Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Metal-Free Pincer Ligand Chemistry: Polycationic Phosphonium Lewis Acids

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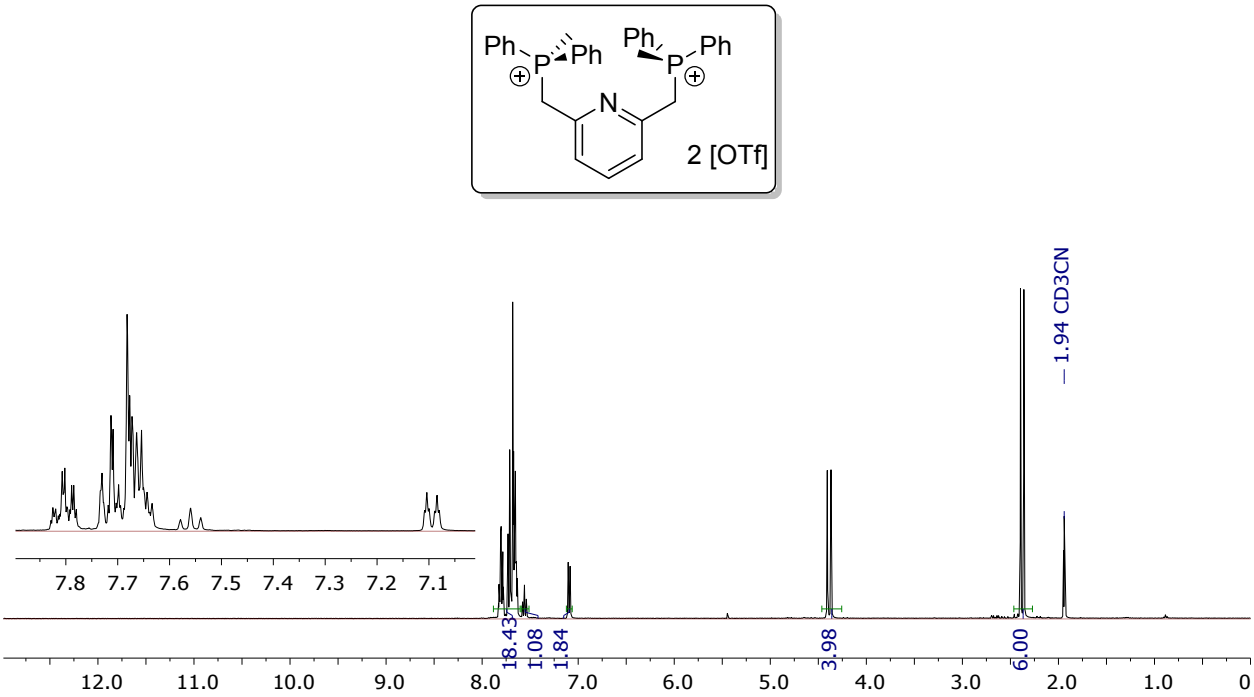


