Reactive FLP-alkyne addition products: A strategy to anionic and zwitterionic phosphines

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Supporting Information

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1 General Information

All preparative procedures were performed in a MB Unilab glovebox produced by MBraun or using standard Schlenk techniques under an inert atmosphere of dry, deoxygenated N_2.

• *Drying of glassware, activated charcoal, molecular sieves, and other items:* All glassware were oven-dried at temperatures greater than 150 °C for at least 4 hours before use and cooled under vacuum before use. Activated charcoal (Sigma-Aldrich) was dried and degassed by initially storing it in a glass beaker in a glassware-drying oven at temperatures greater than 150 °C for at least 48 hours. It was then added to an oven-dried Schlenk flask, which was dried in an 150 °C oil bath for at least 4 hours under dynamic vacuum, and finally shipped into the glovebox. 4 Å molecular sieves were purchased from Sigma-Aldrich, and were activated prior to usage by iteratively heating with 1050 W Haier microwave for 5 min and cooling under vacuum. Items such as plastic syringes, glass microsyringes, needles, and septa were shipped into the glovebox after drying in the antechamber overnight.

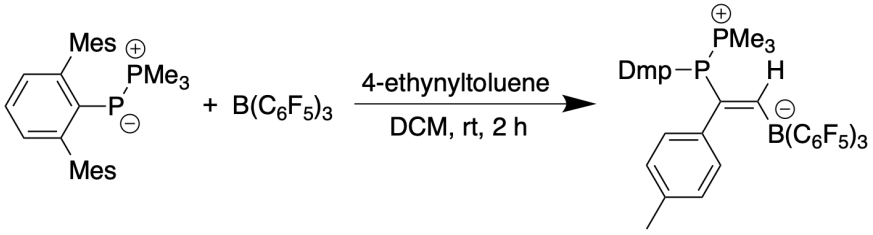
• *Drying solvents:* Anhydrous pentane, hexane, diethyl ether, dichloromethane (DCM), and toluene solvents were dried using a Grubbs-type Innovative Techonologies solvent purification system. Tetrahydrofuran (THF) was dried over Na/benzophenone. Benzene, 1,2-dichloroethane (DCE) and 1,2-difluorobenzene (ODFB) were dried over CaH_2. They were then distilled to an oven-dried Strauss flask under static vacuum, after which it was shipped into the glovebox. All anhydrous solvents in the glovebox were stored over 4 Å molecular sieves for at least 24 hours prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Sigma-Aldrich. They were degassed through 3 freeze-pump-thaw cycles, shipped into the glovebox, and stored over 4 Å molecular sieves for at least 24 hours prior to use.

• *Data collection:* NMR spectra were obtained on a Bruker Avance III 400 MHz spectrometer, an Agilent DD2 600 MHz spectrometer or an Agilent DD2 500 MHz spectrometer. ^{1}H, ^{13}C NMR chemical shifts (δ/ppm) are referenced to the residual solvent resonance of the deuterated solvent. ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 (0 ppm). Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (J) are in Hz. Multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad. High resolution mass spectroscopy (HRMS) studies were performed on an AB Sciex QStarXL (ESI) or a JMS-T100LC JOEL (DART). Elemental analyses were carried out by staff at ANALEST at the University of Toronto on a Flash 2000 CHNS Analyzer.

• *Syntheses or purchase of known compounds:* Mg**A**·3THF (**A** = anthracene),[1] Et_2NP**A**,[2] and $DmpPPMe_3$ (Dmp = 2,6-dimesitylphenyl)[3] were synthesized through literature procedures. All other reagents were purchased from commercial sources, and used as received. 4-ethynyltoluene was dried over 4 Å sieves for 24 hours prior to use.

2 Experimental Procedures and Spectroscopic Data

2.1 Synthesis of 1



Scheme S1: Synthesis of **1**

In the glovebox, DmpPPMe$_3$ (0.0266 g, 0.063 mmol, 1.0 eq) was dissolved in DCM (0.3 mL), and 4-ethynyltoluene (10 μL, 0.076 mmol, 1.2 eq) was added via a microsyringe. A DCM (2.0 mL) solution of B(C$_6$F$_5$)$_3$ (0.0324 g, 0.063 mmol, 1.0 eq) was added dropwise. The reaction was stirred under foil for 2 hours at room temperature, after which the solvent was concentrated under vacuum. Hexanes (4 mL) was added, and the solution was placed in a -20 °C freezer in the glovebox overnight. The solvent was decanted, and the crude product was washed with a minimal amount of benzene. The product was isolated as a white powder (0.0282 g, 0.027 mmol, 43% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.58 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.22 (d, $^3J_{PH}$ = 10.9 Hz, 1H, -PC=C*H*), 7.14–7.09 (m, 2H), 6.90 (br s, 4H), 6.54 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 6.36 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 2.34 (s, 6H), 2.15–1.60 (m, 15H), 1.09 (d, $^2J_{PH}$ = 9.4 Hz, 9H, -P*Me*$_3$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): Due to the insolubility of this compound in most NMR solvents, ^{13}C NMR could not be obtained.

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -15.5 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -129.95 (d, $^3J_{FF}$ = 21.7 Hz, 6F, o-C$_6$*F*$_5$), -162.47 (t, $^3J_{FF}$ = 20.6 Hz, 3F, p-C$_6$*F*$_5$), -166.82 (m, 6F, m-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 8.0 (br s, 1P, Dmp*P*), 7.1 (s, 1P, -*P*Me$_3$).

• The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed, protonated compound DmpP(H)PMe$_3^+$ was observed: MS (ESI) [M]$^+$ C$_{27}$H$_{35}$P$_2^+$ calc. 421.2214 *m/z*, found 421.2207 *m/z*.

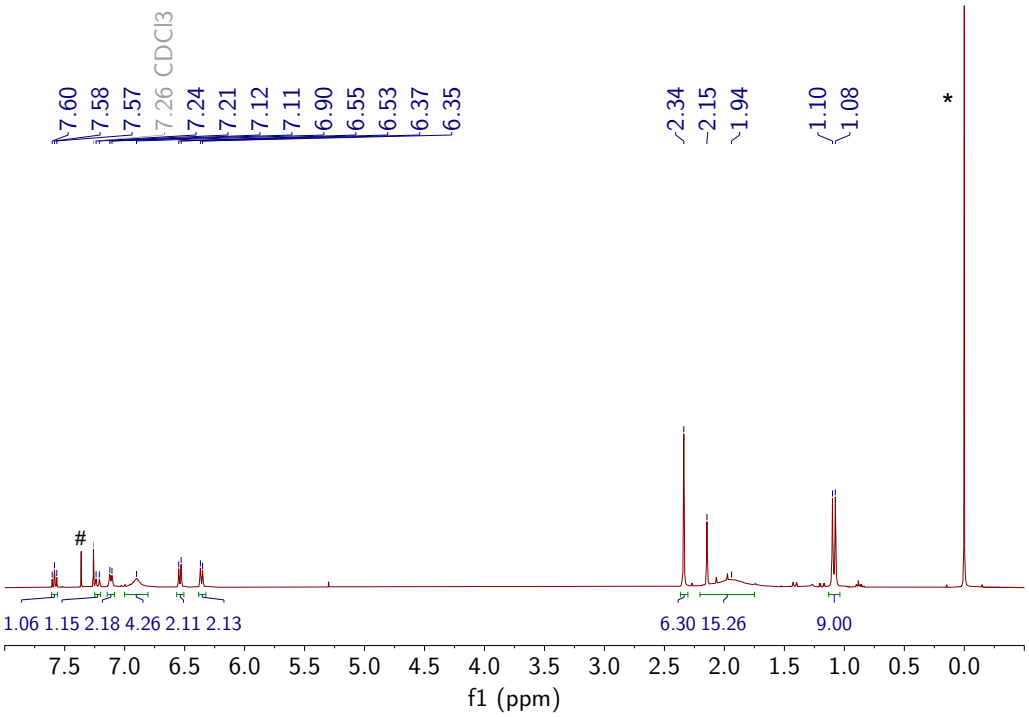


Figure S1: ^{1}H NMR spectrum of **1** with residual benzene (denoted as #). * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

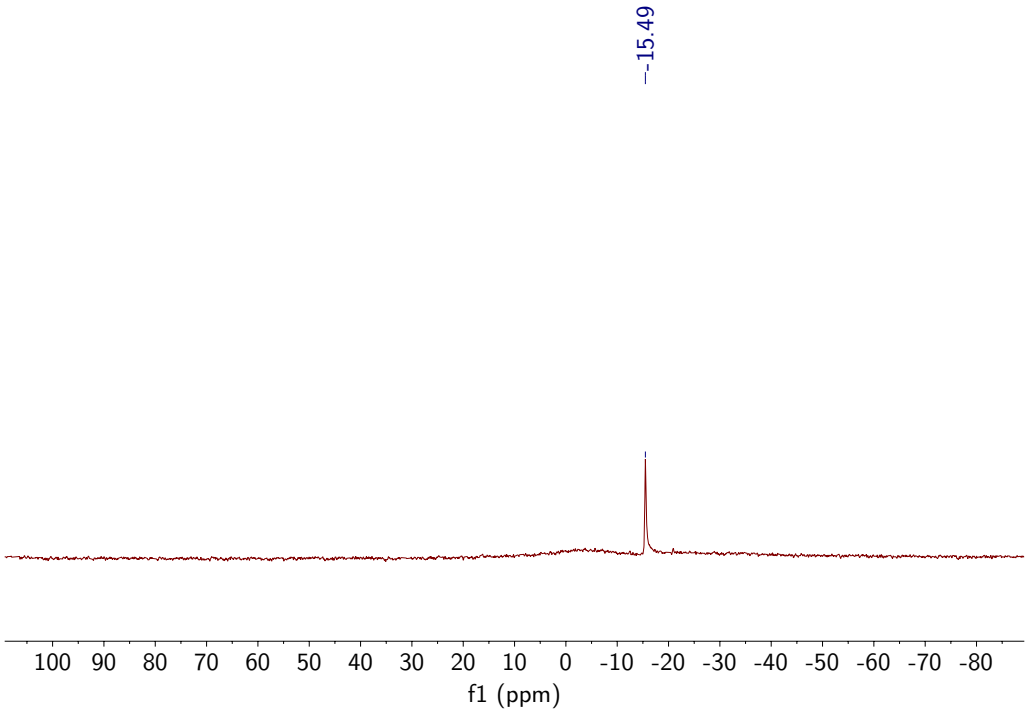


Figure S2: ^{11}B NMR spectrum of **1** (chloroform-*d*, 128 MHz)

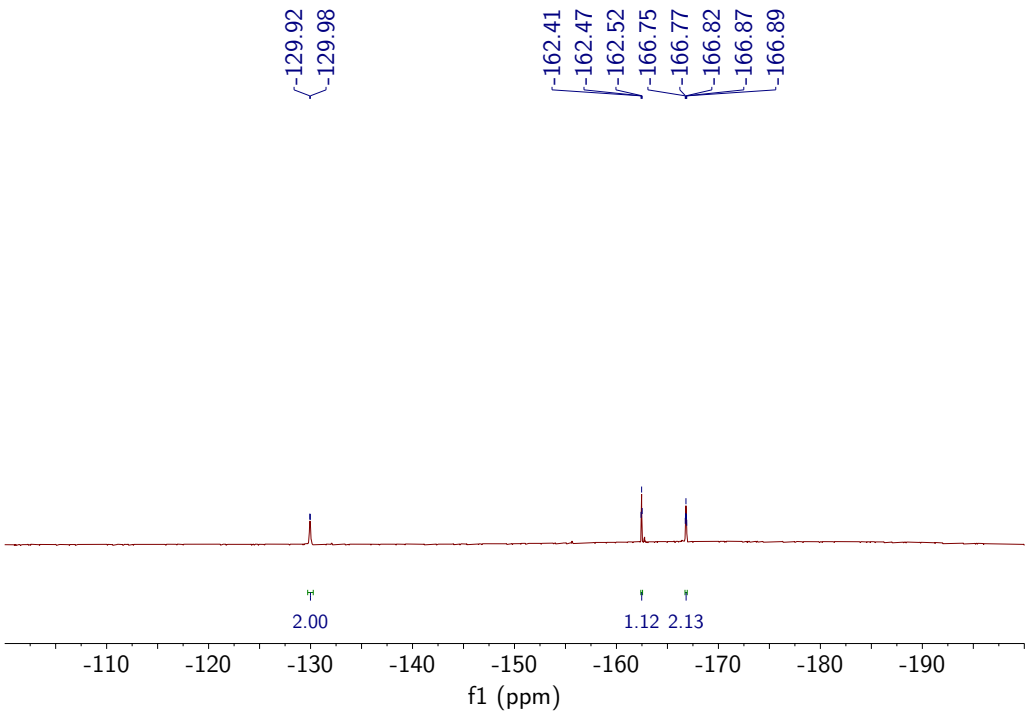


Figure S3: ^{19}F NMR spectrum of **1** (chloroform-*d*, 377 MHz)

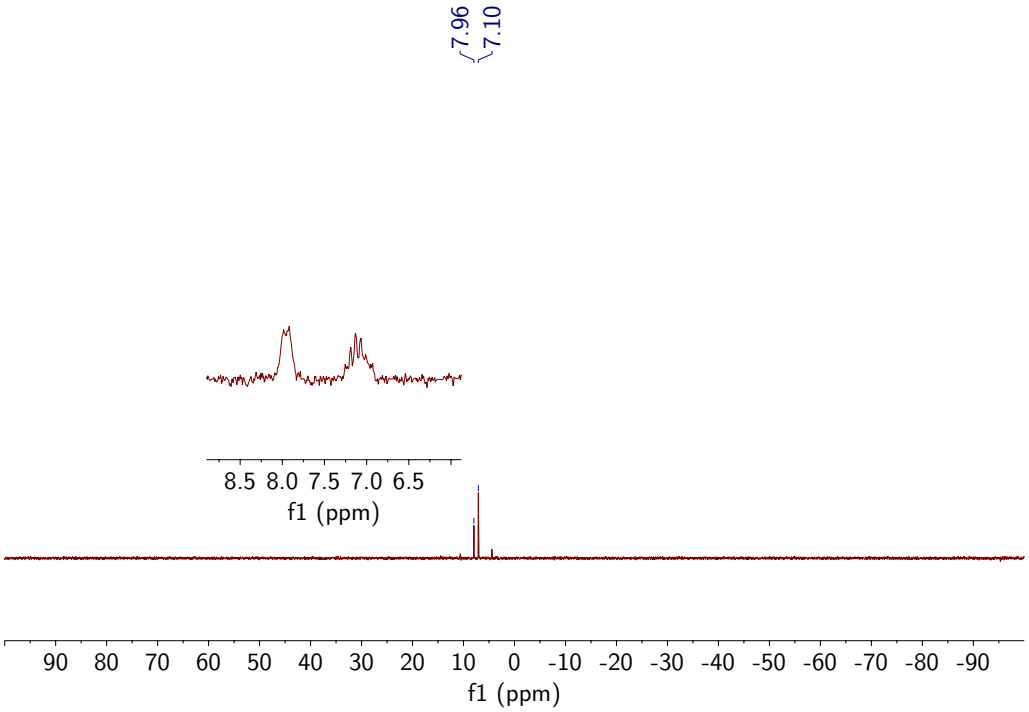
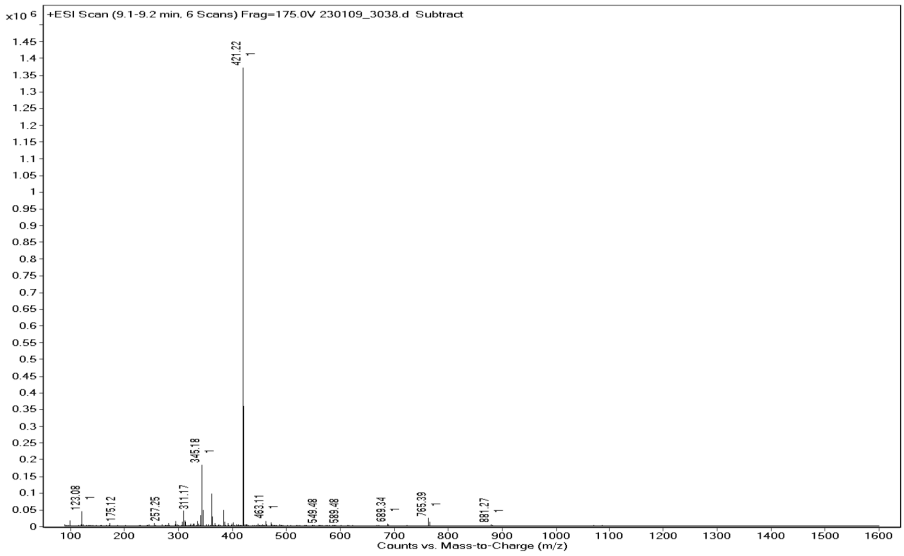


Figure S4: ^{31}P{^{1}H} NMR spectrum of **1**, with inset showing zoomed-in peaks in the ^{31}P NMR (chloroform-*d*, 162 MHz)

ESI Mass Spectrum

Sample Name	WK-05-128	**Data File**	230109_3038.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	09/01/2023 1:38:34 PM
Comment	ESI+				



ESI-MS Report
Molecular Formula Generation (MFG)

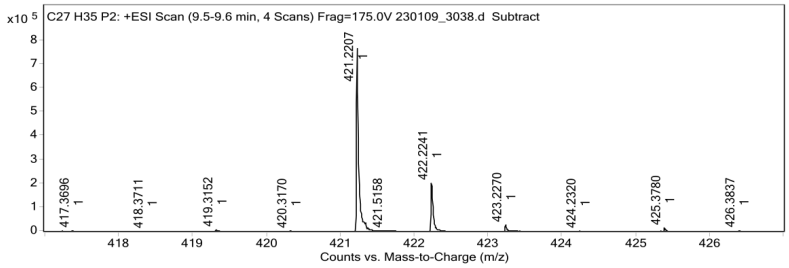
Sample Name	WK-05-128	**Data File**	230109_3038.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	09/01/2023 1:38:34 PM
Comment	ESI+		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M+	421.2207	C27 H35 P2

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
421.2207	C27 H35 P2	421.2209	-0.2	-0.5	11.5	99.87
421.2207	C11 H35 N8 O5 P2	421.2200	0.7	1.7	-0.5	94.67
421.2207	C16 H35 N6 O3 P2	421.2240	-3.3	-7.8	3.5	72.03
421.2207	C22 H35 N2 O2 P2	421.2168	3.9	9.3	7.5	63.12
419.3152	C19 H45 N6 P2	419.3175	-2.3	-5.5	1.5	62.22

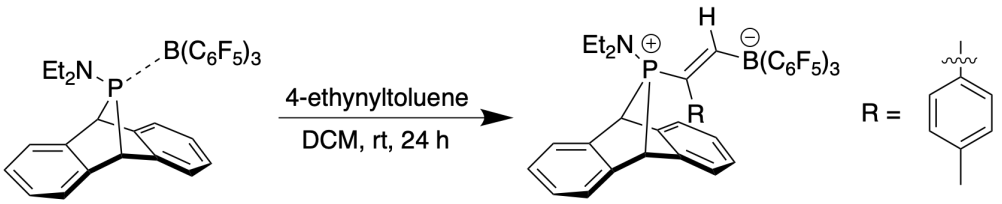


Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	421.2207	421.2209	-0.2	100.0	100.0	0.0
2	422.2241	422.2242	-0.1	28.3	29.6	1.3
3	423.2270	423.2276	-0.6	3.6	4.2	0.6
4	424.2320	424.2310	1.0	0.3	0.4	0.1

Figure S5: ESI-MS(+) of **1**, only showing the hydrolyzed compound $C_{27}H_{35}P_2^+$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.2 Synthesis of 2



Scheme S2: Synthesis of **2**

In the glovebox, 4-ethynyltoluene (19 μL, 0.149 mmol, 1.2 eq) was added to a DCM (0.5 mL) solution of Et_2NP**A** (0.0349 g, 0.124 mmol, 1.0 eq) via a microsyringe. Then, a DCM (2 mL) solution of $B(C_6F_5)_3$ (0.0635 g, 0.124 mmol, 1.0 eq) was added *dropwise* while stirring vigorously. The reaction was stirred under foil for 24 hours. The solution was filtered over activated charcoal, and solvent was removed under vacuum resulting in an orange oil. Hexane (2 mL) was added, after which the supernatant was decanted, and the product was dried under vacuum. The product was obtained as an orange powder (0.1052 g, 0.116 mmol, 93% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 8.21 (d, $^3J_{PH}$ = 35.7 Hz, 1H, -PC=C*H*), 7.48–7.46 (m, 2H), 7.27–7.25 (m, 2H), 7.22–7.20 (m, 2H), 7.10–7.08 (m, 2H) 6.82 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 6.39 (d, $^3J_{HH}$ = 8.1, $^4J_{PH}$ = 1.9 Hz, 2H, Ar-*H*), 4.93 (d, $^2J_{PH}$ = 6.4 Hz, 2H, bridgehead protons), 2.90–2.82 (m, 4H, -N(CH_2CH$_3$)$_2$), 2.23 (s, 3H, Ar-CH_3), 0.69 (t, $^3J_{HH}$ = 7.1 Hz, 6H, -N(CH$_2$CH_3)$_2$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 147.99 (br d, $^1J_{CF}$ = 242.1 Hz, *o*-C_6F_5), 139.54 (d, J = 6.6 Hz), 138.48 (br d, $^1J_{CF}$ = 246.4 Hz, *m*-C_6F_5), 138.02 (d, J = 2.9 Hz), 137.13 (d, J = 13.2 Hz), 136.52 (br d, $^1J_{CF}$ = 250.3 Hz, *p*-C_6F_5), 128.89 (d, J = 1.5 Hz), 128.64 (d, J = 1.8 Hz), 128.49 (s), 128.32 (s), 127.87 (d, J = 5.5 Hz), 125.51 (s), 124.75 (d, J = 7.0 Hz), 124.45 (d, J = 8.1 Hz), 123.46 (d, $^1J_{CP}$ = 62.4 Hz), 50.94 (d, $^1J_{CP}$ = 53.2 Hz, bridgehead carbons), 42.61 (s, -N(*C*H$_2$CH$_3$)$_2$), 21.01 (s, Ar-*C*H$_3$), 13.35 (d, $^3J_{CP}$ = 1.8 Hz, -N(CH$_2$*C*H$_3$)$_2$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.2 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -131.41 (d, $^3J_{FF}$ = 19.5 Hz, 6F, o-C$_6$*F*$_5$), -162.0 (t, $^3J_{FF}$ = 20.0 Hz, 3F, p-C$_6$*F*$_5$), -166.25 (m, 6F, m-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 113.9 (m).

