Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

For

Phosphinodifluoroalkylation of Alkynes Using P(O)H Compounds and Ethyl Difluoroiodoacetate

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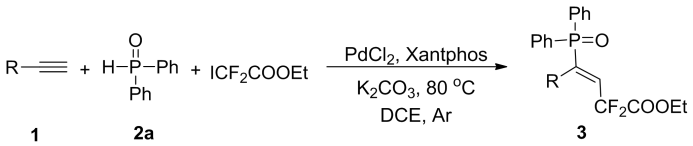
General

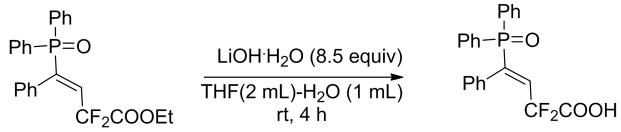
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker AVⅢ 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.23 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Chemical shifts of common trace ^{1}H NMR impurities (ppm): H_2O: 1.56, $CHCl_3$: 7.26. Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

General experimental procedure



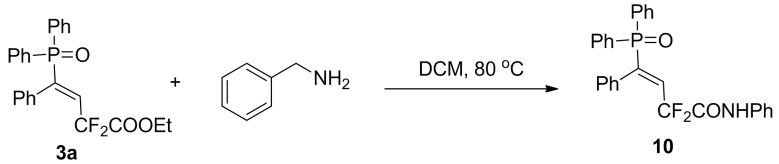
1 **2a** **3**

Diphenylphosphine oxide (0.4 mmol, 2.0 equiv), K_2CO_3(0.4 mmol, 2.0 equiv), $PdCl_2$ (0.02 mmol, 10 mol%) and Xantphos (0.04 mmol, 20 mol%) were placed in a dry Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen three times. Terminalalkyne(0.2mmol, 1.0 equiv), ethyl difluoroiodoacetate (0.4 mmol, 2.0 equiv), DCE (1.5 mL) were sequentially added to the system at room temperature. The reaction mixture was heated with stirring at 80 °C for 8 hours. Upon completion, the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt as the eluent to give the corresponding products.



3a **9**

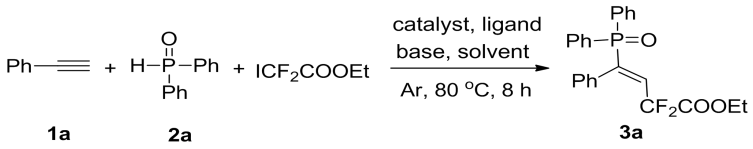
Product **3a** (0.3 mmol) and LiOH-H_2O (2.55 mmol) were stirred in a THF(2 mL)-H_2O (1 mL) mixture at room temperature for 4 h. The mixture was then acidified to pH 1 with a 35% HCl solution and extracted with ethyl acetate (3 × 10 mL), and the combined organic layer was dried over Na_2SO_4. After ethyl acetate was removed under vacuum, the product **9** was obtained without purification.



3a **10**

Product **3a** (0.1 mmol) and phenylmethanamine (0.2 mmol) were stirred in DCM at room temperature for 2 h, and then was heated to 80 °C for 4 h. The reaction was cooled to room temperature and the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt as the eluent to give the corresponding products **10**.

Table S1. Optimization of the Reaction Conditions[a]

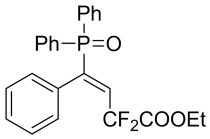


1a 2a 3a

entry	catalyst	ligand	base	solvent	yield (%)
1	CuCl	1,10-Phen	K_2CO_3	1,4-dioxane	trace
2	$CuCl_2$	1,10-Phen	K_2CO_3	1,4-dioxane	trace
3	$CuBr_2$	1,10-Phen	K_2CO_3	1,4-dioxane	trace
4	$Cu(OAc)_2$	1,10-Phen	K_2CO_3	1,4-dioxane	trace
5	CuCl	bpy	K_2CO_3	1,4-dioxane	trace
6	CuCl	1,10-Phen	K_2CO_3	DCE	trace
7	$PdCl_2$	PPh_3	K_2CO_3	DCE	60
8	$PdCl_2$	dppb	K_2CO_3	DCE	47
9	$PdCl_2$	dppe	K_2CO_3	DCE	trace
10	$PdCl_2$	dppp	K_2CO_3	DCE	trace
11	$PdCl_2$	Tri(2-furyl)phosphine	K_2CO_3	DCE	trace
12	$PdCl_2$	Xantphos	K_2CO_3	DCE	78
13	$PdCl_2$	-	K_2CO_3	DCE	trace
14	-	Xantphos	K_2CO_3	DCE	0
15	$Pd(OAc)_2$	Xantphos	K_2CO_3	DCE	74
16	$Pd(TFA)_2$	Xantphos	K_2CO_3	DCE	75
17	$Pd_2(dba)_3$	Xantphos	K_2CO_3	DCE	72
18	$Pd(PPh)_4$	Xantphos	K_2CO_3	DCE	64
19	$PdCl_2$	Xantphos	-	DCE	trace
20	$PdCl_2$	Xantphos	Na_2CO_3	DCE	57
21	$PdCl_2$	Xantphos	NaOAc	DCE	30
22	$PdCl_2$	Xantphos	Cs_2CO_3	DCE	53
23	$PdCl_2$	Xantphos	t-BuOK	DCE	trace
24	$PdCl_2$	Xantphos	NEt_3	DCE	trace
25	$PdCl_2$	Xantphos	pyridine	DCE	trace
26	$PdCl_2$	Xantphos	$i(Pr)_2NH$	DCE	trace
27	$PdCl_2$	Xantphos	K_2CO_3	toluene	23
28	$PdCl_2$	Xantphos	K_2CO_3	MeCN	30
29	$PdCl_2$	Xantphos	K_2CO_3	$CHCl_3$	59
30	$PdCl_2$	Xantphos	K_2CO_3	DCE/H_2O	58
31	$PdCl_2$	Xantphos	K_2CO_3	THF	trace
32	$PdCl_2$	Xantphos	K_2CO_3	EtOH	trace
33	$PdCl_2$	Xantphos	K_2CO_3	DMF	trace
34	$PdCl_2$	Xantphos	K_2CO_3	1,4-dioxane	trace
35[b]	$PdCl_2$	Xantphos	K_2CO_3	DCE	69
36[c]	$PdCl_2$	Xantphos	K_2CO_3	DCE	62
37[d]	$PdCl_2$	Xantphos	K_2CO_3	DCE	65

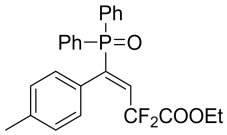
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), ethyl difluoroiodoacetate (0.4 mmol), catalyst (10 mol %), ligand (20 mol %), base (0.4 mmol) in solvent (1.5 mL) stirring at 80 °C under argon for 8 h. Yields of the isolated products. DCE: 1,2-dichloroethane. [b]80 °C. [c]60 °C. [d]$PdCl_2$ (5 mol %).

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-phenylbut-3-enoate (3a)



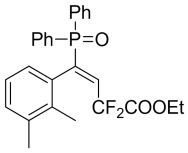
White solid; m.p. 97.1-99.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 4H), 7.56-7.51 (m, 2H), 7.45-7.40 (m, 4H),7.26-7.19 (m, 1H), 7.15-7.11 (m, 2H), 6.87 (td, $J_{C\text{-}F}$ = 10.9 Hz, $J_{C\text{-}P}$ = 18.9 Hz, 1H), 6.85-6.82 (m, 2H), 3.94 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 146.6 (td, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}P}$ = 85.0 Hz), 135.3 (td, $J_{C\text{-}F}$ = 38.7 Hz, $J_{C\text{-}P}$ = 10.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 129.60-129.58 (m), 129.3 (d, $J_{C\text{-}P}$ =105.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.0, 111.7 (td, $J_{C\text{-}F}$ = 249.5 Hz, $J_{C\text{-}P}$ = 19.5 Hz), 63.2, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.87; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.96 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{21}F_2NaO_3P^+$: 449.1089, found: 449.1088.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(p-tolyl)but-3-enoate (3b)



White solid; m.p. 118.1-119.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 4H), 7.55-7.50 (m, 2H), 7.44-7.39 (m, 4H), 6.96-6.93 (m, 2H), 6.84 (td, $J_{C\text{-}F}$ = 10.9 Hz, $J_{C\text{-}P}$ = 18.9 Hz, 1H), 6.73-6.70 (m, 2H), 3.93 (q, J = 7.2 Hz, 2H), 2.23 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 146.7 (td, $J_{C\text{-}F}$ = 7.8 Hz, $J_{C\text{-}P}$ = 85.2 Hz), 138.7 (d, $J_{C\text{-}P}$ = 1.8 Hz), 135.2 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 11.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.61-129.57 (m), 129.5 (d, $J_{C\text{-}P}$ =104.4 Hz), 129.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 128.7, 128.6 (d, $J_{C\text{-}P}$ = 12.4 Hz), 111.7 (td, $J_{C\text{-}F}$ = 248.7 Hz, $J_{C\text{-}P}$ = 19.6 Hz), 63.2, 21.3, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.88; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.62 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{23}F_2NaO_3P^+$: 463.1245, found: 463.1243.

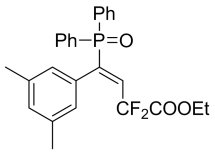
(*E*)-Ethyl 4-(2,3-dimethylphenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3c)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.65 (m, 2H), 7.57-7.50 (m, 2H), 7.48-7.43 (m, 2H), 7.39-7.29 (m, 4H), 7.17-7.08 (m, 1H), 7.00 (d, J = 7.5 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 7.8 Hz, 1H), 4.03-3.98 (m, 2H), 2.05 (s, 3H), 1.51 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.9 (t, $J_{C\text{-}F}$ = 33.1 Hz), 146.7 (ddd, $J_{C\text{-}F}$ = 8.3 Hz, $J_{C\text{-}F}$ = 8.3 Hz, $J_{C\text{-}P}$ = 84.0 Hz), 137.2 (d, $J_{C\text{-}P}$ = 1.3 Hz), 136.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 134.9 (ddd, $J_{C\text{-}F}$ = 30.8 Hz, $J_{C\text{-}F}$ = 30.8 Hz, $J_{C\text{-}P}$ = 10.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 8.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 131.2 (d, $J_{C\text{-}P}$ = 103.8 Hz), 130.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.9 Hz), 128.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.9 (d, $J_{C\text{-}P}$ = 103.3 Hz), 126.35-126.25 (m), 124.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 111.8 (ddd, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 20.0 Hz), 63.2,

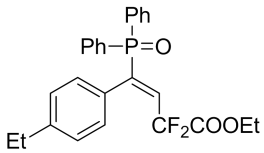
20.3, 16.7, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.77; ^{19}F NMR (377 MHz, $CDCl_3$): δ -97.87 (d, $J_{C\text{-}F}$ = 277.1 Hz, 1F), -99.51 (d, $J_{C\text{-}F}$ = 277.1 Hz, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{25}F_2NaO_3P^+$: 477.1402, found: 477.1397.

(*E*)-Ethyl 4-(3,5-dimethylphenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3d)



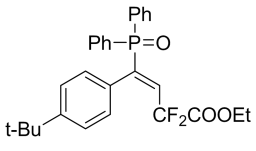
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 4H), 7.56-7.51 (m, 2H), 7.45-7.40 (m, 4H), 6.87-6.78 (m, 2H), 6.40-6.38 (m, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 2.10 (s, 6H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.2 Hz), 146.8 (td, $J_{C\text{-}F}$ = 7.9 Hz, $J_{C\text{-}P}$ = 84.9 Hz), 137.4 (d, $J_{C\text{-}P}$ = 1.4 Hz), 134.9 (td, $J_{C\text{-}F}$ = 28.6 Hz, $J_{C\text{-}P}$ = 10.7 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.2 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 6.9 Hz), 130.3 (d, $J_{C\text{-}P}$ = 2.2 Hz), 129.6 (d, $J_{C\text{-}P}$ =104.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.49-127.45 (m), 111.8 (td, $J_{C\text{-}F}$ = 248.9 Hz, $J_{C\text{-}P}$ = 19.5 Hz), 63.1, 21.3, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.66; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.66 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{25}F_2NaO_3P^+$: 477.1402, found: 477.1406.

(*E*)-Ethyl 4-(diphenylphosphoryl)-4-(4-ethylphenyl)-2,2-difluorobut-3-enoate (3e)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.58 (m, 4H), 7.56-7.52 (m, 2H), 7.46-7.40 (m, 4H), 6.99-6.96 (m, 2H), 6.83 (td, $J_{C\text{-}F}$ = 10.9 Hz, $J_{C\text{-}P}$ = 18.9 Hz, 1H), 6.77-6.75 (m, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.55 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H), 1.15 (q, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 33.1 Hz), 146.7 (td, $J_{C\text{-}F}$ = 7.8 Hz, $J_{C\text{-}P}$ = 85.2 Hz), 145.1 (d, $J_{C\text{-}P}$ = 1.9 Hz), 135.2 (td, $J_{C\text{-}F}$ = 29.1 Hz, $J_{C\text{-}P}$ = 11.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 3.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.67-129.63 (m), 129.6 (d, $J_{C\text{-}P}$ =105.2Hz), 129.3 (d, $J_{C\text{-}P}$ = 7.3 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.6, 111.8 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 19.2 Hz), 63.2, 28.7, 15.4, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.19; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.49 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{25}F_2NaO_3P^+$: 477.1402, found: 477.1400.

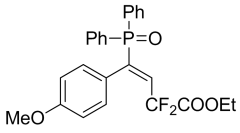
(*E*)-Ethyl 4-(4-(tert-butyl)phenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3f)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.57 (m, 4H), 7.55-7.51 (m, 2H), 7.43-7.39 (m, 4H), 7.16-7.13 (m, 2H), 6.85-6.76 (m, 3H), 3.87 (q, *J* = 7.2 Hz, 2H), 1.22 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.0 Hz), 151.9 (d, $J_{C\text{-}P}$ = 2.3 Hz), 146.6 (td, $J_{C\text{-}F}$ = 8.1 Hz, $J_{C\text{-}P}$ = 85.4 Hz), 135.1 (td, $J_{C\text{-}F}$ = 28.8 Hz, $J_{C\text{-}P}$ = 11.2 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.7 (d, $J_{C\text{-}P}$ =104.5 Hz), 129.38-129.34 (m), 129.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.9, 111.8 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 19.5 Hz), 63.1, 34.7, 31.3,

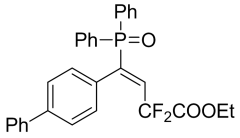
13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.38; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.20 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{28}H_{29}F_2NaO_3P^+$: 505.1715, found: 505.1706.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(4-methoxyphenyl)but-3-enoate (3g)



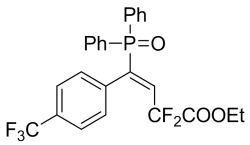
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 4H), 7.55-7.51 (m, 2H), 7.45-7.40 (m, 4H), 6.85-6.75 (m, 3H), 6.69-6.66 (m, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.71 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 160.0, 146.4 (td, $J_{C\text{-}F}$ = 8.3 Hz, $J_{C\text{-}P}$ = 85.7 Hz), 135.3 (td, $J_{C\text{-}F}$ = 28.3 Hz, $J_{C\text{-}P}$ = 11.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.7 Hz), 131.07-131.04 (m), 129.6 (d, $J_{C\text{-}P}$ =104.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.2 Hz), 124.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 113.5, 111.8 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 19.3 Hz), 63.2, 55.3, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.04; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.24 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{23}F_2NaO_4P^+$: 479.1194, found: 479.1188.

(*E*)-Ethyl 4-([1,1'-biphenyl]-4-yl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3h)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.64 (m, 4H), 7.60-7.54 (m, 2H), 7.53-7.50 (m, 2H), 7.48-7.43 (m, 4H), 7.42-7.38 (m, 4H), 7.34-7.30 (m, 1H), 6.97-6.94 (m, 2H), 6.86 (td, $J_{C\text{-}F}$ = 10.8 Hz, $J_{C\text{-}P}$ = 19.0 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 33.0 Hz), 146.5 (td, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}P}$ = 85.0 Hz), 141.5 (d, $J_{C\text{-}P}$ = 2.3 Hz), 140.2, 135.3 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 10.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.4 Hz), 131.1 (d, $J_{C\text{-}P}$ =6.9 Hz), 130.12-130.09(m), 129.4 (d, $J_{C\text{-}P}$ =104.8 Hz), 129.0, 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.9, 127.1, 126.6, 111.8 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ =20.0 Hz), 63.1, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.07; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.72 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{30}H_{25}F_2NaO_3P^+$: 525.1402, found: 525.1398.

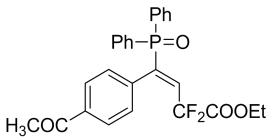
(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(4-(trifluoromethyl)phenyl)but-3-enoate (3i)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.61 (m, 4H), 7.60-7.57 (m, 2H), 7.50-7.45 (m, 4H), 7.44-7.41 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.79 (td, $J_{C\text{-}F}$ = 11.5 Hz, $J_{C\text{-}P}$ = 19.2 Hz, 1H),, 4.06 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 32.9 Hz), 145.8 (td, $J_{C\text{-}F}$ = 6.8 Hz, $J_{C\text{-}P}$ = 84.2 Hz), 136.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 135.6 (td, $J_{C\text{-}F}$ = 27.6 Hz, $J_{C\text{-}P}$ = 10.2 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.8 (qd, $J_{C\text{-}F}$ = 32.7 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 130.01-129.97 (m), 129.0 (d, $J_{C\text{-}P}$ =12.1 Hz), 128.8 (d, $J_{C\text{-}P}$ =100.0 Hz), 124.9 (q, $J_{C\text{-}F}$ = 3.0 Hz), 124.0 (q, $J_{C\text{-}F}$ = 272.2 Hz), 111.7 (td, $J_{C\text{-}F}$ = 251.3 Hz, $J_{C\text{-}P}$ =18.2 Hz), 63.6, 13.9; ^{31}P

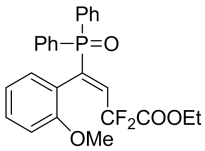
NMR ($CDCl_3$, 162 MHz): δ 27.33; ^{19}F NMR (377 MHz, $CDCl_3$): δ -62.88 (s, 3F), -96.05 (s, 2F). HRMS: $[M+H]^+$ *m/z* calcd for $C_{25}H_{20}F_5HO_3P^+$: 495.1143, found: 495.1139.

(*E*)-Ethyl 4-(4-acetylphenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3j)



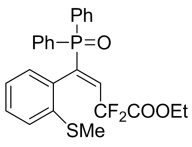
Yellow gum; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.73 (m, 2H), 7.66-7.61 (m, 4H), 7.60-7.56 (m, 2H), 7.49-7.44 (m, 4H), 6.99-6.97 (m, 2H), 6.81 (td, $J_{C\text{-}F}$ = 11.5 Hz, $J_{C\text{-}P}$ = 19.2 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.54 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.63, 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 146.1 (td, $J_{C\text{-}F}$ = 6.0 Hz, $J_{C\text{-}P}$ = 83.9 Hz), 137.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 136.9 (d, $J_{C\text{-}P}$ = 1.6 Hz), 135.3 (td, $J_{C\text{-}F}$ = 27.6 Hz, $J_{C\text{-}P}$ = 10.1 Hz), 133.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.88-129.84 (m), 129.0 (d, $J_{C\text{-}P}$ =105.3 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.9, 111.8 (td, $J_{C\text{-}F}$ = 250.9 Hz, $J_{C\text{-}P}$ = 19.0 Hz), 63.6, 26.8, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.95; ^{19}F NMR (377 MHz, $CDCl_3$): δ -96.20 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{23}F_2NaO_4P^+$: 491.1194, found: 491.1190.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (3l)



Yellow gum; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.55 (m, 4H), 7.52-7.48 (m, 2H), 7.42-7.36 (m, 4H), 7.22-7.17 (m, 1H), 6.96 (td, $J_{C\text{-}F}$ = 11.6 Hz, $J_{C\text{-}P}$ = 19.0 Hz, 1H), 6.86-6.83 (m, 1H), 6.78-6.74 (m, 1H), 6.58 (d, *J* = 8.3 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.27 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 33.5 Hz), 156.40-156.31 (m), 142.8 (td, $J_{C\text{-}F}$ = 7.2 Hz, $J_{C\text{-}P}$ = 87.7 Hz), 135.8 (td, $J_{C\text{-}F}$ = 28.1 Hz, $J_{C\text{-}P}$ = 10.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.4 (br), 132.3, 131.8 (d, $J_{C\text{-}P}$ = 10.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.28-130.18 (m), 128.8 (d, $J_{C\text{-}P}$ =12.7 Hz), 128.4 (br), 121.3 (d, $J_{C\text{-}P}$ = 6.4 Hz), 120.00-119.96 (m), 111.9 (td, $J_{C\text{-}F}$ = 249.9 Hz, $J_{C\text{-}P}$ = 19.7 Hz), 110.3, 63.1, 54.8, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.04; ^{19}F NMR (377 MHz, $CDCl_3$): δ -99.40 (d, $J_{C\text{-}F}$ = 273.4 Hz, 1F), -99.77 (d, $J_{C\text{-}F}$ = 273.4 Hz, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{23}F_2NaO_4P^+$: 479.1194, found: 479.1191.

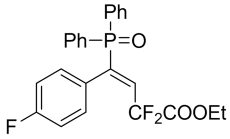
(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(2-(methylthio)phenyl)but-3-enoate (3m)



Light yellow solid; m.p. 191.7-193.6 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.62 (m, 2H), 7.55-7.49 (m, 4H), 7.43-7.34 (m, 4H), 7.23-7.18 (m, 1H), 7.05-6.92 (m, 3H), 6.77-6.74 (m, 1H), 4.19-4.14 (m, 2H), 1.99 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 33.5 Hz), 145.1 (td, $J_{C\text{-}F}$ = 6.5 Hz, $J_{C\text{-}P}$ = 85.7 Hz), 139.35-139.25 (m), 135.9 (td, $J_{C\text{-}F}$ = 26.6 Hz, $J_{C\text{-}P}$ = 10.4 Hz), 133.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.8 Hz),

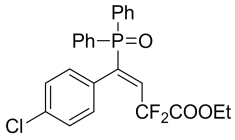
132.2 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.8 (d, $J_{C\text{-}P}$ =104.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.2 (d, $J_{C\text{-}P}$ = 2.2 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.65-128.55 (m), 128.0 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.9 (d, $J_{C\text{-}P}$ = 106.0 Hz), 126.70-126.65 (m), 124.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 111.9 (td, $J_{C\text{-}F}$ = 251.2 Hz, $J_{C\text{-}P}$ = 19.3 Hz), 63.4, 16.5, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.28; ^{19}F NMR (377 MHz, $CDCl_3$): δ -98.66 (d, $J_{C\text{-}F}$ = 272.3 Hz, 1F), -100.19 (d, $J_{C\text{-}F}$ = 272.3 Hz, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{23}F_2NaO_3PS^+$: 495.0966, found: 495.0959.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (3n)



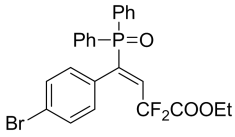
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.60 (m, 4H), 7.58-7.54 (m, 2H), 7.48-7.43 (m, 4H), 6.87-6.84 (m, 4H), 6.80 (td, $J_{C\text{-}F}$ = 11.0 Hz, $J_{C\text{-}P}$ = 19.0 Hz, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.0 (dd, $J_{C\text{-}F}$ = 247.3 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 145.9 (td, $J_{C\text{-}F}$ = 7.5 Hz, $J_{C\text{-}P}$ = 86.3 Hz), 135.6 (td, $J_{C\text{-}F}$ = 27.9 Hz, $J_{C\text{-}P}$ = 10.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.58-131.50 (m), 129.2 (d, $J_{C\text{-}P}$ =104.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.7 Hz), 128.1 (dd, $J_{C\text{-}F}$ = 6.9 Hz, $J_{C\text{-}P}$ = 7.1 Hz), 115.2 (d, $J_{C\text{-}F}$ = 22.8 Hz), 111.7 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 19.3 Hz), 63.4, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.19; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.28 (s, 2F), -113.23 (s, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{20}F_3NaO_3P^+$: 467.0994, found: 467.0988.

(*E*)-ethyl 4-(4-chlorophenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3o)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.55 (m, 6H), 7.49-7.44 (m, 4H), 7.16-7.12 (m, 2H), 6.85-6.74 (m, 3H), 4.03 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 145.8 (td, $J_{C\text{-}F}$ = 7.4 Hz, $J_{C\text{-}P}$ = 84.7 Hz), 135.6 (td, $J_{C\text{-}F}$ = 27.7 Hz, $J_{C\text{-}P}$ = 10.2 Hz), 135.1 (d, $J_{C\text{-}P}$ = 2.1 Hz), 132.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 130.97-130.94 (m), 130.7 (d, $J_{C\text{-}P}$ = 7.3 Hz), 129.0 (d, $J_{C\text{-}P}$ =106.0 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.3, 111.7 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 19.0 Hz), 63.5, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.06; ^{19}F NMR (377 MHz, $CDCl_3$): δ -96.56 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{20}ClF_2NaO_3P^+$: 483.0699, found: 483.0685.

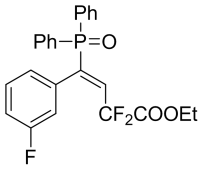
(*E*)-Ethyl 4-(4-bromophenyl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3p)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.55 (m, 6H), 7.49-7.44 (m, 4H), 7.31-7.28 (m, 2H), 6.85-6.74 (m, 3H), 4.04 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.0 Hz), 145.8 (td, $J_{C\text{-}F}$ = 6.7 Hz, $J_{C\text{-}P}$ = 84.7 Hz), 135.5 (td, $J_{C\text{-}F}$ = 27.8

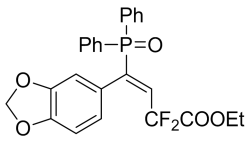
Hz, $J_{C\text{-}P}$ = 10.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.3, 131.27-131.19 (m, 2C), 129.0 (d, $J_{C\text{-}P}$ =105.0 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.1 Hz), 123.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 111.7 (td, $J_{C\text{-}F}$ = 250.4 Hz, $J_{C\text{-}P}$ = 18.6 Hz), 63.5, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.96; ^{19}F NMR (377 MHz, $CDCl_3$): δ -96.60 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{20}BrF_2NaO_3P^+$: 527.0194, found: 527.0185.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(3-fluorophenyl)but-3-enoate (3q)



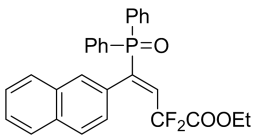
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.55 (m, 6H), 7.48-7.43 (m, 4H), 7.16-7.09 (m, 1H), 6.93 (t, *J* = 8.3 Hz, 1H), 6.82 (td, $J_{C\text{-}F}$ = 11.2 Hz, $J_{C\text{-}P}$ = 19.1 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 9.3 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 H), 162.1 (dd, $J_{C\text{-}F}$ = 248.7 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 145.6 (md, $J_{C\text{-}P}$ = 83.3 Hz), 135.6 (td, $J_{C\text{-}F}$ = 28.0 Hz, $J_{C\text{-}P}$ = 10.2 Hz), 134.3 (dd, J_1 = 8.2 Hz, J_2= 8.2 Hz), 132.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.7 (dd, J_1 =8.1 Hz, J_2 =1.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 105.6 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.1 Hz), 125.59-125.51 (m), 116.7 (md, $J_{C\text{-}P}$ = 22.7 Hz), 115.8 (dd, J_1 = 19.1 Hz, J_2= 2.2 Hz), 111.7 (td, $J_{C\text{-}F}$ = 250.0 Hz, $J_{C\text{-}P}$ = 18.8 Hz), 63.5, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.97; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.28 (s, 2F), -112.52 (s, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{20}F_3NaO_3P^+$: 467.0994, found: 467.0991.

(*E*)-Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-4-(diphenylphosphoryl)-2,2-difluorobut-3-enoate (3r)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.61 (m, 4H), 7.56-7.52 (m, 2H), 7.47-7.42 (m, 4H), 6.73 (td, $J_{C\text{-}F}$ = 10.7 Hz, $J_{C\text{-}P}$ = 18.9 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.37-6.33 (m, 2H), 5.87 (s, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.1 Hz), 148.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 147.4, 146.3 (td, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}P}$ = 86.2 Hz), 135.6 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 11.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.5 (d, $J_{C\text{-}P}$ = 104.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 125.4 (d, $J_{C\text{-}P}$ =7.0 Hz), 123.80-123.76 (m), 111.7 (td, $J_{C\text{-}F}$ = 249.3 Hz, $J_{C\text{-}P}$ = 19.6 Hz), 110.08-109.92 (m), 108.0 (d, $J_{C\text{-}P}$ = 1.2 Hz), 101.4, 63.3, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.18; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.74 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{25}H_{21}F_2NaO_5P^+$: 493.0987, found: 493.0981.

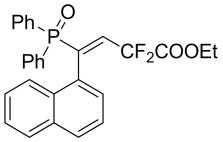
(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(naphthalen-2-yl)but-3-enoate (3s)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.2 Hz, 1H), 7.67-7.58 (m, 6H), 7.56-7.52 (m, 2H), 7.47-7.40 (m, 6H), 7.32-7.28 (m, 1H), 7.00-6.91 (m, 2H), 3.79 (q, *J* = 7.2 Hz,

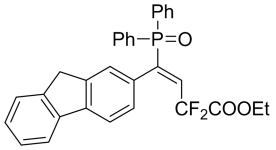
2H), 1.01 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.8 (t, $J_{C\text{-}F}$ = 32.9 Hz), 146.8 (td, $J_{C\text{-}F}$ = 7.6 Hz, $J_{C\text{-}P}$ = 84.5 Hz), 135.6 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 10.6 Hz), 132.9 (d, $J_{C\text{-}P}$ = 1.6 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.8 Hz), 132.4, 129.7 (d, $J_{C\text{-}P}$ = 6.9 Hz), 129.4 (d, $J_{C\text{-}P}$ =104.7 Hz), 129.40-129.35 (m), 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.3, 127.8, 127.6, 127.0, 126.68, 126.65, 111.8 (td, $J_{C\text{-}F}$ = 248.9 Hz, $J_{C\text{-}P}$ = 19.2 Hz), 63.2, 13.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.69; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.83 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{28}H_{23}F_2NaO_3P^+$: 499.1245, found: 499.1239.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(naphthalen-1-yl)but-3-enoate (3t)



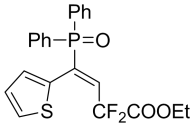
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.71 (m, 3H), 7.66 (d, J = 8.2 Hz, 1H), 7.59-7.55 (m, 1H), 7.50-7.46 (m, 2H), 7.41-7.32 (m, 2H), 7.30-7.21 (m, 5H), 7.12-7.04 (m, 3H), 6.89-6.87 (m, 1H), 3.81-3.74 (m, 1H), 3.65-3.59 (m, 1H), 1.05 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (t, $J_{C\text{-}F}$ = 33.1 Hz), 145.5 (td, $J_{C\text{-}F}$ = 7.4 Hz, $J_{C\text{-}P}$ = 83.5 Hz), 137.0 (td, $J_{C\text{-}F}$ = 28.1 Hz, $J_{C\text{-}P}$ = 9.5 Hz), 133.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 8.9 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 10.2 Hz), 131.94-131.85 (m), 131.0 (d, $J_{C\text{-}P}$ = 104.1 Hz), 129.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 129.3 (d, $J_{C\text{-}P}$ = 3.3 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.9 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.8, 127.1 (d, $J_{C\text{-}P}$ = 104.9 Hz), 127.0 (d, $J_{C\text{-}P}$ = 4.6 Hz), 126.0 (d, $J_{C\text{-}P}$ = 4.6 Hz), 125.9, 124.5 (d, $J_{C\text{-}P}$ = 2.0 Hz), 111.8 (td, $J_{C\text{-}F}$ = 250.4 Hz, $J_{C\text{-}P}$ = 19.1 Hz), 63.1, 13.7; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.98; ^{19}F NMR (377 MHz, $CDCl_3$): δ -96.30 (d, $J_{C\text{-}F}$ = 276.9 Hz, 1F), -98.4 (d, $J_{C\text{-}F}$ = 276.9 Hz, 1F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{28}H_{23}F_2NaO_3P^+$: 499.1245, found: 499.1244.

(*E*)-Ethyl 4-(diphenylphosphoryl)-4-(9H-fluoren-2-yl)-2,2-difluorobut-3-enoate (3u)



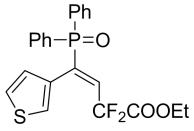
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71-7.63 (m, 5H), 7.58-7.52 (m, 3H), 7.50-7.47 (m, 1H), 7.46-7.41 (m, 4H), 7.35-7.32 (m, 1H), 7.30-7.27 (m, 1H), 7.05-7.03 (m, 1H), 6.94-6.85 (m, 2H), 3.90 (q, J = 7.2 Hz, 2H), 3.73 (s, 2H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.0 Hz), 147.0 (td, $J_{C\text{-}F}$ = 7.8 Hz, $J_{C\text{-}P}$ = 84.9 Hz), 143.5, 142.8, 142.3, 140.9, 135.2 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 11.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 129.5 (d, $J_{C\text{-}P}$ =104.6 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.34-128.30 (m), 127.4, 127.0, 126.47-126.44 (m), 125.2, 120.3, 119.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 111.8 (td, $J_{C\text{-}F}$ = 249.2 Hz, $J_{C\text{-}P}$ = 19.5 Hz), 63.2, 36.9, 13.7; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.93; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.46 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{31}H_{25}F_2NaO_3P^+$: 537.1402, found: 537.1400.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(thiophen-2-yl)but-3-enoate (3v)



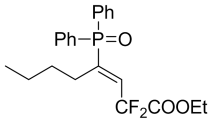
Light yellow solid solid; m.p. 104.4-106.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68-7.57 (m, 6H), 7.50-7.46 (m, 4H), 7.31-7.28 (m, 1H), 6.98 (m, td, $J_{C\text{-}F}$ = 10.8 Hz, $J_{C\text{-}P}$ = 17.9 Hz, 1H), 6.91-6.88 (m, 1H), 6.81-6.78 (m, 1H), 4.03 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.4 (t, $J_{C\text{-}F}$ = 33.2 Hz), 140.4 (td, $J_{C\text{-}F}$ = 8.3 Hz, $J_{C\text{-}P}$ = 89.0 Hz), 137.1 (td, $J_{C\text{-}F}$ = 29.2 Hz, $J_{C\text{-}P}$ = 10.9 Hz), 132.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 7.6 Hz), 131.36-131.30 (m), 129.3 (d, $J_{C\text{-}P}$ =105.6 Hz), 129.1 (d, $J_{C\text{-}P}$ = 1.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.0, 111.7 (td, $J_{C\text{-}F}$ = 248.6 Hz, $J_{C\text{-}P}$ = 18.2 Hz), 63.4, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.68; ^{19}F NMR (377 MHz, $CDCl_3$): δ -93.08 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}F_2NaO_3PS^+$: 455.0653, found: 455.0644.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluoro-4-(thiophen-3-yl)but-3-enoate (3w)



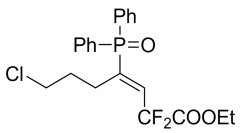
Light yellow solid; m.p. 124.0-126.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 4H), 7.57-7.53 (m, 2H), 7.46-7.42 (m, 4H), 7.14 (dd, J_1 = 2.98 Hz, J_2 =4.95 Hz, 1H), 6.92-6.82 (m, 2H), 6.60 (d, J = 5.0 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (t, $J_{C\text{-}F}$ = 33.1 Hz), 142.2 (td, $J_{C\text{-}F}$ = 7.3 Hz, $J_{C\text{-}P}$ = 87.7 Hz), 135.8 (td, $J_{C\text{-}F}$ = 28.8 Hz, $J_{C\text{-}P}$ = 10.5 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 7.7 Hz), 129.7 (d, $J_{C\text{-}P}$ =105.2 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7, 127.95-127.90 (m), 125.7, 111.8 (td, $J_{C\text{-}F}$ = 248.7 Hz, $J_{C\text{-}P}$ = 19.4 Hz), 63.3, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 26.49; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.13 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}F_2NaO_3PS^+$: 455.0653, found: 455.0649.

(*E*)-Ethyl 4-(diphenylphosphoryl)-2,2-difluorooct-3-enoate (3x)



Colourless gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.64 (m, 4H), 7.58-7.54 (m, 2H), 7.50-7.45 (m, 4H), 6.19 (td, $J_{C\text{-}F}$ = 13.9 Hz, $J_{C\text{-}P}$ = 21.2 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.48-2.41 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.23-1.12 (m, 4H), 0.72-0.68 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.4 (t, $J_{C\text{-}F}$ = 34.0 Hz), 147.7 (td, $J_{C\text{-}F}$ = 5.2 Hz, $J_{C\text{-}P}$ = 86.1 Hz), 133.0 (td, $J_{C\text{-}F}$ = 26.6 Hz, $J_{C\text{-}P}$ = 12.4 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.7 (d, $J_{C\text{-}P}$ =103.2 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.0 Hz), 112.5 (td, $J_{C\text{-}F}$ = 251.3 Hz, $J_{C\text{-}P}$ = 21.6 Hz), 63.6, 32.3, 29.2 (d, $J_{C\text{-}P}$ =7.9 Hz), 23.2, 14.0, 13.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.31; ^{19}F NMR (377 MHz, $CDCl_3$): δ -99.99 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{25}F_2NaO_3P^+$: 429.1402, found: 429.1400.

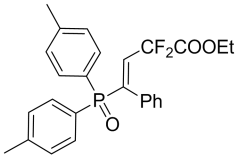
(*E*)-Ethyl 7-chloro-4-(diphenylphosphoryl)-2,2-difluorohept-3-enoate (3y)



Colourless gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.65 (m, 4H), 7.61-7.56 (m, 2H), 7.52-7.48

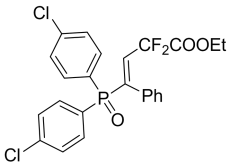
(m, 4H), 6.22 (td, $J_{C\text{-}F}$ = 13.9 Hz, $J_{C\text{-}P}$ = 20.9 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.38 (t, J = 6.4 Hz, 2H), 2.67-2.59 (m, 2H), 1.80-1.73 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.2 (t, $J_{C\text{-}F}$ = 33.7 Hz), 146.3 (td, $J_{C\text{-}F}$ = 5.2 Hz, $J_{C\text{-}P}$ = 86.6 Hz), 134.0 (td, $J_{C\text{-}F}$ = 26.6 Hz, $J_{C\text{-}P}$ = 12.2 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.2 (d, $J_{C\text{-}P}$ =103.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 12.0 Hz), 112.5 (td, $J_{C\text{-}F}$ = 251.7 Hz, $J_{C\text{-}P}$ = 21.1 Hz), 63.8, 44.7, 32.7, 27.0 (d, $J_{C\text{-}P}$ =8.0 Hz), 14.1; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.44; ^{19}F NMR (377 MHz, $CDCl_3$): δ -100.03 (s, 2F). HRMS: $[M+H]^+$ *m/z* calcd for $C_{21}H_{23}ClF_2O_3P^+$: 427.1036, found: 427.1031.

(*E*)-ethyl 4-(di-p-tolylphosphoryl)-2,2-difluoro-4-phenylbut-3-enoate (3ab)



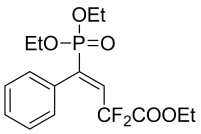
Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.46 (m, 4H), 7.24-7.20 (m, 5H), 7.17-7.13 (m, 2H), 6.89-6.81 (m, 3H), 3.95 (q, J = 7.2 Hz, 2H), 2.39 (s, 6H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.2 Hz), 147.0 (td, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}P}$ = 85.1 Hz), 143.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 134.8 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 10.5 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 132.4 (d, $J_{C\text{-}P}$ =6.9 Hz), 129.64-129.61 (m), 129.4 (d, $J_{C\text{-}P}$ = 12.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 127.9, 126.2 (d, $J_{C\text{-}P}$ =107.5 Hz), 111.9 (td, $J_{C\text{-}F}$ = 249.4 Hz, $J_{C\text{-}P}$ = 19.9 Hz), 63.2, 21.8, 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.18; ^{19}F NMR (377 MHz, $CDCl_3$): δ -94.86 (s, 2H). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{26}H_{25}F_2NaO_3P^+$: 477.1402, found: 477.1398.

(*E*)-ethyl 4-(bis(4-chlorophenyl)phosphoryl)-2,2-difluoro-4-phenylbut-3-enoate (3ac)



Yellow gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.48 (m, 4H), 7.45-7.41 (m, 4H), 7.28-7.25 (m, 1H), 7.21-7.17 (m, 2H), 6.92 (td, $J_{C\text{-}F}$ = 10.9 Hz, $J_{C\text{-}P}$ = 21.8 Hz, 1H), 6.84-6.82 (m, 2H), 3.98 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (t, $J_{C\text{-}F}$ = 33.0 Hz), 145.8 (td, $J_{C\text{-}F}$ = 7.5 Hz, $J_{C\text{-}P}$ = 86.8 Hz), 139.7 (d, $J_{C\text{-}P}$ = 3.5 Hz), 135.9 (td, $J_{C\text{-}F}$ = 28.4 Hz, $J_{C\text{-}P}$ = 10.5 Hz), 133.8 (d, $J_{C\text{-}P}$ = 10.2 Hz), 131.7 (d, $J_{C\text{-}P}$ =7.1 Hz), 129.56-129.52 (m), 129.2 (d, $J_{C\text{-}P}$ = 13.1 Hz), 129.1 (d, $J_{C\text{-}P}$ = 1.8 Hz), 128.2, 127.5 (d, $J_{C\text{-}P}$ =106.5 Hz), 111.7 (td, $J_{C\text{-}F}$ = 250.2 Hz, $J_{C\text{-}P}$ = 19.7 Hz), 63.4, 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 25.14; ^{19}F NMR (377 MHz, $CDCl_3$): δ -95.20 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{24}H_{19}Cl_2F_2NaO_3P^+$: 517.0309, found: 517.0304.

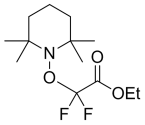
(*E*)-ethyl 4-(diethoxyphosphoryl)-2,2-difluoro-4-phenylbut-3-enoate (3ad)



Colourless gum; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.34 (m, 3H), 7.24-7.22 (m, 2H), 6.86 (td, $J_{C\text{-}F}$ = 10.8 Hz, $J_{C\text{-}P}$ = 23.4 Hz, 1H), 4.09-4.04 (m, 4H), 3.96 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.6 (t, $J_{C\text{-}F}$ = 33.1 Hz), 142.0 (td,

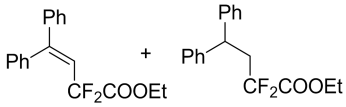
$J_{C\text{-}F}$ = 8.1 Hz, $J_{C\text{-}P}$ = 174.4 Hz), 135.9 (td, $J_{C\text{-}F}$ = 28.3 Hz, $J_{C\text{-}P}$ = 11.1 Hz), 132.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.05-129.01 (m), 128.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 1.4 Hz), 111.5 (td, $J_{C\text{-}F}$ = 249.0 Hz, $J_{C\text{-}P}$ = 26.2 Hz), 63.3, 63.2 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.2 Hz), 13.8; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 13.16; ^{19}F NMR (377 MHz, $CDCl_3$): δ -95.36 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{16}H_{21}F_2NaO_5P^+$: 385.0987, found: 385.0979.

Ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate (5)



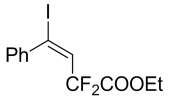
Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.35 (q, *J* = 7.2 Hz, 2H), 1.60-1.54 (m, 5H), 1.37 (t, *J* = 7.2 Hz, 4H, overlap), 1.20-1.16 (m, 12H); ^{19}F NMR (377 MHz, $CDCl_3$): δ -73.54 (s, 2F).

Ethyl 2,2-difluoro-4,4-diphenylbut-3-enoate (6) + Ethyl 2,2-difluoro-4,4-diphenylbutanoate (6+7)



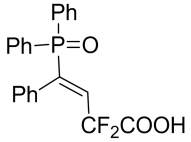
Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.34 (m, 6H), 7.33-7.28 (m, 10H), 7.26-7.19 (m, 4H), 6.32 (t, *J* = 11.8 Hz, 1H), 4.32 (t, *J* = 7.3 Hz, 1H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.87 (q, *J* = 7.2 Hz, 2H), 2.98 (td, J_1 = 15.4 Hz, J_2 = 7.3 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.9 (t, $J_{C\text{-}F}$ = 32.6 Hz), 163.7 (t, $J_{C\text{-}F}$ = 33.2 Hz), 151.2 (t, $J_{C\text{-}F}$ = 9.5 Hz), 143.2, 140.7, 137.3, 130.0, 129.3, 128.8, 128.7, 128.6, 128.2, 128.1, 127.9, 126.9, 119.7 (t, $J_{C\text{-}F}$ = 28.3 Hz), 115.8 (t, $J_{C\text{-}F}$ = 250.2 Hz), 112.7 (t, $J_{C\text{-}F}$ = 247.9 Hz), 62.9, 62.8, 45.0 (t, $J_{C\text{-}F}$ = 4.7 Hz), 40.5 (t, $J_{C\text{-}F}$ =23.2 Hz), 13.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ -90.83 (s, 2F), -103.42 (s, 2F).

(*E*)-Ethyl 2,2-difluoro-4-iodo-4-phenylbut-3-enoate (8)



Oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24-7.21 (m, 5H), 6.64 (t, *J* = 11.0 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.7 (t, $J_{C\text{-}F}$ = 33.2 Hz), 140.9, 133.2 (t, $J_{C\text{-}F}$ = 28.3 Hz), 129.6, 128.4, 128.1 (t, $J_{C\text{-}F}$ = 1.5 Hz), 111.1 (t, $J_{C\text{-}F}$ = 250.3 Hz), 108.9 (t, $J_{C\text{-}F}$ = 10.1 Hz), 63.3, 13.9; ^{19}F NMR (377 MHz, $CDCl_3$): δ -93.84 (s, 2F).

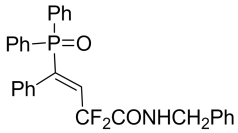
(*E*)-4-(Diphenylphosphoryl)-2,2-difluoro-4-phenylbut-3-enoic acid (9)



Yellow solid; m.p. 213.6-215.3 °C; ^{1}H NMR (CD_3OD, 400 MHz): δ 7.67-7.61 (m, 6H), 7.56-7.51 (m, 4H), 7.26-7.23 (m, 1H), 7.18-7.14 (m, 2H), 6.89-6.86 (m, 2H), 6.69 (td, $J_{C\text{-}F}$ = 11.7 Hz, $J_{C\text{-}P}$ = 19.9 Hz, 1H); ^{13}C NMR (CD_3OD, 100 MHz): δ 163.9 (t, $J_{C\text{-}F}$ = 33.2 Hz), 145.2 (td, $J_{C\text{-}F}$ = 6.8 Hz, $J_{C\text{-}P}$ = 87.4 Hz), 135.8 (td, $J_{C\text{-}F}$ = 27.9 Hz, $J_{C\text{-}P}$ = 11.1 Hz), 132.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.9 (d, $J_{C\text{-}P}$ =

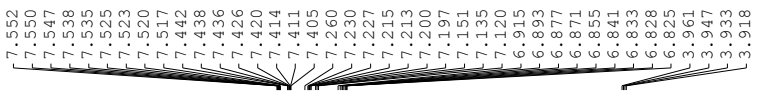
9.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 6.8 Hz), 129.24-129.21 (m), 128.6 (d, $J_{C\text{-}P}$ =12.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 2.3 Hz), 128.2 (d, $J_{C\text{-}P}$ = 106.5 Hz), 127.5 (d, $J_{C\text{-}P}$ = 1.3 Hz), 113.8 (td, $J_{C\text{-}F}$ = 247.6 Hz, $J_{C\text{-}P}$ = 19.3 Hz); ^{31}P NMR (CD_3OD, 162 MHz): δ 30.07; ^{19}F NMR (377 MHz, CD_3OD): δ -98.23 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{22}H_{17}F_2NaO_3P^+$: 421.0776, found: 421.0768.

