

Supporting Information

Catalyst- and solvent-free regiospecific S_N^HAr phosphinylation of pyridines with *H*-phosphinates mediated by benzoylphenylacetylene

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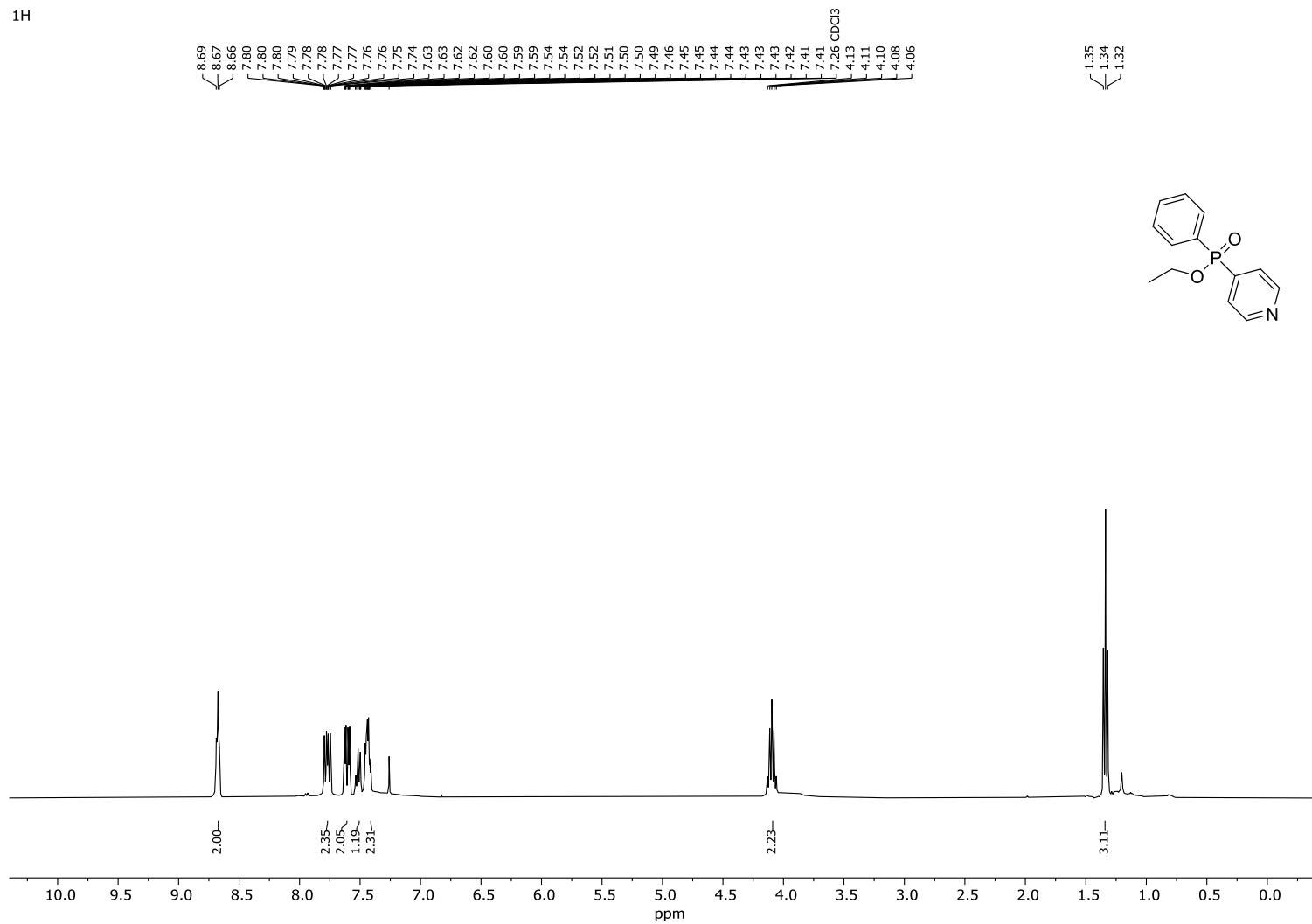
^b *I.Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22/20 S. Kovalevskoi/Akademicheskaya St., Ekaterinburg 620219, Russian Federation*

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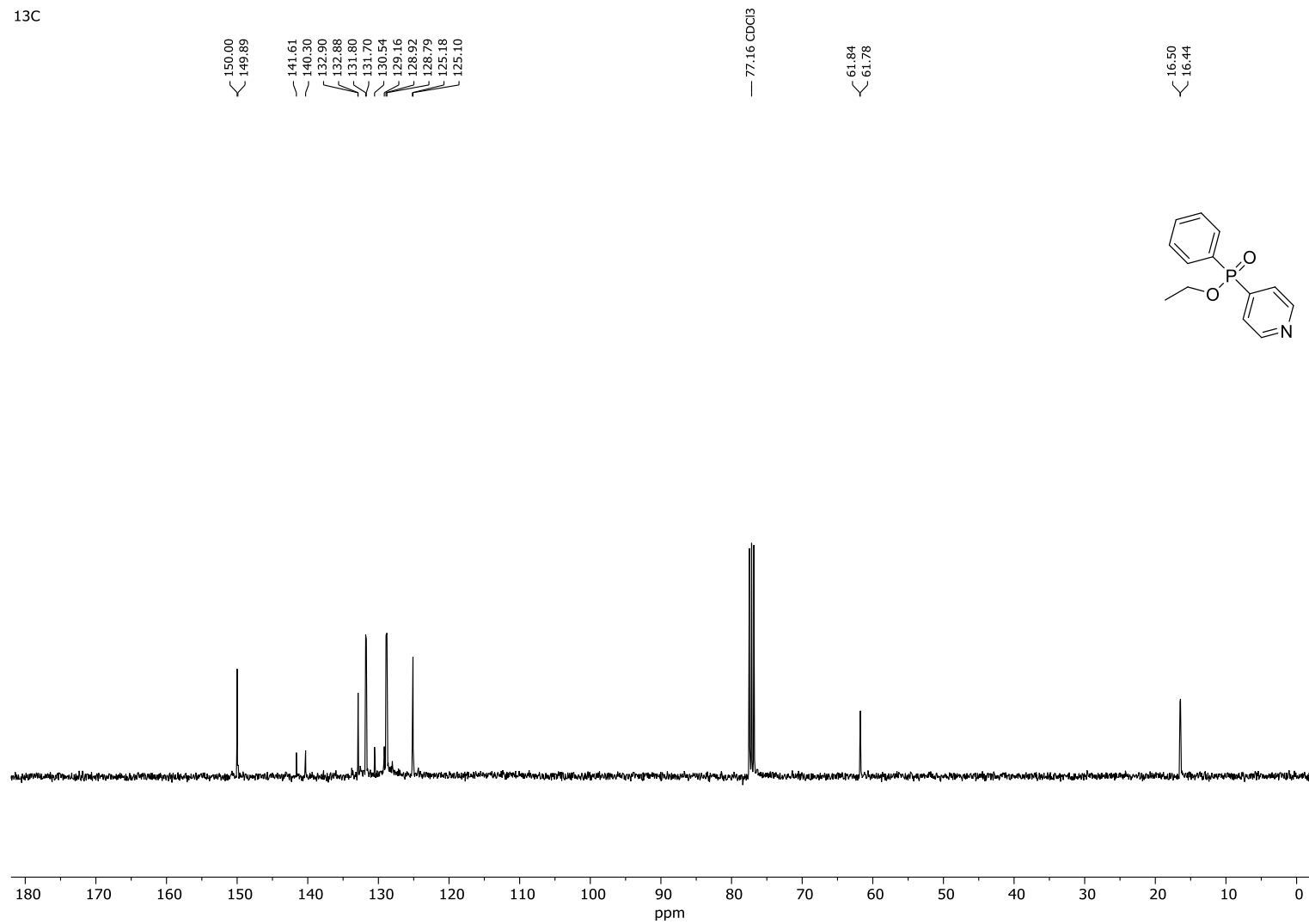
1. NMR Spectra

Ethyl phenyl(pyridin-4-yl)phosphinate (3aa)



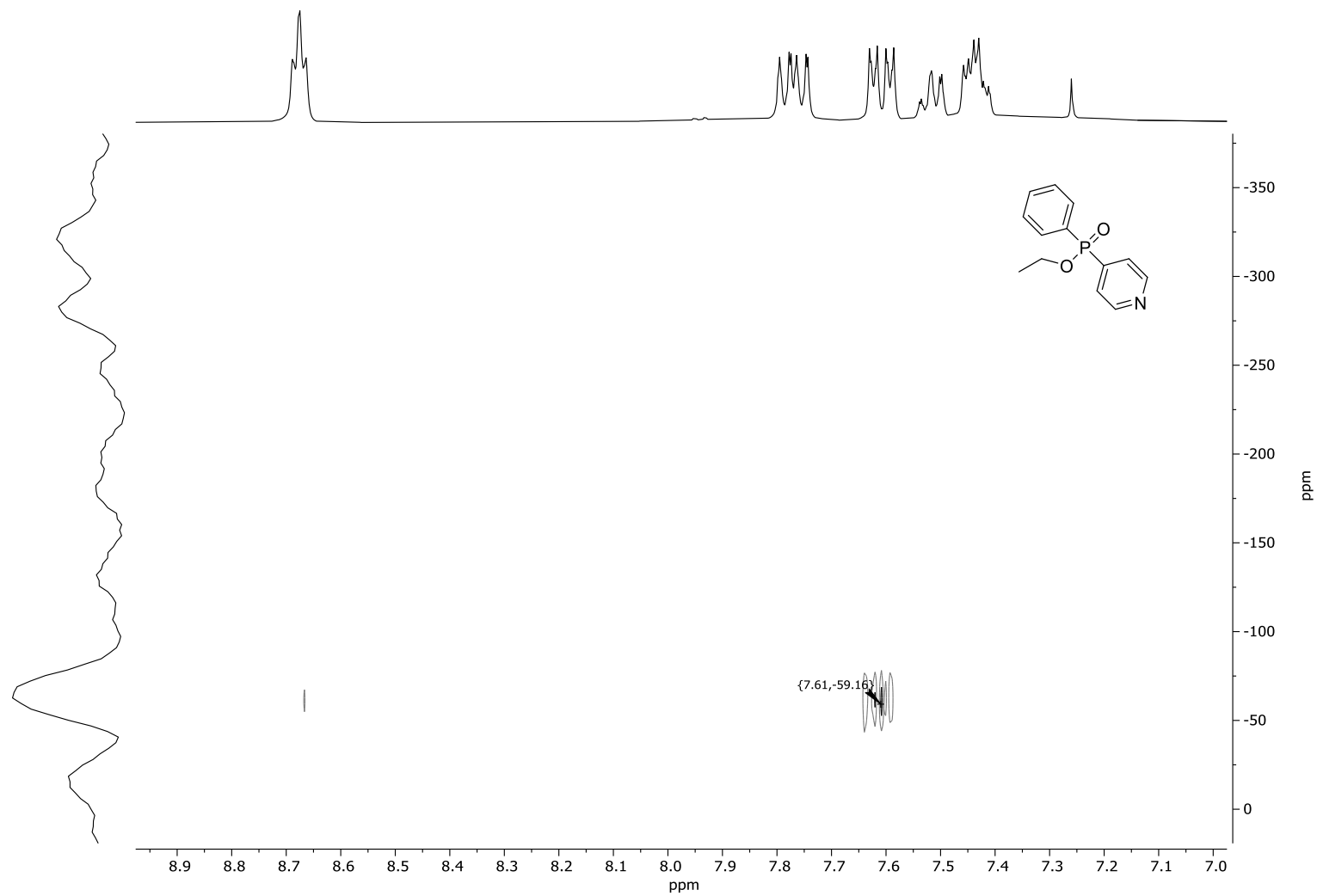
Ethyl phenyl(pyridin-4-yl)phosphinate (3aa)

¹³C



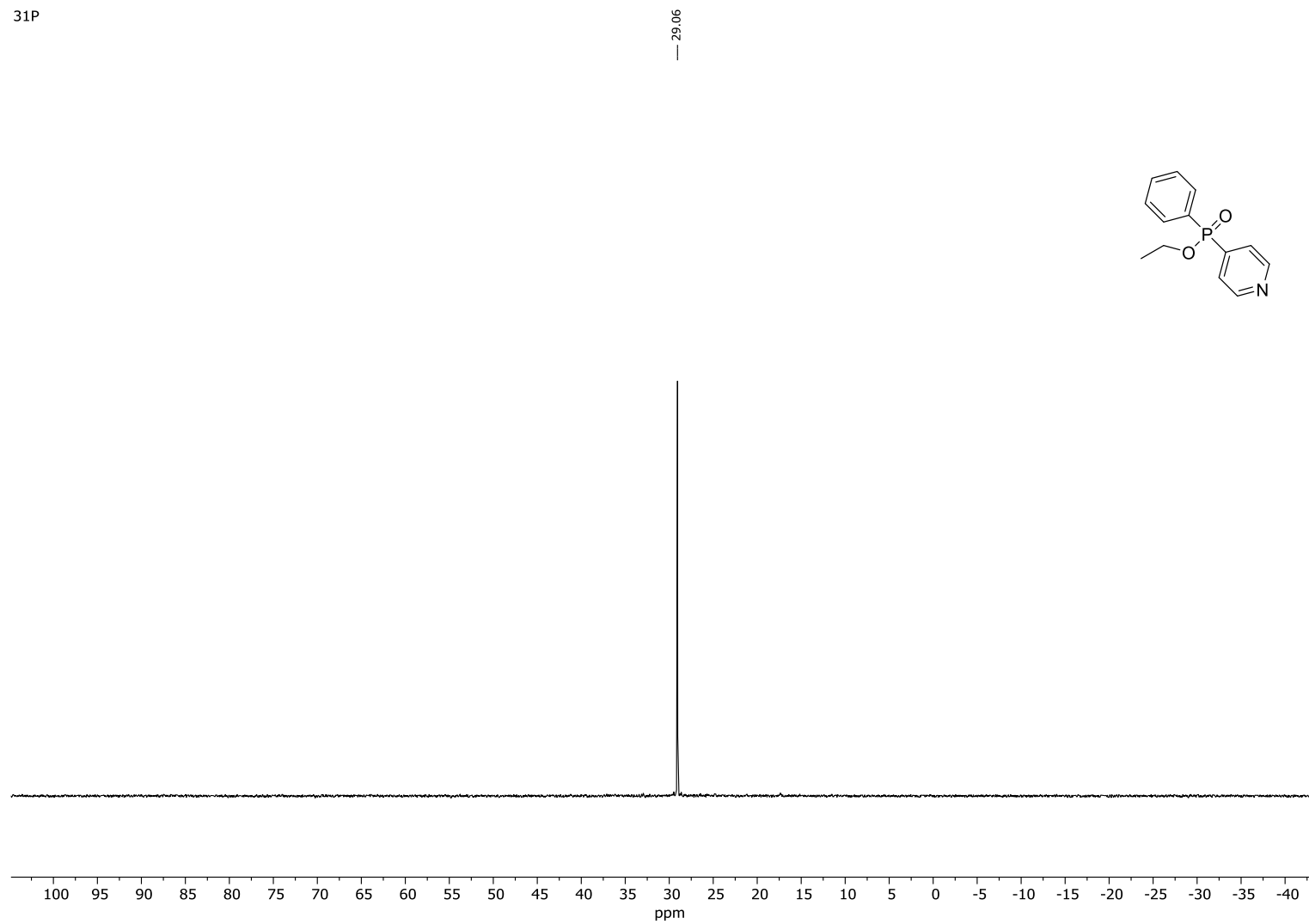
Ethyl phenyl(pyridin-4-yl)phosphinate (3aa)

1H-15N HMBC

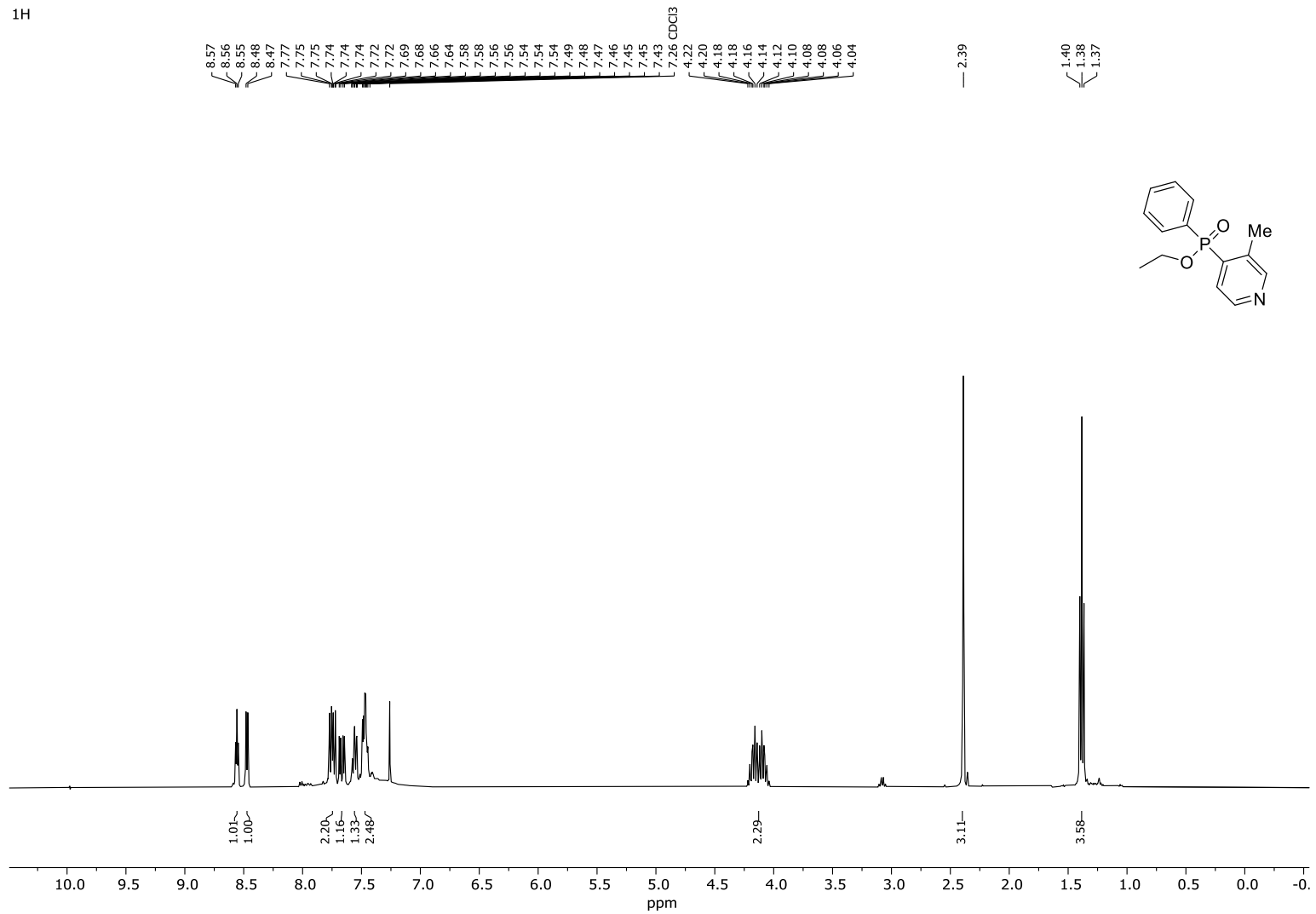


Ethyl phenyl(pyridin-4-yl)phosphinate (3aa)

31P

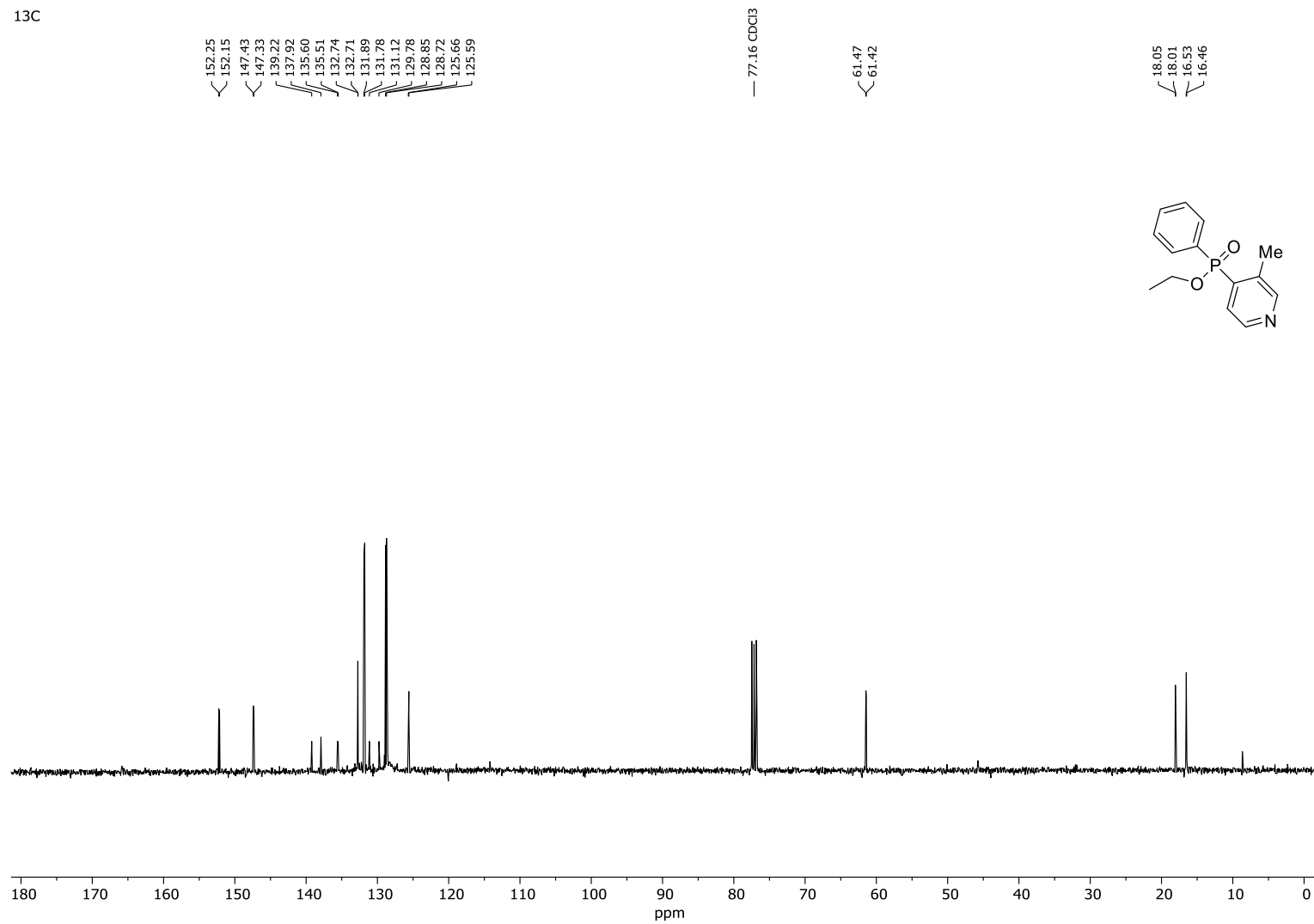


Ethyl (3-methylpyridin-4-yl)phenylphosphinate (3ba)



Ethyl (3-methylpyridin-4-yl)phenylphosphinate (3ba)

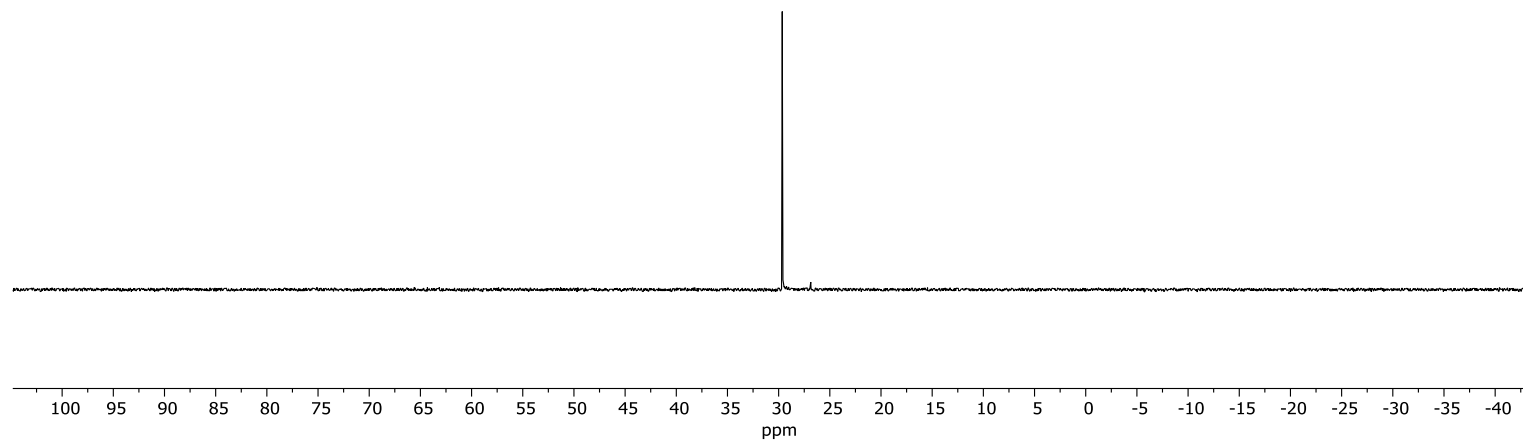
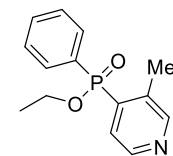
¹³C



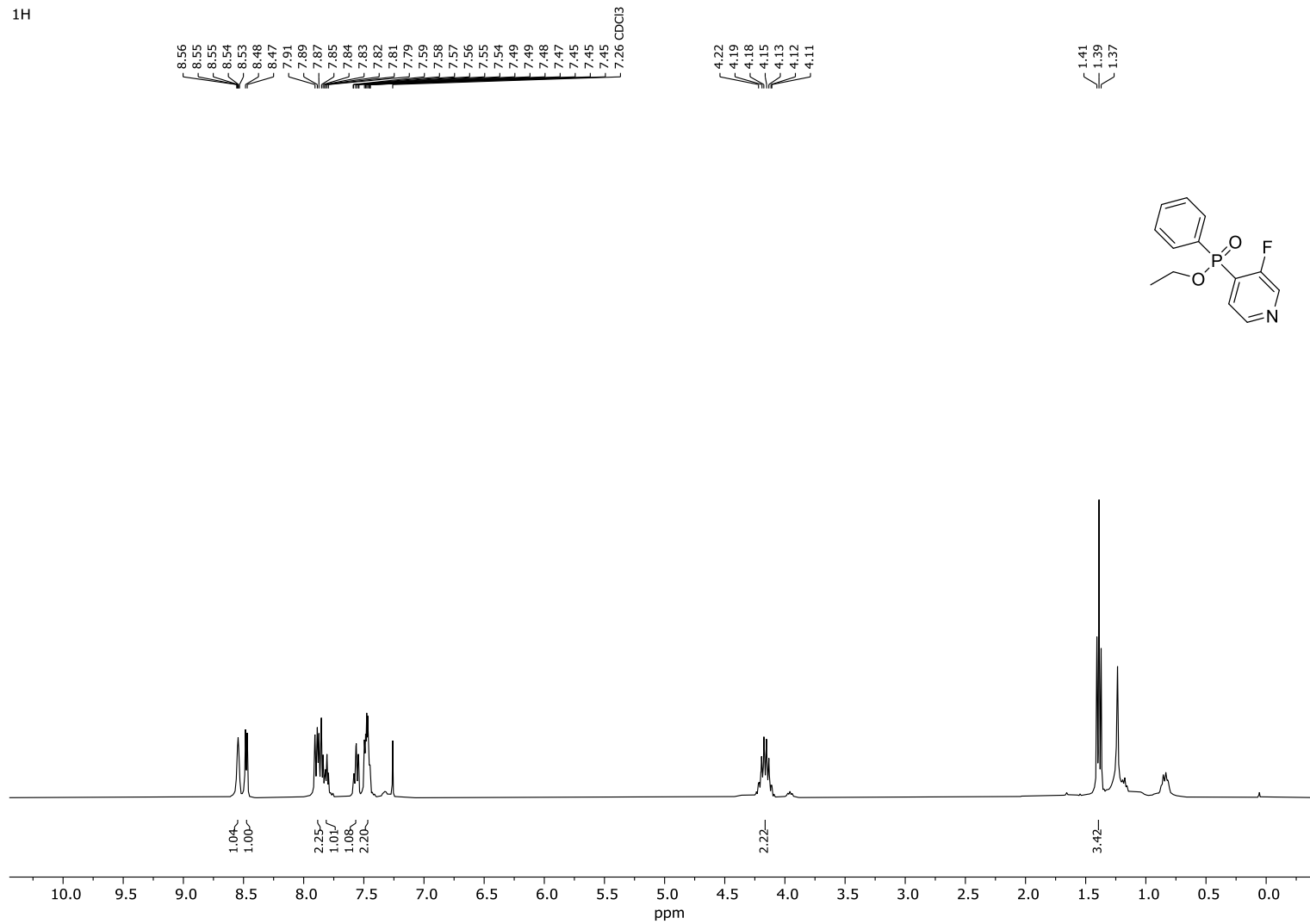
Ethyl (3-methylpyridin-4-yl)phenylphosphinate (3ba)

