

Transition Metal-Free Stereospecific Access to (*E*)-(1-fluoro-2-arylvinyl)phosphine Borane Complexes

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Supporting information

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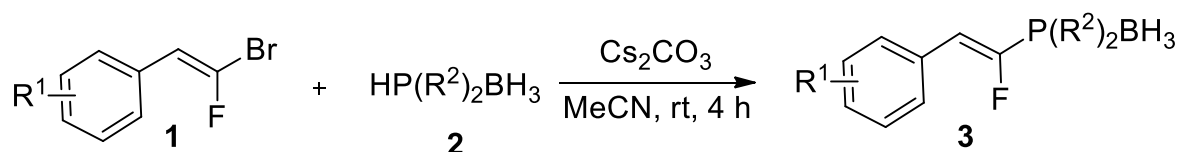
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1. General information

Commercially available reagents were used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich. Chromatography was carried out using neutral alumina 90 (70-230 mesh); the following solvents were used: DCM = dichloromethane, MeCN = acetonitrile. Melting points (mp) were determined on a Fisher Scientific hot stage melting point apparatus and are uncorrected. ^1H , ^{11}B , ^{13}C , ^{19}F and ^{31}P NMR spectra were recorded using a Bruker AC 400 spectrometer operating at 400 MHz (^1H), 160 MHz (^{11}B), 100 MHz (^{13}C), 376 MHz (^{19}F), 162 MHz (^{31}P), or a Bruker AC 300 spectrometer operating at 300 MHz (^1H), 120 MHz (^{11}B), 75 MHz (^{13}C), 282 MHz (^{19}F), 122 MHz (^{31}P), respectively. The chemical shifts (δ) were calibrated on residual proton and carbon resonances of CDCl_3 (^1H , 7.26 ppm and ^{13}C , 77.2 ppm), on boron resonance of $\text{BF}_3\text{-Et}_2\text{O}$ (^{11}B , 0.0 ppm), on fluorine resonance of CFCl_3 (^{19}F , 0.0 ppm) and on phosphorus resonance of PPh_3 (^{31}P , 0.0 ppm). In the ^{13}C NMR spectra, signals corresponding to CH, CH_2 , or CH_3 groups were assigned from DEPT-135. The multiplicity signals were indicated with the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and b (broad) and the combinations thereof. Proton decoupled ^{13}C NMR spectra were indicated with the $\{^1\text{H}\}$ label. IR spectra were recorded on Perkin Elmer Spectrum 100 FT IR spectrometer. High Resolution Mass Spectra (HRMS) were recorded on a JEOL AccuTof 4G spectrometer coupled to a GC HP Agilent 7890 in ElectroSpray Ionisation mode (ESI) or Field Desorption (FD). EPR-ST experiments were carried out using an X-Band spectrometer (MS 400 Magnettech). The ESR spectra simulations were carried out using the WINSIM software. *Gem*-Bromofluoroalkenes were prepared according to our previous report (X. Lei, G. Dutheuil, X. Pannecoucke, J.-C. Quirion *Org. Lett.* **2004**, *6*, 2101).

2. General procedure for the coupling reaction

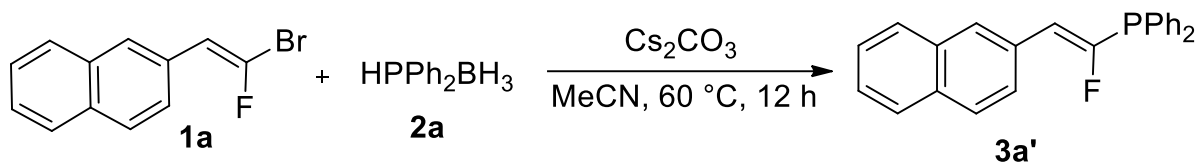
A. General coupling reaction



In a dry vial under argon atmosphere was added *gem*-bromofluoroalkene **1** (1 equiv), phosphine borane **2** (1.1 equiv), and Cs₂CO₃ (1.2 equiv). The vial was then filled with dry and degassed

MeCN (5 mL/mmol), then was stirred for 4 h at room temperature. The crude was then chromatographed on neutral alumina to afford the pure product **3**.

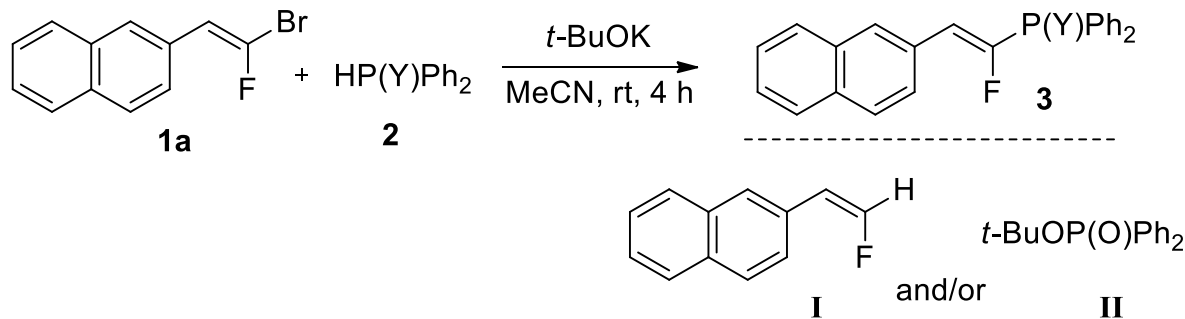
B. One pot coupling/deboration sequence



In a dry vial under argon atmosphere was added *gem*-bromofluoroalkene **1a** (0.20 mmol, 50 mg, 1 equiv), phosphine borane **2a** (0.22 mmol, 44 mg, 1.1 equiv), and Cs₂CO₃ (0.24 mmol, 78 mg, 1.2 equiv). The vial was then filled with dry and degassed MeCN (1 mL, 5 mL/mmol), then was stirred for 12 h at 60 °C. The crude was then chromatographed on silica gel to afford the pure product **3a'** (30 mg, 43%).

3. Optimization of the reaction and control experiments

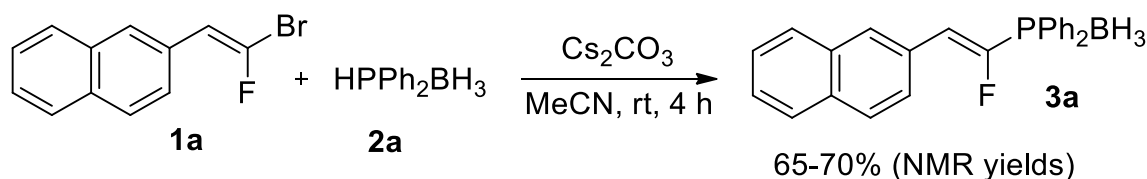
A. Variation of the phosphine



Entry	Y	Yield ^a	Notes
1	BH ₃	21% (3a)	-
2	O	0%	Products I and II
3	-	0%	Product I

^a Isolated yields.

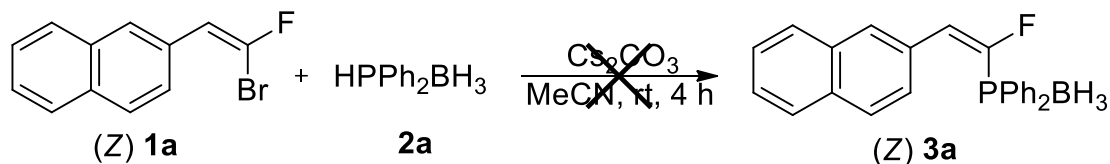
B. Optimization of the purification conditions for the phosphine borane



Entry	Purification method	Yield ^a	Notes
1	Filtration ^b	n.d.	No separation of 3a and HPPH ₂ BH ₃
2	Silica gel pad ^b	n.d.	-
3	Silica gel column ^b	25%	-
4	Dehydrated silica gel column ^b	14%	-
5	Basic alumina column ^b	32%	-
6	Basic alumina pad ^b	45%	-
7	Neutral alumina pad ^b	49%	Few by-products
8	Neutral alumina column ^c	63%	-
9	Neutral alumina column ^c	n.d.	Degradation

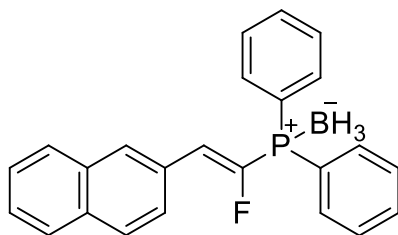
^a Isolated yields. ^b With CH₂Cl₂ stabilized with amylene. ^c With CH₂Cl₂ stabilized with ethanol. n.d.: not determined.

C. Reaction with (*Z*) *gem*-bromofluoroalkènes

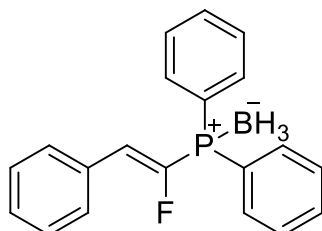


In a dry vial under argon atmosphere was added *gem*-bromofluoroalkene (*Z*) **1a** (1 equiv), phosphine borane **2** (1.1 equiv), and Cs₂CO₃ (1.2 equiv). The vial was then filled with dry and degassed MeCN (5 mL/mmol), then was stirred for 4 h at room temperature. Degradation of starting material (*Z*) **1a** was observed by ¹⁹F NMR, probably because of the basic conditions, according to previous report: X. Lei, G. Dutheuil, X. Pannecoucke, J.-C. Quirion *Org. Lett.* **2004**, *6*, 2101.

4. Experimental data for compounds 3a-3m

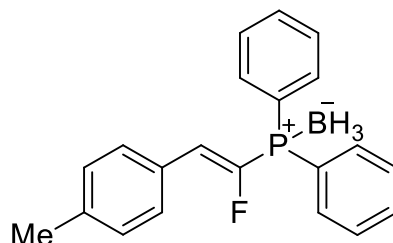


(E)-((1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphonio)trihydroborate 3a: (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (0.2 mmol, 50 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 63% yield (46 mg) as a colourless solid. mp 173-175 °C. IR: 3058, 2923, 2849, 2392, 2348, 1435, 1054, 910, 821 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 1H), 7.86-7.74 (m, 6H), 7.66-7.40 (m, 10H), 7.04 (dd, ³J_{H-F} = 42.7, ³J_{H-P} = 8.9 Hz, 1H), 1.7-0.7 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 153.1 (dd, ¹J_{C-F} = 295.4, ¹J_{C-P} = 62.9 Hz, Cq), 133.6 (d, *J* = 1.7 Hz, Cq), 133.3 (s, Cq), 133.2 (d, ²J_{C-P} = 10.0 Hz, 4xCH), 132.0 (d, ⁴J_{C-P} = 2.4 Hz, 2xCH), 130.4 (d, *J* = 7.7 Hz, CH), 129.3 (dd, ³J = 10.9, 2.4 Hz, Cq), 129.1 (d, ³J_{C-P} = 10.6 Hz, 4xCH), 128.7 (s, CH), 128.5 (s, CH), 127.8 (s, CH), 127.3 (s, CH), 126.9 (d, *J* = 7.9 Hz, CH), 126.72 (d, ¹J_{C-P} = 60.9 Hz, 2xCq), 126.68 (s, CH), 125.3 (d, ²J = 26.6 Hz, CH). ¹¹B NMR (160 MHz, CDCl₃): δ -38.3 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -114.6 (dd, ³J_{F-H} = 42.7, ²J_{F-P} = 17.5 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 21.1 (m). HRMS (ESI-TOF): calcd for C₂₄H₂₁BFNaP *m/z* 393.1356 [M+Na]⁺, found 393.1345.

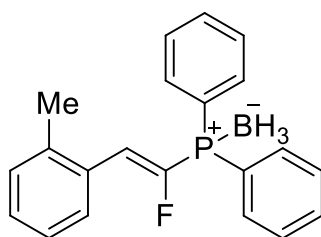


(E)-((1-Fluoro-2-phenylvinyl)diphenylphosphonio)trihydroborate 3b: (*E*)-2-(2-bromo-2-fluorovinyl)benzene (0.2 mmol, 40 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 7/3 to afford the desired compound in 40% yield (25 mg) as a colourless solid.

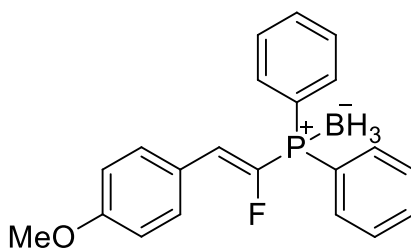
mp 113-115 °C. IR: 3054, 2387, 1485, 1435, 1052, 875, 829 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.77 (dd, *J* = 11.1, 7.6 Hz, 4H), 7.68-7.62 (m, 2H), 7.58-7.45 (m, 6H), 7.43- 7.34 (m, 3H), 6.89 (dd, ³*J*_{H-F} = 42.7, ³*J*_{H-P} = 8.9 Hz, 1H), 1.5-0.7 (bm, 3H). ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 152.9 (dd, ¹*J*_{C-F} = 295.1, ¹*J*_{C-P} = 62.9 Hz, Cq), 133.1 (d, ²*J*_{C-P} = 10.1 Hz, 4xCH), 131.9 (d, ⁴*J*_{C-P} = 2.5 Hz, 2xCH), 131.8 (dd, ³*J* = 11.4, 1.7 Hz, Cq), 130.1 (d, *J* = 7.7 Hz, 2xCH), 129.6 (d, *J* = 2.4 Hz, CH), 129.1 (d, ³*J*_{C-P} = 10.6 Hz, 4xCH), 128.9 (s, 2xCH), 126.7 (d, ¹*J*_{C-P} = 60.9 Hz, 2xCq), 125.2 (d, ²*J* = 26.5 Hz, CH). ¹¹B NMR (120 MHz, CDCl₃): δ -38.2 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -114.7 (dd, ³*J*_{F-H} = 42.7, ²*J*_{F-P} = 17.8 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.1 (m). HRMS (FD-TOF): calcd for C₂₀H₁₆FP *m/z* 306.0973 [M-BH₃]⁺, found 306.0974.



(*E*)-((1-Fluoro-2-(*p*-tolyl)vinyl)diphenylphosphonio)trihydroborate 3c: (*E*)-1-(2-bromo-2-fluorovinyl)-4-methylbenzene (0.20 mmol, 43 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 22% yield (15 mg) as a sticky colourless solid. IR: 2930, 2838, 2388, 1593, 1500, 1291, 1254, 1179, 1107, 1057, 1025, 825, 801 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.74 (dd, *J* = 11.1, 7.4 Hz, 4H), 7.61-7.33 (m, 8H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.84 (dd, ³*J*_{H-F} = 42.9, ³*J*_{H-P} = 8.9 Hz, 1H), 2.36 (s, 3H), 1.4-1.1 (bm, 3H). Selected ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 139.8 (d, *J* = 2.5 Hz, Cq), 133.2 (d, *J* = 10.1 Hz, Cq), 133.0 (d, ²*J*_{C-P} = 10.0 Hz, 4xCH), 131.7 (d, ⁴*J*_{C-P} = 2.5 Hz, 2xCH), 130.0 (d, *J* = 7.6 Hz, 2xCH), 129.4 (s, 2xCH), 128.9 (d, ³*J*_{C-P} = 10.6 Hz, 4xCH), 126.7 (d, ¹*J*_{C-P} = 61.0 Hz, 2xCq), 125.1 (d, ²*J* = 26.7 Hz, CH), 21.5 (s, CH₃). ¹¹B NMR (120 MHz, CDCl₃): δ -37.8 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -116.1 (dd, ³*J*_{F-H} = 43.0, ²*J*_{F-P} = 17.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.1 (m). HRMS (ESI-TOF): calcd for C₂₁H₁₉FP *m/z* 321.1208 [M-BH₃+H]⁺, found 321.1212.

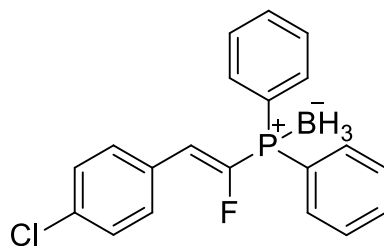


(E)-((1-Fluoro-2-(o-tolyl)vinyl)diphenylphosphonio)trihydroborate 3d: (*E*)-1-(2-bromo-2-fluorovinyl)-2-methylbenzene (0.20 mmol, 43 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 84% yield (56 mg) as a sticky colourless solid. IR: 3058, 2924, 2387, 2340, 1482, 1436, 1107, 1053, 830 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.84-7.75 (m, 5H), 7.64-7.56 (m, 2H), 7.55-7.48 (m, 4H), 7.31-7.25 (m, 3H), 7.17 (dd, ³J_{H-F} = 42.2, ³J_{H-P} = 9.3 Hz, 1H), 2.41 (s, 3H), 1.6-1.2 (bm, 3H). ¹¹B NMR (120 MHz, CDCl₃): δ -38.5 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -116.4 (dd, ³J_{F-H} = 42.2, ²J_{F-P} = 18.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.6 (m). HRMS (ESI-TOF): calcd for C₂₁H₁₉FP *m/z* 321.1208 [M-BH₃+H]⁺, found 321.1209.

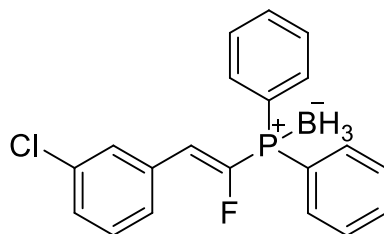


(E)-((2-(4-Methoxyphenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3e: (*E*)-1-(2-bromo-2-fluorovinyl)-4-methoxybenzene (0.2 mmol, 46 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 8/2 to afford the desired compound in 63% yield (46 mg) as a colourless solid. mp 85-87 °C. IR: 3056, 2933, 2837, 2386, 2355, 2342, 1605, 1509, 1436, 1251, 1178, 1055, 1028, 828 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.70-7.54 (m, 4H), 7.53-7.29 (m, 8H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.71 (dd, ³J_{H-F} = 42.3, ³J_{H-P} = 8.5 Hz, 1H), 3.70 (s, 3H), 1.3-0.8 (bm, 3H). ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 160.4 (d, *J* = 3.1 Hz, Cq), 150.9 (dd, ¹J_{C-F} = 291.5, ¹J_{C-P} 64.9 Hz, Cq), 133.0 (d, ²J_{C-P} = 10.0 Hz, 4xCH), 131.7 (m, 4xCH), 128.9 (d, ³J_{C-P} = 10.6 Hz, 4xCH), 126.9 (d, ¹J_{C-P} = 61.2 Hz, 2xCq), 124.8 (d, *J* = 27.1 Hz, CH), 124.5 (dd, *J* = 11.8, 1.5 Hz, Cq), 114.2 (s, 2xCH), 55.3 (s, CH₃). ¹¹B NMR (160 MHz, CDCl₃): δ -38.2 (m). ¹⁹F NMR (376 MHz,

CDCl₃): δ -118.9 (dd, $^3J_{F-H} = 43.3$, $^2J_{F-P} = 18.8$ Hz). ^{31}P NMR (162 MHz, CDCl₃): δ 20.4 (m). HRMS (ESI-TOF): calcd for C₂₁H₁₉FOP m/z 337.1158 [M-BH₃+H]⁺, found 337.1161.

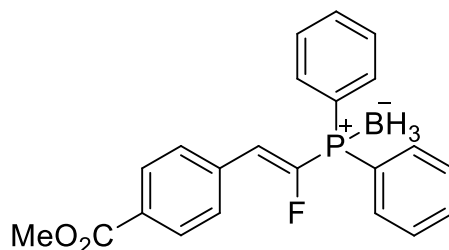


(E)-((2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3f: (*E*)-1-(2-bromo-2-fluorovinyl)-4-chlorobenzene (0.2 mmol, 47 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 9/1 to pentane/DCM 8/2 to afford the desired compound in 64% yield (45 mg) as a colourless solid. mp 119-121 °C. IR: 2376, 1492, 1434, 1108, 1091, 1055, 814 cm⁻¹. ^1H NMR (400 MHz, CDCl₃): δ 7.75 (dd, $J = 11.3$, 7.5 Hz, 4H), 7.59-7.55 (m, 4H), 7.53-7.45 (m, 4H), 7.35 (d, $J = 8.5$ Hz, 2H), 6.84 (dd, $^3J_{H-F} = 42.1$ Hz, $^3J_{H-P} = 8.8$ Hz, 1H), 1.6-0.9 (bm, 3H). ^{13}C NMR { ^1H } (100 MHz, CDCl₃): δ 153.6 (dd, $^1J_{C-F} = 296.2$, $^1J_{C-P} = 61.8$ Hz, Cq), 135.4 (d, $J = 3.6$ Hz, Cq), 133.1 (d, $^2J_{C-P} = 10.1$ Hz, 4xCH), 132.0 (d, $^4J_{C-P} = 2.4$ Hz, 2xCH), 131.3 (d, $J = 7.9$ Hz, 2xCH), 130.2 (dd, $^3J = 11.5$, 1.5 Hz, Cq), 129.4-128.7 (m, 6xCH), 126.4 (d, $^1J_{C-P} = 61.0$ Hz, 2xCq), 123.9 (d, $^2J = 26.6$ Hz, CH). ^{11}B NMR (160 MHz, CDCl₃): δ -38.3 (m). ^{19}F NMR (376 MHz, CDCl₃): δ -113.9 (dd, $^3J_{F-H} = 42.1$, $^2J_{F-P} = 17.0$ Hz). ^{31}P NMR (162 MHz, CDCl₃): δ 21.3 (m). HRMS (ESI-TOF): calcd for C₂₀H₁₆³⁵ClFP m/z 341.0662 [M-BH₃+H]⁺, found 341.0668.