Figure S1. ^{1}H NMR spectrum of **2**, CD_3CN

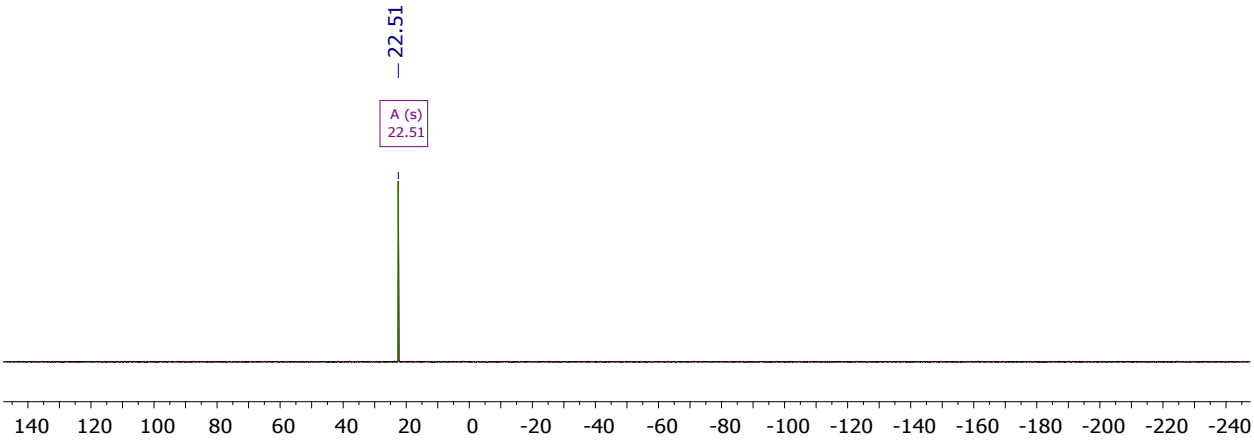


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum of **2**, CD_3CN

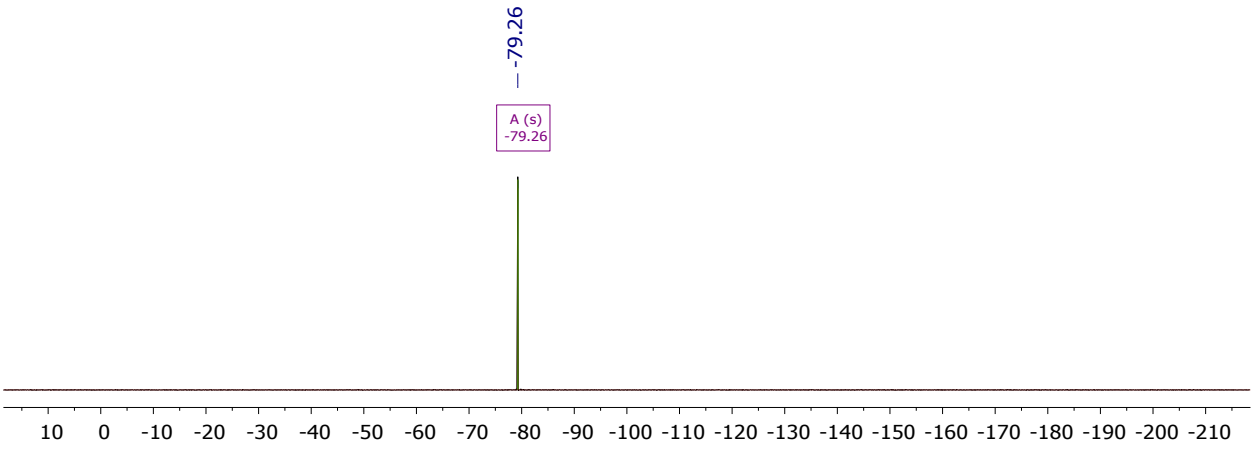


Figure S3. ^{19}F NMR spectrum of **2**, CD_3CN

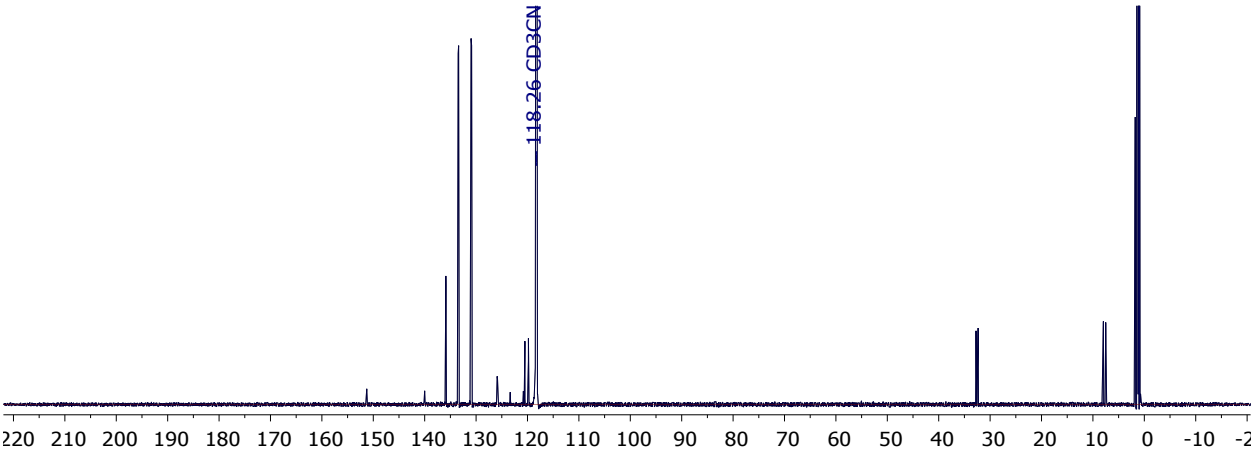


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **2**, CD_3CN

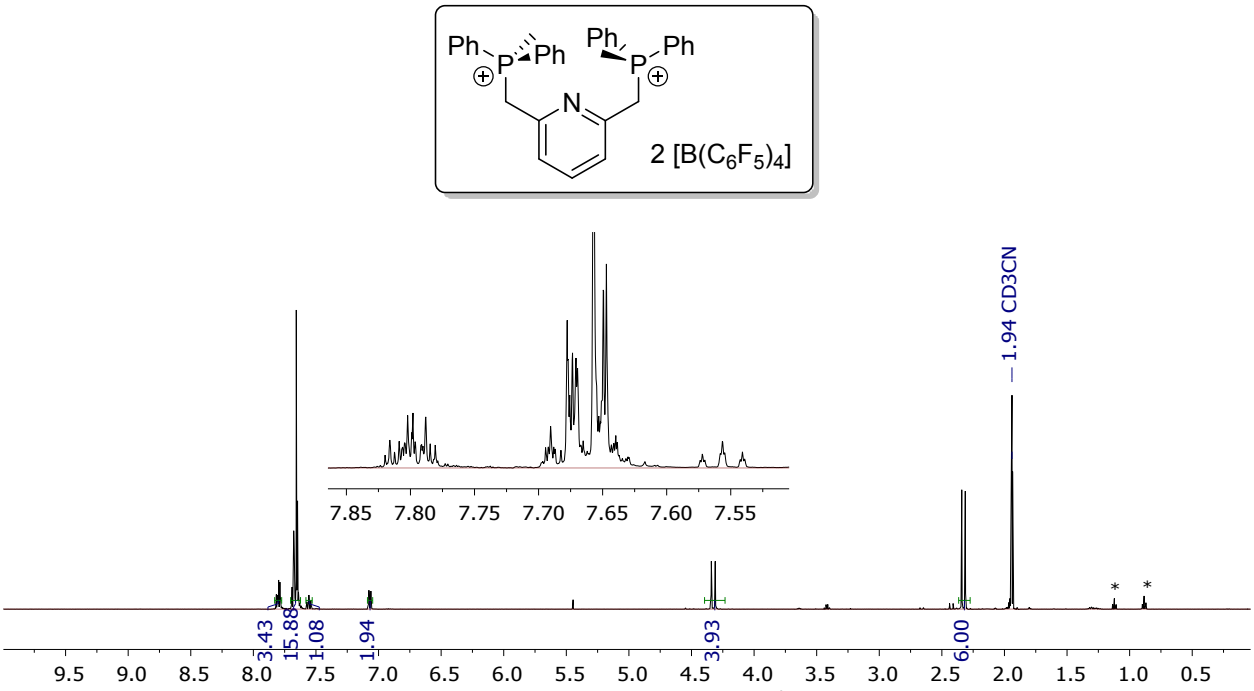


Figure S5. ^{1}H NMR spectrum of **3**, CD_3CN. * = impurities

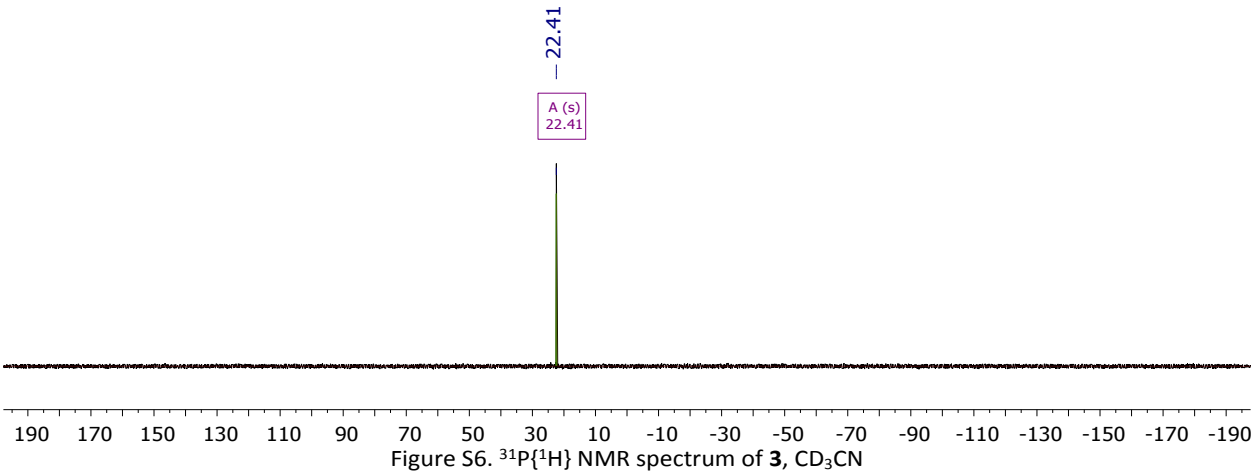


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **3**, CD_3CN

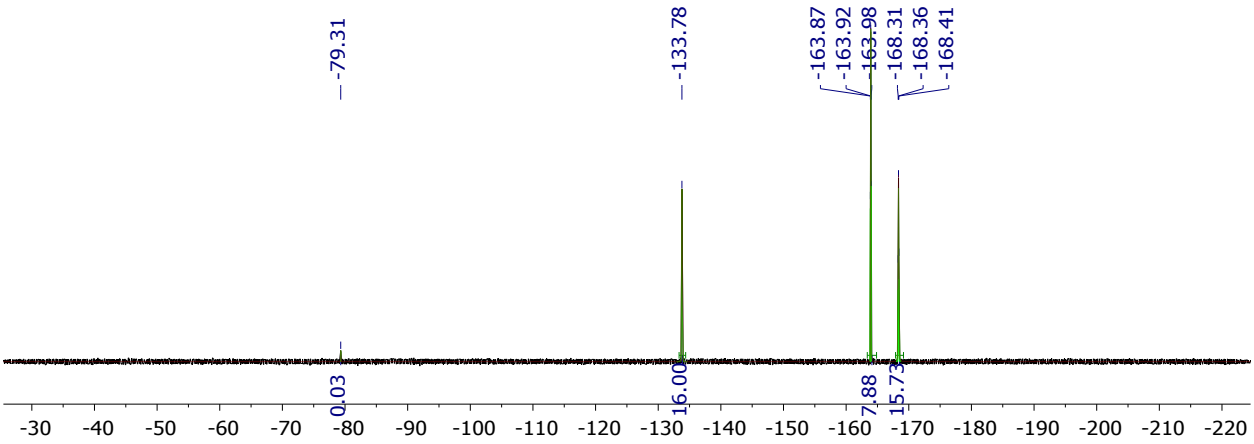


Figure S7. ^{19}F NMR spectrum of **3**, CD_3CN

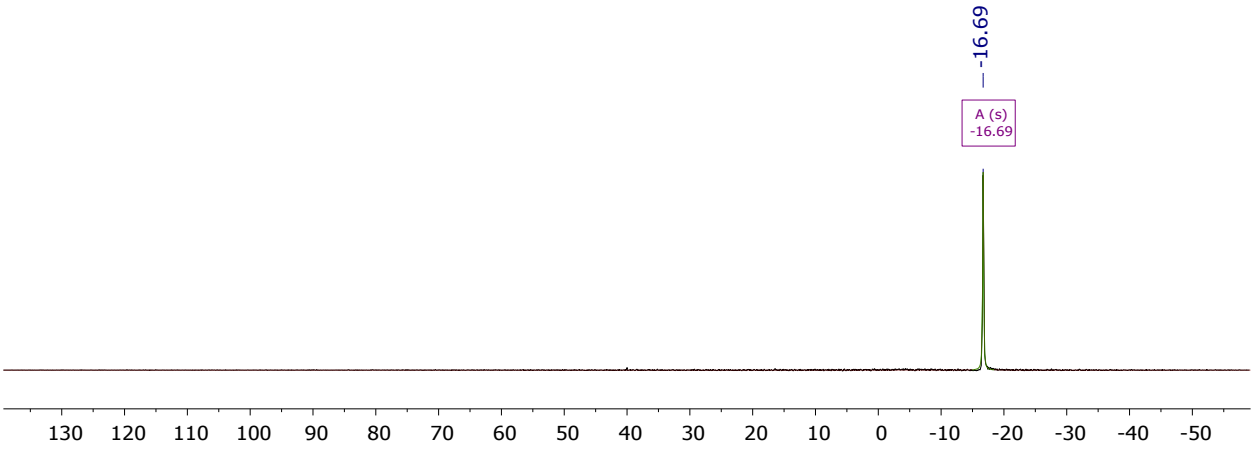


Figure S8. $^{11}B\{^1H\}$ NMR spectrum of **5**, CD_3CN

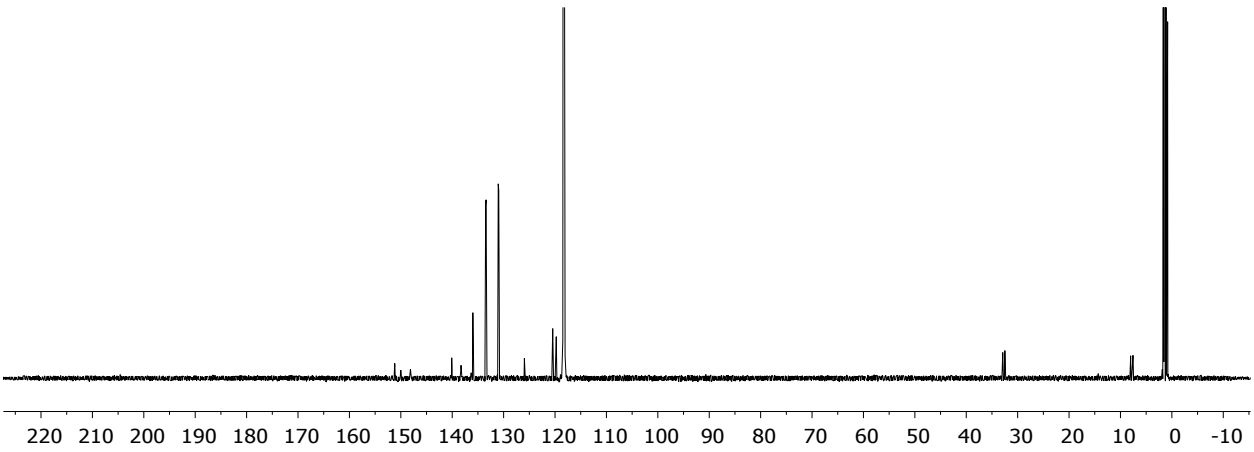


Figure S9. $^{13}C\{^1H\}$ NMR spectrum of **3**, CD_3CN

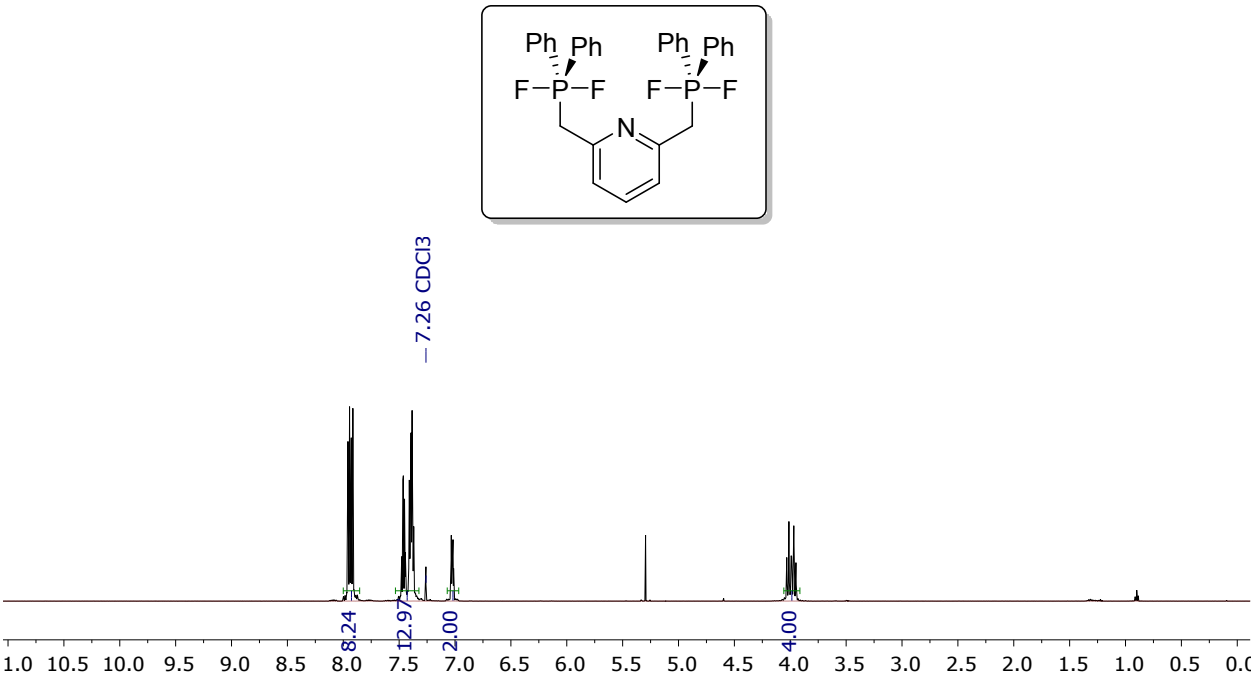


Figure S10. ^{1}H NMR spectrum of **4**, $CDCl_3$

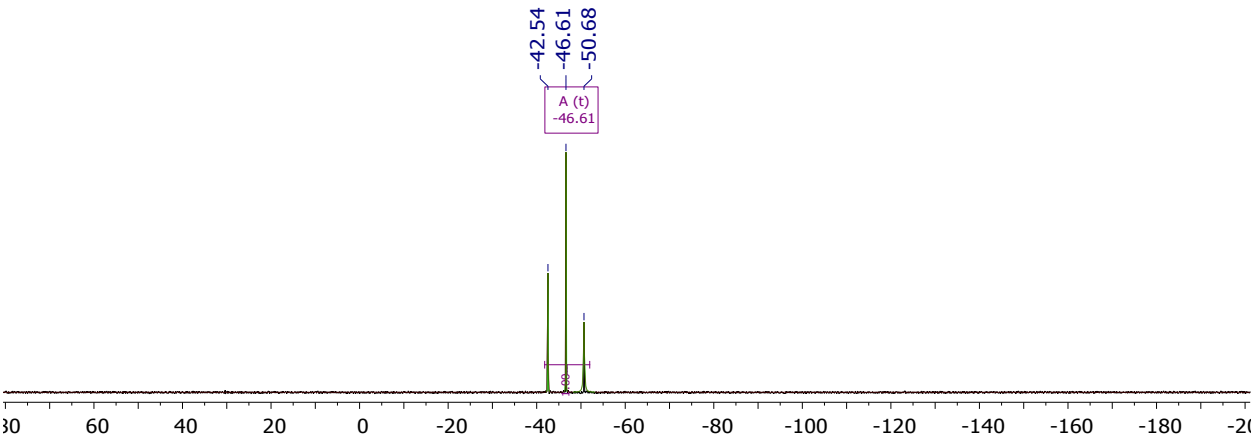


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **4**, $CDCl_3$

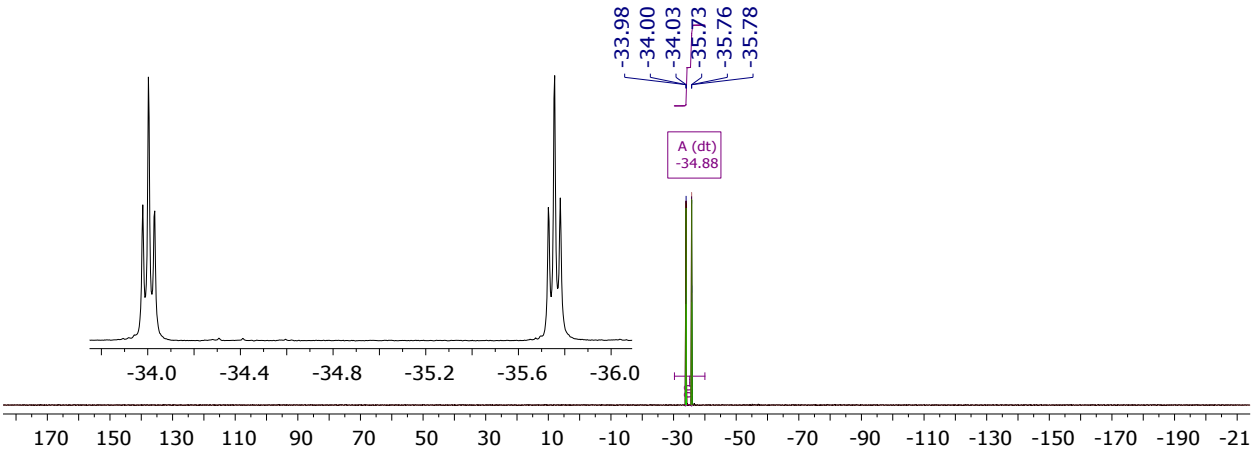


Figure S12. ^{19}F NMR spectrum of **4**, $CDCl_3$

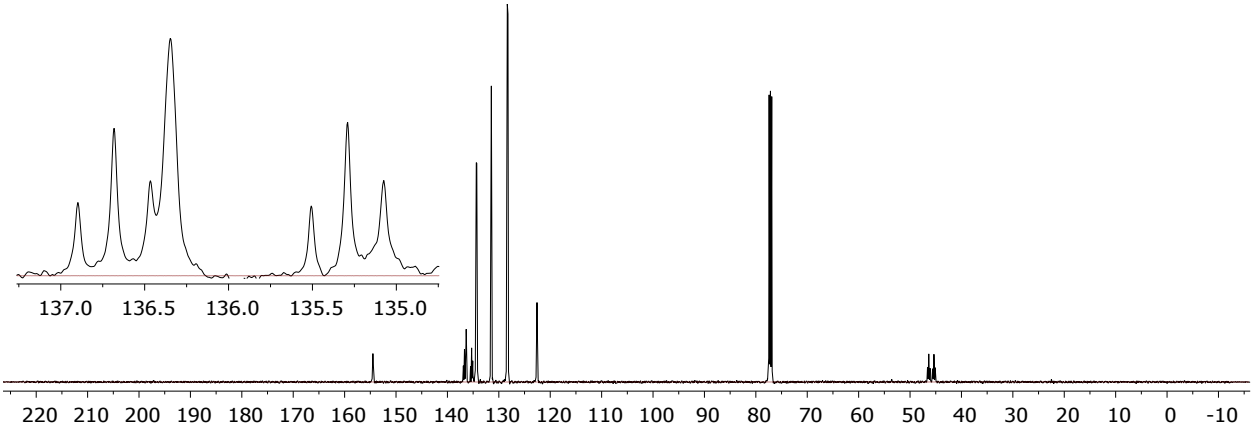


Figure S13. $^{13}C\{^1H\}$ NMR spectrum of **4**, $CDCl_3$

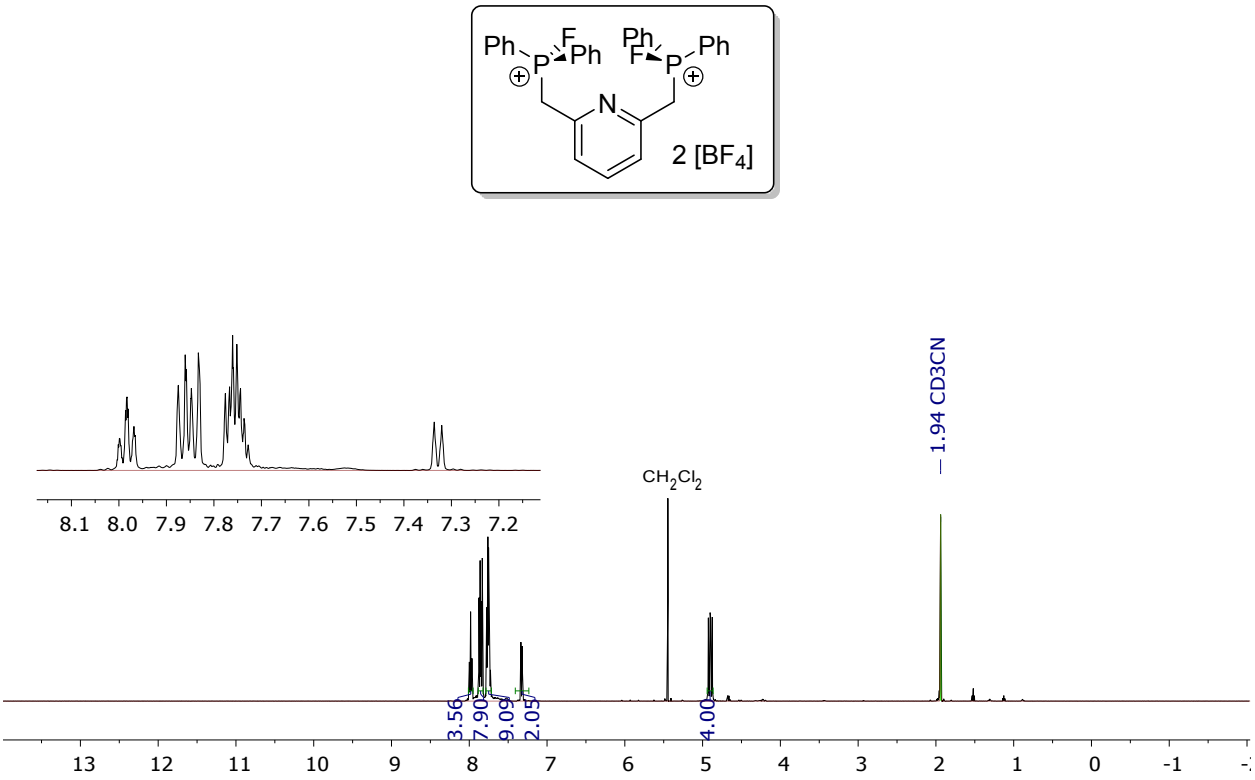


Figure S14. ^{1}H NMR spectrum of **5**, CD_3CN

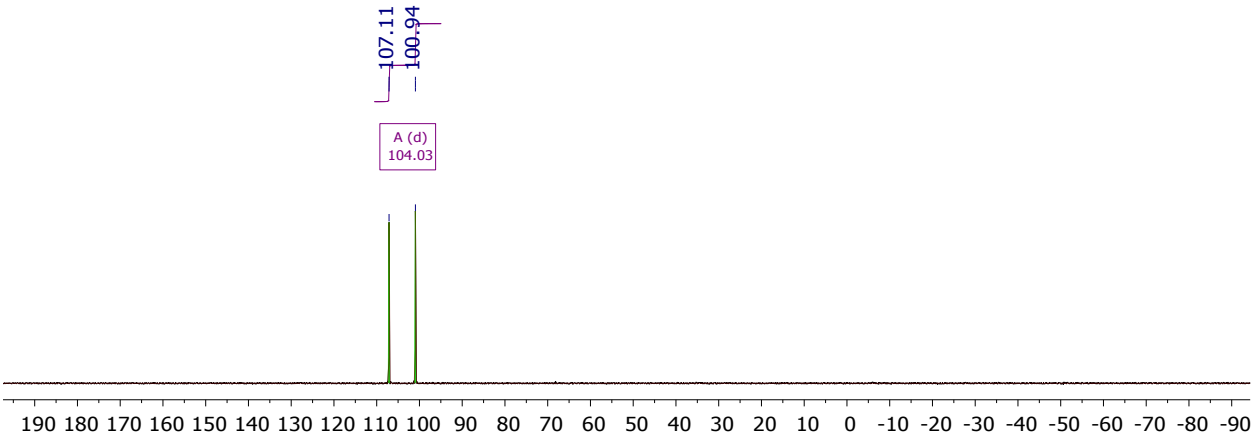


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **5**, CD_3CN

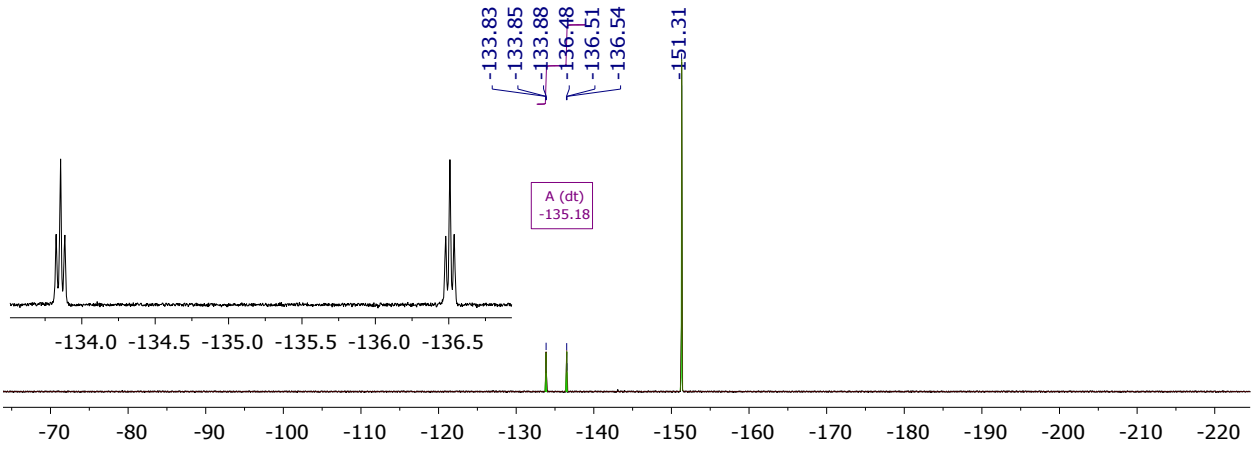


Figure S16. ^{19}F NMR spectrum of **5**, CD_3CN

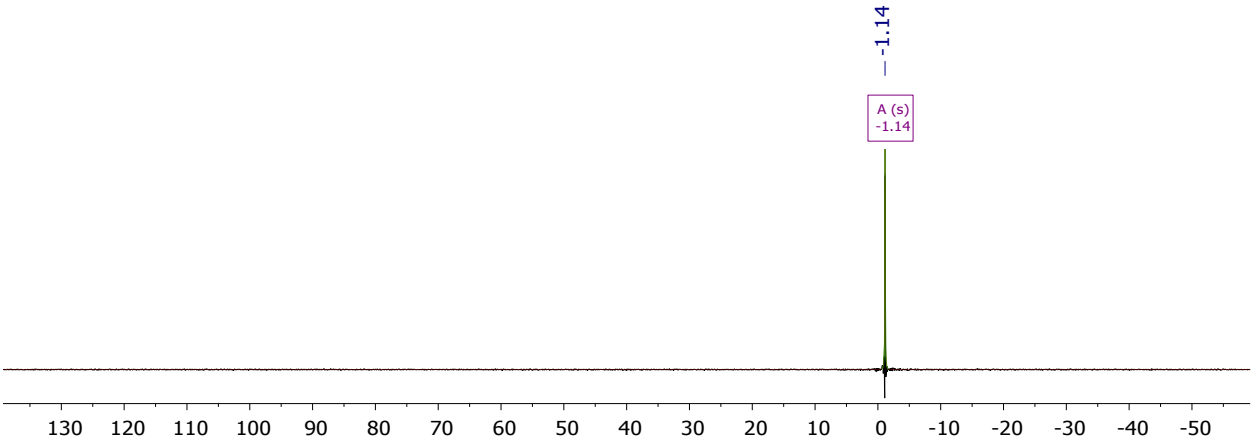


Figure S17. $^{11}B\{^1H\}$ NMR spectrum of **5**, CD_3CN

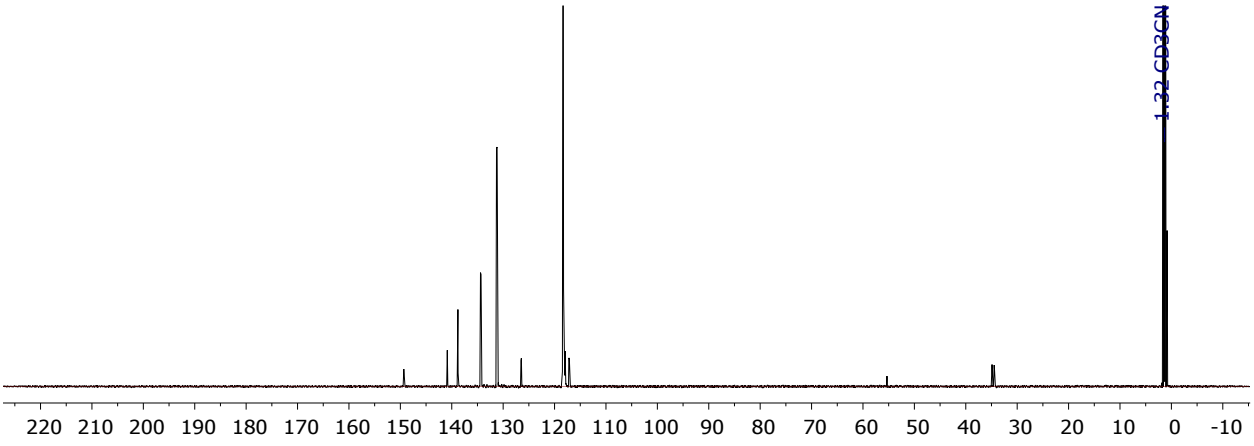


Figure S18. $^{13}C\{^1H\}$ NMR spectrum of **5**, CD_3CN

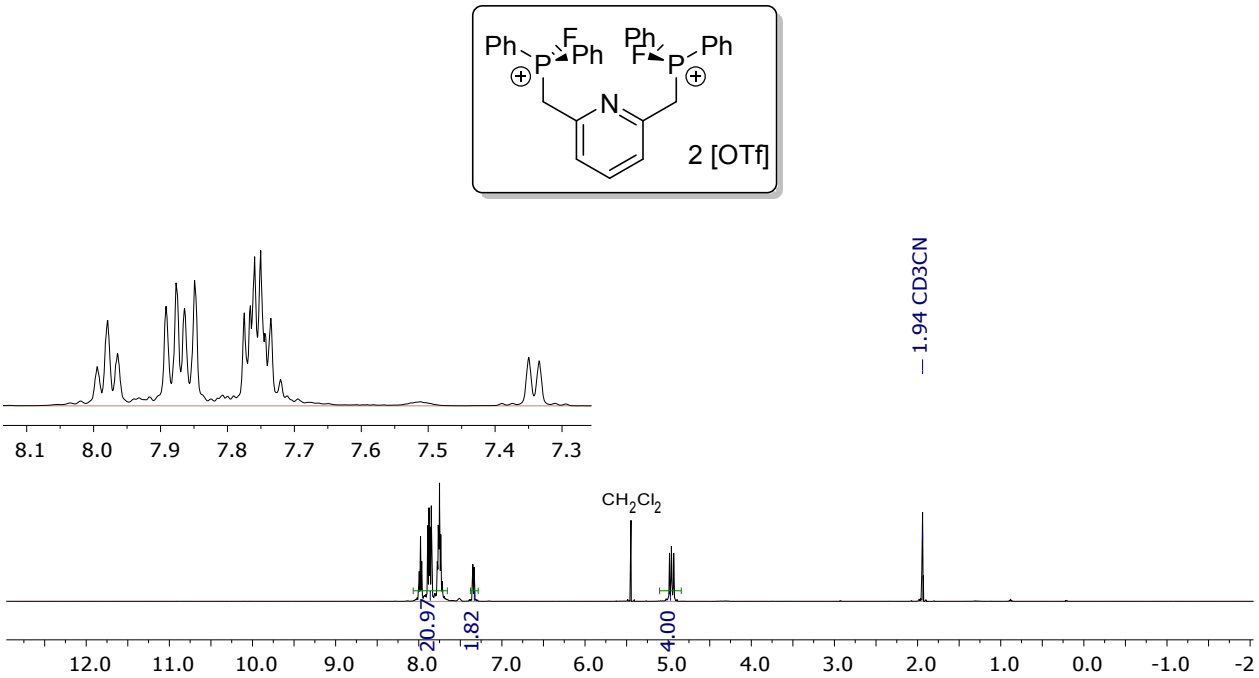


Figure S19. ^{1}H NMR spectrum of **6**, CD_3CN

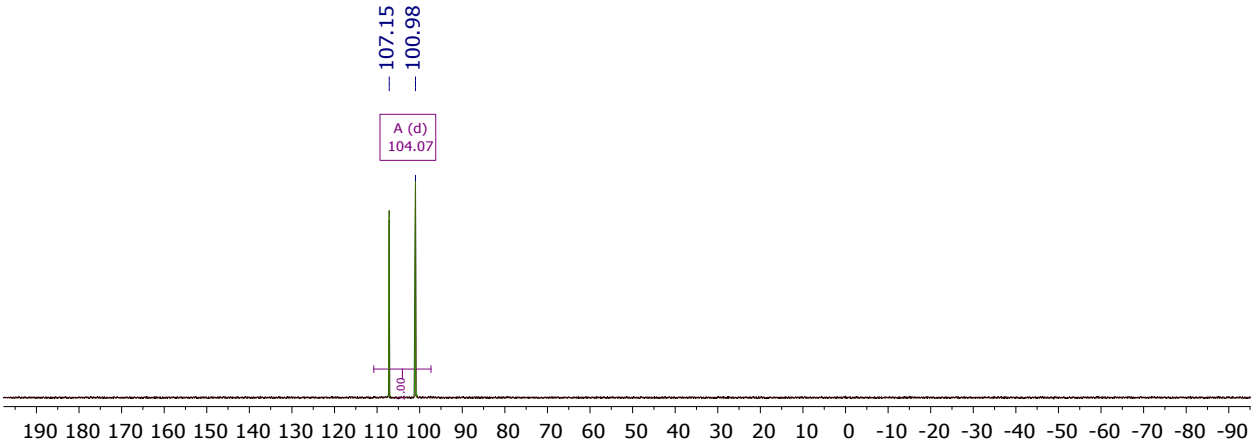


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **6**, CD_3CN

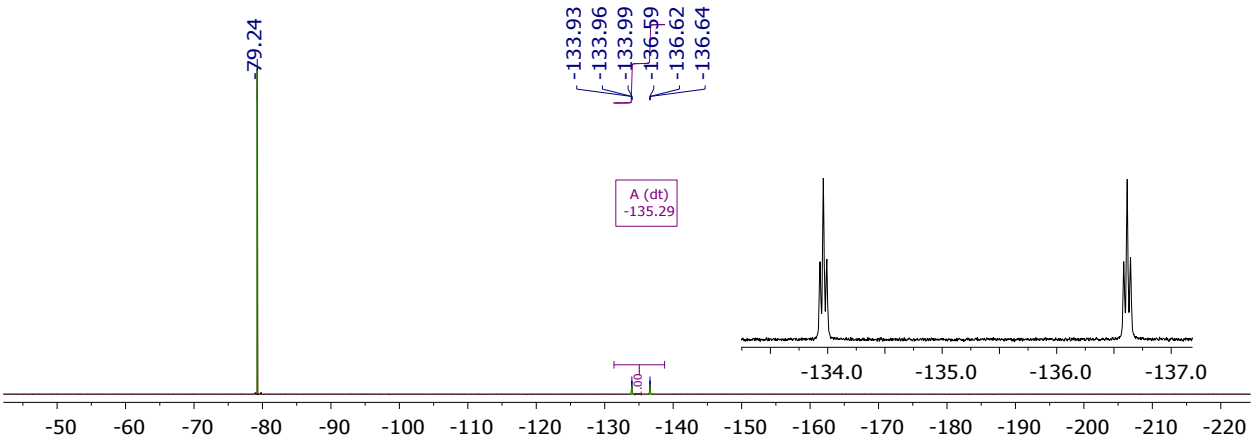


Figure S21. 19F NMR spectrum of 6, CD3CN