(*E*)-N-benzyl-4-(diphenylphosphoryl)-2,2-difluoro-4-phenylbut-3-enamide (10)



Oil; ^{1}H NMR (CD_3OD, 400 MHz): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.61 (m, 4H), 7.57-7.53 (m, 2H), 7.49-7.42 (m, 4H),7.32-7.26 (m, 3H), 7.21-7.18 (m, 1H), 7.14-7.08 (m, 4H), 6.93-6.85 (m, 3H), 6.17 (s, 1H, NH), 4.17 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.1 (t, $J_{C\text{-}F}$ = 29.6 Hz), 146.5 (td, $J_{C\text{-}F}$ = 7.6 Hz, $J_{C\text{-}P}$ = 85.5 Hz), 136.5, 135.8 (td, $J_{C\text{-}F}$ = 27.8 Hz, $J_{C\text{-}P}$ = 10.9 Hz), 132.64 (d, $J_{C\text{-}P}$ = 1.8 Hz), 132.60, 132.59 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.7, 129.3 (d, $J_{C\text{-}P}$ = 99.6 Hz), 129.0, 128.7 (d, $J_{C\text{-}P}$ =12.7 Hz), 128.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.2, 128.1, 127.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 113.4 (td, $J_{C\text{-}F}$ = 251.5 Hz, $J_{C\text{-}P}$ = 19.4 Hz), 43.9; ^{31}P NMR ($CDCl_3$, 162 MHz): δ 27.29; ^{19}F NMR (377 MHz, $CDCl_3$): δ -96.31 (s, 2F). HRMS: $[M+Na]^+$ *m/z* calcd for $C_{29}H_{24}F_2NNaO_2P^+$: 510.1405, found: 510.1399.

3a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7.436
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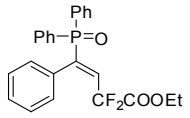
7.420
7.414
7.411
7.405
7.260
7.230
7.227
7.215
7.213
7.200
7.197
7.151
7.135
7.120
6.915
6.893
6.877
6.871
6.855
6.841
6.833
6.828
6.825
3.961
3.947
3.933
3.918
1.183
1.169
1.155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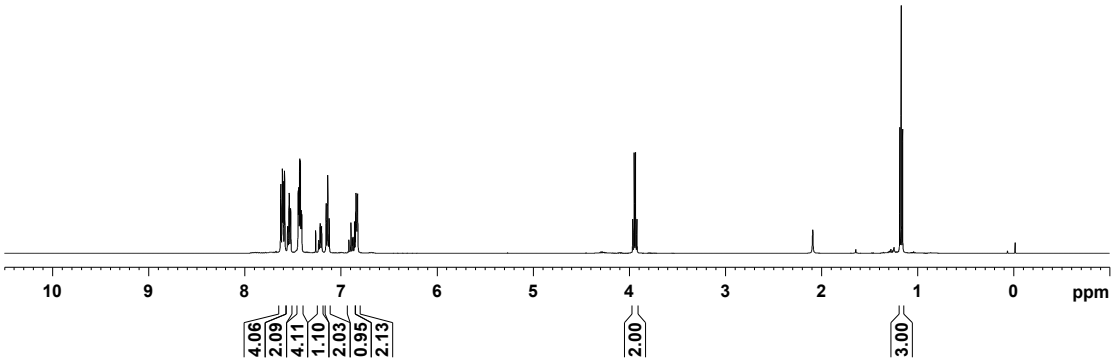
CF2COOEt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6
5
4
3
2
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4.11
1.10
2.03
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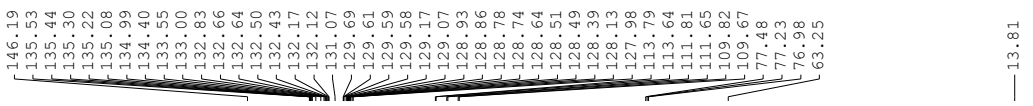
2.13
2.00
3.00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131.07
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129.17
129.07
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128.13
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109.82
109.67
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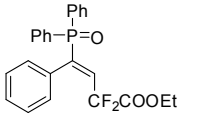
76.98
63.25
13.81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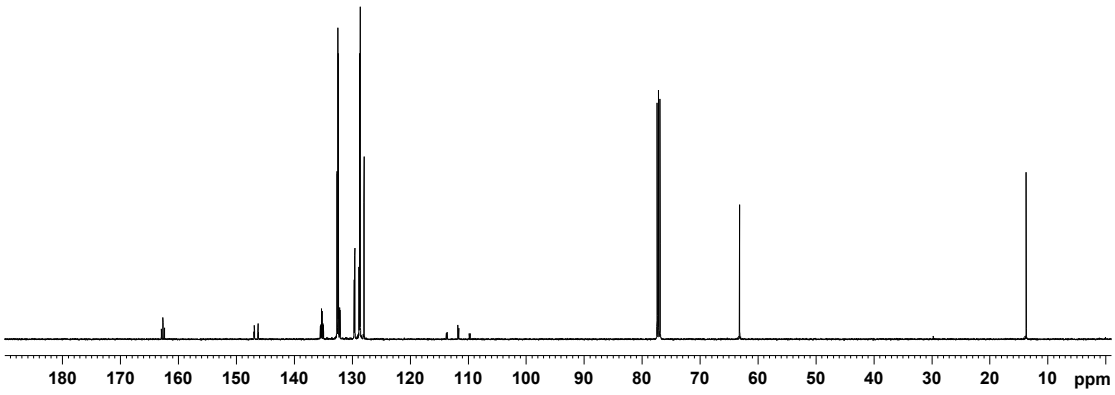
CF2COOEt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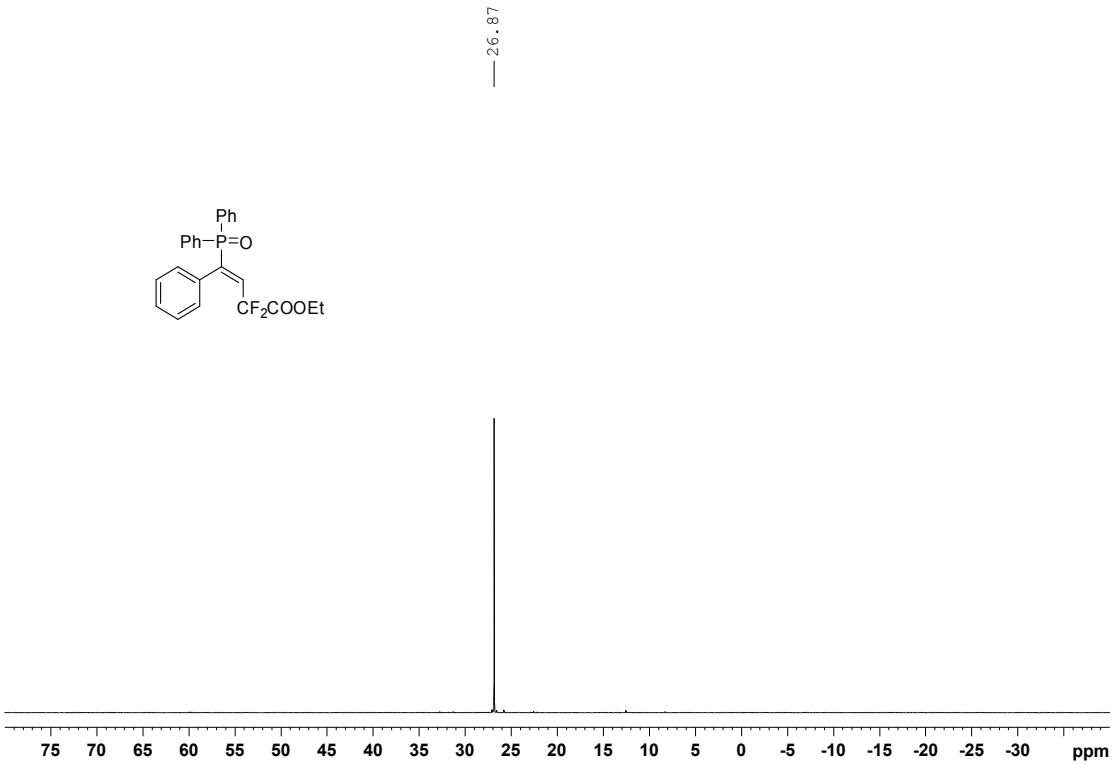
30
20
10
ppm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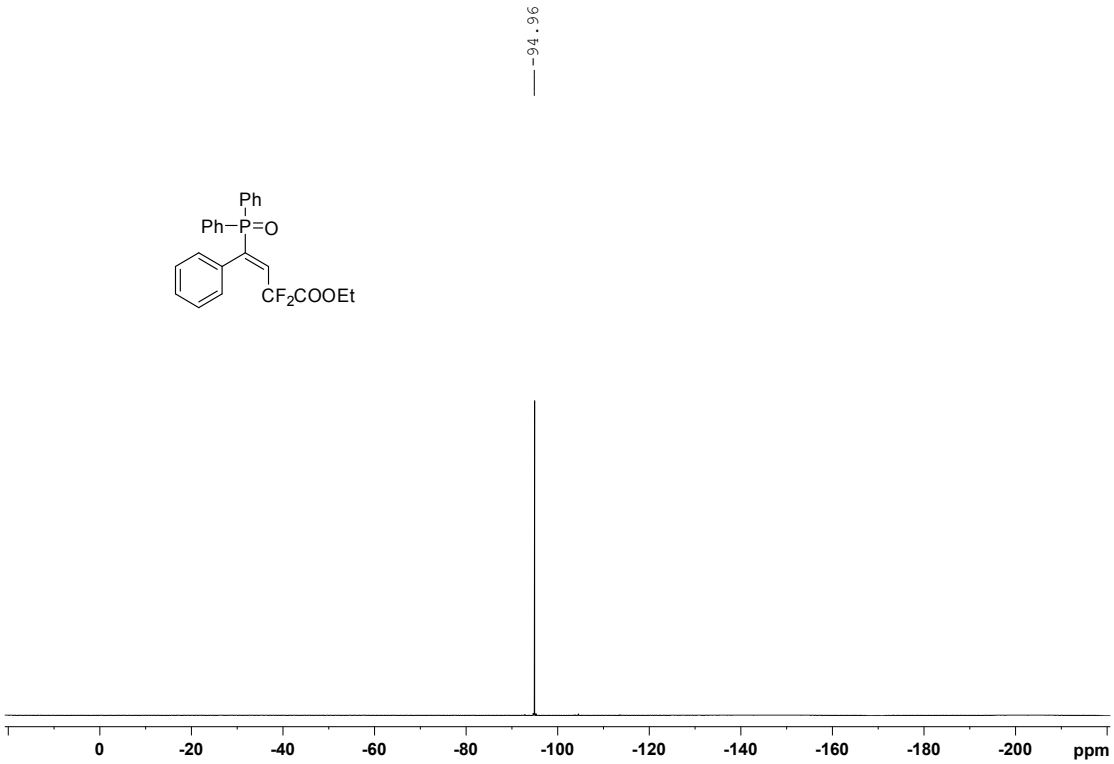
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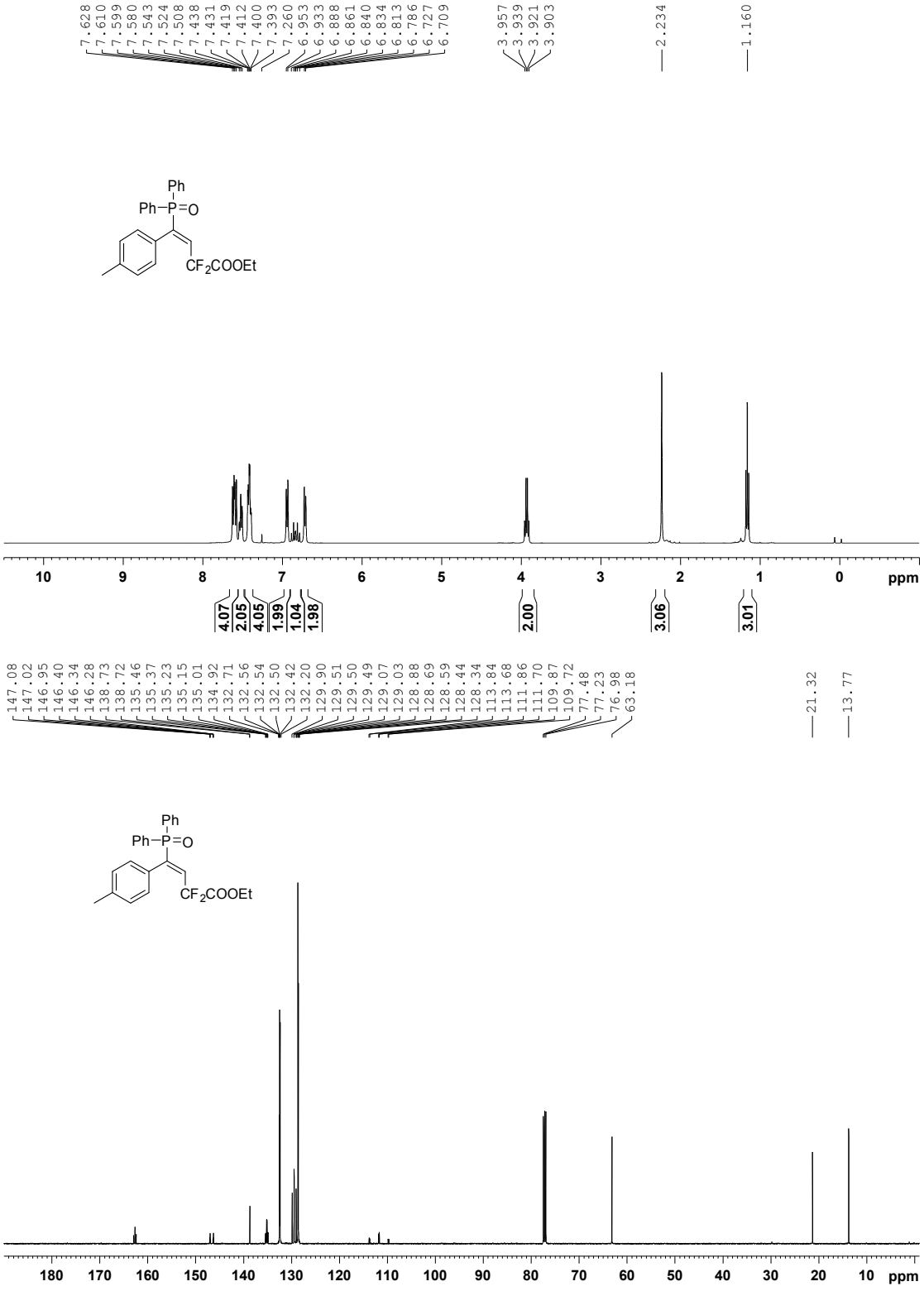
3b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7.260
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6.933
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6.861
6.840
6.834
6.813
6.786
6.727
6.709
3.957
3.939
3.921
3.903
2.234
1.160
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Ph—P=O
CF2COOEt
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2.05
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1.98
2.00
3.06
3.01
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138.72
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135.15
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129.51
129.50
129.49
129.07
129.03
128.88
128.69
128.59
128.44
128.34
113.84
113.68
111.86
111.70
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76.98
63.18
21.32
13.77
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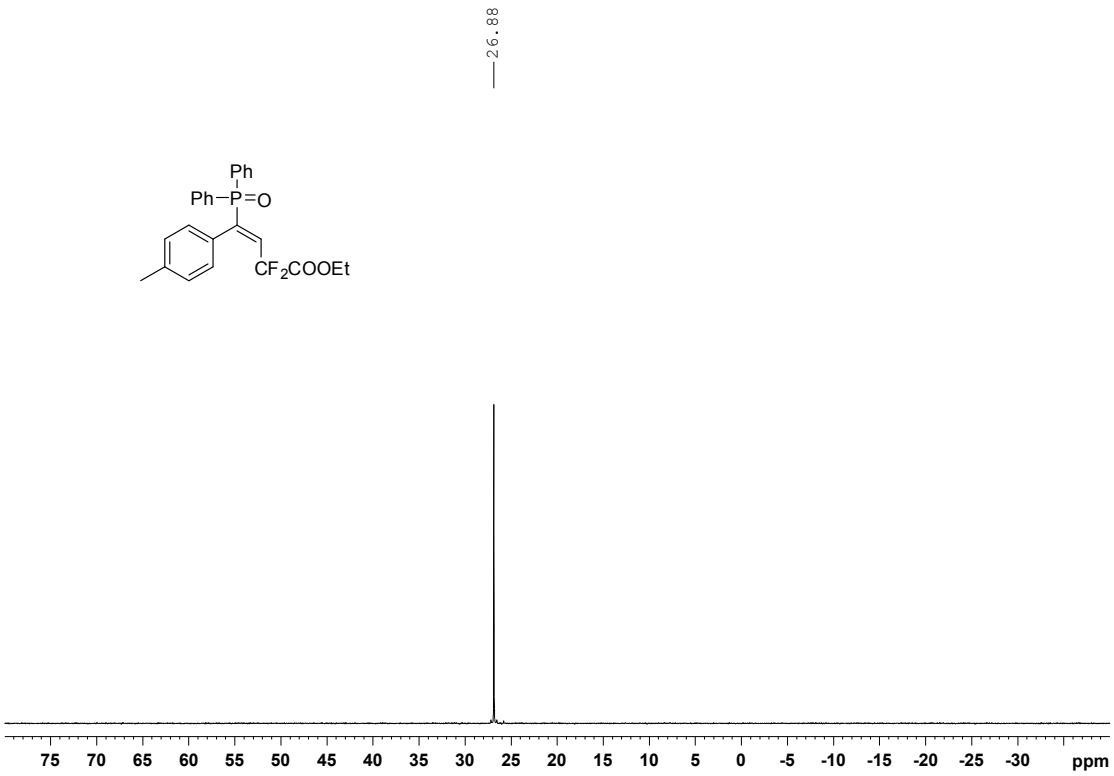
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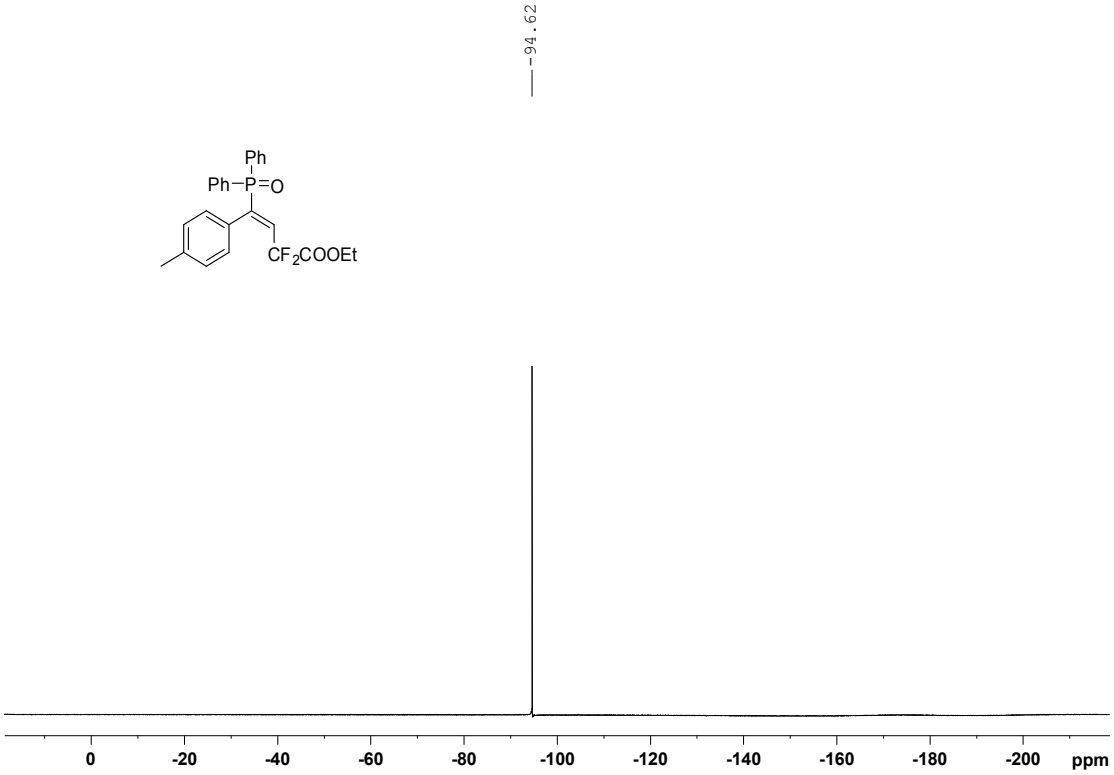
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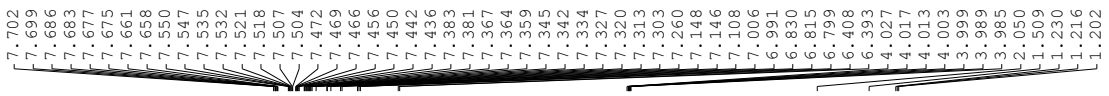
3c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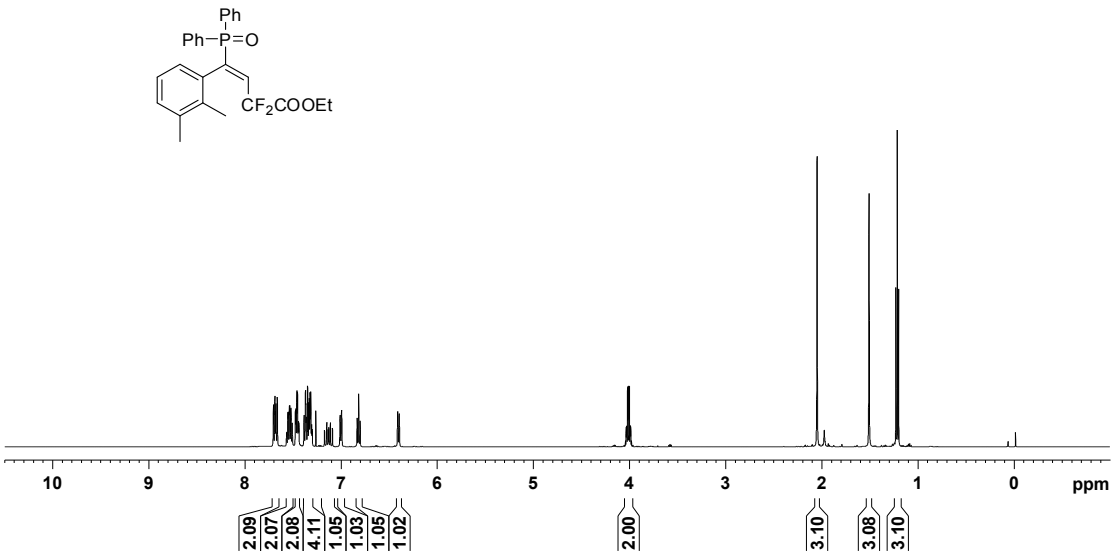
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4
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4.11
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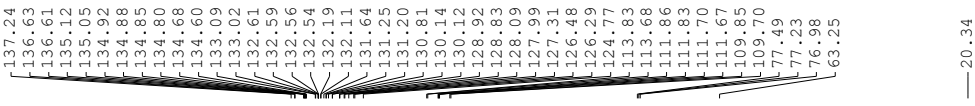
1.03
1.05
1.02
2.00
3.10
3.08
3.10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128.09
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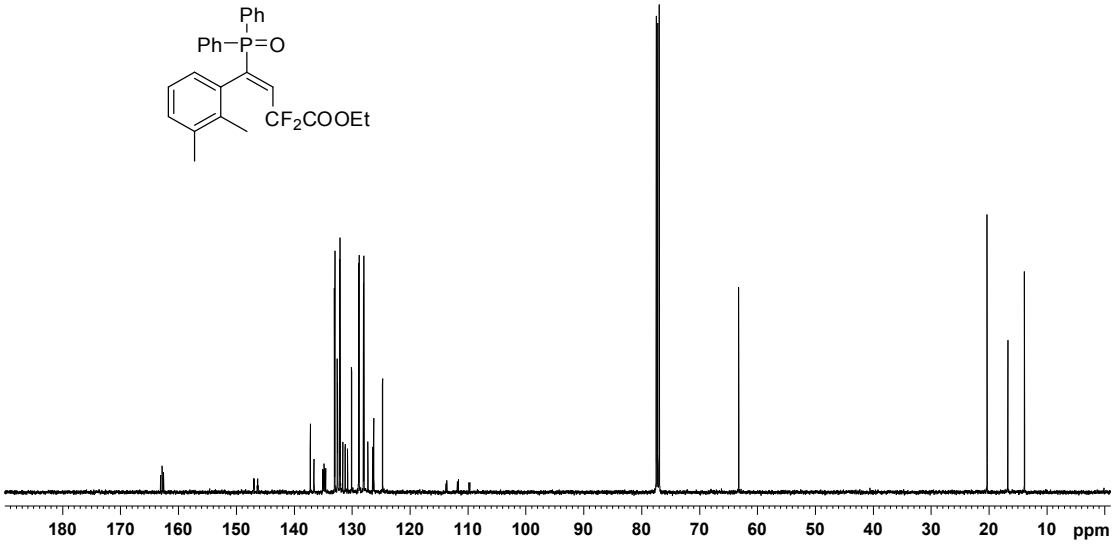
77.23
76.98
63.25
20.34
16.75
13.88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Ph—P=O
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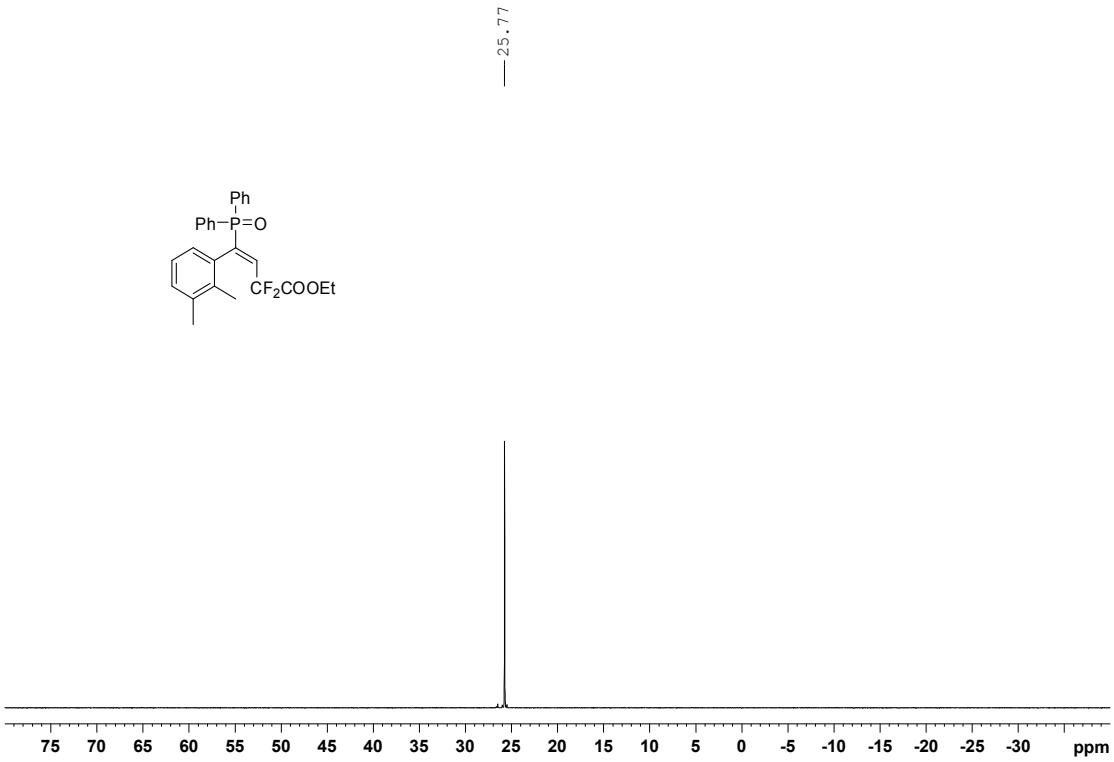
ppm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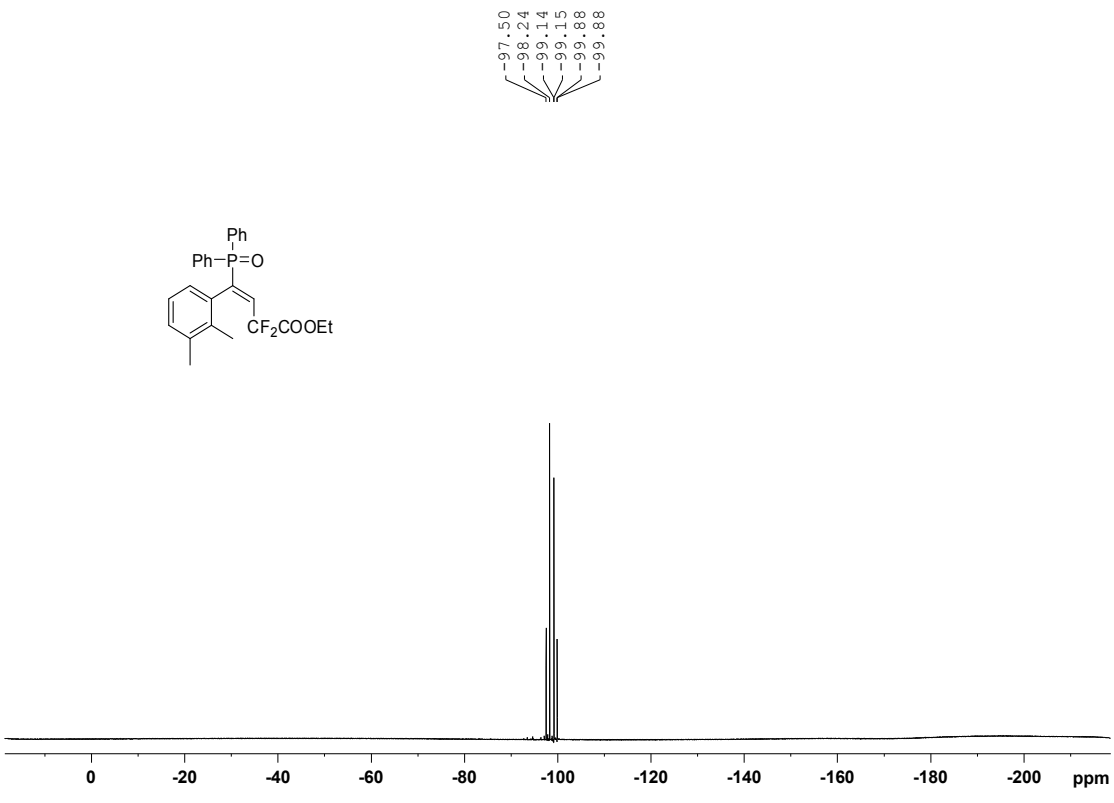
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CF2COOEt
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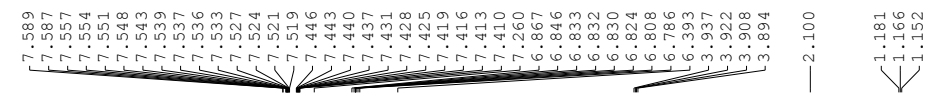
3d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7.419
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7.413
7.410
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6.833
6.832
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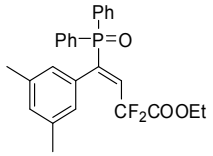
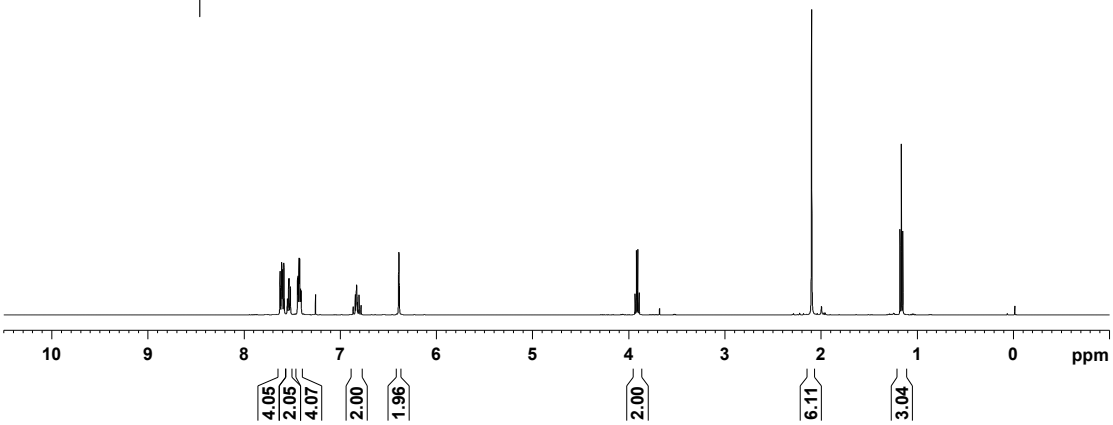
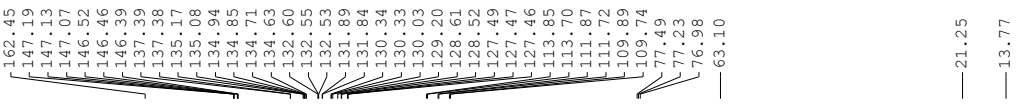
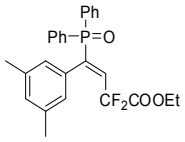
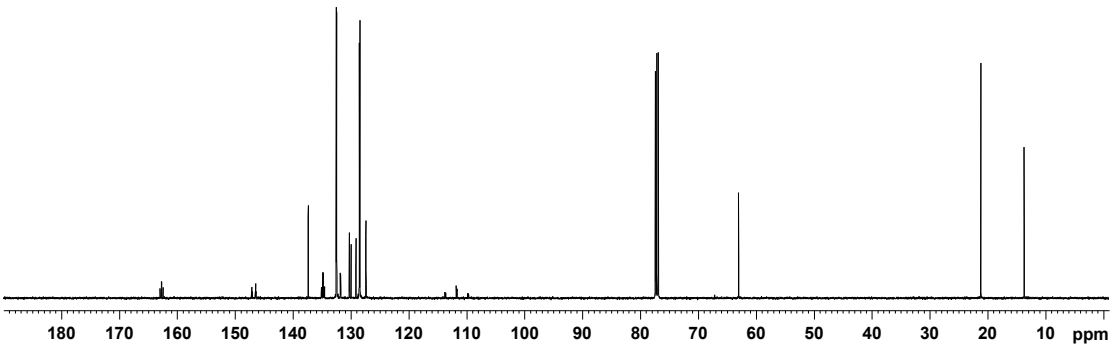
6.824
6.808
6.786
6.393
3.937
3.922
3.908
3.894
2.100
1.181
1.166
1.152


Ph
Ph–P=O
CF2COOEt

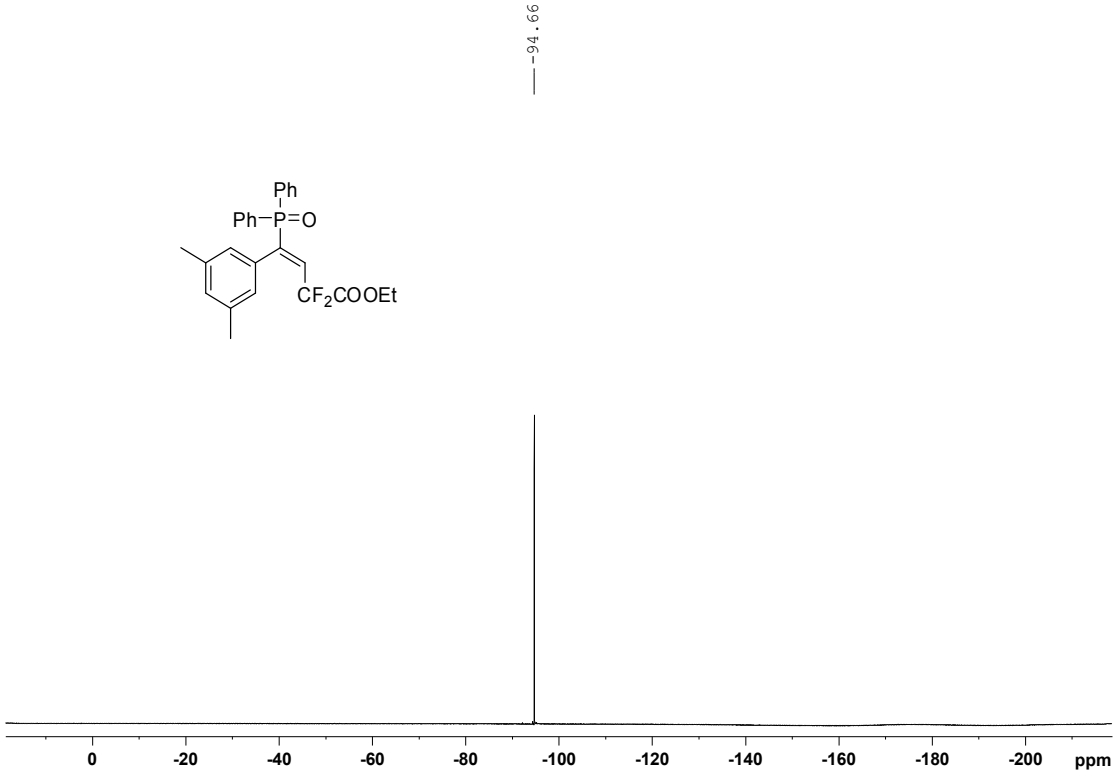

10
9
8
7
6
5
4
3
2
1
0
ppm
4.05
2.05
4.07
2.00
1.96
2.00
6.11
3.04


162.45
147.19
147.13
147.07
146.52
146.46
146.39
137.39
137.38
135.17
135.08
134.94
134.85
134.71
134.63
132.60
132.55
132.53
131.89
131.84
130.34
130.33
130.03
129.20
128.61
128.52
127.49
127.47
127.46
113.85
113.70
111.87
111.72
109.89
109.74
77.49
77.23
76.98
63.10
21.25
13.77