31P

— 29.65

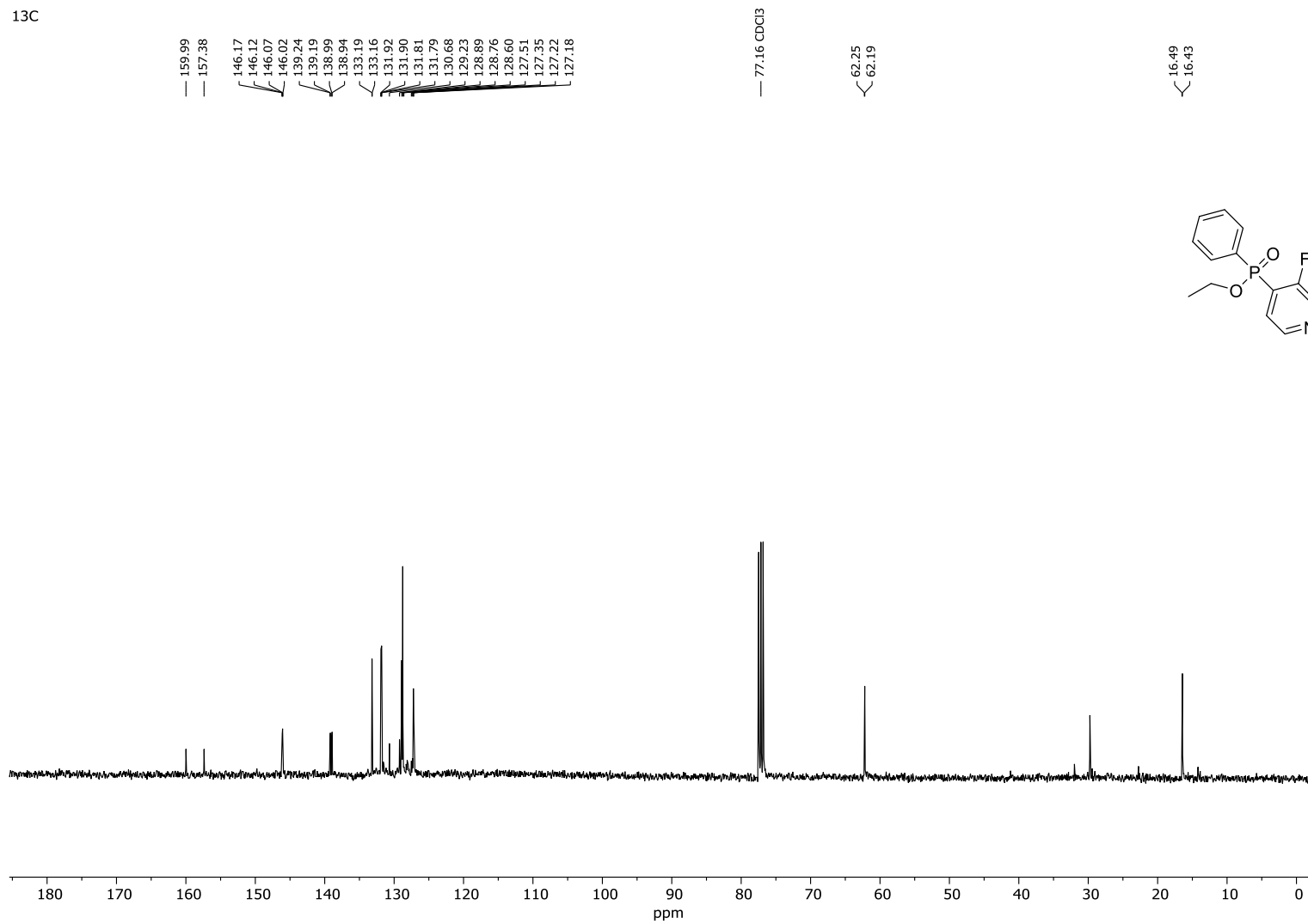


Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)



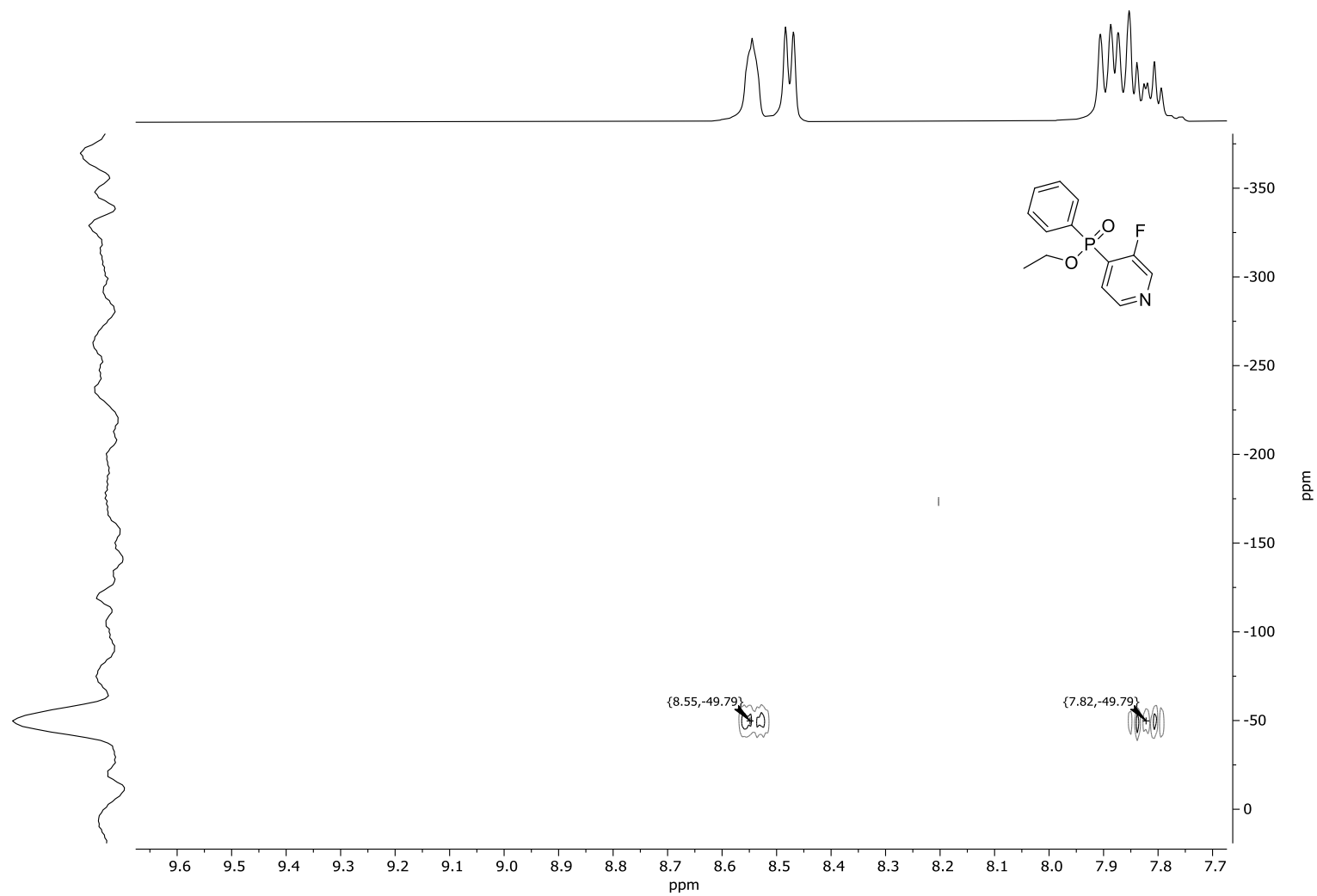
Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)

13C



Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)

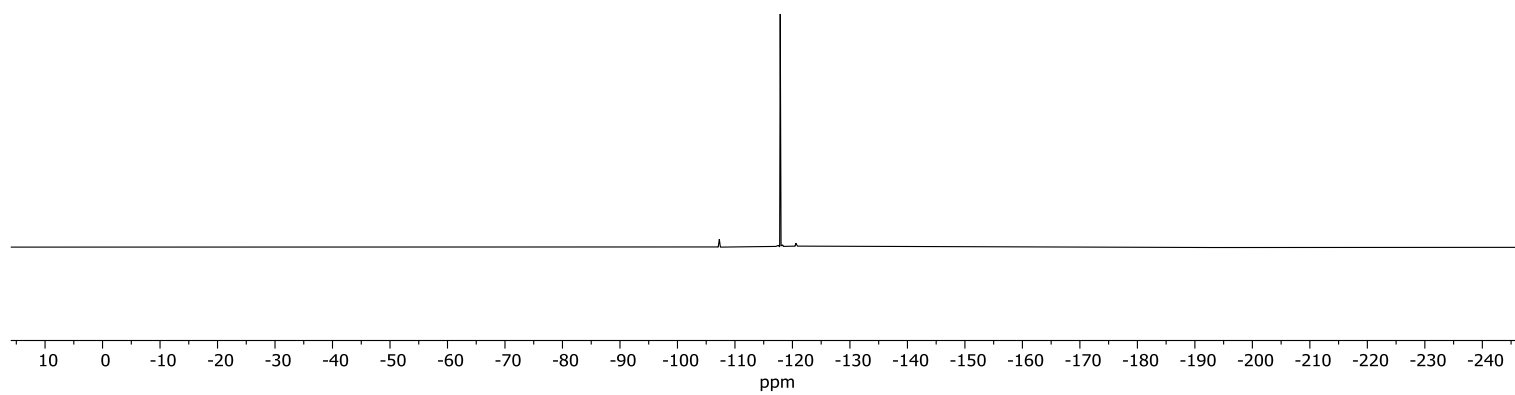
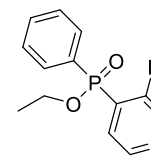
¹H-¹⁵N HMBC



Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)

19F

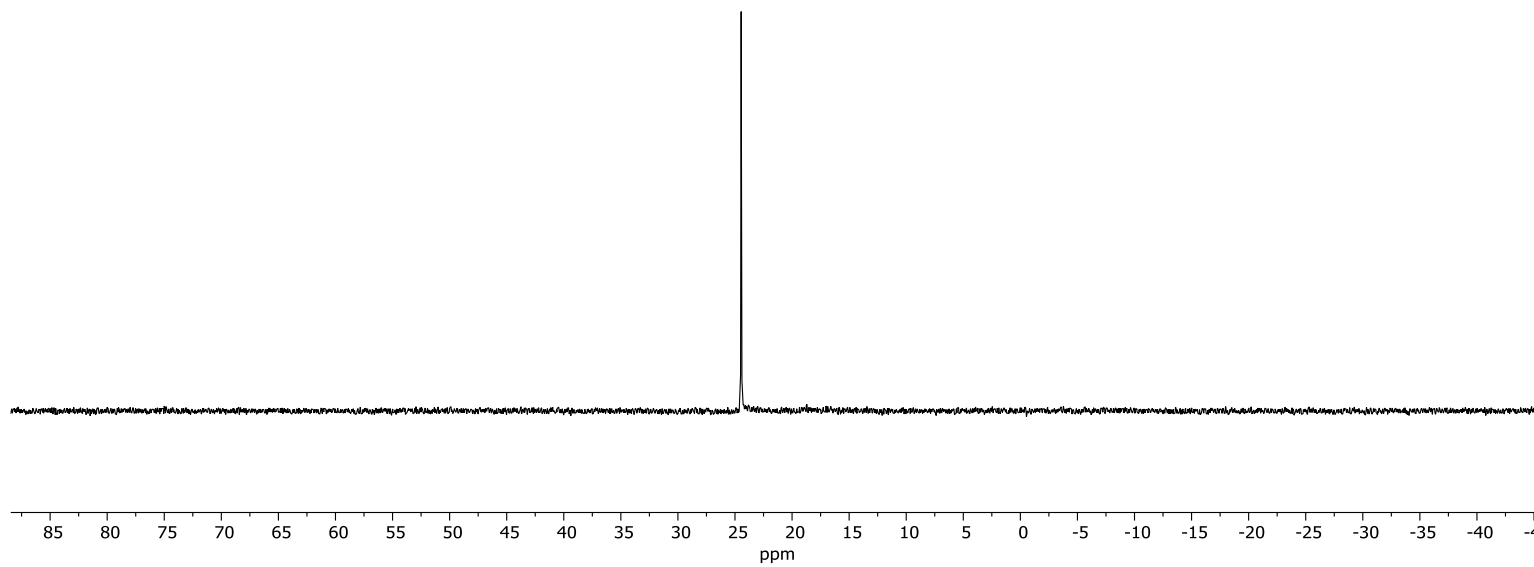
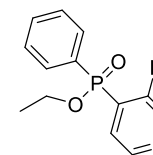
-117.88



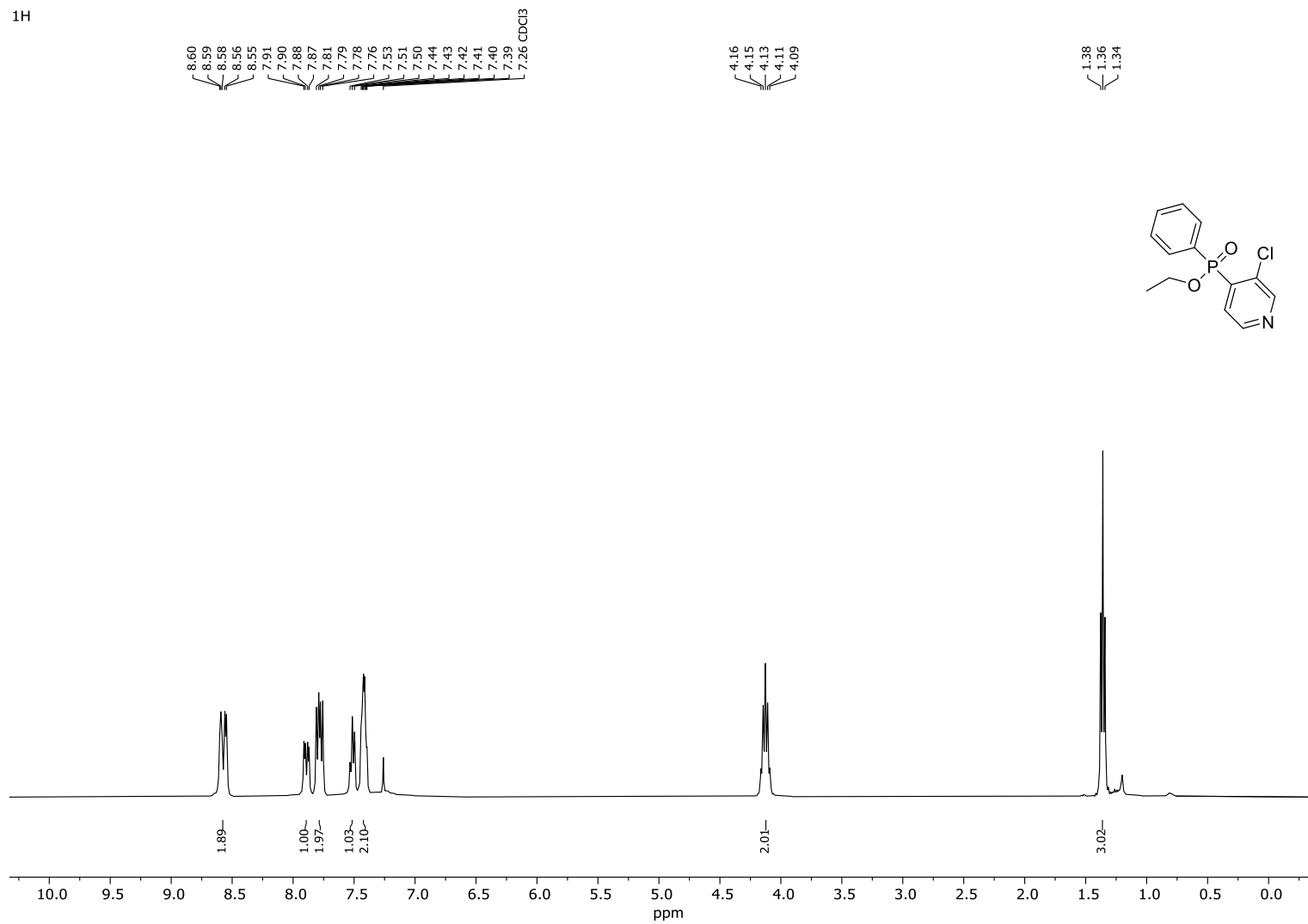
Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)

31P

— 24.46

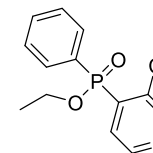
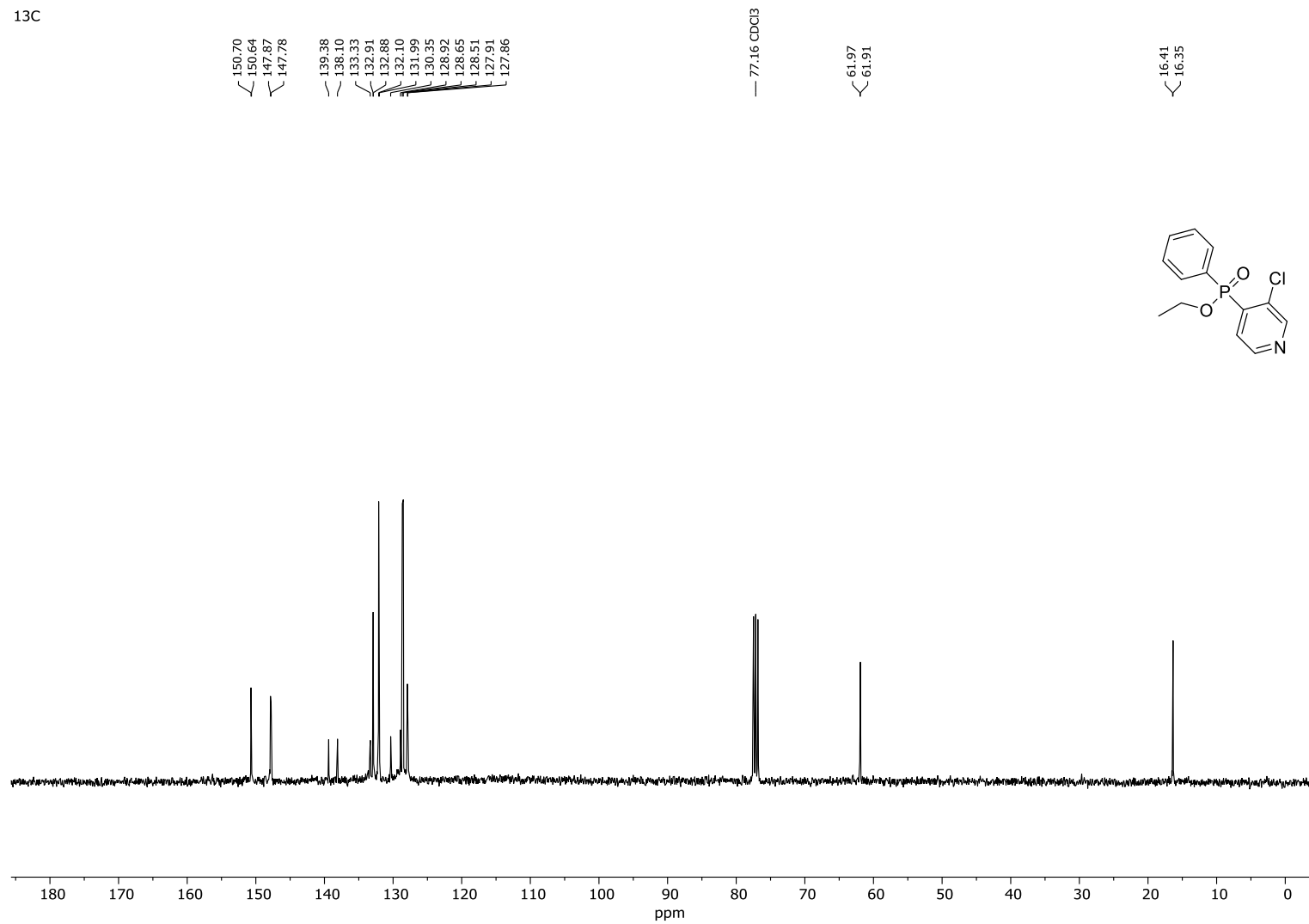


Ethyl (3-chloropyridin-4-yl)phenylphosphinate (3da)



Ethyl (3-chloropyridin-4-yl)phenylphosphinate (3da)

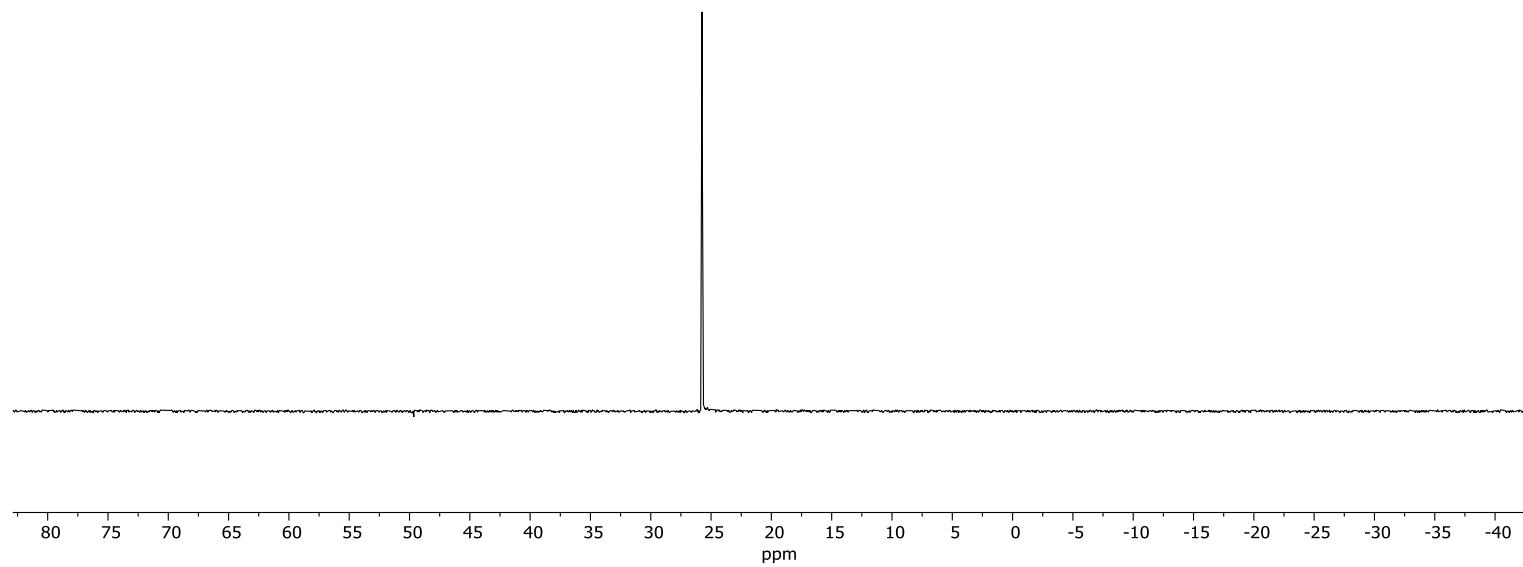
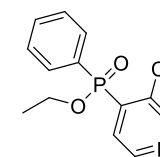
¹³C



Ethyl (3-chloropyridin-4-yl)phenylphosphinate (3da)

