Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective Lewis Base Catalyzed Phosphonyldifluoromethylation of Allylic Fluorides Using C-silyl Latent Pronucleophile

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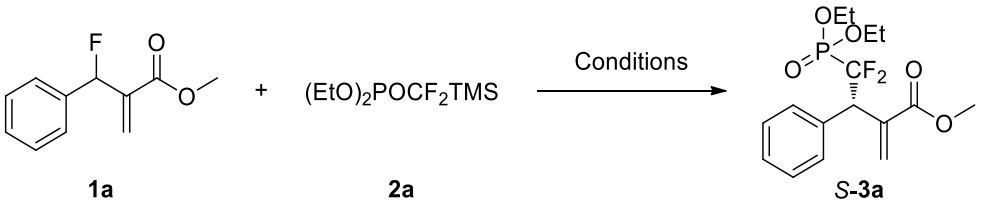
General Remarks

All the chemicals that are not mentioned in the subsequent parts were purchased from Merck, Alfa Aesar, Acros Organics, Fluorochem or TCI and used without further purification. The solvents if needed were dried according to standard conditions. For column chromatography and TLC (SiO_2, 60M, pore size 0.04 – 0.063 mm), products of Machery-Nagel were used. The TLC-glass-plates DURASIL consisted of a 0.25 mm layer of silica 60 with Fluorescence indicator UV254. TLCs were checked under UV-light (254 nm or 365 nm) and stained with an aq. $KMnO_4$-solution, PMA-stain, DNP or PAA. Reaction monitoring by GC-MS was performed using HP 6890, capillary column DB5-MS and Agilent 5973 MSD. The default method was 70 °C (2 min), ramp 20 °C/min to 270 °C, hold 10 min. Injector temperature 250 °C, Aux temperature 275 °C. The preparative TLC-glass-plates DURASIL consisted of a 1.0 mm layer of silica 60 with Fluorescence indicator UV254. All ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were measured with a BRUKER 250 (^{13}C), BRUKER Fourier 300 (^{1}H, ^{13}C) or an BRUKER Avance 400 spectrometer (^{1}H, ^{13}C, ^{19}F, ^{31}P). The chemical shift of each signal was registered in ppm. For 1H and 13C measurements, the chemical shift refers to TMS, showing a signal at 0 ppm. As an internal standard, the remaining protons or respectively the carbons of the corresponding deuterated solvent were used ($CDCl_3$, 7.26 ppm (1H-NMR), 77.16 ppm (^{13}C-NMR)). The chemical shift of the fluorine NMR was determined indirectly. For carbon spectra, a broadband decoupling was performed. Enantiomeric excess was determined by HPLC analysis on Phenomenex Lux Cellulose-1 columns. High-resolution mass spectra (HRMS) were measured with EI or ESI ionisation by the MS plattform. A chromatographic purification was performed before each measurement. The Thermo Q-Exactive plus device for ESI-mass spectra was coupled to a binary UHPLC system. For EI-measurement, a GC-system was coupled to the Thermo Q-Exactive GC device. All the IRs were measured using the Shimadzu IR-Affinity-1 (FTIR) device.

Screening results of Substitution of Allylic Fluorides

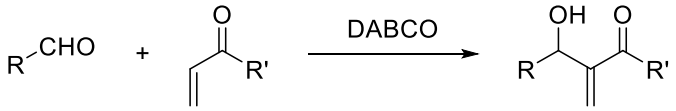


1a **2a** ***S*-3a**

Entry	Catalyst (10 mol%)	Solvent	Ratio	Concentration	Tem. (°C)	t [h]	Yield (%)[a]	er[b]
1	$(DHQD)_2AQN$	$PhCF_3$	1:1.3	0.2M	rt	60	18	94:6
2	$(DHQD)_2PHAL$	$PhCF_3$	1:1.3	0.2M	rt	60	37	94:6
3	$(DHQD)_2PYR$	$PhCF_3$	1:1.3	0.2M	rt	60	30	92:8
4	$(DHQD)_2PHAL$	DCE	1:1.3	0.2M	rt	60	12	93:7
5	$(DHQD)_2PHAL$	DME	1:1.3	0.2M	rt	60	42	94:6
6	$(DHQD)_2PHAL$	THF	1:1.3	0.2M	rt	60	41	94:6
7	$(DHQD)_2PHAL$	CycloHexane	1:1.3	0.2M	rt	60	31	91:9
8	$(DHQD)_2PHAL$	Toluene	1:1.3	0.2M	rt	60	**7**	91:9
9	$(DHQD)_2PHAL$	Dioxane	1:1.3	0.2M	rt	60	40	93:7
10	$(DHQD)_2PHAL$	DME	1:1.3	0.2M	0	40	31	96:4
16	$(DHQD)_2PHAL$	THF	1:1	0.2M	0	60	36	95:5
11	$(DHQD)_2PHAL$	Dioxane:DME (5:1)	1:1.3	0.2M	0	40	32	97:3
12	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:1.3	0.2M	0	40	35	96:4
13	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:1.3	0.5M	0	40	45	95:5
14	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:1	0.5M	0	40	44	95:5
15	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:1	0.2M	0	51	47[c]	98:2
16	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:2	0.2M	0	88	45	96:4
17	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:3	0.2M	0	88	43	95:5
18	$(DHQD)_2PHAL$	Dioxane:THF (5:1)	1:4	0.2M	0	88	38	96:4

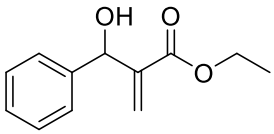
[a] Yield based on NMR with Ph_3CH as the internal standard.
[b] Determined by HPLC analysis using a chiral column.
[c] Isolated yield

Synthesis of Morita Baylis Hillman Alcohols



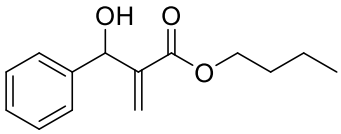
The alcohols were already prepared as following: Aldehyde (1 equiv.) was treated with DABCO (0.5 equiv.) in methyl acrylate (2 equiv.) and stirred at ambient temperature till judged completed by TLC. The crude mixtures were directly subjected to column chromatography (silica) using EA and PE as solvent system to give the corresponding alcohols, which matched the known analytical data.[1]

ethyl 2-(hydroxy(phenyl)methyl)acrylate



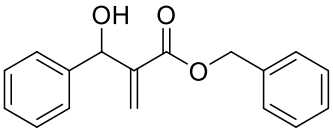
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 5H), 6.35 (d, *J* = 1.0 Hz, 1H), 5.82 (d, *J* = 1.3 Hz, 1H), 5.57 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.06 (s, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.35, 142.14, 141.31, 128.40, 127.79, 126.56, 125.95, 73.39, 60.96, 14.04.

butyl 2-(hydroxy(phenyl)methyl)acrylate



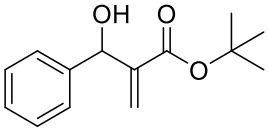
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 5H), 6.35 (t, *J* = 1.0 Hz, 1H), 5.83 (t, *J* = 1.2 Hz, 1H), 5.57 (s, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.06 (s, 1H), 1.68 – 1.53 (m, 2H), 1.41 – 1.24 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.41, 142.12, 141.31, 128.41, 127.79, 126.55, 125.96, 73.40, 64.81, 30.49, 19.09, 13.66.

benzyl 2-(hydroxy(phenyl)methyl)acrylate



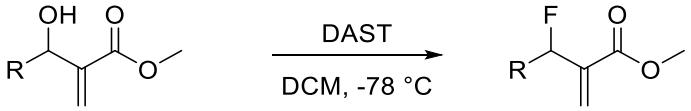
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 8H), 7.29 – 7.24 (m, 2H), 6.42 (t, *J* = 0.9 Hz, 1H), 5.89 (d, *J* = 1.2 Hz, 1H), 5.60 (s, 1H), 5.16 (s, 2H), 3.01 (s, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 166.08, 141.94, 141.21, 135.48, 128.56, 128.47, 128.29, 128.07, 127.88, 126.65, 126.46, 73.28, 66.66.

tert-butyl 2-(hydroxy(phenyl)methyl)acrylate



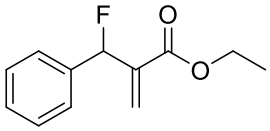
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 6.27 (dd, *J* = 1.3, 0.7 Hz, 1H), 5.73 (t, *J* = 1.3 Hz, 1H), 5.51 (s, 1H), 3.14 (s, 1H), 1.41 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 165.67, 143.36, 141.57, 128.33, 127.65, 126.51, 125.36, 81.67, 73.56, 27.94.

Synthesis of Morita Baylis Hillman Fluorides



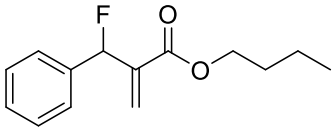
DAST (1.1 or 1.2 equiv.) was added to DCM at -78 °C. To this, a precooled solution of MBH adduct (1 equiv) in DCM was added slowly. The mixture was stirred for 30 minutes and then quenched with sat. $NaHCO_3$ solution. The mixture was extracted twice with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using either EA in PE or Ether in PE.[1]

ethyl 2-(fluoro(phenyl)methyl)acrylate



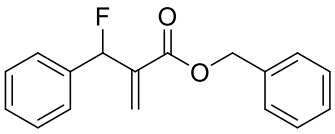
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.31 (m, 5H) 6.47 (dt, *J* = 2.8, 1.0 Hz, 1H), 6.30 (dt, *J* = 46.0, 1.2 Hz, 1H), 6.03 (t, *J* = 1.3 Hz, 1H), 4.18 (qd, *J* = 7.1, 4.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 164.73 (d, $J_{C\text{-}F}$ = 6.4 Hz), 139.60 (d, $J_{C\text{-}F}$ = 22.5 Hz), 137.46 (d, $J_{C\text{-}F}$ = 20.4 Hz), 128.92 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.46 , 127.14 (d, $J_{C\text{-}F}$ = 5.6 Hz), 125.62 (d, $J_{C\text{-}F}$ = 8.9 Hz), 90.85 (d, $J_{C\text{-}F}$ = 173.7 Hz), 60.97 , 14.01. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -170.97 (d, $J_{H\text{-}F}$ = 47.5 Hz).

butyl 2-(fluoro(phenyl)methyl)acrylate



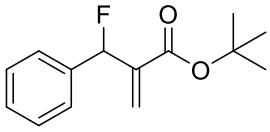
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 5H), 6.47 (dt, *J* = 2.9, 1.1 Hz, 1H), 6.29 (dt, $J_{H\text{-}F}$ = 46.2, 1.3 Hz, 1H), 6.03 (t, *J* = 1.3 Hz, 1H), 4.23 – 3.99 (m, 2H), 1.70 – 1.49 (m, 3H), 1.41 – 1.18 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 164.80 (d, $J_{C\text{-}F}$ = 6.5 Hz), 139.55 (d, $J_{C\text{-}F}$ = 22.5 Hz), 137.43 (d, $J_{C\text{-}F}$ = 20.2 Hz), 128.94 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.47 , 127.17 (d, $J_{C\text{-}F}$ = 5.5 Hz), 125.68 (d, $J_{C\text{-}F}$ = 8.9 Hz), 90.88 (d, $J_{C\text{-}F}$ = 173.7 Hz), 64.83 , 30.46 , 19.04 , 13.64 . **^{19}F-NMR** (377 MHz, $CDCl_3$) -170.52 (d, $J_{H\text{-}F}$ = 48.6 Hz). **HRMS** [EI]: m/z calculated for $C_{14}H_{17}FO_2$ $[M]^+$ 236.1213, found 236.1209. **IR** (ATR): ν = 2958, 1716, 1631, 1454, 1261, 1145, 999, 848, 759 cm^{-1}

benzyl 2-(fluoro(phenyl)methyl)acrylate



^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 8H), 7.27 – 7.20 (m, 2H), 6.53 (dt, *J* = 2.9, 1.0 Hz, 1H), 6.31 (dt, *J* = 46.0, 1.3 Hz, 1H), 6.07 (t, *J* = 1.2 Hz, 1H), 5.16 (q, *J* = 12.4 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 164.54 (d, $J_{C\text{-}F}$ = 6.3 Hz), 139.30 (d, $J_{C\text{-}F}$ = 22.8 Hz), 137.28 (d, $J_{C\text{-}F}$ = 20.2 Hz), 135.40 , 128.53 , 128.51 , 128.28 , 128.07 , 127.23 (d, $J_{C\text{-}F}$ = 5.6 Hz), 126.29 (d, $J_{C\text{-}F}$ = 8.9 Hz), 90.83 (d, $J_{C\text{-}F}$ = 174.2 Hz), 66.71 . **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -170.64 (d, $J_{H\text{-}F}$ = 48.7 Hz). **HRMS** [EI]: m/z calculated for $C_{17}H_{15}FO_2$ $[M]^+$ 270.1056, found 270.1051. **IR** (ATR): ν = 2951, 1724, 1647, 1454, 1269, 1161, 975, 952 cm^{-1}

tert-butyl 2-(fluoro(phenyl)methyl)acrylate



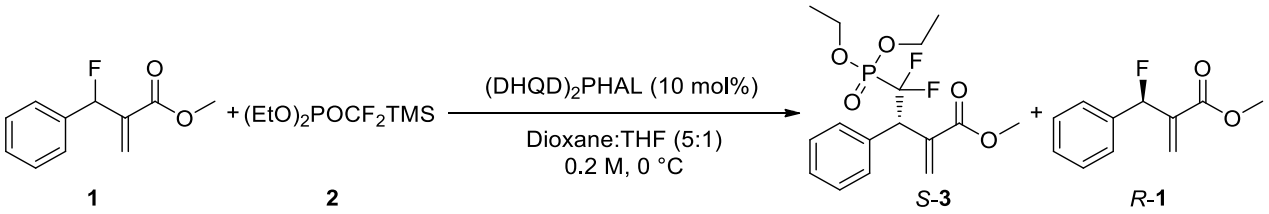
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 6.39 (dt, *J* = 3.2, 1.2 Hz, 1H), 6.23 (dt, *J* = 46.5, 1.4 Hz, 1H), 5.96 (t, *J* = 1.4 Hz, 1H), 1.38 (s, 9H). **^{13}C-NMR** (75

MHz, $CDCl_3$) δ 163.93 (d, J_{C-F} = 6.4 Hz), 140.81 (d, J_{C-F} = 21.8 Hz), 137.67 (d, J_{C-F} = 20.1 Hz), 128.86 (d, J_{C-F} = 2.8 Hz), 128.41 , 127.26 (d, J_{C-F} = 5.4 Hz), 124.84 , 91.09 (d, J_{C-F} = 173.7 Hz), 81.58 , 27.89 .**^{19}F-NMR** (377 MHz, $CDCl_3$) δ -169.88 (d, J_{H-F} = 47.2 Hz).

Synthesis of silylated phasphonate

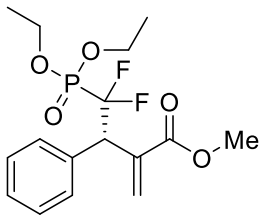
Under nitrogen enviroment a 2.5M solution of n-BuLi in hexane at 0 °C added dropwise to a stirring solution of Diisopropylamine (1 equiv.) in THF. The reaction mixture was sitrred at at 0 °C for additional 30min. Now the solution was cooled to -78 °C and alkanephosphaonate (1 equiv.) was added dropwise to reaction mixture. Stirring continiue at -78 °C for 15 min and a solution of TMS-Cl (1 equiv.) was added and reaction mixture as stirred for additional 20min. A solution of hydrochloric acid (2M) was added to reaction mixture and make it to slightly acidic Ph. The aqueous phase was extracted with diethyl ether. The combined organic layer was dired over Na_2SO_4 and solvents were removed in vacuo and the desired product was obtained by column chromatography with ethyl acetate in petroleum ether.[2]

Substitution of Allylic Fluorides

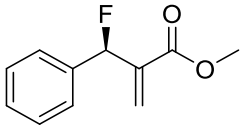


To a dried flask equipped with a stirring bar was added $(DHQD)_2PHAL$ (10 mol%) and then the flask was evaporated and refilled with N_2 for 3 times. The solution (dioxane:THF=5:1) of fluoride **1** was added followed by the addition of $(EtO)_2P(O)CF_2TMS$ (**2**) after which the reaction was stirred at 0 °C. The reaction was monitored by HPLC and after finishing, triphenylmethane was added as the internal standard to confirm the conversion of fluoride by ^{1}H-NMR and then the solvent was removed and the product was purified by preparative thin layer chromatography.

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3a)

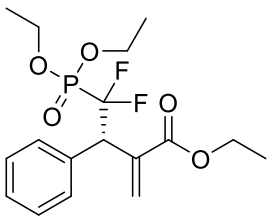


Yield: 47%, 98:2 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 22.18 min, t (minor) = 24.38 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.28 (m, 3H), 6.57 (s, 1H), 6.26 (s, 1H), 4.91 (ddd, *J* = 22.0, 16.3, 2.4 Hz, 1H), 4.26 – 4.09 (m, 2H), 4.06 – 3.83 (m, 2H), 3.72 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.46 , 135.69 (d, *J* = 6.1 Hz), 134.19 , 130.32 , 128.56 , 127.93 , 124.21 – 114.34 (m), 64.49 (d, *J* = 6.6 Hz), 64.06 (d, J = 7.0 Hz), 48.77 (td, *J* = 19.9, 16.6 Hz), 16.24 (d, *J* = 5.7 Hz), 16.10 (d, *J* = 5.8 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 6.18 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.68 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{21}F_2NaO_5P$ $[M+Na]^+$ 385.0992, found 385.1002. **IR** (ATR): ν = 2989, 2360, 1720, 1631, 1438, 1369, 1265, 1165, 1022, 979, 756 cm^{-1}.

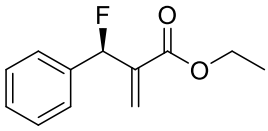


***R*-1a**, 44%, 99:1 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1 *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 9.44 min, t (minor) = 7.56].

ethyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3b)

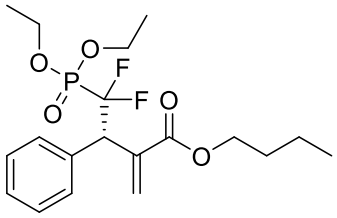


Yield: 40%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 15.35 min, t (minor) = 18.65 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.36 – 7.27 (m, 3H), 6.57 (s, 1H), 6.24 (s, 1H), 4.91 (ddd, *J* = 22.4, 15.8, 2.4 Hz, 1H), 4.26 – 4.09 (m, 4H), 4.07 – 3.83 (m, 2H), 1.29 (td, *J* = 7.0, 0.7 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.97, 135.87 (dd, *J* = 6.9, 4.3 Hz), 134.27 (dd, *J* = 6.2, 3.7 Hz), 130.37, 128.28, 128.25 – 128.16 (m), 127.90, 124.36 – 114.69 (m), 64.51 (d, *J* = 7.5 Hz), 64.06 (d, *J* = 7.6 Hz), 61.28, 48.77 (td, *J* = 20.2, 16.5 Hz), 16.26 (d, *J* = 6.0 Hz), 16.11 (d, *J* = 6.2 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.02 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.66 (m). **HRMS** [ESI]: m/z calculated for $C_{17}H_{23}F_2NaO_5P$ $[M+Na]^+$ 399.1149, found 399.1138. **IR** (ATR): ν = 2985, 2330, 1716, 1631, 1454, 1369, 1253, 1165, 1138, 1022, 979, 794 cm^{-1}.

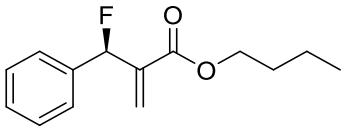


***R*-1b**, 46%, 99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 8.13 min, t (minor) = 6.70 min].

butyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3c)

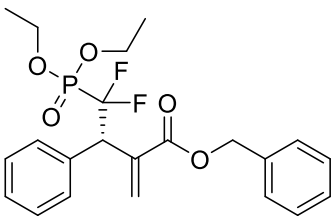


Yield: 43%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 13.12 min, t (minor) = 16.45 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.36 – 7.28 (m, 3H), 6.57 (s, 1H), 6.24 (s, 1H), 4.90 (ddd, *J* = 22.4, 15.7, 2.4 Hz, 1H), 4.25 – 3.97 (m, 5H), 3.95 – 3.84 (m, 1H), 1.64 – 1.58 (m, 2H), 1.36 –1.27 (m, 5H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.04, 135.88 (d, *J* = 7.2 Hz), 134.23 (dd, *J* = 6.4, 3.7 Hz), 130.37, 128.27, 128.20 (d, *J* = 2.7 Hz), 127.90, 122.24 – 115.63 (m), 65.17, 64.49 (d, *J* = 7.5 Hz), 64.05 (d, *J* = 7.4 Hz), 49.21 – 48.43 (m), 30.53, 16.26 (d, *J* = 6.0 Hz), 16.11 (d, *J* = 6.2 Hz), 13.67 . **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.04 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.62 (m). **HRMS** [ESI]: m/z calculated for $C_{19}H_{27}F_2NaO_5P$ $[M+Na]^+$ 427.1462, found 427.1469. **IR** (ATR): ν = 2962, 2364, 1716, 1631, 1454, 1269, 1165, 1026, 960, 765 cm^{-1}.

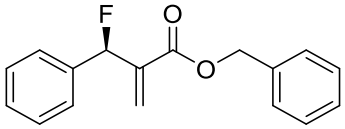


***R*-1c**, 35%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 7.29 min, t (minor) = 6.30 min].

benzyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3d)

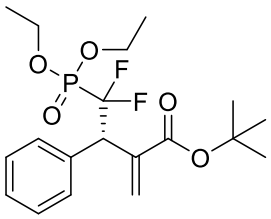


Yield: 39%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 21.26 min, t (minor) = 26.95 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.37 – 7.27 (m, 8H), 6.64 (s, 1H), 6.30 (s, 1H), 5.23 – 5.09 (m, 2H), 4.93 (ddd, *J* = 22.2, 15.9, 2.4 Hz, 1H), 4.25 – 4.09 (m, 2H), 4.07 – 3.98 (m, 1H), 3.95 – 3.83 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.81, 135.62, 134.10 (dd, *J* = 5.5, 3.5 Hz), 130.41, 128.91 – 128.77 (m), 128.49, 128.32, 128.23 – 127.91 (m), 125.24 – 114.28 (m), 67.04, 64.51 (d, *J* = 6.8 Hz), 64.07 (d, *J* = 7.0 Hz), 48.88 (td, *J* = 19.6, 16.6 Hz), 16.25 (d, *J* = 5.7 Hz), 16.10 (d, *J* = 5.8 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.00 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.59 (m). **HRMS** [ESI]: m/z calculated for $C_{22}H_{25}F_2NaO_5P$ $[M+Na]^+$ 461.1305, found 461.1310. **IR** (ATR): ν = 2985, 2360, 1716, 1627, 1454, 1269, 1165, 1026, 960, 794cm^{-1}.

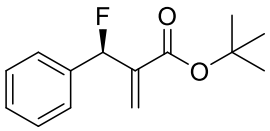


***R*-1d**, 27%, 92:8 *er*, determined by HPLC analysis [Phenomenex Amylose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 10.65 min, t (minor) = 9.54 min].

tert-butyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3e)

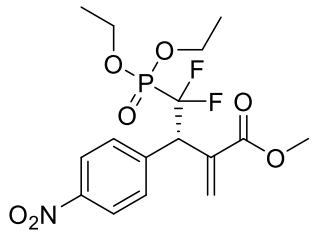


Yield: 34%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 15.11 min, t (minor) = 19.92 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.36 – 7.28 (m, 3H), 6.48 (s, 1H), 6.14 (s, 1H), 4.84 (ddd, *J* = 22.7, 15.5, 2.4 Hz, 1H), 4.29 – 4.11 (m, 2H), 4.06 – 3.83 (m, 2H), 1.40 (s, 9H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.11, 138.18 – 136.58 (m), 134.51, 130.41, 128.20, 127.79, 127.33 (t, *J* = 2.5 Hz), 124.21 – 117.54 (m), 81.36, 64.24 (dd, *J* = 47.7, 6.9 Hz), 48.85 (td, *J* = 19.6, 16.6 Hz), 27.89, 16.27 (d, *J* = 5.7 Hz), 16.11 (d, *J* = 5.9 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.09 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.89 (m). **HRMS** [ESI]: m/z calculated for $C_{19}H_{27}F_2NaO_5P$ $[M+Na]^+$ 427.1462, found 427.1465. **IR** (ATR): ν = 2981, 2360, 1716, 1631, 1454, 1369, 1257, 1153, 1026, 979, 744 cm^{-1}.



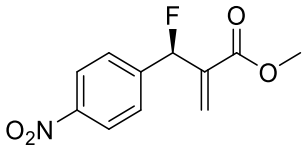
***R*-1e**, 51%, 82:18 *er*, determined by HPLC analysis [Phenomenex Lux Amylose -1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 6.23 min, t (minor) = 5.82 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-nitrophenyl)butanoate (*S*-3g)



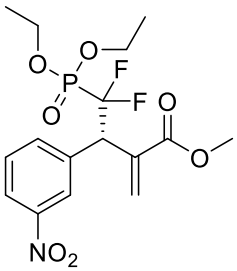
Yield: 55%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 220 nm, t (major) = 21.55 min, t (minor) = 16.46 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 2H), 7.64 – 7.56 (m, 2H), 6.64 (s, 1H), 6.30 (s, 1H), 5.01 (td, *J* = 18.5, 18.0,

2.3 Hz, 1H), 4.29 – 4.15 (m, 2H), 4.15 – 4.00 (m, 2H), 3.73 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.98 , 147.64, 141.70 (t, *J* = 4.2 Hz), 134.85 – 134.38 (m), 131.22, 129.62 (t, *J* = 2.6 Hz), 123.39, 121.90 – 116.67 (m), 64.86 (d, *J* = 6.9 Hz), 64.48 (d, *J* = 7.0 Hz), 52.55, 48.67 (td, *J* = 20.2, 16.6 Hz), 16.29 (d, *J* = 5.5 Hz), 16.16 (d, *J* = 5.6 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.34 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.41 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}F_2NNaO_7P$ $[M+Na]^+$ 430.0843, found 430.0845. **IR** (ATR): ν = 2989, 2360, 1716, 1604, 1523, 1438, 1350, 1253, 1165, 1014, 975, 829 cm^{-1}.

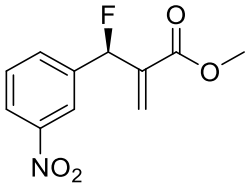


***R*-1g**, 38%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 98/2, 0.7 mL/min, λ = 220 nm, t (major) = 19.04 min, t (minor) = 21.94 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(3-nitrophenyl)butanoate (*S*-3h)

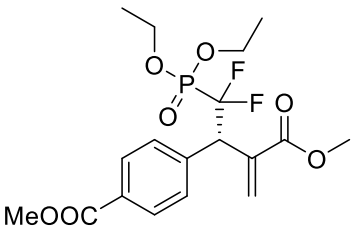


Yield: 46%, 90:10 *er*, determined by HPLC analysis [Phenomenex Cellulose-1, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 220 nm, t (major) = 23.31 min, t (minor) = 16.27 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.31 – 8.24 (m, 1H), 8.18 (ddd, *J* = 8.3, 2.3, 1.1 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 6.67 (s, 1H), 6.34 (s, 1H), 5.14 – 4.91 (m, 1H), 4.30 – 4.15 (m, 2H), 4.15 – 4.01 (m, 2H), 3.73 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.99, 148.18, 136.66, 136.56 – 136.26 (m), 134.56 (d, J = 4.7 Hz), 129.71 (t, *J* = 2.6 Hz), 129.23, 125.01, 123.07, 119.74 (dd, *J* = 267.4, 53.6 Hz), 64.84 (d, *J* = 6.9 Hz), 64.49 (d, *J* = 7.0 Hz), 52.57, 48.52 (td, *J* = 20.3, 16.5 Hz), 16.28 (d, *J* = 5.8 Hz), 16.17 (d, *J* = 5.5 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.39 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.50 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}F_2NNaO_7P$ $[M+Na]^+$ 430.0843, found 430.0845. **IR** (ATR): ν = 2989, 2360, 1720, 1631, 1531, 1442, 1350, 1273, 1165, 1029, 979, 802 cm^{-1}.



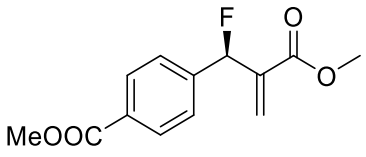
***R*-1h**, 46%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 27.04 min, t (minor) = 18.09 min].

methyl (S)-4-(1-(diethoxyphosphoryl)-1,1-difluoro-3-(methoxycarbonyl)but-3-en-2-yl)benzoate (*S*-3i)



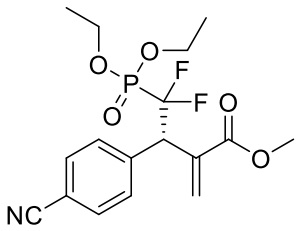
Yield: 42%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 220 nm, t (major) = 19.24 min, t (minor) = 14.66 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 6.60 (s, 1H), 6.27 (s, 1H), 4.96 (td, *J* = 18.8, 2.4 Hz, 1H), 4.27 – 4.11 (m, 2H), 4.10 – 3.93 (m, 2H), 3.91 (s, 3H), 3.72 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.72, 166.23, 139.43 (q, *J* = 3.9 Hz), 135.08 (dd, *J* = 5.7,

2.9 Hz), 130.33, 129.76, 129.53, 129.16, 120.02 (td, *J* = 267.3, 213.9 Hz), 64.68 (d, *J* = 6.8 Hz), 64.26 (d, *J* = 7.1 Hz), 52.42, 52.14, 48.74 (td, *J* = 20.0, 16.7 Hz), 16.27 (d, *J* = 5.6 Hz), 16.14 (d, *J* = 5.7 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.67 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.20 (m). **HRMS** [ESI]: m/z calculated for $C_{18}H_{23}F_2NaO_7P$ $[M+Na]^+$ 443.1047, found 443.1039. **IR** (ATR): ν = 2989, 2360, 1720, 1612, 1438, 1273, 1165, 1107, 1018, 964, 767 cm^{-1}.

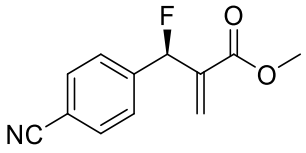


***R*-1i**, 47%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 21.48 min, t (minor) = 24.88 min].

methyl (S)-3-(4-cyanophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3j)

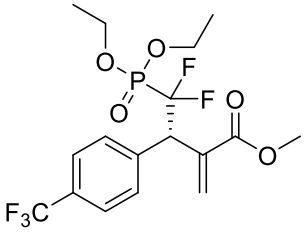


Yield: 54%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 90/10, 0.7 mL/min, λ = 220 nm, t (major) = 21.73 min, t (minor) = 20.20 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.58 – 7.51 (m, 2H), 6.62 (s, 1H), 6.28 (s, 1H), 4.94 (td, *J* = 18.6, 2.4 Hz, 1H), 4.28 – 4.13 (m, 2H), 4.13 – 3.98 (m, 2H), 3.72 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.01, 139.98 – 139.46 (m), 134.64 (dd, *J* = 5.3, 2.2 Hz), 132.02, 131.07, 129.44 (t, *J* = 2.6 Hz), 119.81 (td, J = 267.5, 213.9 Hz), 118.48, 111.97, 64.82 (d, *J* = 6.7 Hz), 64.41 (d, *J* = 7.1 Hz), 52.52, 48.87 (td, *J* = 20.2, 16.7 Hz), 16.28 (d, *J* = 5.6 Hz), 16.15 (d, *J* = 5.6 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.38 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.26 (m). **HRMS** [ESI]: m/z calculated for C17H20F2NNaO5P $[M+Na]^+$ 410.0945, found 410.0950. **IR** (ATR): ν = 2985, 2360, 1716, 1631, 1504, 1438, 1269, 1165, 1014, 975, 798 cm^{-1}.



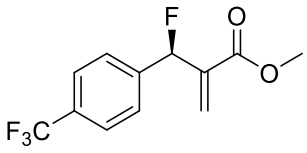
***R*-1j**, 29%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 98/2, 0.7 mL/min, λ = 220 nm, t (major) = 19.39 min, t (minor) = 21.14 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-(trifluoromethyl)phenyl)butanoate (*S*-3k)



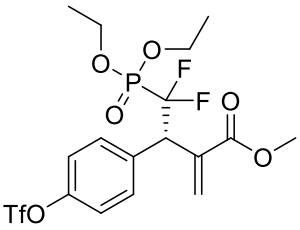
Yield: 49%, 93:7 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 18.50 min, t (minor) = 12.01 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.57 (q, *J* = 8.4 Hz, 4H), 6.62 (s, 1H), 6.29 (s, 1H), 5.08 – 4.85 (m, 1H), 4.27 – 4.12 (m, 2H), 4.10 – 3.92 (m, 2H), 3.72 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.16 (d, *J* = 1.7 Hz), 138.33, 135.16 – 134.65 (m), 130.22 (d, *J* = 32.4 Hz), 129.95 – 128.64 (m), 125.34, 125.21 (q, *J* = 3.9 Hz), 122.95 – 114.36 (m), 64.75 (d, *J* = 7.1 Hz), 64.25 (d, *J* = 7.5 Hz), 52.47, 48.63 (td, *J* = 20.4, 16.3 Hz), 16.23 (d, *J* = 6.2 Hz), 16.03 (d, *J* = 6.5 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.56 (m). **^{19}F-NMR** (377 MHz,

$CDCl_3$) δ -62.73 (s), -110.20 (m). **HRMS** [ESI]: m/z calculated for $C_{17}H_{20}F_5NaO_5P$ $[M+Na]^+$ 453.0866, found 453.0871. **IR** (ATR): ν = 2989, 2360, 1716, 1620, 1442, 1327, 1253, 1165, 1114, 1018, 979, 806 cm^{-1}.

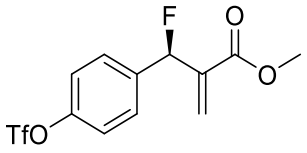


***R*-1k**, 42%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 12.80 min, t (minor) = 14.08 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-(((trifluoromethyl)sulfonyl)oxy) phenyl)butanoate (*S*-3l)

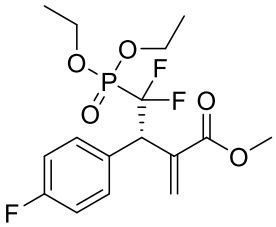


Yield: 38%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 18.45 min, t (minor) = 16.74 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.26 – 7.21 (m, 2H), 6.61 (s, 1H), 6.28 (s, 1H), 4.95 (ddd, *J* = 22.2, 15.1, 2.4 Hz, 1H), 4.27 – 4.12 (m, 2H), 4.09 – 3.88 (m, 2H), 3.73 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.11, 149.20, 135.03 (dd, *J* = 6.0, 3.6 Hz), 134.89 (q, *J* = 3.6 Hz), 132.27, 129.00, 121.21, 118.70 (q, *J* = 320.7 Hz), 64.81 (d, *J* = 6.6 Hz), 64.29 (d, *J* = 7.2 Hz), 52.48, 48.18 (td, *J* = 19.8, 16.8 Hz), 29.70, 16.26 (d, *J* = 5.4 Hz), 16.10 (d, *J* = 5.6 Hz).**^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.56 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -72.96 (s), -110.29 (m). **HRMS** [ESI]: m/z calculated for C17H20F5NaO8PS $[M+Na]^+$ 533.0434, found 533.0433. **IR** (ATR): ν = 2993, 2360, 1720, 1500, 1423, 1273, 1138, 1018, 979, 736 cm^{-1}.

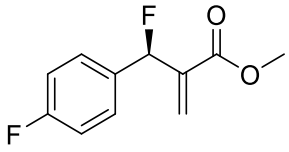


***R*-1l**, 43%, 99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 10.68 min, t (minor) = 11.87 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(4-fluorophenyl)-2-methylenebutanoate (*S*-3m)

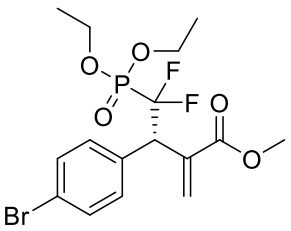


Yield: 42%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 20.26 min, t (minor) = 14.47 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.08 – 6.96 (m, 2H), 6.57 (s, 1H), 6.25 (s, 1H), 4.89 (ddd, *J* = 22.0, 15.7, 2.4 Hz, 1H), 4.28 – 4.12 (m, 2H), 4.11 – 3.89 (m, 2H), 3.72 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.34, 163.77, 161.32, 135.93 – 135.19 (m), 132.01 (d, *J* = 8.7 Hz), 130.06 – 129.76 (m), 128.53, 127.03 – 119.00 (m), 115.23 (d, *J* = 21.6 Hz), 64.41 (dd, *J* = 46.3, 7.3 Hz), 52.39, 48.08 (td, *J* = 20.3, 16.8 Hz), 16.29 (d, *J* = 6.1 Hz), 16.14 (d, *J* = 5.8 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.81 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.01 (m), -114.43 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}F_3NaO_5P$ $[M+Na]^+$ 403.0898, found 403.0891. **IR** (ATR): ν = 2985, 2364, 1716, 1508, 1438, 1269, 1165, 1026, 975, 798 cm^{-1}.

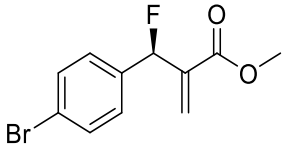


***R*-1m**, 46%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 14.96 min, t (minor) = 16.02 min].

methyl (S)-3-(4-bromophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3n)

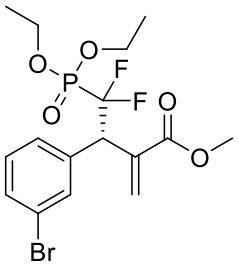


Yield: 49%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 20.91 min, t (minor) = 14.17 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 1.3 Hz, 1H), 6.24 (s, 1H), 4.94 – 4.76 (m, 1H), 4.28 – 4.11 (m, 2H), 4.11 – 3.93 (m, 2H), 3.72 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.25 (d, *J* = 1.8 Hz), 135.20 (dd, *J* = 6.1, 4.6 Hz), 133.22 (dd, *J* = 6.2, 4.1 Hz), 131.99, 131.46, 128.76 (t, *J* = 3.0 Hz), 122.25, 124.61 – 116.07 (m), 64.68 (d, *J* = 7.7 Hz), 64.24 (d, *J* = 7.5 Hz), 52.42, 48.30 (td, *J* = 20.2, 16.4 Hz), 16.27 (d, *J* = 6.2 Hz), 16.12 (d, *J* = 6.3 Hz).**^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.05 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}BrF_2NaO_5P$ $[M+Na]^+$ 463.0097, found 463.0102. **IR** (ATR): ν = 2993, 2360, 1712, 1631, 1489, 1361, 1269, 1165, 1010, 979, 794 cm^{-1}.

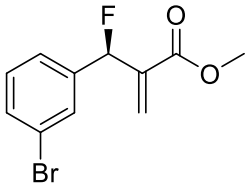


***R*-1n**, 44%, 99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 17.39 min, t (minor) = 22.47 min].

methyl (S)-3-(3-bromophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3o)

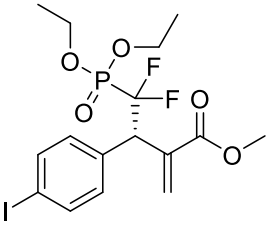


Yield: 42%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 25.09 min, t (minor) = 17.07 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.44 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.20 (t, *J* = 7.9 Hz, 1H), 6.60 (s, 1H), 6.25 (s, 1H), 4.87 (td, *J* = 19.3, 18.8, 2.4 Hz, 1H), 4.27 – 4.12 (m, 2H), 4.12 – 3.93 (m, 2H), 3.73 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) 166.22 , 136.50 (d, *J* = 2.3 Hz), 135.06 (dd, *J* = 5.4, 2.3 Hz), 133.09 , 131.10 , 129.82 , 129.11 (d, *J* = 1.9 Hz), 122.27 , 120.02 (td, *J* = 267.3, 213.8 Hz), 64.67 (d, *J* = 6.7 Hz), 64.23 (d, *J* = 7.0 Hz), 52.44 , 48.42 (td, *J* = 20.1, 16.7 Hz), 16.26 (d, *J* = 5.6 Hz), 16.13 (d, *J* = 5.8 Hz).**^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.70 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.06 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}BrF_2NaO_5P$ $[M+Na]^+$ 463.0097, found 463.0109. **IR** (ATR): ν = 2985, 2364, 1716, 1627, 1570, 1438, 1269, 1165, 1014, 979, 783 cm^{-1}.

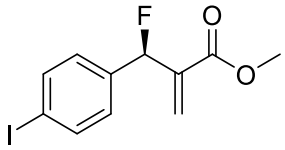


***R*-1o**, 25%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 16.23 min, t (minor) = 14.12 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(4-iodophenyl)-2-methylenebutanoate (*S*-3p)

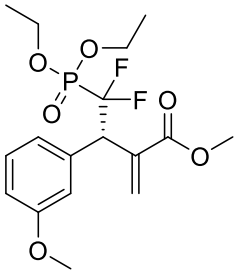


Yield: 44%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 21.62 min, t (minor) = 14.65 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.61 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.57 (s, 1H), 6.24 (s, 1H), 4.84 (ddd, *J* = 20.0, 17.1, 2.3 Hz, 1H), 4.27 – 4.11 (m, 2H), 4.11 – 3.92 (m, 2H), 3.72 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.24, 137.45, 135.45 – 135.01 (m), 134.38 – 133.36 (m), 132.23, 128.76 (t, *J* = 2.5 Hz), 120.03 (td, *J* = 267.4, 213.8 Hz), 93.93, 64.66 (d, *J* = 6.8 Hz), 64.24 (d, *J* = 7.1 Hz), 52.41, 48.43 (td, *J* = 19.9, 16.6 Hz), 16.27 (d, *J* = 5.6 Hz), 16.12 (d, *J* = 5.8 Hz).**^{19}F-NMR** (377 MHz, $CDCl_3$) δ -110.04 (m). **HRMS** [ESI]: m/z calculated for $C_{16}H_{20}F_2INaO_5P$ $[M+Na]^+$ 510.9959, found 510.9973. **IR** (ATR): ν = 2985, 2360, 1716, 1627, 1485, 1438, 1269, 1165, 1026, 979, 794, 748 cm^{-1}.

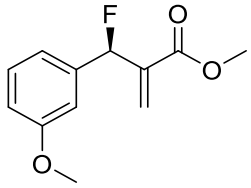


***R*-1p**, 26%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/*i*-PrOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 10.49 min, t (minor) = 11.57 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(3-methoxyphenyl)-2-methylenebutanoate (*S*-3q)

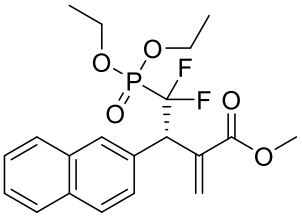


Yield: 44%, 96:4 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 25.16 min, t (minor) = 23.10 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 2.0 Hz, 1H), 6.84 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.57 (s, 1H), 6.25 (s, 1H), 4.88 (td, *J* = 19.0, 2.4 Hz, 1H), 4.28 – 4.11 (m, 2H), 4.11 – 3.89 (m, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.46 (d, *J* = 1.5 Hz), 159.41, 136.21 – 135.11 (m), 129.23, 128.79 (t, *J* = 2.7 Hz), 122.71, 125.01 – 116.38 (m), 116.11, 113.28, 64.54 (d, *J* = 7.4 Hz), 64.15 (d, *J* = 7.3 Hz), 55.23, 52.36, 48.64 (td, *J* = 20.1, 16.6 Hz), 16.27 (d, *J* = 6.6 Hz), 16.14 (d, *J* = 6.3 Hz). a**^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.02 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.87 (m). **HRMS** [ESI]: m/z calculated for $C_{17}H_{23}F_2NaO_6P$ $[M+Na]^+$ 415.1098, found 415.1094. **IR** (ATR): ν = 2985, 2333, 1716, 1600, 1438, 1265, 1165, 1026, 979, 779 cm^{-1}.

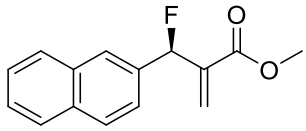


***R*-1q**, 40%, 99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99/1, 0.7 mL/min, λ = 220 nm, t (major) = 11.39 min, t (minor) = 10.31 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(naphthalen-2-yl)butanoate (*S*-3r)

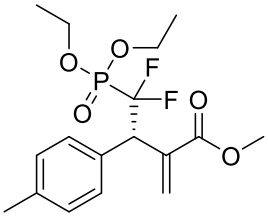


Yield: 45%, 94:6 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 25.07 min, t (minor) = 18.52 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.86 – 7.79 (m, 3H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.44 (m, 2H), 6.62 (s, 1H), 6.34 (s, 1H), 5.09 (ddd, *J* = 20.6, 17.3, 2.4 Hz, 1H), 4.26 – 4.10 (m, 2cH), 4.06 – 3.95 (m, 1H), 3.91 – 3.80 (m, 1H), 3.72 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.48, 135.54, 133.12, 132.87, 131.53 (d, *J* = 4.8 Hz), 129.75, 128.77 (t, *J* = 2.4 Hz), 128.05, 127.92, 127.70, 127.50, 126.26, 126.14, 124.64 – 115.00 (m), 64.59 (d, *J* = 6.6 Hz), 64.11 (d, *J* = 7.0 Hz), 52.38, 48.86 (td, *J* = 19.7, 16.5 Hz), 16.25 (d, *J* = 5.7 Hz), 16.01 (d, *J* = 5.8 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.04 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.74 (m). **HRMS** [ESI]: m/z calculated for $C_{20}H_{23}F_2NaO_5P$ $[M+Na]^+$ 435.1149, found 435.1141. **IR** (ATR): ν = 2947, 2360, 1739, 1365, 1215, 1029 cm^{-1}.

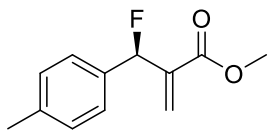


***R*-1r**, 43%, >99:1 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 22.00 min, t (minor) = 23.71 min].

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(p-tolyl)butanoate (*S*-3s)

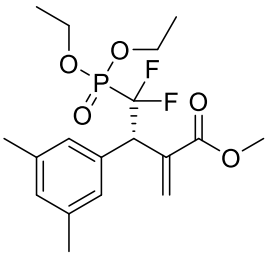


Yield: 40%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 19.10 min, t (minor) = 17.42 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.18 – 7.10 (m, 2H), 6.56 (s, 1H), 6.24 (s, 1H), 4.86 (ddd, *J* = 20.6, 17.4, 2.3 Hz, 1H), 4.29 – 4.09 (m, 2H), 4.09 – 3.85 (m, 2H), 3.72 (s, 3H), 2.33 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.52, 137.70, 136.00 – 135.46 (m), 131.07 (dd, *J* = 5.8, 3.5 Hz), 130.16, 129.04, 128.44 (t, *J* = 2.5 Hz), 120.38 (td, *J* = 267.1, 213.5 Hz), 64.47 (d, *J* = 6.7 Hz), 64.10 (d, *J* = 6.9 Hz), 52.30, 48.39 (td, *J* = 19.9, 16.7 Hz), 21.07, 16.26 (d, *J* = 5.7 Hz), 16.11 (d, *J* = 5.9 Hz). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.54 (m). **HRMS** [ESI]: m/z calculated for $C_{17}H_{23}F_2NaO_5P$ $[M+Na]^+$ 399.1149, found 399.1140. **IR** (ATR): ν = 2985, 2333, 1720, 1631, 1512, 1438, 1469, 1165, 1022, 975, 794 cm^{-1}.

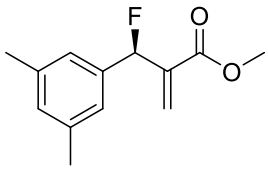


***R*-1s**, 45%, 95:5 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 14.02 min, t (minor) = 16.06 min].

methyl (S)-4-(diethoxyphosphoryl)-3-(3,5-dimethylphenyl)-4,4-difluoro-2-methylenebutanoate (*S*-3t)

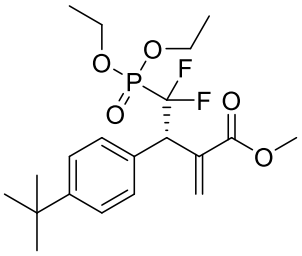


Yield: 41%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 17.93 min, t (minor) = 12.82 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.03 (s, 2H), 6.93 (s, 1H), 6.57 (s, 1H), 6.24 (s, 1H), 4.84 (td, *J* = 19.3, 2.4 Hz, 1H), 4.27 – 4.11 (m, 2H), 4.06 (dp, *J* = 10.1, 7.0 Hz, 1H), 3.92 (ddq, *J* = 10.1, 8.6, 7.1 Hz, 1H), 3.73 (s, 3H), 2.30 (s, 6H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.57, 137.71, 136.00 – 135.39 (m), 133.91, 129.62, 128.74 (t, *J* = 2.3 Hz), 128.02, 126.14 – 116.98 (m), 64.47 (d, *J* = 6.8 Hz), 64.06 (d, *J* = 6.8 Hz), 52.34, 48.49 (td, *J* = 19.8, 16.4 Hz), 21.31, 16.26 (d, *J* = 5.6 Hz), 16.12 (d, *J* = 5.8 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.21 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.52 (m). **HRMS** [ESI]: m/z calculated for $C_{18}H_{25}F_2NaO_5P$ $[M+Na]^+$ 413.1305, found 413.1304. **IR** (ATR): ν = 2985, 2360, 1720, 1604, 1438, 1369, 1269, 1165, 1026, 979, 798 cm^{-1}.

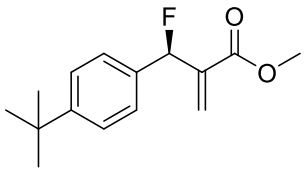


***R*-1t**, 48%, 97:3 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 11.48 min, t (minor) = 10.60 min].

methyl (S)-3-(4-(tert-butyl)phenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3u)

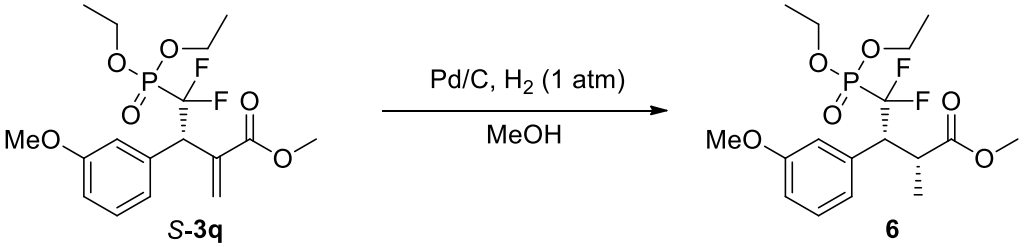


Yield: 30%, 96:4 *er*, determined by HPLC analysis [Phenomenex Cellulose-1, *n*-hexane/*i*-PrOH = 95/5, 0.7 mL/min, λ = 220 nm, t (major) = 15.56 min, t (minor) = 12.08 min]. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 6.56 (s, 1H), 6.26 (s, 1H), 4.89 (ddd, *J* = 23.3, 15.1, 2.4 Hz, 1H), 4.30 – 4.07 (m, 2H), 3.98 (dq, *J* = 9.8, 7.0 Hz, 1H), 3.89 – 3.78 (m, 1H), 3.73 (s, 3H), 1.32 – 1.25 (m, 12H), 1.15 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.57, 150.82, 135.82, 132.62, 131.03, 129.96, 125.29, 64.49 (d, *J* = 7.0 Hz), 63.97 (d, *J* = 7.3 Hz), 52.33, 48.20 (d, *J* = 17.0 Hz), 34.48, 31.29, 16.25 (d, *J* = 6.3 Hz), 16.10 (d, *J* = 6.2 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.096 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -109.72 (m). **HRMS** [ESI]: m/z calculated for $C_{20}H_{29}F_2NaO_5P$ $[M+Na]^+$ 441.1618, found 441.1612. **IR** (ATR): ν = 2966, 2360, 1720, 1631, 1365, 1269, 1026, 979, 798 cm^{-1}.



***R*-1u**, 52%, 91:9 *er*, determined by HPLC analysis [Phenomenex Lux Amylose-1, *n*-hexane/EtOH = 99.9/0.1, 0.7 mL/min, λ = 220 nm, t (major) = 12.62 min, t (minor) = 13.82 min].

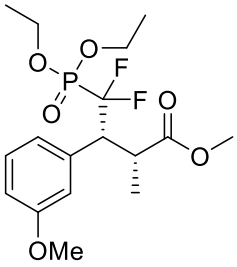
General procedure for Hydrogenation of Substitution products



S-**3q** **6**

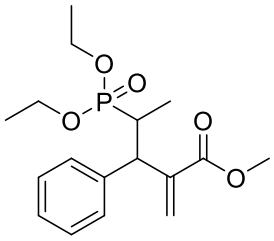
The substrate (1 equiv.) was dissolved in MeOH (1mL) and degassed with nitrogen for 5 minutes. Pd/C (10 mol%) was added and hydrogen was bubbled through the mixture until observed to be completed (by GC-MS). The reaction mixture was filtered on a plug of silica eluting with ethyl acetate if not stated differently.

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (6)



Yield: 96%. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.9 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.81 (dd, *J* = 8.2, 2.6 Hz, 1H), 4.25 – 4.02 (m, 2H), 3.87 – 3.70 (m, 5H), 3.64 – 3.53 (m, 1H), 3.42 (s, 3H), 3.37 – 3.26 (m, 1H), 1.44 (dd, *J* = 7.0, 2.9 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 174.50 (d, *J* = 1.6 Hz), 159.18, 135.84 (d, *J* = 10.1 Hz), 128.97, 122.96 (d, *J* = 2.1 Hz), 119.32 (d, *J* = 214.3 Hz), 116.09 (d, *J* = 2.2 Hz), 113.65, 64.56 (d, *J* = 6.4 Hz), 63.66 (d, *J* = 7.0 Hz), 55.23, 52.25 (td, *J* = 18.8, 15.8 Hz), 51.61, 41.82 (dd, *J* = 7.2, 4.4 Hz), 17.06 (d, *J* = 6.3 Hz), 16.26 (d, *J* = 5.7 Hz), 16.02 (d, *J* = 5.8 Hz).**^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.39 (m). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ -101.54 (m), -116.76 (m). **HRMS** [ESI]: m/z calculated for $C_{17}H_{26}F_2O_6P$ $[M+H]^+$ 395.1435, found 395.1431. **IR** (ATR): ν = 2989, 2360, 1720, 1631, 1438, 1369, 1265, 1165, 1022, 979, 756 cm^{-1}.

methyl 4-(diethoxyphosphoryl)-2-methylene-3-phenylpentanoate (9)



Yield: 19%. **^{1}H-NMR** (300 MHz, $CDCl_3$) 7.29 – 7.26 (m, 2H), 7.20 – 7.10 (m, 3H), 6.22 (s, 1H), 5.69 (s. 1H), 4.02 (t, *J* = 10.5 Hz, 1H), 3.78 –3.65 (m, 4H), 3.62 (s, 3H), 3.45 – 3.37 (m, 1H), 2.74 (ddd, J = 18.5, 11.2, 7.2 Hz, 1H), 1.19 (dd, *J* = 17.8, 7.1 Hz, 4H), 1.06 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.0 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ 167.08, 141.67 (d, *J* = 16.9 Hz), 141.20 (d, *J* = 2.6 Hz), 129.13, 128.17, 126.84, 125.88, 61.45 (d, *J* = 6.9 Hz), 61.31 (d, *J* = 7.1 Hz), 52.04, 49.43, 34.30 (d, 142.1 Hz), 16.35 (d, *J* = 4.0 Hz), 16.29 (d, *J* = 3.8 Hz), 13.89 (d, J = 4.9 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 32.58. **HRMS** [EI]: m/z calculated for $C_{17}H_{25}O_5P$ $[M]^-$ 340.1445, found 340.1446. **IR** (ATR): ν = 2981, 1625, 1438, 1311, 1240, 1056, 761 cm^{-1}. Due to the relatively low yield of the isolated product we refrain from commenting on reaction diastereoselectivity and the relative configuration of the product has not been determined.

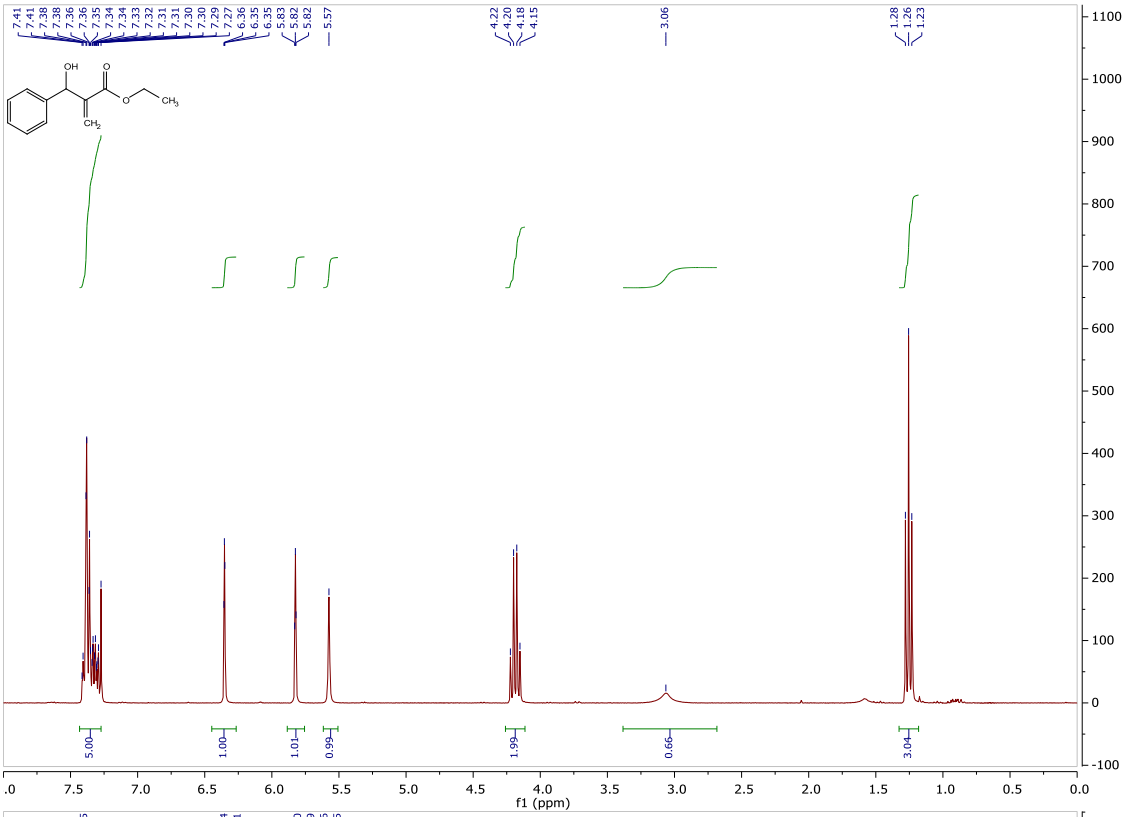
References

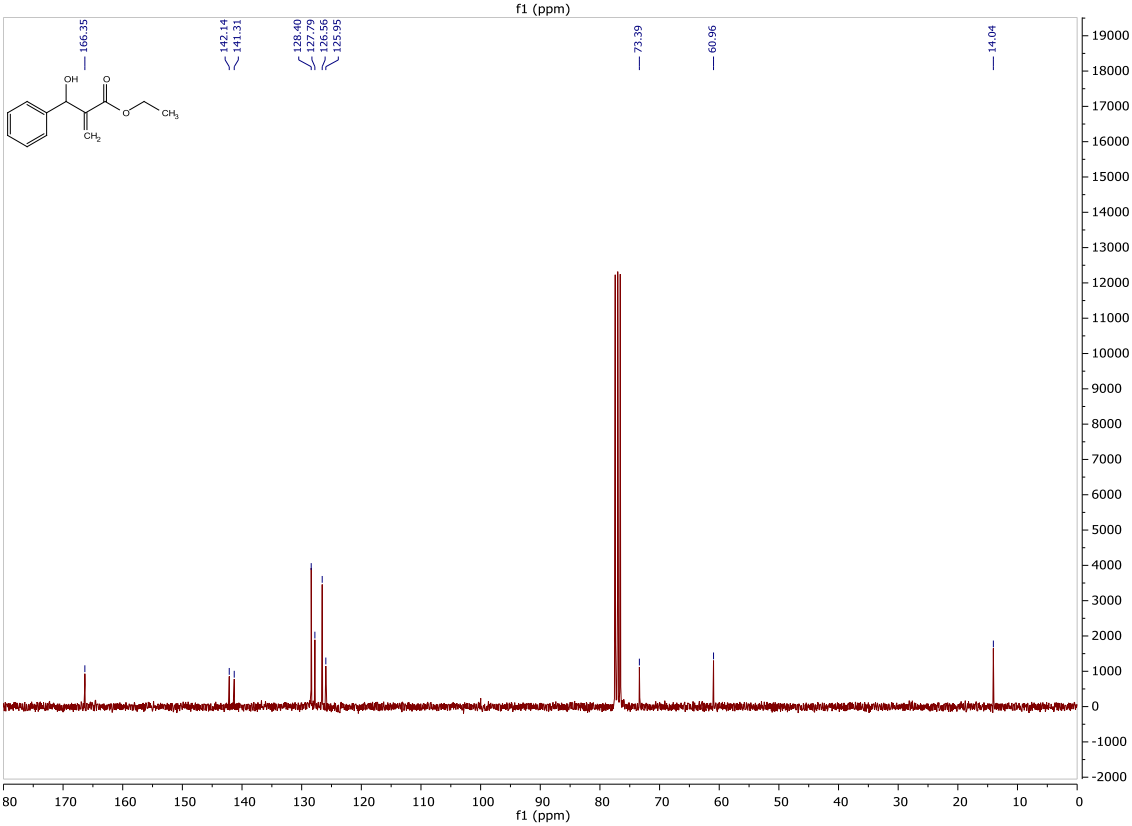
[1] (a) *Angew. Chem. Int. Ed.*, 2019, **58**, 10727; (b) *Angew. Chem. Int. Ed.*, 2014, **53**, 517; (c) *J. Org. Chem.* 2020, **85**, *1259*.