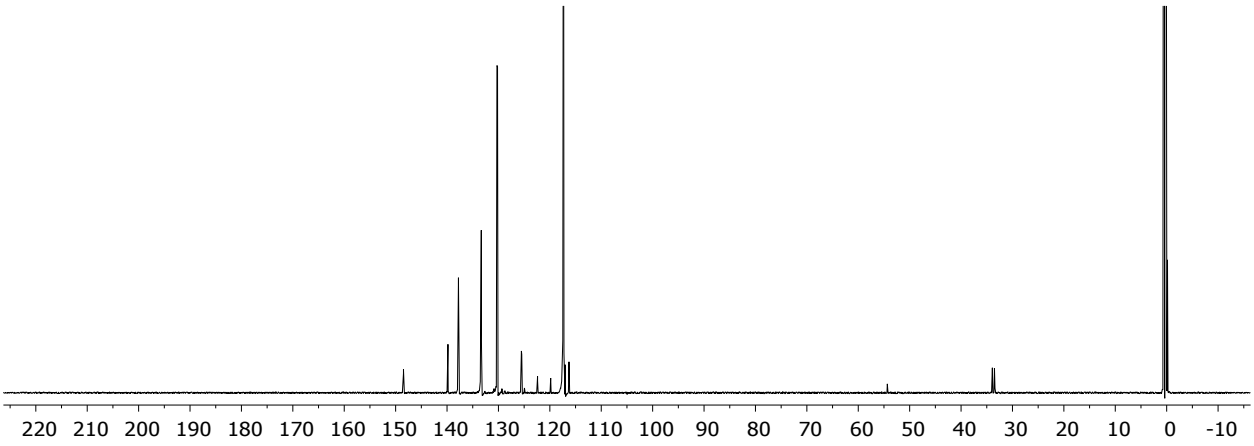


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **6**, CD_3CN

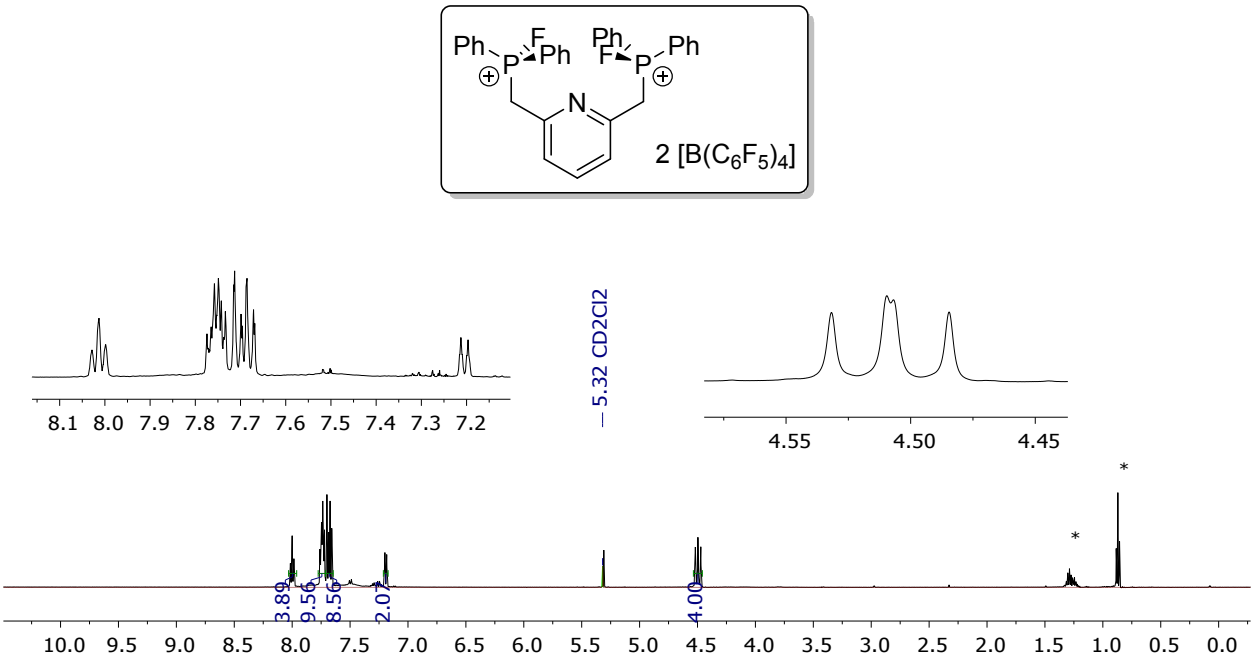


Figure S23. ^{1}H NMR spectrum of **7**, CD_2Cl_2. * = pentane

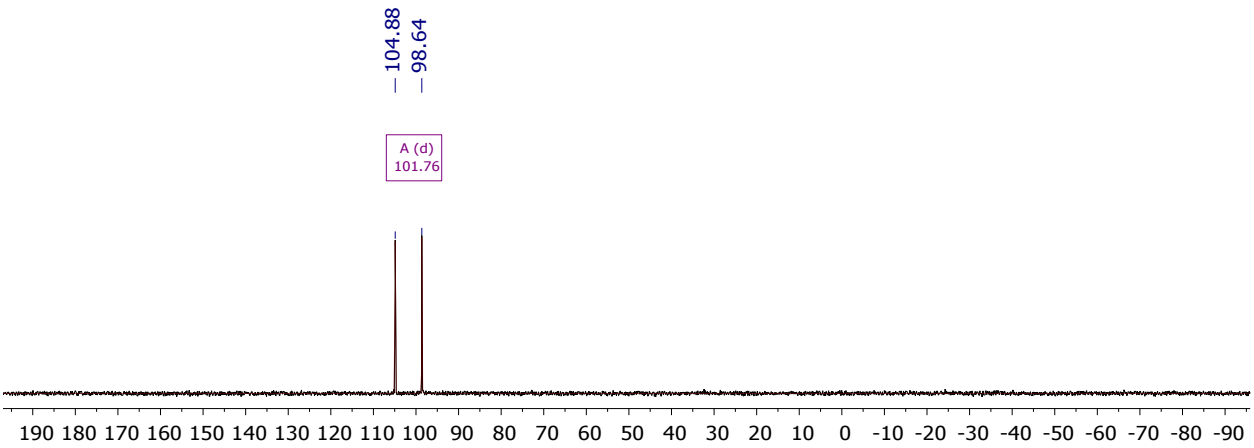


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **7**, CD_2Cl_2

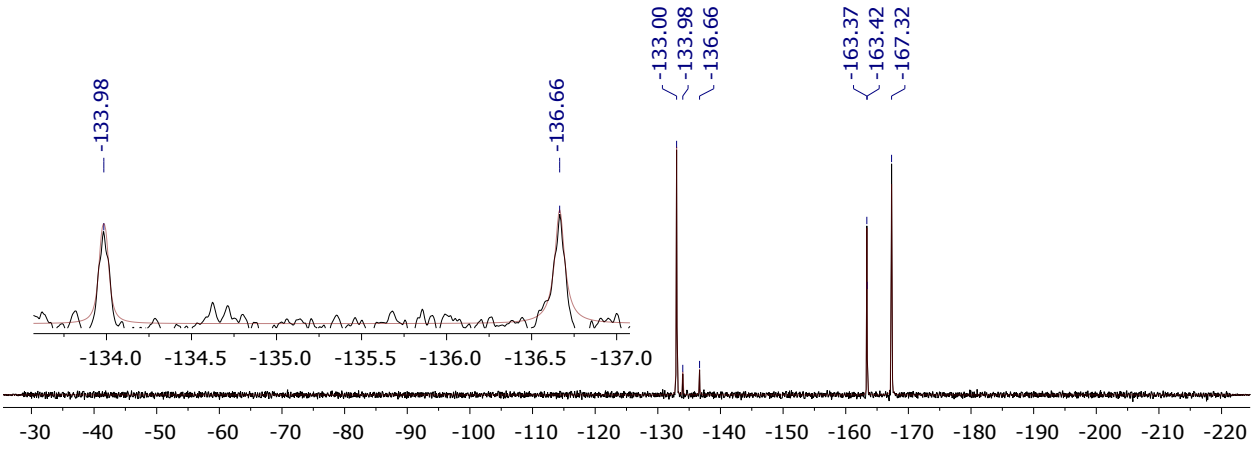


Figure S25. ^{19}F NMR spectrum of **7**, CD_2Cl_2

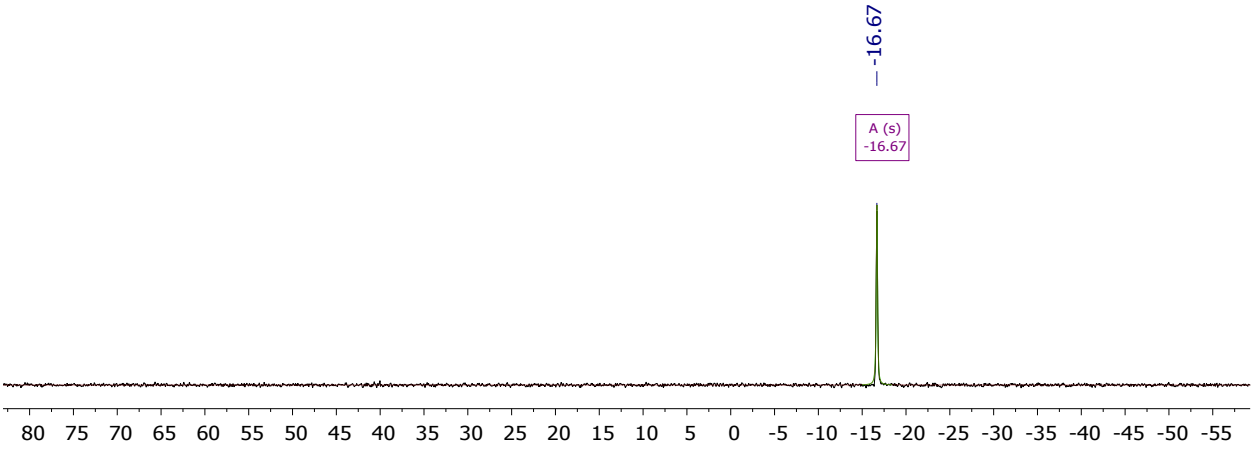


Figure S26. $^{11}B\{^1H\}$ NMR spectrum of **7**, CD_2Cl_2

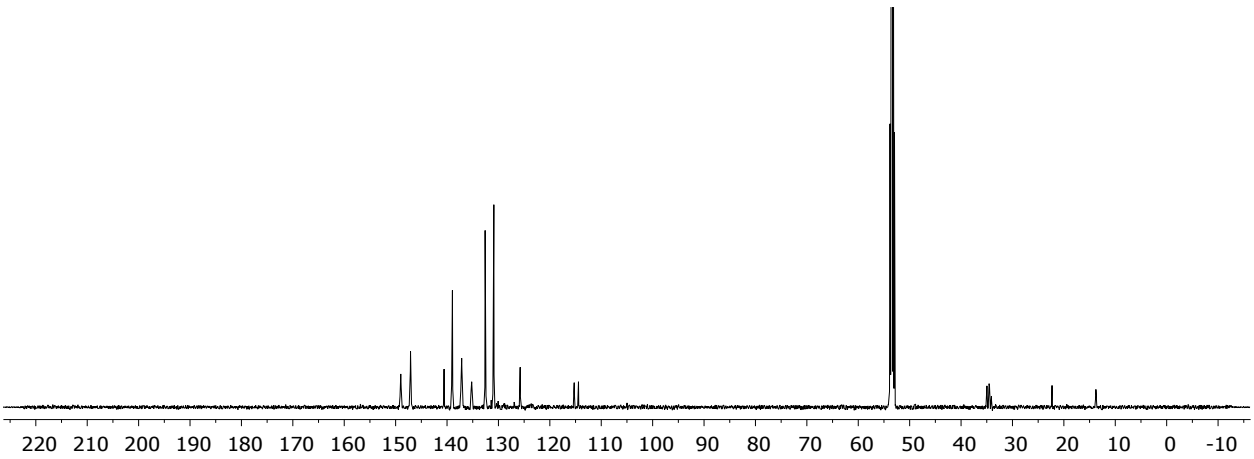


Figure S27. $^{13}C\{^1H\}$ NMR spectrum of **7**, CD_2Cl_2

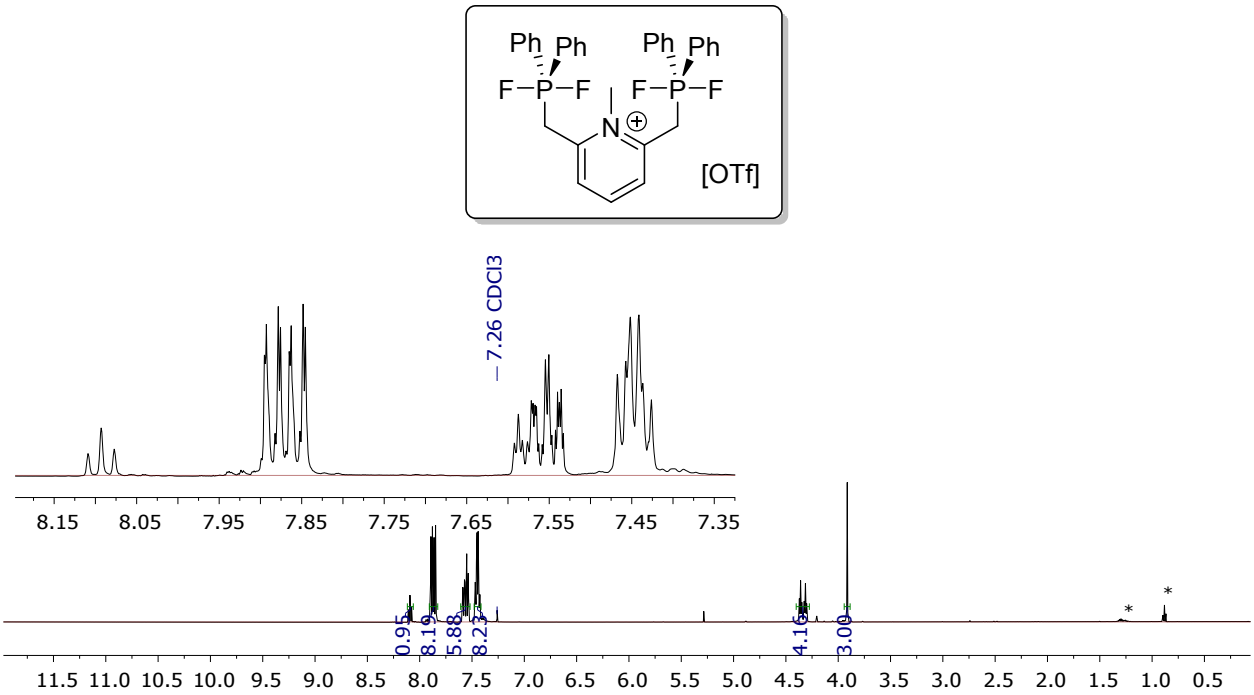


Figure S28. ^{1}H NMR spectrum of **8**, $CDCl_3$. * = pentane

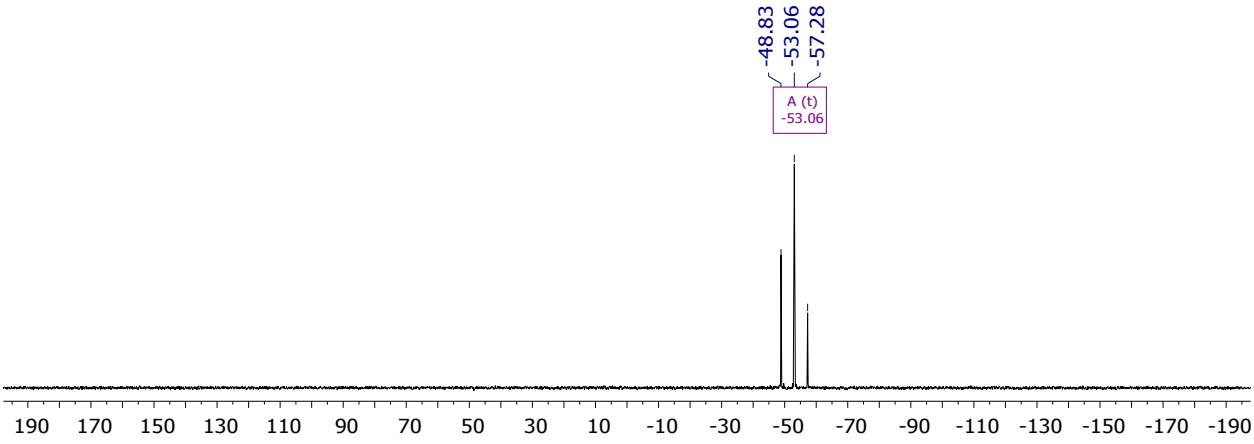


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of **8**, $CDCl_3$

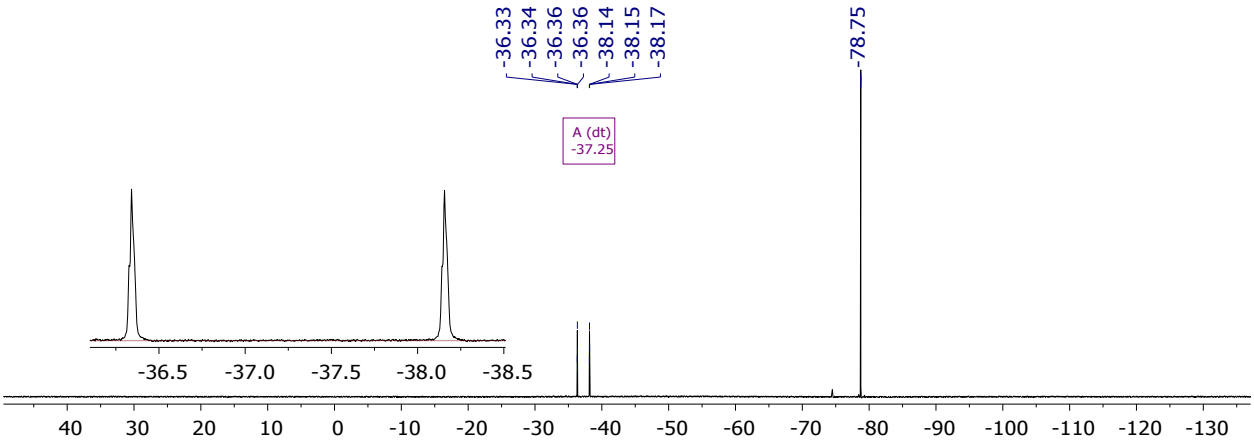


Figure S30. ^{19}F NMR spectrum of **8**, $CDCl_3$

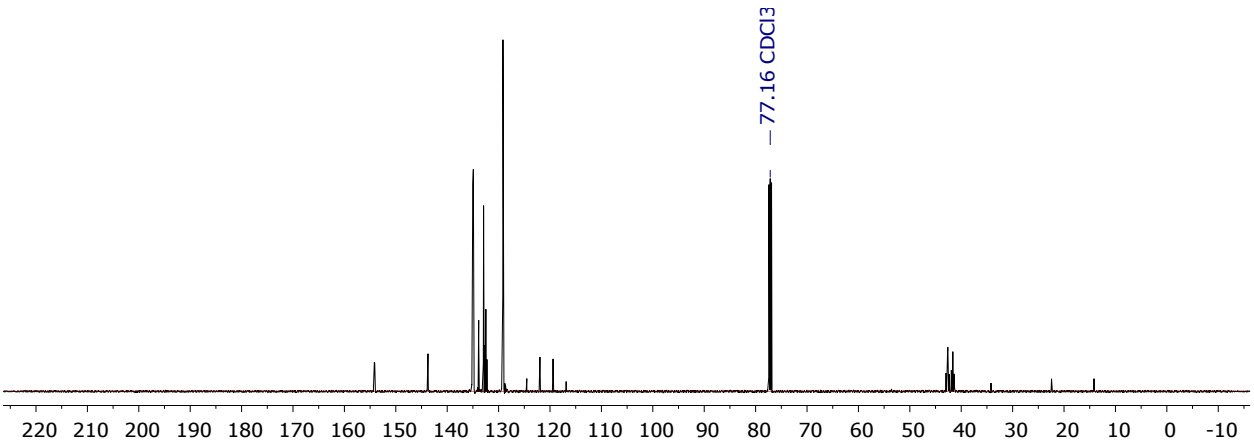


Figure S31. $^{13}C\{^1H\}$ NMR spectrum of **8**, $CDCl_3$

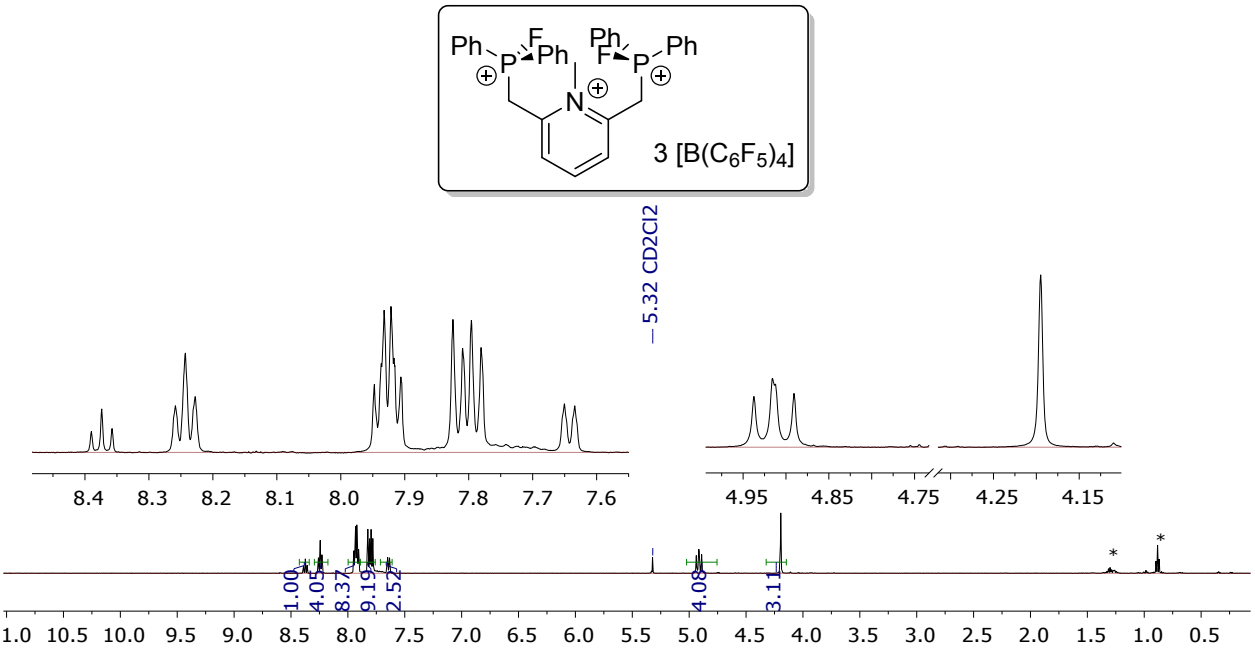


Figure S32. ^{1}H NMR spectrum of **9**, CD_2Cl_2. * = pentane

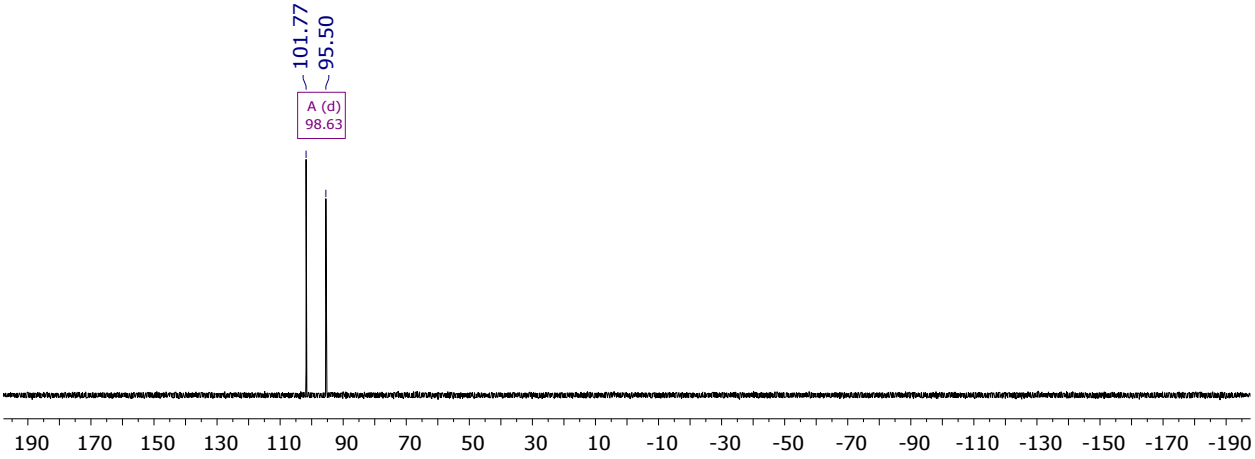


Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum of **9**, CD_2Cl_2

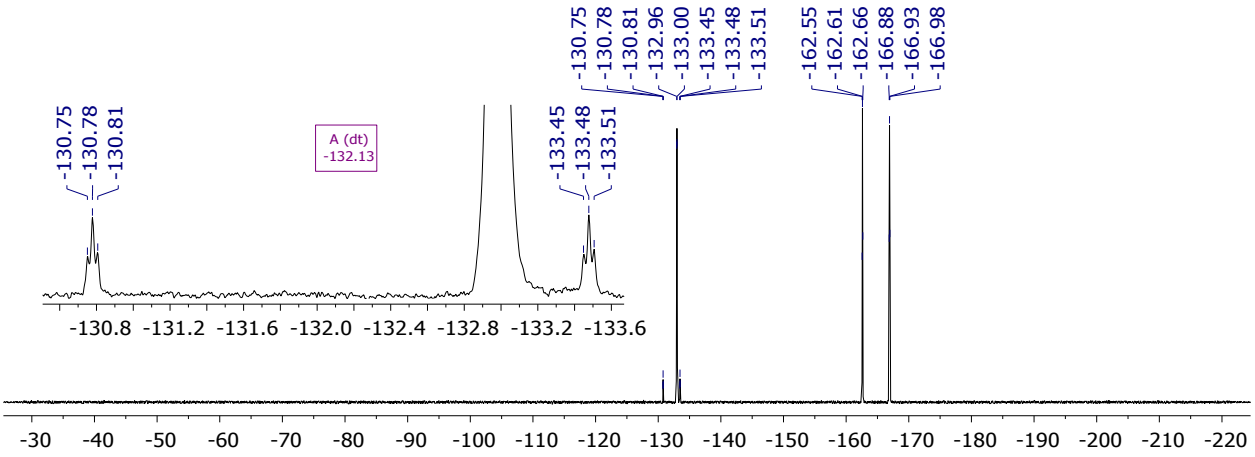


Figure S34. ^{19}F NMR spectrum of **9**, CD_2Cl_2

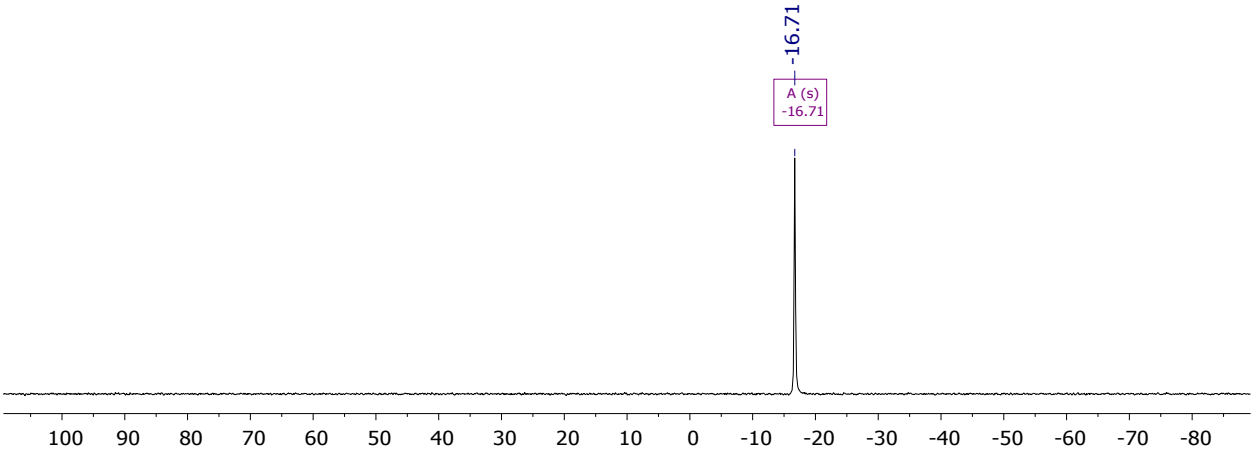


Figure S35. $^{11}B\{^1H\}$ NMR spectrum of **9**, CD_2Cl_2

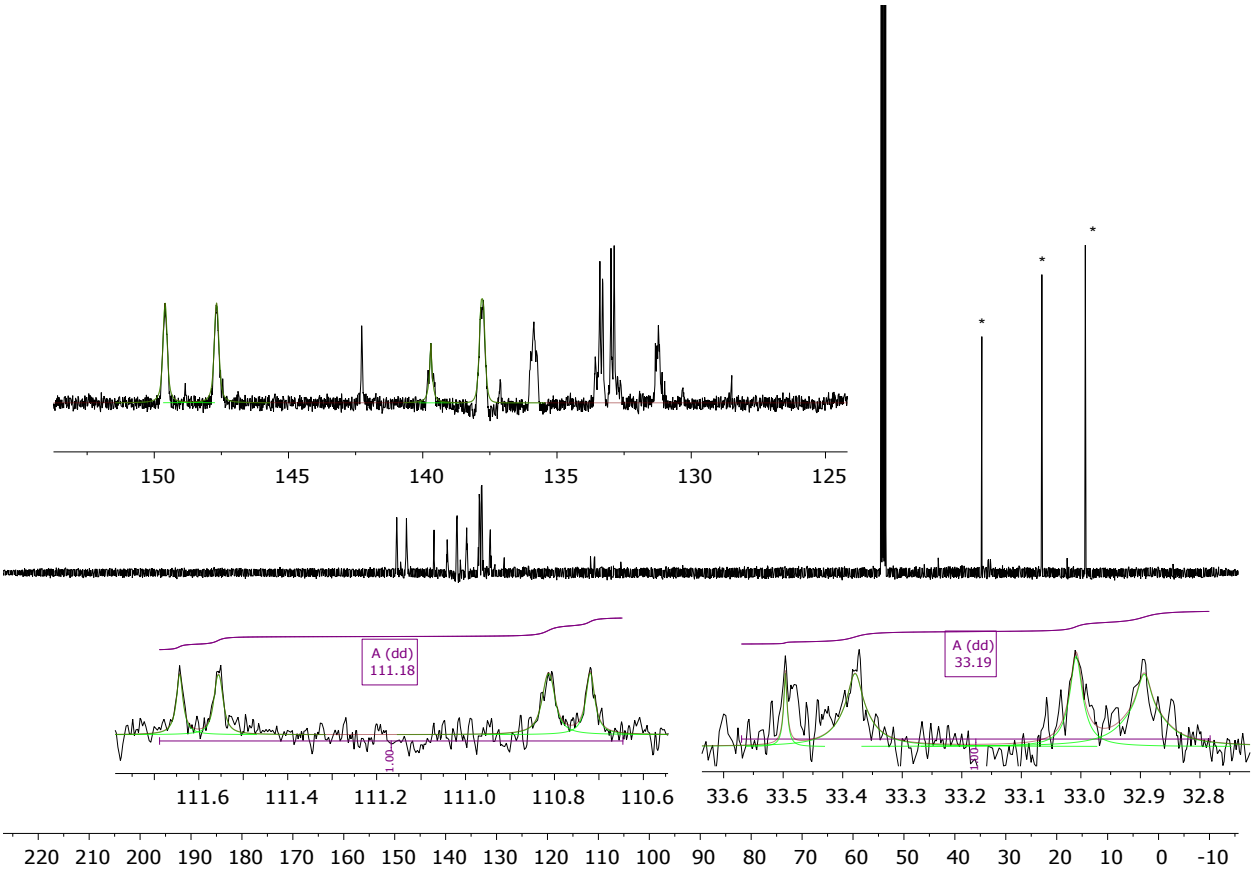


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **8**, CD_2Cl_2. * = pentane

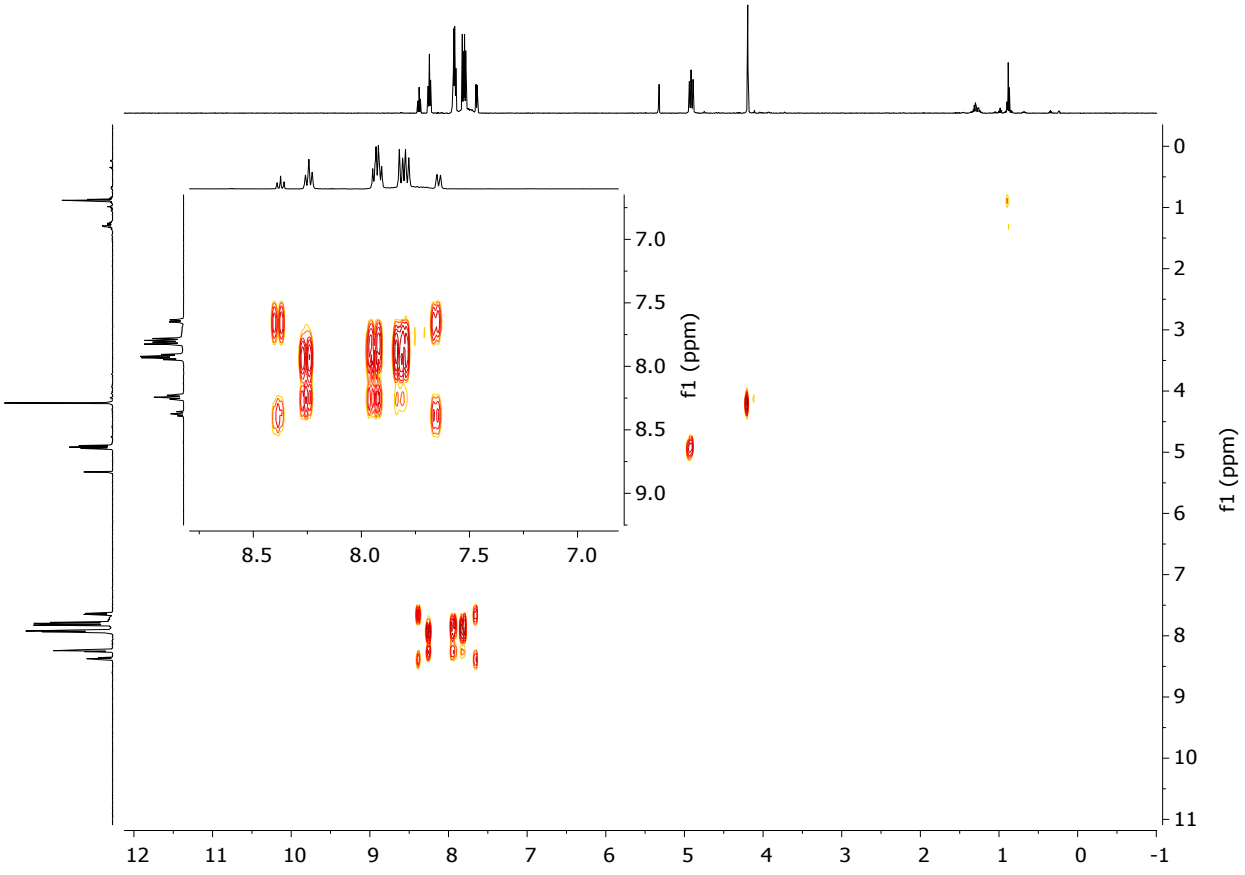


Figure S37. ^{1}H-^{1}H COSY NMR spectrum of **9**, CD_2Cl_2

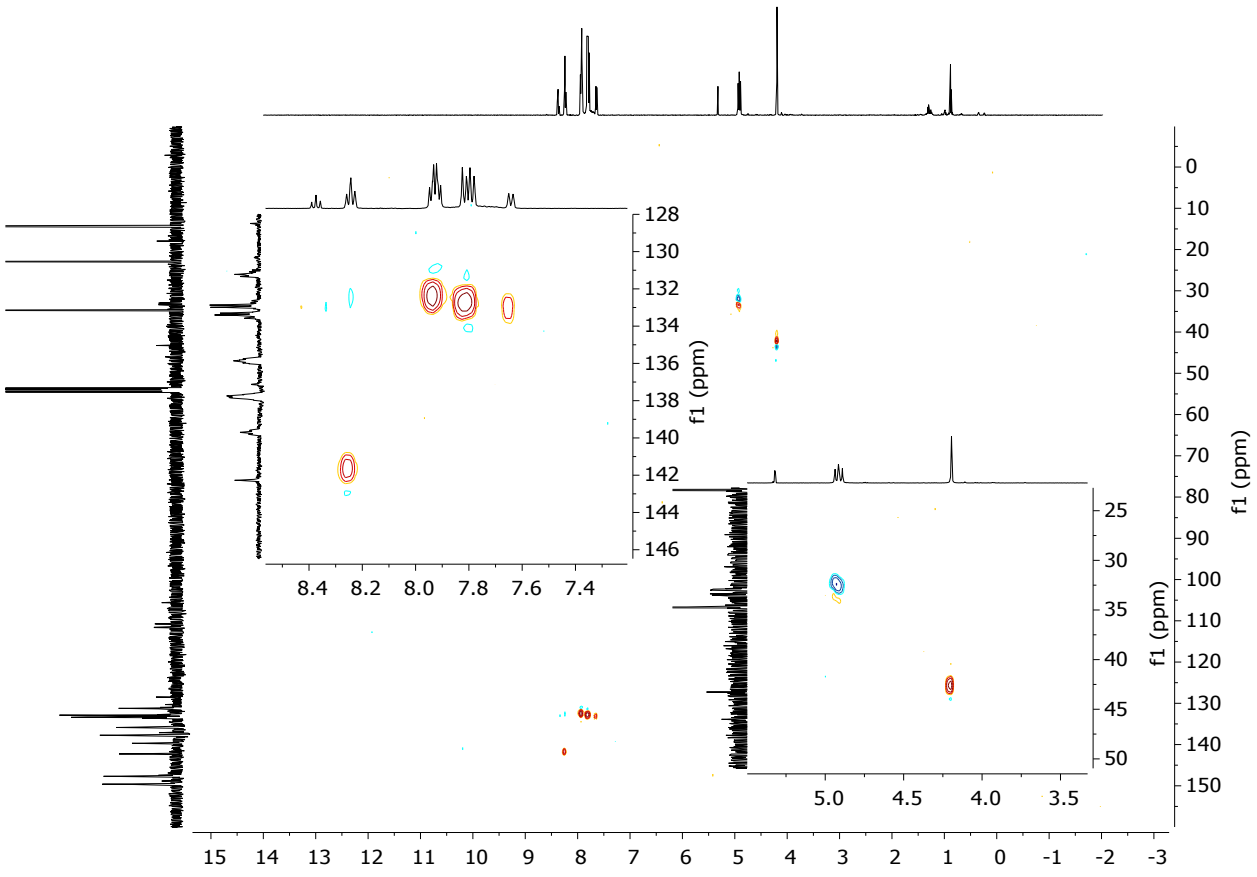
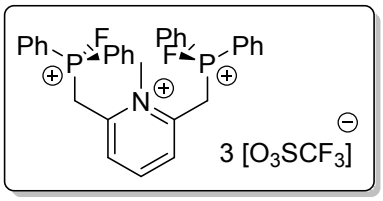


Figure S38. ^{1}H-^{13}C HSQC NMR spectrum of **9**, CD_2Cl_2



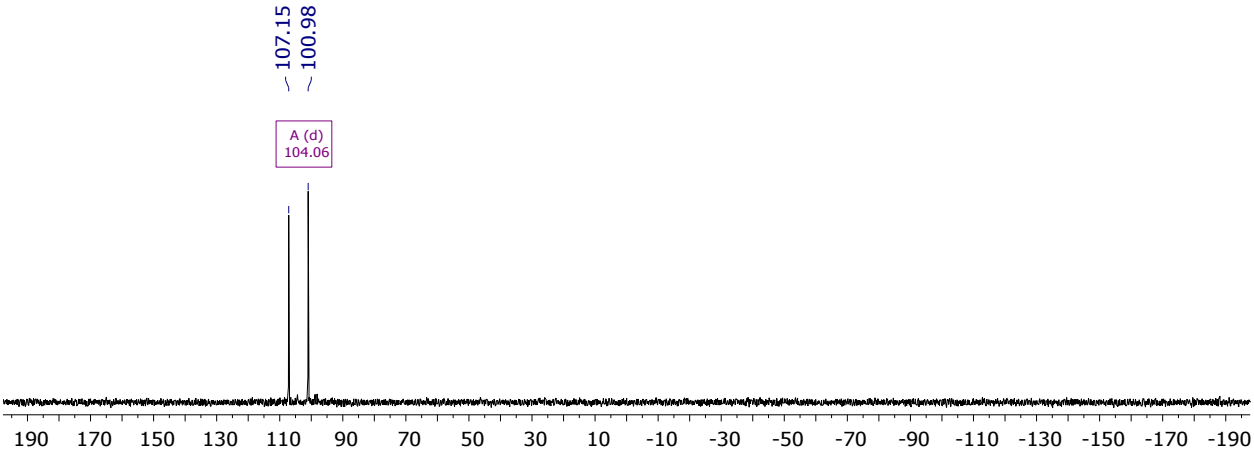


Figure S39. $^{31}P\{^{1}H\}$ NMR spectrum of **10**, CH_2Cl_2

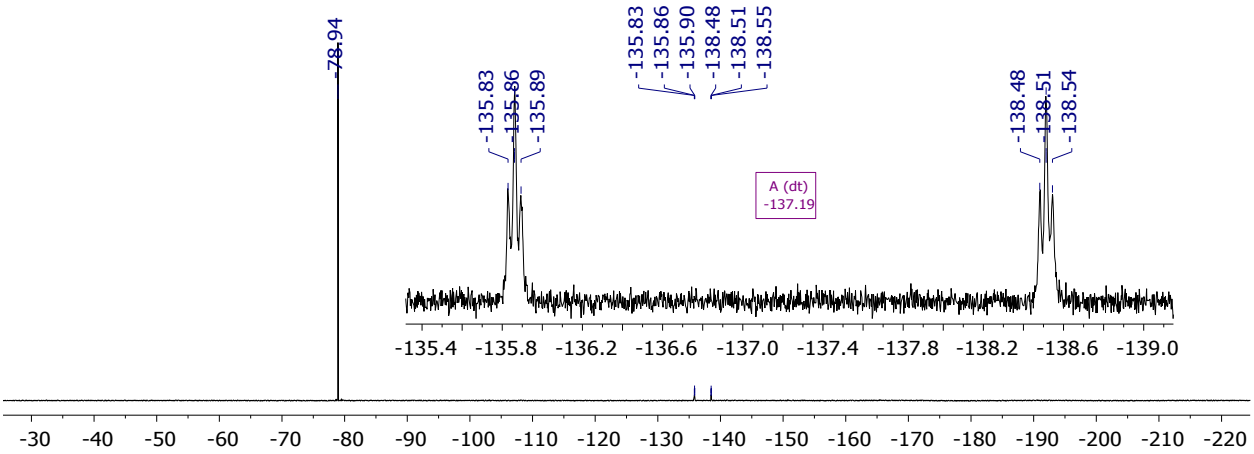
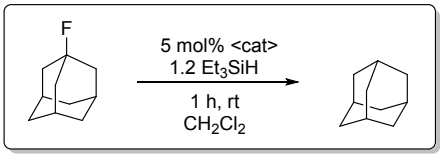


Figure S40. ^{19}F NMR spectrum of **10**, CH_2Cl_2

