Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Palladium-catalyzed phosphonyldifluoromethylation of alkenes with bromodifluoromethylphosphonate

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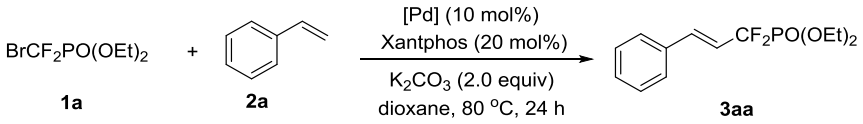
General information: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 and AM500 spectrometer. ^{19}F NMR was recorded on a Bruker AM400 spectrometer ($CFCl_3$ as an external standard and low field is positive). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Materials: All reagents were used as received from commercial sources, unless specified otherwise. All reagents were weighed and handled in air, and refilled with an inert atmosphere of N_2 at room temperature. DCE was distilled from CaH_2. 1,4-Dioxane and toluene were distilled from sodium and benzophenone immediately before use.

Screening for Pd-Catalyzed Heck-Type Reaction of Bromodifluoromethylphosphonate with Styrene (Tables S1-3). To a 25 mL of Schlenk tube were added [Pd] (5-10 mol %), ligand (10-20 mol %) under air, followed by base (2.0 equiv). The mixture was then evacuated and backfilled with N_2 (3 times). Bromodifluoromethylphosphonate **1** (2 equiv), styrene **2a** (0.3 mmol) and solvent (2 mL) were added subsequently. The reaction mixture was heated to 80-120 ^{o}C (oil bath). After stirring for 24 h, the reaction mixture was cooled to room temperature. The yield was determined by ^{19}F NMR before working up. If necessary, the reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1) to give product **3a**.

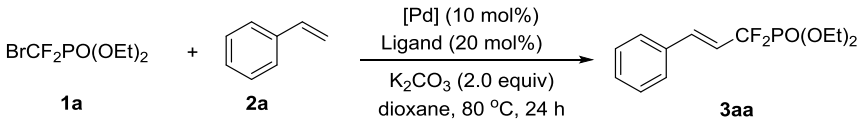
Table S1. Screening of Palladium Sources[a]



Entry	[Pd](mol %)	Ligand (mol %)	Yield (%)[b]
1	$Pd(PhCN)_2Cl_2$ (10)	20	Nd
2	$PdCl_2$ (10)	20	Nd
3	$PdCl_2(PPh_3)_2$ (10)	20	Nd
4	$PdCl_2$(dppf) (10)	20	Nd
5	$PdCl_2(MeCN)_2$ (10)	20	Trace
6	$[PdCl(C_3H_5)]_2$ (5)	20	Nd
7	$Pd(PPh_3)_4$ (10)	20	Nd
8	$Pd_2(dba)_3$ (5)	20	Nd

[a]Reaction conditions (unless otherwise specified): **2a** (0.3 mmol, 1.0 equiv), **1a** (2.0 equiv), dioxane (2 mL), 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as an internal standard.

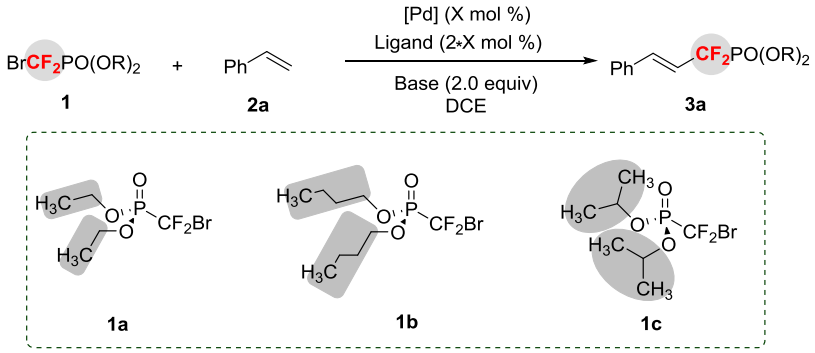
Table S2. Screening of Ligands[a]



Entry	Ligand (20 mol%)	Yield (%)[b]
1	**Xantphos**	Trace
2	DpePhos	Trace
3	dppe	Nd
4	dppp	Nd
5	dppb	Nd
6	dppf	Trace
7	BINAP	Nd
8	JohnPhos	Nd
9	MePhos	Nd
10	DavePhos	Nd
11	XPhos	Nd
12	RuPhos	Nd
13	SPhos	Nd

[a]Reaction conditions (unless otherwise specified): **2a** (0.3 mmol, 1.0 equiv), **1a** (2.0 equiv), dioxane (2 mL), 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as internal standard .

Table S3. Optimization of Palladium-Catalyzed Heck-type Reaction of Bromodifluoromethylphosphonate with Styrene.[a]

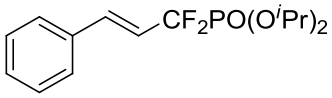


Entry	Substrate	[Pd](mol %)	Solvent	Ligand (mol%)	Base	**3a**, Yield(%)[b]
1	**1a**	$Pd(MeCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3aa**, Trace
3	**1b**	$Pd(MeCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3aa**, 12
4	**1b**	$Pd(PPh_3)_4$ (10)	DCE	Xantphos (20)	K_2CO_3	**3aa**, 10
5	**1c**	$Pd(MeCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3ac**, 21
6	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3ac,** 41
7	**1c**	$PdCl_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3ac**, 39
8	**1c**	$PdCl_2(PPh_3)_2$ (10)	DCE	Xantphos (20)	K_2CO_3	**3ac**, 28
9	**1c**	$PdCl_2$(dppf) (10)	DCE	Xantphos (20)	K_2CO_3	**3ac**, Trace
10	**1c**	$[PdCl(C_3H_5)]_2$ (5)	DCE	Xantphos (20)	K_2CO_3	**3ac**, Nd
11	**1c**	$Pd(PPh_3)_4$ (10)	DCE	Xantphos (20)	K_2CO_3	**3ac**, 31
12	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_3PO_4	**3ac**, 50
13	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	Cs_2CO_3	**3ac**, Nd
14	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	Na_2CO_3	**3ac**, 44
15	**1c**	$Pd(PhCN)_2Cl_2$ (10)	Dioxane	Xantphos (20)	K_3PO_4	**3ac**, 2
16	**1c**	$Pd(PhCN)_2Cl_2$ (10)	toluene	Xantphos (20)	K_3PO_4	**3ac**, 0
17	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	DpePhos (20)	K_3PO_4	**3ac**, 35
18	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	dppf (20)	K_3PO_4	**3ac**, 22
19[c]	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_3PO_4	**3ac**, 47
20[d]	**1c**	$Pd(PhCN)_2Cl_2$ (10)	DCE	Xantphos (20)	K_3PO_4	**3ac**, (94)
21[d]	**1c**	**$Pd(PhCN)_2Cl_2$ (5)**	**DCE**	**Xantphos (10)**	**K_3PO_4**	**3ac, (92)**
22[d]	**2c**	none	DCE	Xantphos (10)	K_3PO_4	**3ac**, Nd
23[d]	**2c**	$Pd(PhCN)_2Cl_2$ (5)	DCE	none	K_3PO_4	**3ac**, Nd

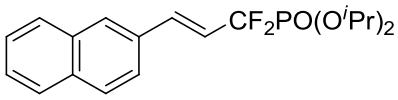
[a]Reaction conditions (unless otherwise specified): **2a** (0.3 mmol, 1.0 equiv), **1** (2.0 equiv), solvent (2 mL), 80 °C, 24 h. [b]Determined by ^{19}F NMR using fluorobenzene as internal standard (isolated yield in parentheses).[c]Reaction run at 100 °C for 12 h. [d]Reaction run at 120 °C for12 h.

General Procedure for Palladium-Catalyzed Heck-type Reaction of Bromodifluoromethylphosphonate with alkenes.

To a 25 mL of Schlenk tube were added $Pd(PhCN)_2Cl_2$ (5 mol %), Xantphos (10 mol %) under air, followed by anhydrous K_2CO_3 (2.0 equiv). The mixture was then evacuated and backfilled with N_2 (3 times). Bromodifluoromethylphosphonate **1c** (2 equiv), alkene **2** (0.3 mmol) and fresh distilled DCE (2 mL) were added subsequently. The reaction mixture was heated to 120 ^oC (oil bath). After stirring for 12 h, the reaction was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1) to give product.

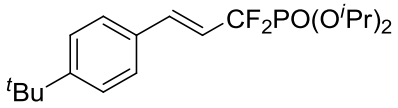


(*E*)-Diisopropyl (1,1-difluoro-3-phenylallyl)phosphonate (3ac). The product (88 mg, 92% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2 H), 7.39-7.32 (m, 3 H), 7.06 (dtd, *J* = 16.4 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1 H), 6.30 (m, 1 H), 4.87 (m, 2 H), 1.38 (d, *J* = 6.4 Hz, 6 H), 1.35 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.3 (ddd, *J* = 114.3 Hz, *J* = 12.8 Hz, *J* = 2.8 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7 (td, *J* = 10.6 Hz, *J* = 6.1 Hz), 134.4 (m), 129.4, 128.8, 127.4 (m), 119.1 (td, *J* = 21.1 Hz, *J* = 13.0 Hz), 117.2 (td, *J* = 258.1 Hz, *J* = 222.3 Hz), 73.8, 73.7, 24.2, 24.1, 23.8, 23.7. MS (EI): *m/z* (%) 318 (M^+), 234, 153 (100). HRMS calcd. for $C_{15}H_{21}F_2O_3P$ (M^+): 318.1196; Found: 318.1197. IR (thin film) ν_{max} 2983, 1653 cm^{-1}.

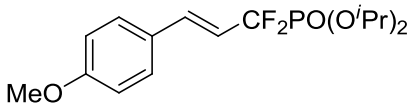


(*E*)-Diisopropyl (1,1-difluoro-3-(naphthalen-2-yl)allyl)phosphonate (3b). The product (95 mg, 86% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 4 H), 7.62 (dd, *J* =8.4 Hz, *J* =1.6 Hz, 1 H), 7.52-7.48 (m, 2 H), 7.22 (dtd, *J* = 16.0 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1 H), 6.43 (m, 1 H), 4.89 (m, 2 H), 1.38 (d, *J* = 6.0 Hz, 6 H), 1.36 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.3 (ddd, *J* = 114.3 Hz, *J* = 12.9 Hz, *J* = 2.8 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8 (td, *J* = 10.6 Hz, *J* =

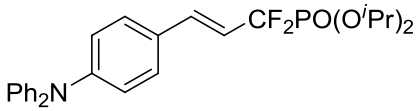
6.1 Hz), 133.8, 133.3, 131.9, 128.6, 128.3, 127.7, 126.8，126.6，123.4，119.3 (td, *J* = 21.1 Hz, *J* = 10.9 Hz), 117.4 (td, *J* = 257.9 Hz, *J* = 222.2 Hz), 73.9, 73.8, 24.21, 24.18, 23.8, 23.7. MS (EI): *m/z* (%) 368 (M^+), 284, 203 (100). HRMS calcd. for $C_{19}H_{23}F_2O_3P$ (M^+): 368.1353; Found: 368.1357. IR (thin film) ν_{max} 2983, 1653cm^{-1}.



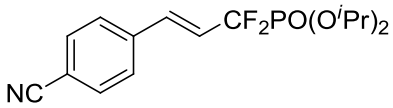
(*E*)-diisopropyl (3-(4-(tert-butyl)phenyl)-1,1-difluoroallyl)phosphonate (3c). The product (107 mg, 95% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 4 H), 6.38 (dtd, *J* = 16.0 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1 H), 6.25 (m, 1 H), 4.86 (m, 2 H), 1.37 (d, *J* = 6.4 Hz, 6 H), 1.34 (d, *J* = 6.0 Hz, 6 H), 1.30 (s, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9 (ddd, *J* = 115.1 Hz, *J* = 12.9 Hz, *J* = 2.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 136.6 (td, *J* = 10.6 Hz, *J* = 6.2 Hz), 131.8, 127.2, 125.7, 118.2 (td, *J* = 21.6 Hz, *J* = 13.4 Hz), 117.4 (td, *J* = 259.2 Hz, *J* = 221.8 Hz), 73.73, 73.66, 34.8, 31.2, 24.2, 24.1, 23.8, 23.7. MS (EI): *m/z* (%) 374 (M^+), 209, 57 (100). HRMS calcd. for $C_{19}H_{29}F_2O_3P$ (M^+): 374.1822; Found: 374.1819. IR (thin film) ν_{max} 2966, 1653, 1509 cm^{-1}.



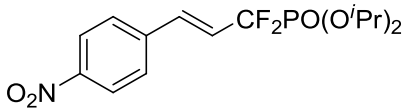
(*E*)-diisopropyl (3-(4-(tert-butyl)phenyl)-1,1-difluoroallyl)phosphonate (3d). The product (100 mg, 96% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 2 H), 6.99 (dtd, *J* = 16.4 Hz, *J* = 2.8 Hz, *J* = 2.8 Hz, 1 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 6.15 (m, 1 H), 4.86 (m, 2 H), 3.82 (s, 3 H), 1.36 (d, *J* = 6.0 Hz, 6 H), 1.33 (d, *J* = 6.4 Hz, 6 H).^{19}F NMR (376 MHz, $CDCl_3$) δ -108.7 (ddd, *J* = 115.7 Hz, *J* = 12.9 Hz, *J* = 2.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 136.2 (td, *J* = 10.7 Hz, *J* = 6.1 Hz), 128.8, 127.3, 117.5 (td, *J* = 259.4 Hz, *J* = 223.1 Hz), 116.6 (td, *J* = 21.2 Hz, *J* = 13.0 Hz), 114.2, 73.7, 73.6, 55.3, 24.19, 24.16, 23.73, 23.68. MS (EI): *m/z* (%) 348 (M^+), 183 (100). HRMS calcd. for $C_{16}H_{23}F_2O_4P$ (M^+): 348.1302; Found: 348.1307. IR (thin film) ν_{max} 2983, 1653, 1607 cm^{-1}.



(*E*)-Diisopropyl (3-(4-(diphenylamino)phenyl)-1,1-difluoroallyl)phosphonate (3e). The product (135 mg, 93% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 7 H), 7.12-7.10 (m, 3 H), 7.08-7.05 (m, 2 H), 7.02-6.95 (m, 3 H), 6.15 (m, 1 H), 4.87 (m, 2 H), 1.38 (d, *J* = 6.4 Hz, 6 H), 1.36 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.5 (ddd, *J* = 116.2 Hz, *J* = 13.0 Hz, *J* = 2.6 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.1, 136.2 (td, *J* = 10.5 Hz, *J* = 6.0 Hz), 129.4, 128.3, 127.9, 124.9, 123.6, 122.4, 117.5 (td, *J* = 259.4 Hz, *J* = 223.2 Hz), 116.5 (td, *J* = 21.0 Hz, *J* = 12.6 Hz), 73.7, 73.6, 24.2, 24.17, 23.8, 23.7. MS (EI): *m/z* (%) 485 (M^+), 320 (100). HRMS calcd. for $C_{27}H_{30}F_2O_3NP$ (M^+): 485.1931; Found: 485.1929. IR (thin film) ν_{max} 2982, 1647, 1592, 1508 cm^{-1}.

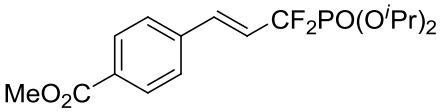


(*E*)-Diisopropyl (3-(4-cyanophenyl)-1,1-difluoroallyl)phosphonate (3f). The product (80 mg, 78% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.53 (d, *J* =8.4 Hz, 2 H), 7.05 (m, 1 H), 6.39 (m, 1 H), 4.86 (m, 2 H), 1.37 (d, *J* = 6.4 Hz, 6 H), 1.33 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3 (ddd, *J* = 111.6 Hz, *J* = 12.5 Hz, *J* = 2.6 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 134.9 (td, *J* = 10.6 Hz, *J* = 5.8 Hz), 132.6, 127.9, 122.9 (td, *J* = 21.4 Hz, *J* = 12.8 Hz), 118.4, 116.7 (td, *J* = 260.1 Hz, *J* = 221.3 Hz), 112.7, 74.1, 74.0, 24.12, 24.08, 23.72, 23.67. MS (EI): *m/z* (%) 343 (M^+), 259, 179, 123 (100). HRMS calcd. for $C_{16}H_{20}F_2O_3PN$ (M^+): 343.1149; Found: 343.1154. IR (thin film) ν_{max} 2984, 2936, 2228, 1654, 1507 cm^{-1}.

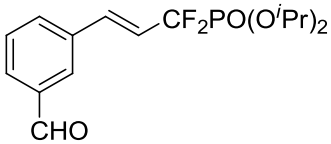


(*E*)-Diisopropyl (1,1-difluoro-3-(4-nitrophenyl)allyl)phosphonate (3g). The product (60 mg, 55% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.11 (dtd, *J* = 16.4, *J* = 12.4, *J* = 2.3 Hz, 1H), 6.45 (m, 1H), 4.86 (m, 2 H), 1.38 (d, *J* = 6.0 Hz, 6 H), 1.35 (d, *J* = 6.0 Hz,

6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.3 (ddd, *J* = 111.2 Hz, *J* = 12.4 Hz, *J* = 2.8 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 140.6, 134.5 (td, *J* = 10.4 Hz, *J* = 5.7 Hz), 128.1, 124.2, 123.7 (td, *J* = 21.4 Hz, *J* = 13.0 Hz), 116.7 (td, *J* = 260.2 Hz, *J* = 221.1 Hz), 74.2, 74.1, 24.2, 24.1, 23.8, 23.7. MS (EI): *m/z* (%) 363 (M^+), 199, 123 (100). HRMS calcd. for $C_{15}H_{20}F_2O_5PN$ (M^+): 363.1047; Found: 363.1049. IR (thin film) ν_{max} 2983, 1517, 1346 cm^{-1}.

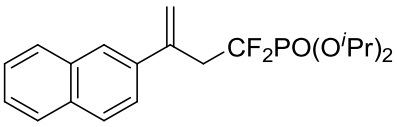


(*E*)-methyl 4-(3-(diisopropoxyphosphoryl)-3,3-difluoroprop-1-en-1-yl)benzoate (3h). The product (79 mg, 70% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.07 (m, 1 H), 6.38 (m, 1 H), 4.86 (m, 2 H), 3.91 (s, 3 H), 1.36 (d, *J* = 6.4 Hz, 6 H), 1.33 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9 (ddd, *J* = 112.8 Hz, *J* = 12.8 Hz, *J* = 2.6 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 138.7, 135.7 (td, *J* = 10.4 Hz, *J* = 6.0 Hz), 130.7, 130.1, 127.3, 121.6 (td, *J* = 21.2 Hz, *J* = 13.0 Hz), 117.0 (td, *J* = 258.1 Hz, *J* = 220.4 Hz), 74.0, 73.9, 52.2, 24.2, 24.1, 23.71, 23.67. MS (EI): *m/z* (%) 376 (M^+), 334, 292 (100). HRMS calcd. for $C_{17}H_{23}F_2O_5P$ (M^+): 376.1251; Found: 376.1248. IR (thin film) ν_{max} 2984, 1723, 1653, 1609 cm^{-1}.

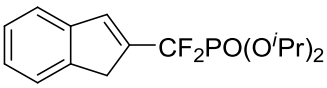


(*E*)-diisopropyl (1,1-difluoro-3-(3-formylphenyl)allyl)phosphonate (3i). The product (78 mg, 75% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 2:1). This compound is known.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1 H), 7.95 (s, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 1 H), 7.55 (t, *J* = 7.6 Hz, 1 H), 7.10 (m, 1 H), 6.39 (m, 1 H), 4.87 (m, 2 H), 1.37 (d, *J* = 6.0 Hz, 6 H), 1.34 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.9 (ddd, *J* = 113.0 Hz, *J* = 12.4 Hz, *J* = 2.6 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 136.9, 135.5, 135.3(td, *J* = 10.4 Hz, *J* = 6.1 Hz), 133.0, 130.5, 129.5, 128.1, 121.1 (td, *J* = 21.6 Hz, *J* = 13.0 Hz), 116.9 (td, *J* = 259.8 Hz, *J* = 221.8 Hz), 74.0, 73.9, 24.14, 24.10, 23.73, 23.67. MS (EI): *m/z* (%) 346 (M^+), 262, 222, 133 (100). HRMS calcd. for $C_{16}H_{21}F_2O_4P$ (M^+): 346.1146; Found: 346.1148. IR

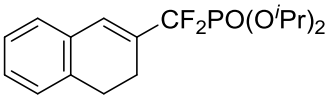
(thin film) ν_{max} 3487, 2984, 1701, 1654 cm^{-1}.



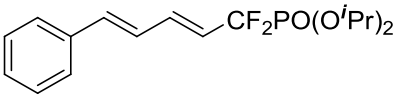
Diisopropyl (1,1-difluoro-3-phenylbut-3-en-1-yl)phosphonate (3j). The product (61 mg, 61% yield) was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (m, 4 H), 7.60 (dd, *J* = 8.6 Hz, *J* = 1.9 Hz, 1 H), 7.49-7.43 (m, 2 H), 5.76 (s, 1 H), 5.42 (s, 1 H), 4.85 (m, 2 H), 3.40 (td, *J* = 20.0 Hz, *J* = 3.5 Hz, 2 H), 1.36 (d, *J* = 6.4 Hz, 6 H), 1.35 (d, *J* = 6.8 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9 (dt, *J* = 107.2 Hz, *J* = 19.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3 (t, *J* = 2.9 Hz), 138.2, 133.3, 132.8, 128.3, 127.8, 127.5, 126.2, 125.9, 125.1, 124.4, 119.8, 119.3 (td, *J* = 261.8 Hz, *J* = 217.0 Hz), 73.7, 73.6, 38.7 (td, *J* = 20.7 Hz, *J* = 15.6 Hz), 24.2, 24.1, 23.8, 23.7. MS (EI): *m/z* (%) 382 (M^+), 340, 298 (100). HRMS calcd. for $C_{20}H_{25}F_2O_3P$ (M^+): 382.1509; Found: 382.1515. IR (thin film) ν_{max} 3057, 2982, 1623 cm^{-1}.



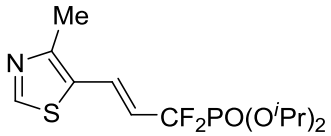
Diisopropyl (difluoro(1H-inden-2-yl)methyl)phosphonate (3k). The product (75 mg, 76% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 13.2 Hz, 1 H), 7.46 (d, *J* = 13.2 Hz, 1 H), 7.33-7.26 (m, 2 H), 7.26 (m, 1 H), 4.85 (m, 2 H), 3.69 (s, 2 H), 1.37 (d, *J* = 6.0 Hz, 6 H), 1.33 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.6 (dd, *J* = 115.4 Hz, *J* = 1.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 142.7, 138.4 (td, *J* = 22.7 Hz, *J* = 13.2 Hz), 134.3 (td, *J* = 8.3 Hz, *J* = 5.5 Hz), 126.7, 126.3, 124.0, 122.4, 117.3 (td, *J* = 257.9 Hz, *J* = 222.5 Hz), 73.9, 73.8, 38.2, 24.2, 24.1, 23.71, 23.66. MS (EI): *m/z* (%) 330 (M^+), 226, 164 (100). HRMS calcd. for $C_{16}H_{21}F_2O_3P$ (M^+): 330.1196; Found: 330.1194. IR (thin film) ν_{max} 2983, 1463cm^{-1}.



(*E*)-Diisopropyl (3-(3,4-dihydronaphthalen-2-yl)-1,1-difluoroallyl)phosphonate (3l). The product (98 mg, 95% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.17 (m, 2 H), 7.16-7.12 (m, 2 H), 6.88 (s, 1 H), 4.86 (m, 2 H), 2.87 (t, *J* = 8.4 Hz, 2 H), 2.53 (t, *J* = 8.4 Hz, 2 H), 1.37 (d, *J* = 6.4 Hz, 6H), 1.34 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.1 (d, *J* = 116.3 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 132.2, 131.4 (td, *J* = 20.1 Hz, *J* = 12.4 Hz), 129.2 (td, *J* = 10.3 Hz, *J* = 6.0 Hz), 128.6, 127.5, 126.7, 118.1 (td, *J* = 260.1 Hz, *J* = 219.4 Hz), 73.7, 73.6, 27.5, 24.21, 24.18, 23.73, 23.68, 21.9. MS (EI): *m/z* (%) 344 (M^+), 260, 240, 179 (100). HRMS calcd. for $C_{17}H_{23}F_2O_3P$ (M^+): 344.1353; Found: 344.1355. IR (thin film) ν_{max} 2983, 1455, 1387 cm^{-1}.

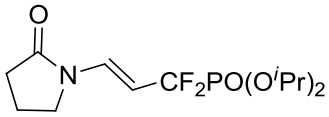


Diisopropyl ((2*E*,4*E*)-1,1-difluoro-5-phenylpenta-2,4-dien-1-yl)phosphonate (3m). The product (67 mg, 65% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2 H), 7.33 (t, *J* = 7.2 Hz, 2 H), 7.29-7.27 (m, 1 H), 6.88-6.73 (m, 3 H), 5.95-5.84 (m, 1 H), 4.86 (m, 2 H), 1.38 (d, *J* = 6.4 Hz, 6 H), 1.35 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.16 (dd, *J* = 114.8 Hz, 13.7 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7 (dt, *J* = 2.4 Hz, *J* = 2.5 Hz), 136.8 (dt, *J* = 10.8 Hz, *J* = 6.2 Hz), 136.1, 128.7, 128.6, 126.9, 126.1 (dt, *J* = 2.3 Hz, *J* = 2.1 Hz), 121.9 (td, *J* = 20.9 Hz, *J* = 12.5 Hz), 117.1 (td, *J* = 259.1 Hz, *J* = 222.7 Hz), 73.8, 73.7, 24.2, 24.1, 23.8, 23.7. MS (EI): *m/z* (%) 344 (M^+), 199, 152, 123 (100). HRMS calcd. for $C_{17}H_{23}F_2O_3P$ (M^+): 344.1353; Found: 344.1352. IR (thin film) ν_{max} 2984, 1641 cm^{-1}.

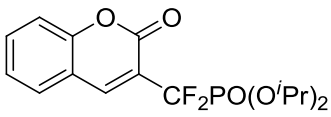


(*E*)-Diisopropyl (1,1-difluoro-3-(4-methylthiazol-5-yl)allyl)phosphonate (3n). The product (46 mg, 45% yield) as a colorless oil was purified with silica gel chromatography (Petroleum

ether/EtOAc = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1 H), 7.18 (dtd, *J* = 16.1 Hz, *J* = 3.2 Hz, *J* = 2.4 Hz, 1 H), 6.03 (m, 1 H), 4.87 (m, 2 H), 2.51 (s, 3 H), 1.38 (d, *J* = 6.0 Hz, 6 H), 1.35 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1 (ddd, *J* = 113.3 Hz, *J* = 12.6 Hz, *J* = 2.0 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7 (d, *J* = 1.3 Hz), 151.7, 127.9, 126.5 (td, *J* = 11.2 Hz, *J* = 5.9 Hz), 120.8 (td, *J* = 21.8 Hz, *J* = 13.2 Hz), 116.6 (td, *J* = 260.0 Hz, *J* = 222.7 Hz), 74.0, 73.9, 24.15, 24.1, 23.73, 23.68, 15.4. MS (EI): *m/z* (%) 339 (M^+), 255, 174 (100). HRMS calcd. for $C_{13}H_{20}F_2NO_3PS$ (M^+): 339.0870; Found: 339.0871. IR (thin film) ν_{max} 2984, 1646 cm^{-1}.