[2] *Synthesis*, 1986, **11**, 934.

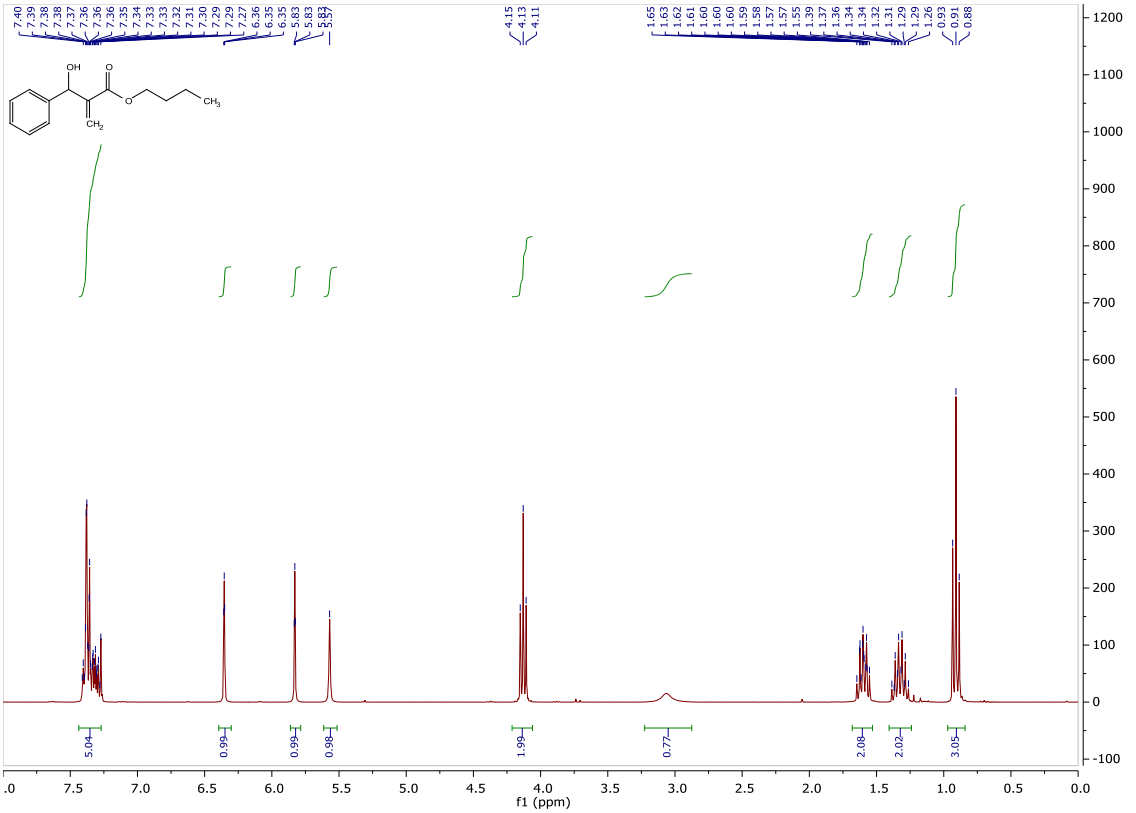
Copies of NMR spectra

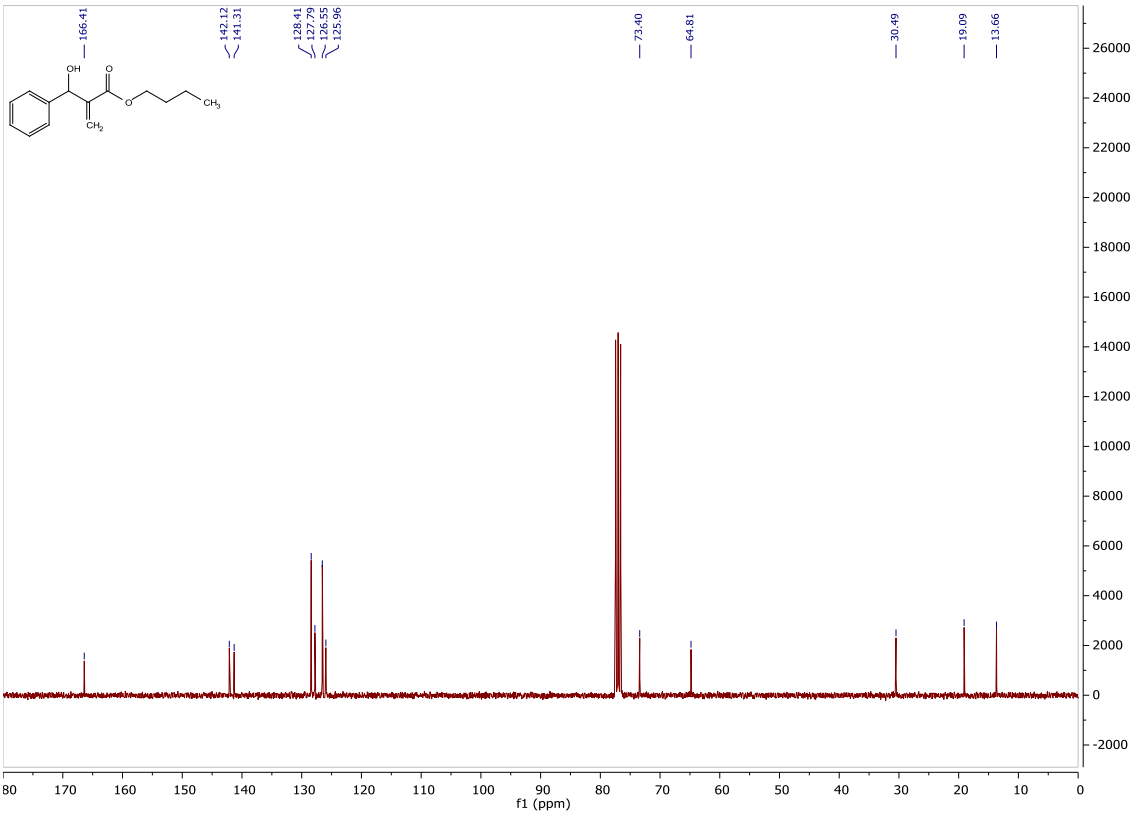
ethyl 2-(hydroxy(phenyl)methyl)acrylate



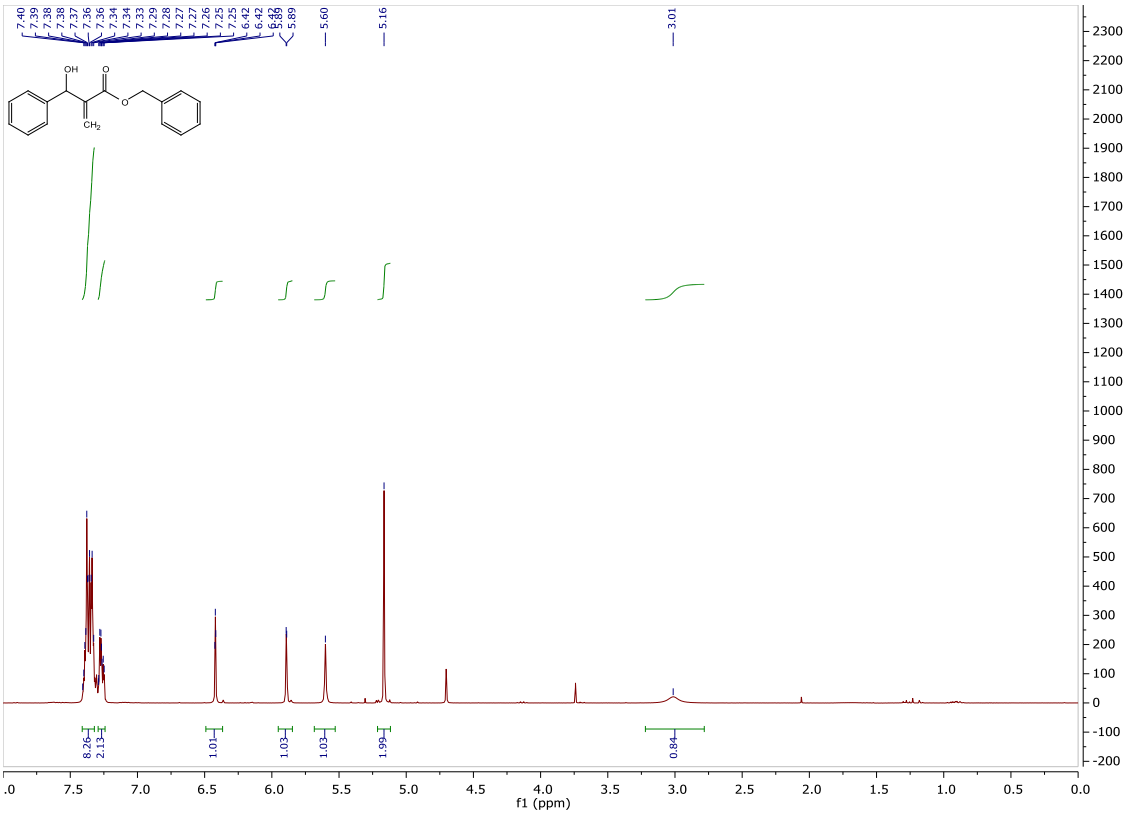


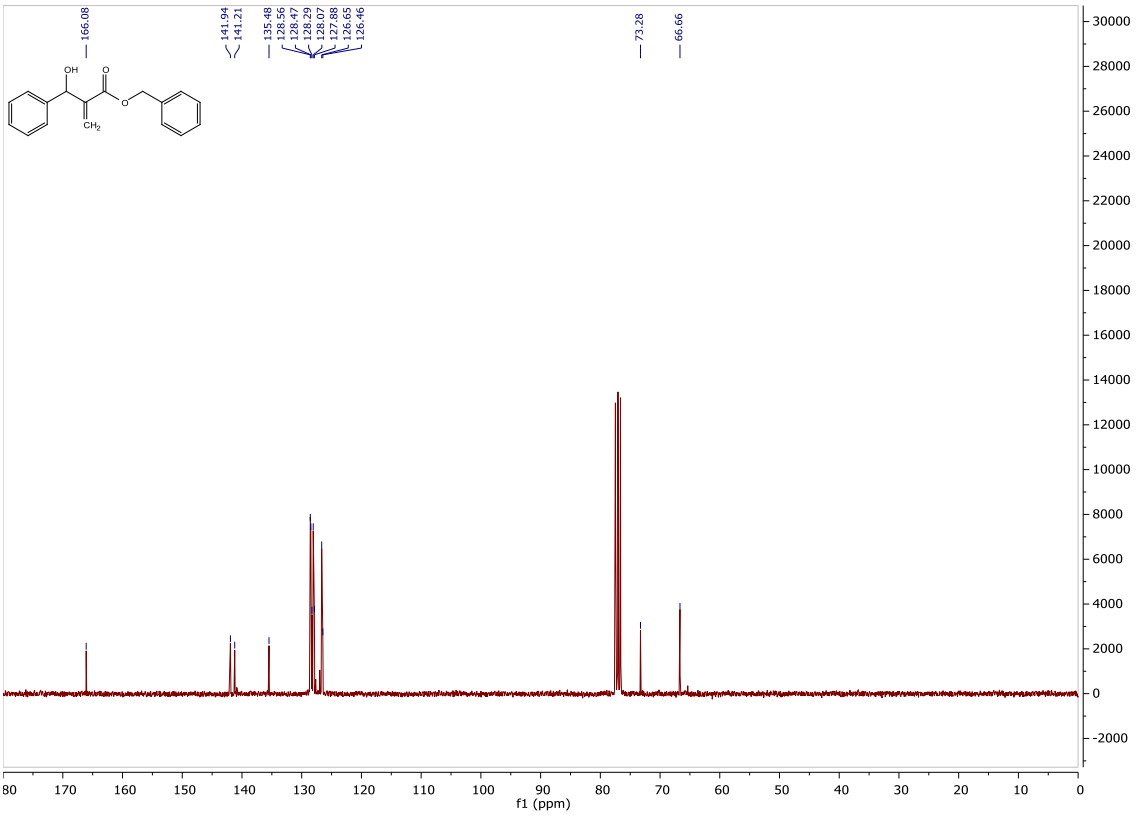
butyl 2-(hydroxy(phenyl)methyl)acrylate



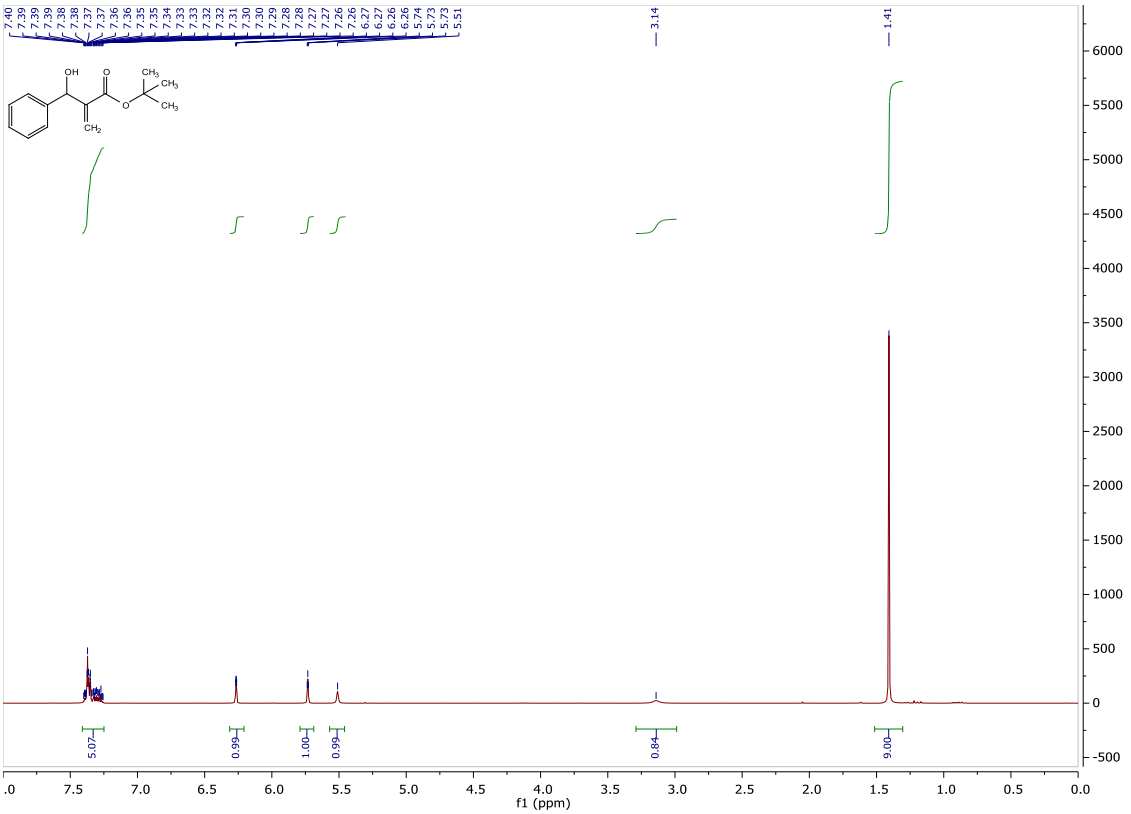


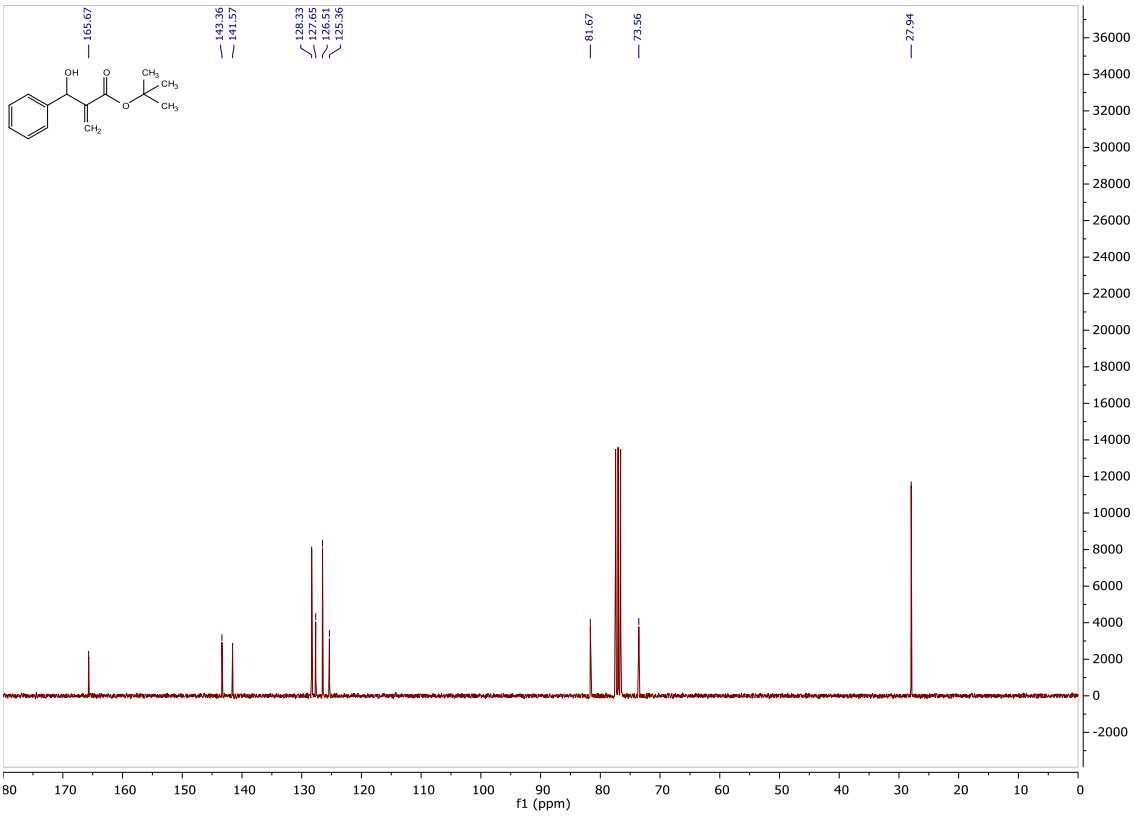
benzyl 2-(hydroxy(phenyl)methyl)acrylate



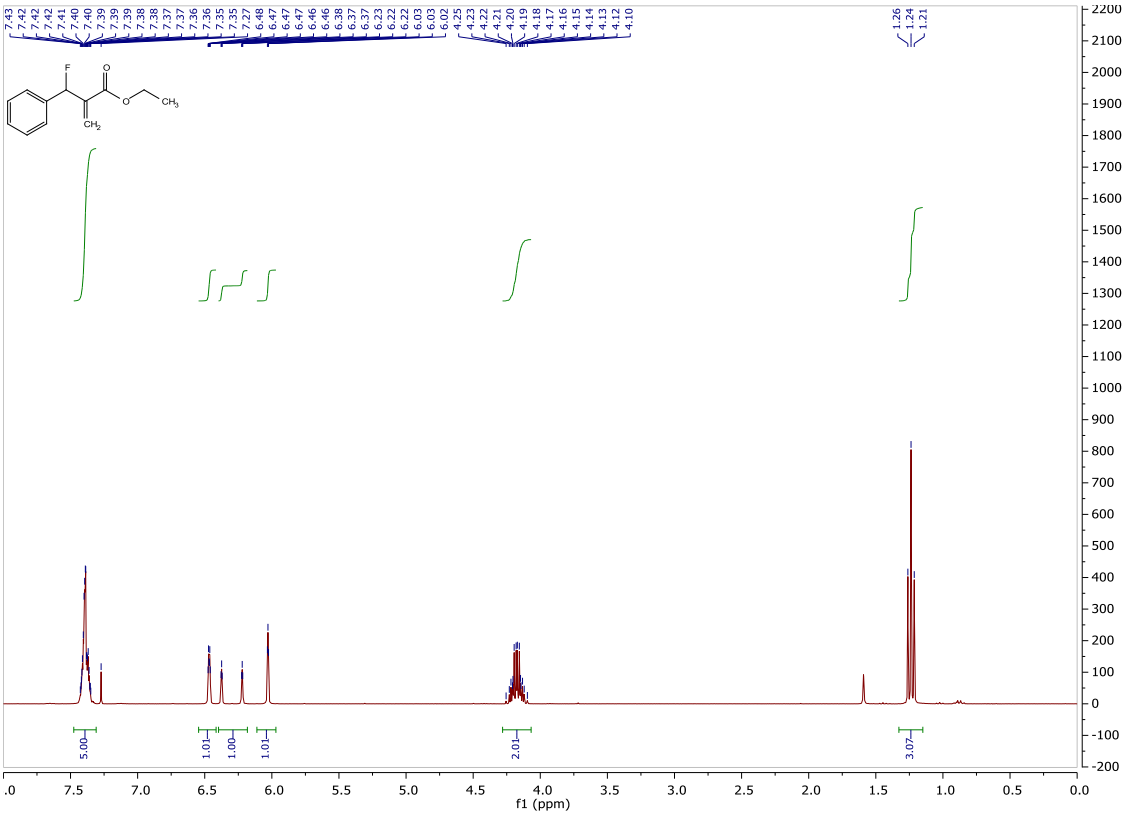


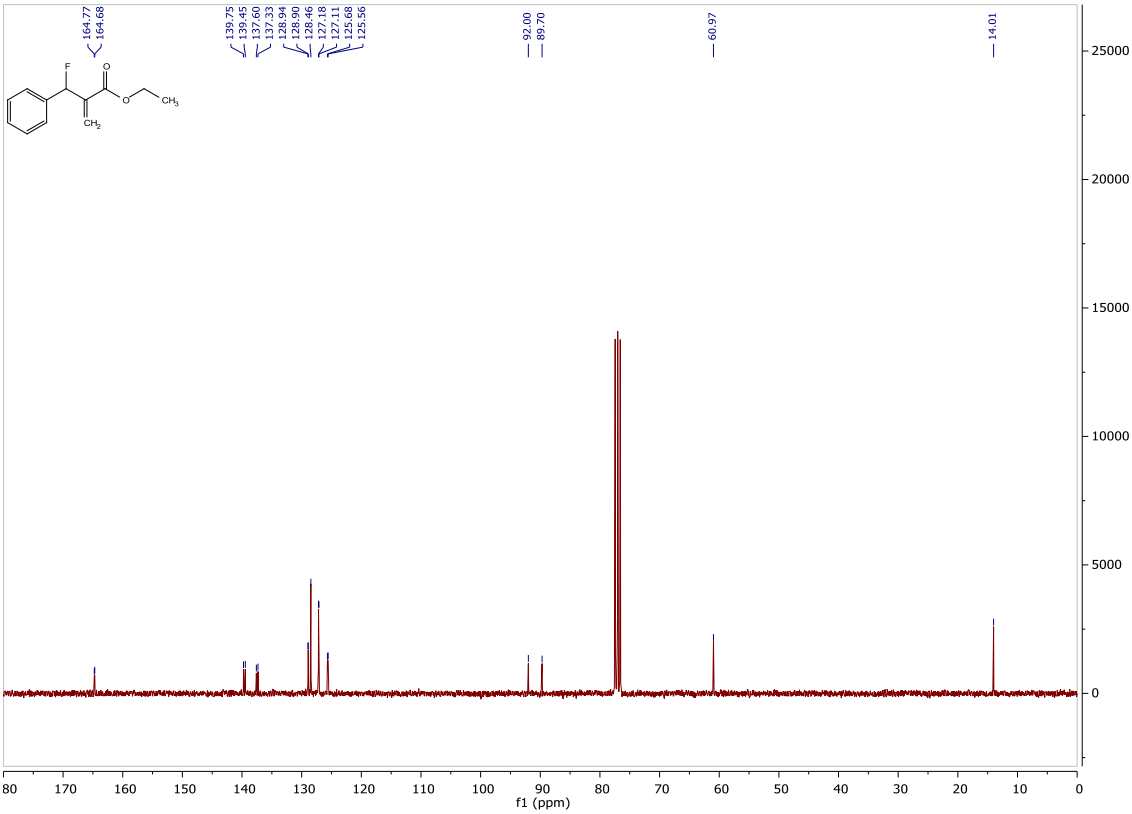
tert-butyl 2-(hydroxy(phenyl)methyl)acrylate

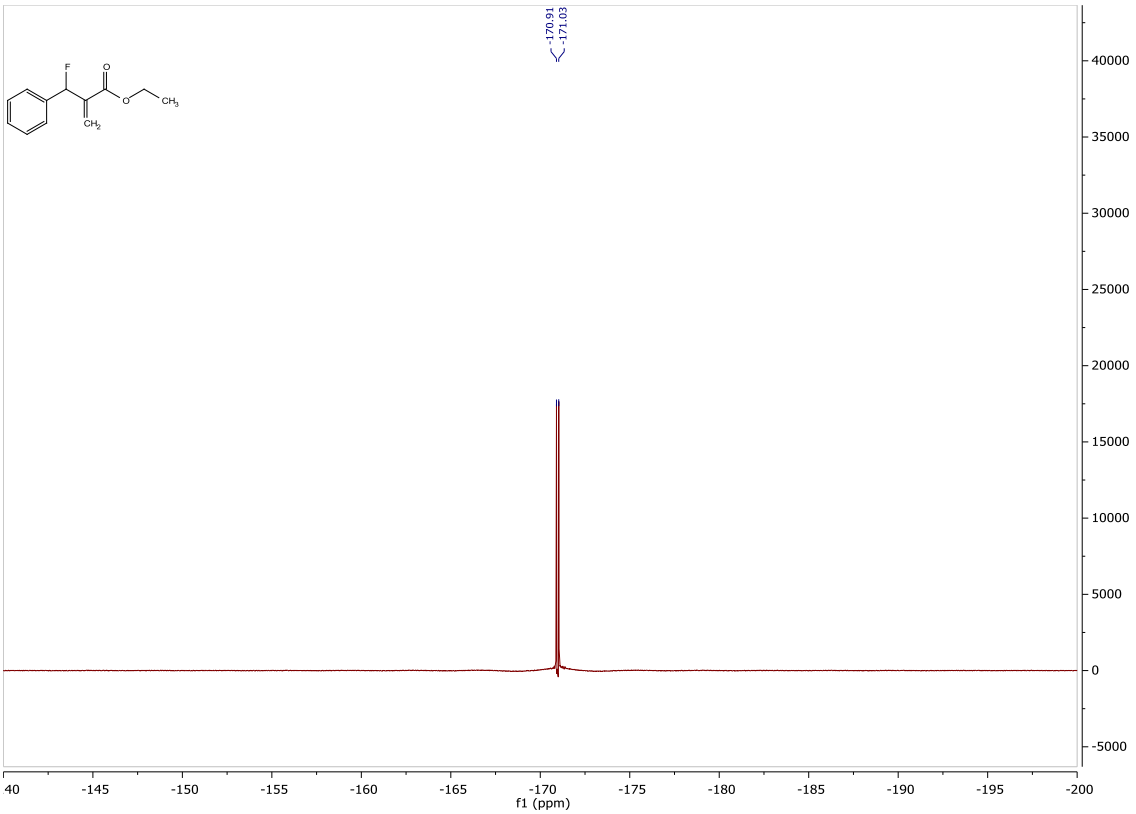




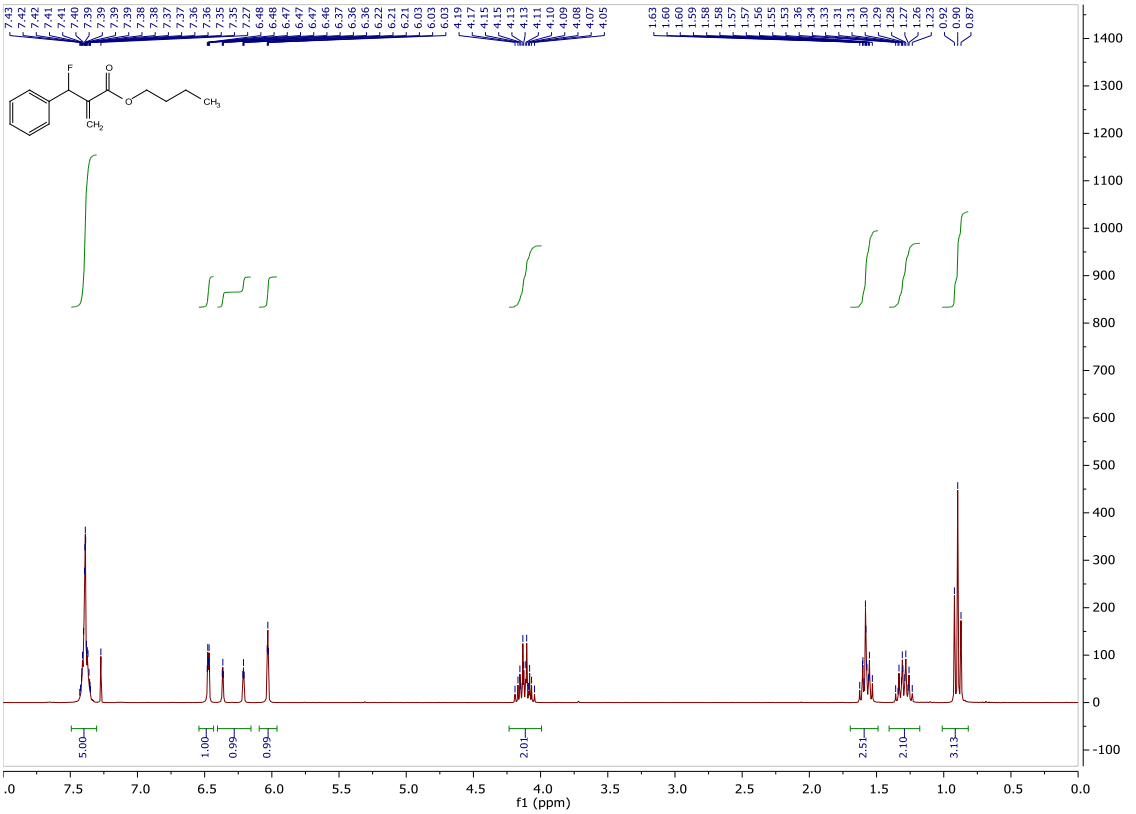
ethyl 2-(fluoro(phenyl)methyl)acrylate

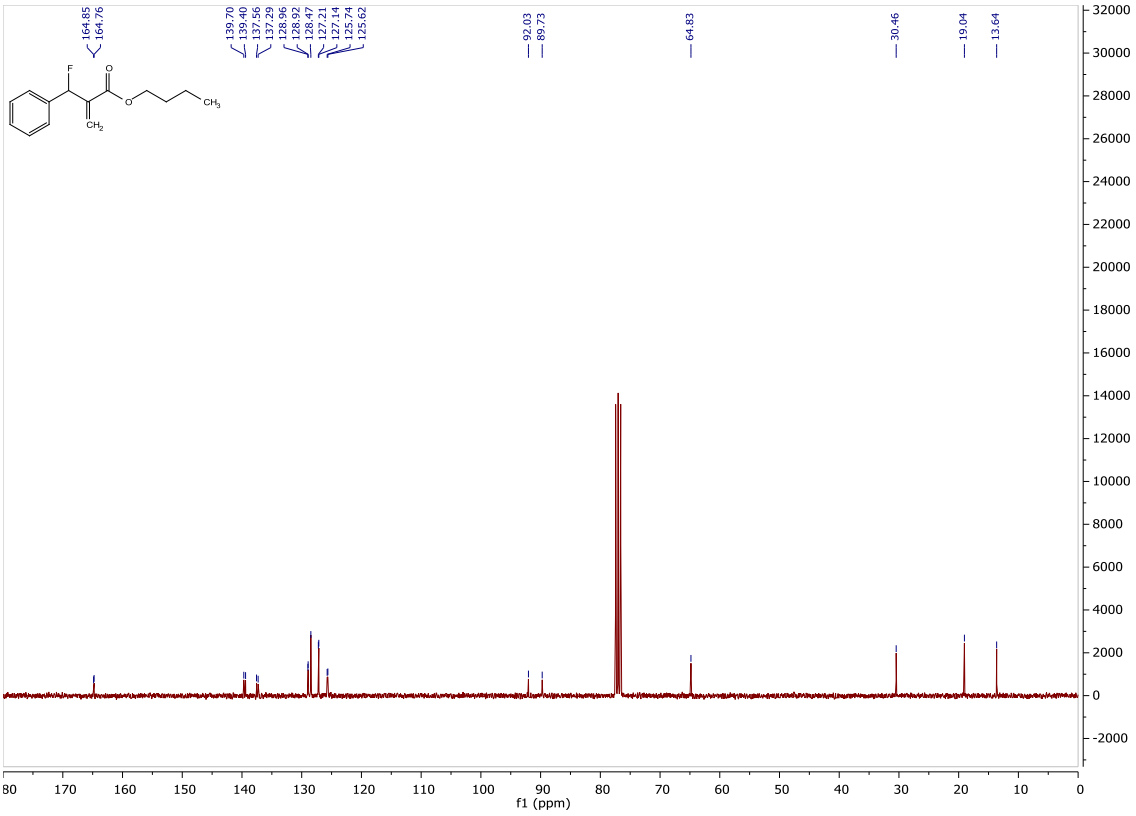






butyl 2-(fluoro(phenyl)methyl)acrylate




164.85
164.76
139.70
139.40
137.56
137.29
128.96
128.92
128.47
127.21
127.14
125.74
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19.04
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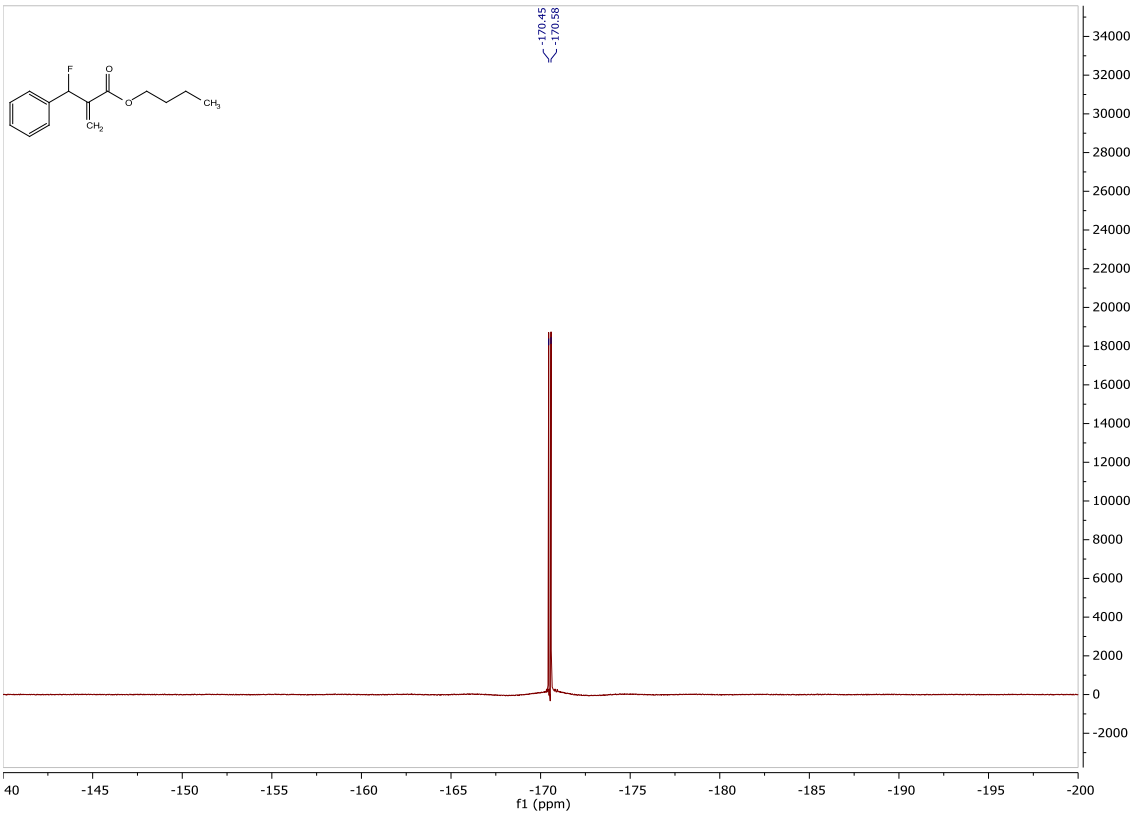
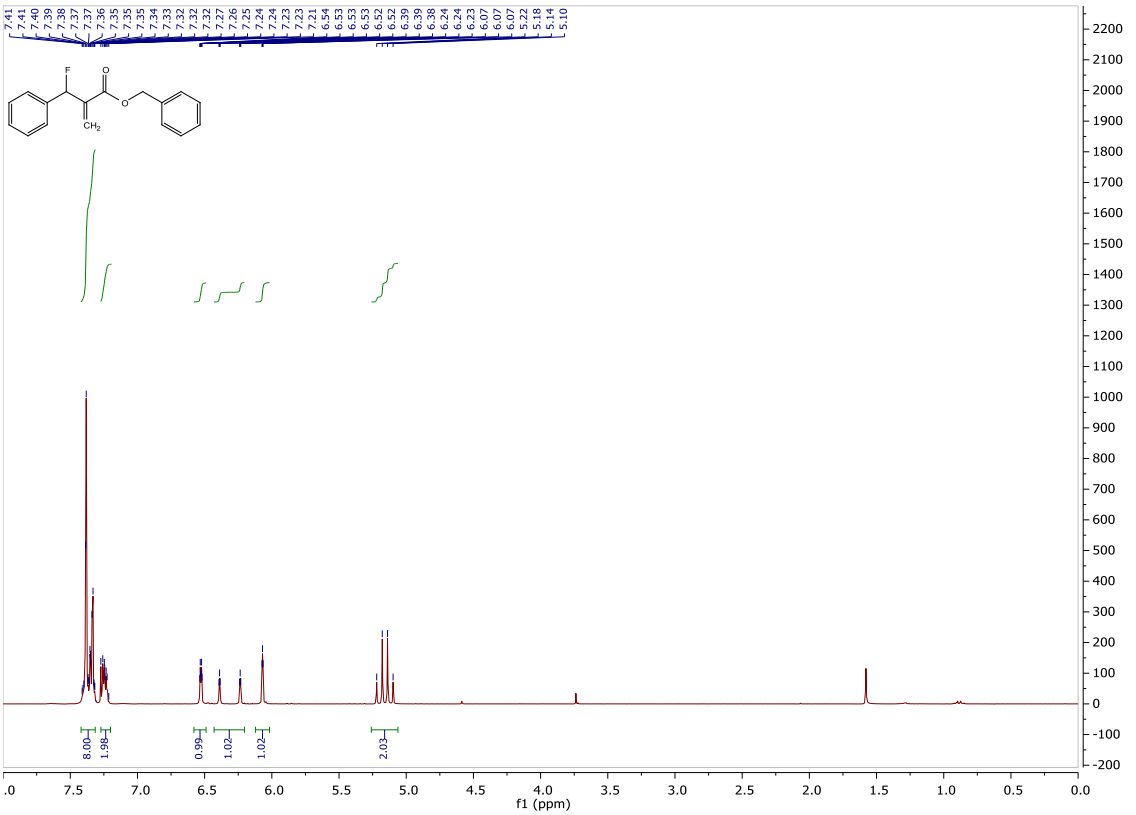
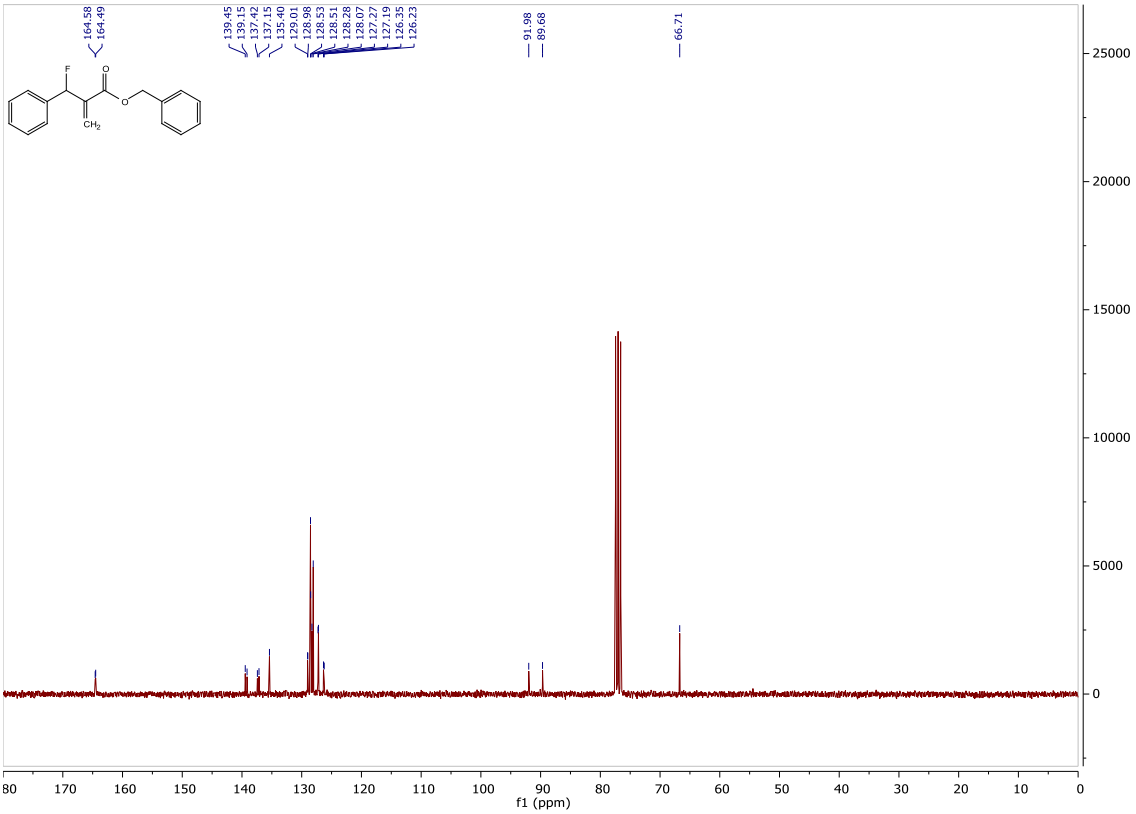
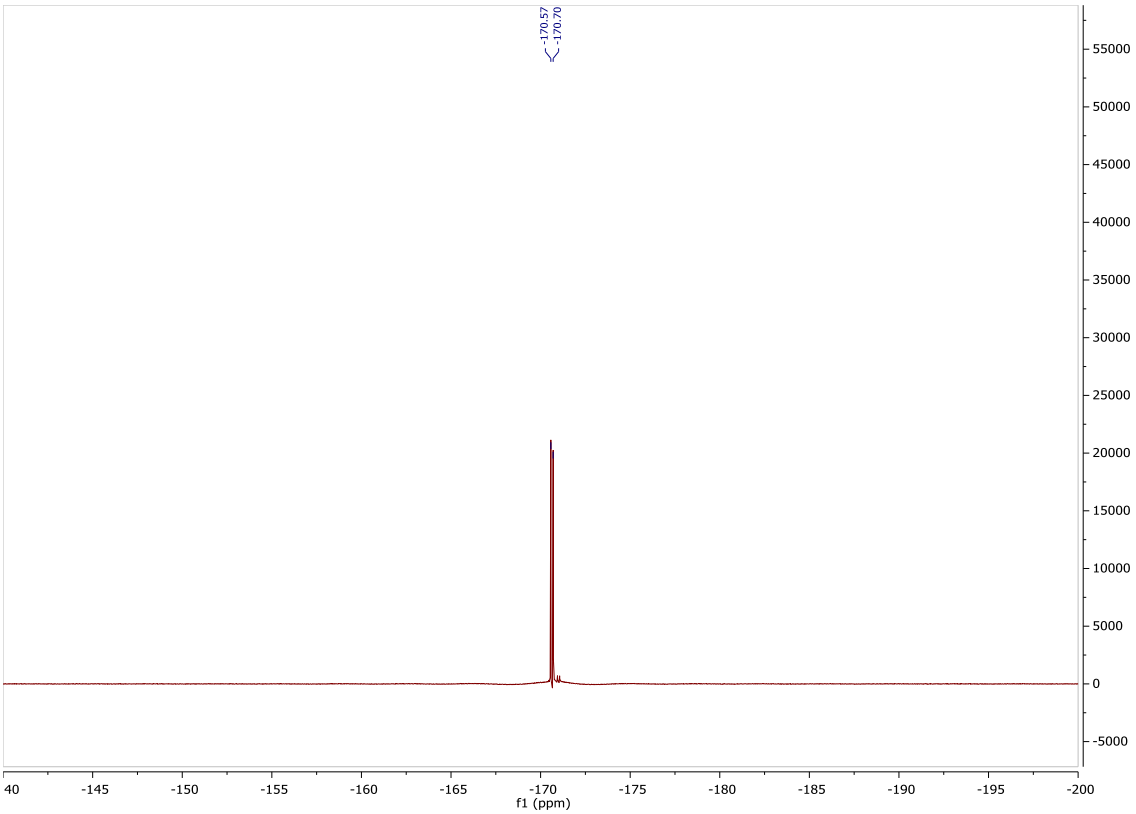
F
O
O
CH3
CH2
f1 (ppm)


-170.45
-170.58
F
O
O
CH3
CH2
f1 (ppm)

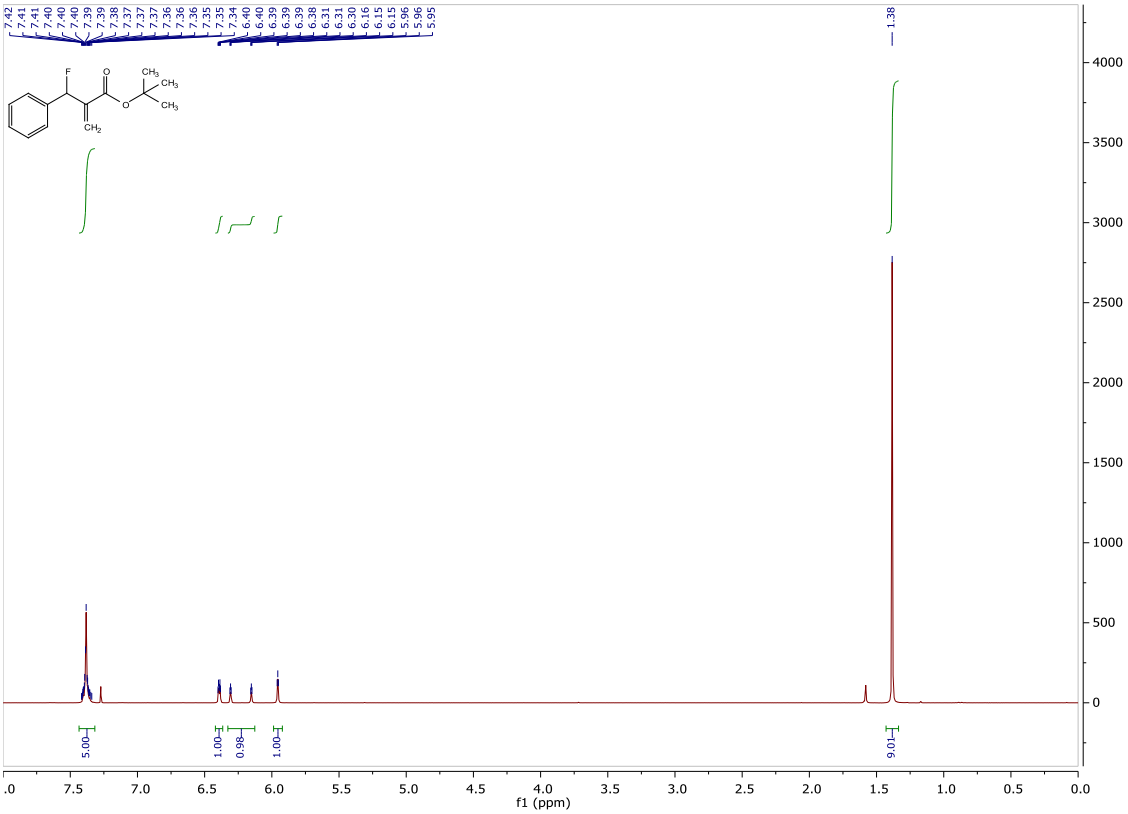
benzyl 2-(fluoro(phenyl)methyl)acrylate

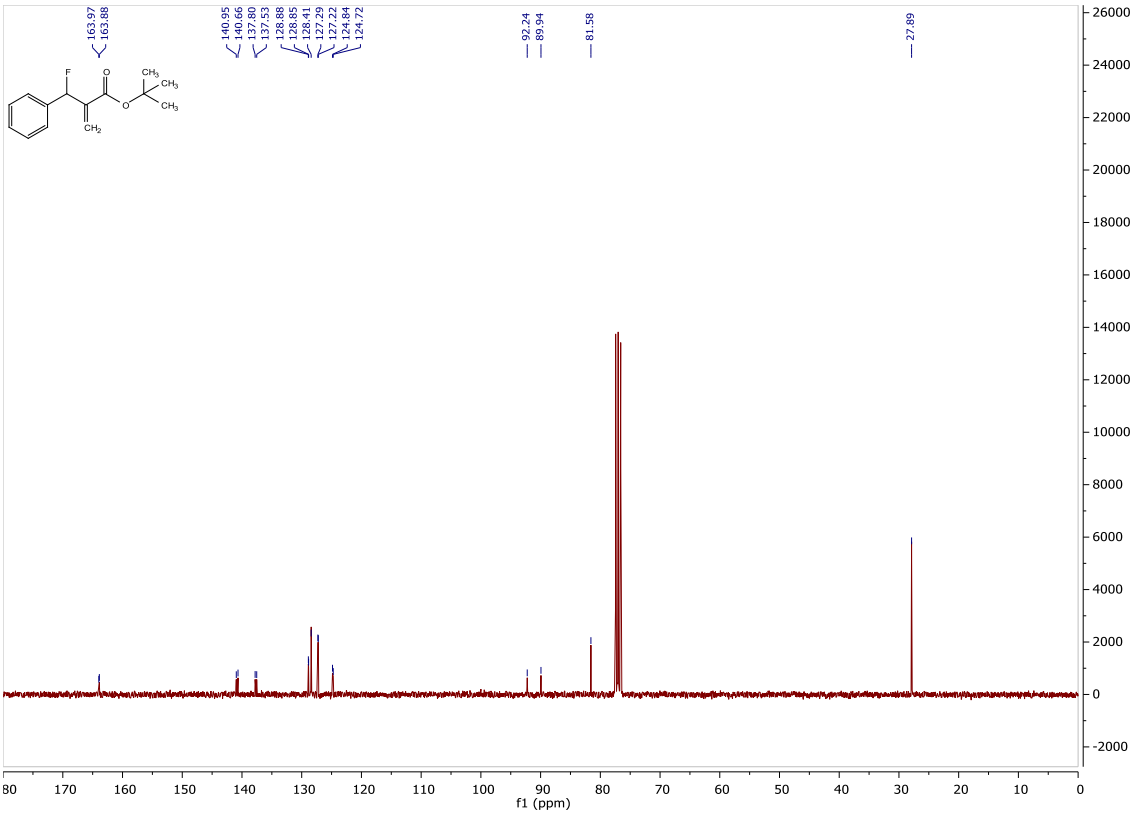


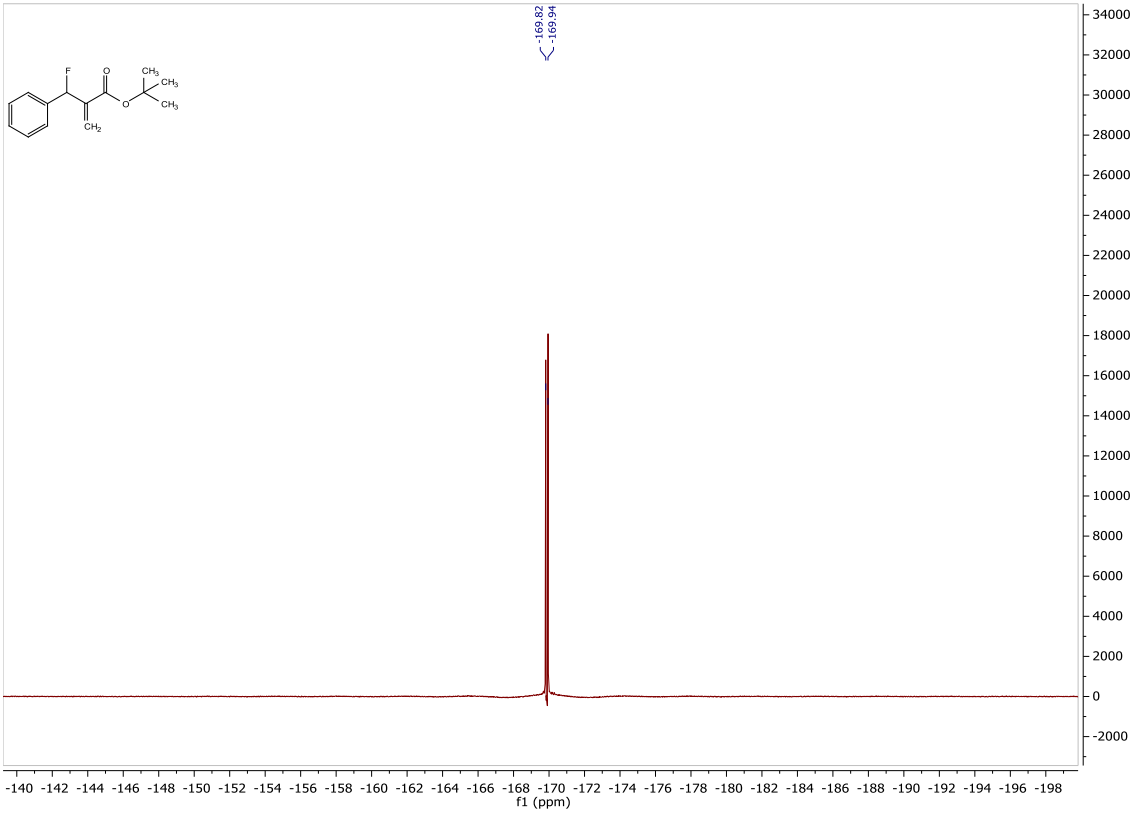




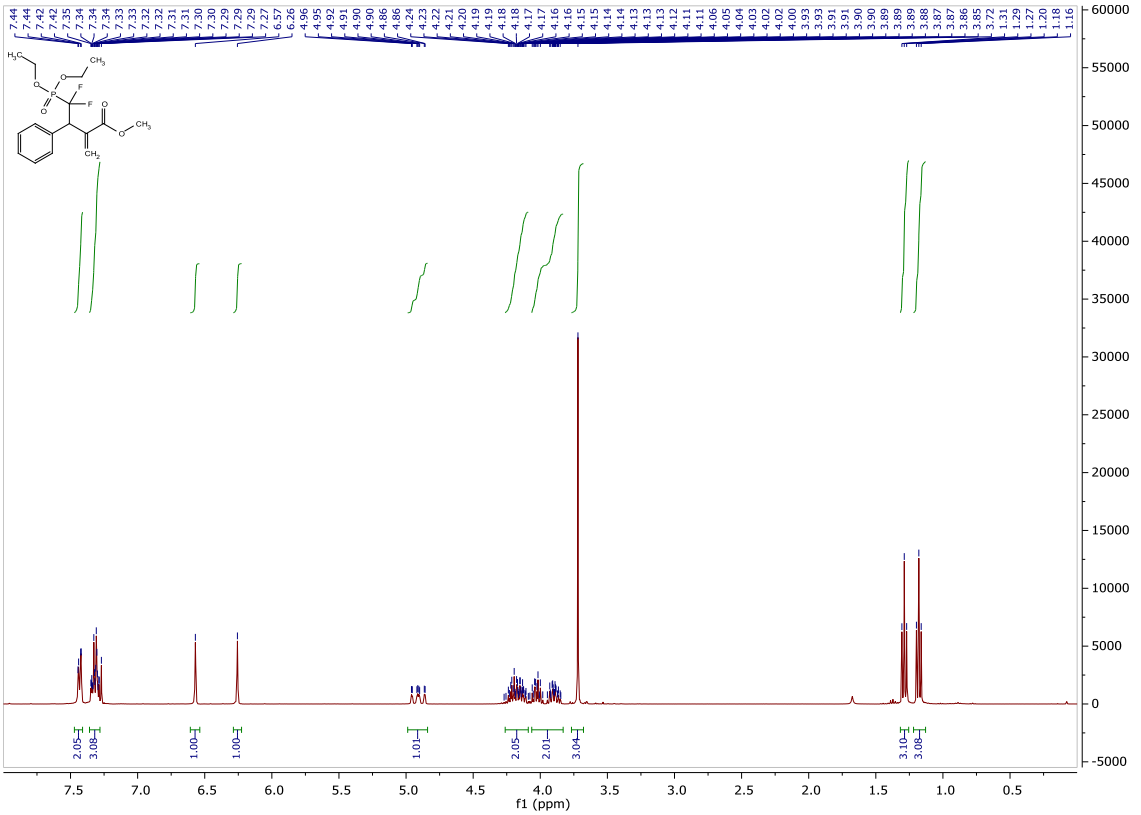
tert-butyl 2-(fluoro(phenyl)methyl)acrylate

