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Supporting information

Photoredox Synthesis of 6-and 7-Membered Ring Scaffolds via N-Centered Radicals

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General Informations

^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on Bruker Avance 300 or 400 MHz spectrometers. For the ^{1}H NMR, the peak due to residual $CDCl_3$ was used as internal reference (fixed at 7.26 ppm). NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, bs = broad signal), and coupling constants *J* (Hz) and number of protons (for ^{1}H NMR). For the ^{13}C NMR, the triplet due to residual $CDCl_3$ was used as internal reference (fixed at 77.16 ppm). Mass spectra were obtained by positive electrospray ionization method. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F254. Visualization was accomplished with short wavelength UV light (254 and 365 nm). Standard flash chromatography was performed using silica gel of particle size 40−63 μm. Photocatalysts were purchased from Aldrich, TCI, and used without any further purification or synthesized as reported in literature. All other commercially available reagents and solvents were used without further purification.

Description of the Visible-Light catalysis apparatus

Our Visible-Light catalysis apparatus consists in an aluminium block in which circulates the cooling fluid linked to the cooling system set at 20°C. The block contains 6 holes and each hole contain a 18W 455 nm LED Cree® XLamp® XT-E Royal Blue LEDs (λ = 455 nm (± 5 nm), 12 V, 1.5 A. The sample are irradiated with a LED through the vial's plane bottom side at a distance of 1 cm. The vials used are WICOM 20mm Crimp Top Vial, 5ml, 38.5mm x 22.0mm, clear. This apparatus is installed on a magnetic stirrer, as shown on the following scheme and picture.

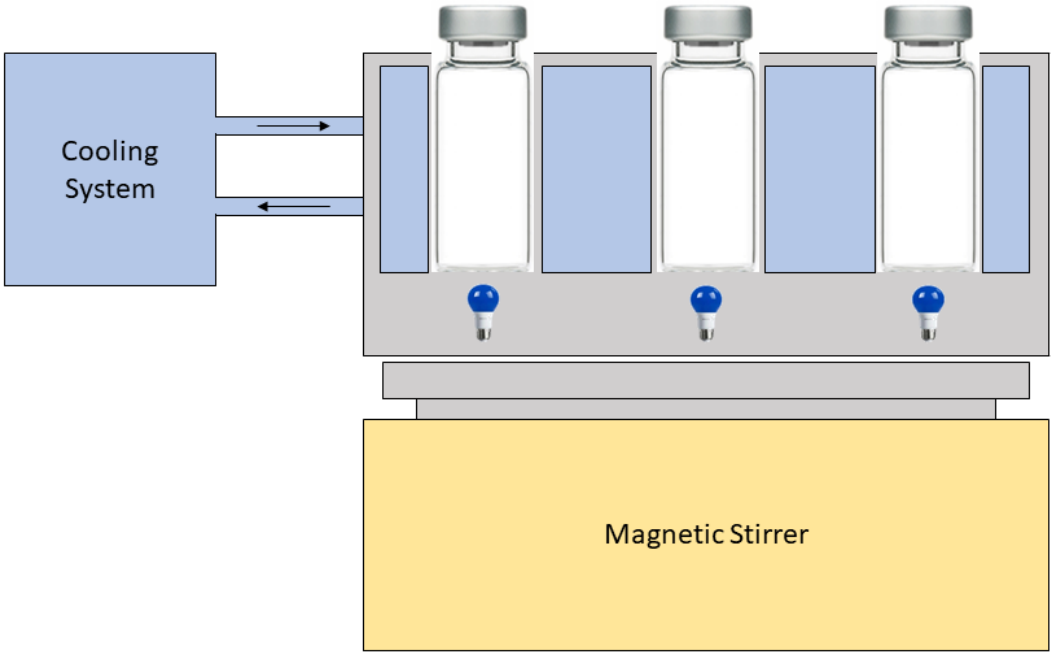


Figure 1 - Sketch of the Visible Light catalysis apparatus

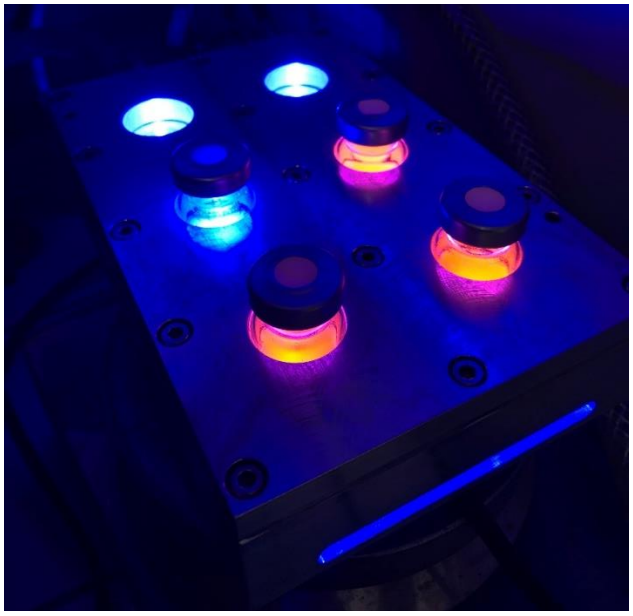
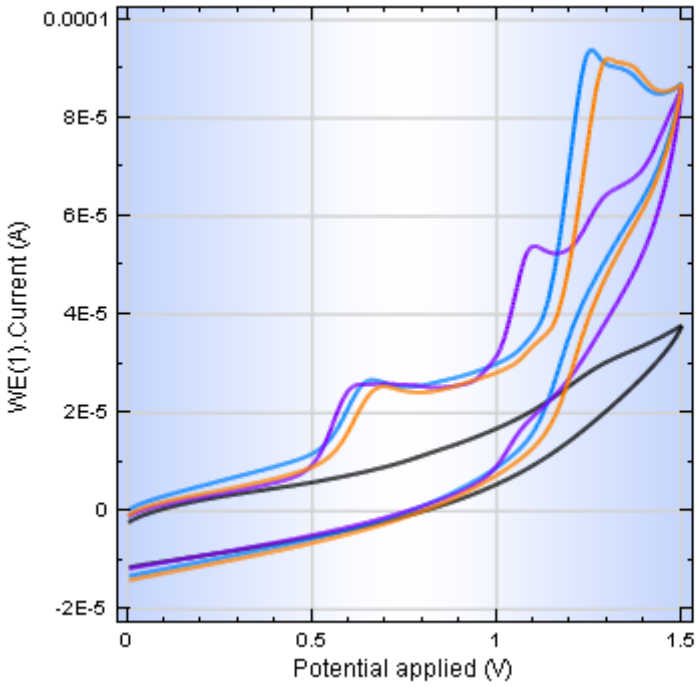
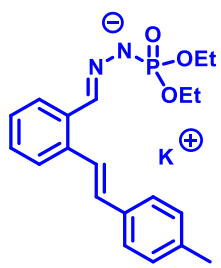


Figure 2 - Picture of the Visible Light catalysis apparatus

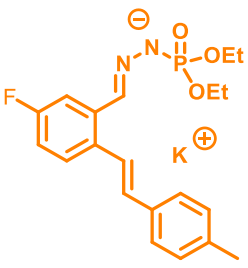
Protocol of cyclic voltammetry experiments

The redox potentials have been measured by cyclic voltammetry using a glassy-carbon electrode in a 10^{-3} M solution of phosphonohydrazones (1 eq.) with 3 eq. of potassium hydroxide, in degassed mixture of methanol. Scan rate: 0.1 V/s, Saturated Calomel Electrode (SCE) used as reference electrode, platinum wire as counter electrode and $LiClO_4$ (0.05 M) as the supporting electrolyte. The cyclic voltammogram were treated using Nova 1.6 software. In the presence of 3 eq. of base, it is worth noting that the oxidation potential corresponds to the anionic form of the starting material.

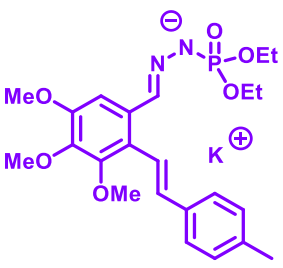




E_{Ox} = +0,67V vs. SCE

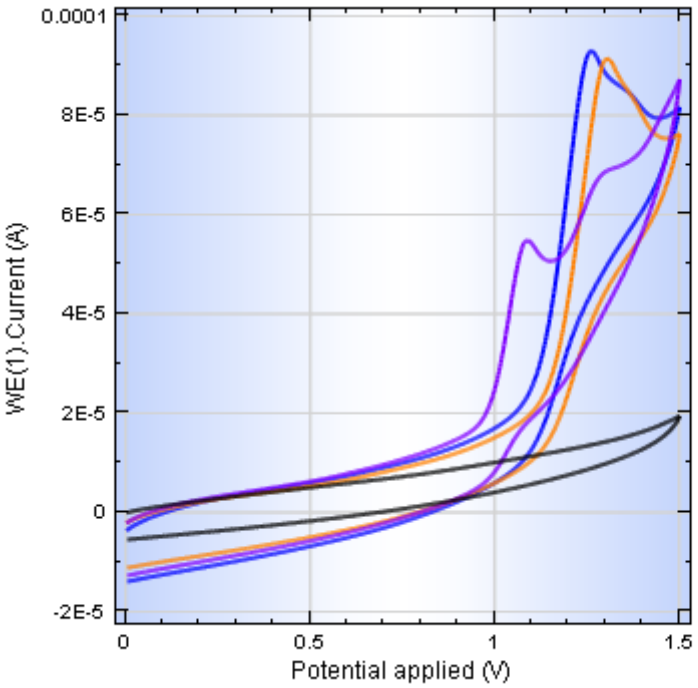


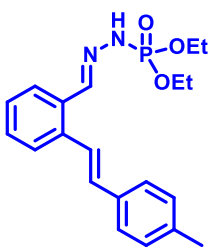
E_{Ox} = +0,69V vs. SCE



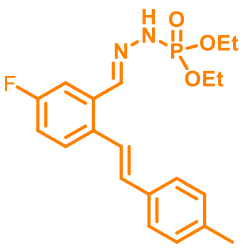
E_{Ox} = +0,61V vs. SCE

The redox potentials have also been measured in the absence of KOH (base), using a glassy carbon electrode in a 10^{-3}M solution of phosphonohydrazones (1 eq.), in degassed mixture of methanol. Scan rate: 0.1 V/s, Saturated Calomel Electrode (SCE) used as reference electrode, platinum wire as counter electrode and $LiClO_4$ (0.05 M) as the supporting electrolyte. Without base, no oxidation potentials are observed under E_{Ox} = 0,77V vs. SCE which is the potential of the used photocatalyst thus indicates that the base is crucial to have cyclisation. The base is generating the N-anion intermediate which has a lower oxidation potential, this N-anion can be oxidized by the photocatalyst.

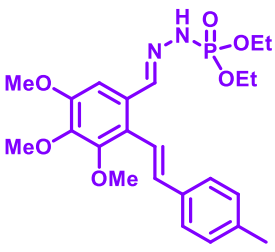




E_{Ox} = +1,26V vs. SCE

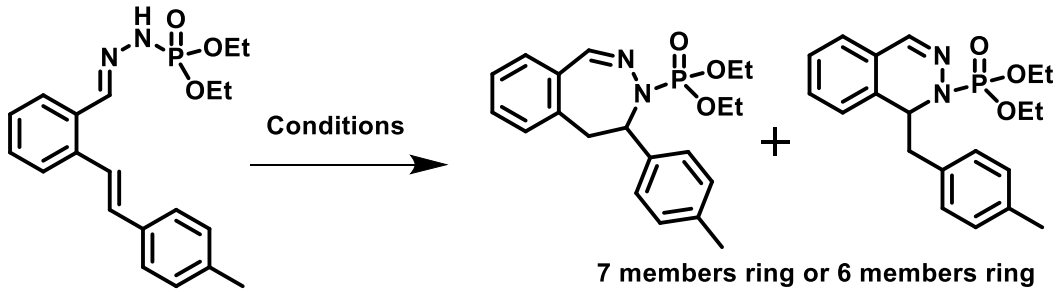


E_{Ox} = +1,30V vs. SCE



E_{Ox} = +1,09V vs. SCE

Optimization of the reaction conditions



Solvent	$V_{(solvent)}$	Photocat. (PC)	PC %	Base	Base eq.	Light	Ratio (6MR):(7MR)	Yield
Methanol	1 mL	**$Ru(bpy)_3(PF_6)_2$**	2,5	tBuONa	3.0	Blue LED	(1:1)	35% (isolated)
Methanol	1 mL	**$Ru(bpz)_3(PF_6)_2$**	2,5	tBuONa	3.0	Blue LED	/	0%
Methanol	1 mL	**Fukuzumi**	5	tBuONa	3.0	Blue LED	/	0%
Methanol	1 mL	**$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$**	2	tBuONa	3.0	Blue LED	(1:1)	20% (isolated)
Methanol	1 mL	**$Ru(phen)_3(PF_6)_2$**	2,5	tBuONa	3.0	Blue LED	(1:1)	26% (NMR)
Methanol	1 mL	**Rhodamine**	5	tBuONa	3.0	Blue LED	/	0%
Methanol	1 mL	**Eosine Y**	5	tBuONa	3.0	Blue LED	(1:1)	20% (NMR)
Methanol	1 mL	**$Ru(bpy)_3Cl_2\,6H_2O$**	2,5	tBuONa	3.0	Blue LED	(1:1)	40% (NMR)
Methanol	1 mL	**4CzIPN**	5	tBuONa	3.0	Blue LED	/	0%
MeCN	2 mL	**Ru cat. on Silica**	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	**Eosine Y**	5	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	**$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$**	1	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	**$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$**	1	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	**$Ir(p\text{-}F\text{-}ppy)_3$**	1	KOH	3.0	Blue LED	/	0%

Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**NaOH**	3.0	Blue LED	(1:1)	40% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**K_2CO_3**	3.0	Blue LED	(1:1)	35% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**Pyridine**	3.0	Blue LED	/	0%
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**LiOH**	3.0	Blue LED	(1:1)	38% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**KOH**	3.0	Blue LED	(1:1)	46% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**CsOH**	3.0	Blue LED	(1:1)	46% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**Cs_2CO_3**	3.0	Blue LED	(1:1)	36% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**Na Acetate**	3.0	Blue LED	/	0%
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**$NaHCO_3$**	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	**LiHMDS**	3.0	Blue LED	/	0%
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	**1.0**	Blue LED	/	0%
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	**2.0**	Blue LED	(1:1)	34% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	**3.0**	Blue LED	(1:1)	46% (NMR)
Methanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	**5.0**	Blue LED	(1:1)	38% (NMR)
Chloroform	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
DMSO	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Ethanol	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Acetonitrile	1 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
DMF	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
THF	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H_2O (4:1)	0,6 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	(1:4)	50% (NMR)
Acetone	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Diethyl Ether	2,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Dioxane	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Toluene	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2 6H_2O$	2,5	KOH	3.0	Blue LED	(1:5)	56% (NMR)

H_2O	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/MeOH (4:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
CH_2Cl_2	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H_2O (1:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(1:1)	40% (NMR)
EtCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	28% (NMR)
Benzyl Alcohol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/CHCl3 (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	14% (NMR)
PhCN/H2O (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeNO2/H2O (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
EtCN/H2O (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
DMSO/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H_2O (16:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	40% (NMR)
Butanone	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Methanol	**0,5 mL**	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(1:1)	48% (NMR)
Methanol	**3 mL**	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
Methanol	**5 mL**	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	/	0%
MeCN/H2O (9:1)	**2 mL**	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(1:3)	62% (NMR)

Photocatalyst additional 2.5 eq. added at mid time of the reaction								
PhCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	27% (NMR)
EtCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	30% (NMR)
EtCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	21% (NMR)
H_2O/MeCN (1:2)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(0:1)	16% (NMR)
MeCN/H2O (9:1)	**2 mL**	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	KOH	3.0	Blue LED	(1:3)	62% (NMR)

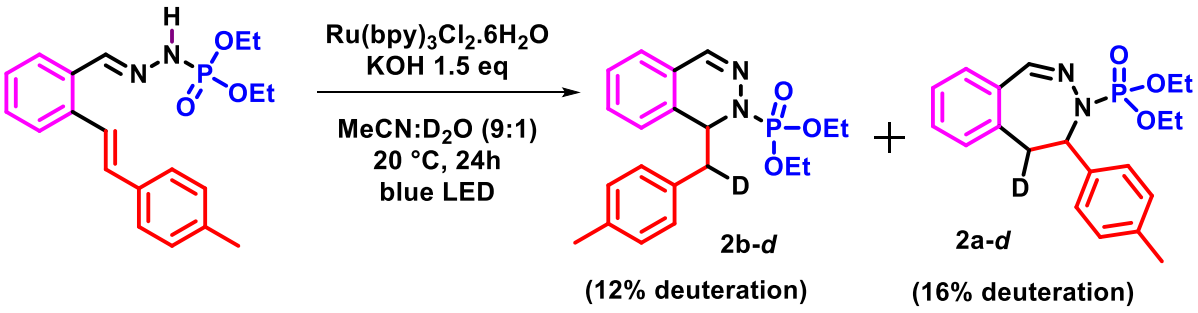
Experiments with additives or other modifications (base is KOH for all)								
Additive or Modification	**Solvent**	**$V_{(solvent)}$**	**Photocat. (PC)**	**PC %**	**Base eq.**	**Light**	**Ratio (6MR):(7MR)**	**Yield**
Molecular Sieve	Methanol	1 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
Without Light	Methanol	1 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	No light	/	0%
H2O 0,050 mL	Methanol/H_2O	1 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
Without PhotoCat.	Methanol	1 mL	No photocatalyst !	0	3.0	Blue LED	/	0%
White LED Light	Methanol	1 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	White LED	(1:1)	48% (NMR)
KOH solution in MeOH	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(1:1)	38% (NMR)
Hantzsch Ester 2eq.	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
18-Crown Ether 2eq.	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(1:1)	44% (NMR)
Thiophenol 2eq.	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
silica 20 mg	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(0:1)	17% (NMR)
Degas.	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(1:1)	50% (NMR)
silica 200 mg	MeCN	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
2 eq. Photocat.	Methanol	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(1:1)	46% (NMR)
silica 200 mg	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	5,0	3.0	Blue LED	/	0%
silica 5 mg	MeCN	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
silica 50 mg	MeCN	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
silica 800 mg	MeCN	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
silica 100 mg	MeCN/H2O (9:1)	2 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
NaClO4	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(0:1)	15% (NMR)
Benzyl-N+Et3Cl-	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(0:1)	15% (NMR)
Cyclohexadiene	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(0:1)	25% (NMR)
Base 1eq./4h (x2)	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	(1:4)	65% (NMR)

Other Photocatalyst	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3(PF_6)_2$	2,5	3.0	Blue LED	(0:4)	48% (NMR)
Diphenyl Sulfide	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	3.0	Blue LED	/	0%
Other Photocatalyst	MeCN/H2O (9:1)	0,5 mL	Eosine Y	5,0	3.0	Blue LED	/	0%
Other Photocatalyst	MeCN/H2O (9:1)	0,5 mL	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	1,0	3.0	Blue LED	/	0%
Other Photocatalyst	MeCN/H2O (9:1)	0,5 mL	$(Ir[dF(CF_3)ppy]_2(bpy))PF_6$	1,0	3.0	Blue LED	/	0%
Other Photocatalyst	MeCN/H2O (9:1)	0,5 mL	Ir(p-F-ppy)3	1,0	3.0	Blue LED	/	0%
Other PC / 1,5eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3(PF_6)_2$	2,5	1.5	Blue LED	(0:1)	40% (NMR)
Other PC / 1eq./ 3W LED	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3(PF_6)_2$	2,5	1.0	Blue LED	(0:1)	40% (NMR)
Other PC / 0,5eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3(PF_6)_2$	2,5	0.5	Blue LED	/	0%
1,5eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	1.5	Blue LED	(0:1)	65% (NMR)
1eq. Base / 3W LED	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	1.0	Blue LED	(0:1)	30% (NMR)
0,5eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	0.5	Blue LED	(0:1)	15% (NMR)
at 0°C / 1eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	1.0	Blue LED	(0:1)	% (NMR)
at 40°C / 1eq. Base	MeCN/H2O (9:1)	0,5 mL	$Ru(bpy)_3Cl_2\,6H_2O$	2,5	1.0	Blue LED	(0:1)	47% (NMR)

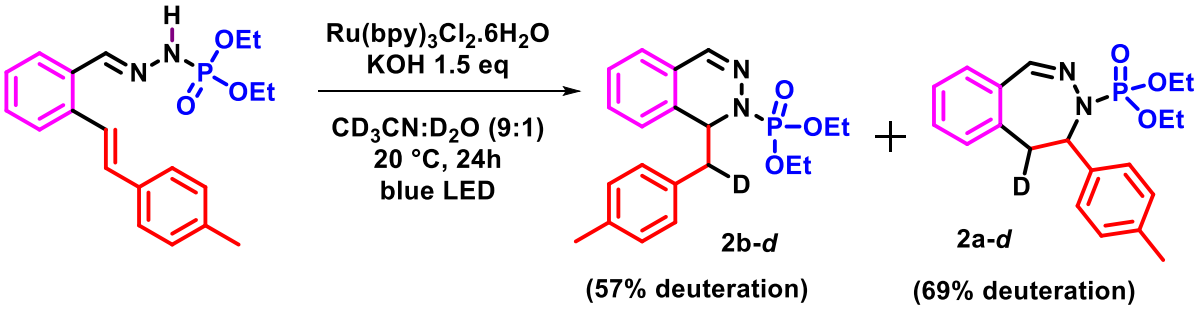
Study of water effect

In order to understand the role of water, particularly for the protonation of the final compound, we have conducted two different deuteration reactions on compound 2:

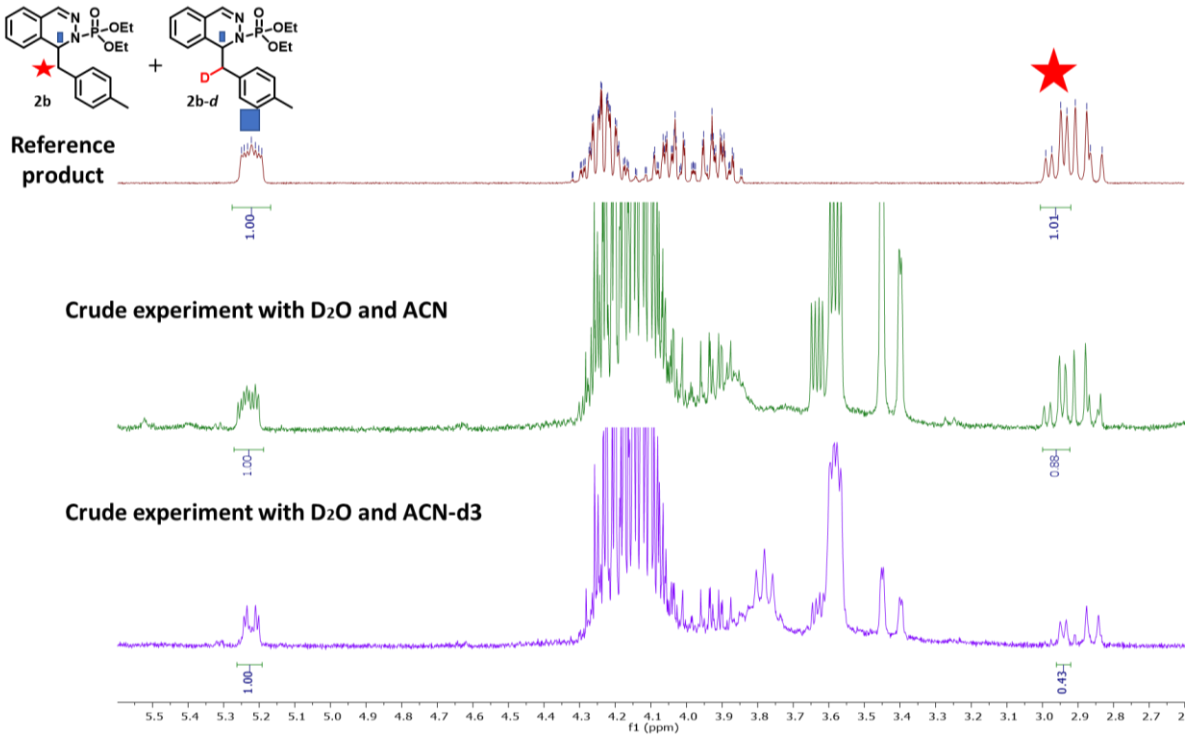
- For the first one we have used ACN and deuterated water.

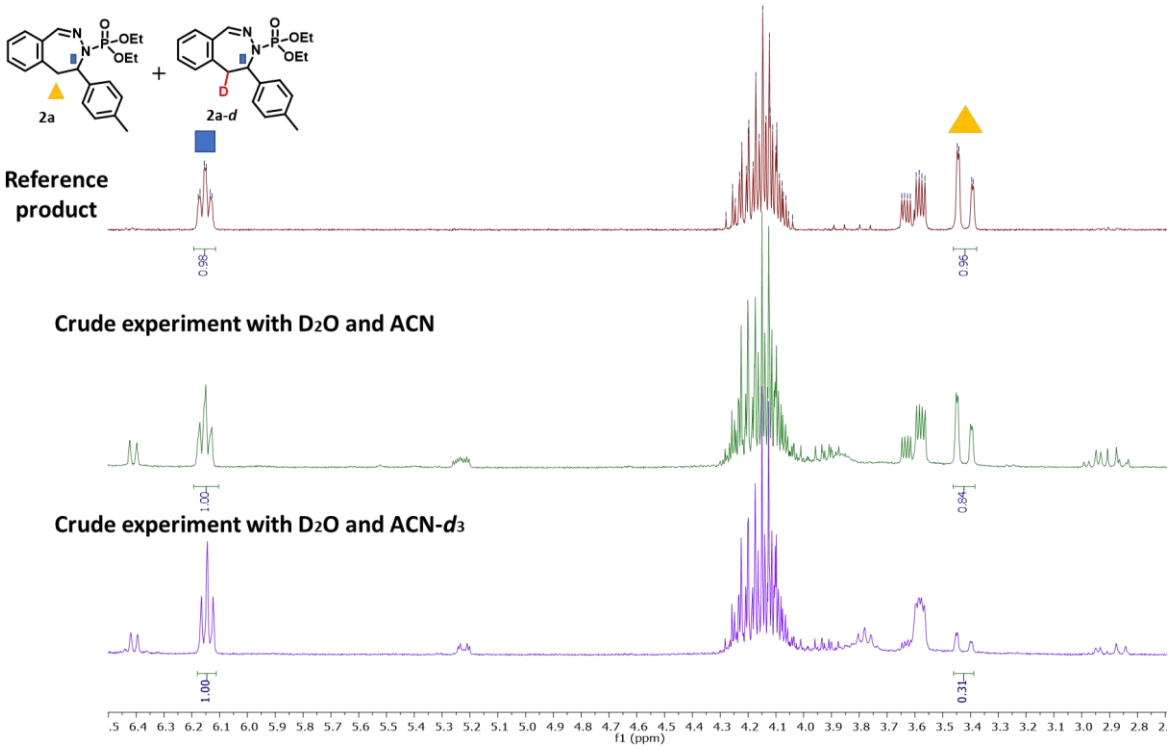


- For the second one, we have used, both, deuterated ACN and water.



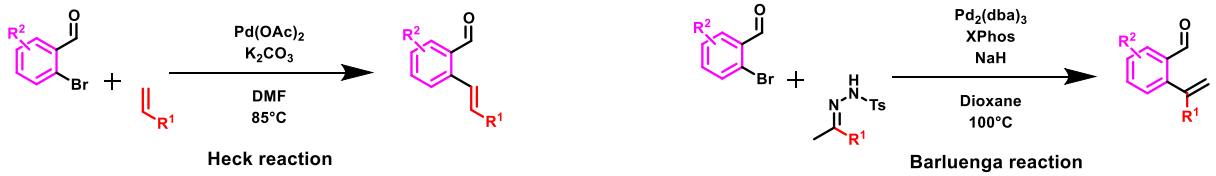
- The first trial (only D_2O) gave us between 12% and 16% deuteration yield for both 7-endo and 6-exo compounds (2a and 2b). However, the second trial (with ACN-$d_3$and D_2O) gave us a 69% for the 7-endo(2a) and a 57% for the 6-exo (2b). This seems to indicate that deuteration (protonation in the mechanism) may come from ACN-$d_3$and D_2O.

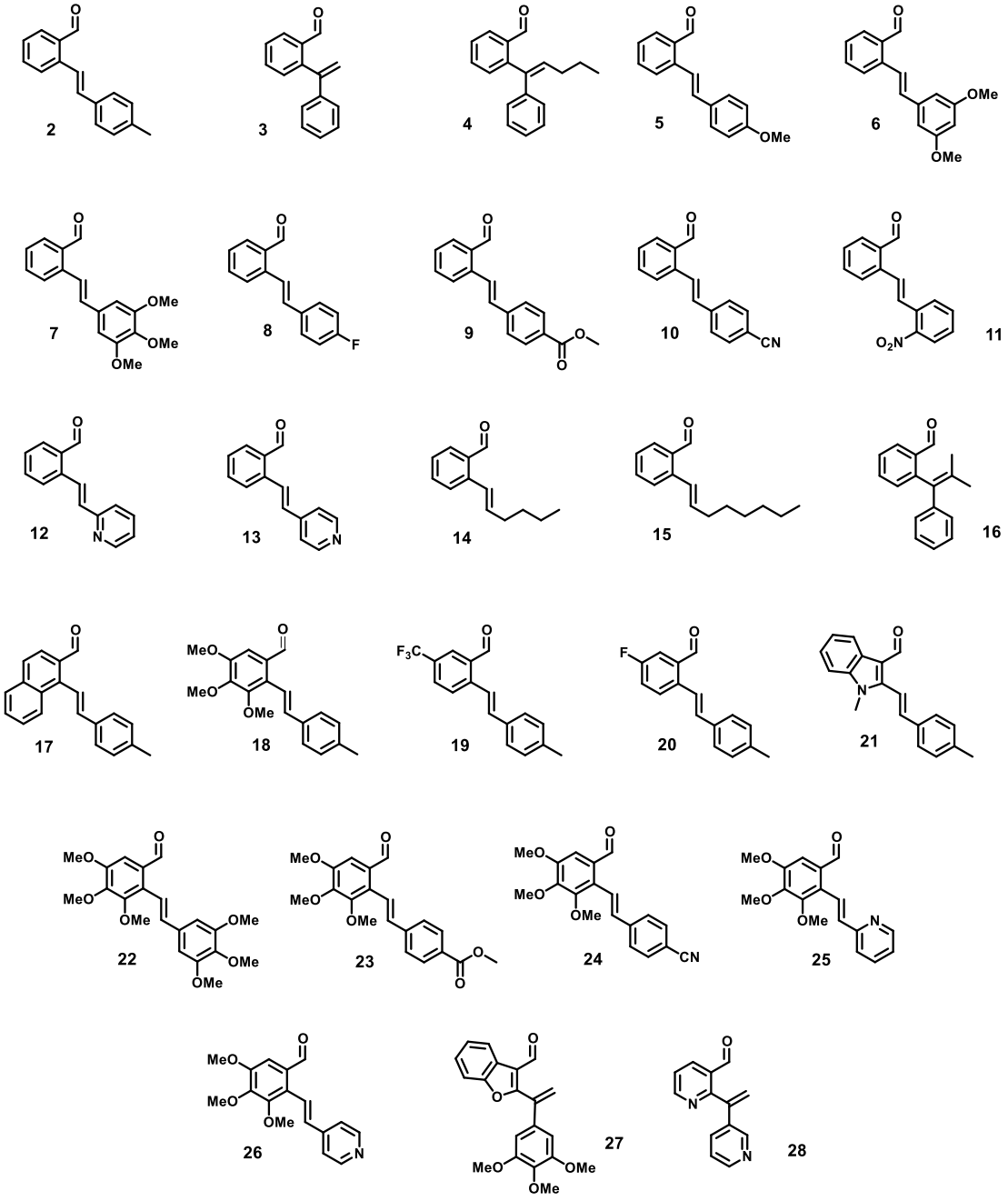

2b
2b-d
Reference product
Crude experiment with D2O and ACN
Crude experiment with D2O and ACN-d3
f1 (ppm)


2a
2a-d
Reference product
Crude experiment with D2O and ACN
Crude experiment with D2O and ACN-d3
f1 (ppm)

Synthesis of the aldehyde precursors

All the aldehydes have been obtained by Heck reaction following the protocol described on the article from W. Zhang *et al. Tetrahedron*, **2019**, *75*, 2, 269-277; or by Barluenga reaction following the protocol described on the article from D; Lamaa et al. *J. Org. Chem.* **2020**, *85*, 21, 13664-13673.


Pd(OAc)2
K2CO3
DMF
85°C
Heck reaction
Pd2(dba)3
XPhos
NaH
Dioxane
100°C
Barluenga reaction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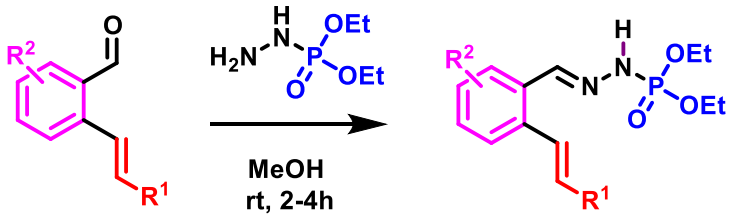
General Procedure A: for the synthesis of phosphonohydrazones and characterization

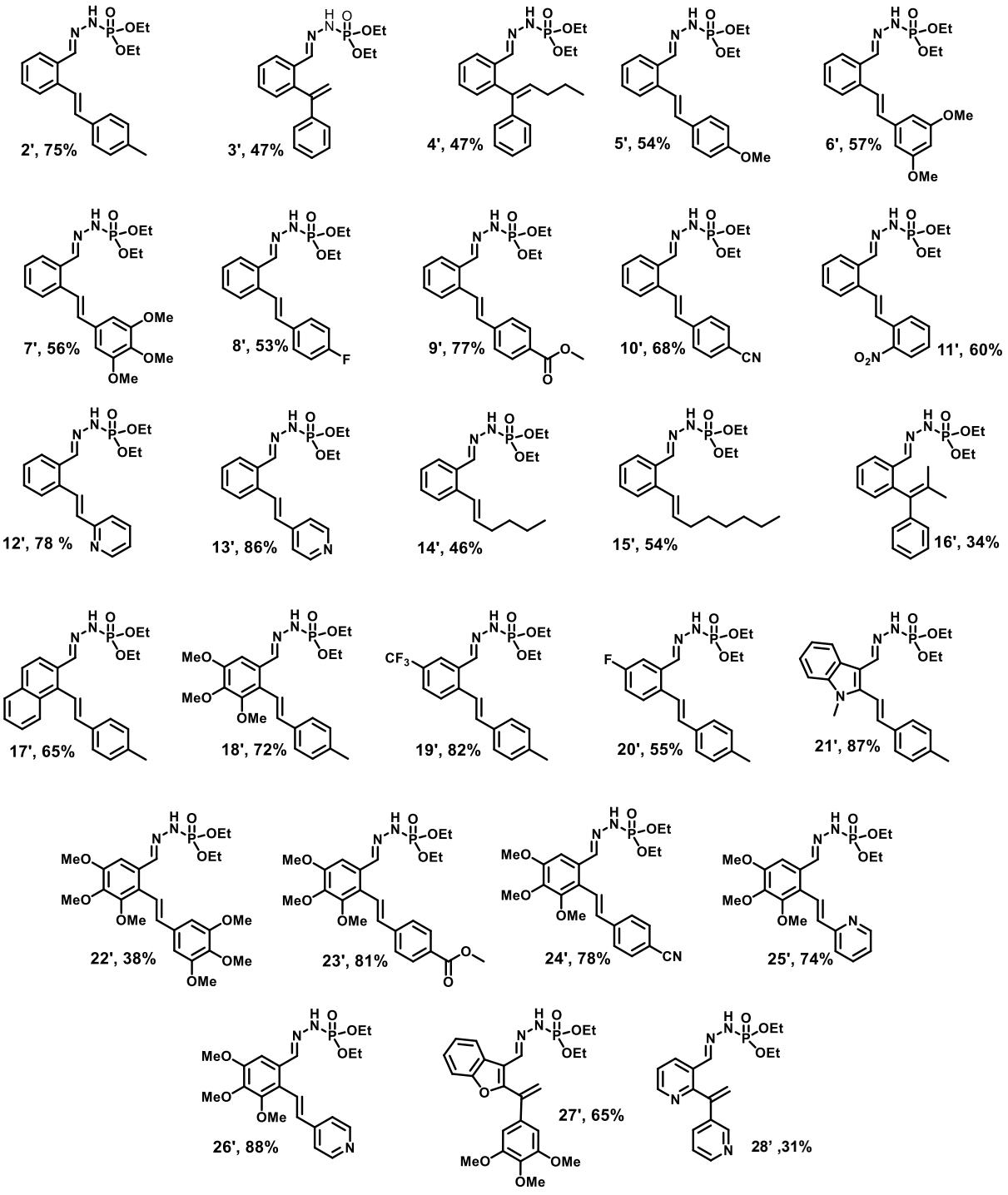


To an oven-dried sealable glass vial were added aldehyde (1 equiv.), phosphonohydrazine (1.5 equiv.) and MeOH (0.8 M). The vial was sealed with 20mm crimp caps with silicone/PTFE septum and stirred at r.t. (for 2 to 4 hours) until completion of the reaction checked by TLC.

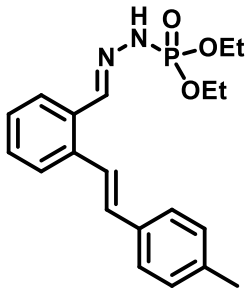
- In case of precipitation of phosphonohydrazone: Reaction medium was filtered using a Büchner funnel. The solid product was then dried under vacuum, characterized and used without any further purification.

- In case of no precipitation of phosphonohydrazone: the mixture was concentrated. The crude product was purified by silica gel column chromatography eluting with a cyclohexane/ethyl acetate mixture to afford the desired pur phosphonohydrazone.

List of phosphonohydrazones:



Diethyl (2-((*E*)-2-((*E*)-4-methylstyryl)benzylidene)hydrazineyl)phosphonate (2'):



The white solid (8.5 mmol, 3.2 g, 75% yield) was obtained following the general procedure A after 5 h starting from the aldehyde 2 (2.5 g, 11.3 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 3:7)

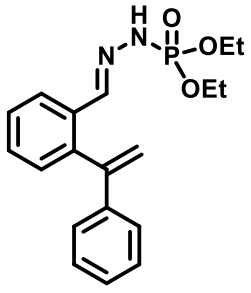
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, *J* = 28.2 Hz, NH), 8.24 (s, 1H), 7.73 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.64 (d, *J* = 16.2 Hz, 1H), 7.61 – 7.58 (dd, J = 7.7, 1.2 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 7.29 – 7.23 (m, 1H, overlapped with $CDCl_3$), 7.18 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 16.1 Hz, 1H), 4.29 – 4.11 (m, 4H), 2.37 (s, 3H), 1.33 (td, *J* = 7.1, 0.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1 (d, J_{C-P} = 19.4 Hz, CN), 137.8, 136.7, 134.7, 131.7, 131.6, 129.4 (2C), 129.2, 127.7, 127.4, 126.7 (2C), 126.6, 125.1, 63.4 (d, J_{C-P} = 5.7 Hz, 2C), 21.3, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.95.

HR-MS (ESI) *m/z*: [M + K]+ Calcd for $C_{20}H_{25}KN_2O_3P$ 411.1234; Found 411.1234.

Diethyl(*E*)-(2-(2-(1-phenylvinyl)benzylidene)hydrazineyl)phosphonate (3'):



The pale-yellow solid (0.80 mmol, 280 mg, 47 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 3 (350 mg, 1.7 mmol).

R*f* = 0.24 (Cyclohexane:Ethyl Acetate, 5:5)

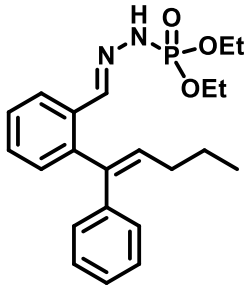
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 1H), 7.68 (s, 1H), 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 5H, overlapped with $CDCl_3$), 7.24 – 7.20 (m, 1H), 6.86 (d, *J* = 27.4 Hz, NH), 5.87 (d, *J* = 0.7 Hz, 1H), 5.22 (d, *J* = 0.7 Hz, 1H), 4.19 – 3.99 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 143.7 (d, J_{C-P} = 18.5 Hz, CN), 141.2, 140.6, 132.3, 130.3, 129.2, 128.5 (2C), 128.0, 127.8, 126.7 (2C), 125.7, 116.7, 63.3 (d, J_{C-P} = 5.5 Hz, 2C), 16.3 (d, J_{C-P} = 6.9 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.10.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{24}N_2O_3P$ 359.1519; Found 359.1513.

Diethyl(2-((*E*)-2-((*E*)-1-phenylpent-1-en-1-yl)benzylidene)hydrazineyl) phosphonate (4'):



The pale-yellow solid (0.4 mmol, 158 mg, 47 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 4 (210 mg, 0.8 mmol).

R*f* = 0.54 (Cyclohexane:Ethyl Acetate, 4:6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 1H), 7.66 (s, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.22 (m, 3H), 7.22 – 7.15 (m, 3H), 7.13 – 7.09 (m, 1H), 6.75 (d, *J* = 27.7 Hz,

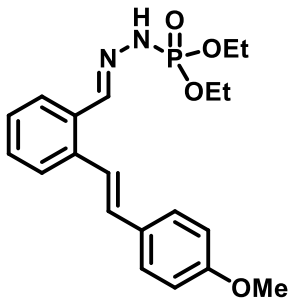
NH), 6.31 (t, *J* = 7.4 Hz, 1H), 4.22 – 4.02 (m, 4H), 1.89 (q, *J* = 7.3 Hz, 2H), 1.42 (h, *J* = 7.3 Hz, 2H), 1.31 (td, *J* = 7.1, 0.9 Hz, 6H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6 (d, J_{C-P} = 18.3 Hz, CN), 141.4, 139.4, 138.5, 132.5, 131.5, 130.5, 129.4, 128.4 (2C), 127.5, 127.1, 126.3 (2C), 125.5, 63.4 (d, J_{C-P} = 5.6 Hz, 2C), 32.0, 22.6, 16.1 (d, J_{C-P} = 6.8 Hz, 2C), 13.9.

^{31}P NMR (121 MHz, $CDCl_3$) δ 0.96.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{22}H_{30}N_2O_3P$ 401.1989; Found 401.1992.

Tetraethyl(4,4'-bis(4-methoxyphenyl)-4,4',5,5'-tetrahydro-3H,3'H-[5,5'-bibenzo[d][1,2]diazepine]-3,3'-diyl)bis(phosphonate) (5'):



The pale-yellow solid (0.9 mmol, 357 mg, 54 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 5 (400 mg, 1.7 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 5:5)

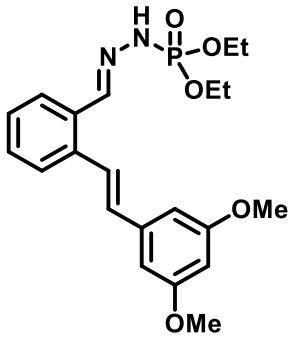
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.84 (d, *J* = 27.4 Hz, 1H), 7.72 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 – 7.46 (m, included 7.52 (d, *J* = 16.1 Hz, 1H) + 7.48 (d, *J* = 8.5 Hz, 2H)), 7.33 (td, *J* = 7.4, 1.3 Hz, 1H), 7.25 (td, *J* = 7.5, 1.3 Hz, 1H, overlap with $CDCl_3$), 6.95 – 6.88 (m, 3H), 4.27 – 4.12 (m, 4H), 3.83 (s, 3H), 1.33 (td, *J* = 7.1, 0.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 144.0 (d, J_{C-P} = 19.1 Hz, CN), 136.9, 131.5, 131.3, 130.2, 129.3, 128.0 (2C), 127.6, 127.2, 126.5, 123.9, 114.1 (2C), 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 55.3, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.55.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{25}N_2NaO_4P$ 411.1444; Found 411.1446.

Diethyl(2-((*E*)-2-((*E*)-3,5-dimethoxystyryl)benzylidene)hydrazineyl) phosphonate (6'):



The brown oil (4.4 mmol, 1.85 g, 59 % yield) was obtained following the general procedure A after 10 h starting from the aldehyde 6 (2 g, 7.5 mmol).

R*f* = 0.33 (Cyclohexane:Ethyl Acetate, 5:5)

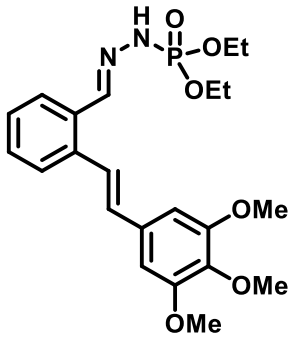
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 28.3 Hz, NH), 8.21 (s, 1H), 7.72 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.66 (d, *J* = 16.1 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.37 – 7.23 (m, 2H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.70 (d, *J* = 2.2 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 1H), 4.27 – 4.08 (m, 4H), 3.83 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (2C), 143.9 (d, J_{C-P} = 19.3 Hz, CN), 139.4, 136.4, 131.9, 131.7, 129.3, 127.7, 127.7, 126.8, 126.6, 104.9 (2C), 100.2, 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 55.4, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.80.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{21}H_{27}N_2NaO_5P$ 441.1550; Found 441.1552.

Diethyl(2-((*E*)-2-((*E*)-3,4,5-trimethoxystyryl)benzylidene)hydrazineyl) phosphonate (7):



The white solid (1.5 mmol, 653 mg, 56 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 7 (1.2 g, 2.7 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 1:9)

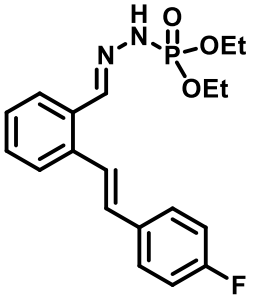
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.39 – 7.28 (m, 2H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.76 (s, 2H), 4.27 – 4.11 (m, 4H), 3.93 (s, 6H), 3.88 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (2C), 143.9 (d, J_{C-P} = 19.1 Hz, CN), 138.3, 136.5, 133.1, 132.0, 131.5, 129.3, 127.7, 127.6, 126.8, 125.5, 103.9 (2C), 63.5 (d, J_{C-P} = 5.5 Hz, 2C), 61.0, 56.3 (2C), 16.2 (d, J_{C-P} = 6.9 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.10.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{22}H_{30}N_2O_6P$ 449.1836; Found 449.1836.

Diethyl (2-((*E*)-2-((*E*)-4-fluorostyryl)benzylidene)hydrazineyl)phosphonate (8'):



The pale yellow solid (0.66 mmol, 247 mg, 53 % yield) was obtained following the general procedure A after 6 h starting from the aldehyde 8 (280 mg, 1.2 mmol).

R*f* = 0.32 (Cyclohexane:Ethyl Acetate, 4:6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.72 – 7.68 (m, 1H), 7.62 – 7.58 (m, 1H), 7.56 (s, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H), 7.06 (t, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 16.1 Hz, 1H), 4.29 – 4.10 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H). 7.72 – 7.68 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.47 (m, 2H), 7.39 – 7.32 (m, 1H), 7.32 – 7.28 (m, 1H).

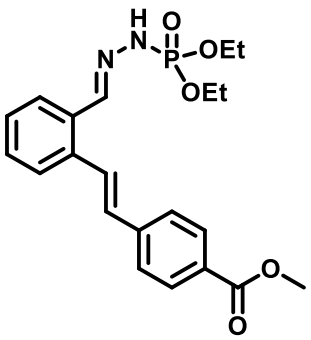
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 247.6 Hz, 1C), 144.2 (d, J_{C-P} = 19.5 Hz, CN), 136.4, 133.7 (d, J_{C-F} = 3.3 Hz, 1C), 131.7, 130.4, 129.2, 128.3 (d, J_{C-F} = 8.0 Hz, 2C), 127.9, 127.6, 126.7, 126.3 (d, J_{C-F} = 2.29 Hz, 1C), 115.6 (d, J_{C-F} = 21.6 Hz, 2C), 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.05.

^{19}F NMR (282 MHz, $CDCl_3$) δ -113.71.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{19}H_{22}FN_2NaO_3P$ 399.1244; Found 399.1247.

Methyl4-((*E*)-2-((*E*)-(2-(diethoxyphosphoryl)hydrazineylidene)methyl)styryl) benzoate (9'):



The white solid (0.72 mmol, 301 mg, 77 % yield) was obtained following the general procedure A after 2 h starting from the aldehyde 9 (250 mg, 0.9 mmol).

R*f* = 0.26 (Cyclohexane:Ethyl Acetate, 4:6)

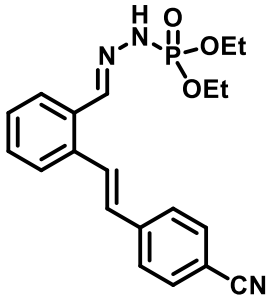
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.06 – 8.00 (m, 2H), 7.86 (d, *J* = 16.2 Hz, 1H), 7.69 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.33 (pd, *J* = 7.3, 1.6 Hz, 2H), 6.99 (d, *J* = 16.2 Hz, 1H), 4.27 – 4.11 (m, 4H), 3.93 (s, 3H), 1.32 (td, *J* = 7.1, 0.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.9 (d, J_{C-P} = 19.0 Hz, CN), 141.9, 136.0, 131.8, 130.5, 130.0 (2C), 129.3, 129.1, 129.1, 128.3, 128.1, 126.9, 126.6 (2C), 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 52.1, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.45.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{21}H_{25}N_2NaO_5P$ 439.1393; Found 439.1394.

Diethyl(2-((*E*)-2-((*E*)-4-cyanostyryl)benzylidene)hydrazineyl)phosphonate (10'):



The white solid (0.73 mmol, 278 mg, 68 % yield) was obtained following the general procedure A after 15 h starting from the aldehyde 10 (250 mg, 1.1 mmol).

R*f* = 0.25 (Cyclohexane:Ethyl Acetate, 5:5)

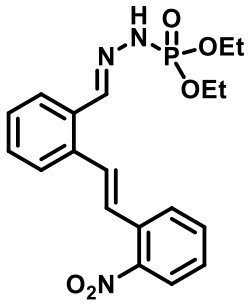
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.69-7.58 (m,6H),7.63 (d, *J* = 4.7 Hz, 6H), 7.40 – 7.31 (m, 2H), 6.95 (d, *J* = 16.1 Hz, 1H), 4.30 – 4.08 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (d, J_{C-P} = 18.7 Hz, CN), 142.0, 135.6, 132.5 (2C), 131.7, 130.6, 129.6, 129.5, 128.7, 128.5, 127.2 (2C), 127.0, 119.0, 110.9, 63.6 (d, J_{C-P} = 5.6 Hz, 2C), 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.19.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{22}N_3NaO_3P$ 406.1291; Found 406.1291.

Diethyl (2-((*E*)-2-((*E*)-2-nitrostyryl)benzylidene)hydrazineyl)phosphonate (11'):



The yellow solid (1.2 mmol, 484 mg, 60 % yield) was obtained following the general procedure A after 16 h starting from the aldehyde 11 (500 mg, 2.0 mmol).

R*f* = 0.20 (Cyclohexane:Ethyl Acetate, 5:5)

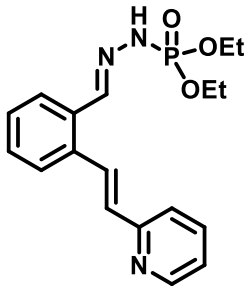
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.3 Hz, 1H), 7.75 – 7.58 (m, 4H), 7.48 – 7.41 (m, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.07 (d, *J* = 27.1 Hz, 1H, NH), 4.29 – 4.10 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 144.2 (d, J_{C-P} = 19.0 Hz, CN), 135.8, 133.3, 133.2, 132.0, 131.7, 129.5, 129.0, 128.5, 128.3, 128.2, 127.6, 126.8, 124.7, 63.5 (d, J_{C-P} = 5.5 Hz, 2C), 16.2 (d, J_{C-P} = 6.9 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.50.

HR-MS (ESI) *m/z*: [M + K]+ Calcd for $C_{19}H_{22}KN_3O_5P$ 442.0929; Found 442.0929.

Diethyl(2-((*E*)-2-((*E*)-2-(pyridin-2-yl)vinyl)benzylidene)hydrazineyl) phosphonate (12'):



The orange oil (2.4 mmol, 869 mg, 78 % yield) was obtained following the general procedure A after 22 h starting from the aldehyde 12 (650 mg, 3.1 mmol).

R*f* = 0.72 (Methanol:Ethyl Acetate, 1:9)

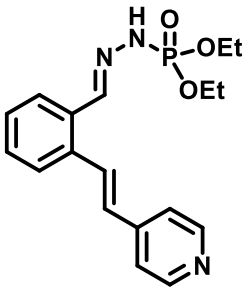
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 – 8.57 (m, 1H), 8.24 (s, 1H), 8.12 (d, *J* = 15.9 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.72 – 7.60 (m, 2H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.33 (pd, *J* = 7.3, 1.5 Hz, 2H), 7.18 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 7.04 (d, *J* = 15.9 Hz, 1H), 4.27 – 4.11 (m, 4H), 1.33 (td, *J* = 7.1, 0.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 149.4, 143.2 (d, J_{C-P} = 18.9 Hz, CN), 136.8, 135.7, 132.1, 130.8, 130.1, 129.4, 128.3, 127.4, 126.9, 122.4, 122.4, 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.16.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{18}H_{23}N_3O_3P$ 360.1472; Found 360.1475.

diethyl(2-((*E*)-2-((*E*)-2-(pyridin-4-yl)vinyl)benzylidene)hydrazineyl) phosphonate (13'):



The brown solid (1.6 mmol, 587 mg, 86 % yield) was obtained following the general procedure A after 22 h starting from the aldehyde 13 (400 mg, 1.9 mmol).

R*f* = 0.42 (Methanol:Ethyl Acetate, 1:9)

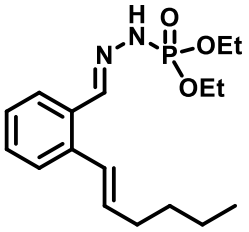
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.3 Hz, 2H), 8.12 – 8.02 (m, 2H), 7.71 – 7.59 (m, 2H), 7.48 (m, *J* = 5.7 Hz, 2H), 7.38 (m, *J* = 6.5, 4.2, 2.4 Hz, 2H), 6.90 (d, *J* = 16.2 Hz, 1H), 4.28 – 4.09 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6 (2C), 145.4, 144.1 (d, J_{C-P} = 19.9 Hz, CN), 135.1, 132.3, 131.9, 129.2, 128.6, 128.3, 128.3, 126.9, 121.3 (2C), 63.4 (d, J_{C-P} = 5.7 Hz, 2C), 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.40.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{18}H_{23}N_3O_3P$ 360.1472; Found 360.1472.

Diethyl (2-((*E*)-2-((*E*)-hex-1-en-1-yl)benzylidene)hydrazineyl)phosphonate (14'):



The yellow oil (1.2 mmol, 406 mg, 46 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 14 (500 mg, 2.6 mmol).

R*f* = 0.23 (Cyclohexane:Ethyl Acetate, 5:5)

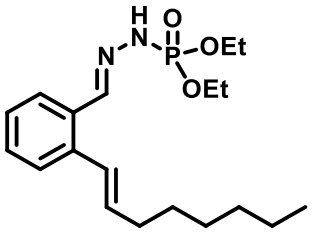
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.66 (d, *J* = 27.2 Hz, NH), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.27 (td, *J* = 7.5, 1.6 Hz, 1H), 7.20 (td, *J* = 7.5, 1.5 Hz, 1H), 6.75 (d, *J* = 15.6 Hz, 1H), 6.06 (dt, *J* = 15.6, 6.9 Hz, 1H), 4.30 – 4.11 (m, 4H), 2.24 (qd, *J* = 7.2, 1.4 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.43 – 1.34 (m, 8H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4 (d, J_{C-P} = 18.8 Hz, CN), 137.3, 135.2, 130.8, 129.2, 126.9 (d, J_{C-P} = 3.3 Hz, 1C), 126.6, 126.5, 63.4 (d, J_{C-P} = 5.6 Hz, 2C), 33.0, 31.4, 22.3, 16.2 (d, J_{C-P} = 6.9 Hz, 2C), 14.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 1.70.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{17}H_{28}N_2O_3P$ 339.1832; Found 339.1837.

Diethyl(2-((*E*)-2-((*E*)-oct-1-en-1-yl)benzylidene)hydrazineyl)phosphonate (15'):



The pale-yellow solid (0.8 mmol, 293 mg, 54 % yield) was obtained following the general procedure A after 16 h starting from the aldehyde 15 (300 mg, 1.4 mmol).

R*f* = 0.24 (Cyclohexane:EtOAc, 5:5)

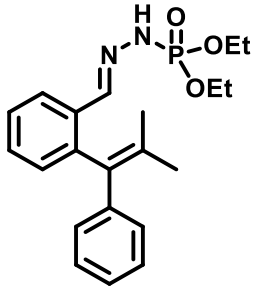
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.76 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.55 (d, *J* = 27.5 Hz, NH), 7.39 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.28 (td, *J* = 7.4, 1.5 Hz, 1H), 7.21 (td, *J* = 7.4, 1.4 Hz, 1H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.06 (dt, *J* = 15.6, 6.9 Hz, 1H), 4.30 – 4.11 (m, 4H), 2.23 (qd, *J* = 7.3, 1.5 Hz, 2H), 1.47 (m, 2H), 1.37 (td, *J* = 7.1, 0.9 Hz, 8H), 1.34 – 1.29 (m, 4H), 0.94 – 0.86 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (d, J_{C-P} = 18.7 Hz, CN), 137.3, 135.3, 130.9, 129.3, 127.0, 126.9, 126.6, 126.4, 63.5 (d, J_{C-P} = 5.7 Hz, 2C), 33.4, 31.8, 29.3, 29.0, 22.7, 16.2 (d, J_{C-P} = 6.9 Hz, 2C), 14.1.

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.31.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{32}N_2O_3P$ 367.2145; Found 367.2146.

Diethyl(*E*)-(2-(2-(2-methyl-1-phenylprop-1-en-1-yl)benzylidene)hydrazineyl) phosphonate (16'):



The pale-yellow solid (0.29 mmol, 112 mg, 34 % yield) was obtained following the general procedure A after 6 h starting from the aldehyde 16 (200 mg, 0.85 mmol).

R*f* = 0.27 (Cyclohexane:Ethyl Acetate, 5:5)

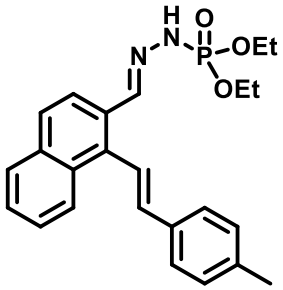
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.32 – 7.20 (m, 4H, overlapped with $CDCl_3$), 7.19 – 7.09 (m, 4H), 4.28 – 4.12 (m, 4H), 1.96 (s, 3H), 1.66 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3 (d, J_{C-P} = 18.4 Hz, CN), 142.9, 142.1, 134.0, 133.5, 132.2, 130.5, 129.5 (2C), 129.3, 128.0 (2C), 126.9, 126.3, 125.5, 63.4 (d, J_{C-P} = 5.6 Hz, 2C), 22.7, 21.9, 16.2 (d, J_{C-P} = 6.9 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.29.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{28}N_2O_3P$ 387.1832; Found 387.1836.

Diethyl(2-((*E*)-(1-((*E*)-4-methylstyryl)naphthalen-2-yl)methylene)hydrazineyl) phosphonate (17'):



The pale-yellow solid solid (1.1 mmol, 449 mg, 65 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 17 (450 mg, 1.7 mmol).

R*f* = 0.29 (Cyclohexane:Ethyl Acetate, 5:5)

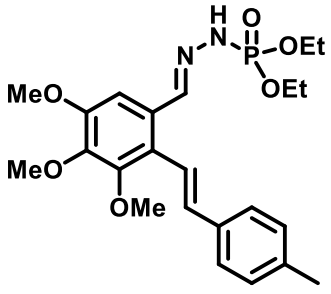
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.15 – 8.07 (m, 2H), 7.87 – 7.80 (m, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.55 – 7.46 (m,5H), 7.24 (d, *J* = 7.9 Hz, 2H, overlapped with $CDCl_3$), 7.17 (d, *J* = 27.3 Hz, NH), 6.67 (d, *J* = 16.4 Hz, 1H), 4.26 – 4.12 (m, 4H), 2.41 (s, 3H), 1.36 (t, *J* = 7.1, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (d, J_{C-P} = 18.5 Hz, CN), 138.4, 137.9, 135.7, 133.9, 133.8, 132.3, 129.6 (2C), 129.4, 128.3, 127.6, 126.7, 126.6 (2C), 126.4, 125.6, 123.4, 122.5, 63.5 (d, J_{C-P} = 5.6 Hz, 2C), 21.3, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.27.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{28}N_2O_3P$ 423.1832; Found 423.1837.

Diethyl(2-((*E*)-3,4,5-trimethoxy-2-((*E*)-4-methylstyryl)benzylidene) hydrazineyl) phosphonate (18'):



The white solid (1.0 mmol, 480 mg, 72 % yield) was obtained following the general procedure A after 20 h starting from the aldehyde 18 (450 mg, 1.4 mmol).

R*f* = 0.20 (Cyclohexane:Ethyl Acetate, 5:5)

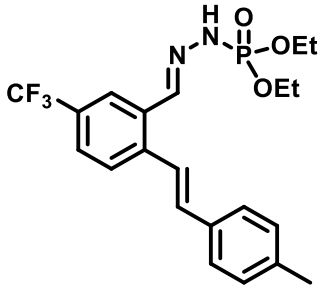
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 11.4 Hz, 2H), 7.20 – 7.12 (m, 2H), 6.68 – 6.56 (m, 1H), 4.28 – 4.13 (m, 4H), 3.95 – 3.90 (m, 6H), 3.83 (s, 3H), 2.38 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 151.7, 144.5 (d, J_{C-P} = 18.5 Hz, CN), 143.4, 137.8, 135.6, 134.7, 129.4 (2C), 127.8, 126.5 (2C), 125.6, 120.3, 105.2, 63.3 (d, J_{C-P} = 5.2 Hz, 2C), 61.0, 60.9, 56.0, 21.2, 16.2 (d, J_{C-P} = 6.7 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.80.

HR-MS (ESI) *m/z*: [M + K]+ Calcd for $C_{23}H_{31}KN_2O_6P$ 501.1551; Found 501.1553.

Diethyl(2-((*E*)-2-((*E*)-4-methylstyryl)-5-(trifluoromethyl)benzylidene) hydrazineyl)phosphonate (19'):



The yellow solid (0.41 mmol, 603 mg, 82 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 19 (500 mg, 1.7 mmol).

R*f* = 0.34 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.98 (s, 1H), 7.83 (d, *J* = 27.6 Hz, NH), 7.68 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 16.2 Hz, 1H), 4.28 – 4.13 (m, 4H), 2.38 (s, 3H), 1.35 (tt, *J* = 7.1, 0.8 Hz, 6H).

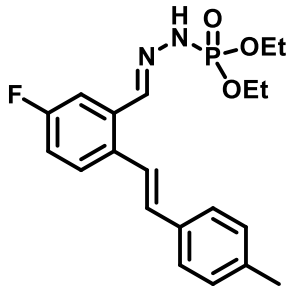
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4 (d, J_{C-P} = 19.2 Hz, CN), 139.8, 138.6, 134.0, 134.0, 131.9, 129.5 (2C), 129.4 (q, J_{C-F} = 32.7 Hz, 1C), 127.1, 126.9 (2C), 125.5 (q, J_{C-F} = 3.4 Hz, 1C), 124.4 (q, J_{C-F} = 3.8 Hz, 1C), 124.0 (q, J_{C-F} = 270 Hz, CF_3), 123.6, 63.7 (d, J_{C-P} = 5.7 Hz, 2C), 21.4, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 0.96.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.66.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{25}F_3N_2O_3P$ 441.1549; Found 441.1550.

Diethyl (2-((*E*)-5-fluoro-2-((*E*)-4-methylstyryl)benzylidene)hydrazineyl) phosphonate (20'):



The pale yellow solid (1.1 mmol, 430 mg, 55% yield) was obtained following the general procedure A after 22 h starting from the aldehyde 20 (500 mg, 2 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.56 – 7.46 (m, 2H), 7.43 – 7.36 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 8.4, 2.7 Hz, 1H), 6.86 (d, *J* = 16.1 Hz, 1H), 4.31 – 4.07 (m, 4H), 2.37 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H).

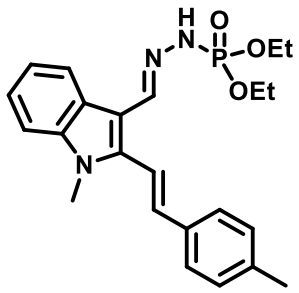
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1 (d, J_{C-P} = 246.5 Hz, CN), 142.5 (d, J_{C-P} = 19.8 Hz, 1C), 137.9, 134.5, 133.6 (d, J_{C-P} = 7.7 Hz, 1C), 132.9 (d, J_{C-P} = 3.1 Hz, 1C), 131.9, 129.5 (2C), 128.5 (d, J_{C-P} = 7.9 Hz, 1C), 126.7 (2C), 123.7, 116.5 (d, J_{C-P} = 22.1 Hz, 1C), 113.1 (d, J_{C-P} = 22.9 Hz, 1C), 63.6 (d, J_{C-P} = 5.7 Hz, 2C), 21.3, 16.2 (d, J_{C-P} = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 0.57.

^{19}F NMR (282 MHz, $CDCl_3$) δ -114.40.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{24}FN_2NaO_3P$ 413.1401; Found 413.1407.

Diethyl(2-((*E*)-(1-methyl-2-((*E*)-4-methylstyryl)-1H-indol-3-yl)methylene) hydrazineyl)phosphonate (21'):



The yellow solid (0.87 mmol, 370 mg, 87 % yield) was obtained following the general procedure A after 26 h starting from the aldehyde 21 (275 mg, 1.0 mmol).

R*f* = 0.29 (Cyclohexane:Ethyl Acetate, 4:6)

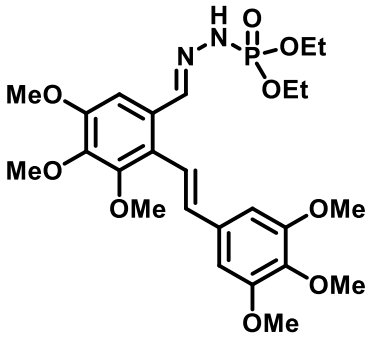
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.8 Hz, 1H), 8.11 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 4.4 Hz, 2H), 7.25 – 7.19 (m, 3H, overlap with $CDCl_3$), 7.13 (d, *J* = 16.2 Hz, 1H), 6.91 (d, *J* = 16.5 Hz, 1H), 6.56 (d, *J* = 25.8 Hz, N-H), 4.24 (m, 4H), 3.79 (s, 3H), 2.40 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7 (d, J_{C-P} = 19.6 Hz, CN), 139.6, 138.8, 137.9, 136.9, 133.8, 129.6 (2C), 126.8 (2C), 125.5, 123.3, 122.5, 121.2, 115.0, 109.7, 109.1, 63.3 (d, J_{C-P} = 5.6 Hz, 2C), 30.8, 21.4, 16.3 (d, J_{C-P} = 7.0 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.83.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{23}H_{29}N_3O_3P$ 426.1941; Found 426.1944.

Diethyl(2-((*E*)-3,4,5-trimethoxy-2-((*E*)-3,4,5-trimethoxystyryl)benzylidene) hydrazineyl)phosphonate (22'):



The pale-yellow solid (0.8 mmol, 415 mg, 38 % yield) was obtained following the general procedure A after 28 h starting from the aldehyde 22 (800 mg, 2.0 mmol).

R*f* = 0.37 (Cyclohexane:Ethyl Acetate, 2:8)

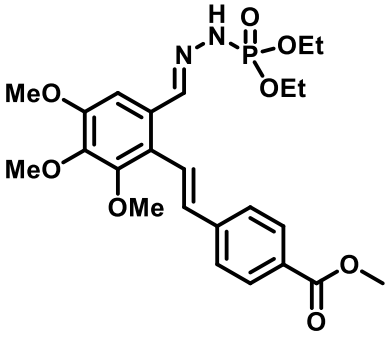
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.27 (s, 1H, overlap with $CDCl_3$), 7.12 (d, *J* = 15.8 Hz, 1H), 6.73 (s, 2H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.27 – 4.13 (m, 4H), 3.92 (s, 12H), 3.88 (s, 3H), 3.84 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5 (2C), 152.8, 151.8, 144.2 (d, J_{C-P} = 18.5 Hz, CN), 143.5, 138.2, 135.6, 133.2, 127.8, 125.3, 120.7, 105.1, 103.7 (2C), 63.4 (d, J_{C-P} = 5.5 Hz, 2C), 61.1, 61.0 (2C), 56.2 (2C), 56.0, 16.2 (d, J_{C-P} = 6.8 Hz, 2C)

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.88.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{25}H_{36}N_2O_9P$ 539.2153; Found 539.2156.

Methyl4-((*E*)-6-((*E*)-(2-(diethoxyphosphoryl)hydrazineylidene)methyl)-2,3,4-trimethoxystyryl)benzoate (23'):



The white solid (0.68 mmol, 344 mg, 81 % yield) was obtained following the general procedure A after 4 h starting from the aldehyde 23 (300 mg, 0.8 mmol).

R*f* = 0.41 (Cyclohexane : Ethyl Acetate, 5:5)

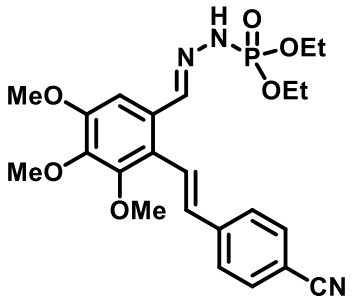
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.02 (s;1H), 8.00 (s, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 16.4 Hz, 1H), 7.23 (s, 1H), 6.85 (d, *J* = 26.1 Hz, NH), 6.73 (d, *J* = 16.4 Hz, 1H), 4.19 (m, 4H), 3.93 (s, 3H), 3.92 (s, 6H), 3.85 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 153.2, 152.0, 143.9 (d, J_{C-P} = 17.7 Hz, CN), 143.5, 141.8, 134.4, 130.1 (2C), 129.2, 127.9, 126.4 (2C), 124.8, 124.1, 105.4, 63.5 (d, J_{C-P} = 5.6 Hz, 2C), 61.1, 61.0, 56.1, 52.2, 16.2 (d, J_{C-P} = 6.7 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.24.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{32}N_2O_8P$ 507.1891; Found 507.1889.

Diethyl(2-((*E*)-2-((*E*)-4-cyanostyryl)-3,4,5-trimethoxybenzylidene)hydrazineyl) phosphonate (24'):



The pale yellow solid (0.72 mmol, 343 mg, 78 % yield) was obtained following the general procedure A after 2 h starting from the aldehyde 2' (300 mg, 0.9 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 7:3)

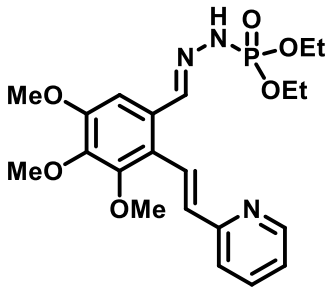
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 16.4 Hz, 1H), 7.21 (s, 1H), 7.11-6.88 (bs, NH), 6.75 (d, *J* = 16.4 Hz, 1H), 4.28-4.05 (m, 4H), 3.92 (s, 6H), 3.85 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 152.1, 144.0 (d, $J_{C\text{-}P}$ = 18.3 Hz, CN), 143.4, 142.2, 133.1, 132.5 (2C), 128.2, 127.0 (2C), 125.5, 124.0, 119.0, 110.7, 105.5, 63.4 (d, $J_{C\text{-}P}$ = 5.6 Hz, 2C), 61.1, 60.9, 56.0, 16.2 (d, $J_{C\text{-}P}$ = 6.5 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.72.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{23}H_{29}N_3O_6P$ 474.1789; Found 474.178.

Diethyl(2-((*E*)-3,4,5-trimethoxy-2-((*E*)-2-(pyridin-2-yl)vinyl)benzylidene) hydrazineyl)phosphonate (25'):



The pale yellow solid (0.62 mmol, 280 mg, 78 % yield) was obtained following the general procedure A after 5 h starting from the aldehyde 25 (240 mg, 0.8 mmol).

R*f* = 0.32 (Methanol:Ethyl Acetate, 1:9)

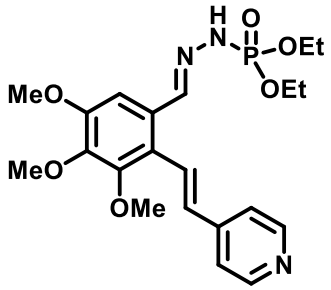
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.7 Hz, 1H), 8.11 (s, 1H), 7.75 (d, *J* = 16.2 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.26 (s, 1H, overlap with $CDCl_3$), 7.20 – 7.13 (m, 1H), 6.85 (d, *J* = 16.1 Hz, 1H), 4.24 – 4.12 (m, 4H), 3.91 (s, 6H), 3.86 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 153.1, 152.2, 149.7, 143.7 (d, $J_{C\text{-}P}$ = 18.1 Hz, CN), 143.5, 136.6, 134.5, 128.2 (d, $J_{C\text{-}P}$ = 3.9 Hz, 1C), 125.5, 124.6 (d, $J_{C\text{-}P}$ = 1.7 Hz, 1C), 122.3, 122.2, 105.1, 63.5 (d, $J_{C\text{-}P}$ = 5.5 Hz, 2C), 61.0 (d, $J_{C\text{-}P}$ = 7.5 Hz, 2C), 56.0, 16.2 (d, $J_{C\text{-}P}$ = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.49.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{29}N_3O_6P$ 450.1789; Found 450.1785.

Diethyl(2-((*E*)-3,4,5-trimethoxy-2-((*E*)-2-(pyridin-4-yl)vinyl)benzylidene) hydrazineyl)phosphonate (26'):



The pale yellow solid (0.48 mmol, 216 mg, 88% yield) was obtained following the general procedure A after 3 h starting from the aldehyde 26 (166mg, 0.55 mmol).

R*f* = 0.45 (Methanol:Ethyl Acetate, 1:9)

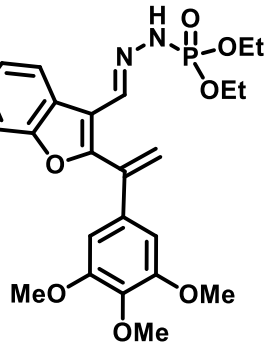
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, *J* = 5.9 Hz, 2H), 8.08 (s, 1H), 8.04-7.79 (bs, 1H, NH), 7.47 (d, *J* = 16.5 Hz, 1H), 7.32 (d, *J* = 5.9 Hz, 2H), 7.23 (s, 1H), 6.67 (d, *J* = 16.4 Hz, 1H), 4.28-4.09 (m, 4H), 3.93 – 3.89 (m, 6H, included 3.92 (s, 3H) + 3.91 (s, 3H)), 3.85 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 152.1, 149.9 (2C), 145.0, 143.7 (d, J_{C-P} = 19.0 Hz, 1C), 143.3, 132.2, 128.4, 126.4, 123.7, 120.9 (2C), 105.4, 63.4 (d, J_{C-P} = 5.6 Hz, 2C), 61.1, 61.0, 56.1, 16.2 (d, J_{C-P} = 6.7 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.64.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{29}N_3O_6P$ 450.1789; Found 450.1793.

Diethyl(*E*)-(2-((2-(1-(3,4,5-trimethoxyphenyl)vinyl)benzofuran-3-yl) methylene)hydrazineyl)phosphonate (27'):



The yellow oil (0.26 mmol, 127 mg, 65 % yield) was obtained following the general procedure A after 5 h starting from the aldehyde 27 (145 mg, 0.4 mmol).

R*f* = 0.24 (Cyclohexane : Ethyl Acetate, 3:7)

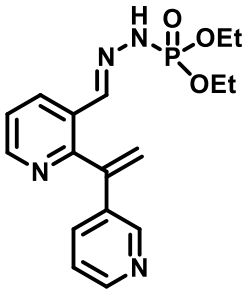
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 7.54 (s, 1H), 7.50 – 7.45 (m, 1H), 7.37 (td, *J* = 8.2, 7.7, 1.6 Hz, 1H), 7.31 (td, *J* = 7.4, 1.2 Hz, 1H), 6.78 (d, *J* = 26.9 Hz, NH), 6.60 (s, 2H), 5.77 (dd, *J* = 25.1, 0.9 Hz, 2H), 4.32 – 4.08 (m, 4H), 3.90 (s, 3H), 3.83 (s, 6H), 1.37 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 154.2, 153.4 (2C), 138.9, 138.8, 138.7 (d, J_{C-P} = 5.5 Hz, CN), 134.1, 126.3, 125.8, 123.7, 123.6, 119.5, 114.6, 111.0, 105.3 (2C), 76.7, 63.4 (d, J_{C-P} = 5.4 Hz, 2C), 61.0, 56.3, 16.2 (d, J_{C-P} = 7.0 Hz, 2C).

^{31}P NMR (162 MHz, $CDCl_3$) δ 1.01.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{28}N_2O_7P$ 487.1629; Found 487.1633.

Diethyl (*E*)-(2-((2-(1-(pyridin-3-yl)vinyl)pyridin-3-yl)methylene)hydrazineyl) phosphonate (28'):



The pale-yellow solid (156 mg with 83% of mass purity, 0.36 mmol adjusted to account for inseparable starting material, 30 % yield) was obtained following the general procedure A after 7 h starting from the aldehyde 28 (250 mg, 1.2 mmol).

R*f* = 0.28 (Methanol:Ethyl Acetate, 1:9)

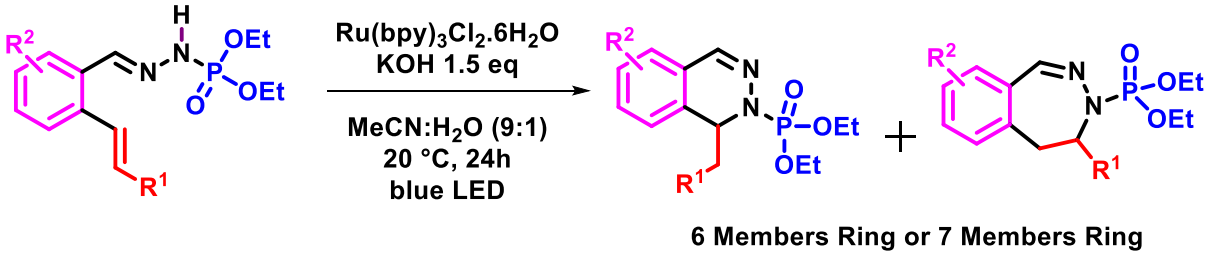
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.55 – 8.51 (bs, 1H), 8.49 – 8.45 (bs, 1H), 8.39 (d, *J* = 28.4 Hz, 1H, NH), 8.27 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.86 (s, 1H), 7.58 – 7.52 (m, 1H), 7.28 (dd, *J* = 8.0, 4.7 Hz, 1H, overlapped with $CDCl_3$), 7.21 (dd, *J* = 8.0, 4.7 Hz, 1H), 6.02 (s, 1H), 5.41 (s, 1H), 4.19 – 3.98 (m, 4H, overlapped with hydrazine), 1.33 – 1.25 (m, 6H, overlapped with hydrazine).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 149.8, 148.9, 147.9, 143.6, 141.2 (d, $J_{C\text{-}P}$ = 19.3 Hz, CN), 135.3, 134.3, 134.0, 129.1, 123.4, 123.1, 120.0, 63.4 (d, $J_{C\text{-}P}$ = 5.5 Hz, 2C), 16.13 (d, $J_{C\text{-}P}$ = 6.8 Hz, 2C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 5.56.

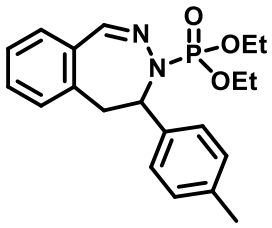
HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{17}H_{22}N_4O_3P$ 361.1424; Found 361.1426.

General Procedure B: for the synthesis of phthalazines and characterization



To an oven-dried sealable glass vial were added phosphonohydrazone (1 equiv.), potassium hydroxide (1.5 equiv.), $Ru(bpy)_3Cl_2.6H_2O$ as a photocatalyst (2.5 mol%) and a mix of MeCN and H_2O (9:1) (1.7 M). The vial was sealed with 20mm crimp caps with silicone/PTFE septum and the mixture was stirred under blue LED irradiation at 20 °C. After completion of the reaction checked by TLC, the resulting suspension was extracted with EtOAc (3 x 50 mL), washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture of 6- and 7-member ring product was purified by silica gel column chromatography eluting with a cyclohexane/ethyl acetate mixture to afford the desired products.

Diethyl (4-(*p*-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (2a):



The brown oil (0.15 mmol, 56 mg, 50% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 2' (112 mg, 0.3 mmol).

R*f* = 0.44 (Cyclohexane:Ethyl Acetate, 3:7)

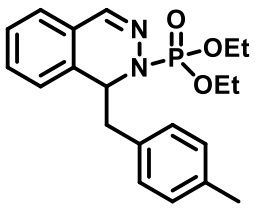
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.21 – 7.15 (m, 1H), 7.14 – 7.07 (m, 2H), 7.02 – 6.97 (m, 1H), 6.91 – 6.84 (m, 4H), 6.15 (td, *J* = 6.4, 2.0 Hz, 1H), 4.31 – 4.01 (m, 4H), 3.61 (ddd, *J* = 15.7, 6.2, 3.1 Hz, 1H), 3.42 (dd, *J* = 15.4, 1.7 Hz, 1H), 2.14 (s, 3H), 1.35 (dtd, *J* = 10.0, 7.1, 1.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7 (d, J_{C-P} = 16.9 Hz, CN), 138.3, 136.7, 135.8, 132.5, 131.5, 130.1, 129.1, 128.7 (2C), 126.4, 125.9 (2C), 63.9 (d, J_{C-P} = 6.0 Hz, 1C), 63.3 (d, J_{C-P} = 5.8 Hz, 1C), 61.8 (d, J_{C-P} = 10.4 Hz, 1C), 41.9 (d, J_{C-P} = 5.3 Hz, 1C), 20.9, 16.2 (d, J_{C-P} = 7.7 Hz, 1C), 16.1 (d, J_{C-P} = 7.8 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.95.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{20}H_{26}N_2O_3P$ 373.1676; Found 373.1679.

Diethyl (1-(4-methylbenzyl)phthalazin-2(1H)-yl)phosphonate (2b):



The brown oil (0.03 mmol, 11.2 mg, 10% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 2' (112mg, 0.3 mmol).

R*f* = 0.56 (Cyclohexane:Ethyl Acetate, 3:7)

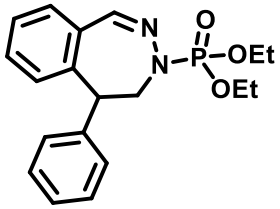
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.31 – 7.24 (m, 1H), 7.22 – 7.12 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.5 Hz, 2H), 6.40 (d, *J* = 7.5 Hz, 1H), 5.22 (ddd, *J* = 8.9, 5.2, 2.5 Hz, 1H), 4.32 – 4.14 (m, 2H), 4.12 – 3.98 (m, 1H), 3.98 – 3.84 (m, 1H), 2.96 (dd, *J* = 12.7, 5.2 Hz, 1H), 2.87 (dd, *J* = 12.8, 9.8 Hz, 1H), 2.27 (s, 3H), 1.40 (tt, *J* = 7.1, 1.0 Hz, 3H), 1.24 (tt, *J* = 7.1, 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9 (d, J_{C-P} = 12.6 Hz, CN), 142.8, 135.9, 133.2, 131.7 (d, J_{C-P} = 6.5 Hz, 1C), 130.5, 129.9 (2C), 128.7 (2C), 127.9, 126.8 (d, J_{C-P} = 1.1 Hz, 1C), 123.0, 123.6 (d, J_{C-P} = 1.7 Hz, 1C), 63.9 (d, J_{C-P} = 6.3 Hz, 1C), 63.1 (d, J_{C-P} = 5.7 Hz, 1C), 55.8 (d, J_{C-P} = 8.7 Hz, 1C), 41.1, 21.1, 16.3 (d, J_{C-P} = 7.2 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.78.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{20}H_{26}N_2O_3P$ 373.1676; Found 373.1676.

Diethyl(5-phenyl-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (3a):



The brown oil (0.15 mmol, 54 mg, 50 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 3' (108 mg, 0.3 mmol).

R*f* = 0.33 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 4.81 (dt, *J* = 13.2, 6.2 Hz, 1H), 4.74 – 4.68 (m, 1H), 4.14 – 4.03 (m, 1H), 4.02 – 3.90 (m, 1H), 3.60 (dd, *J* = 13.7, 2.2 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.12 – 3.00 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H).

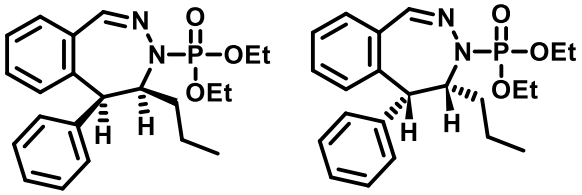
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 141.7, 141.0 (d, J_{C-P} = 17.8 Hz, CN), 133.5, 132.3, 130.5, 129.2, 128.5 (2C), 128.4 (2C), 127.3, 126.5, 63.4 (d, J_{C-P} = 5.9 Hz, 1C), 62.5 (d, J_{C-P} = 5.4 Hz, 1C), 53.5 (d, J_{C-P} = 5.8 Hz, 1C), 52.7 (d, J_{C-P} = 8.9 Hz, 1C), 16.2 (d, J_{C-P} = 7.0 Hz, 1C), 16.0 (d, J_{C-P} = 7.5 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 3.67.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{24}N_2O_3P$ 359.1519; Found 359.1522.

Diethyl (5-phenyl-4-propyl-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (4a):

Enantiomers' pair (S, S) or (R, R) – Dia *syn*:



The brown oil (0.03 mmol, 13 mg, 22 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 4' (60 mg, 0.15 mmol).

R*f* = 0.36 (Cyclohexane:Ethyl Acetate, 7:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.42 (td, *J* = 7.4, 1.6 Hz, 1H), 7.36 (td, *J* = 7.3, 1.7 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.18 (m, 2H), 7.14 – 7.07 (m, 1H), 6.94 – 6.90 (m, 2H), 5.11 – 4.97 (m, 1H), 4.58 (t, *J* = 4.4 Hz, 1H), 4.17 – 4.03 (m, 2H), 3.16 – 3.03 (m, 1H), 2.82 – 2.68 (m, 1H), 1.52 – 1.34 (m, 3H), 1.30 (td, *J*

= 7.1, 1.0 Hz, 3H), 1.27 – 1.14 (m, 1H), 0.93 (td, *J* = 7.1, 1.1 Hz, 3H), 0.83 (t, *J* = 7.1 Hz, 3H).

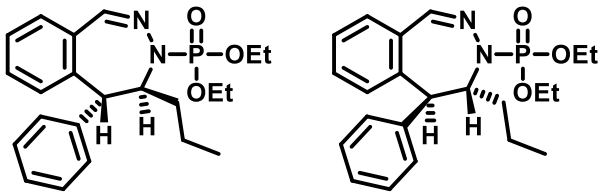
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 139.9 (d, J_{C-P} = 17.9 Hz, CN), 139.1, 133.6, 132.2, 131.4, 129.6, 128.4 (2C), 128.0 (2C), 127.3, 126.3, 64.0 (d, *J* = 6.8 Hz, 1C), 62.0 (d, J_{C-P} = 5.5 Hz, 1C), 62.0 (d, J_{C-P} = 9.0 Hz, 1C), 56.6 (d, J_{C-P} = 6.5 Hz, 1C), 33.6, 19.3, 16.2 (d, J_{C-P} = 6.8 Hz, 1C), 15.9 (d, J_{C-P} = 7.7 Hz, 1C), 13.9.

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.77.

NOESY: A correlation is observed between the two vicinal protons of the 7 members ring

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{22}H_{30}N_2O_3P$ 401.1989; Found 401.1992.

Enantiomers' pair (R, S) or (S, R) – Dia *anti*:



The brown oil (0.03 mmol, 12 mg, 20 % yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 4' (60 mg, 0.15 mmol).

R*f* = 0.30 (Cyclohexane:Ethyl Acetate, 7:3)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.44 – 7.37 (m, 3H), 7.36 – 7.21 (m, 4H, overlapped with $CDCl_3$), 7.18 (td, *J* = 7.5, 1.3 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 5.00 – 4.93 (m, 1H), 4.33 – 4.18 (m, 3H), 4.18 – 4.01 (m, 2H), 1.59 – 1.41 (m, 2H), 1.40 – 1.31 (m, included 1.37 (td, *J* = 7.1, 1.1 Hz, 3H) + 1.34 (td, *J* = 7.1, 1.0 Hz, 3H)), 1.30 – 1.06 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

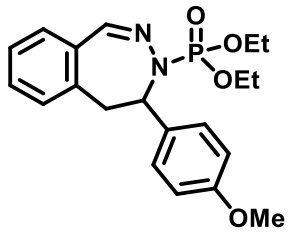
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4 (d, J_{C-P} = 16.3 Hz, CN), 141.3, 141.1, 140.3, 132.0, 131.8, 129.0, 129.0 (2C), 128.9 (2C), 128.6, 127.2, 126.6, 64.1 (d, *J* = 6.4 Hz, 1C), 63.2 (d, J_{C-P} = 5.9 Hz, 1C), 62.9 (d, J_{C-P} = 8.5 Hz, 1C), 55.7 (d, J_{C-P} = 3.9 Hz, 1C), 31.7, 20.1, 16.2 (d, J_{C-P} = 7.1 Hz, 2C), 14.0.

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.98.

NOESY: No correlation observed between the two vicinal protons of the 7 members ring

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{22}H_{30}N_2O_3P$ 401.1989; Found 401.1992.

Diethyl(4-(4-methoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (5a):



The brown oil (0.054 mmol, 21 mg, 18 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 5' (117 mg, 0.3 mmol).

R*f* = 0.39 (Cyclohexane:Ethyl Acetate, 5:5)

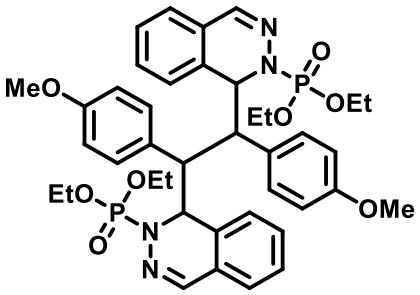
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.11 (m, 2H), 7.05 – 6.98 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 6.12 (t, *J* = 5.7 Hz, 1H), 4.26 – 4.06 (m, 4H), 3.65 (s, 3H), 3.62 – 3.54 (m, 1H), 3.43 (d, *J* = 15.5 Hz, 1H), 1.39-1.30 (m, 6H, included 1.36 (t, *J* = 7.0 Hz, 3H) + 1.33 (t, *J* = 7.0 Hz, 3H)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 141.0 (d, J_{C-P} = 16.6 Hz, CN), 138.4, 132.3, 131.8, 131.7, 130.1, 129.3, 127.2 (2C), 126.5, 113.4 (2C), 64.0 (d, J_{C-P} = 6.0 Hz, 1C), 63.4 (d, J_{C-P} = 5.8 Hz, 1C), 61.4 (d, J_{C-P} = 10.2 Hz, 1C), 55.0, 42.0 (d, J_{C-P} = 5.3 Hz, 1C), 16.2 (d, J_{C-P} = 7.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.3 Hz, 1C).

^{31}P NMR (162 MHz, $CDCl_3$) δ 2.84.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{25}N_2NaO_4P$ 411.1444; Found 411.1446.

Tetraethyl(4,4'-bis(4-methoxyphenyl)-4,4',5,5'-tetrahydro-3H,3'H-[5,5'-bibenzo[d][1,2]diazepine]-3,3'-diyl)bis(phosphonate) (XI):



The brown oil (0.015 mmol, 12 mg, 10 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 5' (117 mg, 0.3 mmol).

R*f* = 0.22 (Cyclohexane:Ethyl Acetate, 2:8)

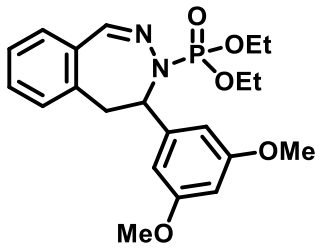
^{1}H NMR (300 MHz, CDCl3) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.01 (dd, *J* = 8.6, 2.6 Hz, 2H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.81 (s, 2H), 6.60 (dd, *J* = 8.4, 2.8 Hz, 2H), 6.40 (dd, *J* = 8.4, 1.9 Hz, 2H), 5.29 (d, *J* = 4.3 Hz, 2H), 4.19 – 4.07 (m, 4H), 3.81 (s, 6H), 3.77 – 3.68 (m, 2H), 3.65 – 3.55 (m, 2H), 3.52 (s, 2H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.02 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 142.26 (d, *J* = 11.4 Hz), 135.20, 131.41, 129.55, 128.90, 127.66 (2C), 125.43, 124.29 (2C), 113.32, 112.24, 63.84 (d, *J* = 6.4 Hz), 62.47 (d, *J* = 5.7 Hz), 55.66, 55.06, 16.28 (d, *J* = 7.7 Hz), 15.68 (d, *J* = 7.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 2.60.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{40}H_{49}N_4O_8P_2$ 775.3020; Found 775.3015.

diethyl(4-(3,5-dimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (6a):



The brown oil (0.07 mmol, 28 mg, 22 % yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 6' (125 mg, 0.3 mmol).

R*f* = 0.40 (Cyclohexane :Ethyl Acetate, 5:5)

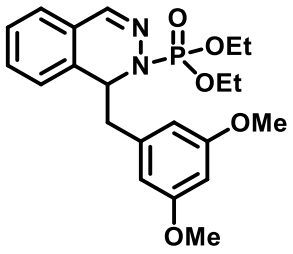
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.24 – 7.19 (m, 1H), 7.18 – 7.10 (m, 2H), 7.03 – 6.98 (m, 1H), 6.18 (d, *J* = 2.1 Hz, 2H), 6.16-6.11 (m, 1H), 6.10 (t, *J* = 2.2 Hz, 1H), 4.29 – 4.06 (m, 4H), 3.63 – 3.53 (m, 7H), 3.41 (dd, *J* = 15.5, 1.7 Hz, 1H), 1.41-1.31 (m, 6H, included 1.38 (td, *J* = 7.0, 0.9 Hz, 3H) + 1.34 (td, *J* = 7.1, 1.0 Hz, 3H))

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (2C), 142.3, 140.8 (d, J_{C-P} = 16.8 Hz, CN), 138.1, 132.4, 131.5, 130.1, 129.2, 126.5, 104.4 (2C), 98.7, 64.0 (d, *J* = 6.0 Hz, 1C), 63.4 (d, J_{C-P} = 5.8 Hz, 1C), 62.2 (d, J_{C-P} = 10.5 Hz, 1C), 55.2 (2C), 41.8 (d, J_{C-P} = 5.3 Hz, 1C), 16.2 (d, J_{C-P} = 7.2 Hz, 1C), 16.1 (d, J_{C-P} = 7.4 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.76.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{21}H_{27}N_2NaO_5P$ 441.1550; Found 441.1556.

Diethyl (1-(3,5-dimethoxybenzyl)phthalazin-2(1H)-yl)phosphonate (6b):



The brown oil (0.07 mmol, 28 mg, 22 % yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 6' (125 mg, 0.3 mmol).

R*f* = 0.30 (Cyclohexane:Ethyl Acetate, 5:5)

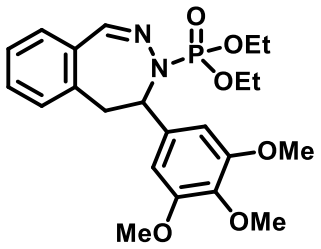
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.32 – 7.27 (m, 1H), 7.23 – 7.16 (m, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 6.27 (t, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 2.3 Hz, 2H), 5.31 – 5.23 (m, 1H), 4.33 – 4.19 (m, 2H), 4.11 – 4.02 (m, 1H), 3.98 – 3.88 (m, 1H), 3.65 (s, 6H), 2.95 (dd, *J* = 12.6, 5.2 Hz, 1H), 2.86 (dd, *J* = 12.5, 9.6 Hz, 1H), 1.41 (td, *J* = 7.0, 0.8 Hz, 3H), 1.26 (td, *J* = 7.1, 0.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4 (2C), 142.9 (d, J_{C-P} = 12.2 Hz, CN), 138.5, 131.6 (d, J_{C-P} = 6.4 Hz, 1C), 130.5, 127.9, 126.9, 125.0, 123.6, 107.7 (2C), 99.3, 63.9 (d, J_{C-P} = 6.3 Hz, 1C), 63.2 (d, J_{C-P} = 5.4 Hz, 1C), 55.5 (d, J_{C-P} = 8.6 Hz, 1C), 55.3 (2C), 41.6, 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.75.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{28}N_2O_5P$ 419.1730; Found 419.1727.

Diethyl(4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (7a):



The brown oil (0.021 mmol, 10 mg, 7 % yield) was obtained following the general procedure B after 27 h starting from the phosphonohydrazone 7' (135mg, 0.3 mmol).