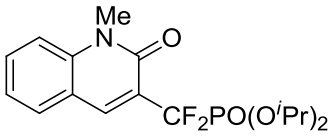


(*E*)-Diisopropyl (1,1-difluoro-3-(2-oxopyrrolidin-1-yl)allyl)phosphonate (3o). The product (74 mg, 76% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 1 H), 5.05 (m, 1 H), 4.82 (m, 2 H), 3.54 (t, *J* = 7.2 Hz, 2 H), 2.51 (t, *J* = 8.4 Hz, 2 H), 2.14 (m, 2 H), 1.34 (d, *J* = 6.4 Hz, 6 H), 1.32 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.6 (ddd, *J* = 117.7 Hz, *J* = 12.4 Hz, *J* = 1.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 130.1(td, *J* = 11.8 Hz, *J* = 6.2 Hz), 117.4 (td, *J* = 259.6 Hz, *J* = 227.1 Hz), 101.1 (td, *J* = 22.3 Hz, *J* = 14.2 Hz), 73.9, 73.8, 44.9, 30.9, 24.10, 24.07, 23.70, 23.65, 17.4. MS (EI): *m/z* (%) 325 (M^+), 160 (100). HRMS calcd. for $C_{13}H_{22}F_2O_4PN$ (M^+): 325.1255; Found: 325.1253. IR (thin film) ν_{max} 2984, 1723, 1655 cm^{-1}.

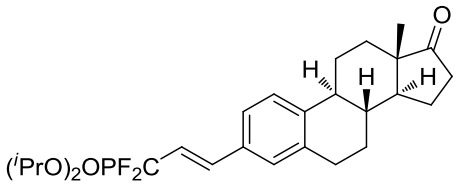


Diisopropyl (difluoro(2-oxo-2H-chromen-3-yl)methyl)phosphonate (3p). The product (49 mg, 45% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 2:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1 H), 7.61 (t, *J* = 7.9 Hz, 1 H), 7.57 (d, *J* = 7.7 Hz, 1 H), 7.36-7.30 (m, 2 H), 4.92 (m, 2 H), 1.39 (d, *J* = 5.6 Hz, 6 H), 1.37 (d, *J* = 5.6 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.9 (d, *J* = 109.1 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2 (m), 154.5, 143.8 (td, *J* = 8.2 Hz, *J* =3.0 Hz), 133.5, 129.2, 124.8, 120.7 (td, *J* = 22.5 Hz, *J* = 13.8 Hz), 117.7, 116.7, 116.1 (td, *J* = 264.3 Hz, *J* = 219.4 Hz), 74.7, 74.6, 24.2, 24.1, 23.7, 23.6. MS (EI): *m/z* (%) 360 (M^+), 276, 196 (100). HRMS calcd. for $C_{16}H_{19}F_2O_5P$ (M^+): 360.0938; Found: 360.0935. IR (thin film)

ν_{max} 2984, 1723, 1653, 1609 cm^{-1}.



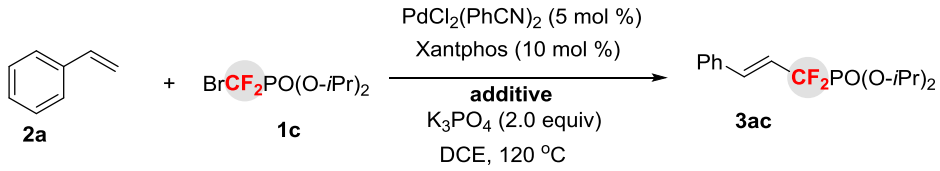
Diisopropyl (difluoro(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)methyl)phosphonate (3q). The product (50 mg, 45%) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1 H), 7.65-7.62 (m, 2 H), 7.35 (d, *J* = 8.8 Hz, 1 H), 7.24 (m, 1 H), 4.94 (m, 2 H), 3.73 (s, 3 H), 1.38 (d, *J* = 6.8 Hz, 6 H), 1.36 (d, *J* = 6.8 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.3 (d, *J* = 109.2 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (m), 140.7, 139.1 (td, *J* = 8.8 Hz, *J* =3.6 Hz), 132.2, 130.1, 128.1 (td, *J* = 10.2 Hz, *J* = 6.8 Hz), 122.4, 118.8, 117.2 (td, *J* = 263.3 Hz, *J* = 217.6 Hz), 114.1, 74.1, 74.0, 29.4, 24.3, 24.2, 23.7, 23.6. MS (EI): *m/z* (%) 373 (M^+), 272, 209 (100). HRMS calcd. for $C_{17}H_{22}F_2O_4PN$ (M^+): 373.1255; Found: 373.1253.



Diisopropyl((*E*)-1,1-difluoro-3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)allyl)phosphonate (5). The product (114 mg, 77% yield) was purified with silica gel chromatography (Petroleum ether/EtOAc = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 1 H), 7.23 (d, *J* = 7.6 Hz, 1 H), 7.18 (s, 1 H), 6.99 (m, 1 H), 6.24 (m, 1 H), 4.84 (m, 2 H), 2.91 (m, 2 H), 2.49 (dd, *J* = 10.0 Hz, 9.2 Hz, 1 H), 2.42-2.40 (m, 1 H), 2.29 (m, 1 H), 2.18-2.11 (m, 1 H), 2.09-2.01 (m, 2 H), 1.97-1.95 (m, 1 H), 1.65-1.58 (m, 2 H), 1.55-1.47 (m, 3 H), 1.43-1.42 (m, 1 H), 1.35 (d, *J* = 6.0 Hz, 6 H), 1.32 (d, *J* = 6.0 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.1 (ddd, *J* = 114.8 Hz, *J* = 12.8 Hz, *J* = 1.9 Hz, 2 F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 141.4, 137.0, 136.6 (td, *J* = 10.3 Hz, *J* = 6.1 Hz), 132.5, 128.1, 125.8, 124.8, 118.3 (td, *J* = 21.1 Hz, *J* = 12.8 Hz), 117.4 (td, *J* = 257.8 Hz, *J* = 221.5 Hz), 73.8, 73.7, 50.5, 47.9, 44.5, 38.0, 35.8, 31.6, 29.3, 26.3, 25.7, 24.2, 24.1, 23.8, 23.7, 21.6, 13.8. IR (thin film) ν_{max} 2982, 2933, 1739, 1653 cm^{-1}. MS (EI): *m/z* (%) 494 (M^+), 401, 329 (100). HRMS calcd. for $C_{27}H_{37}O_4F_2P$:

494.2398; Found: 494.2403.

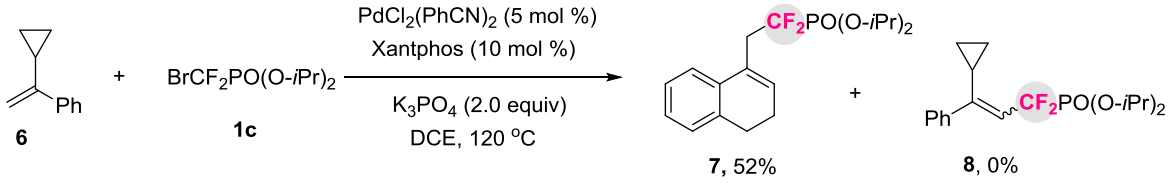
Inhibition Experiments for Pd-Catalyzed Cross-Coupling of 1c with 2a.



Entry	Additive (equiv)	**3ac** Yield(%)[a]
1	Hydroquinone (0.2)	33
2	1,4-dinitrobenzene (0.2)	38
3	none	(92)

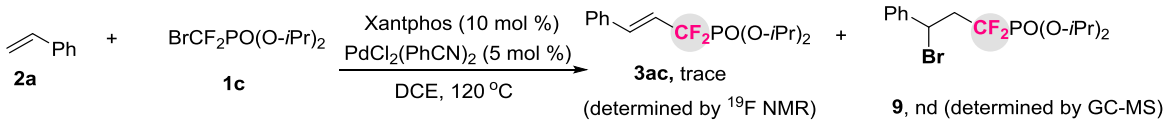
General Procedure: To a 25 mL of Schlenk tube were added $PdCl_2(MeCN)_2$ (5 mol %), Xantphos (10 mol %), additive (0.2 equiv) under air, followed by K_3PO_4 (2.0 equiv). The mixture was then evacuated and backfilled with N_2 (3 times). Bromodifluoromethylphosphonate **1c** (2 equiv), styrene **2a** (0.3 mmol) and fresh distilled DCE (2 mL) were added subsequently. The reaction mixture was heated to 120 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature and fluorobenzene (0.3 mmol) was added. The yield was determined by ^{19}F NMR.

Mechanistic Studies



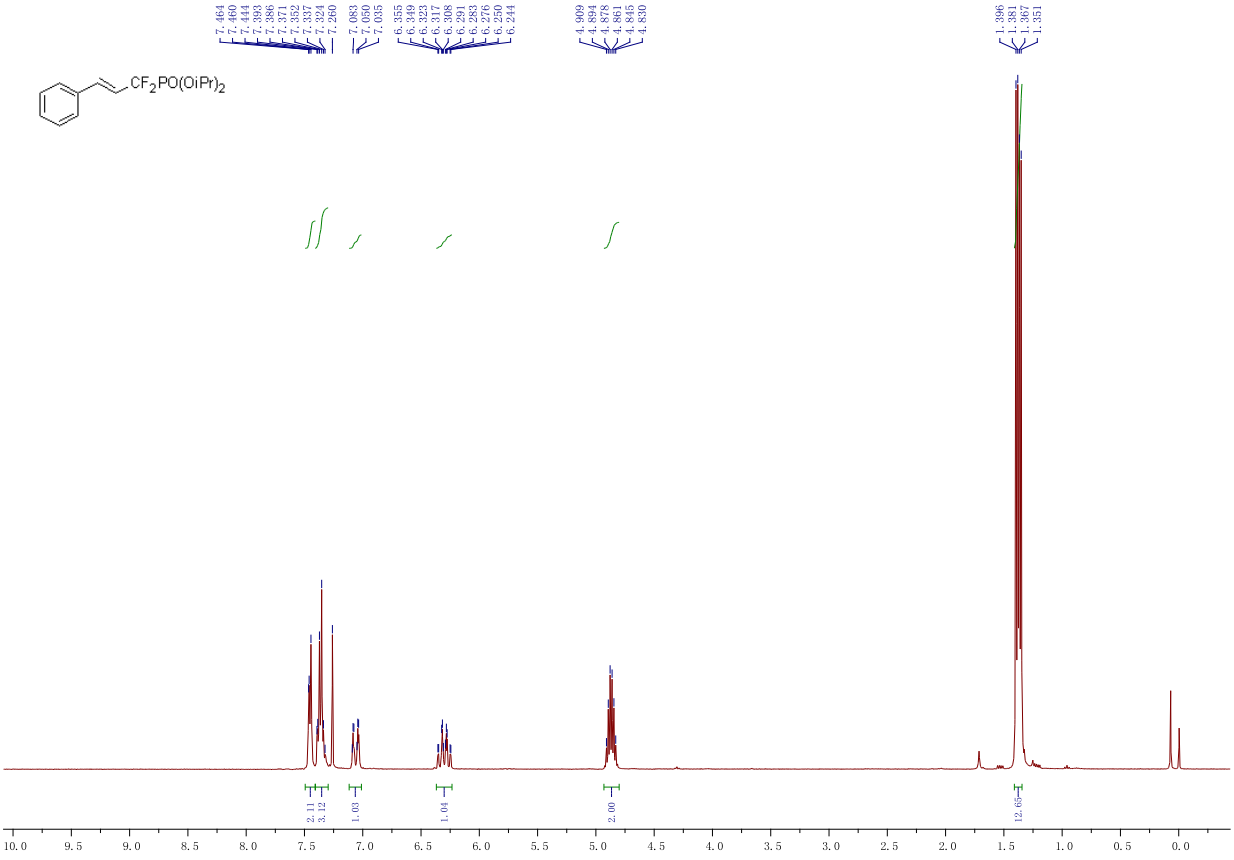
To a 25 mL of Schlenk tube were added $PdCl_2(PhCN)_2$ (5 mol %), Xantphos (10 mol %) under air, followed by by K_3PO_4 (2.0 equiv). The mixture was then evacuated and backfilled with N_2 (3 times). Bromodifluoromethylphosphonate **1c** (2 equiv), alkene **6** (0.3 mmol) and fresh distilled DCE (2 mL) were added subsequently. The reaction mixture was heated to 120 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature. The reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica

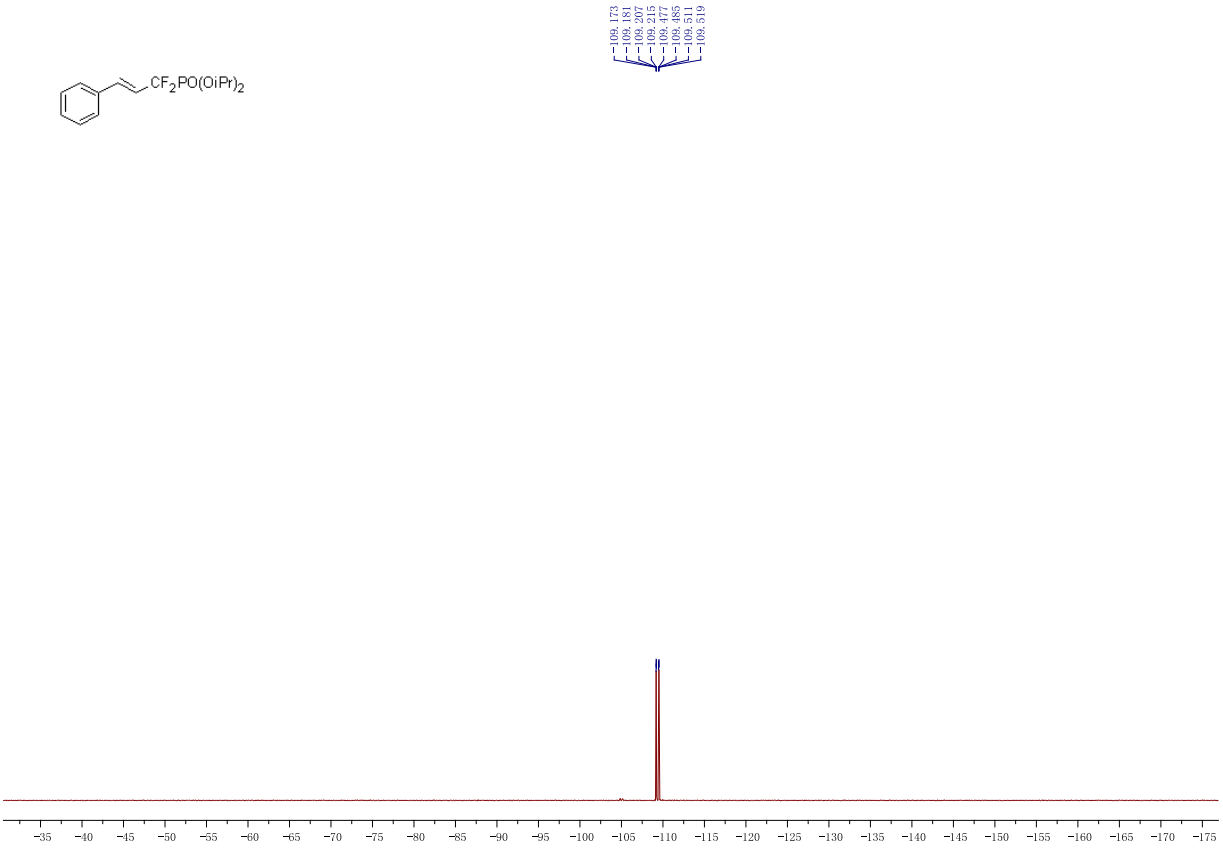
gel chromatography (Petroleum ether/EtOAc = 3:1) to compound **7** (56 mg, 52% yield) as a colorless oil was purified with silica gel chromatography (Petroleum ether/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 1 H), 7.19-7.15 (m, 1 H), 7.12-7.10 (m, 2 H), 6.09 (t, *J* = 4.4 Hz, 1 H), 4.92-4.81 (m, 2 H), 3.21 (td, *J* = 20.4 Hz, *J* = 3.2 Hz, 2 H), 2.76 (t, *J* = 8.2 Hz, 2 H), 2.34-2.29 (m, 2 H), 1.36 (d, *J* = 6.4 Hz, 6 H), 1.35 (d, *J* = 6.4 Hz, 6 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9 (dt, *J* = 108.7 Hz, *J* = 20.0 Hz, 2 F).^{13}C NMR (101.0 MHz, $CDCl_3$) δ 136.1, 134.6, 132.1, 127.4, 126.9, 126.2, 123.3 (t, *J* = 3.1 Hz), 119.3 (td, *J* = 262.3 Hz, *J* = 217.6 Hz), 73.63, 73.56, 36.1 (dt, *J* = 21.1 Hz, *J* = 15.6 Hz), 28.0, 24.10, 24.06, 23.73, 23.68, 23.3. IR (thin film) ν_{max} 1239 cm^{-1} (P=O). MS (EI): m/z (%) 358 (M^+), 274 (100). HRMS: Calculated for $C_{18}H_{25}F_2O_3P$: 358.1509; Found: 358.1506.

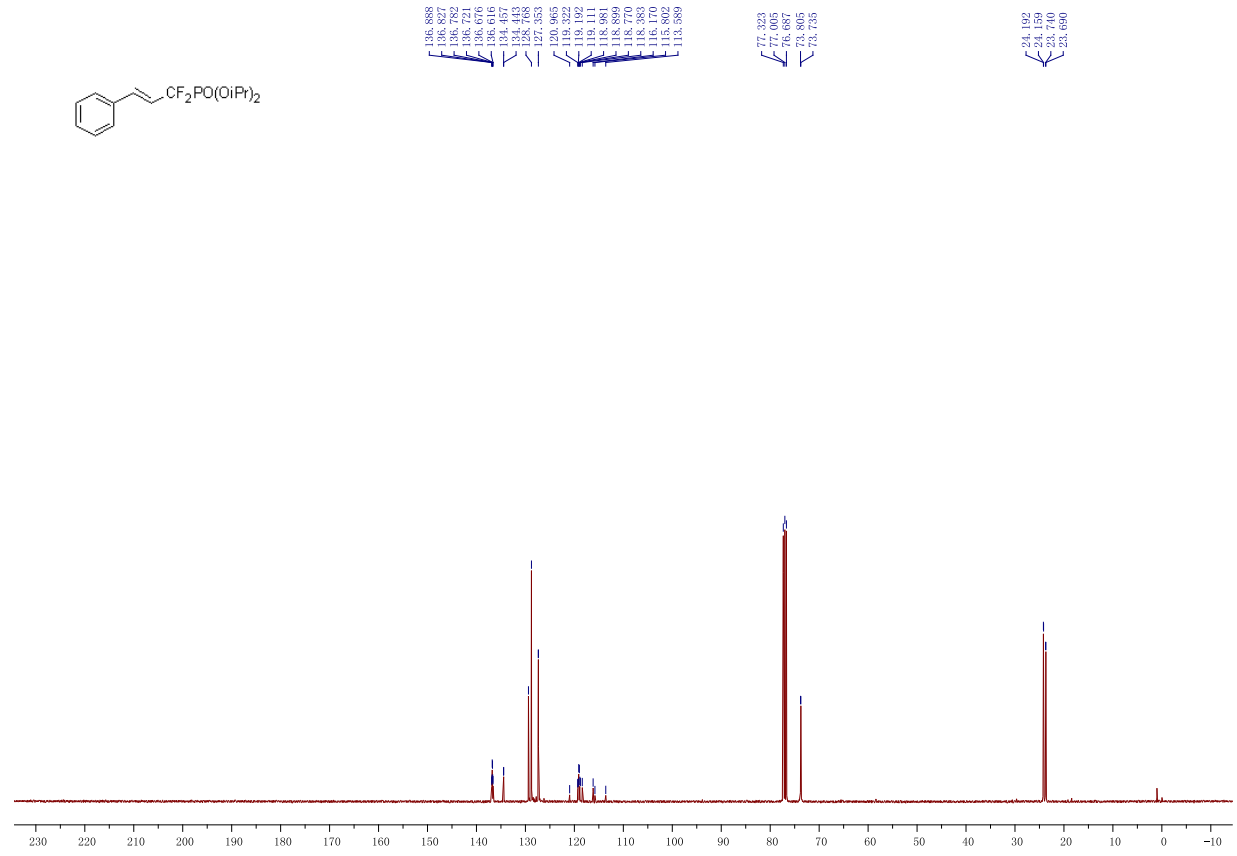


To a 25 mL of Schlenk tube were added $PdCl_2(PhCN)_2$ (5 mol %), Xantphos (10 mol %) under air. The mixture was then evacuated and backfilled with N_2 (3 times). Bromodifluoromethylphosphonate **1c** (2 equiv), alkene **2a** (0.3 mmol) and fresh distilled DCE (2 mL) were added subsequently. The reaction mixture was heated to 120 °C (oil bath). After stirring for 12 h, the reaction was cooled to room temperature, and fluorobenzene (0.3 mmol) was added. The yield was determined by ^{19}F NMR.

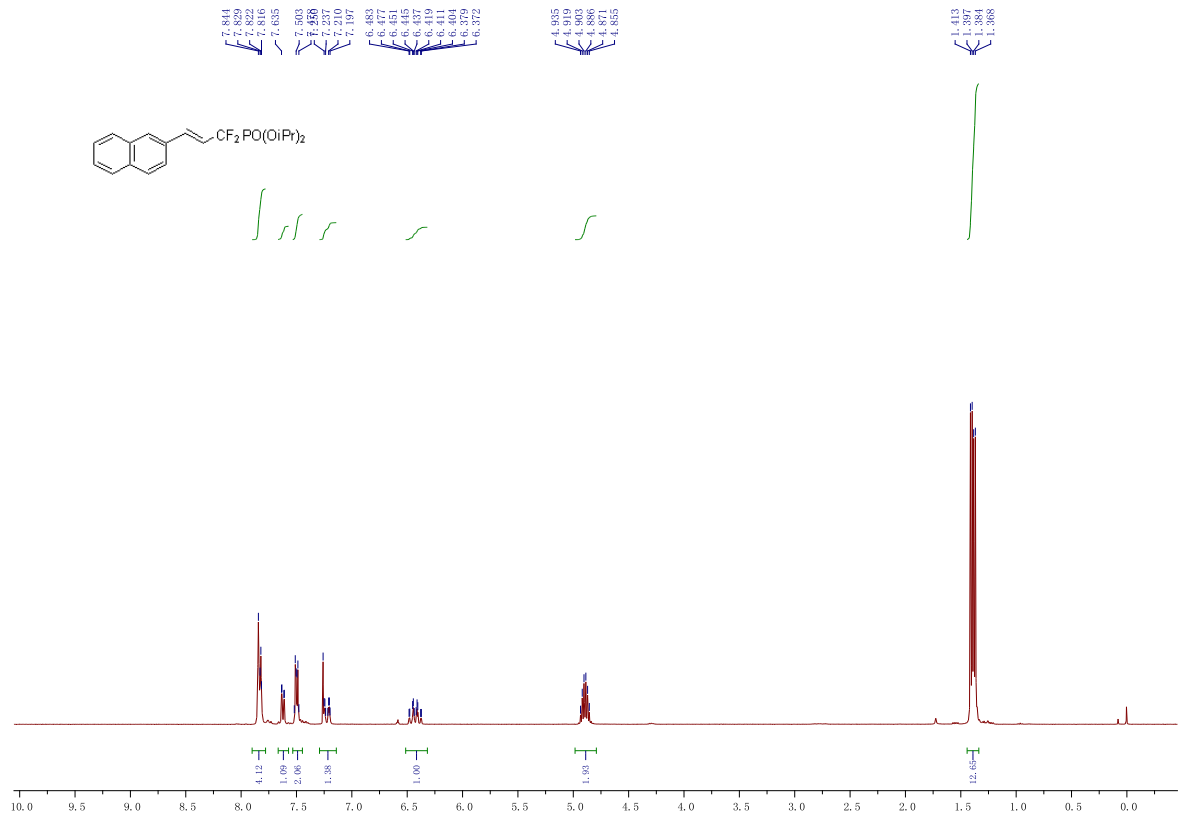
(*E*)-Diisopropyl (1,1-difluoro-3-phenylallyl)phosphonate (3ac).

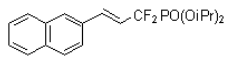


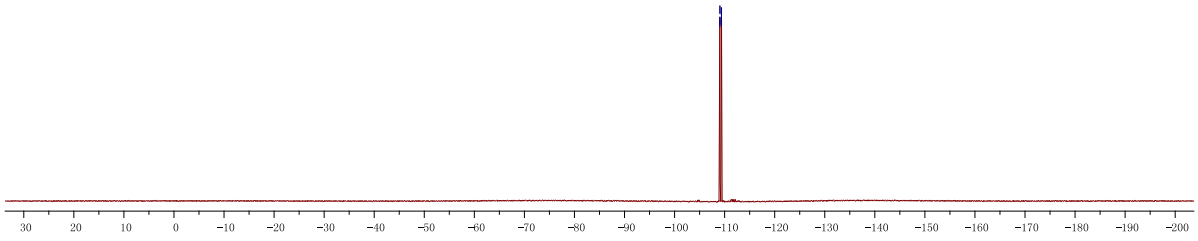


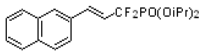


(*E*)-Diisopropyl (1,1-difluoro-3-(naphthalen-2-yl)allyl)phosphonate (3b).