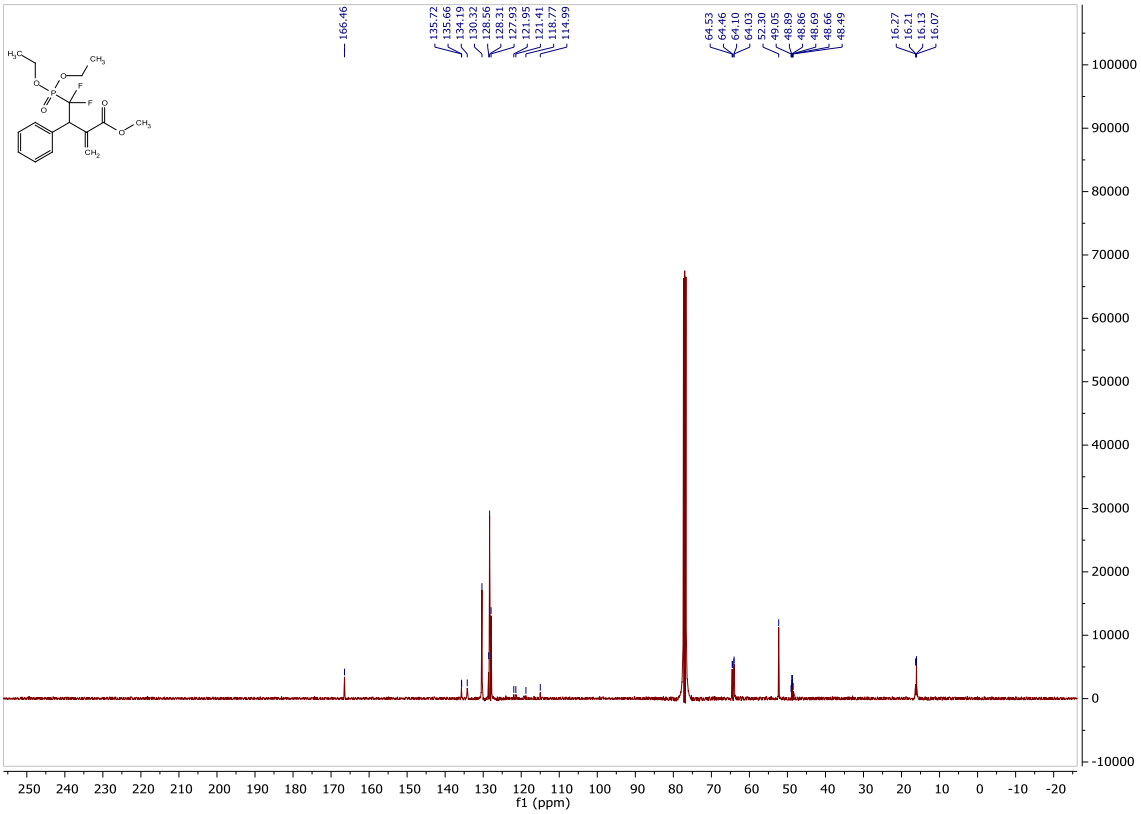


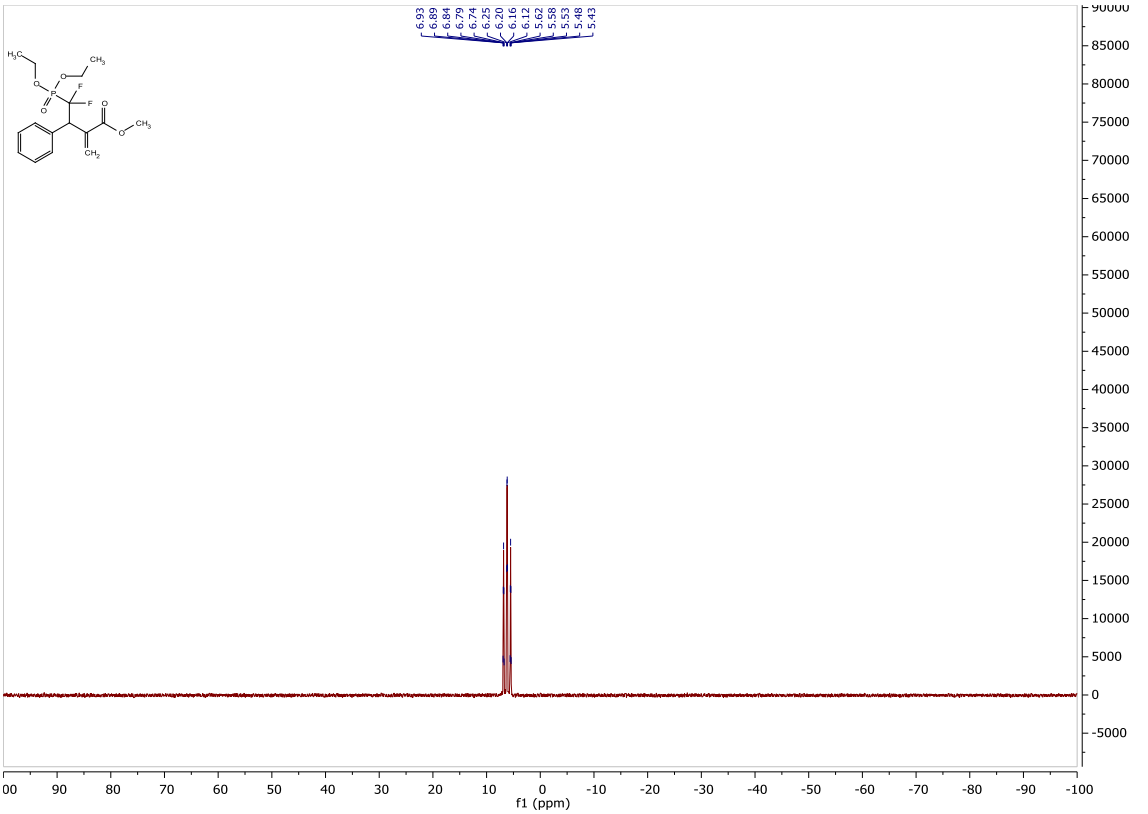

163.97
163.88
140.95
140.66
137.80
137.53
128.88
128.85
128.41
127.29
127.22
124.84
124.72
92.24
89.94
81.58
27.89
F
O
O
CH3
CH3
CH3
CH2
f1 (ppm)

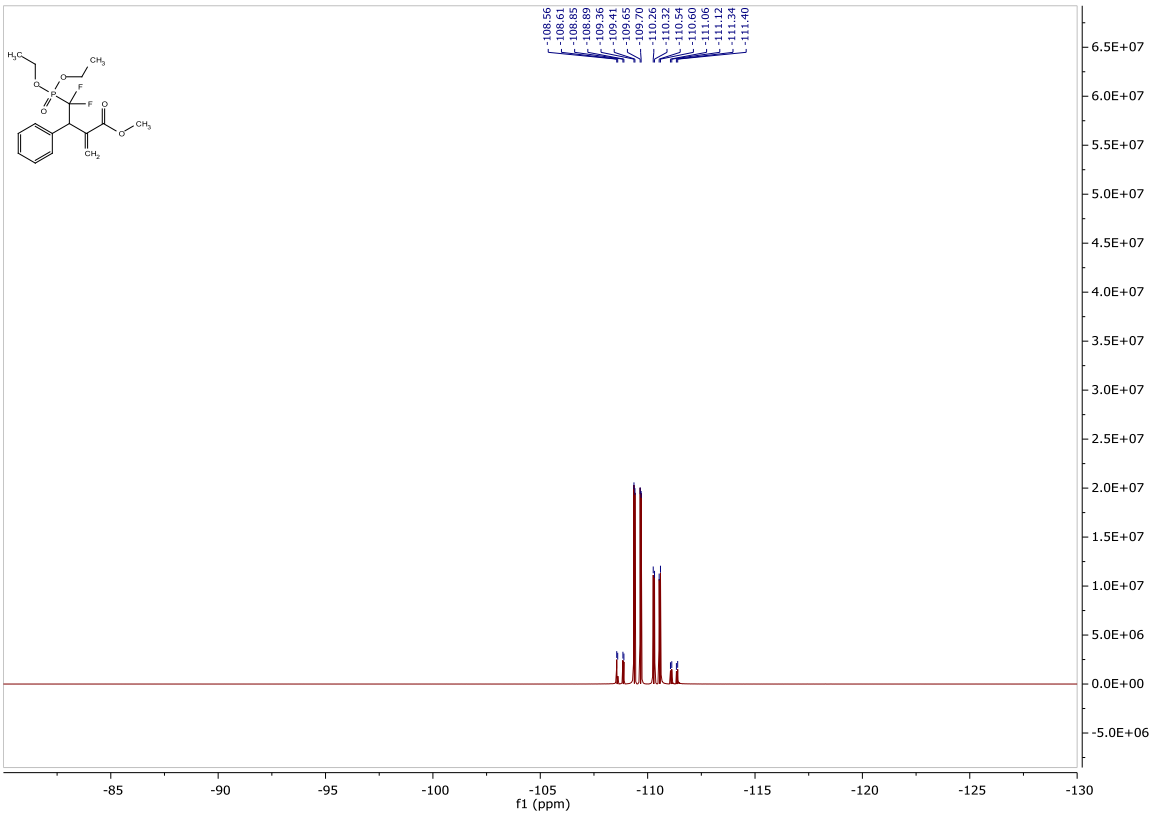

-169.82
-169.94
F
O
O
CH3
CH3
CH3
CH2
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3a)






6.93
6.89
6.84
6.79
6.74
6.25
6.20
6.16
6.12
5.62
5.58
5.53
5.48
5.43
f1 (ppm)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-108.89
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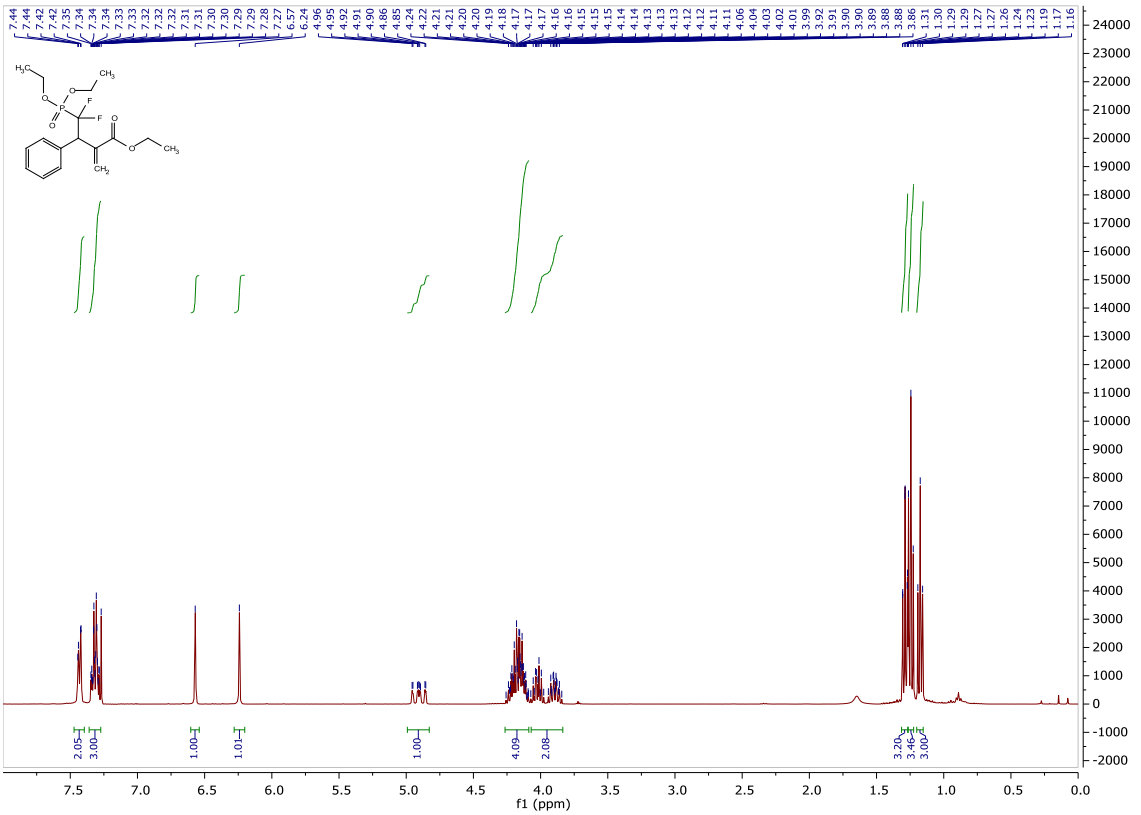
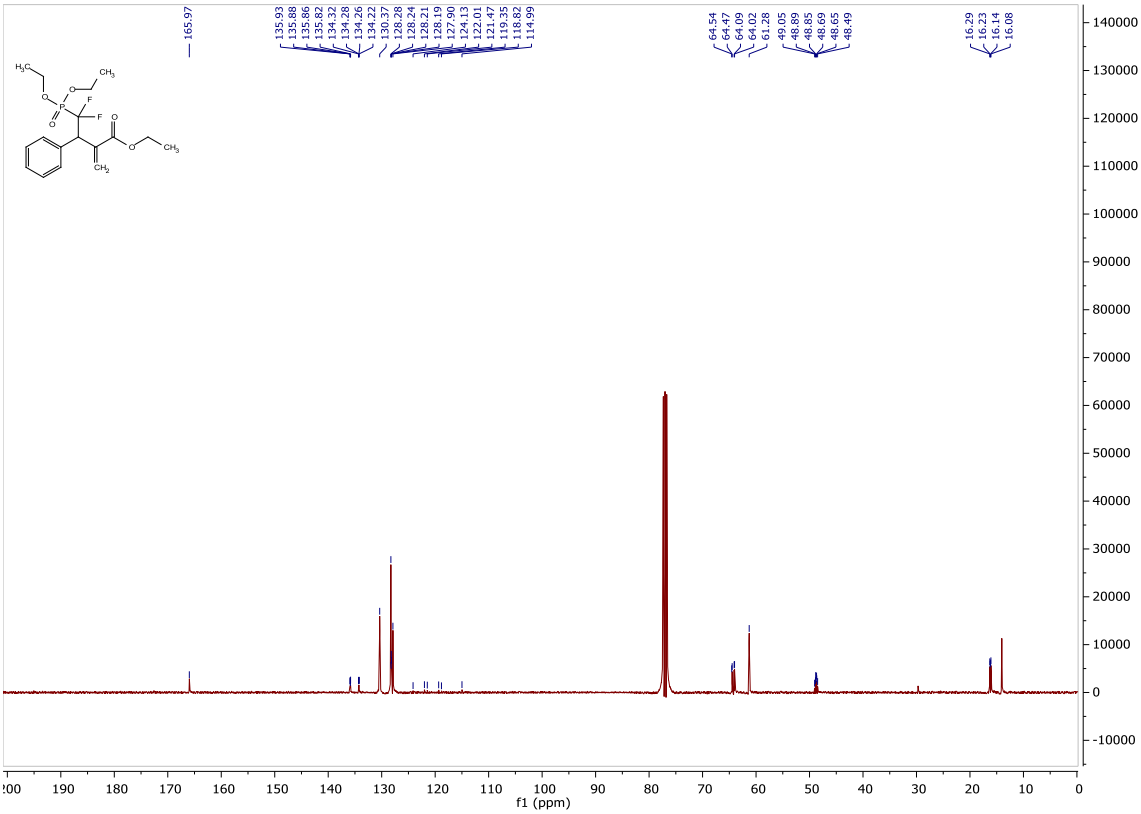
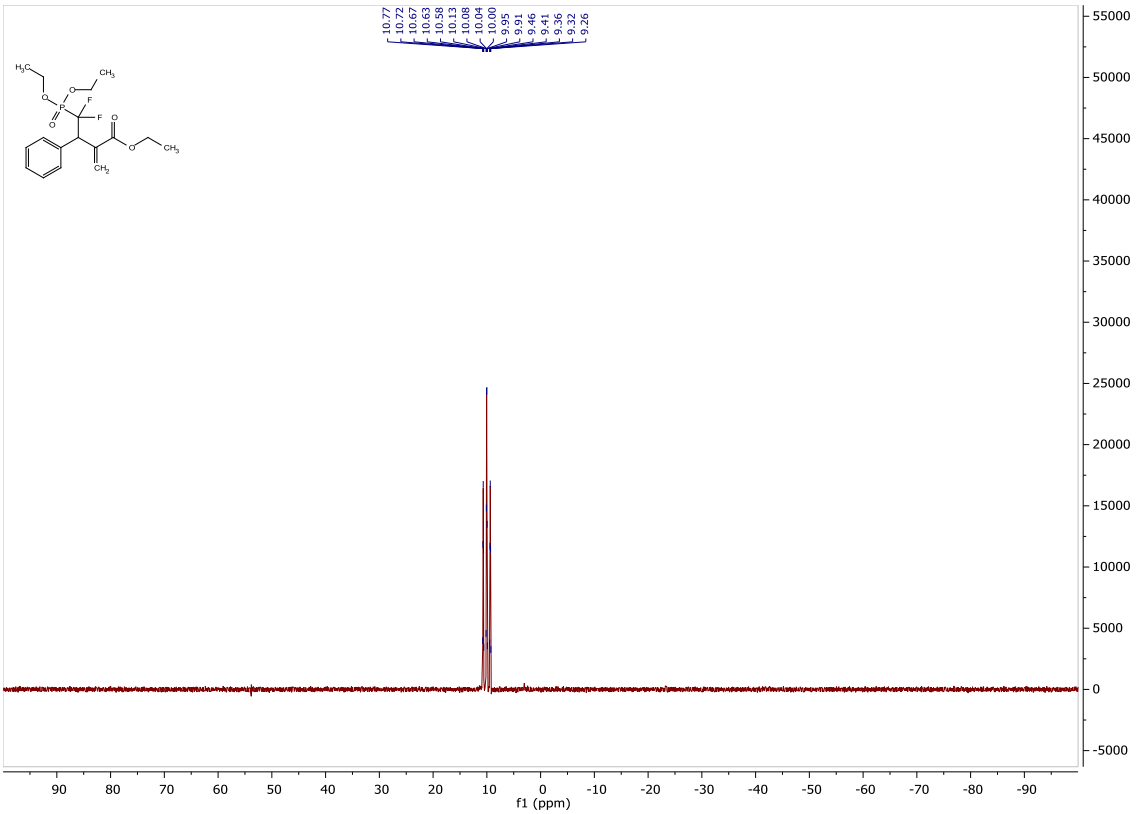
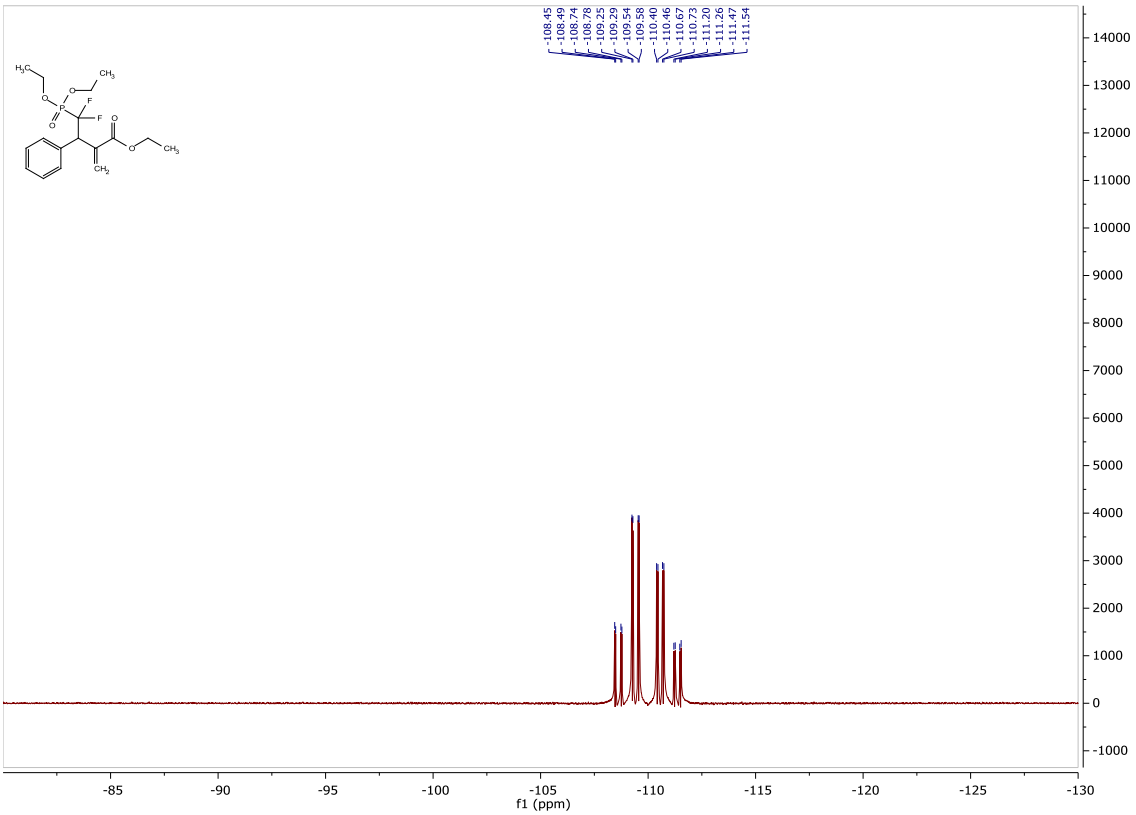
-109.65
-109.70
-110.26
-110.32
-110.54
-110.60
-111.06
-111.12
-111.34
-111.40
f1 (ppm)

ethyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3b)






10.77
10.72
10.67
10.63
10.58
10.13
10.08
10.04
10.00
9.95
9.91
9.46
9.41
9.36
9.32
9.26
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)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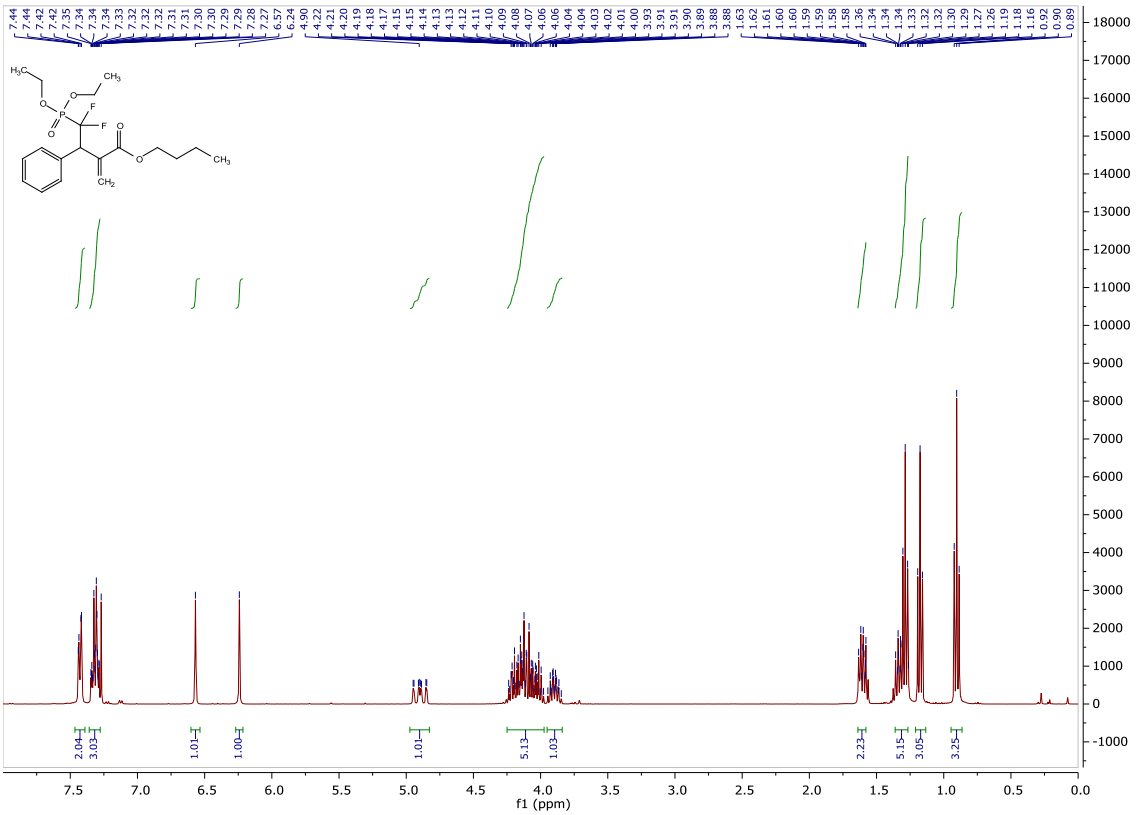
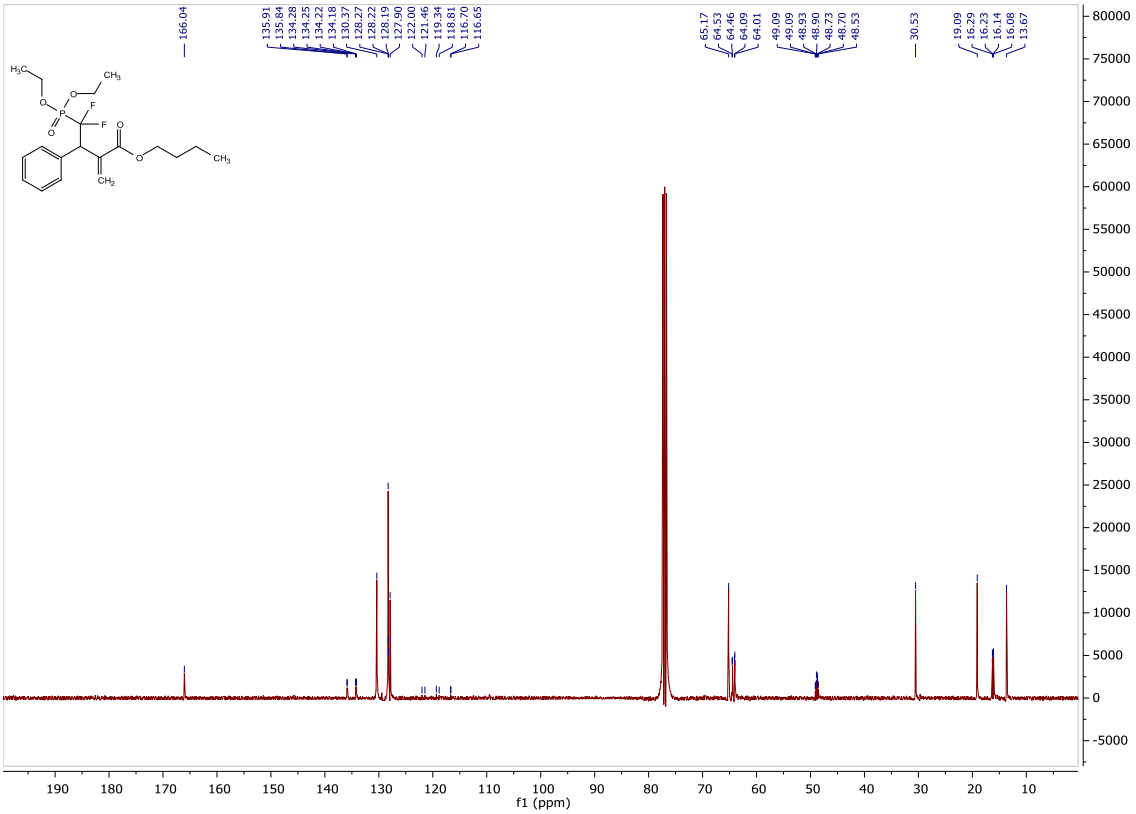
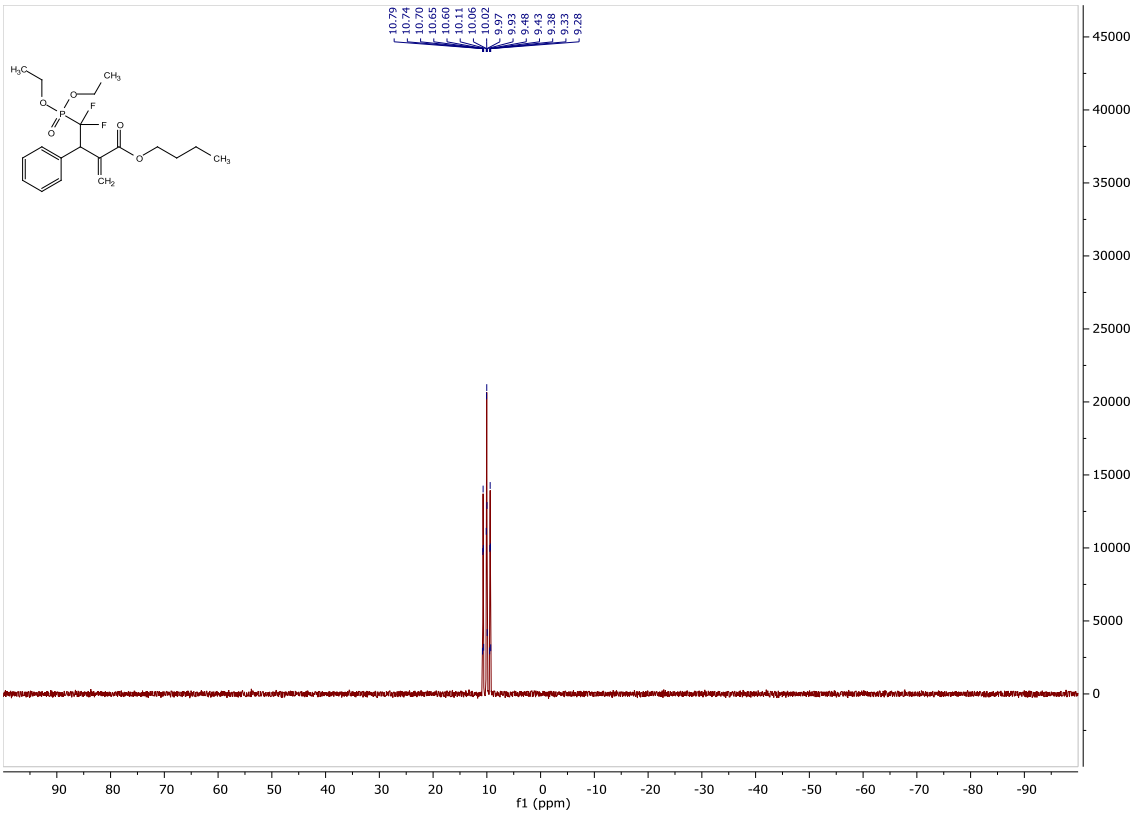
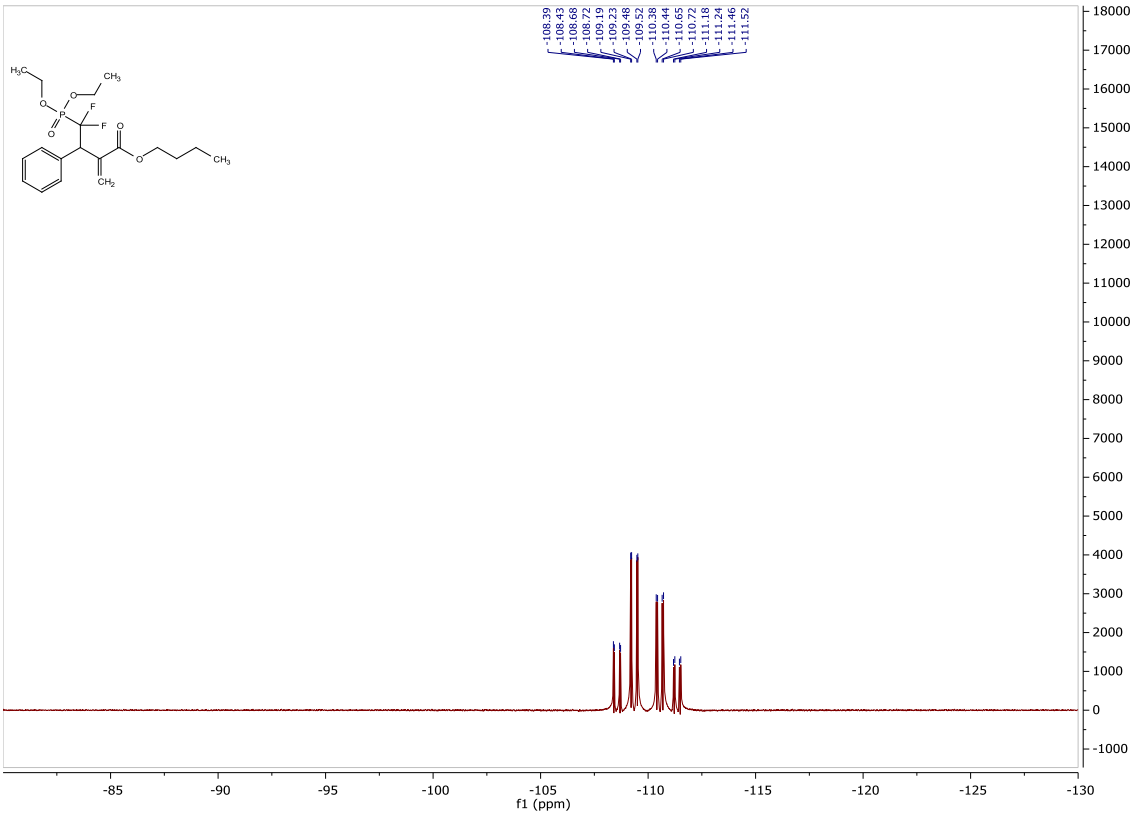
-108.78
-109.25
-109.29
-109.54
-109.58
-110.40
-110.46
-110.67
-110.73
-111.20
-111.26
-111.47
-111.54
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

butyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3c)

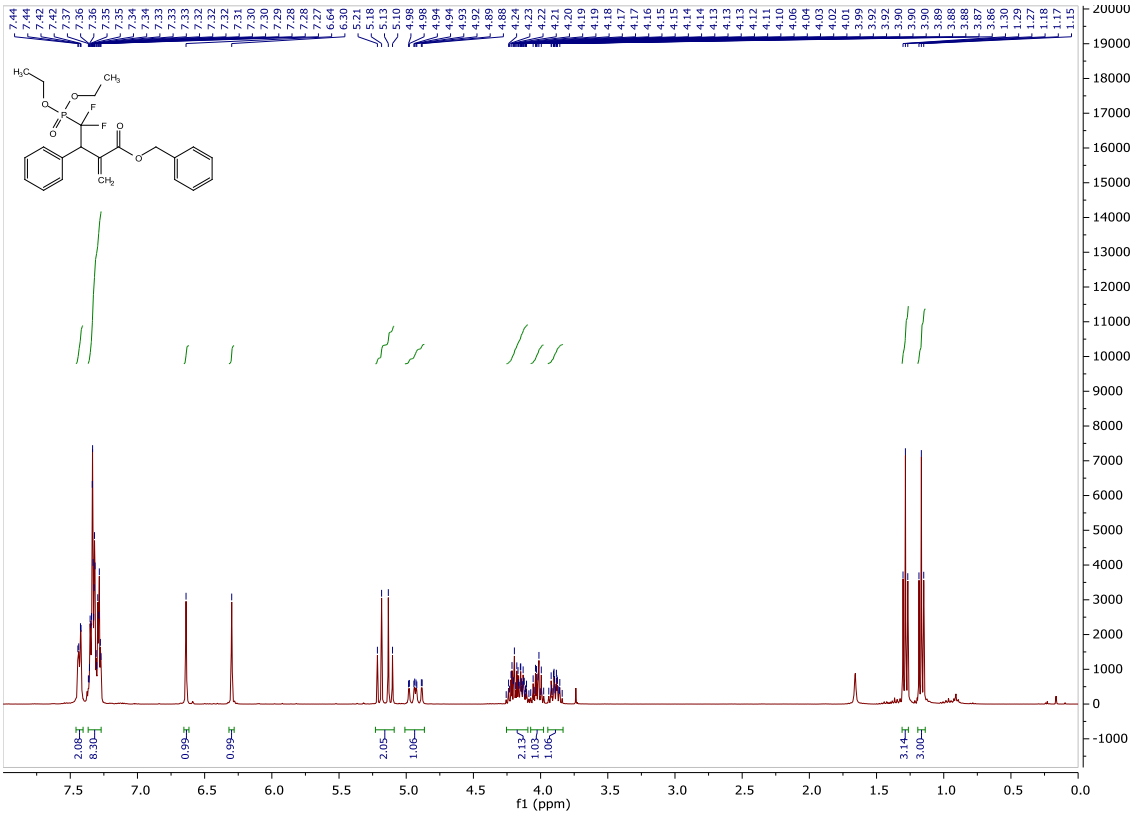


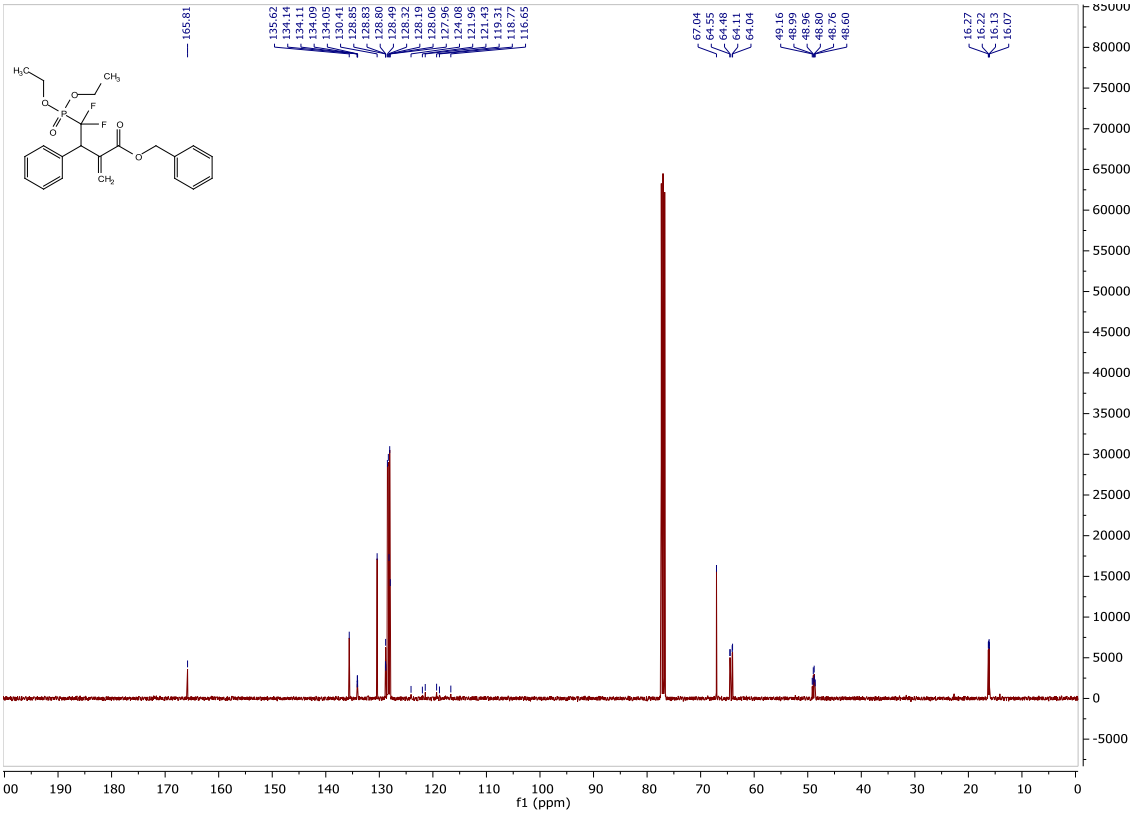


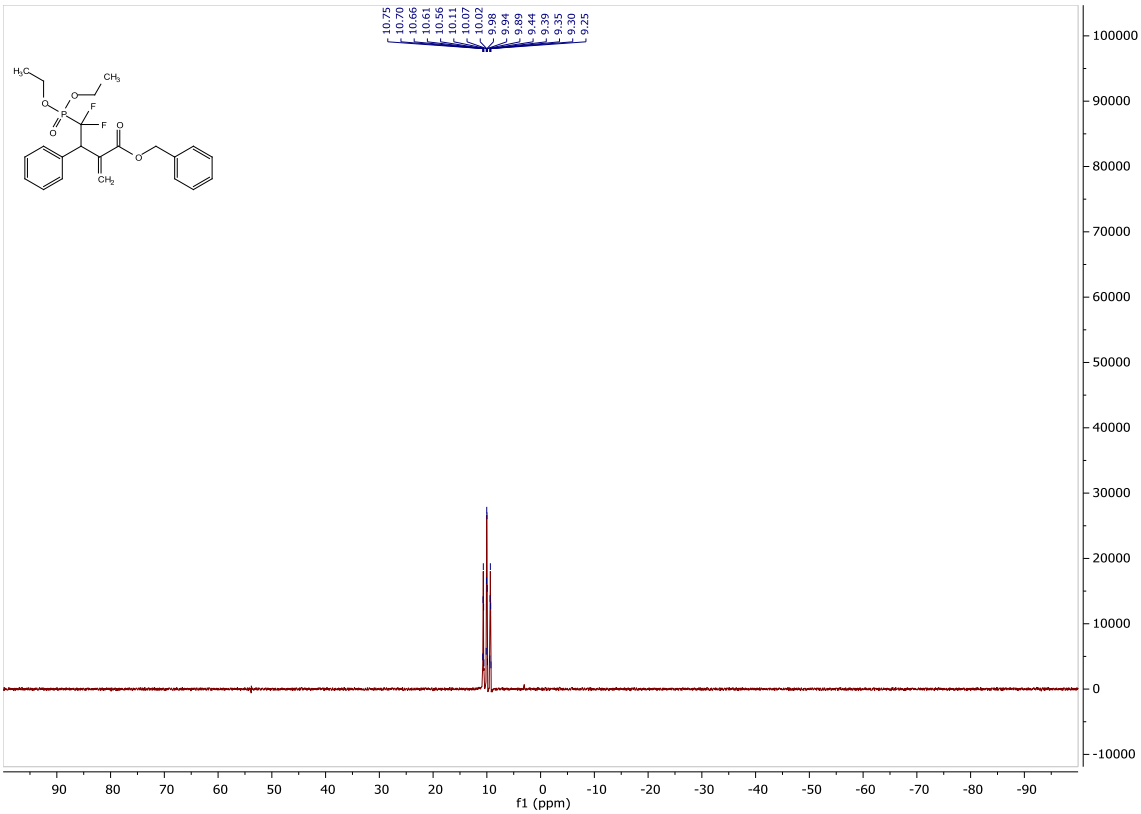

10.79
10.74
10.70
10.65
10.60
10.11
10.06
10.02
9.97
9.93
9.48
9.43
9.38
9.33
9.28
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

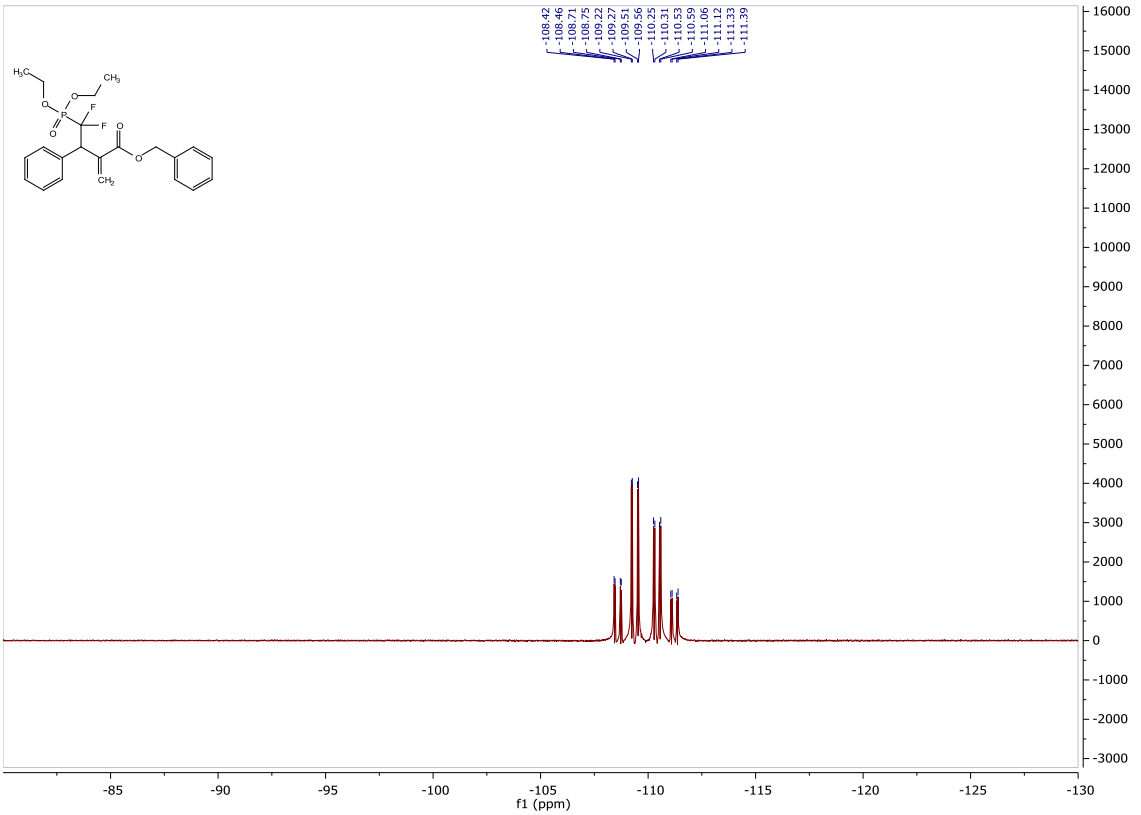

-108.39
-108.43
-108.68
-108.72
-109.19
-109.23
-109.48
-109.52
-110.38
-110.44
-110.65
-110.72
-111.18
-111.24
-111.46
-111.52
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

benzyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3d)

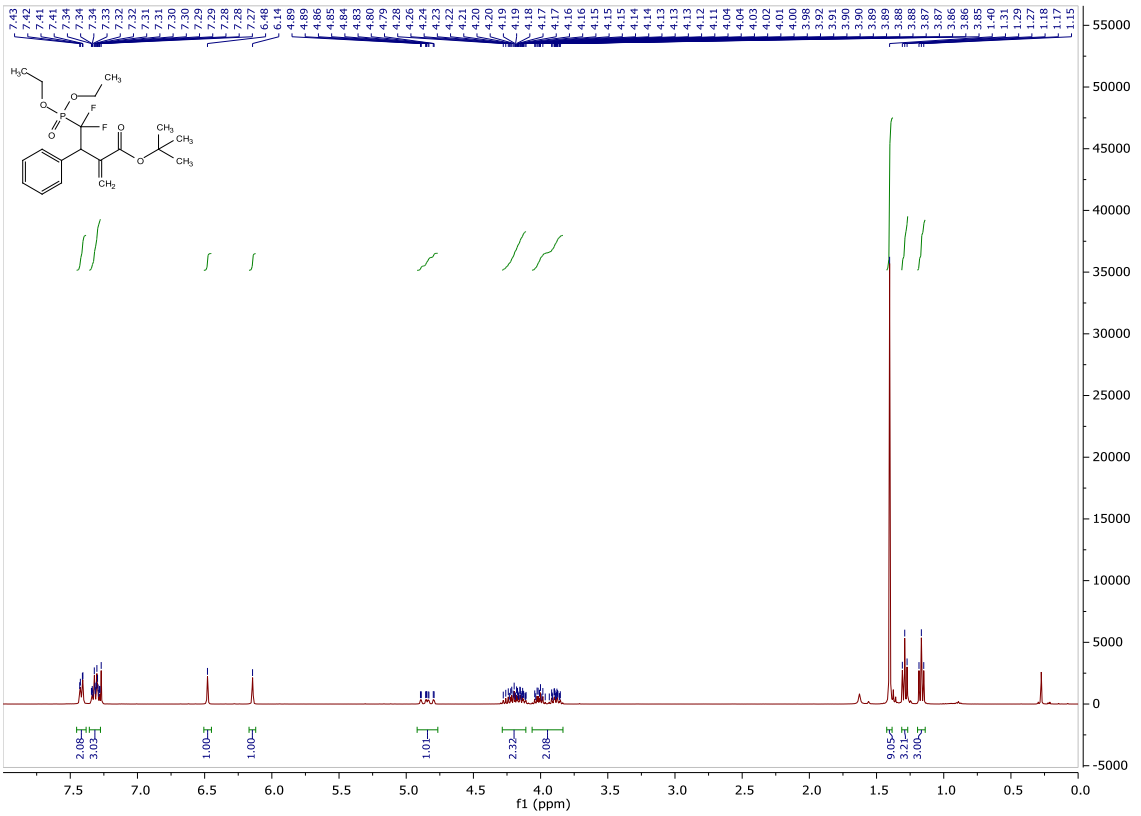


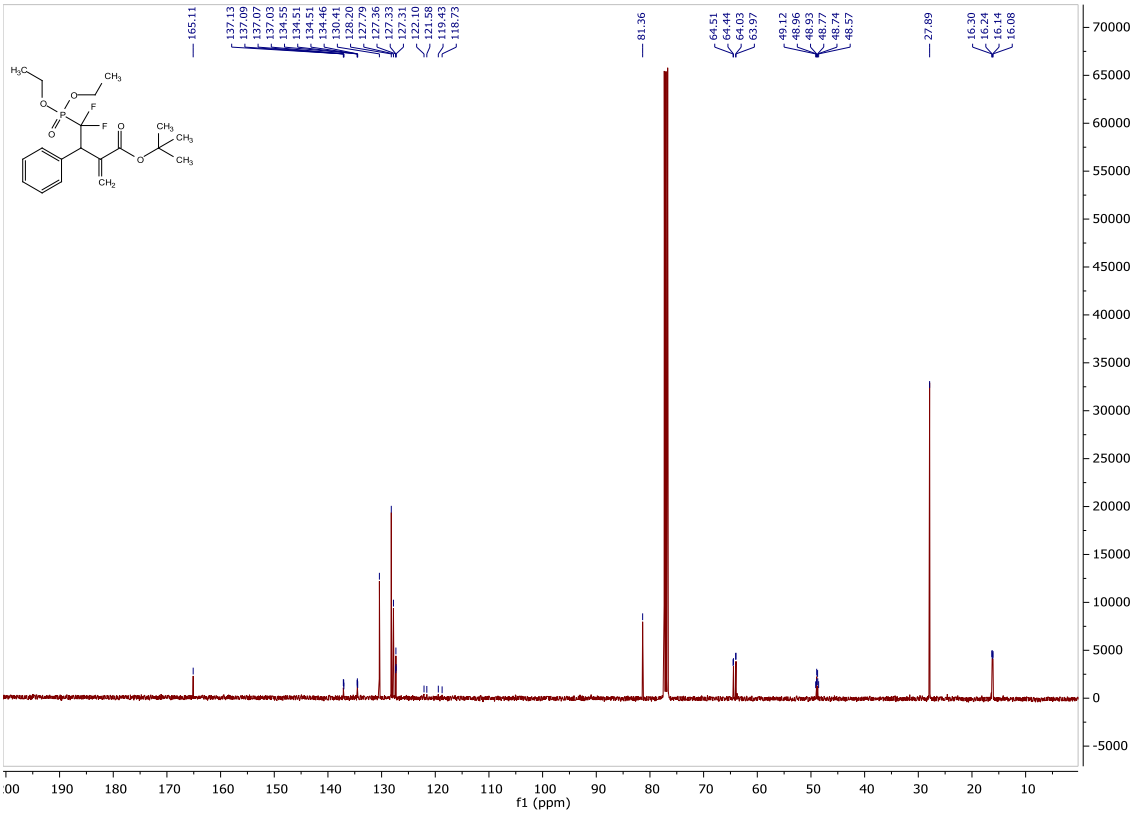


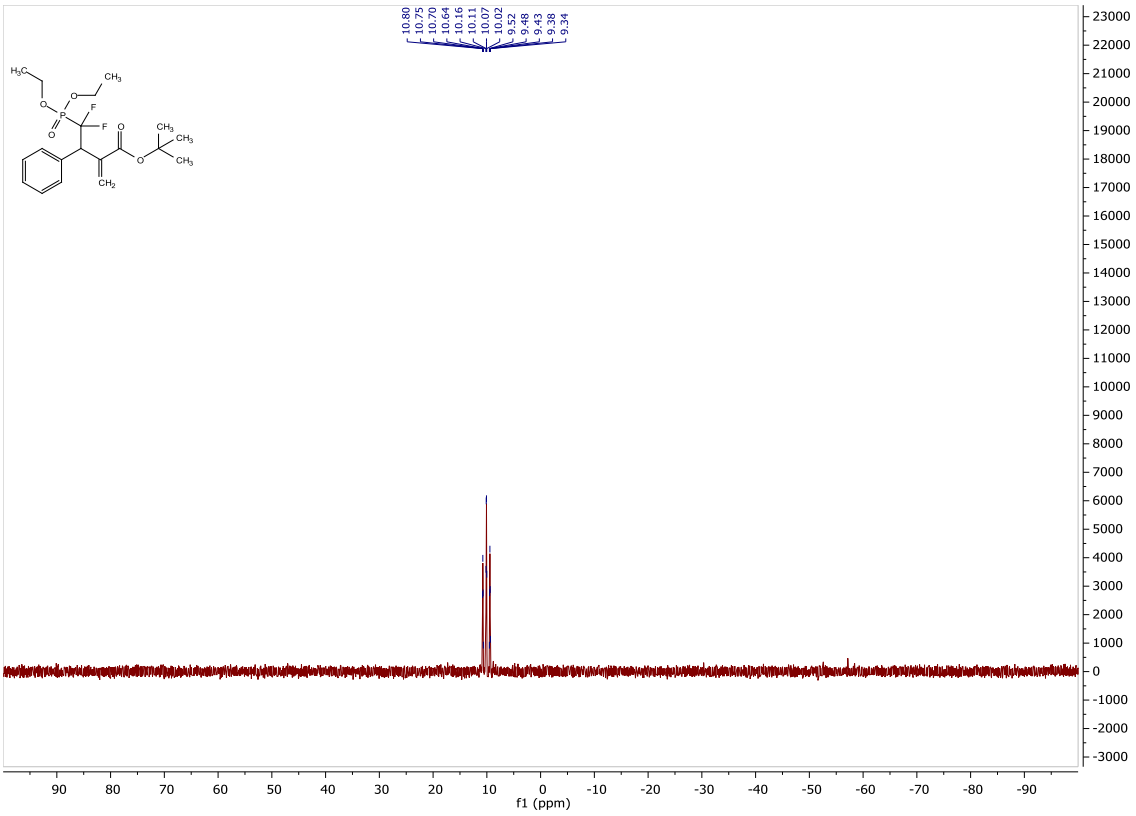

10.75
10.70
10.66
10.61
10.56
10.11
10.07
10.02
9.98
9.94
9.89
9.44
9.39
9.35
9.30
9.25
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

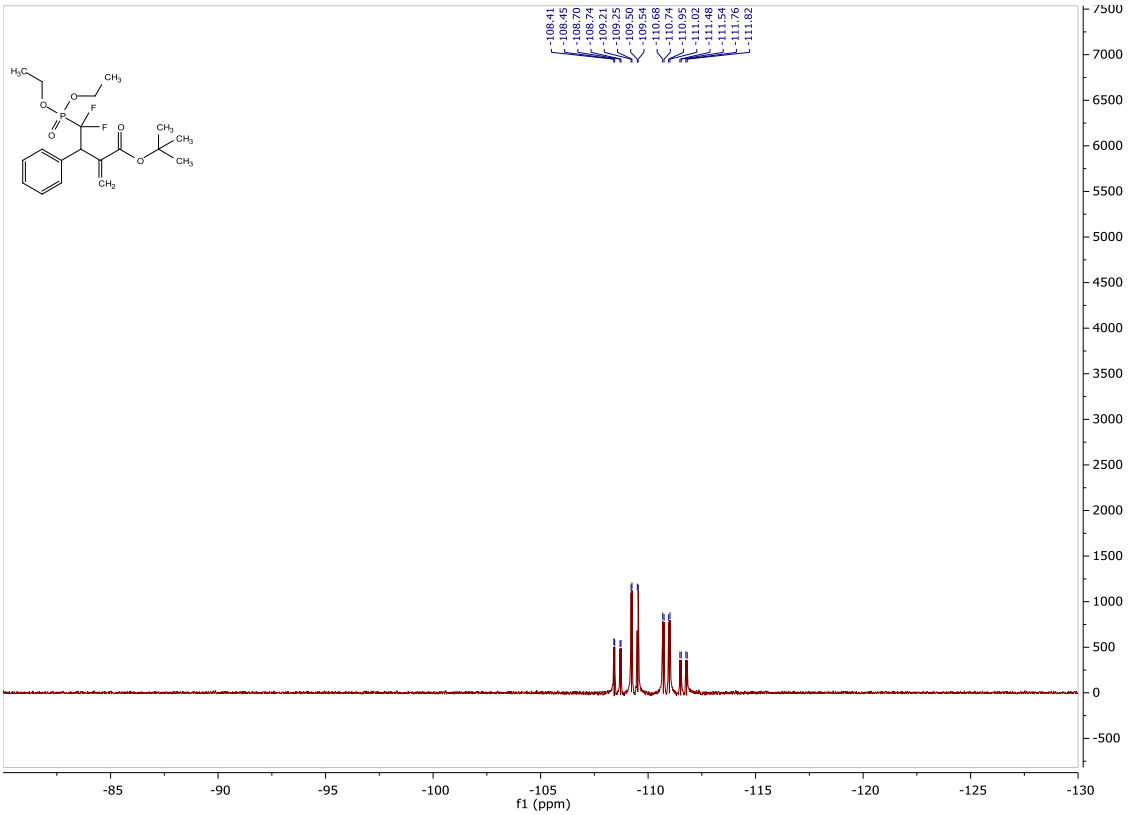

-108.42
-108.46
-108.71
-108.75
-109.22
-109.27
-109.51
-109.56
-110.25
-110.31
-110.53
-110.59
-111.06
-111.12
-111.33
-111.39
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

tert-butyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-phenylbutanoate (*S*-3e)

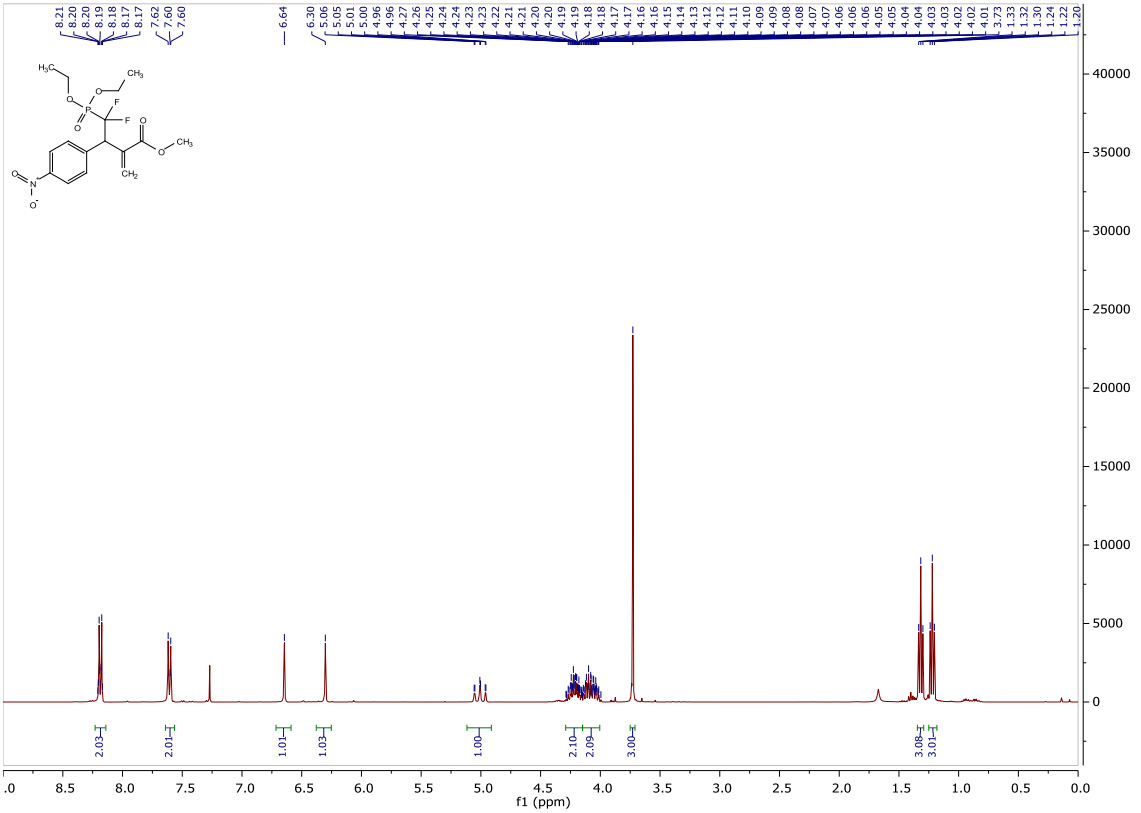


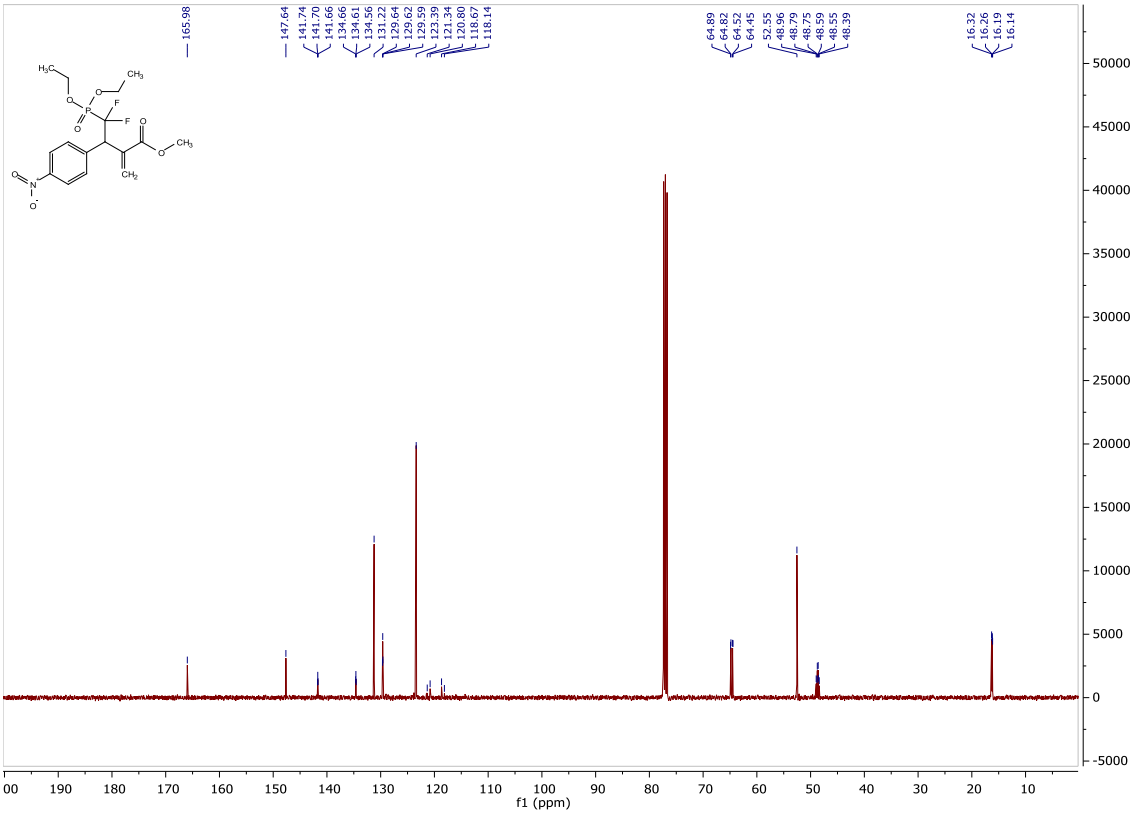


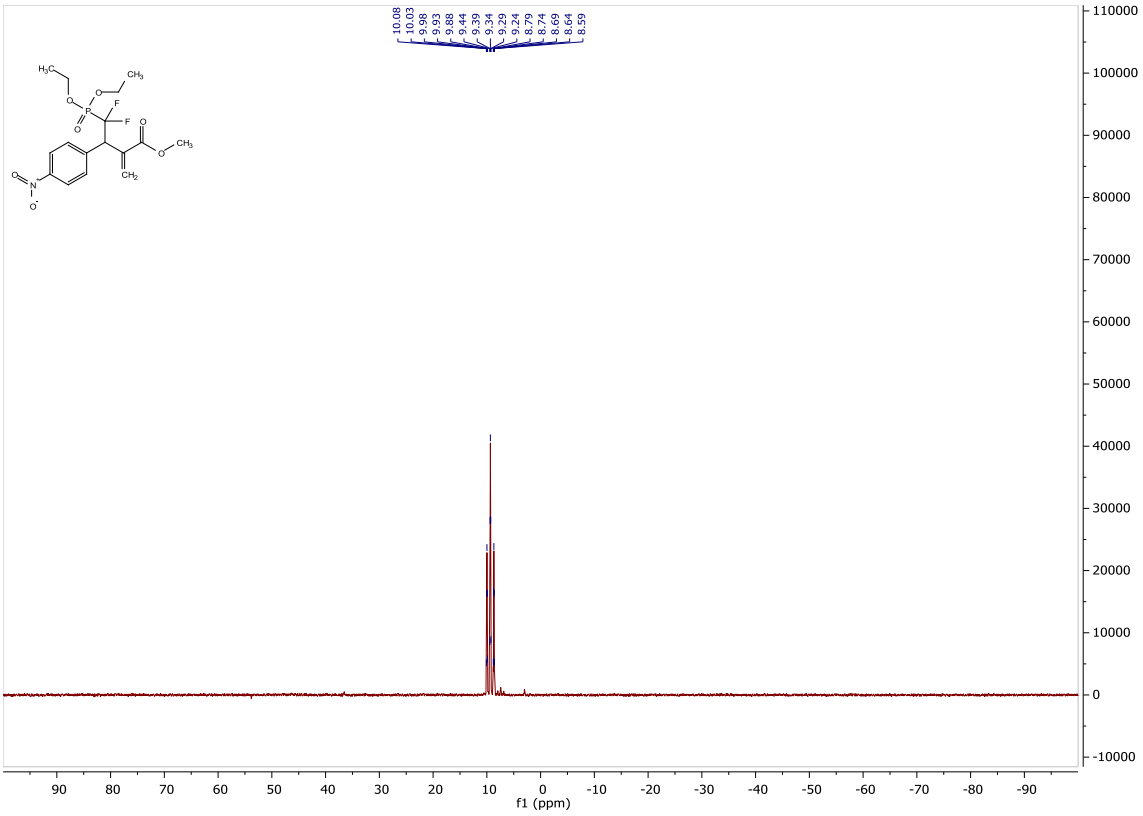

10.80
10.75
10.70
10.64
10.16
10.11
10.07
10.02
9.52
9.48
9.43
9.38
9.34
f1 (ppm)