• MS (ESI) [M+NH$_4$]$^+$ $C_{45}H_{32}BF_{15}N_2P^+$ calc. 927.2159 *m/z*, found 927.2180 *m/z*.

• Elem. Anal. Found (Calc'd) for $C_{45}H_{28}BF_{15}NP$: C 58.15 (59.43), H 3.07 (3.10), N 1.37 (1.54). The observed low C analysis is consistent with incomplete combustion typically seen for boron compounds and is attributed to the formation of boron-carbide.

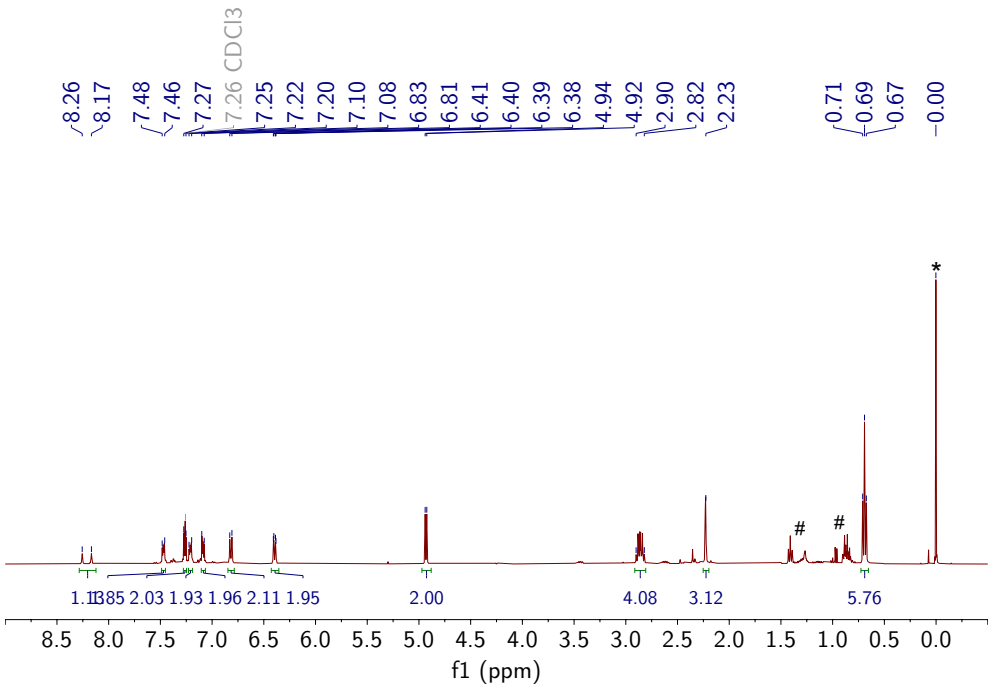


Figure S6: ^{1}H NMR spectrum of **2** with residual hexane (denoted as #). * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

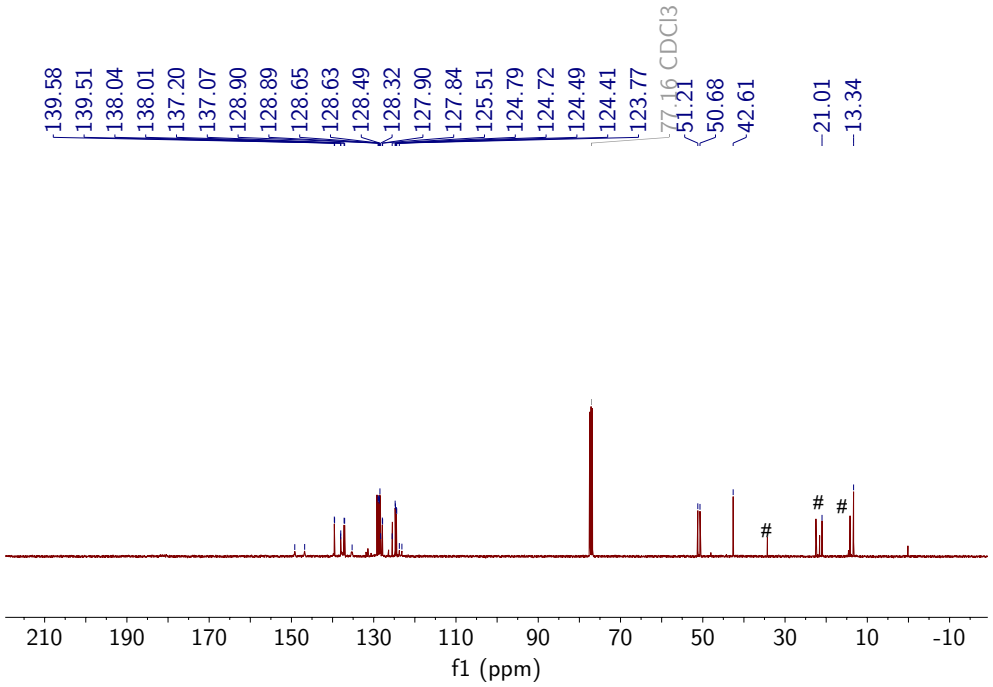


Figure S7: ^{13}C NMR spectrum of **2**, with residual pentane and toluene (denoted as #) (chloroform-*d*, 101 MHz)

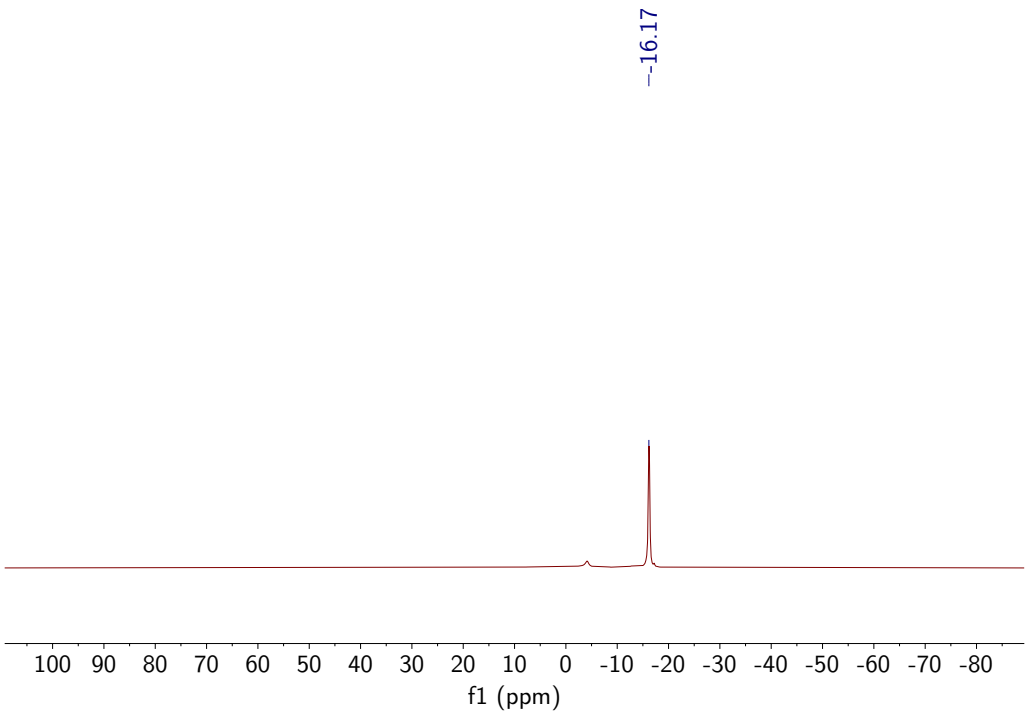


Figure S8: ^{11}B NMR spectrum of **2** (chloroform-*d*, 128 MHz)

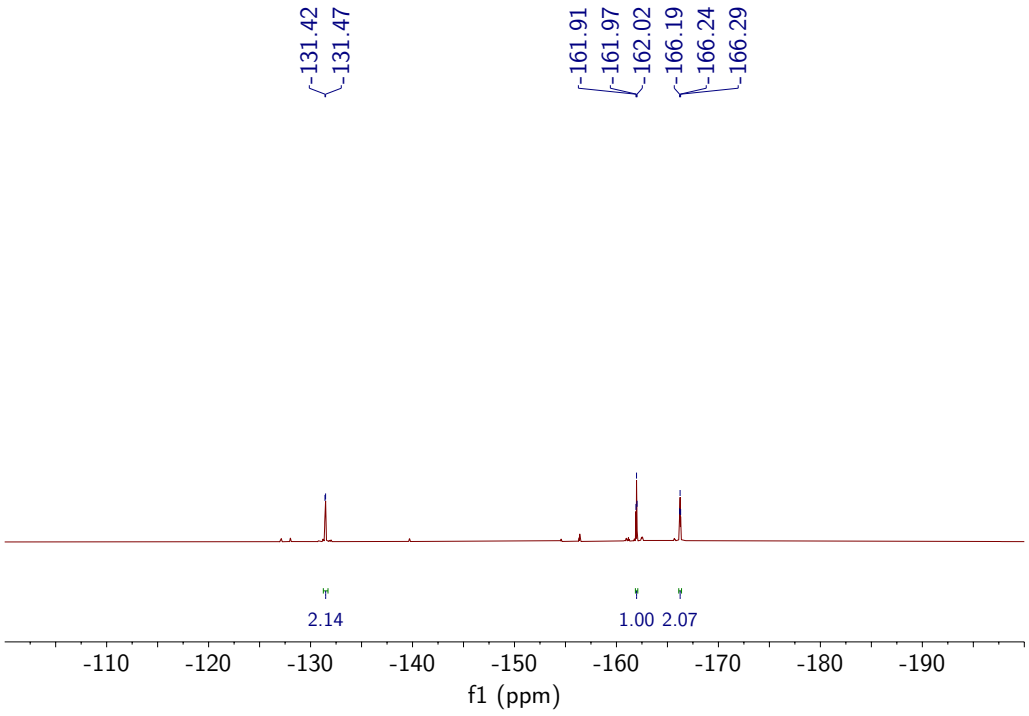


Figure S9: ^{19}F NMR spectrum of **2** (chloroform-*d*, 377 MHz)

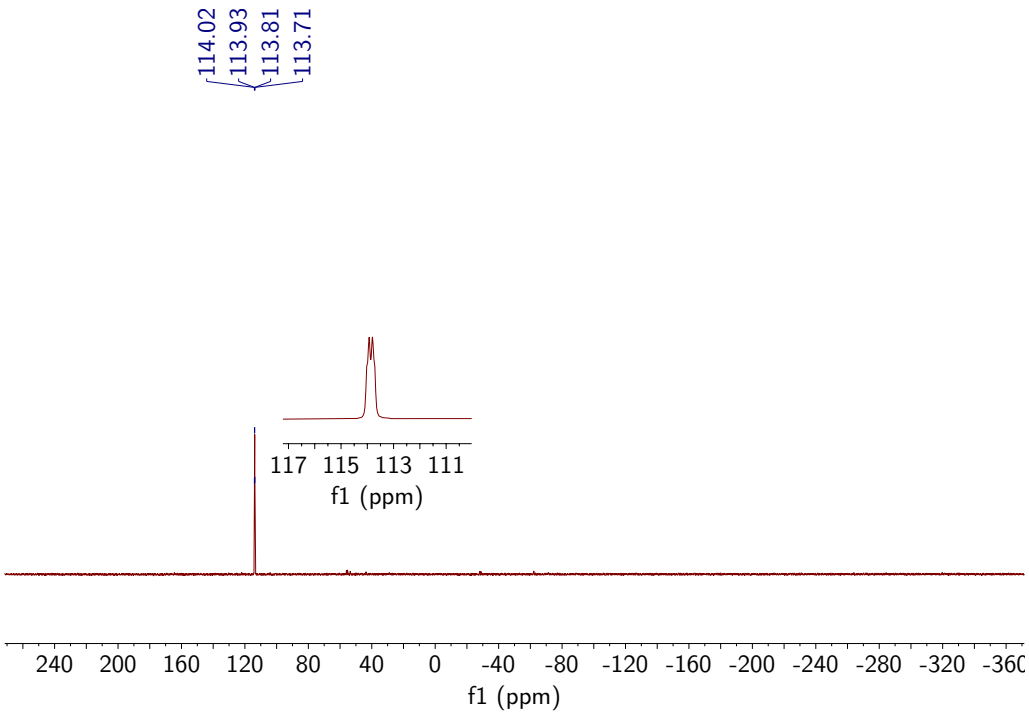


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum of **2** (chloroform-*d*, 162 MHz)

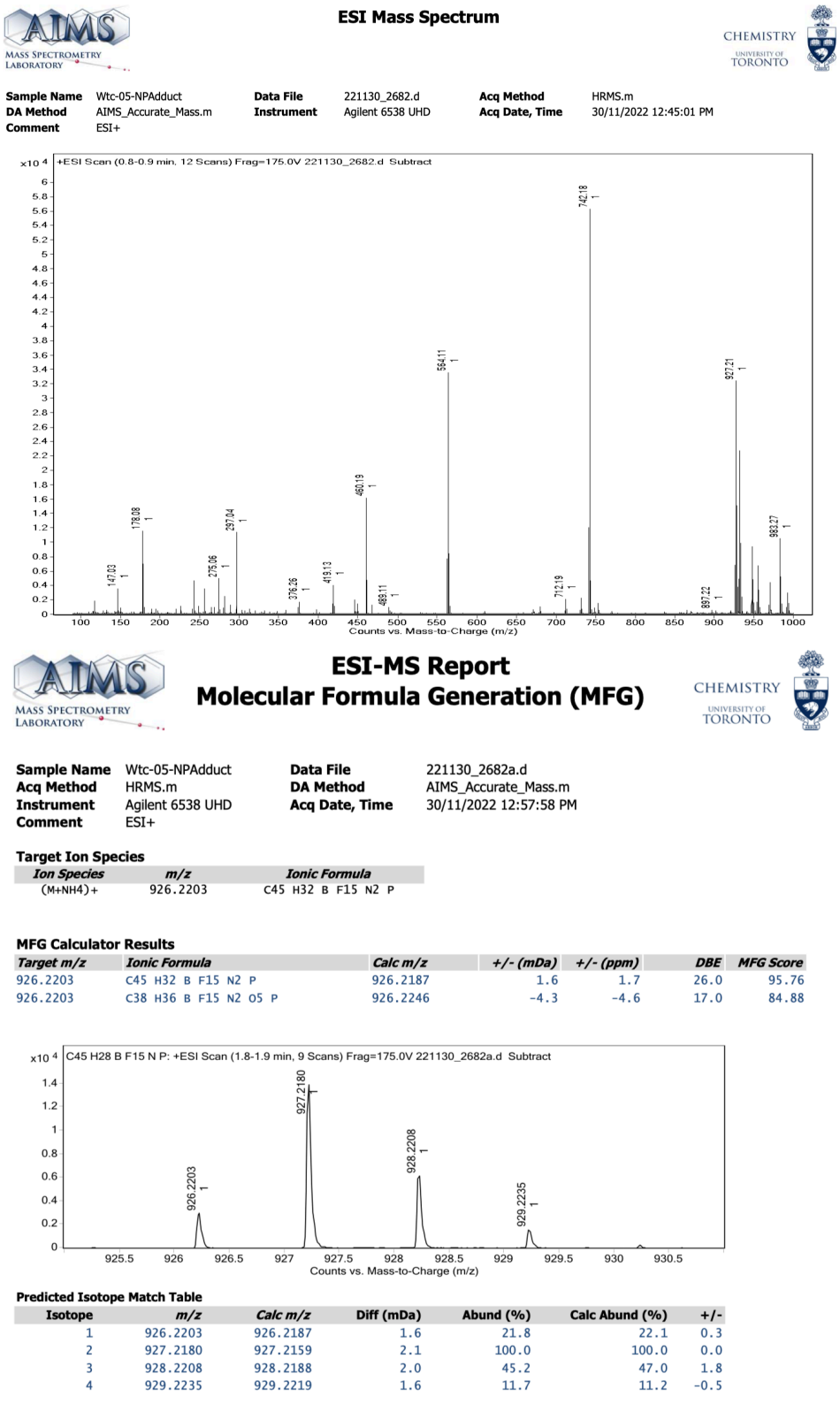
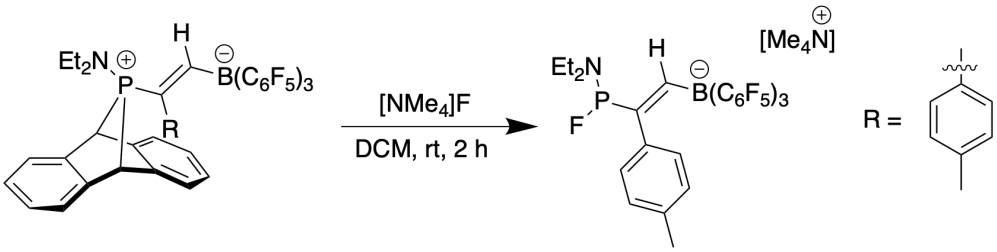


Figure S11: ESI-MS(+) of $C_{45}H_{32}BF_{15}N_2P^+$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.3 Synthesis of 3



Scheme S3: Synthesis of **3**

In the glovebox, compound **2** (0.0214 g, 0.024 mmol, 1.0 eq) was dissolved in DCM (1.0 mL), and tetramethylammonium fluoride (0.0022 g, 0.024 mmol, 1.0 eq) was added. The mixture was stirred at room temperature for 2 hours. The solution was then filtered over an activated charcoal plug to remove the anthracene by-product. Solvent was removed under vacuum, and pentane (1.0 mL) was added to the yellow oil. The pentane layer was decanted, and the product was dried to be obtained as light yellow powder (0.0156 g, 0.019 mmol, 80% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.23 (d, $^{3}J_{PH}$ = 13.1 Hz, 1H, -PC=C*H*), 6.75 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, Ar-*H*), 6.66 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, Ar-*H*), 3.17 (m, 4H, -N(CH_2CH$_3$)$_2$), 3.14 (s, 12H, -N(CH_4)), 2.18 (s, 3H, Ar-CH_3), 0.90 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, -N(CH$_2$CH_3)$_2$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.13 (br d, $^{1}J_{CF}$ = 250.2 Hz, *o*-C_6F$_5$), 138.01 (br d, $^{1}J_{CF}$ = 259.7 Hz, *m*-C_6F$_5$), 137.91 (s), 136.40 (br d, $^{1}J_{CF}$ = 246.1 Hz, *p*-C_6F$_5$), 135.04 (s), 132.17 (s), 128.49 (s), 128.21 (d, J = 5.1 Hz), 127.62 (s), 56.35 (m, N(CH$_3$)$_4$), 42.24 (d, $^{2}J_{CP}$ = 15.0 Hz, -N(CH$_2$CH$_3$)$_2$), 20.92 (s, Ar-CH$_3$), 15.04 (d, $^{3}J_{CP}$ = 3.3 Hz, -N(CH$_2$$CH_3$)$_2$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.0 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -114.05 (d, $^{1}J_{PF}$ = 970 Hz, 1F, P-*F*), -131.37 (dd, $^{3}J_{FF}$ = 25.2 Hz, $^{4}J_{FF}$ = 8.0 Hz, 6F, o-C$_6$*F*$_5$), -163.38 (t, $^{3}J_{FF}$ = 20.6 Hz, 3F, p-C$_6$*F*$_5$), -167.21 (m, 6F, m-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 158.4 (d, $^{1}J_{PF}$ = 970 Hz).

• MS (ESI) [M]$^-$ $C_{31}H_{18}BF_{16}NP^-$ calc. 750.1014 *m/z*, found 750.1026 *m/z*.

• Elem. Anal. Found (Calc'd) for $C_{35}H_{30}BF_{16}N_2P$: C 52.31 (50.99), H 3.37 (3.67), N 2.59 (3.40). The poor agreement of the EA data is attributed to the high sensitivity of this amido-phosphine compound to moisture and oxygen.

