Supplementary Materials: Palladium-Catalyzed Isomerization-Coupling Reactions of Allyl Chloride with Amines to Generate Functionalized Phosphorus Derivatives

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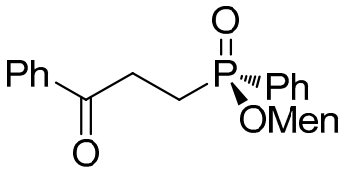
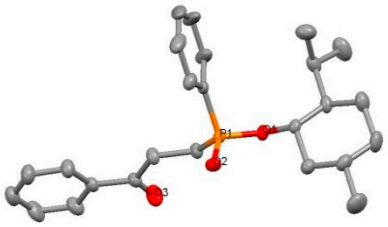
General Chemistry:

The ^{1}H NMR spectrum was recorded on a 400-MHz spectrometer. The chemical shift for ^{1}H NMR spectra is reported (in parts per million) relative to internal tetramethylsilane (Me_4Si, δ = 0.00 ppm) with $CDCl_3$. ^{13}C NMR spectra were recorded at 101 mHz. Chemical shifts for ^{13}C NMR spectra are reported (in parts per million) relative to $CDCl_3$ (δ = 77.0 ppm). ^{31}P NMR spectra were recorded at 162 MHz, and chemical shifts are reported (in parts per million) relative to external 85% phosphoric acid (δ = 0.0 ppm). TLC plates were visualized by UV. All starting materials were purchased from commercial sources and used as received. The solvents were distilled under N_2 and dried according to standard procedures. ^{31}P NMR spectra were referenced to phosphoric acid. The NMR yields of the articles are determined by integration of all of the resonances in the ^{31}P spectra. The yields obtained by the approach are generally accurate and reproducible.

Part 1. Crystallographic Information.

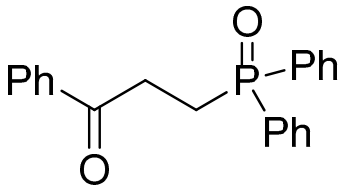
Table S1. (*S*P)-menthxyl 3-oxo-3-phenylpropyl phenylphosphinate, 5a

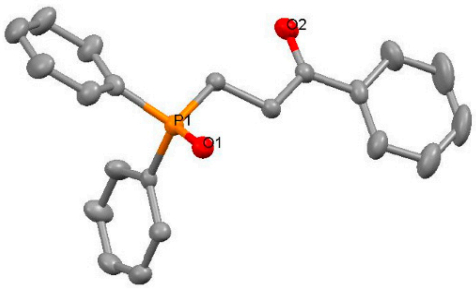




Empirical formula	$C_{25}H_{33}O_3P$
Crystal system	Orthorhombic
Space group	P212121
Formula weight	412.48
a, Å	8.4732(9)
b, Å	11.1296(11)
c, Å	25.186(3)
α, deg	90
β, deg	90
γ, deg	90
V, Å3	2375.1(4)
Z	4
T, K	293(2)
λ, Å	0.71073
ϱ, g cm−3	1.154
Rint	0.0331
R1 [I N 2σ(I)]	0.0425
R1 (all data)	0.0645
wR2 [I N 2σ(I)]	0.0931
wR2 (all data)	0.1029
Flack	-0.02(11)
CCDC	1575335

Table S2. Diphenyl 3-oxo-3-phenyl propylphosphonate, 5f





Empirical formula	$C_{21}H_{19}O_3P$
Crystal system	Monoclinic
Space group	P21
Formula weight	334.33
a, Å	9.4304(7)
b, Å	19.0866(16)
c, Å	10.2263(8)
α, deg	90
β, deg	102.868(3)
γ, deg	90
V, Å3	1794.4(2)
Z	2
T, K	298(2)
λ, Å	0.71073
ϱ, g cm−3	1.238
Rint	0.0478
R1 [I N 2σ(I)]	0.0480
R1 (all data)	0.1024
wR2 [I N 2σ(I)]	0.0724
wR2 (all data)	0.0851
Flack	0.00(10)
CCDC	1575336

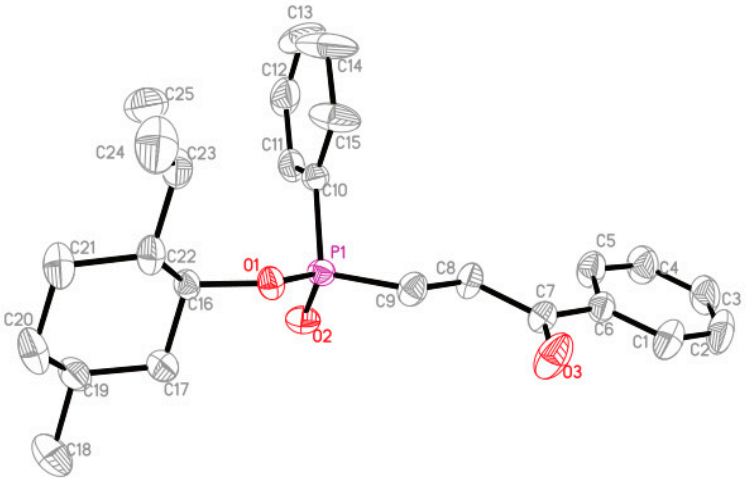


Figure S3. ORTEP drawing of **5a** with thermal ellipsoids at the 50% probability.

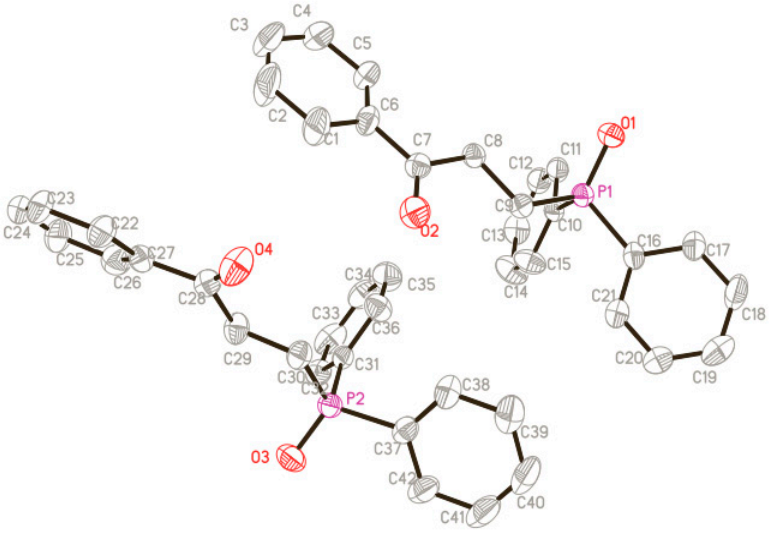
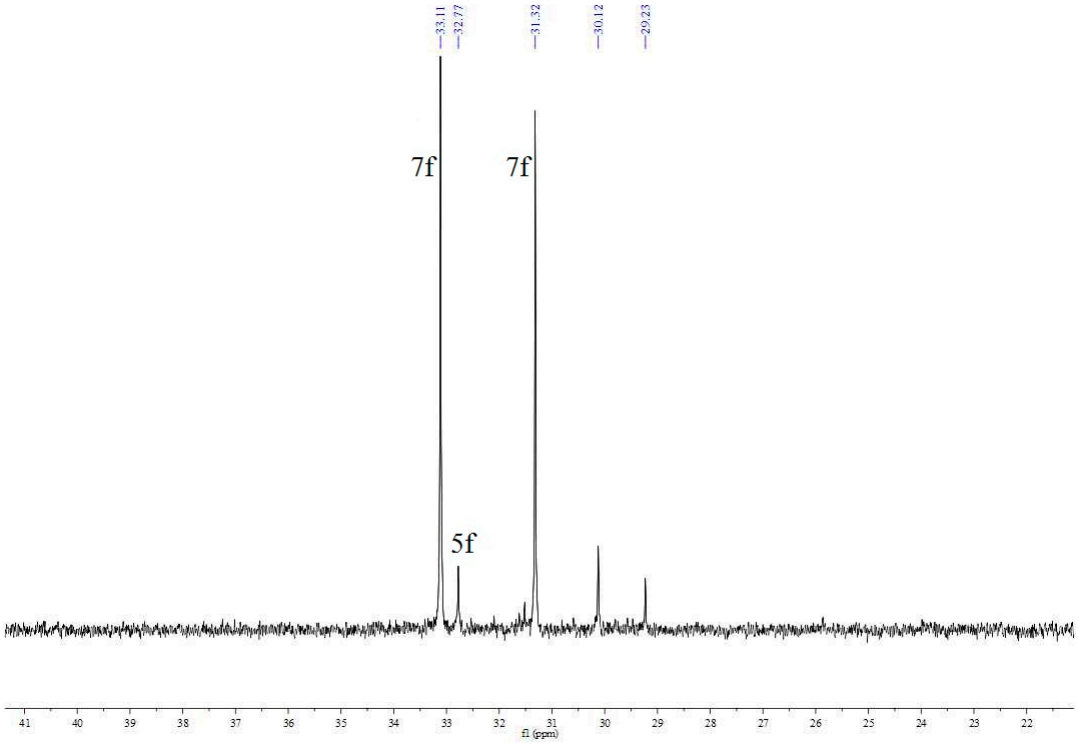


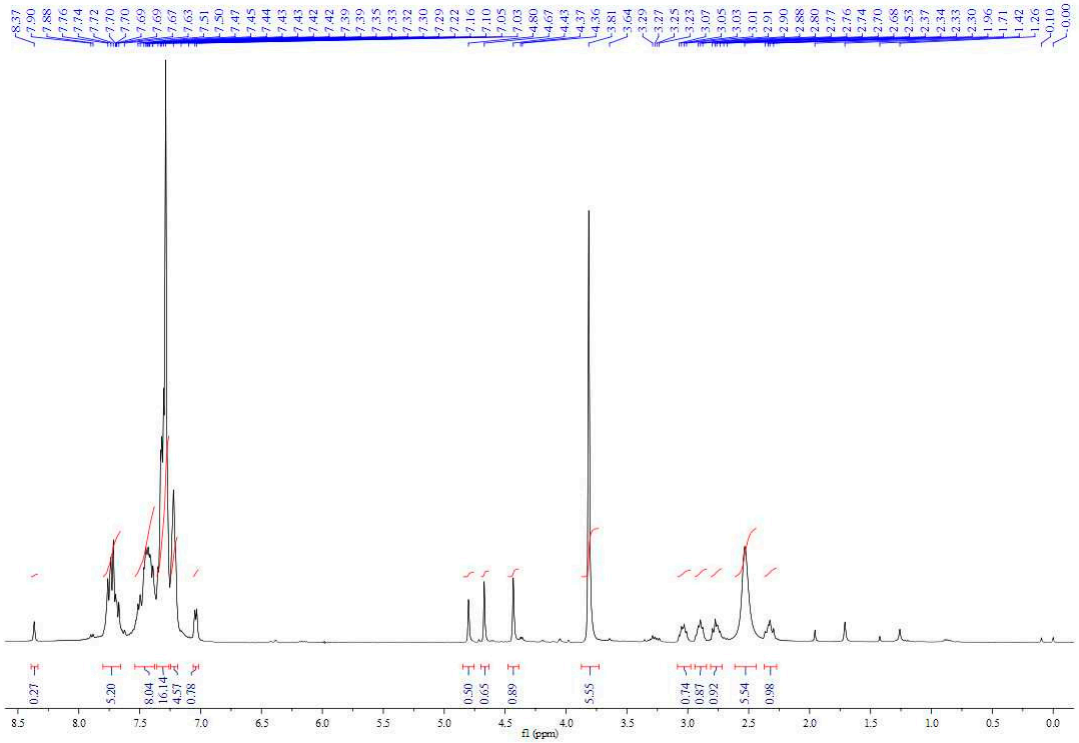
Figure S4. ORTEP drawing of **5f** with thermal ellipsoids at the 50% probability.

Part 2. The NMR spectrum for the mechanism of 1f with benzyl amine.

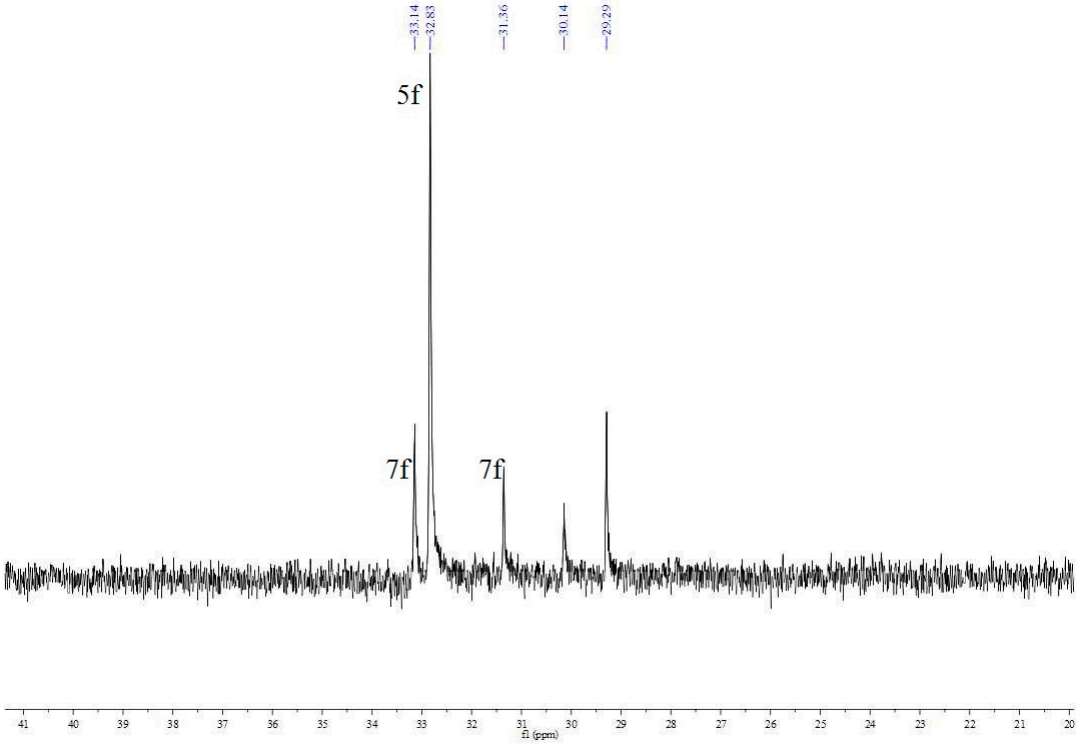
^{31}P-NMR spectroscopy of crude 7f/5f=93:7



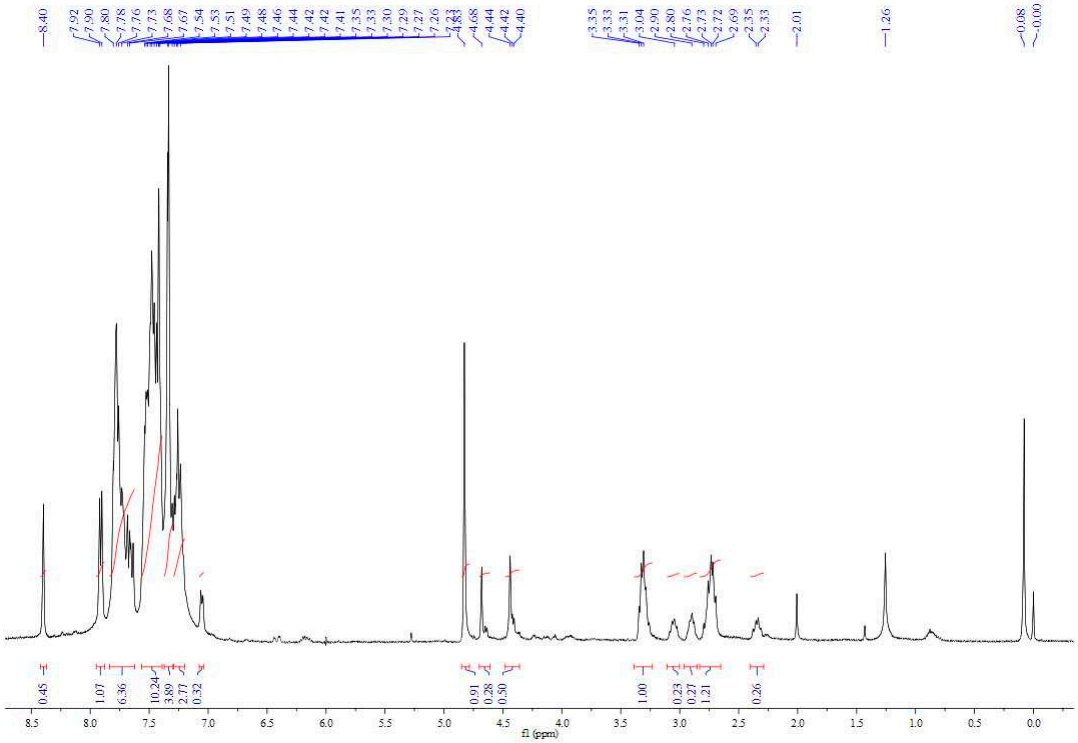
^{1}H-NMR spectroscopy of crude 7f/5f



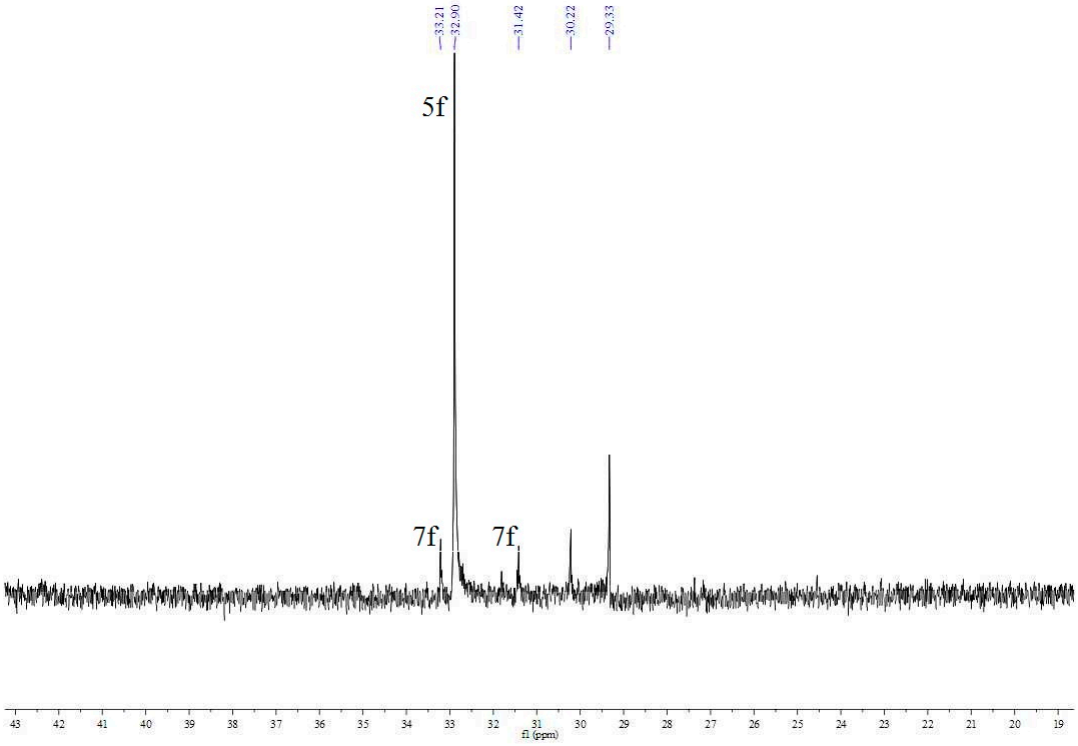
^{31}P-NMR spectroscopy of crude 7f/5f=30:70



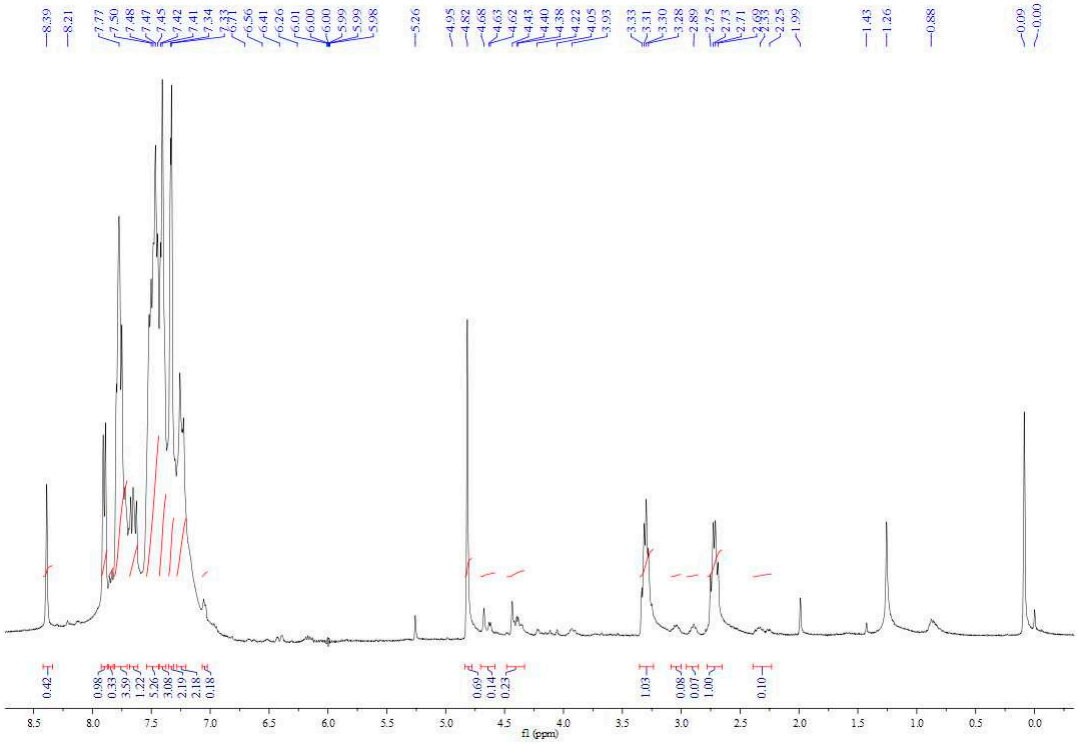
^{1}H-NMR spectroscopy of crude 7f/5f



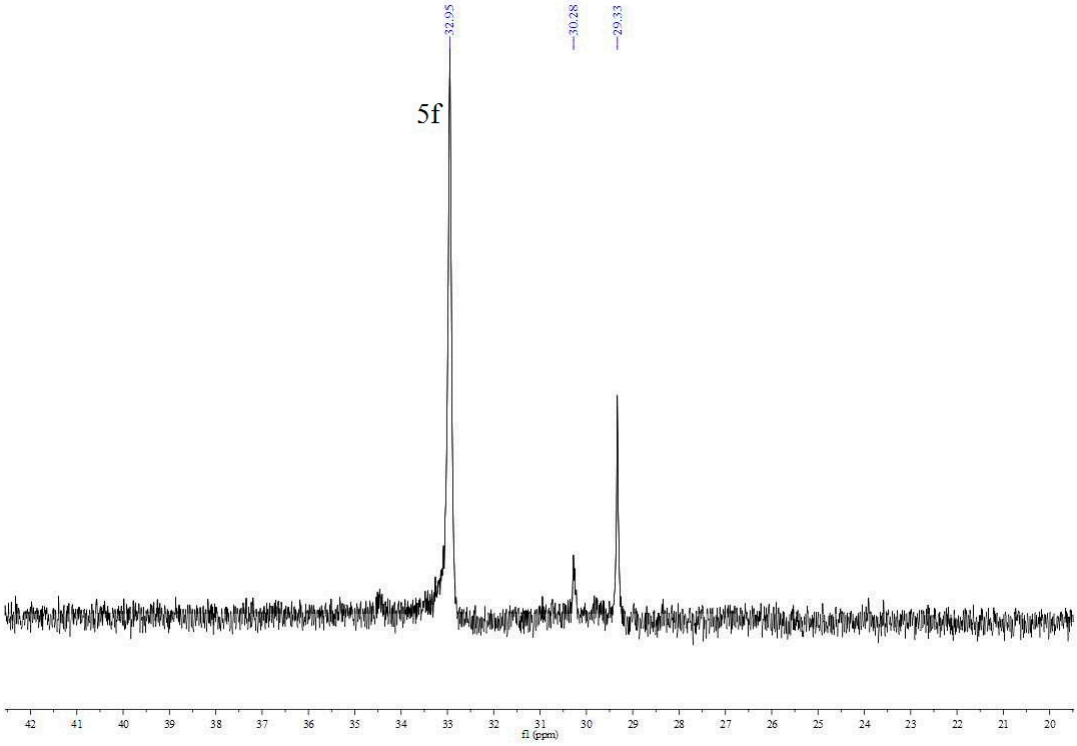
^{31}P-NMR spectroscopy of crude 7f/5f=10:90



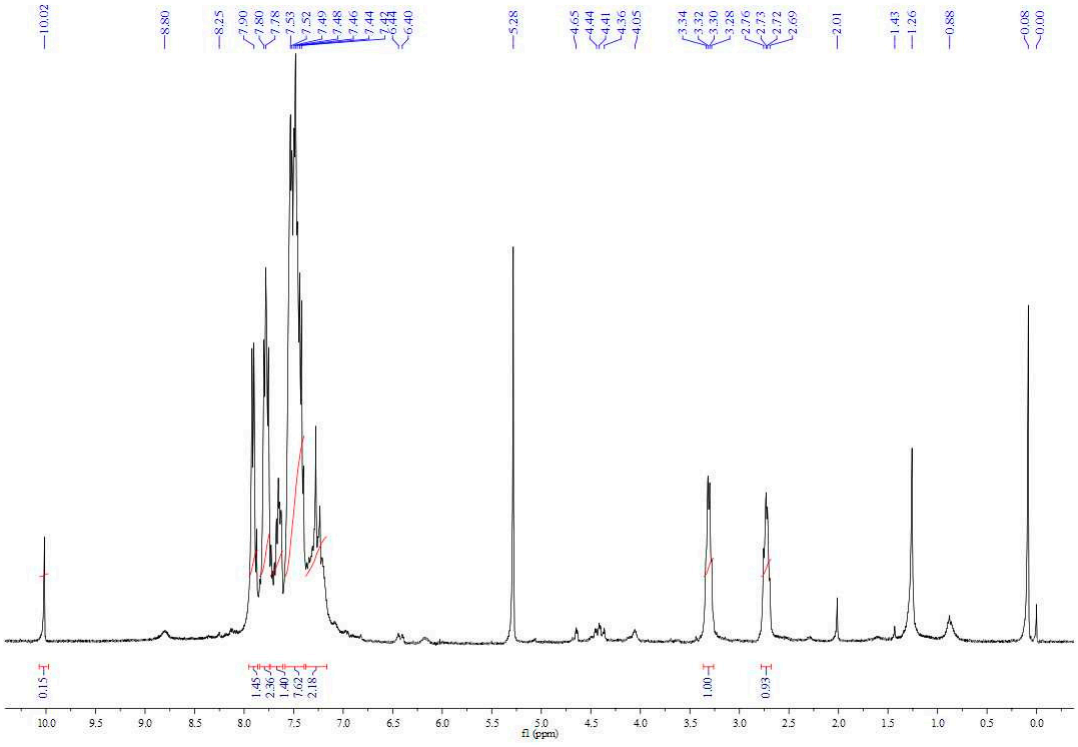
^{1}H-NMR spectroscopy of crude 7f/5f



^{31}P-NMR spectroscopy of crude 5f

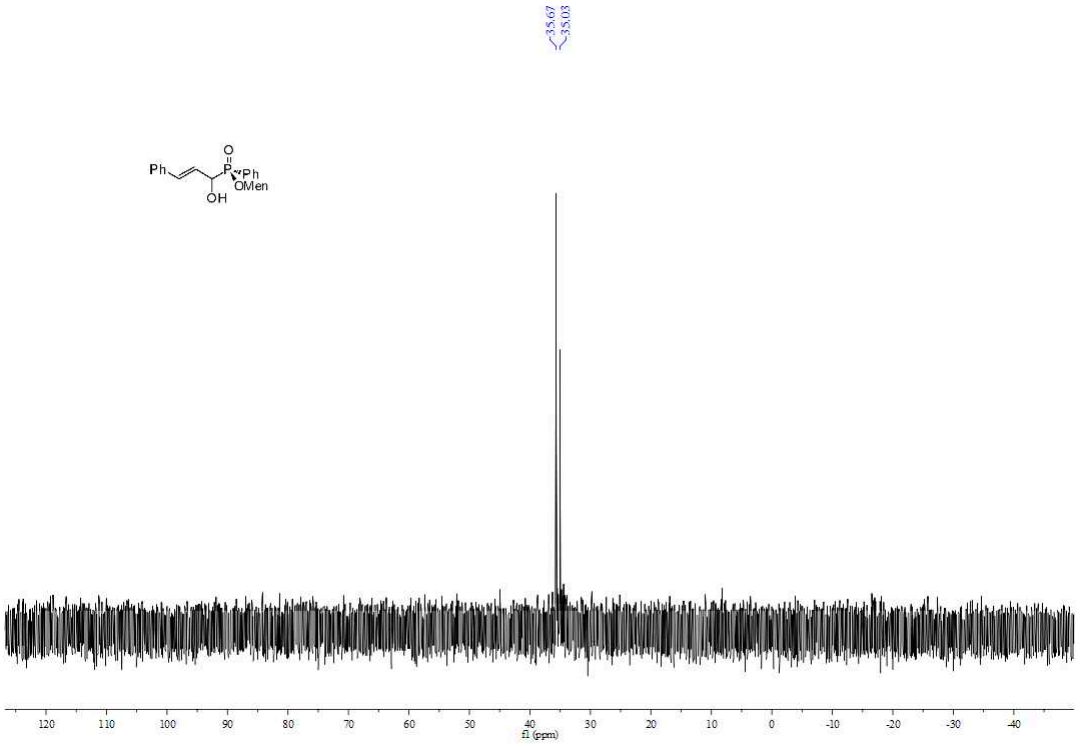


^{1}H-NMR spectroscopy of crude 5f

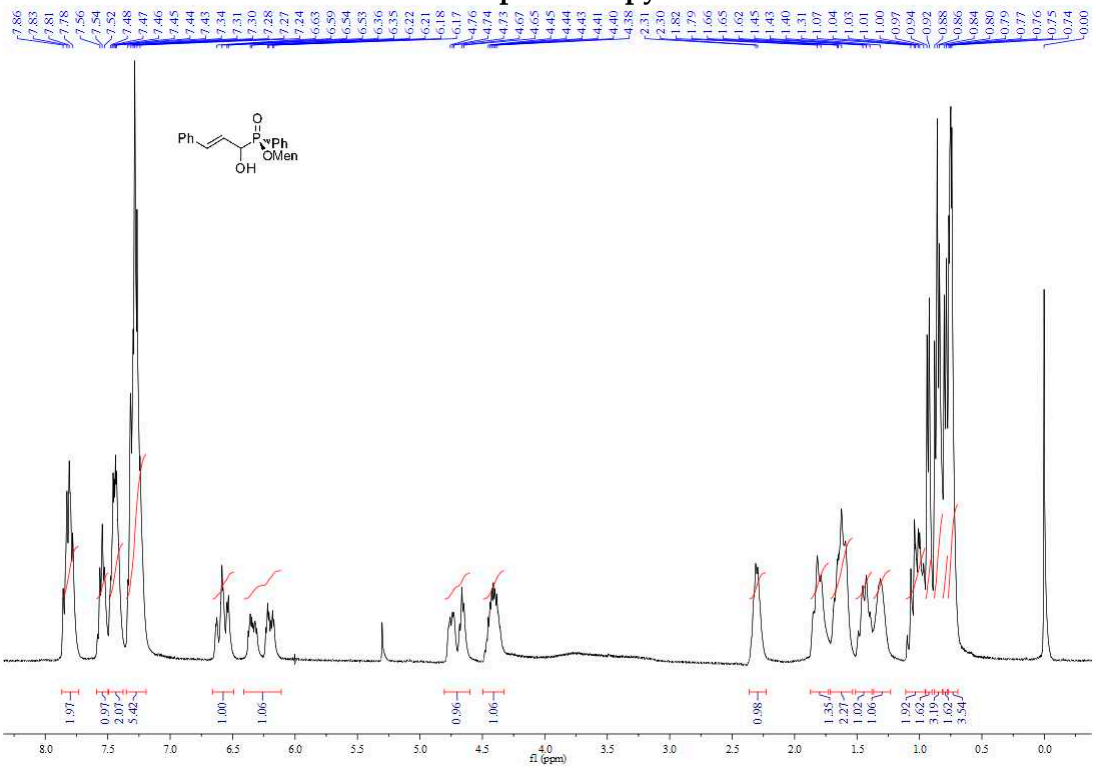


Part 3. Selected 31P, 1H and 13C NMR spectroscopy of 1, 2, 4, 5, 11, 12 and 13.

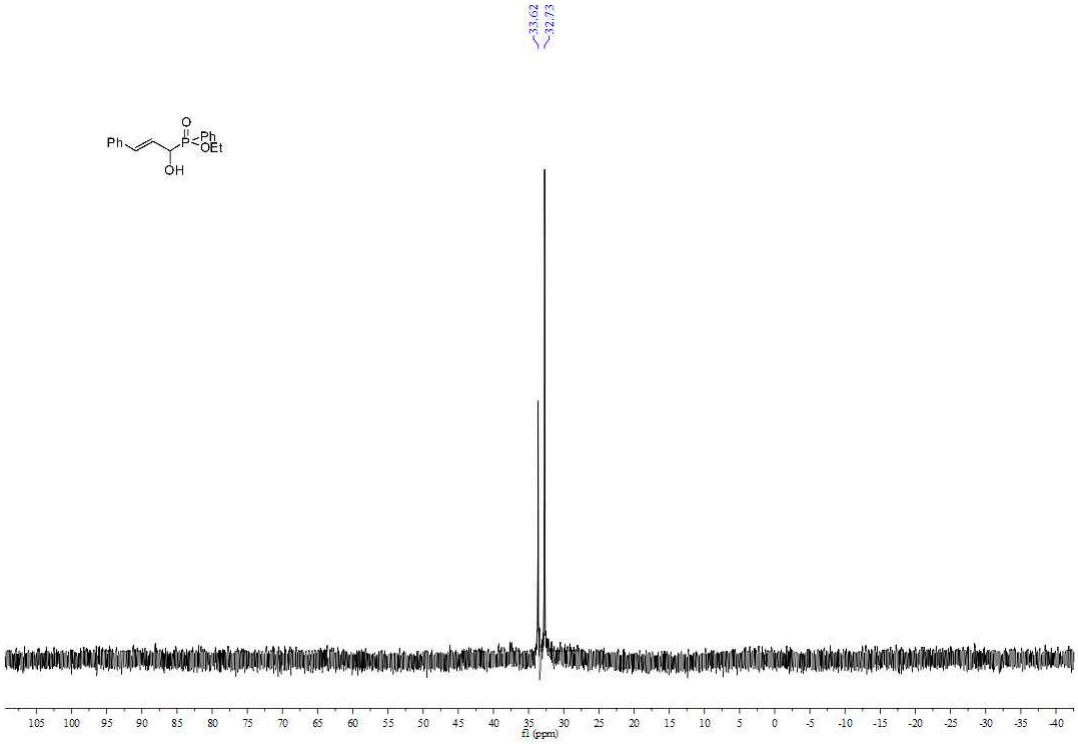
(*S*P)-Menthyl-1-hydroxy-3-phenylallyl phenylphosphinate, 2a, ^{31}P NMR spectroscopy



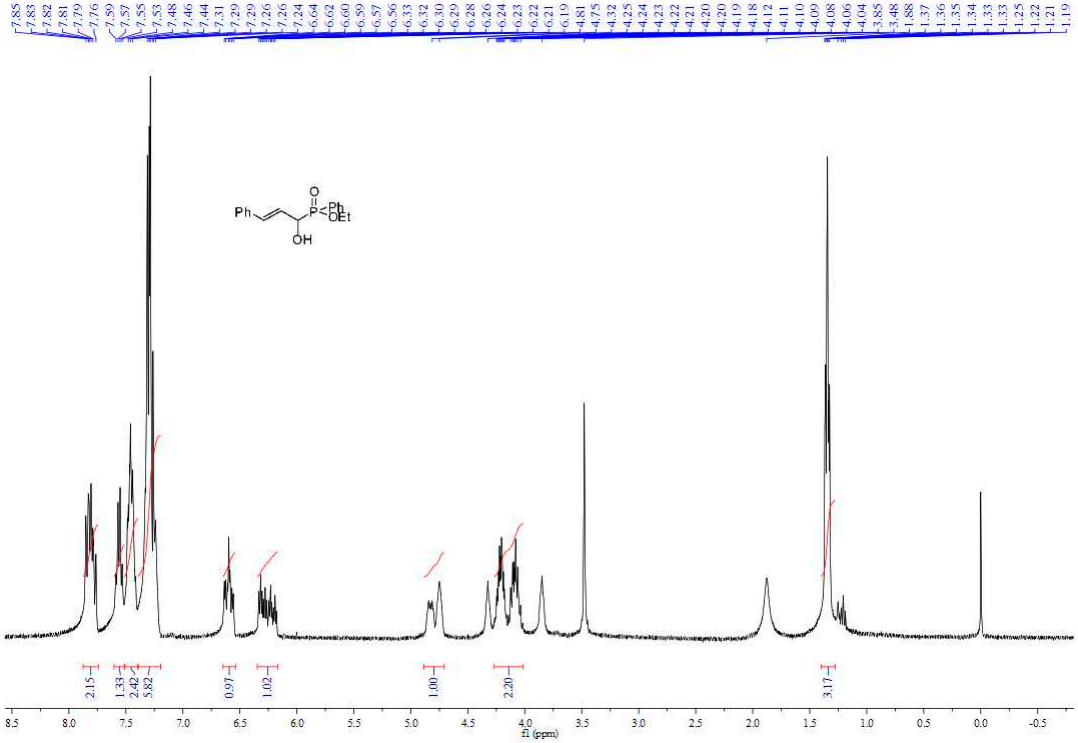
^{1}H NMR spectroscopy of 2a



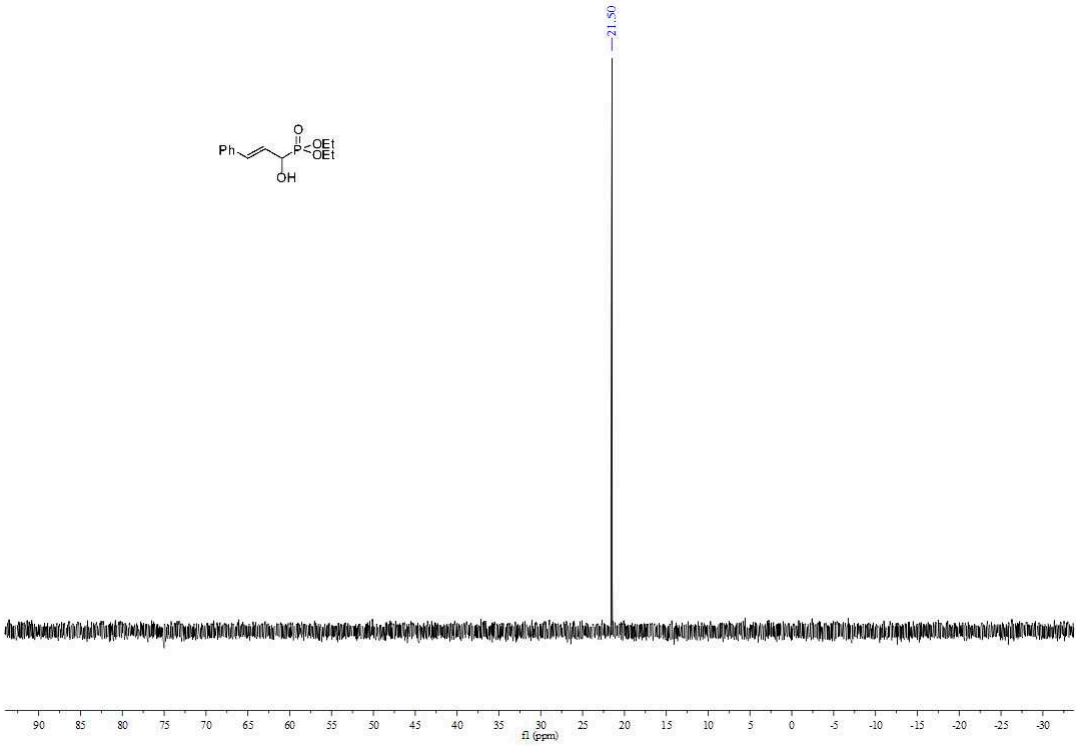
Ethyl 1-hydroxy-3-phenylallyl phenylphosphinate, 2b, 31P NMR spectroscopy



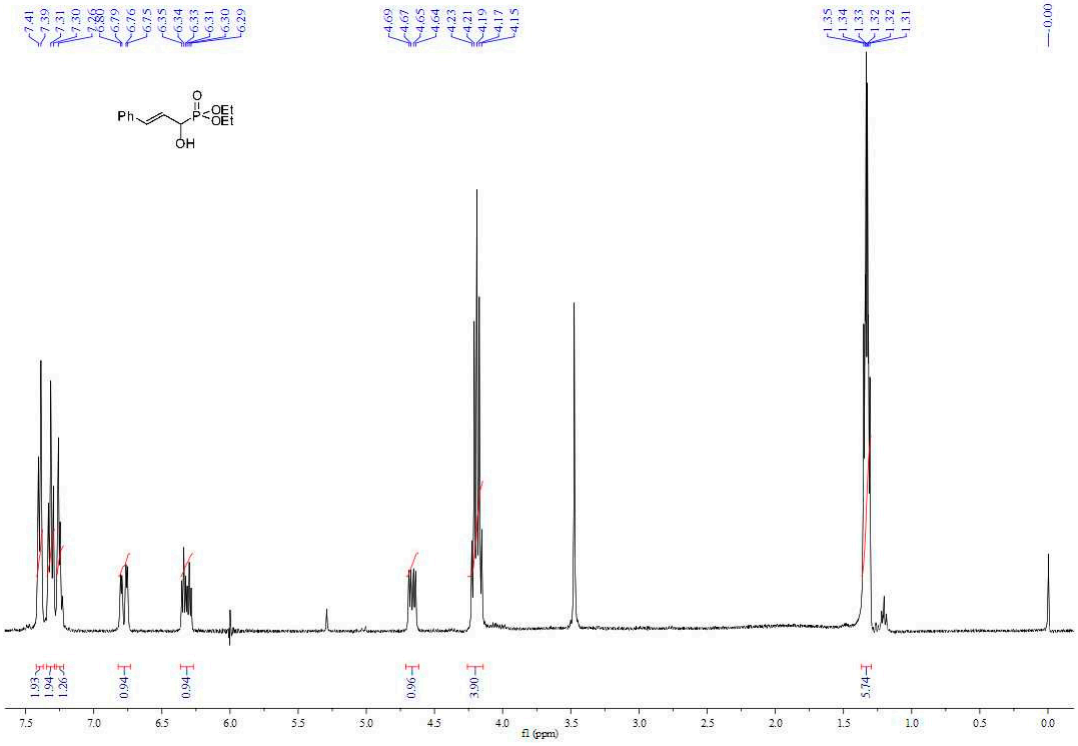
^{1}H NMR spectroscopy of 2b



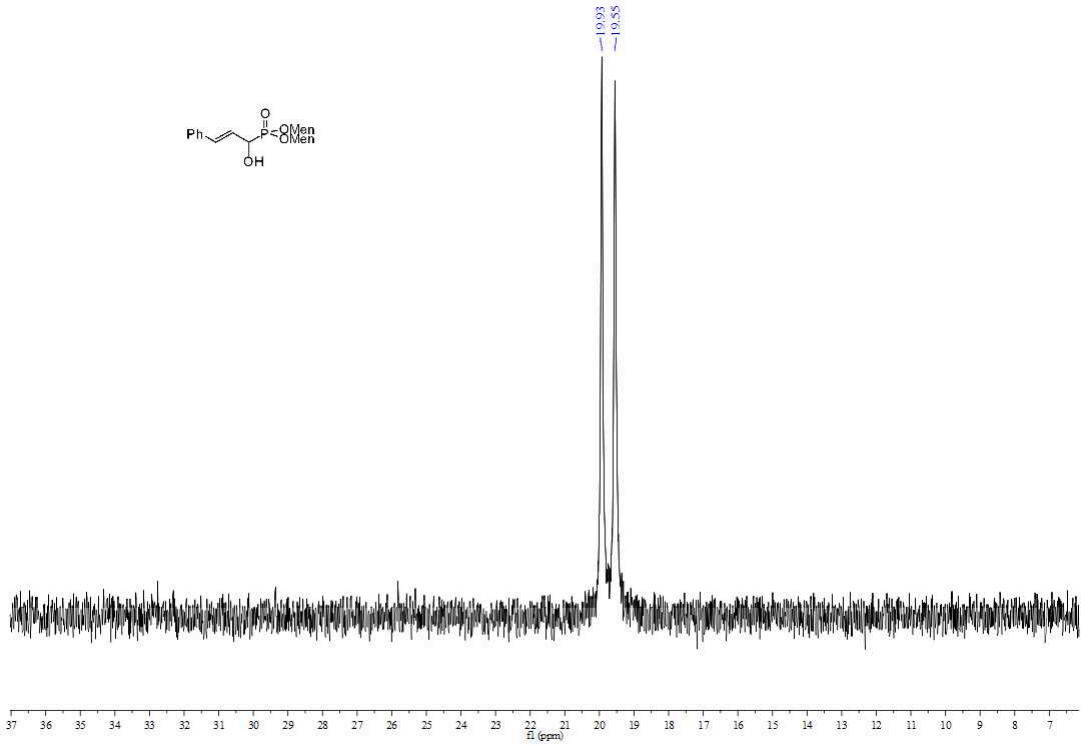
Diethyl 1-hydroxy-3-phenylallylphosphonate, 2c, 31P NMR spectroscopy