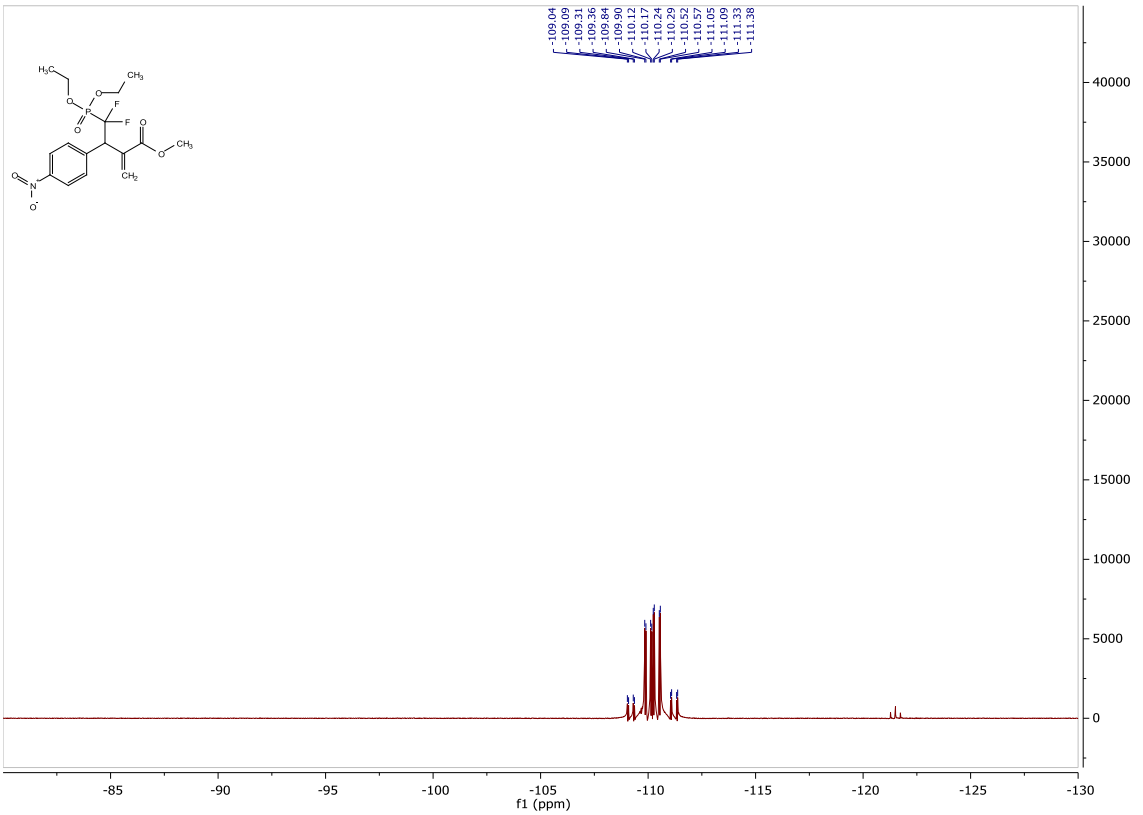

-108.41
-108.45
-108.70
-108.74
-109.21
-109.25
-109.50
-109.54
-110.68
-110.74
-110.95
-111.02
-111.48
-111.54
-111.76
-111.82
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-nitrophenyl)butanoate (*S*-3g)

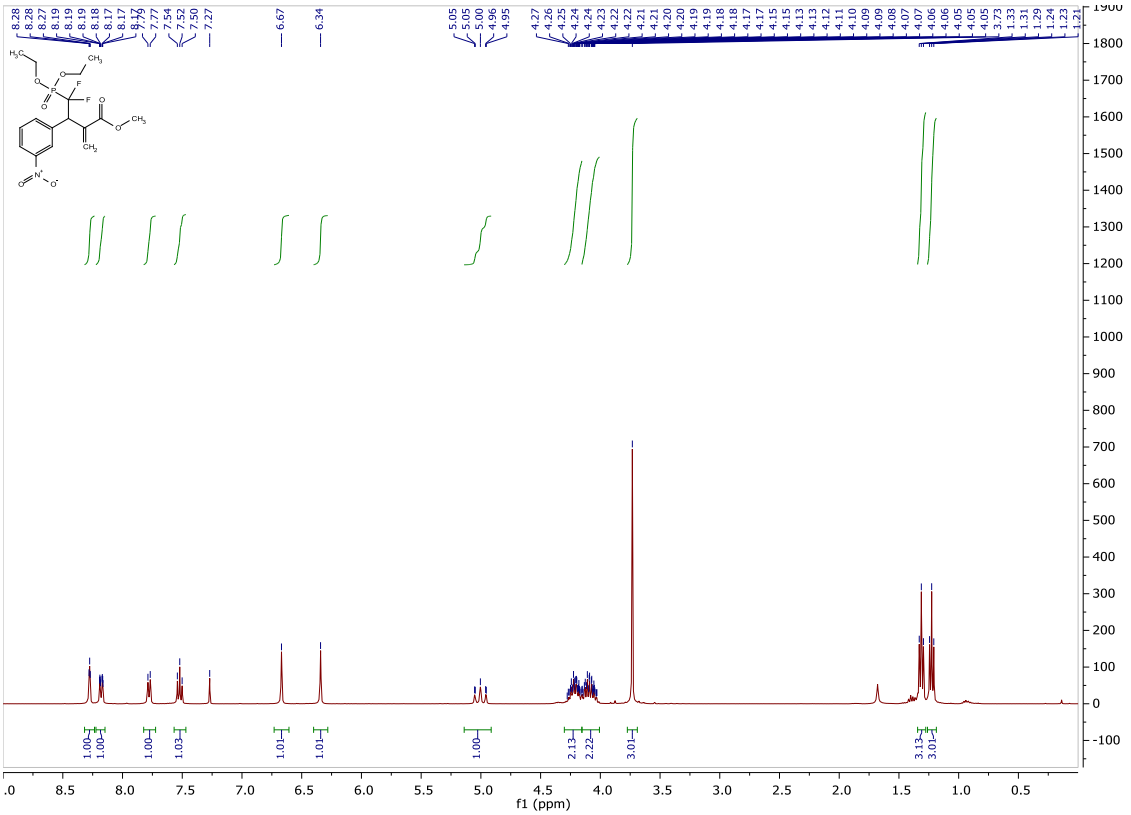


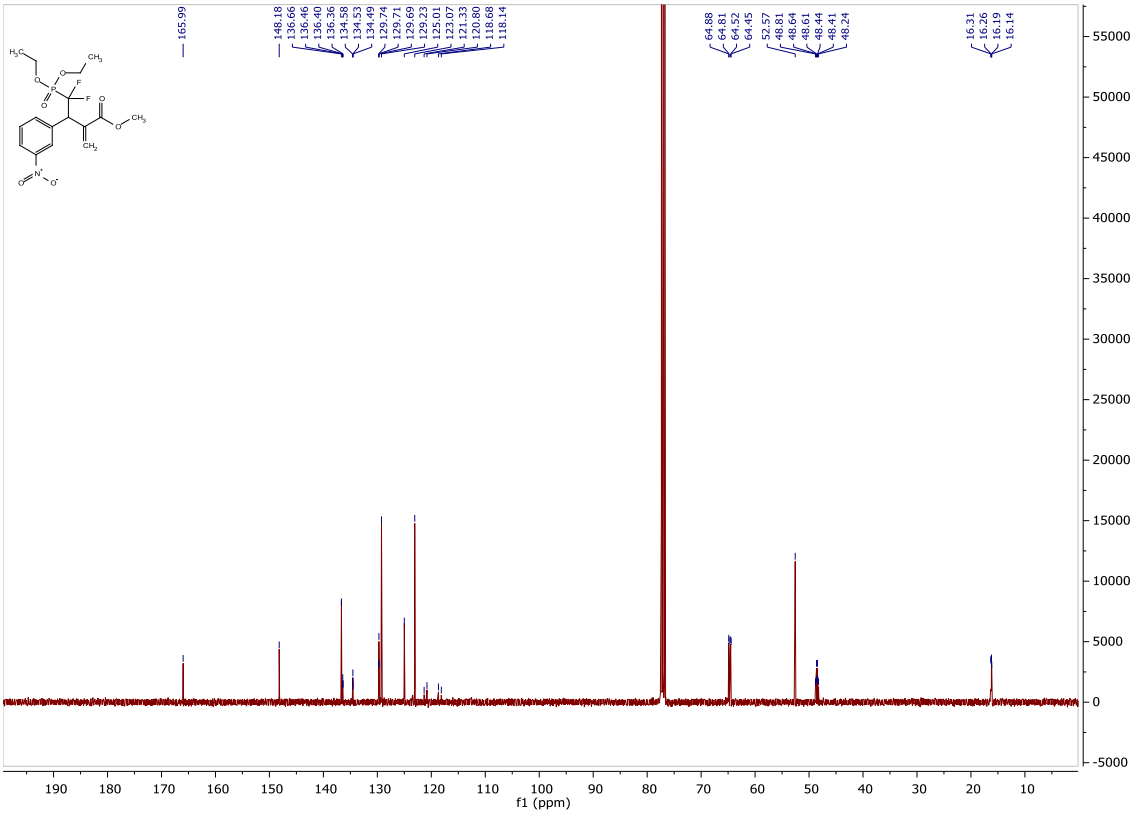


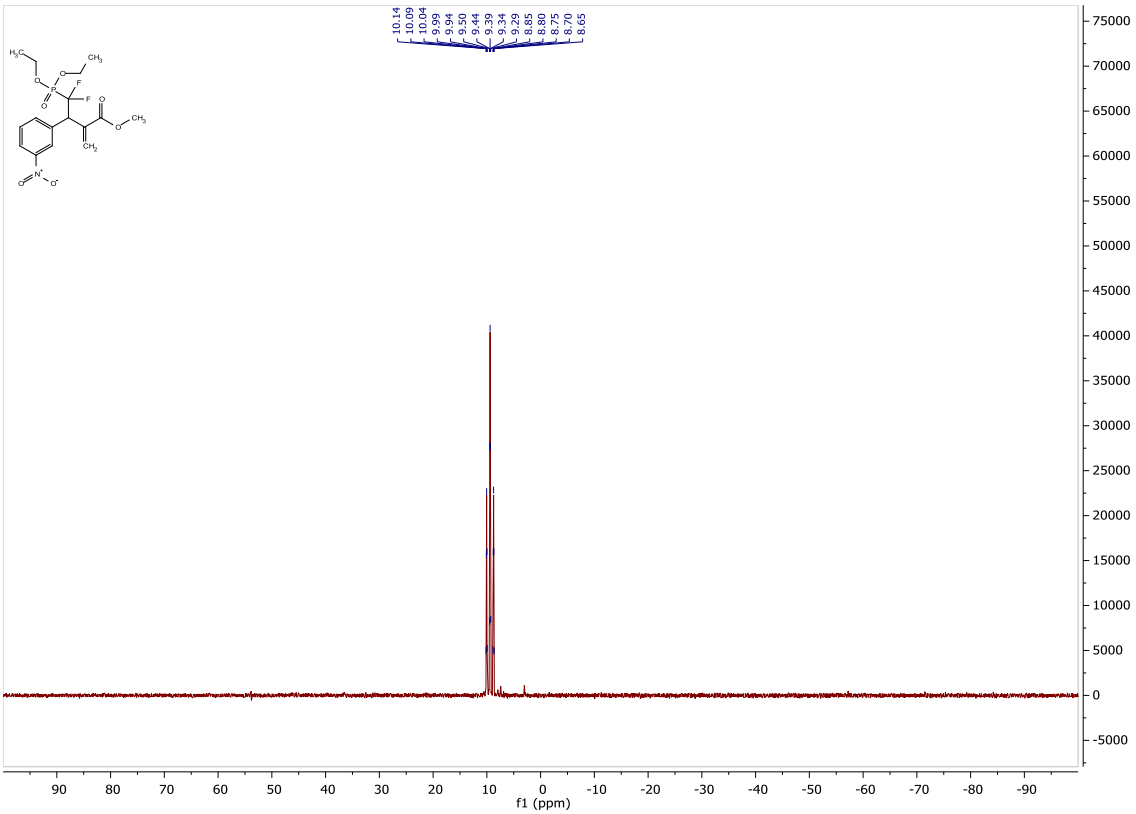

10.08
10.03
9.98
9.93
9.88
9.44
9.39
9.34
9.29
9.24
8.79
8.74
8.69
8.64
8.59
f1 (ppm)

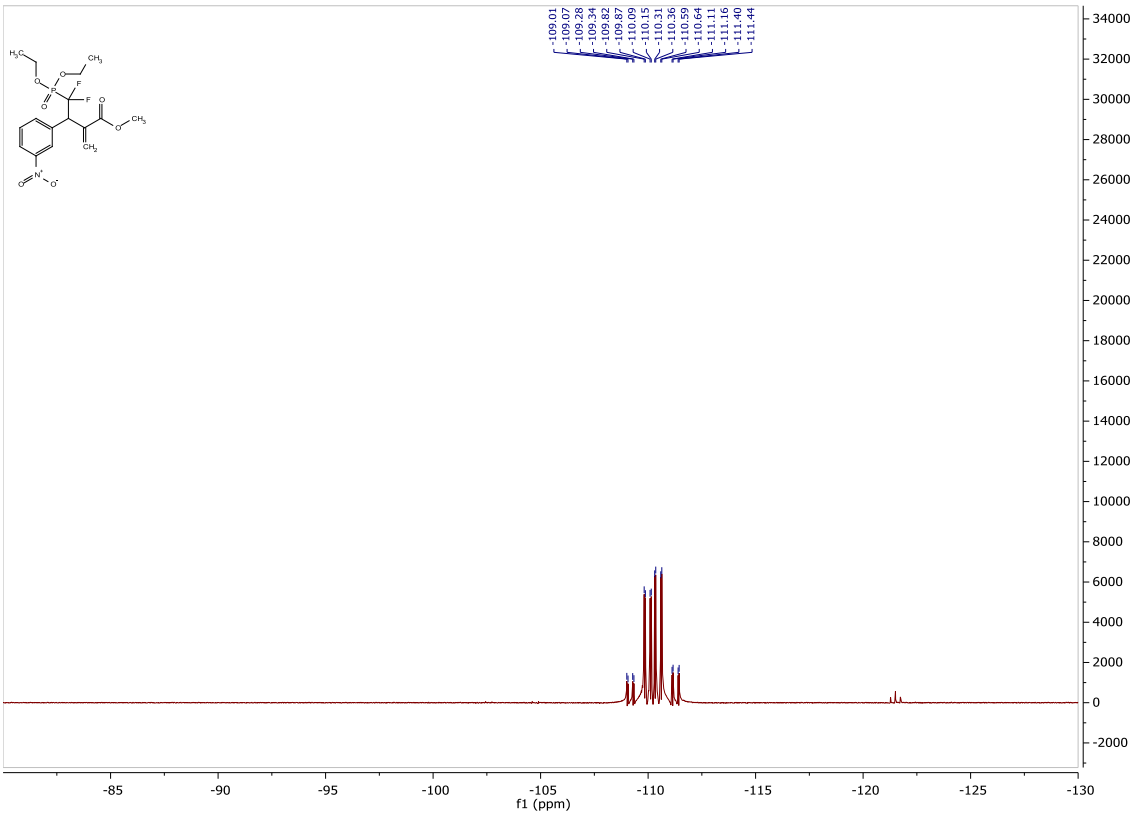

-109.04
-109.09
-109.31
-109.36
-109.84
-109.90
-110.12
-110.17
-110.24
-110.29
-110.52
-110.57
-111.05
-111.09
-111.33
-111.38
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(3-nitrophenyl)butanoate (*S*-3h)

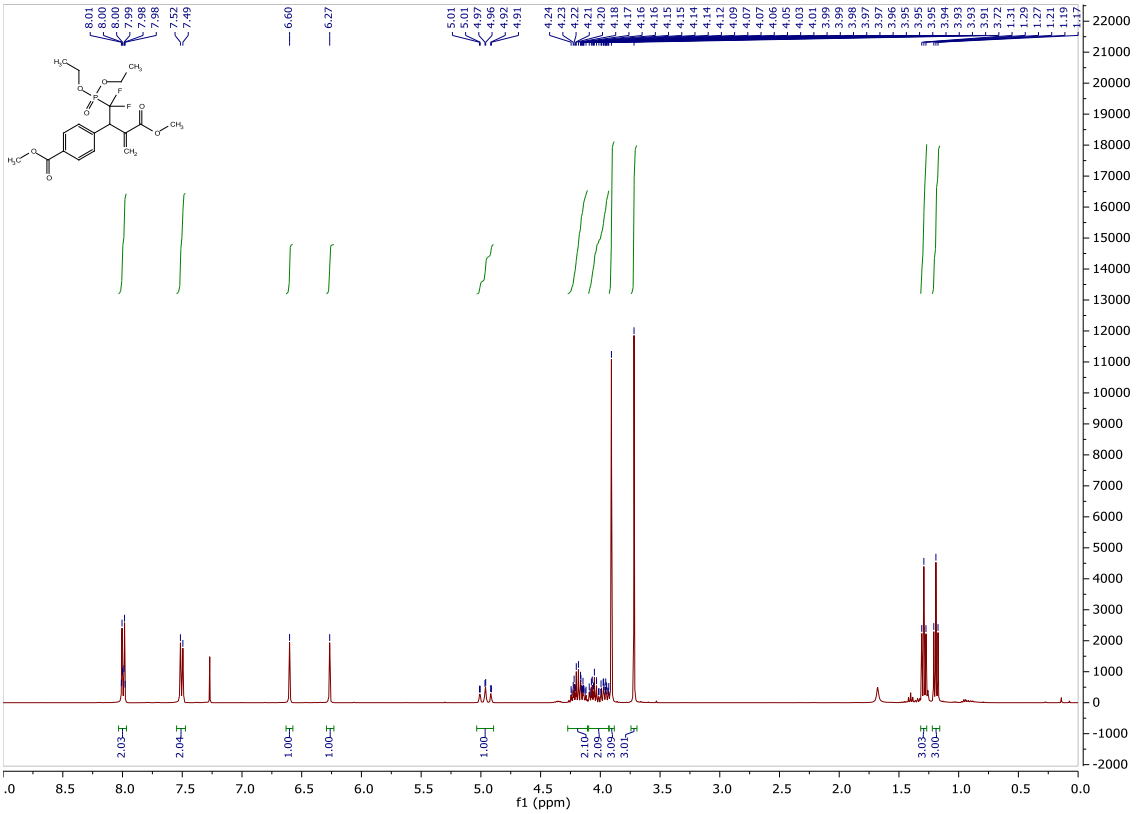


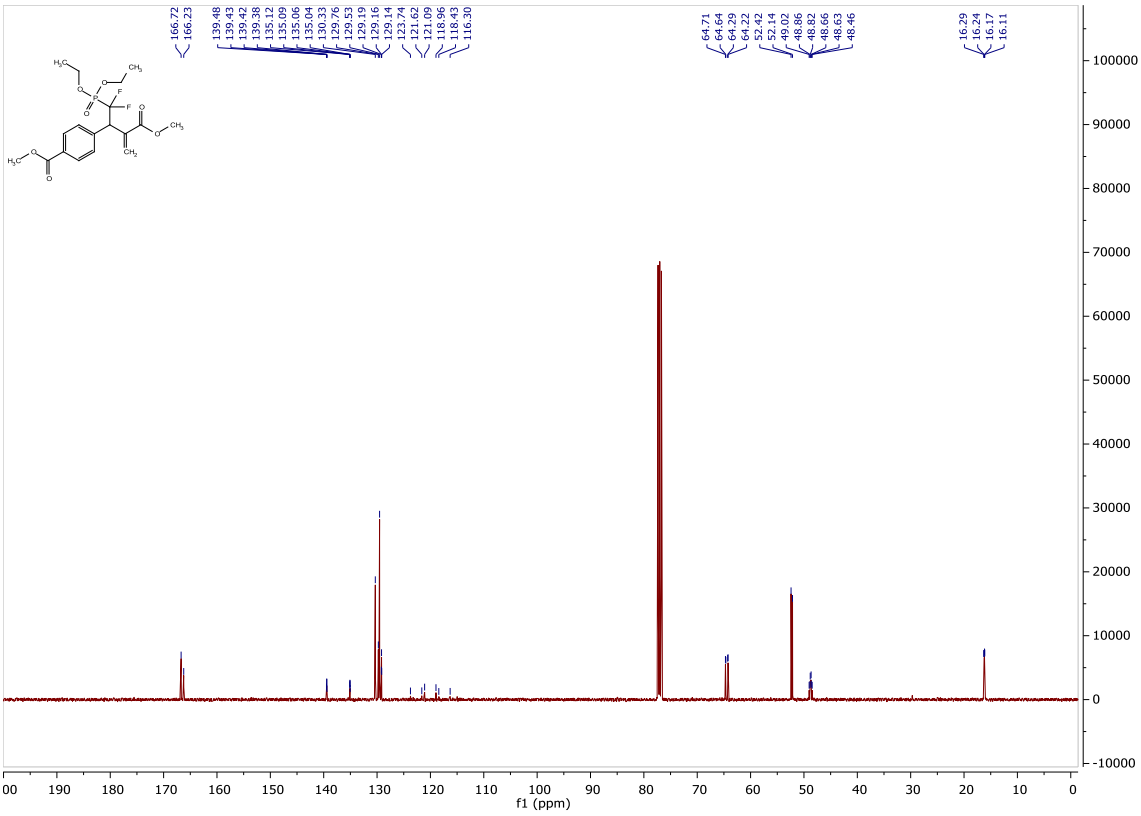


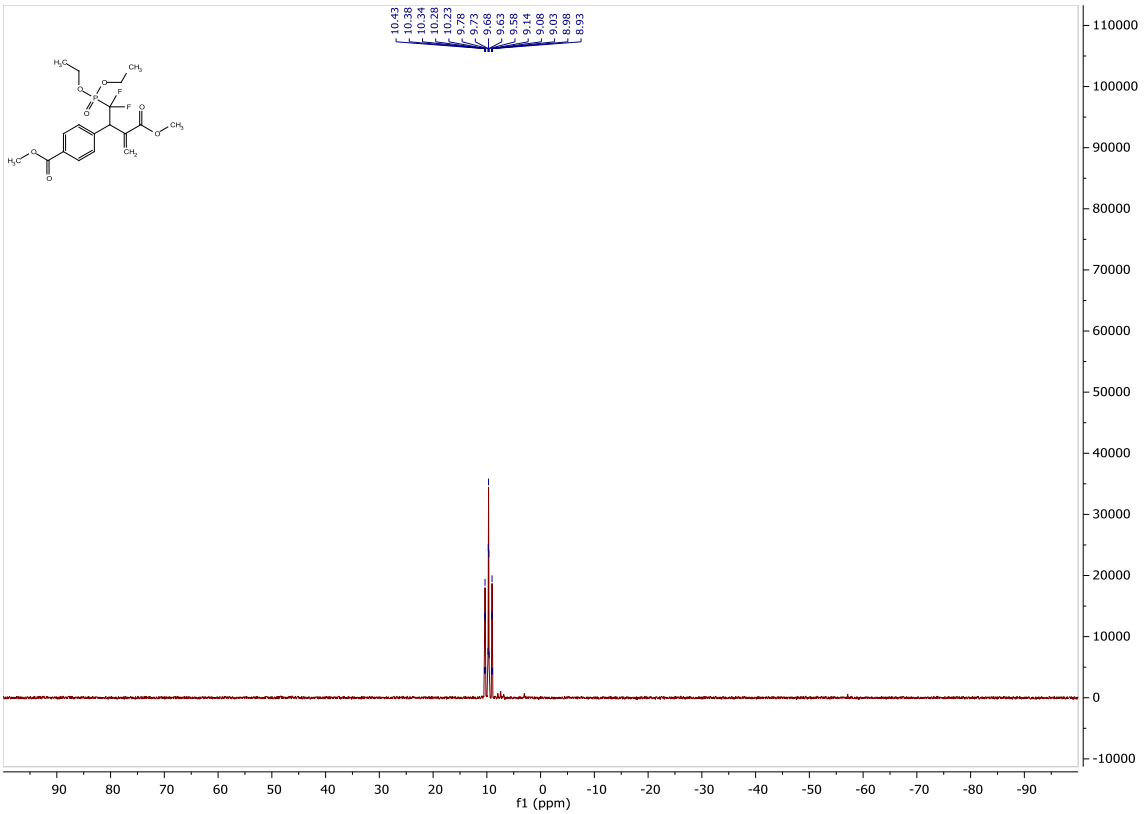

10.14
10.09
10.04
9.99
9.94
9.50
9.44
9.39
9.34
9.29
8.85
8.80
8.75
8.70
8.65
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

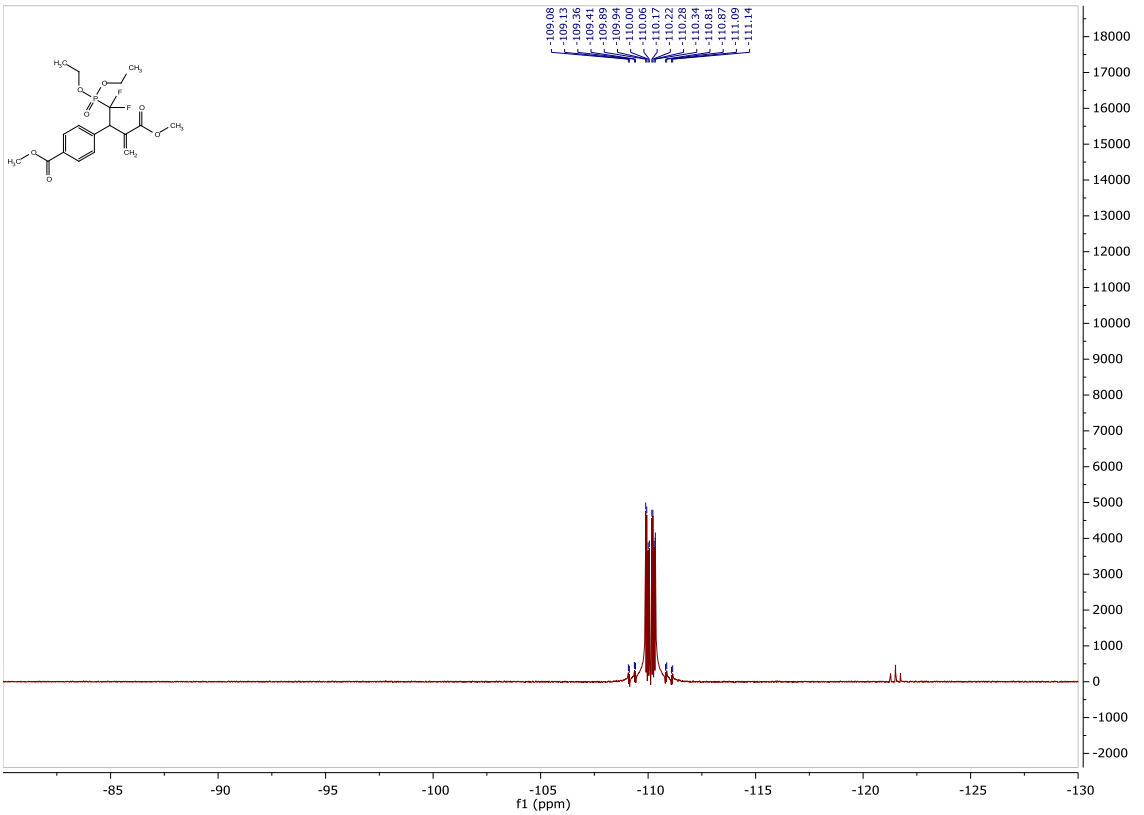

-109.01
-109.07
-109.28
-109.34
-109.82
-109.87
-110.09
-110.15
-110.31
-110.36
-110.59
-110.64
-111.11
-111.16
-111.40
-111.44
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-4-(1-(diethoxyphosphoryl)-1,1-difluoro-3-(methoxycarbonyl)but-3-en-2-yl)benzoate (*S*-3i)

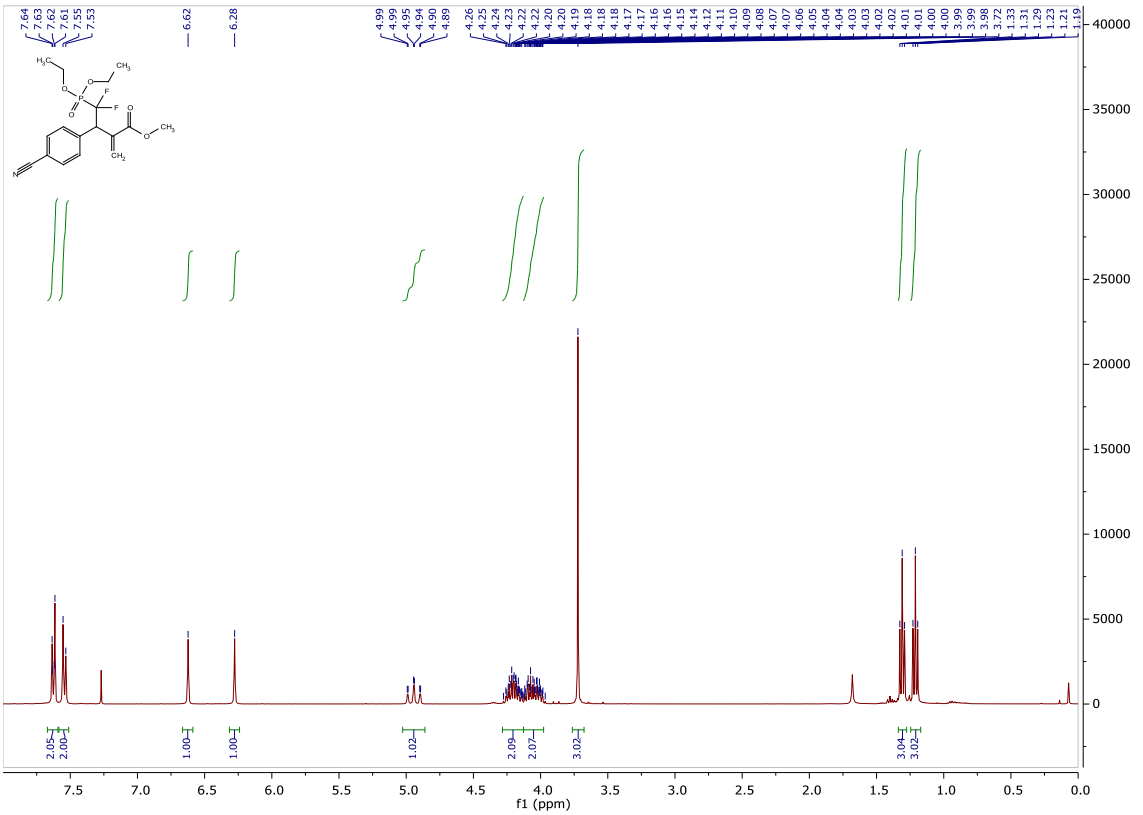


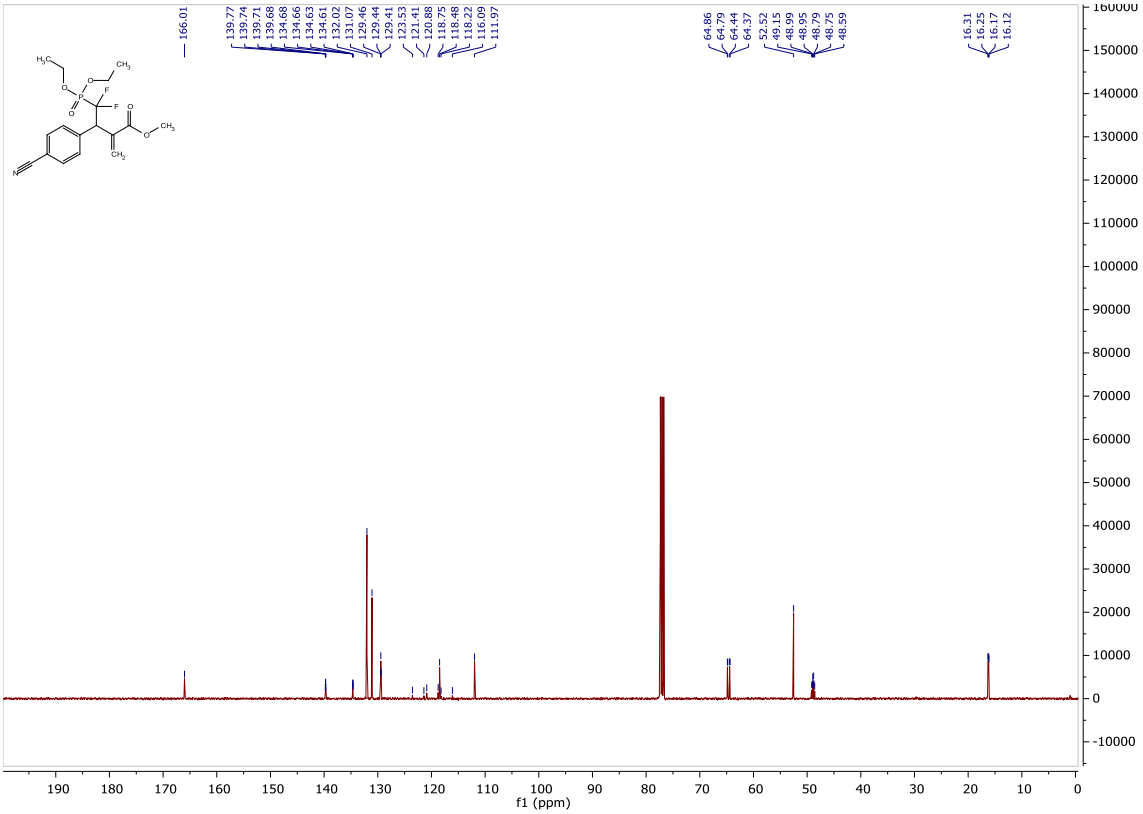


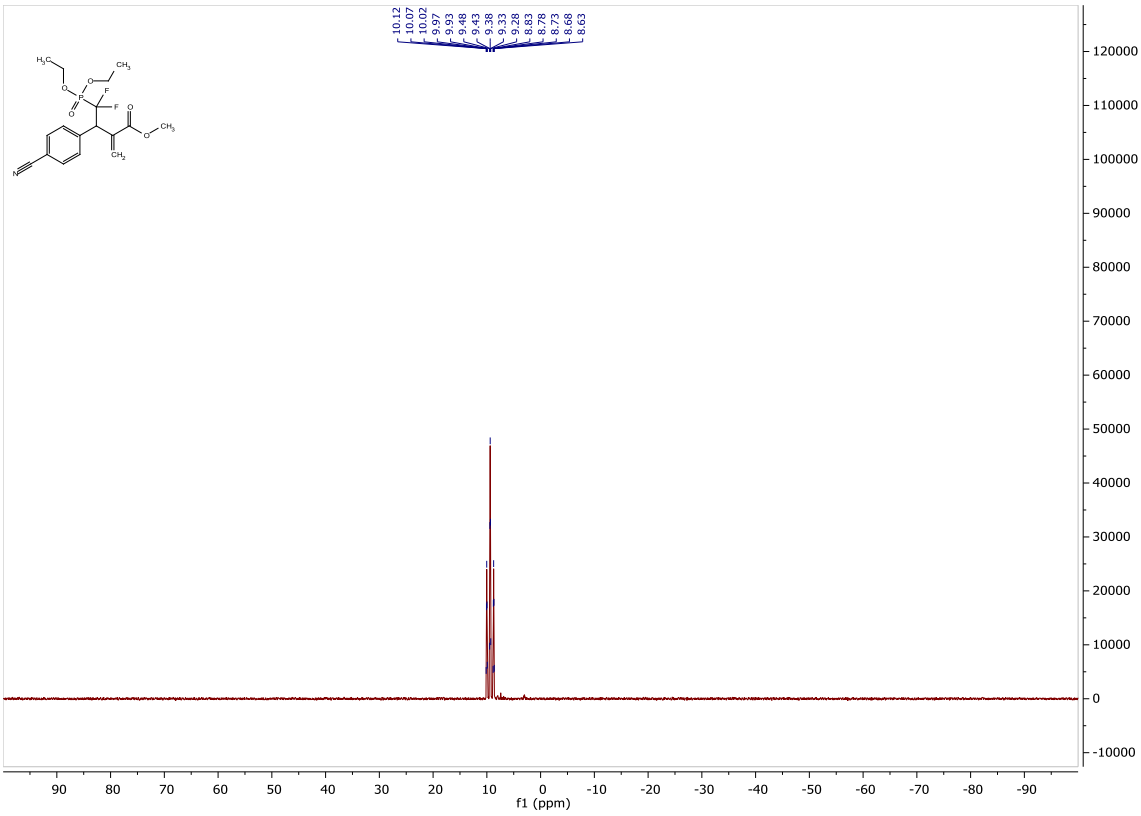

10.43
10.38
10.34
10.28
10.23
9.78
9.73
9.68
9.63
9.58
9.14
9.08
9.03
8.98
8.93
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

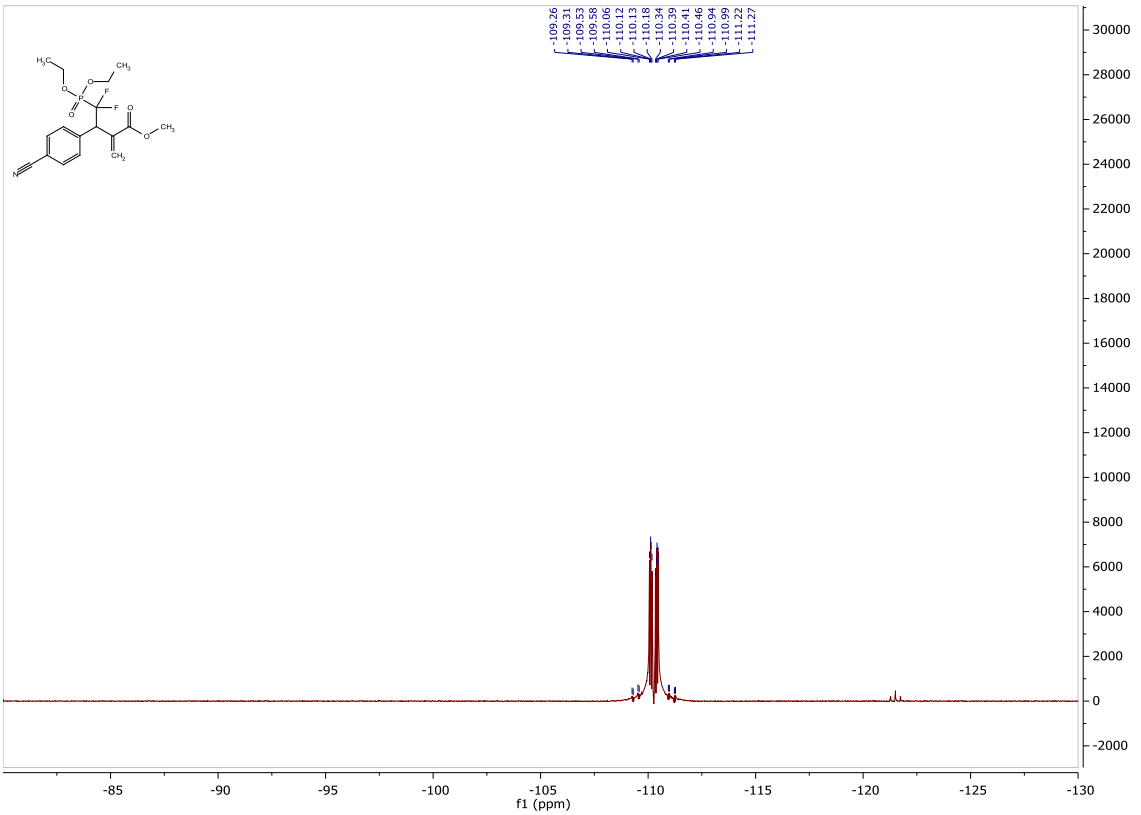

-109.08
-109.13
-109.36
-109.41
-109.89
-109.94
-110.00
-110.06
-110.17
-110.22
-110.28
-110.34
-110.81
-110.87
-111.09
-111.14
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-3-(4-cyanophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3j)

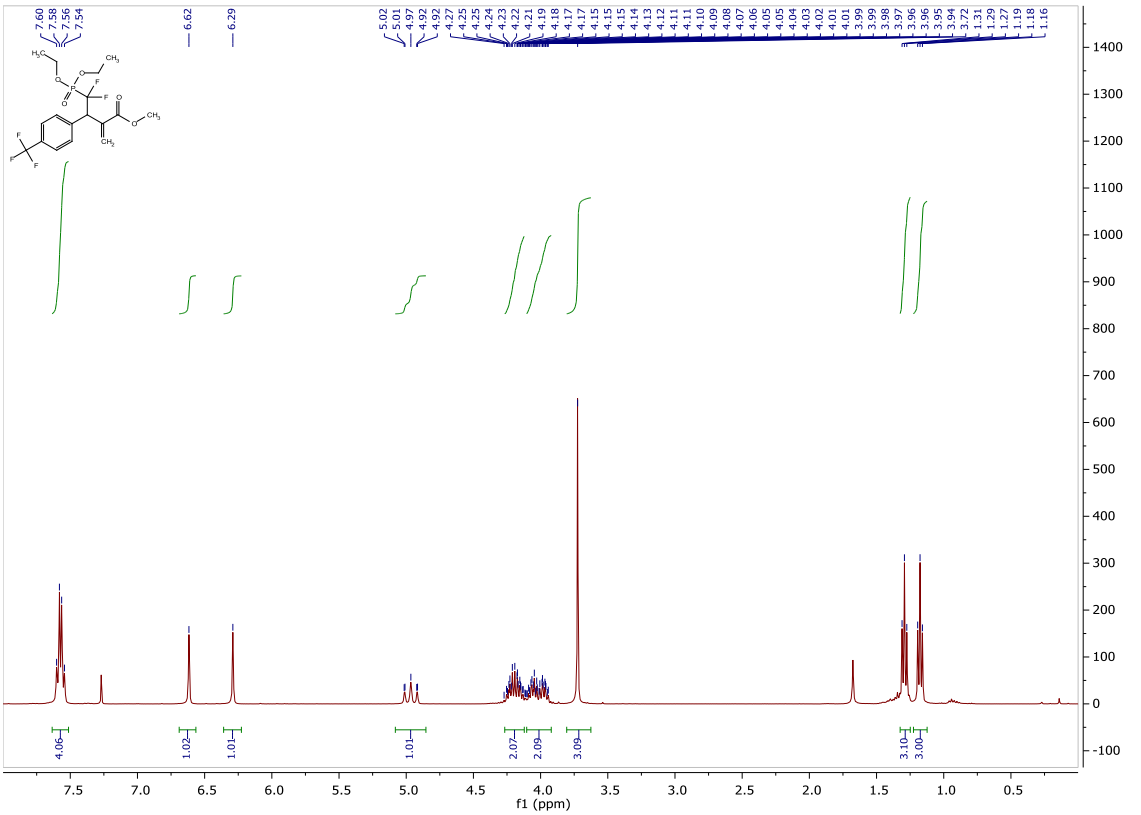


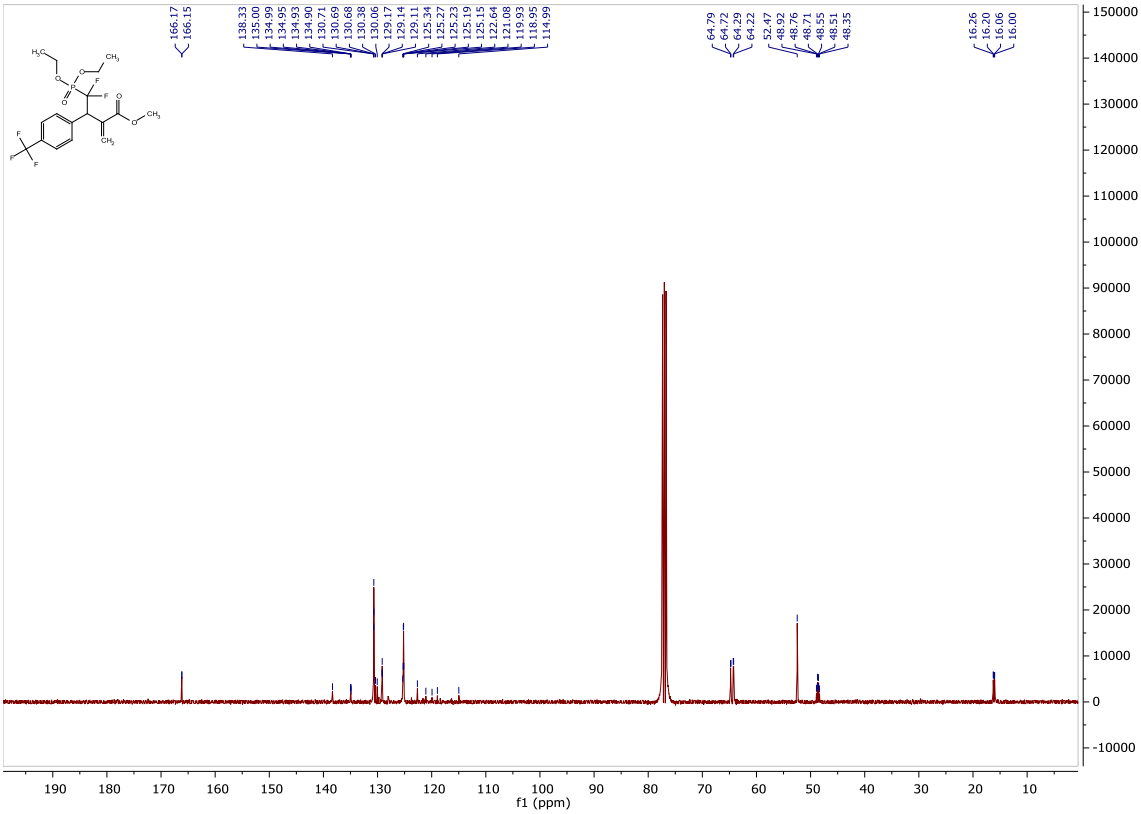


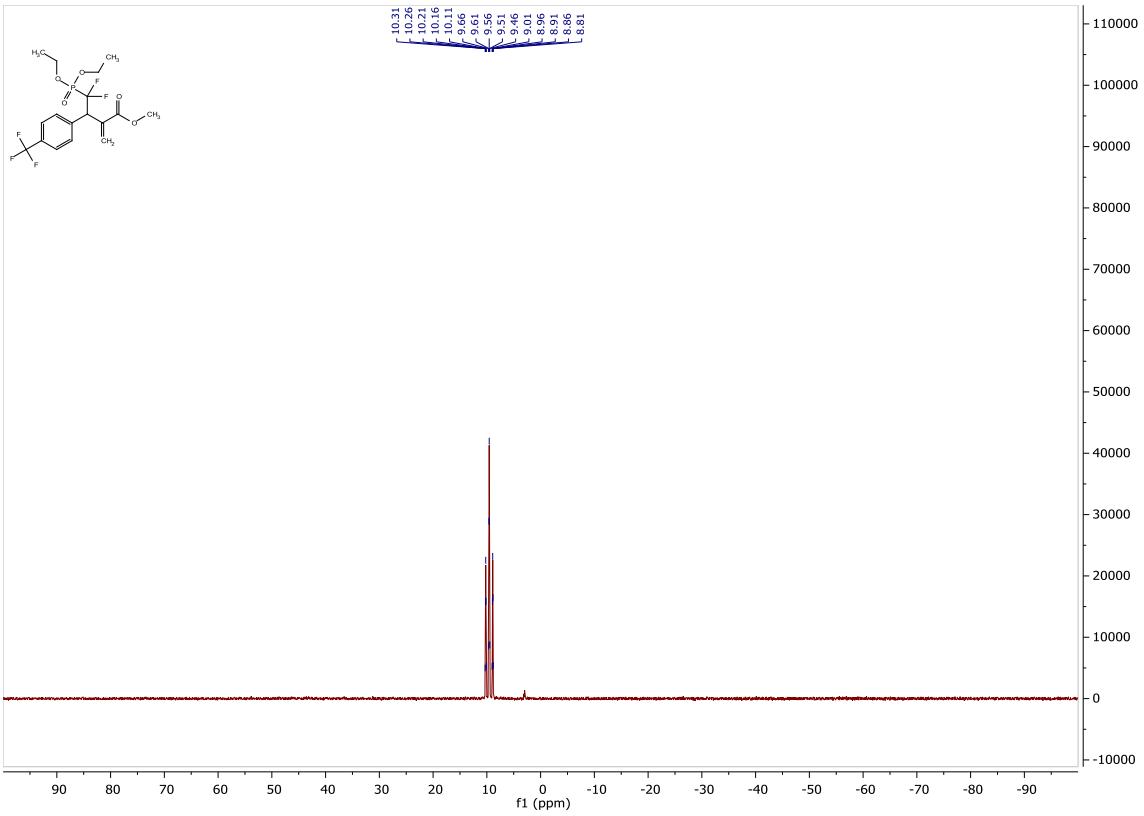

10.12
10.07
10.02
9.97
9.93
9.48
9.43
9.38
9.33
9.28
8.83
8.78
8.73
8.68
8.63
f1 (ppm)

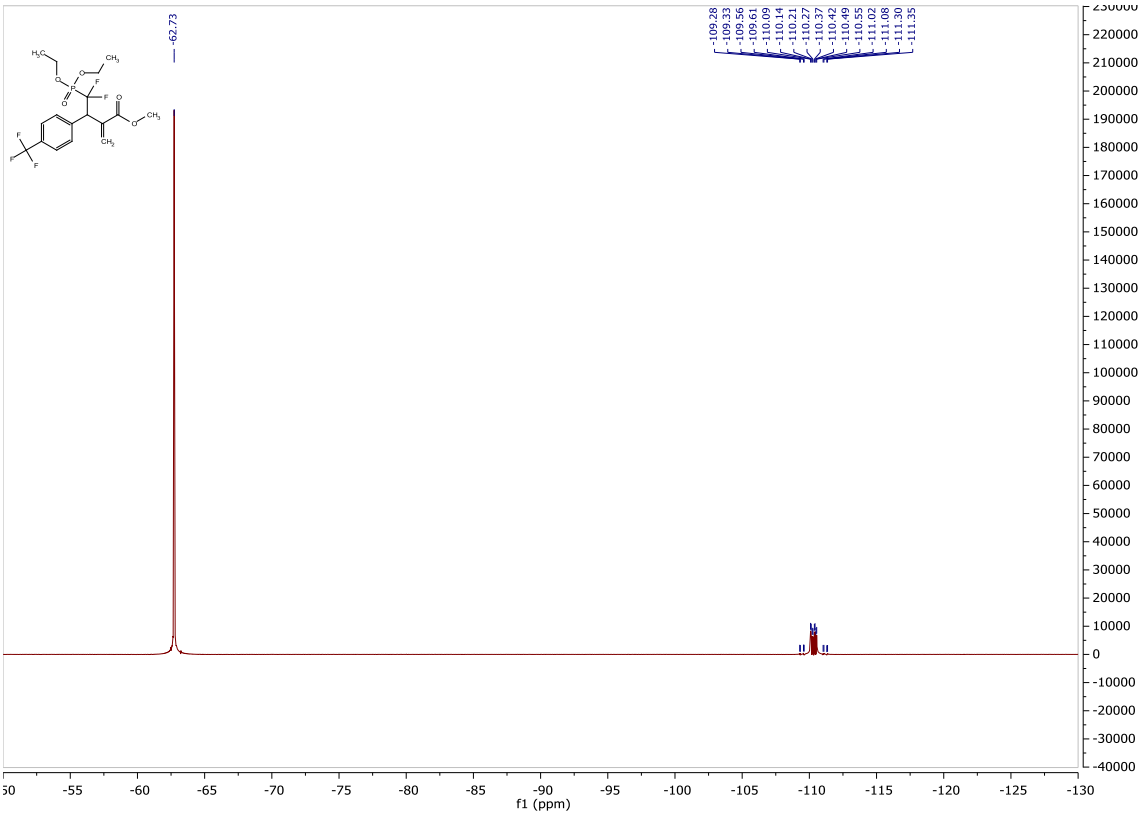

-109.26
-109.31
-109.53
-109.58
-110.06
-110.12
-110.13
-110.18
-110.34
-110.39
-110.41
-110.46
-110.94
-110.99
-111.22
-111.27
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-(trifluoromethyl)phenyl)butanoate (*S*-3k)

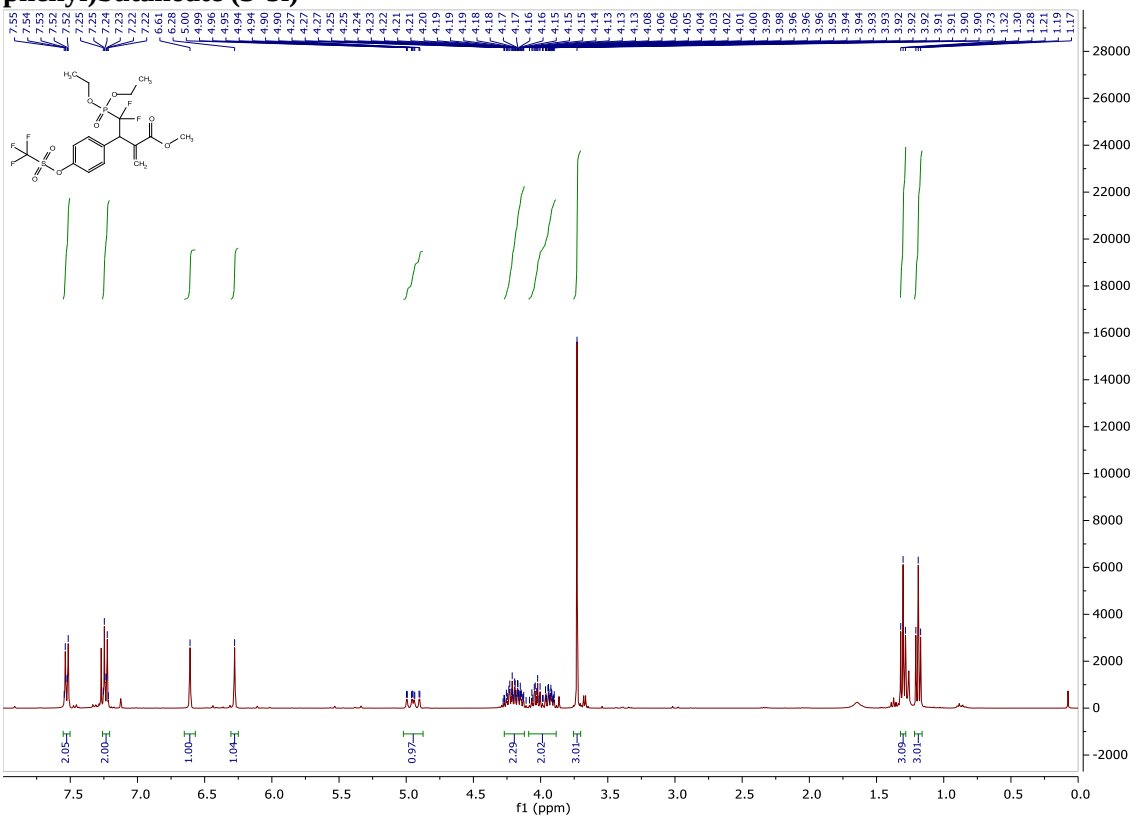


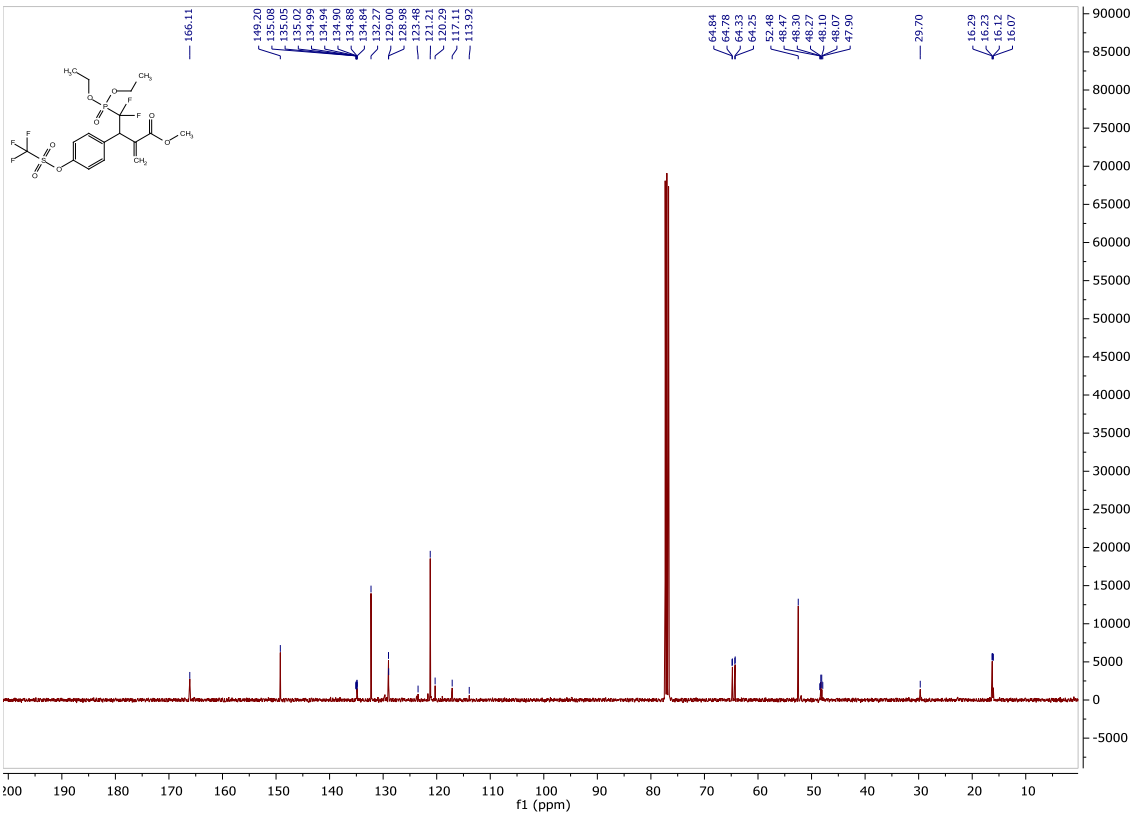


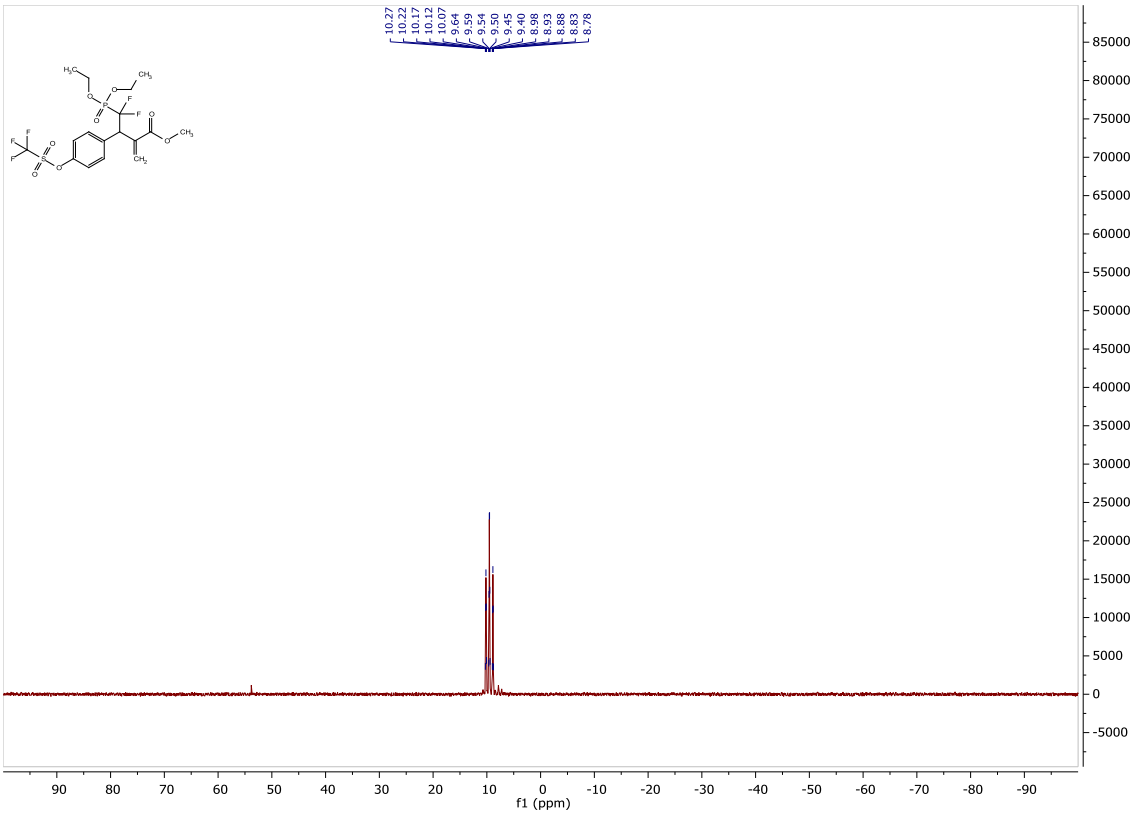

10.31
10.26
10.21
10.16
10.11
9.66
9.61
9.56
9.51
9.46
9.01
8.96
8.91
8.86
8.81
f1 (ppm)

