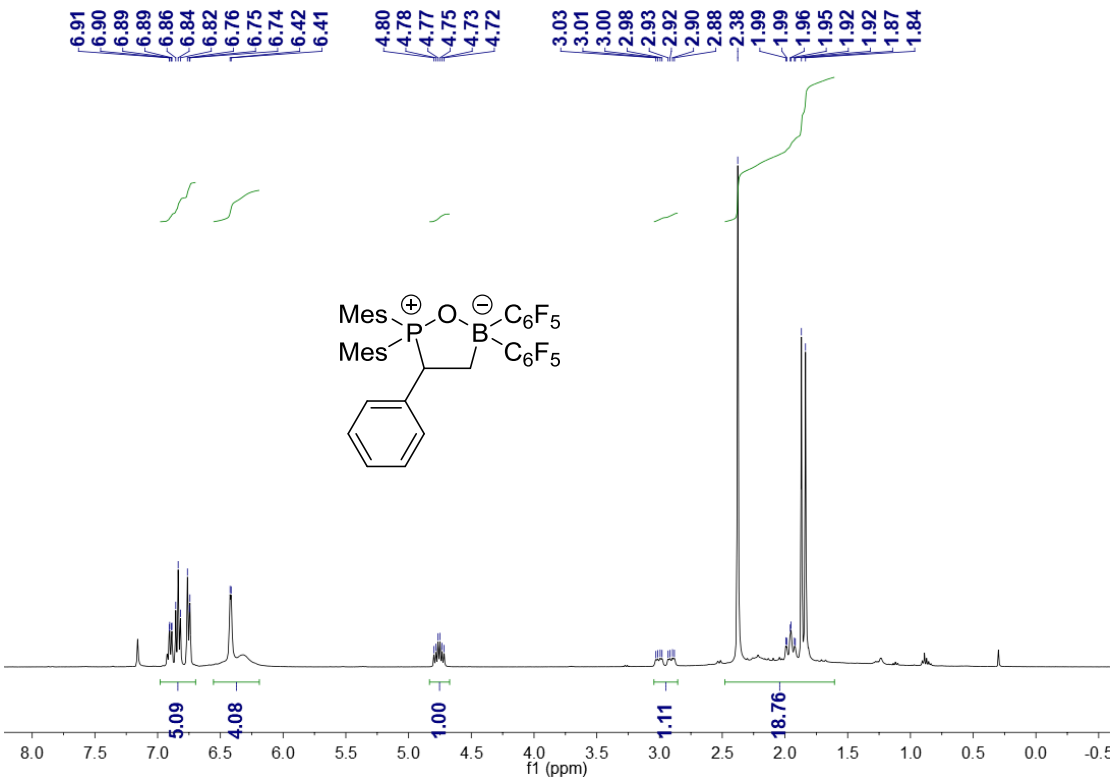


Figure S31. $^{1}$H NMR spectrum of **7** in $C_6D_6$

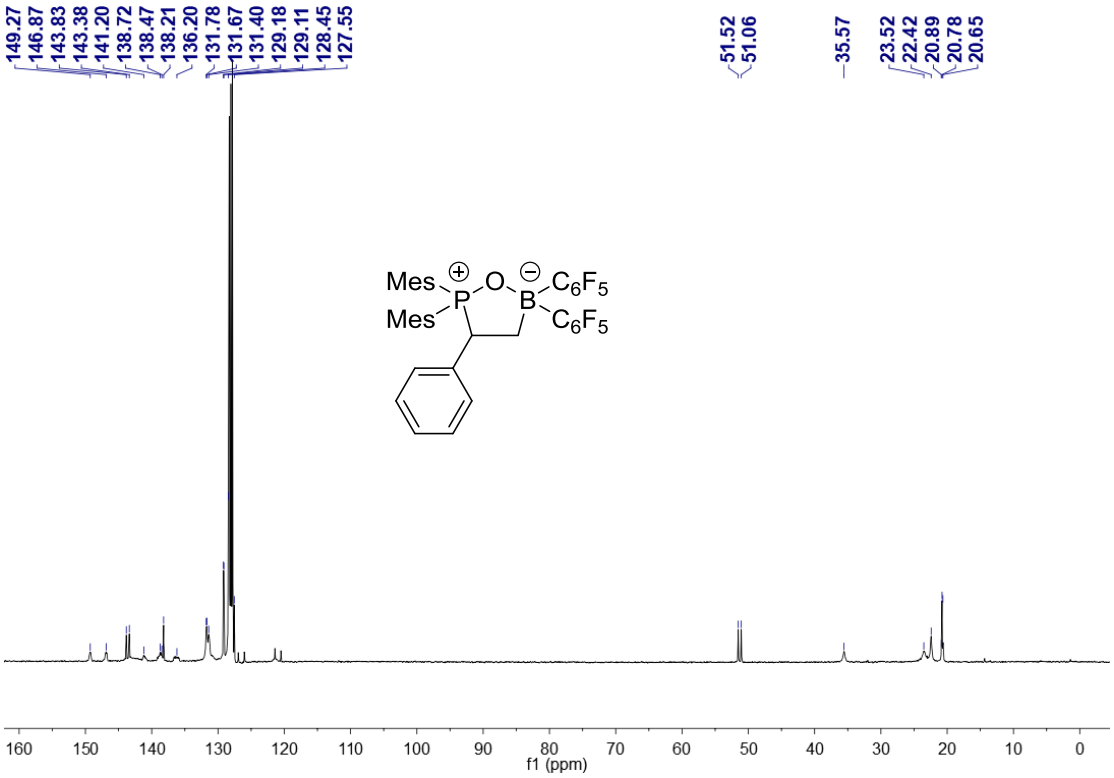