R*f* = 0.35 (Cyclohexane:Ethyl Acetate, 1:9)

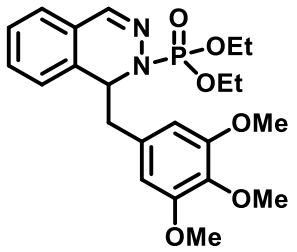
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.25 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 – 6.99 (m, 1H), 6.24 (s, 2H), 6.12 (t, J = 6.0 Hz, 1H), 4.28 – 4.07 (m, 4H), 3.70 (s, 3H), 3.66 (s, 6H), 3.57 (ddd, J = 15.4, 6.0, 3.3 Hz, 1H), 3.44 (dd, J = 15.6, 1.6 Hz, 1H), 1.39 (td, J = 7.1, 1.0 Hz, 3H), 1.33 (td, J = 7.1, 1.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (3C), 140.8 (d, J_{C-P} = 16.6 Hz, CN), 138.2, 136.4, 135.5, 132.5, 131.5, 130.1, 129.3, 126.6, 103.8 (2C), 64.1 (d, J_{C-P} = 6.2 Hz, 1C), 63.4 (d, J_{C-P} = 6.0 Hz, 1C), 62.1 (d, J_{C-P} = 10.4 Hz, 1C), 60.8, 55.9, 41.9 (d, J_{C-P} = 5.6 Hz, 1C), 16.3 (d, J_{C-P} = 7.5 Hz, 1C), 16.1 (d, J_{C-P} = 7.5 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.83.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{22}H_{30}N_2O_6P$ 449.1836; Found 449.1833.

Diethyl(1-(3,4,5-trimethoxybenzyl)phthalazin-2(1H)-yl)phosphonate (7b):



The brown oil (0.045 mmol, 20 mg, 15 % yield) was obtained following the general procedure B after 27 h starting from the phosphonohydrazone 7' (135 mg, 0.3 mmol).

R*f* = 0.45 (Cyclohexane:Ethyl Acetate, 1:9)

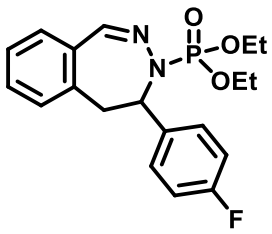
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.16 (m, 2H), 6.49 (d, *J* = 7.4 Hz, 1H), 6.03 (s, 2H), 5.26 (td, *J* = 6.0, 5.4, 2.4 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.09 – 4.03 (m, 1H), 3.97 – 3.88 (m, 1H), 3.79 (s, 3H), 3.67 (s, 6H), 2.96 – 2.81 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (2C), 142.7 (d, J_{C-P} = 12.6 Hz, CN), 136.7, 131.9, 131.5 (d, J_{C-P} = 6.5 Hz, 1C), 130.5, 127.9, 127.1, 125.0, 123.7, 107.0 (2C), 64.0 (d, J_{C-P} = 6.4 Hz, 1C), 63.2 (d, J_{C-P} = 5.8 Hz, 1C), 60.9, 56.0, 55.6 (d, J_{C-P} = 8.7 Hz, 1C), 41.7, 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 15.9 (d, J_{C-P} = 7.1 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.68.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{22}H_{29}N_2NaO_6P$ 471.1655; Found 471.1656.

Diethyl(4-(4-fluorophenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (8a):



The brown oil (0.12 mmol, 45 mg, 40 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 8' (113 mg, 0.3 mmol).

R*f* = 0.43 (Cyclohexane:Ethyl Acetate, 4:6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 7.01 – 6.92 (m, 3H), 6.81 – 6.72 (m, 2H), 6.17 (t, *J* = 6.7 Hz, 1H), 4.28 – 4.06 (m, 4H), 3.58 (ddd, *J* = 15.7, 6.2, 3.1 Hz, 1H), 3.48 – 3.40 (m, 1H), 1.7 Hz, 1H), 1.41-1.31 (m, 6H, included 1.38 (td, *J* = 7.0, 0.9 Hz, 3H) + 1.34 (td, *J* = 7.0, 1.0 Hz, 3H)).

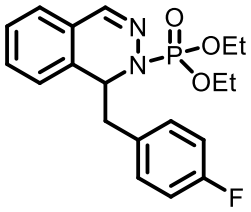
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J_{C-F} = 244.8 Hz, 1C), 140.9 (d, J_{C-P} = 16.7 Hz, CN), 138.0, 135.5 (d, J_{C-F} = 3.2 Hz, 1C), 132.3, 131.6, 130.0, 129.3, 127.7 (d, J_{C-F} = 8.0 Hz, 2C), 126.6, 114.9 (d, J_{C-F} = 21.4 Hz, 2C), 64.1 (d, *J* = 6.1 Hz, 1C), 63.5 (d, *J* = 5.8 Hz, 1C), 61.5 (d, *J* = 10.5 Hz, 1C), 41.9 (d, J_{C-P} = 5.3 Hz, 1C), 16.2 (d, J_{C-P} = 7.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.3 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.65.

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.53.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{23}FN_2O_3P$ 377.1425; Found 377.1423.

Diethyl (1-(4-fluorobenzyl)phthalazin-2(1H)-yl)phosphonate (8b):



The brown oil (0.015 mmol, 6 mg, 5 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 8' (113 mg, 0.3 mmol).

R*f* = 0.59 (Cyclohexane:Ethyl Acetate, 4:6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.35 – 7.28 (m, 1H, overlap with $CDCl_3$), 7.22 – 7.12 (m, 2H), 6.89 – 6.77 (m, 4H), 6.44 (d, *J* = 8.1 Hz, 1H), 5.28 – 5.20 (m, 1H), 4.35-4.15 (m, 2H), 4.11 – 3.99 (m, 1H), 3.99 – 3.87 (m, 1H), 3.01 – 2.85 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H).

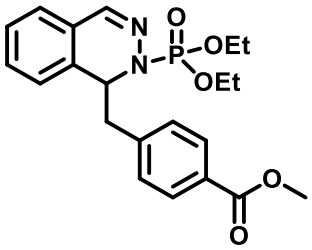
^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F} = 244.6 Hz, 1C), 142.7 (d, J_{C-P} = 12.7 Hz, CN), 132.1 (d, J_{C-F} = 1.1 Hz, 1C), 131.4 (t, J_{C-F} = 7.9 Hz, 2C), 131.3, 130.6, 128.1, 126.7 (d, J_{C-F} = 1.3 Hz, 1C), 125.1, 123.7 (d, J_{C-F} = 2.8 Hz, 1C), 114.9 (d, J_{C-F} = 21.2 Hz, 2C), 64.0 (d, J_{C-P} = 6.5 Hz, 1C), 63.2 (d, J_{C-P} = 5.7 Hz, 1C), 55.7 (d, J_{C-P} = 8.6 Hz, 1C), 40.9, 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 16.0 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.62.

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.39.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{23}FN_2O_3P$ 377.1425; Found 377.1426.

Methyl4-((2-(diethoxyphosphoryl)-1,2-dihydrophthalazin-1-yl)methyl) benzoate (9b):



The brown oil (0.072 mmol, 30 mg, 24 % yield) was obtained following the general procedure B after 15 h starting from the phosphonohydrazone 9' (125 mg, 0.3 mmol).

R*f* = 0.49 (Cyclohexane:Ethyl Acetate, 4:6)

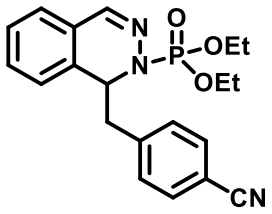
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 2H), 7.64 (s, 1H), 7.32 – 7.25 (m, 1H, overlapped with $CDCl_3$), 7.22 – 7.12 (m, 2H), 6.96 – 6.89 (m, 2H), 6,39 (dd, *J* = 7.5, 0.5 Hz, 1H), 5.30 (ddd, *J* = 8.2, 5.5, 2.4 Hz, 1H), 4.36 – 4.17 (m, 2H), 4.12 – 3.99 (m, 1H), 3.98 – 3.89 (m, 1H), 3.88 (s, 3H), 3.08 – 2.94 (m, 2H), 1.41 (td, *J* = 7.1, 1.0 Hz, 3H), 1.24 (td, *J* = 7.1, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 142.7 (d, J_{C-P} = 12.6 Hz, CN), 141.9, 131.1 (d, J_{C-P} = 6.6 Hz, 1C), 130.7, 130.1 (2C), 129.3 (2C), 128.4, 128.2, 126.6, 125.2, 123.6 (d, J_{C-P} = 1.7 Hz, 1C), 64.1 (d, J_{C-P} = 6.5 Hz, 1C), 63.2 (d, J_{C-P} = 5.8 Hz, 1C), 55.5 (d, J_{C-P} = 8.8 Hz, 1C), 52.0, 41.7, 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.49.

HR-MS (ESI) *m/z*: [M + K]+ Calcd for $C_{21}H_{25}KN_2O_5P$ 455.1133; Found 455.1131.

Diethyl (1-(4-cyanobenzyl)phthalazin-2(1H)-yl)phosphonate (10b):



The brown oil (0.13 mmol, 50 mg, 44 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 10' (114 mg, 0.3 mmol).

R*f* = 0.44 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.46 – 7.41 (m, 2H), 7.36-7.29 (m, 1H), 7.26 – 7.18 (m, 2H, overlapped with $CDCl_3$), 7.01 – 6.95 (m, 2H), 6.50 – 6.45 (m,

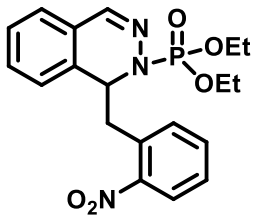
1H), 5.33 (td, *J* = 6.9, 2.5 Hz, 1H), 4.33 – 4.19 (m, 2H), 4.12 – 3.98 (m, 1H), 3.98 – 3.84 (m, 1H), 3.01 (d, *J* = 6.9 Hz, 2H), 1.42 (td, *J* = 7.1, 1.0 Hz, 3H), 1.24 (td, *J* = 7.1, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6 (d, J_{C-P} = 12.5 Hz, CN), 142.1, 131.8 (2C), 130.9, 130.9 (2C), 130.8, 128.4, 126.4 (d, J_{C-P} = 1.2 Hz, 1C), 125.3, 123.6 (d, J_{C-P} = 1.7 Hz, 1C), 118.9, 110.5, 64.2 (d, J_{C-P} = 6.6 Hz, 1C), 63.3 (d, J_{C-P} = 5.8 Hz, 1C), 55.3 (d, J_{C-P} = 9.0 Hz, 1C), 42.1, 16.3 (d, J_{C-P} = 7.0 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.33.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{20}H_{22}N_3NaO_3P$ 406.1291; Found 406.1291.

Diethyl (1-(2-nitrobenzyl)phthalazin-2(1H)-yl)phosphonate (11b):



The brown oil (0.075 mmol, 30 mg, 25 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 11' (121 mg, 0.3 mmol).

R*f* = 0.51 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 12.6, 7.3 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.62 (d, *J* = 7.1 Hz, 1H), 5.46 (td, *J* = 7.5, 3.2 Hz, 1H), 4.21 – 4.07 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.80 (m, 1H), 3.46 (dd, *J* = 13.0, 7.8 Hz, 1H), 3.17 (dd, *J* = 13.1, 7.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

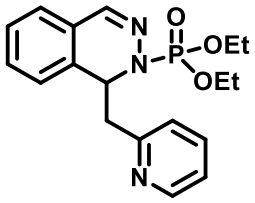
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 143.6 (d, J_{C-P} = 12.3 Hz, CN), 134.0, 132.7, 131.8, 131.2, 131.1 (d, J_{C-P} = 5.9 Hz, 1C), 128.4, 127.8, 125.9 (d, J_{C-P} = 1.3 Hz, 1C), 125.3, 124.7, 123.6 (d, J_{C-P} = 1.8 Hz, 1C), 64.1 (d, J_{C-P} = 6.5 Hz, 1C), 63.1 (d, J_{C-P} =

5.7 Hz, 1C), 54.8 (d, J_{C-P} = 9.0 Hz, 1C), 37.2, 16.2 (d, J_{C-P} = 7.0 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.14.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for C19H22N3NaO5P 426.1189; Found 426.1194.

Diethyl (1-(pyridin-2-ylmethyl)phthalazin-2(1H)-yl)phosphonate (12b):



The brown oil (0.14 mmol, 50 mg, 46 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 12' (108 mg, 0.3 mmol).

R*f* = 0.69 (Methanol:Ethyl Acetate, 1:9)

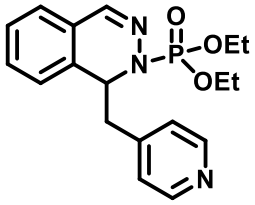
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.1 Hz, 1H), 7.76 (s, 1H), 7.49 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.07 (m, 3H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 1H), 5.55 (ddd, *J* = 8.7, 5.8, 2.7 Hz, 1H), 4.30 – 4.16 (m, 2H), 4.10 – 3.97 (m, 1H), 3.97 – 3.83 (m, 1H), 3.21 (dd, *J* = 12.7, 5.5 Hz, 1H), 3.11 (dd, *J* = 12.7, 9.2 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 149.2, 143.3 (d, J_{C-P} = 12.4 Hz, CN), 136.0, 131.8 (d, J_{C-P} = 6.3 Hz, 1C), 130.7, 128.0, 126.1 (d, J_{C-P} = 1.1 Hz, 1C), 125.2, 124.5, 123.6 (d, J_{C-P} = 1.7 Hz, 1C), 121.5, 63.9 (d, J_{C-P} = 6.3 Hz, 1C), 63.2 (d, J_{C-P} = 5.7 Hz, 1C), 54.6 (d, J_{C-P} = 8.8 Hz, 1C), 43.3, 16.2 (d, J_{C-P} = 7.1 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.58.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{18}H_{23}N_3O_3P$ 360.1472; Found 360.1477.

Diethyl (1-(pyridin-4-ylmethyl)phthalazin-2(1H)-yl)phosphonate (13b):



The brown oil (0.14 mmol, 49 mg, 45 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 13' (108 mg, 0.3 mmol).

R*f* = 0.36 (Methanol:Ethyl Acetate, 1:9)

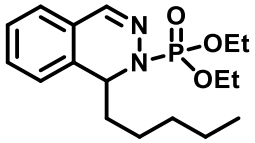
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.29 (m, 2H), 7.63 (s, 1H), 7.33 (td, *J* = 7.5, 1.2 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.92 – 6.78 (m, 2H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.36 (td, *J* = 7.0, 2.2 Hz, 1H), 4.35 – 4.20 (m, 2H), 4.12 – 4.02 (m, 1H), 3.98 – 3.85 (m, 1H), 2.97 (d, *J* = 7.0 Hz, 2H), 1.42 (td, *J* = 7.1, 1.0 Hz, 3H), 1.25 (td, *J* = 7.1, 1.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (2C), 145.6, 142.8 (d, J_{C-P} = 12.5 Hz, CN), 131.0, 130.8 (d, J_{C-P} = 6.5 Hz, 1C), 128.4, 126.5 (d, J_{C-P} = 1.1 Hz, 1C), 125.4 (2C), 125.3, 123.6 (d, J_{C-P} = 1.7 Hz, 1C), 64.2 (d, J_{C-P} = 6.5 Hz, 1C), 63.3 (d, J_{C-P} = 5.8 Hz, 1C), 55.0 (d, J_{C-P} = 8.9 Hz, 1C), 41.3, 16.3 (d, J_{C-P} = 7.0 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.34.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{18}H_{23}N_3O_3P$ 360.1472; Found 360.1474.

Diethyl (1-pentylphthalazin-2(1H)-yl)phosphonate (14b):



The brown oil (0.09 mmol, 30 mg, 30 % yield) was obtained following the general procedure B after 19 h starting from the phosphonohydrazone 14' (102 mg, 0.3 mmol).

R*f* = 0.54 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.38 – 7.34 (m, 1H), 7.30 (dd, *J* = 5.7, 3.2 Hz, 2H), 7.21 – 7.15 (m, 1H), 4.88 – 4.79 (m, 1H), 4.29 – 4.17 (m, 2H), 4.17 – 4.11 (m, 1H), 4.11 – 4.02 (m, 1H), 3.24 – 3.06 (m, 2H), 1.36 (dt, *J* = 14.8, 7.1 Hz, 6H), 1.30 – 1.21 (m, 3H), 1.21 – 1.10 (m, 3H), 0.76 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3 (d, *J* = 17.4 Hz), 137.8, 132.9, 131.8, 130.2, 129.3, 126.6, 63.8 (d, *J* = 6.2 Hz), 63.1 (d, *J* = 5.8 Hz), 57.2 (d, *J* = 9.3 Hz), 41.0 (d, *J* = 5.6 Hz), 30.5, 27.9, 22.4, 16.2 (d, *J* = 7.2 Hz), 16.1 (d, *J* = 7.4 Hz), 13.9.

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.82.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{17}H_{27}N_2NaO_3P$ 361.1652; Found 361.1652.

Diethyl (1-heptylphthalazin-2(1H)-yl)phosphonate (15b):

The brown oil (0.14 mmol, 53 mg, 48 % yield) was obtained following the general procedure B after 15 h starting from the phosphonohydrazone 15' (110 mg, 0.3 mmol).

R*f* = 0.57 (Cyclohexane:EtOAc, 4:6)

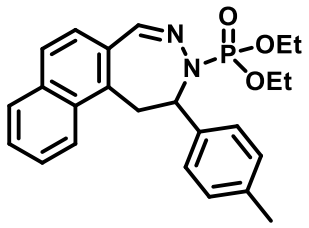
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.34 – 7.30 (m, 1H), 7.33 – 7.21 (m, 2H), 7.18 – 7.11 (m, 1H), 4.87 – 4.76 (m, 1H), 4.29 – 3.97 (m, 4H), 3.20 – 3.04 (m, 1H), 3.12 – 3.03 (m, 1H), 1.38 – 1.32 (m, 3H), 1.33 (dtd, *J* = 10.7, 7.1, 1.0 Hz, 3H), 1.27 – 1.18 (m, 3H), 1.18 – 1.07 (m, 7H), 0.77 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2 (d, $J_{C\text{-}P}$ = 17.3 Hz, CN), 137.8, 132.9, 131.8, 130.2, 129.3, 126.6, 63.8 (d, $J_{C\text{-}P}$ = 6.3 Hz, 1C), 63.1 (d, $J_{C\text{-}P}$ = 5.8 Hz, 1C), 57.2 (d, $J_{C\text{-}P}$ = 9.3 Hz, 1C), 41.0 (d, $J_{C\text{-}P}$ = 5.6 Hz, 1C), 31.6, 30.8, 28.9, 25.6, 22.4, 16.2 (d, $J_{C\text{-}P}$ = 7.8 Hz, 1C), 16.1 (d, $J_{C\text{-}P}$ = 7.9 Hz, 1C), 14.0.

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.73.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{19}H_{32}N_2O_3P$ 367.2145; Found 367.2147.

Diethyl(2-(*p*-tolyl)-1,2-dihydro-3H-naphtho[2,1-d][1,2]diazepin-3-yl) phosphonate (17a):



The brown oil (0.15 mmol, 60 mg, 49 % yield) was obtained following the general procedure B after 7 h starting from the phosphonohydrazone 17' (123 mg, 0.3 mmol).

R*f* = 0.37 (Cyclohexane:Ethyl Acetate, 5:5)

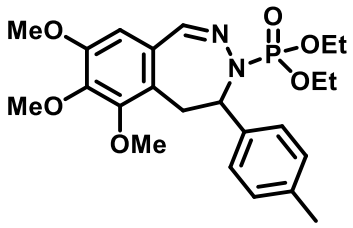
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.59 (t, *J* = 4.2 Hz, 2H), 7.53 (ddd, *J* = 6.8, 8.5, 1.5 Hz, 1H), 7.45 (ddd, *J* = 6.9, 7.9, 1.1 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H, overlapped with $CDCl_3$), 6.87 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.32 (t, *J* = 6.2 Hz, 1H), 4.64 (ddd, *J* = 16.2, 6.6, 2.8 Hz, 1H), 4.33 – 4.08 (m, 4H), 3.37 (d, *J* = 16.1 Hz, 1H), 2.04 (s, 3H), 1.38 (tdd, *J* = 7.1, 1.7, 1.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6 (d, J_{C-P} = 16.8 Hz, CN), 136.3, 135.8, 135.3, 133.1, 131.9, 129.9, 128.6, 128.6 (2C), 128.4, 127.0, 126.8, 126.5, 125.6 (2C), 123.9, 64.1 (d, J_{C-P} = 6.1 Hz, 1C), 63.4 (d, J_{C-P} = 5.8 Hz, 1C), 62.1 (d, J_{C-P} = 10.0 Hz, 1C), 35.1 (d, J_{C-P} = 5.1 Hz, 1C), 20.8, 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.3 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.50.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{28}N_2O_3P$ 423.1832; Found 423.1838.

Diethyl(6,7,8-trimethoxy-4-(*p*-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (18a):



The brown oil (0.18 mmol, 83 mg, 60 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 18' (139 mg, 0.3 mmol).

R*f* = 0.35 (Cyclohexane:Ethyl Acetate, 5:5)

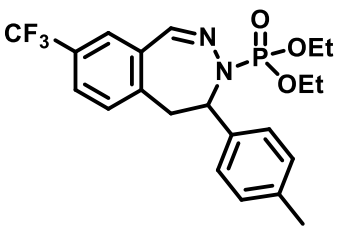
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.89 (s, 4H), 6.48 (s, 1H), 6.08 (t, *J* = 6.1 Hz, 1H), 4.26 – 4.04 (m, 5H), 3.79 (s, 3H), 3.77 (s, 3H), 3.67 (s, 3H), 2.91 (dd, *J* = 15.8, 1.9 Hz, 1H), 2.17 (s, 3H), 1.35 (dtd, *J* = 8.7, 7.1, 1.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.3, 143.0, 140.3 (d, J_{C-P} = 18.3 Hz, CN), 137.2, 135.9, 128.7 (2C), 128.4, 125.8 (2C), 125.0, 110.1, 63.8 (d, J_{C-P} = 5.8 Hz, 1C), 63.3 (d, J_{C-P} = 5.6 Hz, 1C), 62.2 (d, J_{C-P} = 10.0 Hz, 1C), 60.9, 60.7, 55.9, 32.7 (d, J_{C-P} = 5.1 Hz, 1C), 20.9, 16.2 (d, J_{C-P} = 7.6 Hz, 1C), 16.1 (d, J_{C-P} = 7.8 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.90.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{23}H_{32}N_2O_6P$ 463.1993; Found 463.1995.

Diethyl (4-(*p*-tolyl)-8-(trifluoromethyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (19a):



The brown oil (0.14 mmol, 60 mg, 47 % yield) was obtained following the general procedure B after 17 h starting from the phosphonohydrazone 19' (128 mg, 0.3 mmol).

R*f* = 0.38 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.43 (s, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 6.20 (t, *J* = 5.8 Hz, 1H), 4.28 – 4.04 (m, 4H), 3.67 (ddd, *J* = 15.7, 6.3, 3.0 Hz, 1H), 3.40 (d, *J* = 15.7 Hz, 1H), 2.15 (s, 3H), 1.40 – 1.30 (m, 6H, included 1,37 (td, *J* = 7.1, 1.0 Hz, 1H), 1.34 (td, *J* = 7.1, 1.0 Hz, 1H)).

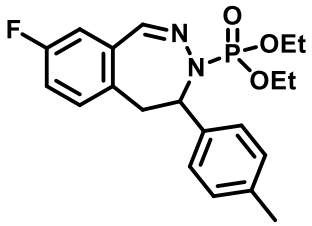
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 138.5 (d, J_{C-P} = 17.0 Hz, CN), 136.2, 136.2, 133.0, 130.7, 129.0 (q, J_{C-F} = 32.8 Hz, 1C), 128.9 (2C), 127.9 (q, J_{C-F} = 3.7 Hz, 1C), 125.6 (2C), 125.3 (q, J_{C-F} = 3.4 Hz, 1C), 123.8 (q, J_{C-F} = 272.3 Hz, CF_3), 64.1 (d, J_{C-P} = 6.0 Hz, 1C), 63.6 (d, J_{C-P} = 5.8 Hz, 1C), 61.9 (d, J_{C-P} = 10.5 Hz, 1C), 41.8 (d, J_{C-P} = 5.3 Hz, 1C), 20.9, 16.2 (d, J_{C-P} = 7.2 Hz, 1C), 16.1 (d, J_{C-P} = 7.4 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.29.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.54.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{25}F_3N_2O_3P$ 441.1549; Found 441.1553.

Diethyl(8-fluoro-4-(*p*-tolyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl) phosphonate (20a):



The brown oil PC-195 RM7 (0.1 mmol, 40 mg, 34% yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 20' (117mg, 0.3 mmol).

R*f* = 0.44 (Cyclohexane:Ethyl Acetate, 5:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H), 6.95 – 6.83 (m, 6H), 6.79 (td, *J* = 8.3, 2.6 Hz, 1H), 6.14 (t, *J* = 6.1 Hz, 1H), 4.29 – 4.03 (m, 4H), 3.57 (ddd, *J* = 15.5, 6.3, 3.1 Hz, 1H), 3.36 (d, *J* = 15.3 Hz, 1H), 2.17 (s, 3H), 1.35 (dtd, *J* = 11.4, 7.1, 0.9 Hz, 6H).

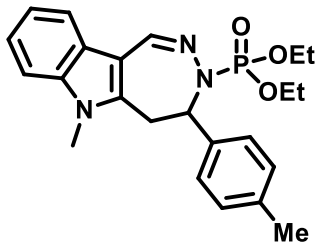
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 244.9 Hz, 1C), 138.7 (dd, $J_{C\text{-}F,C\text{-}P}$ = 17.0, 1.9 Hz, CN), 136.5, 136.0, 134.1 (d, $J_{C\text{-}F}$ = 7.0 Hz, 1C), 134.1 (d, $J_{C\text{-}F}$ = 3.2 Hz, 1C), 131.7 (d, $J_{C\text{-}F}$ = 7.9 Hz, 1C), 128.8 (2C), 125.7 (2C), 117.3 (d, $J_{C\text{-}F}$ = 22.0 Hz, 1C), 116.0 (d, $J_{C\text{-}F}$ = 21.3 Hz, 1C), 64.0 (d, $J_{C\text{-}P}$ = 6.0 Hz, 1C), 63.5 (d, $J_{C\text{-}P}$ = 5.8 Hz, 1C), 62.1 (d, $J_{C\text{-}P}$ = 10.4 Hz, 1C), 41.1 (d, $J_{C\text{-}P}$ = 5.2 Hz, 1C), 20.9, 16.2 (d, $J_{C\text{-}P}$ = 7.1 Hz, 1C), 16.1 (d, $J_{C\text{-}P}$ = 7.3 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.45.

^{19}F NMR (282 MHz, $CDCl_3$) δ -116.89.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{20}H_{25}FN_2O_3P$ 391.1581; Found 391.1583.

Diethyl(6-methyl-4-(*p*-tolyl)-5,6-dihydro-[1,2]diazepino[5,4-b]indol-3(4H)-yl) phosphonate (21a):



The brown oil (0.18 mmol, 76 mg, 59 % yield) was obtained following the general procedure B after 20 h starting from the phosphonohydrazone 21' (128 mg, 0.3 mmol).

R*f* = 0.38 (Cyclohexane:Ethyl Acetate, 2:8)

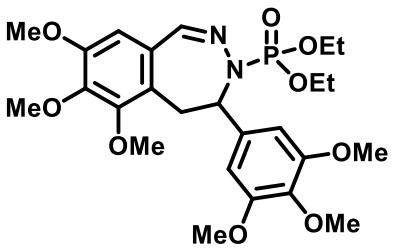
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.30 (m, 1H), 7.37 – 7.26 (m, 1H, overlapped with $CDCl_3$), 7.21 – 7.15 (m, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.15-6.05 (m, 1H), 4.39 – 4.26 (m, 2H), 4.17 – 4.02 (m, 1H), 4.02 – 3.93 (m, 1H), 3.93 – 3.86 (m, 1H), 3.83 (s, 3H), 3.58 (dd, *J* = 17.4, 5.1 Hz, 1H), 2.20 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.8, 136.6 (d, J_{C-P} = 7.5 Hz, CN), 134.3, 128.8 (2C), 127.0 (2C), 126.4, 122.4, 121.1, 117.6, 109.4, 108.8, 64.4 (d, J_{C-P} = 6.8 Hz, 1C), 62.9 (d, J_{C-P} = 5.9 Hz, 1C), 55.5 (d, J_{C-P} = 9.0 Hz, 1C), 33.0 (d, J_{C-P} = 5.8 Hz, 1C), 30.4, 20.9, 16.3 (d, J_{C-P} = 6.9 Hz, 1C), 16.0 (d, J_{C-P} = 7.3 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 4.49.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{23}H_{27}N_3O_3P$ 424.1784; Found 424.1785.

Diethyl(6,7,8-trimethoxy-4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzo[d][1,2]diazepin-3-yl)phosphonate (22a):



The brown oil (0.19 mmol, 101 mg, 63 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 22' (162 mg, 0.3 mmol).

R*f* = 0.40 (Cyclohexane:Ethyl Acetate, 2:8)

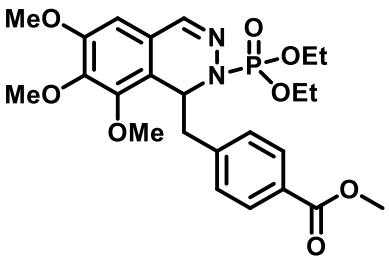
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.47 (s, 1H), 6.29 – 6.28 (m, 2H, included 6.28(s, 1H) + 6.28 (s, 1H)), 6.08 (t, *J* = 6.0 Hz, 1H), 4.28 – 4.07 (m, 5H), 3.79 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.71 – 3.69 (m, 9H, included 3.70 (s, 3H) + 3.70 (s, 6H)), 2.91 (dd, *J* = 15.8, 1.8 Hz, 1H), 1.45-1.30 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7 (2C), 151.6, 151.2, 143.3, 140.3 (d, J_{C-P} = 16.8 Hz, CN), 136.2, 135.6, 128.1, 125.2, 110.3, 103.2 (2C), 64.1 (d, J_{C-P} = 6.2 Hz, 1C), 63.3 (d, J_{C-P} = 5.8 Hz, 1C), 62.2 (d, J_{C-P} = 10.0 Hz, 1C), 61.1, 60.8, 60.8, 56.0, 55.8 (2C), 32.4 (d, J_{C-P} = 5.2 Hz, 1C), 16.3 (d, J_{C-P} = 7.2 Hz, 1C), 16.1 (d, J_{C-P} = 7.3 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.82.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{25}H_{36}N_2O_9P$ 539.2153; Found 539.2153.

Methyl 4-((2-(diethoxyphosphoryl)-6,7,8-trimethoxy-1,2-dihydrophthalazin-1-yl)methyl)benzoate (23b):



The brown oil (0.06 mmol, 32 mg, 21 % yield) was obtained following the general procedure B after 16 h starting from the phosphonohydrazone 23' (152 mg, 0.3 mmol).

R*f* = 0.57 (Cyclohexane:Ethyl Acetate, 5:5)

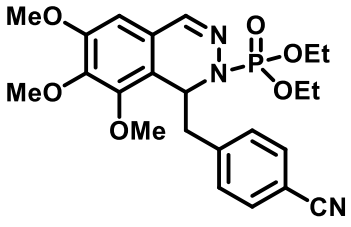
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.40 (s, 1H), 7.01 – 6.96 (m, 2H), 6.44 (s, 1H), 5.63 – 5.56 (m, 1H), 4.27 – 4.14 (m, 2H), 4.12 – 3.97 (m, 1H), 3.96 – 3.89 (m, 1H), 3.87 (s, 6H), 3.75 (s, 3H), 3.62 (s, 3H), 3.03 – 2.89 (m, 2H), 1.40 (td, *J* = 7.1, 1.0 Hz, 3H), 1.25 (td, *J* = 7.1, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 153.5, 148.9, 144.0, 142.5, 142.3 (d, $J_{C\text{-}P}$ = 12.5 Hz, CN), 130.3 (2C), 129.0 (2C), 128.1, 119.9 (d, $J_{C\text{-}P}$ = 1.6 Hz, 1C), 117.3 (d, $J_{C\text{-}P}$ = 6.6 Hz, 1C), 103.6, 64.0 (d, $J_{C\text{-}P}$ = 6.4 Hz, 1C), 63.1 (d, $J_{C\text{-}P}$ = 5.8 Hz, 1C), 60.8, 60.5, 56.1, 52.0, 49.8 (d, $J_{C\text{-}P}$ = 9.5 Hz, 1C), 41.3, 16.3 (d, $J_{C\text{-}P}$ = 7.1 Hz), 15.9 (d, $J_{C\text{-}P}$ = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.69.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{32}N_2O_8P$ 507.1891; Found 507.1897.

Diethyl(1-(4-cyanobenzyl)-6,7,8-trimethoxyphthalazin-2(1H)-yl) phosphonate (24b):



The brown oil (0.22 mmol, 104 mg, 73 % yield) was obtained following the general procedure B after 18 h starting from the phosphonohydrazone 24' (142 mg, 0.3 mmol).

R*f* = 0.29 (Cyclohexane:Ethyl Acetate, 5:5)

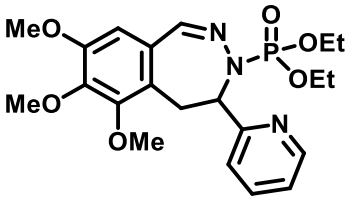
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.44 (s, 1H), 5.65-5.52 (m, 1H), 4.26 – 4.15 (m, 2H), 4.09 – 3.99 (m, 1H), 3.97 – 3.88 (m, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 3.71 (s, 3H), 2.98 (dd, *J* = 13.1, 6.8 Hz, 1H), 2.91 (dd, *J* = 13.2, 5.6 Hz, 1H), 1.40 (td, *J* = 7.1, 1.0 Hz, 3H), 1.24 (td, *J* = 7.1, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 148.7, 144.0, 142.7, 142.2 (d, J_{C-P} = 12.4 Hz, CN), 131.4 (2C), 131.0 (2C), 119.8, 119.1, 116.9 (d, J_{C-P} = 6.7 Hz, 1C), 110.0, 103.7, 64.1 (d, J_{C-P} = 6.5 Hz, 1C), 63.2 (d, J_{C-P} = 5.8 Hz, 1C), 60.8, 60.7, 56.1, 49.8 (d, J_{C-P} = 9.6 Hz, 1C), 41.6, 16.3 (d, J_{C-P} = 7.0 Hz, 1C), 16.0 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.56.

HR-MS (ESI) *m/z*: [M + Na]+ Calcd for $C_{23}H_{28}N_3NaO_6P$ 496.1608; Found 496.1615.

Diethyl(6,7,8-trimethoxy-4-(pyridin-2-yl)-4,5-dihydro-3H-benzo[d][1,2] diazepin-3-yl)phosphonate (25a):



The brown oil (0.06 mmol, 26 mg, 19 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 25' (135 mg, 0.3 mmol).

R*f* = 0.68 (Methanol:Ethyl Acetate, 1:9)

^{1}H NMR (300 MHz, CDCl3) δ 8.34 (d, *J* = 4.8 Hz, 1H), 7.40 (td, *J* = 7.8, 1.8 Hz, 1H), 7.34 (s, 1H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.91 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.41 (s, 1H),

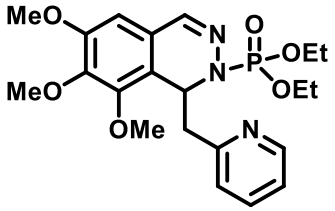
6.17 (t, *J* = 6.2 Hz, 1H), 4.46 (ddd, *J* = 15.7, 6.5, 3.1 Hz, 1H), 4.31 – 4.07 (m, 4H), 3.80 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H), 2.89 (dd, *J* = 15.7, 1.7 Hz, 1H), 1.42 – 1.32 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 151.5, 151.4, 149.0, 143.1, 140.6 (d, J_{C-P} = 16.9 Hz, CN), 136.0, 128.0, 125.6, 121.3, 120.7, 110.1, 64.1 (d, J_{C-P} = 6.0 Hz, 1C), 63.9 (d, J_{C-P} = 9.8 Hz, 1C), 63.4 (d, J_{C-P} = 5.9 Hz, 1C), 60.9, 60.7, 55.9, 32.1 (d, J_{C-P} = 4.8 Hz, 1C), 16.3 (d, J_{C-P} = 7.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.1 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.81.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{29}N_3O_6P$ 450.1789; Found 450.1796.

Diethyl(6,7,8-trimethoxy-1-(pyridin-2-ylmethyl)phthalazin-2(1H)-yl) phosphonate (25b):



The brown oil (0.4 mmol, 60 mg, 45 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 25' (135 mg, 0.3 mmol).

R*f* = 0.51 (Methanol:Ethyl Acetate, 1:9)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 – 8.35 (m, 1H), 7.61 (s, 1H), 7.49 (td, *J* = 7.6, 1.7 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.52 (s, 1H), 5.67 (ddd, *J* = 7.6, 6.1, 3.1 Hz, 1H), 4.23 – 4.12 (m, 2H), 4.08 – 3.98 (m, 1H), 3.97 – 3.88 (m, 1H), 3.86 (s, 3H), 3.72 (s, 3H), 3.61 (s, 3H), 3.12 (dd, *J* = 12.7, 6.1 Hz, 1H), 3.04 (dd, *J* = 12.7, 7.9 Hz, 1H), 1.36 (td, *J* = 7.0, 0.7 Hz, 3H), , 1.26 – 1.20 (m, 3H, overlapped with vacuum grease).

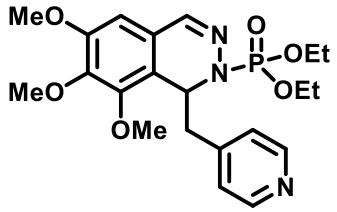
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 153.3, 148.7, 143.9, 143.0 (d, J_{C-P} = 12.3 Hz, CN), 135.7, 124.7, 121.3, 119.8, 117.9, 117.9, 103.8, 63.8 (d, J_{C-P} = 6.0 Hz, 1C),

63.1 (d, J_{C-P} = 5.6 Hz, 1C), 60.7, 60.6, 56.1, 49.3 (d, J_{C-P} = 9.2 Hz, 1C), 43.2, 16.2 (d, J_{C-P} = 7.3 Hz, 1C), 16.0 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.65.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{29}N_3O_6P$ 450.1788; Found 450.1793.

Diethyl(6,7,8-trimethoxy-1-(pyridin-4-ylmethyl)phthalazin-2(1H)-yl) phosphonate (26b):



The brown oil (0.14 mmol, 64 mg, 47% yield) was obtained following the general procedure B after 24 h starting from the phosphonohydrazone 26' (135 mg, 0.3 mmol).

R*f* = 0.5 (Methanol:Ethyl Acetate, 1:9)

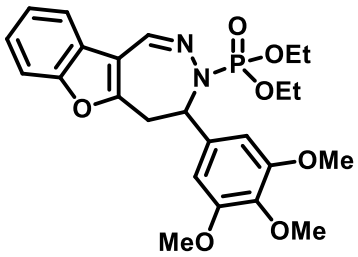
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (bs, 2H), 7.38 (s, 1H), 6.89 (d, *J* = 5.6 Hz, 2H), 6.44 (s, 1H), 5.60 (ddd, *J* = 7.1, 5.6, 2.8 Hz, 1H), 4.27 – 4.14 (m, 2H), 4.08 – 4.00 (m, 1H), 3.97 – 3.88 (m, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 2.94 (dd, *J* = 13.0, 6.9 Hz, 1H), 2.86 (dd, *J* = 12.9, 5.3 Hz, 1H), 1.40 (td, *J* = 7.0, 1.0 Hz, 3H), 1.24 (td, *J* = 6.7, 6.0, 0.9 Hz, 3H, overlapped with vacuum grease).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 148.83 (d, J_{C-P} = 19.1 Hz, CN), 148.67 (d, J_{C-P} = 11.0 Hz, 1C), 147.0, 144.0, 142.3 (d, J_{C-P} = 12.4 Hz, 1C), 126.2, 119.7 (d, J_{C-P} = 1.7 Hz, 1C), 116.4 (d, J_{C-P} = 6.7 Hz, 1C), 103.8, 64.2 (d, J_{C-P} = 6.5 Hz, 1C), 63.2 (d, J_{C-P} = 5.8 Hz, 1C), 60.8, 60.7, 56.1, 49.5 (d, J_{C-P} = 9.6 Hz, 1C), 41.2, 16.3 (d, J_{C-P} = 7.0 Hz, 1C), 15.9 (d, J_{C-P} = 7.0 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.72.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{21}H_{29}N_3O_6P$ 450.1788; Found 450.1787.

Diethyl(4-(3,4,5-trimethoxyphenyl)-4,5-dihydro-3H-benzofuro[3,2-d][1,2]55 diazepin-3-yl)phosphonate (27a):



The brown oil (0.03 mmol, 16 mg, 22 % yield) was obtained following the general procedure B after 22 h starting from the phosphonohydrazone 27' (73 mg, 0.15 mmol).

R*f* = 0.28 (Cyclohexane:Ethyl Acetate, 2:8)

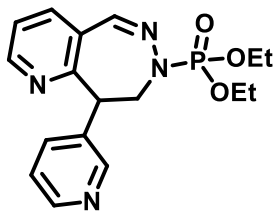
^{1}H NMR (300 MHz, CDCl3) δ 7.98 (d, *J* = 1.2 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.33 (m, 2H), 6.32 (s, 2H), 4.68 – 4.61 (m, 1H), 4.19 – 4.05 (m, 2H), 4.02 – 3.85 (m, 4H), 3.81 (s, 3H), 3.78 (s, 6H), 1.28 (td, *J* = 7.1, 0.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 154.4, 153.4 (2C), 137.5, 126.2 (2C), 125.2, 123.7, 118.5, 112.0 (2C), 111.6, 105.6 (2C), 63.5 (d, J_{C-P} = 5.9 Hz, 1C), 63.5 (d, J_{C-P} = 6.2 Hz, 1C), 61.2 (d, J_{C-P} = 11.7 Hz, 1C), 60.8, 56.2, 48.5 (d, J_{C-P} = 5.1 Hz, 1C), 16.1 (d, J_{C-P} = 3.4 Hz, 1C), 16.1 (d, J_{C-P} = 3.5 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 5.08.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{24}H_{28}N_2O_7P$ 487.1629; Found 487.1628.

Diethyl(9-(pyridin-3-yl)-8,9-dihydro-7H-pyrido[3,2-d][1,2]diazepin-7-yl) phosphonate (28a):



The brown oil (0.06 mmol, 22.5 mg, 50 % yield) was obtained following the general procedure B after 7 h starting from the phosphonohydrazone 28' (54 mg with 83% of mass purity, 0.12 mmol (adjusted to account for inseparable starting material)).

R*f* = 0.25 (Methanol:Ethyl Acetate, 1:9)

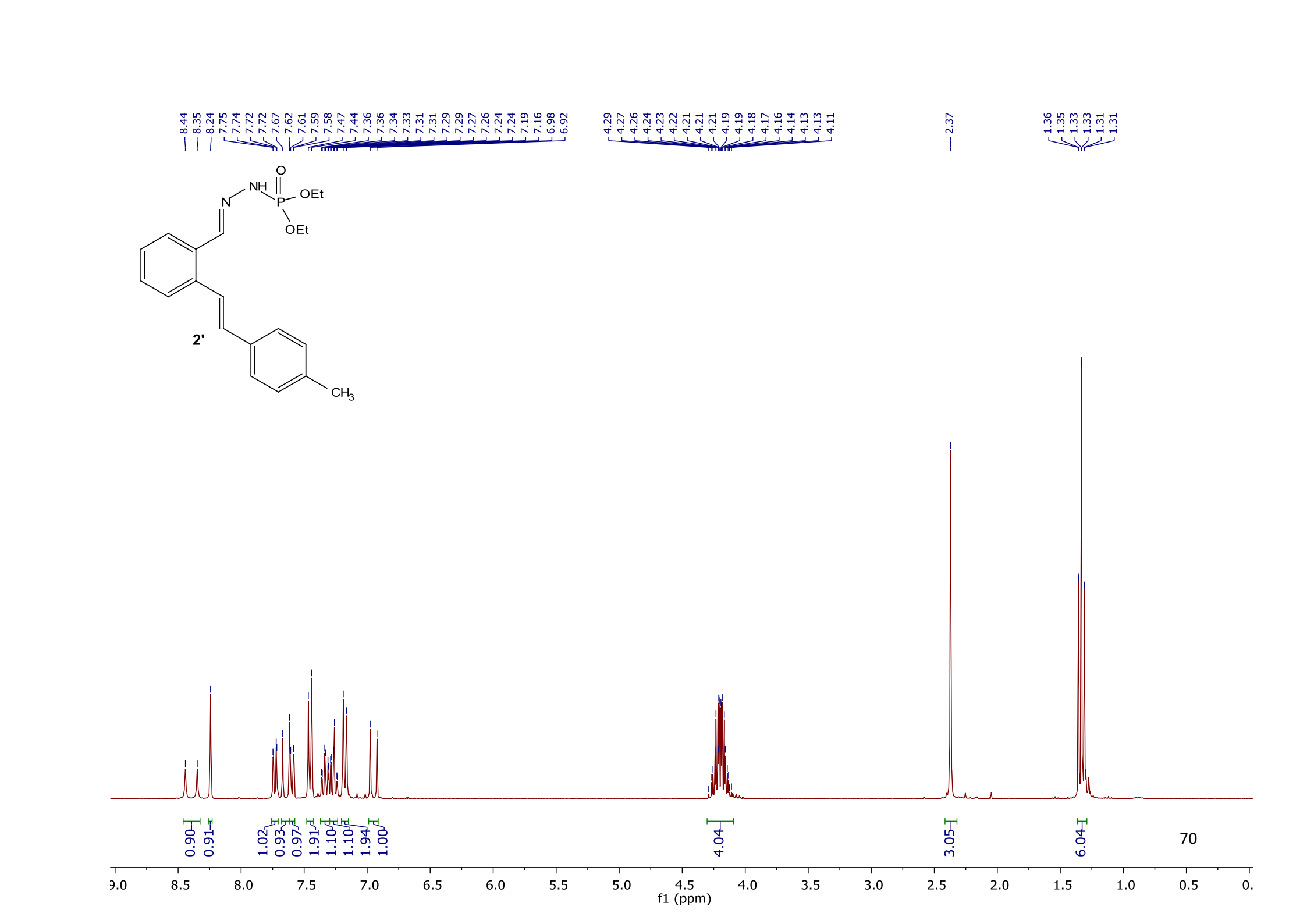
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57-8.45 (m, 2H, included 8.53 (dd, *J* = 4.8, 1.6 Hz, 1H) + 8.51 – 8.48 (m, 1H)), 8.02 (s, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 (dd, *J* = 7.9, 4.7 Hz, 1H), 5.02 (dd, *J* = 5.1, 3.4 Hz, 1H), 4.85 (dt, *J* = 14.1, 6.2 Hz, 1H), 4.20 – 3.93 (m, 2H), 3.68 – 3.56 (m, 2H), 3.55 – 3.40 (m, 1H), 1.30 (td, *J* = 7.1, 0.9 Hz, 3H), 1.10 (td, *J* = 7.1, 1.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 149.4, 146.5, 145.1, 140.9, 139.4, 138.4 (d, J_{C-P} = 17.2 Hz, CN), 138.0, 127.4, 124.5, 123.0, 63.9 (d, J_{C-P} = 6.2 Hz, 1C), 63.6 (d, J_{C-P} = 6.1 Hz, 1C), 54.5 (d, J_{C-P} = 5.2 Hz, 1C), 50.7 (d, J_{C-P} = 9.1 Hz, 1C), 16.1 (d, J_{C-P} = 7.8 Hz, 1C), 16.0 (d, J_{C-P} = 7.5 Hz, 1C).

^{31}P NMR (121 MHz, $CDCl_3$) δ 2.98.

HR-MS (ESI) *m/z*: [M + H]+ Calcd for $C_{17}H_{22}N_4O_3P$ 361.1424; Found 361.1423.

NMR Spectrum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1.33
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1.31
1.31
O
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P
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OEt
2'
CH3
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0.91
1.02
0.93
0.97
1.91
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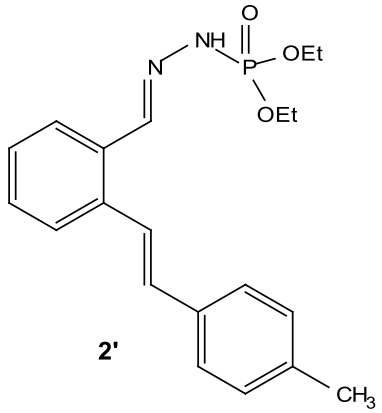
6.04
70
f1 (ppm)



2'

144.20
144.00
137.77
136.70
134.68
131.72
131.62
129.40
129.20
127.67
127.37
126.71
126.60
125.11

63.48
63.42

21.29
16.22
16.16

71

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

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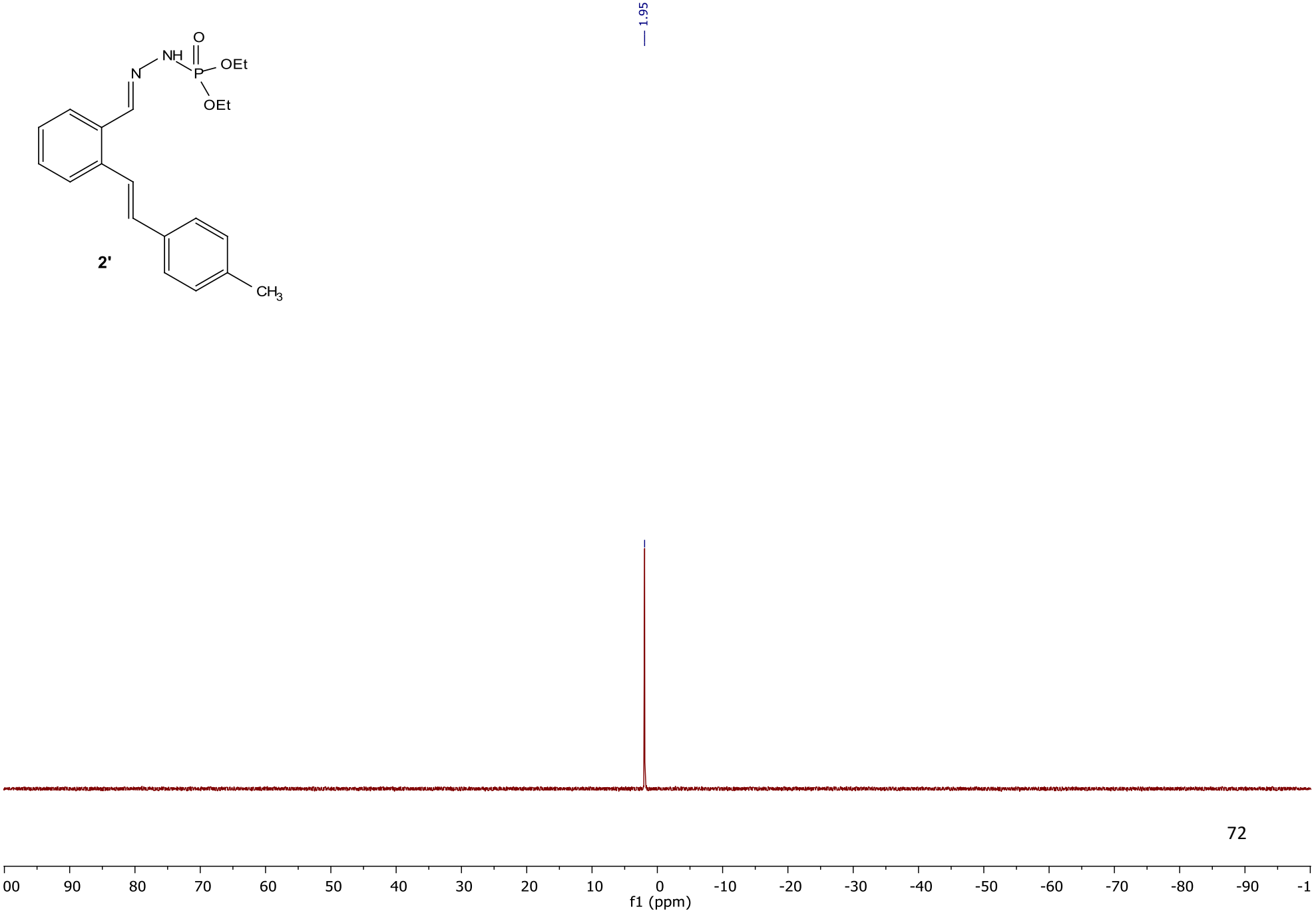
NH
N
P
OEt
OEt
CH3

2'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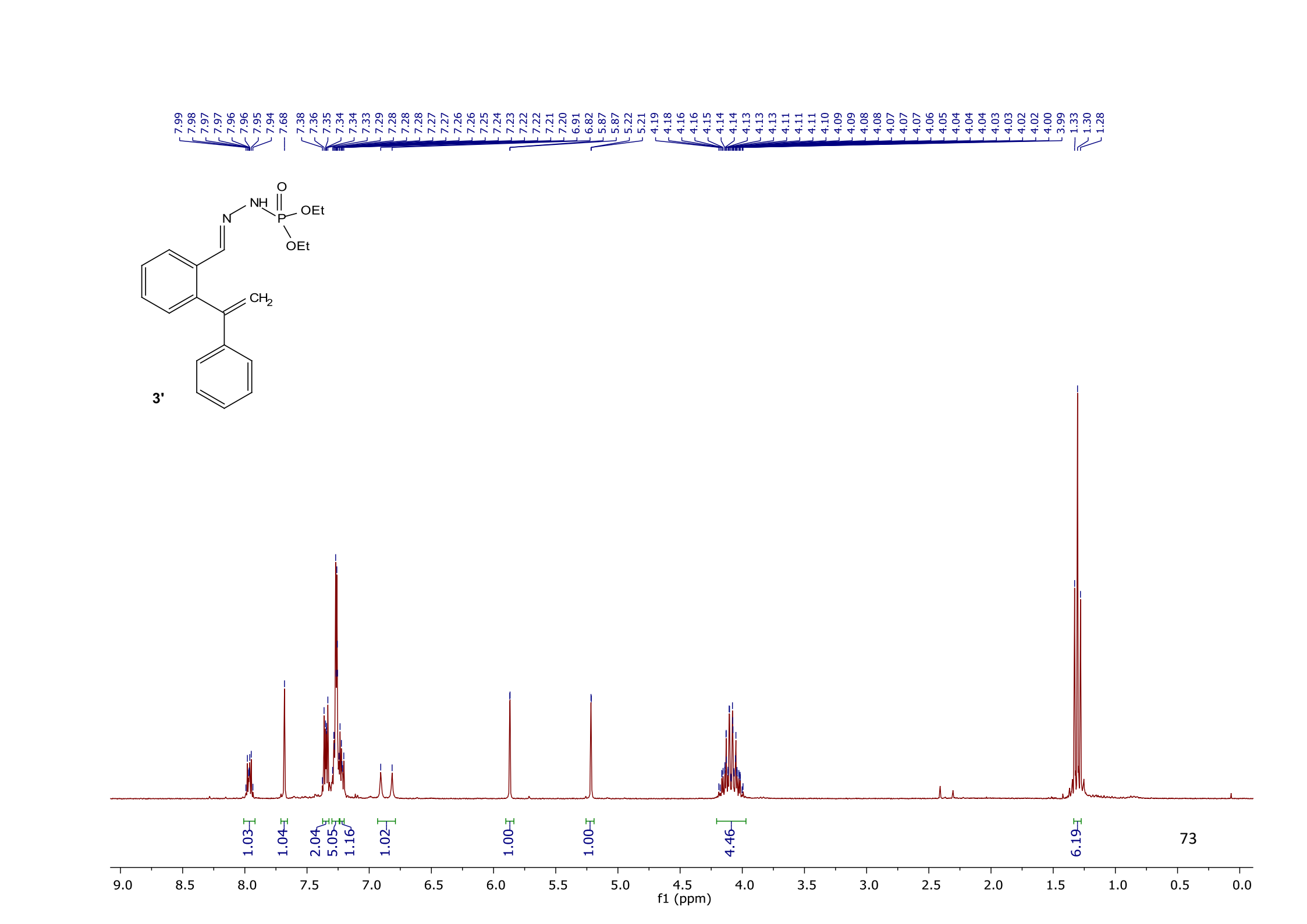
f1 (ppm)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NH
P
OEt
OEt
N
CH2
3'
1.03
1.04
2.04
5.05
1.16
1.02
1.00
1.00
4.46
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73
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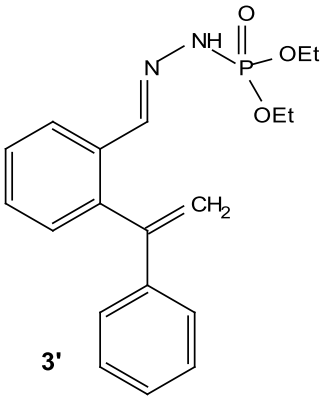
f1 (ppm)



3'

147.1
143.8
143.6
141.2
140.6
132.3
130.3
129.2
128.5
128.0
127.8
126.7
125.7
116.7
63.4
63.3
16.2
16.1

74

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

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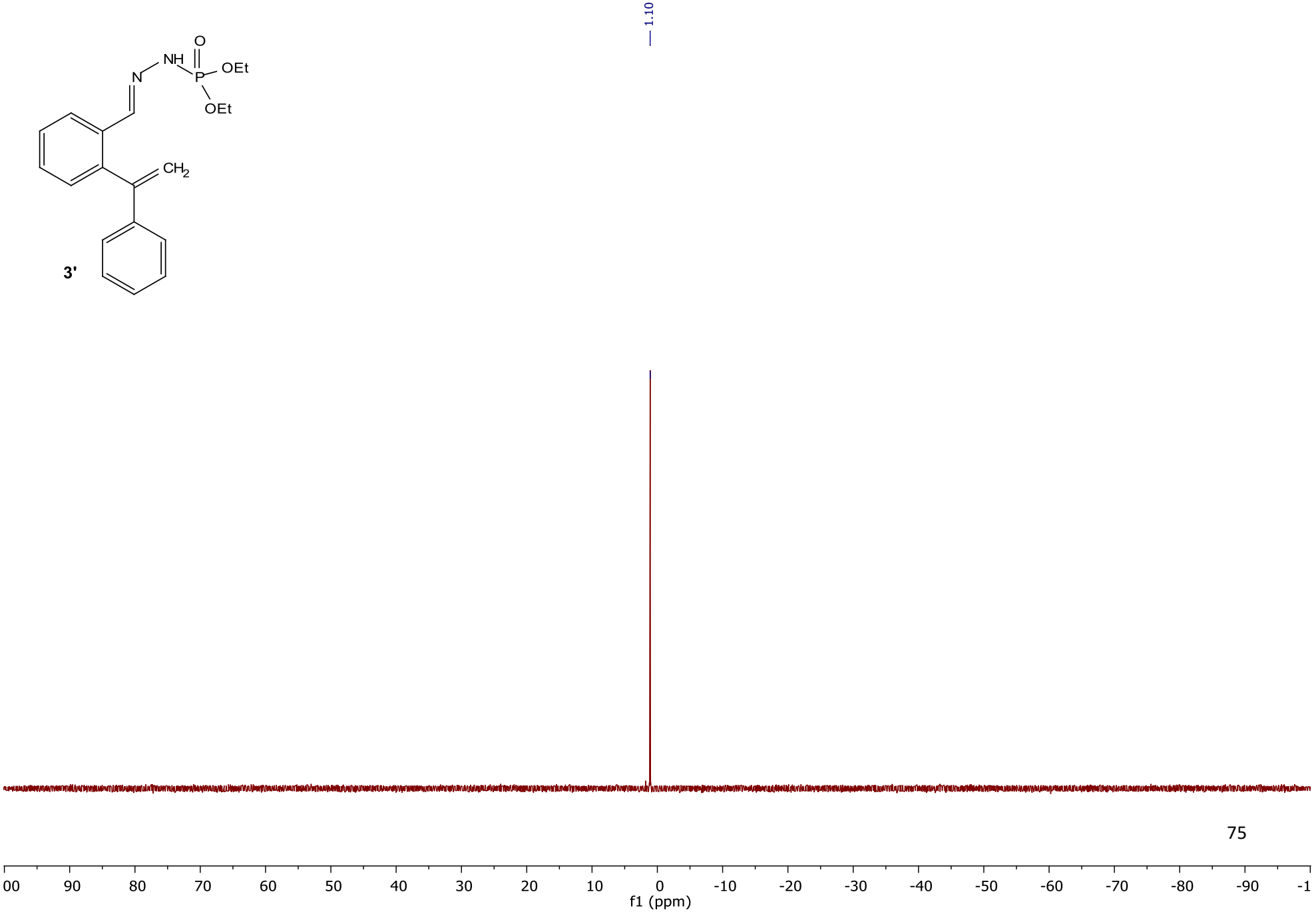
NH
N
P
OEt
OEt
CH2

3'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-70
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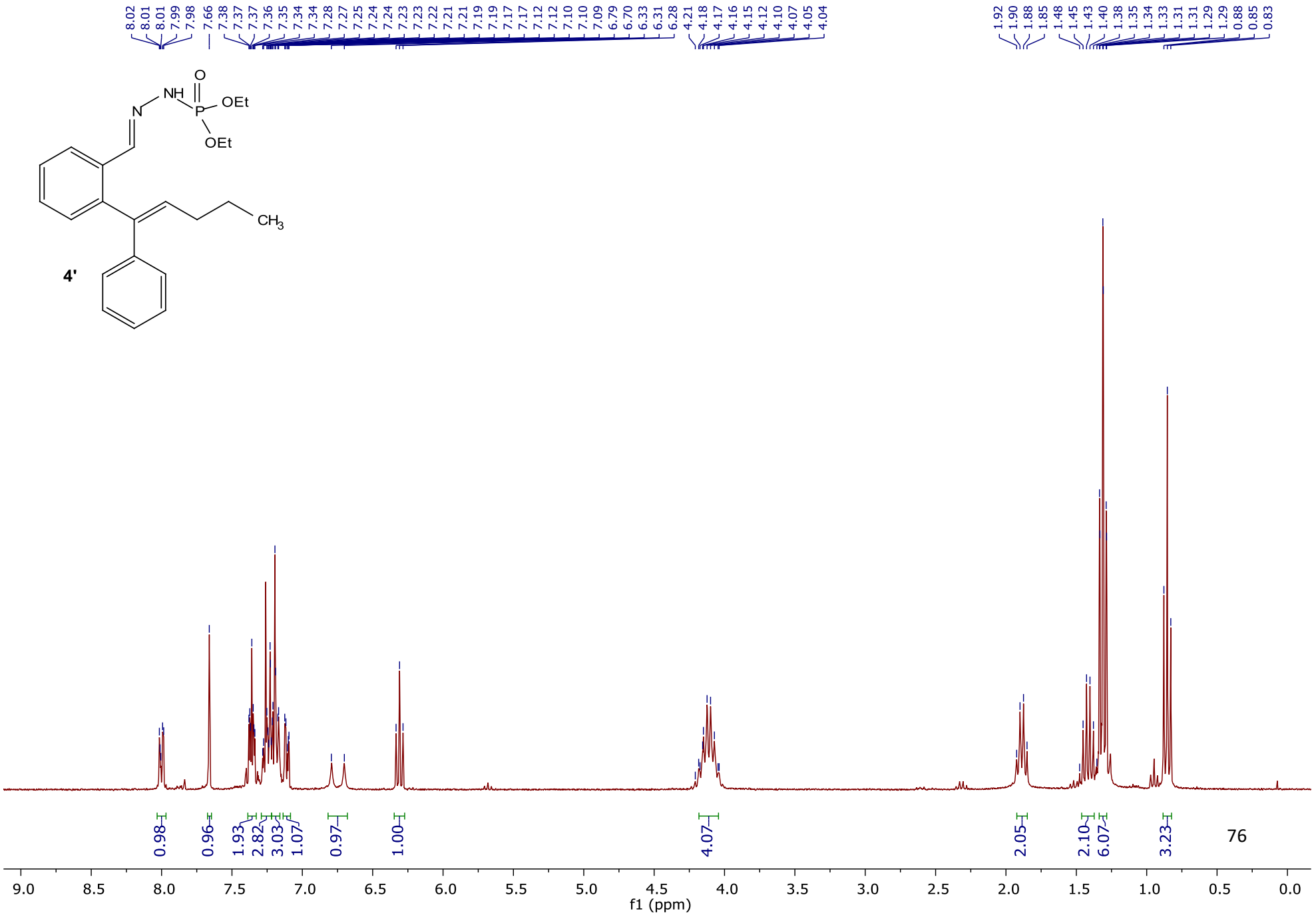
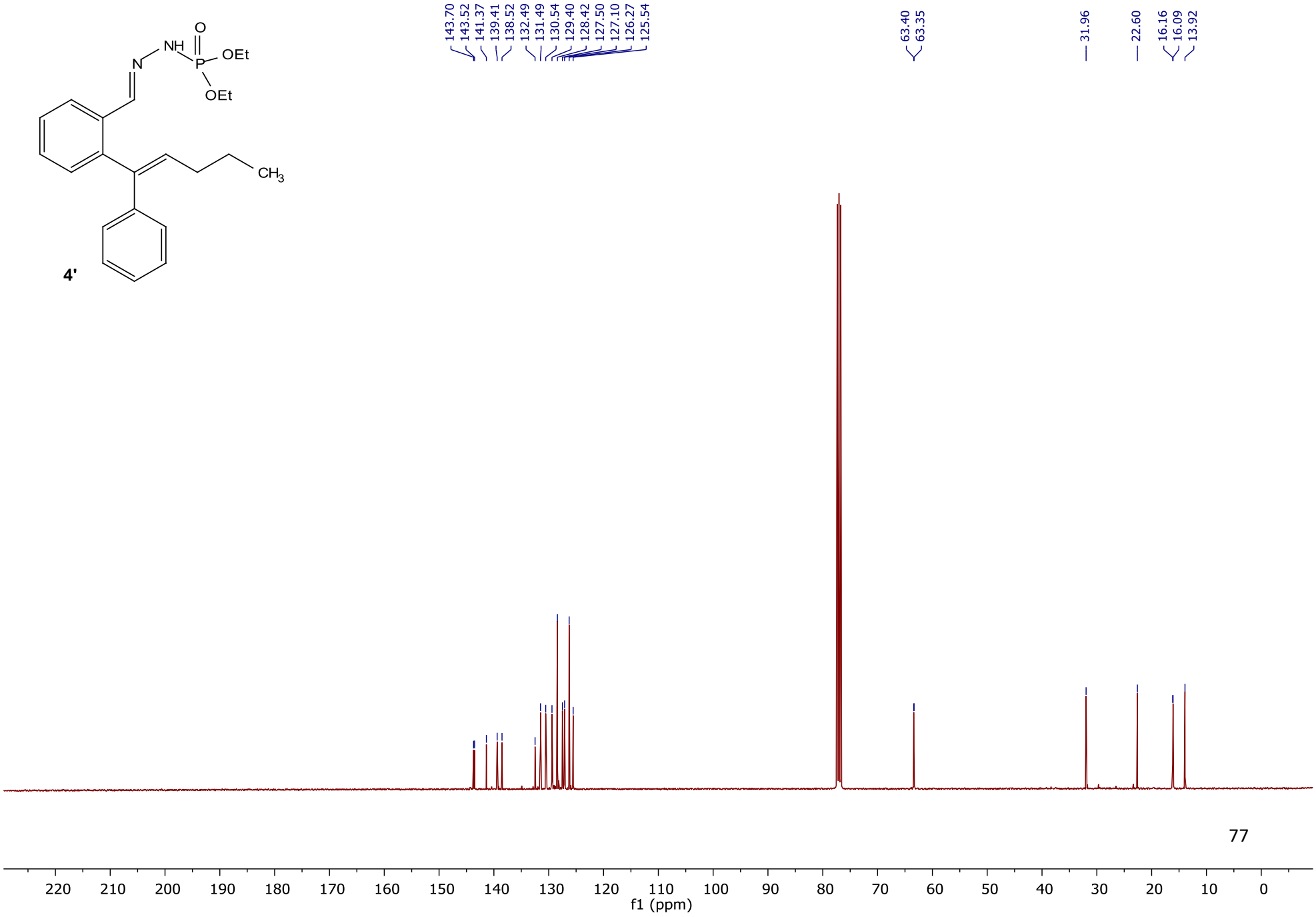
-90
-1
f1 (ppm)


8.02 8.01 8.01 7.99 7.98 7.66 7.38 7.37 7.37 7.36 7.35 7.34 7.34 7.28 7.27 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.19 7.19 7.17 7.17 7.12 7.12 7.10 7.10 7.09 6.79 6.70 6.33 6.31 6.28 4.21 4.18 4.17 4.16 4.15 4.12 4.10 4.07 4.05 4.04
1.92 1.90 1.88 1.85 1.48 1.45 1.43 1.40 1.38 1.35 1.34 1.33 1.31 1.31 1.29 1.29 0.88 0.85 0.83
O
NH
P
OEt
OEt
N
CH3
4'
0.98 0.96 1.93 2.82 3.03 1.07 0.97 1.00 4.07 2.05 2.10 6.07 3.23
76
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

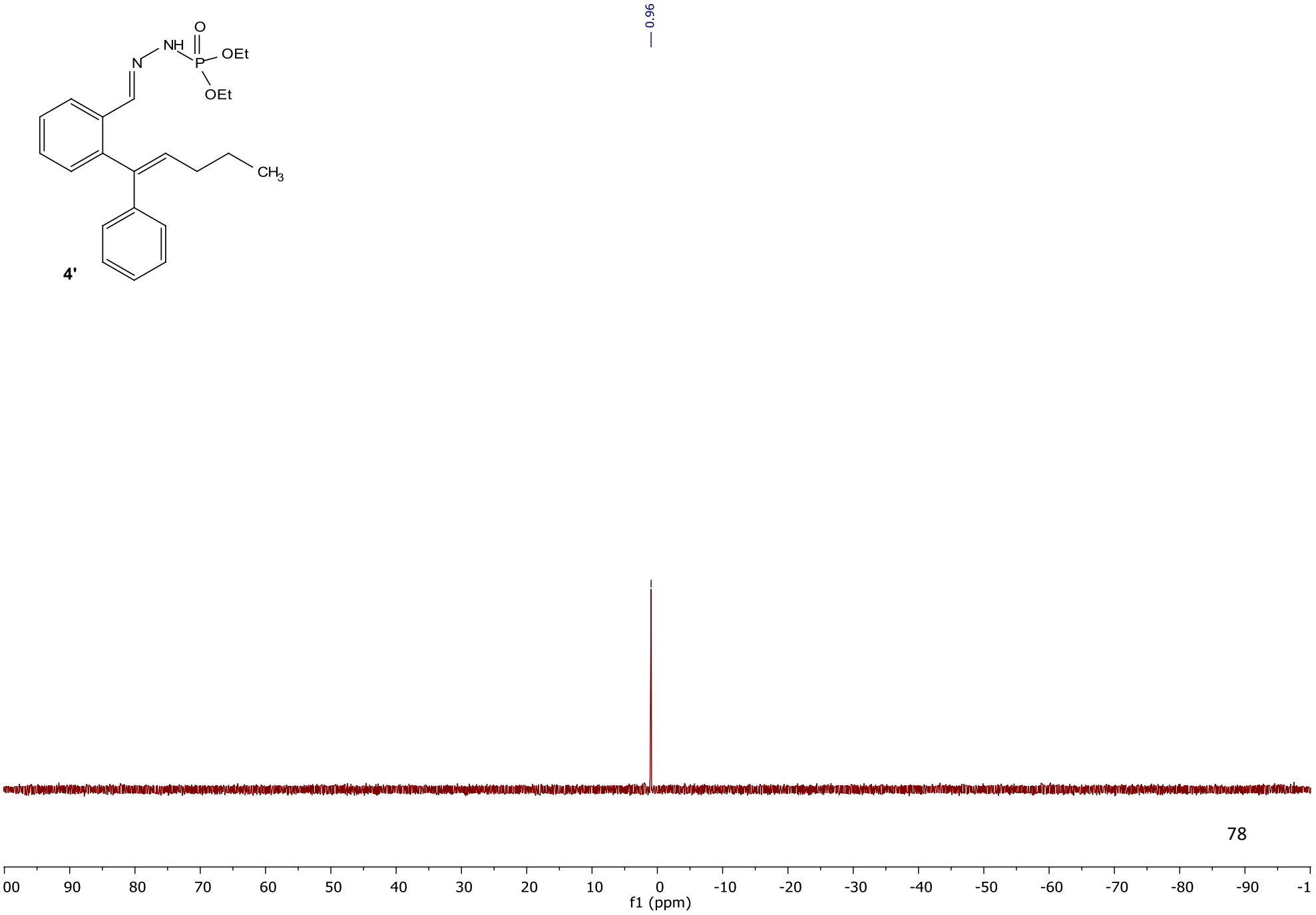
NH
O
OEt
N
P
OEt
CH3

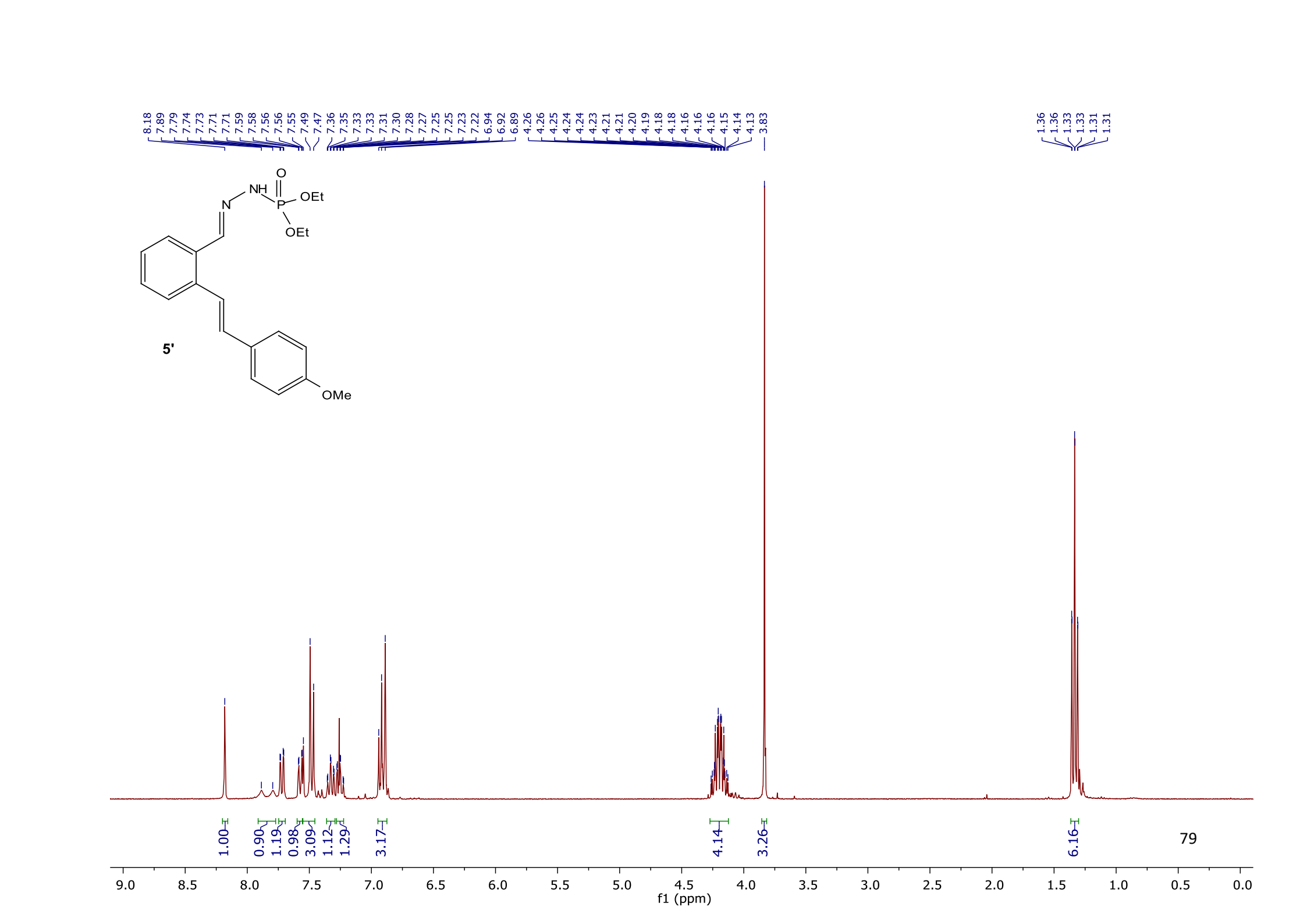
4'


143.70
143.52
141.37
139.41
138.52
132.49
131.49
130.54
129.40
128.42
127.50
127.10
126.27
125.54
63.40
63.35
31.96
22.60
16.16
16.09
13.92
77
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
P
OEt
N
OEt
CH3

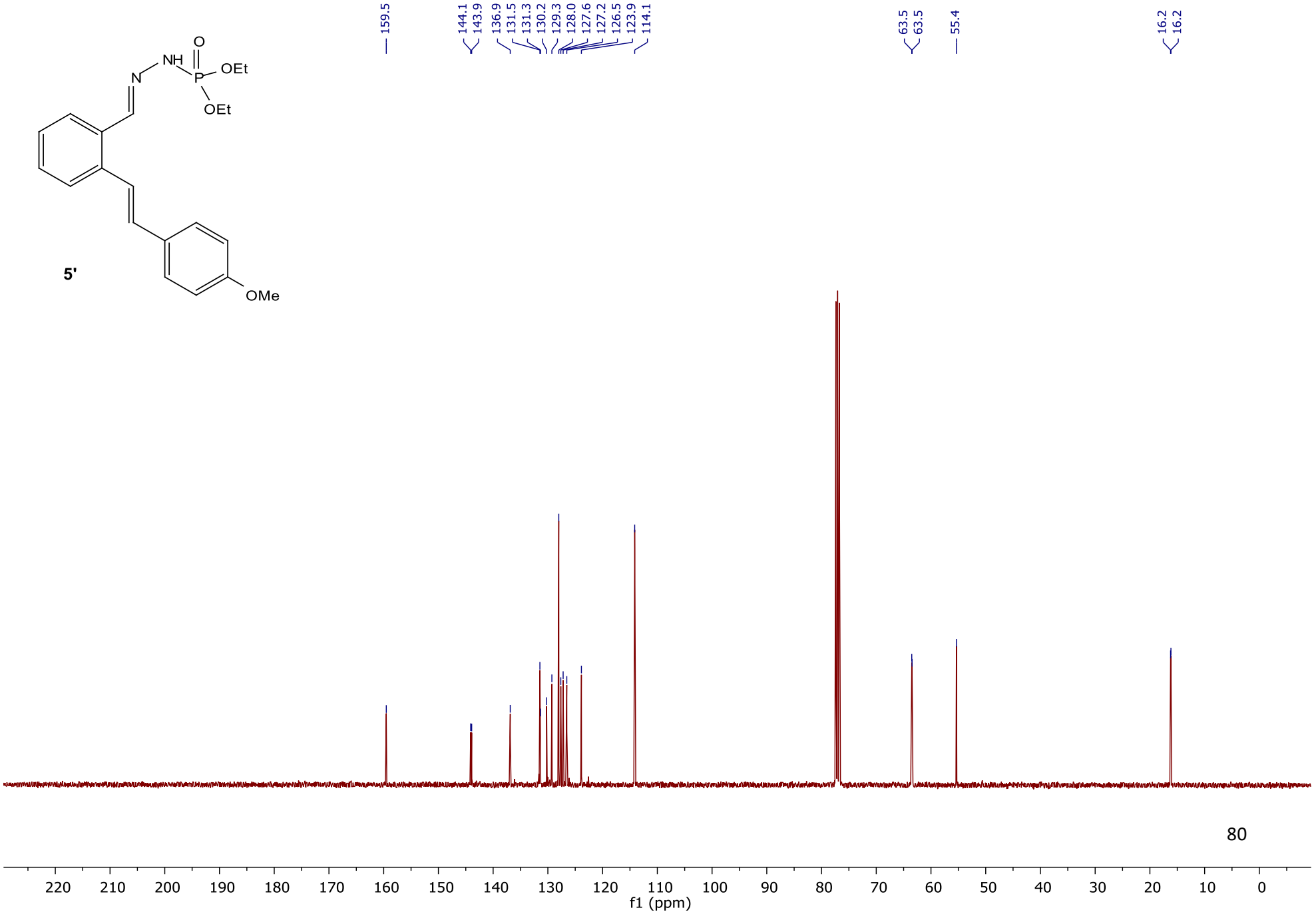
4'


0.96
78
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.18
7.89
7.79
7.74
7.73
7.71
7.71
7.59
7.58
7.56
7.56
7.55
7.49
7.47
7.36
7.35
7.33
7.33
7.31
7.30
7.28
7.27
7.25
7.25
7.23
7.22
6.94
6.92
6.89
4.26
4.26
4.25
4.24
4.24
4.23
4.21
4.21
4.20
4.19
4.18
4.18
4.16
4.16
4.16
4.15
4.14
4.13
3.83
1.36
1.36
1.33
1.33
1.31
1.31
O
NH
N
P
OEt
OEt
5'
OMe
1.00
0.90
1.19
0.98
3.09
1.12
1.29
3.17
4.14
3.26
6.16
79
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

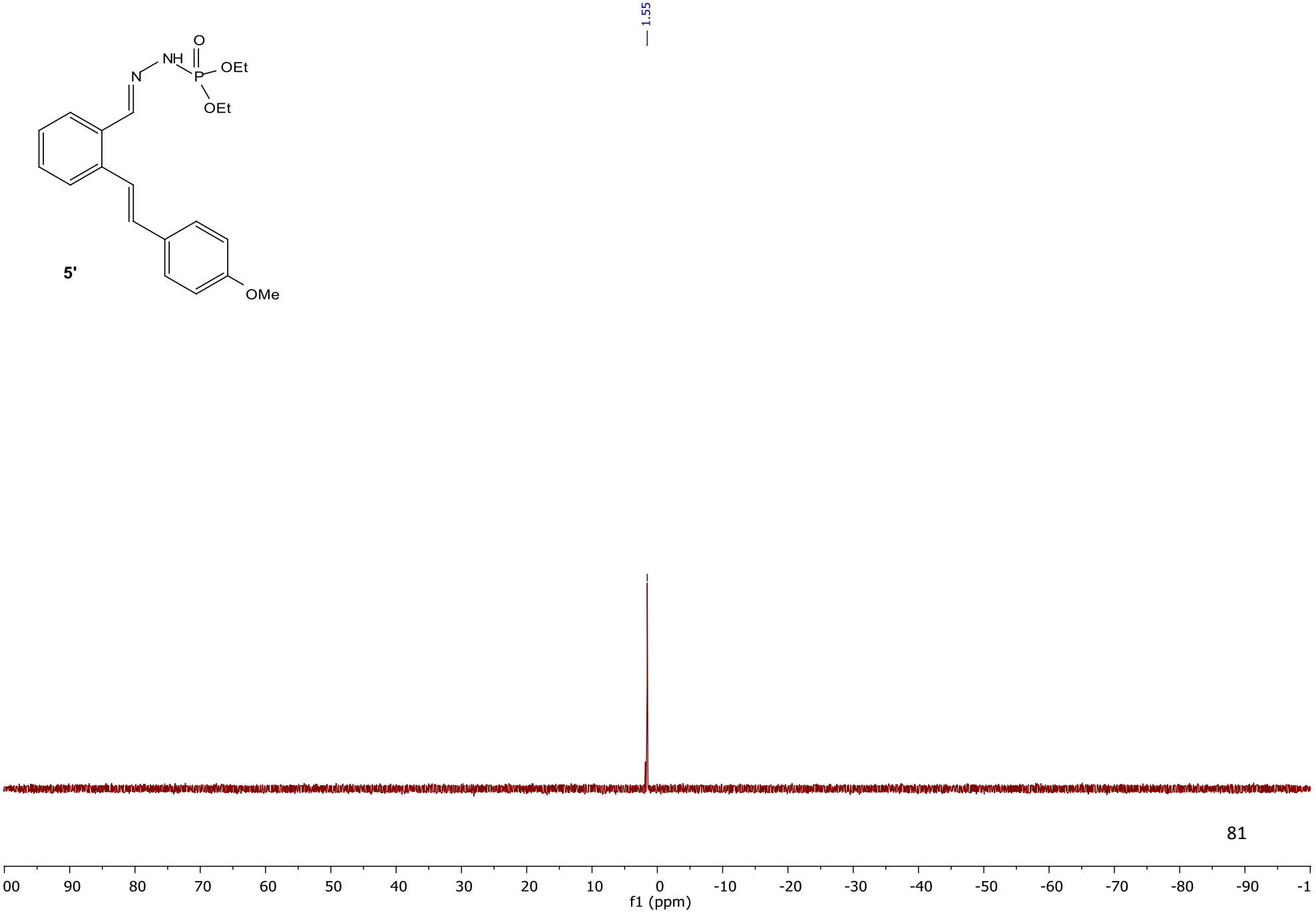
O
NH
N
P
OEt
OEt
OMe

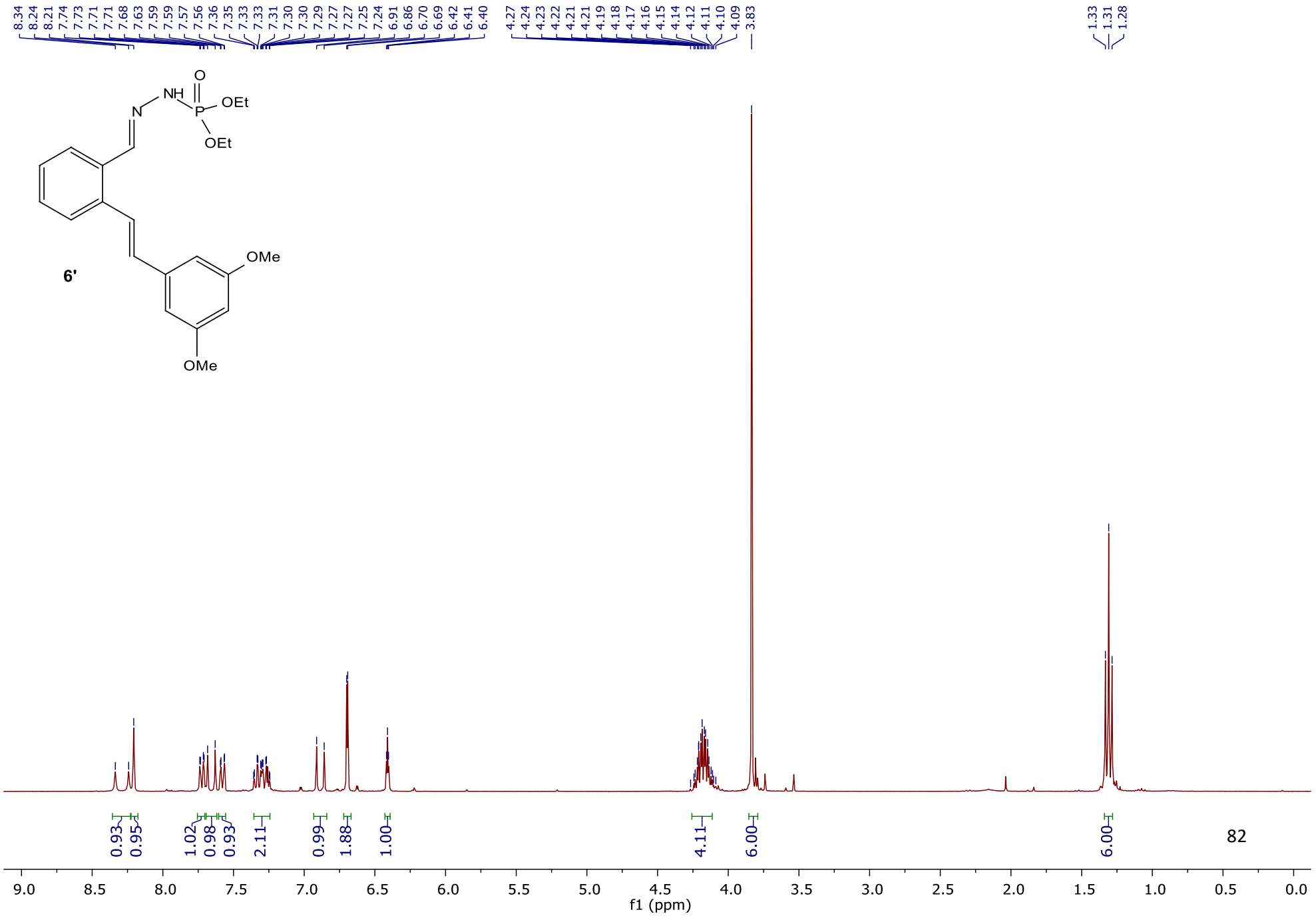
5'

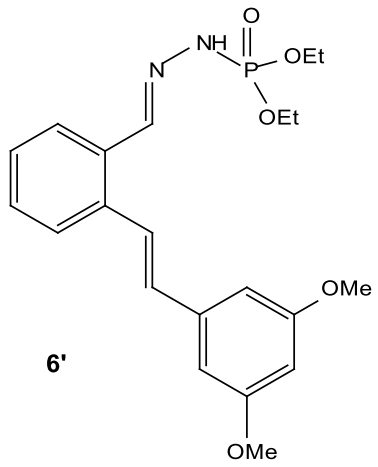

159.5
144.1
143.9
136.9
131.5
131.3
130.2
129.3
128.0
127.6
127.2
126.5
123.9
114.1
63.5
63.5
55.4
16.2
16.2
80
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
N
P
OEt
OEt
OMe

5'

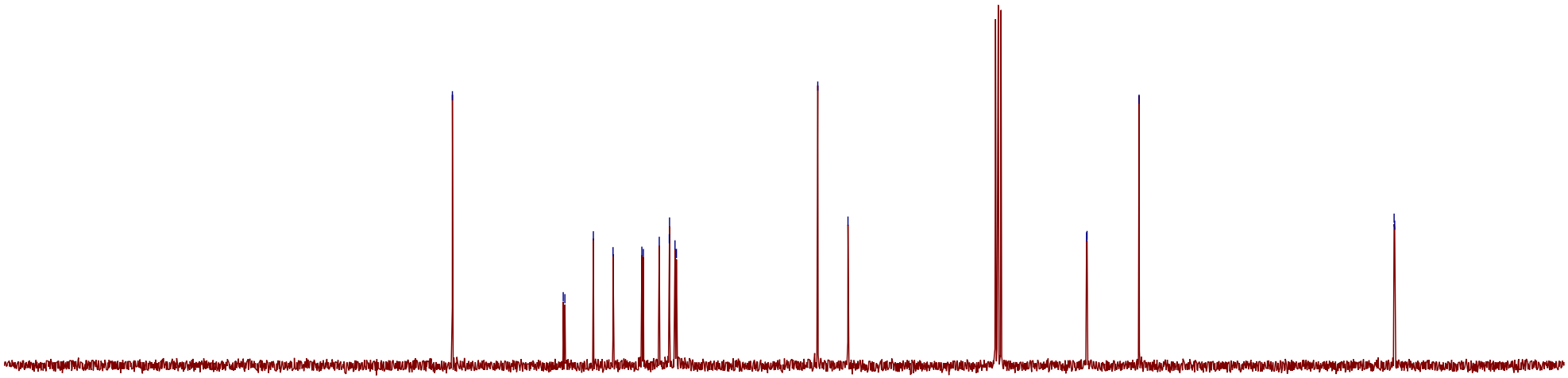

1.55
81
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

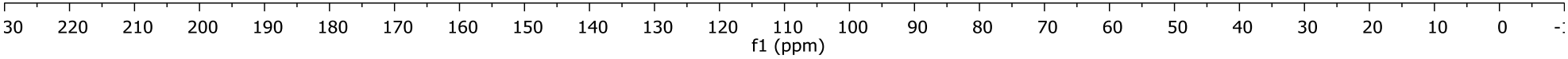

8.34
8.24
8.21
7.74
7.73
7.71
7.71
7.68
7.63
7.59
7.59
7.57
7.56
7.36
7.35
7.33
7.33
7.31
7.30
7.30
7.29
7.27
7.27
7.25
7.24
6.91
6.86
6.70
6.69
6.42
6.41
6.40
4.27
4.24
4.23
4.22
4.21
4.21
4.19
4.18
4.17
4.16
4.15
4.14
4.12
4.11
4.10
4.09
3.83
1.33
1.31
1.28
O
NH
P
OEt
N
OEt
OMe
OMe
6'
0.93
0.95
1.02
0.98
0.93
2.11
0.99
1.88
1.00
4.11
6.00
6.00
82
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



6'

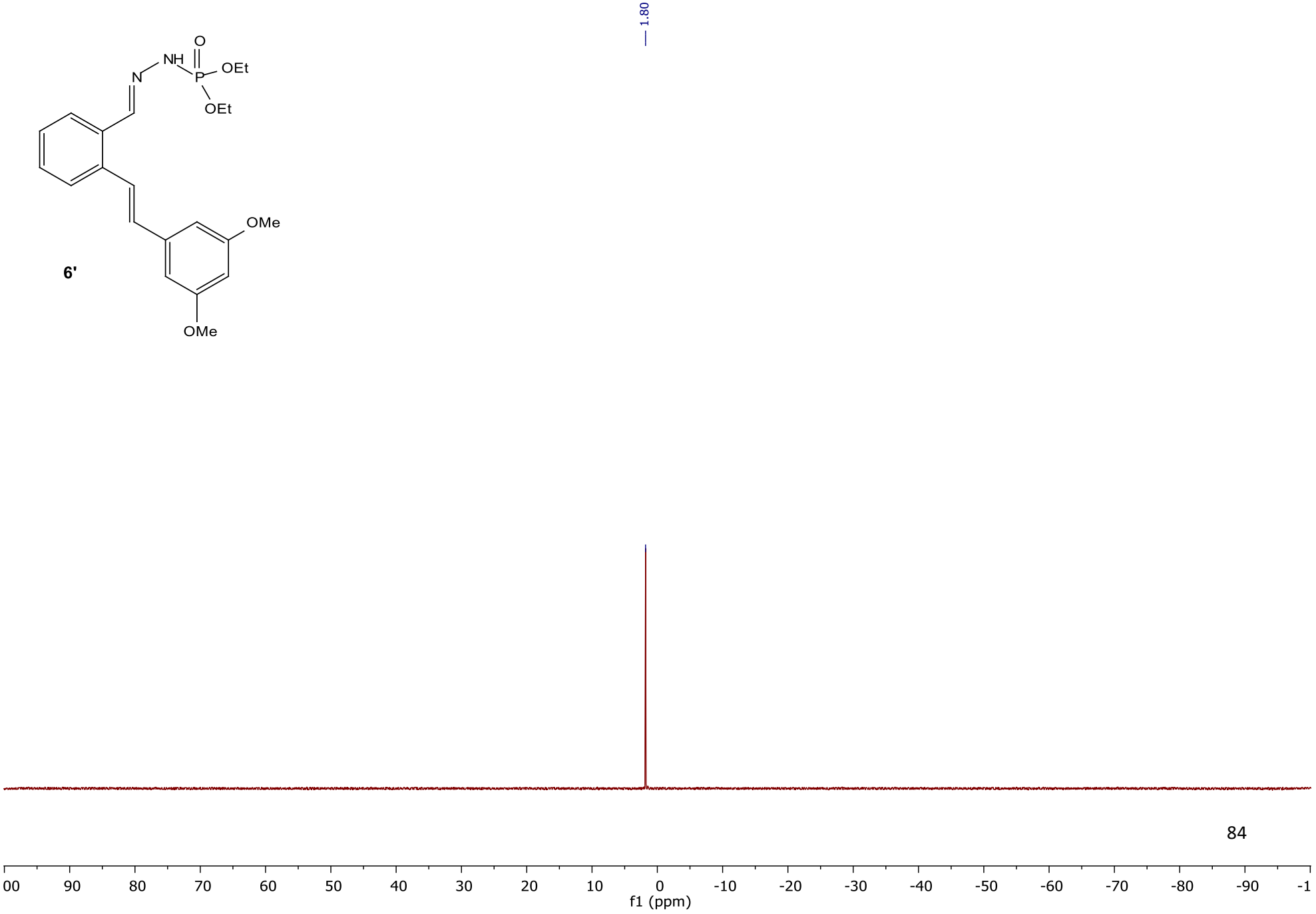
161.09
144.04
143.78
139.41
136.38
131.94
131.71
129.27
127.72
127.68
126.84
126.62
104.88
100.23
63.52
63.45
55.44
16.20
16.11