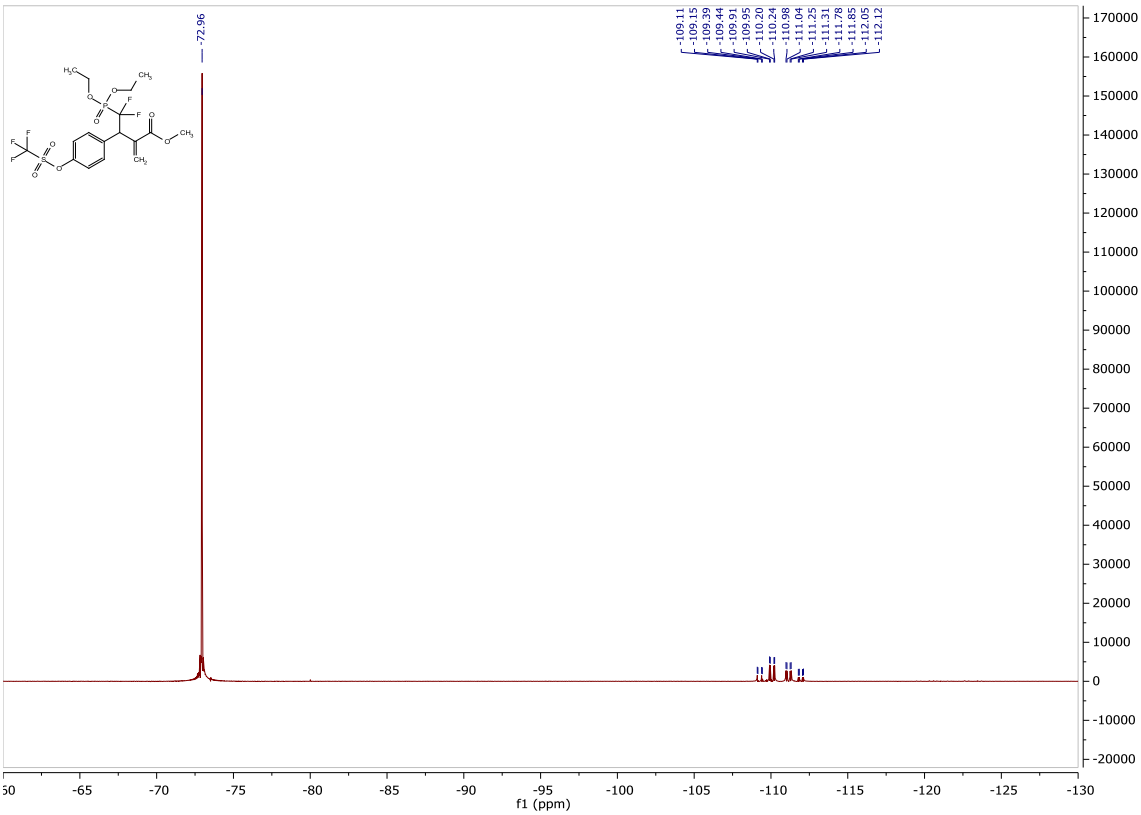

-62.73
-109.28
-109.33
-109.56
-109.61
-110.09
-110.14
-110.21
-110.27
-110.37
-110.42
-110.49
-110.55
-111.02
-111.08
-111.30
-111.35
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(4-(((trifluoromethyl)sulfonyl)oxy) phenyl)butanoate (*S*-3l)

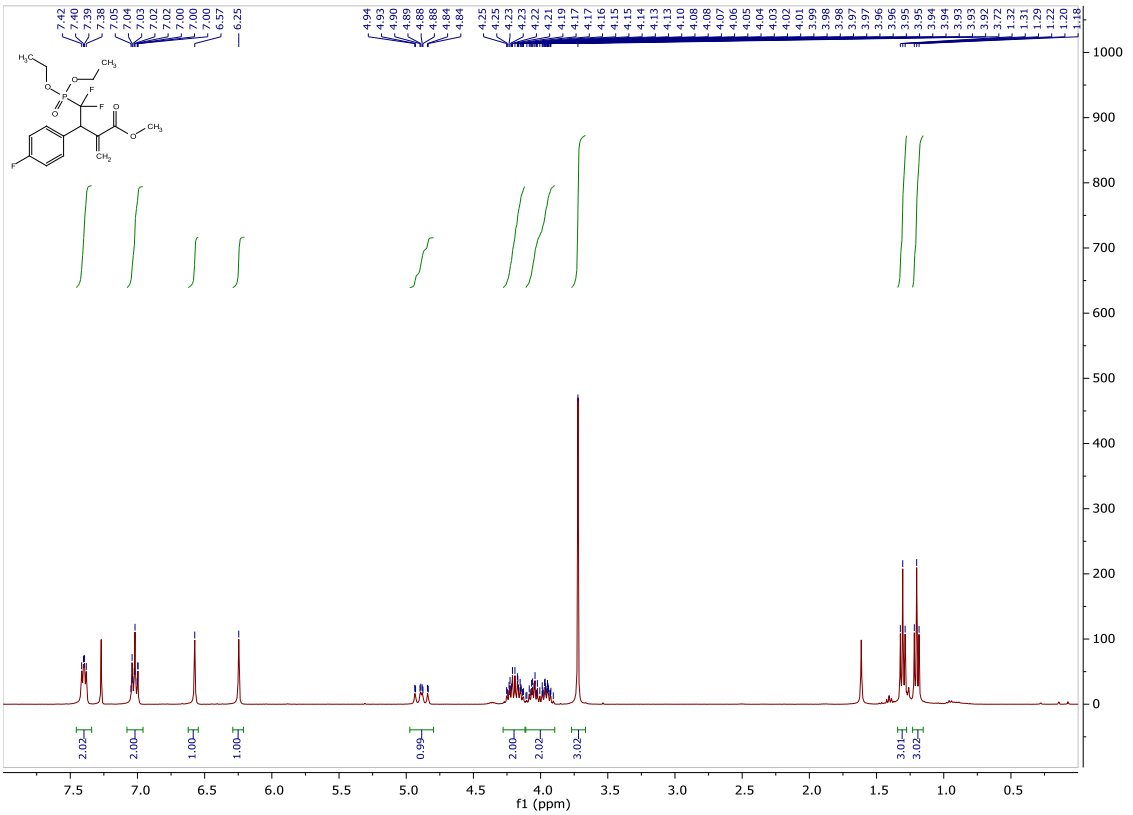


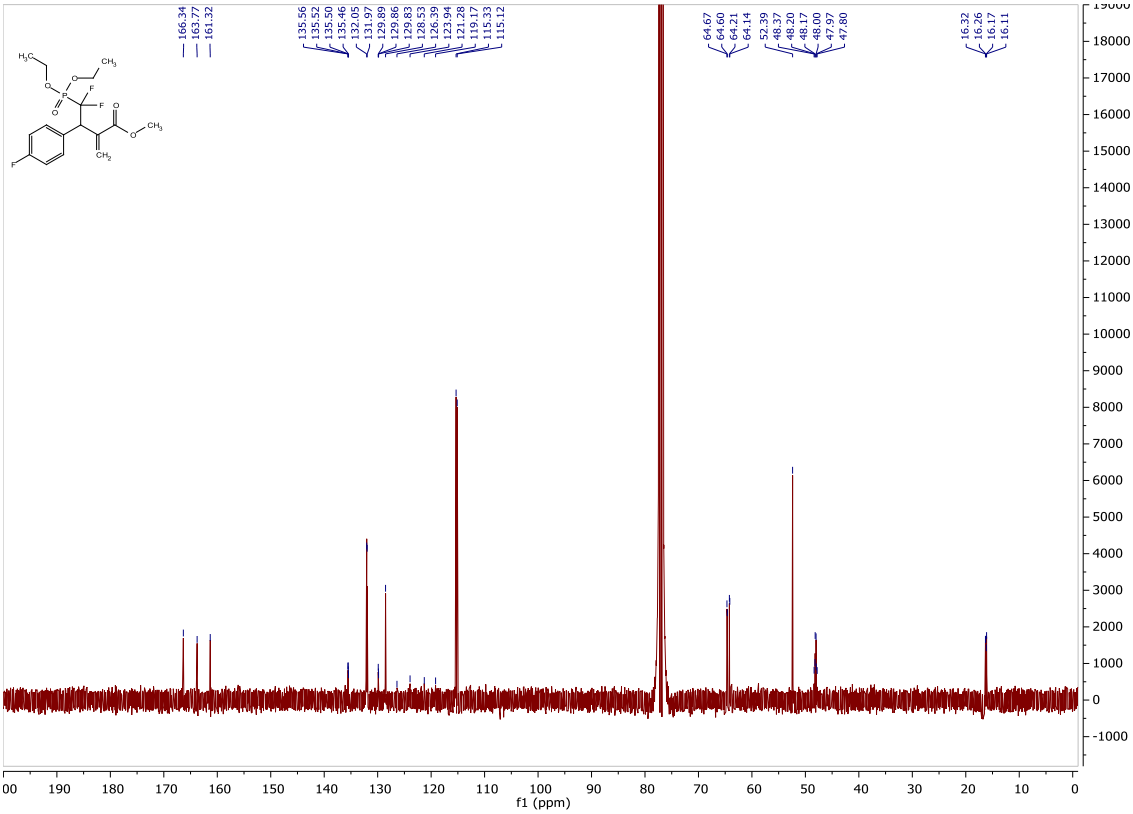


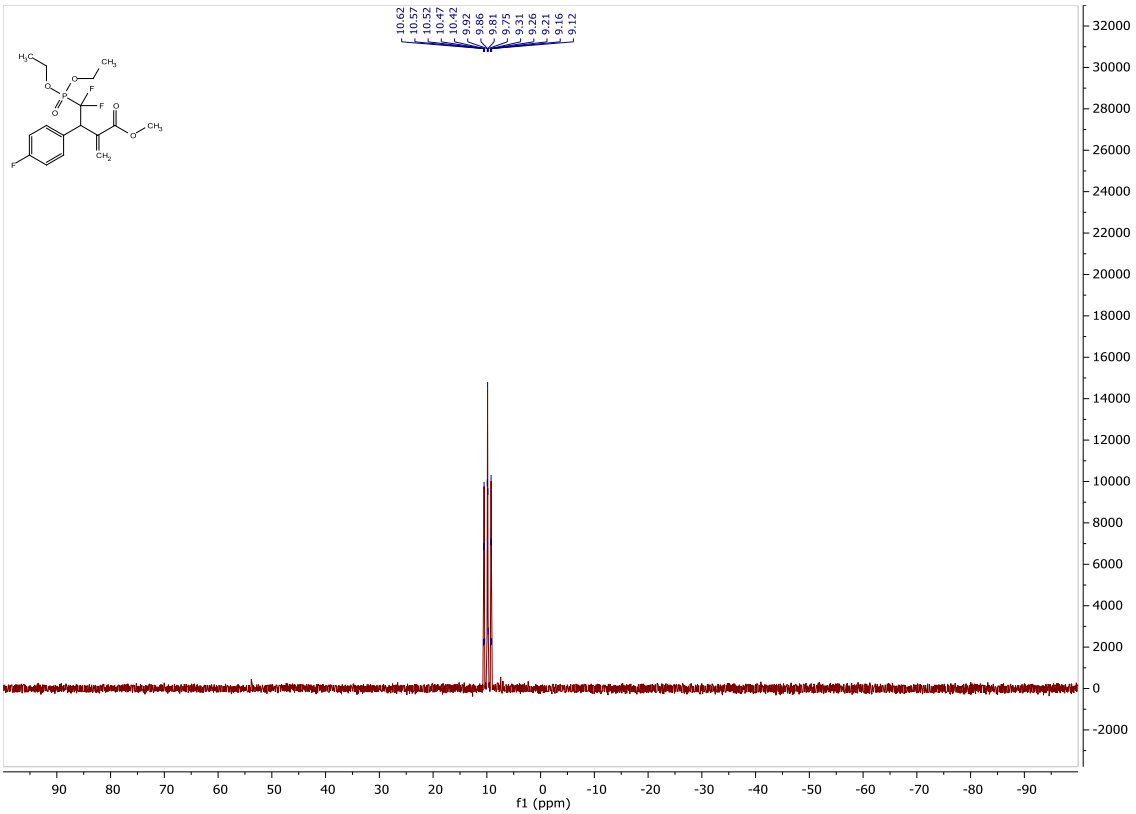

10.27
10.22
10.17
10.12
10.07
9.64
9.59
9.54
9.50
9.45
9.40
8.98
8.93
8.88
8.83
8.78
f1 (ppm)

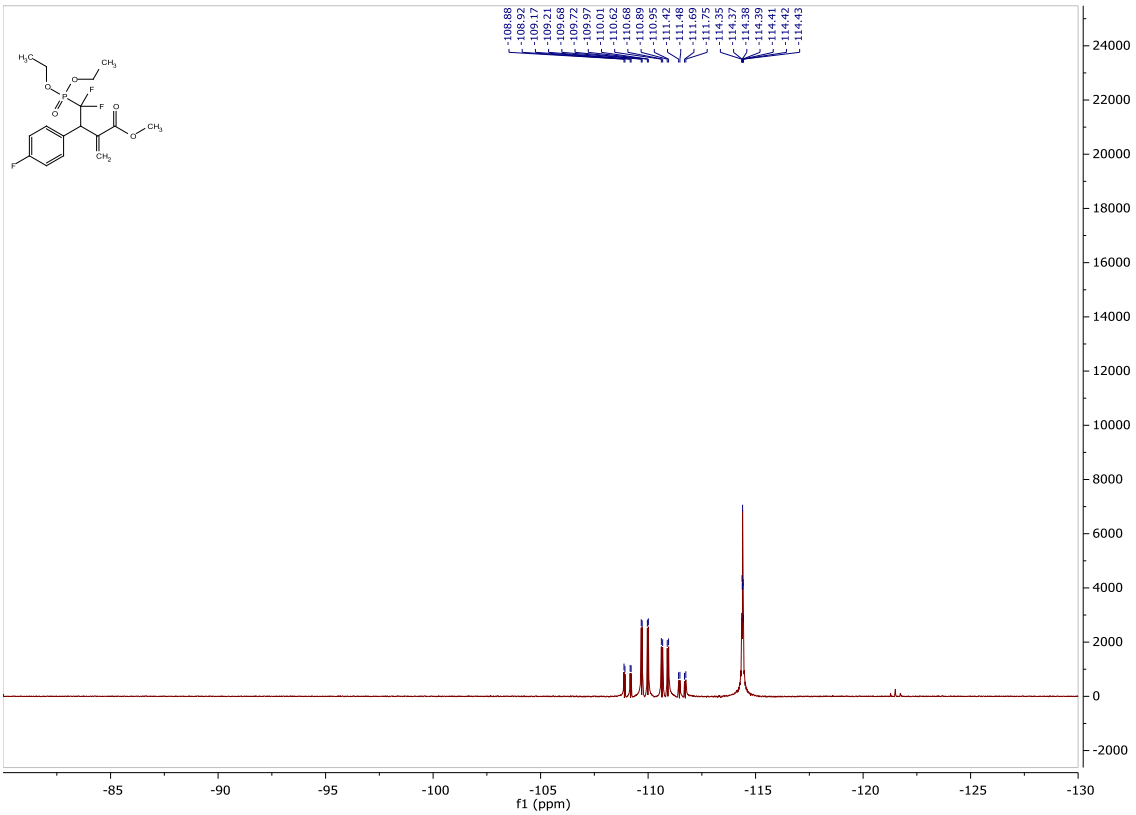

-72.96
-109.11
-109.15
-109.39
-109.44
-109.91
-109.95
-110.20
-110.24
-110.98
-111.04
-111.25
-111.31
-111.78
-111.85
-112.05
-112.12
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(4-fluorophenyl)-2-methylenebutanoate (*S*-3m)

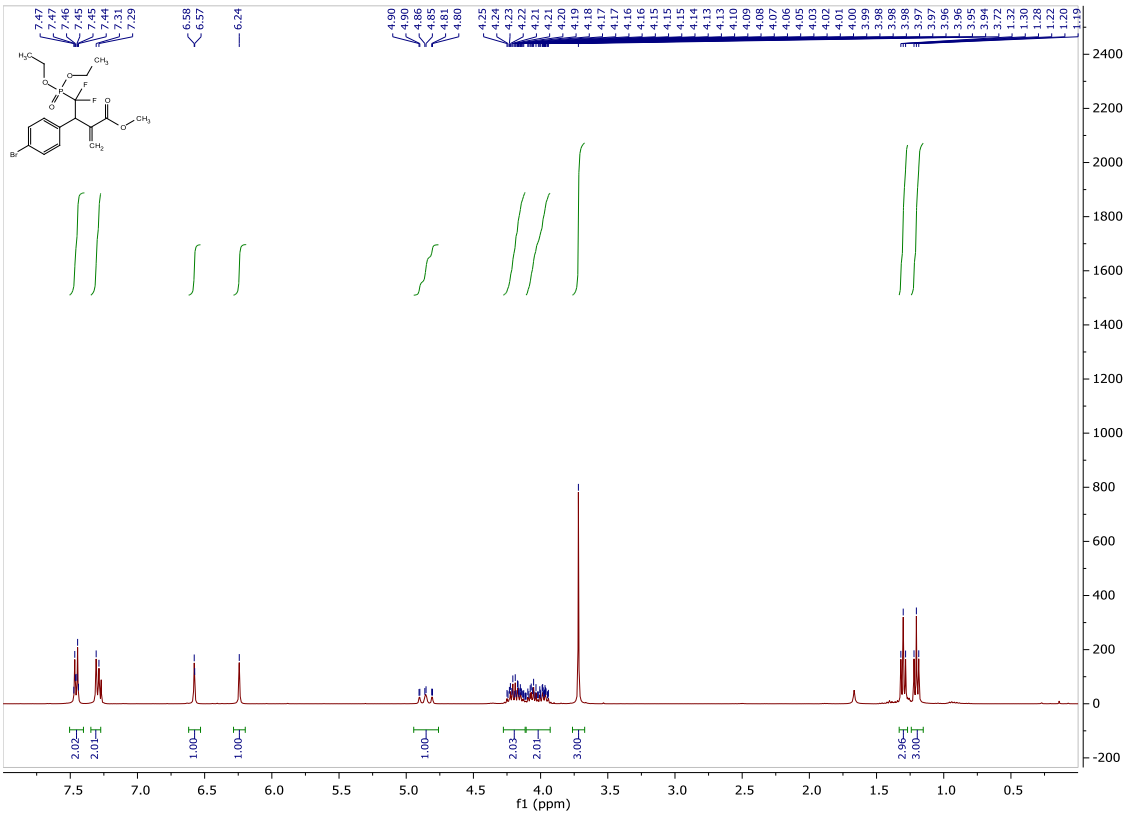


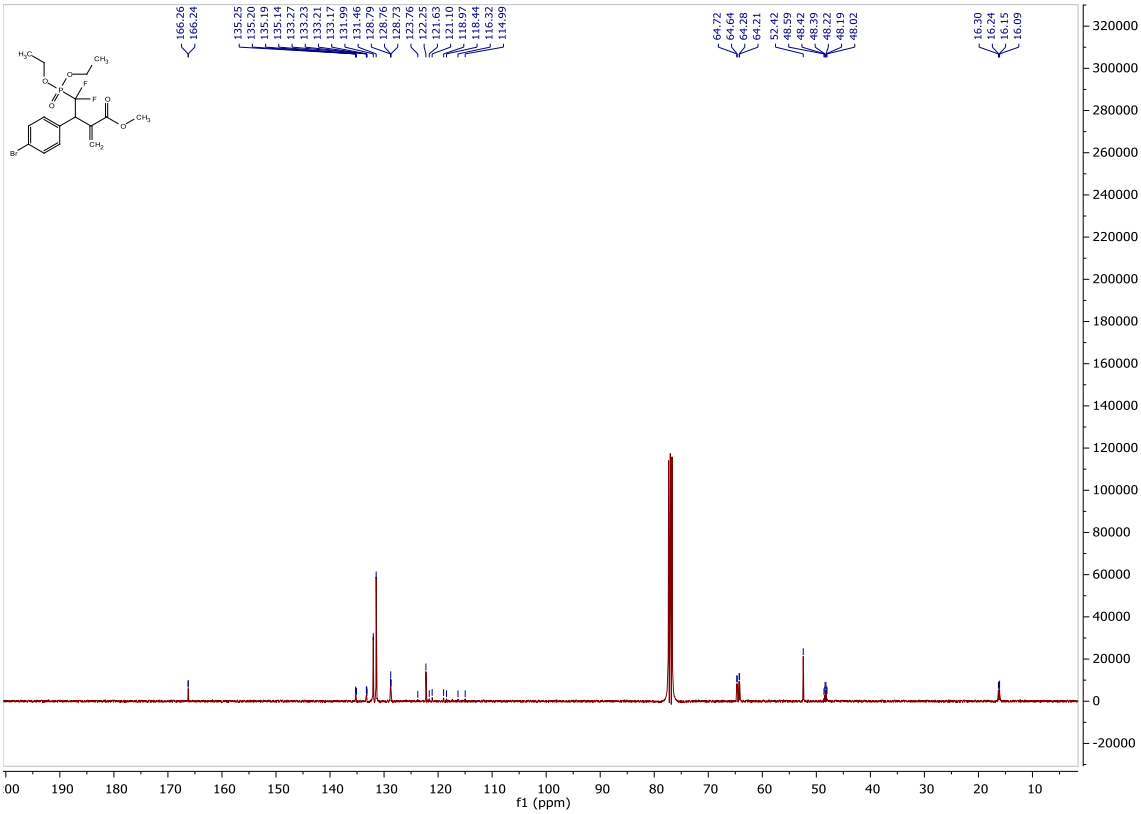


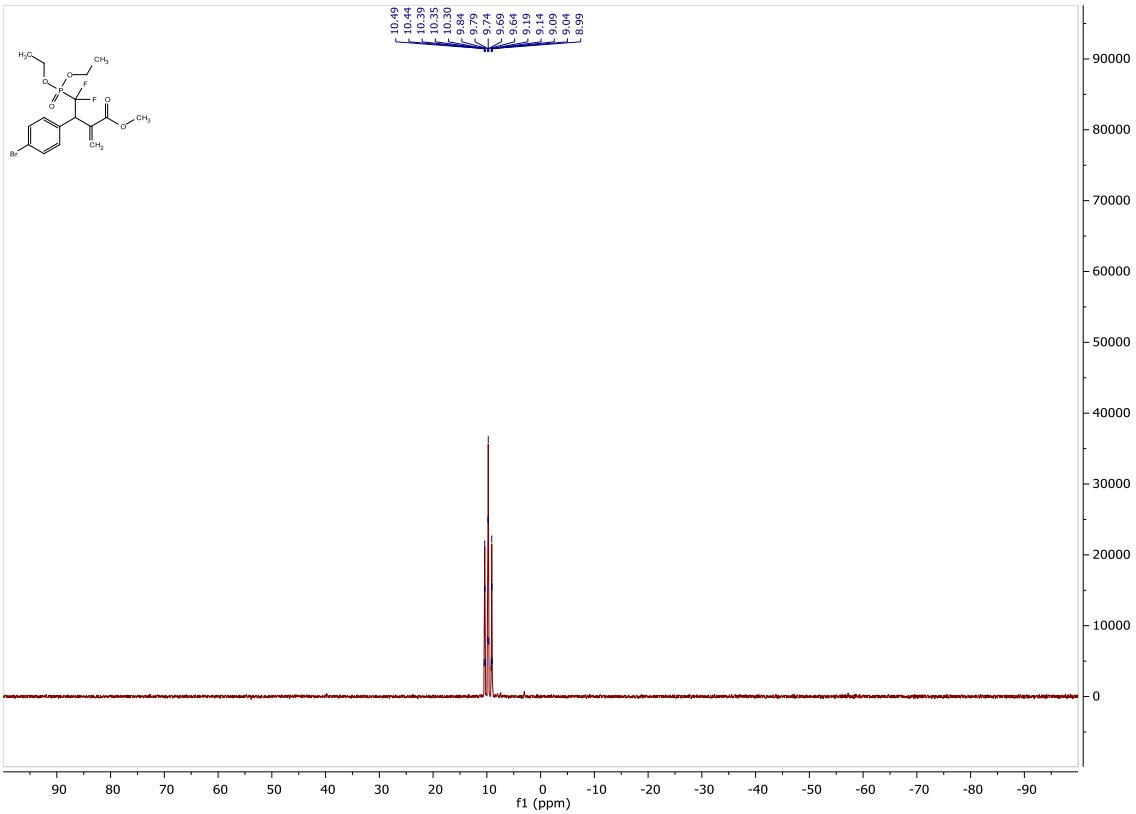

10.62
10.57
10.52
10.47
10.42
9.92
9.86
9.81
9.75
9.31
9.26
9.21
9.16
9.12
f1 (ppm)

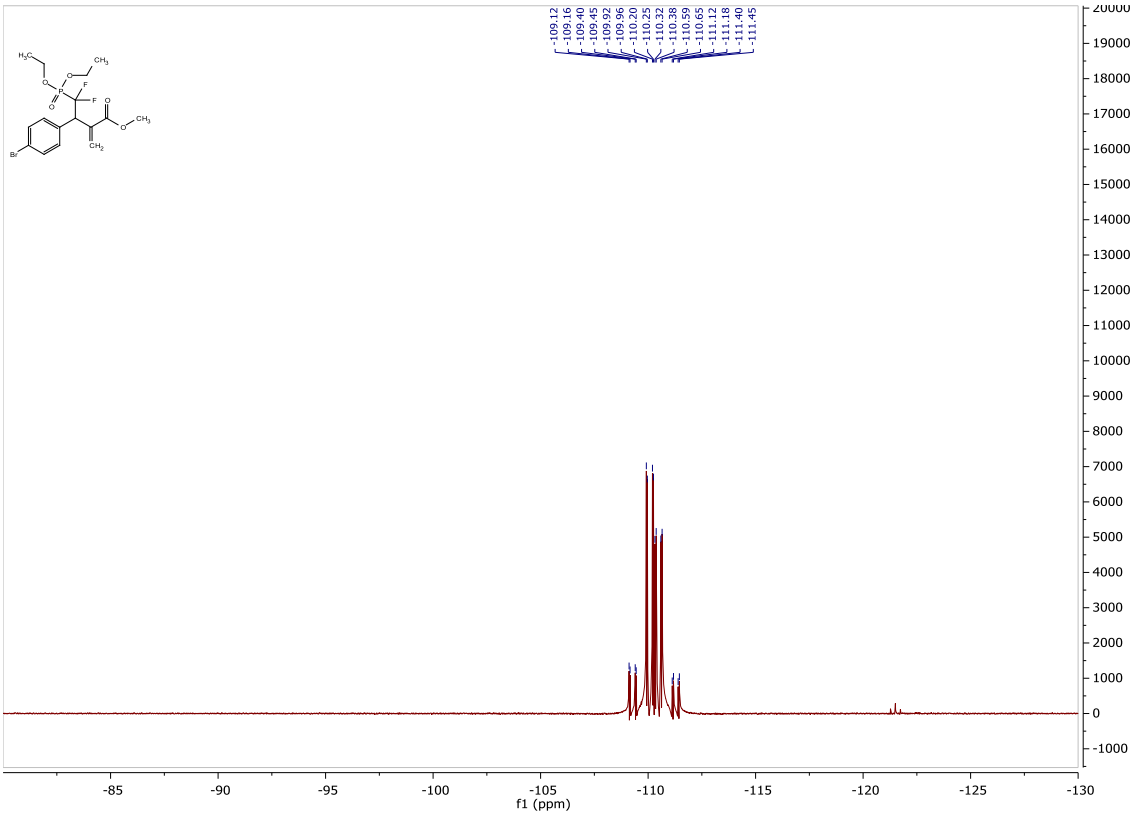

-108.88
-108.92
-109.17
-109.21
-109.68
-109.72
-109.97
-110.01
-110.62
-110.68
-110.89
-110.95
-111.42
-111.48
-111.69
-111.75
-114.35
-114.37
-114.38
-114.39
-114.41
-114.42
-114.43
f1 (ppm)

methyl (S)-3-(4-bromophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3n)

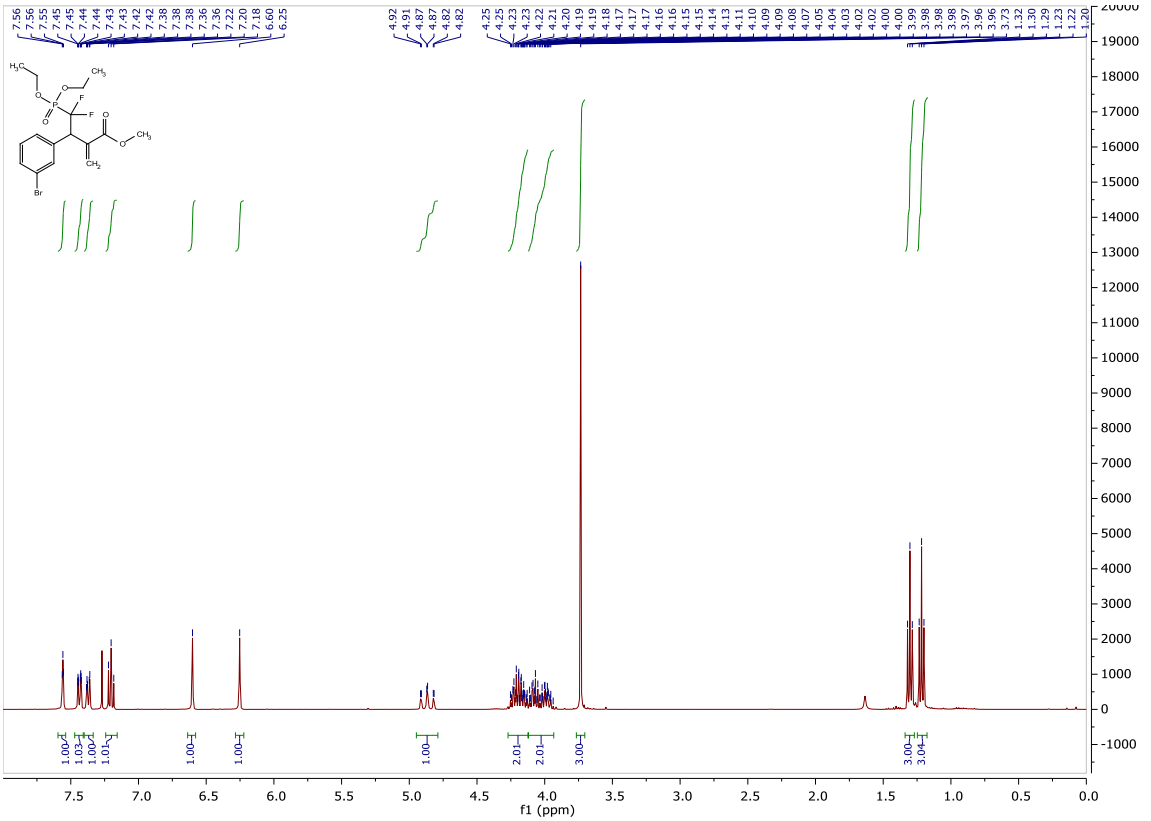


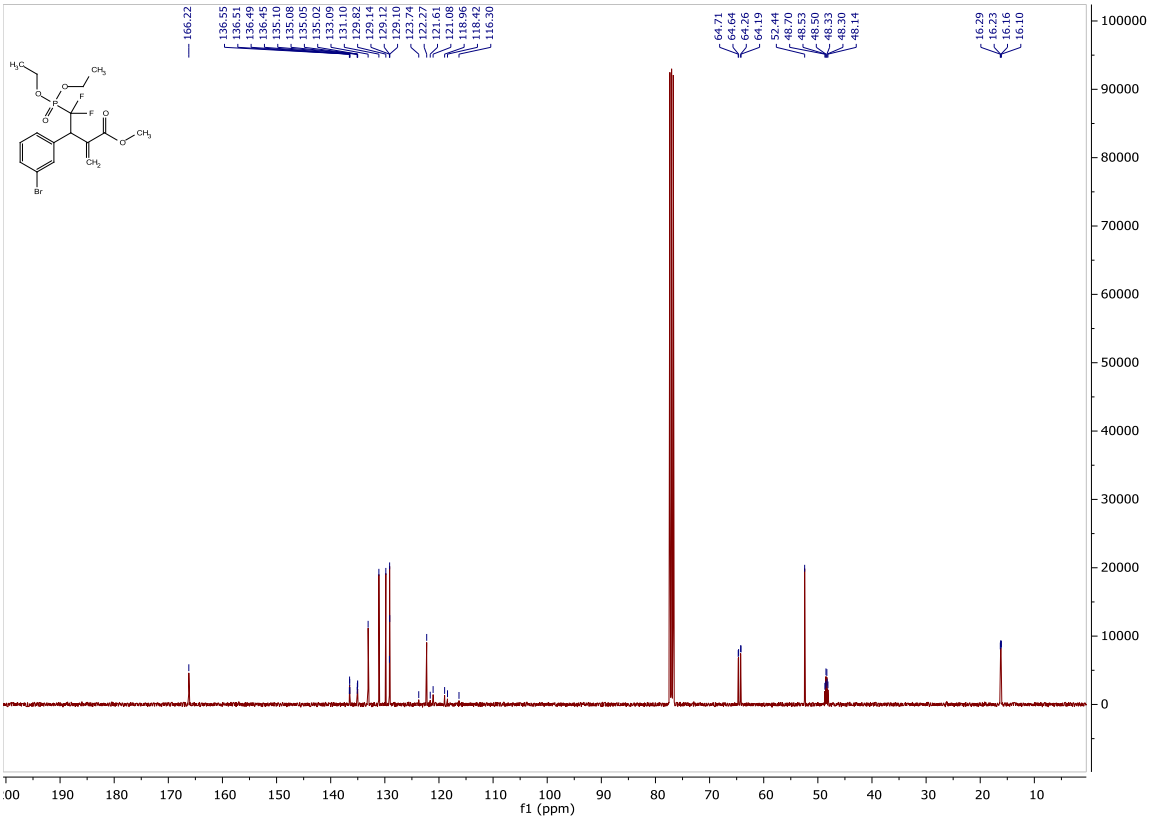


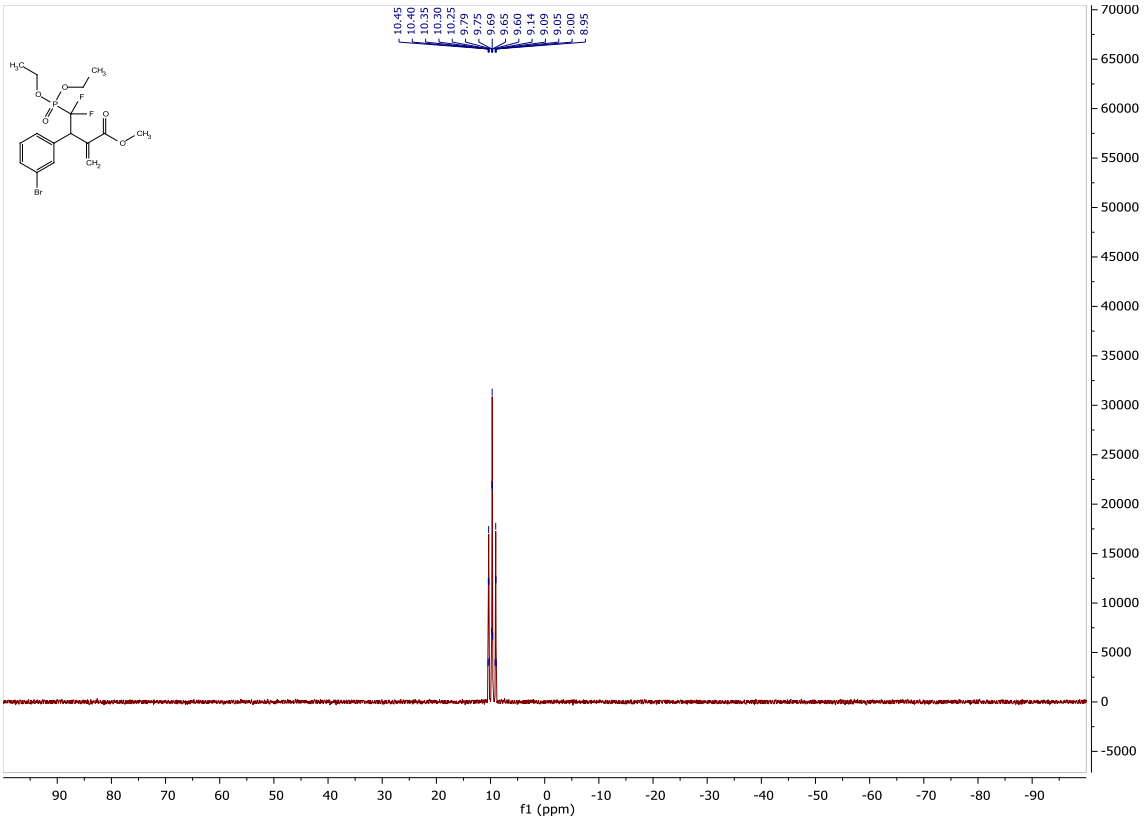

10.49
10.44
10.39
10.35
10.30
9.84
9.79
9.74
9.69
9.64
9.19
9.14
9.09
9.04
8.99
f1 (ppm)

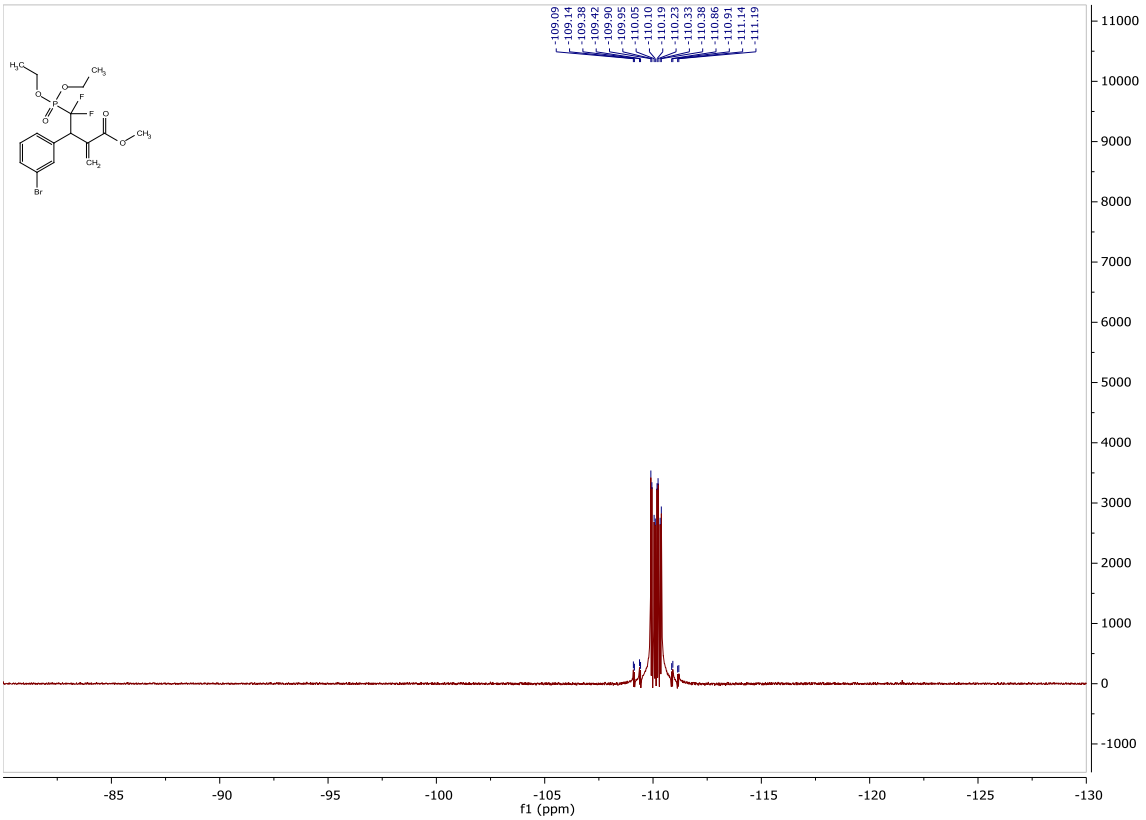

-109.12
-109.15
-109.40
-109.45
-109.92
-109.96
-110.20
-110.25
-110.32
-110.38
-110.59
-110.65
-111.12
-111.18
-111.40
-111.45
f1 (ppm)

methyl (S)-3-(3-bromophenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3o)

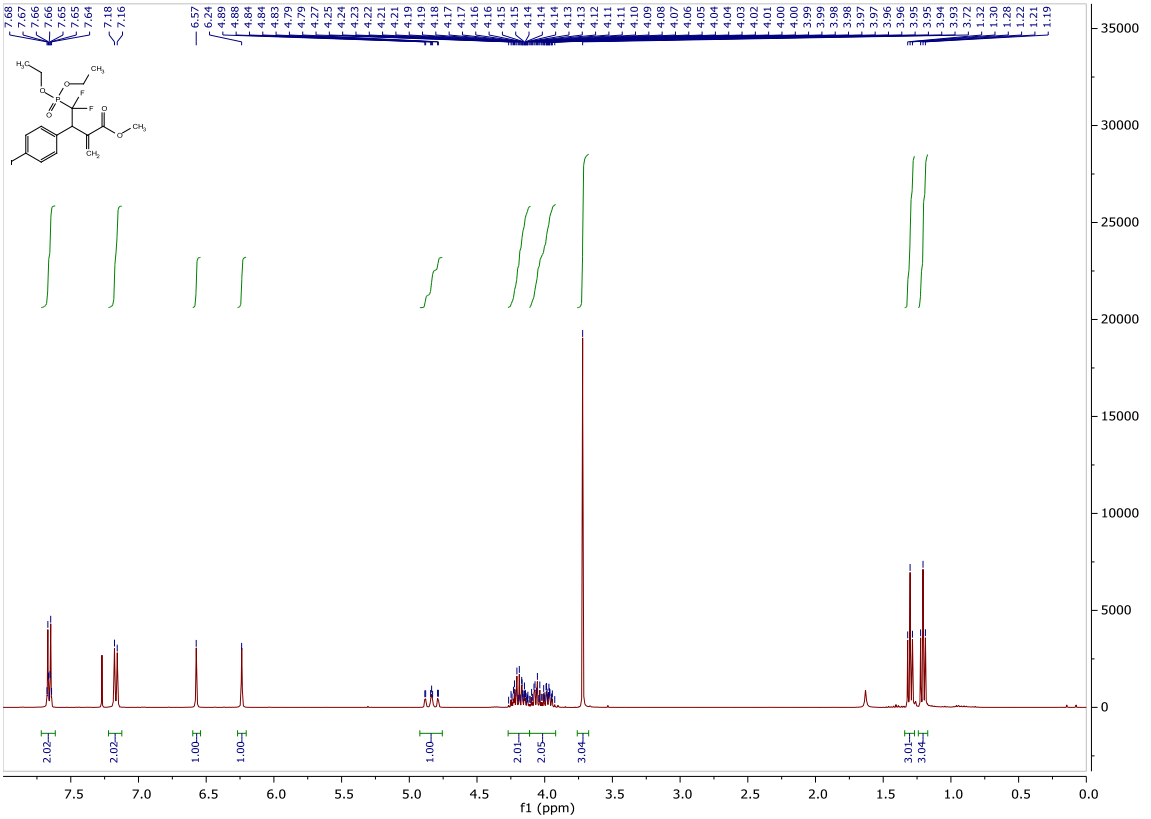


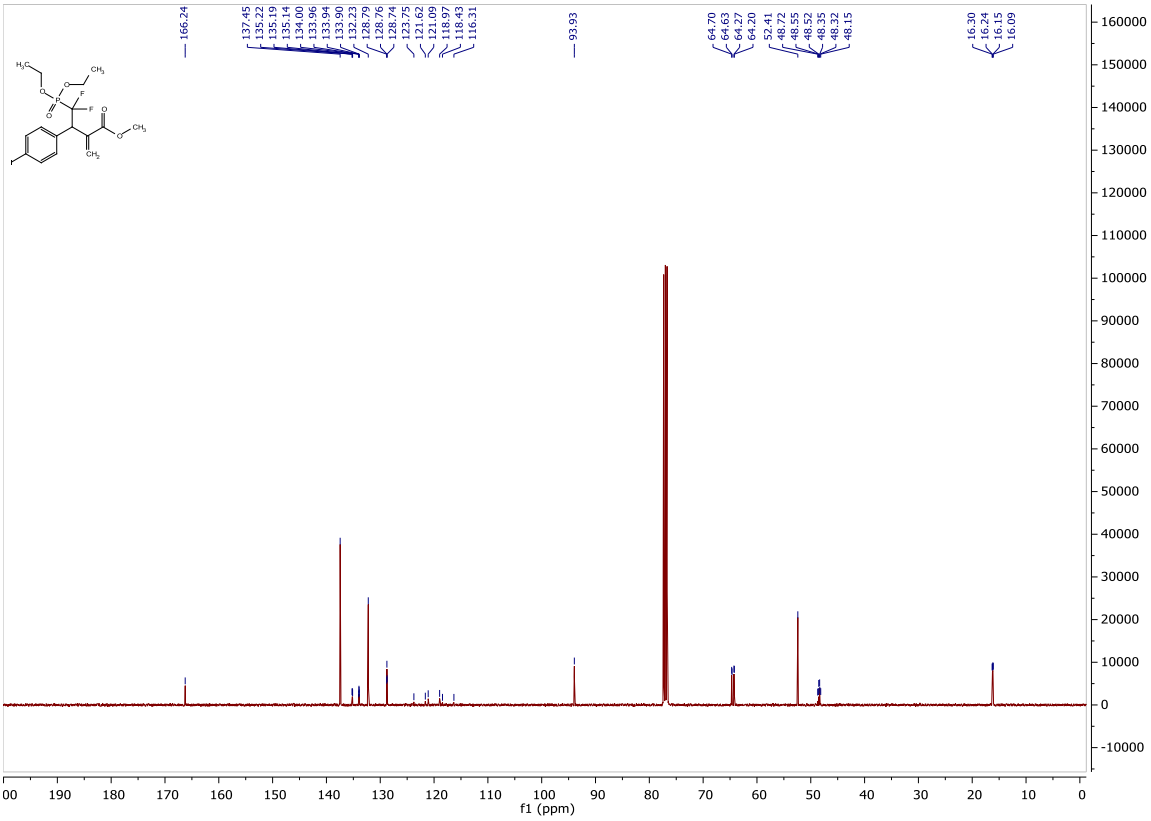


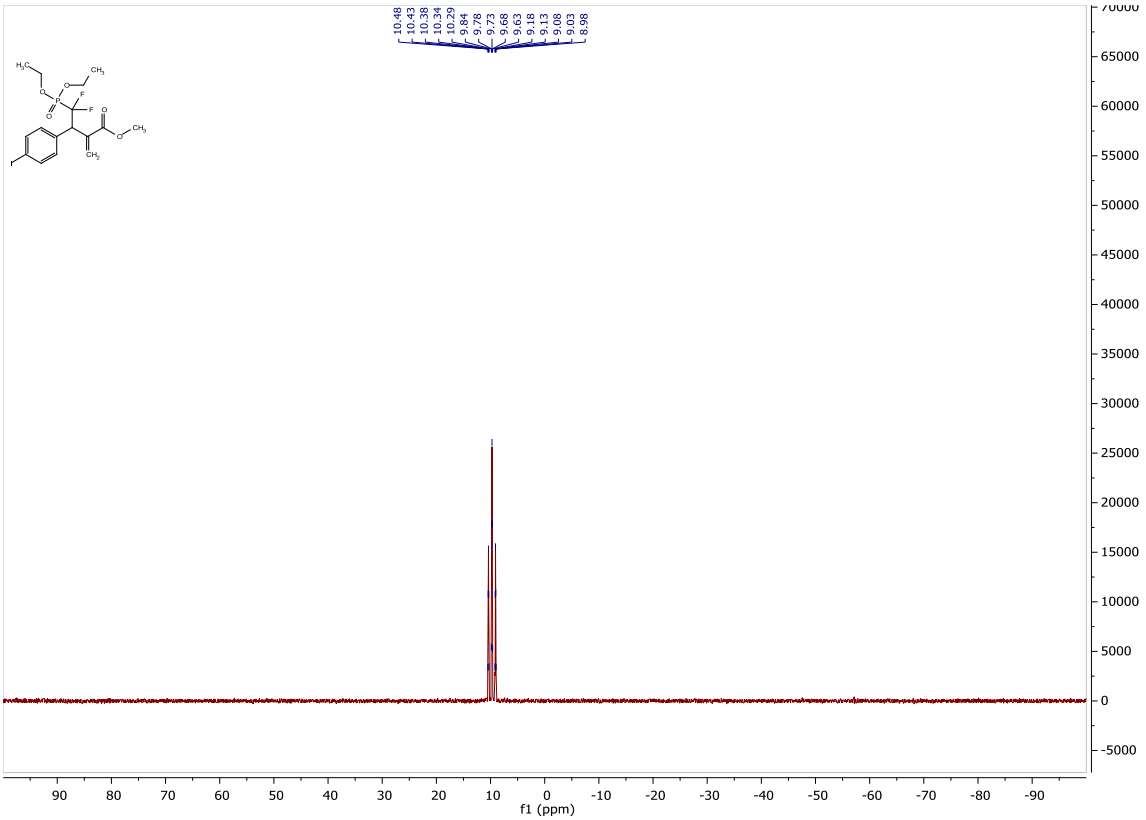

10.45
10.40
10.35
10.30
10.25
9.79
9.75
9.69
9.65
9.60
9.14
9.09
9.05
9.00
8.95
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

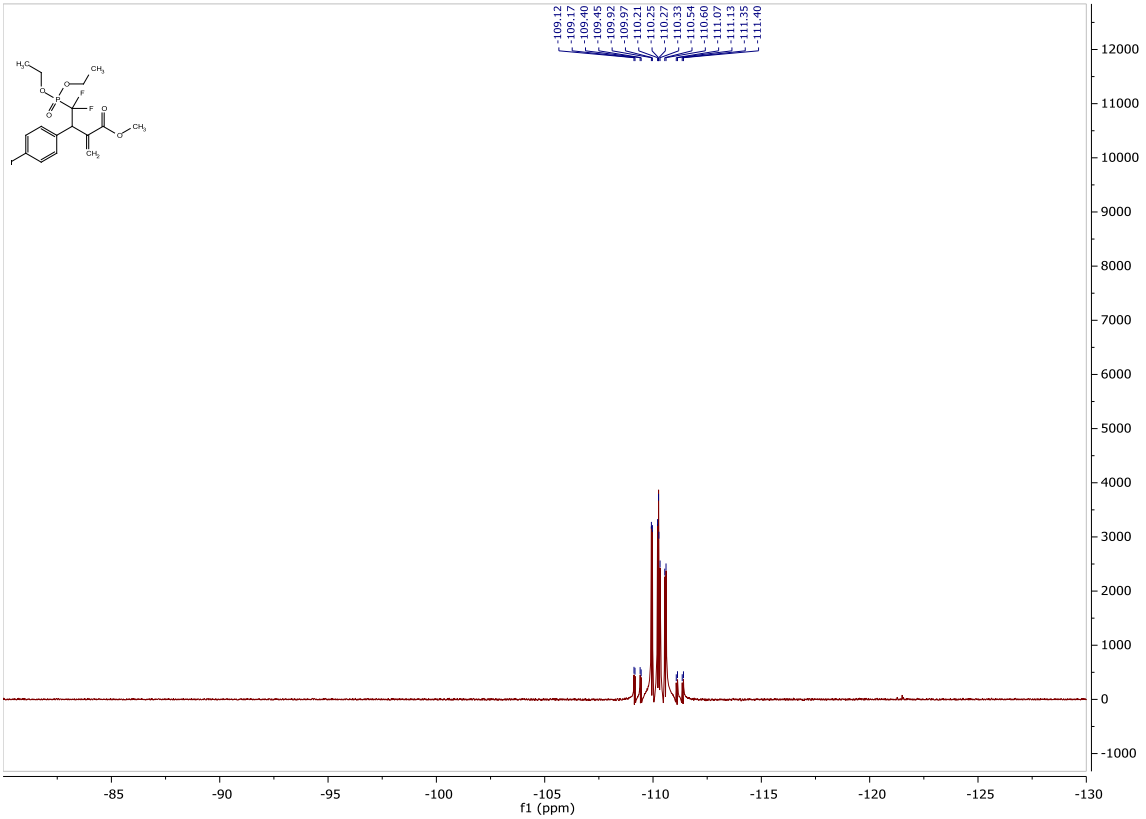

-109.09
-109.14
-109.38
-109.42
-109.90
-109.95
-110.05
-110.10
-110.19
-110.23
-110.33
-110.38
-110.86
-110.91
-111.14
-111.19
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(4-iodophenyl)-2-methylenebutanoate (*S*-3p)

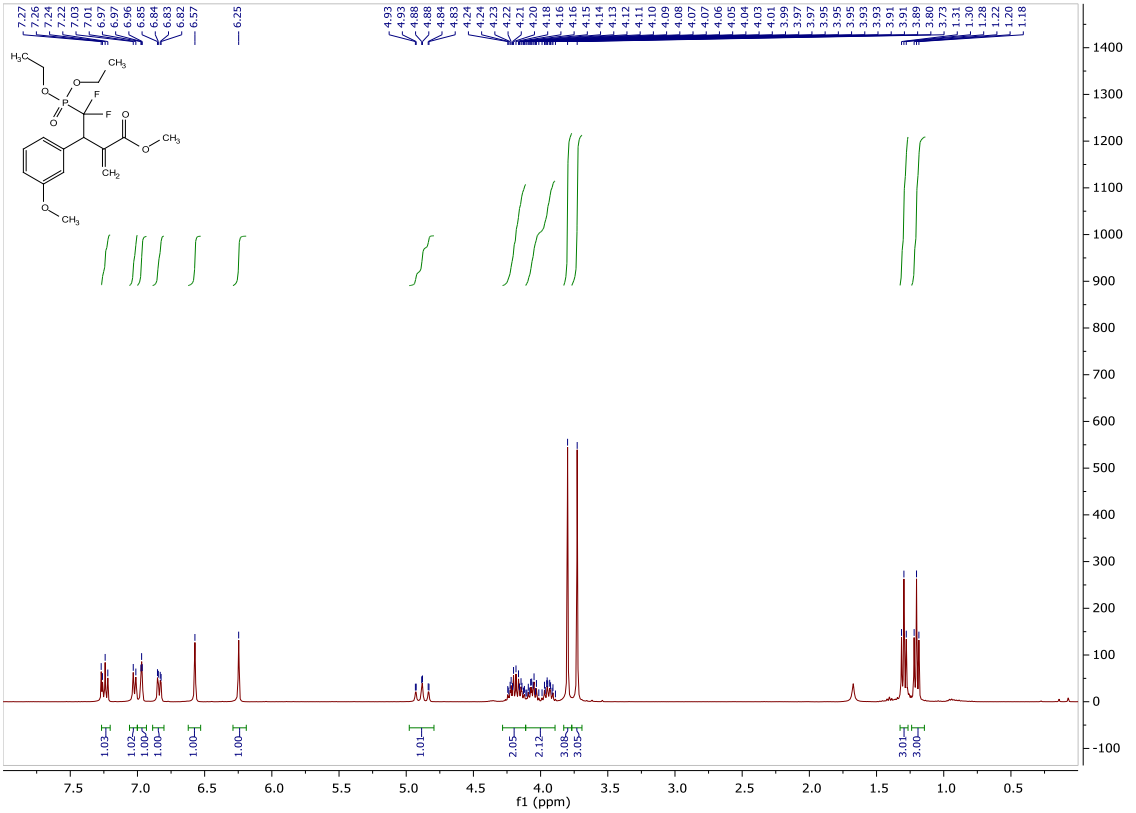


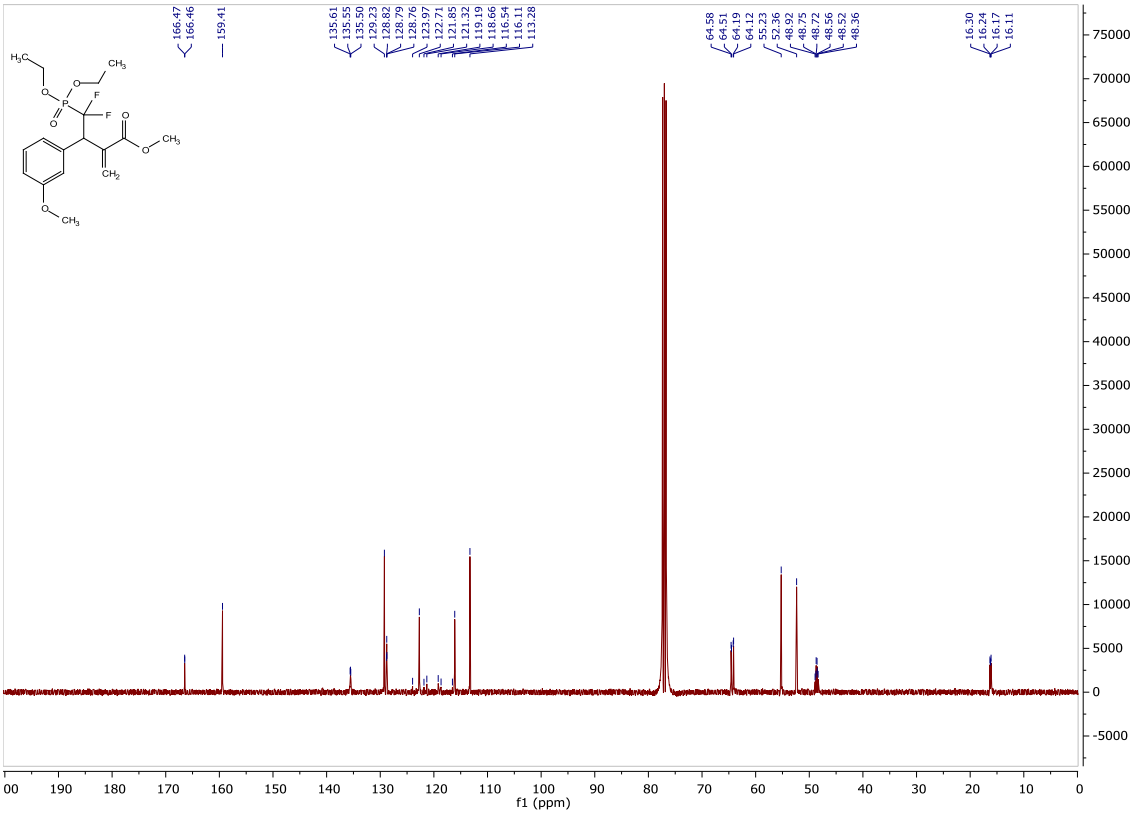


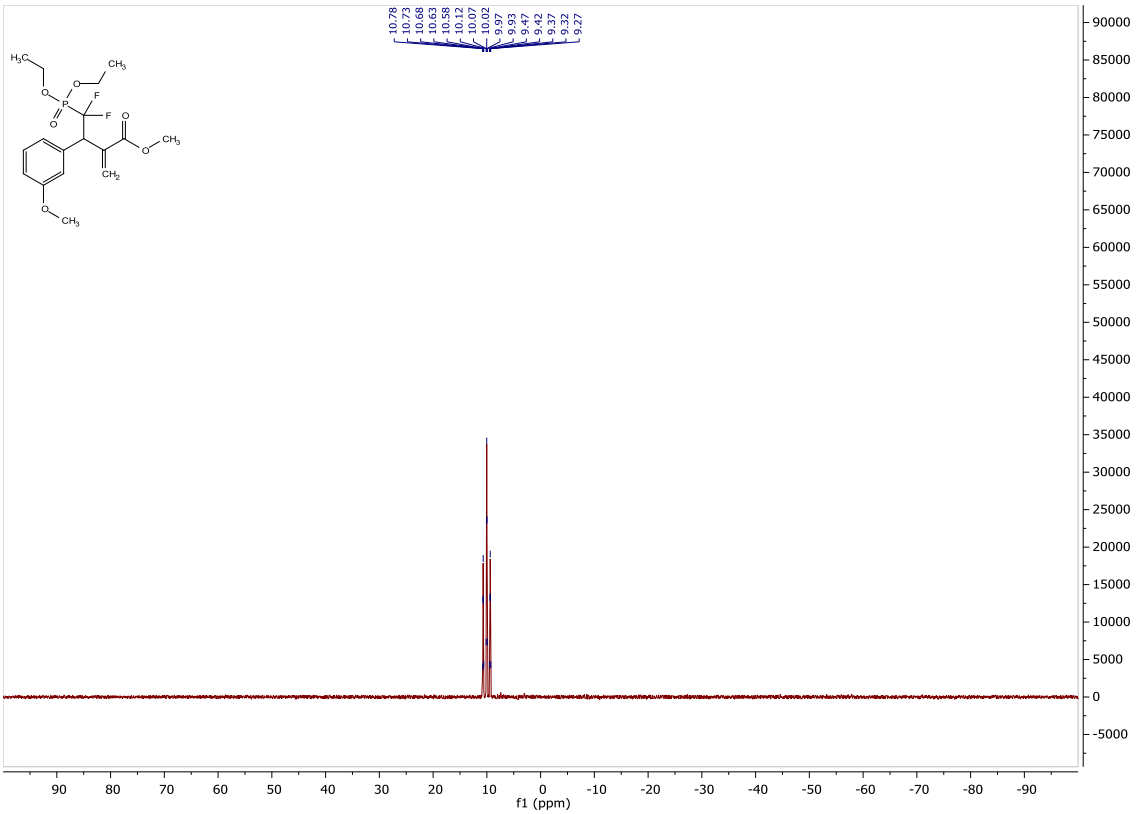

10.48
10.43
10.38
10.34
10.29
9.84
9.78
9.73
9.68
9.63
9.18
9.13
9.08
9.03
8.98
f1 (ppm)