Figure S32. $^{13}$C NMR spectrum of **7** in $C_6D_6$

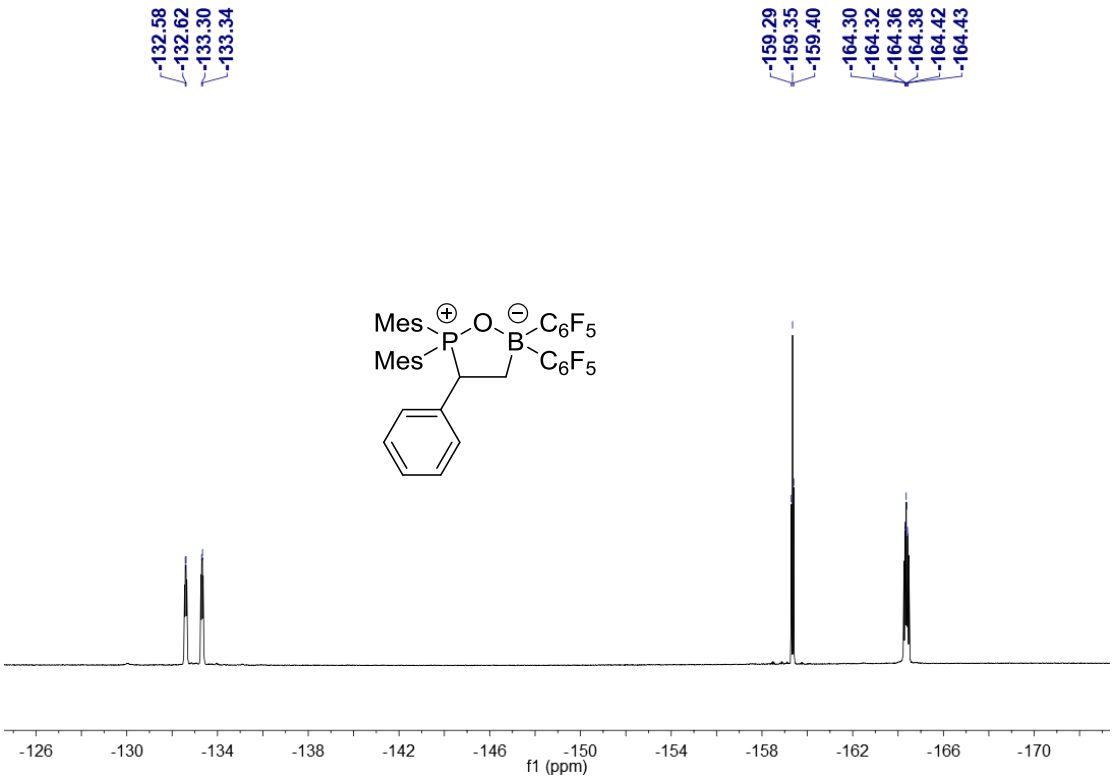


Figure S33. $^{19}F$ NMR spectrum of **7** in $C_6D_6$

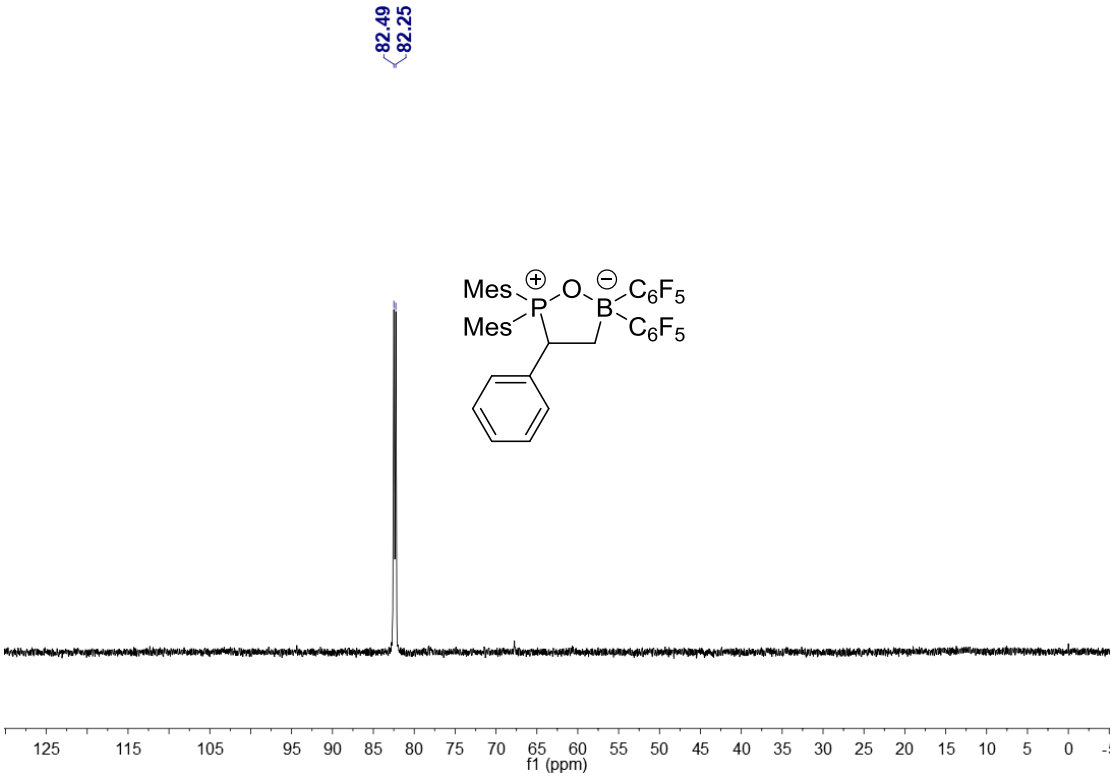