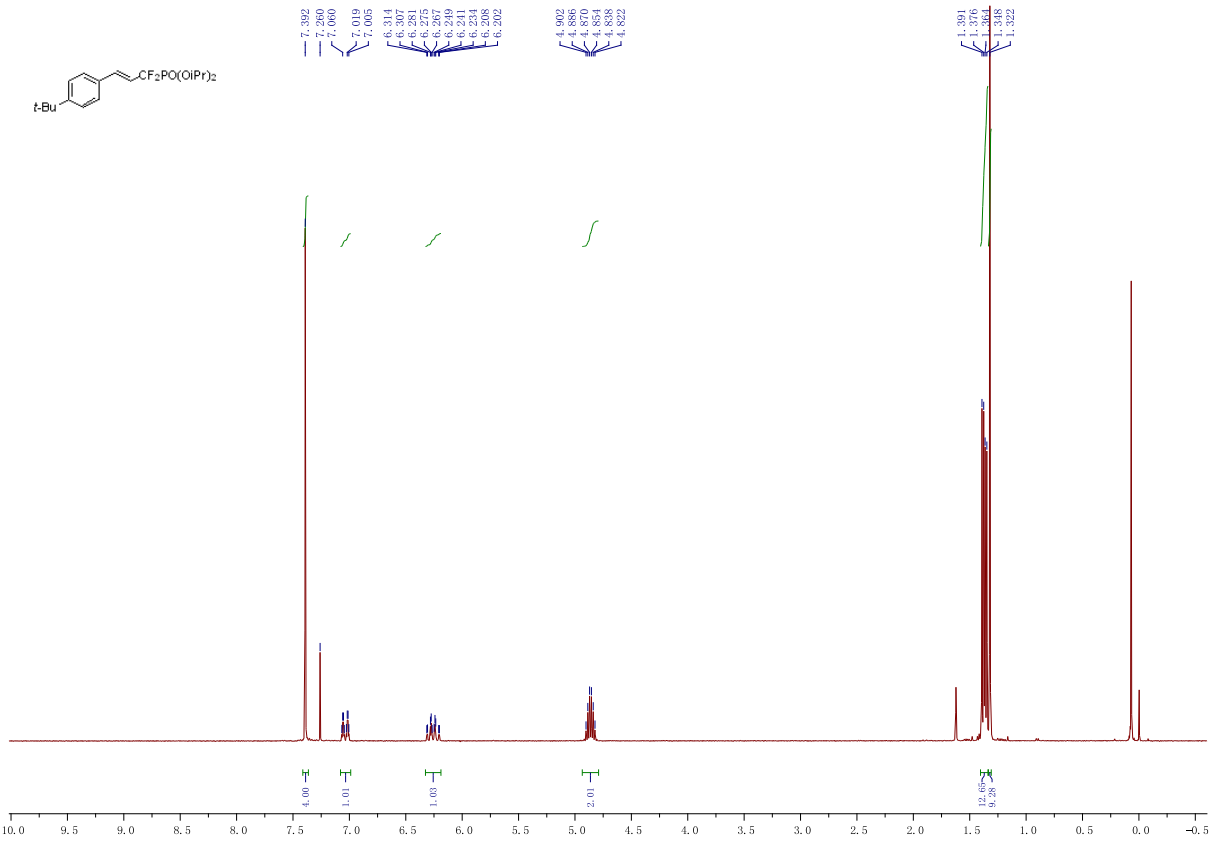


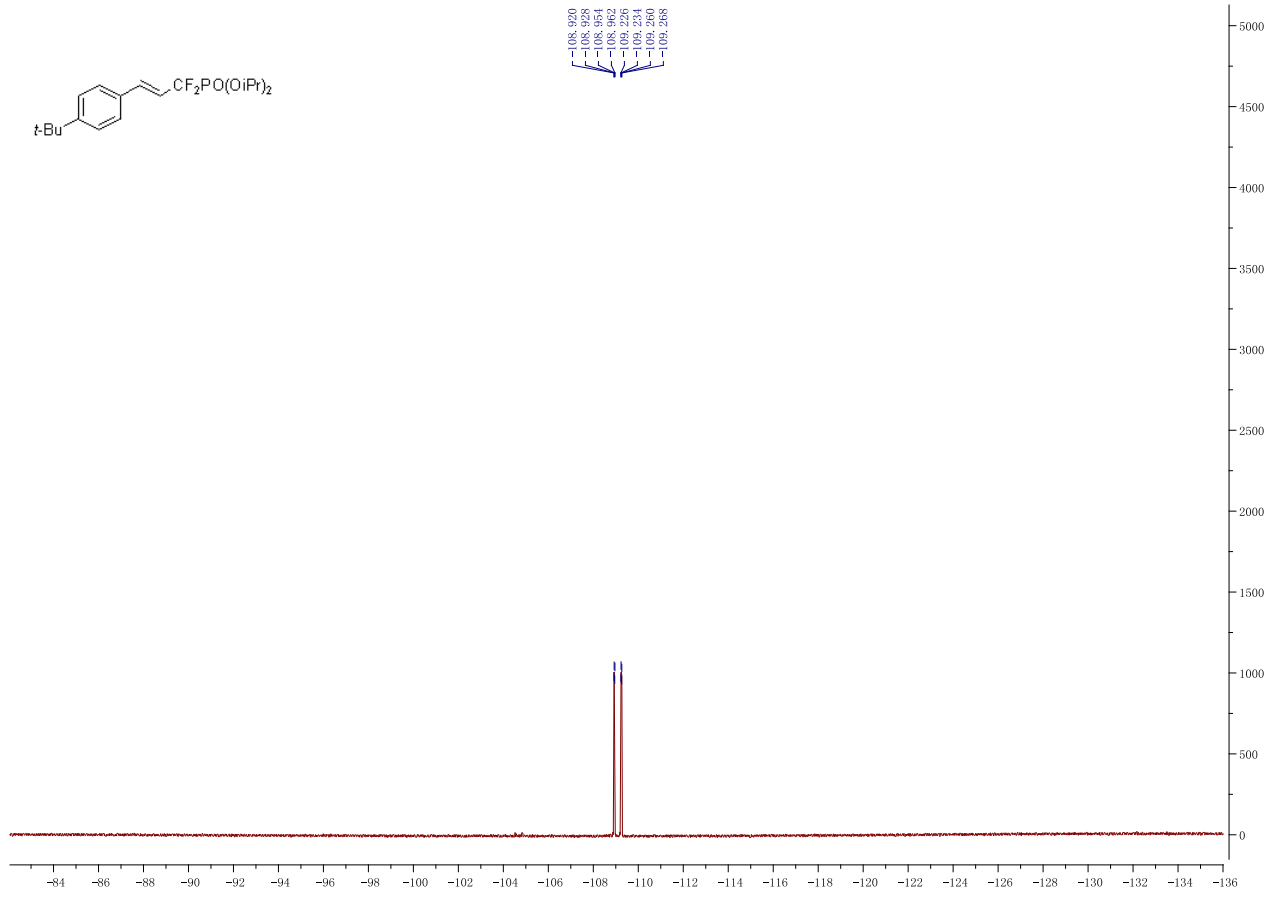

CF2PO(OiPr)2

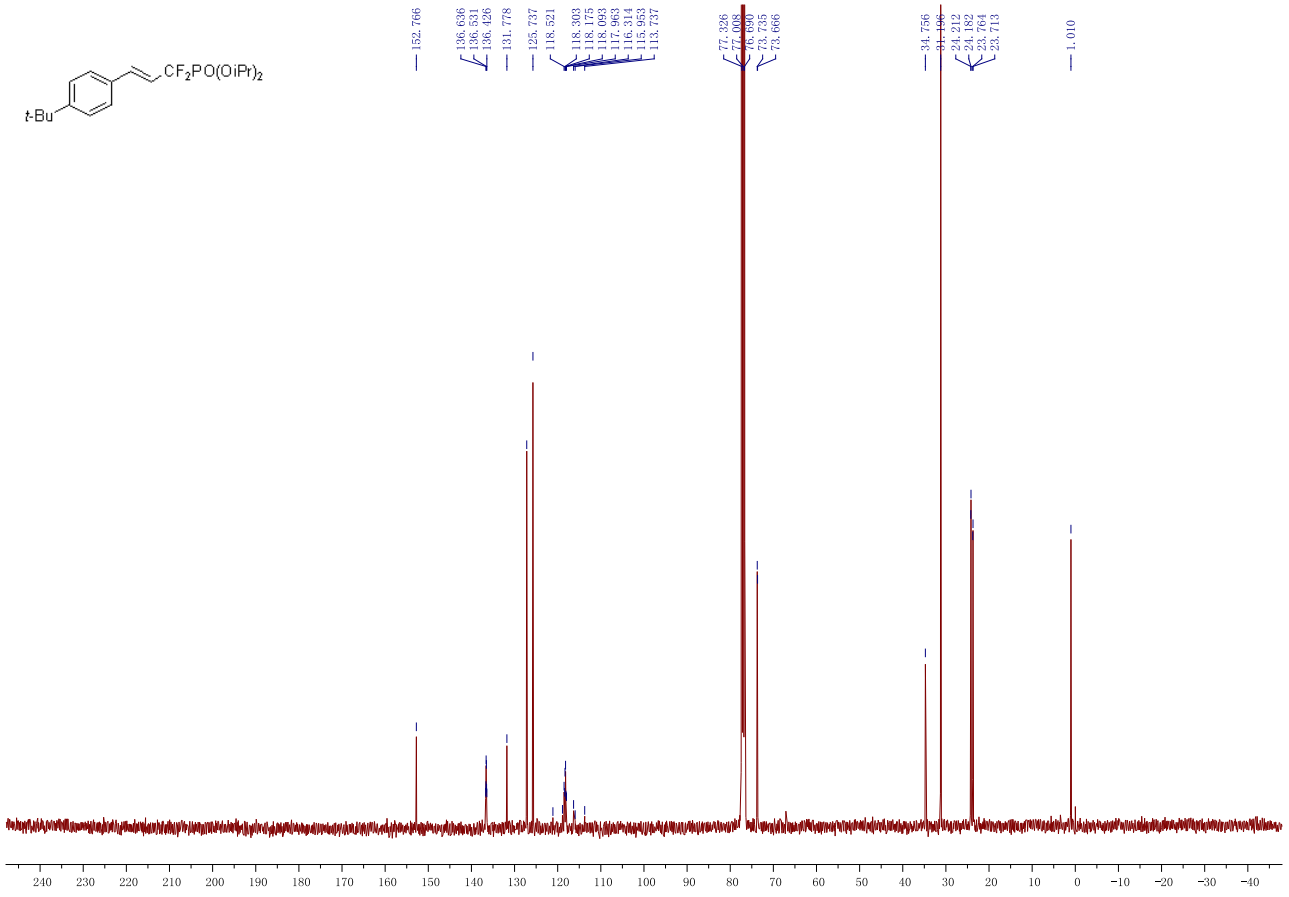



CF2PO(OiPr)2

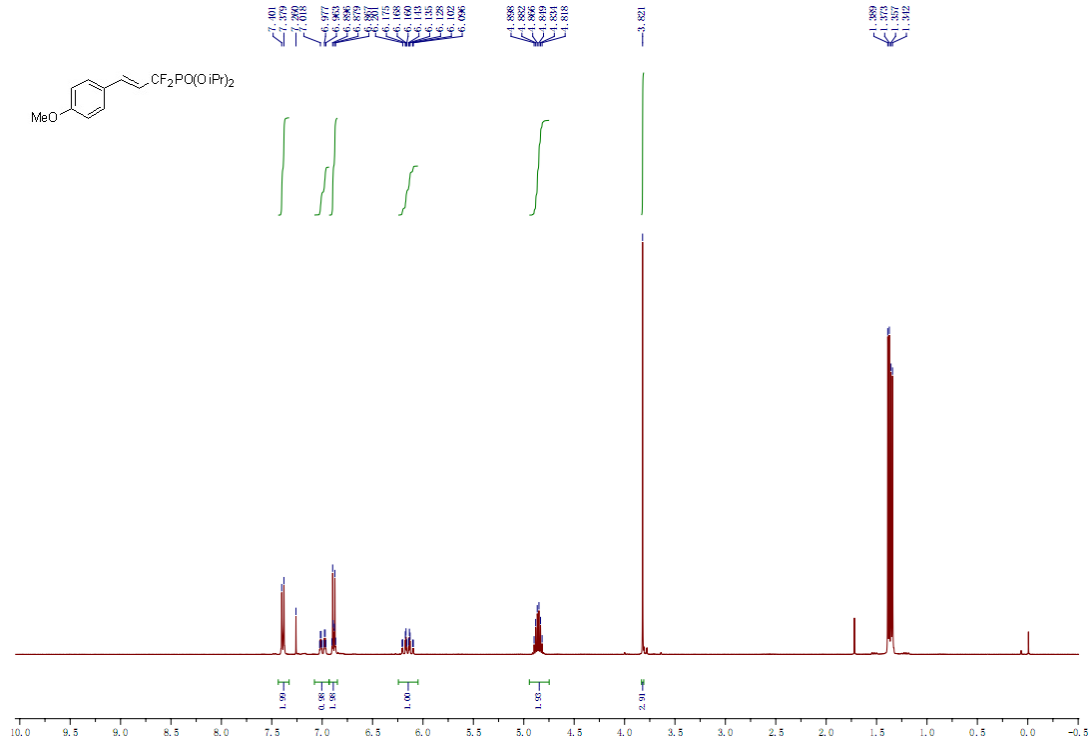
(*E*)-diisopropyl (3-(4-(tert-butyl)phenyl)-1,1-difluoroallyl)phosphonate (3c).

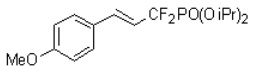


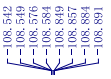


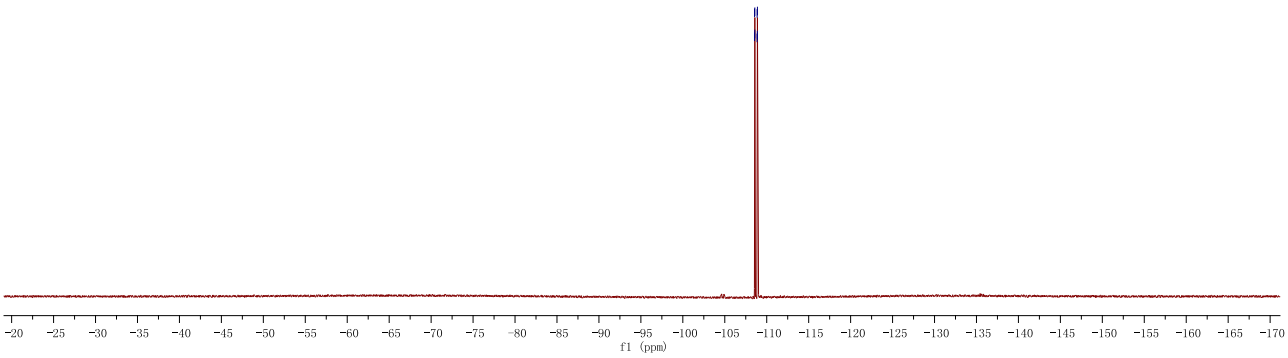


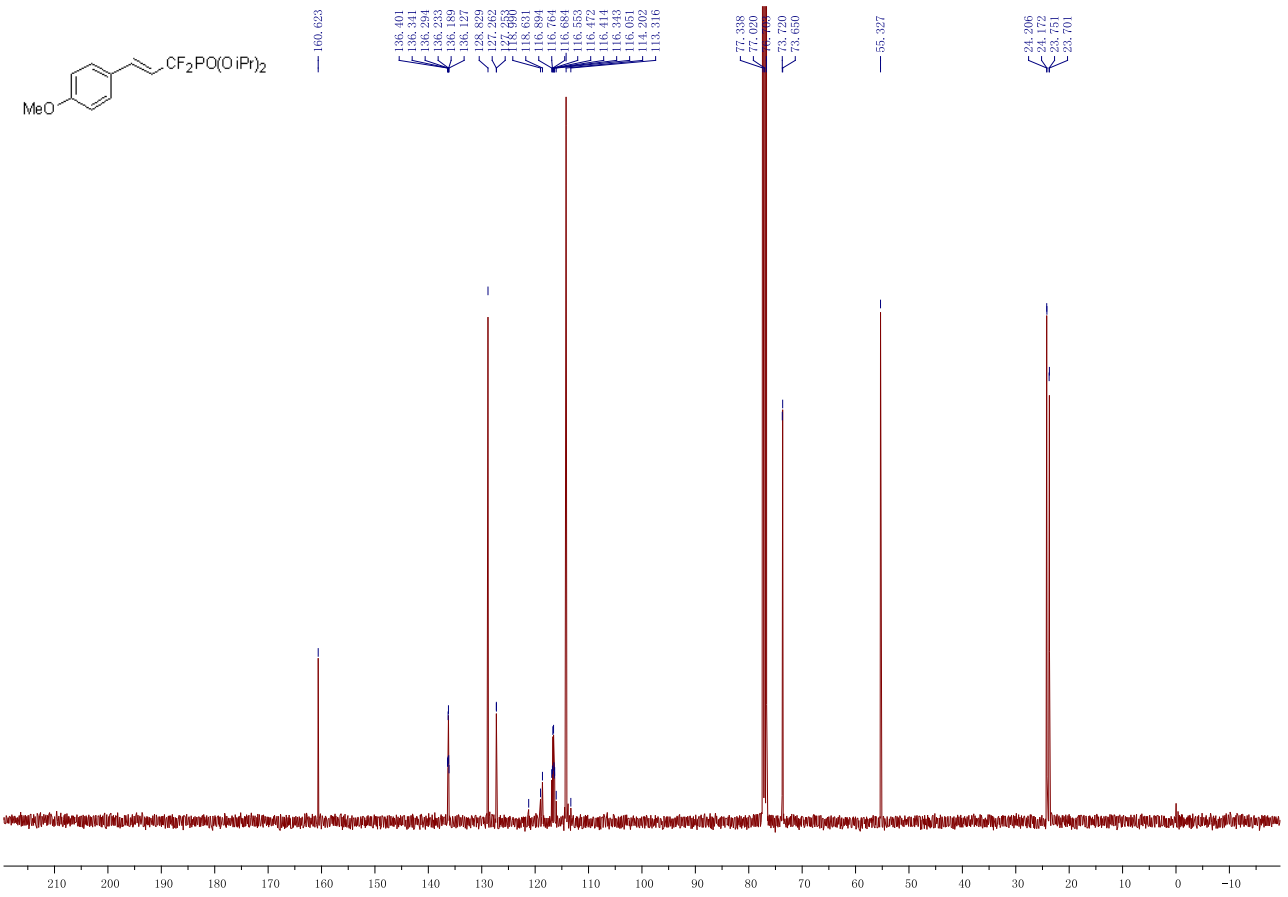
(*E*)-diisopropyl (3-(4-(tert-butyl)phenyl)-1,1-difluoroallyl)phosphonate (3d).



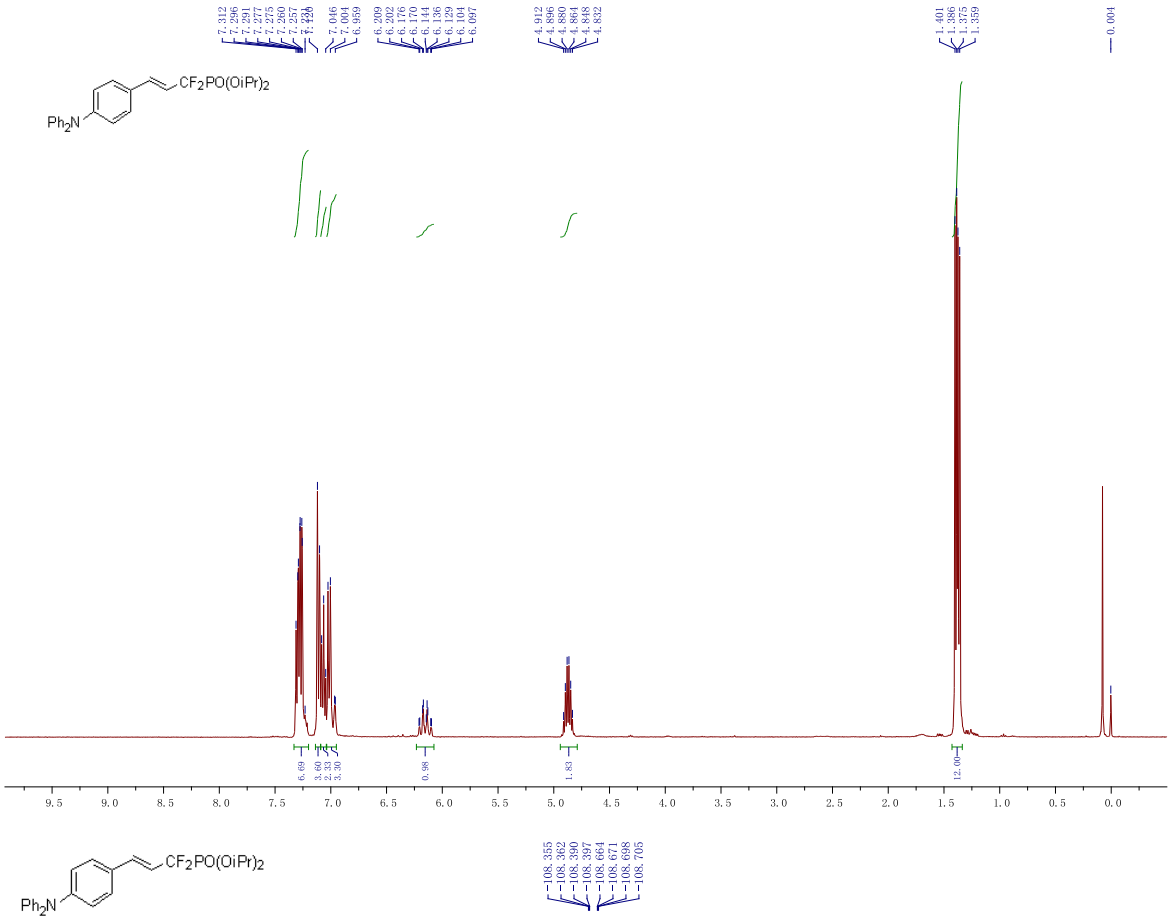

MeO
CF2PO(OiPr)2

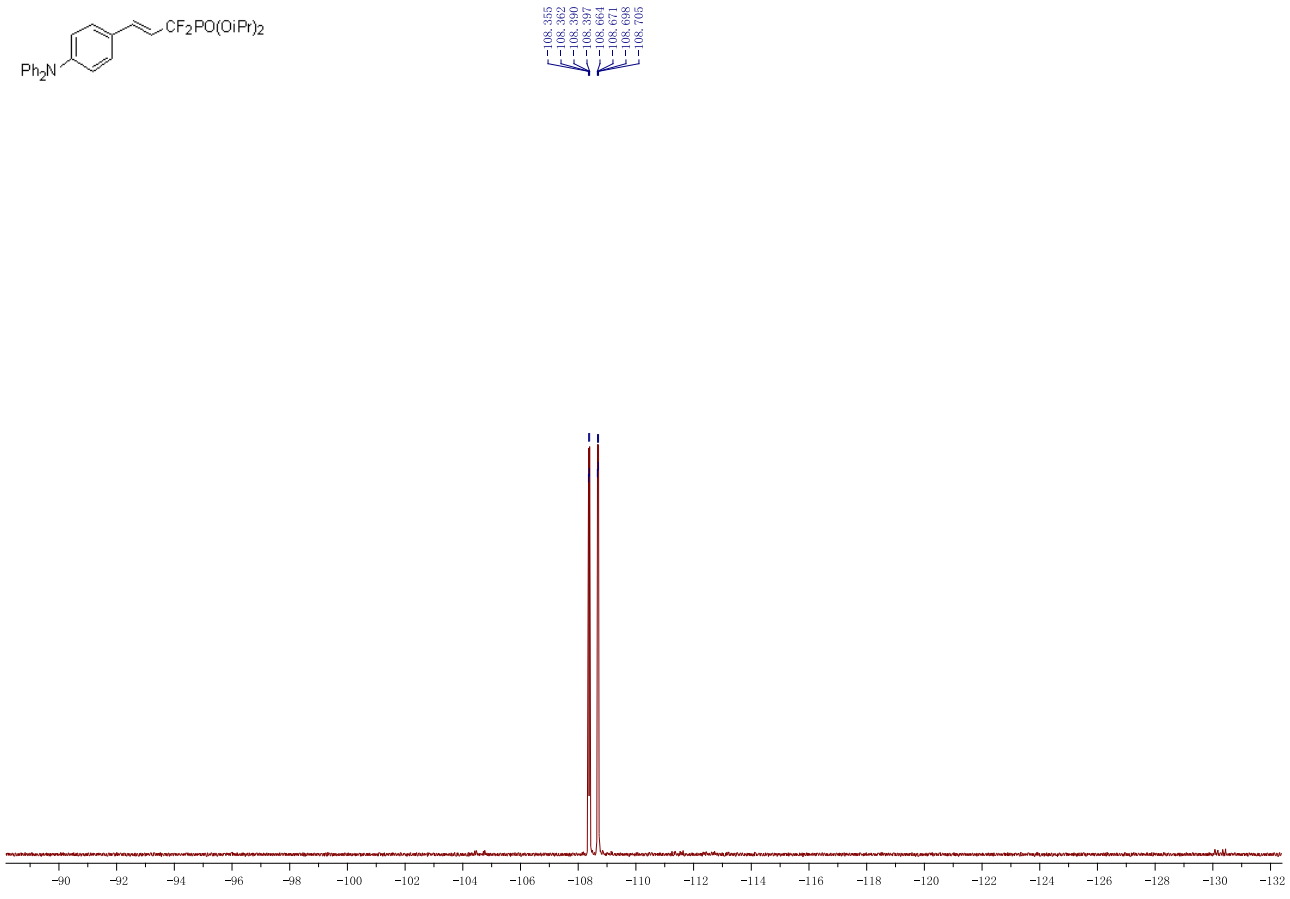

-108.542
-108.549
-108.576
-108.584
-108.849
-108.857
-108.884
-108.891

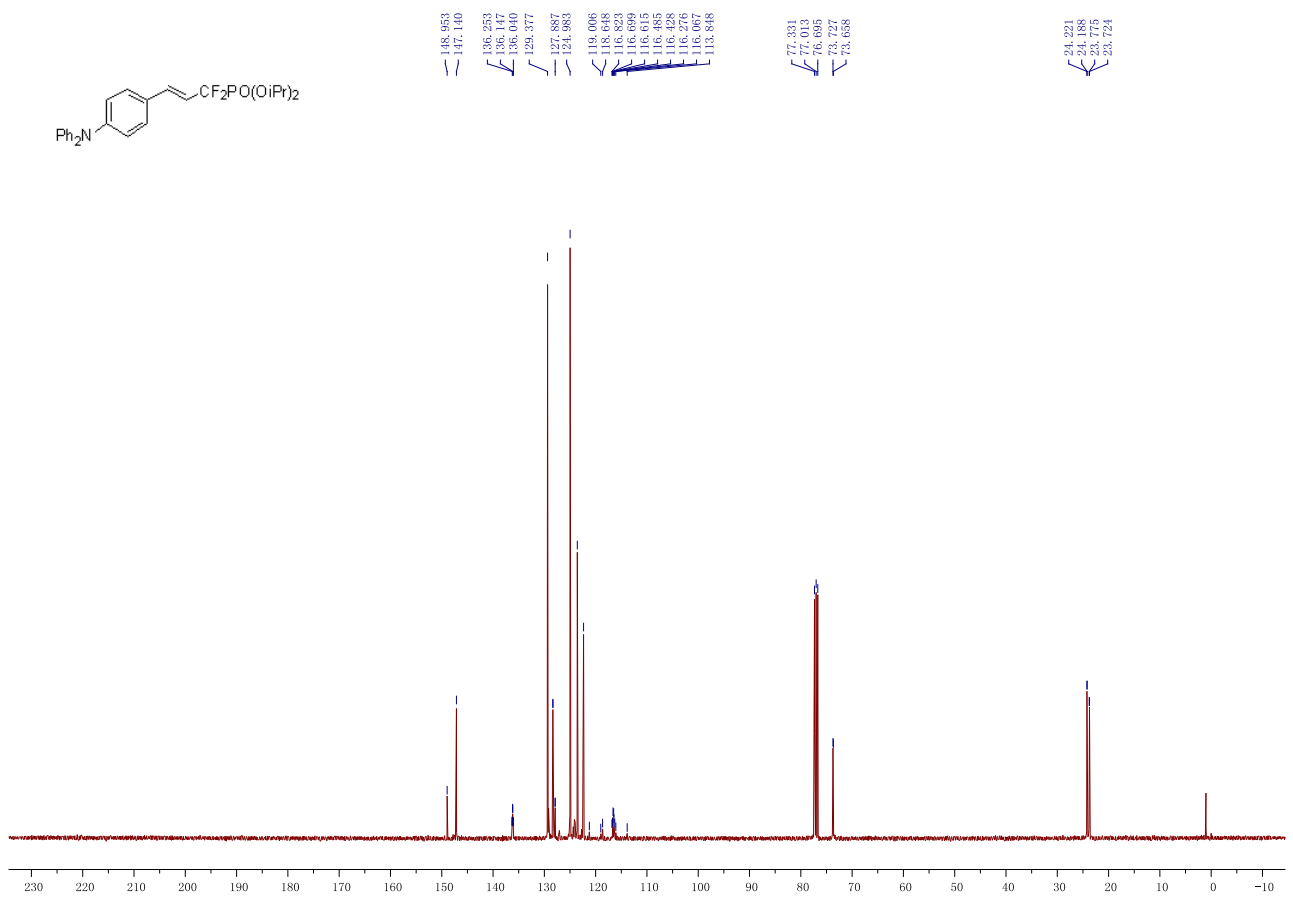

f1 (ppm)


MeO
CF2PO(OiPr)2
160.623
136.401
136.341
136.294
136.233
136.189
136.127
128.829
127.262
118.631
116.894
116.764
116.684
116.553
116.472
116.414
116.343
116.051
114.202
113.316
77.338
77.020
73.720
73.650
55.327
24.206
24.172
23.751
23.701

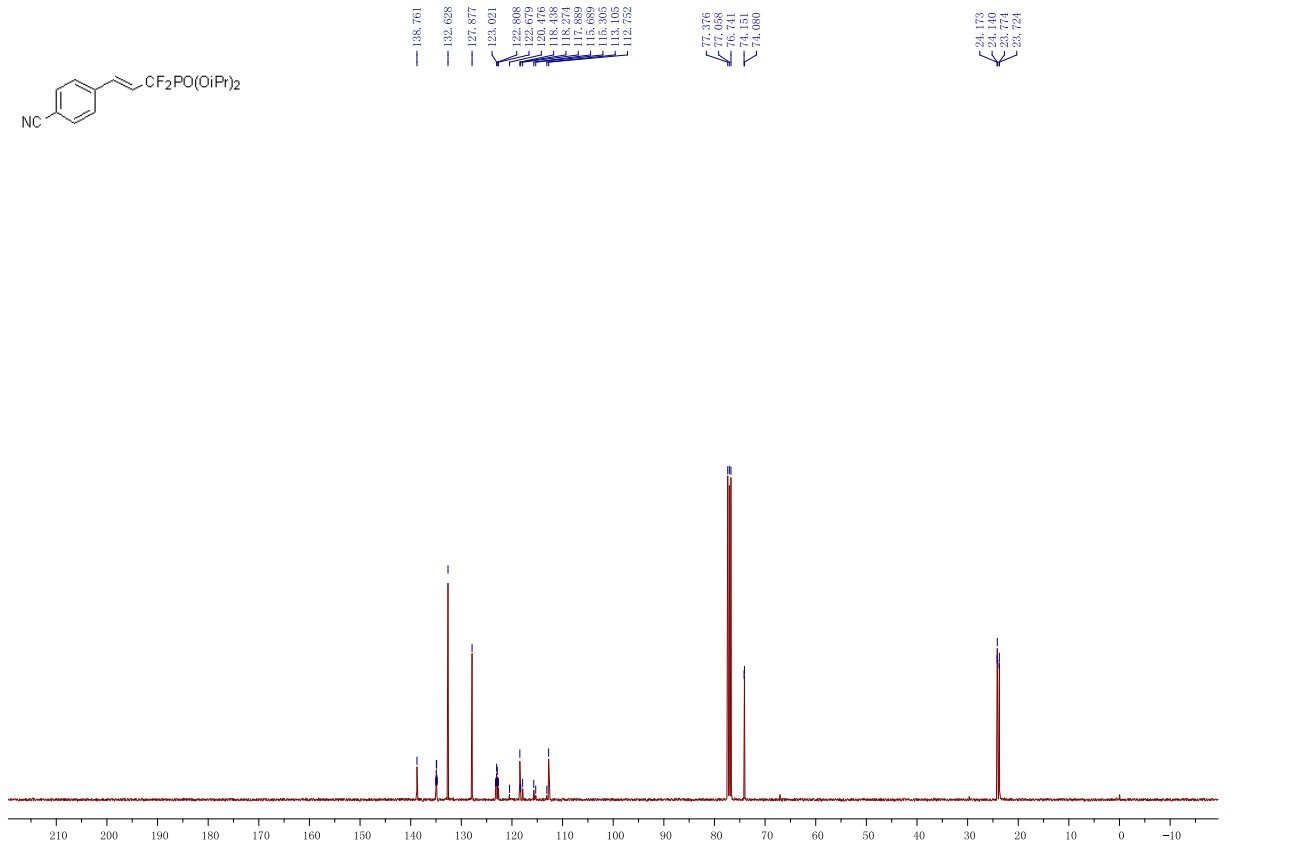
(*E*)-Diisopropyl (3-(4-(diphenylamino)phenyl)-1,1-difluoroallyl)phosphonate (3e).

