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Supporting Information

for

Silver-catalyzed synthesis of β-fluorovinylphosphonates by phosphonofluorination of aromatic alkynes

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Experimental procedures, full characterization of products, and NMR spectra

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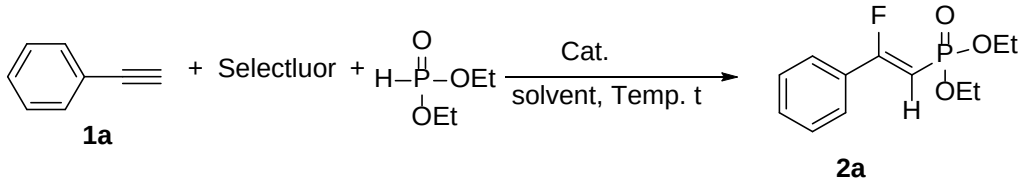
Catalyst screening



1a **2a**

entry	catalyst	yield (%)[a]
1	CuI	trace
2	$AuCl_3$	9%
3	$(MeCN)_2PdCl_2$	no reaction
4	$[Rh(OH)(COD)]_2$	no reaction
5	$Cu(MeCN)_4PF_4$	3%
6	CuOAc	trace

[a]Yields determined by ^1H NMR analysis with an internal standard (diethyl phthalate).

2 General Information

All reagents were obtained from commercial sources and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). ^{1}H NMR spectra were obtained at 400 MHz and recorded relative to the tetramethylsilane signal (0 ppm) or residual proton solvent. ^{13}C NMR spectra were obtained at 100 MHz, and chemical shifts were recorded relative to the solvent resonance ($CDCl_3$, 77.16ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ, ppm) and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration).

General procedure for the silver-catalyzed fluorophosphorylation of alkynes

In a vial, **1a** (20.4 mg, 0.2 mmol), Selectfluor® (141.7 mg, 0.4 mmol), diethyl phosphonate (55.2 mg, 0.4 mmol), and silver acetate (3.3 mg, 0.02 mmol) were dissolved in DEC/H_2O 1 mL:1 mL. The resulting mixture was stirred under N_2 atmosphere at 60 °C for 24 h. After completion, the reaction was quenched, and the suspension was extracted with CH_2Cl_2. Volatile solvent was evaporated in vacuo, and the residual oil was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate to afford the fluorine product **2a**. Note: A single *Z*-isomer of the product **2a** was established by comparison with previous reports [1,2].

Diethyl (*Z*)-(2-fluoro-2-phenylvinyl)phosphonate (2a)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (40.9 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.51-7.42 (m, 3H), 5.51 (dd, *J* = 25.6, 3.3 Hz, 1H), 4.05-3.95 (m, 4H), 1.20-1.17 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (dd, *J* = 272.8, 26.0 Hz), 131.5, 130.4 (d, *J* = 28.7 Hz), 128.83 128.78, 128.2, 95.2 (dd, *J* = 202.3, 22.5 Hz), 62.3, 62.2, 16.23, 16.16; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.9 (dd, *J* = 72.9, 25.6 Hz, 1F); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.5 (d, *J* = 72.7 Hz, 1P); HR-MS *m/z*: Calcd for $C_{12}H_{17}FO_3P$ $[M + H]^+$ calcd. 259.0905 found 259.0896

Diethyl (*Z*)-(2-fluoro-2-(*p*-tolyl)vinyl)phosphonate (2b)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (37.0 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.44 (dd, *J* = 26.0, 3.6 Hz, 1H), 4.05-3.96 (m, 4H), 2.39 (s, 3H), 1.20 (t, J = 7.0 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1 (dd, *J* = 272.0, 26.3Hz), 142.0, 128.9, 128.7 (d, *J* =6.0 Hz), 127.5 (d, *J* = 29.4 Hz), 94.3 (dd, *J* = 203.1, 23.2 Hz), 62.2, 62.1, 21.7, 16.24, 16.17; ^{19}F (376 MHz, $CDCl_3$) δ -67.0 (dd, *J* = 73.7, 25.9 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.9 (d, *J* = 72.7 Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{19}FO_3P$ $[M + H]^+$ calcd. 273.1061 found 273.1053

Diethyl (*Z*)-(2-fluoro-2-(*m*-tolyl)vinyl)phosphonate (2c)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE:EA=10:1) to give a colorless oil (36.4 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.34-7.30 (m, 2H), 5.48 (dd, *J* = 25.2, 3.2 Hz, 1H), 4.05-3.95 (m, 4H), 2.39 (s, 3H), 1.19 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ170.1 (dd, *J* = 272.9, 26.1 Hz), 137.9, 132.3, 130.4 (d, *J* = 28.9 Hz), 129.2 (d, *J* = 5.8Hz), 128.1, 126.1 (d, *J* = 6.2 Hz), 95.1 (dd, *J* = 203.3, 22.6 Hz), 62.22, 62.16, 21.5, 16.25, 16.19; ^{19}F (376 MHz, $CDCl_3$) δ -66.6 (dd, *J* = 72.9, 25.2 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.7 (d, *J* = 73.2 Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{19}FO_3P$ $[M + H]^+$ calcd. 273.1061 found 273.1050

Diethyl (*Z*)-(2-(4-(*tert*-butyl)phenyl)-2-fluorovinyl)phosphonate (2d)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (47.1 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.46-7.44 (m, 2H), 5.45 (dd, *J* = 25.6, 3.2 Hz, 1H), 4.05-3.96 (m, 4H), 1.33 (s, 9H), 1.19 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1 (dd, *J* = 271.8, 26.2 Hz), 155.1, 128.6 (d, *J* = 6.1 Hz), 127.4 (dd, *J* = 28.8, 1.4 Hz), 125.2, 94.2 (dd, *J* = 202.6, 23.0 Hz), 62.2, 62.1, 35.1, 31.2, 16.2, 16.1; ^{19}F (376 MHz, $CDCl_3$) δ -67.2 (dd, *J* = 73.3, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.8 (d, *J* = 73.4 Hz, 1P); HR-MS *m/z*: Calcd for $C_{16}H_{25}FO_3P$ $[M + H]^+$ calcd. 315.1531 found 315.1543

Diethyl (*Z*)-(2-fluoro-2-(4-methoxyphenyl)vinyl)phosphonate (2e)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (34.6 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.38 (dd, *J* = 26.0, 3.2 Hz, 1H), 4.05-3.98 (m, 4H), 3.85 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (dd, J = 270.5, 26.5Hz), 162.1, 130.6 (d, *J* = 6.7 Hz), 122.6 (dd, *J* = 29.2, 1.4 Hz), 113.6, 92.9 (dd, *J* = 202.9, 23.7 Hz), 62.2, 62.1, 55.5, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -67.4 (dd, *J* = 74.1, 26.3 Hz, 1F); ^{31}P (162

MHz, $CDCl_3$) δ 16.3 (d, *J* = 74.0 Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{19}FO_4P$ $[M + H]^+$ calcd. 289.1010 found 289.1001

Diethyl (*Z*)-(2-([1,1'-biphenyl]-4-yl)-2-fluorovinyl)phosphonate (2f)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (46.1 mg, 69%).

^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.68-7.61 (m, 4H), 7.49-7.45 (m, 2H), 7.41-7.37 (m, 1H), 5.52 (dd, *J* = 26.0, 3.2 Hz, 1H), 4.08-4.00 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6 (dd, J = 271.4, 26.1Hz), 144.2, 140.1, 129.3 (d, *J* = 6.3 Hz), 129.1, 128.2, 127.3, 126.9, 95.0 (dd, *J* = 202.4, 22.8 Hz), 62.31, 62.25, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -67.8 (dd, *J* = 72.9, 25.9 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.6 (d, *J* = 72.9 Hz, 1P); HR-MS *m/z*: Calcd for $C_{18}H_{21}FO_3P$ $[M + H]^+$ calcd. 335.1218 found 335.1209

Diethyl (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl)phosphonate (2g)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (42.5 mg, 77%).

^1H NMR (400 MHz, $CDCl_3$) δ7.87-7.84 (m, 2H), 7.14-7.10 (m, 2H), 5.49 (dd, *J* = 25.6, 2.8 Hz, 1H), 4.06-3.97 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7(dd, *J* = 271.6, 26.0Hz), 164.6 (dd, *J* = 253.9, 1.1Hz), 131.2 (ddd, *J* = 8.8, 6.3, 0.8 Hz), 126.6 (ddd, J = 29.5, 3.2, 1.6Hz), 115.5 (d, *J* = 22.1 Hz), 95.2 (dd, *J* = 202.3, 22.6Hz), 62.3, 62.2, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) -107.43- -107.36 (m, 1F), δ -66.8 (dd, *J* = 72.6, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.3 (d, *J* = 72.6 Hz, 1P); HR-MS *m/z*: Calcd for $C_{12}H_{16}F_2O_3P$ $[M + H]^+$calcd. 277.0811 found 277.0800

Diethyl (*Z*)-(2-fluoro-2-(3-fluorophenyl)vinyl)phosphonate (2h)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (44.1 mg, 80%).

^1H NMR (400 MHz, $CDCl_3$) δ7.66 (d, *J* = 8.0 Hz, 1H), 7.54 (dt, *J* = 11.6, 1.6 Hz, 1H), 7.44-7.39(m, 1H), 7.19 (td, *J* = 8.4, 2.4 Hz, 1H), 5.56 (dd, *J* = 25.6, 2.8 Hz, 1H), 4.08-3.99 (m, 4H), 1.22 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) 168.1 (ddd, *J* = 272.1, 25.5, 2.5Hz), 162.2 (d, *J* = 247.8 Hz), 132.3 (ddd, *J* = 29.7, 8.2, 1.5 Hz), 130.8(d, *J* = 8.8 Hz), 129.9 (d, *J* = 8.1Hz), 124.8 (q, *J* = 2.3 Hz), 118.5 (d, *J* =21.2 Hz), 115.8 (dd, *J* = 327.2, 21.6 Hz), 115.8 (dd, *J* = 24.0, 6.0 Hz), 96.4 (dd, *J* = 202.1, 21.9Hz), 62.4, 62.3, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) -112.27-112.20 (m, 1F), δ -67.9 (dd, *J* = 71.8, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 14.7 (d, *J* = 71.9 Hz, 1P);

HR-MS *m/z*: Calcd for $C_{12}H_{16}F_2O_3P$ [M + H] $^+$calcd. 277.0811 found 277.0796

Diethyl (*Z*)-(2-(4-chlorophenyl)-2-fluorovinyl)phosphonate (2i)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (48.5 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.79 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.52 (dd, *J* = 26.0, 2.8 Hz, 1H), 4.07-3.98 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (dd, *J* = 271.6, 25.9 Hz), 137.8, 130.2 (dd, *J* = 6.1, 0.8 Hz), 128.8 (dd, *J* = 29.5, 1.7 Hz), 128.6, 95.8 (dd, *J* = 202.0, 22.2 Hz), 62.4, 62.3, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -67.9 (dd, *J* = 71.8, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.0 (d, *J* = 72.1Hz, 1P); HR-MS *m/z*: Calcd for $C_{12}H_{16}ClFO_3P$ [M + H] $^+$calcd. 293.0515 found 293.0521

Diethyl (*Z*)-(2-(3-chlorophenyl)-2-fluorovinyl)phosphonate (2j)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (41.5 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.79-7.74 (m, 2H), 7.47-7.45 (m, 1H), 7.40-7.36(m, 1H), 5.56 (dd, *J* = 25.6, 2.0 Hz, 1H), 4.07-3.97 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 (dd, *J* = 272.6, 25.4 Hz), 134.3, 132.0 (dd, *J* = 29.4, 1.3 Hz), 131.5, 129.6, 127.9 (dd, *J* = 160.5, 6.1Hz), 96.6 (dd, *J* = 202.1, 21.7 Hz), 62.4, 62.4, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -68.1 (dd, *J* = 71.4, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 14.7 (d, *J* = 71.6Hz, 1P); HR-MS *m/z*: Calcd for $C_{12}H_{16}ClFO_3P$ [M + H] $^+$calcd. 293.0515 found 293.0505

Diethyl (*Z*)-(2-(2-chlorophenyl)-2-fluorovinyl)phosphonate (2k)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (32.7 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.57-7.56 (m, 1H), 7.46-7.40 (m, 2H), 7.35-7.31(m, 1H), 5.68 (dd, *J* = 20.8, 5.2 Hz, 1H), 4.02-3.86 (m, 4H), 1.17 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1 (dd, *J* = 279.0, 24.8Hz), 133.3, 132.4, 132.1 (d, *J* = 2.3 Hz), 130.5 (dd, *J* = 25.6, 1.7 Hz), 129.6 (d, *J* = 1.9 Hz), 99.4 (dd, *J* = 200.5, 19.7 Hz), 62.14, 62.10, 16.22, 16.15; ^{19}F (376 MHz, $CDCl_3$) δ -69.1 (dd, *J* = 66.6, 21.1 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 13.7 (d, *J* = 66.7 Hz, 1P); HR-MS *m/z*: Calcd for $C_{12}H_{16}ClFO_3P$ [M + H] $^+$calcd. 293.0515 found 293.0507

Diethyl (*Z*)-(2-(4-bromophenyl)-2-fluorovinyl)phosphonate (2l)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The

desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (45.7 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 5.53 (dd, *J* = 25.6, 2.8 Hz, 1H), 4.07-3.98 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6 (dd, *J* = 271.7, 25.6 Hz), 131.6, 130.4 (dd, *J* = 6.1, 0.8Hz), 129.2 (dd, *J* = 29.5, 1.7 Hz), 126.2 (d, *J* = 1.3Hz), 96.0 (dd, *J* = 202.0, 22.2 Hz), 62.4, 62.3, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -68.2 (dd, *J* = 71.8, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 15.0 (d, *J* = 72.1Hz, 1P)； HR-MS *m/z*: Calcd for $C_{12}H_{16}BrFO_3P$ [M + H] $^{+}$ calcd. 336.9926 found 236.9941

Diethyl (*Z*)-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)phosphonate (2m)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 10:1) to give a colorless oil (55.4 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ7.96 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 5.63 (dd, *J* = 25.6, 2.4 Hz, 1H), 4.07-4.00(m, 4H), 1.22 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101MHz, $CDCl_3$) δ 168.0 (dd, *J* = 272.5 25.6 Hz), 133.4 (d, *J* = 66.4, 29.6 Hz), 129.3 (d, *J* = 5.6 Hz), 125.2 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 273.8 Hz), 97.5 (dd, *J* = 201.6, 21.3 Hz), 62.5, 62.4, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -63.2 (s, 1F), -68.2 (dd, *J* = 71.1, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 14.3 (d, *J* = 71.1Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{16}F_4O_3P$ [M + H] $^{+}$ calcd. 327.0779 found 327.0789

Diethyl (*Z*)-(2-(4-cyanophenyl)-2-fluorovinyl)phosphonate (2n)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 3:1) to give a colorless oil (39.1 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 5.66 (dd, *J* = 25.6, 2.0 Hz, 1H), 4.07- 3.99 (m, 4H), 3.95 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (d, *J* = 348.45 Hz), 134.1, 131.8, 129.3 (d, *J* = 5.05 Hz), 117.9, 114.8, 98.1 (dd, *J* = 201.0, 21.2 Hz), 62.42, 62.36, 16.14, 16.07; ^{19}F (376 MHz, $CDCl_3$) δ -69.6 (dd, *J* = 70.3, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 14.3 (d, *J* = 71.1Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{16}FNO_3P$ [M + H] $^{+}$ calcd. 284.0857 found 2 284.0861

Methyl (*Z*)-4-(2-(diethoxyphosphoryl)-1-fluorovinyl)benzoate (2o)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 1:1) to give a colorless oil (46.8 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 5.61

(dd, *J* = 25.6, 2.8 Hz, 1H), 4.08-4.01(m, 4H), 1.24 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4 (dd, *J* = 272.5, 25.5 Hz), 166.3, 134.4 (dd, *J* = 28.0, 1.1 Hz), 132.6, 129.3, 128.9 (d, *J* = 5.8 Hz), 97.2 (dd, *J* = 202.0, 21.7 Hz), 62.4, 62.3, 52.5, 16.3, 16.2; ^{19}F (376 MHz, $CDCl_3$) δ -68.3 (dd, *J* = 71.4, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 14.5 (d, *J* = 71.4Hz, 1P); HR-MS *m/z*: Calcd for $C_{14}H_{19}FO_5P$ $[M + H]^+$ calcd. 317.0960 found 317.0957

Diethyl (*Z*)-(1-fluoro-1-phenylprop-1-en-2-yl)phosphonate (2p)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 3:1) to give a colorless oil (32.6 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.45-7.37 (m, 3H), 4.00-3.82 (m, 4H), 2.05-2.01 (m, 3H), 1.12 (td, *J* = 6.8, 1.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (dd, *J* = 270.4, 33.5 Hz), 132.1 (d, *J* = 28.9 Hz), 130.4, 129.4, 129.3, 127.8, 104.8 (dd, *J* = 193.1, 17.8 Hz), 61.94, 61.88, 16.1, 16.0, 12.5 (dd, *J* = 9.9, 5.1 Hz); ^{19}F (376 MHz, $CDCl_3$) δ -67.8 (d, *J* = 54.1 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 18.7 (d, *J* = 53.8 Hz, 1P); HR-MS *m/z*: Calcd for $C_{13}H_{19}FO_3P$ $[M + H]^+$calcd. 273.1061 found 273.1060

Diethyl (*Z*)-(1-fluoro-1-phenylbut-1-en-2-yl)phosphonate (2q)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 3:1) to give a colorless oil (29.2 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.43-7.39 (m, 3H), 3.99-3.84 (m, 4H), 2.52-2.46 (m, 2H), 1.22 (t, *J* = 7.4 Hz, 3H) 1.11 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ165.7 (dd, *J* = 270.5, 34.4 Hz), 132.2 (dd, *J* = 28.9, 1.6 Hz), 130.4 (d, *J* = 2.1 Hz), 129.4 (dd, *J* = 3.8, 0.9 Hz), 127.8, 111.3 (dd, *J* = 190.0, 6.8 Hz), 61.9, 61.8, 21.0 (dd, *J* = 8.2, 5.2 Hz), 16.14, 16.07, 14.3; ^{19}F (376 MHz, $CDCl_3$) δ -70.4 (d, *J* = 55.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 19.2 (d, *J* = 55.9 Hz, 1P); HR-MS *m/z*: Calcd for $C_{14}H_{21}FO_3P$ $[M + H]^+$calcd. 287.1218 found 287.1219

Dimethyl (*Z*)-(2-fluoro-2-phenylvinyl)phosphonate (3a)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (34.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.52-7.42 (m, 3H), 5.48 (dd, *J* = 25.2, 2.0 Hz, 1H), 3.63 (d, *J* = 11.6Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4 (dd, *J* = 273.4, 26.6 Hz), 131.7, 130.2 (d, *J* = 28.8 Hz), 128.7 (d, *J* = 6.1 Hz), 128.3, 93.8 (dd, *J* = 203.7, 23.3 Hz), 52.72, 52.66; ^{19}F (376 MHz, $CDCl_3$) δ -65.8 (dd, *J* =

72.9, 25.2 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 18.5 (d, *J* = 73.4Hz, 1P); HR-MS *m/z*: Calcd for $C_{10}H_{13}FO_3P$ $[M + H]^+$ calcd. 231.0592 found 231.0595

Dimethyl (*Z*)-(2-fluoro-2-(*p*-tolyl)vinyl) phosphonate (3b)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (29.3 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), δ 7.24 (d, *J* = 8.0 Hz, 2H), 5.42 (dd, *J* = 25.2, 3.2 Hz, 1H), 3.64 (d, *J* = 11.6Hz, 6H) 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (dd, *J* = 272.7, 26.8 Hz), 142.2, 129.0, 128.6 (d, *J* = 6.3 Hz), 127.3 (dd, *J* = 28.8, 1.5 Hz), 92.8 (dd, *J* = 204.0, 23.9 Hz), 52.7, 52.6, 21.7; ^{19}F (376 MHz, $CDCl_3$) δ -65.9 (dd, *J* = 74.1, 25.6 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 18.9 (d, *J* = 74.0Hz, 1P); HR-MS *m/z*: Calcd for $C_{11}H_{15}FO_3P$ $[M + H]^+$calcd.245.0748 found 245.0743

Dimethyl (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl) phosphonate (3c)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (34.2 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 9.2 Hz, 1H), δ 7.45-7.40 (m, 1H), 7.22-7.18 (m, 1H), 5.57-5.51 (m, 1H), 3.67(d, *J* = 11.2Hz, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ168.6 (ddd, *J* =271.8, 25.9, 2.6 Hz), 162.3 (d, *J* = 248.1 Hz), 132.1 (ddd, *J* =29.3, 8.2, 1.6 Hz), 130.0 (d, *J* =8.2 Hz), 124.7(dd, *J* = 6.0, 3.1 Hz), 118.7(d, *J* = 21.2 Hz), 115.6 (dd, *J* = 24.0, 6.2 Hz), 95.1(dd, *J* =203.2, 22.6 Hz), 52.8, 52.7; ^{19}F (376 MHz, $CDCl_3$) δ-112.0 (m, 1F), -66.7 (dd, *J* = 72.2, 25.2 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 17.1 (d, *J* = 72.3 Hz, 1P); HR-MS *m/z*: Calcd for $C_{10}H_{12}F_2O_3P$ $[M + H]^+$ calcd.249.0498 found 249.0501

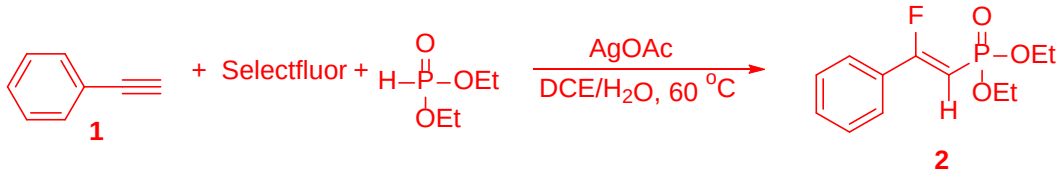
Dimethyl (*Z*)-(2-(4-bromophenyl)-2-fluorovinyl)phosphonate (3d)

The reaction was conducted on a 0.2 mmol scale following the general procedure. The desired product was purified by column chromatography (PE/EA 5:1) to give a colorless oil (44.4 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), δ 7.74 (d, *J* = 8.4 Hz, 2H), 5.64 (dd, *J* = 25.6, 2.0 Hz, 1H), 3.68(d, *J* = 11.6Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9 (dd, *J* = 272.9, 26.1 Hz), 134.2 (d, *J* = 29.4, 1.7 Hz), 132.1, 129.4 (d, *J* = 6.0, 0.7 Hz), 96.9 (dd, *J* = 202.1, 21.8Hz), 52.94, 52.88; ^{19}F (376 MHz, $CDCl_3$) δ -68.1 (dd, *J* = 71.1, 25.2 Hz, 1F); ^{31}P (162 MHz, $CDCl_3$) δ 16.8 (d, *J* = 71.1Hz, 1P); HR-MS *m/z*: Calcd for $C_{10}H_{12}BrFO_3P$ $[M + H]^+$calcd.308.9613 found 308.9625

2.1 Gram-scale reaction

In a vial, **1a** (816 mg, 8 mmol), Selectfluor® (5.6 g, 16 mmol), diethyl phosphonate (2.2 mg, 16 mmol), and silver acetate (132 mg, 0.8 mmol) were dissolved in DEC/H_2O 25 mL:25 mL. The resulting mixture was stirred under N_2 atmosphere at 60 °C for 48 h. After completion, the reaction was quenched and the residual oil was purified by column chromatography on silica gel, affording the product **2a** (1.4 g, yield 67%).



1 **2**

3 References

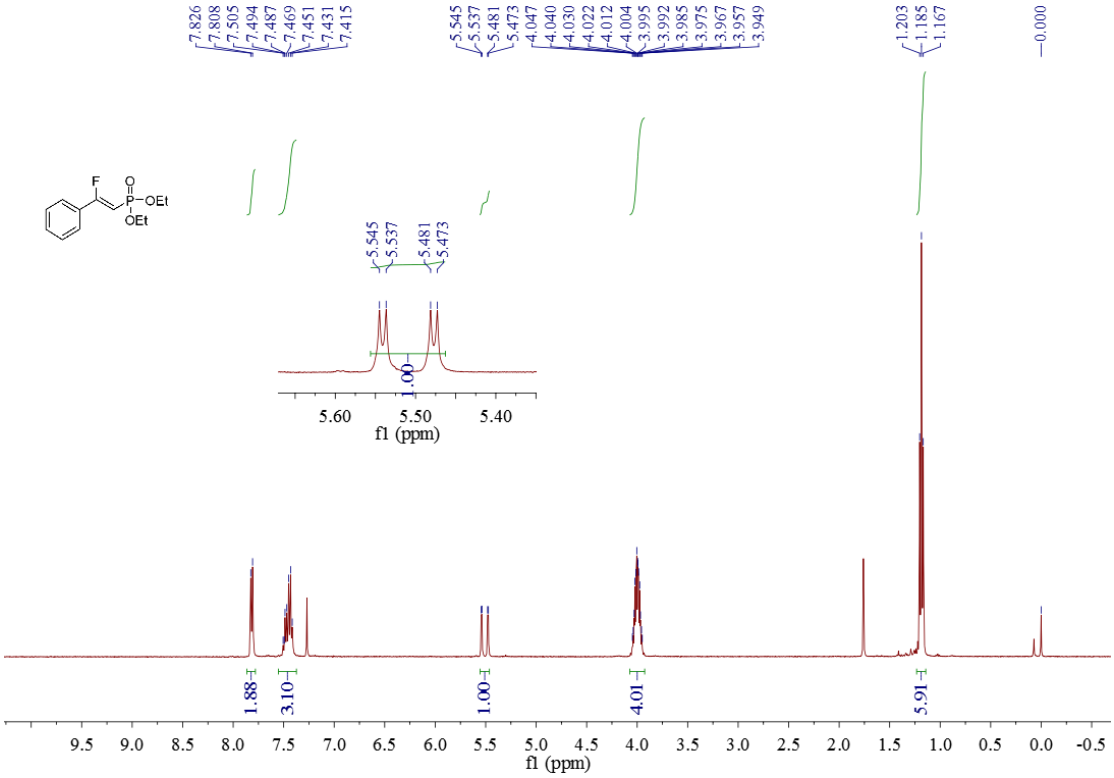
1. Okoromoba, O. -E.; Han, J. -B.; Hammond, G. B.; Xu, B. J. Am. Chem. Soc. **2014**, 136, 14381-14384

2. Xu, J.-J.; Burton, D.-J. J.Org.Chem. **2006**, 71, 3743-3747

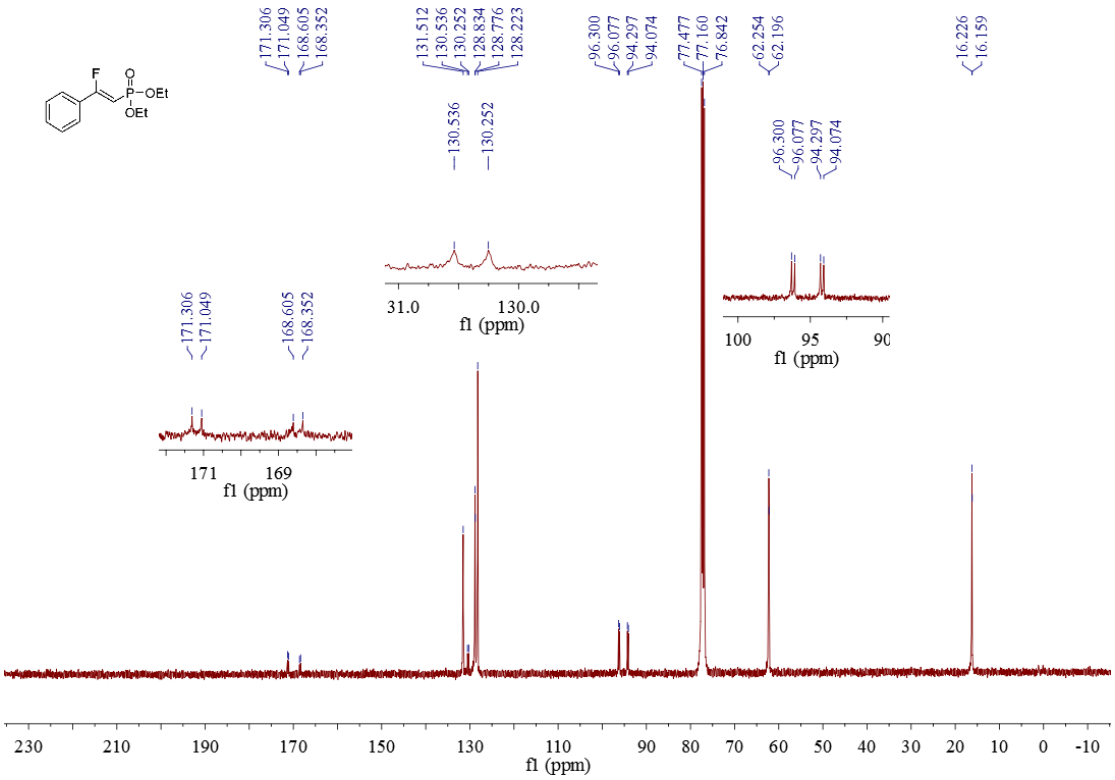
4 Copies of NMR spectra

Diethyl (*Z*)-(2-fluoro-2-phenylvinyl)phosphonate (2a)