Figure S34. $^{31}P$ NMR spectrum of **7** in $C_6D_6$

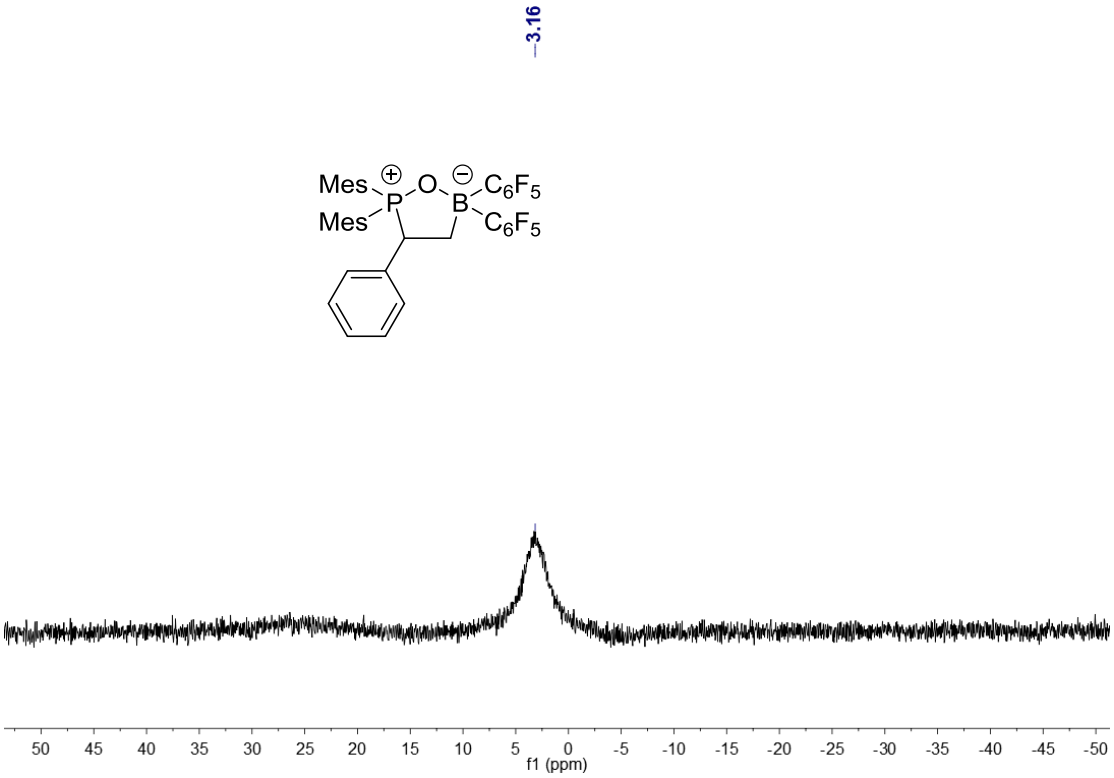


Figure S35. $^{11}B$ NMR spectrum of **7** in $C_6D_6$