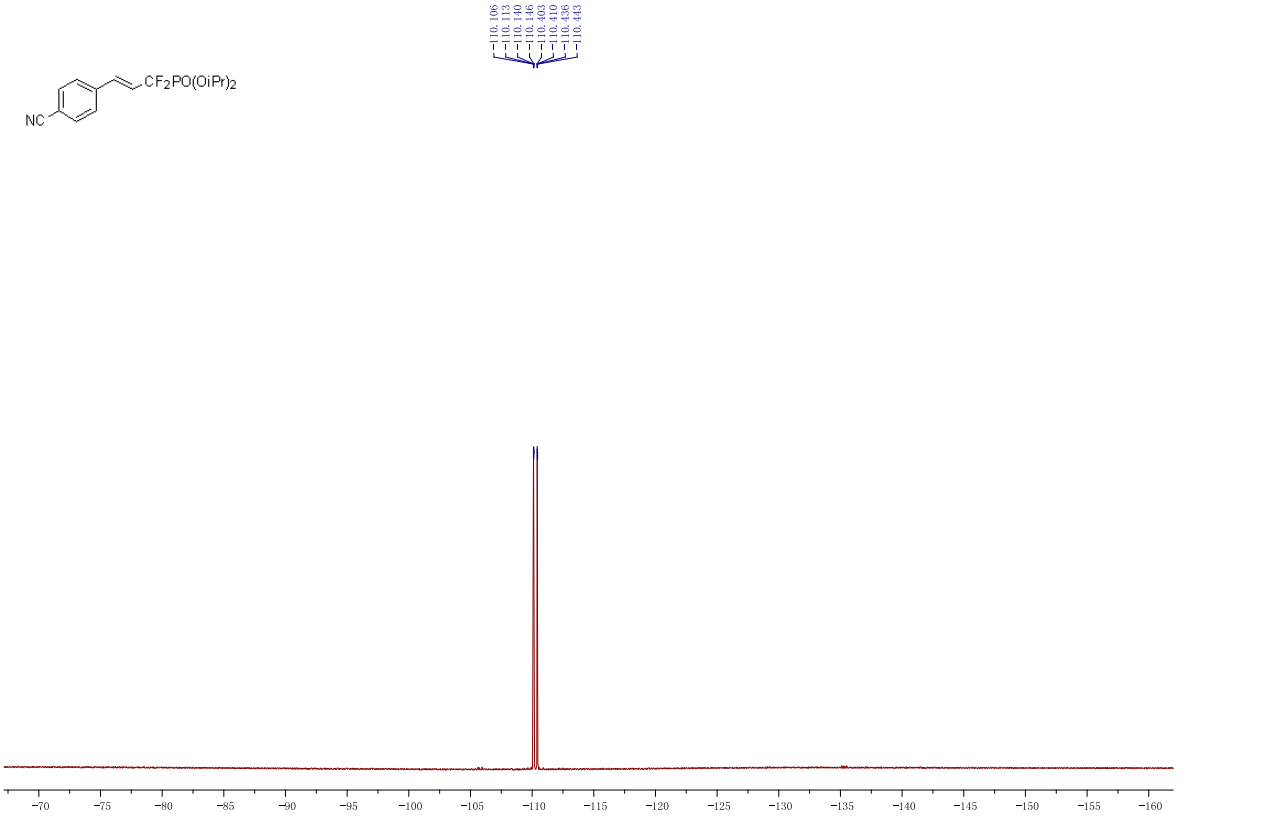


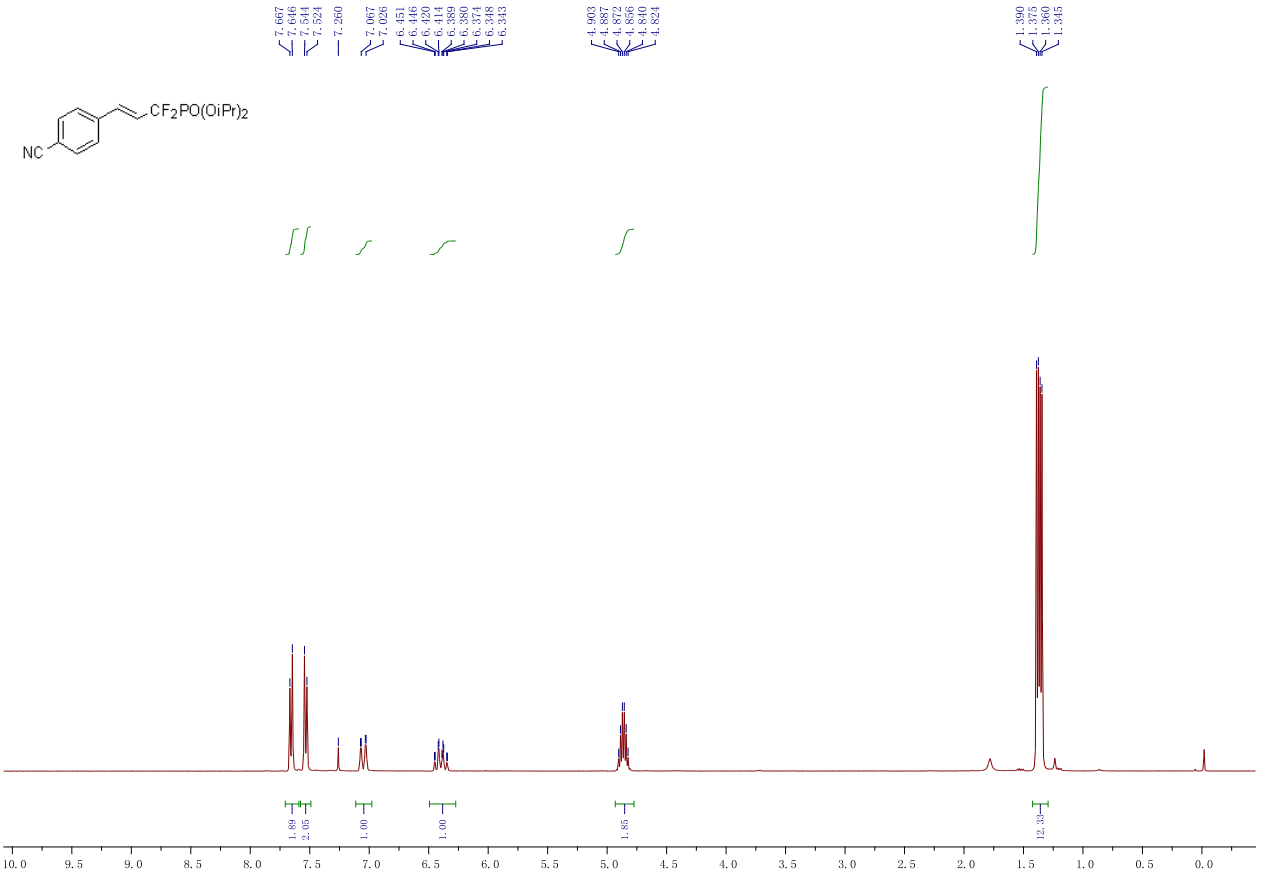




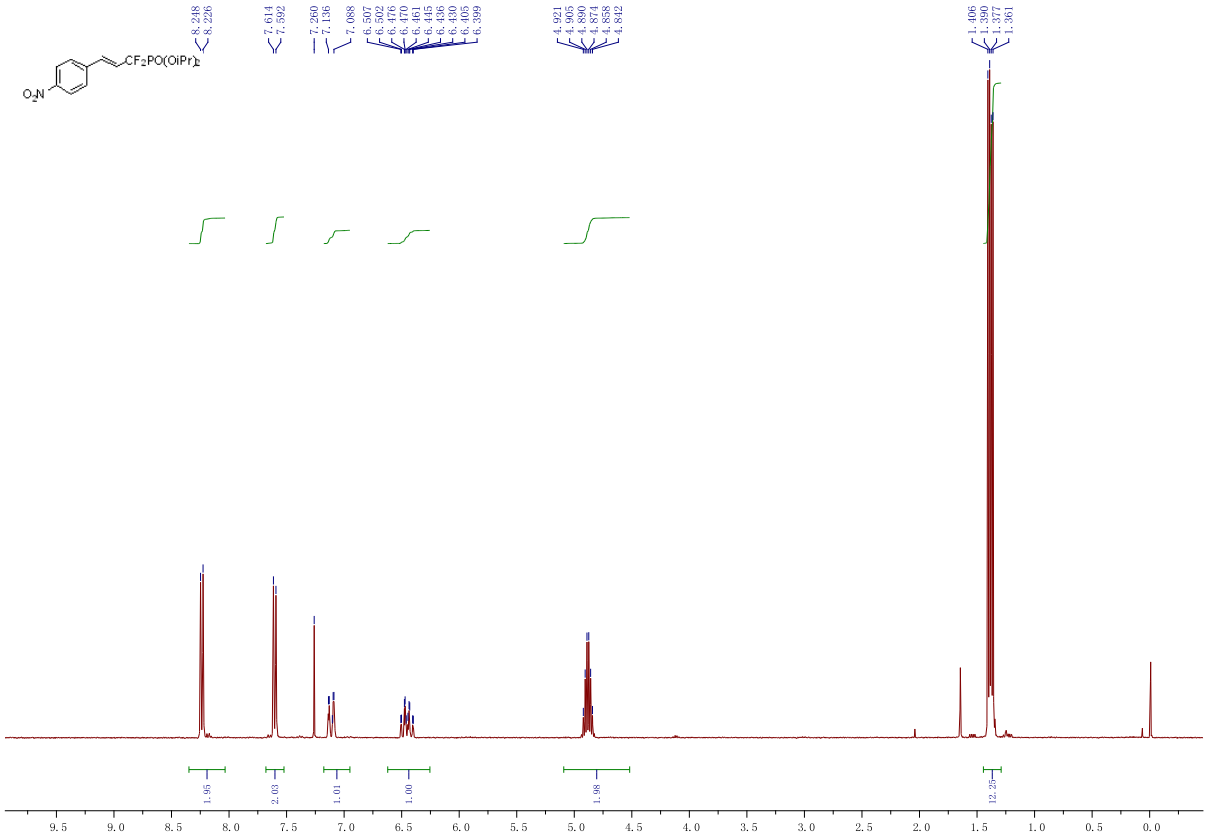
(*E*)-Diisopropyl (3-(4-cyanophenyl)-1,1-difluoroallyl)phosphonate (3f).

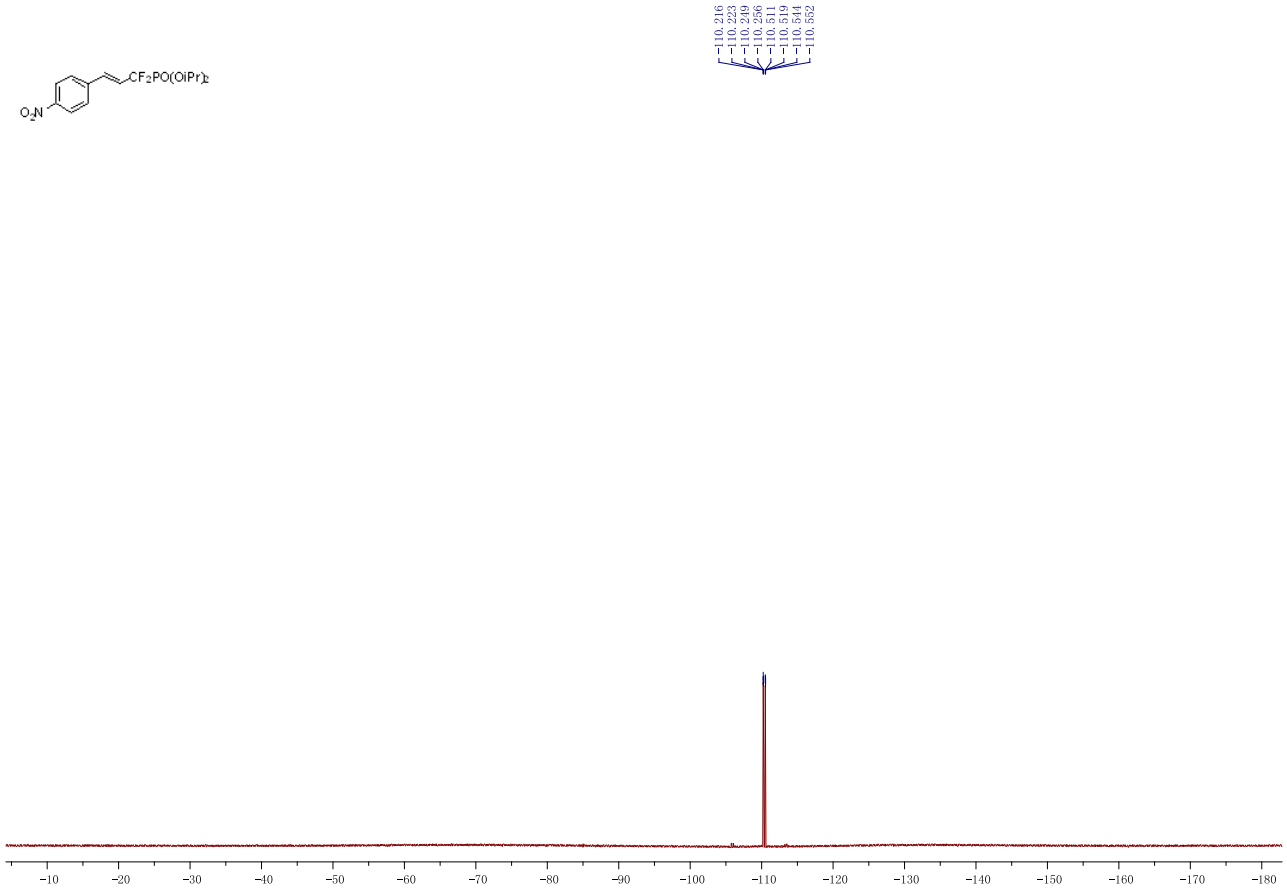


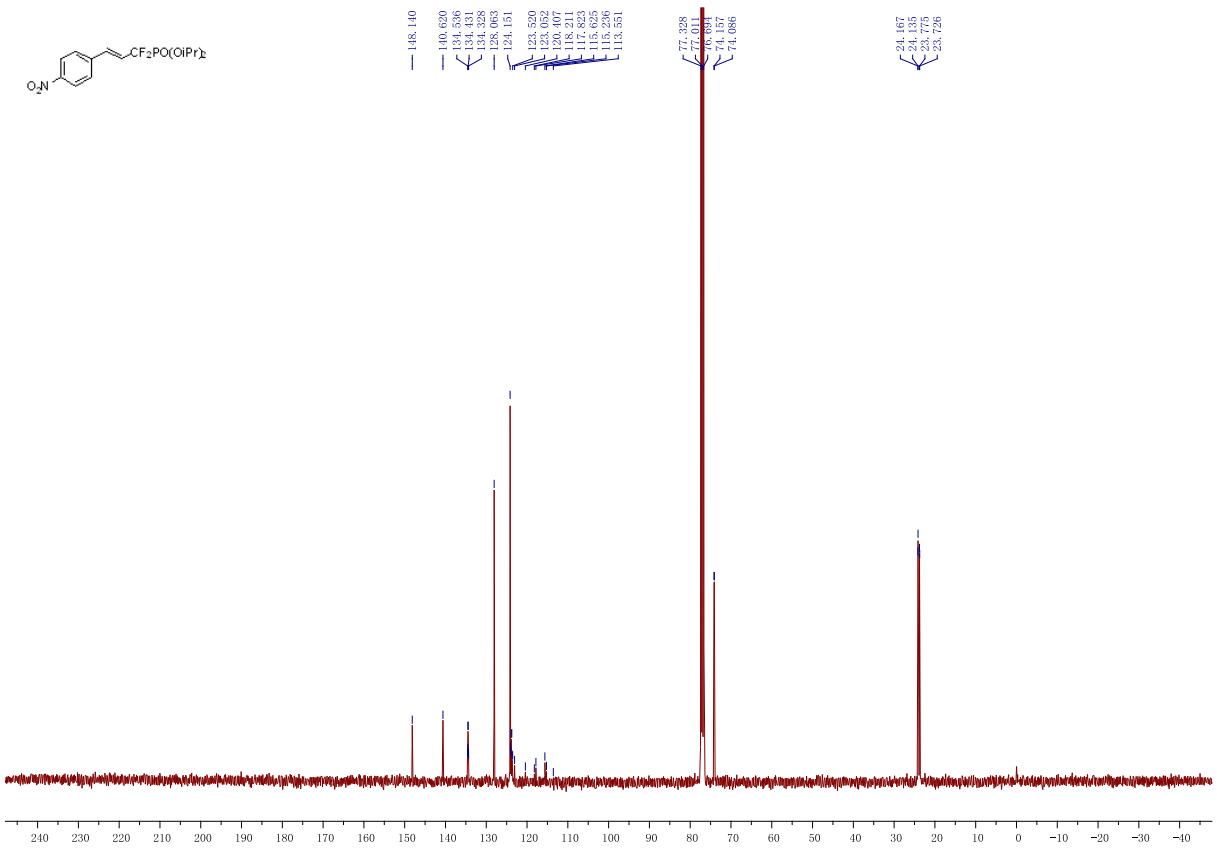

-110.106
-110.113
-110.119
-110.140
-110.146
-110.403
-110.410
-110.436
-110.443
CF2PO(OiPr)2
NC
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160


7.667
7.646
7.544
7.524
7.260
7.067
7.026
6.451
6.446
6.420
6.414
6.389
6.380
6.374
6.348
6.343
4.903
4.877
4.872
4.856
4.840
4.824
1.390
1.375
1.360
1.345
CF2PO(OiPr)2
NC
1.89
2.05
1.00
1.00
1.85
12.33
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

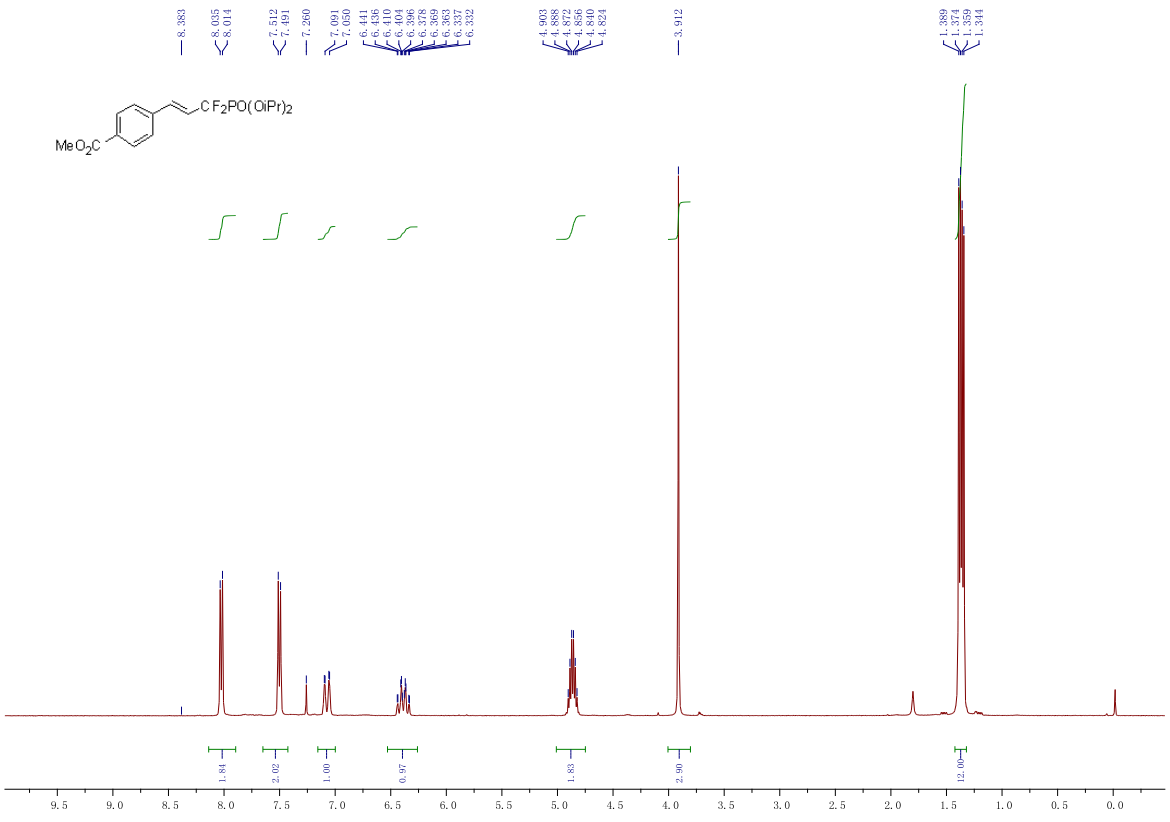
(*E*)-Diisopropyl (1,1-difluoro-3-(4-nitrophenyl)allyl)phosphonate (3g).

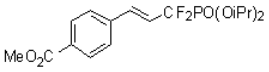


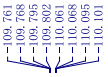


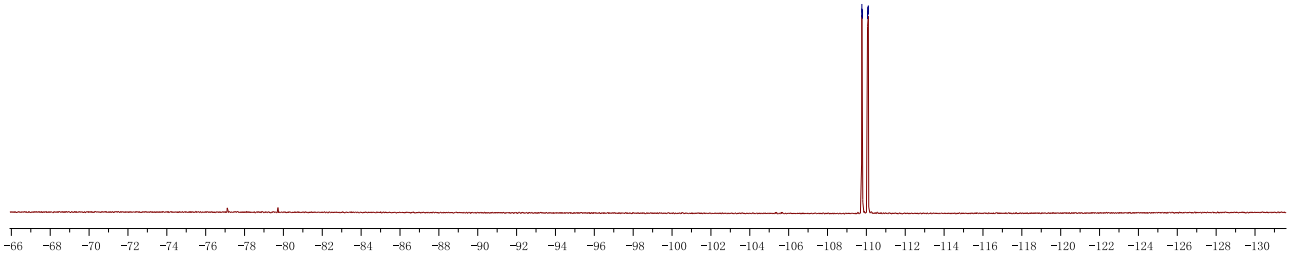


(*E*)-methyl 4-(3-(diisopropoxyphosphoryl)-3,3-difluoroprop-1-en-1-yl)benzoate (3h).