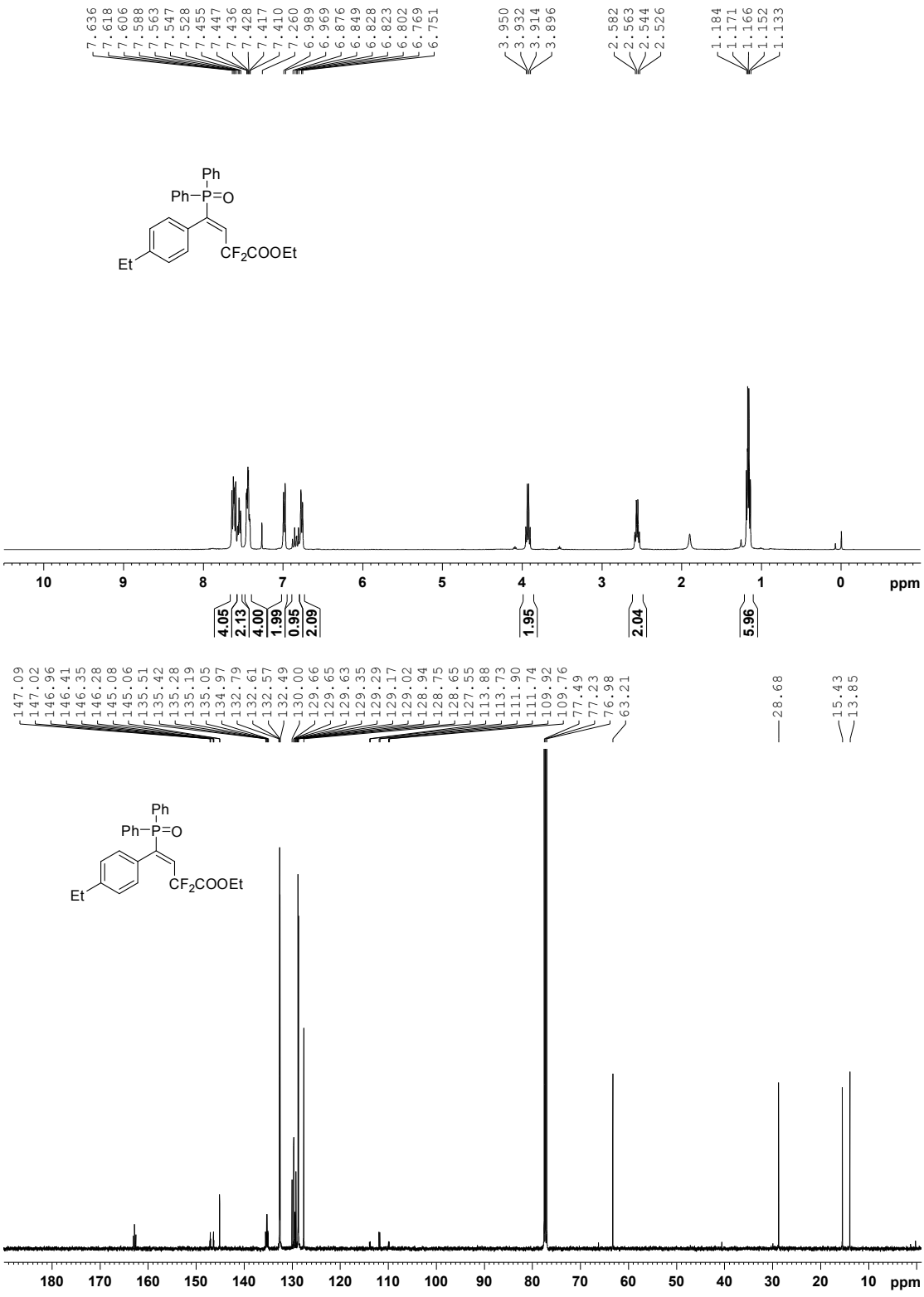

Ph
Ph–P=O
CF2COOEt


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.66
Ph
Ph—P=O
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.66
Ph
Ph—P=O
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3e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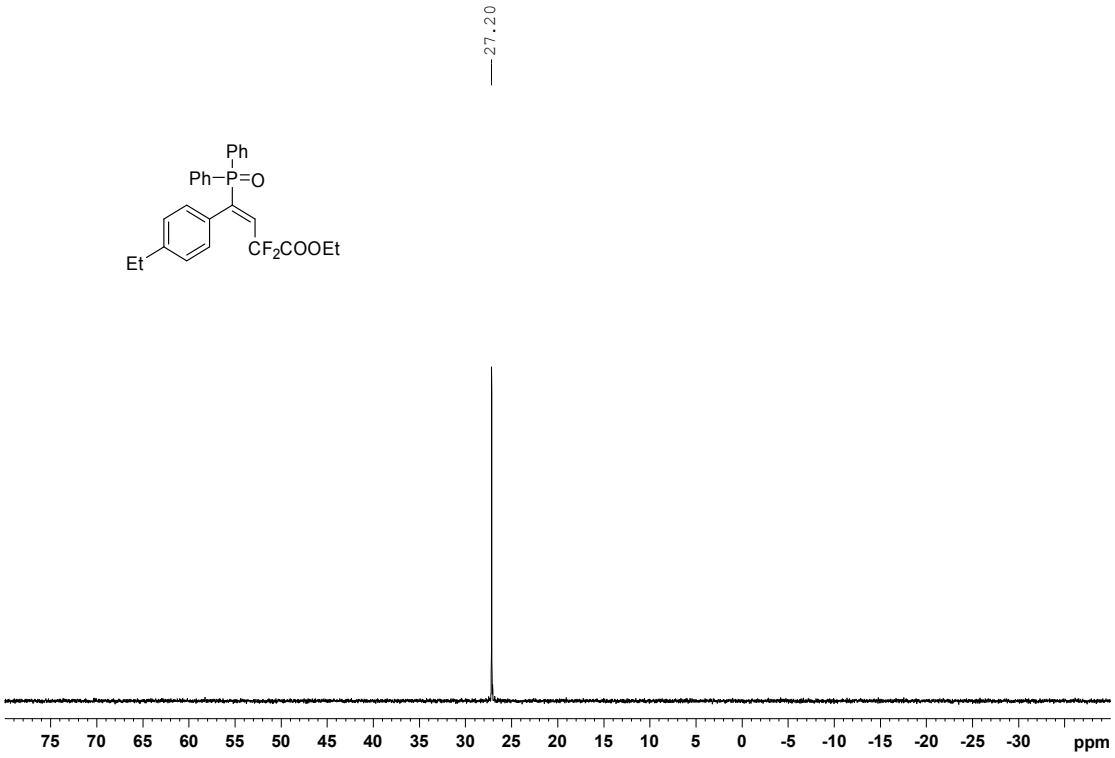
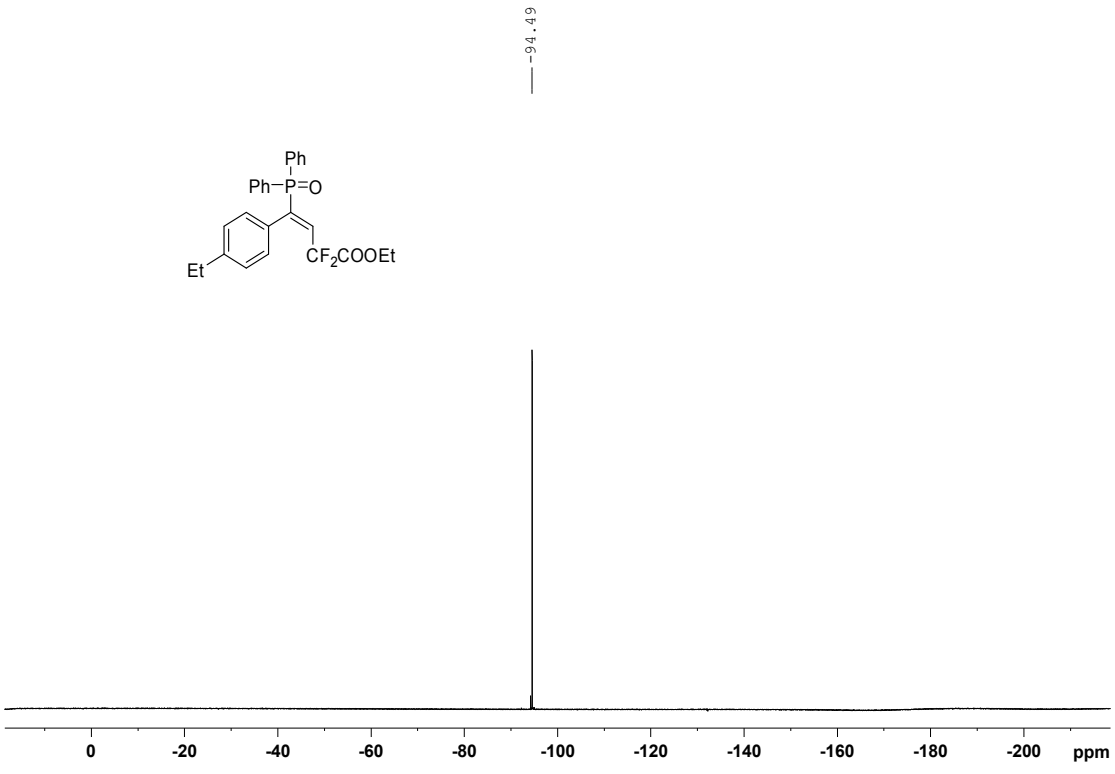
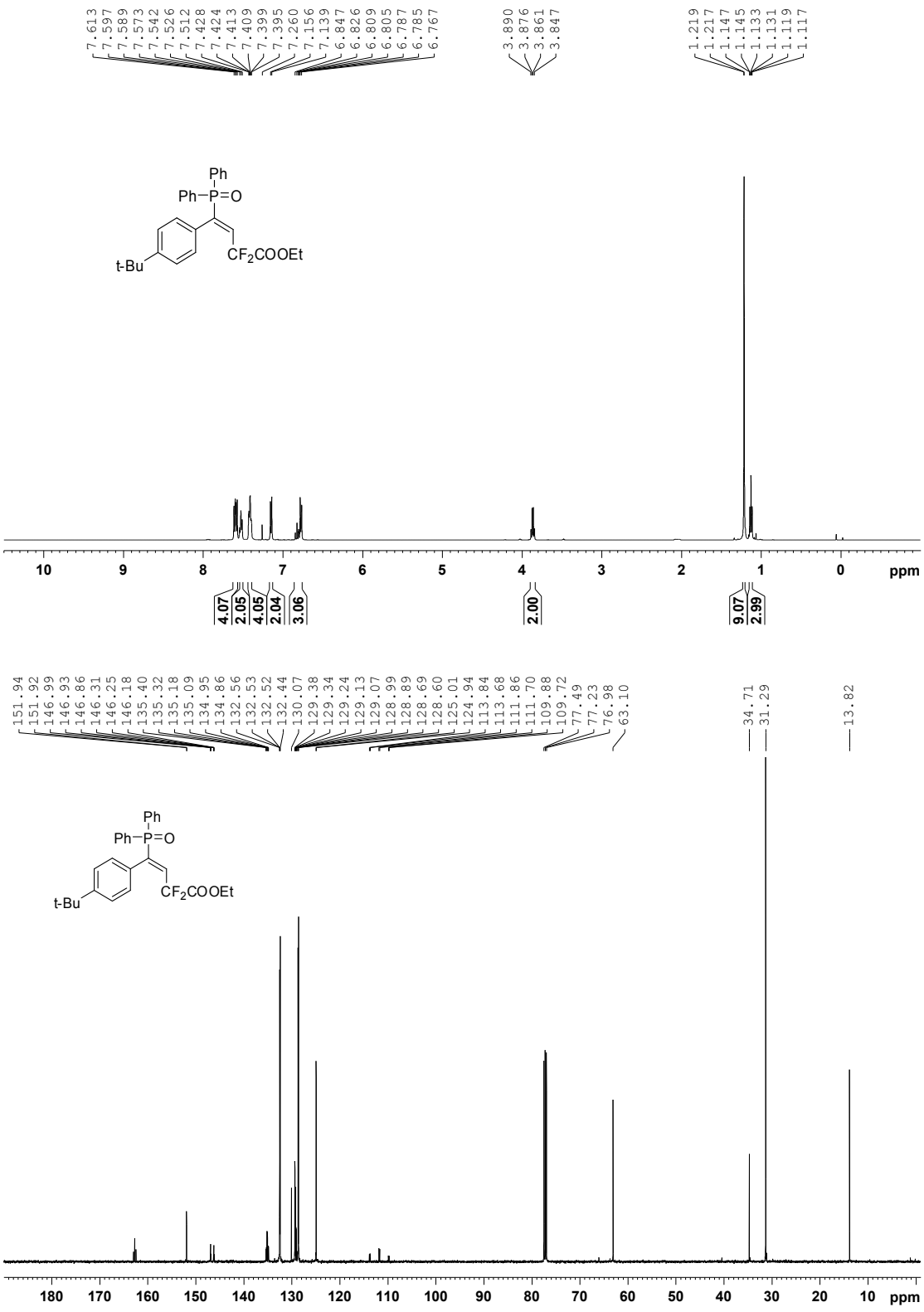
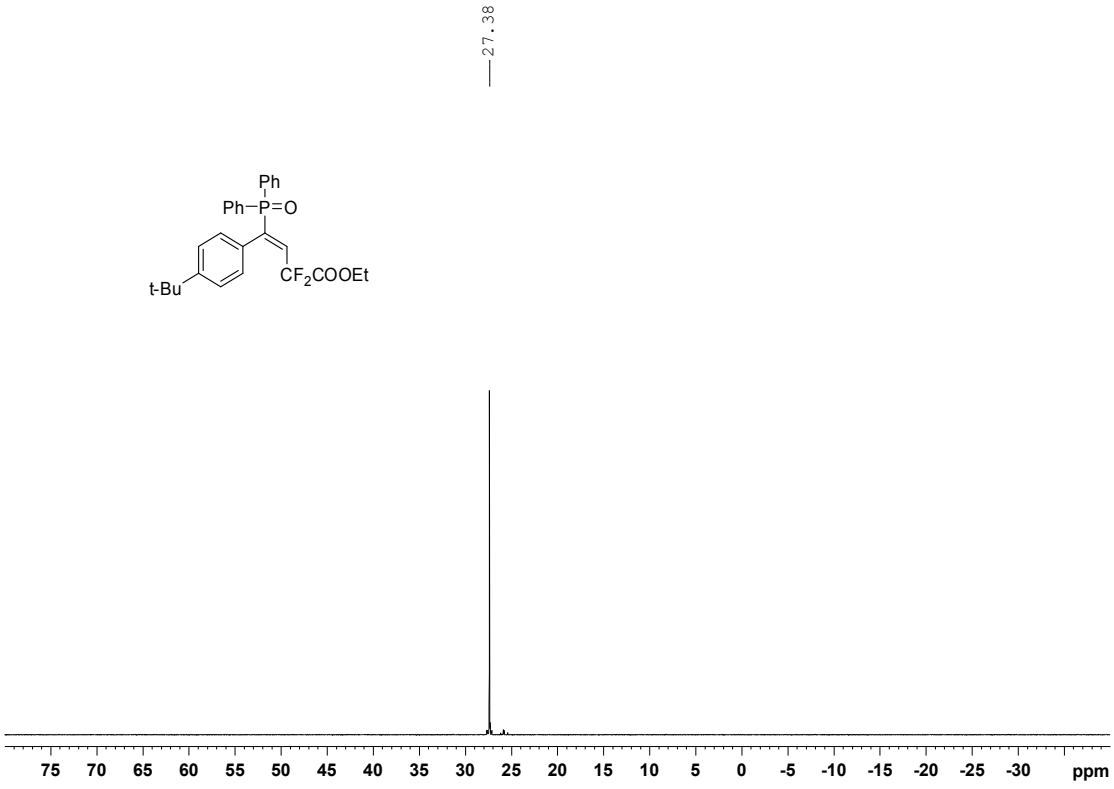
7.618
7.606
7.588
7.563
7.547
7.528
7.455
7.447
7.436
7.428
7.417
7.410
7.260
6.989
6.969
6.876
6.849
6.828
6.823
6.802
6.769
6.751
3.950
3.932
3.914
3.896
2.582
2.563
2.544
2.526
1.184
1.171
1.166
1.152
1.133
Ph
Ph—P=O
Et
CF2COOEt
ppm
4.05
2.13
4.00
1.99
0.95
2.09
1.95
2.04
5.96
147.09
147.02
146.96
146.41
146.35
146.28
145.08
145.06
135.51
135.42
135.28
135.19
135.05
134.97
132.79
132.61
132.57
132.49
130.00
129.66
129.65
129.63
129.35
129.29
129.17
129.02
128.94
128.75
128.65
127.55
113.88
113.73
111.90
111.74
109.92
109.76
77.49
77.23
76.98
63.21
28.68
15.43
13.85

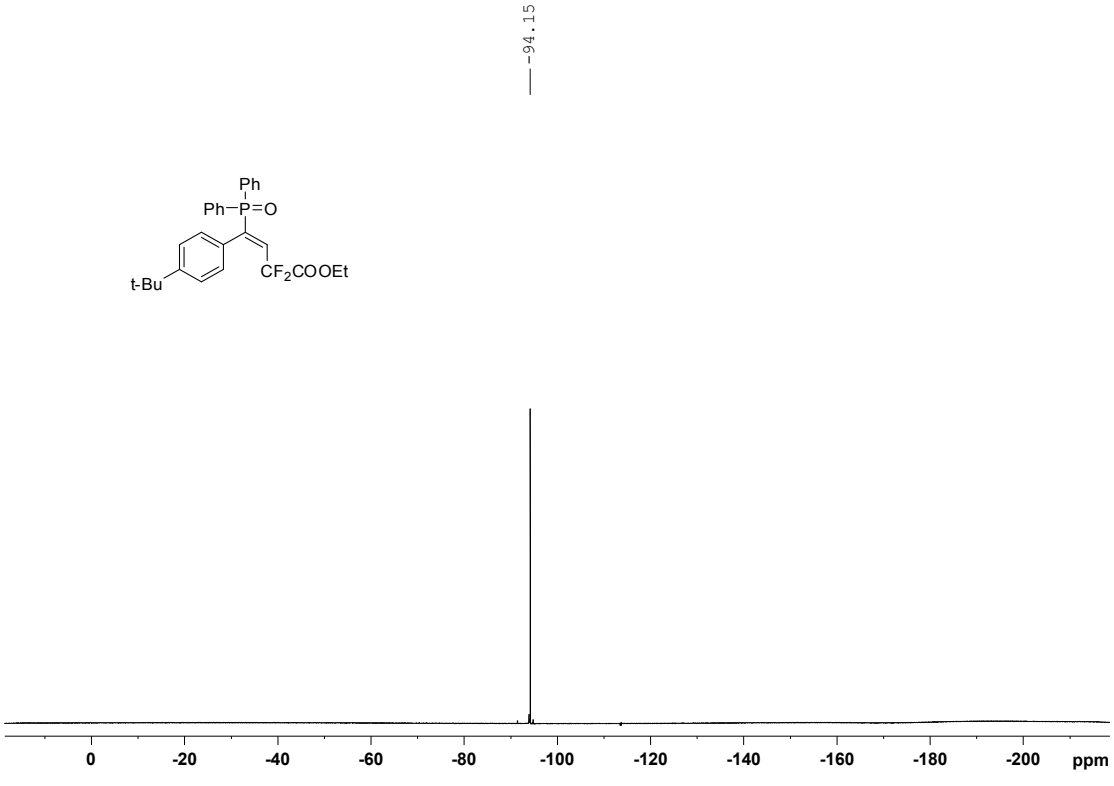

27.20
Ph
Ph—P=O
Et
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.49
Ph
Ph—P=O
Et
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

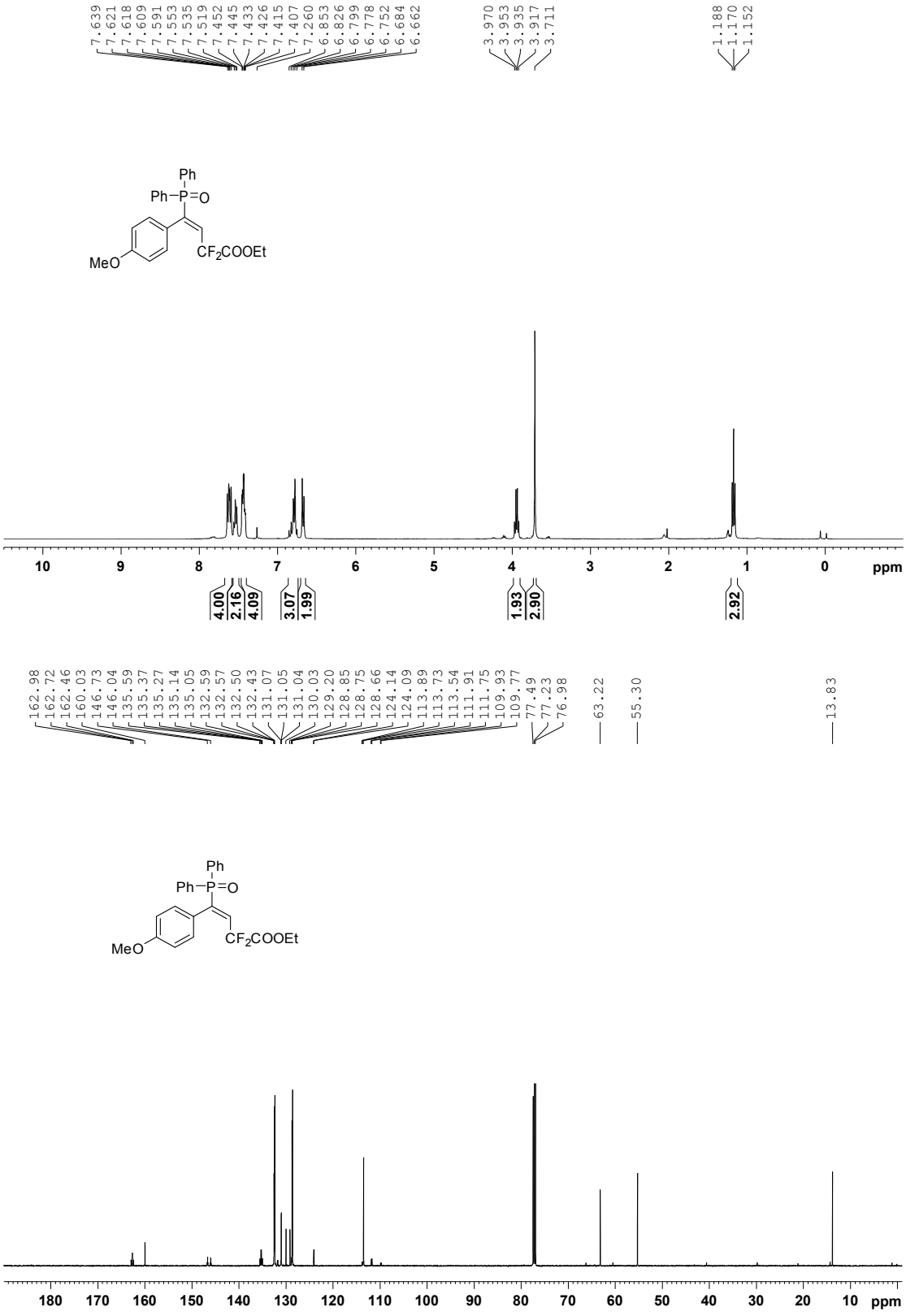
3f

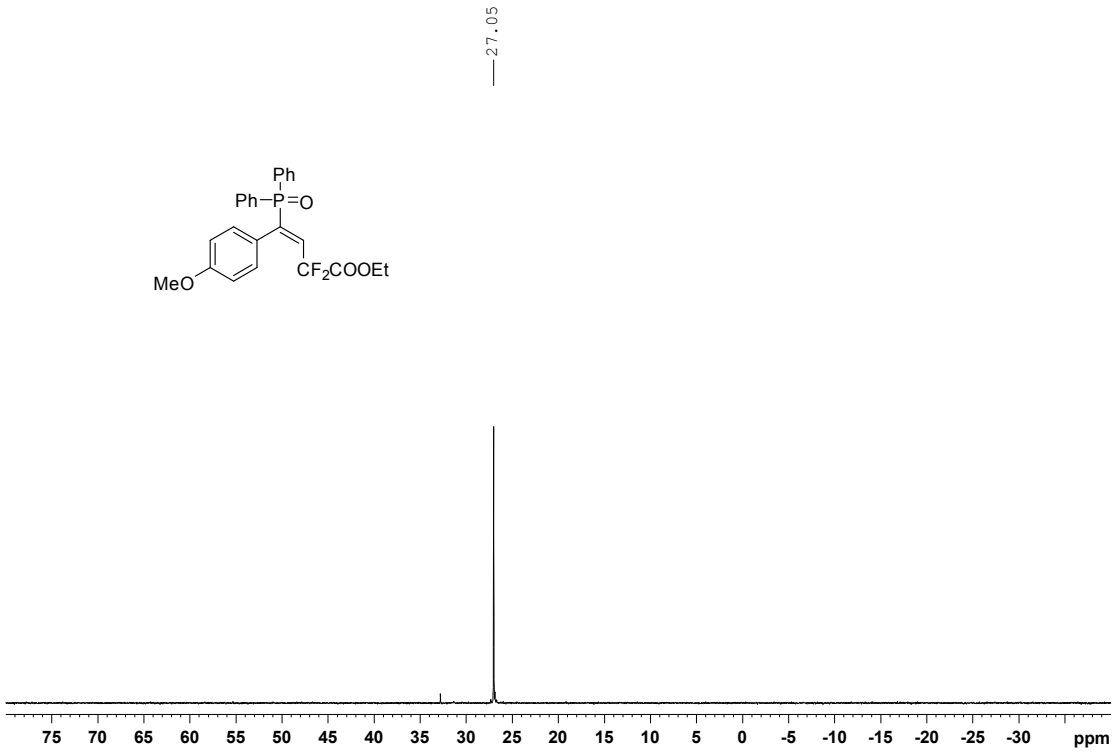

7.613
7.597
7.589
7.573
7.542
7.526
7.512
7.428
7.424
7.413
7.409
7.399
7.395
7.260
7.156
7.139
6.847
6.826
6.809
6.805
6.787
6.785
6.767
3.890
3.876
3.861
3.847
1.219
1.217
1.147
1.145
1.133
1.131
1.119
1.117
Ph
Ph—P=O
t-Bu
CF2COOEt
ppm
4.07
2.05
4.05
2.04
3.06
2.00
9.07
2.99
151.94
151.92
146.99
146.93
146.86
146.31
146.25
146.18
135.40
135.32
135.18
135.09
134.95
134.86
132.56
132.53
132.52
132.44
130.07
129.38
129.34
129.24
129.13
129.07
128.99
128.89
128.69
128.60
125.01
124.94
113.84
113.68
111.86
111.70
109.88
109.72
77.49
77.23
76.98
63.10
34.71
31.29
13.82
Ph
Ph—P=O
t-Bu
CF2COOEt
ppm

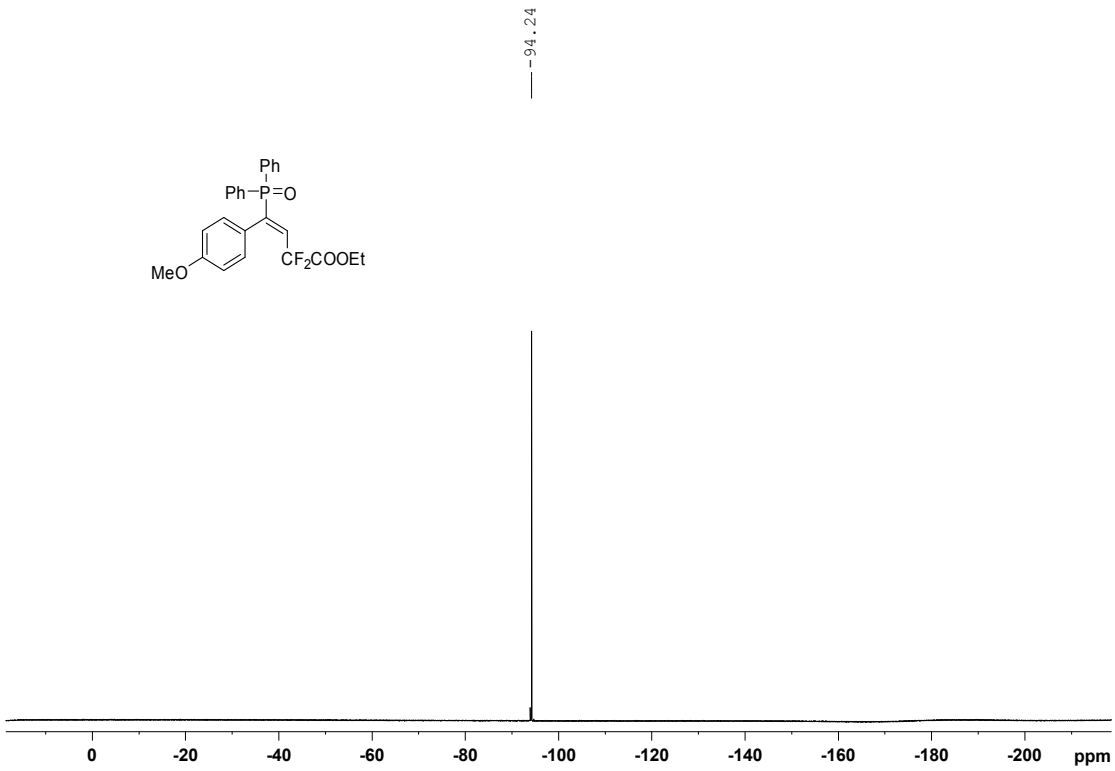

27.38
Ph
Ph–P=O
t-Bu
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.15
Ph
Ph–P=O
t-Bu
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

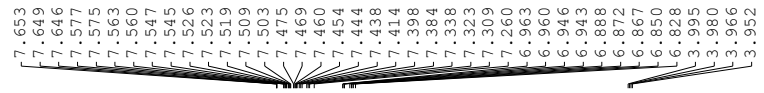
3g


7.639
7.621
7.618
7.609
7.591
7.553
7.535
7.519
7.452
7.445
7.433
7.426
7.415
7.407
7.260
6.853
6.826
6.799
6.778
6.752
6.684
6.662
3.970
3.953
3.935
3.917
3.711
1.188
1.170
1.152
Ph
Ph—P=O
MeO
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
2.16
4.09
3.07
1.99
1.93
2.90
2.92
162.98
162.72
162.46
160.03
146.73
146.04
135.59
135.37
135.27
135.14
135.05
132.59
132.57
132.50
132.43
131.07
131.05
131.04
130.03
129.20
128.85
128.75
128.66
124.14
124.09
113.89
113.73
113.54
111.91
111.75
109.93
109.77
77.49
77.23
76.98
63.22
55.30
13.83
Ph
Ph—P=O
MeO
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


27.05
Ph
Ph–P=O
MeO
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.24
Ph
Ph–P=O
MeO
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3h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7.649
7.646
7.577
7.575
7.563
7.560
7.547
7.545
7.526
7.523
7.519
7.509
7.503
7.475
7.469
7.460
7.454
7.444
7.438
7.414
7.398
7.384
7.338
7.323
7.309
7.260
6.963
6.960
6.946
6.943
6.888
6.872
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6.850
6.828
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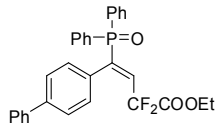
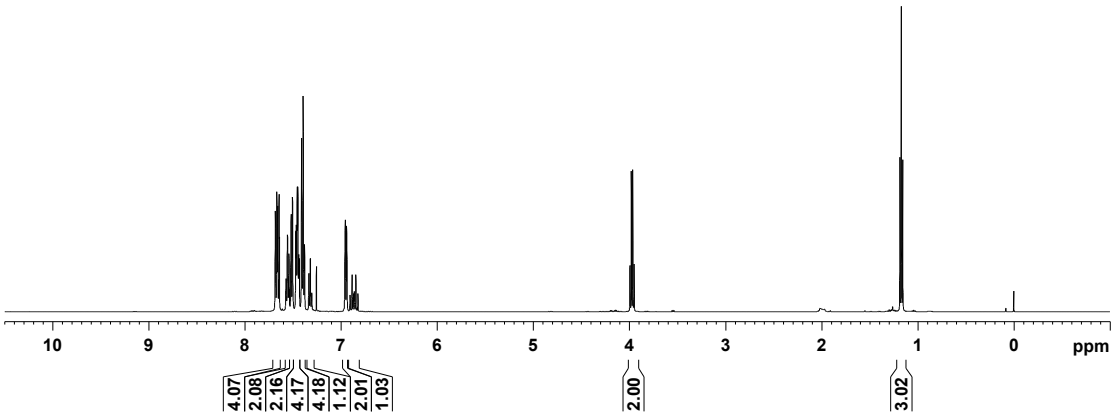
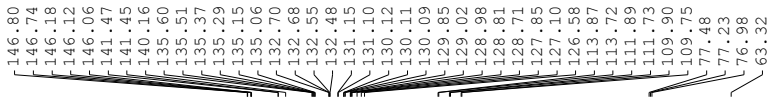
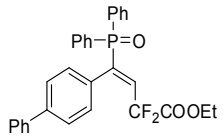
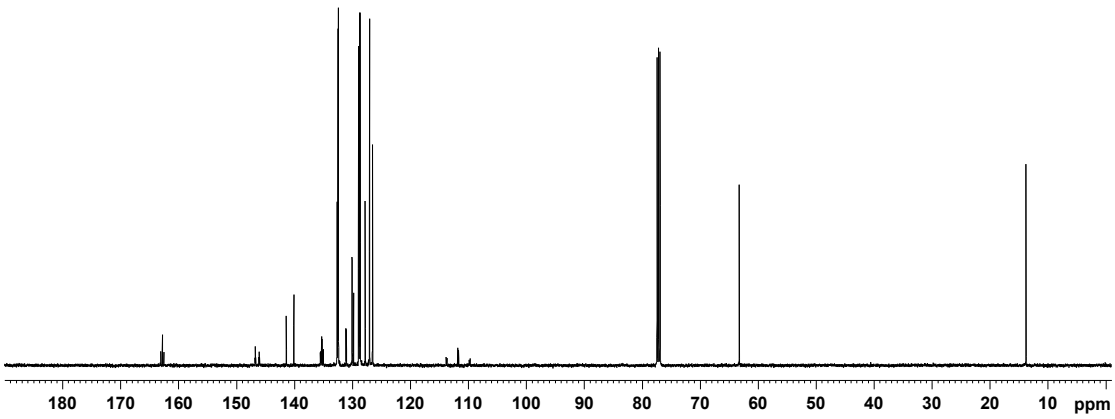
3.980
3.966
3.952
1.186
1.172
1.157

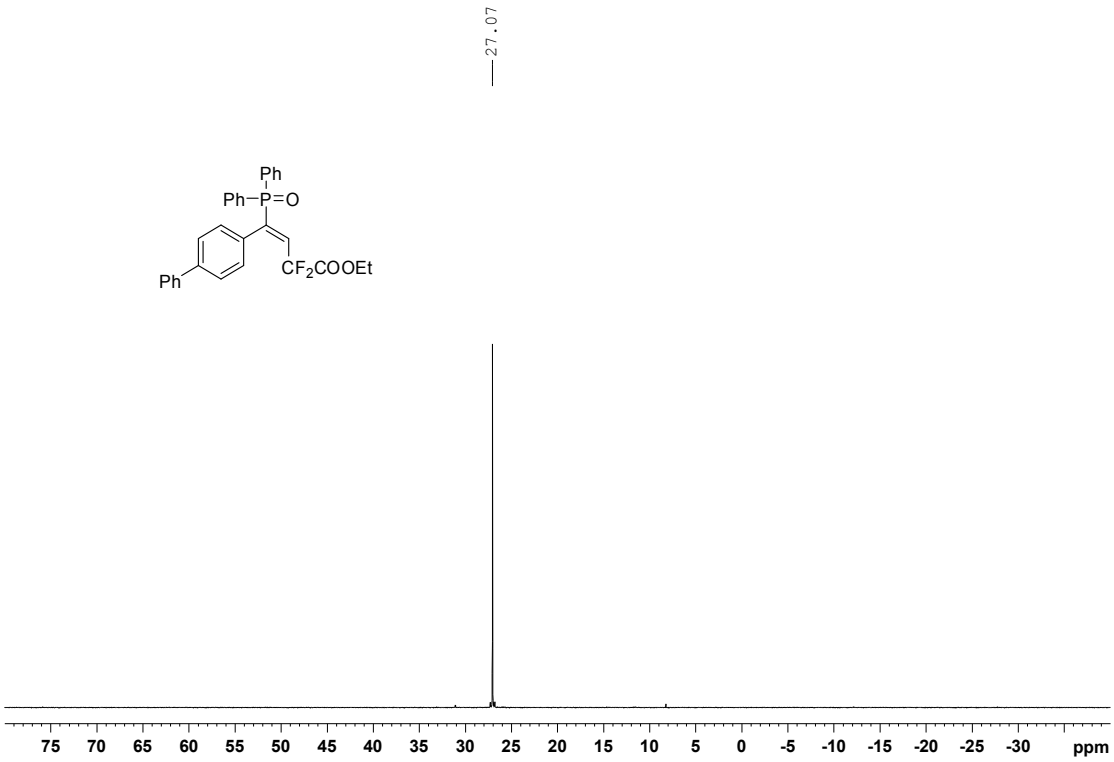

Ph
Ph–P=O
CF2COOEt
Ph

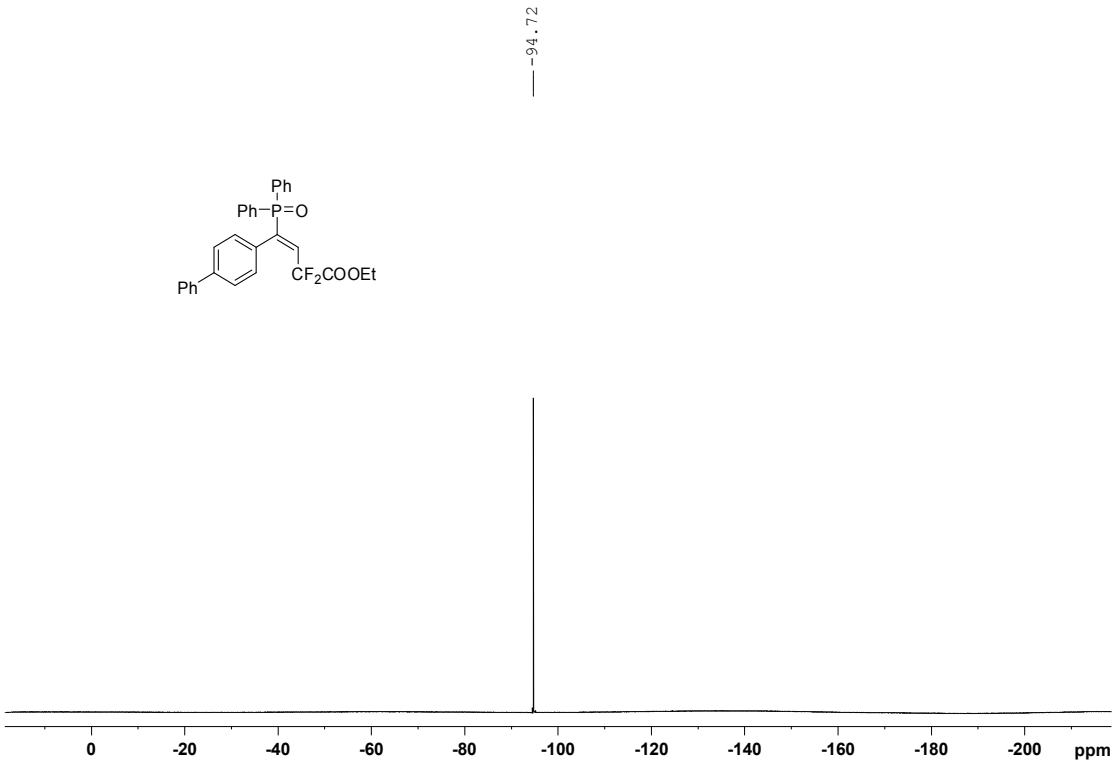

10
9
8
7
6
5
4
3
2
1
0
ppm
4.07
2.08
2.16
4.17
4.18
1.12
2.01
1.03
2.00
3.02


146.80
146.74
146.18
146.12
146.06
141.47
141.45
140.16
135.60
135.51
135.37
135.29
135.15
135.06
132.70
132.68
132.55
132.48
131.15
131.10
130.12
130.11
130.09
129.85
129.02
128.98
128.81
128.71
127.85
127.10
126.58
113.87
113.72
111.89
111.73
109.90
109.75
77.48
77.23
76.98
63.32
13.85

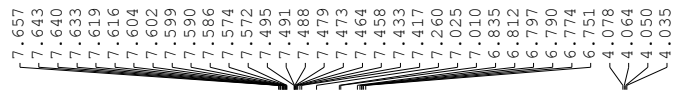

Ph
Ph–P=O
CF2COOEt
Ph


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


27.07
Ph
Ph–P=O
CF2COOEt
Ph
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.72
Ph
Ph–P=O
CF2COOEt
Ph
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3i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7.643
7.640
7.633
7.619
7.616
7.604
7.602
7.599
7.590
7.586
7.574
7.572
7.495
7.491
7.488
7.479
7.473
7.464
7.458
7.433
7.417
7.260
7.025
7.010
6.835
6.812
6.797
6.790
6.774
6.751
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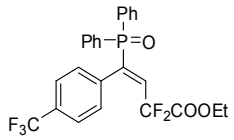
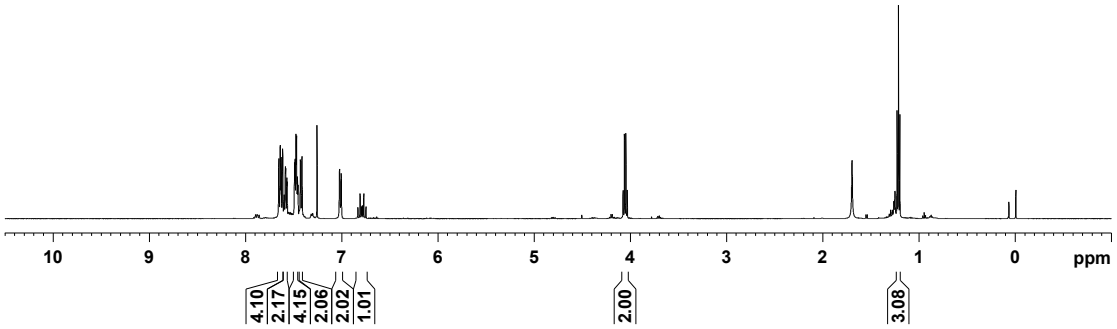
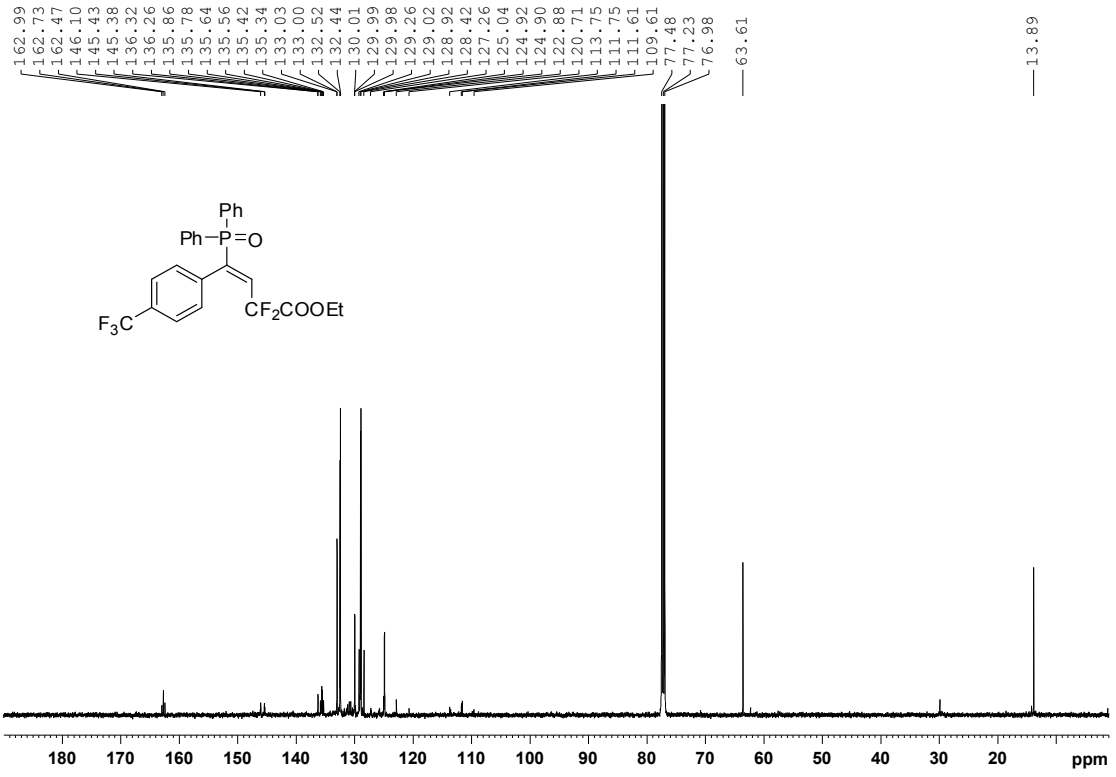
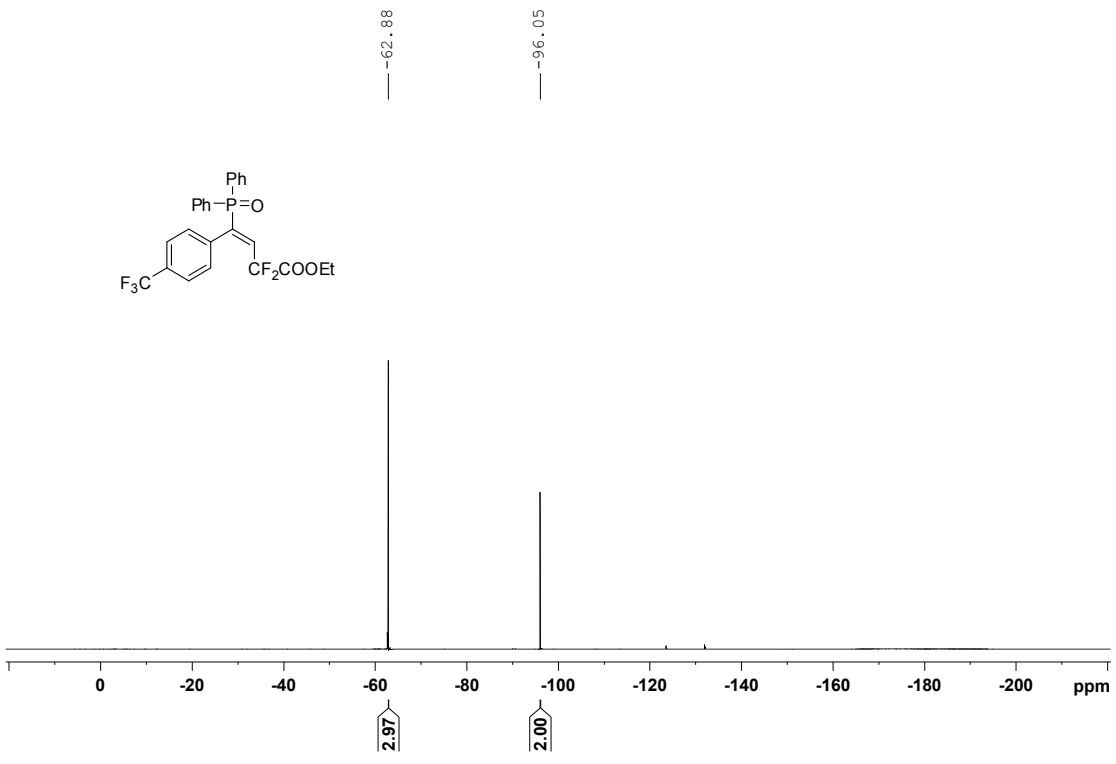
4.064
4.050
4.035
1.230
1.216
1.201


Ph
Ph—P=O
F3C
CF2COOEt

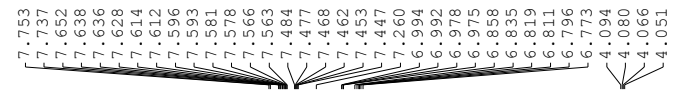

10
9
8
7
6
5
4
3
2
1
0
ppm
4.10
2.17
4.15
2.06
2.02
1.01
2.00
3.08

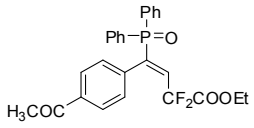

162.99
162.73
162.47
146.10
145.43
145.38
136.32
136.26
135.86
135.78
135.64
135.56
135.42
135.34
133.03
133.00
132.52
132.44
130.01
129.99
129.98
129.26
129.02
128.92
128.42
127.26
125.04
124.92
124.90
122.88
120.71
113.75
111.75
111.61
109.61
77.48
77.23
76.98
63.61
13.89
Ph
Ph—P=O
F3C
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

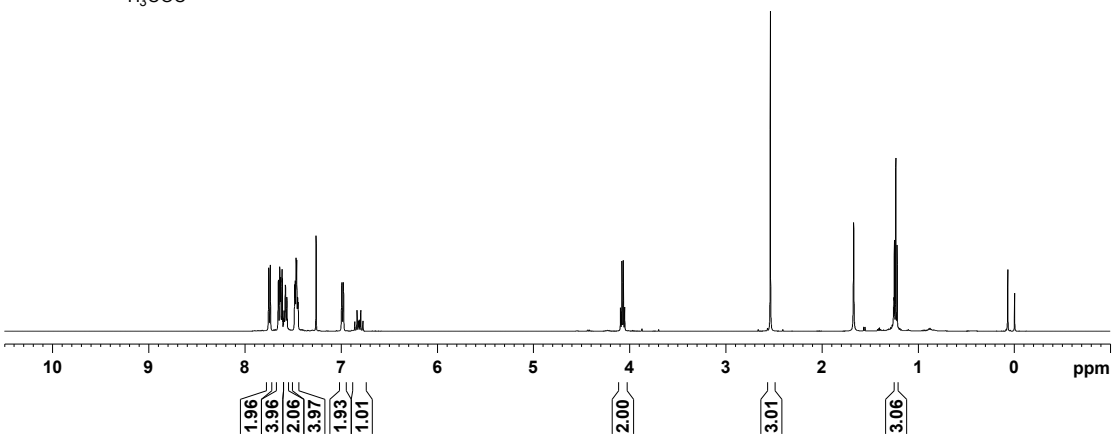

27.33
Ph
Ph—P=O
F3C
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

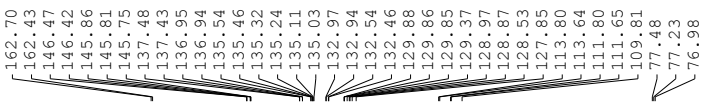

-62.88
-96.05
Ph
Ph—P=O
F3C
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm
2.97
2.00

3j

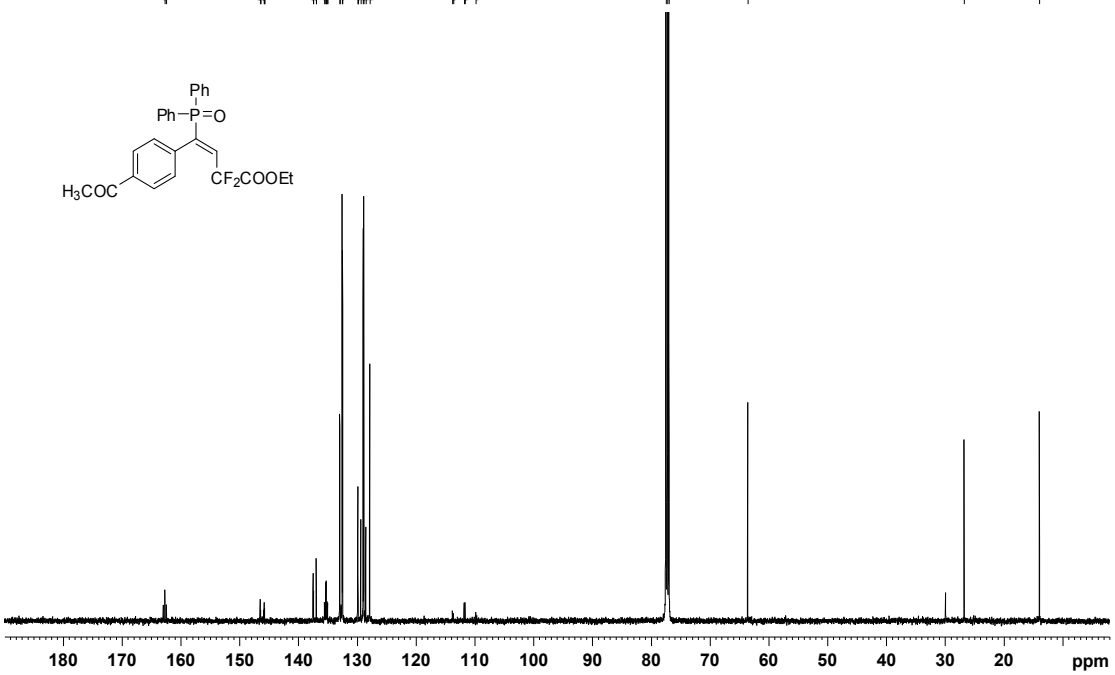

7.753
7.737
7.652
7.638
7.636
7.628
7.614
7.612
7.596
7.593
7.581
7.578
7.566
7.563
7.484
7.477
7.468
7.462
7.453
7.447
7.260
6.994
6.992
6.978
6.975
6.858
6.835
6.819
6.811
6.796
6.773
4.094
4.080
4.066
4.051
2.536
1.246
1.232
1.217