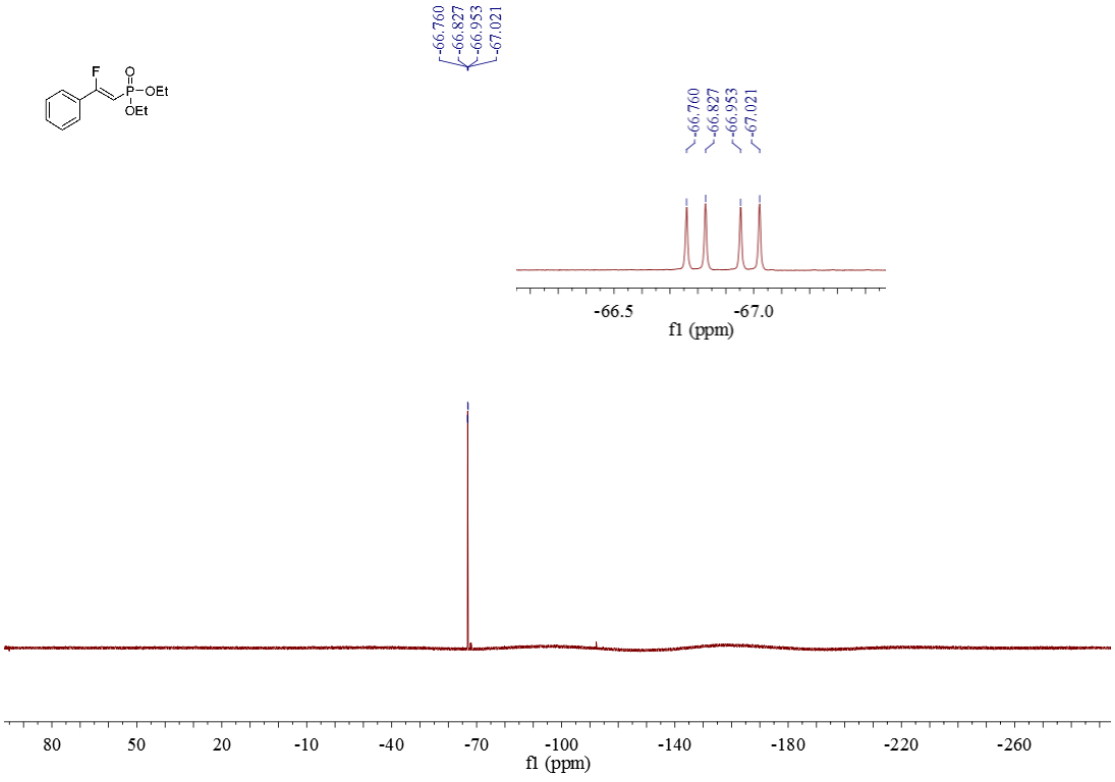
^{1}H NMR



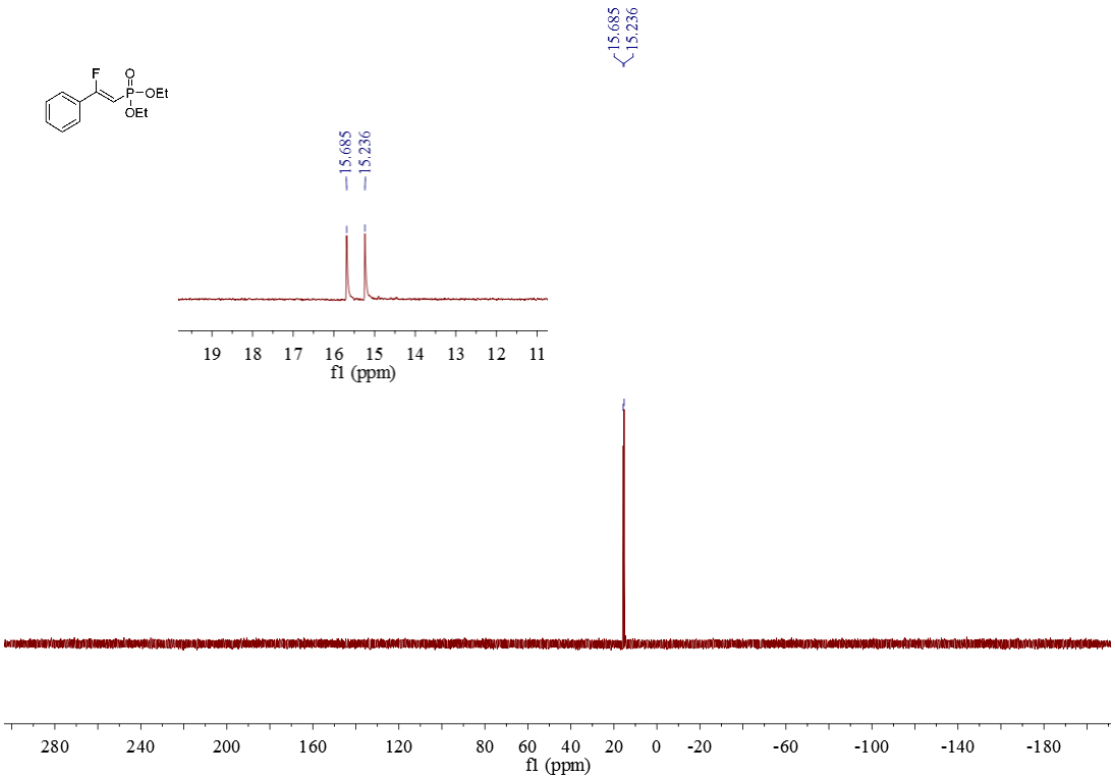
^{13}C NMR



^{19}F NMR

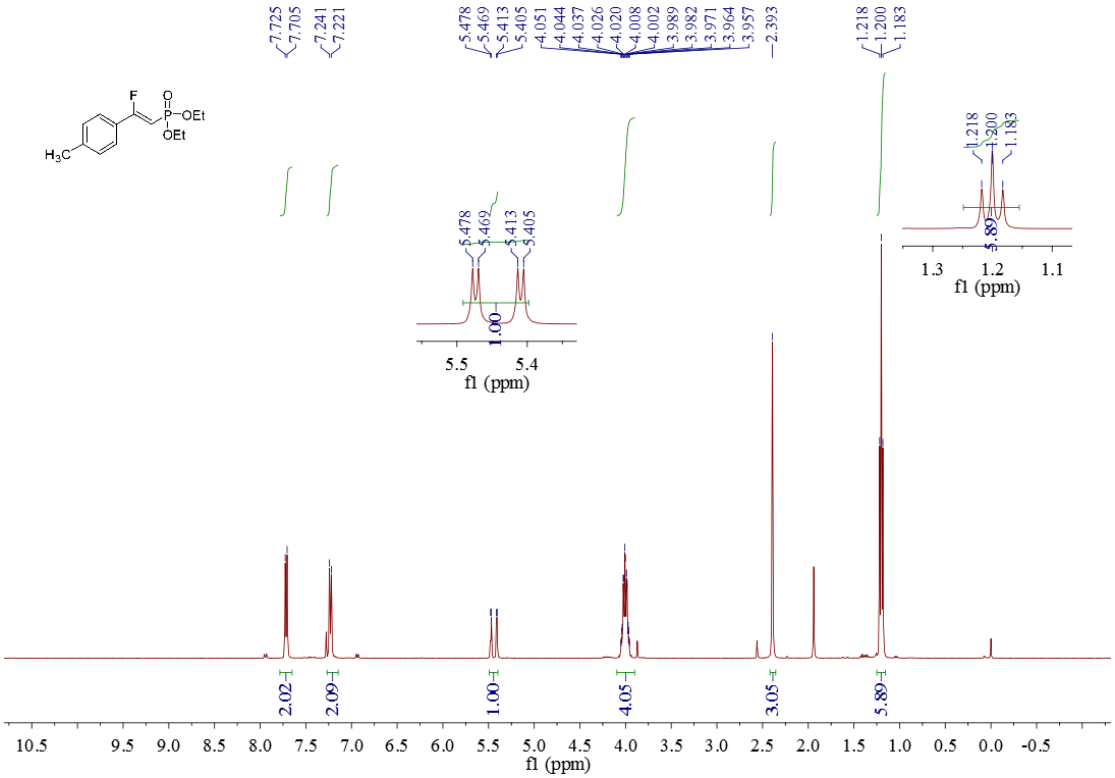


^{31}P NMR



Diethyl (*Z*)-(2-fluoro-2-(*p*-tolyl)vinyl)phosphonate (2b)

^{1}H NMR



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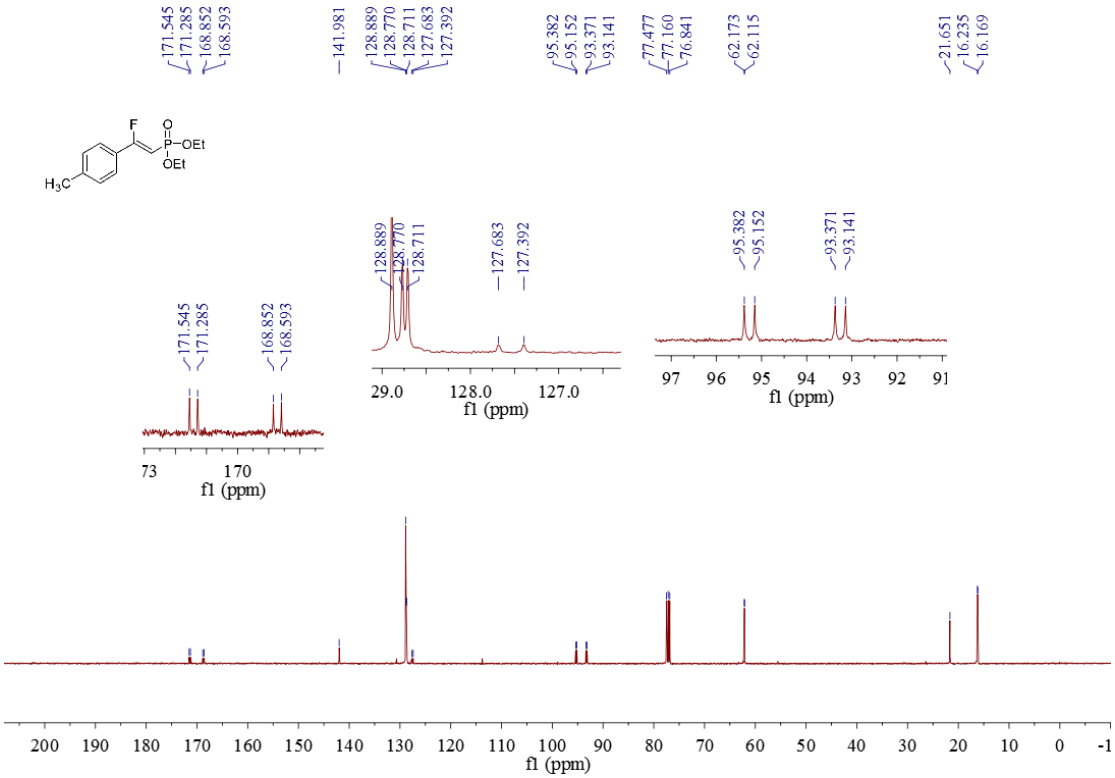

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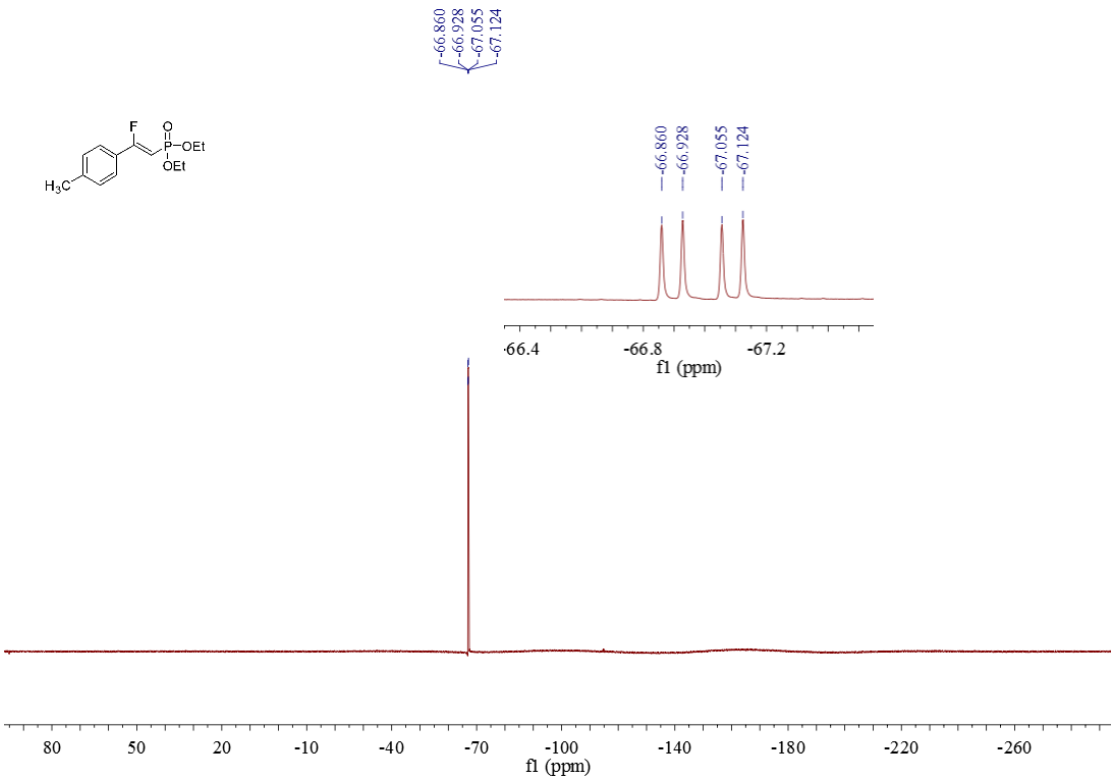
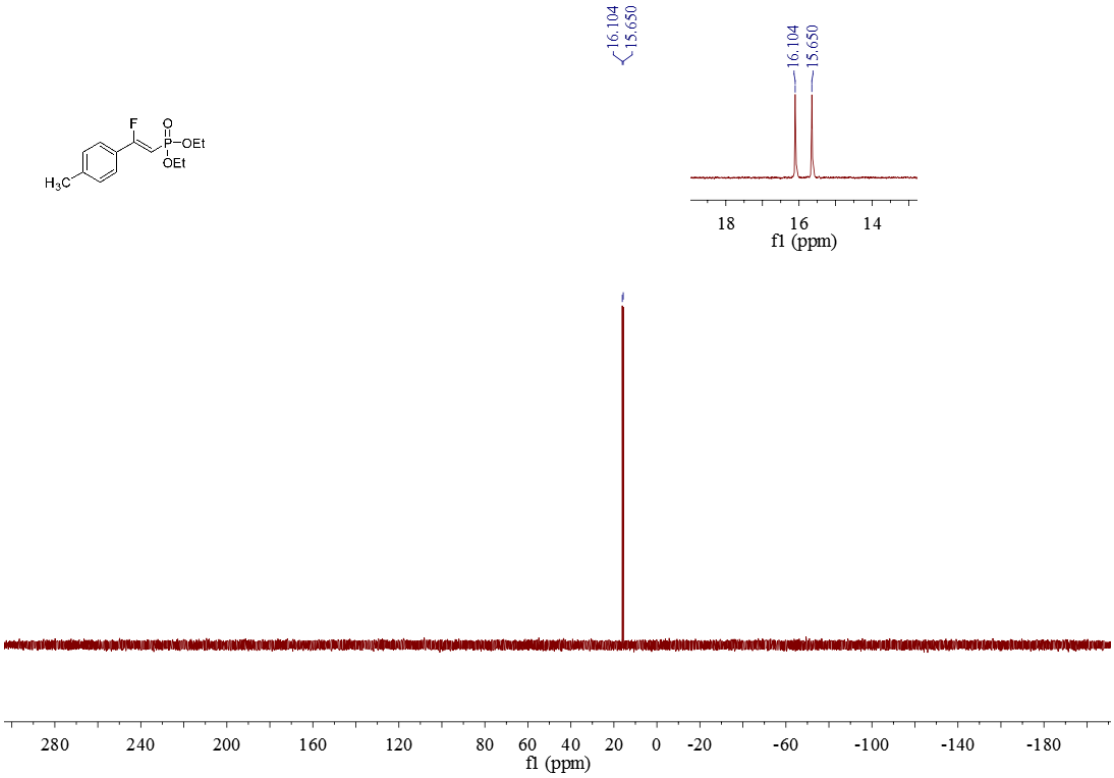
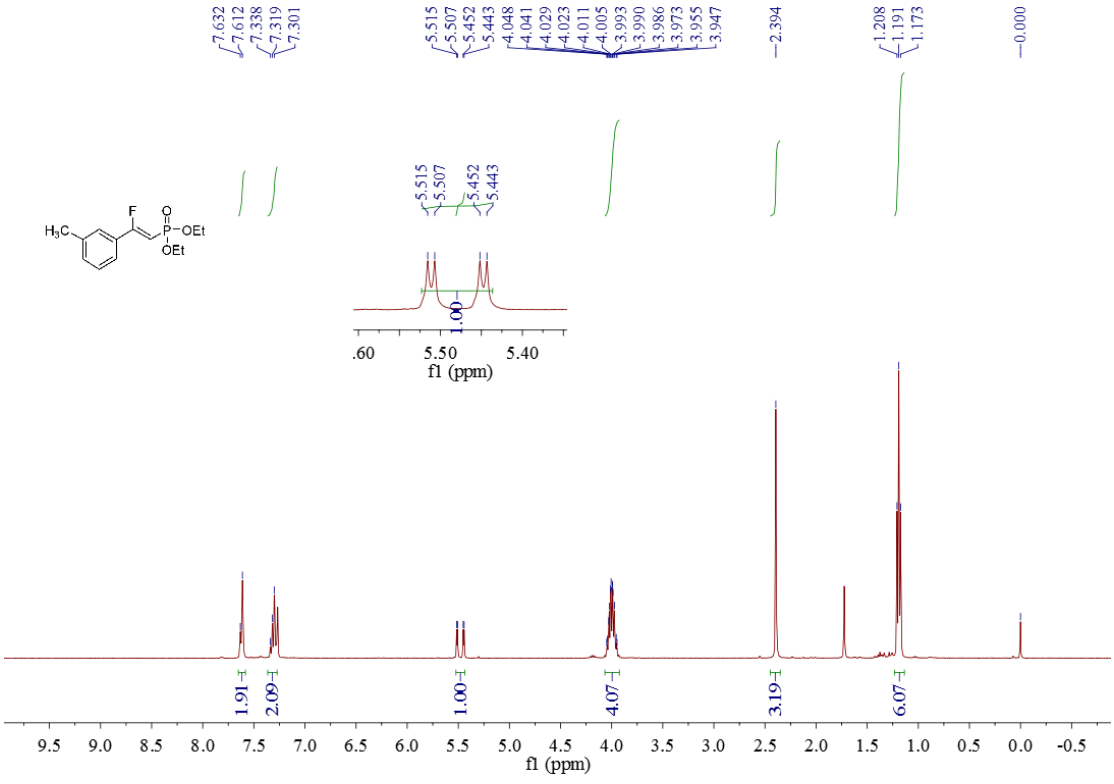


^{31}P NMR

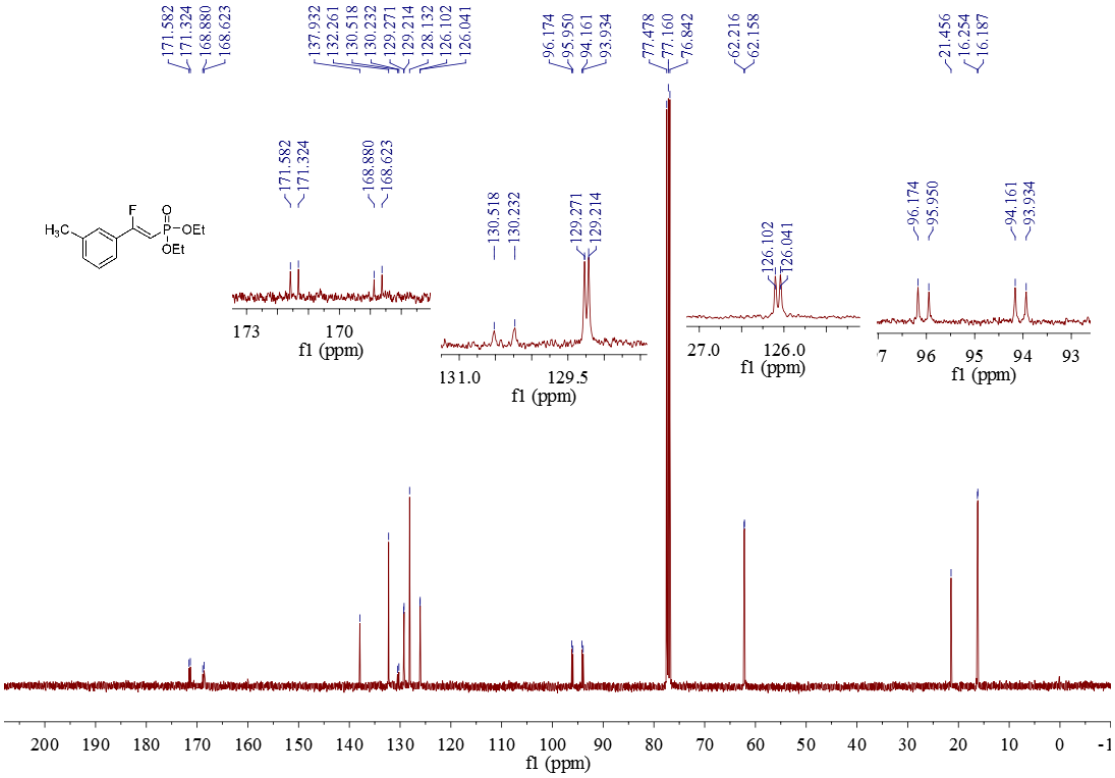


Diethyl (*Z*)-(2-fluoro-2-(*m*-tolyl)vinyl)phosphonate (2c)

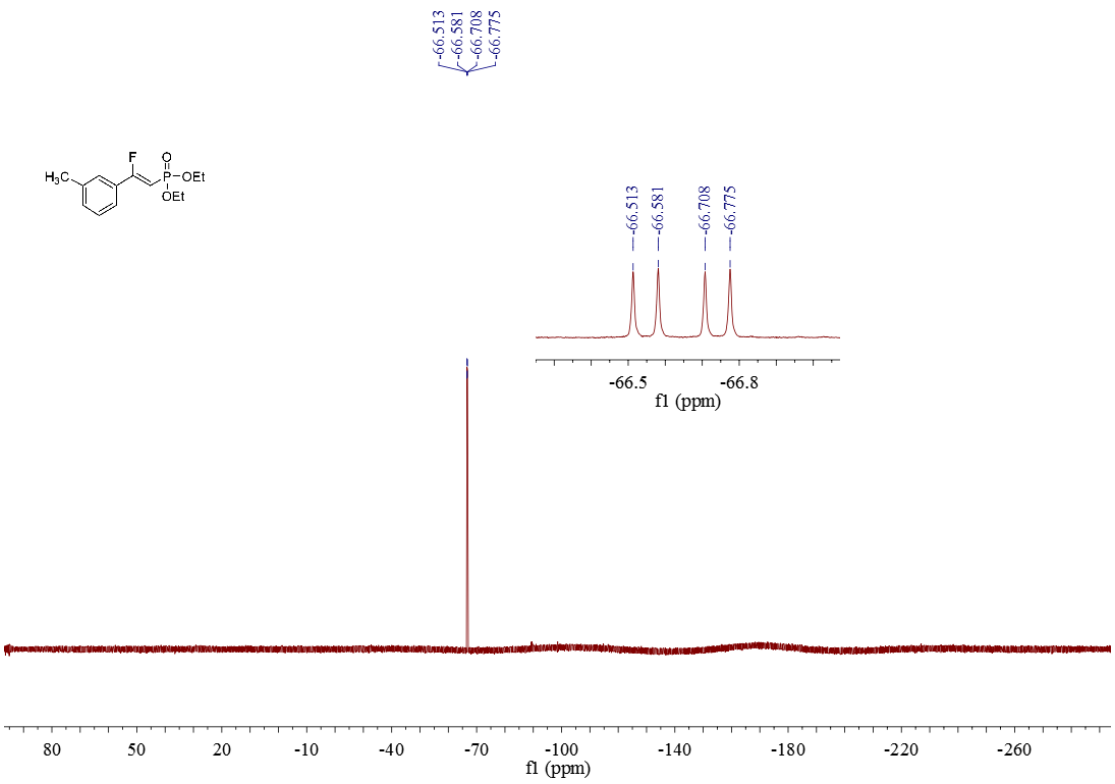
^{1}H NMR



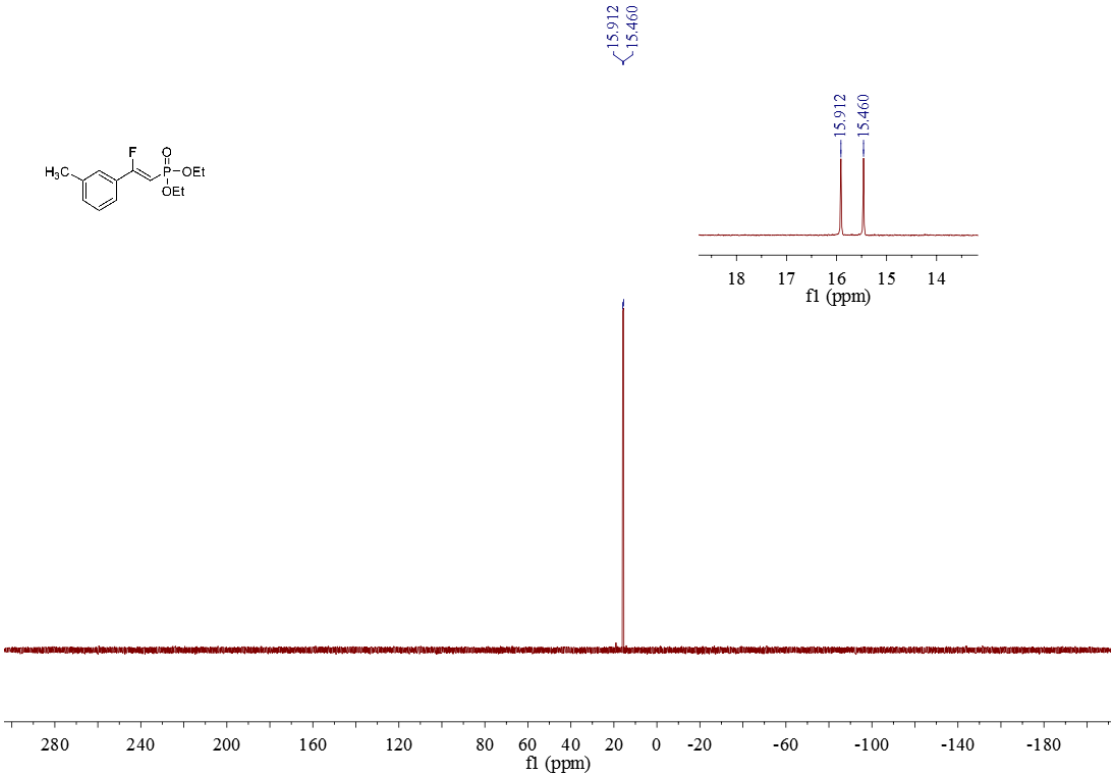
^{13}C NMR



^{19}F NMR

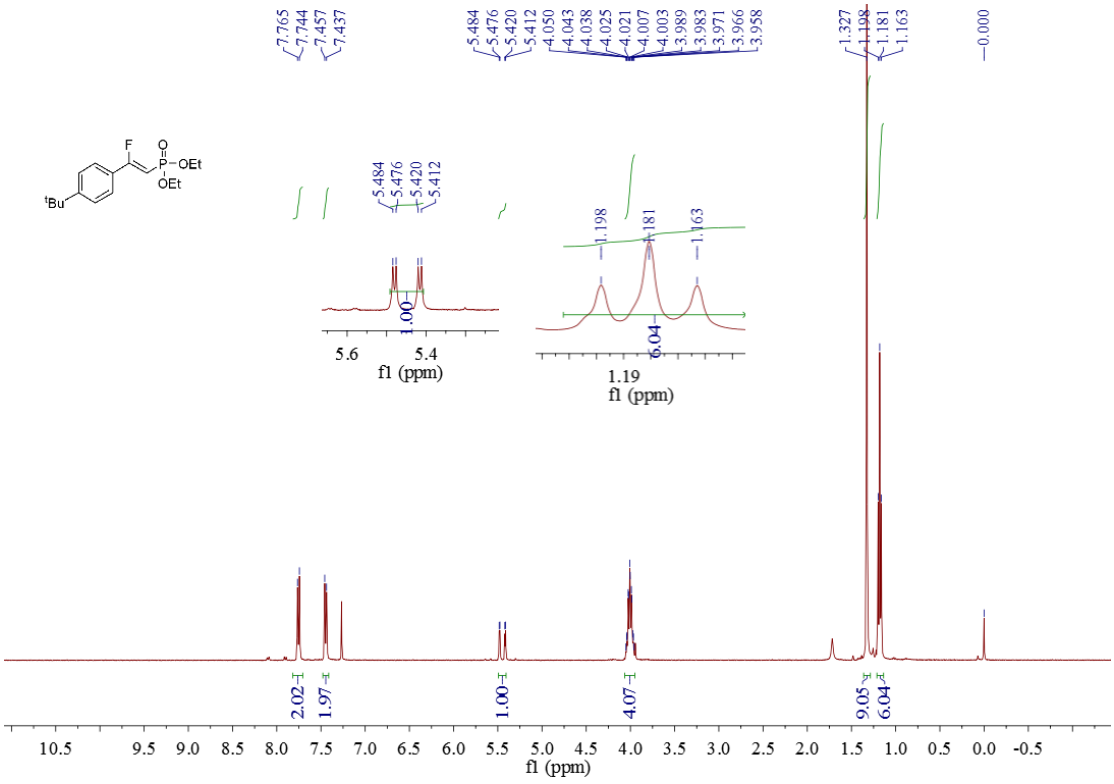


^{31}P NMR

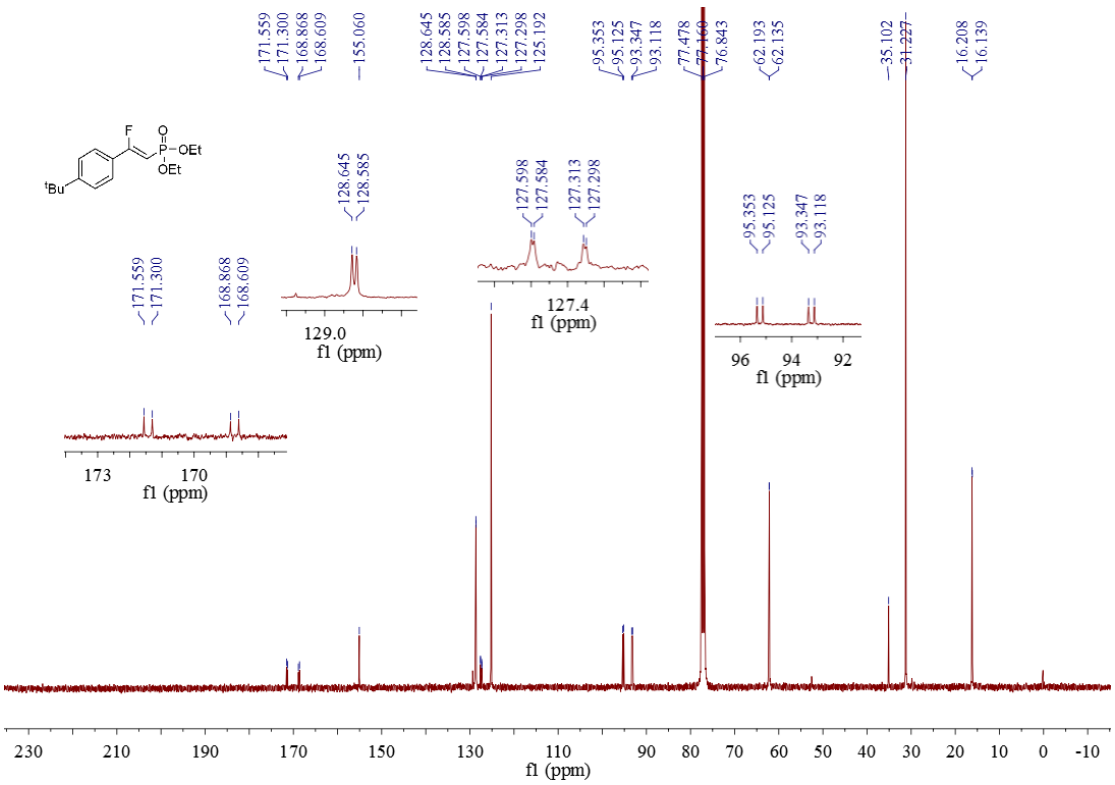


Diethyl (*Z*)-(2-(4-(tert-butyl)phenyl)-2-fluorovinyl)phosphonate (2d)