Hydrodefluorination of 1-fluoroadamantane with bis(fluorophosphonium)pyridine 2[B(C_6F_5)$_4$]



Procedure:

1-fluoroadamantane (15 mg, 0.10 mmol) and Et_3SiH (triethylsilane, 20 µL, 0.12 mmol) were dissolved in CH_2Cl_2 (0.5 mL). The solution was transferred to an NMR tube charged with the title catalyst (9 mg, 5 mol %) and left at ambient temperature for 1 hour, at which time the reaction mixture was analyzed by ^{19}F NMR. Conversion was determined by consumption of 1-fluoroadamantane and production of triethylsilyl fluoride. Additionally, no starting material is observed by ^{19}F NMR.

Average conversion after 1 hour: > 99%

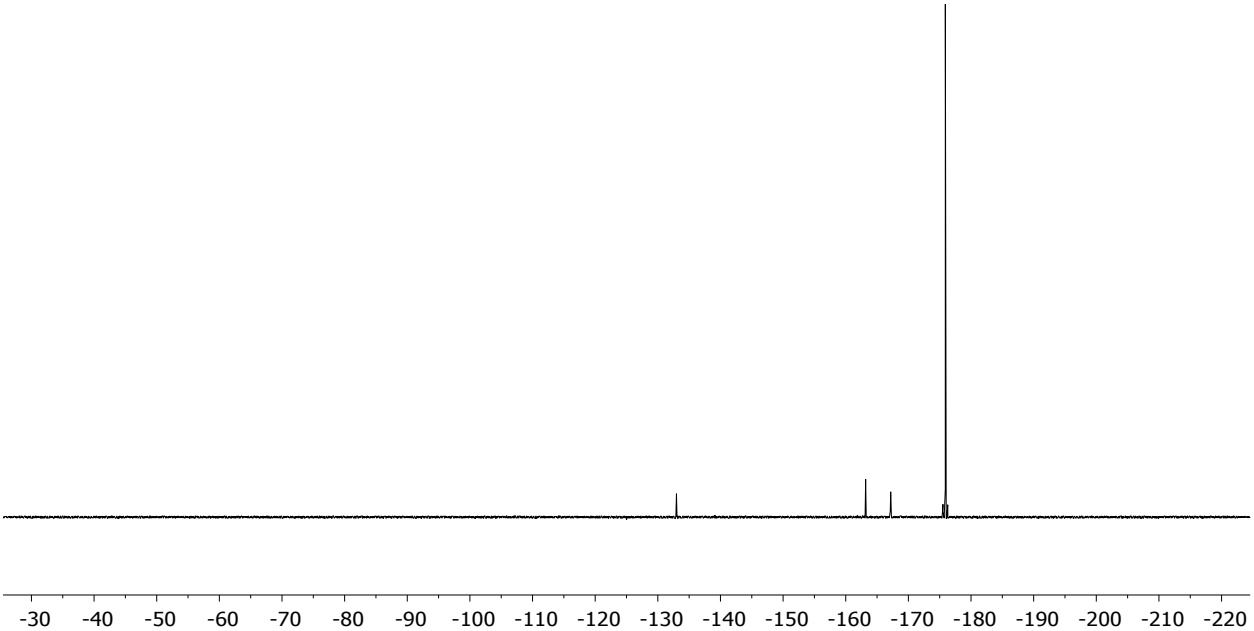
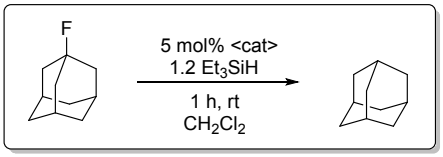


Figure S41. $^{19}F\{^1H\}$ NMR spectrum of reaction with title catalyst after 1 hour. Three minor resonances correspond to *ortho*, *meta*, *para* fluorines of [B(C_6F_5)$_4$] counterions. Note: resonance corresponding to the P-F doublet is not observed in this view as it may be buried in the baseline.

Hydrodefluorination of 1-fluoroadamantane with bis(fluorophosphonium)pyridinium 3[$B(C_6F_5)_4$]



Procedure:

1-fluoroadamantane (15 mg, 0.10 mmol) and Et_3SiH (triethylsilane, 20 µL, 0.12 mmol) were dissolved in CH_2Cl_2 (0.5 mL). The solution was transferred to an NMR tube charged with the title catalyst (12 mg, 5 mol %) and left at ambient temperature for 1 hour, at which time the reaction mixture was analyzed by ^{19}F NMR. Conversion was determined by consumption of 1-fluoroadamantane and production of triethylsilyl fluoride. Additionally, no starting material is observed by ^{19}F NMR.

Average conversion after 1 hour: > 99%

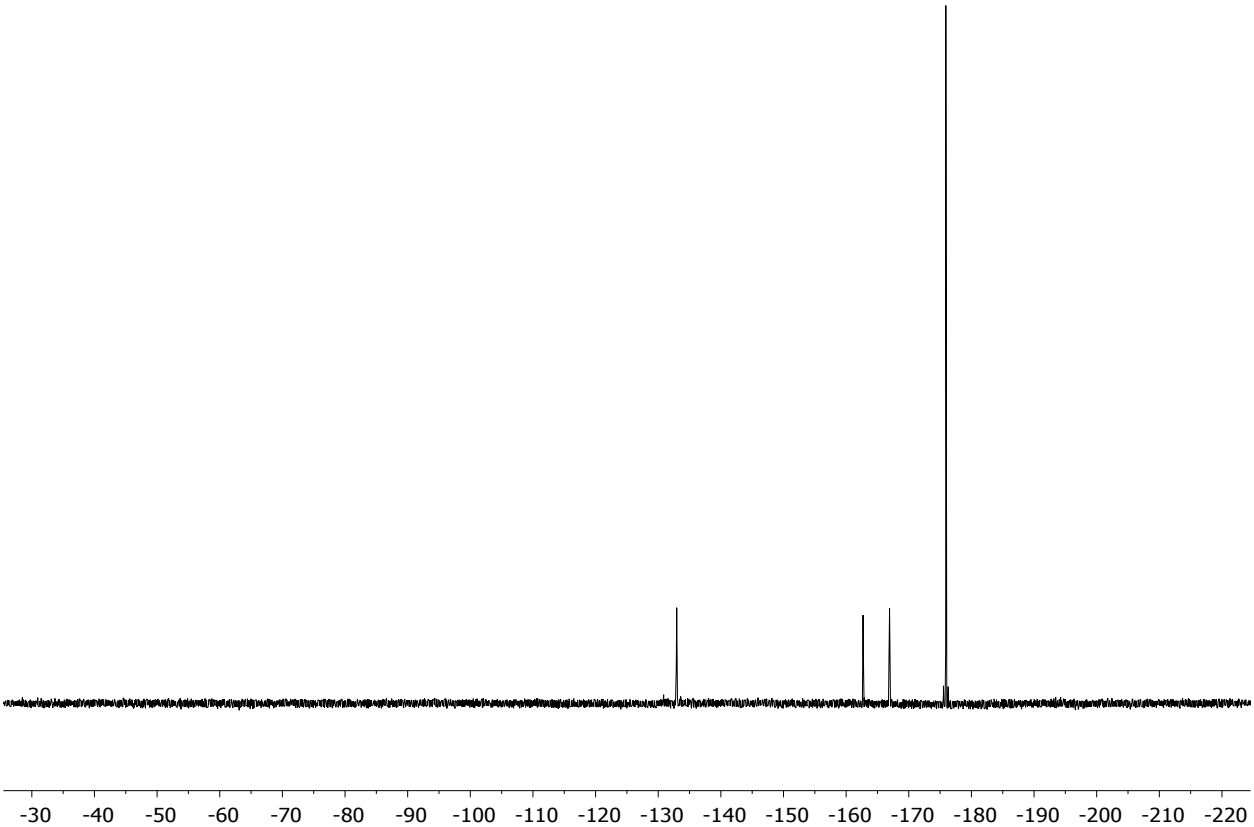
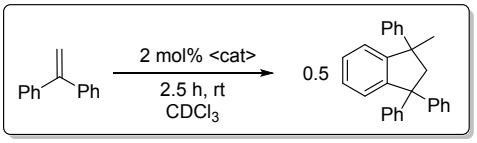


Figure S42. $^{19}F\{^1H\}$ NMR spectrum of reaction with title catalyst after 1 hour. Three minor resonances correspond to ortho, meta, para fluorines of [$B(C_6F_5)_4$] counterions. Note: resonance corresponding to the P-F doublet is not observed in this view as it may be buried in the baseline.