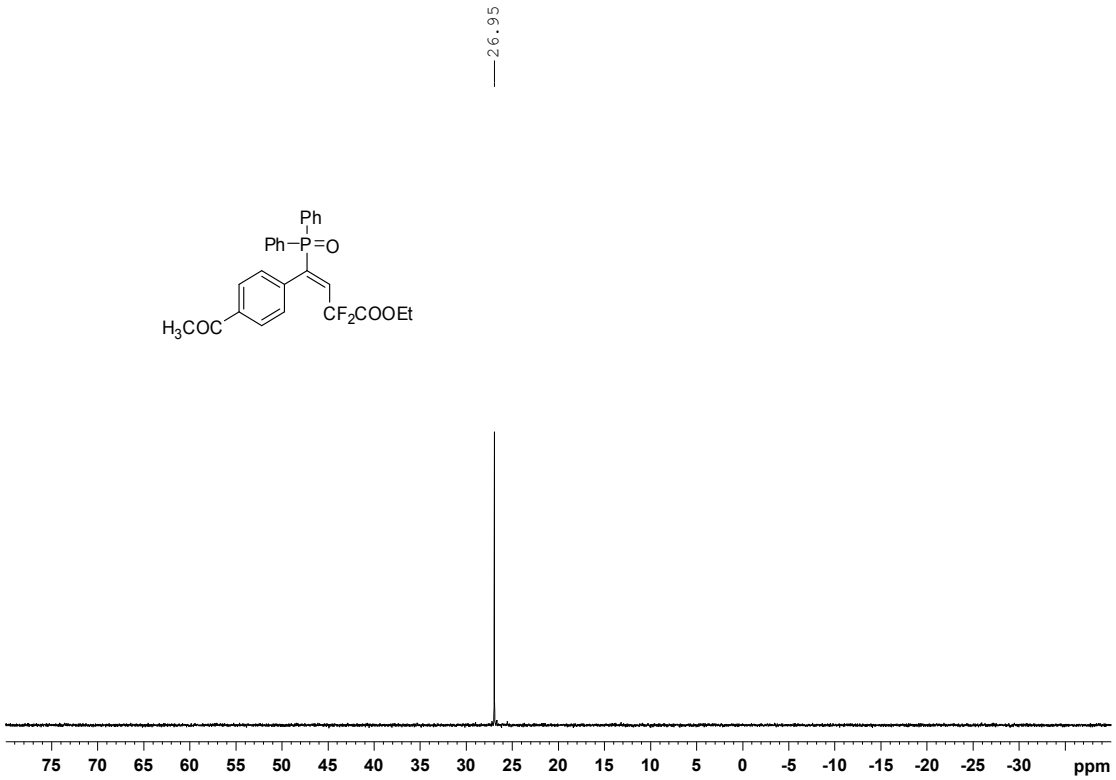

Ph
Ph–P=O
H3COC
CF2COOEt

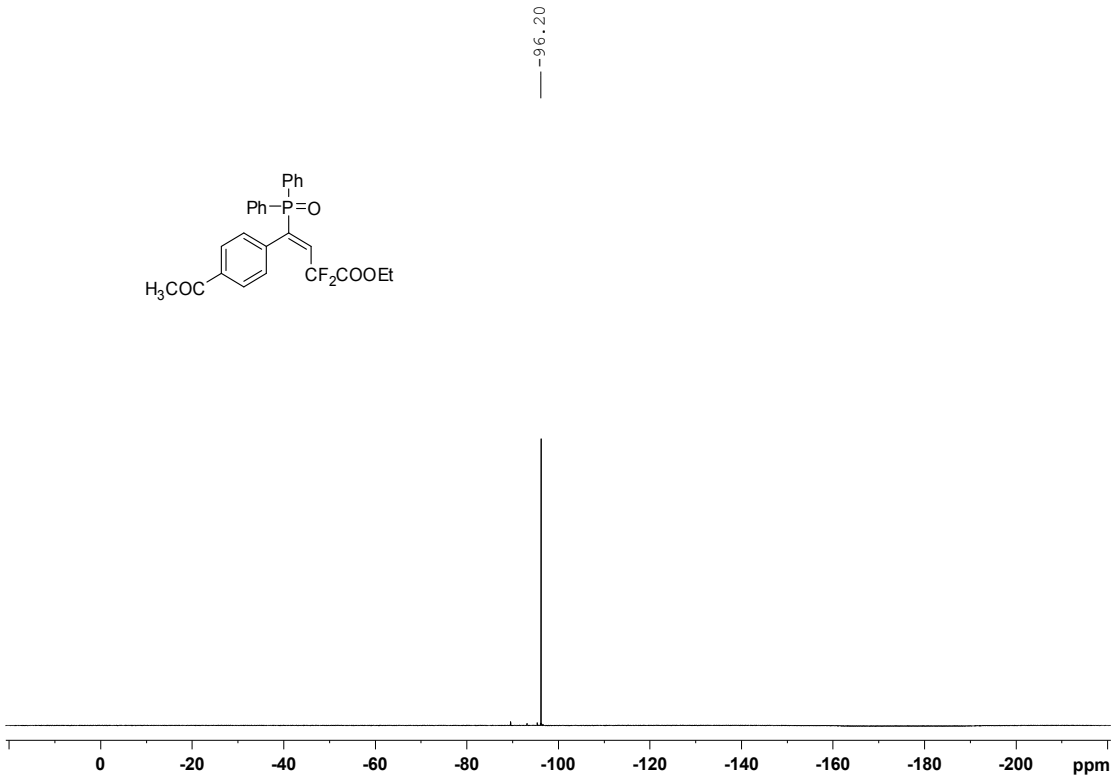

10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
3.96
2.06
3.97
1.93
1.01
2.00
3.01
3.06


162.70
162.43
146.47
146.42
145.86
145.81
145.75
137.48
137.43
136.95
136.94
135.54
135.46
135.32
135.24
135.11
135.03
132.97
132.94
132.54
132.46
129.88
129.86
129.85
129.37
128.97
128.87
128.53
127.85
113.80
113.64
111.80
111.65
109.81
77.48
77.23
76.98
63.57
26.78
13.96

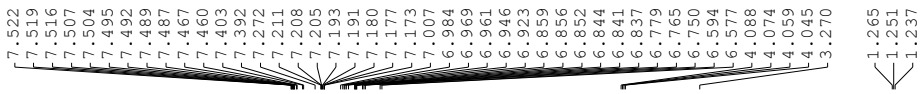
Ph
Ph–P=O
H3COC
CF2COOEt

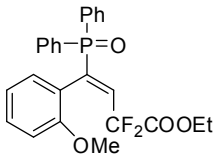

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

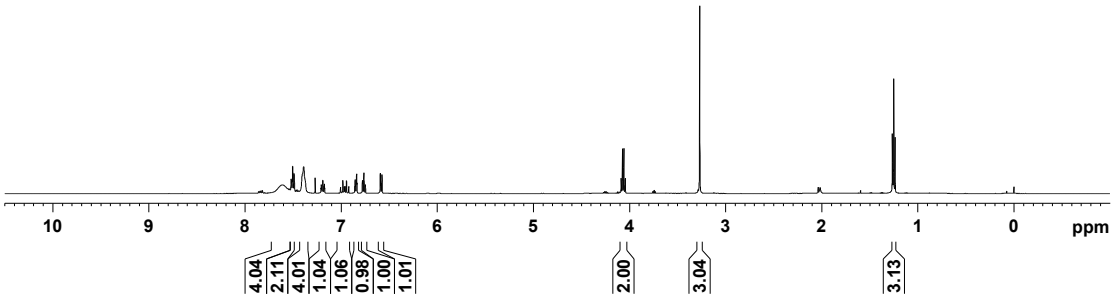

26.95
Ph
Ph—P=O
H3COC
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

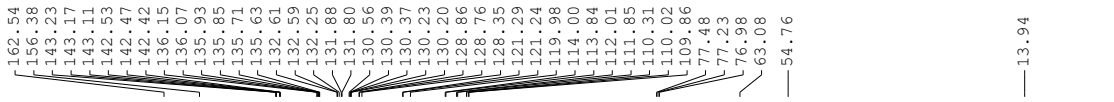

-96.20
Ph
Ph—P=O
H3COC
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

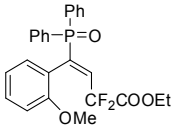
3l

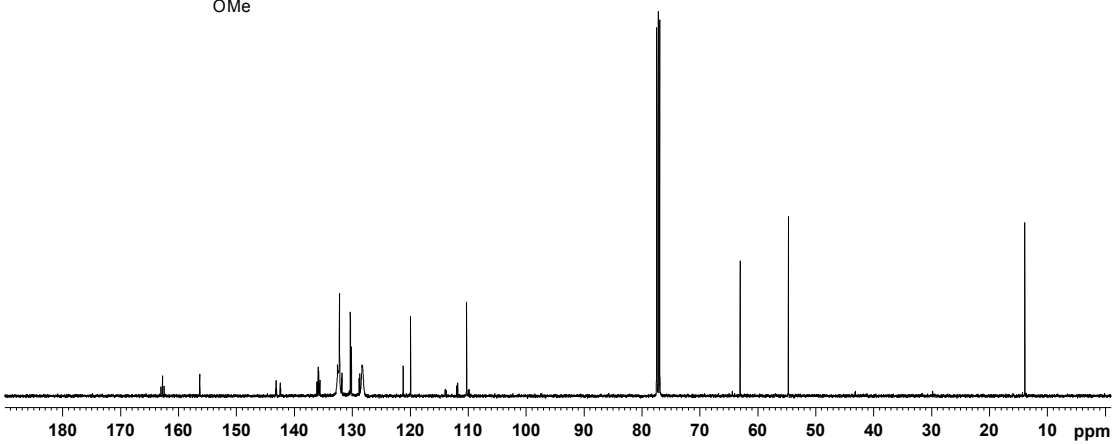

7.522
7.519
7.516
7.507
7.504
7.495
7.492
7.489
7.487
7.467
7.460
7.403
7.392
7.272
7.211
7.208
7.205
7.193
7.191
7.180
7.177
7.173
7.007
6.984
6.969
6.961
6.946
6.923
6.859
6.856
6.852
6.844
6.841
6.837
6.779
6.765
6.750
6.594
6.577
4.088
4.074
4.059
4.045
3.270
1.265
1.251
1.237

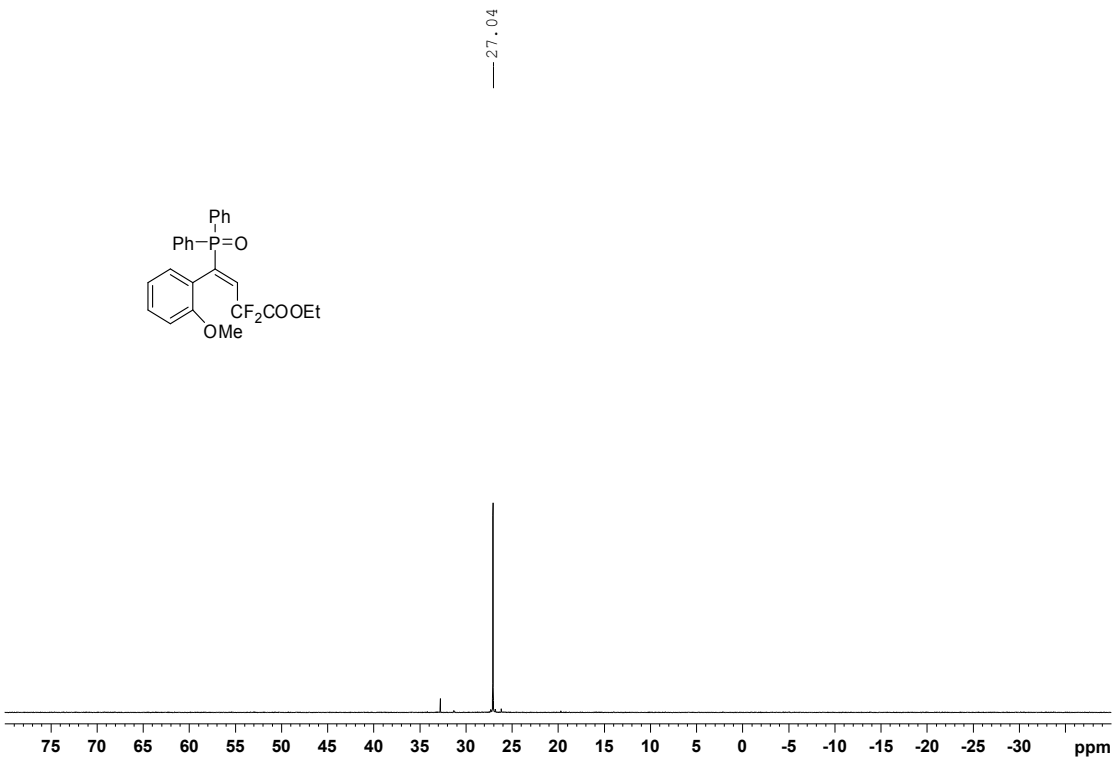

Ph
Ph—P=O
CF2COOEt
OMe

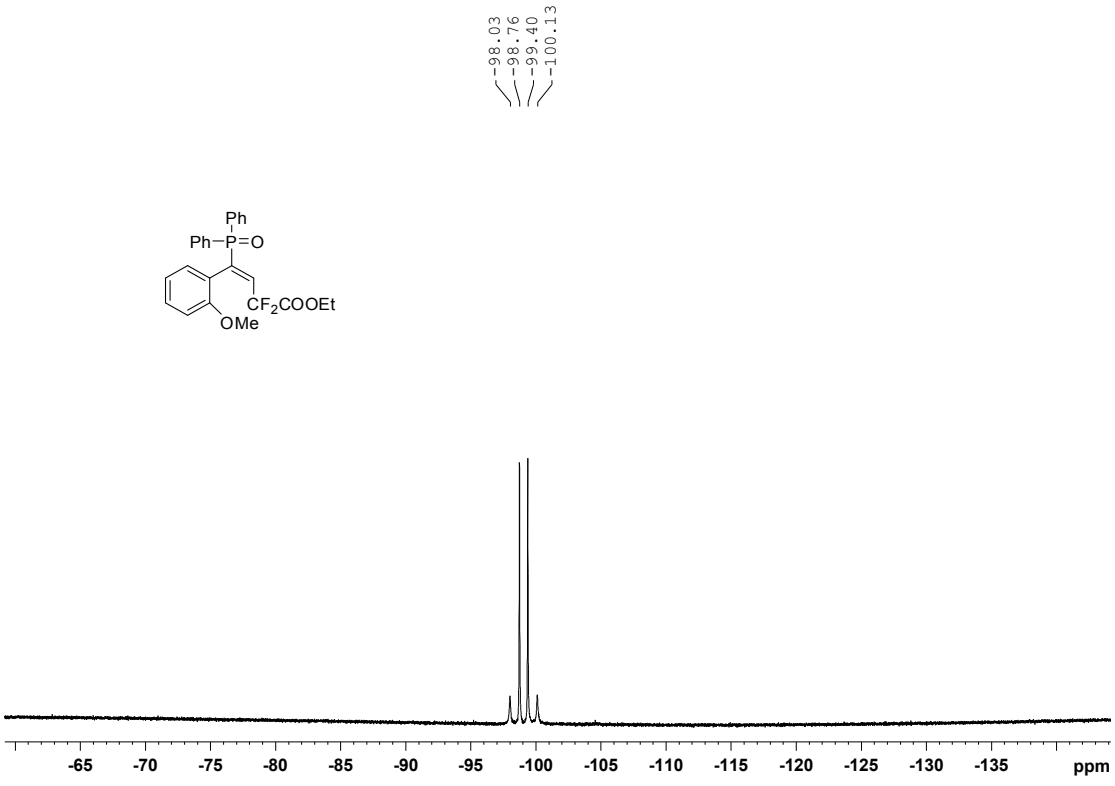

10
9
8
7
6
5
4
3
2
1
0
ppm
4.04
2.11
4.01
1.04
1.06
0.98
1.00
1.01
2.00
3.04
3.13


162.54
156.38
143.23
143.17
143.11
142.53
142.47
142.42
136.15
136.07
135.93
135.85
135.71
135.63
132.61
132.59
132.25
131.88
131.80
130.56
130.39
130.37
130.23
130.20
128.86
128.76
128.35
121.29
121.24
119.98
114.00
113.84
112.01
111.85
110.31
110.02
109.86
77.48
77.23
76.98
63.08
54.76
13.94

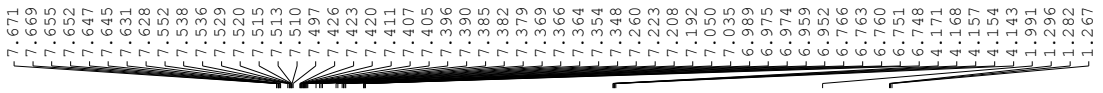

Ph
Ph—P=O
CF2COOEt
OMe

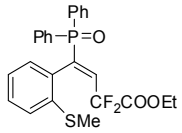

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

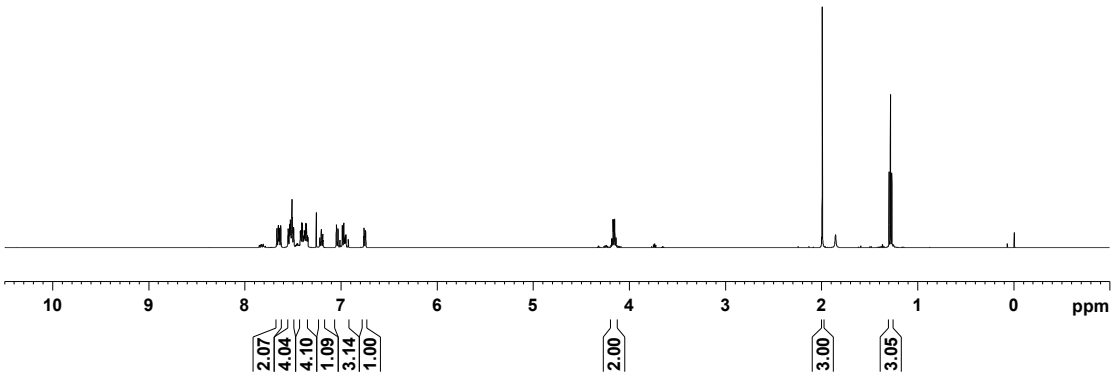

27.04
Ph
Ph—P=O
CF2COOEt
OMe
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

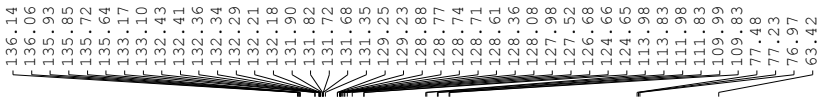

-98.03
-98.76
-99.40
-100.13
Ph
Ph—P=O
CF2COOEt
OMe
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 ppm

3m

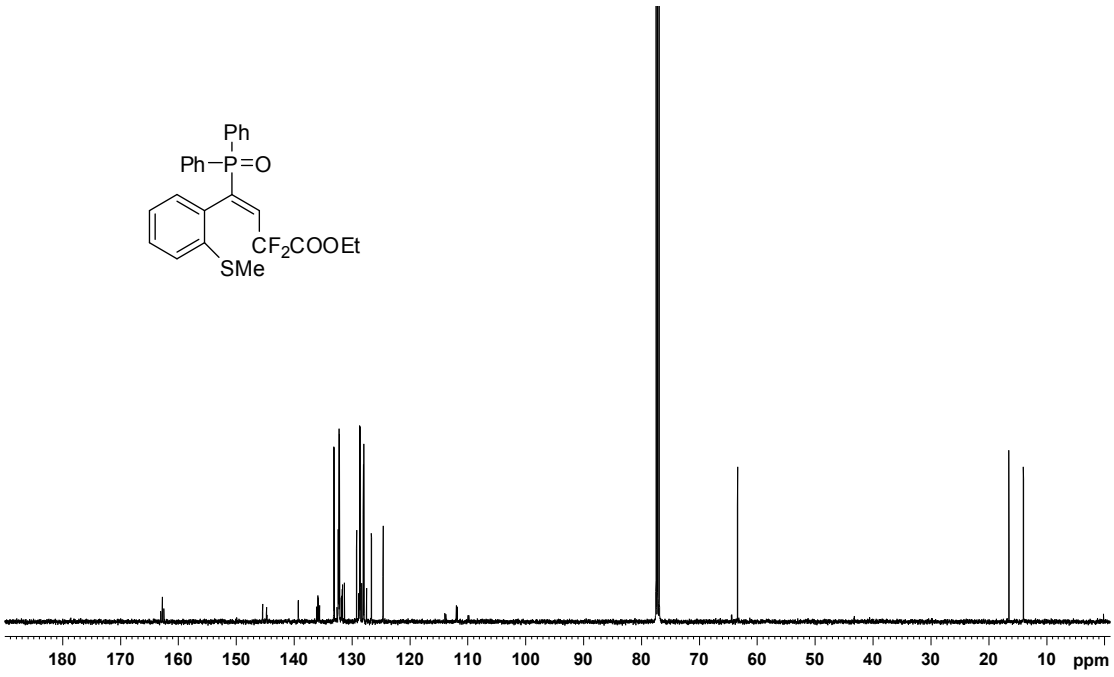

7.671
7.669
7.655
7.652
7.647
7.645
7.631
7.628
7.552
7.538
7.536
7.529
7.520
7.515
7.513
7.510
7.497
7.426
7.423
7.420
7.411
7.407
7.405
7.396
7.390
7.385
7.382
7.379
7.369
7.366
7.364
7.354
7.348
7.260
7.223
7.208
7.192
7.050
7.035
6.989
6.975
6.974
6.959
6.952
6.766
6.763
6.760
6.751
6.748
4.171
4.168
4.157
4.154
4.143
1.991
1.296
1.282
1.267

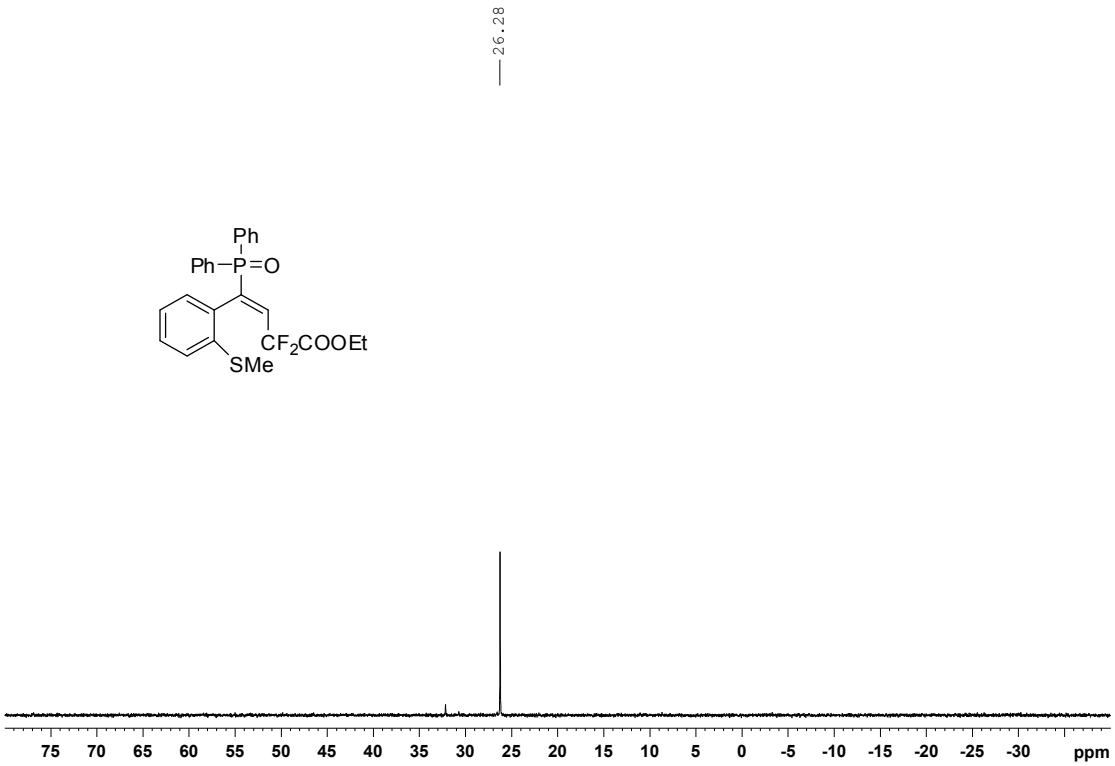

Ph
Ph—P=O
CF2COOEt
SMe

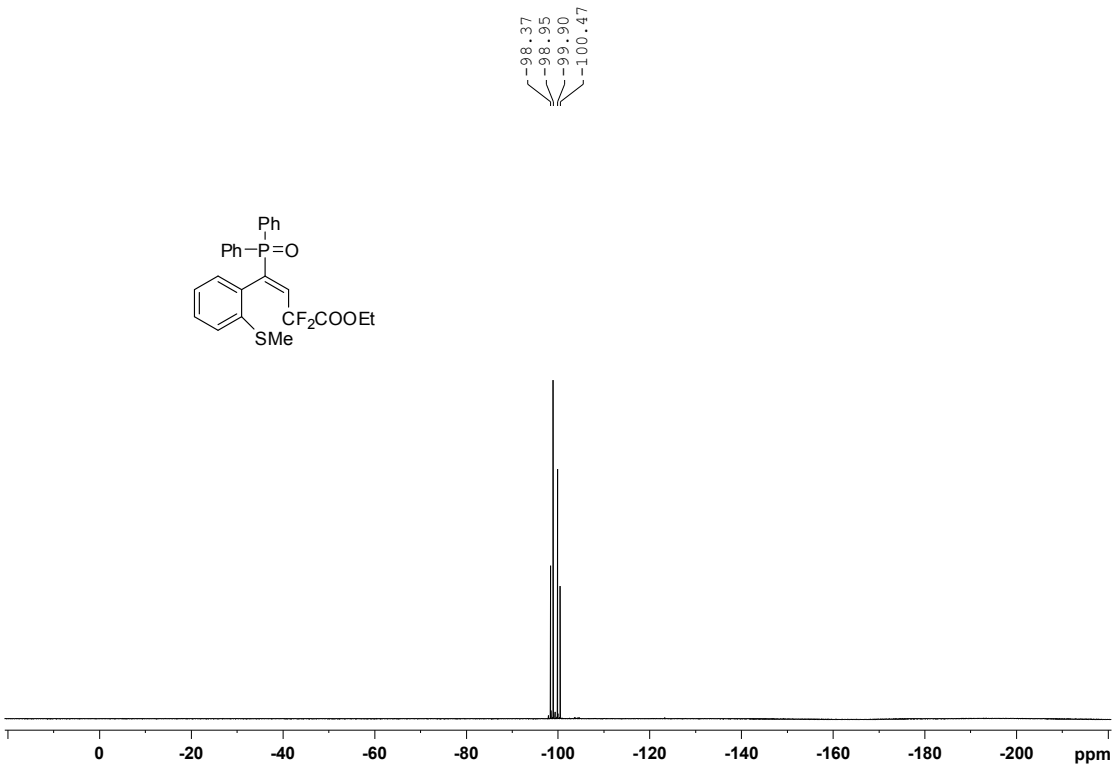

10
9
8
7
6
5
4
3
2
1
0
ppm
2.07
4.04
4.10
1.09
3.14
1.00
2.00
3.00
3.05


136.14
136.06
135.93
135.85
135.72
135.64
133.17
133.10
132.43
132.41
132.36
132.34
132.29
132.21
132.18
131.90
131.82
131.72
131.68
131.35
129.25
129.23
128.88
128.77
128.74
128.71
128.61
128.36
128.08
127.98
127.52
126.68
124.66
124.65
113.98
113.83
111.98
111.83
109.99
109.83
77.48
77.23
76.97
63.42
16.53
14.02

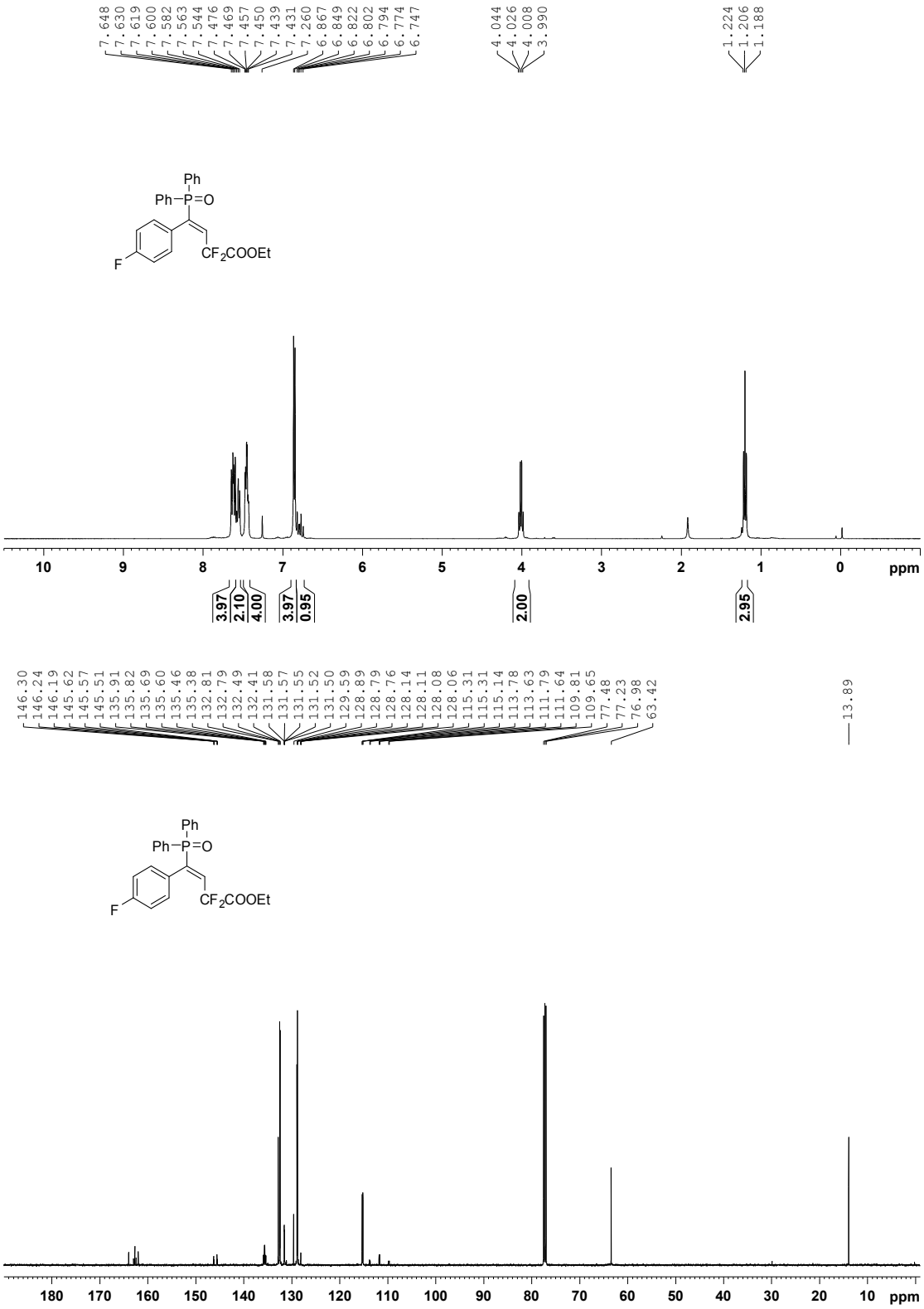
Ph
Ph—P=O
CF2COOEt
SMe

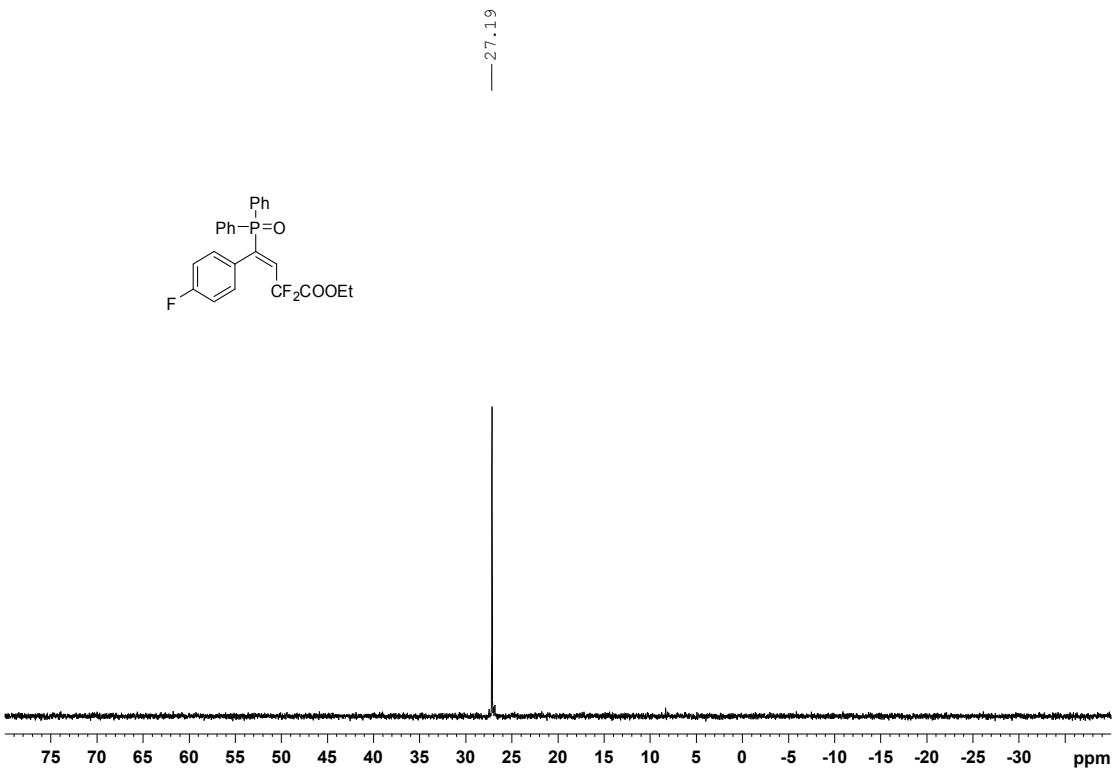

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

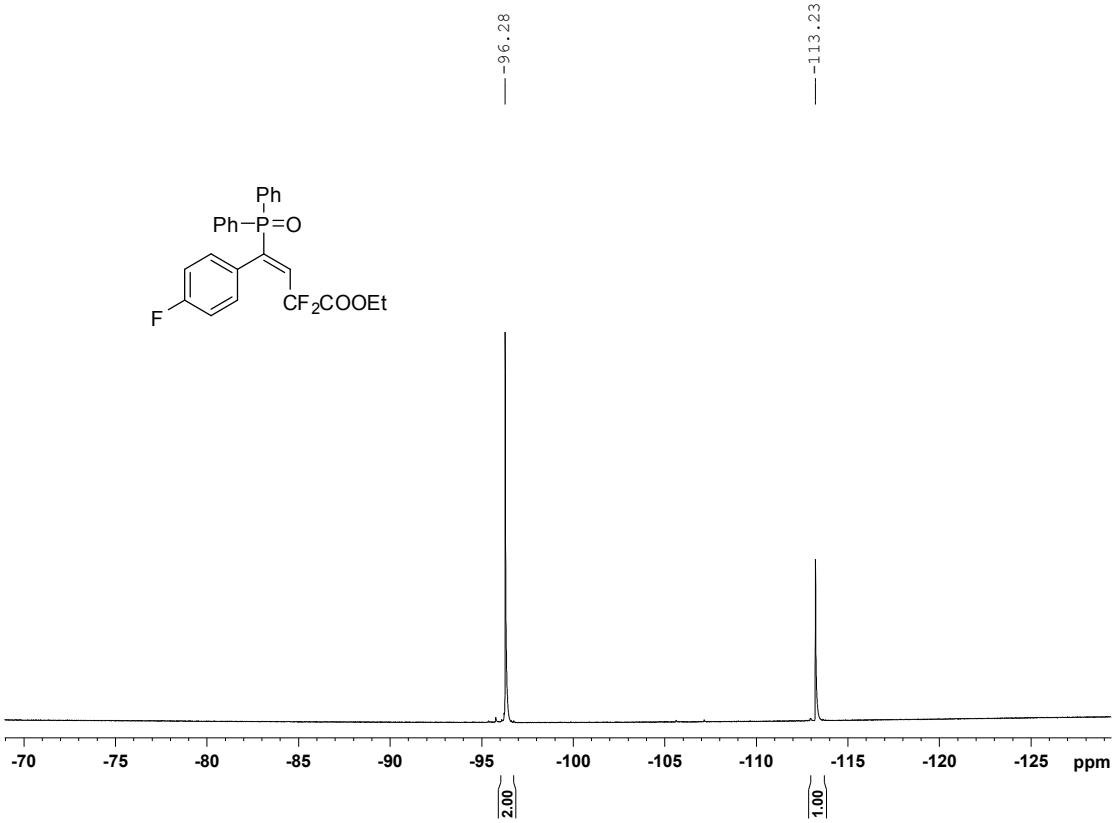

26.28
Ph
Ph—P=O
CF2COOEt
SMe
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-98.37
-98.95
-99.90
-100.47
Ph
Ph—P=O
CF2COOEt
SMe
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

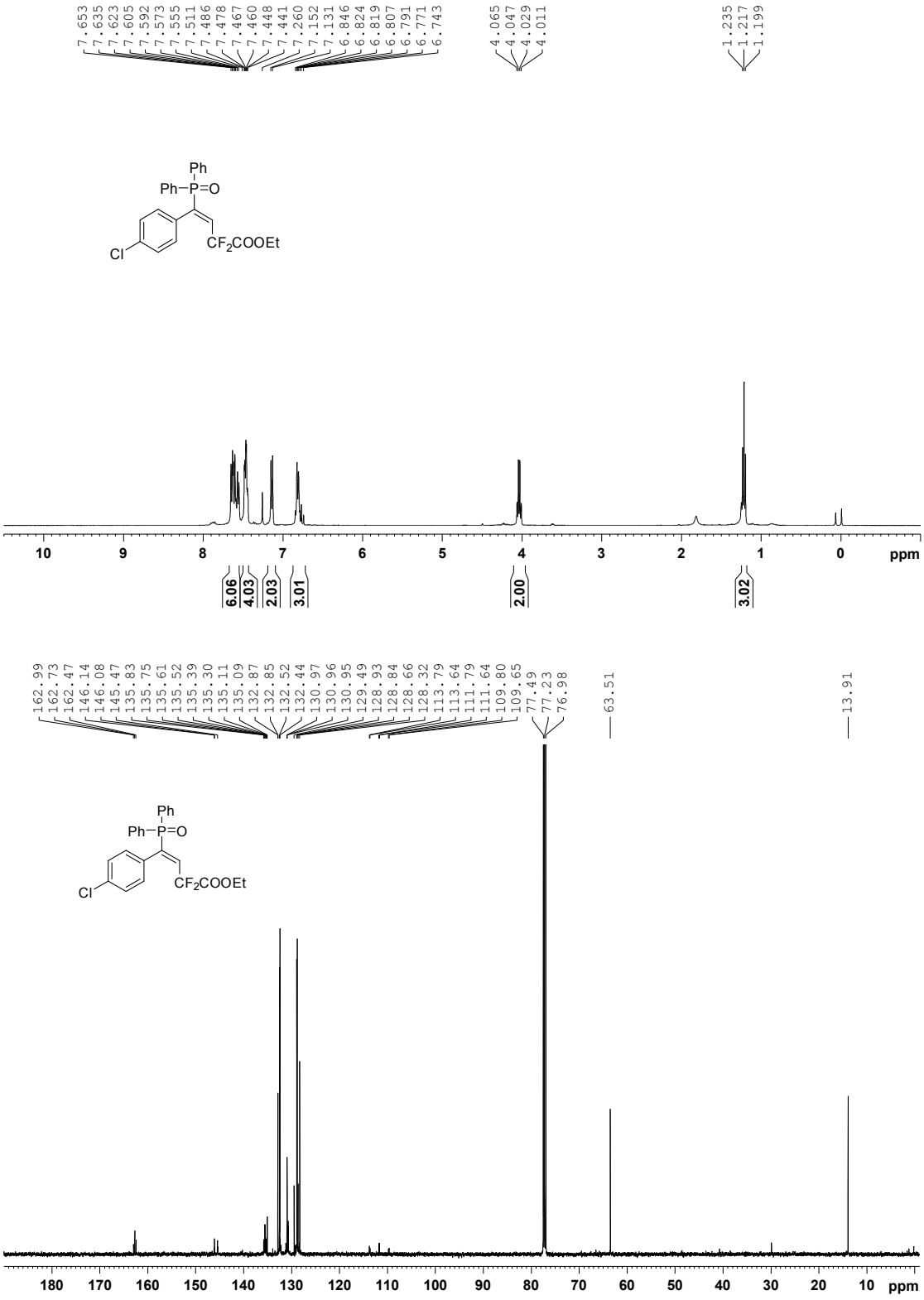
3n

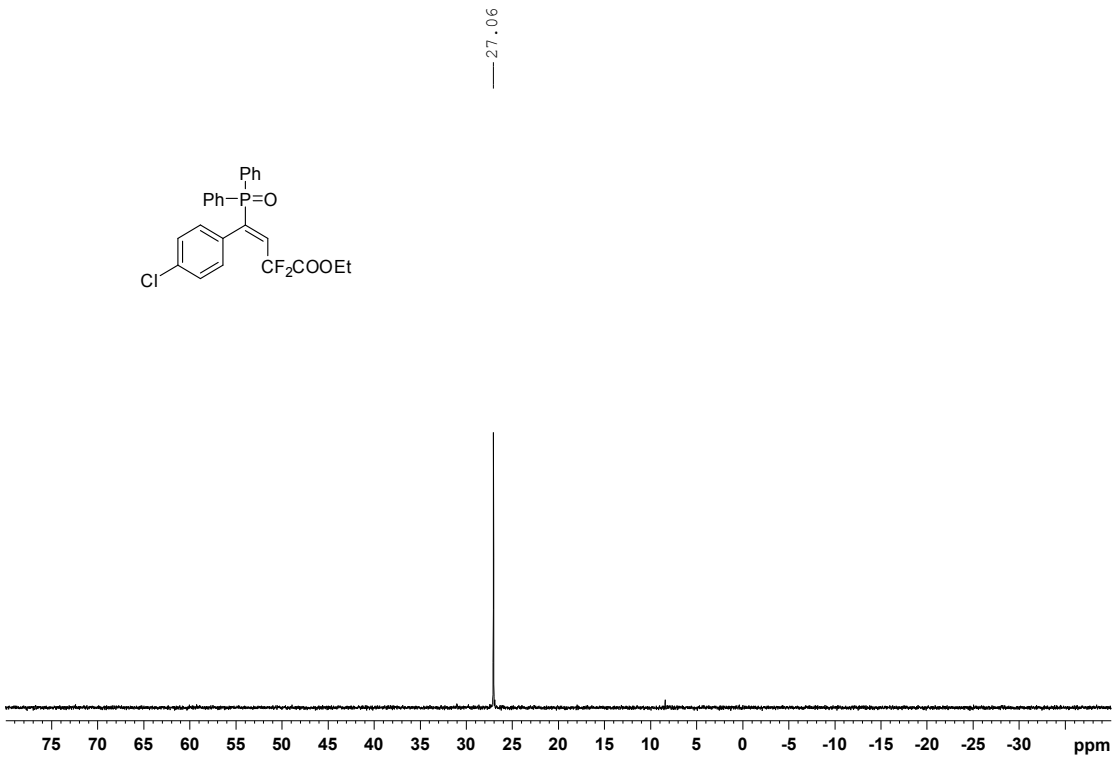

7.648
7.630
7.619
7.600
7.582
7.563
7.544
7.476
7.469
7.457
7.450
7.439
7.431
7.260
6.867
6.849
6.822
6.802
6.794
6.774
6.747
4.044
4.026
4.008
3.990
1.224
1.206
1.188
Ph
Ph—P=O
F
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
3.97
2.10
4.00
3.97
0.95
2.00
2.95
146.30
146.24
146.19
145.62
145.57
145.51
135.91
135.82
135.69
135.60
135.46
135.38
132.81
132.79
132.49
132.41
131.58
131.57
131.55
131.52
131.50
129.59
128.89
128.79
128.76
128.14
128.11
128.08
128.06
115.31
115.31
115.14
113.78
113.63
111.79
111.64
109.81
109.65
77.48
77.23
76.98
63.42
13.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

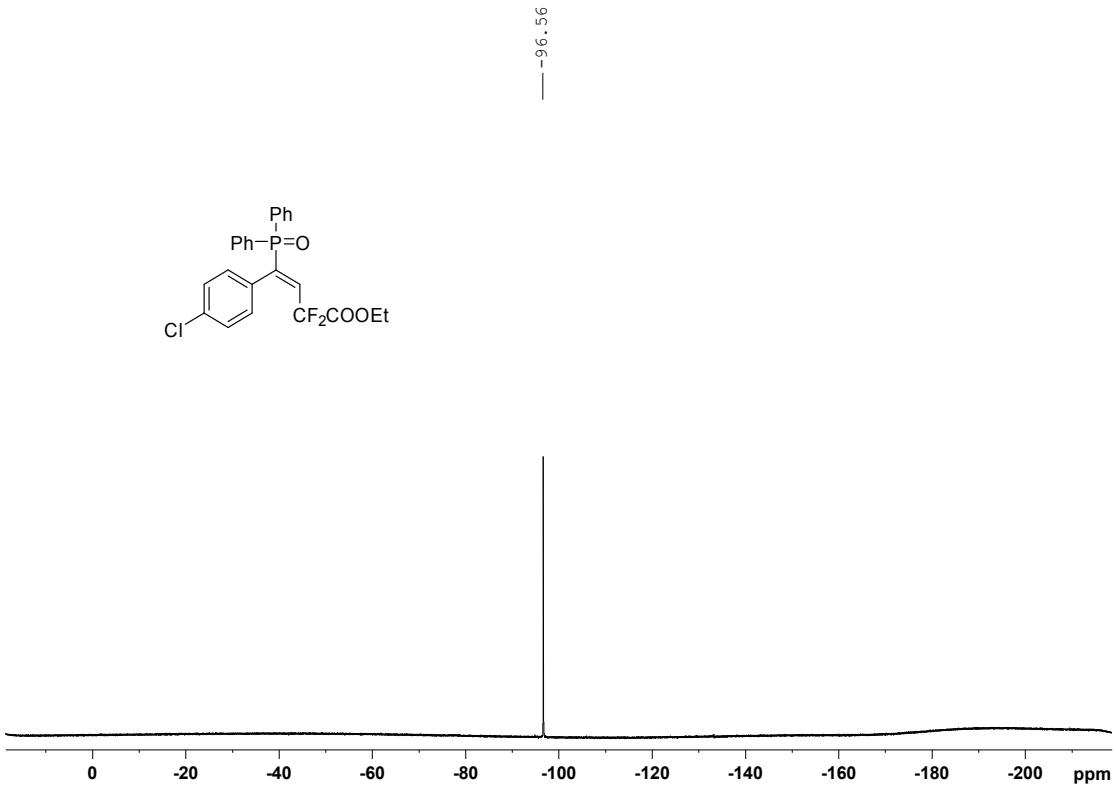

27.19
Ph
Ph—P=O
F
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-96.28
-113.23
Ph
Ph—P=O
F
CF2COOEt
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 ppm
2.00
1.00