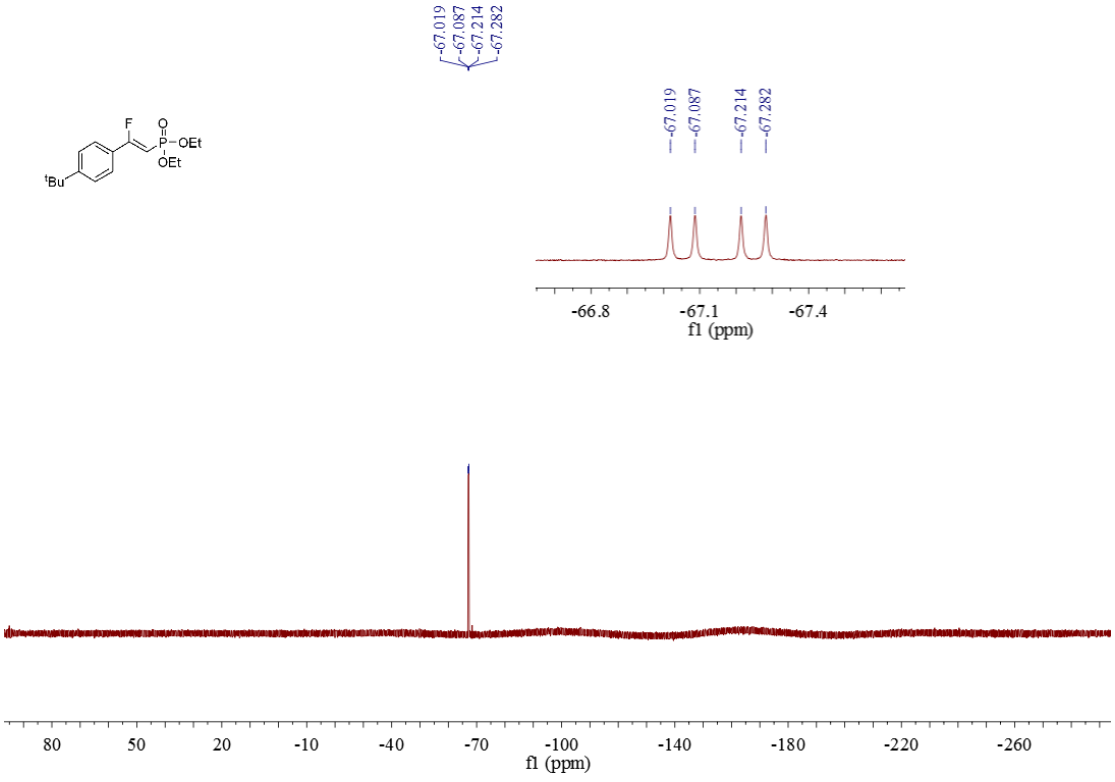
^{1}H NMR



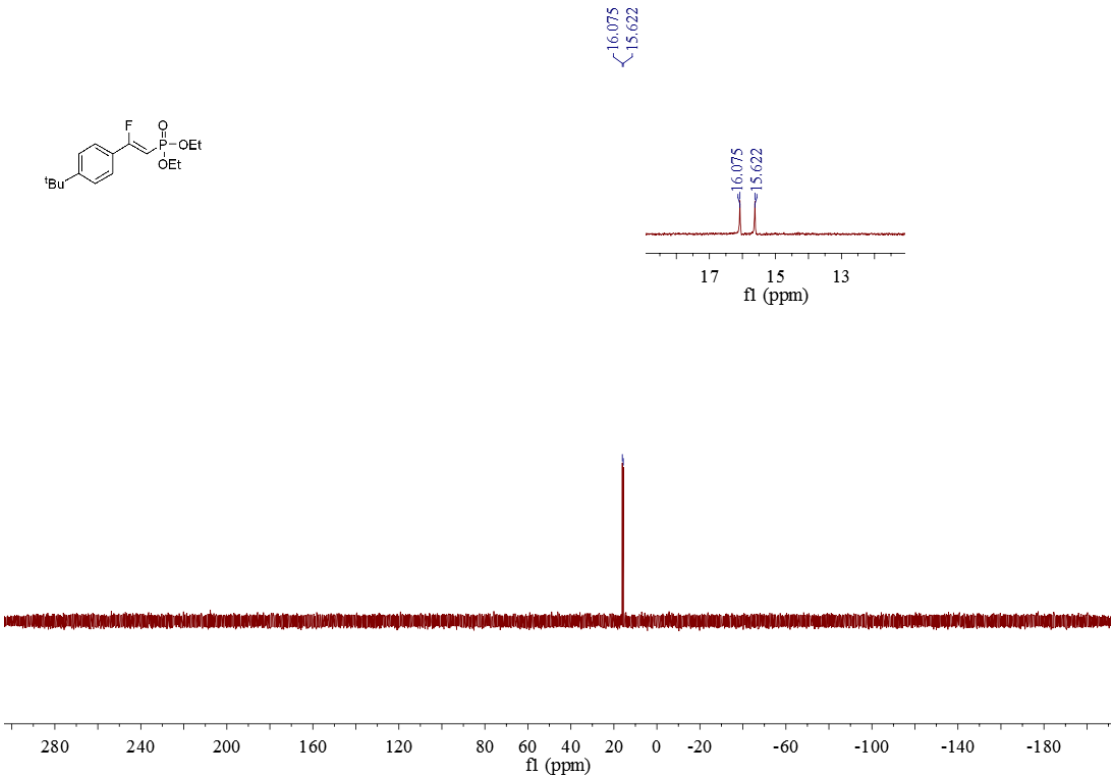
^{13}C NMR



^{19}F NMR

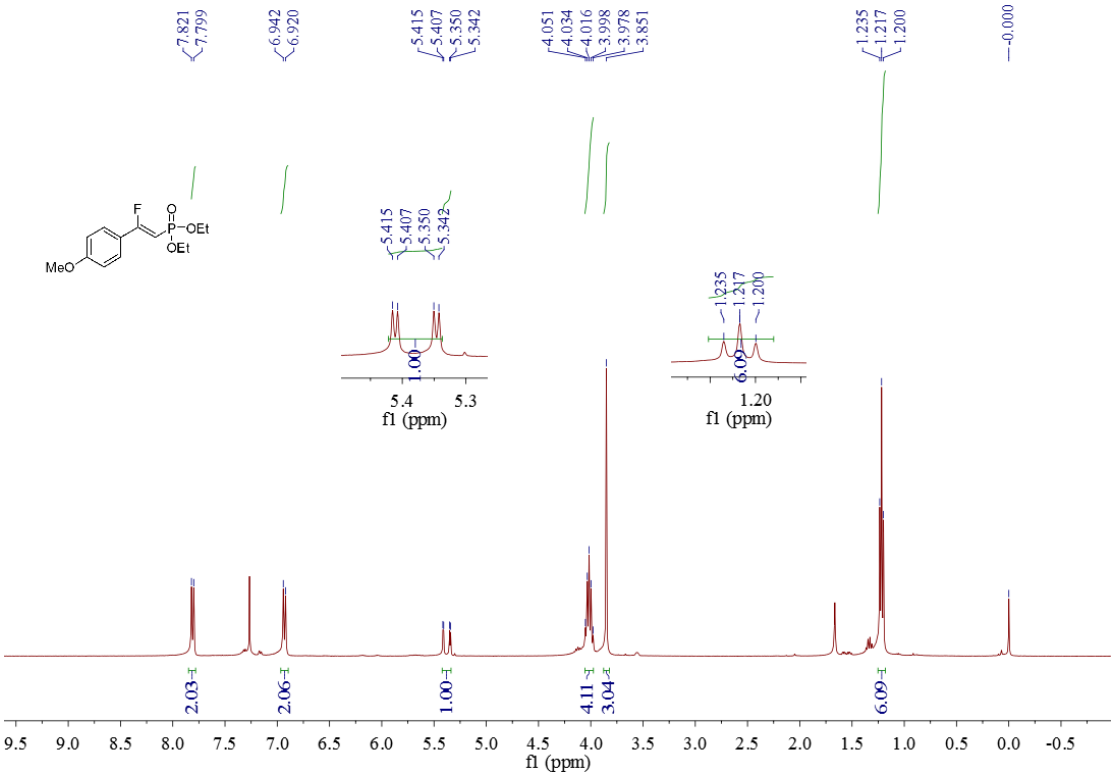


^{31}P NMR

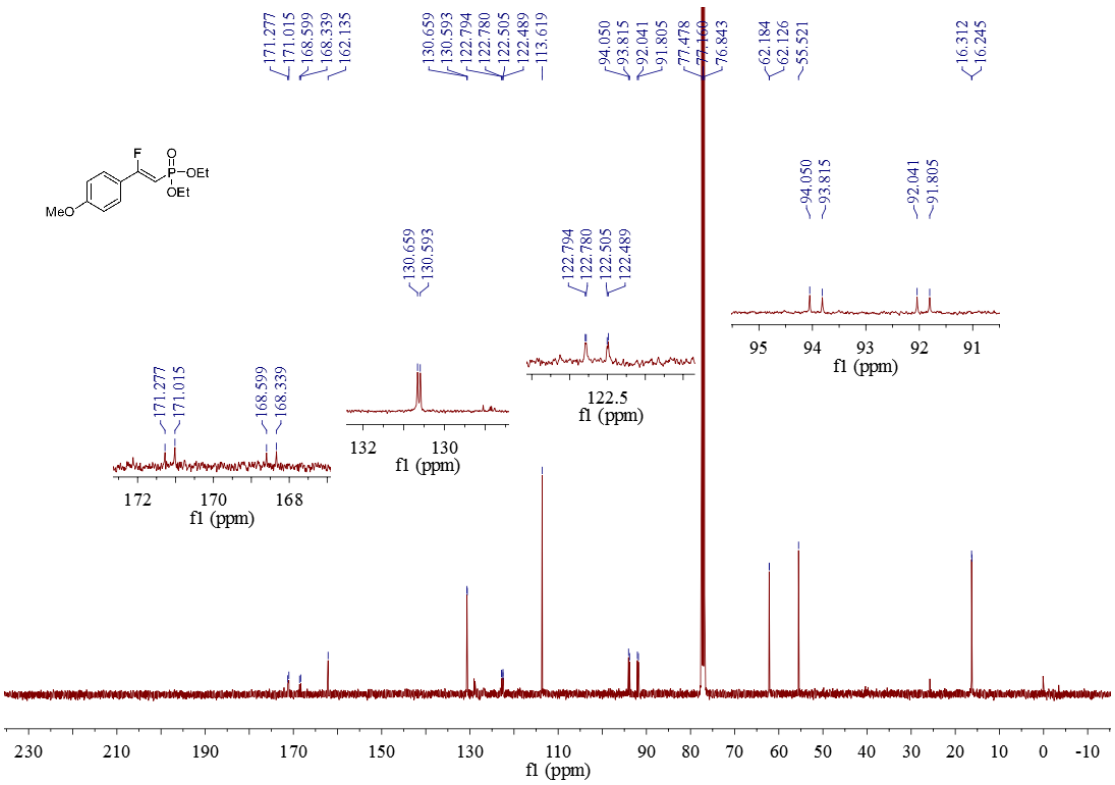


Diethyl (*Z*)-(2-fluoro-2-(4-methoxyphenyl)vinyl)phosphonate (2e)

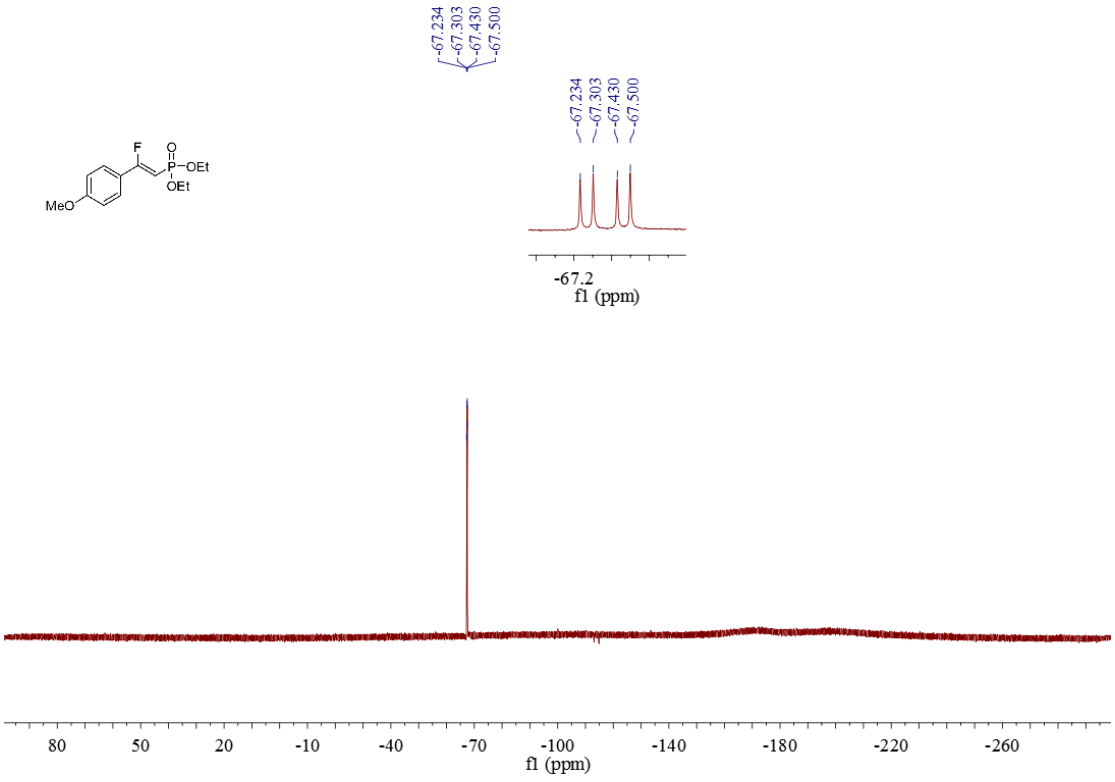
^{1}H NMR



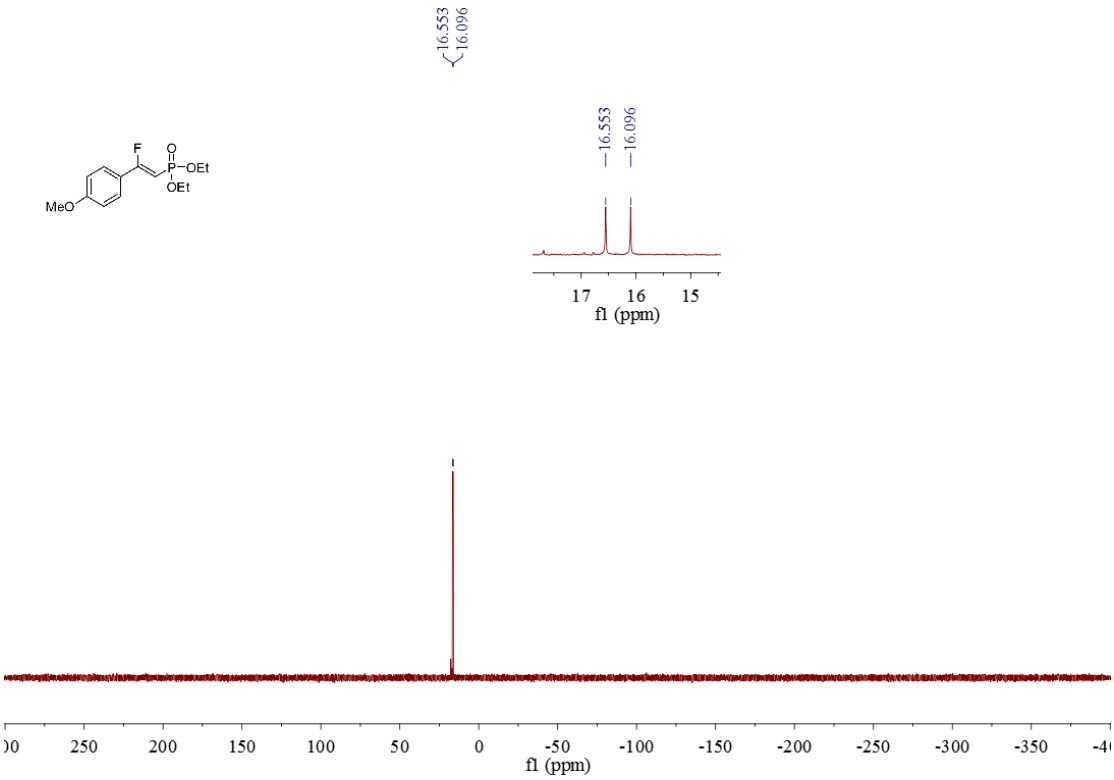
^{13}C NMR



^{19}F NMR

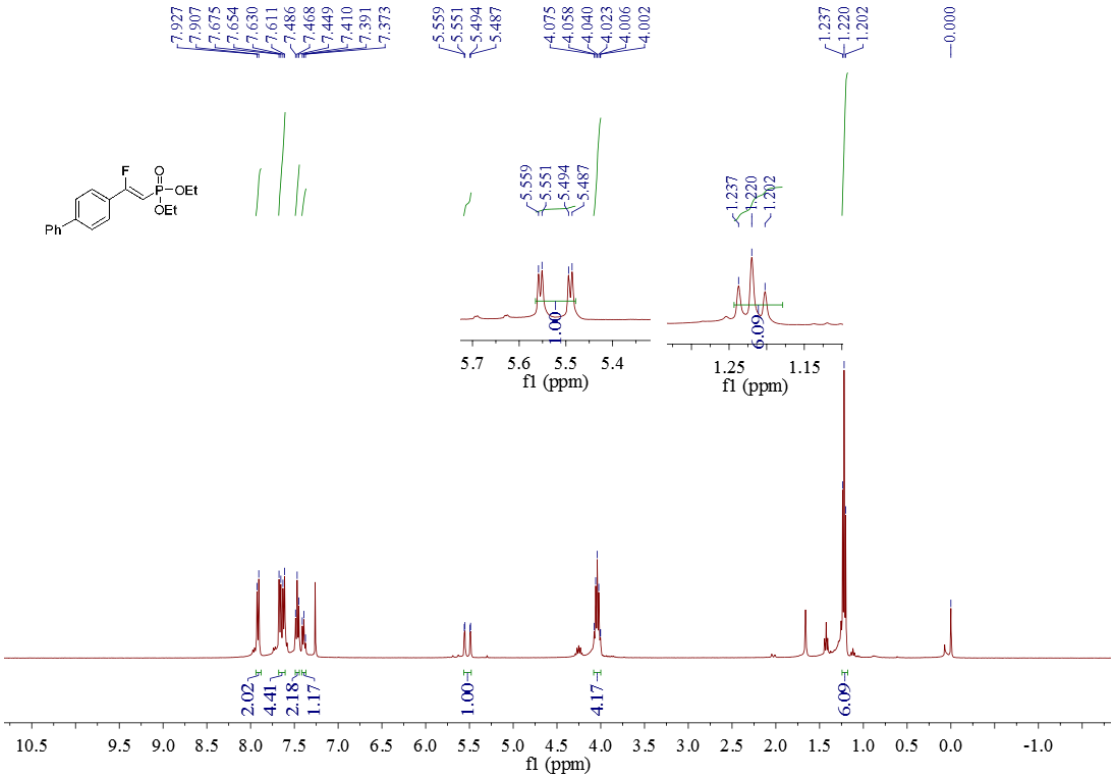


^{31}P NMR

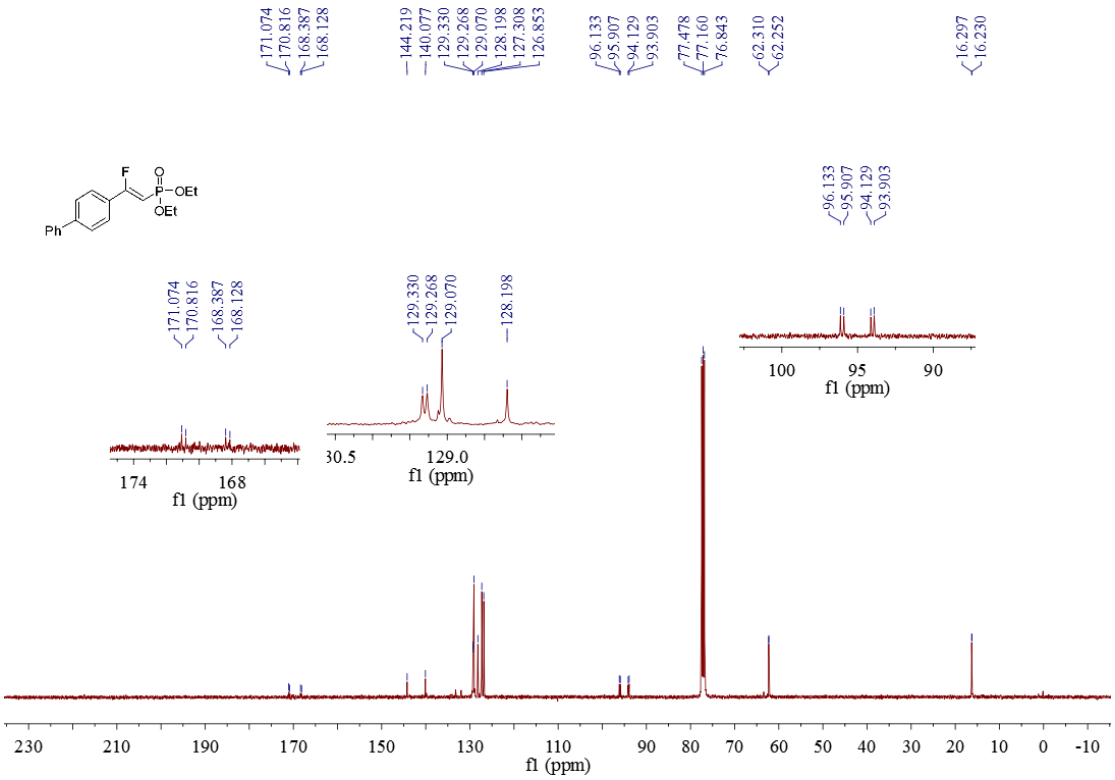


Diethyl (*Z*)-(2-([1,1'-biphenyl]-4-yl)-2-fluorovinyl)phosphonate (2f)

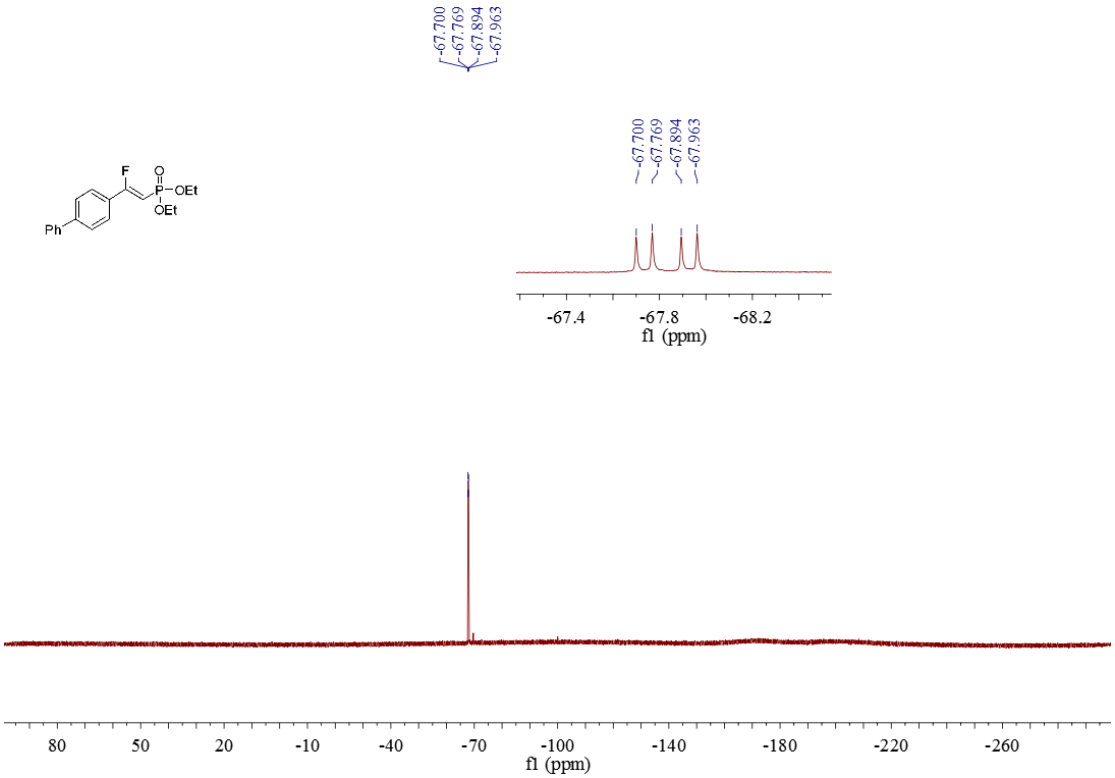
^{1}H NMR



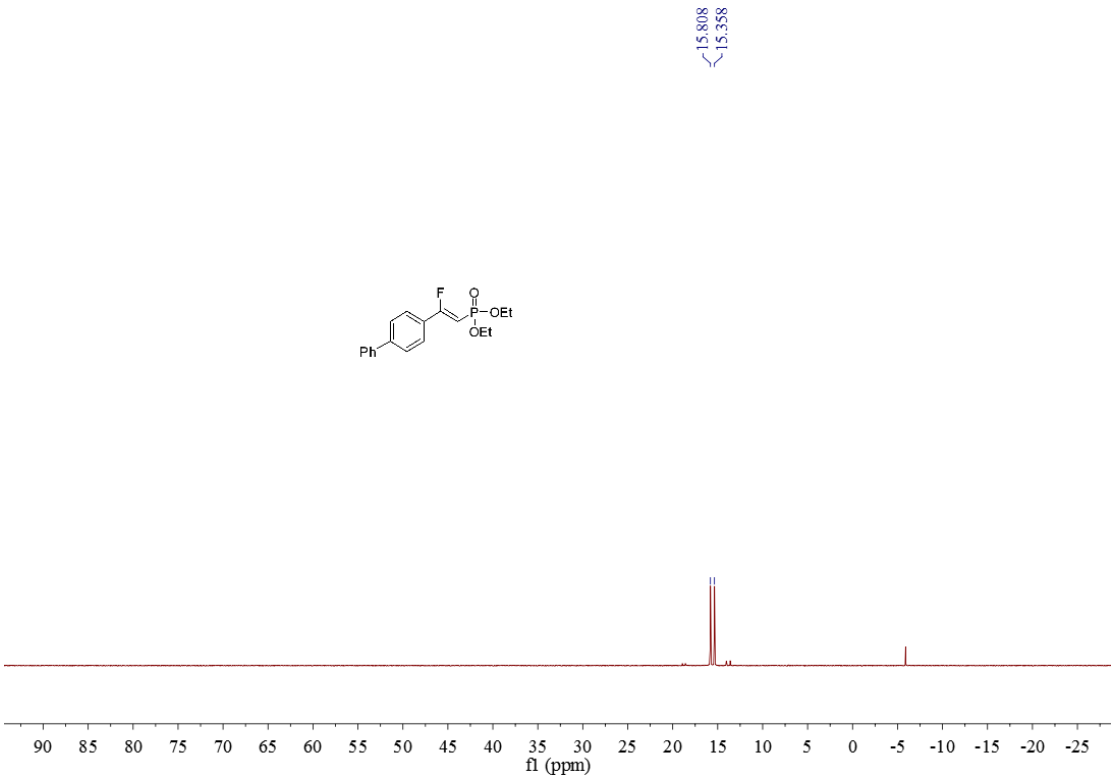
^{13}C NMR



^{19}F NMR

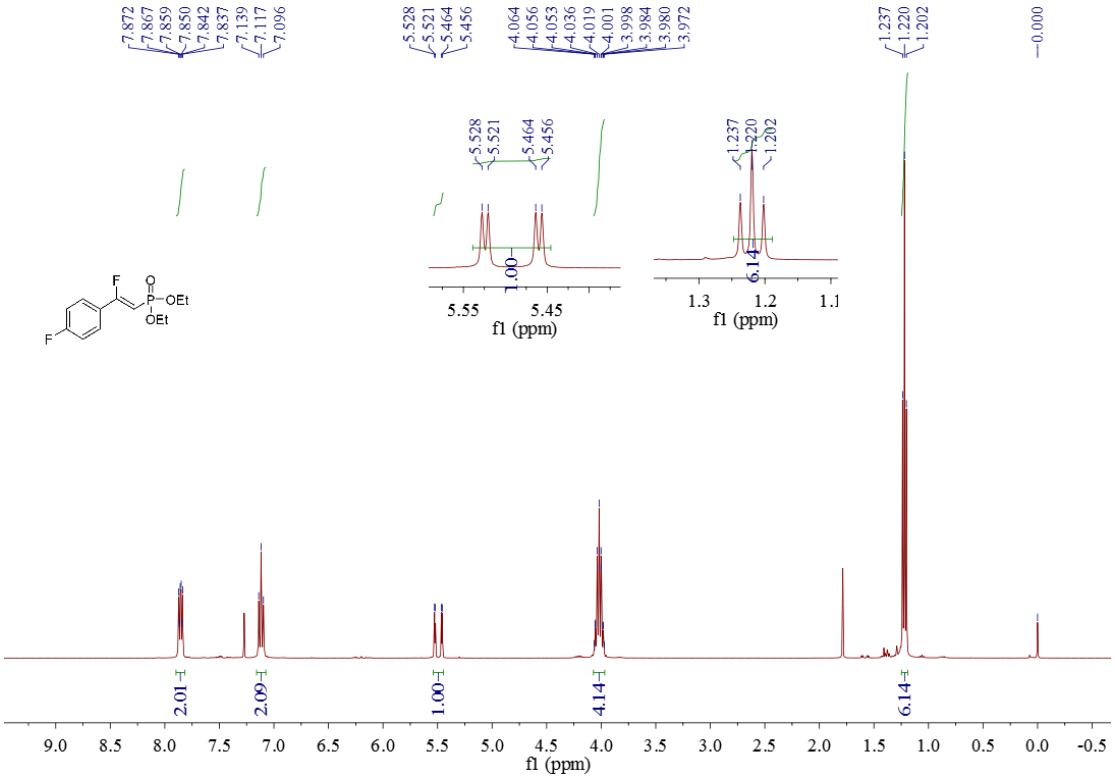


^{31}P NMR

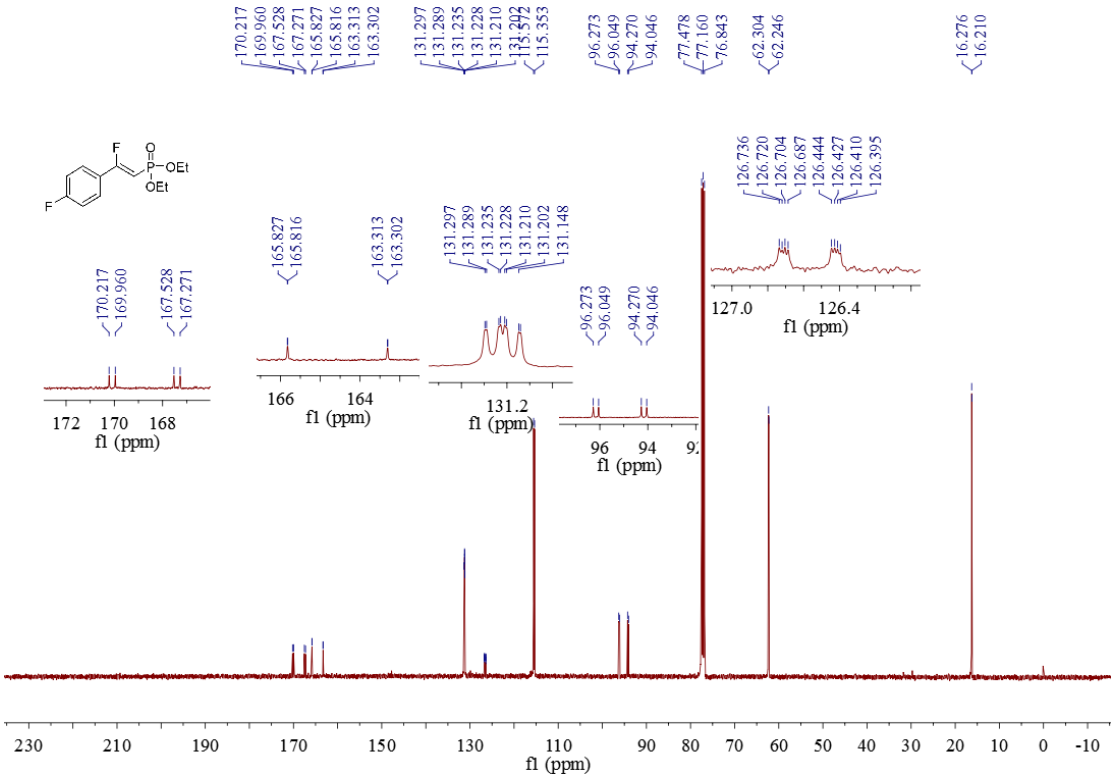


Diethyl (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl)phosphonate (2g)