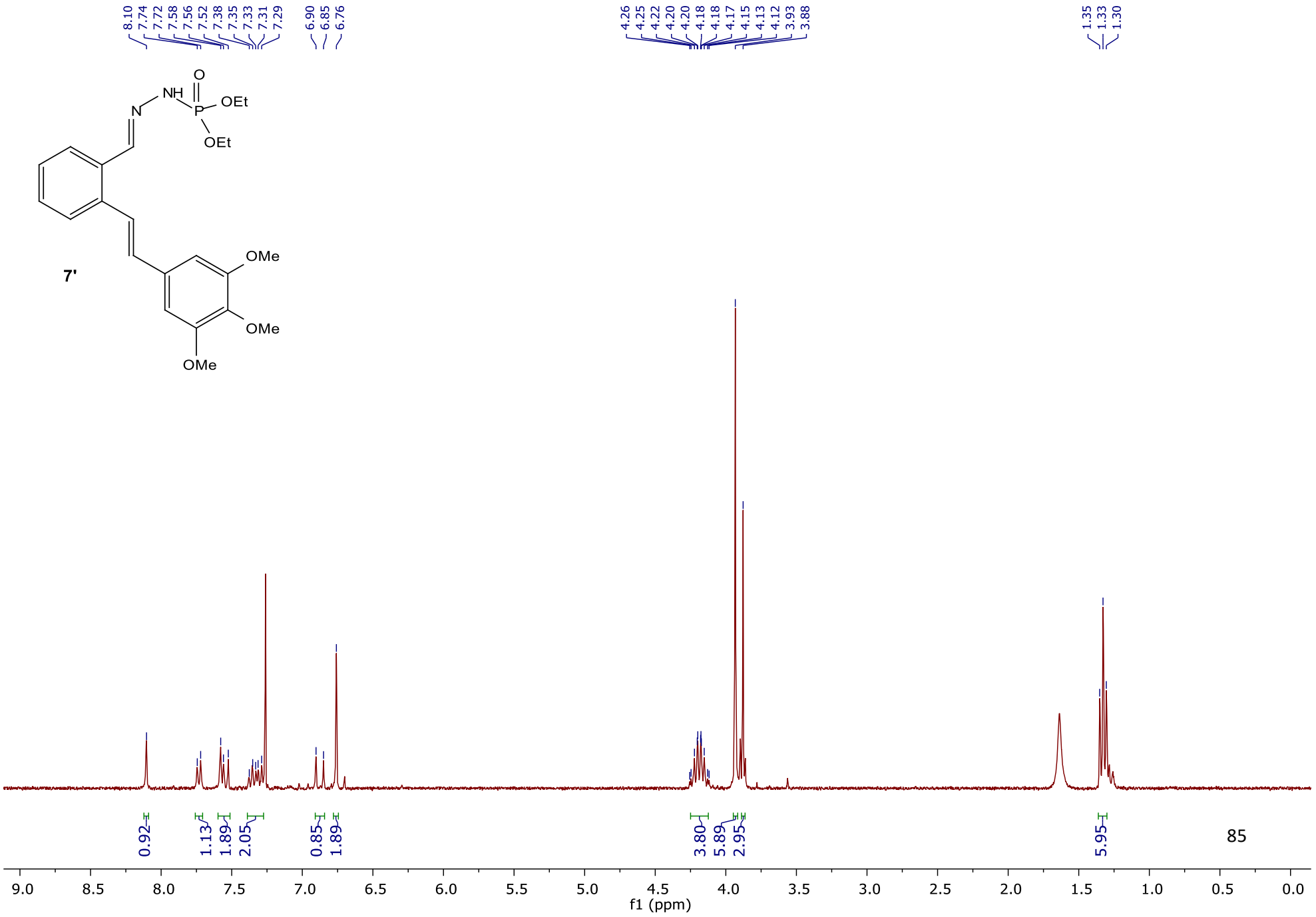


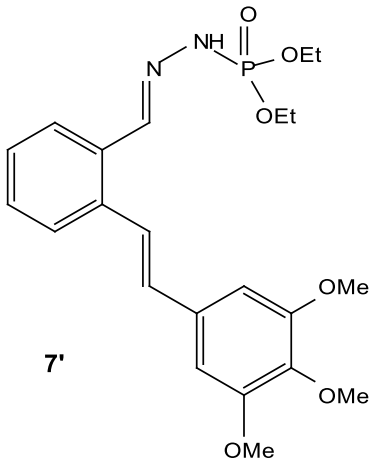


O
NH
N
P
OEt
OEt
OMe
OMe

6'

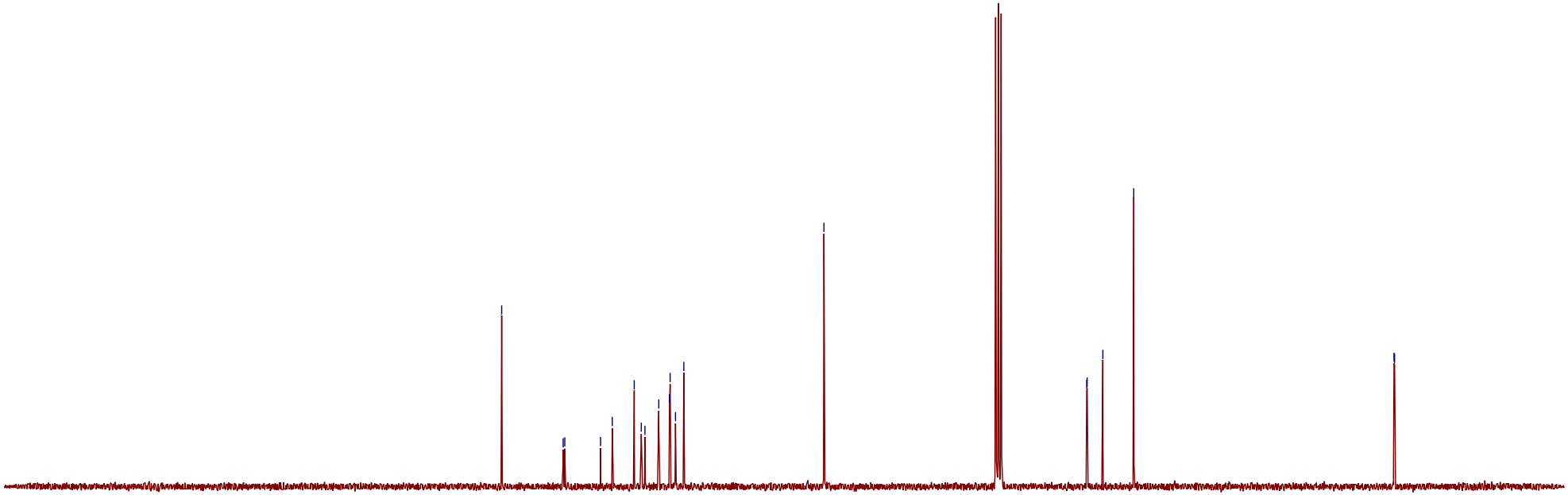

1.80
84
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.10
7.74
7.72
7.58
7.56
7.52
7.38
7.35
7.33
7.31
7.29
6.90
6.85
6.76
4.26
4.25
4.22
4.20
4.20
4.18
4.18
4.17
4.15
4.13
4.12
3.93
3.88
1.35
1.33
1.30
O
NH
P
OEt
N
OEt
OMe
OMe
OMe
7'
0.92
1.13
1.89
2.05
0.85
1.89
3.80
5.89
2.95
5.95
85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

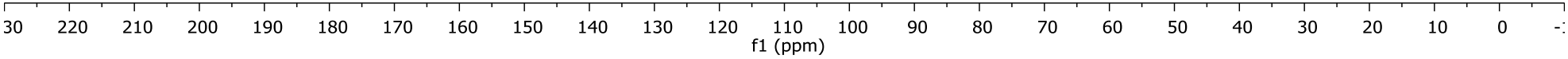


7'

153.5
144.0
143.8
138.3
136.5
133.1
132.0
131.5
129.3
127.7
127.6
126.8
125.5
103.9
63.5
63.4
61.0
56.3
16.2
16.1

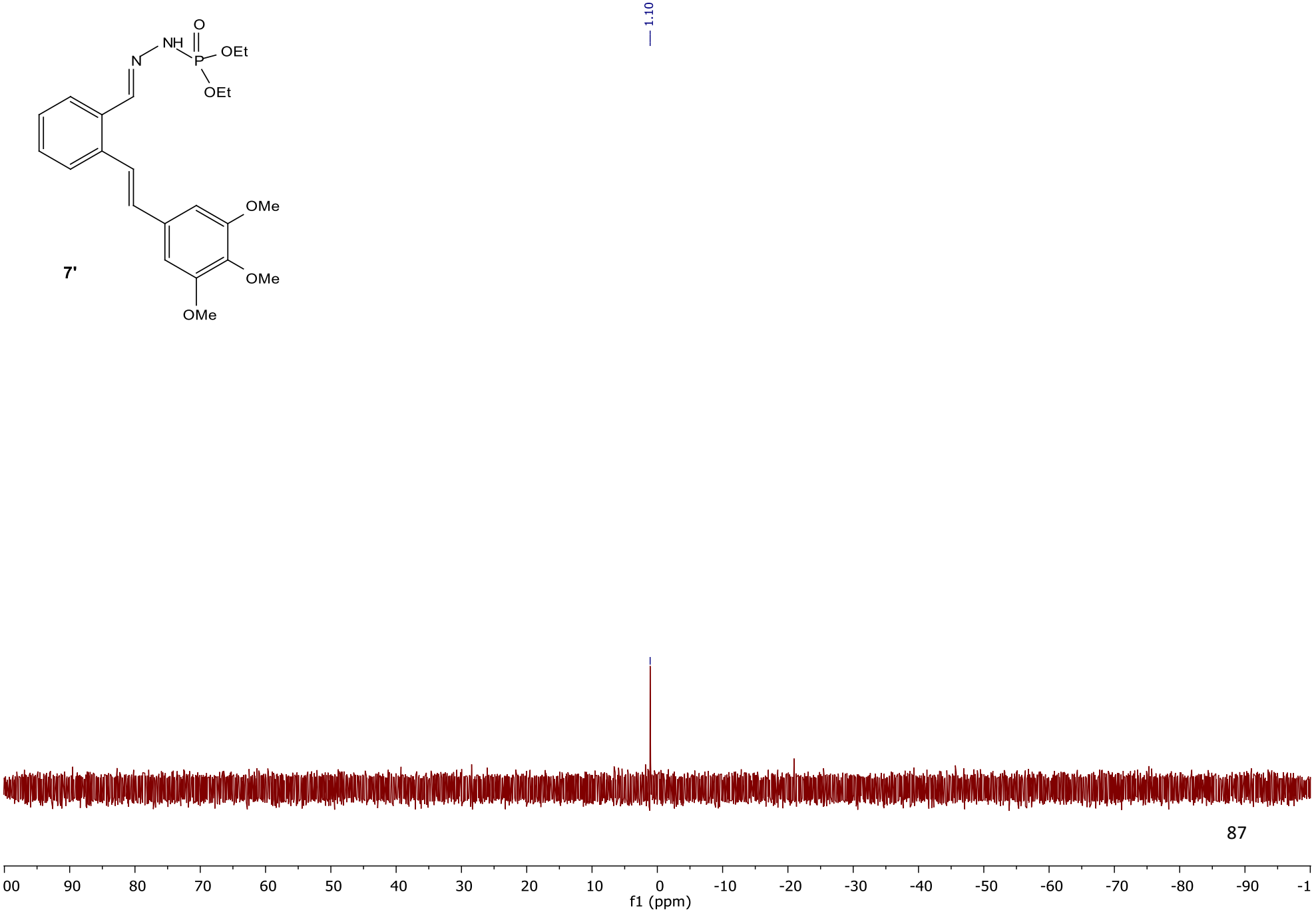


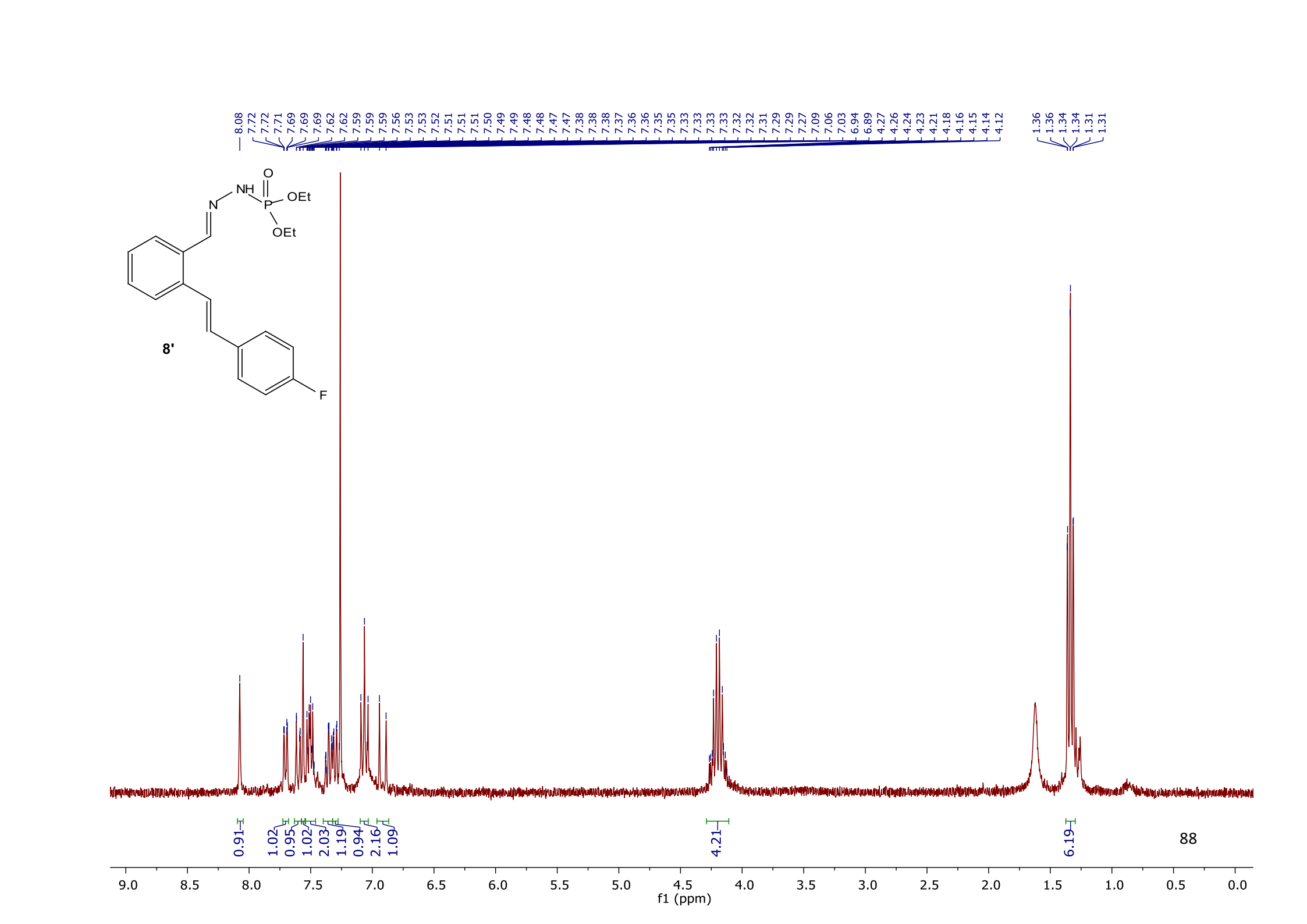
86

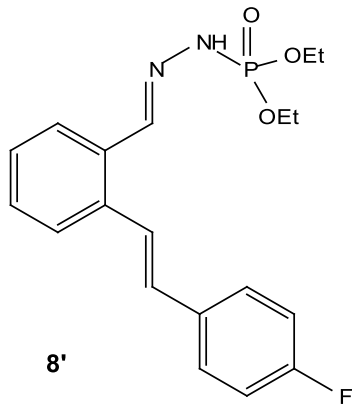


O
NH
OEt
N
P
OEt
OMe
OMe
OMe

7'

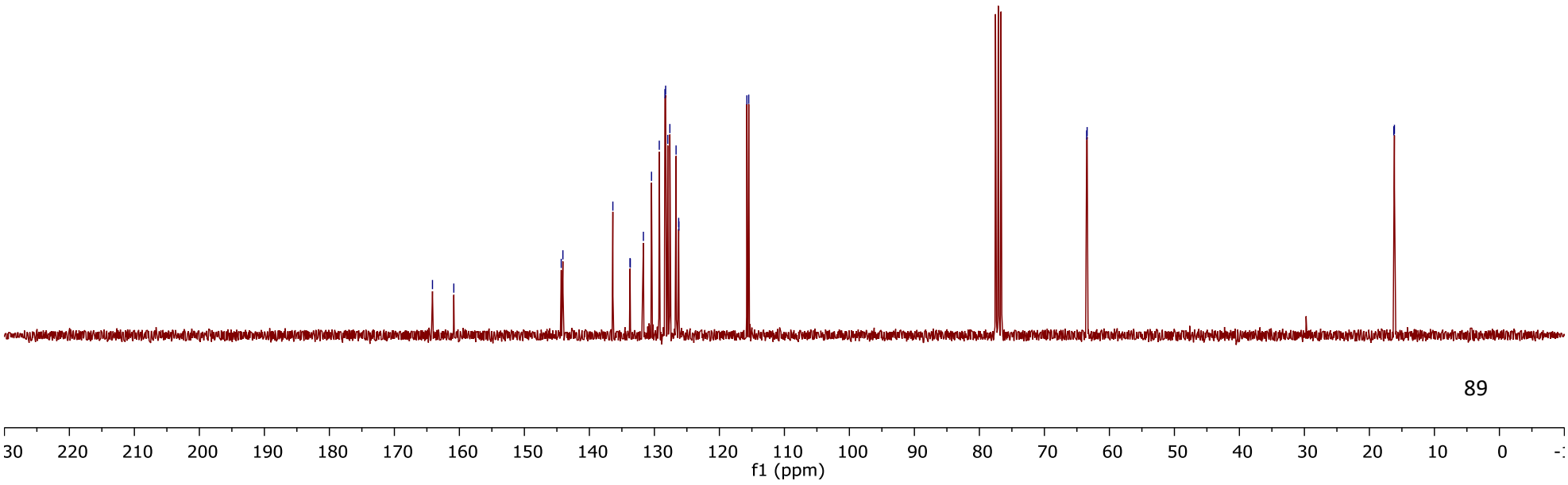

1.10
87
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.08 7.72 7.72 7.71 7.69 7.69 7.69 7.62 7.62 7.59 7.59 7.59 7.56 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.29 7.29 7.27 7.09 7.06 7.03 6.94 6.89 4.27 4.26 4.24 4.23 4.21 4.18 4.16 4.15 4.14 4.12 1.36 1.36 1.34 1.34 1.31 1.31
NH
O
P
OEt
OEt
N
F
8'
0.91 1.02 0.95 1.02 2.03 1.19 0.94 2.16 1.09 4.21 6.19
88
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

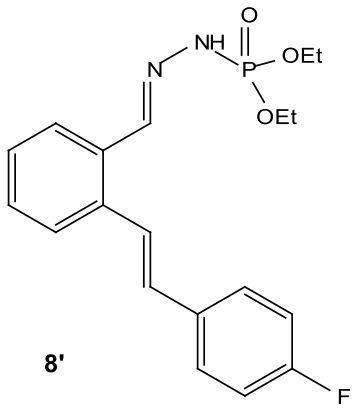


8'

164.1
160.9
144.3
144.1
136.4
133.7
133.7
131.7
130.4
129.2
128.4
128.3
127.9
127.6
126.7
126.3
126.2
115.8
115.5
63.5
63.4
16.2
16.2



31P dec 1H



8'

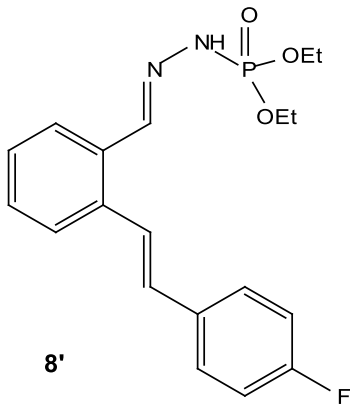
1.05

90

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

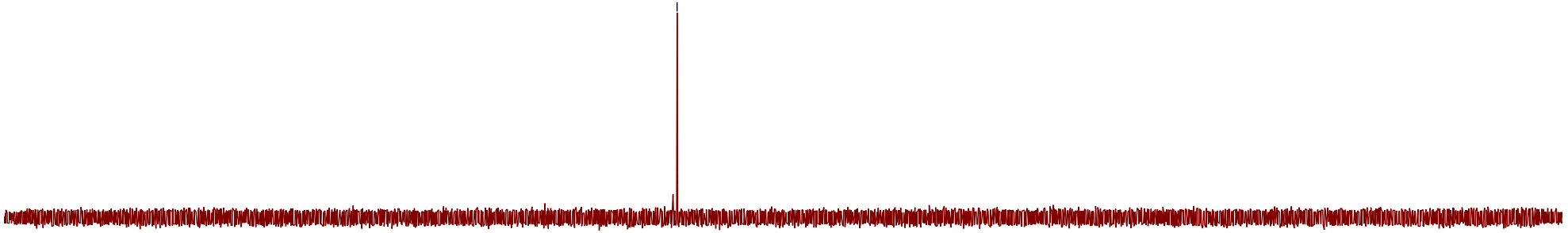
f1 (ppm)

19F

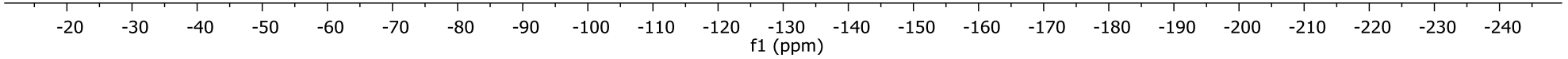


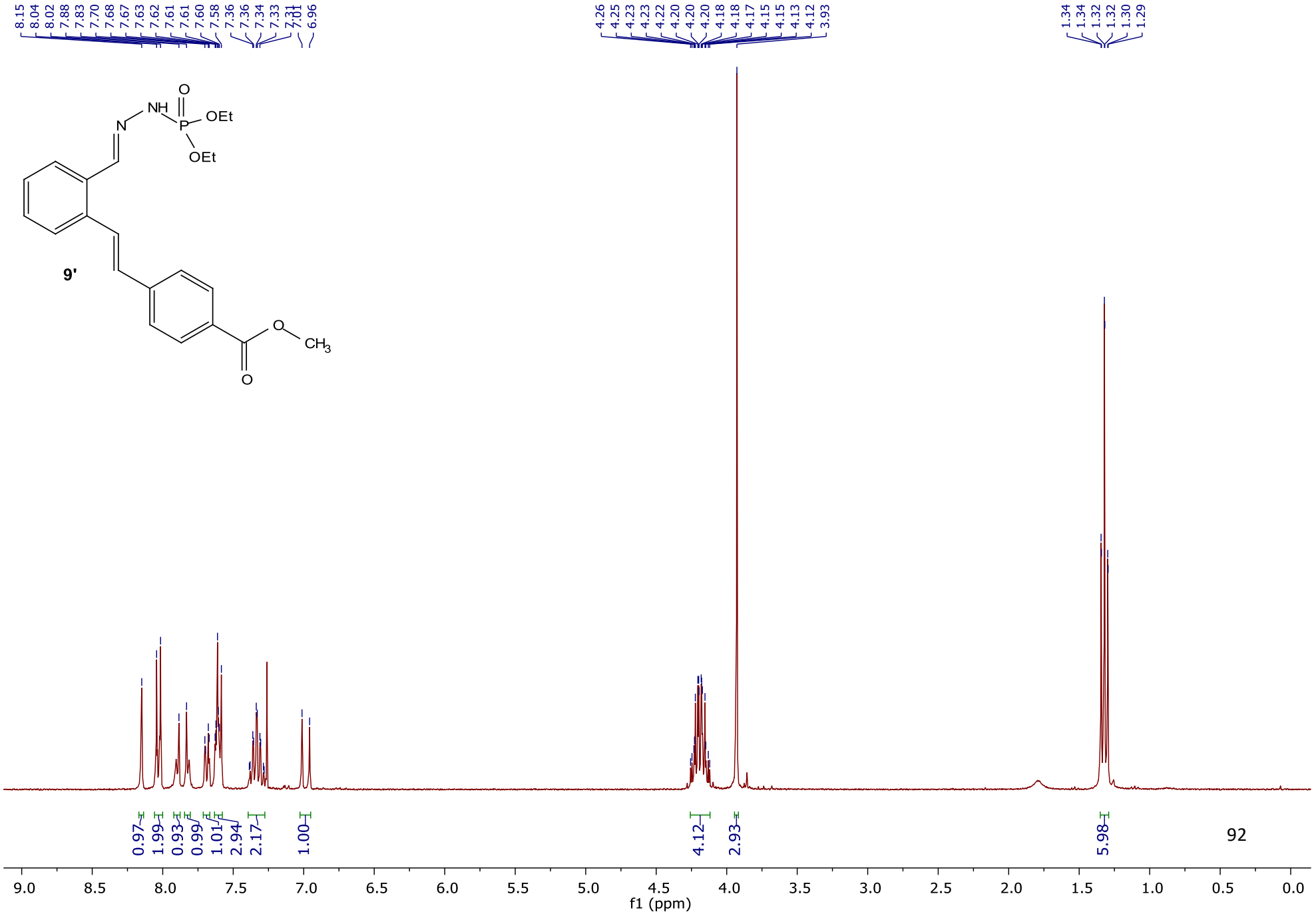
8'

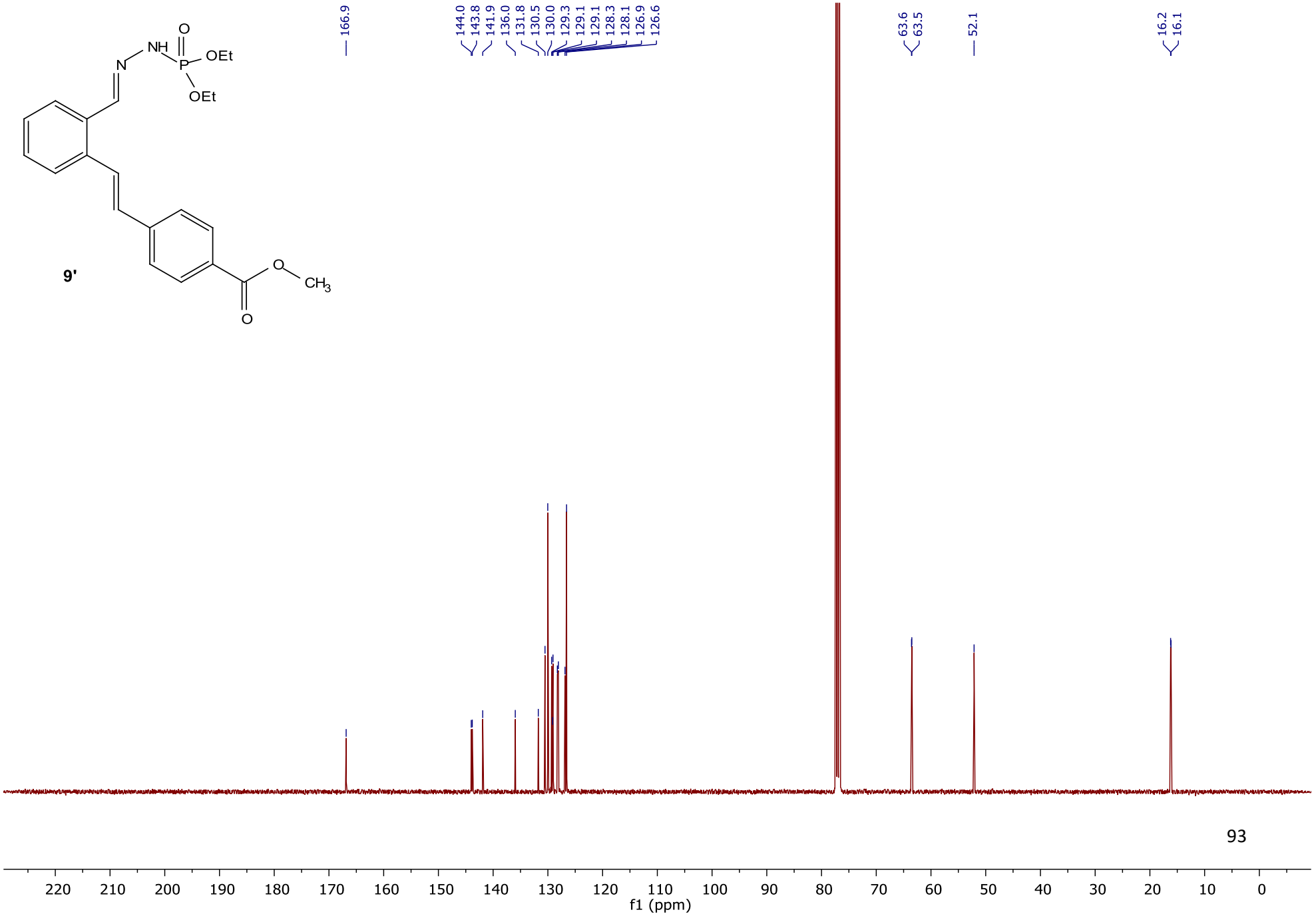
-113.71



91

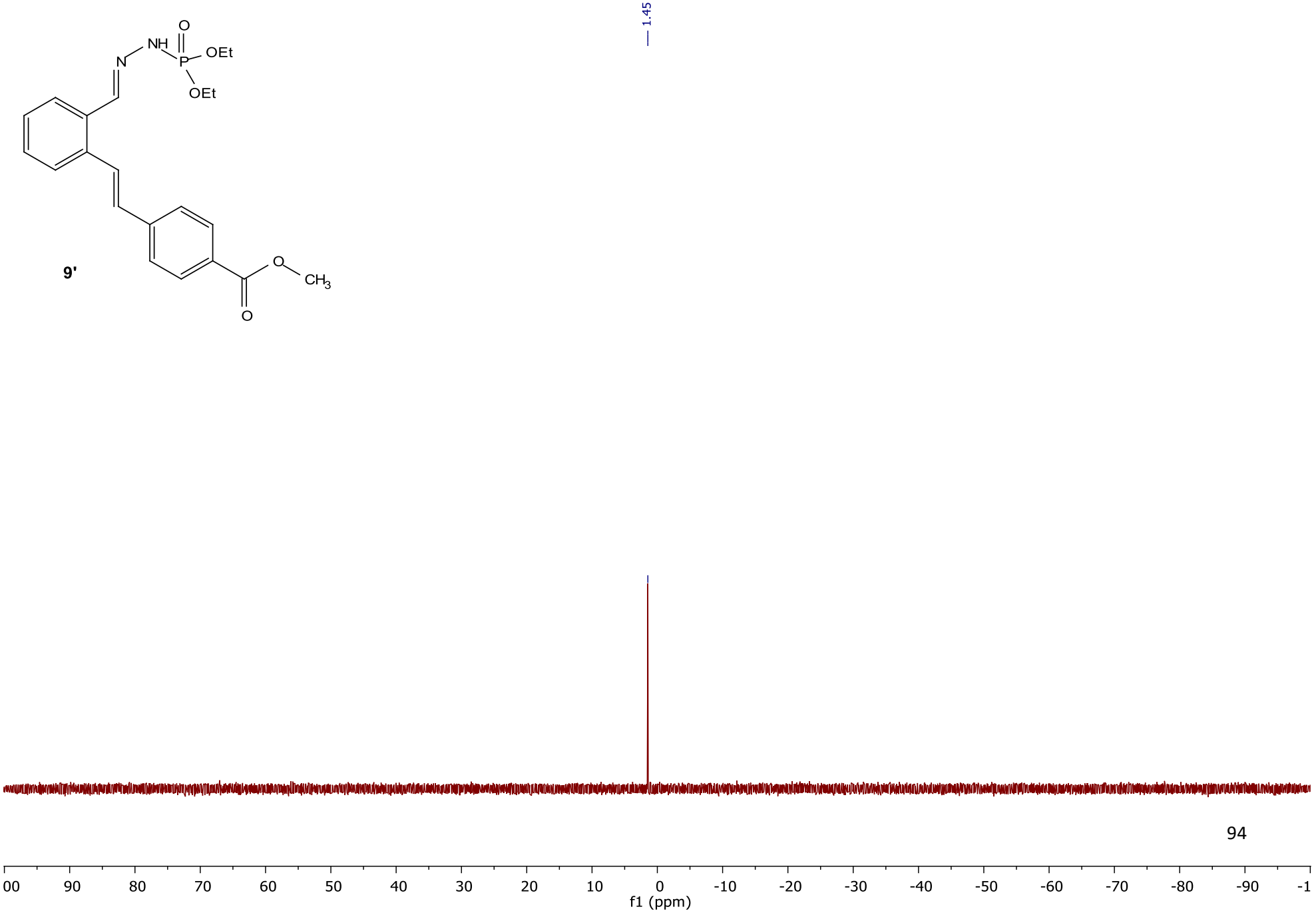


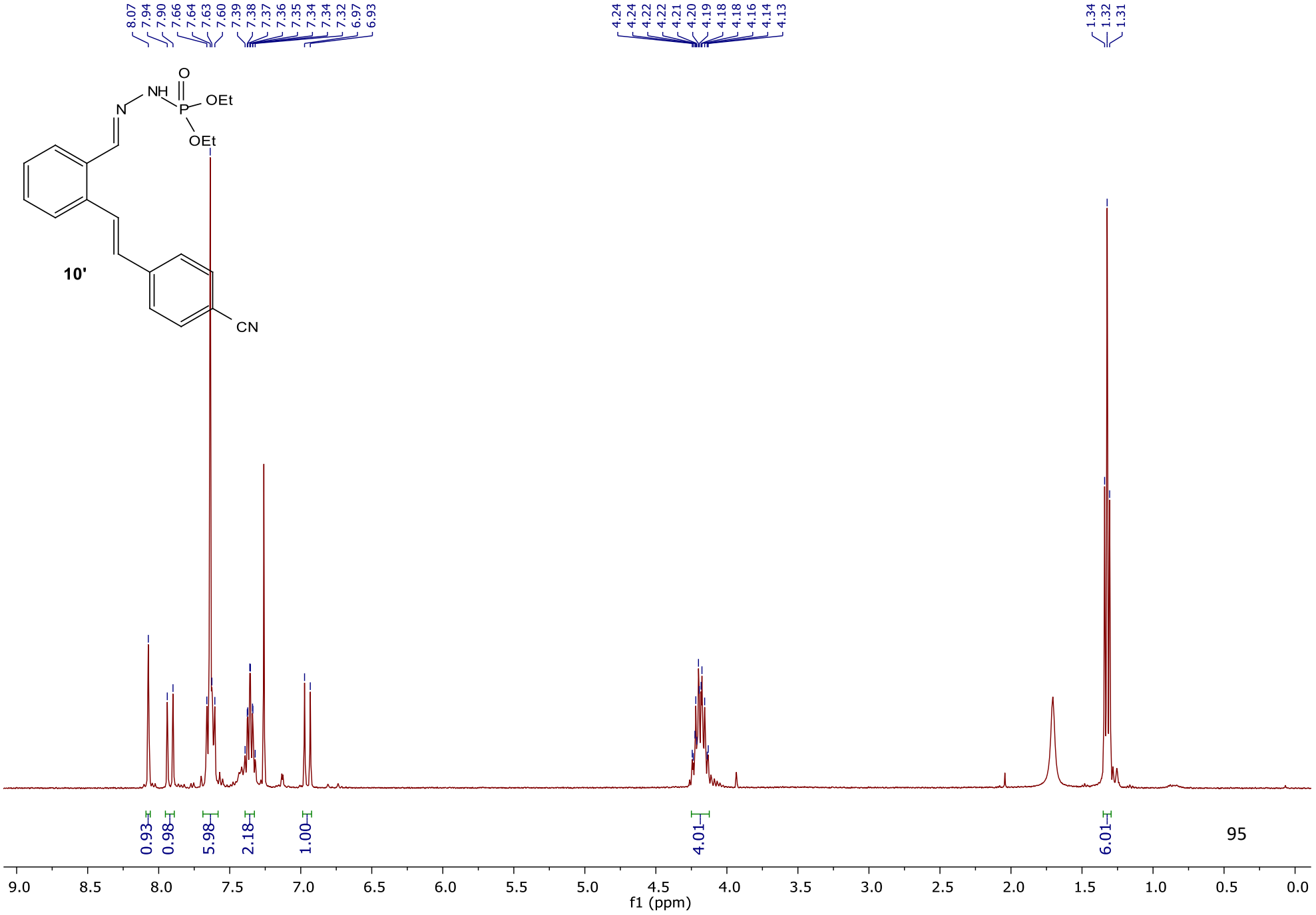

8.15
8.04
8.02
7.88
7.83
7.70
7.68
7.67
7.63
7.62
7.61
7.61
7.60
7.58
7.36
7.36
7.34
7.33
7.31
7.01
6.96
4.26
4.25
4.23
4.23
4.22
4.20
4.20
4.20
4.18
4.18
4.17
4.15
4.15
4.13
4.12
3.93
1.34
1.34
1.32
1.32
1.30
1.29
NH
N
O
P
OEt
OEt
9'
O
O
CH3
O
0.97
1.99
0.93
0.99
1.01
2.94
2.17
1.00
4.12
2.93
5.98
92
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

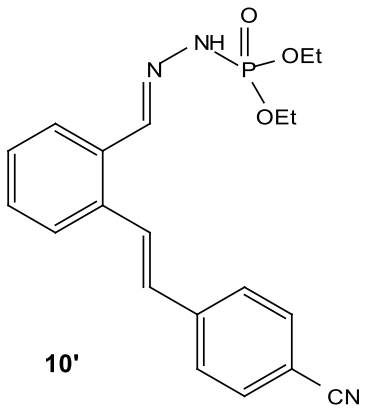

166.9
144.0
143.8
141.9
136.0
131.8
130.5
130.0
129.3
129.1
129.1
128.3
128.1
126.9
126.6
63.6
63.5
52.1
16.2
16.1
NH
N
P
O
OEt
OEt
O
CH3
O
9'
93
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
N
P
OEt
OEt
O
O
CH3
O

9'


1.45
94
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.07
7.94
7.90
7.66
7.64
7.63
7.60
7.39
7.38
7.37
7.36
7.35
7.34
7.34
7.32
6.97
6.93
4.24
4.24
4.22
4.22
4.21
4.20
4.19
4.18
4.18
4.16
4.14
4.13
1.34
1.32
1.31
O
NH
N
P
OEt
OEt
10'
CN
0.93
0.98
5.98
2.18
1.00
4.01
6.01
95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



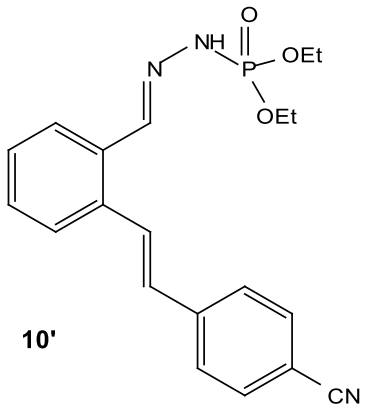
10'

144.1
143.8
142.0
135.6
132.5
131.7
130.6
129.6
129.4
128.7
128.5
127.2
127.0
119.0
110.9
63.6
63.5
16.3
16.2

96

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)



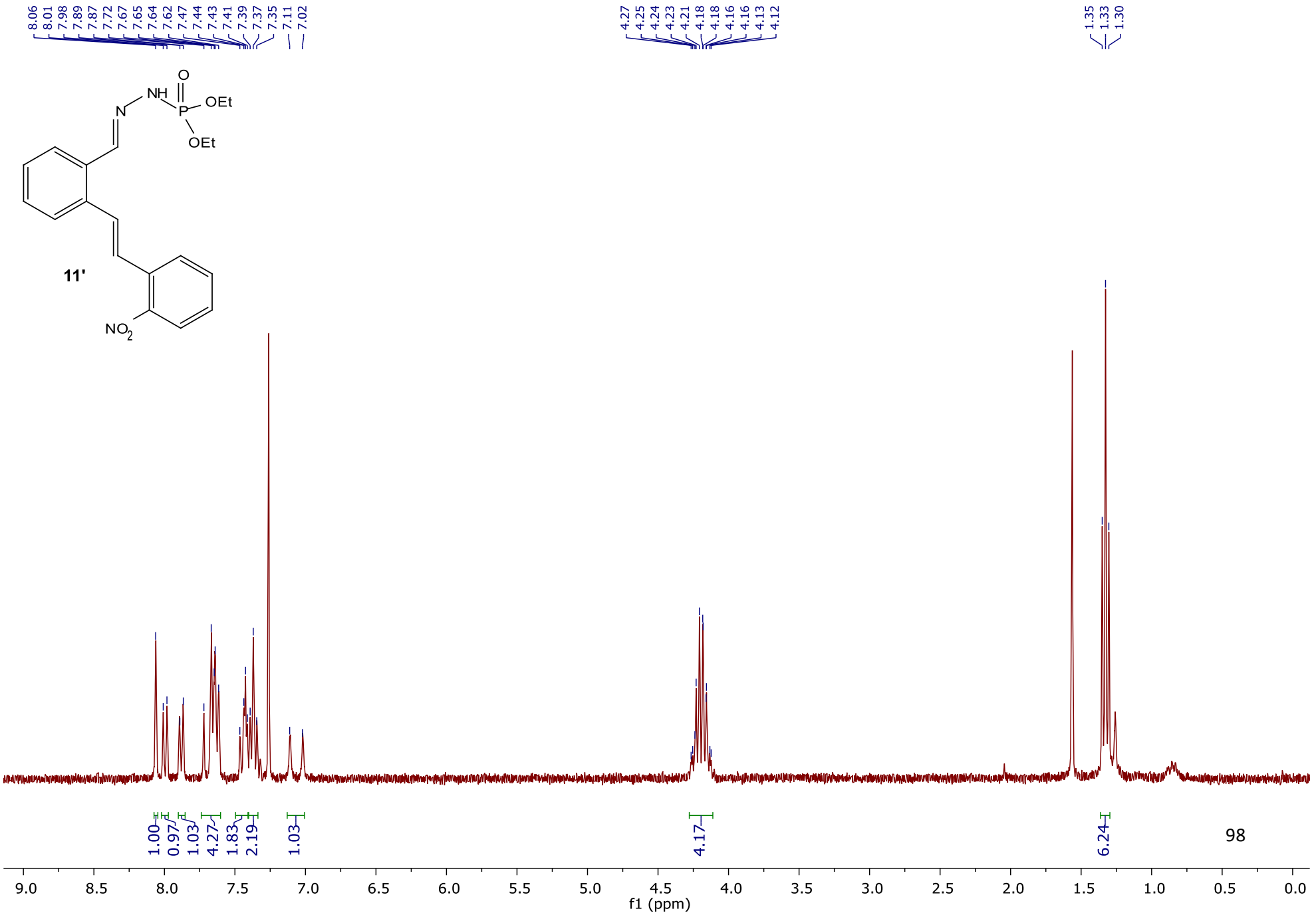
10'

1.19

97

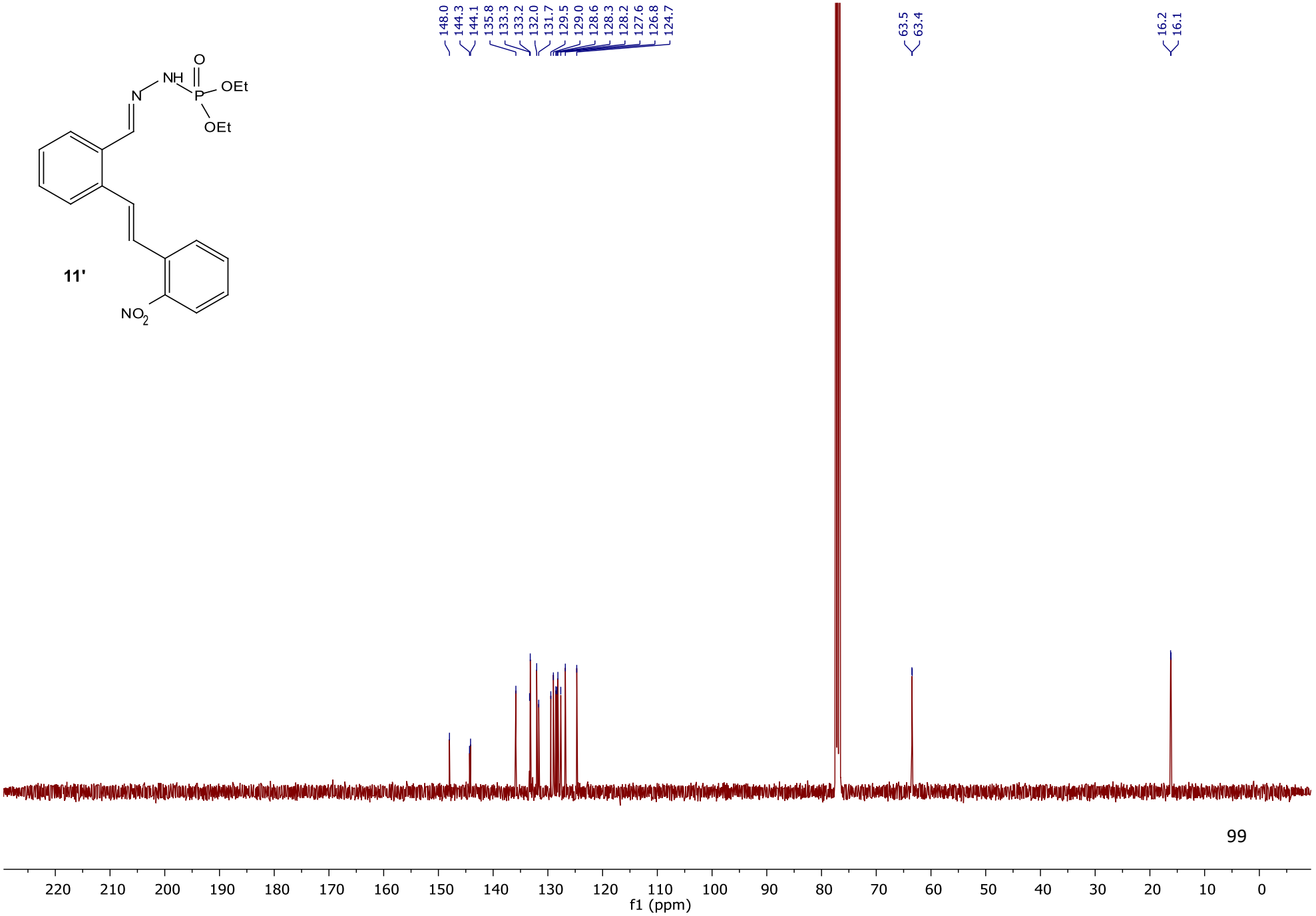
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


8.06
8.01
7.98
7.89
7.87
7.72
7.67
7.65
7.64
7.62
7.47
7.44
7.43
7.41
7.39
7.37
7.35
7.11
7.02
4.27
4.25
4.24
4.23
4.21
4.18
4.18
4.16
4.16
4.13
4.12
1.35
1.33
1.30
O
NH
P
OEt
OEt
N
11'
NO2
1.00
0.97
1.03
4.27
1.83
2.19
1.03
4.17
6.24
98
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

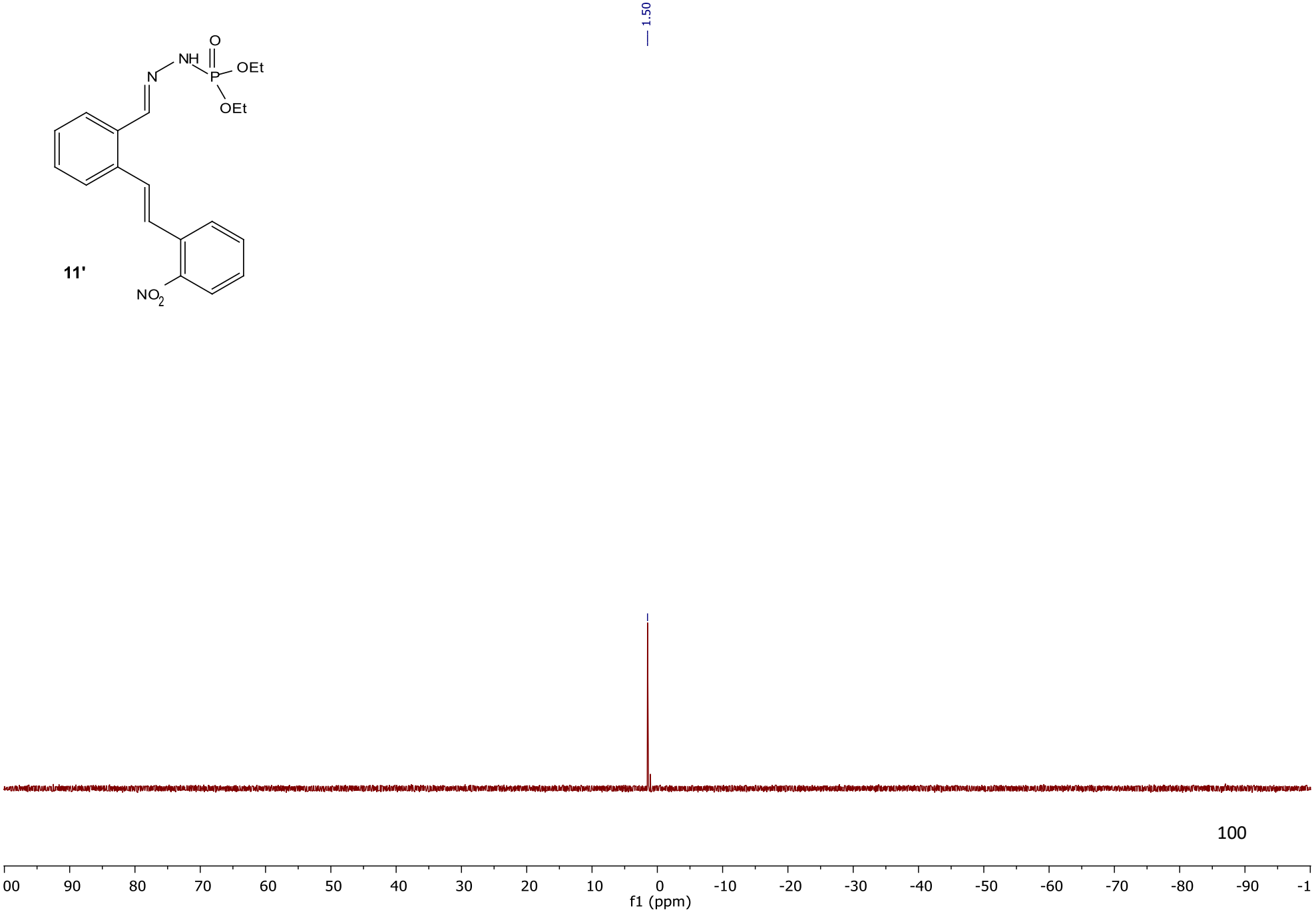
O
NH
P
OEt
N
OEt
NO2

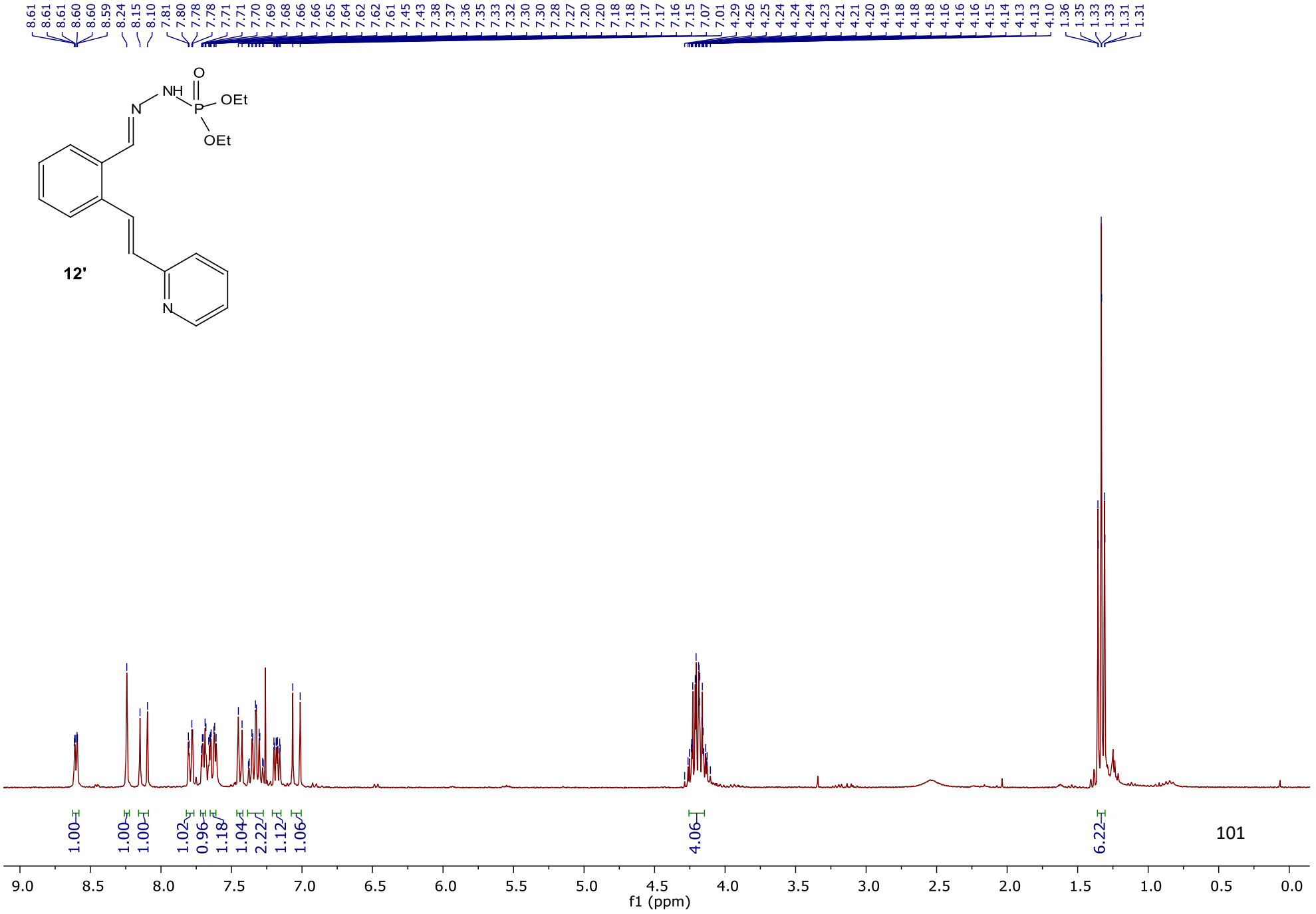
11'

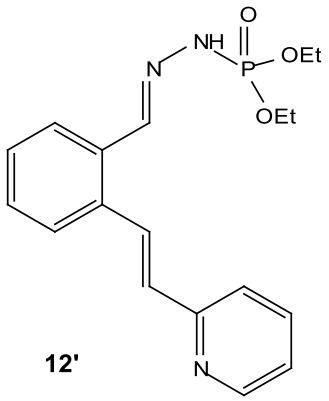

148.0
144.3
144.1
135.8
133.3
133.2
132.0
131.7
129.5
129.0
128.6
128.3
128.2
127.6
126.8
124.7
63.5
63.4
16.2
16.1
99
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
P
OEt
N
OEt
NO2

11'


1.50
100
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.61 8.61 8.61 8.60 8.60 8.59 8.24 8.15 8.10 7.81 7.80 7.78 7.78 7.71 7.71 7.70 7.69 7.68 7.66 7.66 7.65 7.64 7.62 7.62 7.61 7.45 7.43 7.38 7.37 7.36 7.35 7.33 7.32 7.30 7.30 7.28 7.27 7.20 7.20 7.18 7.18 7.17 7.17 7.16 7.15 7.07 7.01 4.29 4.26 4.25 4.24 4.24 4.24 4.23 4.21 4.21 4.20 4.19 4.18 4.18 4.18 4.16 4.16 4.16 4.15 4.14 4.13 4.13 4.10 1.36 1.35 1.33 1.33 1.31 1.31
O
NH
P
OEt
OEt
N
N
12'
1.00 1.00 1.00 1.02 0.96 1.18 1.04 2.22 1.12 1.06 4.06 6.22
101
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



12'

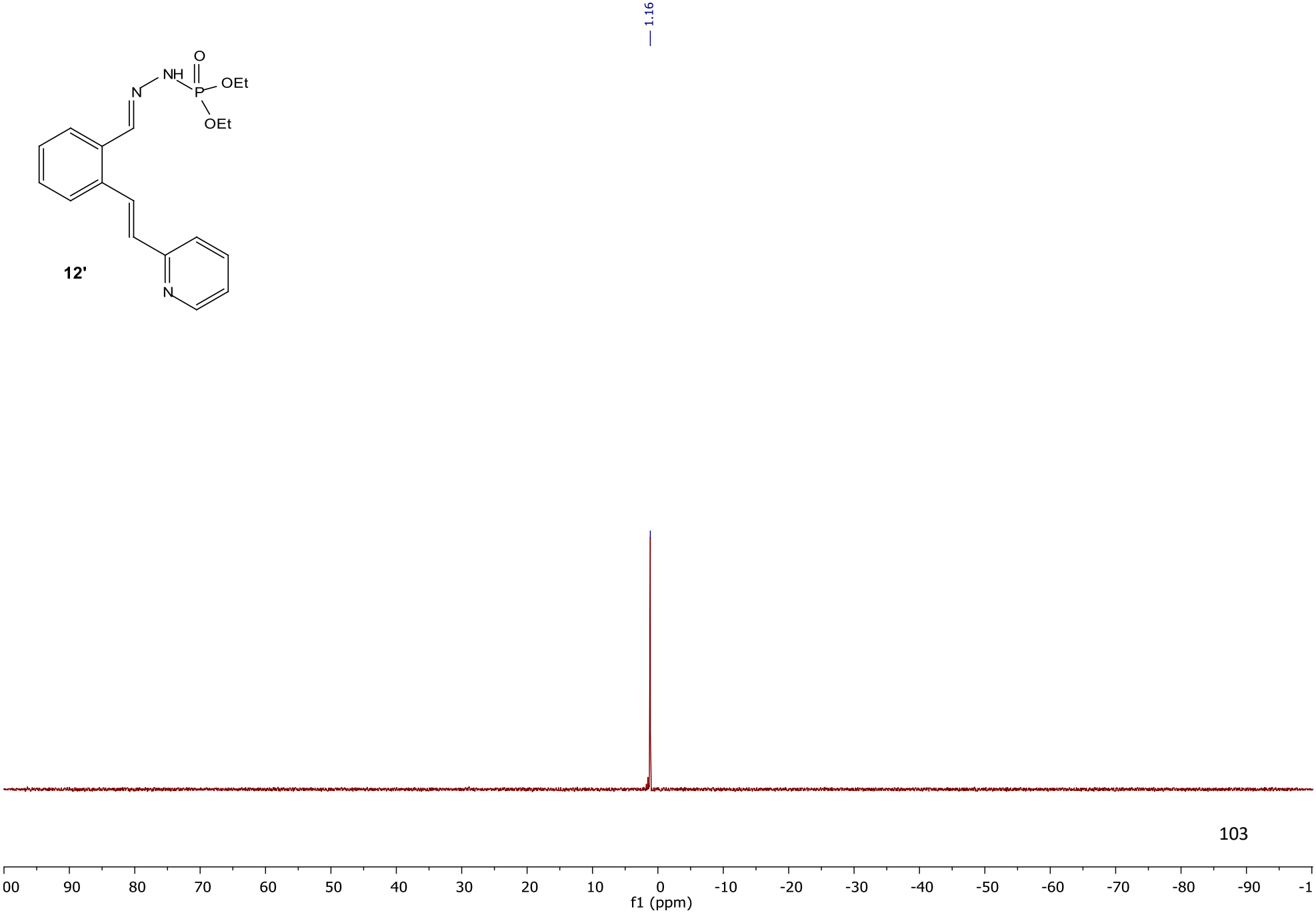
155.4
149.5
143.4
143.1
136.9
135.7
132.1
130.8
130.1
129.4
128.3
127.4
126.9
122.4
122.4
63.6
63.5
16.2
16.2

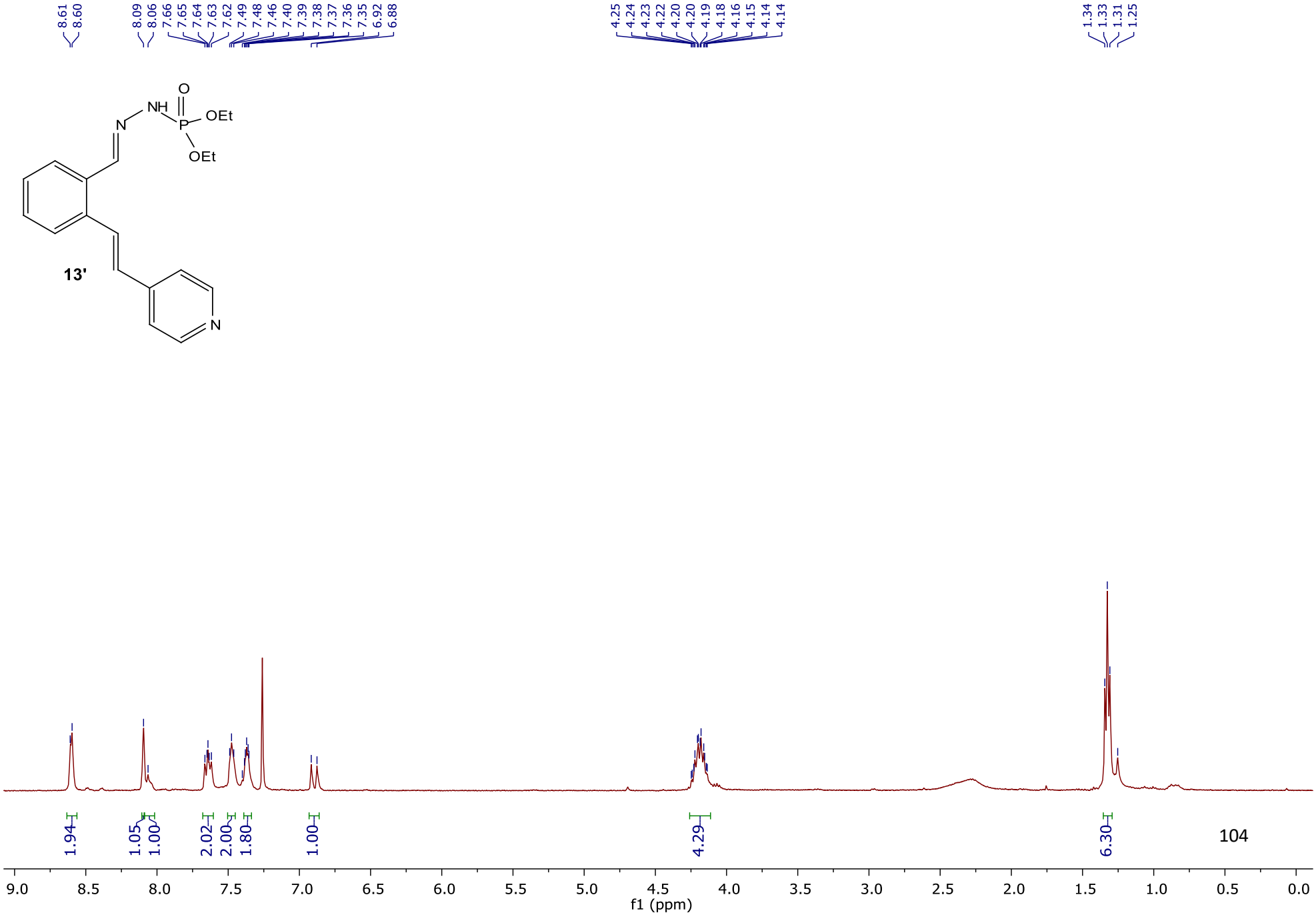
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

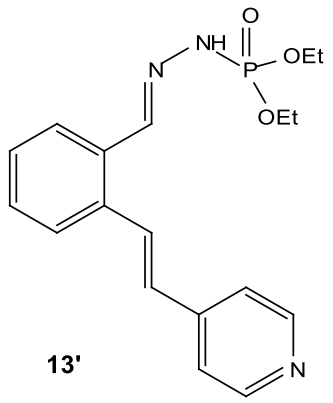
f1 (ppm)

O
NH
N
P
OEt
OEt
N

12'


1.16
103
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.61
8.60
8.09
8.06
7.66
7.65
7.64
7.63
7.62
7.49
7.48
7.46
7.40
7.39
7.38
7.37
7.36
7.35
6.92
6.88
4.25
4.24
4.23
4.22
4.20
4.20
4.19
4.18
4.16
4.15
4.14
4.14
1.34
1.33
1.31
1.25
NH
O
OEt
N
P
OEt
13'
N
1.94
1.05
1.00
2.02
2.00
1.80
1.00
4.29
6.30
104
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



13'

149.5
145.4
144.3
144.0
135.1
132.3
131.9
129.2
128.6
128.3
128.2
126.9
121.3

63.5
63.4

16.2
16.1

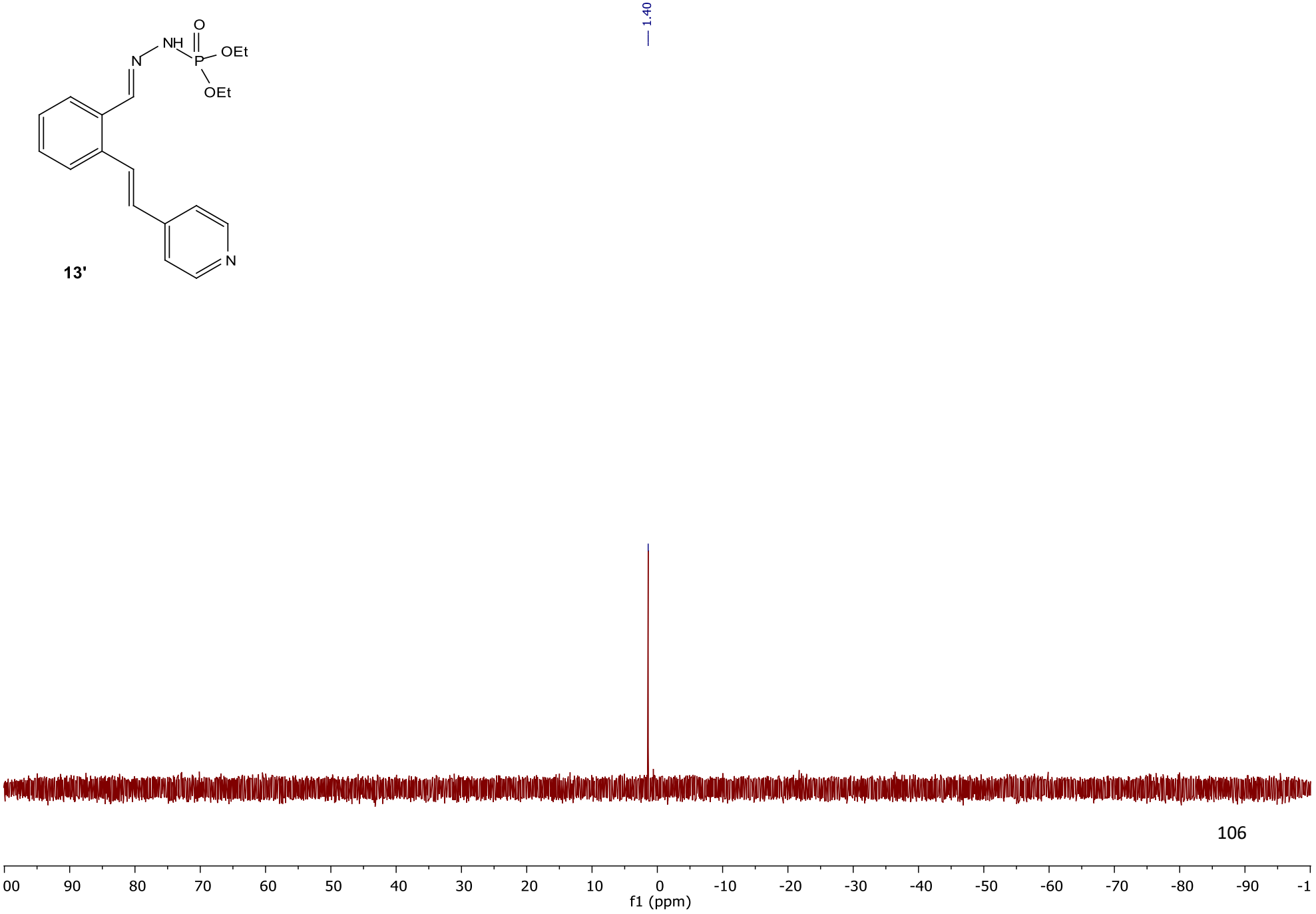
105

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

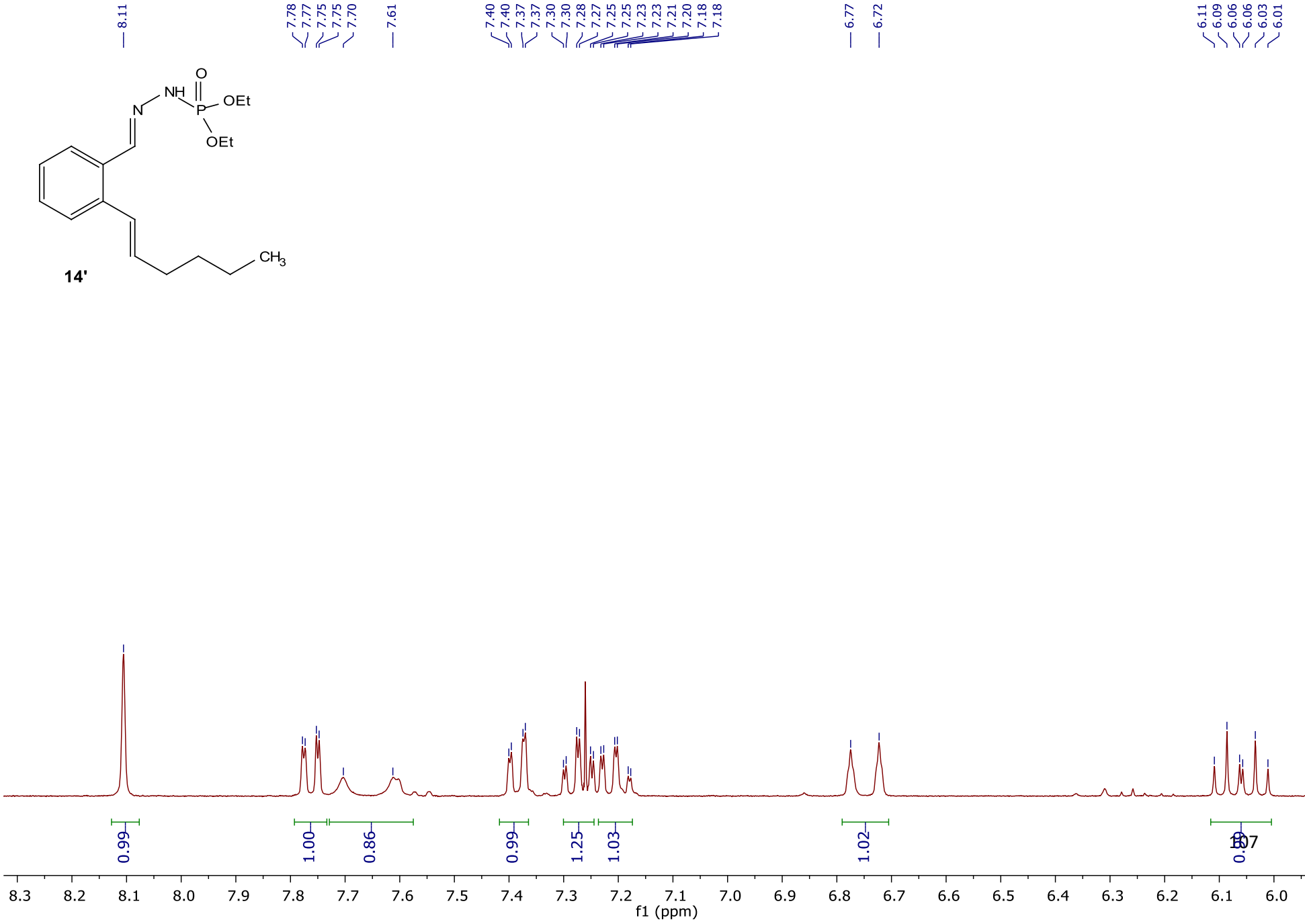
O
NH
OEt
N
P
OEt
N

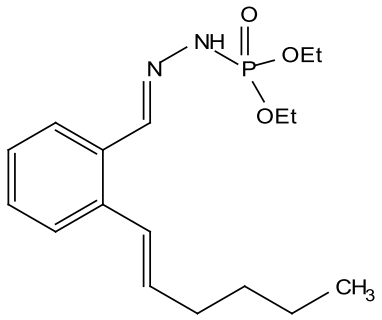
13'


1.40
106
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

O
NH
P
OEt
N
OEt
CH3

14'


8.11
7.78
7.77
7.75
7.75
7.70
7.61
7.40
7.40
7.37
7.37
7.30
7.30
7.28
7.27
7.25
7.25
7.23
7.23
7.21
7.20
7.18
7.18
6.77
6.72
6.11
6.09
6.06
6.06
6.03
6.01
0.99
1.00
0.86
0.99
1.25
1.03
1.02
0.
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
f1 (ppm)



14'

143.5
143.4
137.3
135.2
130.8
129.2
126.9
126.9
126.6
126.5
63.5
63.4
33.1
31.4
22.3
16.2
16.2
14.0

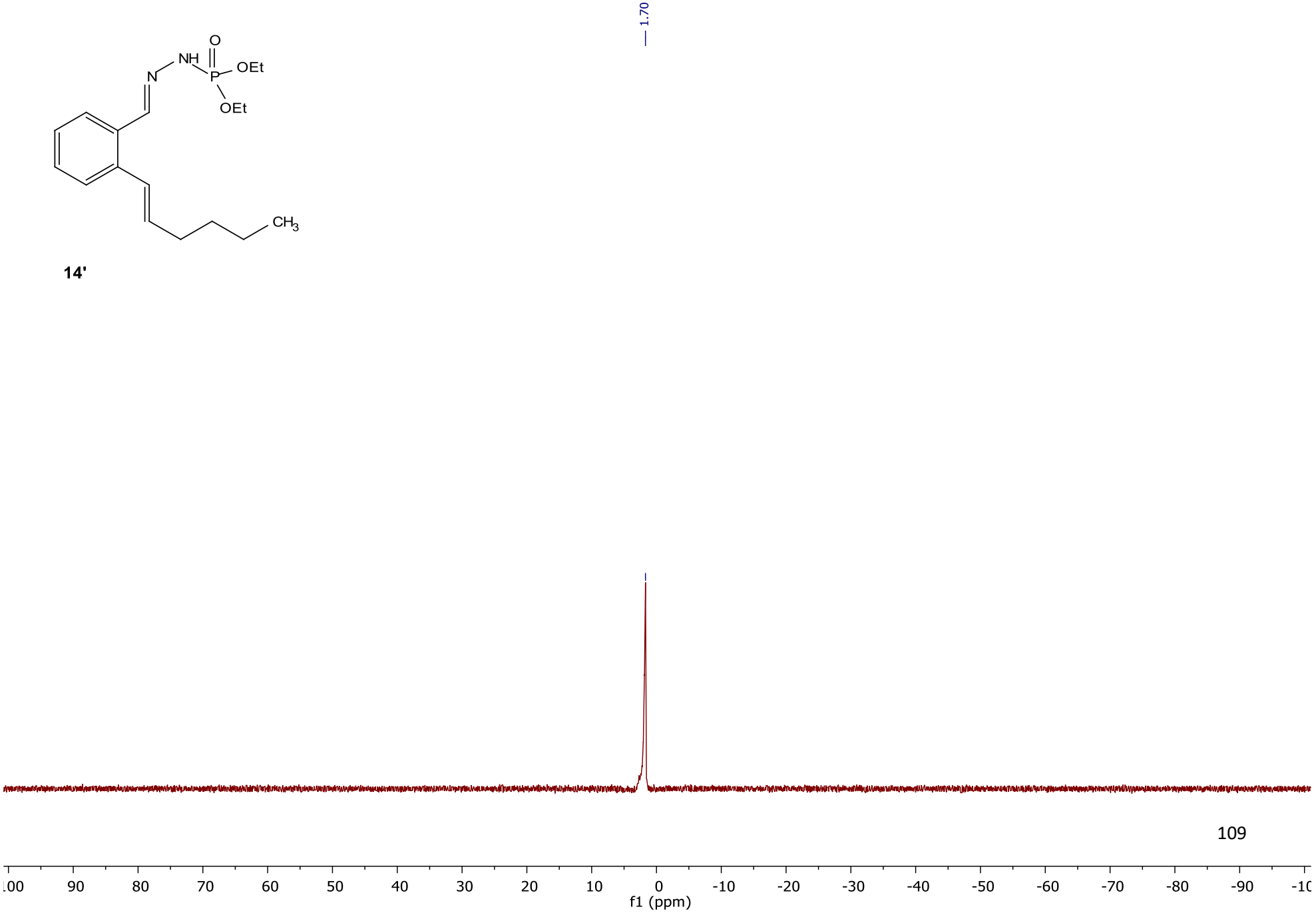
108

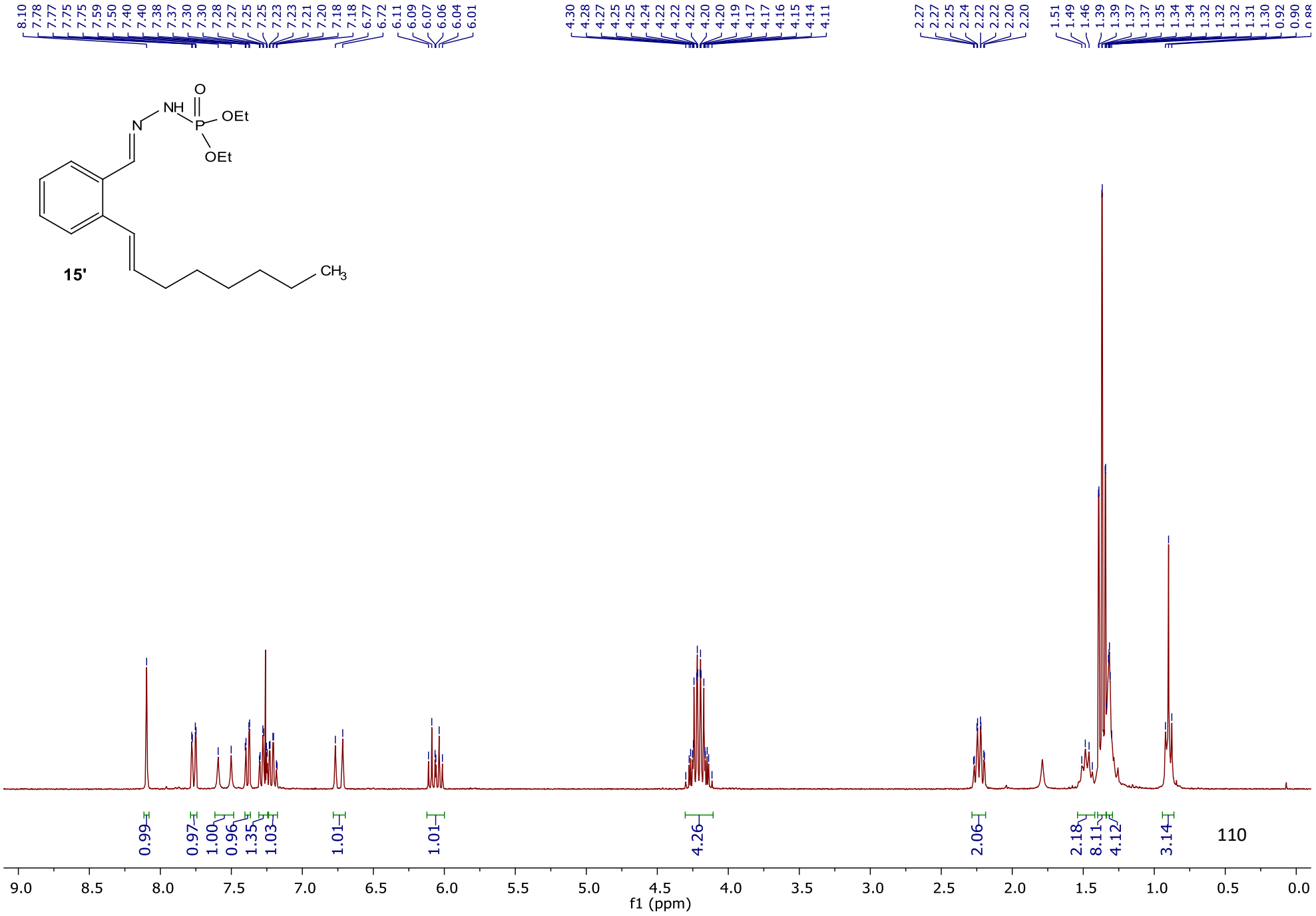
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

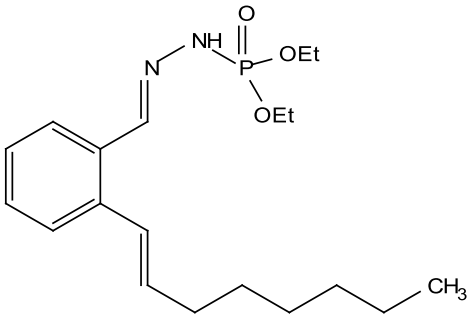
f1 (ppm)

O
NH
N
P
OEt
OEt
CH3

14'


1.70
109
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


8.10 7.78 7.77 7.75 7.75 7.59 7.50 7.40 7.40 7.38 7.37 7.30 7.30 7.28 7.27 7.25 7.25 7.23 7.23 7.21 7.20 7.18 7.18 6.77 6.72 6.11 6.09 6.07 6.06 6.04 6.01
4.30 4.28 4.27 4.25 4.25 4.24 4.22 4.22 4.22 4.20 4.20 4.19 4.17 4.17 4.16 4.15 4.14 4.11
2.27 2.27 2.25 2.24 2.22 2.22 2.20 2.20
1.51 1.49 1.46 1.39 1.39 1.37 1.37 1.35 1.34 1.34 1.32 1.32 1.31 1.30 0.92 0.90
O
NH
P
OEt
OEt
N
CH3
15'
0.99 0.97 1.00 0.96 1.35 1.03 1.01 1.01 4.26 2.06 2.18 8.11 4.12 3.14
110
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



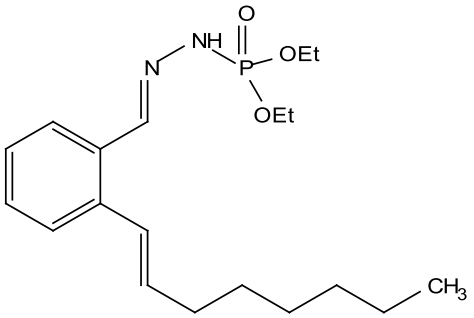
15'

143.5
143.3
137.3
135.3
130.9
129.3
127.0
126.9
126.6
126.4
63.5
63.4
33.4
31.8
29.3
29.0
22.7
16.3
16.2
14.1

111

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

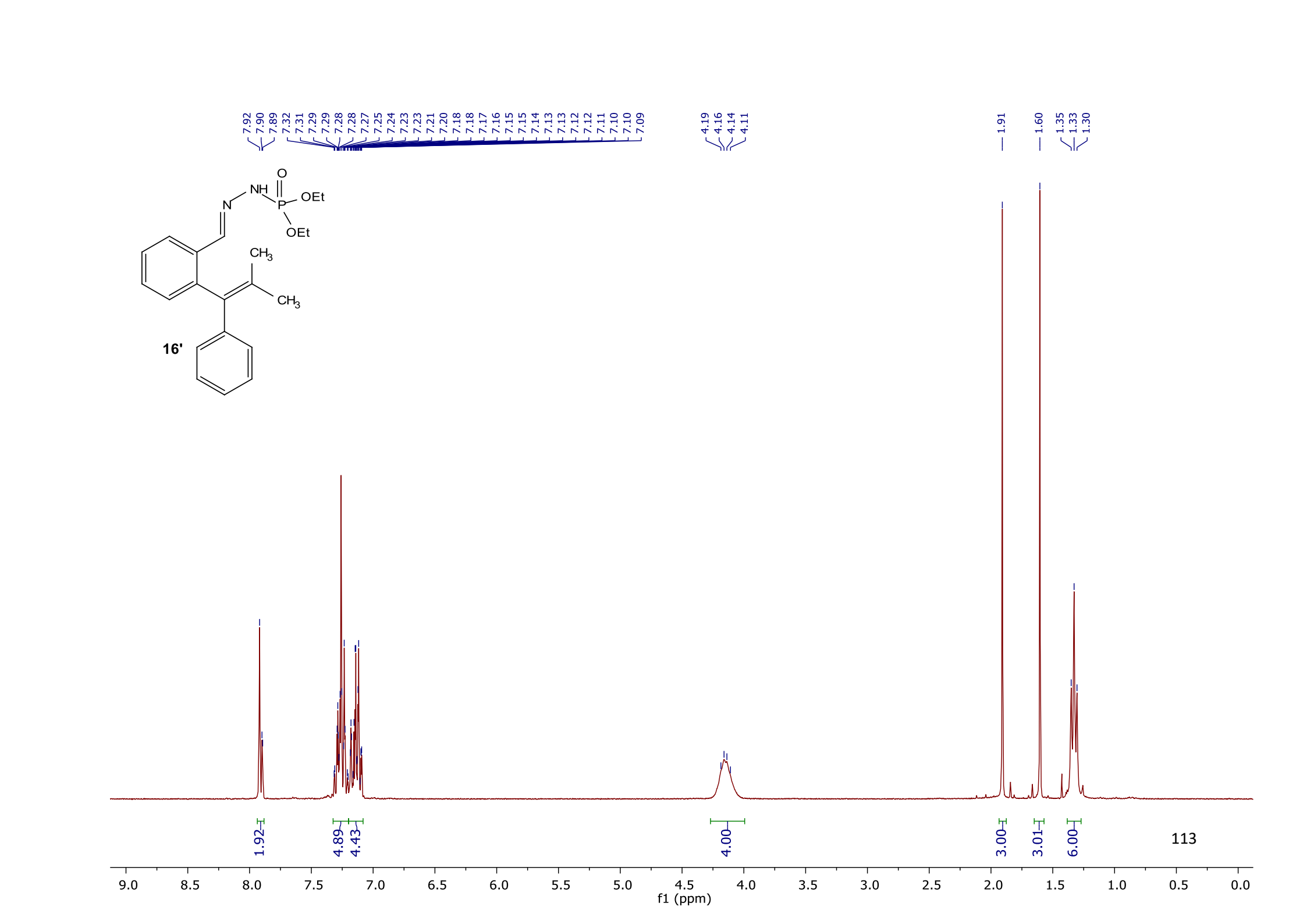


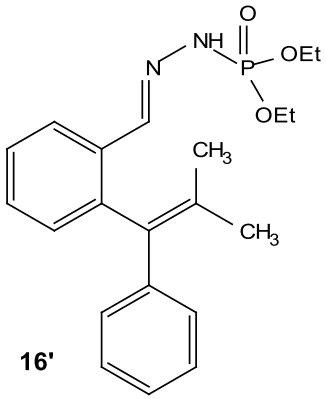
15'

1.31

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

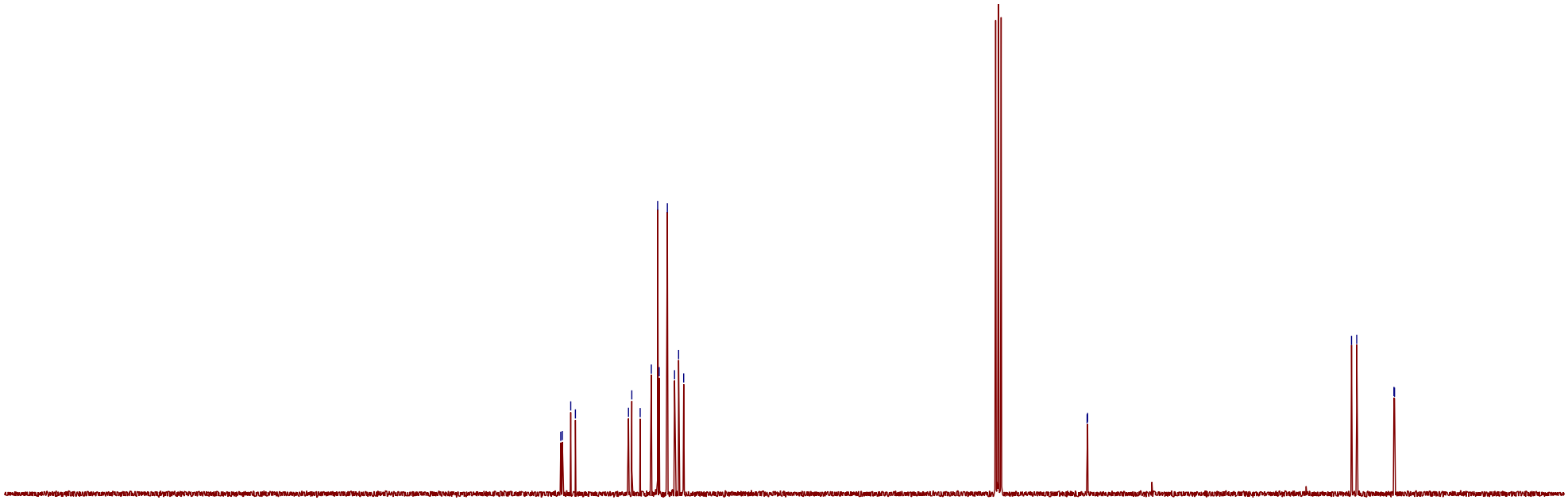
f1 (ppm)


7.92
7.90
7.89
7.32
7.31
7.29
7.29
7.28
7.28
7.27
7.25
7.24
7.23
7.23
7.21
7.20
7.18
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
4.19
4.16
4.14
4.11
1.91
1.60
1.35
1.33
1.30
O
NH
P
OEt
OEt
N
CH3
CH3
16'
1.92
4.89
4.43
4.00
3.00
3.01
6.00
113
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

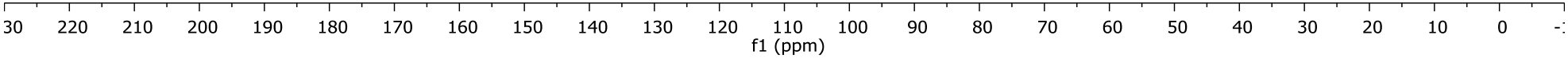


16'

144.4
144.2
142.9
142.2
134.0
133.5
132.2
130.5
129.5
129.3
128.0
126.9
126.3
125.5
63.4
63.4
22.8
22.0
16.2
16.1

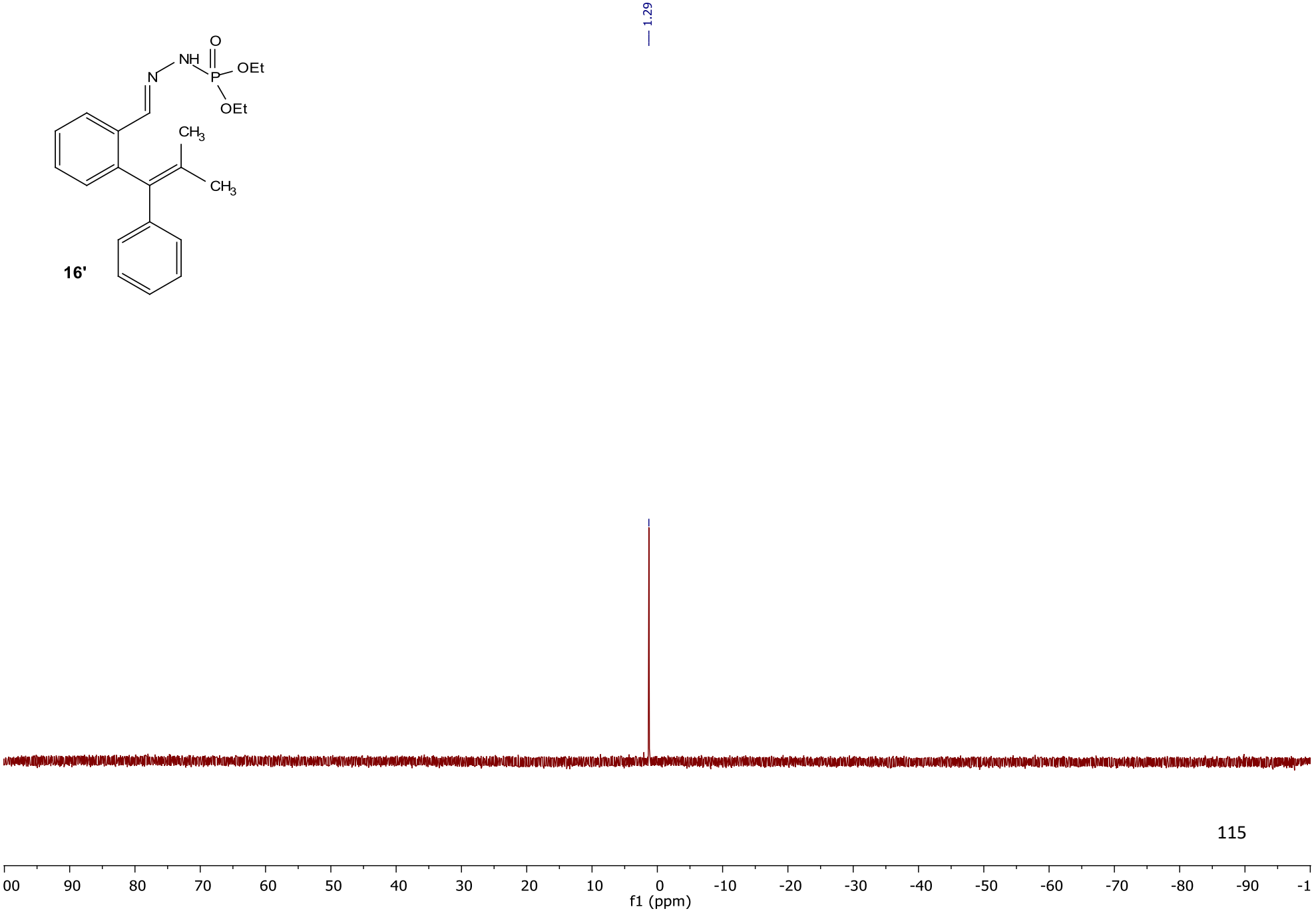


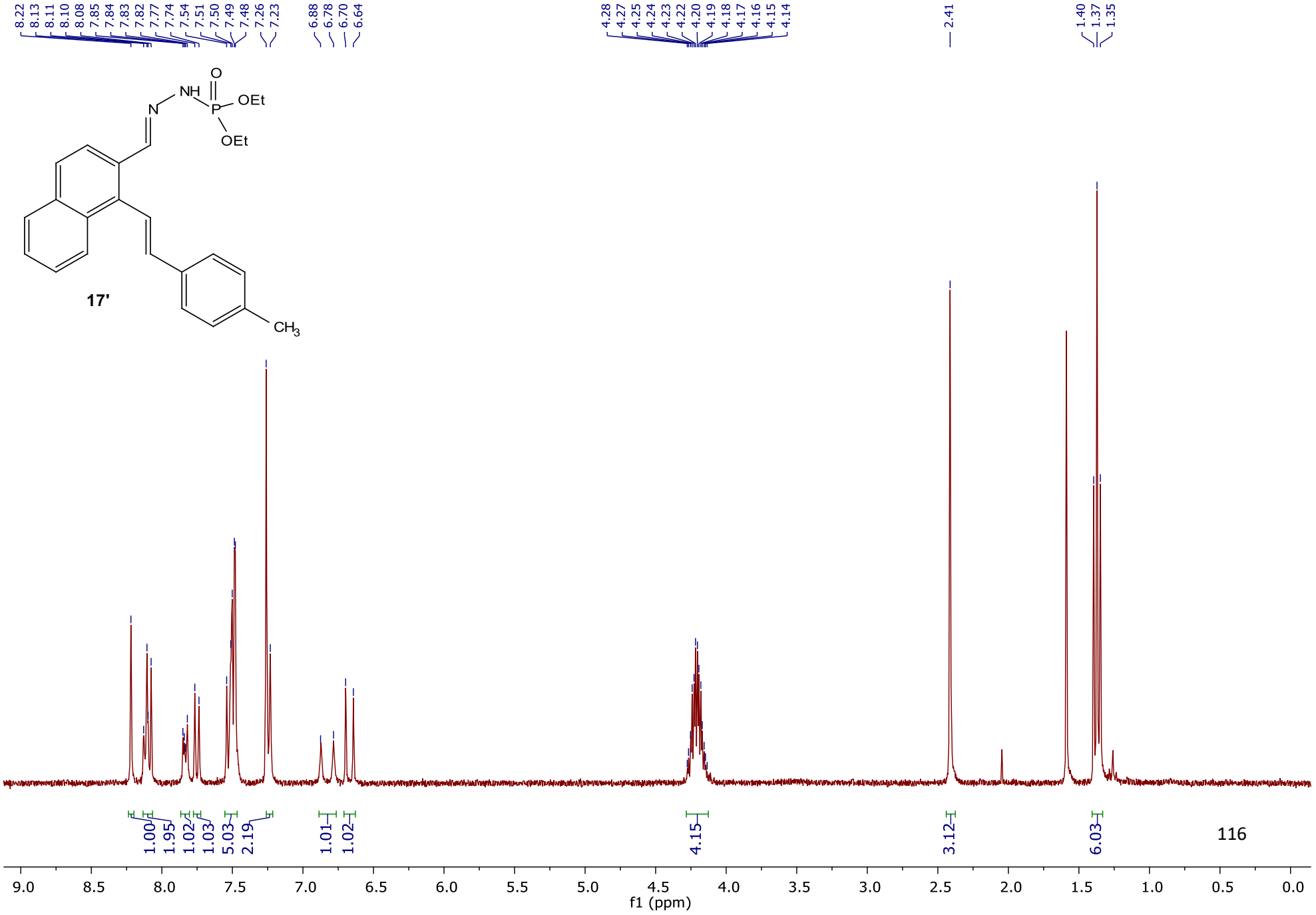
114



O
NH
N
P
OEt
OEt
CH3
CH3

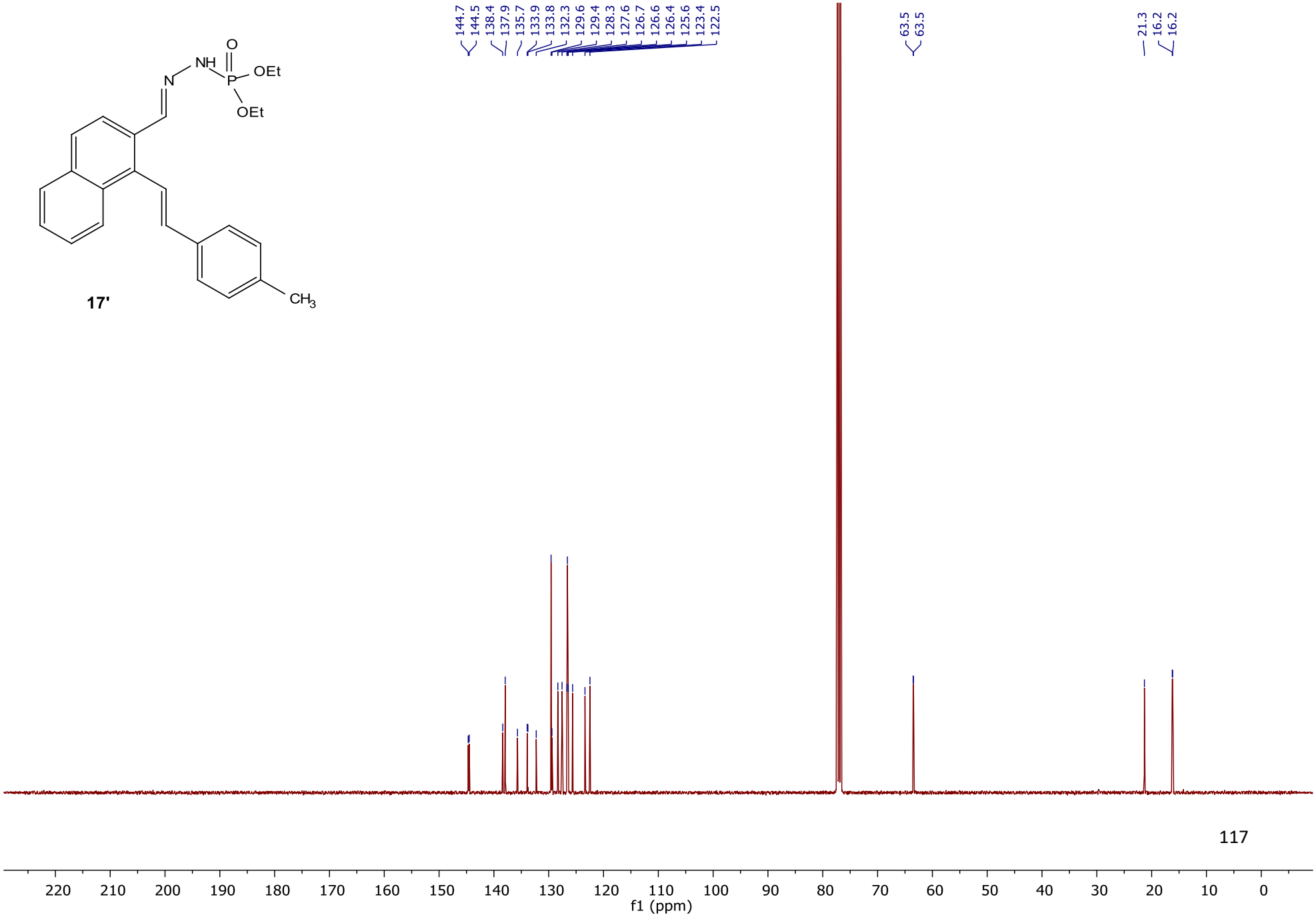
16'


