

Supporting information

Oxidative [3+2]cycloaddition of alkynylphosphonates to heterocyclic *N*-imines: synthesis of pyrazolo[1,5-*a*]pyridine-3-phosphonates

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Crystallographic data

Crystallographic data for diethyl (2,7-diphenylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (3d). Formula $C_{23}H_{19}N_2O_3P$ (without solvent), $M = 402.37$, triclinic, space group $P-1$, $a = 7.7535(4)$, $b = 10.9029(7)$, $c = 14.0556(9)$ Å, $\alpha = 94.892(3)$, $\beta = 97.428(3)$, $\gamma = 103.153(3)^\circ$, $V = 1139.19(12)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.173$ g·cm⁻³, $\mu = 0.144$ mm⁻¹, min/max transmission = 0.8816/0.9391, $\theta_{\text{max}} = 26.1^\circ$, measured 21669, unique 4514 ($R_{\text{int}} = 0.0467$), observed [$I_o > 2\sigma(I)$] 3004 reflections, $R_1 = 0.0481$ (I_o), $wR_2 = 0.1339$ (all), Gof = 1.023, $\Delta\rho_{\text{max}} = 0.32$, $\Delta\rho_{\text{min}} = -0.31$ e·Å⁻³. CCDC 2001188.

Crystallographic data for diethyl (2-phenoxy[1,5-a]pyridin-3-yl)phosphonate (5u). Formula $C_{17}H_{19}N_2O_4P$, $M = 346.31$, monoclinic space group $P2_1/n$, $a = 9.9416(5)$, $b = 12.9865(5)$, $c = 13.7882(8)$ Å, $\beta = 92.659(2)$, $V = 1778.23(15)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.294$ g·cm⁻³, $\mu = 0.177$ mm⁻¹, min/max transmission = 0.756/0.801, $\theta_{\text{max}} = 27.2^\circ$, measured 23274, unique 3933 ($R_{\text{int}} = 0.047$), observed [$I_o > 2\sigma(I)$] 3185 reflections, $R_1 = 0.071$ (I_o), $wR_2 = 0.211$ (all), Gof = 1.05, $\Delta\rho_{\text{max}} = 0.51$, $\Delta\rho_{\text{min}} = -0.50$ e·Å⁻³. CCDC 2122366.

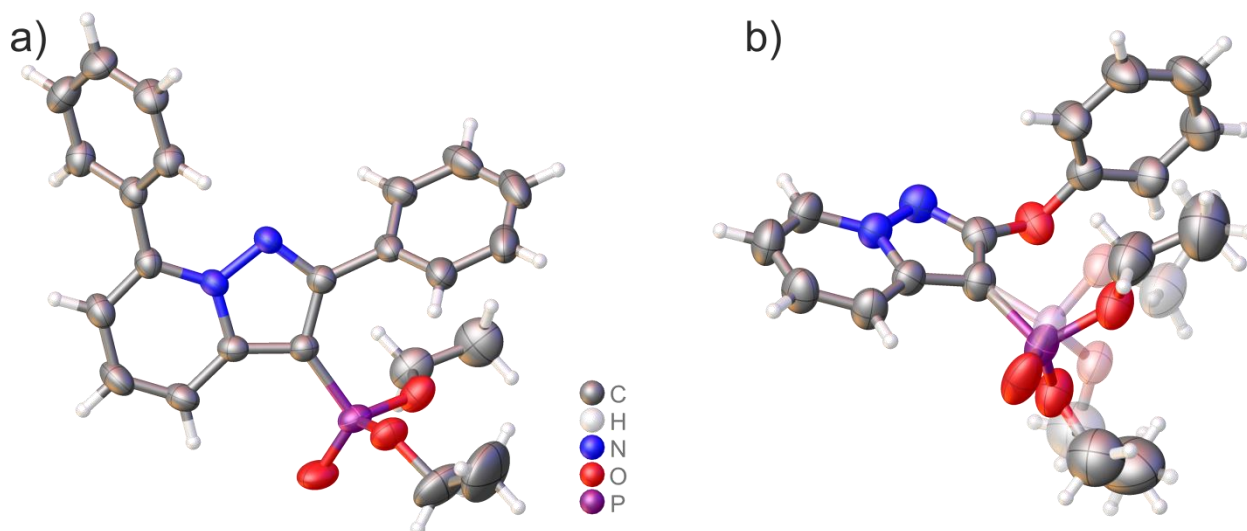
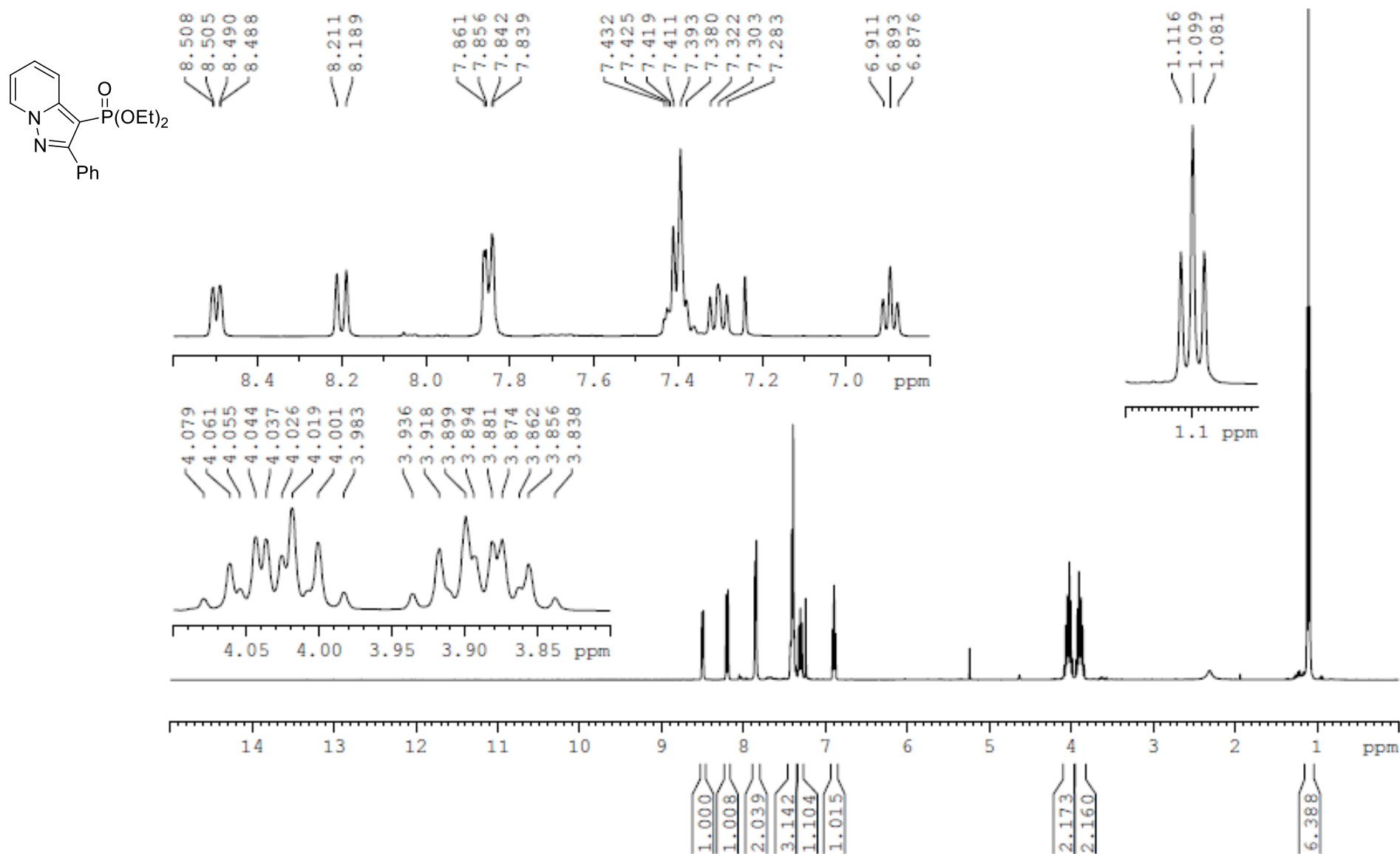


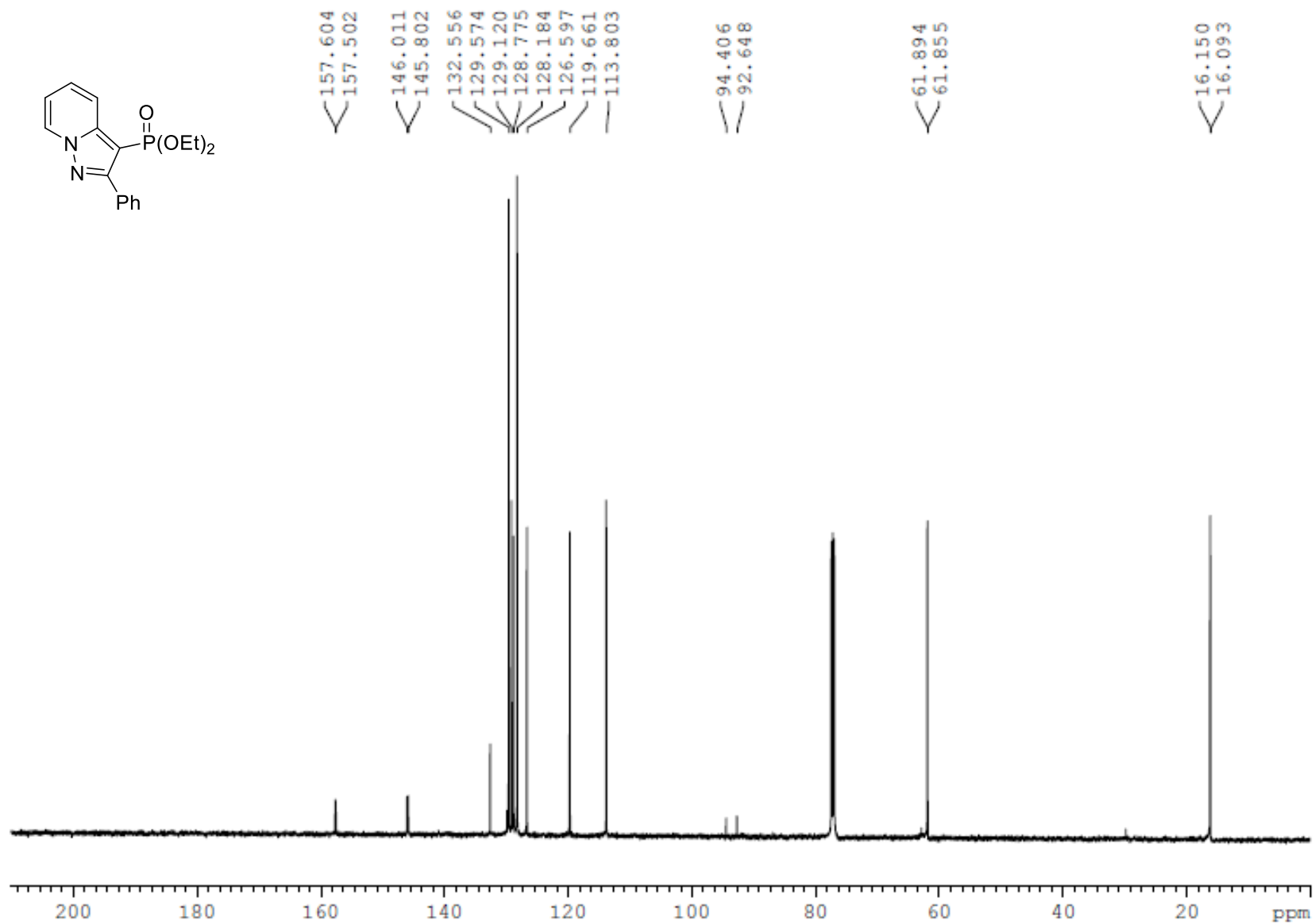
Figure S1. Crystal structures of pyrazolopyridines **3d** (A) and **5u** (B)

Copies of NMR spectra.

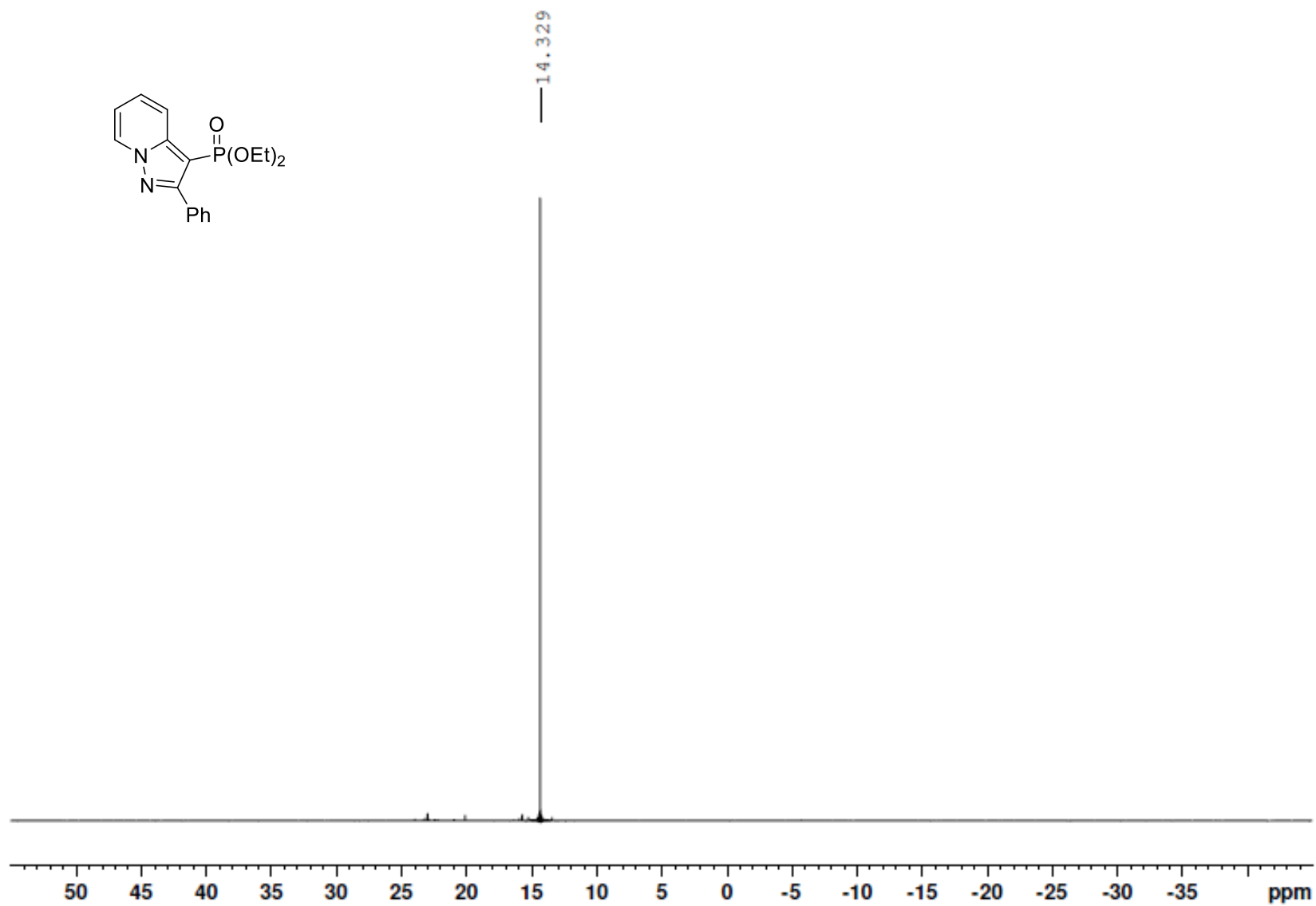
Diethyl (2-phenylpyrazolo[1,5-*a*]pyridin-3-yl)phosphonate (3a) ¹H NMR.



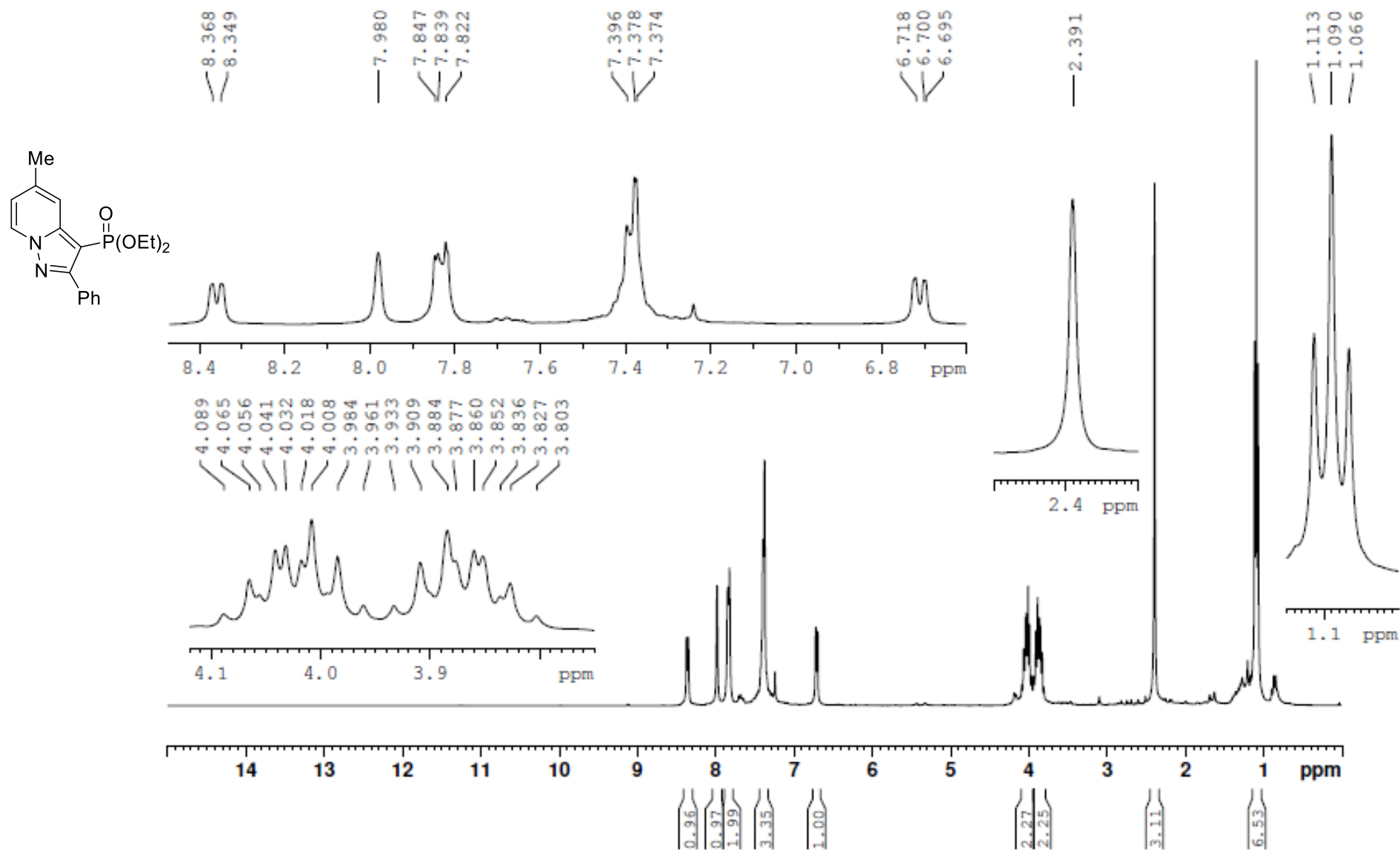
Diethyl (2-phenylpyrazolo[1,5-*a*]pyridin-3-yl)phosphonate (3a) ^{13}C NMR.