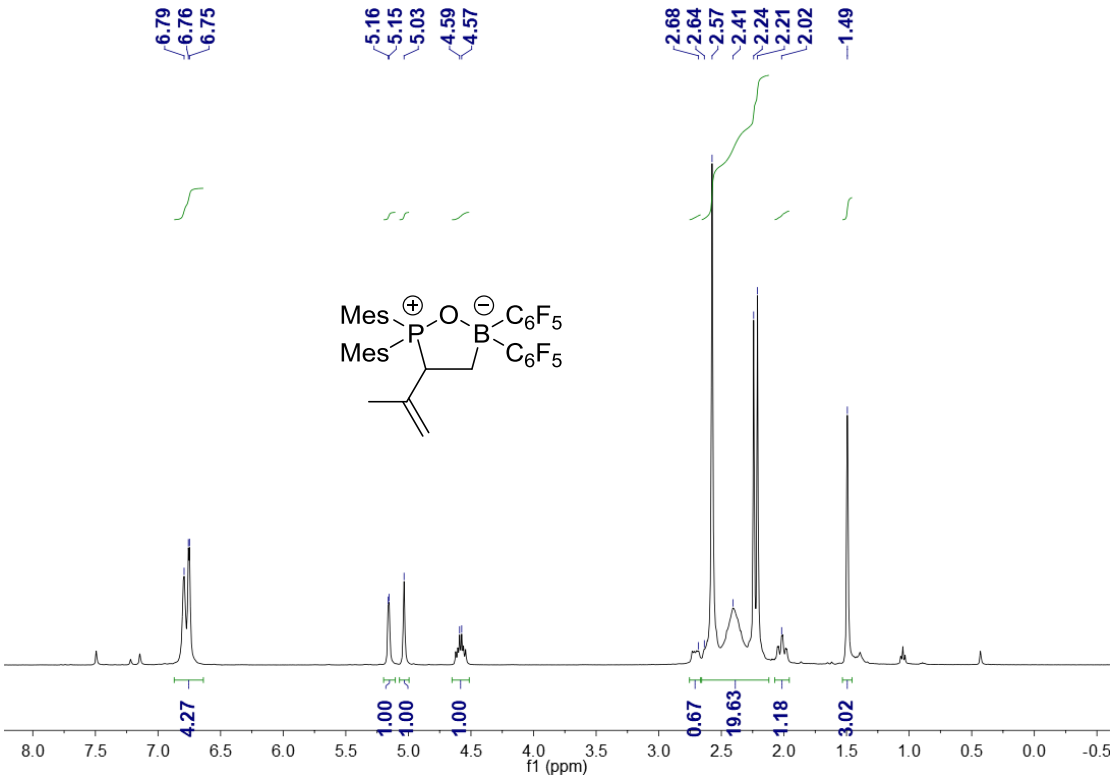


Figure S36. $^{1}H$ NMR spectrum of **8** in $C_6D_5Br$

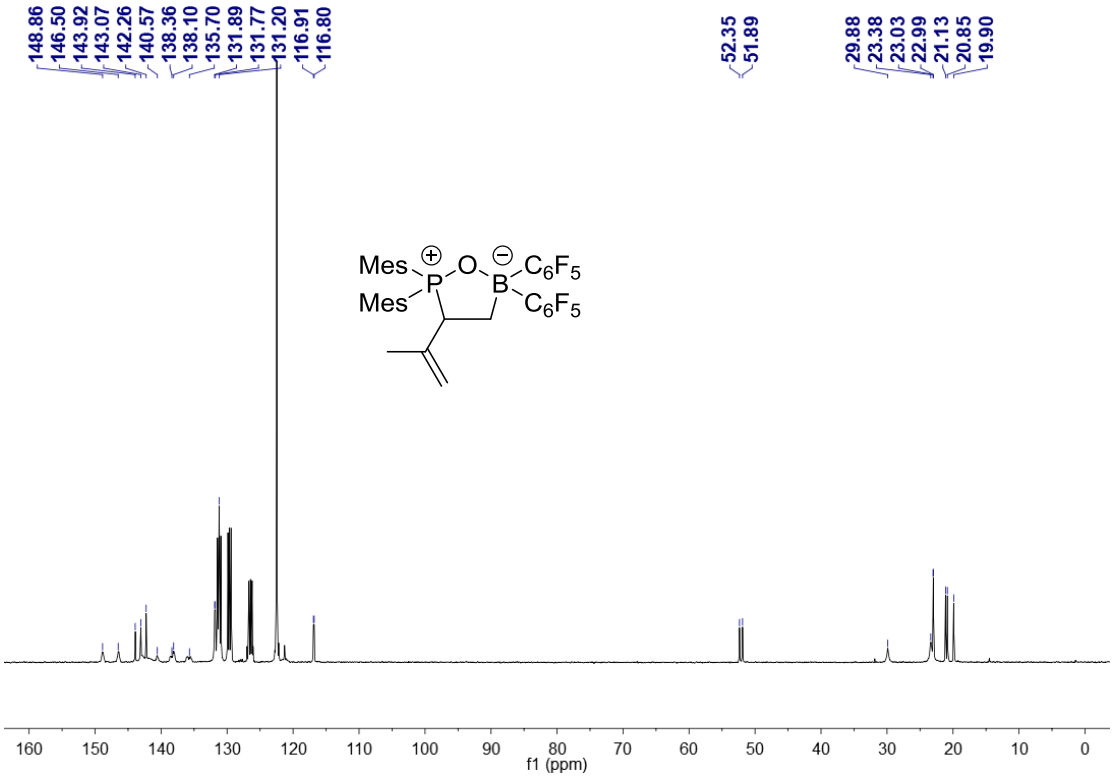