1.29
115
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.22
8.13
8.11
8.10
8.08
7.85
7.84
7.83
7.82
7.77
7.74
7.54
7.51
7.50
7.49
7.48
7.26
7.23
6.88
6.78
6.70
6.64
4.28
4.27
4.25
4.24
4.23
4.22
4.20
4.19
4.18
4.17
4.16
4.15
4.14
2.41
1.40
1.37
1.35
NH
O
P
OEt
N
OEt
17'
CH3
1.00
1.95
1.02
1.03
5.03
2.19
1.01
1.02
4.15
3.12
6.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

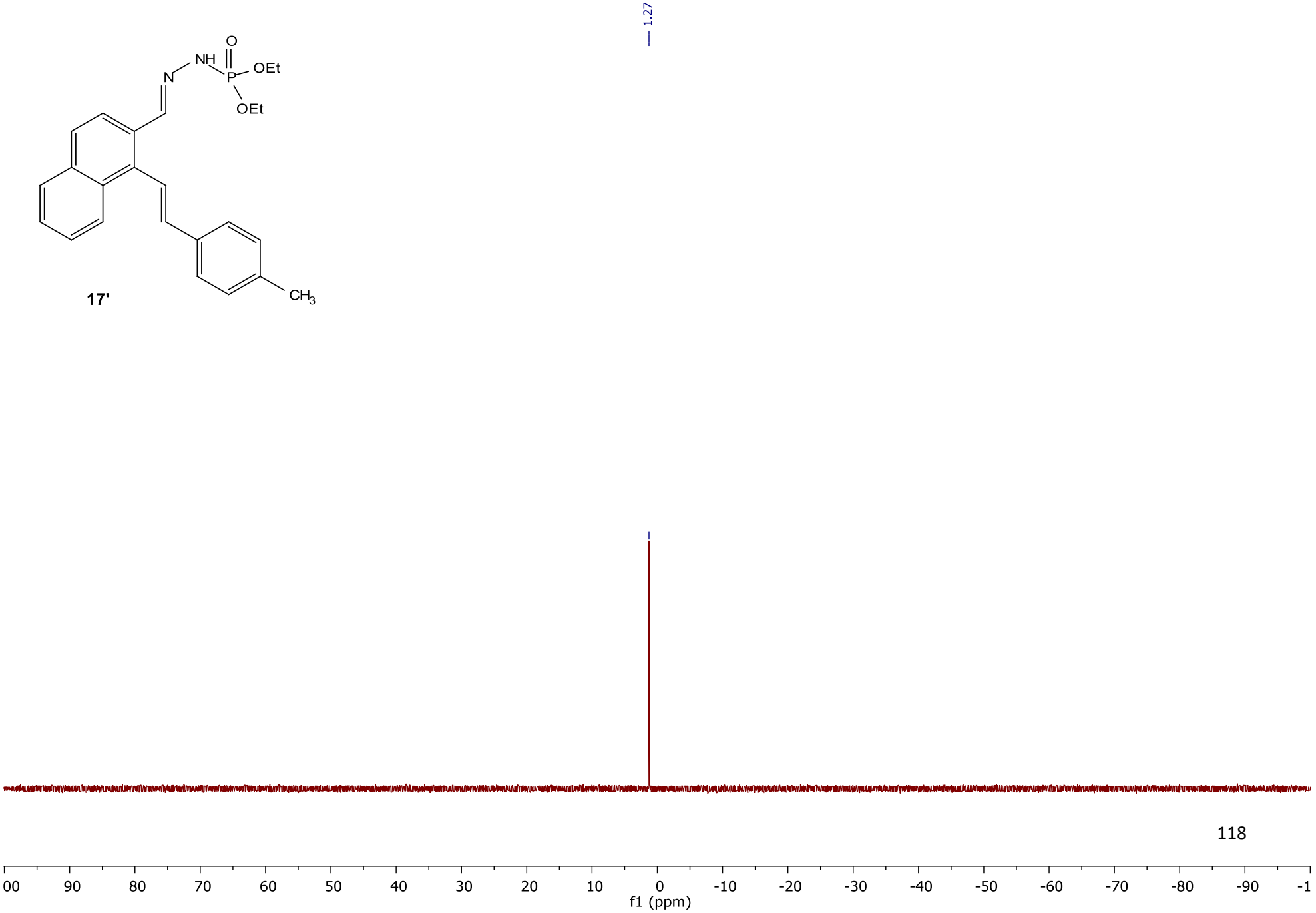
O
NH
N
P
OEt
OEt
CH3

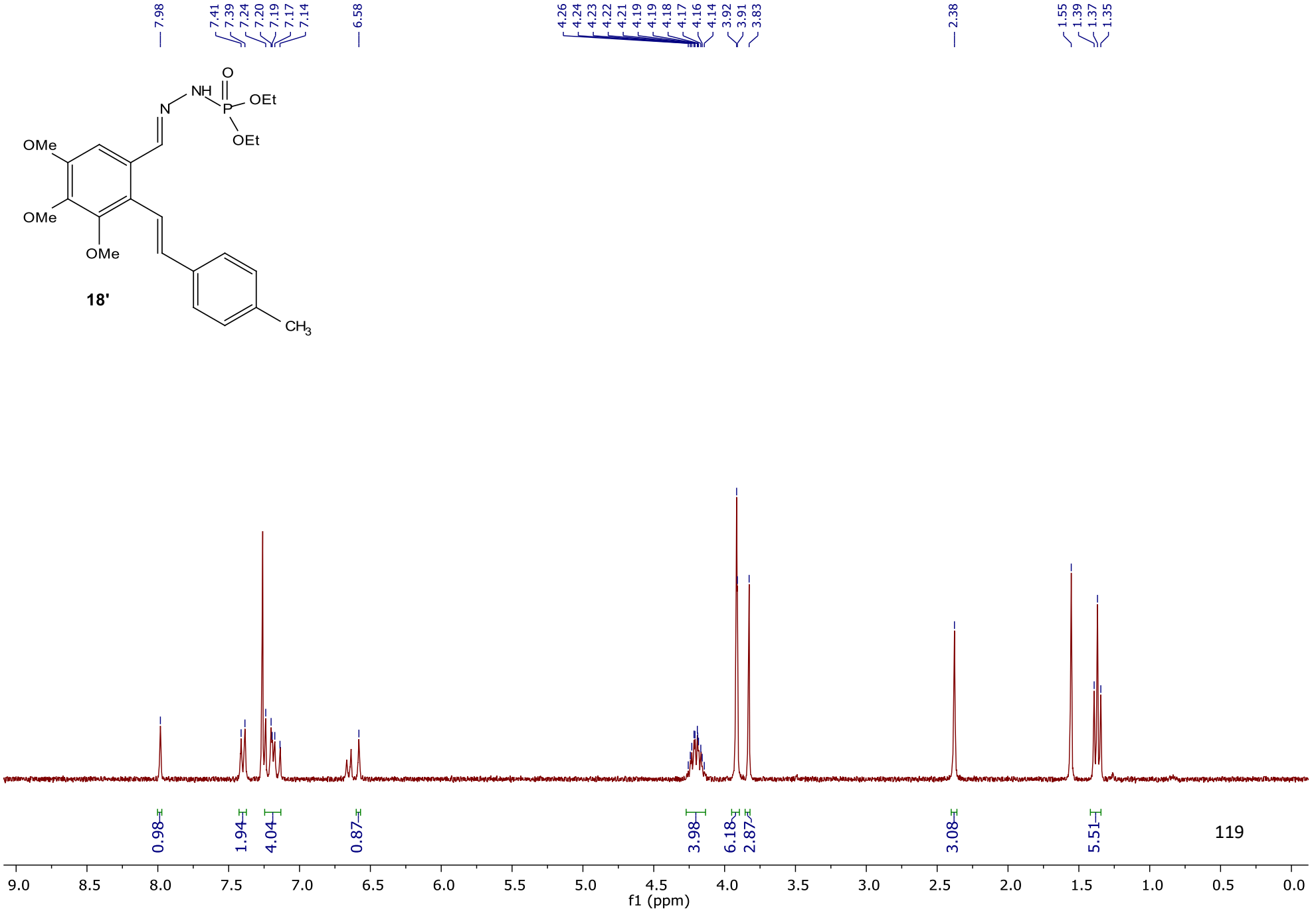
17'


144.7
144.5
138.4
137.9
135.7
133.9
133.8
132.3
129.6
129.4
128.3
127.6
126.7
126.6
126.4
125.6
123.4
122.5
63.5
63.5
21.3
16.2
16.2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
N
P
OEt
OEt
CH3

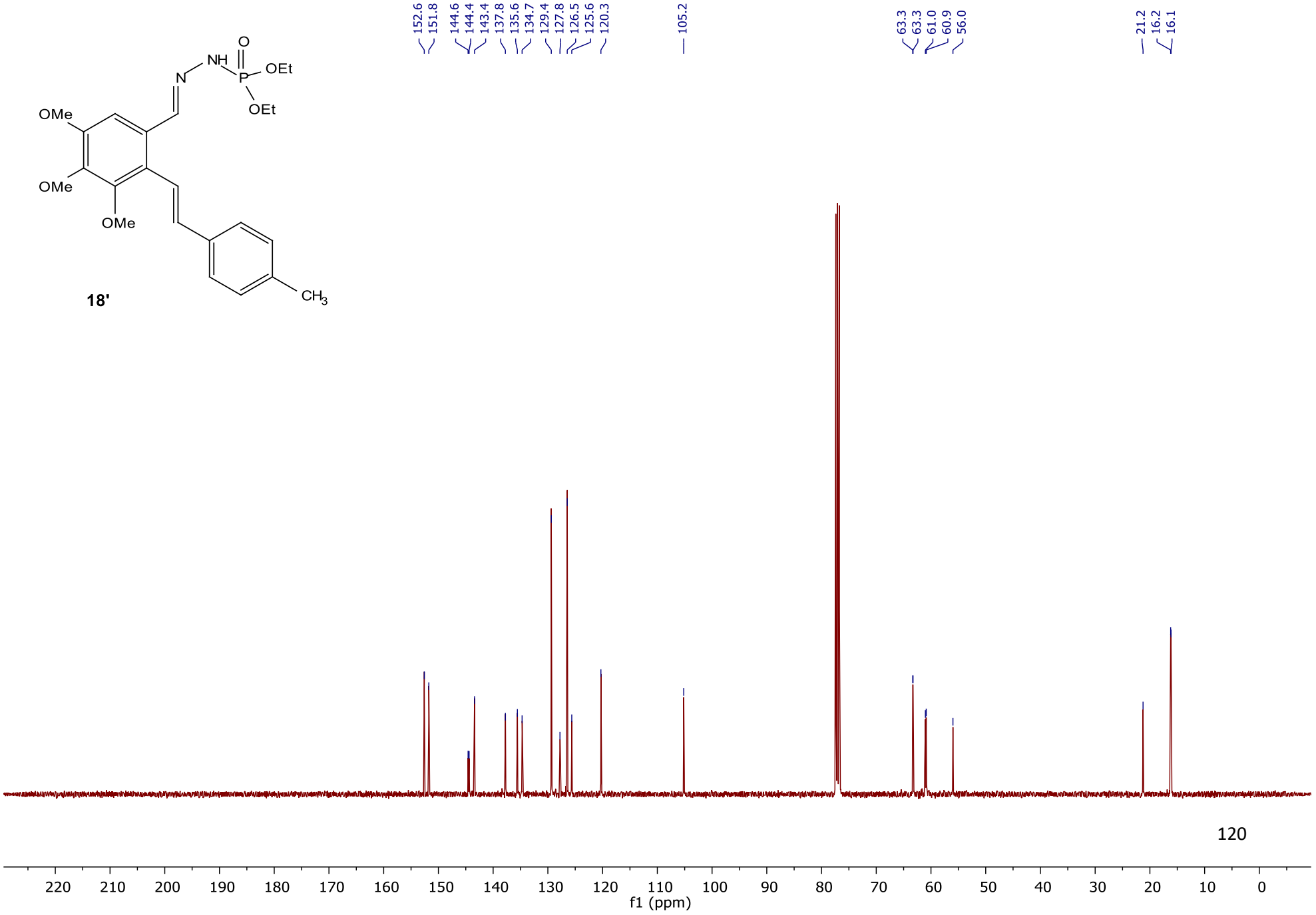
17'


1.27
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.98
7.41
7.39
7.24
7.20
7.19
7.17
7.14
6.58
4.26
4.24
4.23
4.22
4.21
4.19
4.19
4.18
4.17
4.16
4.14
3.92
3.91
3.83
2.38
1.55
1.39
1.37
1.35
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
18'
CH3
0.98
1.94
4.04
0.87
3.98
6.18
2.87
3.08
5.51
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

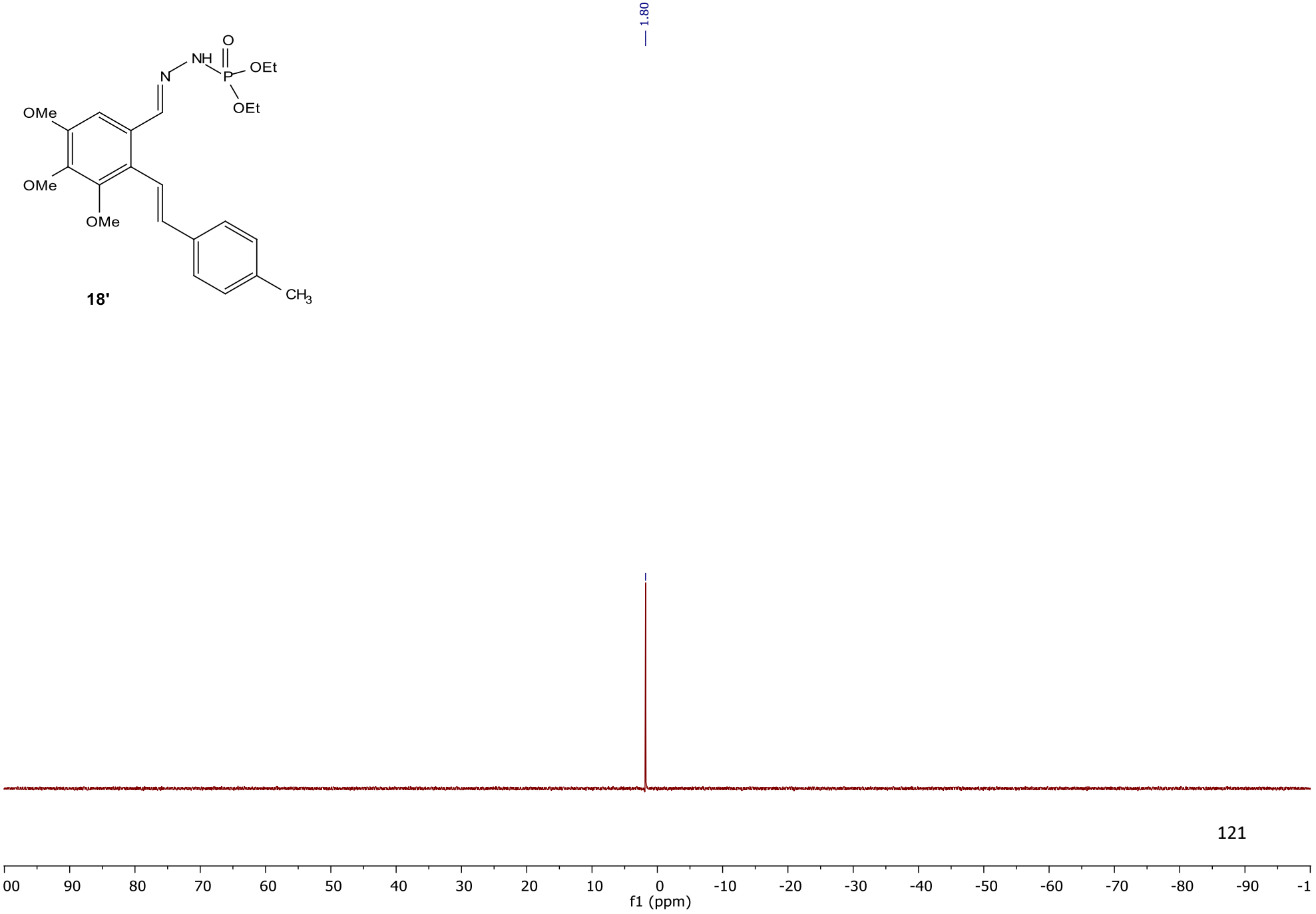
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
CH3

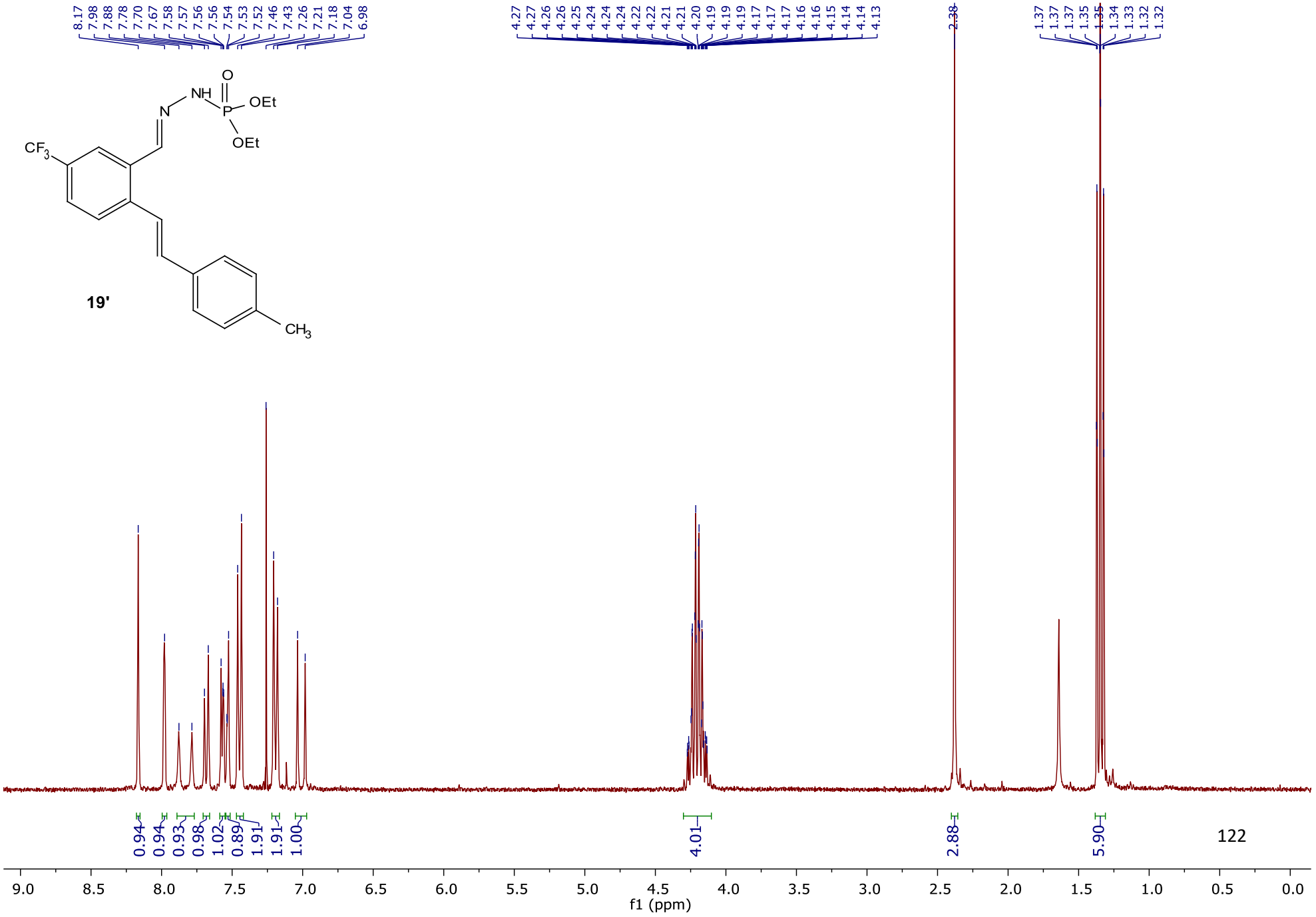
18'

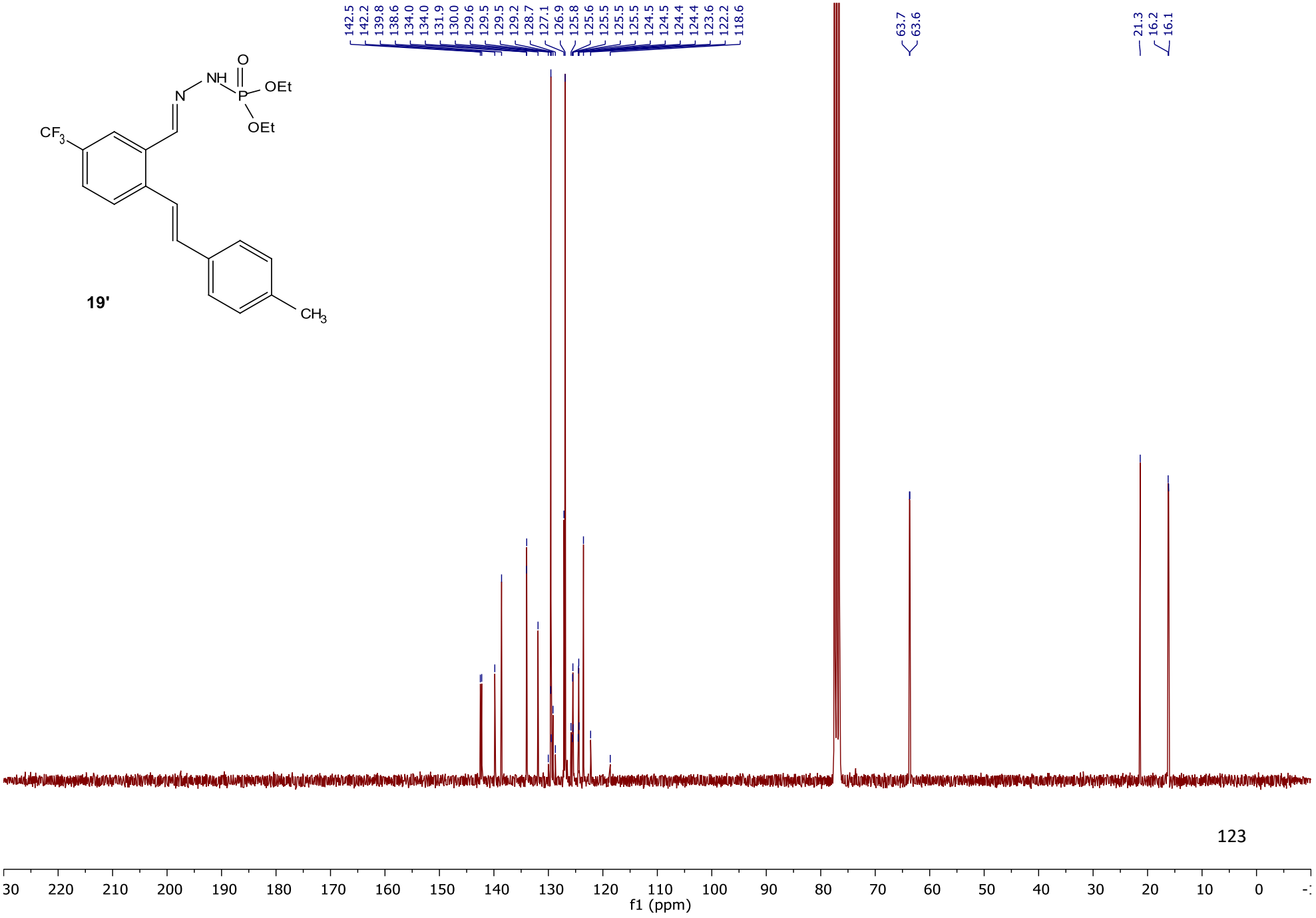

152.6
151.8
144.6
144.4
143.4
137.8
135.6
134.7
129.4
127.8
126.5
125.6
120.3
105.2
63.3
63.3
61.0
60.9
56.0
21.2
16.2
16.1
120
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
N
P
OEt
OEt
OMe
OMe
OMe
CH3

18'


1.80
121
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

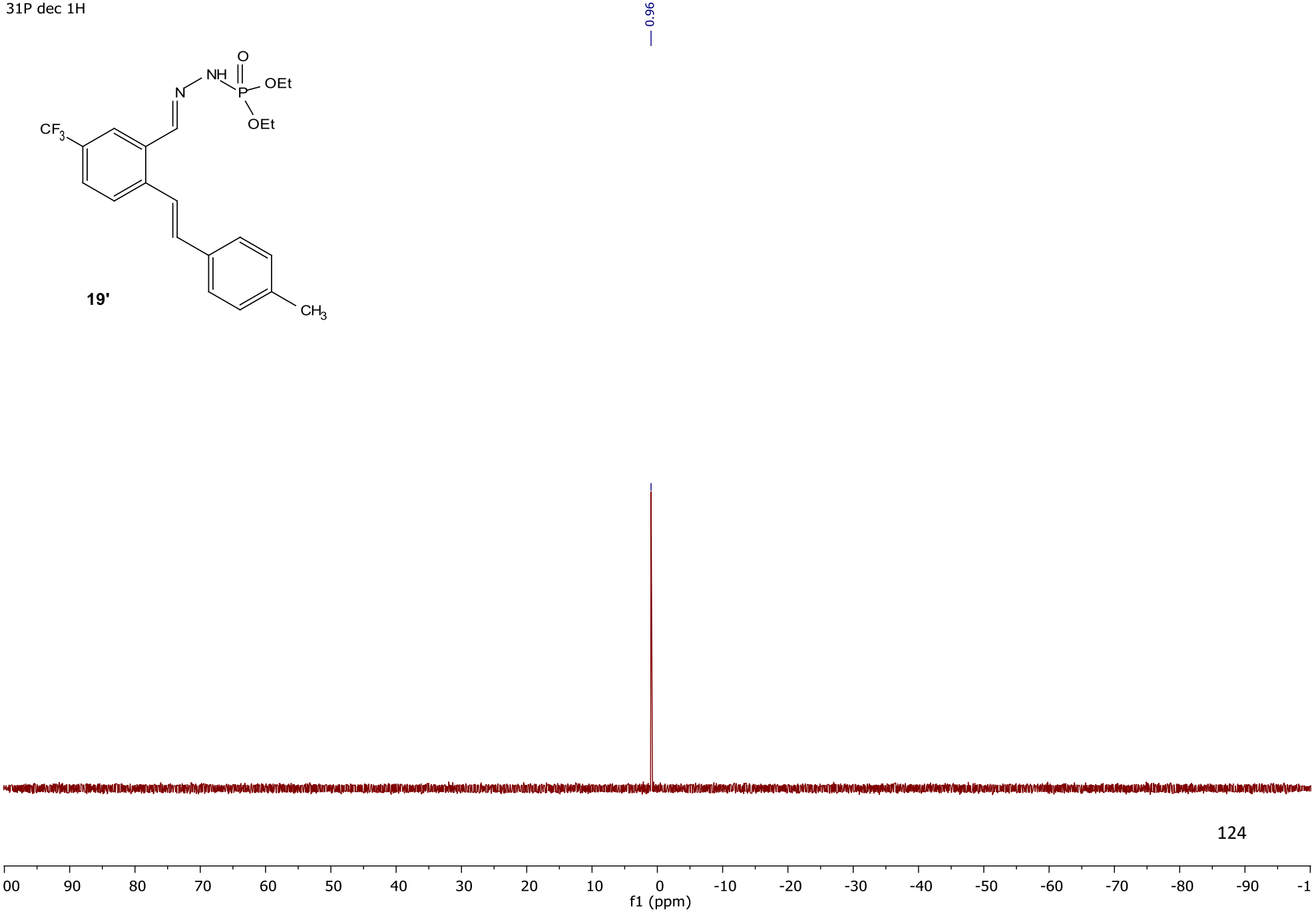

8.17 7.98 7.88 7.78 7.70 7.67 7.58 7.57 7.56 7.56 7.54 7.53 7.52 7.46 7.43 7.26 7.21 7.18 7.04 6.98
4.27 4.27 4.26 4.26 4.25 4.24 4.24 4.24 4.22 4.22 4.21 4.21 4.20 4.19 4.19 4.19 4.17 4.17 4.16 4.16 4.15 4.14 4.14 4.13
2.38
1.37 1.37 1.37 1.35 1.35 1.34 1.33 1.32 1.32
O
NH
N
P
OEt
OEt
CF3
CH3
19'
0.94 0.94 0.93 0.98 1.02 0.89 1.91 1.91 1.00
4.01
2.88
5.90
122
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.5
142.2
139.8
138.6
134.0
134.0
131.9
130.0
129.6
129.5
129.5
129.2
128.7
127.1
126.9
125.8
125.6
125.5
125.5
125.5
124.5
124.5
124.4
124.4
123.6
122.2
118.6
63.7
63.6
21.3
16.2
16.1
NH
O
OEt
N
P
OEt
CF3
CH3
19'
123
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

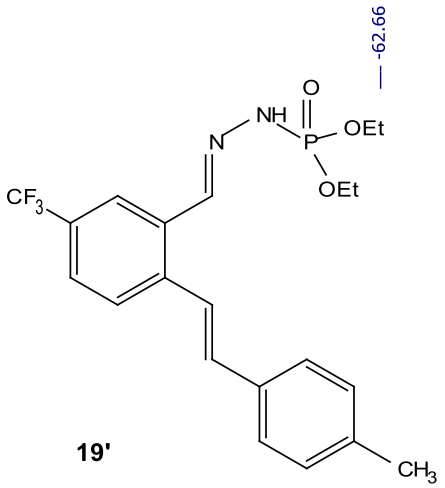
31P dec 1H

O
NH
N
P
OEt
OEt
CF3
CH3

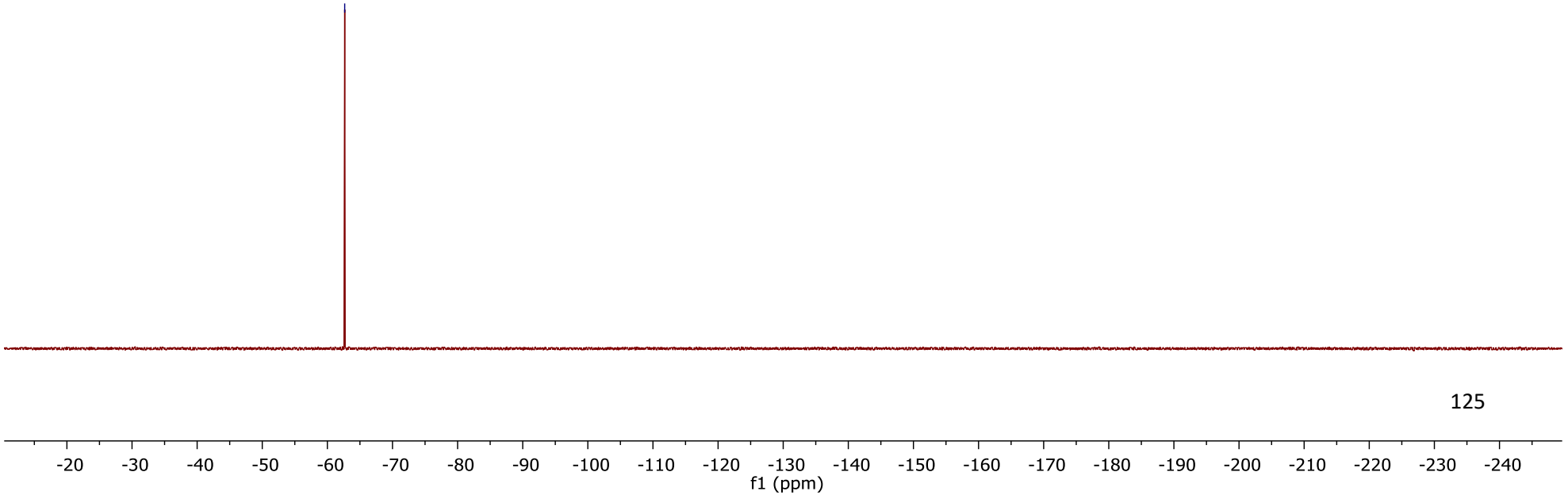
19'

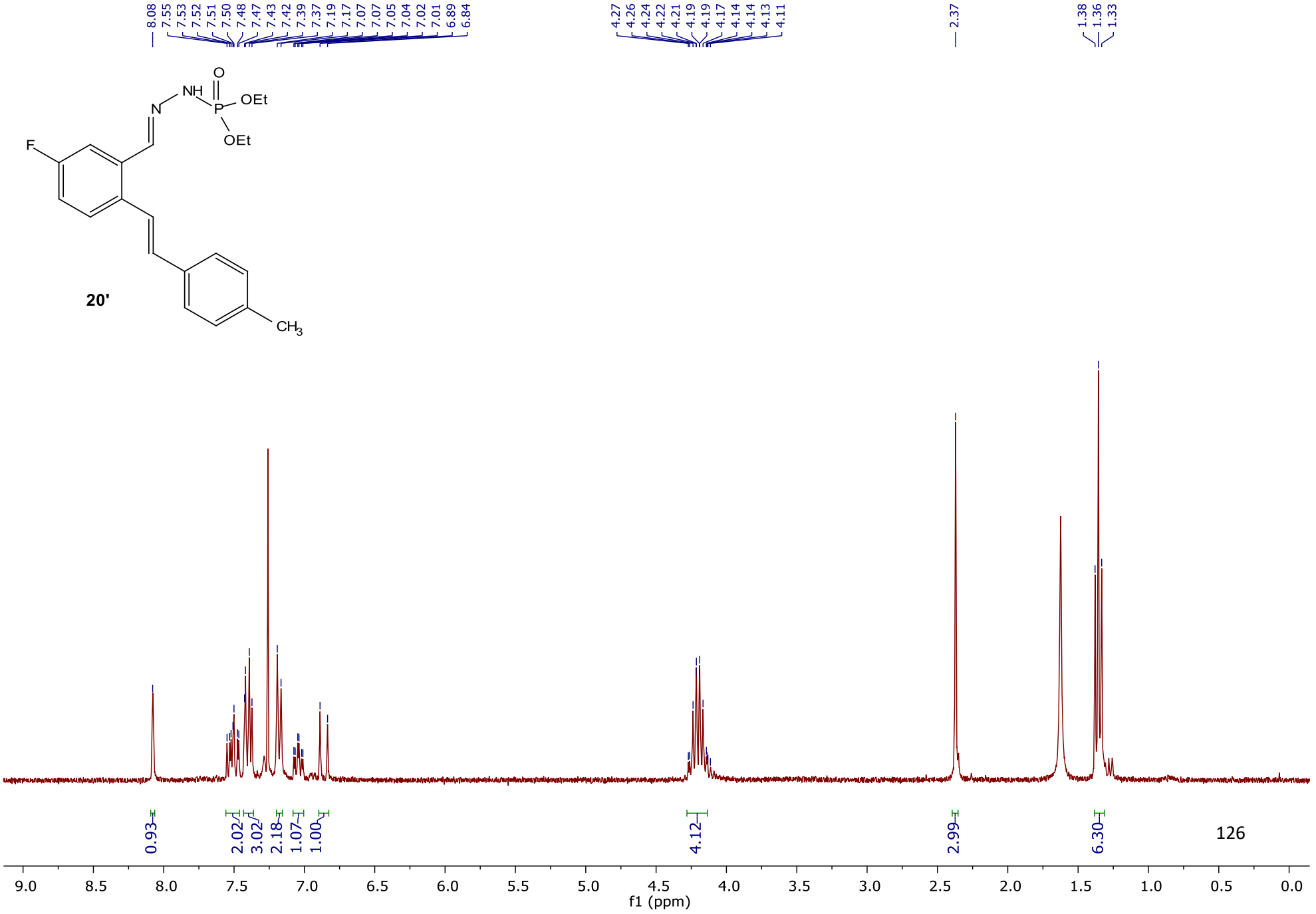

0.96
124
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

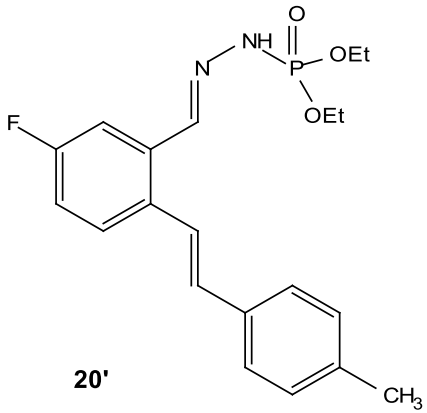
19F


-62.66
O
NH
N
P
OEt
OEt
CF3
CH3

19'


125
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


8.08
7.55
7.53
7.52
7.51
7.50
7.48
7.47
7.43
7.42
7.39
7.37
7.19
7.17
7.07
7.07
7.05
7.04
7.02
7.01
6.89
6.84
4.27
4.26
4.24
4.22
4.21
4.19
4.19
4.17
4.14
4.14
4.13
4.11
2.37
1.38
1.36
1.33
O
NH
N
P
OEt
OEt
F
CH3
20'
0.93
2.02
3.02
2.18
1.07
1.00
4.12
2.99
6.30
126
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



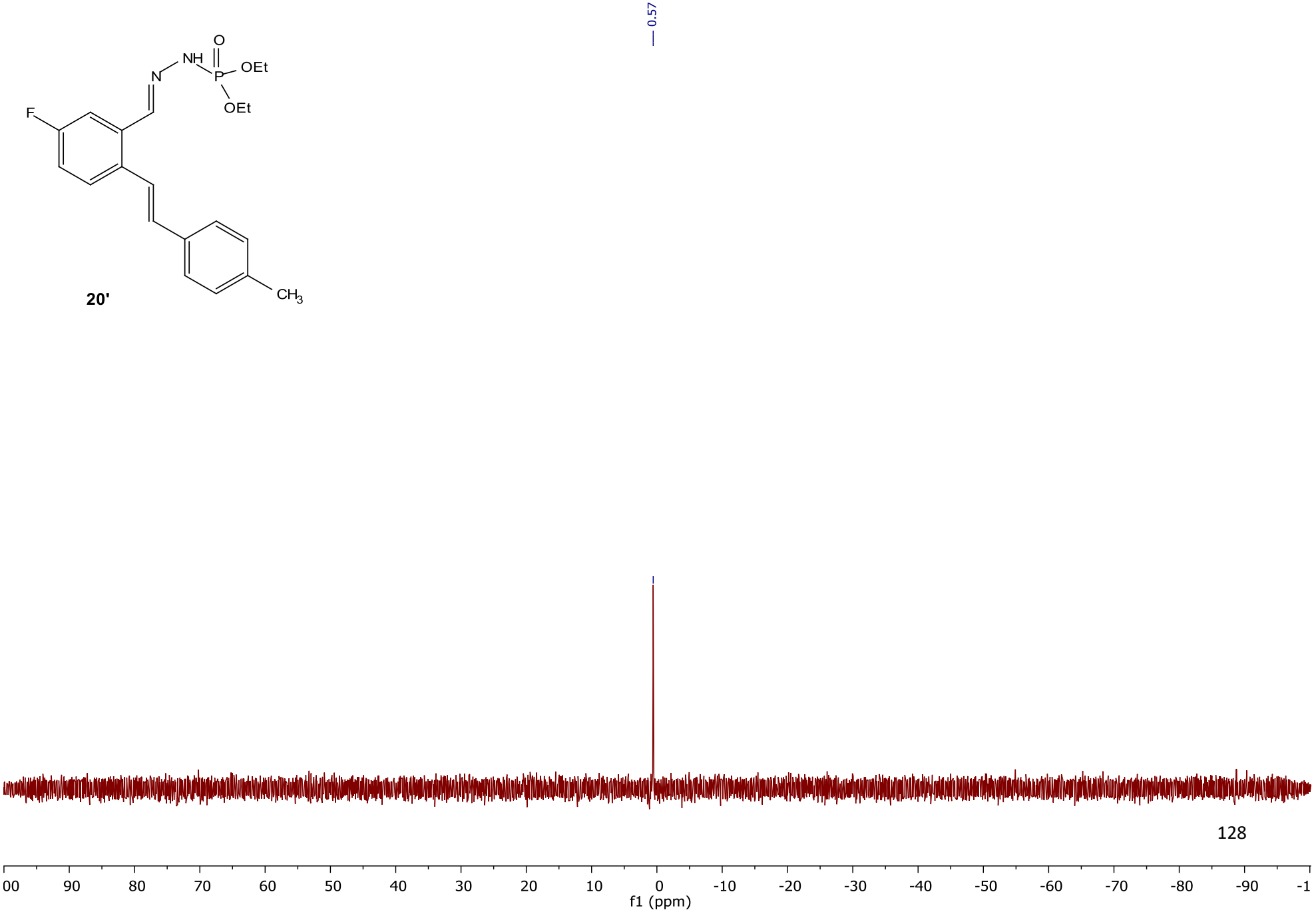
20'

163.75
160.49
142.64
142.38
137.92
134.47
133.61
133.50
132.94
132.89
131.87
129.46
128.56
128.45
126.65
123.70
116.64
116.35
113.20
112.90
63.61
63.54
21.31
16.24
16.15

f1 (ppm)

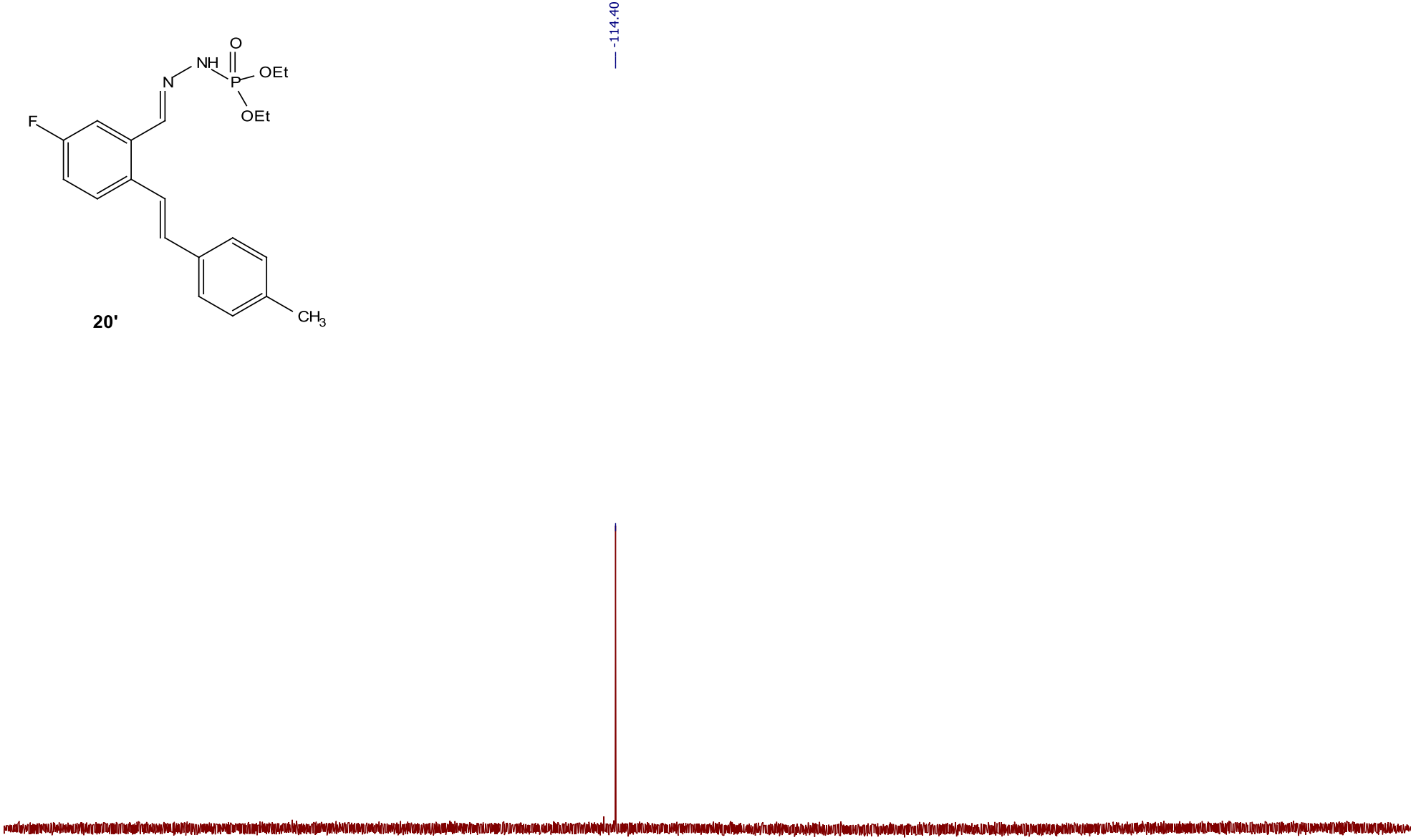
O
NH
N
P
OEt
OEt
F
CH3

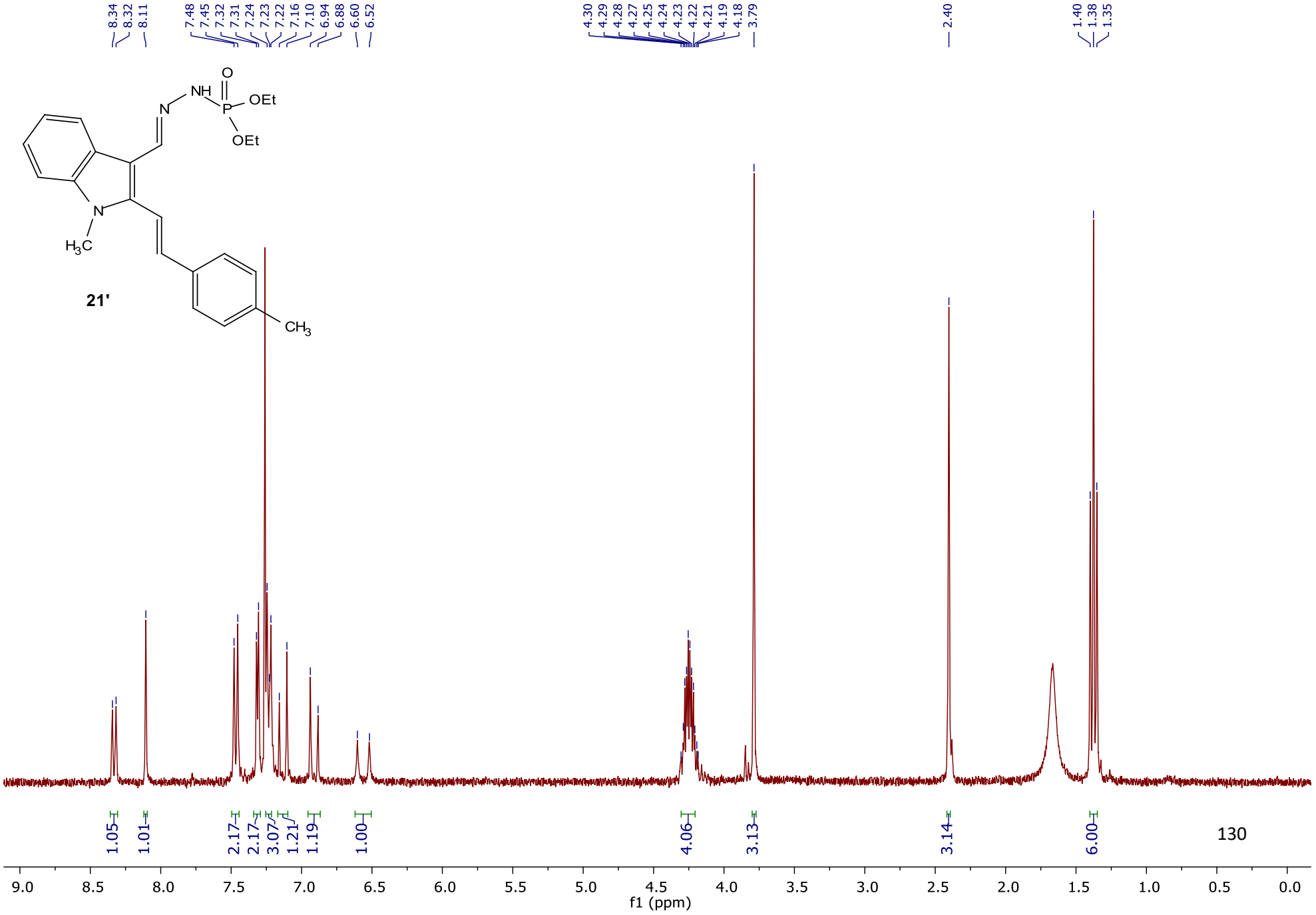
20'

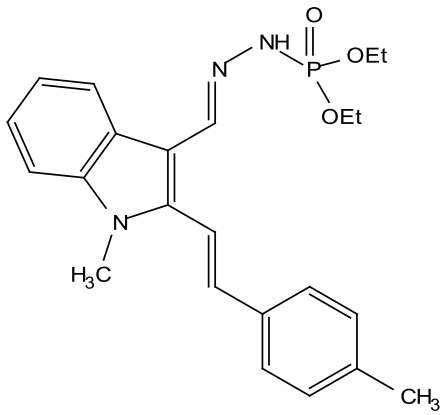

0.57
128
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

O
NH
N
P
OEt
OEt
F
CH3

20'

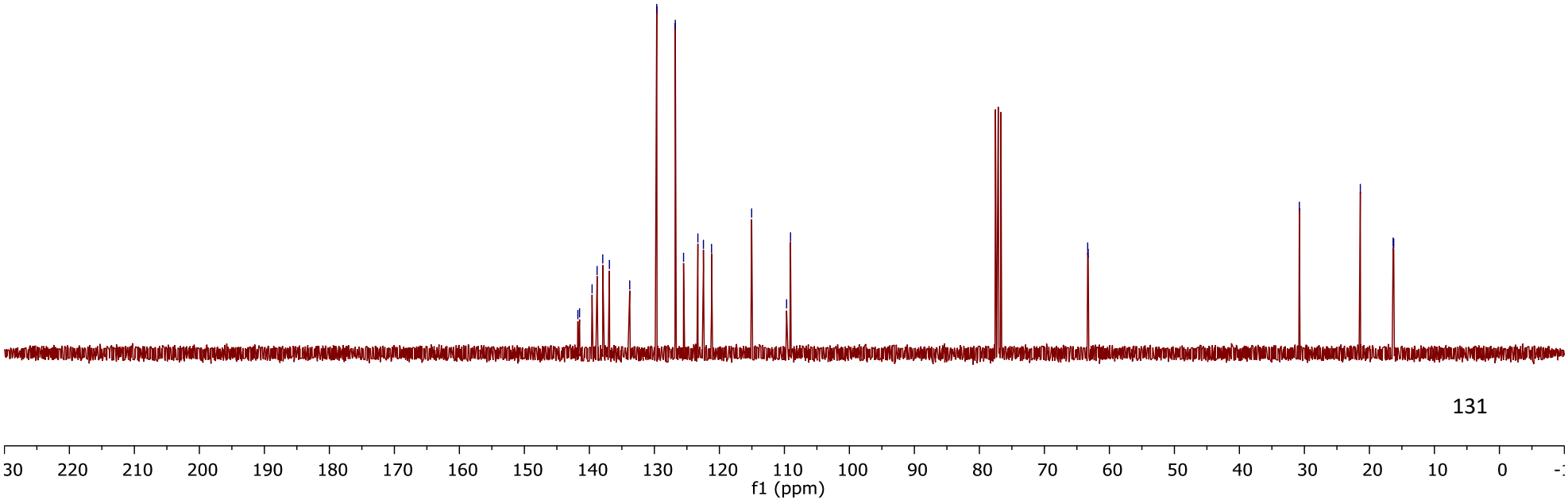

-114.40
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


8.34
8.32
8.11
7.48
7.45
7.32
7.31
7.24
7.23
7.22
7.16
7.10
6.94
6.88
6.60
6.52
4.30
4.29
4.28
4.27
4.25
4.24
4.23
4.22
4.21
4.19
4.18
3.79
2.40
1.40
1.38
1.35
O
NH
N
P
OEt
OEt
N
H3C
21'
CH3
1.05
1.01
2.17
2.17
3.07
1.21
1.19
1.00
4.06
3.13
3.14
6.00
130
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



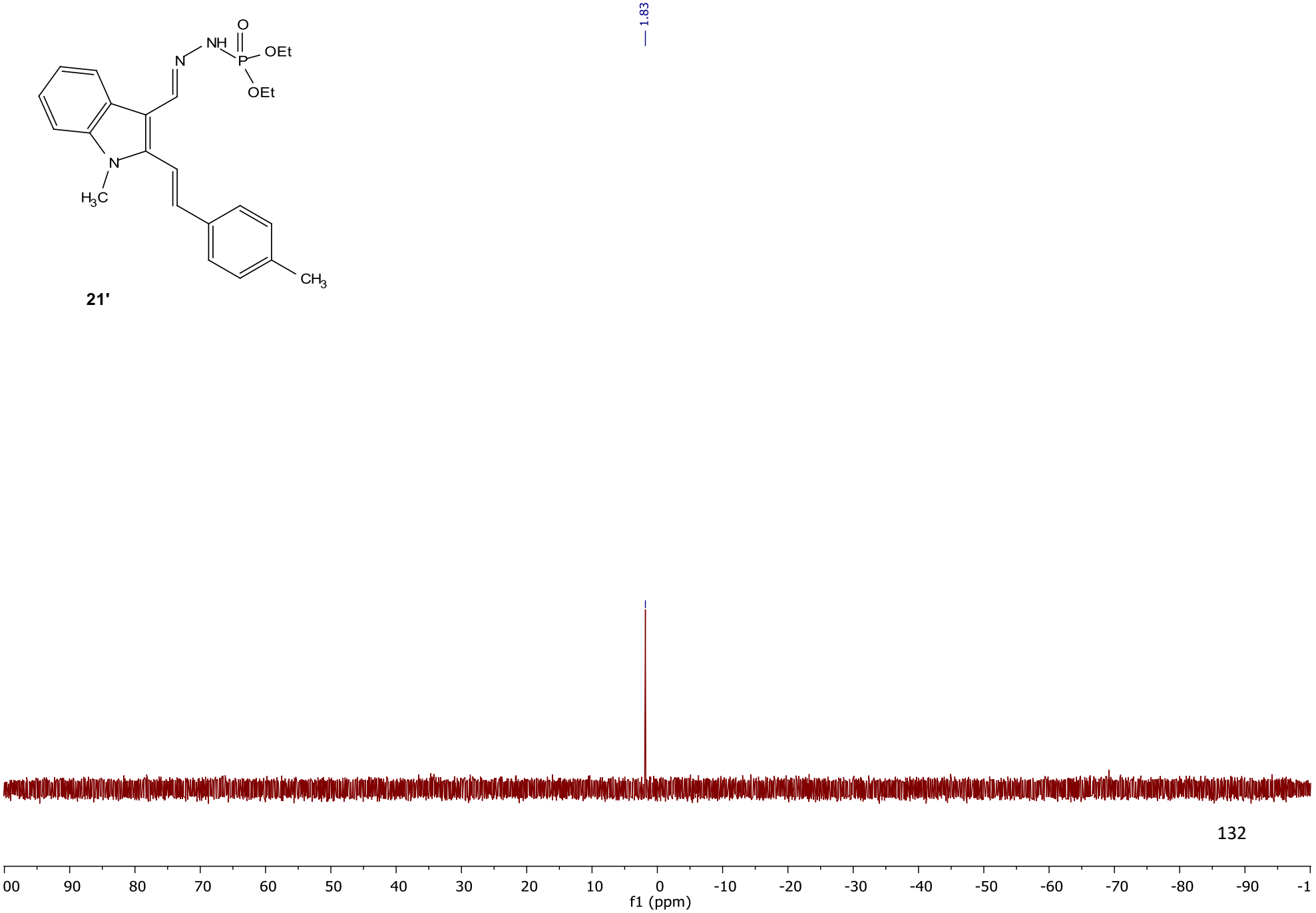
21'

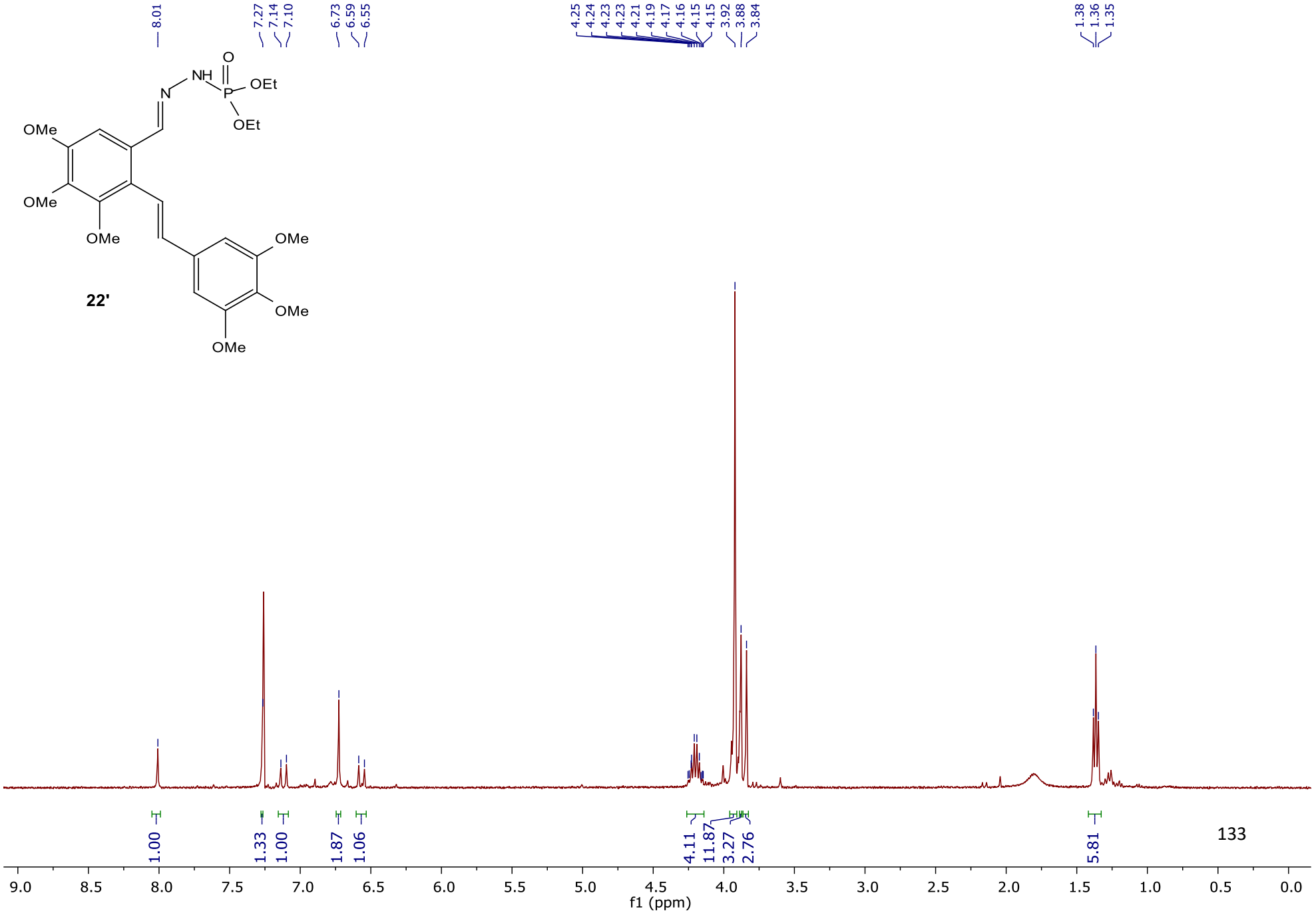
141.8
141.5
139.6
138.8
137.9
136.9
133.8
129.6
126.8
125.5
123.3
122.5
121.2
115.0
109.7
109.1
63.3
63.3
30.8
21.4
16.4
16.3

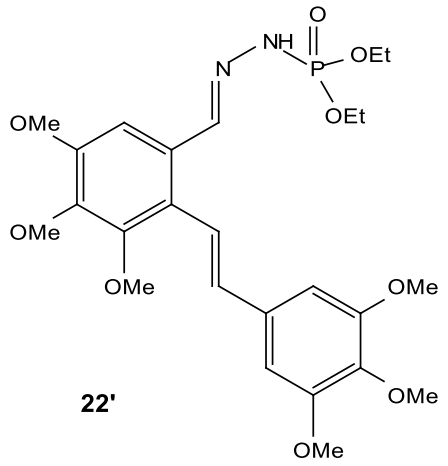


O
NH
N
P
OEt
OEt
N
H3C
CH3

21'

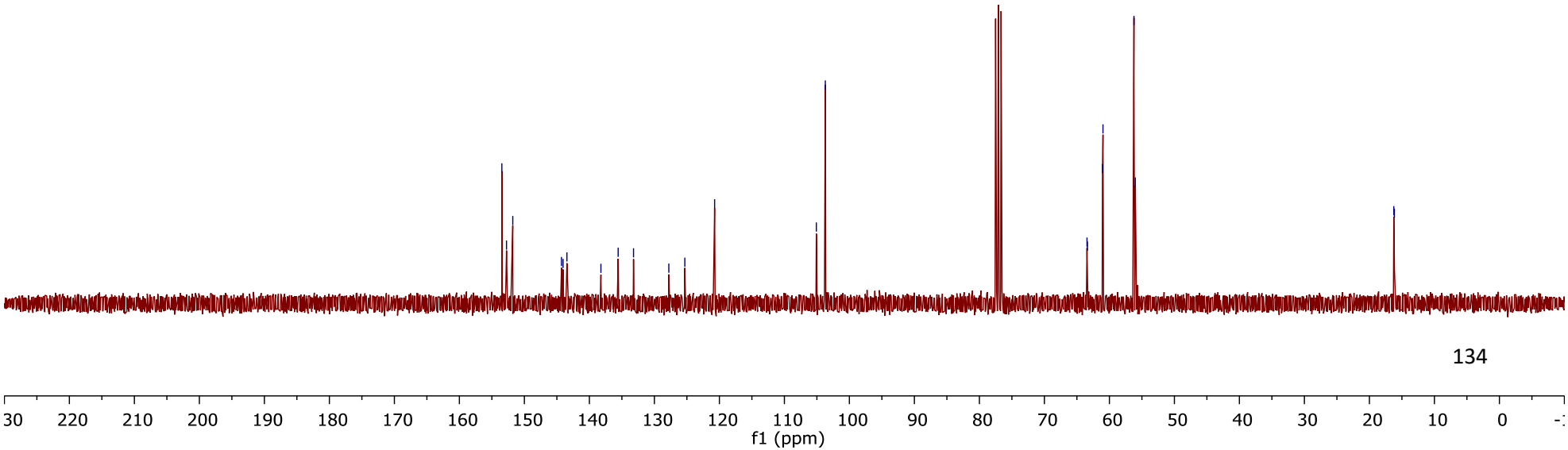

1.83
132
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.01
7.27
7.14
7.10
6.73
6.59
6.55
4.25
4.24
4.23
4.23
4.21
4.19
4.17
4.16
4.15
4.15
3.92
3.88
3.84
1.38
1.36
1.35
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
OMe
OMe
OMe
22'
1.00
1.33
1.00
1.87
1.06
4.11
11.87
3.27
2.76
5.81
133
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



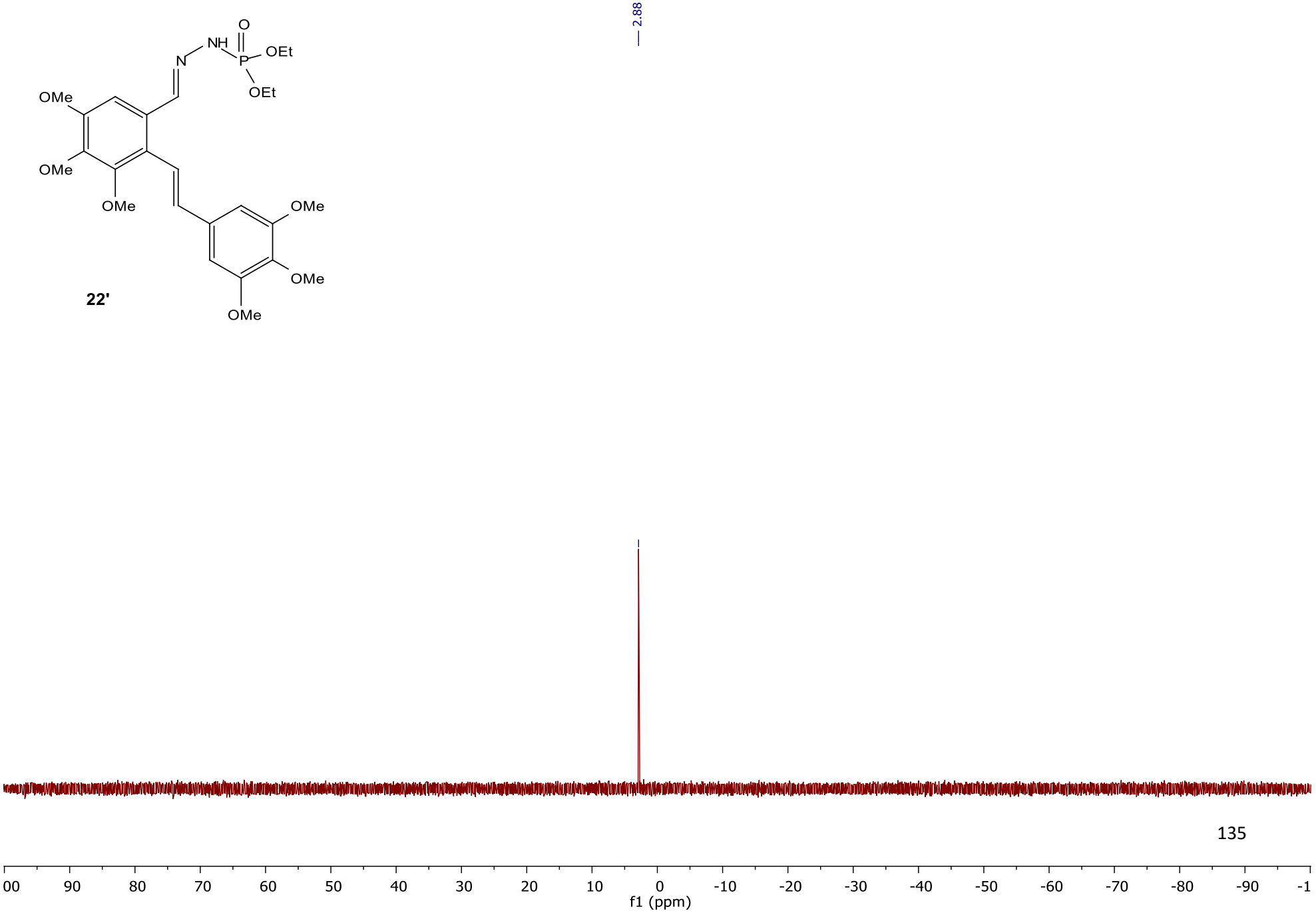
22'

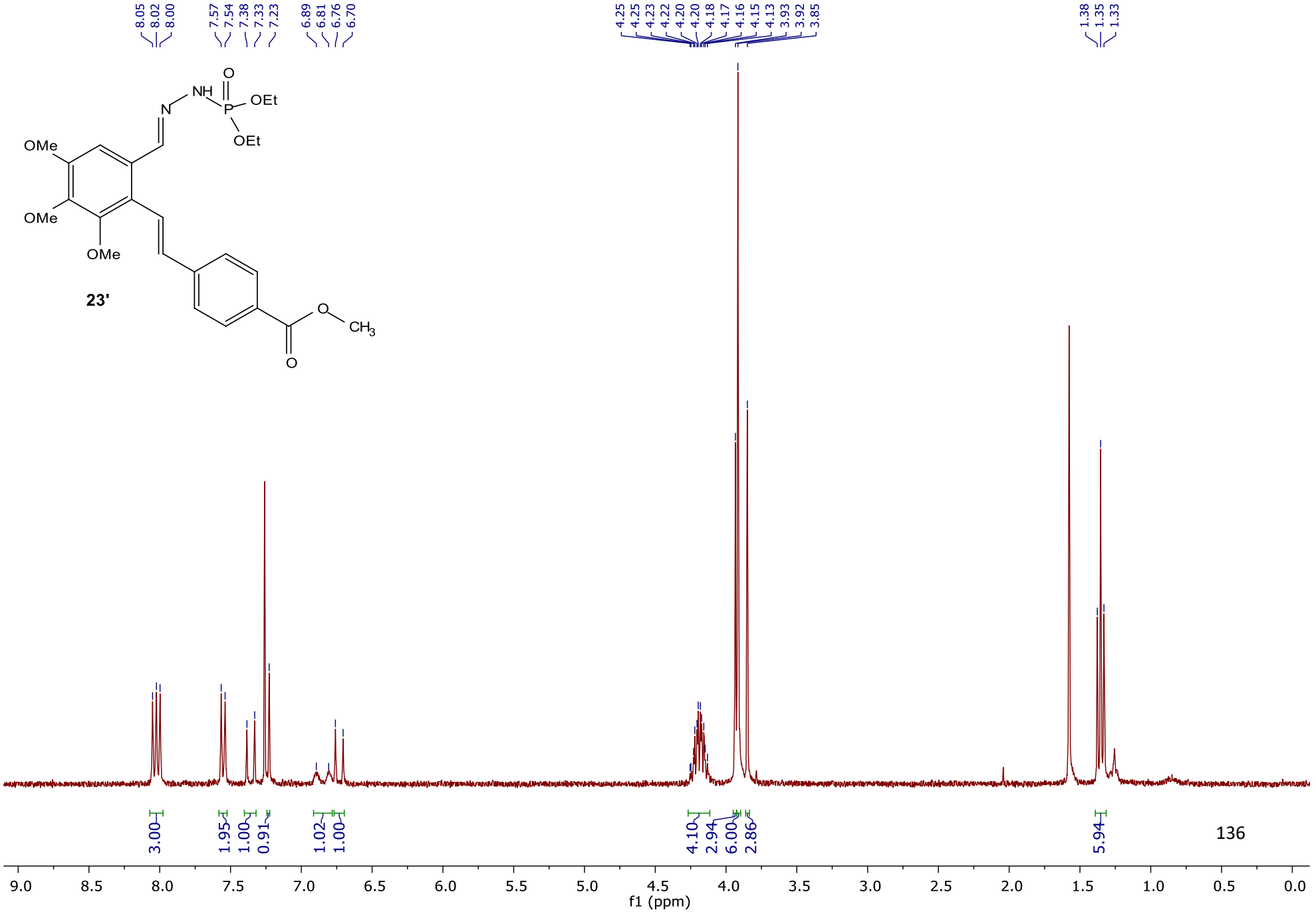
153.46
152.75
151.79
144.30
144.05
143.45
138.23
135.57
133.21
127.78
125.32
120.73
105.08
103.70
63.45
63.37
61.07
60.99
56.22
56.01
16.24
16.15

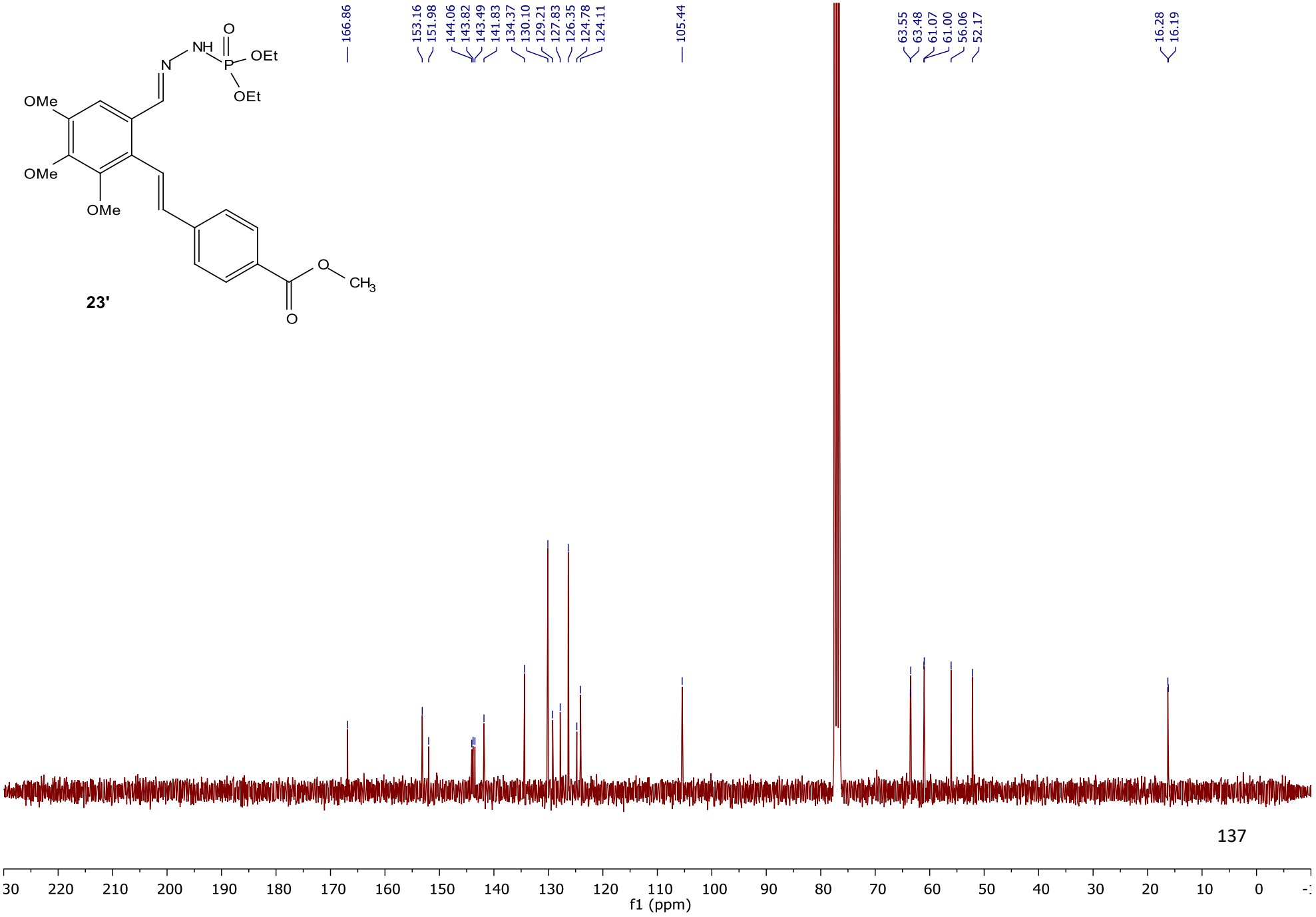


O
NH
N
P
OEt
OEt
OMe
OMe
OMe
OMe
OMe
OMe

22'

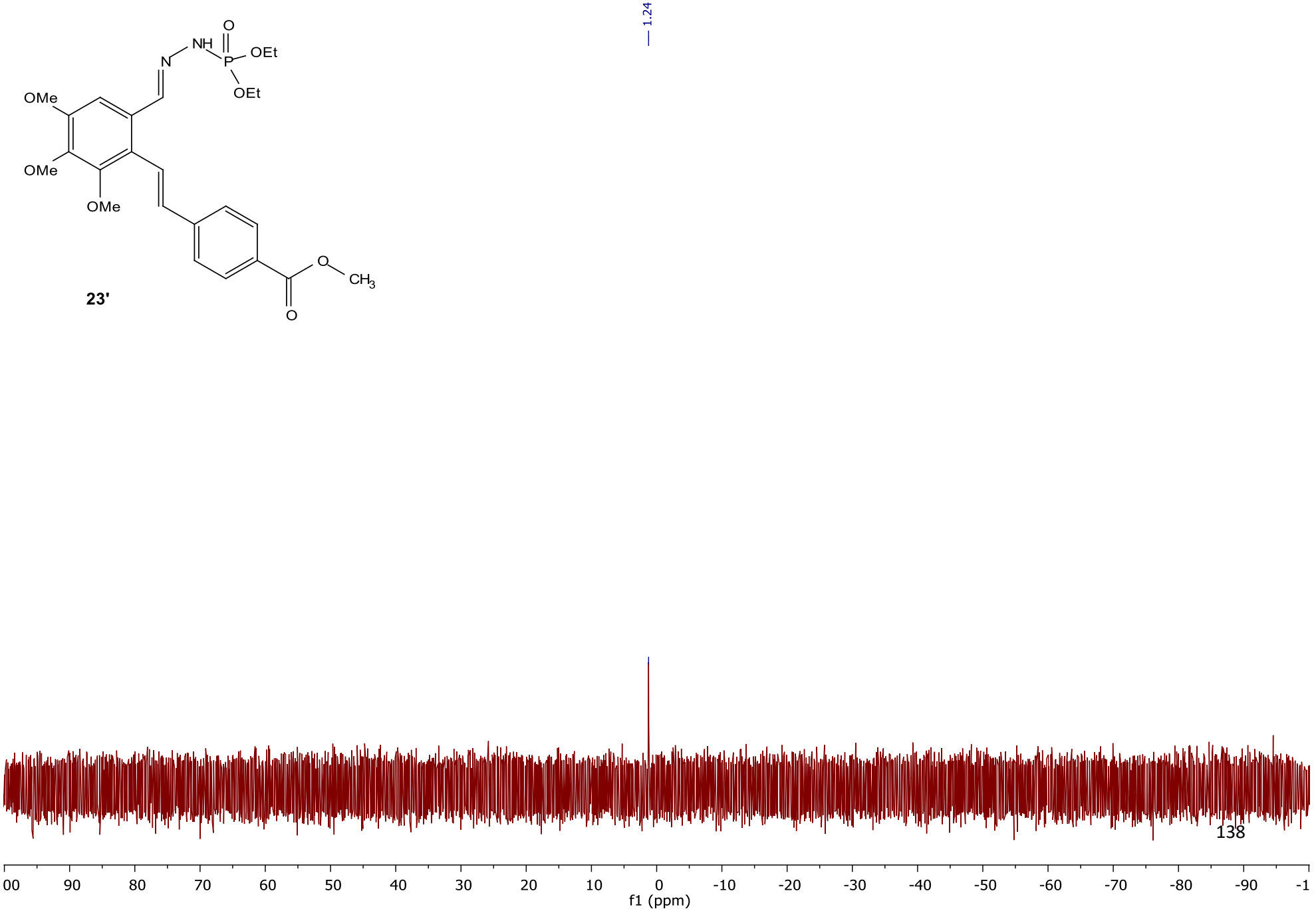

2.88
135
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

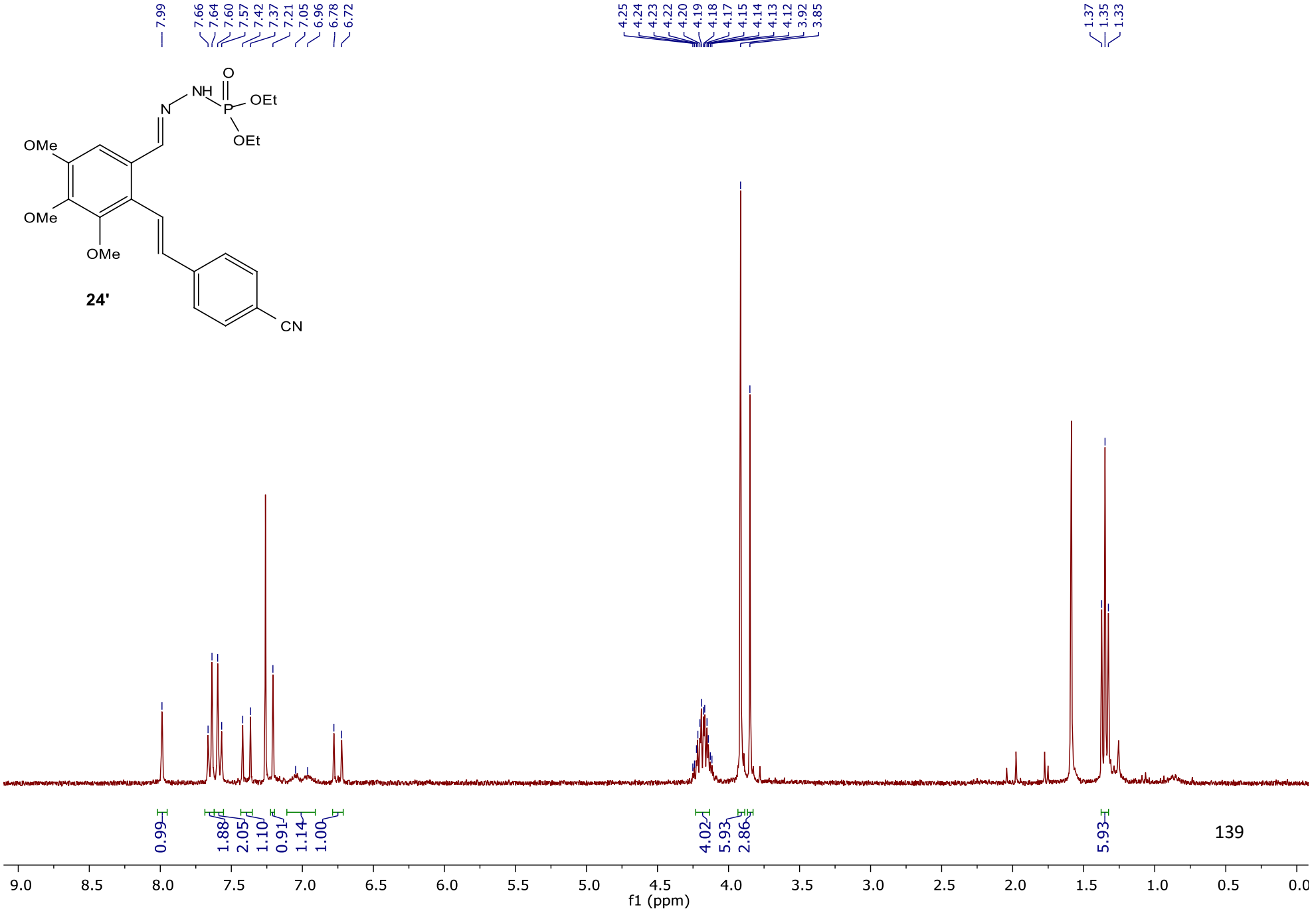

8.05
8.02
8.00
7.57
7.54
7.38
7.33
7.23
6.89
6.81
6.76
6.70
4.25
4.25
4.23
4.22
4.20
4.20
4.18
4.17
4.16
4.15
4.13
3.93
3.92
3.85
1.38
1.35
1.33
NH
O
P
N
OEt
OEt
OMe
OMe
OMe
23'
O
CH3
O
3.00
1.95
1.00
0.91
1.02
1.00
4.10
2.94
6.00
2.86
5.94
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

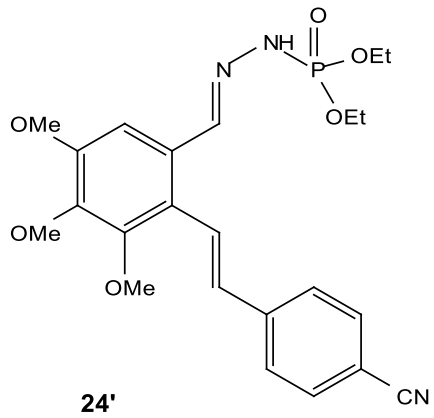

166.86
153.16
151.98
144.06
143.82
143.49
141.83
134.37
130.10
129.21
127.83
126.35
124.78
124.11
105.44
63.55
63.48
61.07
61.00
56.06
52.17
16.28
16.19
OMe
OMe
OMe
NH
N
P
O
OEt
OEt
O
CH3
O
23'
137
f1 (ppm)

O
NH
OEt
N
P
OEt
OMe
OMe
OMe
O
CH3
O

23'

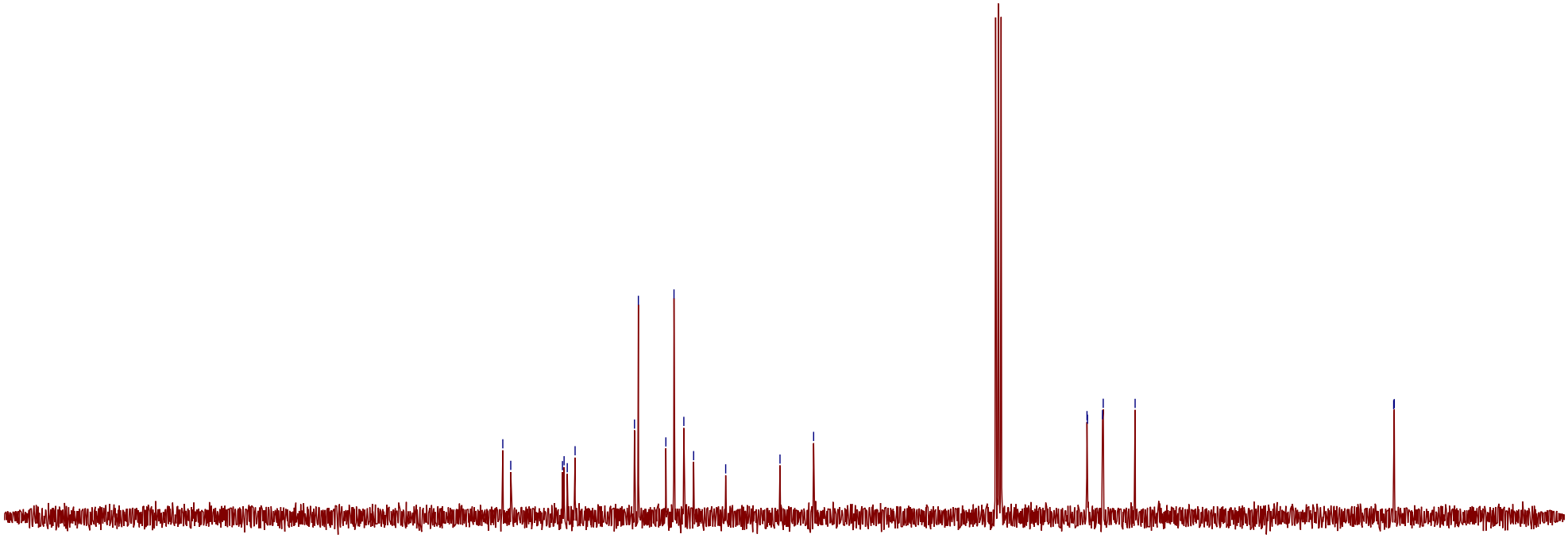

1.24
138
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

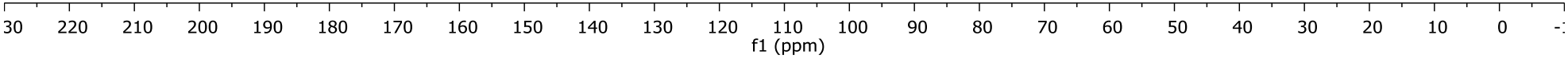

7.99
7.66
7.64
7.60
7.57
7.42
7.37
7.21
7.05
6.96
6.78
6.72
4.25
4.24
4.23
4.22
4.20
4.19
4.18
4.17
4.15
4.14
4.13
4.12
3.92
3.85
1.37
1.35
1.33
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
24'
CN
0.99
1.88
2.05
1.10
0.91
1.14
1.00
4.02
5.93
2.86
5.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



24'

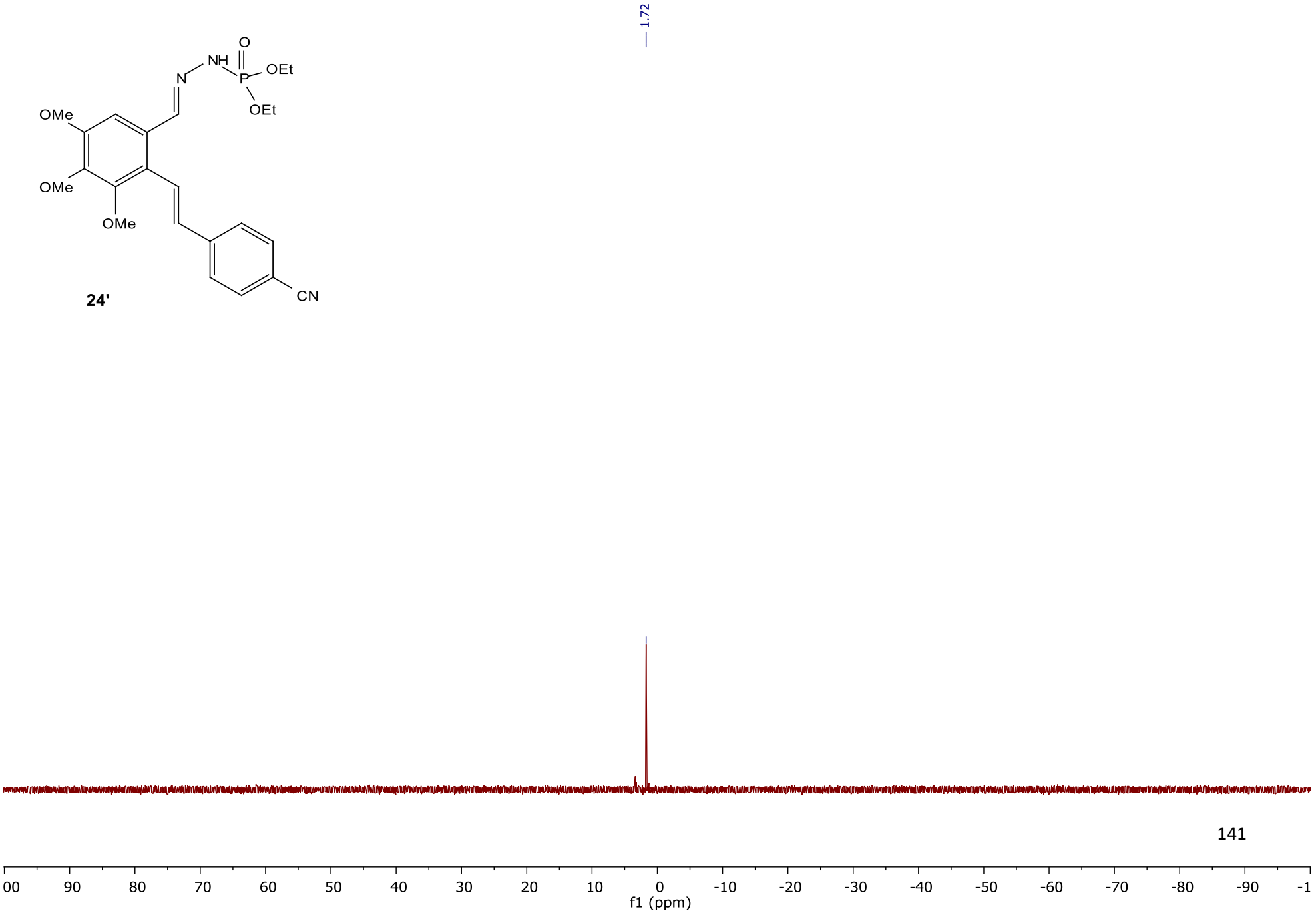
153.3
152.1
144.1
143.9
143.4
142.2
133.1
132.5
128.2
127.0
125.5
124.0
119.0
110.7
105.5
63.4
63.4
61.1
60.9
56.0
16.3
16.2

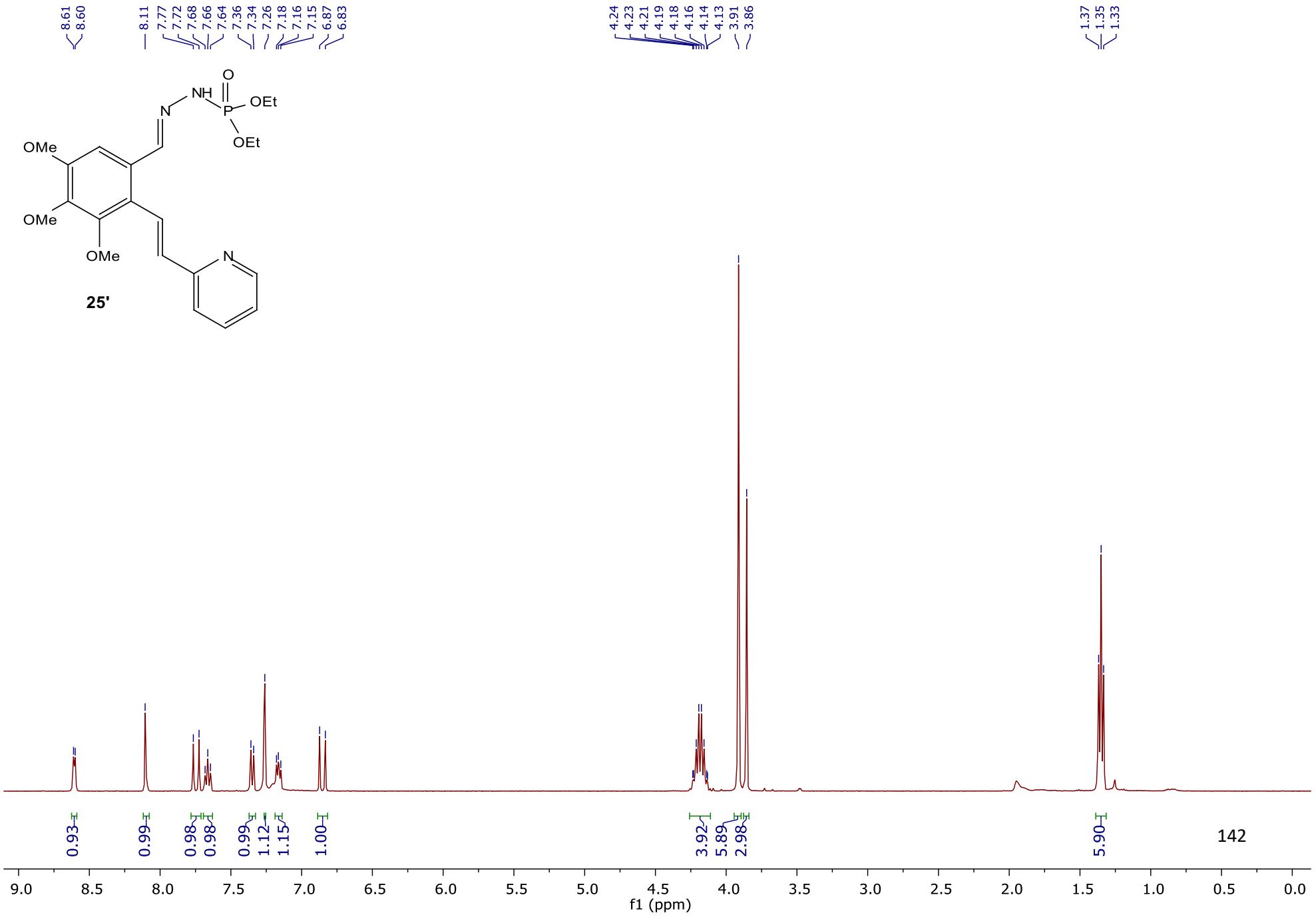


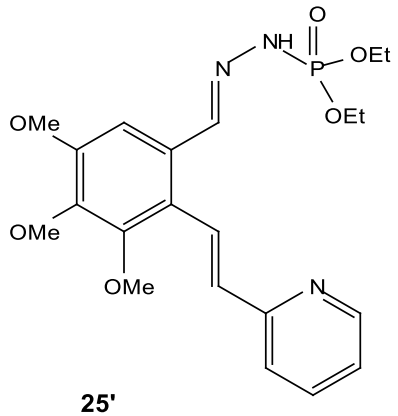


O
NH
N
P
OEt
OEt
OMe
OMe
OMe
CN

24'