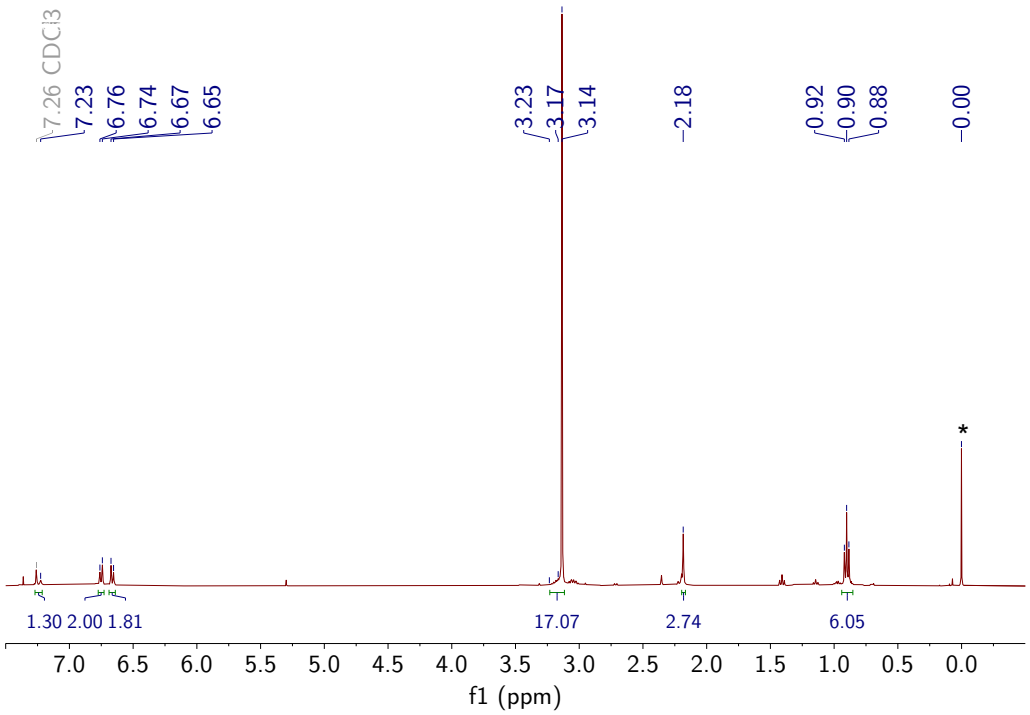


Figure S12: ^{1}H NMR spectrum of **3**. * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

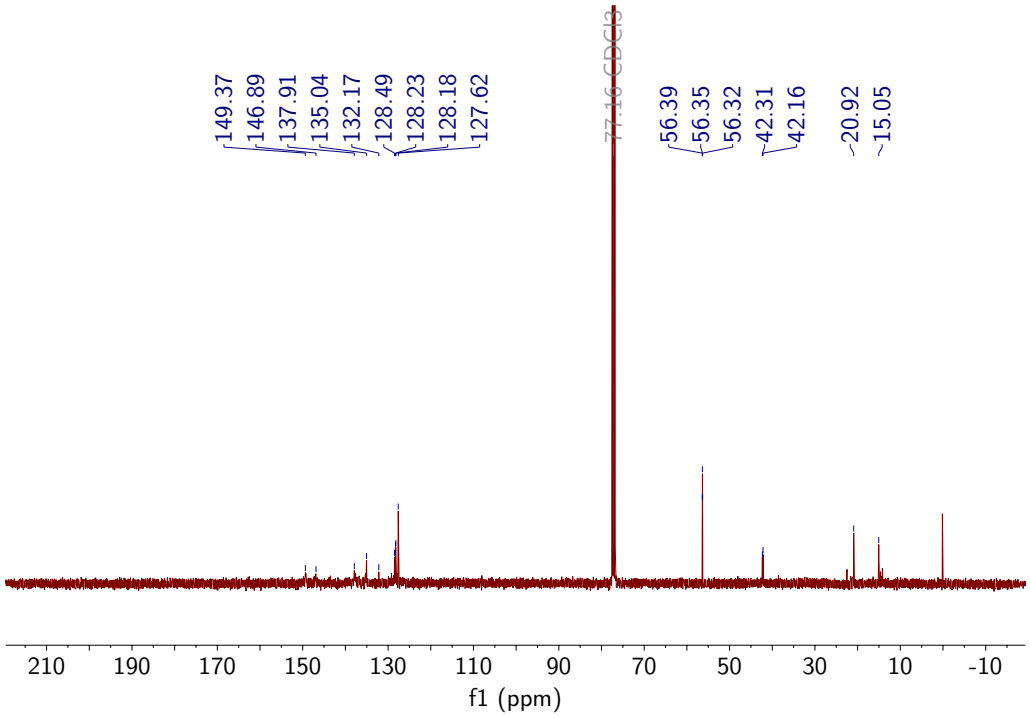


Figure S13: ^{13}C NMR spectrum of **3** (chloroform-*d*, 101 MHz)

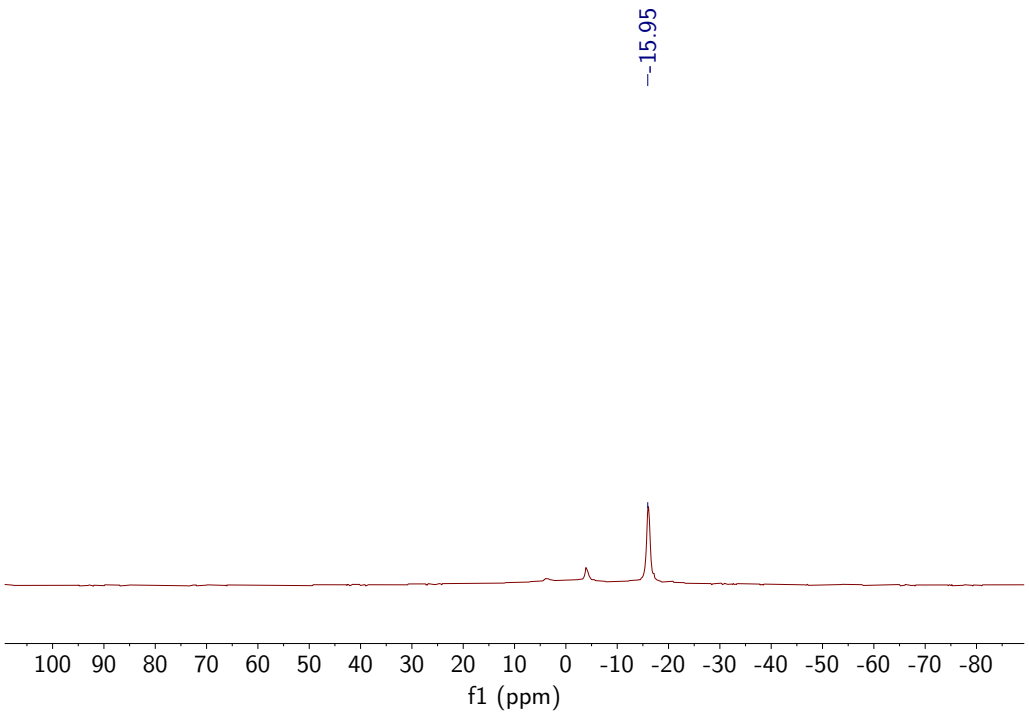


Figure S14: ^{11}B NMR spectrum of **3** (chloroform-*d*, 128 MHz)

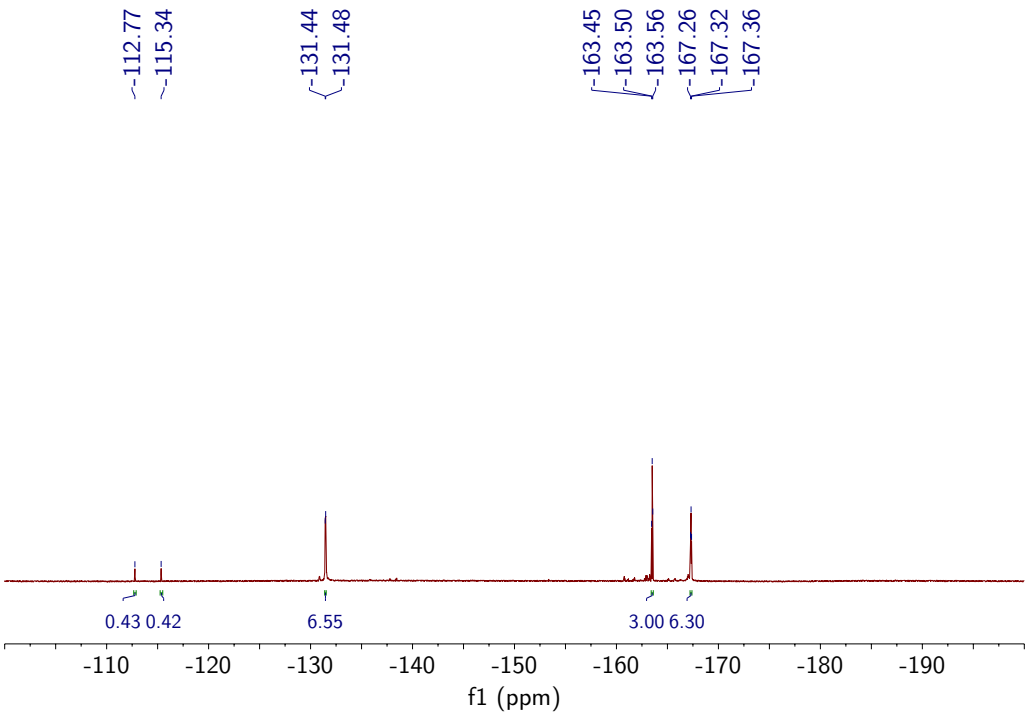


Figure S15: ^{19}F NMR spectrum of **3** (chloroform-*d*, 377 MHz)

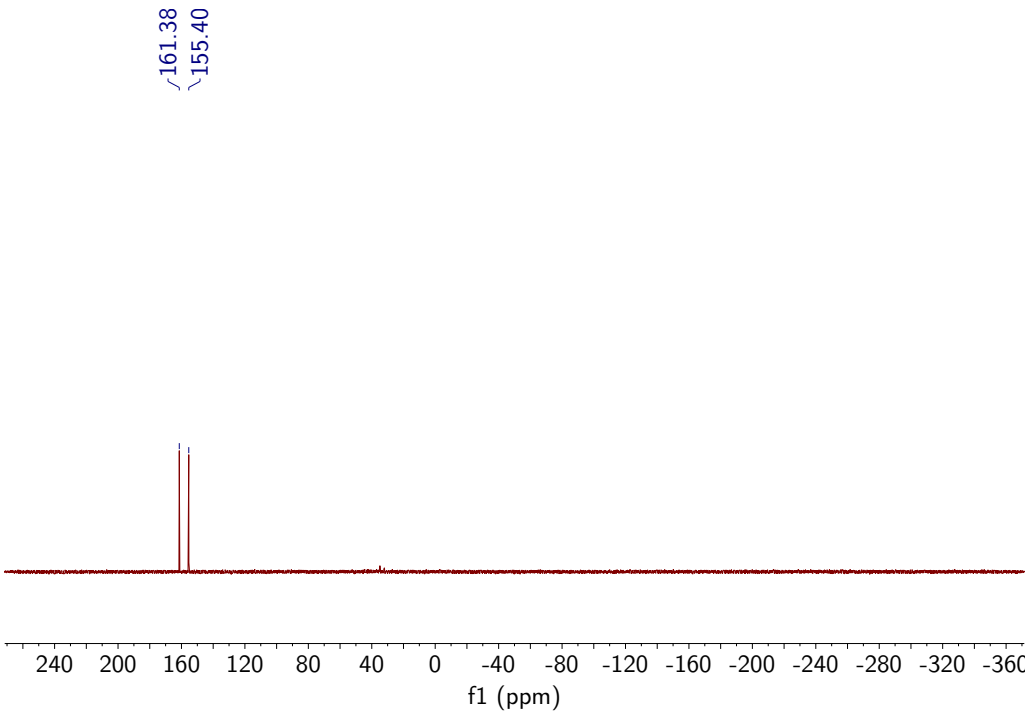


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of **3** (chloroform-*d*, 162 MHz)

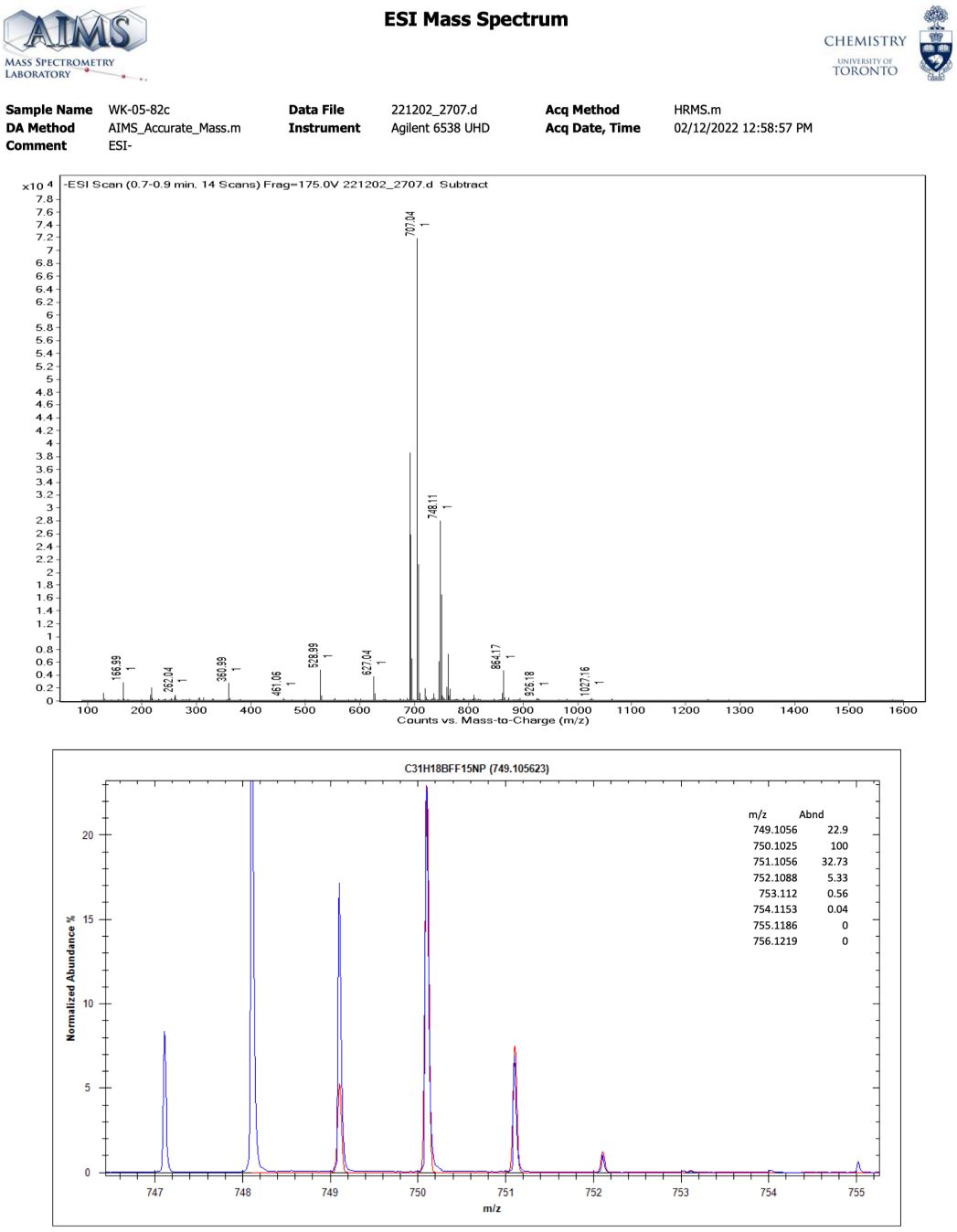
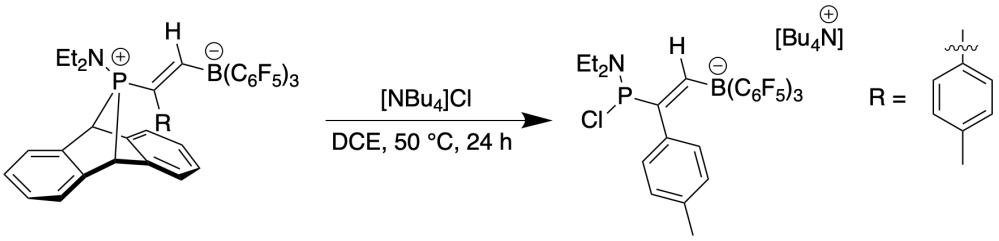


Figure S17: ESI-MS(-) of $C_{31}H_{18}BF_{16}NP^-$ with zoomed in portion of the molecular ion, and predicted isotope pattern superimposed (red)

2.4 Synthesis of 4



Scheme S4: Synthesis of **4**

In the glovebox, compound **2** (0.0381 g, 0.042 mmol, 1.0 eq) was dissolved in dichloroethane (1.0 mL), and tetrabutylammonium chloride (0.0116 g, 0.042 mmol, 1.0 eq) was added. The solution was heated at 50 °C for 24 hours. The solution was then filtered over an activated charcoal plug to remove the anthracene by-product. Solvent was removed under vacuum, and pentane (1.0 mL) was added to the yellow oil. The pentane layer was decanted, and the product was dried to be obtained as light yellow powder (0.0383 g, 0.038 mmol, 91% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.71 (d, $^{3}J_{PH}$ = 15.2 Hz, 1H, -PC=C*H*), 6.73 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 6.69 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 3.14–3.06 (m, 12H, overlapping signals of -N(C*H*$_2$CH$_3$)$_2$ and N*Bu*$_4$), 2.19 (s, 3H, -ArC*H*$_3$), 1.62–1.54 (m, 8H, N*Bu*$_4$), 1.41–1.32 (m, 8H, N*Bu*$_4$), 0.98–0.93 (m, 18H, overlapping signals of -N(CH$_2$C*H*$_3$)$_2$ and N*Bu*$_4$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.18 (br d, $^{1}J_{CF}$ = 241.7 Hz, *o*-*C*$_6$F$_5$), 138.38 (s), 138.12 (s), 137.83 (br d, $^{1}J_{CF}$ = 247.5 Hz, *m*-*C*$_6$F$_5$), 136.36 (br d, $^{1}J_{CF}$ = 247.5 Hz, *p*-*C*$_6$F$_5$), 135.06 (d, J = 2.2 Hz), 128.65 (d, J = 5.1 Hz), 127.53 (s), 58.98 (s, N*Bu*$_4$), 43.10 (d, $^{2}J_{CP}$ = 12.1 Hz, -N(*C*H$_2$CH$_3$)$_2$), 23.98 (s, N*Bu*$_4$), 20.96 (s, Ar-*C*H$_3$), 19.72 (s, N*Bu*$_4$), 13.64 (d, $^{3}J_{CP}$ = 5.5 Hz, -N(CH$_2$*C*H$_3$)$_2$), 13.55 (s, N*Bu*$_4$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -15.9 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -130.94 (dd, $^{3}J_{FF}$ = 25.7 Hz, $^{4}J_{FF}$ = 8.6 Hz, 6F, *o*-C$_6$*F*$_5$), -163.98 (t, $^{3}J_{FF}$ = 20.6 Hz, 3F, *p*-C$_6$*F*$_5$), -167.49 (m, 6F, *m*-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 155.4 (s).

• The molecular ion peak was not observed for this molecule. Rather, only the hydrolyzed compound $C_{31}H_{19}BF_{15}NOP^{-}$ was observed: MS (ESI) $[M]^{-}$ $C_{31}H_{19}BF_{15}NOP^{-}$ calc. 748.1058 *m/z*, found 748.1065 *m/z*.

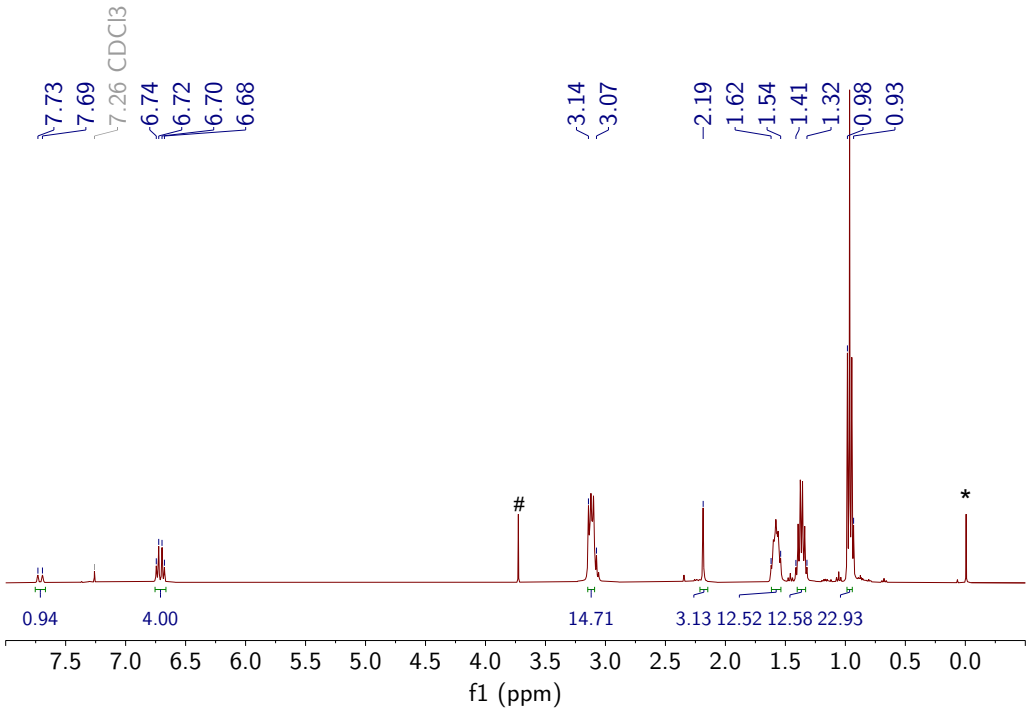


Figure S18: ^{1}H NMR spectrum of **4** with residual dichloroethane (denoted as #). * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

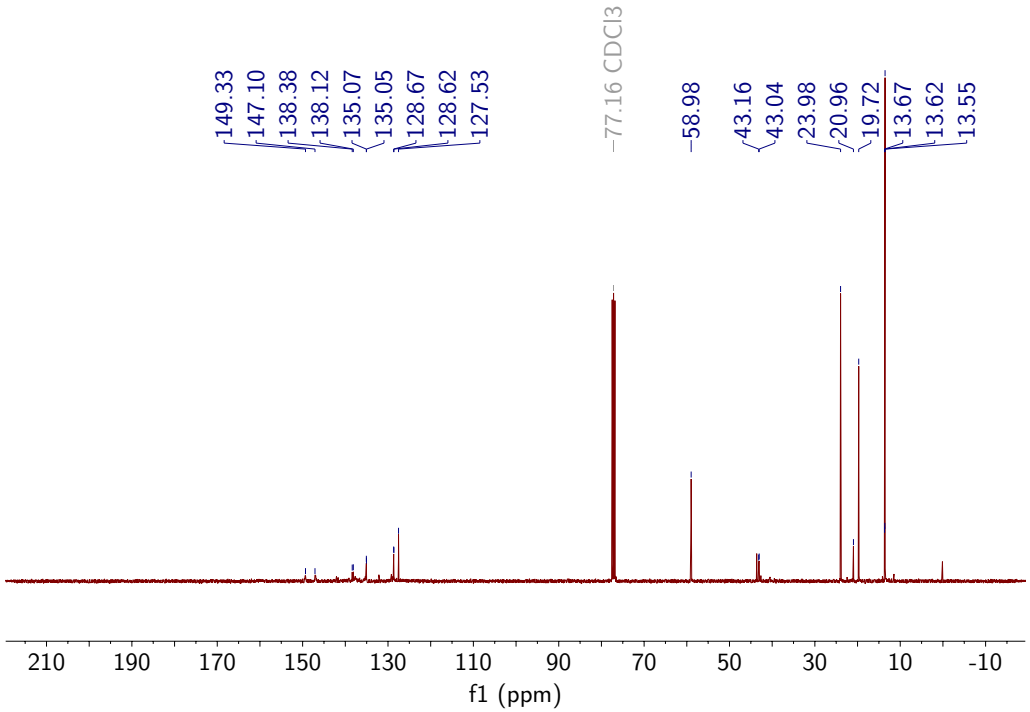


Figure S19: ^{13}C NMR spectrum of **4** (chloroform-*d*, 101 MHz)