Figure S37. $^{13}C$ NMR spectrum of **8** in $C_6D_5Br$

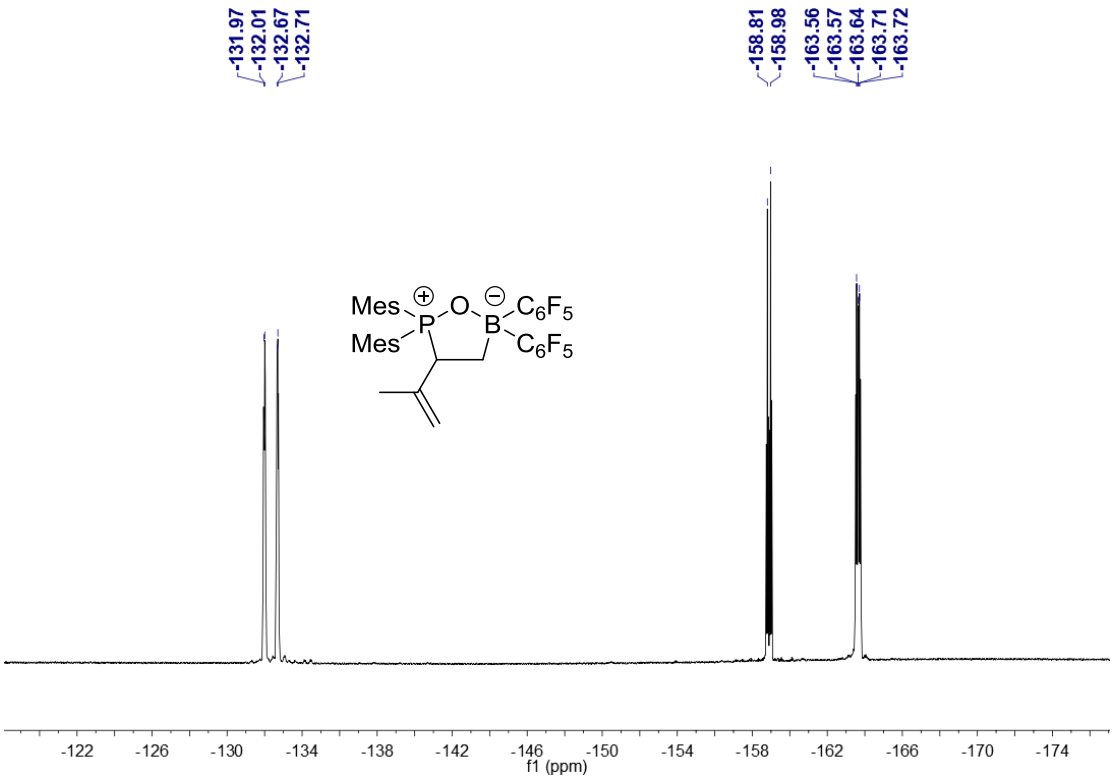


Figure S38. $^{19}F$ NMR spectrum of **8** in $C_6D_5Br$

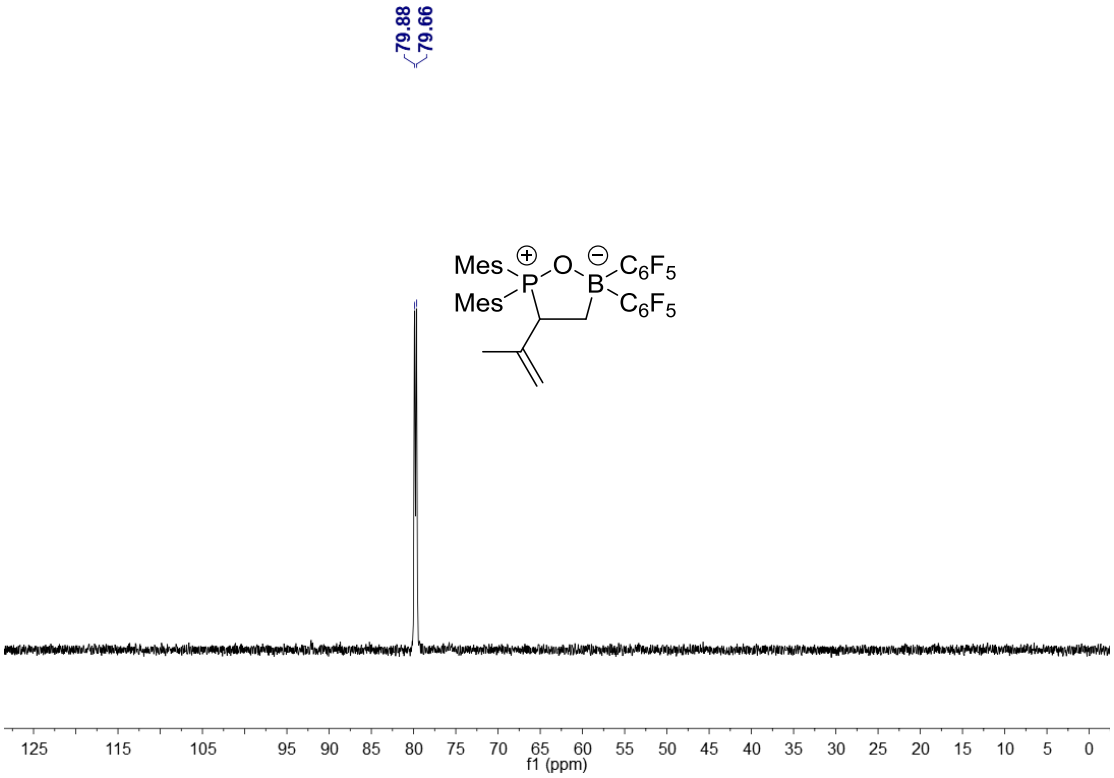