1.72
141
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.61
8.60
8.11
7.77
7.72
7.68
7.66
7.64
7.36
7.34
7.26
7.18
7.16
7.15
6.87
6.83
4.24
4.23
4.21
4.19
4.18
4.16
4.14
4.13
3.91
3.86
1.37
1.35
1.33
O
NH
P
OEt
N
OEt
OMe
OMe
OMe
N
25'
0.93
0.99
0.98
0.98
0.99
1.12
1.15
1.00
3.92
5.89
2.98
5.90
142
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



25'

155.6
153.2
152.2
149.7
143.8
143.6
143.5
136.6
134.5
128.2
125.5
124.6
122.3
122.2
105.1
63.5
63.4
61.0
60.9
56.0
16.3
16.2

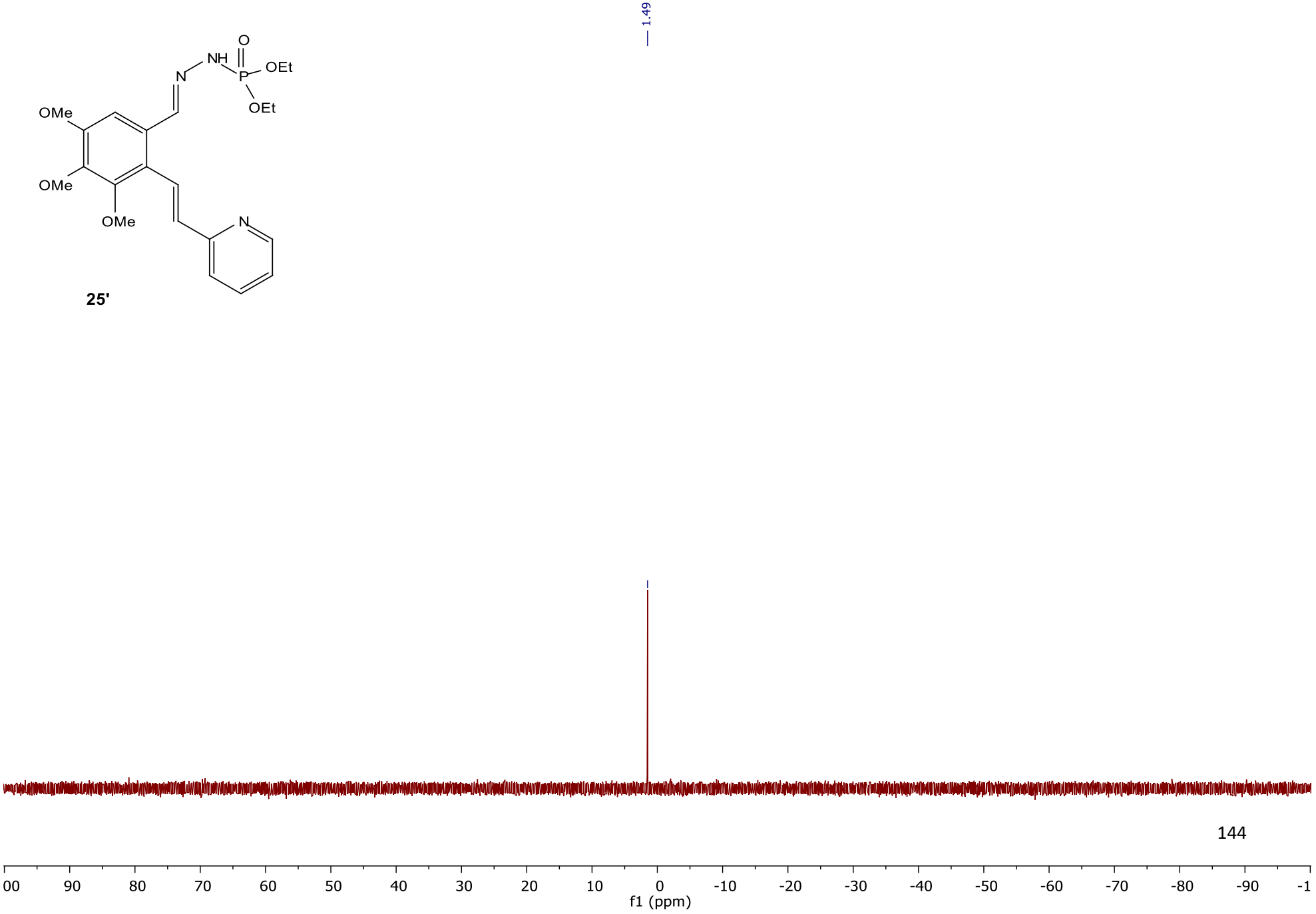
143

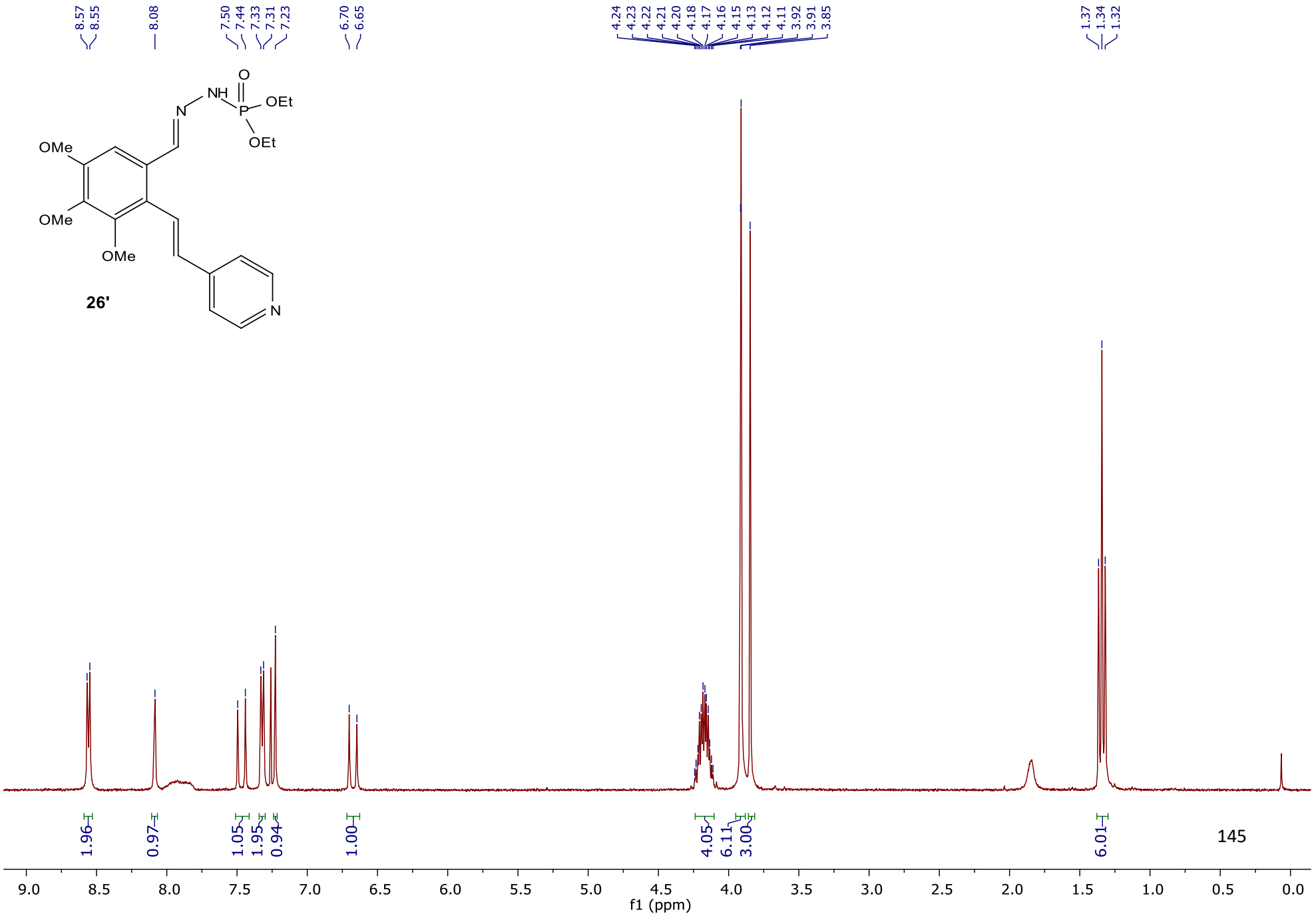
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

O
NH
N
P
OEt
OEt
OMe
OMe
OMe
N

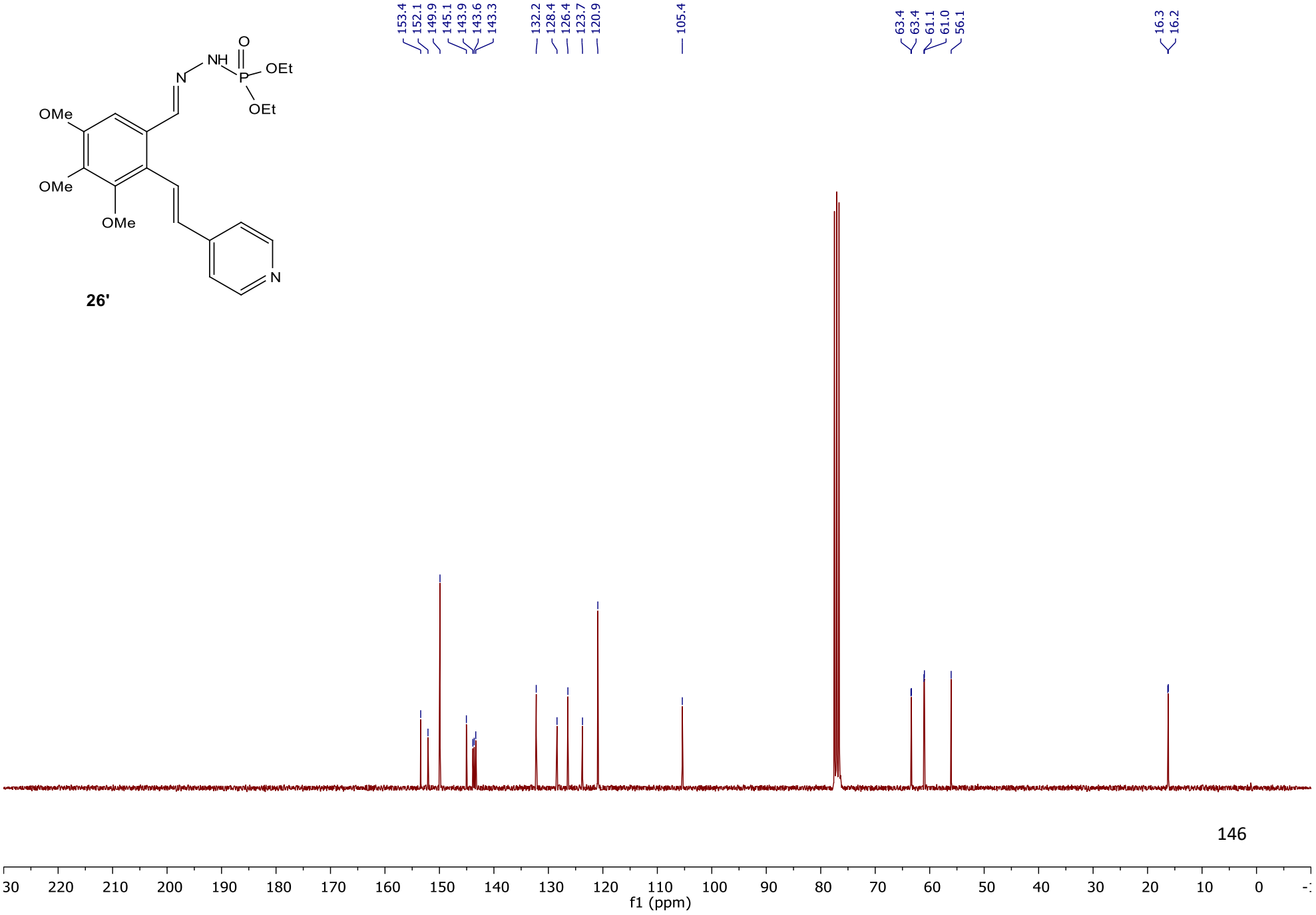
25'


1.49
144
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.57
8.55
8.08
7.50
7.44
7.33
7.31
7.23
6.70
6.65
4.24
4.23
4.22
4.21
4.20
4.18
4.17
4.16
4.15
4.13
4.12
4.11
3.92
3.91
3.85
1.37
1.34
1.32
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
N
26'
1.96
0.97
1.05
1.95
0.94
1.00
4.05
6.11
3.00
6.01
145
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

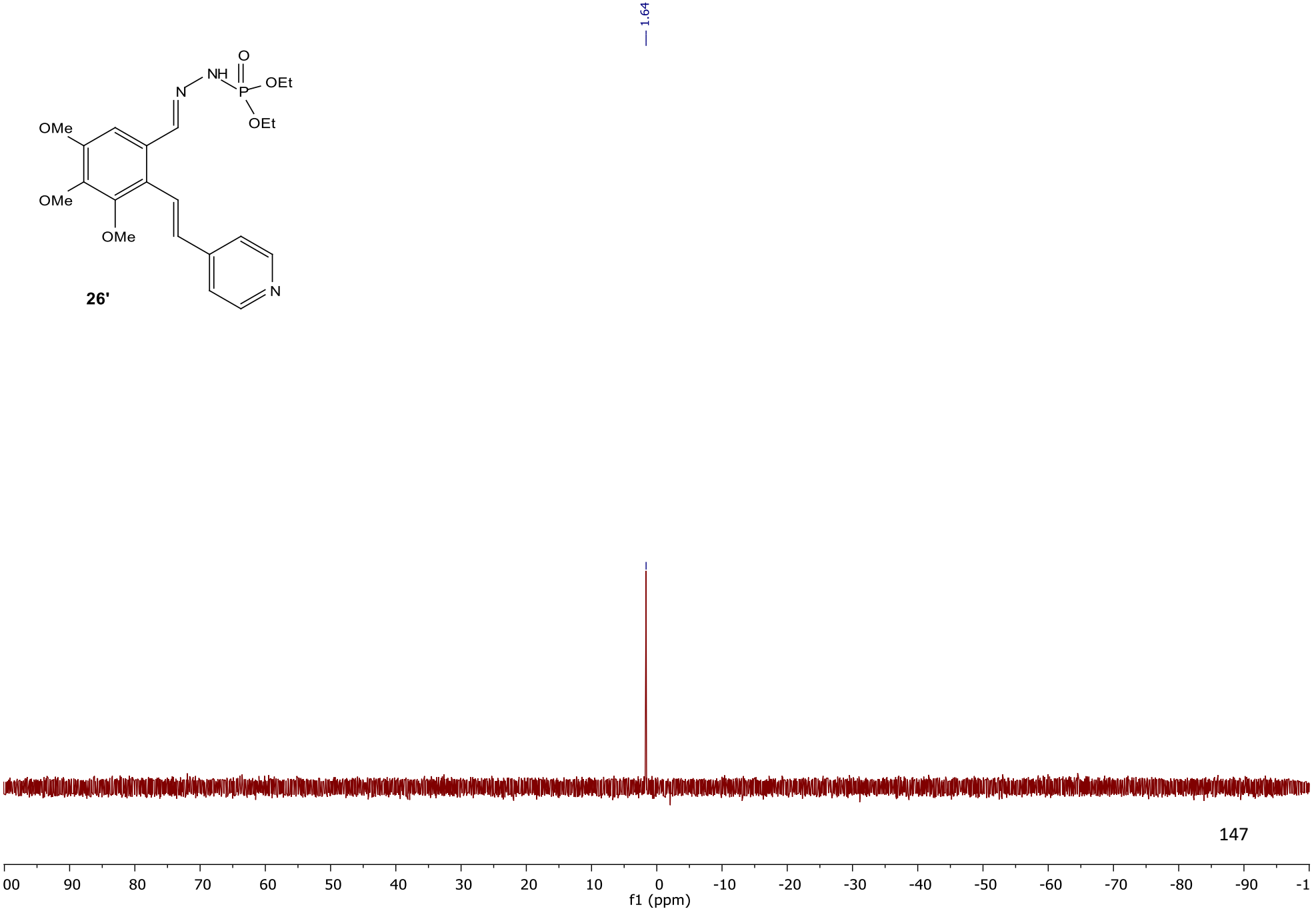
O
NH
N
P
OEt
OEt
OMe
OMe
OMe
N

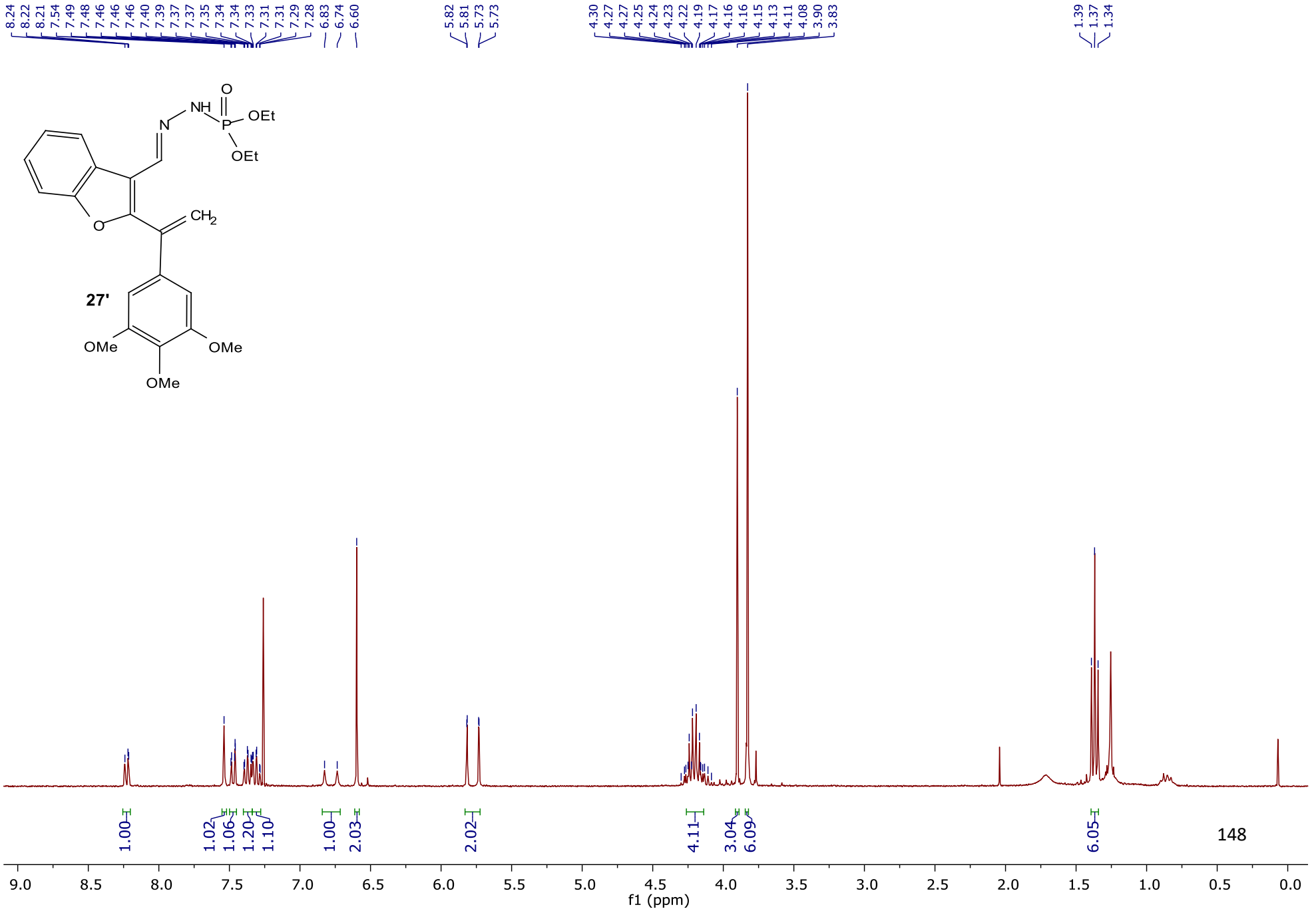
26'


153.4
152.1
149.9
145.1
143.9
143.6
143.3
132.2
128.4
126.4
123.7
120.9
105.4
63.4
63.4
61.1
61.0
56.1
16.3
16.2
146
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
N
P
OEt
OEt
OMe
OMe
OMe
N

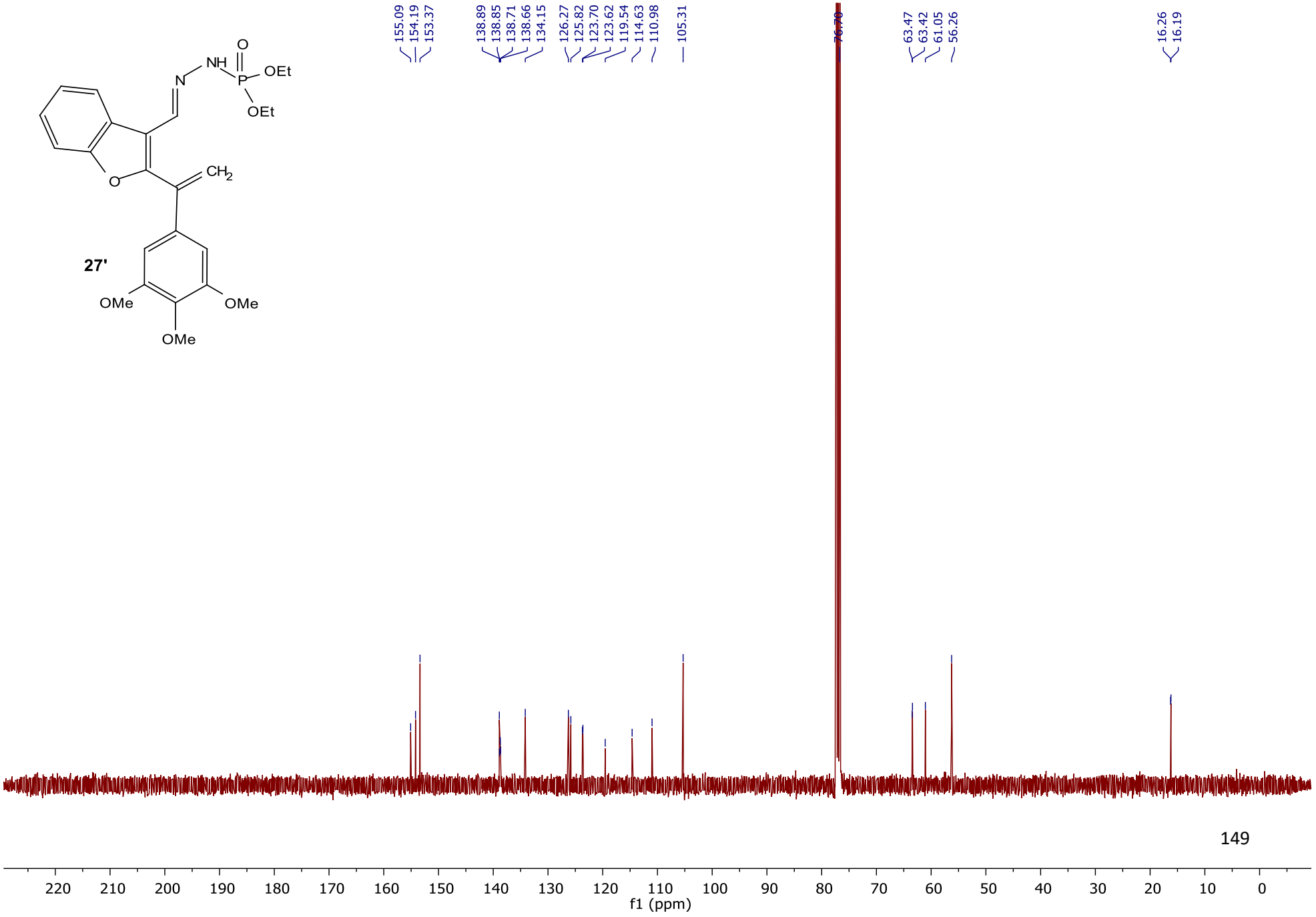
26'


1.64
147
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.24
8.22
8.21
7.54
7.49
7.48
7.46
7.46
7.46
7.40
7.39
7.37
7.37
7.35
7.34
7.34
7.33
7.31
7.31
7.29
7.28
6.83
6.74
6.60
5.82
5.81
5.73
5.73
4.30
4.27
4.27
4.25
4.24
4.23
4.22
4.19
4.17
4.16
4.16
4.15
4.13
4.11
4.08
3.90
3.83
1.39
1.37
1.34
O
NH
N
P
OEt
OEt
O
CH2
27'
OMe
OMe
OMe
1.00
1.02
1.06
1.20
1.10
1.00
2.03
2.02
4.11
3.04
6.09
6.05
148
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

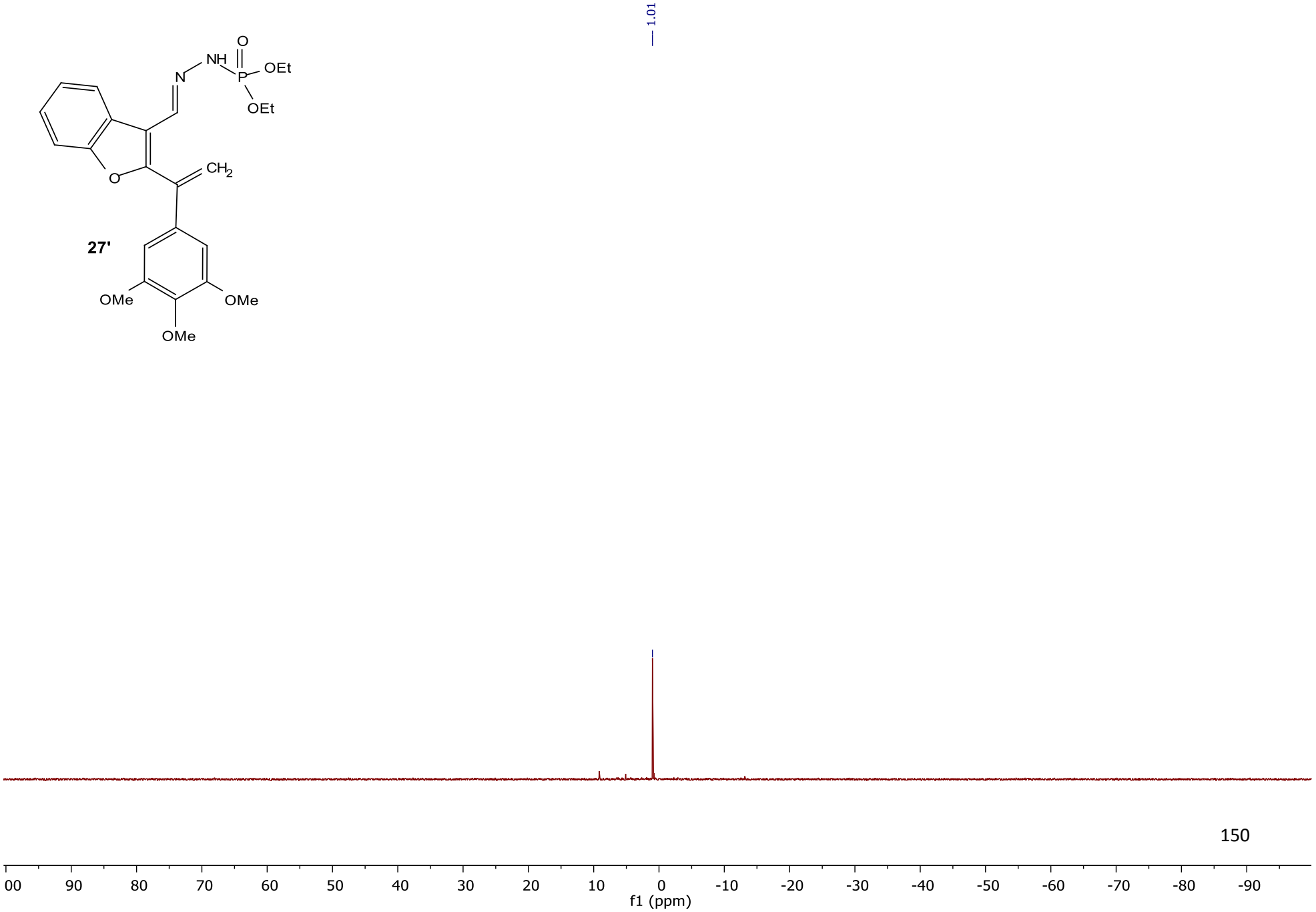
O
NH
N
P
OEt
OEt
O
CH2
OMe
OMe
OMe

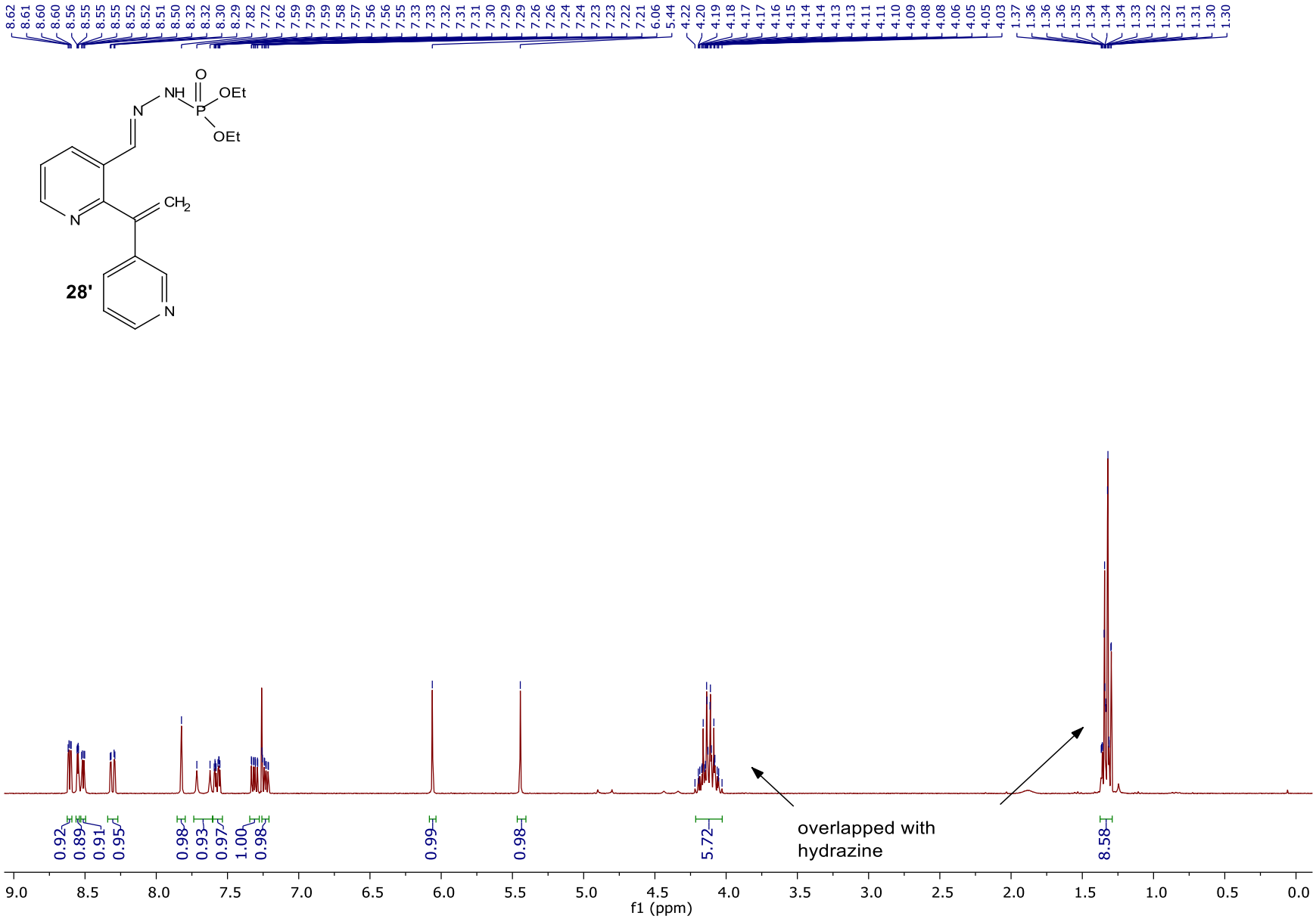
27'

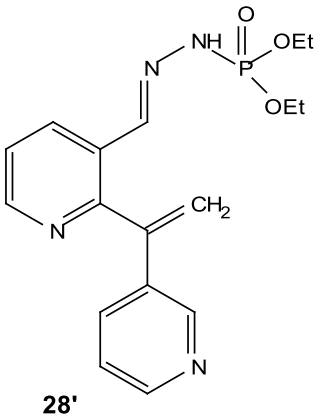

155.09
154.19
153.37
138.89
138.85
138.71
138.66
134.15
126.27
125.82
123.70
123.62
119.54
114.63
110.98
105.31
76.79
63.47
63.42
61.05
56.26
16.26
16.19
149
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
NH
P
OEt
N
OEt
CH2
O
OMe
OMe
OMe

27'


1.01
150
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


8.62 8.61 8.60 8.60 8.56 8.55 8.55 8.55 8.52 8.52 8.51 8.50 8.32 8.32 8.30 8.29 7.82 7.72 7.62 7.59 7.59 7.59 7.58 7.57 7.56 7.56 7.55 7.33 7.33 7.32 7.31 7.31 7.30 7.29 7.29 7.26 7.24 7.24 7.23 7.23 7.22 7.21 6.06 5.44 4.22 4.20 4.19 4.18 4.17 4.17 4.16 4.15 4.14 4.14 4.13 4.13 4.11 4.11 4.10 4.09 4.08 4.08 4.06 4.05 4.05 4.03 1.37 1.36 1.36 1.36 1.35 1.34 1.34 1.34 1.33 1.32 1.32 1.31 1.31 1.30 1.30
NH
O
OEt
OEt
P
N
N
CH2
N
28'
0.92
0.89
0.91
0.95
0.98
0.93
0.97
1.00
0.98
0.99
0.98
5.72
8.58
overlapped with
hydrazine
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

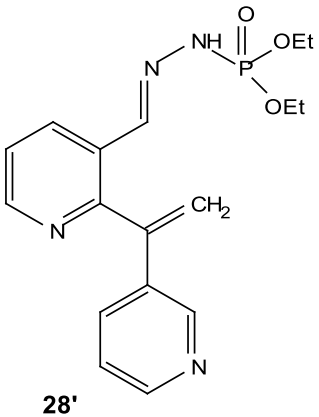


28'

157.03
149.81
148.90
147.89
143.63
141.31
141.12
135.30
134.28
134.03
129.09
123.37
123.09
120.06
63.43
63.38
16.16
16.09

152

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



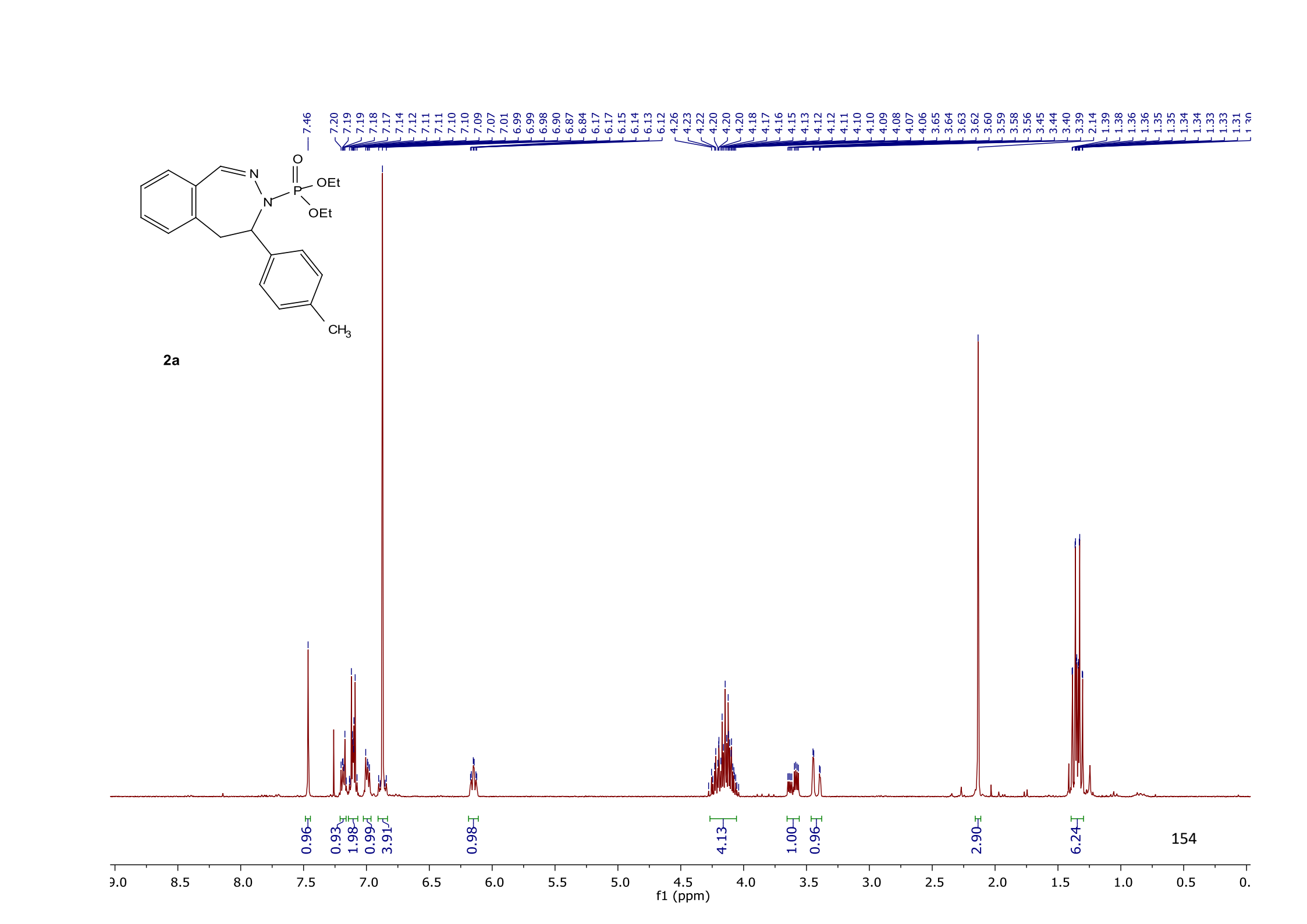
28'

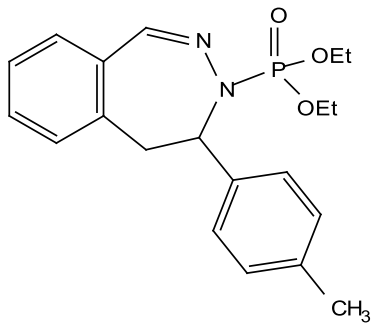
5.56

153

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


7.46
7.20
7.19
7.19
7.18
7.17
7.14
7.12
7.11
7.11
7.10
7.10
7.09
7.07
7.01
6.99
6.99
6.98
6.90
6.87
6.84
6.17
6.17
6.15
6.14
6.13
6.12
4.26
4.23
4.22
4.20
4.20
4.20
4.18
4.17
4.16
4.15
4.13
4.12
4.12
4.11
4.10
4.10
4.09
4.08
4.07
4.06
3.65
3.64
3.63
3.62
3.60
3.59
3.58
3.56
3.45
3.44
3.40
3.39
2.14
1.39
1.38
1.36
1.36
1.35
1.35
1.34
1.34
1.33
1.33
1.31
O
N
N
P
OEt
OEt
CH3
2a
0.96
0.93
1.98
0.99
3.91
0.98
4.13
1.00
0.96
2.90
6.24
154
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)



2a

140.80
140.64
138.29
136.73
135.80
132.50
131.48
130.08
129.08
128.69
126.38
125.92
63.93
63.87
63.35
63.29
61.89
61.79
41.95
41.90
20.87
16.24
16.16
16.08

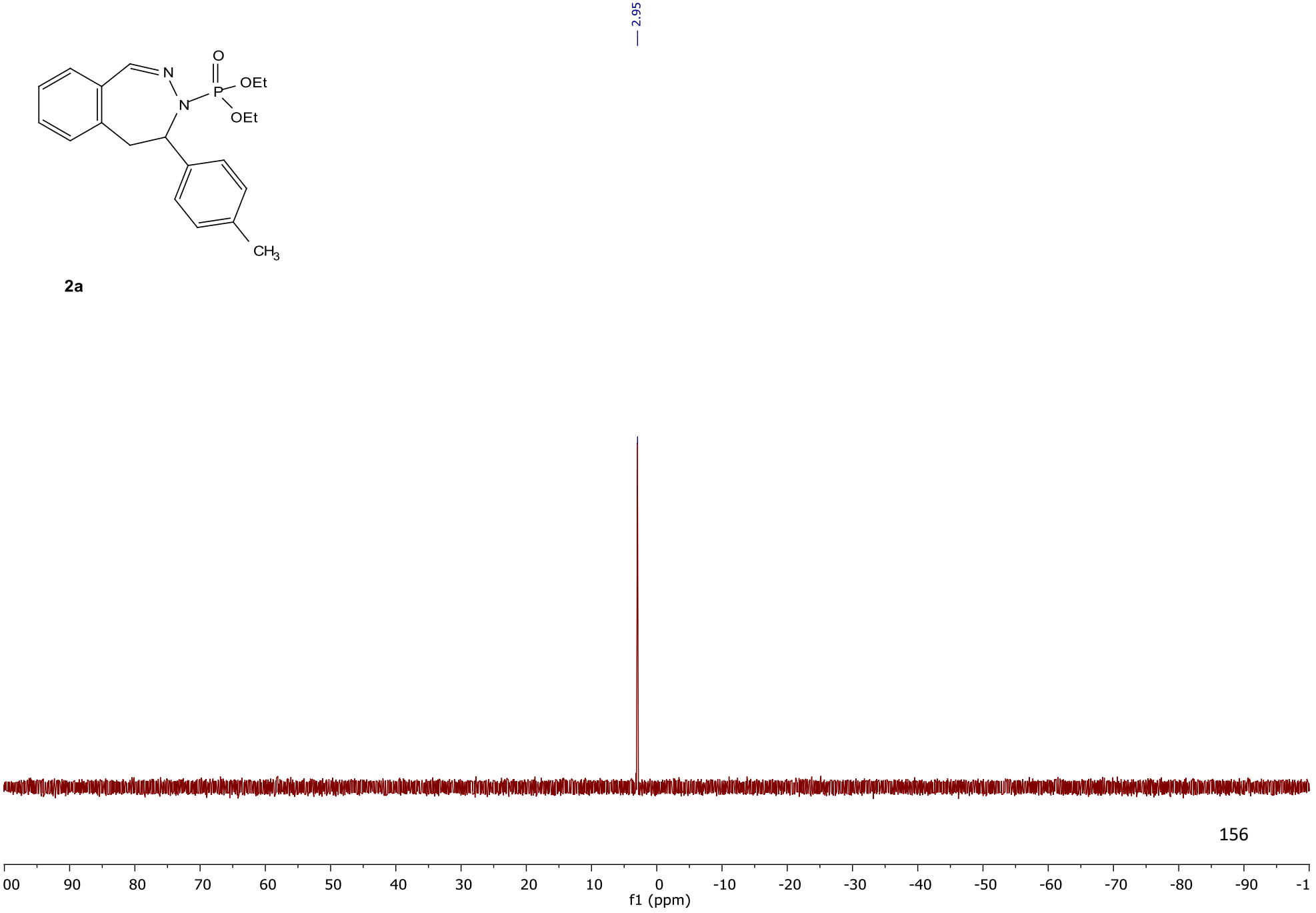
155

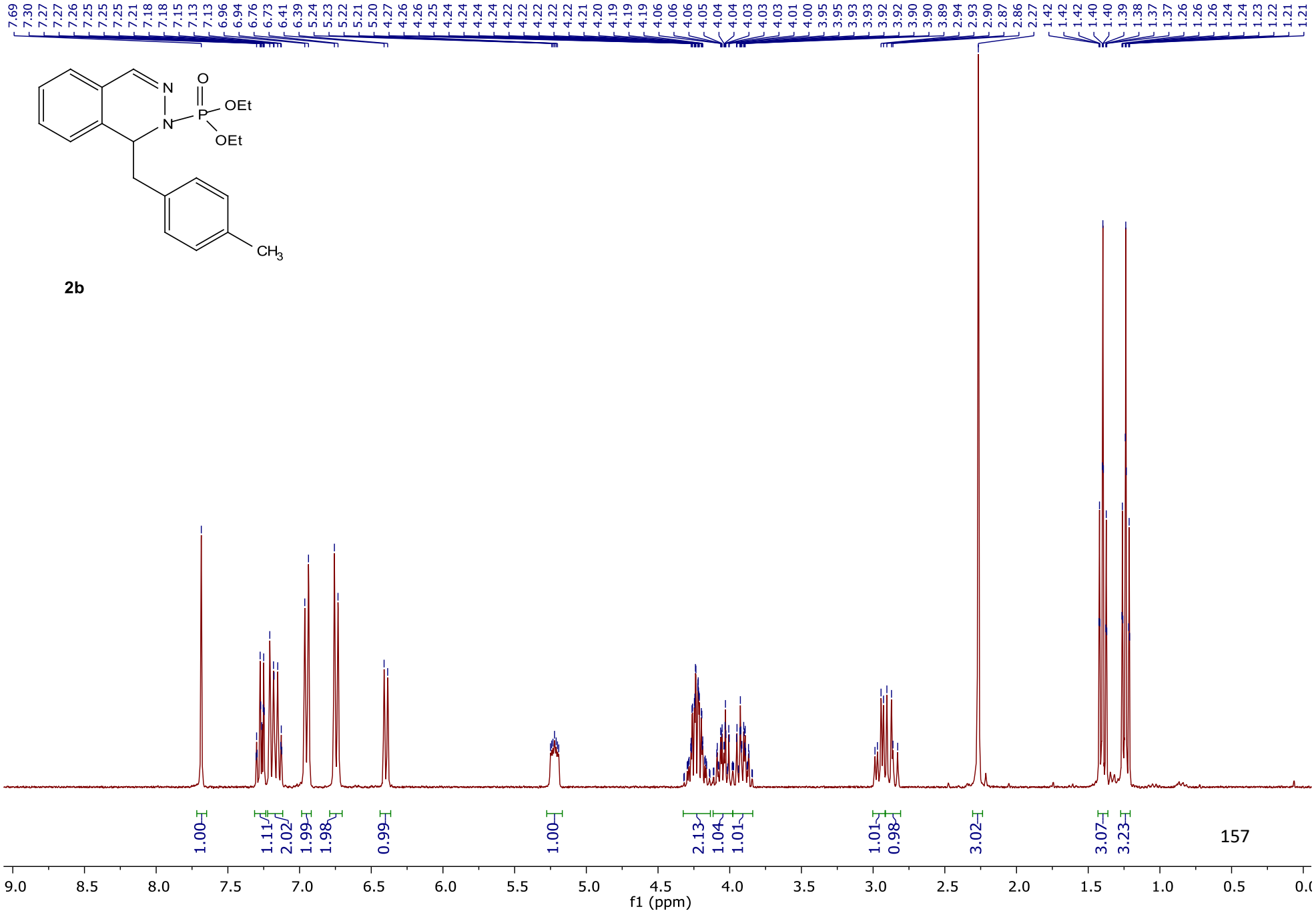
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

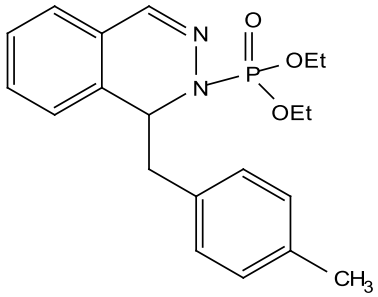
f1 (ppm)

O
N
OEt
P
N
OEt
CH3

2a


2.95
156
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.69 7.30 7.27 7.27 7.26 7.25 7.25 7.21 7.18 7.18 7.15 7.13 7.13 6.96 6.94 6.76 6.73 6.41 6.39 5.24 5.23 5.22 5.21 5.20 4.27 4.26 4.26 4.25 4.24 4.24 4.24 4.24 4.22 4.22 4.22 4.22 4.21 4.20 4.19 4.19 4.19 4.06 4.06 4.06 4.05 4.04 4.04 4.03 4.03 4.03 4.01 4.00 3.95 3.95 3.93 3.93 3.92 3.92 3.90 3.90 3.89 2.94 2.93 2.90 2.87 2.86 2.27 1.42 1.42 1.42 1.40 1.40 1.39 1.38 1.37 1.37 1.26 1.26 1.26 1.24 1.24 1.23 1.22 1.21 1.21
N
N
O
P
OEt
OEt
CH3
2b
1.00 1.11 2.02 1.99 1.98 0.99 1.00 2.13 1.04 1.01 1.01 0.98 3.02 3.07 3.23
157
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



2b

142.96
142.84
135.93
133.19
131.78
131.72
130.46
129.87
128.74
127.86
126.86
124.96
123.60

63.89
63.83
63.13
63.08
55.83
55.74

41.13

21.06
16.31
16.23
15.98
15.91

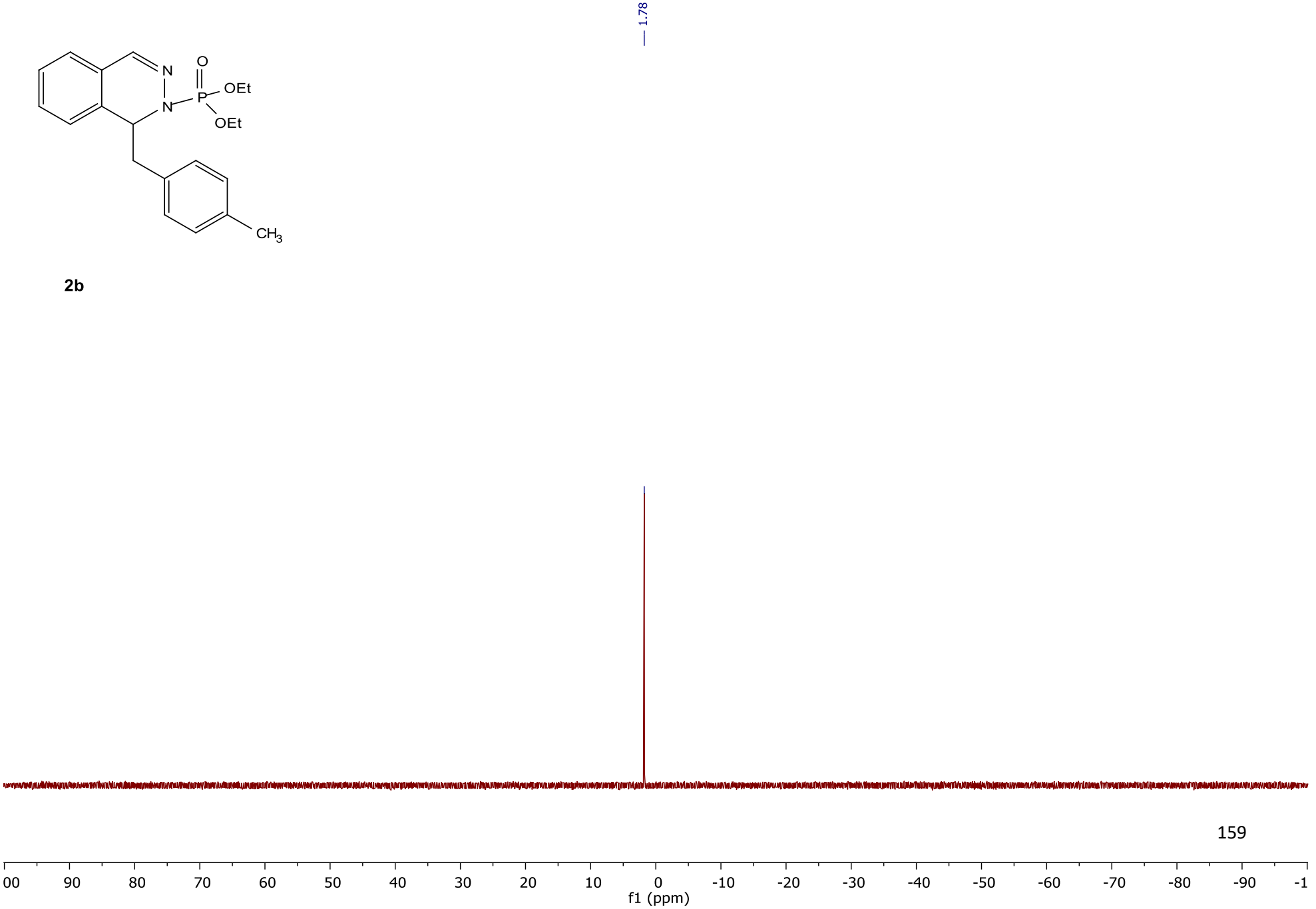
158

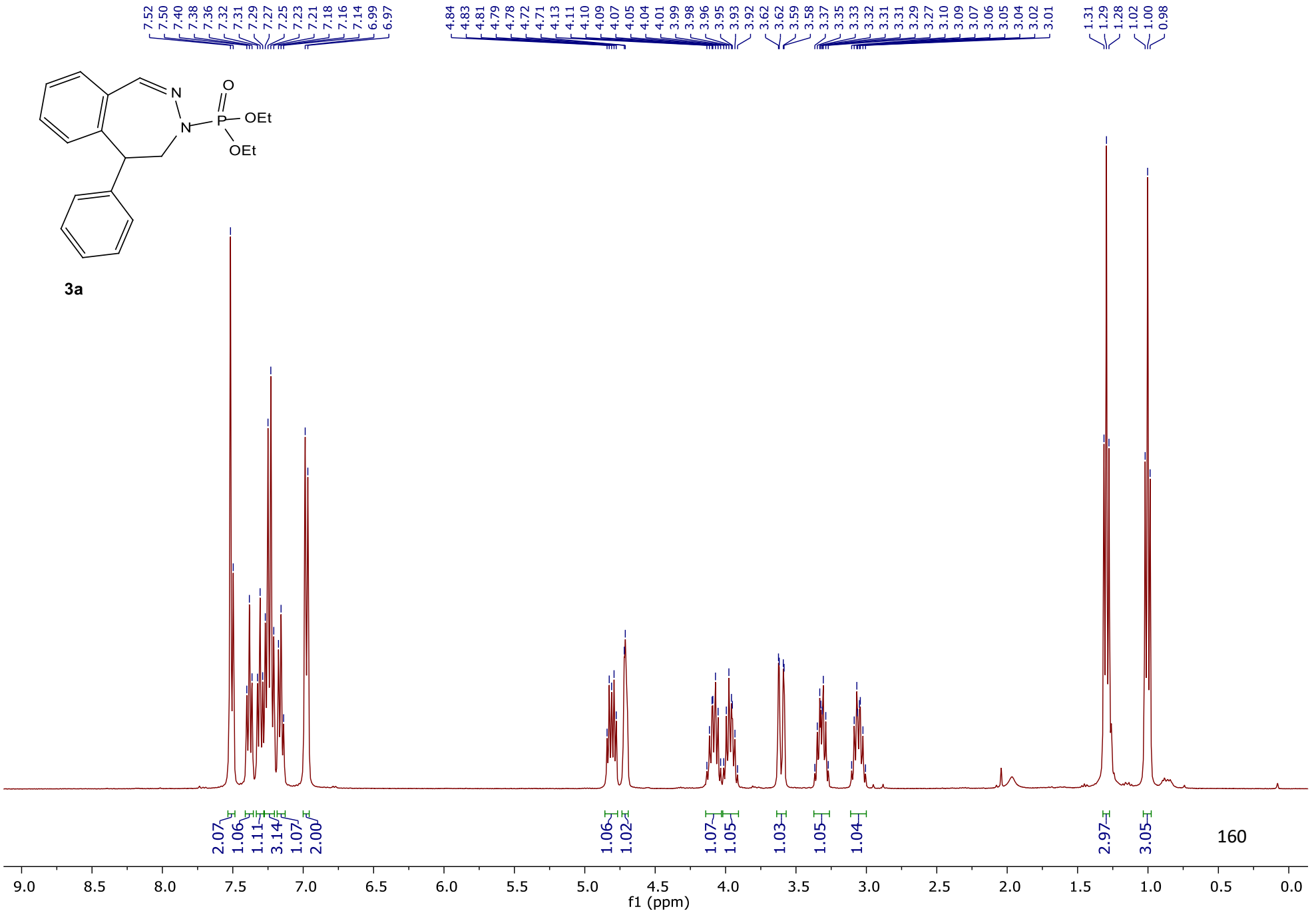
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

N
O
OEt
N
P
OEt
CH3

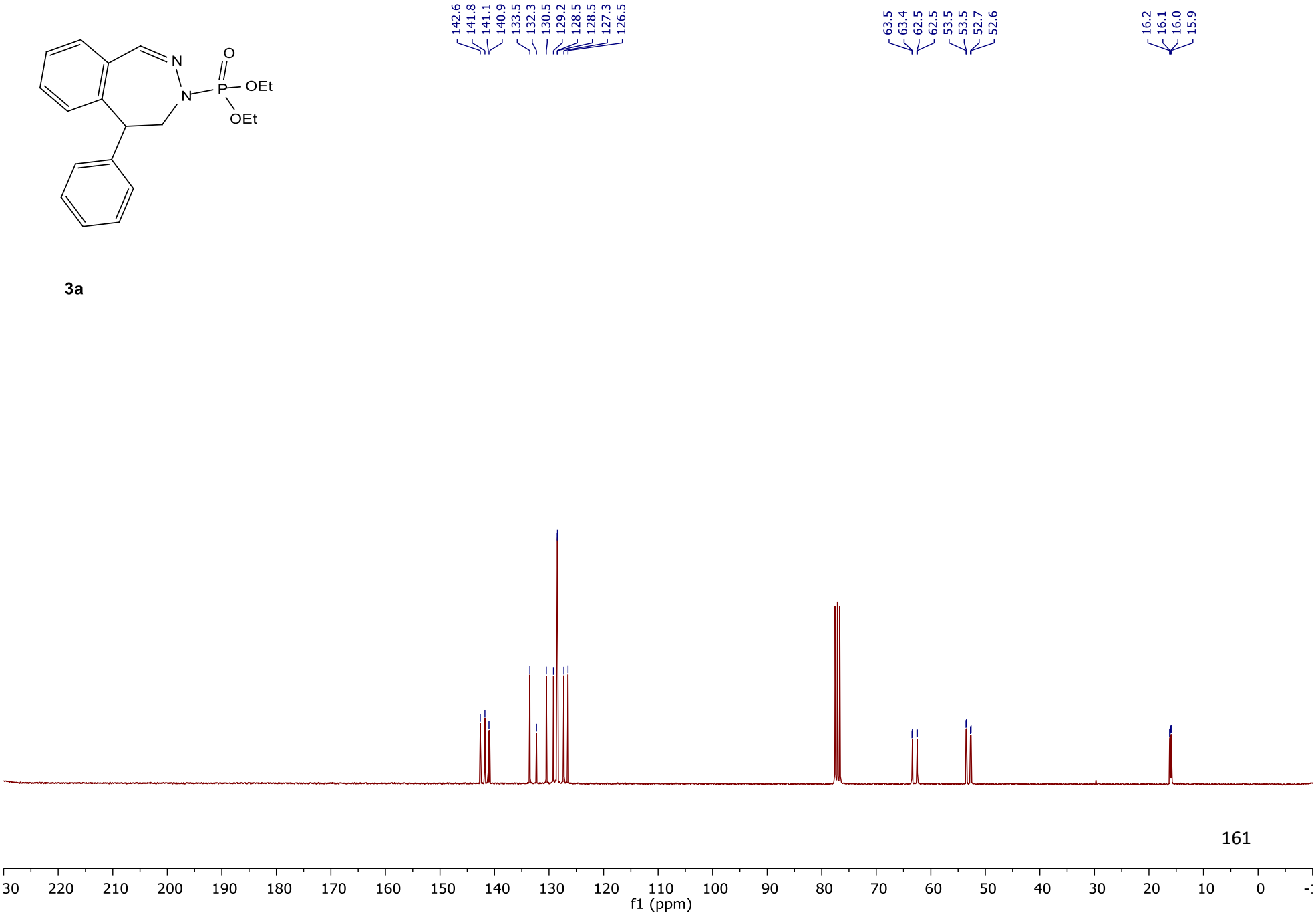
2b


1.78
159
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.52 7.50 7.40 7.38 7.36 7.32 7.31 7.29 7.27 7.25 7.23 7.21 7.18 7.16 7.14 6.99 6.97
4.84 4.83 4.81 4.79 4.78 4.72 4.71 4.13 4.11 4.10 4.09 4.07 4.05 4.04 4.01 3.99 3.98 3.96 3.95 3.93 3.92 3.62 3.62 3.59 3.58 3.37 3.35 3.33 3.32 3.31 3.31 3.29 3.27 3.10 3.09 3.07 3.06 3.05 3.04 3.02 3.01
1.31 1.29 1.28 1.02 1.00 0.98
N
N
P
O
OEt
OEt
3a
2.07 1.06 1.11 3.14 1.07 2.00
1.06 1.02
1.07 1.05
1.03
1.05
1.04
2.97
3.05
160
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

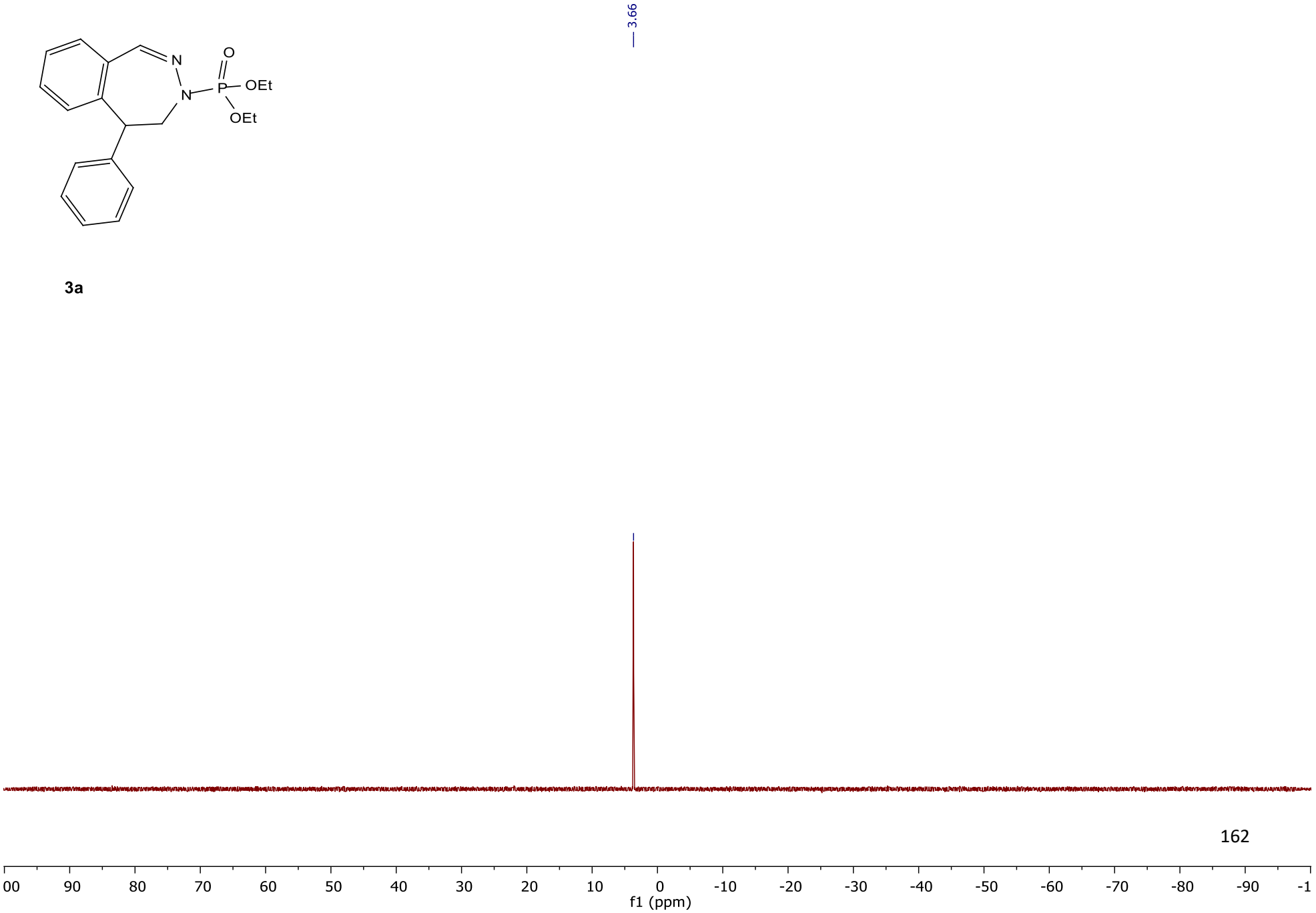
N
N
P
O
OEt
OEt

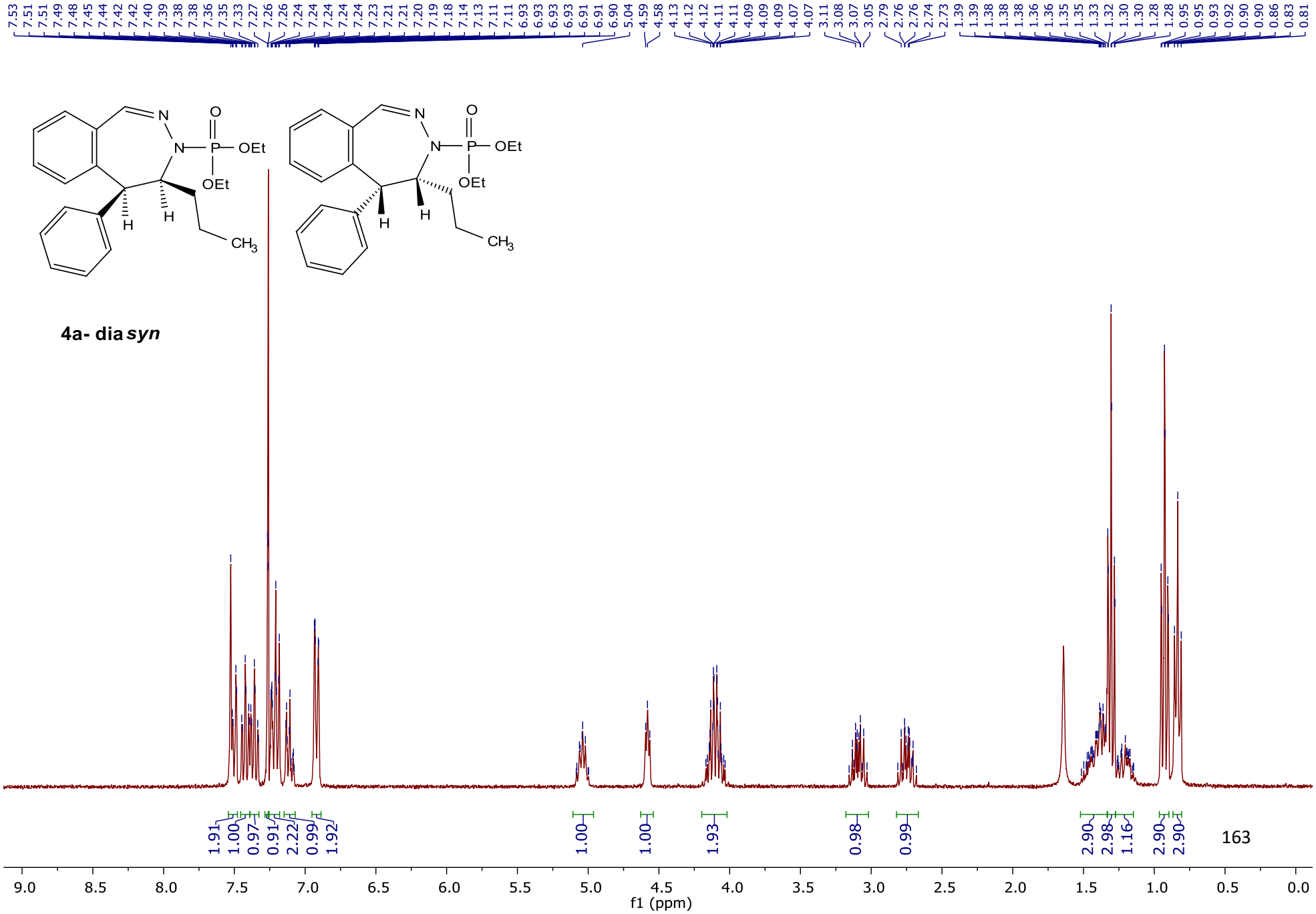
3a

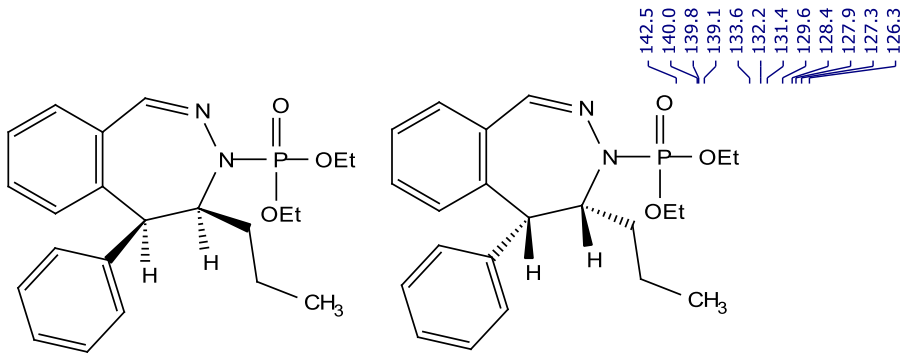

142.6
141.8
141.1
140.9
133.5
132.3
130.5
129.2
128.5
128.5
127.3
126.5
63.5
63.4
62.5
62.5
53.5
53.5
52.7
52.6
16.2
16.1
16.0
15.9
161
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

N
O
N
P
OEt
OEt

3a

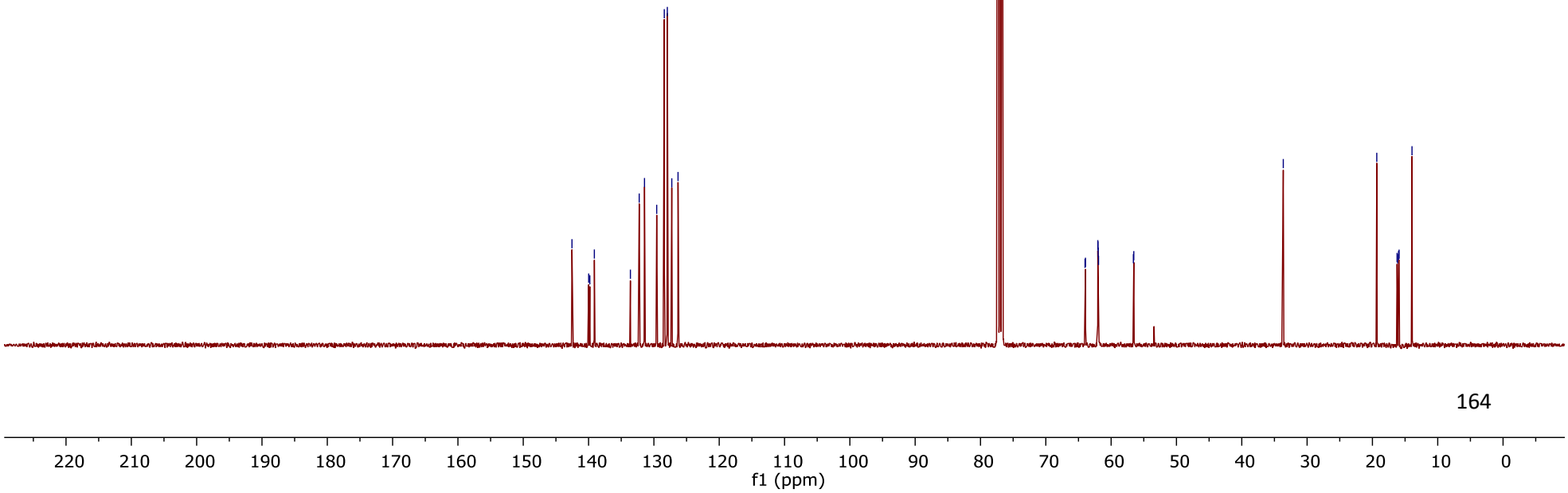

3,66
162
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

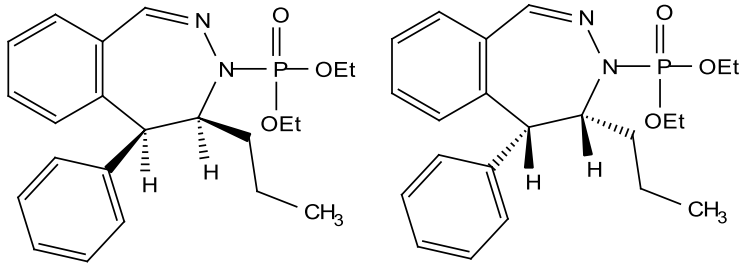

7.53 7.51 7.51 7.49 7.48 7.45 7.44 7.42 7.42 7.40 7.39 7.38 7.38 7.36 7.35 7.33 7.27 7.26 7.26 7.24 7.24 7.24 7.24 7.24 7.23 7.21 7.21 7.20 7.19 7.18 7.14 7.13 7.11 7.11 6.93 6.93 6.93 6.91 6.91 6.90 5.04 4.59 4.58 4.13 4.12 4.12 4.11 4.11 4.09 4.09 4.09 4.07 4.07 3.11 3.08 3.07 3.05 2.79 2.76 2.76 2.74 2.73 1.39 1.39 1.38 1.38 1.38 1.36 1.36 1.35 1.35 1.33 1.32 1.30 1.30 1.28 1.28 0.95 0.95 0.93 0.92 0.90 0.90 0.86 0.83 0.81
N
O
N
P
OEt
OEt
H
H
CH3
4a- dia syn
1.91 1.00 0.97 0.91 2.22 0.99 1.92
1.00
1.00
1.93
0.98
0.99
2.90 2.98 1.16 2.90 2.90
163
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
N
P
O
OEt
OEt
H
H
CH3
N
N
P
O
OEt
OEt
H
H
CH3

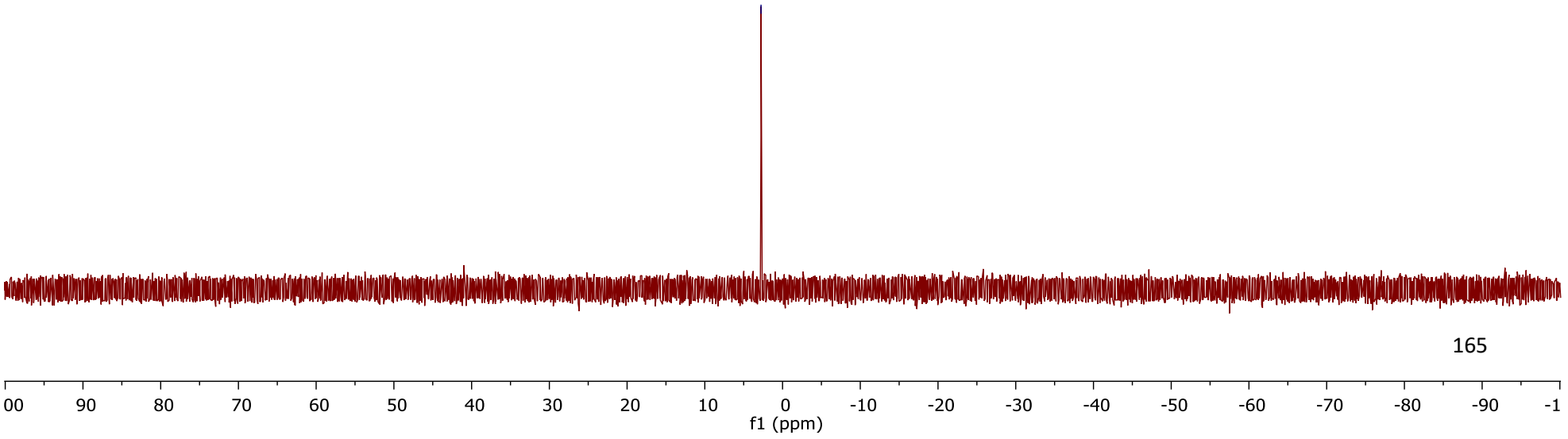

142.5
140.0
139.8
139.1
133.6
132.2
131.4
129.6
128.4
127.9
127.3
126.3
64.0
63.9
62.0
62.0
62.0
61.9
56.6
56.5
33.6
19.3
16.2
16.2
16.0
15.9
13.9

4a- dia *syn*

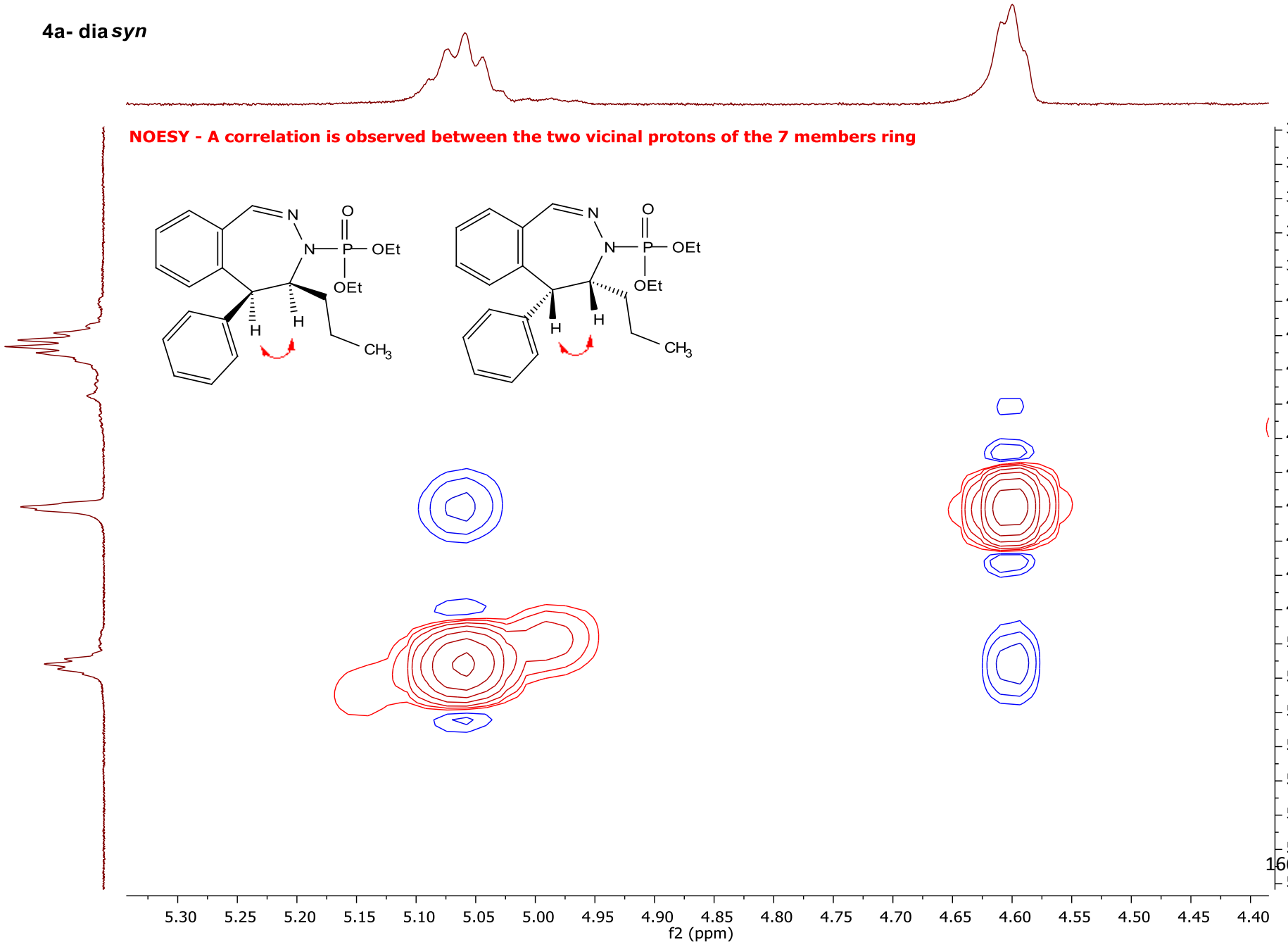

164
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

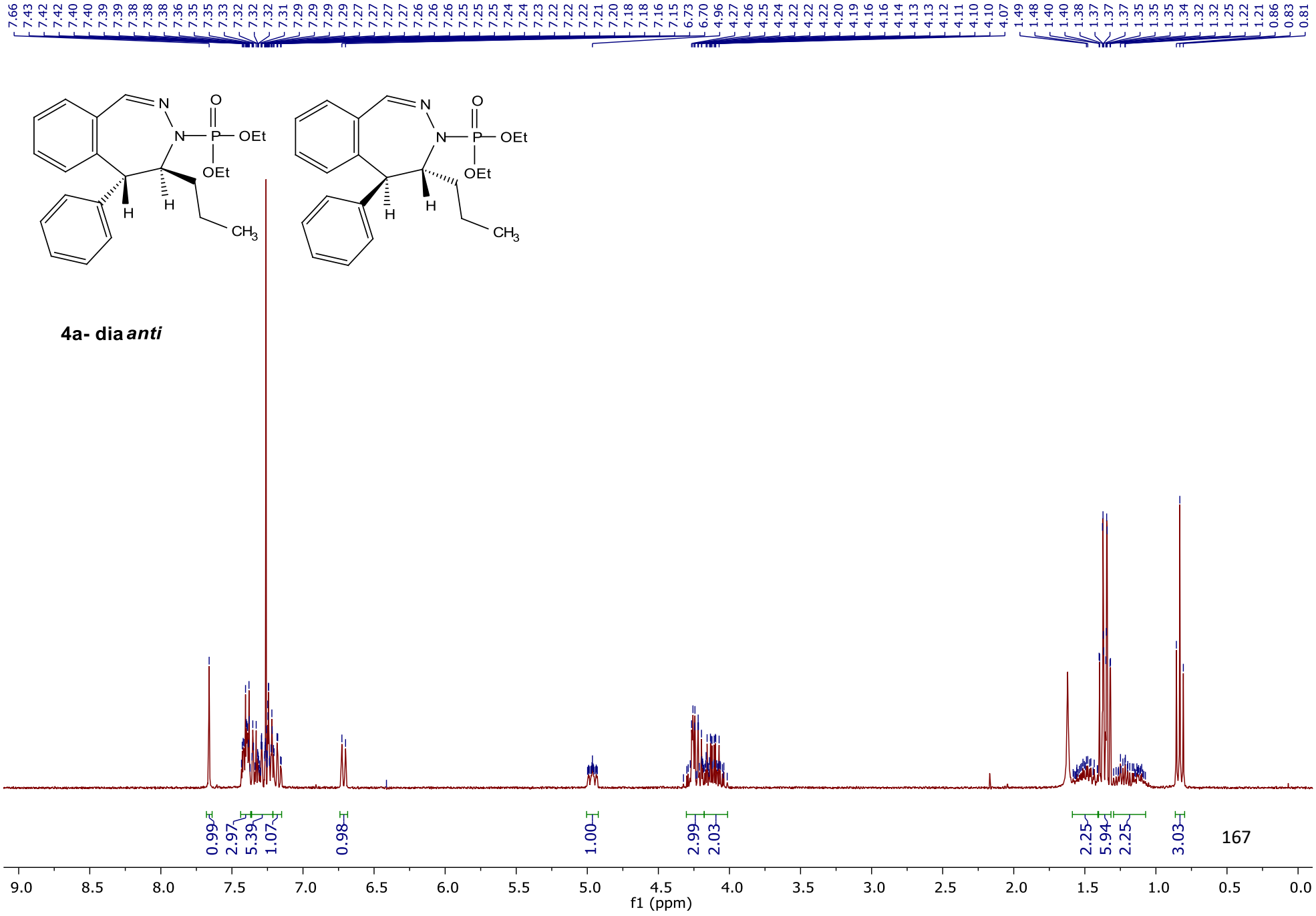

N
O
N
P
OEt
OEt
H
H
CH3
N
O
N
P
OEt
OEt
H
H
CH3

4a- dia *syn*


2.77
165
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

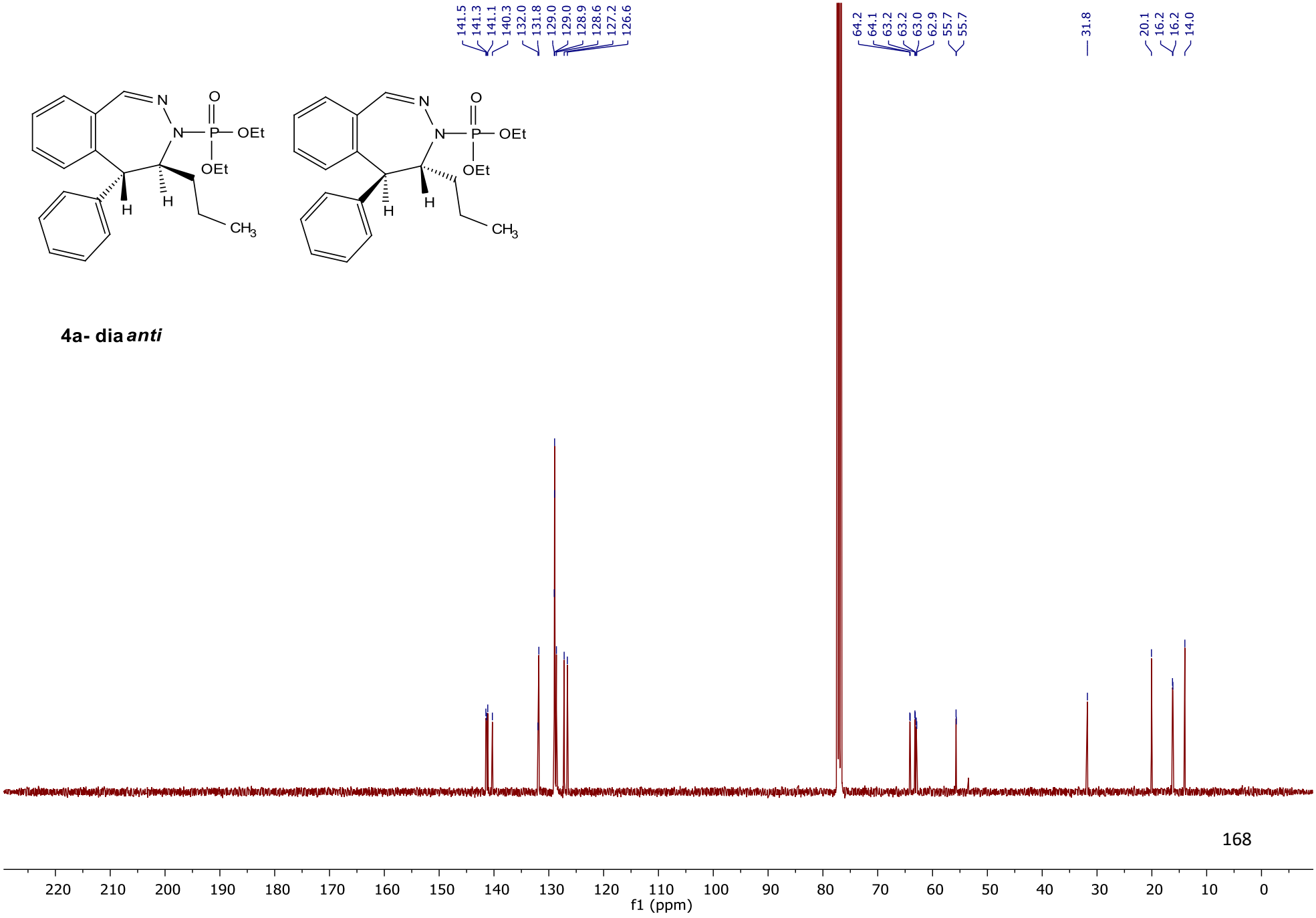
4a- dia *syn*

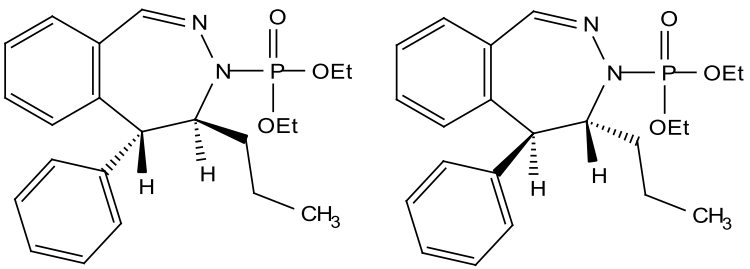

NOESY - A correlation is observed between the two vicinal protons of the 7 members ring
N
N
O
P
OEt
OEt
H
H
CH3
f2 (ppm)
f1 (ppm)


7.66 7.43 7.42 7.42 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.36 7.35 7.35 7.33 7.32 7.32 7.32 7.31 7.29 7.29 7.29 7.29 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.22 7.22 7.22 7.21 7.20 7.18 7.16 7.15 6.73 6.70 4.96 4.27 4.26 4.25 4.24 4.22 4.22 4.22 4.20 4.19 4.16 4.16 4.14 4.13 4.13 4.12 4.11 4.10 4.10 4.07 1.49 1.48 1.40 1.40 1.38 1.37 1.37 1.37 1.35 1.35 1.35 1.34 1.32 1.32 1.25 1.22 1.21 0.86 0.83 0.81
N
O
N
P
OEt
OEt
H
H
CH3
4a- dia anti
0.99
2.97
5.39
1.07
0.98
1.00
2.99
2.03
2.25
5.94
2.25
3.03
167
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

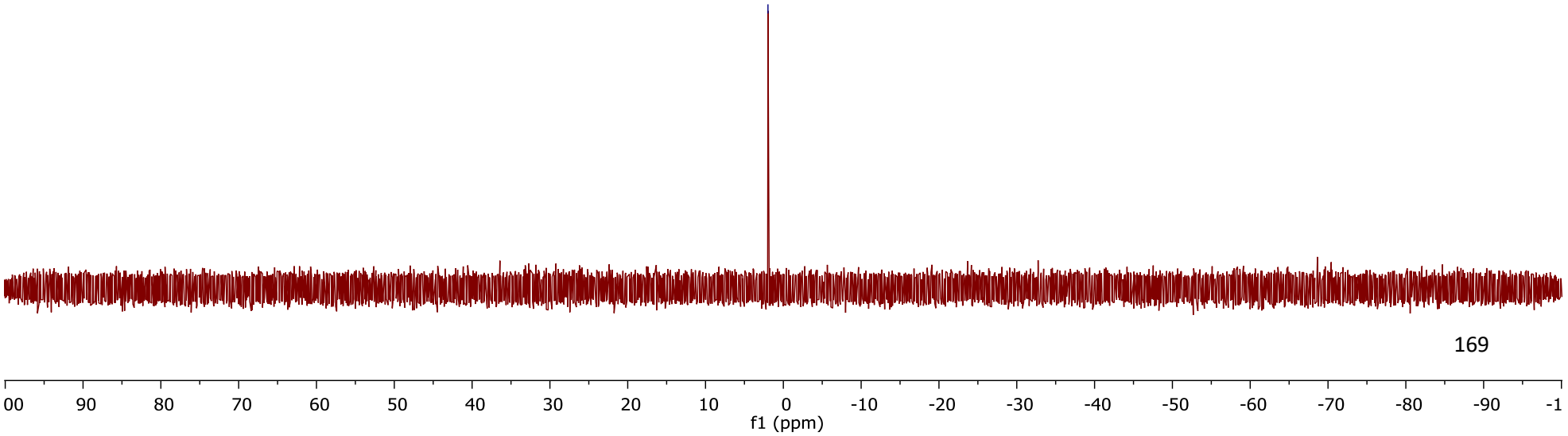
N
N
P
O
OEt
OEt
H
H
CH3

4a- dia *anti*

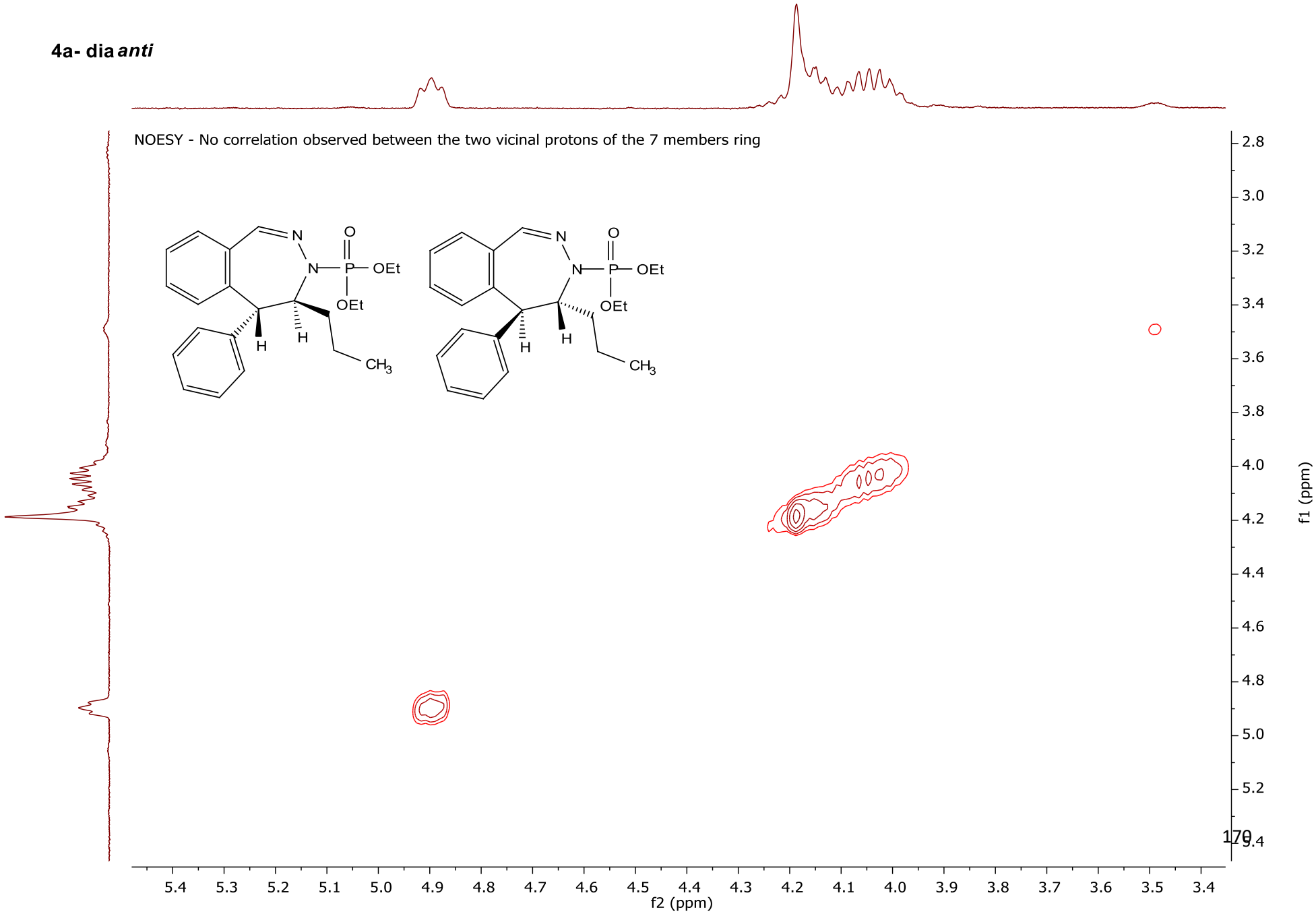

141.5
141.3
141.1
140.3
132.0
131.8
129.0
129.0
128.9
128.6
127.2
126.6
64.2
64.1
63.2
63.2
63.0
62.9
55.7
55.7
31.8
20.1
16.2
16.2
14.0
168
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