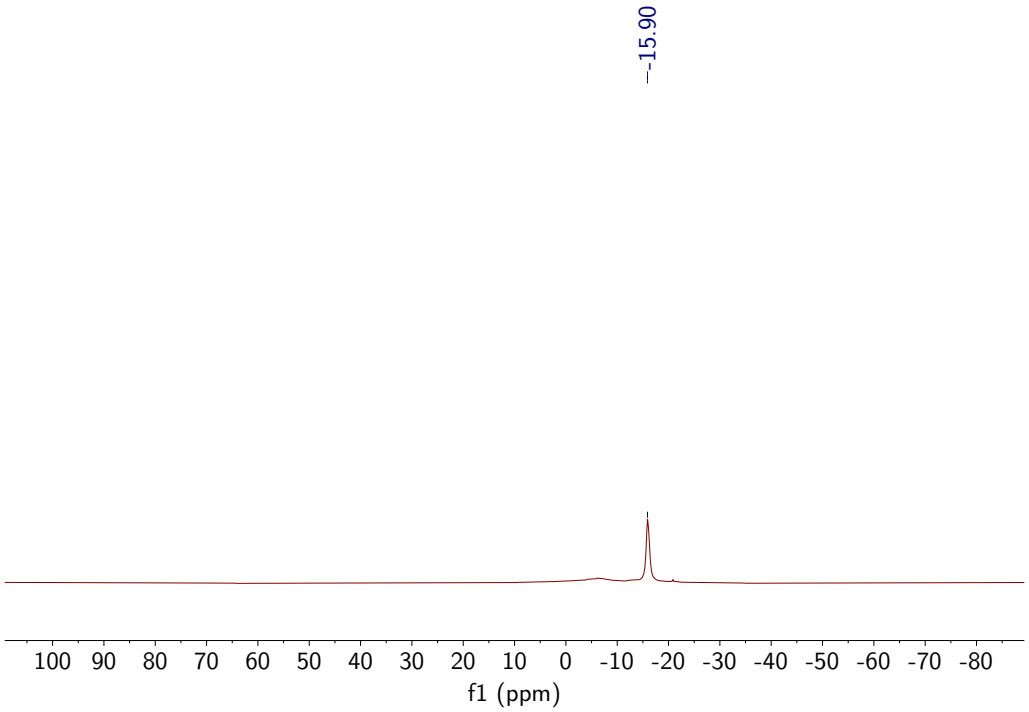


Figure S20: ^{11}B NMR spectrum of **4** (chloroform-*d*, 128 MHz)

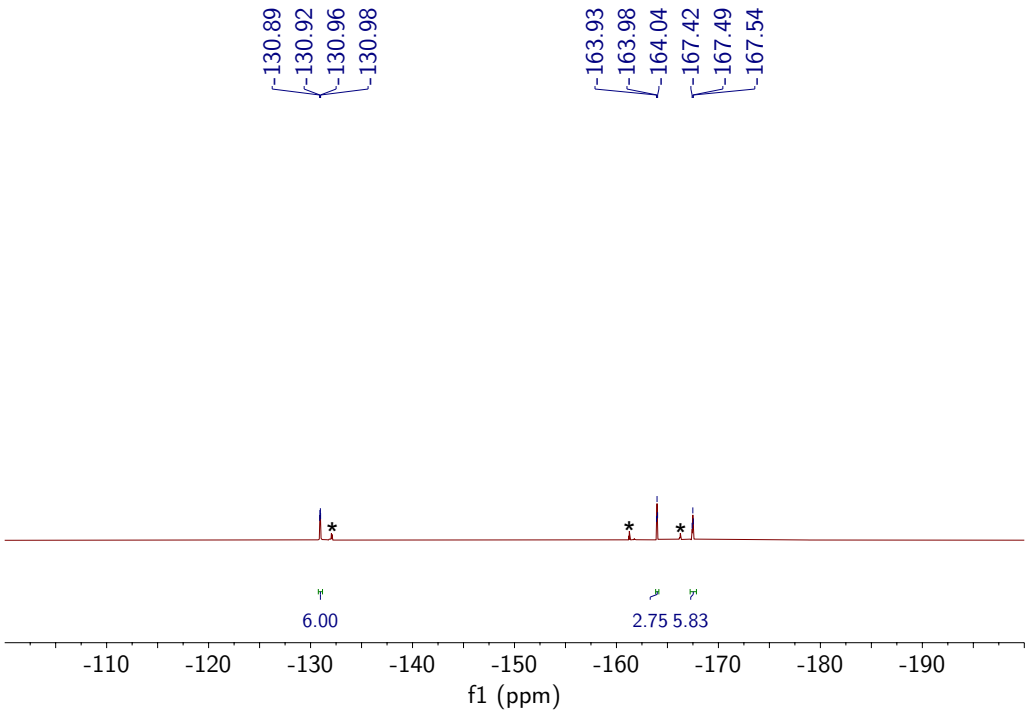


Figure S21: ^{19}F NMR spectrum of **4**. Minor unidentifiable impurities have been labelled with *s. (chloroform-*d*, 377 MHz)

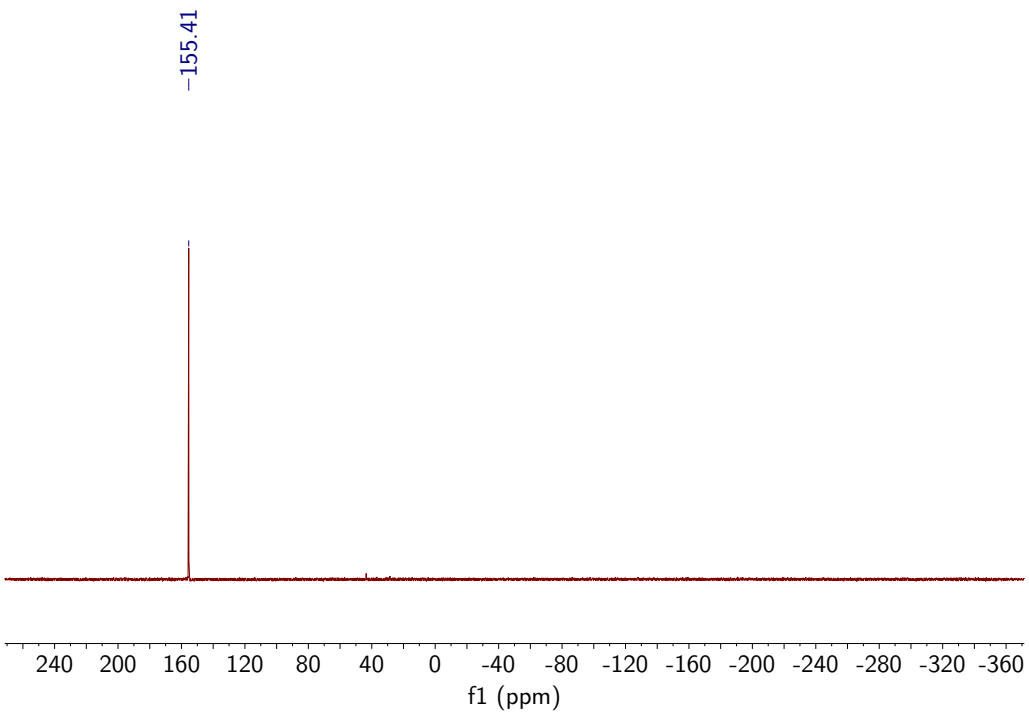
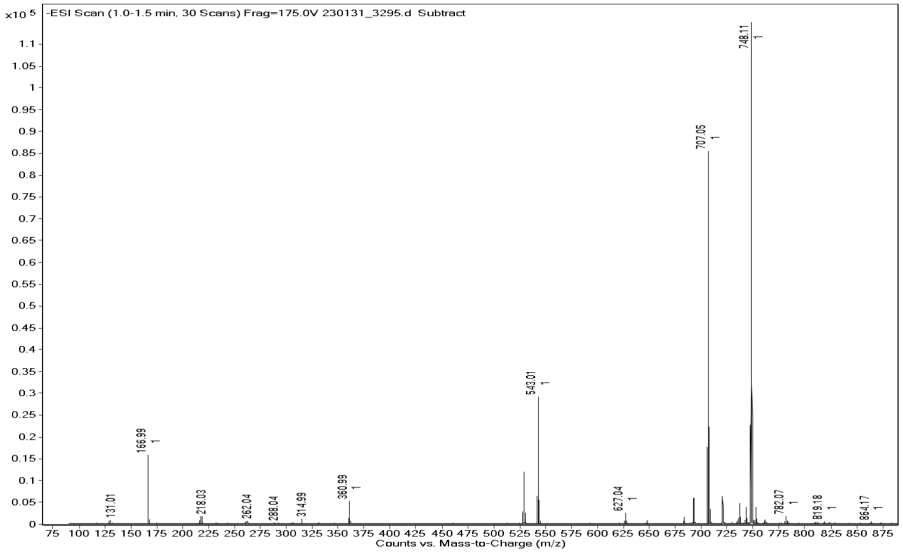


Figure S22: $^{31}P\{^{1}H\}$ NMR spectrum of **4** (chloroform-*d*, 162 MHz)

ESI Mass Spectrum

Sample Name	WK-05-136re	**Data File**	230131_3295.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	31/01/2023 1:00:23 PM
Comment	ESI-				



ESI-MS Report
Molecular Formula Generation (MFG)

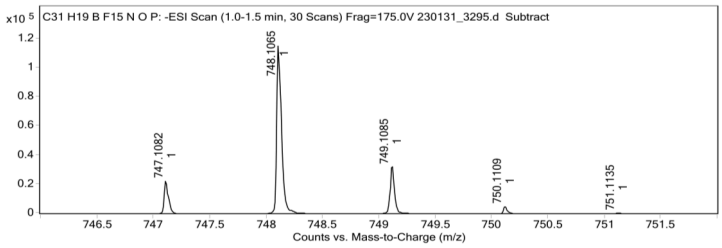
Sample Name	WK-05-136re	**Data File**	230131_3295.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	31/01/2023 1:00:23 PM
Comment	ESI-		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	747.1082	C31 H19 B F15 N O P

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
747.1082	C31 H19 B F15 N O P	747.1100	-1.8	-2.4	16.5	95.93
747.1082	C33 H14 B F15 N3	747.1083	-0.1	-0.1	21.5	93.51
747.1082	C21 H18 B F15 N5 O7	747.1102	-2.0	-2.7	8.5	92.47
747.1082	C22 H14 B F15 N9 O3	747.1115	-3.3	-4.4	13.5	90.53
747.1082	C20 H22 B F15 N O11	747.1088	-0.6	-0.8	3.5	89.71
747.1082	C26 H19 B F15 N3 O3 P	747.1059	2.3	3.1	12.5	85.08
747.1082	C15 H19 B F15 N9 O6 P	747.1091	-0.9	-1.2	4.5	84.15
747.1082	C19 H23 B F15 N3 O8 P	747.1118	-3.6	-4.8	3.5	82.22
747.1082	C20 H19 B F15 N7 O4 P	747.1131	-4.9	-6.6	8.5	77.93
747.1082	C14 H23 B F15 N5 O10 P	747.1078	0.4	0.5	-0.5	77.40

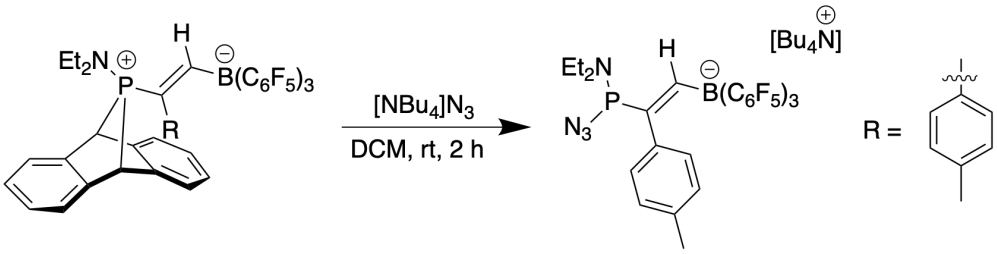


Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	747.1082	747.1100	-1.8	19.8	22.9	3.1
2	748.1065	748.1069	-0.4	100.0	100.0	0.0
3	749.1085	749.1099	-1.4	28.4	32.8	4.4
4	750.1109	750.1130	-2.1	4.3	5.6	1.3

Figure S23: ESI-MS(-) of the product, only showing the hydrolyzed compound $C_{31}H_{19}BF_{15}NOP^-$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.5 Synthesis of 5



Scheme S5: Synthesis of **5**

In the glovebox, compound **2** (0.0201 g, 0.022 mmol, 1.0 eq) was dissolved in DCM (1.0 mL), and [TBA]N_3 (0.0063 g, 0.022 mmol, 1.0 eq) was added at once. The mixture was stirred at room temperature for 2 hours. The solution was then filtered over an activated charcoal plug to remove the anthracene by-product. The solution was dried, and pentane (1.0 mL) was added to the orange oil. The pentane layer was decanted, and the product was dried to be obtained as light orange powder (0.0170 g, 0.017 mmol, 76% yield).

- ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.36 (d, $^{3}J_{PH}$ = 15.4 Hz, 1H, -PC=C*H*), 6.72 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 6.68 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 3.18–3.14 (m, 8H, N*Bu*$_4$), 3.11–2.99 (m, 4H, -N(C*H*$_2$CH$_3$)$_2$), 2.18 (s, 3H, -ArC*H*$_3$), 1.63–1.56 (m, 8H, N*Bu*$_4$), 1.42–1.33 (m, 8H, N*Bu*$_4$), 0.98–0.91 (m, 18H, overlapping signals of -N(CH$_2$C*H*$_3$)$_2$ and N*Bu*$_4$).
- ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.12 (br d, $^{1}J_{CF}$ = 241.8 Hz, *o*-*C*$_6$F$_5$), 138.69 (s), 138.45 (s), 138.00 (br d, $^{1}J_{CF}$ = 241.8 Hz, *m*-*C*$_6$F$_5$), 136.34 (br d, $^{1}J_{CF}$ = 251.4 Hz, *p*-*C*$_6$F$_5$), 134.67 (s), 128.43 (d, J = 5.1 Hz), 127.44 (s), 58.99 (s, N*Bu*$_4$), 42.61 (d, $^{2}J_{CP}$ = 14.7 Hz, -N(*C*H$_2$CH$_3$)$_2$), 23.99 (s, N*Bu*$_4$), 20.95 (s, Ar-*C*H$_3$), 19.75 (s, N*Bu*$_4$), 14.69 (d, $^{3}J_{CP}$ = 3.7 Hz, -N(CH$_2$*C*H$_3$)$_2$), 13.57 (s, N*Bu*$_4$).
- ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.0 (s, -*B*(C$_6$F$_5$)$_3$).
- ^{19}F NMR (chloroform-*d*, 377 MHz): δ -130.94 (dd, $^{3}J_{FF}$ = 25.2 Hz, $^{4}J_{FF}$ = 8.0 Hz, 6F, *o*-C$_6$*F*$_5$), -164.22 (t, $^{3}J_{FF}$ = 20.0 Hz, 3F, *p*-C$_6$*F*$_5$), -167.61 (m, 6F, *m*-C$_6$*F*$_5$).
- ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 129.1 (s).
- MS (ESI) [M]$^-$ $C_{31}H_{18}BF_{15}N_4P^-$ calc. 773.1123 *m/z*, found 773.1153 *m/z*.

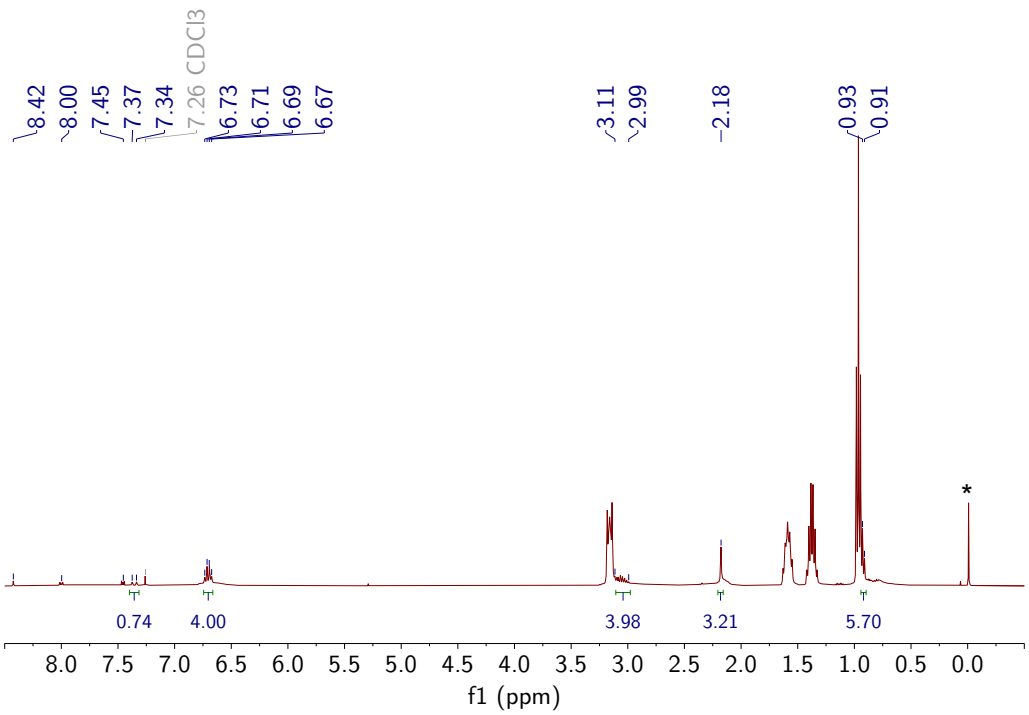


Figure S24: ^{1}H NMR spectrum of **5** with minor residual anthracene at 8.42, 8.00, and 7.45 ppm. * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

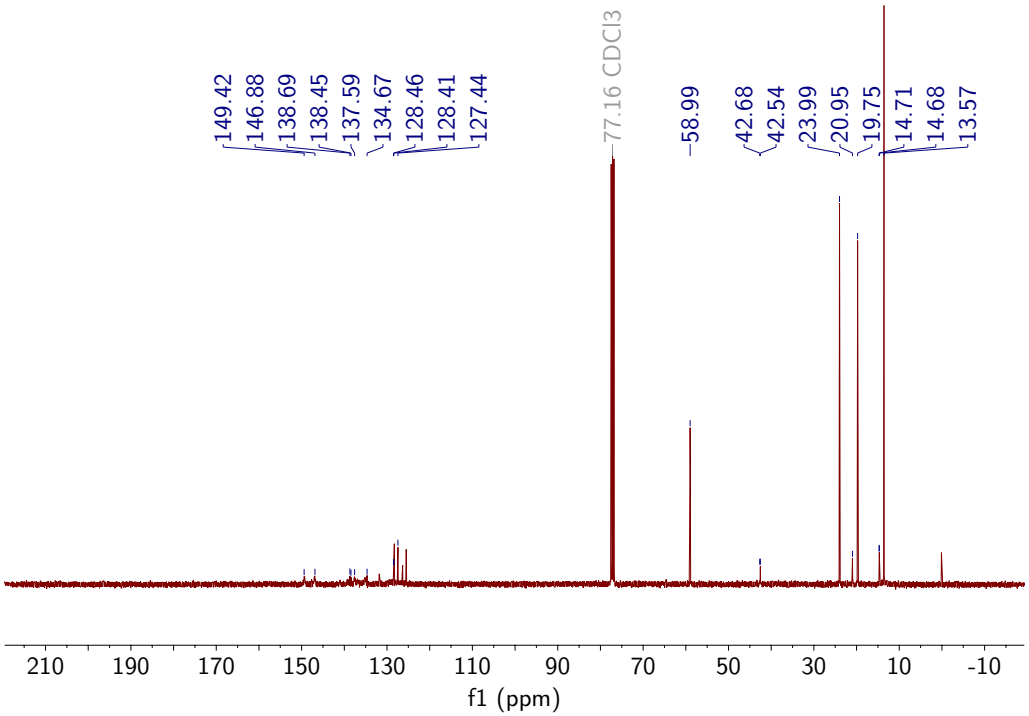


Figure S25: ^{13}C NMR spectrum of **5** (chloroform-*d*, 101 MHz)

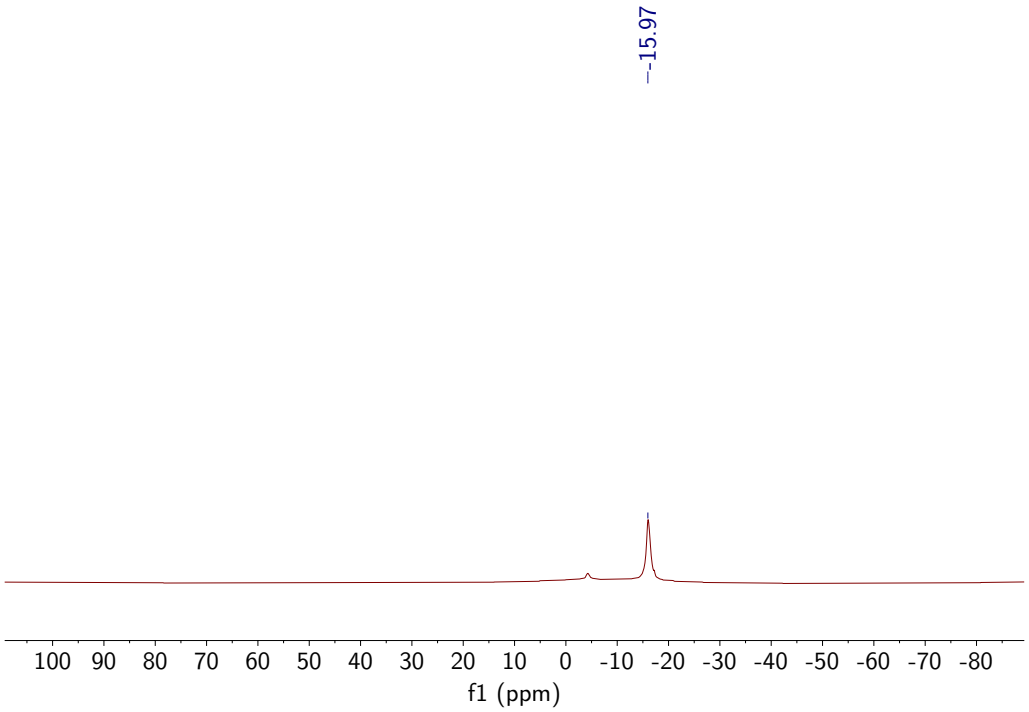


Figure S26: ^{11}B NMR spectrum of **5** (chloroform-*d*, 128 MHz)