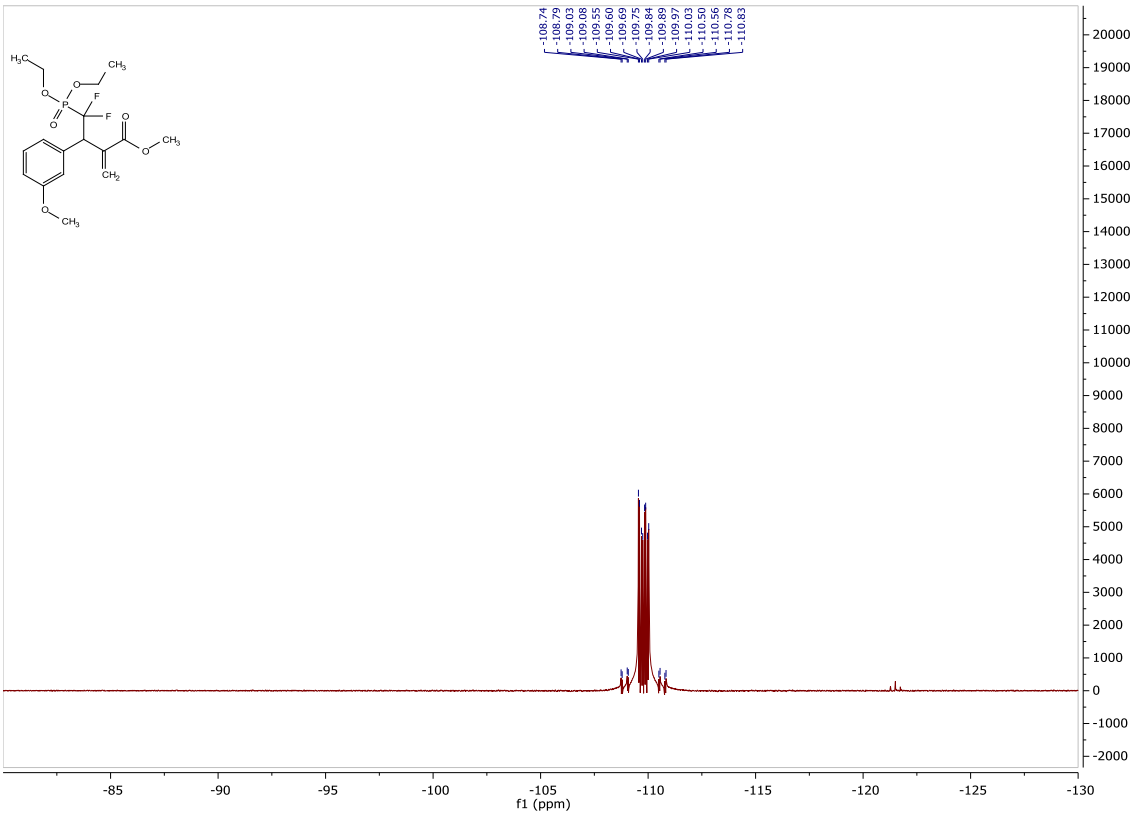

-109.12
-109.17
-109.40
-109.45
-109.92
-109.97
-110.21
-110.25
-110.27
-110.33
-110.54
-110.60
-111.07
-111.13
-111.35
-111.40
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-3-(3-methoxyphenyl)-2-methylenebutanoate (*S*-3q)

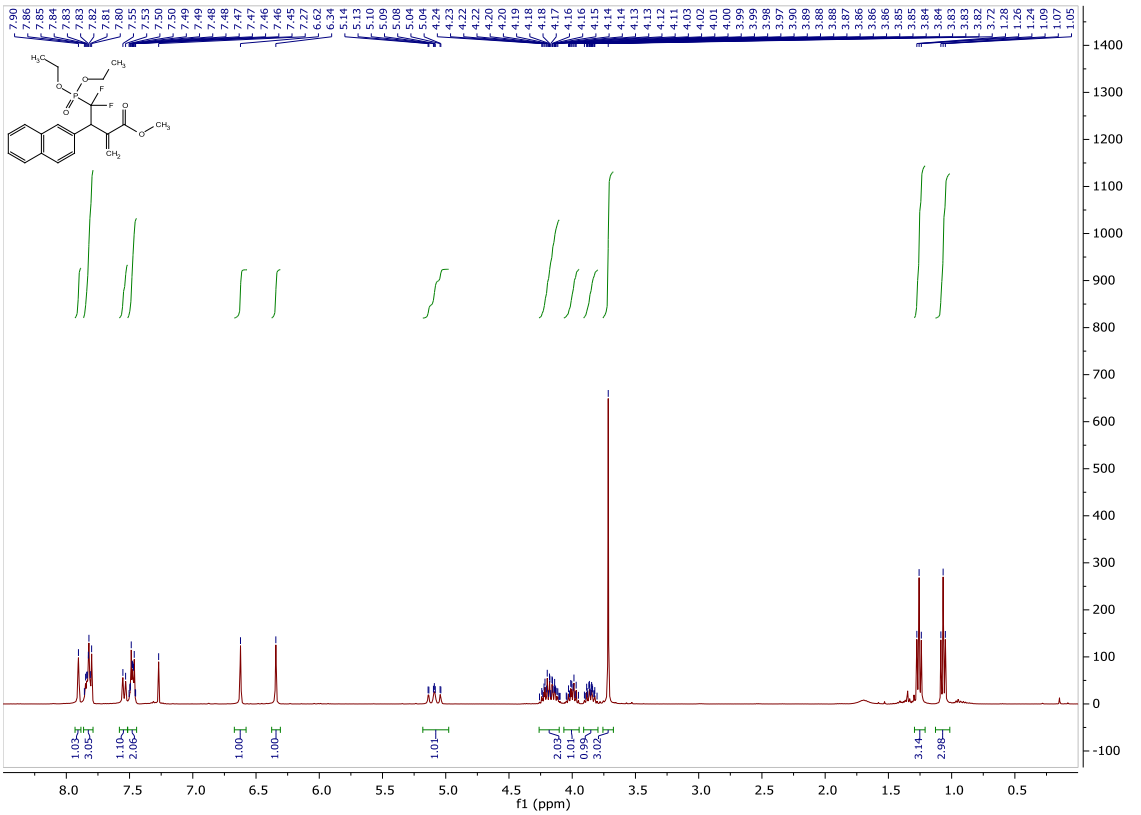


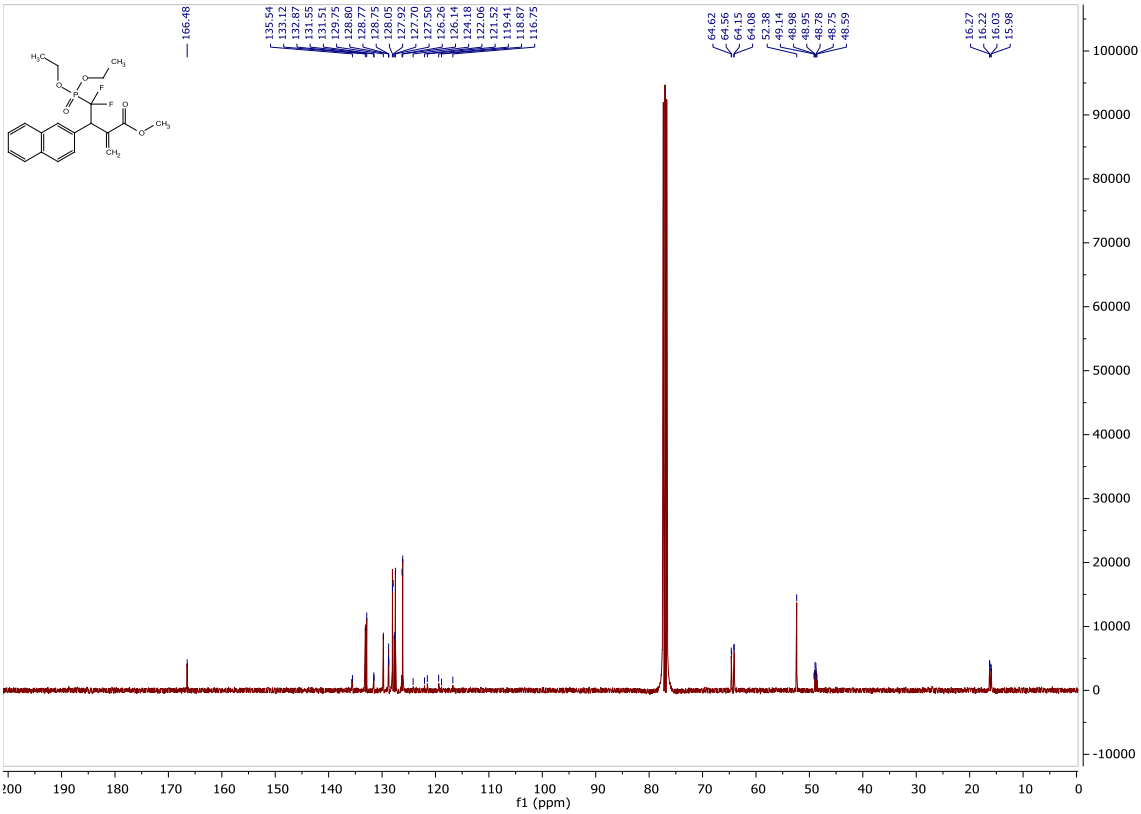


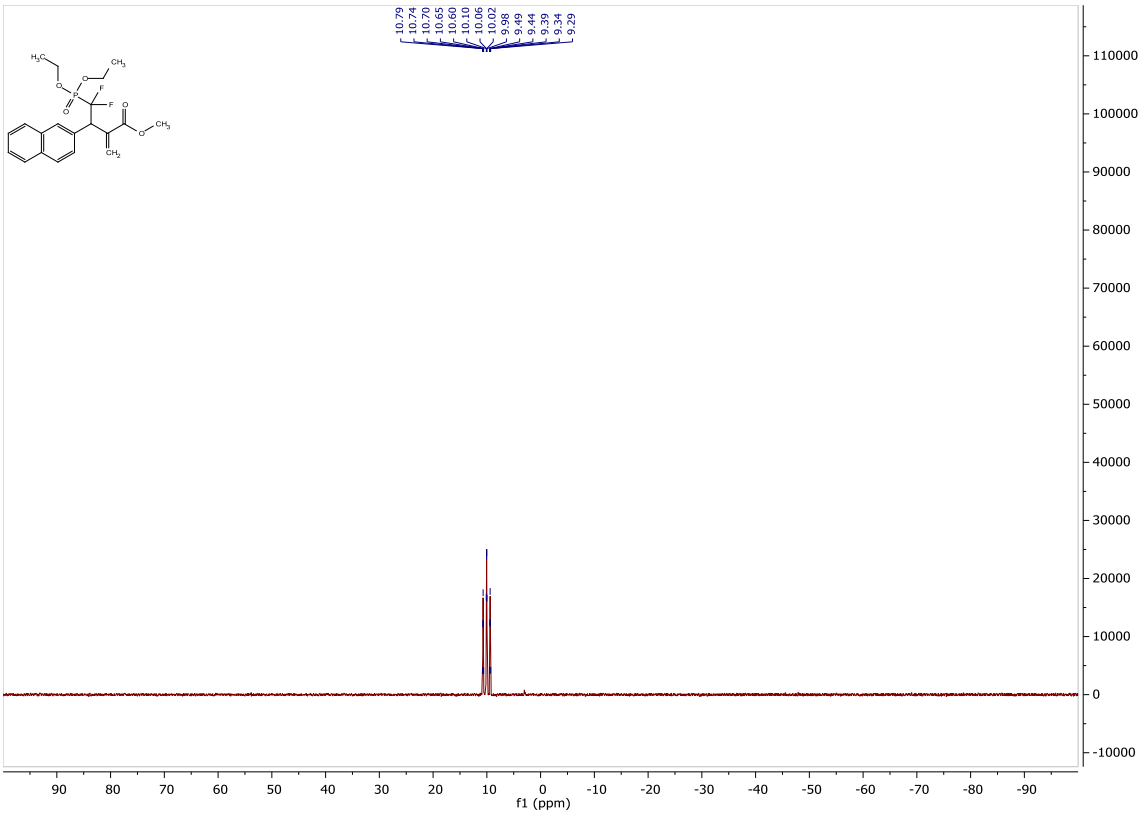

10.78
10.73
10.68
10.63
10.58
10.12
10.07
10.02
9.97
9.93
9.47
9.42
9.37
9.32
9.27
f1 (ppm)

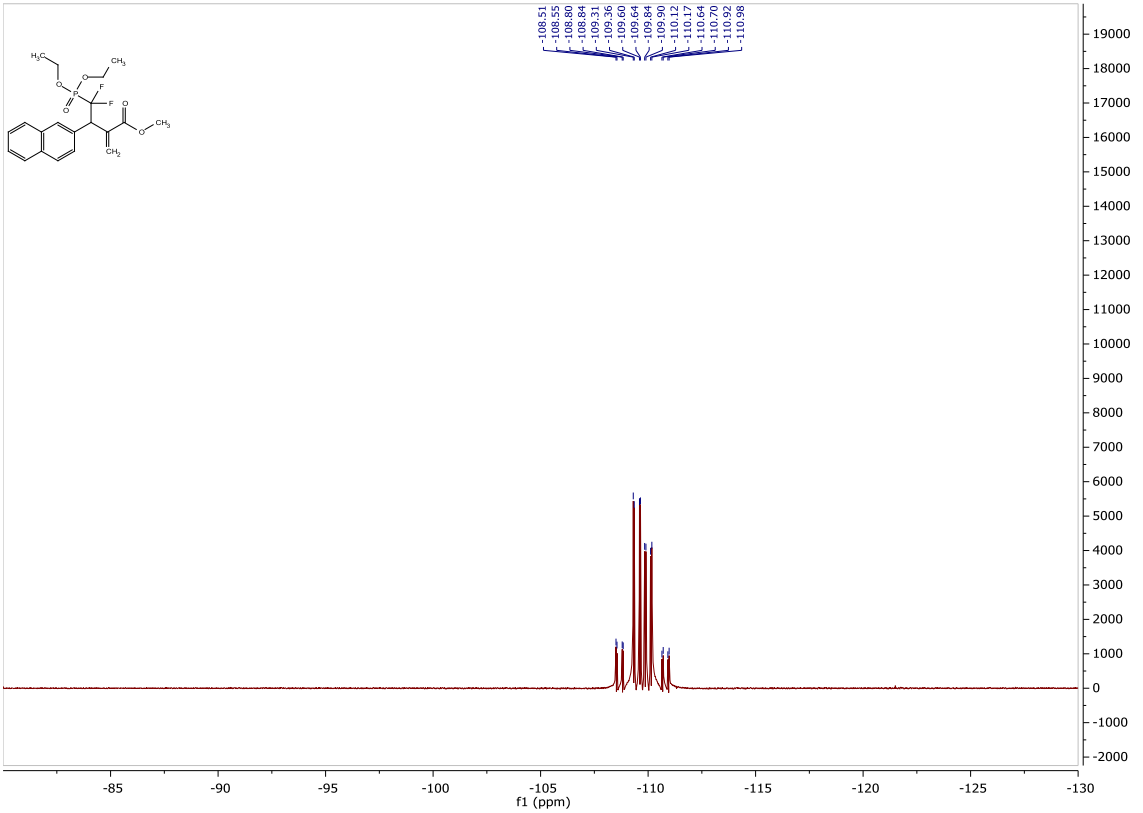

-108.74
-108.79
-109.03
-109.08
-109.55
-109.60
-109.69
-109.75
-109.84
-109.89
-109.97
-110.03
-110.50
-110.56
-110.78
-110.83
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(naphthalen-2-yl)butanoate (*S*-3r)

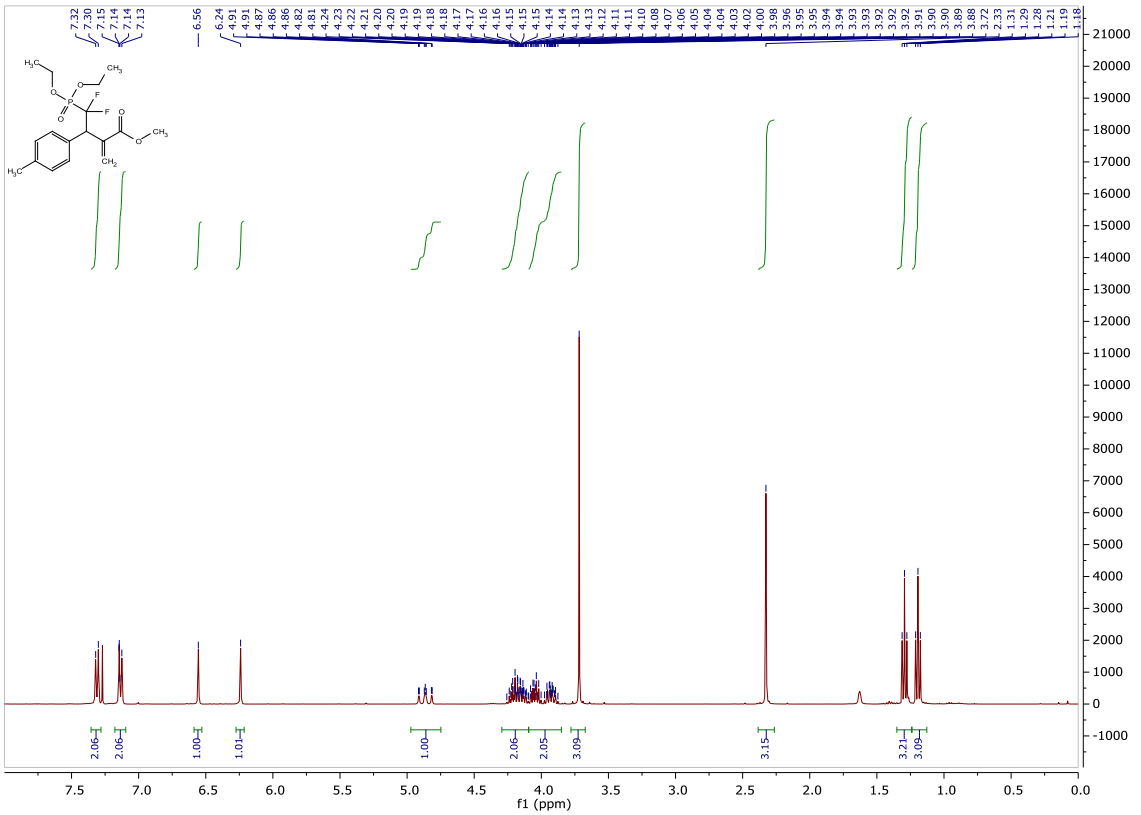


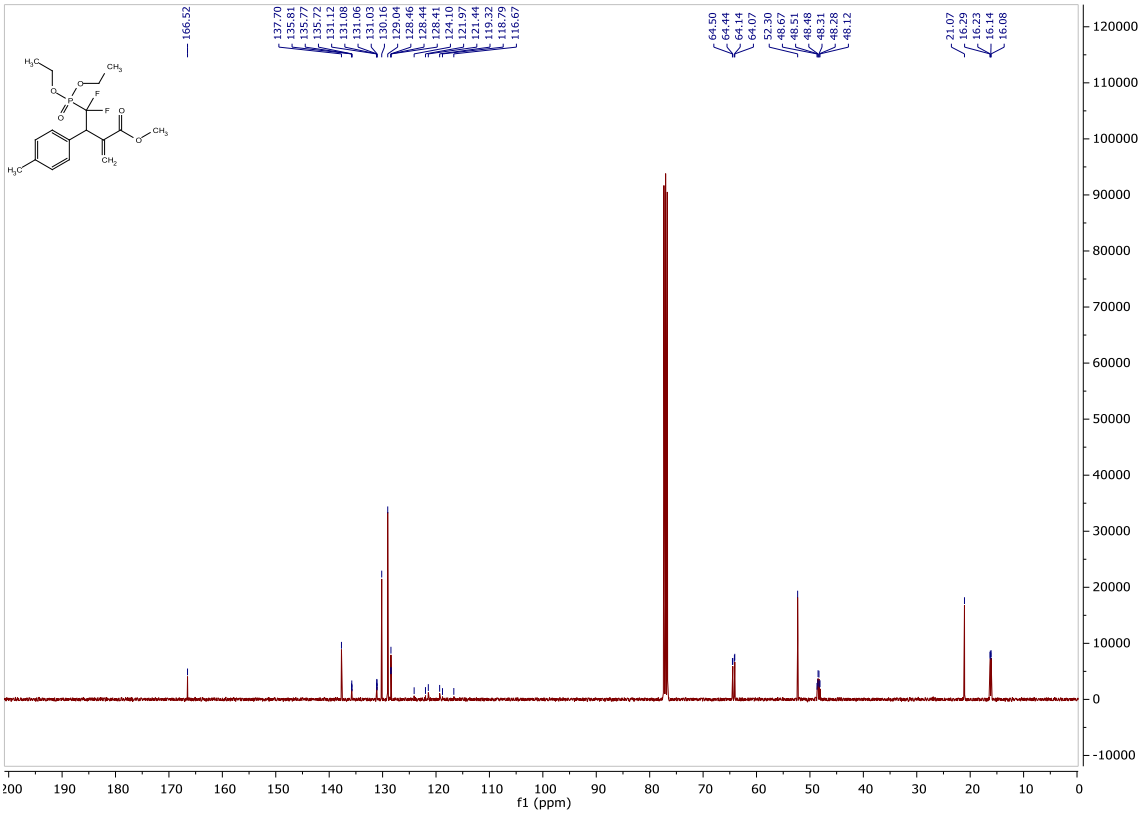


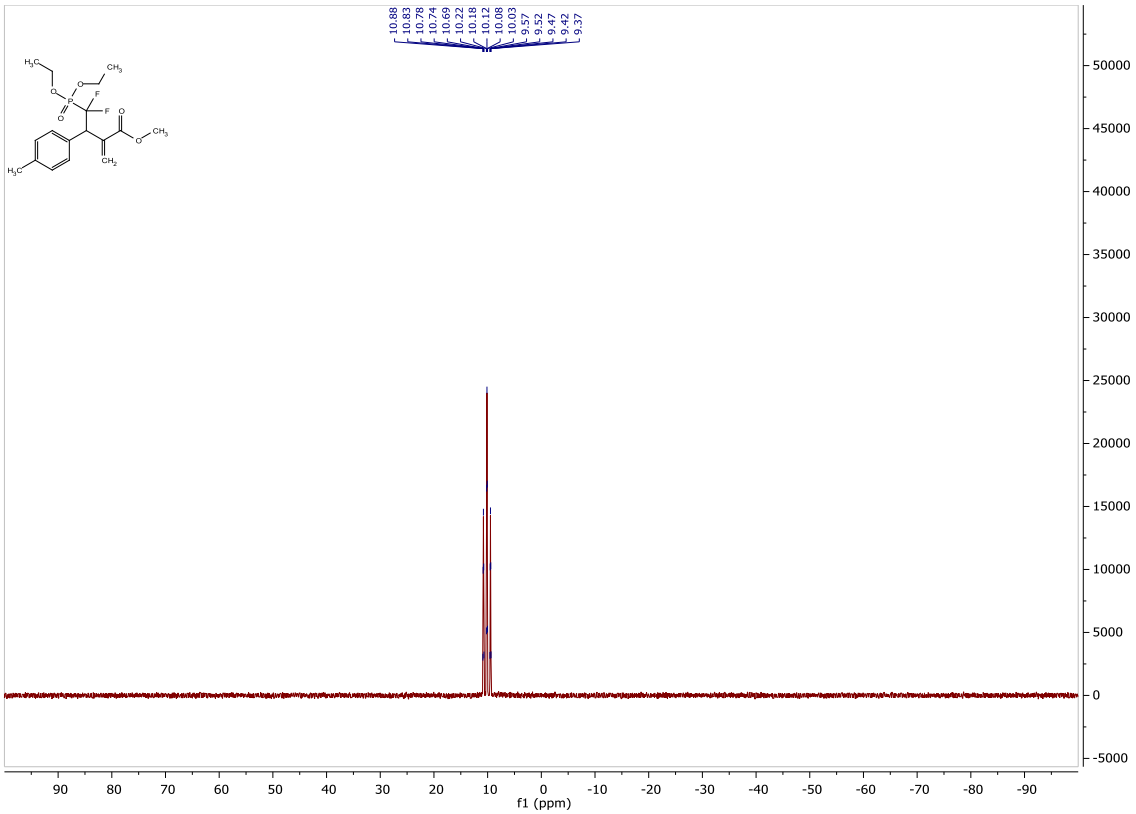

10.79
10.74
10.70
10.65
10.60
10.10
10.06
10.02
9.98
9.49
9.44
9.39
9.34
9.29
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

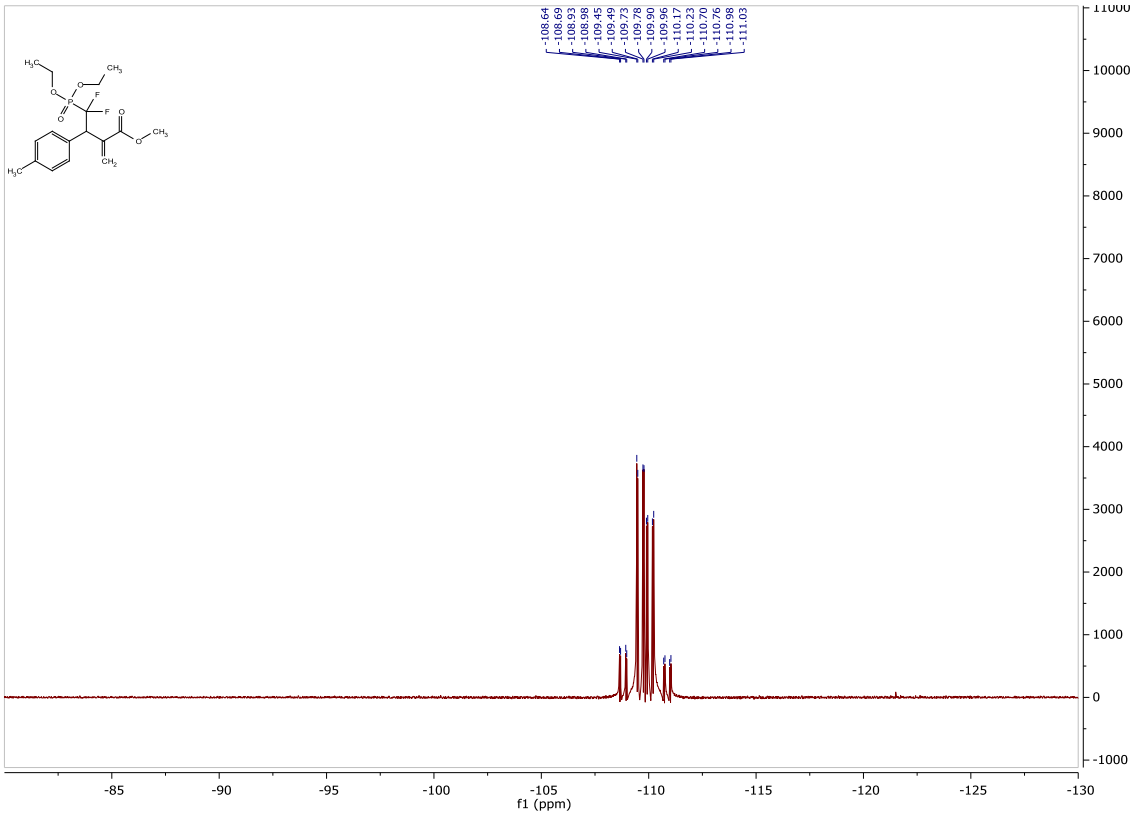

-108.51
-108.55
-108.80
-108.84
-109.31
-109.36
-109.60
-109.64
-109.84
-109.90
-110.12
-110.17
-110.64
-110.70
-110.92
-110.98
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylene-3-(p-tolyl)butanoate (*S*-3s)

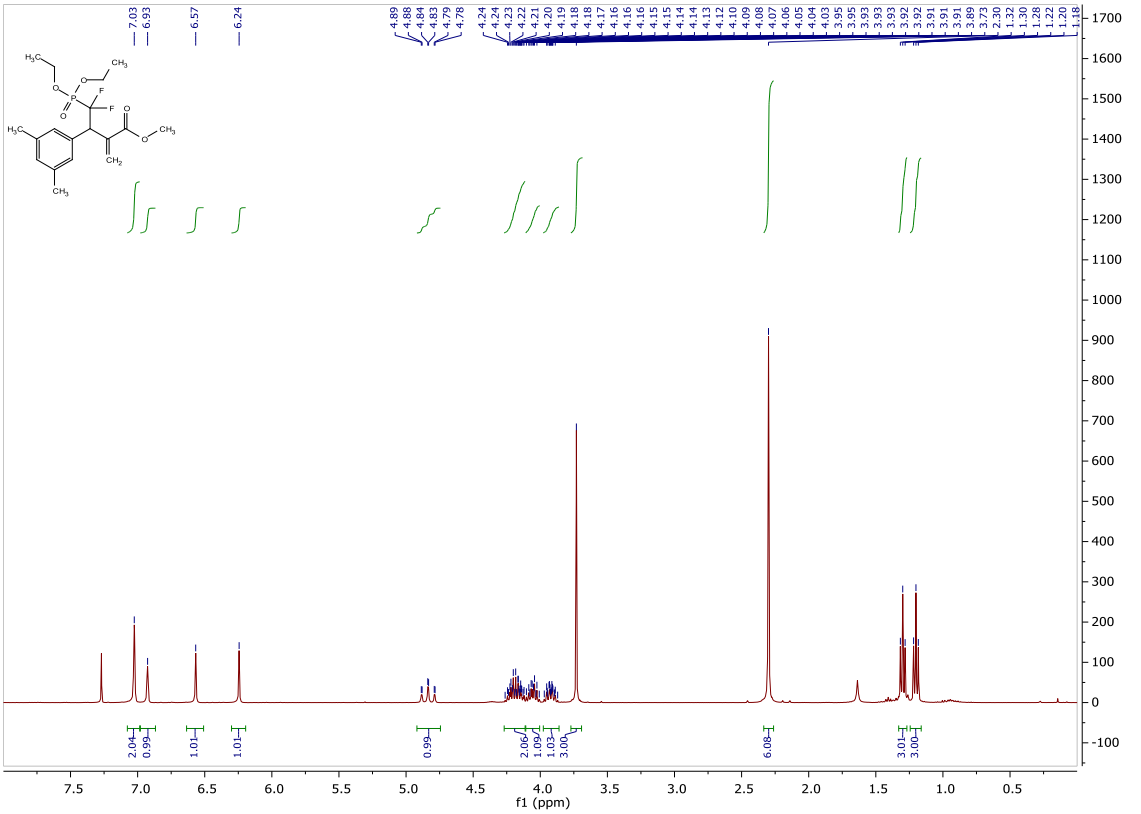


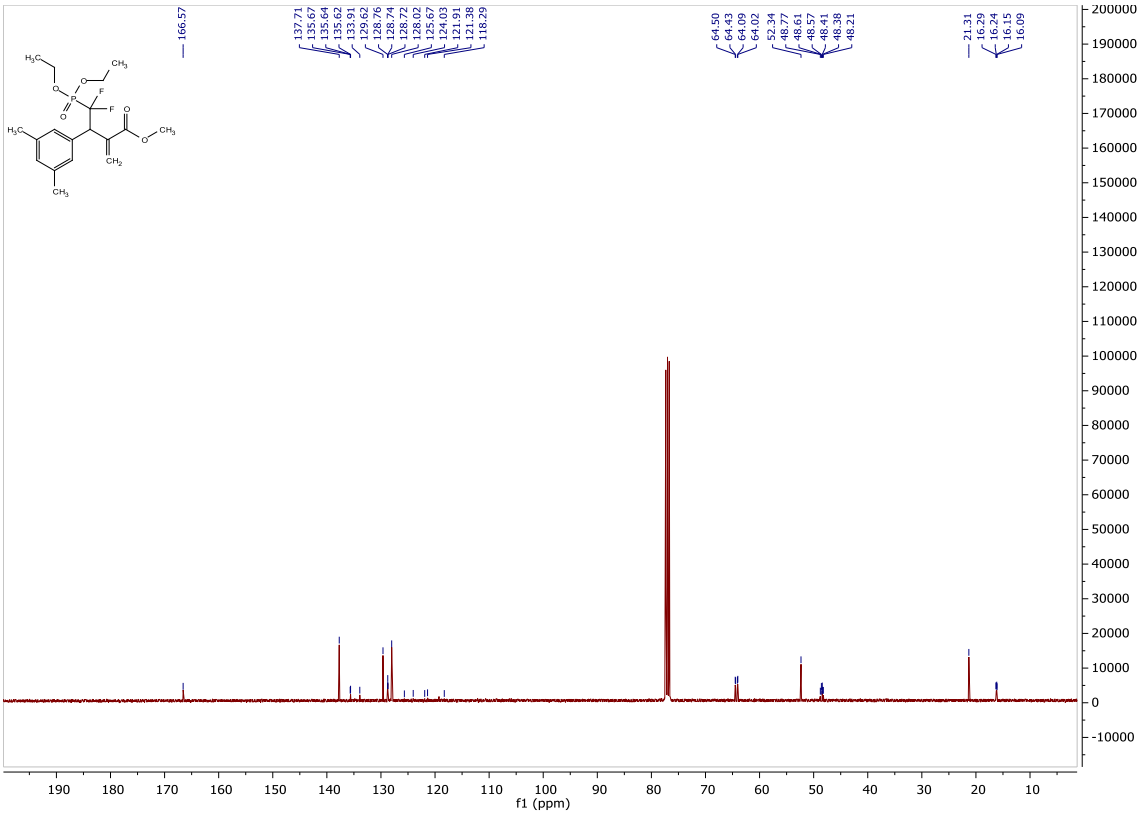


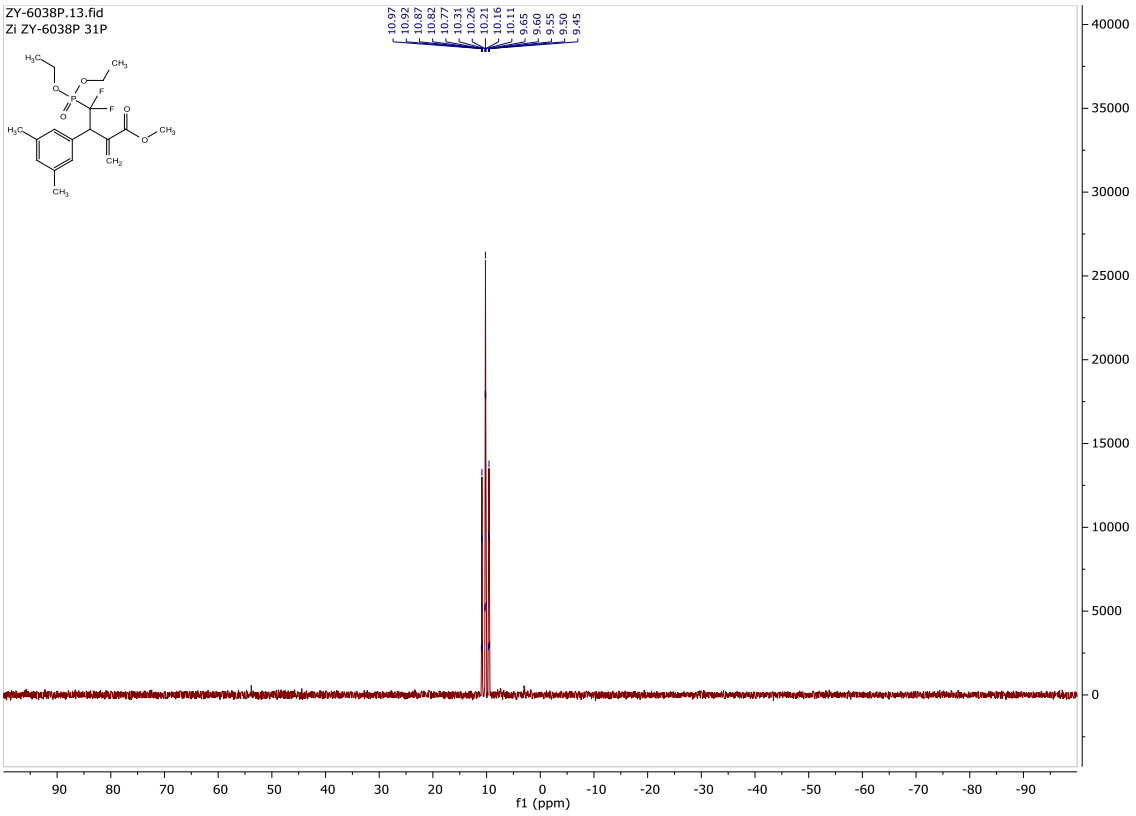

10.88
10.83
10.78
10.74
10.69
10.22
10.18
10.12
10.08
10.03
9.57
9.52
9.47
9.42
9.37
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

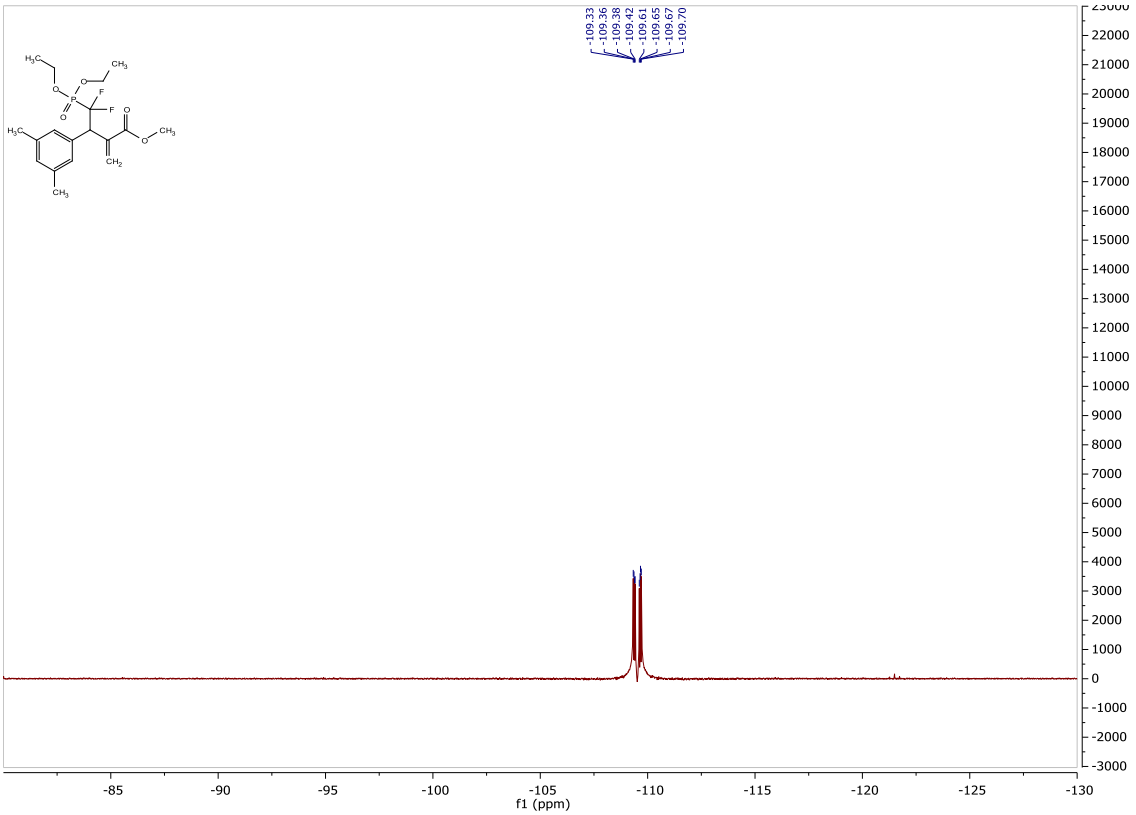

-108.64
-108.69
-108.93
-108.98
-109.45
-109.49
-109.73
-109.78
-109.86
-109.96
-110.17
-110.23
-110.70
-110.76
-110.98
-111.03
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-4-(diethoxyphosphoryl)-3-(3,5-dimethylphenyl)-4,4-difluoro-2-methylenebutanoate (*S*-3t)

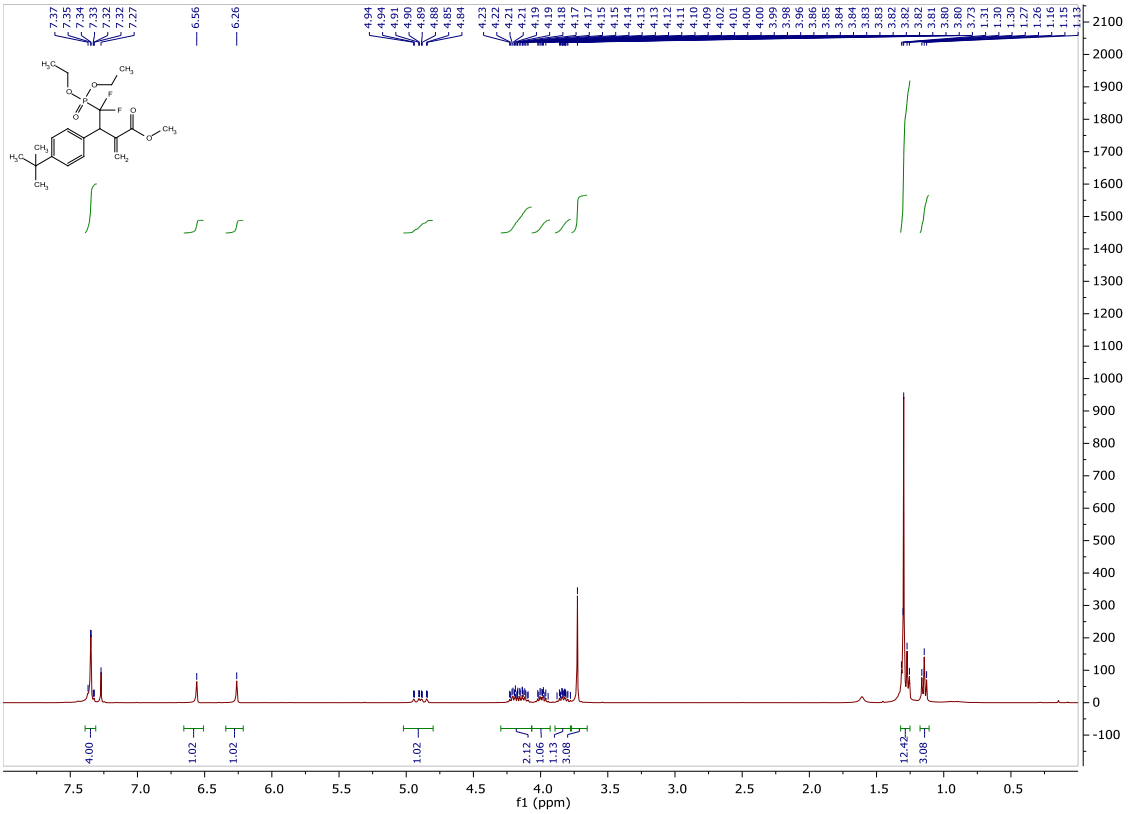


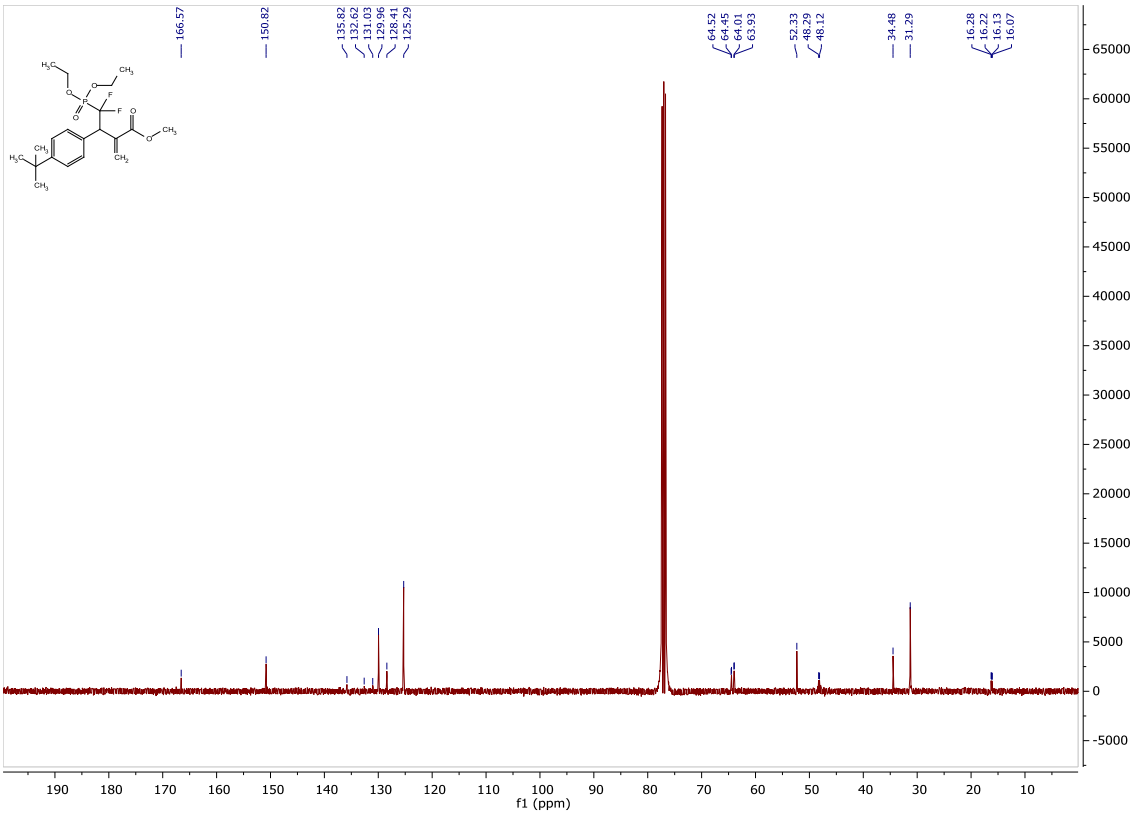


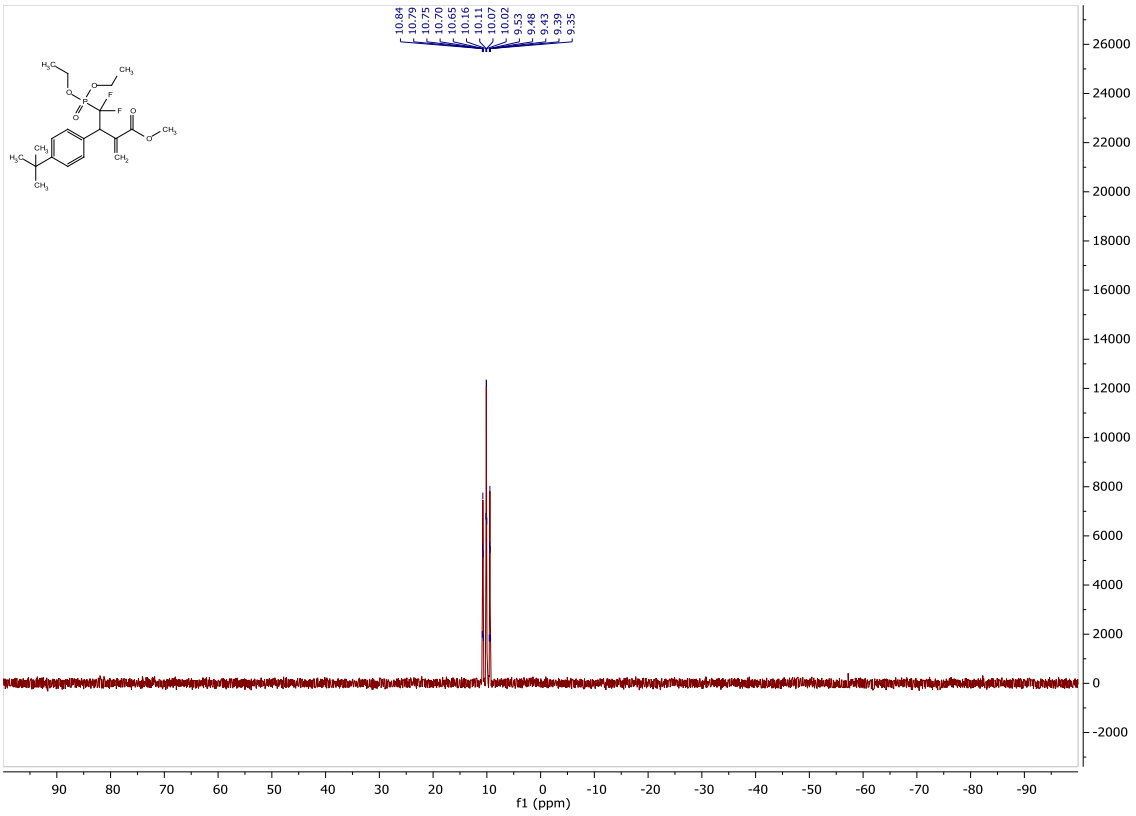

ZY-6038P.13.fid
Zi ZY-6038P 31P
10.97
10.92
10.87
10.82
10.77
10.31
10.26
10.21
10.16
10.11
9.65
9.60
9.55
9.50
9.45
40000
35000
30000
25000
20000
15000
10000
5000
0
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

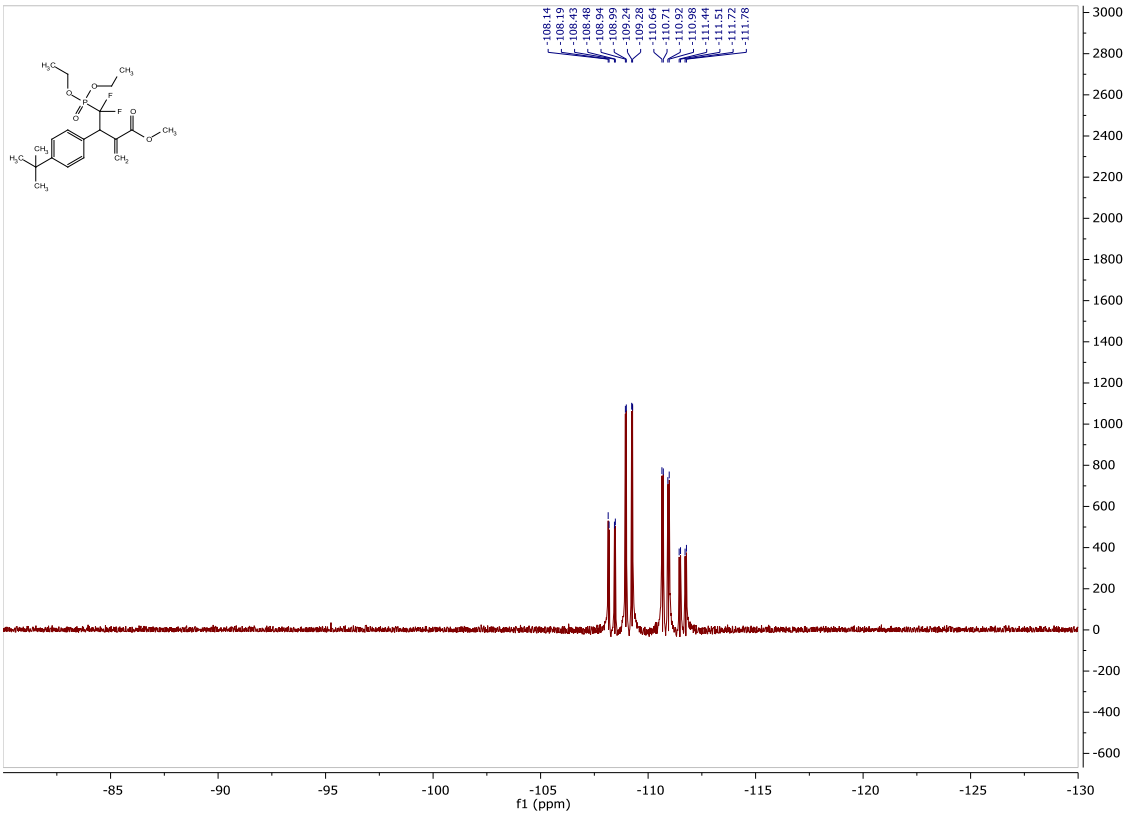

-109.33
-109.36
-109.38
-109.42
-109.61
-109.65
-109.67
-109.70
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl (S)-3-(4-(tert-butyl)phenyl)-4-(diethoxyphosphoryl)-4,4-difluoro-2-methylenebutanoate (*S*-3u)

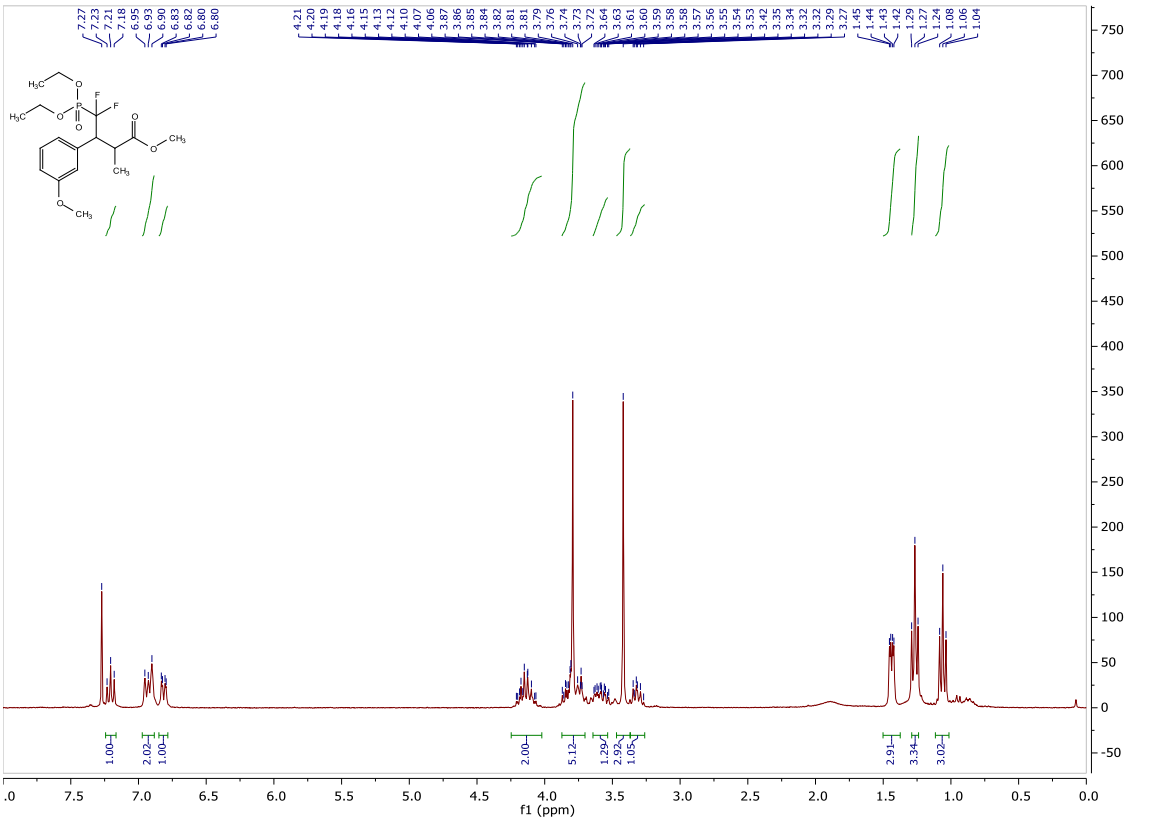


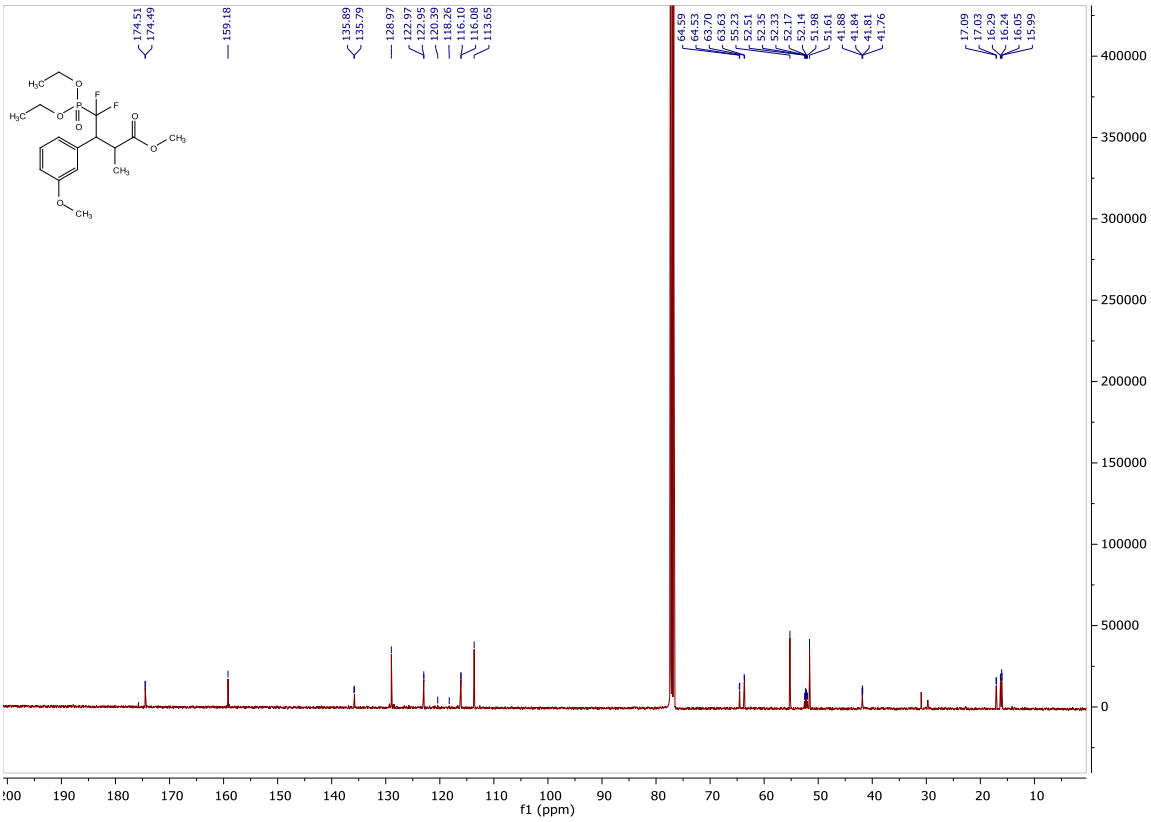


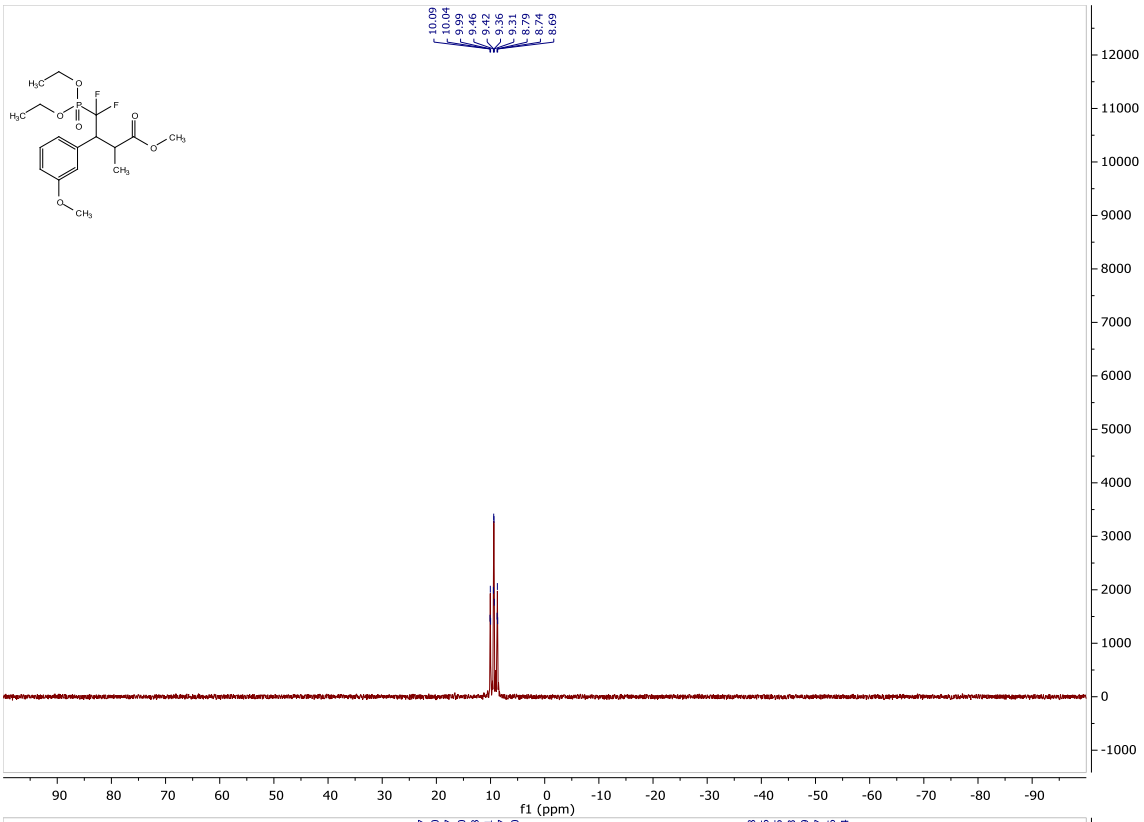

10.84
10.79
10.75
10.70
10.65
10.16
10.11
10.07
10.02
9.53
9.48
9.43
9.39
9.35
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