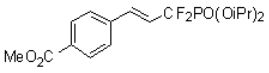


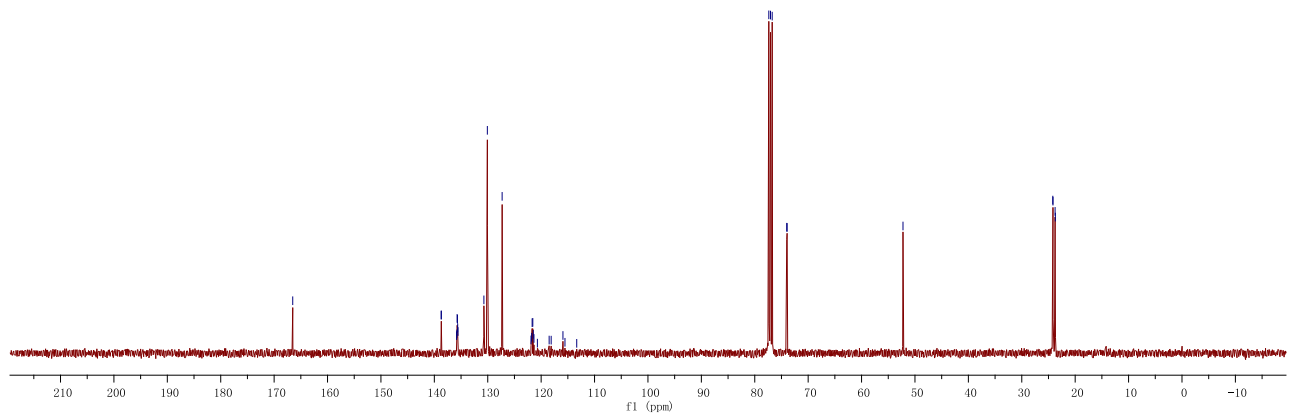

CF2PO(OiPr)2
MeO2C


-109.761
-109.768
-109.795
-109.802
-110.061
-110.068
-110.095
-110.101

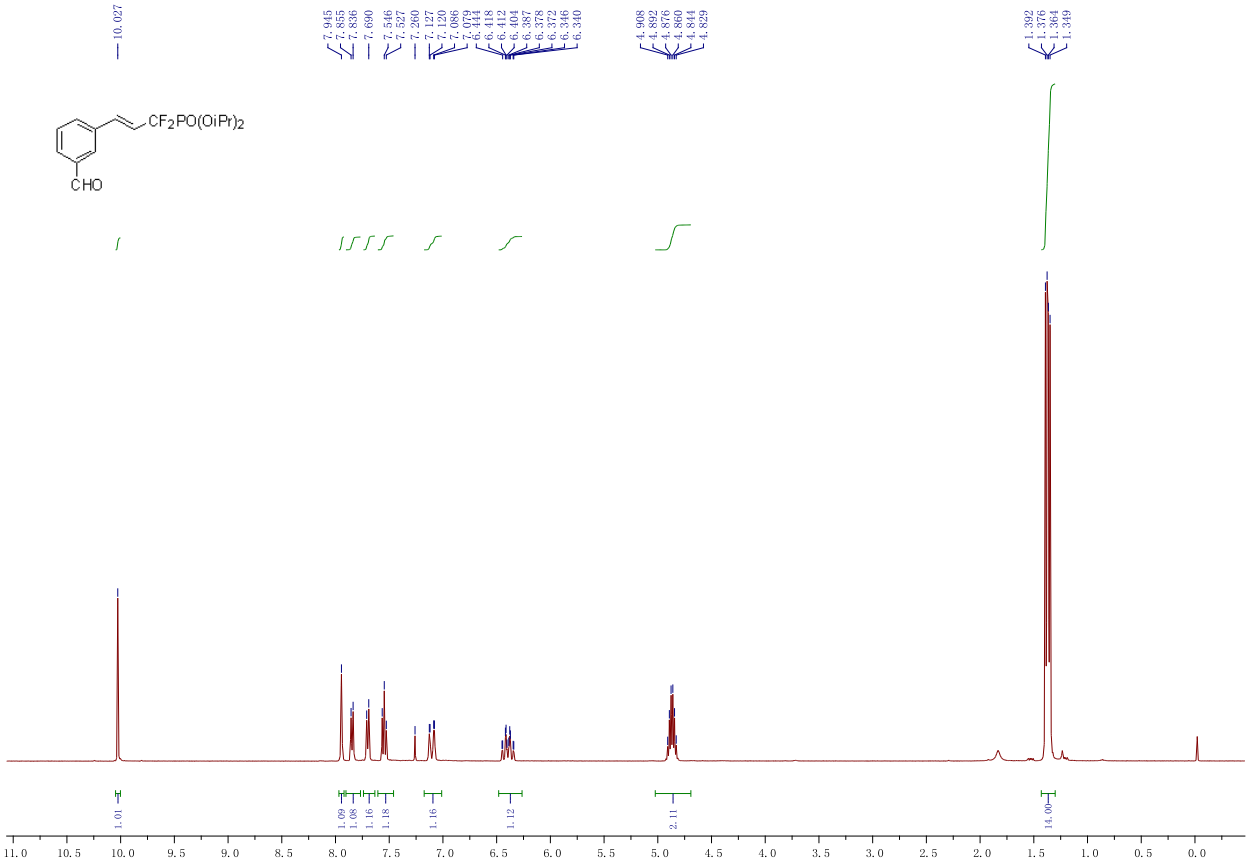

-66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130

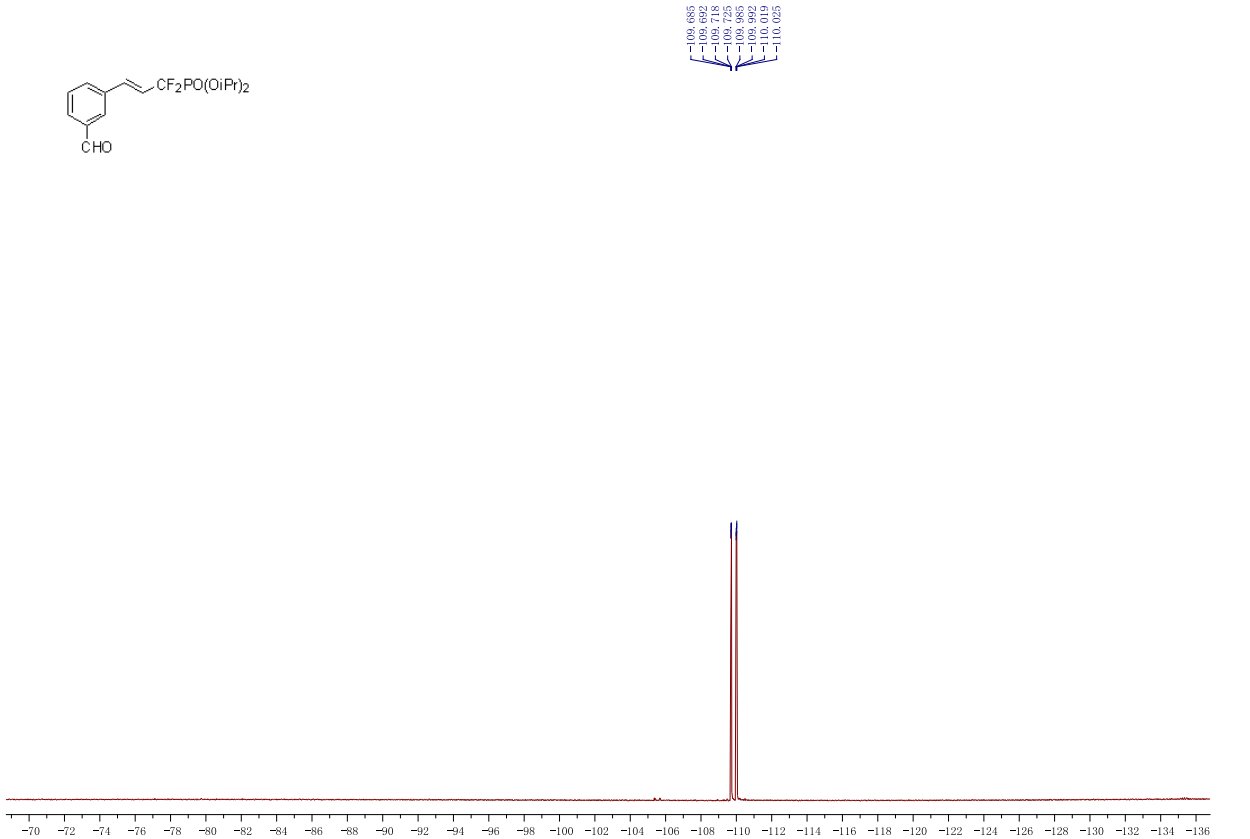

166.517
138.709
138.700
135.569
130.074
127.304
121.898
121.769
121.687
121.560
121.477
121.348
120.704
118.501
118.122
115.918
115.540
113.337
77.369
77.052
76.734
74.011
73.941
52.242
24.190
24.156
23.762
23.711

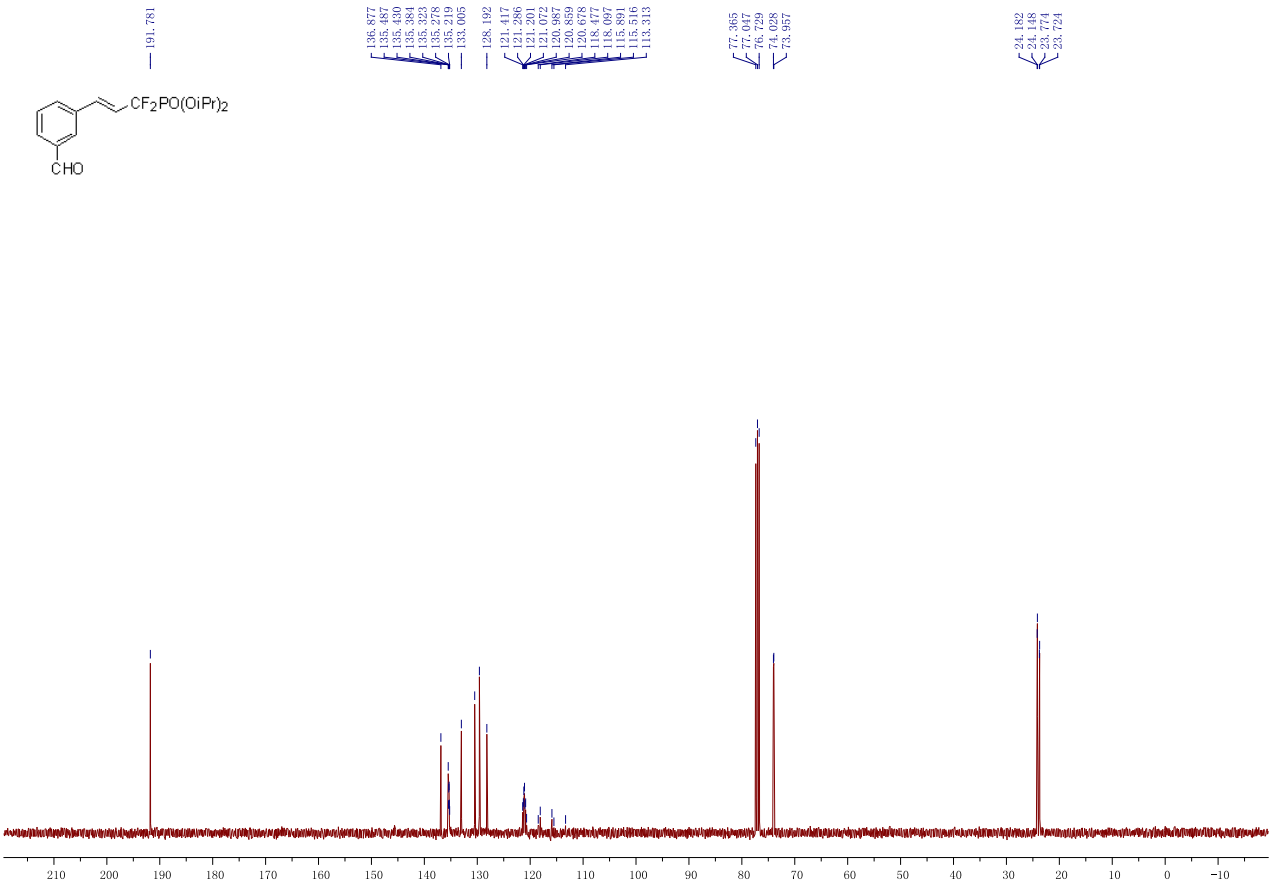

CF2PO(OiPr)2
MeO2C


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

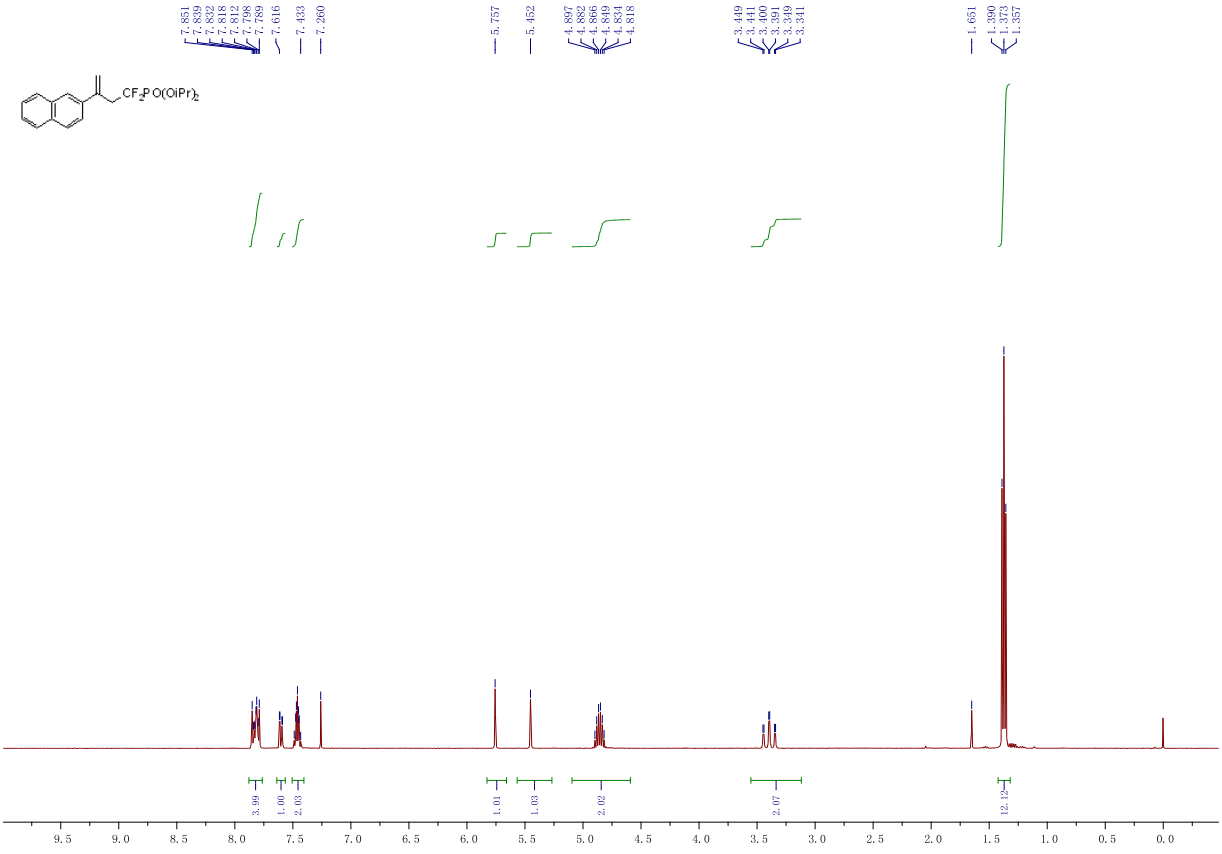
(*E*)-diisopropyl (1,1-difluoro-3-(3-formylphenyl)allyl)phosphonate (3i)

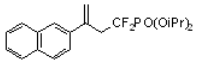




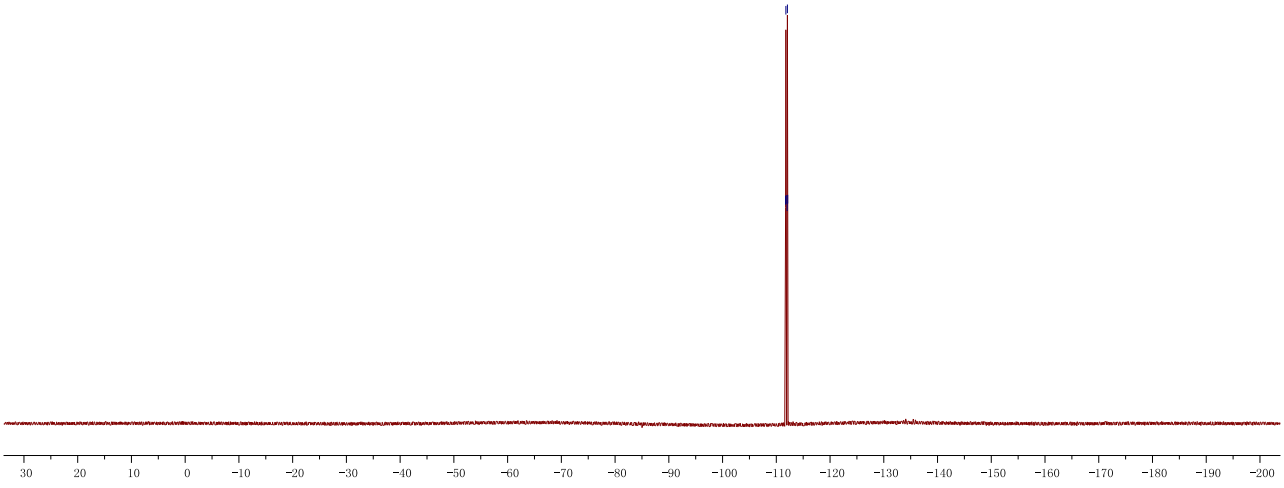


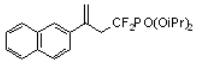
Diisopropyl (1,1-difluoro-3-phenylbut-3-en-1-yl)phosphonate (3j).




CF2PO(OiPr)2


-111.727
-111.780
-111.833
-112.012
-112.065
-112.118


30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200


CF2PO(OiPr)2


138.271
138.252
138.223
138.172
133.273
132.836
128.264
127.506
126.173
125.983
125.112
124.437
122.949
120.792
120.349
119.845
118.193
117.748
115.589
77.335
77.018
76.700
73.732
73.661
39.046
38.890
38.840
38.686
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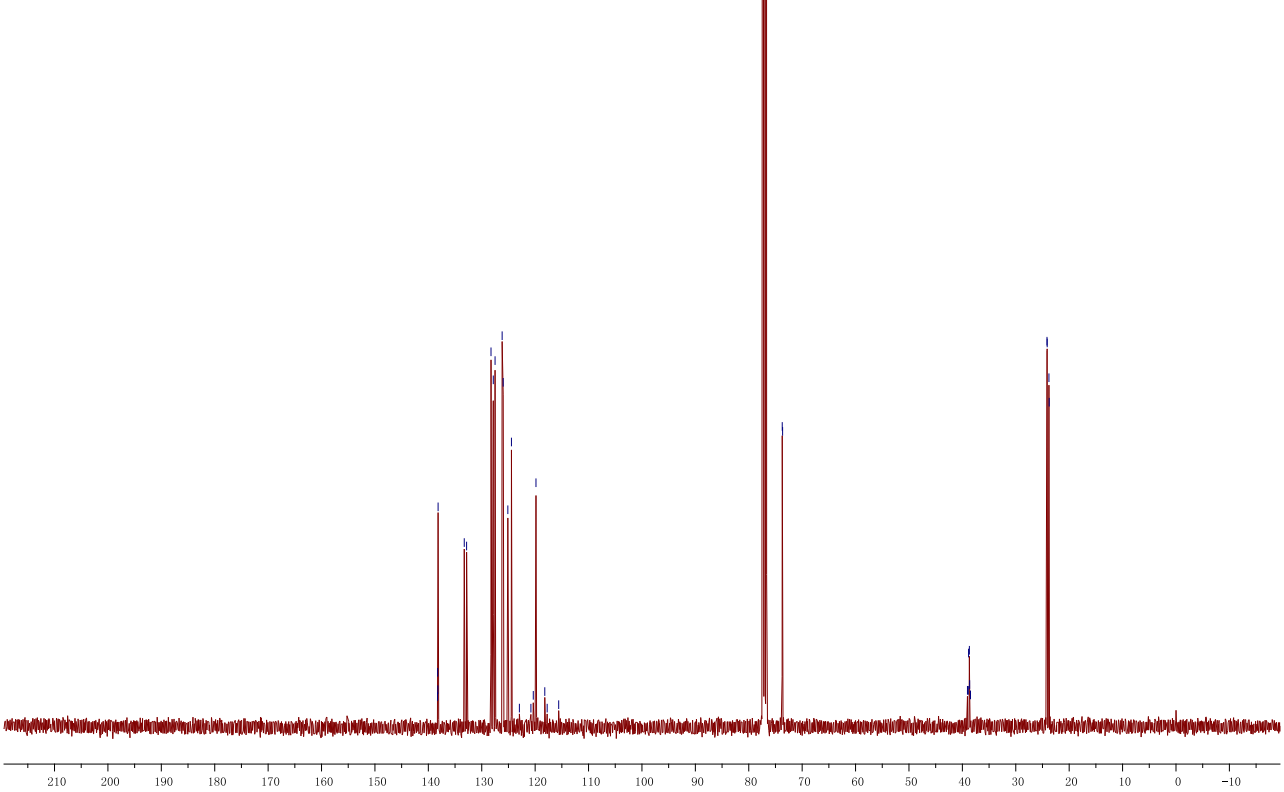
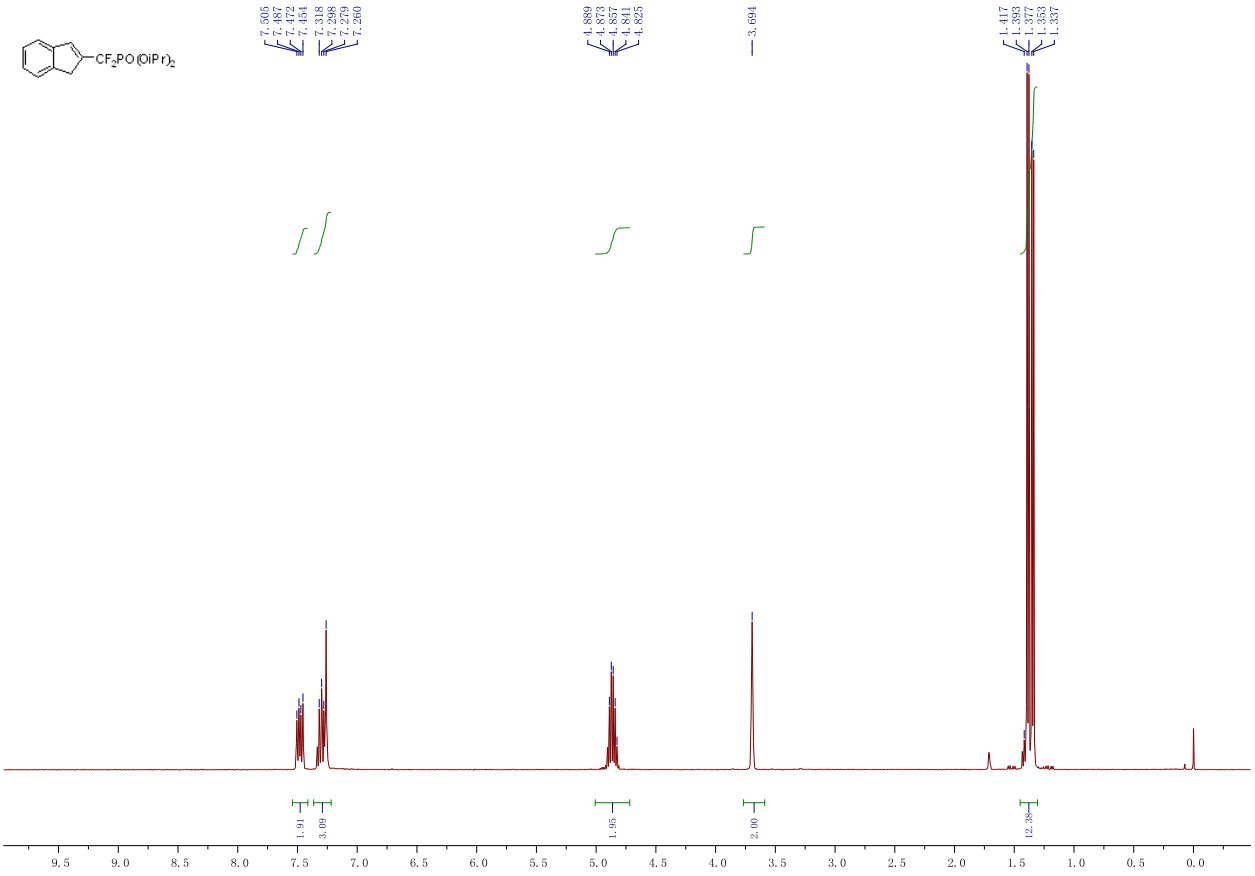
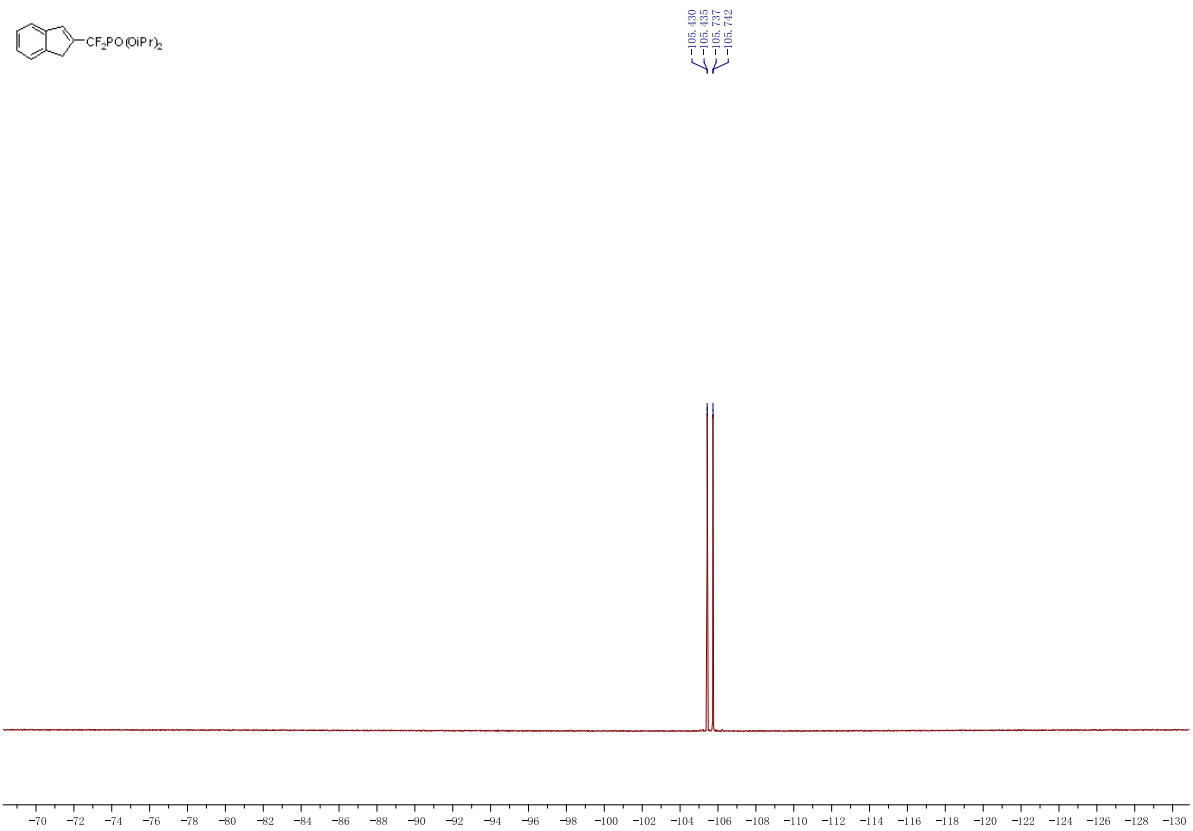
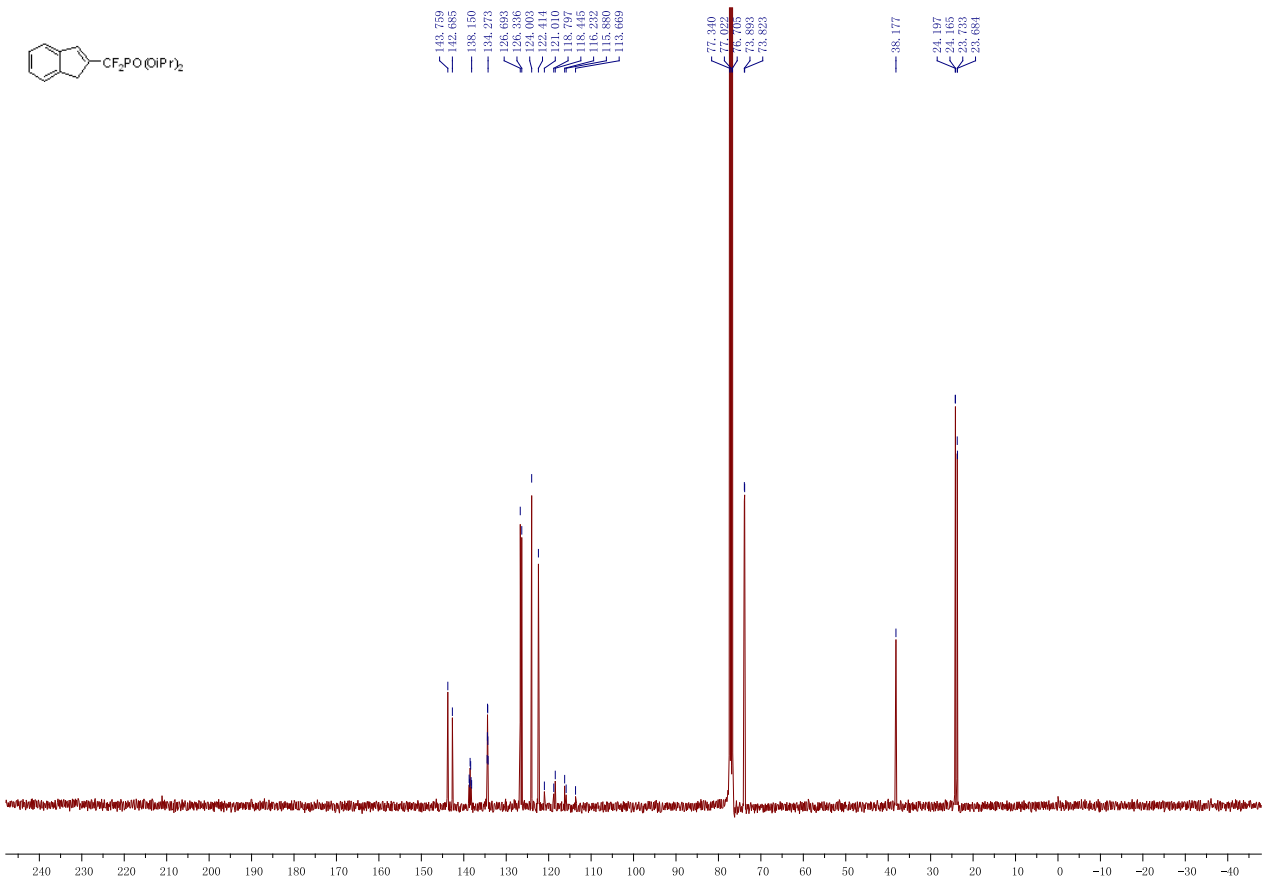
38.481
24.154
24.119
23.792
23.743