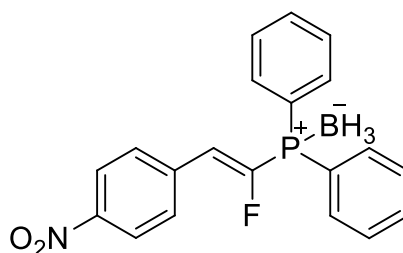


(E)-((2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3g: (*E*)-1-(2-bromo-2-fluorovinyl)-3-chlorobenzene (0.2 mmol, 47 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 8/2 to afford the desired compound in 49% yield (34 mg) as a

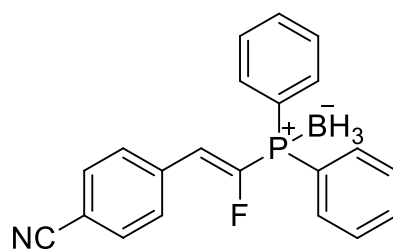
colourless solid. mp 99-101 °C. IR: 3057, 2924, 2388, 1561, 1472, 1435, 1053, 888, 820 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (dd, *J* = 11.2, 7.6 Hz, 4H), 7.68 (s, 1H), 7.59-7.54 (m, 2H), 7.53-7.46 (m, 5H), 7.35-7.28 (m, 2H), 6.83 (dd, ³*J*_{H-F} = 41.7, ³*J*_{H-P} = 8.7 Hz, 1H), 1.6-0.9 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 154.3 (dd, ¹*J*_{C-F} = 297.5, ¹*J*_{C-P} = 61.0 Hz, Cq), 134.8 (s, Cq), 133.3 (dd, ³*J* = 11.4, 1.3 Hz, Cq), 133.1 (d, ²*J*_{C-P} = 10.0 Hz, 4xCH), 132.1 (d, ⁴*J*_{C-P} = 2.5 Hz, 2xCH), 130.1 (s, CH), 129.8 (d, *J* = 9.1 Hz, CH), 129.6 (d, *J* = 2.1 Hz, CH), 129.2 (d, ³*J*_{C-P} = 10.6 Hz, 4xCH), 128.2 (d, *J* = 6.9 Hz, CH), 126.3 (d, ¹*J*_{C-P} = 60.9 Hz, 2xCq), 123.7 (d, *J* = 26.4 Hz, CH). ¹¹B NMR (160 MHz, CDCl₃): δ -38.3 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -112.3 (dd, ³*J*_{F-H} = 41.7, ²*J*_{F-P} = 17.2 Hz). ³¹P NMR (162 MHz, CDCl₃): δ 21.6 (m). HRMS (ESI-TOF): calcd for C₂₀H₁₆³⁵ClFP *m/z* 341.0662 [M-BH₃+H]⁺, found 341.0659.



(E)-((2-(4-(Methoxycarbonyl)phenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate
3h: (*E*)-methyl 4-(2-bromo-2-fluorovinyl)benzoate (0.2 mmol, 52 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 9/1 to pentane/DCM 8/2 to afford the desired compound in 85% yield (64 mg) as a colourless solid. mp 147-149 °C. IR: 2924, 2849, 2384, 1717, 1436, 1412, 1280, 1185, 1107, 1053, 894, 828 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, ³*J*_{H-H} = 8.4 Hz, 2H), 7.79-7.72 (m, 4H), 7.69 (d, ³*J*_{H-H} = 8.4 Hz, 2H), 7.59-7.54 (m, 2H), 7.53-7.46 (m, 4H), 6.91 (dd, ³*J*_{H-F} = 41.9, ³*J*_{H-P} = 8.7 Hz, 1H), 3.92 (s, 3H), 1.6-0.8 (bm, 3H). ¹³C NMR {¹H} (100 MHz, CDCl₃): δ 166.6 (s, Cq), 155.0 (dd, ¹*J*_{C-F} = 299.1, ¹*J*_{C-P} = 60.4 Hz, Cq), 135.9 (d, ³*J* = 11.2 Hz, Cq), 133.1 (d, ²*J*_{C-P} = 10.1 Hz, 4xCH), 132.1 (d, ⁴*J*_{C-P} = 2.5 Hz, 2xCH), 130.6 (d, *J* = 2.4 Hz, Cq), 130.0 (s, 2xCH), 129.9 (d, *J* = 7.9 Hz, 2xCH), 129.2 (d, ³*J*_{C-P} = 10.7 Hz, 4xCH), 126.2 (d, ¹*J*_{C-P} = 60.8 Hz, 2xCq), 123.9 (d, ²*J* = 26.2 Hz, CH), 52.4 (s, OCH₃). ¹¹B NMR (160 MHz, CDCl₃): δ -38.5 (m). ¹⁹F NMR (376 MHz, CDCl₃): δ -111.0 (dd, ³*J*_{F-H} = 41.9, ²*J*_{F-P} = 17.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 21.7 (m). HRMS (ESI-TOF): calcd for C₂₂H₁₉FO₂P *m/z* 365.1107 [M-BH₃+H]⁺, found 365.1106.

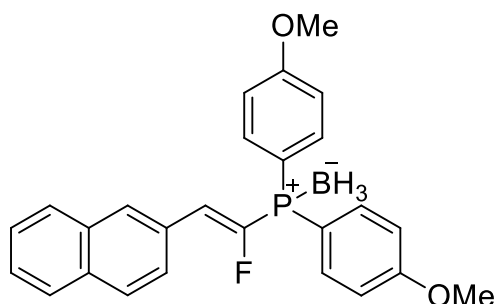


(E)-((2-(4-Nitrophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3i: (*E*)-1-(2-bromo-2-fluorovinyl)-4-nitrobenzene (0.20 mmol, 49 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 53% yield (39 mg) as a colourless solid. mp 153-155 °C. IR: 3061, 2418, 1644, 1594, 1511, 1436, 1344, 1289, 1107, 1056, 885, 859, 843, 827 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.89-7.67 (m, 6H), 7.65-7.38 (m, 6H), 6.94 (dd, ³*J*_{H-F} = 41.0, ³*J*_{H-P} = 8.6 Hz, 1H), 1.4-0.7 (bm, 3H). ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 156.7 (dd, ¹*J*_{C-F} = 302.4, ¹*J*_{C-P} = 58.1 Hz, Cq), 147.8 (s, Cq), 137.8 (d, ³*J* = 11.3 Hz, Cq), 133.1 (d, ²*J*_{C-P} = 10.1 Hz, 4xCH), 132.3 (s, 2xCH), 130.7 (d, *J* = 8.0 Hz, 2xCH), 129.3 (d, ³*J*_{C-P} = 10.7 Hz, 4xCH), 125.8 (d, ¹*J* = 60.7 Hz, 2xCq), 124.1 (s, 2xCH), 122.6 (d, ²*J* = 26.1 Hz, CH). ¹¹B NMR (120 MHz, CDCl₃): δ -38.5 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -108.6 (dd, ³*J*_{F-H} = 41.0, ³*J*_{F-P} = 16.5 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 22.2 (m). HRMS (FD-TOF): calcd for C₂₀H₁₅FNO₂P *m/z* 351.0824 [M-BH₃]⁺, found 351.0826.



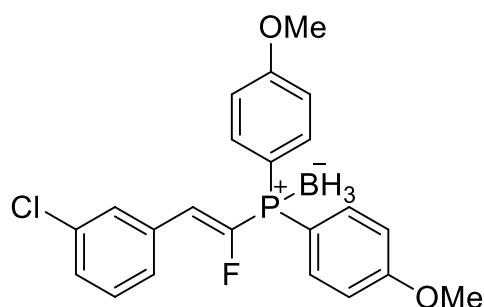
(E)-((2-(4-Cyanophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3j: (*E*)-4-(2-bromo-2-fluorovinyl)benzonitrile (0.2 mmol, 45 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pentane/DCM 8/2 to afford the desired compound in 82% yield (51 mg) as a colourless solid. mp 131-133 °C. IR: 3053, 2401, 2350, 2230, 1435, 1050, 887, 839, 828 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.98- 7.37 (m, 14H), 6.89 (dd, ³*J*_{H-F} = 41.2, ³*J*_{H-P} = 8.2 Hz, 1H), 1.5-0.8 (bm, 3H). ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 156.1 (dd, ¹*J*_{C-F} = 301.3, ¹*J*_{C-P} = 58.6 Hz, Cq), 135.9 (d, *J* = 11.3 Hz, Cq), 133.0 (d, ²*J*_{C-P} = 10.1 Hz, 4xCH), 132.5 (s, 2xCH), 132.2 (d, ⁴*J*_{C-P} = 2.4

Hz, 2xCH), 130.4 (d, $J = 8.0$ Hz, 2xCH), 129.2 (d, $^3J_{C-P} = 10.7$ Hz, 4xCH), 125.8 (d, $^1J_{C-P} = 60.8$ Hz, 2xCq), 123.0 (d, $J = 26.1$ Hz, CH), 118.5 (s, Cq), 112.7 (d, $J = 3.0$ Hz, Cq). ^{11}B NMR (160 MHz, CDCl_3): δ -38.4 (m). ^{19}F NMR (376 MHz, CDCl_3): δ -109.7 (dd, $^3J_{F-H} = 41.2$, $^2J_{F-P} = 19.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3): δ -21.9 (m). HRMS (ESI-TOF): calcd for $\text{C}_{21}\text{H}_{16}\text{FNP}$ m/z 332.1004 $[\text{M-BH}_3+\text{H}]^+$, found 332.1002.

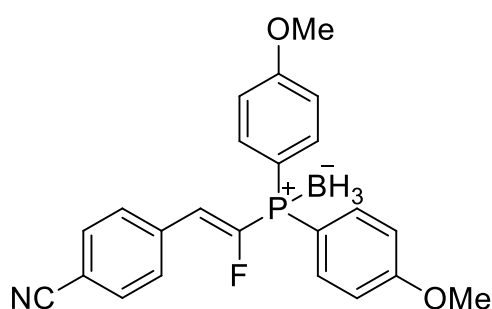


(E)-((1-Fluoro-2-(naphth-2-yl)vinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate

3k: (*E*)-2-(2-bromo-2-fluorovinyl)naphthalene (0.20 mmol, 50 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs_2CO_3 (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 38% yield (30 mg) as a sticky colourless solid. IR: 2923, 2355, 1593, 1569, 1500, 1455, 1300, 1257, 1177, 1108, 1054, 1028, 903, 826 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.08 (s, 1H), 7.84-7.68 (m, 8H), 7.54-7.44 (m, 2H), 7.05-6.83 (m, 5H), 3.85 (s, 6H), 1.4-0.9 (bm, 3H). ^{13}C NMR $\{^1\text{H}\}$ (75 MHz, CDCl_3): δ 162.6 (d, $^4J_{C-P} = 2.4$ Hz, 2xCq), 154.1 (dd, $^1J_{C-F} = 295.0$, $^1J_{C-P} = 63.3$ Hz, Cq), 134.8 (d, $J_{C-P} = 11.3$ Hz, 4xCH), 133.5 (d, $J = 1.8$ Hz, Cq), 133.3 (s, Cq), 130.2 (d, $J = 7.6$ Hz, CH), 129.5 (dd, $J = 11.2, 1.7$ Hz, Cq), 128.6 (s, $J = 16.2$ Hz, CH), 128.4 (s, CH), 127.7 (s, CH), 127.2 (s, CH), 126.9 (d, $J = 7.9$ Hz, CH), 126.6 (s, CH), 124.2 (d, $^2J = 26.0$ Hz, CH), 117.5 (d, $^1J_{C-P} = 66.4$ Hz, 2xCq), 114.8 (d, $J_{C-P} = 11.6$ Hz, 4xCH), 55.5 (s, 2xOCH₃). ^{11}B NMR (120 MHz, CDCl_3): δ -38.0 (m). ^{19}F NMR (282 MHz, CDCl_3): δ -114.8 (dd, $^3J_{F-H} = 42.8$, $^2J_{F-P} = 20.6$ Hz). ^{31}P NMR (122 MHz, CDCl_3): δ 18.4 (m). HRMS (FD-TOF): calcd for $\text{C}_{26}\text{H}_{22}\text{FO}_2\text{P}$ m/z 416.1341 $[\text{M-BH}_3]^+$, found 416.1349.

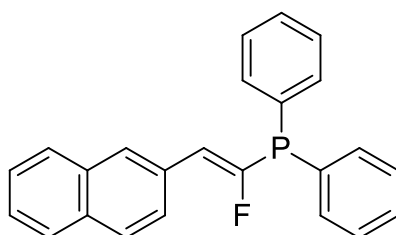


(E)-((2-(3-Chlorophenyl)-1-fluorovinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate 3l: (*E*)-1-(2-bromo-2-fluorovinyl)-3-chlorobenzene (0.20 mmol, 47 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 7/3 to afford the desired compound in 18% yield (12 mg) as a sticky colourless solid. IR: 2924, 2389, 1725, 1436, 1107, 1054, 812 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.66 (m, 5H), 7.44 (m, 1H), 7.30 (m, 2H), 6.98 (m, 4H), 6.72 (dd, ³J_{H-F} = 41.9, ³J_{H-P} = 8.5 Hz, 1H), 3.85 (s, 6H), 1.4-0.8 (bm, 3H). Selected ¹³C NMR {¹H} (75 MHz, CDCl₃): δ 162.7 (d, ⁴J_{C-P} = 2.4 Hz, 2xCq), 134.8 (m, 4xCH+Cq), 133.5 (dd, *J* = 11.1, 1.3 Hz, Cq), 130.0 (s, CH), 129.8 (d, *J* = 9.0 Hz, CH), 129.4 (d, *J* = 2.1 Hz, CH), 128.2 (d, *J* = 7.0 Hz, CH), 122.6 (d, ²*J* = 25.9 Hz, CH), 117.1 (d, ¹J_{C-P} = 66.4 Hz, 2xCq), 114.8 (d, ³J_{C-P} = 11.6 Hz, 4xCH), 55.5 (s, CH₃). ¹¹B NMR (120 MHz, CDCl₃): δ -38.7 (m). ¹⁹F NMR (282 MHz, CDCl₃): δ -112.6 (dd, ³J_{F-H} = 41.9, ²J_{F-P} = 20.2 Hz). ³¹P NMR (122 MHz, CDCl₃): δ 18.7 (m). HRMS (ESI-TOF): calcd for C₂₂H₂₀³⁵ClFO₂P *m/z* 401.0873 [M-BH₃+H]⁺, found 401.0867.



(E)-((2-(4-Cyanophenyl)-1-fluorovinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate 3m: (*E*)-4-(2-bromo-2-fluorovinyl)benzotrinitrile (0.20 mmol, 45 mg), bis(4-methoxyphenyl)phosphine borane (0.22 mmol, 57 mg), Cs₂CO₃ (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure. The crude product was chromatographed on neutral alumina eluting with pure pentane to pentane/DCM 1/1 to afford the desired compound in 47% yield (42 mg) as a sticky colourless solid. IR: 2932, 2839, 2388, 2228, 1594, 1500, 1292, 1254, 1179, 1107, 826, 800 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 7.71-

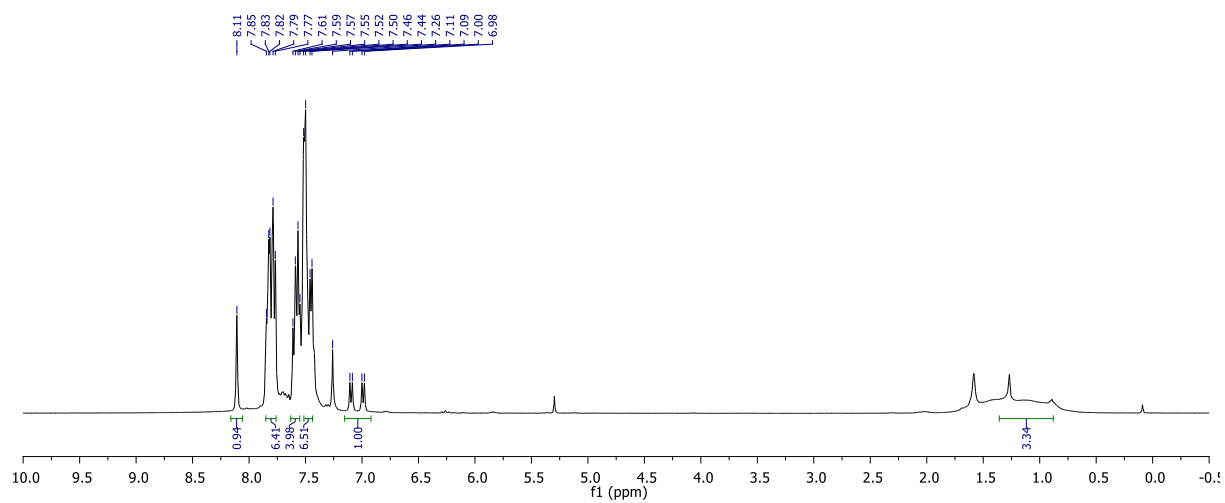
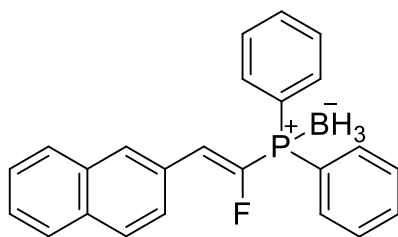
7.61 (m, 8H), 7.00 (dd, $J = 8.3, 1.7$ Hz, 4H), 6.79 (dd, $^3J_{\text{H-F}} = 41.4, ^3J_{\text{H-P}} = 8.3$ Hz, 1H), 3.85 (s, 6H), 1.4-0.9 (bm, 3H). ^{13}C NMR $\{^1\text{H}\}$ (75 MHz, CDCl_3): δ 162.7 (d, $^4J_{\text{C-P}} = 2.4$ Hz, 2xCq), 157.1 (dd, $^1J_{\text{C-F}} = 301.0, ^1J_{\text{C-P}} = 59.2$ Hz, Cq), 136.1 (d, $J = 11.0$ Hz, Cq), 134.8 (d, $^2J_{\text{C-P}} = 11.5$ Hz, 4xCH), 132.5 (s, 2xCH), 130.3 (d, $J = 8.1$ Hz, 2xCH), 121.9 (d, $^2J = 25.5$ Hz, CH), 118.6 (s, Cq), 116.5 (d, $^1J_{\text{C-P}} = 66.3$ Hz, 2xCq), 114.9 (d, $^3J_{\text{C-P}} = 11.6$ Hz, 4xCH), 112.5 (d, $J = 3.0$ Hz, Cq), 55.5 (s, 2xOCH₃). ^{11}B NMR (120 MHz, CDCl_3): δ -38.1 (m). ^{19}F NMR (282 MHz, CDCl_3): δ -109.4 (dd, $^3J_{\text{F-H}} = 41.4, ^2J_{\text{F-P}} = 19.8$ Hz). ^{31}P NMR (122 MHz, CDCl_3): δ 19.1 (m). HRMS (FD-TOF): calcd for $\text{C}_{23}\text{H}_{19}\text{FNO}_2\text{P}$ m/z 391.1137 $[\text{M-BH}_3]^+$, found 391.1148.



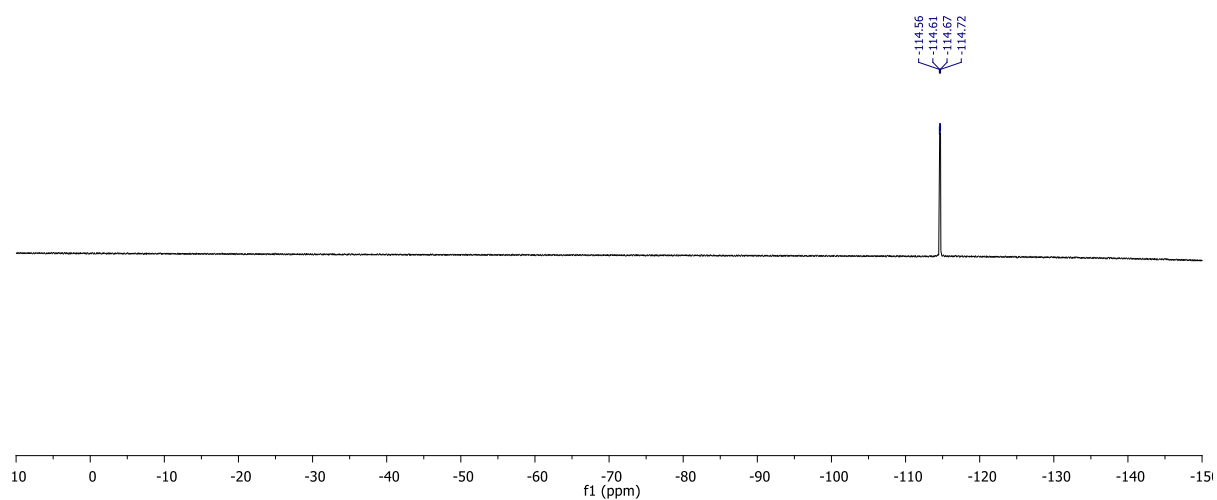
(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphine 3a': *(E)*-2-(2-bromo-2-fluorovinyl)naphthalene (0.20 mmol, 50 mg), diphenylphosphine borane (0.22 mmol, 44 mg), Cs_2CO_3 (0.24 mmol, 78 mg) in MeCN (1 mL) were reacted according to the general procedure, at 60 °C overnight. The crude product was chromatographed on silica gel eluting with pentane/toluene 9/1 to 5/5 to afford the desired compound in 43% yield (31 mg) as a colourless solid. mp 139-141 °C. IR: 3058, 2924, 2852, 1727, 1584, 1479, 1430, 1273, 1042, 906, 828 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.04 (s, 1H), 7.9-7.7 (m, 4H), 7.7-7.6 (m, 4H), 7.5-7.3 (m, 8H), 6.51 (dd, $^3J_{\text{H-F}} = 41.0, ^3J_{\text{H-P}} = 9.4$ Hz, 1H). ^{13}C NMR $\{^1\text{H}\}$ (75 MHz, CDCl_3): δ 161.6 (dd, $^1J_{\text{C-F}} = 313.6, ^1J_{\text{C-P}} = 28.9$ Hz, Cq), 134.4 (dd, $J = 6.4, 2.8$ Hz, 2xCq), 133.6 (d, $^2J_{\text{C-P}} = 19.3$ Hz, 4xCH), 133.4 (s, Cq), 133.1 (d, $J = 1.9$ Hz, Cq), 130.7 (dd, $^3J = 11.9, 2.1$ Hz, Cq), 129.4 (s, 2xCH), 129.0 (d, $J = 8.1$ Hz, CH), 128.8 (d, $^3J_{\text{C-P}} = 7.1$ Hz, 4xCH), 128.4 (s, CH), 128.2 (s, CH), 127.7 (s, CH), 126.9 (d, $J = 8.0$ Hz, CH), 126.6 (s, CH), 126.4 (s, CH), 123.8 (dd, $^2J_{\text{C-F}} = 39.3, ^2J_{\text{C-P}} = 4.3$ Hz, CH). ^{19}F NMR (282 MHz, CDCl_3): δ -104.4 (dd, $^3J_{\text{F-H}} = 41.1, ^2J_{\text{F-P}} = 14.5$ Hz). ^{31}P NMR (122 MHz, CDCl_3): δ -5.4 (m). HRMS (ESI-TOF): calcd for $\text{C}_{24}\text{H}_{19}\text{OFP}$ m/z 373.1158 $[\text{M}(\text{O})+\text{H}]^+$, found 373.1163.