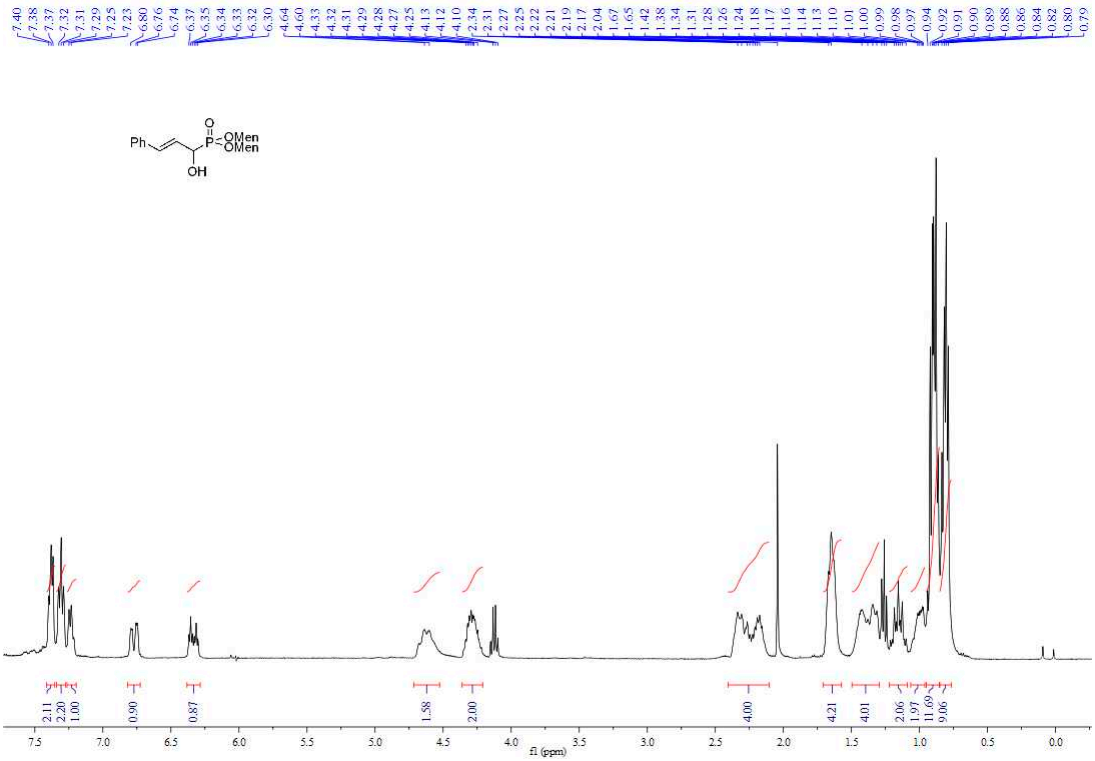
^{1}H NMR spectroscopy of 2c



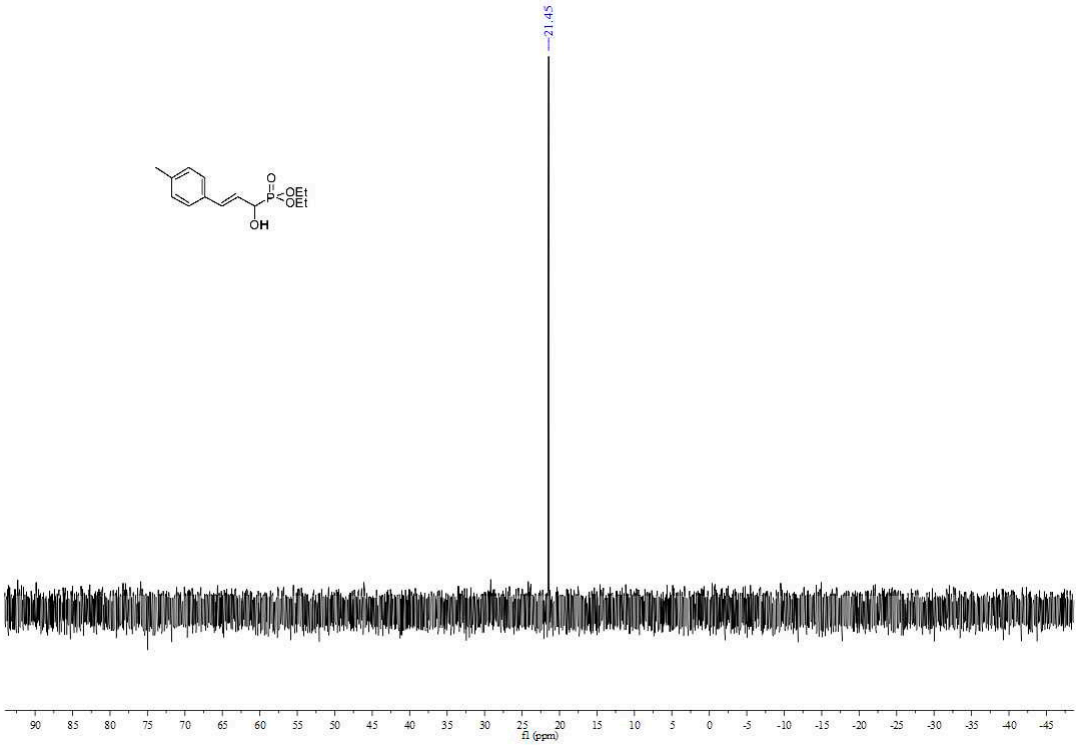
Dimenthyl 1-hydroxy-3-phenylallylphosphonate, 2d, 31P NMR spectroscopy



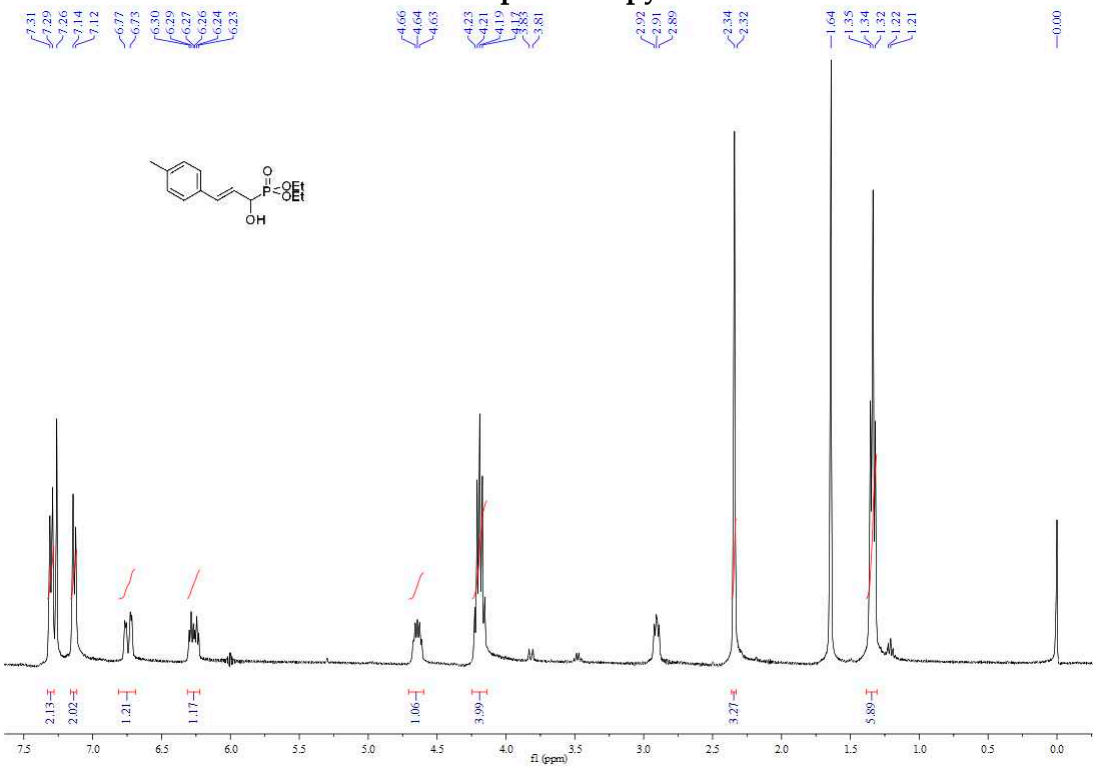
^{1}H NMR spectroscopy of 2d



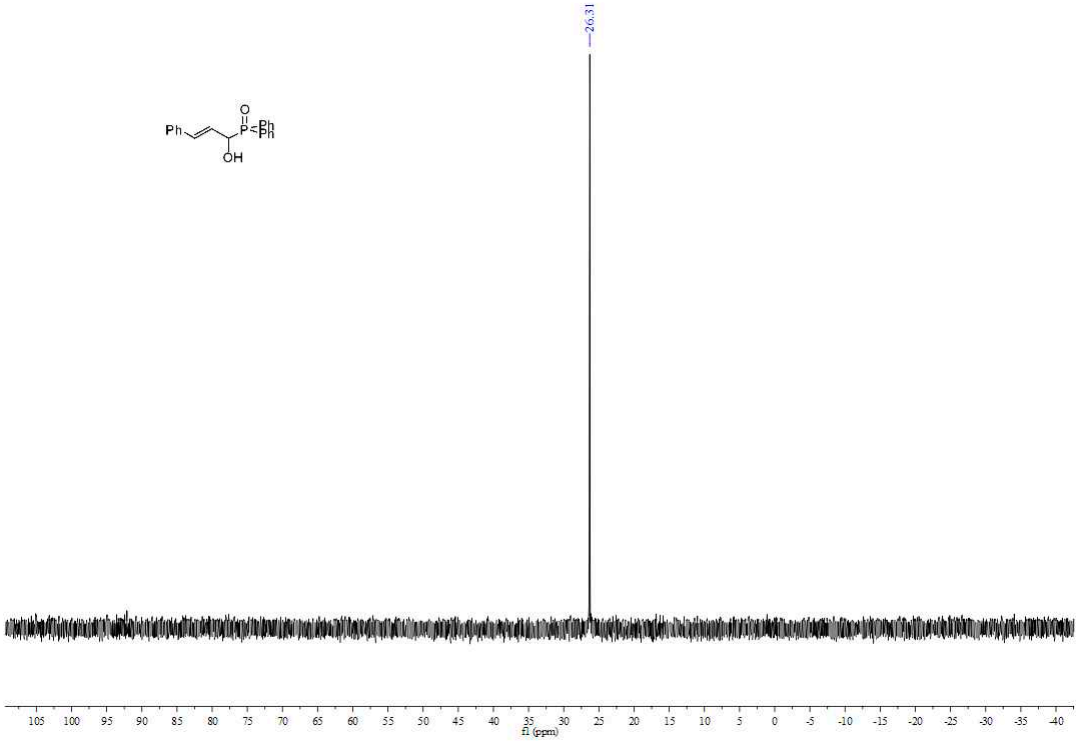
Diethyl 1-hydroxy-3-p-tolyl allylphosphonate, 2e, 31P NMR spectroscopy



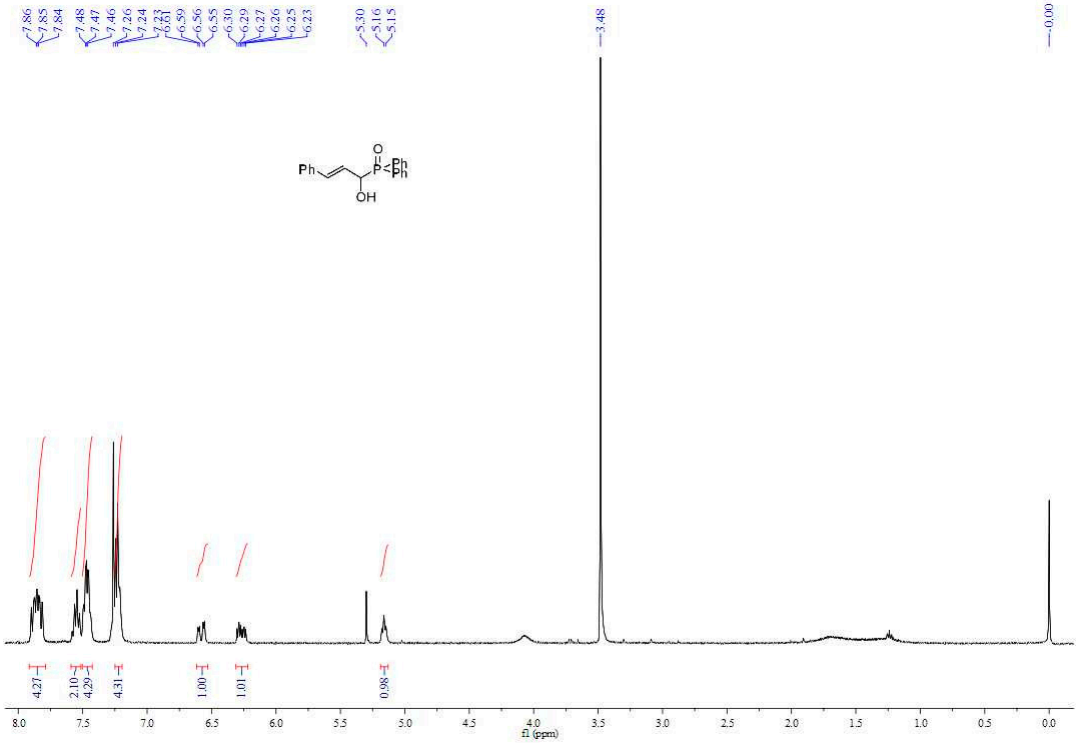
^{1}H NMR spectroscopy of 2e



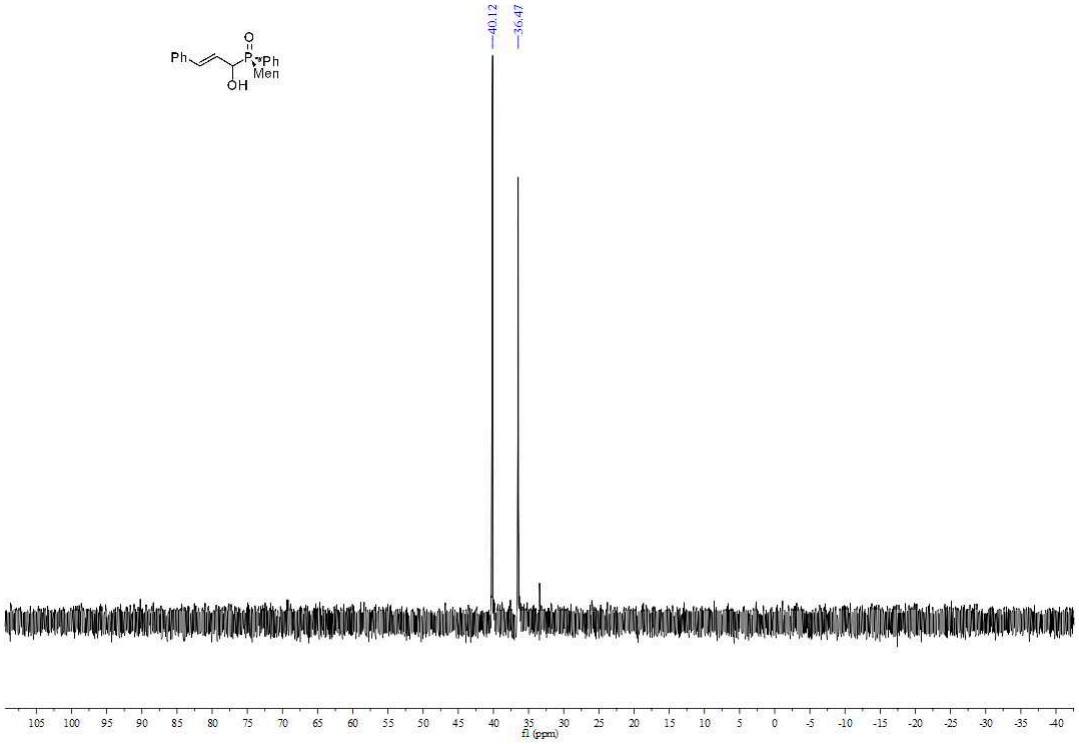
Diphenyl 1-hydroxy-3-phenylallylphosphine oxide, 2f, 31P NMR spectroscopy



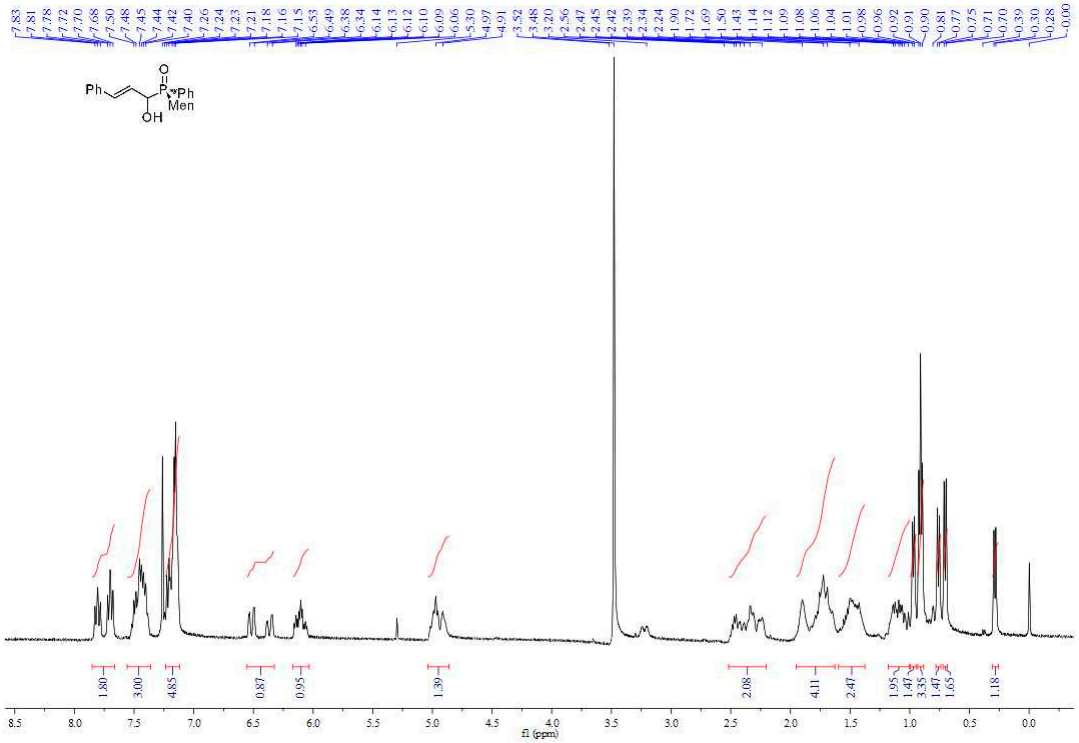
^{1}H NMR spectroscopy of 2f



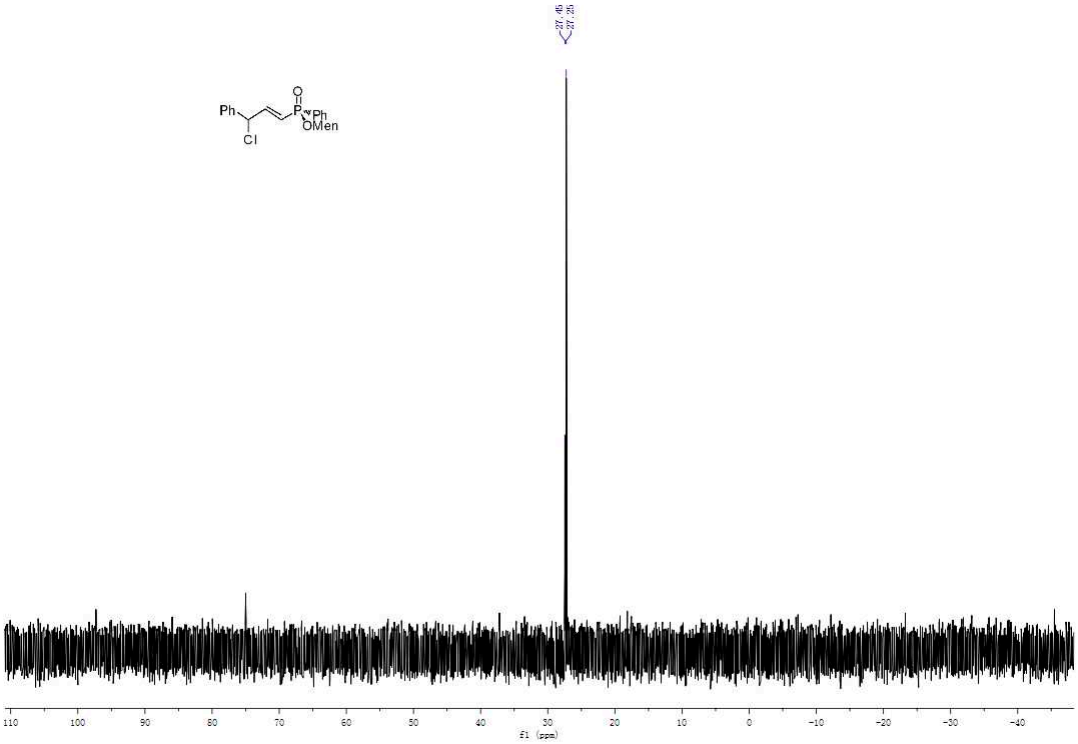
(*S*P)-Menthyl 1-hydroxy-3-phenylallylphenylphosphine oxide, 2g, ^{31}P NMR spectroscopy



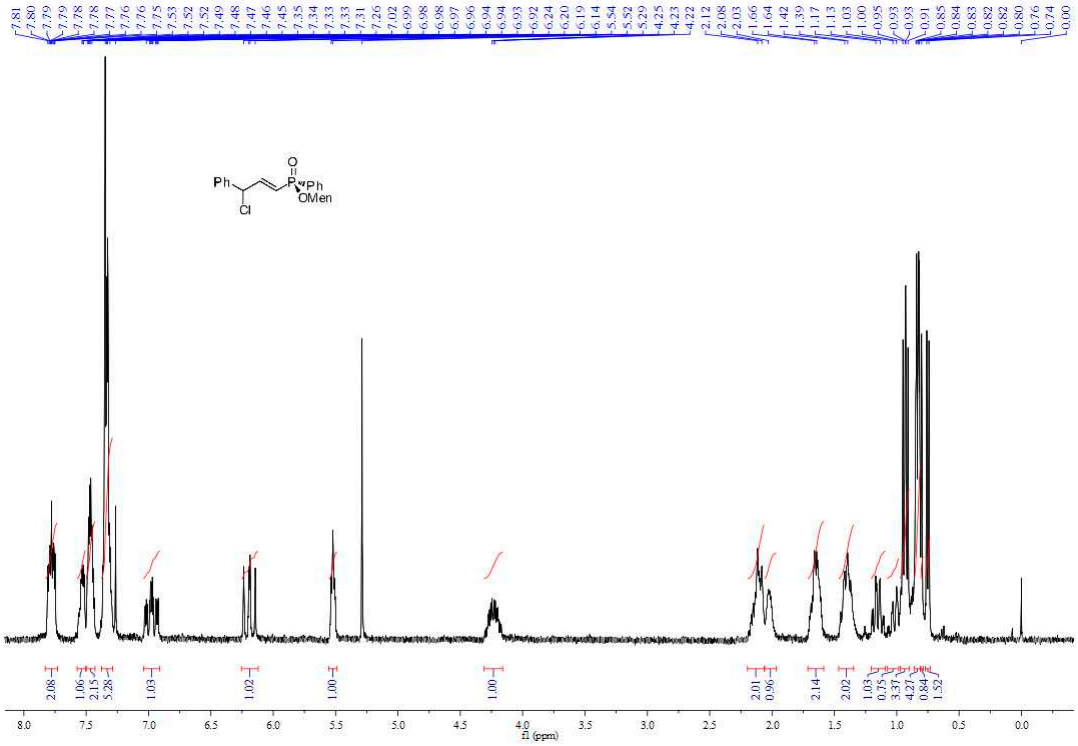
^{1}H NMR spectroscopy of 2g



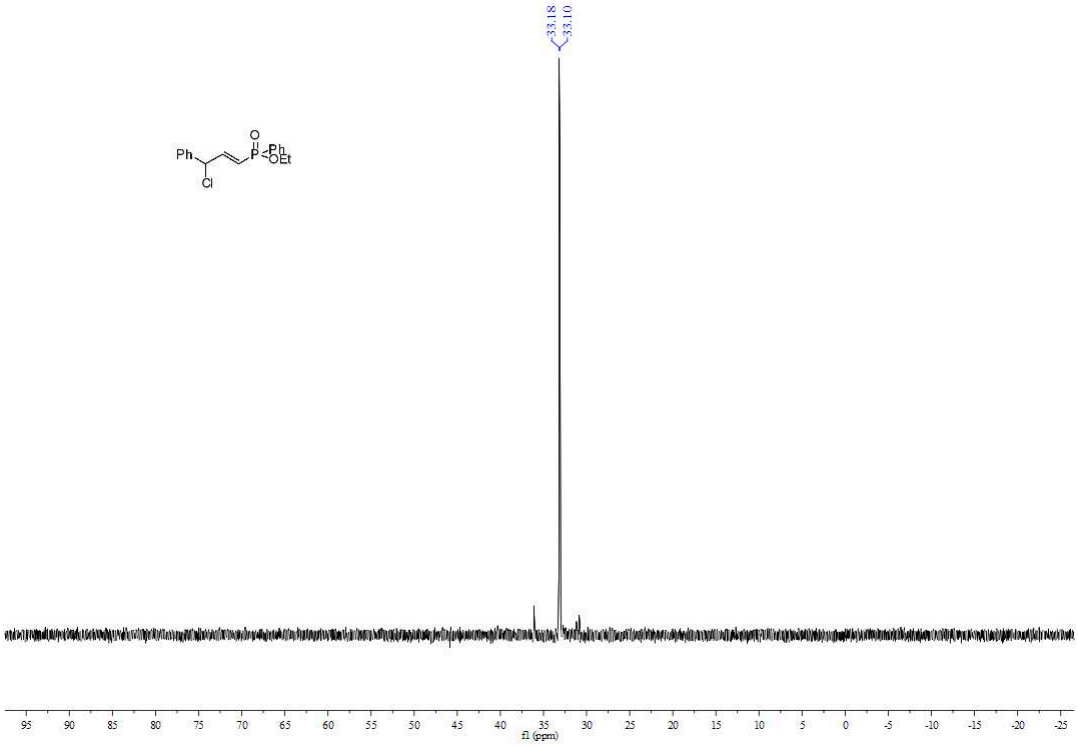
(*S*P)-Menthyl 3-chloro-3-phenylprop-1-en-1-ylphenylphosphinate, 1a, ^{31}P NMR spectroscopy



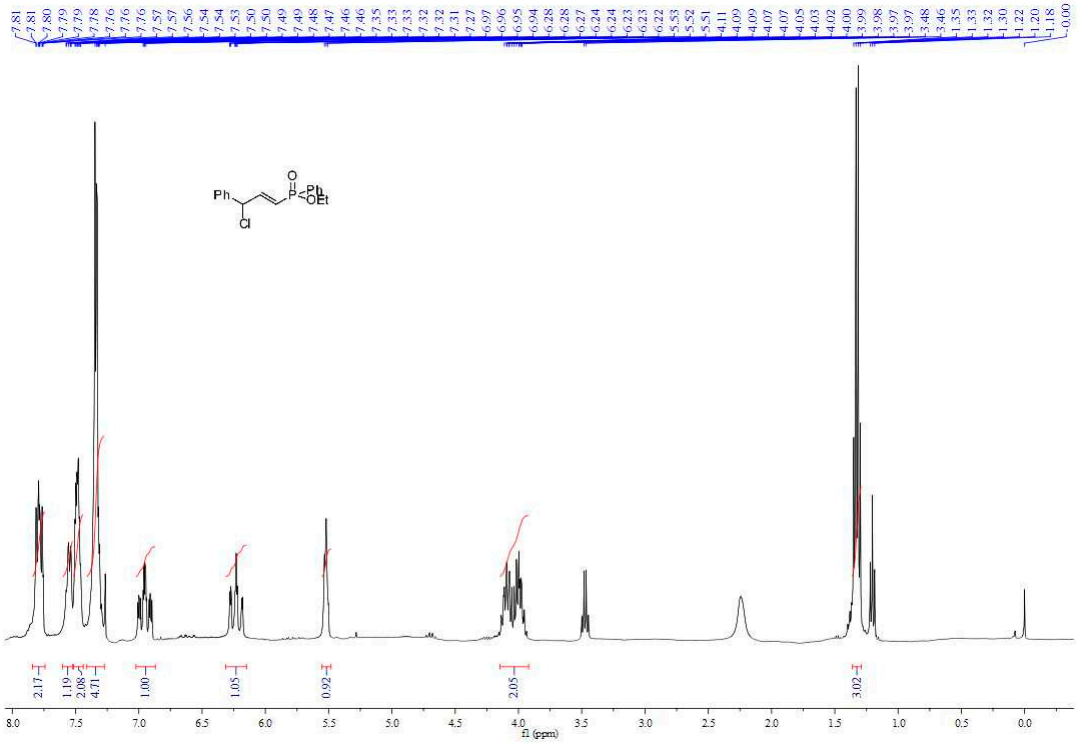
^{1}H NMR spectroscopy of 1a



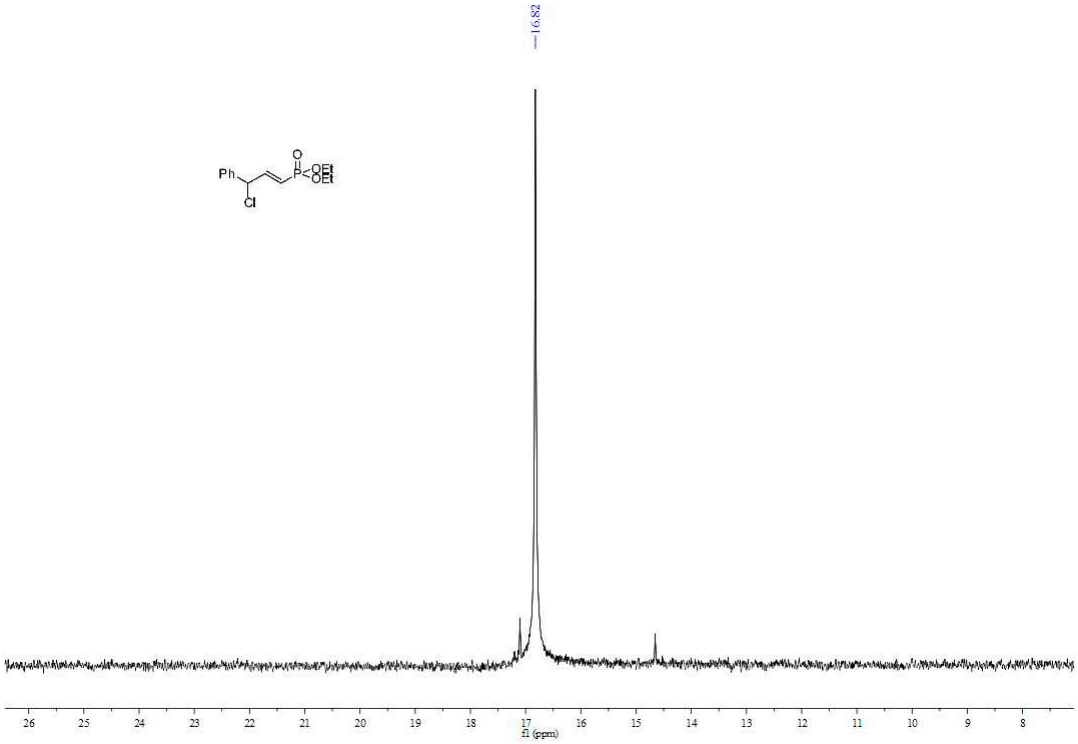
Ethyl 3-chloro-3-phenylprop-1-en-1-ylphenylphosphinate, 1b, 31P NMR spectroscopy



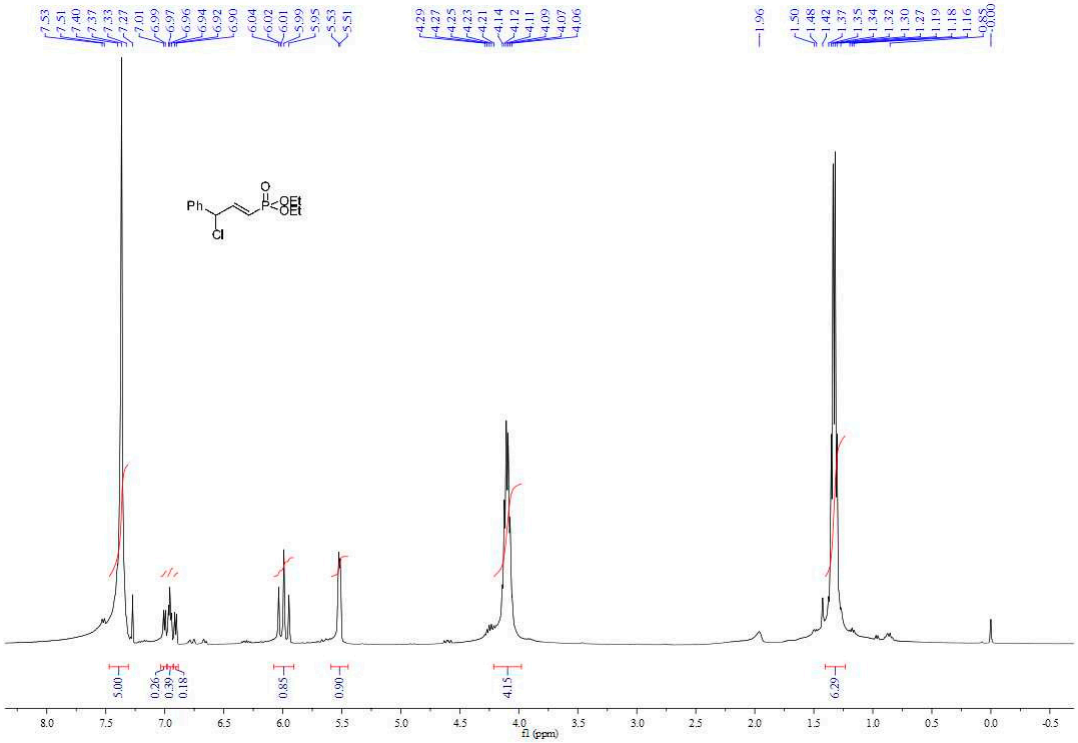
^{1}H NMR spectroscopy of 1b



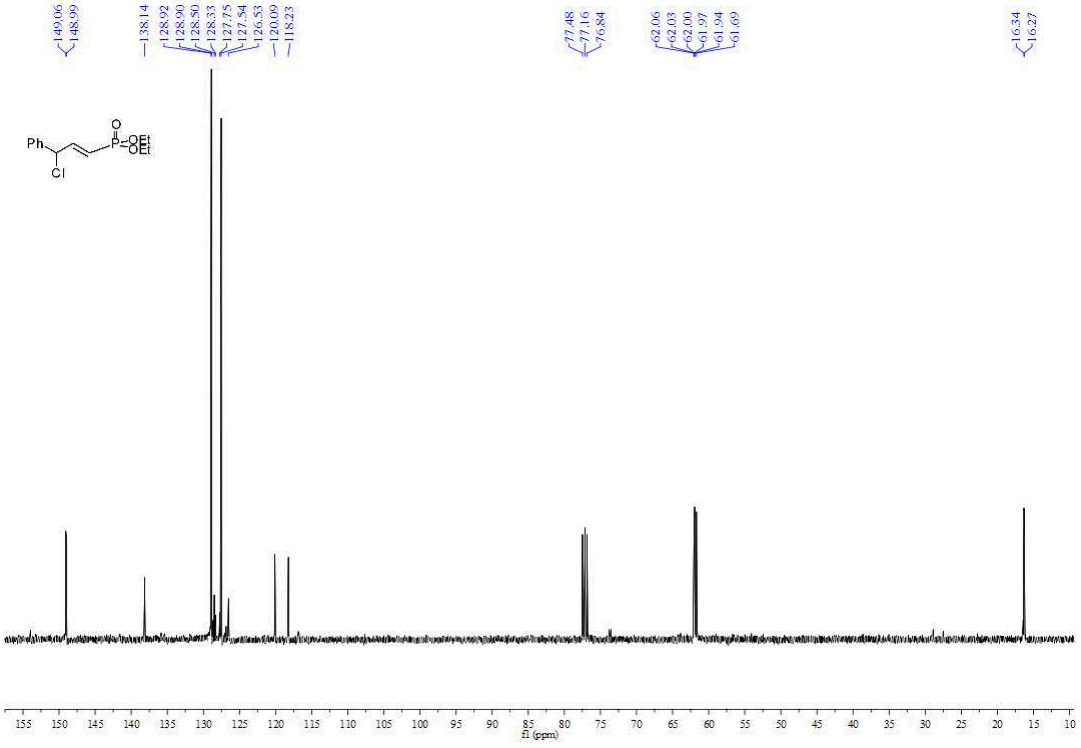
Diethyl 3-chloro-3-phenylprop-1-en-1-ylphosphonate, 1c, 31P NMR spectroscopy