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

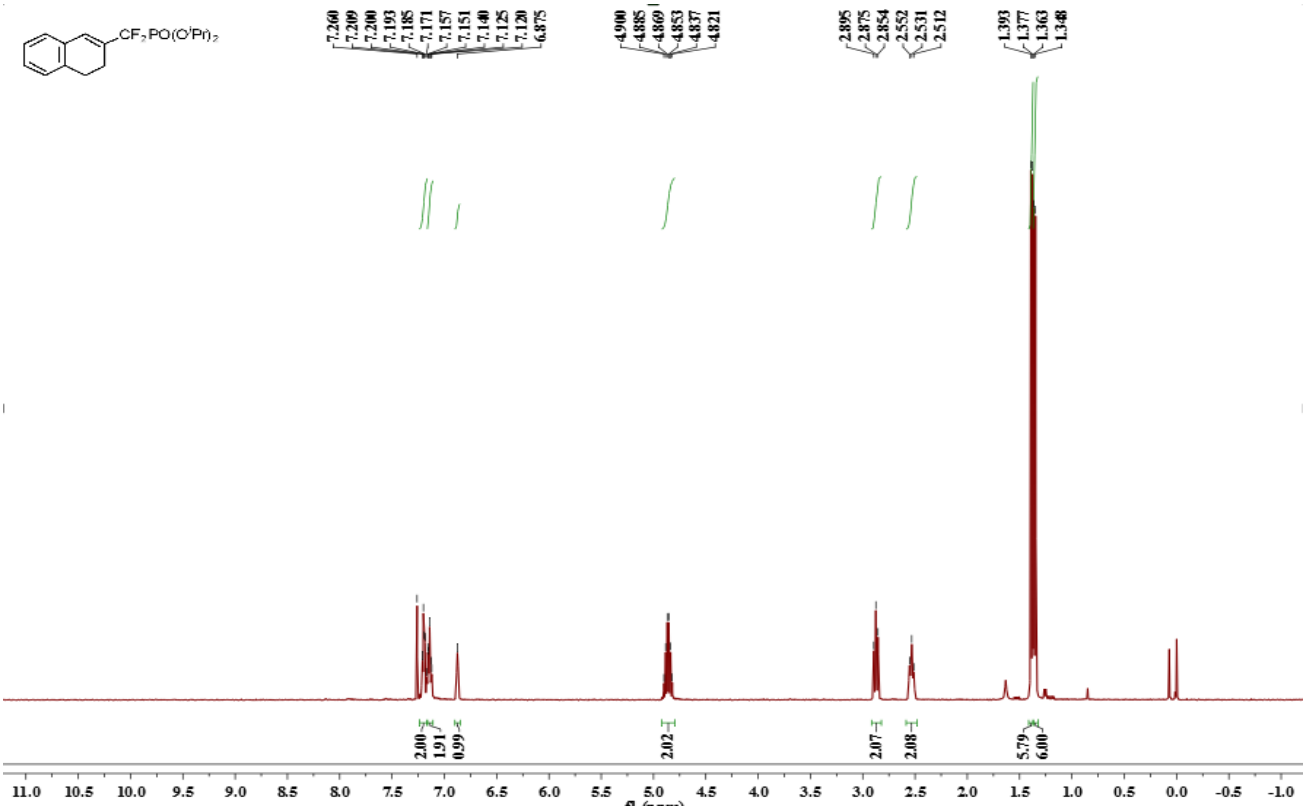
Diisopropyl (difluoro(1H-inden-2-yl)methyl)phosphonate (3k).

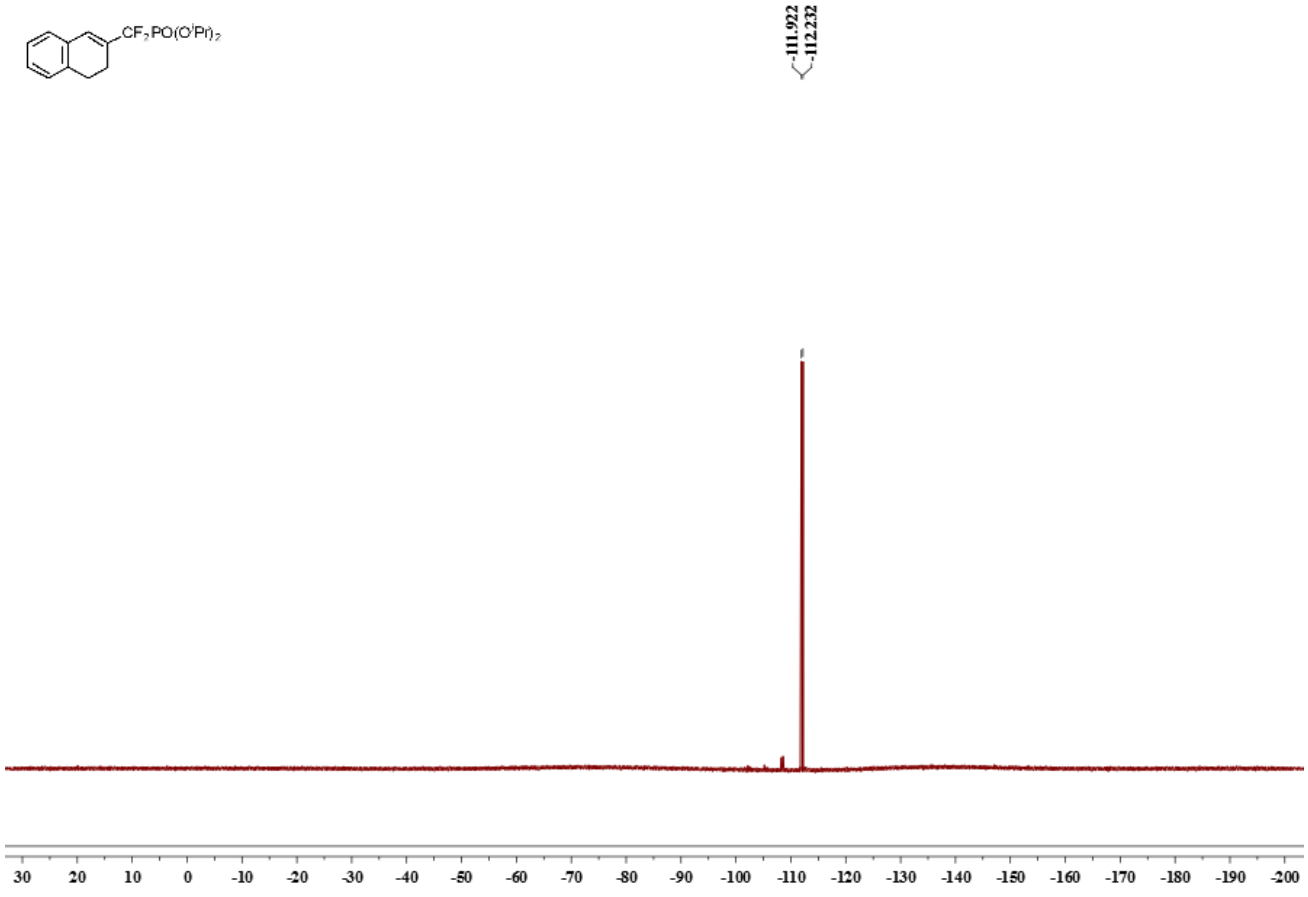


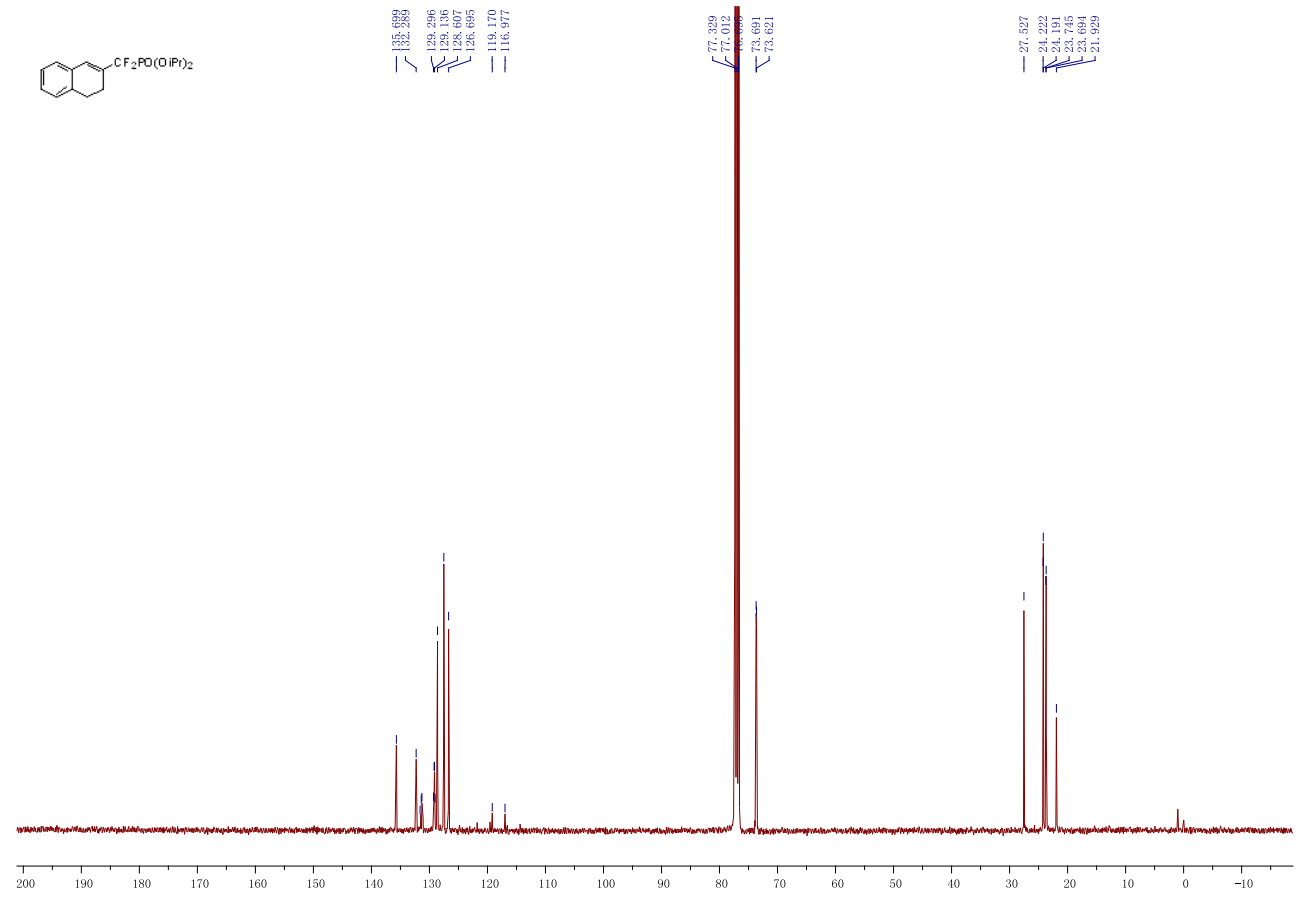




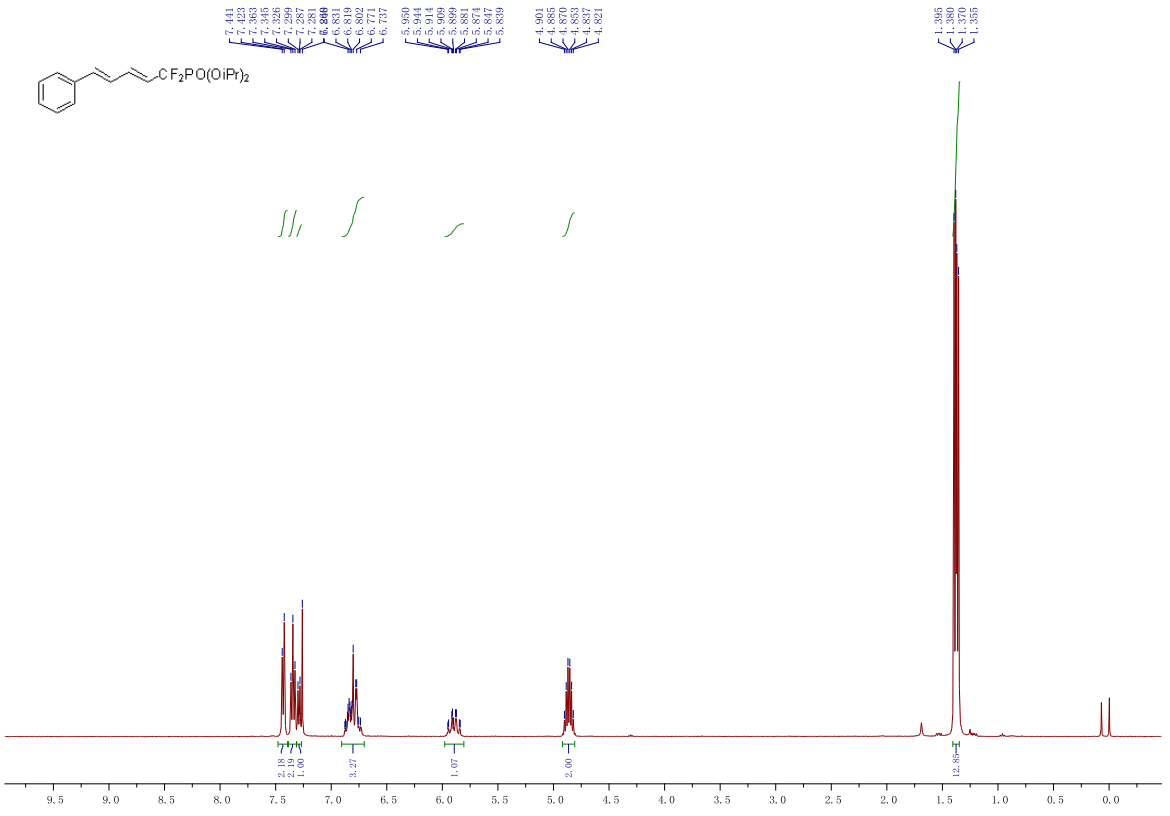
(*E*)-Diisopropyl (3-(3,4-dihydronaphthalen-2-yl)-1,1-difluoroallyl)phosphonate (3l).

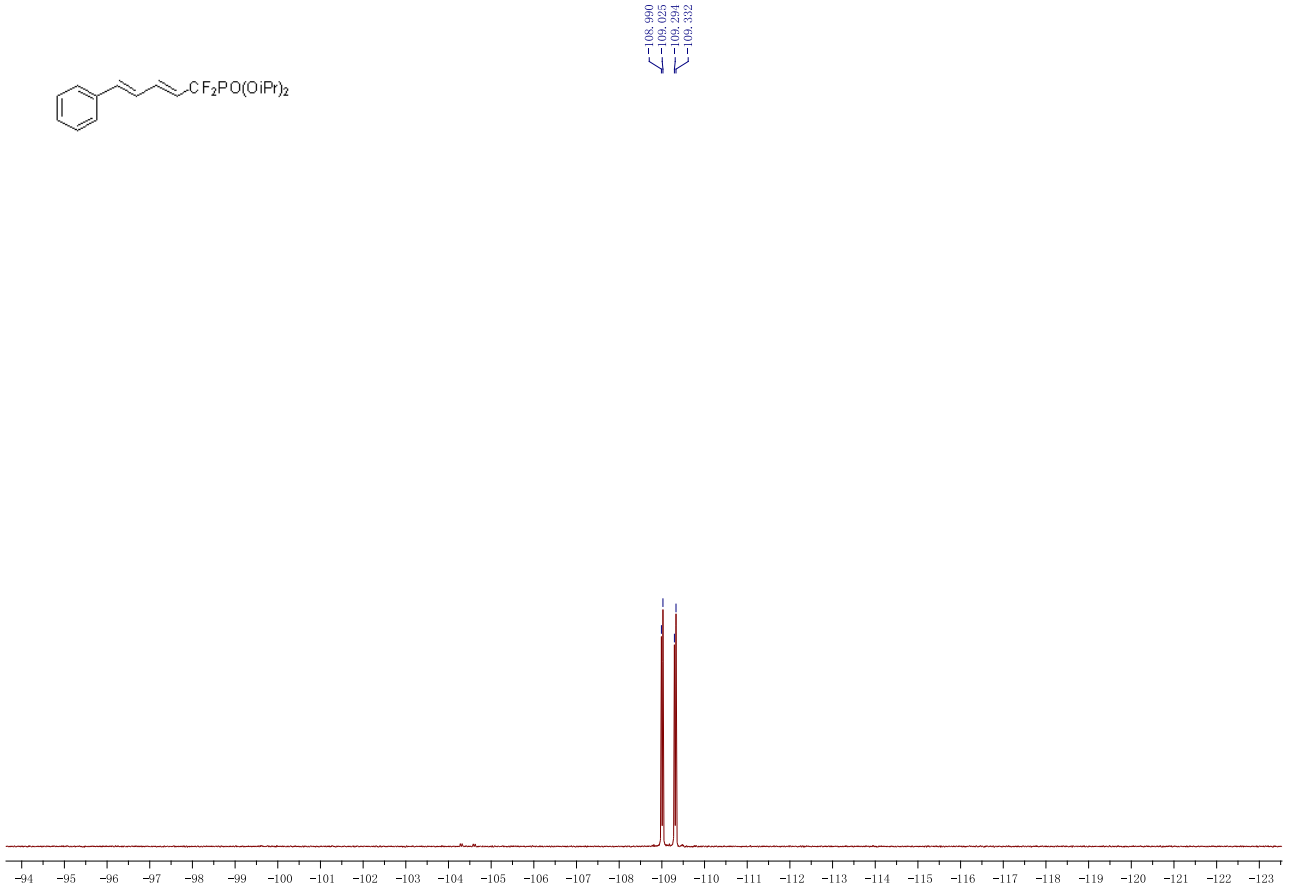


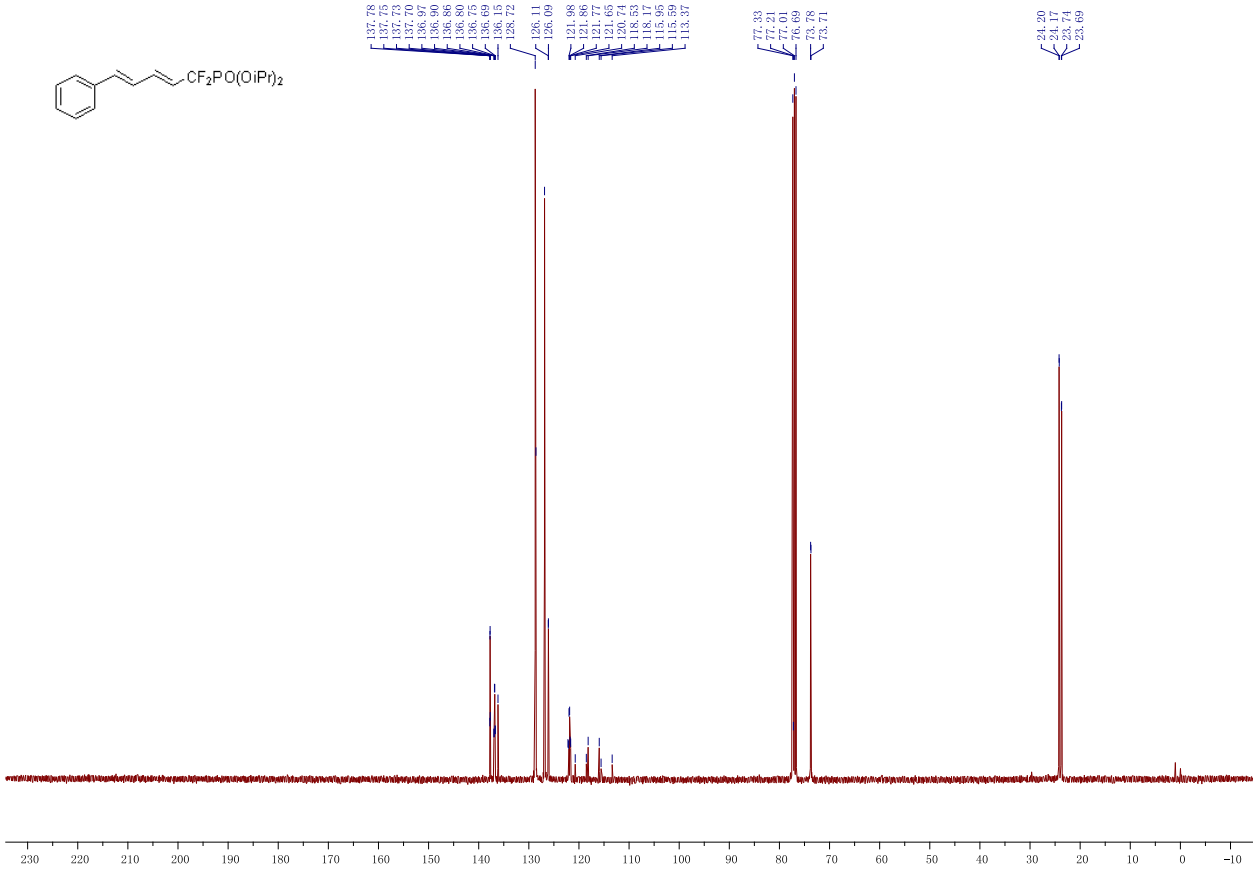

CF2PO(OiPr)2
-111.922
-112.232
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200


CF2PO(OiPr)2
135.689
132.269
129.296
129.136
128.607
126.695
119.170
116.977
77.329
77.012
76.695
73.691
73.621
27.527
24.222
24.191
23.745
23.694
21.929
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

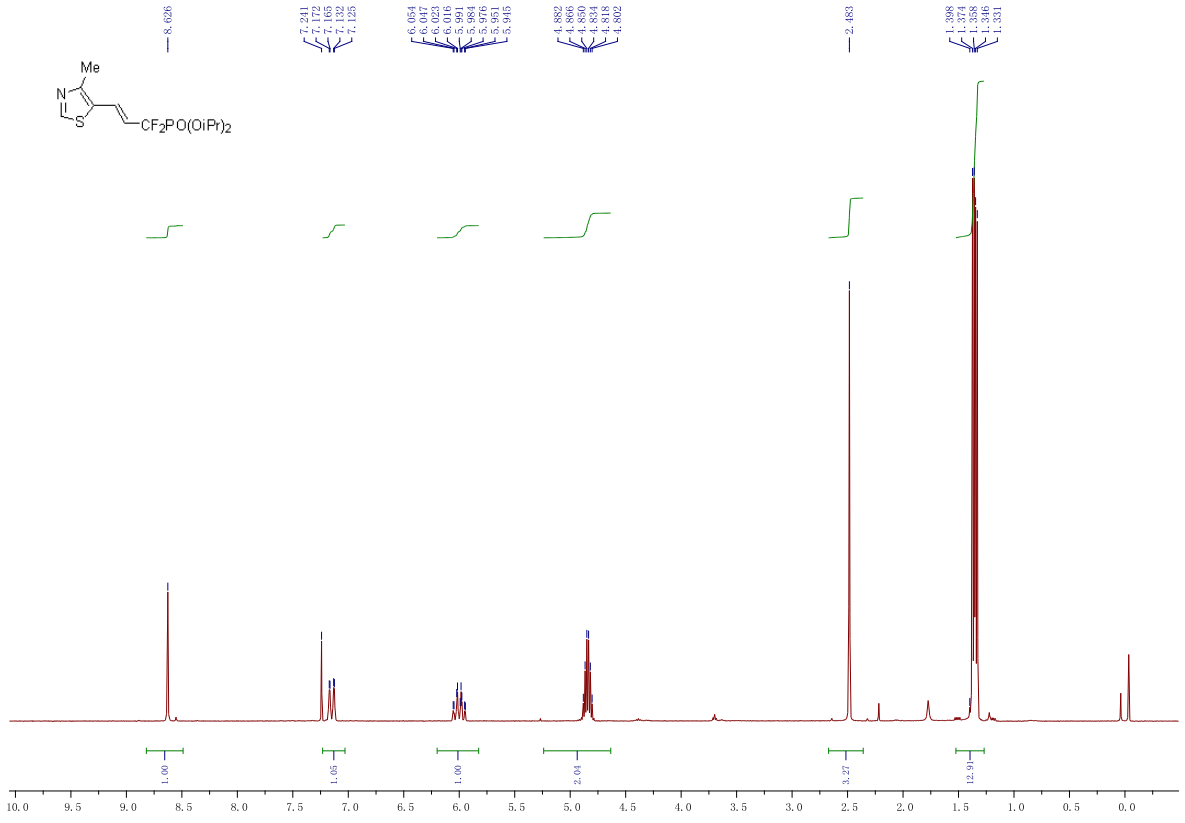
Diisopropyl ((2*E*,4*E*)-1,1-difluoro-5-phenylpenta-2,4-dien-1-yl)phosphonate (3m).