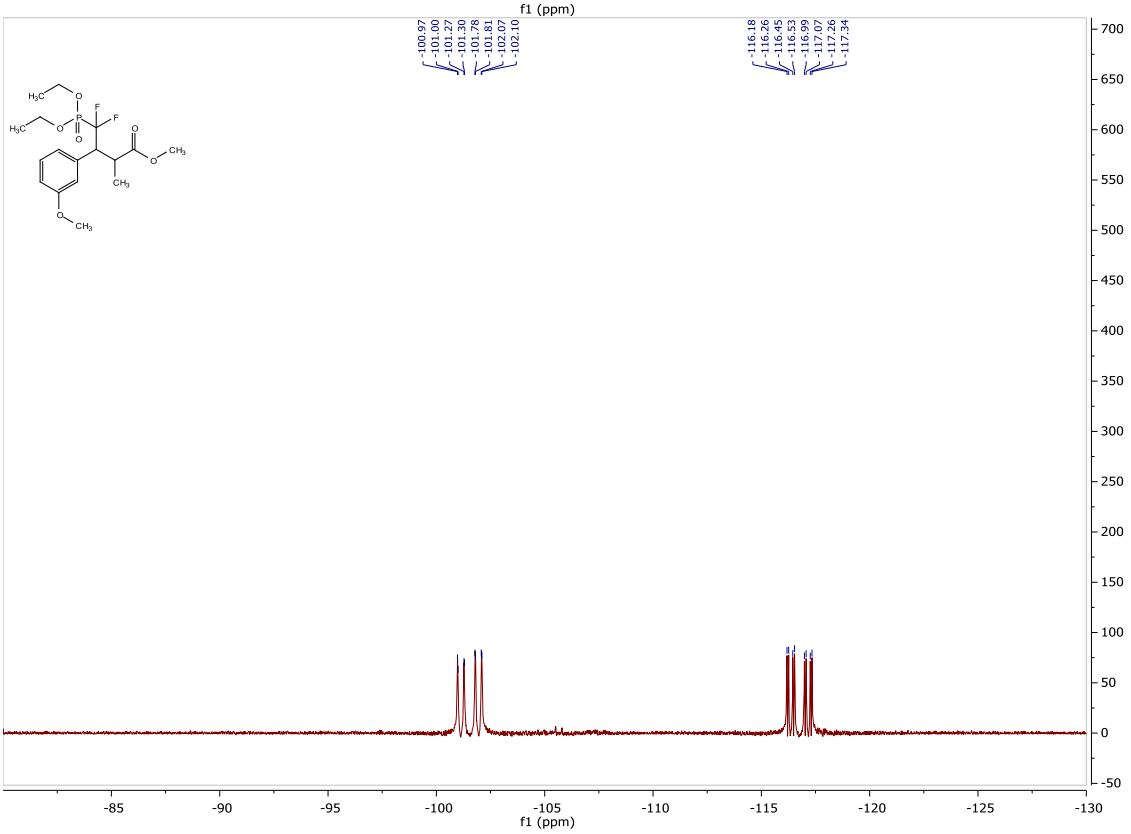

-108.14
-108.19
-108.43
-108.48
-108.94
-108.99
-109.24
-109.28
-110.64
-110.71
-110.93
-110.98
-111.44
-111.51
-111.72
-111.78
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

methyl 4-(diethoxyphosphoryl)-4,4-difluoro-3-(3-methoxyphenyl)-2-methylbutanoate (6)

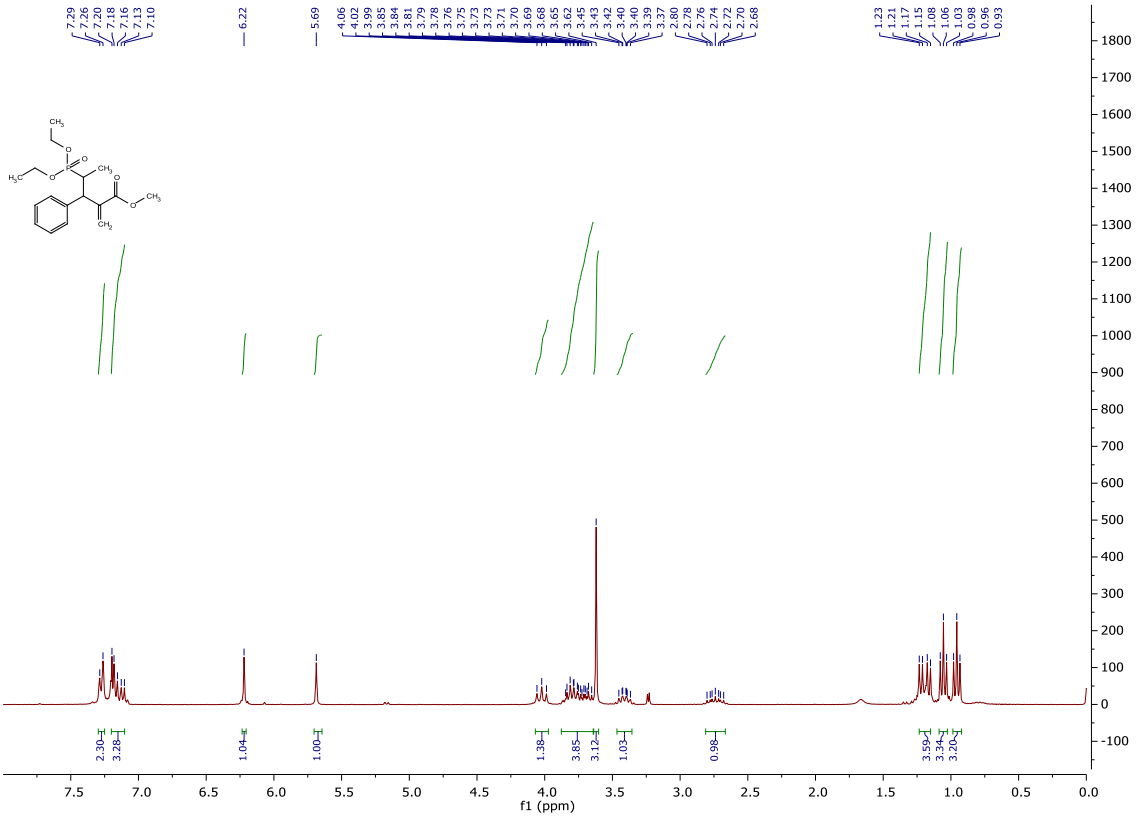


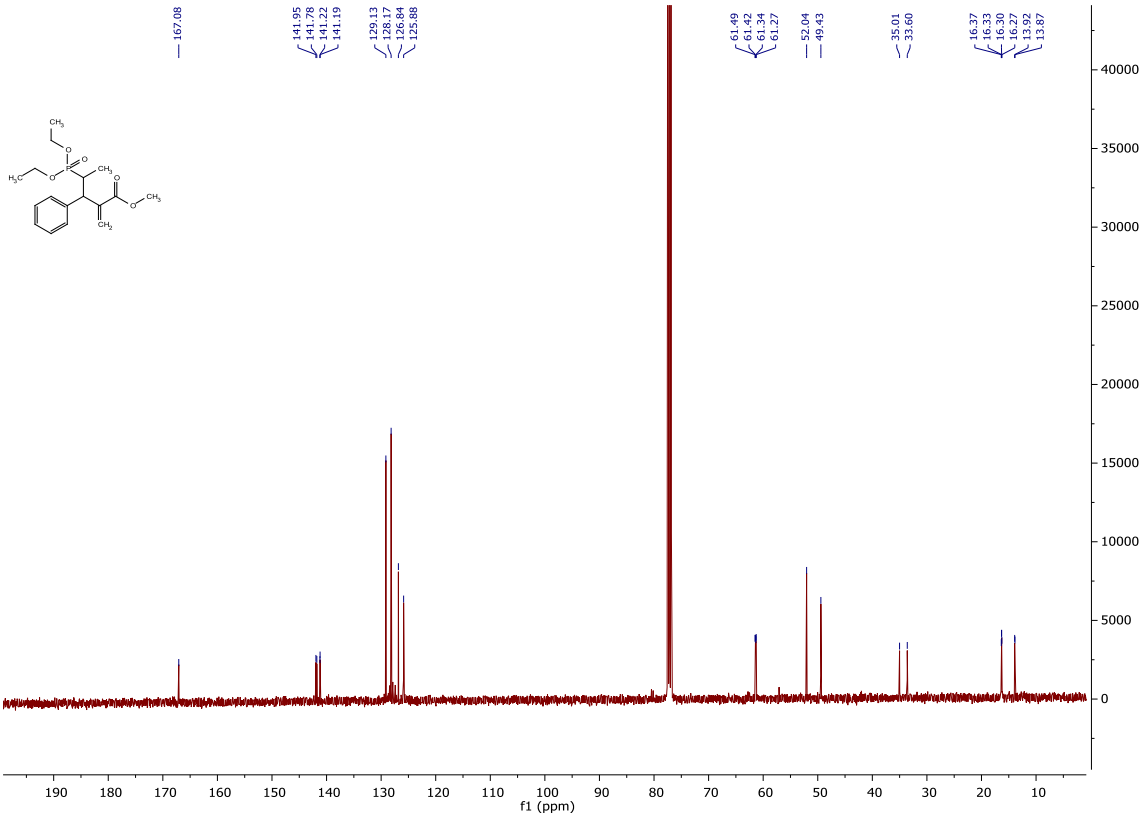


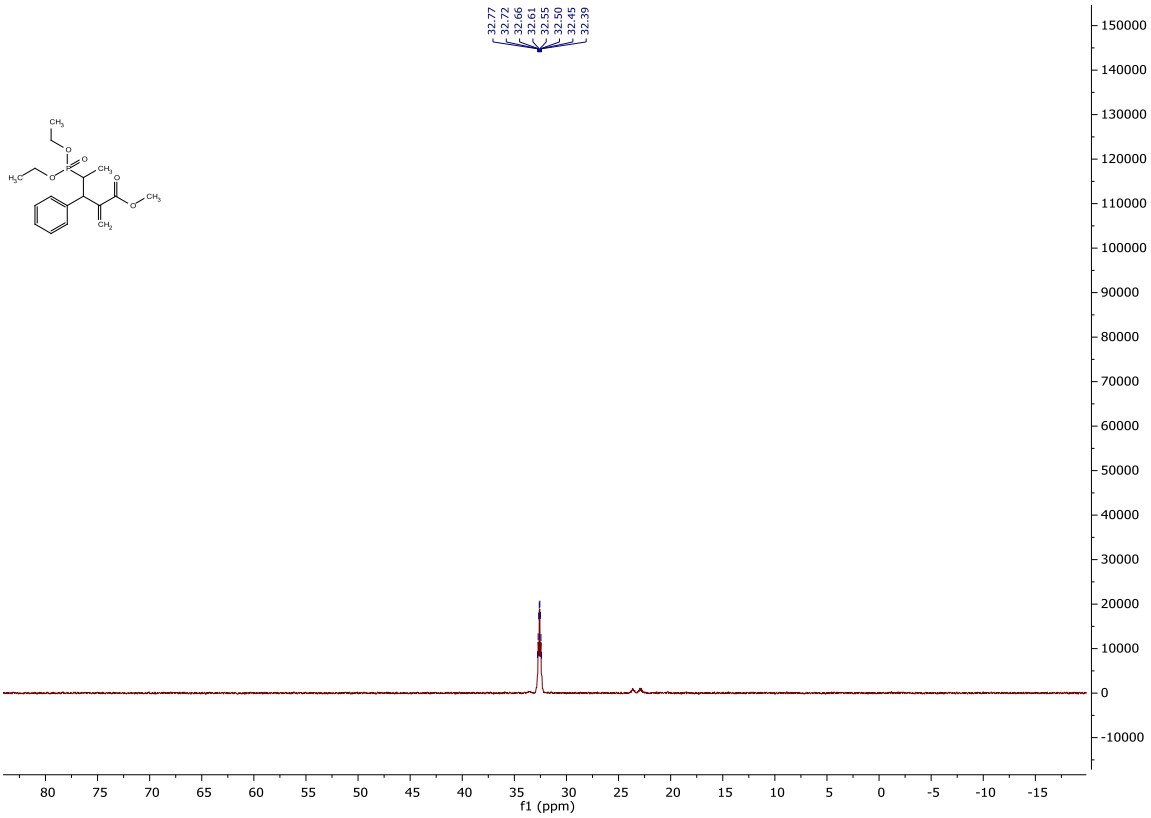

10.09
10.04
9.99
9.46
9.42
9.36
9.31
8.79
8.74
8.69
f1 (ppm)


-100.97
-101.00
-101.27
-101.30
-101.78
-101.81
-102.07
-102.10
-116.18
-116.26
-116.45
-116.53
-116.99
-117.07
-117.26
-117.34
f1 (ppm)

methyl 4-(diethoxyphosphoryl)-2-methylene-3-phenylpentanoate (9)



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32.61
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32.39
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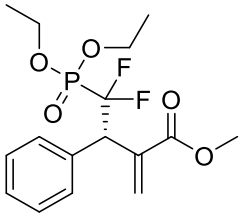
f1 (ppm)

Copies of HPLC spectra



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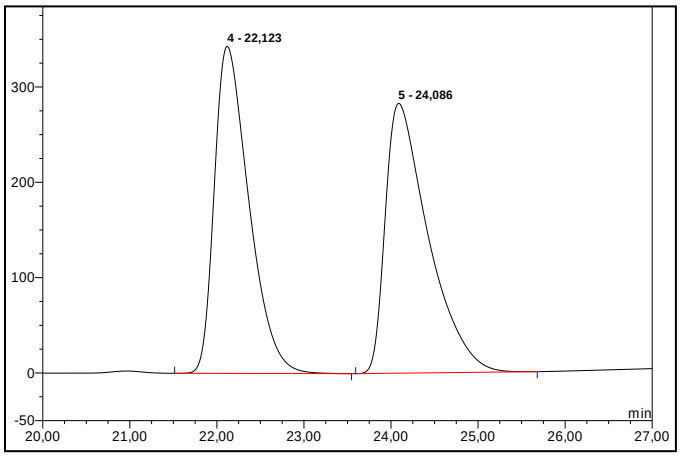
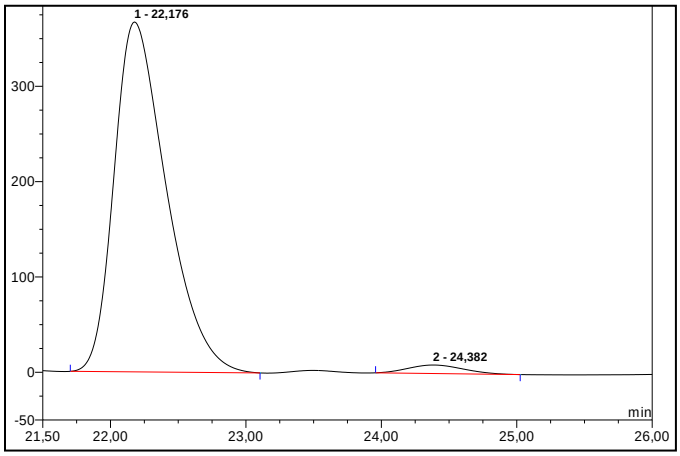
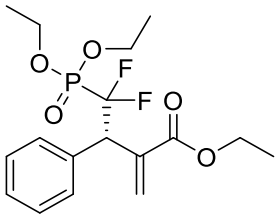


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.12	n.a.	343.095	157.854	49.42	n.a.	BMB
2	24.09	n.a.	283.095	161.587	50.58	n.a.	BMB
Total:			626.190	319.441	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.18	n.a.	367.030	164.652	97.51	n.a.	BMB*
2	24.38	n.a.	8.910	4.199	2.49	n.a.	BMB*
Total:			375.940	168.850	100.00	0.000	



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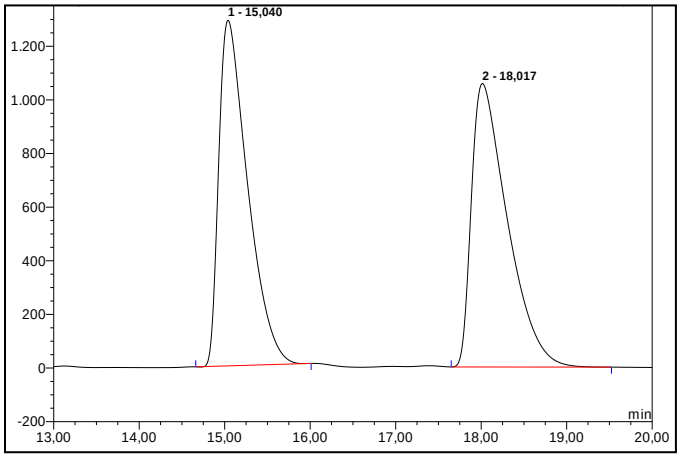
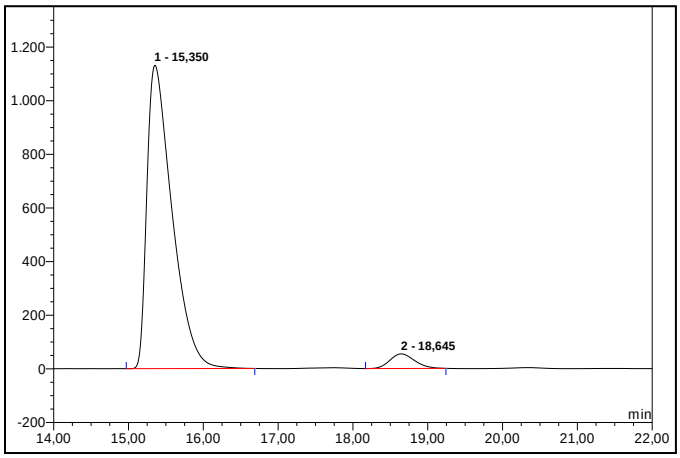
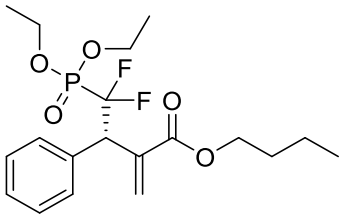


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.04	n.a.	1289.449	503.878	49.48	n.a.	BMB*
2	18.02	n.a.	1057.423	514.545	50.52	n.a.	BMB*
Total:			2346.872	1018.422	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.35	n.a.	1131.240	440.450	95.47	n.a.	BMB*
2	18.65	n.a.	54.457	20.875	4.53	n.a.	BMB*
Total:			1185.697	461.325	100.00	0.000	



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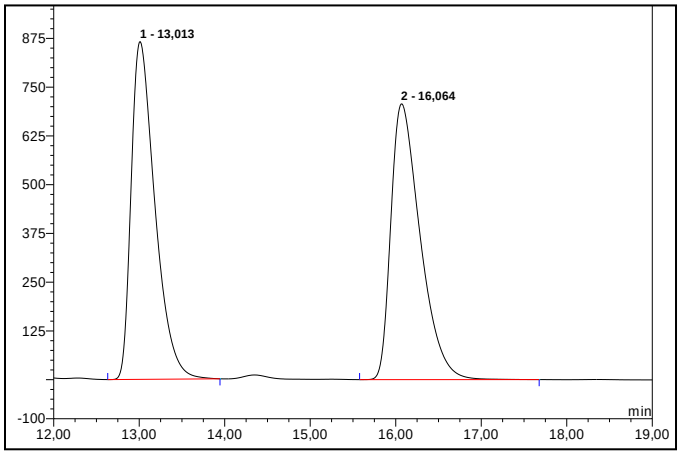
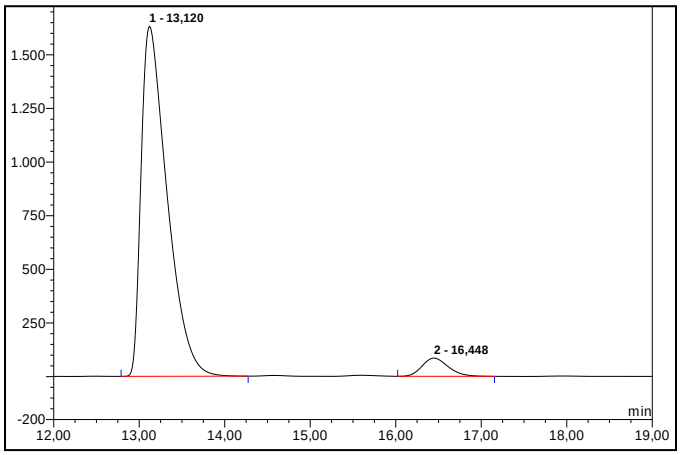
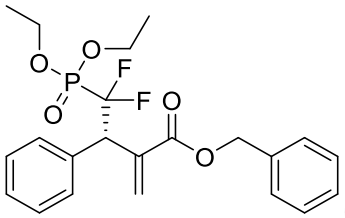


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.01	n.a.	865.953	279.368	49.88	n.a.	BMB*
2	16.06	n.a.	706.900	280.658	50.12	n.a.	BMB*
Total:			1572.853	560.027	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.12	n.a.	1631.512	573.908	95.02	n.a.	BMB*
2	16.45	n.a.	84.824	30.085	4.98	n.a.	BMB*
Total:			1716.336	603.993	100.00	0.000	



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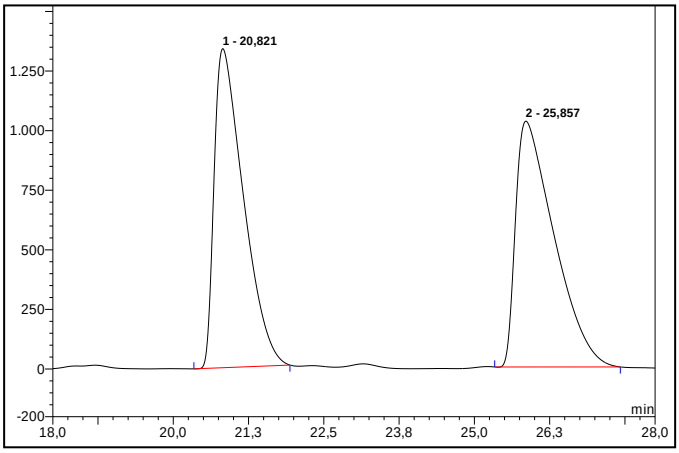
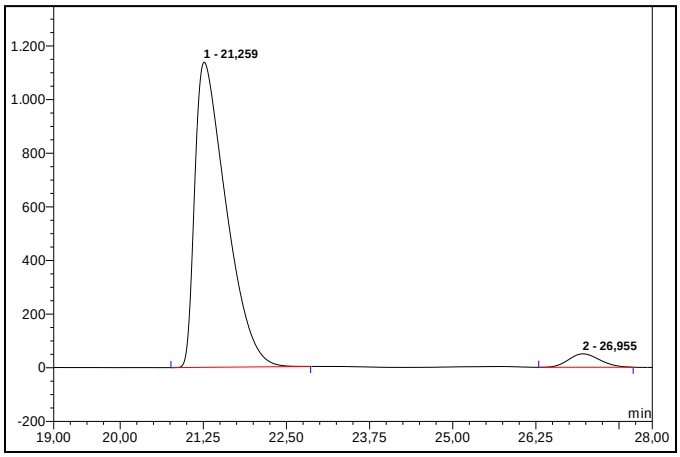
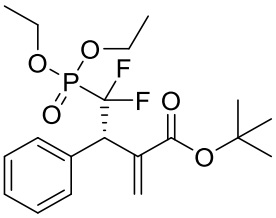
2.5



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.82	n.a.	1338.707	753.962	49.66	n.a.	BMB*
2	25.86	n.a.	1031.282	764.320	50.34	n.a.	BMB*
Total:			2369.989	1518.282	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.26	n.a.	1138.004	622.808	95.82	n.a.	BMB*
2	26.95	n.a.	50.086	27.186	4.18	n.a.	BMB*
Total:			1188.090	649.995	100.00	0.000	



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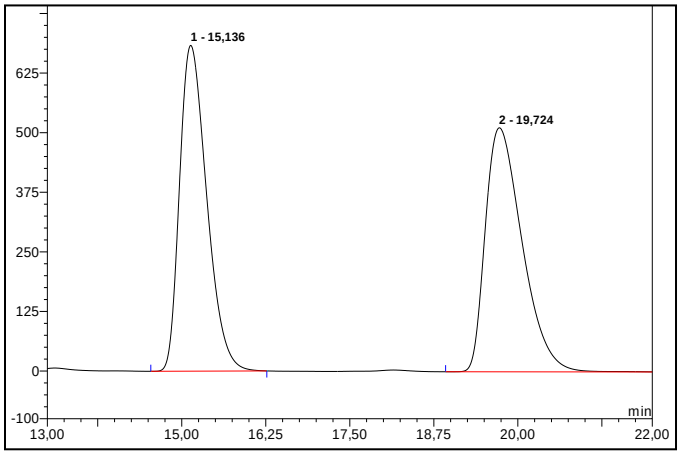
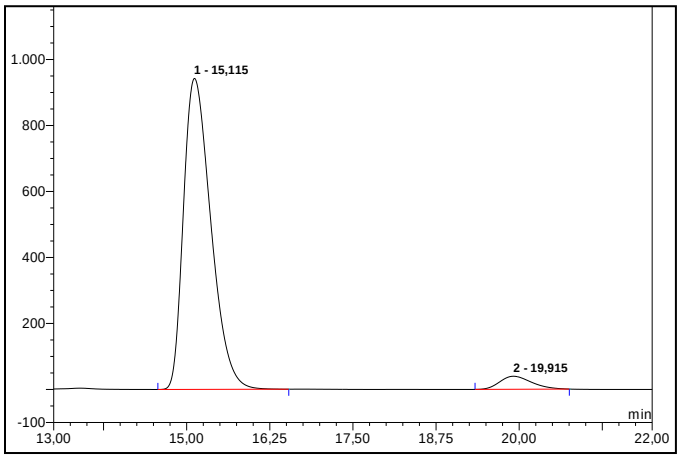
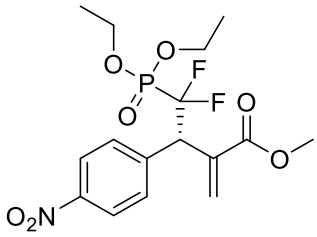


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.14	n.a.	683.451	320.318	49.64	n.a.	BMB*
2	19.72	n.a.	511.827	324.962	50.36	n.a.	BMB*
Total:			1195.278	645.280	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.11	n.a.	942.498	449.649	95.37	n.a.	BMB
2	19.92	n.a.	39.482	21.847	4.63	n.a.	BMB*
Total:			981.980	471.496	100.00	0.000	



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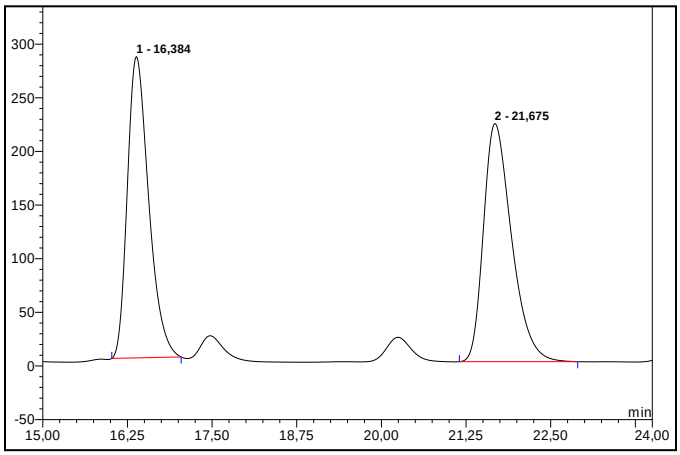
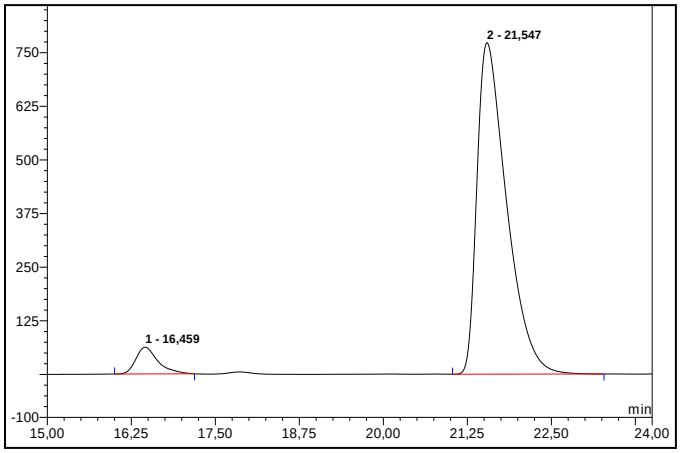
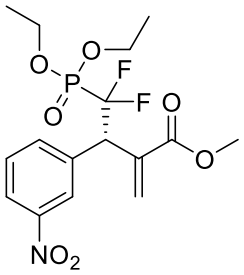


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.38	n.a.	280.869	102.745	49.03	n.a.	BMB*
2	21.67	n.a.	221.936	106.797	50.97	n.a.	BMB*
Total:			502.805	209.542	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.46	n.a.	62.192	23.775	5.67	n.a.	BMB*
2	21.55	n.a.	772.536	395.709	94.33	n.a.	BMB*
Total:			834.728	419.484	100.00	0.000	



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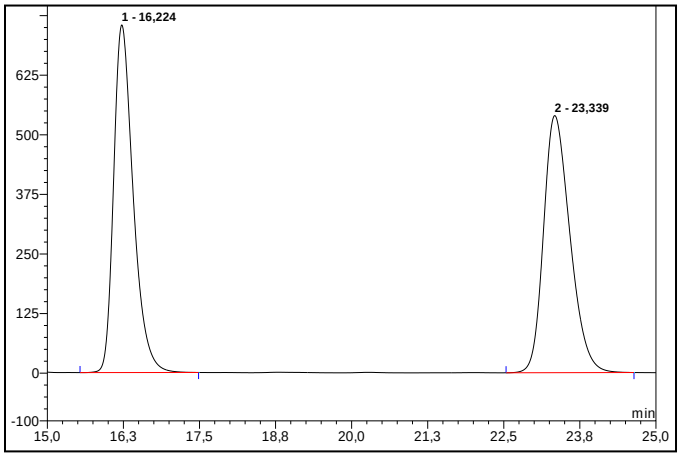
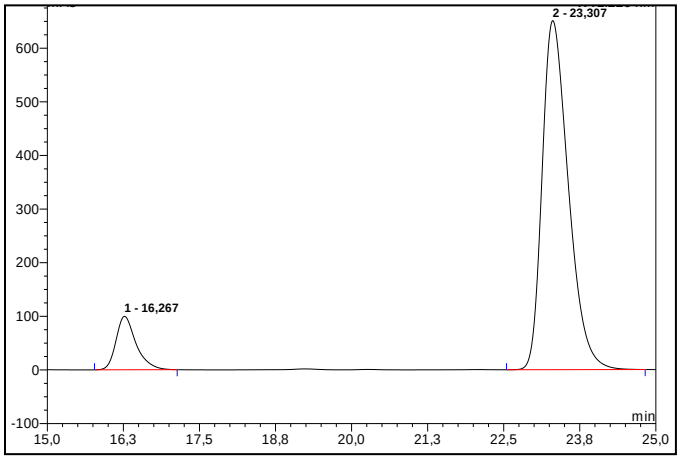
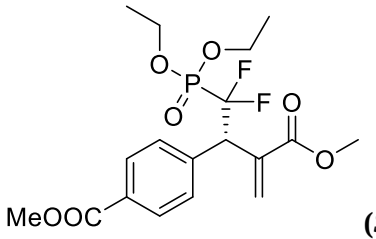


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.22	n.a.	729.433	271.715	49.97	n.a.	BMB*
2	23.34	n.a.	539.350	272.014	50.03	n.a.	BMB*
Total:			1268.783	543.729	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.27	n.a.	99.692	38.010	10.45	n.a.	BMB*
2	23.31	n.a.	651.095	325.686	89.55	n.a.	BMB*
Total:			750.787	363.696	100.00	0.000	



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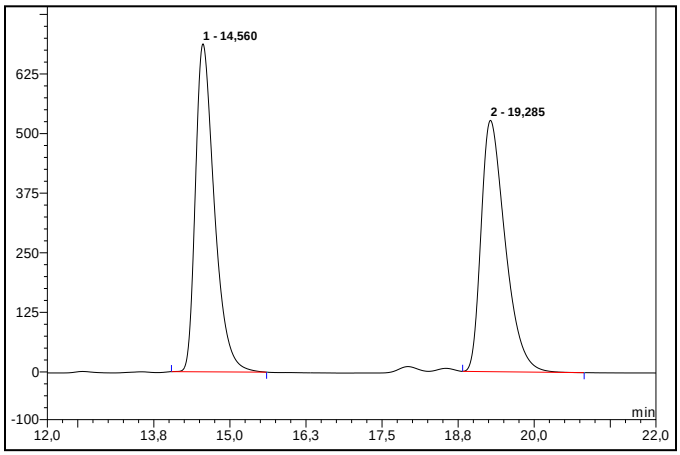
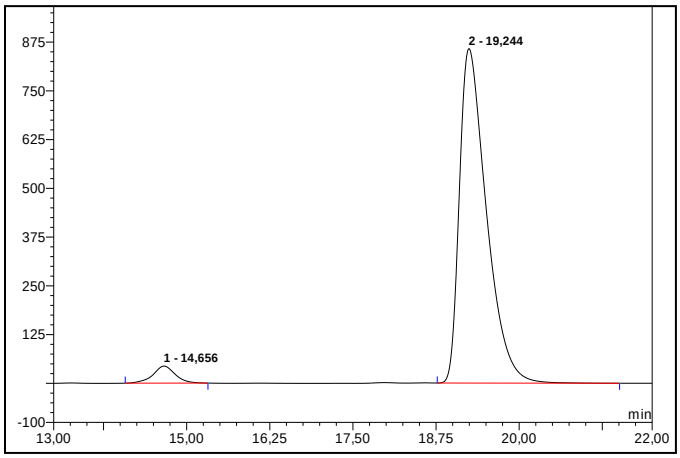
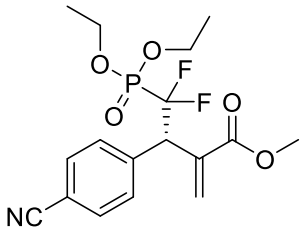


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.56	n.a.	688.005	248.454	50.66	n.a.	BMB*
2	19.29	n.a.	527.109	242.003	49.34	n.a.	BMB
Total:			1215.114	490.457	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.66	n.a.	43.646	16.857	4.01	n.a.	BMB*
2	19.24	n.a.	857.694	403.679	95.99	n.a.	BMB
Total:			901.340	420.536	100.00	0.000	



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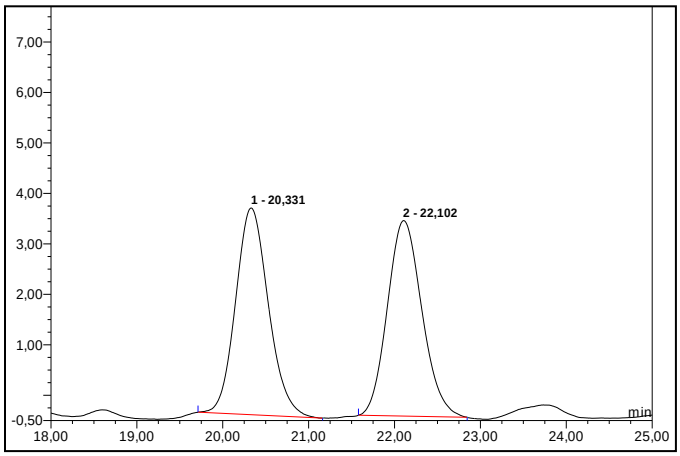
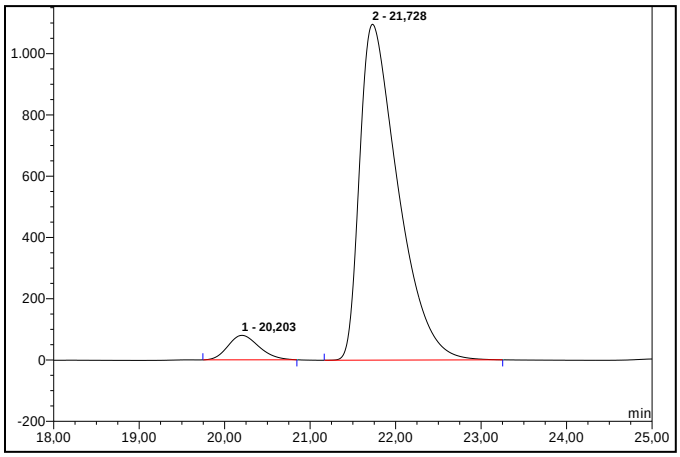
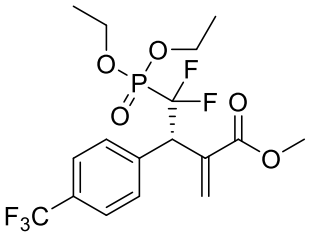


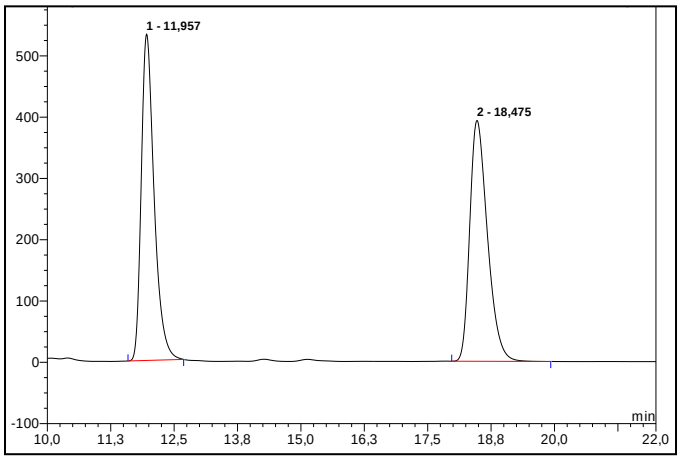
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.33	n.a.	4.095	1.811	50.09	n.a.	BMB*
2	22.10	n.a.	3.872	1.805	49.91	n.a.	BMB*
Total:			7.967	3.616	100.00	0.000	



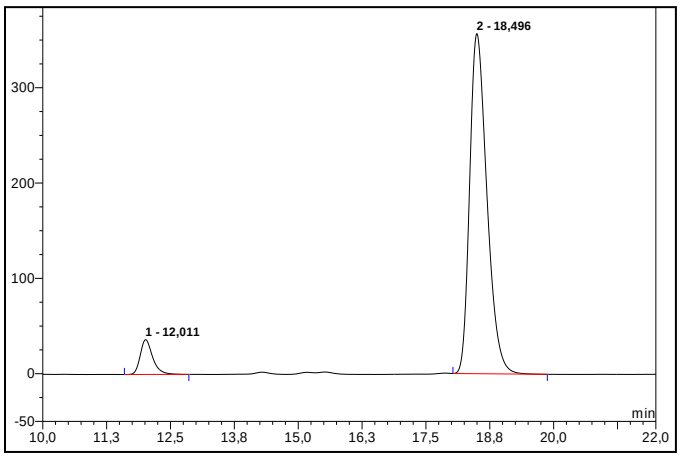
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.20	n.a.	79.891	33.624	5.56	n.a.	BMB*
2	21.73	n.a.	1096.400	571.226	94.44	n.a.	BMB*
Total:			1176.291	604.850	100.00	0.000	



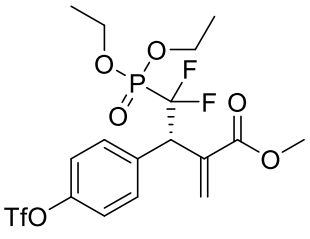
(*S*-3k)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.96	n.a.	532.716	156.681	49.66	n.a.	BMB*
2	18.47	n.a.	393.080	158.825	50.34	n.a.	BMB
Total:			925.796	315.506	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.01	n.a.	36.467	10.306	6.88	n.a.	BMB
2	18.50	n.a.	356.779	139.548	93.12	n.a.	BMB
Total:			393.246	149.854	100.00	0.000	



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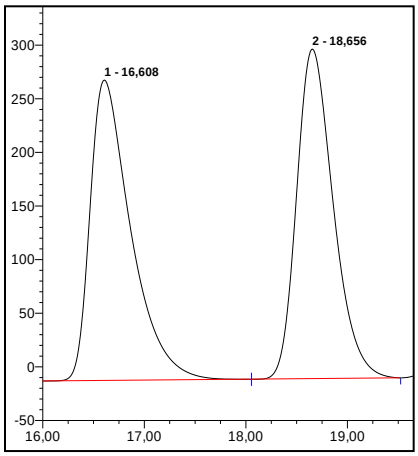
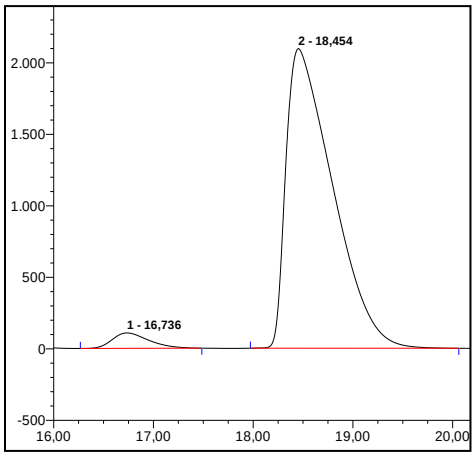
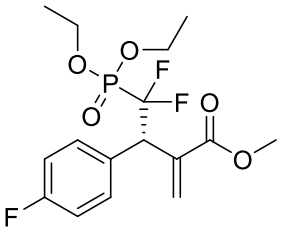


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.61	n.a.	280.121	129.903	50.27	n.a.	BM *
2	18.66	n.a.	307.317	128.526	49.73	n.a.	MB*
Total:			587.438	258.429	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.74	n.a.	107.860	45.626	3.86	n.a.	BMB*
2	18.45	n.a.	2095.988	1136.964	96.14	n.a.	BMB*
Total:			2203.848	1182.590	100.00	0.000	



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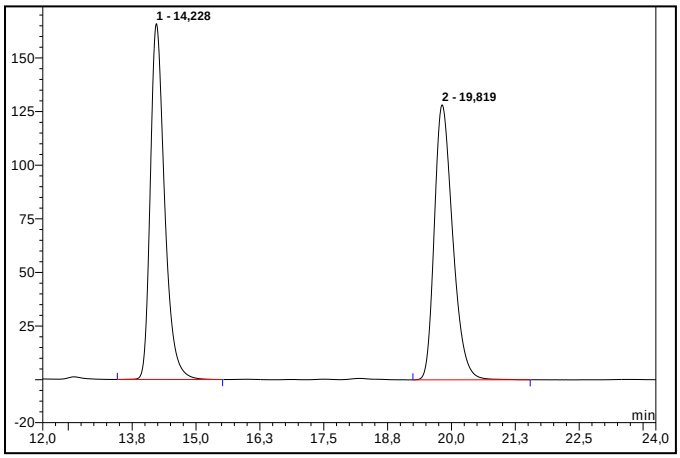
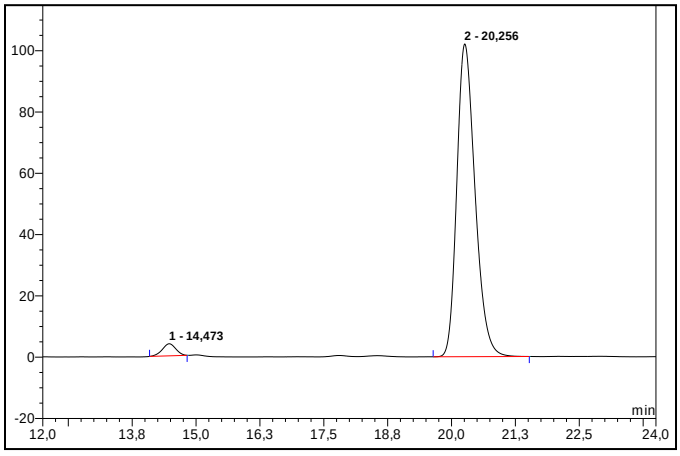
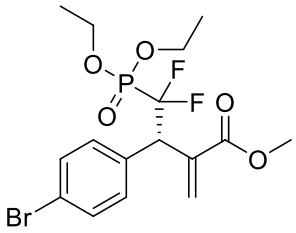


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.23	n.a.	165.849	53.859	50.15	n.a.	BMB
2	19.82	n.a.	128.212	53.538	49.85	n.a.	BMB
Total:			294.061	107.396	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.47	n.a.	3.942	1.210	2.79	n.a.	BMB*
2	20.26	n.a.	102.064	42.189	97.21	n.a.	BMB
Total:			106.006	43.400	100.00	0.000	



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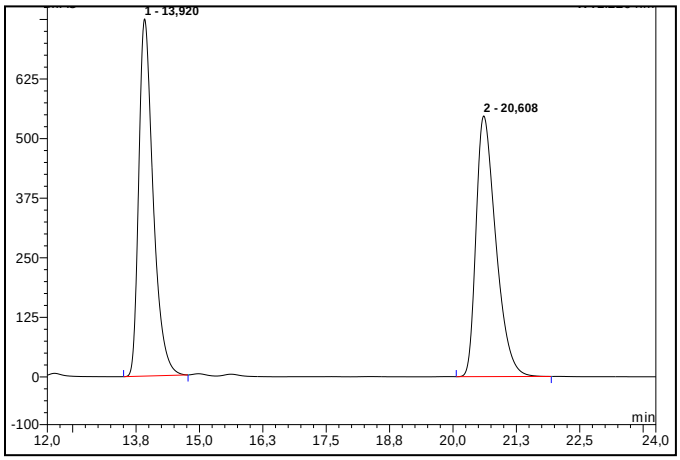
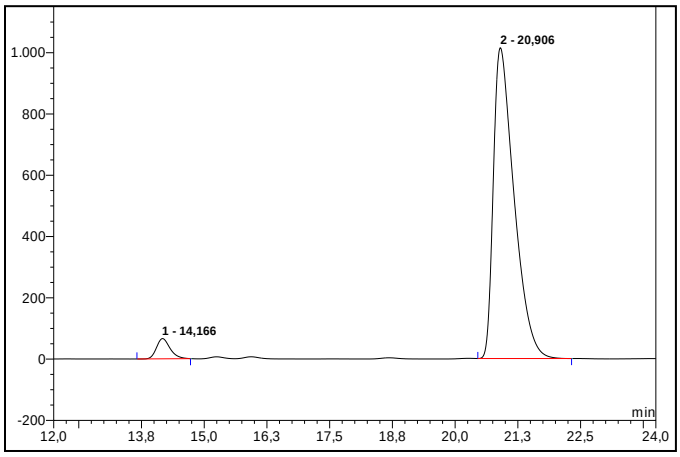
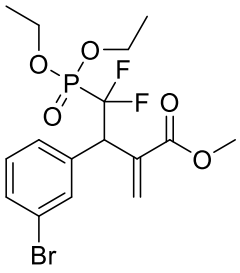


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.92	n.a.	749.575	246.293	49.89	n.a.	BMB
2	20.61	n.a.	547.037	247.411	50.11	n.a.	BMB
Total:			1296.612	493.705	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.17	n.a.	66.065	20.677	4.08	n.a.	BMB*
2	20.91	n.a.	1014.189	485.596	95.92	n.a.	BMB
Total:			1080.254	506.273	100.00	0.000	



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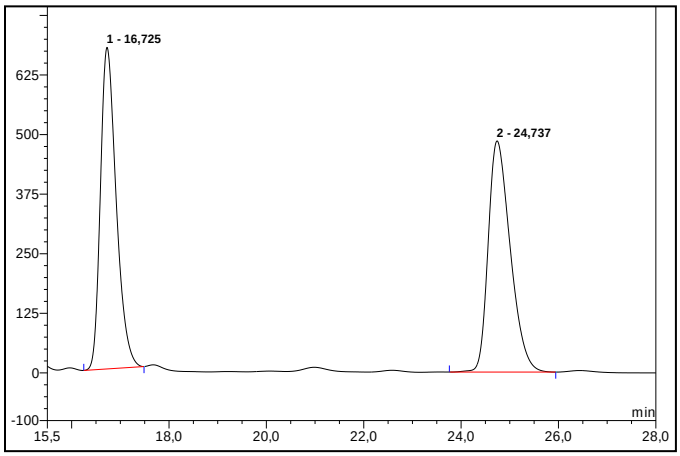
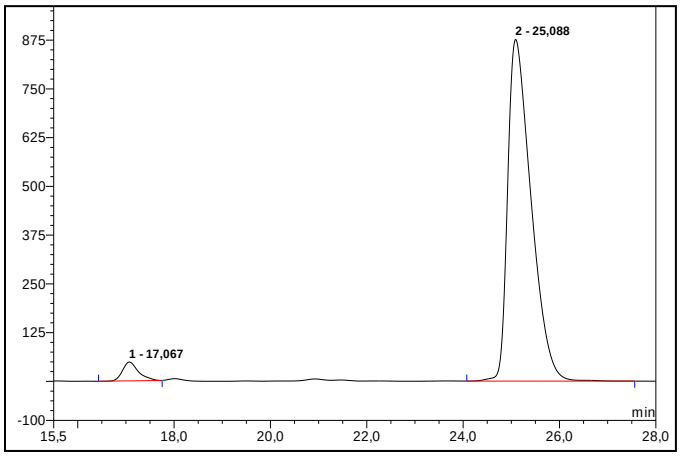
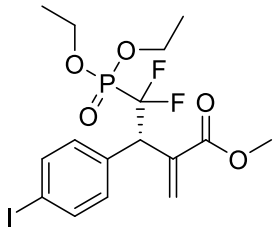


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.73	n.a.	674.775	253.826	49.91	n.a.	BMB
2	24.74	n.a.	484.936	254.770	50.09	n.a.	BMB*
Total:			1159.711	508.596	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.07	n.a.	48.222	18.488	3.61	n.a.	BMB*
2	25.09	n.a.	876.162	493.151	96.39	n.a.	BMB*
Total:			924.384	511.639	100.00	0.000	



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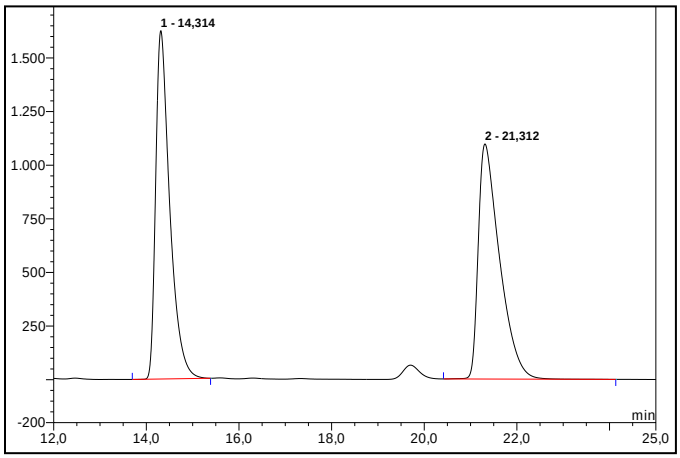
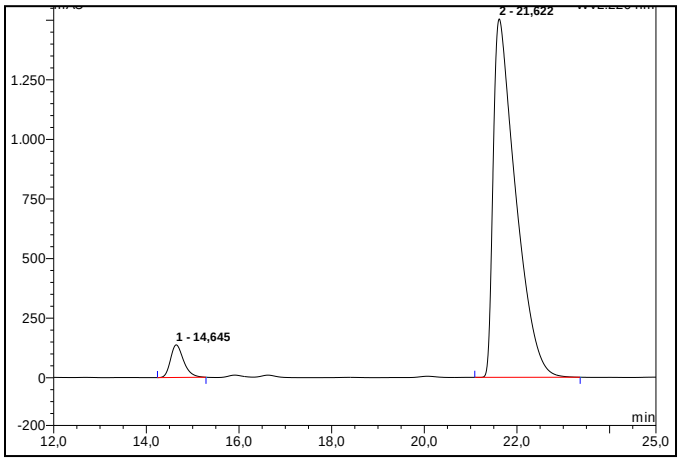
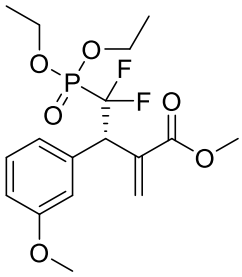


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.31	n.a.	1624.417	572.947	49.53	n.a.	BMB*
2	21.31	n.a.	1096.317	583.816	50.47	n.a.	BMB*
Total:			2720.734	1156.764	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.65	n.a.	136.774	44.790	5.04	n.a.	BMB*
2	21.62	n.a.	1503.576	843.680	94.96	n.a.	BMB*
Total:			1640.350	888.470	100.00	0.000	



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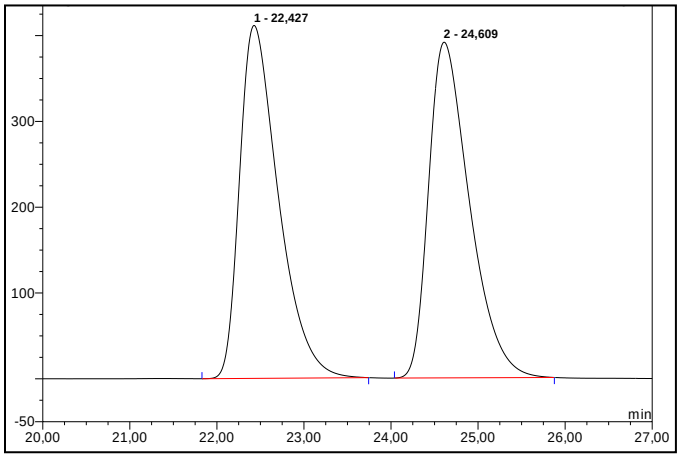
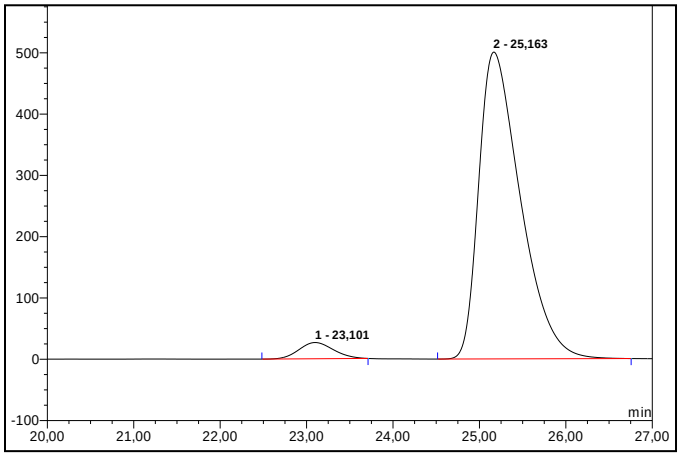
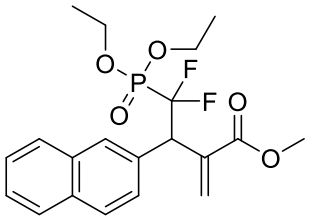


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.43	n.a.	411.287	212.609	49.90	n.a.	BMB*
2	24.61	n.a.	391.307	213.424	50.10	n.a.	BMB*
Total:			802.594	426.033	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.10	n.a.	26.513	12.309	4.22	n.a.	BMB*
2	25.16	n.a.	500.602	279.577	95.78	n.a.	BMB*
Total:			527.115	291.886	100.00	0.000	



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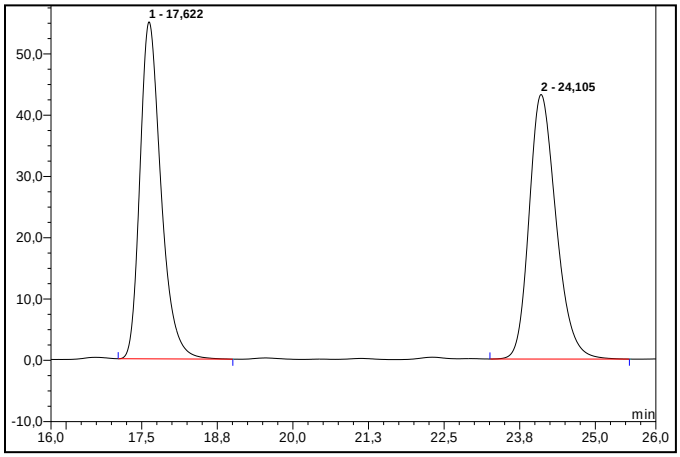
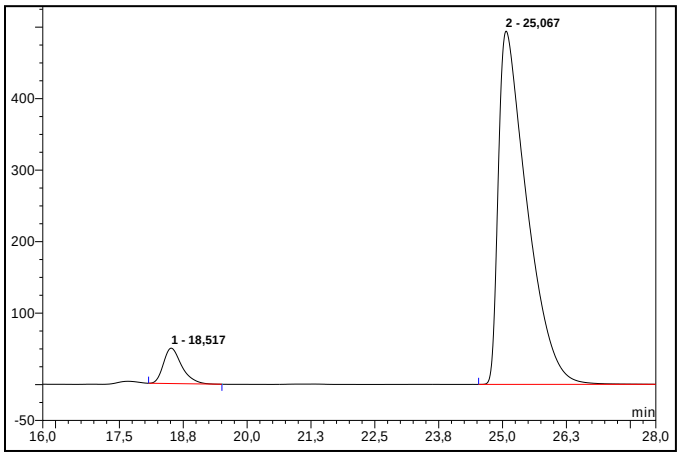
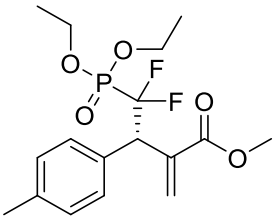