5. NMR spectra for compounds 3a-3m

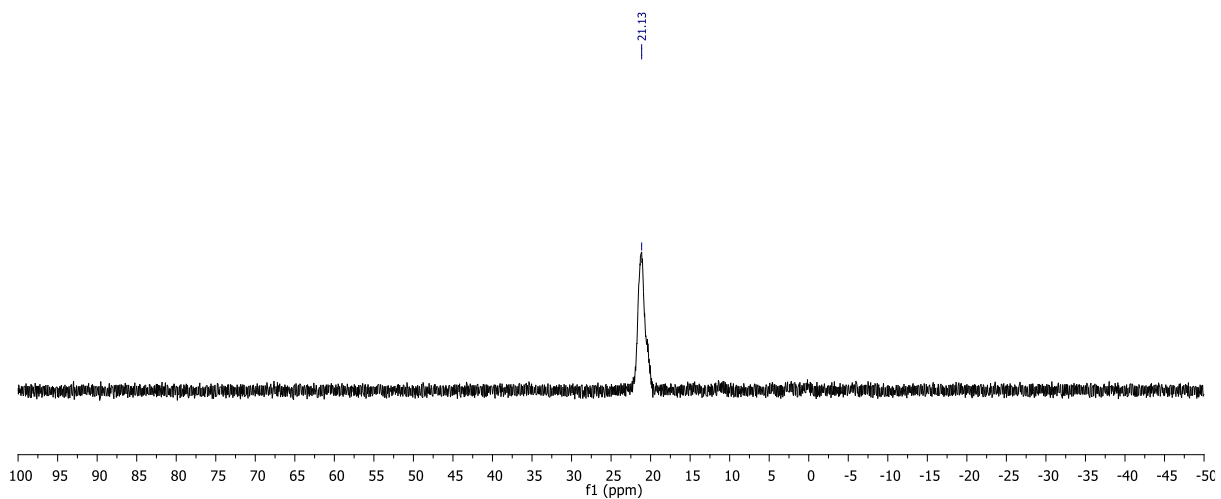
(*E*)-((1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphonio)trihydroborate 3a



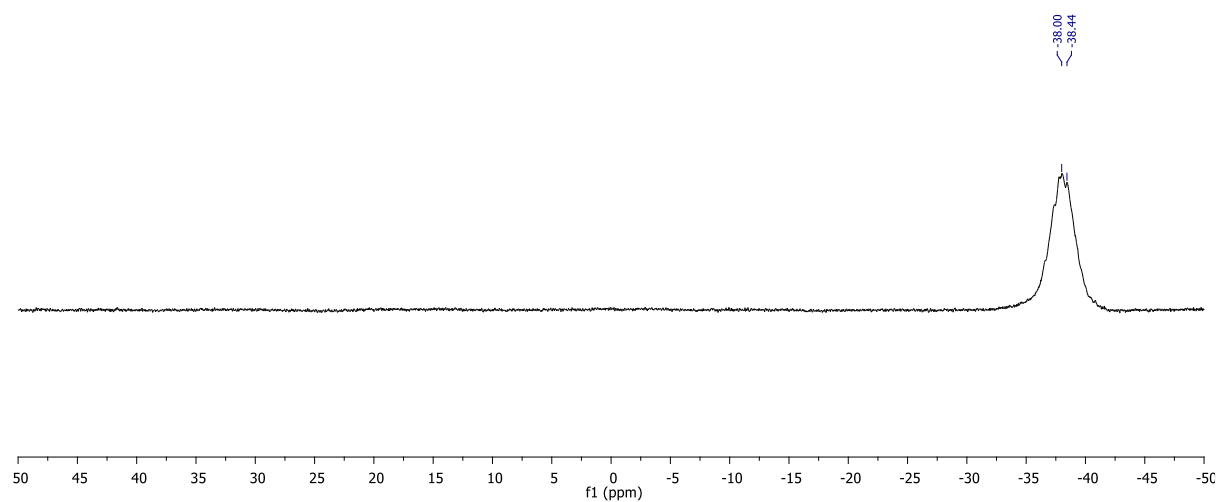
¹H NMR in CDCl₃



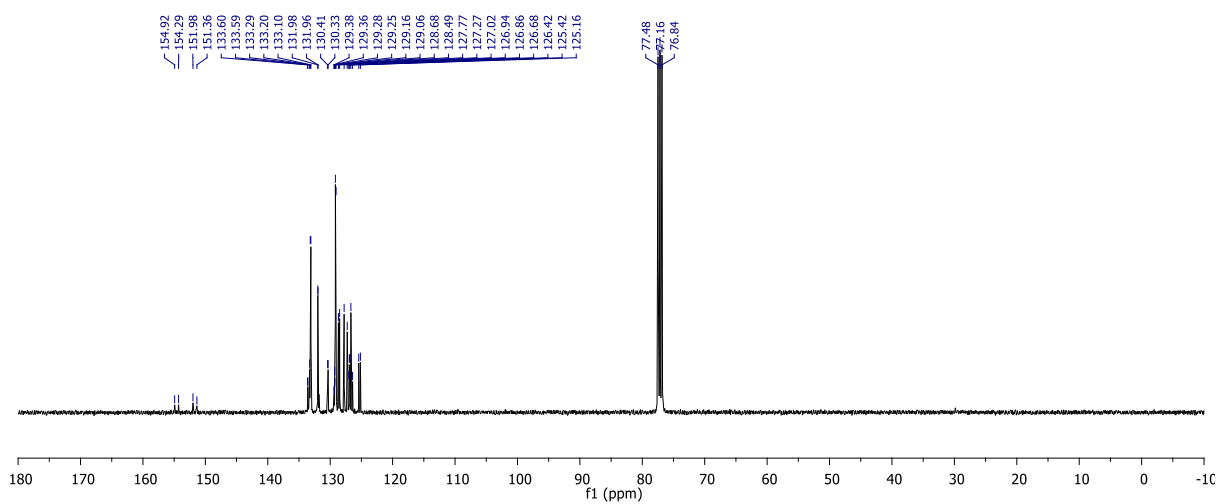
¹⁹F NMR in CDCl₃



³¹P NMR in CDCl₃

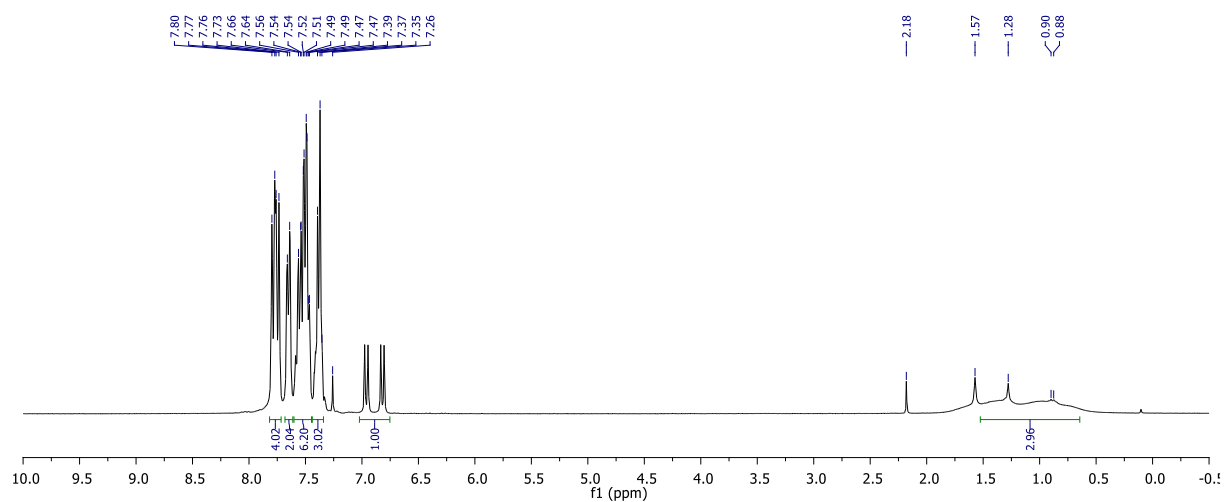
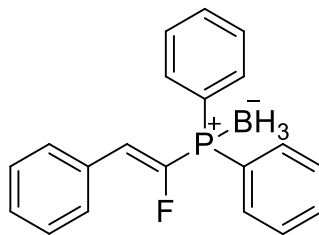


¹¹B NMR in CDCl₃

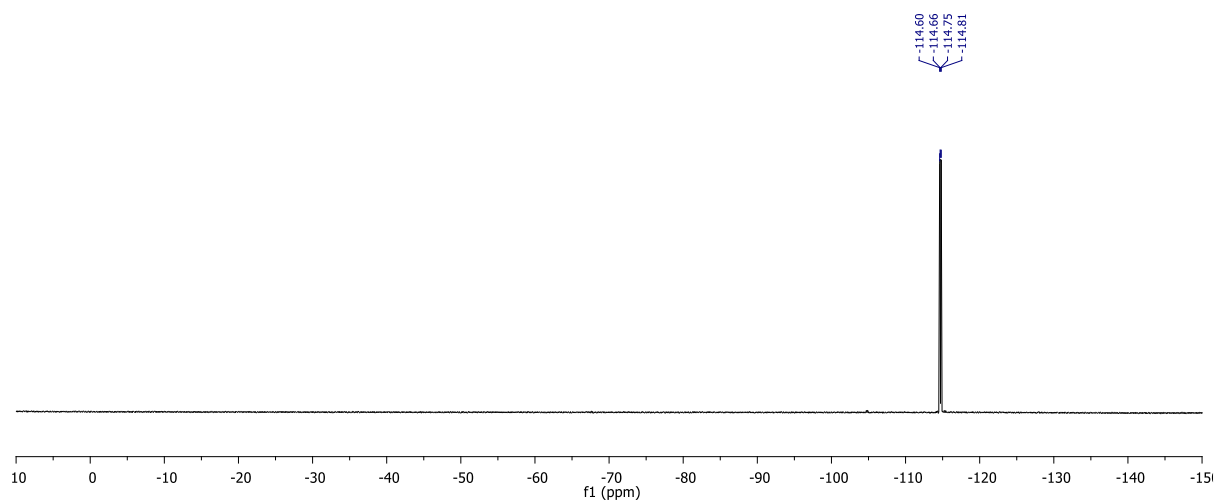


¹³C NMR {¹H} in CDCl₃

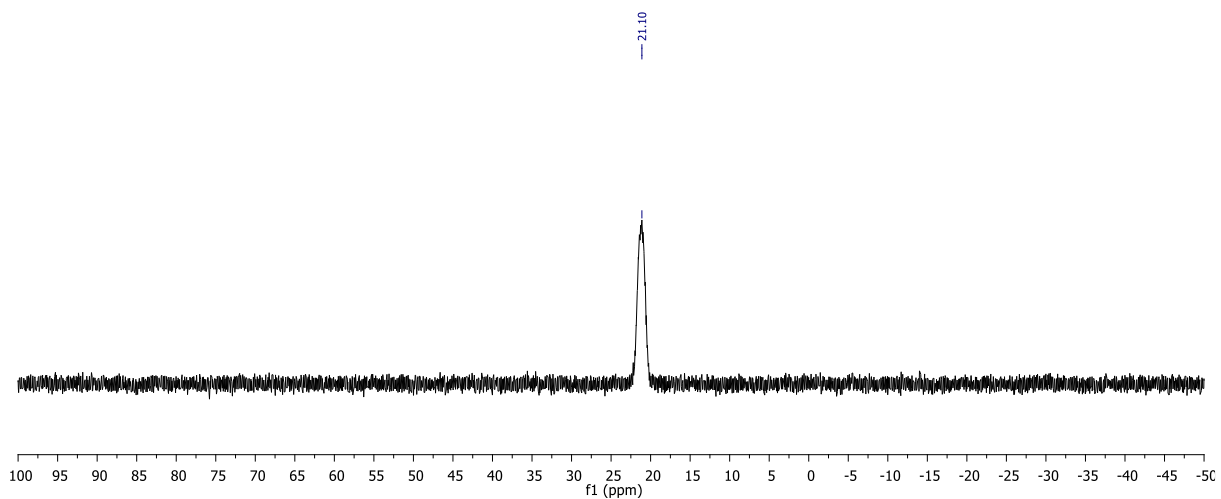
(E)-((1-Fluoro-2-phenylvinyl)diphenylphosphonio)trihydroborate 3b



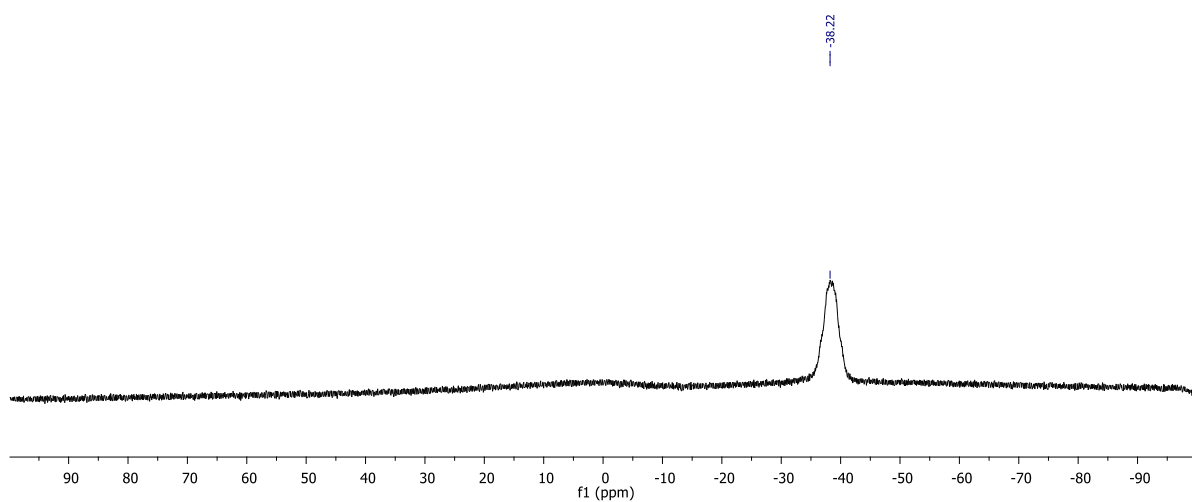
¹H NMR in CDCl₃



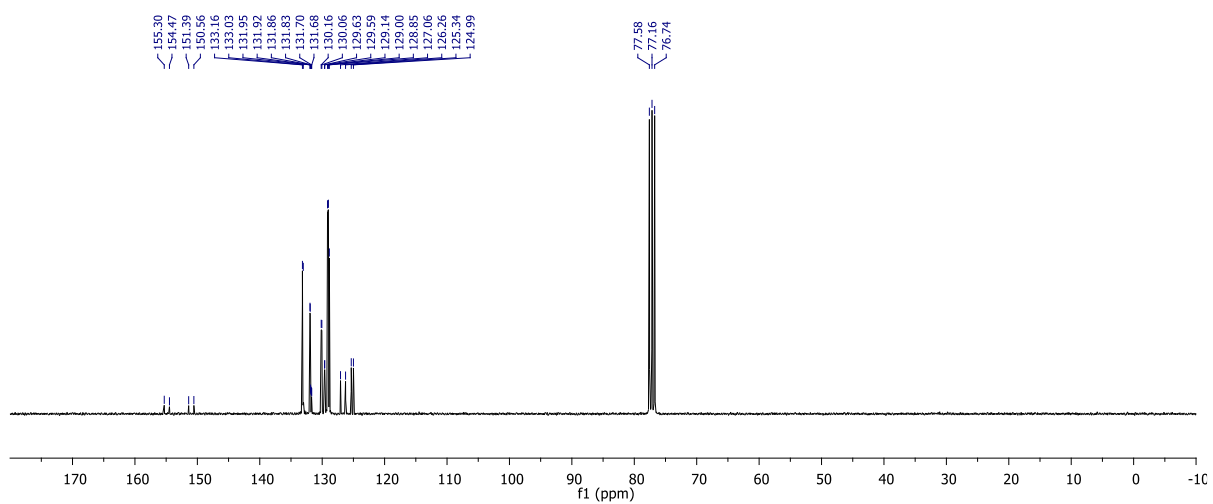
¹⁹F NMR in CDCl₃



^{31}P NMR in CDCl_3

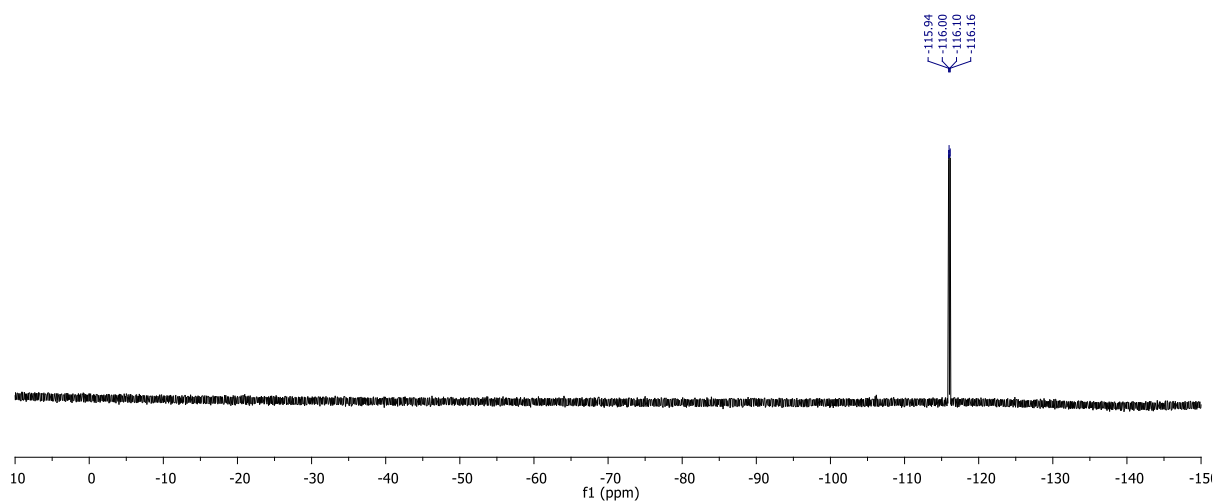
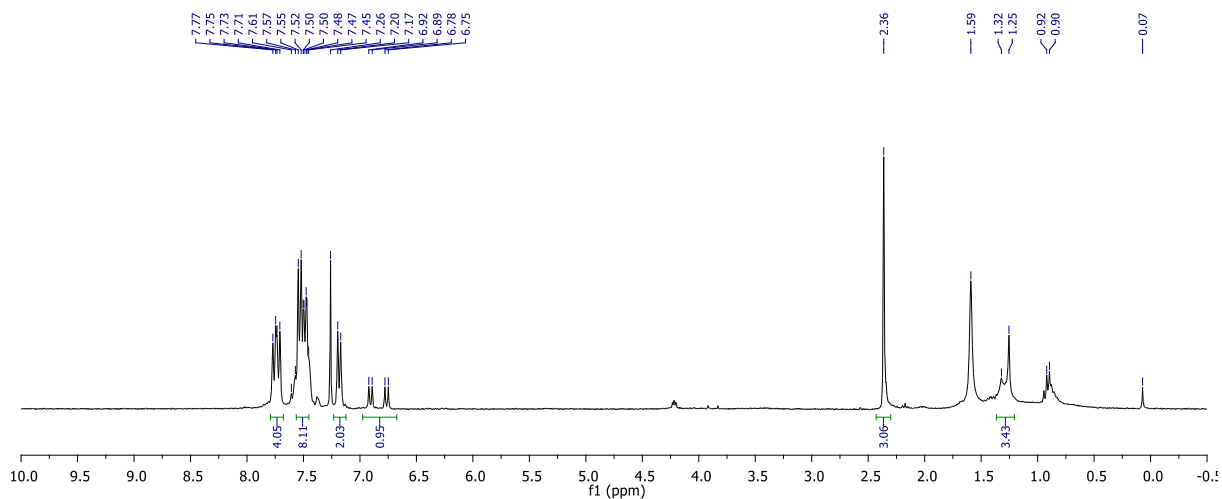
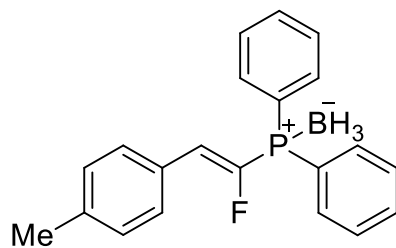