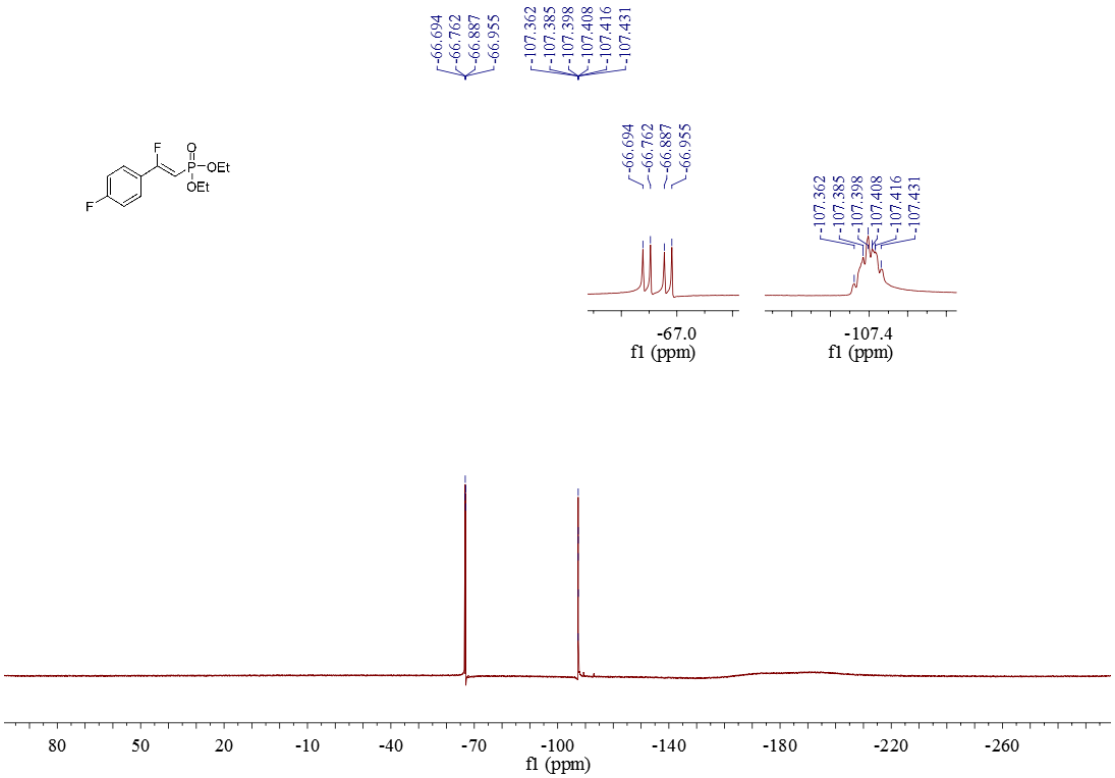
^{1}H NMR



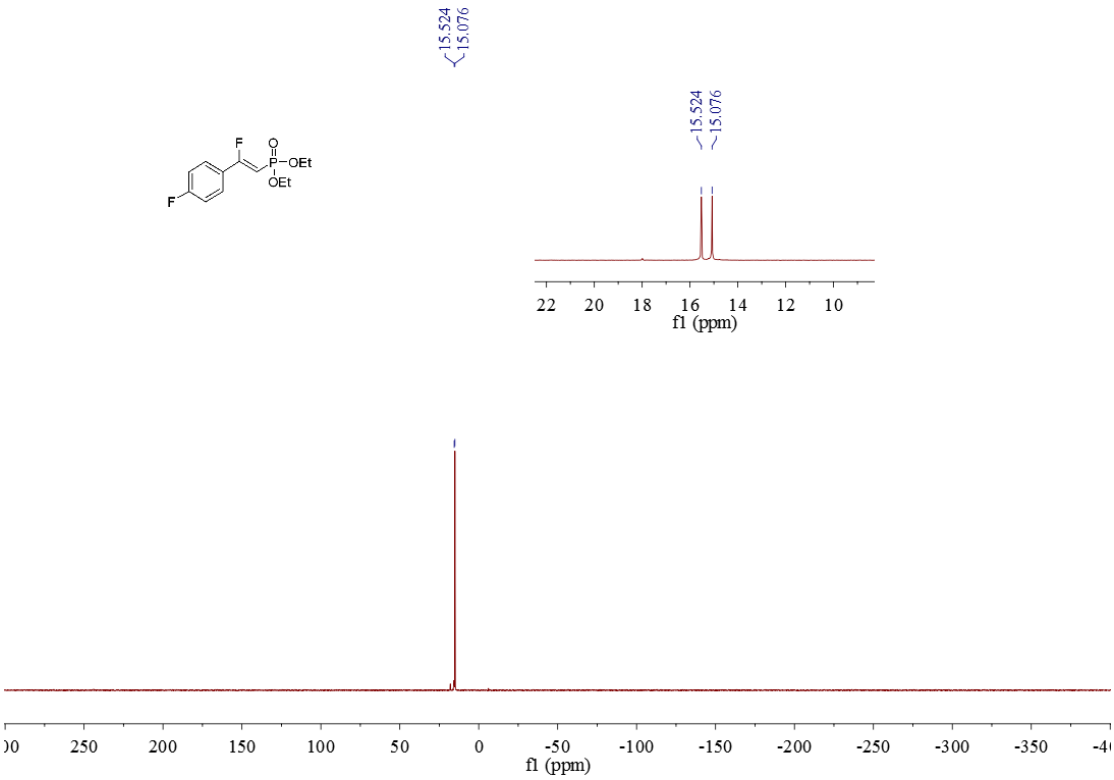
^{13}C NMR



^{19}F NMR

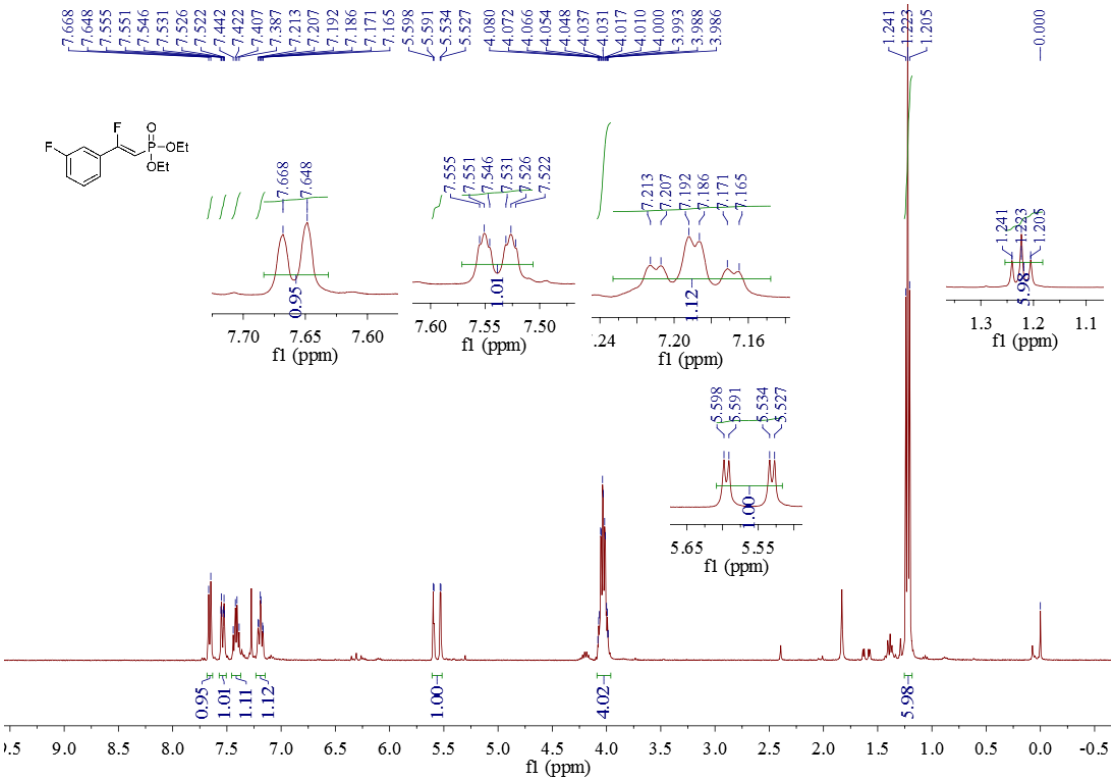


^{31}P NMR

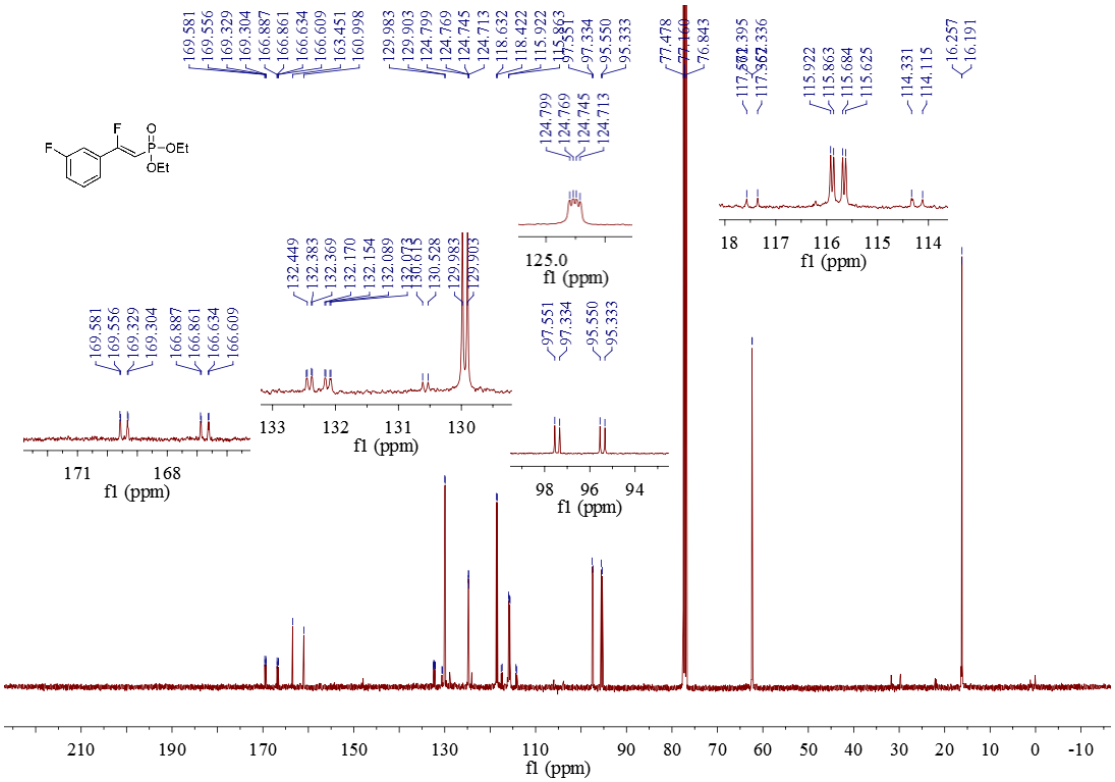


Diethyl (*Z*)-(2-fluoro-2-(3-fluorophenyl)vinyl)phosphonate (2h)

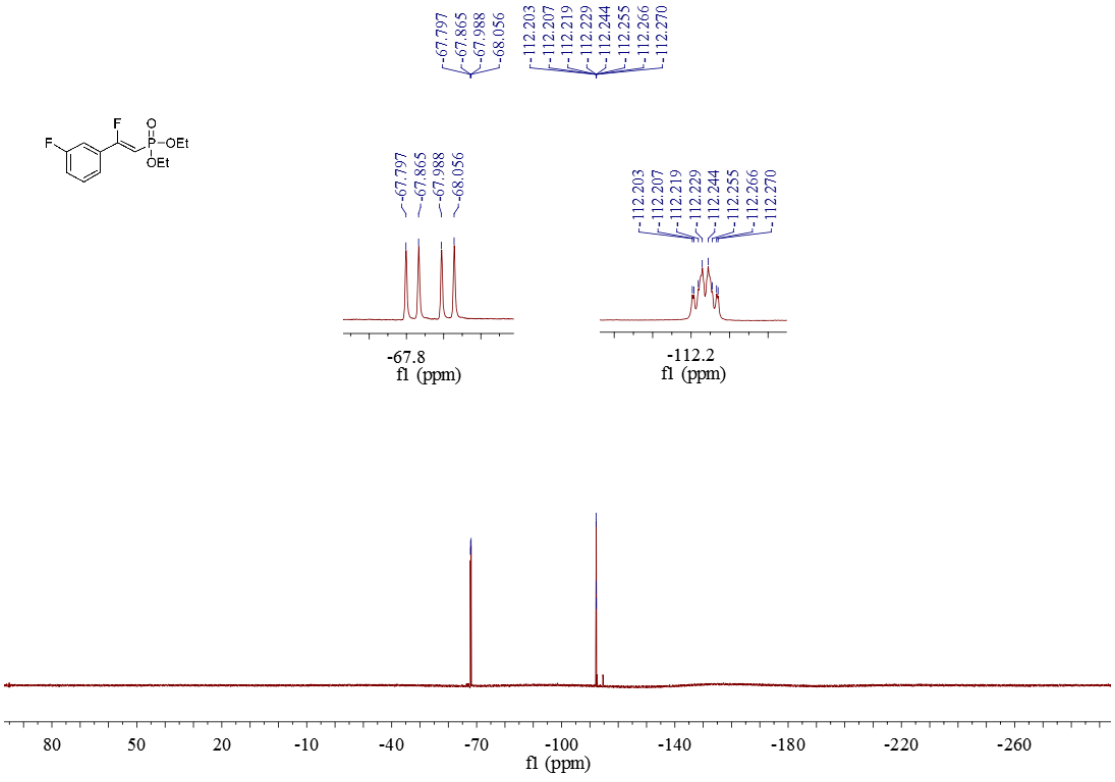
^{1}H NMR



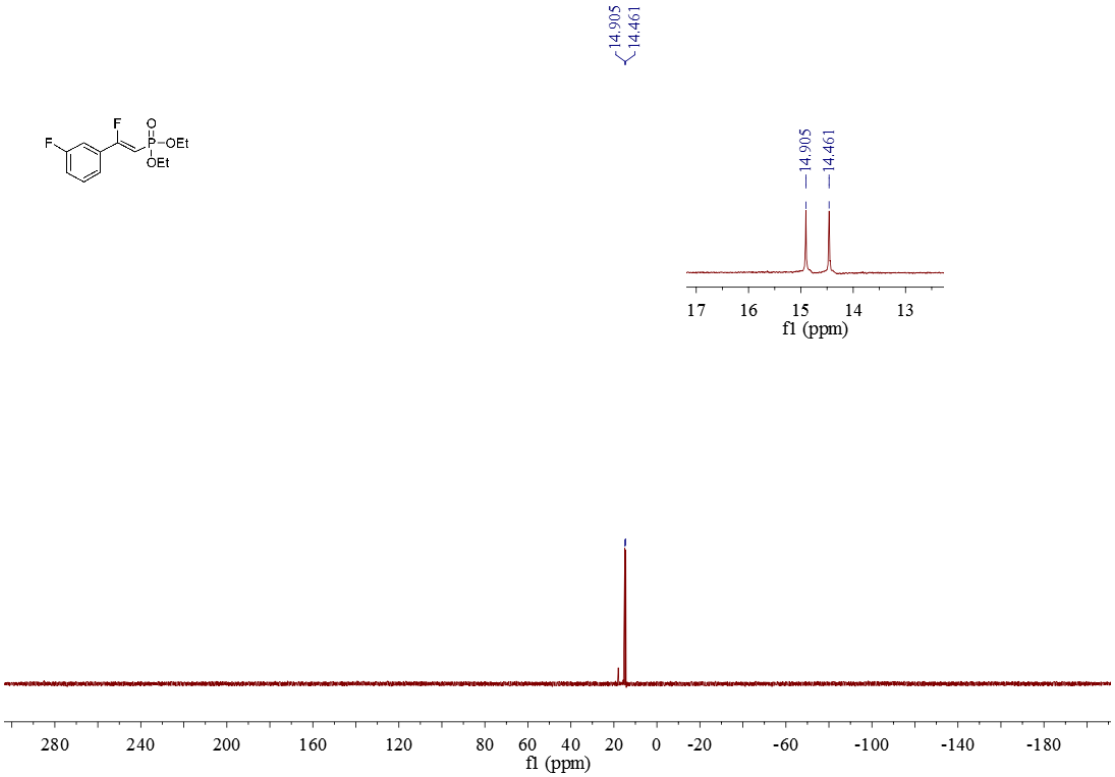
^{13}C NMR



^{19}F NMR

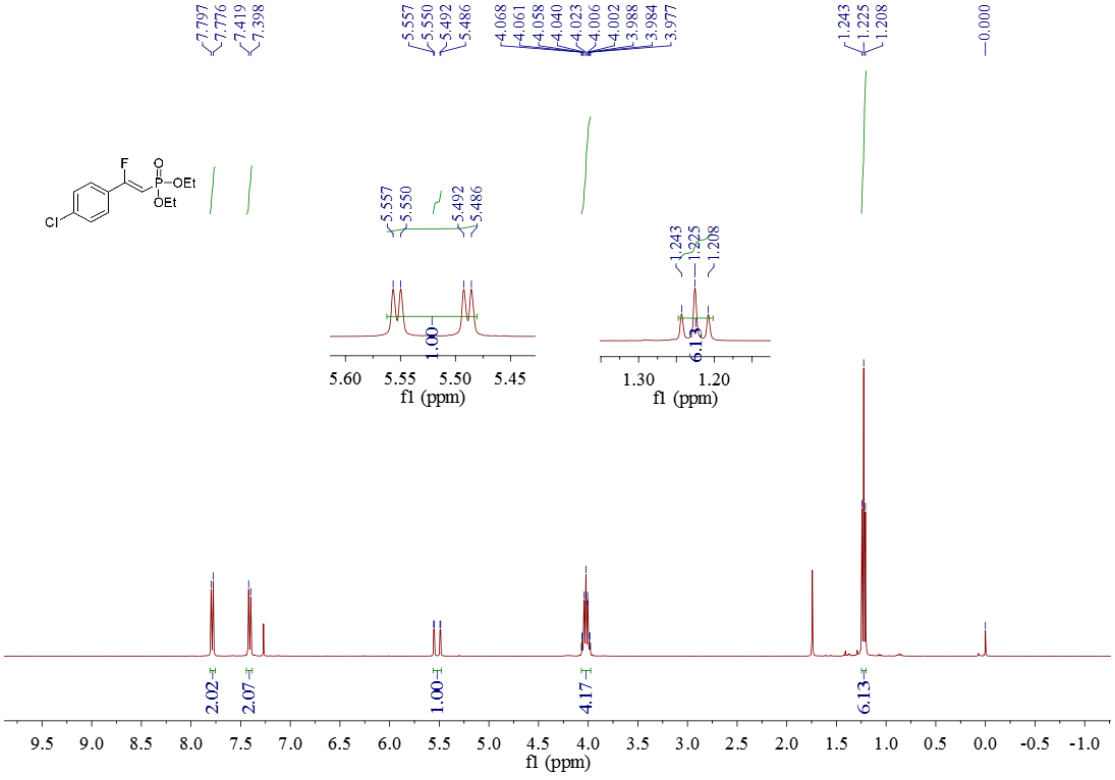


^{31}P NMR



Diethyl (*Z*)-(2-(4-chlorophenyl)-2-fluorovinyl)phosphonate (2i)

^{1}H NMR



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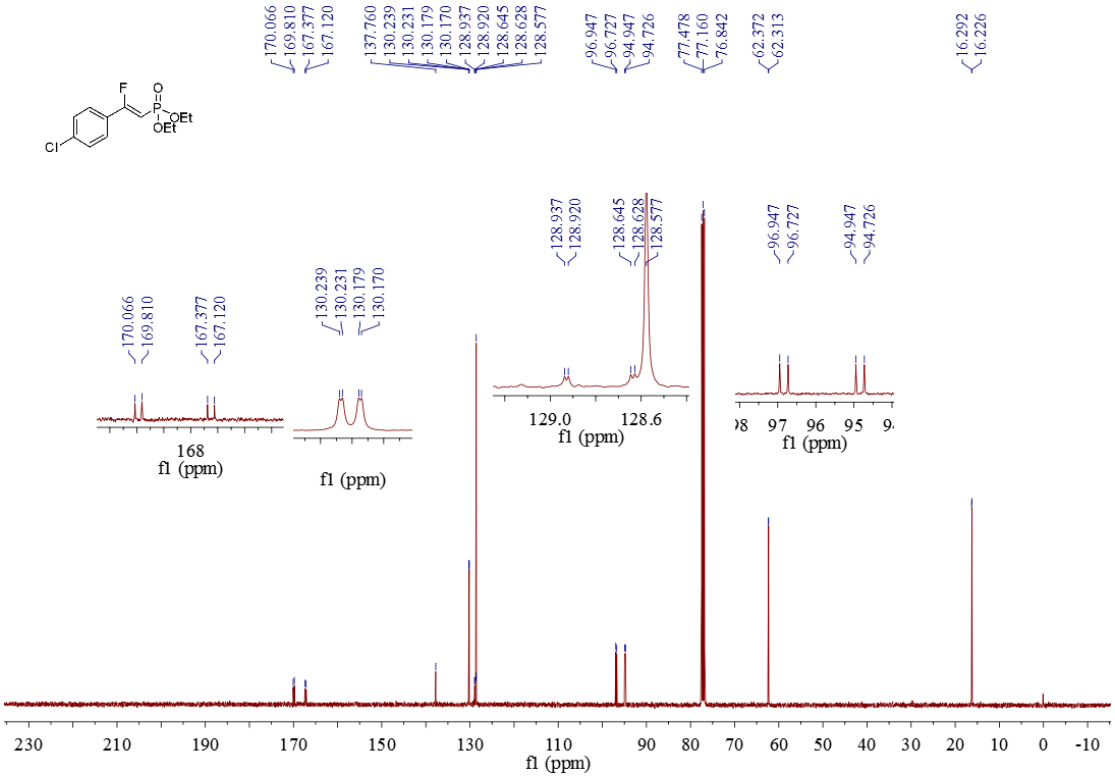
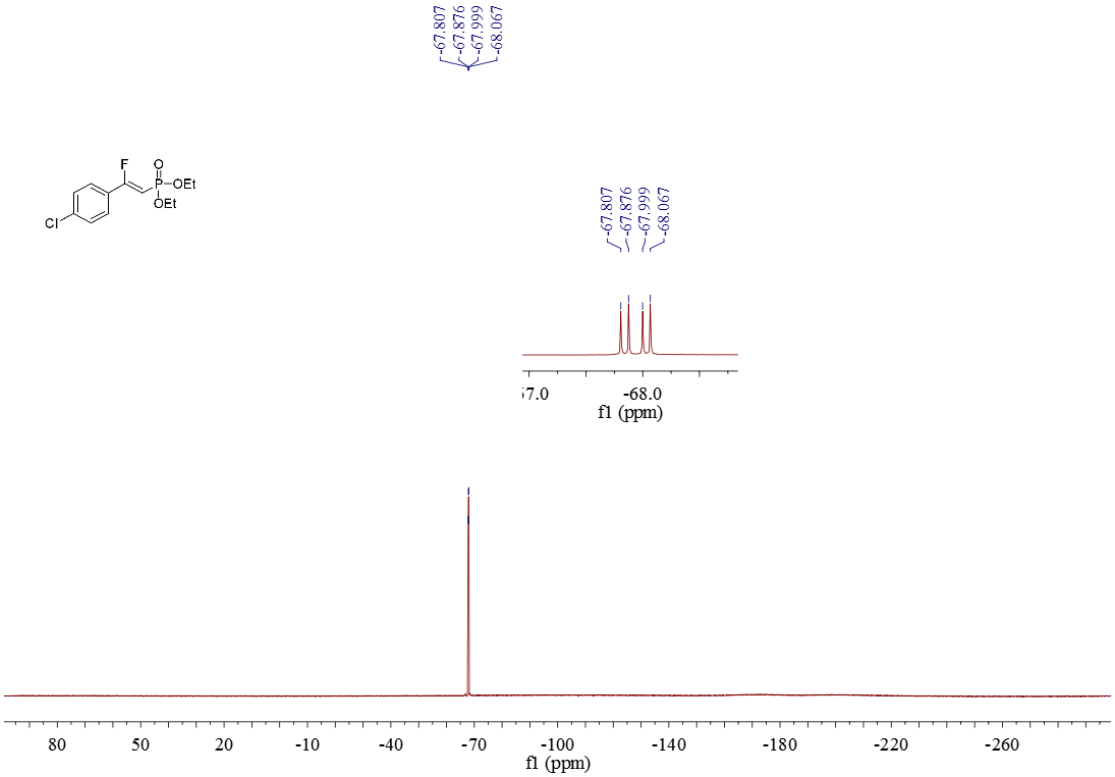


^{19}F NMR



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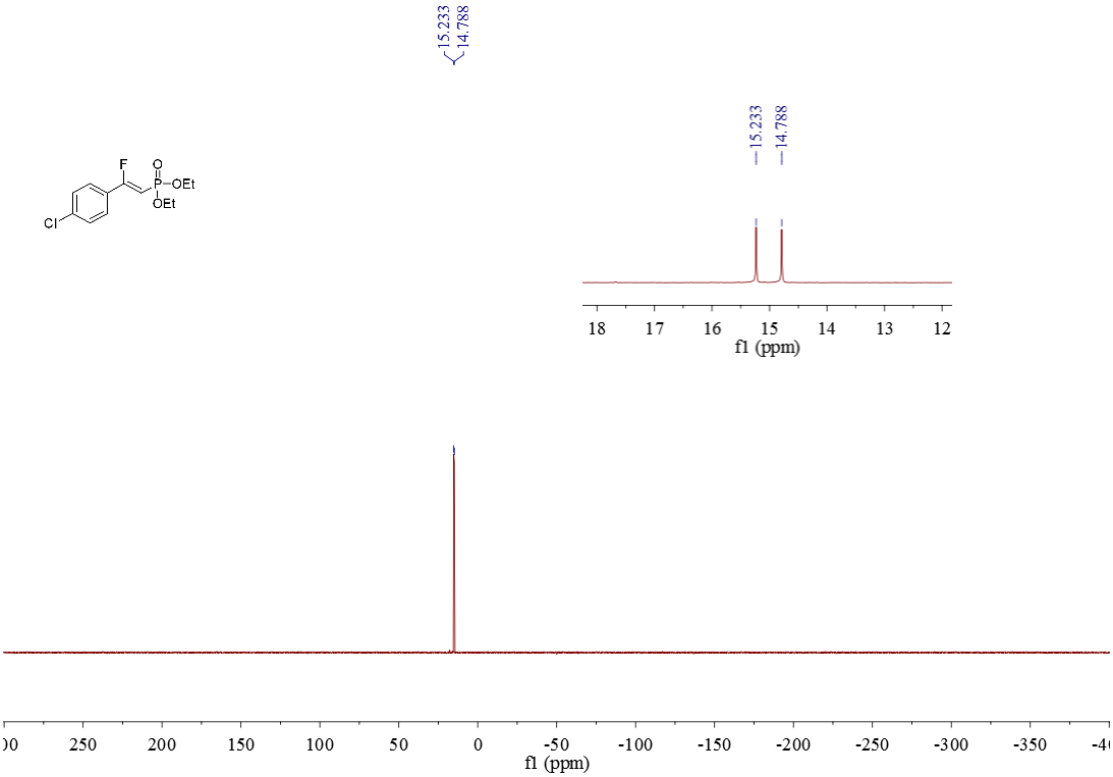
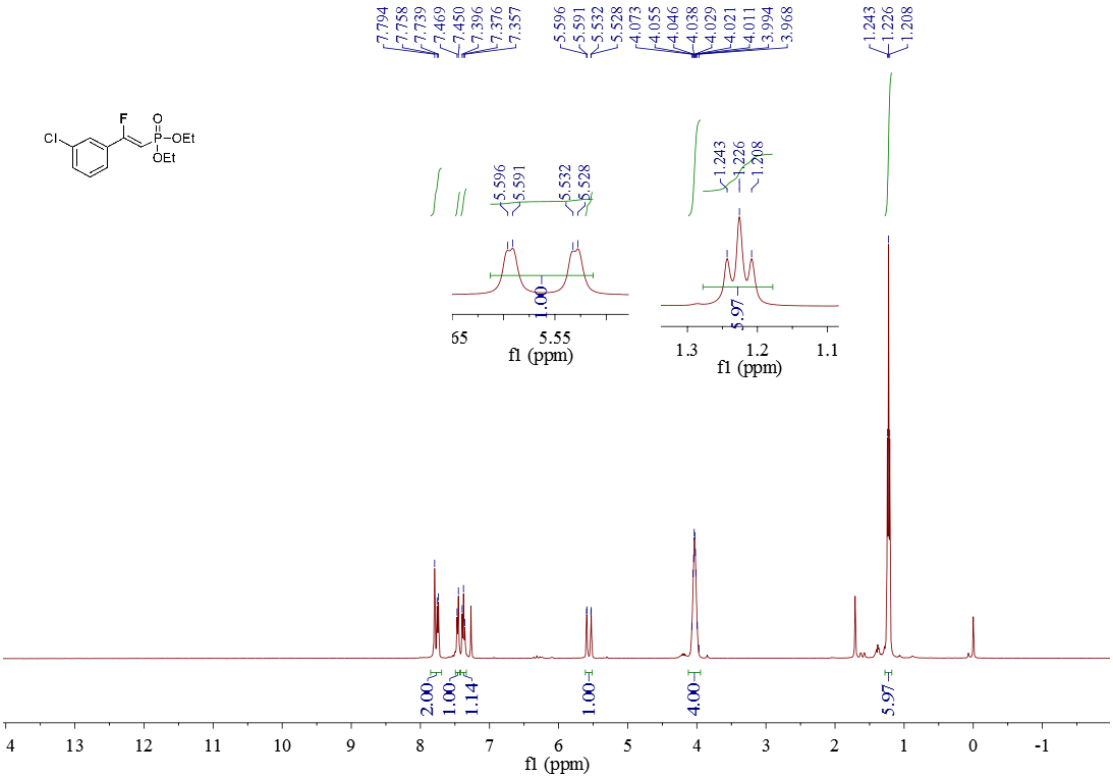