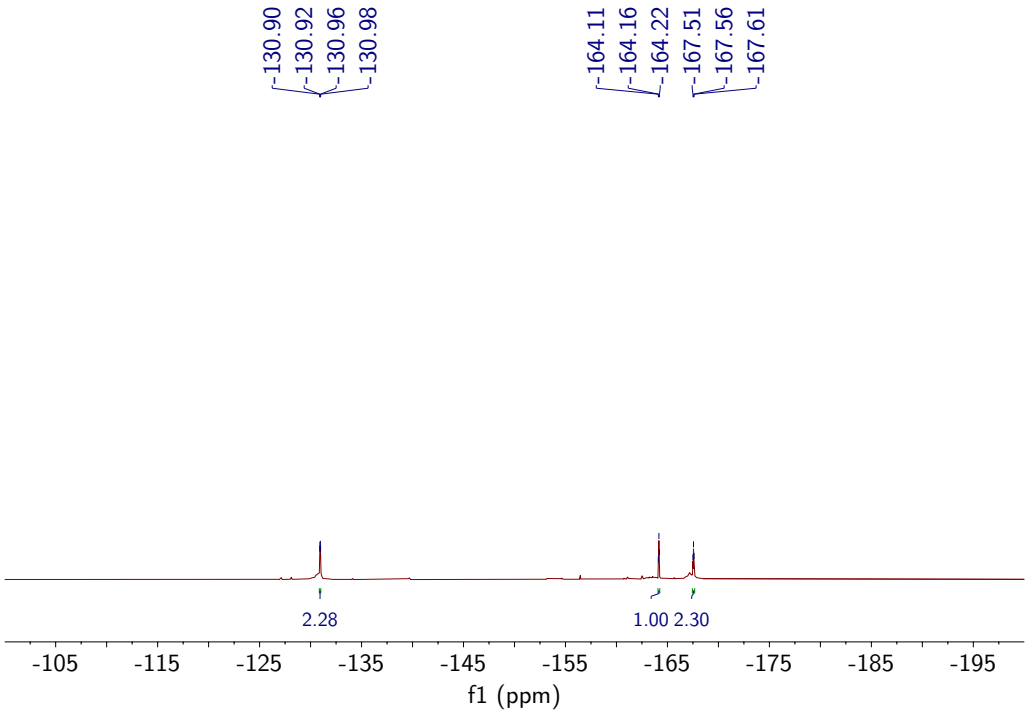


Figure S27: ^{19}F NMR spectrum of **5** (chloroform-*d*, 377 MHz)

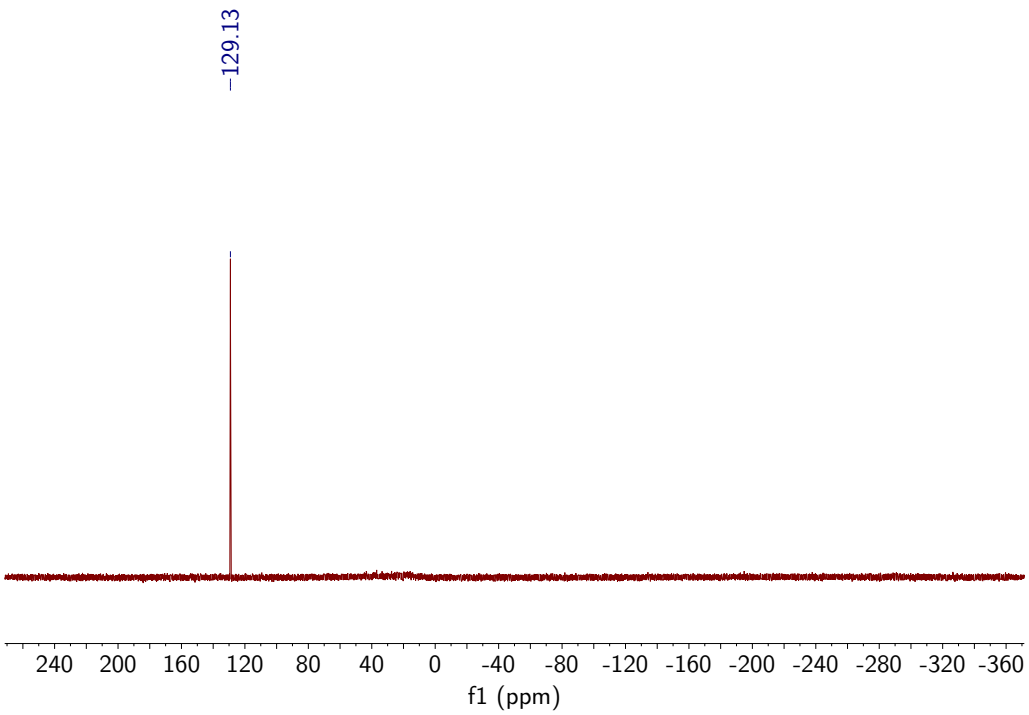
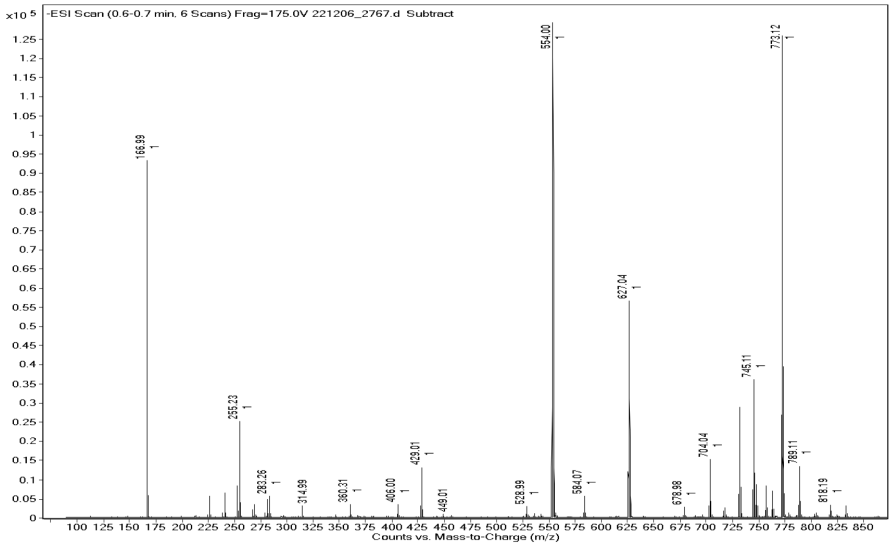


Figure S28: $^{31}P\{^{1}H\}$ NMR spectrum of **5** (chloroform-*d*, 162 MHz)

ESI Mass Spectrum

Sample Name	wk-05-91	**Data File**	221206_2767.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	06/12/2022 2:33:20 PM
Comment	ESI-				



ESI-MS Report
Molecular Formula Generation (MFG)

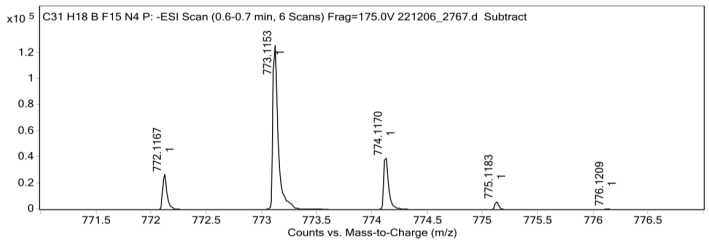
Sample Name	wk-05-91	**Data File**	221206_2767.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	06/12/2022 2:33:20 PM
Comment	ESI-		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	772.1167	C31 H18 B F15 N4 P

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
772.1167	C31 H18 B F15 N4 P	772.1164	0.3	0.4	18.5	95.97
772.1167	C30 H22 B F15 O4 P	772.1151	1.6	2.1	13.5	90.33
772.1167	C20 H18 B F15 N10 O3 P	772.1196	-2.9	-3.8	10.5	87.78
772.1167	C19 H22 B F15 N6 O7 P	772.1183	-1.6	-2.1	5.5	86.78
772.1167	C18 H26 B F15 N2 O11 P	772.1170	-0.3	-0.4	0.5	81.88
772.1167	C23 H26 B F15 O9 P	772.1210	-4.3	-5.6	4.5	80.74
772.1167	C24 H22 B F15 N4 O5 P	772.1223	-5.6	-7.3	9.5	76.03
772.1167	C14 H22 B F15 N8 O9 P	772.1143	2.4	3.1	1.5	63.55

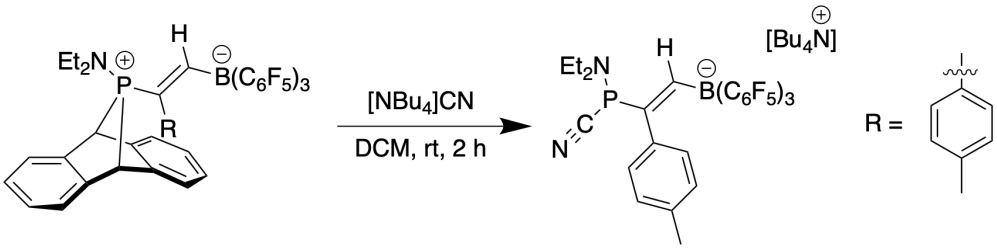


Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	772.1167	772.1164	0.3	21.5	22.8	1.3
2	773.1153	773.1134	1.9	100.0	100.0	0.0
3	774.1170	774.1162	0.8	31.9	33.7	1.8
4	775.1183	775.1192	-0.9	4.9	5.7	0.8

Figure S29: ESI-MS(-) of $C_{31}H_{18}BF_{15}N_4P^-$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.6 Synthesis of 6



Scheme S6: Synthesis of **6**

In the glovebox, compound **2** (0.0248 g, 0.027 mmol, 1.0 eq) was dissolved in DCM (1.0 mL), and [TBA]CN (0.0073 g, 0.027 mmol, 1.0 eq) was added at once. The mixture was stirred at room temperature for 2 hours. The solution was then filtered over an activated charcoal plug to remove the anthracene by-product. The solution was dried, and pentane (1.0 mL) was added to the yellow oil. The pentane layer was decanted, and the product was dried to be obtained as an off-white powder (0.0232 g, 0.023 mmol, 85% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.50 (d, $^{3}J_{PH}$ = 18.9 Hz, 1H, -PC=C*H*), 6.75 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 6.72 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H, Ar-*H*), 3.10–3.03 (m, 12H, overlapping signals of -N(C*H*$_2$CH$_3$)$_2$ and N*Bu*$_4$), 2.19 (s, 3H, -ArC*H*$_3$), 1.59–1.51 (m, 8H, N*Bu*$_4$), 1.39–1.30 (m, 8H, N*Bu*$_4$), 0.99 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, -N(CH$_2$C*H*$_3$)$_2$), 0.96 (t, $^{3}J_{HH}$ = 7.3 Hz, 12H, N*Bu*$_4$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.19 (br d, $^{1}J_{CF}$ = 239.3 Hz, *o*-*C*$_6$F$_5$), 138.04 (br d, $^{1}J_{CF}$ = 244.3 Hz, *m*-*C*$_6$F$_5$), 137.56 (s), 137.31 (s), 136.67 (s), 136.40 (br d, $^{1}J_{CF}$ = 247.8 Hz, *p*-*C*$_6$F$_5$), 135.28 (d, J = 2.5 Hz), 128.38 (d, J = 5.2 Hz), 127.74 (s), 124.03 (d, $^{1}J_{CP}$ = 103.3 Hz, -P*C*N), 58.90 (s, N*Bu*$_4$), 44.58 (d, $^{2}J_{CP}$ = 14.0 Hz, -N(*C*H$_2$CH$_3$)$_2$), 23.86 (s, N*Bu*$_4$), 21.00 (s, Ar-*C*H$_3$), 19.69 (s, N*Bu*$_4$), 13.63 (d, $^{3}J_{CP}$ = 4.0 Hz, -N(CH$_2$*C*H$_3$)$_2$), 13.51 (s, N*Bu*$_4$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.0 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -131.16 (dd, $^{3}J_{FF}$ = 25.2 Hz, $^{4}J_{FF}$ = 8.0 Hz, 6F, *o*-C$_6$*F*$_5$), -163.89 (t, $^{3}J_{FF}$ = 20.6 Hz, 3F, *p*-C$_6$*F*$_5$), -167.45 (m, 6F, *m*-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 51.9 (s).

• MS (ESI) [M]$^{-}$ $C_{32}H_{18}BF_{15}N_2P^{-}$ calc. 757.1061 *m/z*, found 757.1087 *m/z*.

• Elem. Anal. Found (Calc'd) for $C_{48}H_{54}N_3BF_{15}P$: C 57.13 (57.67), H 5.02 (5.44), N 3.48 (4.20). The poor agreement of the EA data is attributed to the high sensitivity of this amido-phosphine compound to moisture and oxygen.

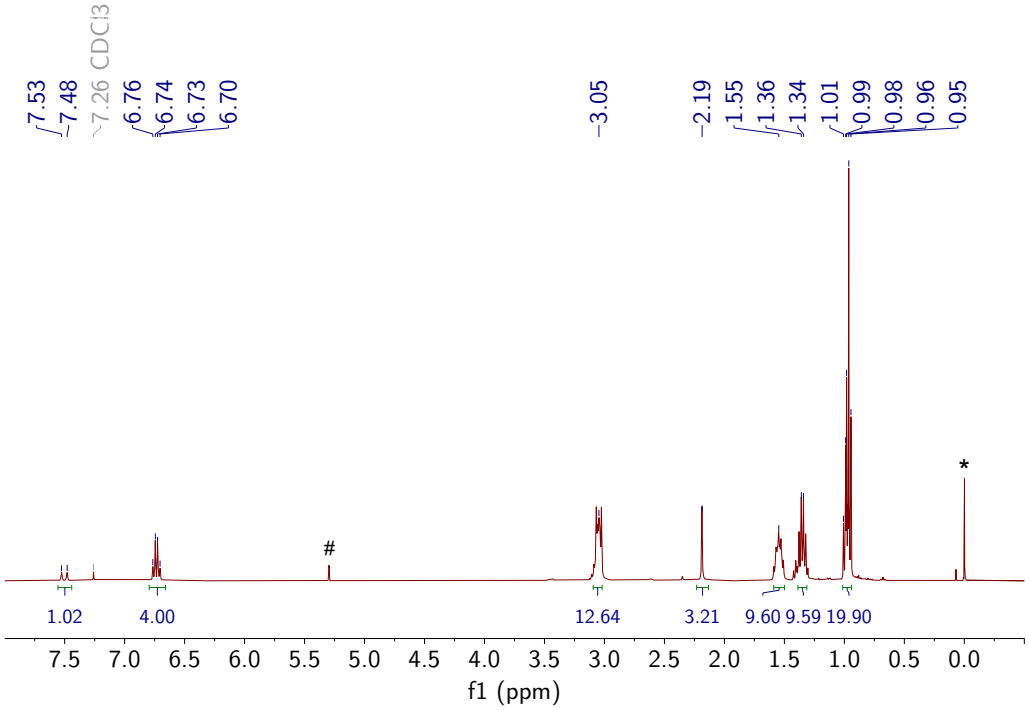


Figure S30: ^{1}H NMR spectrum of **6** with residual DCM (denoted as #). * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

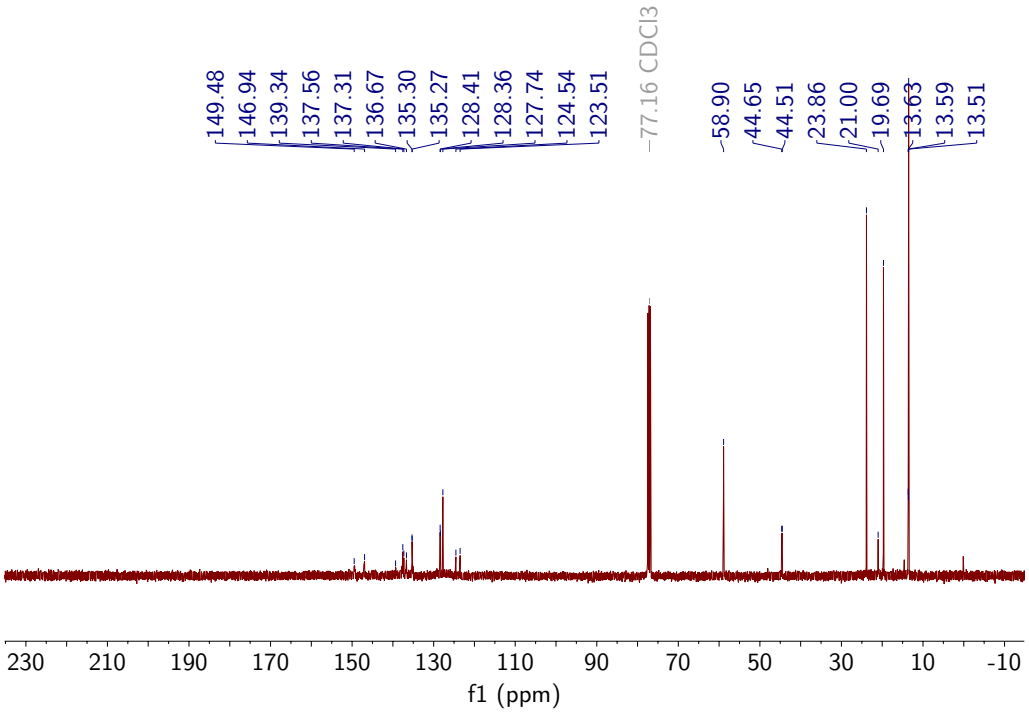


Figure S31: ^{13}C NMR spectrum of **6** (chloroform-*d*, 101 MHz)

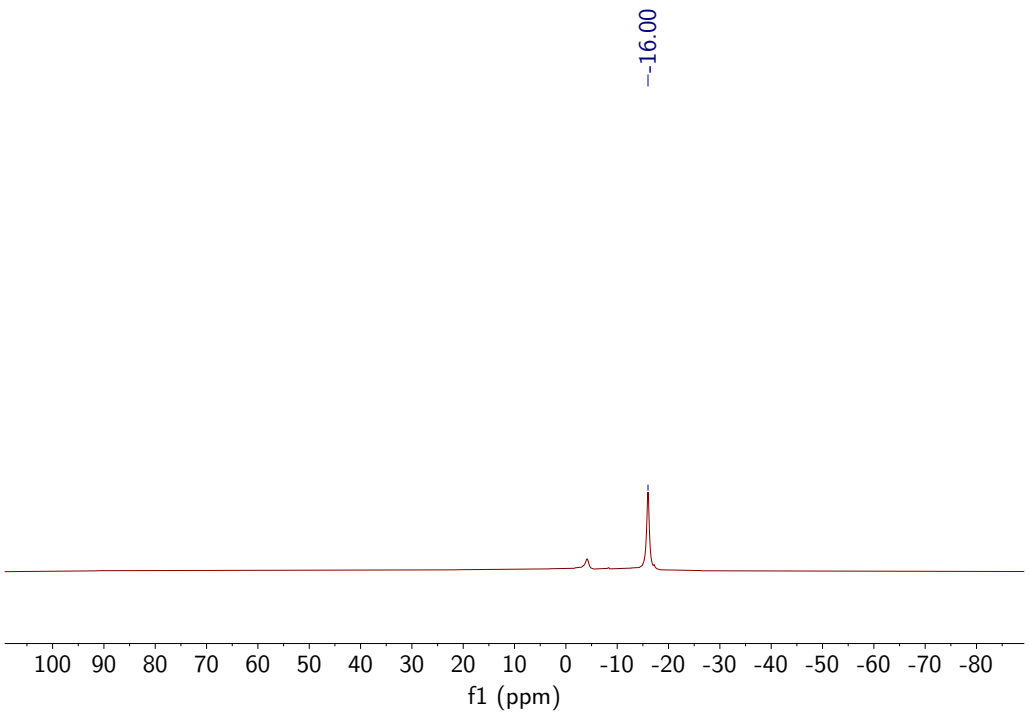


Figure S32: ^{11}B NMR spectrum of **6** (chloroform-*d*, 128 MHz)

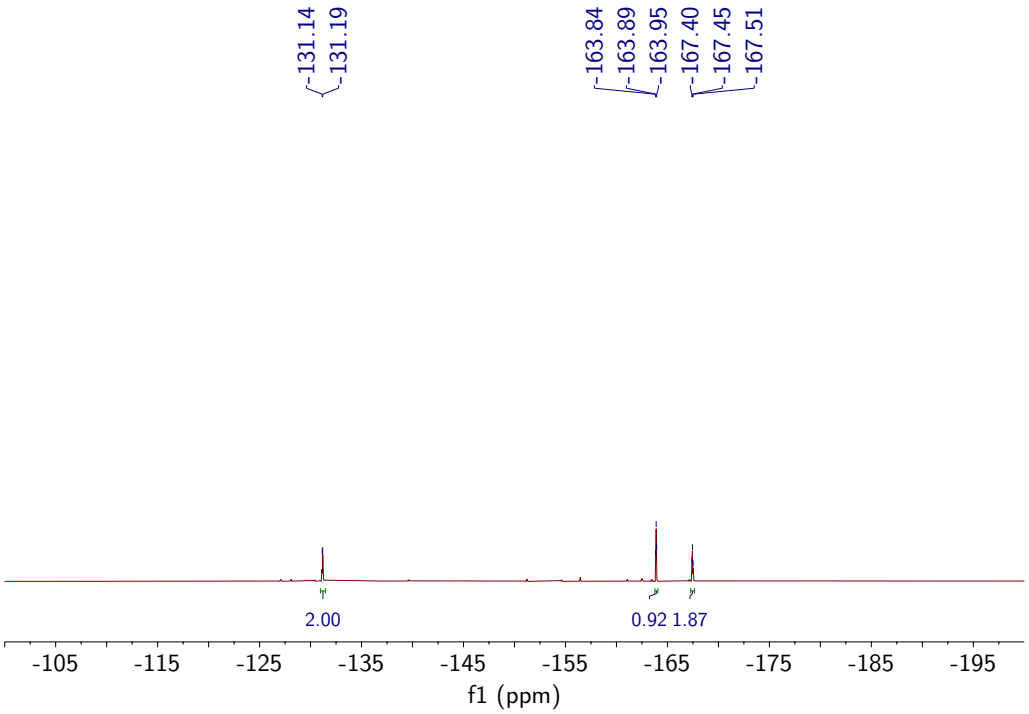


Figure S33: ^{19}F NMR spectrum of **6** (chloroform-*d*, 377 MHz)