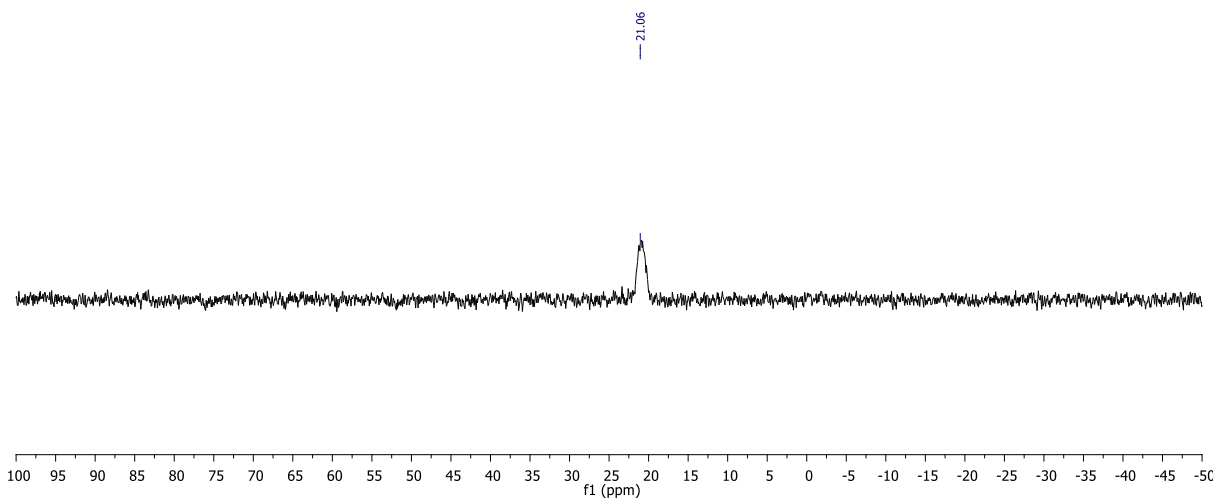
^{11}B NMR in CDCl_3



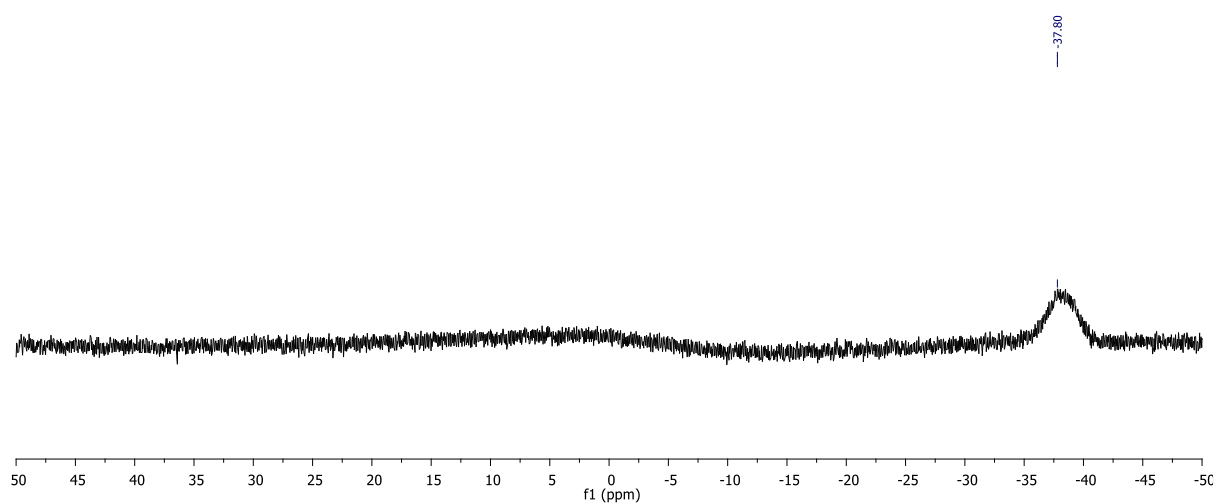
^{13}C NMR (^1H) in CDCl_3

(E)-((1-Fluoro-2-(p-tolyl)vinyl)diphenylphosphonio)trihydroborate 3c

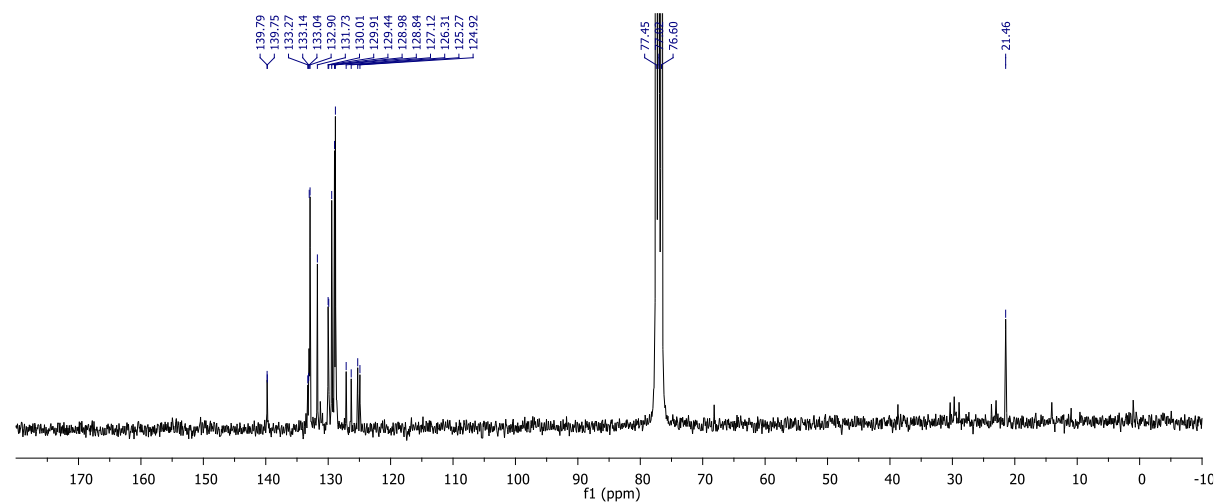




^{31}P NMR in CDCl_3

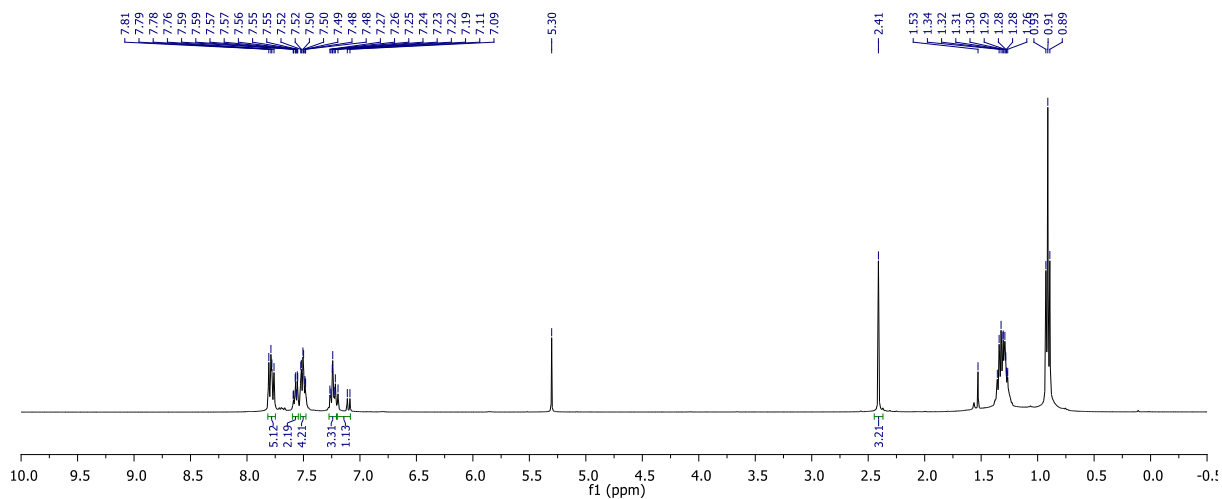
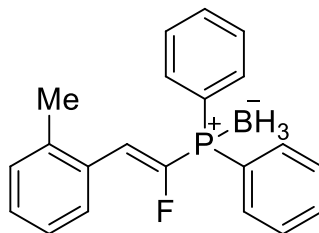


^{11}B NMR in CDCl_3

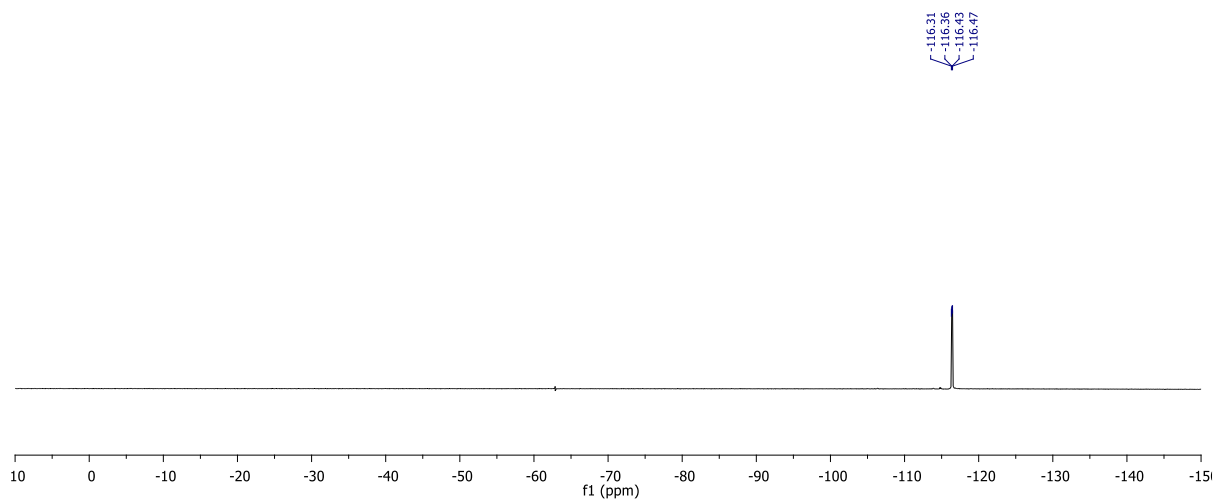


^{13}C NMR ($\{^1\text{H}\}$) in CDCl_3

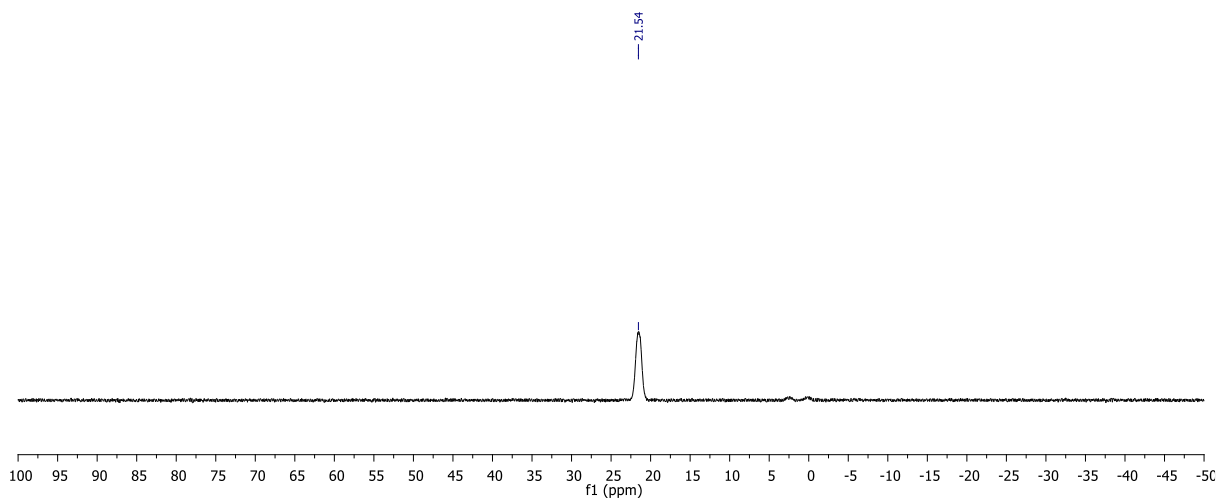
(E)-((1-Fluoro-2-(*o*-tolyl)vinyl)diphenylphosphonio)trihydroborate 3d



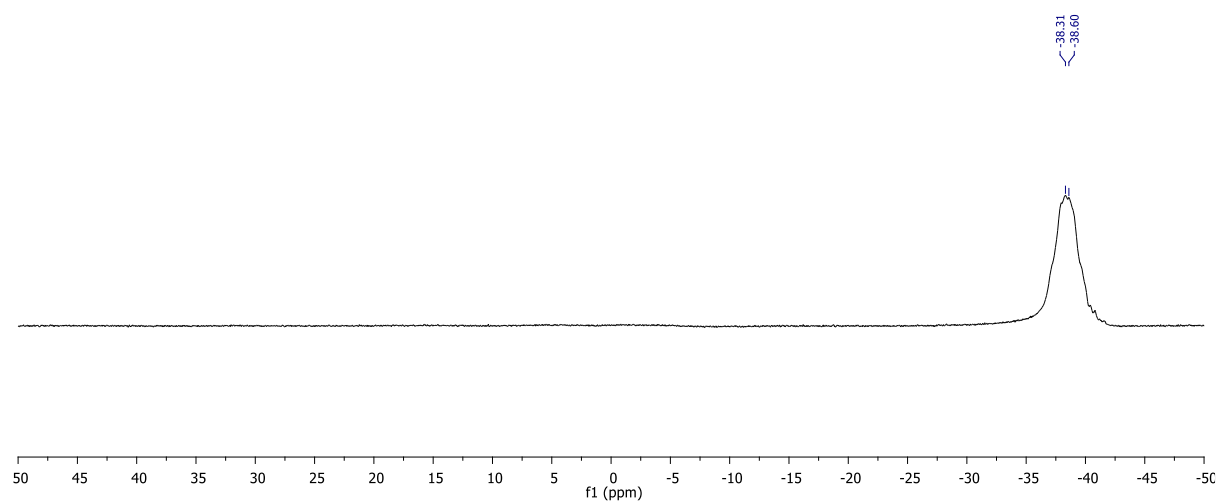
¹H NMR in CDCl₃



¹⁹F NMR in CDCl₃

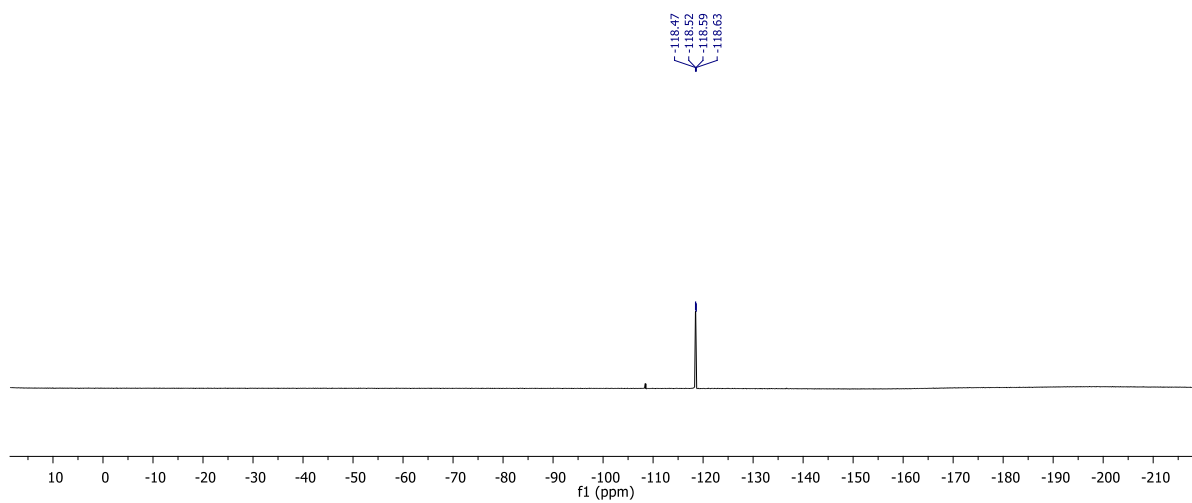
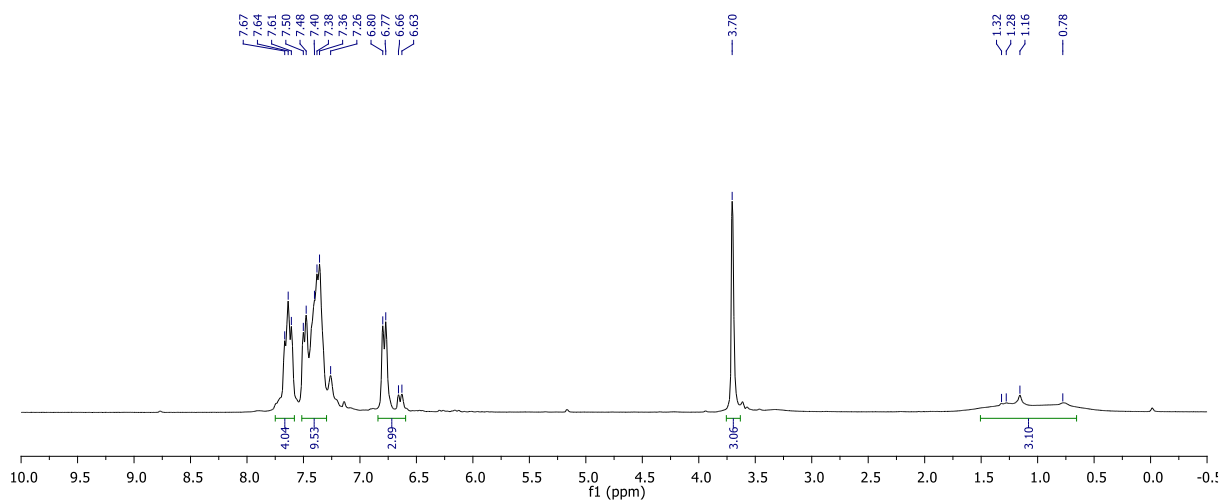
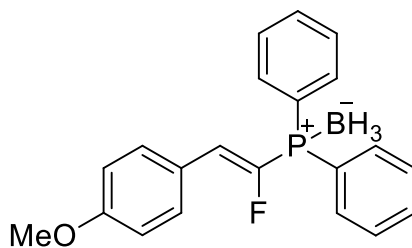