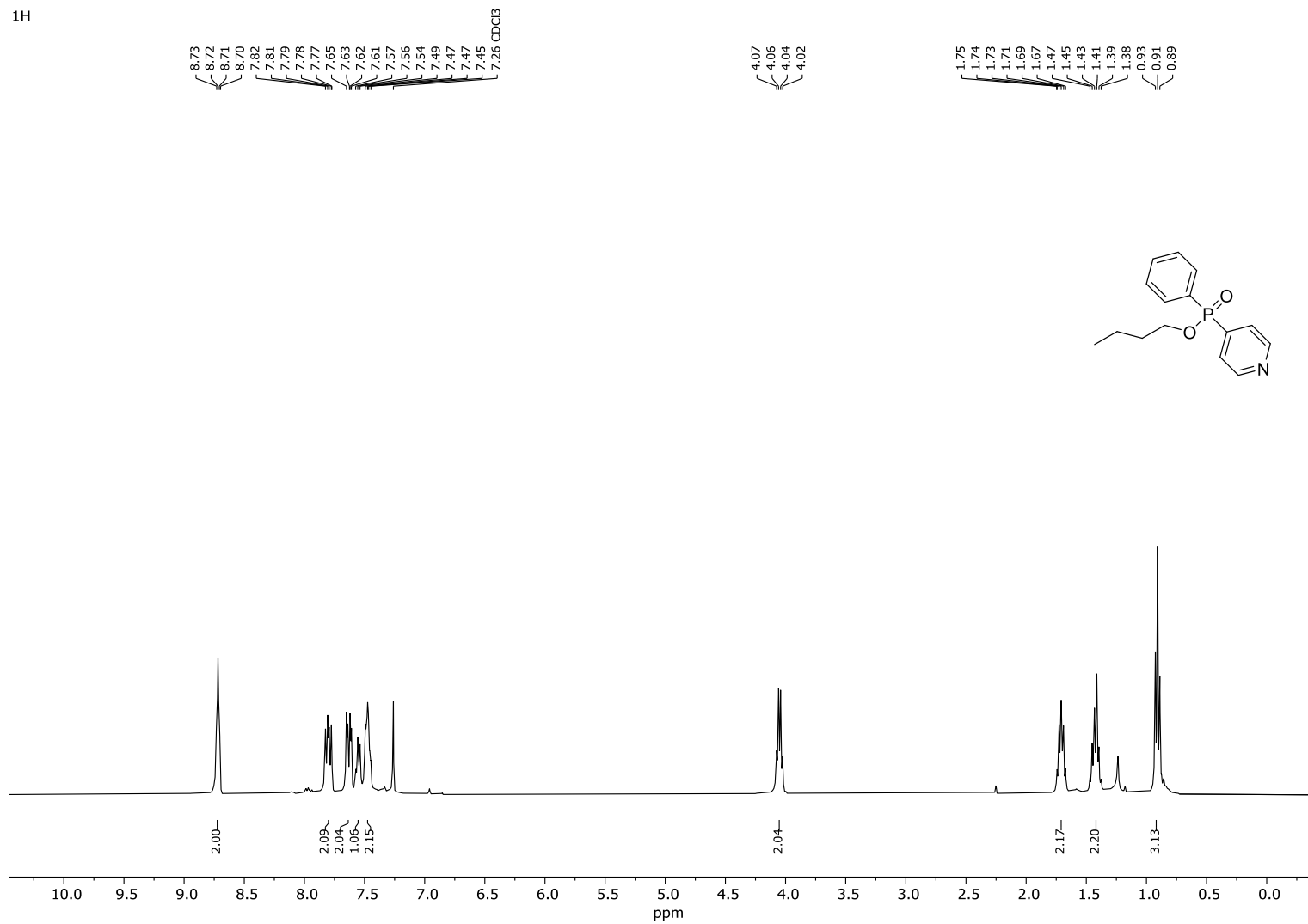
31P

— 25.75



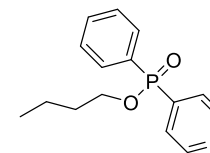
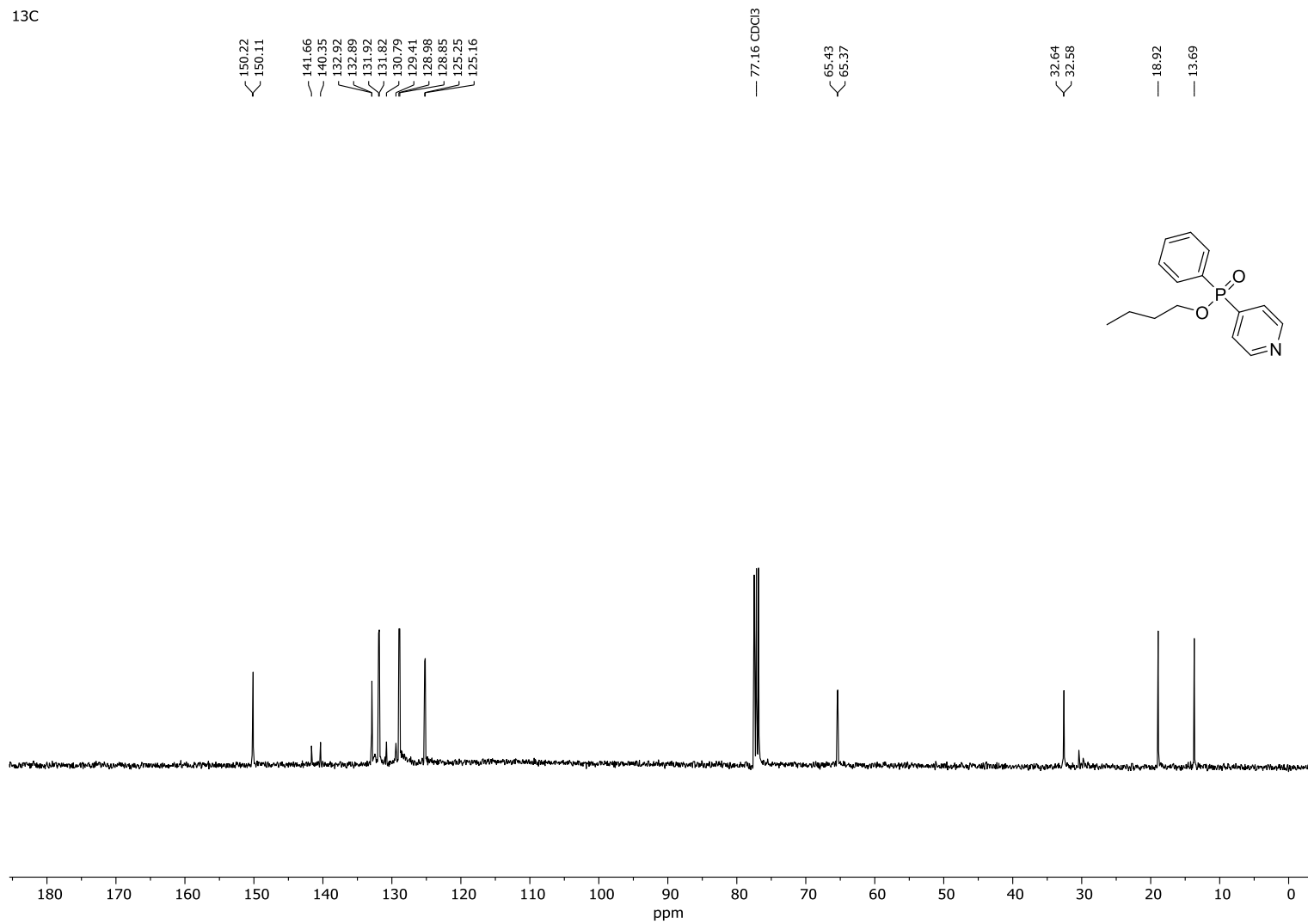
Butyl phenyl(pyridin-4-yl)phosphinate (3ab)

¹H



Butyl phenyl(pyridin-4-yl)phosphinate (3ab)

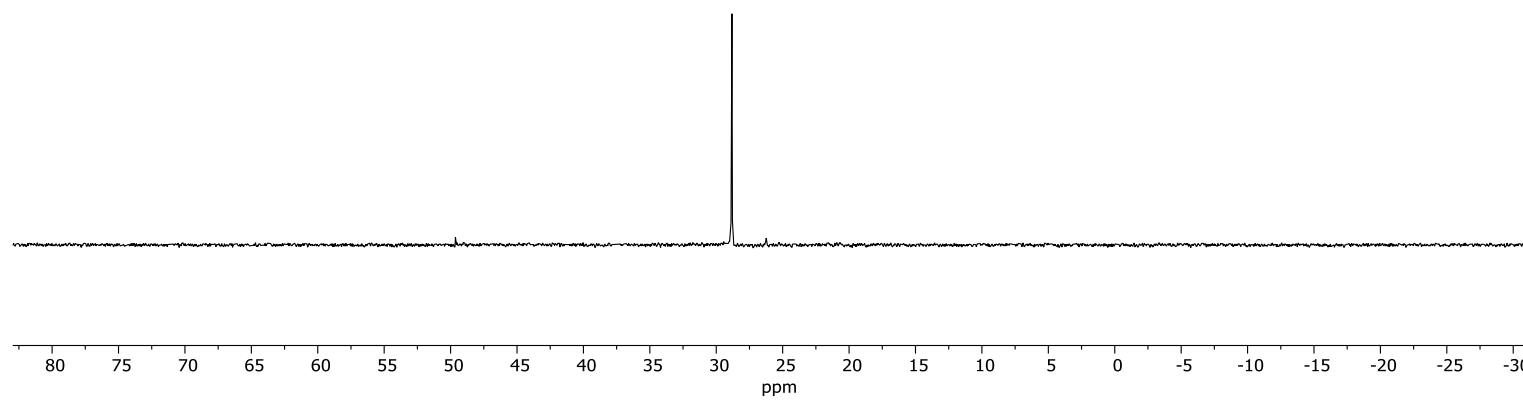
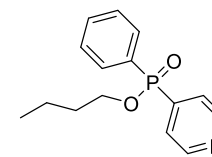
¹³C



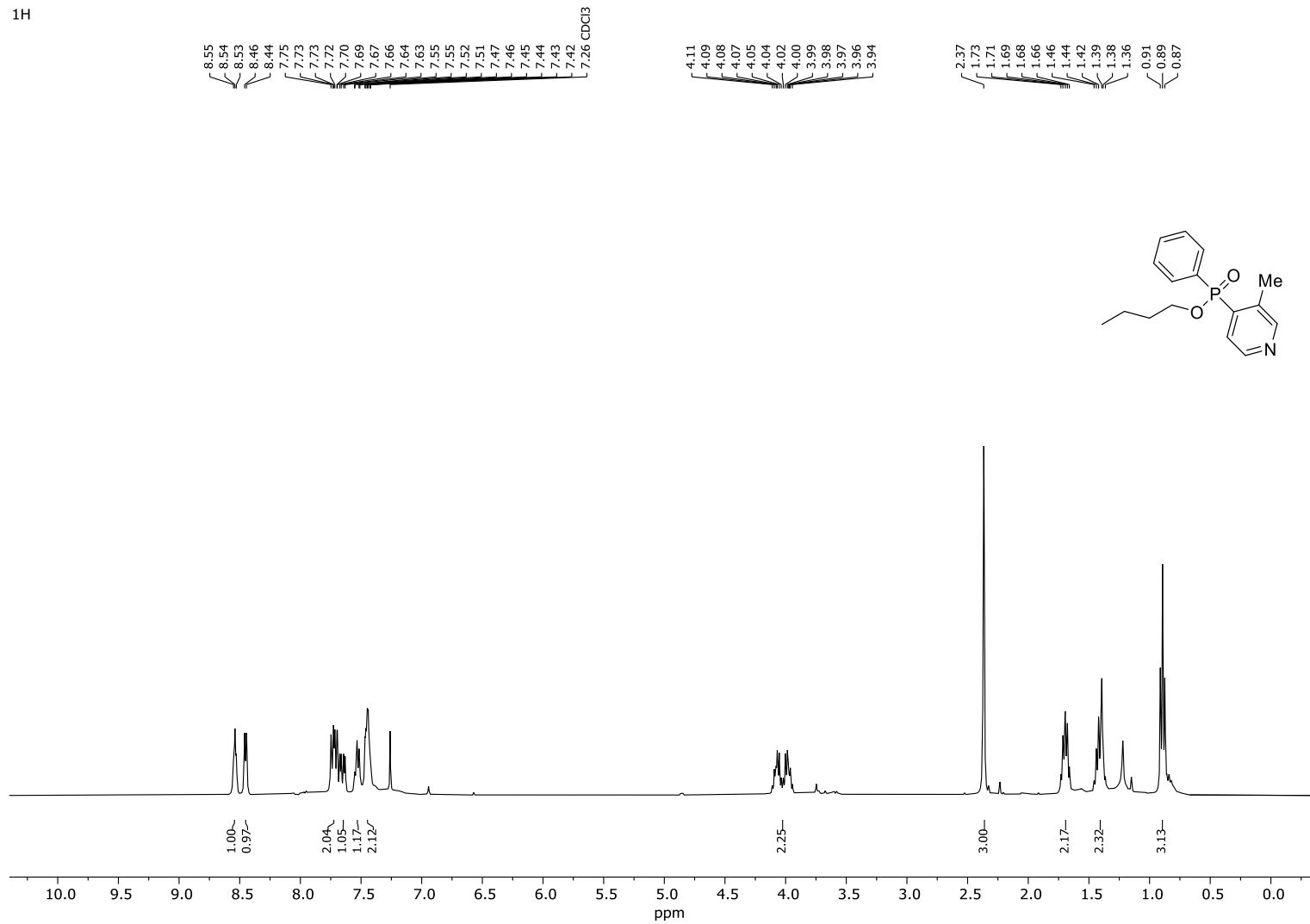
Butyl phenyl(pyridin-4-yl)phosphinate (3ab)

31P

28.82

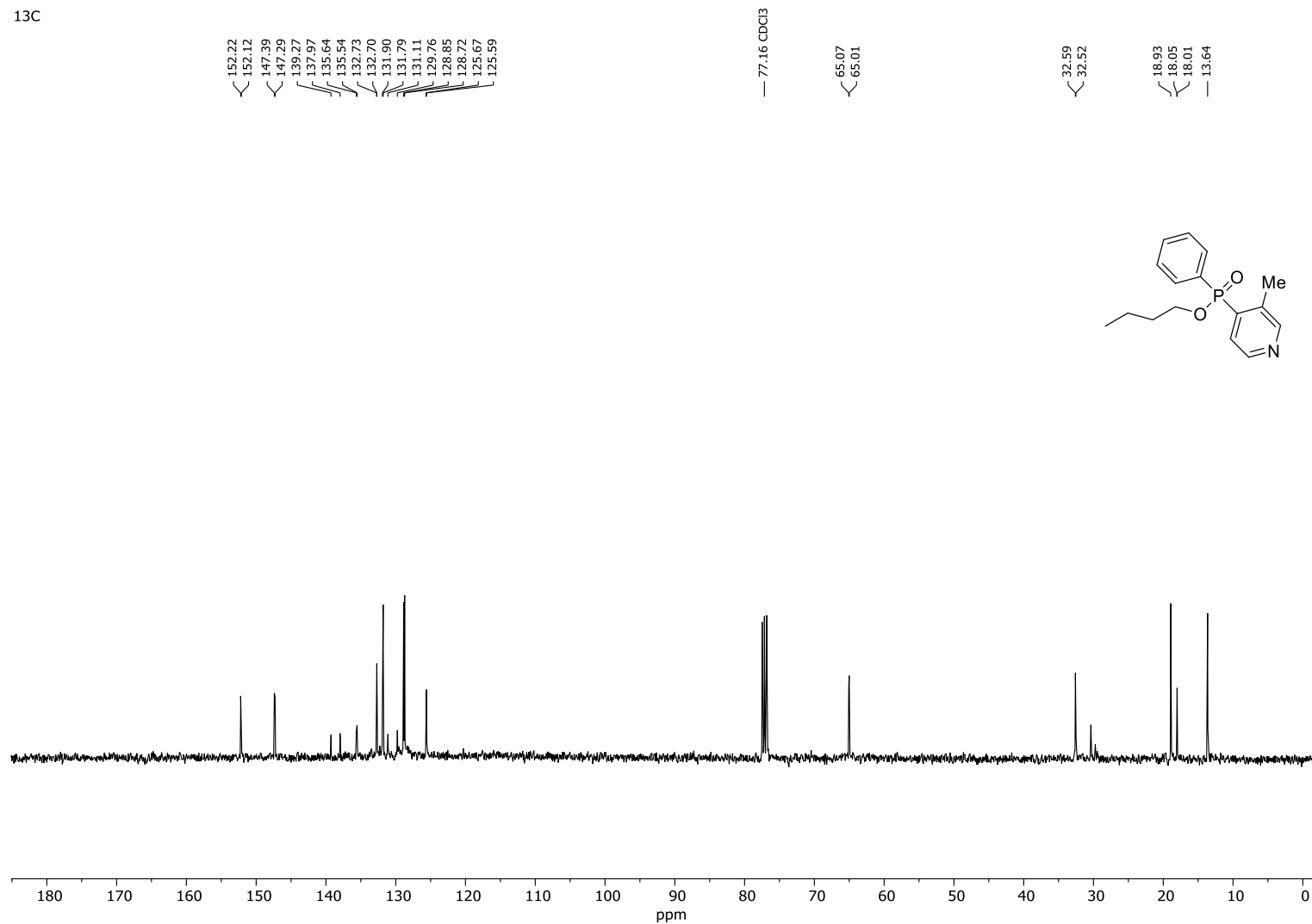


Butyl (3-methylpyridin-4-yl)phenylphosphinate (3bb)



Butyl (3-methylpyridin-4-yl)phenylphosphinate (3bb)

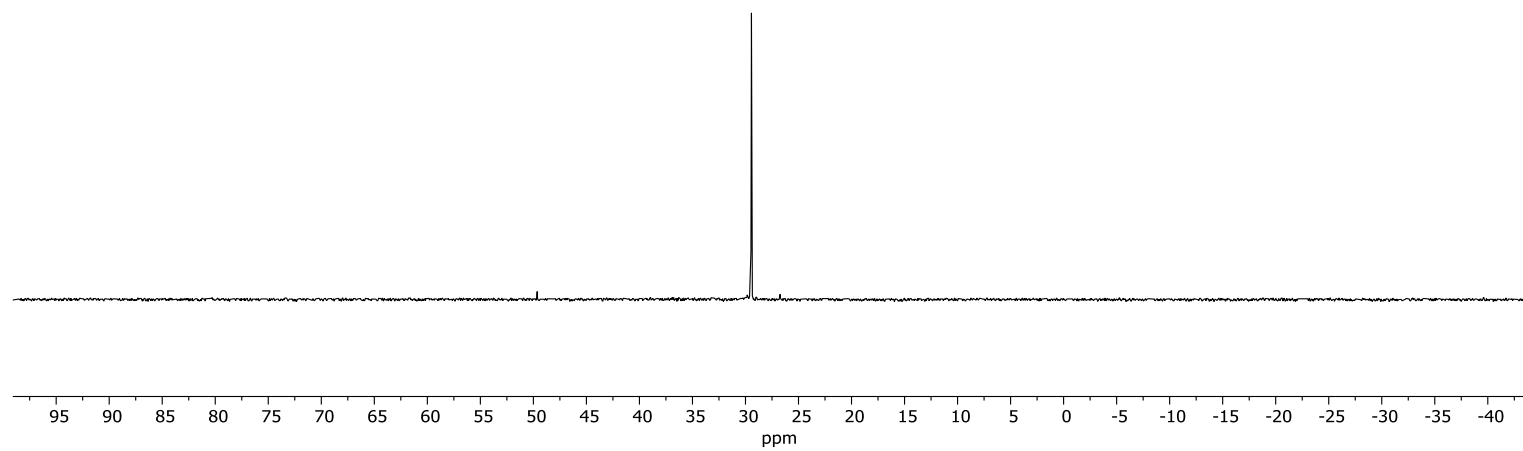
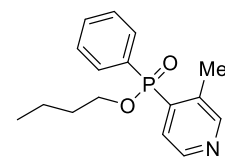
¹³C



Butyl (3-methylpyridin-4-yl)phenylphosphinate (3bb)

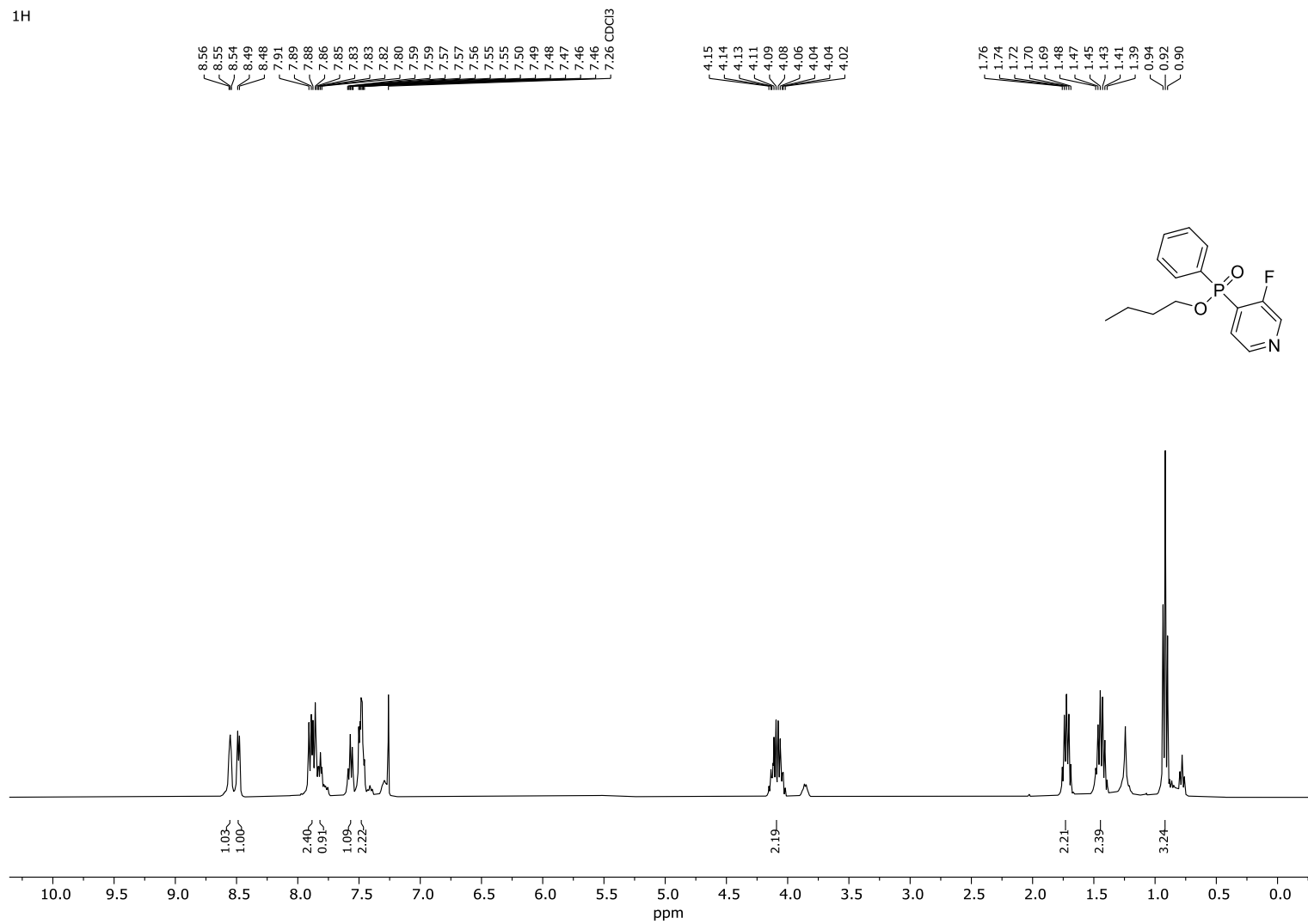
31P

— 29.44



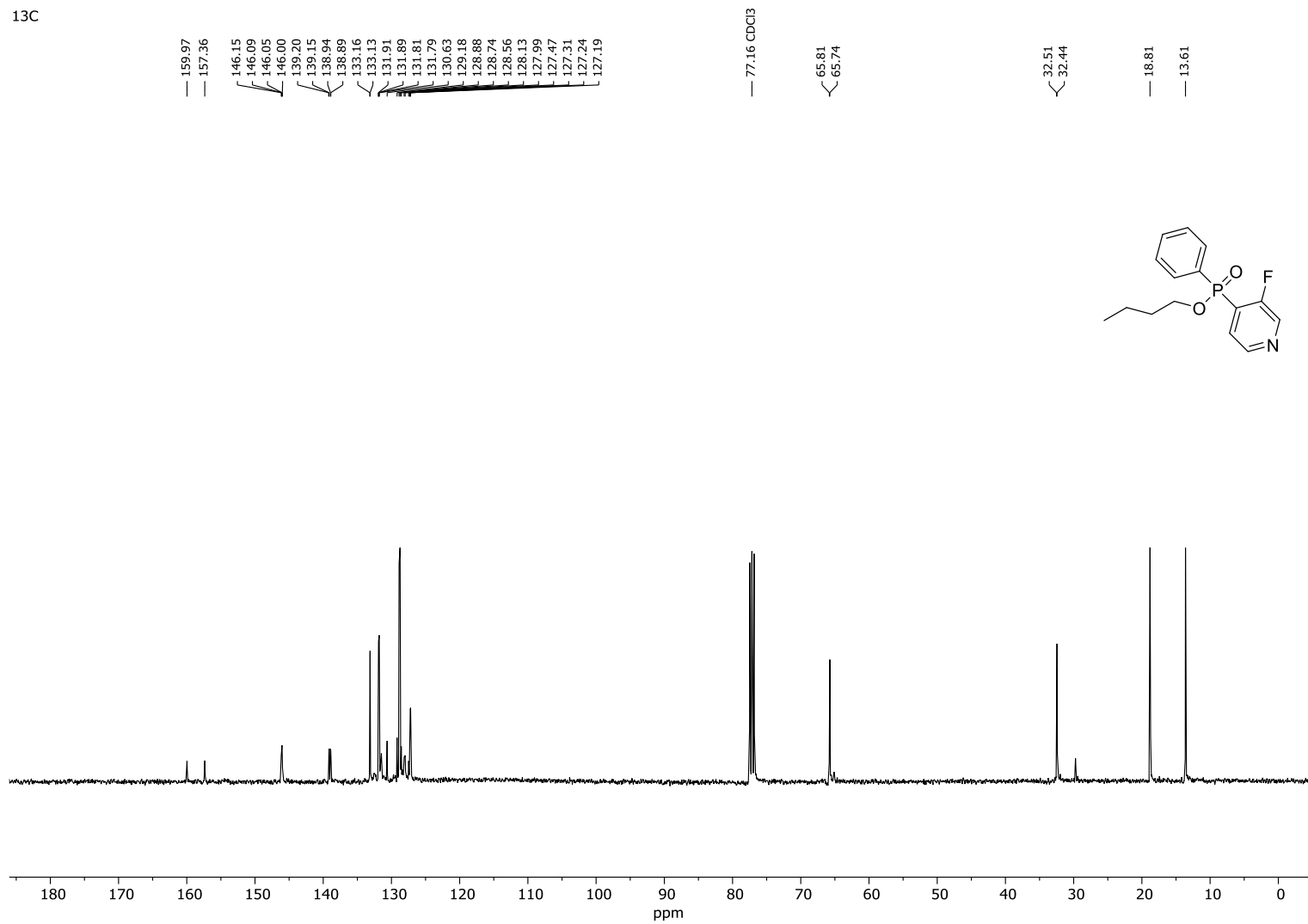
Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)

¹H



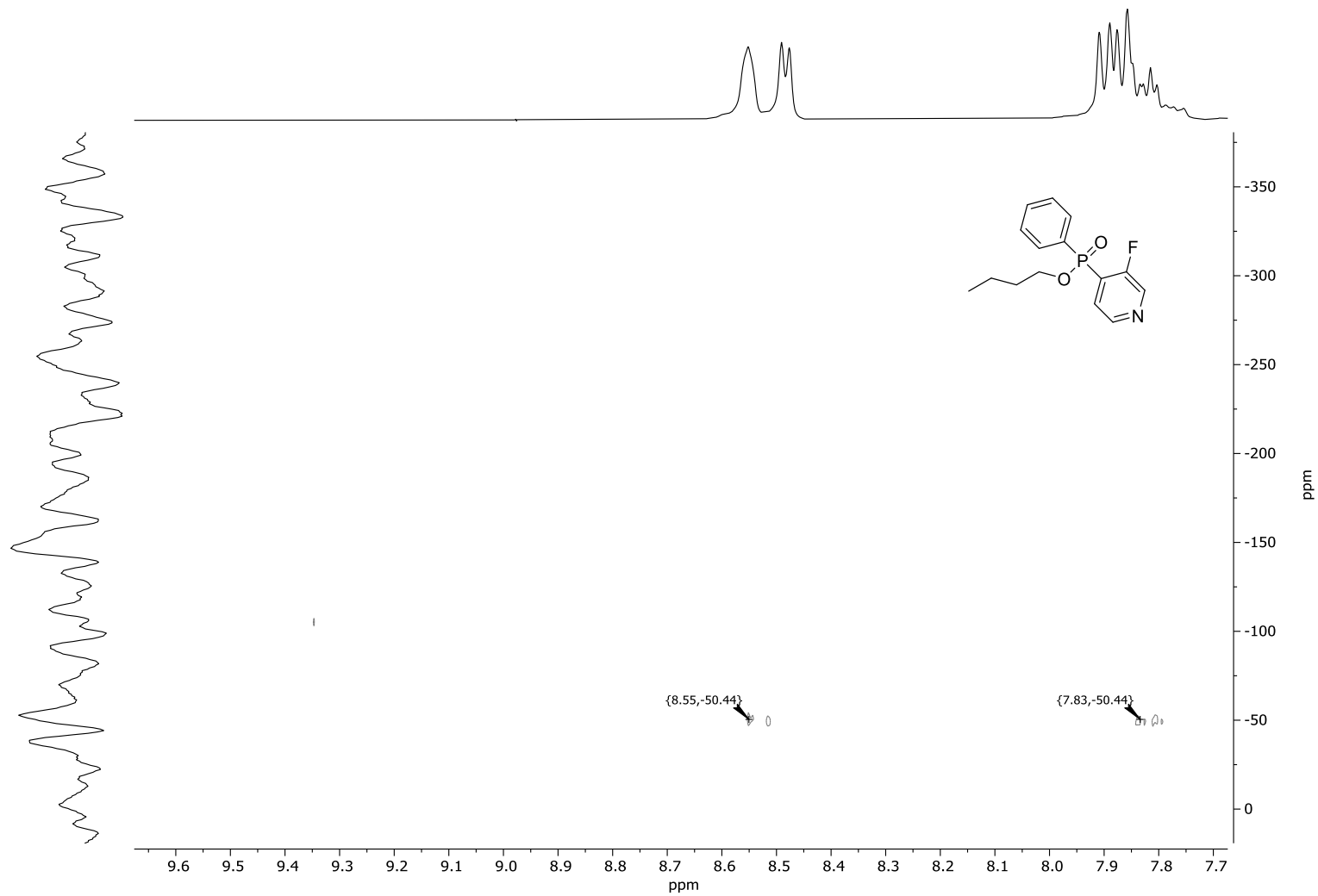
Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)

¹³C



Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)