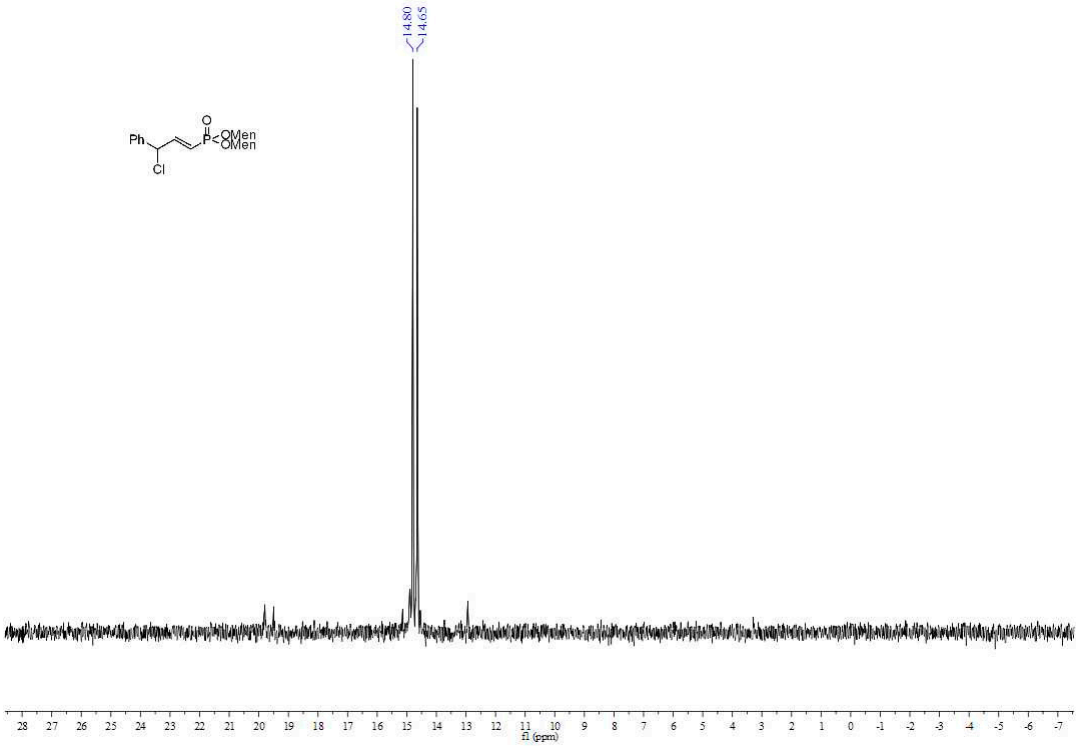
^{1}H NMR spectroscopy of 1c



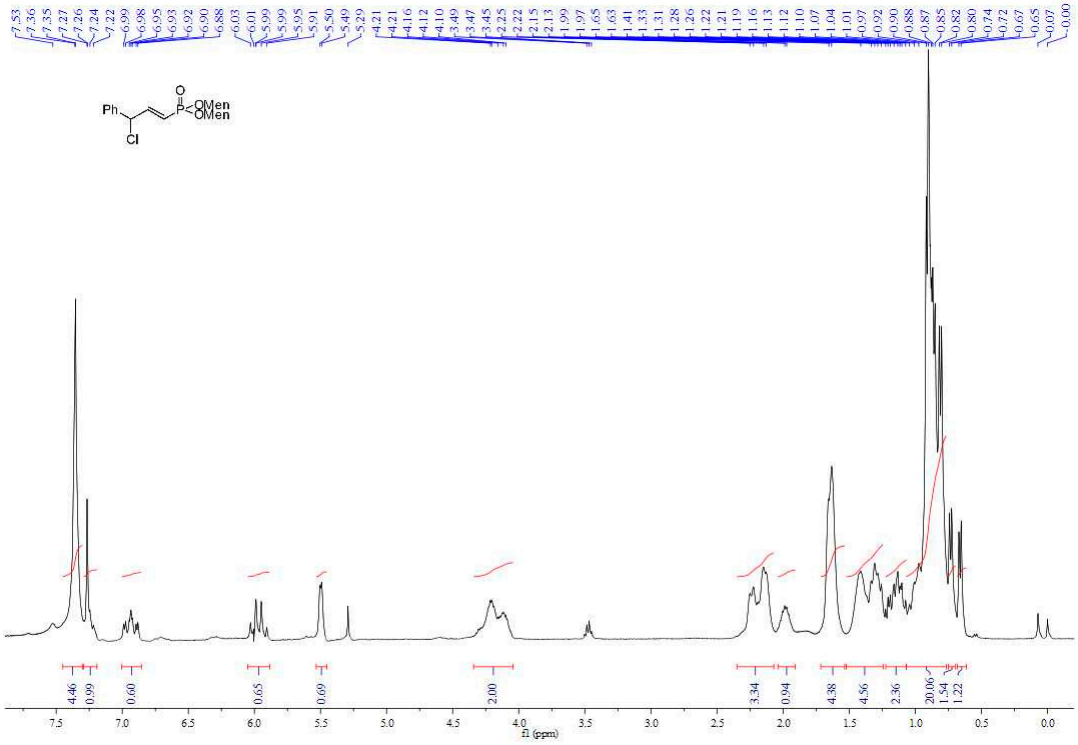
^{13}C NMR spectroscopy of 1c



Dimenthyl 3-chloro-3-phenylprop-1-en-1-ylphosphonate, 1d, 31P NMR spectroscopy



^{1}H NMR spectroscopy of 1d



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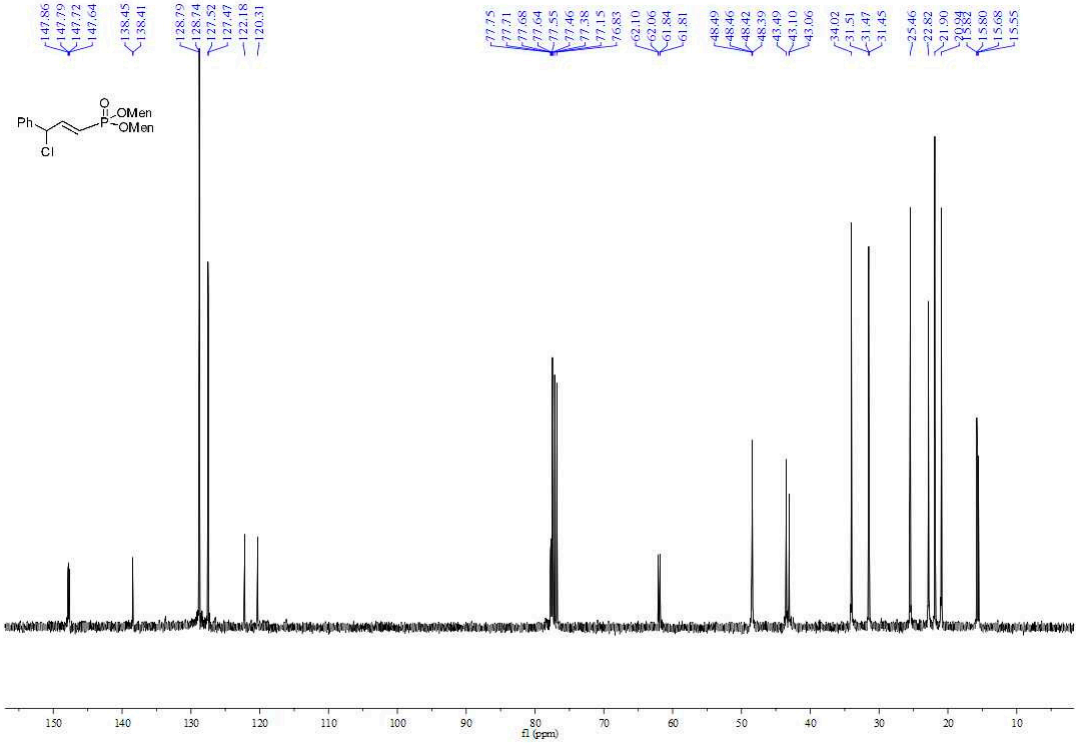
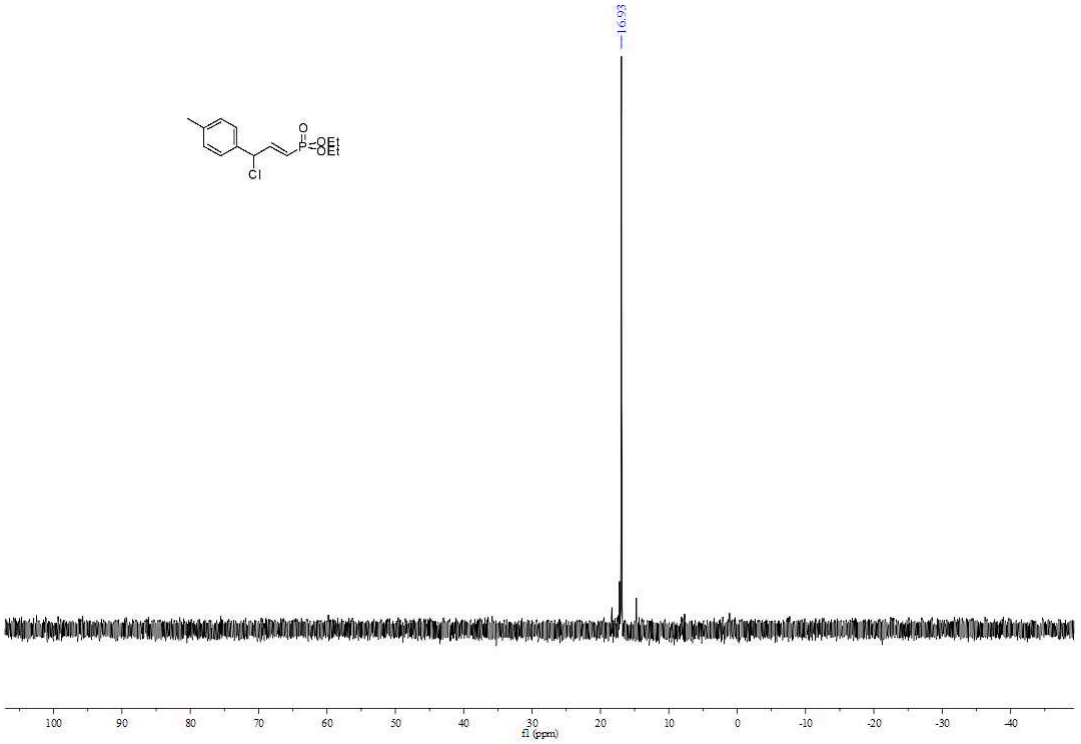
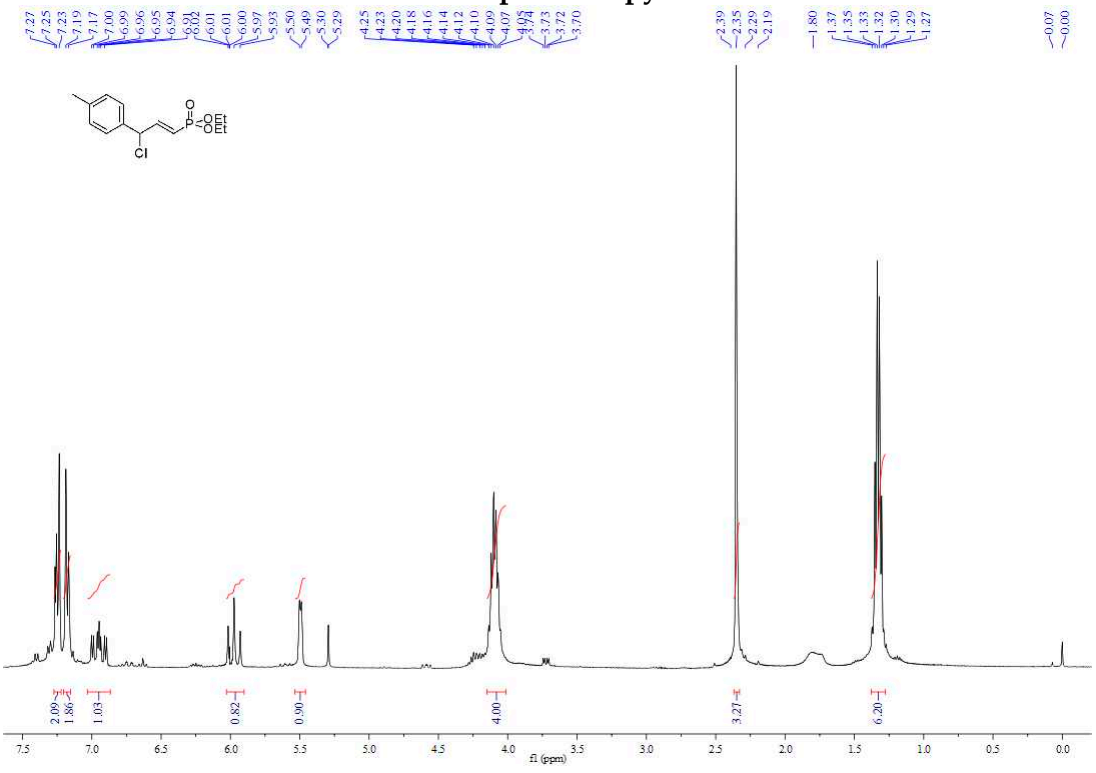


Diethyl 3-chloro-3-p-tolylprop-1-en-1-ylphosphonate, 1e, 31P NMR spectroscopy



^{1}H NMR spectroscopy of 1e



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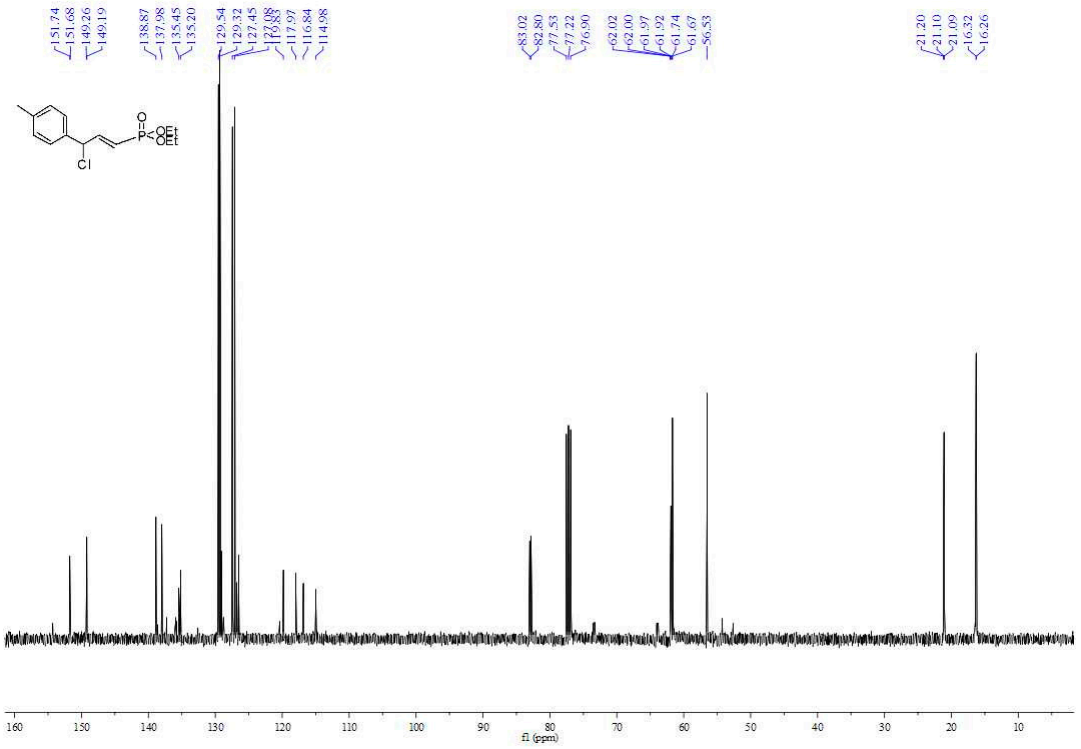
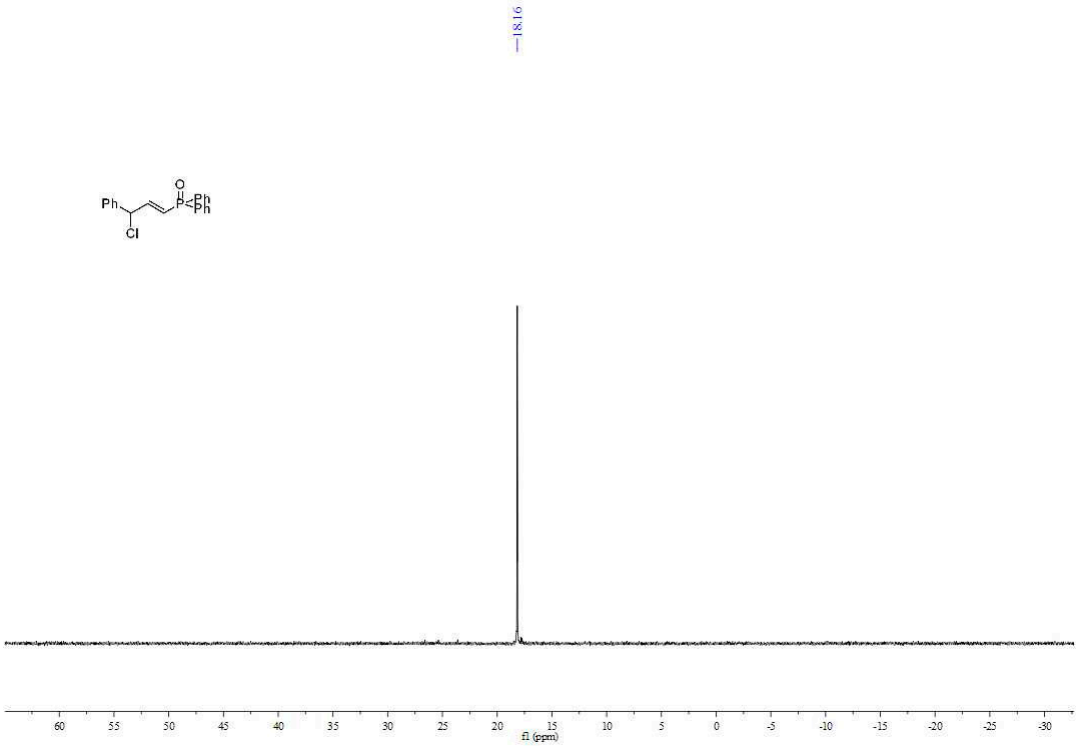
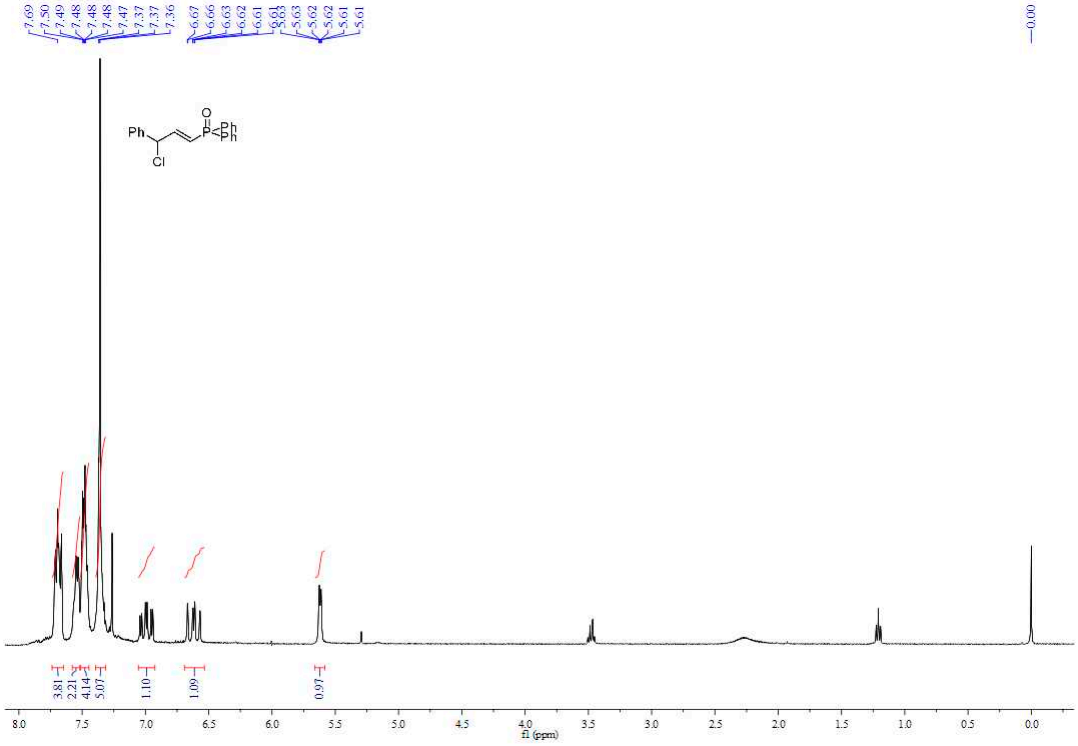


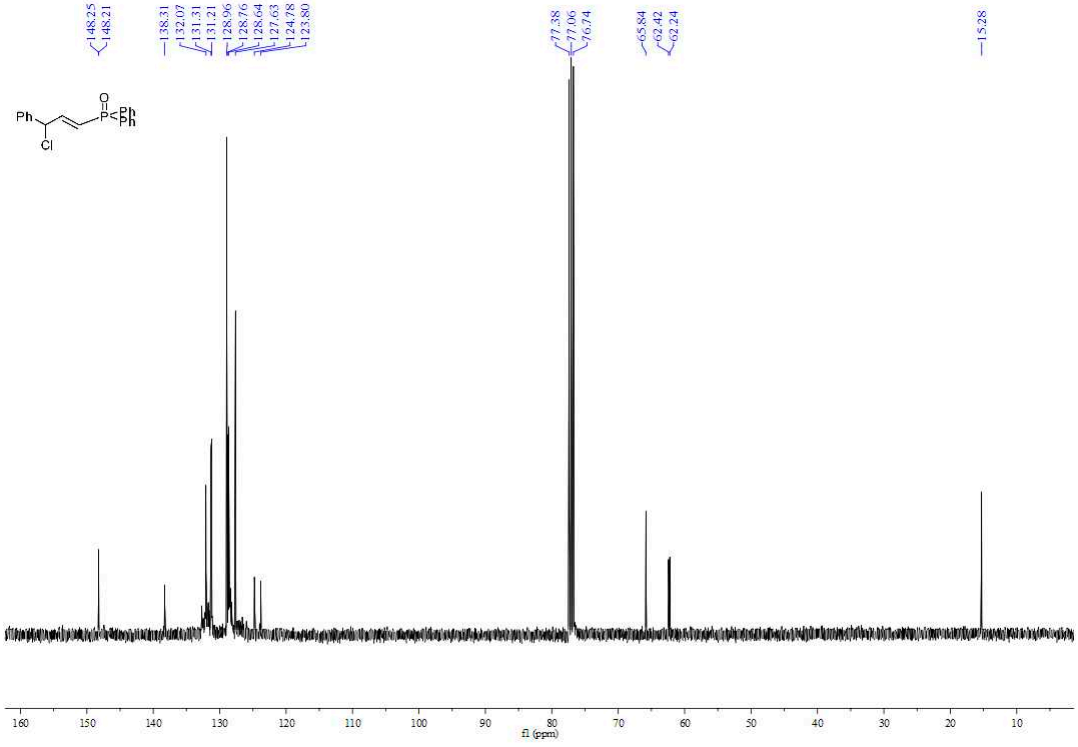
Diphenyl 3-chloro-3-phenylprop-1-en-1-ylphosphine oxide, 1f, 31P NMR spectroscopy



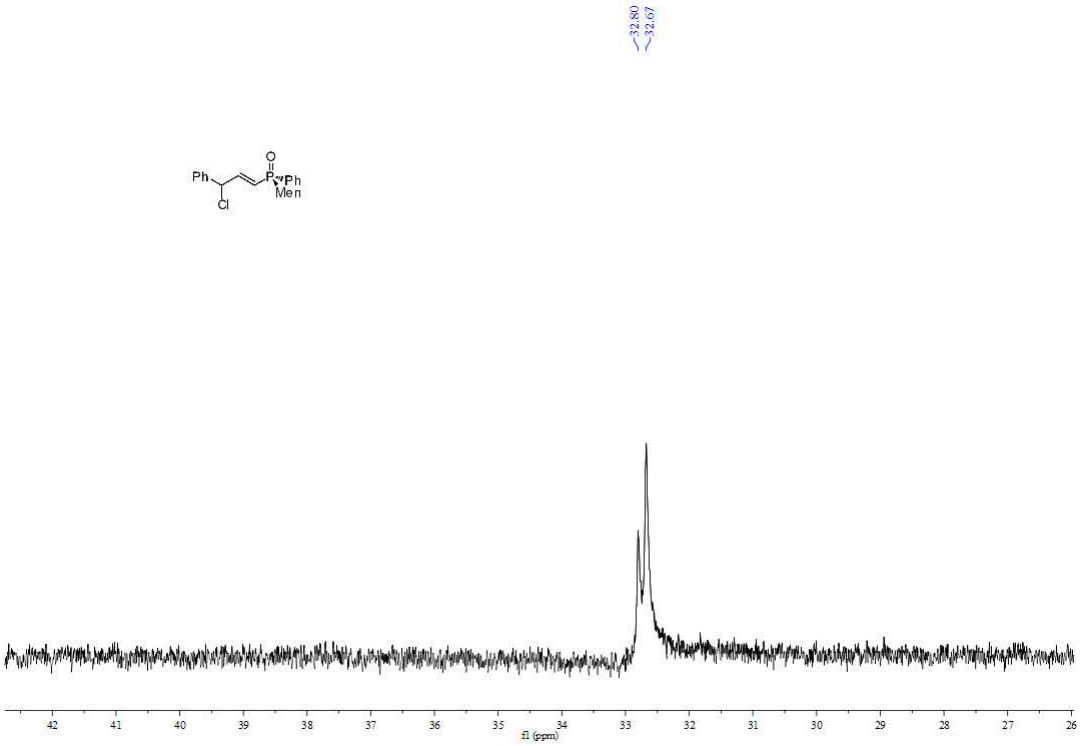
^{1}H NMR spectroscopy of 1f



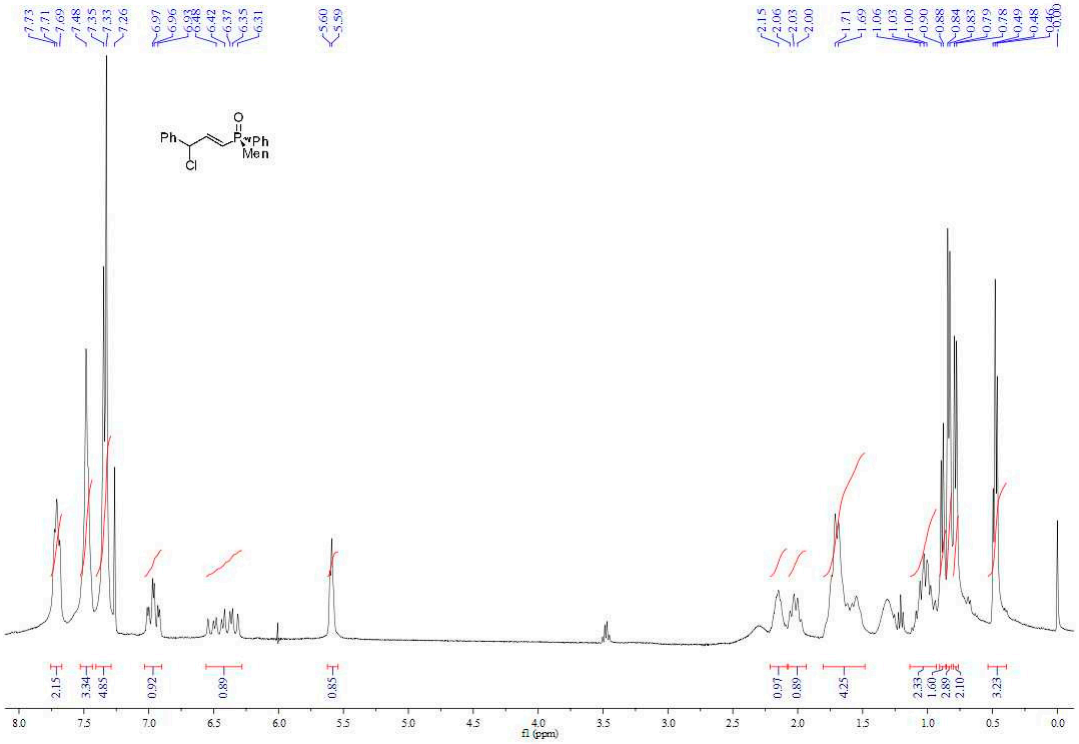
^{13}C NMR spectroscopy of 1f



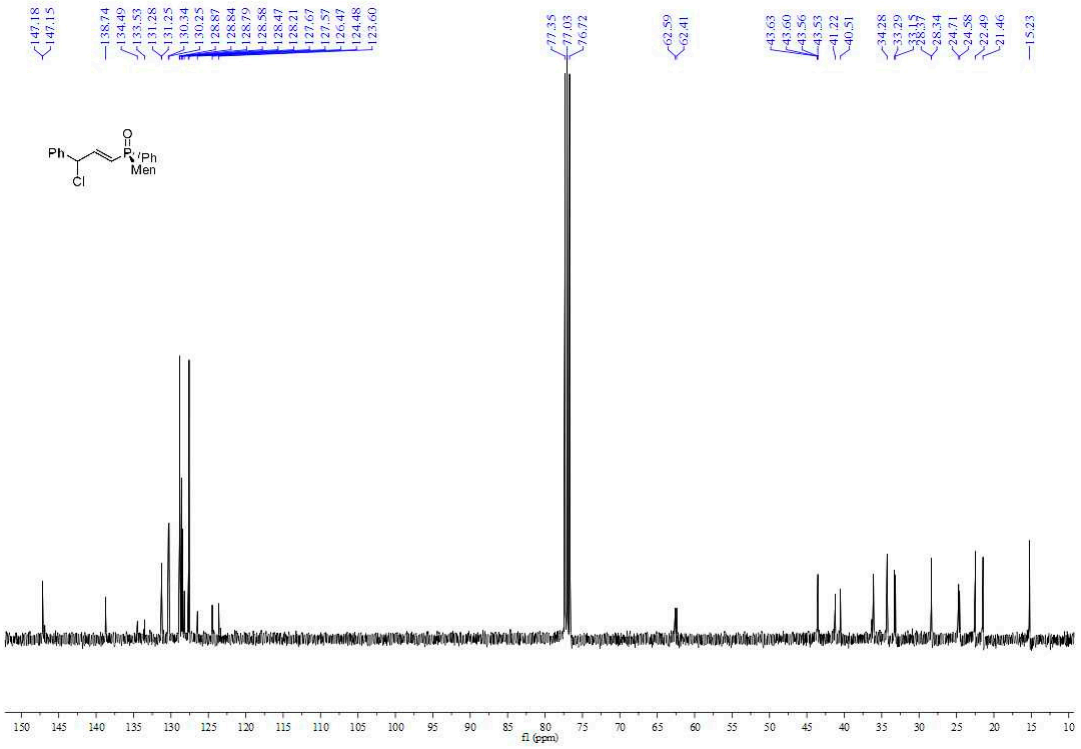
(*S*P)-Menthyl-3-chloro-3-phenylprop-1-en-1-yl phenylphosphine oxide, 1g, ^{31}P NMR spectroscopy



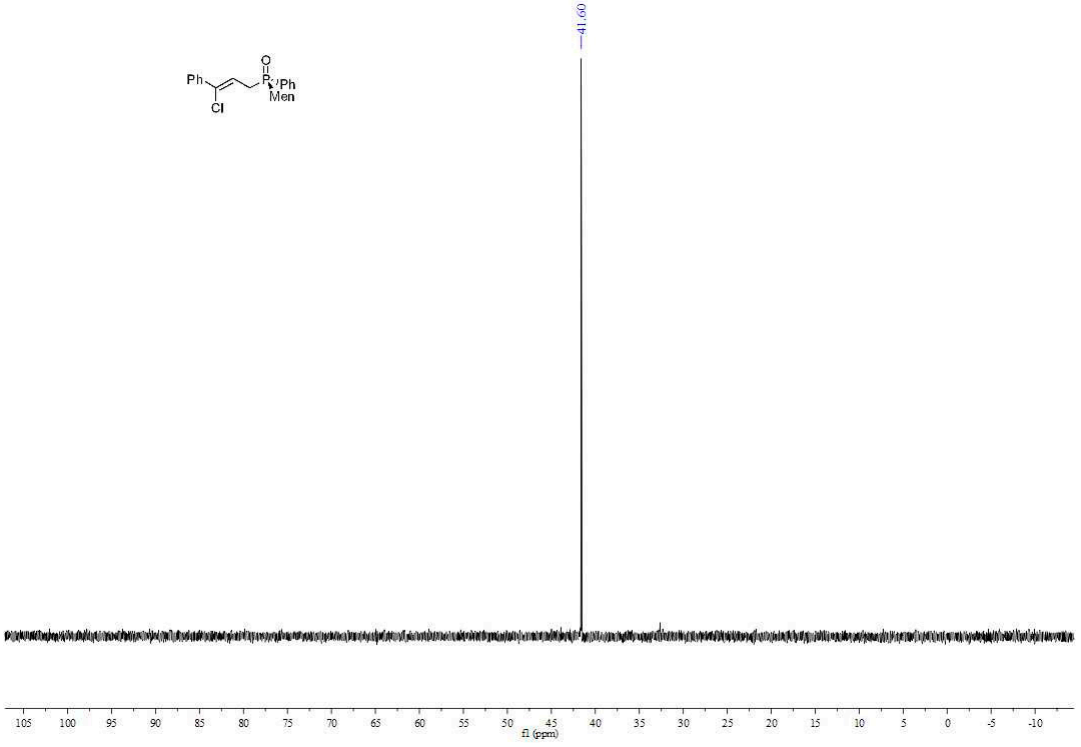
^{1}H NMR spectroscopy of 1g



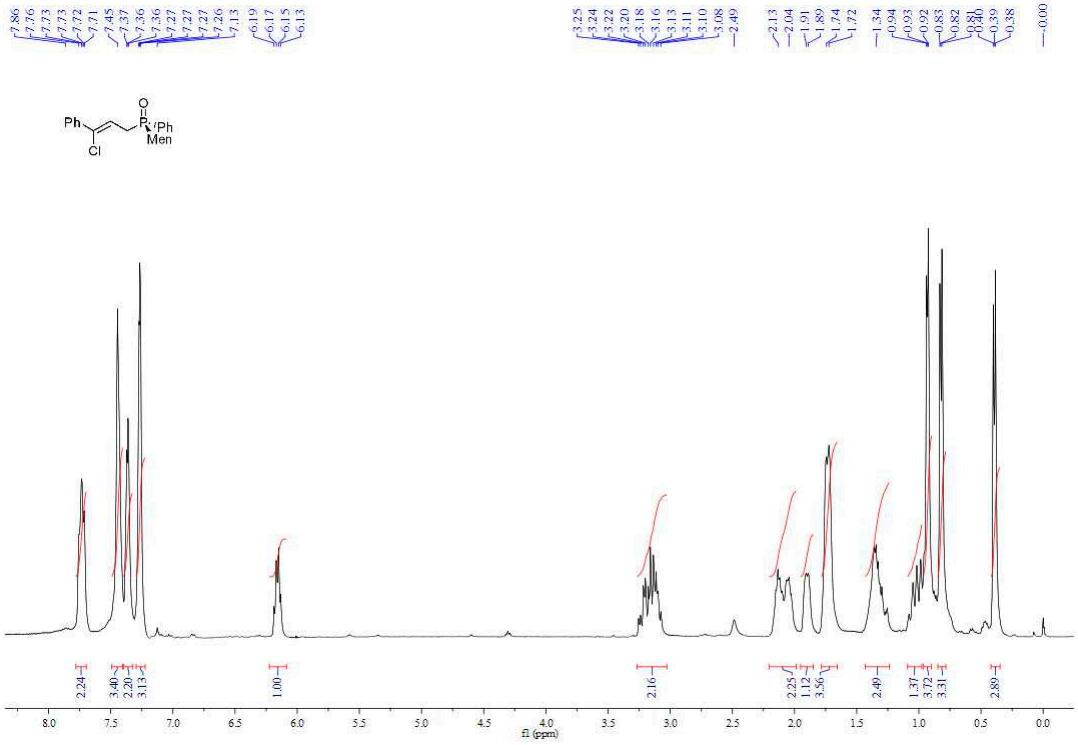
^{13}C NMR spectroscopy of 1g



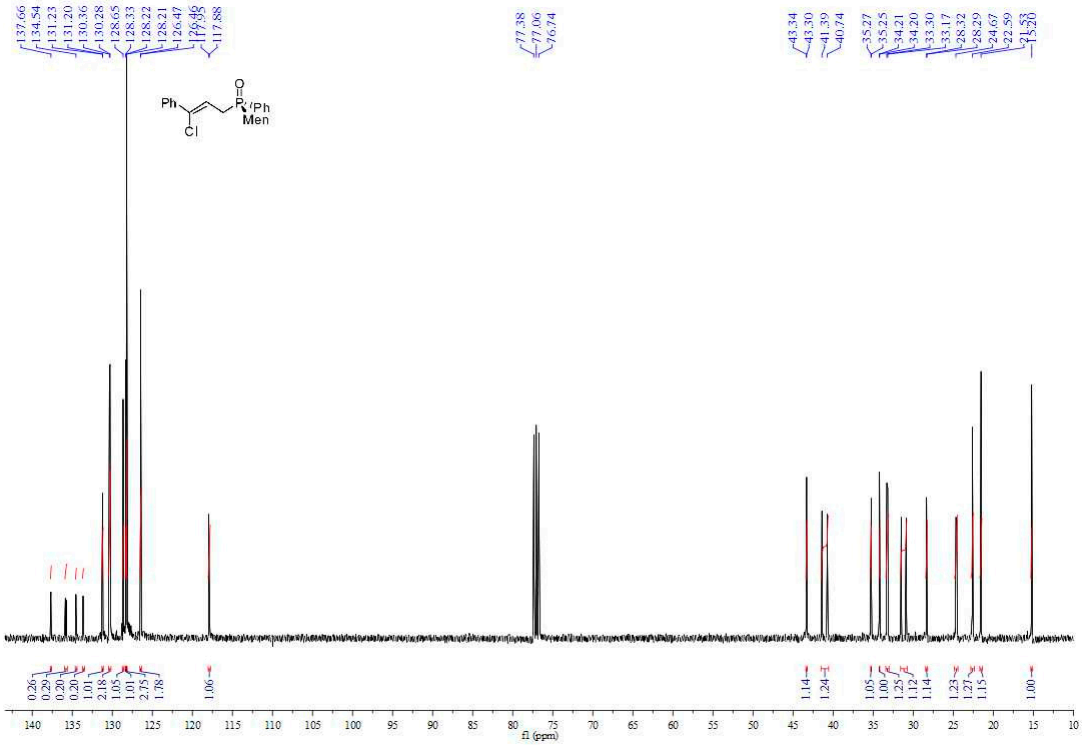
^{31}P NMR spectroscopy of 4g



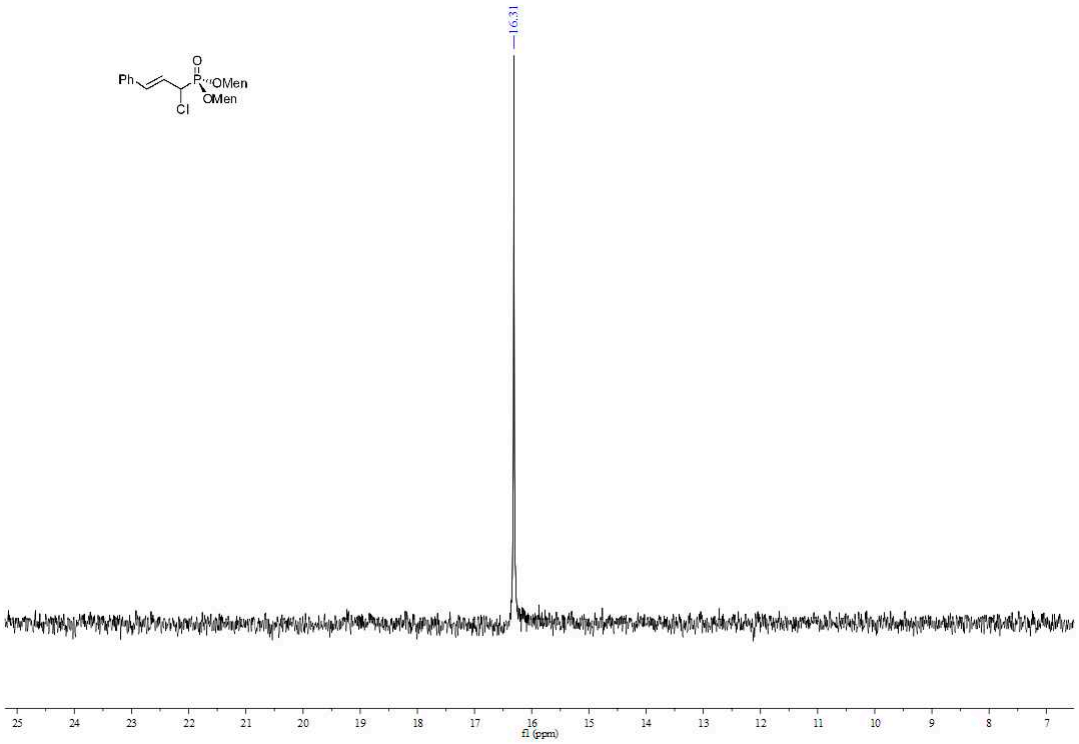
^{1}H NMR spectroscopy of 4g



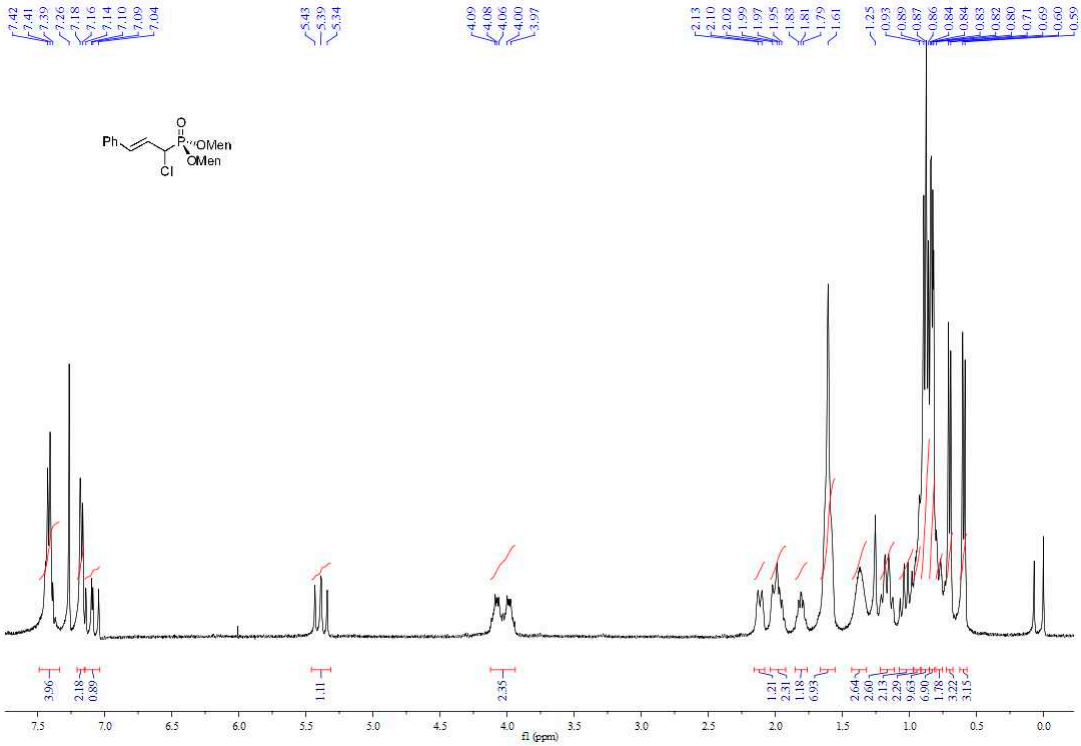
^{13}C NMR spectroscopy of 4g



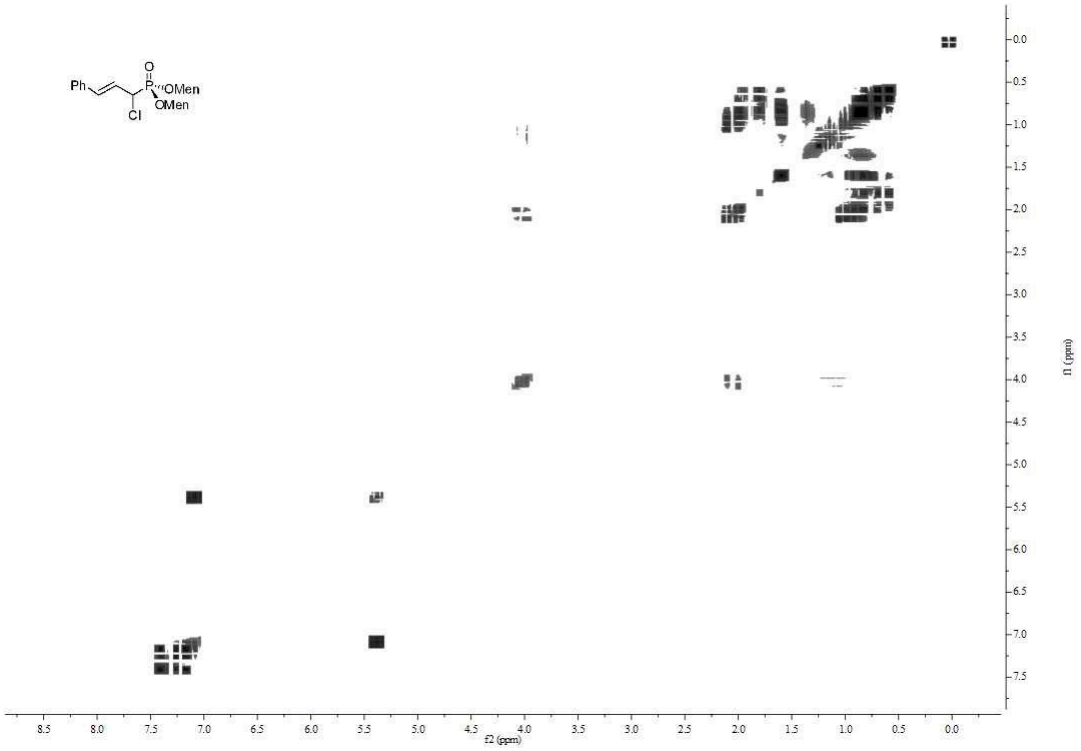
Dimenthyl 1-chloro-3-phenylprop-1-en-1-ylphosphonate, 4d', 31P NMR spectroscopy