Diethyl (*Z*)-(2-(3-chlorophenyl)-2-fluorovinyl)phosphonate (2j)

^{1}H NMR



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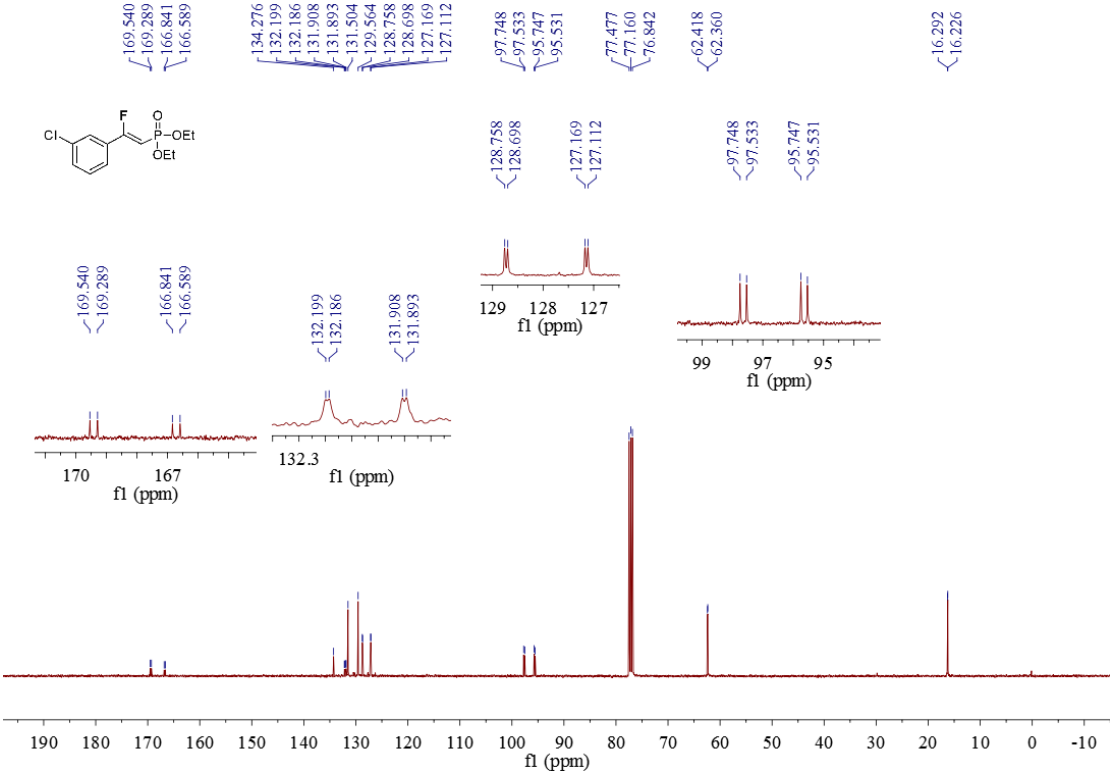
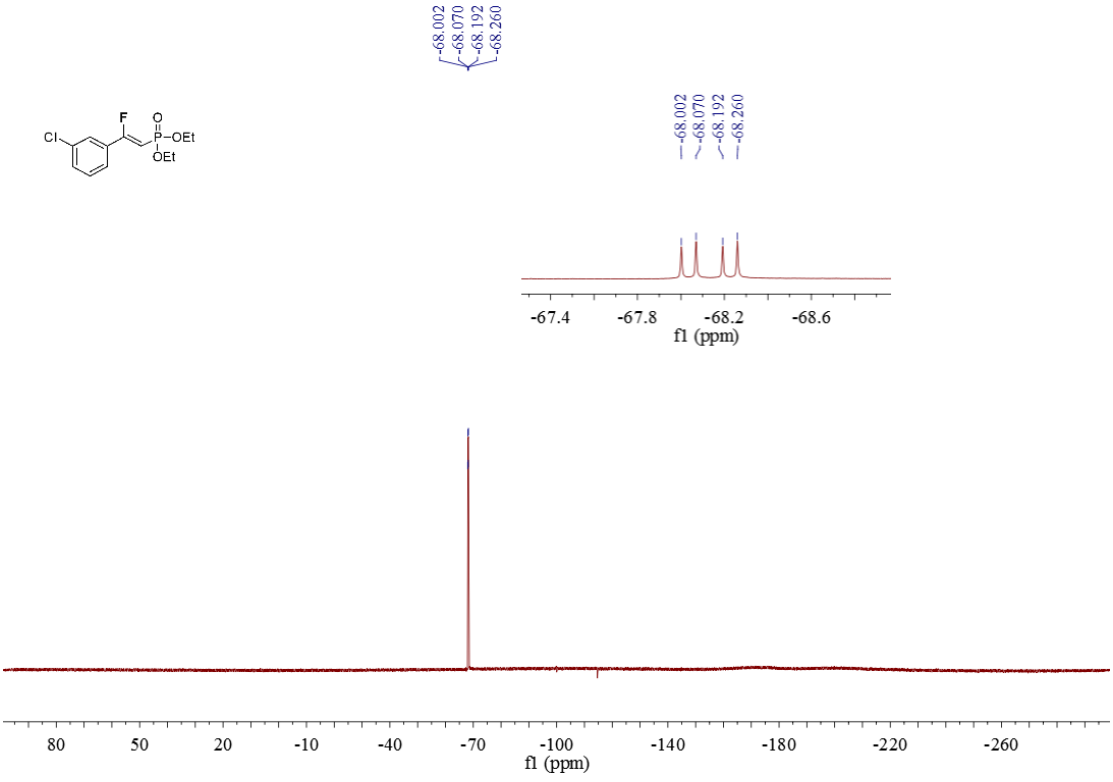
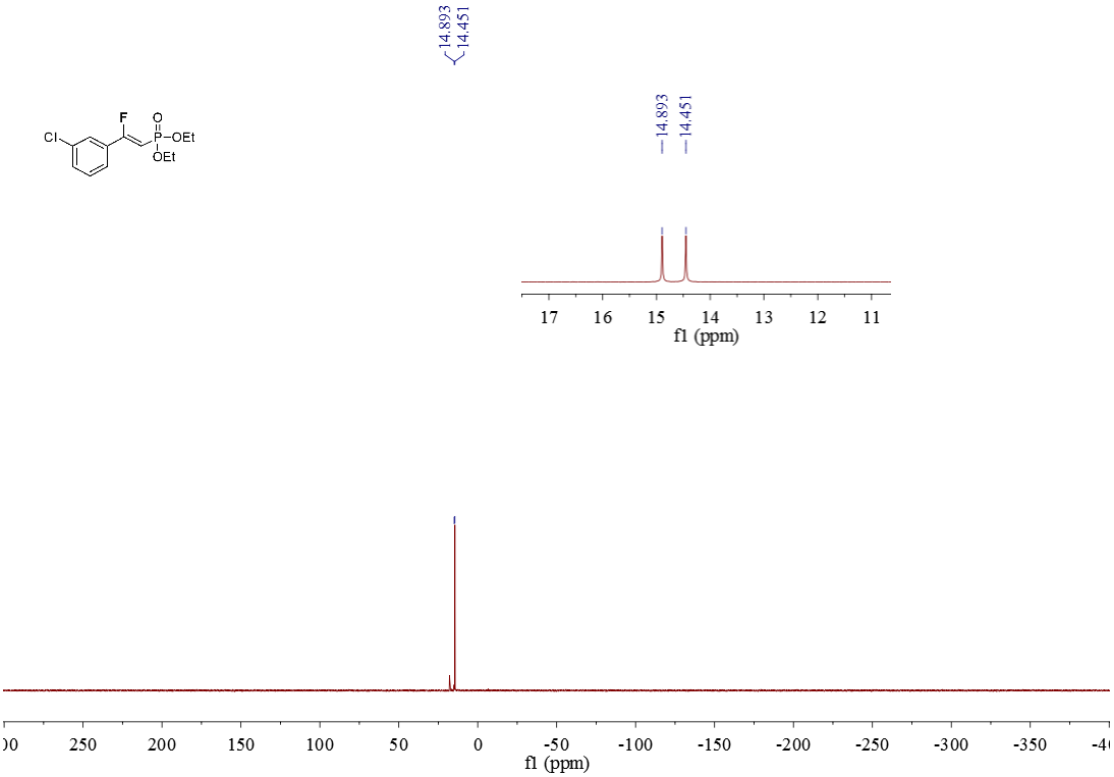


^{19}F NMR

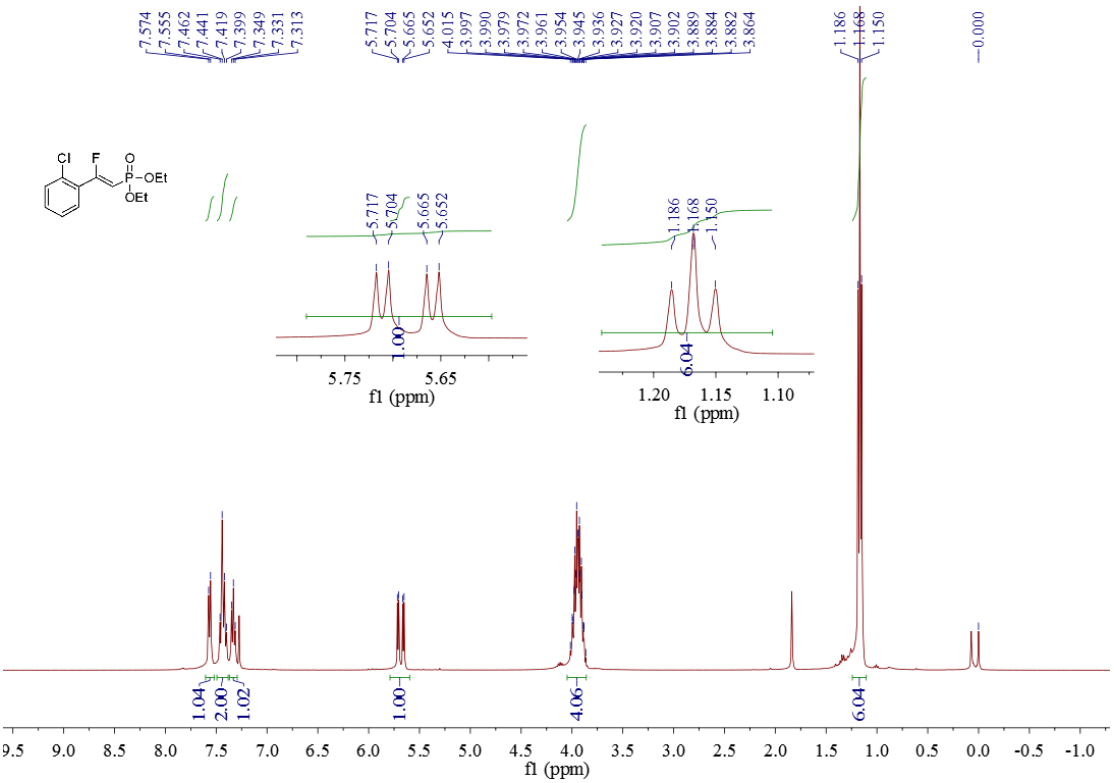


^{31}P NMR

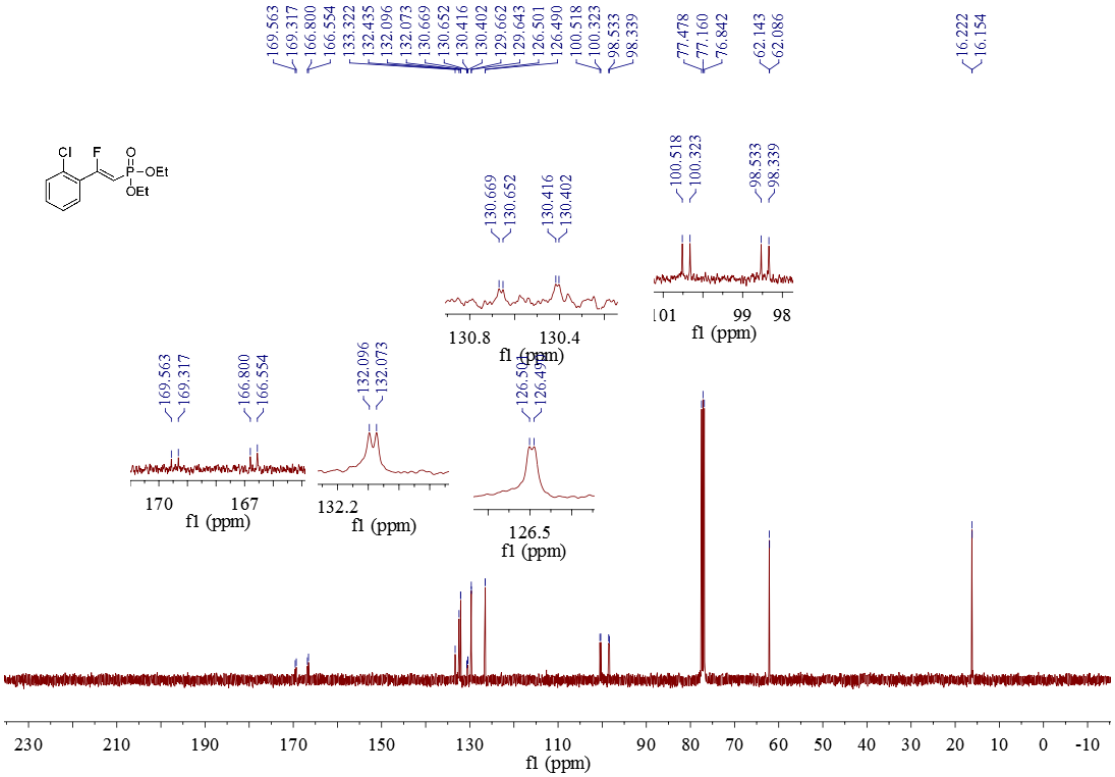


Diethyl (*Z*)-(2-(2-chlorophenyl)-2-fluorovinyl)phosphonate (2k)

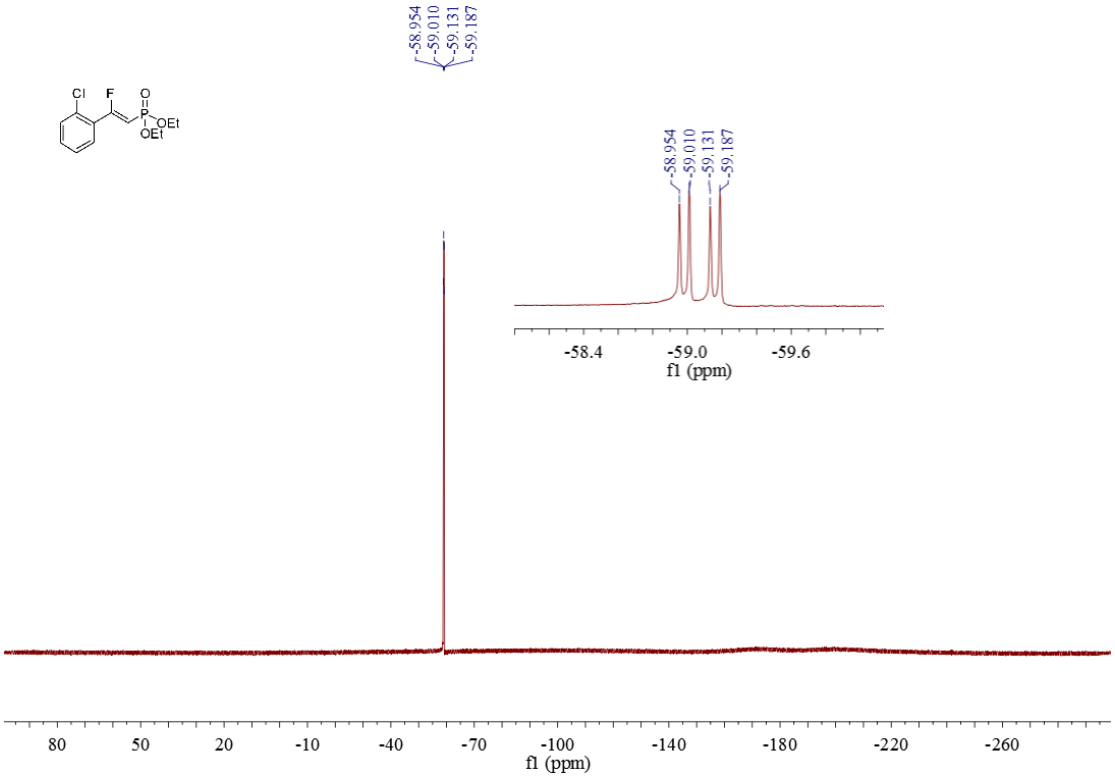
^{1}H NMR



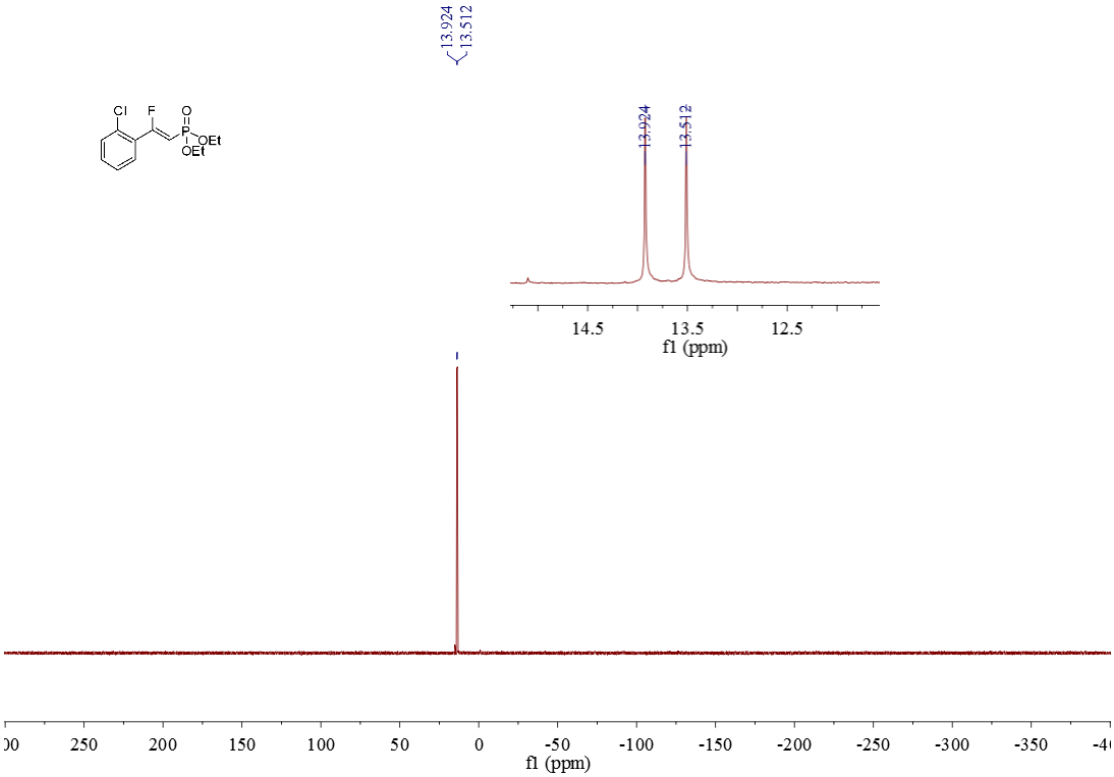
^{13}C NMR



^{19}F NMR

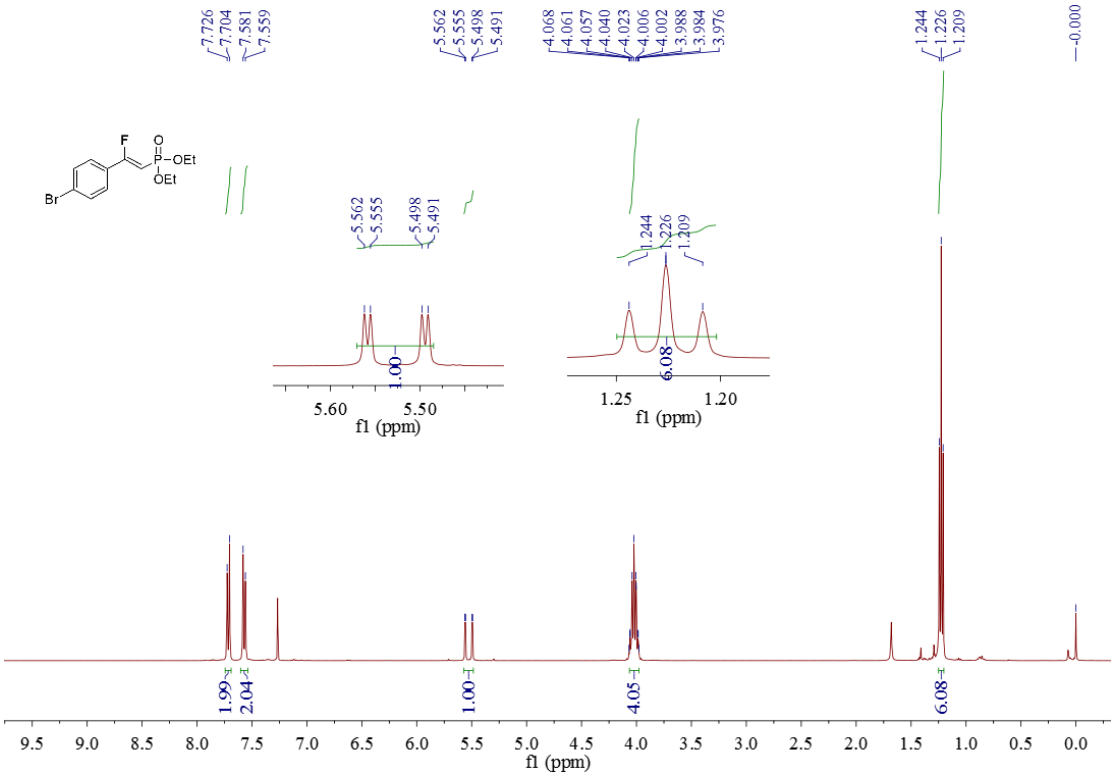


^{31}P NMR

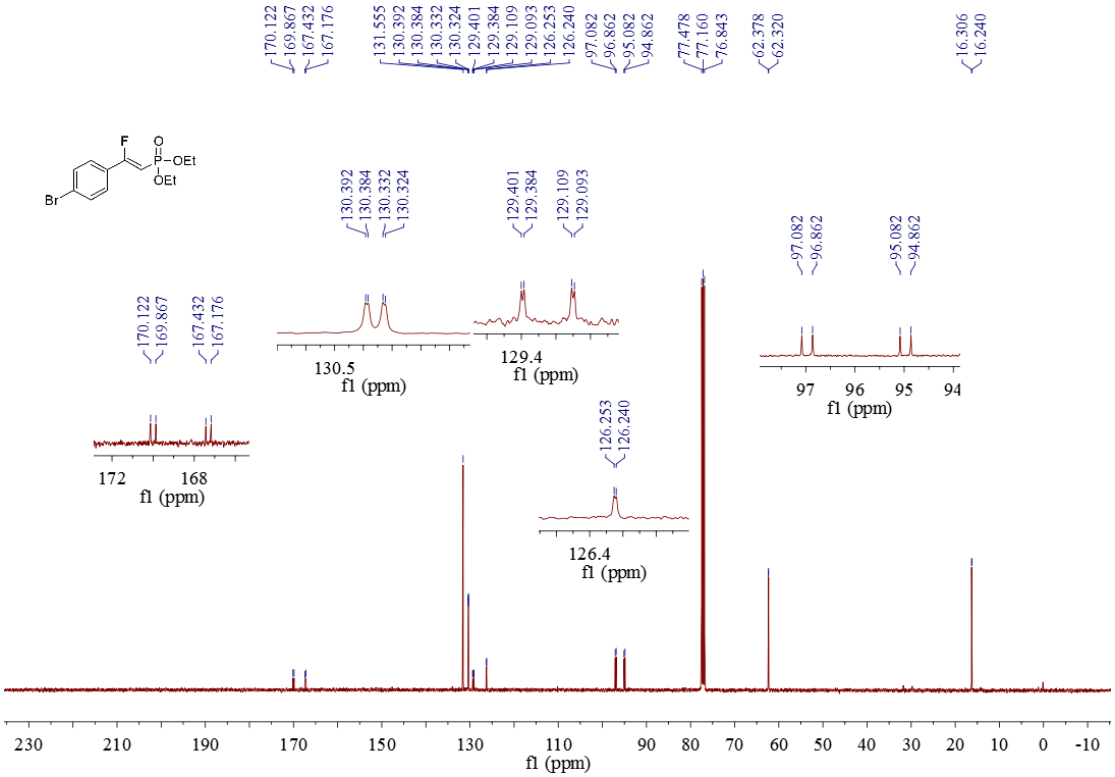


Diethyl (*Z*)-(2-(4-bromophenyl)-2-fluorovinyl)phosphonate (2l)

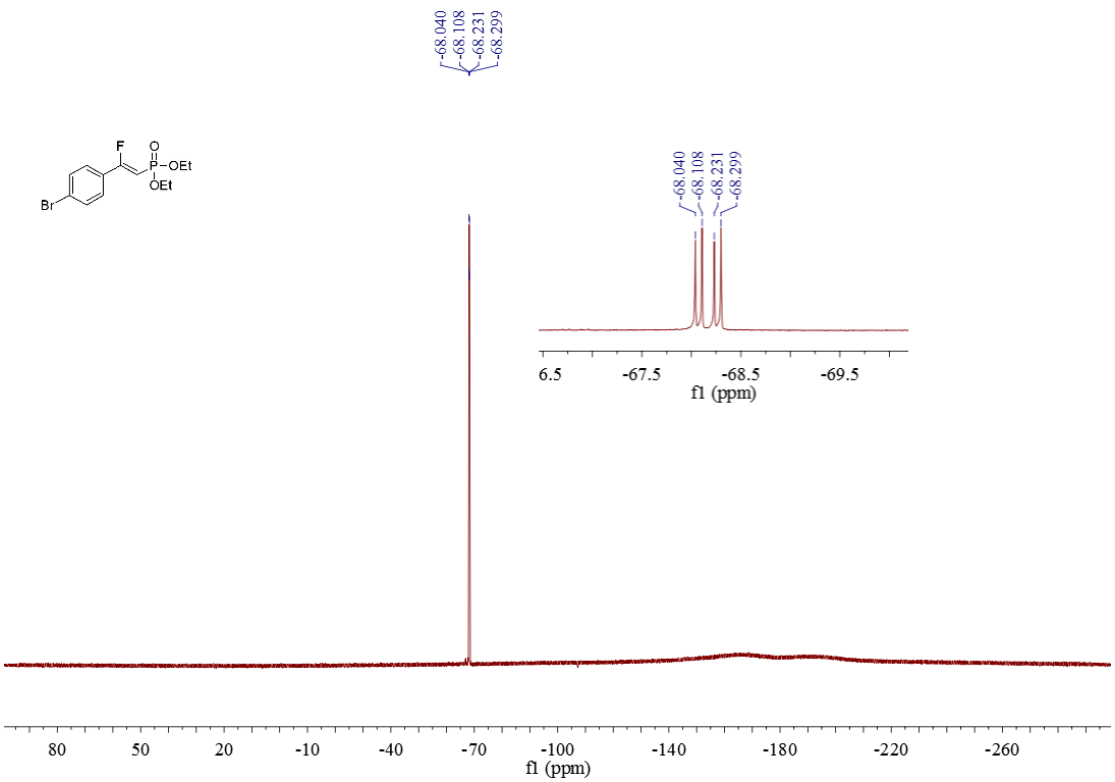
^{1}H NMR



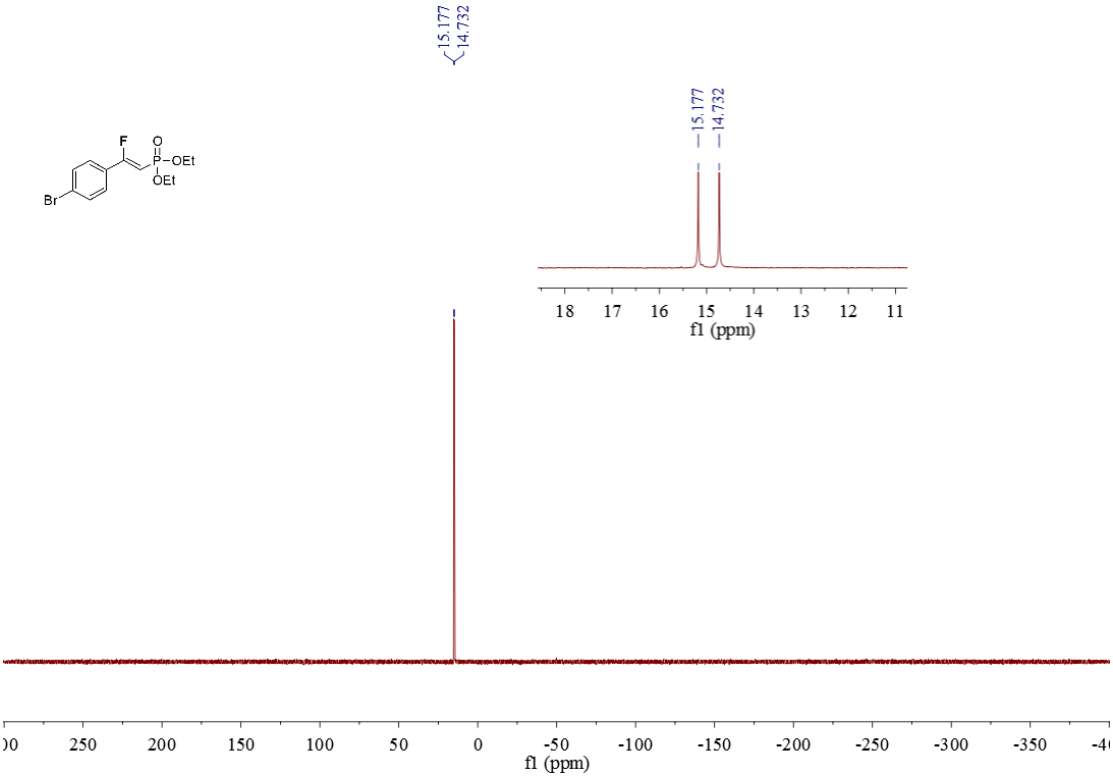
^{13}C NMR



^{19}F NMR

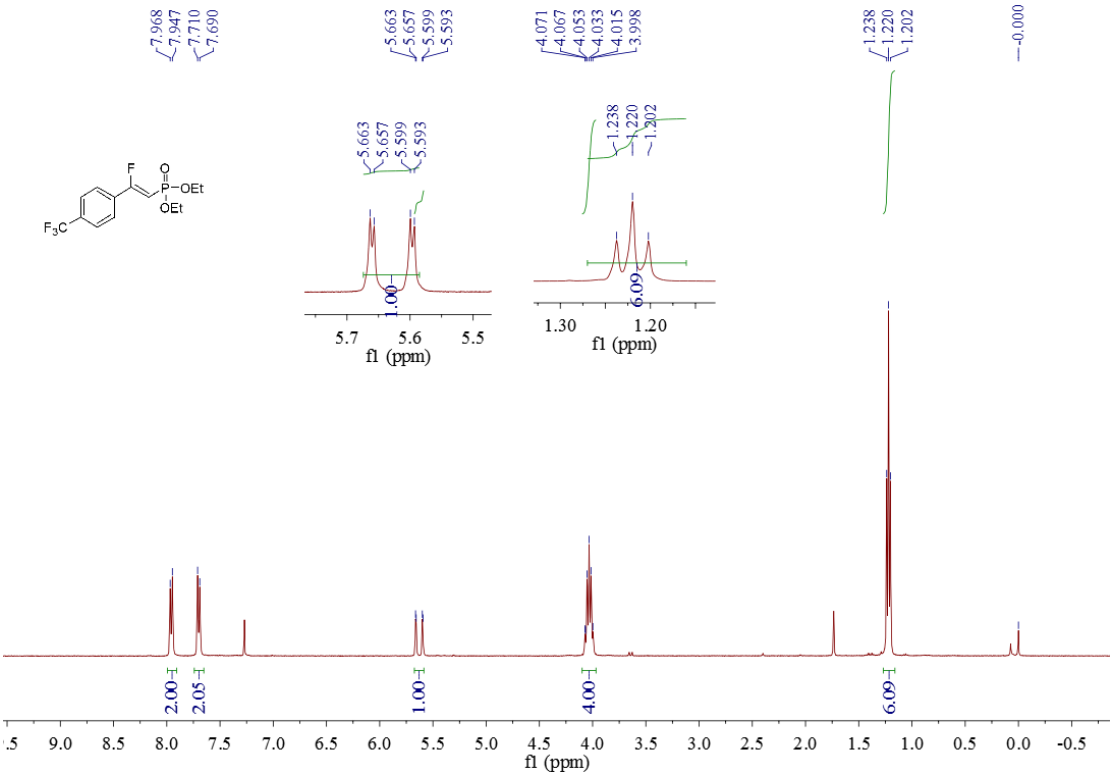


^{31}P NMR

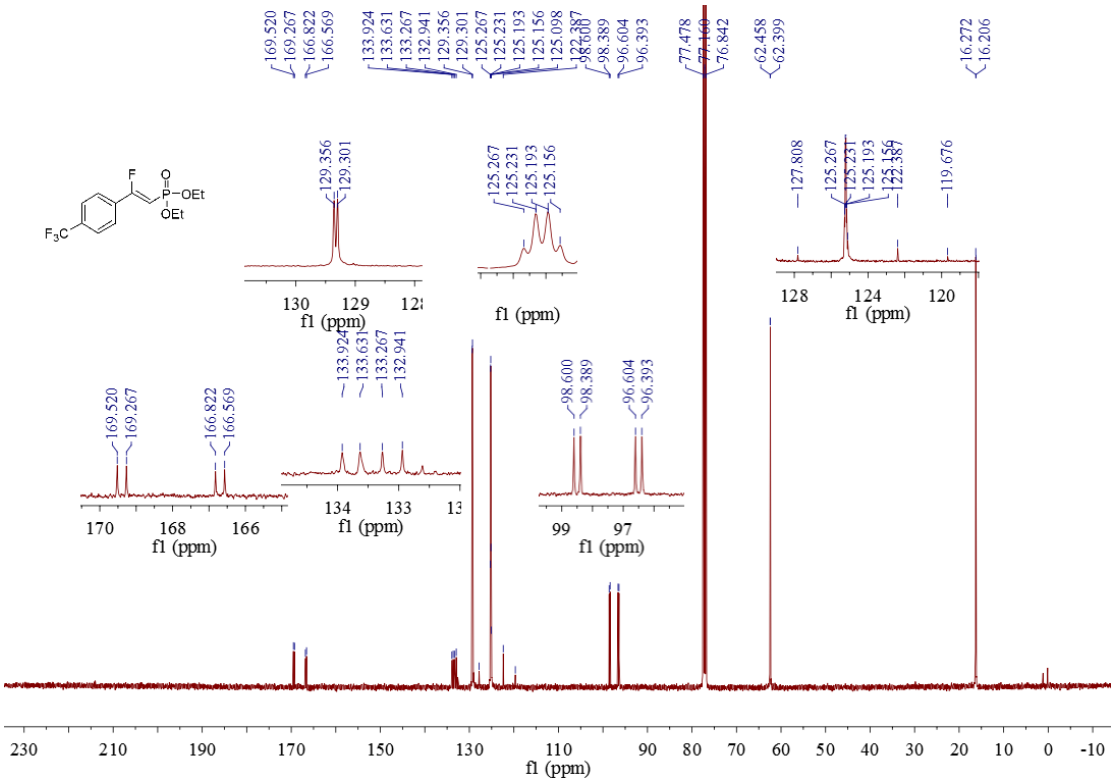


Diethyl (*Z*)-(2-fluoro-2-(4-(trifluoromethyl)phenyl)vinyl)phosphonate (2m)