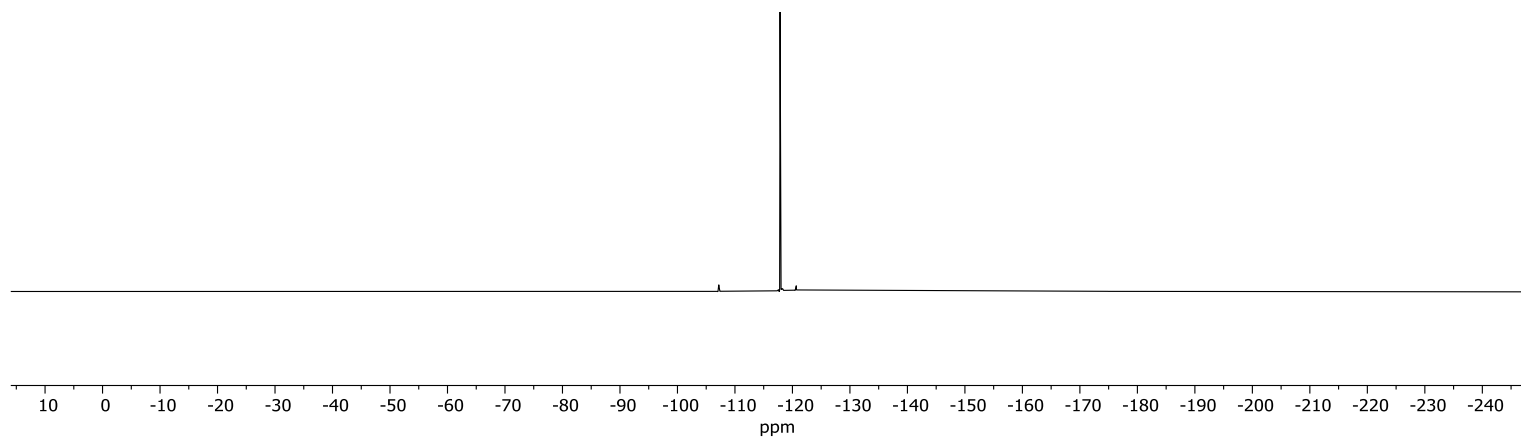
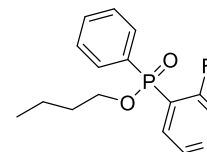
1H-15N HMBC



Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)

19F

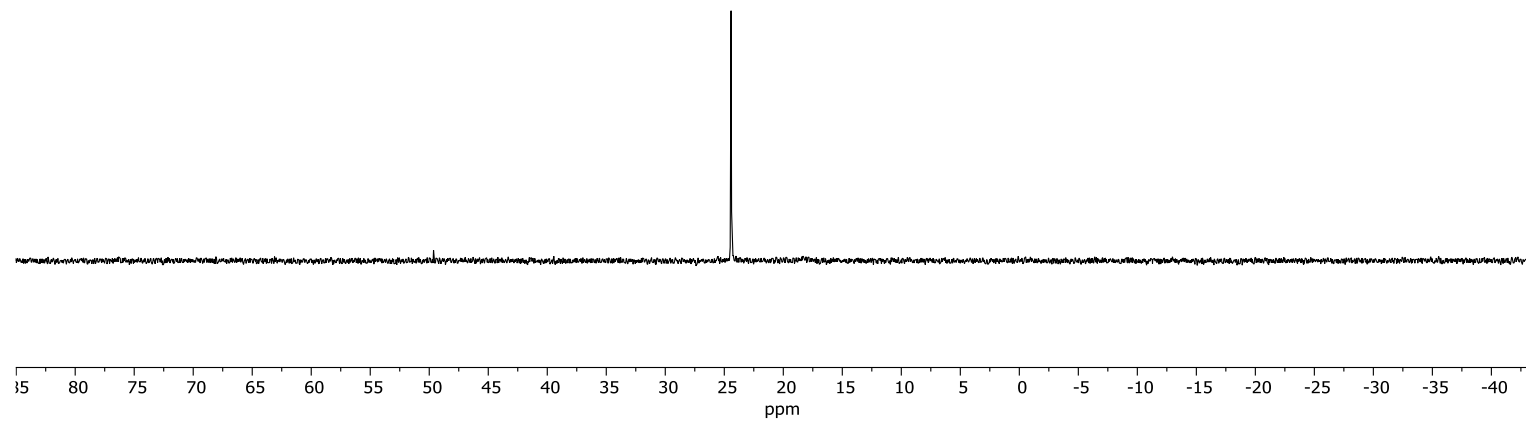
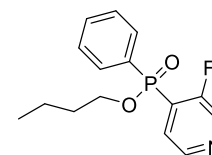
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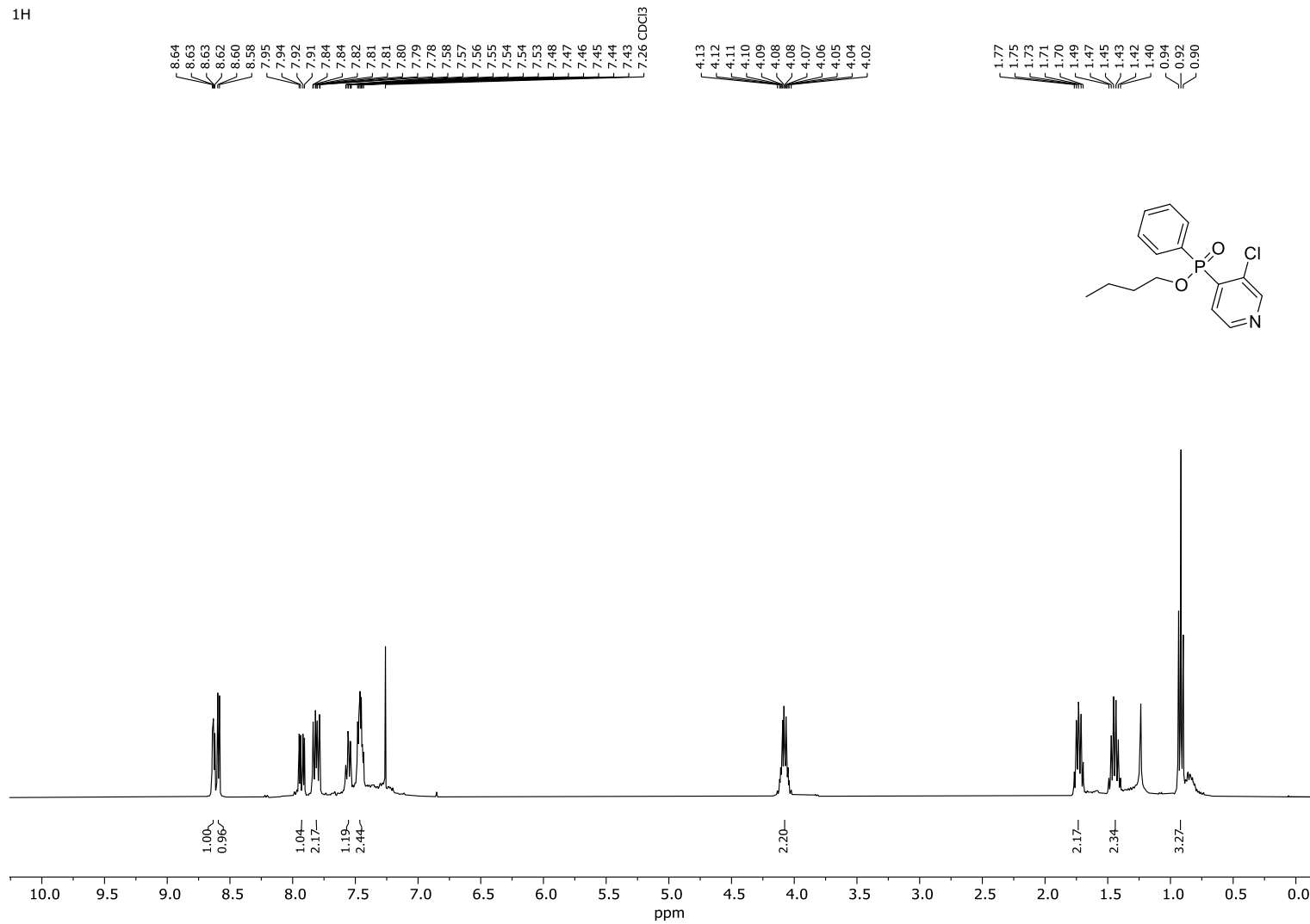
Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)

31P

— 24.42

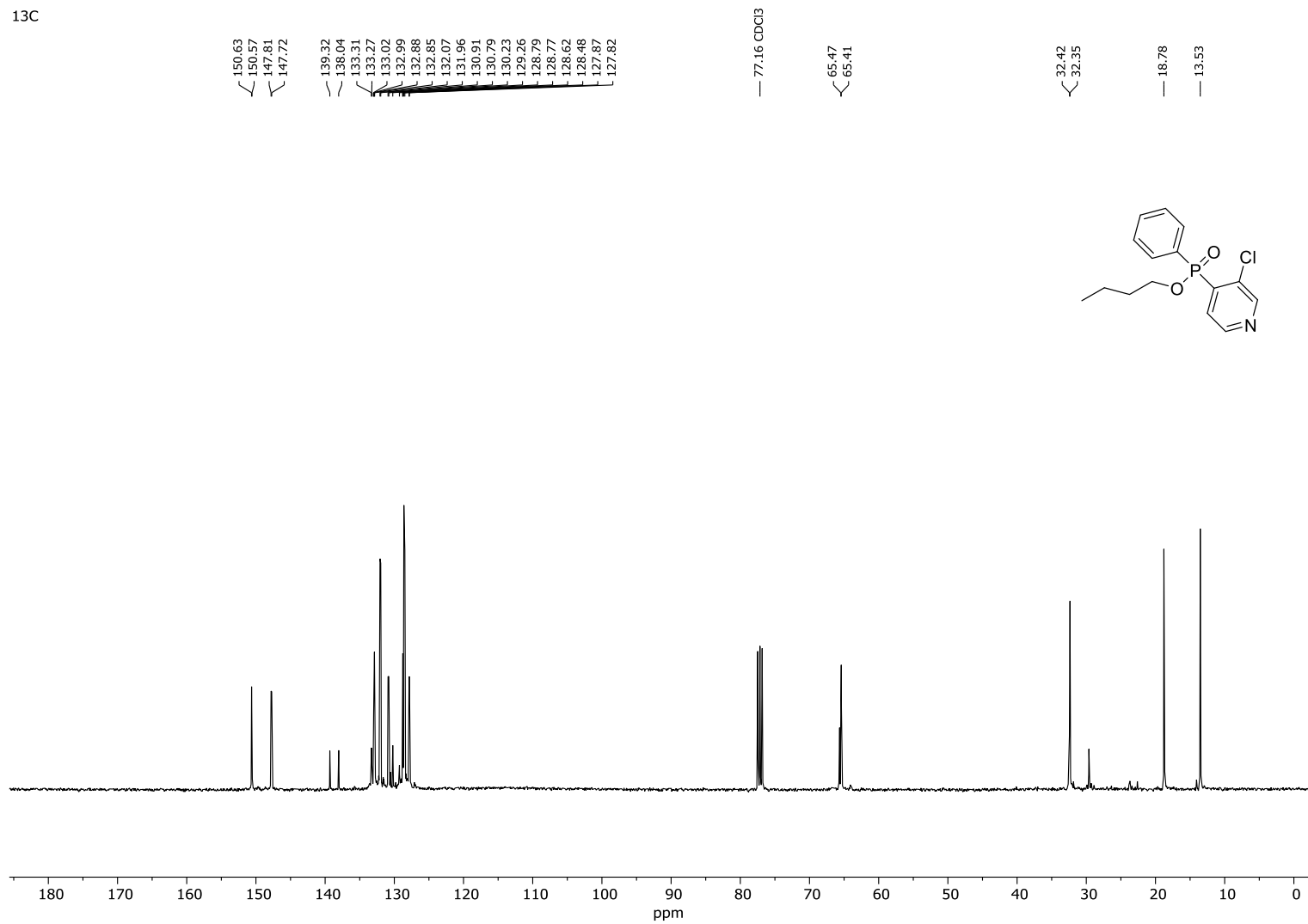


Butyl (3-chloropyridin-4-yl)phenylphosphinate (3db)



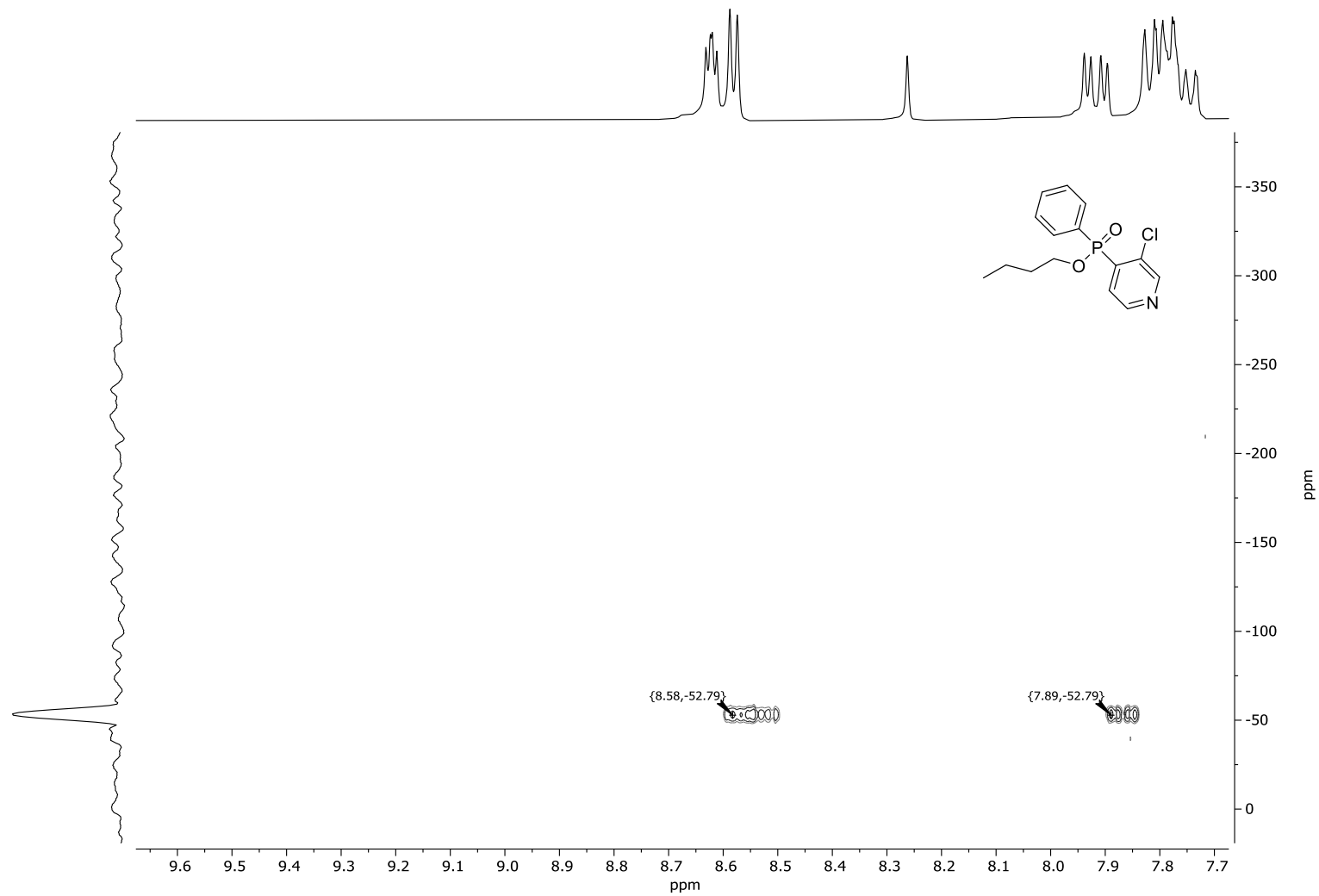
Butyl (3-chloropyridin-4-yl)phenylphosphinate (3db)

¹³C



Butyl (3-chloropyridin-4-yl)phenylphosphinate (3db)

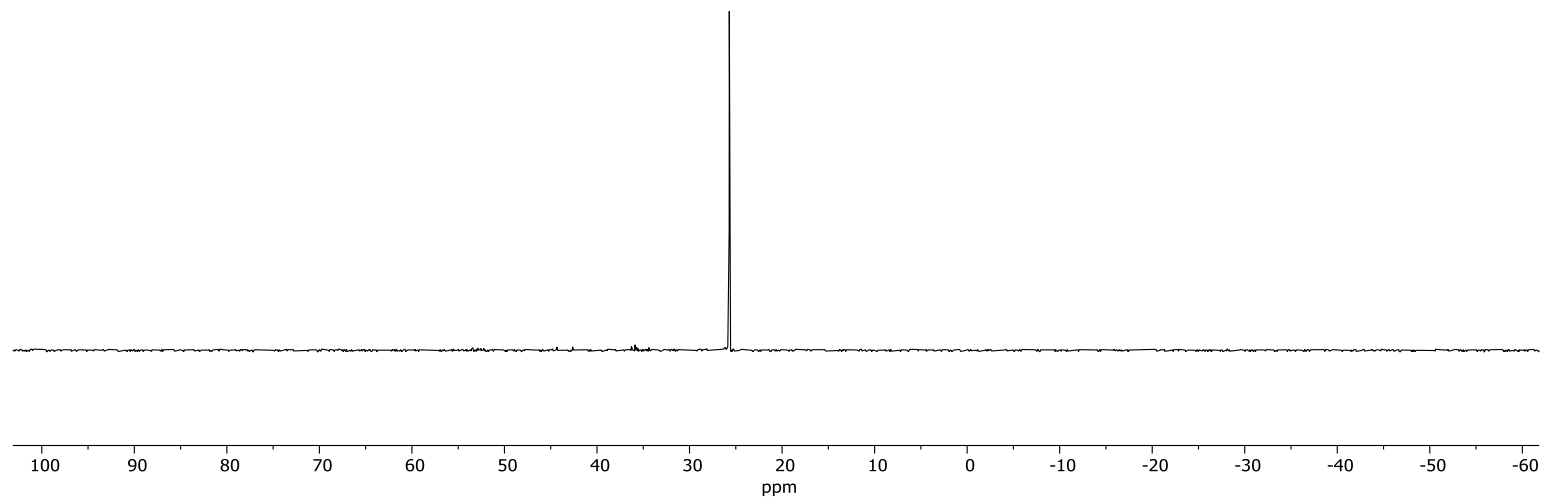
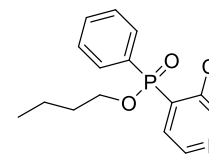
1H-15N HMBC



Butyl (3-chloropyridin-4-yl)phenylphosphinate (3db)

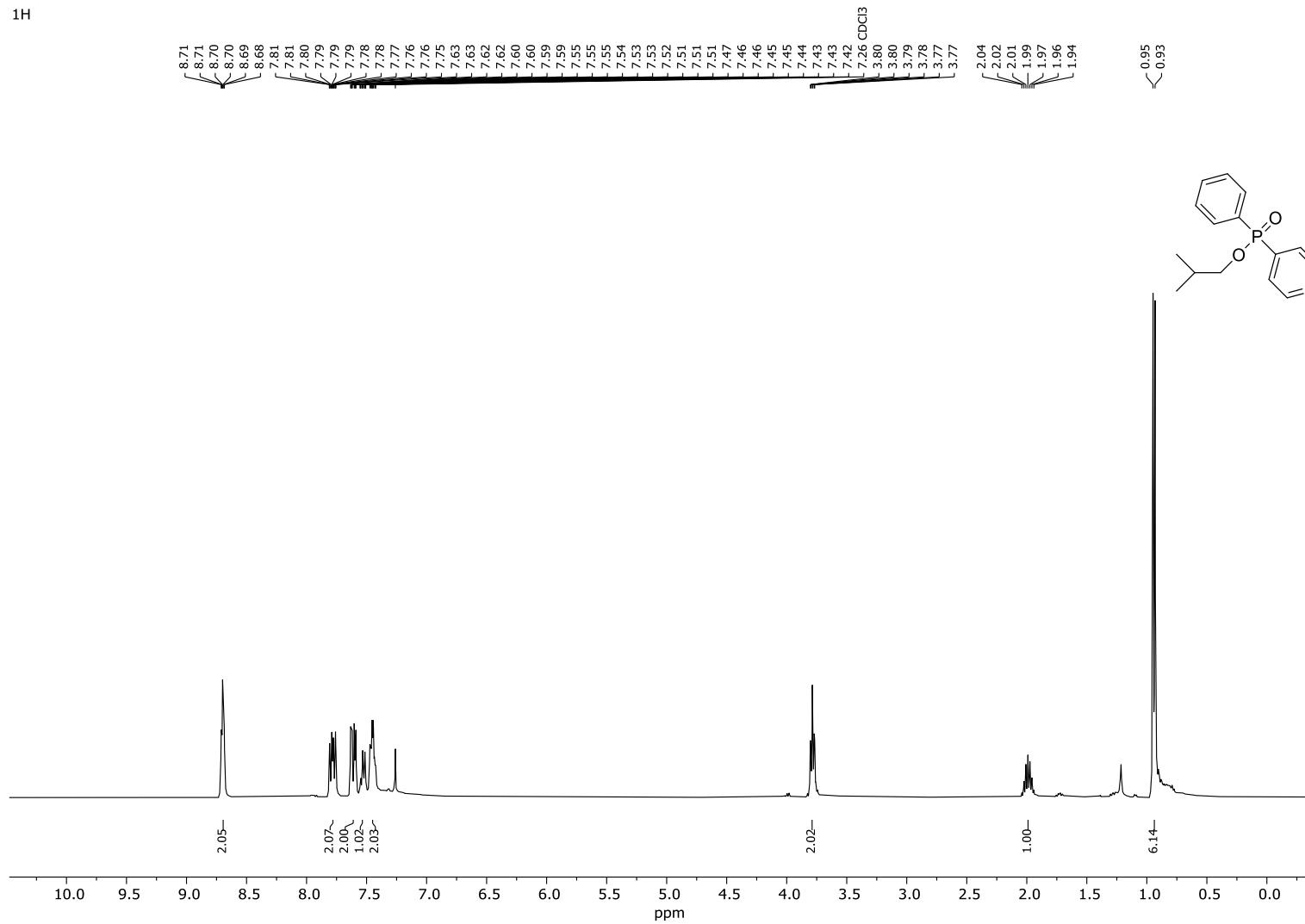
31P

— 25.70



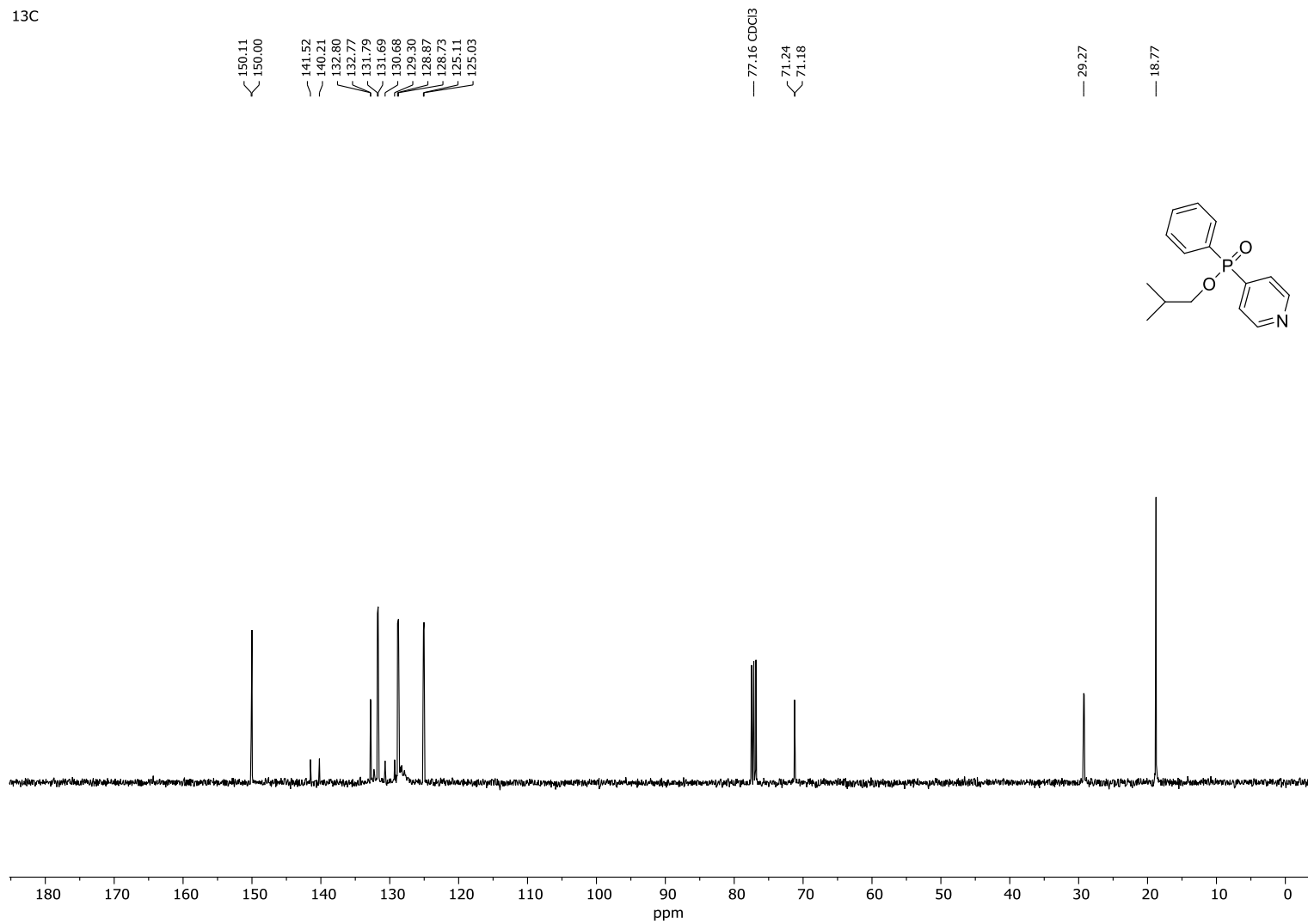
2-Methylpropyl phenyl(pyridin-4-yl)phosphinate (3ac)

¹H



2-Methylpropyl phenyl(pyridin-4-yl)phosphinate (3ac)

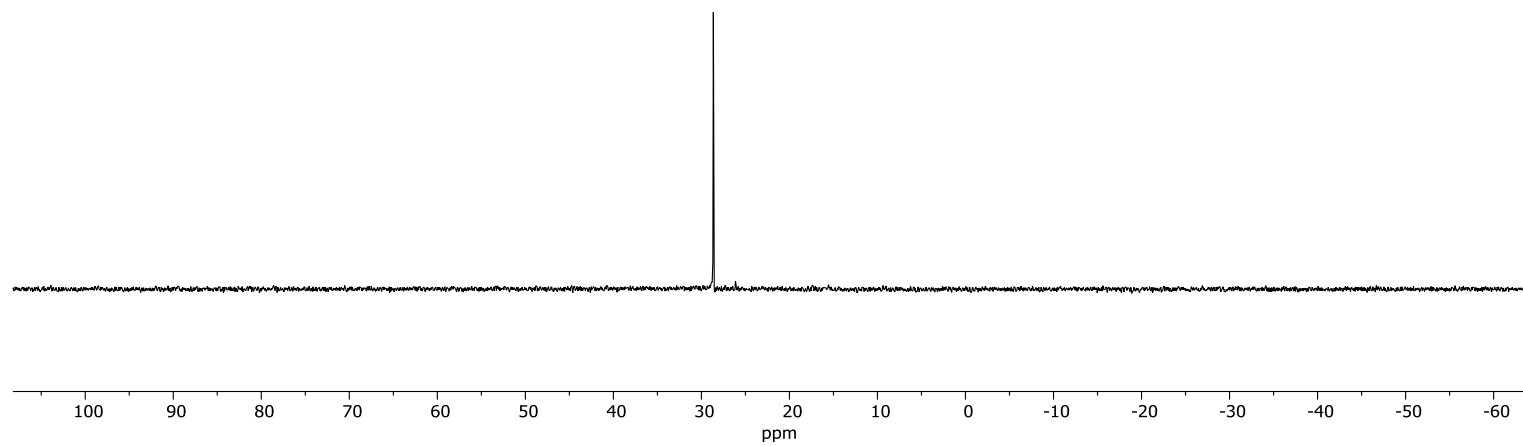
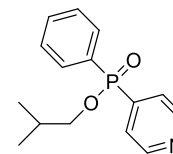
¹³C