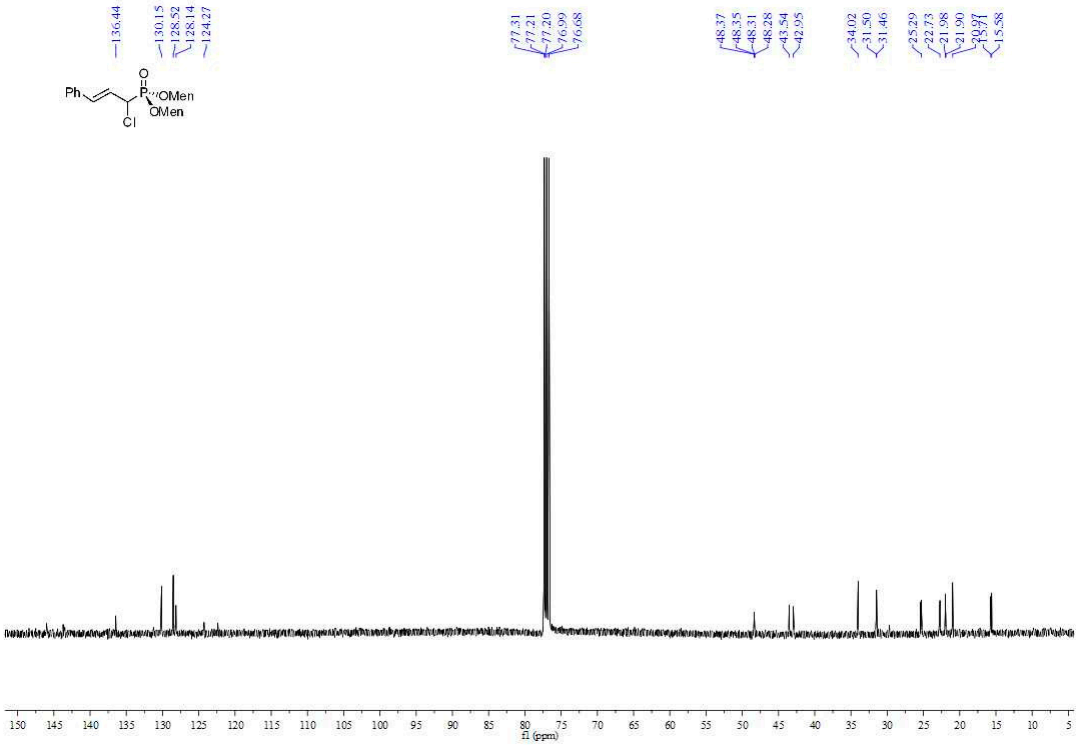
^{1}H NMR spectroscopy of 4d'



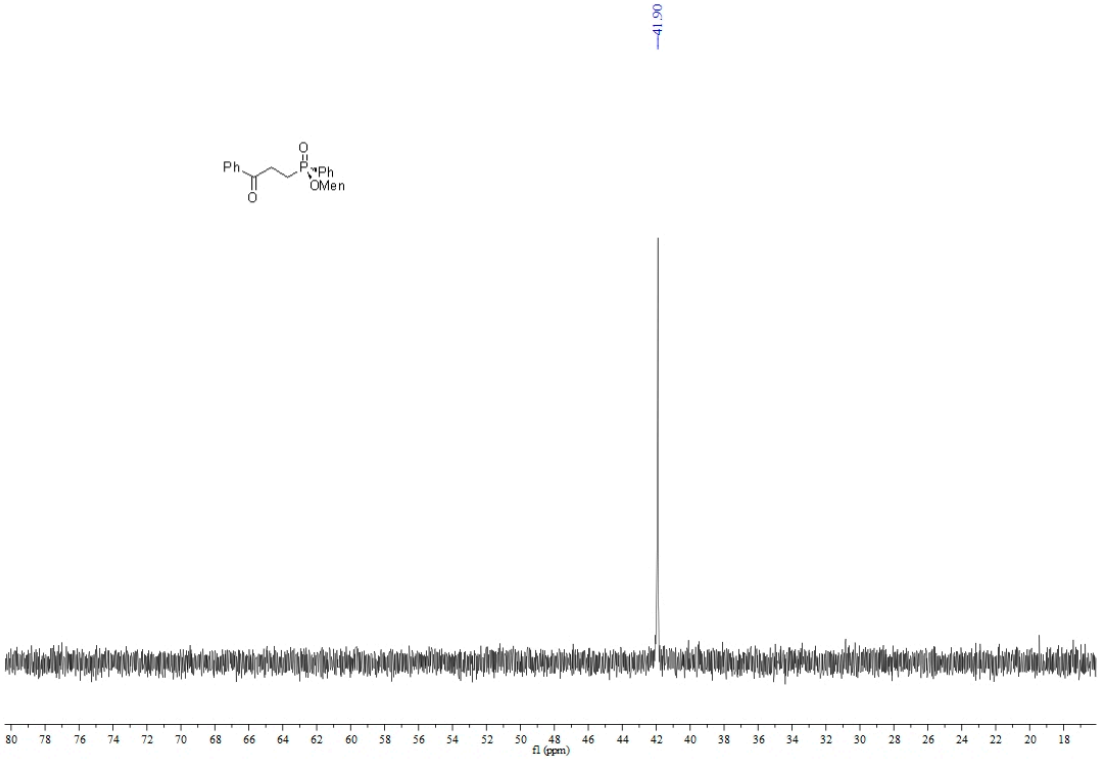
gCOSY NMR spectroscopy of 4d'



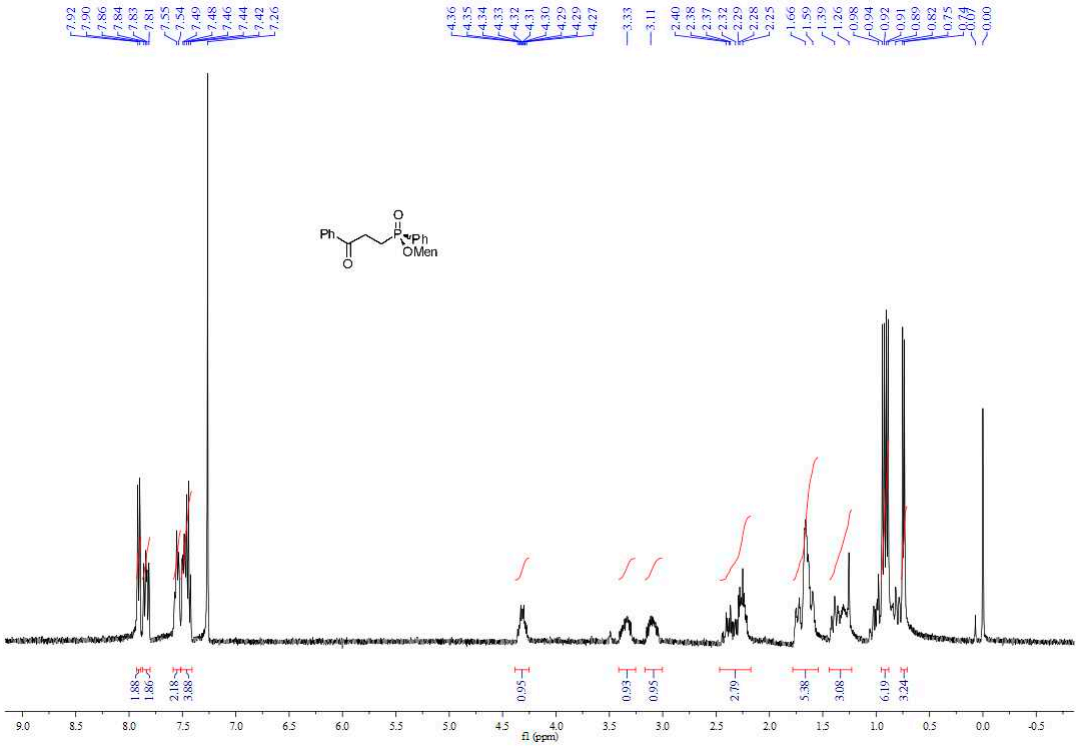
^{13}C NMR spectroscopy of 4d'



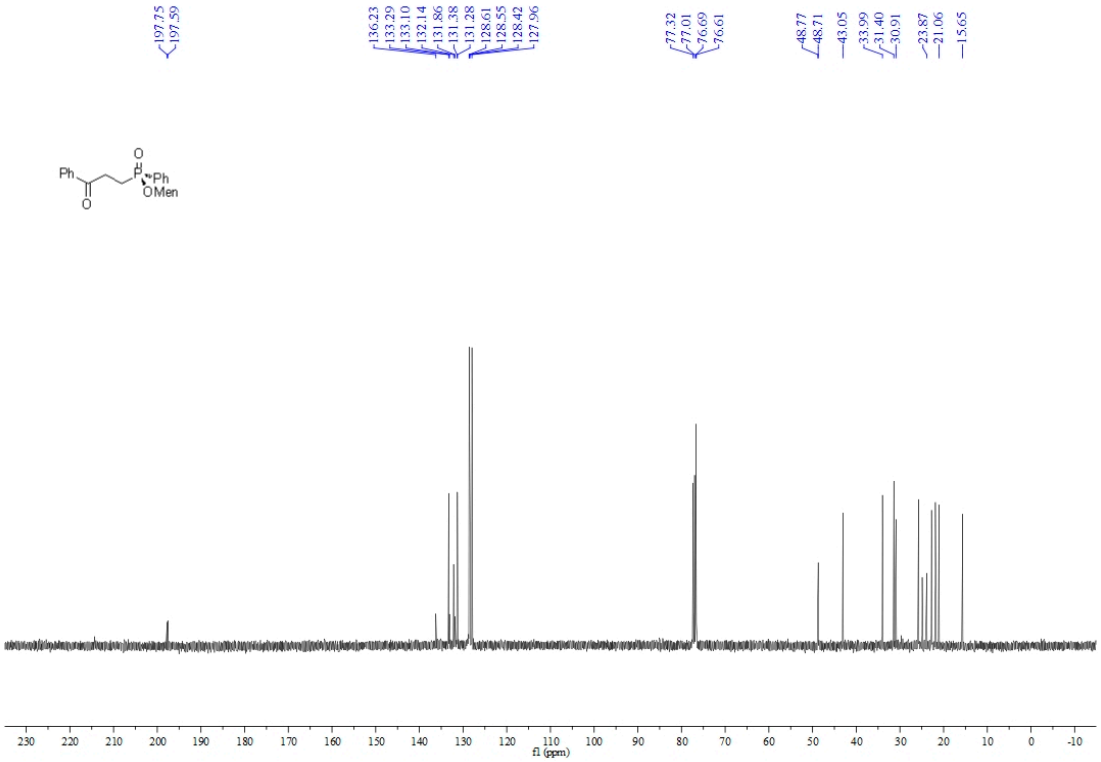
(*S*P)-Menthyl 3-oxo-3-phenylpropyl phenylphosphinate, 5a, ^{31}P NMR spectroscopy



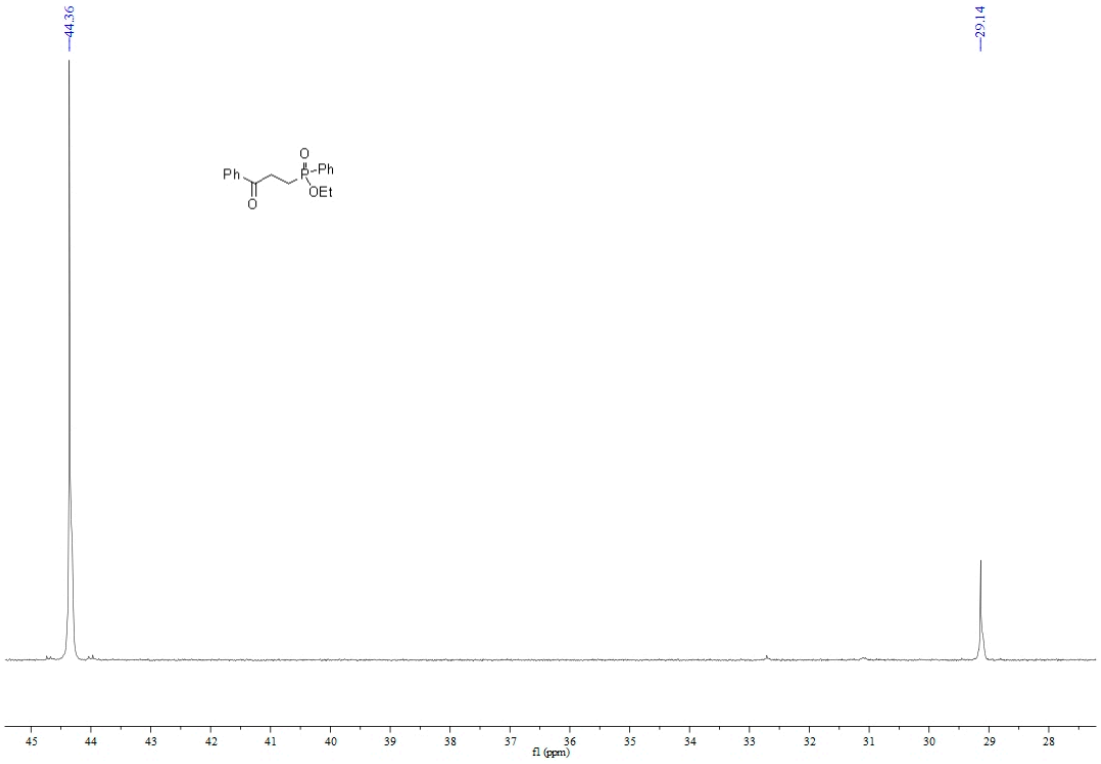
^{1}H NMR spectroscopy of 5a



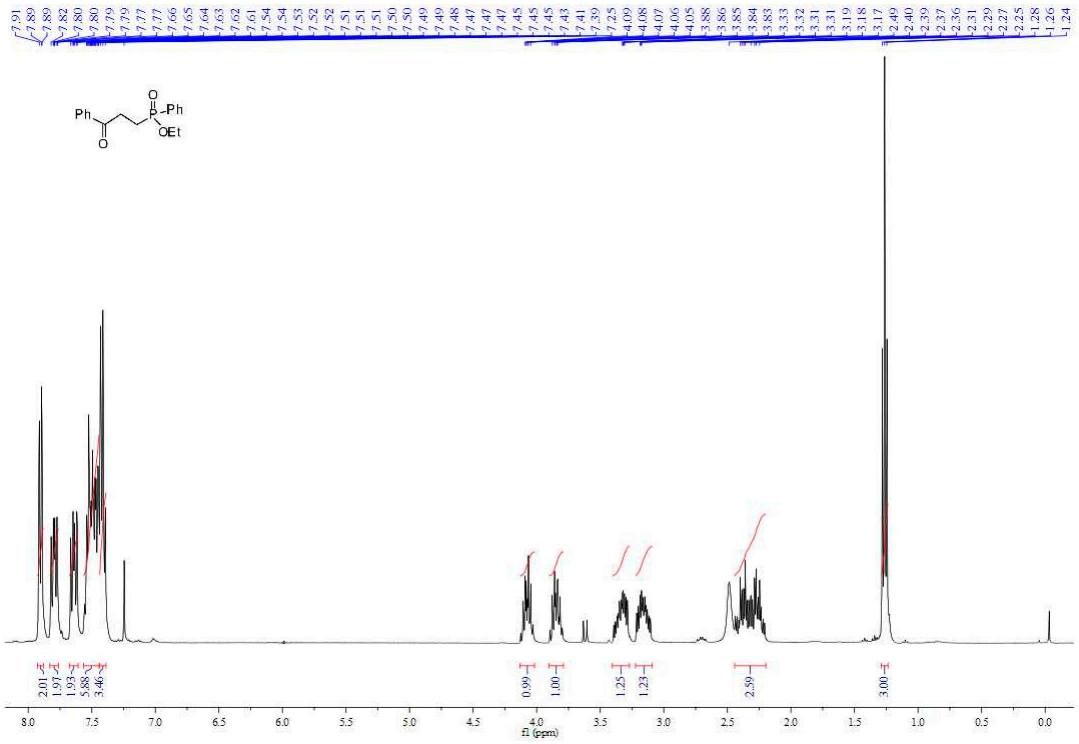
^{13}C NMR spectroscopy of 5a



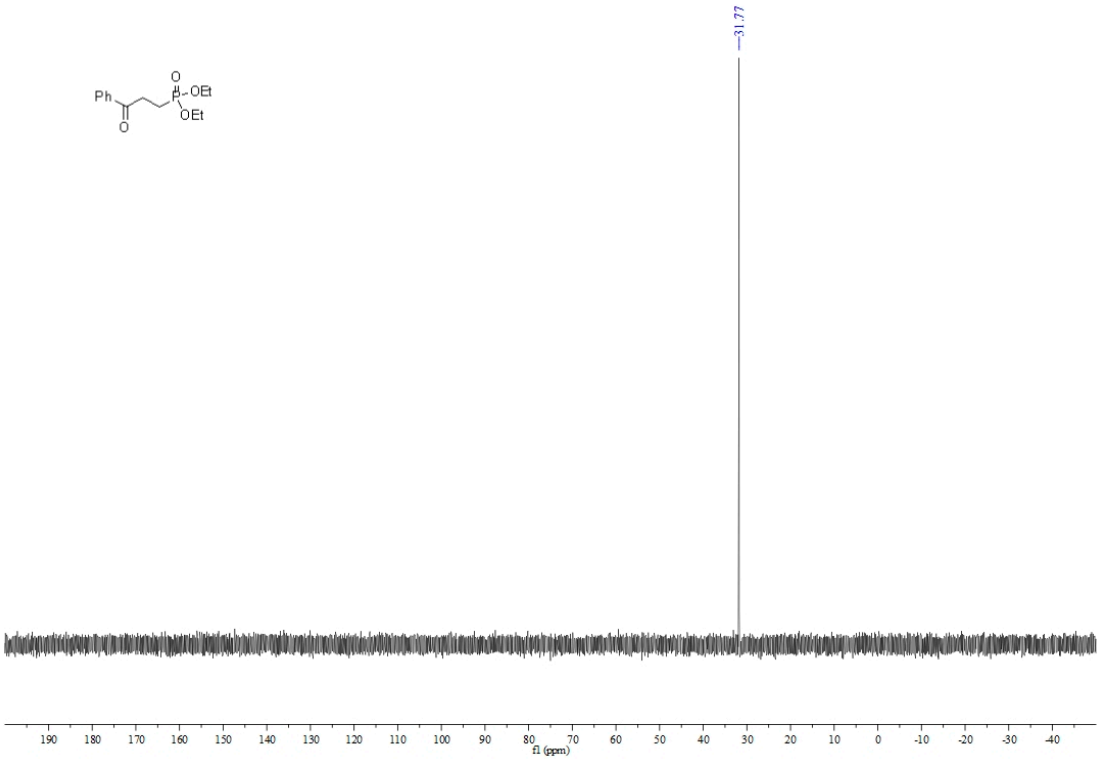
Ethyl 3-oxo-3-phenylpropyl phenylphosphinate, 5b, ^{31}P NMR spectroscopy



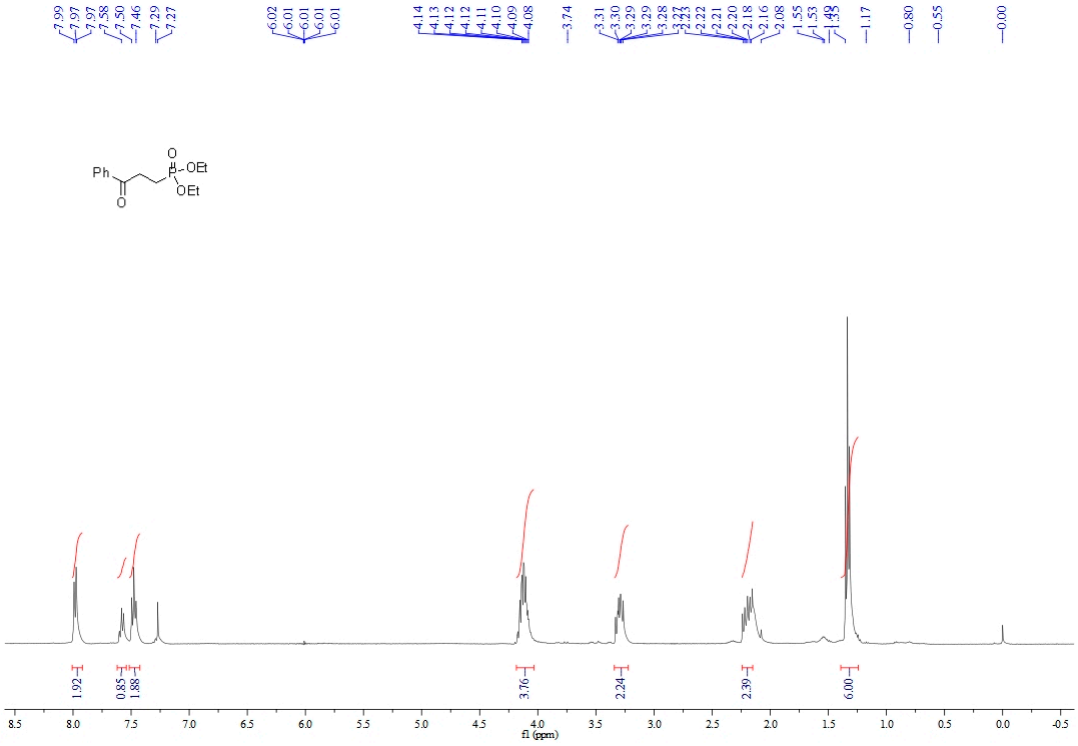
^{1}H NMR spectroscopy of 5b



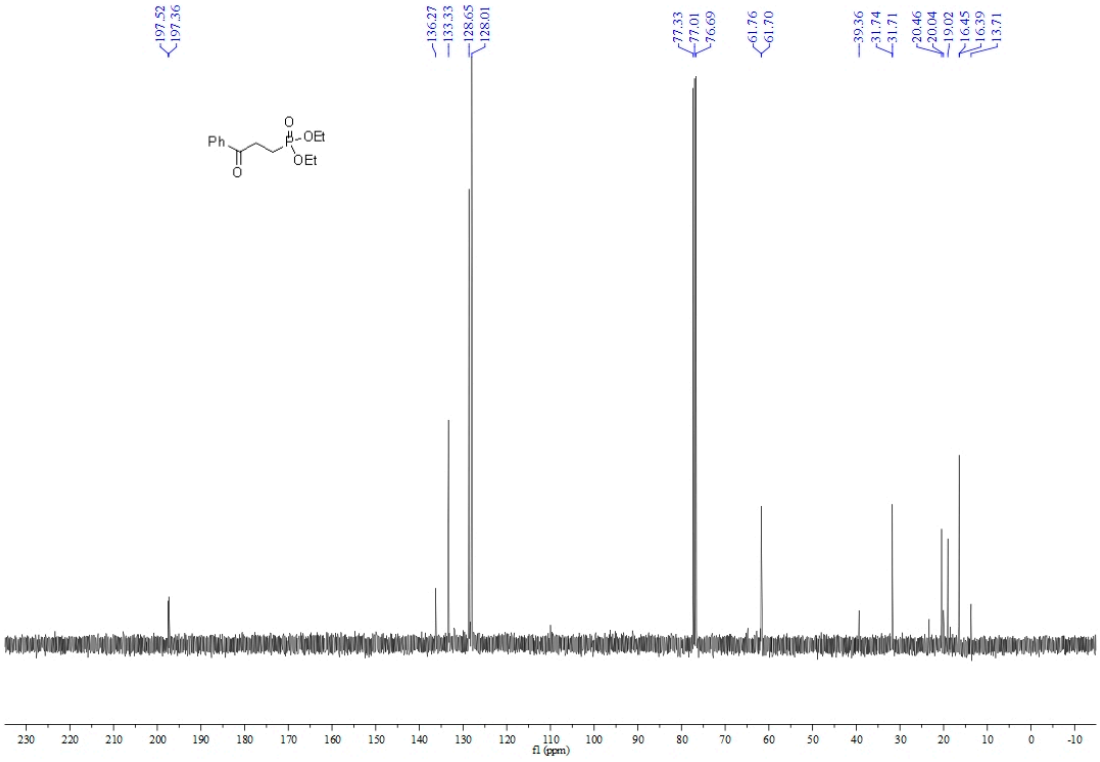
Diethyl 3-oxo-3-phenyl propylphosphonate, 5c, ^{31}P NMR spectroscopy



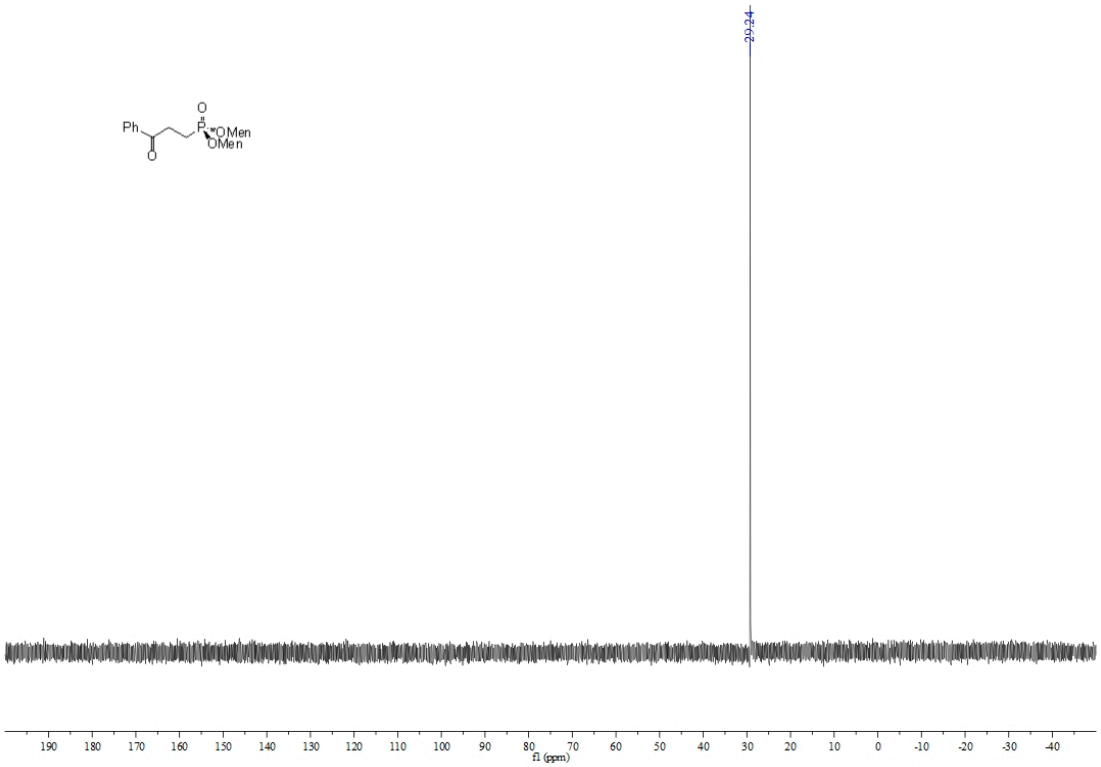
^{1}H NMR spectroscopy of 5c



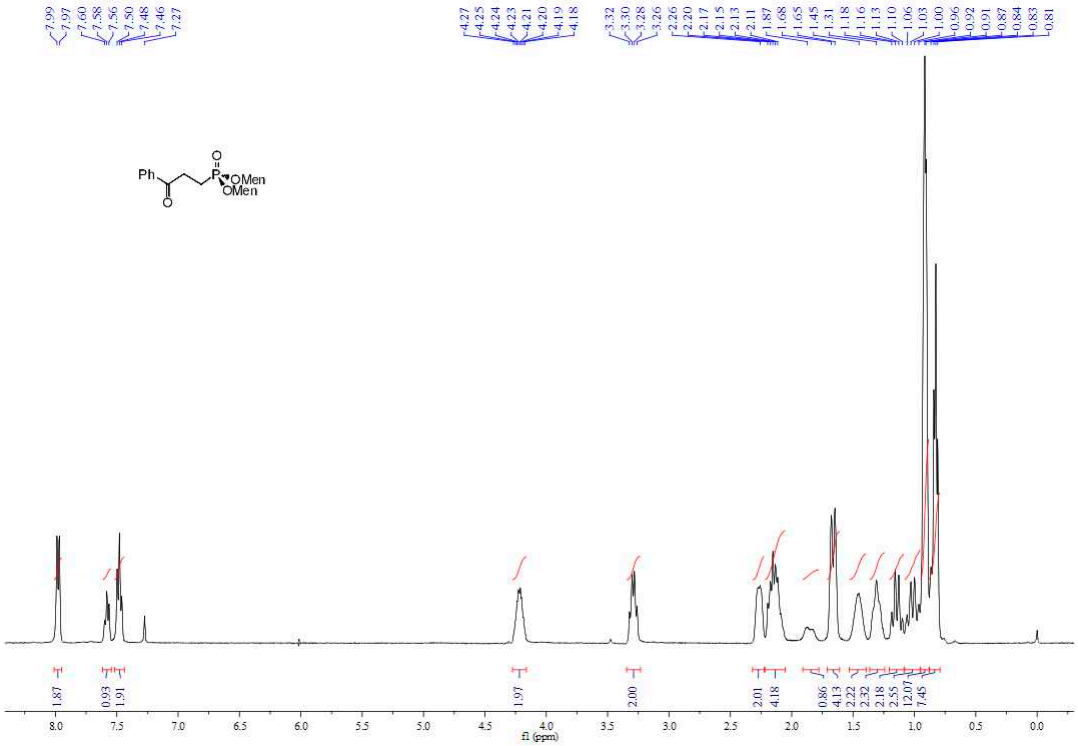
^{13}C NMR spectroscopy of 5c



Dimenthyl 3-oxo-3-phenylpropyl phenylphosphonate, 5d, ^{31}P NMR spectroscopy



^{1}H NMR spectroscopy of 5d



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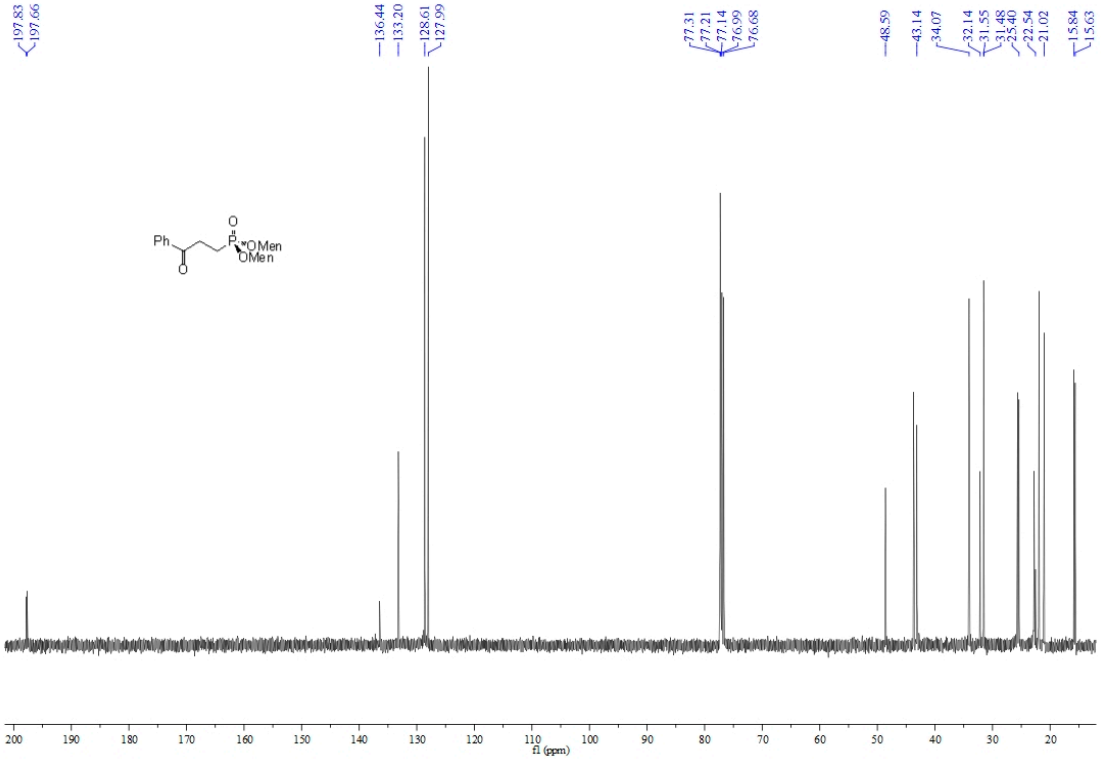
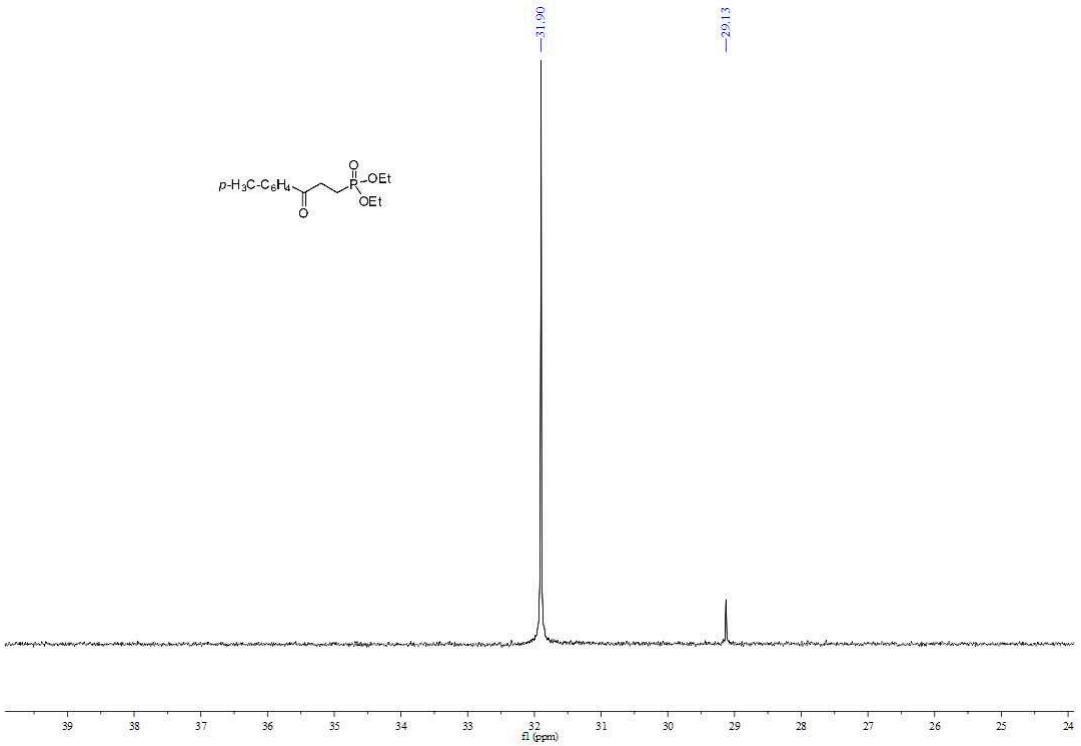
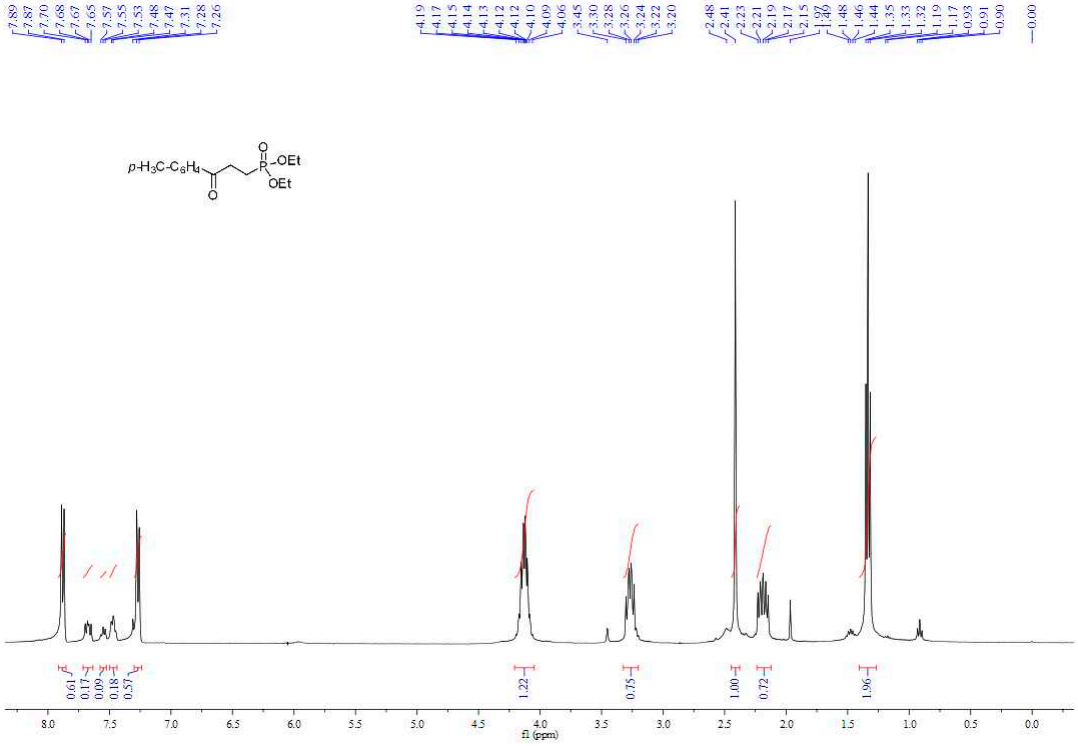


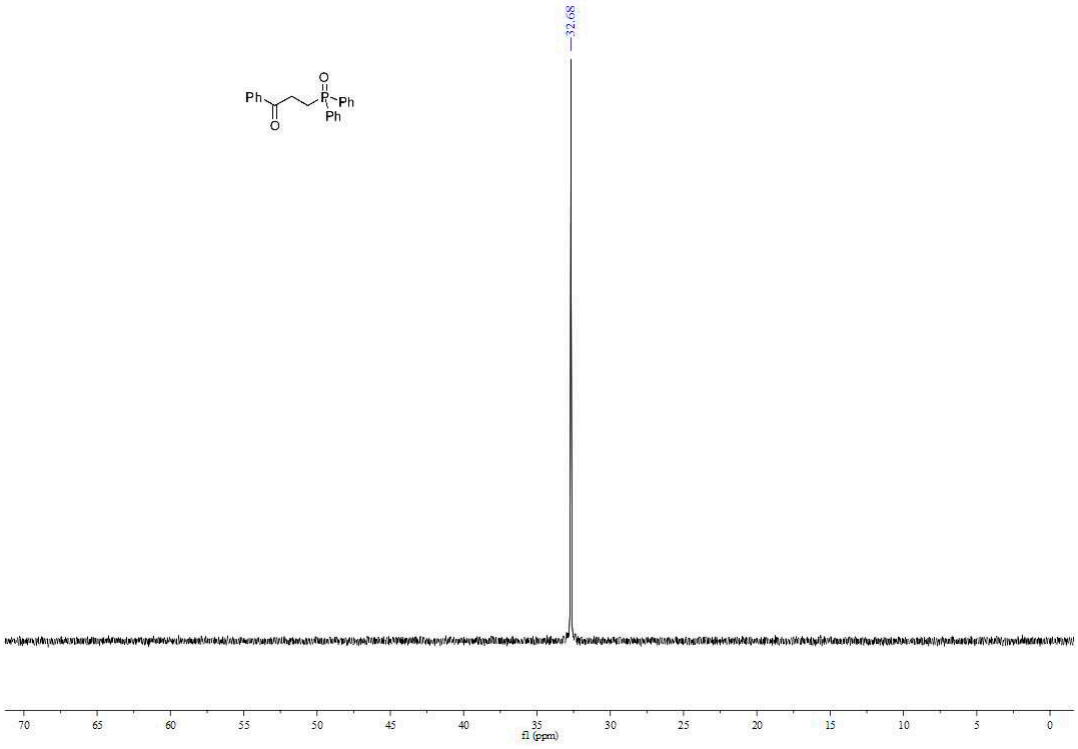
Diethyl 3-oxo-3-p-tolyl propylphosphonate, 5e, ^{31}P NMR spectroscopy