Dimerization of 1,1-diphenylethylene with bis(fluorophosphonium)pyridine 2[B(C_6F_5)$_4$]



Procedure:

A solution of 1,1-diphenylethylene (18 mg, 0.10 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube charged with the title catalyst (4 mg, 2 mol %). The reaction which became opaque and orange-green, was allowed to proceed at ambient temperature for 2.5 hours, after which time the reaction was analyzed by ^{1}H NMR spectroscopy and again at 20 hours. Conversion was determined by integration of diagnostic peaks in the ^{1}H NMR spectra – specifically the disappearance of the singlet resonance of the olefin -CH_2 protons of the starting material (δ 5.51 ppm) and the emergence of a methyl singlet resonance of the product (δ 1.59 ppm).

Average conversion: 61% (2.5 hours) and 99% (20 hours).

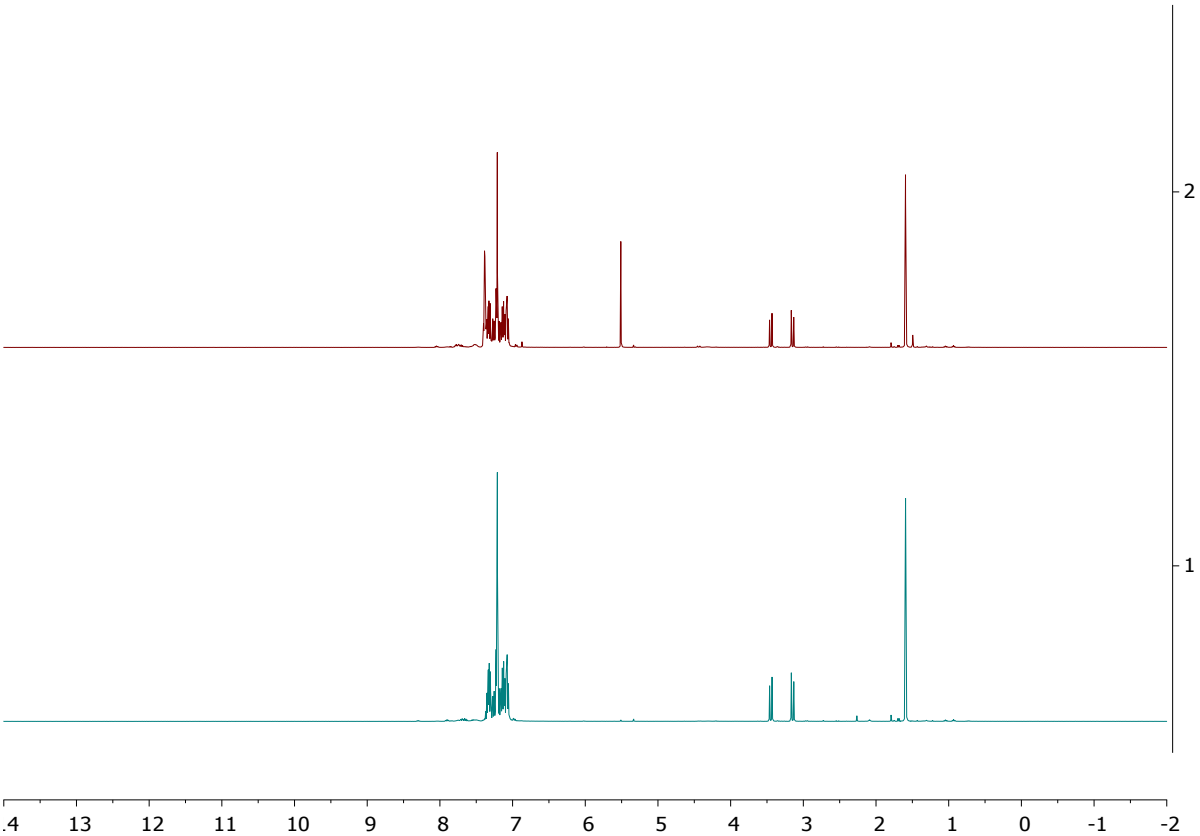
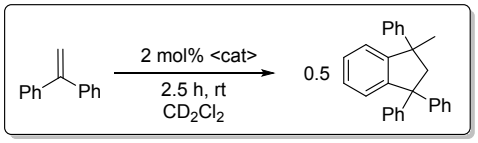


Figure S43. ^{1}H NMR spectra of title reaction. Top spectrum at reaction time of 2.5 hours (average: 61% conversion) and bottom spectrum at reaction time of 20 hours (average: 99% conversion).

Dimerization of 1,1-diphenylethylene with bis(fluorophosphonium)pyridinium 3[$B(C_6F_5)_4$] in CD_2Cl_2



Procedure:

A solution of 1,1-diphenylethylene (18 mg, 0.10 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube charged with the title catalyst (5 mg, 2 mol %). The reaction which became opaque and orange-green, was allowed to proceed at ambient temperature and analyzed at intervals by ^1H NMR spectroscopy. For NMR determination procedure, see previous page. It is noteworthy to note that the catalyst is fully soluble in this solvent, in stark difference to $CDCl_3$.

Average conversion: > 99% (1 hour)

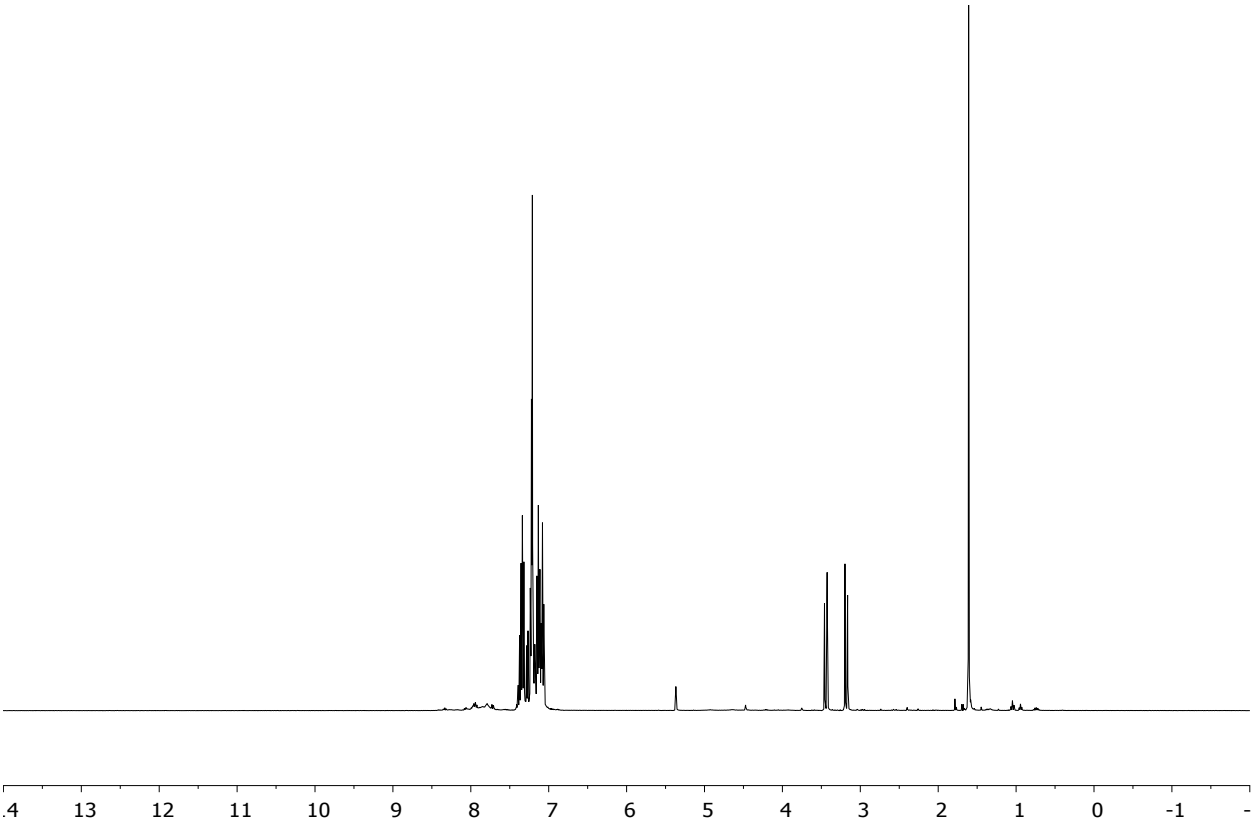
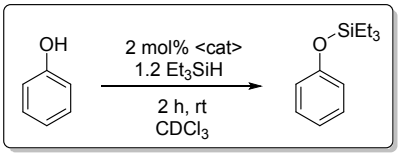


Figure S44. ^1H NMR spectra of title reaction at reaction time of 1 hour (average: 99% conversion).

Dehydrocoupling of phenol and triethylsilane with bis(fluorophosphonium)pyridine 2[$B(C_6F_5)_4$]



Procedure:

A solution containing phenol (9 mg, 0.10 mmol), Et_3SiH (triethylsilane, 20 µL, 0.12 mmol) and mesityl (14 µL, 0.10 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube charged with the title catalyst (4 mg, 2 mol %). The immediate production of a gas, H_2, was noticed. The clear, colourless and vigorously bubbling reaction was allowed to proceed at ambient temperature for 2 hours, after which time the reaction was analyzed by ^1H NMR spectroscopy. Conversion was determined by integration of diagnostic peaks in the ^1H NMR spectra – namely the singlet resonance of the methyl protons of the internal standard to the resonances corresponding to both the aromatic and aliphatic protons of the product. Additionally, the O-H phenol resonance is not observed at the end of the reaction.

Average conversion after 2 hours: > 99%

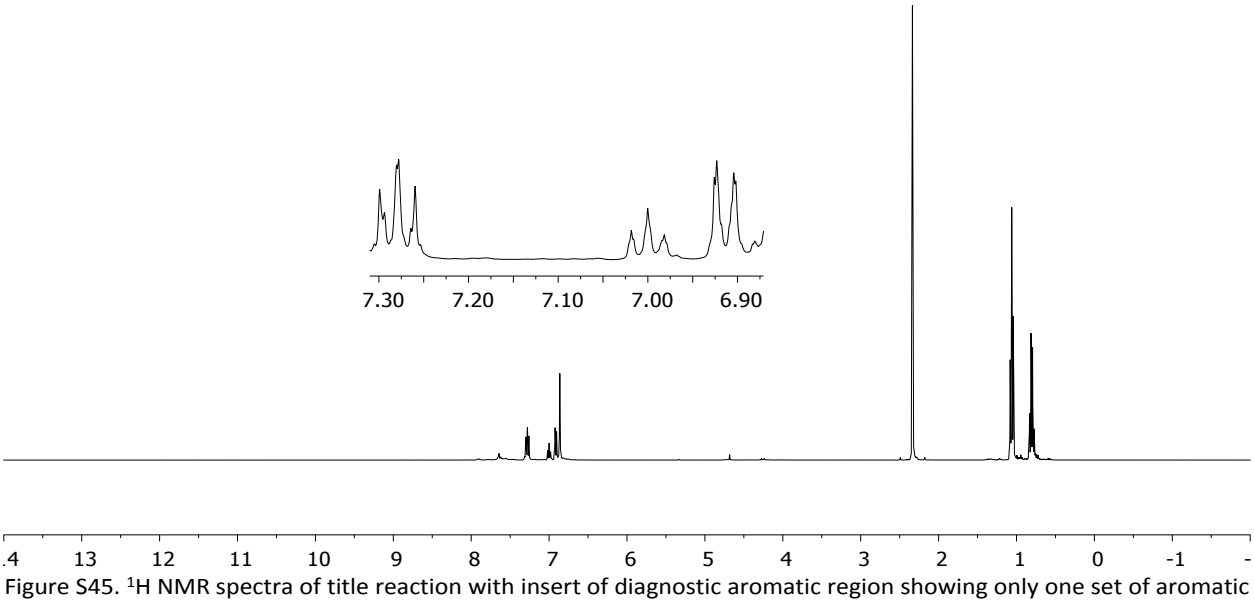
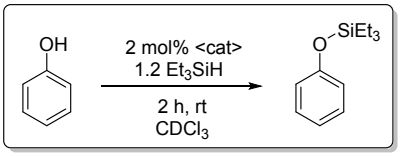


Figure S45. ^1H NMR spectra of title reaction with insert of diagnostic aromatic region showing only one set of aromatic resonance signals corresponding to the product.

Dehydrocoupling of phenol and triethylsilane with bis(fluorophosphonium)pyridinium 3[$B(C_6F_5)_4$]



Procedure:

A solution containing phenol (9 mg, 0.10 mmol), Et_3SiH (triethylsilane, 20 µL, 0.12 mmol) and mesityl (14 µL, 0.10 mmol) in $CDCl_3$ (0.5 mL) was added to an NMR tube charged with the title catalyst (5 mg, 2 mol %). The immediate production of a gas, H_2, was noticed. It was noticed that the catalyst was not fully in solution during the duration of the reaction. The clear and colourless reaction was allowed to proceed at ambient temperature for 2 hours, after which time the reaction was analyzed by ^1H NMR spectroscopy. For NMR determination procedure, see previous page.

Average conversion after 2 hours: > 99%

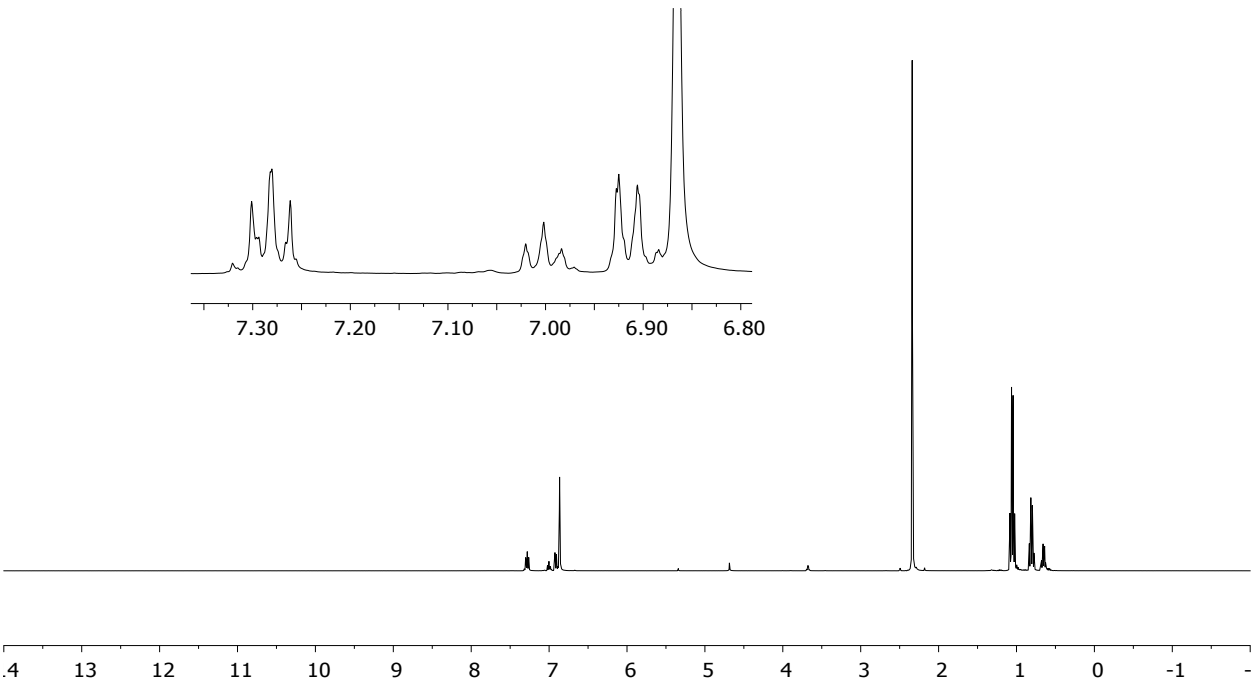


Figure S46. ^1H NMR spectra of title reaction with insert of diagnostic aromatic region showing only one set of aromatic resonance signals corresponding to the product.

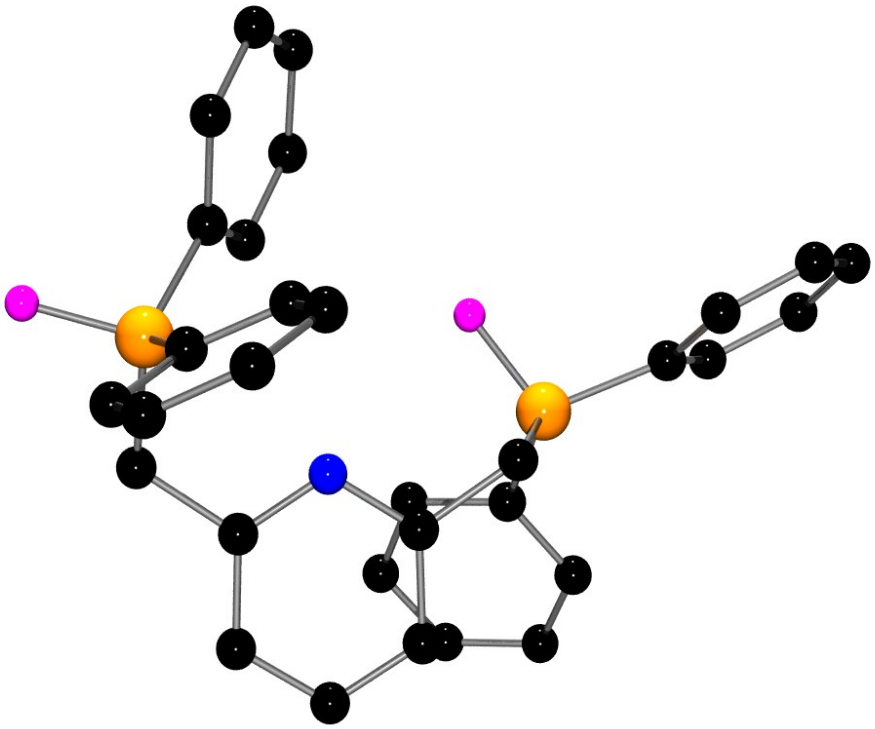


Figure S47. POV-RAY depiction of molecular structure of 2,6-bis(fluorophosphonium) pyridine **5**. P: orange, F: pink, C: black, N: blue. Hydrogen atoms and BF_4^- counterions omitted for clarity.

Table 1. Crystal data and structure refinement for **2**.

Identification code	pre1	
Empirical formula	$C_{35}\ H_{33}\ F_6\ N\ O_6\ P_2\ S_2$	
Formula weight	803.68	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.5221(10) Å	α= 90°.
	b = 10.1677(6) Å	β= 100.283(2)°.
	c = 21.9637(12) Å	γ = 90°.
Volume	3630.5(4) $Å^3$	
Z	4	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	0.312 mm^{-1}	
F(000)	1656	
Crystal size	0.280 x 0.140 x 0.140 mm^3	
Theta range for data collection	2.214 to 27.596°.	
Index ranges	-21<=h<=21, -13<=k<=13, -28<=l<=28	
Reflections collected	56971	
Independent reflections	8357 [R(int) = 0.0391]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8357 / 0 / 471	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1103	
R indices (all data)	R1 = 0.0628, wR2 = 0.1206	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.739 and -0.561 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pre1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	-824(1)	-845(1)	3259(1)	29(1)
S(2)	4666(1)	6568(1)	1320(1)	25(1)
P(1)	1735(1)	1726(1)	3508(1)	21(1)
P(2)	3967(1)	1117(1)	1674(1)	18(1)
F(1)	-174(2)	-862(3)	4432(1)	102(1)
F(2)	-1237(2)	-2057(4)	4191(1)	163(2)
F(3)	-1367(2)	-24(4)	4214(2)	158(2)
F(4)	4628(1)	6457(2)	128(1)	72(1)
F(5)	5481(1)	7858(2)	595(1)	56(1)
F(6)	5766(1)	5822(2)	688(1)	72(1)
O(1)	-238(1)	-1846(2)	3181(1)	63(1)
O(2)	-505(1)	442(2)	3211(1)	47(1)
O(3)	-1645(1)	-1067(2)	2929(1)	47(1)
O(4)	4433(1)	5217(2)	1336(1)	45(1)
O(5)	3986(1)	7455(2)	1171(1)	46(1)
O(6)	5295(1)	6998(2)	1813(1)	57(1)
C(7)	2917(1)	-547(2)	2174(1)	19(1)
C(1)	-40(2)	4685(3)	4123(1)	45(1)
C(2)	437(2)	5057(3)	3698(1)	41(1)
C(3)	976(2)	4161(2)	3509(1)	32(1)
C(4)	1033(1)	2888(2)	3752(1)	24(1)
C(5)	1230(1)	1018(2)	2789(1)	22(1)
C(6)	1710(1)	-2(2)	2499(1)	20(1)
N(1)	2492(1)	301(2)	2466(1)	19(1)
C(8)	3810(1)	-217(2)	2185(1)	20(1)
C(9)	3494(1)	703(2)	896(1)	21(1)
C(10)	3957(2)	158(2)	491(1)	27(1)
C(11)	3576(2)	-220(2)	-98(1)	34(1)
C(12)	2743(2)	-59(2)	-282(1)	35(1)
C(13)	2418(2)	-1472(3)	4965(1)	42(1)
C(14)	1838(2)	-1726(3)	4449(1)	42(1)

C(15)	1614(2)	-762(2)	3999(1)	33(1)
C(16)	1989(1)	466(2)	4081(1)	25(1)
C(17)	2642(1)	2605(2)	3416(1)	28(1)
C(18)	8(2)	3419(3)	4360(1)	42(1)
C(19)	546(1)	2516(3)	4178(1)	31(1)
C(20)	1336(1)	-1160(2)	2263(1)	26(1)
C(21)	1771(2)	-2003(2)	1949(1)	30(1)
C(22)	2570(1)	-1690(2)	1893(1)	26(1)
C(23)	2279(2)	470(3)	118(1)	41(1)
C(24)	2648(2)	855(3)	709(1)	35(1)
C(25)	5048(1)	1353(2)	1699(1)	20(1)
C(26)	5632(1)	569(2)	2066(1)	28(1)
C(27)	6464(2)	807(3)	2084(1)	34(1)
C(28)	6711(1)	1813(2)	1734(1)	32(1)
C(29)	6137(2)	2597(2)	1368(1)	31(1)
C(30)	5303(1)	2375(2)	1351(1)	26(1)
C(31)	3524(1)	2606(2)	1897(1)	24(1)
C(32)	2564(1)	728(3)	4616(1)	33(1)
C(33)	2775(2)	-244(3)	5052(1)	40(1)
C(34)	-911(3)	-949(5)	4061(2)	76(1)
C(35)	5151(2)	6680(3)	645(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for pre1.