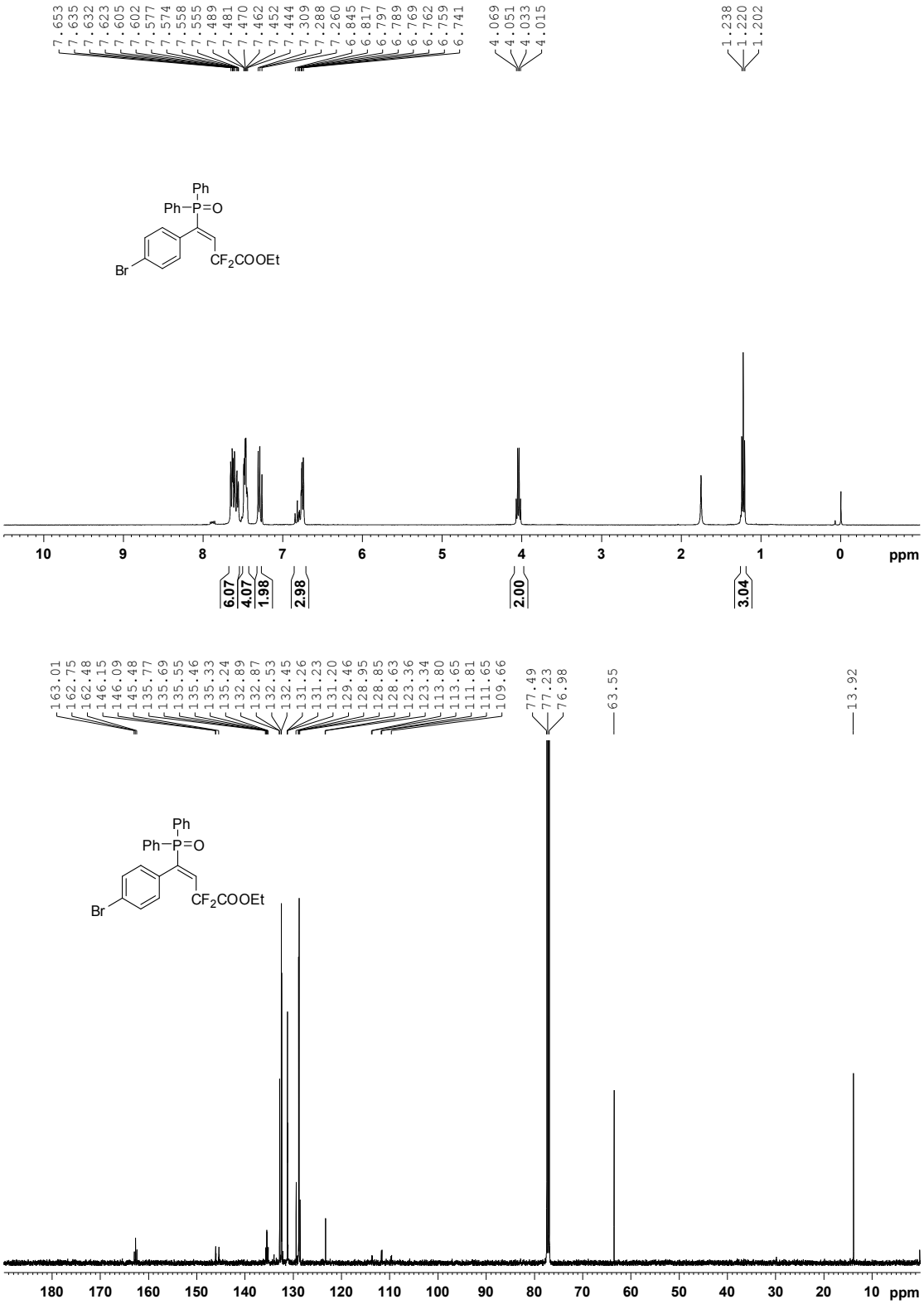
3o

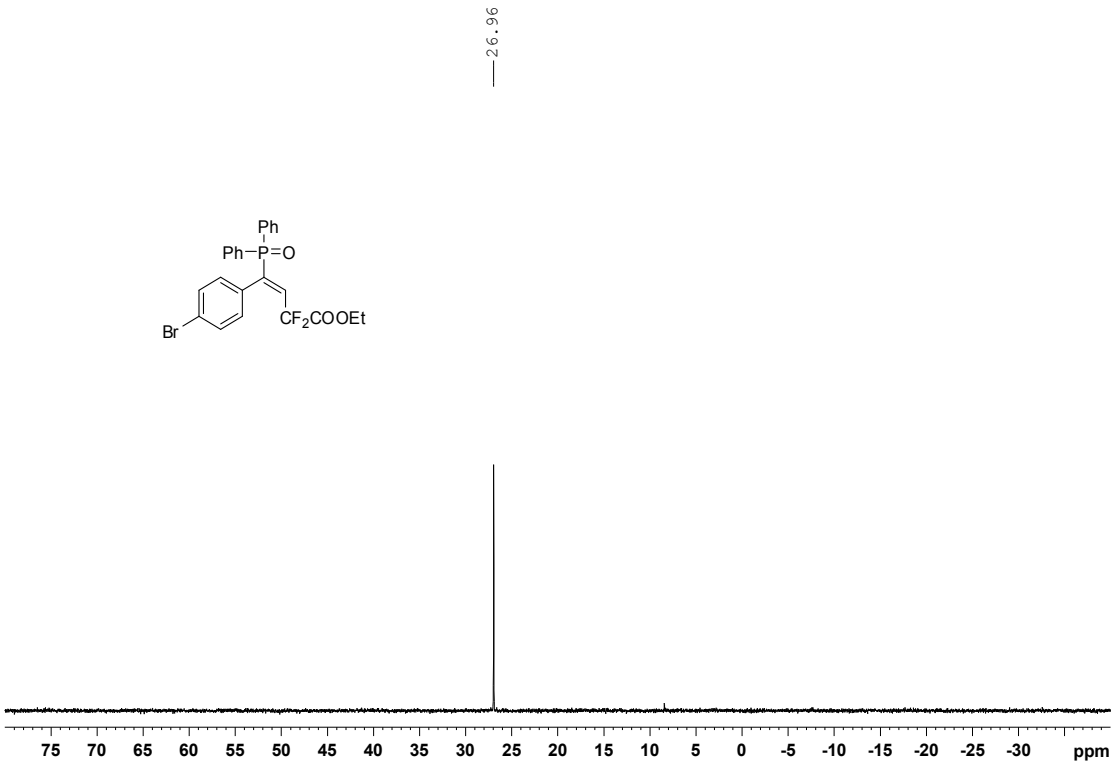

7.653
7.635
7.623
7.605
7.592
7.573
7.555
7.511
7.486
7.478
7.467
7.460
7.448
7.441
7.260
7.152
7.131
6.846
6.824
6.819
6.807
6.791
6.771
6.743
4.065
4.047
4.029
4.011
1.235
1.217
1.199
Ph
Ph–P=O
Cl
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
6.06
4.03
2.03
3.01
2.00
3.02
162.99
162.73
162.47
146.14
146.08
145.47
135.83
135.75
135.61
135.52
135.39
135.30
135.11
135.09
132.87
132.85
132.52
132.44
130.97
130.96
130.95
129.49
128.93
128.84
128.66
128.32
113.79
113.64
111.79
111.64
109.80
109.65
77.49
77.23
76.98
63.51
13.91
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

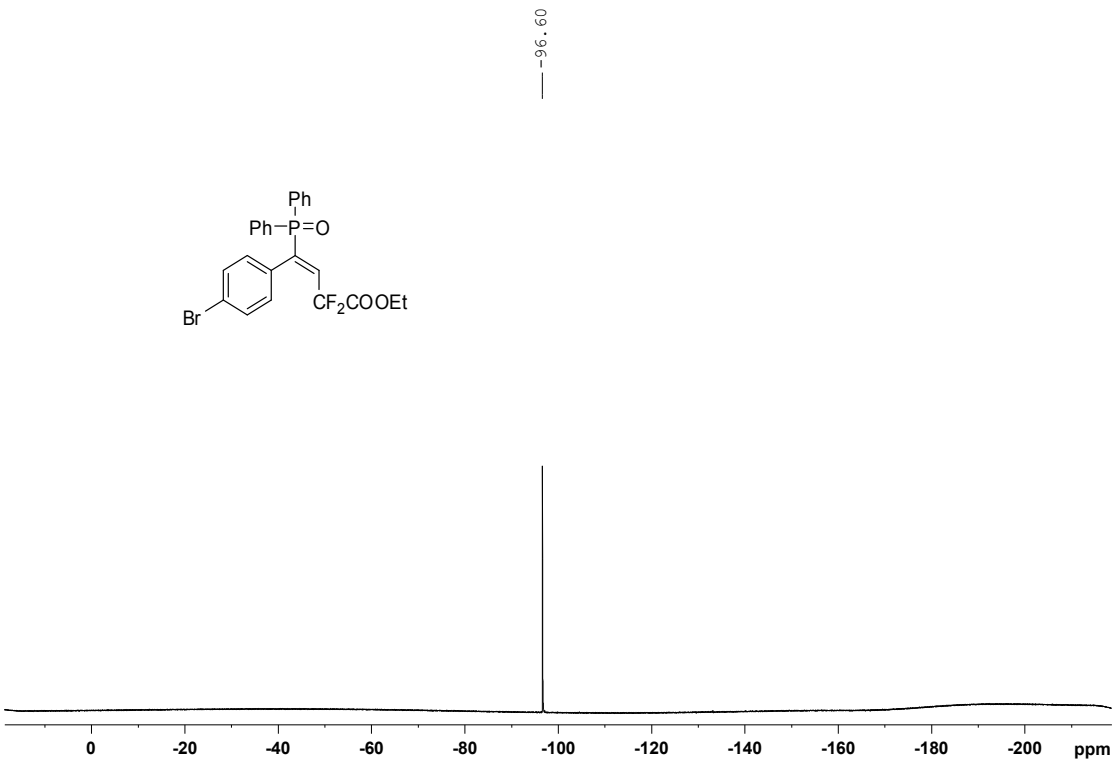

27.06
Ph
Ph—P=O
Cl
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-96.56
Ph
Ph—P=O
Cl
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

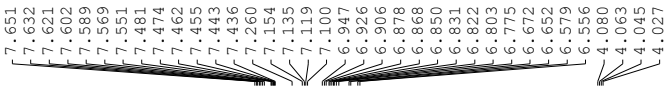
3p


7.653
7.635
7.632
7.623
7.605
7.602
7.577
7.574
7.558
7.555
7.489
7.481
7.470
7.462
7.452
7.444
7.309
7.288
7.260
6.845
6.817
6.797
6.789
6.769
6.762
6.759
6.741
4.069
4.051
4.033
4.015
1.238
1.220
1.202
Ph
Ph—P=O
Br
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
6.07
4.07
1.98
2.98
2.00
3.04
163.01
162.75
162.48
146.15
146.09
145.48
135.77
135.69
135.55
135.46
135.33
135.24
132.89
132.87
132.53
132.45
131.26
131.23
131.20
129.46
128.95
128.85
128.63
123.36
123.34
113.80
113.65
111.81
111.65
109.66
77.49
77.23
76.98
63.55
13.92
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

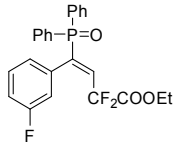

26.96
Ph
Ph–P=O
Br
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

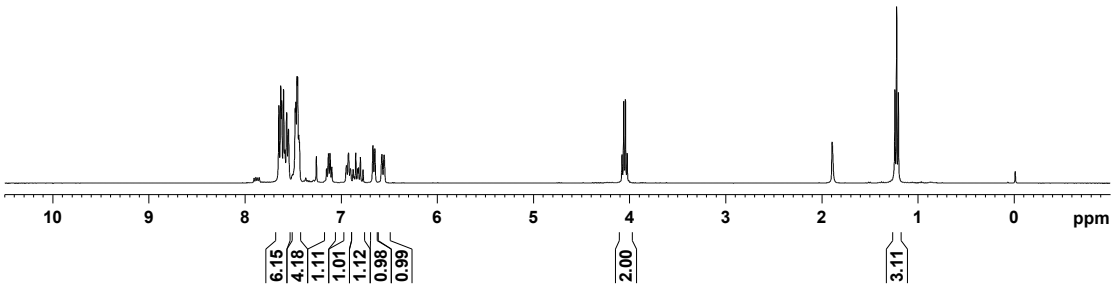

-96.60
Ph
Ph–P=O
Br
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3q


7.651
7.632
7.621
7.602
7.589
7.569
7.551
7.481
7.474
7.462
7.455
7.443
7.436
7.260
7.154
7.135
7.119
7.100
6.947
6.926
6.906
6.878
6.868
6.850
6.831
6.822
6.803
6.775
6.672
6.652
6.579
6.556
4.080
4.063
4.045
4.027


1.241
1.223
1.205


Ph
Ph–P=O
CF2COOEt
F


10
9
8
7
6
5
4
3
2
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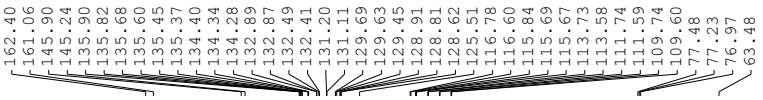
ppm
6.15
4.18
1.11
1.01
1.12
0.98
0.99
2.00
3.11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161.06
145.90
145.24
135.90
135.82
135.68
135.60
135.45
135.37
134.40
134.34
134.28
132.89
132.87
132.49
132.41
131.20
131.11
129.69
129.63
129.45
128.91
128.81
128.62
125.51
116.78
116.60
115.84
115.69
115.67
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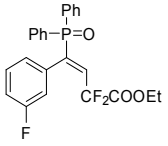
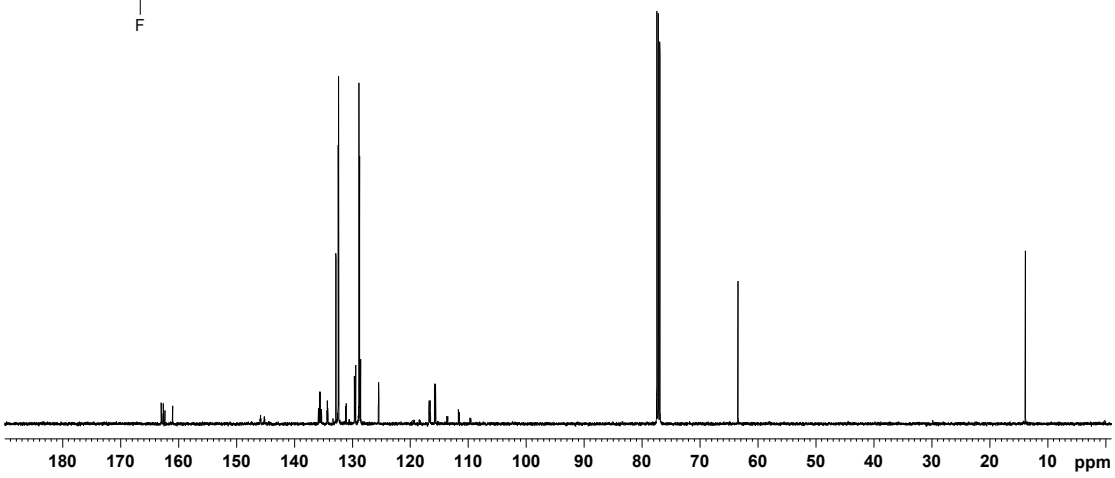
113.58
111.74
111.59
109.74
109.60
77.48
77.23
76.97
63.48

13.88


Ph
Ph–P=O
CF2COOEt
F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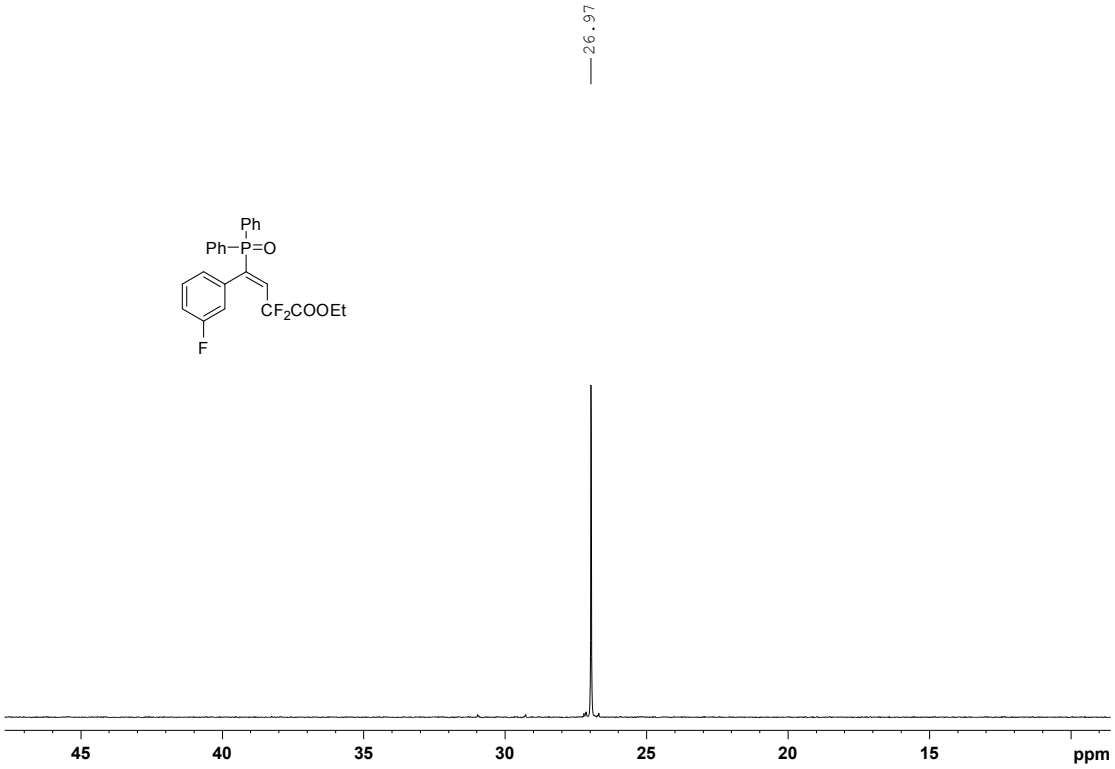
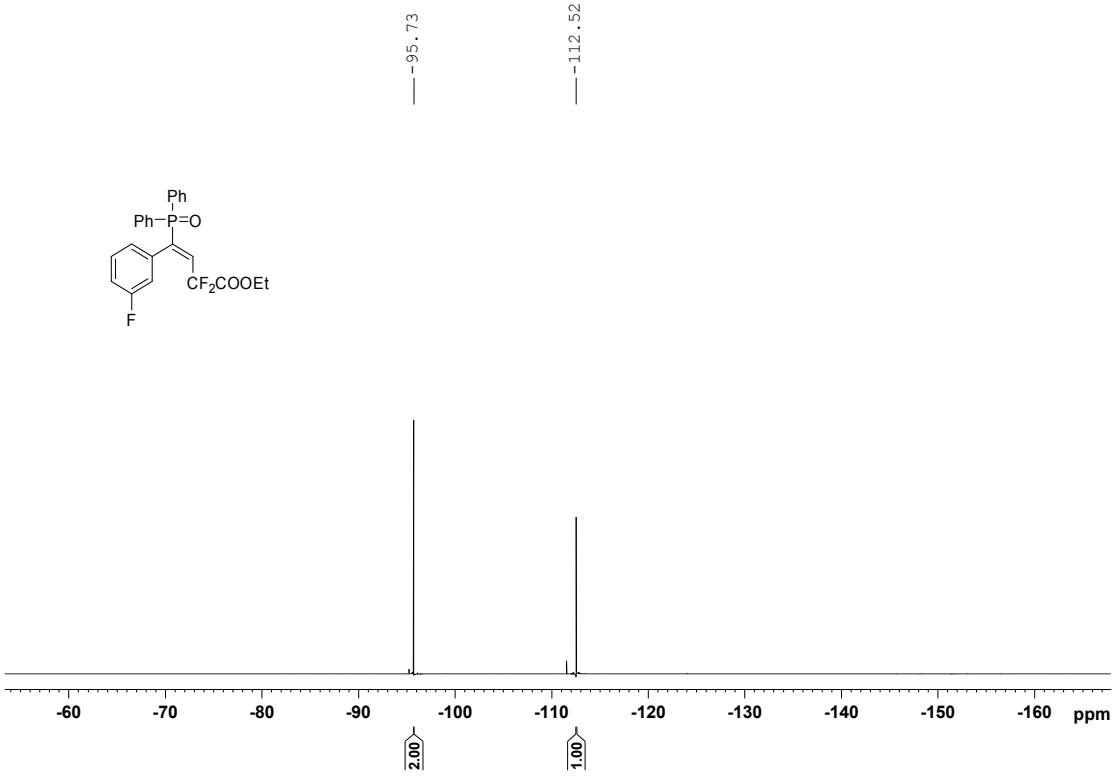
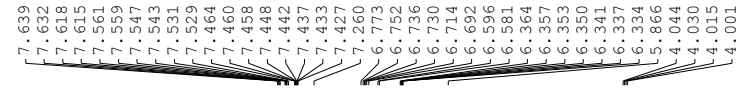
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.97
Ph
Ph—P=O
CF2COOEt
F
45
40
35
30
25
20
15
ppm


-95.73
-112.52
Ph
Ph—P=O
CF2COOEt
F
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
ppm
2.00
1.00

3r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7.632
7.618
7.615
7.561
7.559
7.547
7.543
7.531
7.529
7.464
7.460
7.458
7.448
7.442
7.437
7.433
7.427
7.260
6.773
6.752
6.736
6.730
6.714
6.692
6.596
6.581
6.364
6.357
6.353
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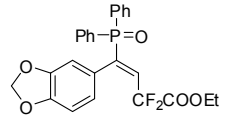
6.337
6.334
5.866
4.044
4.030
4.015
4.001
1.221
1.207
1.192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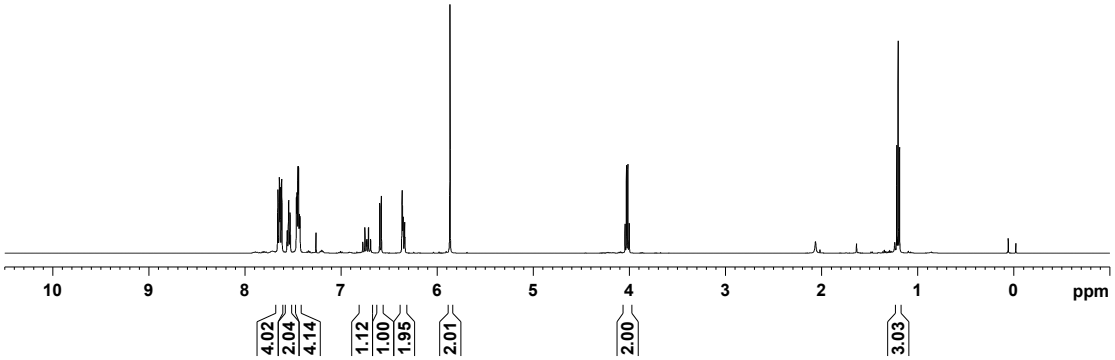
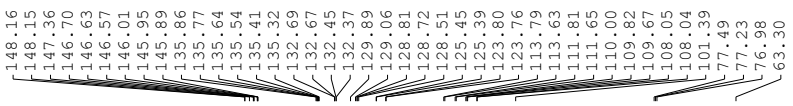
O
O
CF2COOEt


10
9
8
7
6
5
4
3
2
1
0
ppm
4.02
2.04
4.14
1.12
1.00
1.95
2.01
2.00
3.03


148.16
148.15
147.36
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146.63
146.57
146.01
145.95
145.89
135.86
135.77
135.64
135.54
135.41
135.32
132.69
132.67
132.45
132.37
129.89
129.06
128.81
128.72
128.51
125.45
125.39
123.80
123.76
113.79
113.63
111.81
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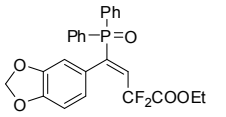
101.39
77.49
77.23
76.98
63.30
13.86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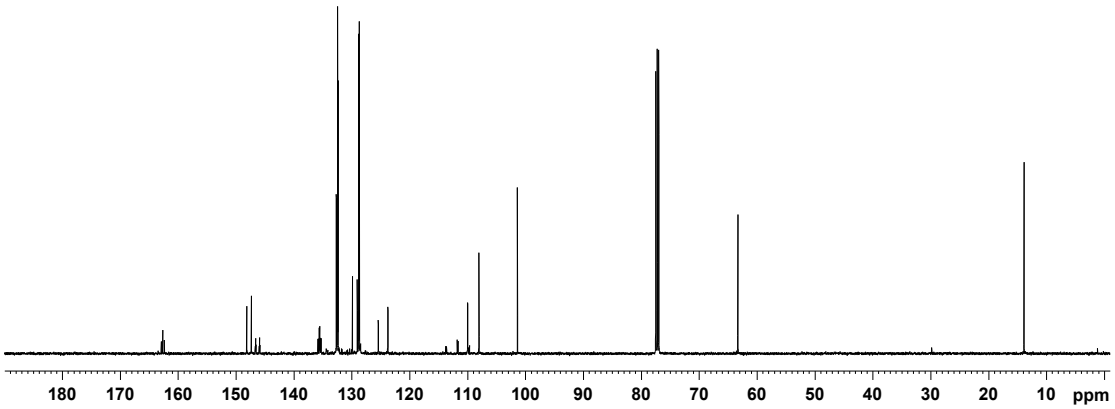
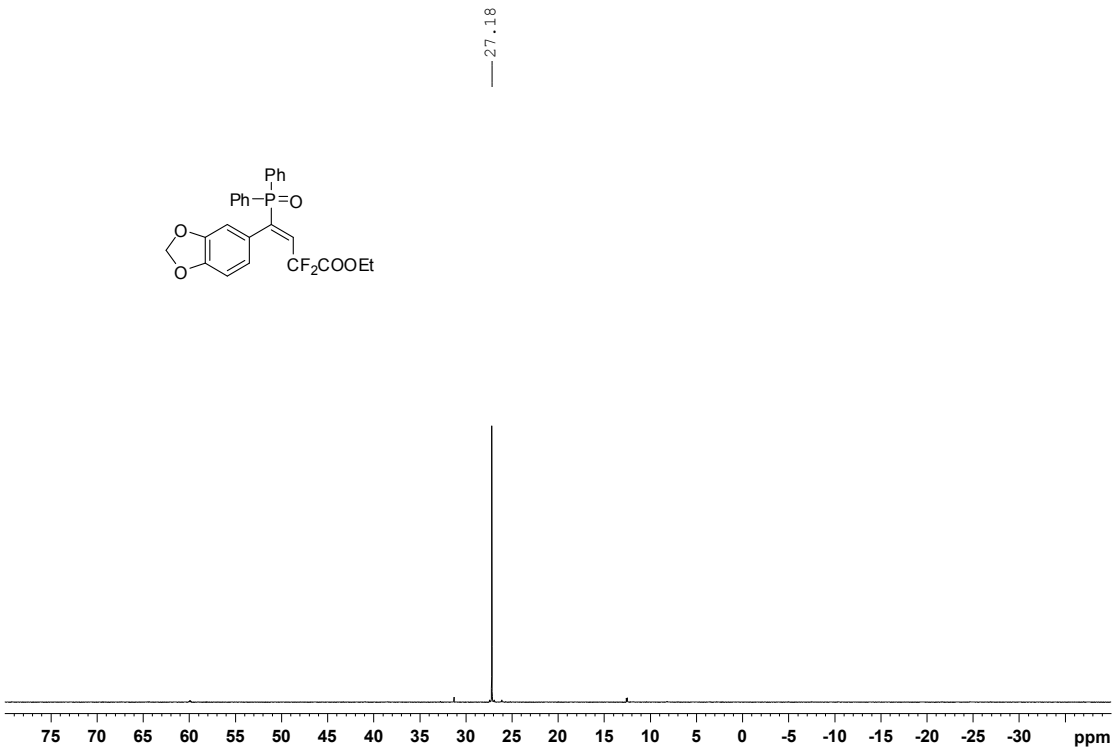
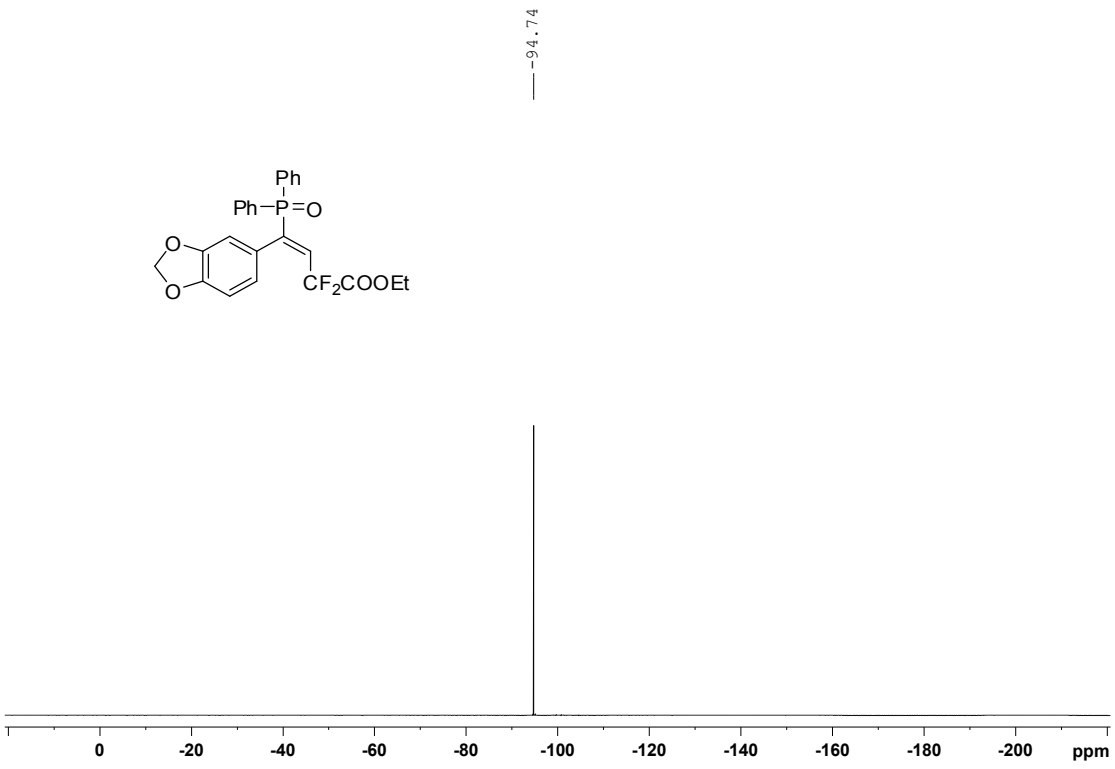
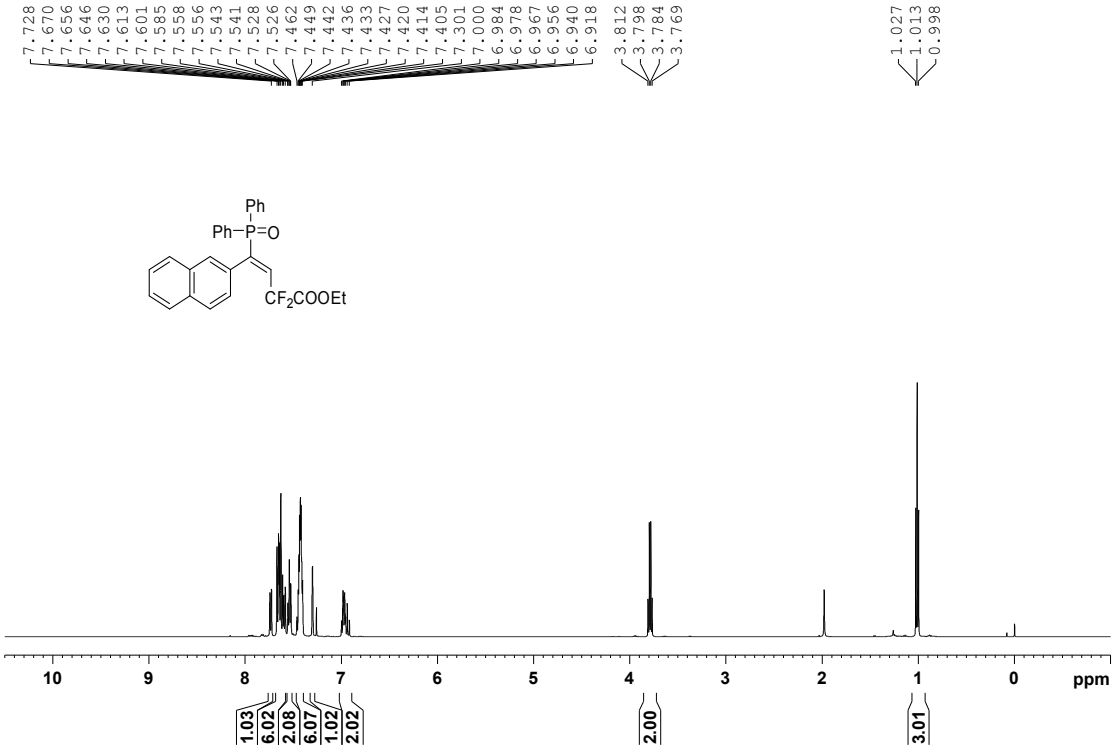
Ph—P=O
O
O
CF2COOEt


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


27.18
Ph
Ph—P=O
O
O
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.74
Ph
Ph—P=O
O
O
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3s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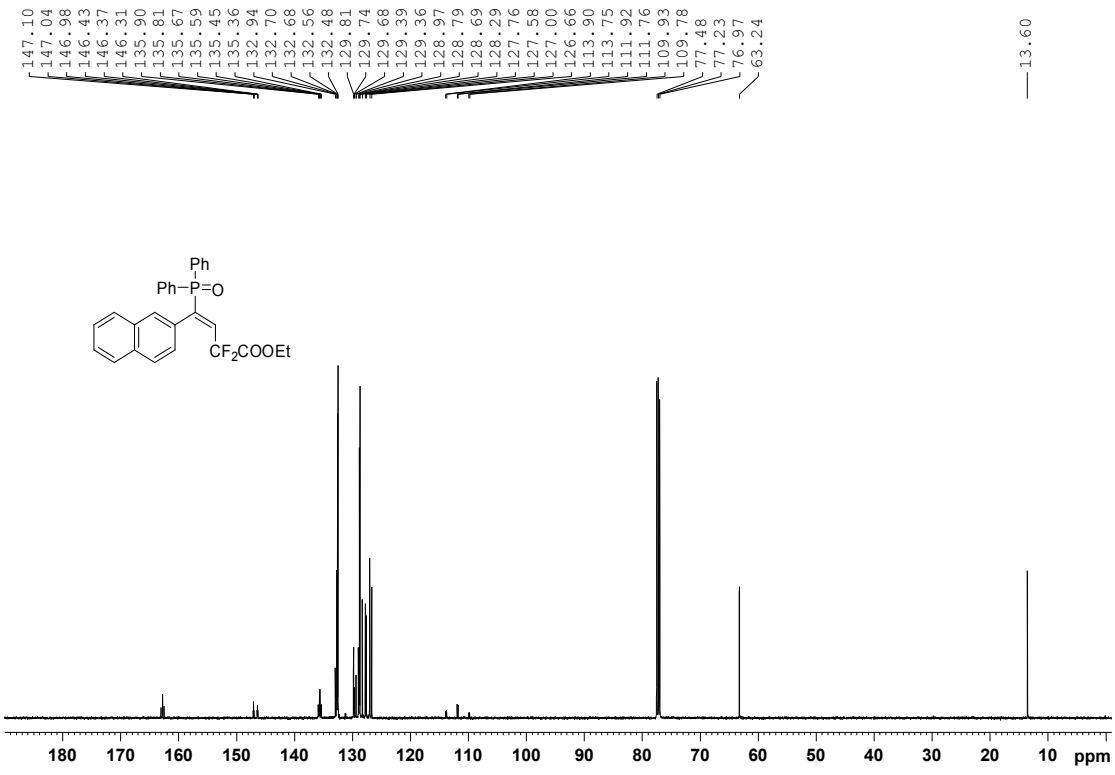
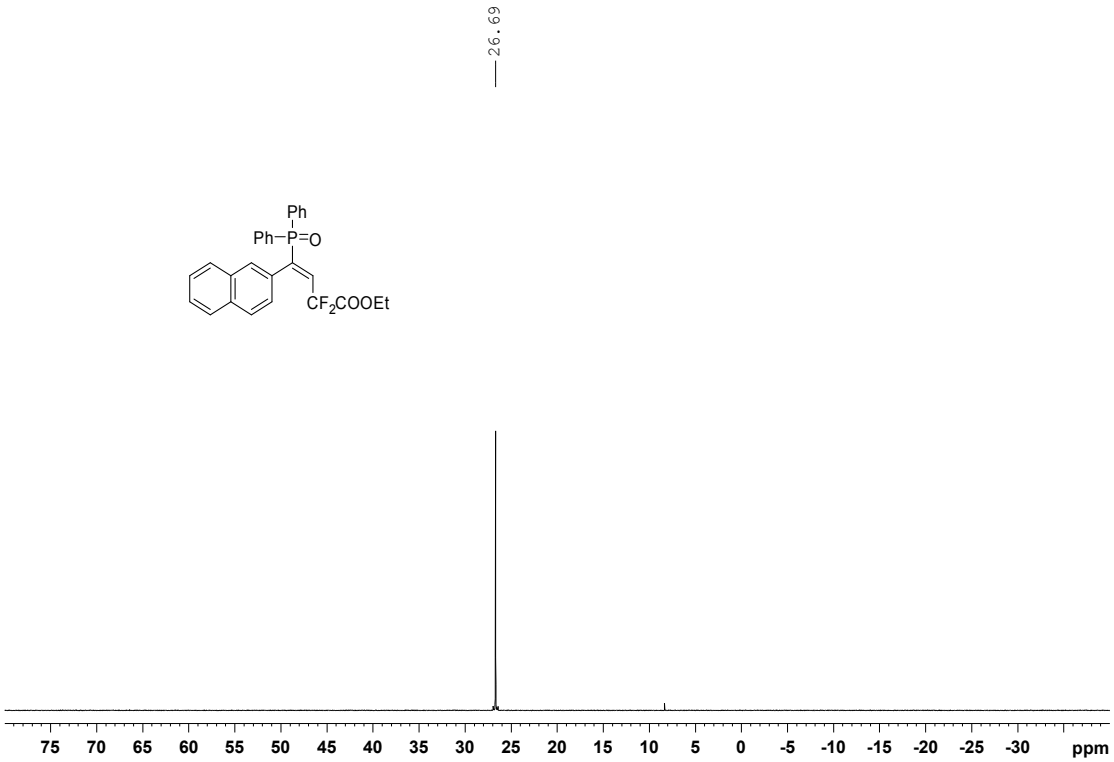
7.630
7.613
7.601
7.585
7.558
7.556
7.543
7.541
7.528
7.526
7.462
7.449
7.442
7.436
7.433
7.427
7.420
7.414
7.405
7.301
7.000
6.984
6.978
6.967
6.956
6.940
6.918
3.812
3.798
3.784
3.769
1.027
1.013
0.998
Ph
Ph–P=O
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
1.03
6.02
2.08
6.07
1.02
2.02
2.00
3.01


147.10
147.04
146.98
146.43
146.37
146.31
135.90
135.81
135.67
135.59
135.45
135.36
132.94
132.70
132.68
132.56
132.48
129.81
129.74
129.68
129.39
129.36
128.97
128.79
128.69
128.29
127.76
127.58
127.00
126.66
113.90
113.75
111.92
111.76
109.93
109.78
77.48
77.23
76.97
63.24
13.60
Ph
Ph–P=O
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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Ph
Ph–P=O
CF2COOEt
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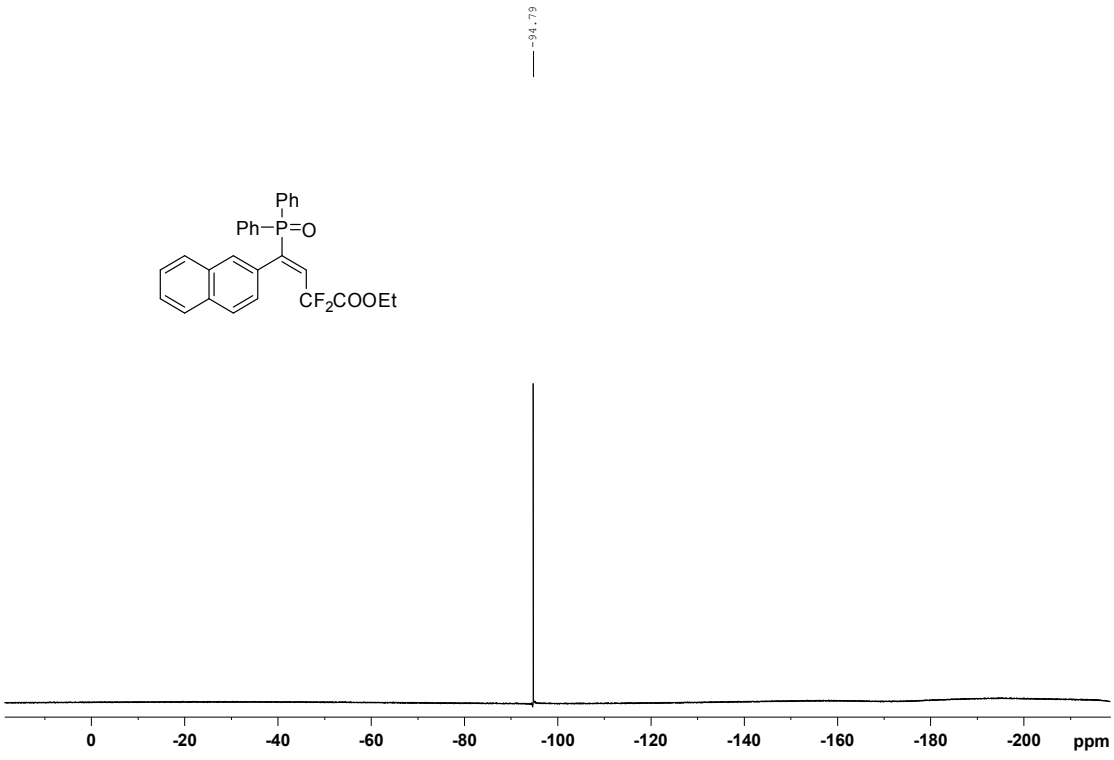
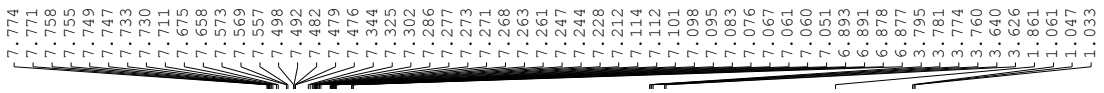

-94.79
Ph
Ph–P=O
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3t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7.771
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7.755
7.749
7.747
7.733
7.730
7.711
7.675
7.658
7.573
7.569
7.557
7.498
7.492
7.482
7.479
7.476
7.344
7.325
7.302
7.286
7.277
7.273
7.271
7.268
7.263
7.261
7.247
7.244
7.228
7.212
7.114
7.112
7.101
7.098
7.095
7.083
7.076
7.067
7.061
7.060
7.051
6.893
6.891
6.878
6.877
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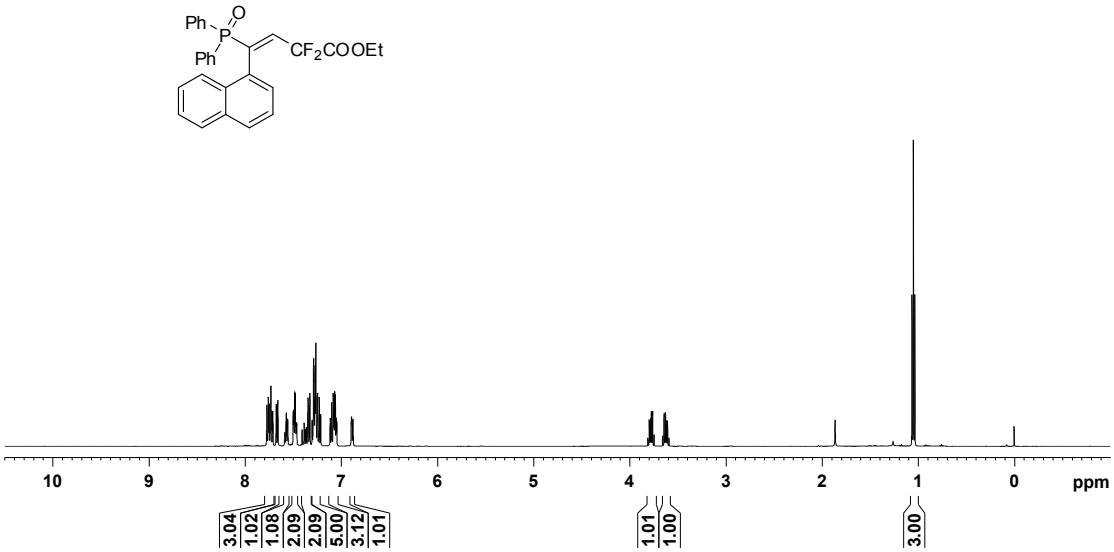
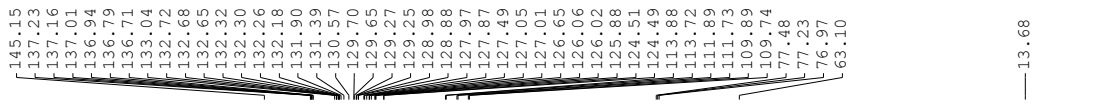
3.781
3.774
3.760
3.640
3.626
1.861
1.061
1.047
1.033


Ph
P
O
Ph
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
3.04
1.02
1.08
2.09
2.09
5.00
3.12
1.01
1.01
1.00
3.00