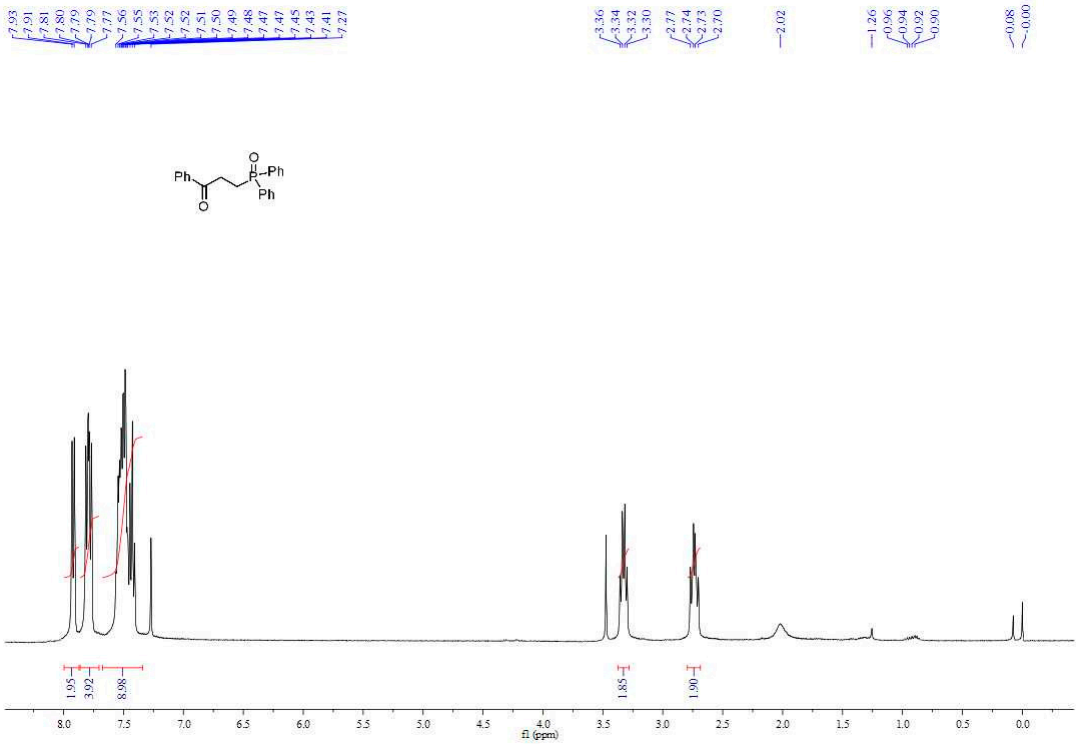
^{1}H NMR spectroscopy of 5e



Diphenyl 3-oxo-3-phenyl propylphosphonate, 5f, ^{31}P NMR spectroscopy



^{1}H NMR spectroscopy of 5f



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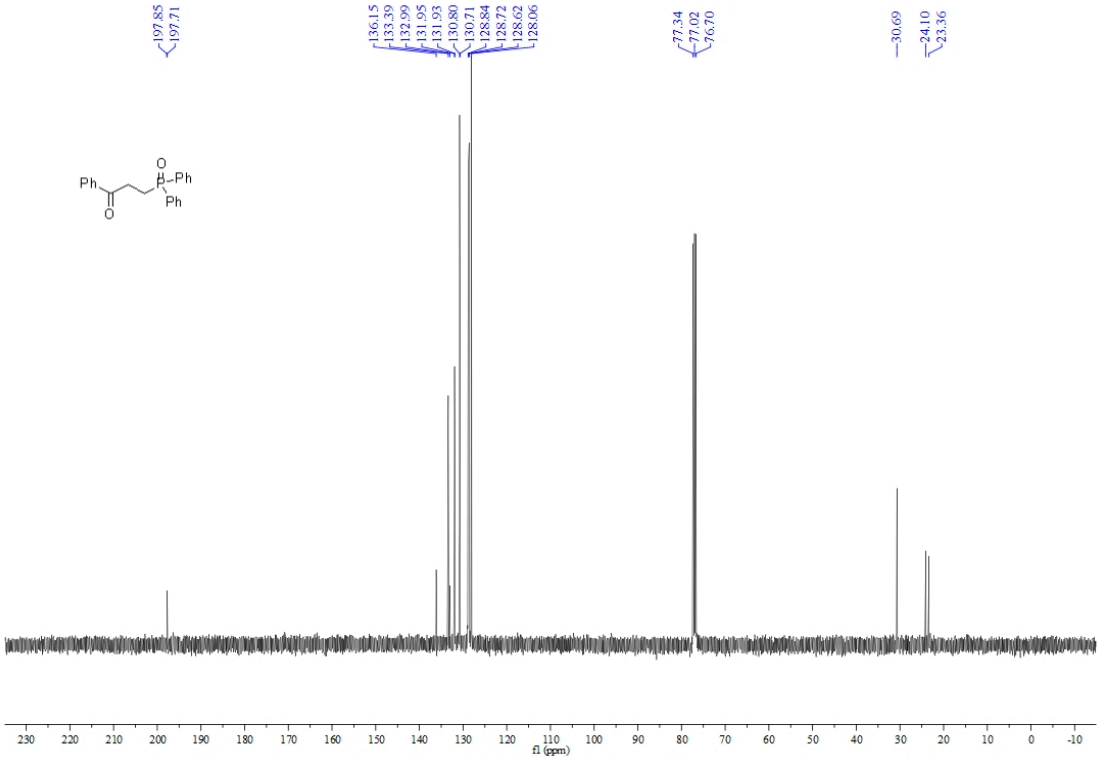
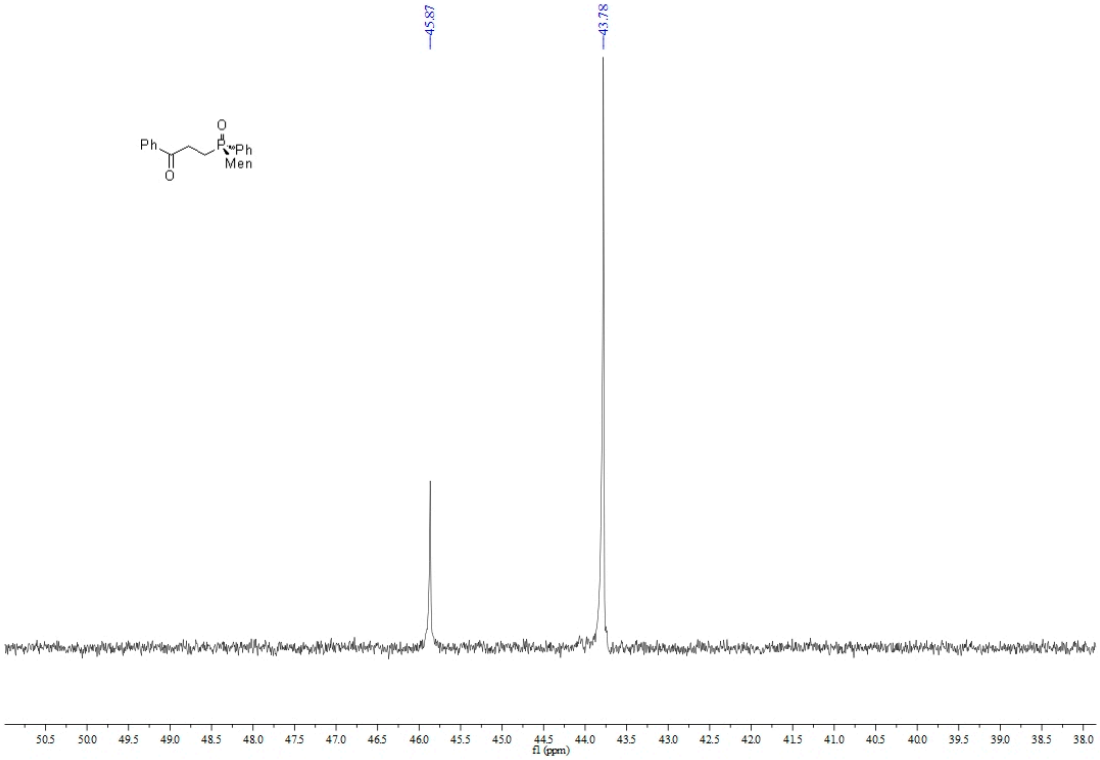
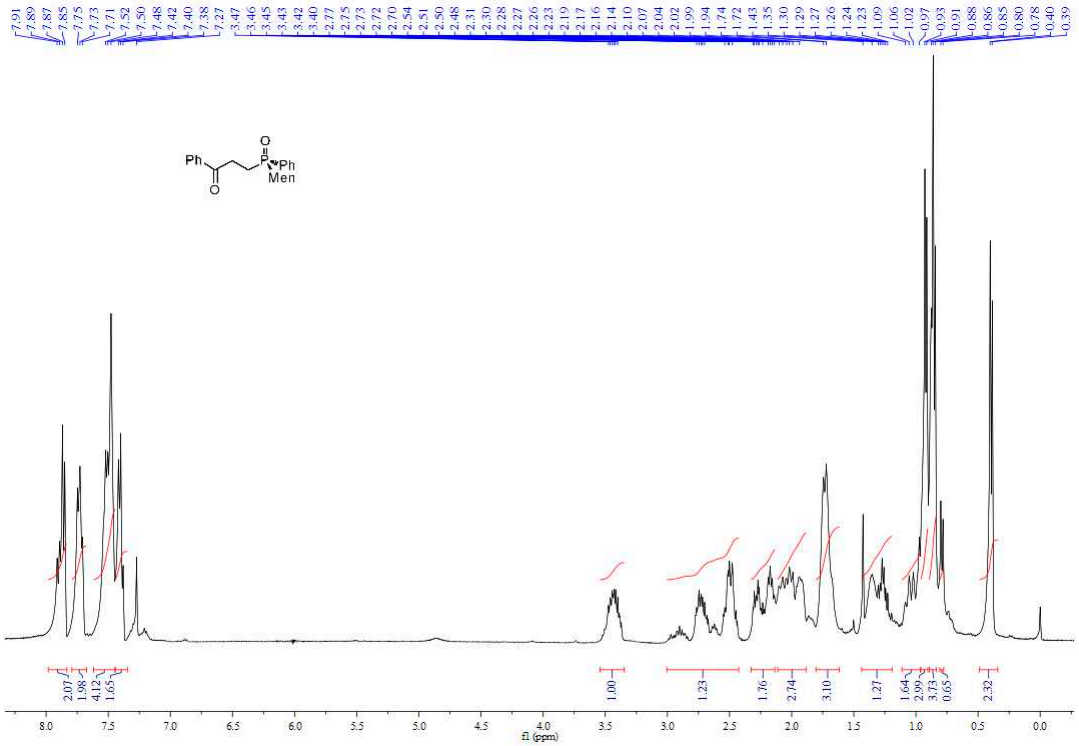


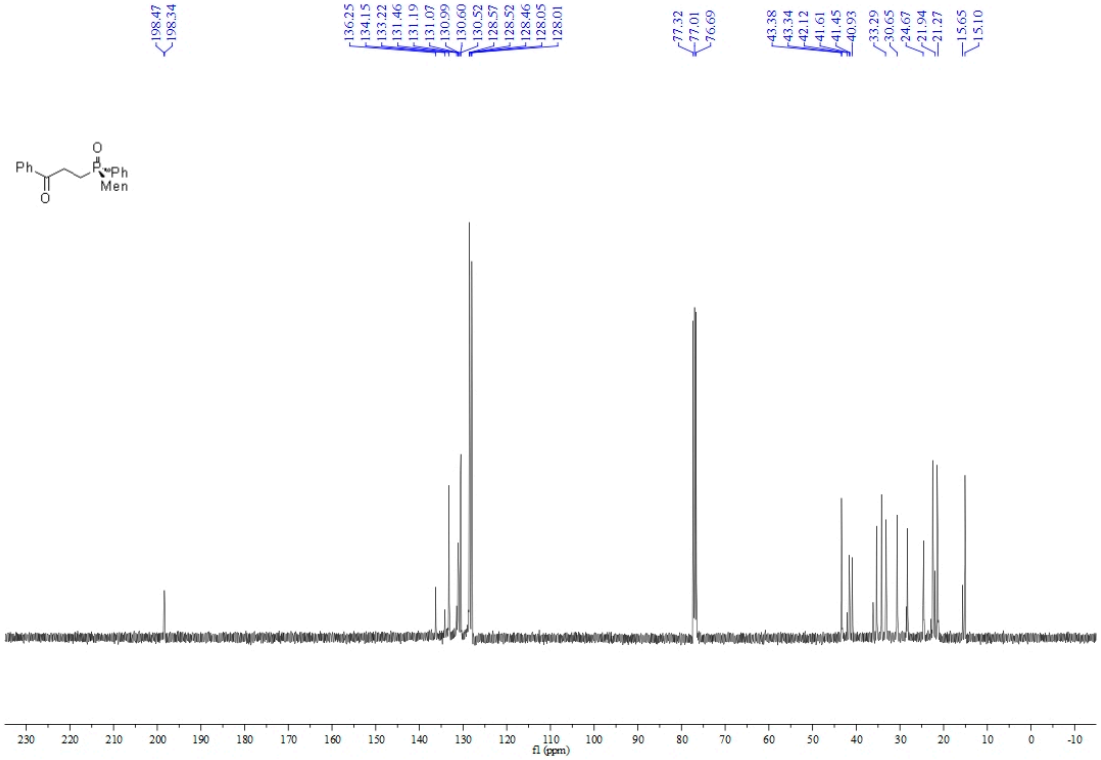
(*S*P)-Menthyl 3-oxo-3-phenylpropyl phenylphosphinate, 5g/5g', ^{31}P NMR spectroscopy



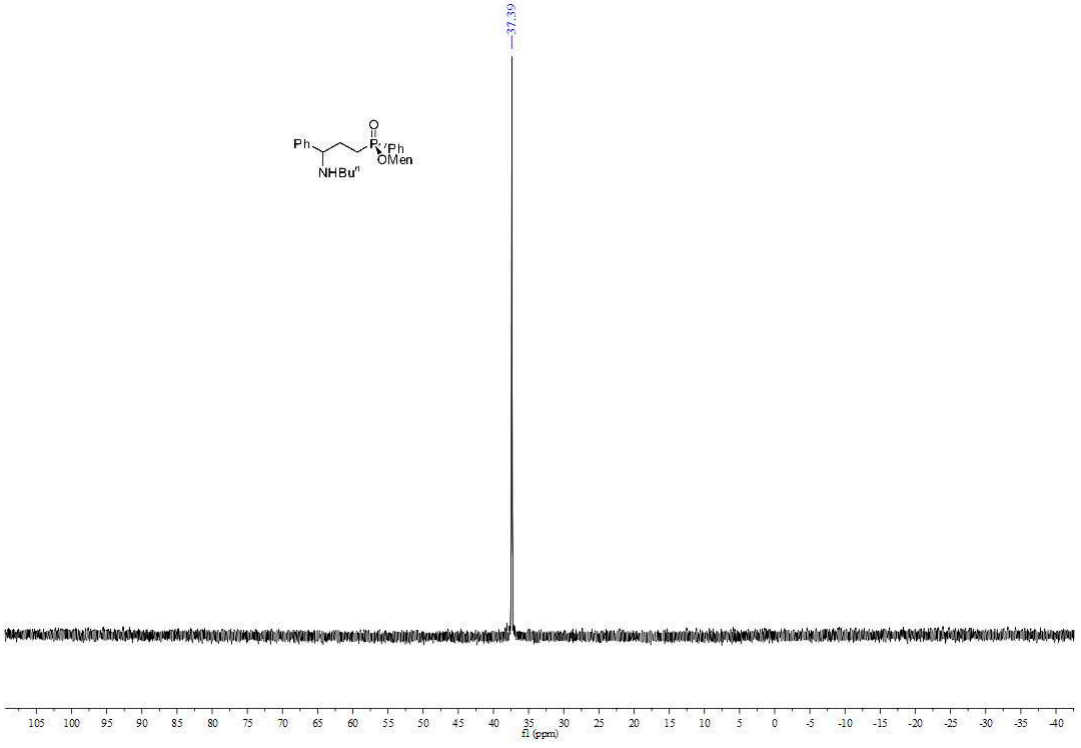
^{1}H NMR spectroscopy of 5g/5g'



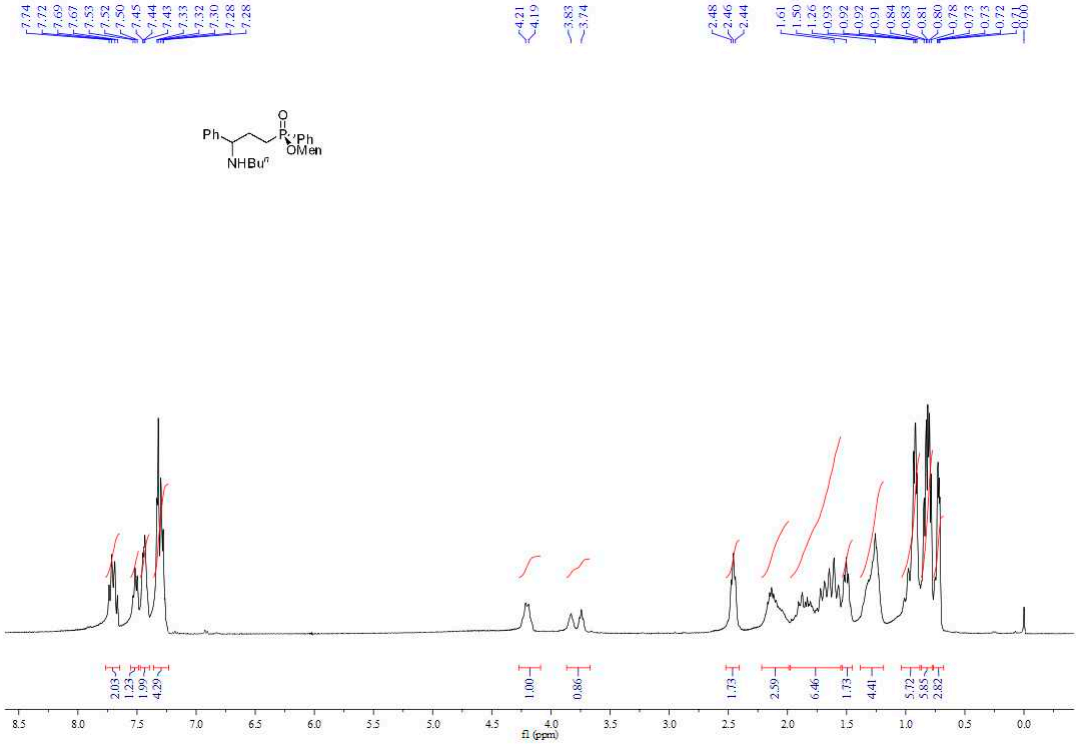
^{13}C NMR spectroscopy of 5g/5g'



(*S*$_P$)-Menthyl-3-butylamino-3-phenylpropyl phenylphosphinate, 11aa, ^{31}P NMR spectroscopy



^{1}H NMR spectroscopy of 11aa



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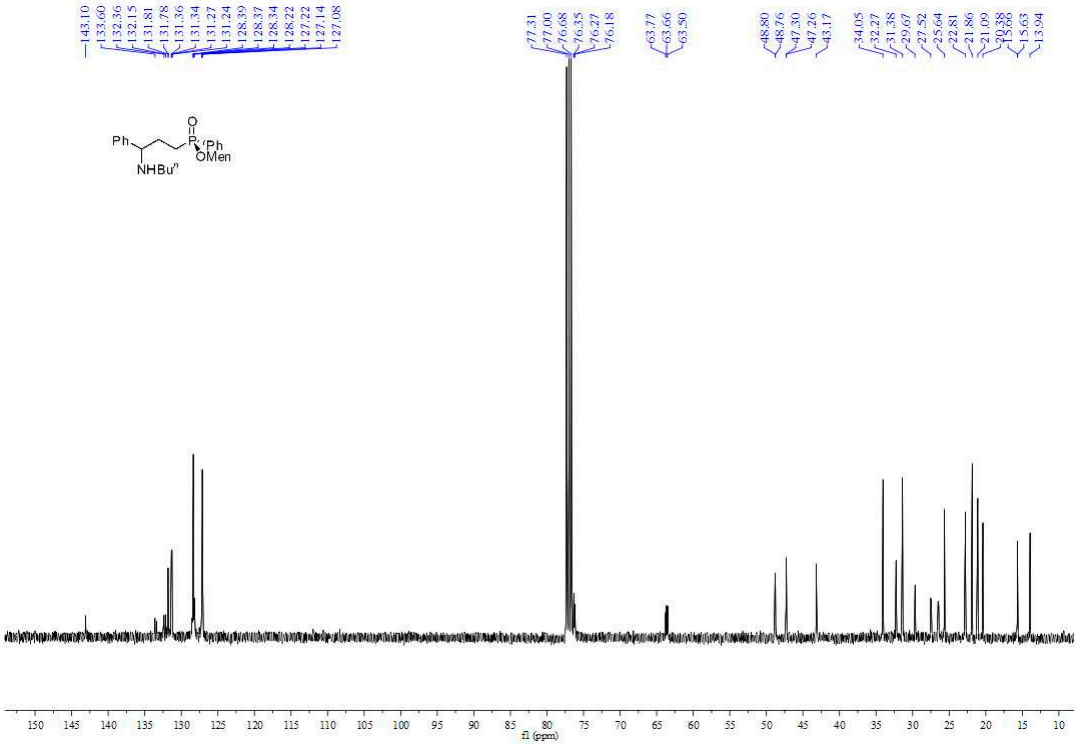
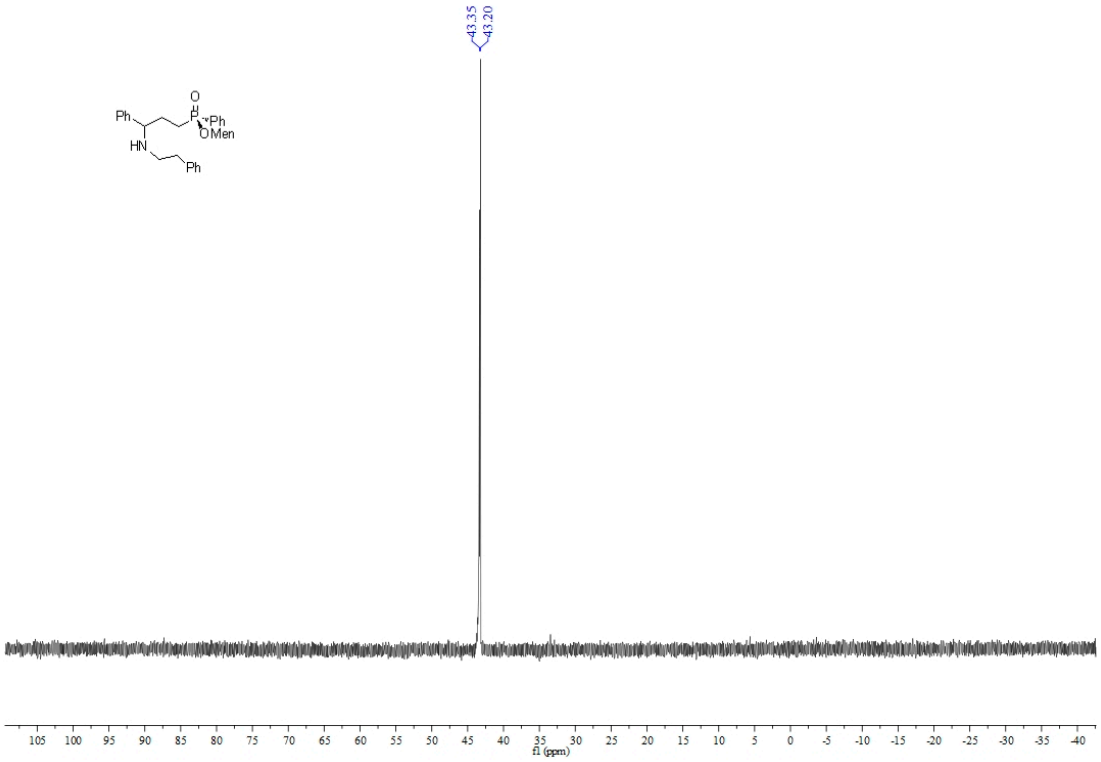
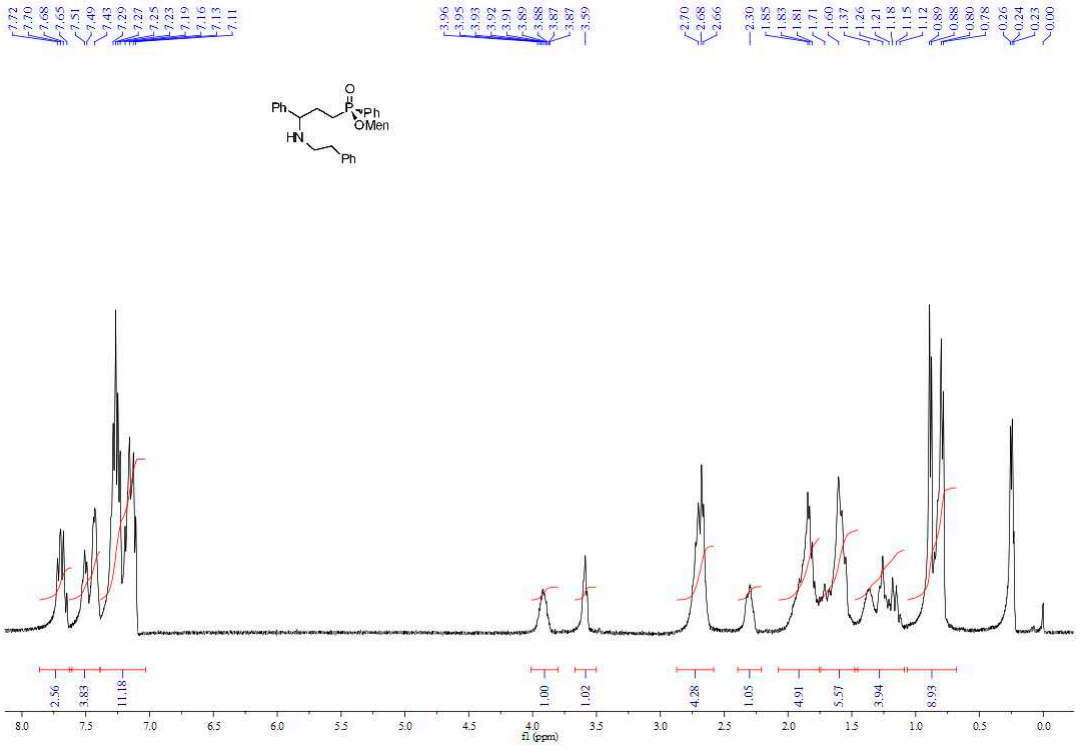


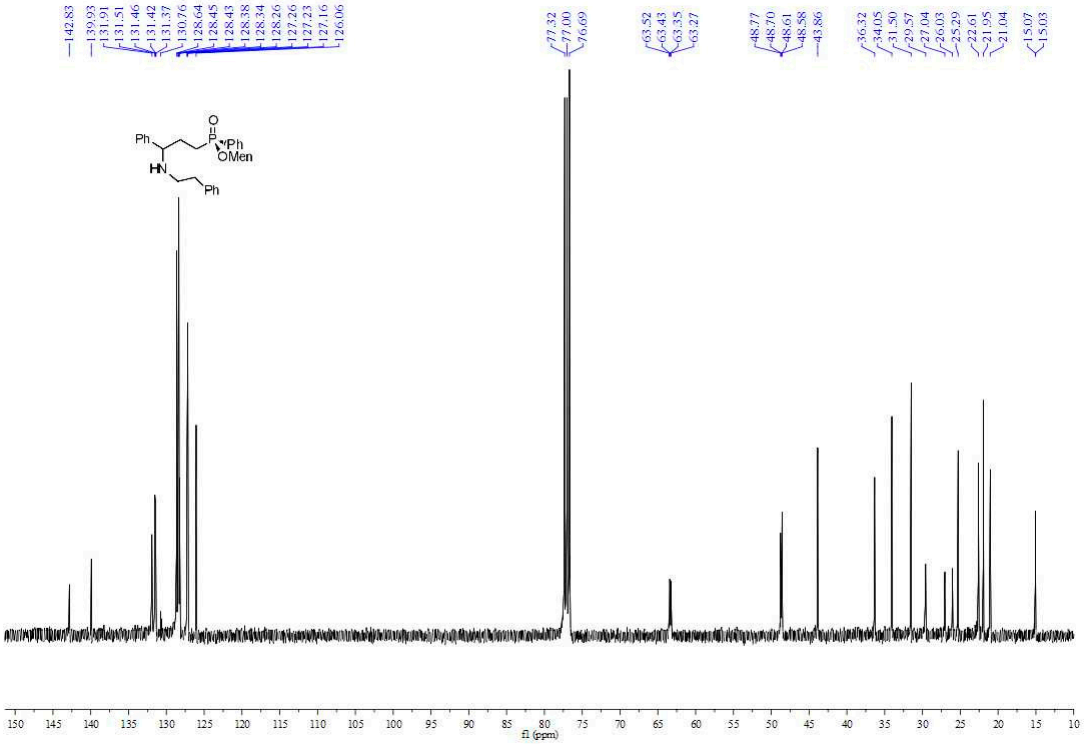
(*S*P)-Menthyl-3-phenethylamino-3-phenylpropyl phenylphosphinate, 11ab, ^{31}P NMR spectroscopy



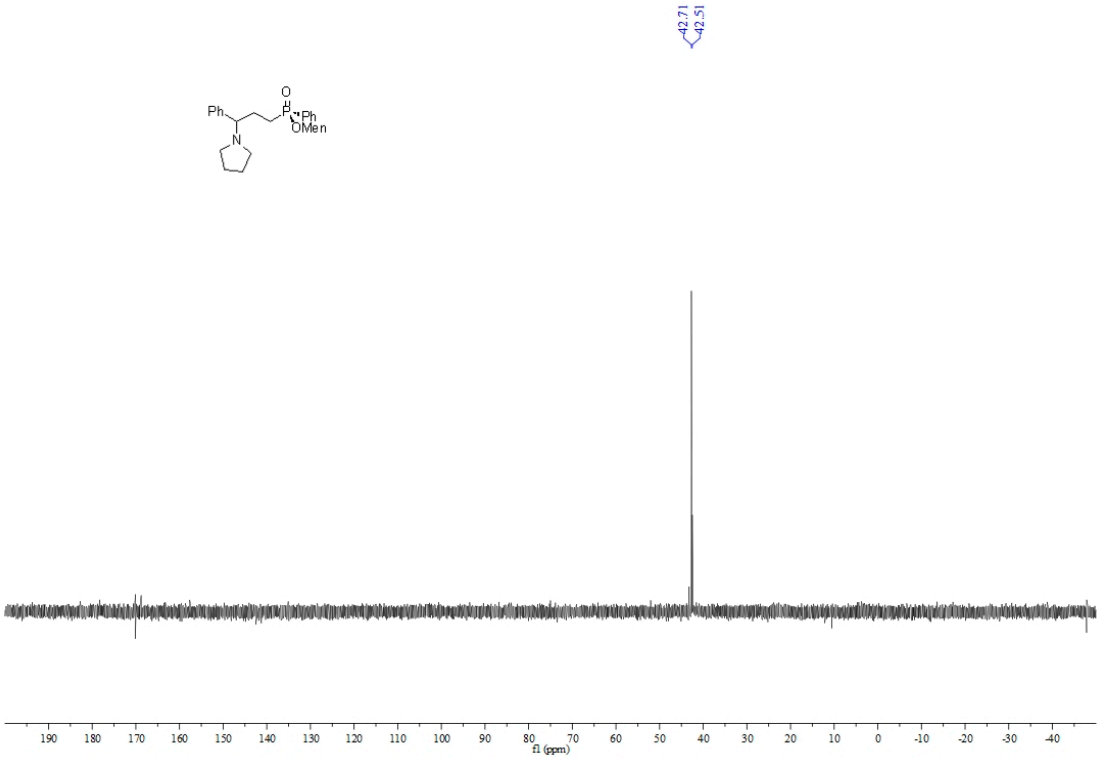
^{1}H NMR spectroscopy of 11ab



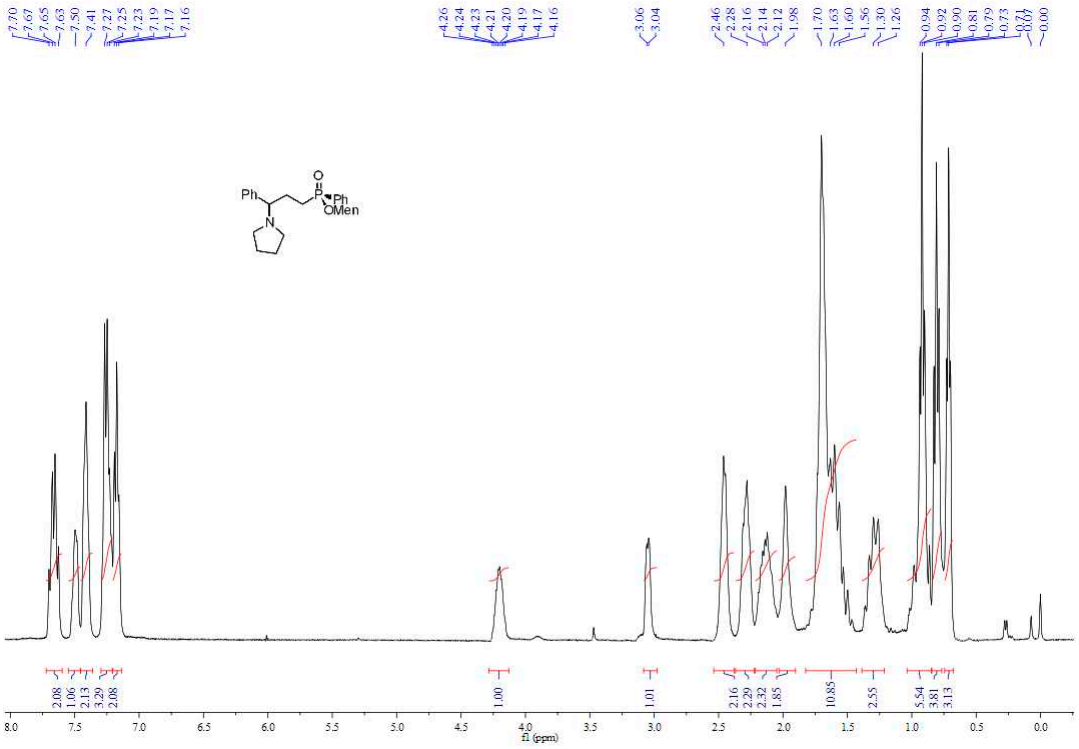
^{13}C NMR spectroscopy of 11ab



(*S*P)-Menthyl-3-phenyl-3-pyrrolidin-1-yl propylphosphinate, 11ac, ^{31}P NMR spectroscopy



^{1}H NMR spectroscopy of 11ac



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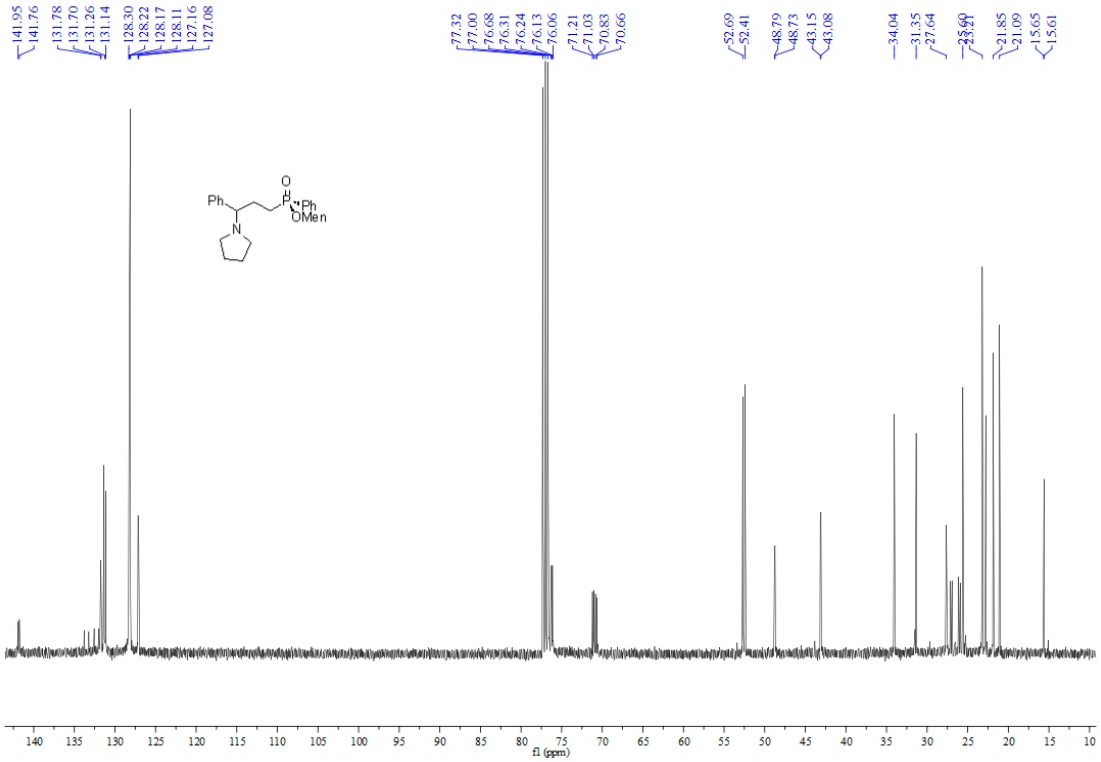
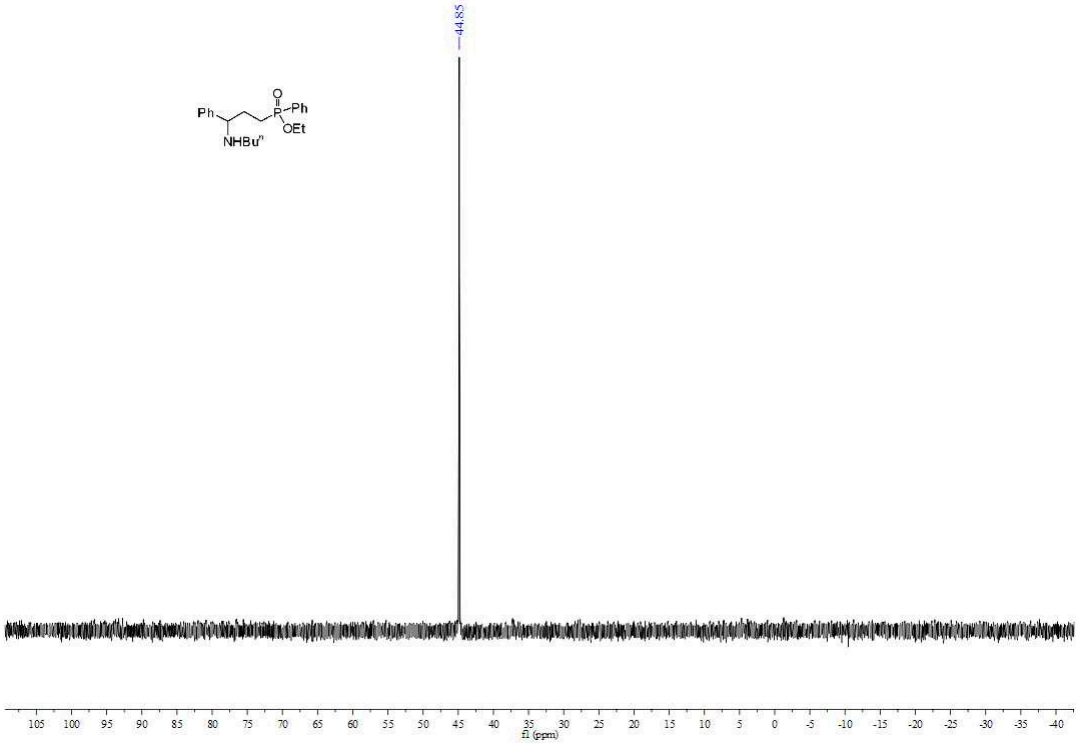
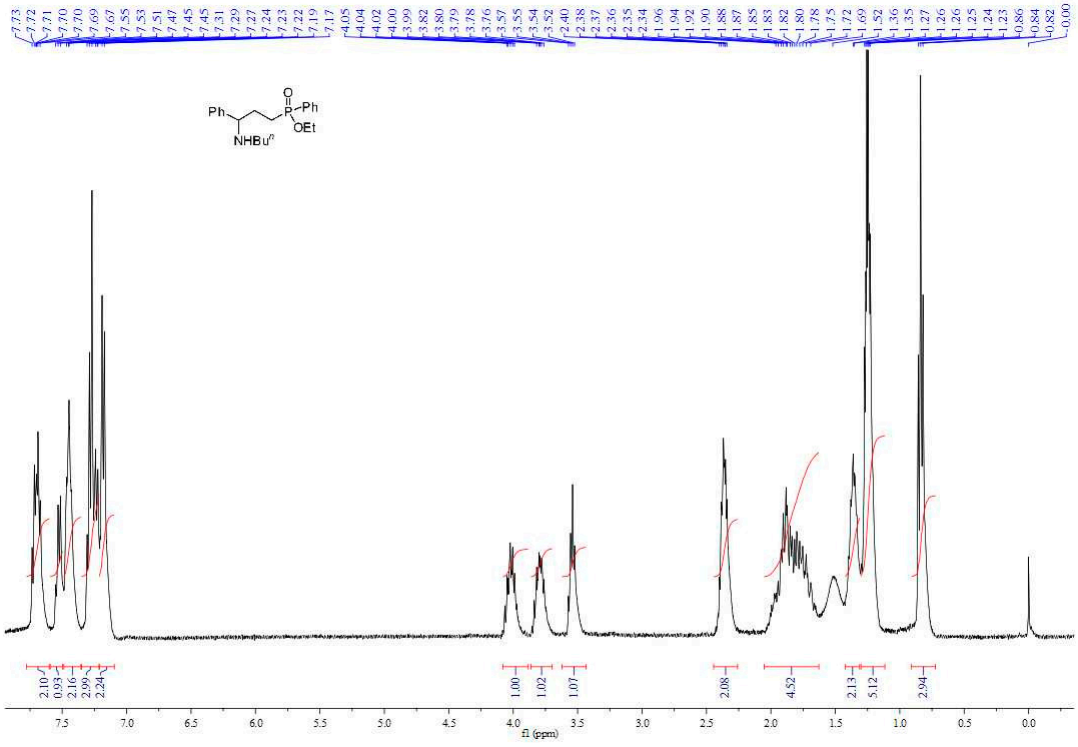


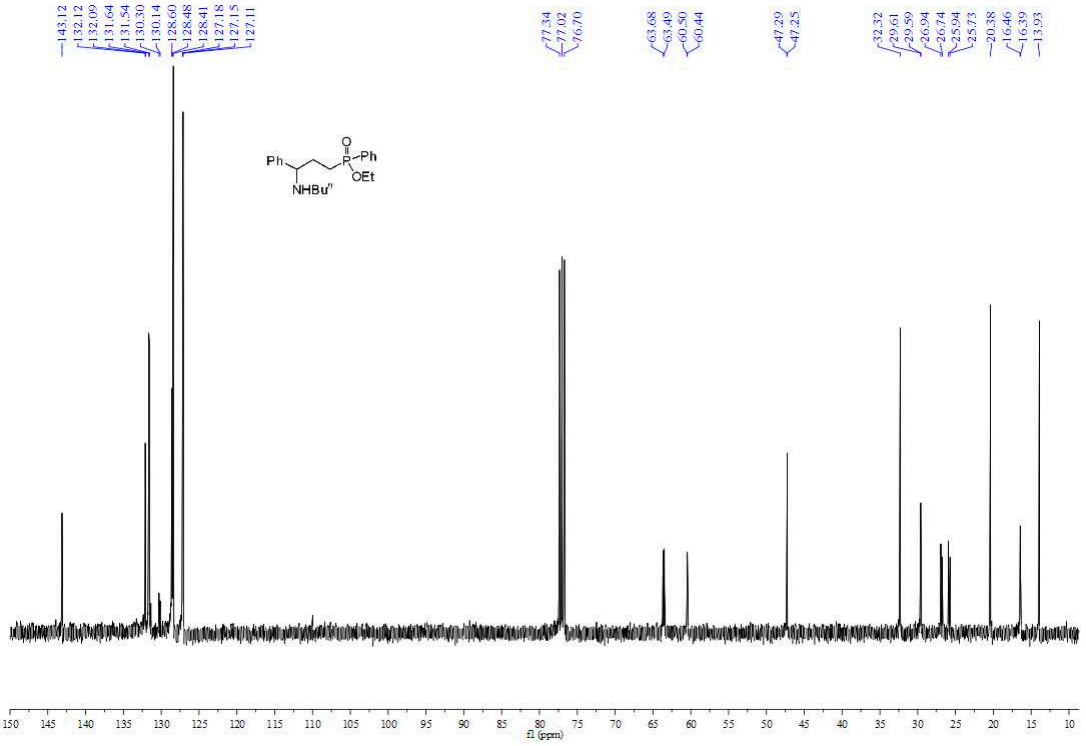
Ethyl 3-butylamino-3-phenylpropyl phenylphosphinate, 11ba, ^{31}P NMR spectroscopy