Figure S39. $^{31}$P NMR spectrum of **8** in $C_6D_5Br$

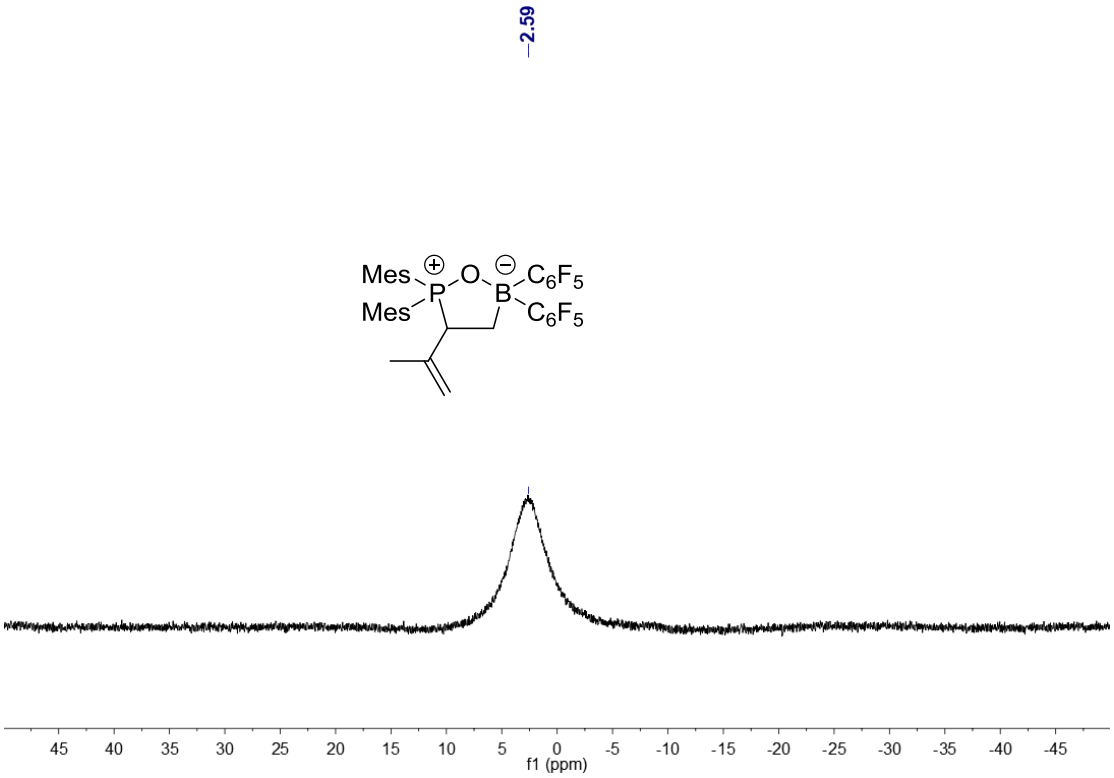


Figure S40. $^{11}$B NMR spectrum of **8** in $C_6D_5Br$