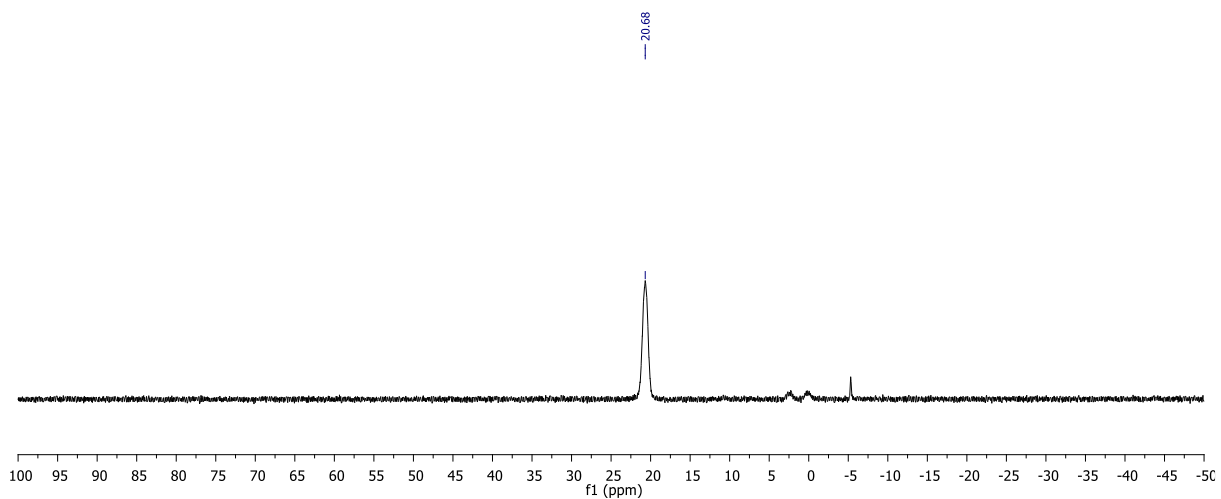
^{31}P NMR in CDCl_3



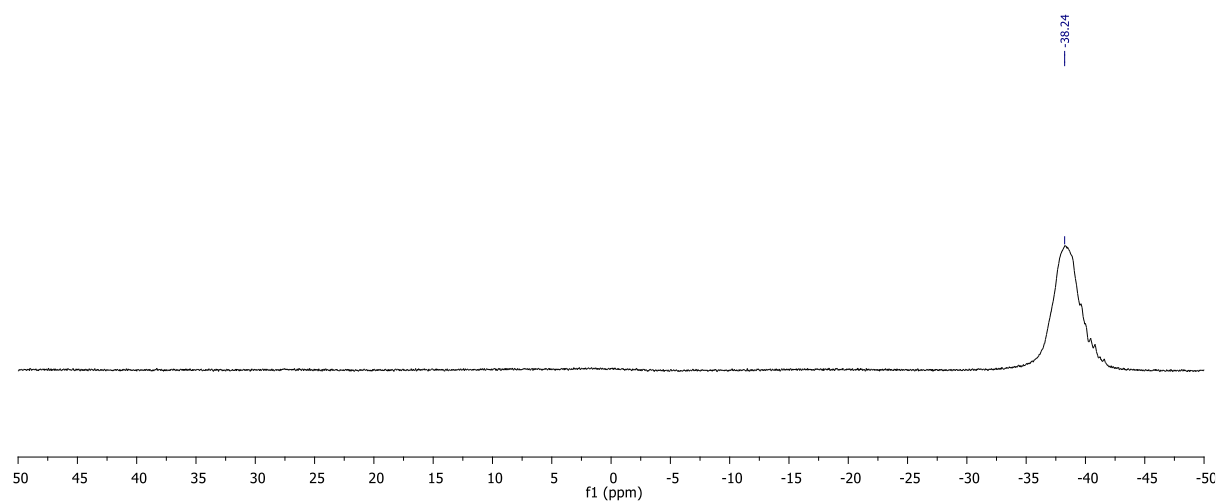
^{11}B NMR in CDCl_3

(E)-((2-(4-Methoxyphenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3e

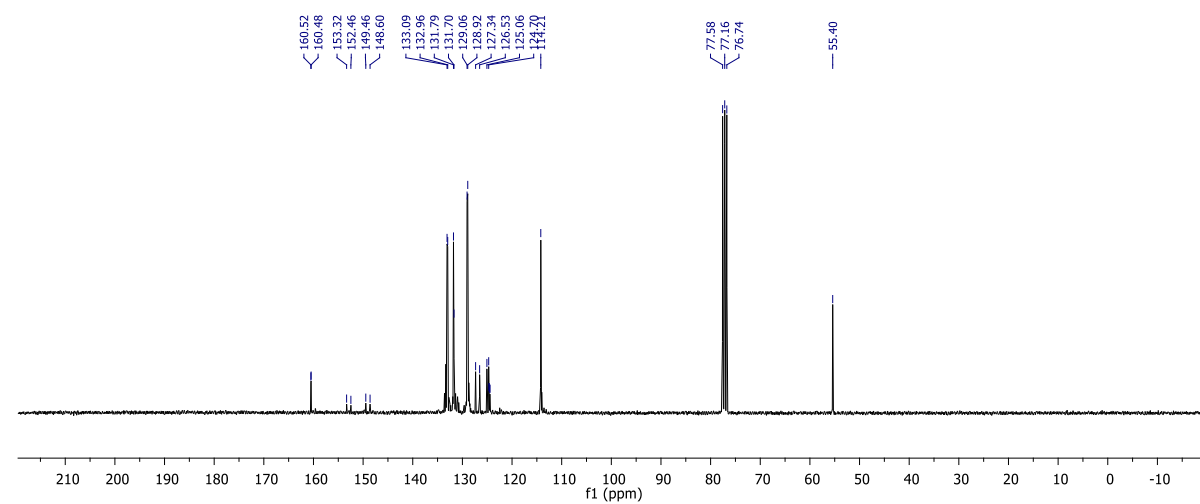




³¹P NMR in CDCl₃

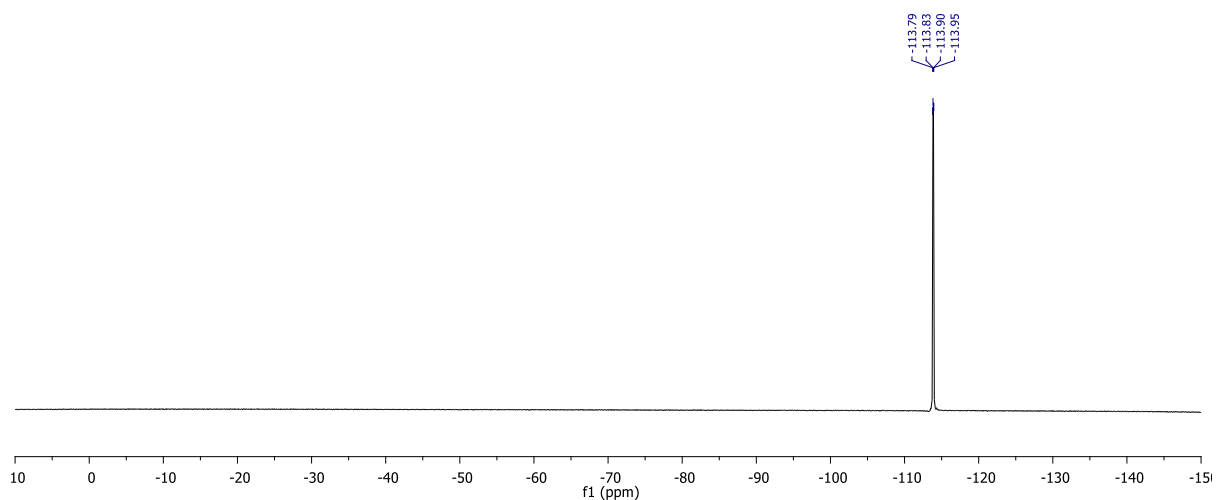
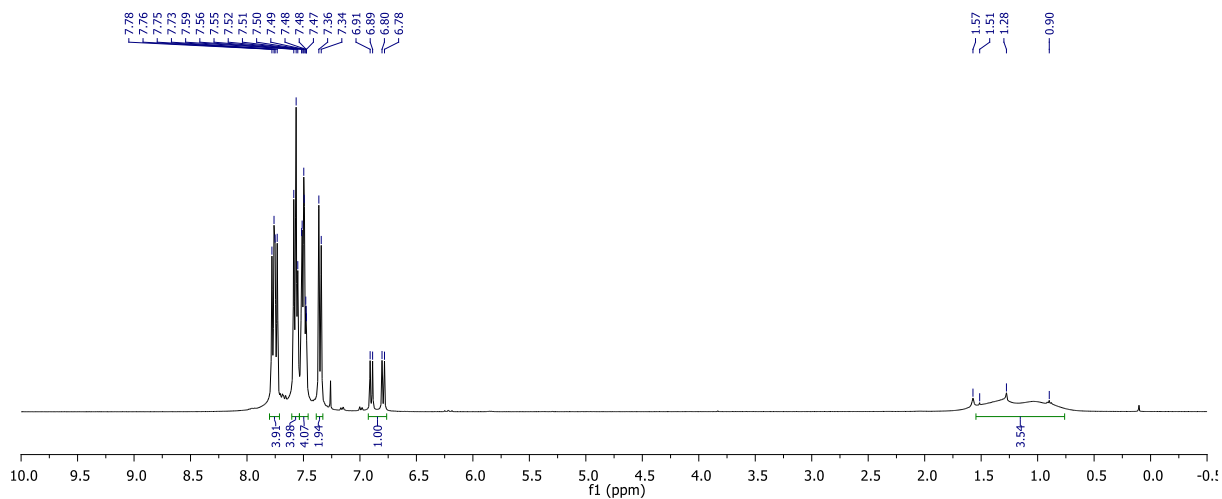
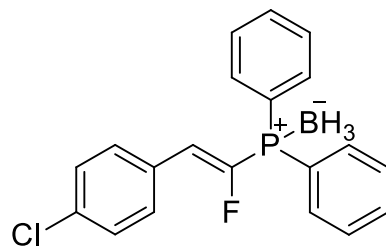


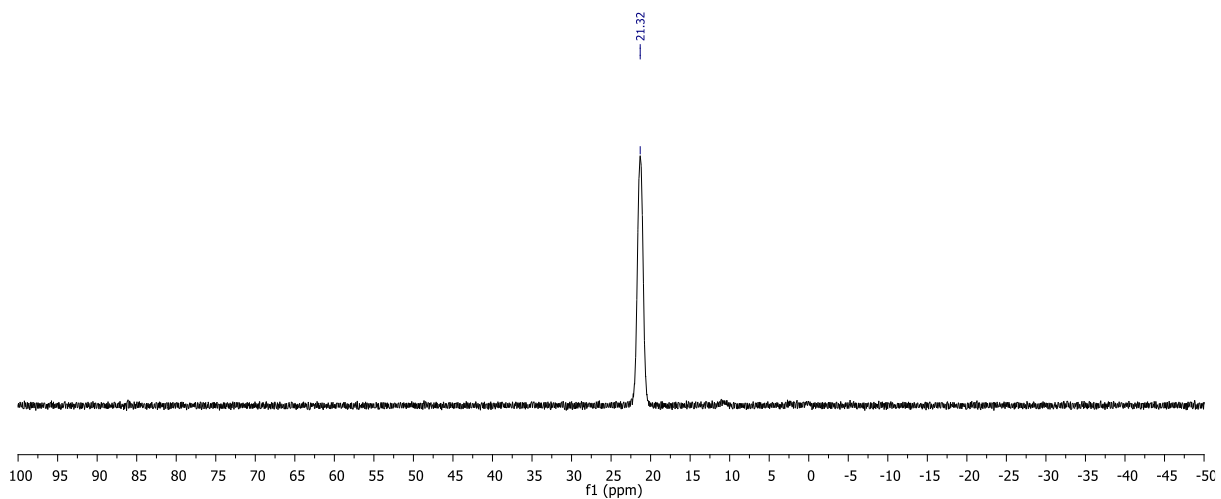
¹¹B NMR in CDCl₃



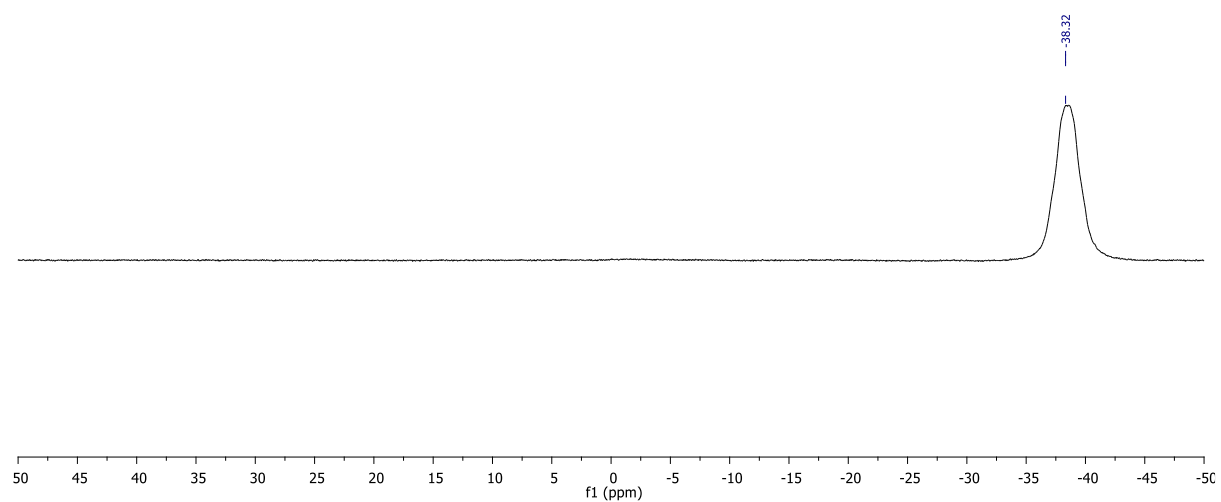
¹³C NMR {¹H} in CDCl₃

(E)-((2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3f

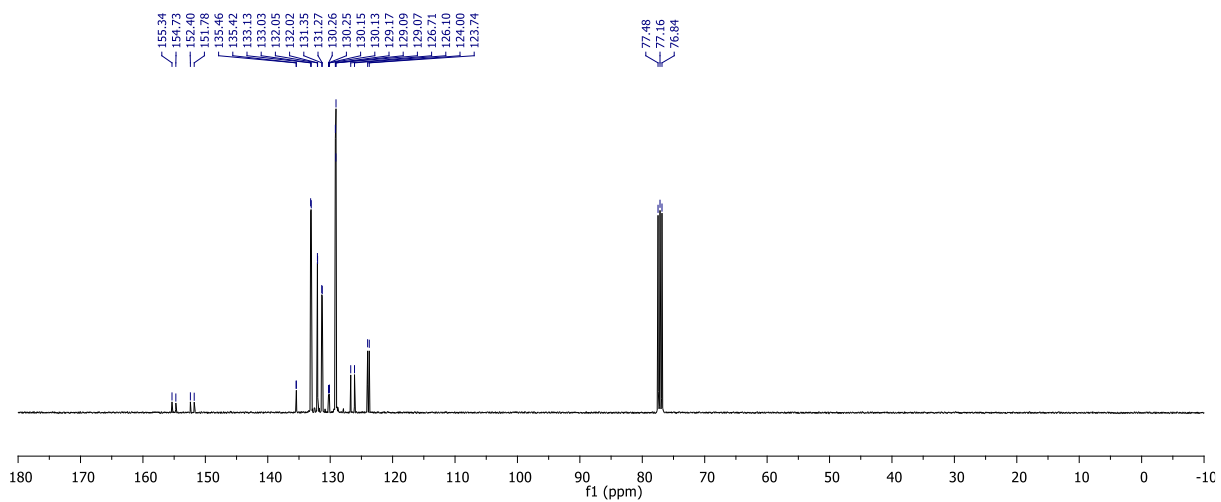




³¹P NMR in CDCl₃

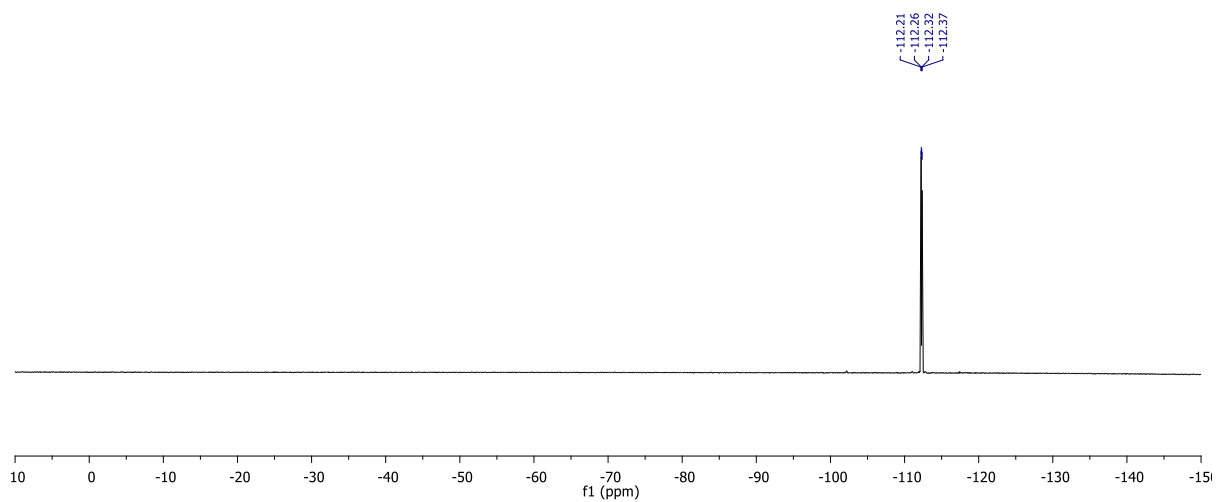
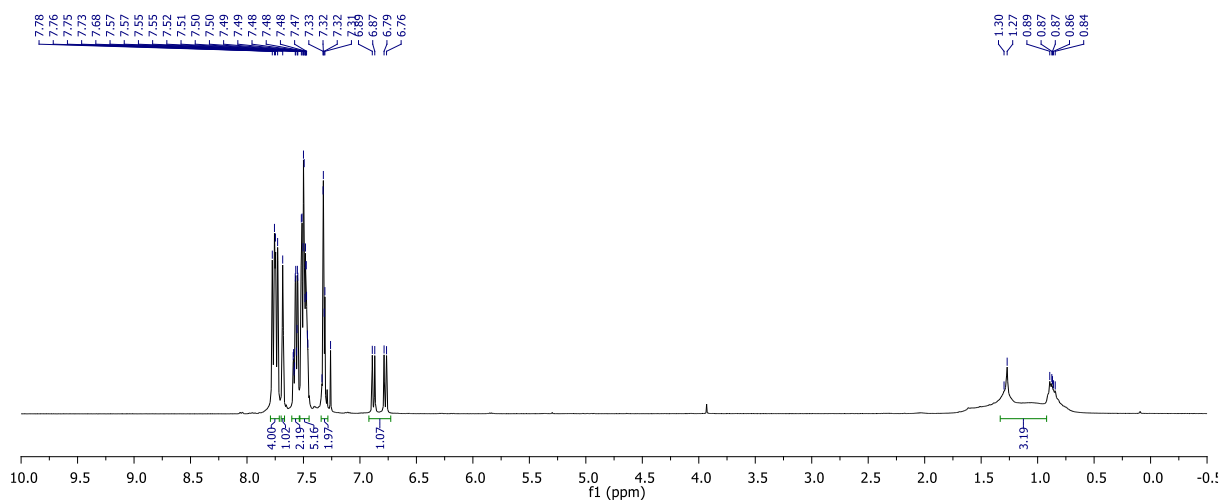
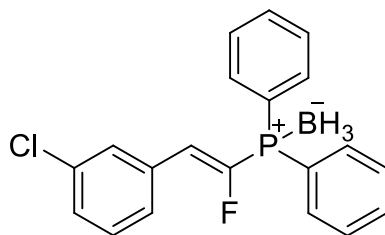