145.15
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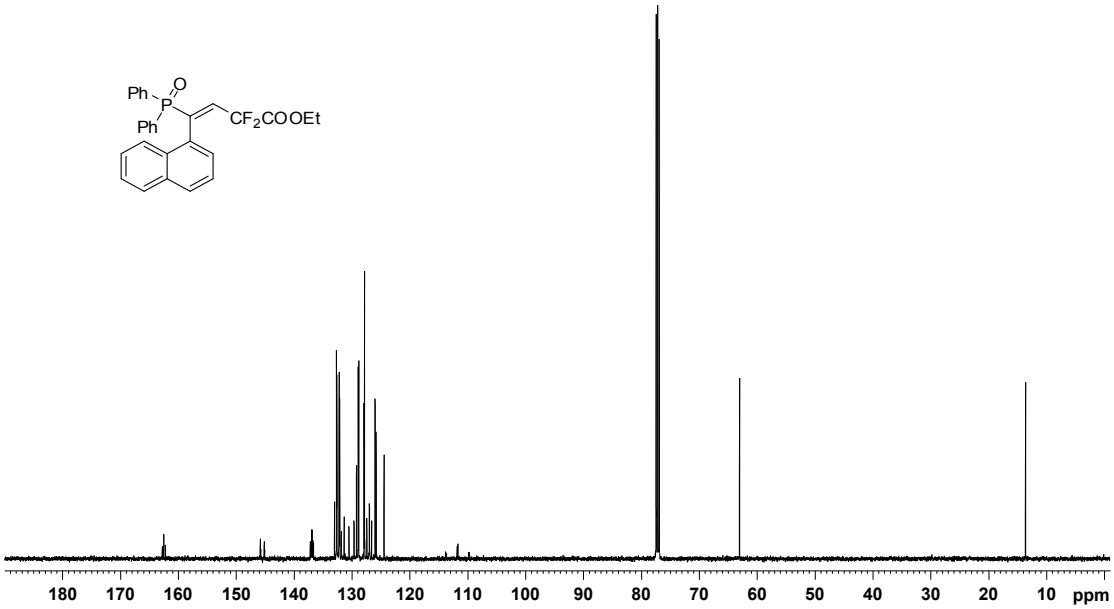
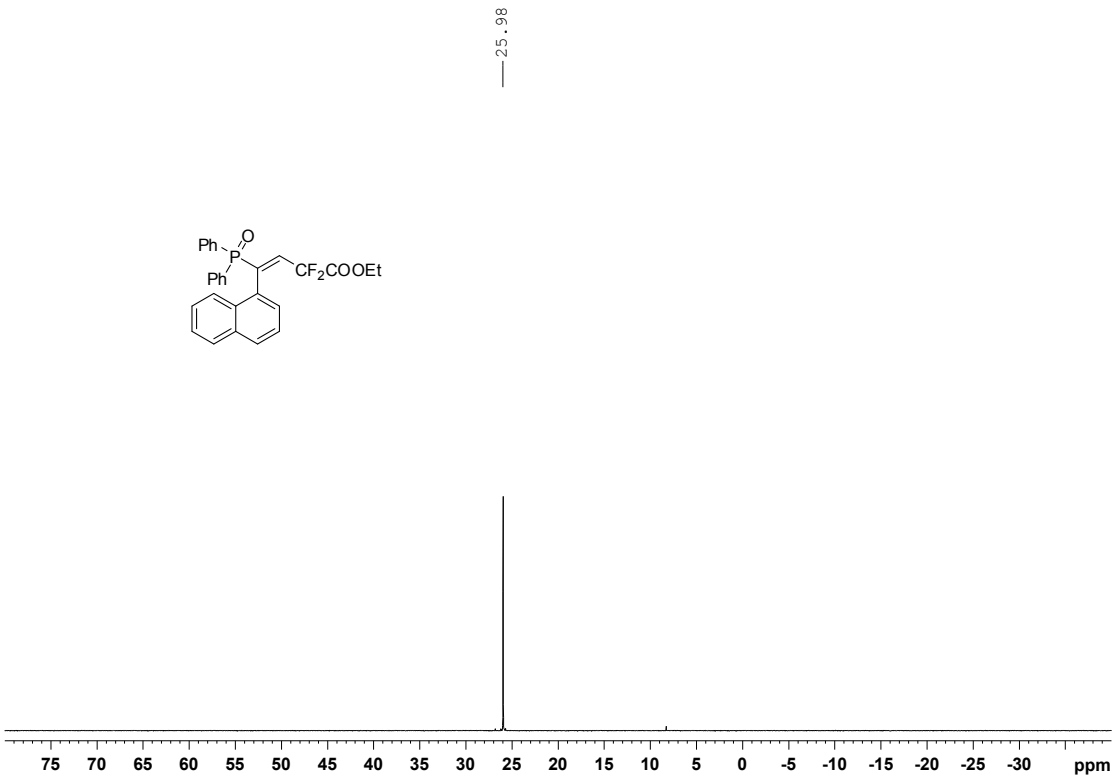
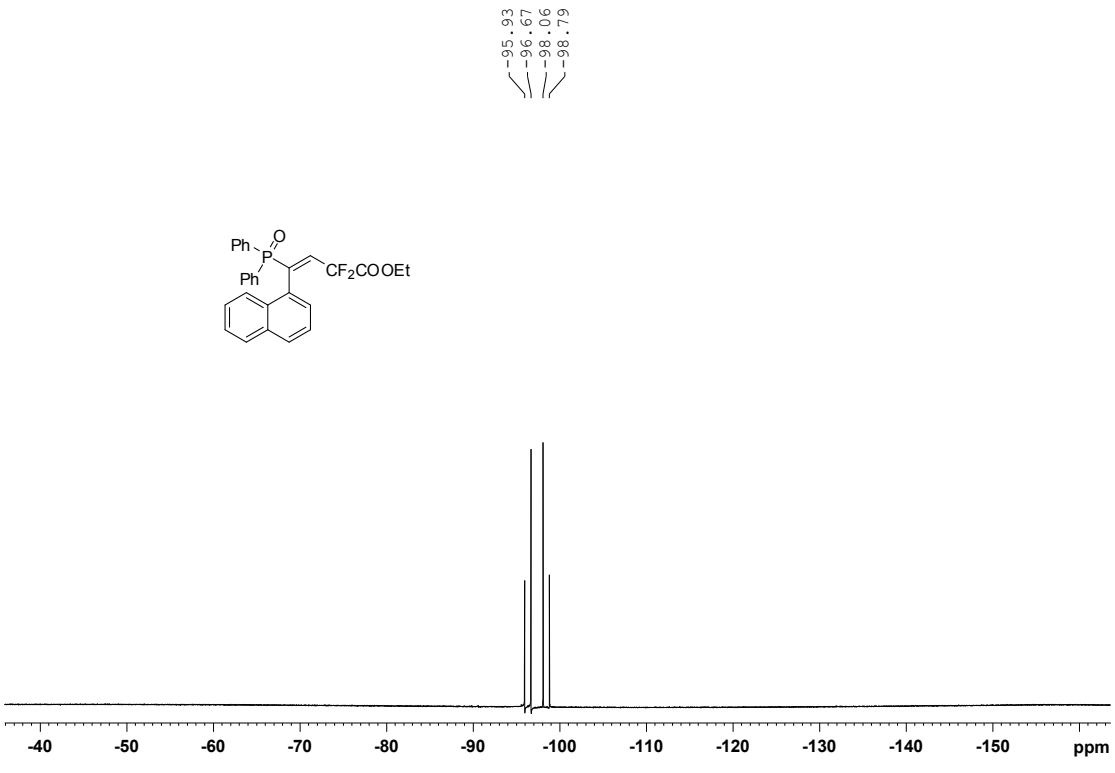
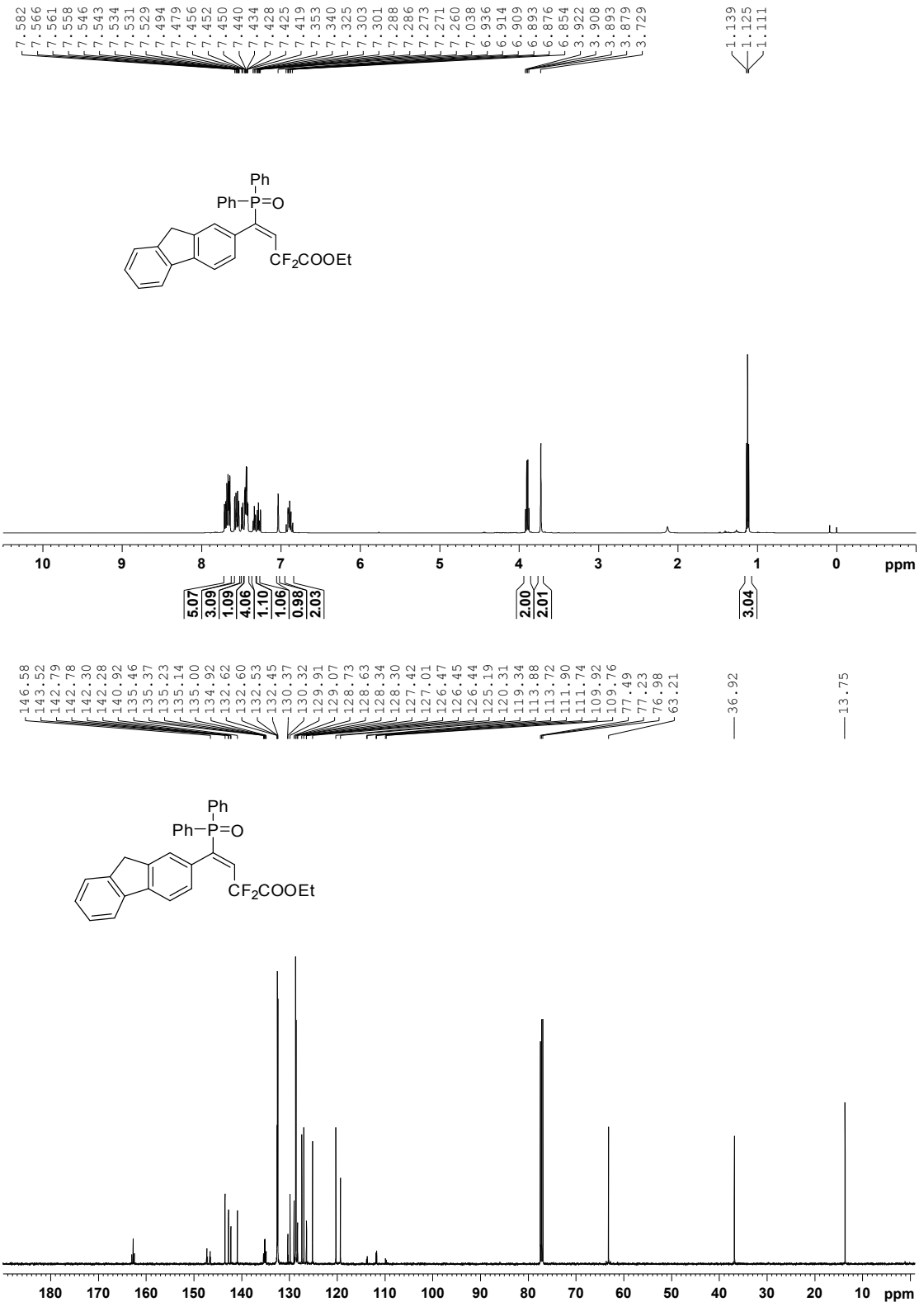
137.16
137.01
136.94
136.79
136.71
133.04
132.72
132.68
132.65
132.32
132.30
132.26
132.18
131.90
131.39
130.57
129.70
129.65
129.27
129.25
128.98
128.88
127.97
127.87
127.49
127.05
127.01
126.65
126.06
126.02
125.88
124.51
124.49
113.88
113.72
111.89
111.73
109.89
109.74
77.48
77.23
76.97
63.10
13.68


Ph
P
O
Ph
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


25.98
Ph
O
P
Ph
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-95.93
-96.67
-98.06
-98.79
Ph
O
P
Ph
CF2COOEt
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 ppm

3u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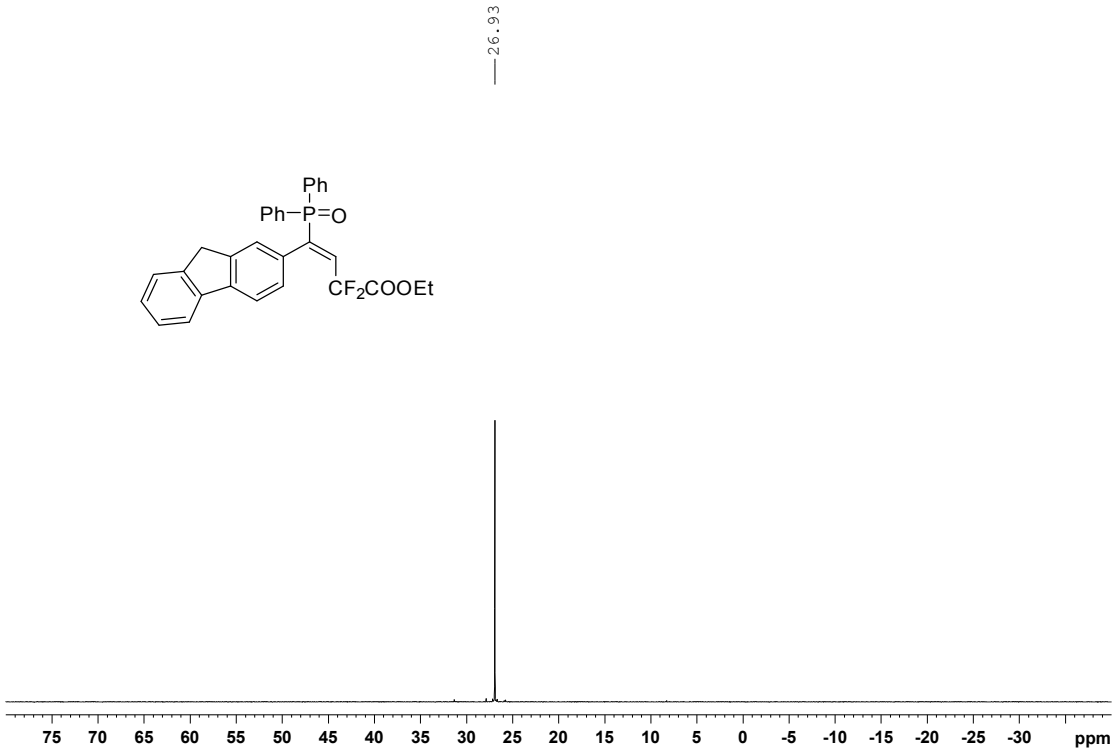
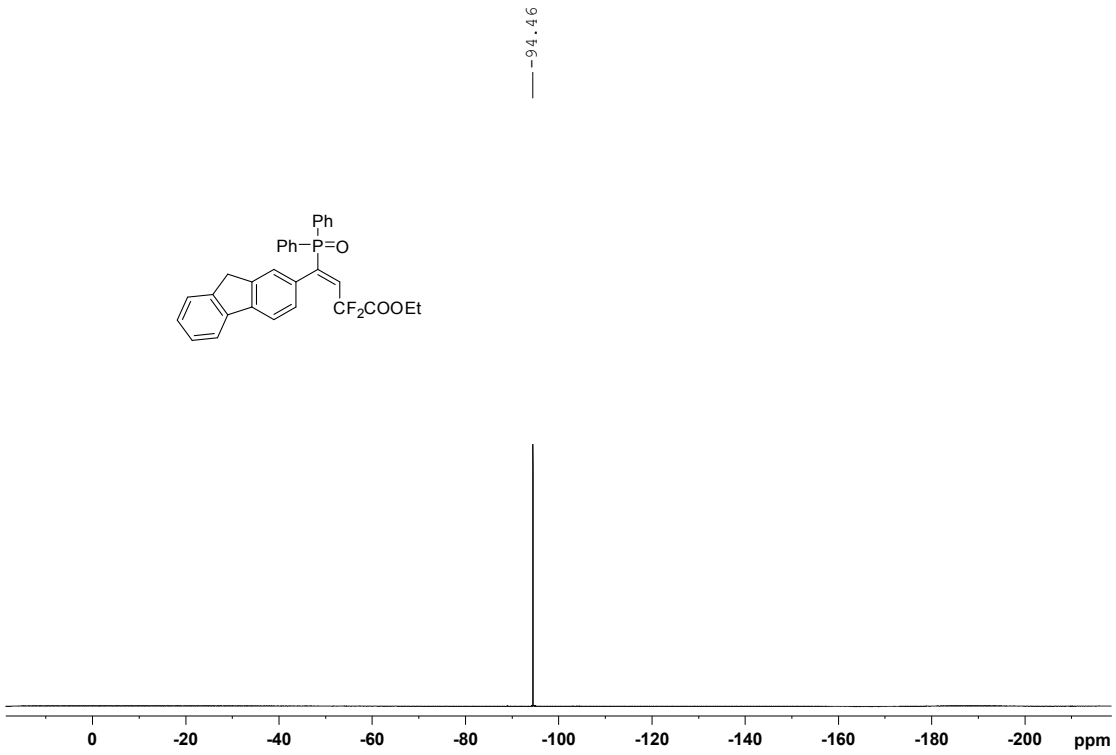
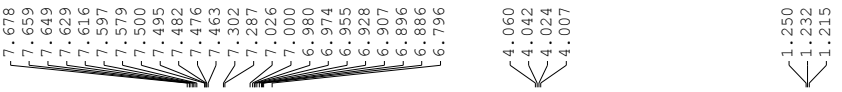
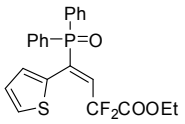
7.566
7.561
7.558
7.546
7.543
7.534
7.531
7.529
7.494
7.479
7.456
7.452
7.450
7.440
7.434
7.428
7.425
7.419
7.353
7.340
7.325
7.303
7.301
7.288
7.286
7.273
7.271
7.260
7.038
6.936
6.914
6.909
6.893
6.876
6.854
3.922
3.908
3.893
3.879
3.729
1.139
1.125
1.111
Ph
Ph—P=O
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
5.07
3.09
1.09
4.06
1.10
1.06
0.98
2.03
2.00
2.01
3.04
146.58
143.52
142.79
142.78
142.30
142.28
140.92
135.46
135.37
135.23
135.14
135.00
134.92
132.62
132.60
132.53
132.45
130.37
130.32
129.91
129.07
128.73
128.63
128.34
128.30
127.42
127.01
126.47
126.45
126.44
125.19
120.31
119.34
113.88
113.72
111.90
111.74
109.92
109.76
77.49
77.23
76.98
63.21
36.92
13.75
Ph
Ph—P=O
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


26.93
Ph
Ph—P=O
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.46
Ph
Ph—P=O
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

3v


7.678
7.659
7.649
7.629
7.616
7.597
7.579
7.500
7.495
7.482
7.476
7.463
7.302
7.287
7.026
7.000
6.980
6.974
6.955
6.928
6.907
6.896
6.886
6.796
4.060
4.042
4.024
4.007
1.250
1.232
1.215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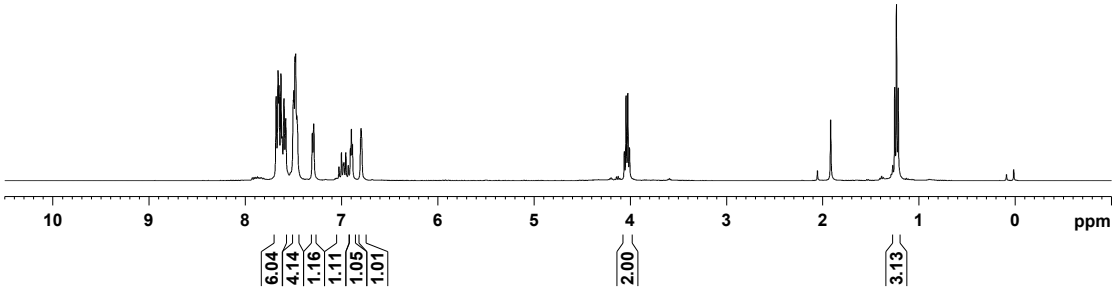
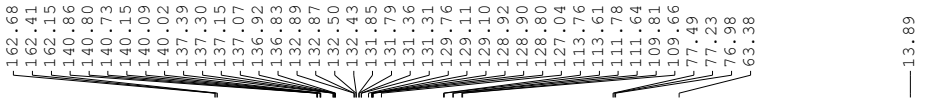
S
CF2COOEt


10
9
8
7
6
5
4
3
2
1
0
ppm
6.04
4.14
1.16
1.11
1.05
1.01
2.00
3.13


162.68
162.41
162.15
140.86
140.80
140.73
140.15
140.09
140.02
137.39
137.30
137.15
137.07
136.92
136.83
132.89
132.87
132.50
132.43
131.85
131.79
131.36
131.31
129.76
129.11
129.10
128.92
128.90
128.80
127.04
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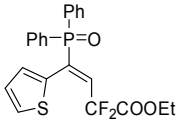
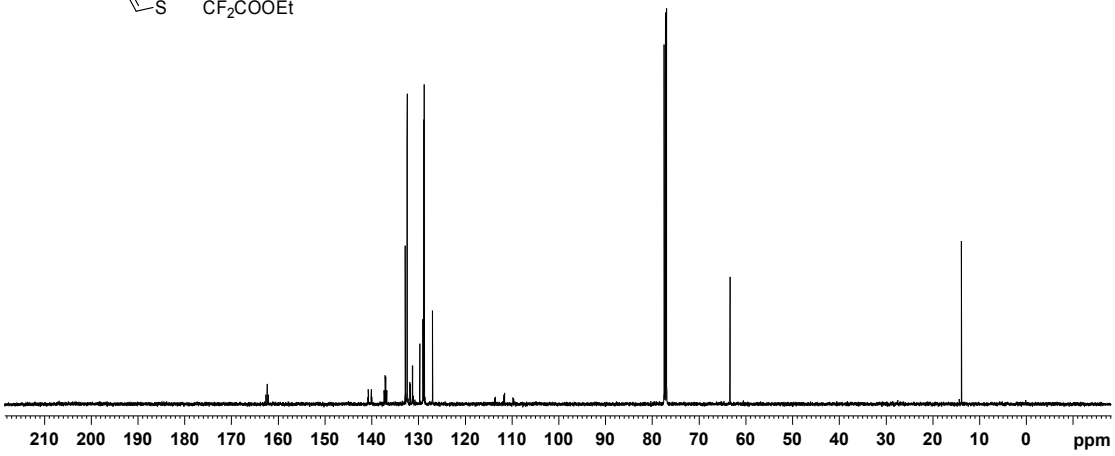
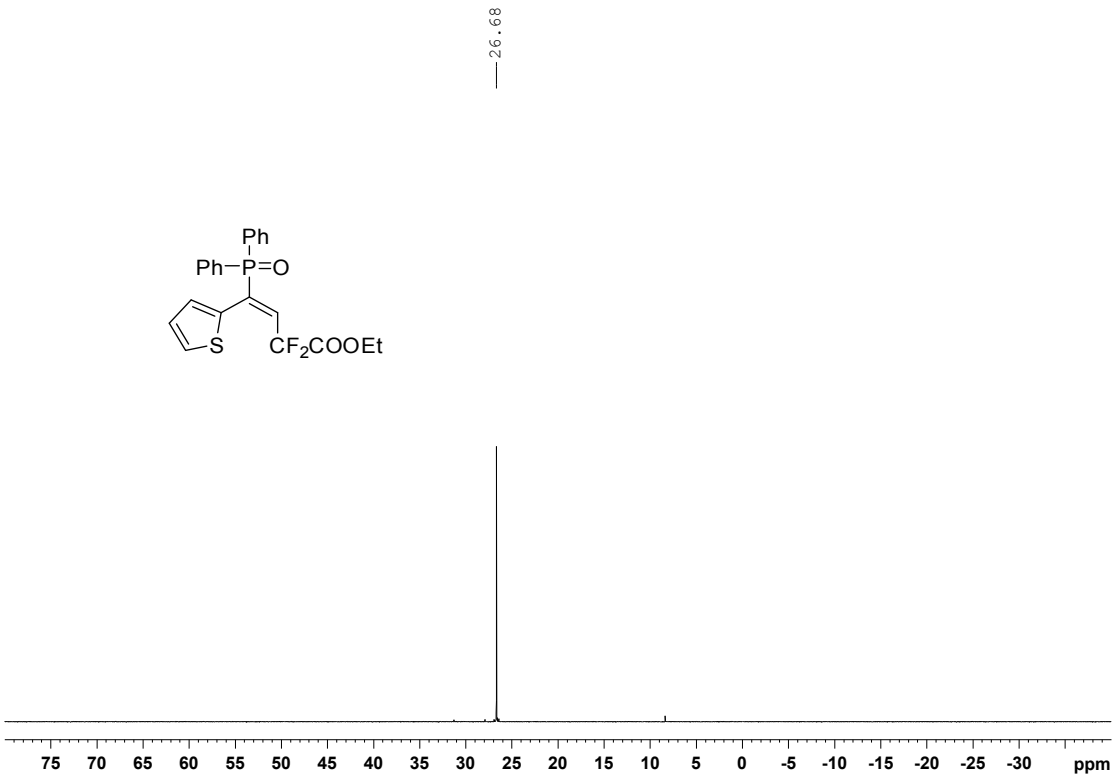
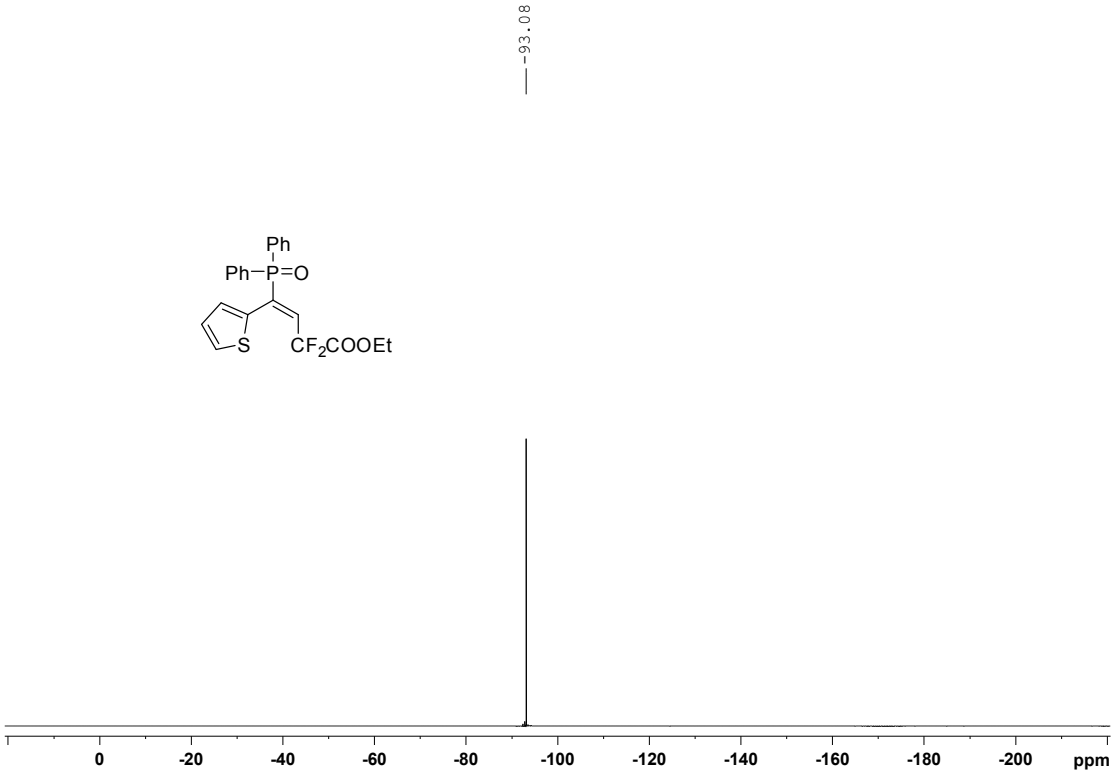
109.81
109.66
77.49
77.23
76.98
63.38
13.89

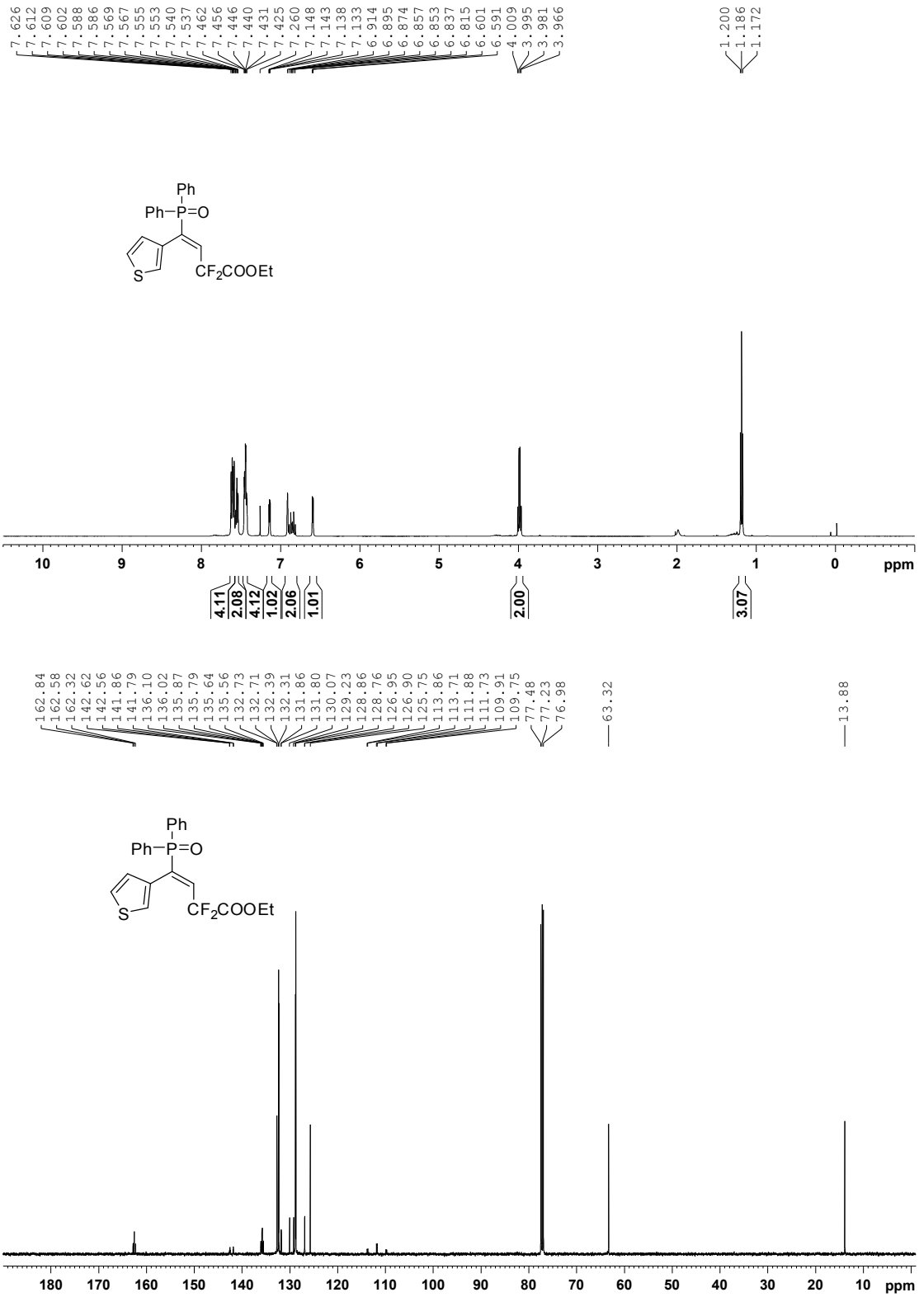

Ph
Ph—P=O
S
CF2COOEt

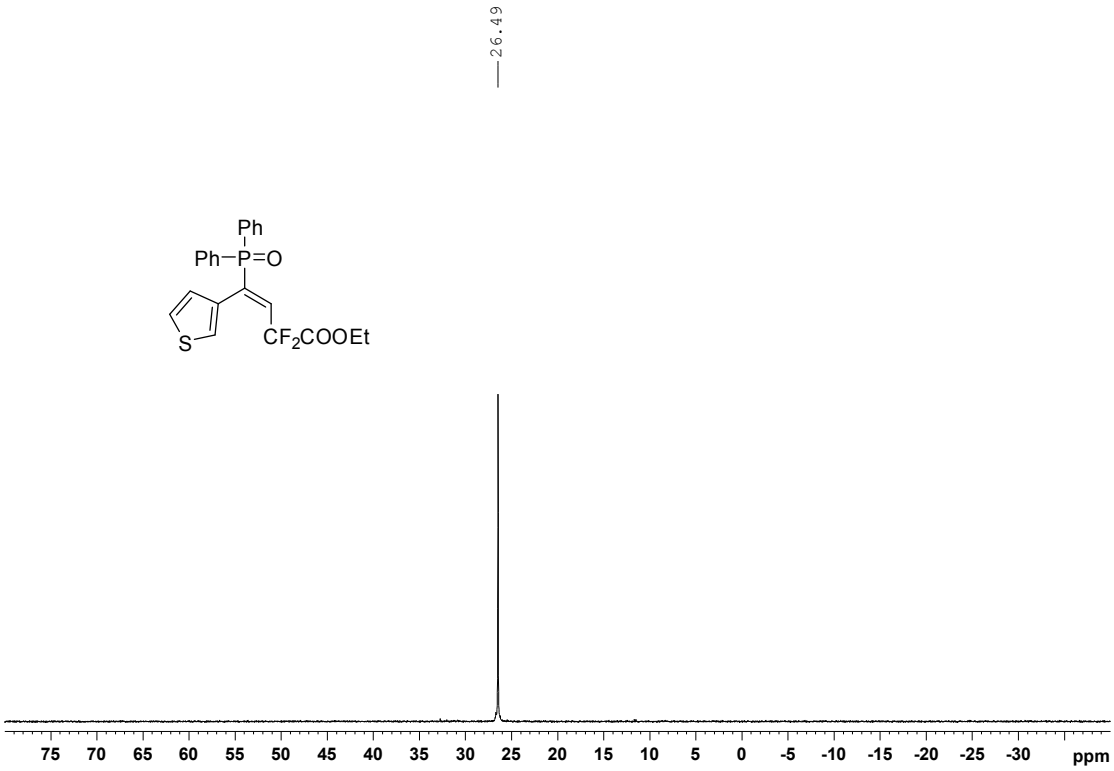

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

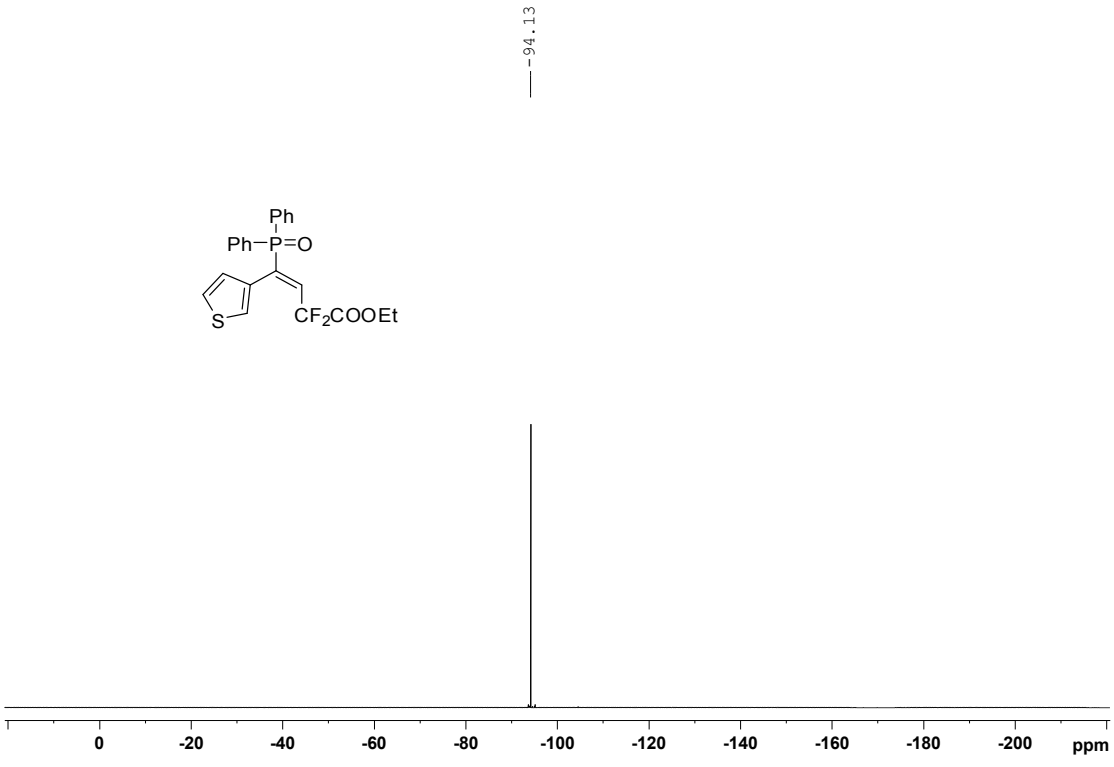

26.68
Ph
Ph—P=O
S
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-93.08
Ph
Ph—P=O
S
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

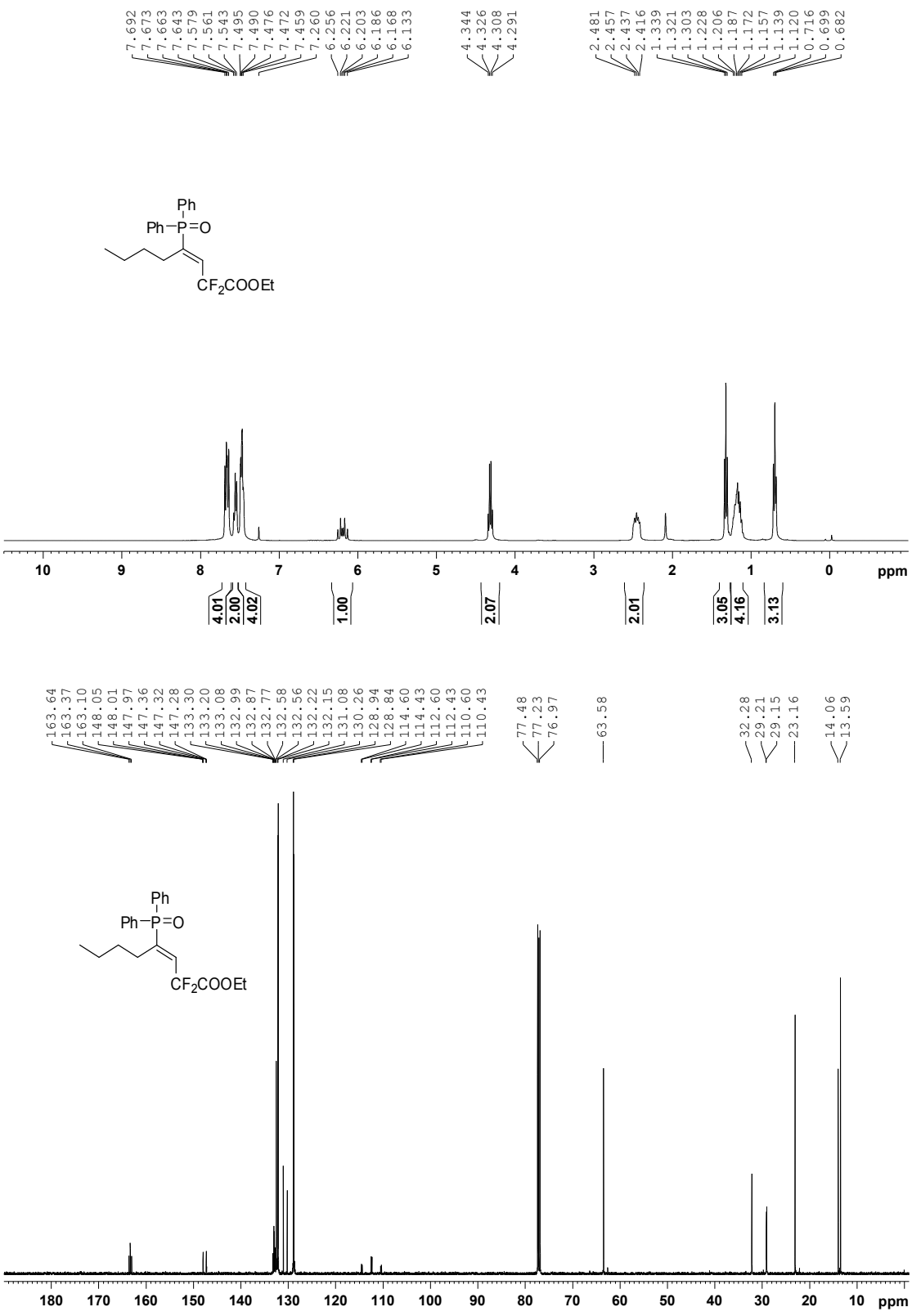
3w

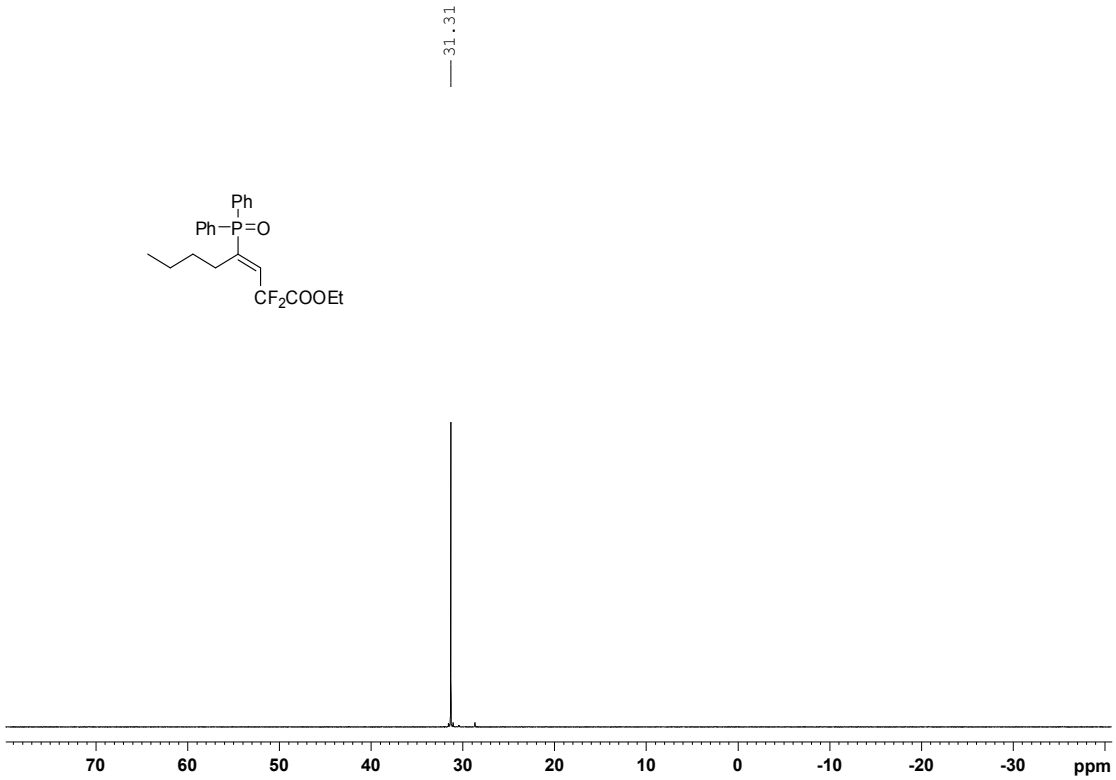

7.626
7.612
7.609
7.602
7.588
7.586
7.569
7.567
7.555
7.553
7.540
7.537
7.462
7.456
7.446
7.440
7.431
7.425
7.260
7.148
7.143
7.138
7.133
6.914
6.895
6.874
6.857
6.853
6.837
6.815
6.601
6.591
4.009
3.995
3.981
3.966
1.200
1.186
1.172
Ph
Ph−P=O
S
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
4.11
2.08
4.12
1.02
2.06
1.01
2.00
3.07
162.84
162.58
162.32
142.62
142.56
141.86
141.79
136.10
136.02
135.87
135.79
135.64
135.56
132.73
132.71
132.39
132.31
131.86
131.80
130.07
129.23
128.86
128.76
126.95
126.90
125.75
113.86
113.71
111.88
111.73
109.91
109.75
77.48
77.23
76.98
63.32
13.88
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

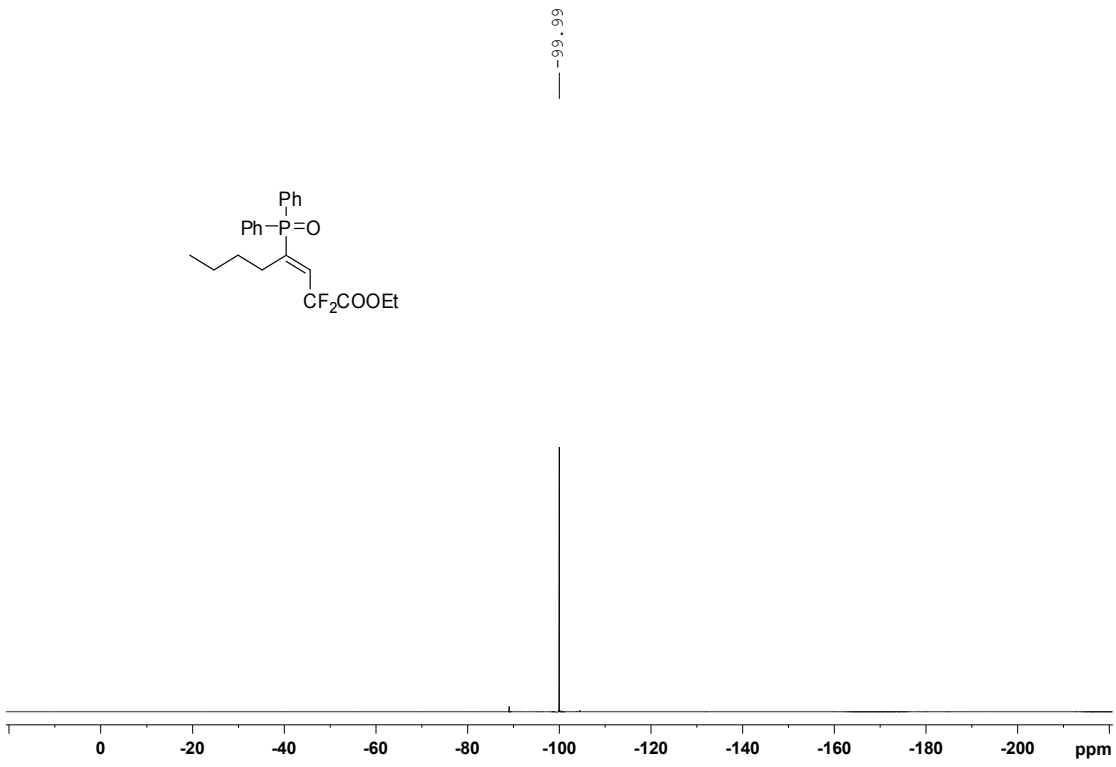

26.49
Ph
Ph—P=O
S
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-94.13
Ph
Ph—P=O
S
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

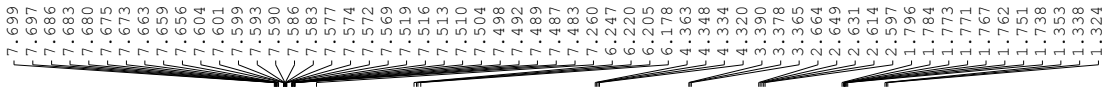
3x

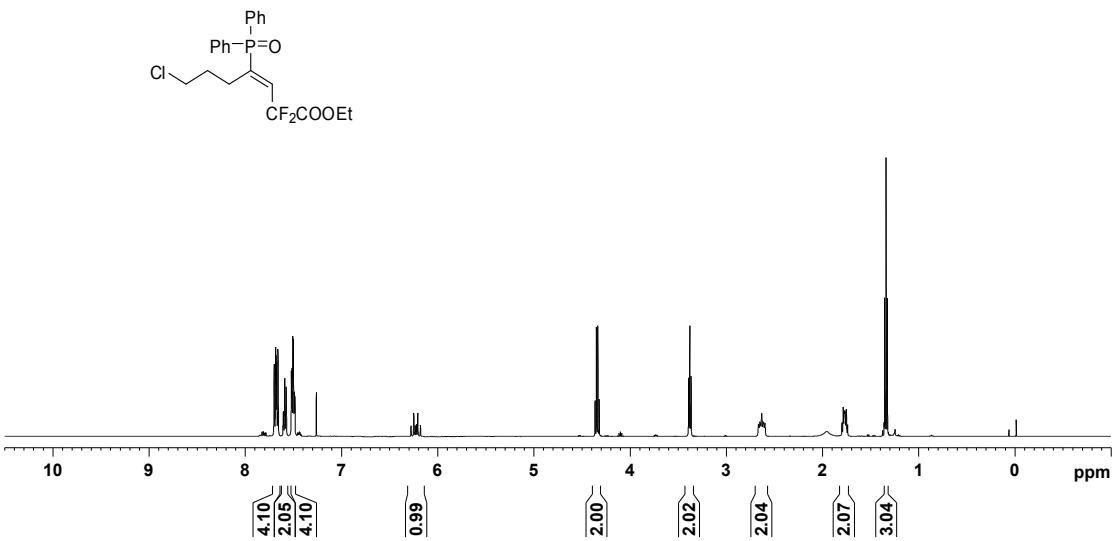

7.692
7.673
7.663
7.643
7.579
7.561
7.543
7.495
7.490
7.476
7.472
7.459
7.260
6.256
6.221
6.203
6.186
6.168
6.133
4.344
4.326
4.308
4.291
2.481
2.457
2.437
2.416
1.339
1.321
1.303
1.228
1.206
1.187
1.172
1.157
1.139
1.120
0.716
0.699
0.682
Ph
Ph—P=O
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
4.01
2.00
4.02
1.00
2.07
2.01
3.05
4.16
3.13
163.64
163.37
163.10
148.05
148.01
147.97
147.36
147.32
147.28
133.30
133.20
133.08
132.99
132.87
132.77
132.58
132.56
132.22
132.15
131.08
130.26
128.94
128.84
114.60
114.43
112.60
112.43
110.60
110.43
77.48
77.23
76.97
63.58
32.28
29.21
29.15
23.16
14.06
13.59
Ph
Ph—P=O
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