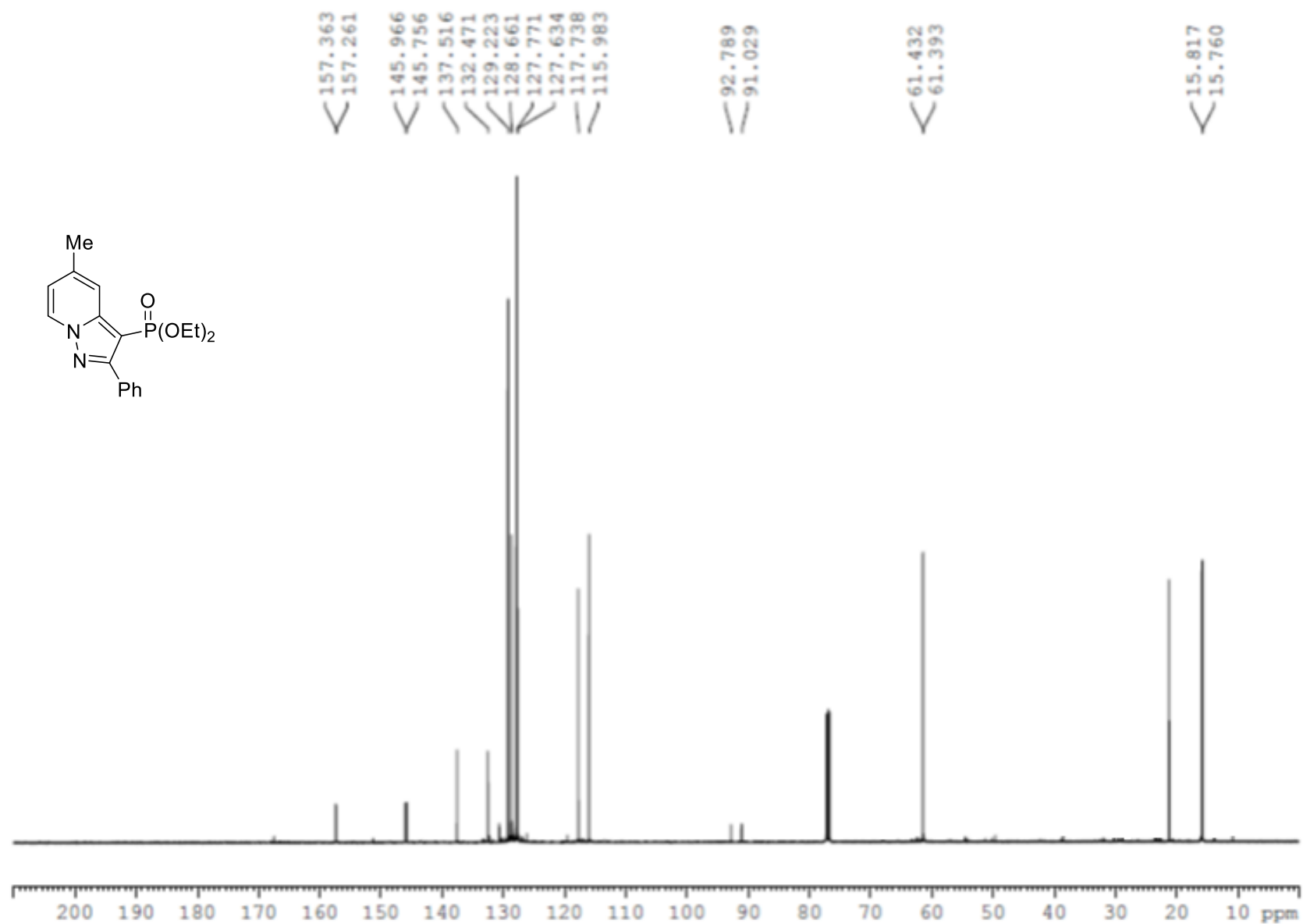
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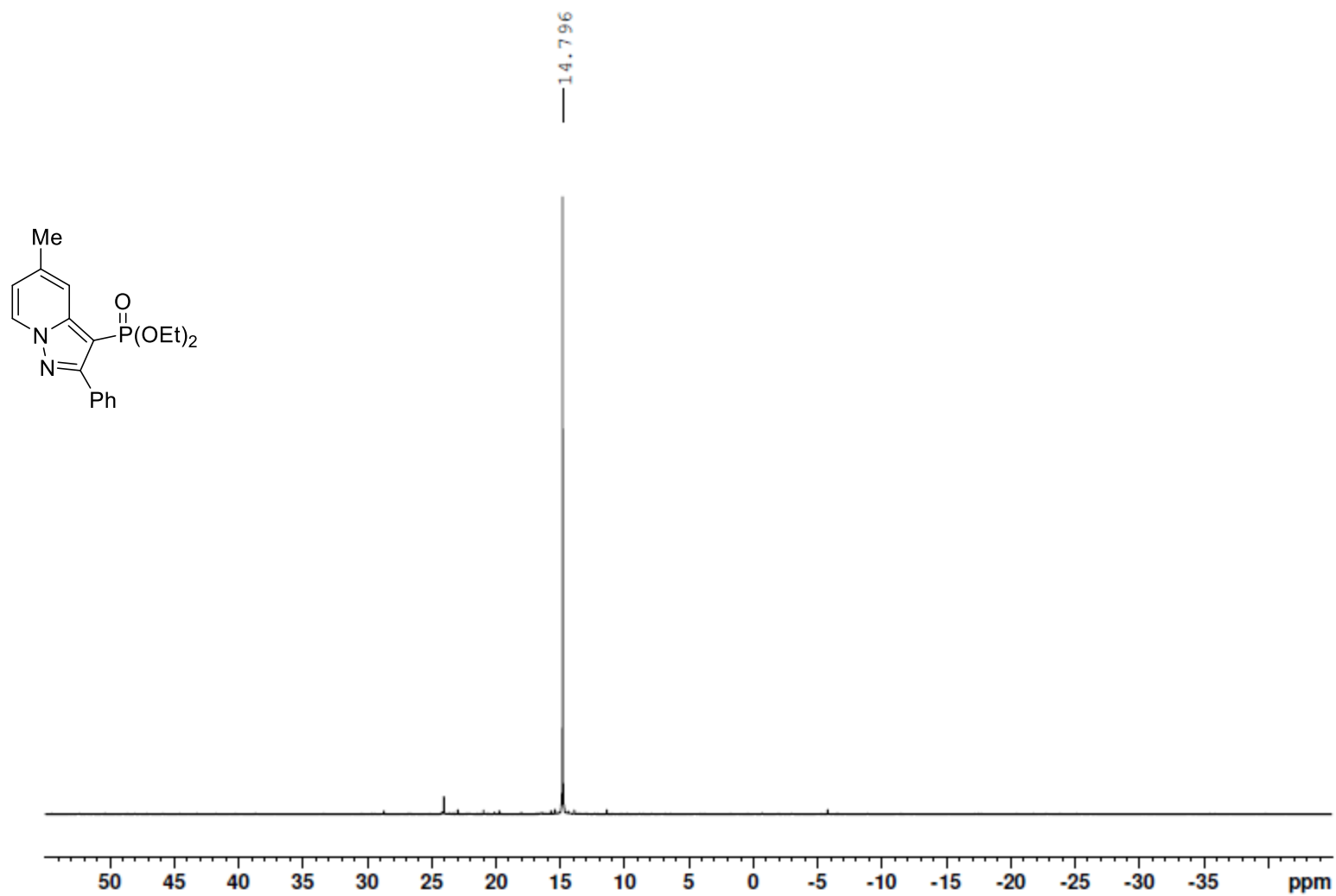
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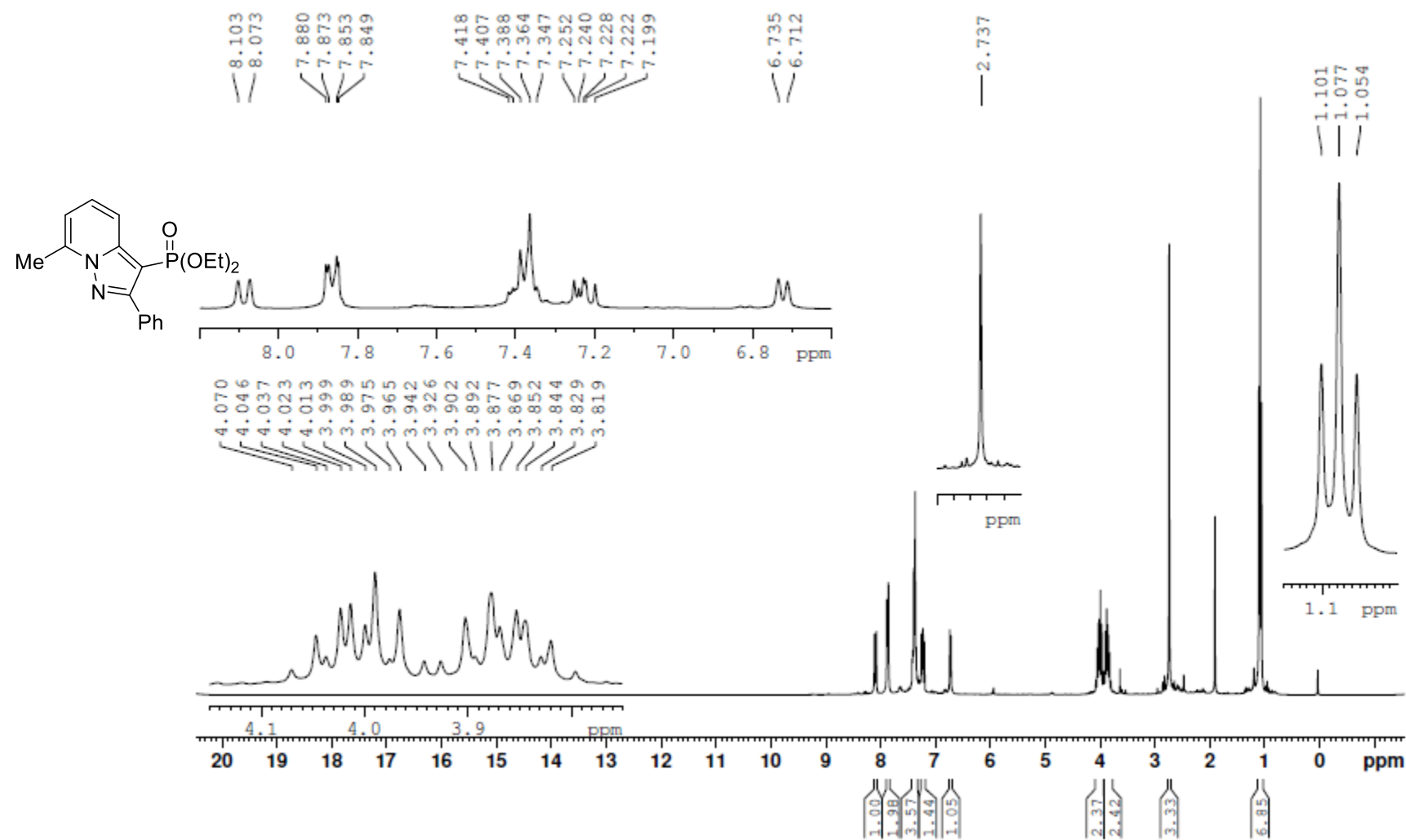
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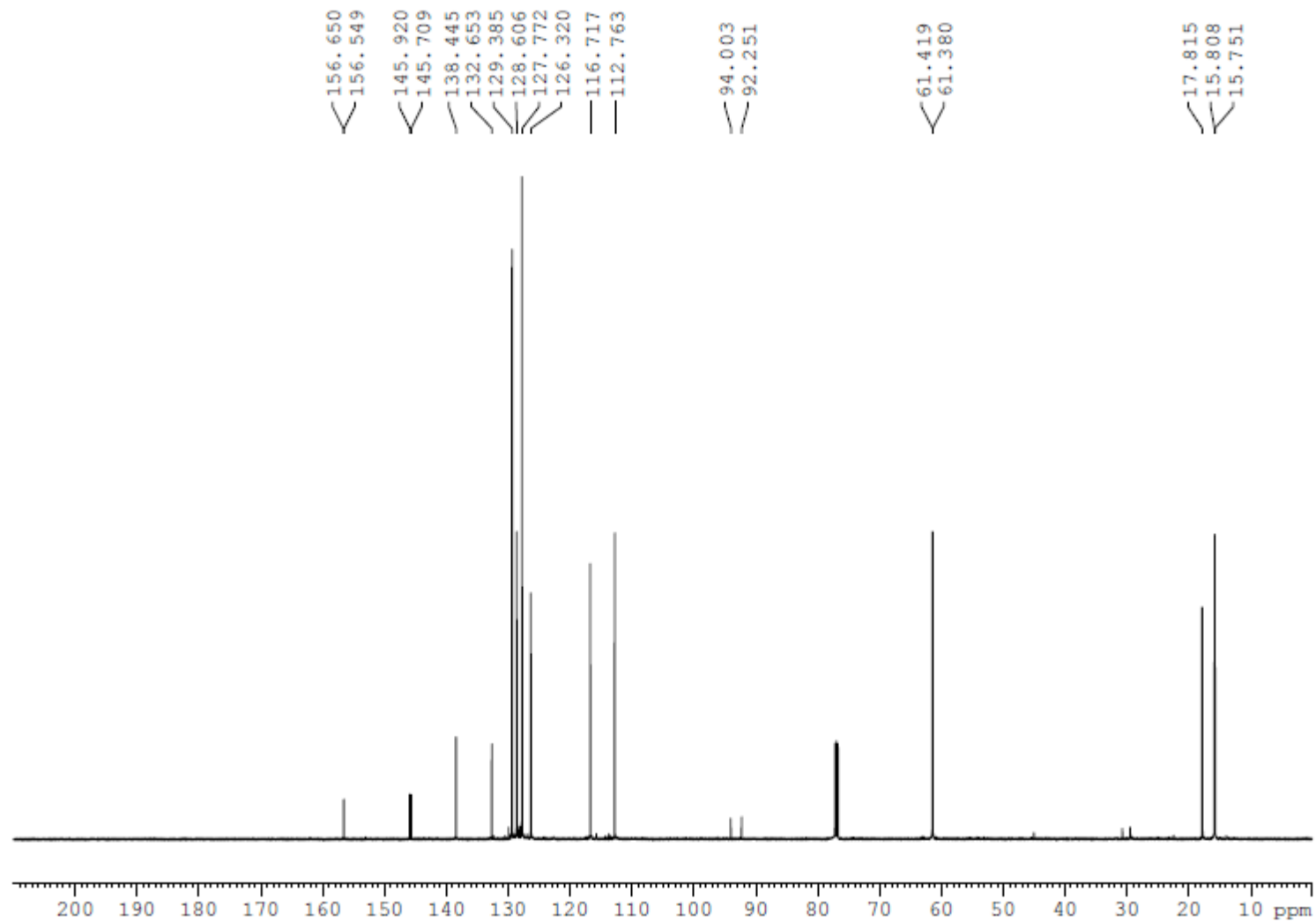
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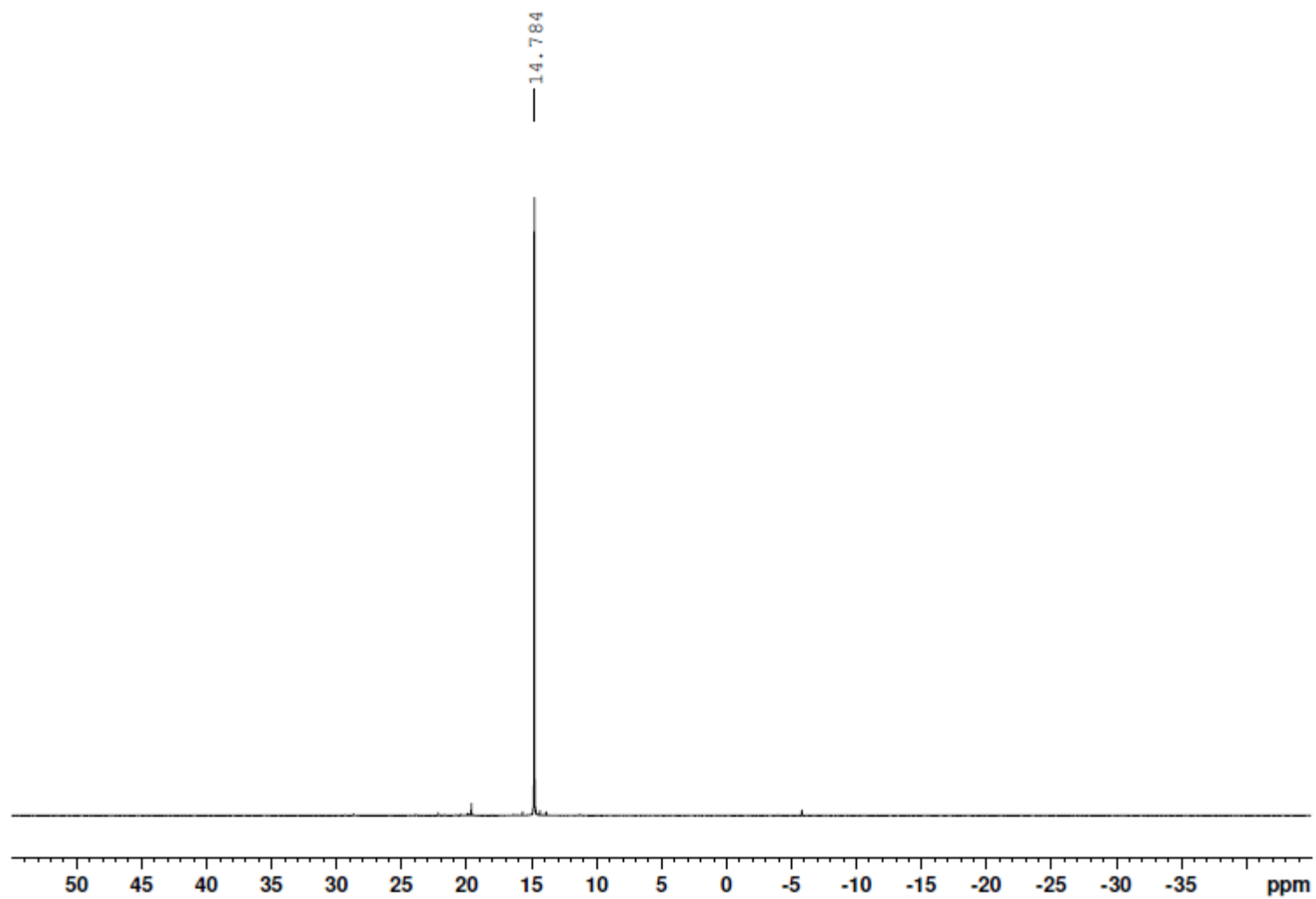
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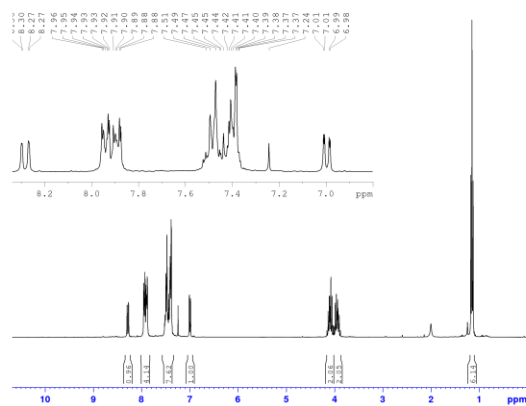
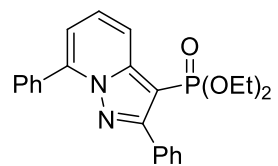
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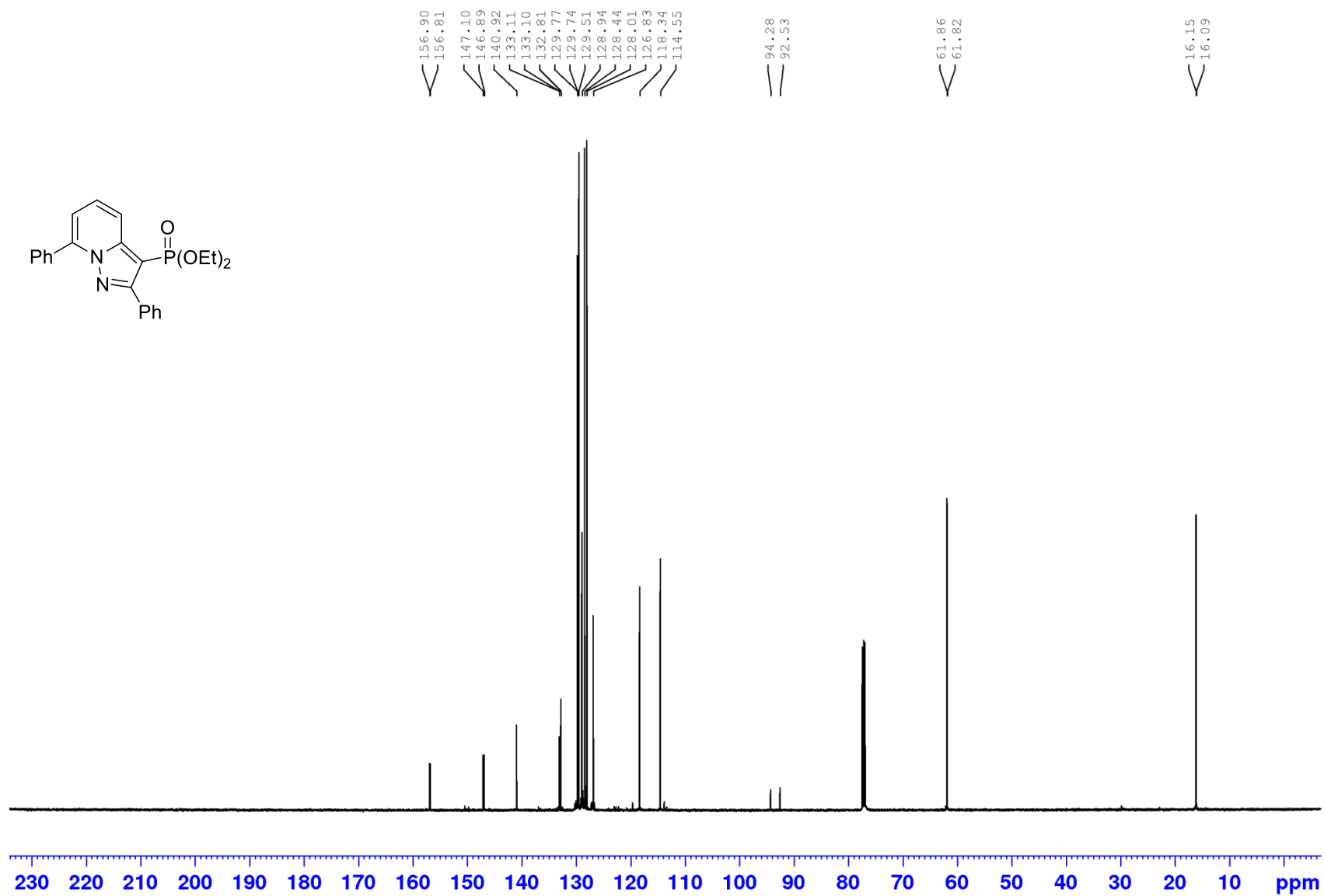
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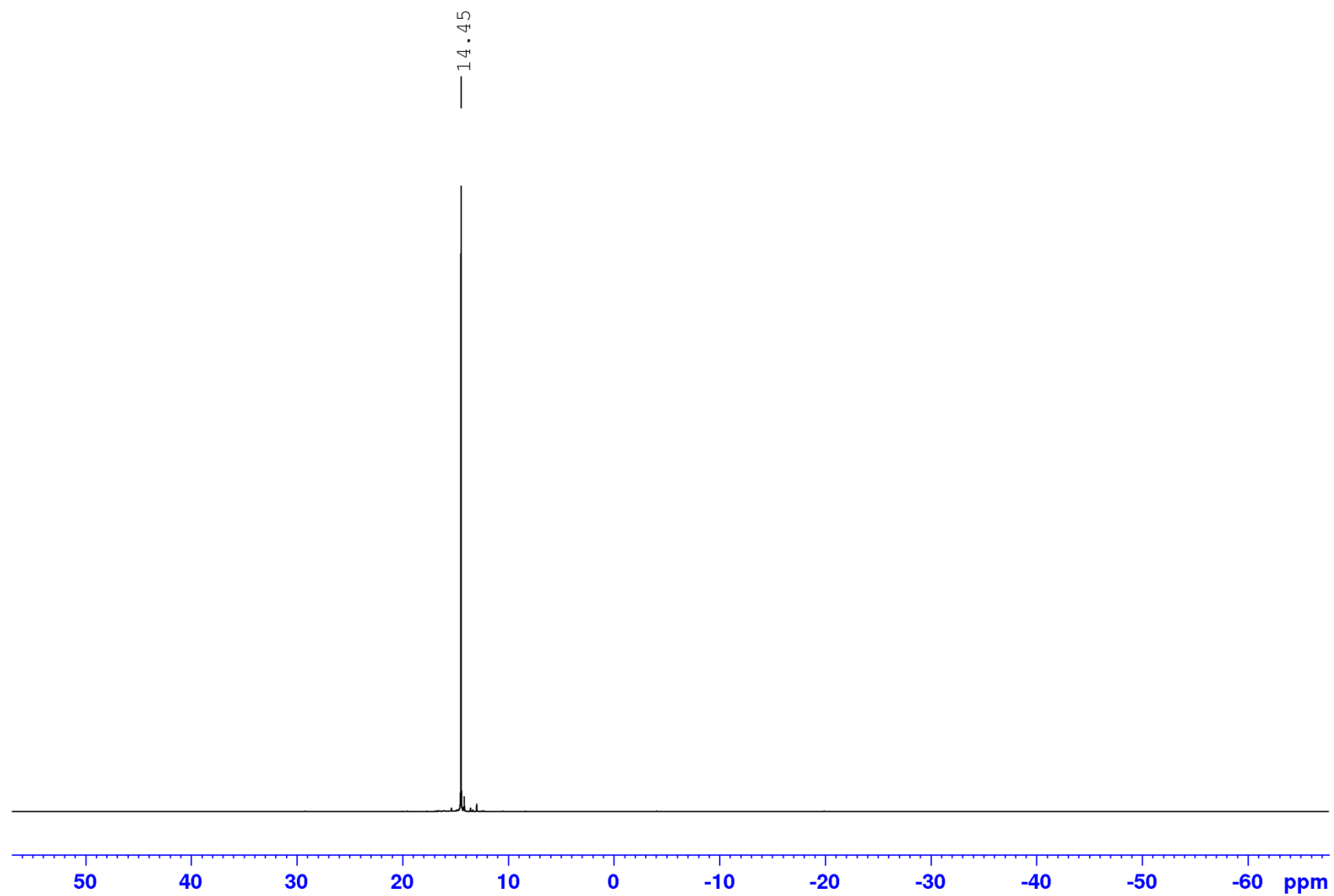
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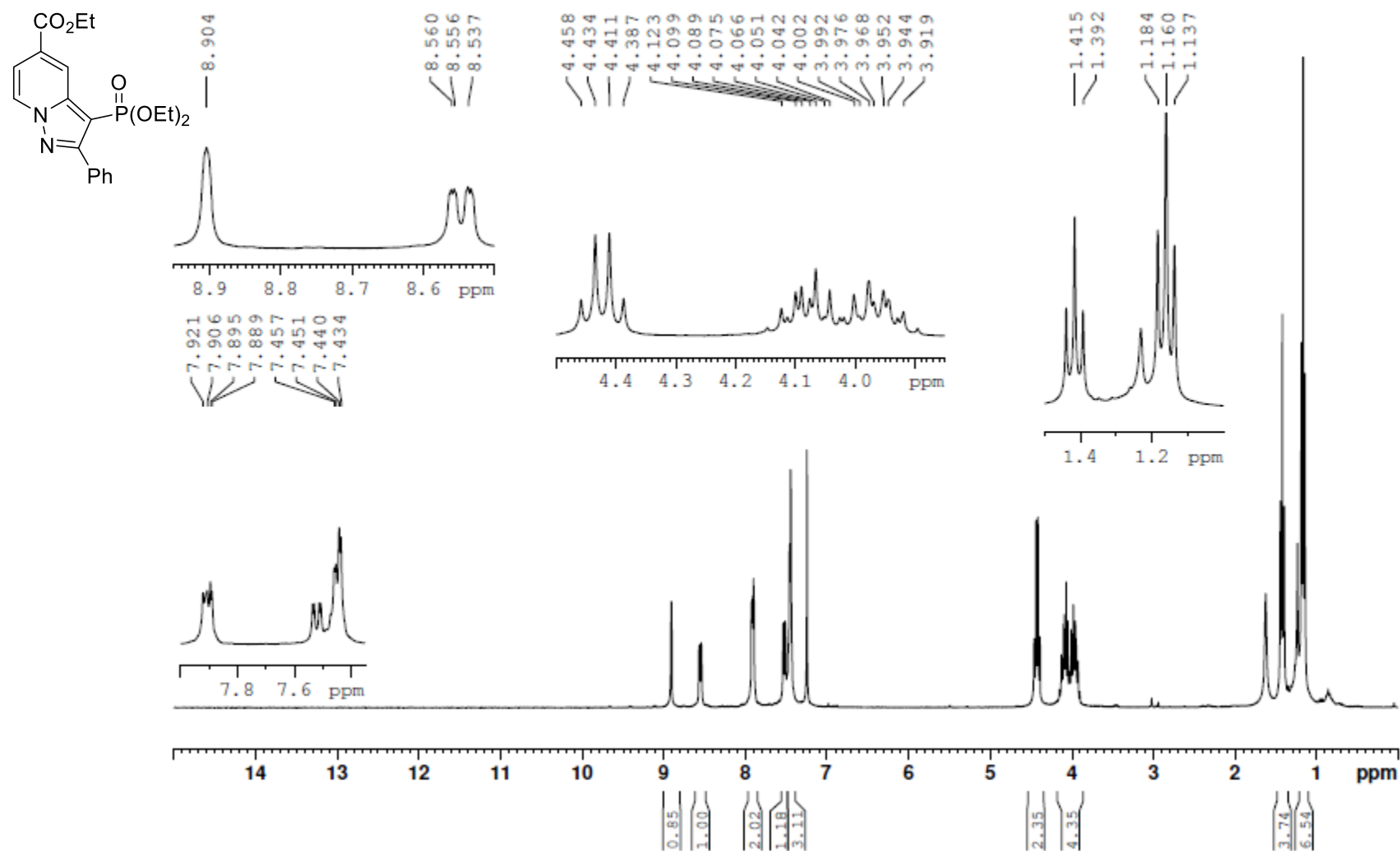
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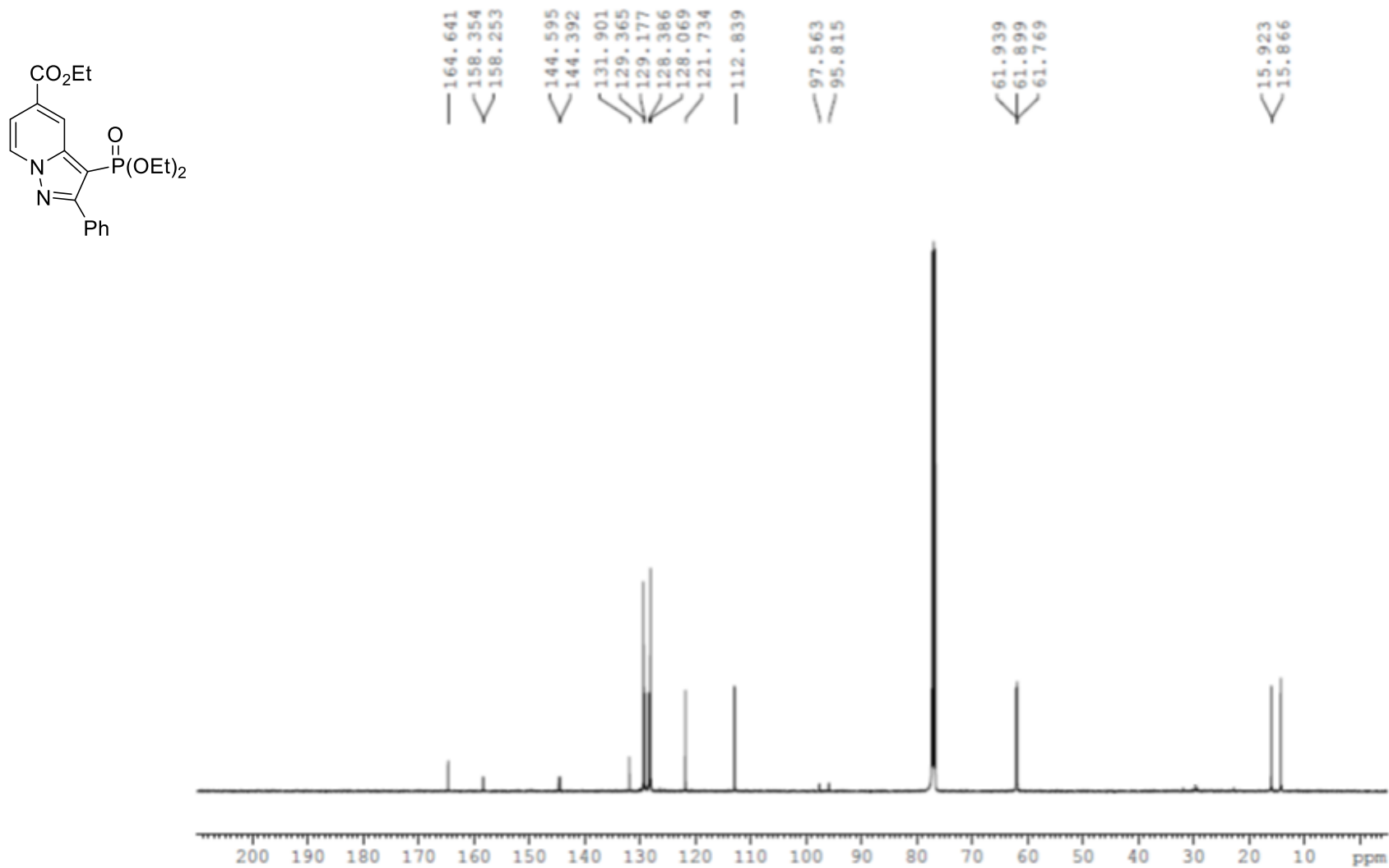
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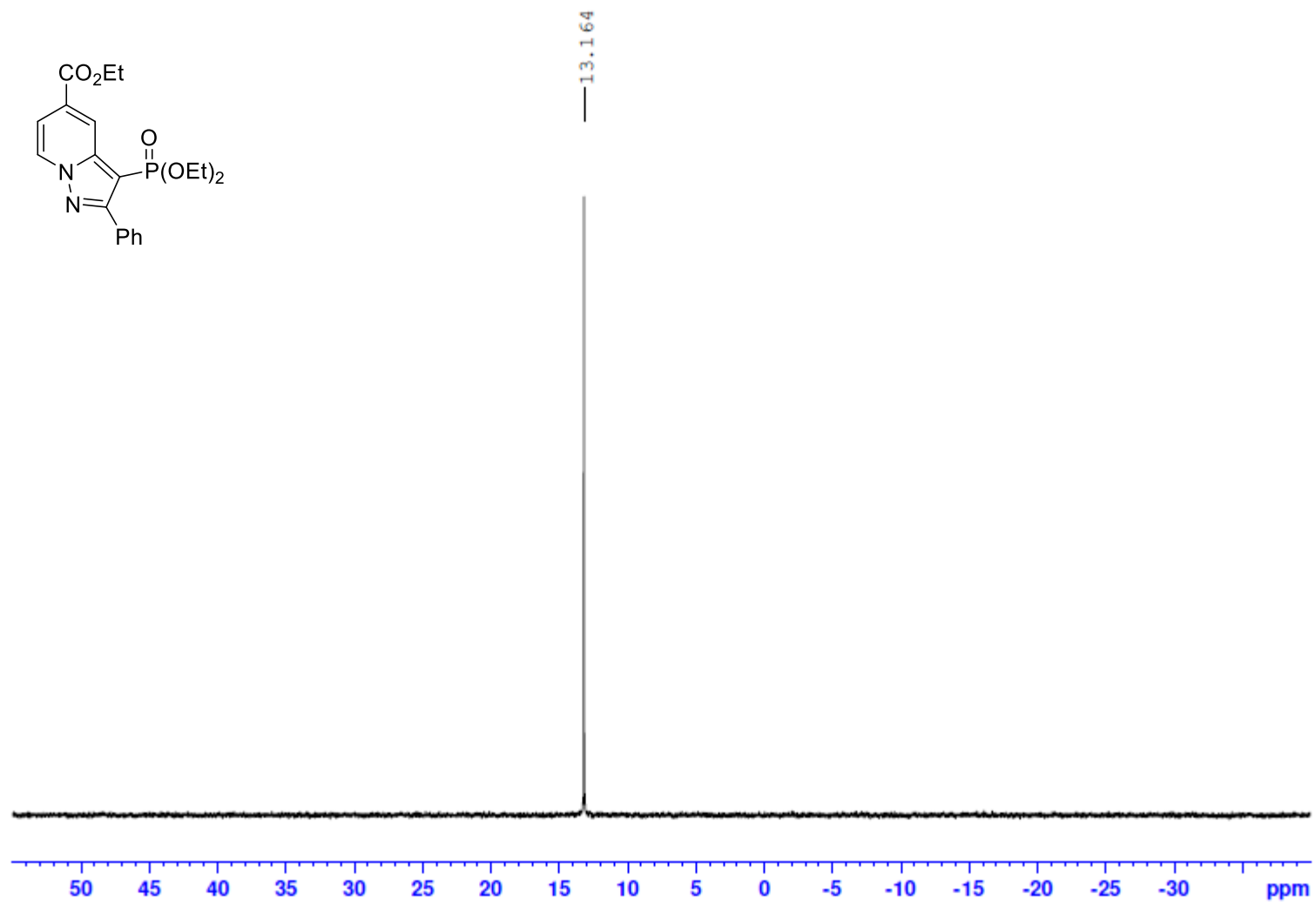
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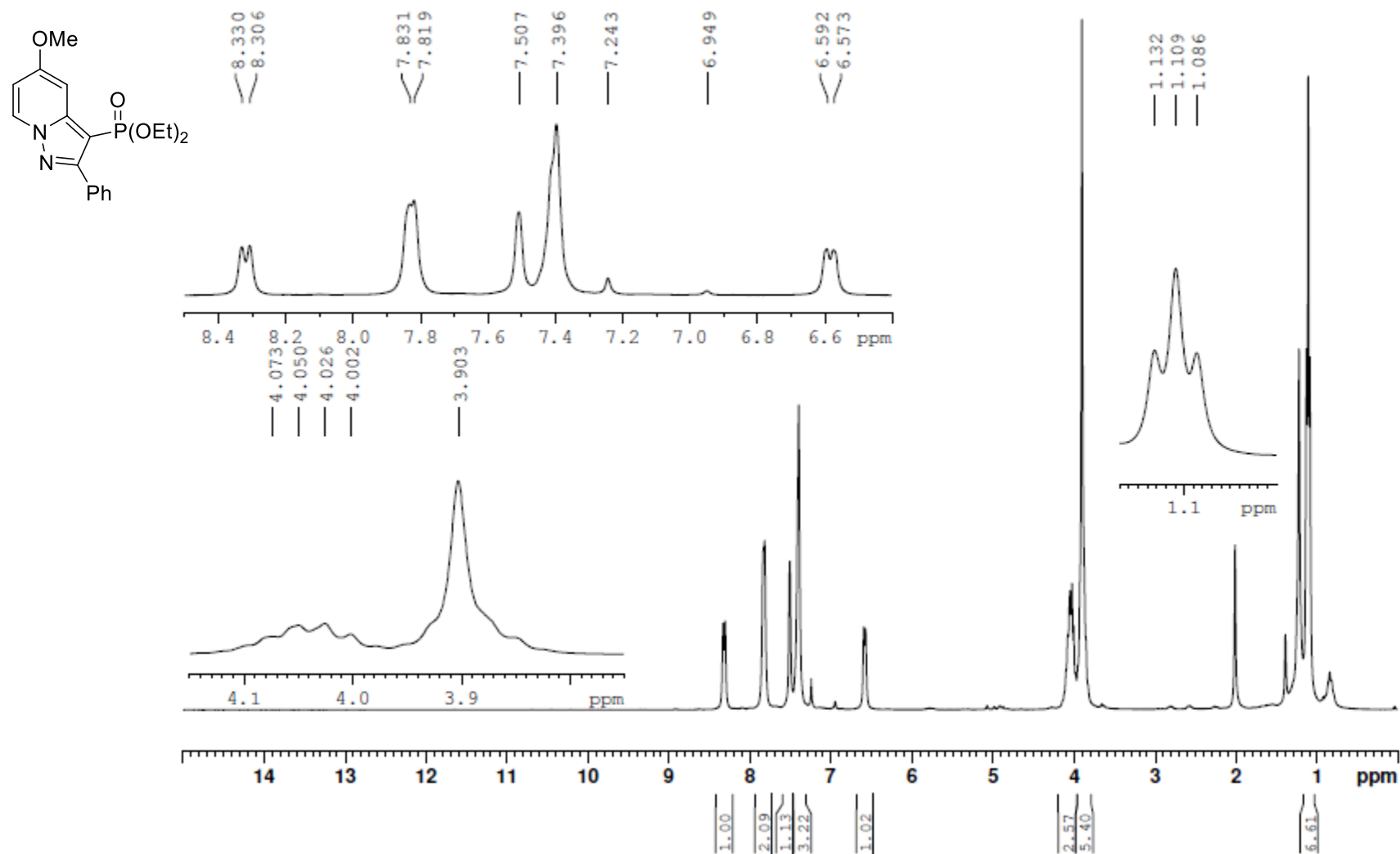
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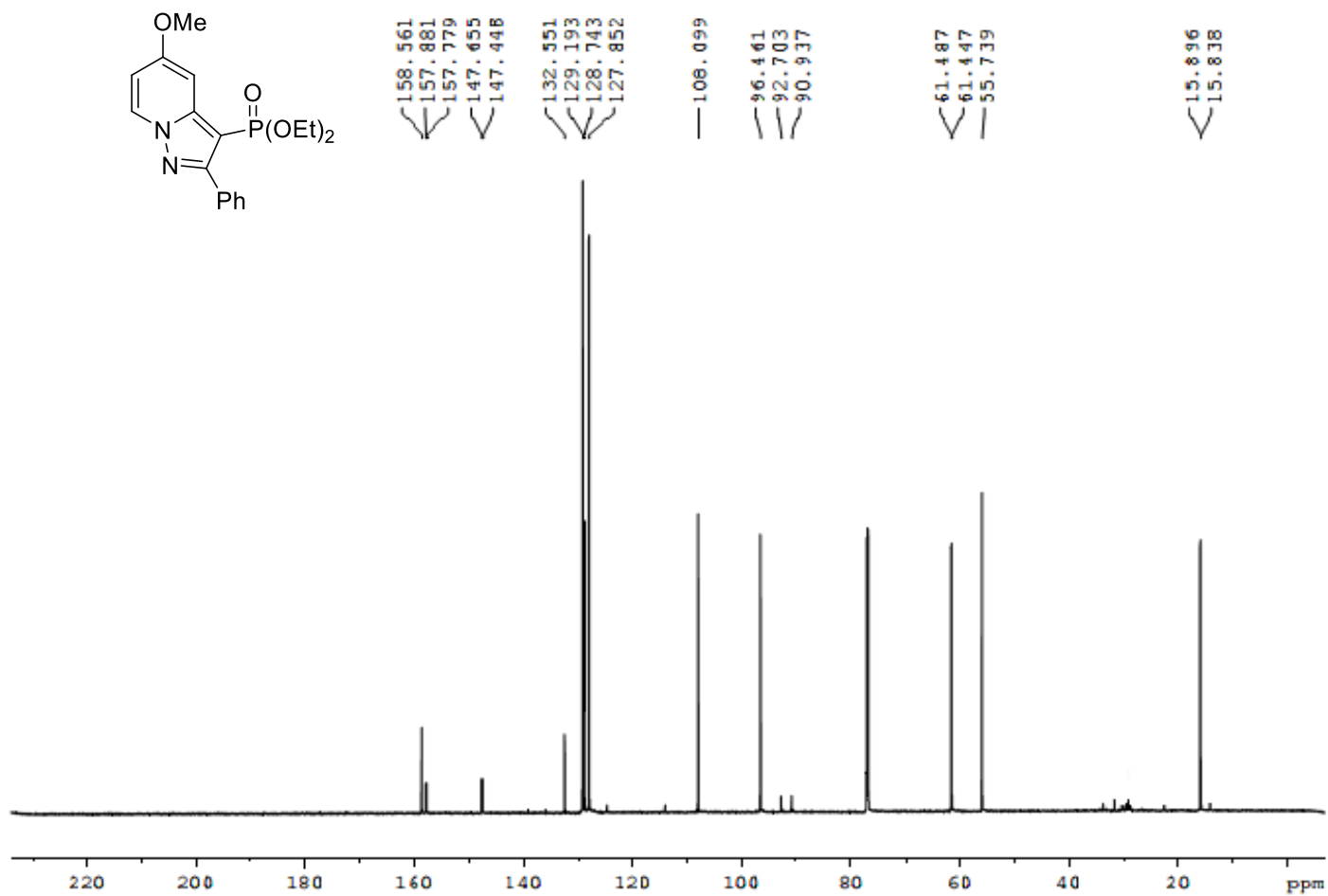
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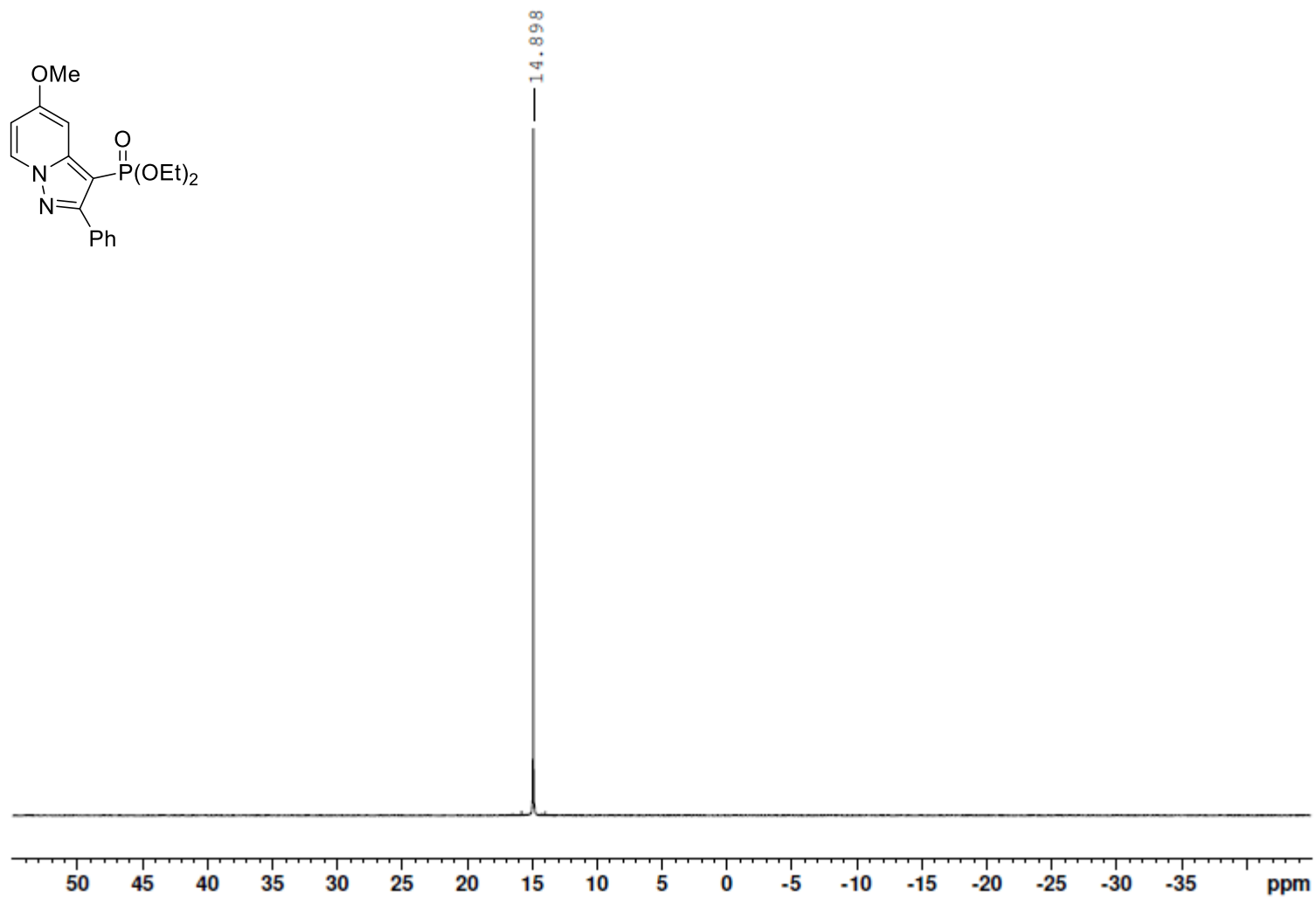
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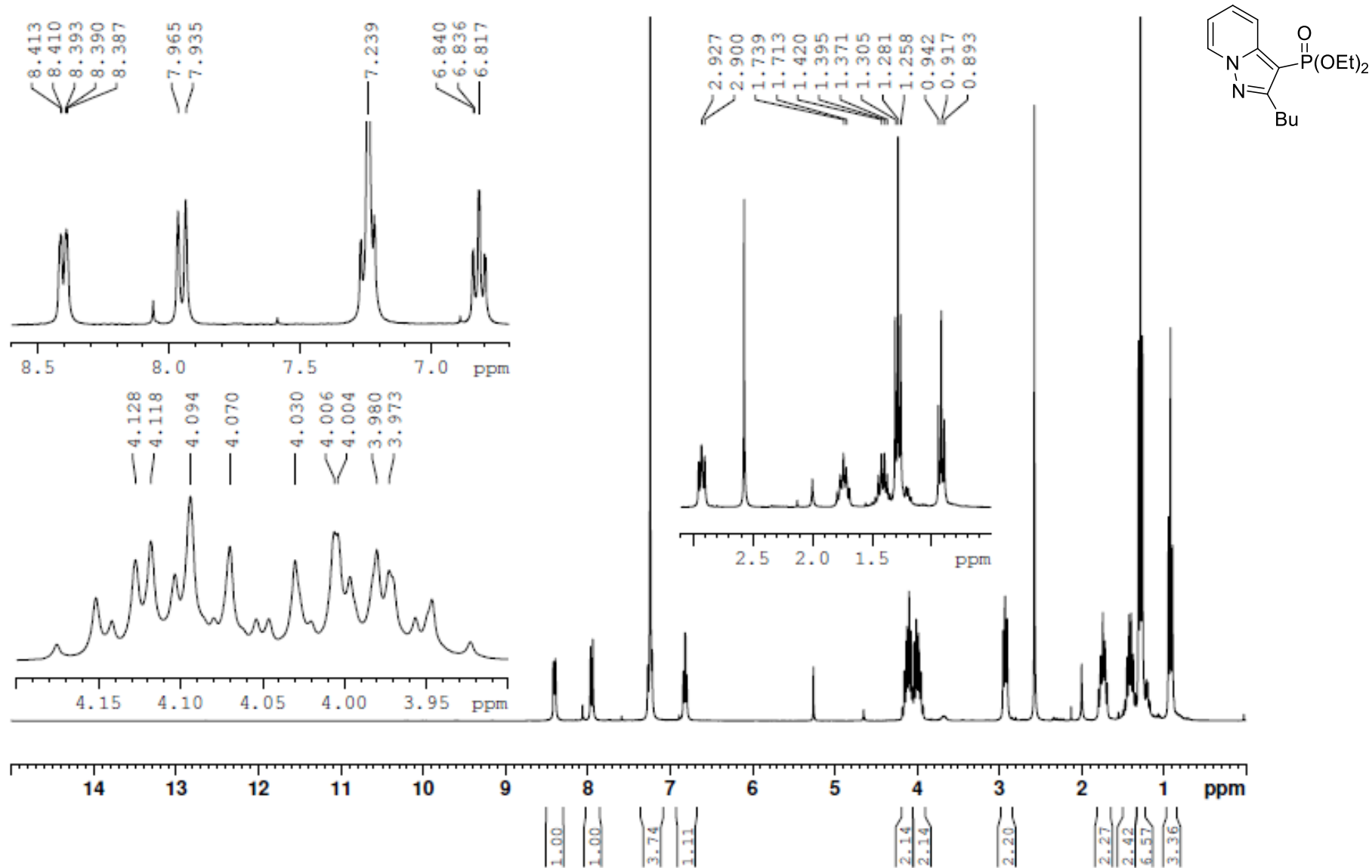
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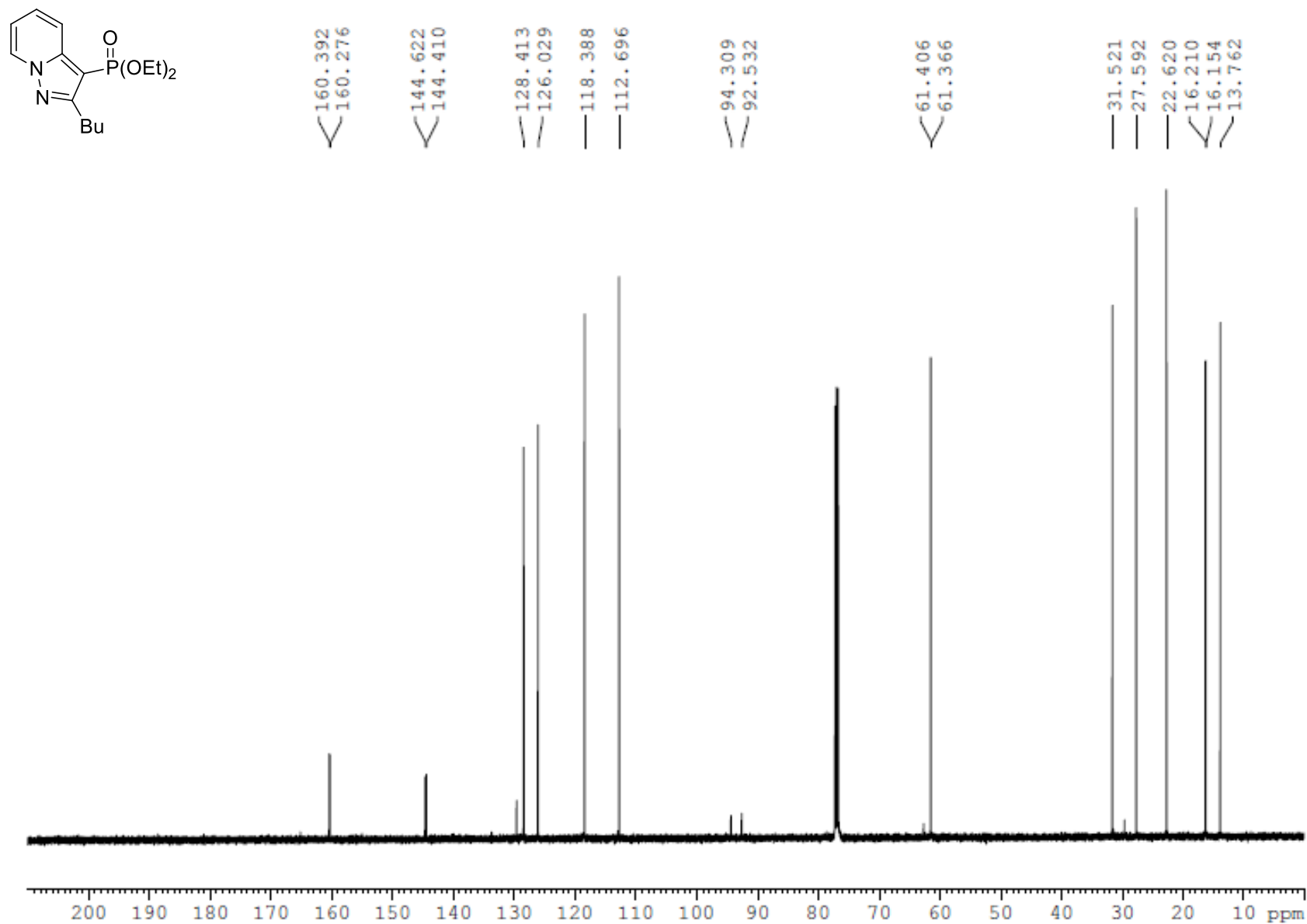
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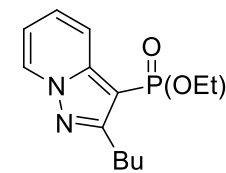
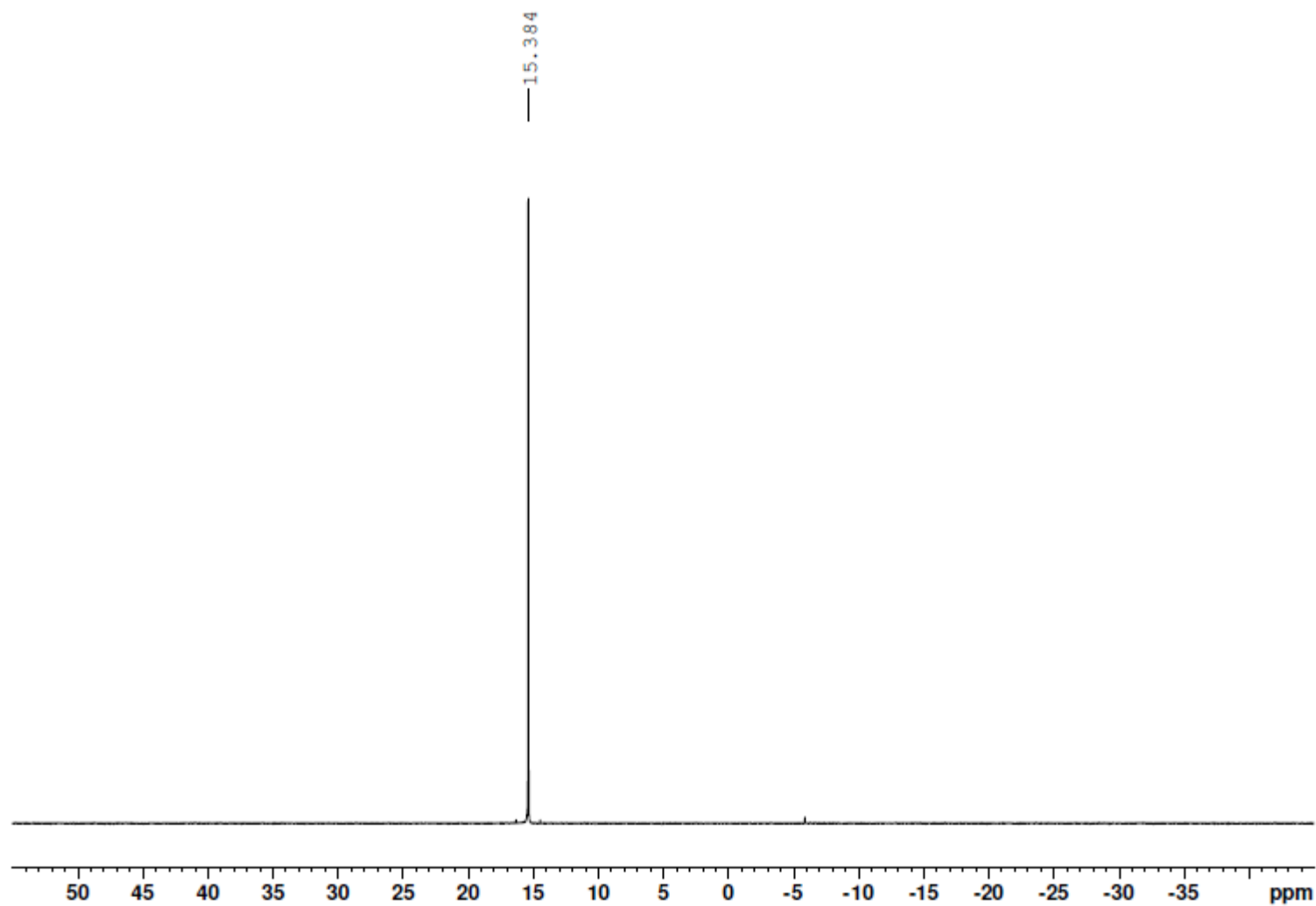
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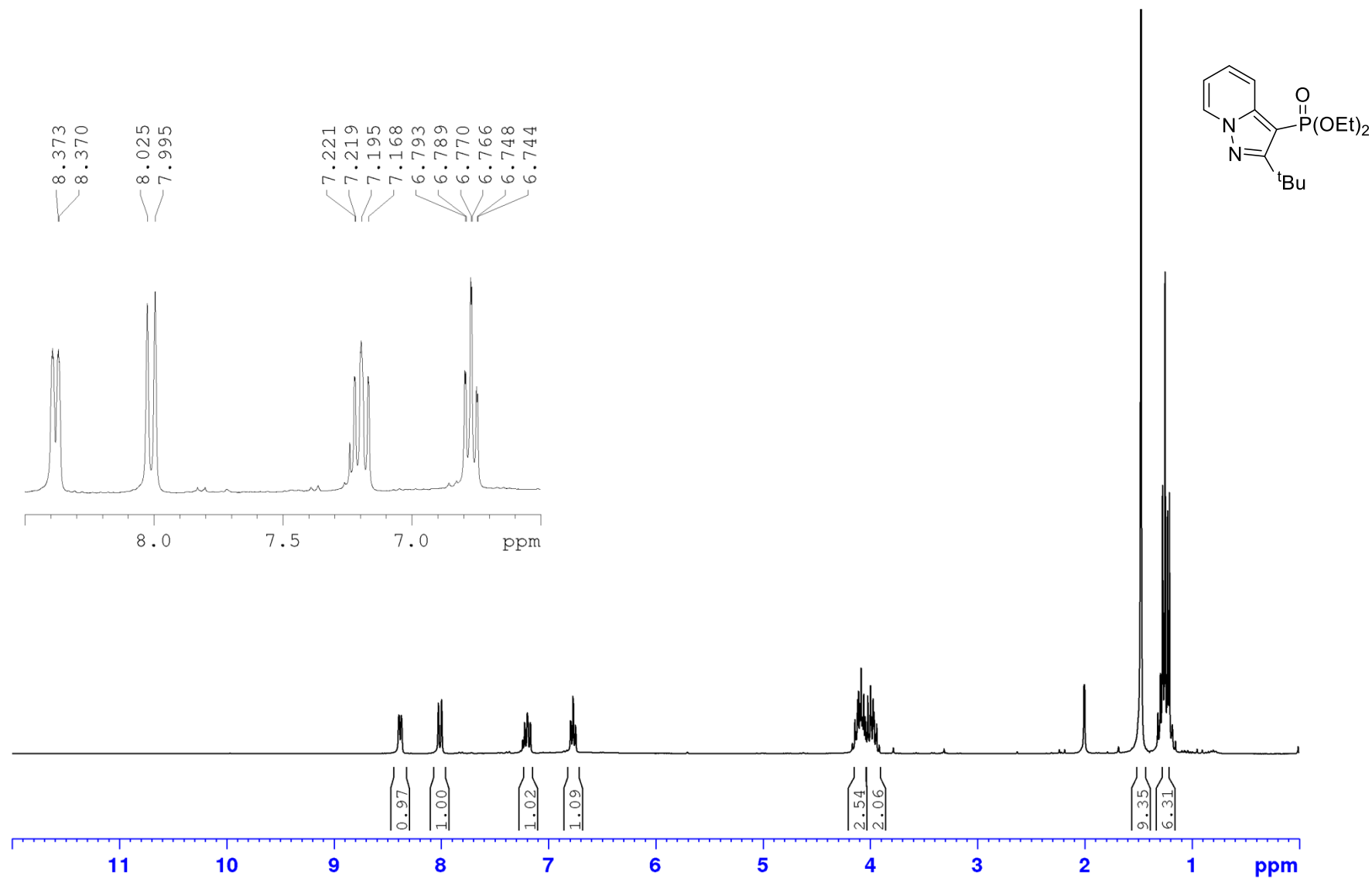
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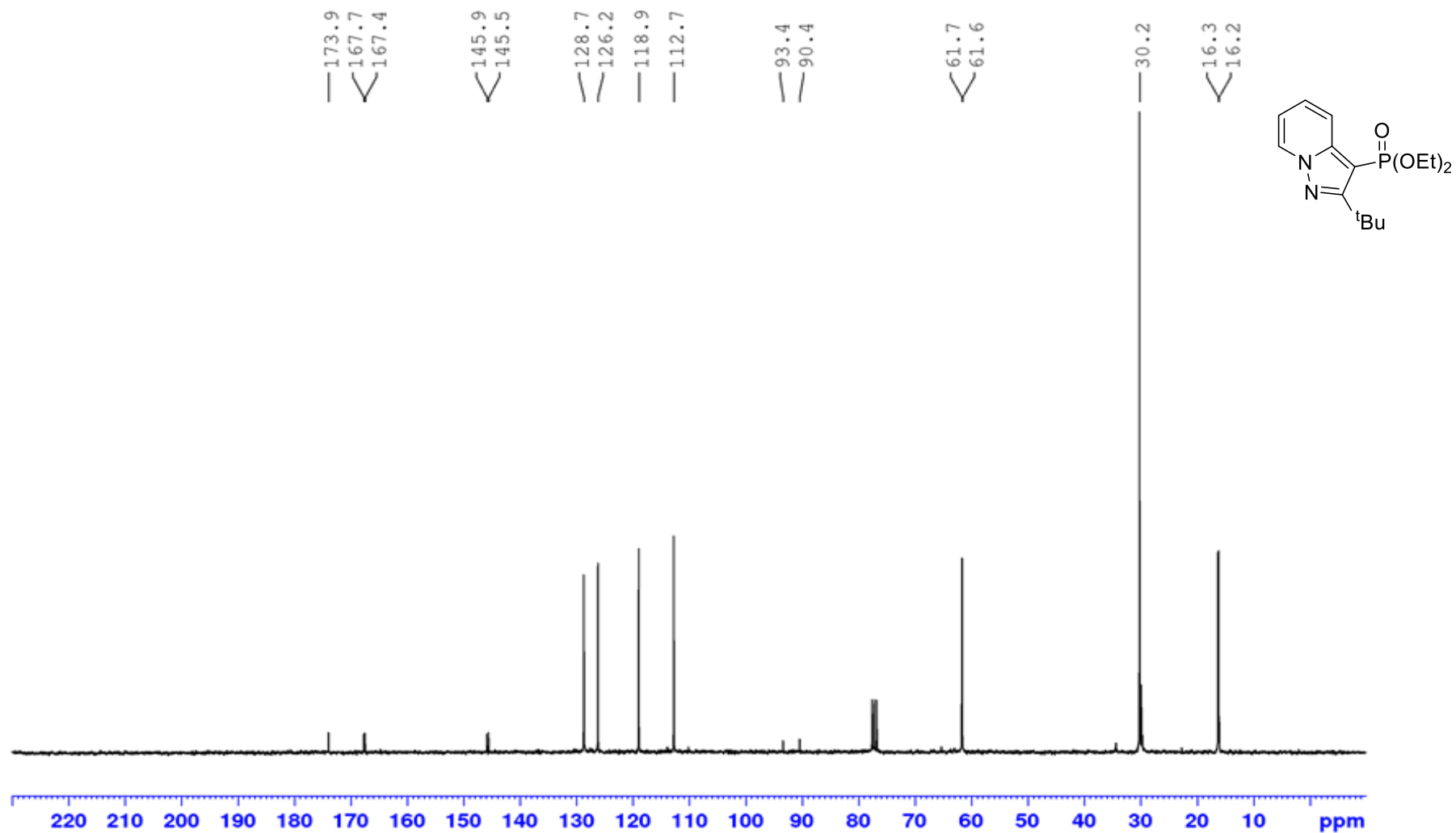
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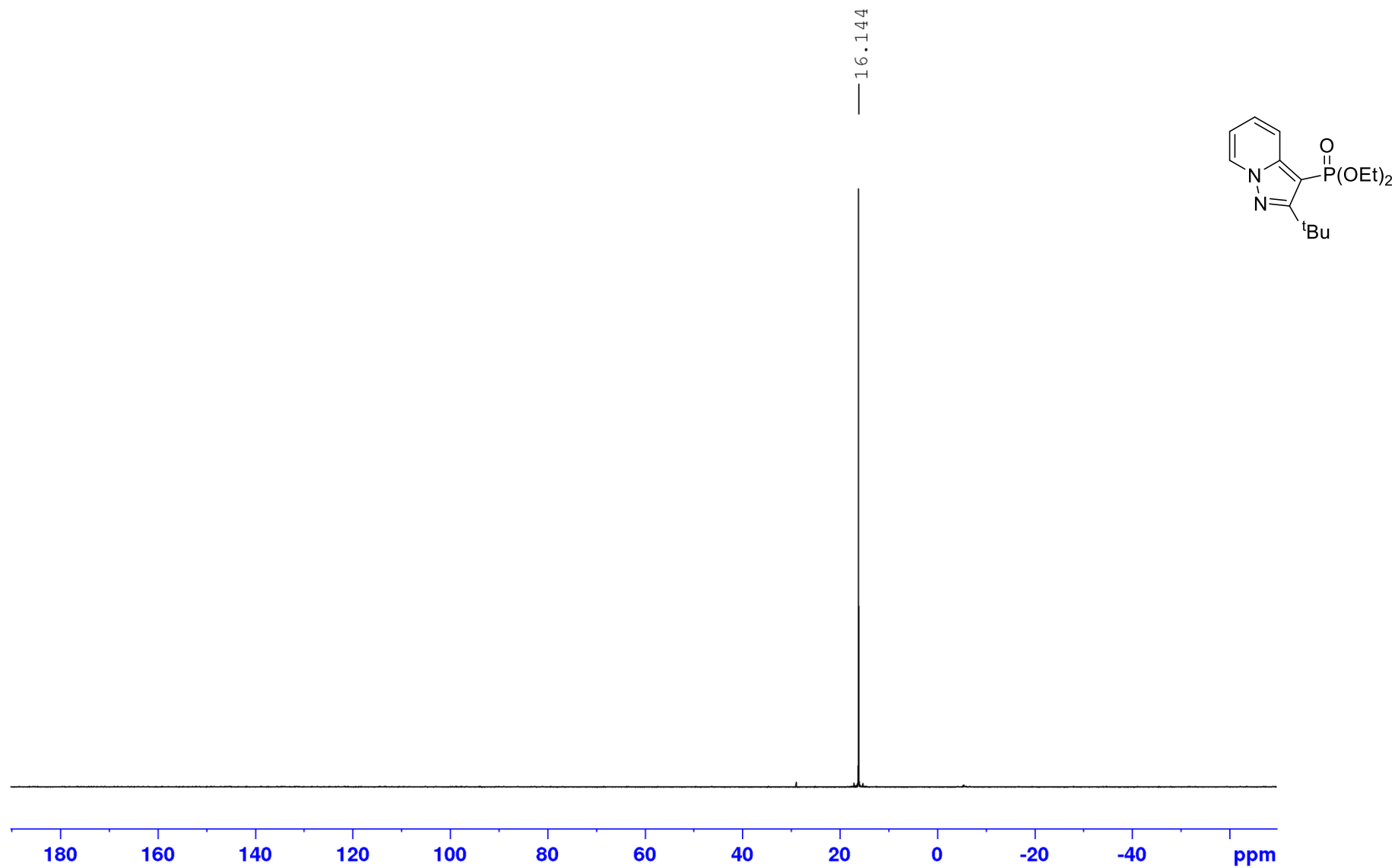
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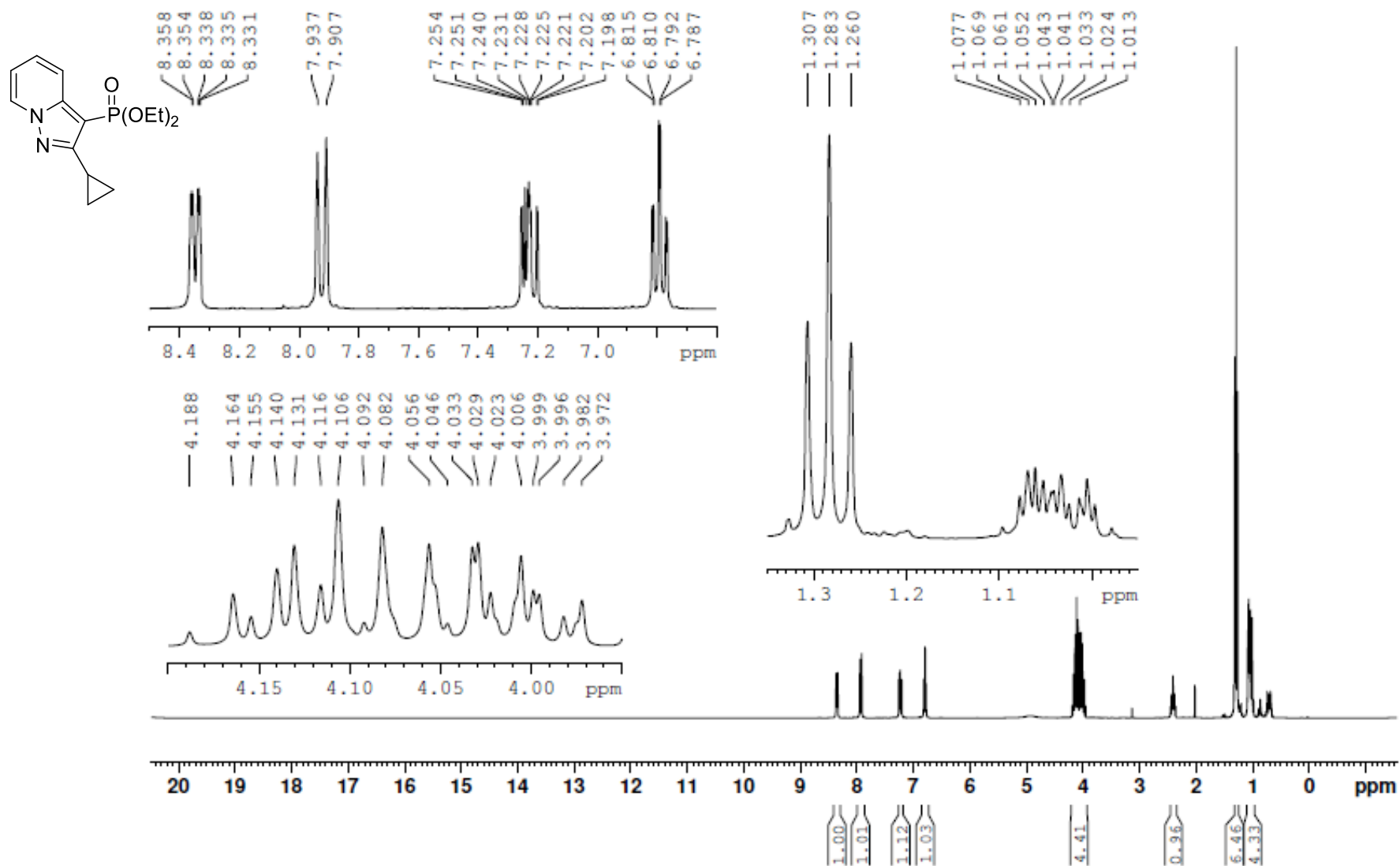
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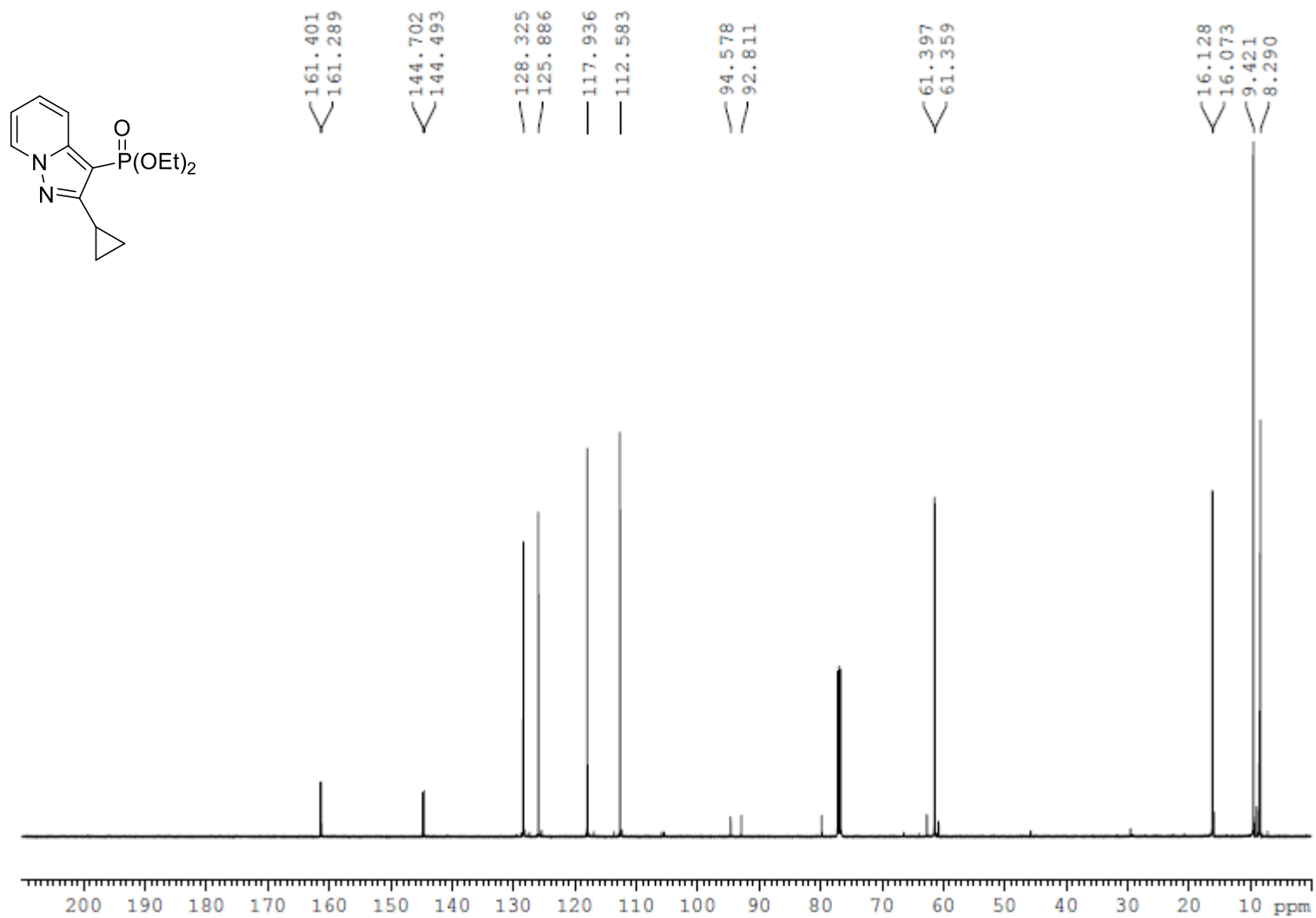
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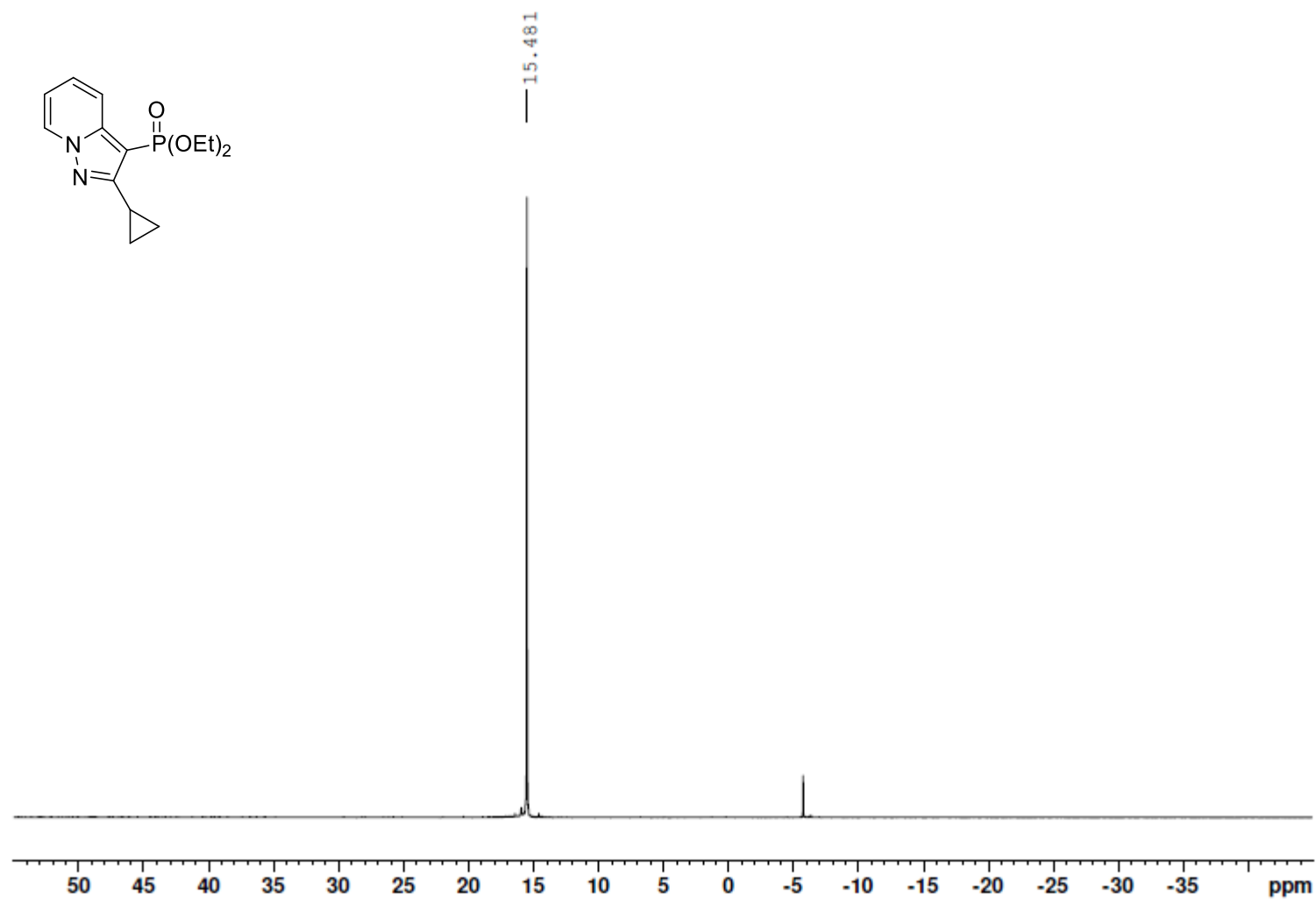
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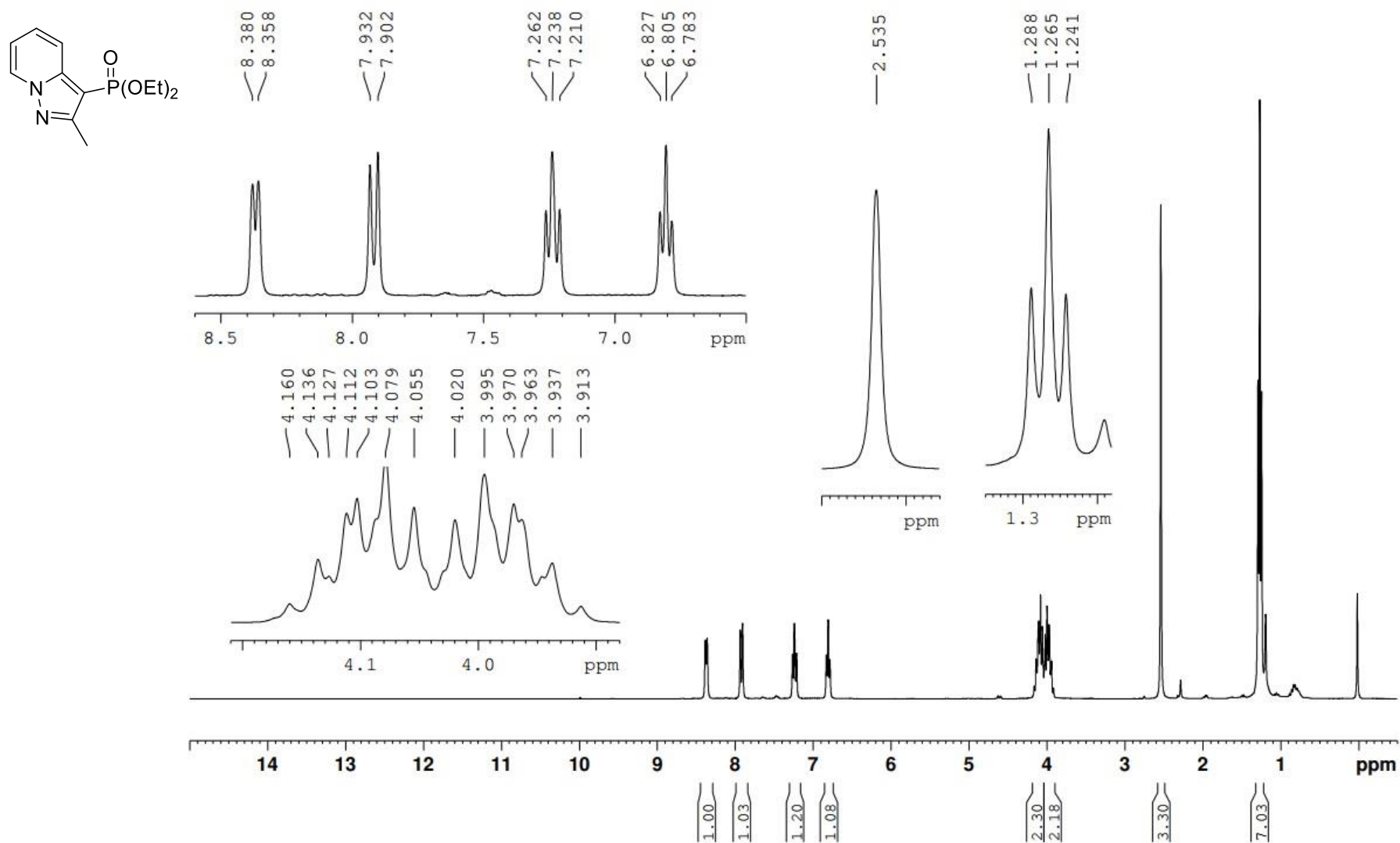
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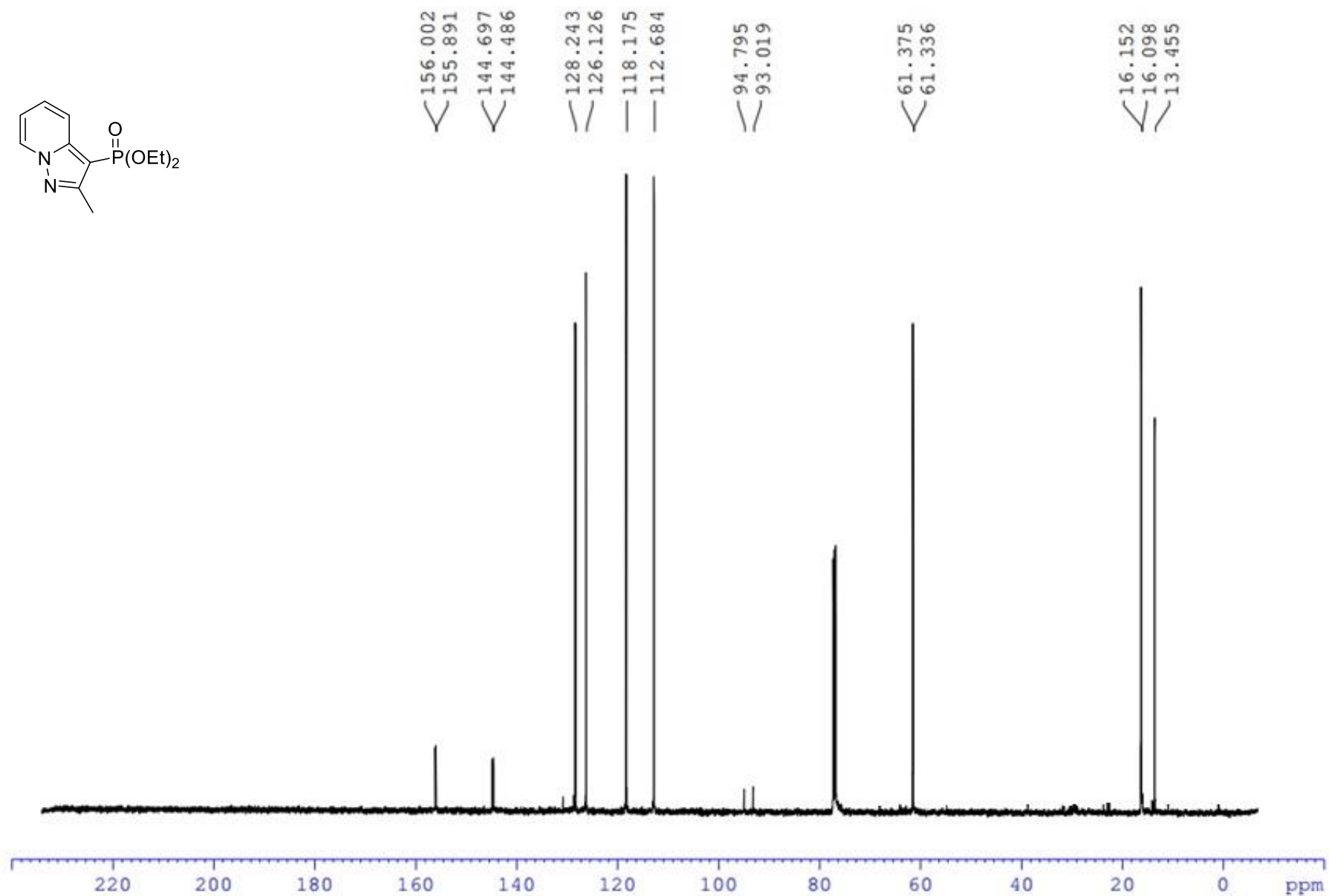
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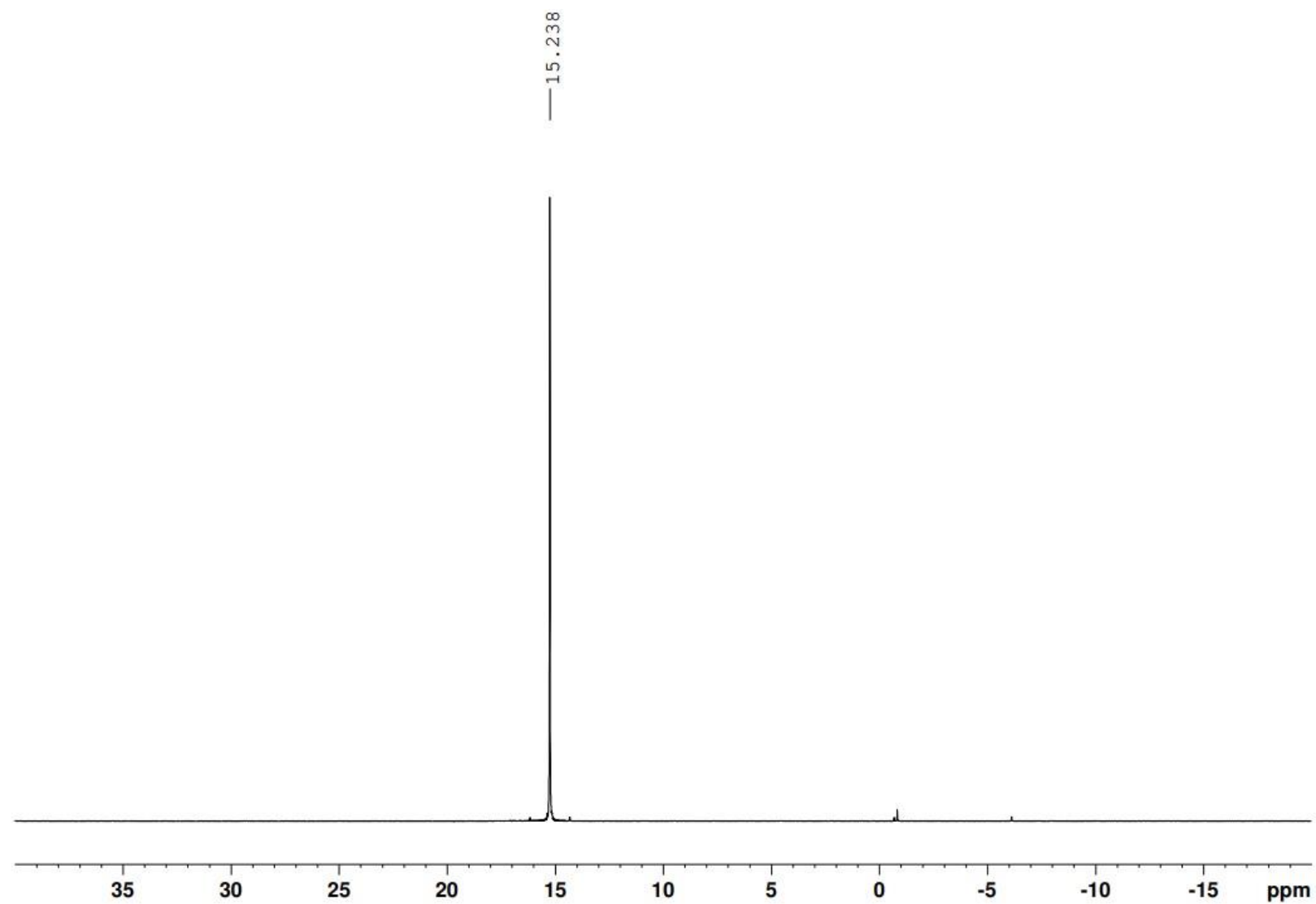
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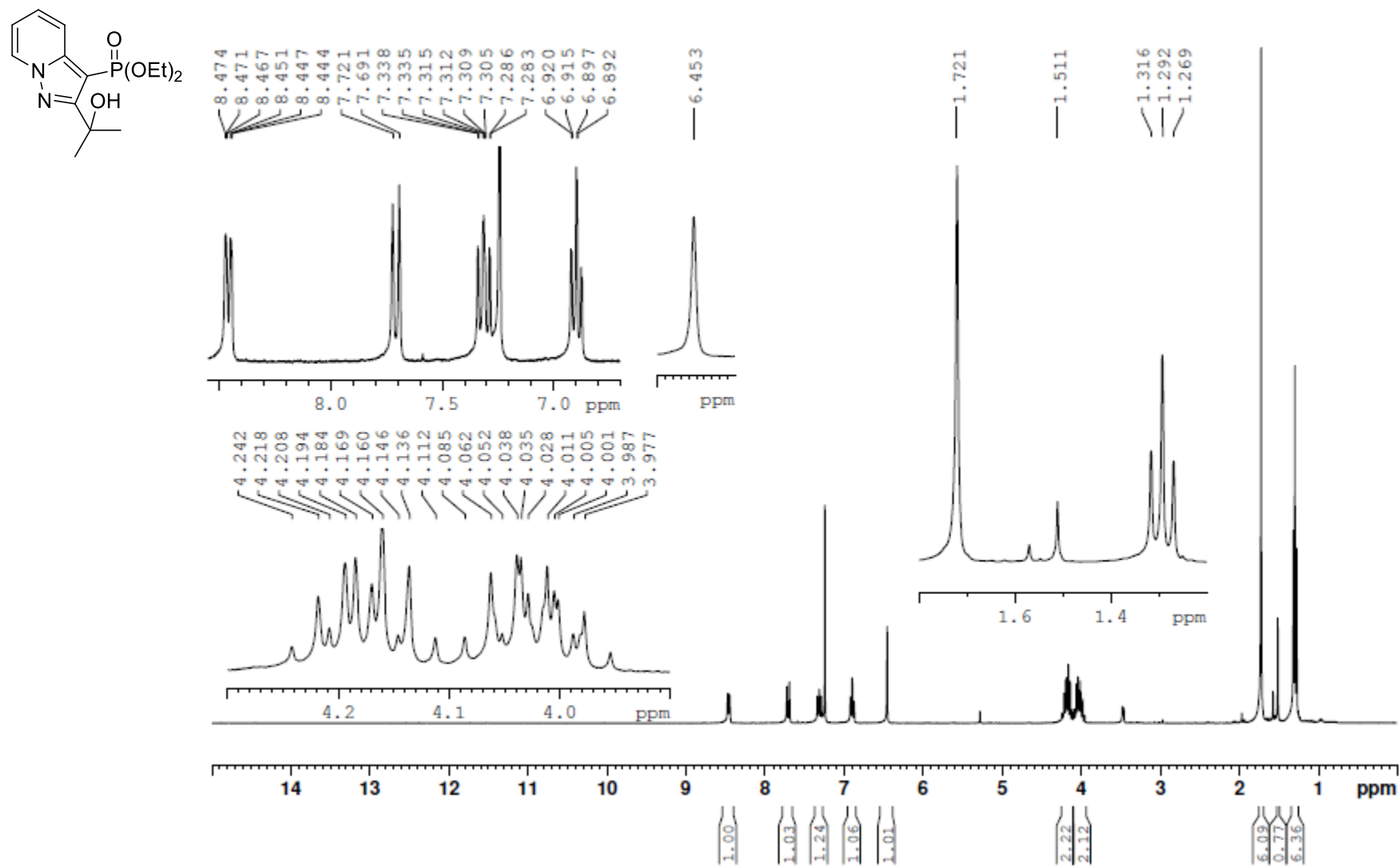
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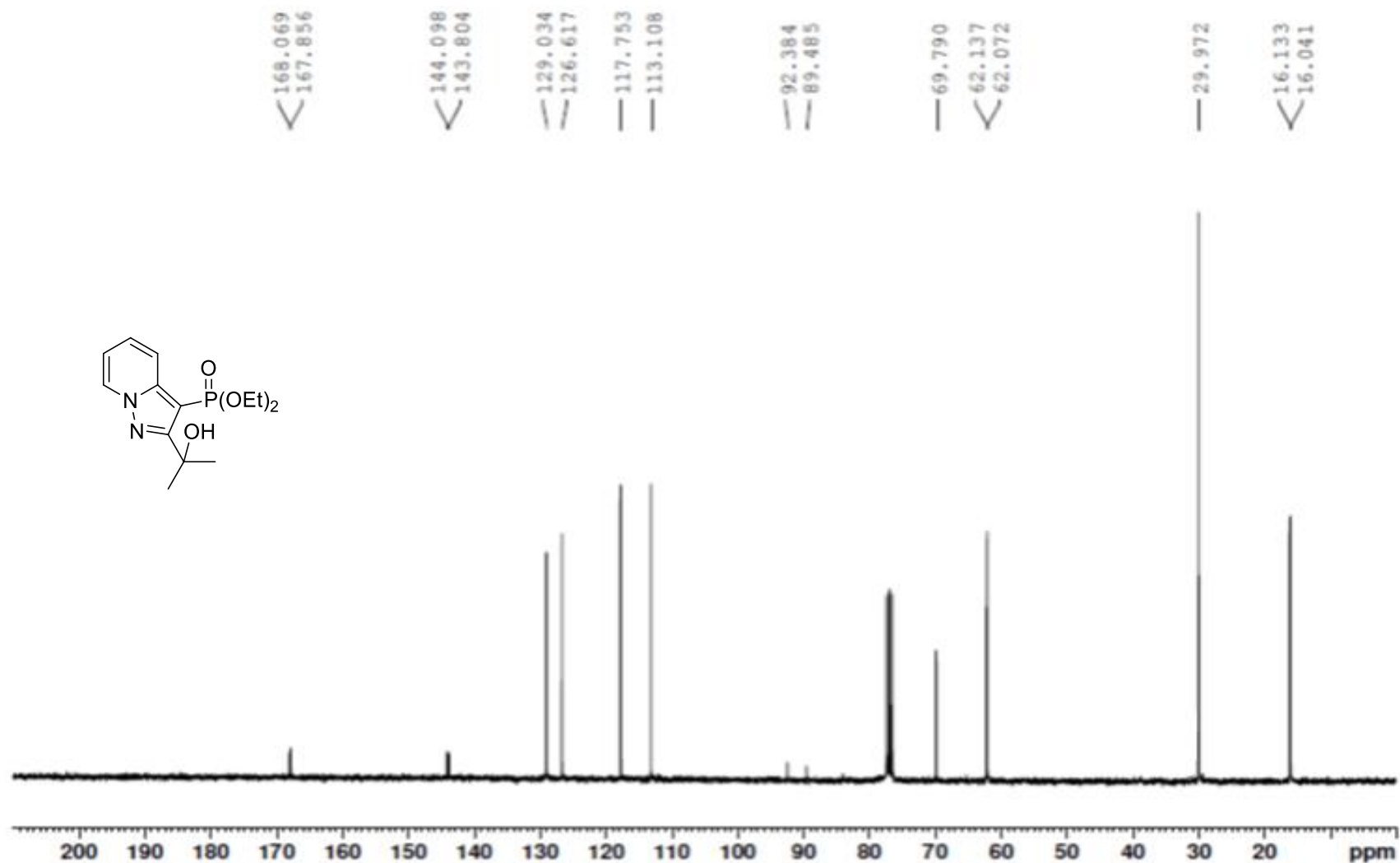
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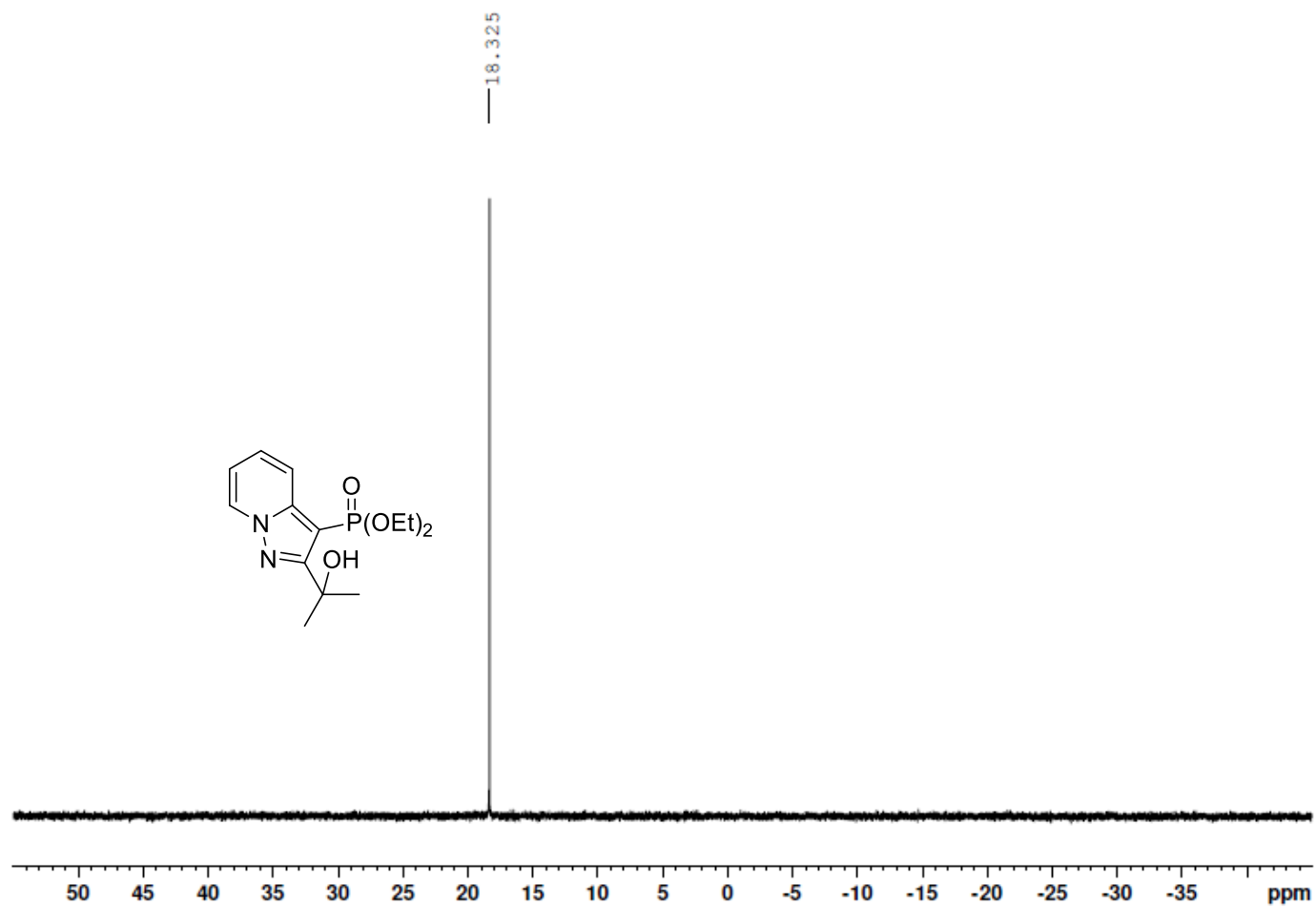
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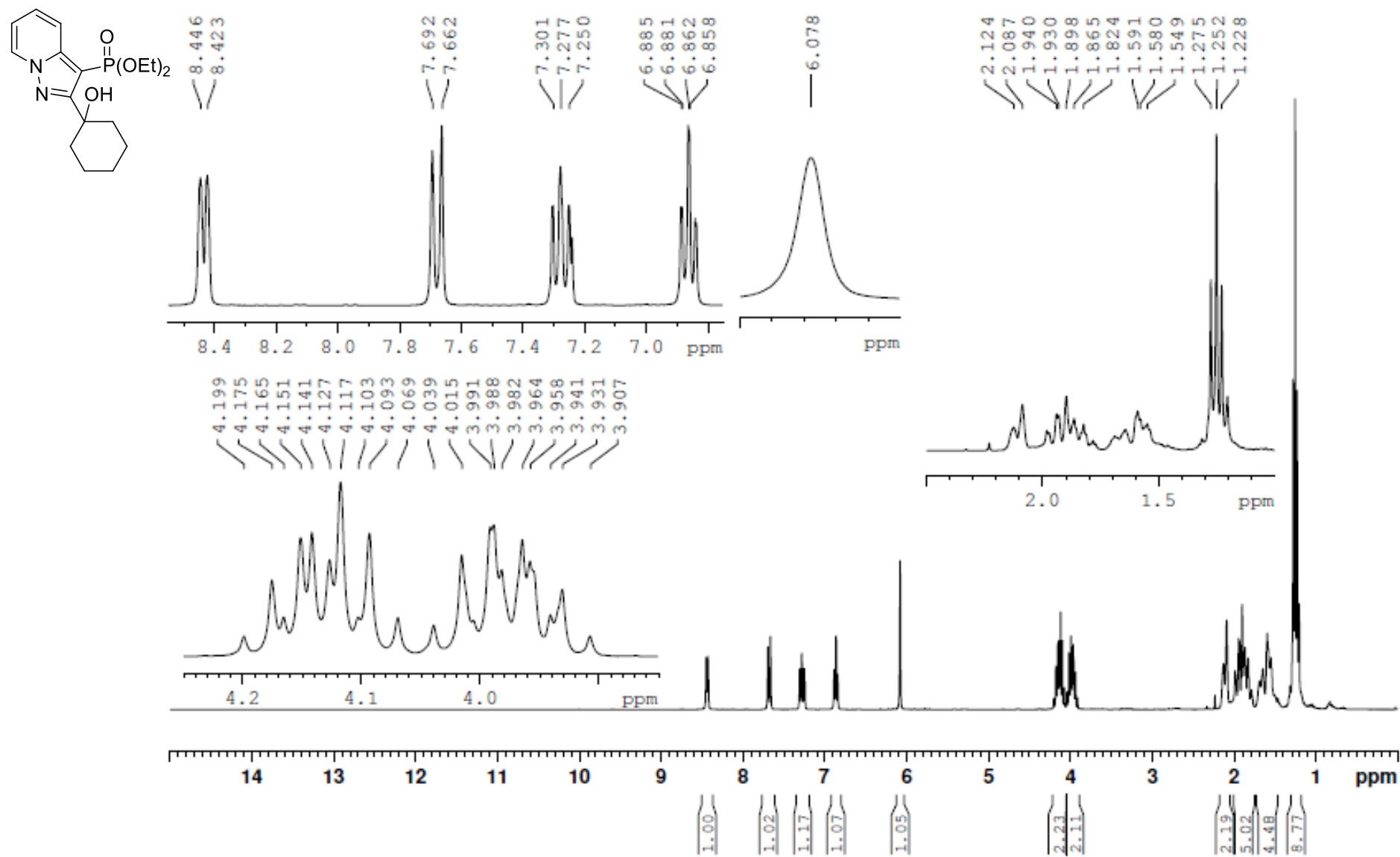
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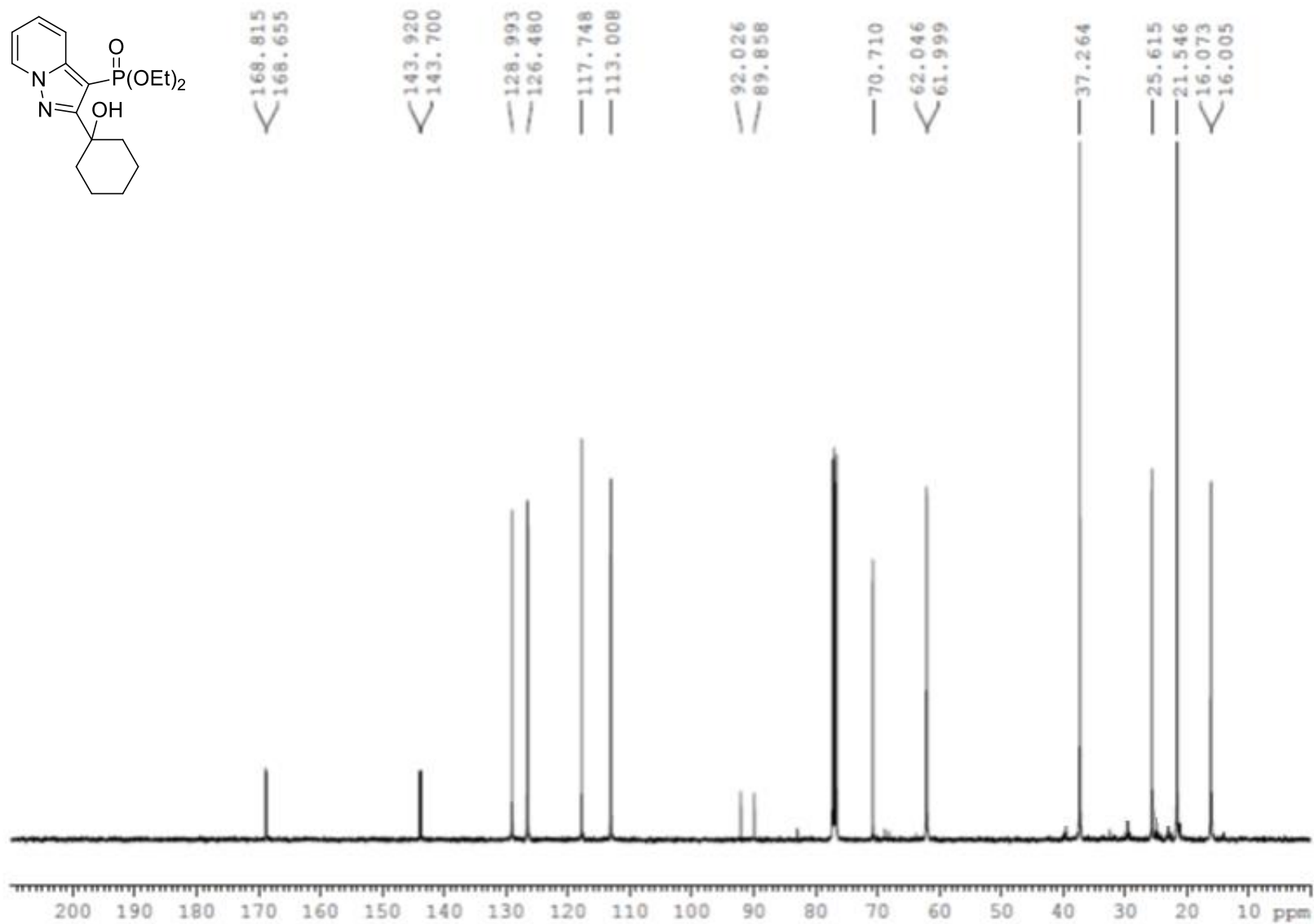
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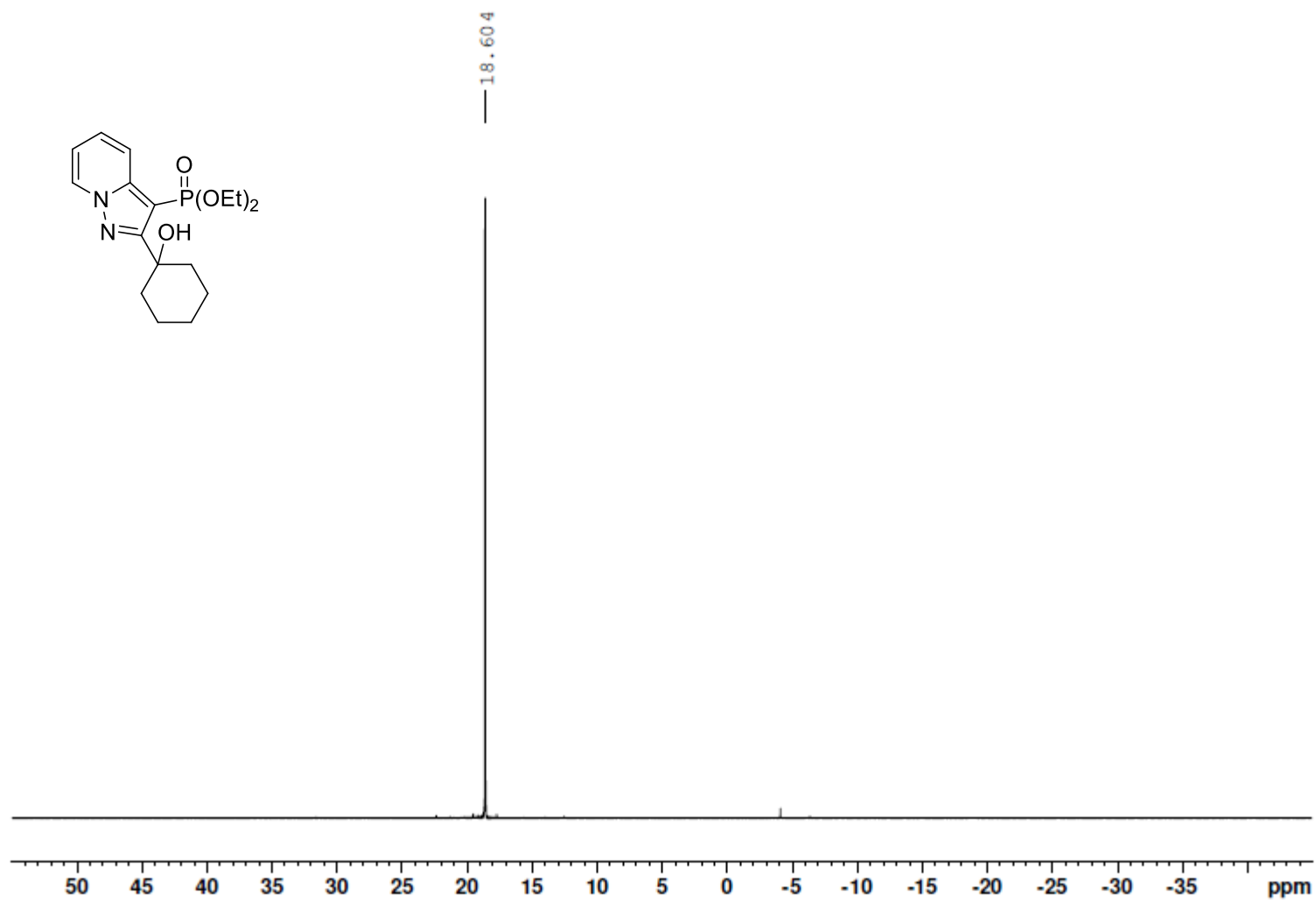
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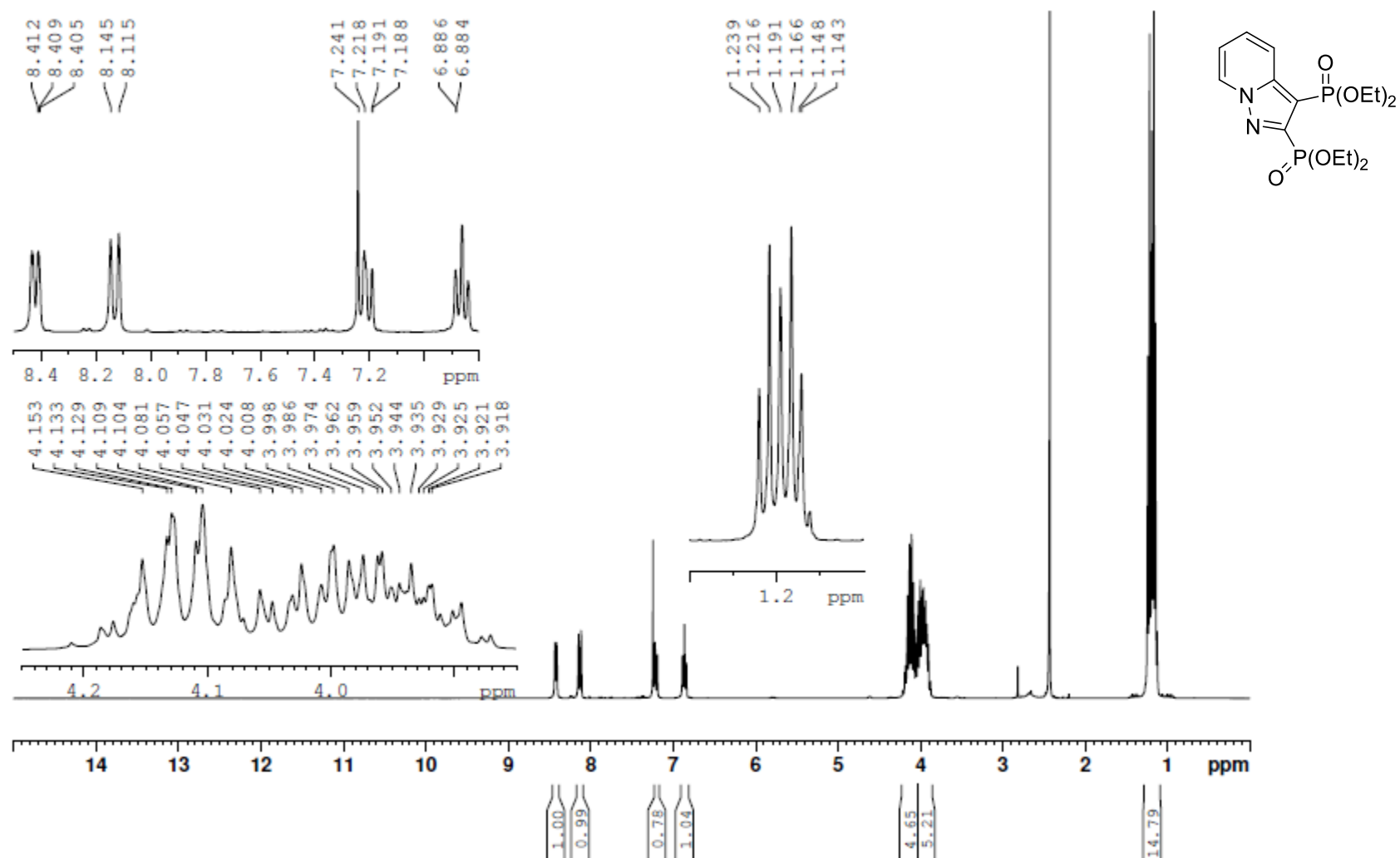
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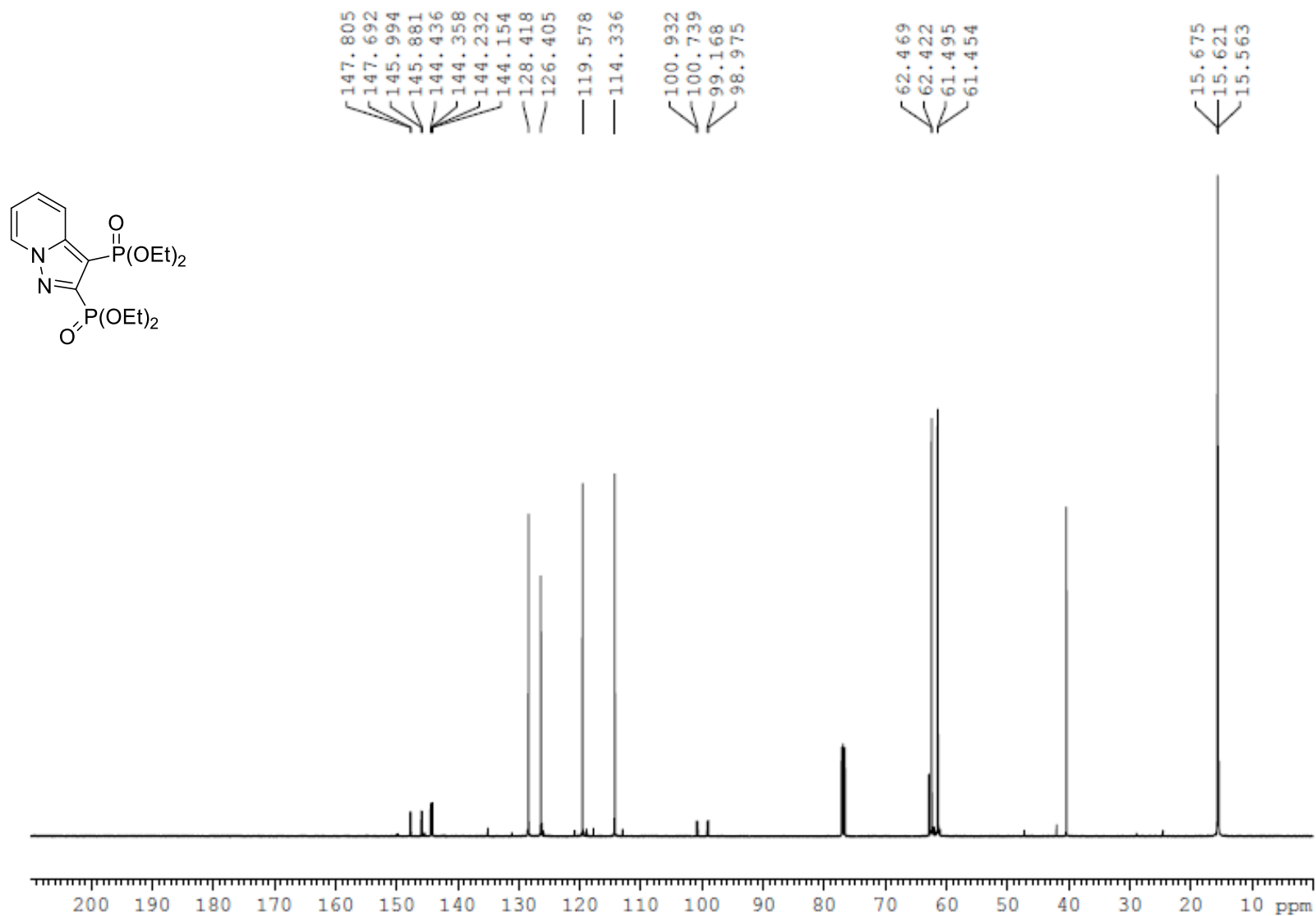
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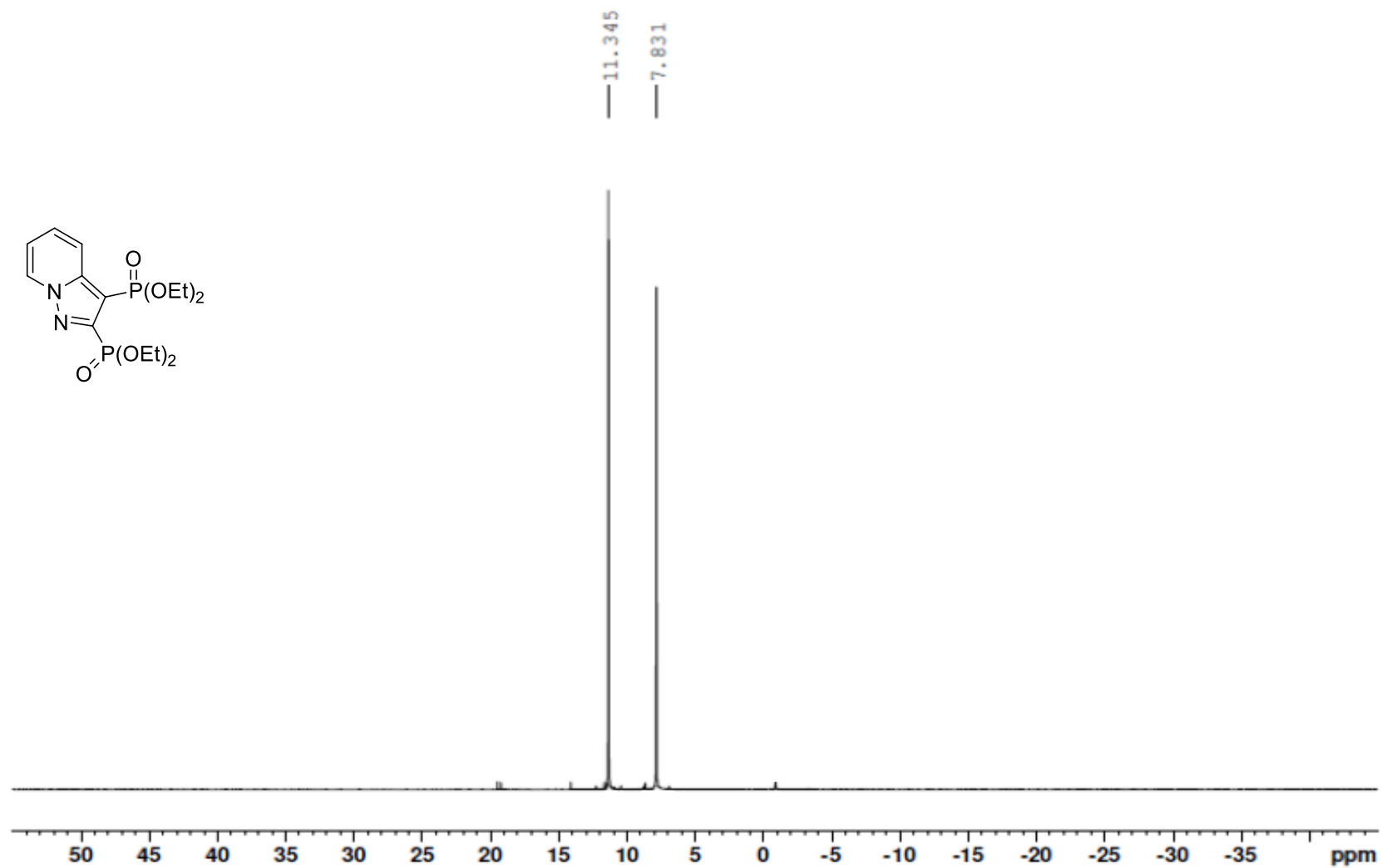
Tetraethyl pyrazolo[1,5-a]pyridine-2,3-diylbis(phosphonate) (5a) ^1H NMR.