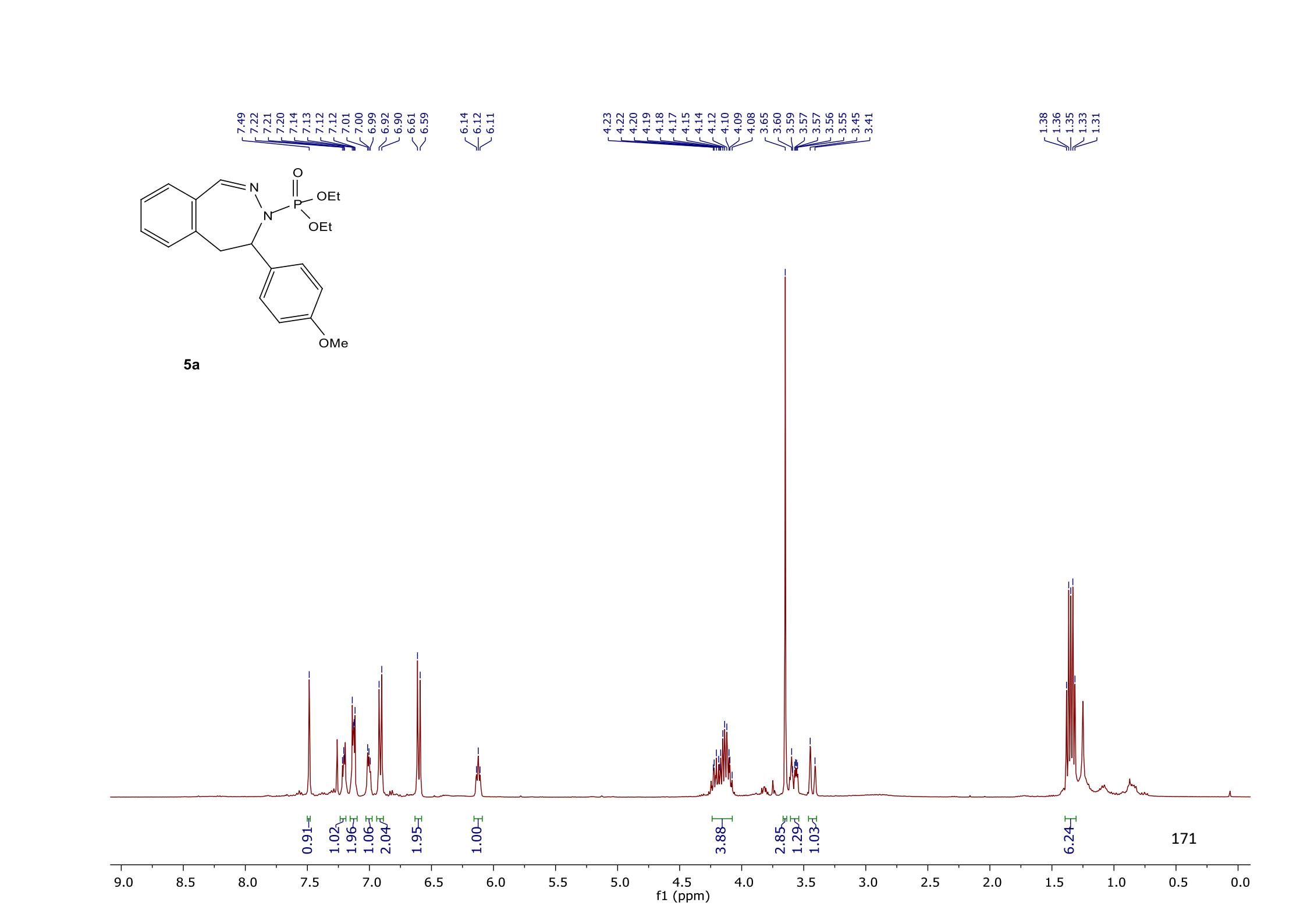

N
O
N
P
OEt
OEt
H
H
CH3
N
O
N
P
OEt
OEt
H
H
CH3

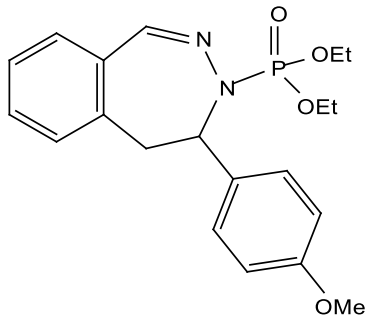
4a- dia *anti*


1.98
169
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

4a- dia *anti*

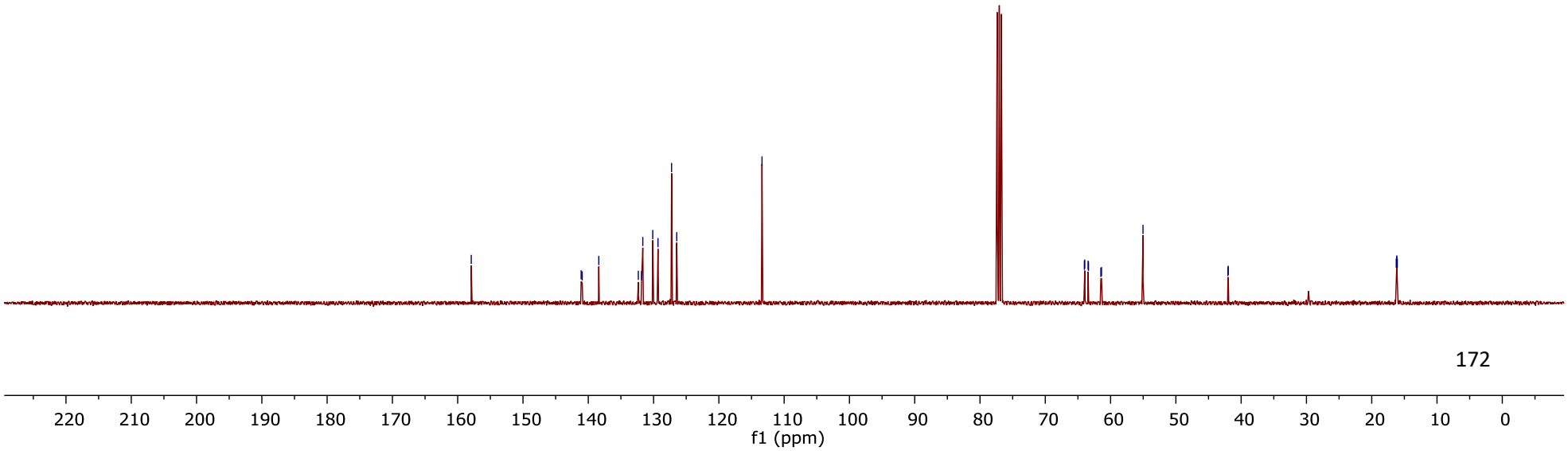

NOESY - No correlation observed between the two vicinal protons of the 7 members ring
N
O
P
OEt
OEt
H
H
CH3
f1 (ppm)
f2 (ppm)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4


7.49
7.22
7.21
7.20
7.14
7.13
7.12
7.12
7.01
7.00
6.99
6.92
6.90
6.61
6.59
6.14
6.12
6.11
4.23
4.22
4.20
4.19
4.18
4.17
4.15
4.14
4.12
4.10
4.09
4.08
3.65
3.60
3.59
3.57
3.57
3.56
3.55
3.45
3.41
1.38
1.36
1.35
1.33
1.31
O
N
P
OEt
N
OEt
OMe
5a
0.91
1.02
1.96
1.06
2.04
1.95
1.00
3.88
2.85
1.29
1.03
6.24
171
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



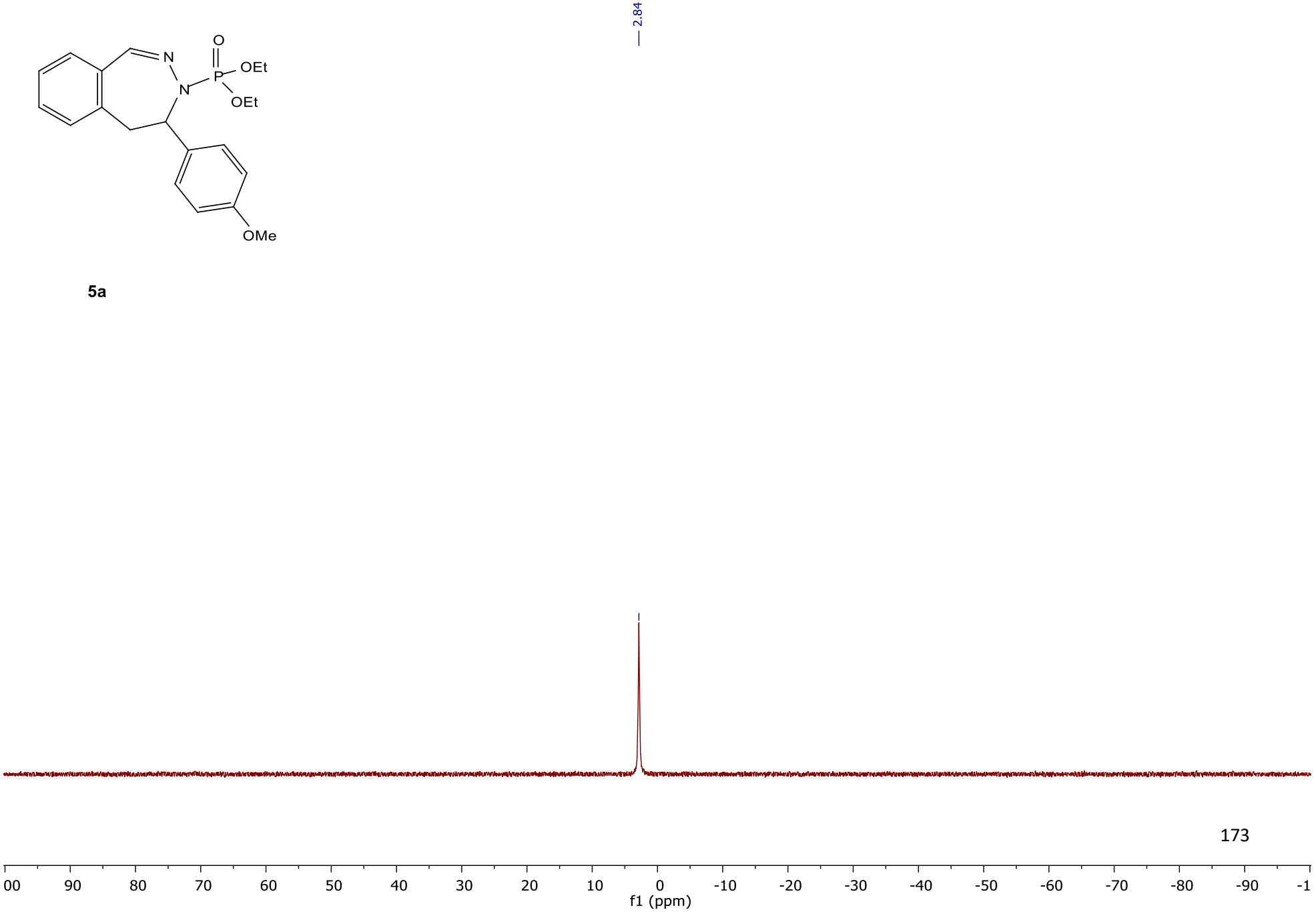
5a

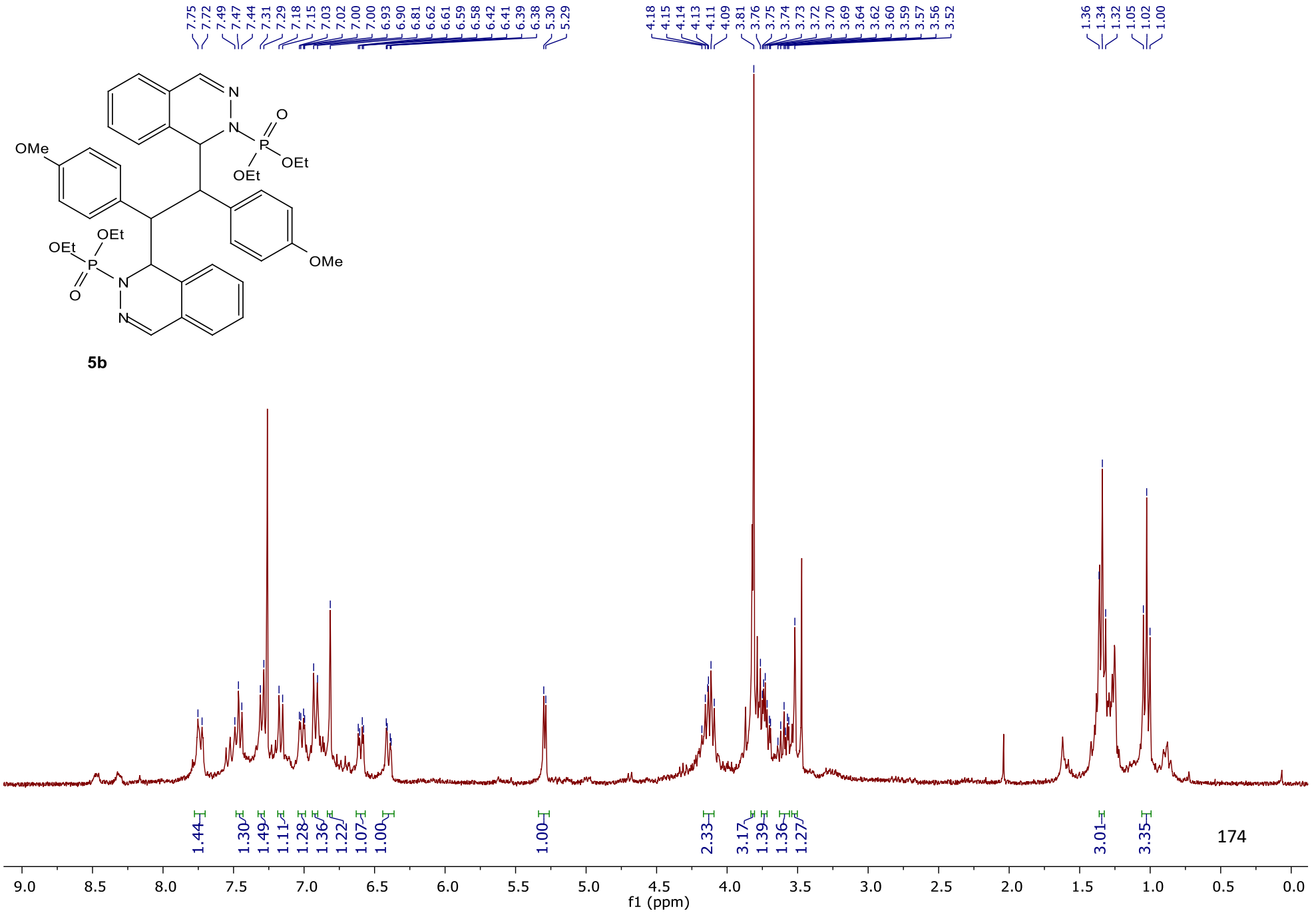
157.9
141.1
140.9
138.4
132.3
131.8
131.7
130.1
129.3
127.2
126.5
113.4
64.0
64.0
63.4
63.4
61.5
61.4
55.0
42.0
42.0
16.2
16.2
16.2
16.1

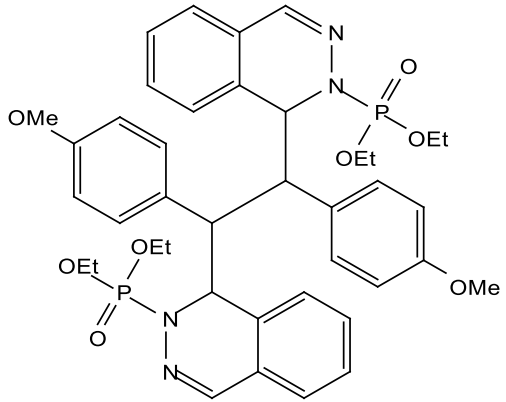


O
N
OEt
P
N
OEt
OMe

5a


2.84
173
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.75
7.72
7.49
7.47
7.44
7.31
7.29
7.18
7.15
7.03
7.02
7.00
7.00
6.93
6.90
6.81
6.62
6.61
6.59
6.58
6.42
6.41
6.39
6.38
5.30
5.29
4.18
4.15
4.14
4.13
4.11
4.09
3.81
3.76
3.75
3.74
3.73
3.72
3.70
3.69
3.64
3.62
3.60
3.59
3.57
3.56
3.52
1.36
1.34
1.32
1.05
1.02
1.00
OMe
N
N
O
P
OEt
OEt
OEt
OEt
P
O
N
N
OMe
5b
1.44
1.30
1.49
1.11
1.28
1.36
1.22
1.07
1.00
1.00
2.33
3.17
1.39
1.36
1.27
3.01
3.35
174
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



5b

158.88
142.32
142.20
135.20
131.41
129.55
128.90
127.66
125.43
124.29
113.32
112.24
63.87
63.81
62.49
62.44
55.66
55.06
16.32
16.25
15.72
15.64

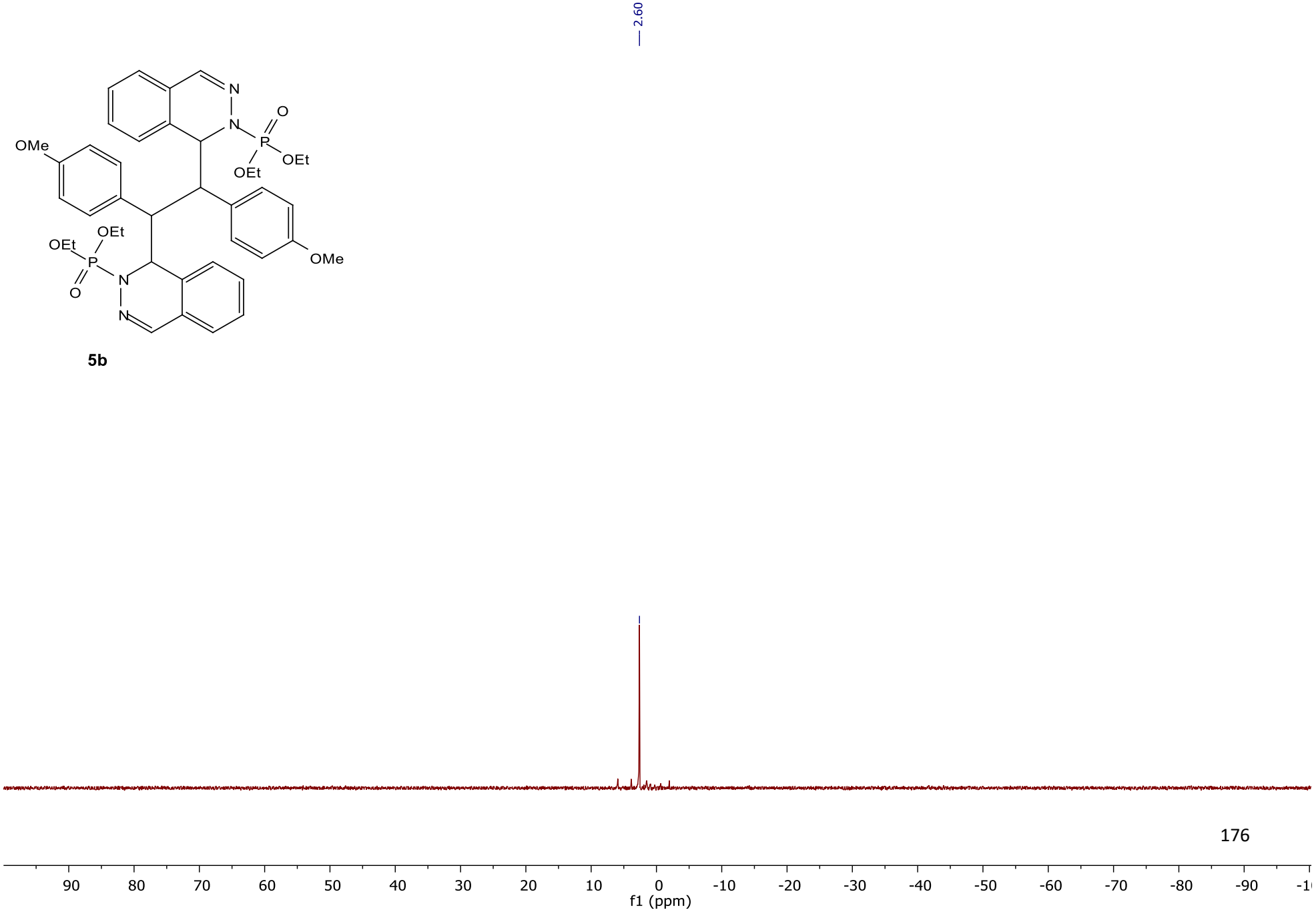
175

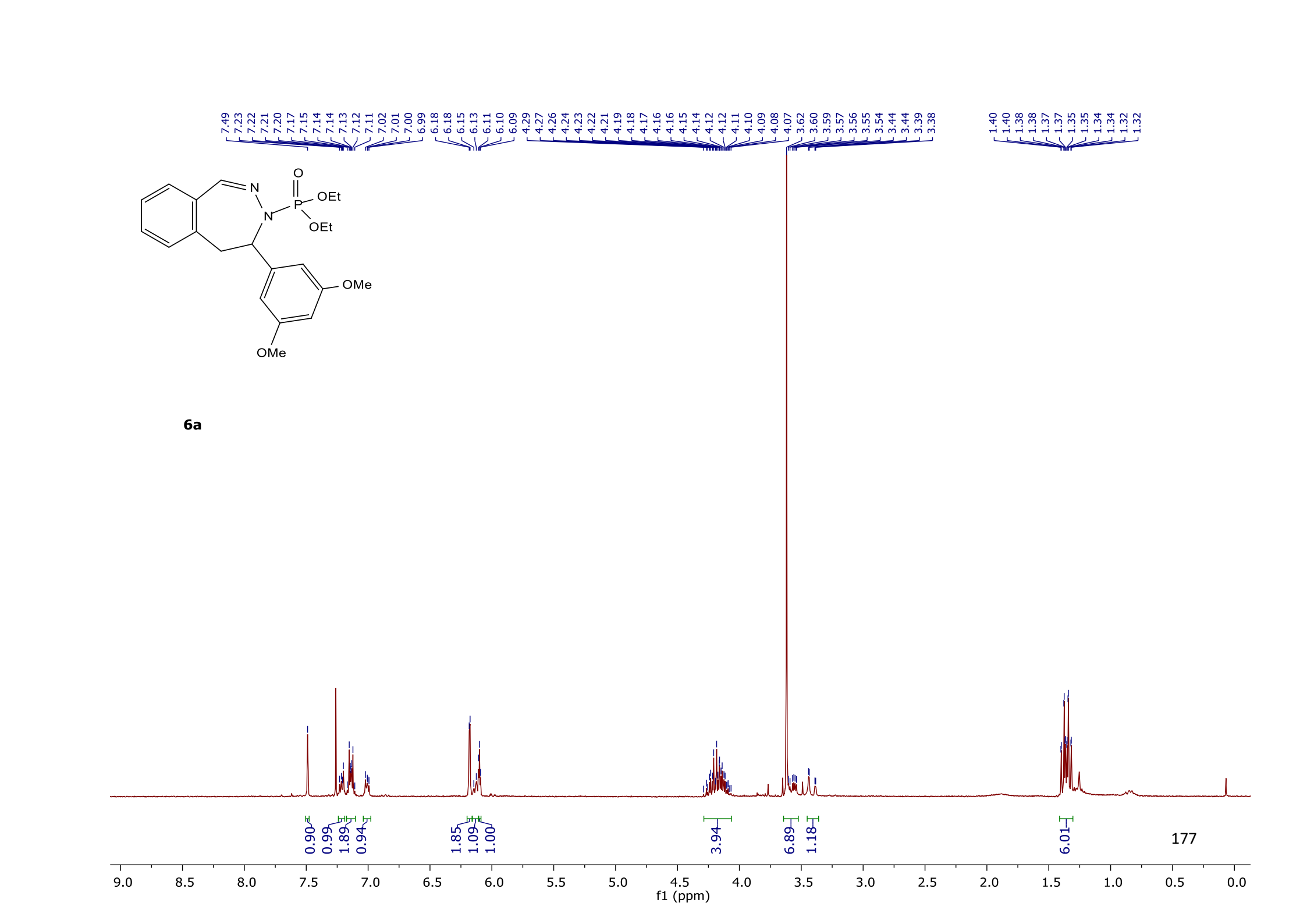
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

OMe
N
N
O
P
OEt
OEt
OEt
OEt
P
O
N
N
OMe

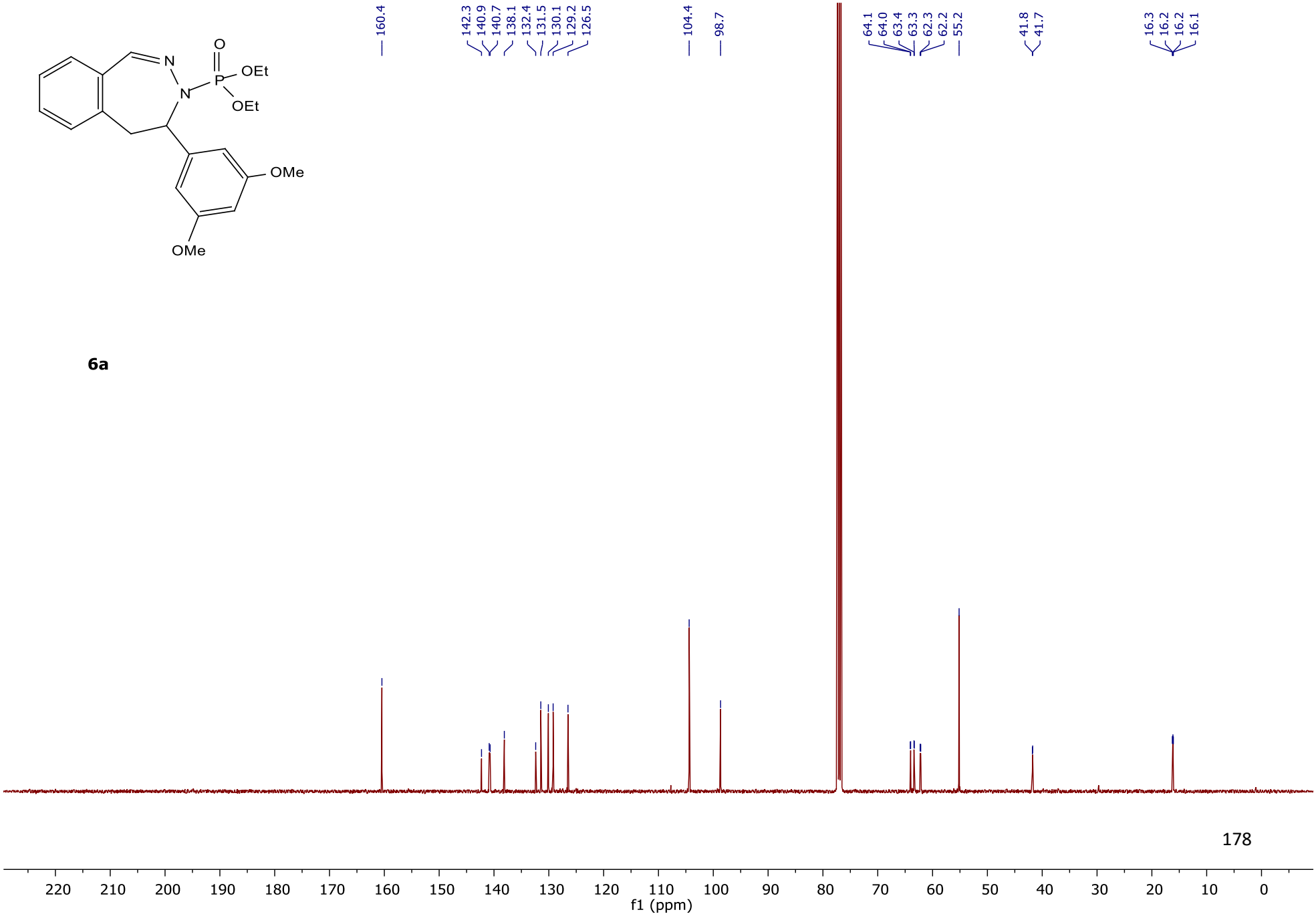
5b

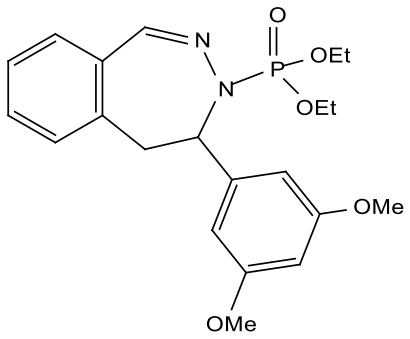

2.60
176
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)


7.49 7.23 7.22 7.21 7.20 7.17 7.15 7.14 7.14 7.13 7.12 7.11 7.02 7.01 7.00 6.99 6.18 6.18 6.15 6.13 6.11 6.10 6.09 4.29 4.27 4.26 4.24 4.23 4.22 4.21 4.19 4.18 4.17 4.16 4.16 4.15 4.14 4.12 4.12 4.11 4.10 4.09 4.08 4.07 3.62 3.60 3.59 3.57 3.56 3.55 3.54 3.44 3.44 3.39 3.38 1.40 1.40 1.38 1.38 1.37 1.37 1.35 1.35 1.34 1.34 1.32 1.32
O
N
P
OEt
N
OEt
OMe
OMe
6a
0.90 0.99 1.89 0.94 1.85 1.09 1.00 3.94 6.89 1.18 6.01
177
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

O
N
P
OEt
N
OEt
OMe
OMe

6a


160.4
142.3
140.9
140.7
138.1
132.4
131.5
130.1
129.2
126.5
104.4
98.7
64.1
64.0
63.4
63.3
62.3
62.2
55.2
41.8
41.7
16.3
16.2
16.2
16.1
178
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



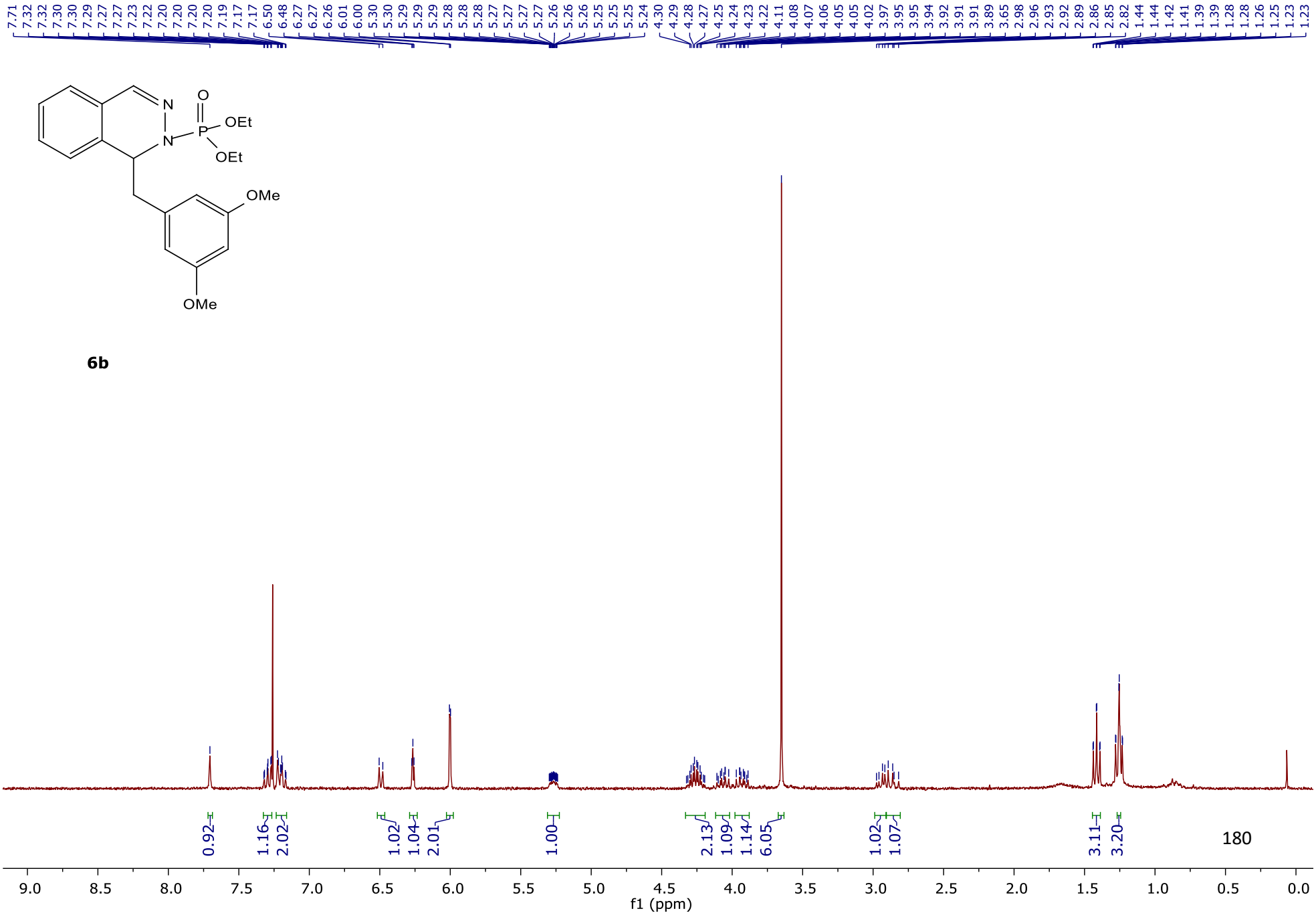
2.76

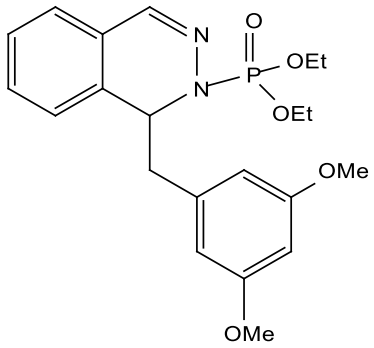
6a

179

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


7.71 7.32 7.32 7.30 7.30 7.29 7.27 7.27 7.23 7.22 7.20 7.20 7.20 7.19 7.17 7.17 6.50 6.48 6.27 6.27 6.26 6.01 6.00 5.30 5.30 5.29 5.29 5.28 5.28 5.27 5.27 5.27 5.27 5.26 5.26 5.25 5.25 5.24
4.30 4.29 4.28 4.27 4.25 4.24 4.23 4.22 4.11 4.08 4.07 4.06 4.05 4.05 4.02 3.97 3.95 3.95 3.94 3.92 3.91 3.91 3.89 3.65 2.98 2.96 2.93 2.92 2.89 2.86 2.85 2.82 1.44 1.44 1.42 1.41 1.39 1.39 1.28 1.28 1.26 1.25 1.23 1.23
N
N
O
P
OEt
OEt
OMe
OMe
6b
0.92
1.16
2.02
1.02
1.04
2.01
1.00
2.13
1.09
1.14
6.05
1.02
1.07
3.11
3.20
180
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

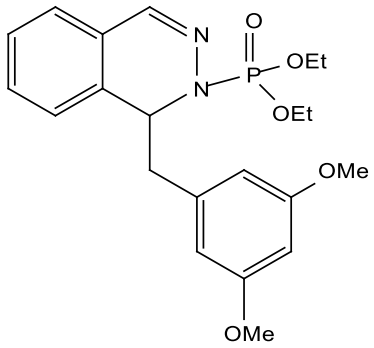


6b

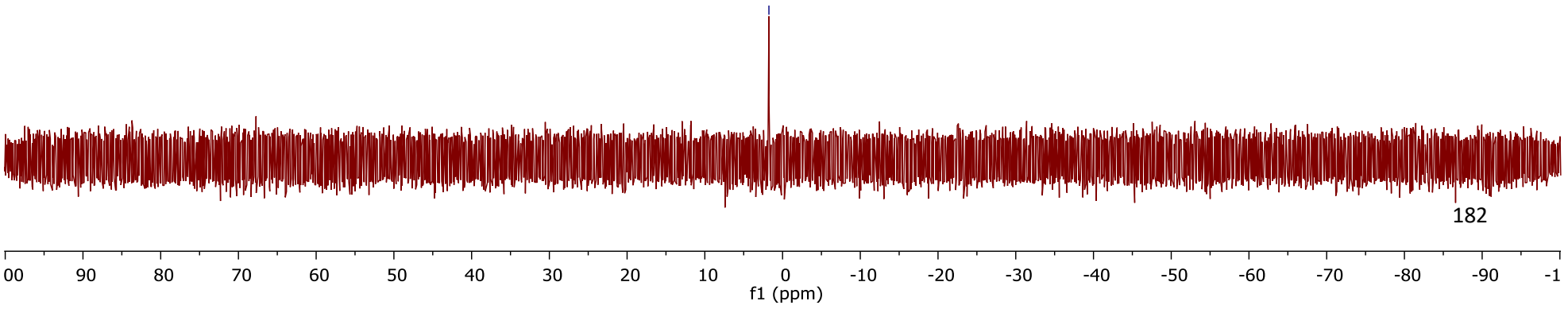
160.41
142.92
142.80
138.52
131.60
131.53
130.53
127.94
126.93
124.98
123.60
107.74
99.26
63.97
63.90
63.21
63.15
55.59
55.51
55.26
41.65
16.32
16.25
15.99
15.92

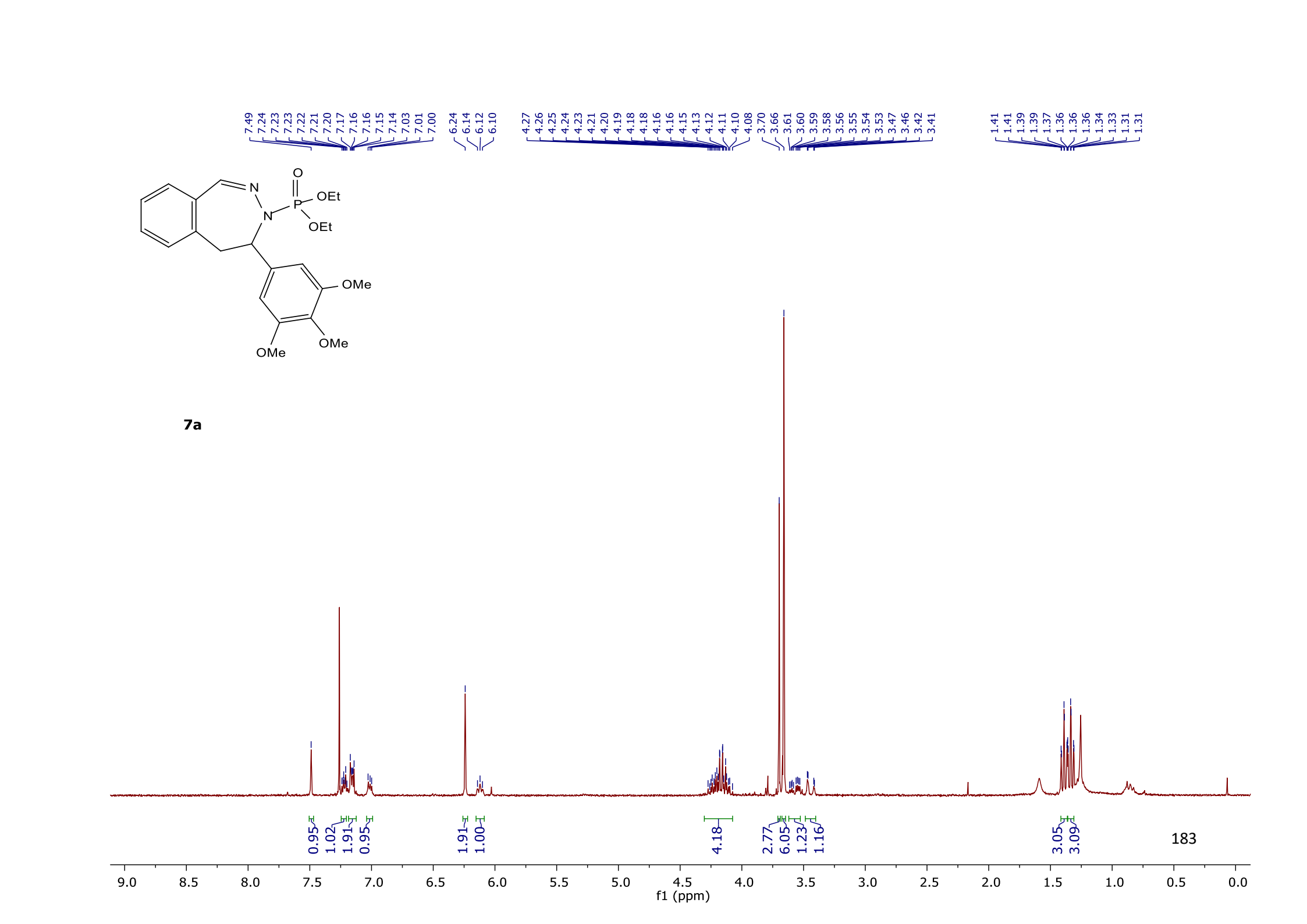
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


N
O
OEt
N
P
OEt
OMe
OMe

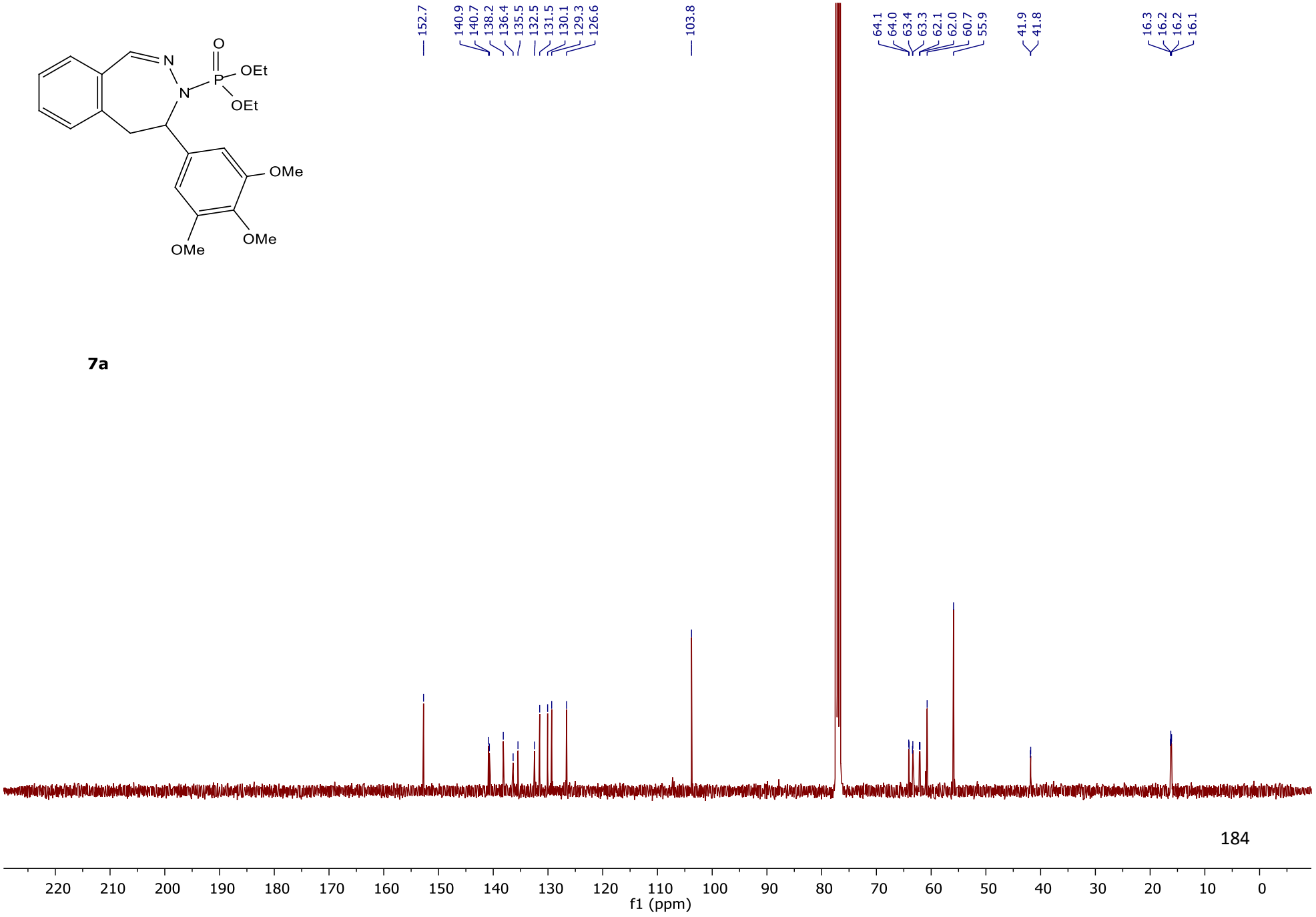
6b


1.75
182
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.49 7.24 7.23 7.23 7.22 7.21 7.20 7.17 7.16 7.16 7.15 7.14 7.03 7.01 7.00
6.24 6.14 6.12 6.10
4.27 4.26 4.25 4.24 4.23 4.21 4.20 4.19 4.18 4.18 4.16 4.16 4.15 4.13 4.12 4.11 4.10 4.08
3.70 3.66 3.61 3.60 3.59 3.58 3.56 3.55 3.54 3.53 3.47 3.46 3.42 3.41
1.41 1.41 1.39 1.39 1.37 1.36 1.36 1.36 1.34 1.33 1.31 1.31
O
N
P
OEt
N
OEt
OMe
OMe
OMe
7a
0.95 1.02 1.91 0.95 1.91 1.00 4.18 2.77 6.05 1.23 1.16 3.05 3.09
183
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

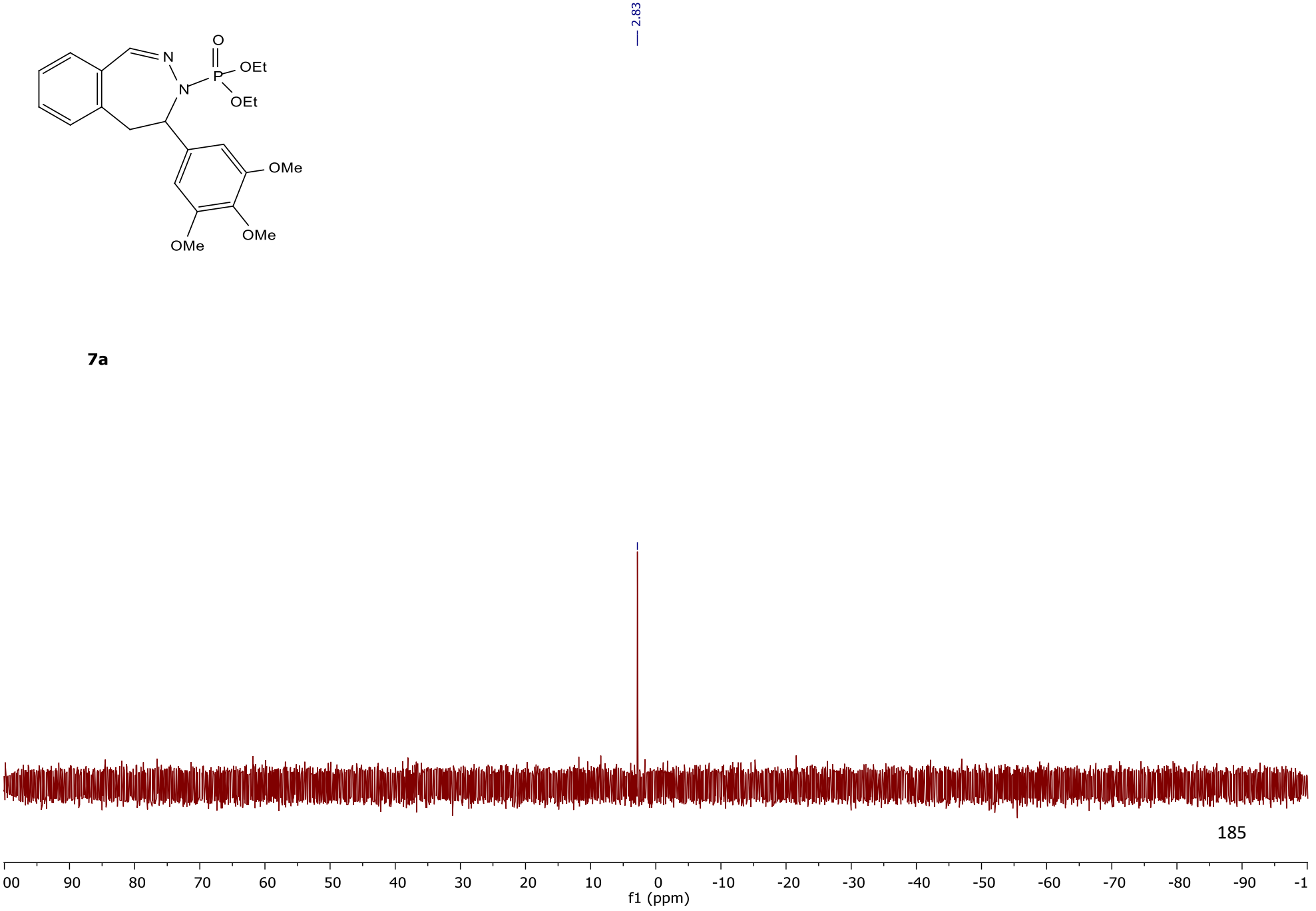
O
N
P
OEt
N
OEt
OMe
OMe
OMe

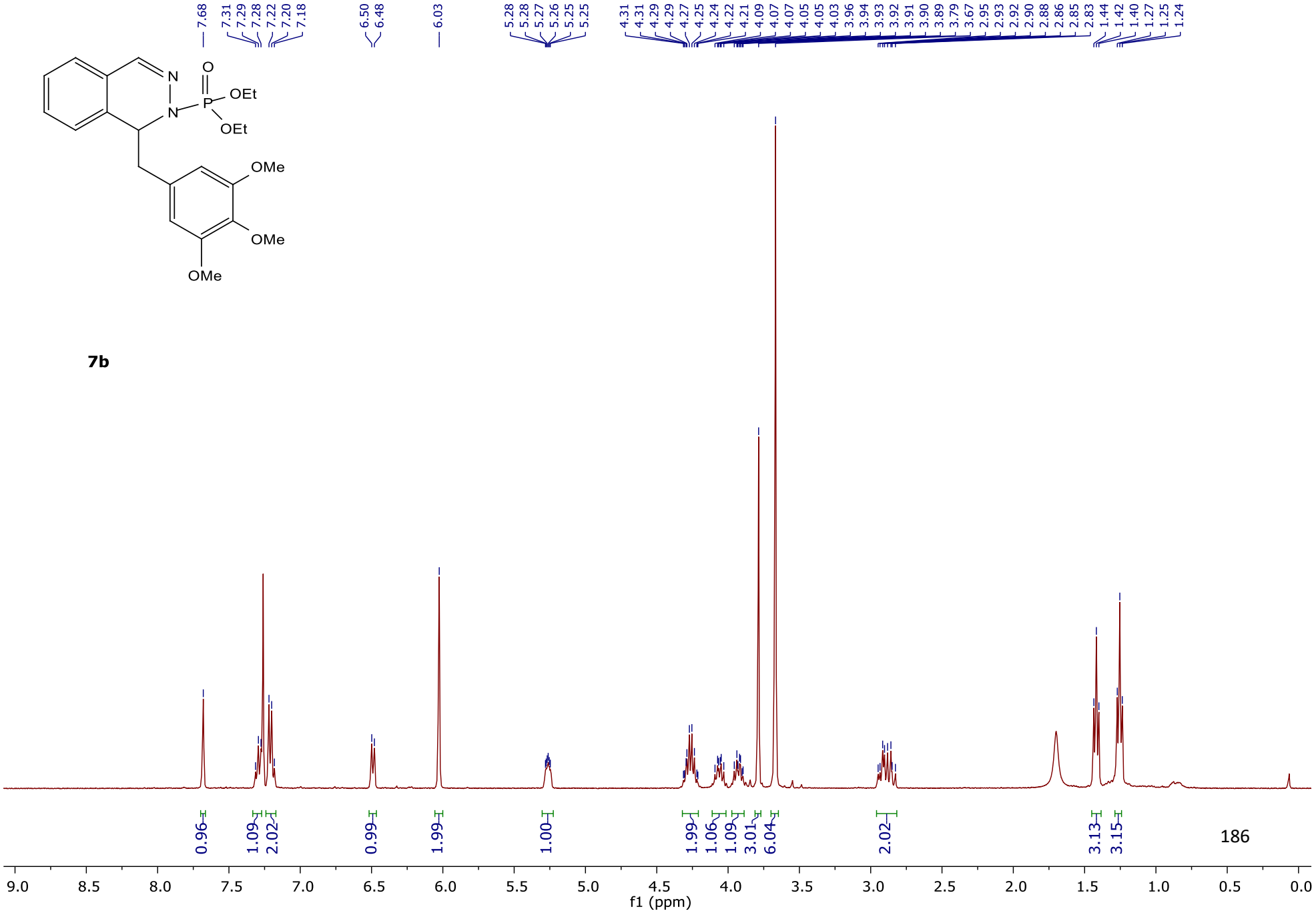
7a

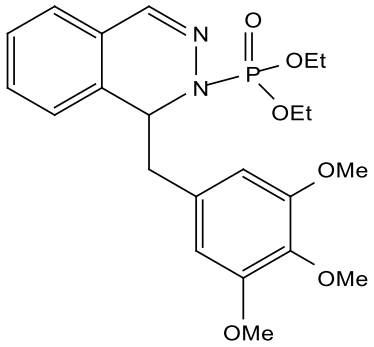

152.7
140.9
140.7
138.2
136.4
135.5
132.5
131.5
130.1
129.3
126.6
103.8
64.1
64.0
63.4
63.3
62.1
62.0
60.7
55.9
41.9
41.8
16.3
16.2
16.2
16.1
184
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

O
N
OEt
P
N
OEt
OMe
OMe
OMe

7a

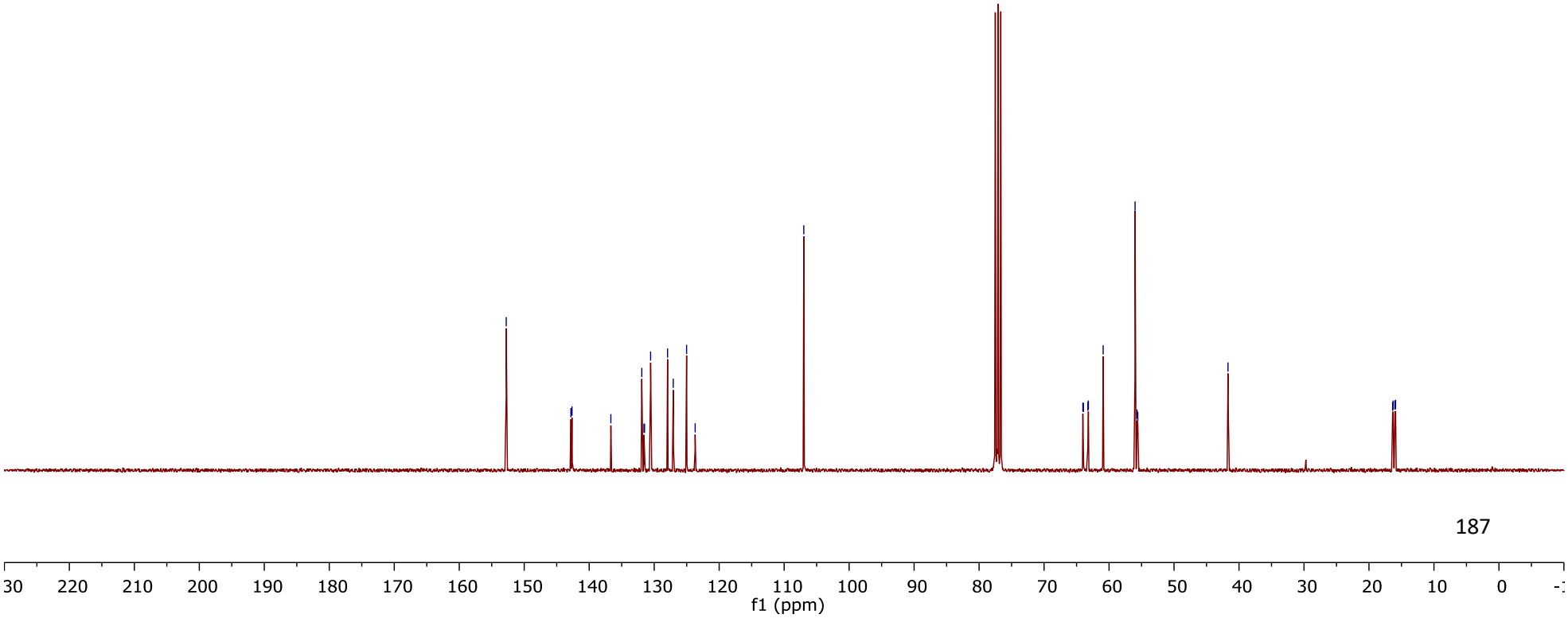

2.83
185
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.68
7.31
7.29
7.28
7.22
7.20
7.18
6.50
6.48
6.03
5.28
5.28
5.27
5.26
5.25
5.25
4.31
4.31
4.29
4.29
4.27
4.25
4.24
4.22
4.21
4.09
4.07
4.07
4.05
4.05
4.03
3.96
3.94
3.93
3.92
3.91
3.90
3.89
3.79
3.67
2.95
2.93
2.92
2.90
2.88
2.86
2.85
2.83
1.44
1.42
1.40
1.27
1.25
1.24
N
N
O
P
OEt
OEt
OMe
OMe
OMe
7b
0.96
1.09
2.02
0.99
1.99
1.00
1.99
1.06
1.09
3.01
6.04
2.02
3.13
3.15
186
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



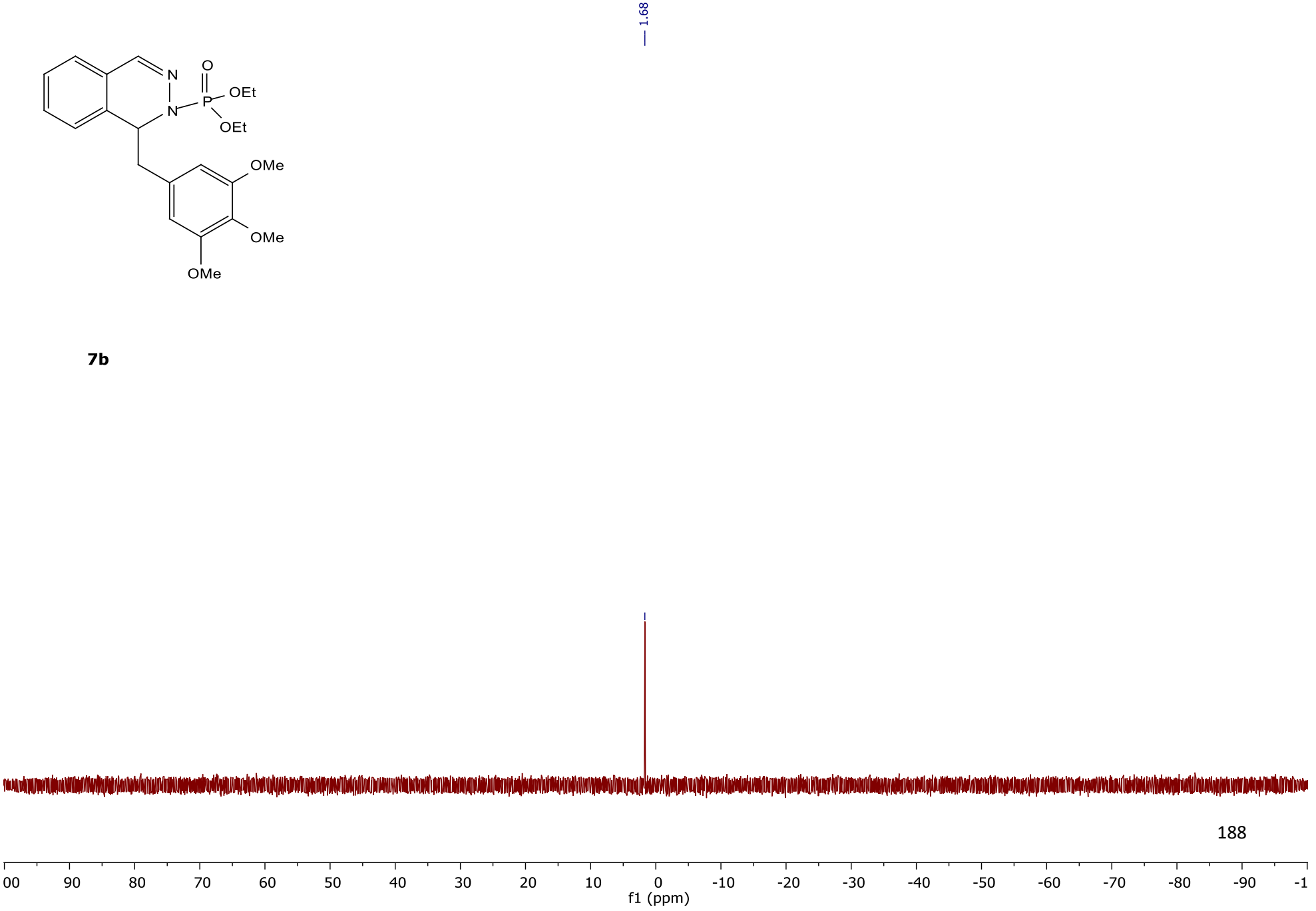
152.8
142.8
142.6
136.7
131.9
131.6
131.5
130.6
127.9
127.1
125.0
123.7
107.0
64.0
63.9
63.3
63.2
60.9
56.0
55.7
55.6
41.7
16.4
16.3
16.0
15.9

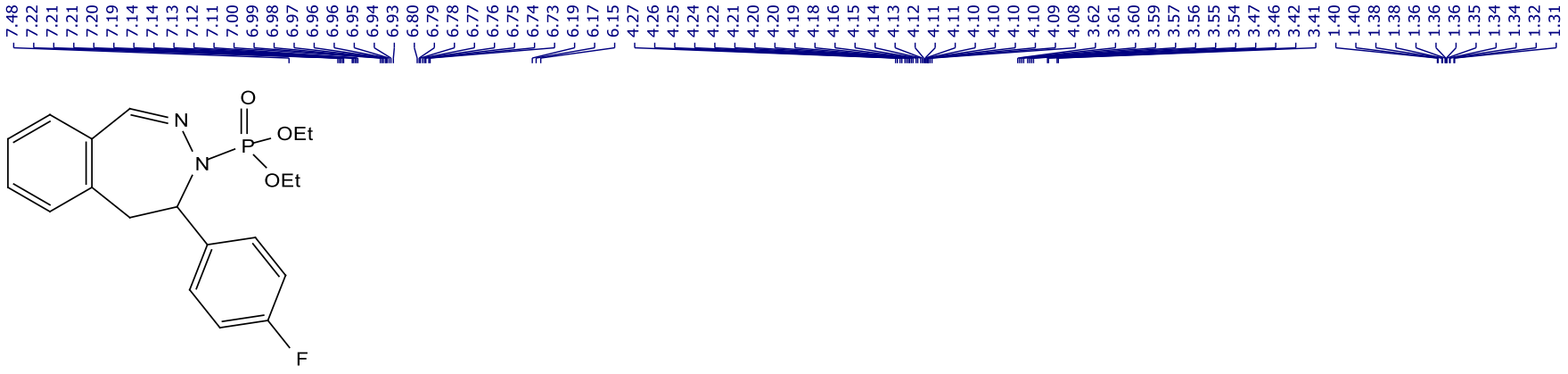
7b



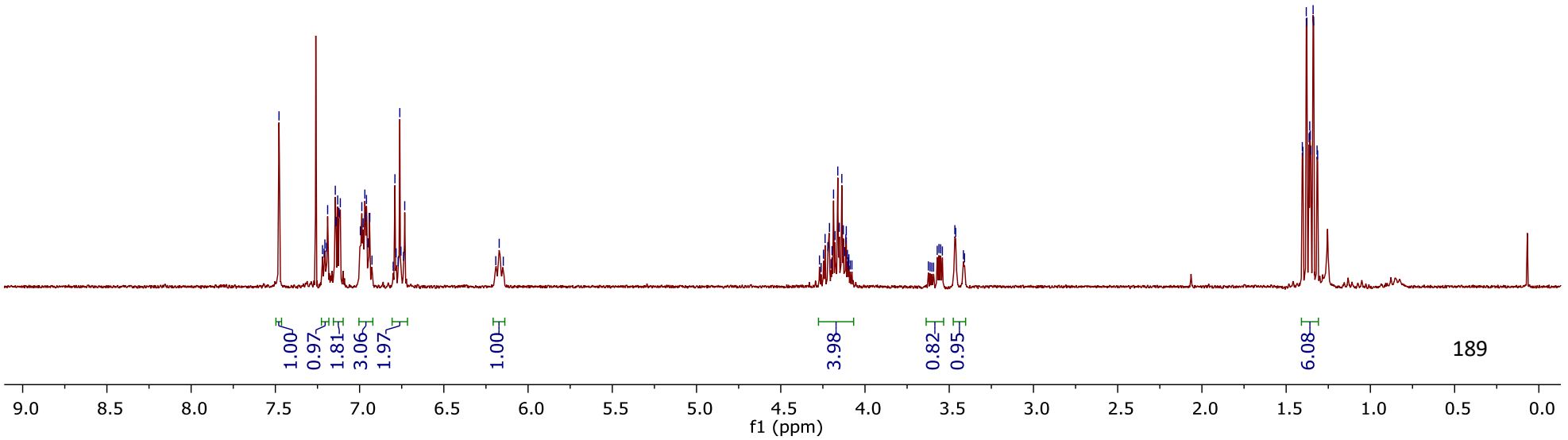
N
O
OEt
N
P
OEt
OMe
OMe
OMe

7b


1.68
188
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

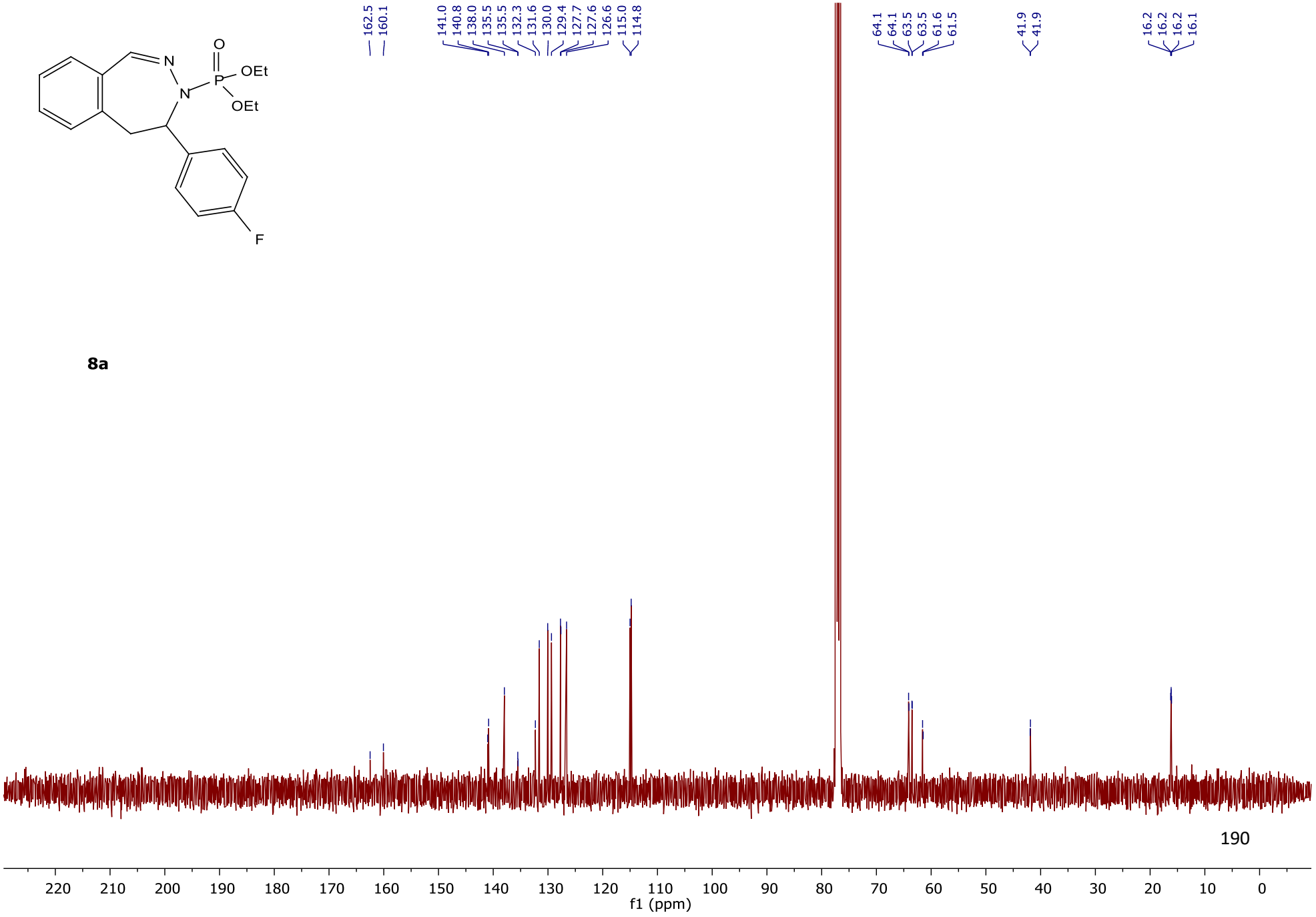

7.48 7.22 7.21 7.21 7.20 7.19 7.14 7.14 7.13 7.12 7.11 7.00 6.99 6.98 6.97 6.96 6.96 6.95 6.94 6.93 6.80 6.79 6.78 6.77 6.76 6.75 6.74 6.73 6.19 6.17 6.15 4.27 4.26 4.25 4.24 4.22 4.21 4.20 4.20 4.19 4.18 4.16 4.15 4.14 4.13 4.12 4.11 4.11 4.10 4.10 4.10 4.10 4.09 4.08 3.62 3.61 3.60 3.59 3.57 3.56 3.55 3.54 3.47 3.46 3.42 3.41 1.40 1.40 1.38 1.38 1.36 1.36 1.35 1.34 1.34 1.32 1.31
O
N
P
OEt
N
OEt
F

8a

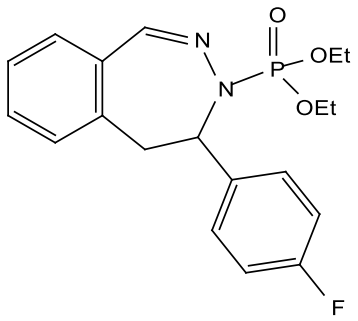

1.00
0.97
1.81
3.06
1.97
1.00
3.98
0.82
0.95
6.08
189
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

O
N
P
OEt
N
OEt
F

8a


162.5
160.1
141.0
140.8
138.0
135.5
135.5
132.3
131.6
130.0
129.4
127.7
127.6
126.6
115.0
114.8
64.1
64.1
63.5
63.5
61.6
61.5
41.9
41.9
16.2
16.2
16.2
16.1
190
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

31P dec 1H



2.65

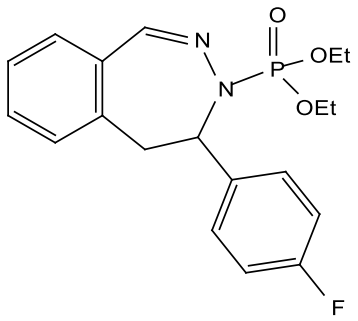
8a

191

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)

19F



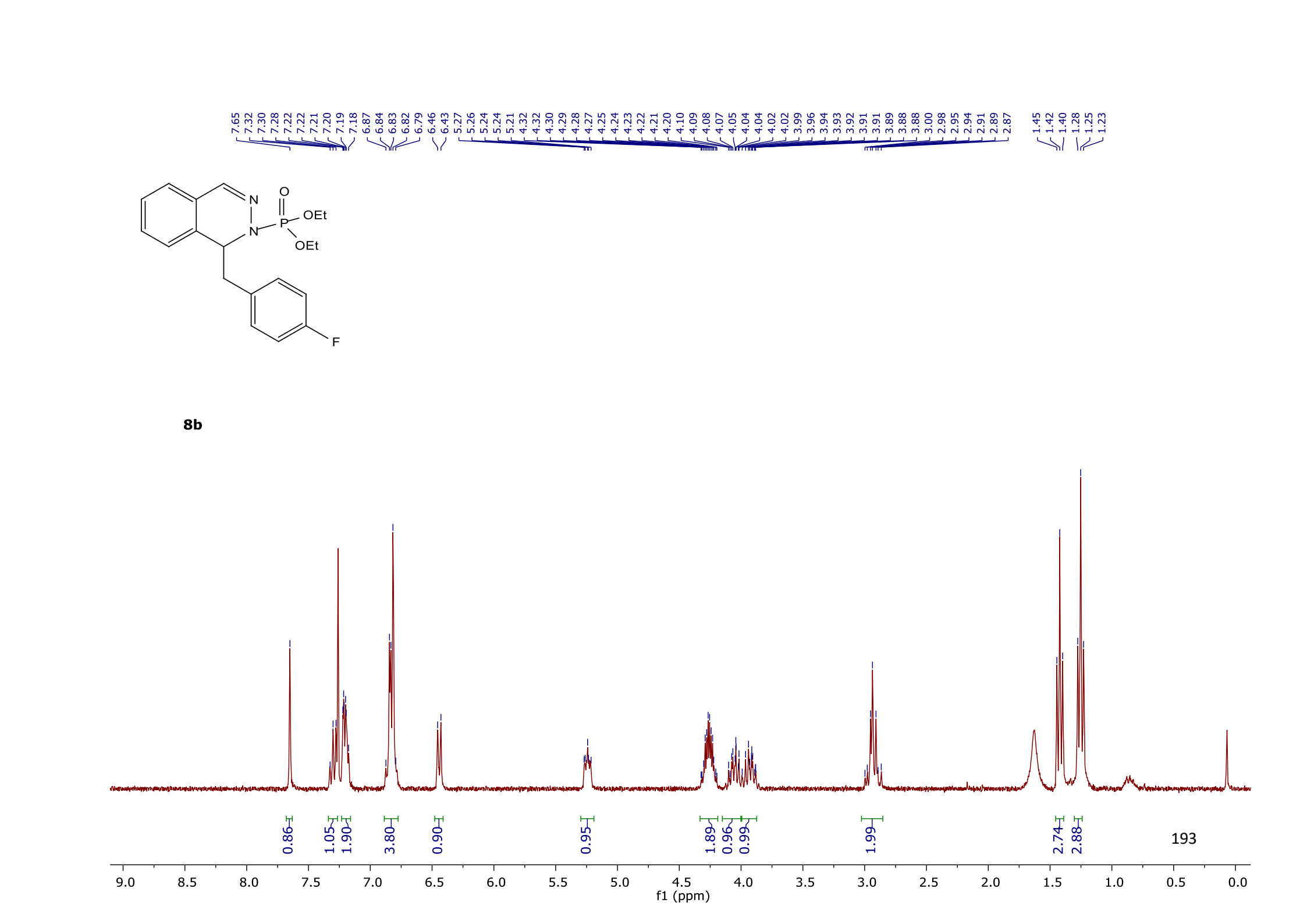
-116.53

8a

192

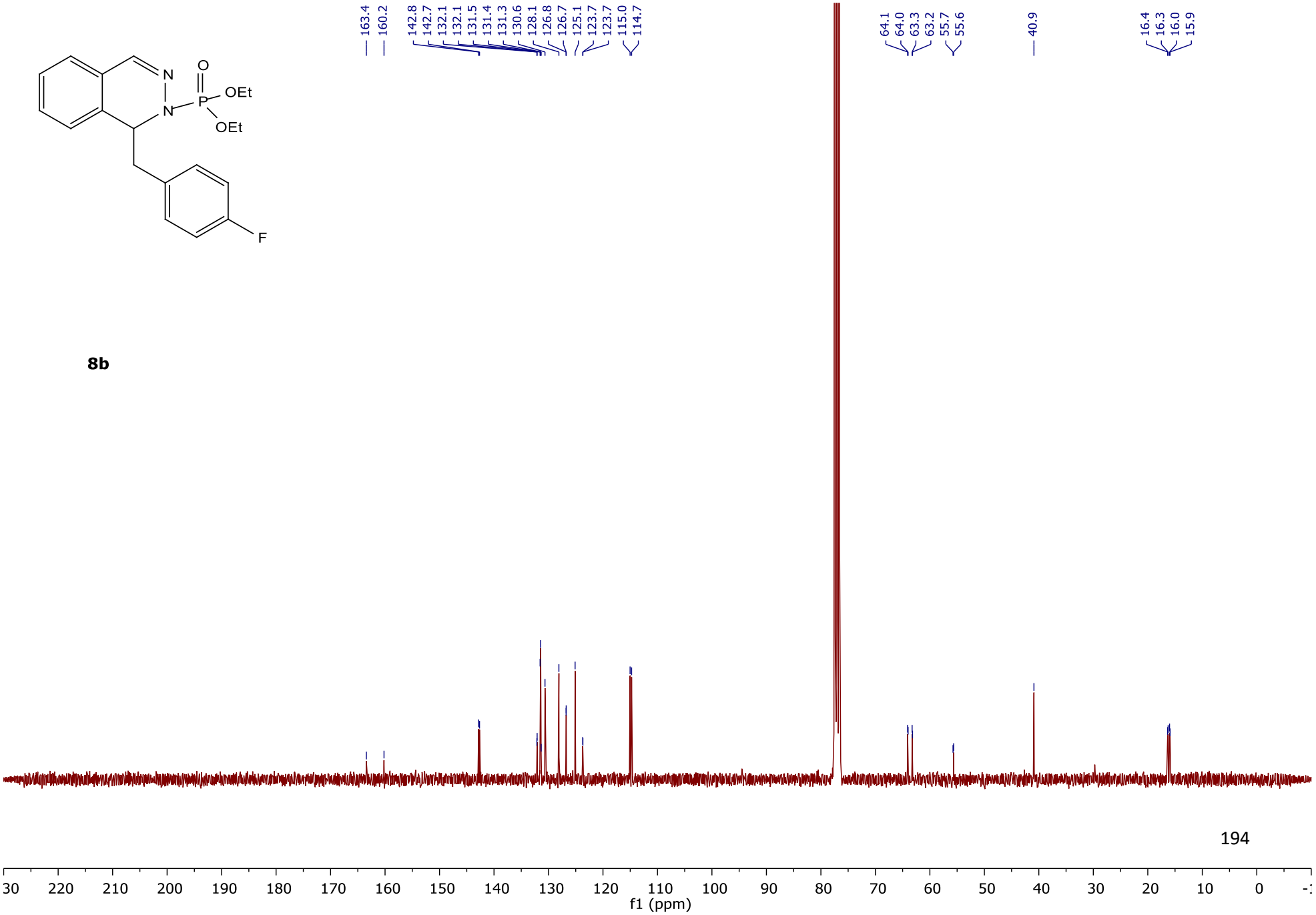
-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240

f1 (ppm)

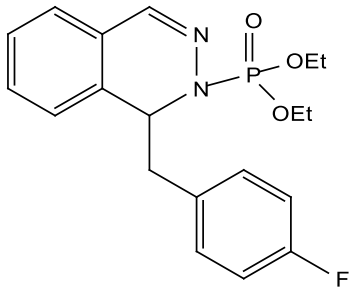

7.65 7.32 7.30 7.28 7.22 7.22 7.21 7.20 7.19 7.18 6.87 6.84 6.83 6.82 6.79 6.46 6.43 5.27 5.26 5.24 5.24 5.21 4.32 4.32 4.30 4.29 4.28 4.27 4.25 4.24 4.23 4.22 4.21 4.20 4.10 4.09 4.08 4.07 4.05 4.04 4.04 4.02 4.02 3.99 3.96 3.94 3.93 3.92 3.91 3.91 3.89 3.88 3.88 3.00 2.98 2.95 2.94 2.91 2.89 2.87 1.45 1.42 1.40 1.28 1.25 1.23
N
O
P
OEt
N
OEt
F
8b
0.86 1.05 1.90 3.80 0.90 0.95 1.89 0.96 0.99 1.99 2.74 2.88
193
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

N
O
OEt
N
P
OEt
F

8b

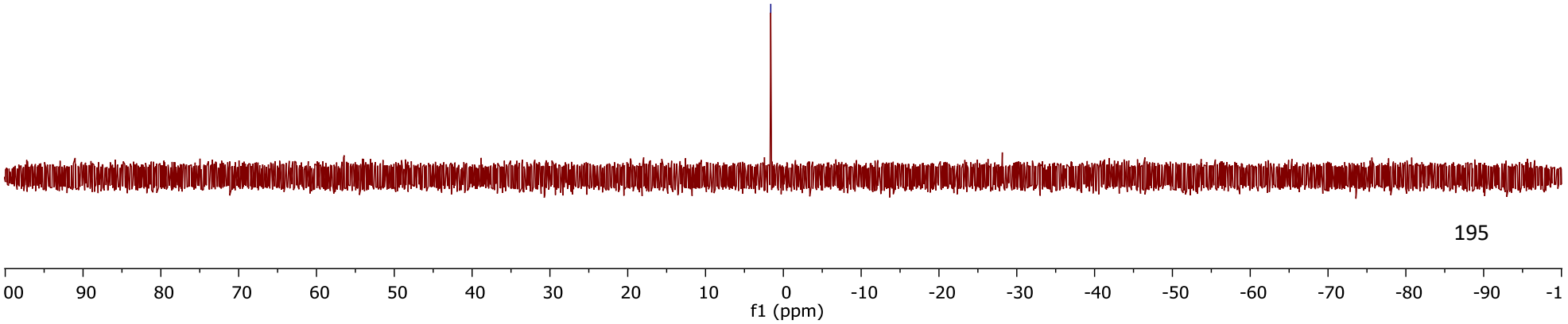

163.4
160.2
142.8
142.7
132.1
132.1
131.5
131.4
131.3
130.6
128.1
126.8
126.7
125.1
123.7
123.7
115.0
114.7
64.1
64.0
63.3
63.2
55.7
55.6
40.9
16.4
16.3
16.0
15.9
194
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

31P dec 1H



1.62

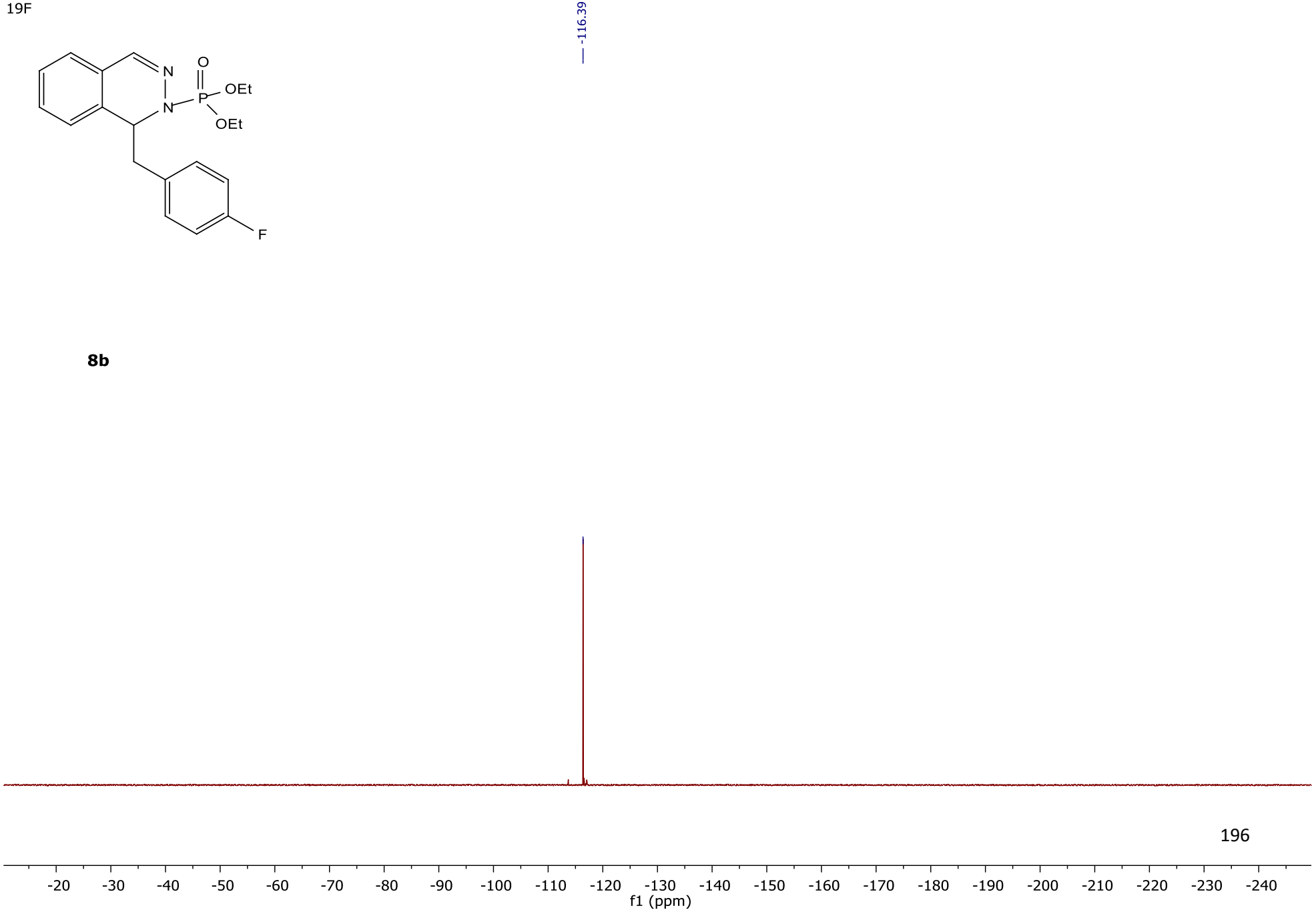
8b

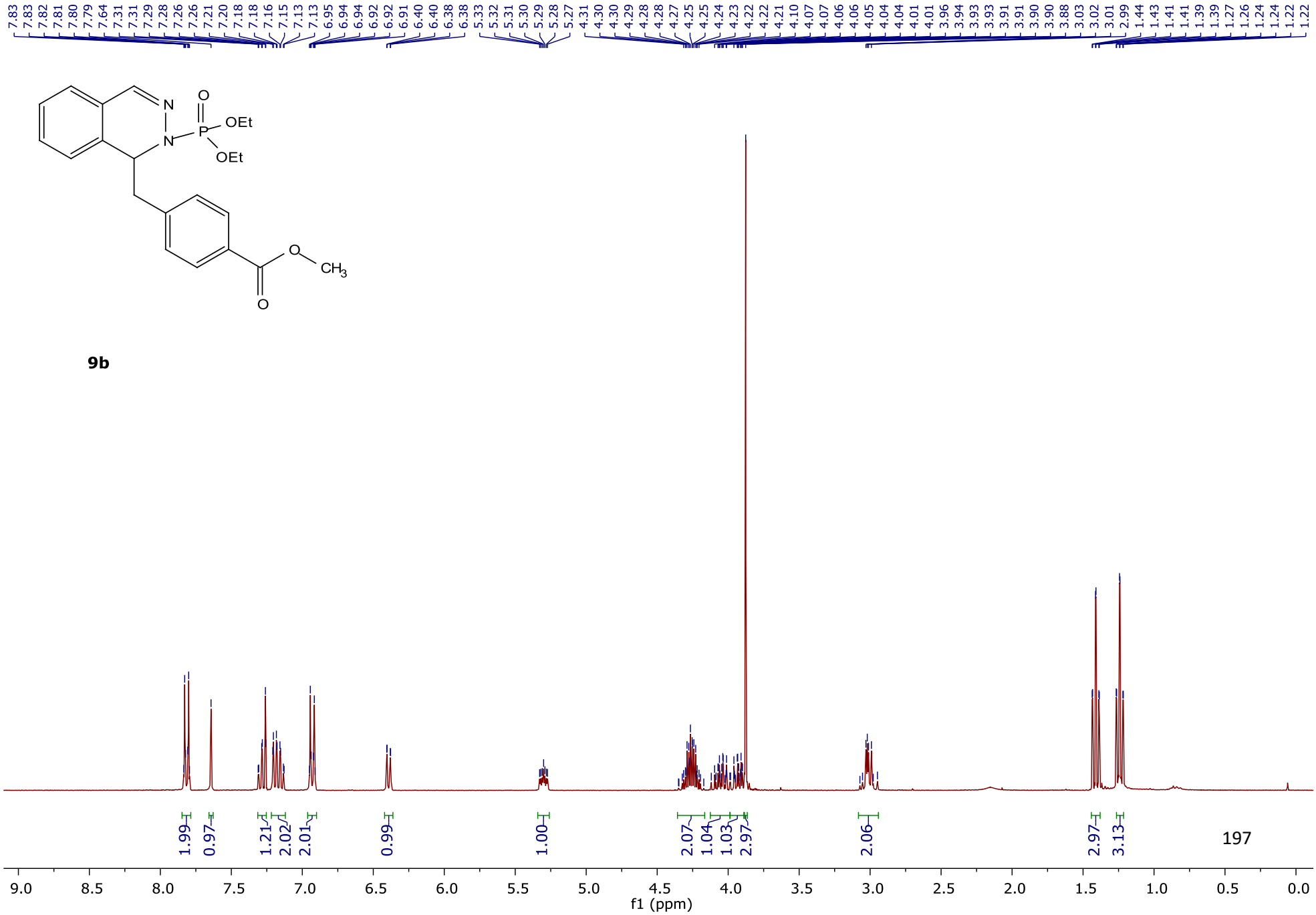


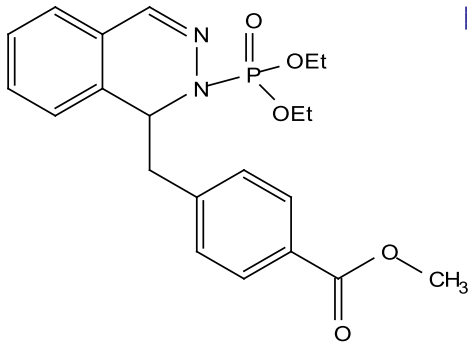
19F

N
O
OEt
N
P
OEt
F

8b

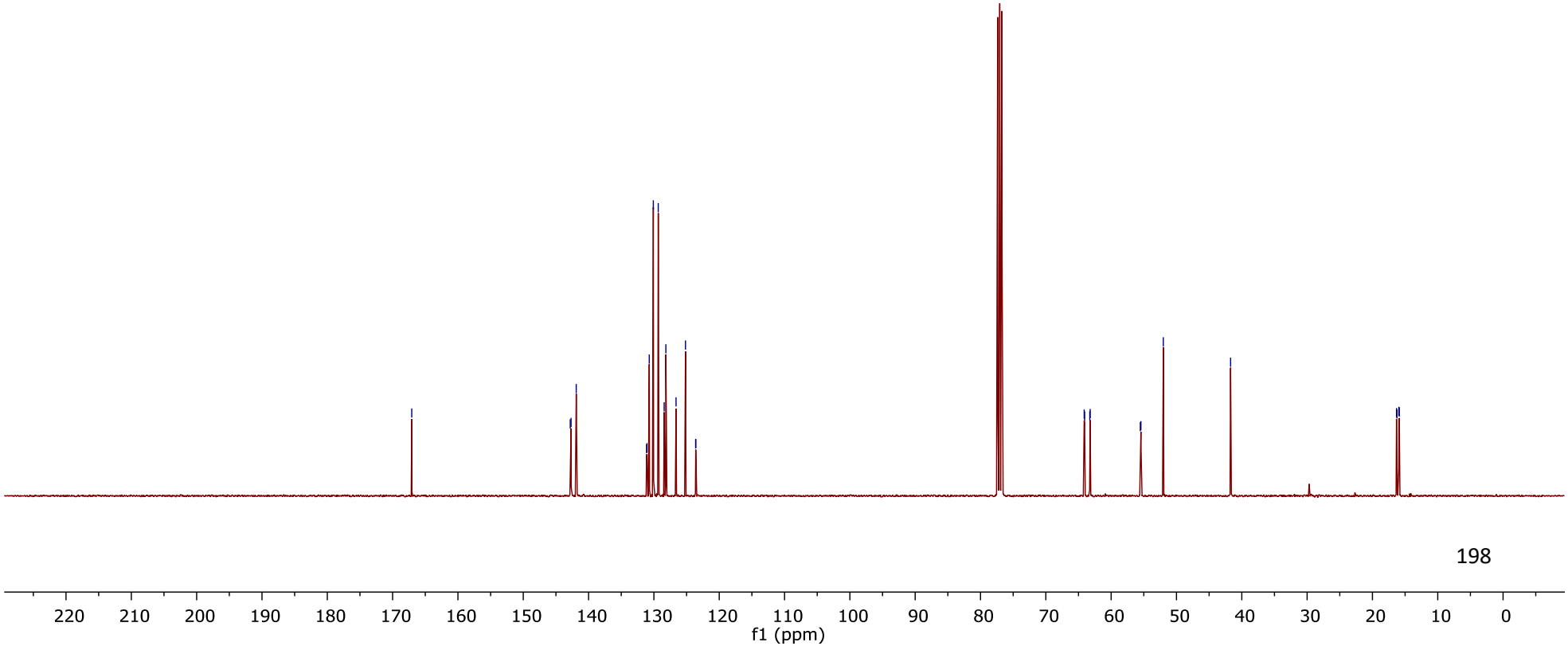

-116.39
196
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

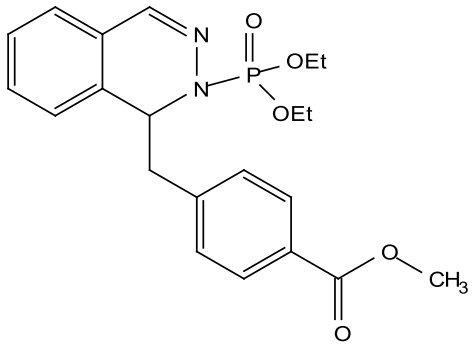

7.83 7.83 7.82 7.81 7.80 7.79 7.64 7.31 7.31 7.29 7.28 7.26 7.26 7.21 7.20 7.18 7.18 7.16 7.15 7.13 7.13 6.95 6.94 6.94 6.92 6.92 6.91 6.40 6.40 6.38 6.38 5.33 5.32 5.31 5.30 5.29 5.28 5.27 4.31 4.30 4.30 4.29 4.28 4.28 4.27 4.25 4.25 4.24 4.23 4.22 4.22 4.21 4.10 4.07 4.07 4.06 4.06 4.05 4.04 4.04 4.01 4.01 3.96 3.94 3.93 3.93 3.91 3.90 3.90 3.88 3.03 3.02 3.01 2.99 1.44 1.43 1.41 1.41 1.39 1.39 1.27 1.26 1.24 1.24 1.22 1.22
N
N
O
P
OEt
OEt
O
O
CH3
9b
1.99
0.97
1.21
2.02
2.01
0.99
1.00
2.07
1.04
1.03
2.97
2.06
2.97
3.13
197
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



167.1
142.8
142.7
141.9
131.1
131.1
130.7
130.1
129.3
128.4
128.2
126.6
125.2
123.6
123.6
64.1
64.1
63.3
63.2
55.5
55.4
52.0
41.7
16.3
16.2
16.0
15.9

9b





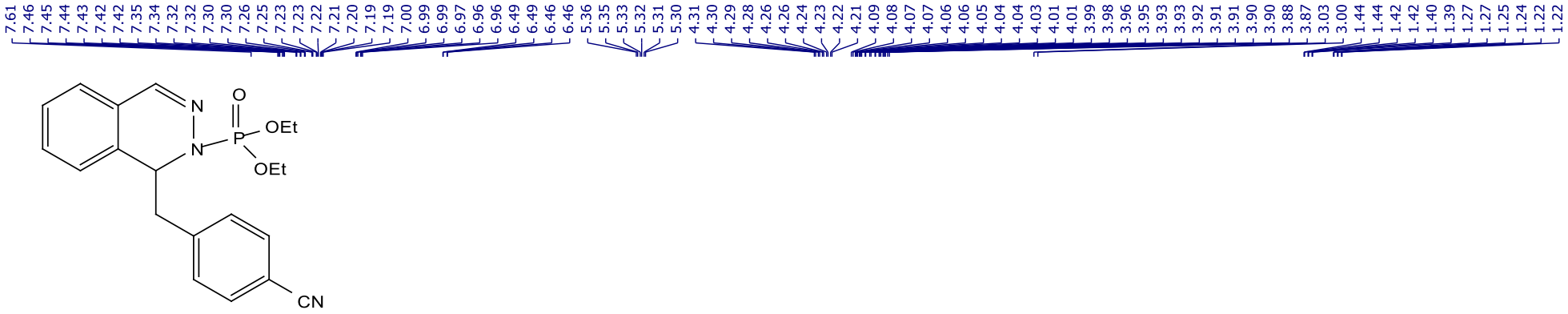
1.49

9b

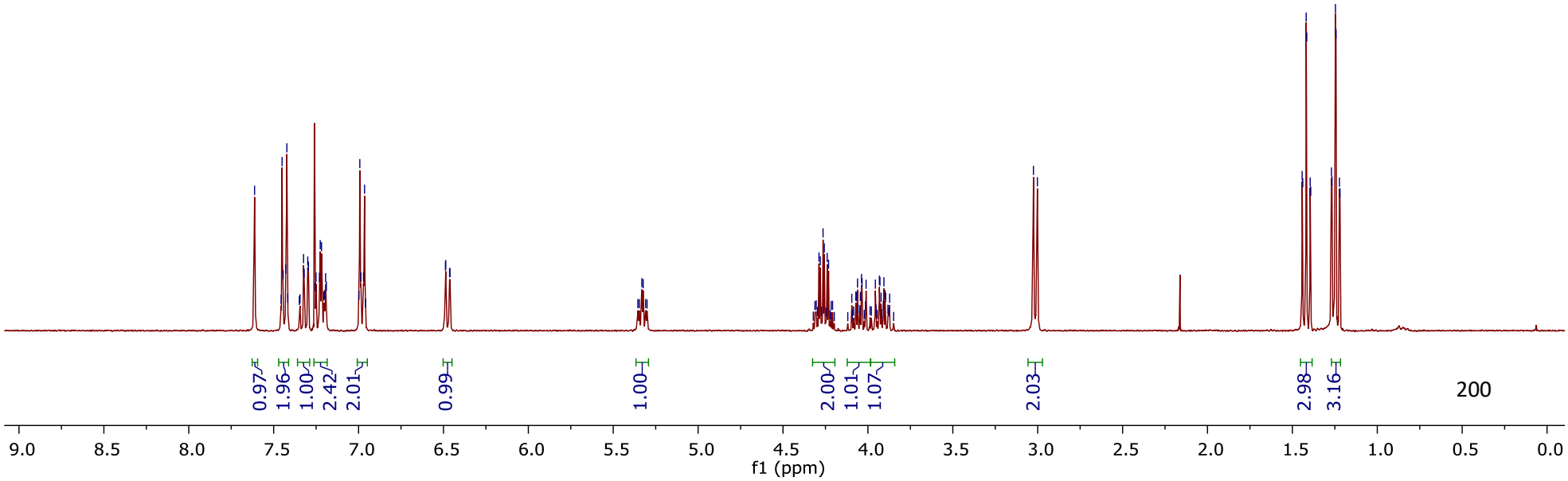
199

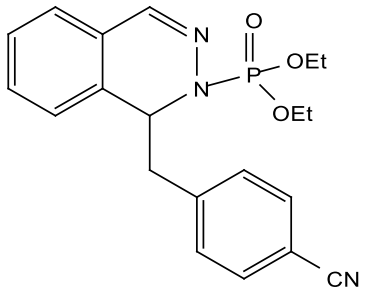
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