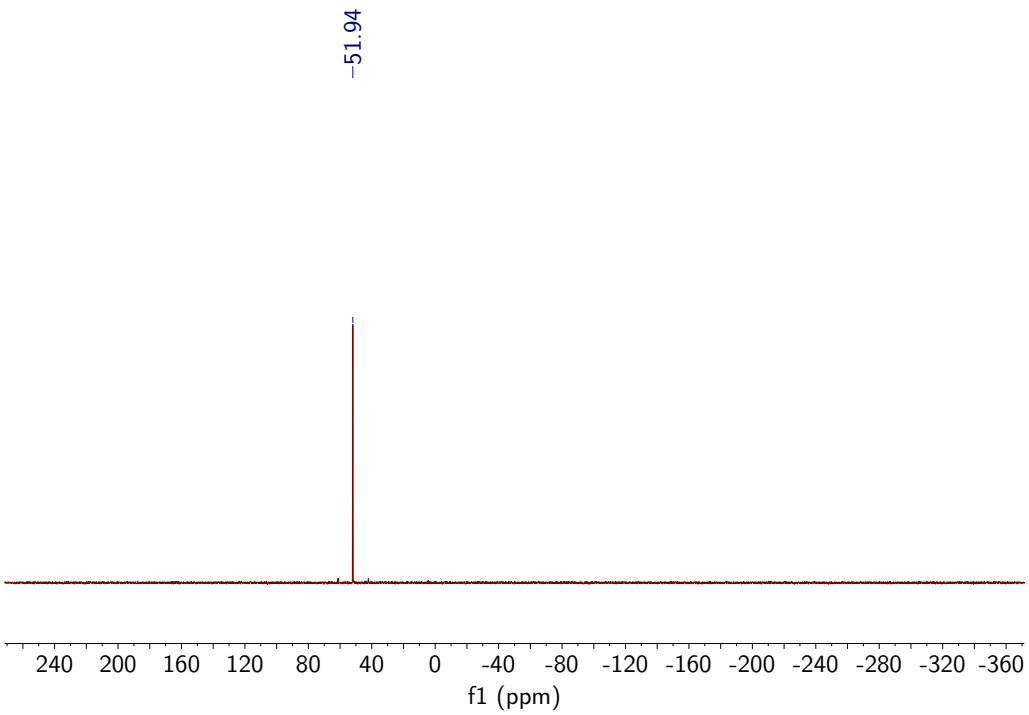
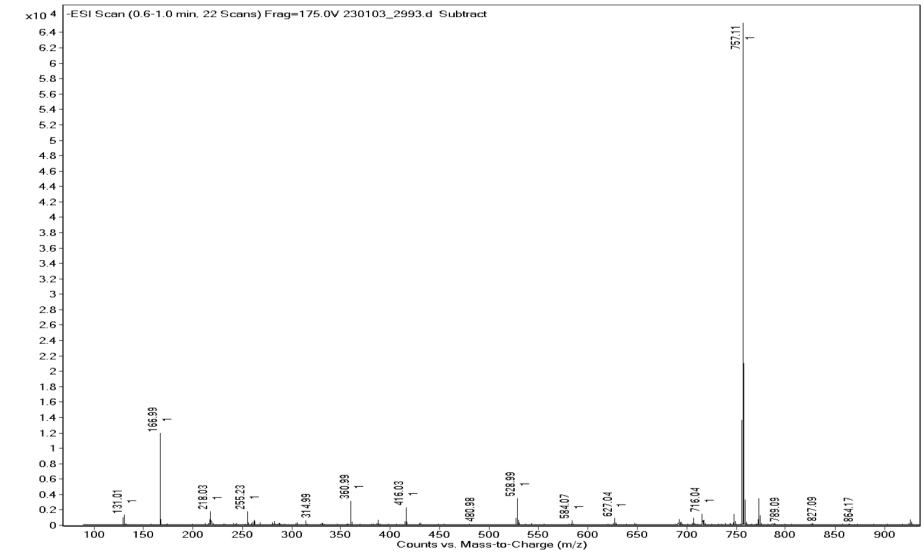


Figure S34: $^{31}P\{^{1}H\}$ NMR spectrum of **6** (chloroform-*d*, 162 MHz)



ESI Mass Spectrum

Sample Name	WK-05-116	**Data File**	230103_2993.d	**Acq Method**	HRMS.m
DA Method	AIMS_Accurate_Mass.m	**Instrument**	Agilent 6538 UHD	**Acq Date, Time**	03/01/2023 12:01:19 PM
Comment	ESI-				

ESI-MS Report
Molecular Formula Generation (MFG)

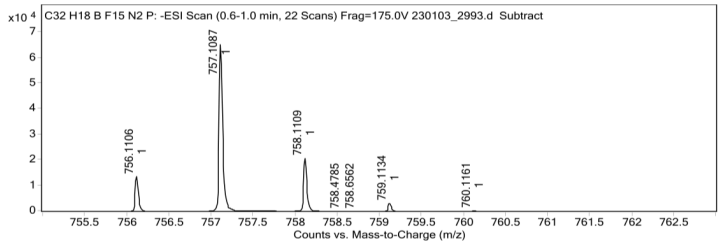
Sample Name	WK-05-116	**Data File**	230103_2993.d
Acq Method	HRMS.m	**DA Method**	AIMS_Accurate_Mass.m
Instrument	Agilent 6538 UHD	**Acq Date, Time**	03/01/2023 12:01:19 PM
Comment	ESI-		

Target Ion Species

Ion Species	*m/z*	*Ionic Formula*
M-	756.1106	C32 H18 B F15 N2 P

MFG Calculator Results

Target m/z	*Ionic Formula*	*Calc m/z*	*+/- (mDa)*	*+/- (ppm)*	*DBE*	*MFG Score*
756.1106	C32 H18 B F15 N2 P	756.1103	0.3	0.4	18.5	97.28
756.1106	C20 H22 B F15 N4 O7 P	756.1121	-1.5	-2.0	5.5	86.97
756.1106	C21 H18 B F15 N8 O3 P	756.1135	-2.9	-3.8	10.5	86.97
756.1106	C19 H26 B F15 O11 P	756.1108	-0.2	-0.3	0.5	83.03
756.1106	C16 H18 B F15 N10 O5 P	756.1095	1.1	1.5	6.5	76.39
756.1106	C25 H22 B F15 N2 O5 P	756.1162	-5.6	-7.4	9.5	74.01
756.1106	C15 H22 B F15 N6 O9 P	756.1081	2.5	3.3	1.5	65.94

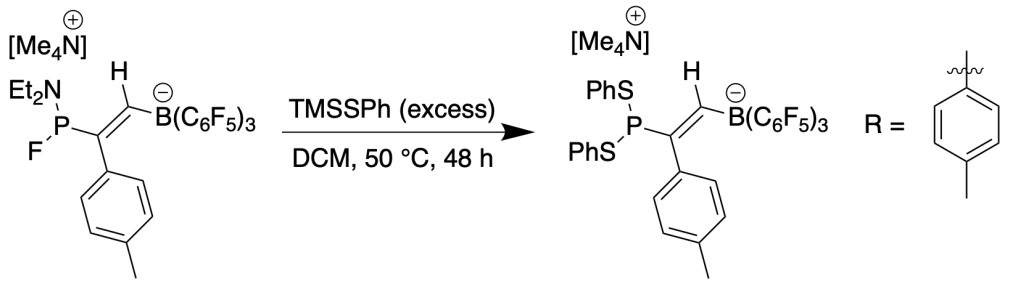


Predicted Isotope Match Table

Isotope	*m/z*	*Calc m/z*	Diff (mDa)	Abund (%)	Calc Abund (%)	+/-
1	756.1106	756.1103	0.3	20.8	22.8	2.0
2	757.1087	757.1072	1.5	100.0	100.0	0.0
3	758.1109	758.1102	0.7	32.0	34.1	2.1
4	759.1134	759.1133	0.1	5.1	5.8	0.7

Figure S35: ESI-MS(-) of $C_{32}H_{18}BF_{15}N_2P^-$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.7 Synthesis of 7



Scheme S7: Synthesis of **7**

In the glovebox, compound **3** (0.0160 g, 0.019 mmol, 1.0 eq) was dissolved in DCM (0.7 mL), and TMSSPh (9.2 μL, 0.049 mmol, 2.5 eq) was added to the solution. The mixture was heated at 50 °C for 48 hours. Solvent was removed under vacuum to afford the product as a pale yellow oil (0.0171 g, 0.018 mmol, 93% yield).

- ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.88 (d, $^{3}J_{PH}$ = 31.0 Hz, 1H, -PC=C*H*), 7.39–7.36 (m, 4H, -S*Ph*), 7.18–7.16 (m, 6H, -S*Ph*), 6.83 (s, 4H, Ar-*H*), 2.95 (s, 12H, -N*Me*$_4$), 2.23 (s, 3H, -ArC*H*$_3$).
- ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.19 (br d, $^{1}J_{CF}$ = 240.0 Hz, *o*-*C*$_6$F$_5$), 138.18 (br d, $^{1}J_{CF}$ = 256.1 Hz, *m*-*C*$_6$F$_5$), 137.72 (s), 136.48 (br d, $^{1}J_{CF}$ = 241.7 Hz, *p*-*C*$_6$F$_5$), 135.57 (s), 135.33 (s), 135.20 (s), 132.60 (s), 132.54 (s), 129.04 (s), 128.44 (d, J = 2.1 Hz), 127.60 (s), 127.12 (d, J = 1.8 Hz), 56.24 (m, N(*C*H$_3$)$_4$), 21.05 (s, Ar-*C*H$_3$).
- ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.1 (s, -*B*(C$_6$F$_5$)$_3$).
- ^{19}F NMR (chloroform-*d*, 377 MHz): δ -131.22 (dd, $^{3}J_{FF}$ = 25.2 Hz, $^{4}J_{FF}$ = 8.0 Hz, 6F, *o*-C$_6$*F*$_5$), -162.96 ($^{3}J_{FF}$ = 20.6 Hz, 3F, *p*-C$_6$*F*$_5$), -166.95 (m, 6F, *m*-C$_6$*F*$_5$).
- ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 102.8 (s).
- MS (ESI) [M]$^{-}$ $C_{39}H_{18}BF_{15}PS_2^{-}$ calc. 877.0441 *m/z*, found 877.0457 *m/z*.
- Elem. Anal. Found (Calc'd) for $C_{43}H_{30}BF_{15}NPS_2$: C 54.38 (54.27), H 3.24 (3.18), N 1.63 (1.47)

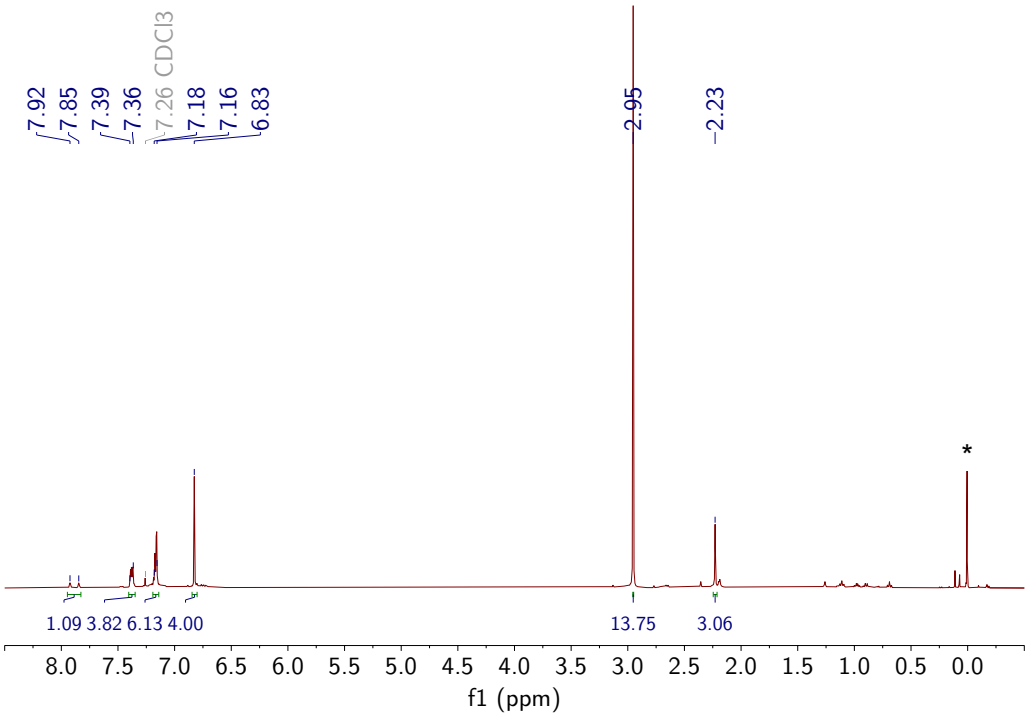


Figure S36: ^{1}H NMR spectrum of **7**. * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

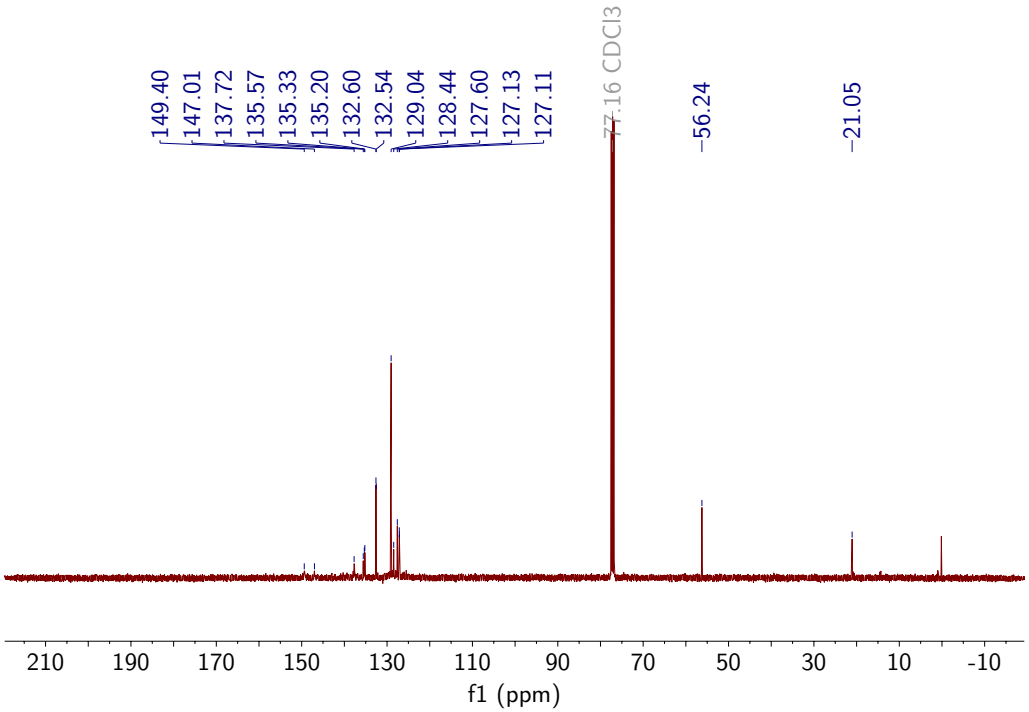


Figure S37: ^{13}C NMR spectrum of **7** (chloroform-*d*, 101 MHz)

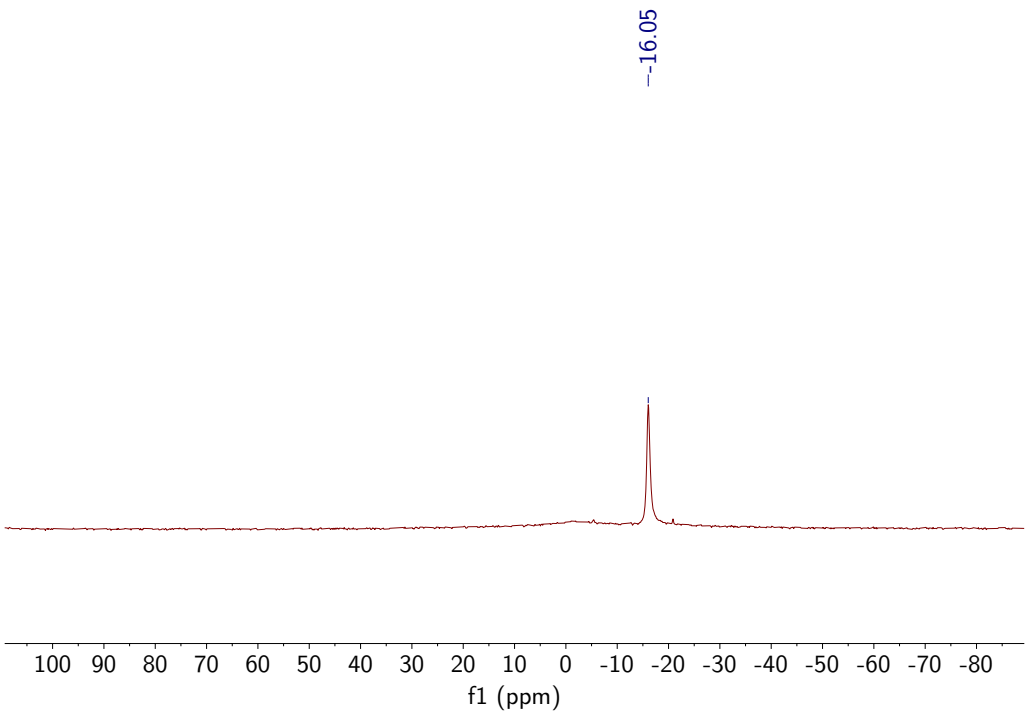


Figure S38: ^{11}B NMR spectrum of **7** (chloroform-*d*, 128 MHz)

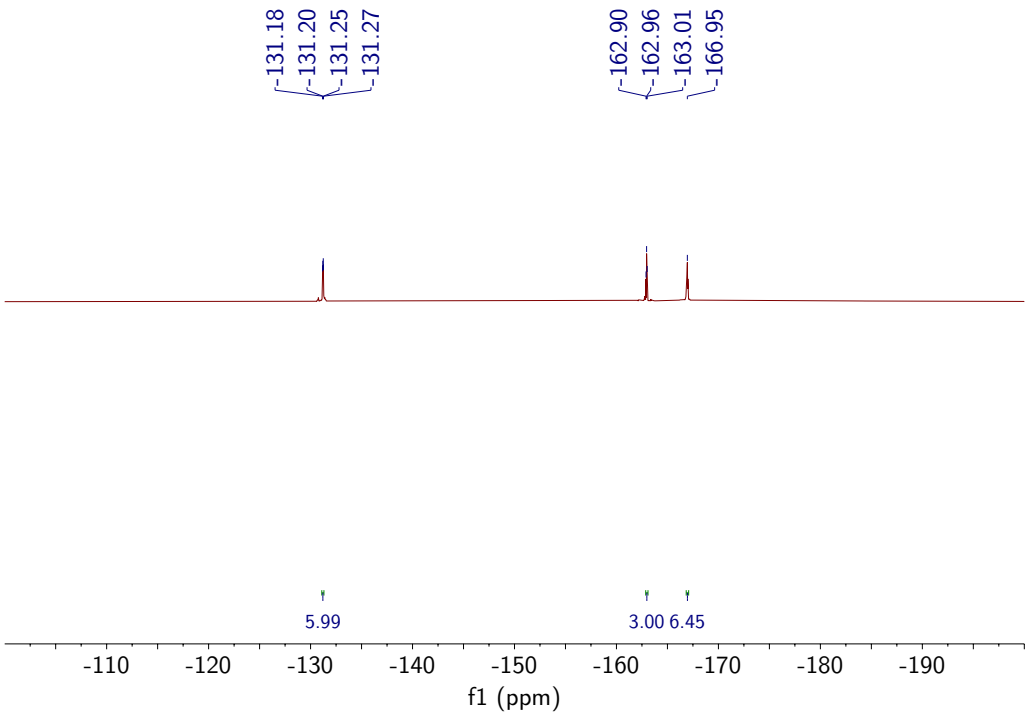


Figure S39: ^{19}F NMR spectrum of **7** (chloroform-*d*, 377 MHz)

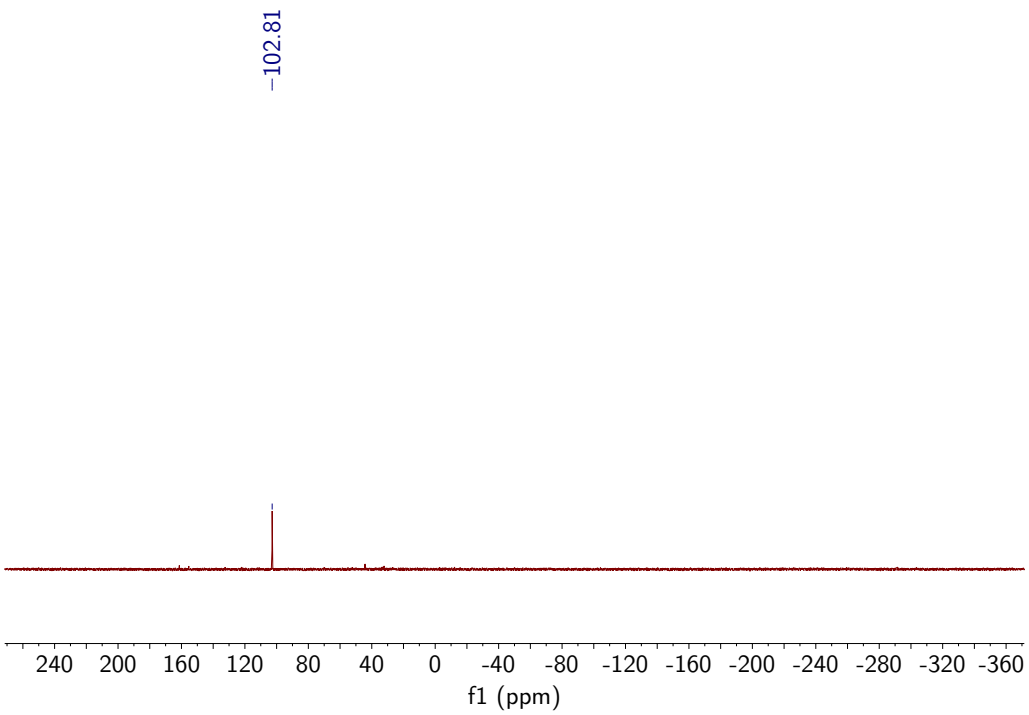


Figure S40: $^{31}P\{^{1}H\}$ NMR spectrum of **7** (chloroform-*d*, 162 MHz)