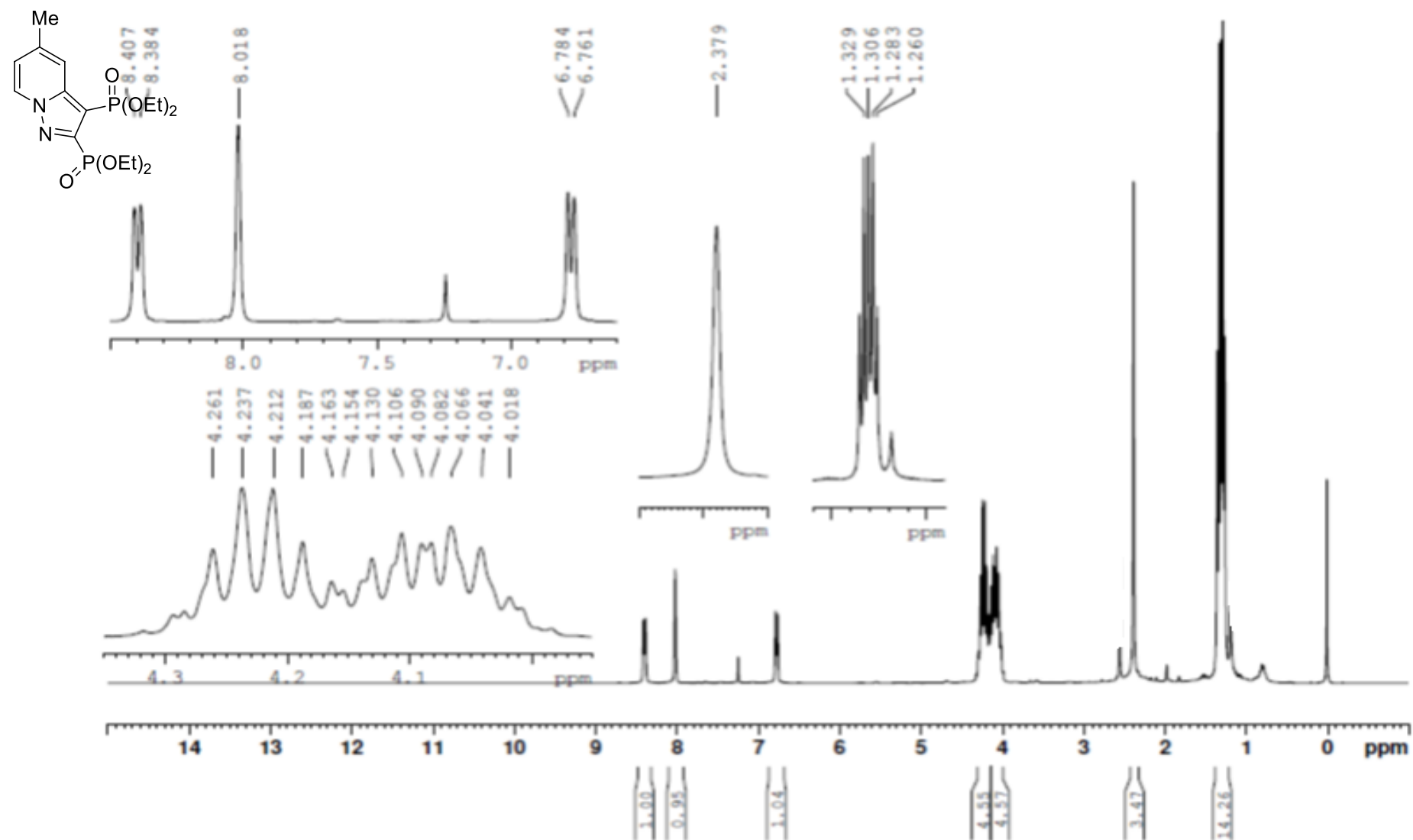
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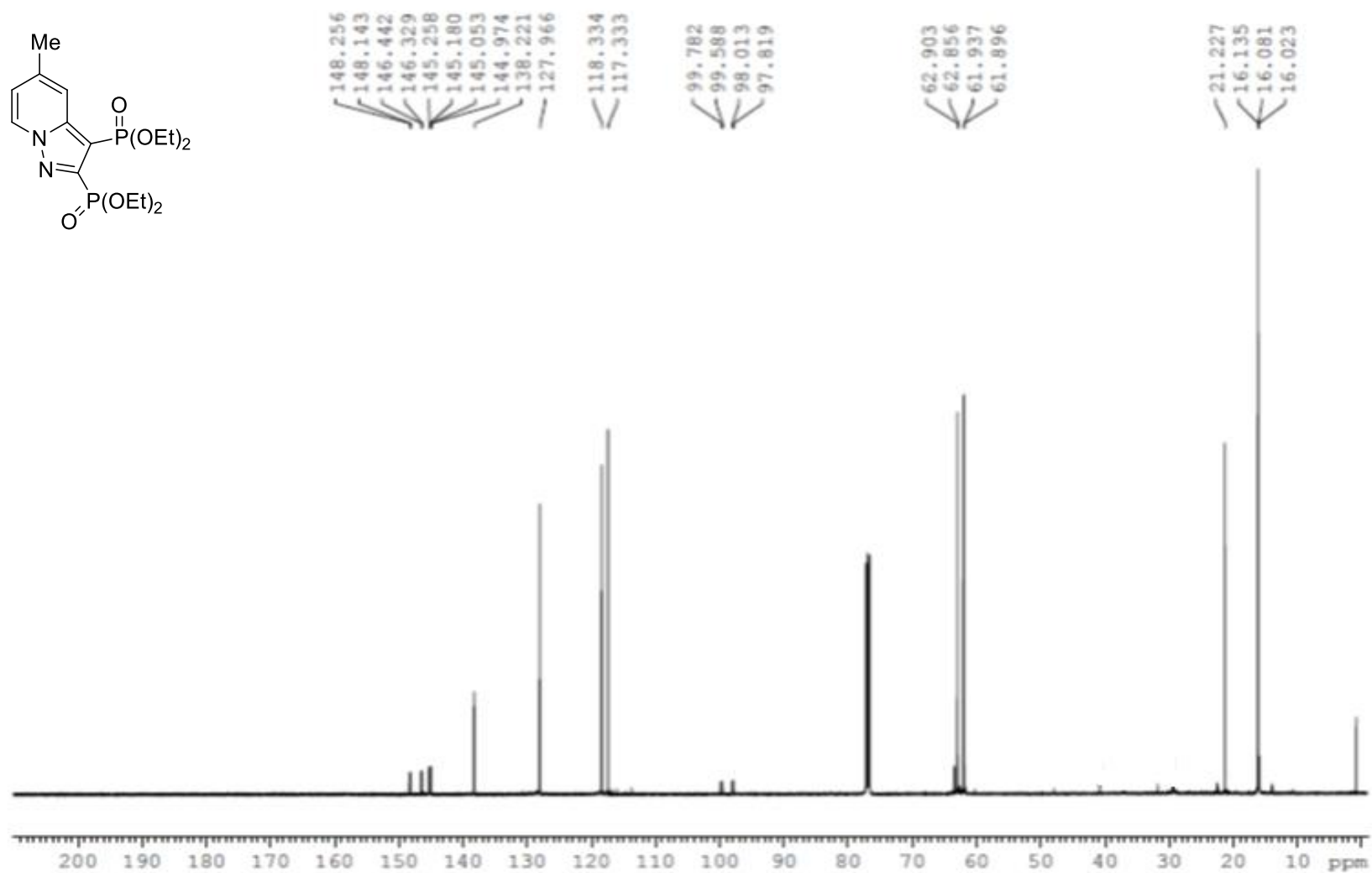
Tetraethyl pyrazolo[1,5-a]pyridine-2,3-diylbis(phosphonate) (5a) ^{31}P NMR.