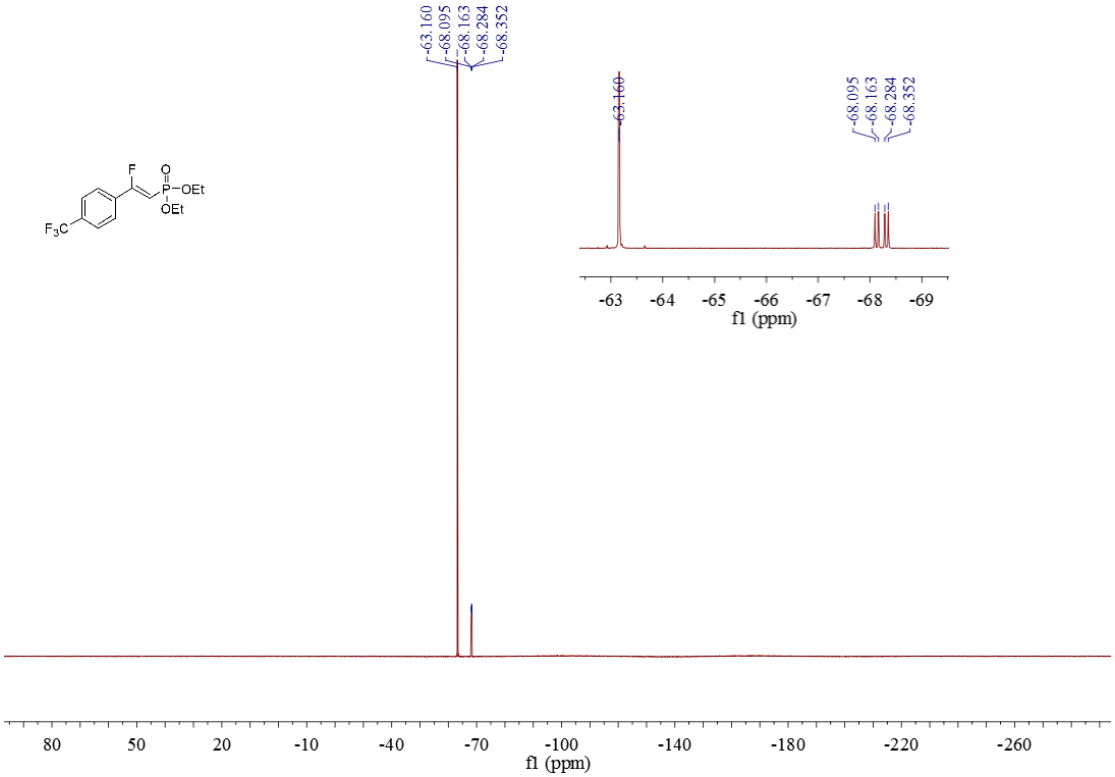
^{1}H NMR



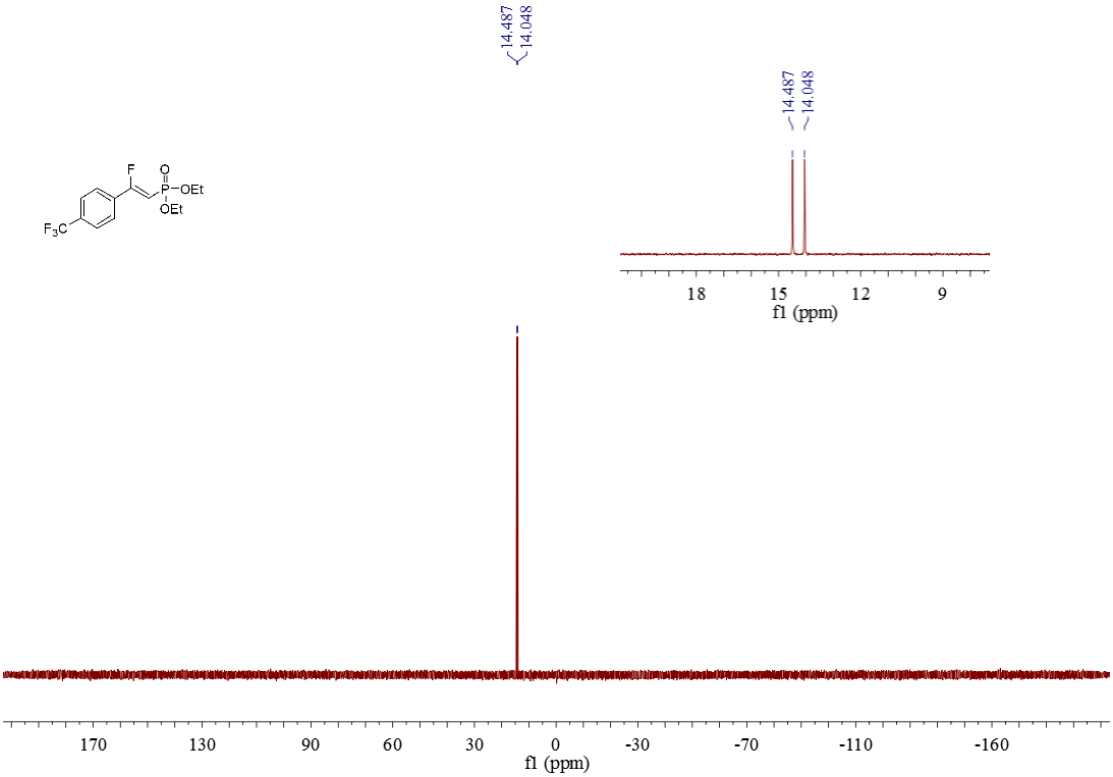
^{13}C NMR



^{19}F NMR

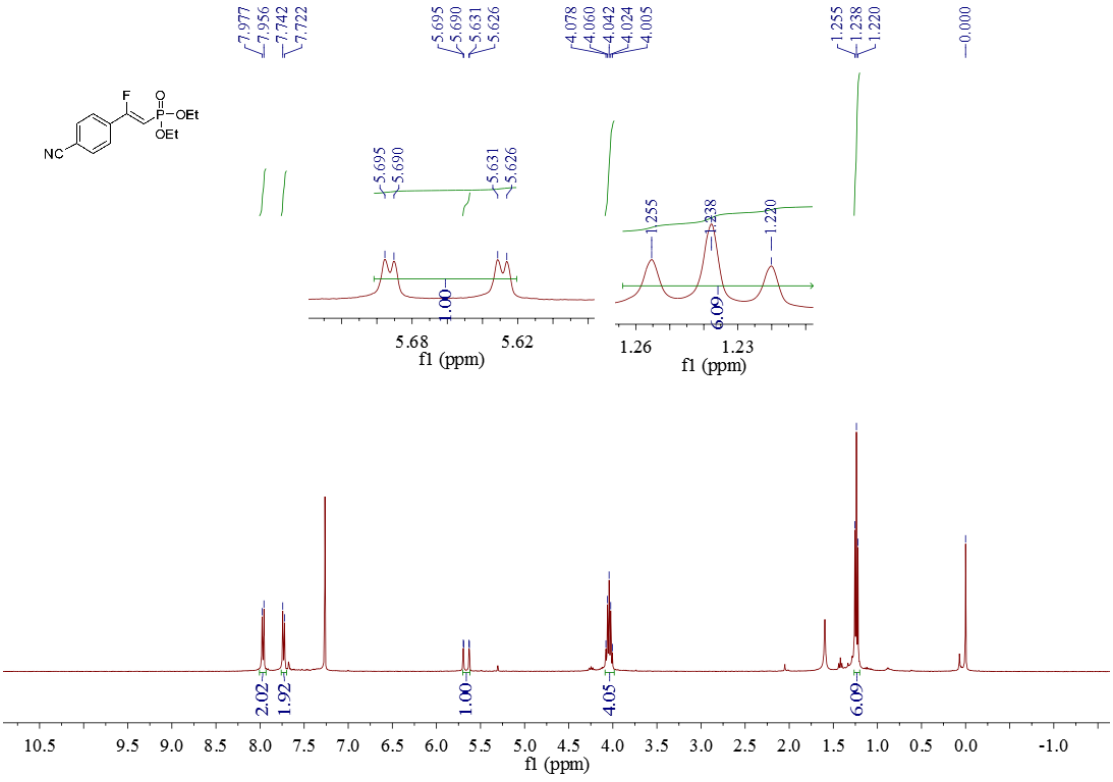


^{31}P NMR

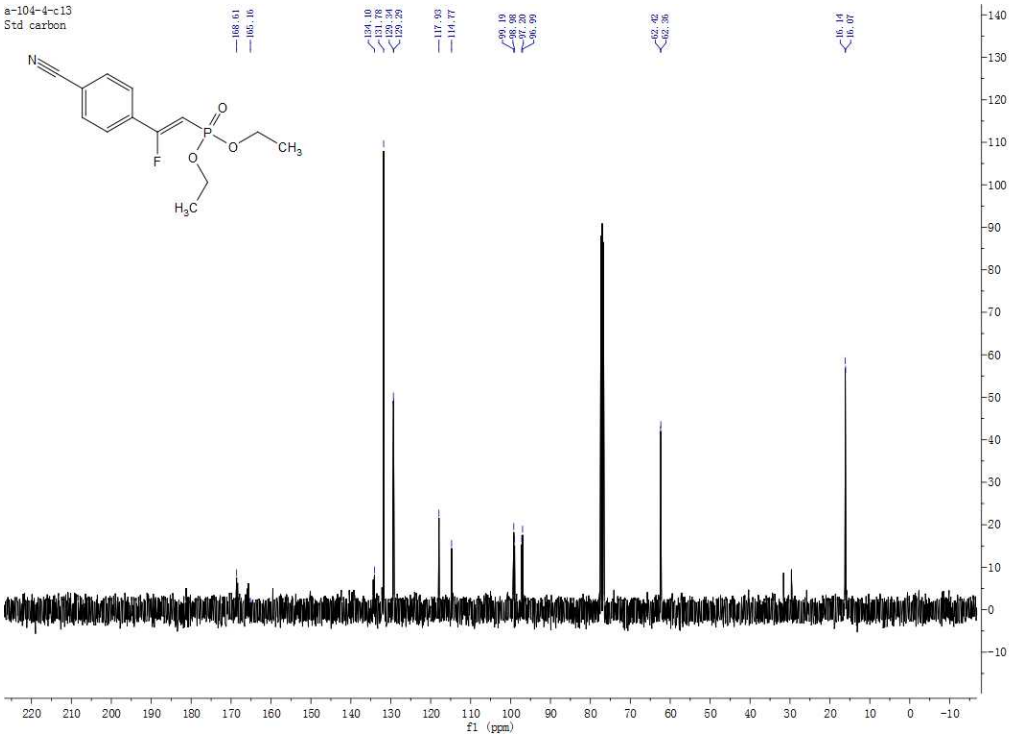


Diethyl (*Z*)-(2-(4-cyanophenyl)-2-fluorovinyl)phosphonate (2n)

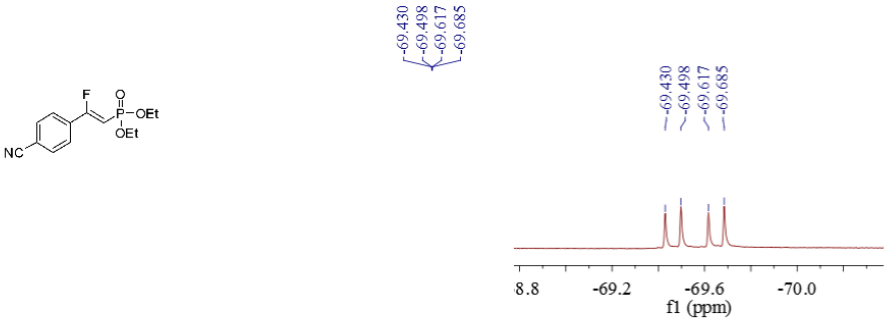
^{1}H NMR

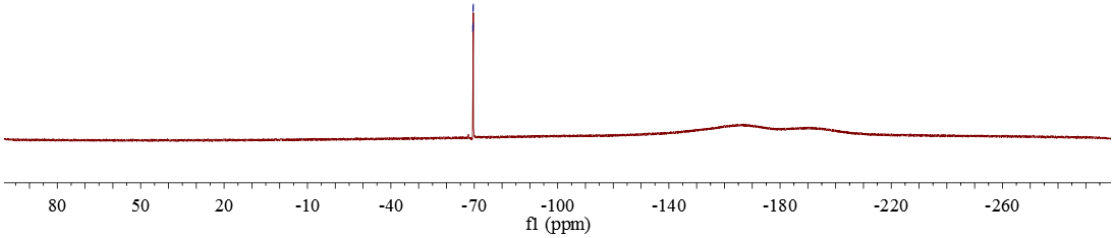


^{13}C NMR

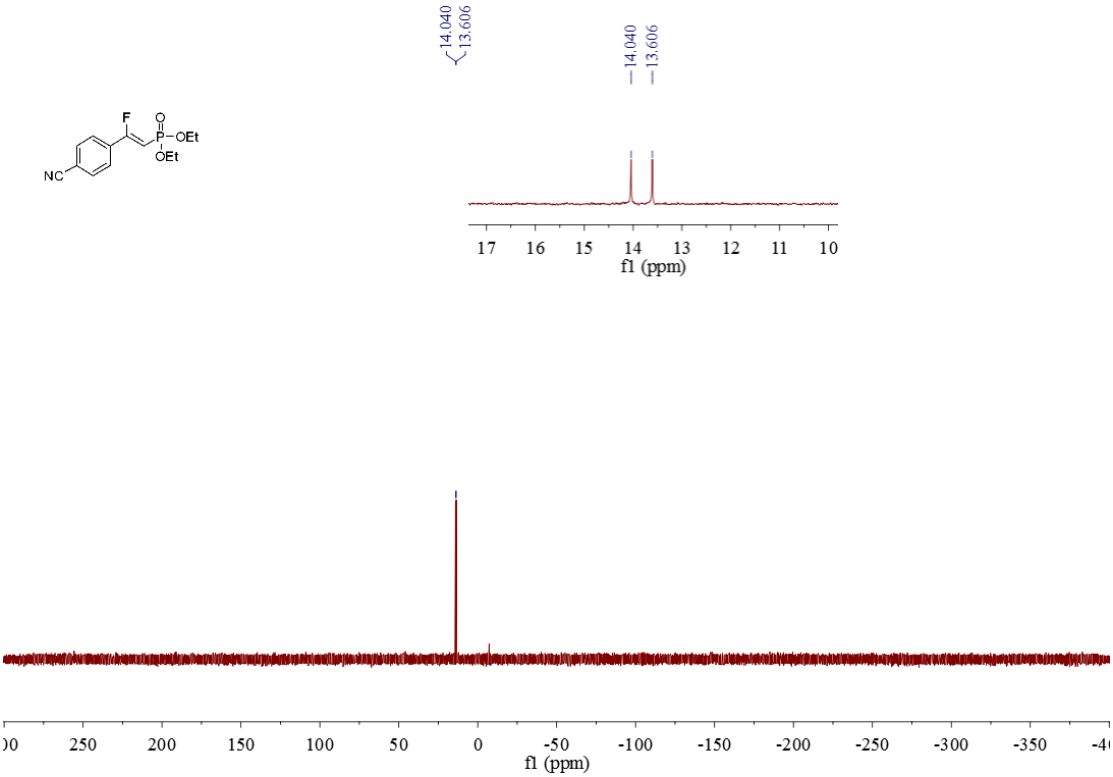


^{19}F NMR



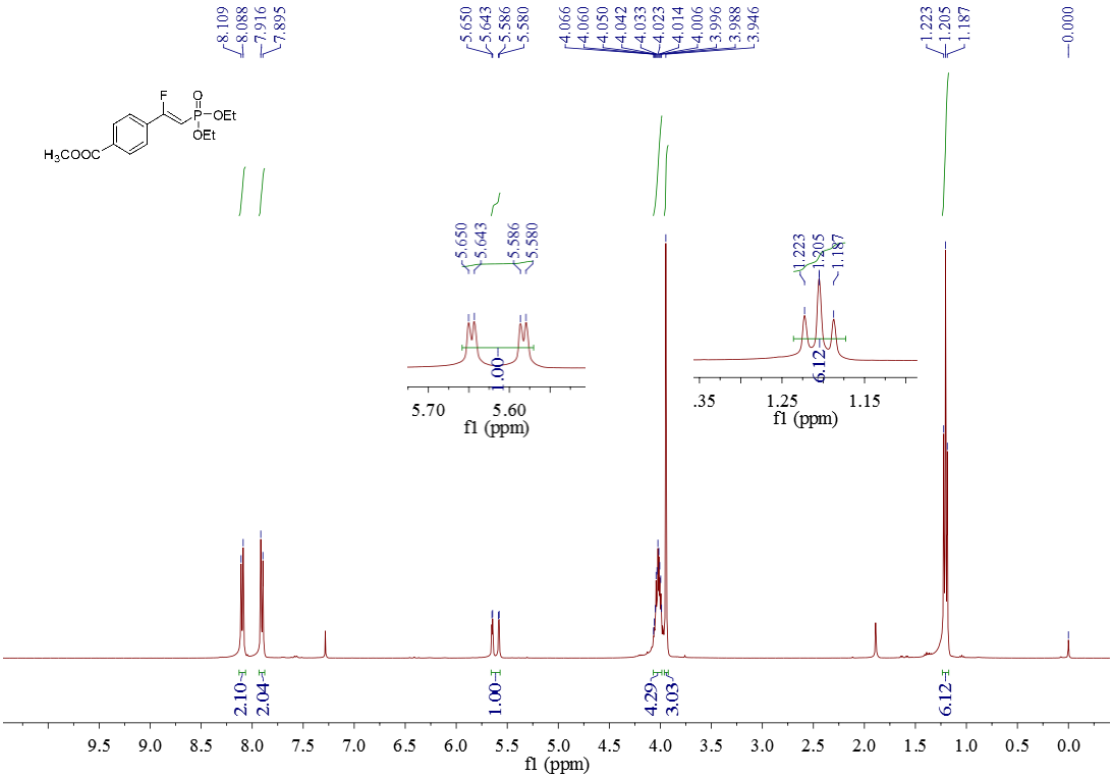


^{31}P NMR

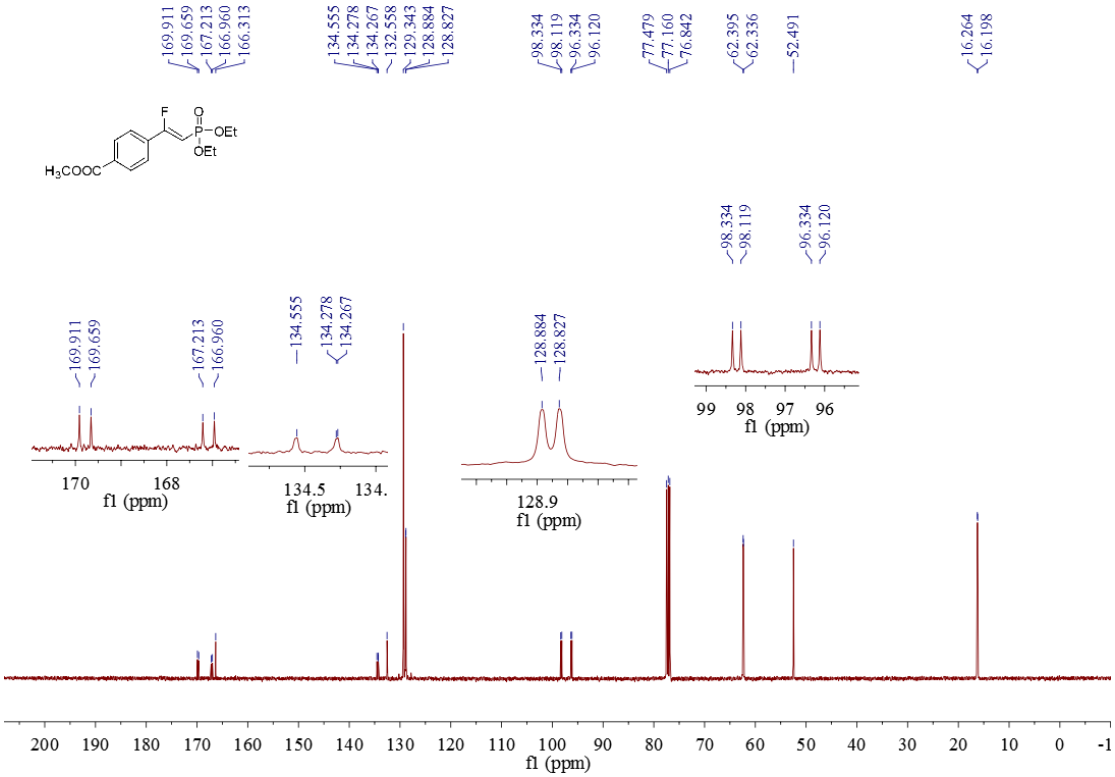


Methyl (*Z*)-4-(2-(diethoxyphosphoryl)-1-fluorovinyl)benzoate (2o)