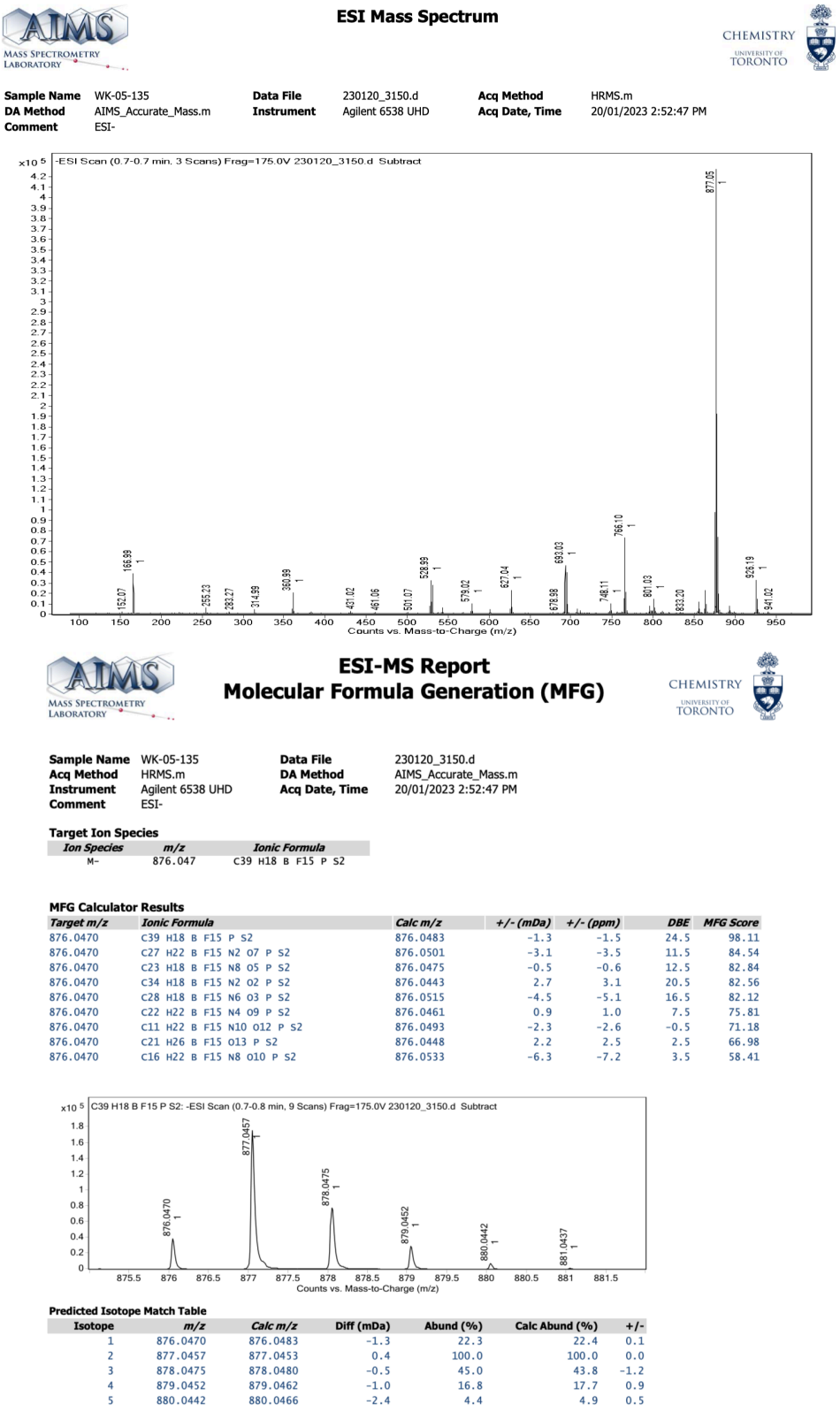
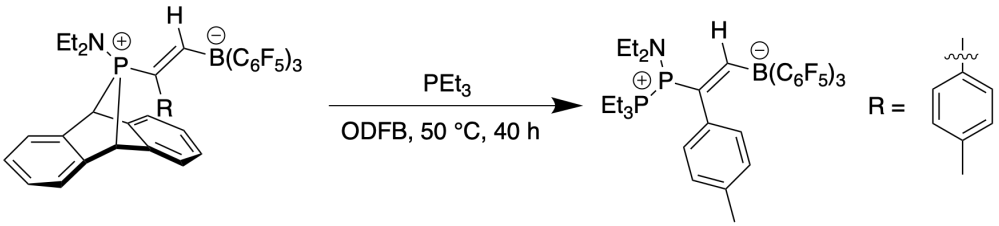


Figure S41: ESI-MS(-) of $C_{39}H_{18}BF_{15}PS_2^-$ with zoomed in portion of the molecular ion, and predicted isotope pattern

2.8 Synthesis of 8



Scheme S8: Synthesis of **8**

In the glovebox, compound **2** (0.0457 g, 0.050 mmol, 1.0 eq) was dissolved in ODFB (1.0 mL), and PEt_3 (15 μL, 0.100 mmol, 2.0 eq) was added via a microsyringe. The orange solution was heated at 50 °C for 40 hours. The solution was then filtered over an activated charcoal plug to remove the anthracene by-product. The crude material was dissolved in DCM (0.3 mL), layered with hexanes (2 mL), and stored in a -20 °C freezer overnight. The supernatant was decanted, and the product was obtained as colourless solids after drying under vacuum (0.0251 g, 0.030 mmol, 59% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 7.36 (dd, $^{3}J_{PH}$ = 15.0, $^{4}J_{PH}$ = 4.9 Hz, 1H, -PC=C*H*), 6.84 (d, J = 2.6 Hz, 4H, Ar-*H*), 3.32–3.06 (m, 4H, -N(CH_2CH$_3$)$_2$), 2.23 (s, 3H, -ArCH_3), 1.89–1.67 (m, 6H, -P(CH_2CH$_3$)$_3$), 1.18 (dt, $^{3}J_{PH}$ = 16.6, $^{4}J_{PH}$ = 7.7 Hz, 9H, -P(CH$_2$CH_3)$_3$), 1.06 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, -N(CH$_2$CH_3)$_2$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 148.07 (br d, $^{1}J_{CF}$ = 240.3 Hz, *o*-C_6F$_5$), 138.28 (br d, $^{1}J_{CF}$ = 245.0 Hz, *m*-C_6F$_5$), 137.74 (d, J = 2.6 Hz), 136.52 (br d, $^{1}J_{CF}$ = 241.6 Hz, *p*-C_6F$_5$), 128.89 (s), 128.53 (s), 128.42 (d, J = 7.0 Hz), 46.32 (dd, $^{2}J_{CP}$ = 14.7 Hz, $^{3}J_{CP}$ = 2.9 Hz, -N(*C*H$_2$CH$_3$)$_2$), 21.00 (s, Ar-*C*H$_3$), 14.52 (t, $^{3}J_{CP}$ = 2.9 Hz, -N(CH$_2$*C*H$_3$)$_2$), 13.96 (dd, $^{1}J_{CP}$ = 29.3 Hz, $^{2}J_{CP}$ = 5.5 Hz, -P(*C*H$_2$CH$_3$)$_3$), 7.16 (dd, $^{2}J_{CP}$ = 6.6 Hz, $^{3}J_{CP}$ = 2.9 Hz, -P(CH$_2$*C*H$_3$)$_3$), 0.14 (s, −Si(*C*H$_3$)$_3$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -16.3 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -131.76 (dd, $^{3}J_{FF}$ = 25.2 Hz, $^{4}J_{FF}$ = 8.0 Hz, 6F, *o*-C$_6$*F*$_5$), -162.85 ($^{3}J_{FF}$ = 20.3 Hz, 3F, *p*-C$_6$*F*$_5$), -166.85 (m, 6F, *m*-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 78.7 (d, $^{1}J_{PP}$ = 443.1 Hz, -*P*NEt$_2$), 18.8 (d, $^{1}J_{PP}$ = 443.1 Hz, *P*Et$_3$).

• The molecular ion peak was not observed for this molecule.

• Elem. Anal. Found (Calc'd) for $C_{37}H_{33}BF_{15}NP_2$: C 51.76 (52.32), H 3.99 (3.92), N 1.41 (1.65)

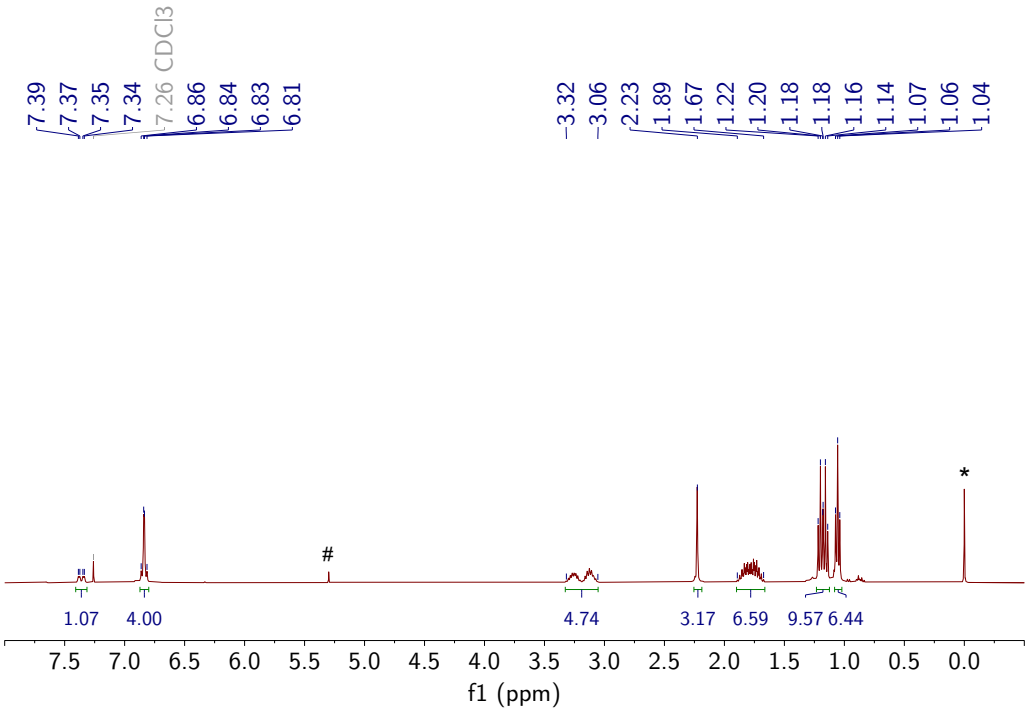


Figure S42: ^{1}H NMR spectrum of **8** with residual DCM (denoted as #). * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

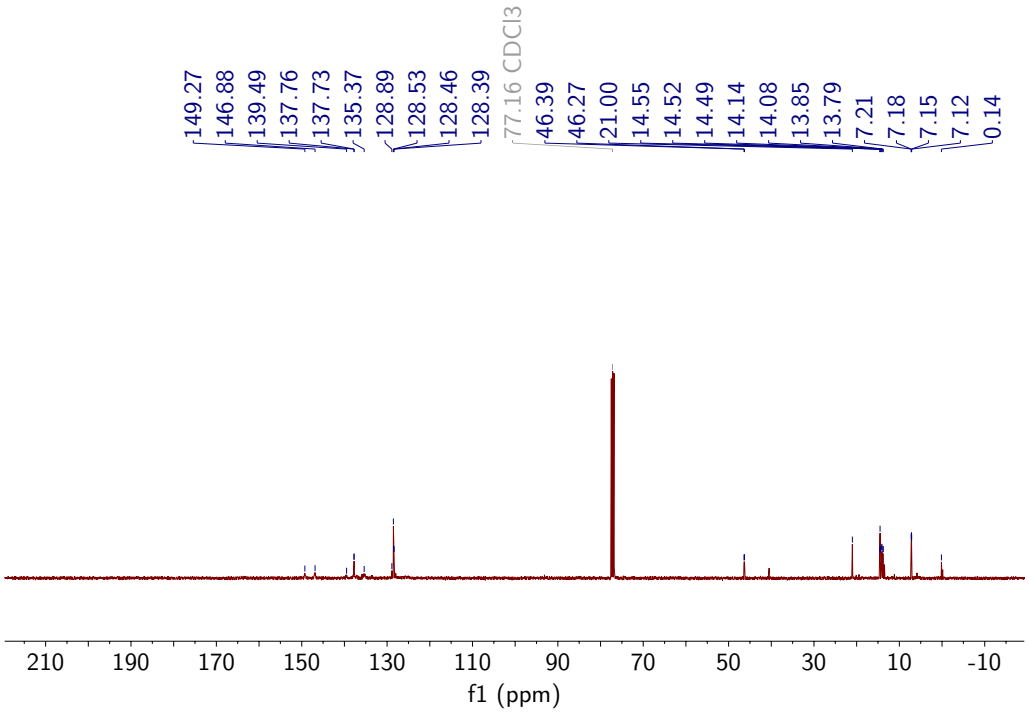


Figure S43: ^{13}C NMR spectrum of **8** (chloroform-*d*, 101 MHz)

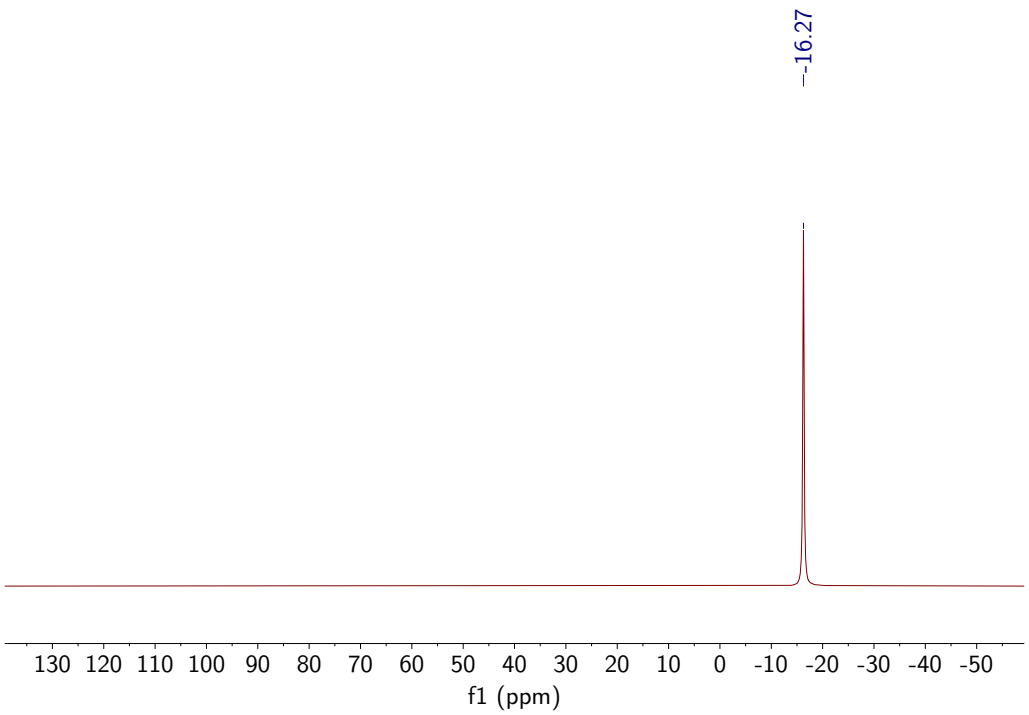


Figure S44: ^{11}B NMR spectrum of **8** (chloroform-*d*, 128 MHz)

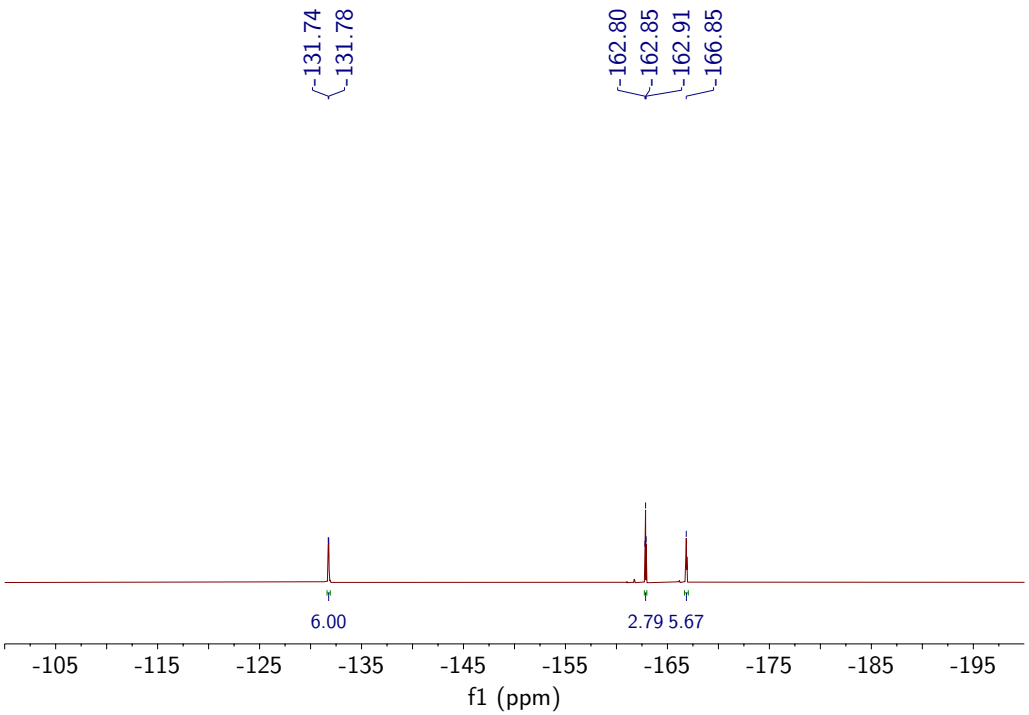


Figure S45: ^{19}F NMR spectrum of **8** (chloroform-*d*, 377 MHz)

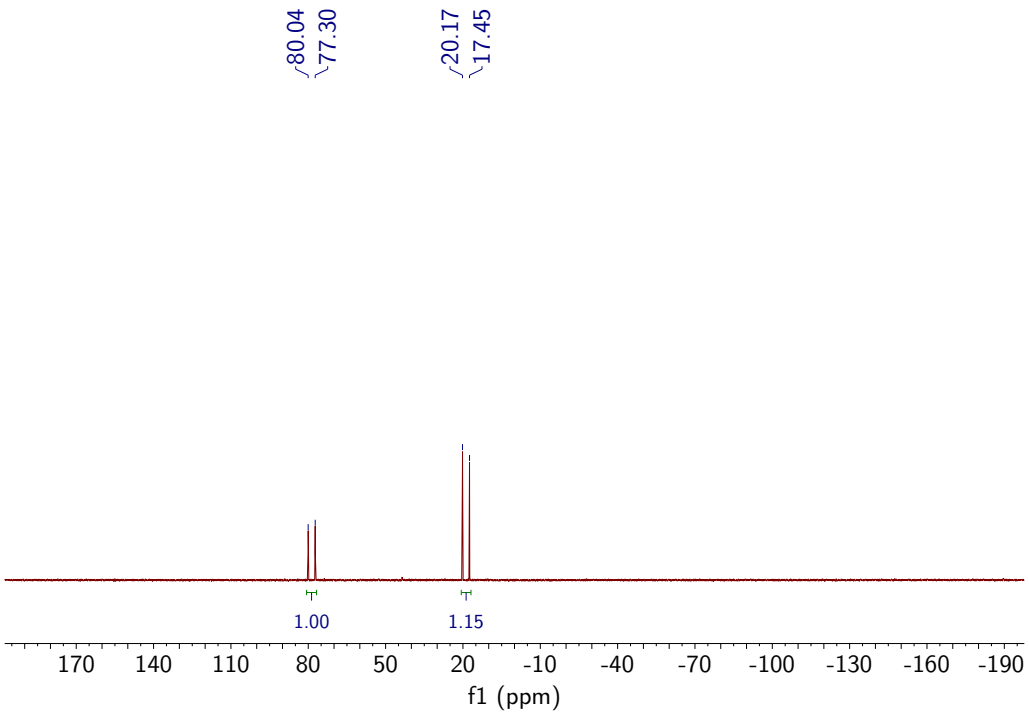


Figure S46: $^{31}P\{^{1}H\}$ NMR spectrum of **8** (chloroform-*d*, 162 MHz)

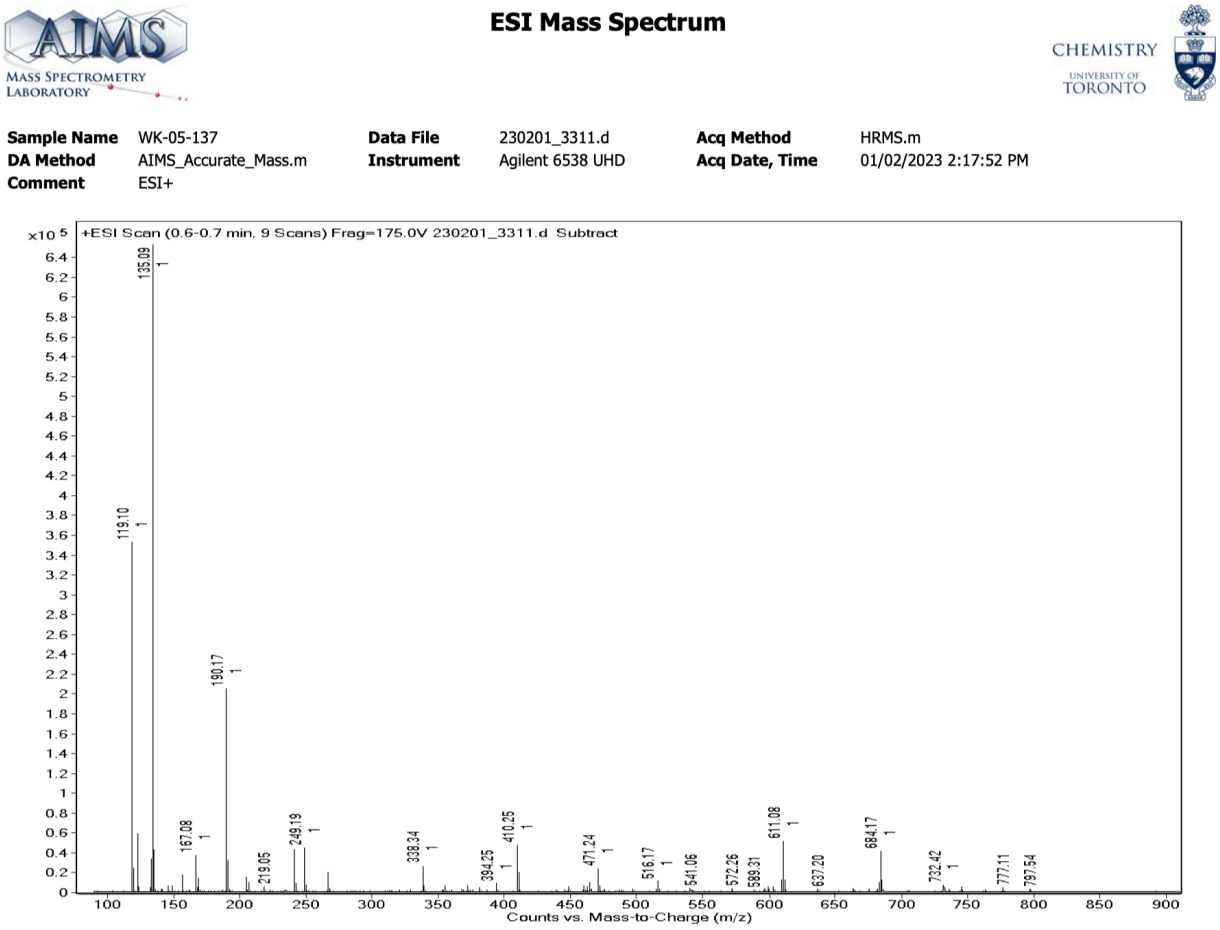
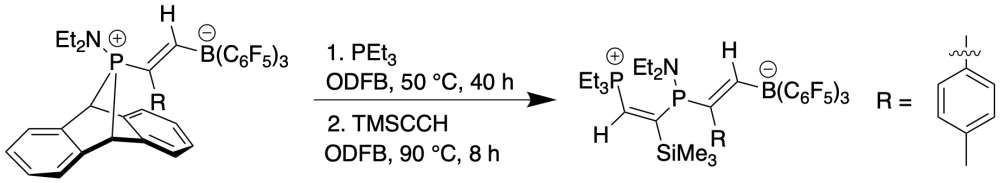


Figure S47: ESI-MS(+) of compound **8**

2.9 Synthesis of 9



Scheme S9: Synthesis of **9**

In the glovebox, compound **2** (0.0758 g, 0.083 mmol, 1.0 eq) was dissolved in ODFB (1.0 mL), and PEt_3 (25 μL, 0.17 mmol, 2.0 eq) was added via a microsyringe. The mixture was heated at 50 °C for 40 hours. Solvent and excess PEt_3 were removed under vacuum, affording crude compound **8**. ODFB (0.7 mL) and excess Me_3SiCCH (0.3 mL) were added, and the solution was heated at 90 °C for 8 hours. The orange solution was then filtered over an activated charcoal plug to remove the anthracene by-product. Solvent and excess

Me_3SiCCH were removed under vacuum. The product was dissolved in DCM (0.3 mL), and layered with hexanes (2.0 mL). The solution was placed in a -20 °C freezer overnight, after the solution separated into a dark orange oil and a light orange supernatant. The supernatant was decanted, and the orange oil was dried under vacuum. The product was obtained as an orange powder (0.0361 g, 0.038 mmol, 46% yield).