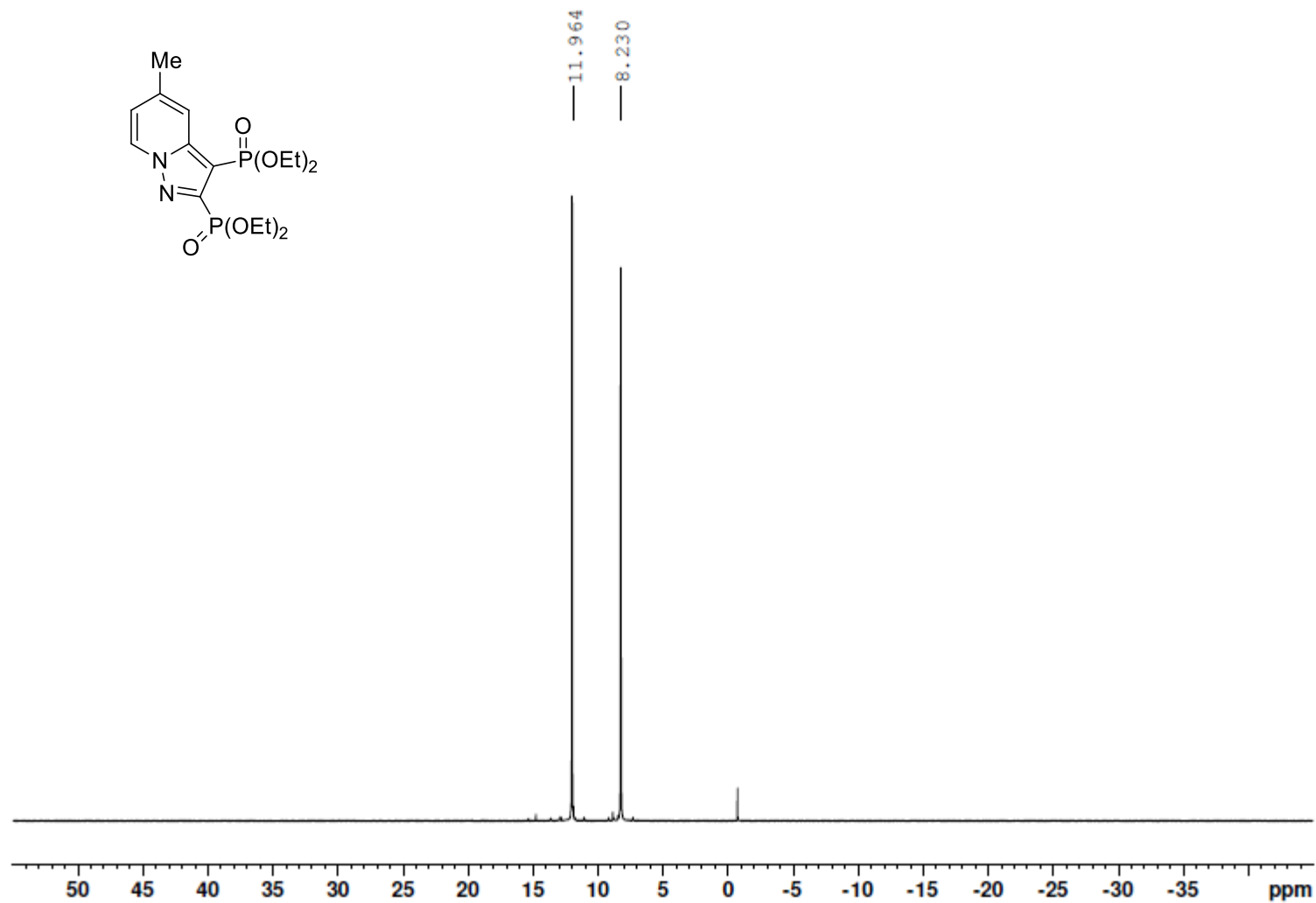
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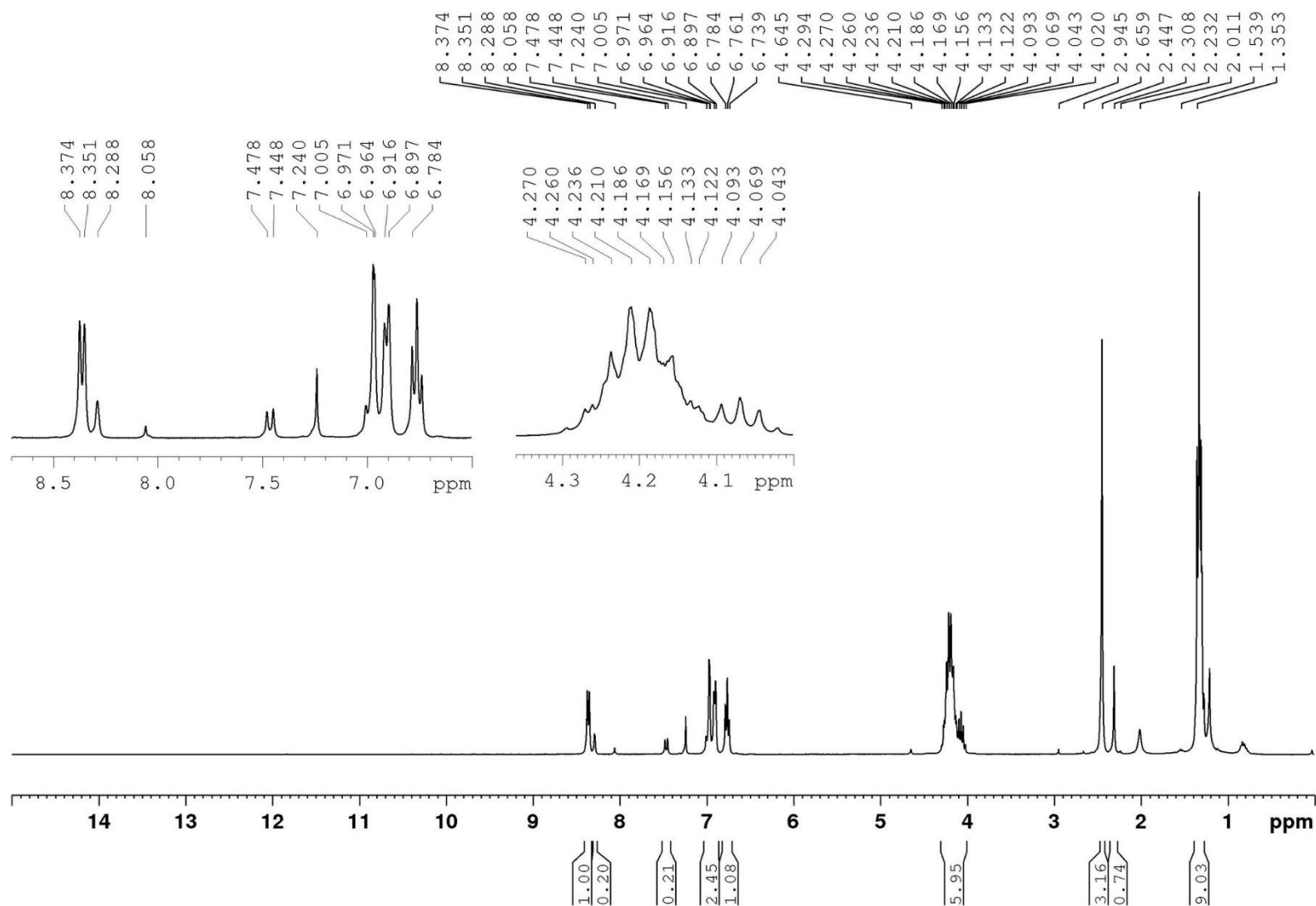
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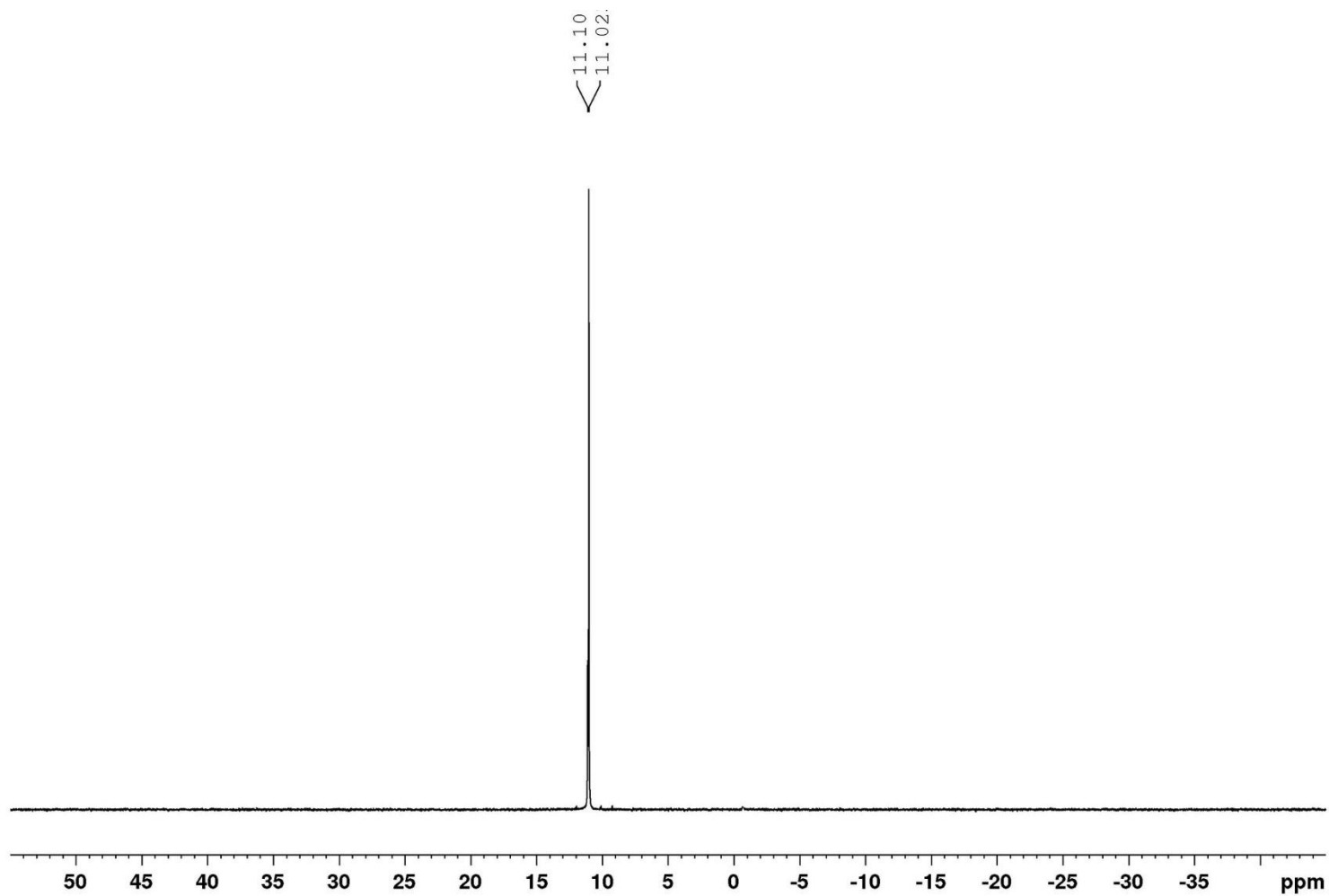
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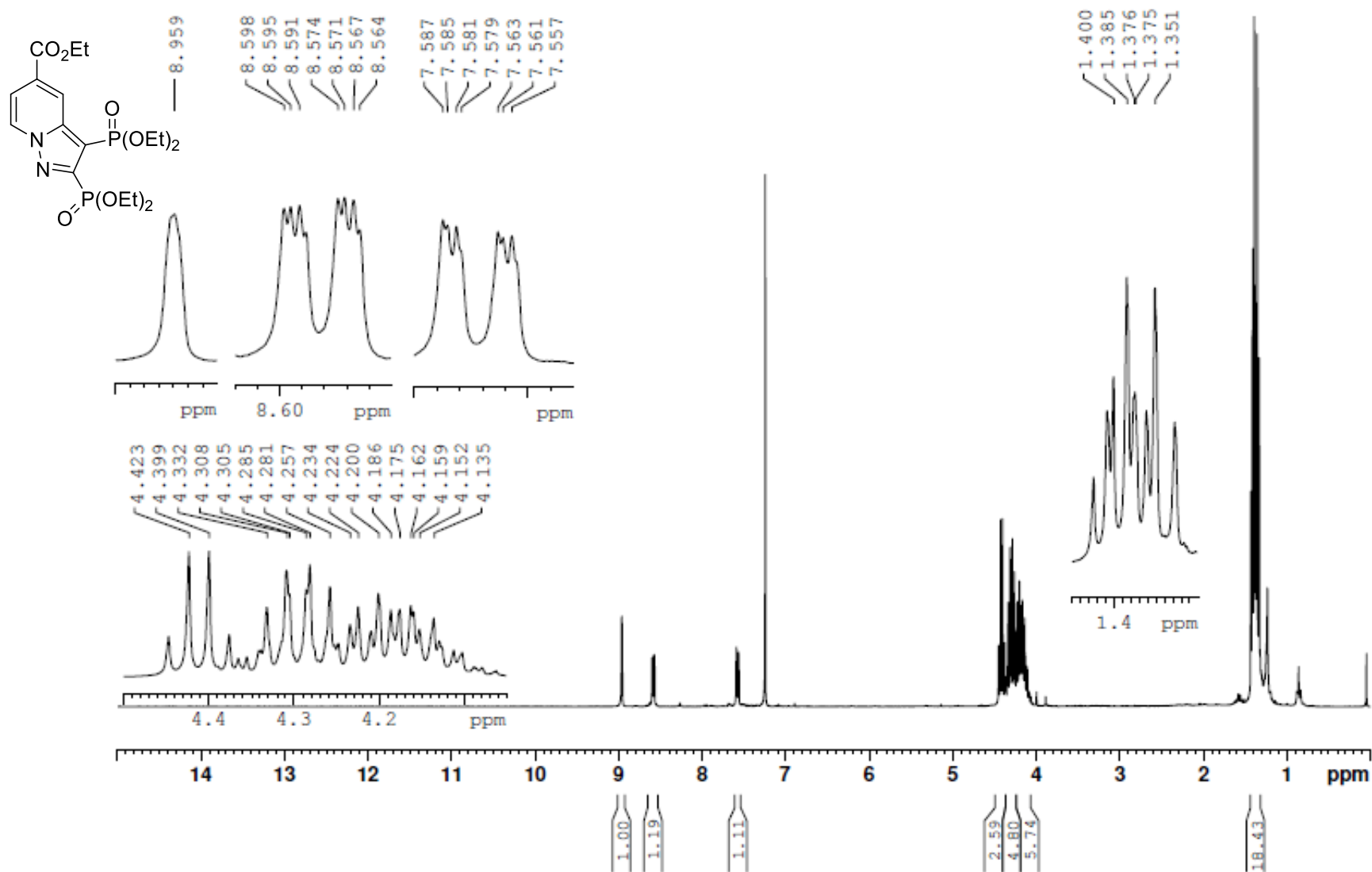
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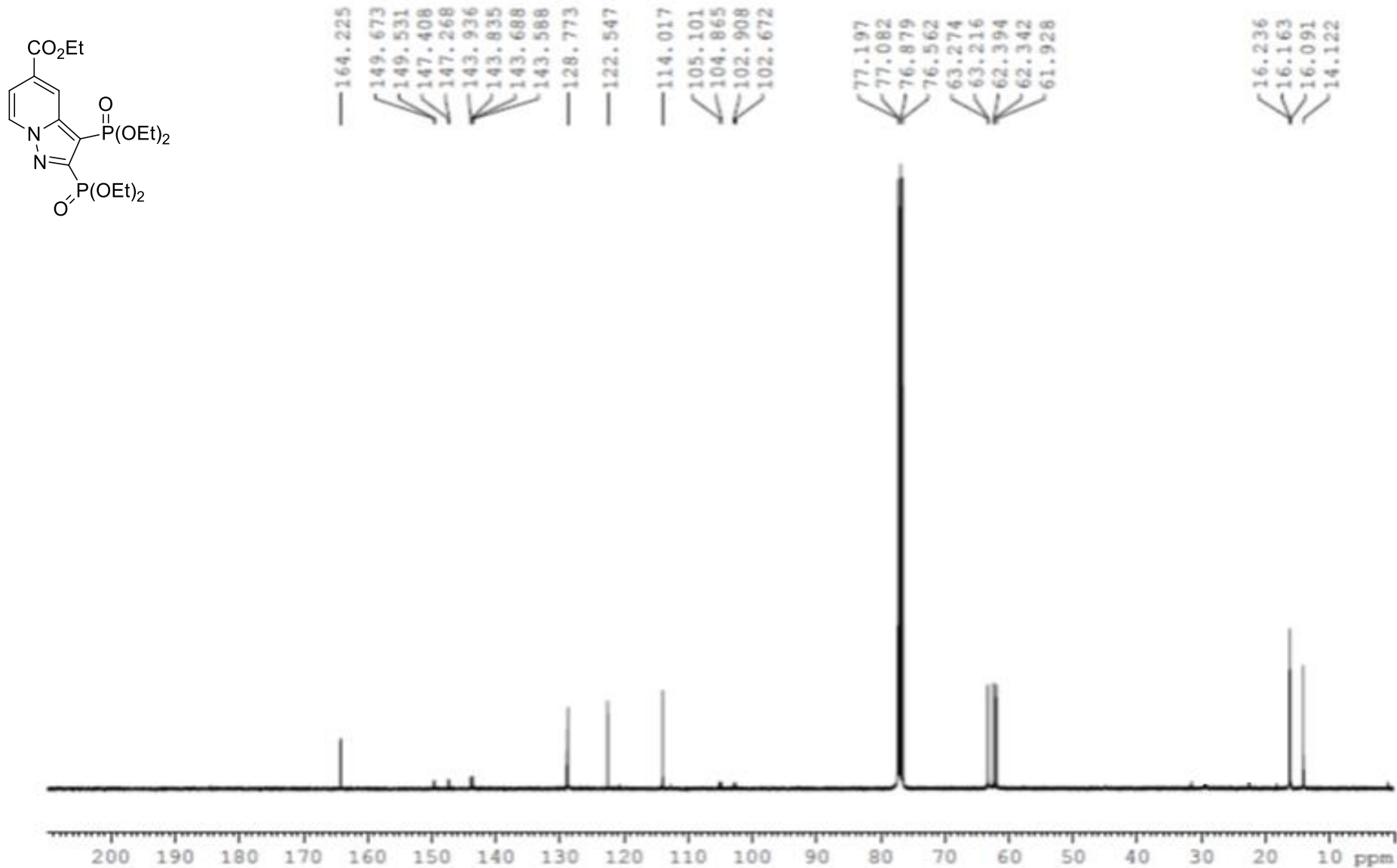
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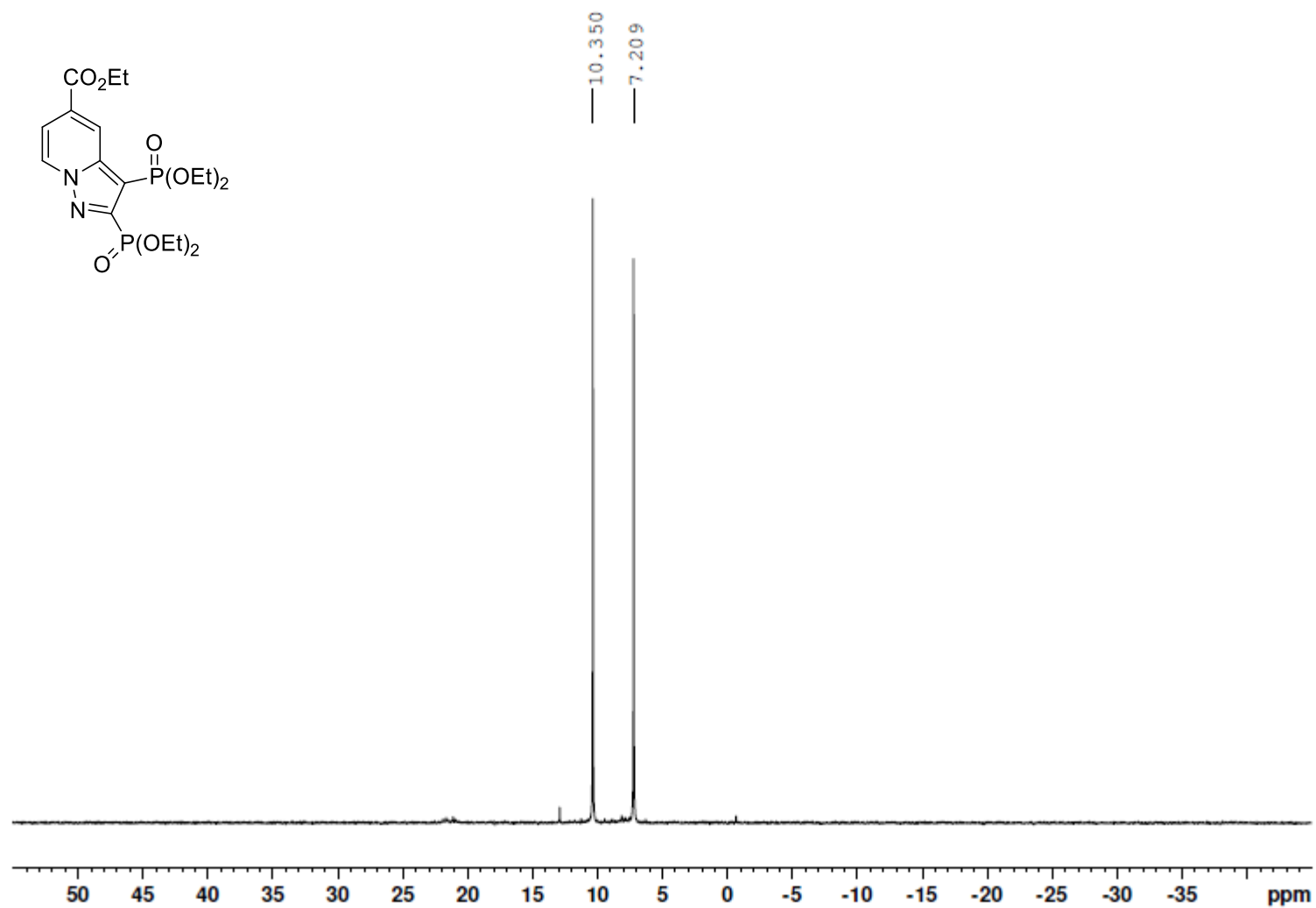
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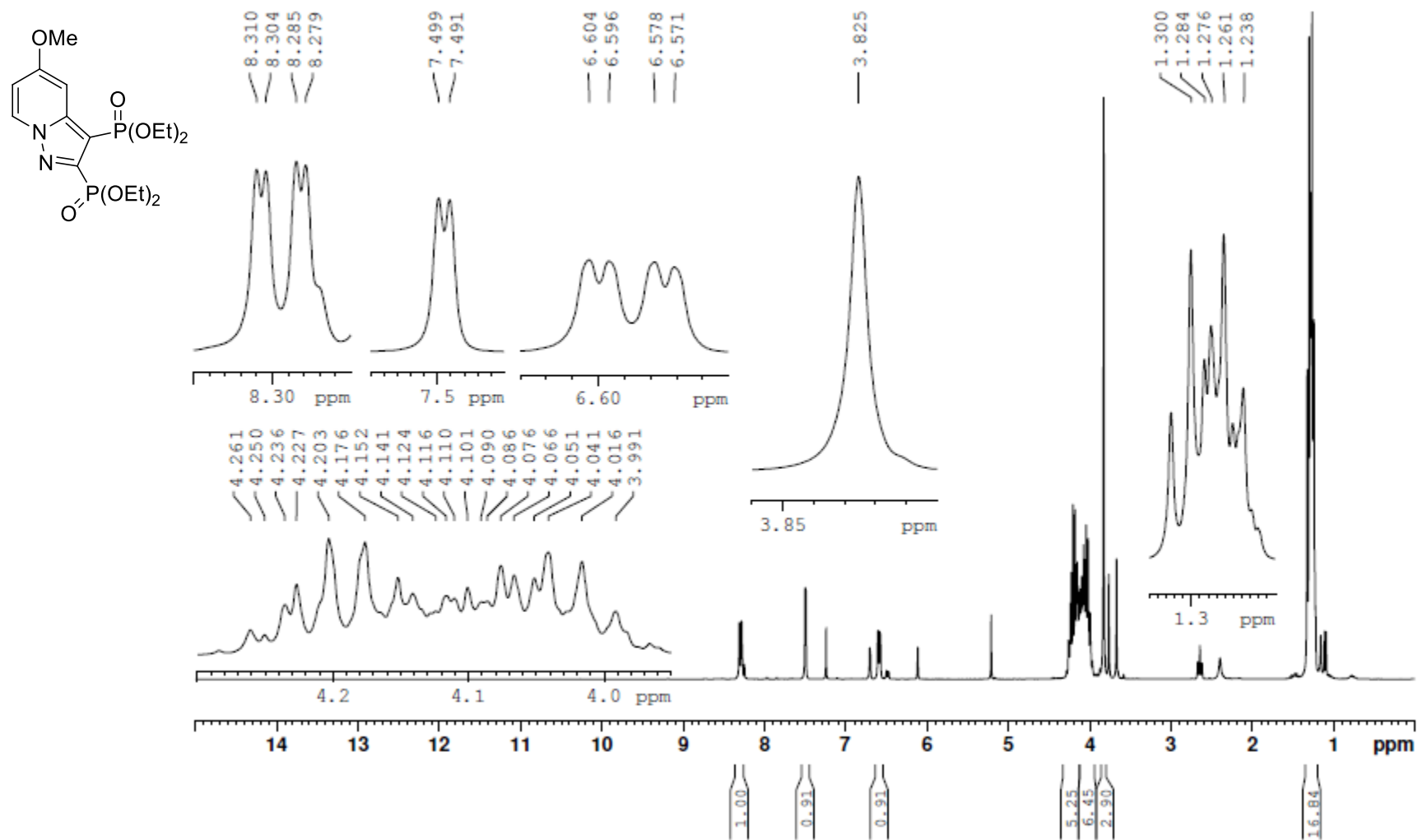
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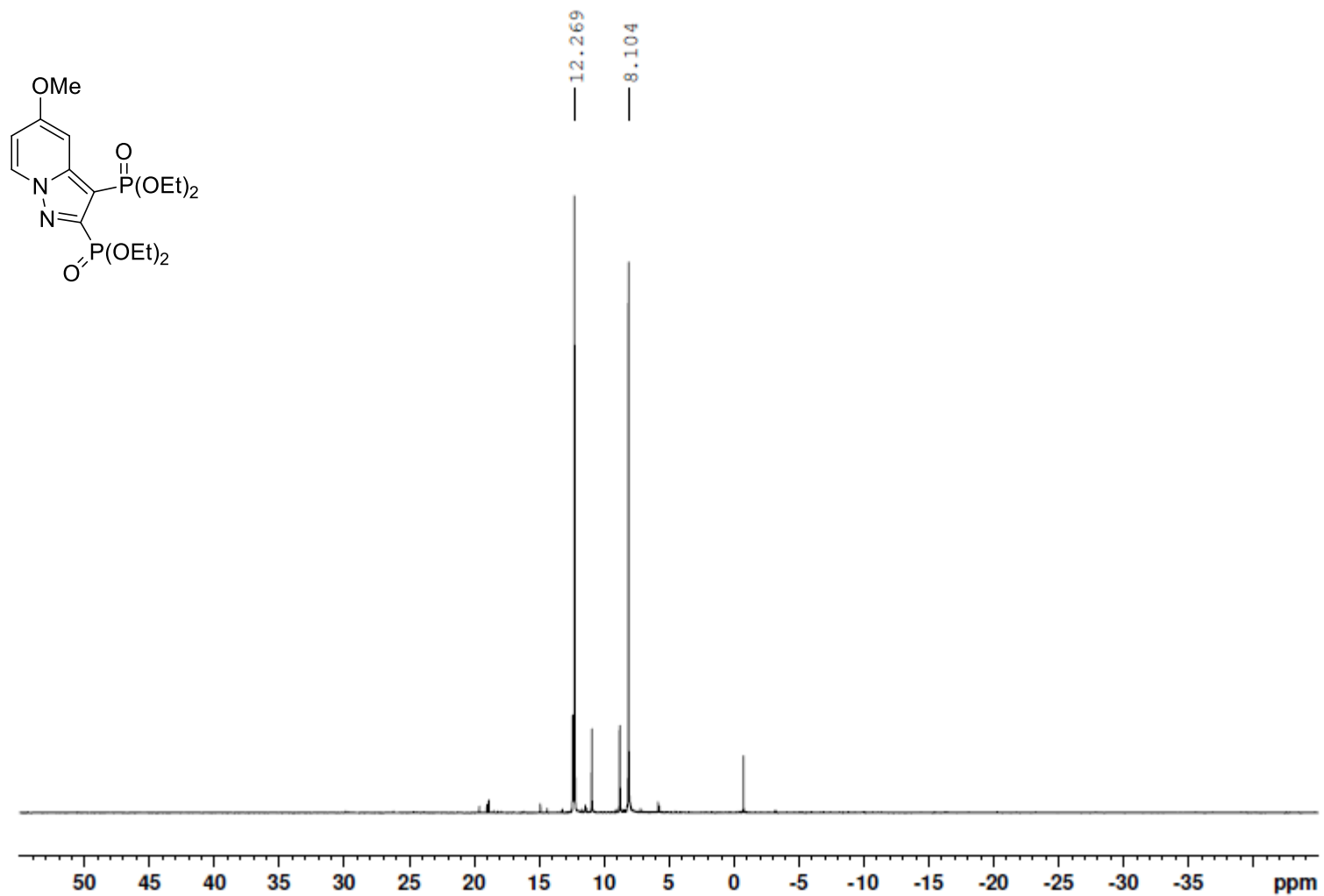
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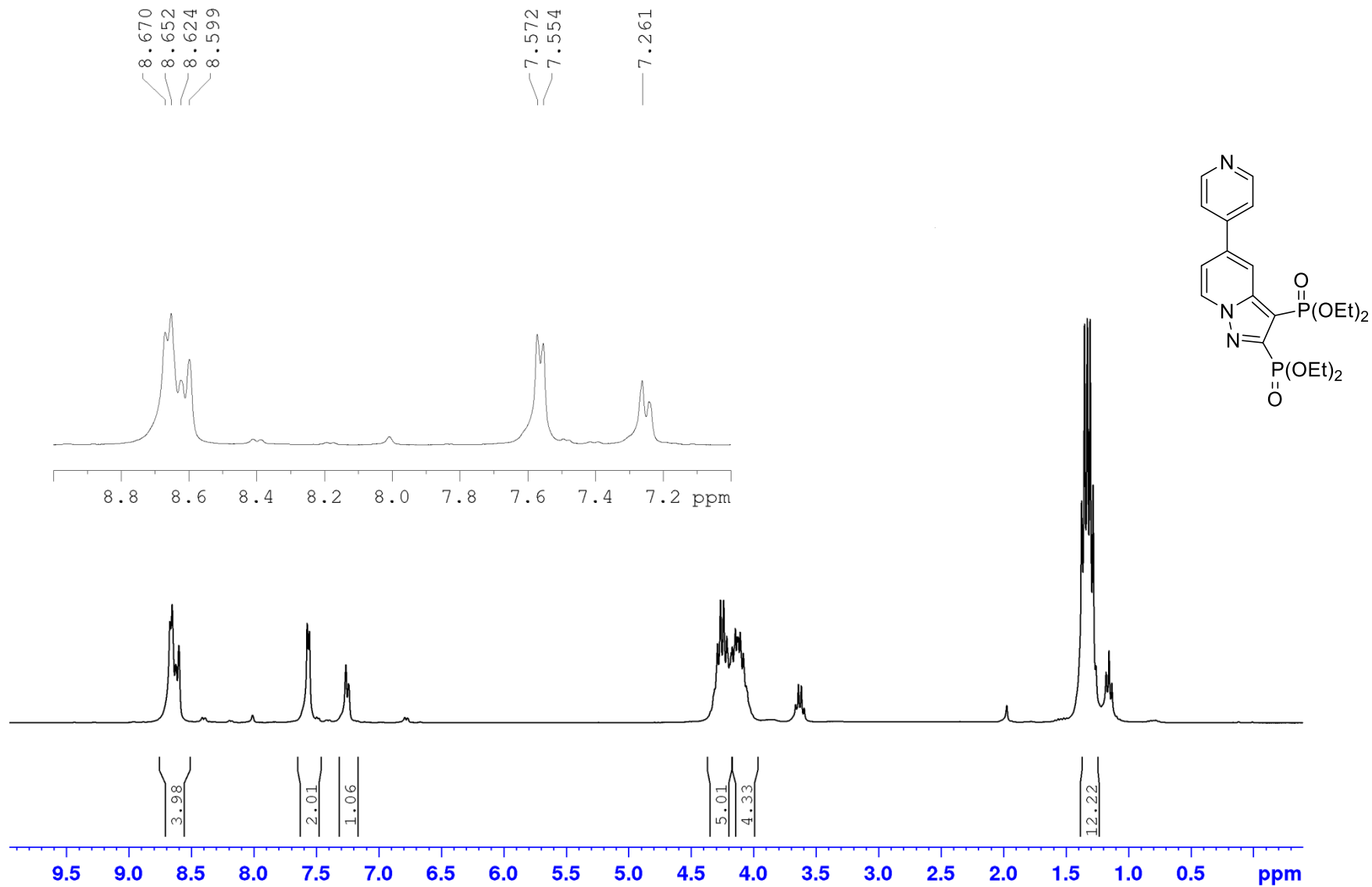
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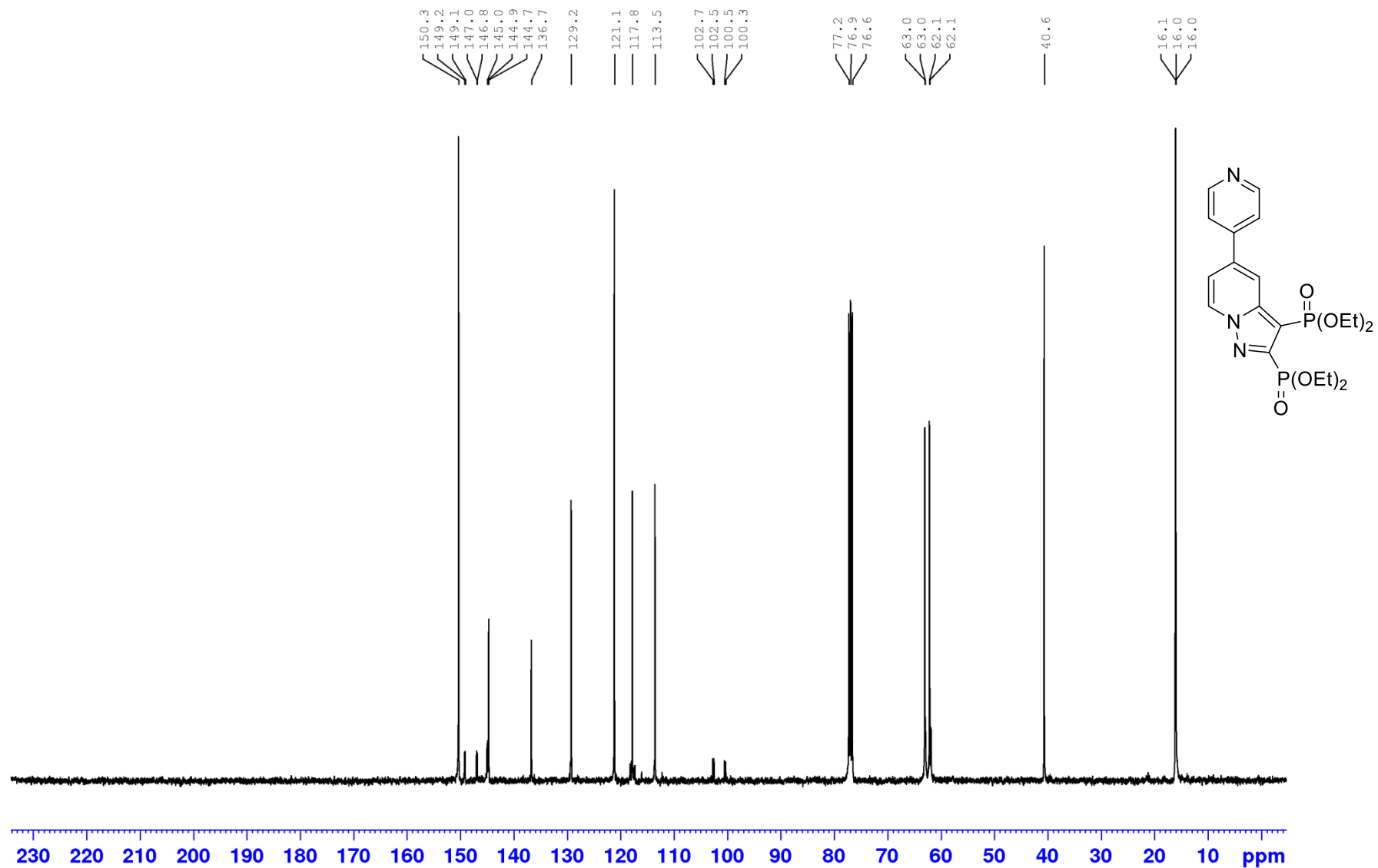
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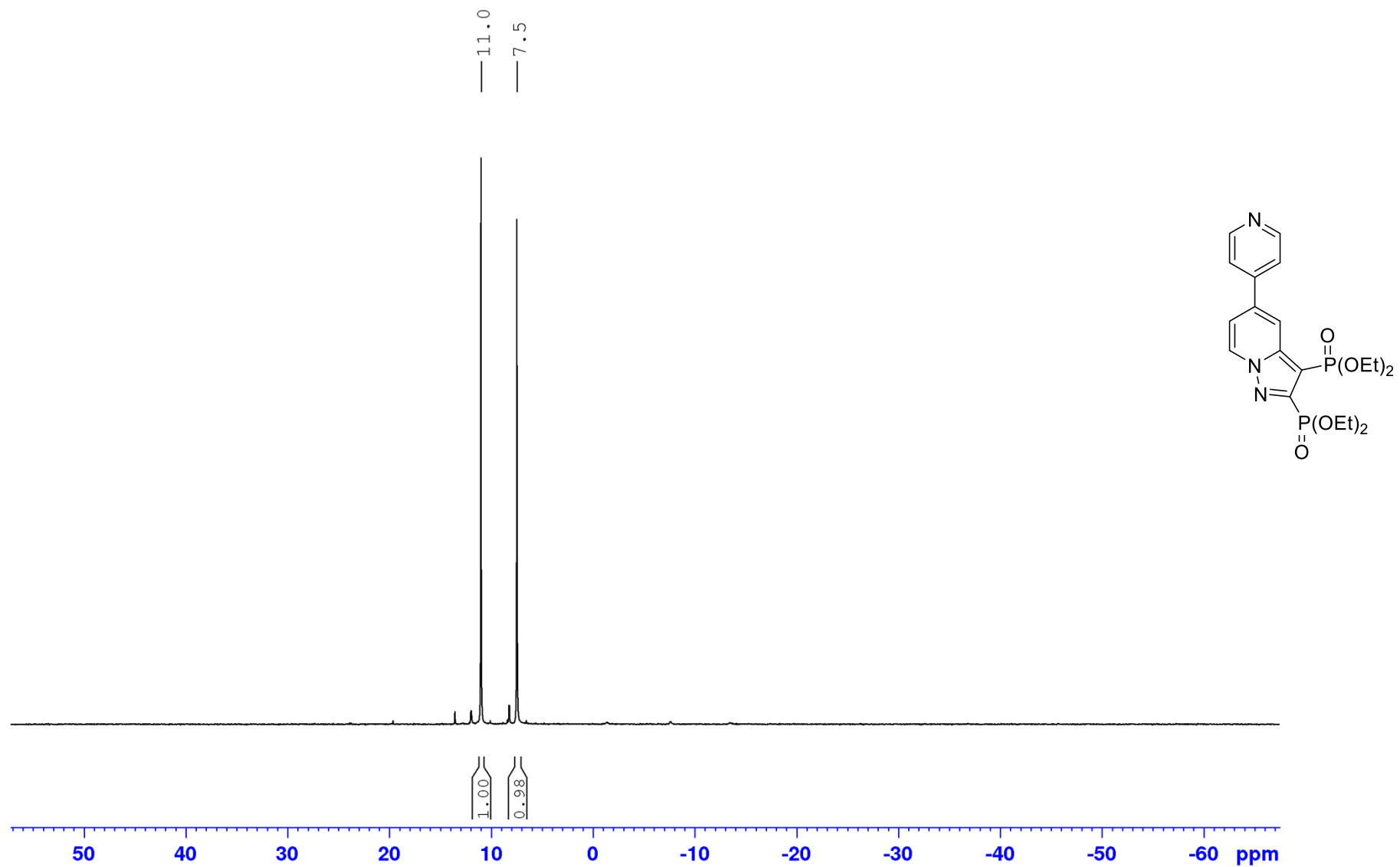
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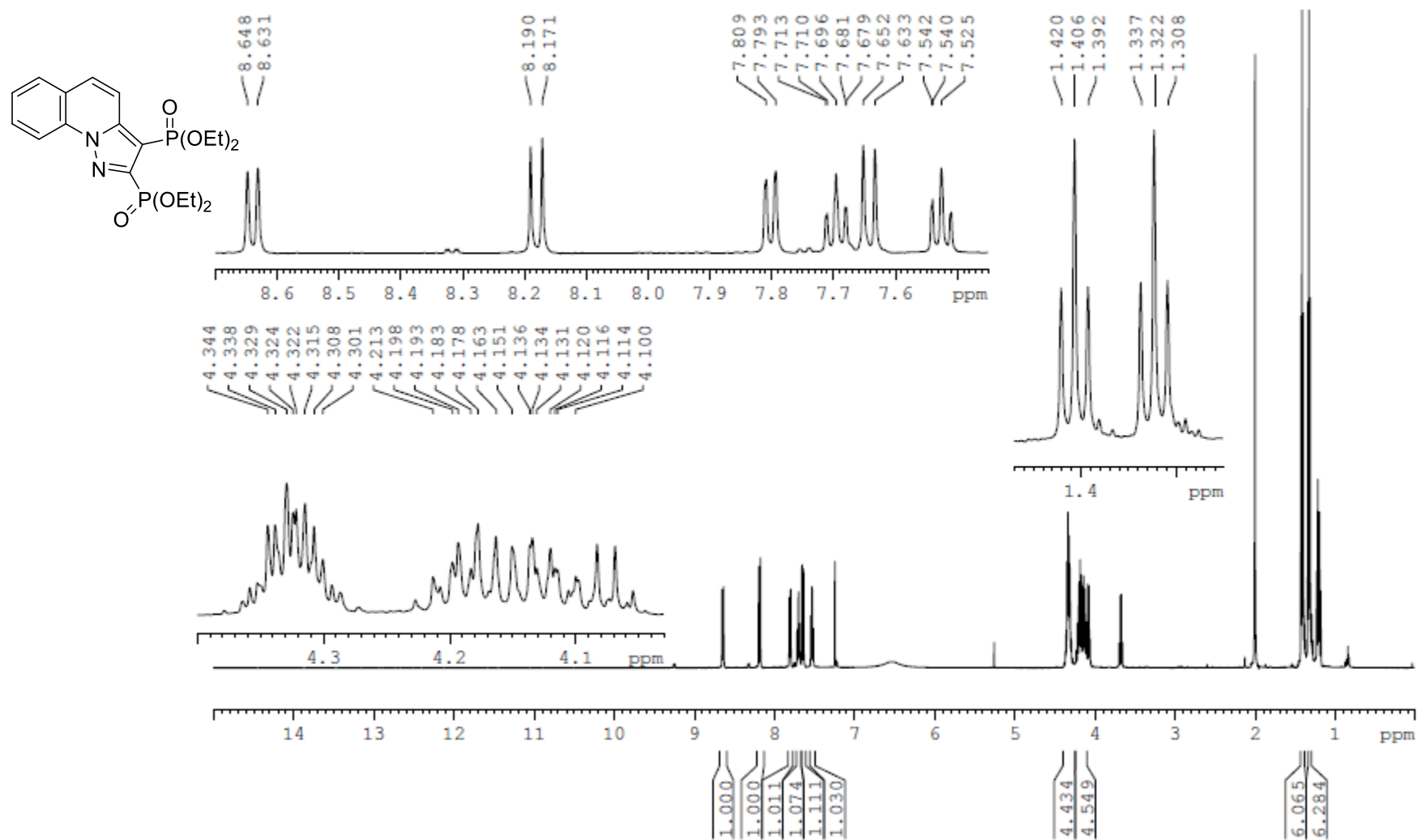
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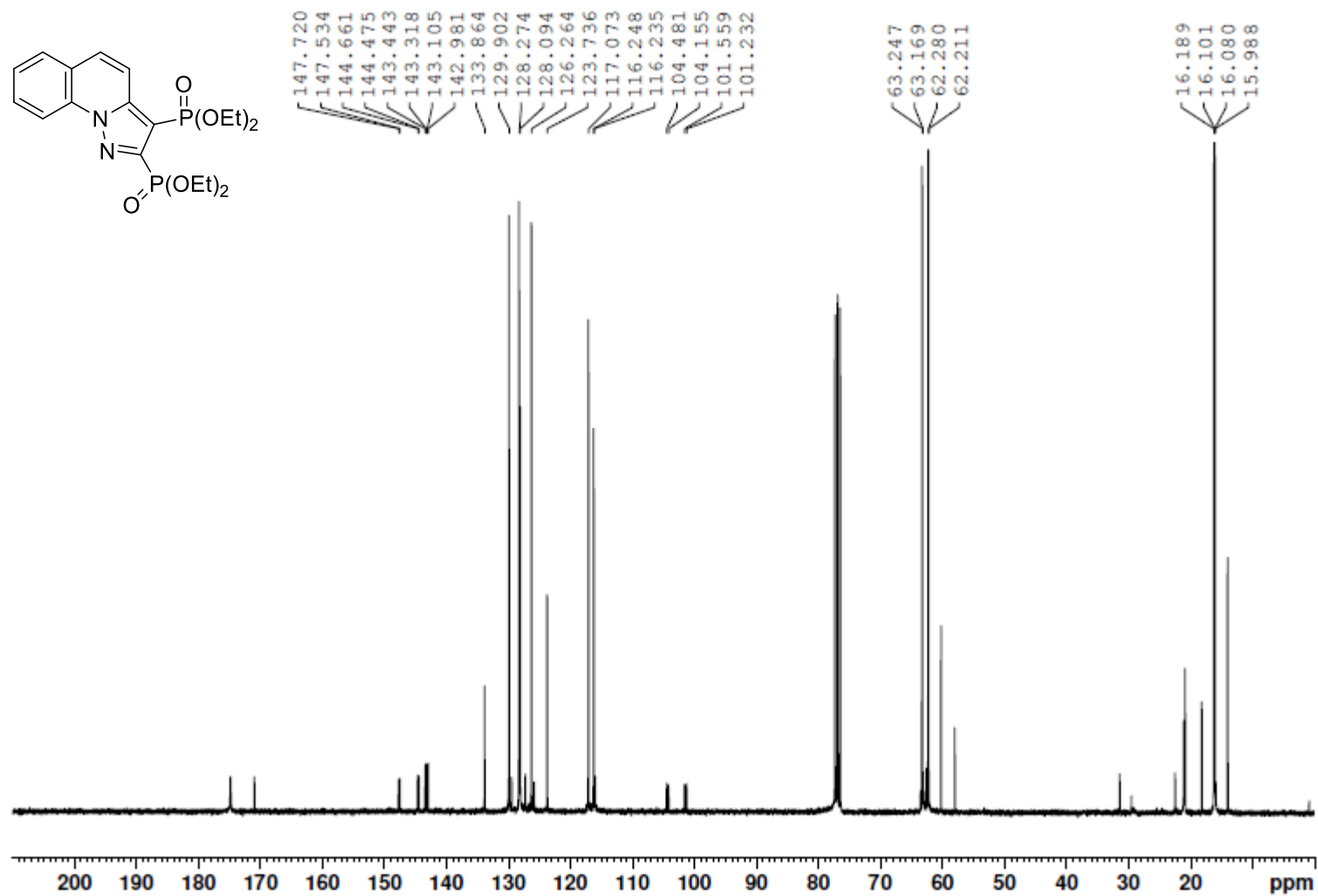
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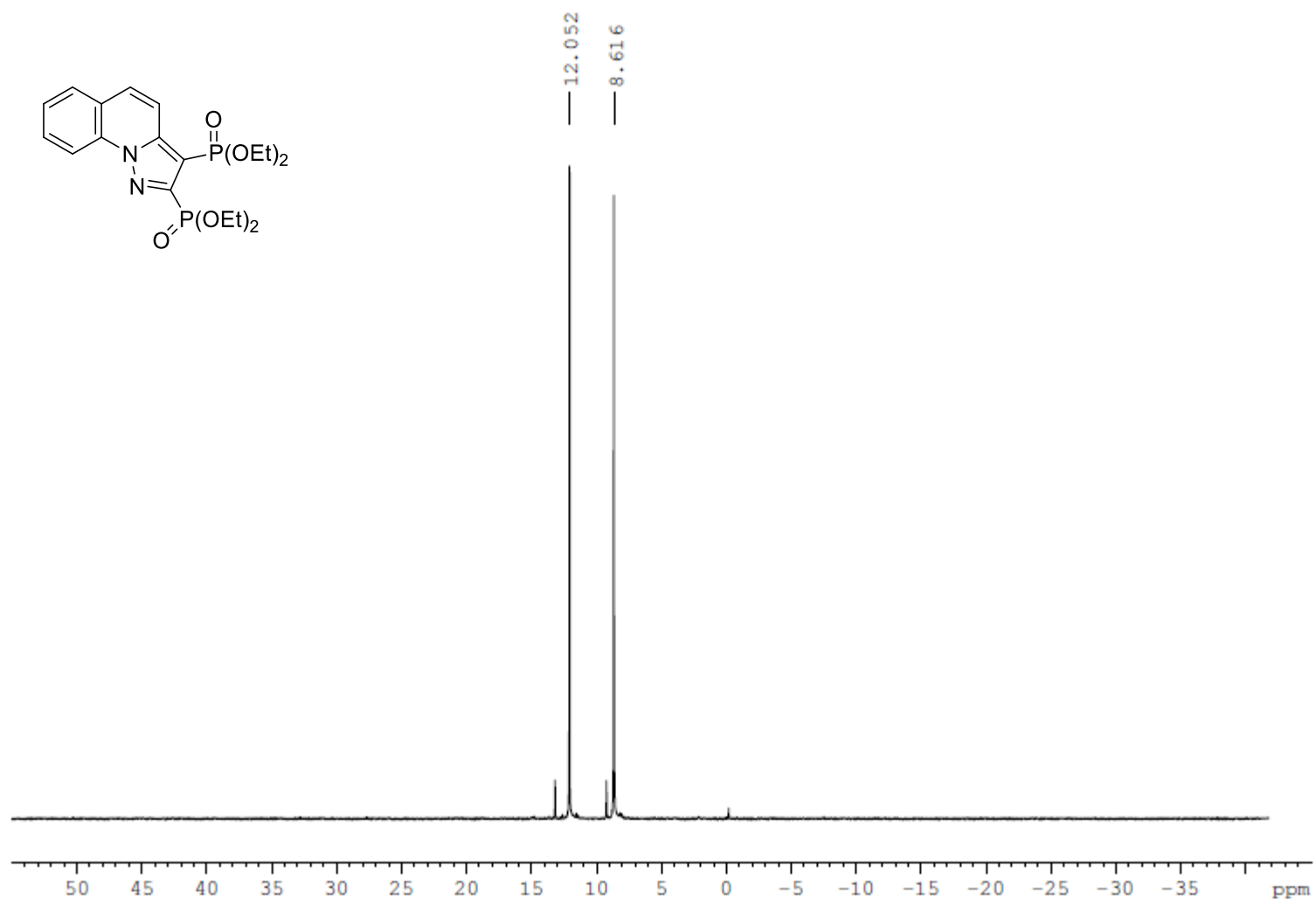
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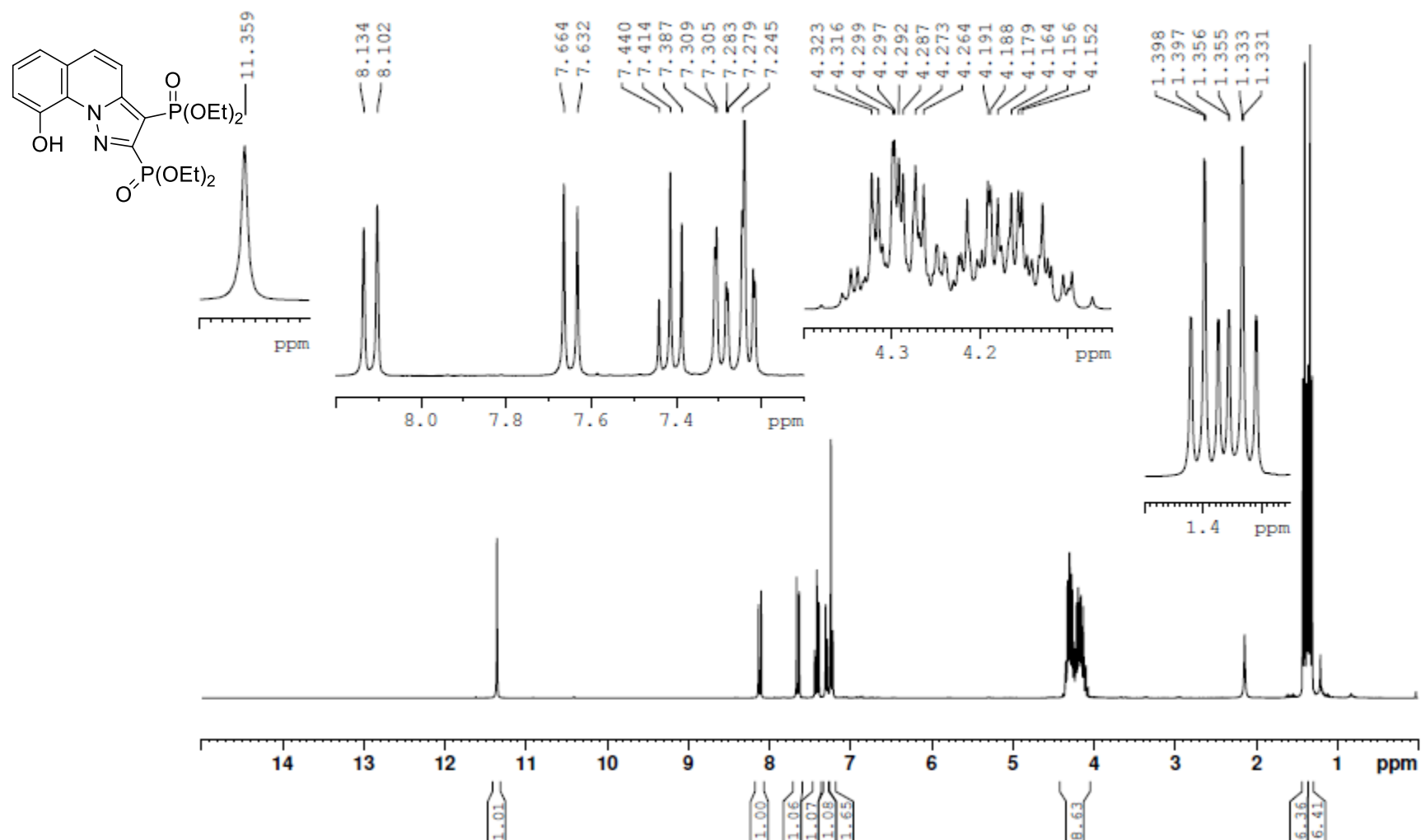
Tetraethyl pyrazolo[1,5-a]quinoline-2,3-diylldiphosphonate (5g) ^{13}C NMR