## XRD structure

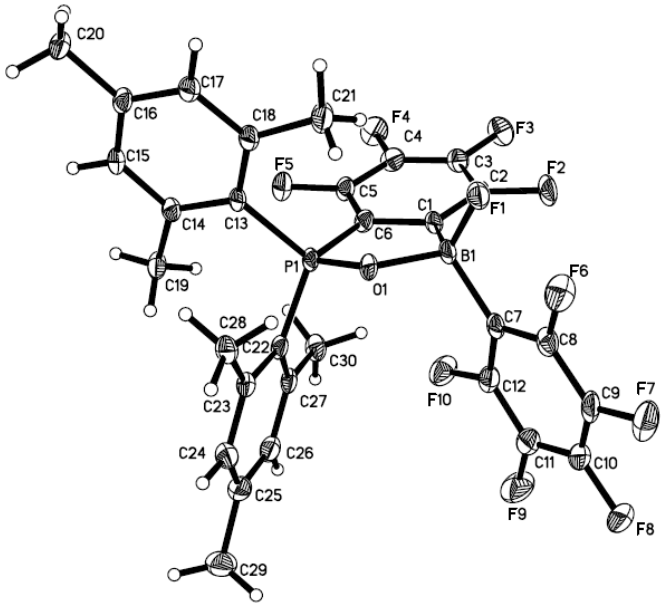


Figure S41. Molecular structure of **3** (thermal ellipsoids are shown with 30% probability).