7.61 7.46 7.45 7.44 7.43 7.42 7.42 7.35 7.34 7.32 7.32 7.30 7.30 7.26 7.25 7.23 7.23 7.22 7.21 7.20 7.19 7.19 7.00 6.99 6.99 6.97 6.96 6.96 6.49 6.49 6.46 6.46 5.36 5.35 5.33 5.32 5.31 5.30 4.31 4.30 4.29 4.28 4.26 4.26 4.24 4.23 4.22 4.21 4.09 4.08 4.07 4.07 4.06 4.06 4.05 4.04 4.04 4.03 4.01 4.01 3.99 3.98 3.96 3.95 3.93 3.93 3.92 3.91 3.91 3.90 3.90 3.88 3.87 3.03 3.00 1.44 1.44 1.42 1.42 1.40 1.39 1.27 1.27 1.25 1.24 1.22 1.22
N
N
O
P
OEt
OEt
CN

10b


0.97
1.96
1.00
2.42
2.01
0.99
1.00
2.00
1.01
1.07
2.03
2.98
3.16
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



10b

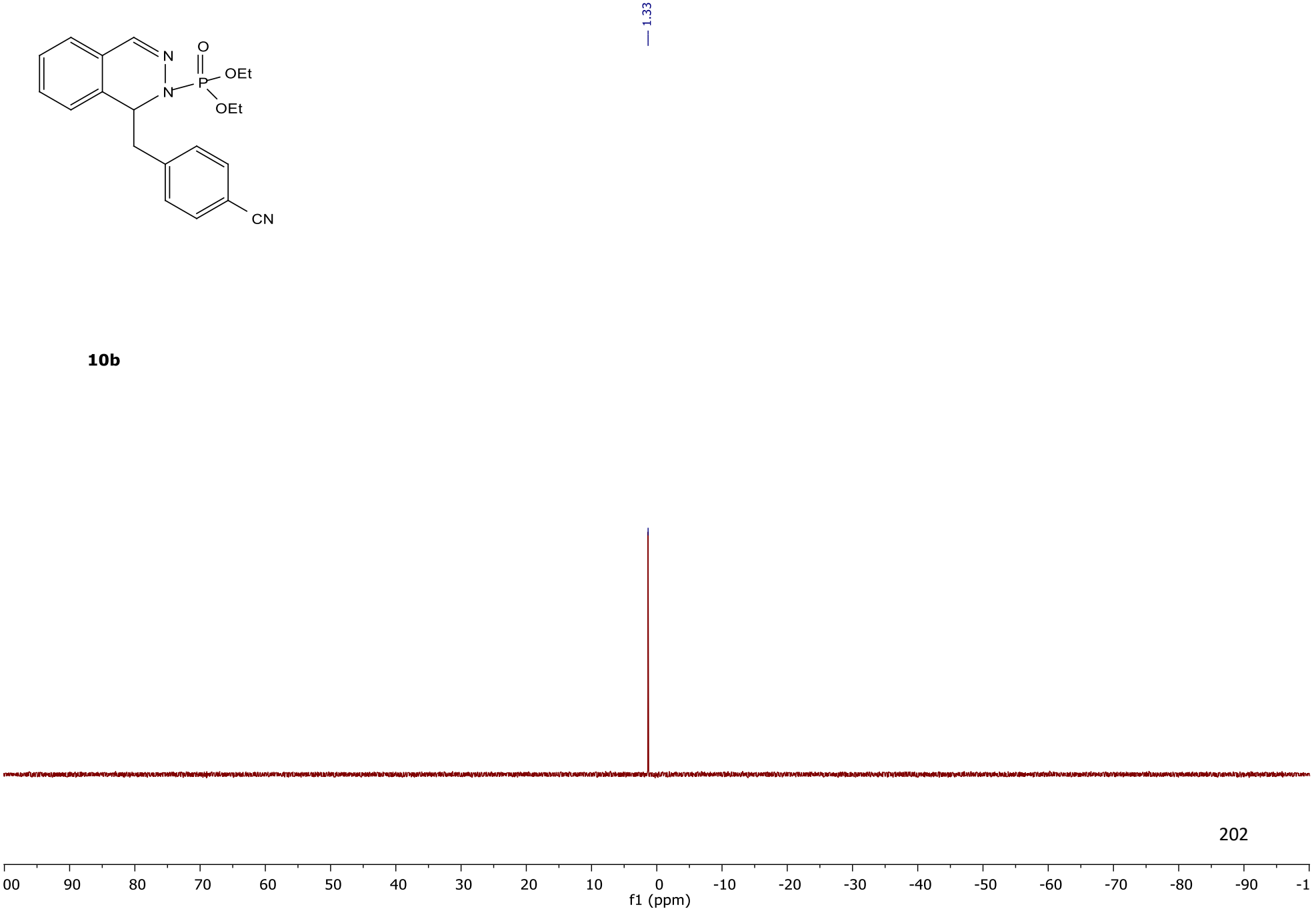
142.70
142.58
142.15
131.78
130.92
130.85
130.75
128.40
126.42
126.41
125.31
123.66
123.65
118.91
110.48
64.27
64.21
63.34
63.28
55.34
55.26
42.06
16.33
16.26
15.94
15.87

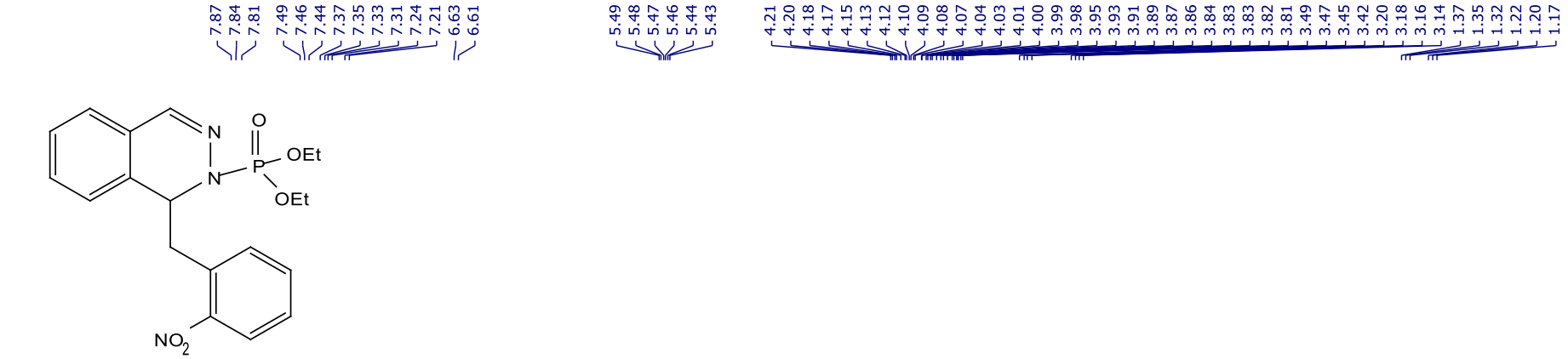
201

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

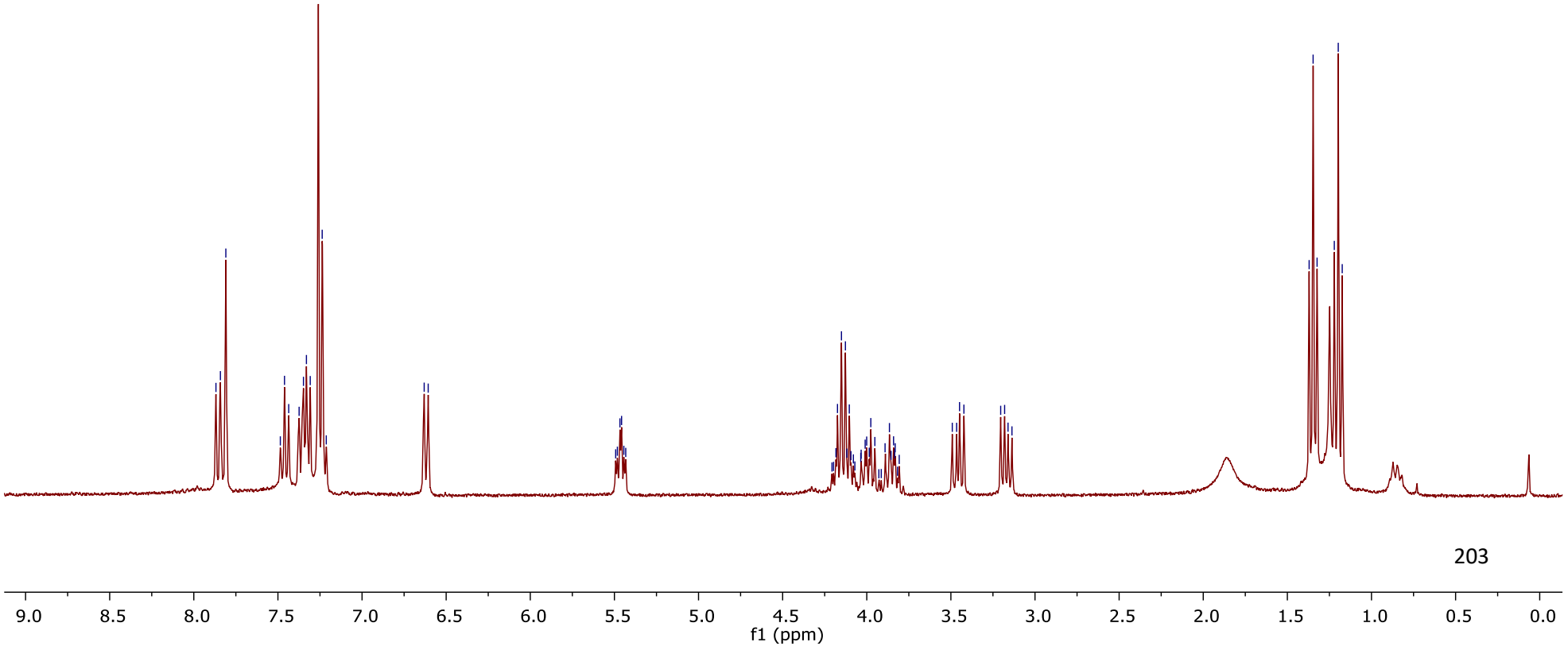
N
O
OEt
N
P
OEt
CN

10b


1.33
202
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

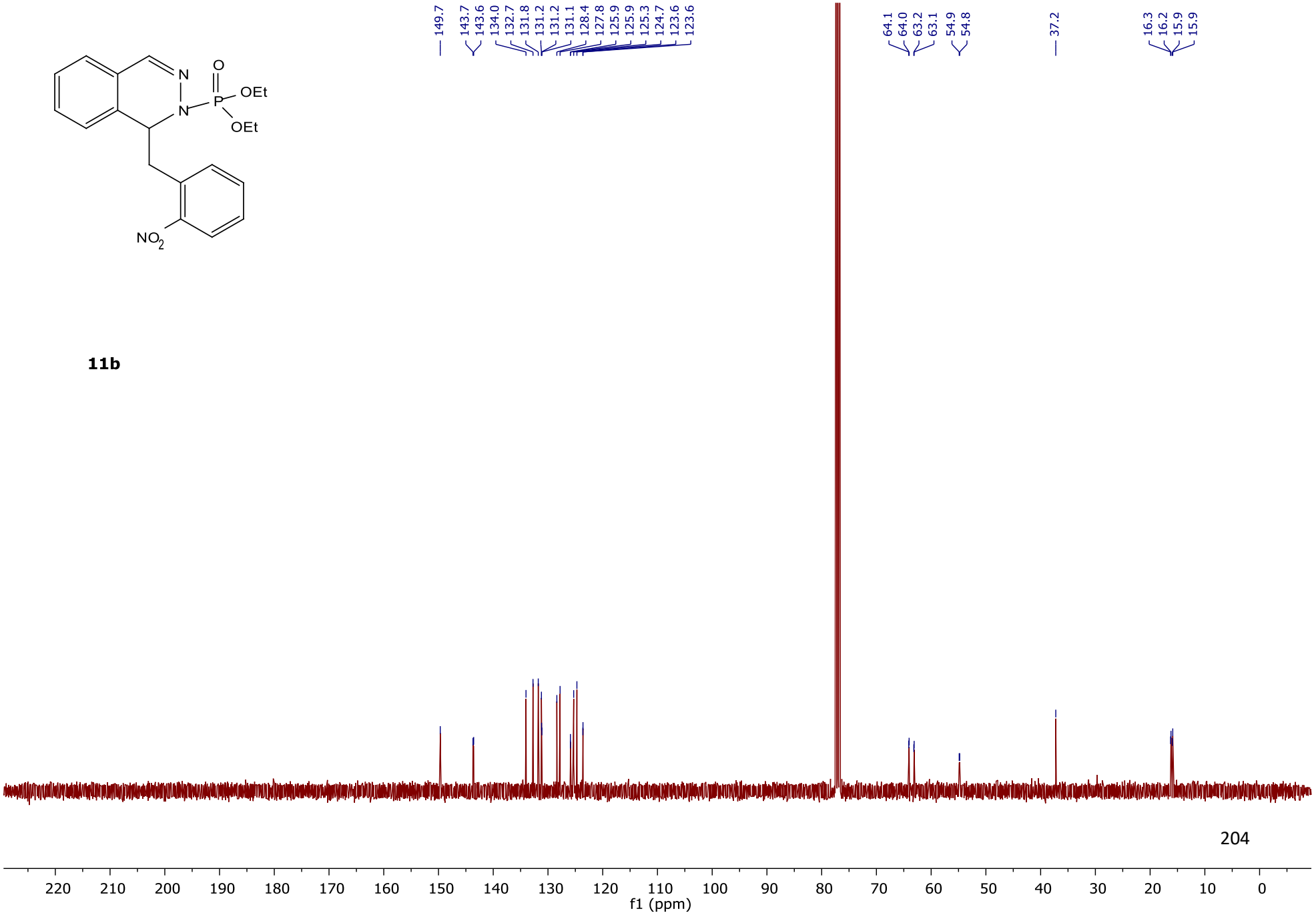

7.87
7.84
7.81
7.49
7.46
7.44
7.37
7.35
7.33
7.31
7.24
7.21
6.63
6.61
5.49
5.48
5.47
5.46
5.44
5.43
4.21
4.20
4.18
4.17
4.15
4.13
4.12
4.10
4.09
4.08
4.07
4.04
4.03
4.01
4.00
3.99
3.98
3.95
3.93
3.91
3.89
3.87
3.86
3.84
3.83
3.83
3.82
3.81
3.49
3.47
3.45
3.42
3.20
3.18
3.16
3.14
1.37
1.35
1.32
1.22
1.20
1.17
O
N
N
P
OEt
OEt
NO2

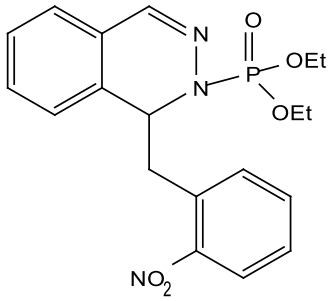
11b


203
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

N
N
O
P
OEt
OEt
NO2

11b


149.7
143.7
143.6
134.0
132.7
131.8
131.2
131.2
131.1
128.4
127.8
125.9
125.9
125.3
124.7
123.6
123.6
64.1
64.0
63.2
63.1
54.9
54.8
37.2
16.3
16.2
15.9
15.9
204
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



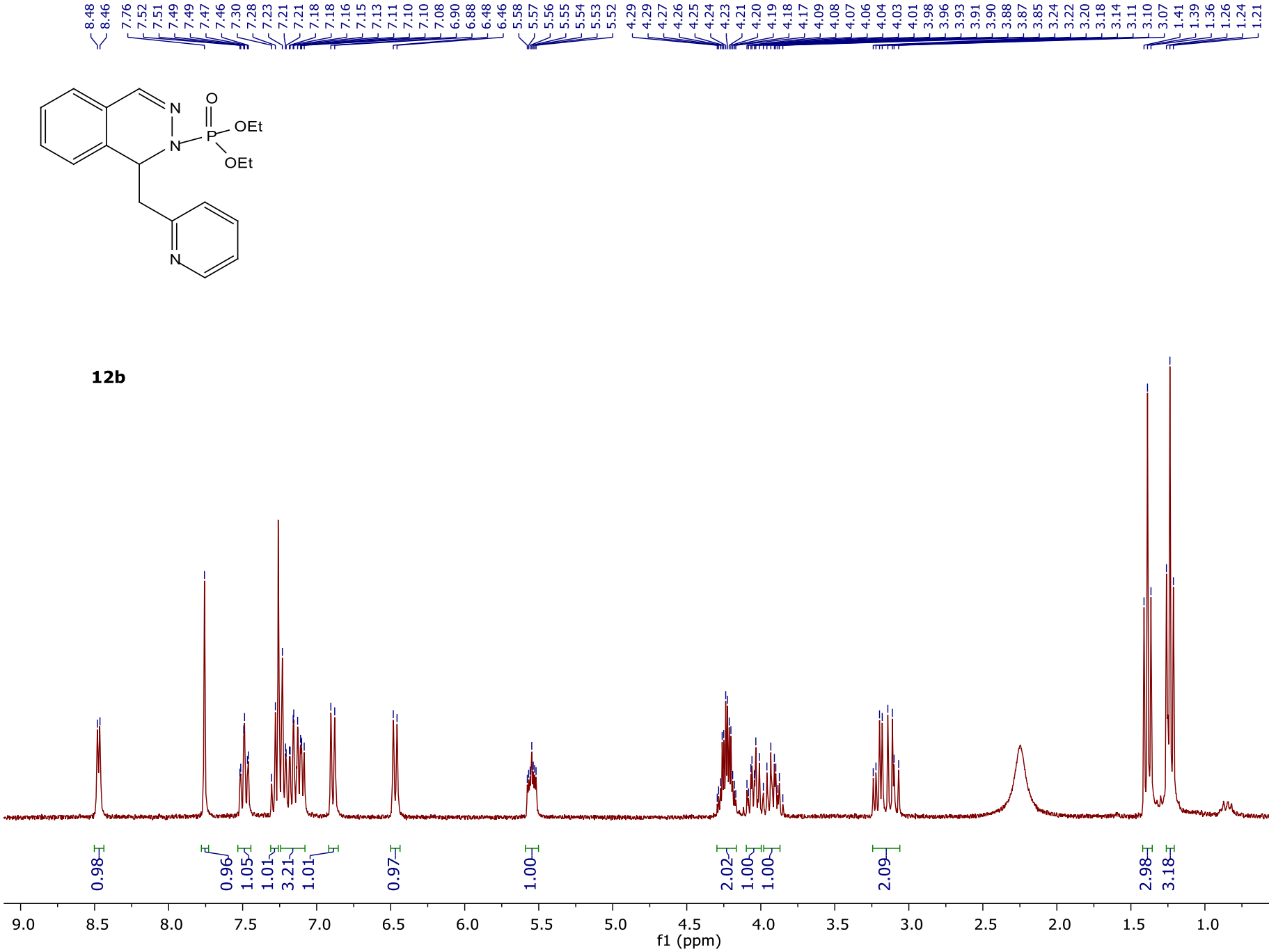
1.14

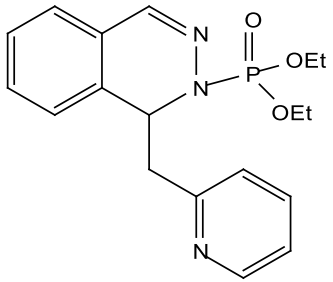
11b

205

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

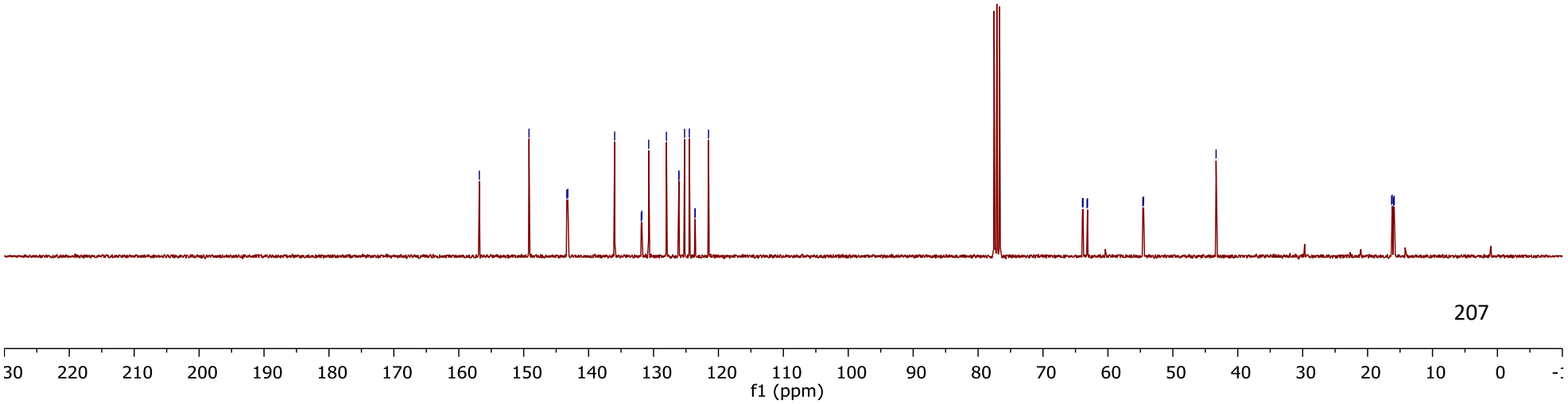
f1 (ppm)

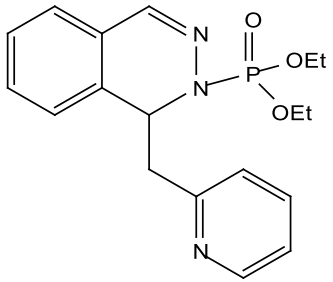

8.48 8.46 7.76 7.52 7.51 7.49 7.49 7.47 7.46 7.30 7.28 7.23 7.21 7.21 7.18 7.18 7.16 7.15 7.13 7.11 7.10 7.10 7.08 6.90 6.88 6.48 6.46 5.58 5.57 5.56 5.55 5.54 5.53 5.52 4.29 4.29 4.27 4.26 4.25 4.24 4.23 4.21 4.20 4.19 4.18 4.17 4.09 4.08 4.07 4.06 4.04 4.03 4.01 3.98 3.96 3.93 3.91 3.90 3.88 3.87 3.85 3.24 3.22 3.20 3.18 3.14 3.11 3.10 3.07 1.41 1.39 1.36 1.26 1.24 1.21
O
OEt
P
OEt
N
N
N
12b
0.98 0.96 1.05 1.01 3.21 1.01 0.97 1.00 2.02 1.00 1.00 2.09 2.98 3.18
206
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



156.8
149.2
143.4
143.2
136.0
131.9
131.8
130.7
128.0
126.1
126.1
125.2
124.5
123.6
123.6
121.5
63.9
63.8
63.2
63.1
54.6
54.5
43.3
16.3
16.2
16.0
15.9

12b





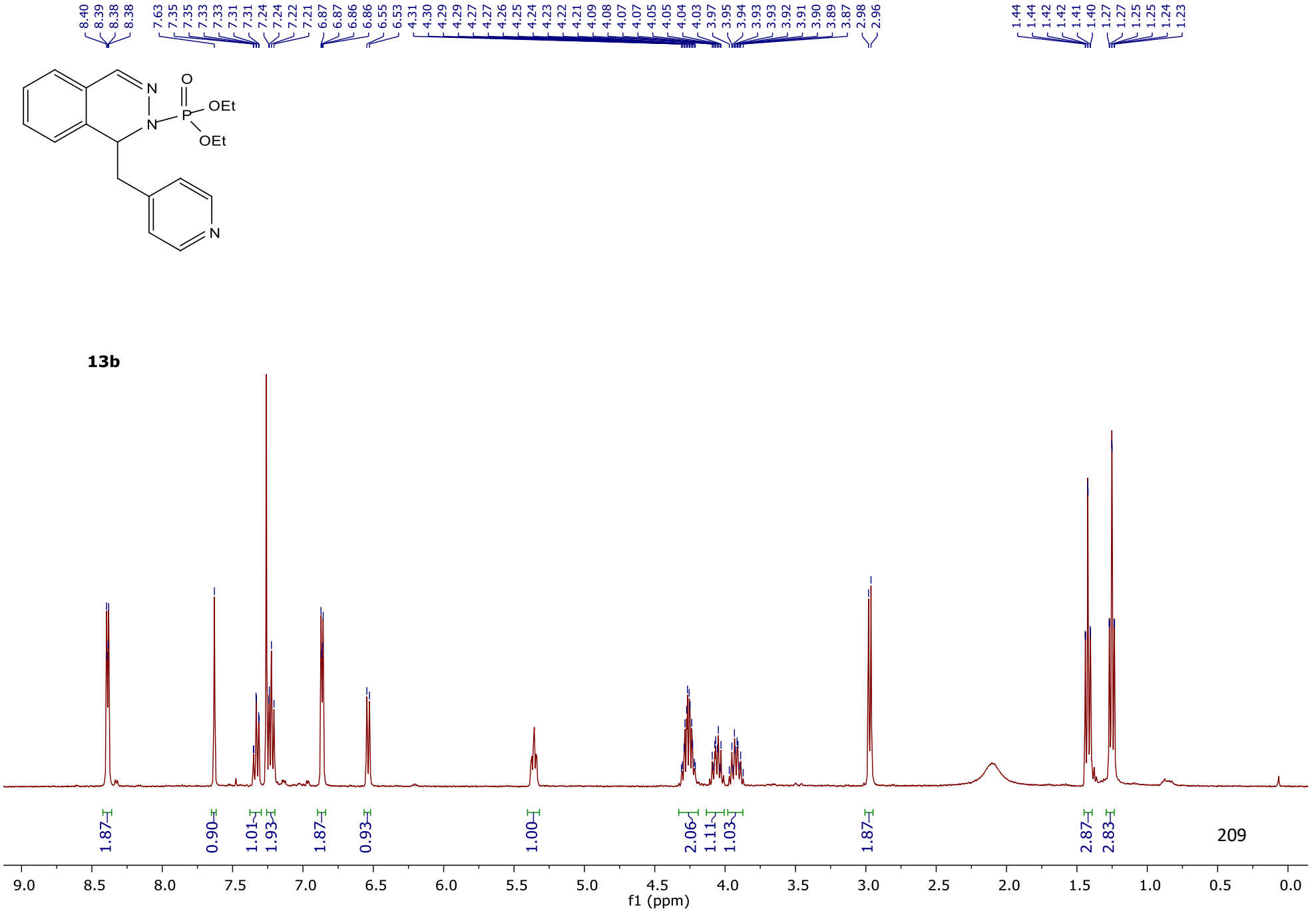
1.58

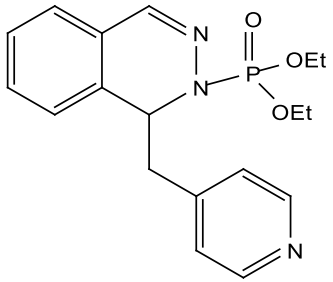
12b

208

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


8.40 8.39 8.38 8.38
7.63 7.35 7.35 7.33 7.33 7.31 7.31 7.24 7.24 7.22 7.21
6.87 6.87 6.86 6.86 6.55 6.53
4.31 4.30 4.29 4.29 4.27 4.27 4.26 4.25 4.24 4.24 4.23 4.22 4.21 4.09 4.08 4.07 4.07 4.05 4.05 4.04 4.03 3.97 3.95 3.94 3.93 3.93 3.92 3.91 3.90 3.89 3.87
2.98 2.96
1.44 1.44 1.42 1.42 1.41 1.40
1.27 1.27 1.25 1.25 1.24 1.23
O
N
N
P
OEt
OEt
N
13b
1.87
0.90
1.01
1.93
1.87
0.93
1.00
2.06
1.11
1.03
1.87
2.87
2.83
209
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



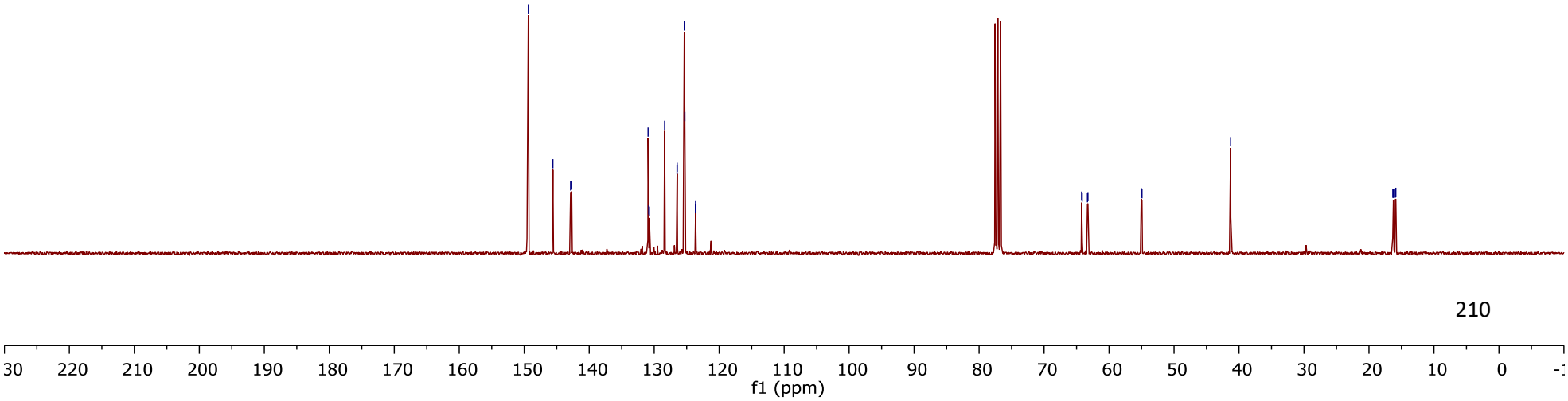
149.4
145.6
142.9
142.7
130.9
130.8
130.7
128.4
126.5
126.5
125.4
125.3
123.7
123.6

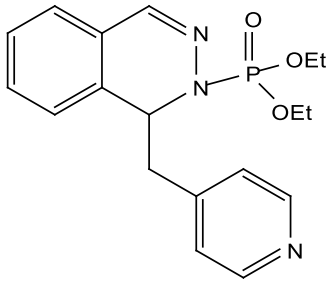
64.2
64.1
63.3
63.2
55.1
54.9

41.3

16.3
16.2
16.0
15.9

13b





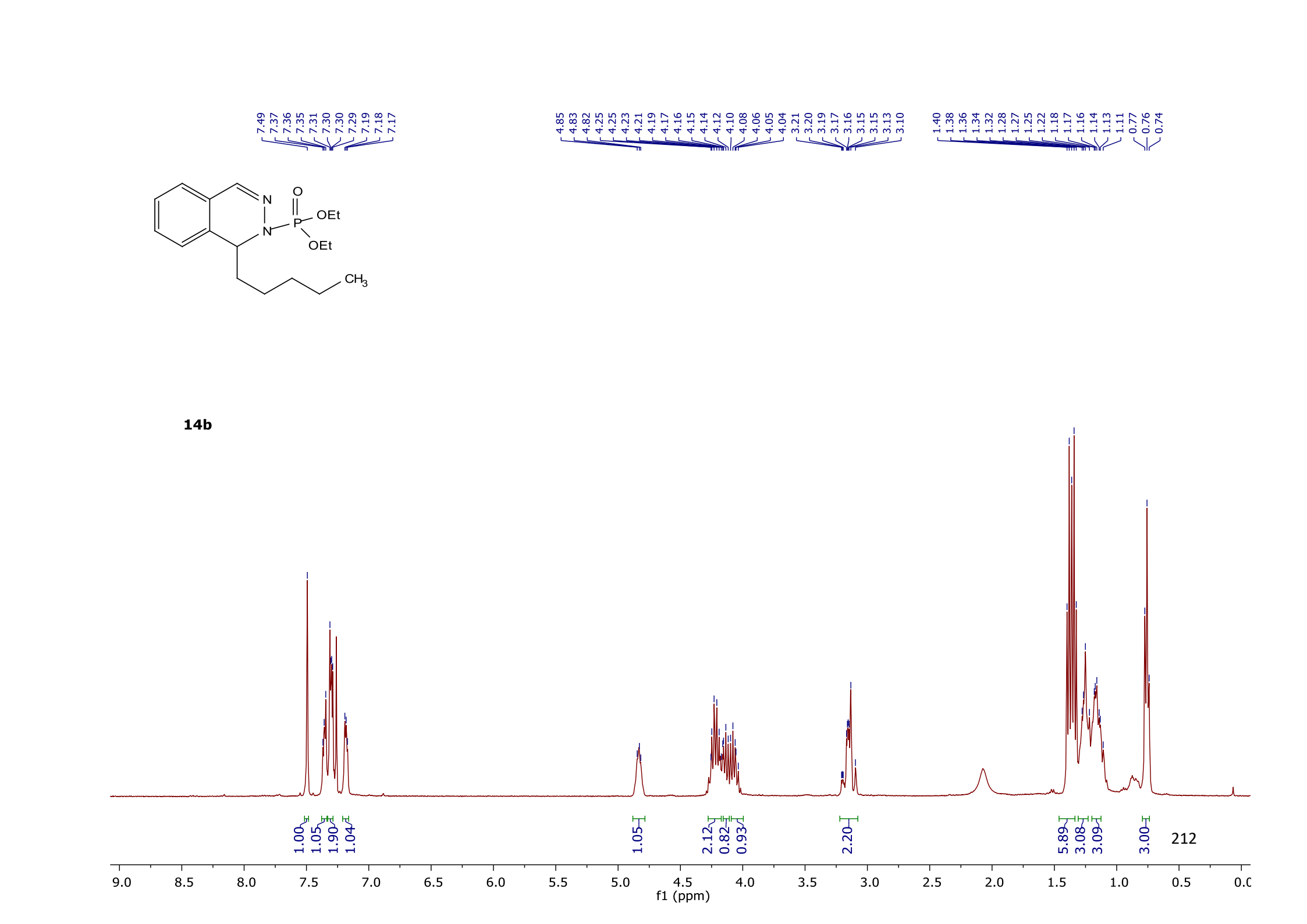
1.34

13b

211

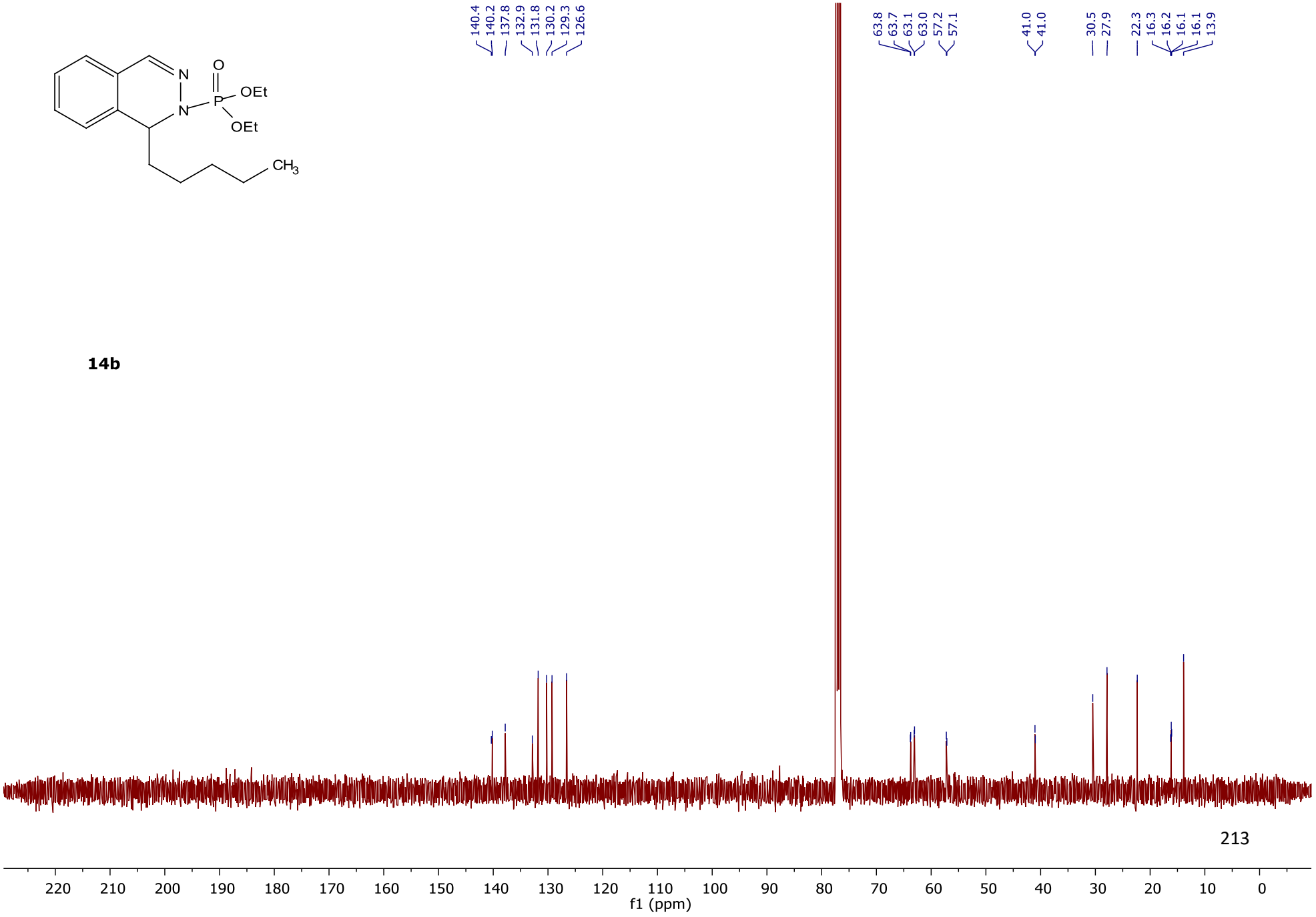
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

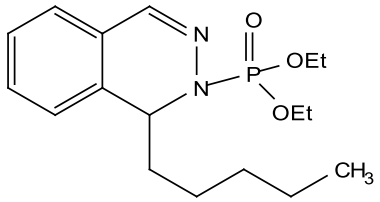
f1 (ppm)


7.49
7.37
7.36
7.35
7.31
7.30
7.30
7.29
7.19
7.18
7.17
4.85
4.83
4.82
4.25
4.25
4.23
4.21
4.19
4.17
4.16
4.15
4.14
4.12
4.10
4.08
4.06
4.05
4.04
3.21
3.20
3.19
3.17
3.16
3.15
3.15
3.13
3.10
1.40
1.38
1.36
1.34
1.32
1.28
1.27
1.25
1.22
1.18
1.17
1.16
1.14
1.13
1.11
0.77
0.76
0.74
N
N
O
P
OEt
OEt
CH3
14b
1.00
1.05
1.90
1.04
1.05
2.12
0.82
0.93
2.20
5.89
3.08
3.09
3.00
212
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

O
N
N
P
OEt
OEt
CH3

14b


140.4
140.2
137.8
132.9
131.8
130.2
129.3
126.6
63.8
63.7
63.1
63.0
57.2
57.1
41.0
41.0
30.5
27.9
22.3
16.3
16.2
16.1
16.1
13.9
213
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



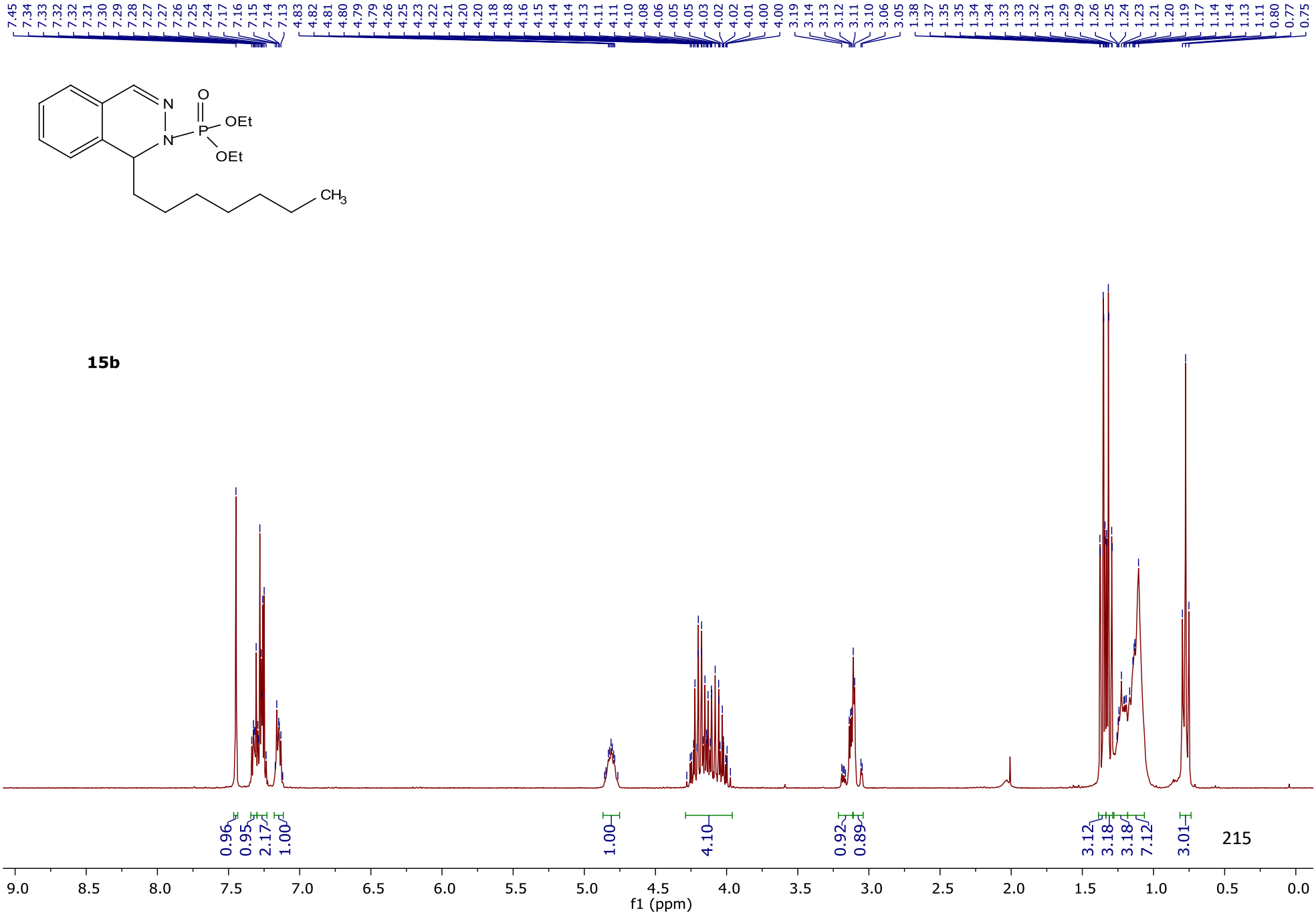
2.82

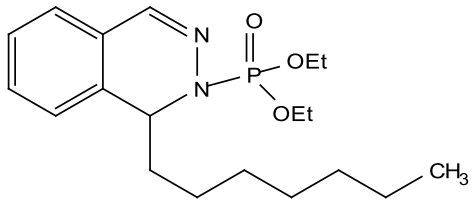
14b

214

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

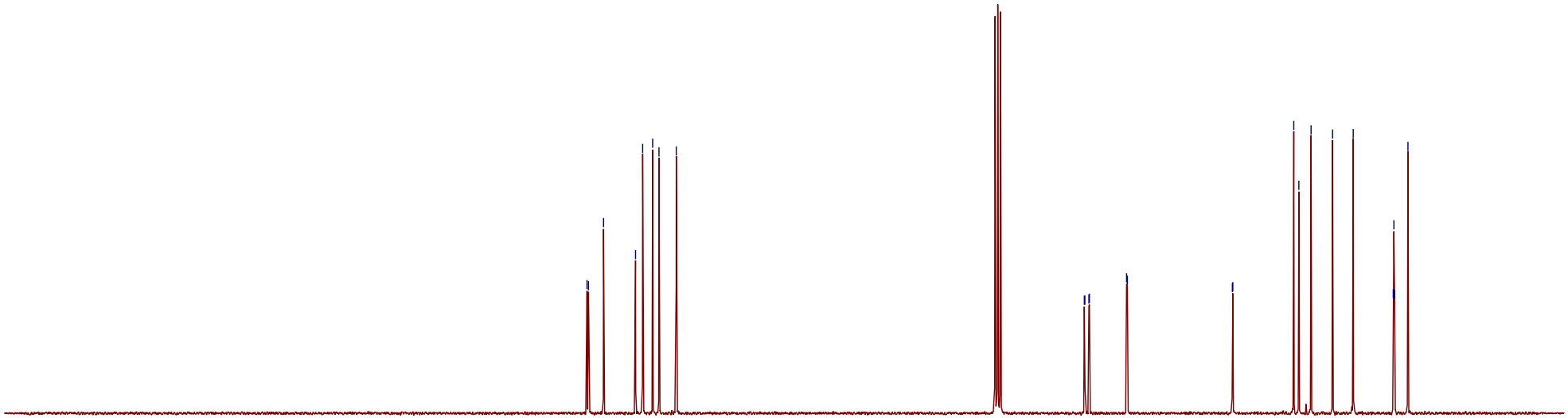
f1 (ppm)

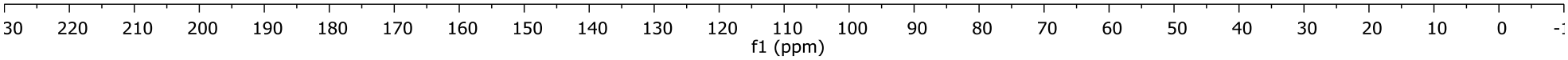

7.45 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.28 7.27 7.27 7.26 7.25 7.24 7.17 7.16 7.15 7.14 7.13
4.83 4.82 4.81 4.80 4.79 4.79 4.26 4.25 4.23 4.22 4.21 4.20 4.20 4.18 4.18 4.16 4.15 4.14 4.14 4.13 4.11 4.11 4.10 4.08 4.06 4.05 4.05 4.03 4.02 4.02 4.01 4.00 4.00
3.19 3.14 3.13 3.12 3.11 3.10 3.06 3.05
1.38 1.37 1.35 1.35 1.34 1.34 1.33 1.33 1.32 1.31 1.29 1.29 1.26 1.25 1.24 1.23 1.21 1.20 1.19 1.17 1.14 1.14 1.13 1.11 0.80 0.77 0.75
N
N
O
P
OEt
OEt
CH3
15b
0.96
0.95
2.17
1.00
1.00
4.10
0.92
0.89
3.12
3.18
3.18
7.12
3.01
215
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



140.3
140.1
137.8
132.9
131.8
130.2
129.3
126.6
63.8
63.7
63.1
63.0
57.3
57.2
41.0
41.0
31.6
30.8
28.9
25.6
22.4
16.3
16.2
16.1
14.0

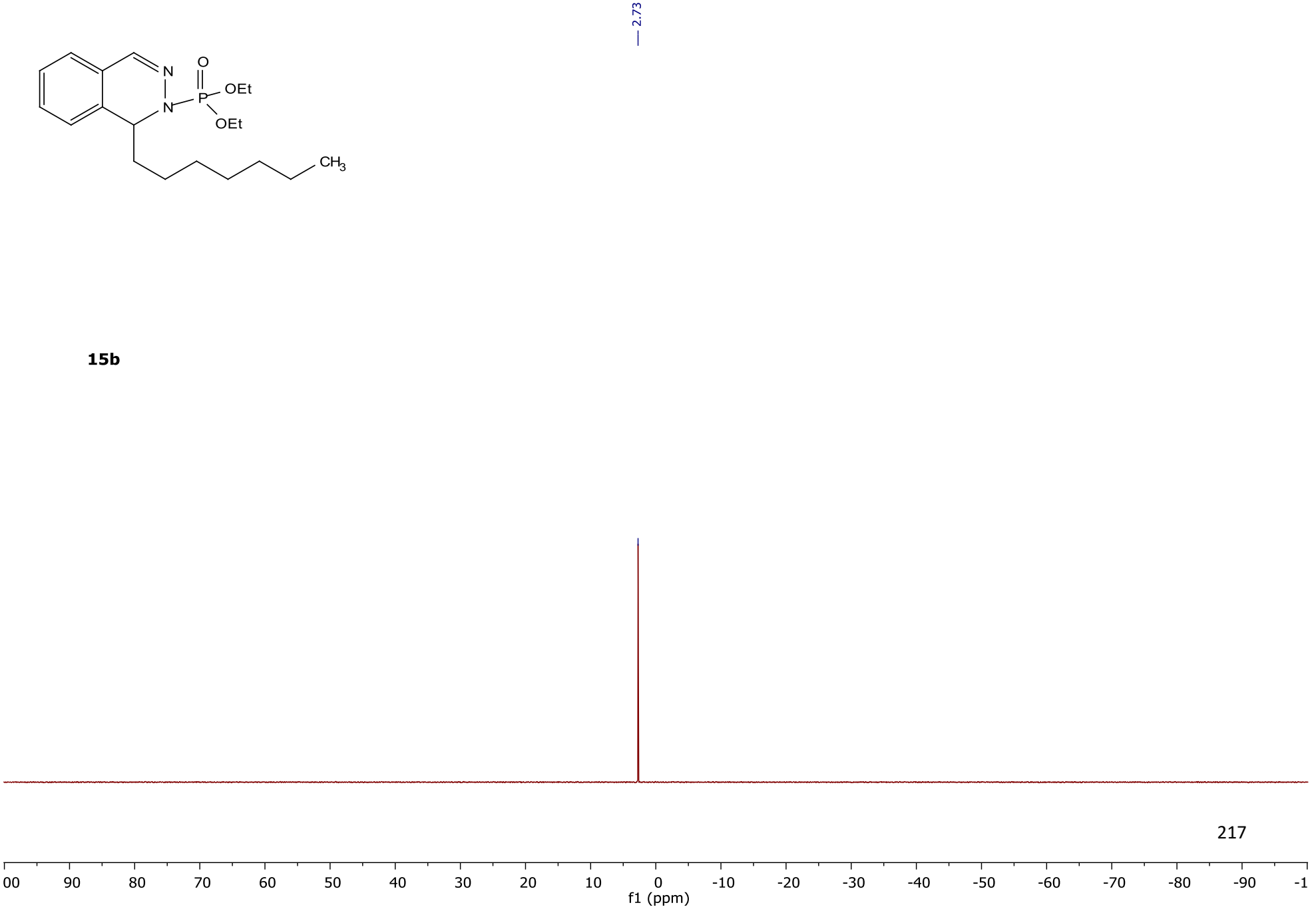
15b

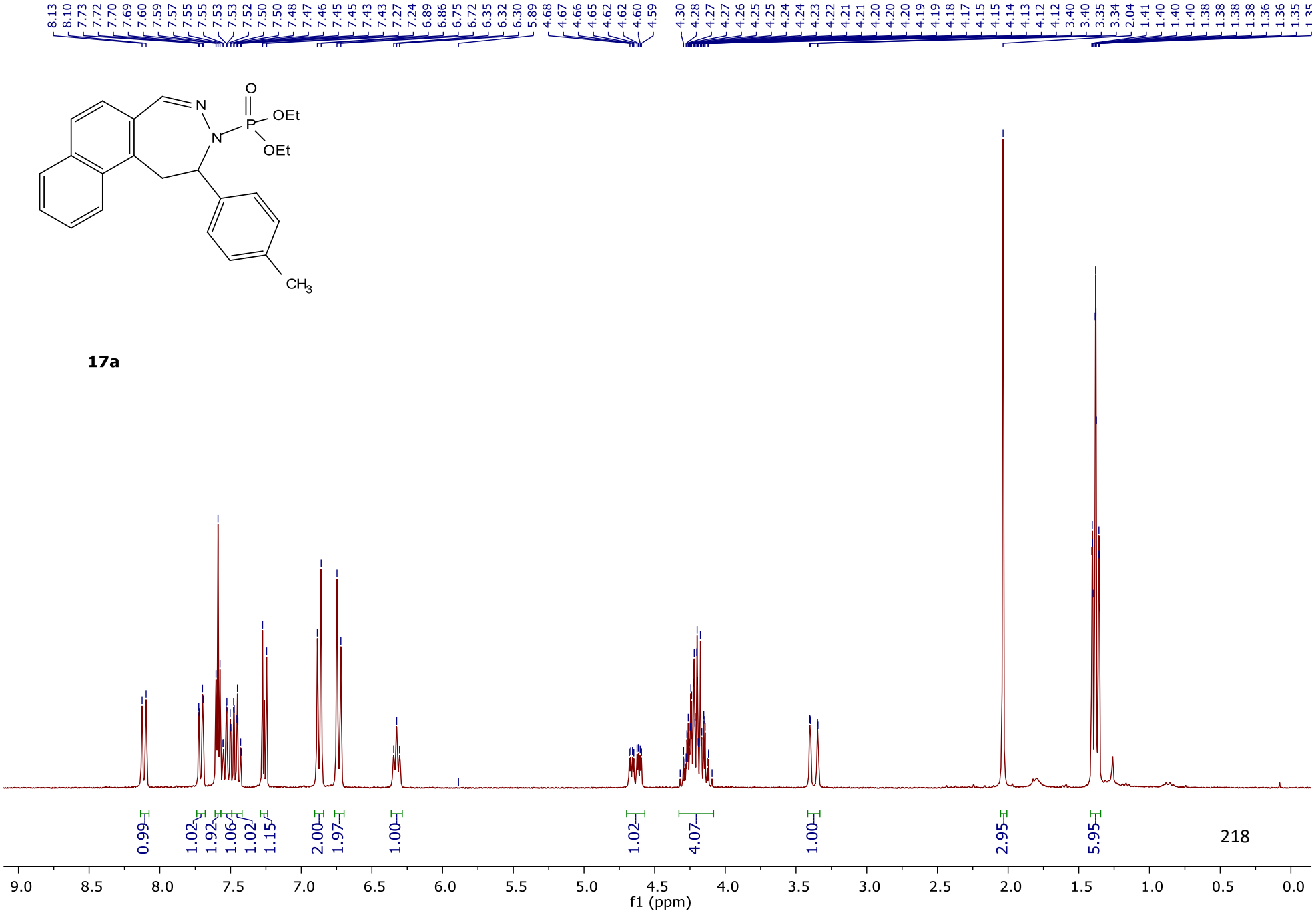


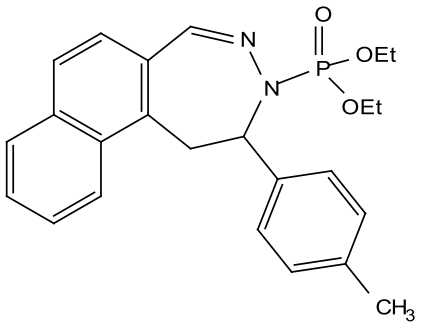


N
O
OEt
N
P
OEt
CH3

15b


2.73
217
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.13 8.10 7.73 7.72 7.70 7.69 7.60 7.59 7.57 7.55 7.55 7.53 7.53 7.52 7.50 7.50 7.48 7.47 7.46 7.45 7.45 7.43 7.43 7.27 7.24 6.89 6.86 6.75 6.72 6.35 6.32 6.30 5.89 4.68 4.67 4.66 4.65 4.62 4.62 4.60 4.59 4.30 4.28 4.27 4.27 4.26 4.25 4.25 4.24 4.24 4.23 4.22 4.21 4.21 4.20 4.20 4.20 4.19 4.19 4.18 4.17 4.15 4.15 4.14 4.13 4.12 4.12 3.40 3.40 3.35 3.34 2.04 1.41 1.40 1.40 1.40 1.38 1.38 1.38 1.38 1.36 1.35
O
N
P
OEt
N
OEt
CH3
17a
0.99
1.02
1.92
1.06
1.02
1.15
2.00
1.97
1.00
1.02
4.07
1.00
2.95
5.95
218
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



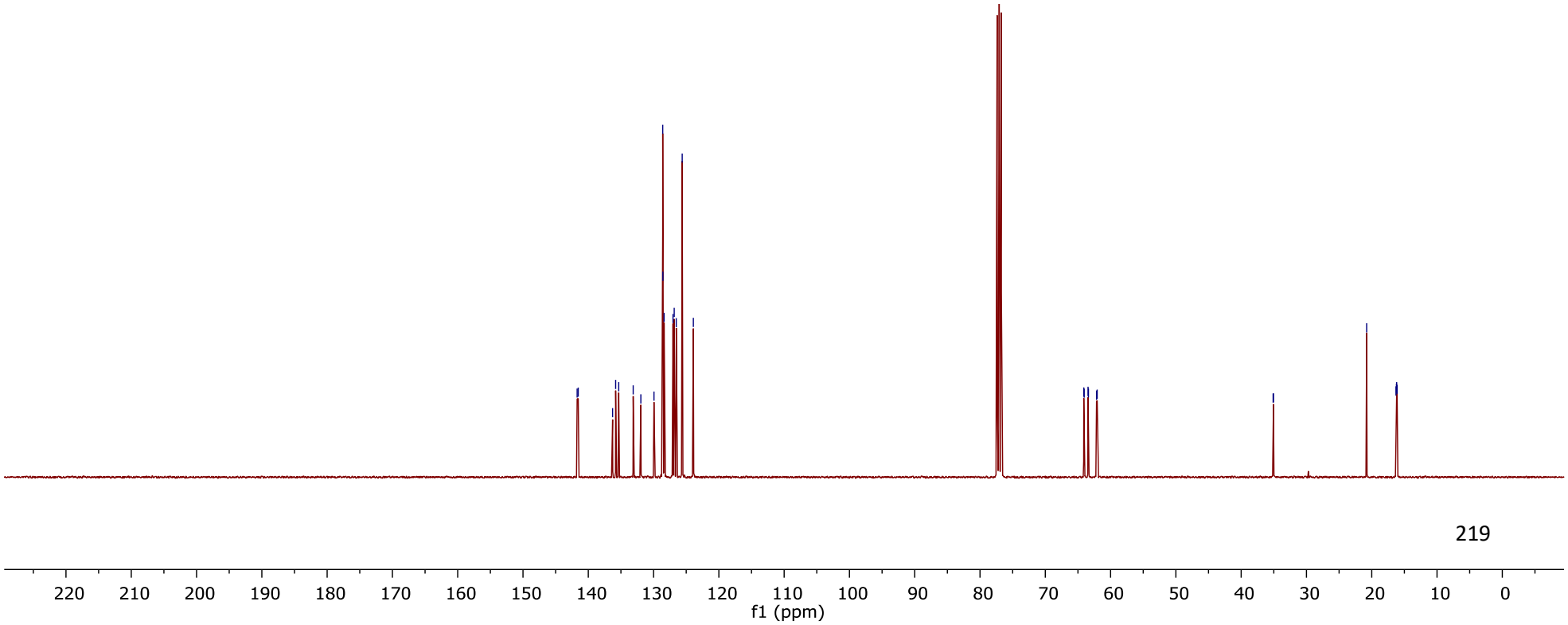
141.7
141.5
136.3
135.8
135.3
133.1
131.9
129.9
128.6
128.6
128.4
127.0
126.8
126.5
125.6
123.9

64.1
64.0
63.4
63.4
62.2
62.1

35.1
35.1

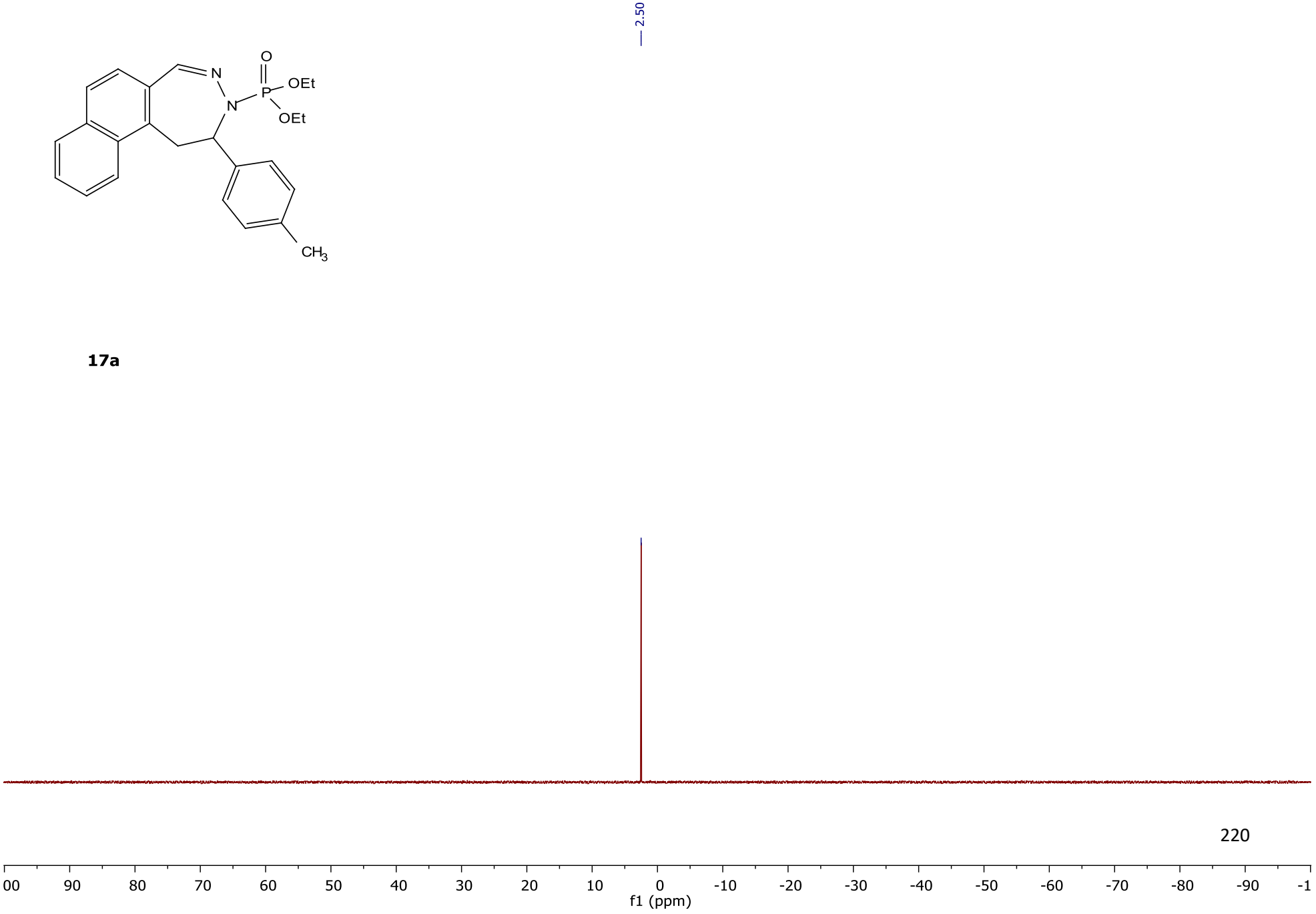
20.8
16.3
16.2
16.2
16.1

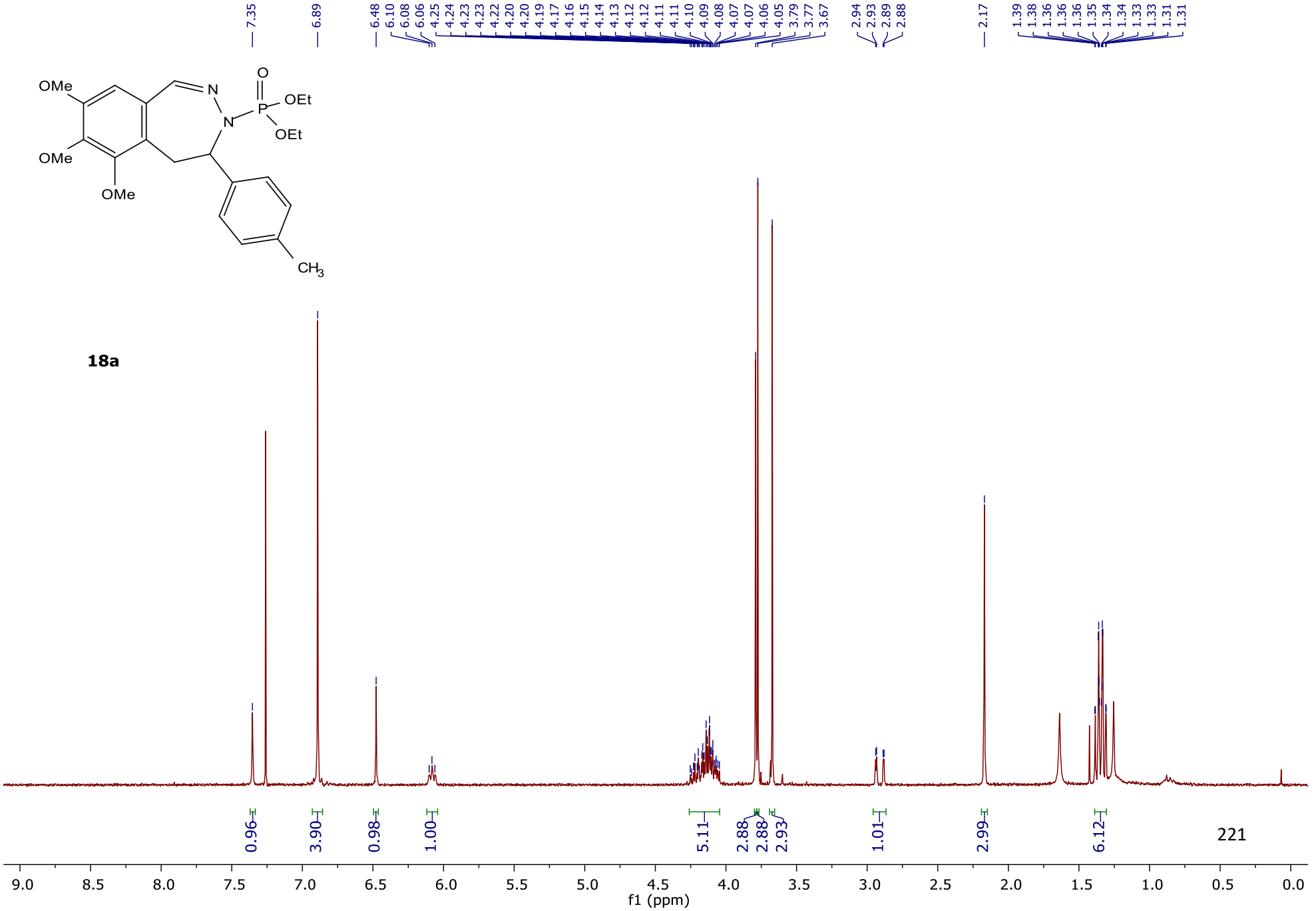
17a



O
N
OEt
P
N
OEt
CH3

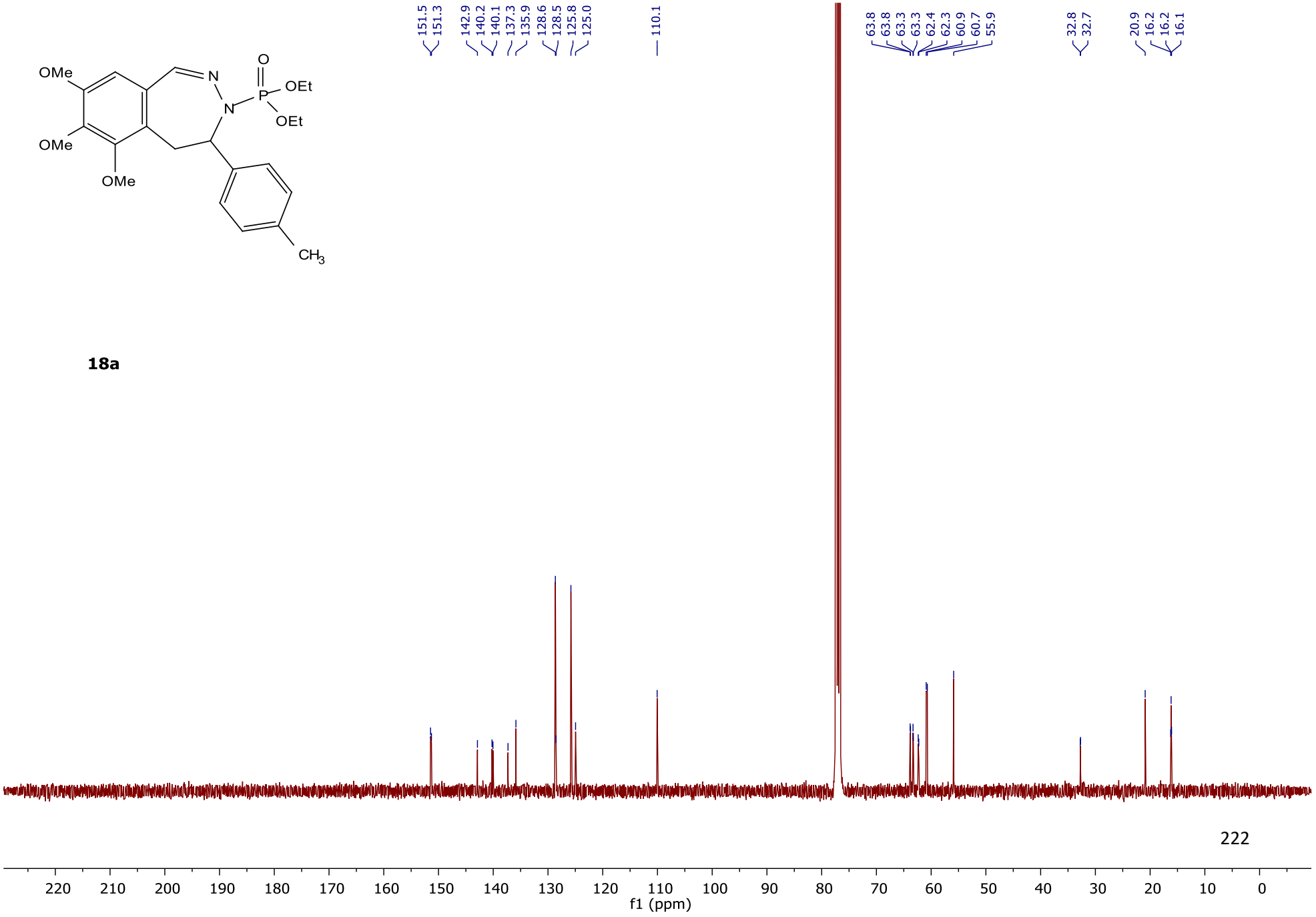
17a


2.50
220
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.35
6.89
6.48
6.10
6.08
6.06
4.25
4.24
4.23
4.23
4.22
4.20
4.20
4.19
4.17
4.16
4.15
4.14
4.13
4.12
4.12
4.11
4.11
4.10
4.09
4.08
4.07
4.07
4.06
4.05
3.79
3.77
3.67
2.94
2.93
2.89
2.88
2.17
1.39
1.38
1.36
1.36
1.36
1.35
1.34
1.34
1.33
1.33
1.31
1.31
OMe
OMe
OMe
N
N
P
O
OEt
OEt
CH3
18a
0.96
3.90
0.98
1.00
5.11
2.88
2.88
2.93
1.01
2.99
6.12
221
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

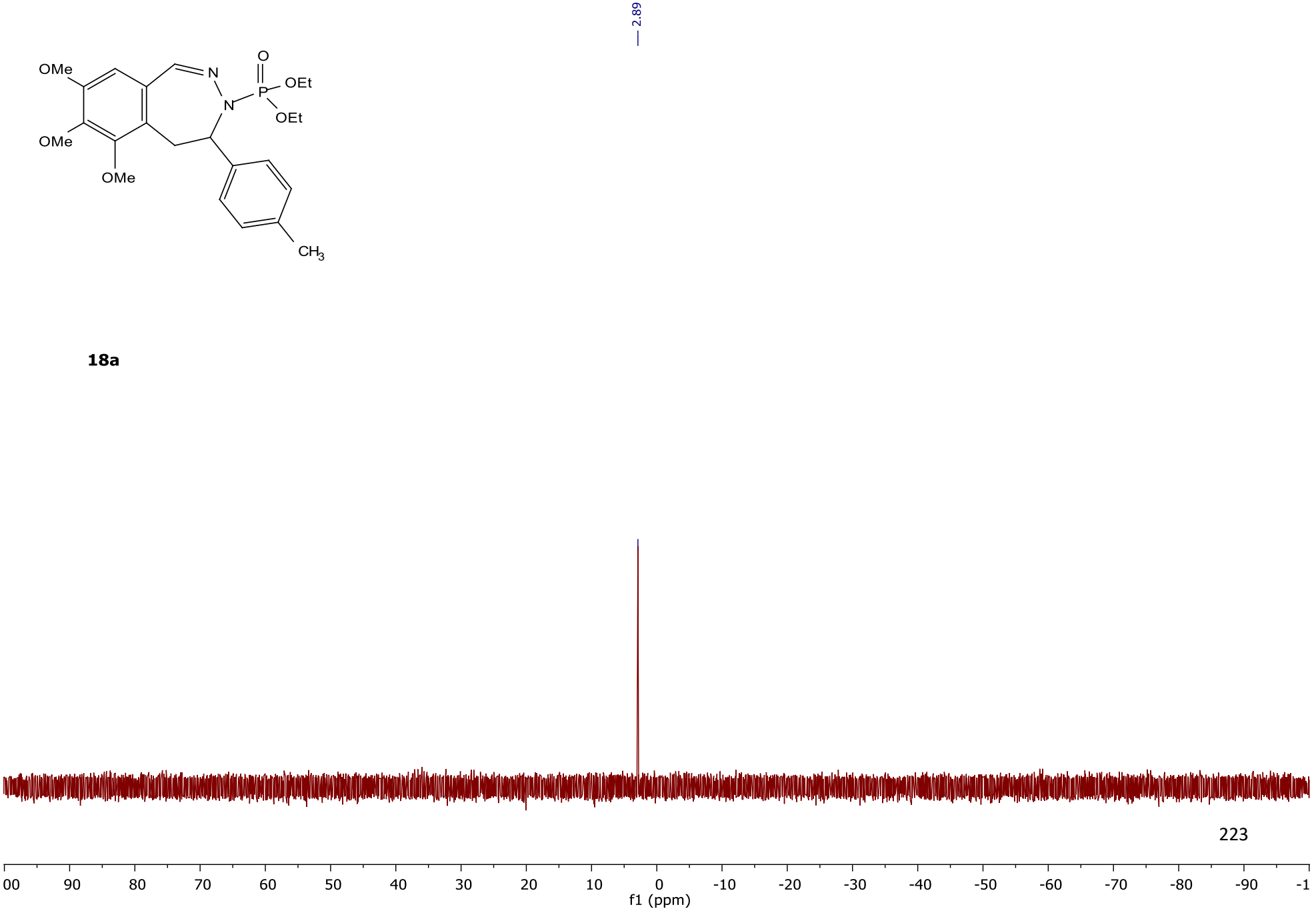
OMe
OMe
OMe
N
N
P
O
OEt
OEt
CH3

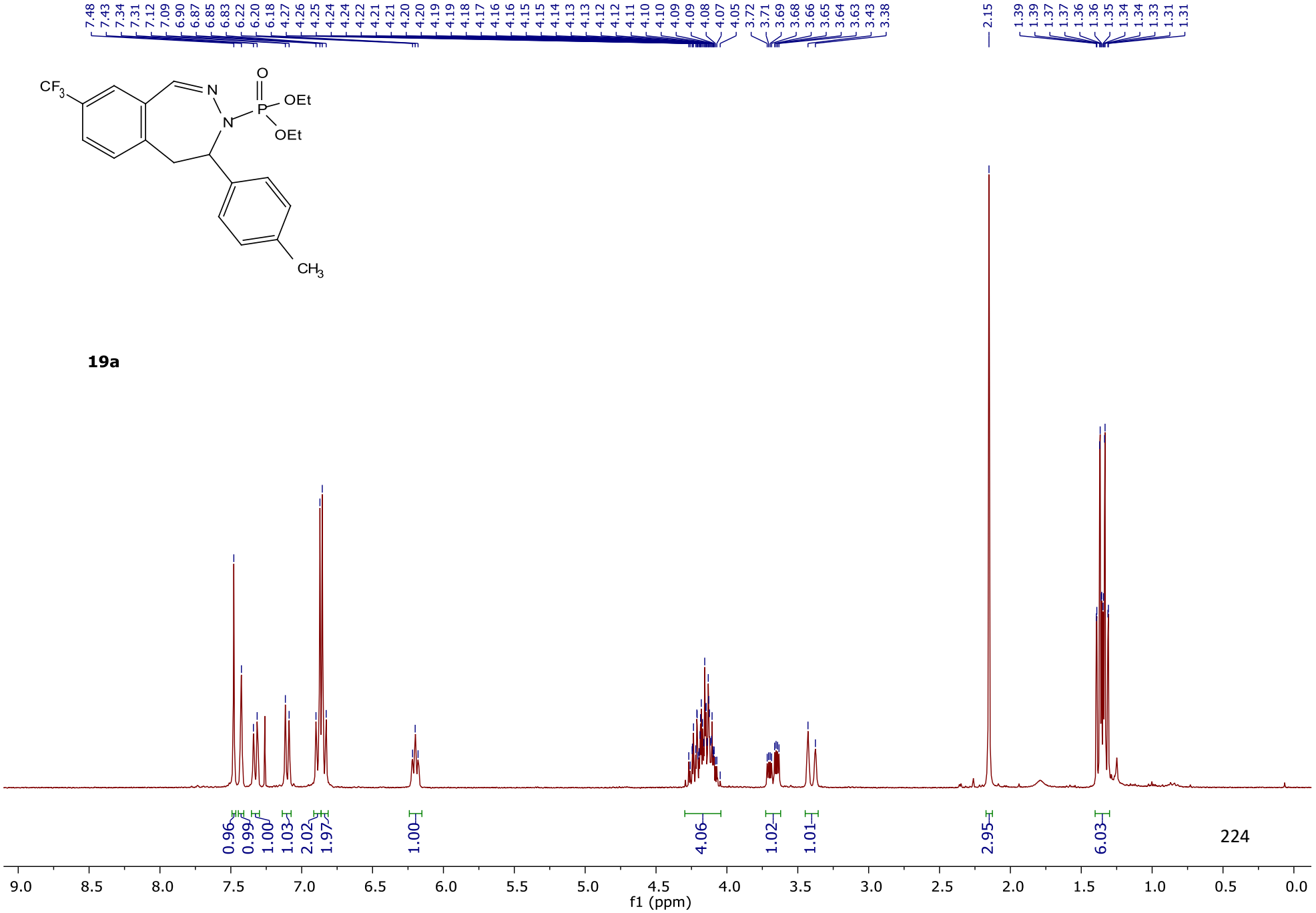
18a

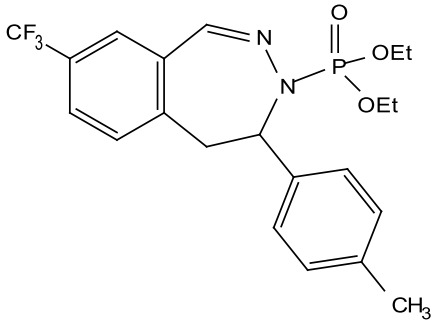

151.5
151.3
142.9
140.2
140.1
137.3
135.9
128.6
128.5
125.8
125.0
110.1
63.8
63.8
63.3
63.3
62.4
62.3
60.9
60.7
55.9
32.8
32.7
20.9
16.2
16.2
16.1
222
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OMe
OMe
OMe
N
N
P
O
OEt
OEt
CH3

18a


2.89
223
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.48 7.43 7.34 7.31 7.12 7.09 6.90 6.87 6.85 6.83 6.22 6.20 6.18 4.27 4.26 4.25 4.24 4.24 4.22 4.21 4.21 4.20 4.20 4.19 4.19 4.18 4.17 4.16 4.16 4.15 4.15 4.14 4.13 4.13 4.12 4.12 4.11 4.10 4.10 4.09 4.09 4.08 4.07 4.05 3.72 3.71 3.69 3.68 3.66 3.65 3.64 3.63 3.43 3.38
2.15
1.39 1.39 1.37 1.37 1.36 1.36 1.35 1.34 1.34 1.33 1.31 1.31
CF3
N
O
P
OEt
OEt
N
CH3
19a
0.96 0.99 1.00 1.03 2.02 1.97 1.00 4.06 1.02 1.01 2.95 6.03
224
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



142.0
138.6
138.5
136.2
136.2
133.0
130.7
129.5
129.1
128.9
128.8
128.5
128.0
127.9
127.9
127.9
125.6
125.4
125.4
125.3
125.3
125.1
122.4
119.7

64.1
64.1
63.6
63.5
62.0
61.9

41.9
41.8

20.9
16.2
16.1
16.1

19a

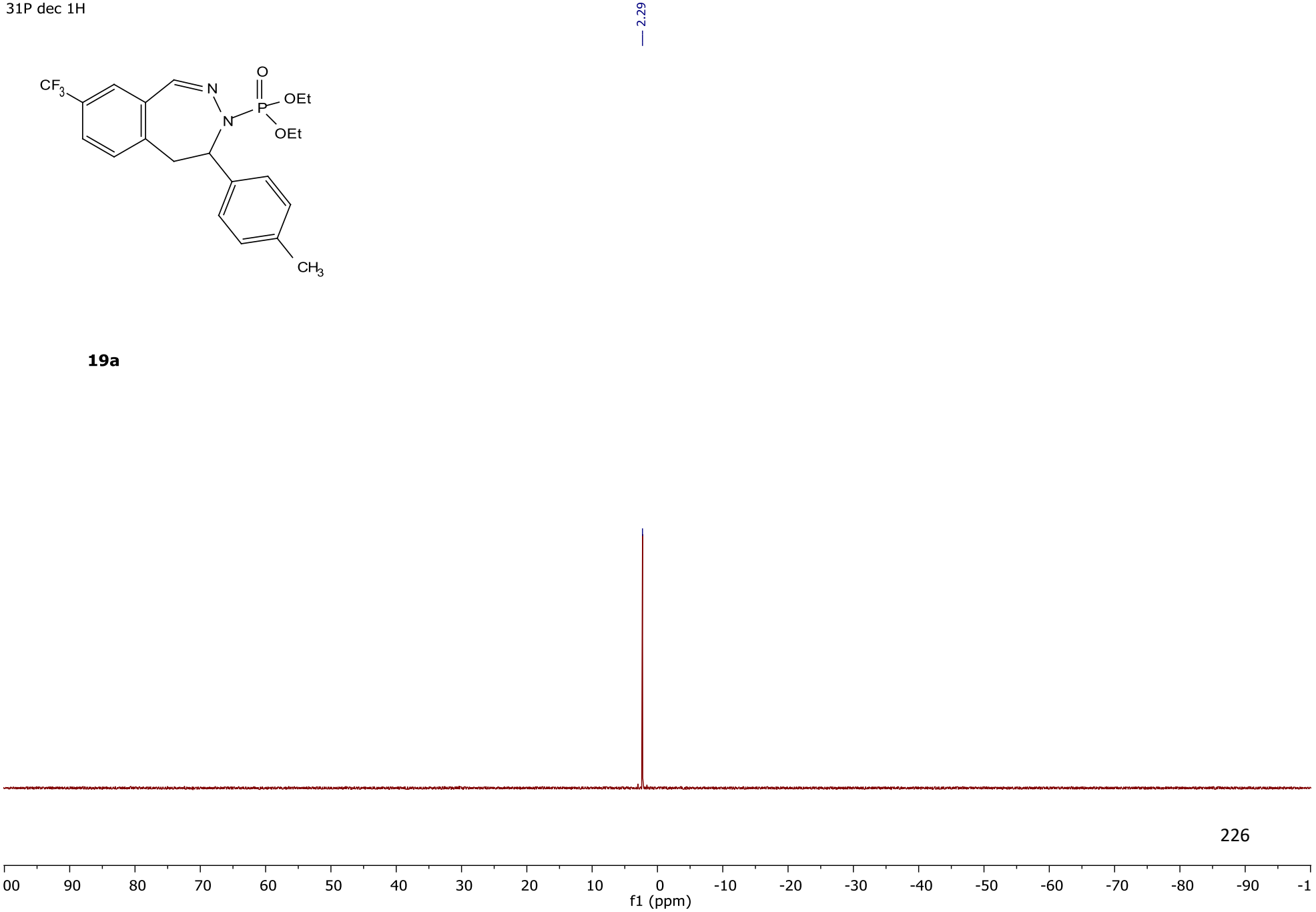
225

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

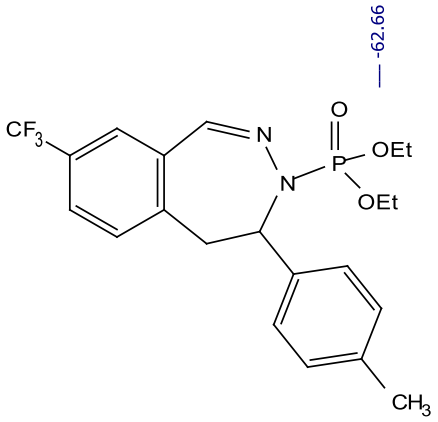
f1 (ppm)

31P dec 1H

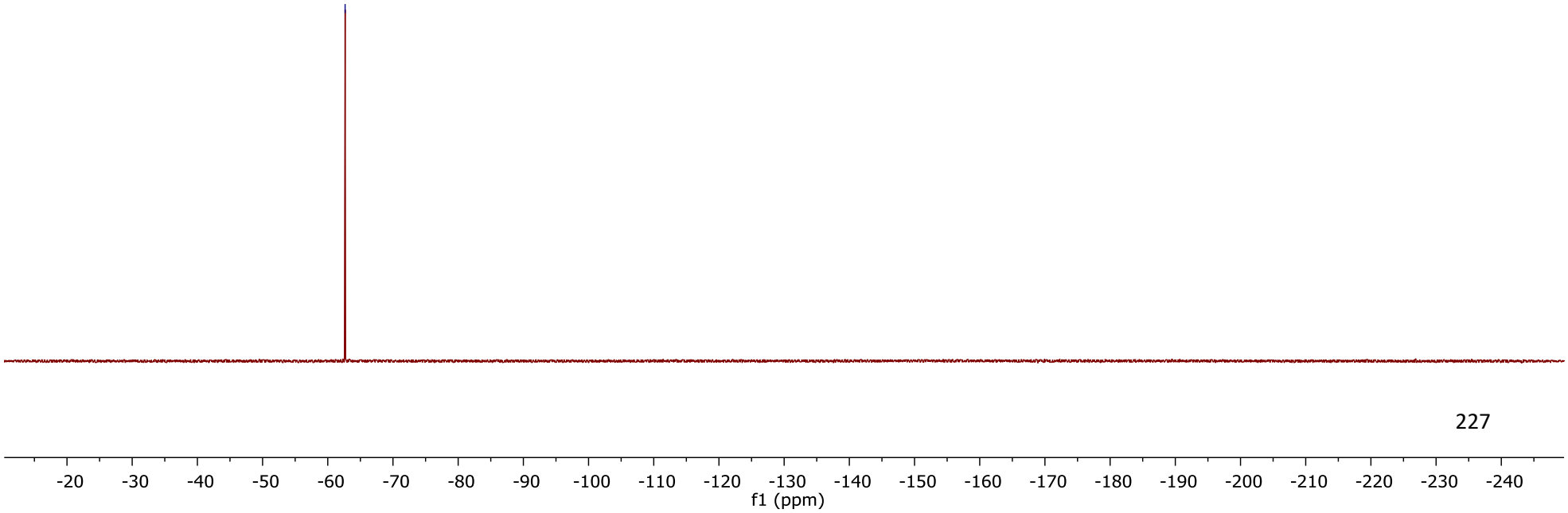
19a

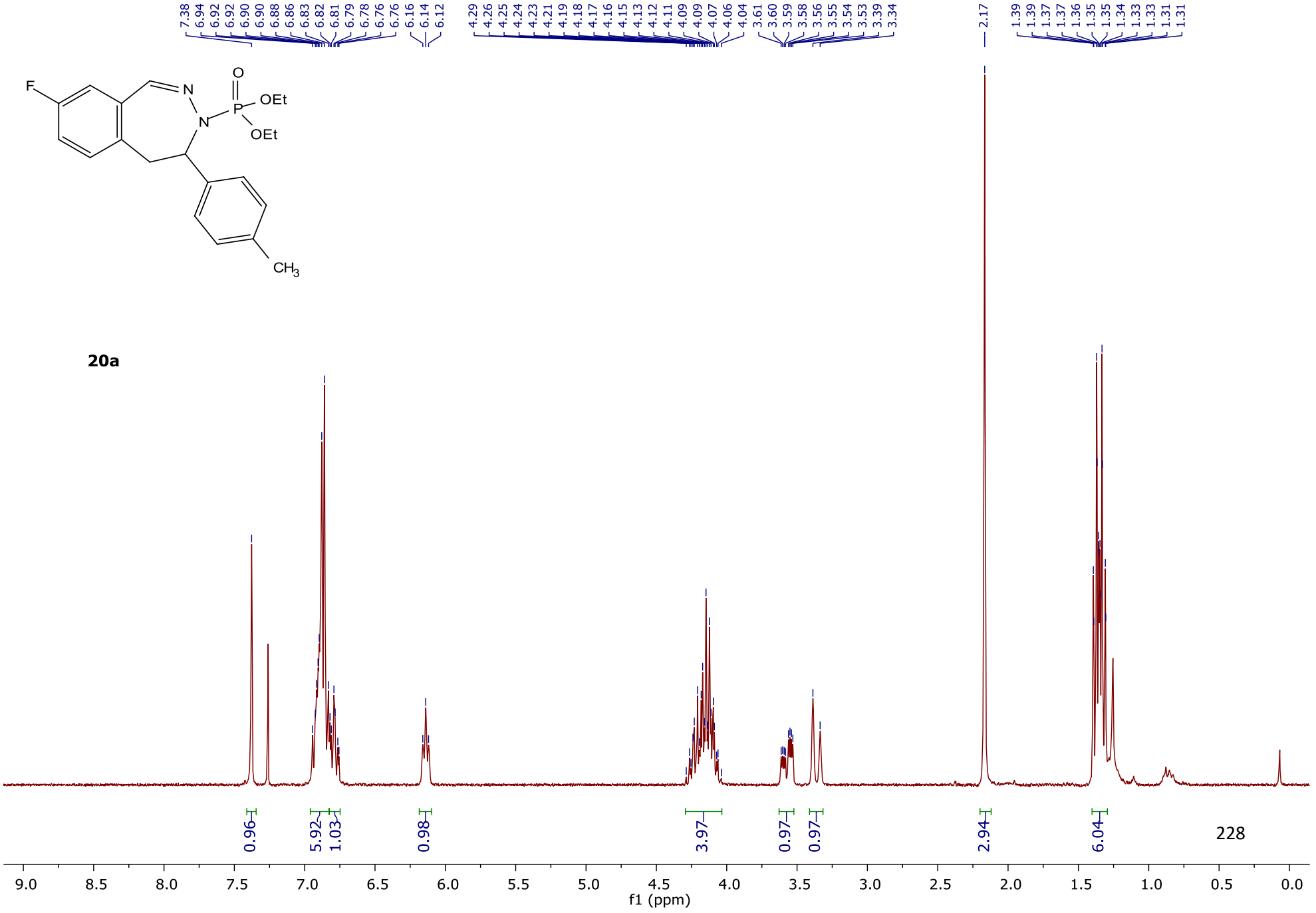


19F


-62.66
CF3
N
O
P
OEt
N
OEt
CH3

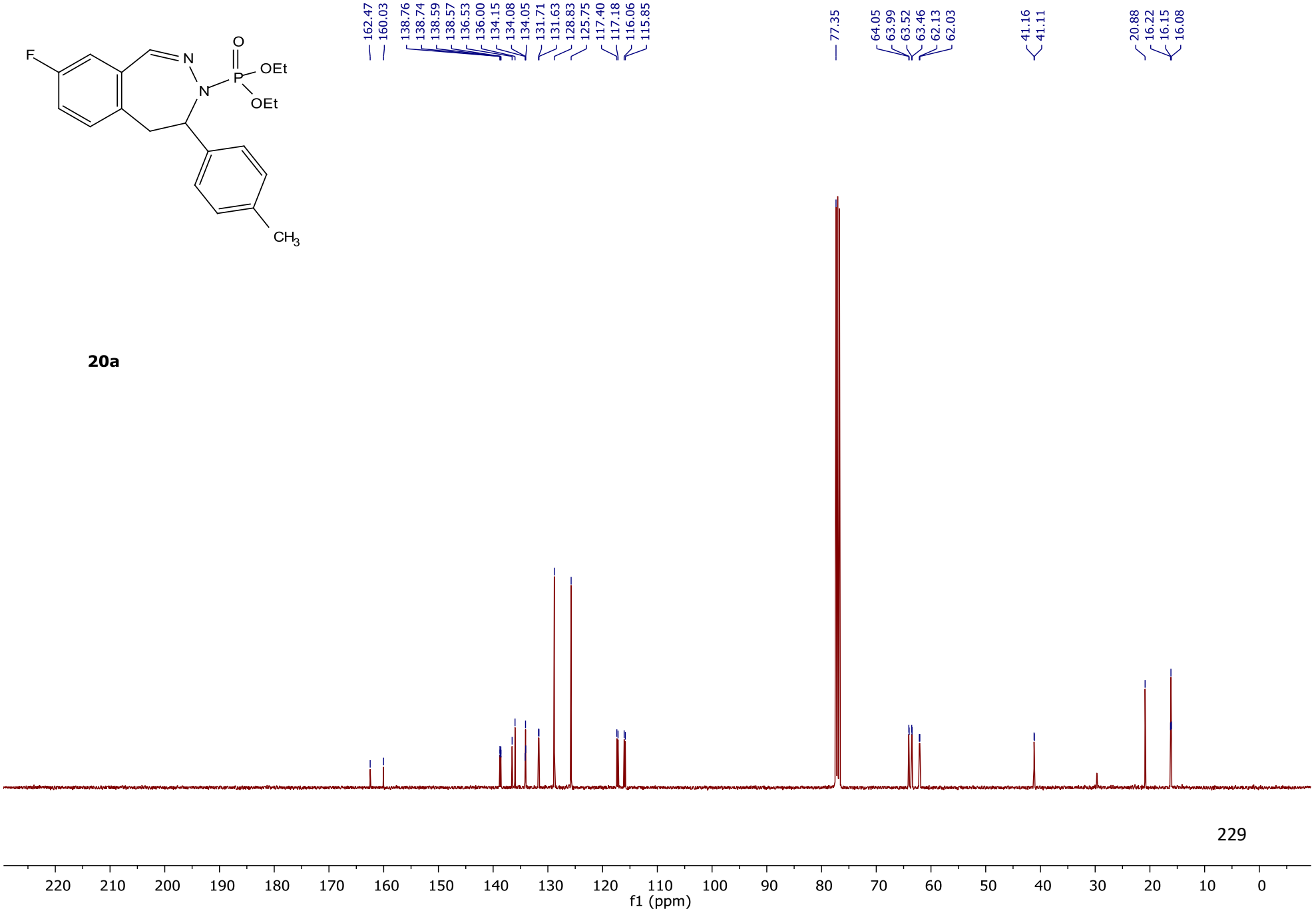
19a


227
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


7.38 6.94 6.92 6.92 6.90 6.90 6.88 6.86 6.83 6.82 6.81 6.79 6.78 6.76 6.76 6.16 6.14 6.12
4.29 4.26 4.25 4.24 4.23 4.21 4.19 4.18 4.17 4.16 4.15 4.13 4.12 4.11 4.09 4.09 4.07 4.06 4.04 3.61 3.60 3.59 3.58 3.56 3.55 3.54 3.53 3.39 3.34
2.17
1.39 1.39 1.37 1.37 1.36 1.35 1.35 1.34 1.33 1.33 1.31 1.31
F
N
O
P
OEt
OEt
N
CH3
20a
0.96
5.92
1.03
0.98
3.97
0.97
0.97
2.94
6.04
228
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