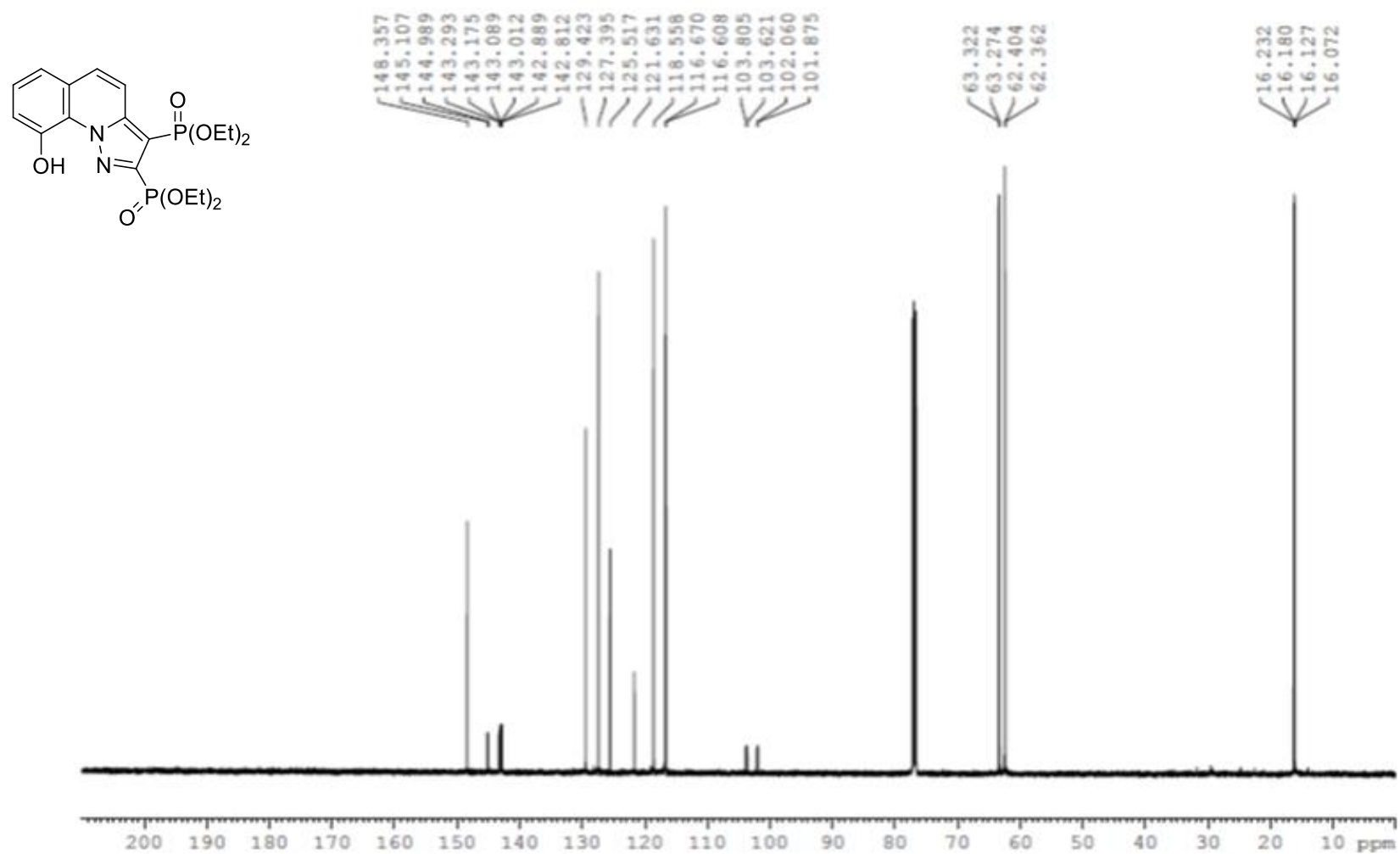
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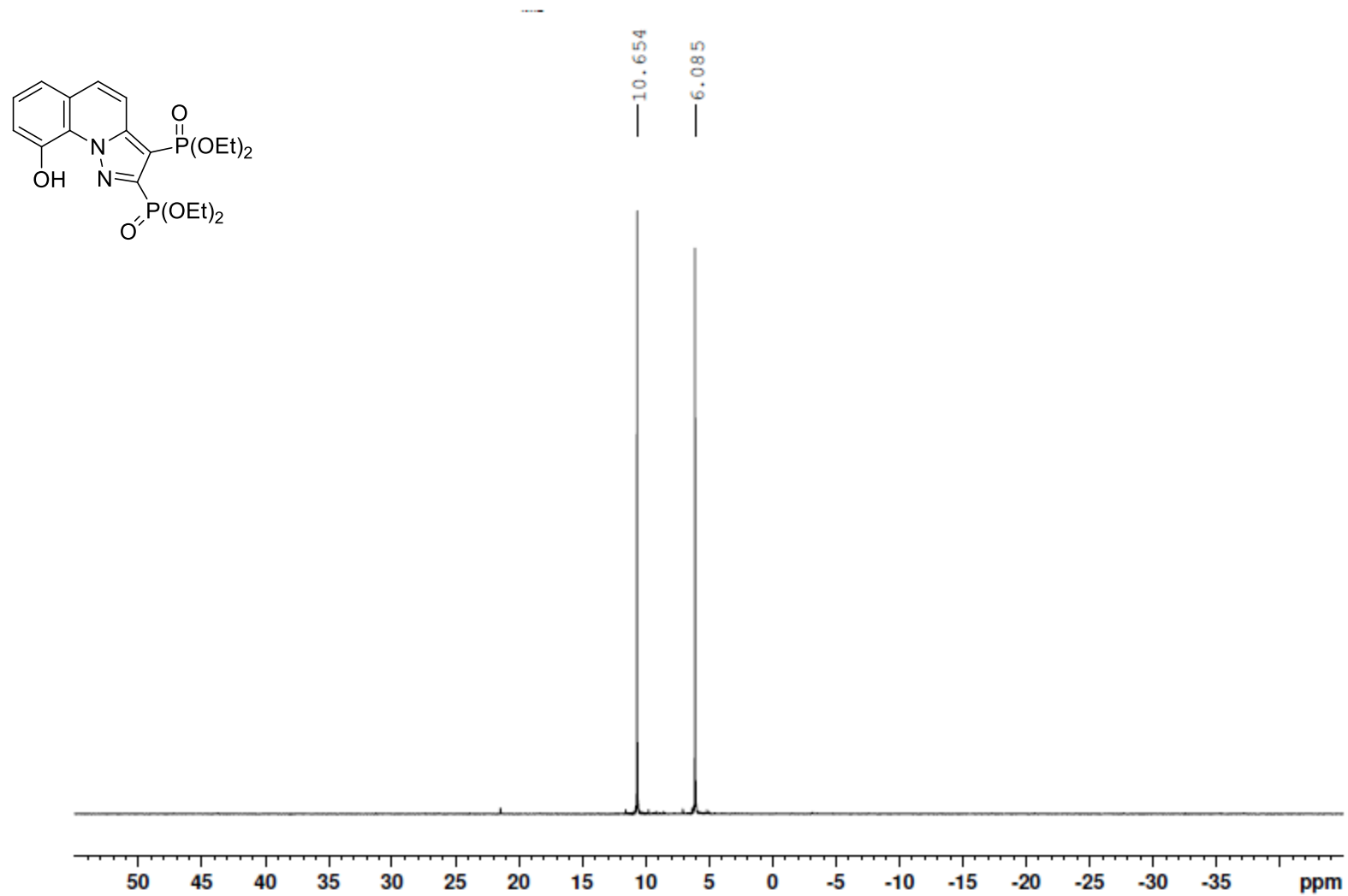
Tetraethyl (9-hydroxypyrazolo[1,5-a]quinoline-2,3-diyl)bis(phosphonate) (5h) ^1H NMR