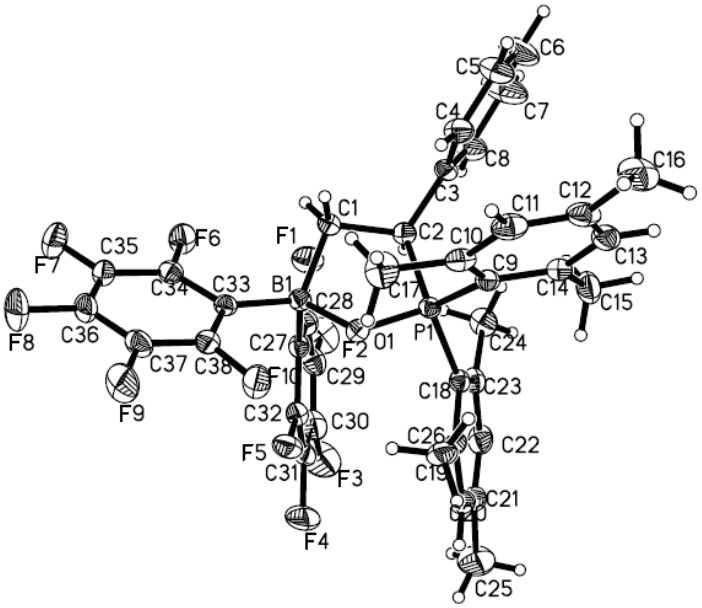


Figure S42. Molecular structure of **7** (thermal ellipsoids are shown with 30% probability).

## Computation details

Quantum chemical calculations were all performed at the density functional theory (DFT) level using the hybrid meta-GGA M06-2x functional,[3] which has been proven to give reliable results to the structural and energetic properties of non-covalent systems and reaction energy barriers.[4] The M06-2x functional has a mean absolute error in energy barriers of about 1.3 kcal/mol. The 6-31+G(d,p) basis set[5] was used for the atoms directly involved in the reaction, the 6-31G basis set was used for the F atoms, and the 6-31G(d) basis set was used for the other atoms. All the DFT calculations were performed with a pruned (99,590) integration grid.

Full geometry optimization were carried out in the benzene solution which was modelled by the polarizable continuum solvation model (IEFPCM)[6] with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.[7] This solvation model is by far the most reliable one in predicting solvation free energies. The convergence criteria used for the geometry optimization are $4.50\times10^{-4}$ au. for gradients, and $1.80\times10^{-3}$ au. for displacements. Harmonic vibrational analyses were carried out to confirm if the optimized structure is a genuine minima. All the calculations were performed by using the Gaussian 09 program.[8]

**Cartesian coordinates of compound 1**

0,1
F,0,-0.454621,-1.985341,-2.242012
F,0,1.555348,-1.325838,1.988442
F,0,3.037125,-1.161777,-2.064138
F,0,2.258144,1.821025,1.520298
F,0,-1.318348,-4.393731,-1.447392
F,0,0.722112,-3.772376,2.756344
F,0,5.692032,-0.711199,-1.850678
F,0,4.89392,2.266564,1.715336
F,0,-0.737345,-5.314708,1.041519
F,0,6.628805,1.010382,0.042734
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C,0,0.879767,-2.083606,1.097904
C,0,3.473509,-0.302972,-1.120665
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C,0,-0.576435,-3.650234,-0.619176
C,0,0.454518,-3.333263,1.522882
C,0,4.839575,-0.089076,-1.031115
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C,0,-2.95717,-1.935379,1.28263

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H,0,-4.135109,-2.655381,-1.810183
C,0,-3.121413,3.153962,0.1461
C,0,-0.854493,3.847182,-0.484739
C,0,-3.405006,4.489734,0.437985
C,0,-1.191716,5.160831,-0.16835
C,0,-2.457689,5.502697,0.30457
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H,0,-2.249997,-0.21768,3.132433
H,0,-0.680842,-0.179636,2.311763
C,0,-3.124349,-0.327685,-2.704955
H,0,-3.416842,0.729001,-2.717396
H,0,-2.158704,-0.408785,-3.216495
H,0,-3.860004,-0.883365,-3.292017
C,0,-4.07492,-4.062406,0.524935
H,0,-4.537351,-4.140981,1.513097
H,0,-4.805621,-4.370878,-0.227231
H,0,-3.244806,-4.779056,0.493372
C,0,-4.23974,2.153996,0.327387
H,0,-4.423636,1.559839,-0.572527
H,0,-4.035711,1.453036,1.142499
H,0,-5.164864,2.683249,0.568941
C,0,0.540187,3.580318,-1.002461
H,0,0.987012,4.510154,-1.363255
H,0,1.179176,3.172388,-0.213489
H,0,0.547574,2.865769,-1.834317
C,0,-2.78487,6.925569,0.669005
H,0,-3.865016,7.086806,0.714689
H,0,-2.367637,7.176853,1.650818
H,0,-2.36188,7.628434,-0.054761
B,0,0.994037,-0.022259,-0.437765
C,0,0.606257,-1.568245,-0.162105
C,0,2.54686,0.321442,-0.295706
O,0,0.08403,0.925927,0.124047
P,0,-1.266469,1.160856,-0.760302
C,0,-2.37747,-0.191105,-0.271895
C,0,-1.820595,2.827034,-0.296694

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