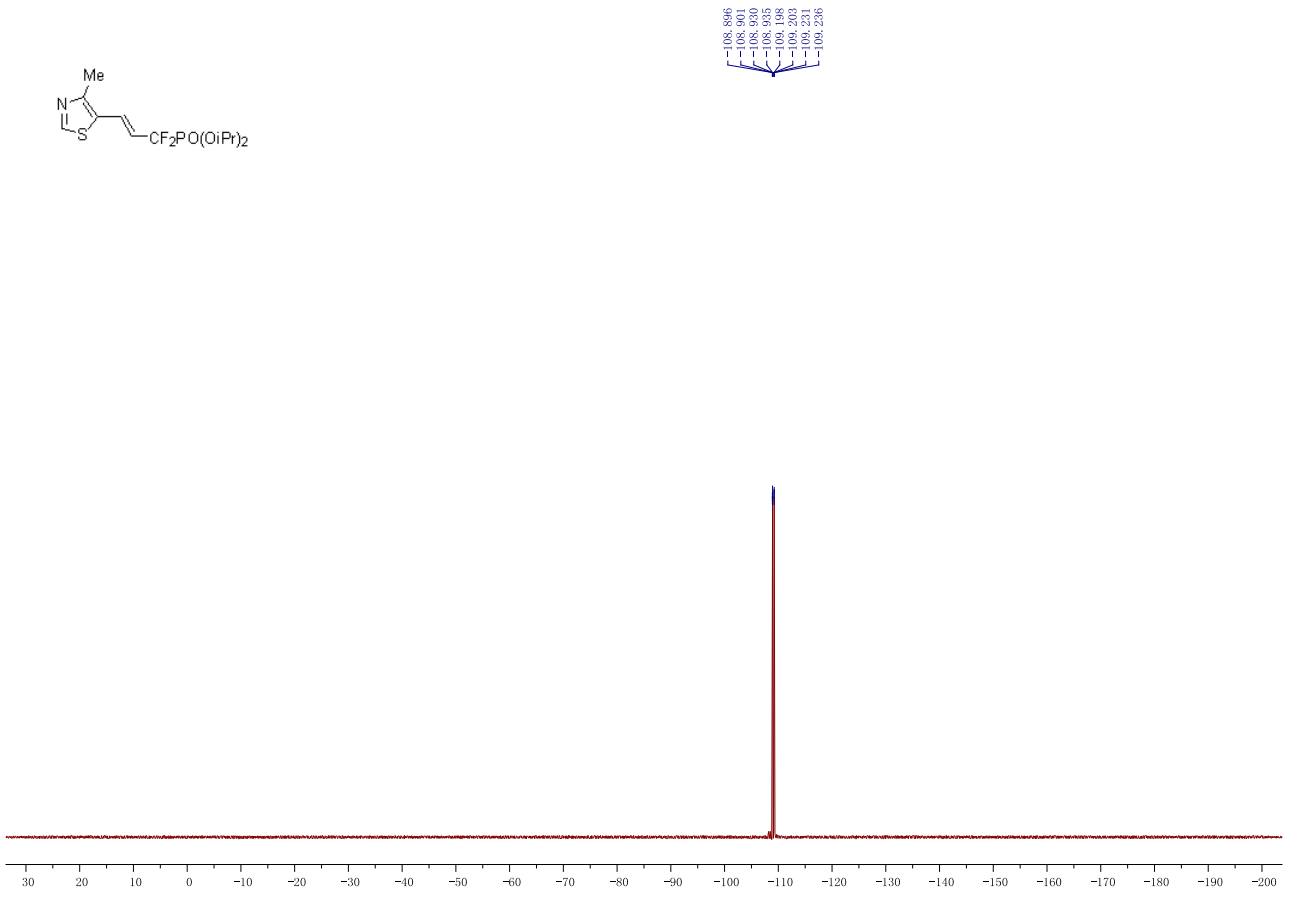


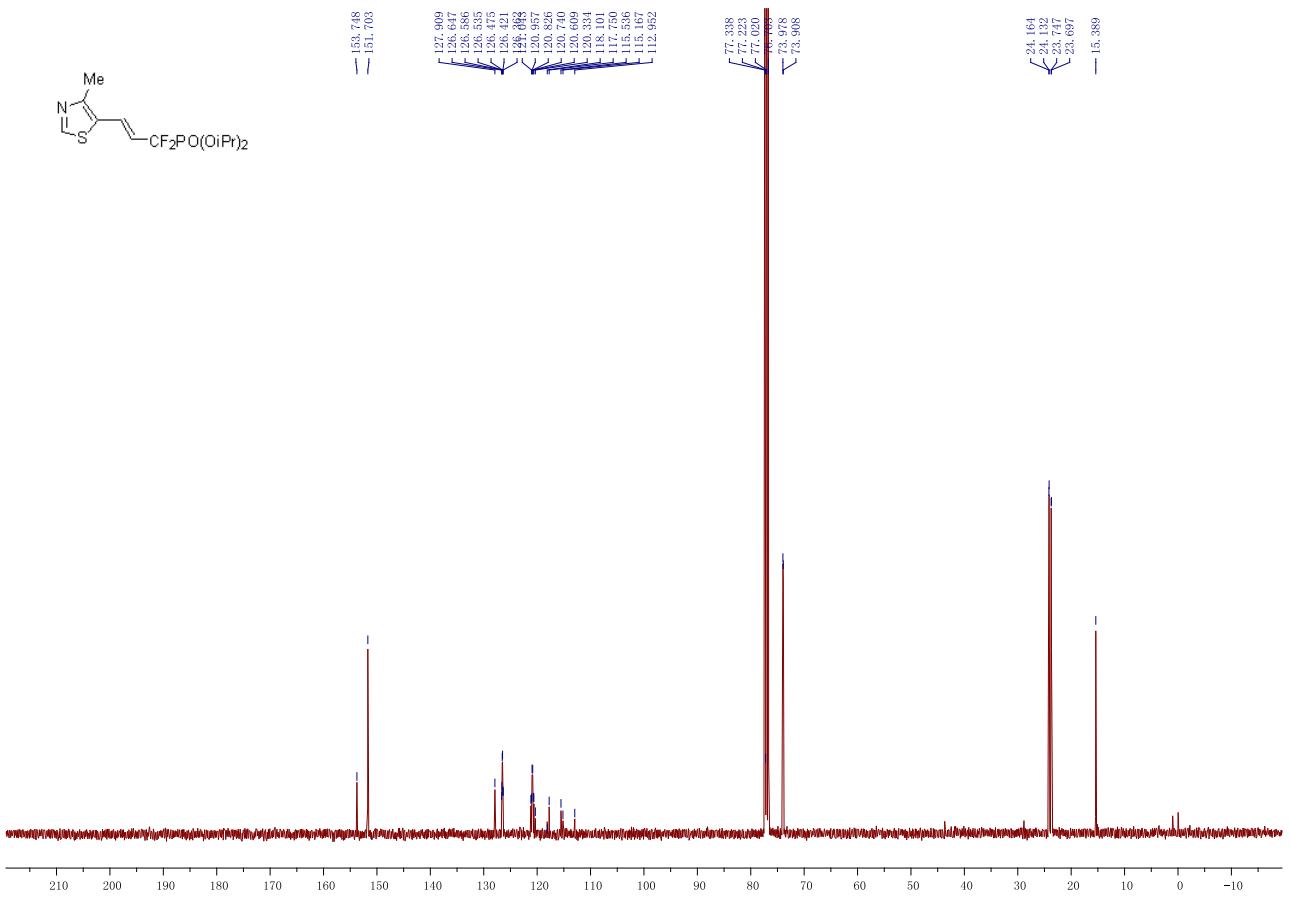




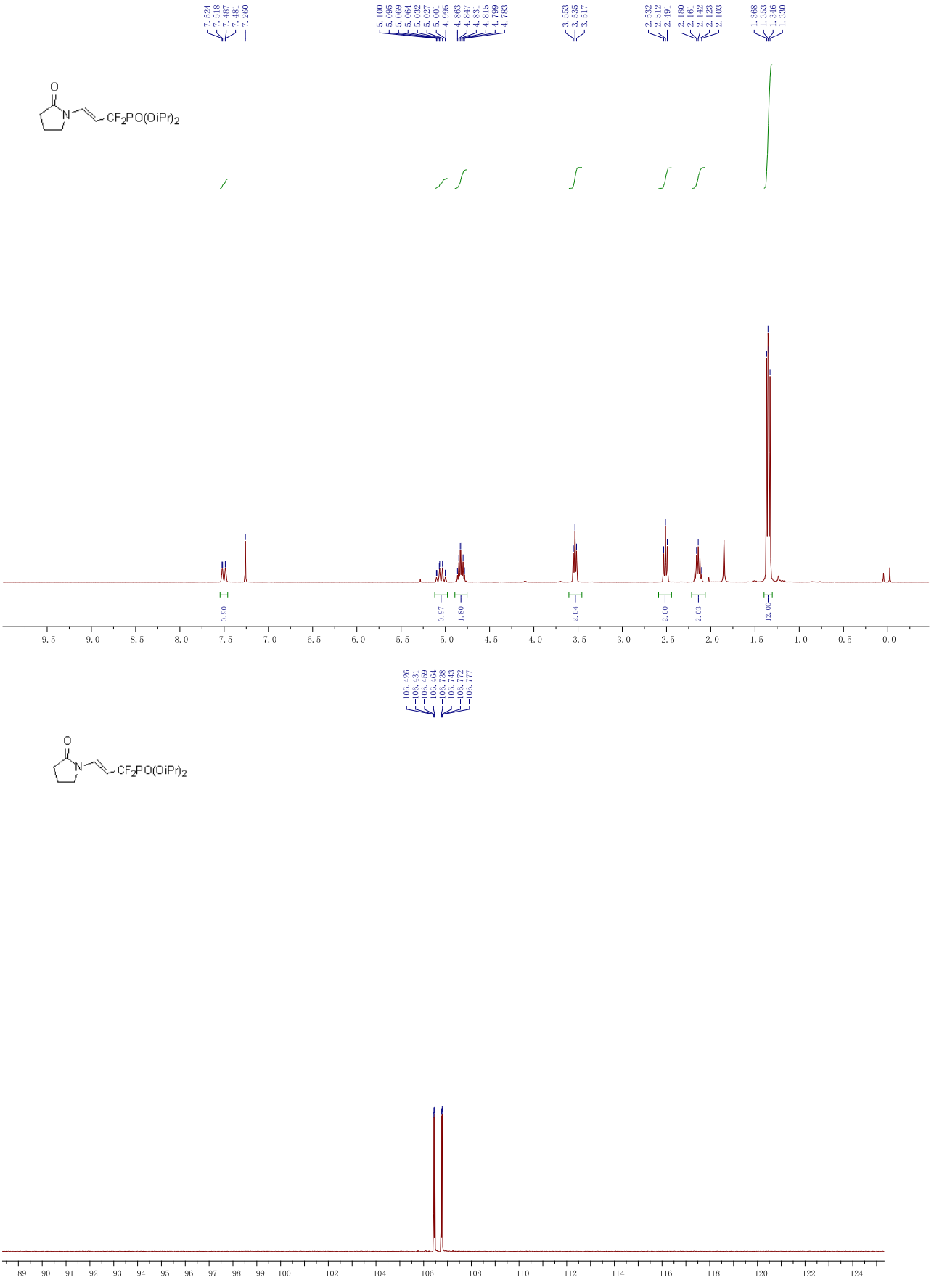
(*E*)-Diisopropyl (1,1-difluoro-3-(4-methylthiazol-5-yl)allyl)phosphonate (3n).

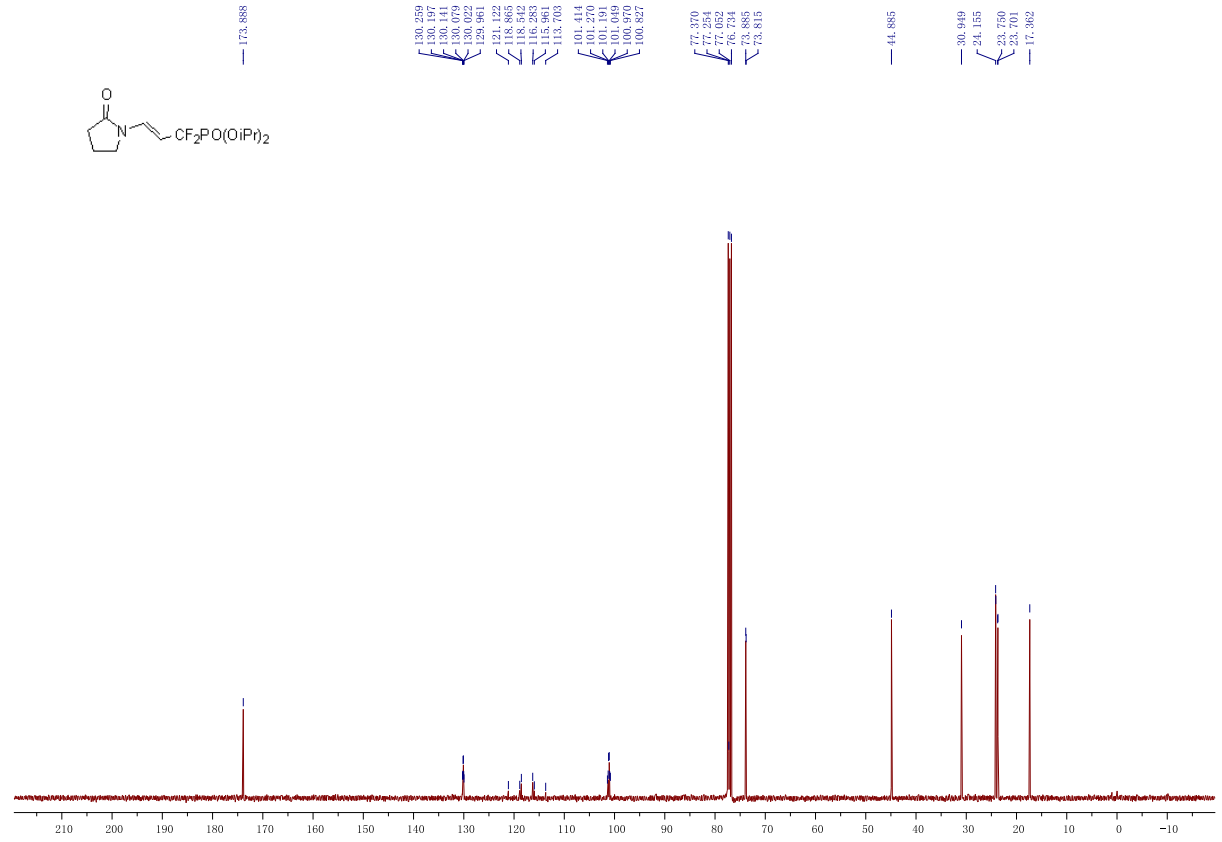



Me
N
S
CF2PO(OiPr)2
-108.896
-108.901
-108.930
-108.935
-109.198
-109.203
-109.231
-109.236
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

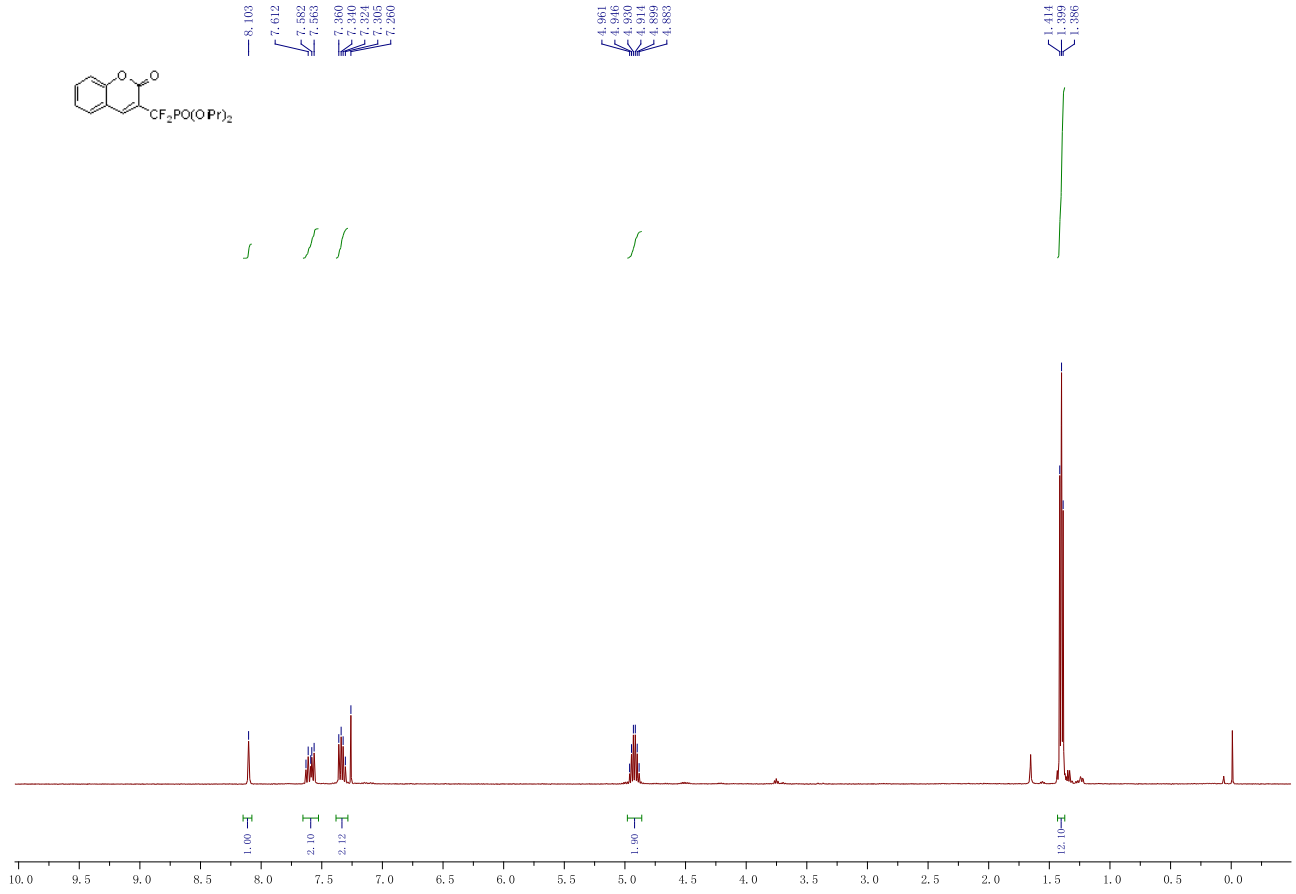

Me
N
S
CF2PO(OiPr)2
153.748
151.703
127.909
126.647
126.586
126.535
126.475
126.421
121.957
120.826
120.740
120.609
120.334
118.101
117.750
115.536
115.167
112.962
77.338
77.223
77.020
73.978
73.908
24.164
24.132
23.747
23.697
15.389
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

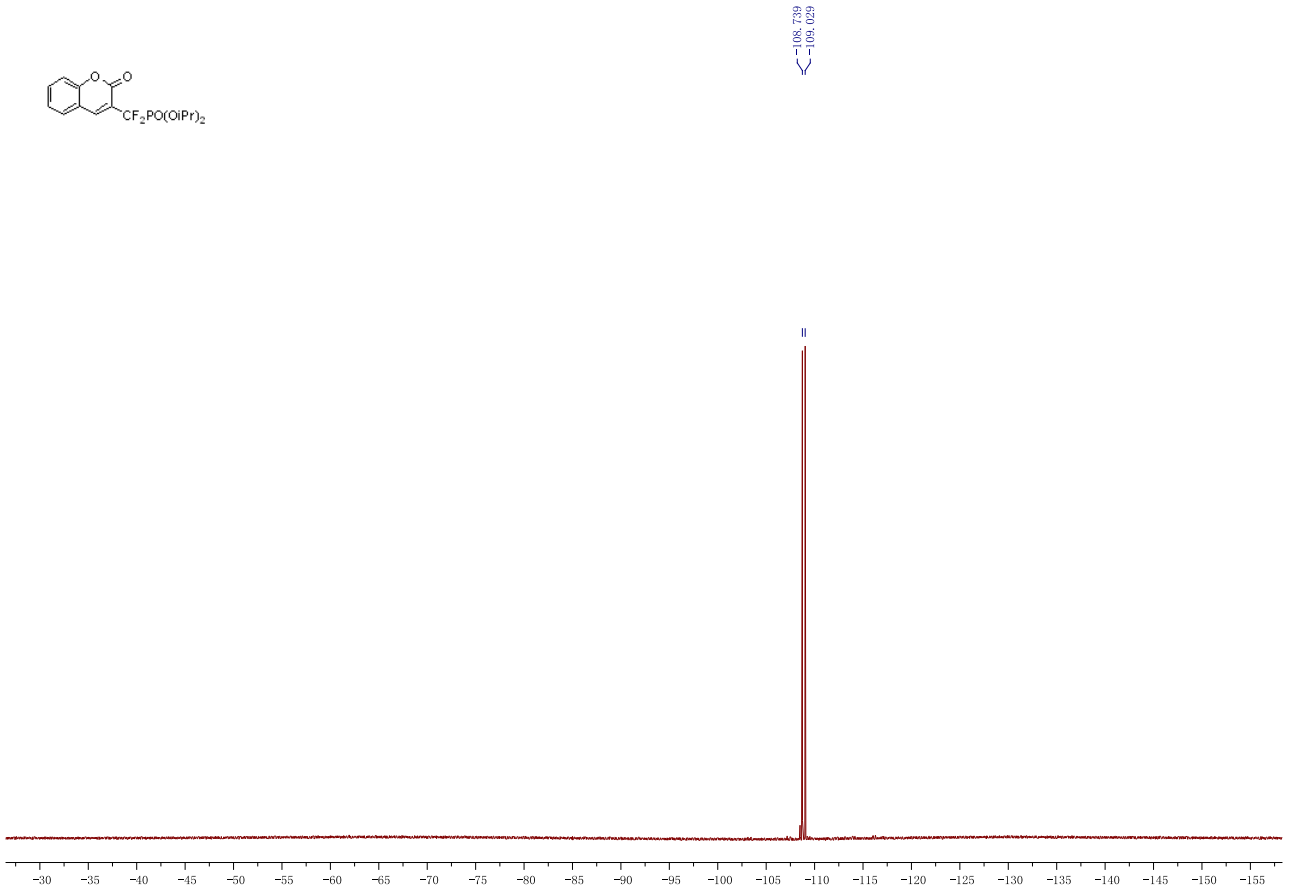
(*E*)-Diisopropyl (1,1-difluoro-3-(2-oxopyrrolidin-1-yl)allyl)phosphonate (3o).

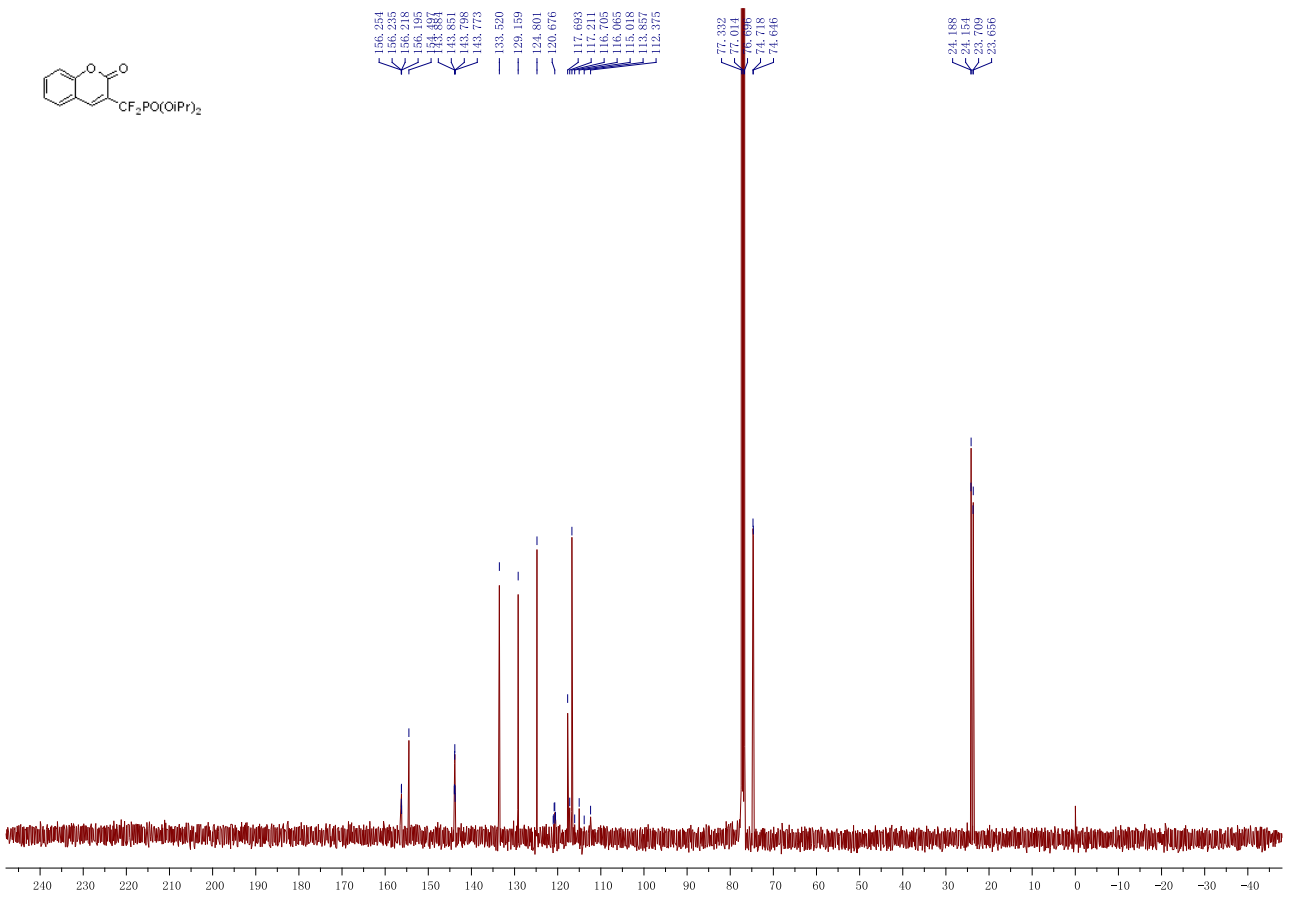




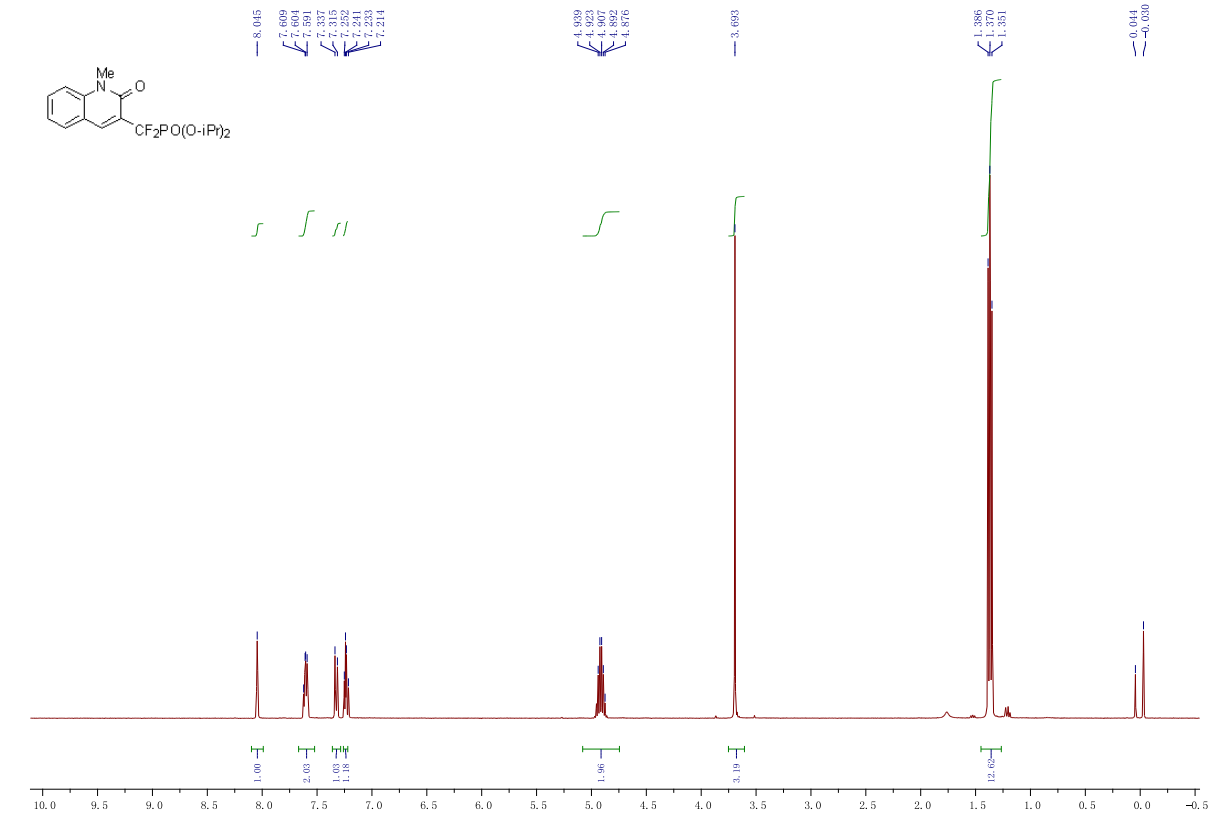
Diisopropyl (difluoro(2-oxo-2H-chromen-3-yl)methyl)phosphonate (3p).