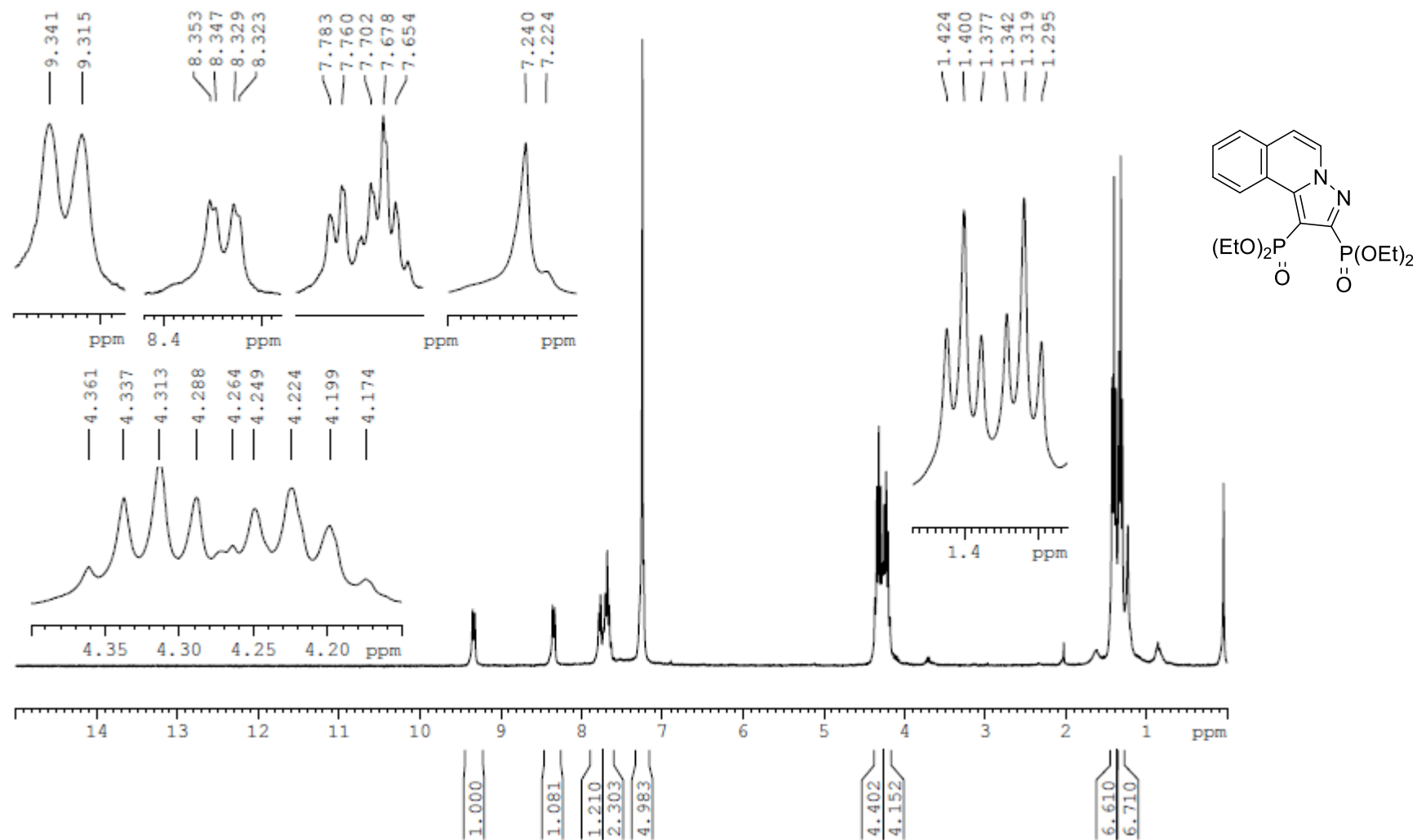
Tetraethyl (9-hydroxypyrazolo[1,5-a]quinoline-2,3-diyl)bis(phosphonate) (5h) ^{13}C NMR



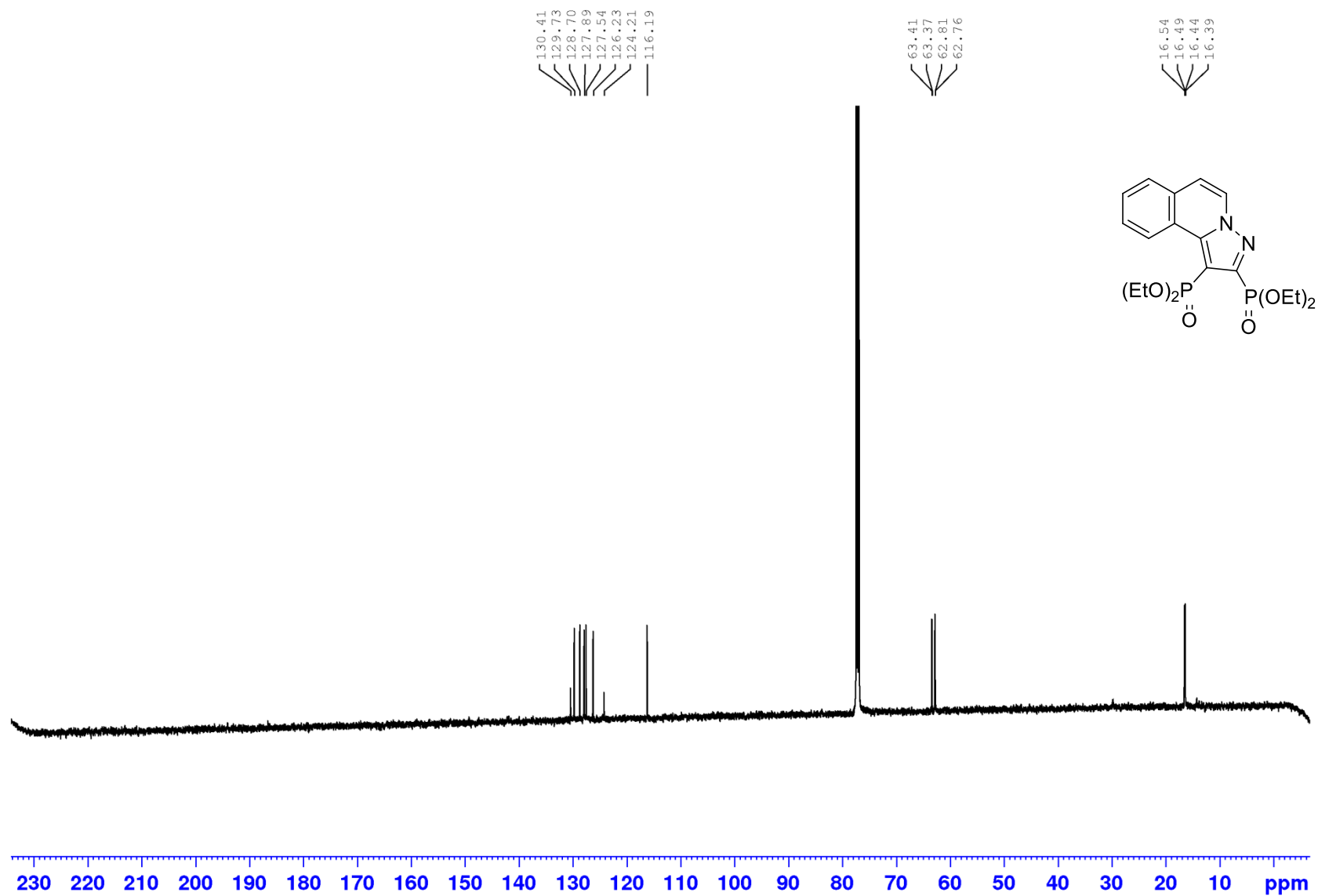
Tetraethyl (9-hydroxypyrazolo[1,5-a]quinoline-2,3-diyl)bis(phosphonate) (5h) ^{31}P NMR



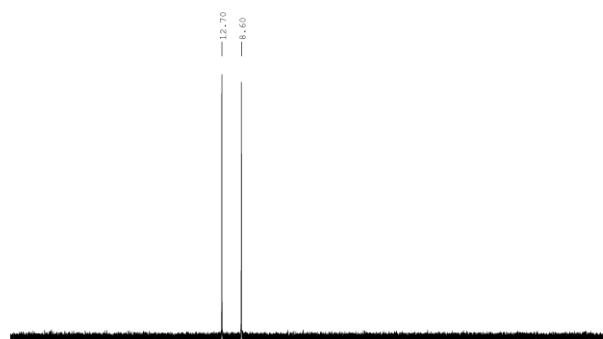
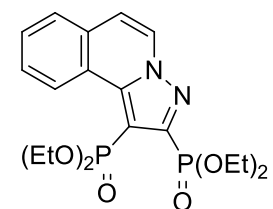
Tetraethyl pyrazolo[5,1-a]isoquinoline-1,2-diylbis(phosphonate) (5i) ^1H NMR



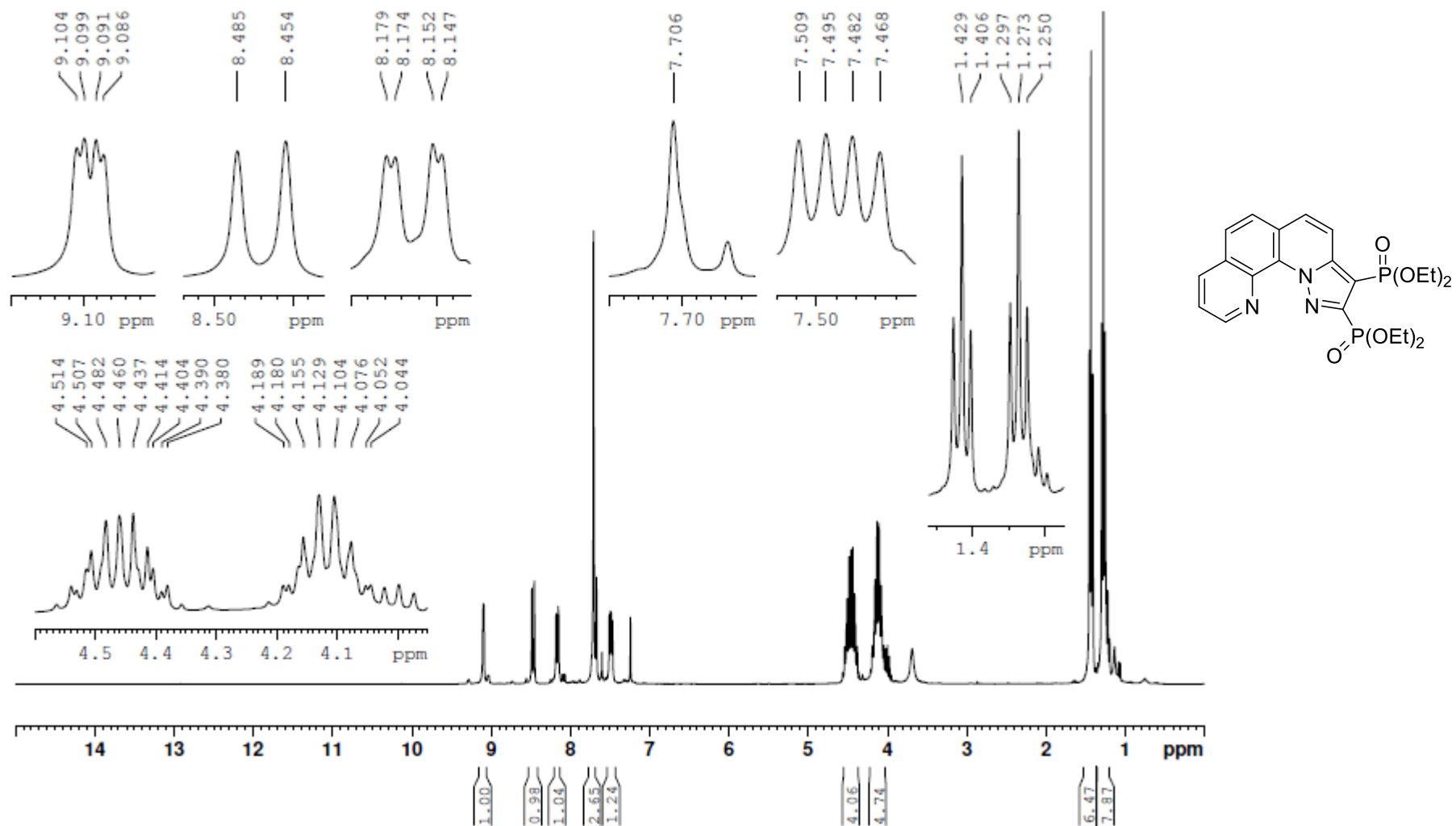
Tetraethyl pyrazolo[5,1-a]isoquinoline-1,2-diylbis(phosphonate) (5i) ^{13}C NMR



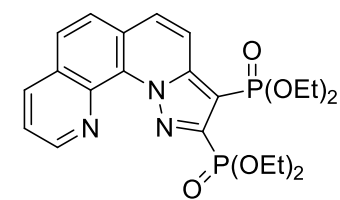
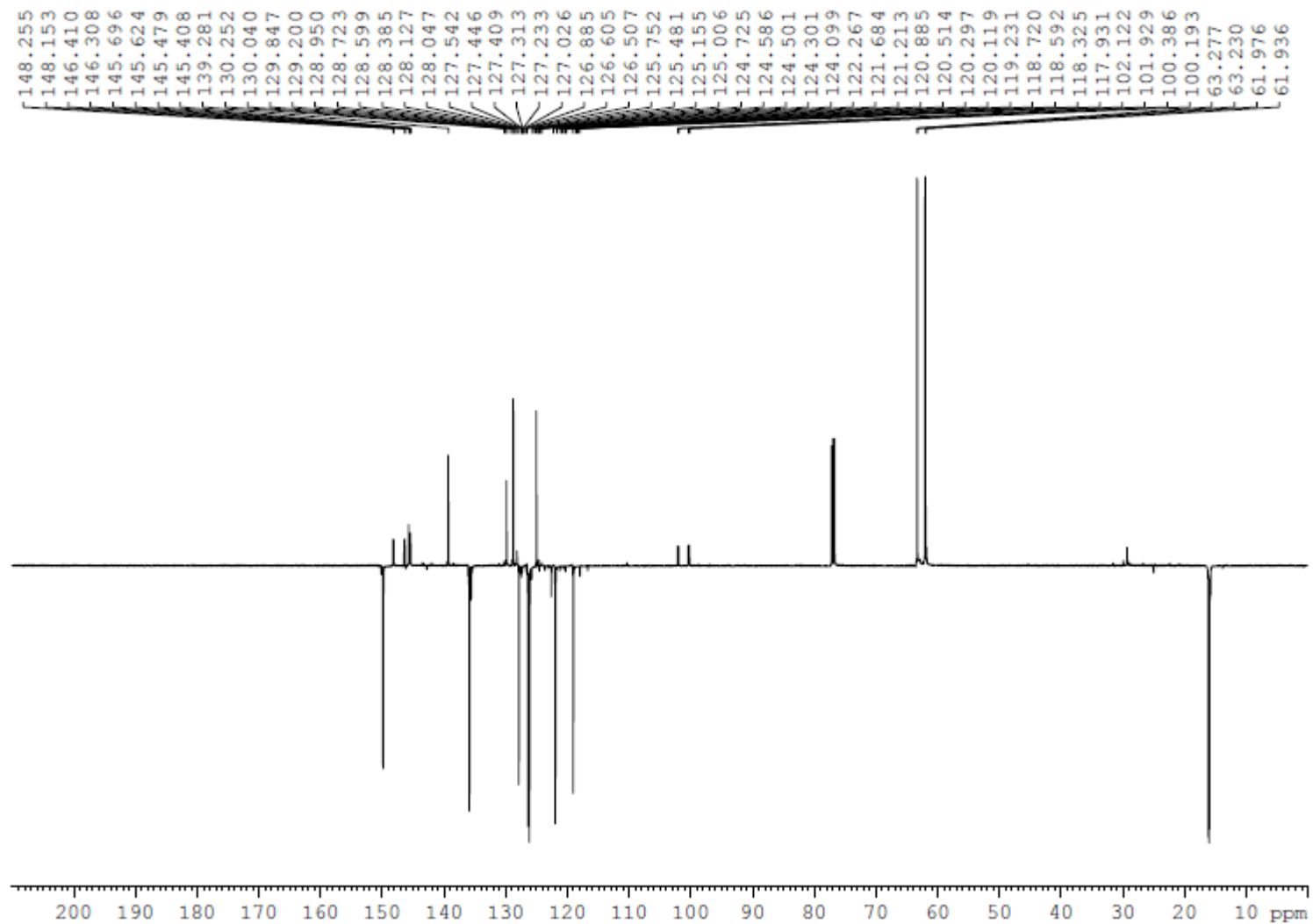
Tetraethyl pyrazolo[5,1-a]isoquinoline-1,2-diylbis(phosphonate) (5i) ^{31}P NMR



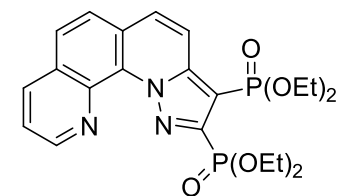
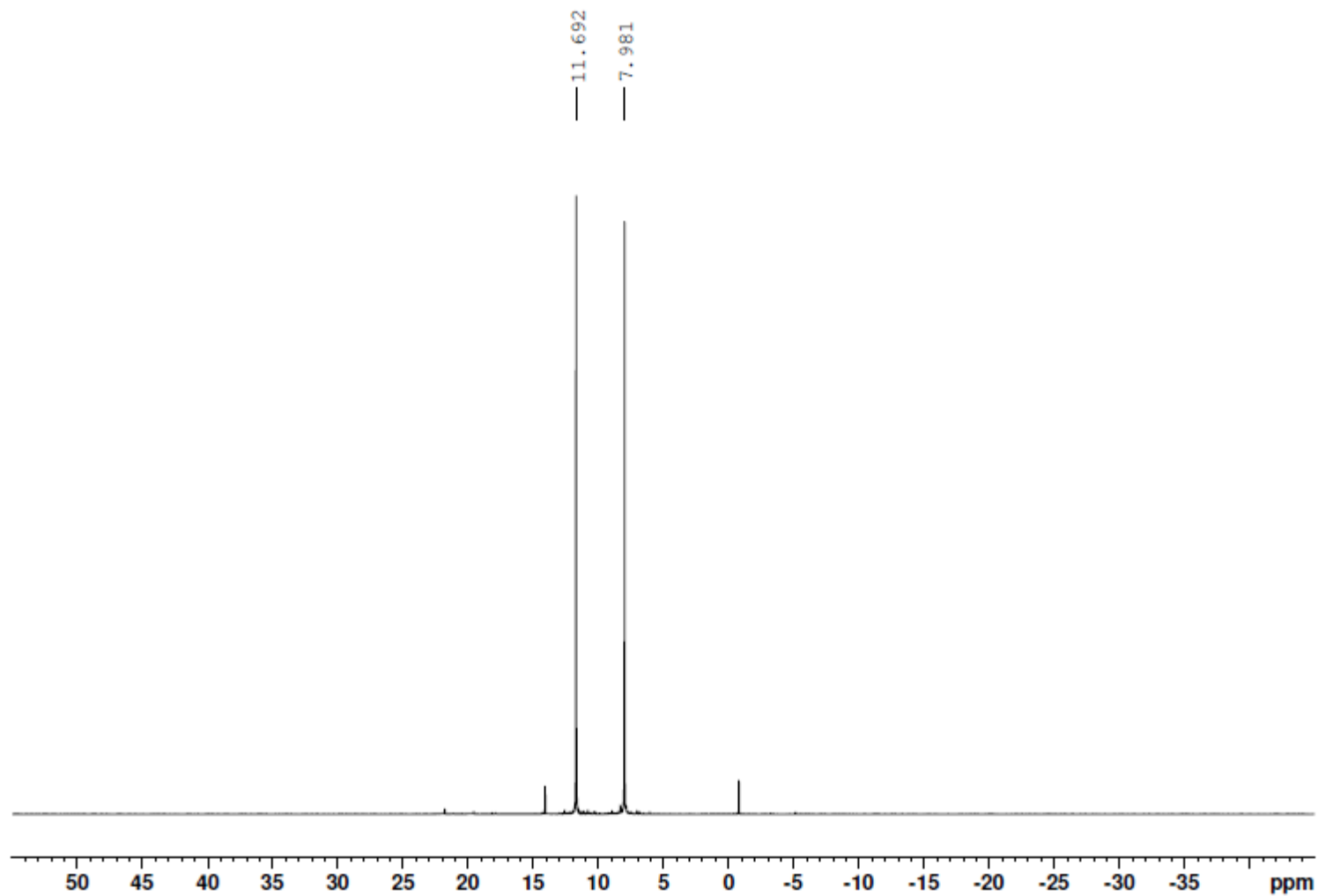
Tetraethyl pyrazolo[1,5-a][1,10]phenanthroline-2,3-diylbis(phosphonate) (5j) ^1H NMR