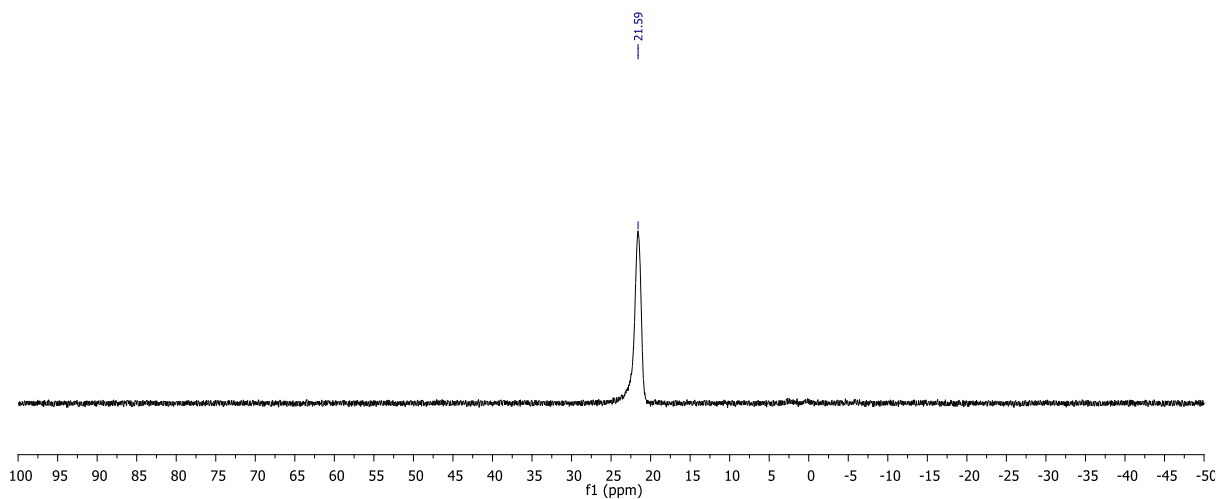
¹¹B NMR in CDCl₃



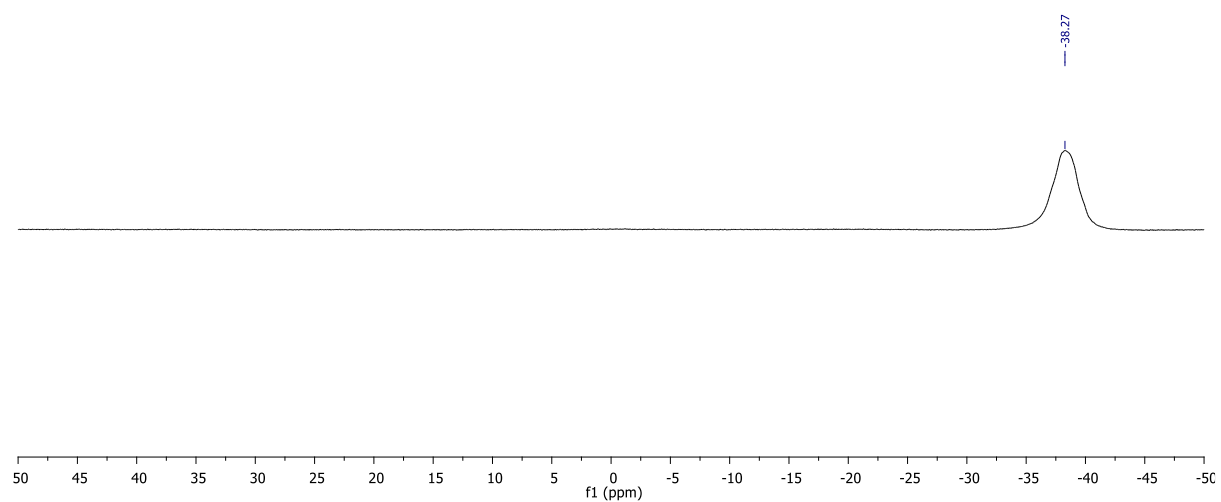
¹³C NMR {¹H} in CDCl₃

(E)-((2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3g

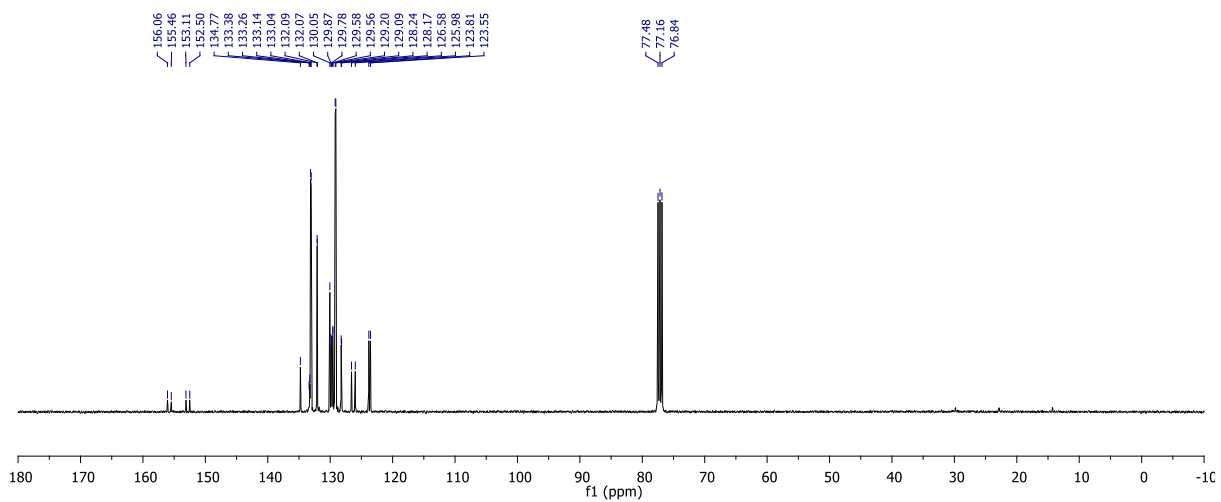




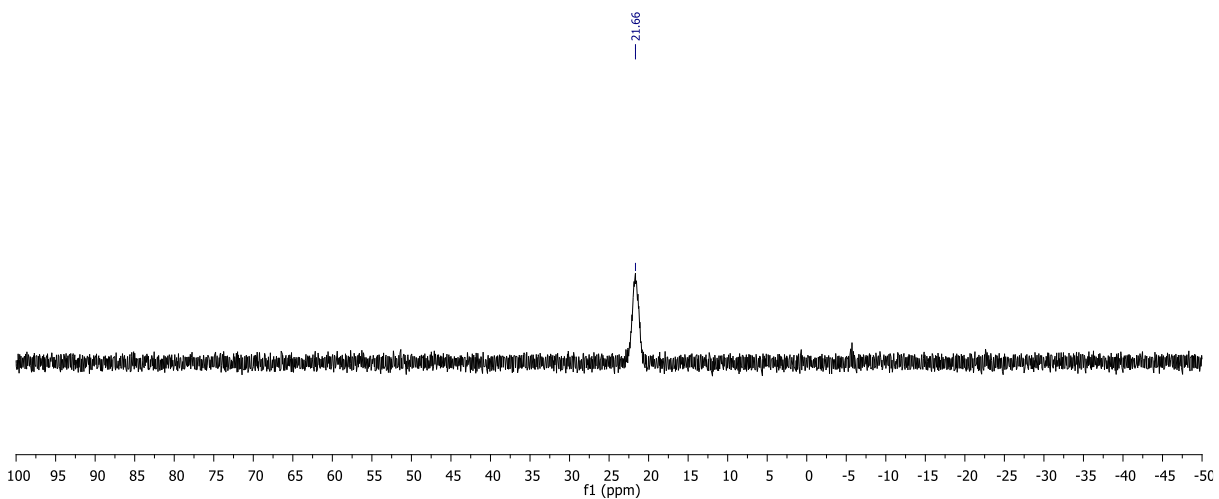
³¹P NMR in CDCl₃



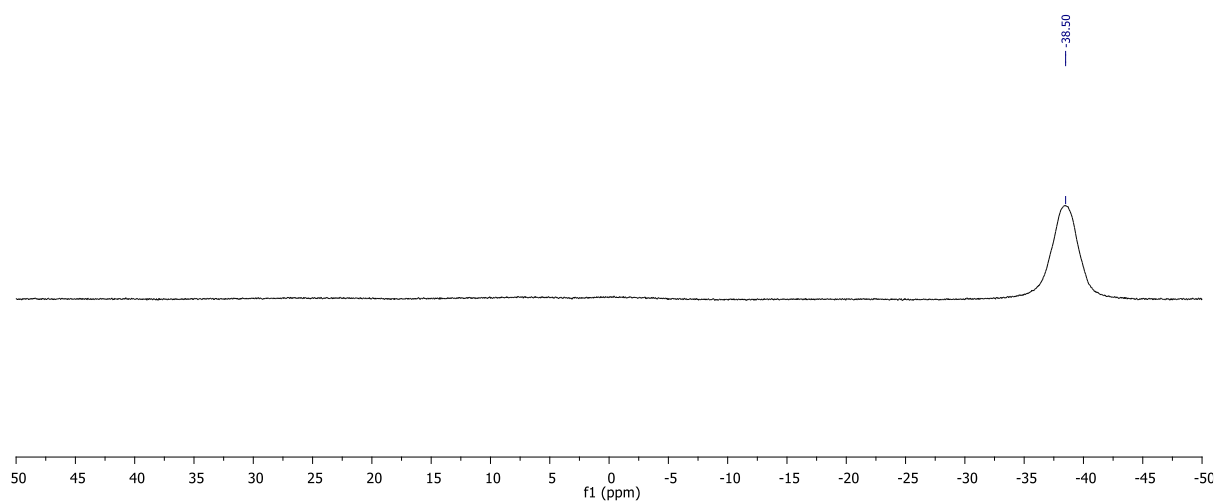
¹¹B NMR in CDCl₃



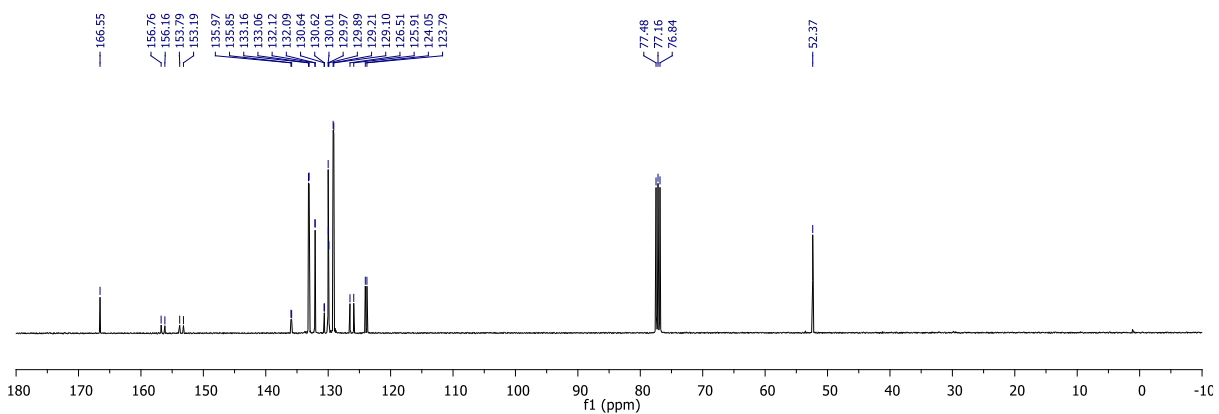
¹³C NMR {¹H} in CDCl₃



^{31}P NMR in CDCl_3

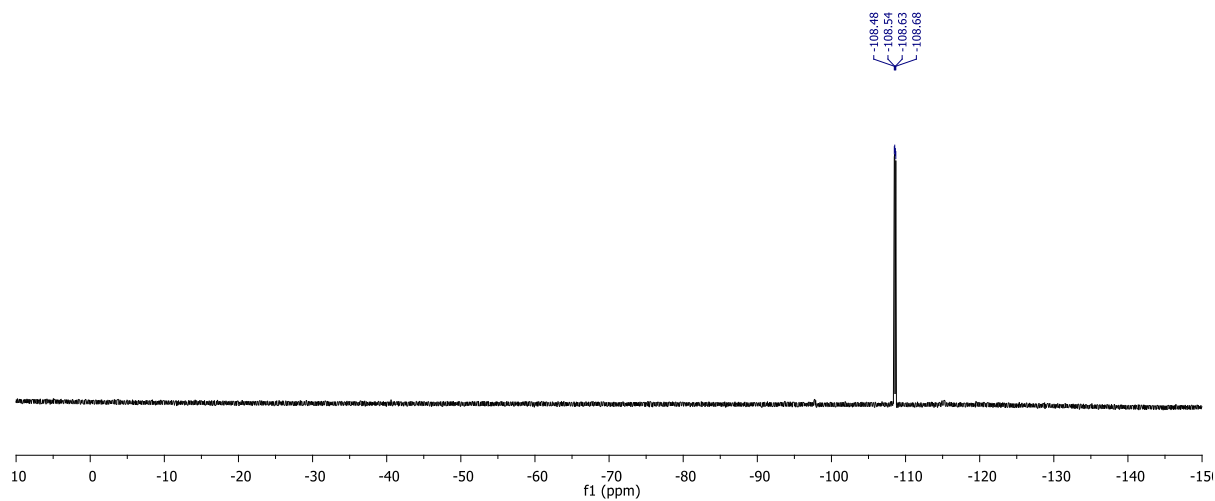
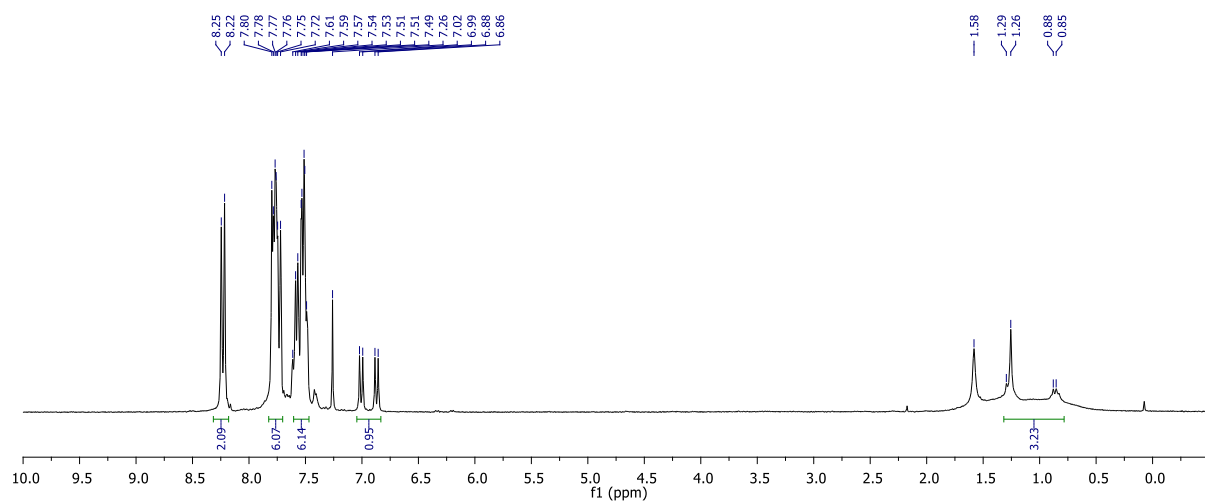
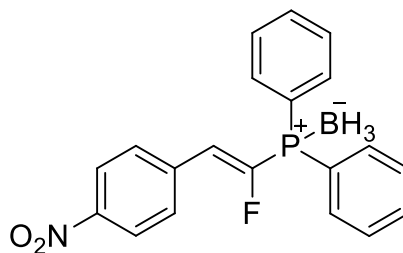


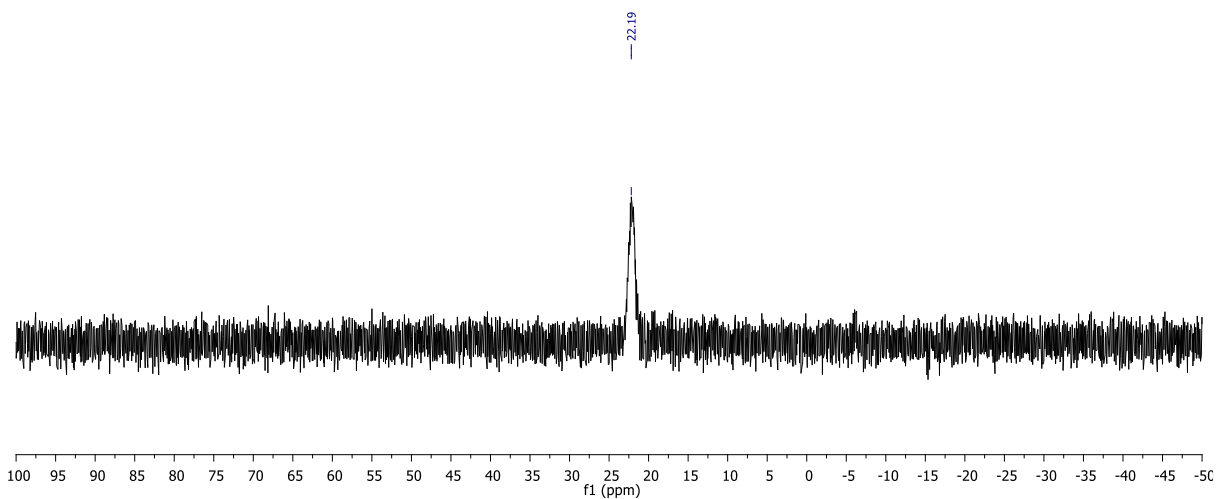
^{11}B NMR in CDCl_3



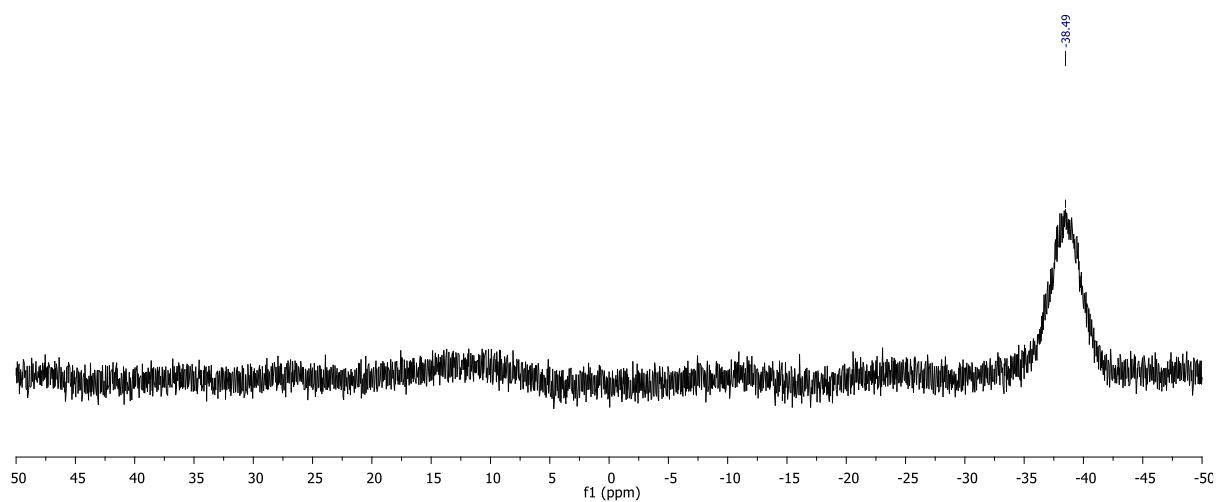
^{13}C NMR (^1H) in CDCl_3

(E)-((2-(4-Nitrophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3i

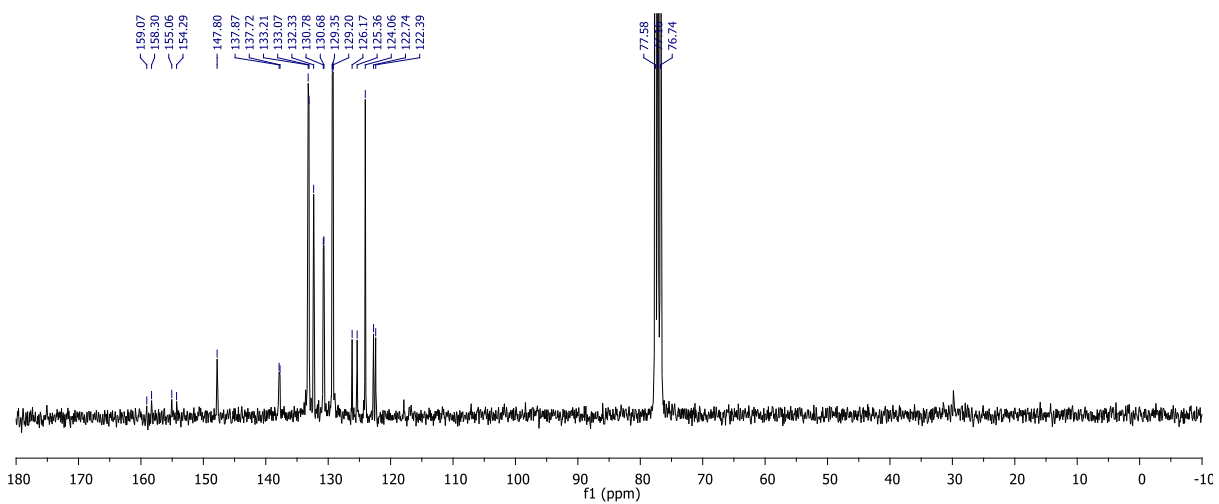




^{31}P NMR in CDCl_3

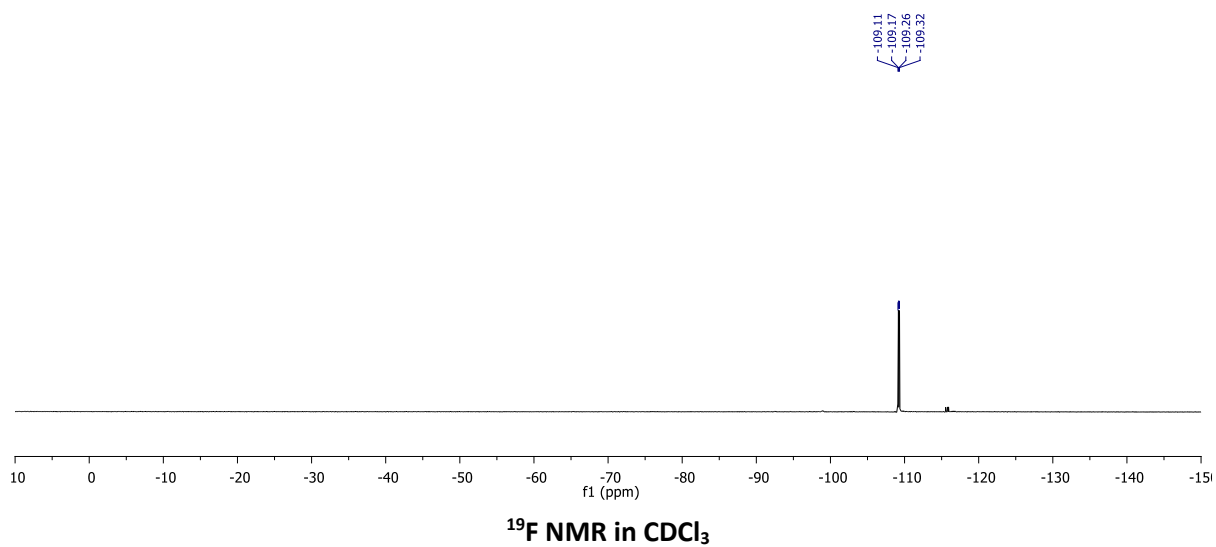
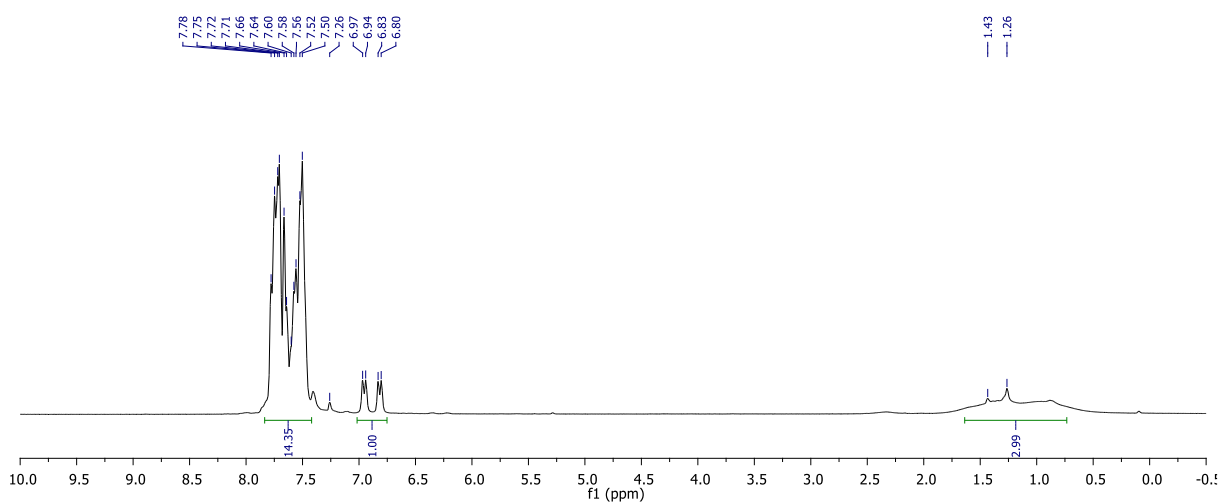
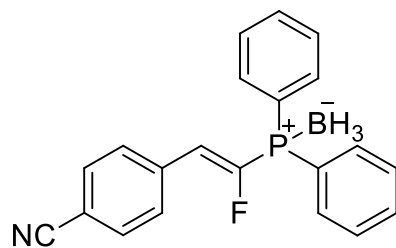


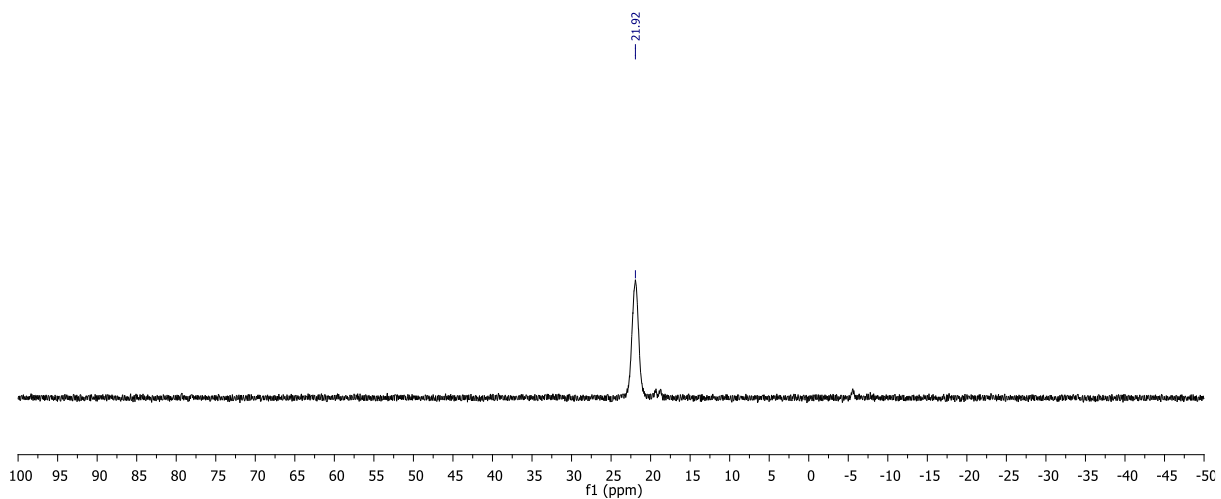
^{11}B NMR in CDCl_3



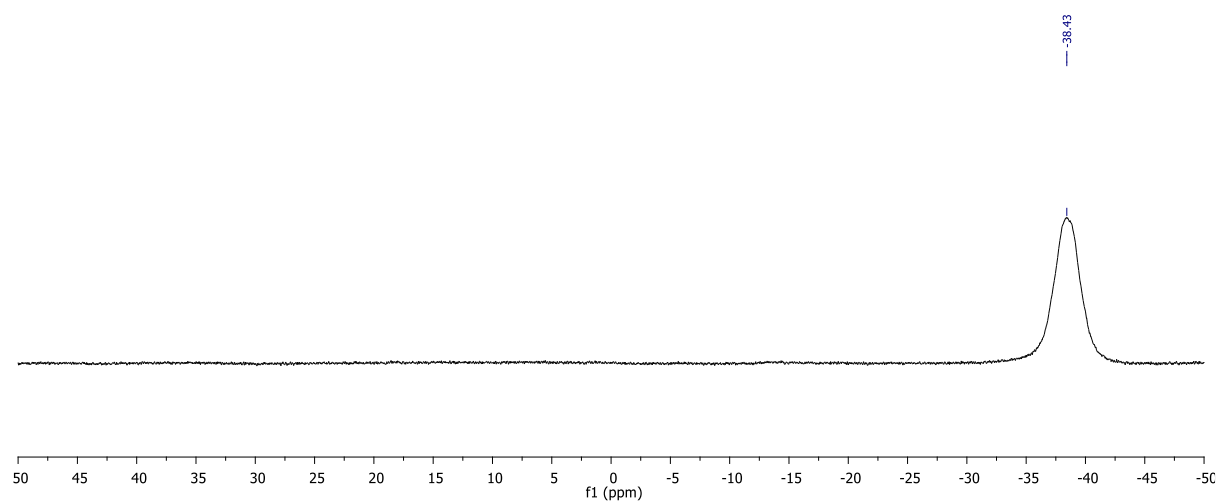
^{13}C NMR $\{^1\text{H}\}$ in CDCl_3

(E)-((2-(4-Cyanophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate 3j

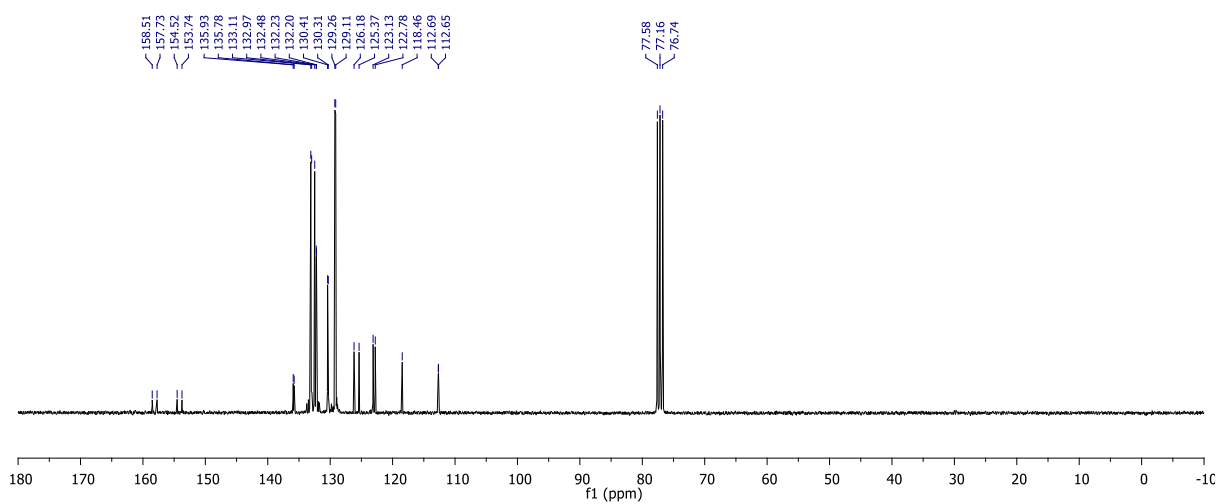




^{31}P NMR in CDCl_3



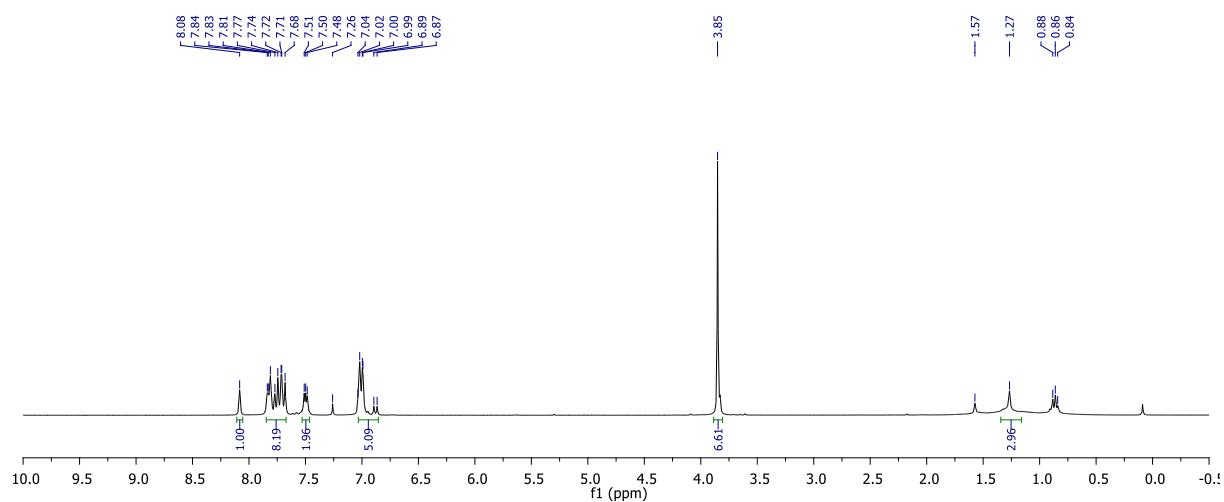
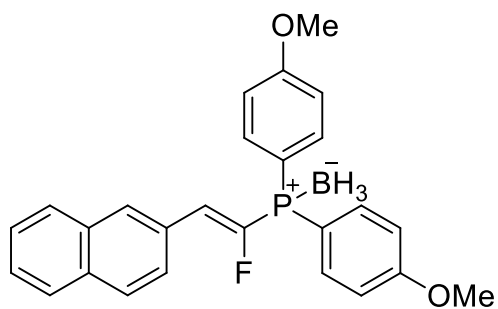
^{11}B NMR in CDCl_3