S(1)-O(2)	1.422(2)
S(1)-O(1)	1.436(2)
S(1)-O(3)	1.4371(19)
S(1)-C(34)	1.795(3)
S(2)-O(4)	1.4279(18)
S(2)-O(6)	1.4304(19)
S(2)-O(5)	1.4318(19)
S(2)-C(35)	1.811(2)
P(1)-C(17)	1.787(2)
P(1)-C(16)	1.792(2)
P(1)-C(5)	1.799(2)
P(1)-C(4)	1.803(2)
P(2)-C(31)	1.787(2)
P(2)-C(25)	1.795(2)
P(2)-C(9)	1.798(2)
P(2)-C(8)	1.808(2)
F(1)-C(34)	1.342(4)
F(2)-C(34)	1.303(4)
F(3)-C(34)	1.287(6)
F(4)-C(35)	1.317(3)
F(5)-C(35)	1.329(3)
F(6)-C(35)	1.331(3)
C(7)-N(1)	1.345(3)
C(7)-C(22)	1.391(3)
C(7)-C(8)	1.509(3)
C(1)-C(2)	1.378(4)
C(1)-C(18)	1.384(4)
C(1)-H(1)	0.9500
C(2)-C(3)	1.389(3)
C(2)-H(9)	0.9500
C(3)-C(4)	1.396(3)
C(3)-H(10)	0.9500
C(4)-C(19)	1.392(3)
C(5)-C(6)	1.514(3)

C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-N(1)	1.344(3)
C(6)-C(20)	1.387(3)
C(8)-H(23)	0.9900
C(8)-H(24)	0.9900
C(9)-C(10)	1.389(3)
C(9)-C(24)	1.392(3)
C(10)-C(11)	1.388(3)
C(10)-H(11)	0.9500
C(11)-C(12)	1.372(4)
C(11)-H(14)	0.9500
C(12)-C(23)	1.374(4)
C(12)-H(2)	0.9500
C(13)-C(14)	1.373(4)
C(13)-C(33)	1.380(4)
C(13)-H(3)	0.9500
C(14)-C(15)	1.395(3)
C(14)-H(33)	0.9500
C(15)-C(16)	1.391(3)
C(15)-H(32)	0.9500
C(16)-C(32)	1.398(3)
C(17)-H(4)	0.9800
C(17)-H(6)	0.9800
C(17)-H(5)	0.9800
C(18)-C(19)	1.387(3)
C(18)-H(7)	0.9500
C(19)-H(8)	0.9500
C(20)-C(21)	1.381(3)
C(20)-H(28)	0.9500
C(21)-C(22)	1.384(3)
C(21)-H(27)	0.9500
C(22)-H(26)	0.9500
C(23)-C(24)	1.390(3)
C(23)-H(13)	0.9500
C(24)-H(12)	0.9500

C(25)-C(26)	1.392(3)
C(25)-C(30)	1.399(3)
C(26)-C(27)	1.390(3)
C(26)-H(19)	0.9500
C(27)-C(28)	1.382(3)
C(27)-H(18)	0.9500
C(28)-C(29)	1.381(3)
C(28)-H(17)	0.9500
C(29)-C(30)	1.390(3)
C(29)-H(16)	0.9500
C(30)-H(15)	0.9500
C(31)-H(20)	0.9800
C(31)-H(22)	0.9800
C(31)-H(21)	0.9800
C(32)-C(33)	1.377(4)
C(32)-H(31)	0.9500
C(33)-H(30)	0.9500

O(2)-S(1)-O(1)	112.16(13)
O(2)-S(1)-O(3)	115.83(13)
O(1)-S(1)-O(3)	115.07(12)
O(2)-S(1)-C(34)	102.91(16)
O(1)-S(1)-C(34)	104.4(2)
O(3)-S(1)-C(34)	104.59(15)
O(4)-S(2)-O(6)	115.99(13)
O(4)-S(2)-O(5)	114.10(12)
O(6)-S(2)-O(5)	114.51(14)
O(4)-S(2)-C(35)	103.93(12)
O(6)-S(2)-C(35)	103.49(13)
O(5)-S(2)-C(35)	102.49(12)
C(17)-P(1)-C(16)	109.97(11)
C(17)-P(1)-C(5)	111.61(10)
C(16)-P(1)-C(5)	110.11(10)
C(17)-P(1)-C(4)	107.61(11)
C(16)-P(1)-C(4)	110.00(10)
C(5)-P(1)-C(4)	107.46(10)

C(31)-P(2)-C(25)	109.44(10)
C(31)-P(2)-C(9)	109.23(10)
C(25)-P(2)-C(9)	108.80(9)
C(31)-P(2)-C(8)	110.72(10)
C(25)-P(2)-C(8)	109.45(10)
C(9)-P(2)-C(8)	109.17(10)
N(1)-C(7)-C(22)	122.55(19)
N(1)-C(7)-C(8)	116.19(18)
C(22)-C(7)-C(8)	121.23(18)
C(2)-C(1)-C(18)	120.6(2)
C(2)-C(1)-H(1)	119.7
C(18)-C(1)-H(1)	119.7
C(1)-C(2)-C(3)	119.8(3)
C(1)-C(2)-H(9)	120.1
C(3)-C(2)-H(9)	120.1
C(2)-C(3)-C(4)	119.8(2)
C(2)-C(3)-H(10)	120.1
C(4)-C(3)-H(10)	120.1
C(19)-C(4)-C(3)	120.1(2)
C(19)-C(4)-P(1)	120.09(18)
C(3)-C(4)-P(1)	119.82(17)
C(6)-C(5)-P(1)	116.56(14)
C(6)-C(5)-H(5A)	108.2
P(1)-C(5)-H(5A)	108.2
C(6)-C(5)-H(5B)	108.2
P(1)-C(5)-H(5B)	108.2
H(5A)-C(5)-H(5B)	107.3
N(1)-C(6)-C(20)	122.91(19)
N(1)-C(6)-C(5)	116.54(18)
C(20)-C(6)-C(5)	120.51(19)
C(6)-N(1)-C(7)	117.89(18)
C(7)-C(8)-P(2)	113.88(14)
C(7)-C(8)-H(23)	108.8
P(2)-C(8)-H(23)	108.8
C(7)-C(8)-H(24)	108.8
P(2)-C(8)-H(24)	108.8

H(23)-C(8)-H(24)	107.7
C(10)-C(9)-C(24)	119.6(2)
C(10)-C(9)-P(2)	120.48(17)
C(24)-C(9)-P(2)	119.79(17)
C(11)-C(10)-C(9)	119.9(2)
C(11)-C(10)-H(11)	120.1
C(9)-C(10)-H(11)	120.1
C(12)-C(11)-C(10)	120.3(2)
C(12)-C(11)-H(14)	119.9
C(10)-C(11)-H(14)	119.9
C(11)-C(12)-C(23)	120.2(2)
C(11)-C(12)-H(2)	119.9
C(23)-C(12)-H(2)	119.9
C(14)-C(13)-C(33)	120.2(2)
C(14)-C(13)-H(3)	119.9
C(33)-C(13)-H(3)	119.9
C(13)-C(14)-C(15)	120.7(3)
C(13)-C(14)-H(33)	119.7
C(15)-C(14)-H(33)	119.7
C(16)-C(15)-C(14)	118.9(2)
C(16)-C(15)-H(32)	120.5
C(14)-C(15)-H(32)	120.5
C(15)-C(16)-C(32)	120.0(2)
C(15)-C(16)-P(1)	120.52(17)
C(32)-C(16)-P(1)	119.51(19)
P(1)-C(17)-H(4)	109.5
P(1)-C(17)-H(6)	109.5
H(4)-C(17)-H(6)	109.5
P(1)-C(17)-H(5)	109.5
H(4)-C(17)-H(5)	109.5
H(6)-C(17)-H(5)	109.5
C(1)-C(18)-C(19)	120.2(3)
C(1)-C(18)-H(7)	119.9
C(19)-C(18)-H(7)	119.9
C(18)-C(19)-C(4)	119.4(2)
C(18)-C(19)-H(8)	120.3

C(4)-C(19)-H(8)	120.3
C(21)-C(20)-C(6)	118.5(2)
C(21)-C(20)-H(28)	120.7
C(6)-C(20)-H(28)	120.7
C(20)-C(21)-C(22)	119.4(2)
C(20)-C(21)-H(27)	120.3
C(22)-C(21)-H(27)	120.3
C(21)-C(22)-C(7)	118.5(2)
C(21)-C(22)-H(26)	120.7
C(7)-C(22)-H(26)	120.7
C(12)-C(23)-C(24)	120.4(2)
C(12)-C(23)-H(13)	119.8
C(24)-C(23)-H(13)	119.8
C(23)-C(24)-C(9)	119.6(2)
C(23)-C(24)-H(12)	120.2
C(9)-C(24)-H(12)	120.2
C(26)-C(25)-C(30)	119.8(2)
C(26)-C(25)-P(2)	121.65(17)
C(30)-C(25)-P(2)	118.49(16)
C(27)-C(26)-C(25)	119.7(2)
C(27)-C(26)-H(19)	120.1
C(25)-C(26)-H(19)	120.1
C(28)-C(27)-C(26)	120.1(2)
C(28)-C(27)-H(18)	120.0
C(26)-C(27)-H(18)	120.0
C(29)-C(28)-C(27)	120.7(2)
C(29)-C(28)-H(17)	119.6
C(27)-C(28)-H(17)	119.6
C(28)-C(29)-C(30)	119.8(2)
C(28)-C(29)-H(16)	120.1
C(30)-C(29)-H(16)	120.1
C(29)-C(30)-C(25)	119.9(2)
C(29)-C(30)-H(15)	120.1
C(25)-C(30)-H(15)	120.1
P(2)-C(31)-H(20)	109.5
P(2)-C(31)-H(22)	109.5

H(20)-C(31)-H(22)	109.5
P(2)-C(31)-H(21)	109.5
H(20)-C(31)-H(21)	109.5
H(22)-C(31)-H(21)	109.5
C(33)-C(32)-C(16)	119.9(2)
C(33)-C(32)-H(31)	120.1
C(16)-C(32)-H(31)	120.1
C(32)-C(33)-C(13)	120.2(2)
C(32)-C(33)-H(30)	119.9
C(13)-C(33)-H(30)	119.9
F(3)-C(34)-F(2)	106.9(4)
F(3)-C(34)-F(1)	107.6(3)
F(2)-C(34)-F(1)	106.8(4)
F(3)-C(34)-S(1)	111.5(3)
F(2)-C(34)-S(1)	112.1(3)
F(1)-C(34)-S(1)	111.7(2)
F(4)-C(35)-F(5)	107.5(2)
F(4)-C(35)-F(6)	108.9(2)
F(5)-C(35)-F(6)	106.0(2)
F(4)-C(35)-S(2)	112.13(17)
F(5)-C(35)-S(2)	111.84(18)
F(6)-C(35)-S(2)	110.18(19)

Table 4. Crystal data and structure refinement for **4**.

Identification code	ortho	
Empirical formula	$C_{31}\ H_{27}\ F_4\ N\ P_2$	
Formula weight	551.47	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 8.716(2) Å	α= 90°.
	b = 23.262(6) Å	β= 90°.
	c = 6.4438(14) Å	γ = 90°.
Volume	1306.6(5) $Å^3$	
Z	2	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	572	
Crystal size	0.080 x 0.060 x 0.060 mm^3	
Theta range for data collection	2.495 to 27.490°.	
Index ranges	-11<=h<=10, -29<=k<=30, -6<=l<=8	
Reflections collected	12003	
Independent reflections	3004 [R(int) = 0.0938]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3004 / 0 / 173	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.0849	
R indices (all data)	R1 = 0.0916, wR2 = 0.0960	
Absolute structure parameter	-0.07(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.475 and -0.357 $e.Å^{-3}$	

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ortho. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	1761(1)	971(1)	7045(2)	18(1)
F(1)	2543(2)	978(1)	4677(3)	27(1)
F(2)	1074(2)	955(1)	9486(3)	23(1)
C(1)	2294(4)	216(2)	7335(6)	22(1)
C(11)	-157(5)	1094(2)	6003(6)	19(1)
C(12)	-1336(4)	1298(2)	7276(6)	22(1)
C(13)	-2813(5)	1357(2)	6513(7)	28(1)
C(14)	-3139(6)	1209(2)	4494(7)	32(1)
C(15)	-1979(5)	1018(2)	3204(7)	27(1)
C(16)	-489(5)	958(2)	3943(6)	22(1)
C(21)	2952(4)	1584(2)	7761(6)	19(1)
C(22)	3253(5)	2011(2)	6297(6)	24(1)
C(23)	4131(5)	2486(2)	6788(8)	31(1)
C(24)	4746(6)	2542(2)	8758(7)	34(1)
C(25)	4468(5)	2119(2)	10238(7)	31(1)
C(26)	3551(5)	1652(2)	9756(6)	22(1)
N(1)	5000	0	7533(7)	19(1)
C(31)	3714(5)	107(2)	8616(6)	20(1)
C(32)	3679(5)	119(2)	10776(6)	24(1)
C(33)	5000	0	11854(10)	24(1)

Table 6. Bond lengths [Å] and angles [°] for ortho.

P(1)-F(1)	1.671(2)
P(1)-F(2)	1.683(2)
P(1)-C(21)	1.823(4)
P(1)-C(11)	1.824(4)
P(1)-C(1)	1.826(4)
C(1)-C(31)	1.509(5)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(11)-C(16)	1.395(5)
C(11)-C(12)	1.398(5)
C(12)-C(13)	1.385(6)
C(12)-H(12)	0.9500
C(13)-C(14)	1.375(6)
C(13)-H(13)	0.9500
C(14)-C(15)	1.382(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.390(6)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(21)-C(22)	1.395(5)
C(21)-C(26)	1.397(6)
C(22)-C(23)	1.381(6)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(6)
C(23)-H(23)	0.9500
C(24)-C(25)	1.392(6)
C(24)-H(24)	0.9500
C(25)-C(26)	1.383(6)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
N(1)-C(31)#1	1.344(5)
N(1)-C(31)	1.344(5)
C(31)-C(32)	1.393(5)
C(32)-C(33)	1.372(5)

C(32)-H(32)	0.9500
C(33)-C(32)#1	1.372(5)
C(33)-H(33)	0.9500

F(1)-P(1)-F(2)	176.71(13)
F(1)-P(1)-C(21)	89.50(16)
F(2)-P(1)-C(21)	89.07(16)
F(1)-P(1)-C(11)	92.06(15)
F(2)-P(1)-C(11)	91.22(15)
C(21)-P(1)-C(11)	119.48(19)
F(1)-P(1)-C(1)	89.95(17)
F(2)-P(1)-C(1)	88.48(16)
C(21)-P(1)-C(1)	125.57(19)
C(11)-P(1)-C(1)	114.94(18)
C(31)-C(1)-P(1)	115.2(3)
C(31)-C(1)-H(1A)	108.5
P(1)-C(1)-H(1A)	108.5
C(31)-C(1)-H(1B)	108.5
P(1)-C(1)-H(1B)	108.5
H(1A)-C(1)-H(1B)	107.5
C(16)-C(11)-C(12)	118.9(4)
C(16)-C(11)-P(1)	120.3(3)
C(12)-C(11)-P(1)	120.7(3)
C(13)-C(12)-C(11)	120.6(4)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	120.2(4)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	119.9(4)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.6(4)
C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7
C(15)-C(16)-C(11)	119.8(4)

C(15)-C(16)-H(16)	120.1
C(11)-C(16)-H(16)	120.1
C(22)-C(21)-C(26)	118.1(4)
C(22)-C(21)-P(1)	119.6(3)
C(26)-C(21)-P(1)	122.3(3)
C(23)-C(22)-C(21)	121.3(4)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(22)-C(23)-C(24)	120.0(4)
C(22)-C(23)-H(23)	120.0
C(24)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	119.6(4)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(26)-C(25)-C(24)	120.1(4)
C(26)-C(25)-H(25)	119.9
C(24)-C(25)-H(25)	119.9
C(25)-C(26)-C(21)	120.7(4)
C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6
C(31)#1-N(1)-C(31)	117.4(5)
N(1)-C(31)-C(32)	122.8(4)
N(1)-C(31)-C(1)	115.5(3)
C(32)-C(31)-C(1)	121.7(4)
C(33)-C(32)-C(31)	118.9(4)
C(33)-C(32)-H(32)	120.6
C(31)-C(32)-H(32)	120.6
C(32)-C(33)-C(32)#1	119.2(6)
C(32)-C(33)-H(33)	120.4
C(32)#1-C(33)-H(33)	120.4

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z

Table 7. Crystal data and structure refinement for **5**.

Identification code	q1	
Empirical formula	$C_{31}\ H_{27}\ B_2\ F_{10}\ N\ P_2$	
Formula weight	687.09	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.205(3) Å	α= 90°.
	b = 15.0893(11) Å	β= 130.351(7)°.
	c = 19.149(2) Å	γ = 90°.
Volume	6210.9(11) $Å^3$	
Z	8	
Density (calculated)	1.470 Mg/m^3	
Absorption coefficient	0.224 mm^{-1}	
F(000)	2800	
Crystal size	0.200 x 0.200 x 0.100 mm^3	
Theta range for data collection	2.129 to 27.721°.	
Index ranges	-35<=h<=36, -19<=k<=19, -24<=l<=24	
Reflections collected	49190	
Independent reflections	7222 [R(int) = 0.0474]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7222 / 0 / 416	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.0931	
R indices (all data)	R1 = 0.0693, wR2 = 0.1048	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.361 and -0.388 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for q1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	1468(1)	4291(1)	4677(1)	26(1)
P(2)	702(1)	1996(1)	6276(1)	24(1)
F(1)	1622(1)	4543(1)	4059(1)	41(1)
F(2)	1138(1)	1717(1)	6083(1)	35(1)
F(11)	248(1)	1378(1)	3251(1)	71(1)
F(12)	452(1)	2432(1)	2642(1)	82(1)
F(21)	476(1)	6014(1)	2714(1)	56(1)
F(22)	204(1)	7066(1)	3240(1)	55(1)
F(31)	2828(1)	-1249(1)	6103(1)	50(1)
F(32)	2744(1)	-1347(1)	7195(1)	39(1)
F(33)	3349(1)	-285(1)	7293(1)	36(1)
F(34)	2306(1)	-191(1)	6198(1)	46(1)
B(1)	0	1894(2)	2500	37(1)
B(2)	0	6551(2)	2500	29(1)
B(3)	2808(1)	-768(2)	6693(2)	28(1)
N(1)	654(1)	3725(1)	5061(1)	22(1)
C(1)	645(1)	4175(1)	3842(1)	29(1)
C(2)	757(1)	3178(1)	6343(1)	26(1)
C(101)	370(1)	3594(1)	5406(1)	24(1)
C(102)	-250(1)	3802(1)	4925(1)	31(1)
C(103)	-589(1)	4170(1)	4064(2)	37(1)
C(104)	-305(1)	4311(1)	3701(1)	33(1)
C(105)	315(1)	4072(1)	4218(1)	25(1)
C(201)	989(1)	1492(1)	7311(1)	28(1)
C(202)	788(1)	652(2)	7318(2)	42(1)
C(203)	1062(1)	241(2)	8151(2)	52(1)
C(204)	1533(1)	656(2)	8952(2)	44(1)
C(205)	1730(1)	1483(2)	8948(1)	44(1)
C(206)	1457(1)	1914(2)	8132(1)	38(1)
C(301)	-37(1)	1610(1)	5315(1)	26(1)
C(302)	-166(1)	1552(1)	4480(1)	33(1)

C(303)	-756(1)	1321(2)	3704(1)	43(1)
C(304)	-1209(1)	1135(2)	3758(2)	48(1)
C(305)	-1082(1)	1191(2)	4585(2)	45(1)
C(306)	-497(1)	1441(1)	5369(1)	34(1)
C(401)	1896(1)	3323(1)	5260(1)	27(1)
C(402)	2546(1)	3386(2)	5882(2)	35(1)
C(403)	2900(1)	2631(2)	6325(2)	40(1)
C(404)	2607(1)	1832(2)	6157(2)	38(1)
C(405)	1968(1)	1761(1)	5531(2)	38(1)
C(406)	1607(1)	2512(1)	5076(2)	31(1)
C(501)	1727(1)	5208(1)	5414(1)	27(1)
C(502)	1619(1)	6058(1)	5046(2)	37(1)
C(503)	1830(1)	6778(2)	5620(2)	48(1)
C(504)	2151(1)	6661(2)	6547(2)	46(1)
C(505)	2258(1)	5825(2)	6908(2)	40(1)
C(506)	2042(1)	5093(1)	6342(1)	32(1)

Table 9. Bond lengths [Å] and angles [°] for q1.

P(1)-F(1)	1.5504(12)
P(1)-C(401)	1.760(2)
P(1)-C(501)	1.762(2)
P(1)-C(1)	1.780(2)
P(2)-F(2)	1.5512(12)
P(2)-C(201)	1.756(2)
P(2)-C(301)	1.7621(19)
P(2)-C(2)	1.787(2)
F(11)-B(1)	1.364(3)
F(12)-B(1)	1.381(3)
F(21)-B(2)	1.383(2)
F(22)-B(2)	1.374(2)
F(31)-B(3)	1.374(3)
F(32)-B(3)	1.395(3)
F(33)-B(3)	1.381(2)
F(34)-B(3)	1.387(2)
B(1)-F(11)#1	1.364(3)
B(1)-F(12)#1	1.381(3)
B(2)-F(22)#1	1.374(2)
B(2)-F(21)#1	1.383(2)
N(1)-C(105)	1.339(2)
N(1)-C(101)	1.342(2)
C(1)-C(105)	1.508(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(101)	1.508(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(101)-C(102)	1.387(3)
C(102)-C(103)	1.378(3)
C(102)-H(102)	0.9500
C(103)-C(104)	1.376(3)
C(103)-H(103)	0.9500
C(104)-C(105)	1.387(3)

C(104)-H(104)	0.9500
C(201)-C(206)	1.390(3)
C(201)-C(202)	1.394(3)
C(202)-C(203)	1.388(3)
C(202)-H(202)	0.9500
C(203)-C(204)	1.368(3)
C(203)-H(203)	0.9500
C(204)-C(205)	1.367(3)
C(204)-H(204)	0.9500
C(205)-C(206)	1.378(3)
C(205)-H(205)	0.9500
C(206)-H(206)	0.9500
C(301)-C(306)	1.389(3)
C(301)-C(302)	1.395(3)
C(302)-C(303)	1.377(3)
C(302)-H(302)	0.9500
C(303)-C(304)	1.376(3)
C(303)-H(303)	0.9500
C(304)-C(305)	1.381(3)
C(304)-H(304)	0.9500
C(305)-C(306)	1.383(3)
C(305)-H(305)	0.9500
C(306)-H(306)	0.9500
C(401)-C(406)	1.384(3)
C(401)-C(402)	1.400(3)
C(402)-C(403)	1.384(3)
C(402)-H(402)	0.9500
C(403)-C(404)	1.376(3)
C(403)-H(403)	0.9500
C(404)-C(405)	1.379(3)
C(404)-H(404)	0.9500
C(405)-C(406)	1.390(3)
C(405)-H(405)	0.9500
C(406)-H(406)	0.9500
C(501)-C(506)	1.392(3)
C(501)-C(502)	1.397(3)

C(502)-C(503)	1.377(3)
C(502)-H(502)	0.9500
C(503)-C(504)	1.385(4)
C(503)-H(503)	0.9500
C(504)-C(505)	1.375(3)
C(504)-H(504)	0.9500
C(505)-C(506)	1.382(3)
C(505)-H(505)	0.9500
C(506)-H(506)	0.9500

F(1)-P(1)-C(401)	105.69(8)
F(1)-P(1)-C(501)	104.06(8)
C(401)-P(1)-C(501)	112.73(10)
F(1)-P(1)-C(1)	100.69(8)
C(401)-P(1)-C(1)	116.65(10)
C(501)-P(1)-C(1)	114.86(9)
F(2)-P(2)-C(201)	107.10(8)
F(2)-P(2)-C(301)	104.28(8)
C(201)-P(2)-C(301)	113.83(9)
F(2)-P(2)-C(2)	104.06(8)
C(201)-P(2)-C(2)	113.26(9)
C(301)-P(2)-C(2)	113.18(9)
F(11)-B(1)-F(11)#1	110.3(3)
F(11)-B(1)-F(12)#1	108.68(10)
F(11)#1-B(1)-F(12)#1	110.48(12)
F(11)-B(1)-F(12)	110.48(12)
F(11)#1-B(1)-F(12)	108.68(10)
F(12)#1-B(1)-F(12)	108.2(3)
F(22)-B(2)-F(22)#1	111.1(3)
F(22)-B(2)-F(21)#1	108.40(8)
F(22)#1-B(2)-F(21)#1	110.29(9)
F(22)-B(2)-F(21)	110.29(9)
F(22)#1-B(2)-F(21)	108.40(8)
F(21)#1-B(2)-F(21)	108.3(3)
F(31)-B(3)-F(33)	110.56(18)
F(31)-B(3)-F(34)	109.76(17)