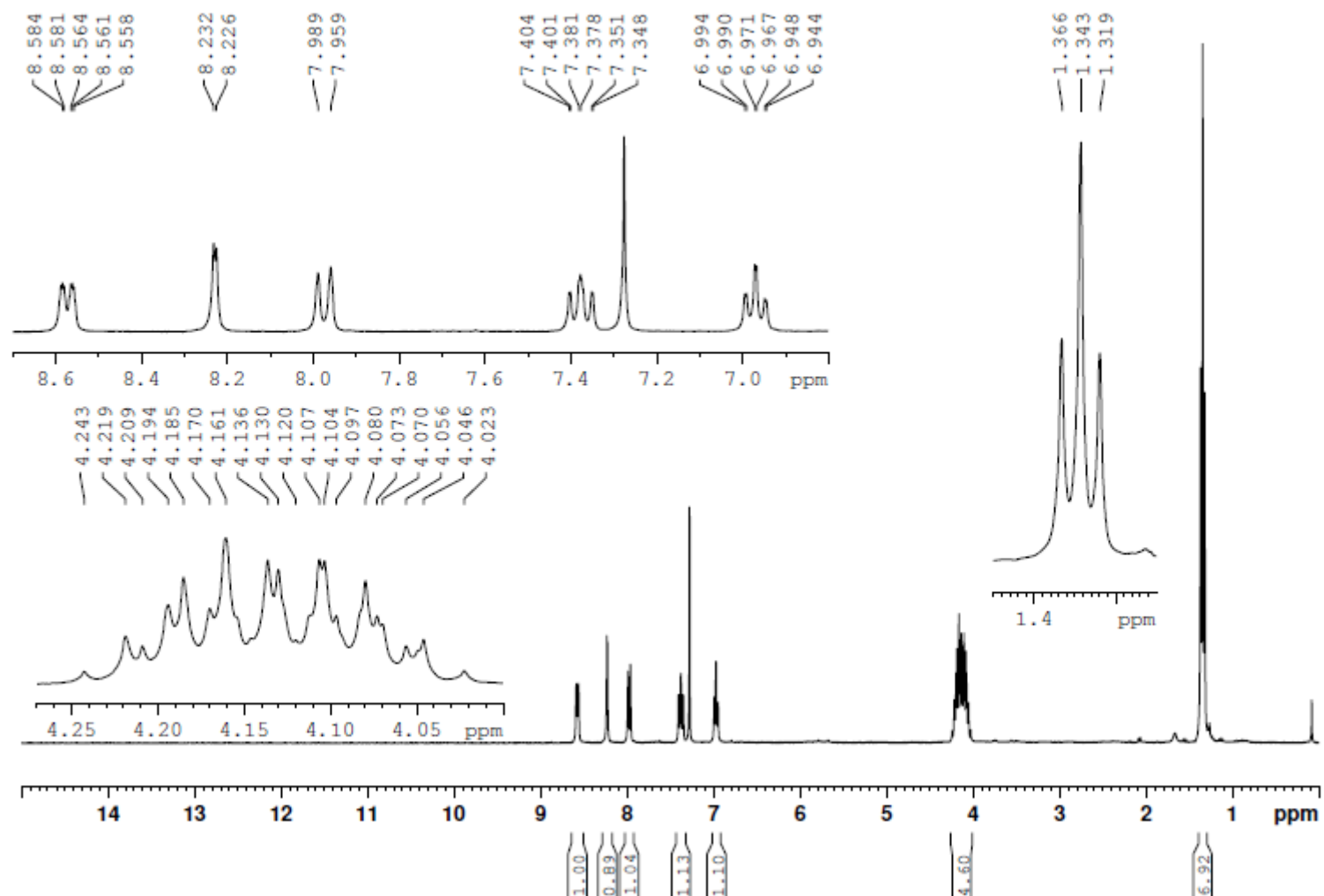
Tetraethyl pyrazolo[1,5-a][1,10]phenanthroline-2,3-diylbis(phosphonate) (5j) ^{13}C NMR



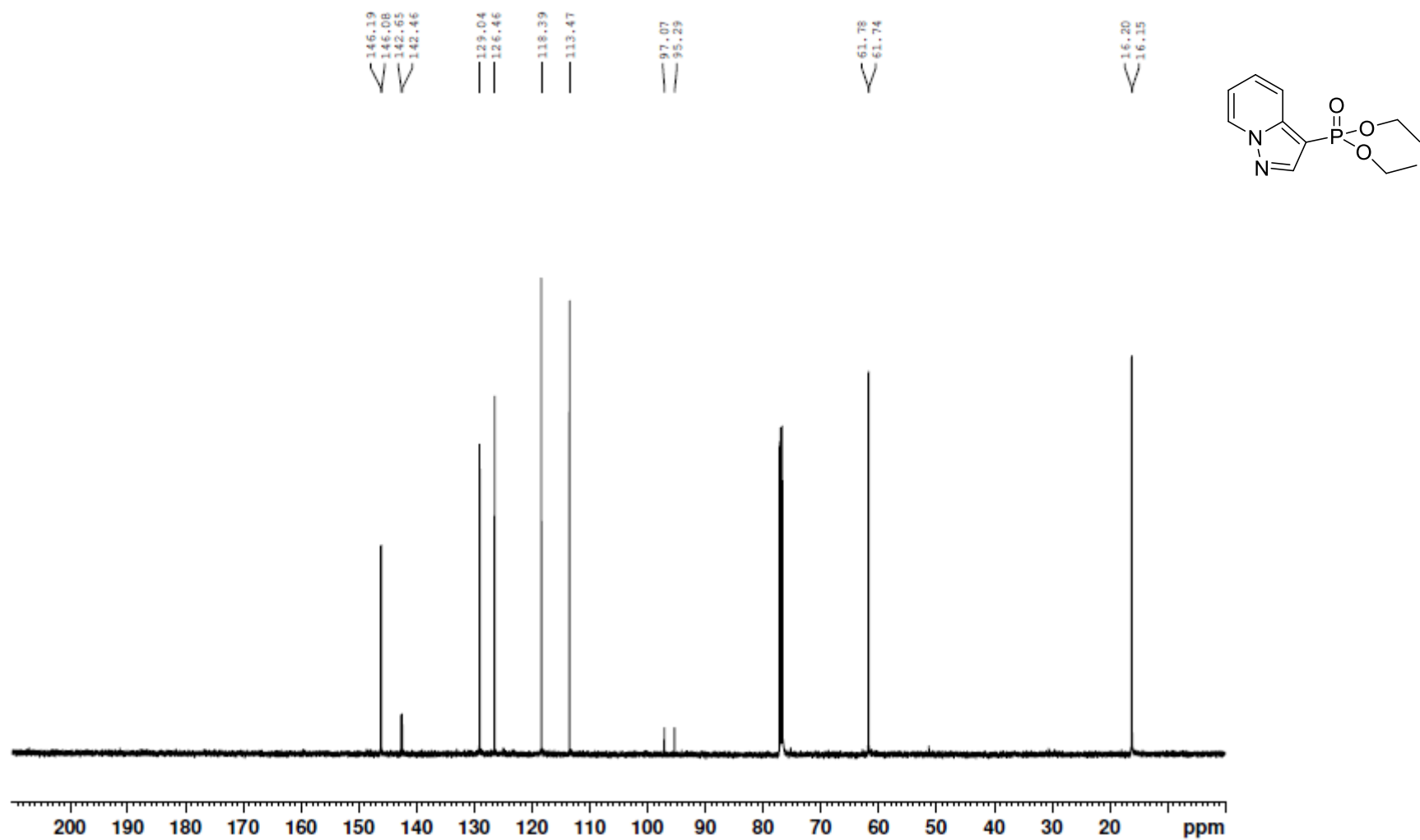
Tetraethyl pyrazolo[1,5-a][1,10]phenanthroline-2,3-diylbis(phosphonate) (5j) ^{31}P NMR



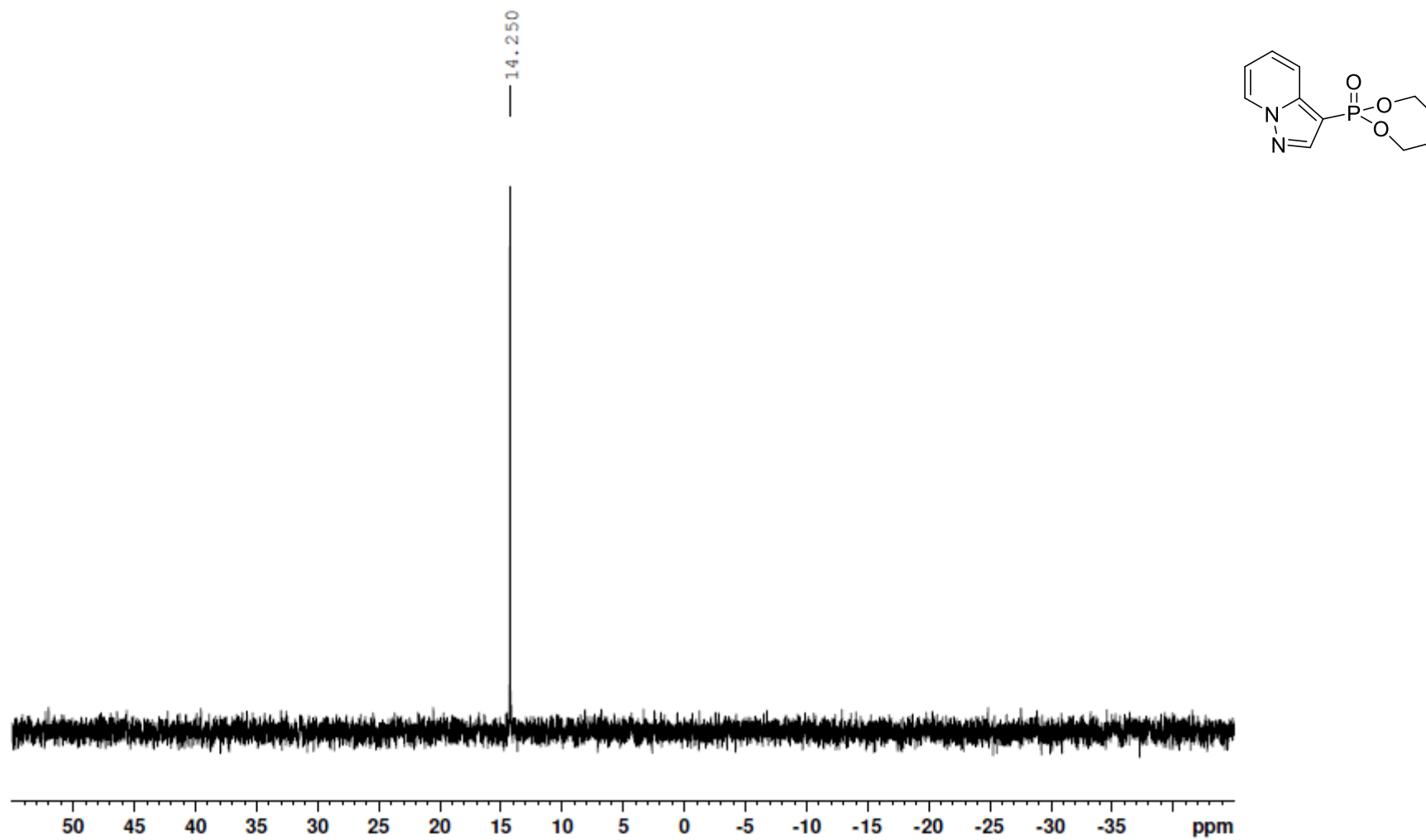
Diethyl (pyrazolo[1,5-a]pyridin-3-yl)phosphonate ¹H NMR (5k).



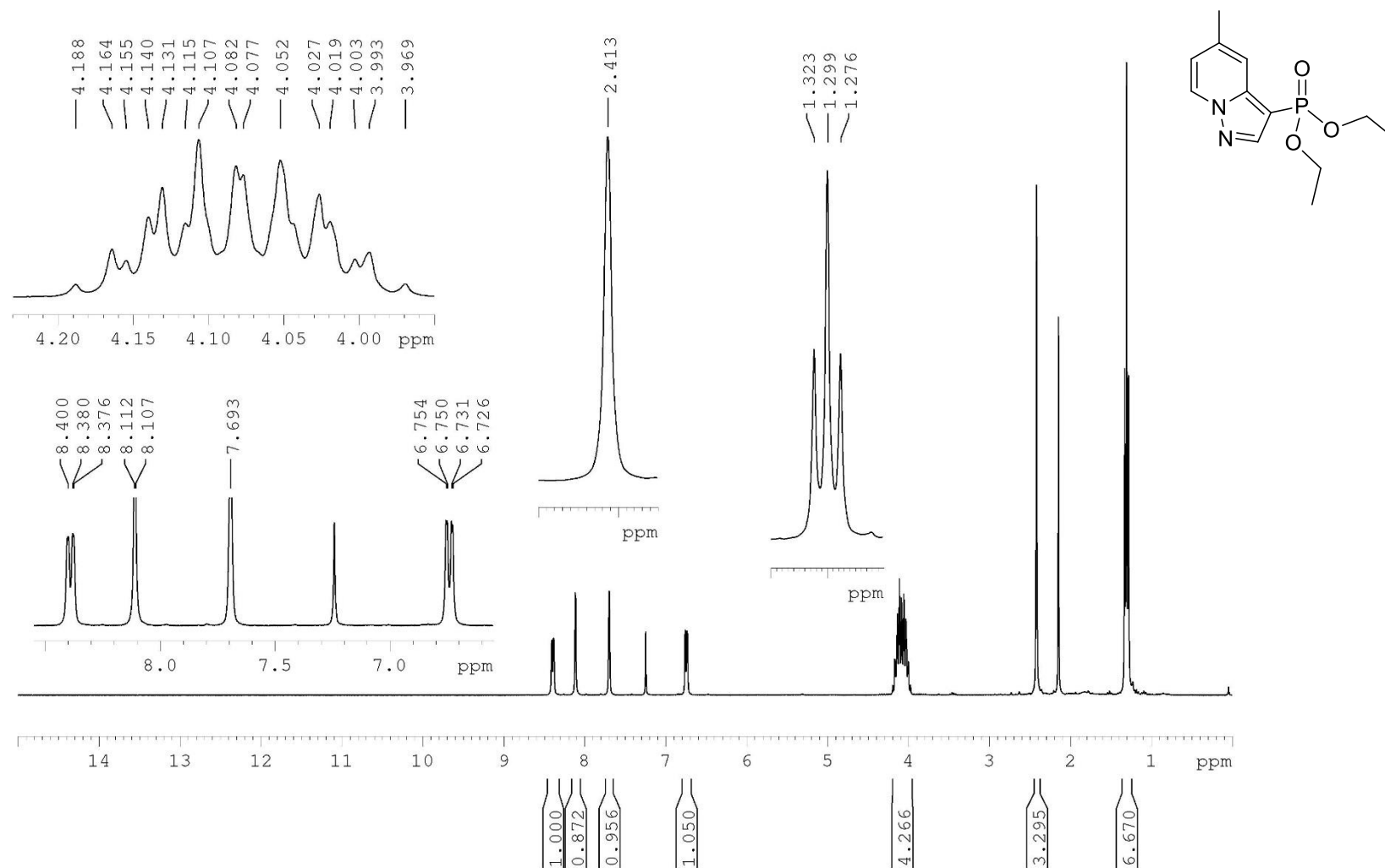
Diethyl (pyrazolo[1,5-a]pyridin-3-yl)phosphonate ^{13}C NMR (5k).



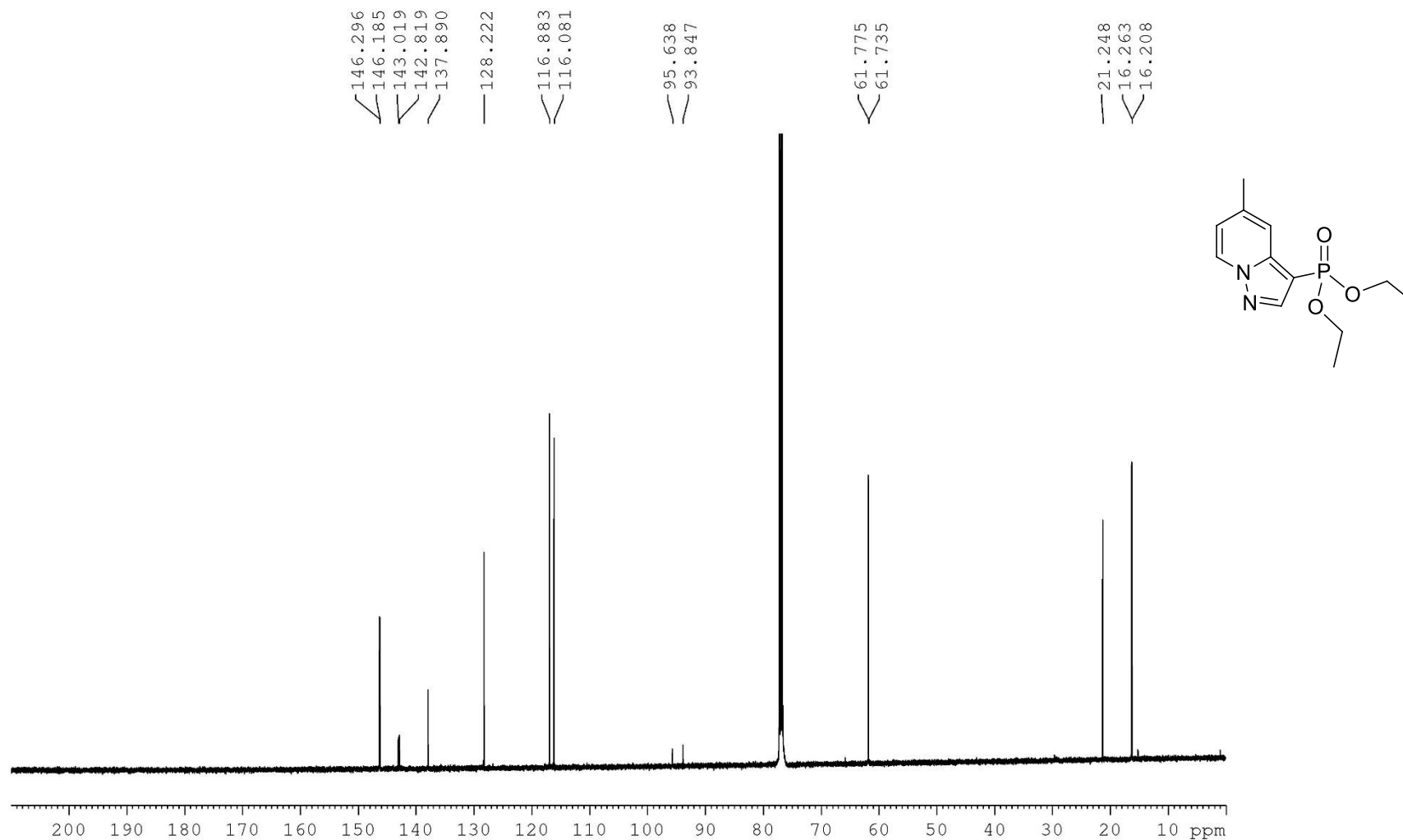
Diethyl (pyrazolo[1,5-a]pyridin-3-yl)phosphonate ^{31}P NMR (5k).



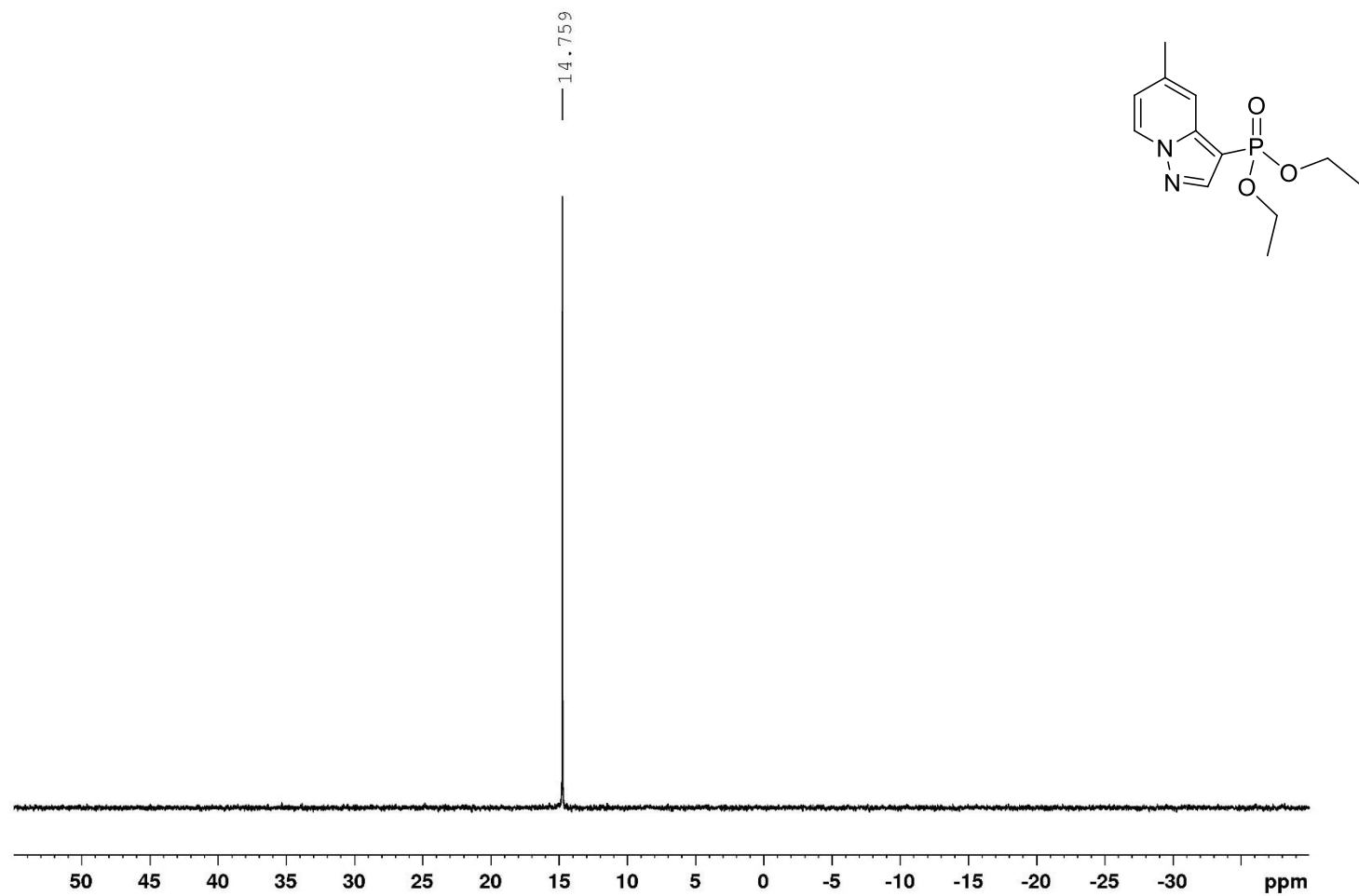
Diethyl (5-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5l) ^1H NMR.



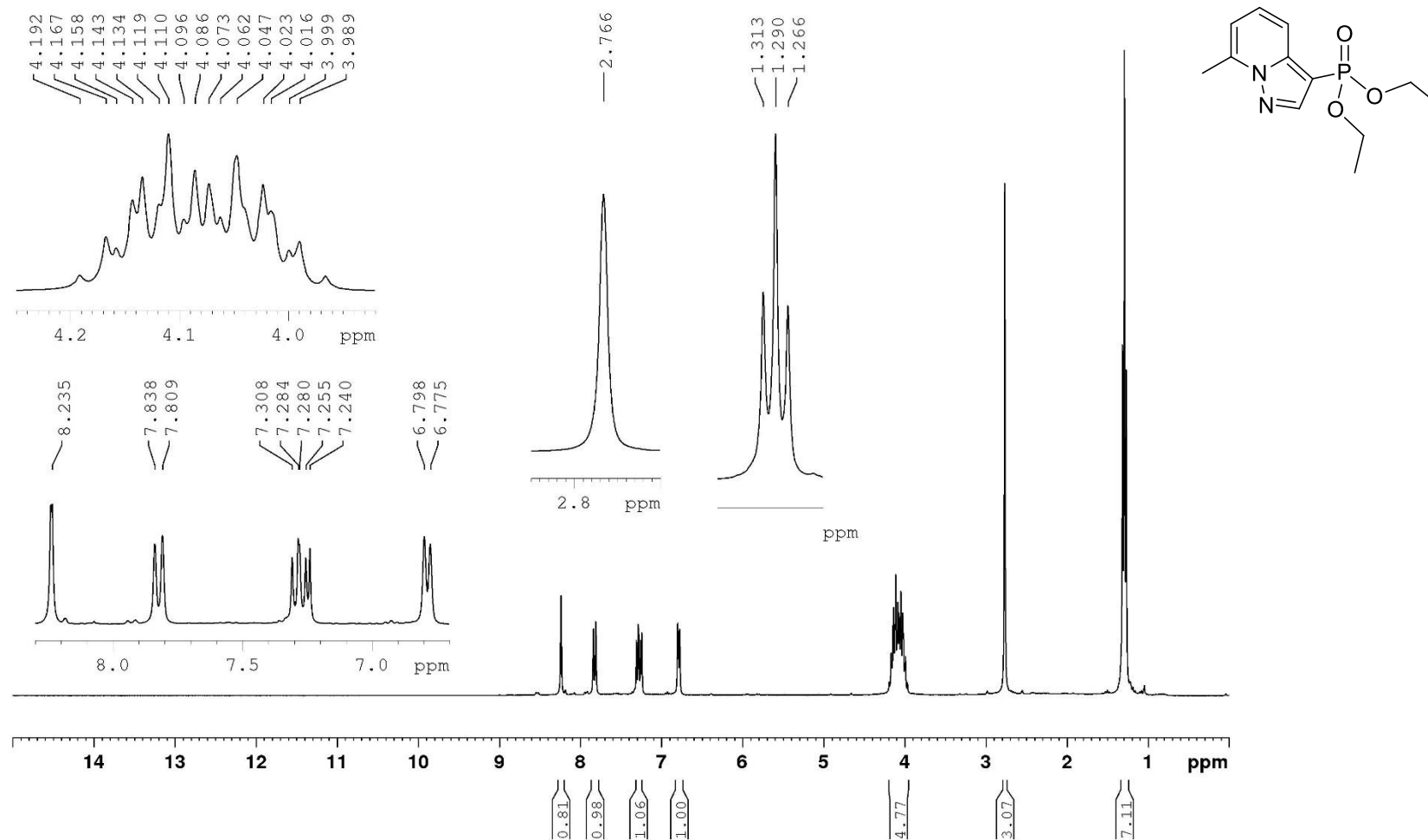
Diethyl (5-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5l) ^{13}C NMR.



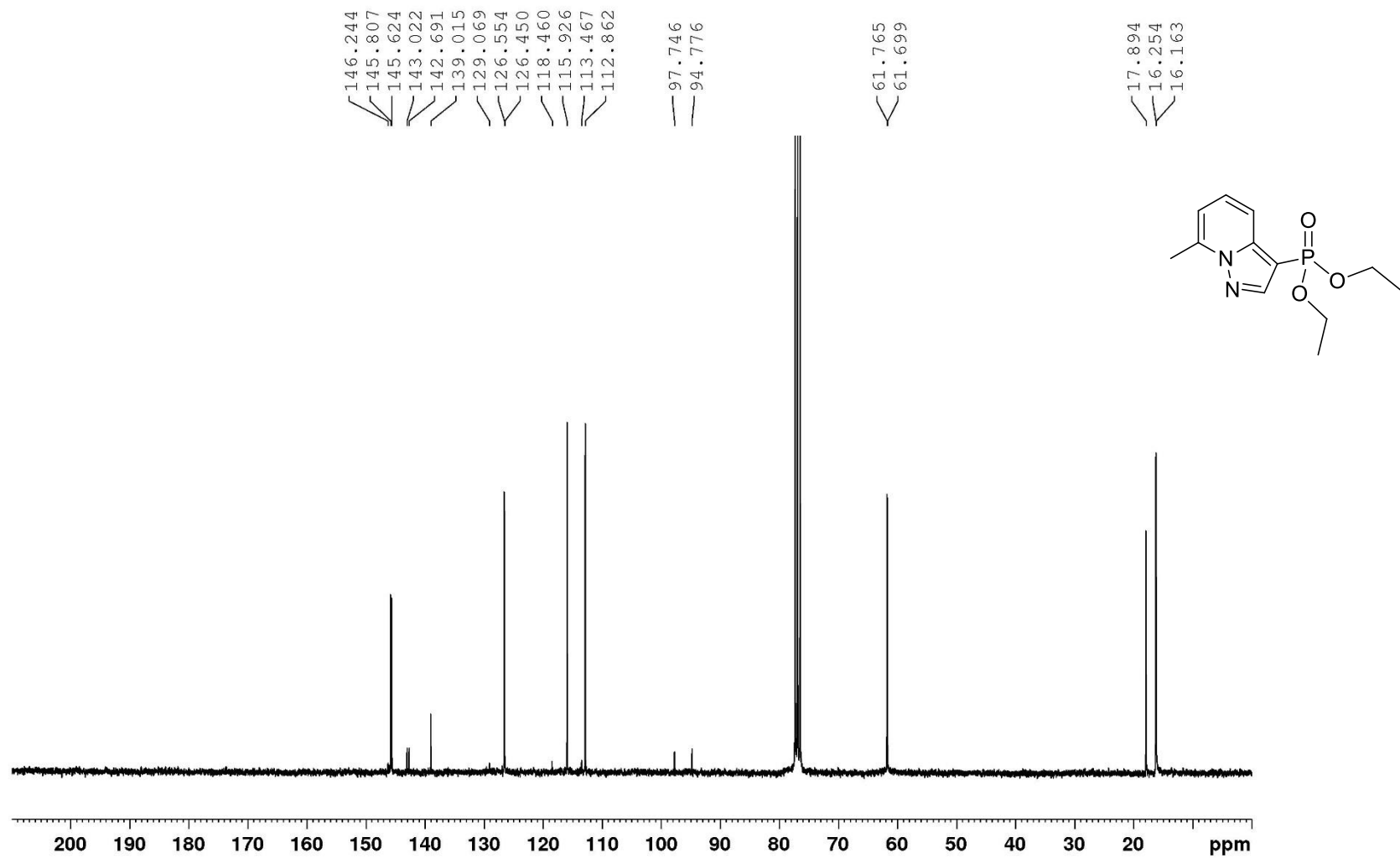
Diethyl (5-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5l) ^{31}P NMR.



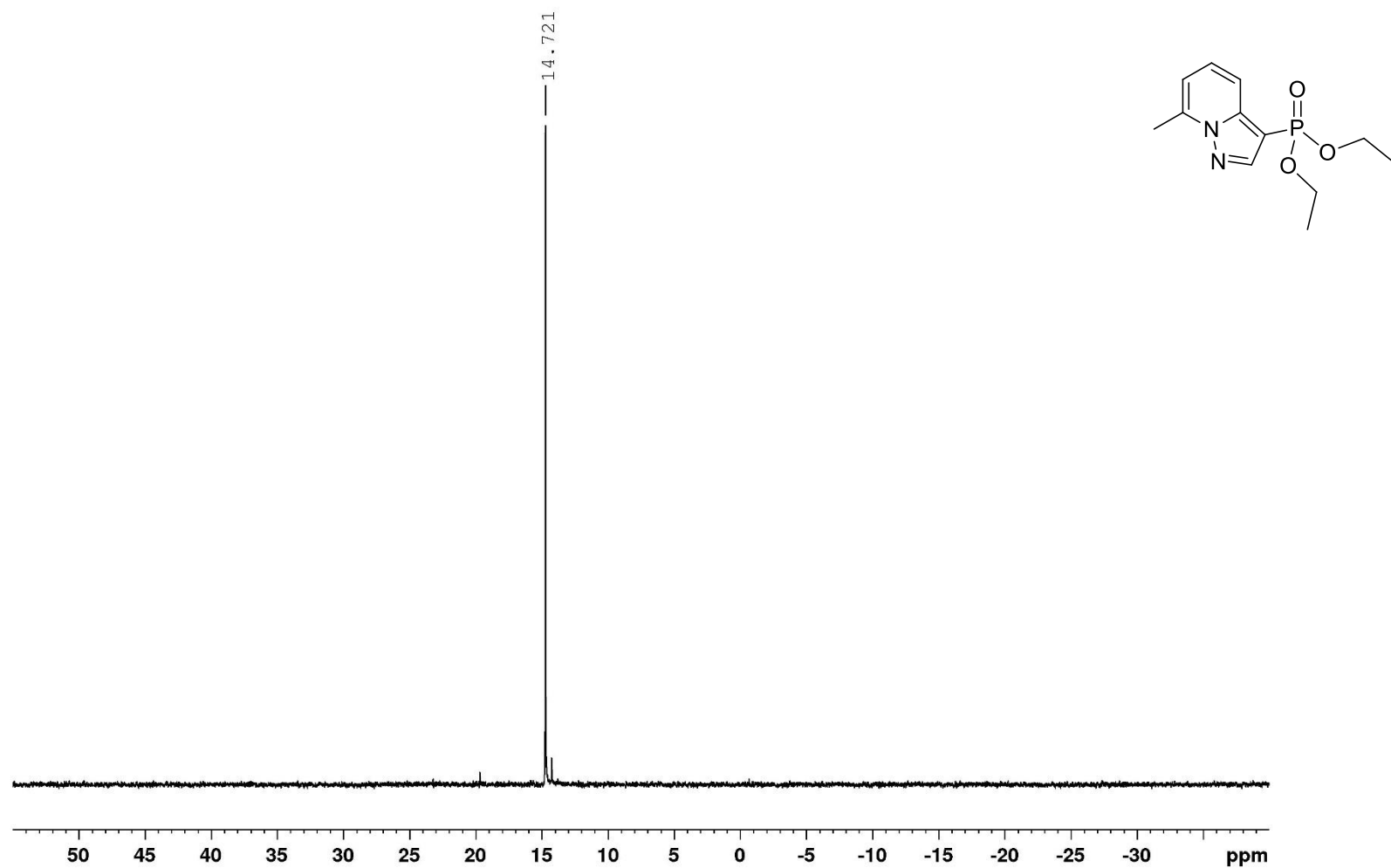
Diethyl (7-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5m) ^1H NMR.



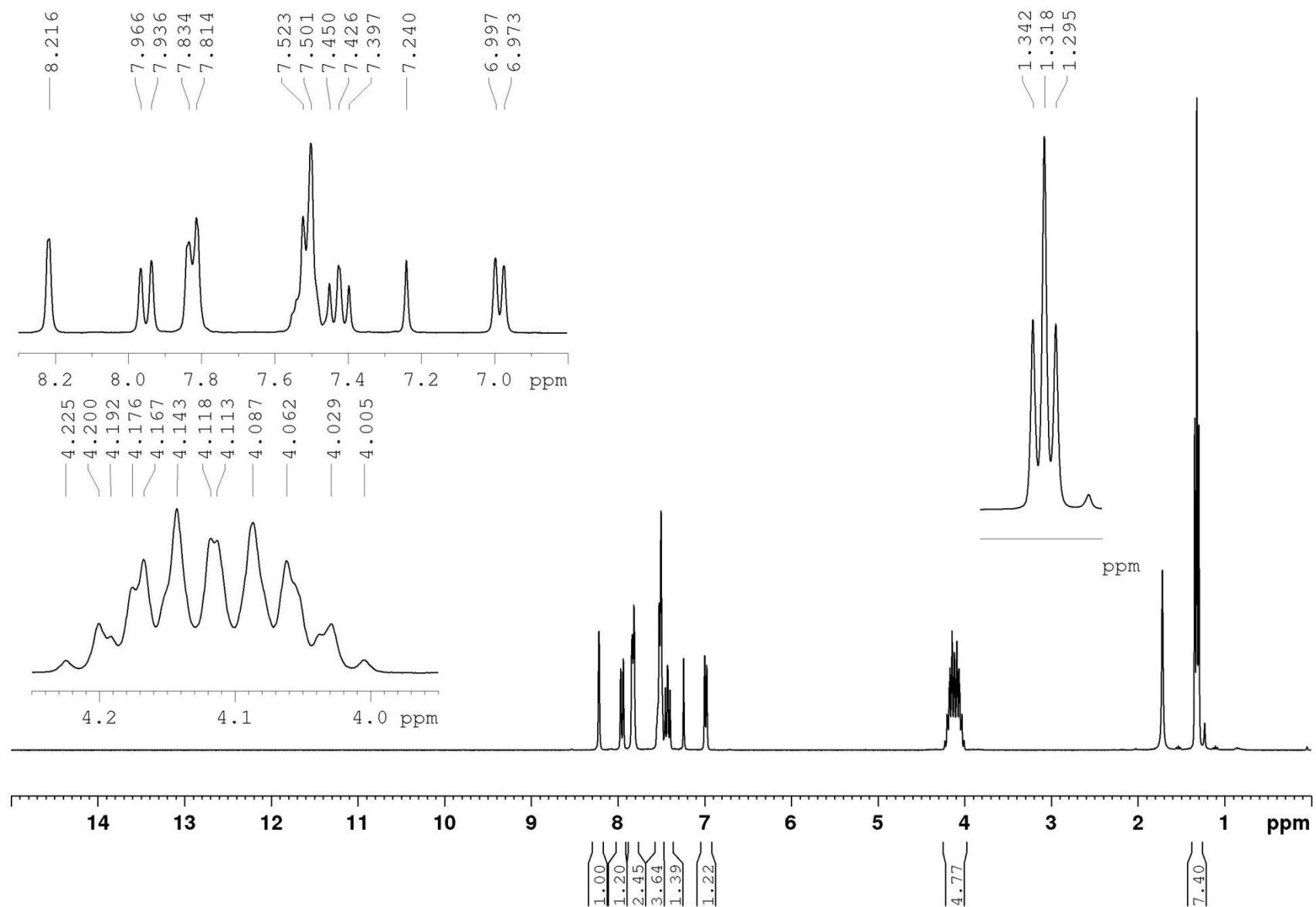
Diethyl (7-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5m) ^{13}C NMR.



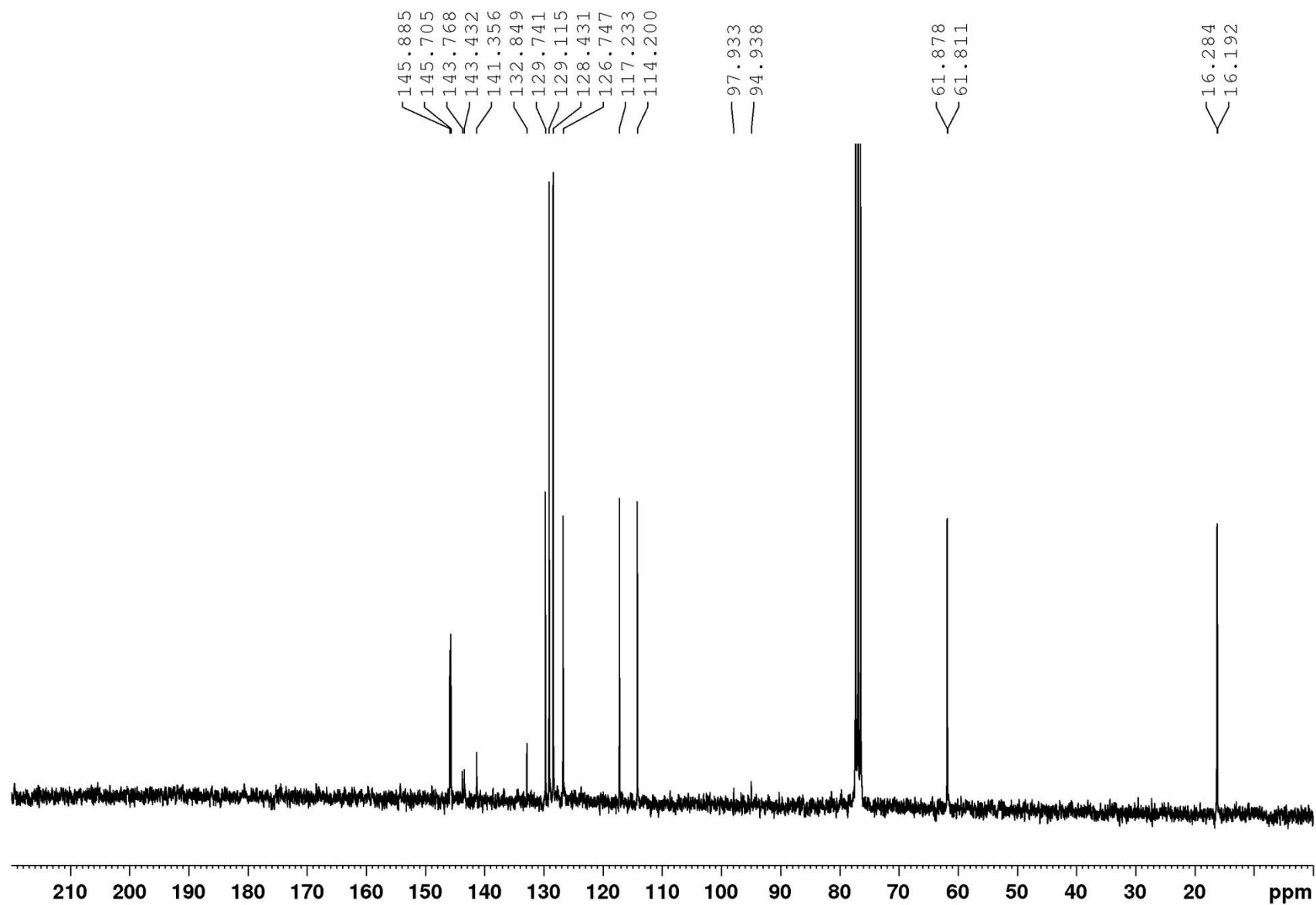
Diethyl (7-methylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5m) ^{31}P NMR.