• ^{1}H NMR (chloroform-*d*, 400 MHz): δ 6.94 (dd, $^3J_{HH}$ = 8.1, $^4J_{PH}$ = 1.8 Hz, 2H, Ar-*H*), 6.77 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-*H*), 6.61 (d, $^3J_{PH}$ = 15.0 Hz, 1H, -PC=C*H*), 6.35 (dd, $^2J_{PH}$ = 46.2 Hz, $^3J_{PH}$ = 32.9 Hz, 1H, Et_3P-C*H*), 2.95–2.80 (m, 4H, -N(CH_2CH$_3$)$_2$), 2.57–2.46 (m, 3H, -P(CH_2CH$_3$)$_3$), 2.20 (s, 3H, Ar-CH_3), 2.14–2.03 (m, 3H, -P(CH_2CH$_3$)$_3$), 1.15 (dt, $^3J_{PH}$ = 18.6, $^4J_{PH}$ = 7.6 Hz, 9H, -P(CH$_2$CH_3)$_3$), 0.65 (t, $^3J_{HH}$ = 7.1 Hz, 6H, -N(CH$_2$CH_3)$_2$), 0.32 (s, 9H, -Si(CH_3)$_3$).

• ^{13}C NMR (chloroform-*d*, 101 MHz): δ 194.10 (dd, $^1J_{CP}$ = 49.9 Hz, ^2J_CP = 4.8 Hz), 148.14 (br d, $^1J_{CF}$ = 240.1 Hz, *o*-C_6F_5), 140.75 (s), 138.47 (s), 138.21 (s), 138.08 (br d, $^1J_{CF}$ = 252.2 Hz, *m*-C_6F_5), 136.48 (br d, $^1J_{CF}$ = 252.2 Hz, *p*-C_6F_5), 135.72 (d, J = 2.6 Hz), 128.45 (d, J = 8.1 Hz), 127.53 (s), 123.86 (dd, J = 67.3, 42.4 Hz), 45.23 (d, $^2J_{CP}$ = 13.6 Hz, -N(*C*H$_2$CH$_3$)$_2$), 20.96 (s, Ar-*C*H$_3$), 15.75 (dd, $^1J_{CP}$ = 49.2 Hz, $^2J_{CP}$ = 13.9 Hz, -P(*C*H$_2$CH$_3$)$_3$), 14.36 (d, $^3J_{CP}$ = 2.2 Hz, -N(CH$_2$*C*H$_3$)$_2$), 5.94 (dd, $^2J_{CP}$ = 5.5 Hz, $^3J_{CP}$ = 1.8 Hz, -P(CH$_2$*C*H$_3$)$_3$), 0.17 (s, −Si(*C*H$_3$)$_3$).

• ^{11}B NMR (chloroform-*d*, 128 MHz): δ -15.7 (s, -*B*(C$_6$F$_5$)$_3$).

• ^{19}F NMR (chloroform-*d*, 377 MHz): δ -130.87 (dd, $^3J_{FF}$ = 25.2 Hz, $^4J_{FF}$ = 8.0 Hz, 6F, *o*-C$_6$*F*$_5$), -163.28 (t, $^3J_{FF}$ = 20.6 Hz, 3F, *p*-C$_6$*F*$_5$), -167.03 (m, 6F, *m*-C$_6$*F*$_5$).

• ^{31}P{^{1}H} NMR (chloroform-*d*, 162 MHz): δ 82.9 (d, $^3J_{PP}$ = 26.6 Hz, -*P*NEt$_2$), 24.9 (d, $^3J_{PP}$ = 26.6 Hz, *P*Et$_3$).

• MS (ESI) [M+H]$^+$ $C_{42}H_{44}BF_{15}NP_2Si^+$ calc. 948.2571 *m/z*, found 948.2585 *m/z*.

• Elem. Anal. Found (Calc'd) for $C_{42}H_{43}BF_{15}NP_2Si$: C 53.41 (53.23), H 4.48 (4.57), N 1.39 (1.48)

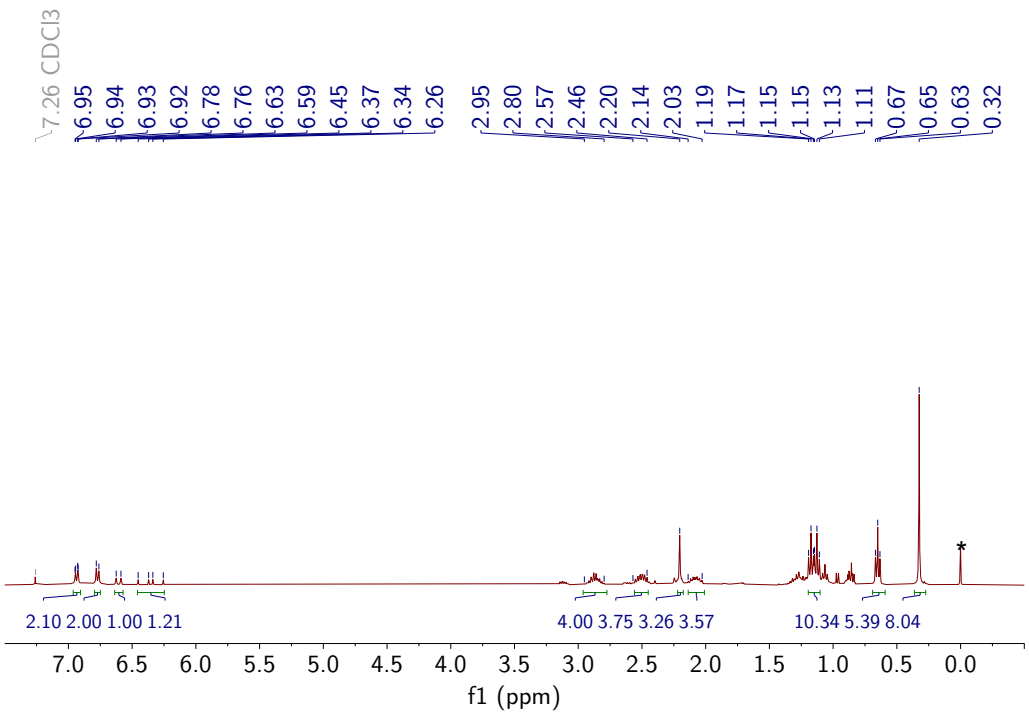


Figure S48: ^{1}H NMR spectrum of **9**. * indicates $SiMe_4$ that is present in the NMR solvent. (chloroform-*d*, 400 MHz)

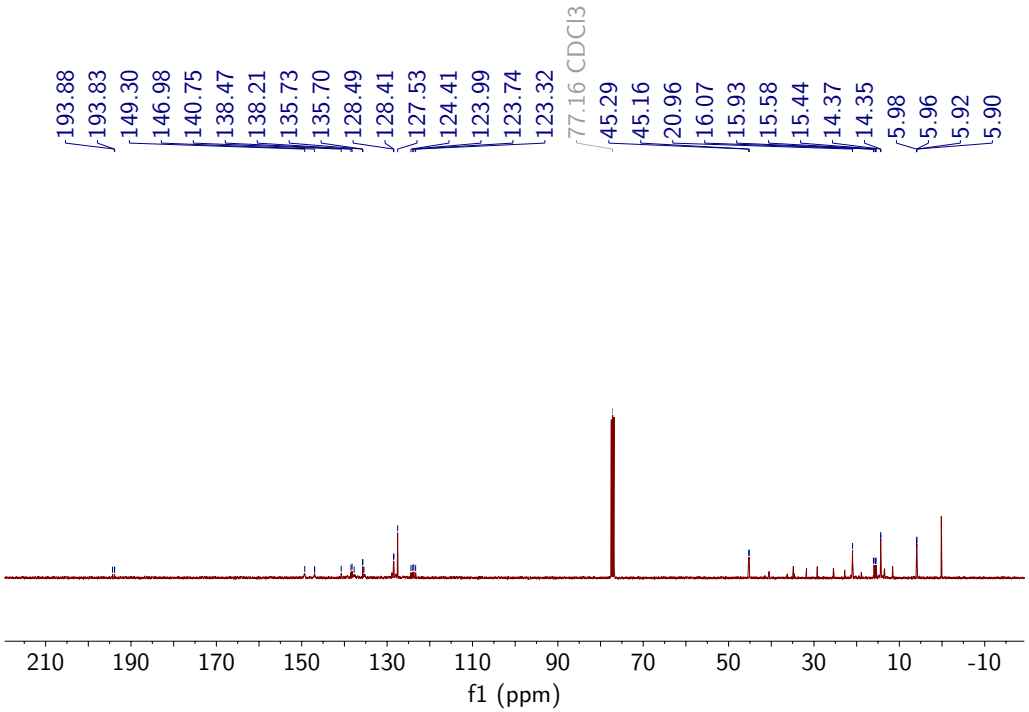


Figure S49: ^{13}C NMR spectrum of **9** (chloroform-*d*, 101 MHz)

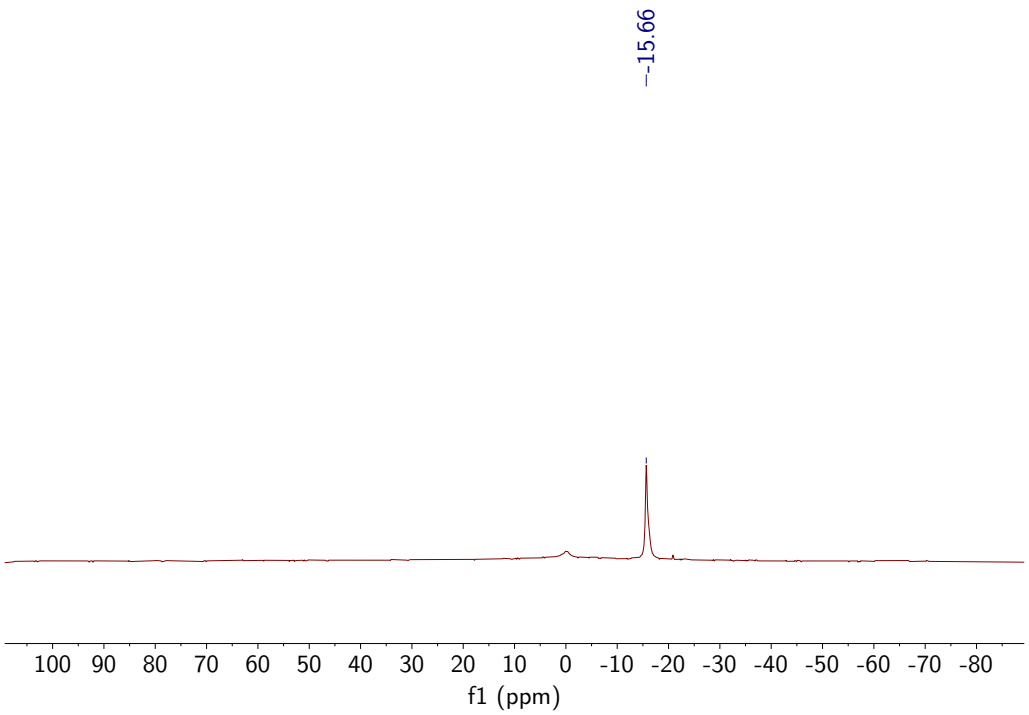


Figure S50: ^{11}B NMR spectrum of **9** (chloroform-*d*, 128 MHz)

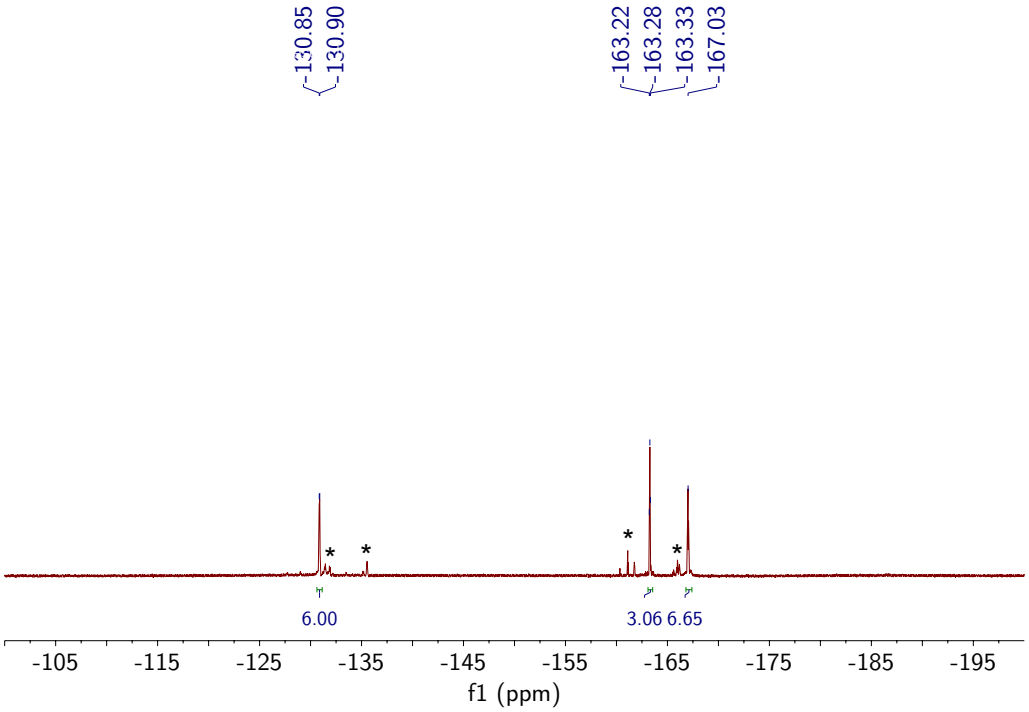


Figure S51: ^{19}F NMR spectrum of **9**. Minor unidentifiable impurities have been labelled with *s. (chloroform-*d*, 377 MHz)

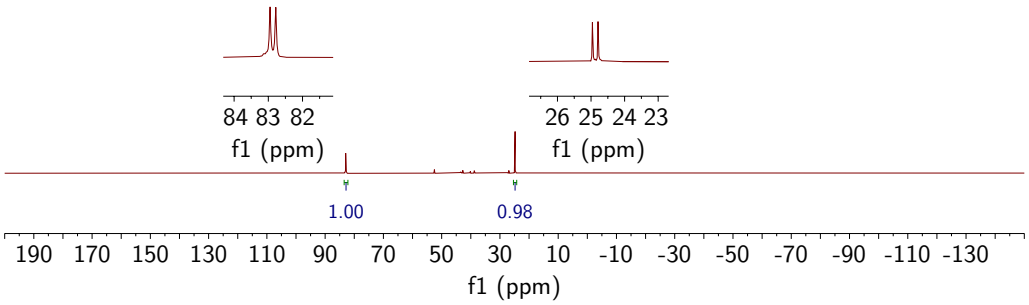


Figure S52: $^{31}P\{^{1}H\}$ NMR spectrum of **9** (chloroform-*d*, 162 MHz)

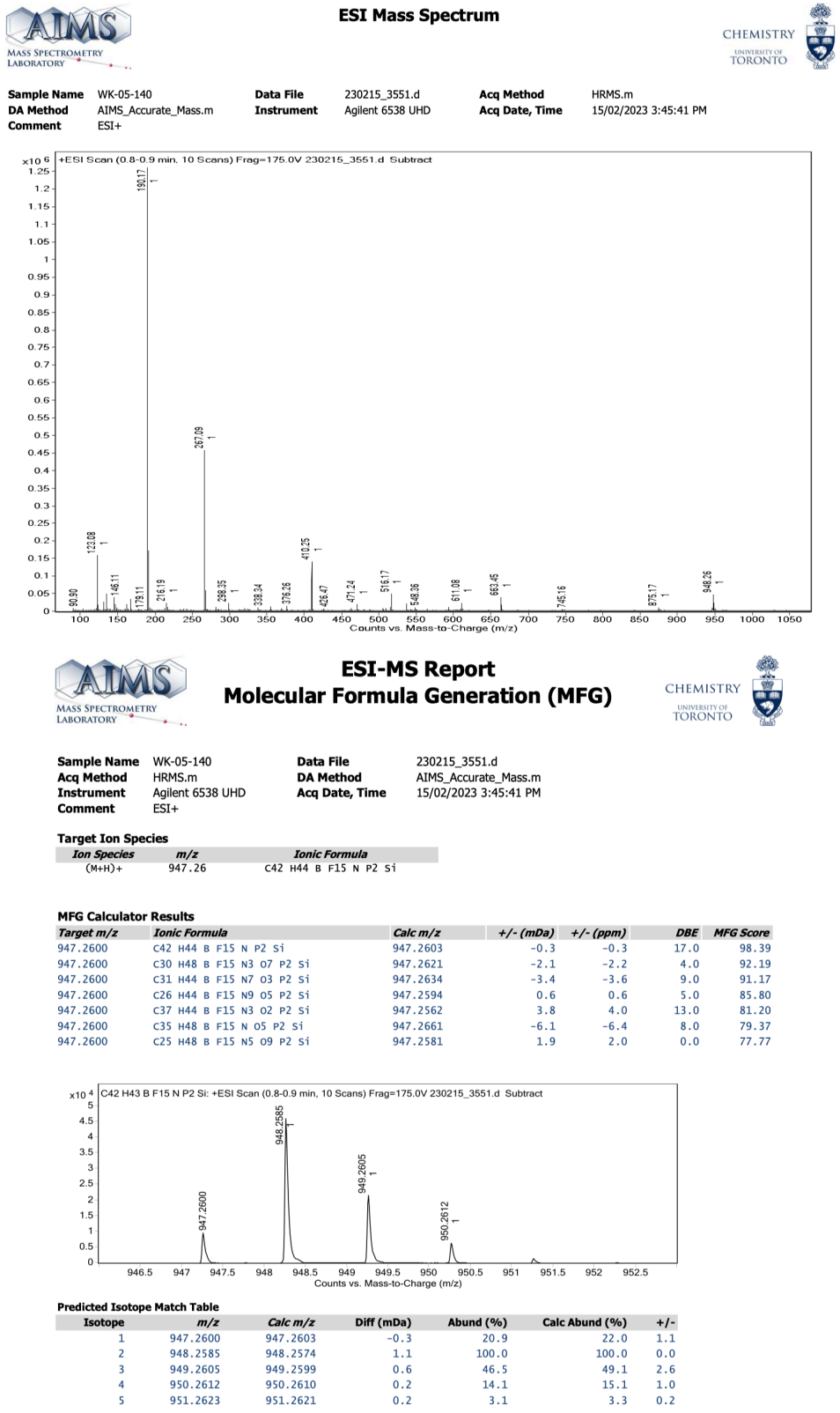


Figure S53: ESI-MS(+) of $C_{42}H_{44}BF_{15}NP_2Si^+$ with zoomed in portion of the molecular ion, and predicted isotope pattern

3 X-ray Diffraction Studies

Crystals were coated in Paratone-N oil in an N_2 filled glovebox, brought out of the glovebox, mounted on a MiTegen Micromount, and placed under a cold N_2 stream to maintain a dry, O_2-free environment for each crystal during data collection. All data were collected on a Bruker Kappa Apex II diffractometer using a graphite monochromator with Mo κ_α radiation (λ = 0.7103 Å). Data were collected at 150 K for all crystals. A semi-empirical absorption correction was applied to the diffraction data using SADABS.[4] The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[5,6] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Descriptions of the individual refinements follow below and details of the data quality and a summary of the residual values of the refinements for all structures are given. Further details can be found in the form of .cif files available from the CCDC.

• Crystals of **1** were grown from slow evaporation of a saturated toluene solution.

• Crystals of **2** were grown from slow evaporation of a saturated pentane solution.

• Crystals of **8** were grown from layering a saturated benzene solution with hexane and placing the vial in a -20 °C freezer overnight.

• Crystals of **9** were grown slow evaporation of a saturated pentane solution.

4 References

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