F(33)-B(3)-F(34)	109.09(17)
F(31)-B(3)-F(32)	109.14(17)
F(33)-B(3)-F(32)	108.79(16)
F(34)-B(3)-F(32)	109.47(18)
C(105)-N(1)-C(101)	117.48(16)
C(105)-C(1)-P(1)	115.48(13)
C(105)-C(1)-H(1A)	108.4
P(1)-C(1)-H(1A)	108.4
C(105)-C(1)-H(1B)	108.4
P(1)-C(1)-H(1B)	108.4
H(1A)-C(1)-H(1B)	107.5
C(101)-C(2)-P(2)	111.57(13)
C(101)-C(2)-H(2A)	109.3
P(2)-C(2)-H(2A)	109.3
C(101)-C(2)-H(2B)	109.3
P(2)-C(2)-H(2B)	109.3
H(2A)-C(2)-H(2B)	108.0
N(1)-C(101)-C(102)	122.65(18)
N(1)-C(101)-C(2)	116.42(16)
C(102)-C(101)-C(2)	120.91(17)
C(103)-C(102)-C(101)	118.98(19)
C(103)-C(102)-H(102)	120.5
C(101)-C(102)-H(102)	120.5
C(104)-C(103)-C(102)	119.14(19)
C(104)-C(103)-H(103)	120.4
C(102)-C(103)-H(103)	120.4
C(103)-C(104)-C(105)	118.44(19)
C(103)-C(104)-H(104)	120.8
C(105)-C(104)-H(104)	120.8
N(1)-C(105)-C(104)	123.30(18)
N(1)-C(105)-C(1)	115.74(16)
C(104)-C(105)-C(1)	120.94(17)
C(206)-C(201)-C(202)	120.00(19)
C(206)-C(201)-P(2)	119.01(16)
C(202)-C(201)-P(2)	120.81(15)
C(203)-C(202)-C(201)	119.3(2)

C(203)-C(202)-H(202)	120.3
C(201)-C(202)-H(202)	120.3
C(204)-C(203)-C(202)	119.9(2)
C(204)-C(203)-H(203)	120.0
C(202)-C(203)-H(203)	120.0
C(205)-C(204)-C(203)	120.9(2)
C(205)-C(204)-H(204)	119.6
C(203)-C(204)-H(204)	119.6
C(204)-C(205)-C(206)	120.5(2)
C(204)-C(205)-H(205)	119.8
C(206)-C(205)-H(205)	119.8
C(205)-C(206)-C(201)	119.4(2)
C(205)-C(206)-H(206)	120.3
C(201)-C(206)-H(206)	120.3
C(306)-C(301)-C(302)	120.72(18)
C(306)-C(301)-P(2)	120.97(15)
C(302)-C(301)-P(2)	118.09(15)
C(303)-C(302)-C(301)	119.2(2)
C(303)-C(302)-H(302)	120.4
C(301)-C(302)-H(302)	120.4
C(304)-C(303)-C(302)	120.2(2)
C(304)-C(303)-H(303)	119.9
C(302)-C(303)-H(303)	119.9
C(303)-C(304)-C(305)	120.7(2)
C(303)-C(304)-H(304)	119.7
C(305)-C(304)-H(304)	119.7
C(304)-C(305)-C(306)	120.1(2)
C(304)-C(305)-H(305)	119.9
C(306)-C(305)-H(305)	119.9
C(305)-C(306)-C(301)	119.02(19)
C(305)-C(306)-H(306)	120.5
C(301)-C(306)-H(306)	120.5
C(406)-C(401)-C(402)	120.52(18)
C(406)-C(401)-P(1)	121.54(15)
C(402)-C(401)-P(1)	117.83(16)
C(403)-C(402)-C(401)	119.6(2)

C(403)-C(402)-H(402)	120.2
C(401)-C(402)-H(402)	120.2
C(404)-C(403)-C(402)	119.4(2)
C(404)-C(403)-H(403)	120.3
C(402)-C(403)-H(403)	120.3
C(403)-C(404)-C(405)	121.4(2)
C(403)-C(404)-H(404)	119.3
C(405)-C(404)-H(404)	119.3
C(404)-C(405)-C(406)	119.8(2)
C(404)-C(405)-H(405)	120.1
C(406)-C(405)-H(405)	120.1
C(401)-C(406)-C(405)	119.29(19)
C(401)-C(406)-H(406)	120.4
C(405)-C(406)-H(406)	120.4
C(506)-C(501)-C(502)	120.62(19)
C(506)-C(501)-P(1)	121.02(15)
C(502)-C(501)-P(1)	118.35(16)
C(503)-C(502)-C(501)	118.7(2)
C(503)-C(502)-H(502)	120.6
C(501)-C(502)-H(502)	120.6
C(502)-C(503)-C(504)	120.6(2)
C(502)-C(503)-H(503)	119.7
C(504)-C(503)-H(503)	119.7
C(505)-C(504)-C(503)	120.6(2)
C(505)-C(504)-H(504)	119.7
C(503)-C(504)-H(504)	119.7
C(504)-C(505)-C(506)	119.8(2)
C(504)-C(505)-H(505)	120.1
C(506)-C(505)-H(505)	120.1
C(505)-C(506)-C(501)	119.6(2)
C(505)-C(506)-H(506)	120.2
C(501)-C(506)-H(506)	120.2

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2

Table 10. Crystal data and structure refinement for **6**.

Identification code	pre1	
Empirical formula	$C_{66}\ H_{54}\ F_{16}\ N_2\ O_{12}\ P_4\ S_4$	
Formula weight	1623.23	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 23.497(2) Å	α= 90°.
	b = 16.0412(15) Å	β= 91.850(3)°.
	c = 18.2355(14) Å	γ = 90°.
Volume	6869.9(10) $Å^3$	
Z	4	
Density (calculated)	1.569 Mg/m^3	
Absorption coefficient	0.339 mm^{-1}	
F(000)	3312	
Crystal size	0.080 x 0.090 x 0.090 mm^3	
Theta range for data collection	0.867 to 27.514°.	
Index ranges	-30<=h<=30, -20<=k<=20, -17<=l<=23	
Reflections collected	62904	
Independent reflections	15715 [R(int) = 0.0445]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15715 / 85 / 1001	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1098	
R indices (all data)	R1 = 0.0733, wR2 = 0.1211	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.547 and -0.629 $e.Å^{-3}$	

Table 11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pre1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(4)	8945(1)	2767(1)	10918(1)	20(1)
S(2)	10205(1)	3422(1)	13522(1)	28(1)
S(3)	7860(1)	1019(1)	13761(1)	23(1)
S(5)	7044(1)	8875(1)	18826(1)	23(1)
P(1)	6400(1)	11844(1)	18735(1)	21(1)
P(2)	4000(1)	12411(1)	19175(1)	23(1)
P(3)	11365(1)	3240(1)	11283(1)	19(1)
F(1)	6967(1)	11866(1)	18316(1)	31(1)
F(2)	4352(1)	12702(1)	18521(1)	32(1)
F(3)	9363(1)	2495(1)	11543(1)	31(1)
F(4)	11955(1)	3235(1)	11697(1)	29(1)
F(5)	10164(1)	4834(1)	14236(1)	40(1)
F(6)	10263(1)	3749(1)	14924(1)	66(1)
F(7)	9455(1)	4026(1)	14401(1)	57(1)
F(8)	7691(1)	1869(1)	12537(1)	52(1)
F(9)	8324(1)	2387(1)	13271(1)	67(1)
F(10)	8509(1)	1286(2)	12650(1)	69(1)
F(14)	6580(1)	8761(2)	17511(1)	74(1)
F(15)	7431(1)	8295(1)	17599(1)	59(1)
F(16)	6751(1)	7579(1)	18028(1)	62(1)
O(1)	10062(1)	2583(1)	13742(1)	37(1)
O(2)	10808(1)	3588(1)	13464(1)	39(1)
O(3)	9866(1)	3759(1)	12924(1)	41(1)
O(4)	8378(1)	883(1)	14197(1)	36(1)
O(5)	7647(1)	289(1)	13389(1)	42(1)
O(6)	7445(1)	1526(1)	14111(1)	37(1)
O(10)	6475(1)	8898(1)	19110(1)	34(1)
O(11)	7431(1)	8338(2)	19229(1)	42(1)
O(12)	7266(1)	9677(1)	18624(1)	38(1)
N(1)	5254(1)	11304(1)	19023(1)	21(1)
N(2)	10197(1)	3812(1)	10943(1)	18(1)

C(44A)	6947(1)	11204(2)	21075(1)	29(1)
C(43A)	6821(1)	10584(2)	20572(1)	26(1)
C(42A)	6628(1)	10790(2)	19869(1)	24(1)
C(41A)	6581(1)	11627(2)	19666(1)	20(1)
C(111)	6059(1)	10969(2)	18294(1)	25(1)
C(11A)	5517(1)	10702(2)	18650(1)	22(1)
C(15A)	4765(1)	11103(2)	19342(1)	24(1)
C(222)	4473(1)	11800(2)	19746(1)	27(1)
C(31A)	3788(1)	13326(2)	19633(1)	24(1)
C(32A)	3878(1)	14107(2)	19317(2)	31(1)
C(33A)	3724(1)	14818(2)	19696(2)	38(1)
C(34A)	3480(1)	14754(2)	20377(2)	37(1)
C(51A)	6092(1)	12839(2)	18574(1)	25(1)
C(56A)	5734(1)	13202(2)	19074(2)	28(1)
C(55A)	5487(1)	13967(2)	18917(2)	38(1)
C(54A)	5595(2)	14365(2)	18265(2)	49(1)
C(53A)	5953(2)	14009(2)	17769(2)	49(1)
C(52A)	6207(1)	13241(2)	17913(2)	37(1)
C(45A)	6892(1)	12033(2)	20880(2)	32(1)
C(46A)	6715(1)	12256(2)	20172(1)	27(1)
C(12A)	5311(1)	9891(2)	18585(2)	30(1)
C(13A)	4812(1)	9694(2)	18920(2)	36(1)
C(14A)	4533(1)	10310(2)	19304(2)	32(1)
C(21A)	3422(1)	11829(2)	18774(1)	22(1)
C(22A)	3527(1)	11274(2)	18198(1)	27(1)
C(23A)	3081(1)	10831(2)	17882(1)	30(1)
C(24A)	2530(1)	10926(2)	18139(2)	30(1)
C(25A)	2430(1)	11468(2)	18709(2)	32(1)
C(26A)	2873(1)	11927(2)	19030(2)	26(1)
C(36A)	3548(1)	13256(2)	20321(2)	29(1)
C(35A)	3394(1)	13980(2)	20687(2)	34(1)
C(24B)	7635(2)	4361(2)	12038(2)	42(1)
C(23B)	7512(1)	4033(2)	11356(2)	42(1)
C(22B)	7916(1)	3562(2)	11001(2)	32(1)
C(21B)	8443(1)	3415(2)	11347(1)	23(1)
C(444)	9358(1)	3312(2)	10266(1)	22(1)

C(15B)	9687(1)	4019(2)	10632(1)	20(1)
C(11B)	10495(1)	4414(2)	11290(1)	19(1)
C(333)	11045(1)	4144(2)	11672(1)	21(1)
C(51B)	11531(1)	3374(2)	10352(1)	21(1)
C(52B)	11979(1)	3924(2)	10201(2)	31(1)
C(53B)	12121(1)	4065(2)	9486(2)	37(1)
C(54B)	11820(1)	3677(2)	8918(2)	32(1)
C(34B)	8182(1)	366(2)	10017(2)	31(1)
C(33B)	8083(1)	1105(2)	9646(2)	31(1)
C(32B)	8314(1)	1849(2)	9908(2)	27(1)
C(31B)	8649(1)	1830(2)	10559(1)	21(1)
C(25B)	8158(2)	4235(2)	12376(2)	46(1)
C(26B)	8574(1)	3762(2)	12039(2)	36(1)
C(41B)	11045(1)	2277(2)	11492(1)	20(1)
C(42B)	10602(1)	2250(2)	11980(1)	24(1)
C(43B)	10398(1)	1485(2)	12209(2)	29(1)
C(44B)	10622(1)	755(2)	11941(2)	32(1)
C(45B)	11054(1)	787(2)	11442(2)	35(1)
C(46B)	11272(1)	1542(2)	11213(2)	30(1)
C(55B)	11376(1)	3135(2)	9059(2)	28(1)
C(56B)	11233(1)	2981(2)	9781(1)	25(1)
C(12B)	10312(1)	5237(2)	11323(1)	23(1)
C(13B)	9790(1)	5441(2)	11000(2)	26(1)
C(14B)	9465(1)	4822(2)	10655(1)	25(1)
C(36B)	8751(1)	1079(2)	10929(2)	27(1)
C(35B)	8518(1)	349(2)	10652(2)	32(1)
C(63)	10017(1)	4042(2)	14311(2)	33(1)
C(64)	8107(1)	1676(2)	13020(2)	37(1)
C(66)	6946(1)	8349(2)	17948(2)	36(1)
C(1S)	5114(1)	7949(2)	13150(2)	32(1)
S(1A)	4600(1)	8186(1)	13815(1)	28(1)
O(1A)	4896(3)	8788(4)	14277(3)	78(2)
O(2A)	4114(3)	8500(4)	13392(3)	66(2)
O(3A)	4507(1)	7398(2)	14150(2)	49(1)
F(11A)	5589(1)	7655(4)	13423(2)	77(1)
F(12A)	5236(2)	8600(2)	12719(2)	78(1)

F(13A)	4928(2)	7381(3)	12666(2)	71(1)
S(1B)	4569(2)	8573(5)	13720(3)	45(1)
O(1B)	4630(6)	9386(7)	13425(7)	73(4)
O(2B)	4070(11)	8263(17)	13468(16)	88(6)
O(3B)	4774(9)	8439(12)	14456(9)	74(5)
F(11B)	5147(10)	7205(7)	13413(7)	131(8)
F(12B)	4966(4)	7936(9)	12508(4)	52(3)
F(13B)	5585(4)	8388(11)	13228(9)	93(5)

Table 12. Bond lengths [Å] and angles [°] for pre1.

P(4)-F(3)	1.5432(16)
P(4)-C(31B)	1.773(3)
P(4)-C(21B)	1.774(3)
P(4)-C(444)	1.788(2)
S(2)-O(3)	1.435(2)
S(2)-O(1)	1.447(2)
S(2)-O(2)	1.450(2)
S(2)-C(63)	1.815(3)
S(3)-O(6)	1.434(2)
S(3)-O(5)	1.436(2)
S(3)-O(4)	1.448(2)
S(3)-C(64)	1.822(3)
S(5)-O(11)	1.437(2)
S(5)-O(12)	1.441(2)
S(5)-O(10)	1.4506(19)
S(5)-C(66)	1.817(3)
P(1)-F(1)	1.5572(15)
P(1)-C(41A)	1.772(2)
P(1)-C(51A)	1.774(3)
P(1)-C(111)	1.794(3)
P(2)-F(2)	1.5442(16)
P(2)-C(31A)	1.769(3)
P(2)-C(21A)	1.784(3)
P(2)-C(222)	1.792(3)
P(3)-F(4)	1.5567(15)
P(3)-C(41B)	1.765(3)
P(3)-C(51B)	1.767(3)
P(3)-C(333)	1.791(2)
F(5)-C(63)	1.324(3)
F(6)-C(63)	1.328(3)
F(7)-C(63)	1.336(4)
F(8)-C(64)	1.332(3)
F(9)-C(64)	1.326(4)
F(10)-C(64)	1.336(4)

F(14)-C(66)	1.331(4)
F(15)-C(66)	1.326(4)
F(16)-C(66)	1.327(4)
N(1)-C(15A)	1.342(3)
N(1)-C(11A)	1.343(3)
N(2)-C(11B)	1.340(3)
N(2)-C(15B)	1.351(3)
C(44A)-C(43A)	1.379(4)
C(44A)-C(45A)	1.381(4)
C(44A)-H(44A)	0.9500
C(43A)-C(42A)	1.385(4)
C(43A)-H(43A)	0.9500
C(42A)-C(41A)	1.396(4)
C(42A)-H(42A)	0.9500
C(41A)-C(46A)	1.396(4)
C(111)-C(11A)	1.510(4)
C(111)-H(11A)	0.9900
C(111)-H(11B)	0.9900
C(11A)-C(12A)	1.393(4)
C(15A)-C(14A)	1.384(4)
C(15A)-C(222)	1.516(4)
C(222)-H(22A)	0.9900
C(222)-H(22B)	0.9900
C(31A)-C(36A)	1.396(4)
C(31A)-C(32A)	1.398(4)
C(32A)-C(33A)	1.388(4)
C(32A)-H(32A)	0.9500
C(33A)-C(34A)	1.389(5)
C(33A)-H(33A)	0.9500
C(34A)-C(35A)	1.380(4)
C(34A)-H(34A)	0.9500
C(51A)-C(56A)	1.389(4)
C(51A)-C(52A)	1.401(4)
C(56A)-C(55A)	1.384(4)
C(56A)-H(56A)	0.9500
C(55A)-C(54A)	1.381(5)

C(55A)-H(55A)	0.9500
C(54A)-C(53A)	1.380(5)
C(54A)-H(54A)	0.9500
C(53A)-C(52A)	1.390(5)
C(53A)-H(53A)	0.9500
C(52A)-H(52A)	0.9500
C(45A)-C(46A)	1.389(4)
C(45A)-H(45A)	0.9500
C(46A)-H(46A)	0.9500
C(12A)-C(13A)	1.377(4)
C(12A)-H(12A)	0.9500
C(13A)-C(14A)	1.387(4)
C(13A)-H(13A)	0.9500
C(14A)-H(14A)	0.9500
C(21A)-C(26A)	1.395(4)
C(21A)-C(22A)	1.405(4)
C(22A)-C(23A)	1.378(4)
C(22A)-H(22C)	0.9500
C(23A)-C(24A)	1.398(4)
C(23A)-H(23A)	0.9500
C(24A)-C(25A)	1.381(4)
C(24A)-H(24A)	0.9500
C(25A)-C(26A)	1.390(4)
C(25A)-H(25A)	0.9500
C(26A)-H(26A)	0.9500
C(36A)-C(35A)	1.394(4)
C(36A)-H(36A)	0.9500
C(35A)-H(35A)	0.9500
C(24B)-C(23B)	1.371(5)
C(24B)-C(25B)	1.372(5)
C(24B)-H(24B)	0.9500
C(23B)-C(22B)	1.390(4)
C(23B)-H(23B)	0.9500
C(22B)-C(21B)	1.391(4)
C(22B)-H(22D)	0.9500
C(21B)-C(26B)	1.403(4)

C(444)-C(15B)	1.516(3)
C(444)-H(44B)	0.9900
C(444)-H(44C)	0.9900
C(15B)-C(14B)	1.391(3)
C(11B)-C(12B)	1.390(3)
C(11B)-C(333)	1.512(3)
C(333)-H(33B)	0.9900
C(333)-H(33C)	0.9900
C(51B)-C(56B)	1.387(4)
C(51B)-C(52B)	1.408(4)
C(52B)-C(53B)	1.375(4)
C(52B)-H(52B)	0.9500
C(53B)-C(54B)	1.382(4)
C(53B)-H(53B)	0.9500
C(54B)-C(55B)	1.389(4)
C(54B)-H(54B)	0.9500
C(34B)-C(33B)	1.381(4)
C(34B)-C(35B)	1.381(4)
C(34B)-H(34B)	0.9500
C(33B)-C(32B)	1.390(4)
C(33B)-H(33D)	0.9500
C(32B)-C(31B)	1.402(4)
C(32B)-H(32B)	0.9500
C(31B)-C(36B)	1.399(4)
C(25B)-C(26B)	1.394(5)
C(25B)-H(25B)	0.9500
C(26B)-H(26B)	0.9500
C(41B)-C(42B)	1.392(4)
C(41B)-C(46B)	1.397(4)
C(42B)-C(43B)	1.386(4)
C(42B)-H(42B)	0.9500
C(43B)-C(44B)	1.380(4)
C(43B)-H(43B)	0.9500
C(44B)-C(45B)	1.384(4)
C(44B)-H(44D)	0.9500
C(45B)-C(46B)	1.385(4)

C(45B)-H(45B)	0.9500
C(46B)-H(46B)	0.9500
C(55B)-C(56B)	1.392(4)
C(55B)-H(55B)	0.9500
C(56B)-H(56B)	0.9500
C(12B)-C(13B)	1.383(4)
C(12B)-H(12B)	0.9500
C(13B)-C(14B)	1.391(4)
C(13B)-H(13B)	0.9500
C(14B)-H(14B)	0.9500
C(36B)-C(35B)	1.382(4)
C(36B)-H(36B)	0.9500
C(35B)-H(35B)	0.9500
C(1S)-F(12B)	1.211(9)
C(1S)-F(11B)	1.288(11)
C(1S)-F(11A)	1.295(4)
C(1S)-F(13B)	1.314(11)
C(1S)-F(13A)	1.333(4)
C(1S)-F(12A)	1.343(4)
C(1S)-S(1A)	1.780(3)
C(1S)-S(1B)	1.950(6)
S(1A)-O(3A)	1.425(4)
S(1A)-O(1A)	1.446(6)
S(1A)-O(2A)	1.446(6)
S(1B)-O(2B)	1.34(3)
S(1B)-O(1B)	1.421(14)
S(1B)-O(3B)	1.427(18)

F(3)-P(4)-C(31B)	105.48(11)
F(3)-P(4)-C(21B)	104.77(11)
C(31B)-P(4)-C(21B)	113.67(12)
F(3)-P(4)-C(444)	106.50(11)
C(31B)-P(4)-C(444)	112.61(12)
C(21B)-P(4)-C(444)	112.93(12)
O(3)-S(2)-O(1)	115.66(14)
O(3)-S(2)-O(2)	113.36(14)

O(1)-S(2)-O(2)	115.28(13)
O(3)-S(2)-C(63)	104.62(13)
O(1)-S(2)-C(63)	102.96(13)
O(2)-S(2)-C(63)	102.74(14)
O(6)-S(3)-O(5)	116.10(14)
O(6)-S(3)-O(4)	114.40(13)
O(5)-S(3)-O(4)	114.24(13)
O(6)-S(3)-C(64)	103.82(14)
O(5)-S(3)-C(64)	103.64(14)
O(4)-S(3)-C(64)	102.24(13)
O(11)-S(5)-O(12)	116.01(14)
O(11)-S(5)-O(10)	114.11(13)
O(12)-S(5)-O(10)	114.41(12)
O(11)-S(5)-C(66)	103.43(14)
O(12)-S(5)-C(66)	103.01(13)
O(10)-S(5)-C(66)	103.58(14)
F(1)-P(1)-C(41A)	107.03(10)
F(1)-P(1)-C(51A)	104.36(11)
C(41A)-P(1)-C(51A)	114.80(12)
F(1)-P(1)-C(111)	100.05(11)
C(41A)-P(1)-C(111)	111.50(12)
C(51A)-P(1)-C(111)	117.15(13)
F(2)-P(2)-C(31A)	106.27(11)
F(2)-P(2)-C(21A)	105.15(11)
C(31A)-P(2)-C(21A)	113.94(12)
F(2)-P(2)-C(222)	106.02(11)
C(31A)-P(2)-C(222)	111.01(13)
C(21A)-P(2)-C(222)	113.65(13)
F(4)-P(3)-C(41B)	105.66(10)
F(4)-P(3)-C(51B)	104.22(10)
C(41B)-P(3)-C(51B)	115.03(12)
F(4)-P(3)-C(333)	101.01(10)
C(41B)-P(3)-C(333)	115.80(12)
C(51B)-P(3)-C(333)	112.99(12)
C(15A)-N(1)-C(11A)	117.5(2)
C(11B)-N(2)-C(15B)	117.6(2)