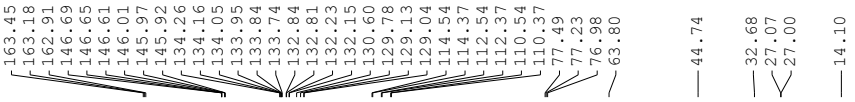

31.31
Ph
Ph—P=O
CF2COOEt
70
60
50
40
30
20
10
0
-10
-20
-30
ppm

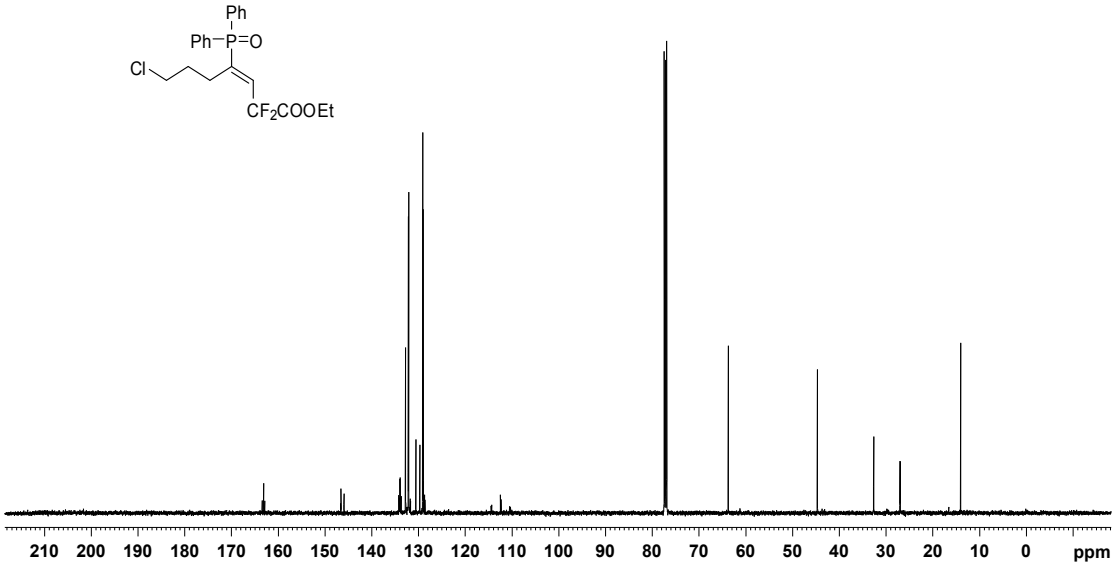

-99.99
Ph
Ph—P=O
CF2COOEt
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

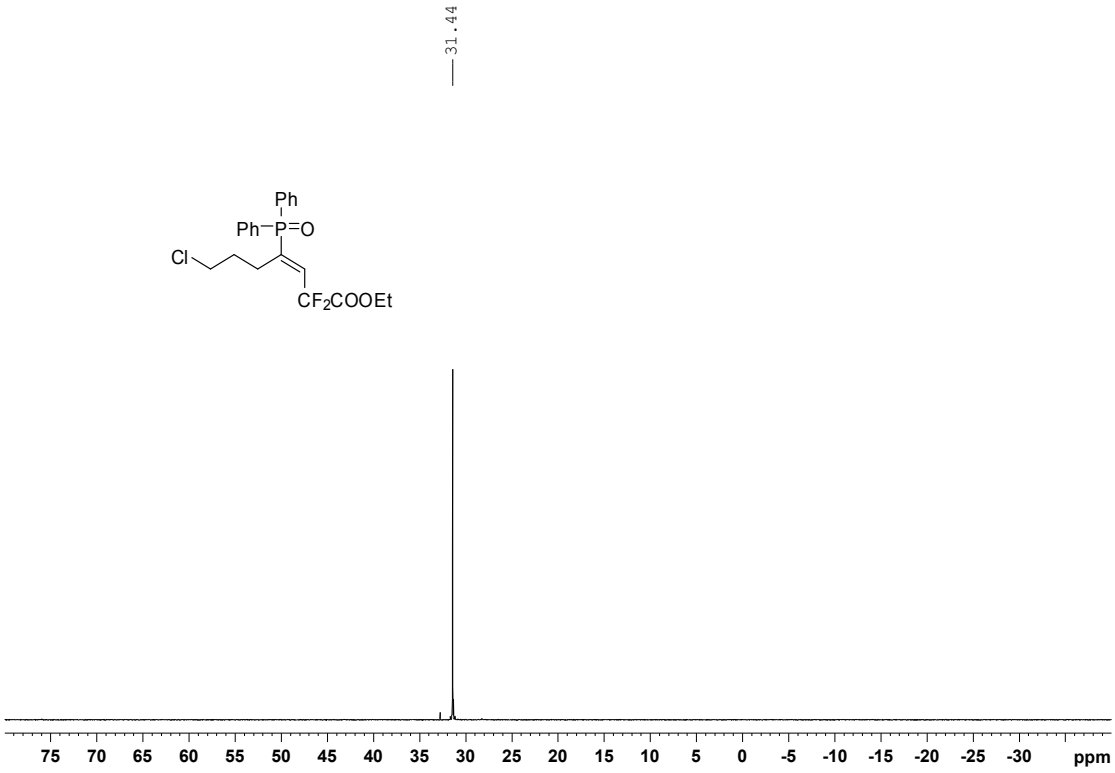
3y

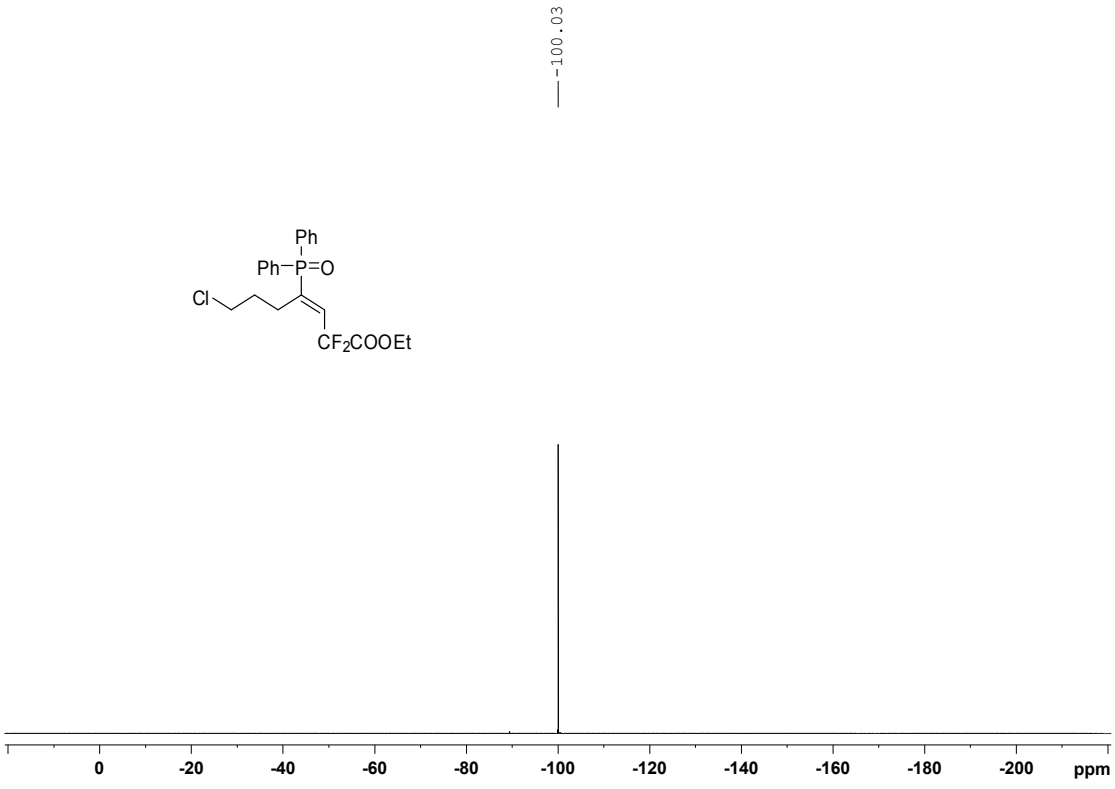

7.699
7.697
7.686
7.683
7.680
7.675
7.673
7.663
7.659
7.656
7.604
7.601
7.599
7.593
7.590
7.586
7.583
7.577
7.574
7.572
7.569
7.519
7.516
7.513
7.510
7.504
7.498
7.492
7.489
7.487
7.483
7.260
6.247
6.220
6.205
6.178
4.363
4.348
4.334
4.320
3.390
3.378
3.365
2.664
2.649
2.631
2.614
2.597
1.796
1.784
1.773
1.771
1.767
1.762
1.751
1.738
1.353
1.338
1.324


Ph
Ph–P=O
Cl
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
4.10
2.05
4.10
0.99
2.00
2.02
2.04
2.07
3.04

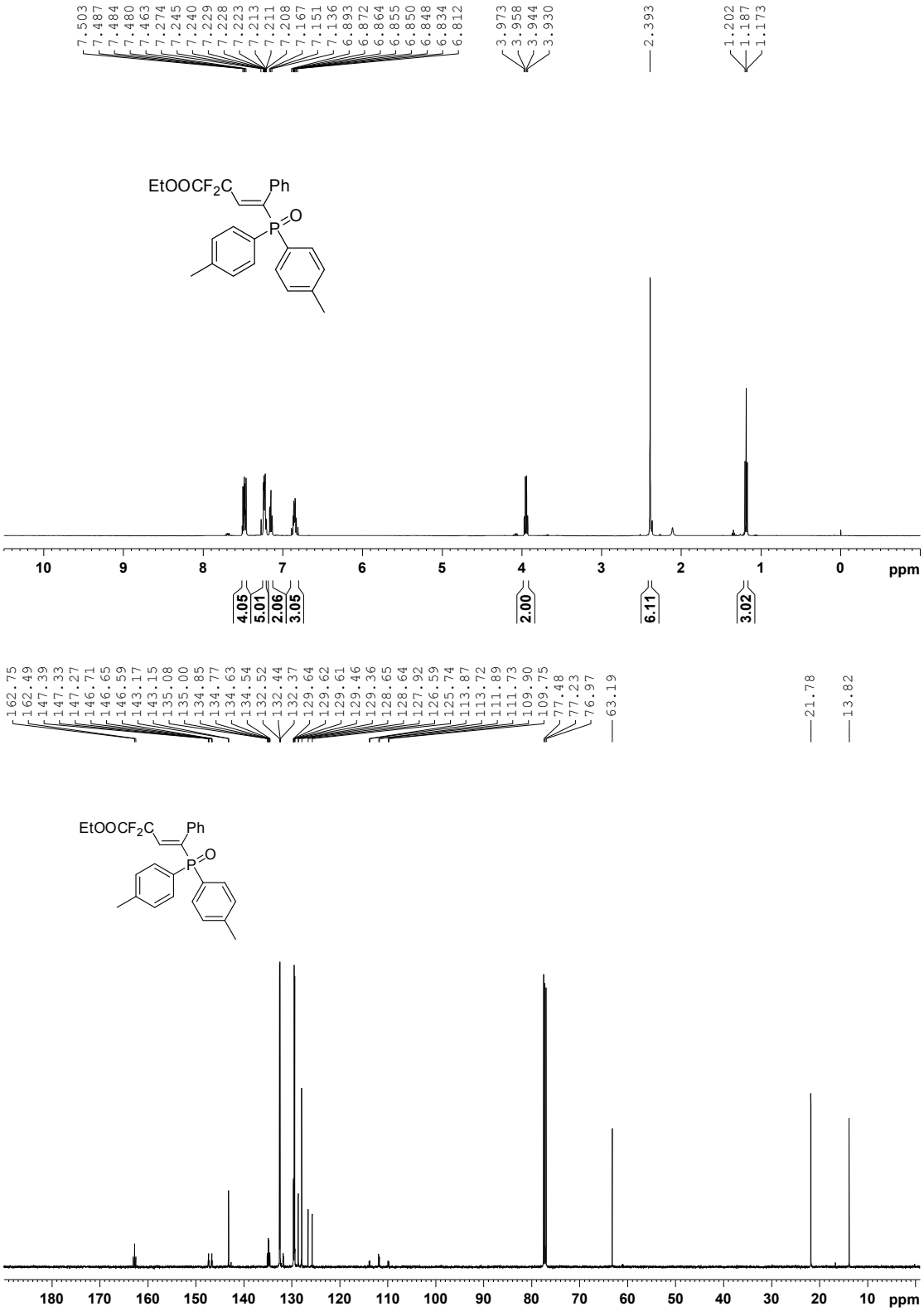

163.45
163.18
162.91
146.69
146.65
146.61
146.01
145.97
145.92
134.26
134.16
134.05
133.95
133.84
133.74
132.84
132.81
132.23
132.15
130.60
129.78
129.13
129.04
114.54
114.37
112.54
112.37
110.54
110.37
77.49
77.23
76.98
63.80
44.74
32.68
27.07
27.00
14.10

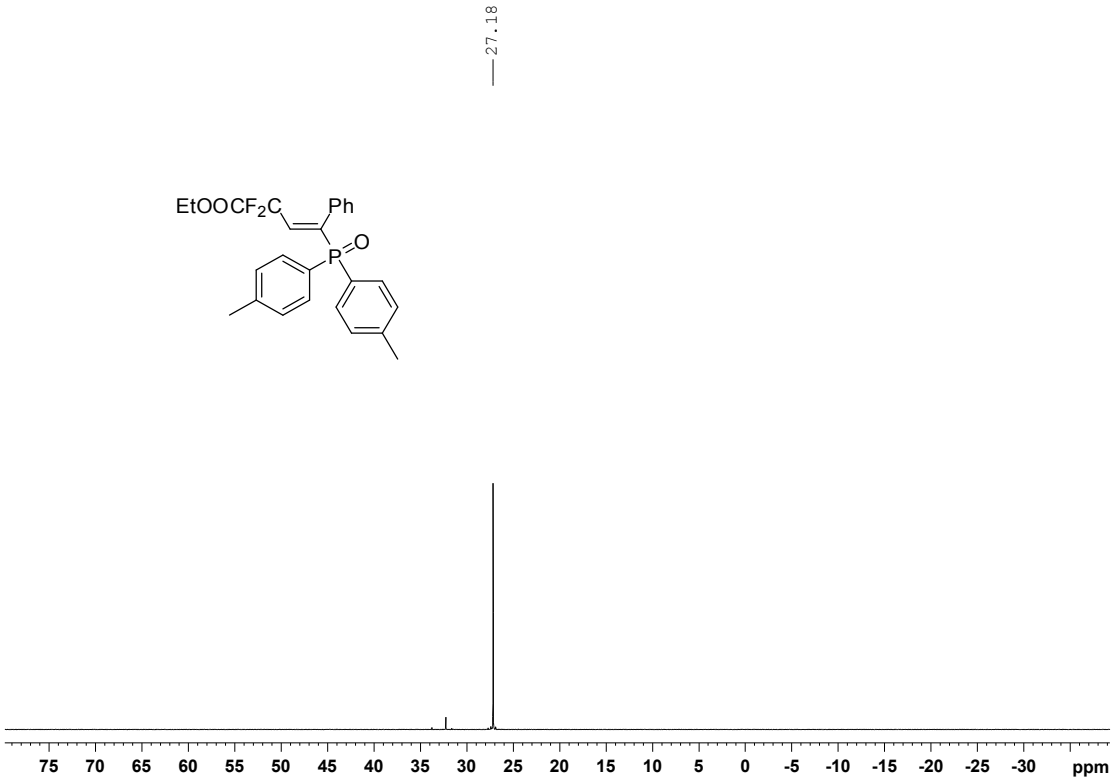

Ph
Ph–P=O
Cl
CF2COOEt
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

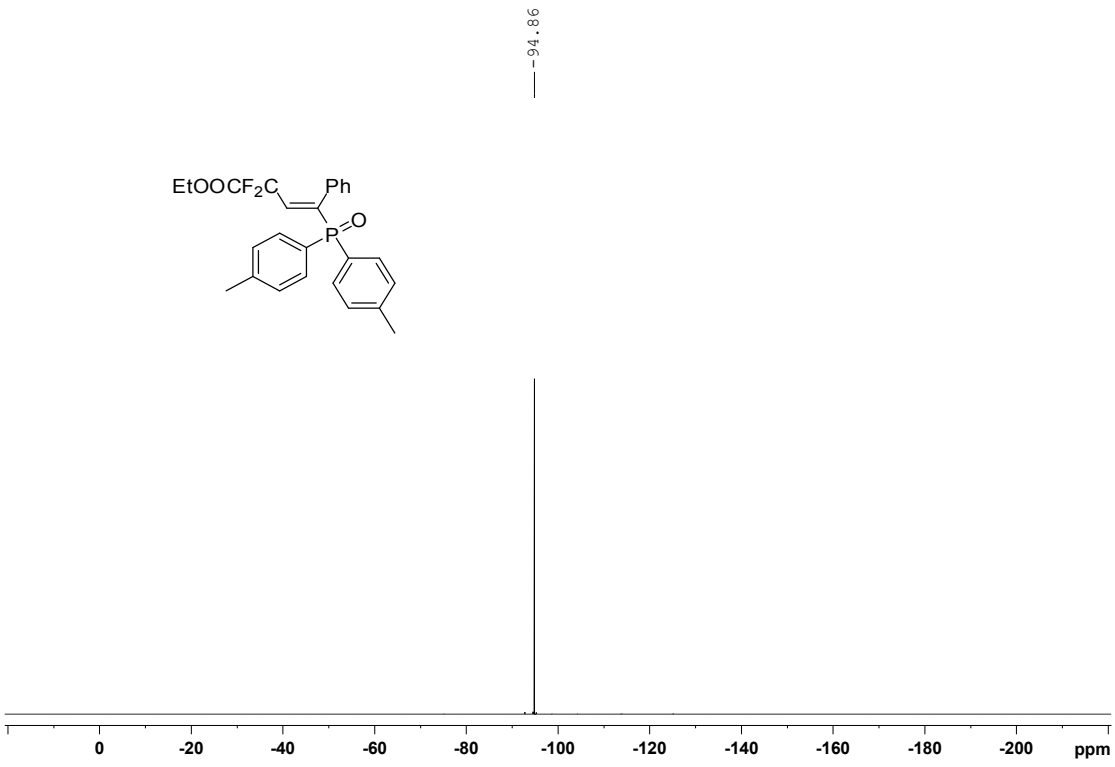

31.44
Ph
Ph—P=O
Cl
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-100.03
Ph
Ph—P=O
Cl
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

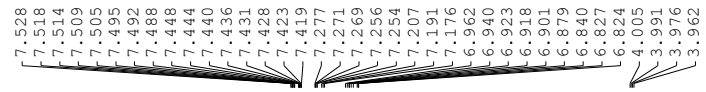
3ab

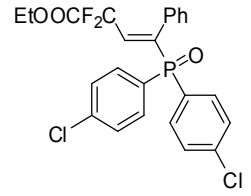

7.503
7.487
7.484
7.480
7.463
7.274
7.245
7.240
7.229
7.228
7.223
7.213
7.211
7.208
7.167
7.151
7.136
6.893
6.872
6.864
6.855
6.850
6.848
6.834
6.812
3.973
3.958
3.944
3.930
2.393
1.202
1.187
1.173
EtOOCF2C
Ph
P
O
10
9
8
7
6
5
4
3
2
1
0
ppm
4.05
5.01
2.06
3.05
2.00
6.11
3.02
162.75
162.49
147.39
147.33
147.27
146.71
146.65
146.59
143.17
143.15
135.08
135.00
134.85
134.77
134.63
134.54
132.52
132.44
132.37
129.64
129.62
129.61
129.46
129.36
128.65
128.64
127.92
126.59
125.74
113.87
113.72
111.89
111.73
109.90
109.75
77.48
77.23
76.97
63.19
21.78
13.82
EtOOCF2C
Ph
P
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

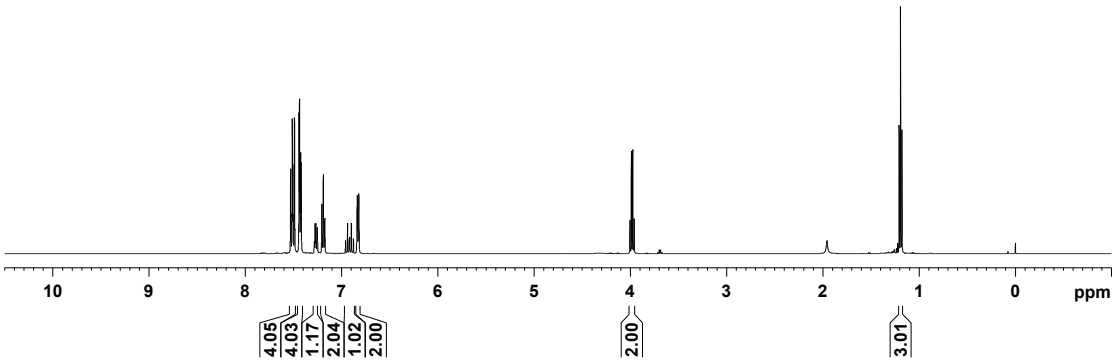

27.18
EtOOCF2C
Ph
P
O
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm

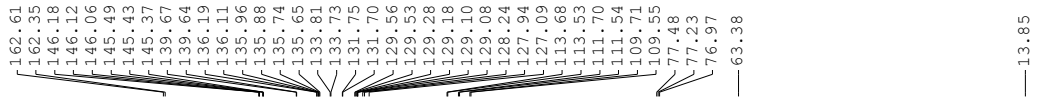

-94.86
EtOOCF2C
Ph
P
O
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

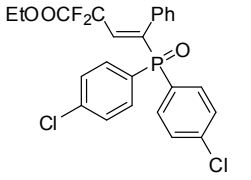
3ac

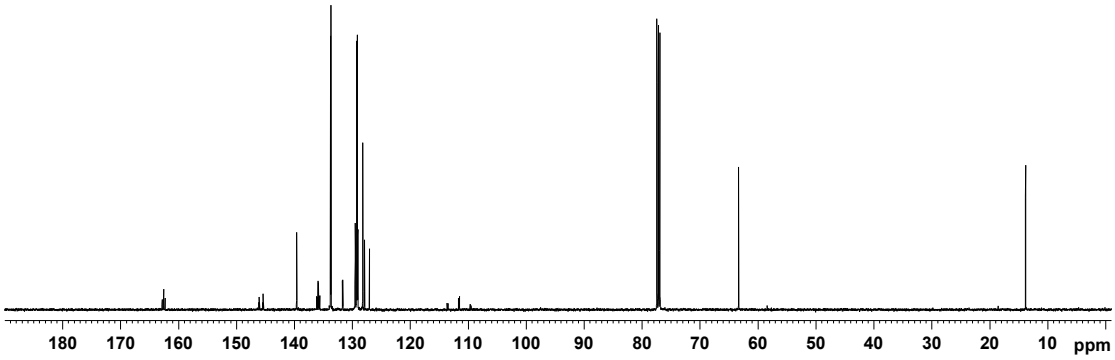

7.528
7.518
7.514
7.509
7.505
7.495
7.492
7.488
7.448
7.444
7.440
7.436
7.431
7.428
7.423
7.419
7.277
7.271
7.269
7.256
7.254
7.207
7.191
7.176
6.962
6.940
6.923
6.918
6.901
6.879
6.840
6.827
6.824
4.005
3.991
3.976
3.962
1.208
1.194
1.179

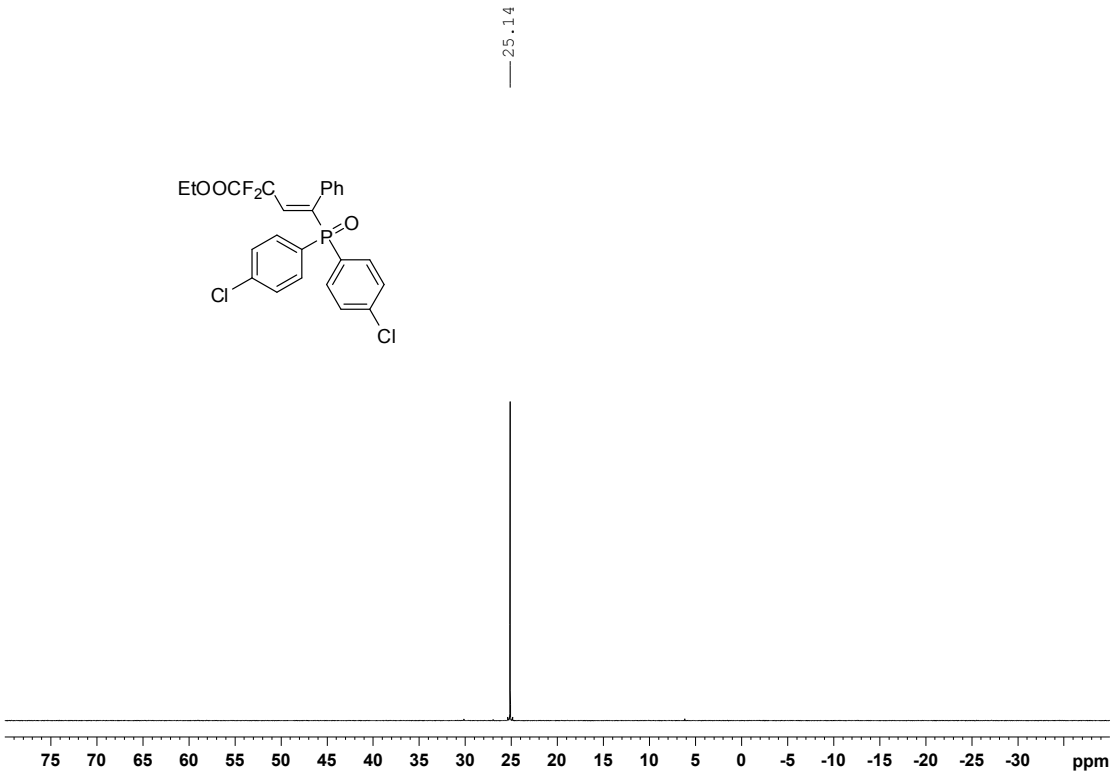

EtOOCF2C
Ph
P
O
Cl
Cl

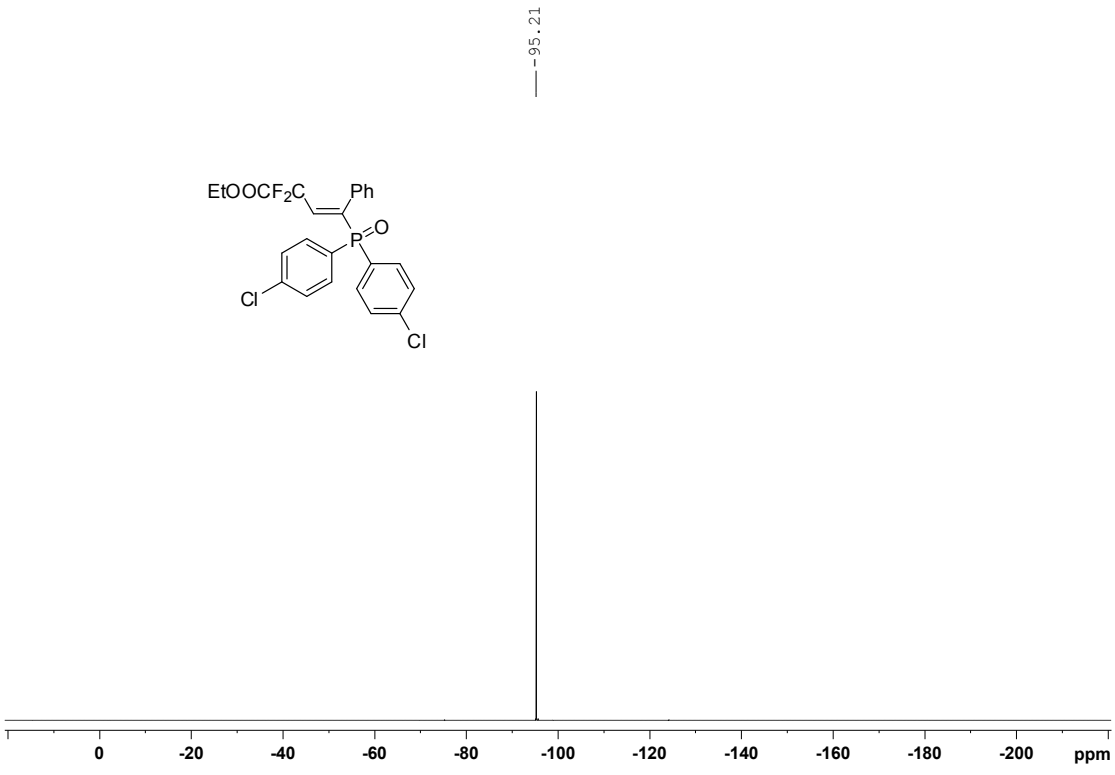

10
9
8
7
6
5
4
3
2
1
0
ppm
4.05
4.03
1.17
2.04
1.02
2.00
2.00
3.01


162.61
162.35
146.18
146.12
146.06
145.49
145.43
145.37
139.67
139.64
136.19
136.11
135.96
135.88
135.74
135.65
133.81
133.73
131.75
131.70
129.56
129.53
129.28
129.18
129.10
129.08
128.24
127.94
127.09
113.68
113.53
111.70
111.54
109.71
109.55
77.48
77.23
76.97
63.38
13.85

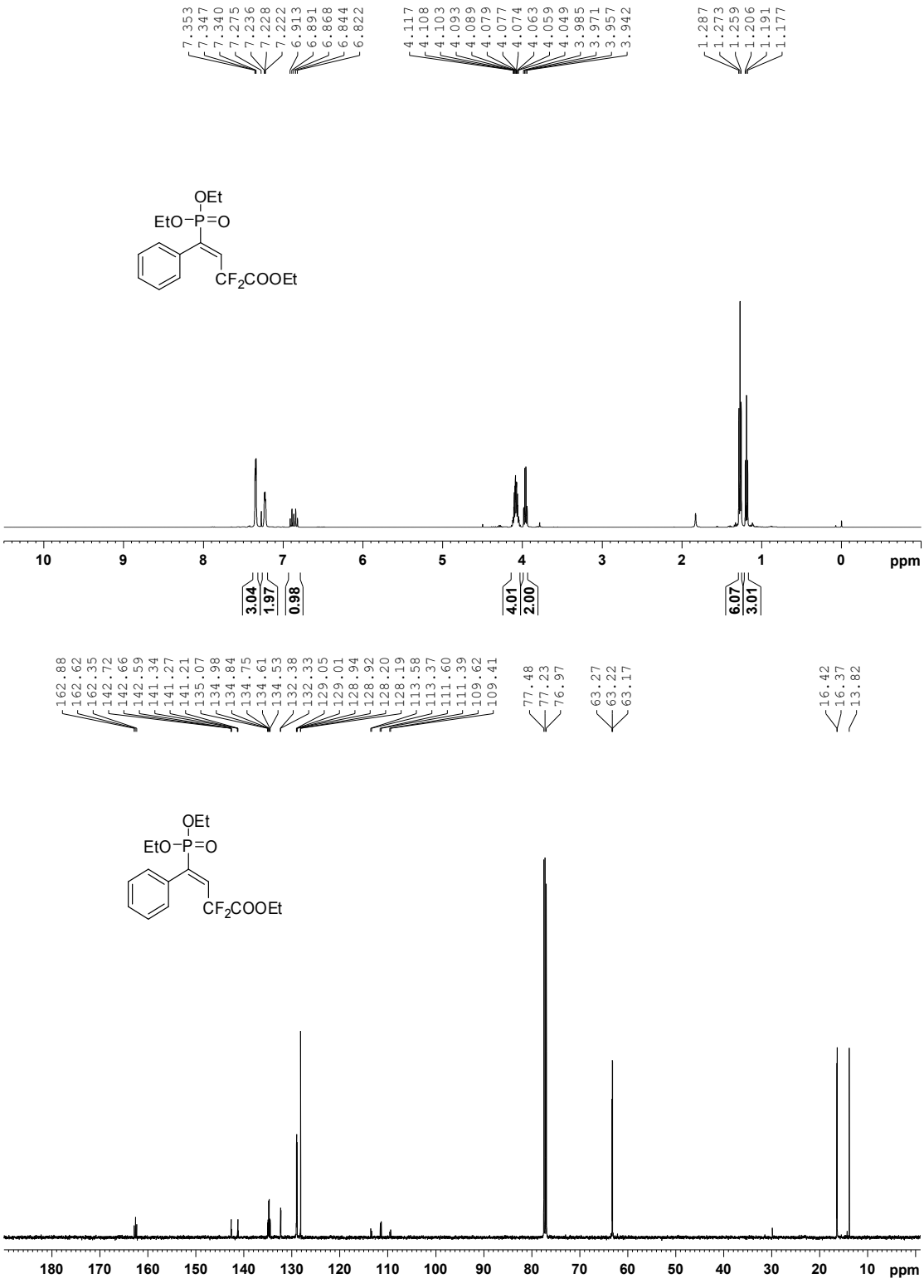

EtOOCF2C
Ph
P
O
Cl
Cl

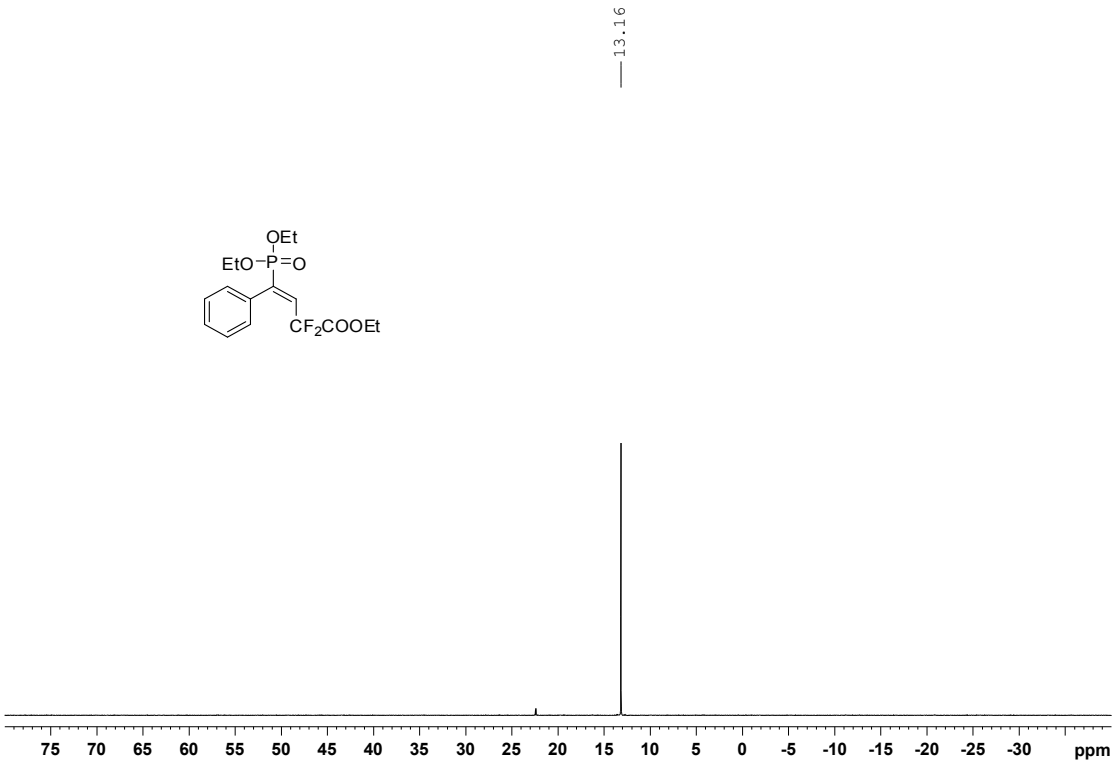

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

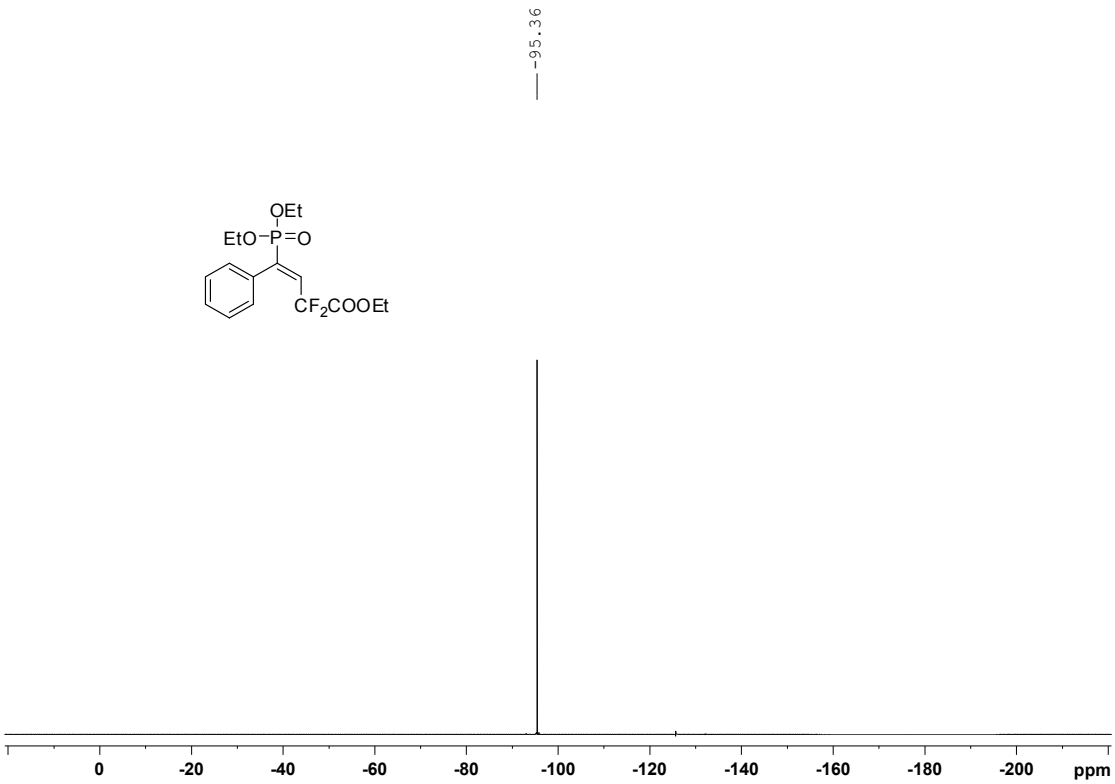

25.14
EtOOCF2C
Ph
P
O
Cl
Cl
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-95.21
EtOOCF2C
Ph
P
O
Cl
Cl
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

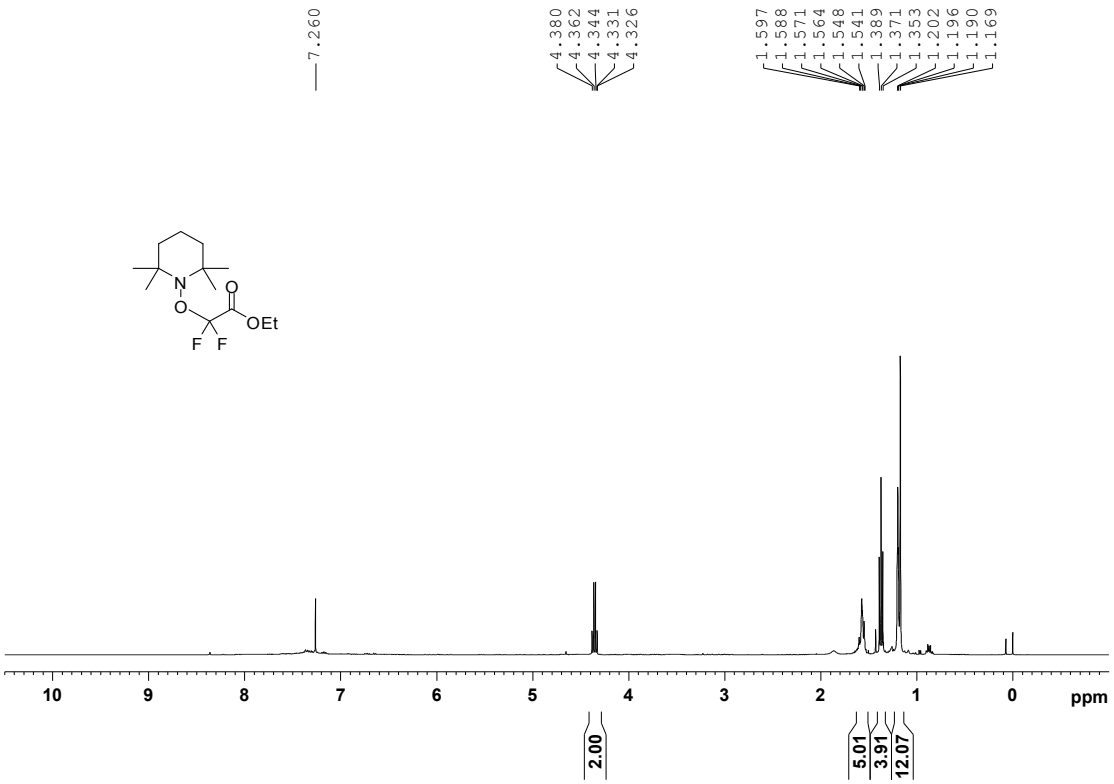
3ad


7.353
7.347
7.340
7.275
7.236
7.228
7.222
6.913
6.891
6.868
6.844
6.822
4.117
4.108
4.103
4.093
4.089
4.079
4.077
4.074
4.063
4.059
4.049
3.985
3.971
3.957
3.942
1.287
1.273
1.259
1.206
1.191
1.177
OEt
EtO−P=O
CF2COOEt
10
9
8
7
6
5
4
3
2
1
0
ppm
3.04
1.97
0.98
4.01
2.00
6.07
3.01
162.88
162.62
162.35
142.72
142.66
142.59
141.34
141.27
141.21
135.07
134.98
134.84
134.75
134.61
134.53
132.38
132.33
129.05
129.01
128.94
128.92
128.20
128.19
113.58
113.37
111.60
111.39
109.62
109.41
77.48
77.23
76.97
63.27
63.22
63.17
16.42
16.37
13.82
OEt
EtO−P=O
CF2COOEt
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.16
OEt
EtO
P
O
CF2COOEt
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 ppm


-95.36
OEt
EtO
P
O
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

5


7.260
4.380
4.362
4.344
4.331
4.326
1.597
1.588
1.571
1.564
1.548
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1.389
1.371
1.353
1.202
1.196
1.190
1.169
N
O
O
OEt
F F
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7
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ppm
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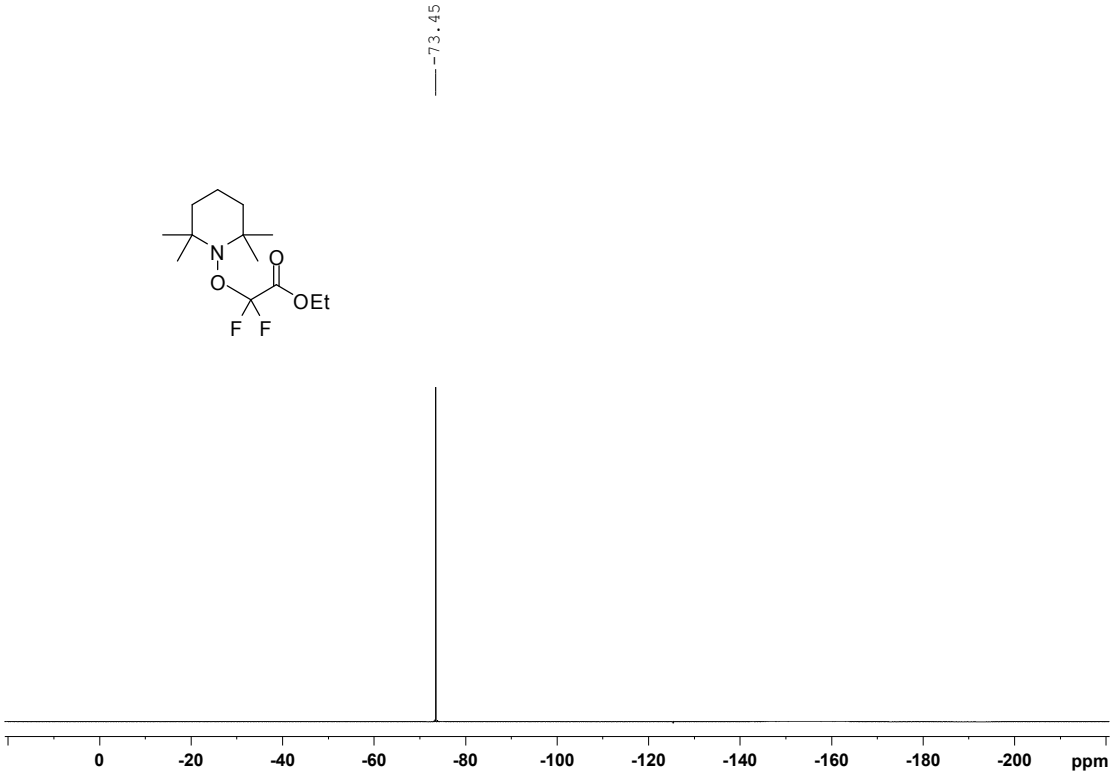
5.01
3.91
12.07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N
O
O
OEt
F F
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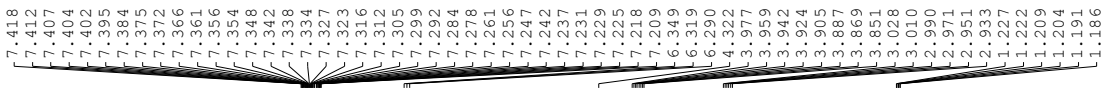
-200
ppm