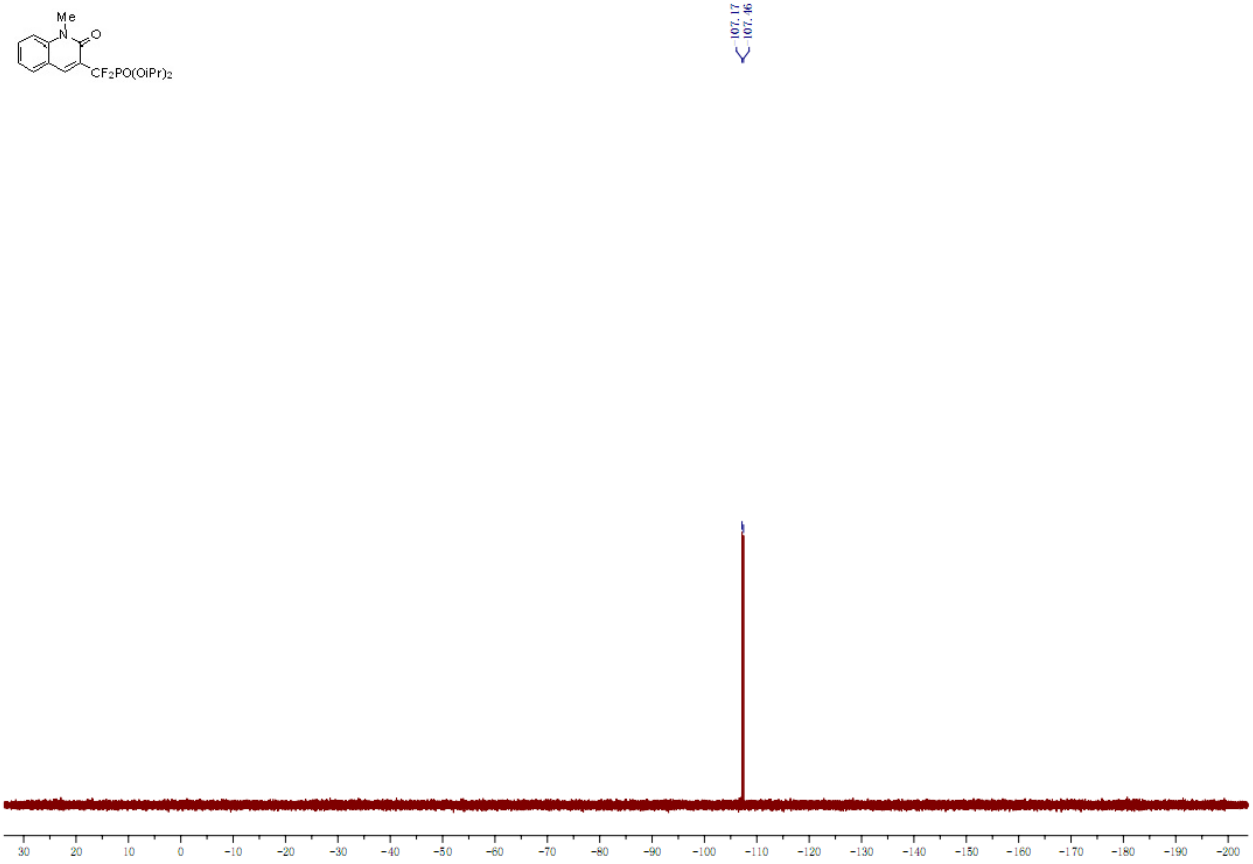


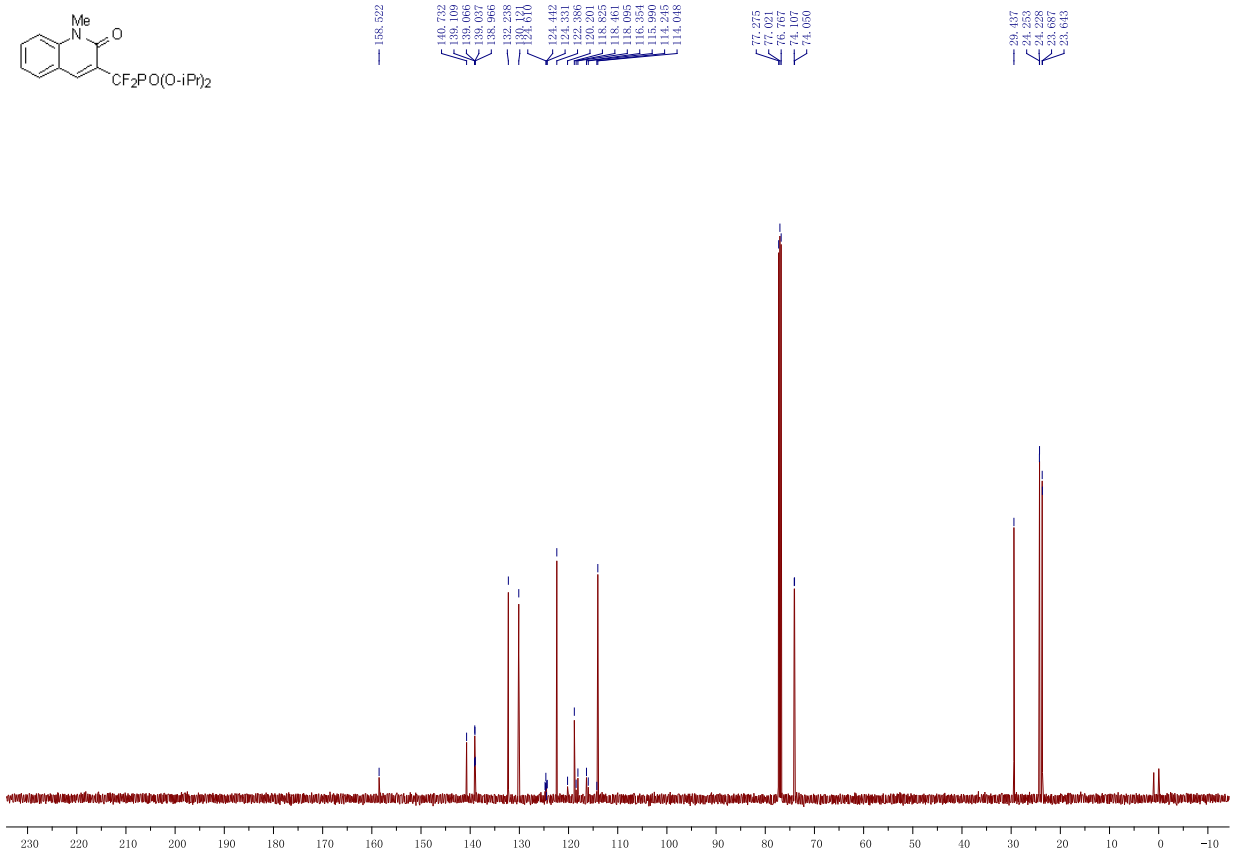

-108.739
-109.029
CF2PO(OiPr)2


156.254
156.235
156.218
156.195
133.520
129.159
124.801
120.676
117.693
117.211
116.705
116.065
115.018
113.857
112.375
77.332
77.014
76.696
74.718
74.696
24.188
24.154
23.709
23.656
CF2PO(OiPr)2

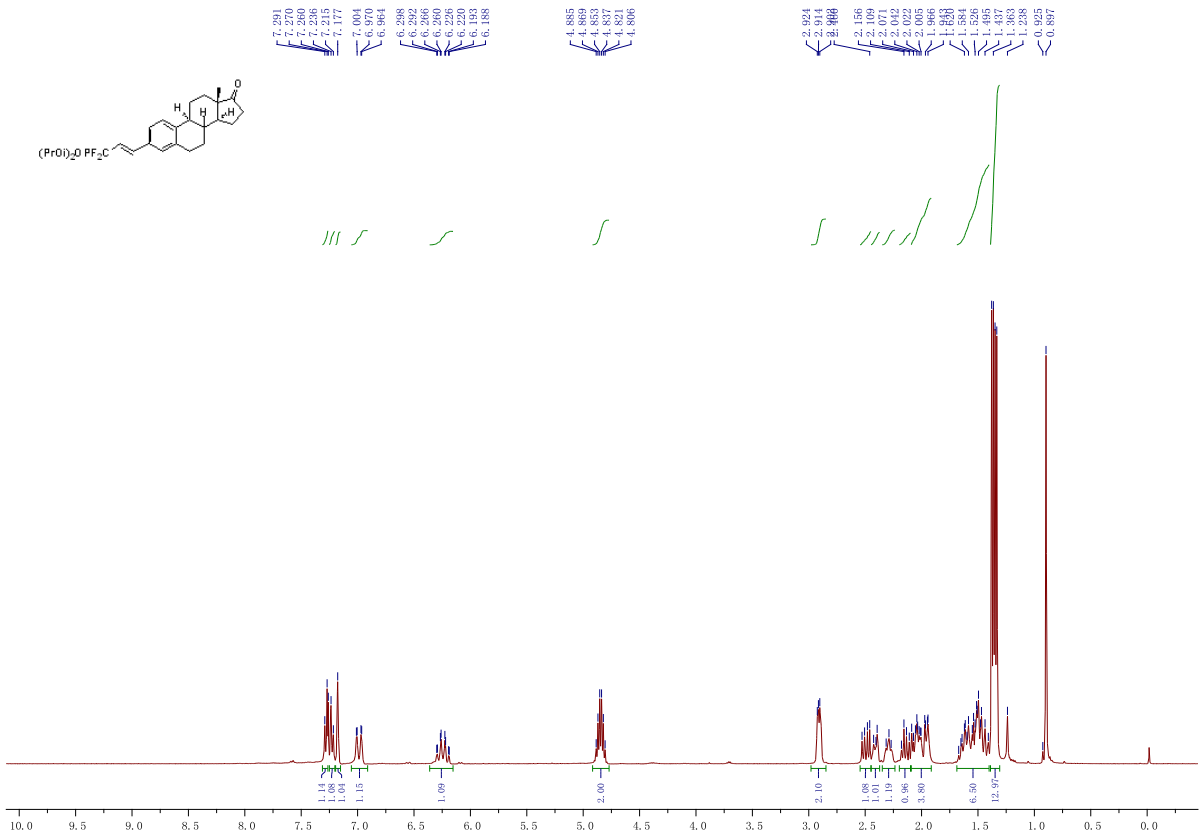
Diisopropyl(difluoro(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)methyl)phosphonate (3q).

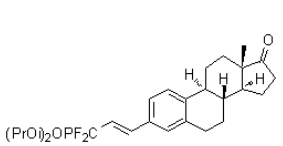


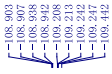


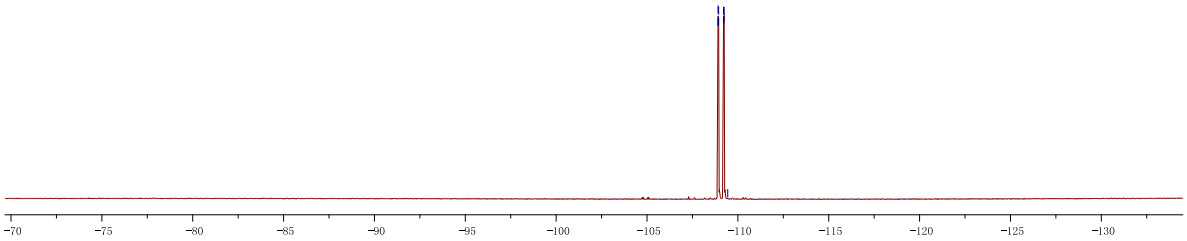


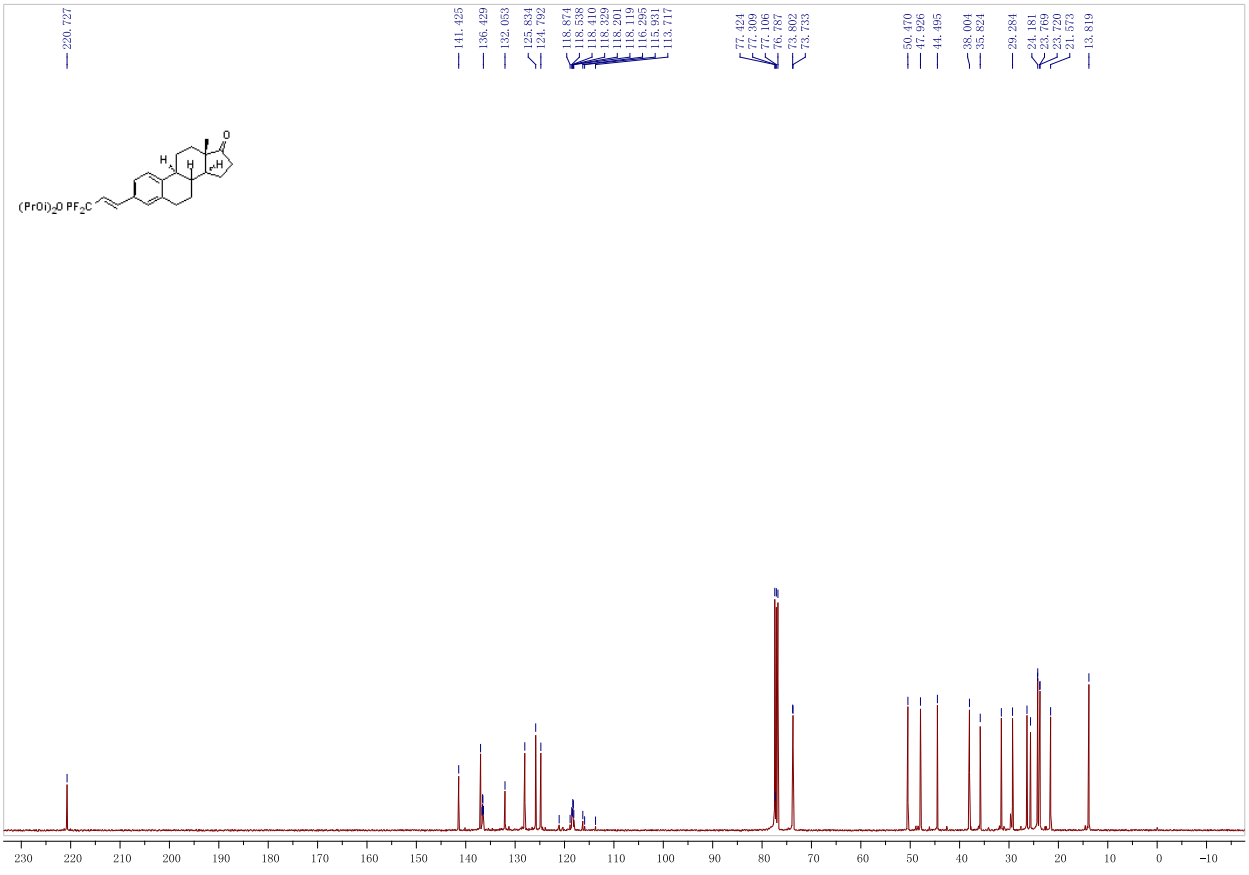
Diisopropyl((*E*)-1,1-difluoro-3-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)allyl)phosphonate (5).



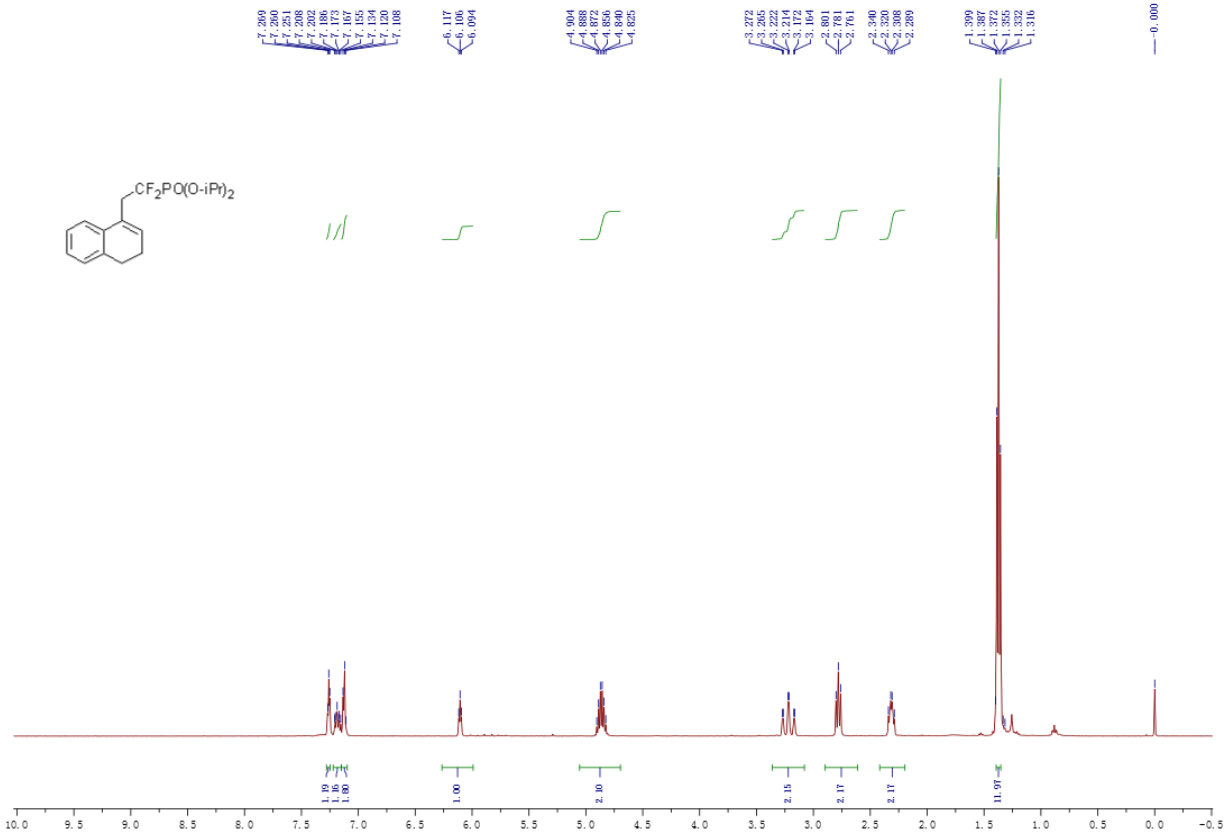

O
H
H
H
(PrOi)2OPF2C

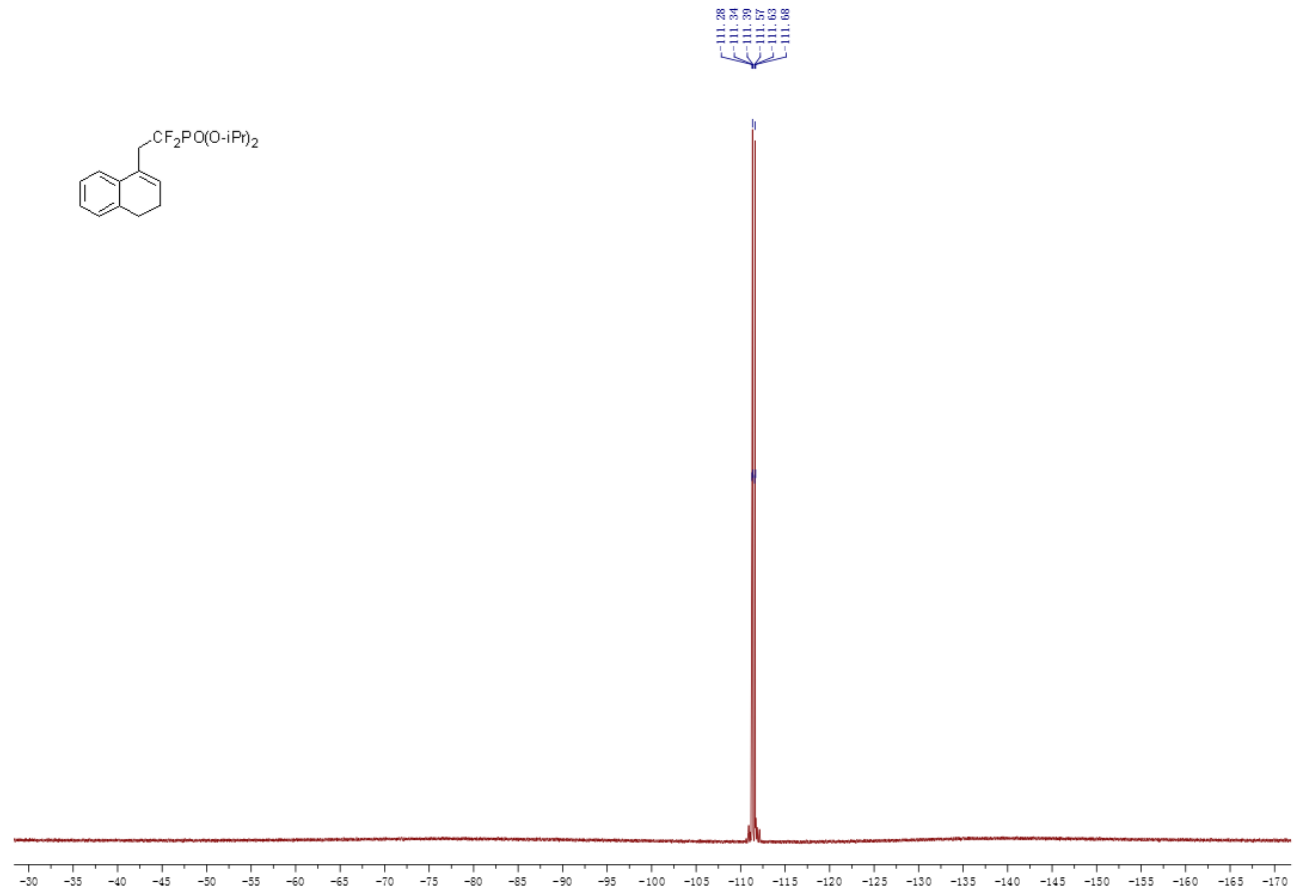

108.903
108.907
108.938
108.942
109.208
109.213
109.242
109.247
109.442

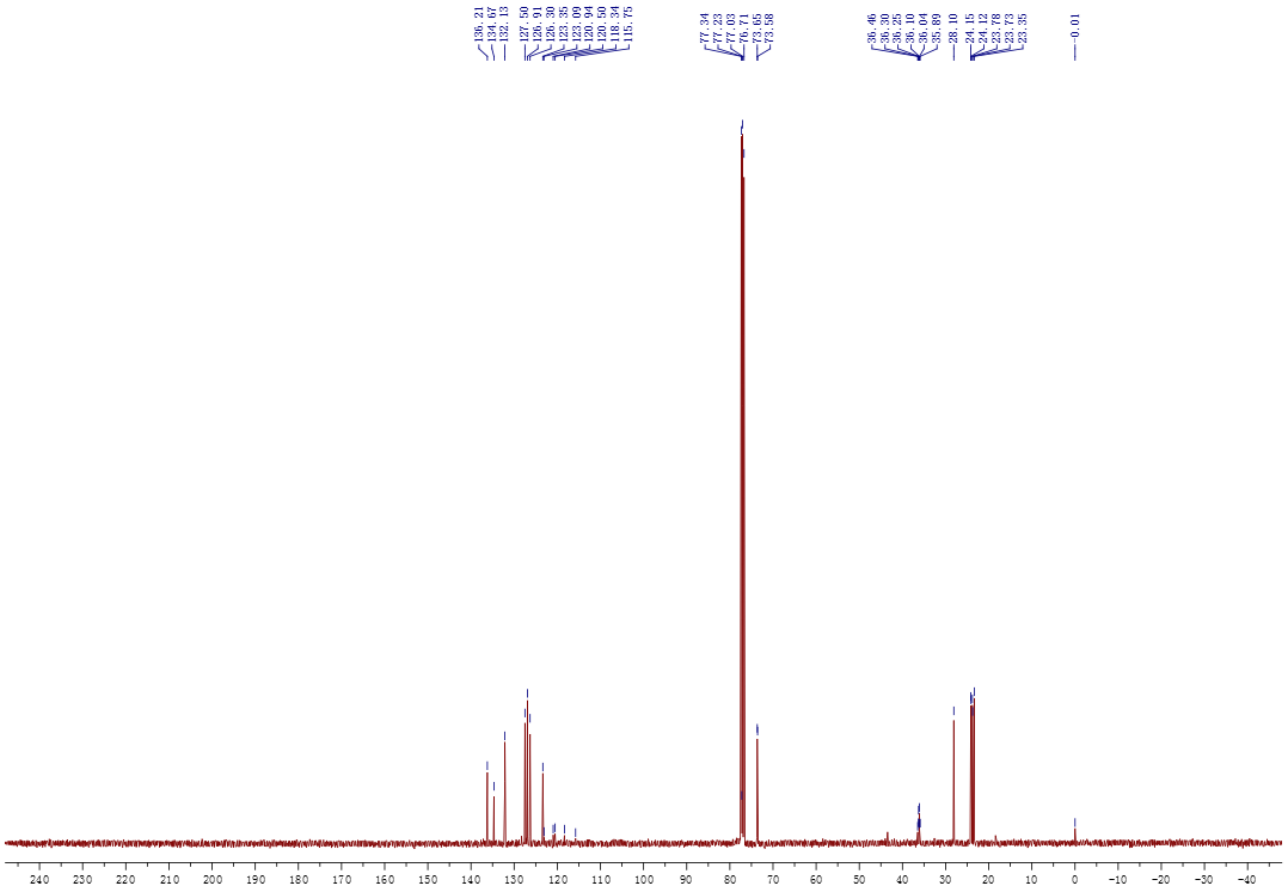

−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130


220.727
141.425
136.429
132.053
125.834
124.792
118.874
118.538
118.410
118.329
118.201
118.119
116.295
115.931
113.717
77.424
77.309
77.106
76.787
73.802
73.733
50.470
47.926
44.495
38.004
35.824
29.284
24.181
23.769
23.720
21.573
13.819
O
H
H
H
(PrOi)2O PF2C
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

Diisopropyl (2-(3,4-dihydronaphthalen-1-yl)-1,1-difluoroethyl)phosphonate (7).






136.21
134.67
132.13
127.50
126.91
126.30
125.35
123.09
120.94
120.50
118.34
115.75
77.34
77.23
77.03
76.71
73.65
73.58
36.46
36.39
36.25
36.10
36.04
35.89
28.10
24.15
24.12
23.78
23.73
23.35
0.01
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40