C(43A)-C(44A)-C(45A)	120.4(2)
C(43A)-C(44A)-H(44A)	119.8
C(45A)-C(44A)-H(44A)	119.8
C(44A)-C(43A)-C(42A)	120.0(3)
C(44A)-C(43A)-H(43A)	120.0
C(42A)-C(43A)-H(43A)	120.0
C(43A)-C(42A)-C(41A)	119.7(2)
C(43A)-C(42A)-H(42A)	120.2
C(41A)-C(42A)-H(42A)	120.2
C(42A)-C(41A)-C(46A)	120.4(2)
C(42A)-C(41A)-P(1)	117.21(19)
C(46A)-C(41A)-P(1)	122.2(2)
C(11A)-C(111)-P(1)	113.47(17)
C(11A)-C(111)-H(11A)	108.9
P(1)-C(111)-H(11A)	108.9
C(11A)-C(111)-H(11B)	108.9
P(1)-C(111)-H(11B)	108.9
H(11A)-C(111)-H(11B)	107.7
N(1)-C(11A)-C(12A)	123.3(2)
N(1)-C(11A)-C(111)	115.1(2)
C(12A)-C(11A)-C(111)	121.6(2)
N(1)-C(15A)-C(14A)	122.6(3)
N(1)-C(15A)-C(222)	116.1(2)
C(14A)-C(15A)-C(222)	121.2(2)
C(15A)-C(222)-P(2)	113.74(18)
C(15A)-C(222)-H(22A)	108.8
P(2)-C(222)-H(22A)	108.8
C(15A)-C(222)-H(22B)	108.8
P(2)-C(222)-H(22B)	108.8
H(22A)-C(222)-H(22B)	107.7
C(36A)-C(31A)-C(32A)	121.0(3)
C(36A)-C(31A)-P(2)	119.0(2)
C(32A)-C(31A)-P(2)	120.0(2)
C(33A)-C(32A)-C(31A)	119.0(3)
C(33A)-C(32A)-H(32A)	120.5
C(31A)-C(32A)-H(32A)	120.5

C(32A)-C(33A)-C(34A)	120.4(3)
C(32A)-C(33A)-H(33A)	119.8
C(34A)-C(33A)-H(33A)	119.8
C(35A)-C(34A)-C(33A)	120.2(3)
C(35A)-C(34A)-H(34A)	119.9
C(33A)-C(34A)-H(34A)	119.9
C(56A)-C(51A)-C(52A)	120.7(3)
C(56A)-C(51A)-P(1)	121.4(2)
C(52A)-C(51A)-P(1)	117.9(2)
C(55A)-C(56A)-C(51A)	119.6(3)
C(55A)-C(56A)-H(56A)	120.2
C(51A)-C(56A)-H(56A)	120.2
C(54A)-C(55A)-C(56A)	120.1(3)
C(54A)-C(55A)-H(55A)	120.0
C(56A)-C(55A)-H(55A)	120.0
C(53A)-C(54A)-C(55A)	120.4(3)
C(53A)-C(54A)-H(54A)	119.8
C(55A)-C(54A)-H(54A)	119.8
C(54A)-C(53A)-C(52A)	120.7(3)
C(54A)-C(53A)-H(53A)	119.6
C(52A)-C(53A)-H(53A)	119.6
C(53A)-C(52A)-C(51A)	118.4(3)
C(53A)-C(52A)-H(52A)	120.8
C(51A)-C(52A)-H(52A)	120.8
C(44A)-C(45A)-C(46A)	120.7(3)
C(44A)-C(45A)-H(45A)	119.7
C(46A)-C(45A)-H(45A)	119.7
C(45A)-C(46A)-C(41A)	118.8(3)
C(45A)-C(46A)-H(46A)	120.6
C(41A)-C(46A)-H(46A)	120.6
C(13A)-C(12A)-C(11A)	118.4(3)
C(13A)-C(12A)-H(12A)	120.8
C(11A)-C(12A)-H(12A)	120.8
C(12A)-C(13A)-C(14A)	118.8(3)
C(12A)-C(13A)-H(13A)	120.6
C(14A)-C(13A)-H(13A)	120.6

C(15A)-C(14A)-C(13A)	119.3(3)
C(15A)-C(14A)-H(14A)	120.3
C(13A)-C(14A)-H(14A)	120.3
C(26A)-C(21A)-C(22A)	120.5(2)
C(26A)-C(21A)-P(2)	120.2(2)
C(22A)-C(21A)-P(2)	119.3(2)
C(23A)-C(22A)-C(21A)	119.3(3)
C(23A)-C(22A)-H(22C)	120.3
C(21A)-C(22A)-H(22C)	120.3
C(22A)-C(23A)-C(24A)	120.3(3)
C(22A)-C(23A)-H(23A)	119.8
C(24A)-C(23A)-H(23A)	119.8
C(25A)-C(24A)-C(23A)	120.2(3)
C(25A)-C(24A)-H(24A)	119.9
C(23A)-C(24A)-H(24A)	119.9
C(24A)-C(25A)-C(26A)	120.4(3)
C(24A)-C(25A)-H(25A)	119.8
C(26A)-C(25A)-H(25A)	119.8
C(25A)-C(26A)-C(21A)	119.3(3)
C(25A)-C(26A)-H(26A)	120.4
C(21A)-C(26A)-H(26A)	120.4
C(35A)-C(36A)-C(31A)	118.8(3)
C(35A)-C(36A)-H(36A)	120.6
C(31A)-C(36A)-H(36A)	120.6
C(34A)-C(35A)-C(36A)	120.6(3)
C(34A)-C(35A)-H(35A)	119.7
C(36A)-C(35A)-H(35A)	119.7
C(23B)-C(24B)-C(25B)	120.7(3)
C(23B)-C(24B)-H(24B)	119.6
C(25B)-C(24B)-H(24B)	119.6
C(24B)-C(23B)-C(22B)	120.2(3)
C(24B)-C(23B)-H(23B)	119.9
C(22B)-C(23B)-H(23B)	119.9
C(23B)-C(22B)-C(21B)	119.5(3)
C(23B)-C(22B)-H(22D)	120.3
C(21B)-C(22B)-H(22D)	120.3

C(22B)-C(21B)-C(26B)	120.4(3)
C(22B)-C(21B)-P(4)	119.6(2)
C(26B)-C(21B)-P(4)	120.0(2)
C(15B)-C(444)-P(4)	110.67(17)
C(15B)-C(444)-H(44B)	109.5
P(4)-C(444)-H(44B)	109.5
C(15B)-C(444)-H(44C)	109.5
P(4)-C(444)-H(44C)	109.5
H(44B)-C(444)-H(44C)	108.1
N(2)-C(15B)-C(14B)	123.0(2)
N(2)-C(15B)-C(444)	115.7(2)
C(14B)-C(15B)-C(444)	121.3(2)
N(2)-C(11B)-C(12B)	123.3(2)
N(2)-C(11B)-C(333)	115.9(2)
C(12B)-C(11B)-C(333)	120.9(2)
C(11B)-C(333)-P(3)	114.42(17)
C(11B)-C(333)-H(33B)	108.7
P(3)-C(333)-H(33B)	108.7
C(11B)-C(333)-H(33C)	108.7
P(3)-C(333)-H(33C)	108.7
H(33B)-C(333)-H(33C)	107.6
C(56B)-C(51B)-C(52B)	120.0(2)
C(56B)-C(51B)-P(3)	122.97(19)
C(52B)-C(51B)-P(3)	117.0(2)
C(53B)-C(52B)-C(51B)	119.6(3)
C(53B)-C(52B)-H(52B)	120.2
C(51B)-C(52B)-H(52B)	120.2
C(52B)-C(53B)-C(54B)	120.2(3)
C(52B)-C(53B)-H(53B)	119.9
C(54B)-C(53B)-H(53B)	119.9
C(53B)-C(54B)-C(55B)	120.8(3)
C(53B)-C(54B)-H(54B)	119.6
C(55B)-C(54B)-H(54B)	119.6
C(33B)-C(34B)-C(35B)	120.7(3)
C(33B)-C(34B)-H(34B)	119.6
C(35B)-C(34B)-H(34B)	119.6

C(34B)-C(33B)-C(32B)	120.7(3)
C(34B)-C(33B)-H(33D)	119.6
C(32B)-C(33B)-H(33D)	119.6
C(33B)-C(32B)-C(31B)	118.3(3)
C(33B)-C(32B)-H(32B)	120.8
C(31B)-C(32B)-H(32B)	120.8
C(36B)-C(31B)-C(32B)	120.7(2)
C(36B)-C(31B)-P(4)	119.5(2)
C(32B)-C(31B)-P(4)	119.8(2)
C(24B)-C(25B)-C(26B)	120.8(3)
C(24B)-C(25B)-H(25B)	119.6
C(26B)-C(25B)-H(25B)	119.6
C(25B)-C(26B)-C(21B)	118.4(3)
C(25B)-C(26B)-H(26B)	120.8
C(21B)-C(26B)-H(26B)	120.8
C(42B)-C(41B)-C(46B)	120.6(2)
C(42B)-C(41B)-P(3)	119.93(19)
C(46B)-C(41B)-P(3)	119.3(2)
C(43B)-C(42B)-C(41B)	119.6(2)
C(43B)-C(42B)-H(42B)	120.2
C(41B)-C(42B)-H(42B)	120.2
C(44B)-C(43B)-C(42B)	120.3(3)
C(44B)-C(43B)-H(43B)	119.9
C(42B)-C(43B)-H(43B)	119.9
C(43B)-C(44B)-C(45B)	119.9(3)
C(43B)-C(44B)-H(44D)	120.1
C(45B)-C(44B)-H(44D)	120.1
C(44B)-C(45B)-C(46B)	121.1(3)
C(44B)-C(45B)-H(45B)	119.5
C(46B)-C(45B)-H(45B)	119.5
C(45B)-C(46B)-C(41B)	118.6(3)
C(45B)-C(46B)-H(46B)	120.7
C(41B)-C(46B)-H(46B)	120.7
C(54B)-C(55B)-C(56B)	119.5(3)
C(54B)-C(55B)-H(55B)	120.3
C(56B)-C(55B)-H(55B)	120.3

C(51B)-C(56B)-C(55B)	119.9(2)
C(51B)-C(56B)-H(56B)	120.1
C(55B)-C(56B)-H(56B)	120.1
C(13B)-C(12B)-C(11B)	118.5(2)
C(13B)-C(12B)-H(12B)	120.8
C(11B)-C(12B)-H(12B)	120.8
C(12B)-C(13B)-C(14B)	119.4(2)
C(12B)-C(13B)-H(13B)	120.3
C(14B)-C(13B)-H(13B)	120.3
C(15B)-C(14B)-C(13B)	118.3(2)
C(15B)-C(14B)-H(14B)	120.9
C(13B)-C(14B)-H(14B)	120.9
C(35B)-C(36B)-C(31B)	119.5(3)
C(35B)-C(36B)-H(36B)	120.2
C(31B)-C(36B)-H(36B)	120.2
C(34B)-C(35B)-C(36B)	119.9(3)
C(34B)-C(35B)-H(35B)	120.0
C(36B)-C(35B)-H(35B)	120.0
F(5)-C(63)-F(6)	108.5(3)
F(5)-C(63)-F(7)	106.9(2)
F(6)-C(63)-F(7)	107.1(3)
F(5)-C(63)-S(2)	111.94(19)
F(6)-C(63)-S(2)	111.3(2)
F(7)-C(63)-S(2)	110.7(2)
F(9)-C(64)-F(8)	107.1(3)
F(9)-C(64)-F(10)	107.8(3)
F(8)-C(64)-F(10)	106.9(2)
F(9)-C(64)-S(3)	111.7(2)
F(8)-C(64)-S(3)	112.4(2)
F(10)-C(64)-S(3)	110.6(2)
F(15)-C(66)-F(16)	107.2(3)
F(15)-C(66)-F(14)	107.2(3)
F(16)-C(66)-F(14)	107.9(3)
F(15)-C(66)-S(5)	111.6(2)
F(16)-C(66)-S(5)	111.7(2)
F(14)-C(66)-S(5)	111.0(2)

F(12B)-C(1S)-F(11B)	110.9(9)
F(12B)-C(1S)-F(13B)	109.1(10)
F(11B)-C(1S)-F(13B)	114.5(12)
F(11A)-C(1S)-F(13A)	105.4(4)
F(11A)-C(1S)-F(12A)	108.1(4)
F(13A)-C(1S)-F(12A)	102.4(3)
F(11A)-C(1S)-S(1A)	114.3(2)
F(13A)-C(1S)-S(1A)	112.4(2)
F(12A)-C(1S)-S(1A)	113.2(2)
F(12B)-C(1S)-S(1B)	110.5(5)
F(11B)-C(1S)-S(1B)	108.0(7)
F(13B)-C(1S)-S(1B)	103.5(5)
O(3A)-S(1A)-O(1A)	114.8(3)
O(3A)-S(1A)-O(2A)	114.2(4)
O(1A)-S(1A)-O(2A)	115.8(5)
O(3A)-S(1A)-C(1S)	102.63(18)
O(1A)-S(1A)-C(1S)	102.3(3)
O(2A)-S(1A)-C(1S)	104.6(3)
O(2B)-S(1B)-O(1B)	108.0(14)
O(2B)-S(1B)-O(3B)	122.1(16)
O(1B)-S(1B)-O(3B)	117.3(11)
O(2B)-S(1B)-C(1S)	102.2(14)
O(1B)-S(1B)-C(1S)	101.1(5)
O(3B)-S(1B)-C(1S)	102.5(9)

Table 13. Crystal data and structure refinement for **8**.

Identification code	pbca_sq	
Empirical formula	$C_{33}\ H_{30}\ F_7\ N\ O_3\ P_2\ S$	
Formula weight	715.58	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 16.7886(16) Å	α= 90°.
	b = 16.6604(15) Å	β= 90°.
	c = 27.550(2) Å	γ = 90°.
Volume	7705.9(12) $Å^3$	
Z	8	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.231 mm^{-1}	
F(000)	2944	
Crystal size	0.150 x 0.150 x 0.080 mm^3	
Theta range for data collection	1.912 to 23.255°.	
Index ranges	-18<=h<=15, -18<=k<=17, -30<=l<=30	
Reflections collected	35388	
Independent reflections	5536 [R(int) = 0.0639]	
Completeness to theta = 23.255°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5536 / 3 / 425	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0630, wR2 = 0.1467	
R indices (all data)	R1 = 0.1026, wR2 = 0.1665	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.551 and -0.509 $e.Å^{-3}$	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for pbca_sq. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	8252(1)	10322(1)	1191(1)	35(1)
F(1)	7561(2)	9421(2)	3494(1)	65(1)
N(1)	7680(2)	9606(2)	2349(1)	36(1)
C(1A)	7326(3)	8998(3)	2602(2)	44(1)
C(1)	7319(3)	10424(3)	2348(2)	46(1)
C(2)	7687(4)	8249(3)	2611(2)	57(1)
C(22)	5985(4)	11091(3)	3509(2)	72(2)
C(21)	6641(3)	10606(3)	3575(2)	57(1)
C(3)	8394(4)	8124(3)	2383(2)	66(2)
C(4)	8729(3)	8741(3)	2117(2)	51(1)
C(25)	7403(5)	11809(5)	3761(2)	99(2)
C(1B)	8362(3)	9479(3)	2092(1)	36(1)
C(24)	6744(6)	12254(5)	3692(3)	105(3)
C(23)	6051(5)	11913(4)	3563(2)	95(2)
C(26)	7357(4)	10966(4)	3700(2)	83(2)
C(11)	6492(3)	8863(3)	4003(2)	45(1)
C(12)	5942(3)	8244(3)	4013(2)	51(1)
C(13)	5898(3)	7741(3)	4416(2)	62(2)
C(14)	6393(4)	7872(4)	4805(2)	70(2)
C(15)	6936(4)	8479(4)	4801(2)	78(2)
C(16)	6993(4)	8978(3)	4398(2)	68(2)
C(33)	6287(4)	11677(4)	893(2)	76(2)
C(222)	6555(3)	9134(3)	2860(2)	50(1)
C(31)	7569(3)	11158(3)	1126(2)	42(1)
C(41)	8488(3)	9702(2)	672(2)	38(1)
C(46)	9275(3)	9588(3)	534(2)	48(1)
C(45)	9455(4)	9105(3)	134(2)	65(2)
C(36)	7817(3)	11933(3)	1224(2)	58(1)
C(42)	7886(3)	9339(3)	404(2)	54(1)
C(44)	8843(6)	8767(3)	-129(2)	79(2)
C(32)	6794(3)	11040(3)	966(2)	57(1)

C(34)	6541(5)	12444(4)	994(2)	80(2)
C(35)	7293(5)	12568(3)	1162(2)	80(2)
C(43)	8067(5)	8876(3)	5(2)	73(2)
C(111)	8715(3)	10123(3)	1782(2)	39(1)
C(1T)	5258(5)	6110(5)	3003(4)	148(5)
P(2)	6577(1)	9526(1)	3483(1)	46(1)
F(2)	5584(1)	9559(2)	3445(1)	47(1)
F(3)	9023(1)	10913(1)	1082(1)	44(1)
F(4)	7488(1)	9709(1)	1328(1)	40(1)
S(1)	5603(1)	6918(1)	2667(1)	75(1)
O(1)	5257(3)	7595(2)	2889(2)	102(2)
F(1T)	5389(4)	6145(3)	3468(2)	178(3)
F(2T)	5542(4)	5415(2)	2863(2)	230(4)
O(2)	6428(3)	6817(3)	2722(3)	154(3)
O(3)	5415(6)	6770(4)	2195(2)	210(4)
F(3T)	4458(4)	6082(5)	2963(4)	272(5)

Table 15. Bond lengths [Å] and angles [°] for pbca_sq.

P(1)-F(3)	1.654(3)
P(1)-F(4)	1.682(3)
P(1)-C(41)	1.807(4)
P(1)-C(31)	1.812(5)
P(1)-C(111)	1.833(4)
F(1)-P(2)	1.661(3)
N(1)-C(1B)	1.362(5)
N(1)-C(1A)	1.366(5)
N(1)-C(1)	1.492(5)
C(1A)-C(2)	1.388(7)
C(1A)-C(222)	1.495(6)
C(2)-C(3)	1.358(7)
C(22)-C(21)	1.378(8)
C(22)-C(23)	1.383(8)
C(21)-C(26)	1.387(8)
C(21)-P(2)	1.820(6)
C(3)-C(4)	1.382(7)
C(4)-C(1B)	1.377(6)
C(25)-C(24)	1.346(10)
C(25)-C(26)	1.416(10)
C(1B)-C(111)	1.494(6)
C(24)-C(23)	1.343(10)
C(11)-C(12)	1.386(6)
C(11)-C(16)	1.389(7)
C(11)-P(2)	1.813(5)
C(12)-C(13)	1.394(7)
C(13)-C(14)	1.374(7)
C(14)-C(15)	1.362(8)
C(15)-C(16)	1.390(8)
C(33)-C(34)	1.375(9)
C(33)-C(32)	1.376(7)
C(222)-P(2)	1.837(4)
C(31)-C(36)	1.382(6)
C(31)-C(32)	1.388(7)

C(41)-C(46)	1.389(6)
C(41)-C(42)	1.391(6)
C(46)-C(45)	1.398(7)
C(45)-C(44)	1.377(9)
C(36)-C(35)	1.388(7)
C(42)-C(43)	1.377(7)
C(44)-C(43)	1.365(9)
C(34)-C(35)	1.361(9)
C(1T)-F(1T)	1.301(12)
C(1T)-F(2T)	1.311(8)
C(1T)-F(3T)	1.349(11)
C(1T)-S(1)	1.731(10)
P(2)-F(2)	1.672(3)
S(1)-O(3)	1.360(6)
S(1)-O(2)	1.403(5)
S(1)-O(1)	1.409(4)

F(3)-P(1)-F(4)	177.24(14)
F(3)-P(1)-C(41)	91.40(17)
F(4)-P(1)-C(41)	89.82(17)
F(3)-P(1)-C(31)	91.15(18)
F(4)-P(1)-C(31)	90.38(18)
C(41)-P(1)-C(31)	120.0(2)
F(3)-P(1)-C(111)	86.39(16)
F(4)-P(1)-C(111)	90.86(16)
C(41)-P(1)-C(111)	120.3(2)
C(31)-P(1)-C(111)	119.7(2)
C(1B)-N(1)-C(1A)	121.1(4)
C(1B)-N(1)-C(1)	118.8(3)
C(1A)-N(1)-C(1)	120.0(4)
N(1)-C(1A)-C(2)	119.0(4)
N(1)-C(1A)-C(222)	120.6(4)
C(2)-C(1A)-C(222)	120.4(4)
C(3)-C(2)-C(1A)	120.8(5)
C(21)-C(22)-C(23)	120.1(7)
C(22)-C(21)-C(26)	118.1(6)

C(22)-C(21)-P(2)	120.9(4)
C(26)-C(21)-P(2)	121.0(5)
C(2)-C(3)-C(4)	119.1(5)
C(1B)-C(4)-C(3)	120.6(5)
C(24)-C(25)-C(26)	119.0(7)
N(1)-C(1B)-C(4)	119.2(4)
N(1)-C(1B)-C(111)	121.3(4)
C(4)-C(1B)-C(111)	119.5(4)
C(23)-C(24)-C(25)	121.1(8)
C(24)-C(23)-C(22)	121.2(8)
C(21)-C(26)-C(25)	120.5(7)
C(12)-C(11)-C(16)	119.4(5)
C(12)-C(11)-P(2)	121.4(4)
C(16)-C(11)-P(2)	119.2(4)
C(11)-C(12)-C(13)	119.9(5)
C(14)-C(13)-C(12)	119.7(5)
C(15)-C(14)-C(13)	121.0(5)
C(14)-C(15)-C(16)	119.8(5)
C(11)-C(16)-C(15)	120.1(5)
C(34)-C(33)-C(32)	119.8(6)
C(1A)-C(222)-P(2)	118.8(3)
C(36)-C(31)-C(32)	118.5(5)
C(36)-C(31)-P(1)	120.5(4)
C(32)-C(31)-P(1)	121.0(4)
C(46)-C(41)-C(42)	119.0(4)
C(46)-C(41)-P(1)	120.3(3)
C(42)-C(41)-P(1)	120.7(4)
C(41)-C(46)-C(45)	120.1(5)
C(44)-C(45)-C(46)	119.2(6)
C(31)-C(36)-C(35)	119.8(5)
C(43)-C(42)-C(41)	120.6(6)
C(43)-C(44)-C(45)	121.0(5)
C(33)-C(32)-C(31)	121.1(5)
C(35)-C(34)-C(33)	119.8(6)
C(34)-C(35)-C(36)	121.0(6)
C(44)-C(43)-C(42)	120.1(6)

C(1B)-C(111)-P(1)	118.0(3)
F(1T)-C(1T)-F(2T)	105.5(11)
F(1T)-C(1T)-F(3T)	104.4(7)
F(2T)-C(1T)-F(3T)	107.9(7)
F(1T)-C(1T)-S(1)	115.8(6)
F(2T)-C(1T)-S(1)	114.1(5)
F(3T)-C(1T)-S(1)	108.5(10)
F(1)-P(2)-F(2)	175.03(16)
F(1)-P(2)-C(11)	90.01(19)
F(2)-P(2)-C(11)	89.54(18)
F(1)-P(2)-C(21)	92.5(2)
F(2)-P(2)-C(21)	92.0(2)
C(11)-P(2)-C(21)	119.8(2)
F(1)-P(2)-C(222)	89.91(19)
F(2)-P(2)-C(222)	86.10(18)
C(11)-P(2)-C(222)	121.3(2)
C(21)-P(2)-C(222)	118.8(2)
O(3)-S(1)-O(2)	108.1(5)
O(3)-S(1)-O(1)	117.7(4)
O(2)-S(1)-O(1)	117.1(4)
O(3)-S(1)-C(1T)	107.0(5)
O(2)-S(1)-C(1T)	100.3(4)
O(1)-S(1)-C(1T)	104.7(3)