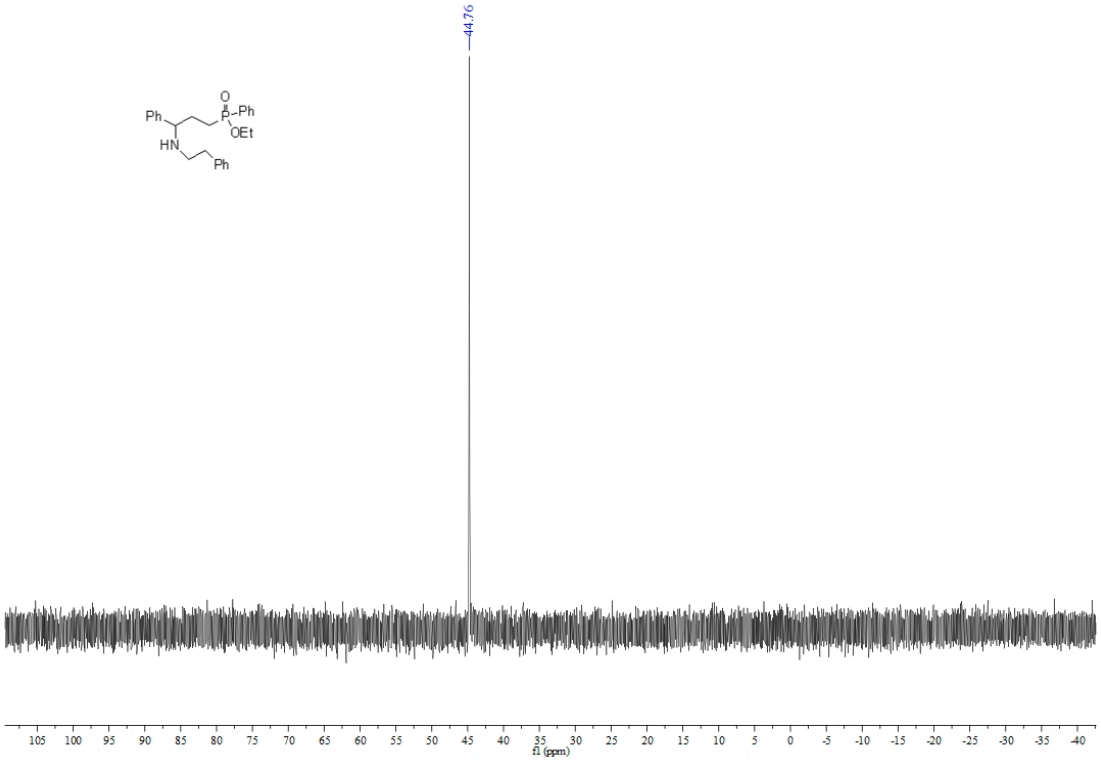
^{1}H NMR spectroscopy of 11ba



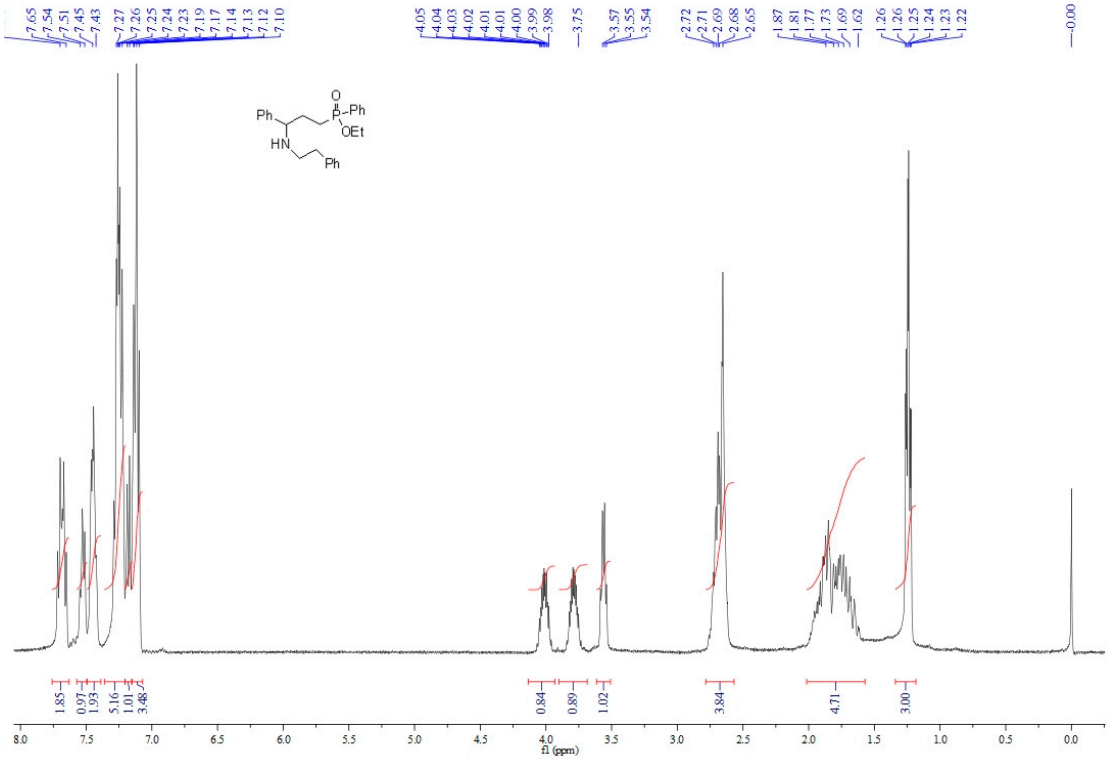
^{13}C NMR spectroscopy of 11ba



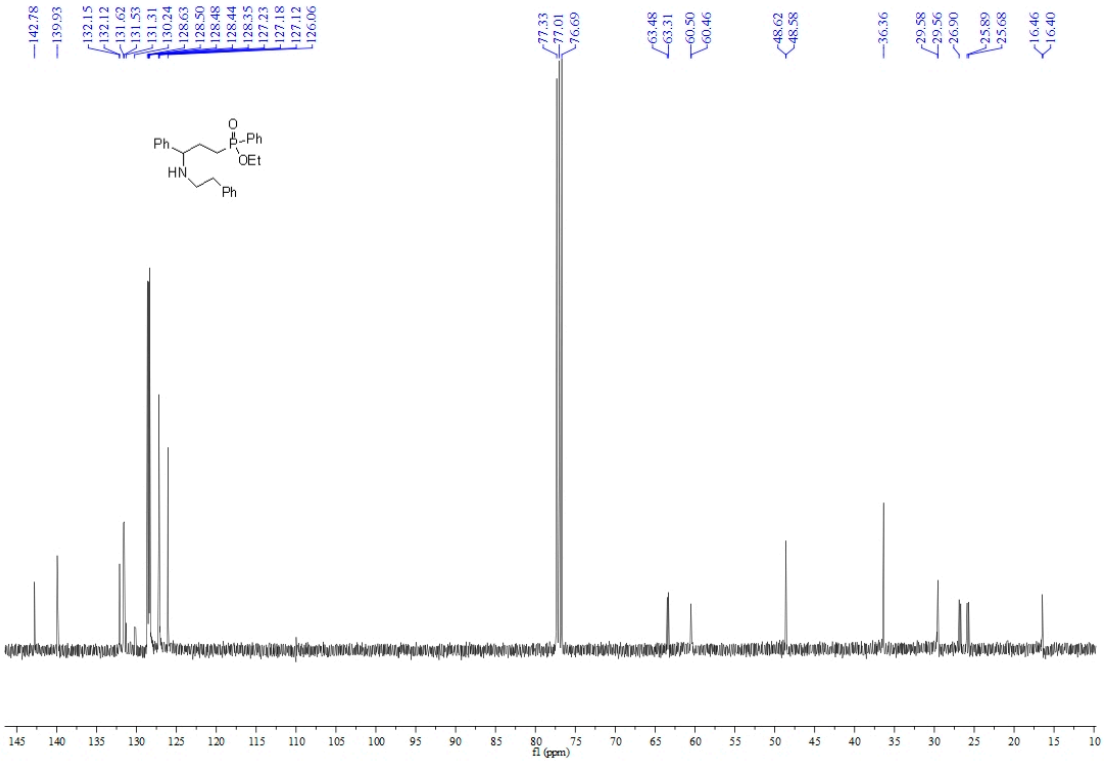
Ethyl 3-phenethylamino-3-phenylpropyl phenylphosphinate, 11bb, ^{31}P NMR spectroscopy



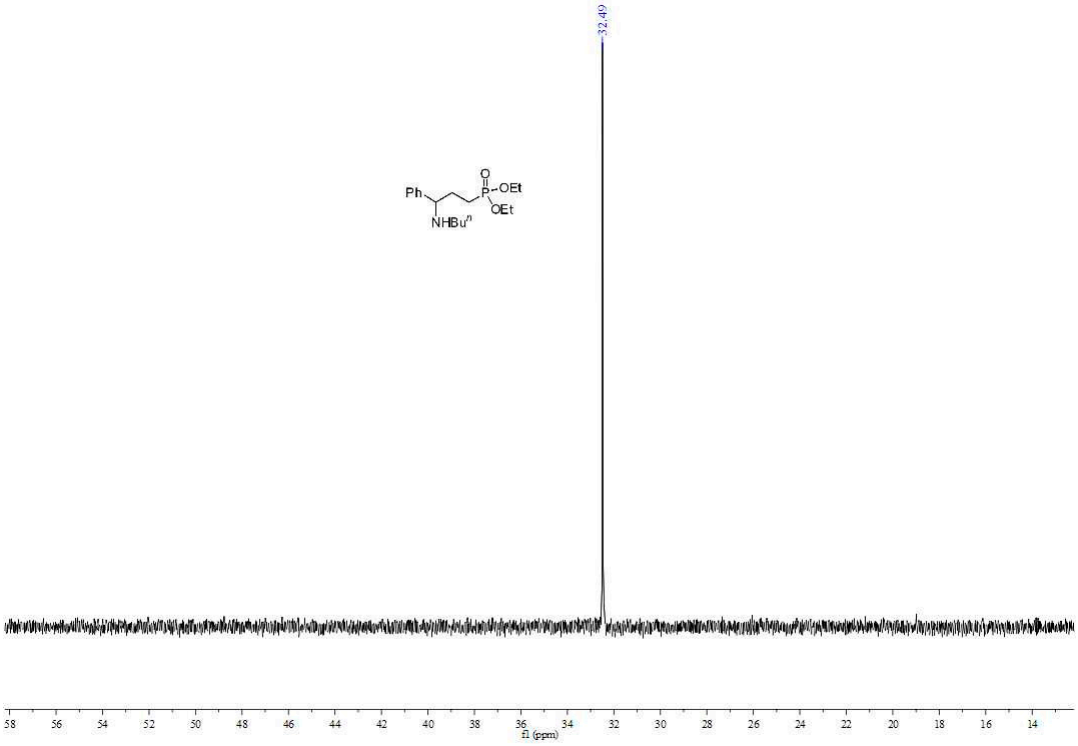
^{1}H NMR spectroscopy of 11bb



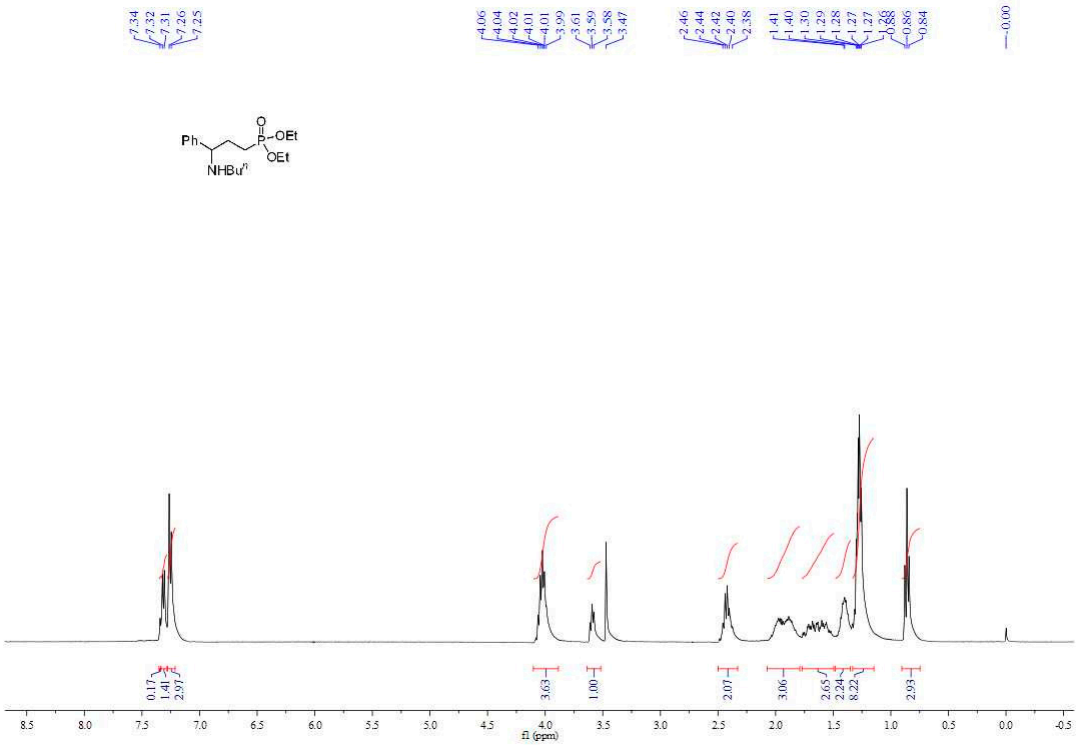
^{13}C NMR spectroscopy of 11bb



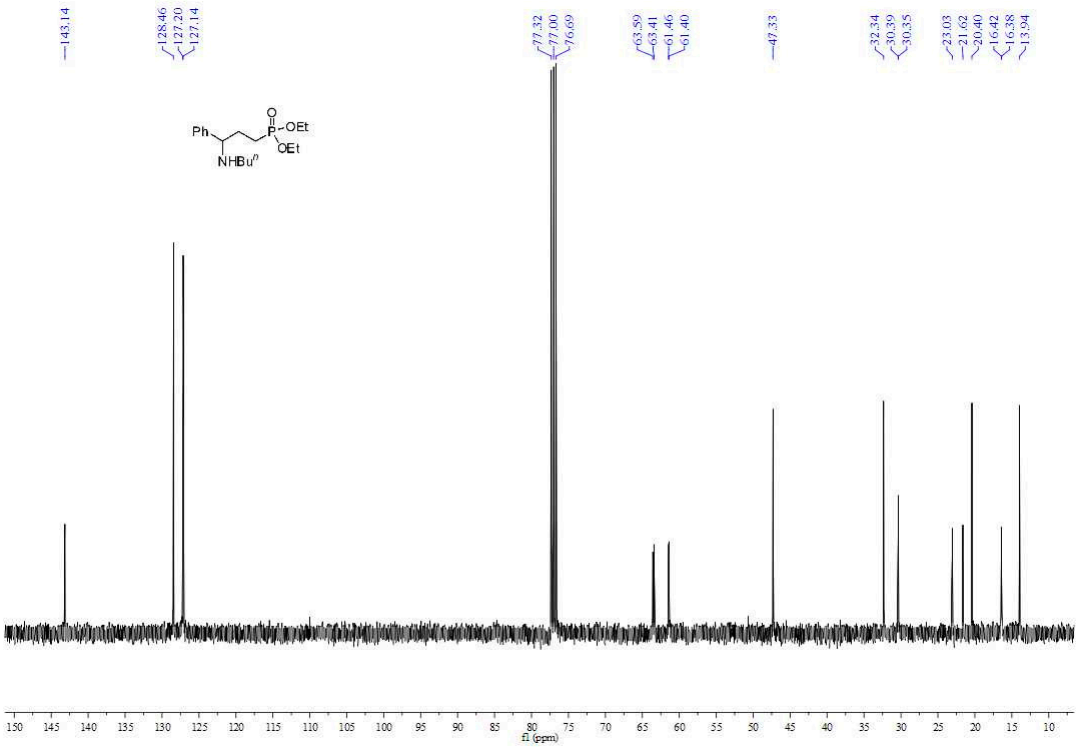
Diethyl 3-butylamino-3-phenyl propylphosphonate, 11ca, ^{31}P NMR spectroscopy



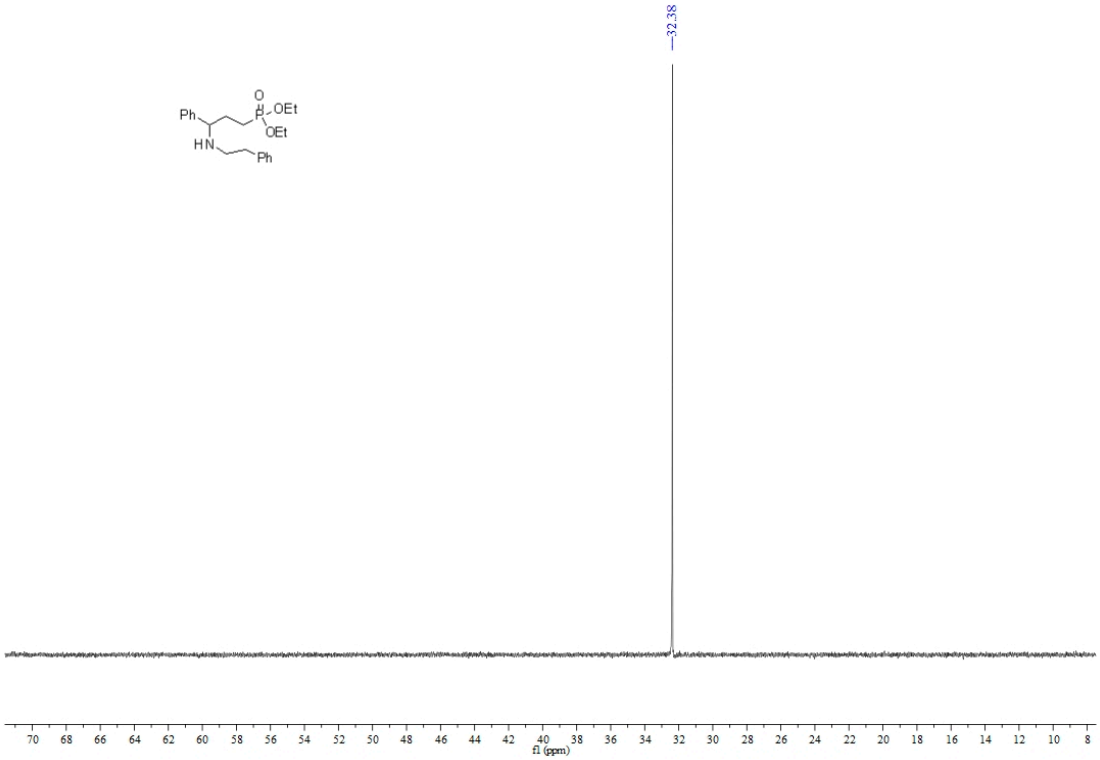
^{1}H NMR spectroscopy of 11ca



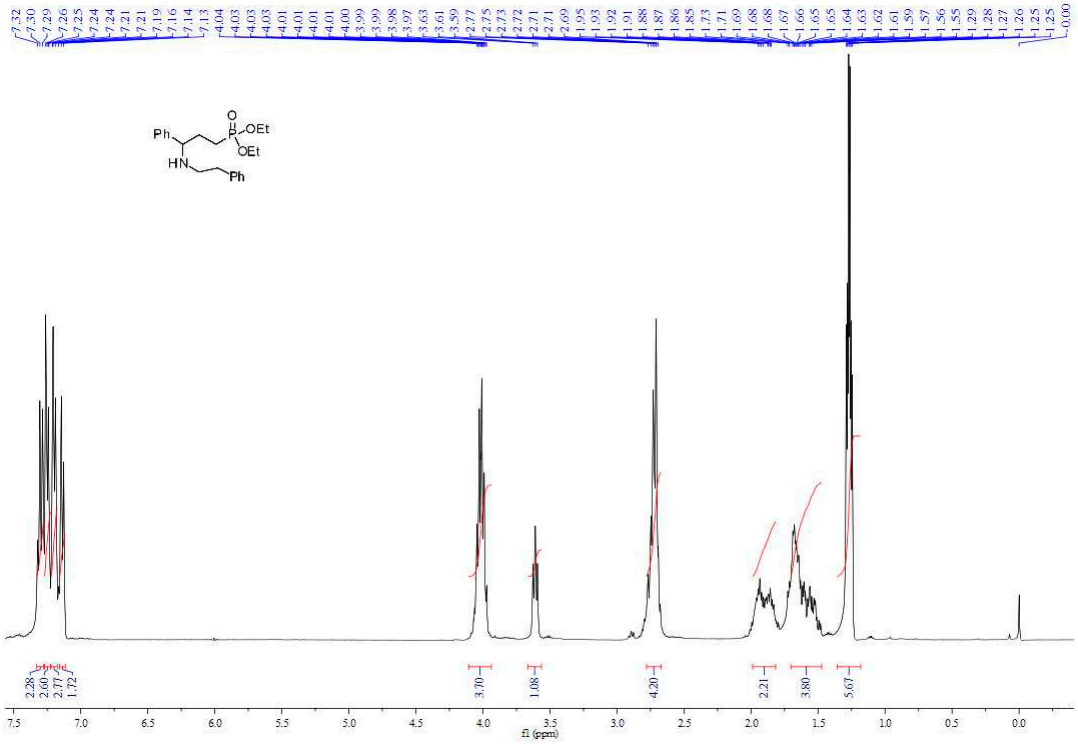
^{13}C NMR spectroscopy of 11ca



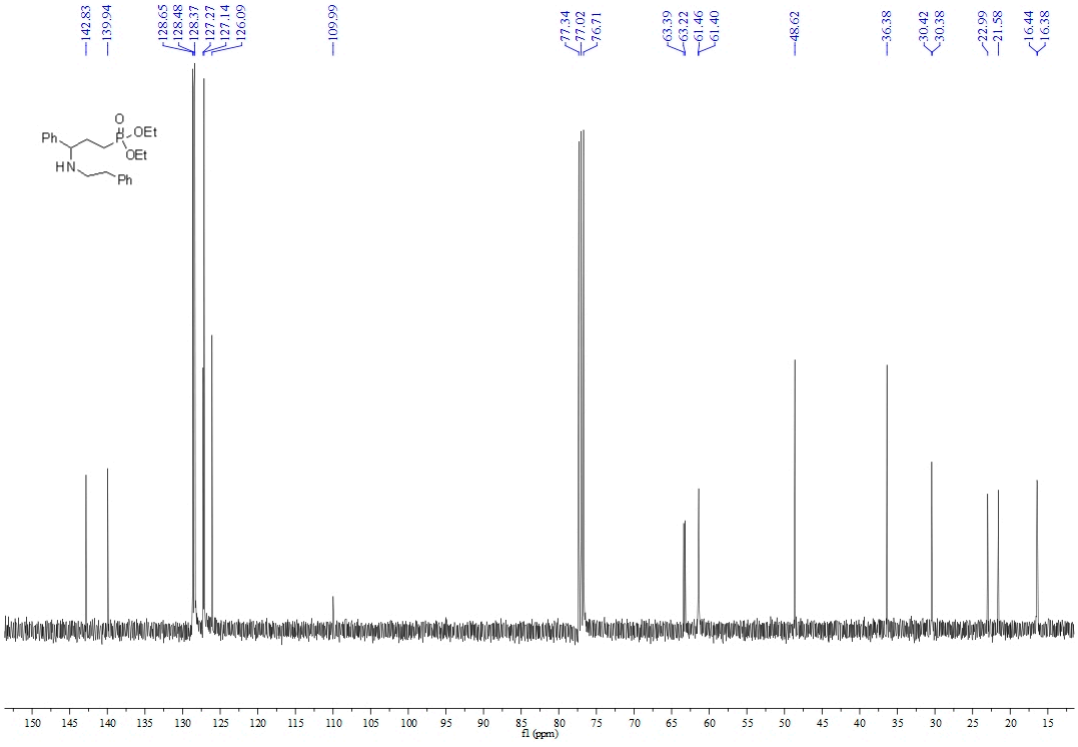
Diethyl 3-phenethylamino-3-phenyl propylphosphonate, 11cb, ^{31}P NMR spectroscopy



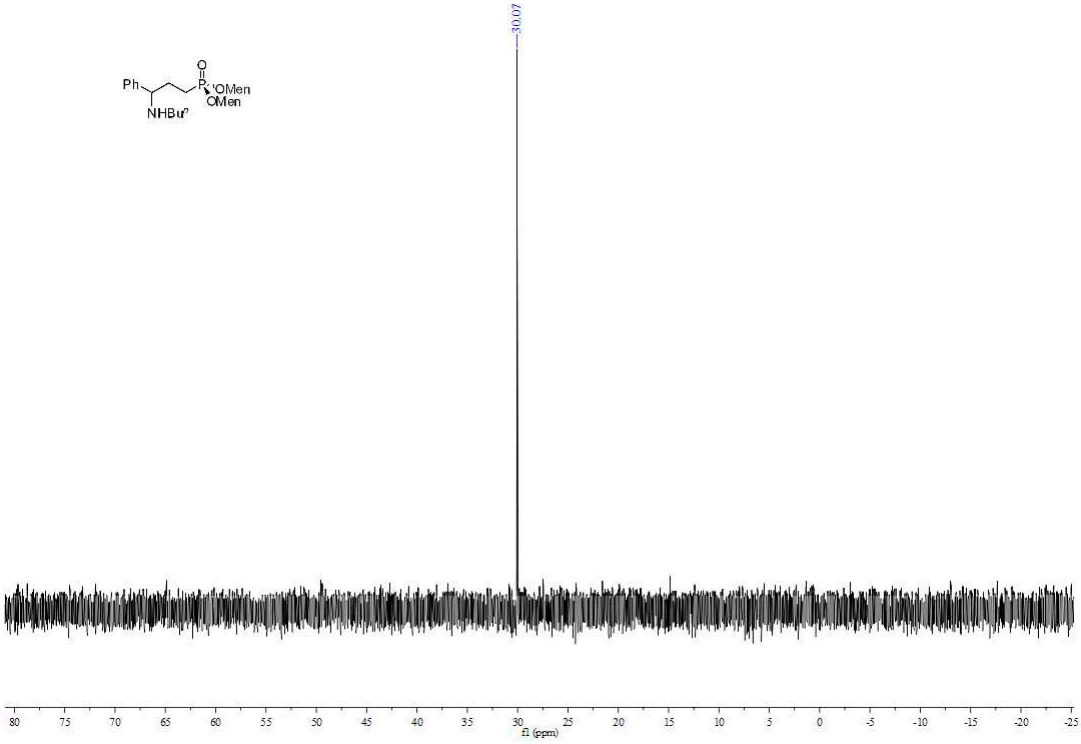
^{1}H NMR spectroscopy of 11cb



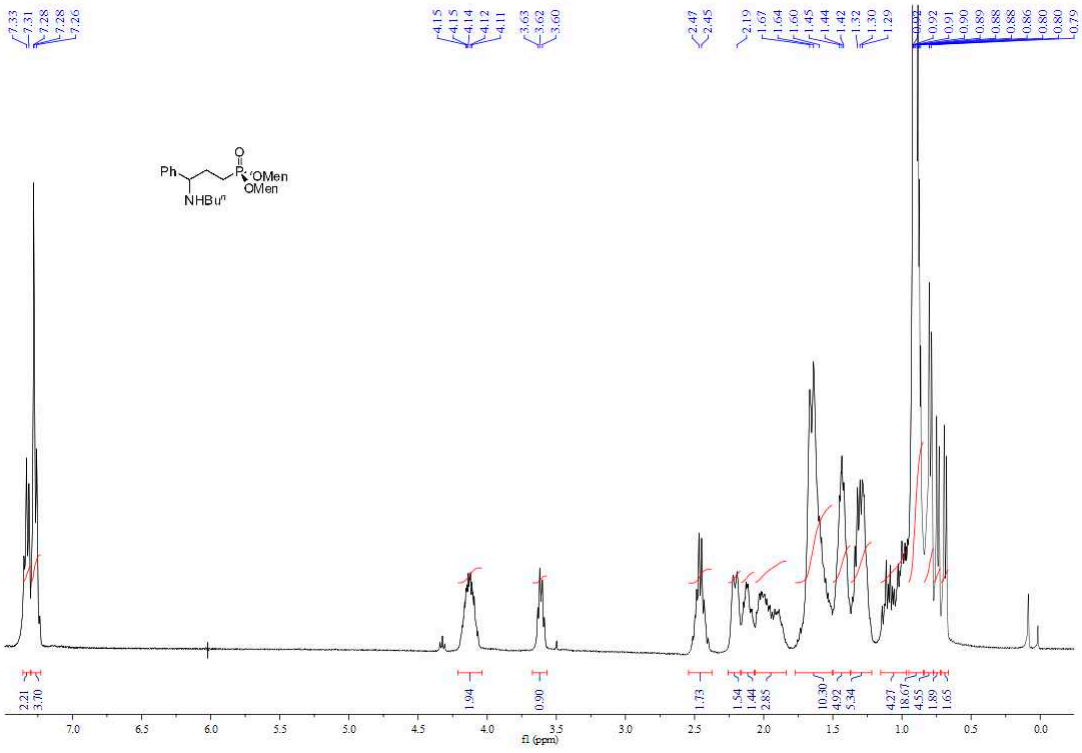
^{13}C NMR spectroscopy of 11cb



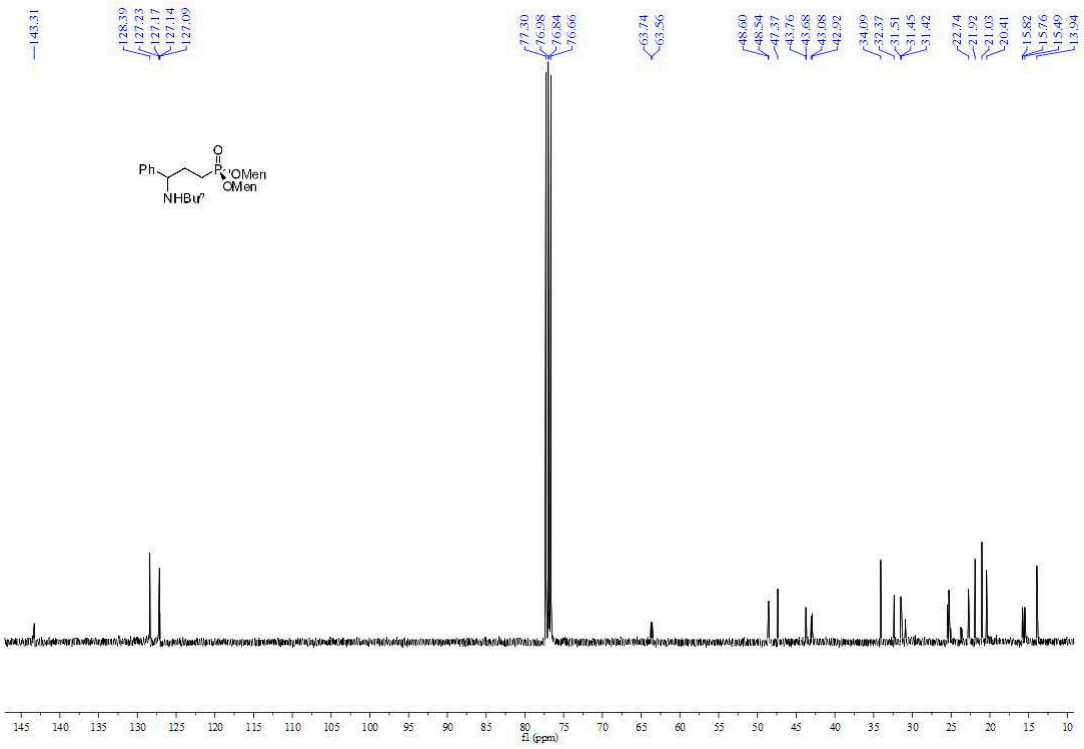
Dimenthyl 3-butylamino-3-phenyl propylphosphonate, 11da, ^{31}P NMR spectroscopy



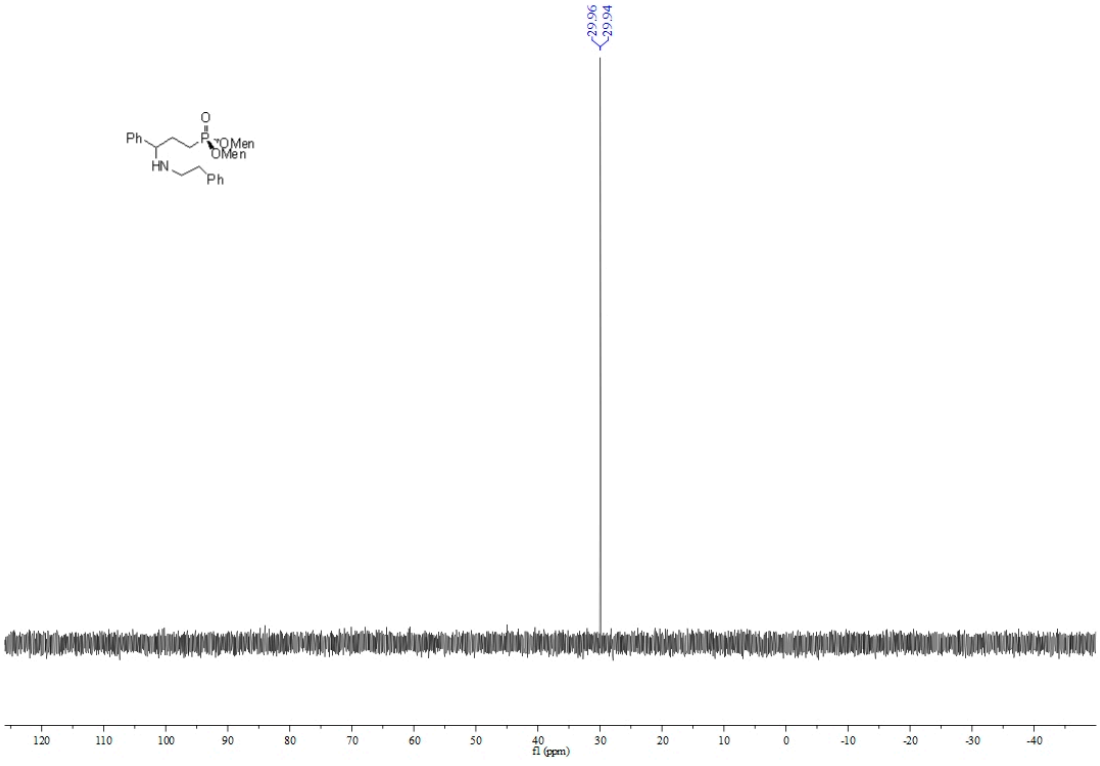
^{1}H NMR spectroscopy of 11da



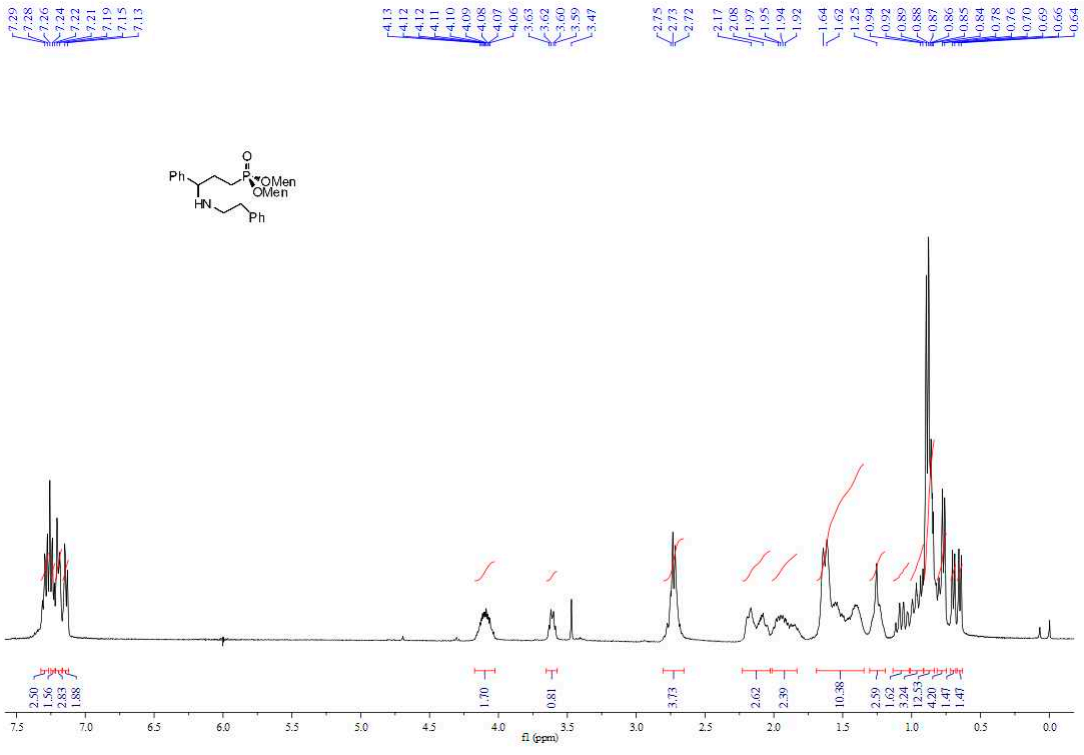
^{13}C NMR spectroscopy of 11da



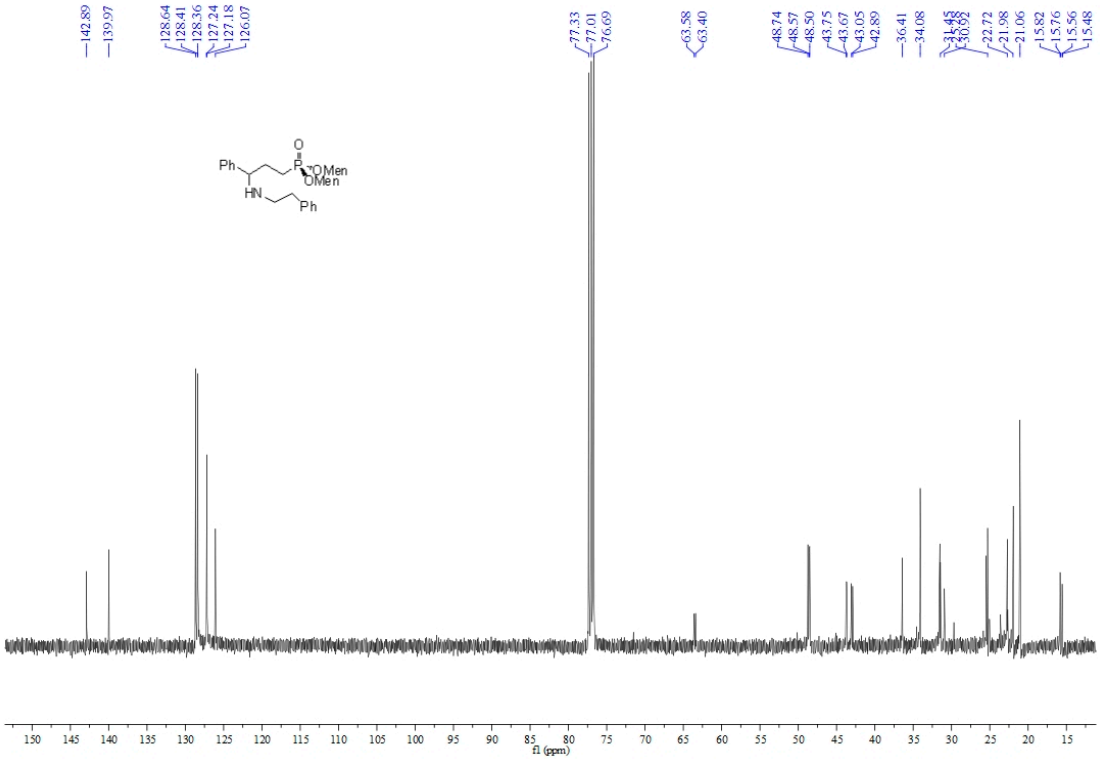
Dimenthyl 3-phenylethylamino-3-phenyl propylphosphonate, 11db, ^{31}P NMR spectroscopy



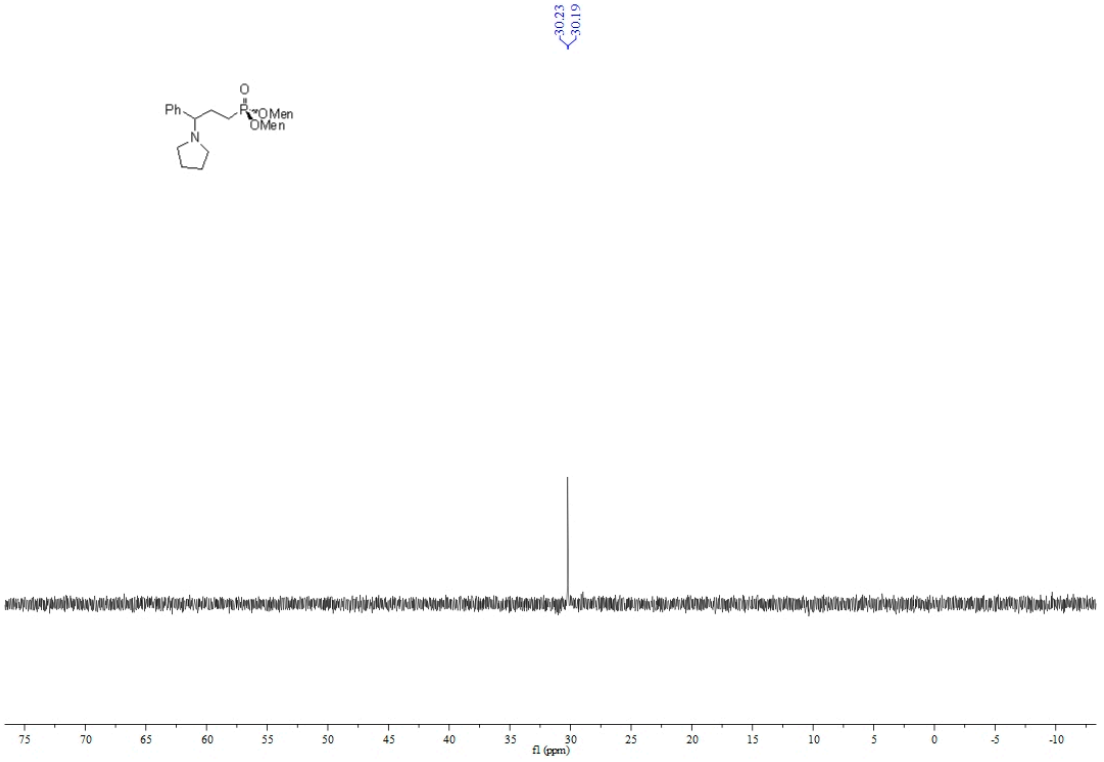
^{1}H NMR spectroscopy of 11db



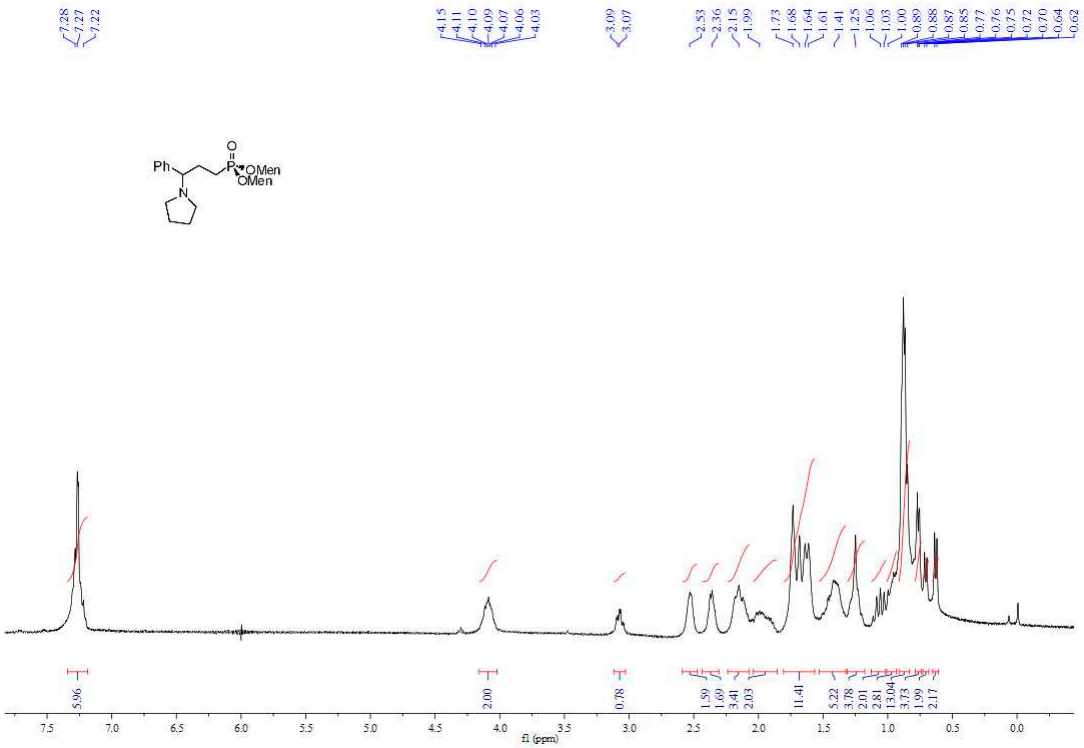
^{13}C NMR spectroscopy of 11db



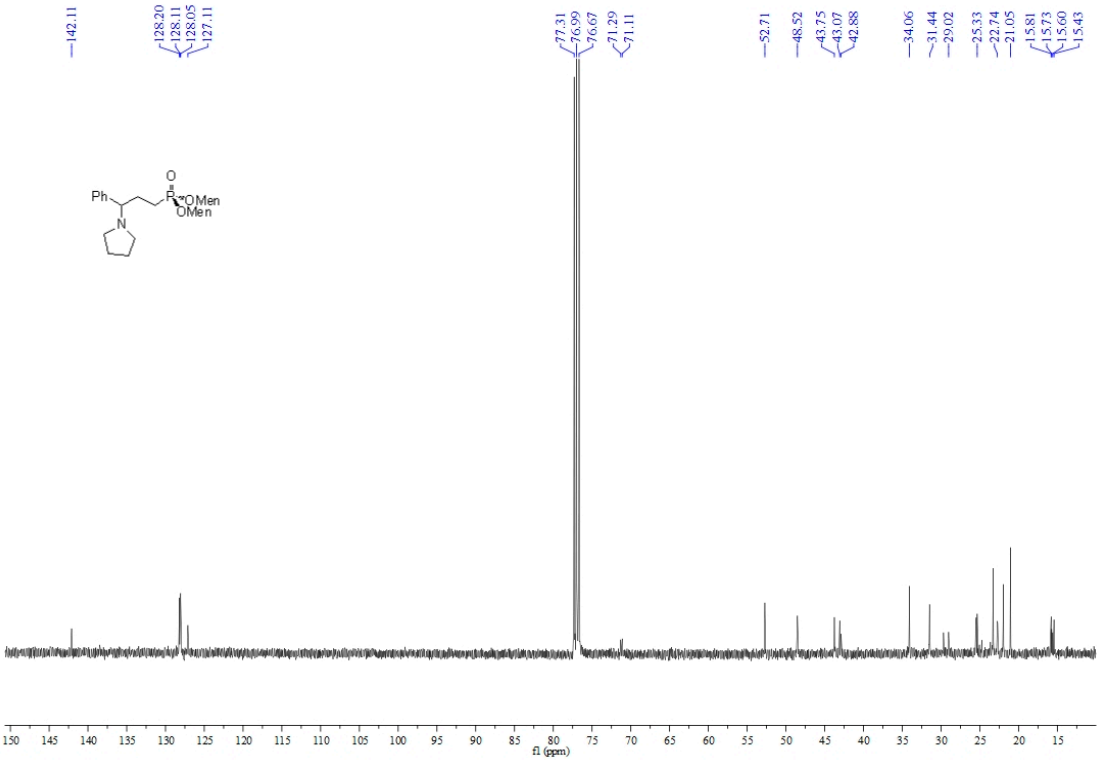
Dimenthyl 3-phenyl-3-pyrrolidin-1-yl propylphosphonate, 11dc, ^{31}P NMR spectroscopy