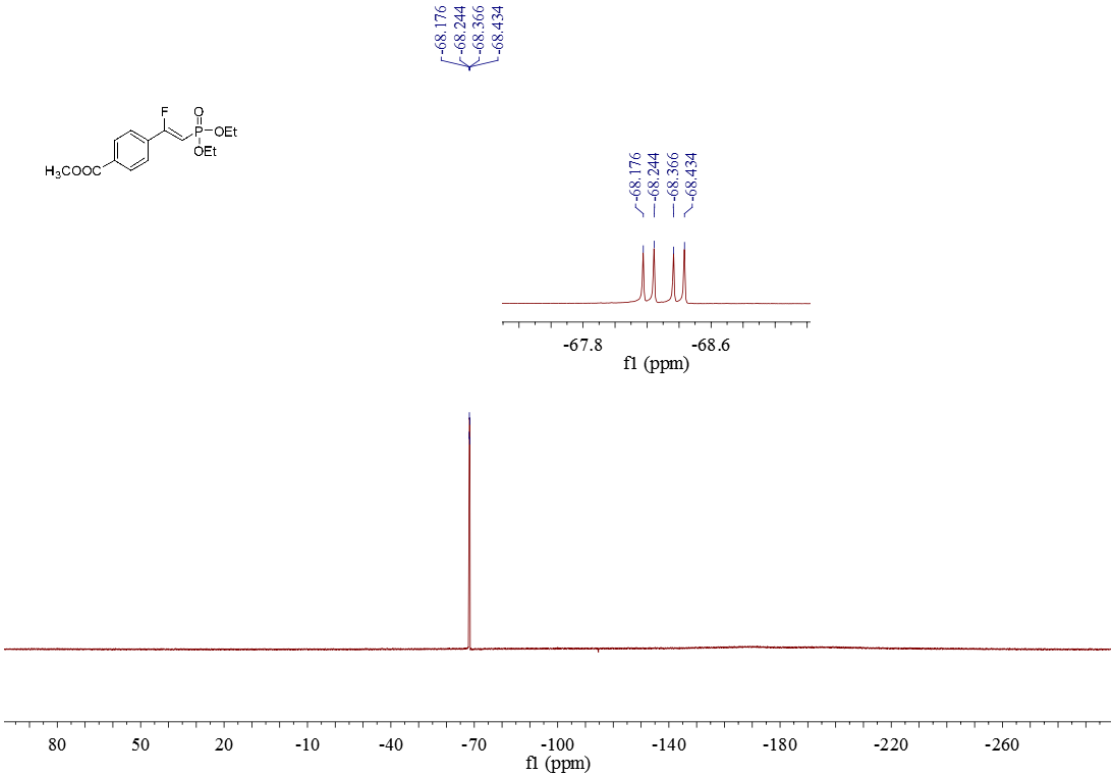
^{1}H NMR



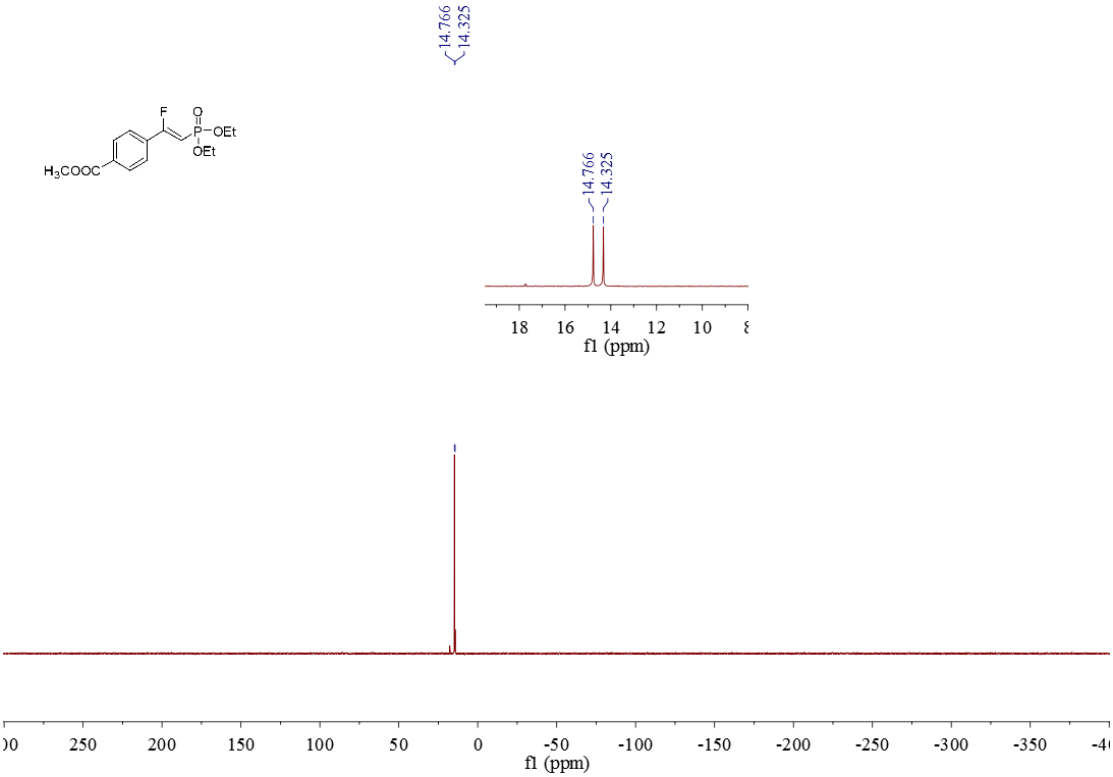
^{13}C NMR



^{19}F NMR

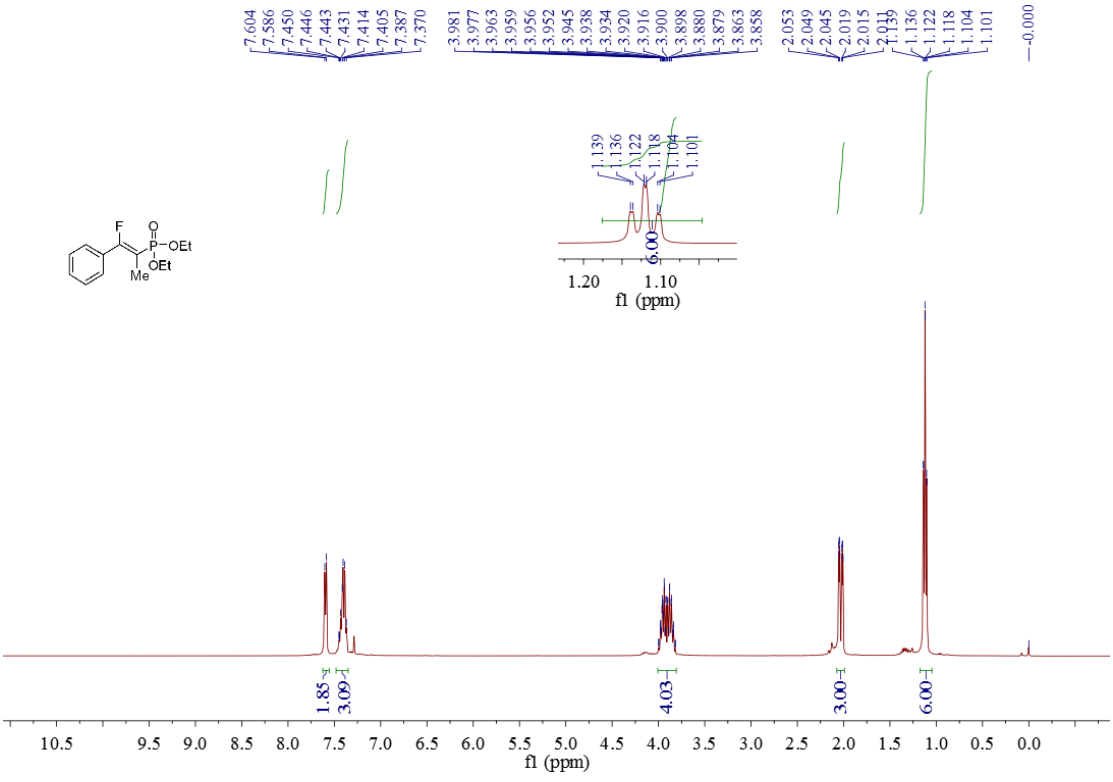


^{31}P NMR

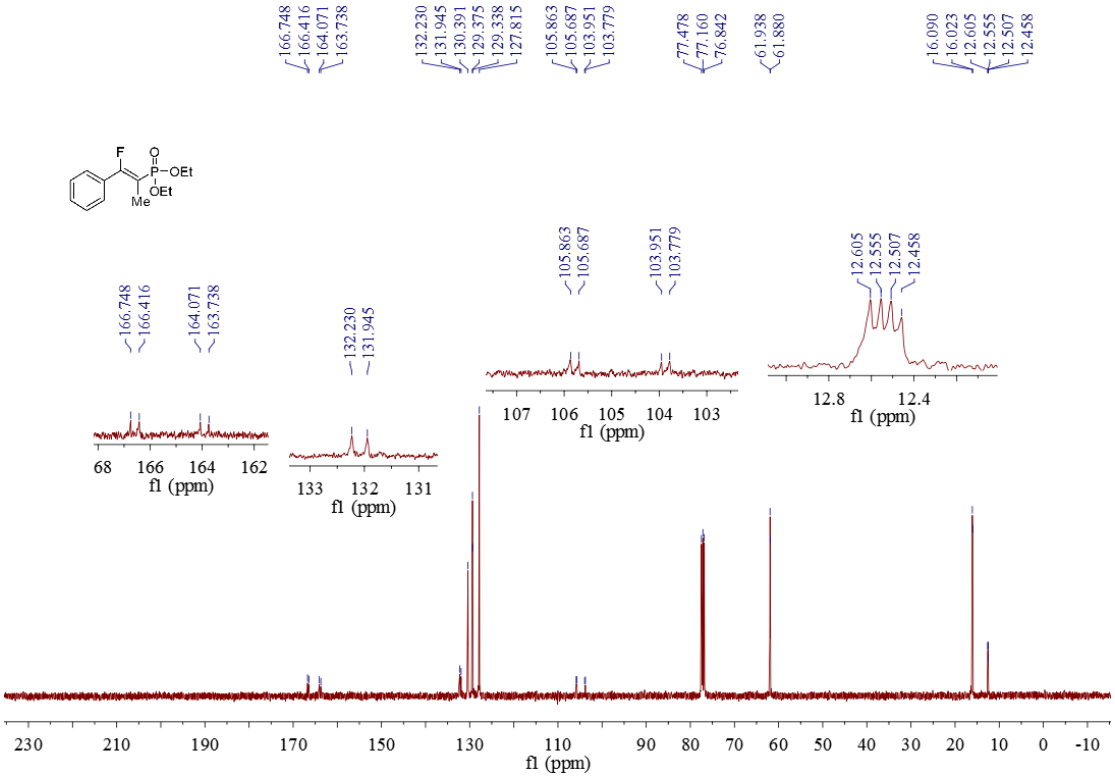


Diethyl (*Z*)-(1-fluoro-1-phenylprop-1-en-2-yl)phosphonate (2p)

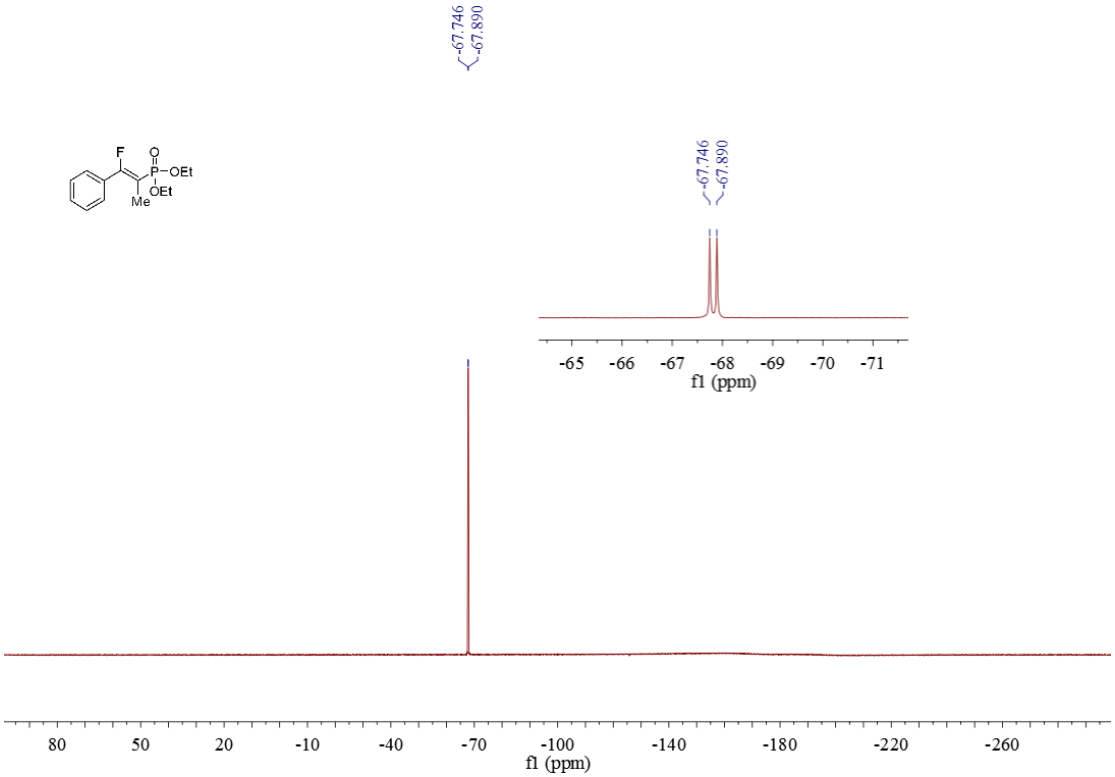
^{1}H NMR



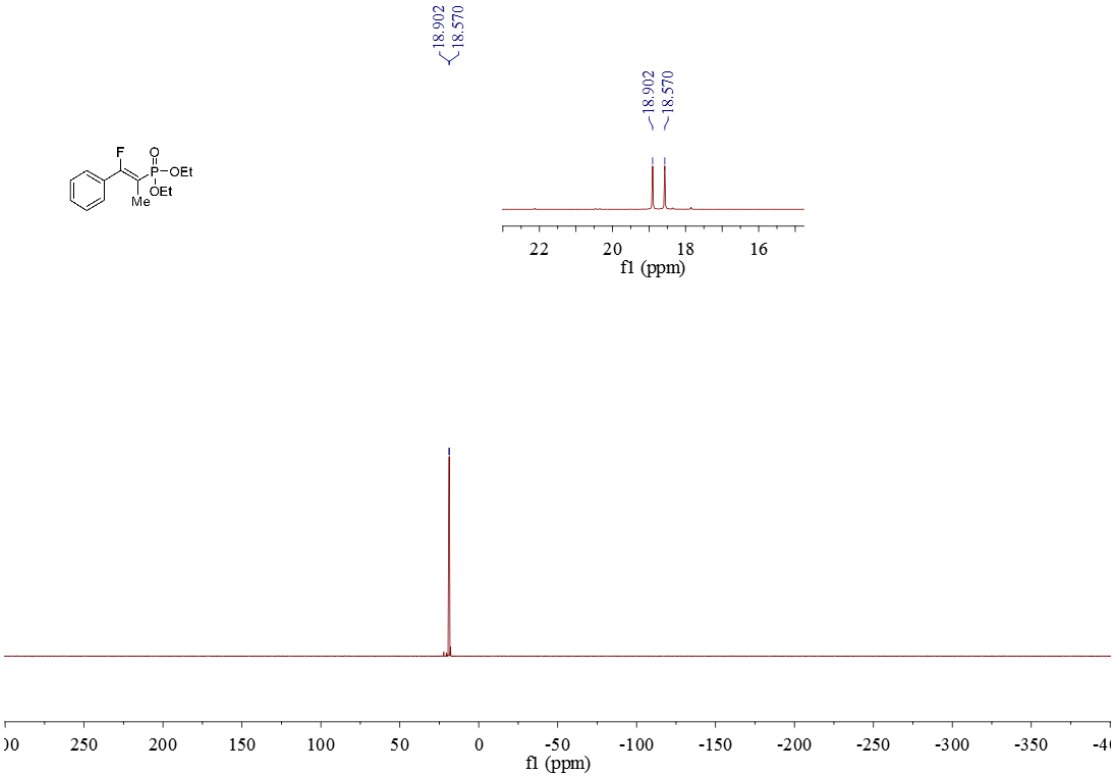
^{13}C NMR



^{19}F NMR

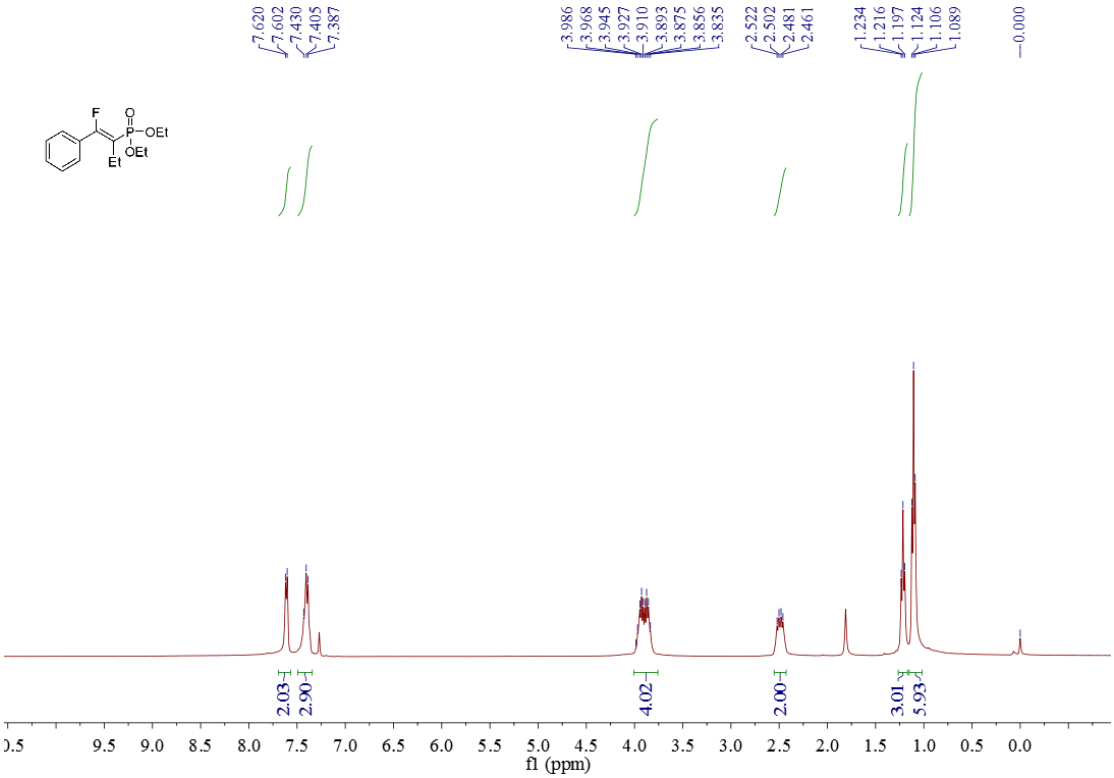


^{31}P NMR

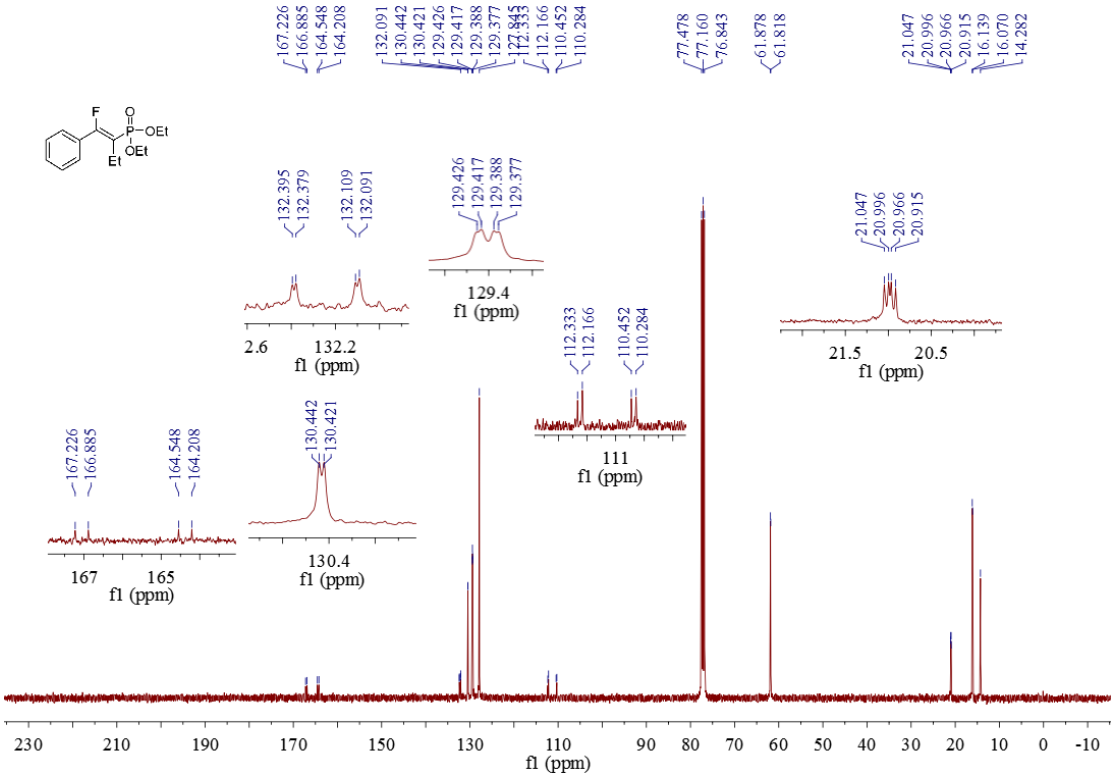


Diethyl (*Z*)-(1-fluoro-1-phenylbut-1-en-2-yl)phosphonate (2q)

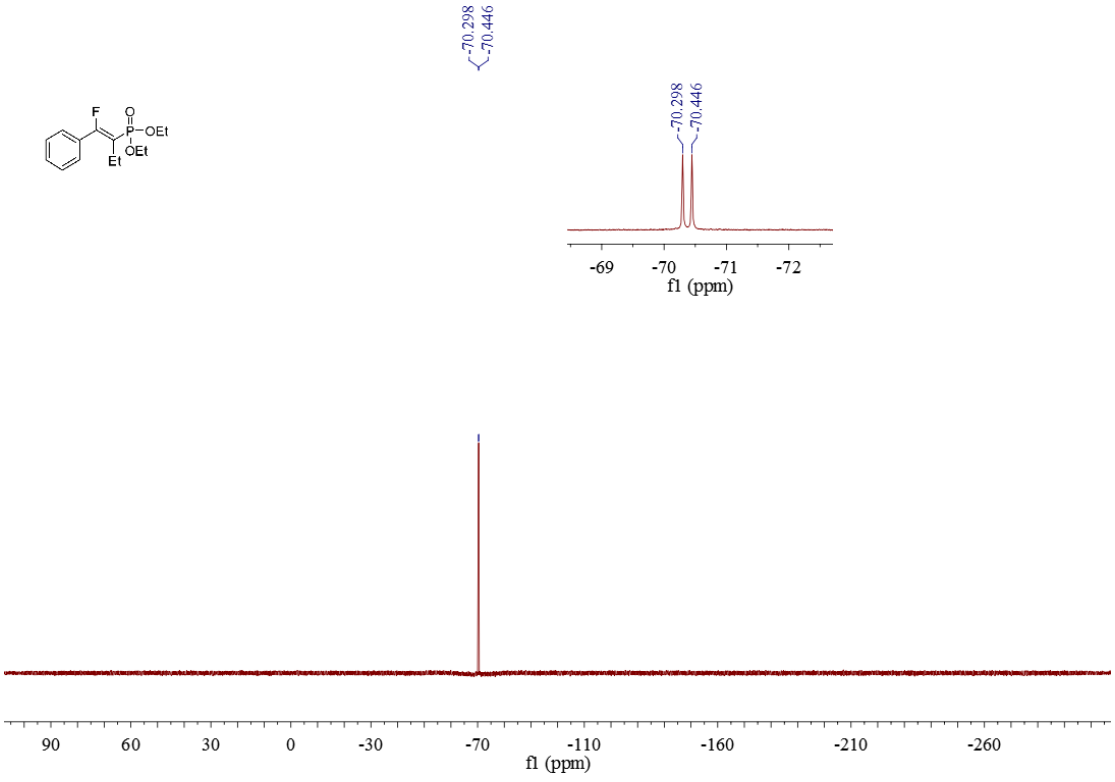
^{1}H NMR



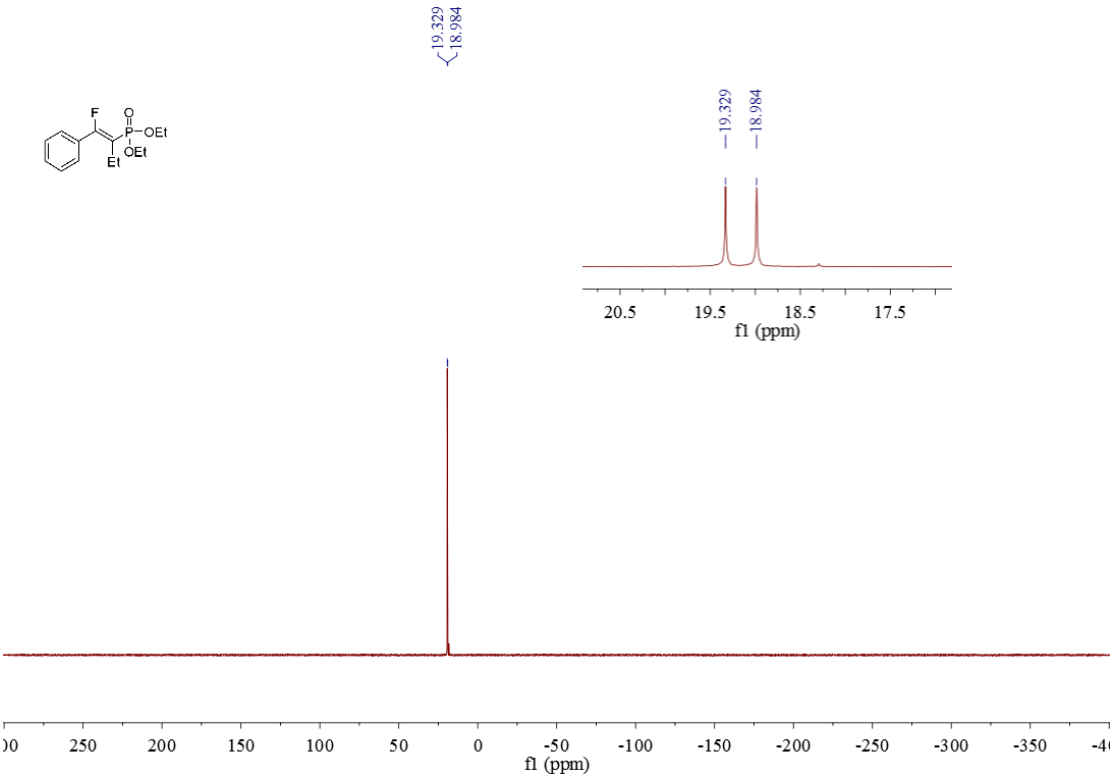
^{13}C NMR



^{19}F NMR

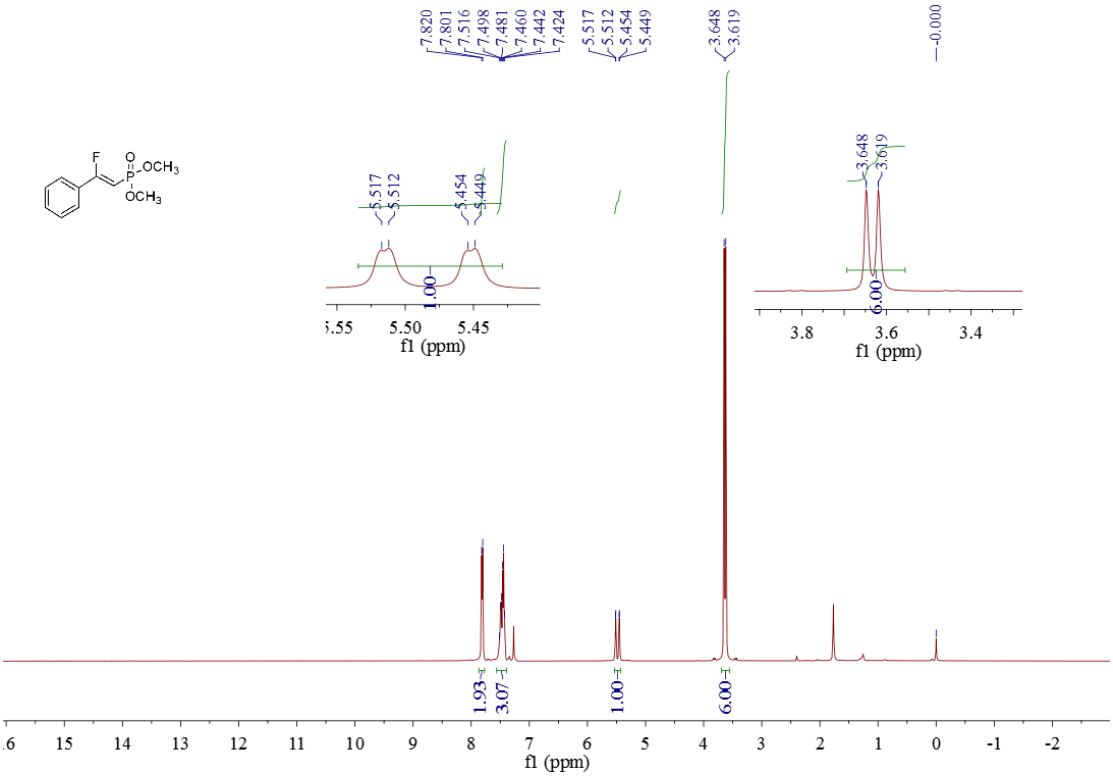


^{31}P NMR

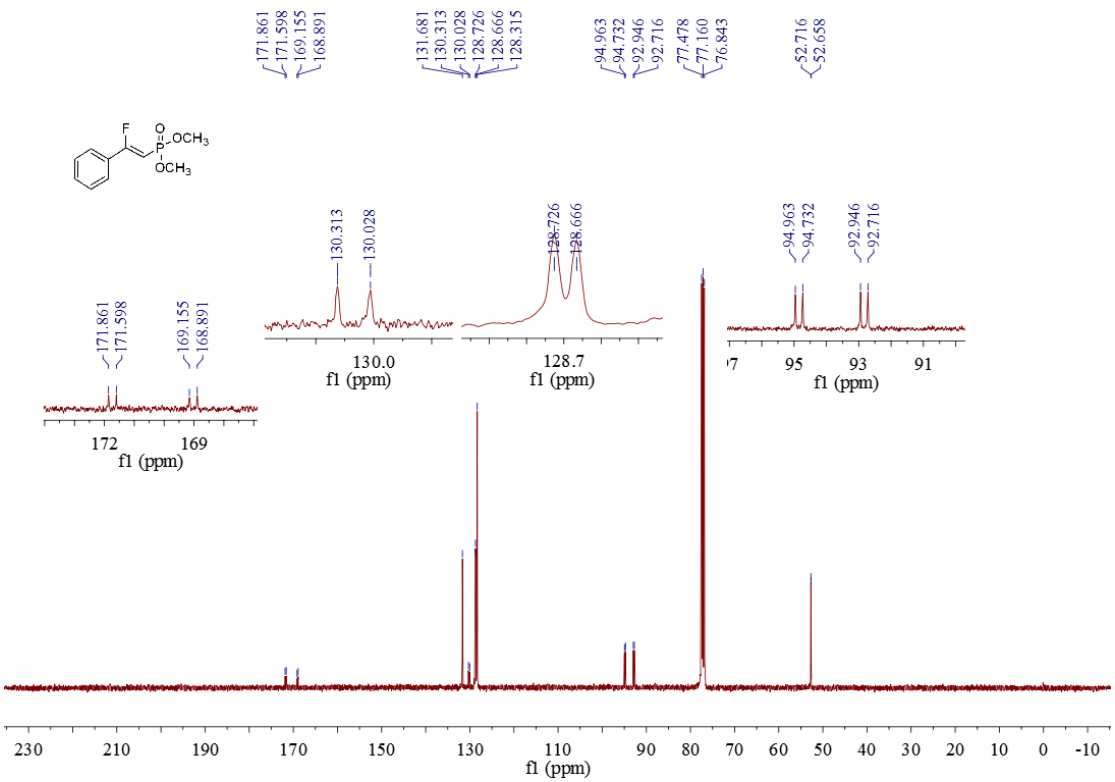


Dimethyl (*Z*)-(2-fluoro-2-phenylvinyl)phosphonate (3a)