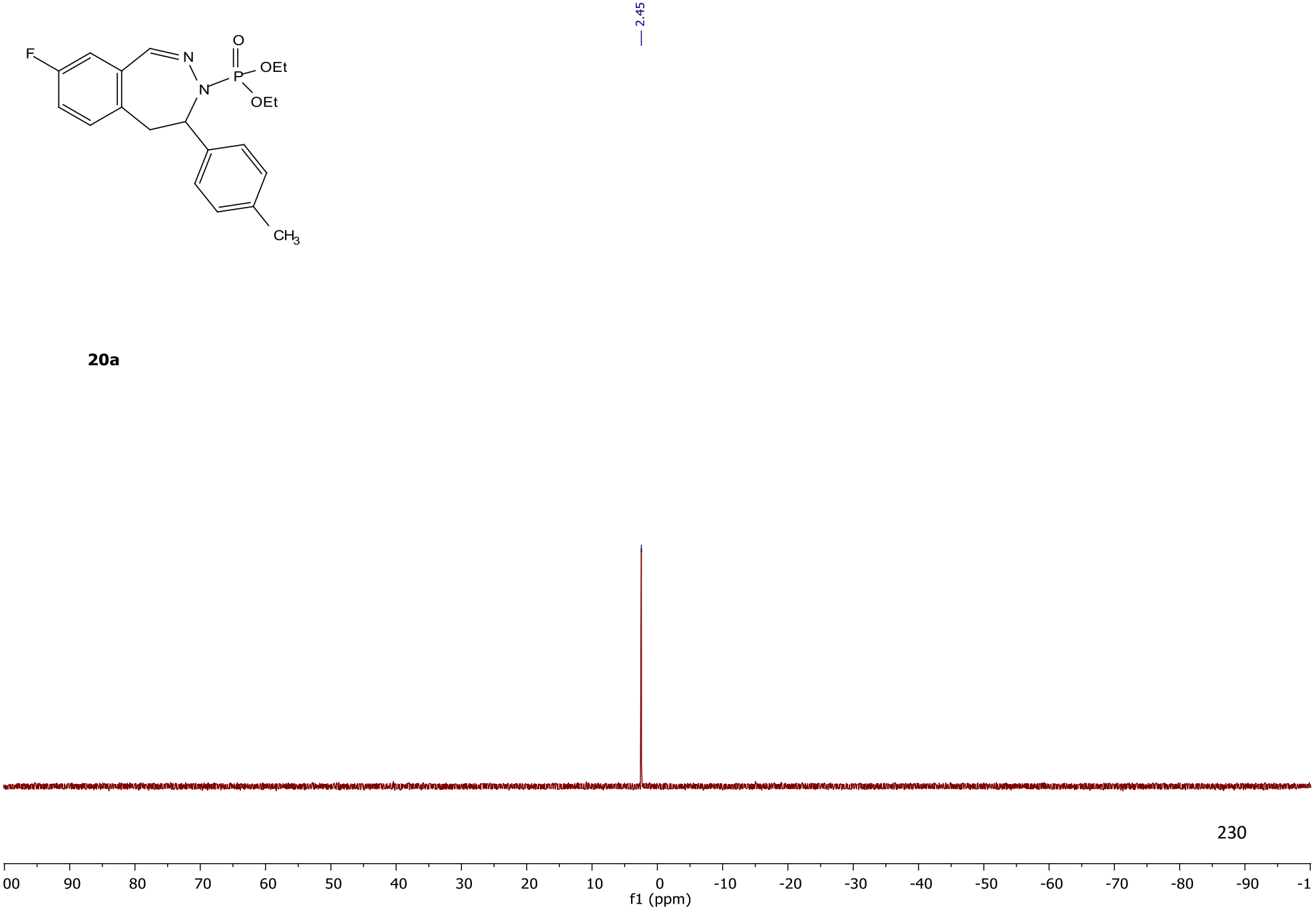
F
N
O
P
OEt
N
OEt
CH3

20a


162.47
160.03
138.76
138.74
138.59
138.57
136.53
136.00
134.15
134.08
134.05
131.71
131.63
128.83
125.75
117.40
117.18
116.06
115.85
77.35
64.05
63.99
63.52
63.46
62.13
62.03
41.16
41.11
20.88
16.22
16.15
16.08
229
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

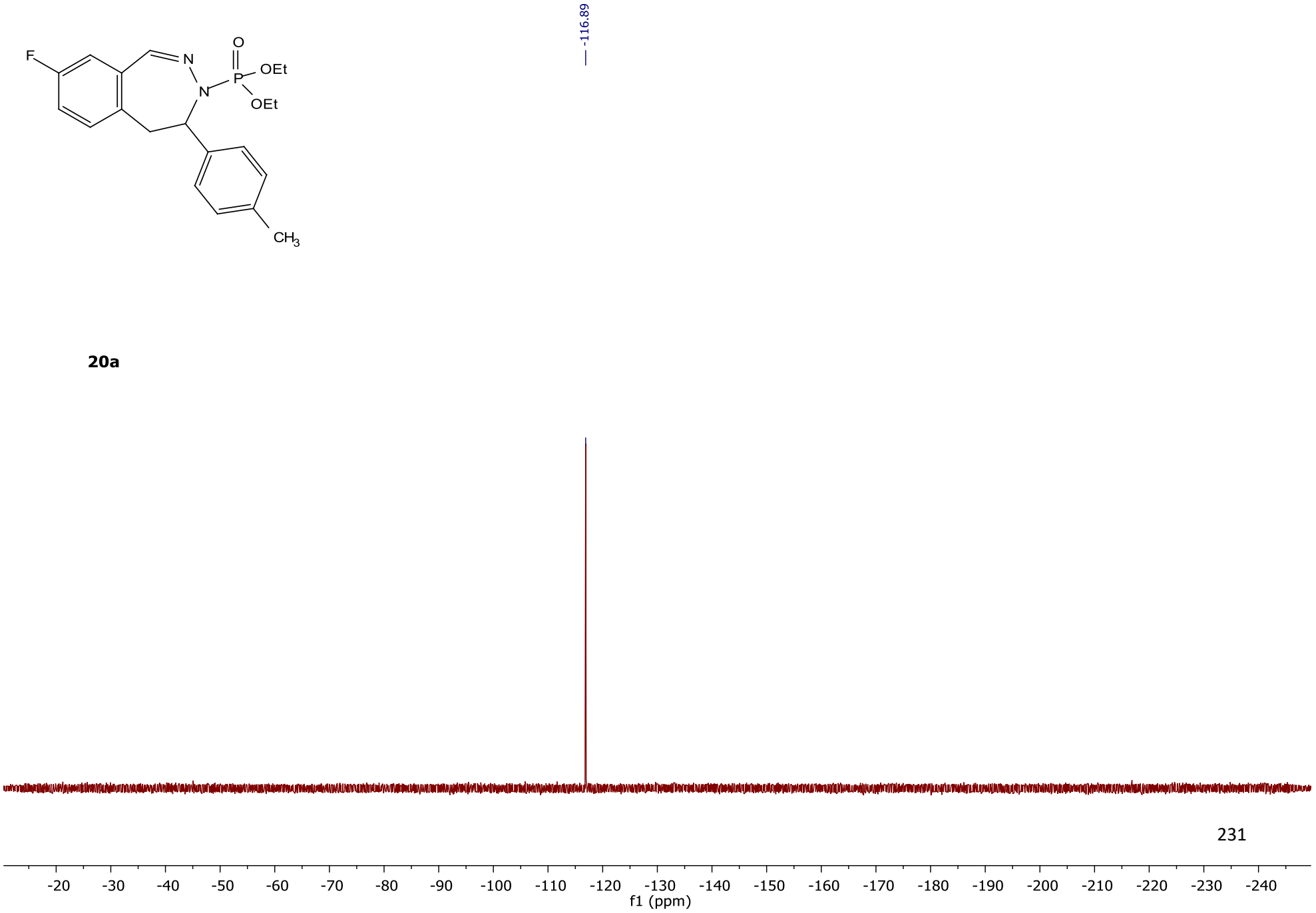
F
N
O
P
OEt
N
OEt
CH3

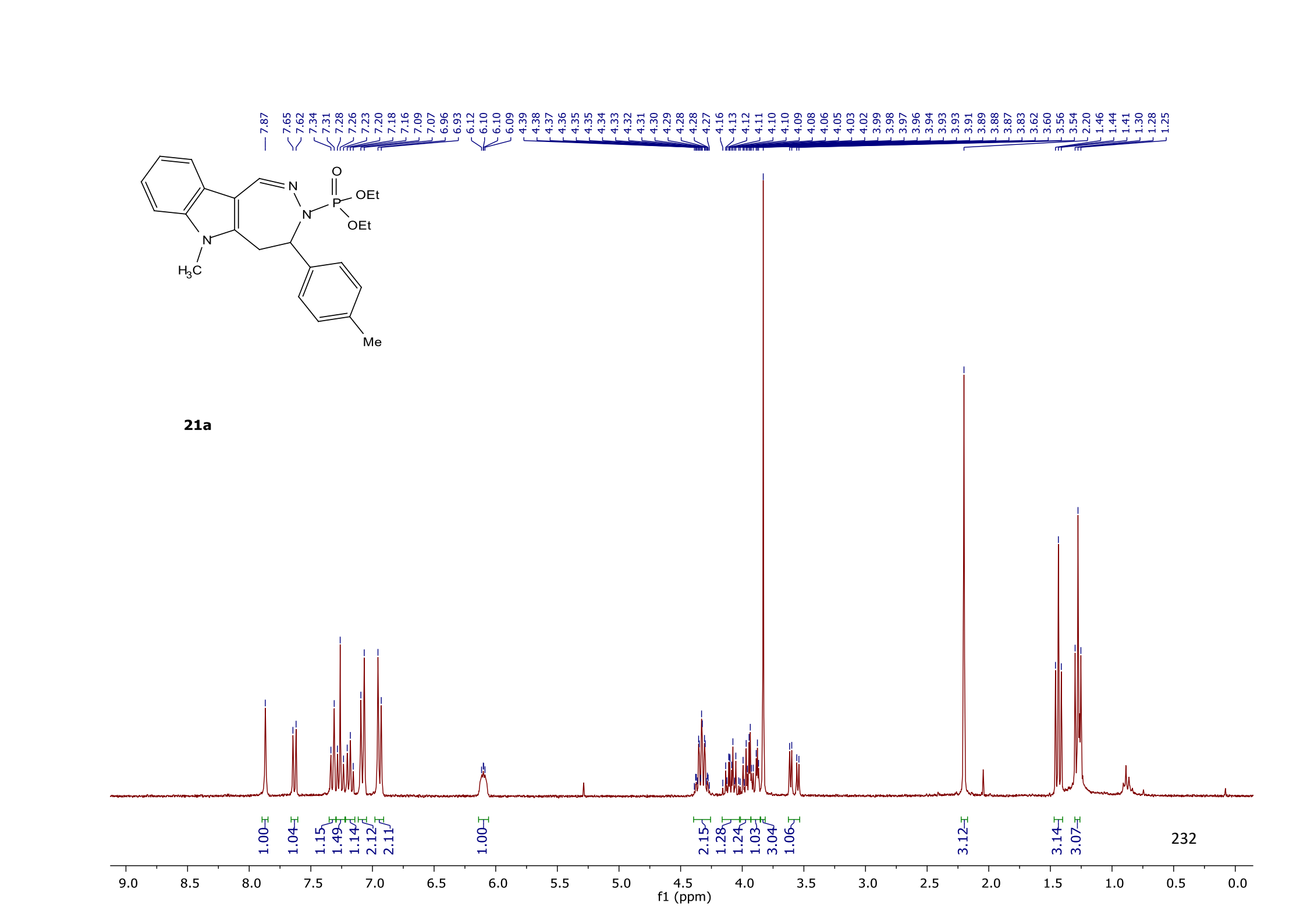
20a


2.45
230
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

F
N
O
P
OEt
N
OEt
CH3

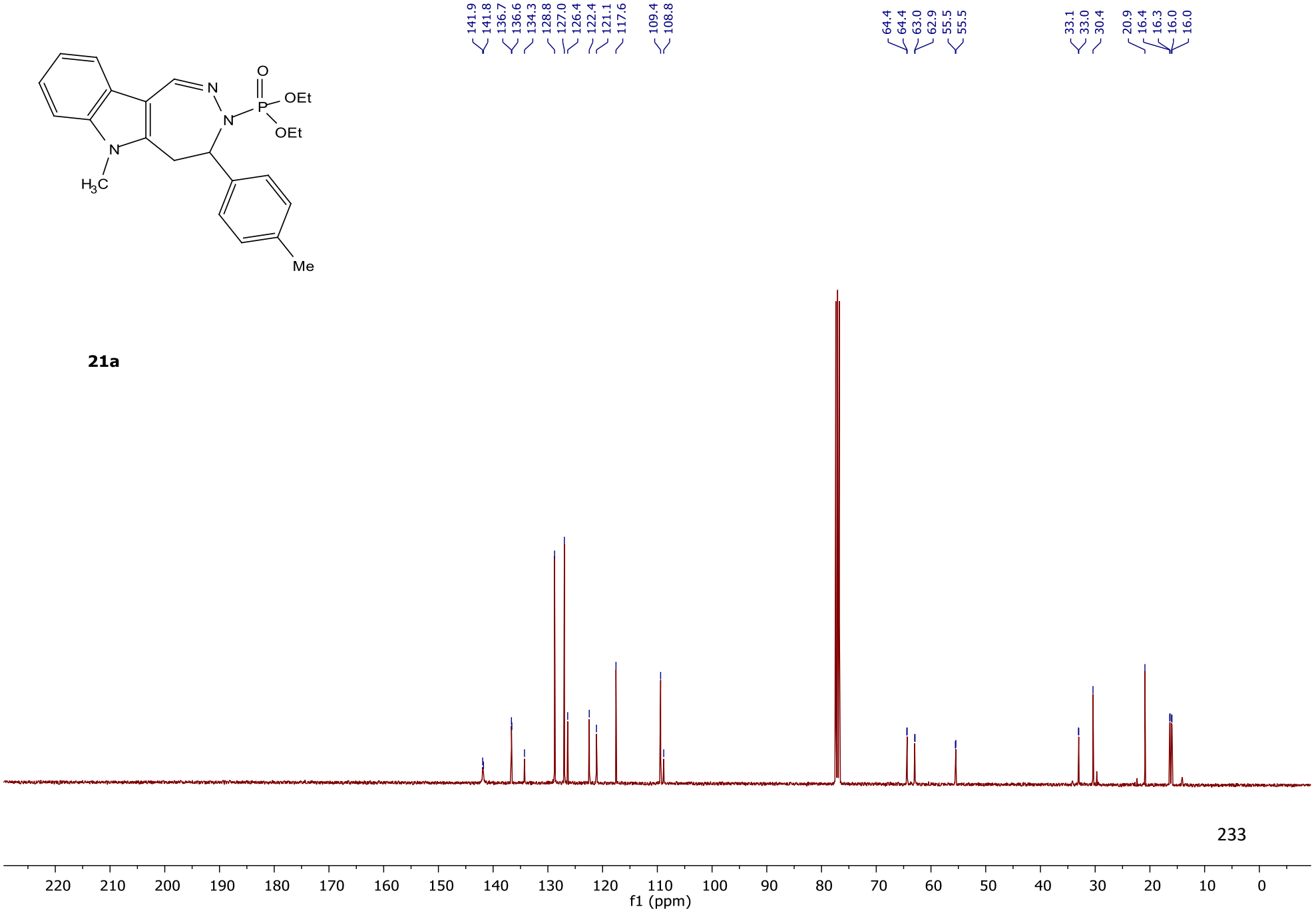
20a


-116.89
231
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


7.87 7.65 7.62 7.34 7.31 7.28 7.26 7.23 7.20 7.18 7.16 7.09 7.07 6.96 6.93 6.12 6.10 6.10 6.09 4.39 4.38 4.37 4.36 4.35 4.35 4.34 4.33 4.32 4.31 4.30 4.29 4.28 4.28 4.27 4.16 4.13 4.12 4.11 4.10 4.10 4.09 4.08 4.06 4.05 4.03 4.02 3.99 3.98 3.97 3.96 3.94 3.93 3.93 3.91 3.89 3.88 3.87 3.83 3.62 3.60 3.56 3.54 2.20 1.46 1.44 1.41 1.30 1.28 1.25
O
N
P
OEt
OEt
N
N
H3C
Me
21a
1.00 1.04 1.15 1.49 1.14 2.12 2.11 1.00 2.15 1.28 1.24 1.03 3.04 1.06 3.12 3.14 3.07
232
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

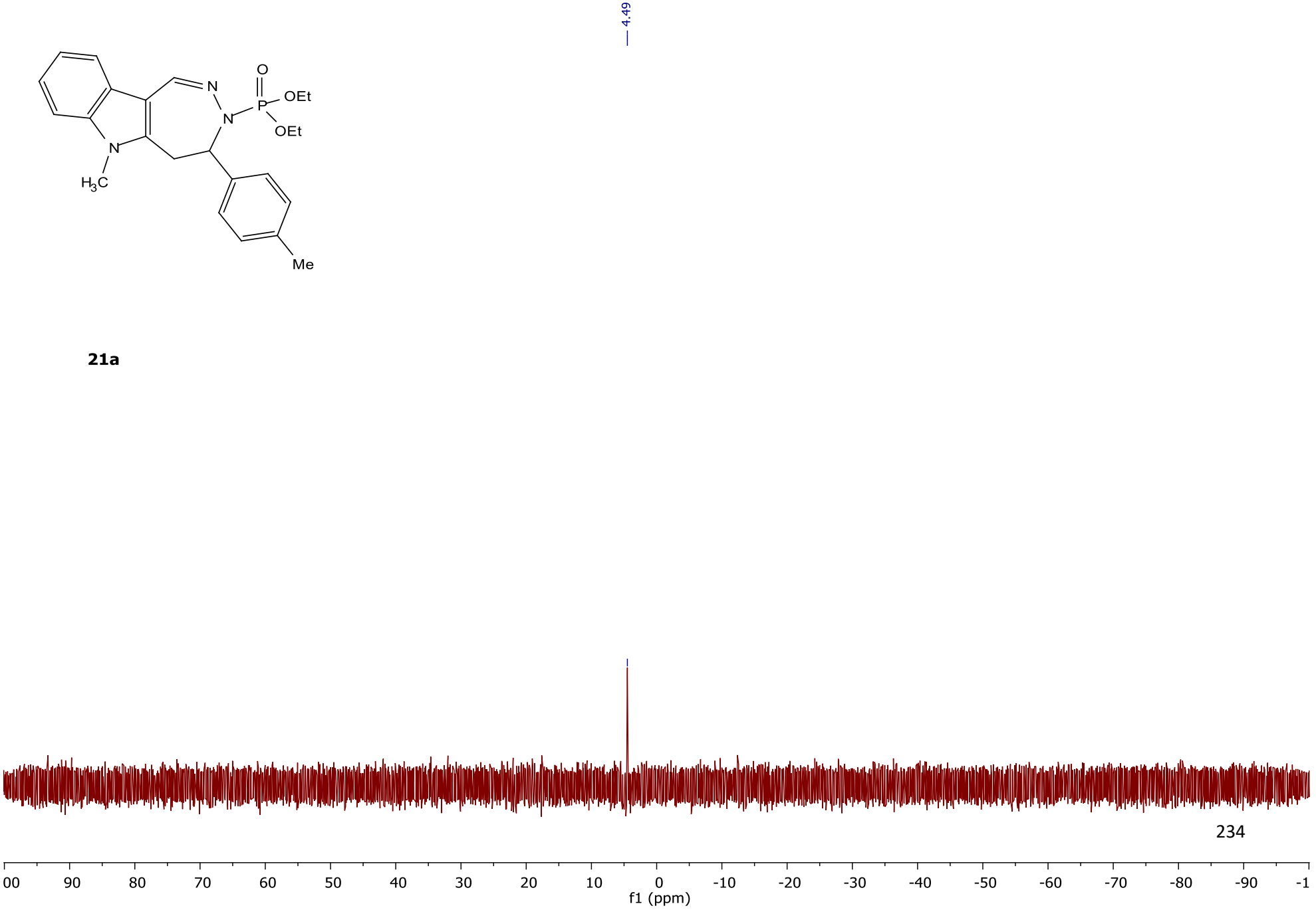
O
N
P
OEt
N
OEt
N
H3C
Me

21a


141.9
141.8
136.7
136.6
134.3
128.8
127.0
126.4
122.4
121.1
117.6
109.4
108.8
64.4
64.4
63.0
62.9
55.5
55.5
33.1
33.0
30.4
20.9
16.4
16.3
16.0
16.0
233
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

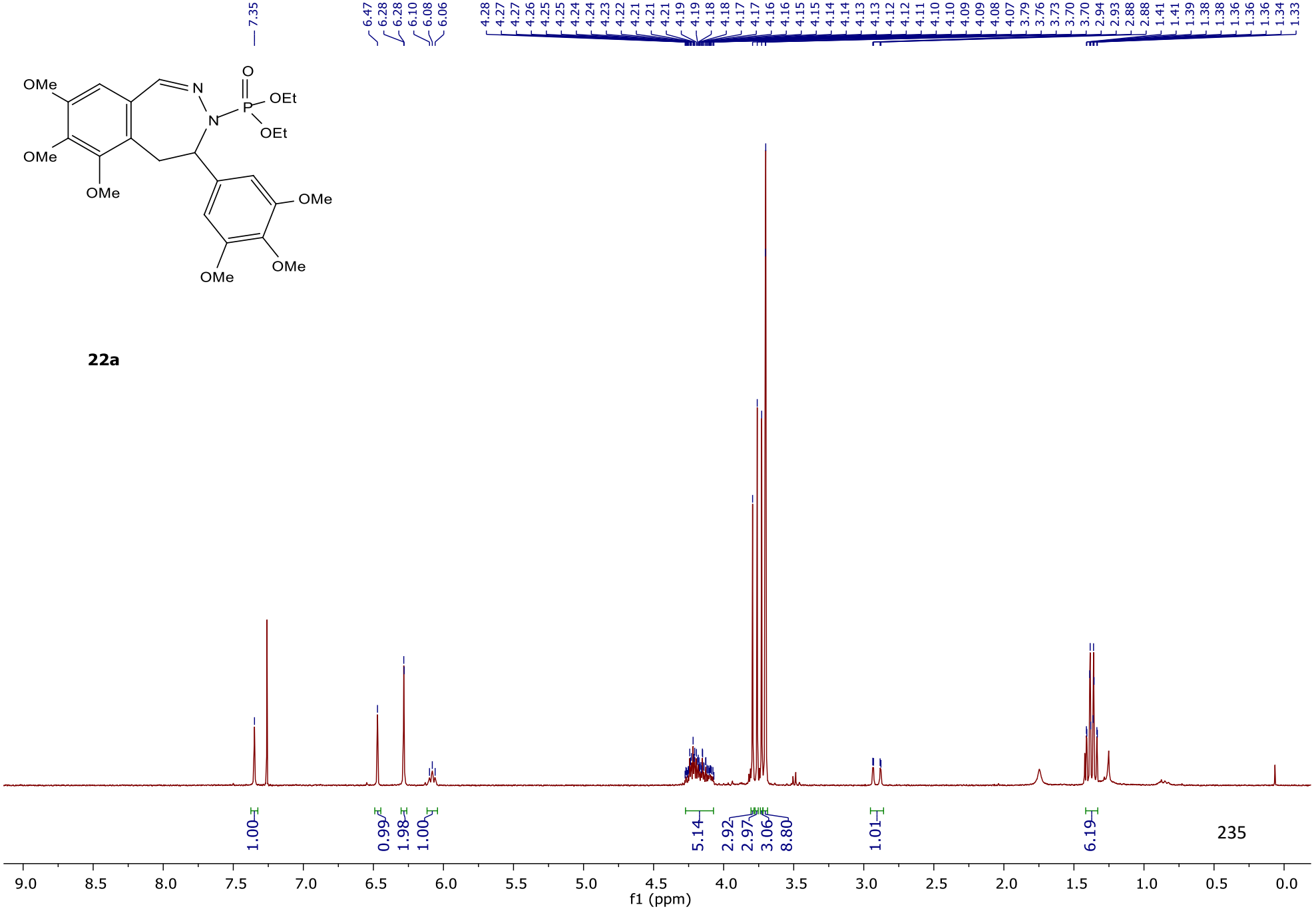
O
N
OEt
P
N
OEt
N
H3C
Me

21a


4.49
234
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)

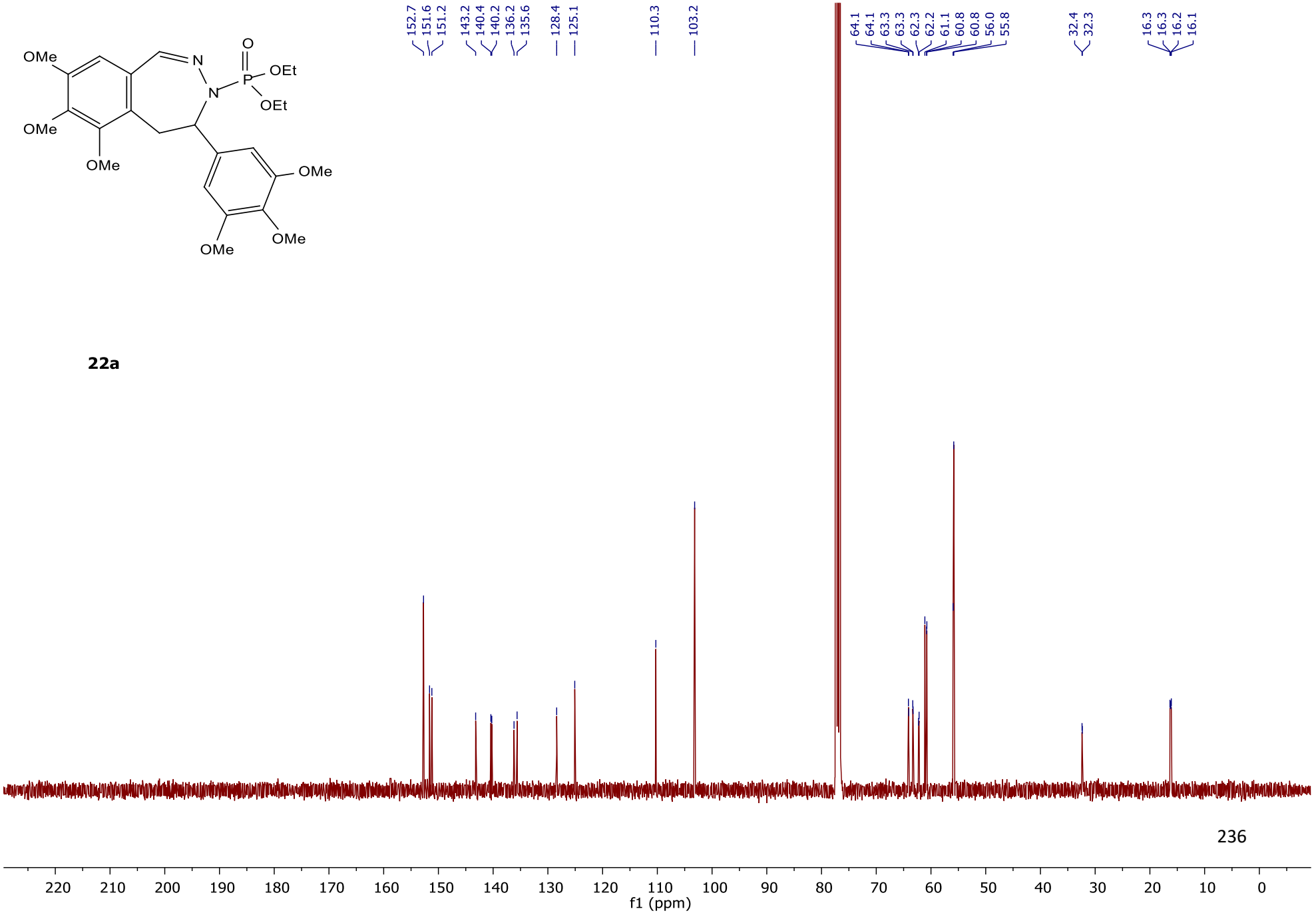
OMe
OMe
OMe
N
O
P
OEt
OEt
N
OMe
OMe
OMe
OMe

22a


7.35
6.47
6.28
6.28
6.10
6.08
6.06
4.28
4.27
4.27
4.26
4.25
4.25
4.24
4.24
4.23
4.22
4.21
4.21
4.21
4.19
4.19
4.18
4.18
4.17
4.17
4.16
4.16
4.15
4.15
4.14
4.14
4.13
4.13
4.12
4.12
4.11
4.10
4.10
4.09
4.09
4.08
4.07
3.79
3.76
3.73
3.70
3.70
2.94
2.93
2.88
2.88
1.41
1.41
1.39
1.38
1.38
1.36
1.36
1.36
1.34
1.33
1.00
0.99
1.98
1.00
5.14
2.92
2.97
3.06
8.80
1.01
6.19
235
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

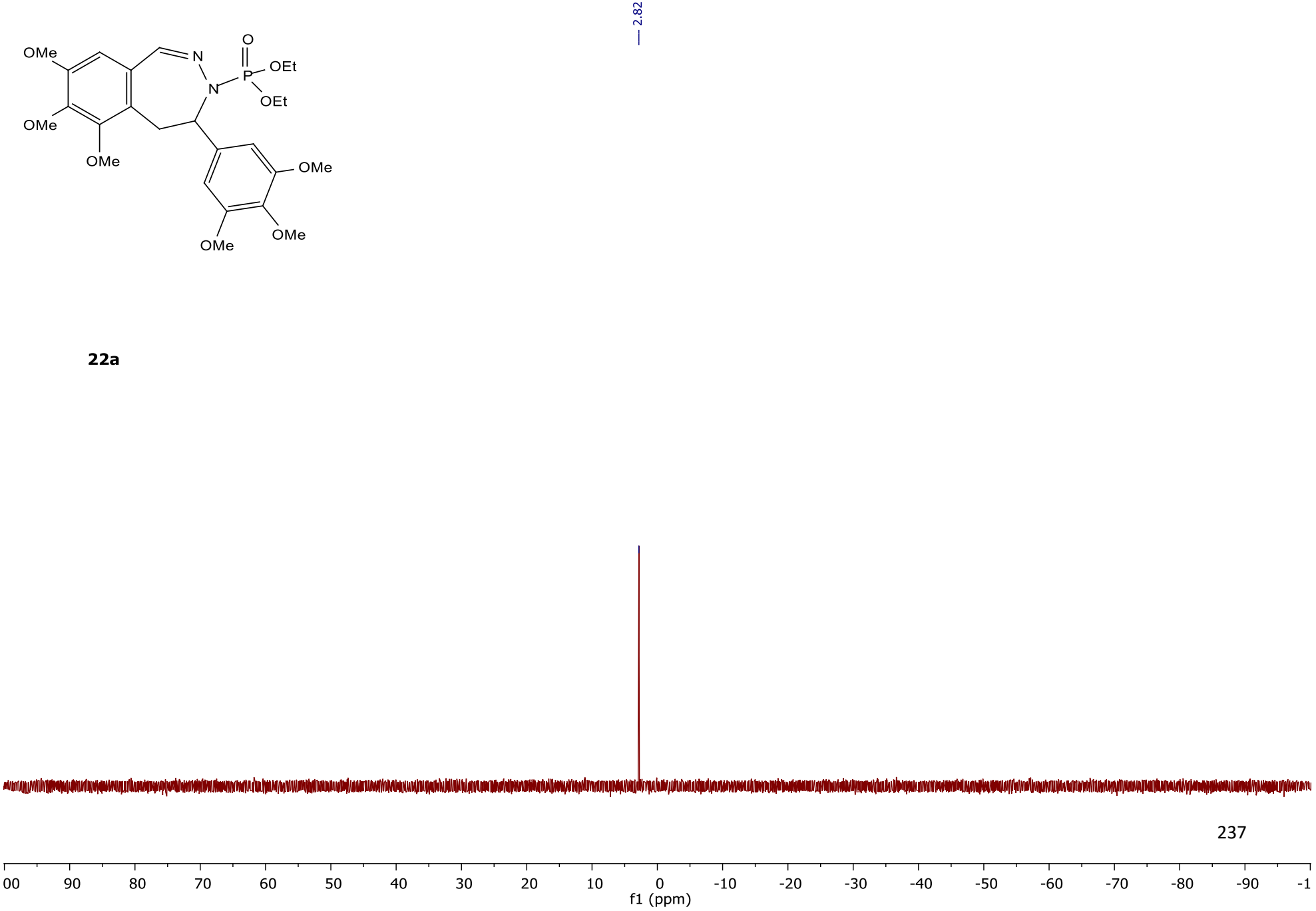
OMe
OMe
OMe
N
N
P
O
OEt
OEt
OMe
OMe
OMe
OMe

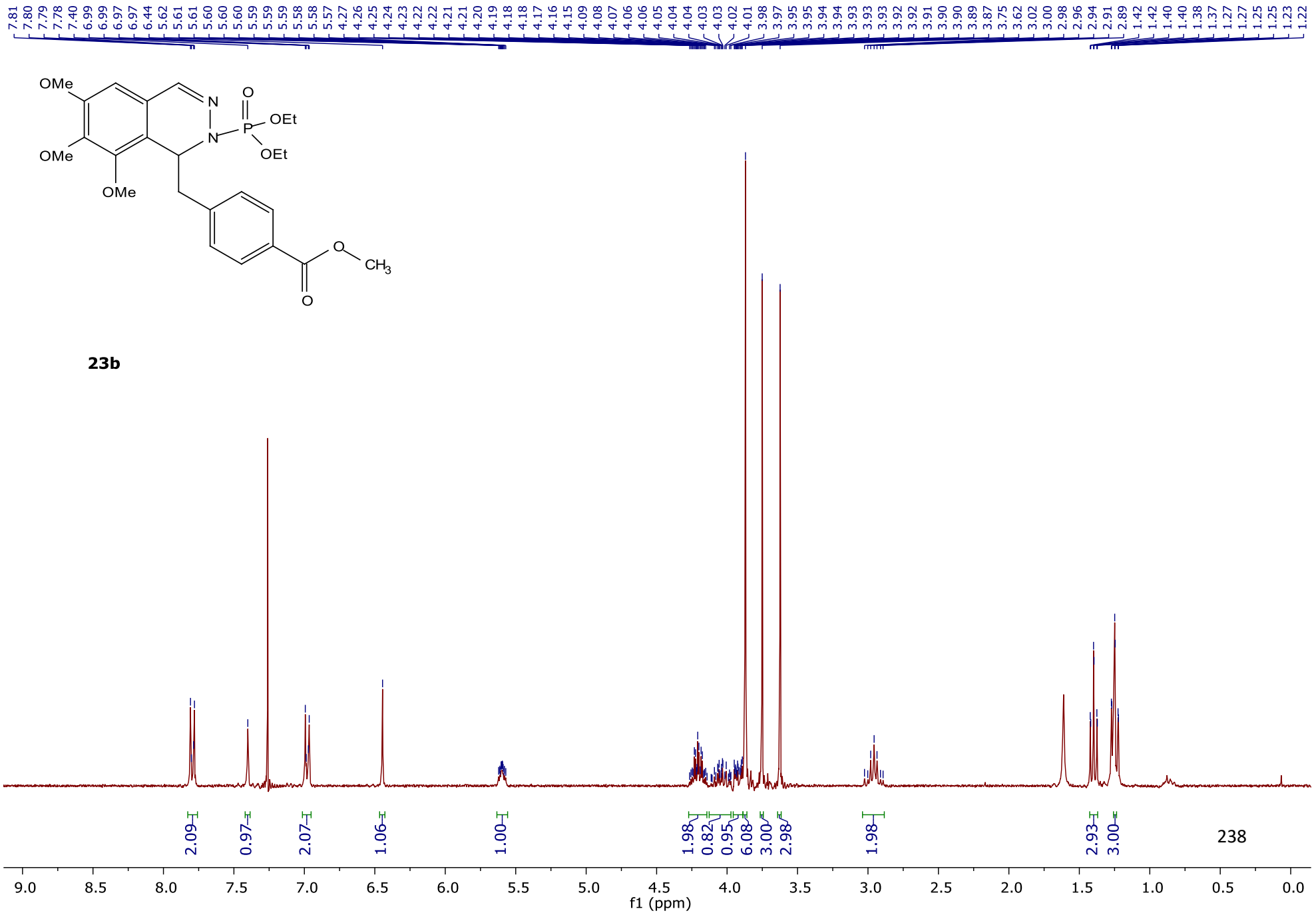
22a


152.7
151.6
151.2
143.2
140.4
140.2
136.2
135.6
128.4
125.1
110.3
103.2
64.1
64.1
63.3
63.3
62.3
62.2
61.1
60.8
60.8
56.0
55.8
32.4
32.3
16.3
16.3
16.2
16.1
236
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OMe
OMe
OMe
N
N
P
O
OEt
OEt
OMe
OMe
OMe

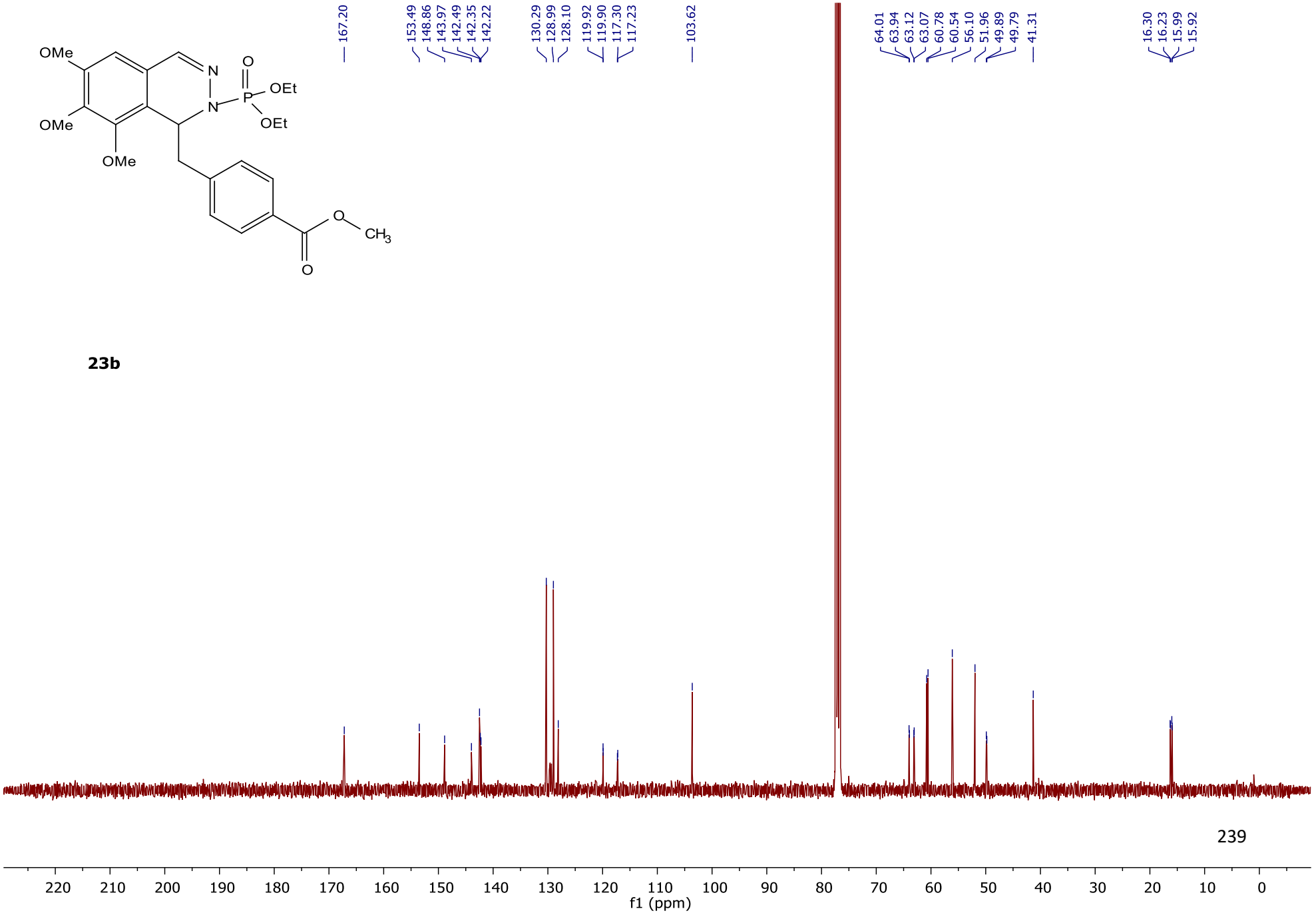
22a


2.82
237
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.81 7.80 7.79 7.78 7.40 6.99 6.99 6.97 6.97 6.44 5.62 5.61 5.61 5.60 5.60 5.60 5.59 5.59 5.59 5.58 5.58 5.57 4.27 4.26 4.25 4.24 4.23 4.22 4.22 4.21 4.21 4.20 4.19 4.18 4.18 4.17 4.16 4.15 4.09 4.08 4.07 4.06 4.06 4.05 4.04 4.04 4.04 4.03 4.03 4.02 4.01 3.98 3.97 3.95 3.95 3.94 3.94 3.93 3.93 3.93 3.92 3.92 3.91 3.90 3.90 3.89 3.87 3.75 3.62 3.02 3.00 2.98 2.96 2.94 2.91 2.89 1.42 1.42 1.40 1.40 1.38 1.37 1.27 1.27 1.25 1.25 1.23 1.22
OMe
OMe
OMe
N
N
P
O
OEt
OEt
O
O
CH3
23b
2.09
0.97
2.07
1.06
1.00
1.98
0.82
0.95
6.08
3.00
2.98
1.98
2.93
3.00
238
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

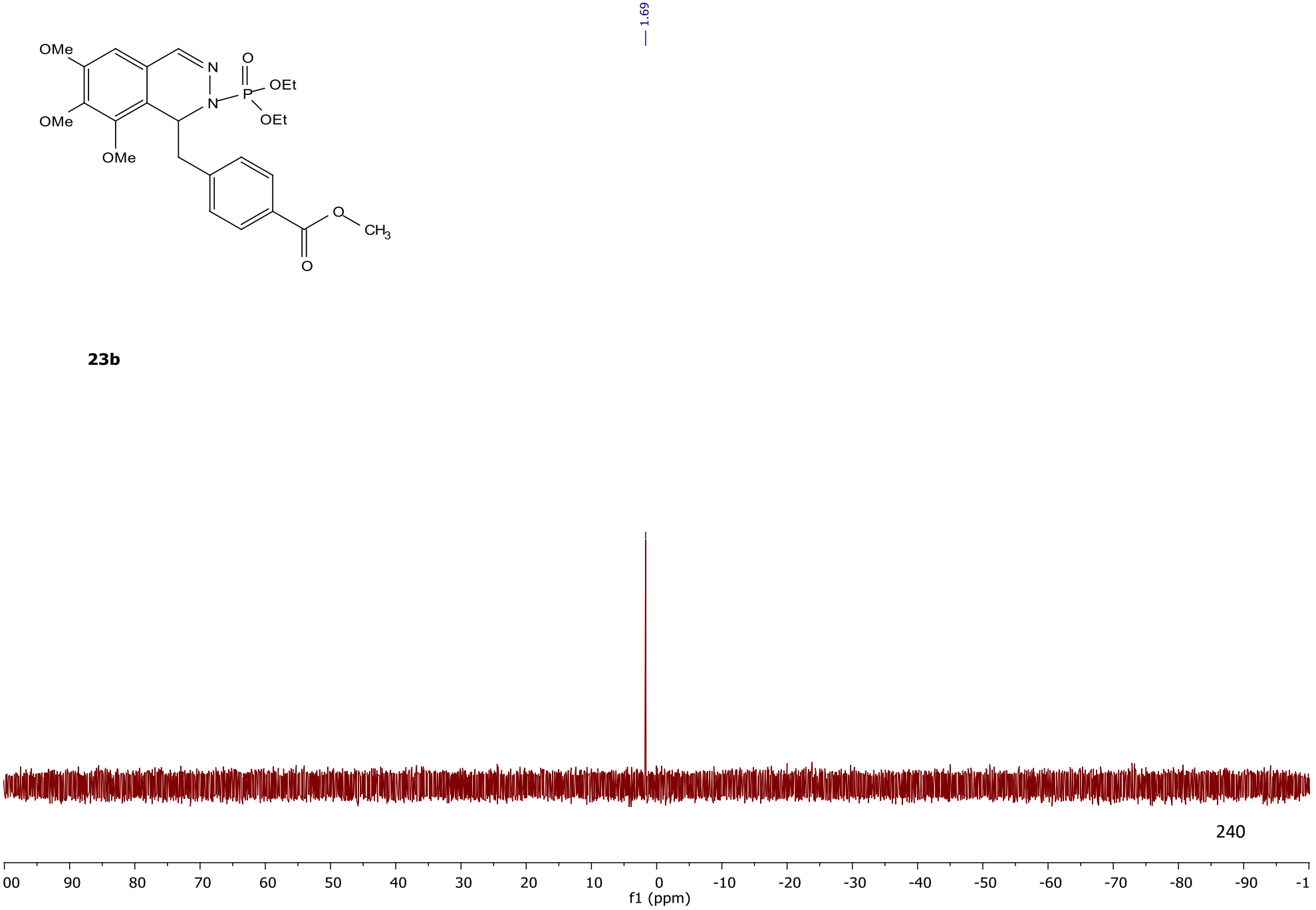
OMe
OMe
OMe
N
N
P
O
OEt
OEt
O
CH3
O

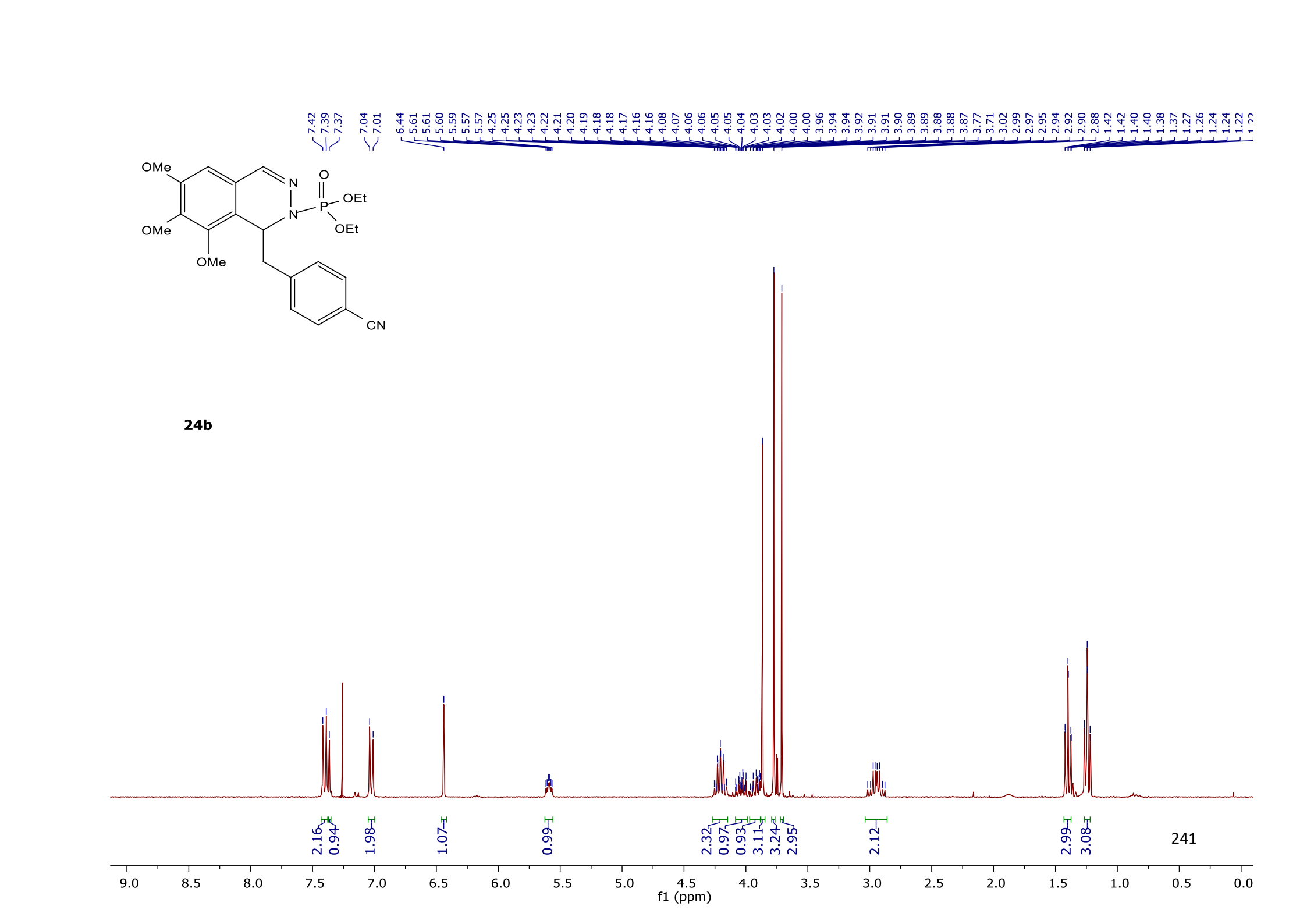
23b

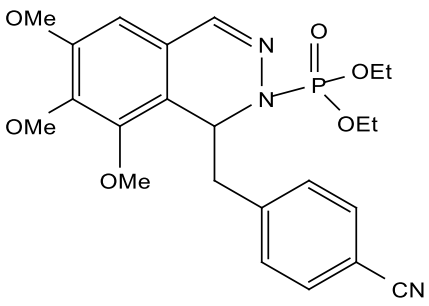

167.20
153.49
148.86
143.97
142.49
142.35
142.22
130.29
128.99
128.10
119.92
119.90
117.30
117.23
103.62
64.01
63.94
63.12
63.07
60.78
60.54
56.10
51.96
49.89
49.79
41.31
16.30
16.23
15.99
15.92
239
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OMe
OMe
OMe
N
N
O
P
OEt
OEt
O
CH3
O

23b


1.69
240
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.42 7.39 7.37 7.04 7.01 6.44 5.61 5.61 5.60 5.59 5.57 5.57 4.25 4.23 4.23 4.22 4.21 4.20 4.19 4.18 4.18 4.17 4.16 4.16 4.08 4.07 4.06 4.06 4.05 4.05 4.04 4.03 4.03 4.02 4.00 4.00 3.96 3.94 3.94 3.92 3.91 3.91 3.90 3.89 3.89 3.88 3.88 3.87 3.77 3.71 3.02 2.99 2.97 2.95 2.94 2.92 2.90 2.88 1.42 1.42 1.40 1.40 1.38 1.37 1.27 1.26 1.24 1.24 1.22
OMe
OMe
OMe
N
N
O
P
OEt
OEt
CN
24b
2.16 0.94 1.98 1.07 0.99 2.32 0.97 0.93 3.11 3.24 2.95 2.12 2.99 3.08
241
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



24b

153.63
148.75
144.03
142.74
142.23
142.10
131.38
131.03
119.81
119.11
116.91
116.84
110.05
103.71
64.12
64.06
63.19
63.13
60.82
60.69
56.12
49.81
49.72
41.60
16.31
16.24
15.97
15.90

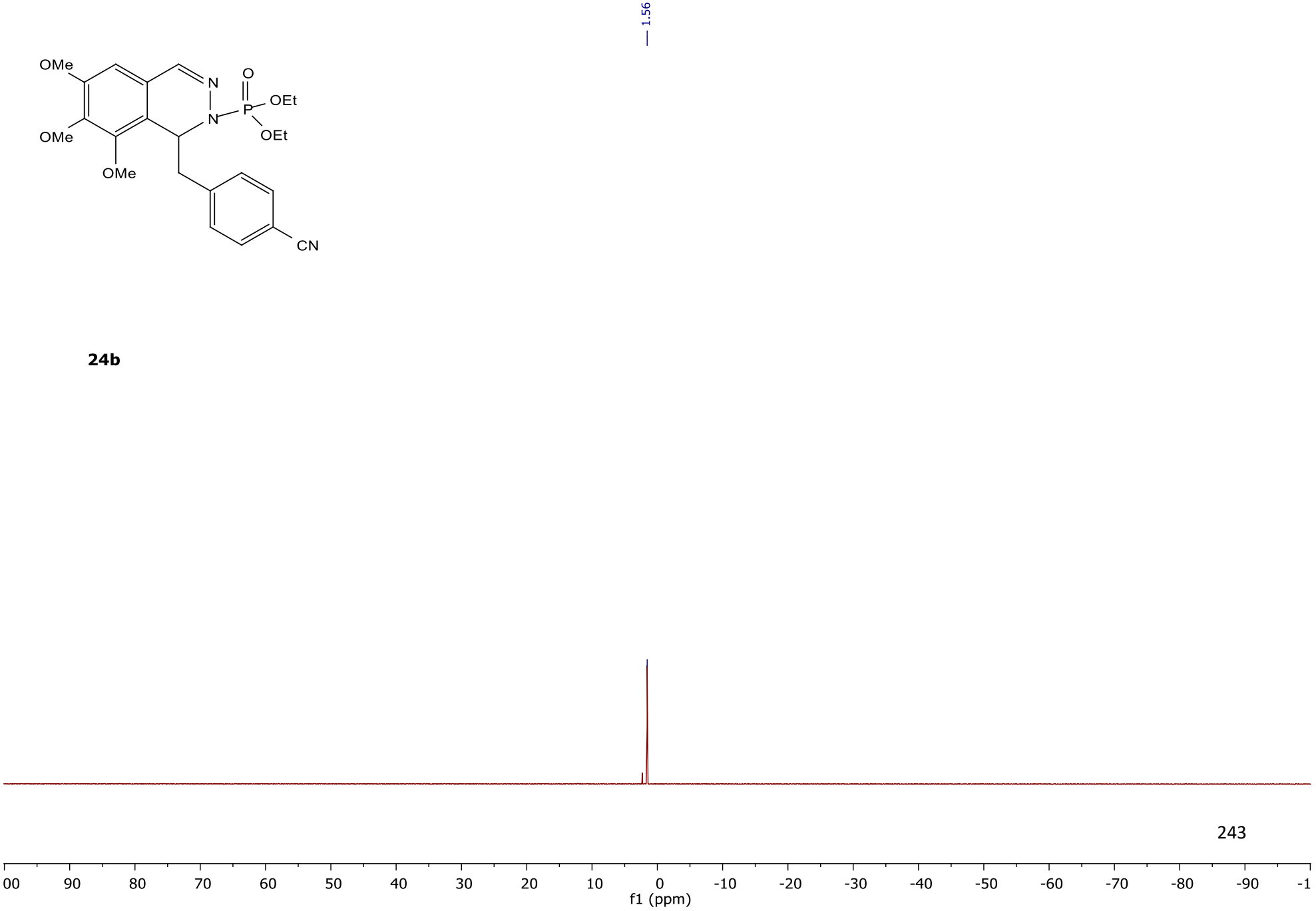
242

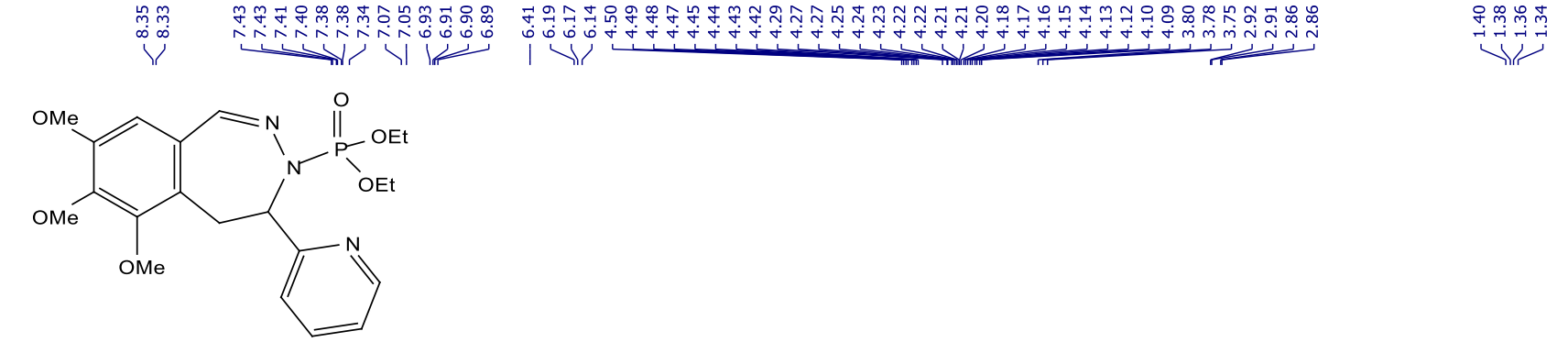
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

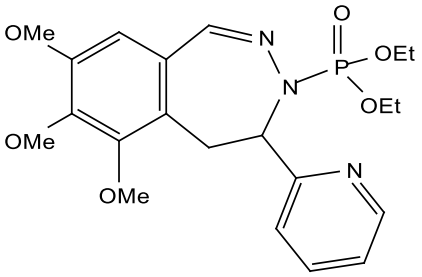
OMe
OMe
OMe
N
N
O
P
OEt
OEt
CN

24b


1.56
243
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)



25a



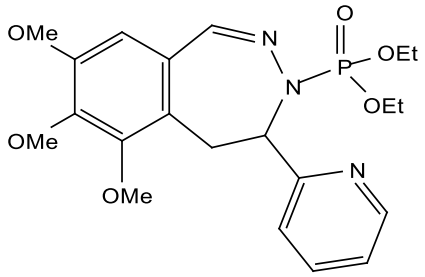
159.0
151.5
151.4
149.0
143.1
140.7
140.5
136.0
128.0
125.6
121.3
120.7
110.1
64.2
64.1
63.9
63.8
63.4
63.4
60.9
60.7
55.9
32.2
32.1
16.3
16.2
16.2
16.1

25a

245

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)



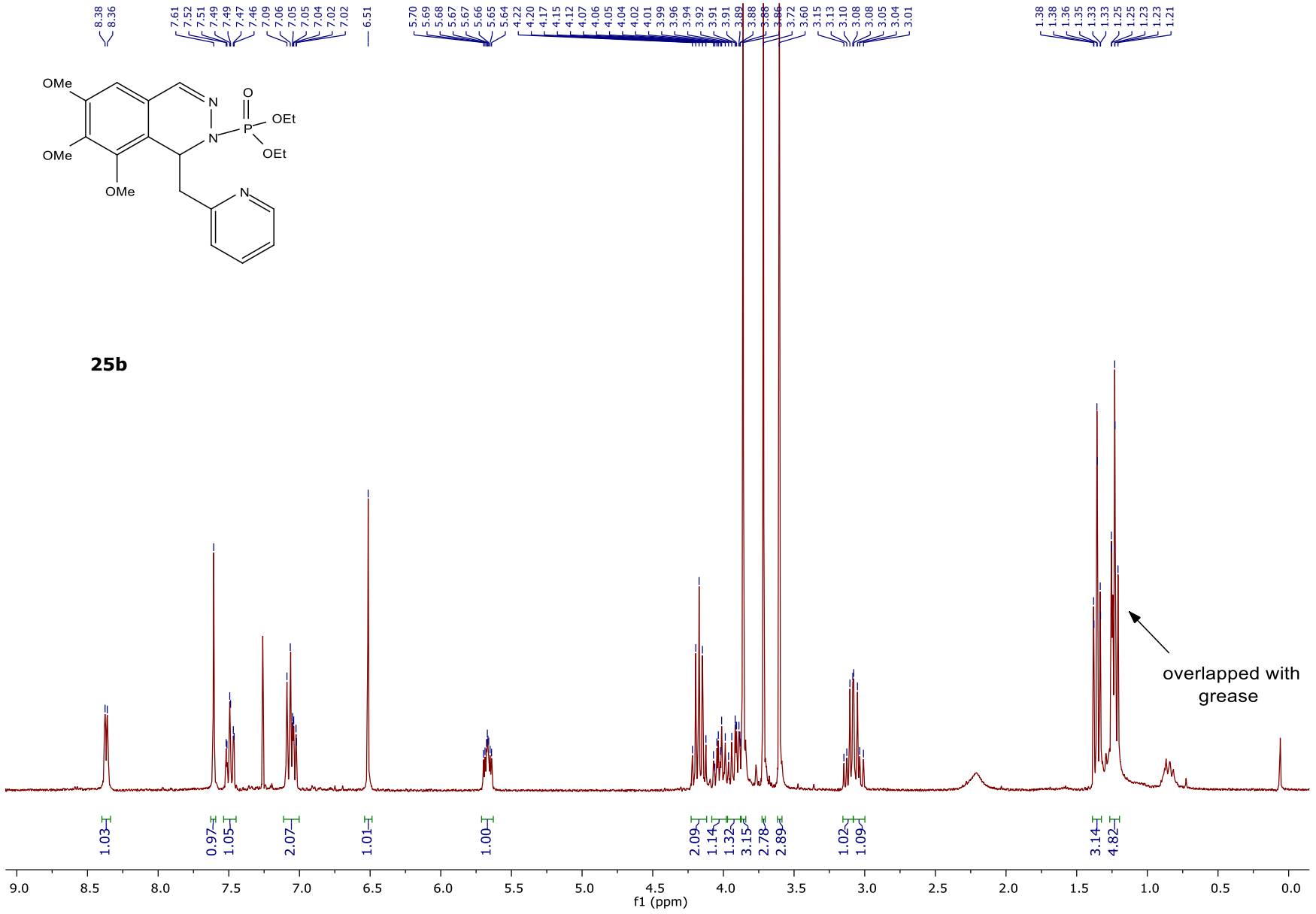
2.81

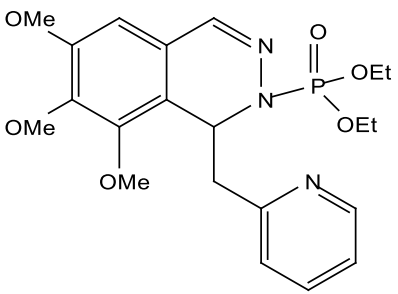
25a

246

00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -1

f1 (ppm)


25b
OMe
OMe
OMe
N
N
P
O
OEt
OEt
N
overlapped with grease
f1 (ppm)



25b

157.2
153.3
148.7
143.9
143.0
142.9
135.7
124.7
121.3
119.8
117.9
117.9
103.8
63.8
63.7
63.1
63.1
60.7
60.6
56.1
49.4
49.3
43.2
16.2
16.2
16.0
15.9

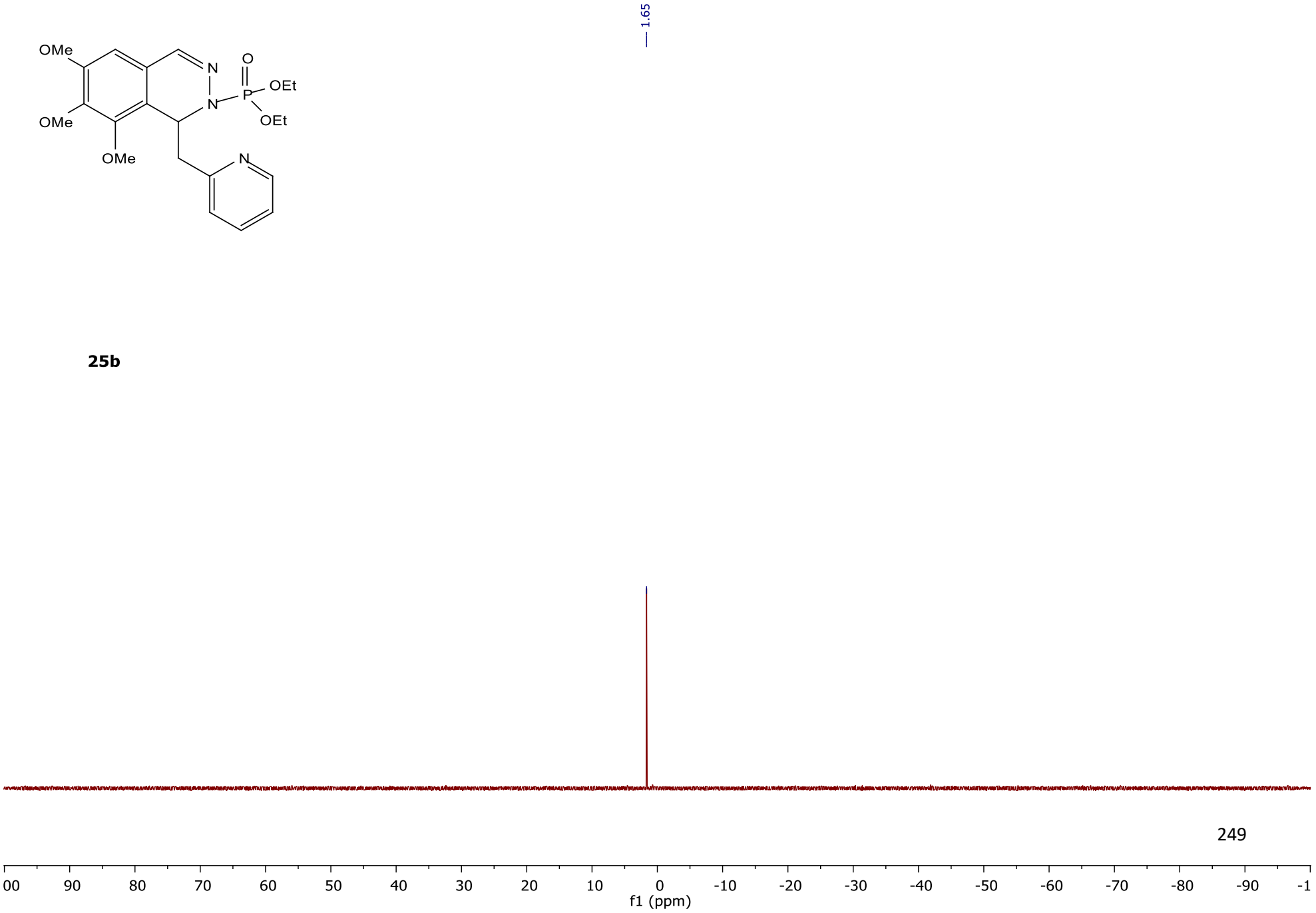
248

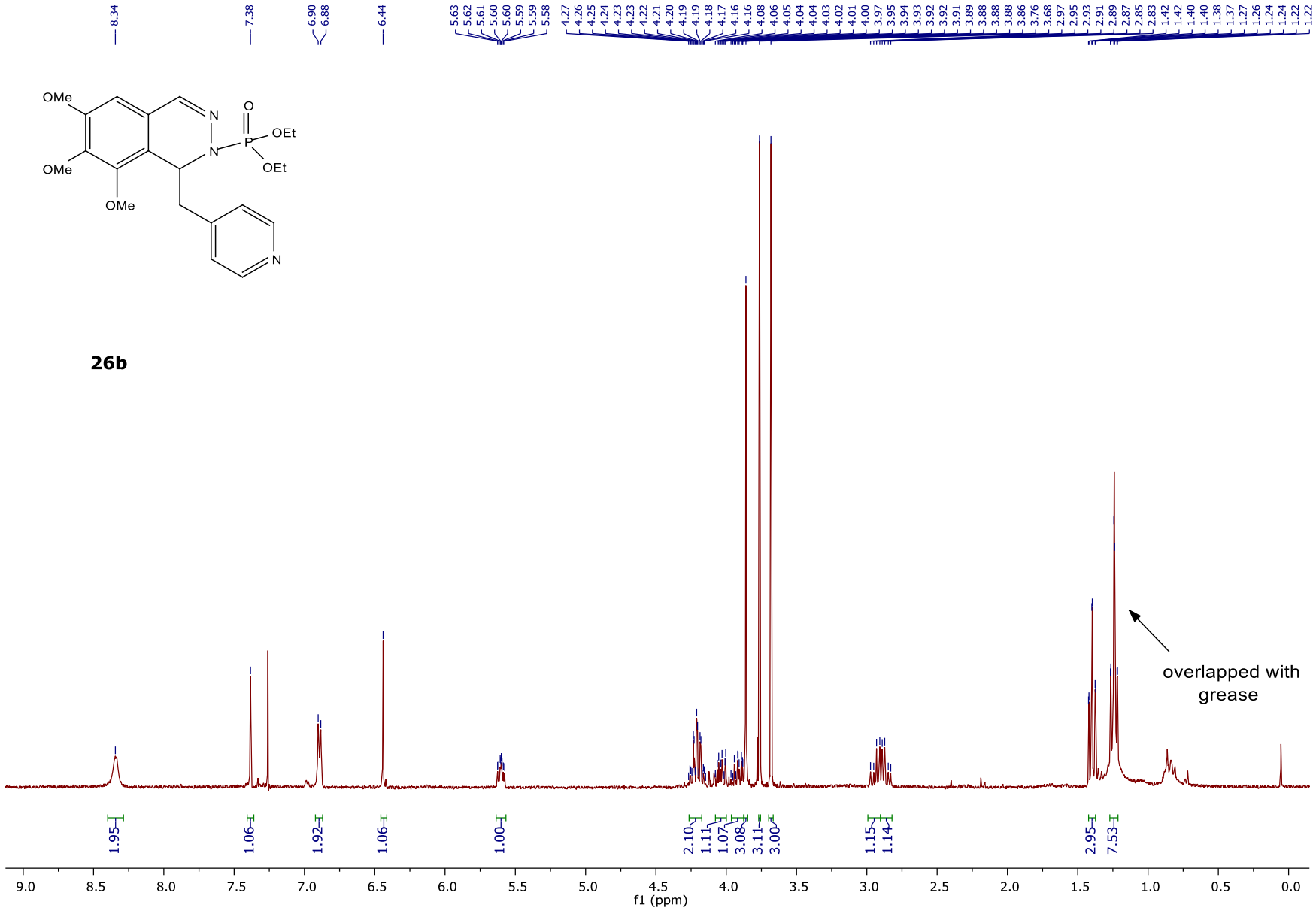
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

OMe
OMe
OMe
N
N
O
P
OEt
OEt
N

25b

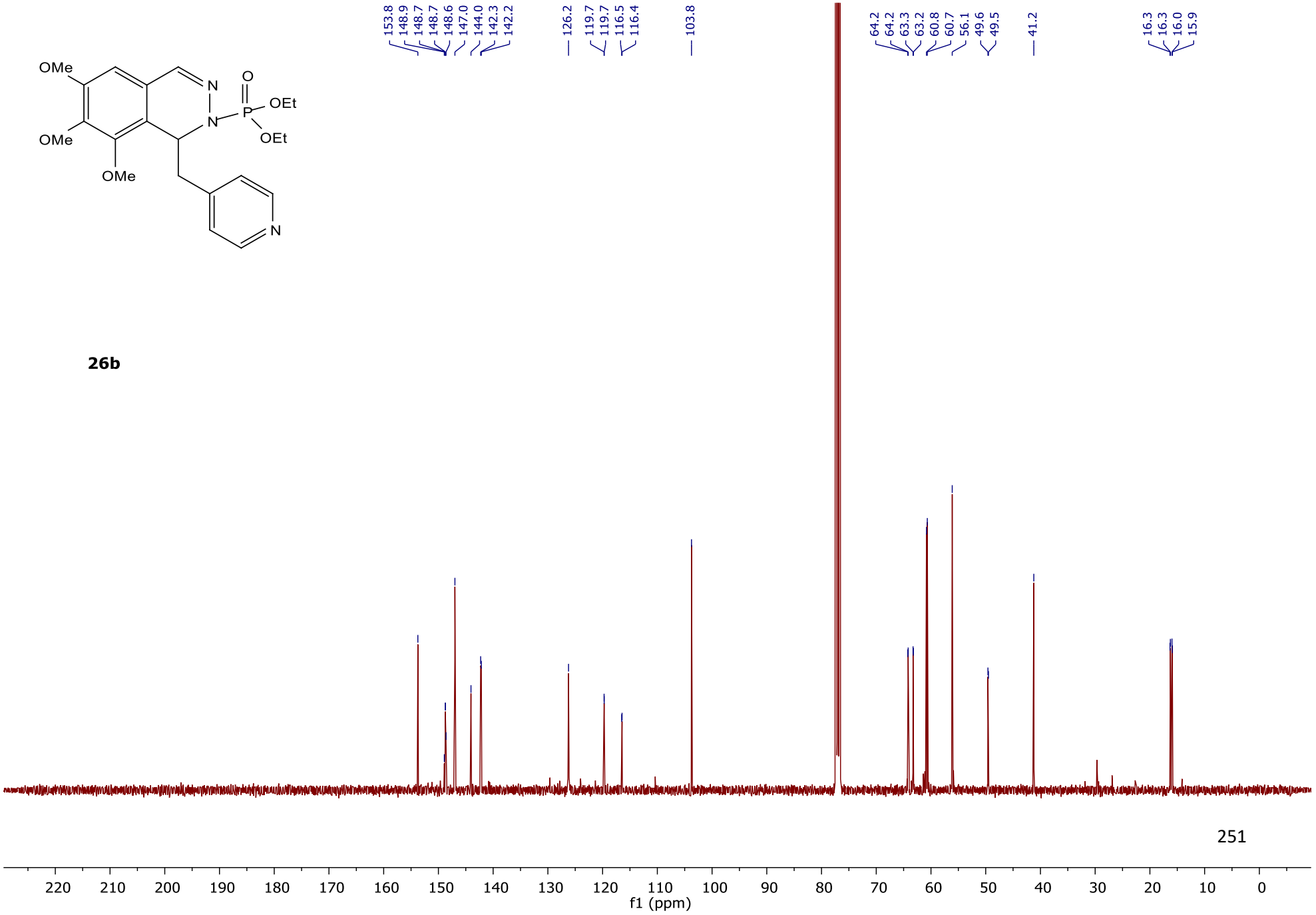

1.65
249
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.34
7.38
6.90
6.88
6.44
OMe
OMe
OMe
N
N
P
O
OEt
OEt
N
overlapped with grease
1.95
1.06
1.92
1.06
1.00
2.10
1.11
1.07
3.08
3.11
3.00
1.15
1.14
2.95
7.53
f1 (ppm)

26b

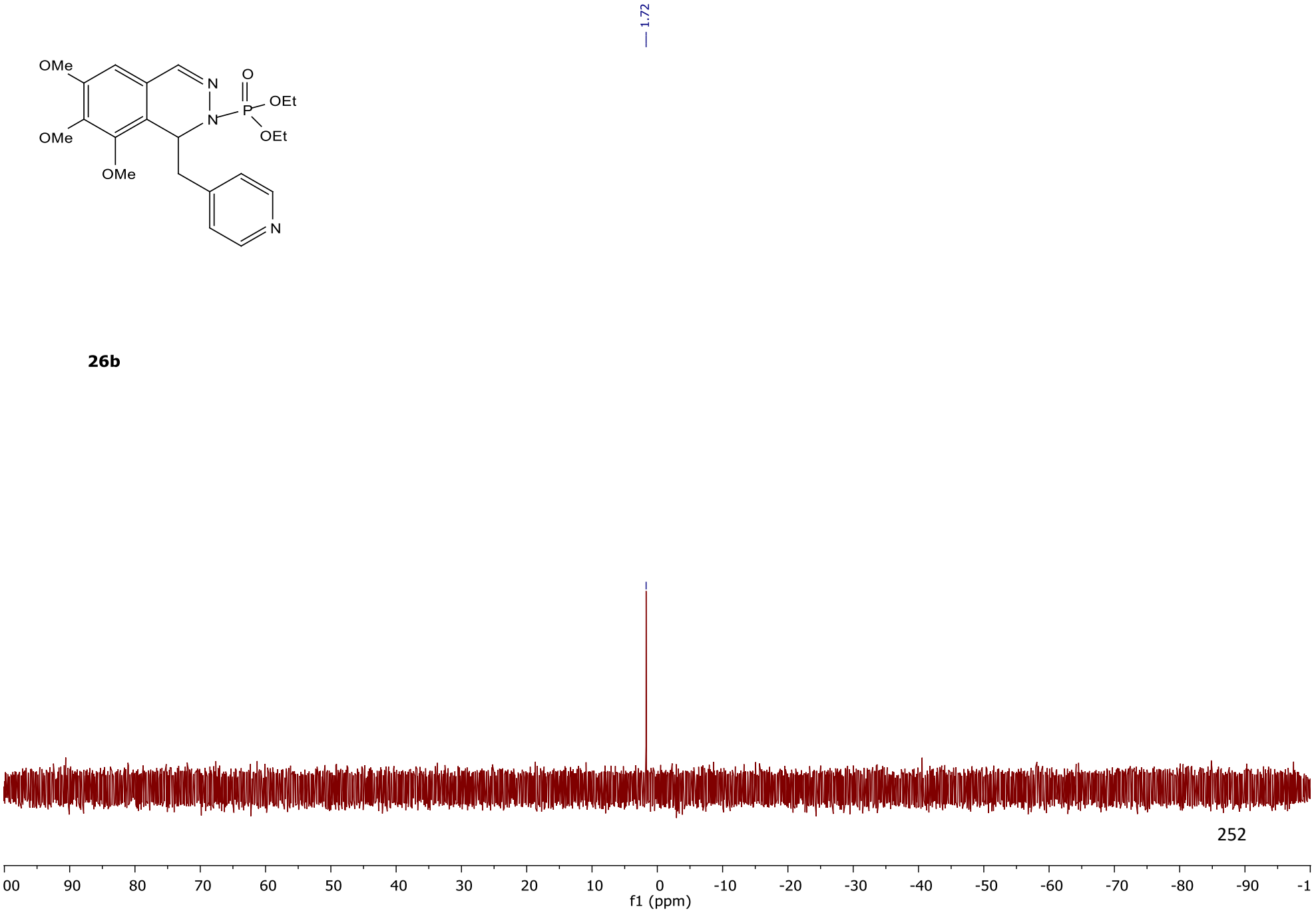
OMe
OMe
OMe
N
N
P
O
OEt
OEt
N

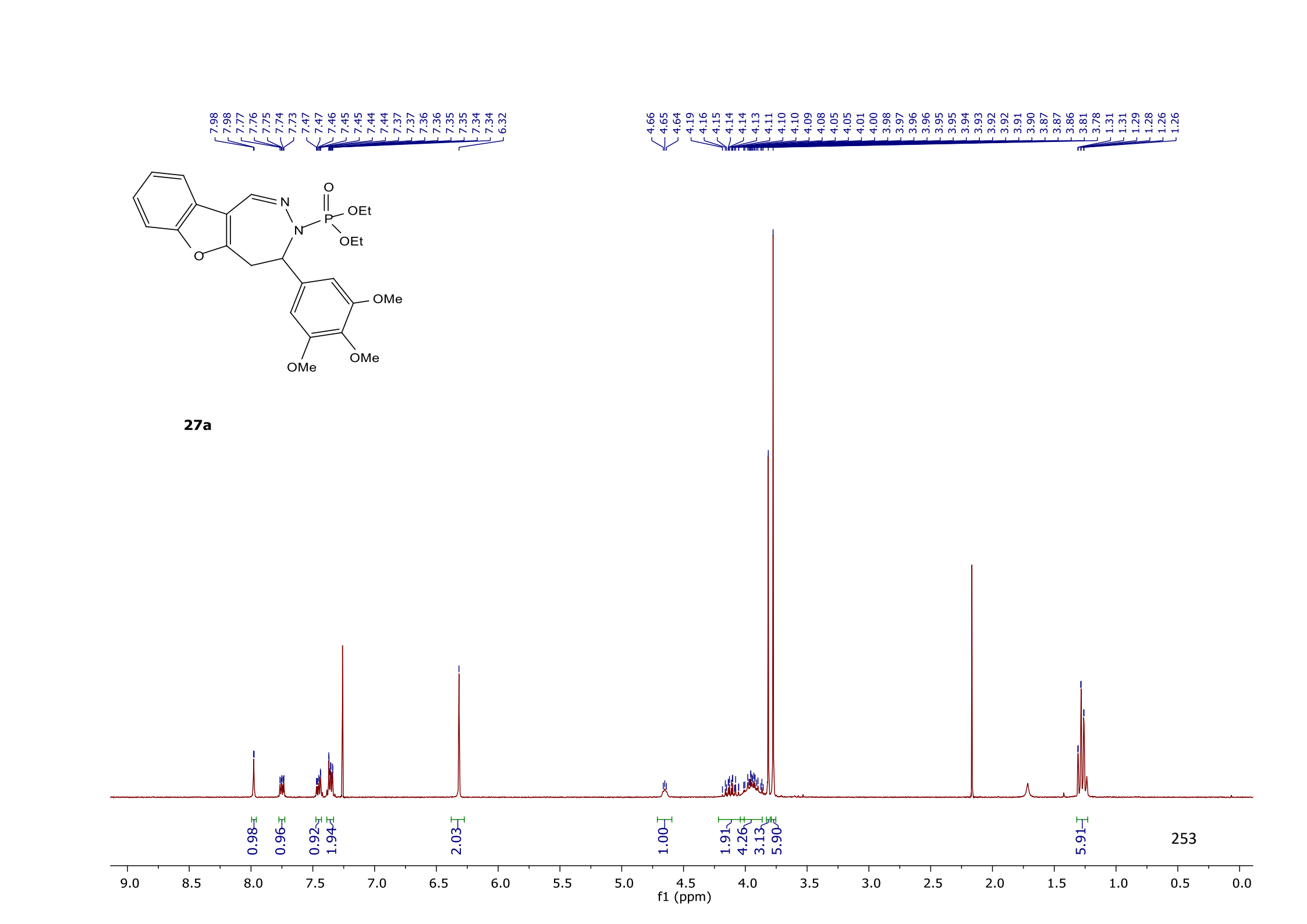
26b


153.8
148.9
148.7
148.7
148.6
147.0
144.0
142.3
142.2
126.2
119.7
119.7
116.5
116.4
103.8
64.2
64.2
63.3
63.2
60.8
60.7
56.1
49.6
49.5
41.2
16.3
16.3
16.0
15.9
251
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OMe
OMe
OMe
N
N
O
P
OEt
OEt
N

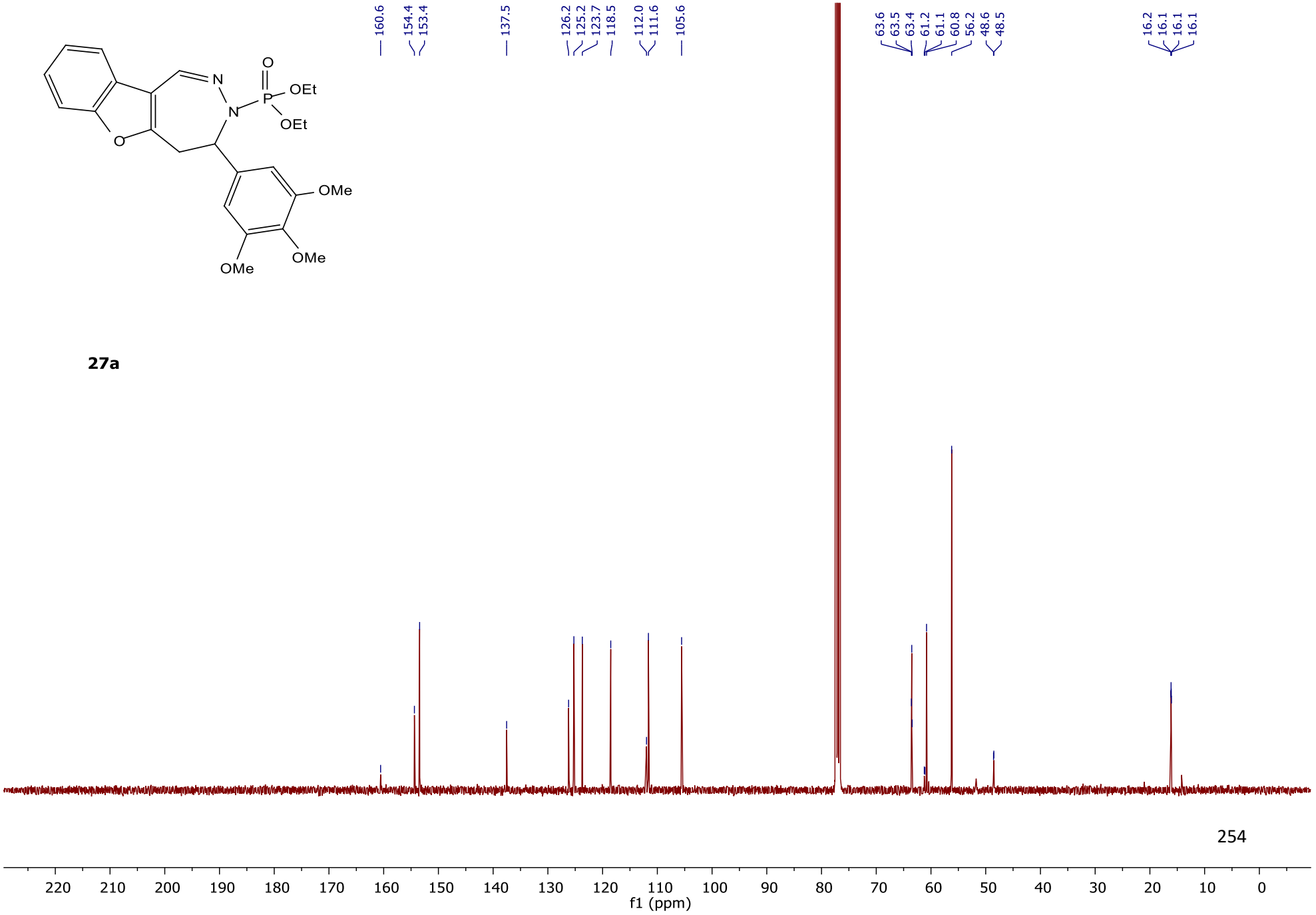
26b

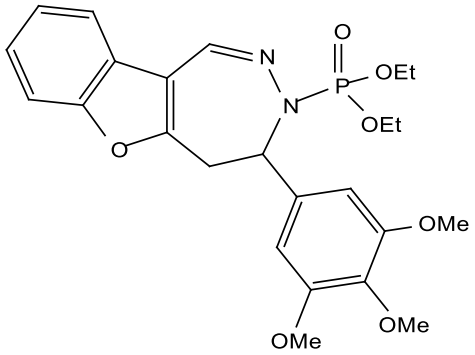

1.72
252
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


7.98 7.98 7.77 7.76 7.75 7.74 7.73 7.47 7.47 7.46 7.45 7.45 7.44 7.44 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 6.32
4.66 4.65 4.64 4.19 4.16 4.15 4.14 4.14 4.13 4.11 4.10 4.10 4.09 4.08 4.05 4.05 4.01 4.00 3.98 3.97 3.96 3.96 3.95 3.95 3.94 3.93 3.92 3.92 3.91 3.90 3.87 3.87 3.86 3.81 3.78 1.31 1.31 1.29 1.28 1.26 1.26
O
N
P
OEt
OEt
N
O
OMe
OMe
OMe
27a
0.98
0.96
0.92
1.94
2.03
1.00
1.91
4.26
3.13
5.90
5.91
253
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

O
N
OEt
N
P
OEt
O
OMe
OMe
OMe

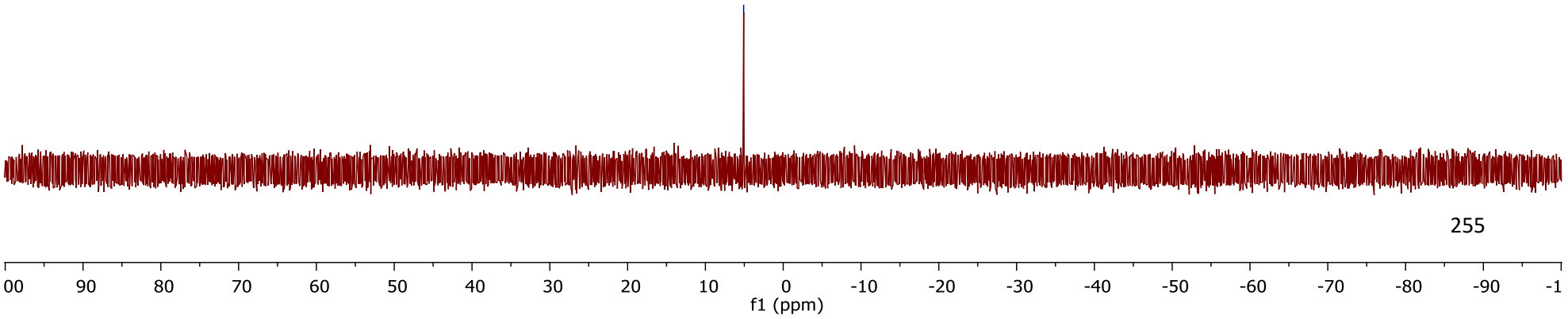
27a

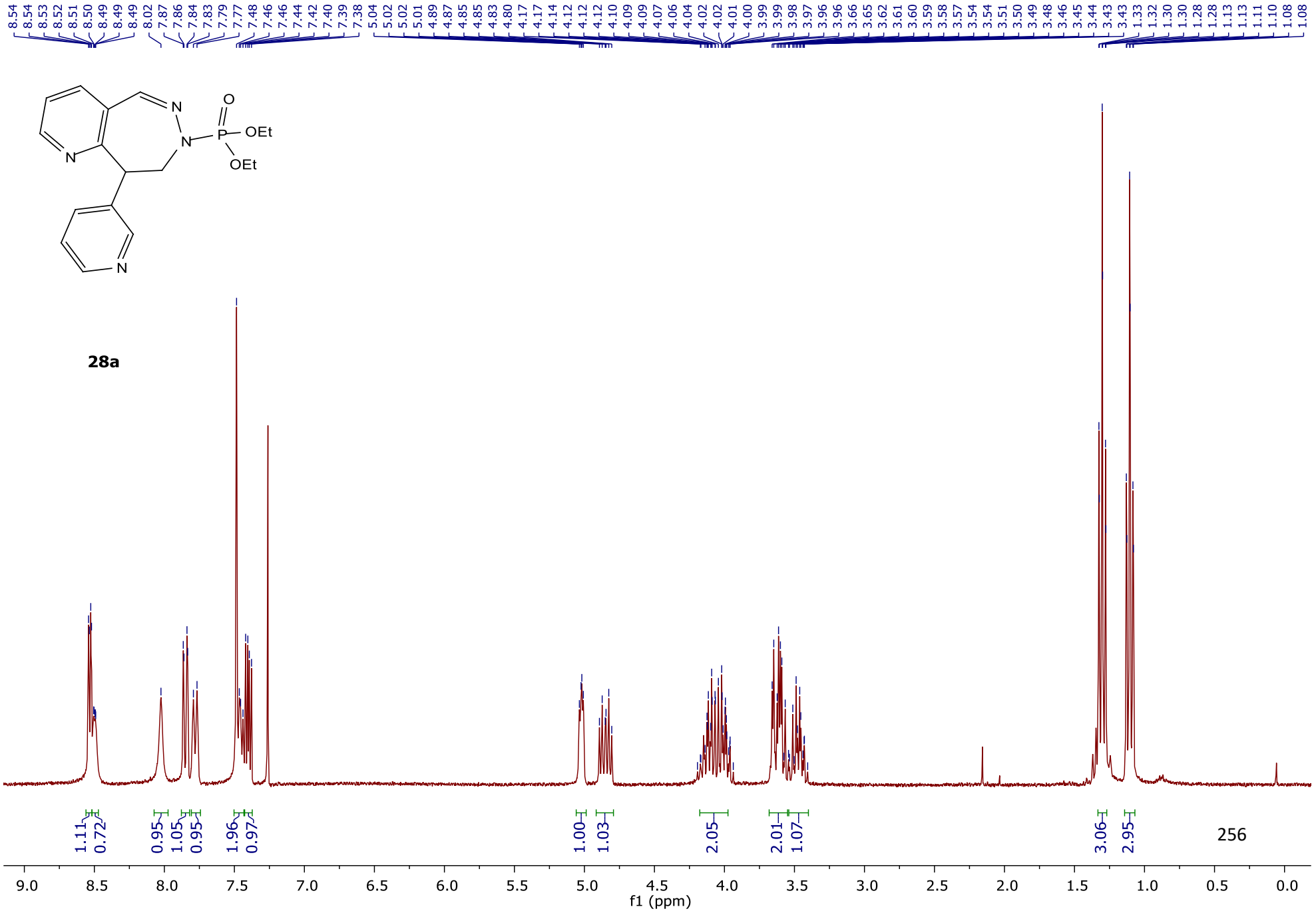

160.6
154.4
153.4
137.5
126.2
125.2
123.7
118.5
112.0
111.6
105.6
63.6
63.5
63.4
61.2
61.1
60.8
56.2
48.6
48.5
16.2
16.1
16.1
16.1
254
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

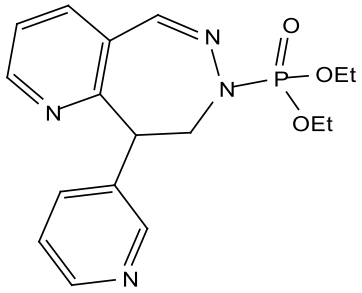

O
N
OEt
P
N
OEt
O
OMe
OMe
OMe

5.08

27a


255
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)


8.54 8.54 8.53 8.52 8.51 8.50 8.49 8.49 8.49 8.02 7.87 7.86 7.84 7.83 7.79 7.77 7.48 7.46 7.46 7.44 7.42 7.40 7.39 7.38 5.04 5.02 5.02 5.01 4.89 4.87 4.85 4.85 4.83 4.80 4.17 4.17 4.14 4.12 4.12 4.12 4.10 4.09 4.09 4.07 4.06 4.04 4.02 4.02 4.01 4.00 3.99 3.99 3.98 3.97 3.96 3.96 3.66 3.65 3.62 3.61 3.60 3.59 3.58 3.57 3.54 3.54 3.51 3.50 3.49 3.48 3.46 3.45 3.44 3.43 3.43 1.33 1.32 1.30 1.30 1.28 1.28 1.13 1.13 1.11 1.10 1.08 1.08
N
N
O
P
OEt
OEt
N
28a
1.11
0.72
0.95
1.05
0.95
1.96
0.97
1.00
1.03
2.05
2.01
1.07
3.06
2.95
256
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



28a

158.78
149.36
146.52
145.10
140.94
139.43
138.48
138.25
138.02
127.44
124.55
123.05
63.94
63.86
63.67
63.59
54.51
54.44
50.77
50.65
16.17
16.06
15.96

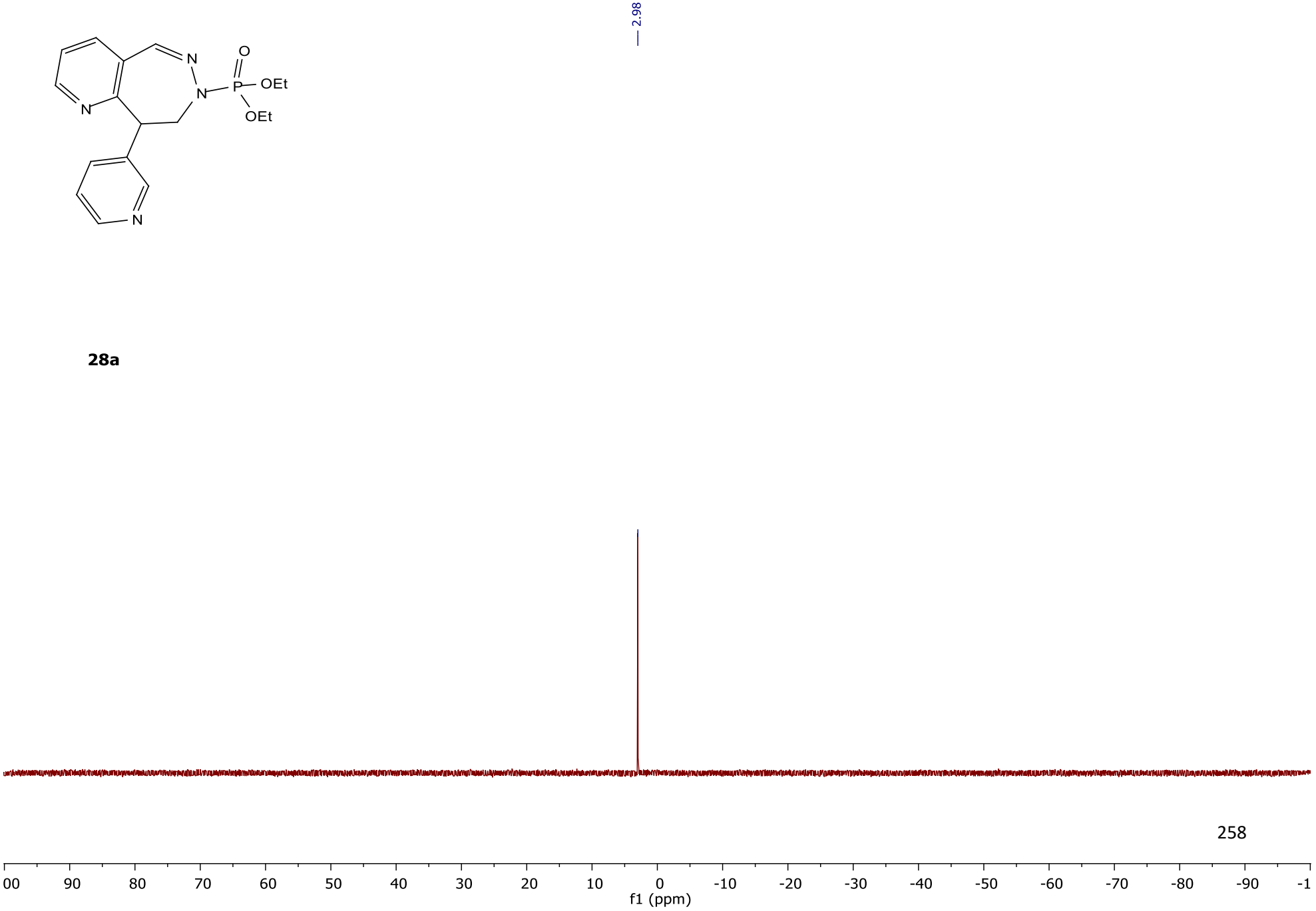
257

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

N
O
N
P
OEt
OEt
N
N

28a


2.98
258
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-1
f1 (ppm)