6+7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7.312
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7.292
7.284
7.278
7.261
7.256
7.247
7.242
7.237
7.231
7.229
7.225
7.218
7.209
6.349
6.319
6.290
4.322
3.977
3.959
3.942
3.924
3.905
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3.869
3.851
3.028
3.010
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2.933
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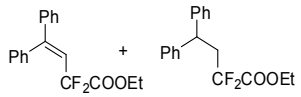
1.191
1.186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Ph
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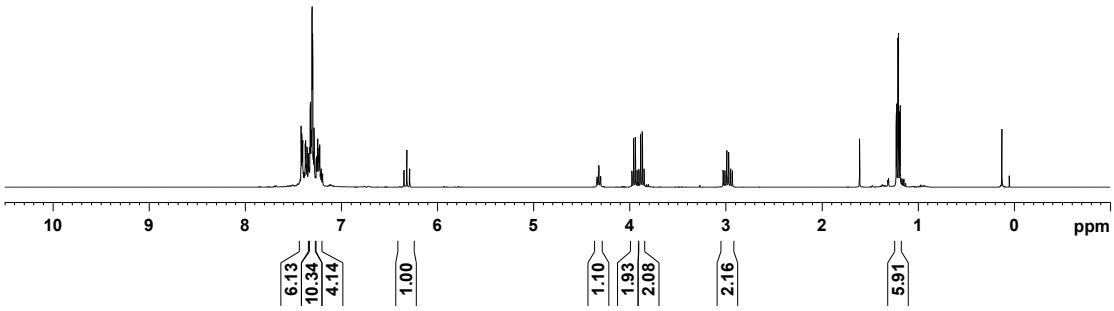
+
Ph
Ph
CF2COOEt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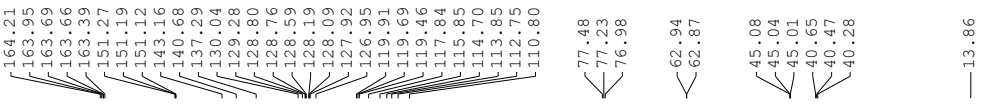
1.10
1.93
2.08
2.16
5.91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151.12
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129.28
128.80
128.76
128.59
128.19
128.09
127.92
126.95
119.91
119.69
119.46
117.84
115.85
114.70
113.85
112.75
110.80
77.48
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76.98
62.94
62.87
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45.04
45.01
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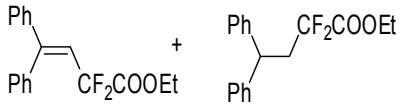
40.47
40.28
13.86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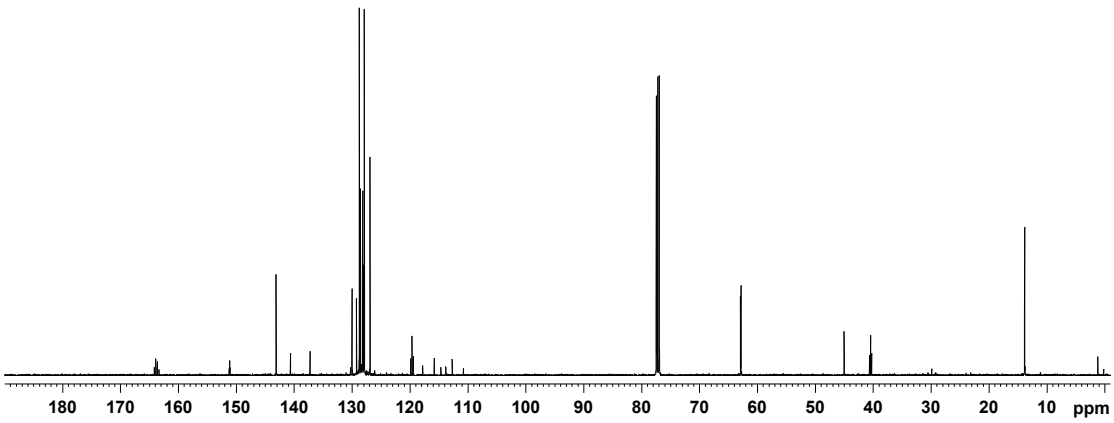
+
Ph
CF2COOEt
Ph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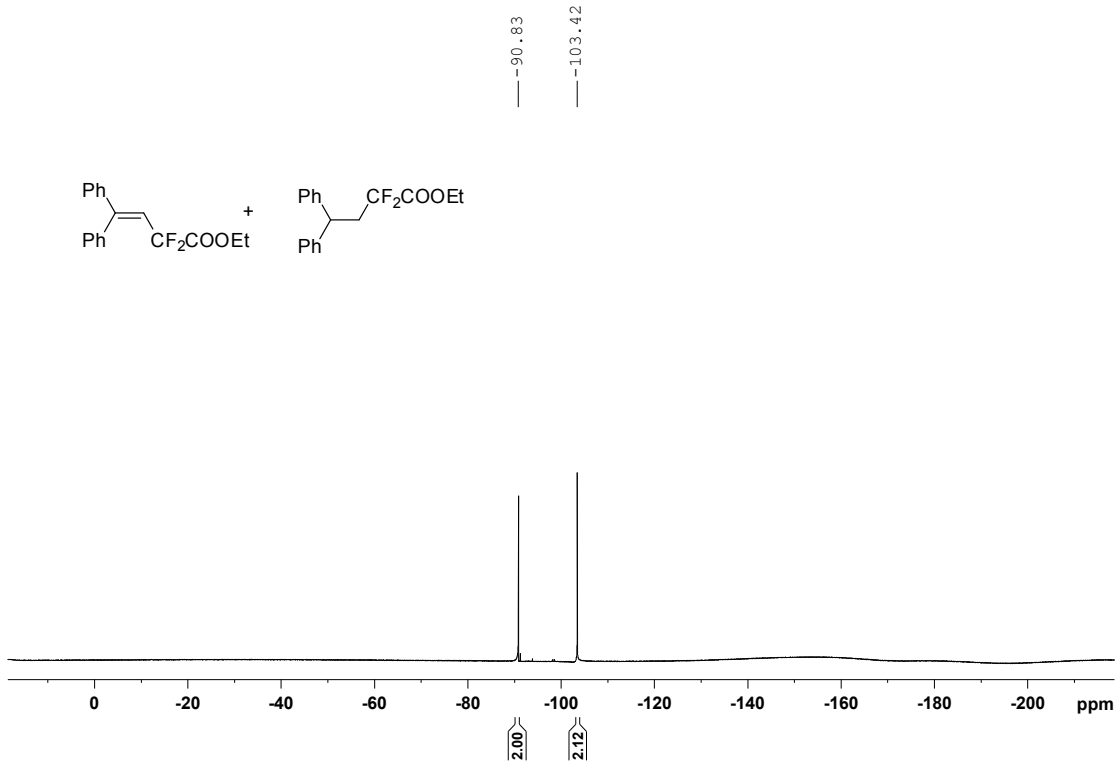
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Ph
CF2COOEt
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-180
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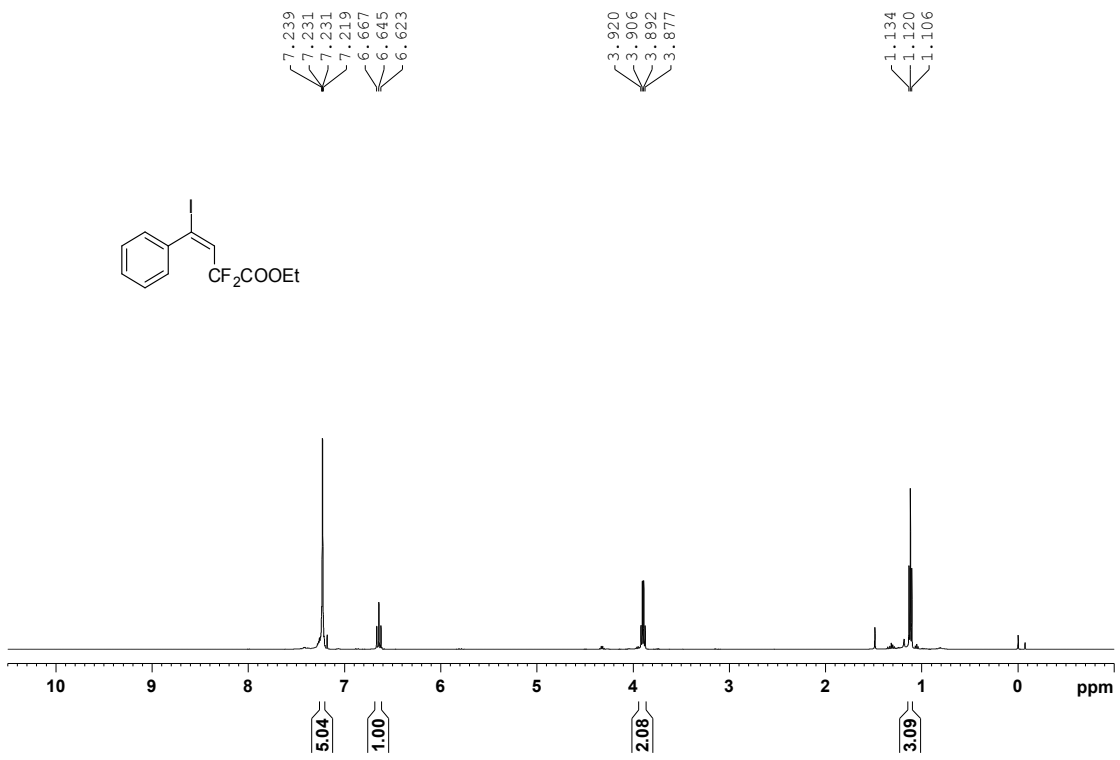
ppm
2.00
2.12

8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6.623
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3.877
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1.120
1.106
I
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9
8
7
6
5
4
3
2
1
0
ppm
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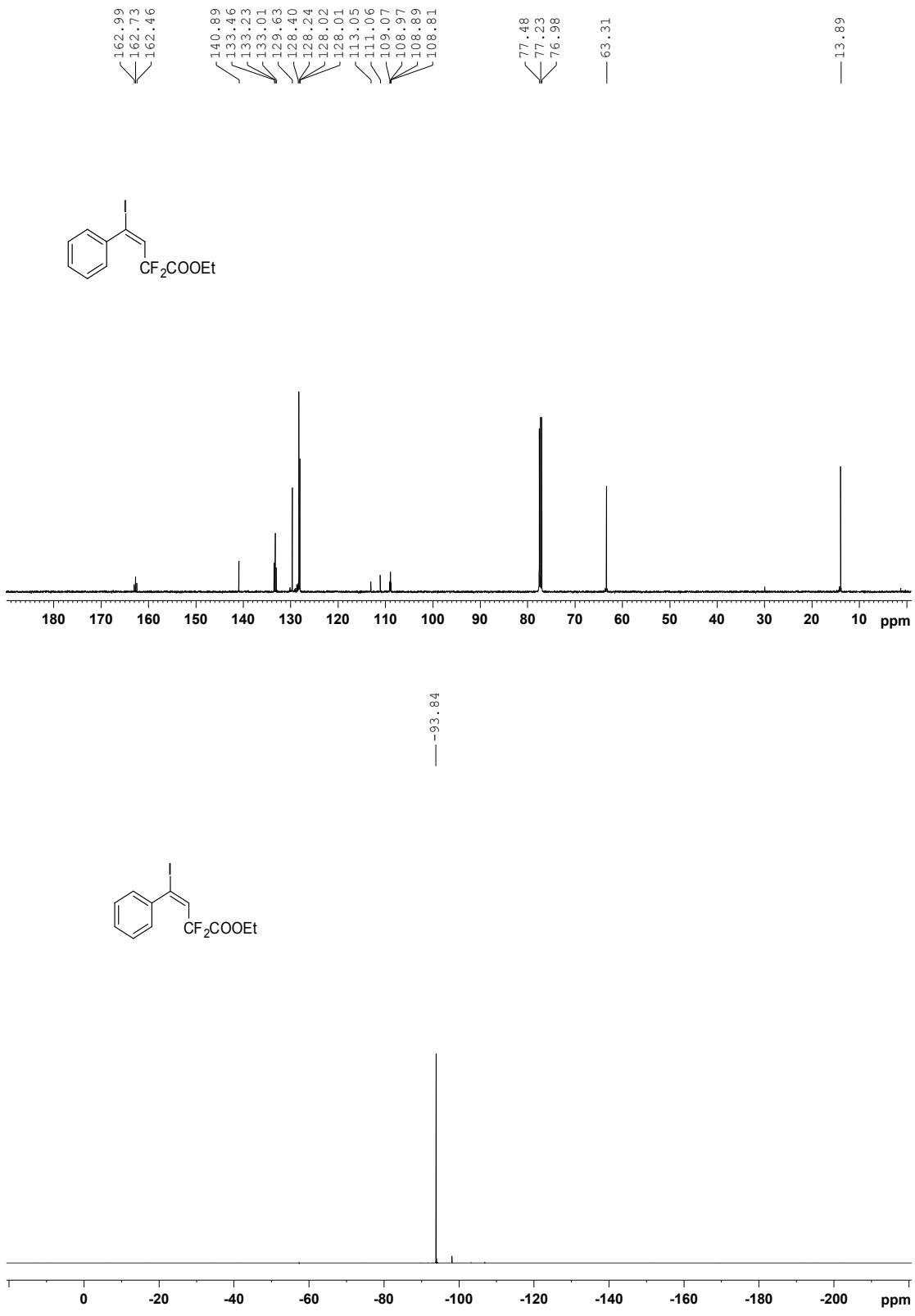
1.00
2.08
3.09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129.63
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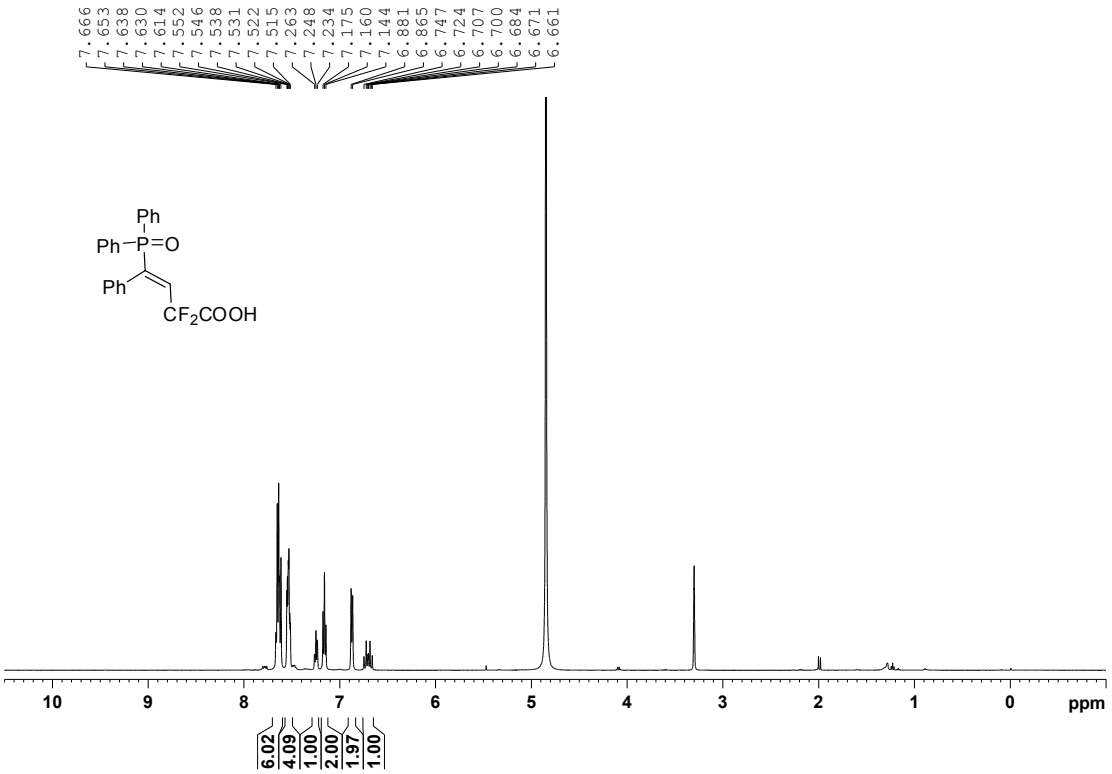
128.24
128.02
128.01
113.05
111.06
109.07
108.97
108.89
108.81
77.48
77.23
76.98
63.31
13.89
I
CF2COOEt
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
-93.84
I
CF2COOEt
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

9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7.538
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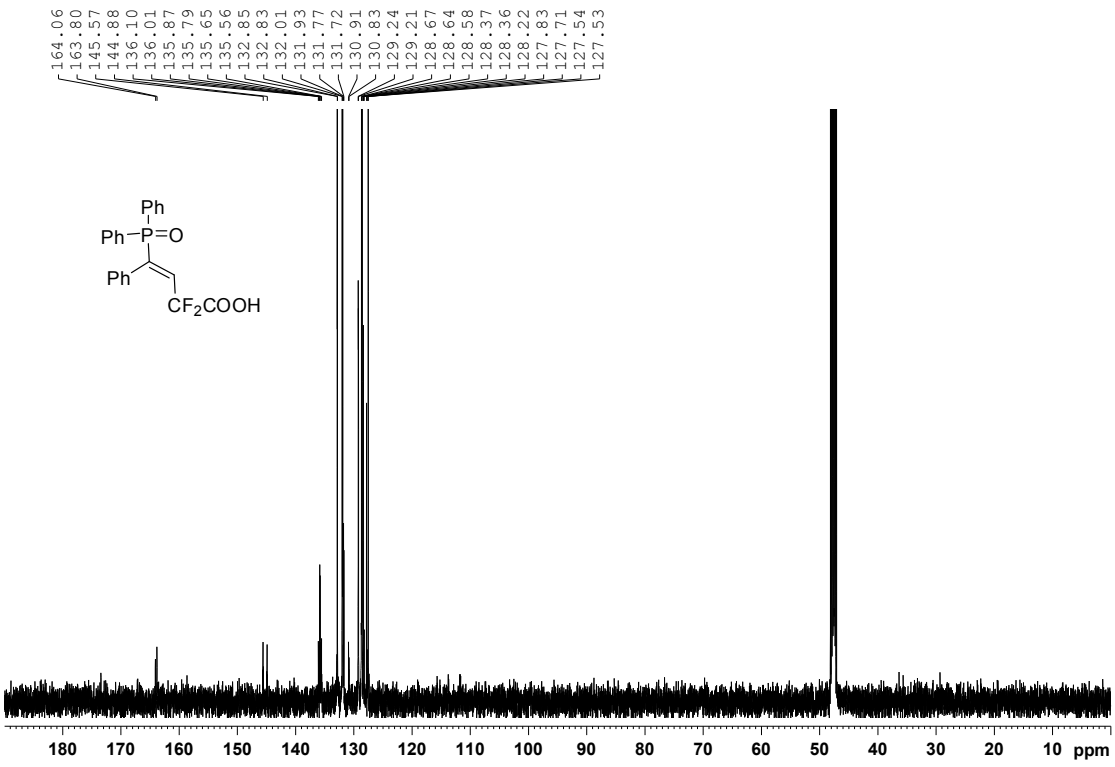
7.522
7.515
7.263
7.248
7.234
7.175
7.160
7.144
6.881
6.865
6.747
6.724
6.707
6.700
6.684
6.671
6.661
Ph
Ph–P=O
Ph
CF2COOH
10
9
8
7
6
5
4
3
2
1
0
ppm
6.02
4.09
1.00
2.00
1.97
1.00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136.01
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135.79
135.65
135.56
132.85
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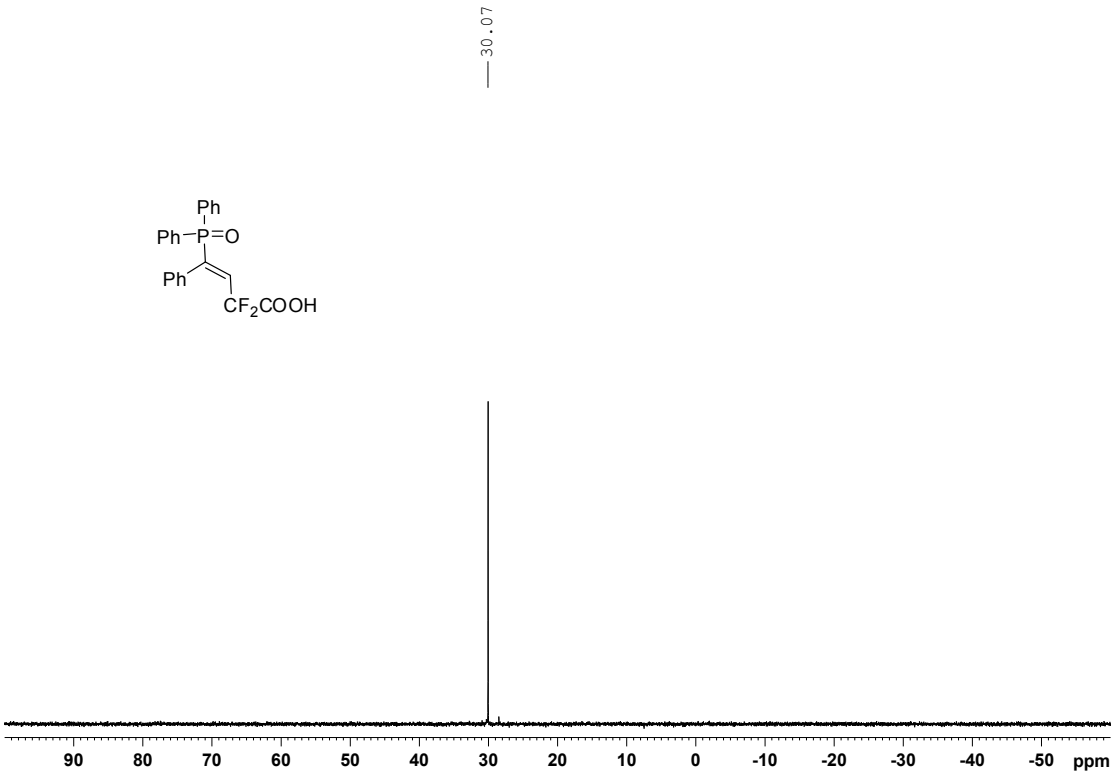
132.01
131.93
131.77
131.72
130.91
130.83
129.24
129.21
128.67
128.64
128.58
128.37
128.36
128.22
127.83
127.71
127.54
127.53
Ph
Ph–P=O
Ph
CF2COOH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


30.07
Ph
Ph
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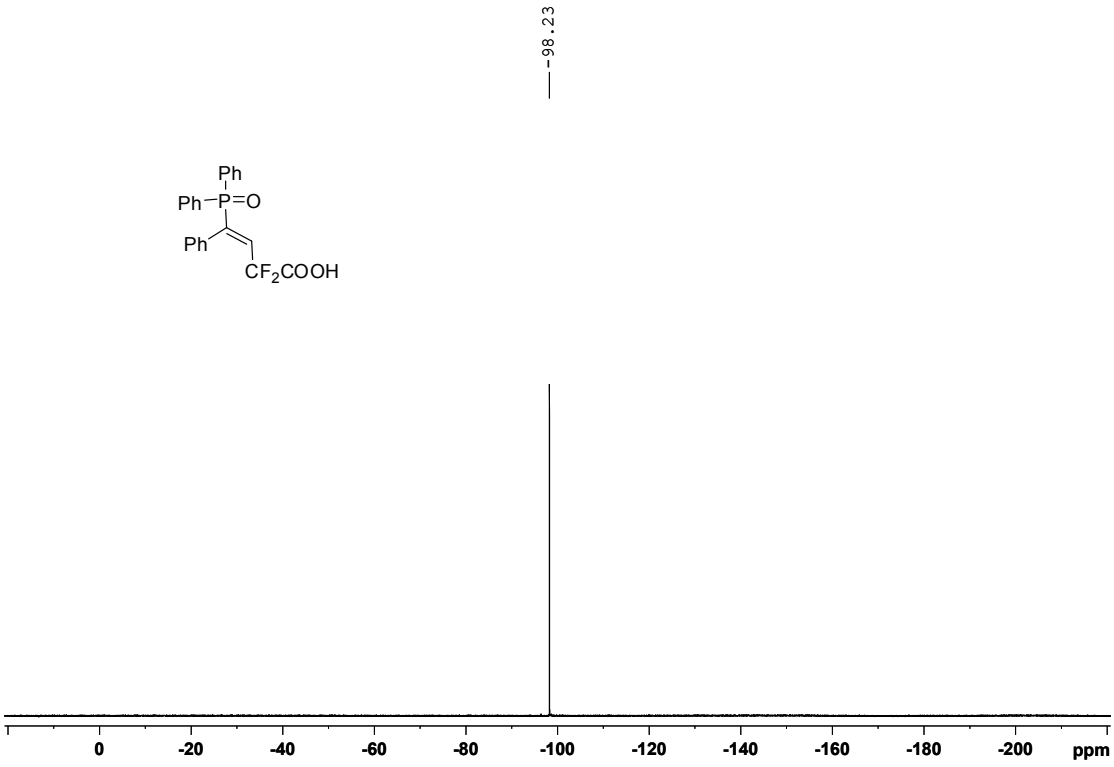
CF2COOH
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 ppm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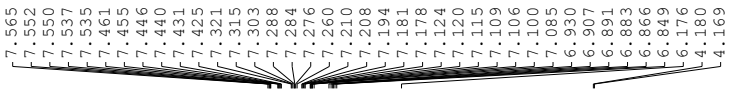
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7.455
7.446
7.440
7.431
7.425
7.321
7.315
7.303
7.288
7.284
7.276
7.260
7.210
7.208
7.194
7.181
7.178
7.124
7.120
7.115
7.109
7.106
7.100
7.085
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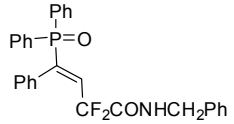
6.907
6.891
6.883
6.866
6.849
6.176
4.180
4.169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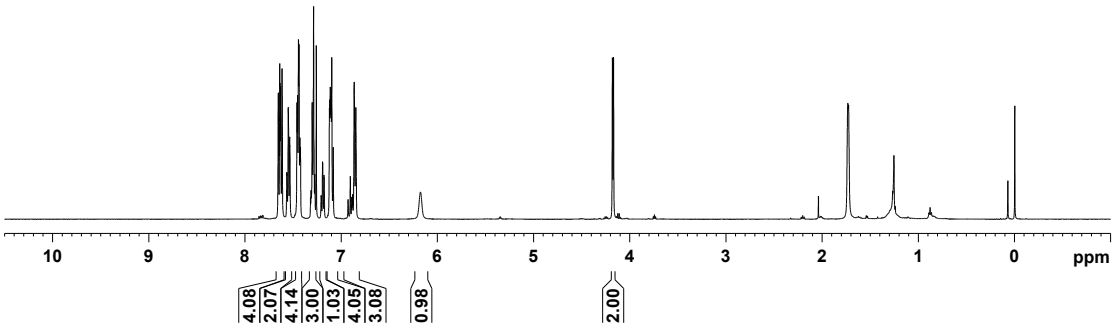
P=O
Ph
CF2CONHCH2Ph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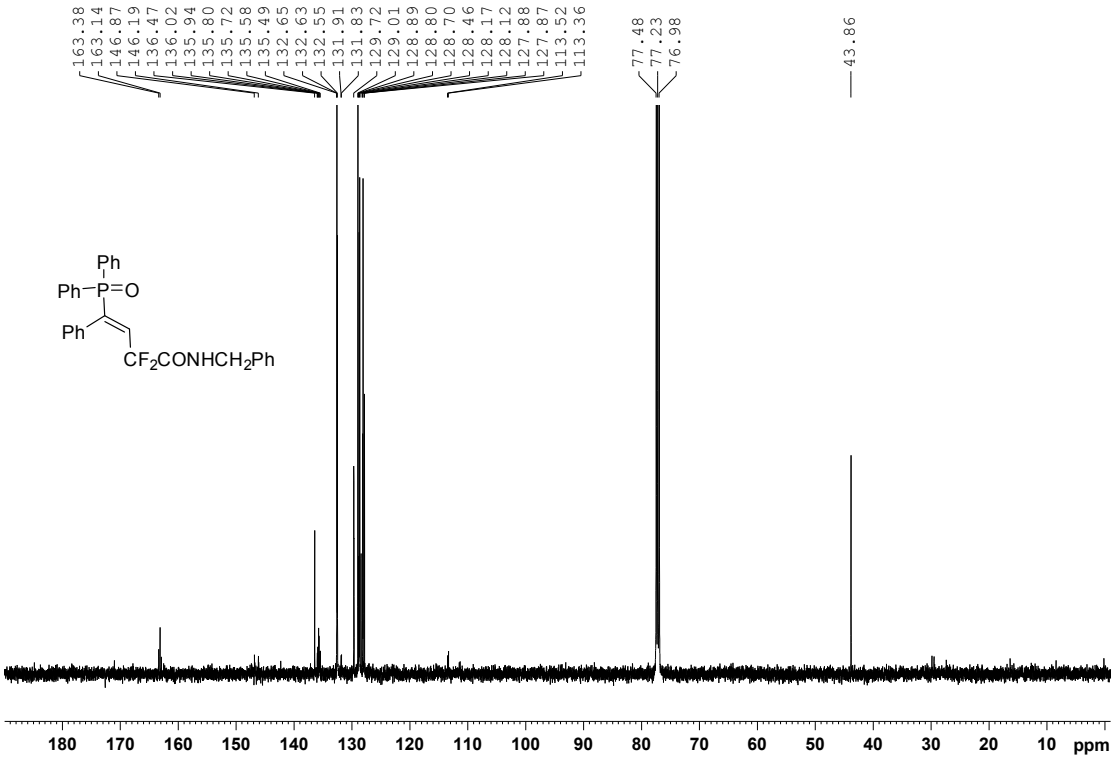
9
8
7
6
5
4
3
2
1
0
ppm
4.08
2.07
4.14
3.00
1.03
4.05
3.08
0.98
2.00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135.58
135.49
132.65
132.63
132.55
131.91
131.83
129.72
129.01
128.89
128.80
128.70
128.46
128.17
128.12
127.88
127.87
113.52
113.36
77.48
77.23
76.98
43.86
Ph
Ph
P=O
Ph
CF2CONHCH2Ph
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150
140
130
120
110
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80
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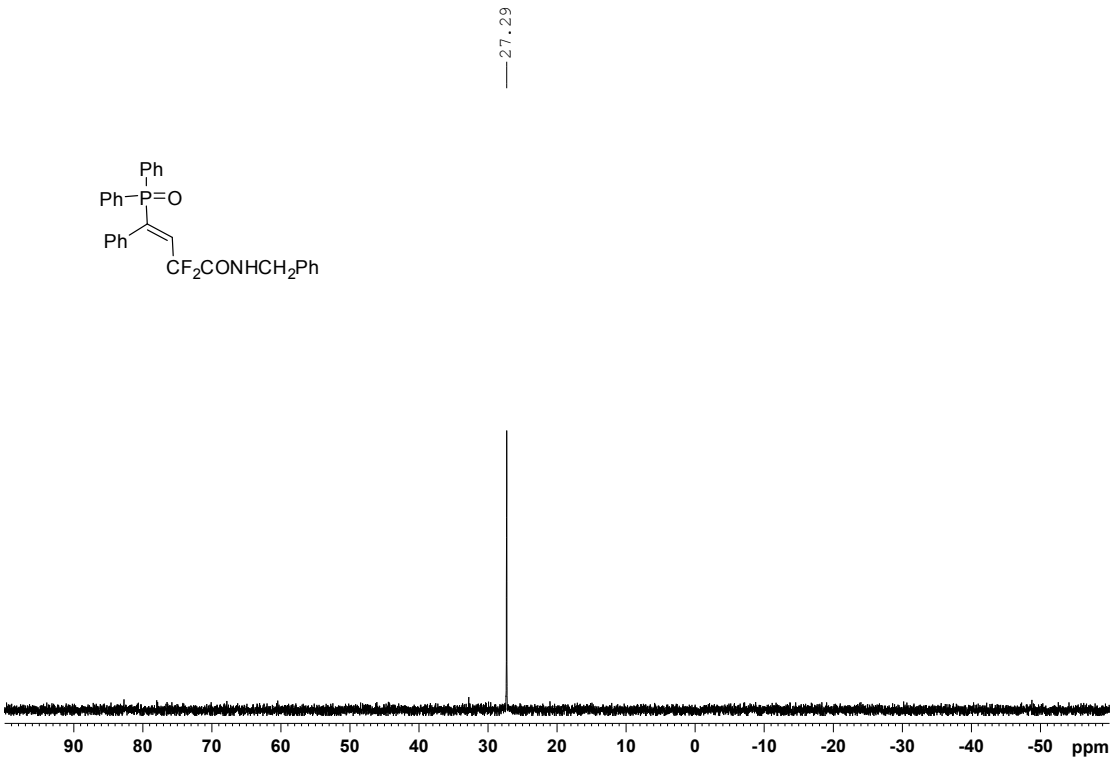
60
50
40
30
20
10
ppm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Ph
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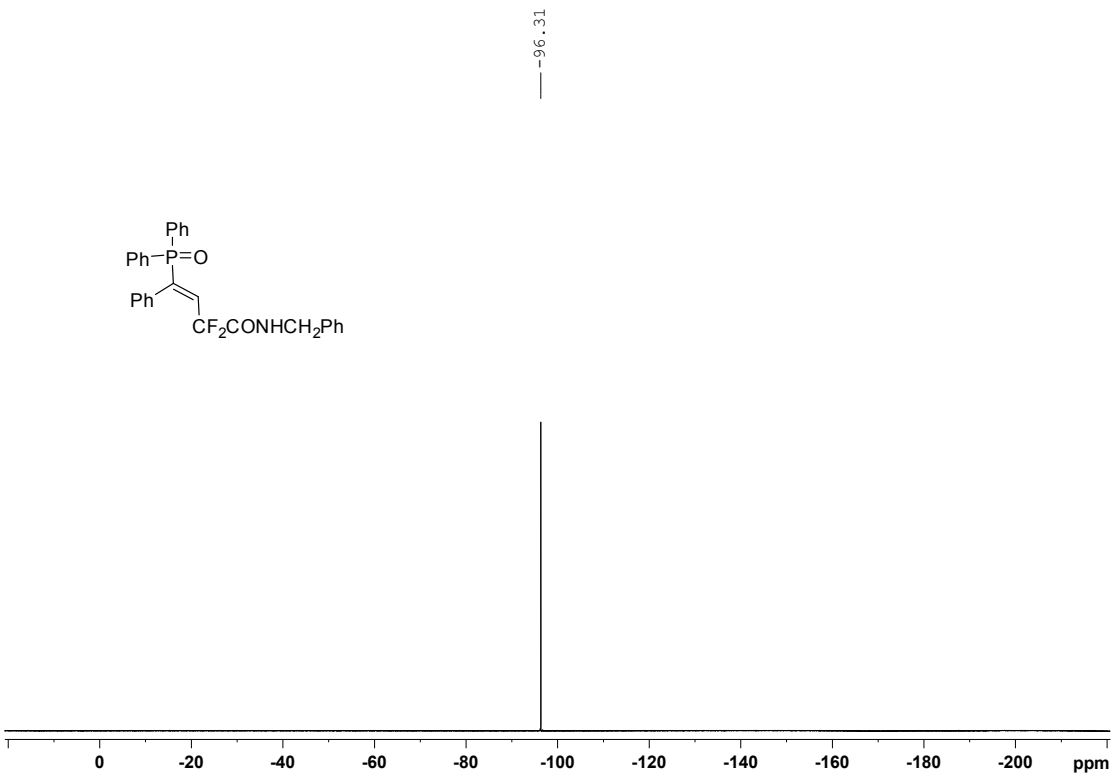
-10
-20
-30
-40
-50
ppm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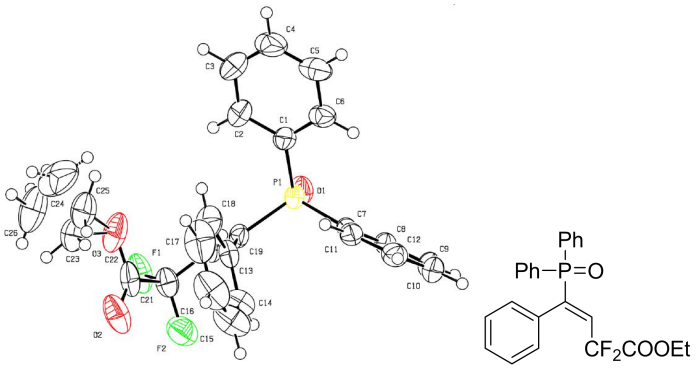
ppm



CCDC: 1537201

Table 1 Crystal data and structure refinement for z0223m.

Identification code	z0223m
Empirical formula	$C_{24}H_{21}F_2O_3P$
Formula weight	426.40
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	25.317(4)
b/Å	8.8649(15)
c/Å	22.042(4)
α/°	90
β/°	120.571(2)
γ/°	90
Volume/Å^3	4259.4(12)
Z	8
ρ_{calc}g/cm^3	1.3298
μ/mm^{-1}	0.169
F(000)	1777.9
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.74 to 52
Index ranges	-33 ≤ h ≤ 32, -12 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	17795
Independent reflections	4161 [R_{int} = 0.0330, R_{sigma} = 0.0431]
Data/restraints/parameters	4161/0/291
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1296
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.1347
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for z0223m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	630.6(2)	7291.7(5)	1264.3(2)	36.35(16)
O1	59.4(6)	6415.5(17)	899.4(7)	48.2(3)
C19	1091.5(8)	6720(2)	2181.1(9)	35.7(4)
F1	683.9(6)	4465.2(18)	3210.8(7)	69.0(4)
C13	1724.8(9)	7292(2)	2620.7(9)	40.3(4)
C11	1631.0(9)	7875(2)	1084.3(10)	40.7(4)
C7	1101.1(8)	7057.9(19)	880.7(9)	34.8(4)
F2	1460.1(7)	3806.6(17)	3115.3(8)	72.2(4)
C20	834.1(9)	5723(2)	2391.6(9)	41.2(4)
C8	894.9(9)	6057(2)	324.6(9)	40.5(4)
O2	2052.3(8)	5629(2)	4171.8(8)	76.5(6)
C12	1941.7(10)	7713(2)	727.6(12)	48.9(5)
O3	1253.6(8)	7164(2)	3751.5(9)	73.6(5)
C9	1211.7(11)	5894(2)	-26.4(11)	51.7(5)
C1	510.8(9)	9285(2)	1278.3(10)	46.6(5)
C21	1131.5(10)	5015(3)	3101.3(11)	49.2(5)
C5	425.6(11)	11779(2)	812.4(13)	61.5(6)
C6	569.6(9)	10267(2)	833.5(10)	46.7(5)
C4	222.1(15)	12311(3)	1232.0(14)	85.9(10)
C22	1548.8(11)	5971(3)	3744.2(11)	56.3(6)
C14	2210(1)	6385(3)	2757.6(12)	53.3(5)
C10	1730.6(11)	6724(3)	172.5(12)	54.5(5)
C18	1840.1(12)	8730(3)	2891.6(12)	60.2(6)
C15	2803.8(11)	6891(3)	3155.1(15)	73.5(8)
C3	165(2)	11367(4)	1670.9(18)	115.9(15)
C17	2445.5(17)	9195(3)	3305.5(15)	84.9(9)
C16	2918.9(13)	8270(4)	3428.9(15)	83.4(9)
C25	1527(4)	8549(11)	4246(4)	74(2)
C26	1397(4)	8323(10)	4793(4)	95(2)
C2	308.0(18)	9846(4)	1703.9(16)	92.5(11)
C24	1212(5)	9134(11)	4374(6)	113(4)
C23	1651(4)	7857(9)	4445(4)	62.5(17)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for z0223m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P1	40.0(3)	38.8(3)	28.3(2)	-0.03(18)	16.0(2)	-4.32(17)

O1	43.0(7)	59.5(9)	35.9(7)	-6.0(6)	15.6(6)	-5.9(6)
C19	40.9(9)	37.4(9)	28.7(8)	-2.0(7)	17.6(7)	-6.2(7)
F1	66.6(8)	93.3(11)	49.4(7)	-31.8(7)	31.3(6)	4.0(7)
C13	48.6(11)	42.7(10)	27.7(8)	-11.3(8)	18.1(8)	-1.7(7)
C11	48.7(11)	34.2(9)	38.0(9)	2.4(8)	21.1(8)	0.2(7)
C7	44.2(10)	30.3(8)	28.9(8)	4.9(7)	17.8(7)	2.2(7)
F2	82.9(10)	63.0(9)	64.0(9)	8.2(7)	32.4(8)	12.9(7)
C20	41.4(10)	49.9(11)	31.7(9)	-8.5(8)	18.3(8)	-6.5(8)
C8	50.7(11)	35.1(9)	32.3(9)	5.7(8)	18.7(8)	0.2(7)
O2	55.8(10)	117.2(16)	40.6(8)	-17.9(10)	12.9(8)	13.2(9)
C12	51.8(12)	45.8(11)	53.8(12)	6.8(9)	30.4(10)	11.0(9)
O3	63.1(10)	109.0(15)	54.5(10)	-24.7(10)	34.2(9)	-38.5(10)
C9	71.5(14)	48.2(11)	38.6(10)	12(1)	30.4(10)	-3.4(9)
C1	51.8(11)	46.5(11)	33.6(9)	10.9(9)	15.8(9)	-5.2(8)
C21	50.8(11)	58.2(12)	41.4(10)	-10(1)	25.4(9)	2.4(9)
C5	56.5(13)	41.4(11)	54.4(13)	8.3(10)	4.8(11)	-3.1(10)
C6	42.4(10)	41(1)	42.9(10)	4.5(8)	11.6(9)	-3.7(8)
C4	111(2)	57.4(15)	49.3(14)	37.8(15)	12.0(15)	-9.1(12)
C22	53.2(13)	88.2(17)	32.4(10)	-17.8(12)	25.2(10)	0.3(10)
C14	46.1(11)	49.1(12)	55.6(12)	-5.2(9)	19.1(10)	6.5(10)
C10	69.8(14)	59.2(13)	49.8(12)	16.2(11)	41.6(11)	8.7(10)
C18	74.8(15)	51.7(12)	53.3(12)	-19.7(11)	32.2(12)	-18.6(10)
C15	45.0(13)	76.4(17)	76.7(17)	-11.4(12)	14.5(12)	19.4(14)
C3	186(4)	99(2)	74.3(19)	78(3)	74(2)	3.2(18)
C17	111(2)	69.6(18)	68.0(17)	-53.1(18)	40.9(17)	-31.0(14)
C16	58.1(16)	95(2)	68.2(17)	-32.1(16)	11.4(14)	0.7(16)
C25	85(5)	85(6)	51(4)	-11(5)	34(4)	-23(4)
C26	104(5)	118(6)	84(4)	-47(5)	63(4)	-53(4)
C2	150(3)	83.3(19)	68.3(17)	57(2)	73(2)	15.9(14)
C24	107(6)	102(7)	102(7)	10(6)	33(6)	-56(6)
C23	67(4)	69(4)	45(4)	-14(4)	23(3)	-21(3)

Table 4 Bond Lengths for z0223m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.4691(14)	O3	C22	1.300(3)
P1	C19	1.8175(18)	O3	C25	1.552(8)
P1	C7	1.7892(18)	O3	C23	1.469(7)
P1	C1	1.796(2)	C9	C10	1.369(3)
C19	C13	1.479(2)	C1	C6	1.374(3)
C19	C20	1.315(3)	C1	C2	1.371(3)

F1	C21	1.363(2)	C21	C22	1.523(3)
C13	C14	1.367(3)	C5	C6	1.383(3)
C13	C18	1.374(3)	C5	C4	1.352(4)
C11	C7	1.383(3)	C4	C3	1.342(5)
C11	C12	1.374(3)	C14	C15	1.374(3)
C7	C8	1.383(2)	C18	C17	1.389(4)
F2	C21	1.347(3)	C15	C16	1.329(4)
C20	C21	1.487(3)	C3	C2	1.389(4)
C8	C9	1.376(3)	C17	C16	1.361(5)
O2	C22	1.176(3)	C25	C26	1.417(11)
C12	C10	1.373(3)	C24	C23	1.538(11)

Table 5 Bond Angles for z0223m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	P1	O1	110.97(8)	C2	C1	C6	118.2(2)
C7	P1	O1	112.74(8)	F2	C21	F1	105.72(18)
C7	P1	C19	106.73(8)	C20	C21	F1	108.40(16)
C1	P1	O1	113.70(9)	C20	C21	F2	109.65(17)
C1	P1	C19	105.88(8)	C22	C21	F1	106.26(16)
C1	P1	C7	106.31(9)	C22	C21	F2	107.06(19)
C13	C19	P1	120.14(13)	C22	C21	C20	118.96(19)
C20	C19	P1	115.25(14)	C4	C5	C6	120.0(3)
C20	C19	C13	124.47(17)	C5	C6	C1	121.0(2)
C14	C13	C19	119.76(17)	C3	C4	C5	119.7(2)
C18	C13	C19	121.5(2)	O3	C22	O2	126.6(2)
C18	C13	C14	118.7(2)	C21	C22	O2	123.9(3)
C12	C11	C7	120.20(18)	C21	C22	O3	109.47(19)
C11	C7	P1	123.71(14)	C15	C14	C13	121.2(2)
C8	C7	P1	116.83(14)	C9	C10	C12	120.25(19)
C8	C7	C11	119.35(17)	C17	C18	C13	118.7(3)
C21	C20	C19	125.35(17)	C16	C15	C14	120.4(3)
C9	C8	C7	120.04(19)	C2	C3	C4	121.4(3)
C10	C12	C11	120.0(2)	C16	C17	C18	121.2(3)
C25	O3	C22	126.8(4)	C17	C16	C15	119.8(2)
C10	C9	C8	120.15(19)	C26	C25	O3	105.8(6)
C6	C1	P1	122.02(15)	C3	C2	C1	119.7(3)
C2	C1	P1	119.6(2)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for z0223m.

Atom	*x*	*y*	*z*	U(eq)

H11	1777.4(9)	8535(2)	1463.9(10)	48.9(5)
H20	433.2(9)	5437(2)	2070.2(9)	49.4(5)
H8	541.9(9)	5493(2)	187.6(9)	48.6(5)
H12	2295(1)	8273(2)	861.9(12)	58.7(6)
H9	1072.9(11)	5218(2)	-399.5(11)	62.0(6)
H5	468.8(11)	12429(2)	509.4(13)	73.8(8)
H6	708.3(9)	9909(2)	542.3(10)	56.0(6)
H4	122.6(15)	13325(3)	1216.4(14)	103.0(12)
H14	2136.9(10)	5409(3)	2578.5(12)	64.0(6)
H10	1940.9(11)	6618(3)	-69.3(12)	65.4(7)
H18	1518.9(12)	9378(3)	2799.7(12)	72.2(7)
H15	3126.9(11)	6264(3)	3232.9(15)	88.2(9)
H3	26(2)	11740(4)	1959.4(18)	139.1(18)
H17	2528.8(17)	10157(3)	3501.7(15)	101.8(11)
H16	3321.6(13)	8602(4)	3704.0(15)	100.1(11)
H25a	1967(4)	8610(11)	4437(4)	89(3)
H25b	1339(4)	9475(11)	3993(4)	89(3)
H26a	962(4)	8230(60)	4594(4)	142(3)
H26b	1600(20)	7420(30)	5047(17)	142(3)
H26c	1540(20)	9170(30)	5109(16)	142(3)
H2	266.7(18)	9211(4)	2013.1(16)	111.0(13)
H24a	1110(30)	9730(50)	3960(20)	170(5)
H24b	845(15)	8709(12)	4330(40)	170(5)
H24c	1407(14)	9760(50)	4780(20)	170(5)
H23a	1739(4)	7175(9)	4829(4)	75(2)
H23b	2031(4)	8236(9)	4496(4)	75(2)

Table 7 Atomic Occupancy for z0223m.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C25	0.500000	H25a	0.500000	H25b	0.500000
C26	0.550000	H26a	0.550000	H26b	0.550000
H26c	0.550000	C24	0.450000	H24a	0.450000
H24b	0.450000	H24c	0.450000	C23	0.500000
H23a	0.500000	H23b	0.500000		

z0223m

Table 1 Crystal data and structure refinement for z0223m.

Identification code	z0223m
Empirical formula	$C_{24}H_{21}F_2O_3P$
Formula weight	426.40
Temperature/K	100

Crystal system	monoclinic
Space group	C2/c
a/Å	25.317(4)
b/Å	8.8649(15)
c/Å	22.042(4)
α/°	90
β/°	120.571(2)
γ/°	90
Volume/Å^3	4259.4(12)
Z	8
ρ_{calc}g/cm^3	1.3298
μ/mm^{-1}	0.169
F(000)	1777.9
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.74 to 52
Index ranges	-33 ≤ h ≤ 32, -12 ≤ k ≤ 11, -28 ≤ l ≤ 28
Reflections collected	17795
Independent reflections	4161 [R_{int} = 0.0330, R_{sigma} = 0.0431]
Data/restraints/parameters	4161/0/291
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1296
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.1347
Largest diff. peak/hole / e Å^{-3}	0.28/-0.27