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.62	n.a.	55.000	22.200	49.84	n.a.	BMB
2	24.10	n.a.	43.163	22.340	50.16	n.a.	BMB
Total:			98.163	44.540	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.52	n.a.	49.495	20.525	6.01	n.a.	BMB
2	25.07	n.a.	494.083	320.866	93.99	n.a.	BMB
Total:			543.578	341.392	100.00	0.000	



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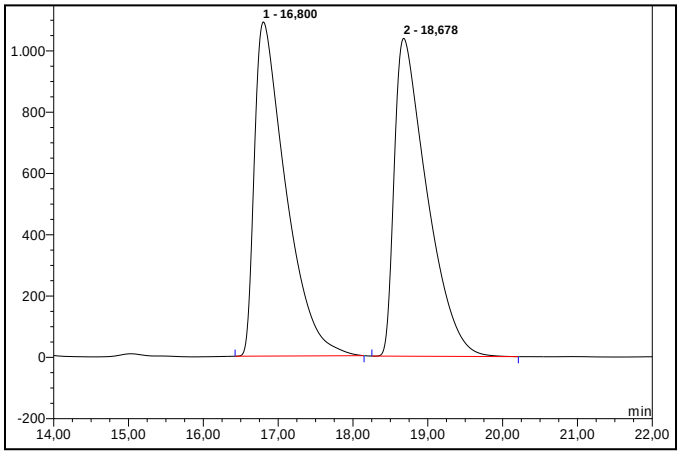
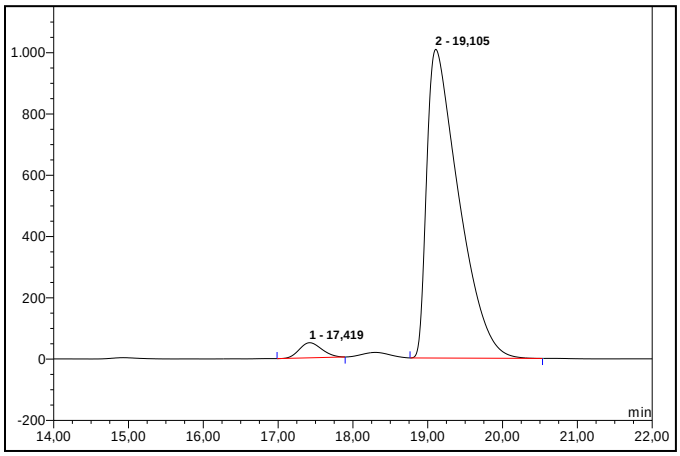
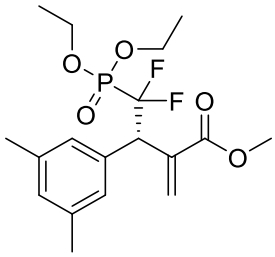


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.80	n.a.	1090.619	530.073	50.25	n.a.	BMB*
2	18.68	n.a.	1037.445	524.728	49.75	n.a.	BMB*
Total:			2128.064	1054.801	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.42	n.a.	49.278	17.111	3.30	n.a.	BMB*
2	19.10	n.a.	1007.448	501.053	96.70	n.a.	BMB*
Total:			1056.726	518.164	100.00	0.000	



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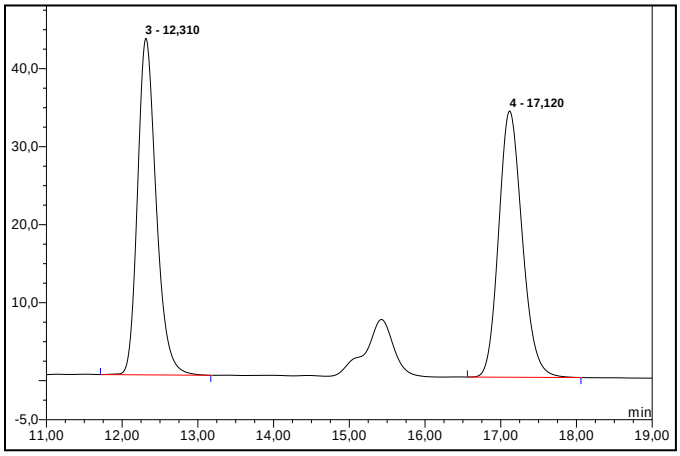
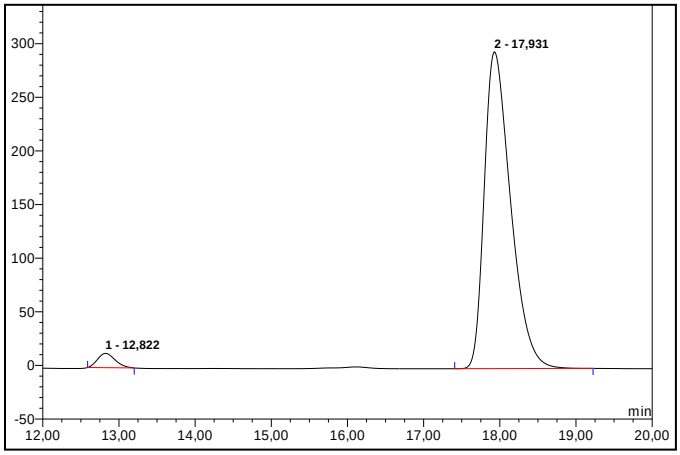
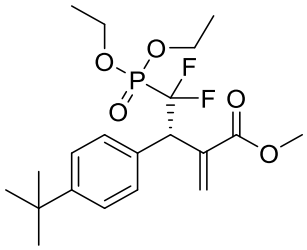


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.31	n.a.	43.144	12.306	49.98	n.a.	BMB
2	17.12	n.a.	34.133	12.317	50.02	n.a.	BMB
Total:			77.321	24.623	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.82	n.a.	13.282	3.558	2.92	n.a.	BMB*
2	17.93	n.a.	295.436	118.492	97.08	n.a.	BMB*
Total:			308.718	122.051	100.00	0.000	



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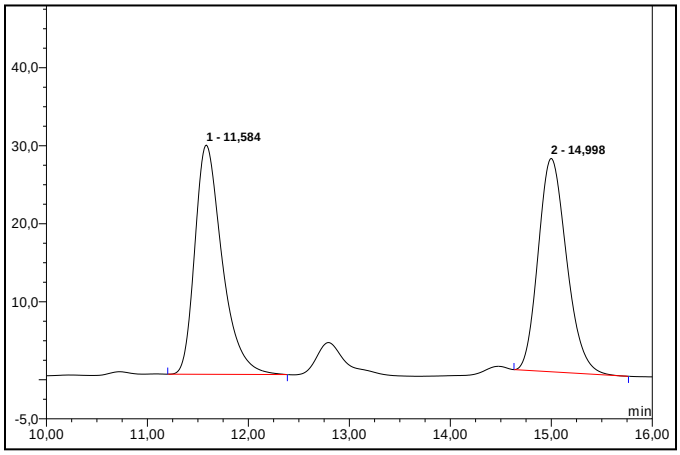
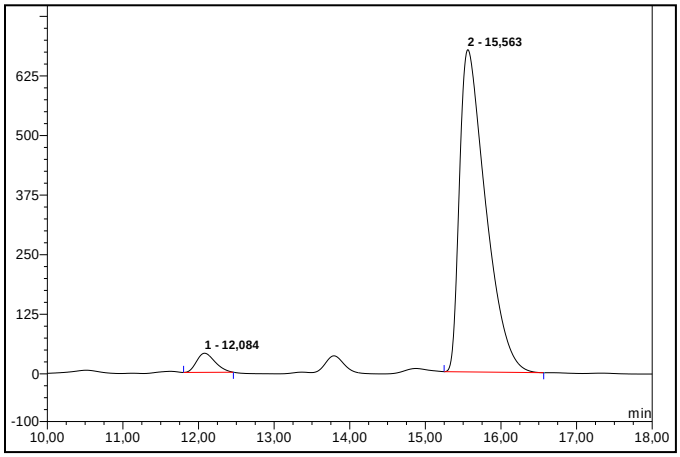
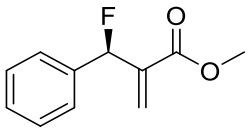


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.58	n.a.	29.386	9.195	50.78	n.a.	BMB*
2	15.00	n.a.	27.352	8.913	49.22	n.a.	BMB*
Total:			56.738	18.108	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.08	n.a.	40.151	11.374	4.02	n.a.	BMB*
2	15.56	n.a.	676.204	271.226	95.98	n.a.	BMB*
Total:			716.355	282.600	100.00	0.000	



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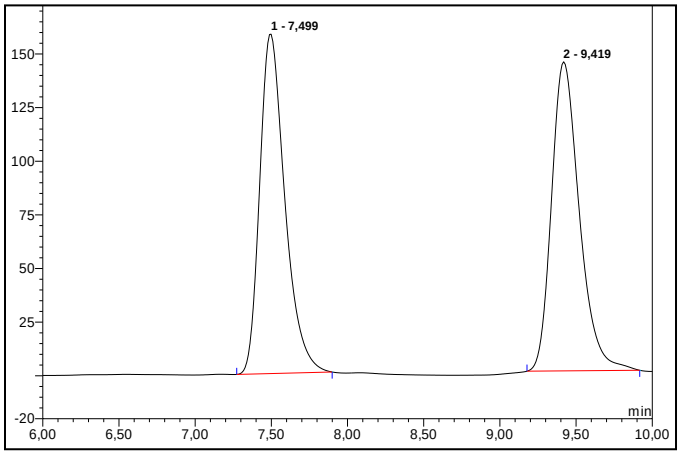
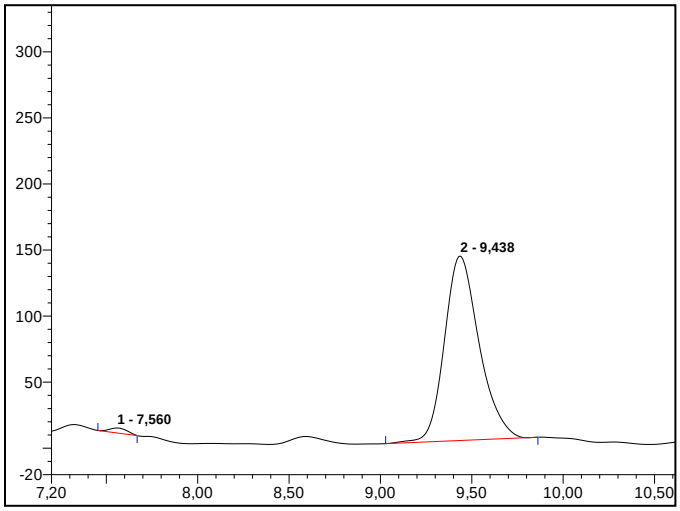
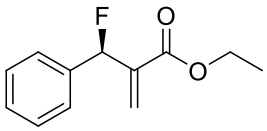


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.50	n.a.	158.223	30.284	49.83	n.a.	BMB*
2	9.42	n.a.	144.092	30.488	50.17	n.a.	BMB*
Total:			302.315	60.772	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.56	n.a.	3.777	0.425	1.36	n.a.	BMB*
2	9.44	n.a.	139.499	30.735	98.64	n.a.	BMB*
Total:			143.276	31.160	100.00	0.000	



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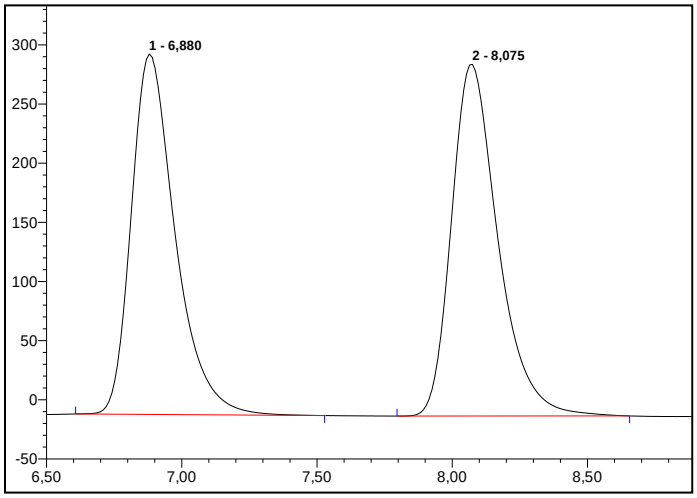
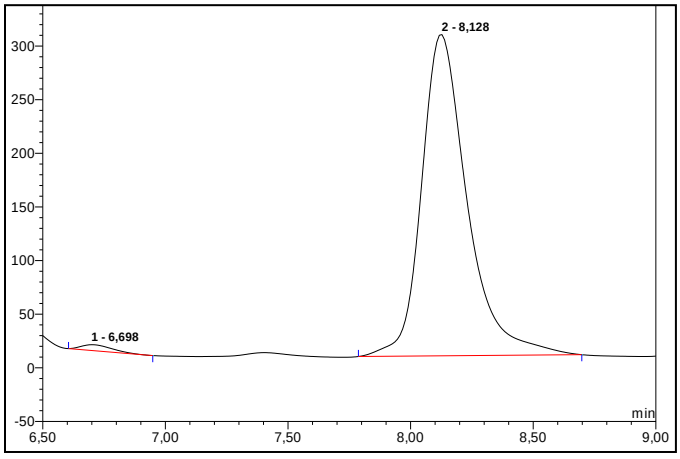
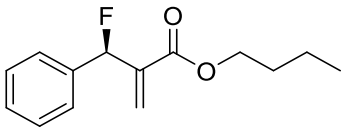


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.88	n.a.	304.687	57.309	49.17	n.a.	BMB*
2	8.07	n.a.	297.303	59.250	50.83	n.a.	BMB*
Total:			601.990	116.559	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.70	n.a.	5.372	0.791	1.21	n.a.	BMB*
2	8.13	n.a.	299.563	64.603	98.79	n.a.	BMB*
Total:			304.935	65.394	100.00	0.000	



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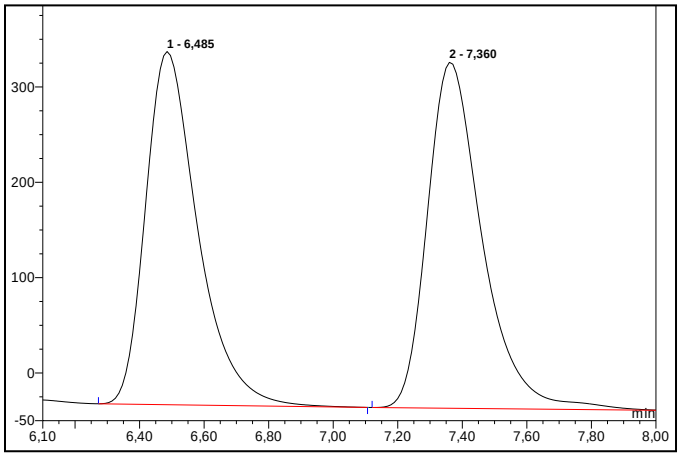
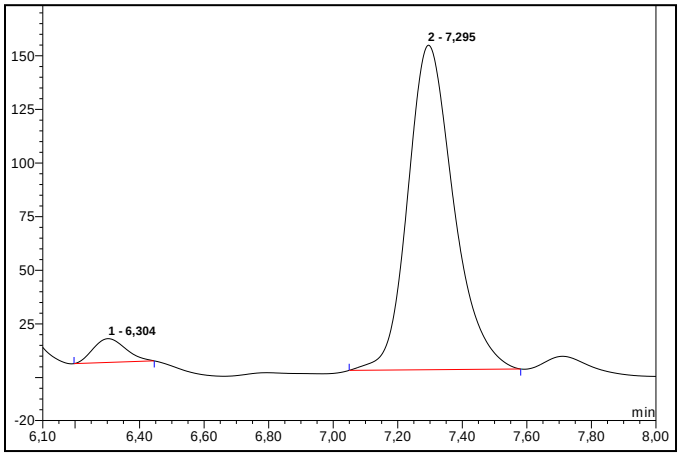
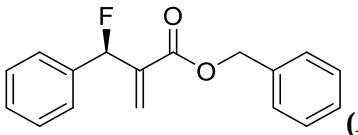


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.49	n.a.	370.430	69.416	49.28	n.a.	BMB
2	7.36	n.a.	362.769	71.436	50.72	n.a.	BMB*
Total:			733.199	140.852	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.30	n.a.	11.079	1.292	4.94	n.a.	BMB*
2	7.29	n.a.	151.271	24.883	95.06	n.a.	BMB*
Total:			162.350	26.175	100.00	0.000	



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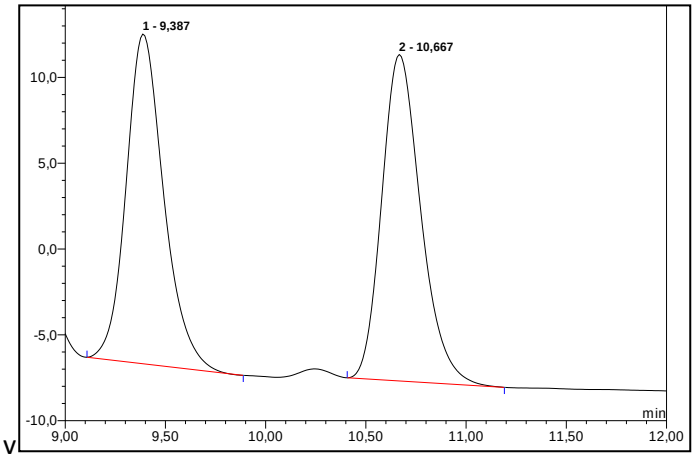
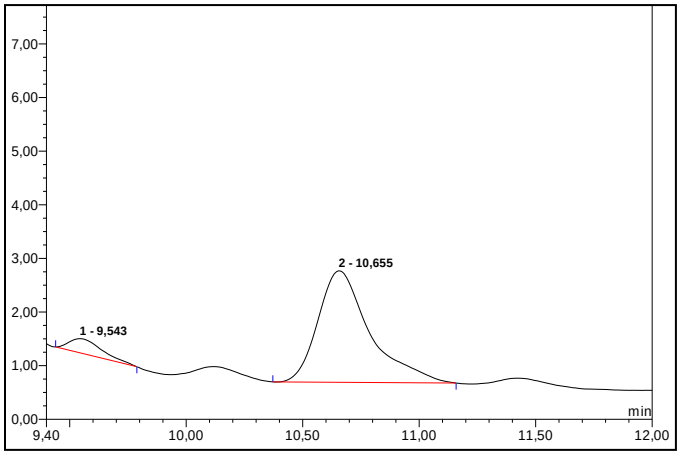
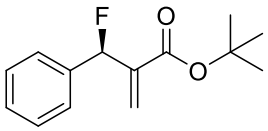


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.39	n.a.	19.210	4.193	49.39	n.a.	BMB*
2	10.67	n.a.	19.022	4.296	50.61	n.a.	BMB
Total:			38.232	8.489	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.54	n.a.	0.263	0.045	7.76	n.a.	BMB*
2	10.65	n.a.	2.078	0.535	92.24	n.a.	BMB*
Total:			2.341	0.580	100.00	0.000	



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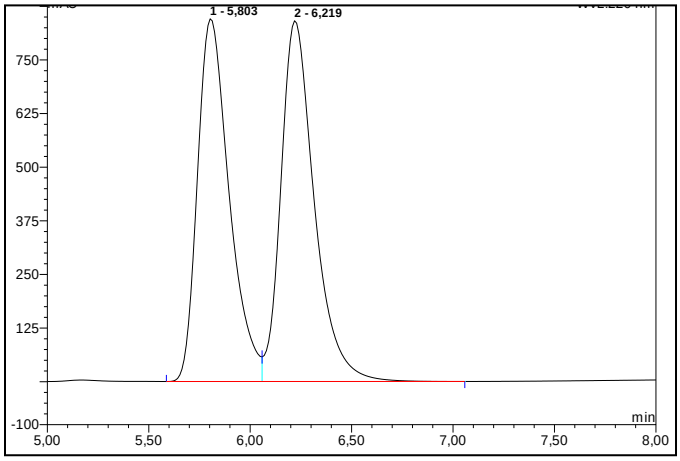
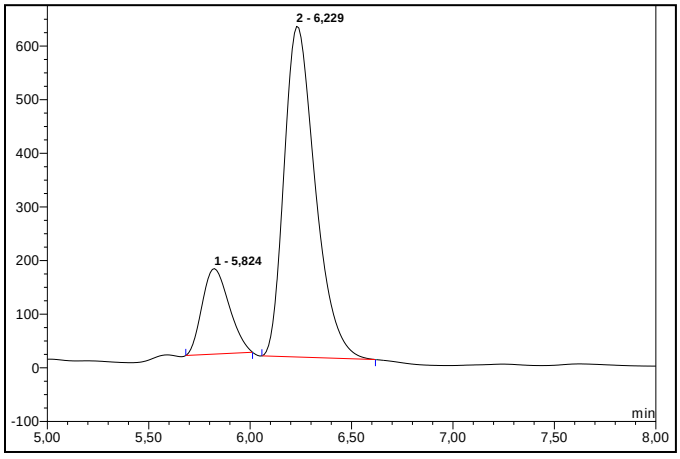
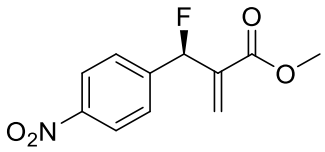


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.80	n.a.	845.457	153.230	48.84	n.a.	BM
2	6.22	n.a.	840.838	160.493	51.16	n.a.	MB*
Total:			1686.295	313.723	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.82	n.a.	159.441	24.558	18.26	n.a.	BMB*
2	6.23	n.a.	616.628	109.919	81.74	n.a.	BMB*
Total:			776.069	134.477	100.00	0.000	



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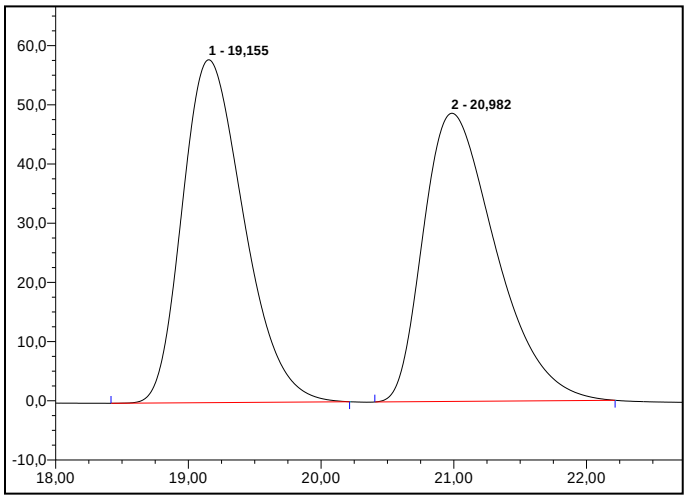
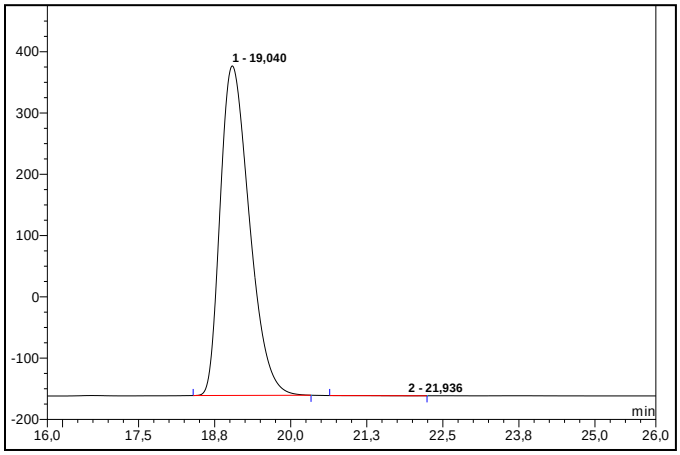
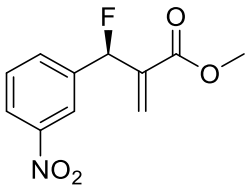


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.15	n.a.	57.929	31.169	50.27	n.a.	BMB*
2	20.98	n.a.	48.687	30.839	49.73	n.a.	BMB*
Total:			106.616	62.008	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.04	n.a.	537.799	298.323	99.97	n.a.	BMB*
2	21.94	n.a.	0.110	0.101	0.03	n.a.	BMB*
Total:			537.909	298.423	100.00	0.000	



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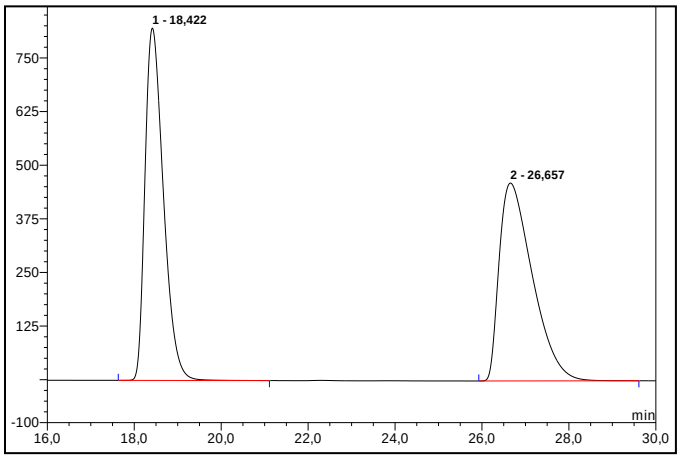
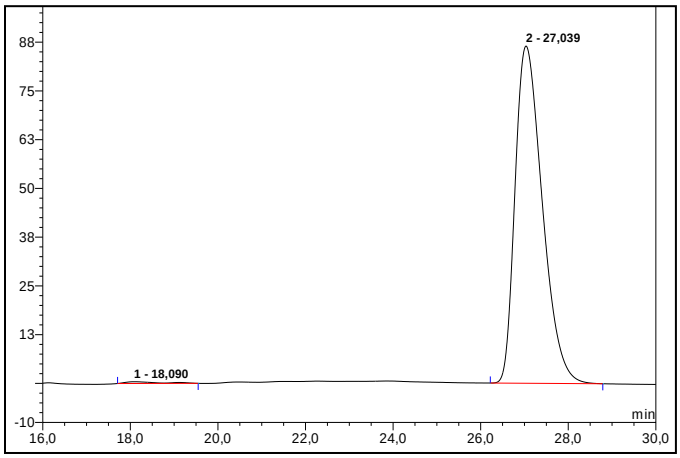
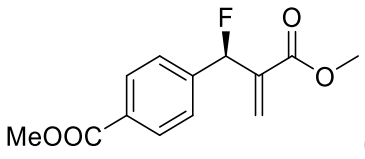


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.42	n.a.	821.161	403.459	49.77	n.a.	BMB
2	26.66	n.a.	461.288	407.259	50.23	n.a.	BMB
Total:			1282.449	810.718	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.09	n.a.	0.446	0.399	0.64	n.a.	BMB*
2	27.04	n.a.	86.465	62.249	99.36	n.a.	BMB
Total:			86.911	62.648	100.00	0.000	



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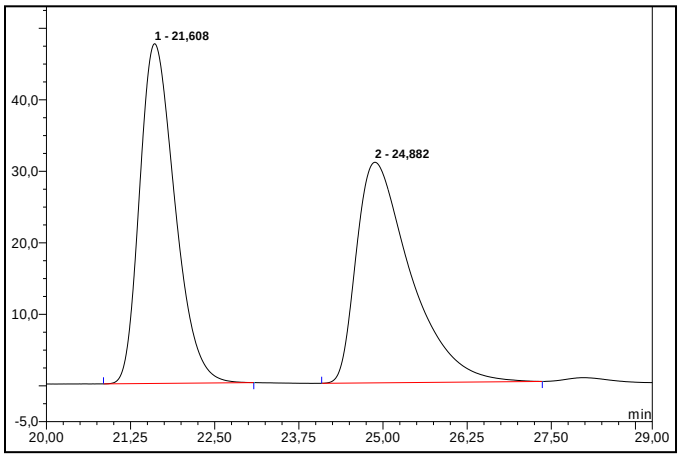
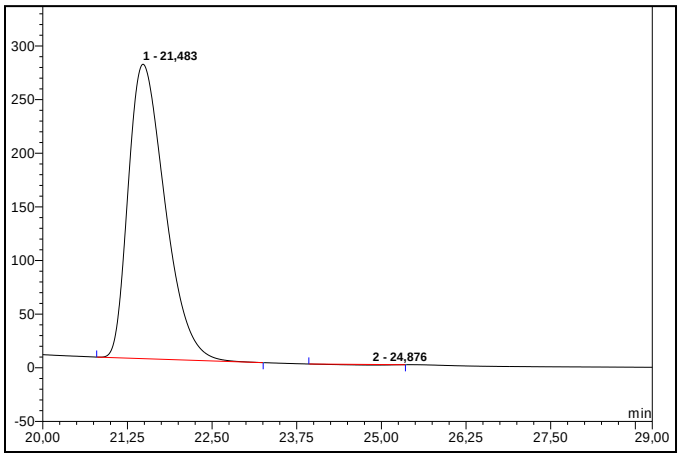
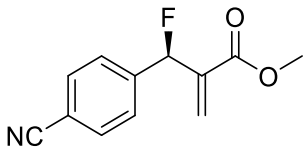


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.61	n.a.	47.512	28.872	50.06	n.a.	BMB
2	24.88	n.a.	30.845	28.803	49.94	n.a.	BMB
Total:			78.357	57.676	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	21.48	n.a.	274.453	172.535	99.71	n.a.	BMB*
2	24.88	n.a.	0.571	0.507	0.29	n.a.	BMB*
Total:			275.024	173.042	100.00	0.000	



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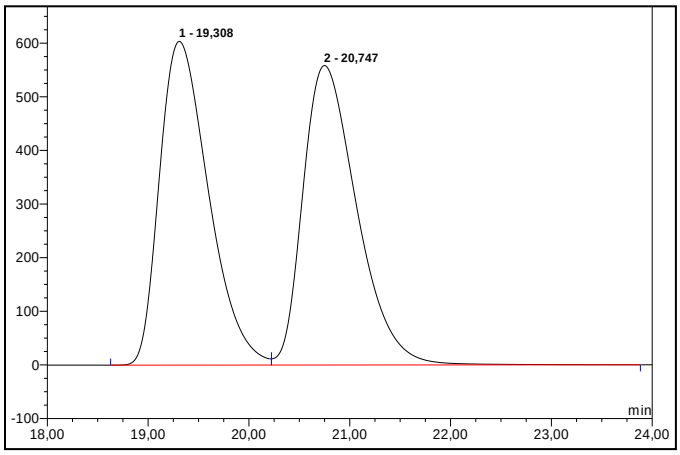
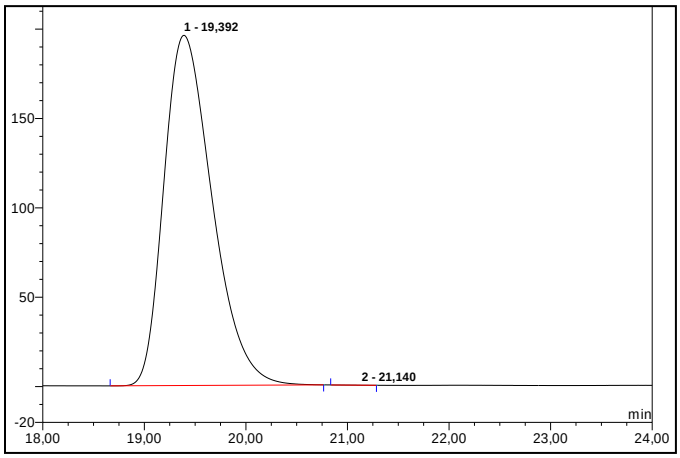
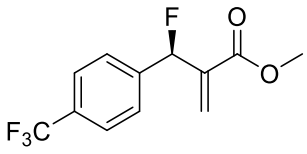


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.31	n.a.	603.722	340.246	49.60	n.a.	BM
2	20.75	n.a.	558.516	345.764	50.40	n.a.	MB
Total:			1162.238	686.010	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.39	n.a.	195.925	108.011	100.00	n.a.	BMB*
2	21.14	n.a.	0.020	0.005	0.00	n.a.	BMB*
Total:			195.945	108.016	100.00	0.000	



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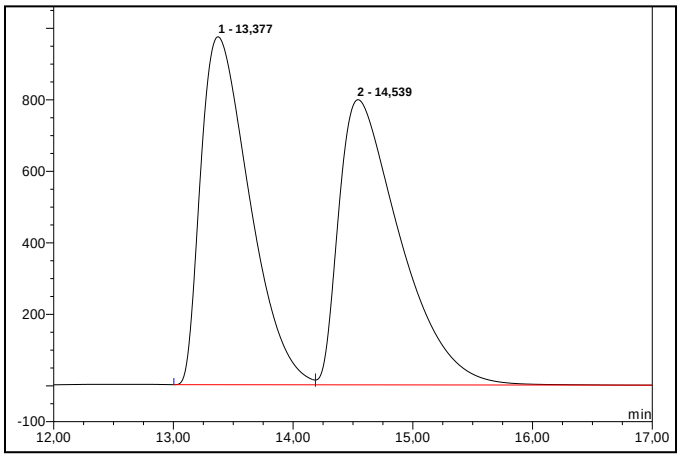
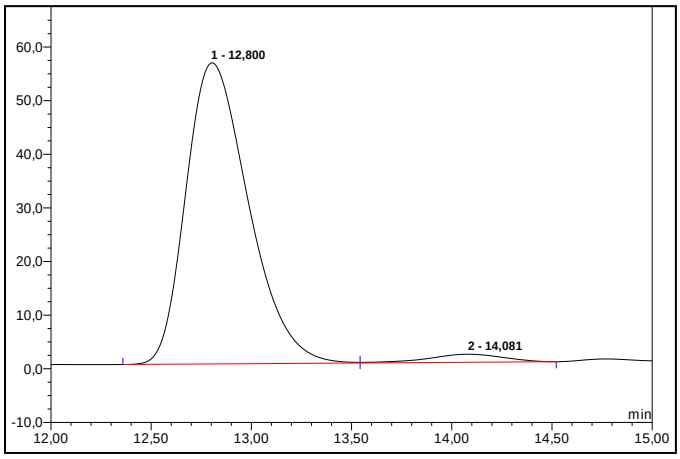
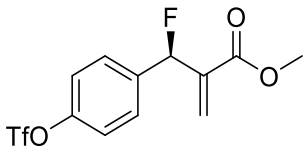


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.38	n.a.	973.116	460.721	49.27	n.a.	BM
2	14.54	n.a.	797.724	474.376	50.73	n.a.	MB
Total:			1770.840	935.097	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.80	n.a.	56.156	20.337	96.90	n.a.	BM
2	14.08	n.a.	1.507	0.651	3.10	n.a.	MB
Total:			57.663	20.988	100.00	0.000	



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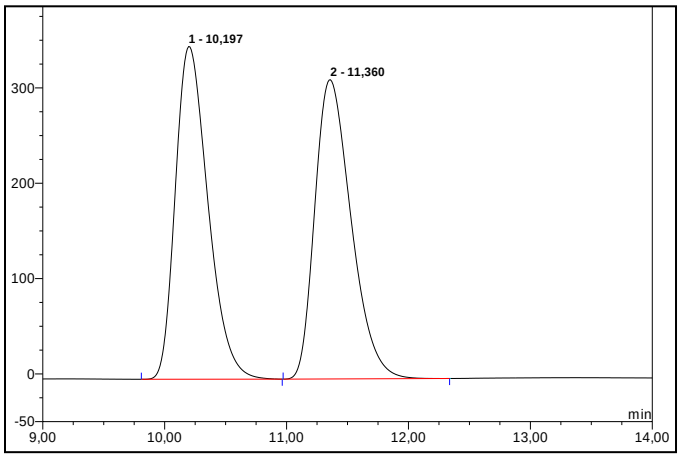
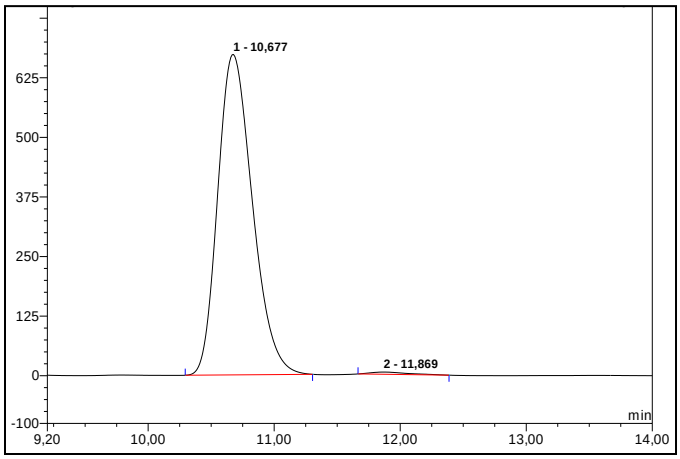
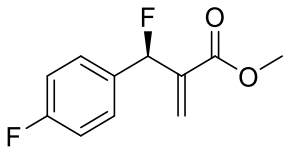


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.20	n.a.	349.035	108.221	50.00	n.a.	BMB
2	11.36	n.a.	313.811	108.222	50.00	n.a.	BMB
Total:			662.846	216.443	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.68	n.a.	672.144	214.302	99.24	n.a.	BMB*
2	11.87	n.a.	4.651	1.637	0.76	n.a.	BMB*
Total:			676.795	215.939	100.00	0.000	



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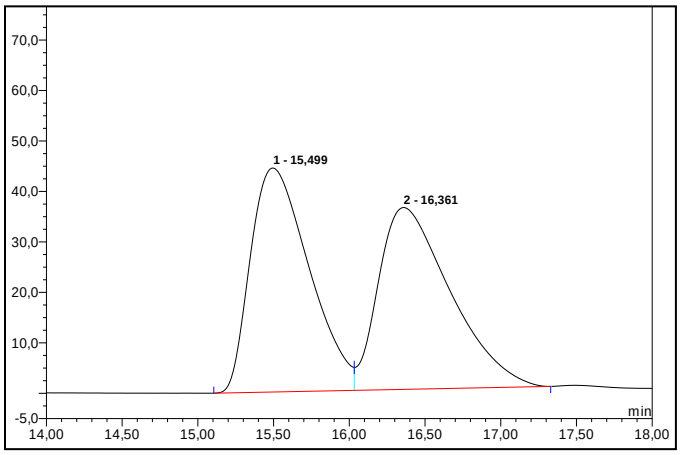
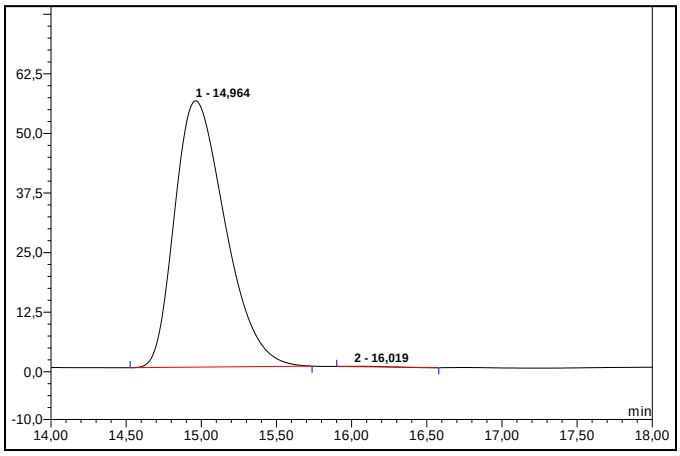
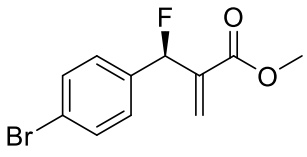


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.50	n.a.	44.377	19.888	50.06	n.a.	BM
2	16.36	n.a.	36.030	19.841	49.94	n.a.	MB
Total:			80.407	39.729	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.96	n.a.	55.881	21.829	99.90	n.a.	BMB*
2	16.02	n.a.	0.072	0.022	0.10	n.a.	BMB*
Total:			55.953	21.851	100.00	0.000	



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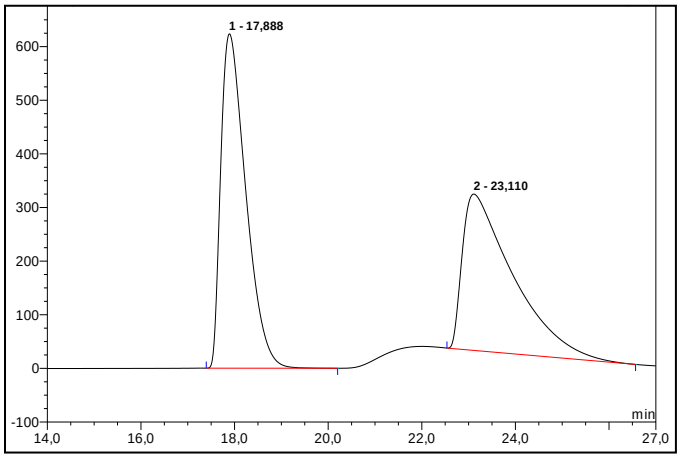
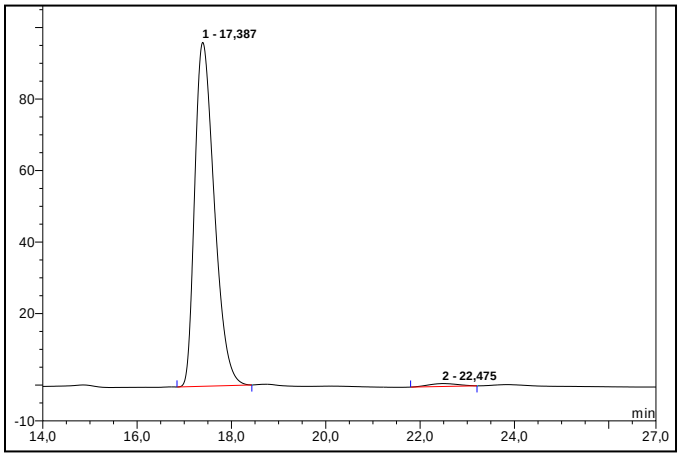
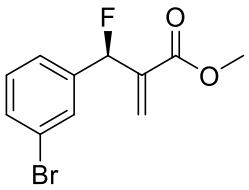


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.89	n.a.	623.508	386.173	51.29	n.a.	BMB
2	23.11	n.a.	291.522	366.709	48.71	n.a.	BMB*
Total:			915.030	752.882	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	17.39	n.a.	96.176	46.201	98.76	n.a.	BMB
2	22.47	n.a.	0.809	0.581	1.24	n.a.	BMB*
Total:			96.985	46.781	100.00	0.000	



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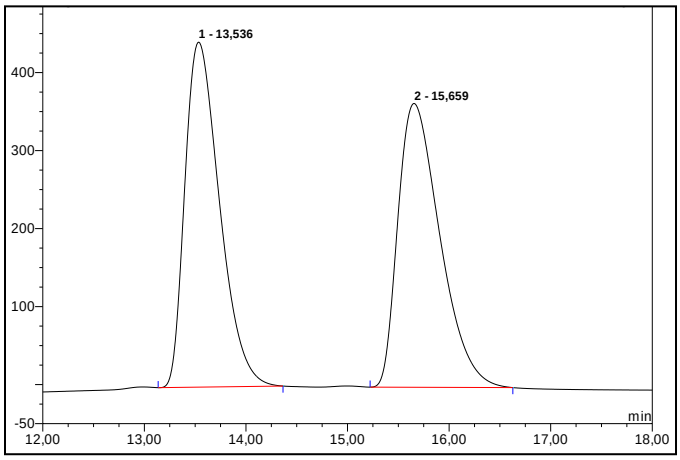
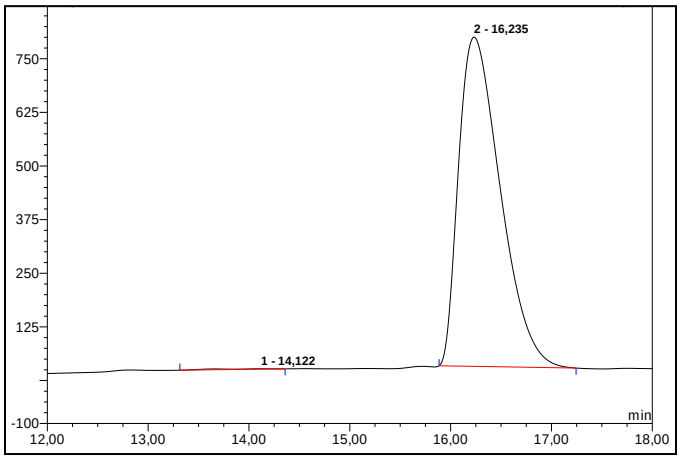
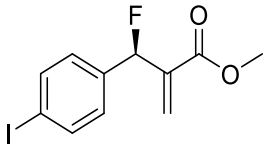


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.54	n.a.	442.308	174.972	50.10	n.a.	BMB*
2	15.66	n.a.	363.803	174.278	49.90	n.a.	BMB*
Total:			806.111	349.251	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.12	n.a.	0.902	0.951	0.26	n.a.	BMB*
2	16.23	n.a.	767.432	368.421	99.74	n.a.	BMB*
Total:			768.334	369.372	100.00	0.000	



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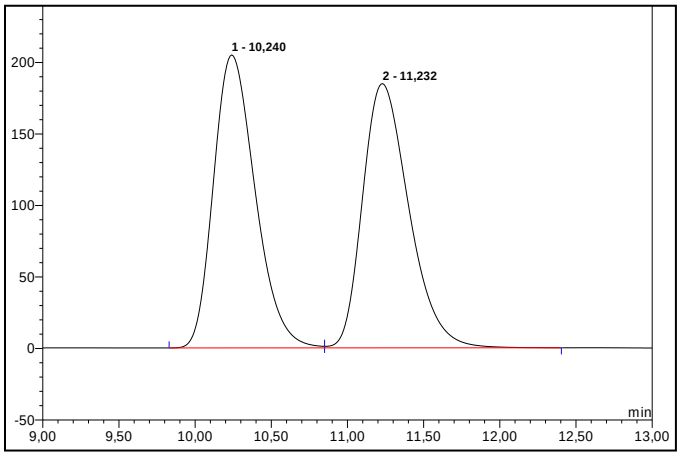
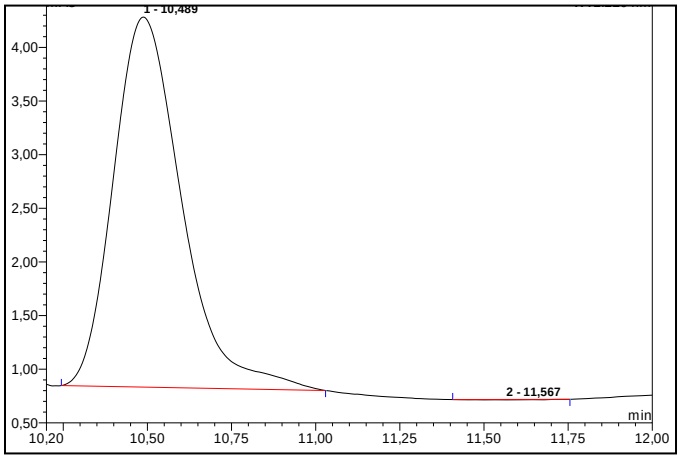
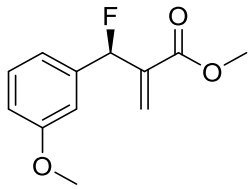


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.24	n.a.	204.889	65.093	49.97	n.a.	BM
2	11.23	n.a.	184.752	65.172	50.03	n.a.	MB
Total:			389.641	130.265	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.49	n.a.	3.450	0.811	99.91	n.a.	BMB*
2	11.57	n.a.	0.004	0.001	0.09	n.a.	BMB*
Total:			3.453	0.812	100.00	0.000	



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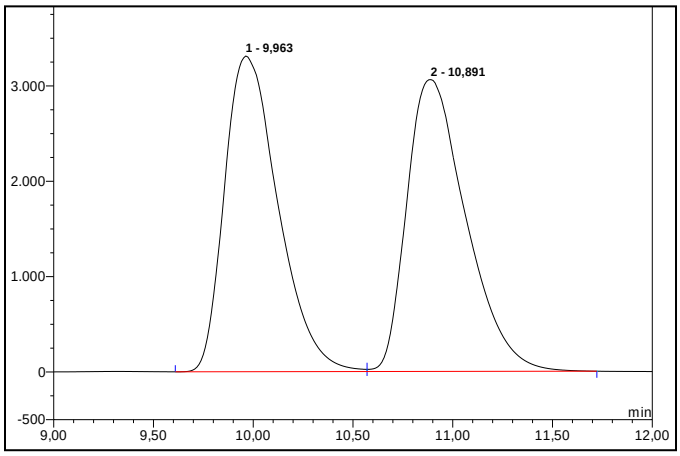
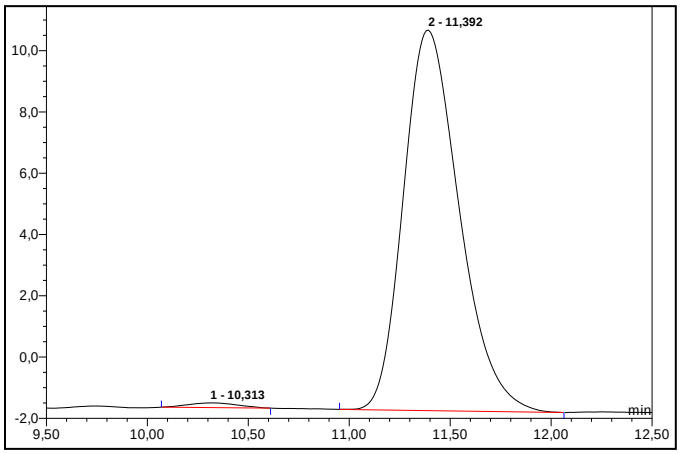
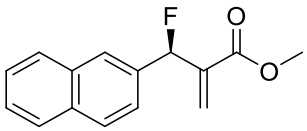


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.96	n.a.	3311.506	1032.927	49.54	n.a.	BM *
2	10.89	n.a.	3060.351	1051.921	50.46	n.a.	MB*
Total:			6371.857	2084.848	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.31	n.a.	0.152	0.043	1.07	n.a.	BMB*
2	11.39	n.a.	12.420	3.993	98.93	n.a.	BMB
Total:			12.572	4.036	100.00	0.000	



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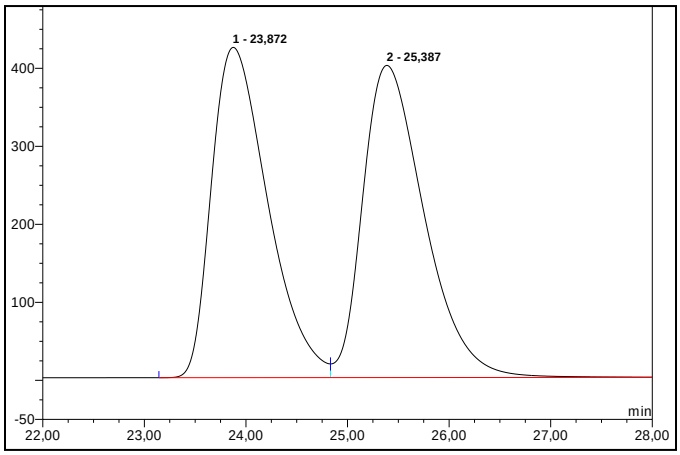
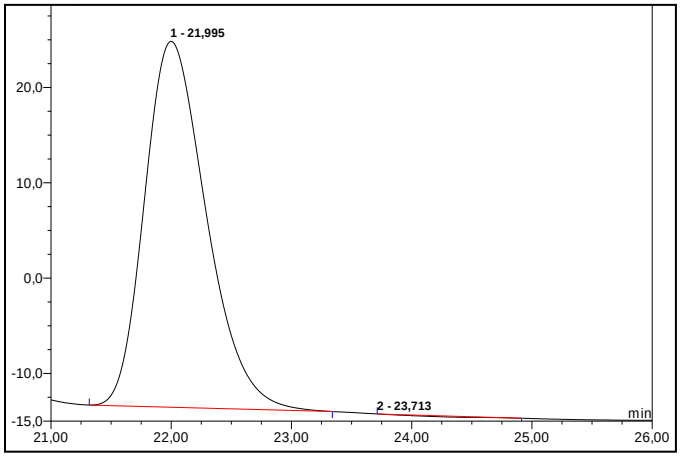
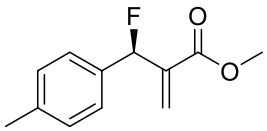


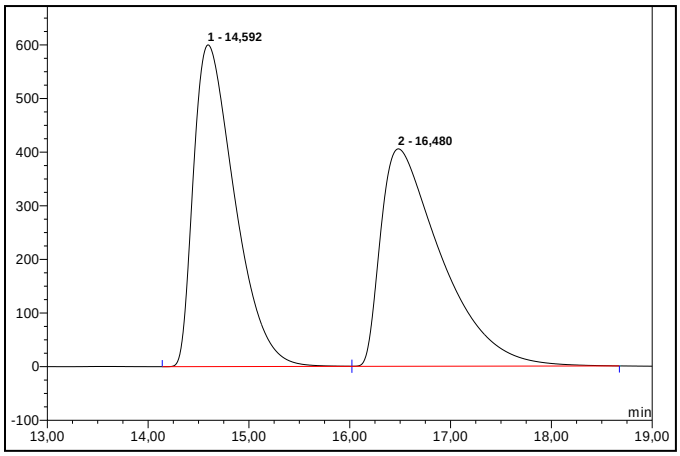
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	23.87	n.a.	423.375	271.742	49.17	n.a.	BM
2	25.39	n.a.	400.192	280.876	50.83	n.a.	MB
Total:			823.567	552.618	100.00	0.000	



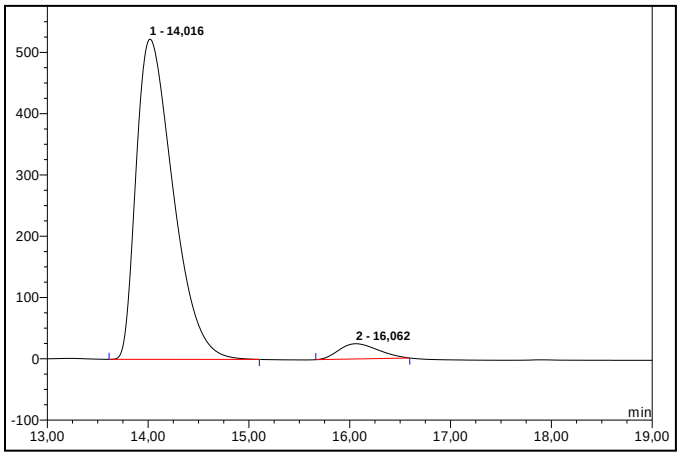
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.00	n.a.	38.379	22.861	99.72	n.a.	BMB*
2	23.71	n.a.	0.000	0.064	0.28	n.a.	BMB*
Total:			38.379	22.925	100.00	0.000	



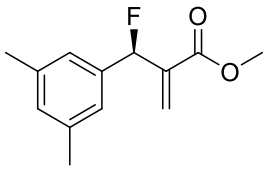
(*R*-1s)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.59	n.a.	600.048	284.348	50.11	n.a.	BM *
2	16.48	n.a.	405.487	283.139	49.89	n.a.	MB*
Total:			1005.535	567.486	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	14.02	n.a.	522.592	221.903	95.21	n.a.	BMB*
2	16.06	n.a.	24.789	11.163	4.79	n.a.	BMB*
Total:			547.381	233.066	100.00	0.000	



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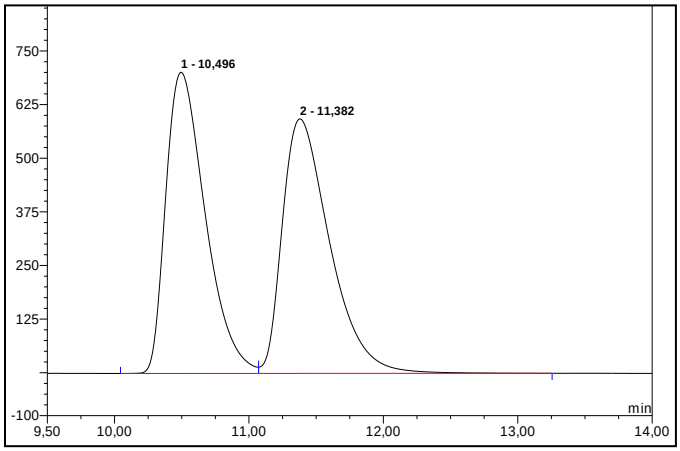
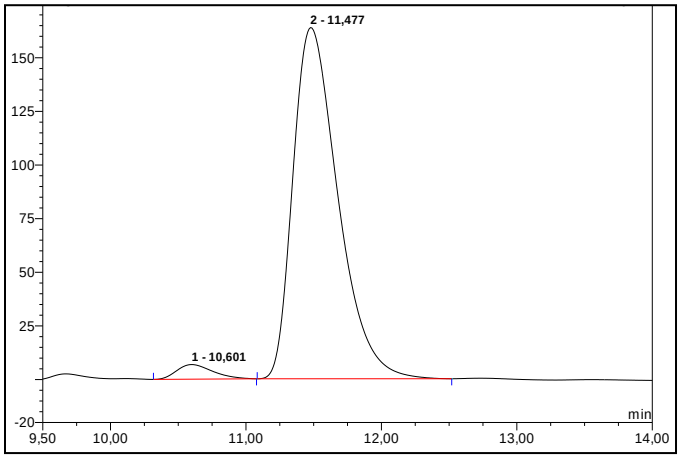
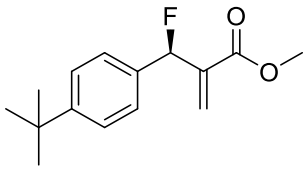


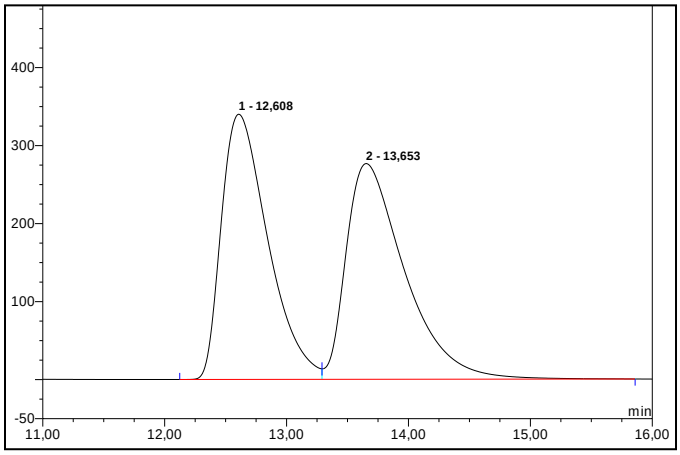
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.50	n.a.	702.377	239.147	49.64	n.a.	BM
2	11.38	n.a.	593.384	242.604	50.36	n.a.	MB
Total:			1295.761	481.751	100.00	0.000	



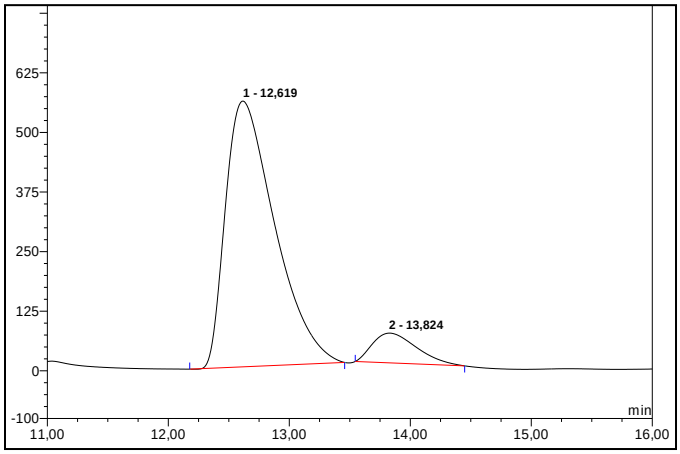
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.60	n.a.	6.813	2.095	3.22	n.a.	BMB
2	11.48	n.a.	163.720	62.956	96.78	n.a.	BMB
Total:			170.533	65.051	100.00	0.000	



(*R*-1u)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.61	n.a.	339.992	150.164	49.36	n.a.	BM *
2	13.65	n.a.	276.582	154.045	50.64	n.a.	MB*
Total:			616.574	304.209	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	12.62	n.a.	557.511	263.415	90.88	n.a.	BMB*
2	13.82	n.a.	62.249	26.423	9.12	n.a.	BMB*
Total:			619.760	289.838	100.00	0.000	