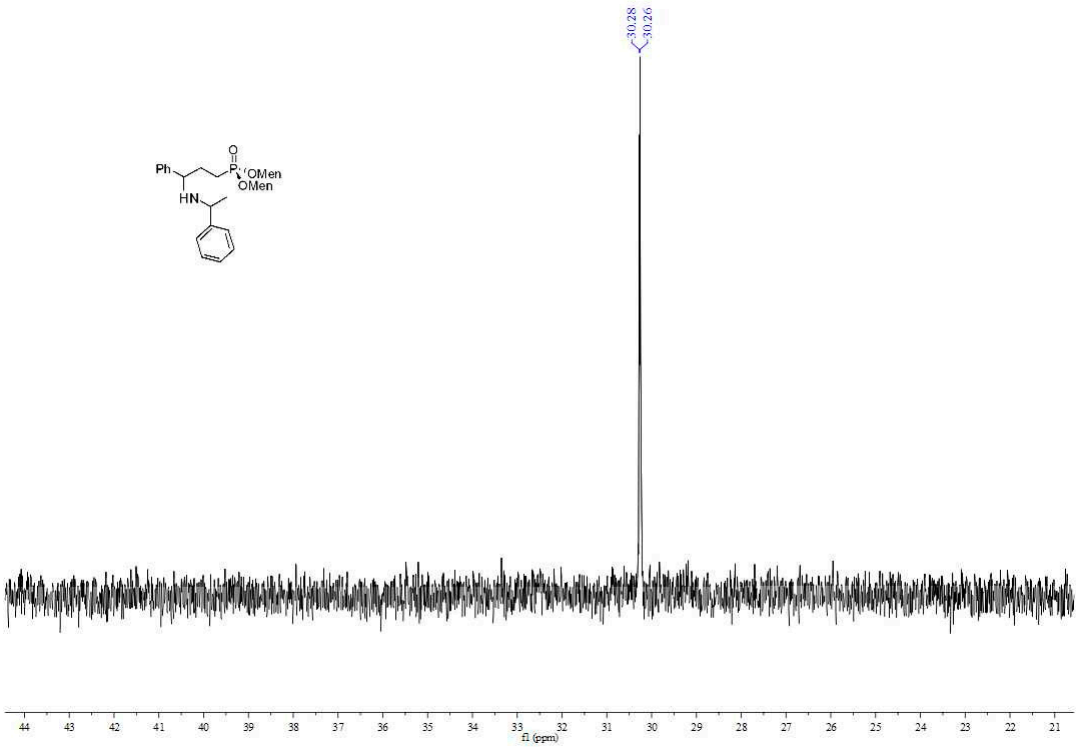
^{1}H NMR spectroscopy of 11dc



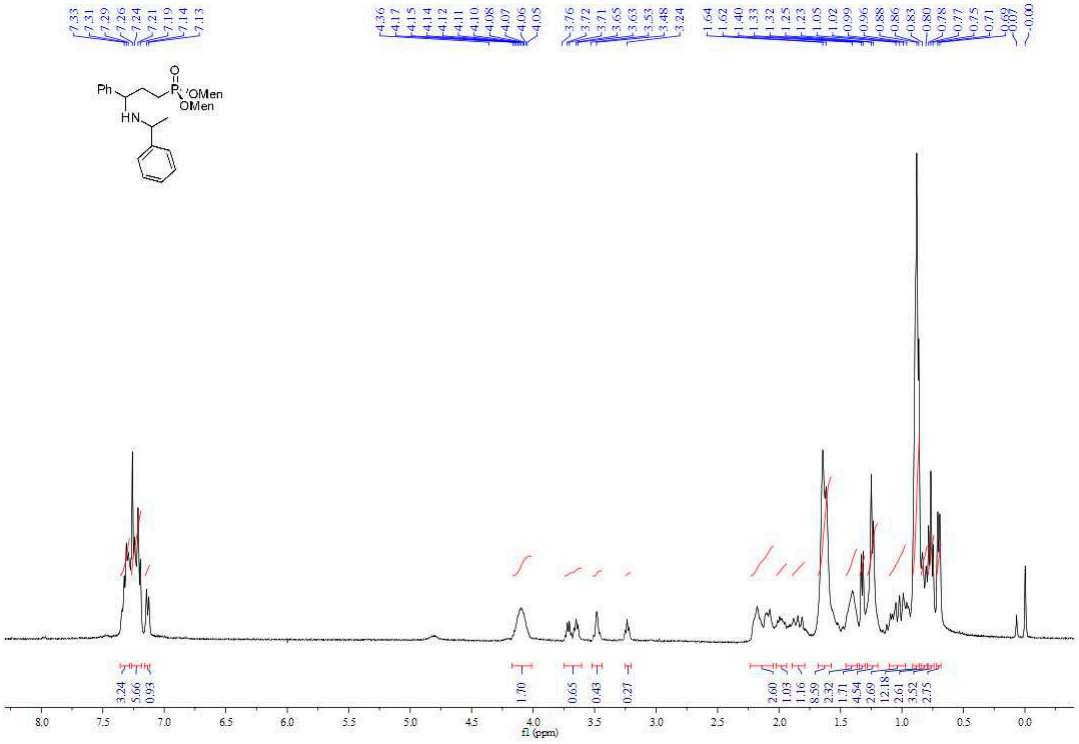
^{13}C NMR spectroscopy of 11dc



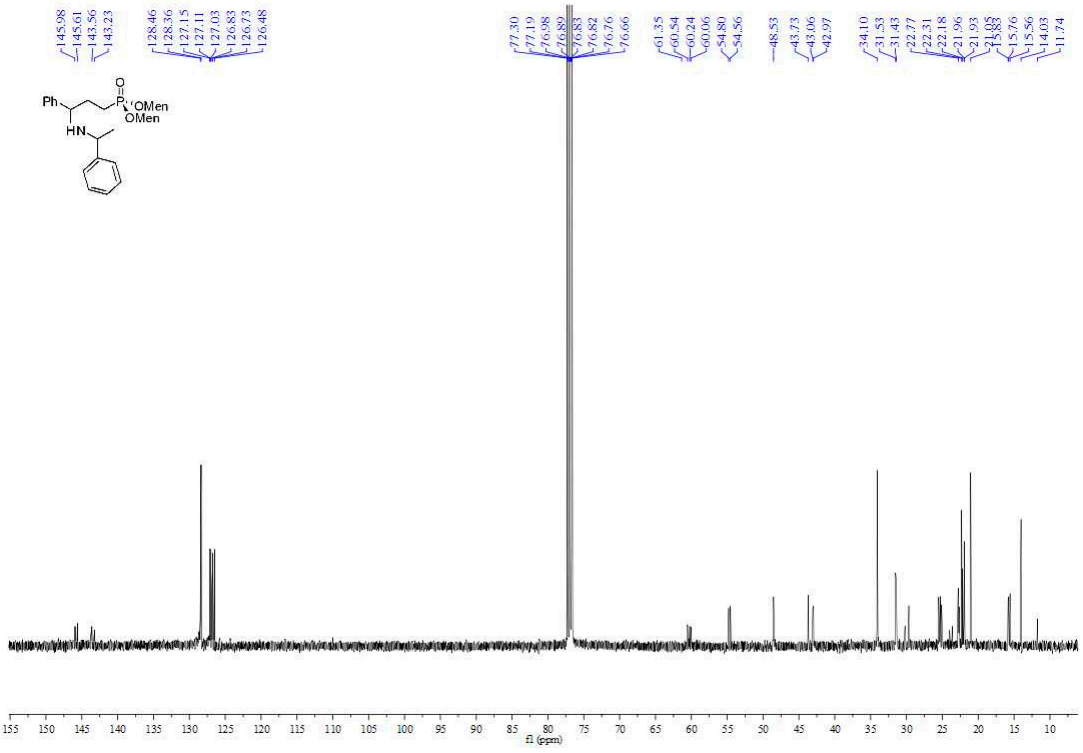
Dimenthyl-3-methyl phenylamino-3-phenyl propylphosphonate, 11dd, ^{31}P NMR spectroscopy



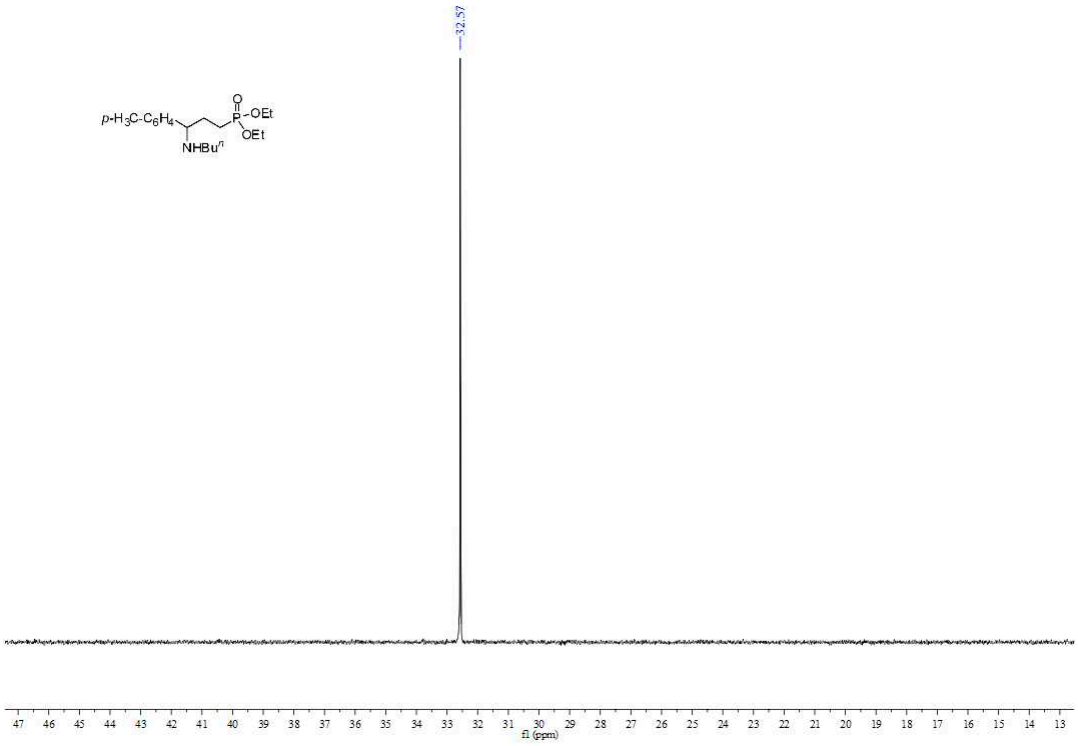
^{1}H NMR spectroscopy of 11dd



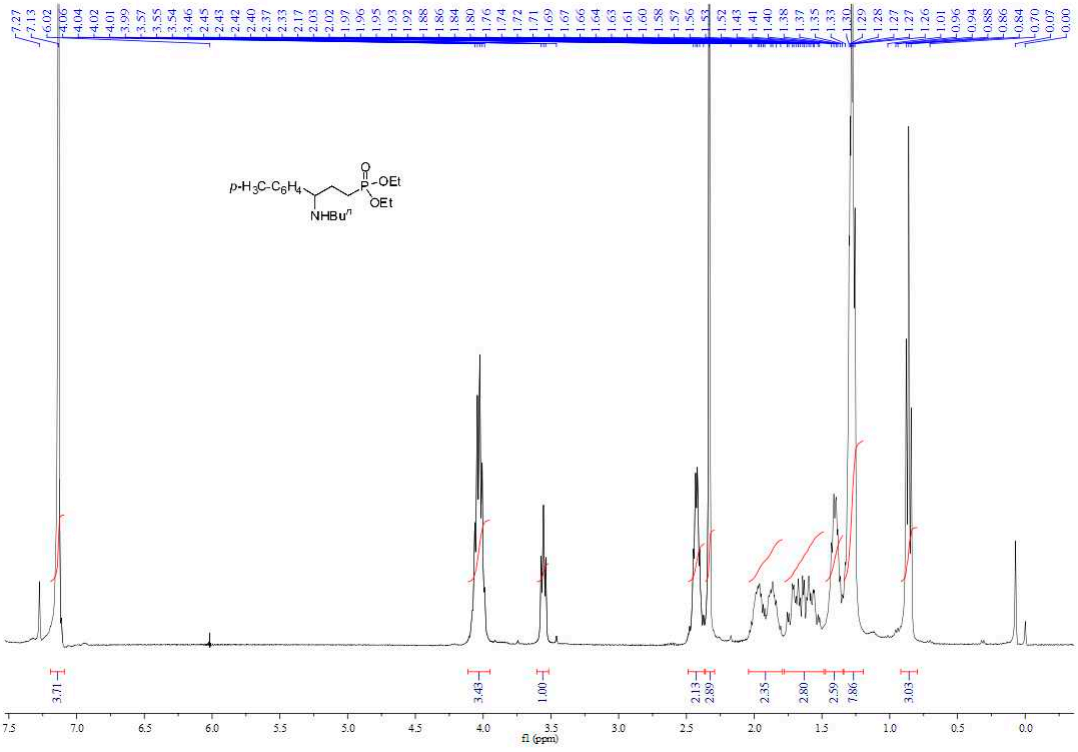
^{13}C NMR spectroscopy of 11dd



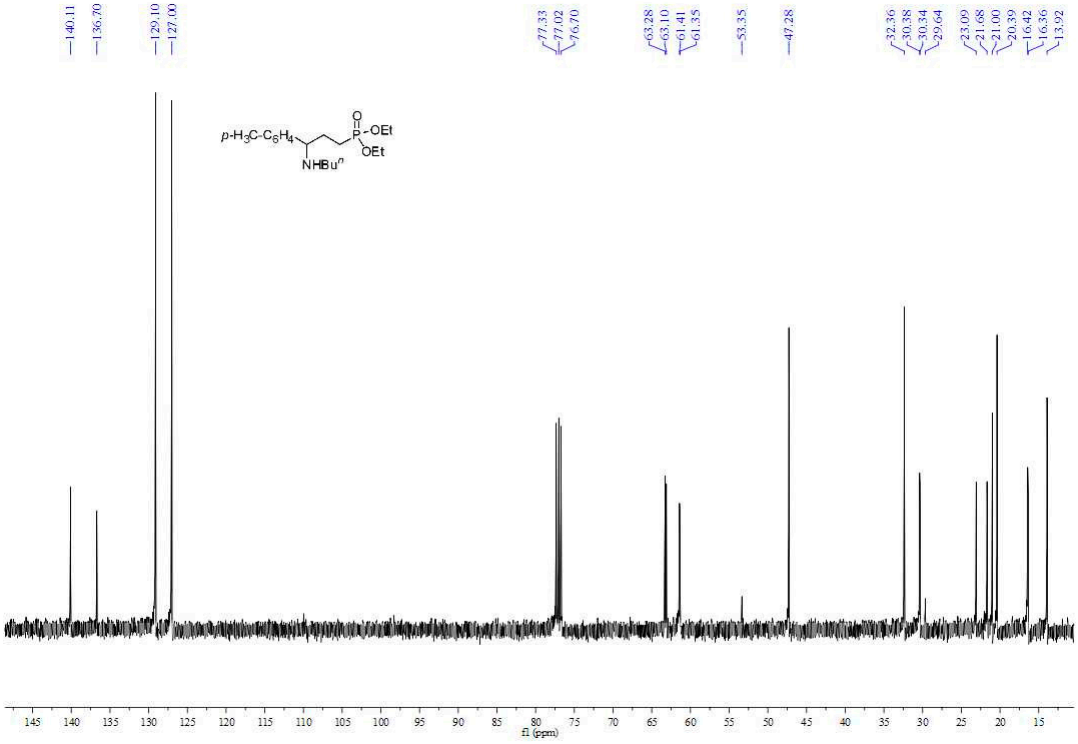
Diethyl 3-butylamino-3-p-tolyl propylphosphonate, 11ea, ^{31}P NMR spectroscopy



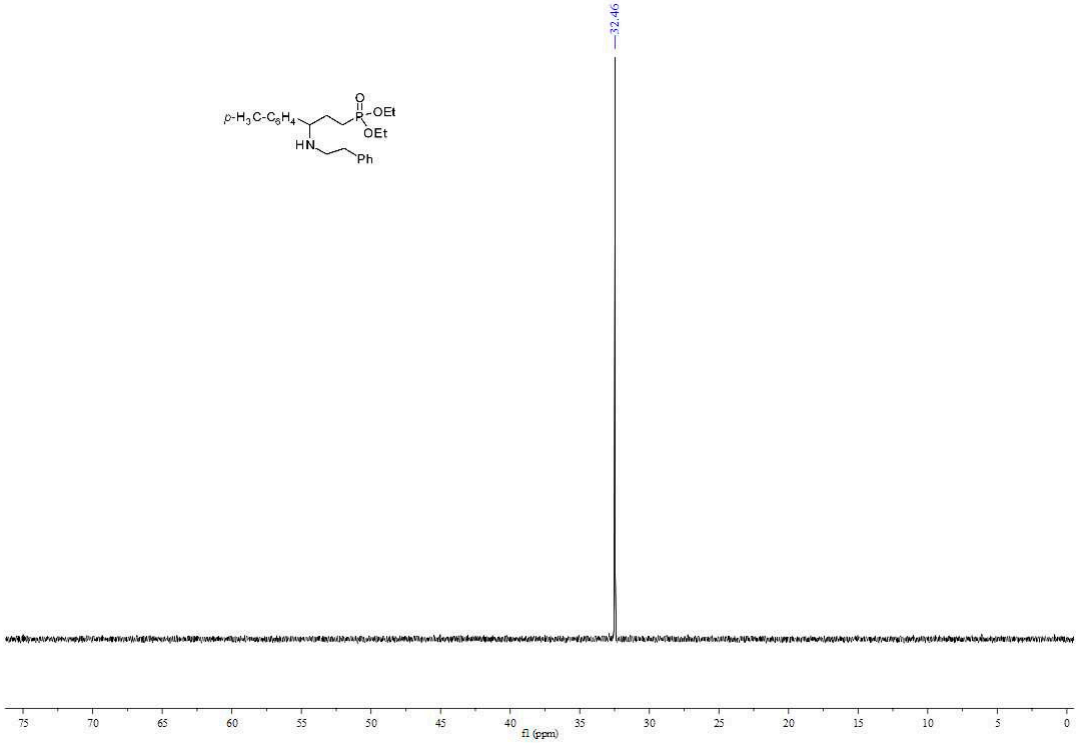
^{1}H NMR spectroscopy of 11ea



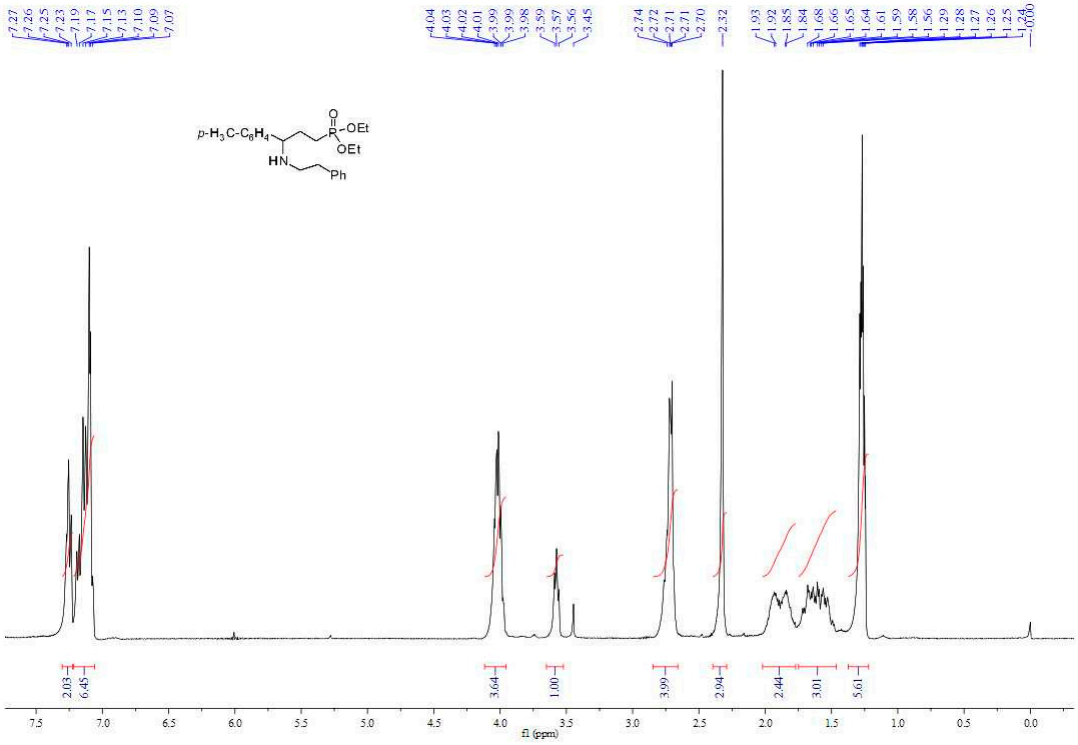
^{13}C NMR spectroscopy of 11ea



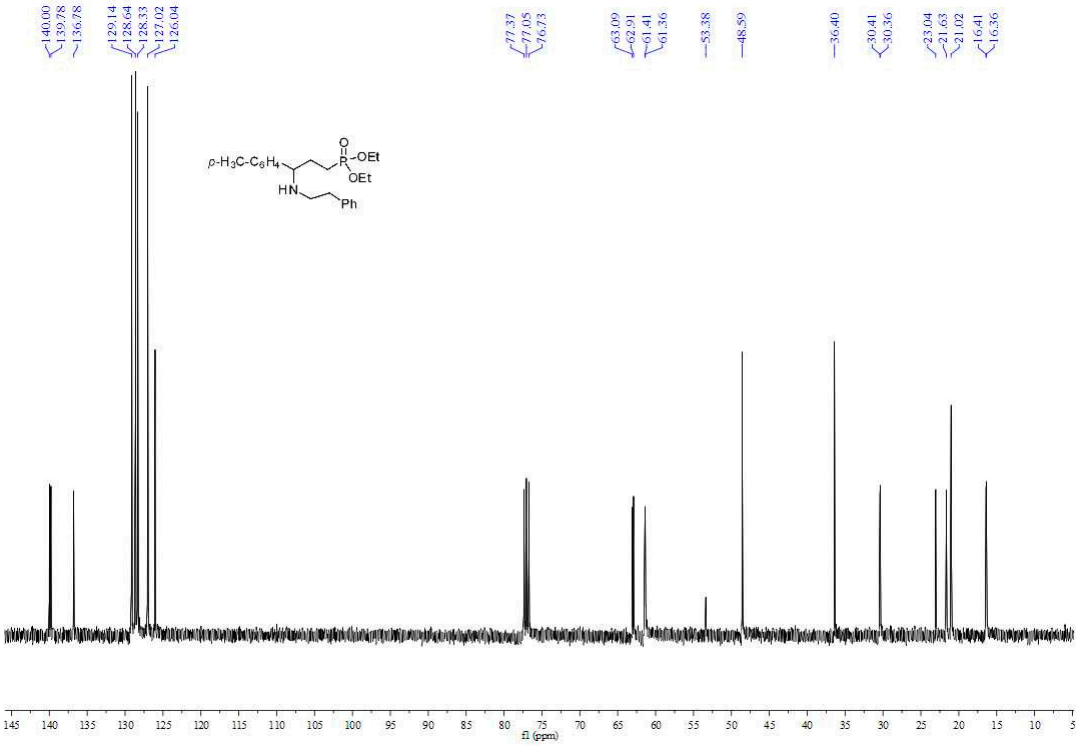
Diethyl 3-phenethylamino-3-*p*-tolyl propylphosphonate, 11eb, ^{31}P NMR spectroscopy



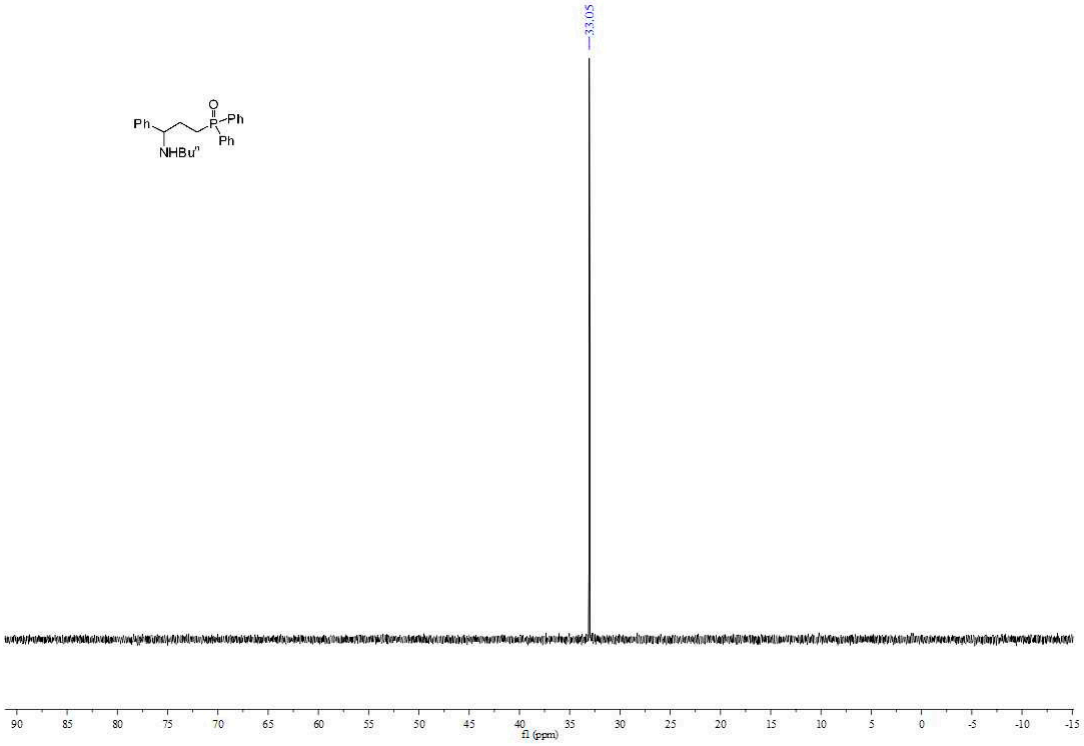
^{1}H NMR spectroscopy of 11eb



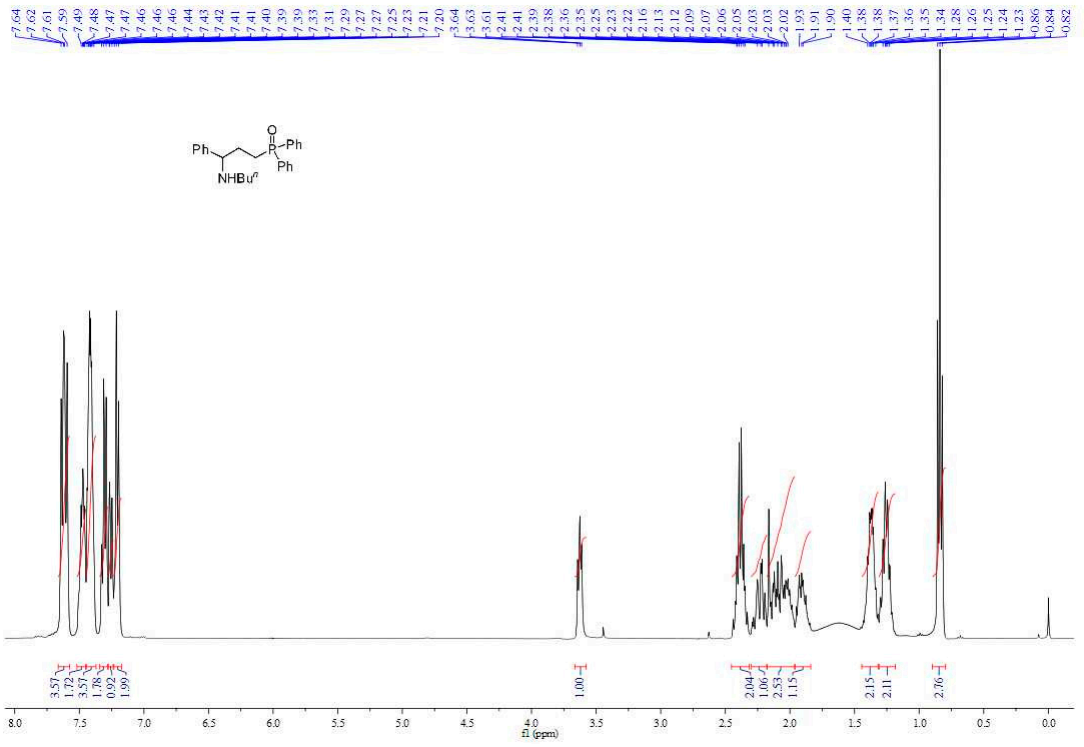
^{13}C NMR spectroscopy of 11eb



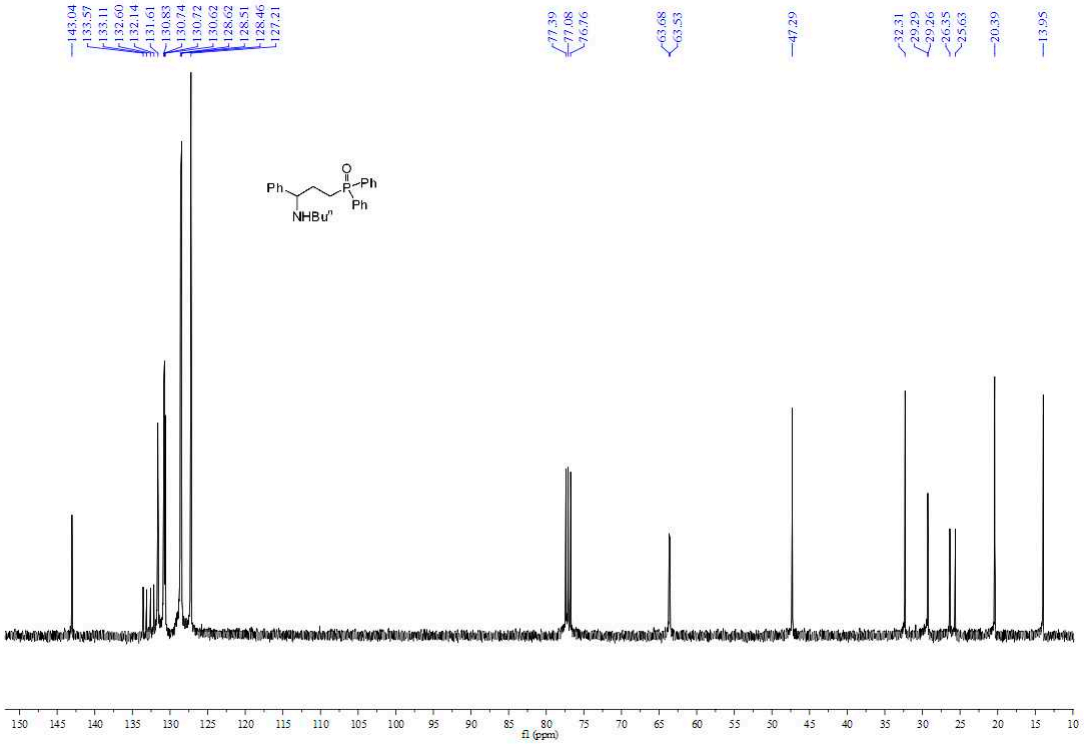
Diphenyl 3-butylamino-3-phenylpropyl phosphine oxide, 11fa, ^{31}P NMR spectroscopy



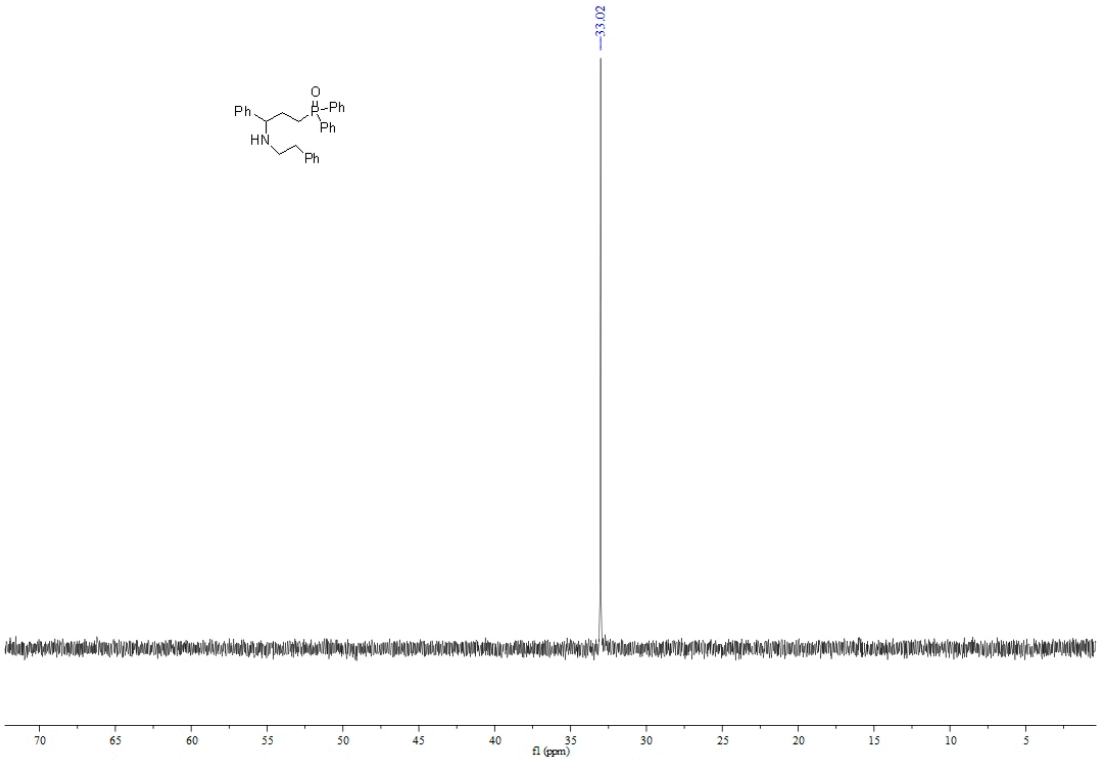
^{1}H NMR spectroscopy of 11fa



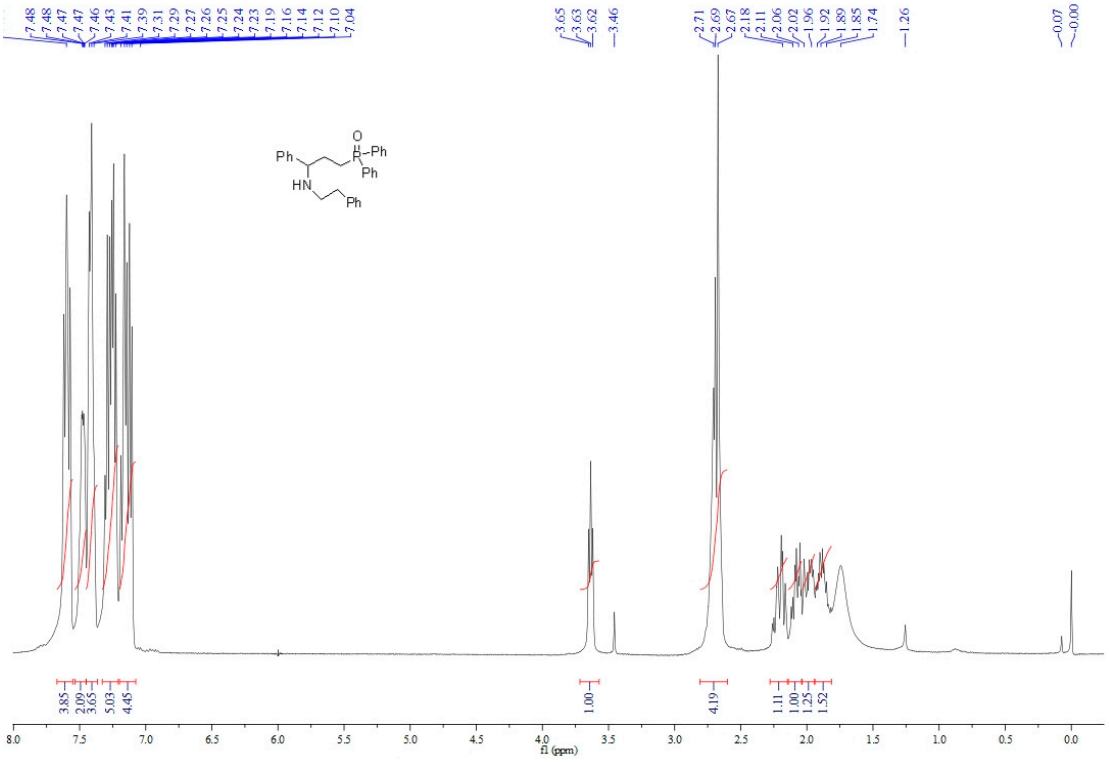
^{13}C NMR spectroscopy of 11fa



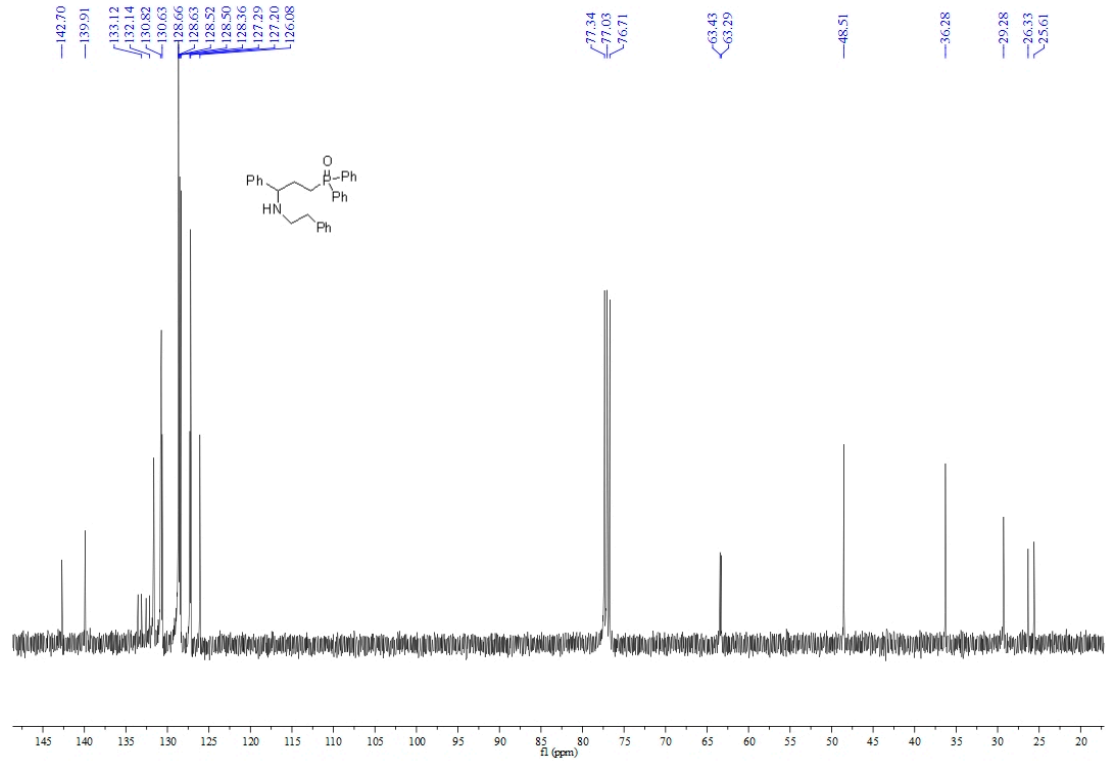
Diphenyl 3-phenethylamino-3-phenylpropyl phosphine oxide, 11fb, ^{31}P NMR spectroscopy