2-Methylpropyl phenyl(pyridin-4-yl)phosphinate (3ac)

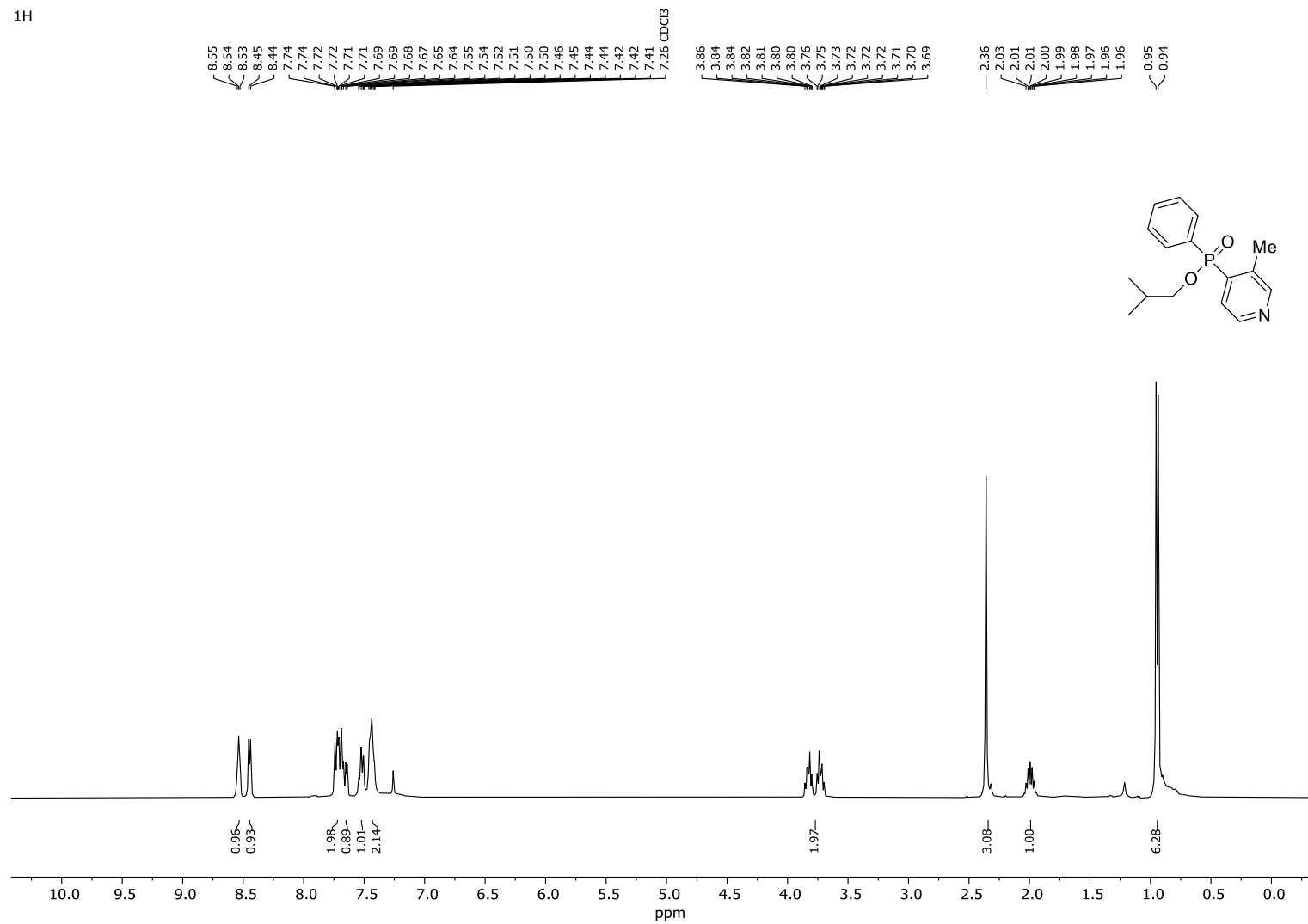
31P

— 28.64



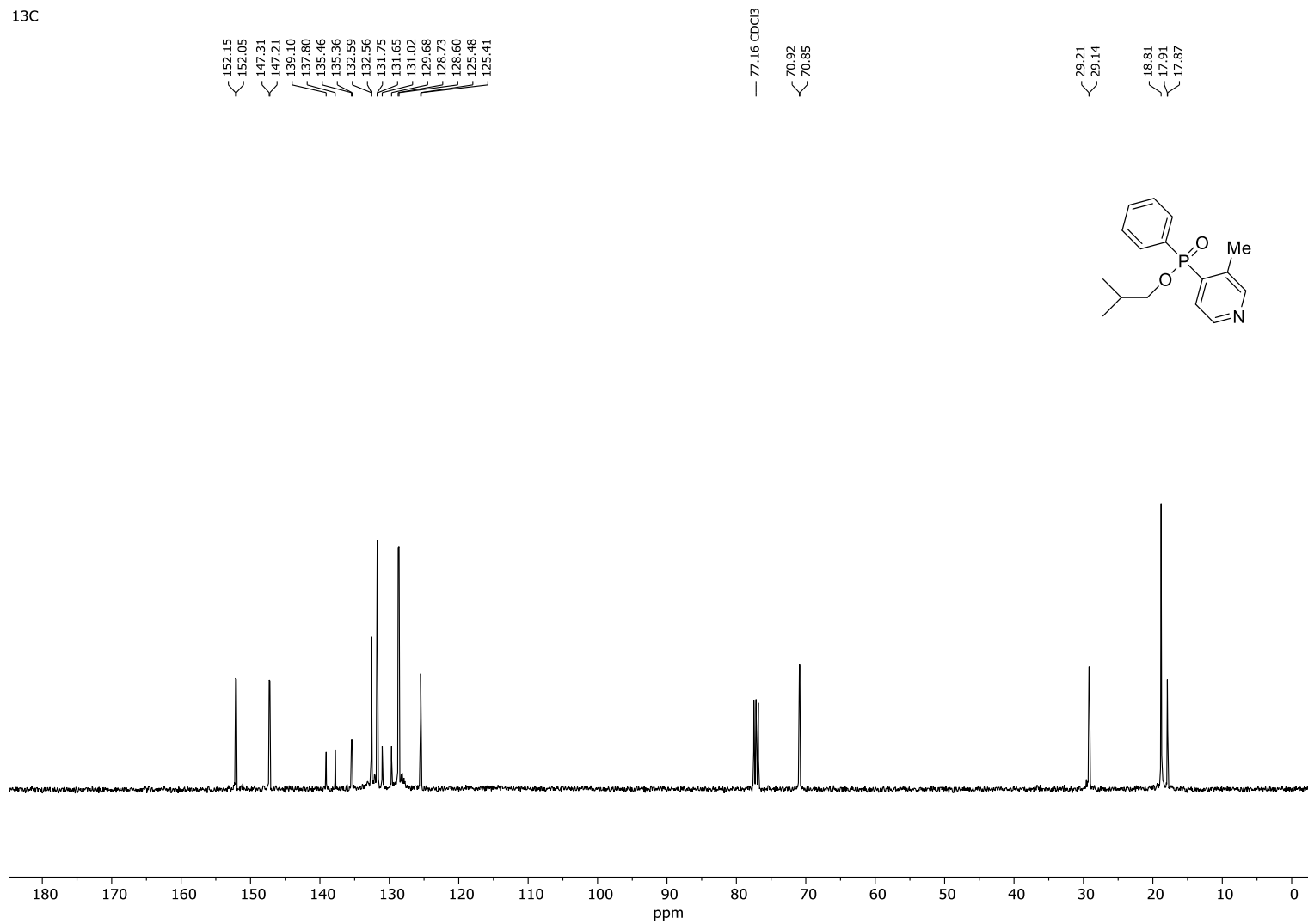
2-Methylpropyl (3-methylpyridin-4-yl)phenylphosphinate (3bc)

¹H



2-Methylpropyl (3-methylpyridin-4-yl)phenylphosphinate (3bc)

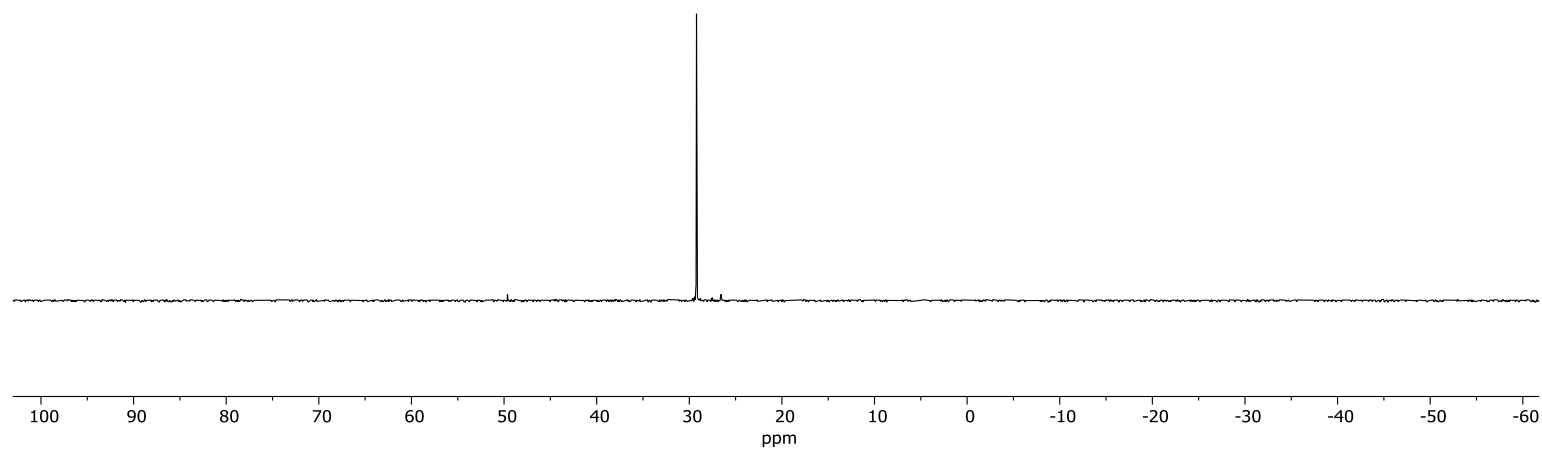
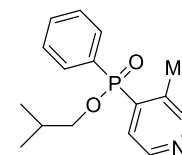
¹³C



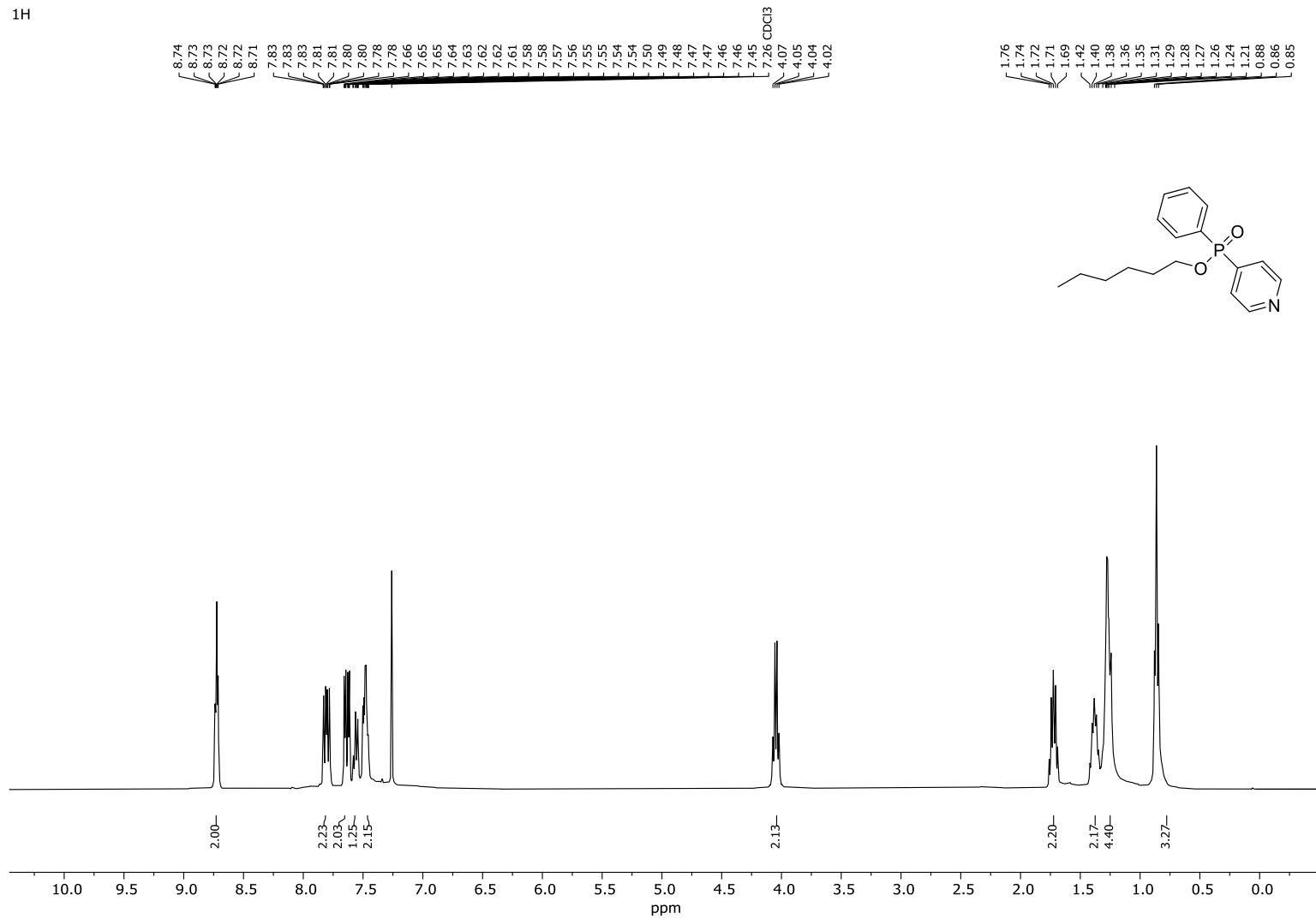
2-Methylpropyl (3-methylpyridin-4-yl)phenylphosphinate (3bc)

31P

— 29.22

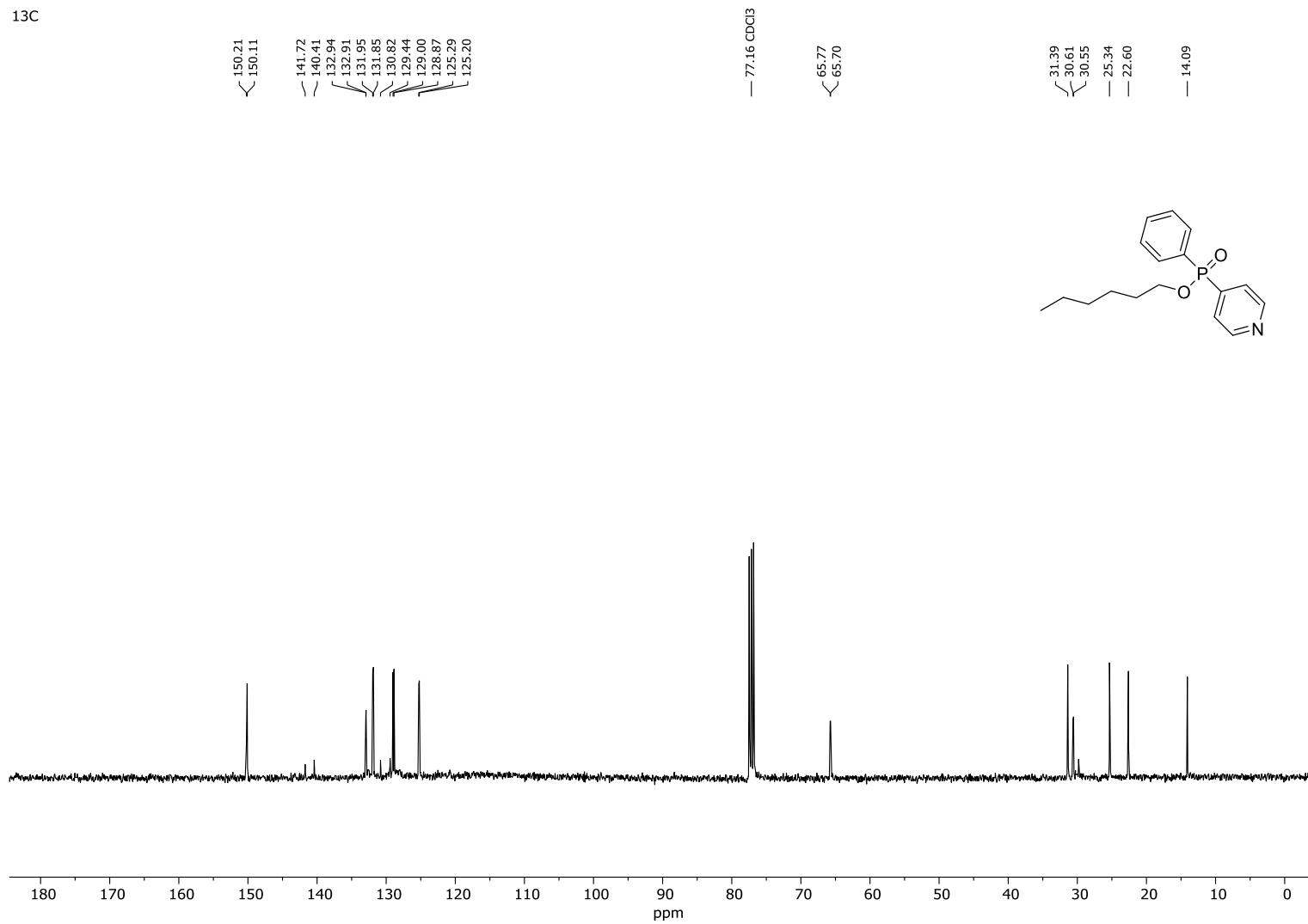


Hexyl phenyl(pyridin-4-yl)phosphinate (3ad)



Hexyl phenyl(pyridin-4-yl)phosphinate (3ad)

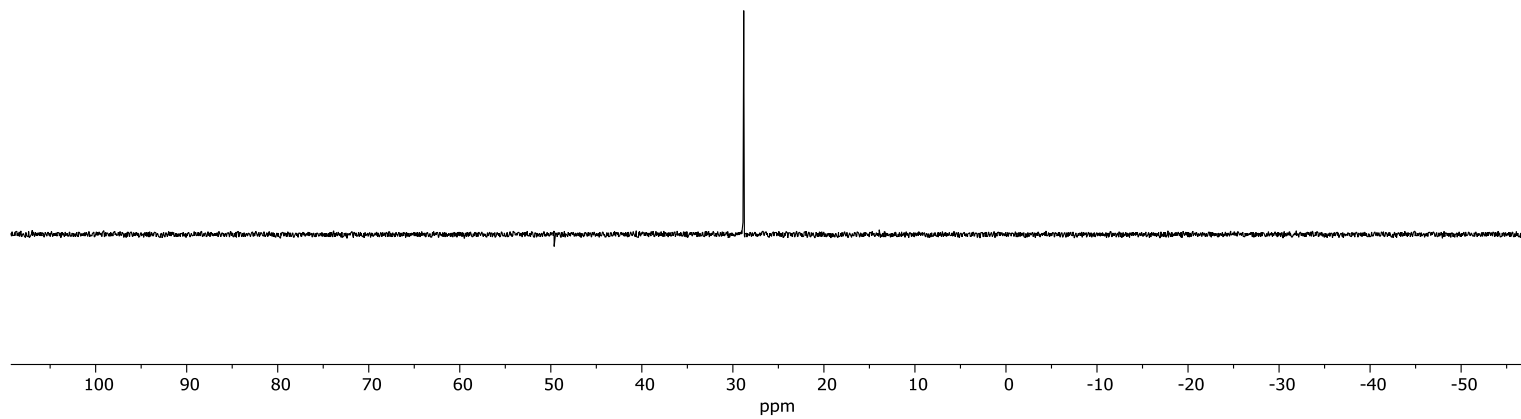
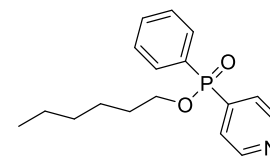
¹³C



Hexyl phenyl(pyridin-4-yl)phosphinate (3ad)

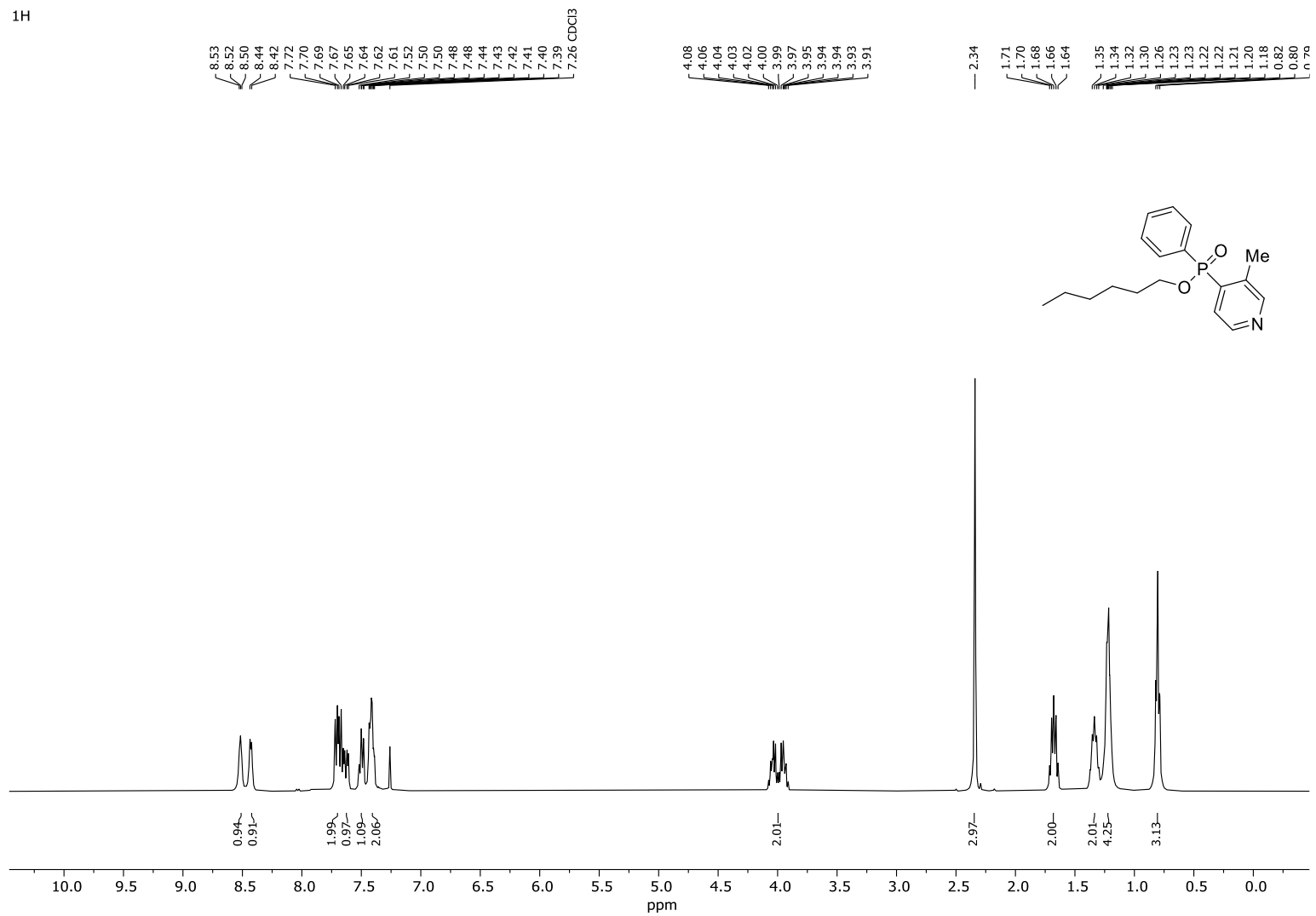
31P

28.81



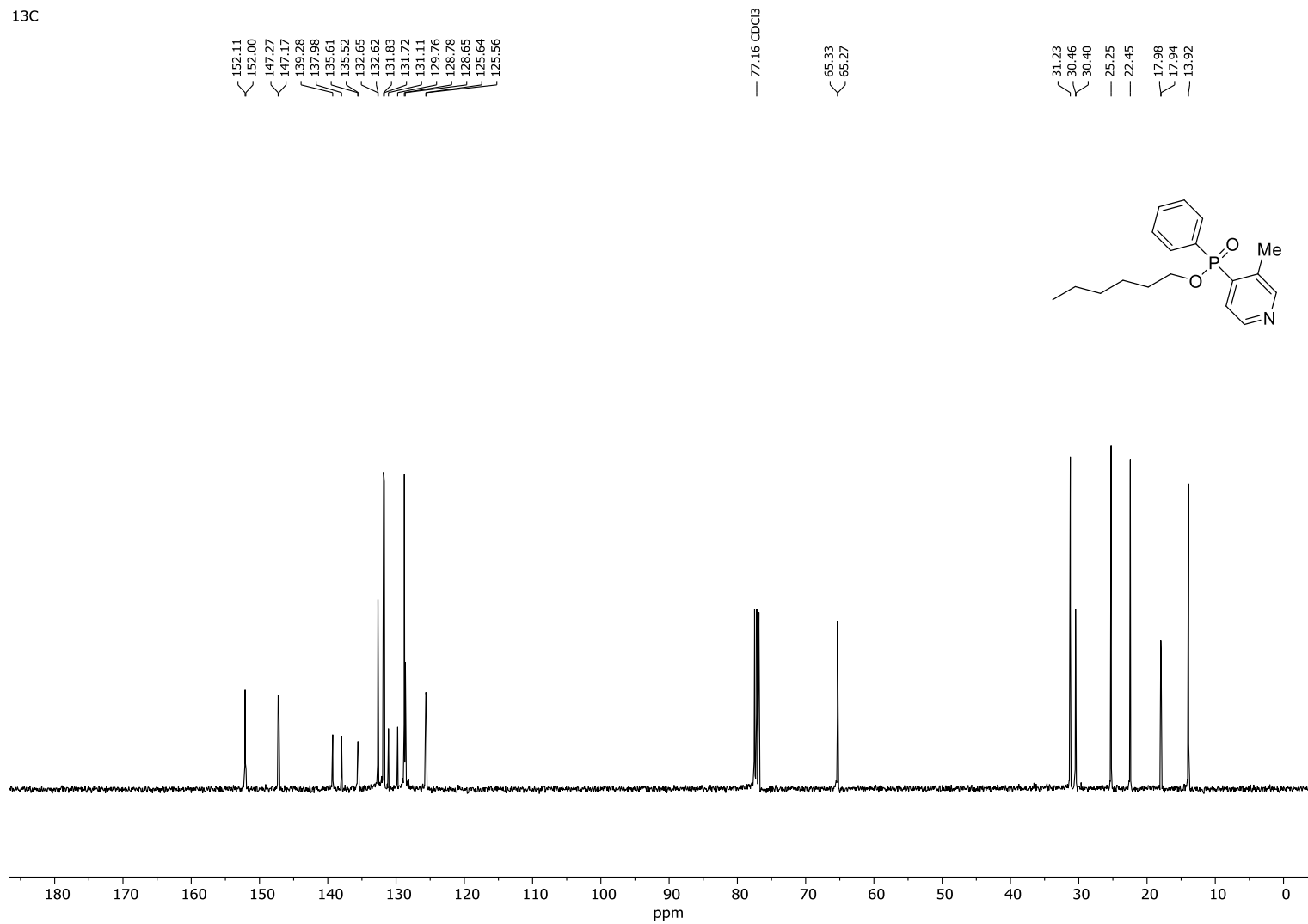
Hexyl (3-methylpyridin-4-yl)phenylphosphinate (3bd)