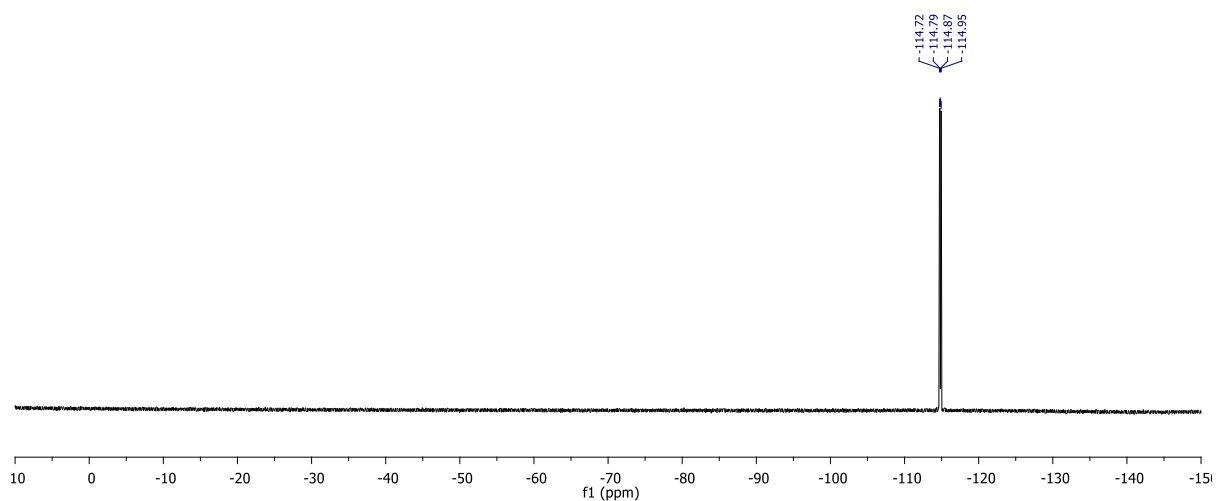
^{13}C NMR $\{^1\text{H}\}$ in CDCl_3

(E)-((1-Fluoro-2-(naphth-2-yl)vinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate

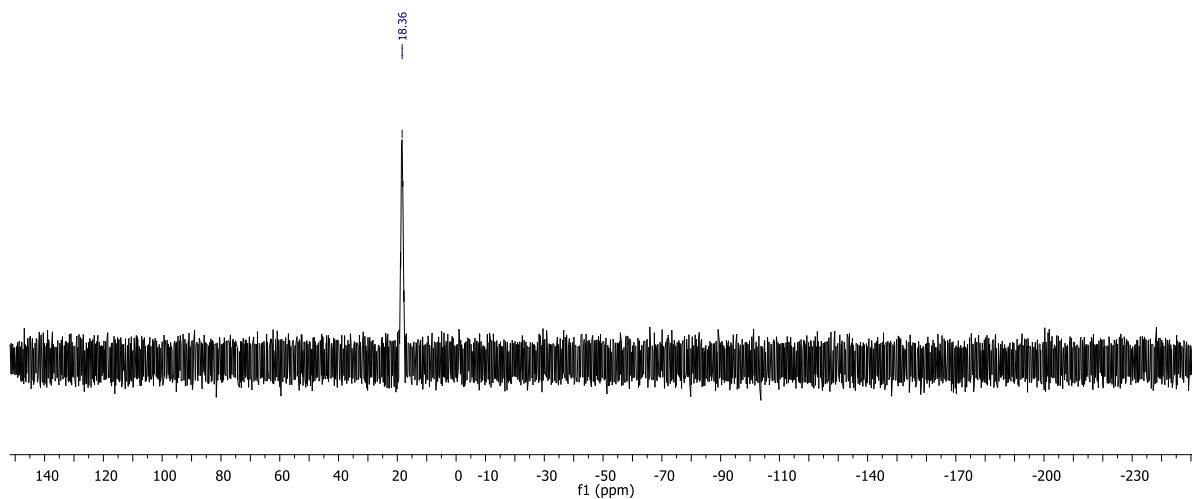
3k



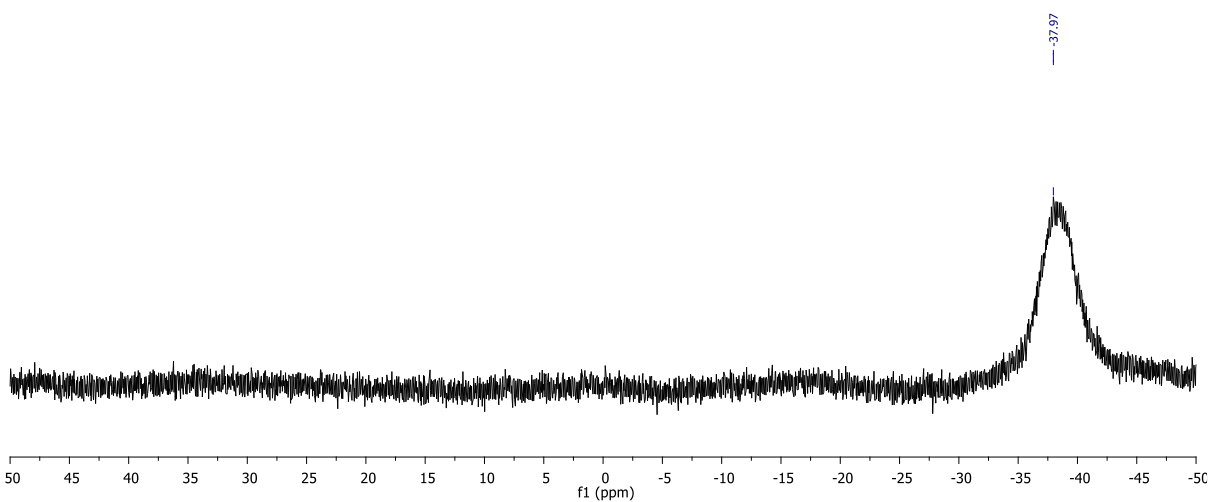
¹H NMR in CDCl₃



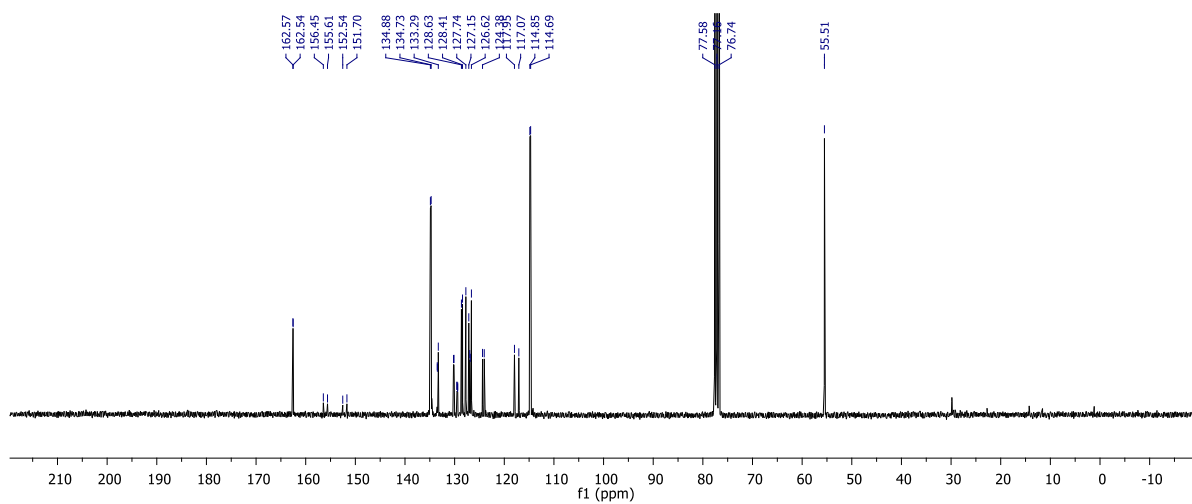
¹⁹F NMR in CDCl₃



^{31}P NMR in CDCl_3

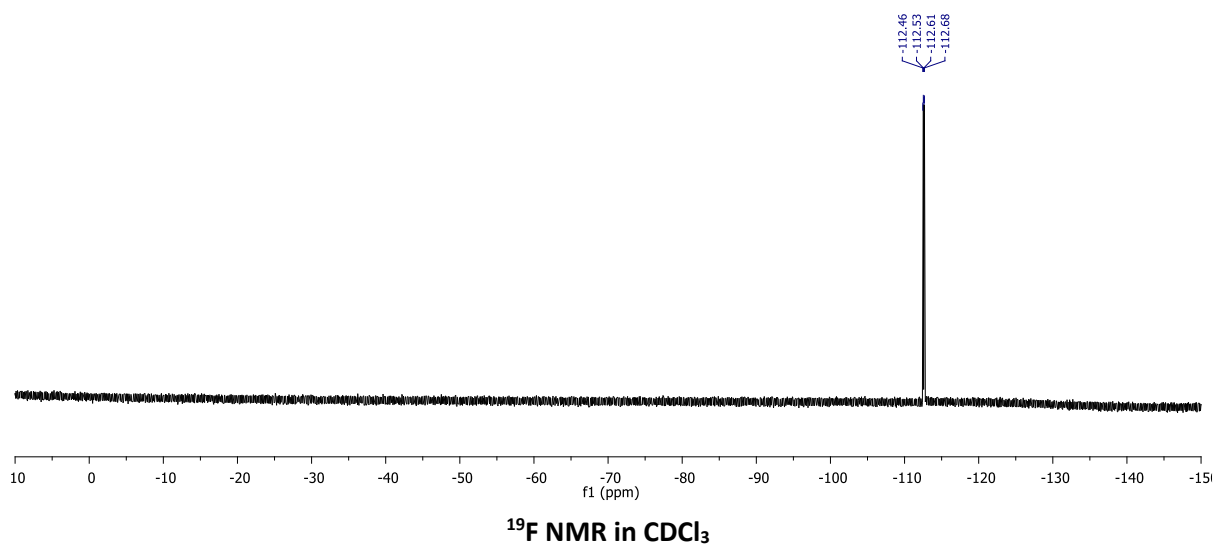
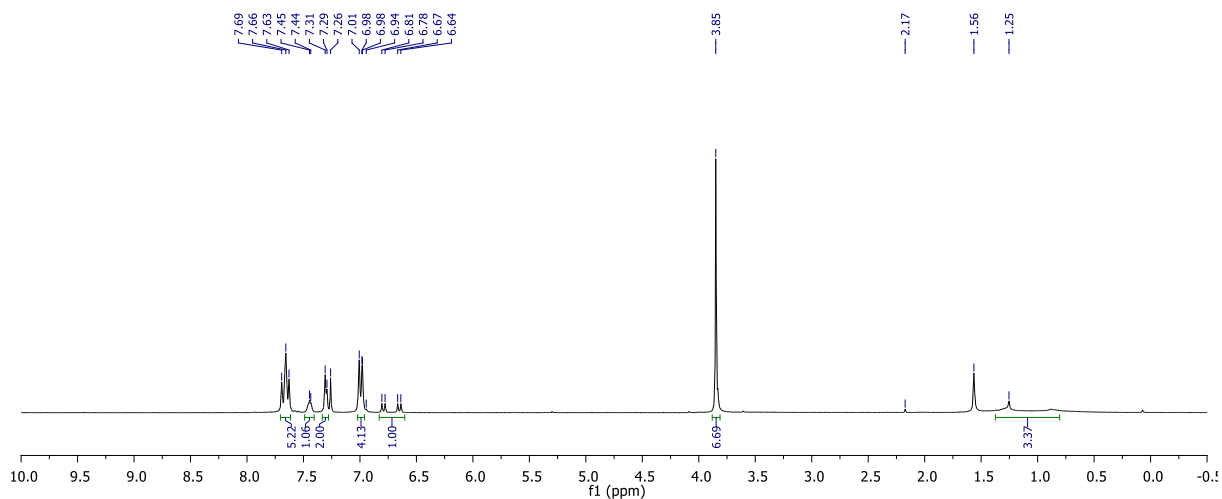
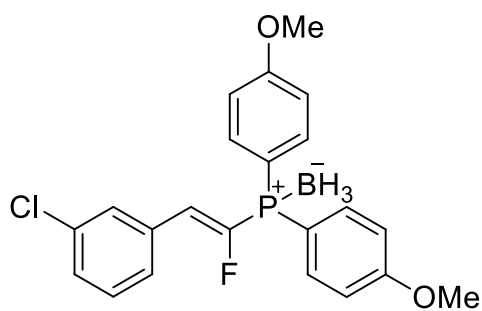


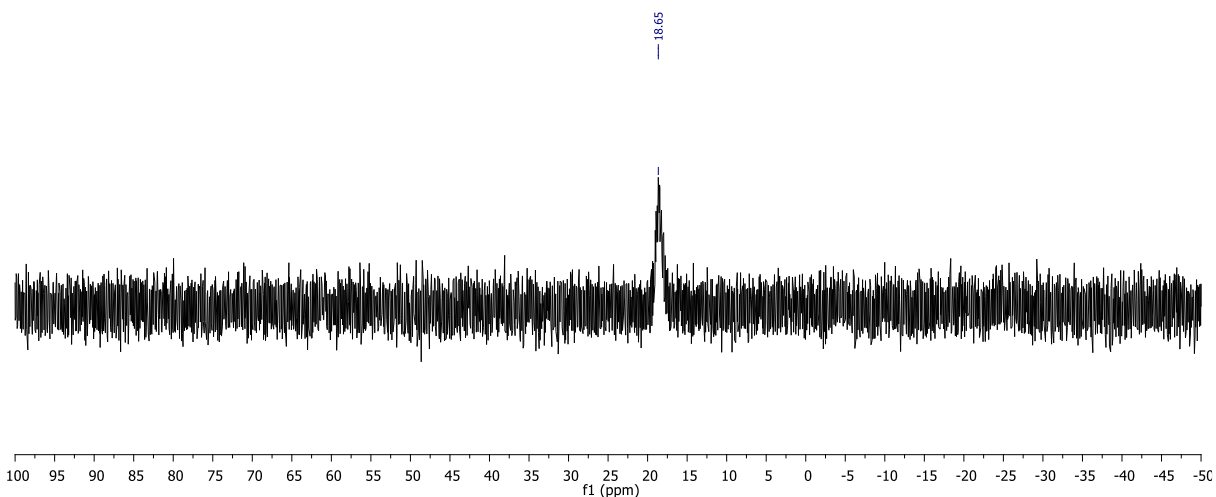
^{11}B NMR in CDCl_3



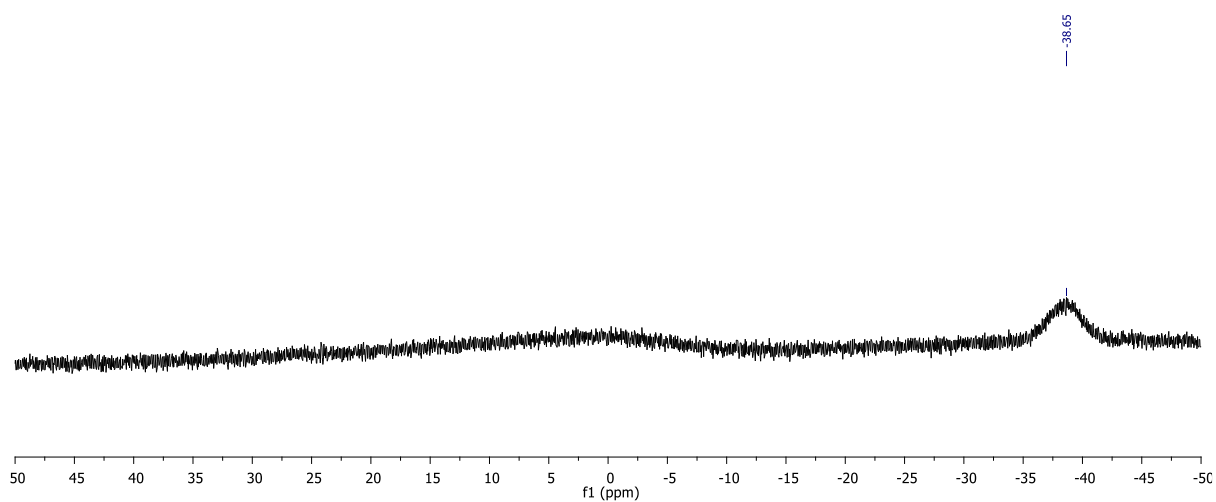
^{13}C NMR (^1H) in CDCl_3

(E)-((2-(3-Chlorophenyl)-1-fluorovinyl)-bis(4-methoxyphenyl)phosphonio)trihydroborate 3l

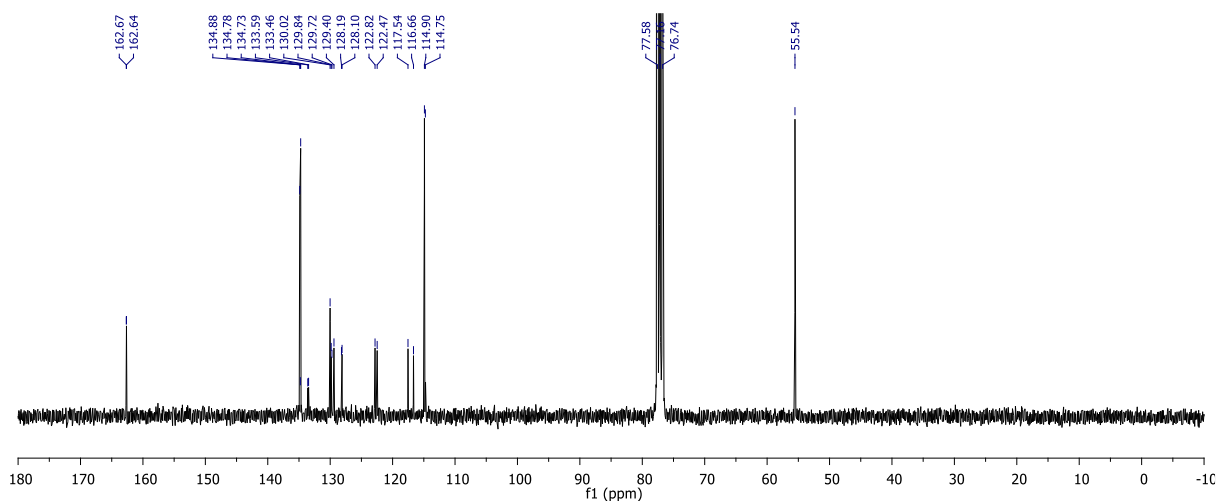




^{31}P NMR in CDCl_3

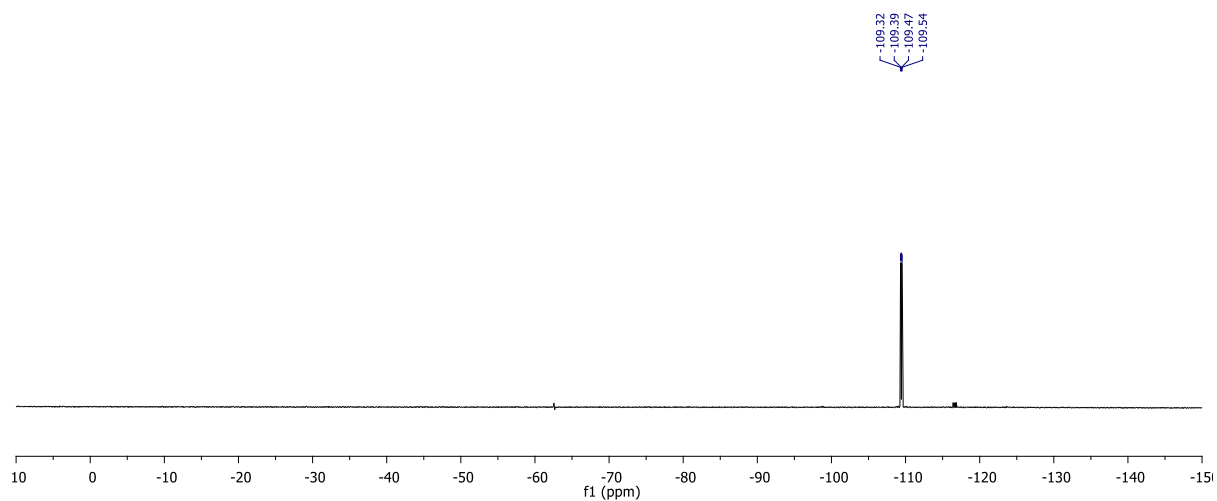
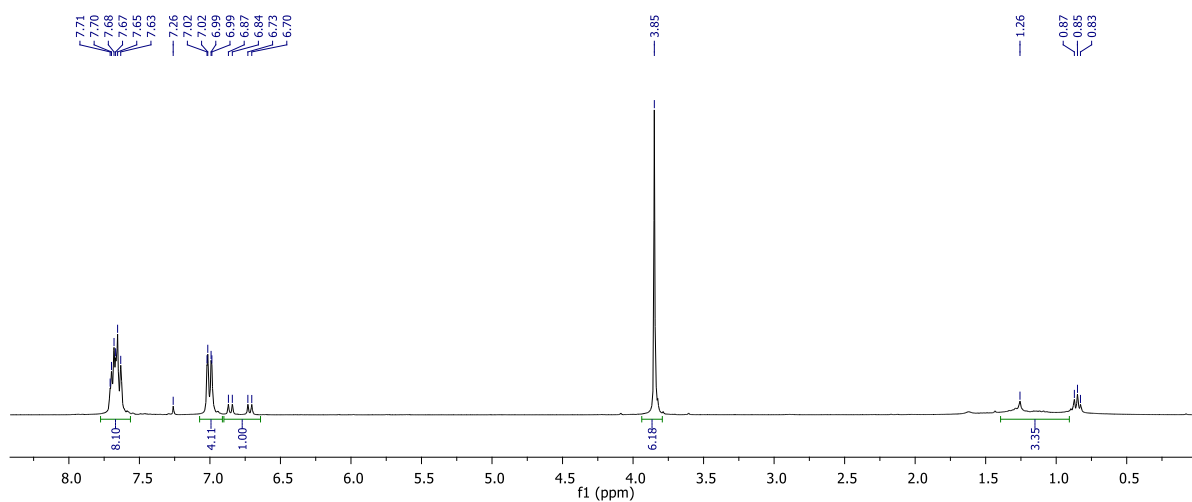
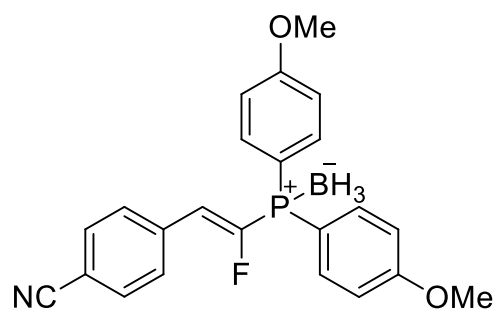