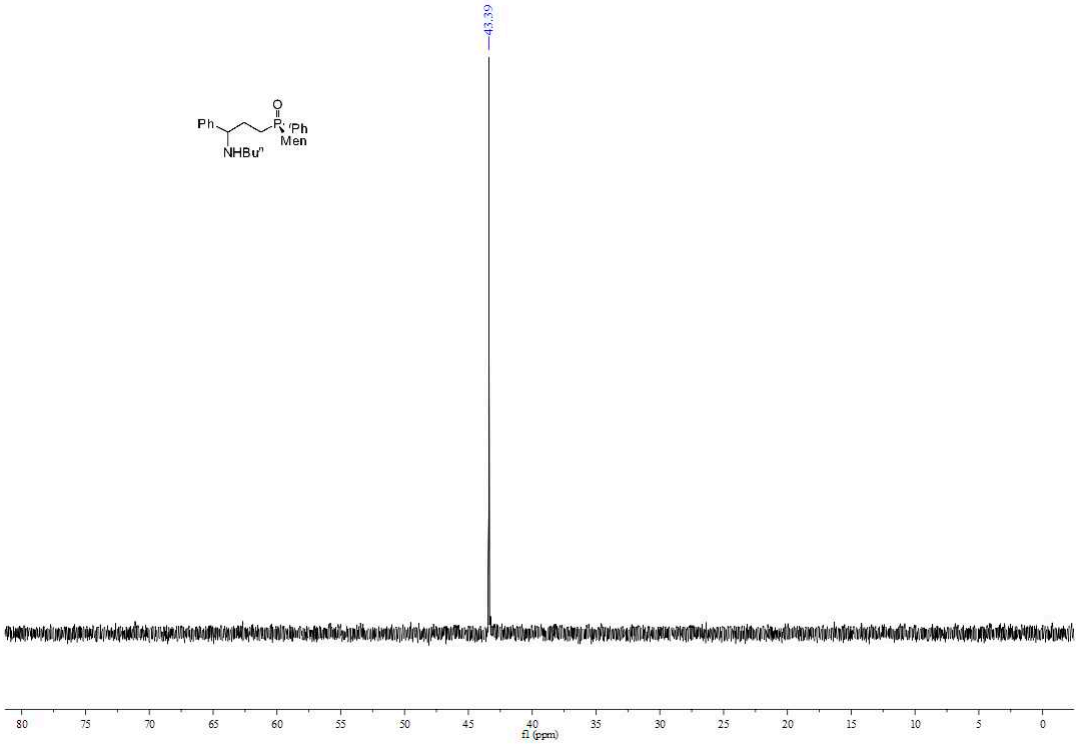
^{1}H NMR spectroscopy of 11fb



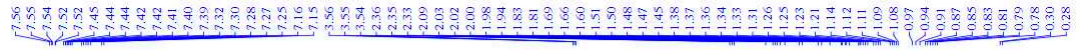
^{13}C NMR spectroscopy of 11fb

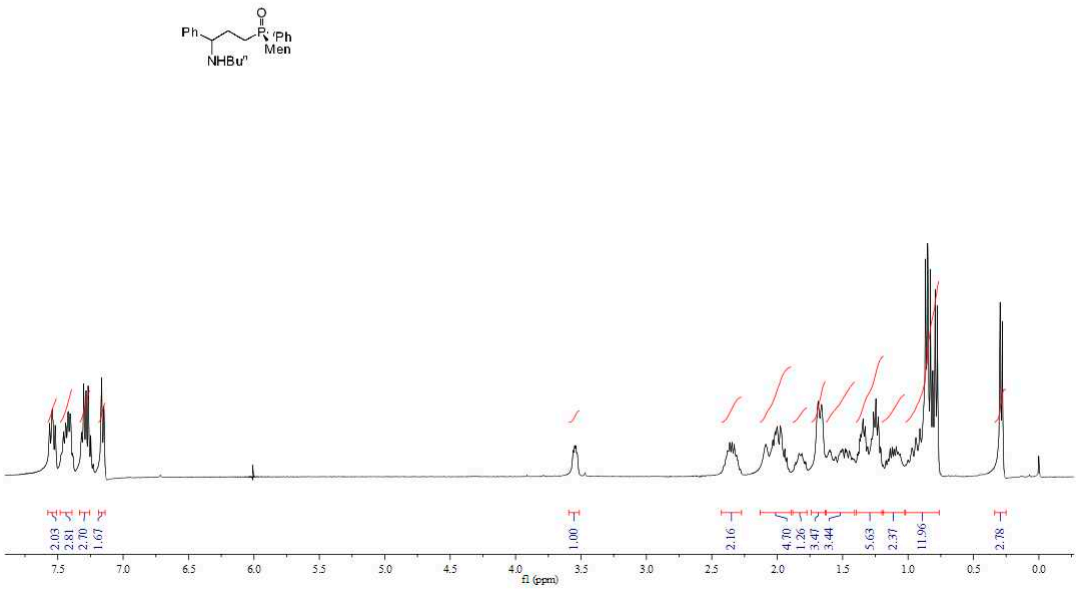


(*S*P)-Menthyl-3-butylamino-3-phenylpropyl phenylphosphine oxide, 11gaA/11gaB, ^{31}P NMR spectroscopy

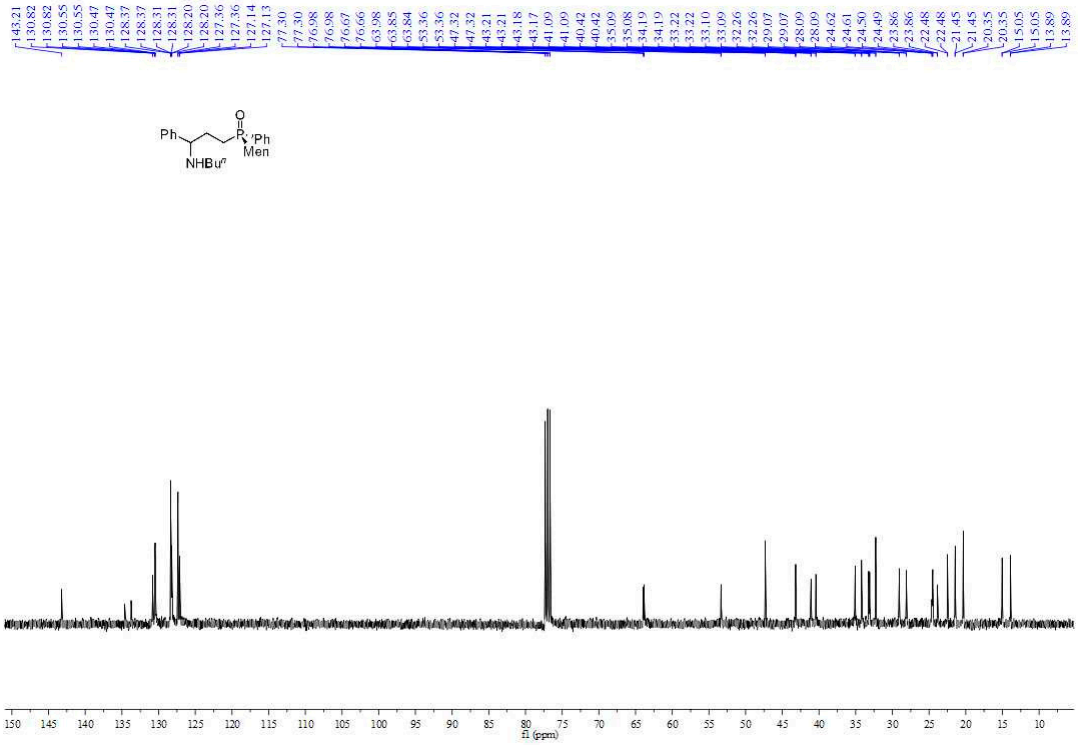


^{1}H NMR spectroscopy of 11gaA/11gaB

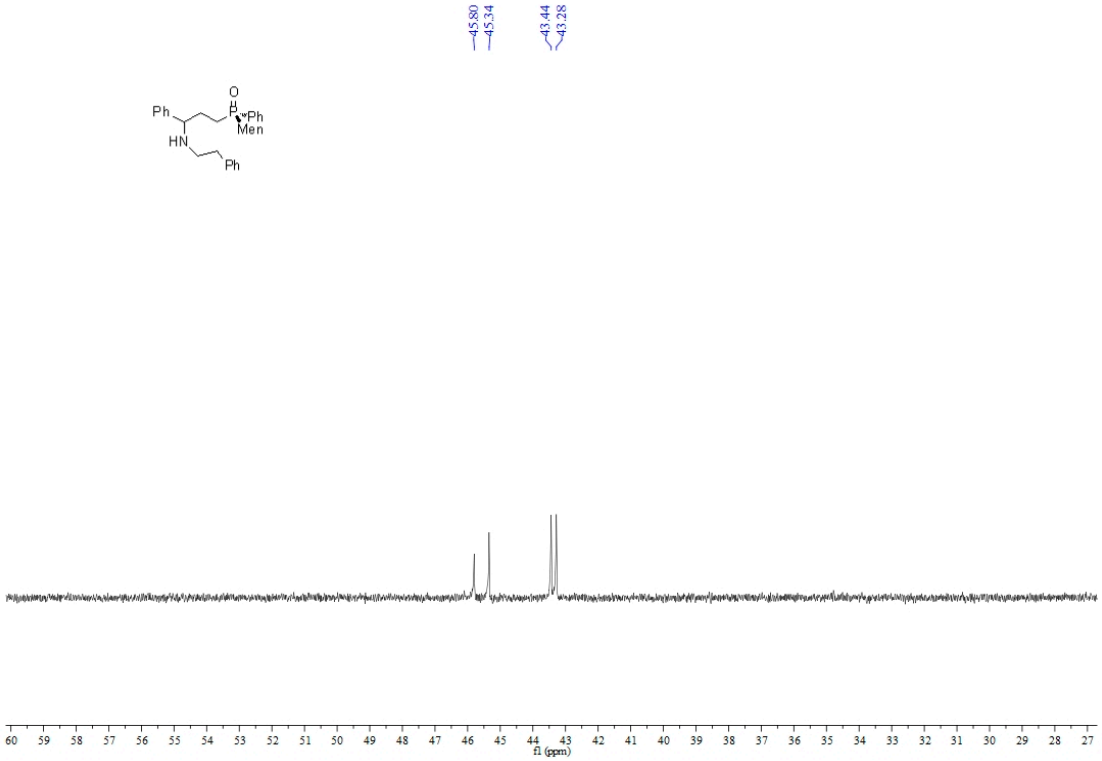




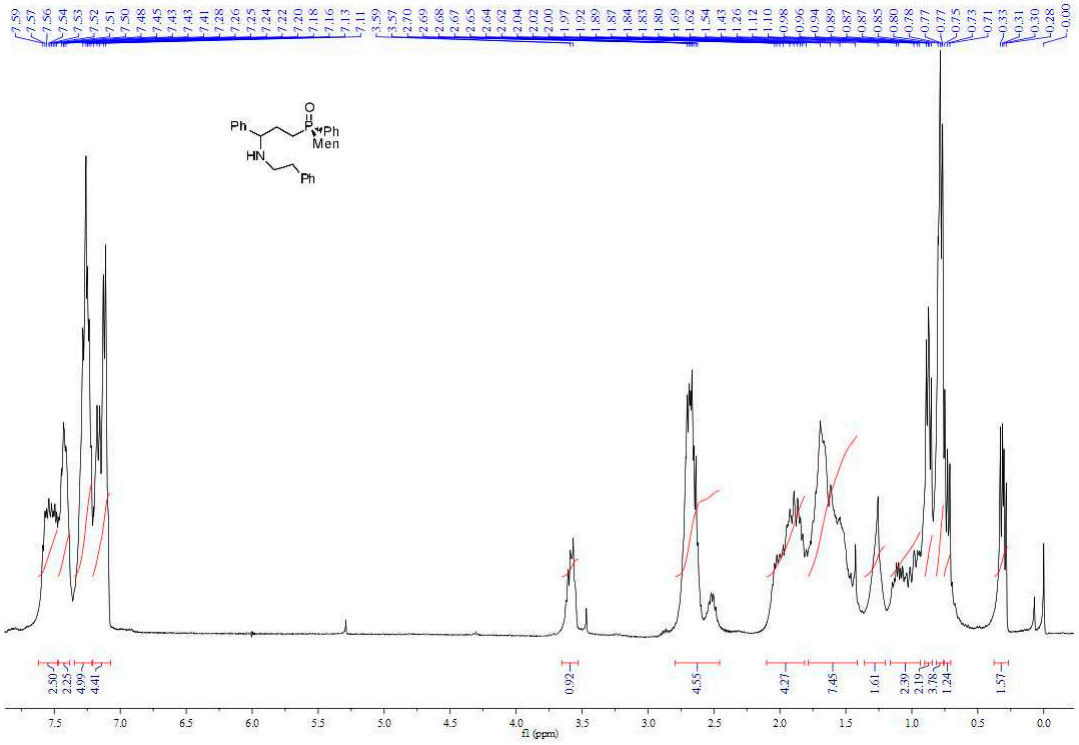
^{13}C NMR spectroscopy of 11ga$_A$/11ga$_B$



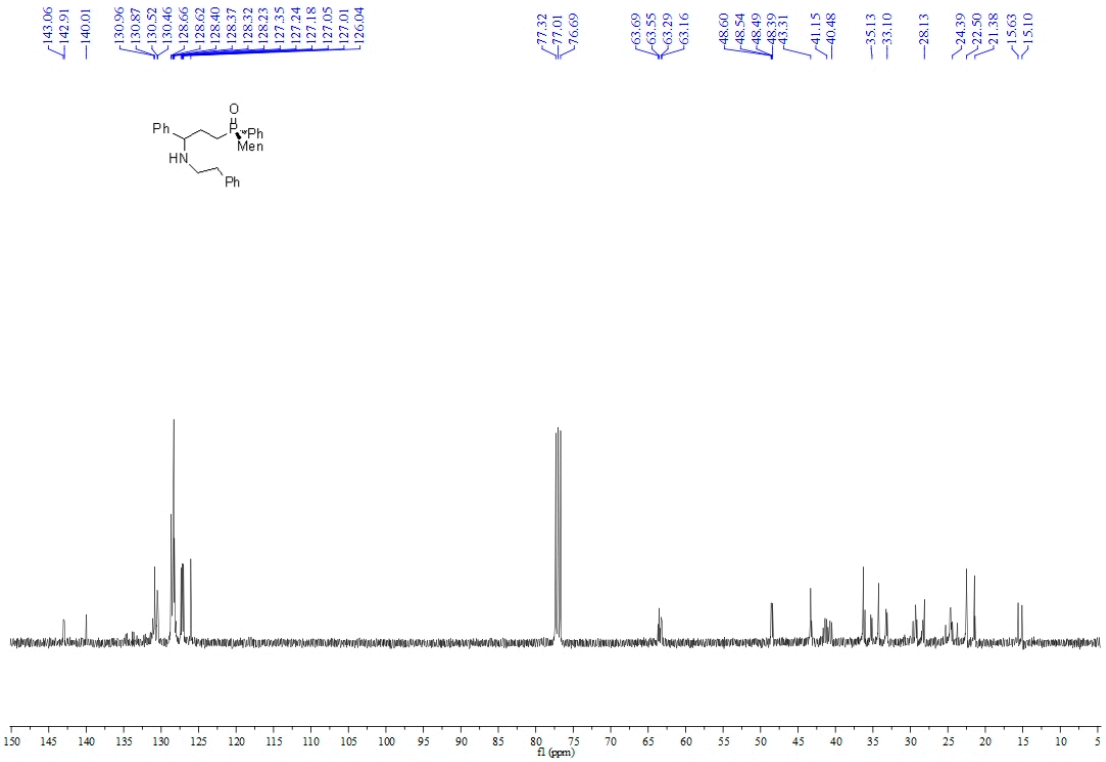
(*S*$_P$)-Menthyl-3-phenethylamino-3-phenylpropyl phenylphosphine oxide, 11gb$_A$/11gb$_B$, 11gb$_A$'/11gb$_B$', ^{31}P NMR spectroscopy



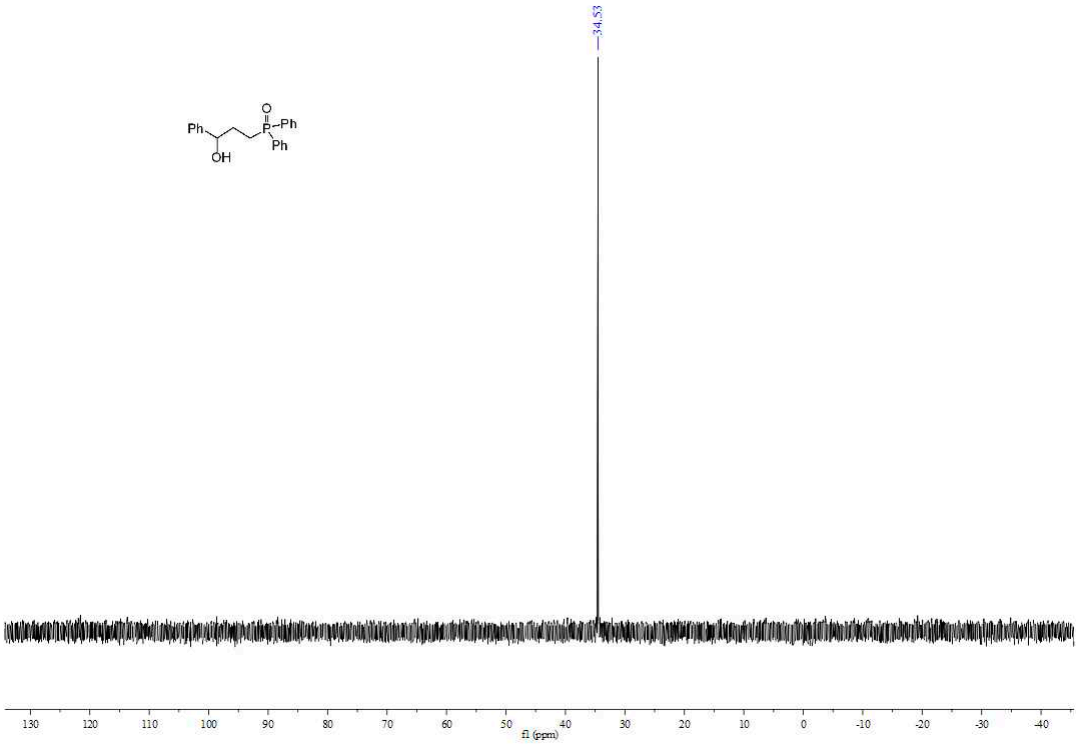
^{1}H NMR spectroscopy of 11gb$_{A}$/11gb$_{B}$, 11gb$_{A}$'/11gb$_{B}$'



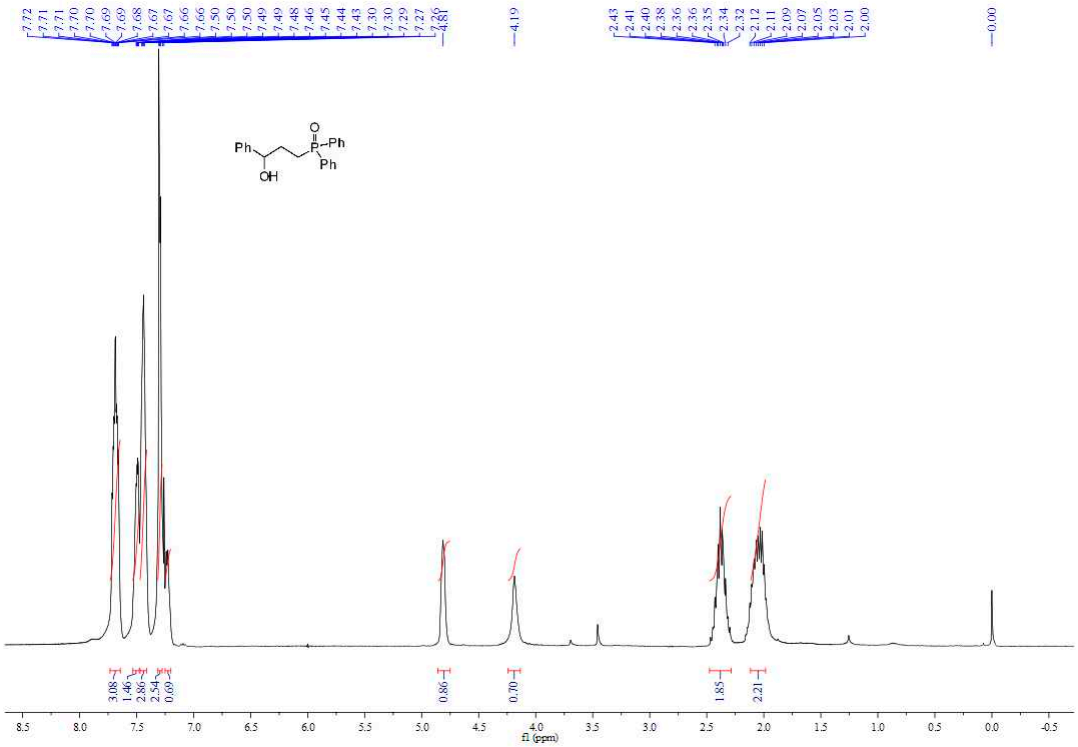
^{13}C NMR spectroscopy of 11gb$_{A}$/11gb$_{B}$, 11gb$_{A}$'/11gb$_{B}$'



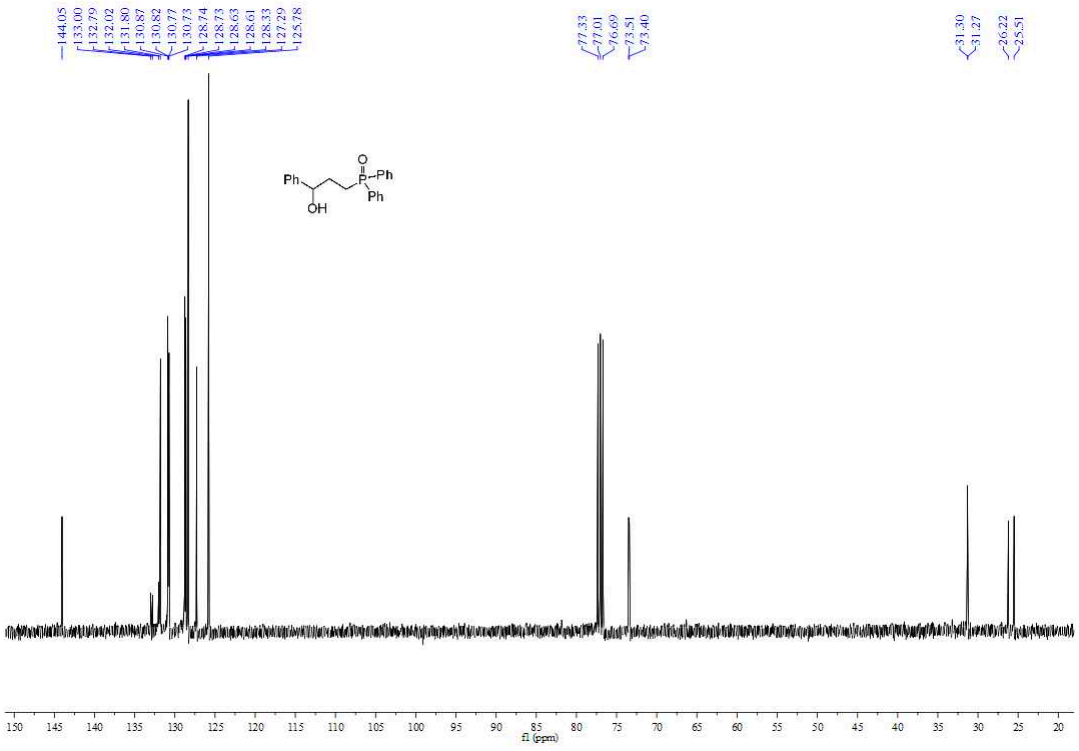
Diphenyl 3-hydroxy-3-phenylprop-1-en-1-ylphosphine oxide, 12a, ^{31}P NMR spectroscopy



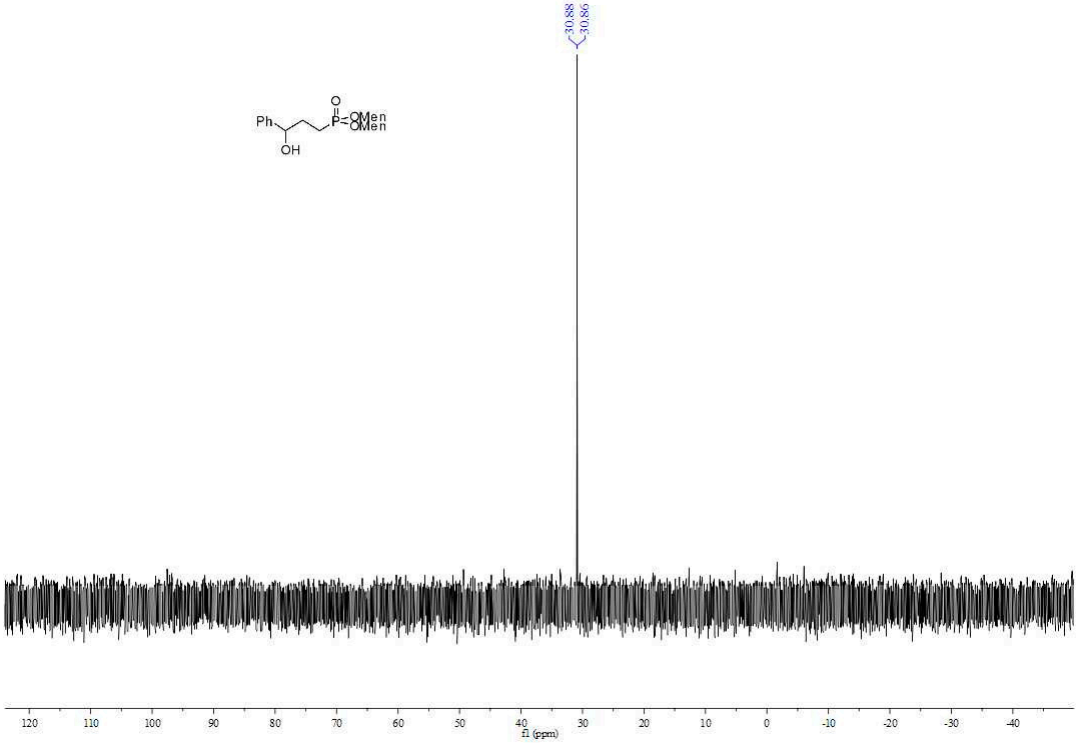
^{1}H NMR spectroscopy of 12a



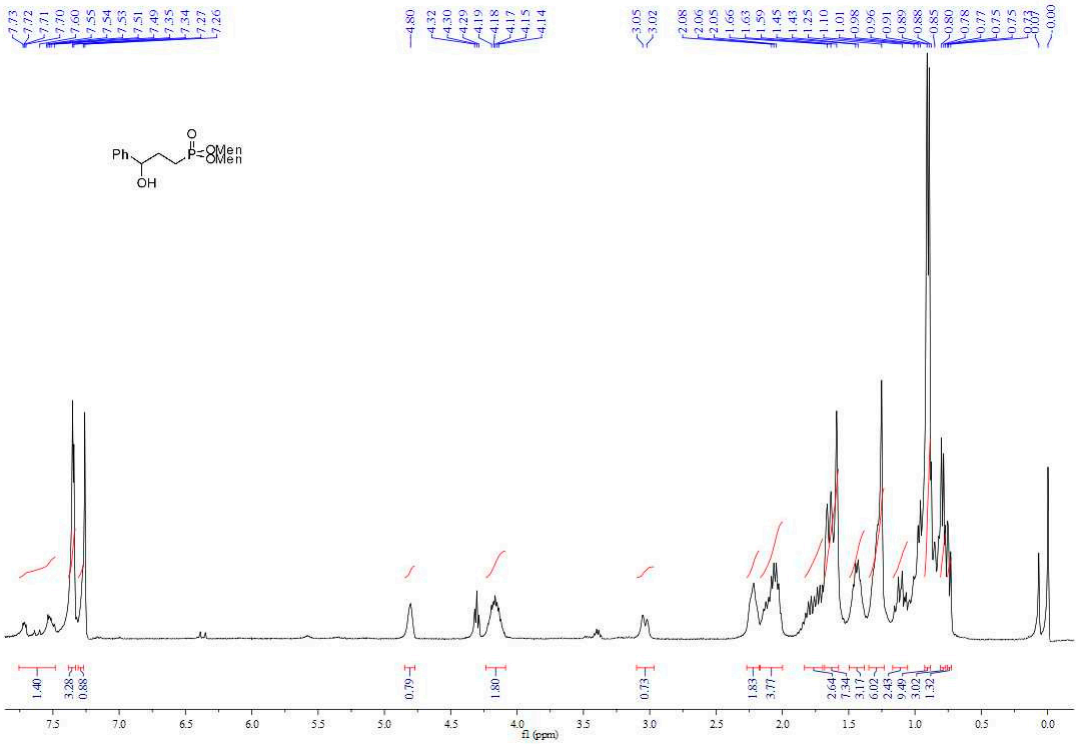
^{13}C NMR spectroscopy of 12a



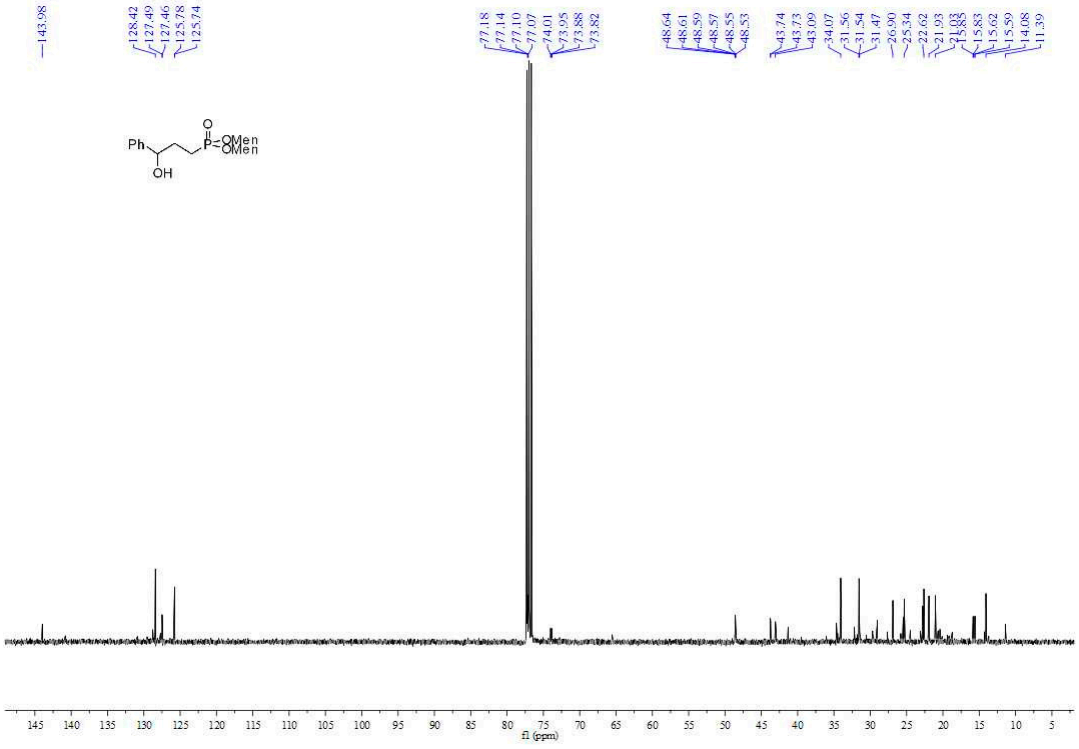
Dimenthyl 3-hydroxy-3-phenylprop-1-en-1-ylphosphonate, 12b, ^{31}P NMR spectroscopy



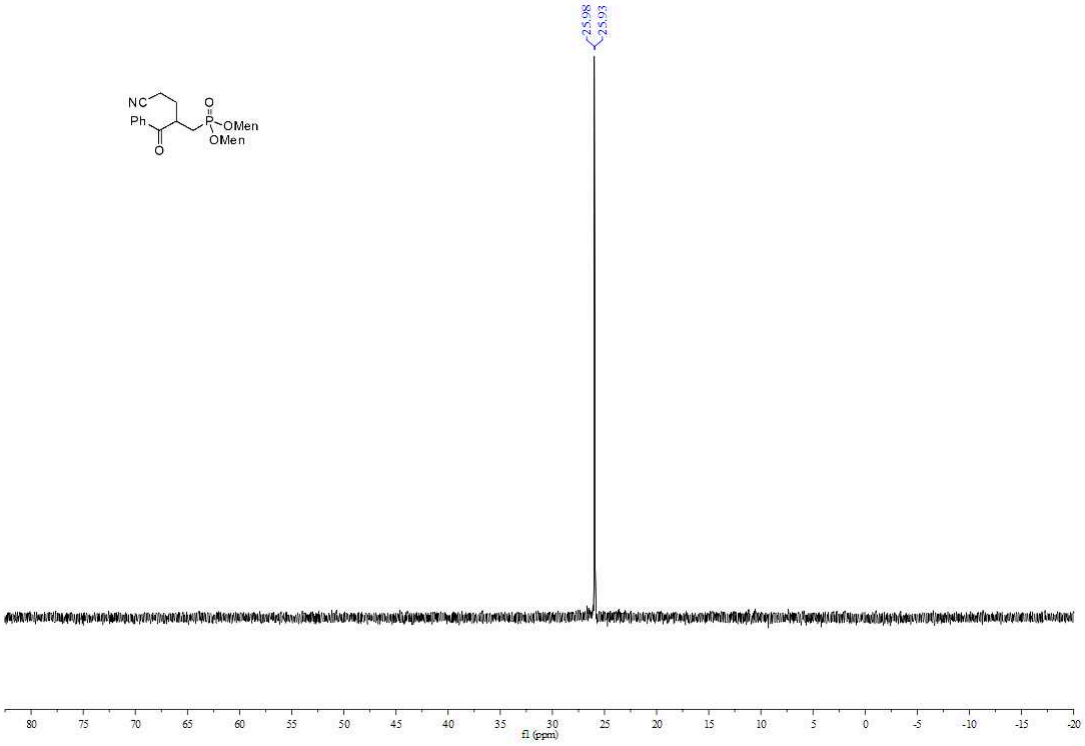
^{1}H NMR spectroscopy of 12b



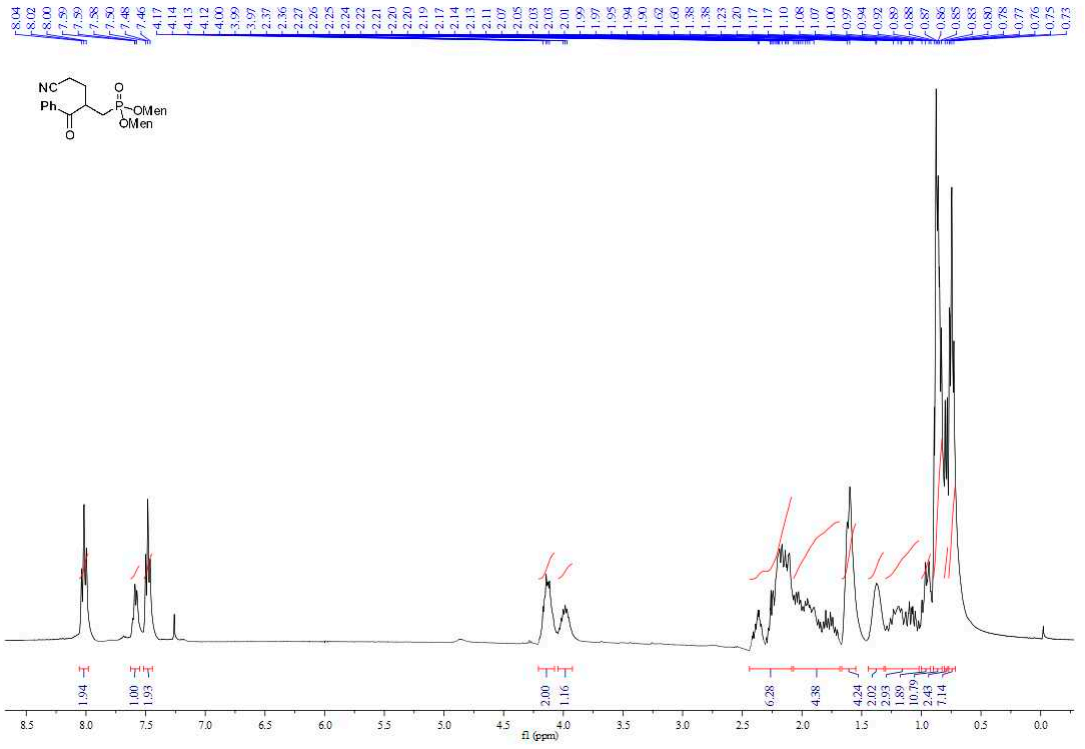
^{13}C NMR spectroscopy of 12b



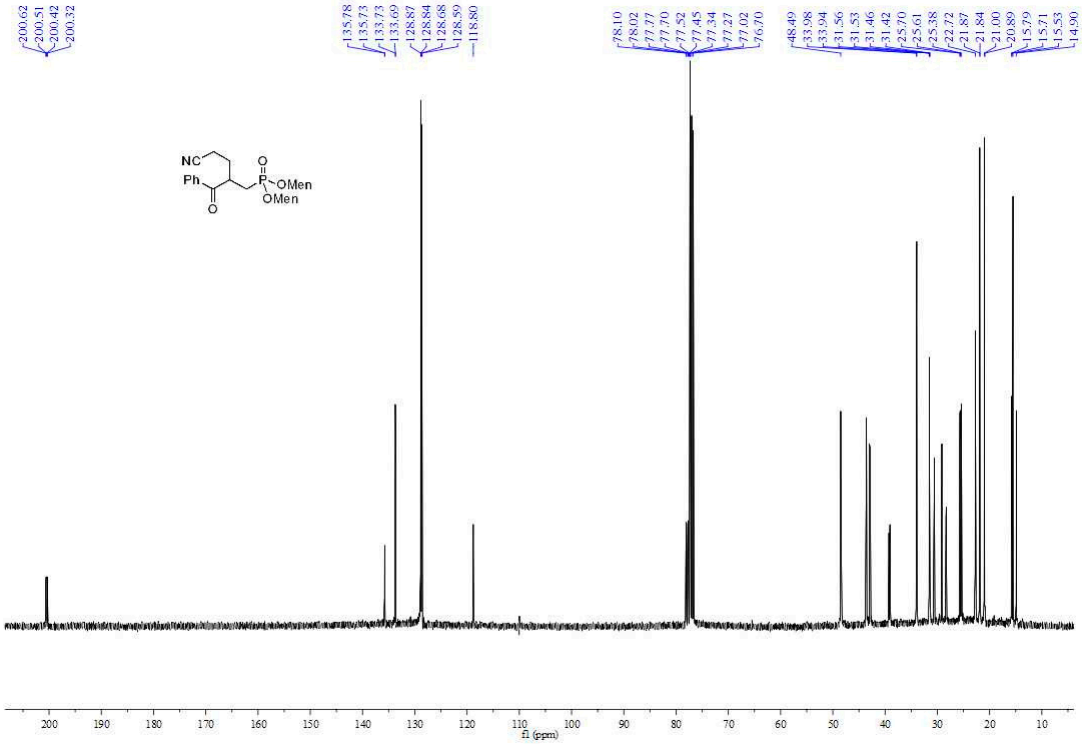
Dimenthoxyl 2-benzoyl-4-cyanobutylphosphonate, 13a, ^{31}P NMR spectroscopy



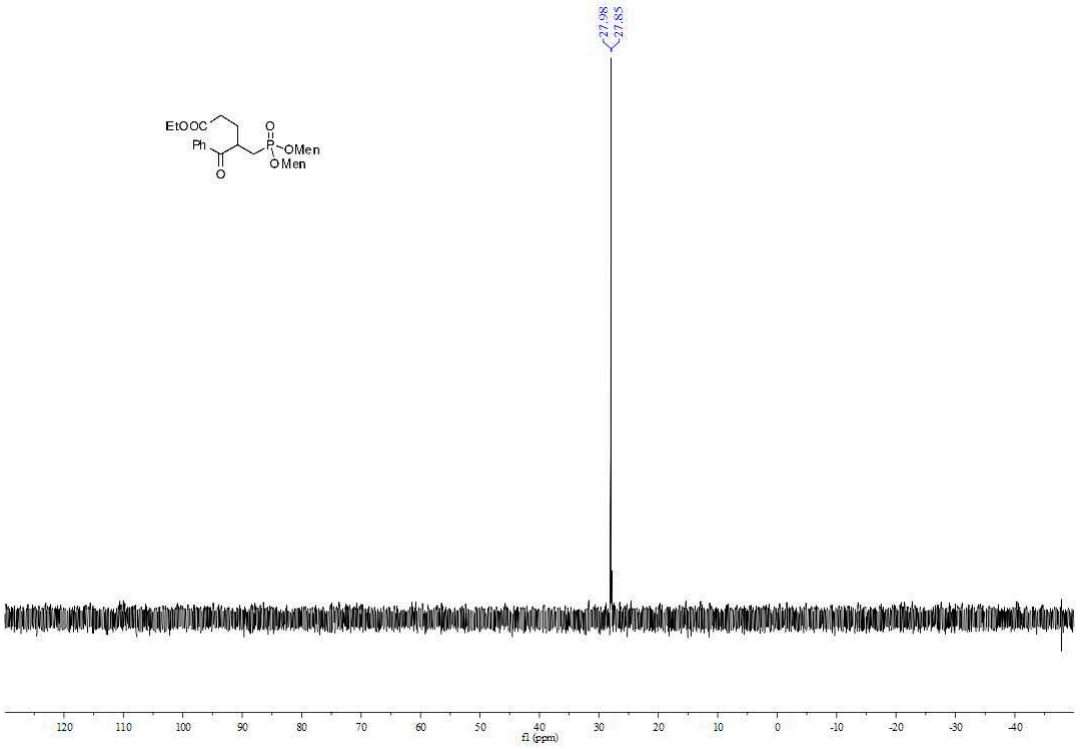
^{1}H NMR spectroscopy of 13a



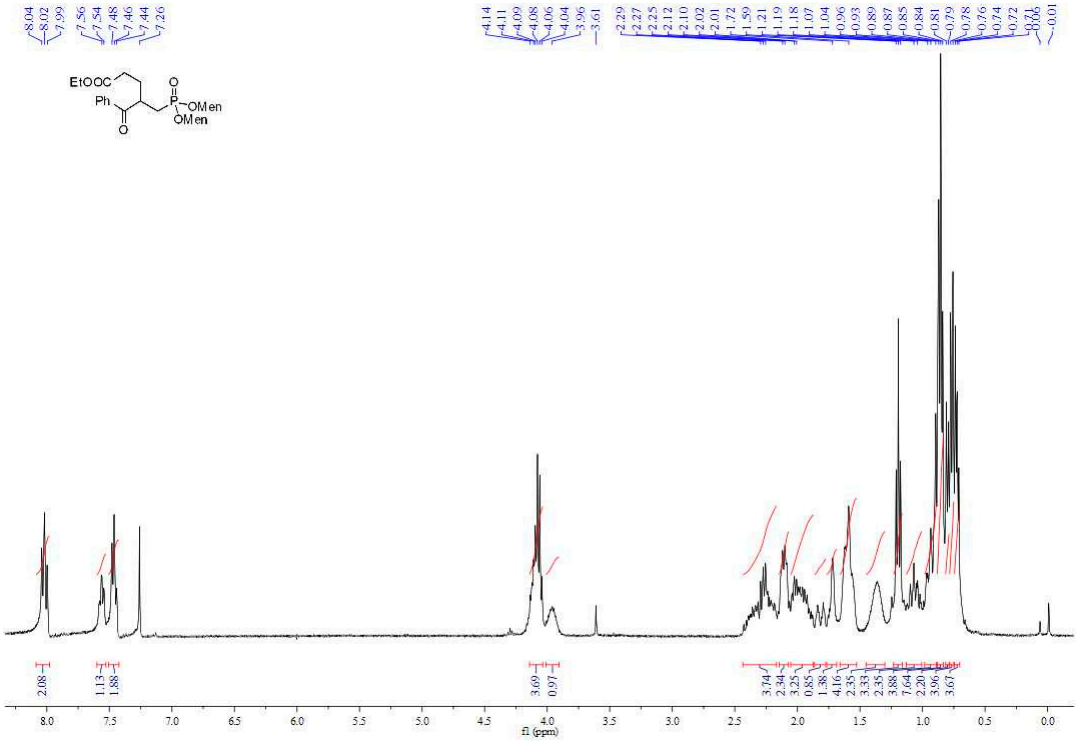
^{13}C NMR spectroscopy of 13a



Ethyl 4-dimenthoxyphosphorylmethyl-5-oxo-5-phenylpentanoate, 13b, ^{31}P NMR spectroscopy



^{1}H NMR spectroscopy of 13b



^{13}C NMR spectroscopy of 13b