¹H



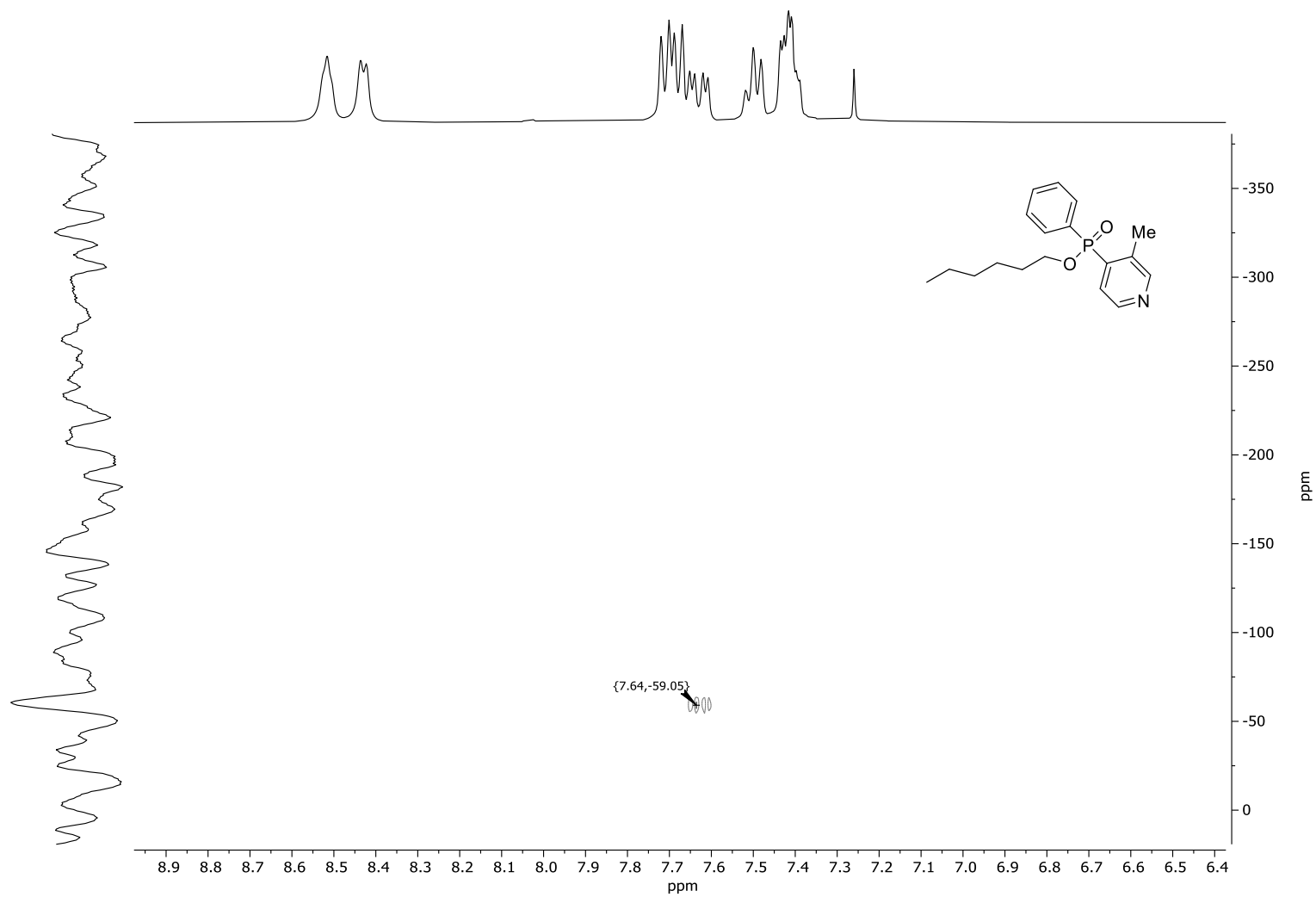
Hexyl (3-methylpyridin-4-yl)phenylphosphinate (3bd)

¹³C



Hexyl (3-methylpyridin-4-yl)phenylphosphinate (3bd)

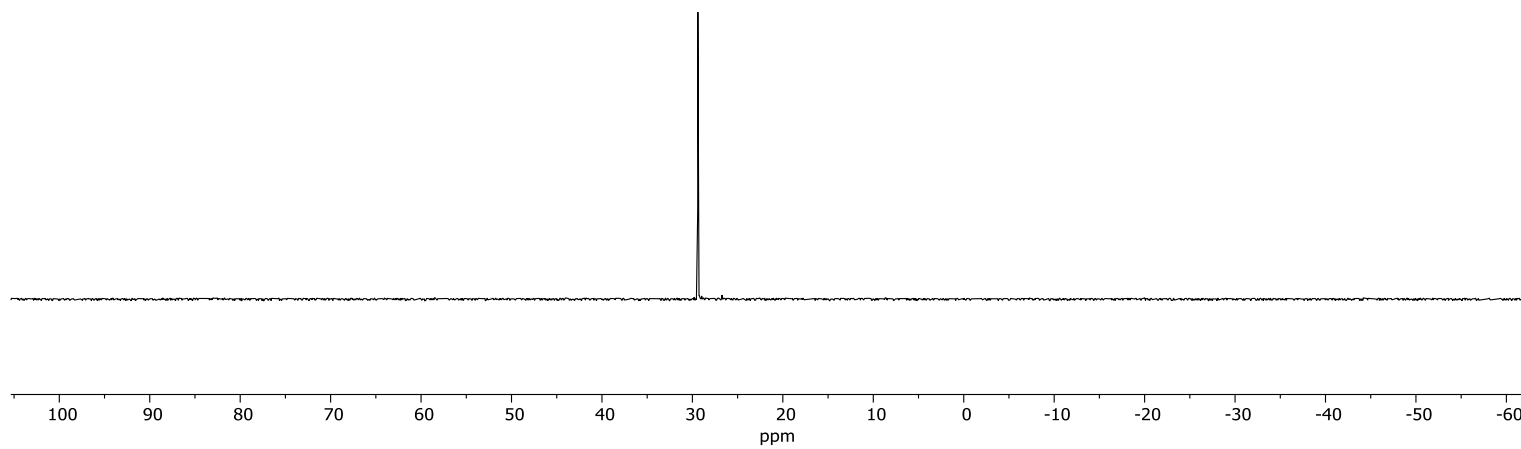
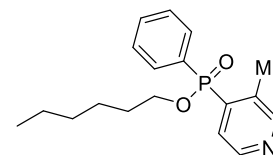
1H-15N HMBC



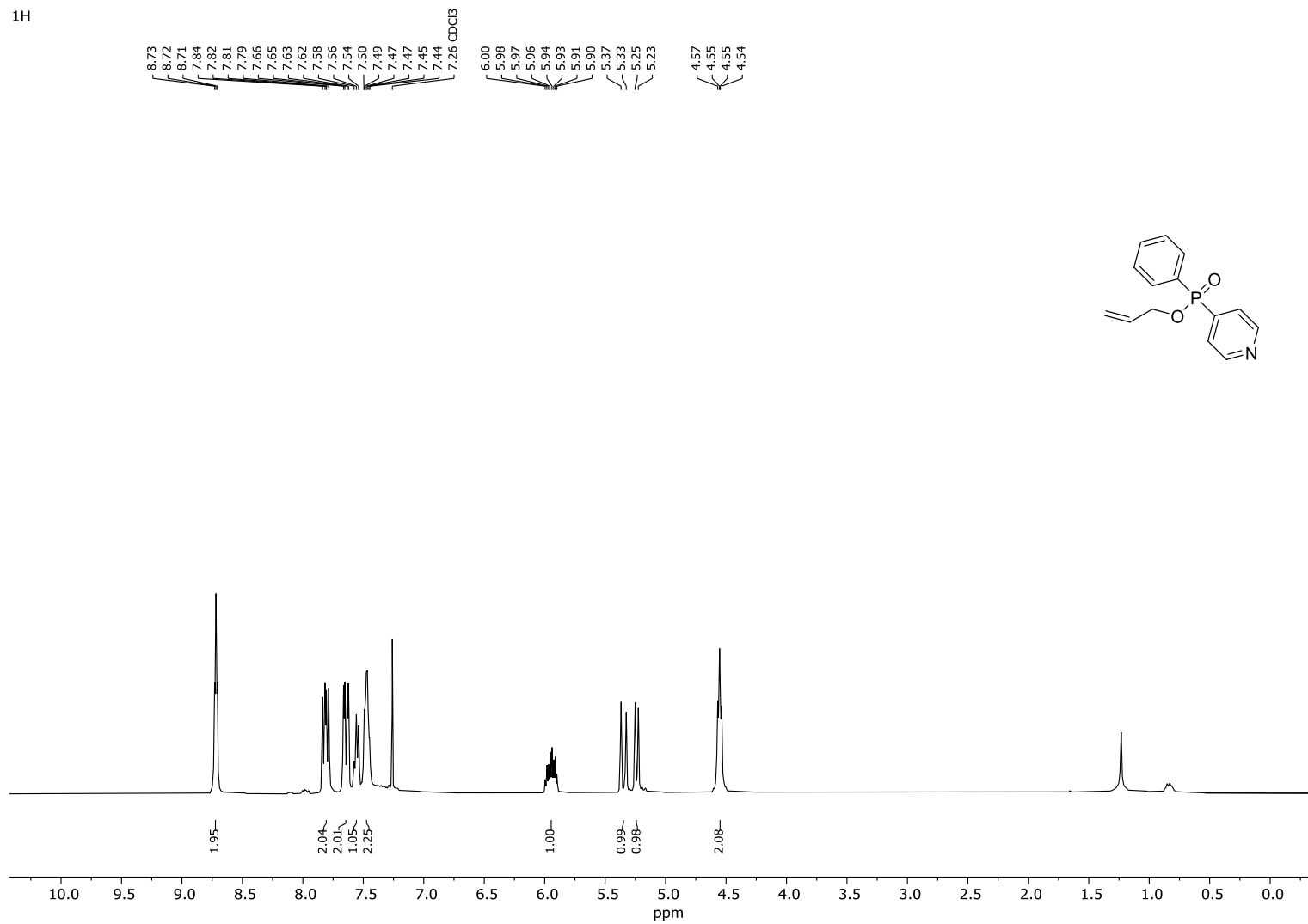
Hexyl (3-methylpyridin-4-yl)phenylphosphinate (3bd)

31P

— 29.40

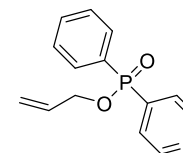
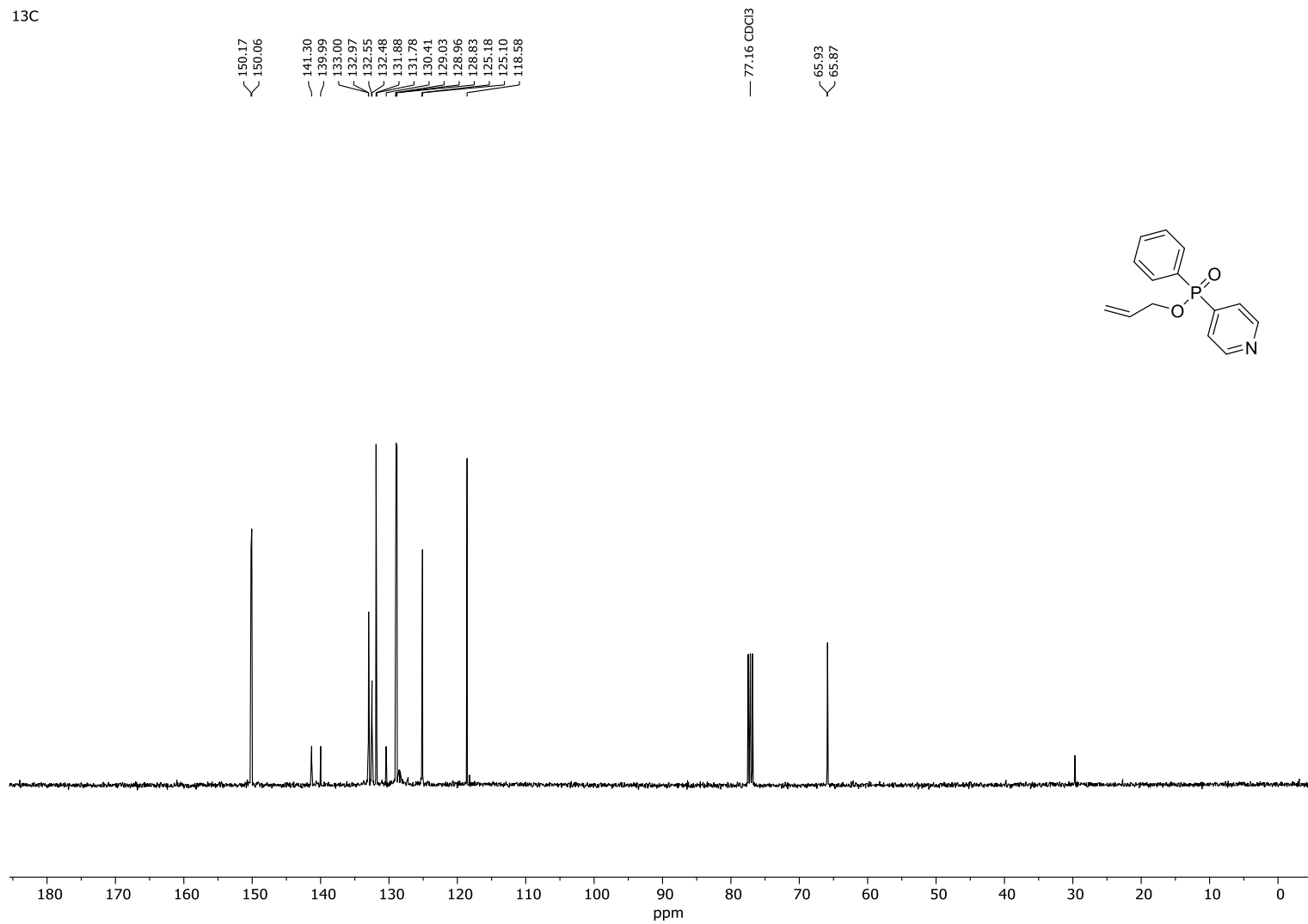


Prop-2-en-1-yl phenyl(pyridin-4-yl)phosphinate (3ae)



Prop-2-en-1-yl phenyl(pyridin-4-yl)phosphinate (3ae)

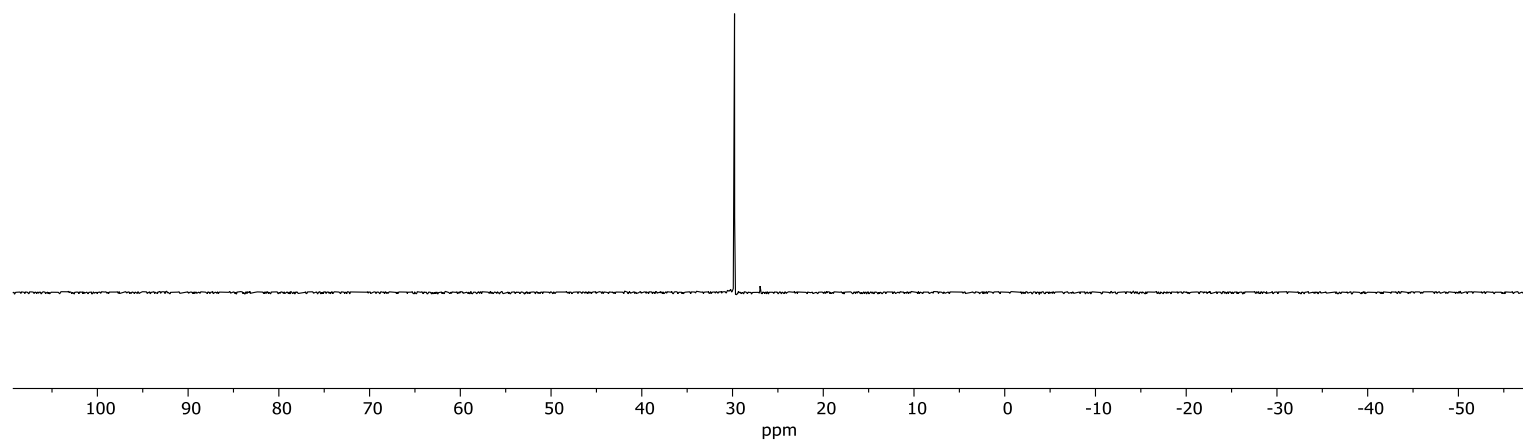
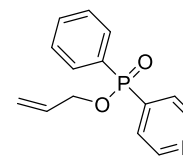
¹³C



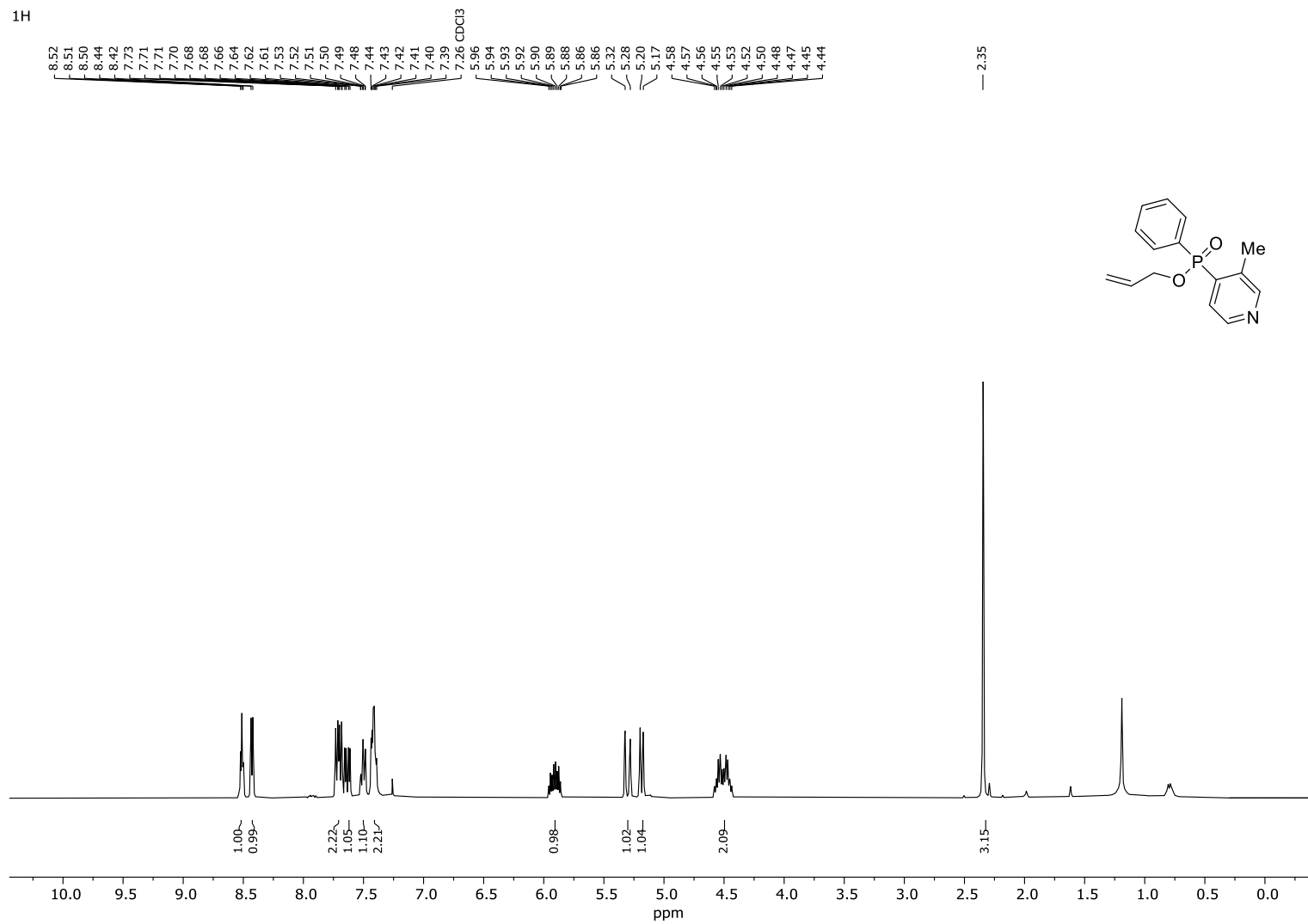
Prop-2-en-1-yl phenyl(pyridin-4-yl)phosphinate (3ae)

31P

— 29.78

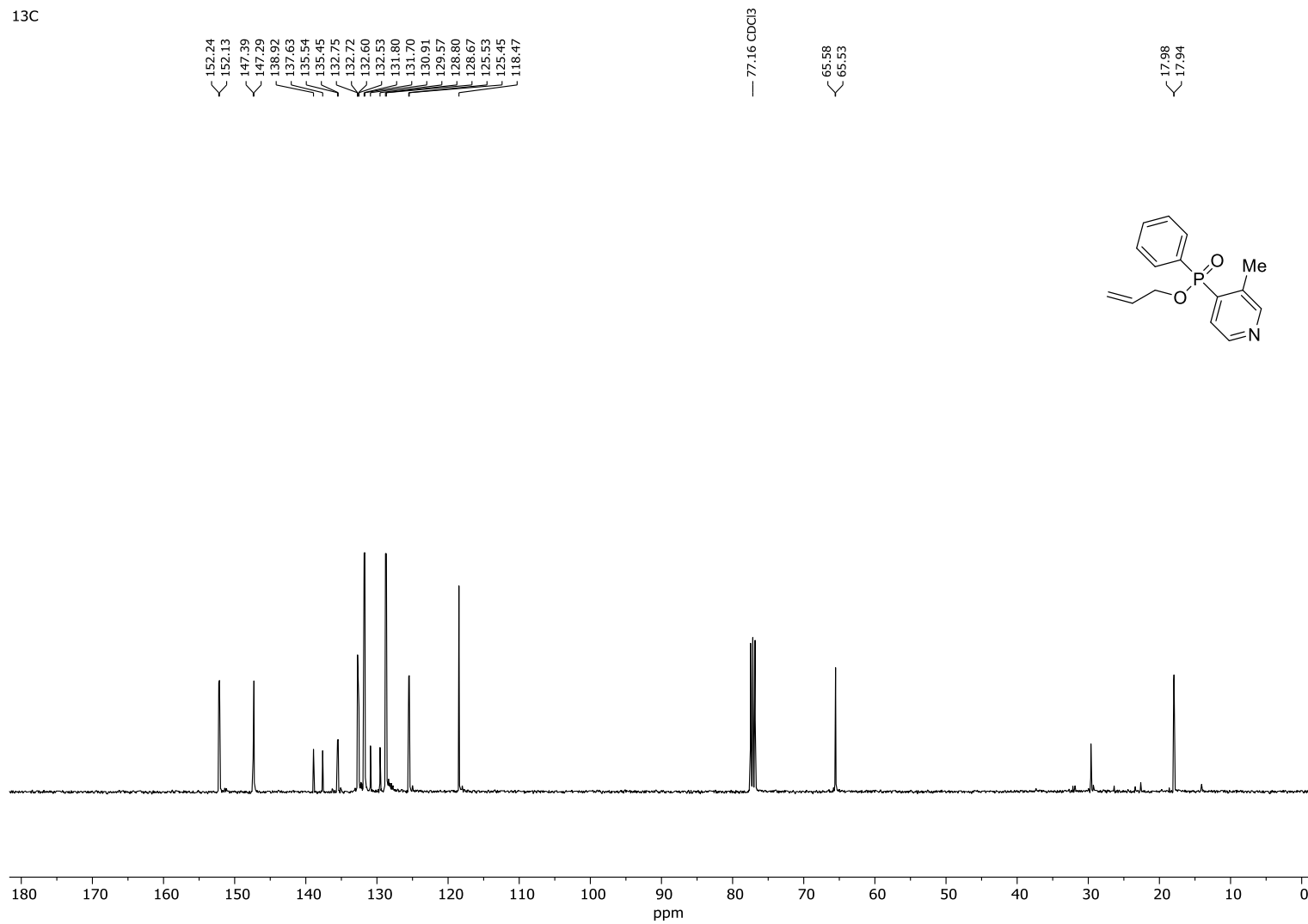


Prop-2-en-1-yl (3-methylpyridin-4-yl)phenylphosphinate (3be)



Prop-2-en-1-yl (3-methylpyridin-4-yl)phenylphosphinate (3be)

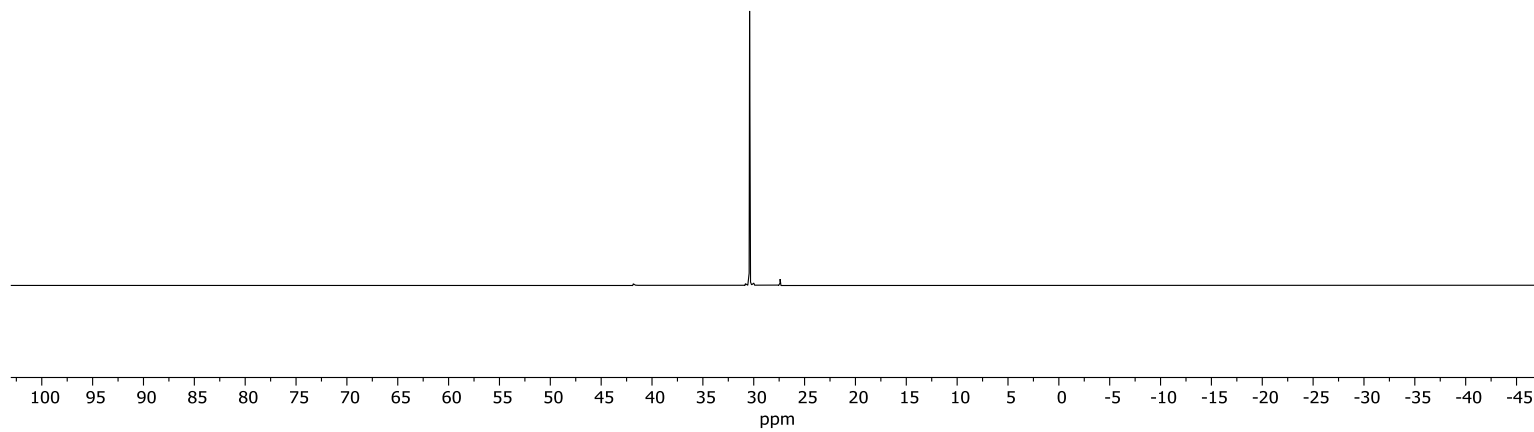
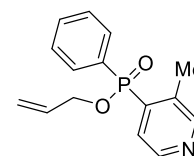
¹³C



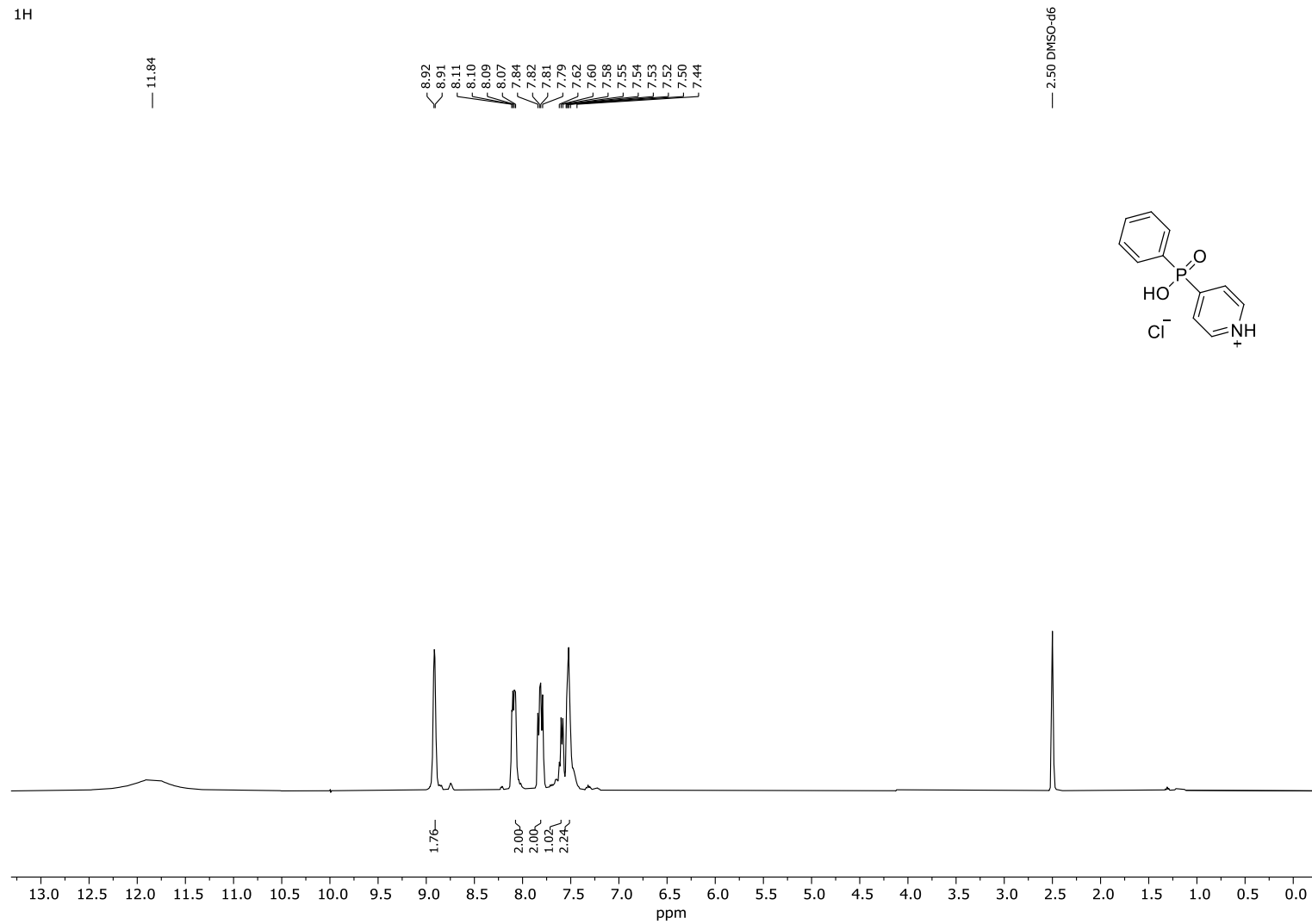
Prop-2-en-1-yl (3-methylpyridin-4-yl)phenylphosphinate (3be)