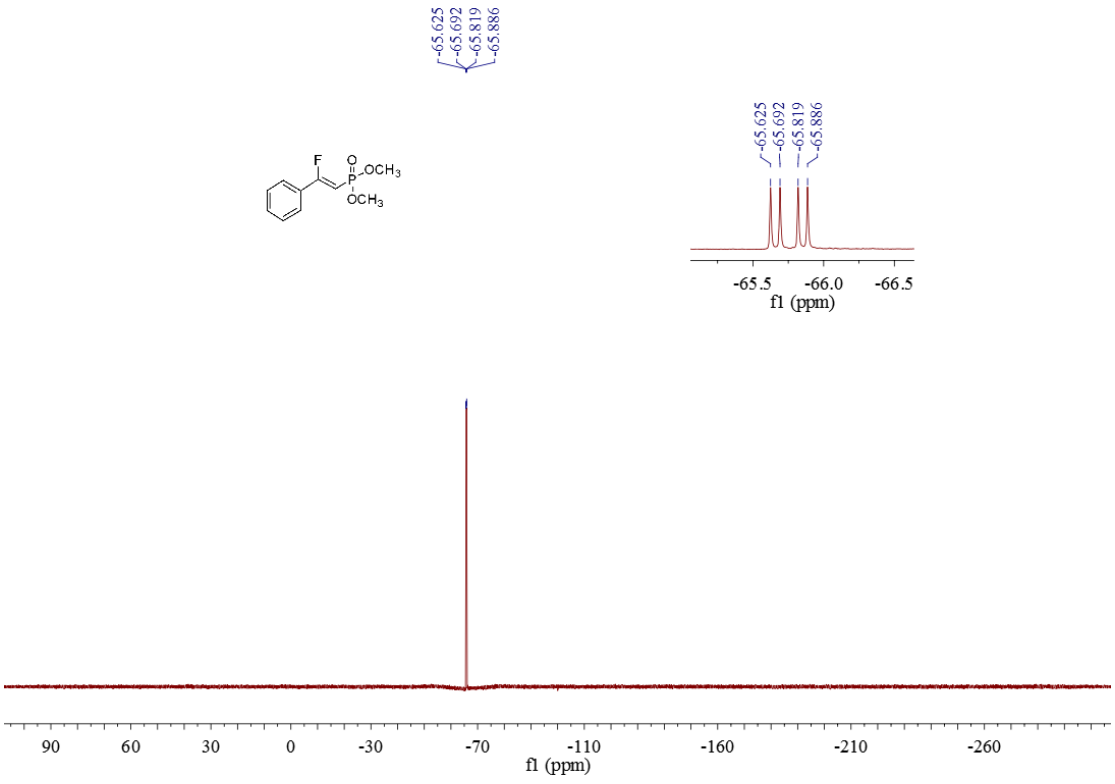
^{1}H NMR



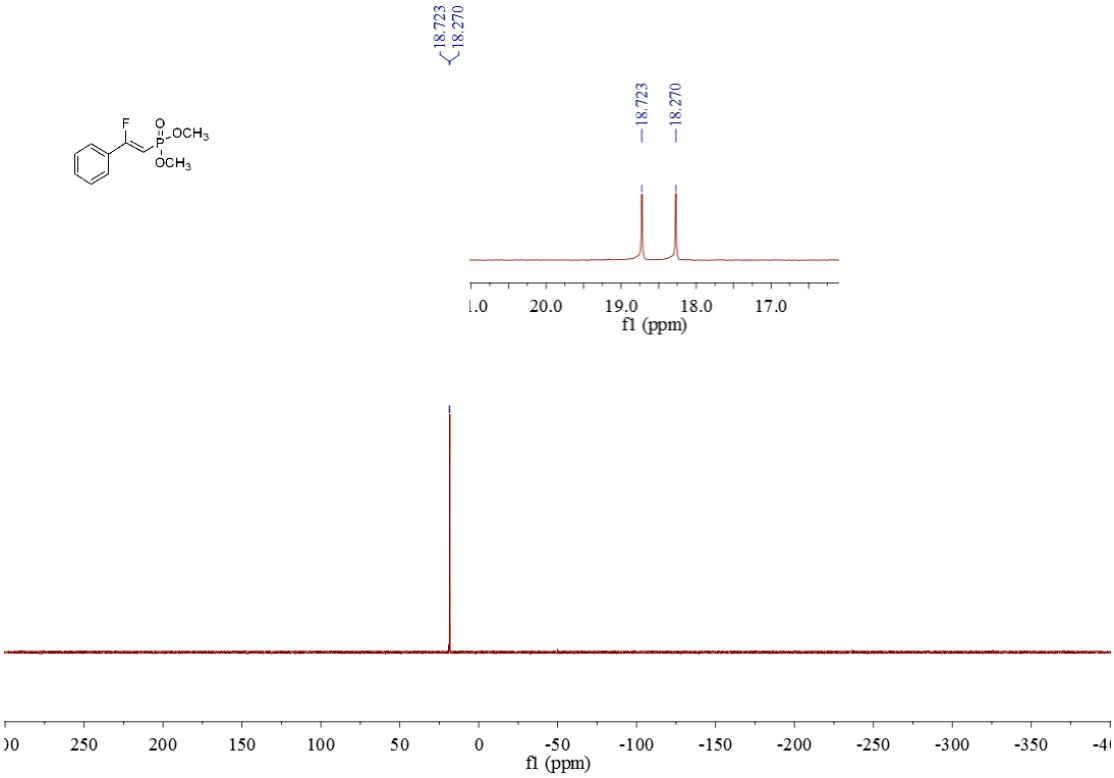
^{13}C NMR



^{19}F NMR

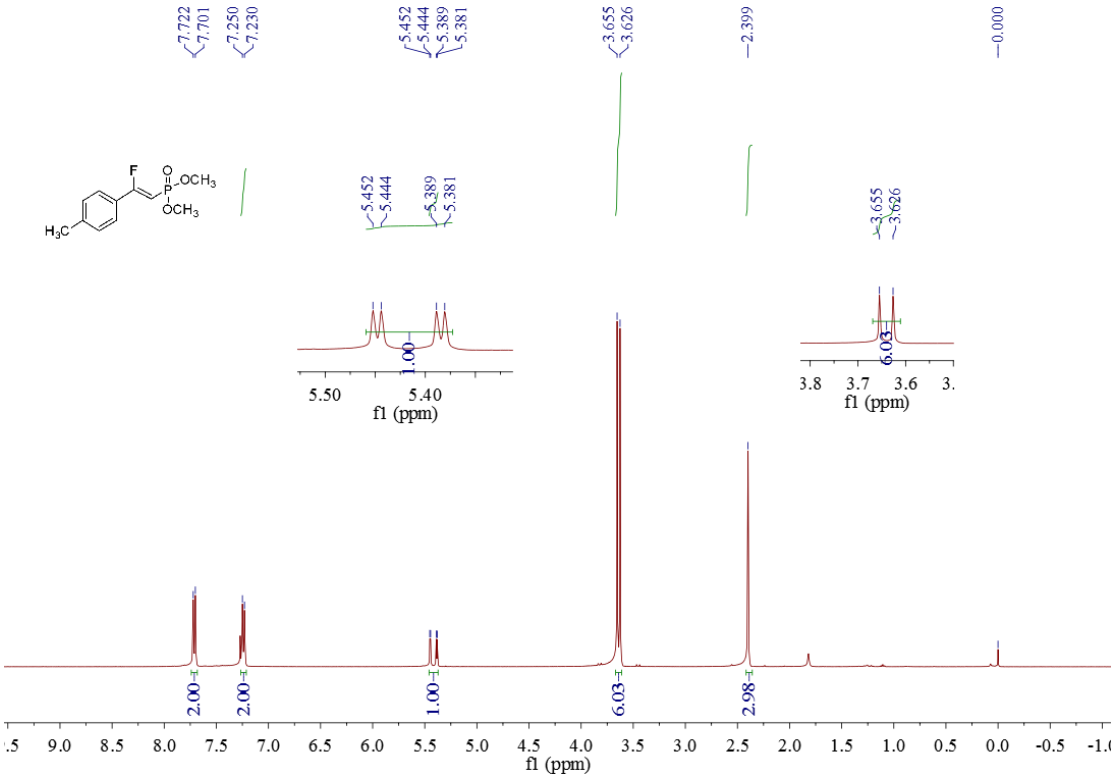


^{31}P NMR

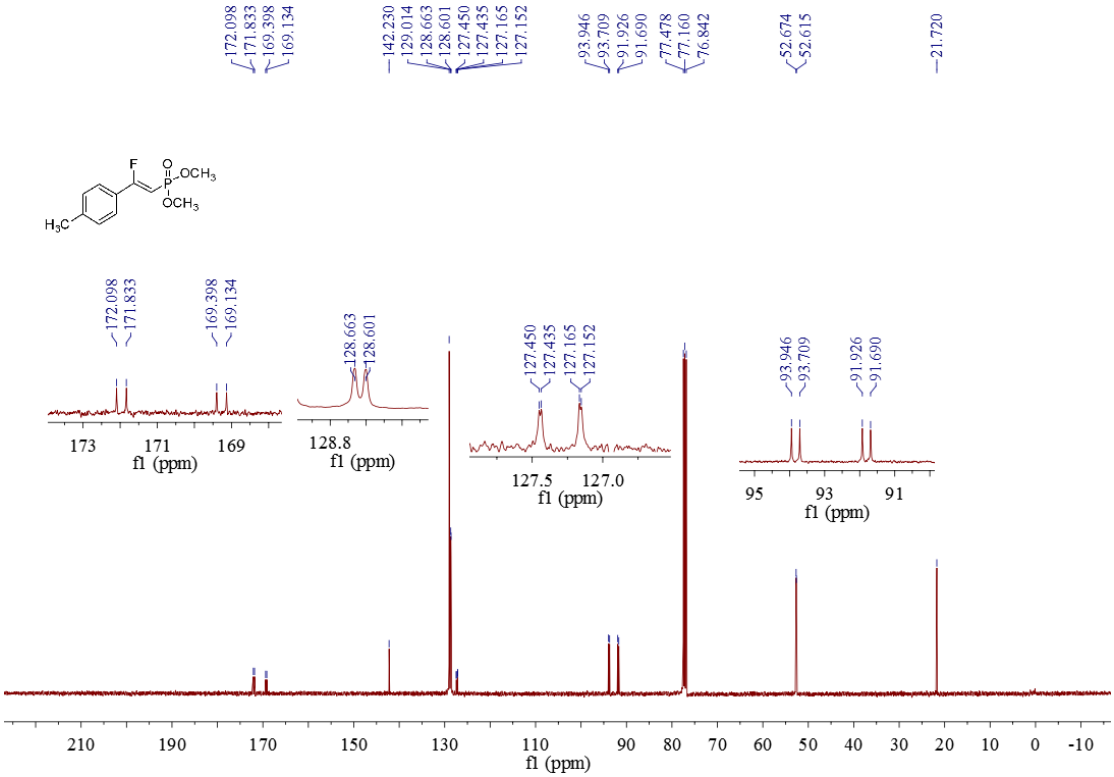


Dimethyl (*Z*)-(2-fluoro-2-(*p*-tolyl)vinyl) phosphonate (3b)

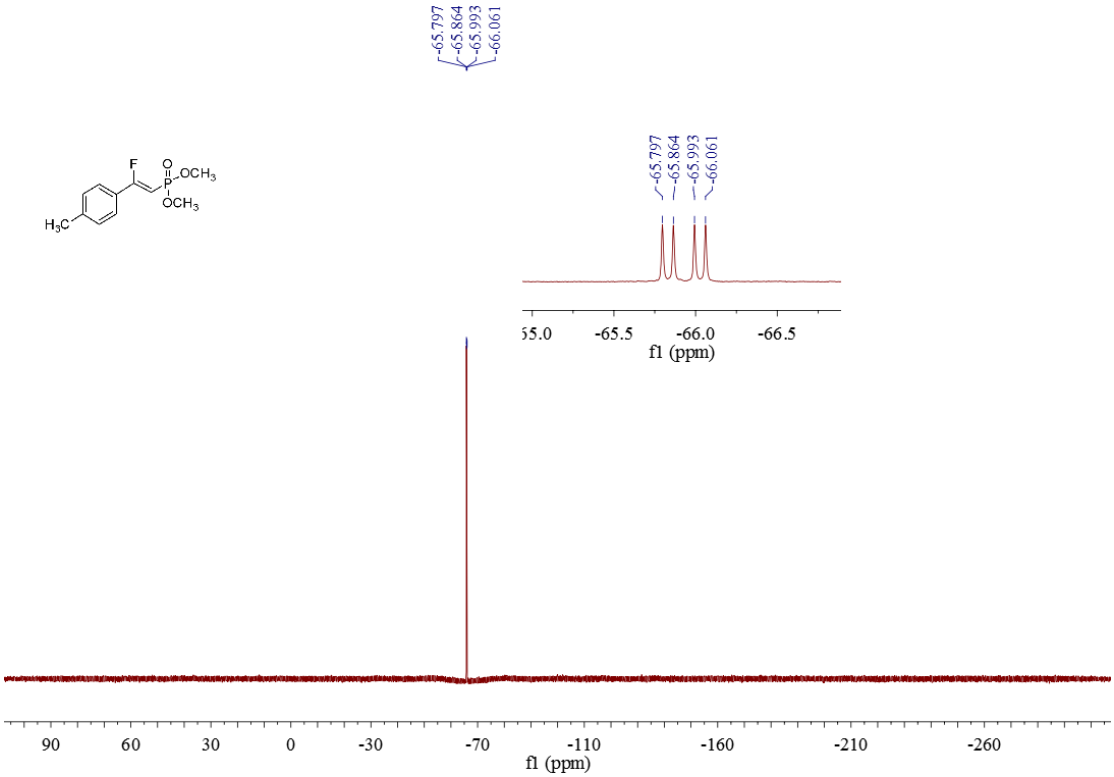
^{1}H NMR



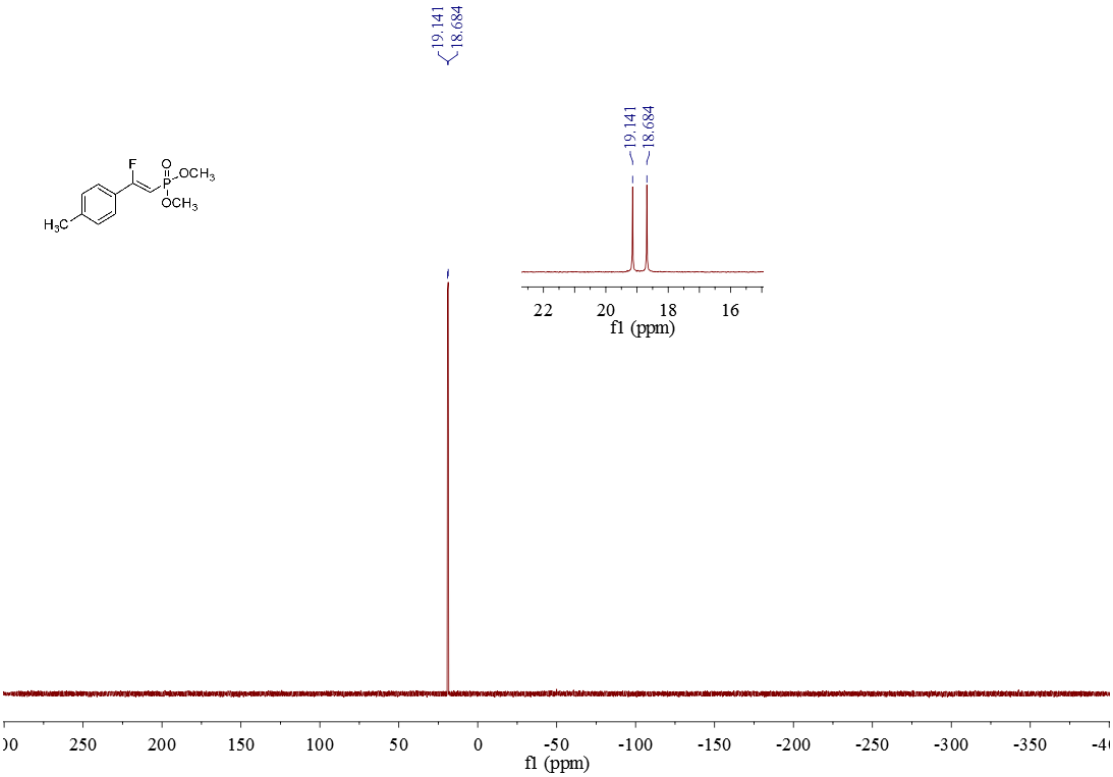
^{13}C NMR



^{19}F NMR

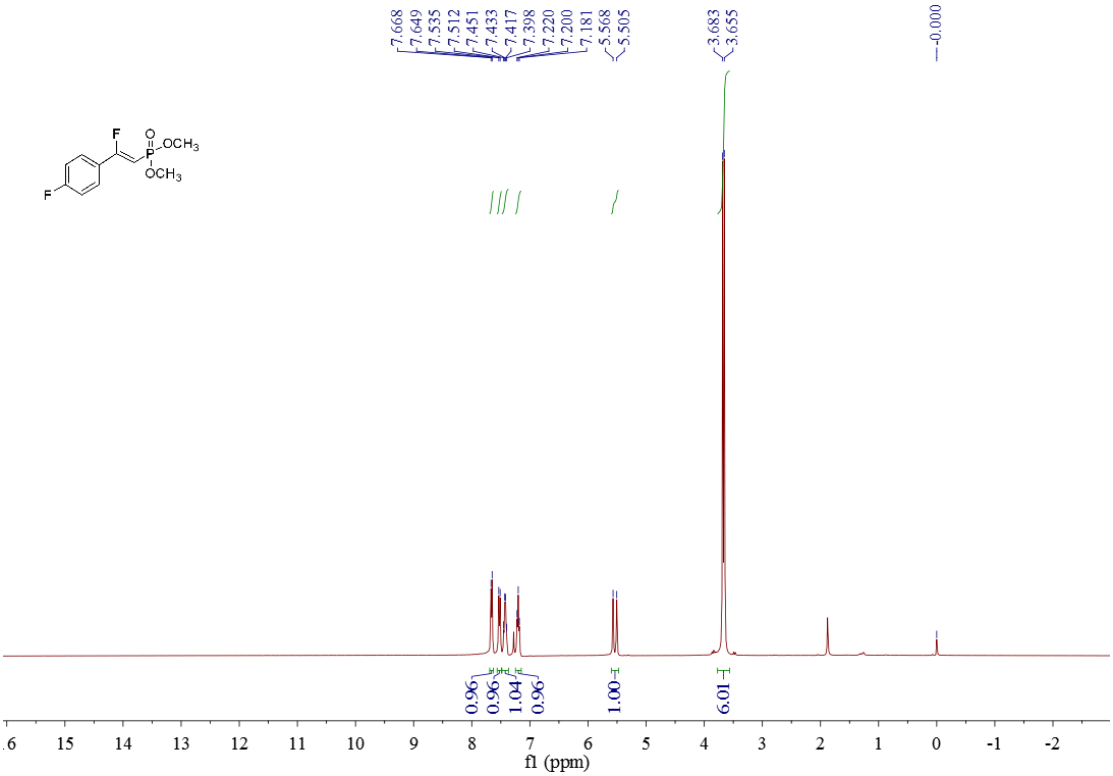


^{31}P NMR

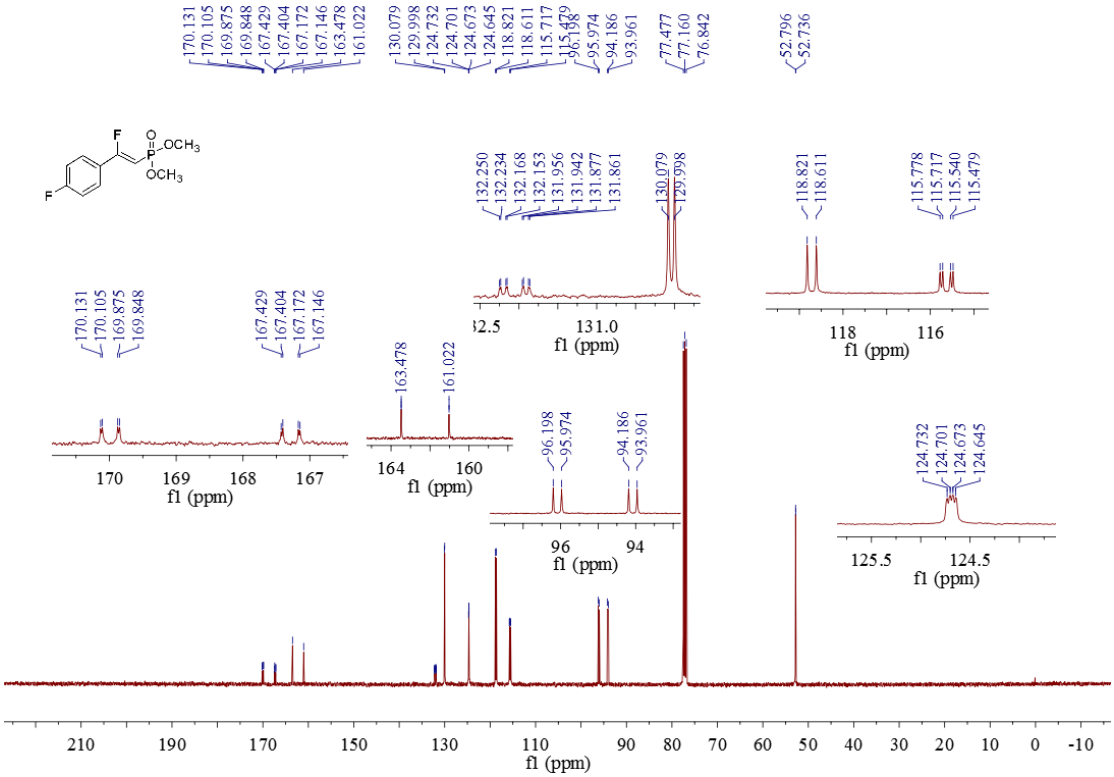


Dimethyl (*Z*)-(2-fluoro-2-(4-fluorophenyl)vinyl) phosphonate (3c)

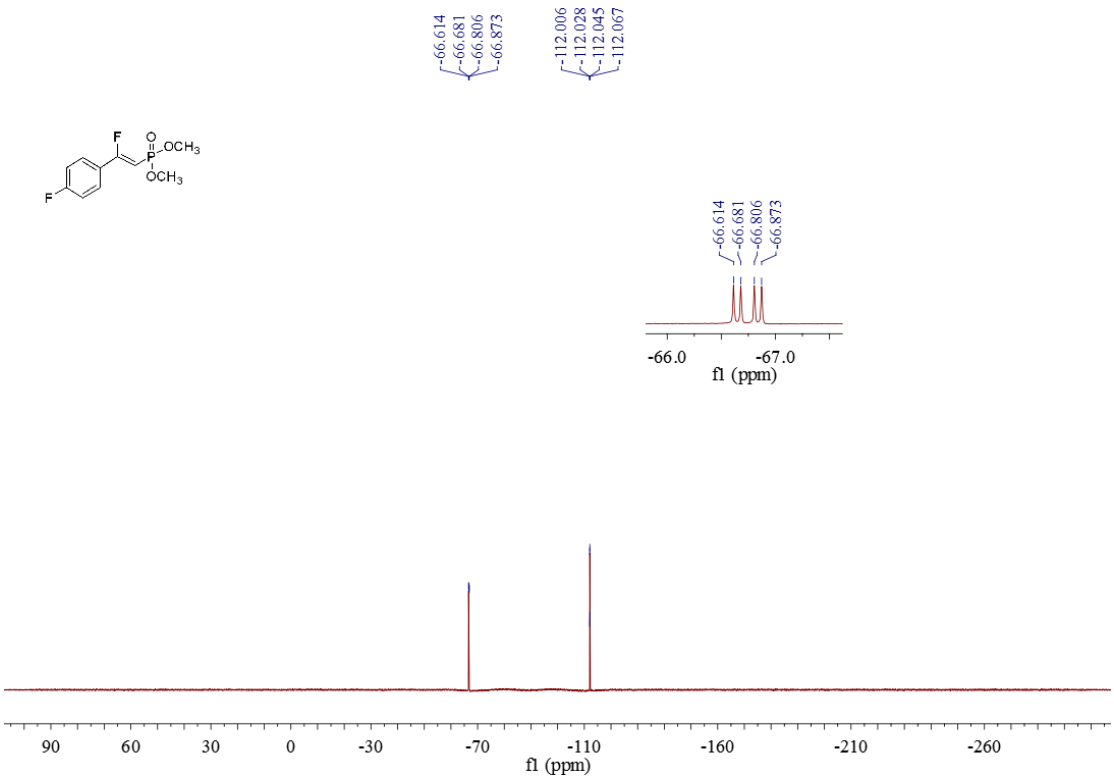
^{1}H NMR



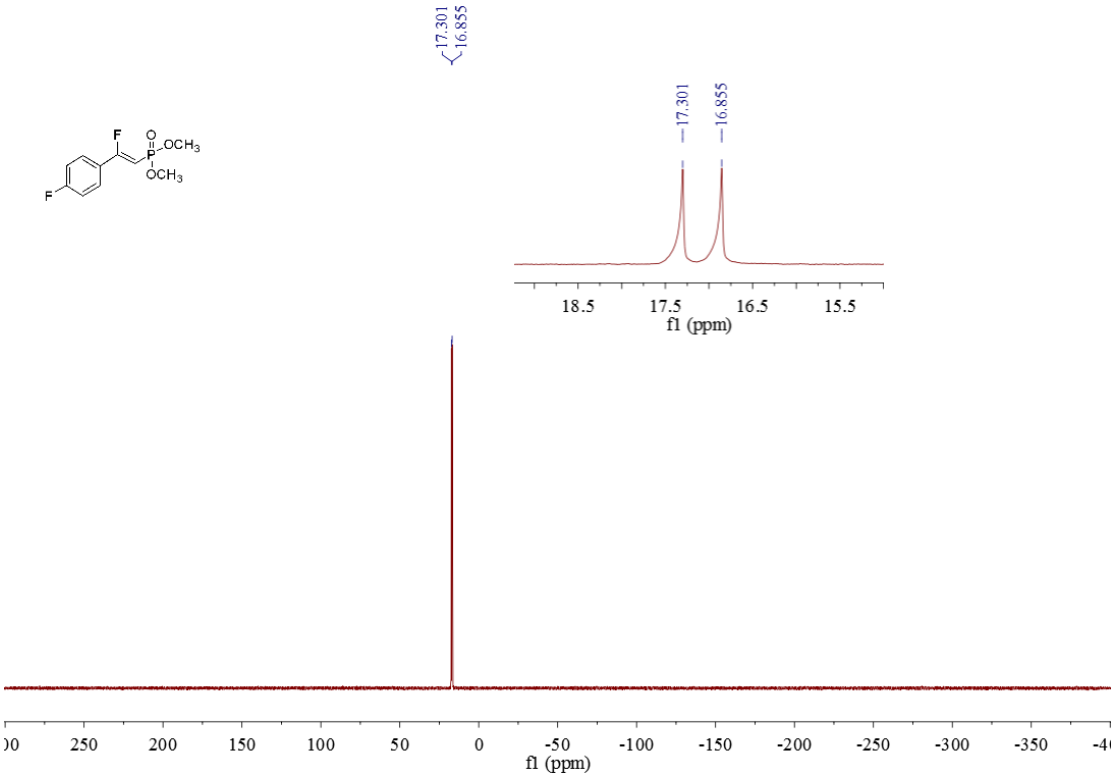
^{13}C NMR



^{19}F NMR

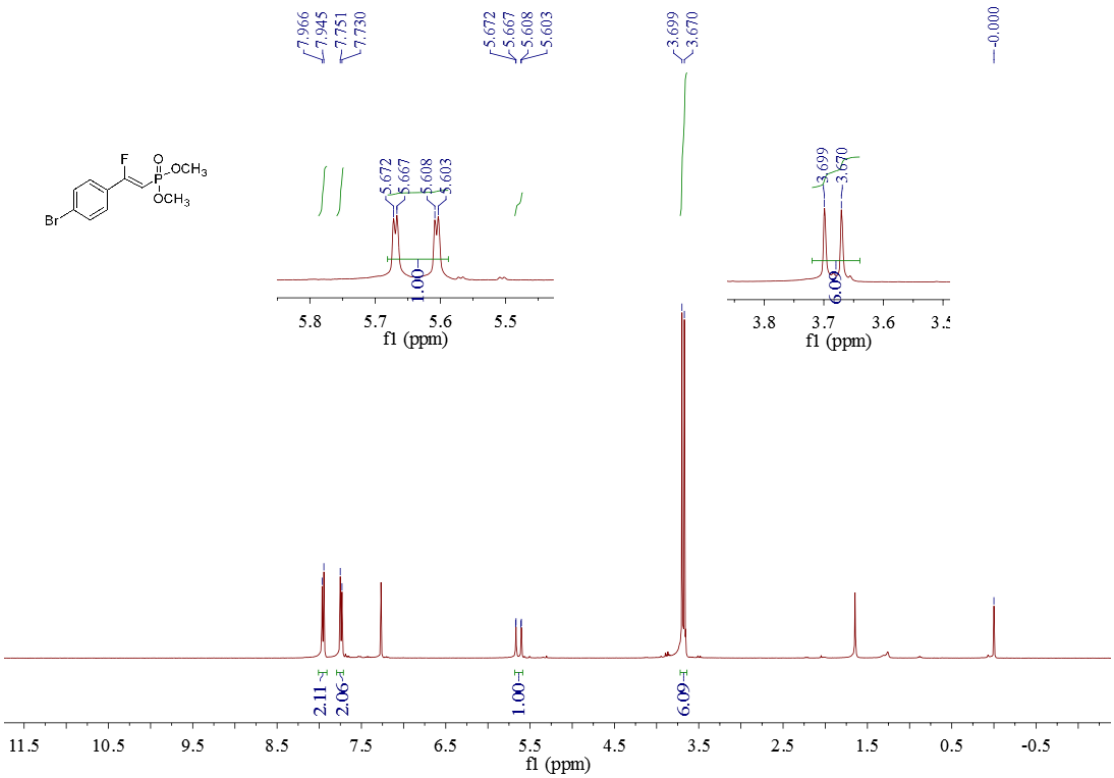


^{31}P NMR

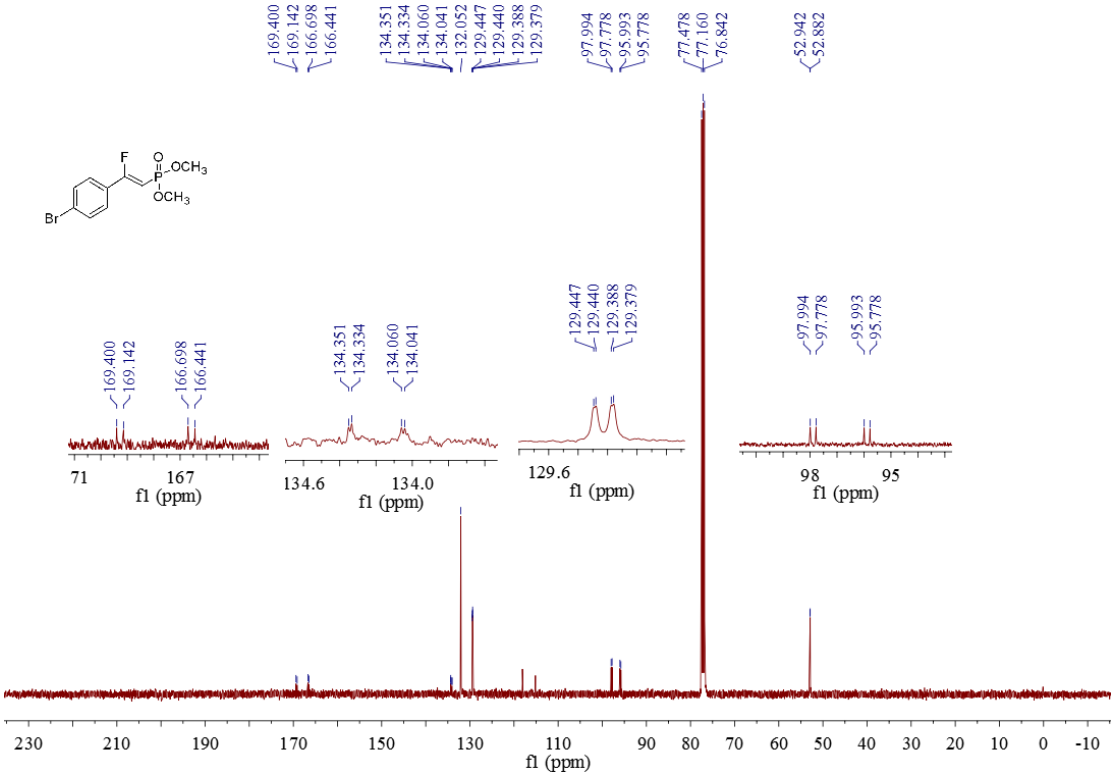

17.301
16.855
F
O
OCH3
P
OCH3
F
17.301
16.855
18.5
17.5
16.5
15.5
f1 (ppm)
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
f1 (ppm)

Dimethyl (*Z*)-(2-(4-bromophenyl)-2-fluorovinyl)phosphonate (3d)

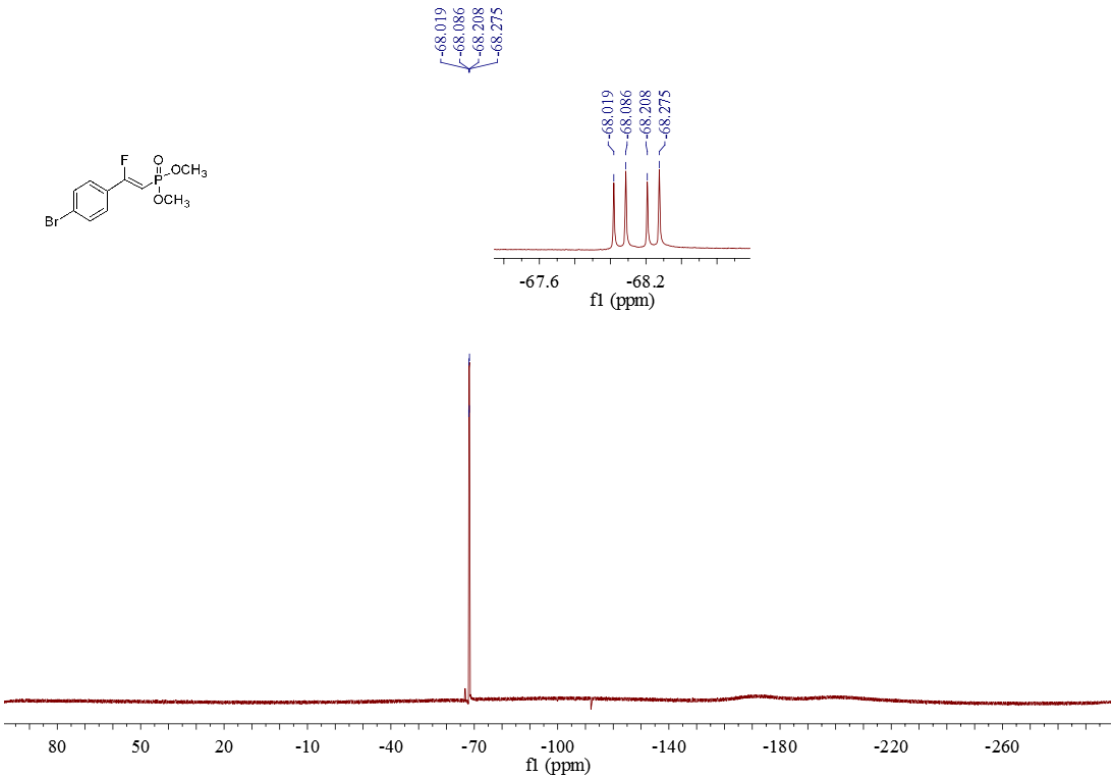
^{1}H NMR



^{13}C NMR



^{19}F NMR



^{31}P NMR