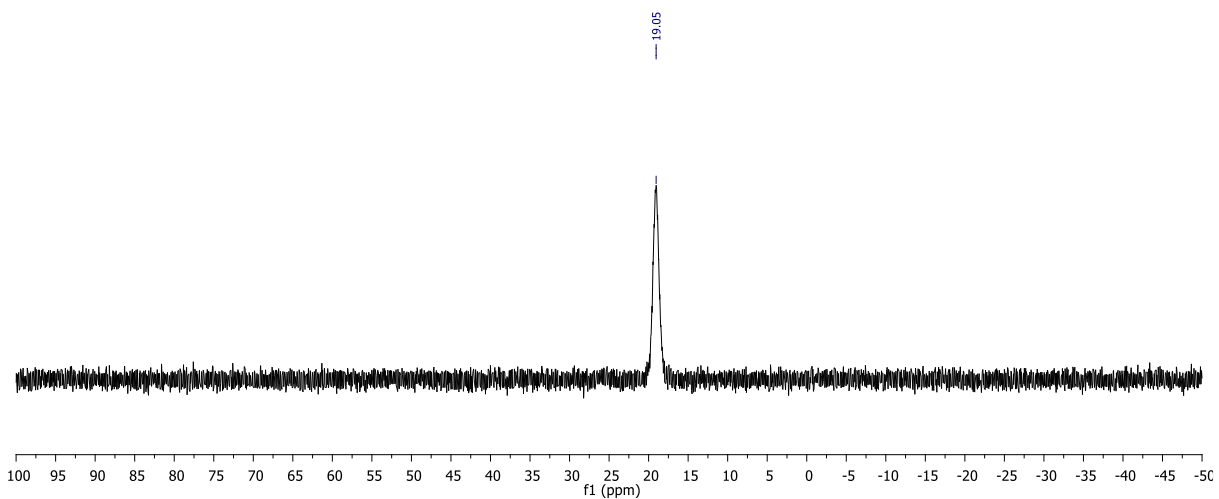
^{11}B NMR in CDCl_3



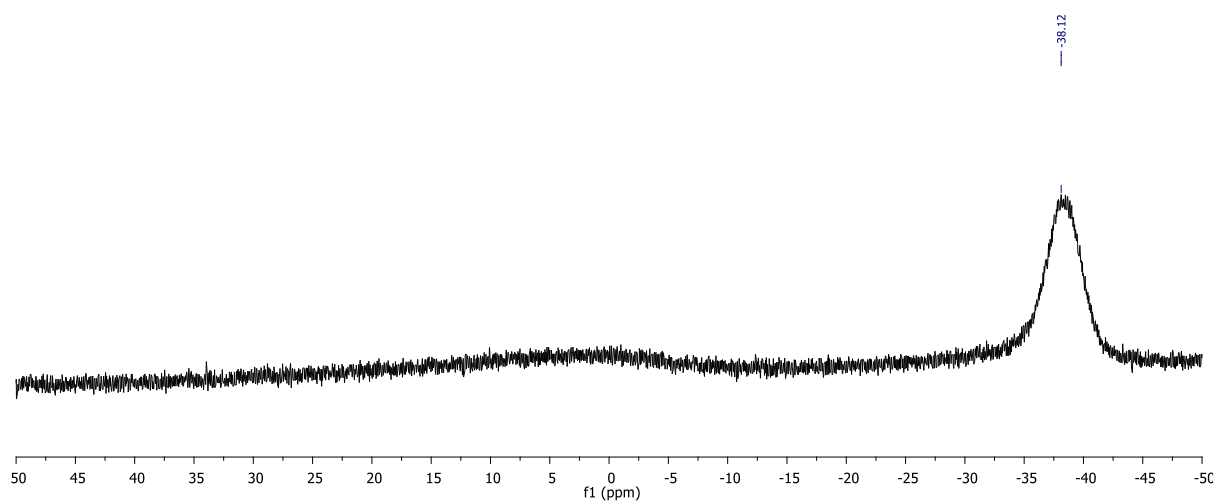
^{13}C NMR $\{^1\text{H}\}$ in CDCl_3

(E)-((2-(4-Cyanophenyl)-1-fluorovinyl) bis(4-methoxyphenyl)phosphonio)trihydroborate
3m

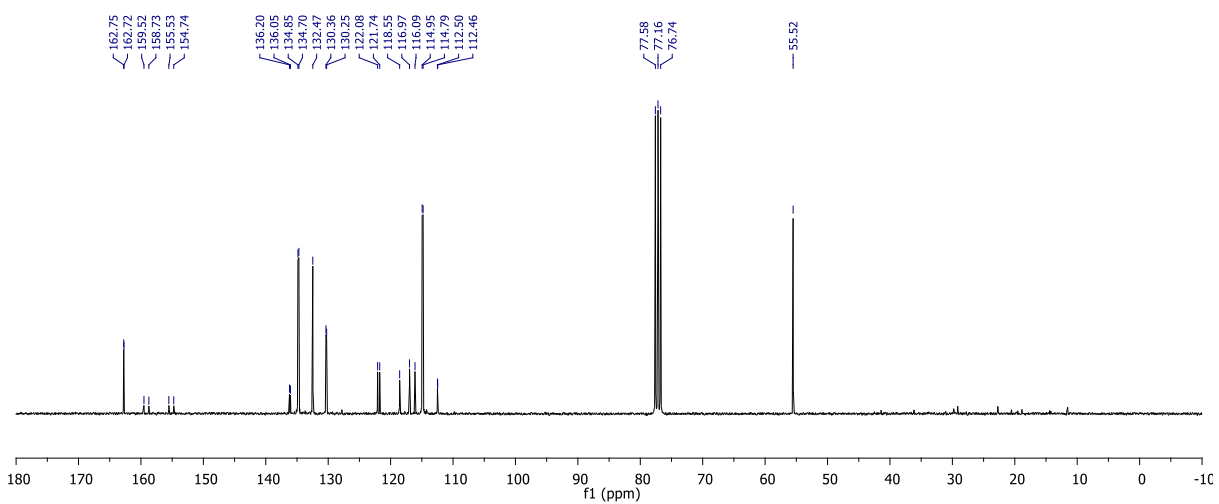




^{31}P NMR in CDCl_3

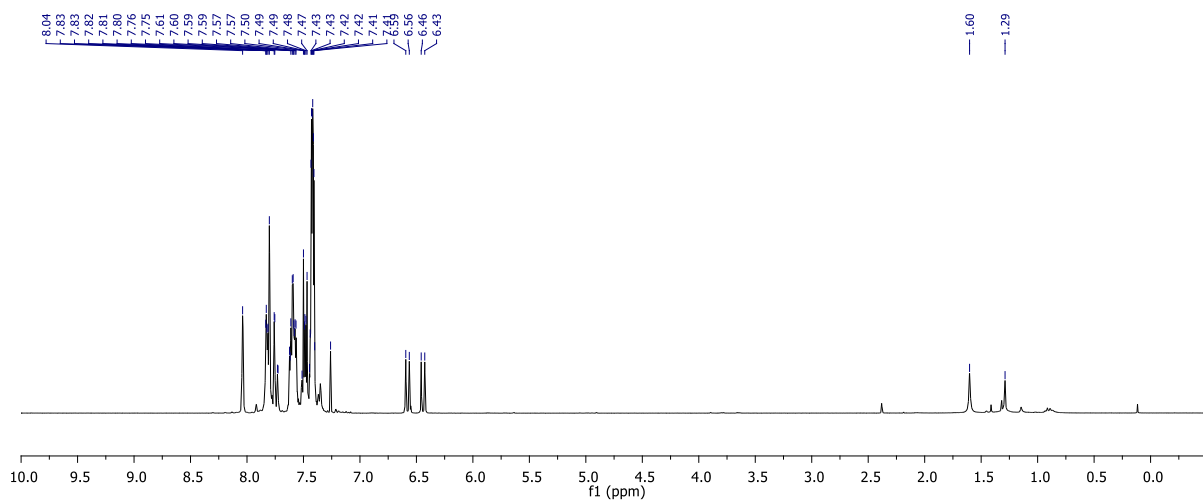
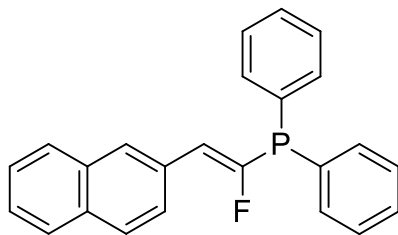


^{11}B NMR in CDCl_3

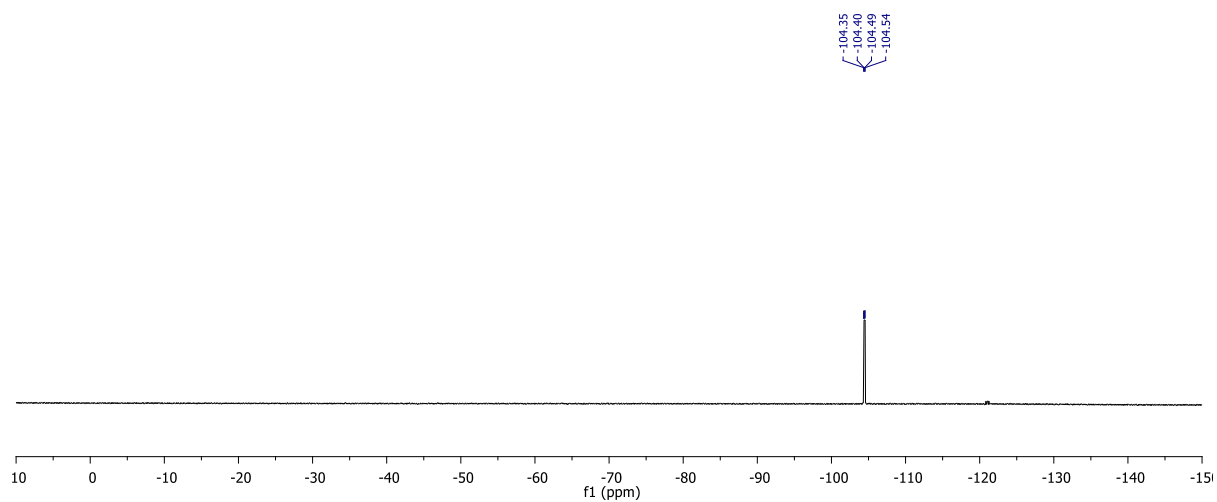


^{13}C NMR $\{^1\text{H}\}$ in CDCl_3

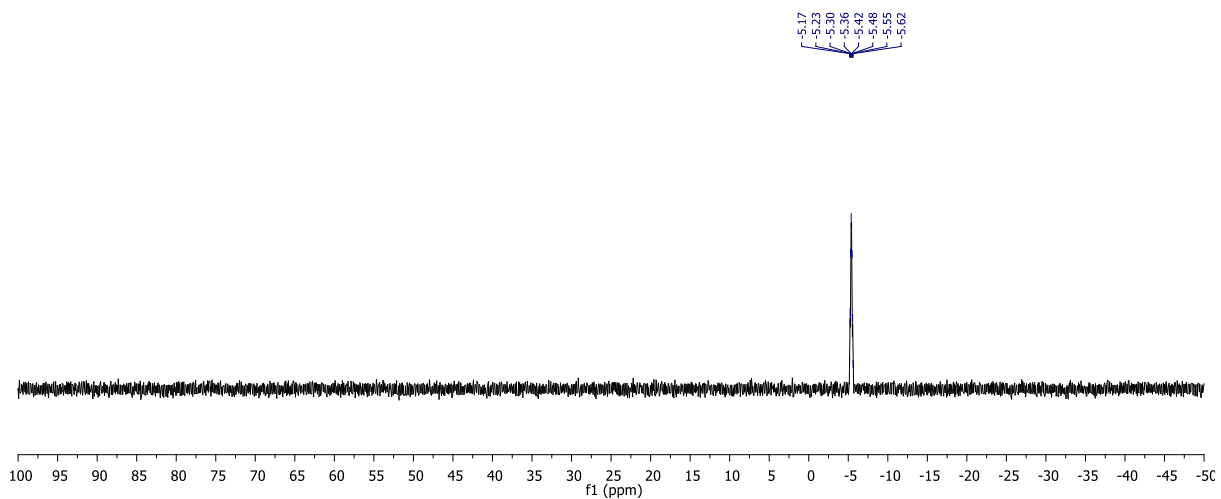
(E)-(1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphine 3a'



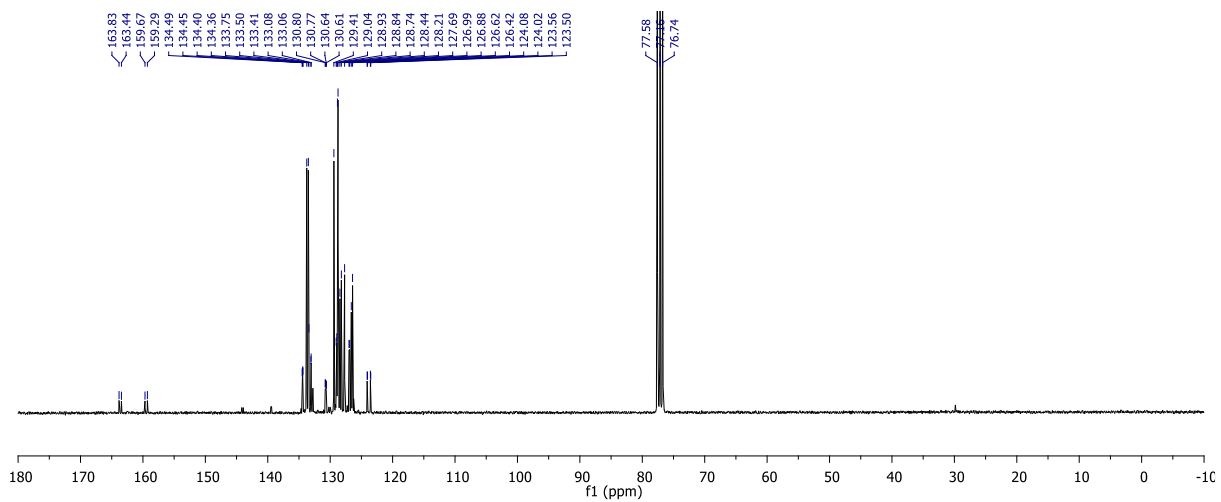
^1H NMR in CDCl_3



^{19}F NMR in CDCl_3

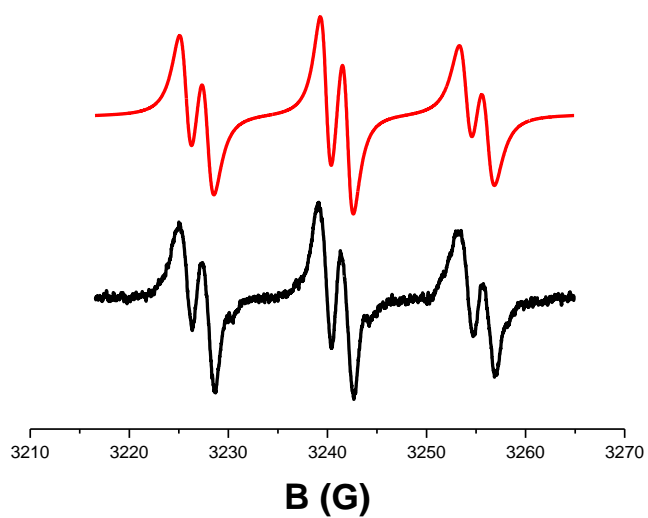
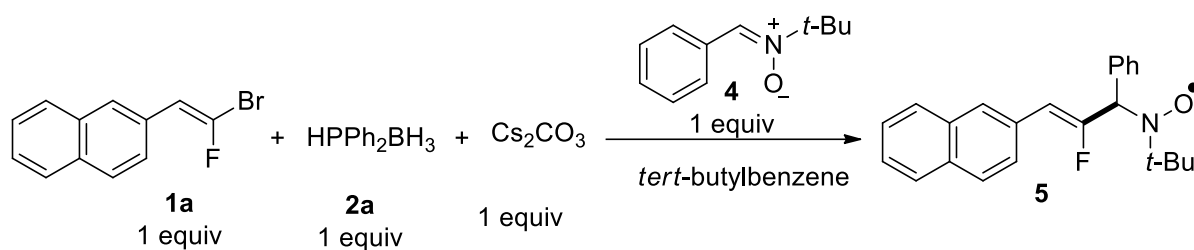


^{31}P NMR in CDCl_3



^{13}C NMR ($\{^1\text{H}\}$) in CDCl_3

6. Electron paramagnetic resonance (EPR) experiment



$$a_N = 14.5; a_H = 2.3 \text{ G}$$

7. X-Ray structures

(E)-((1-Fluoro-2-(naphth-2-yl)vinyl)diphenylphosphonio)trihydroborate **3a**

Hydrogen atoms are omitted for clarity.

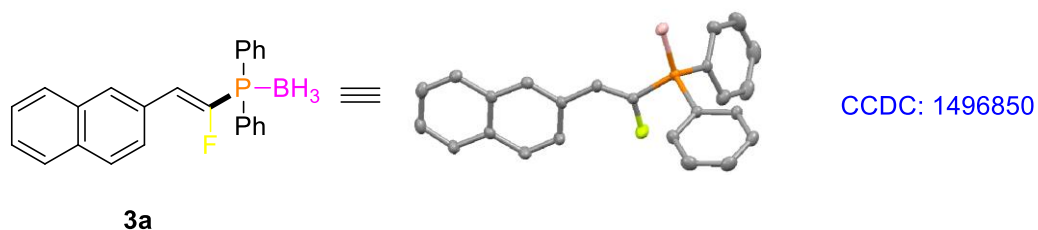


Figure 1 : X-Ray Structure of **3a**

(E)-((2-(4-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate **3f**

Hydrogen atoms are omitted for clarity.

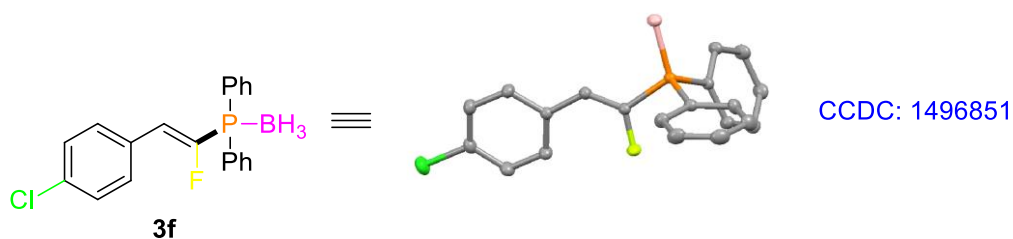


Figure 2 : X-Ray Structure of **3f**

(E)-((2-(3-Chlorophenyl)-1-fluorovinyl)diphenylphosphonio)trihydroborate **3g**

Hydrogen atoms are omitted for clarity.

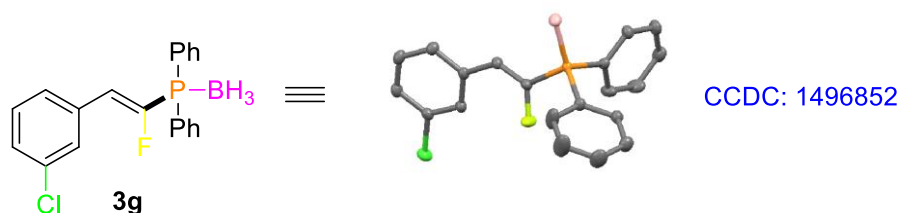


Figure 3 : X-Ray Structure of **3g**