31P

— 30.41

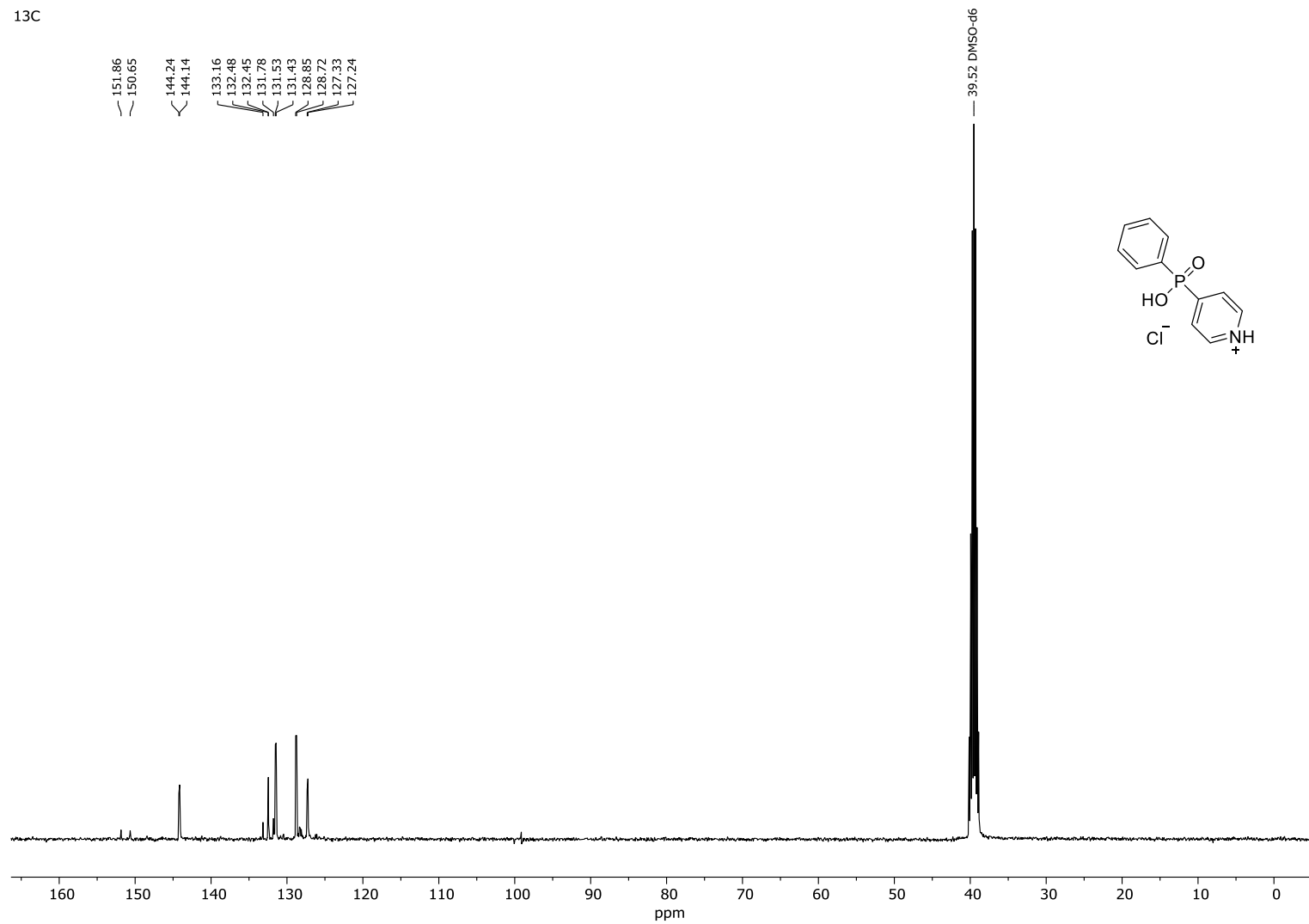


4-[Hydroxy(phenyl)phosphoryl]pyridin-1-ium chloride (5a)



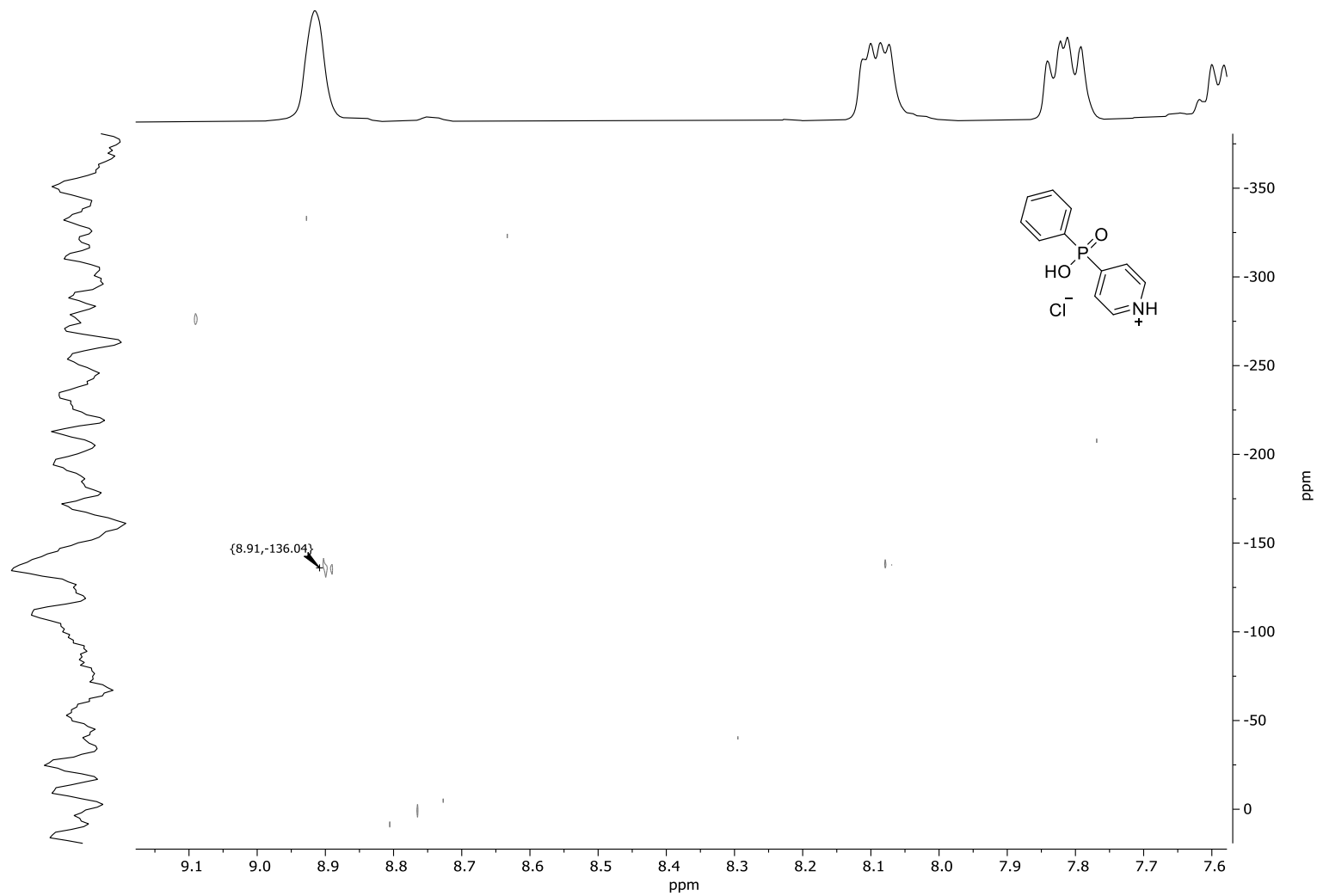
4-[Hydroxy(phenyl)phosphoryl]pyridin-1-ium chloride (5a)

¹³C



4-[Hydroxy(phenyl)phosphoryl]pyridin-1-ium chloride (5a)

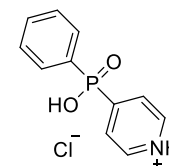
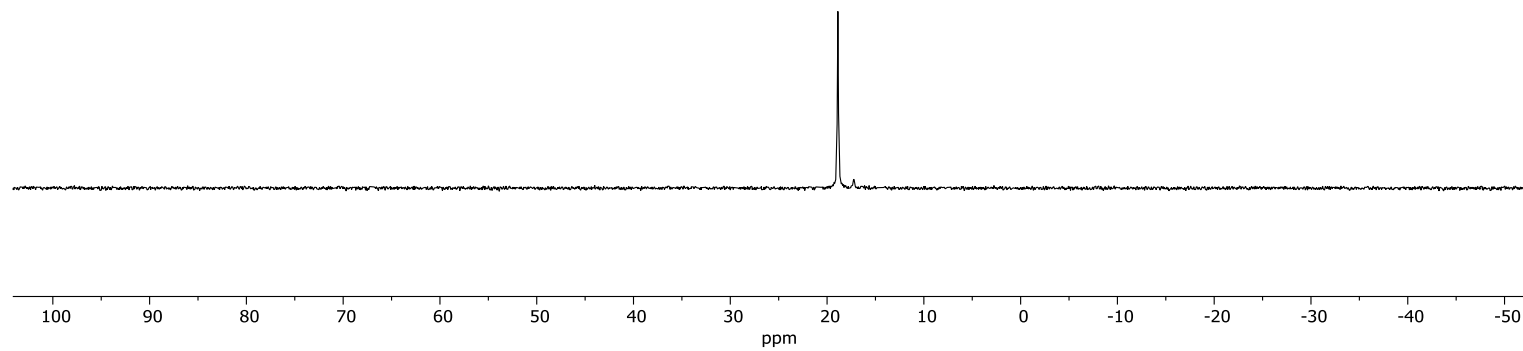
1H-15N HMBC



4-[Hydroxy(phenyl)phosphoryl]pyridin-1-ium chloride (5a)

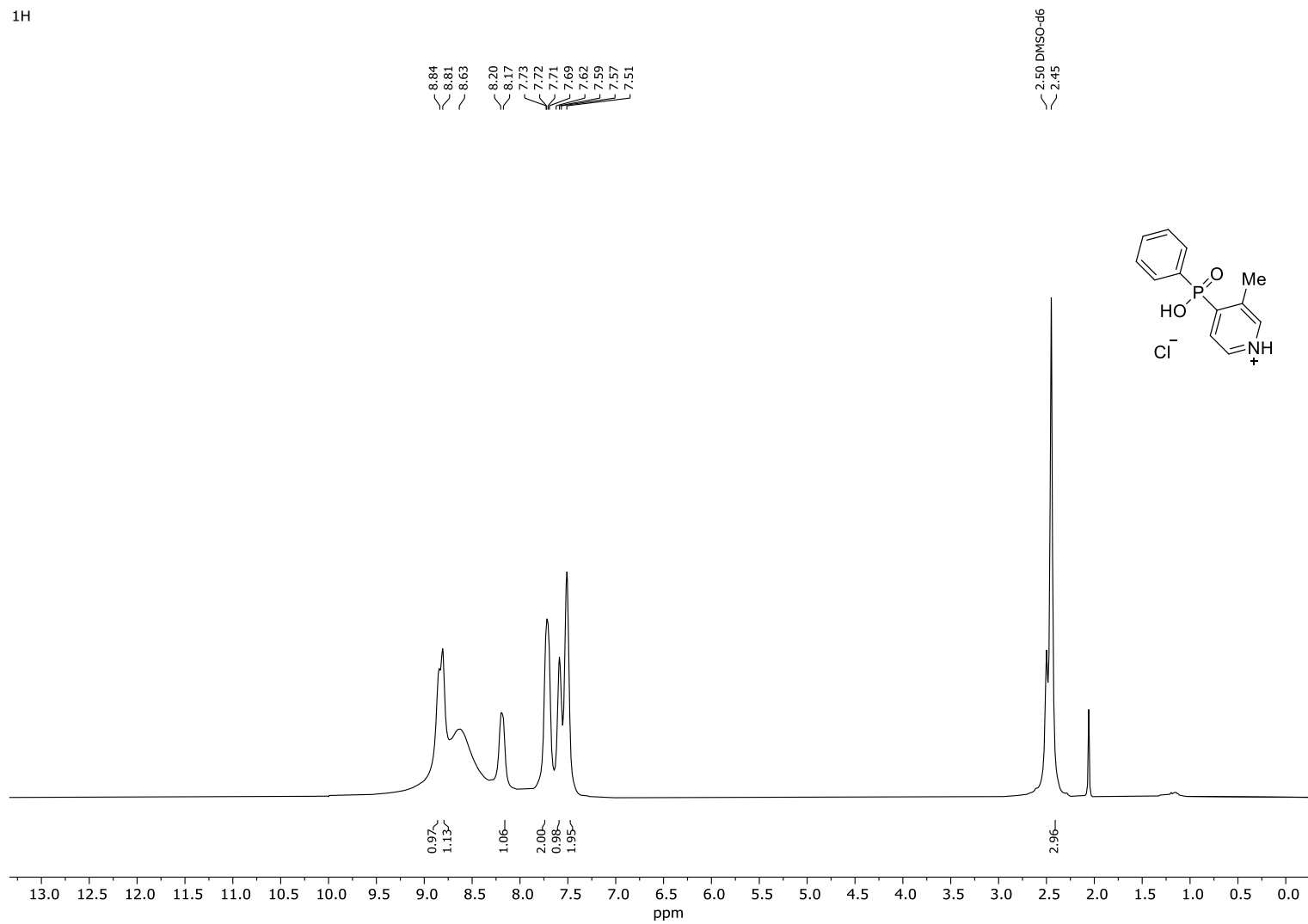
31P

18.88



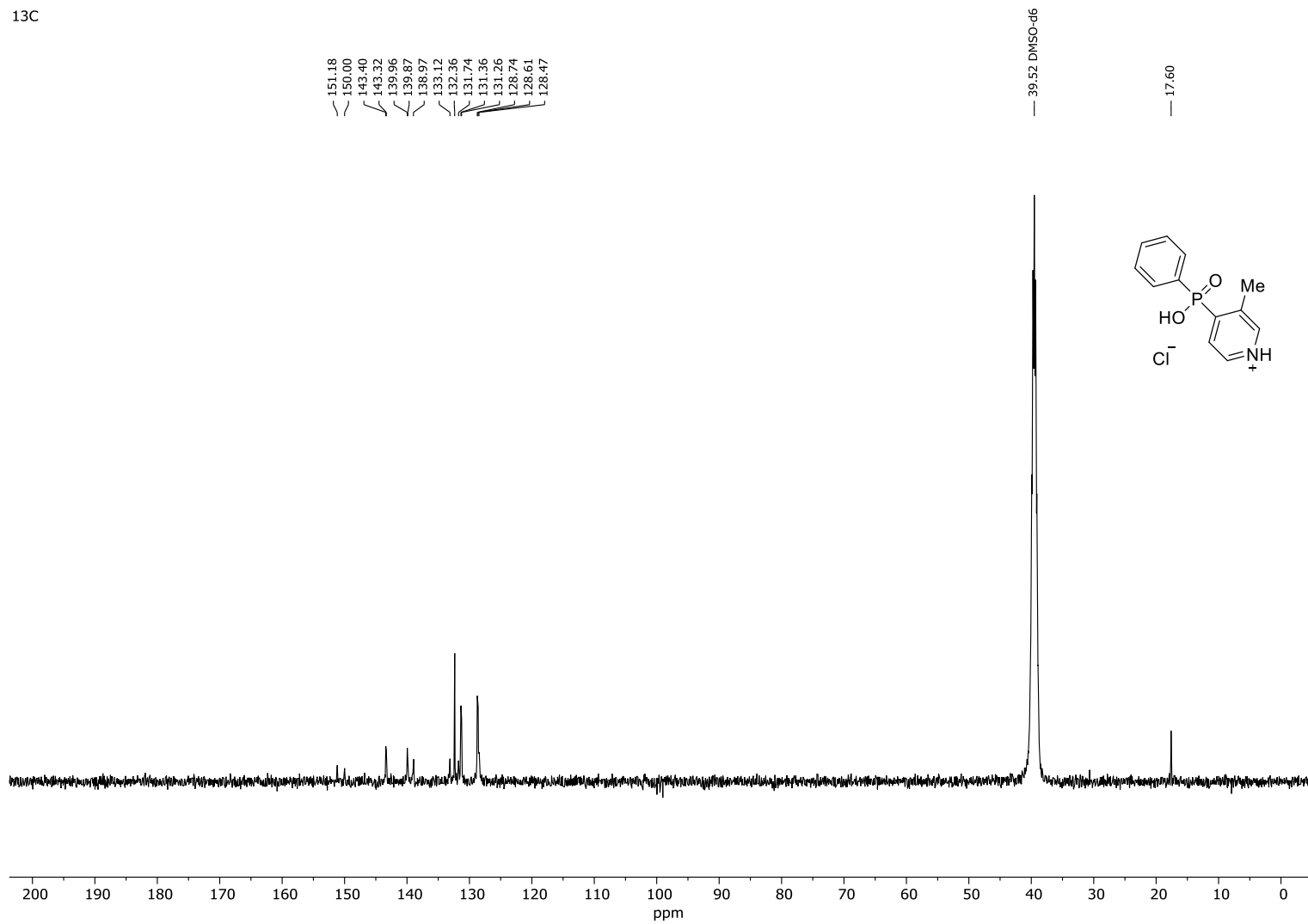
4-[Hydroxy(phenyl)phosphoryl]-3-methylpyridin-1-ium chloride (5b)

¹H



4-[Hydroxy(phenyl)phosphoryl]-3-methylpyridin-1-ium chloride (5b)

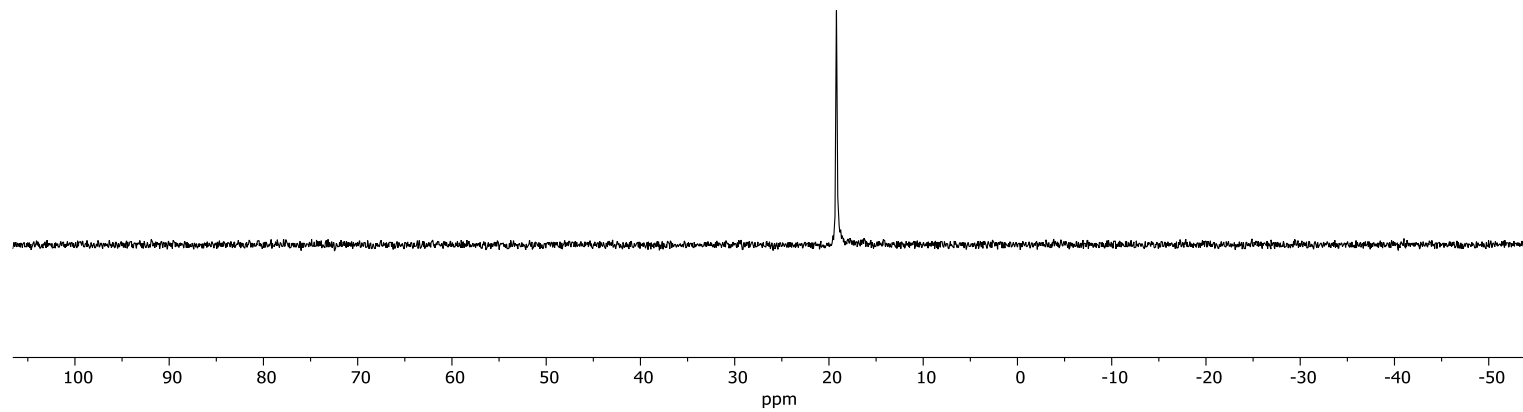
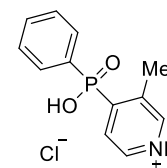
13C



4-[Hydroxy(phenyl)phosphoryl]-3-methylpyridin-1-ium chloride (5b)

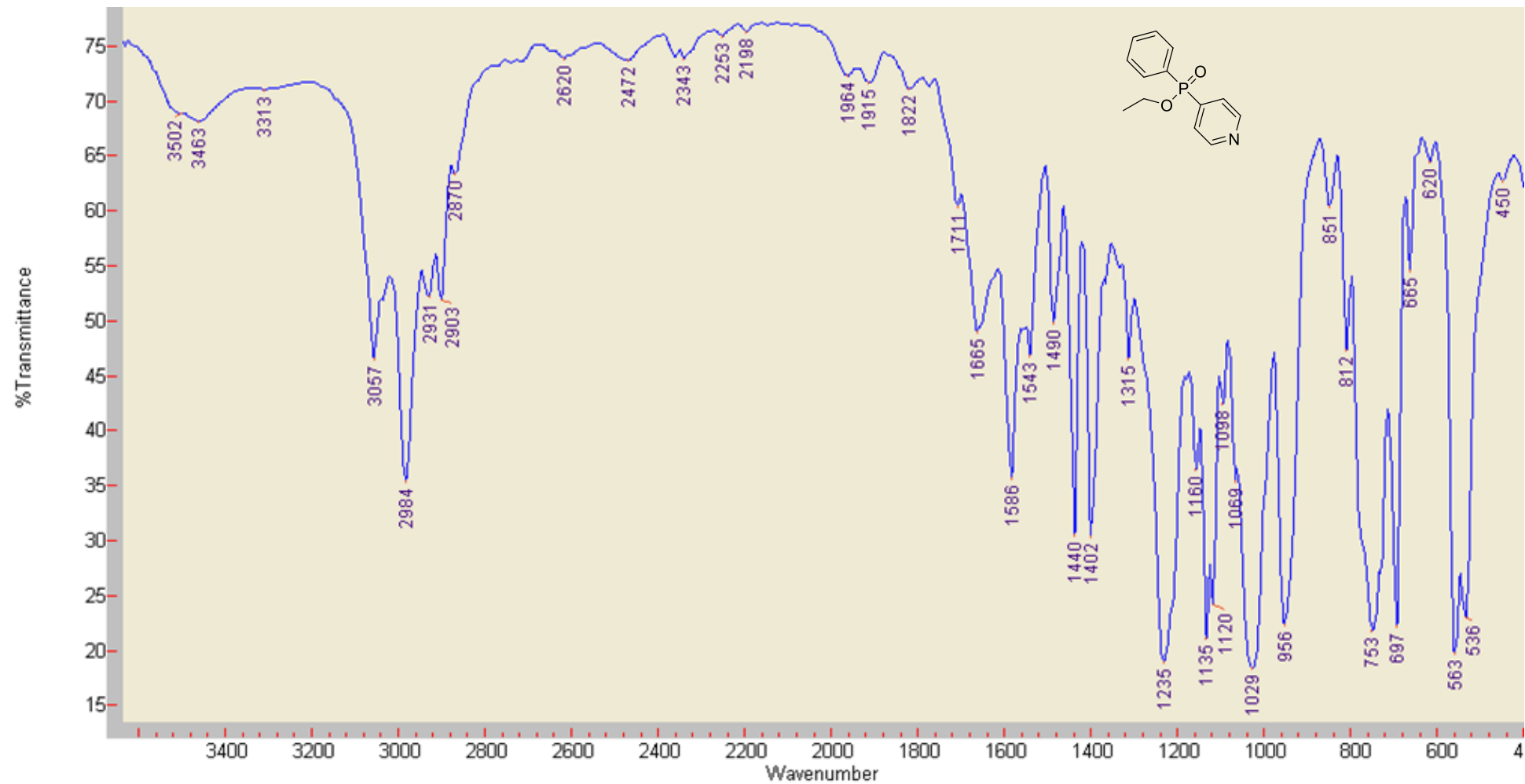
31P

19.20

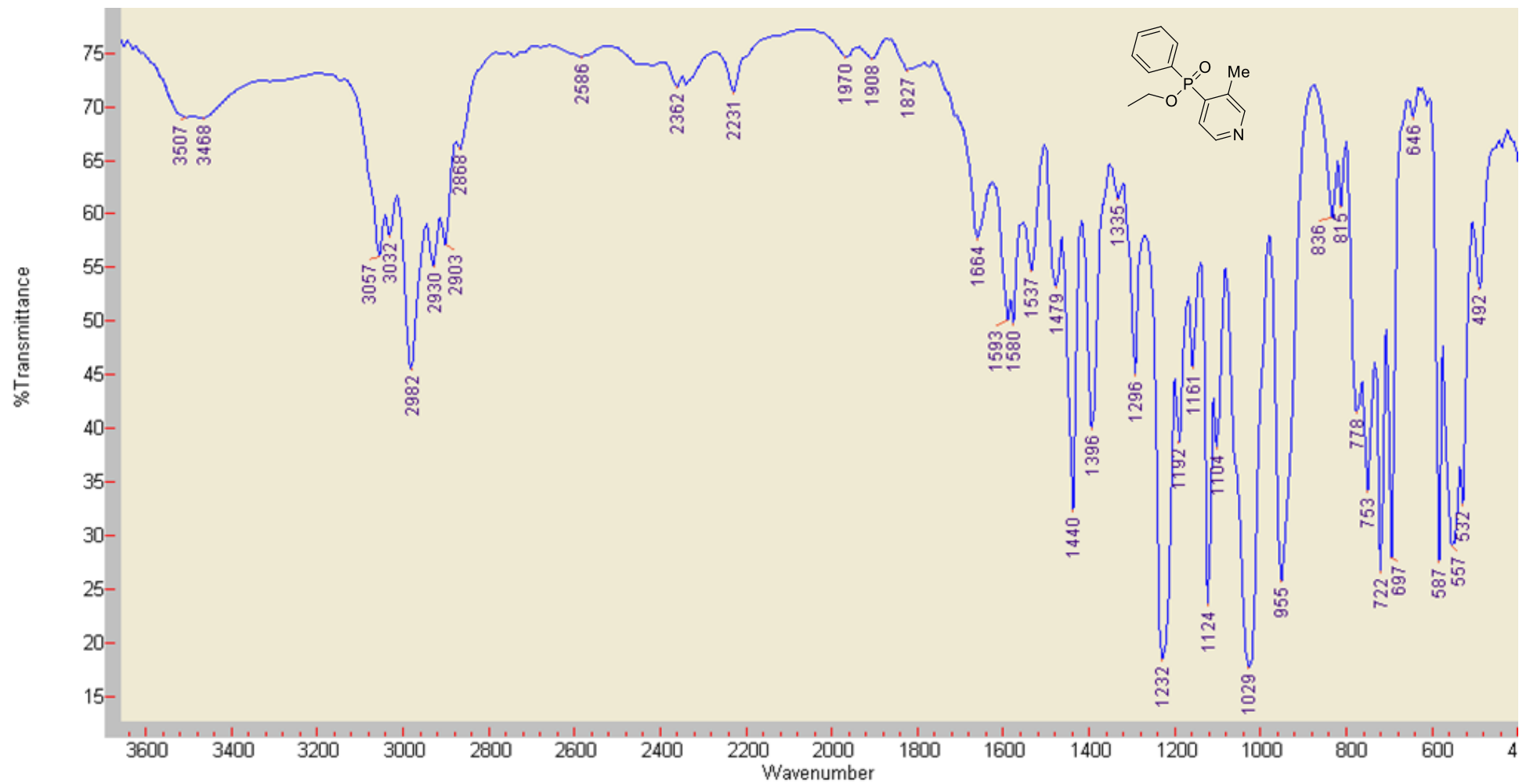


2. IR Spectra

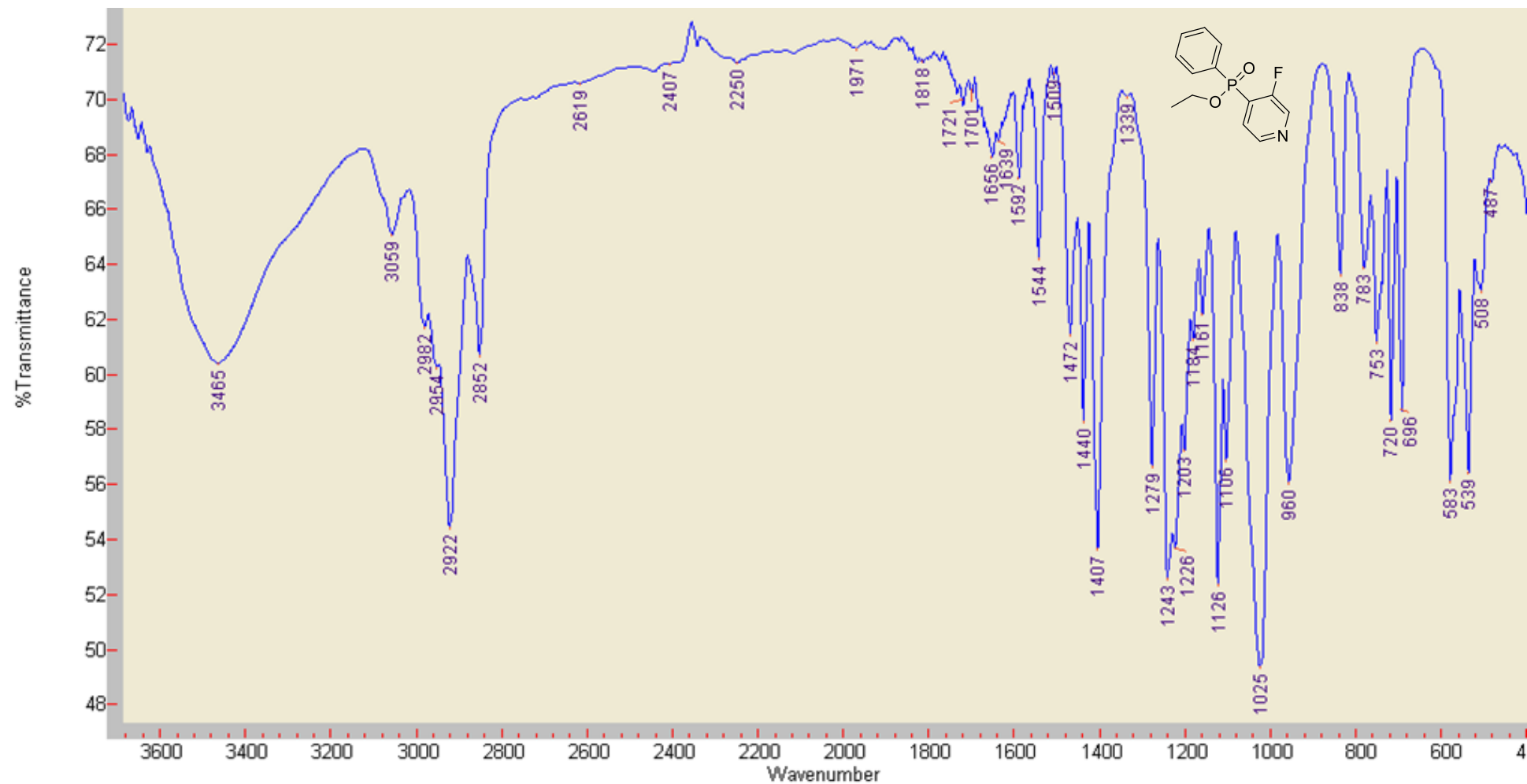
Ethyl phenyl(pyridin-4-yl)phosphinate (3aa)



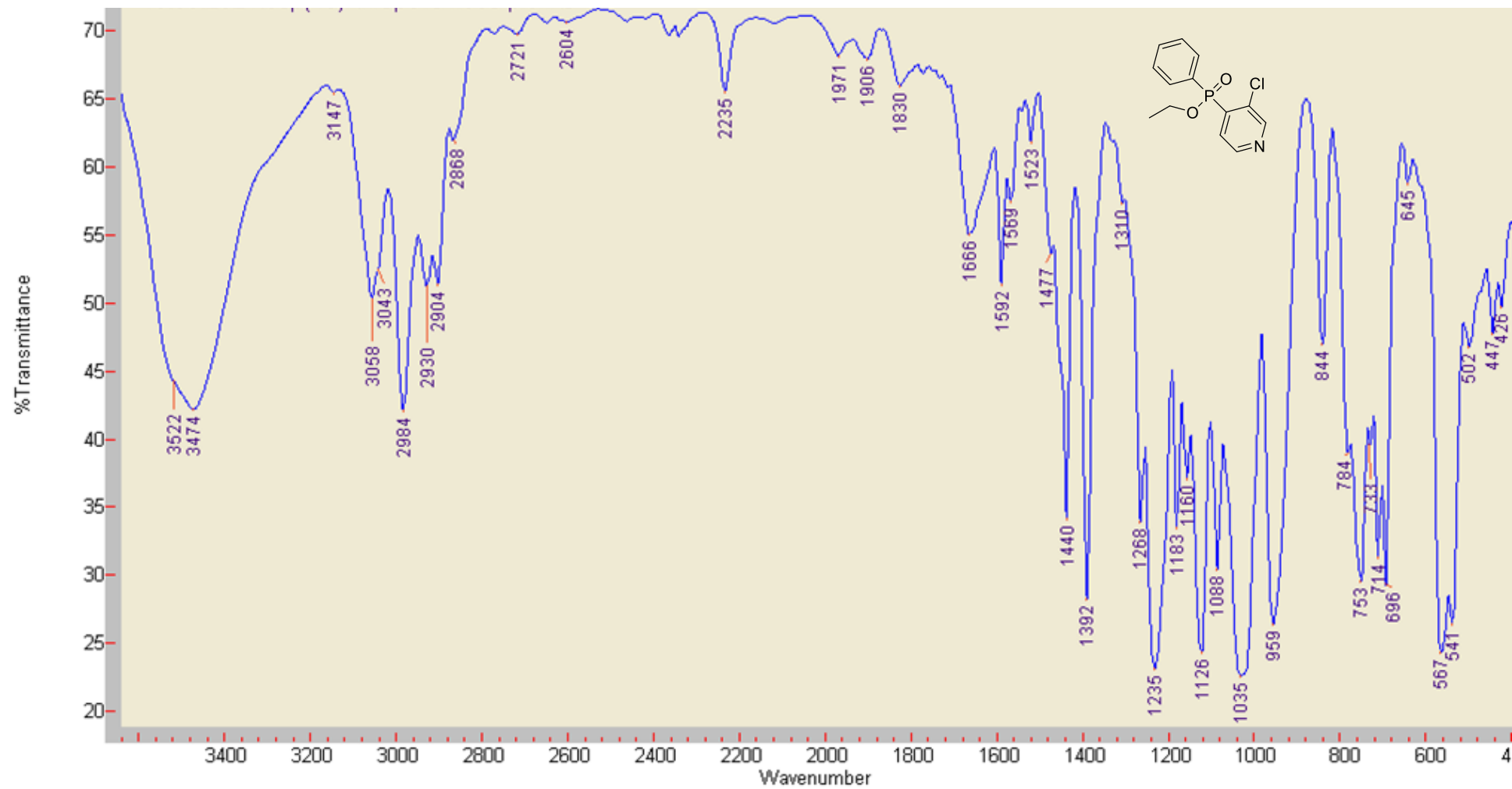
Ethyl (3-methylpyridin-4-yl)phenylphosphinate (3ba)



Ethyl (3-fluoropyridin-4-yl)phenylphosphinate (3ca)



Ethyl (3-chloropyridin-4-yl)phenylphosphinate (3da)



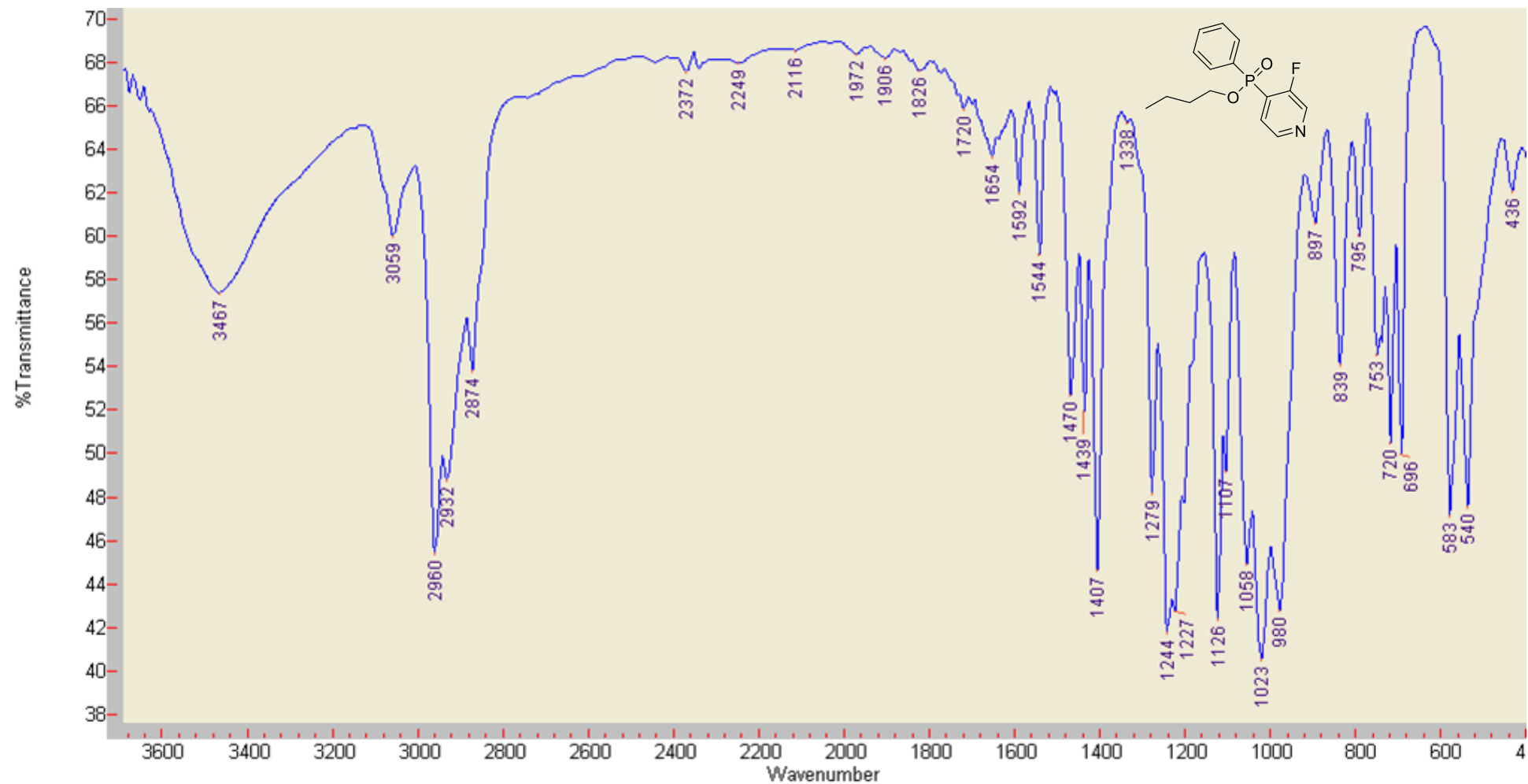
Butyl phenyl(pyridin-4-yl)phosphinate (3ab)



Butyl (3-methylpyridin-4-yl)phenylphosphinate (3bb)



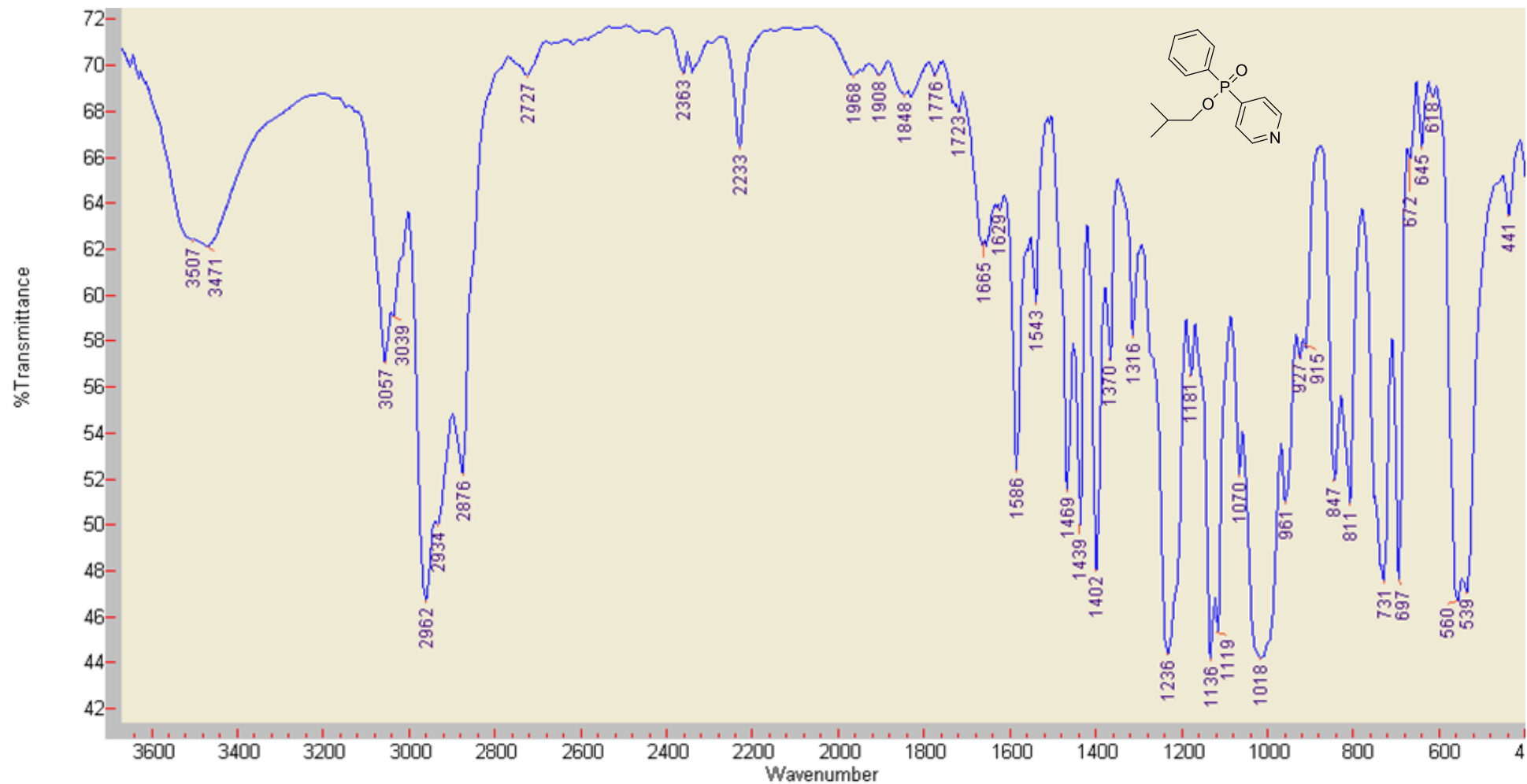
Butyl (3-fluoropyridin-4-yl)phenylphosphinate (3cb)



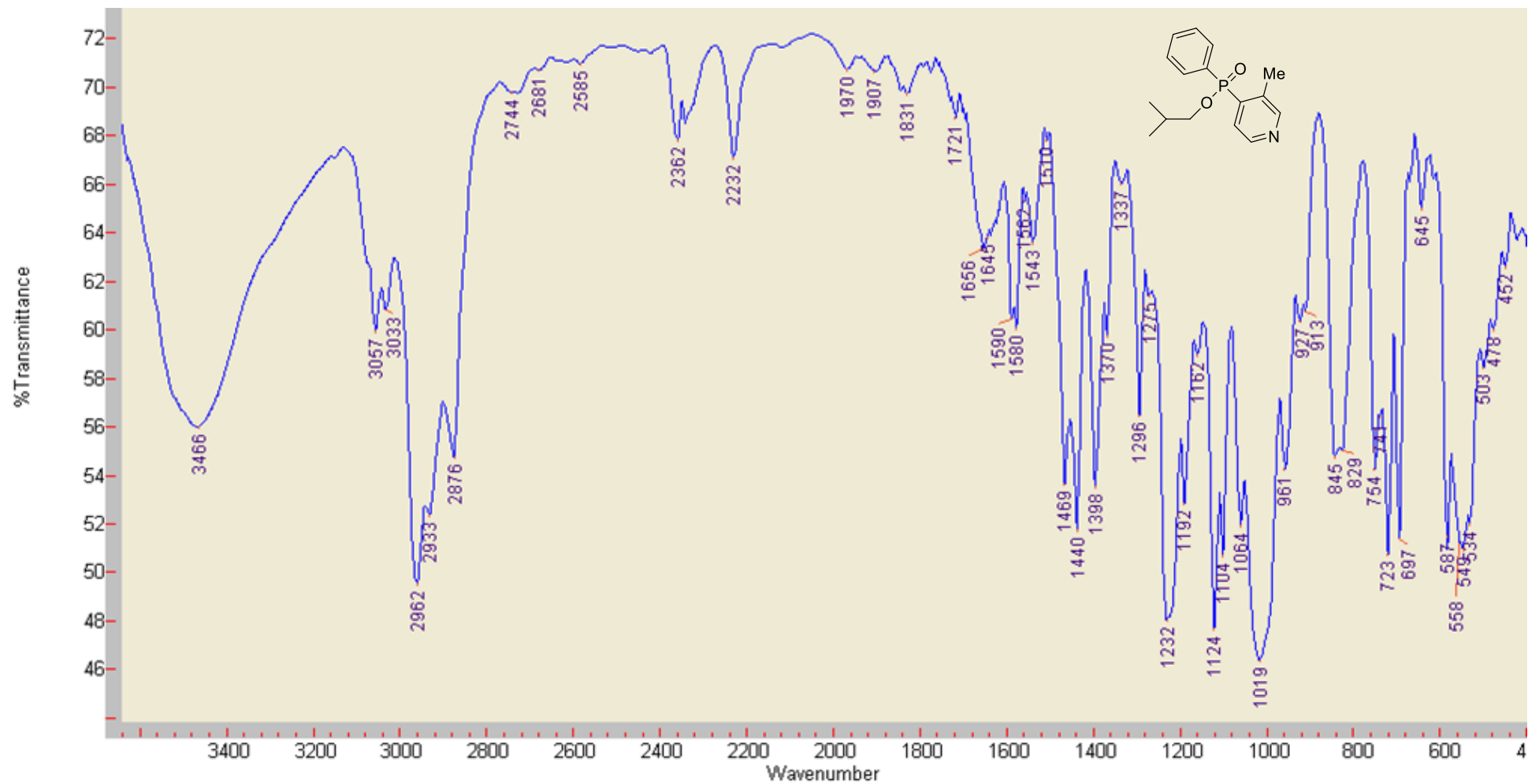
Butyl (3-chloropyridin-4-yl)phenylphosphinate (3db)



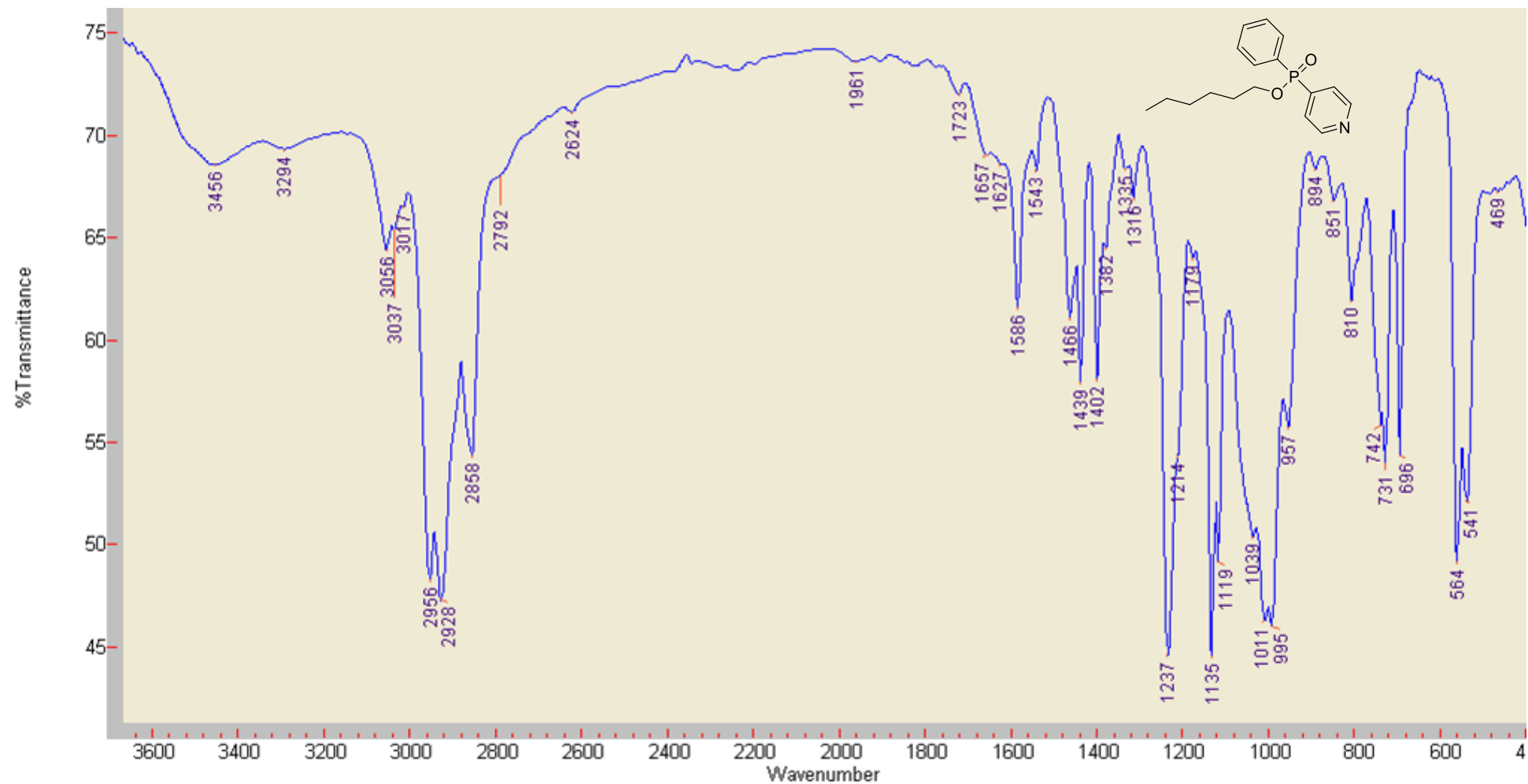
2-Methylpropyl phenyl(pyridin-4-yl)phosphinate (3ac)



2-Methylpropyl (3-methylpyridin-4-yl)phenylphosphinate (3bc)



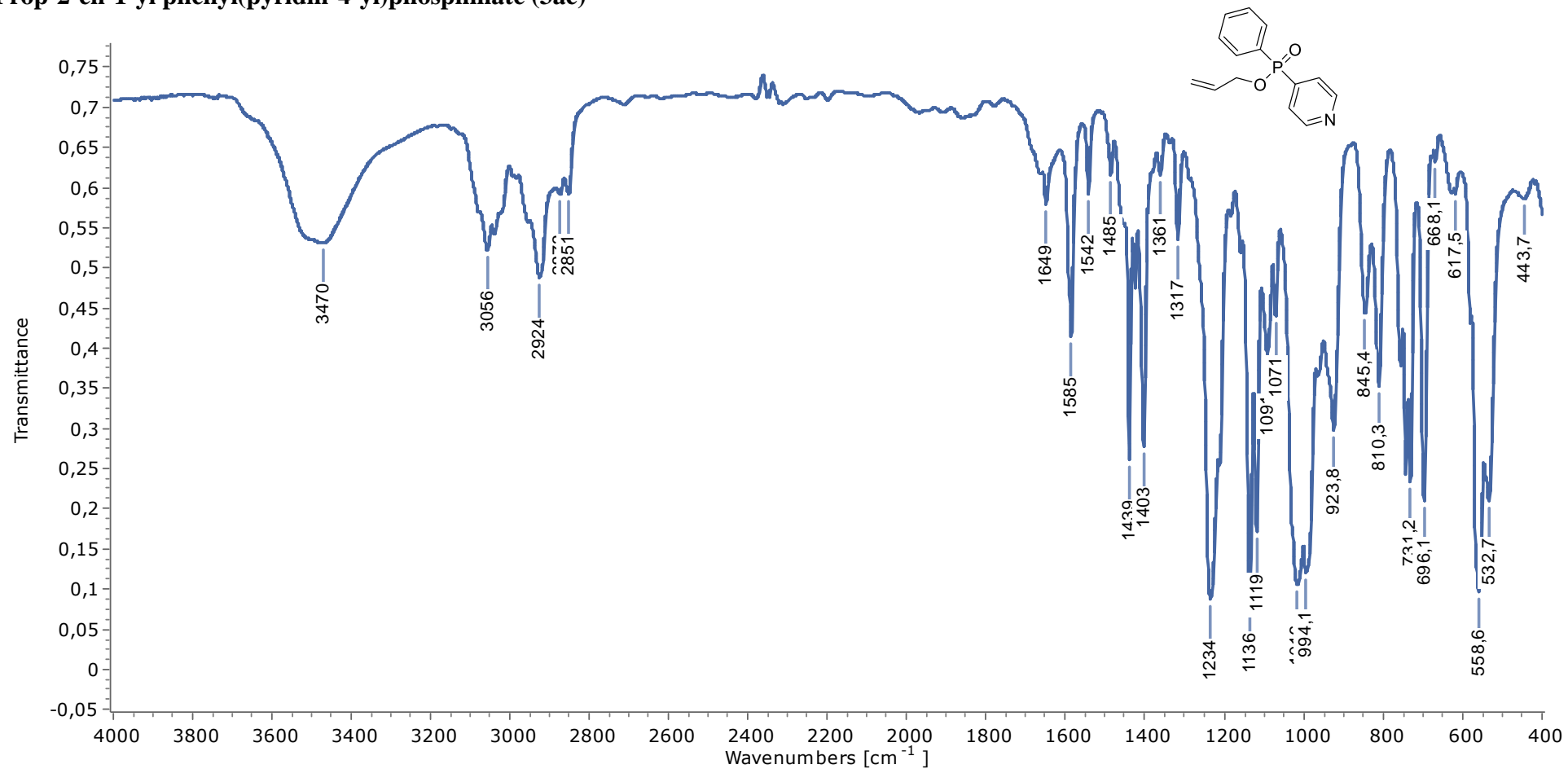
Hexyl phenyl(pyridin-4-yl)phosphinate (3ad)



Hexyl (3-methylpyridin-4-yl)phenylphosphinate (3bd)



Prop-2-en-1-yl phenyl(pyridin-4-yl)phosphinate (3ae)



Prop-2-en-1-yl (3-methylpyridin-4-yl)phenylphosphinate (3be)