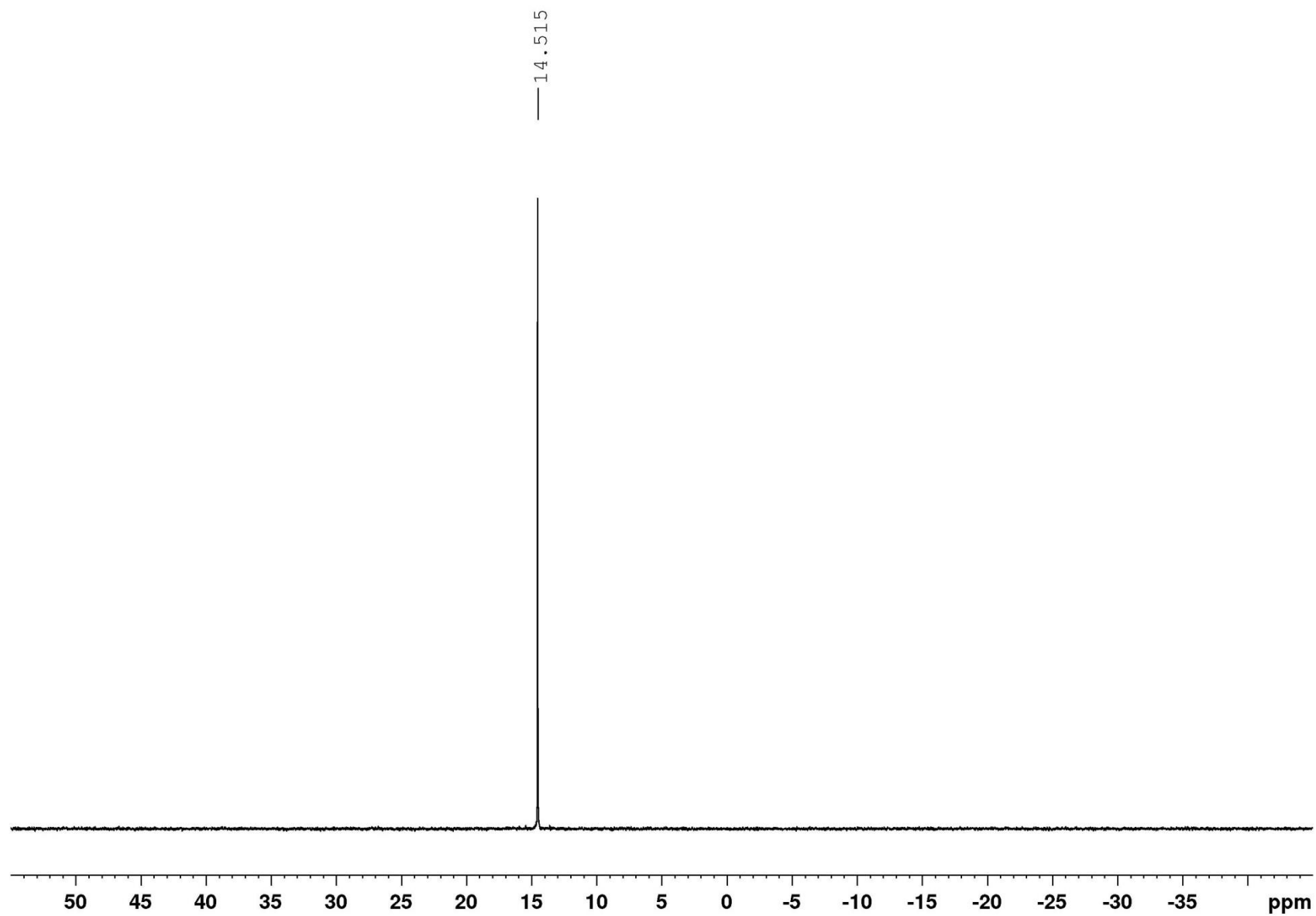
Diethyl (7-phenylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5n) ^1H NMR.



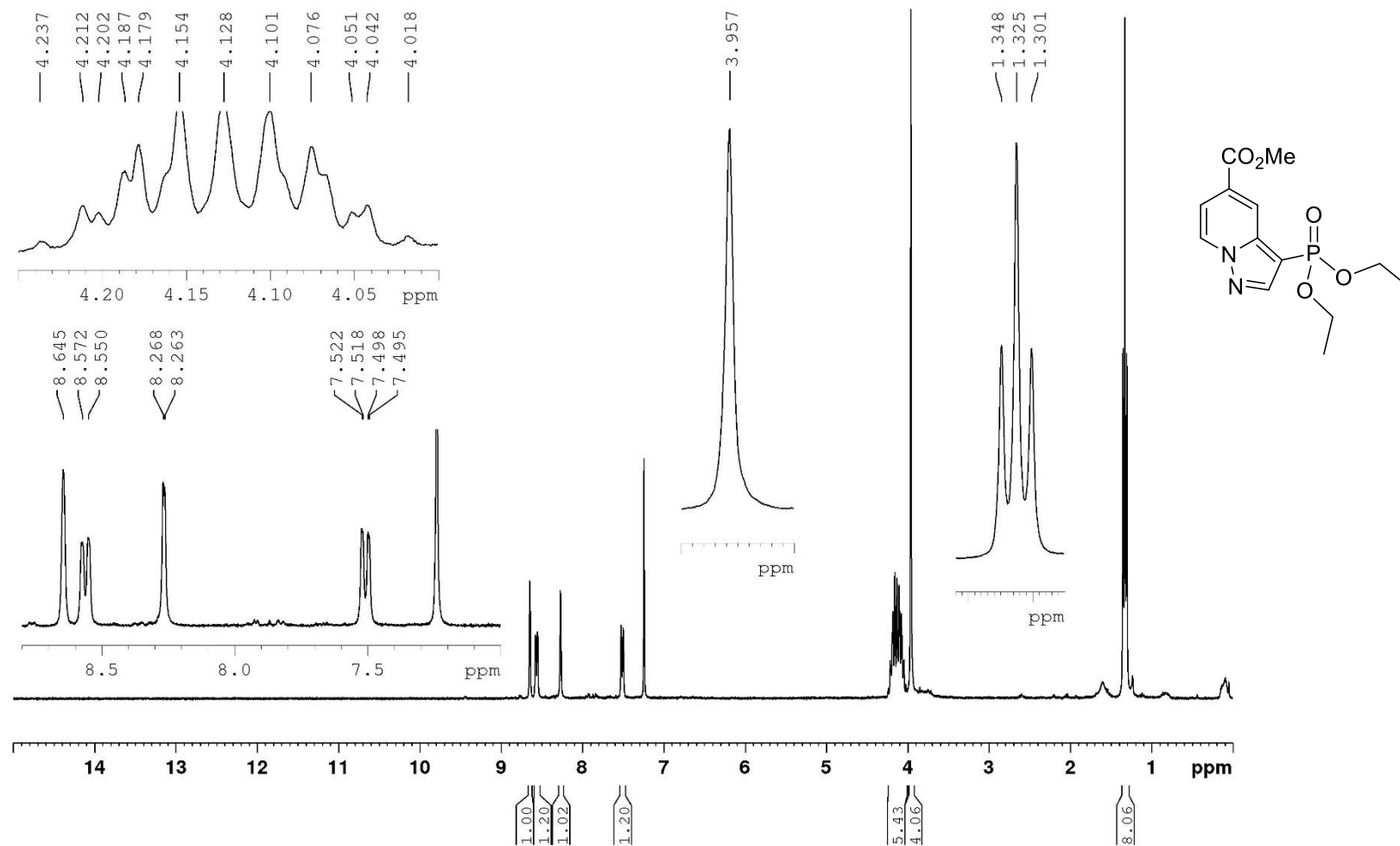
Diethyl (7-phenylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5n) ^{13}C NMR.



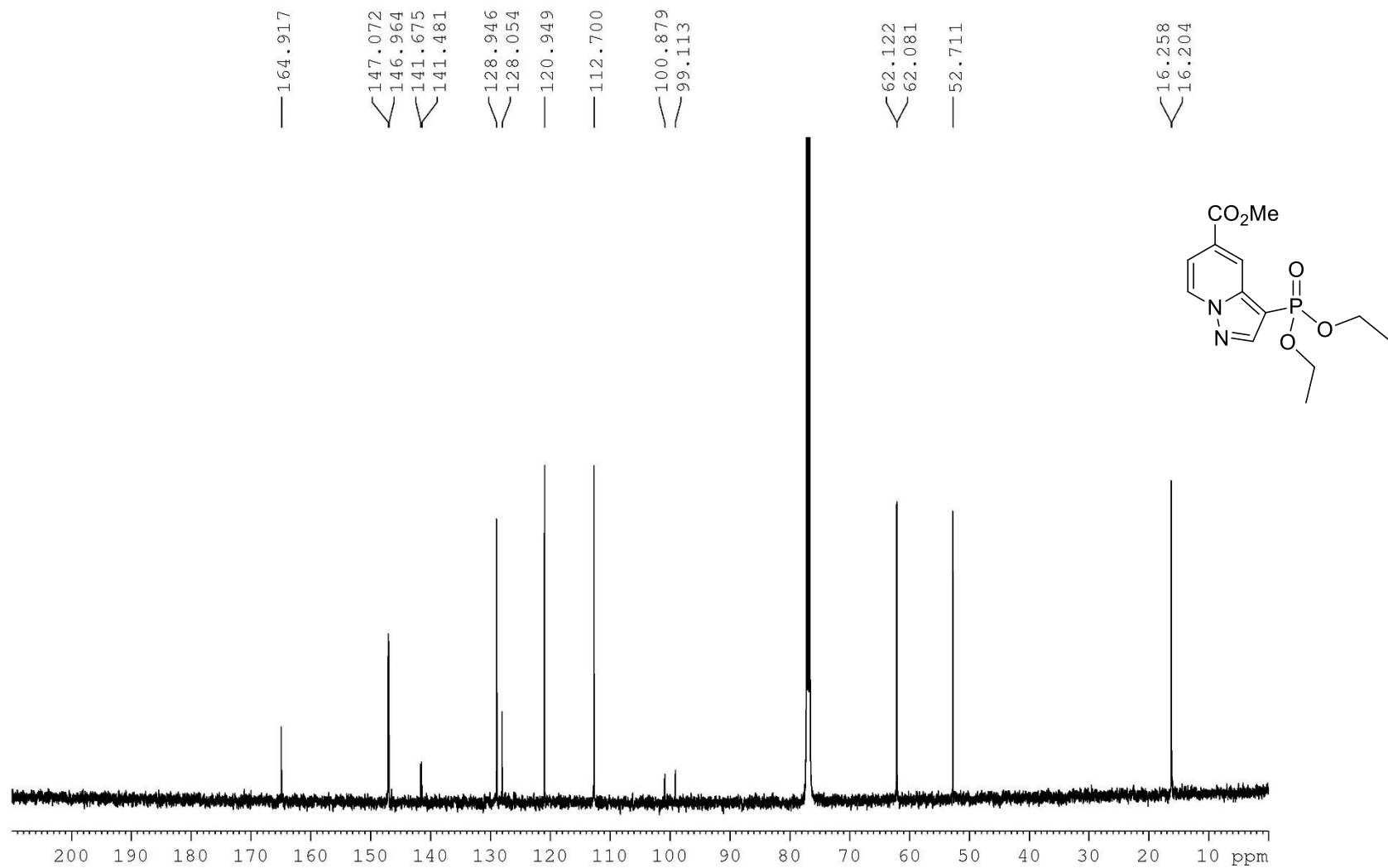
Diethyl (7-phenylpyrazolo[1,5-a]pyridin-3-yl)phosphonate (5n) ^{31}P NMR.



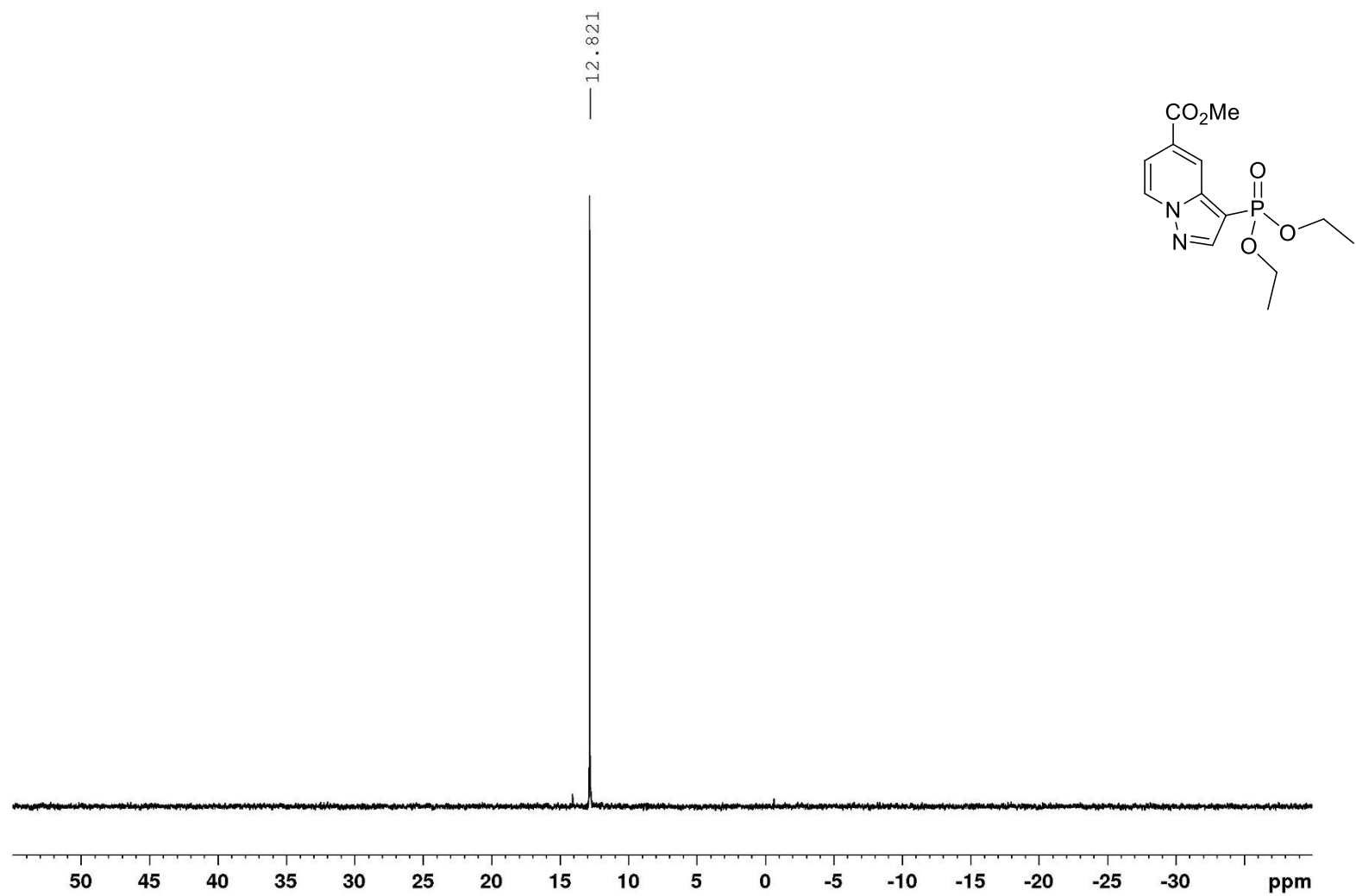
Methyl 3-diethoxyphosphorylpyrazolo[1,5-a]pyridine-5-carboxylate (5o) ^1H NMR.



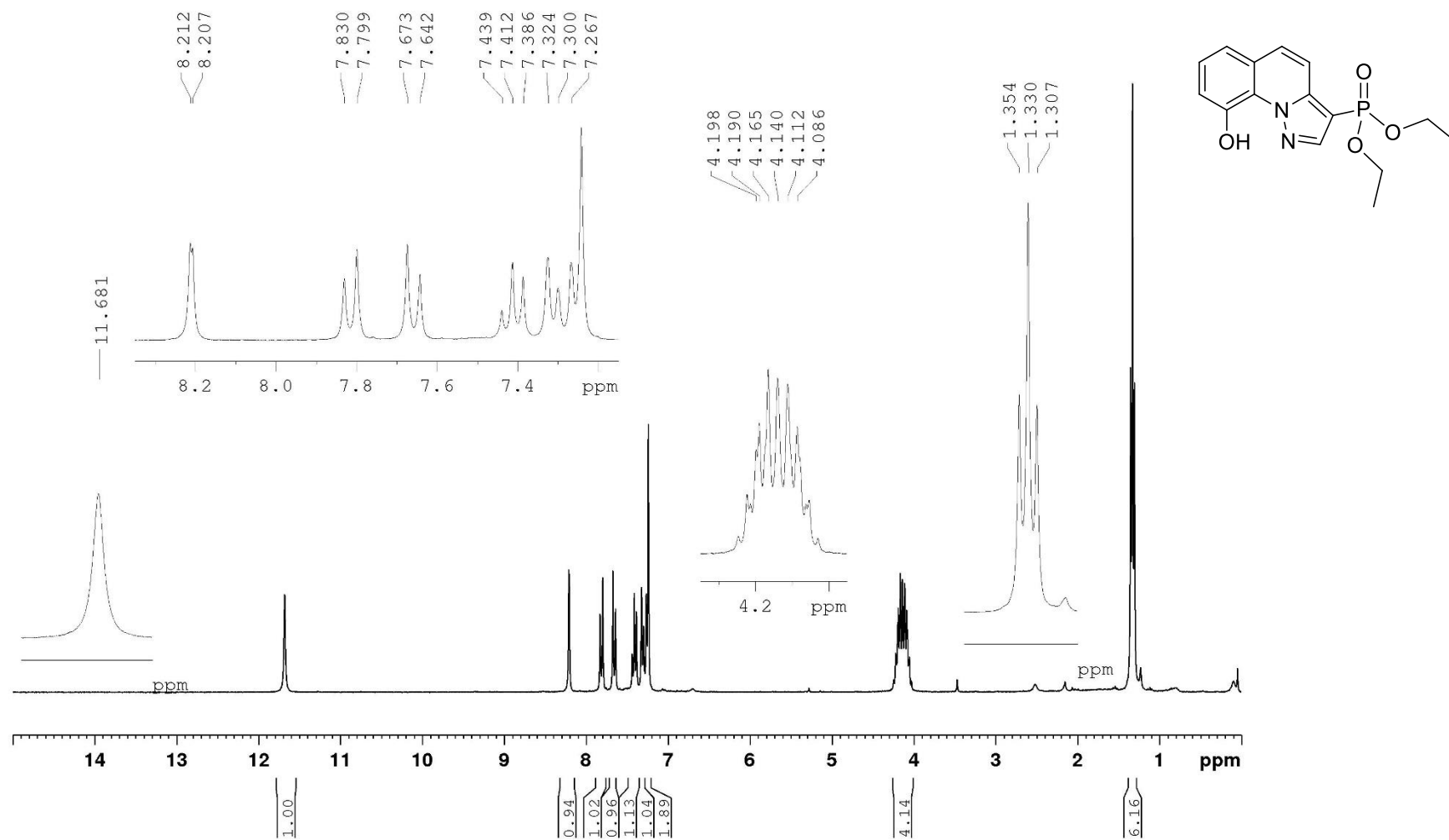
Methyl 3-diethoxyphosphorylpyrazolo[1,5-a]pyridine-5-carboxylate (5o) ^{13}C NMR.



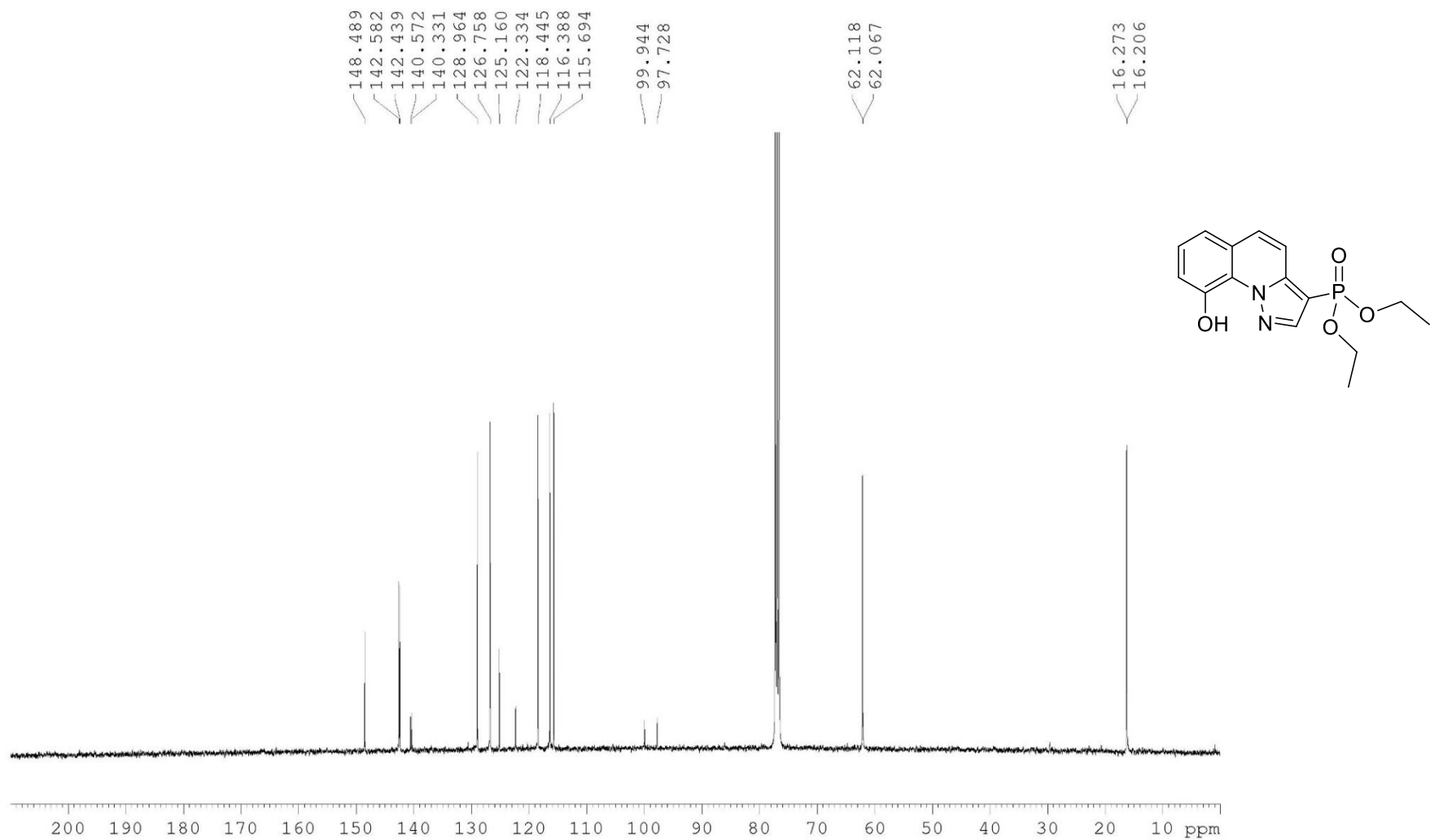
Methyl 3-diethoxyphosphorylpyrazolo[1,5-a]pyridine-5-carboxylate (5o) ^{31}P NMR.



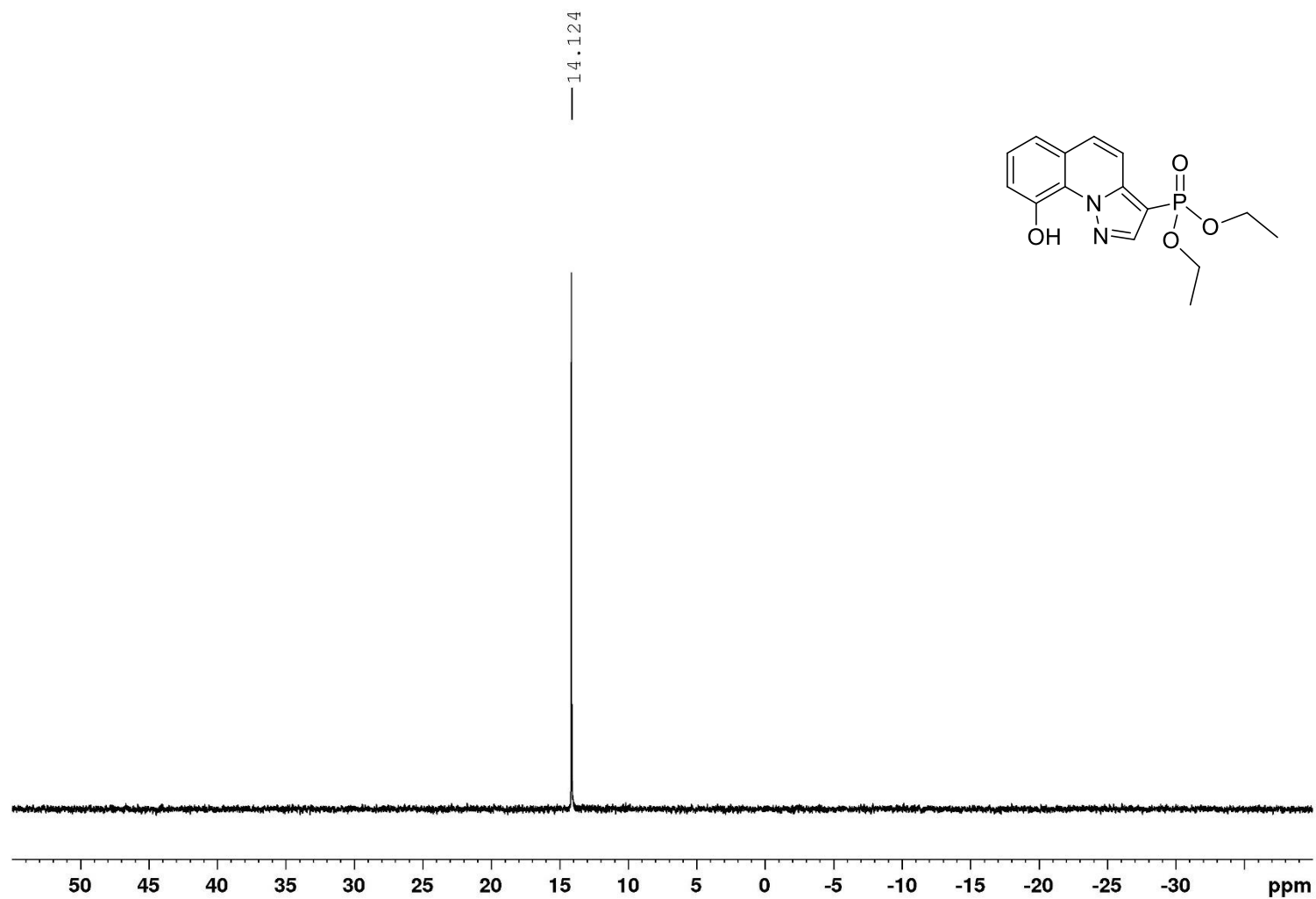
Diethyl (9-hydroxypyrazolo[1,5-a]quinoline-3-yl)phosphonate (5p) ^1H NMR.



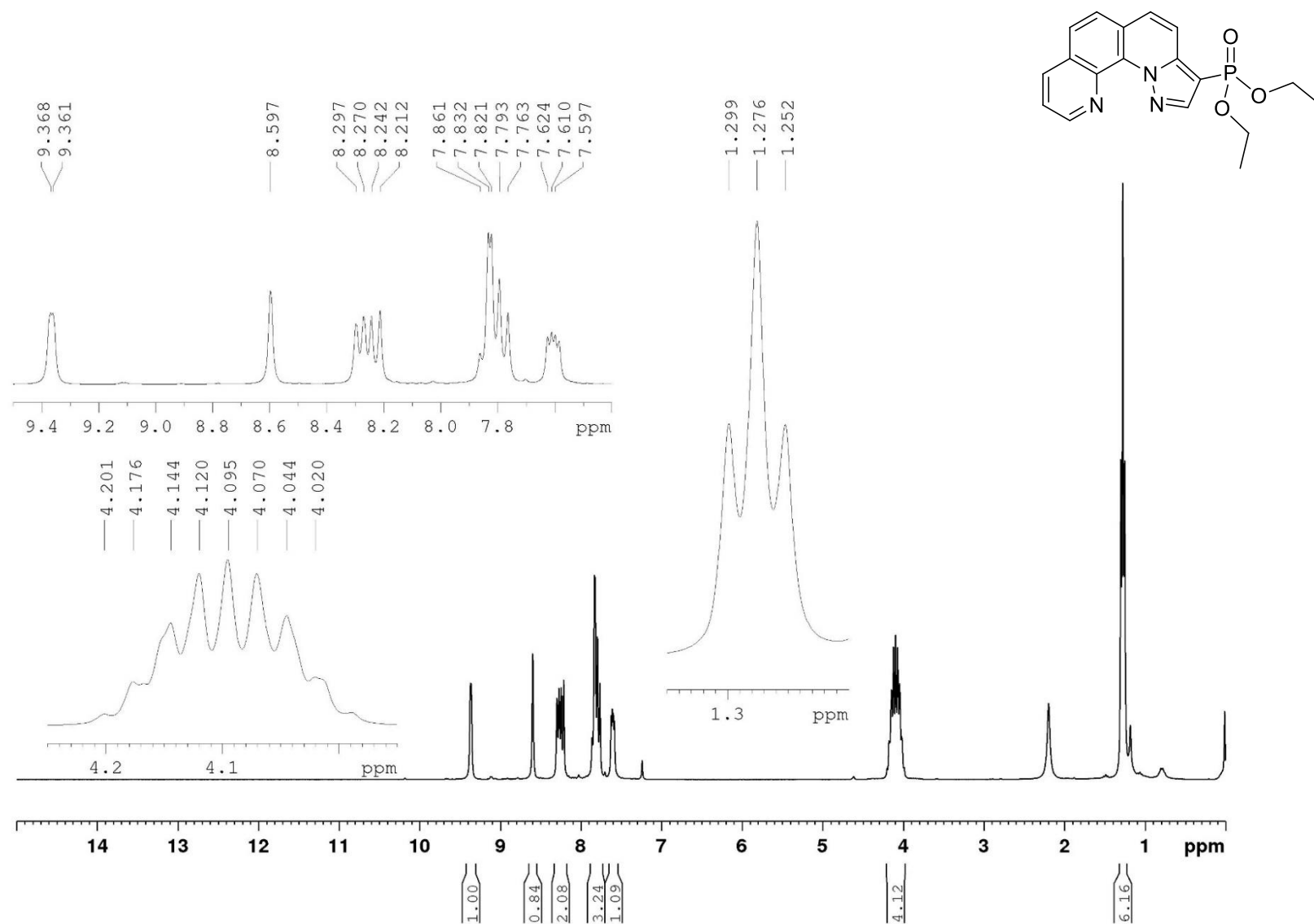
Diethyl (9-hydroxypyrazolo[1,5-a]quinoline-3-yl)phosphonate (5p) ^{13}C NMR.



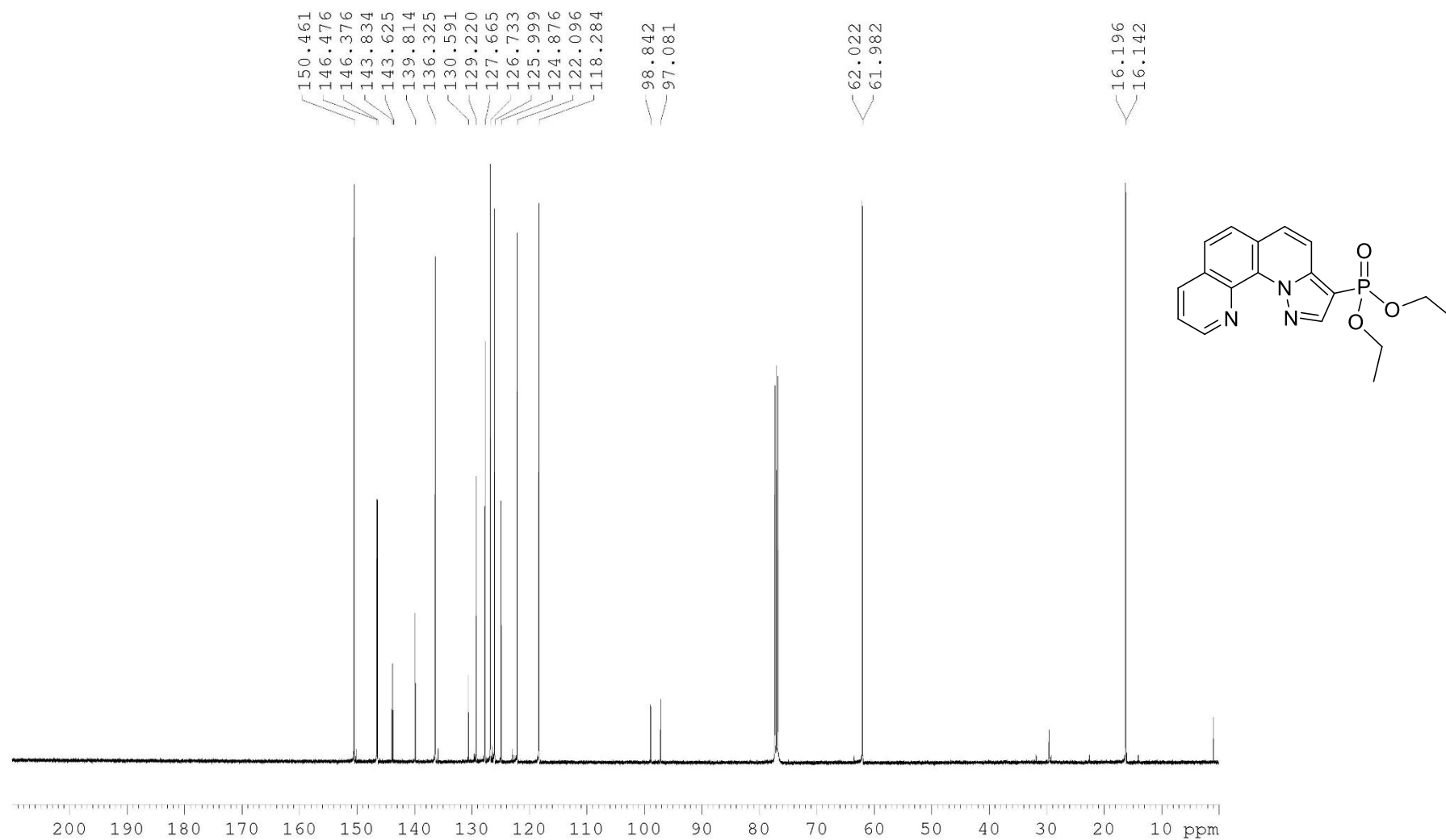
Diethyl (9-hydroxypyrazolo[1,5-a]quinoline-3-yl)phosphonate (5p) ^{31}P NMR.



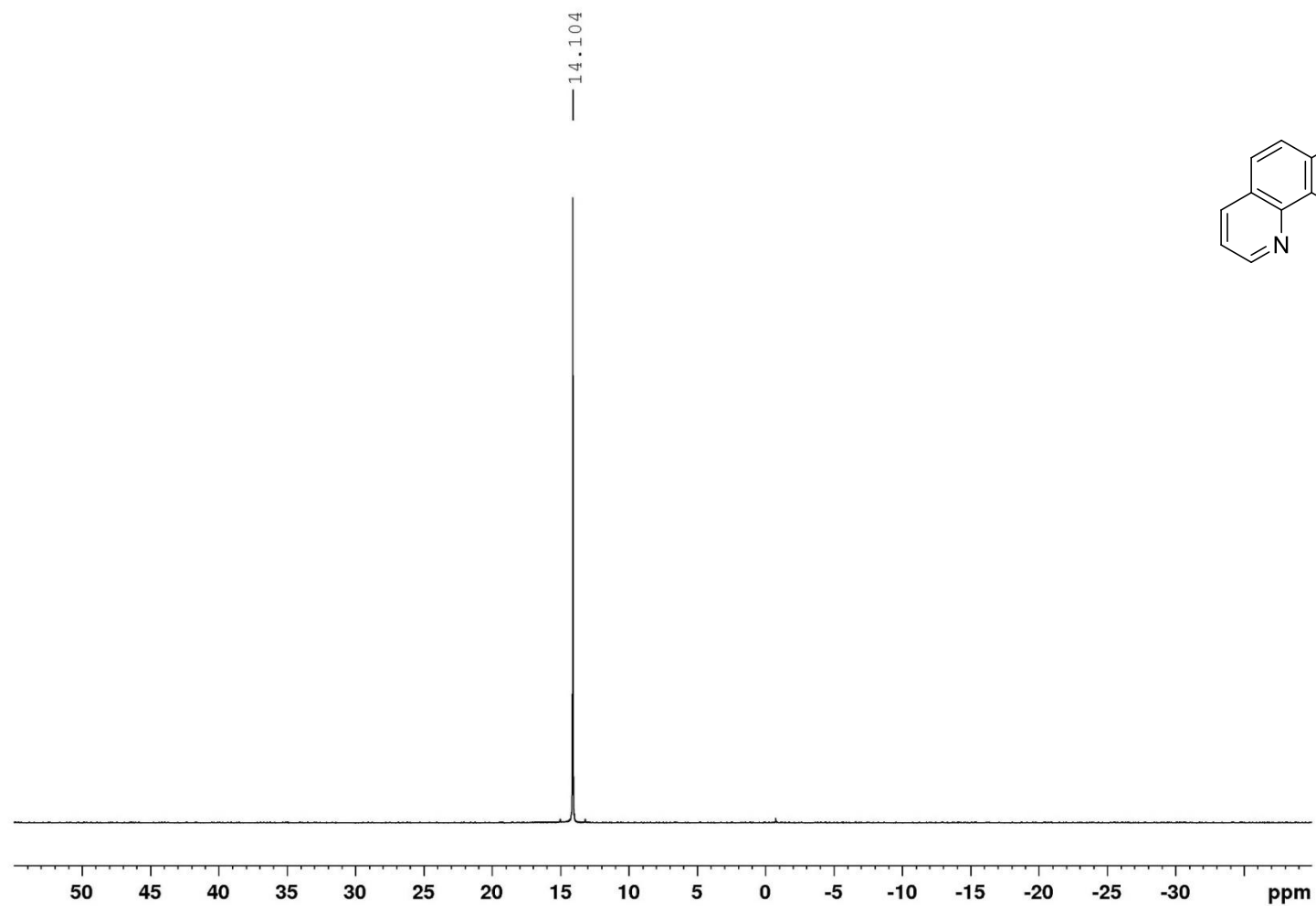
Diethyl (pyrazolo[1,5-a][1,10]phenantroline-3-yl)phosphonate (5q) ^1H NMR.



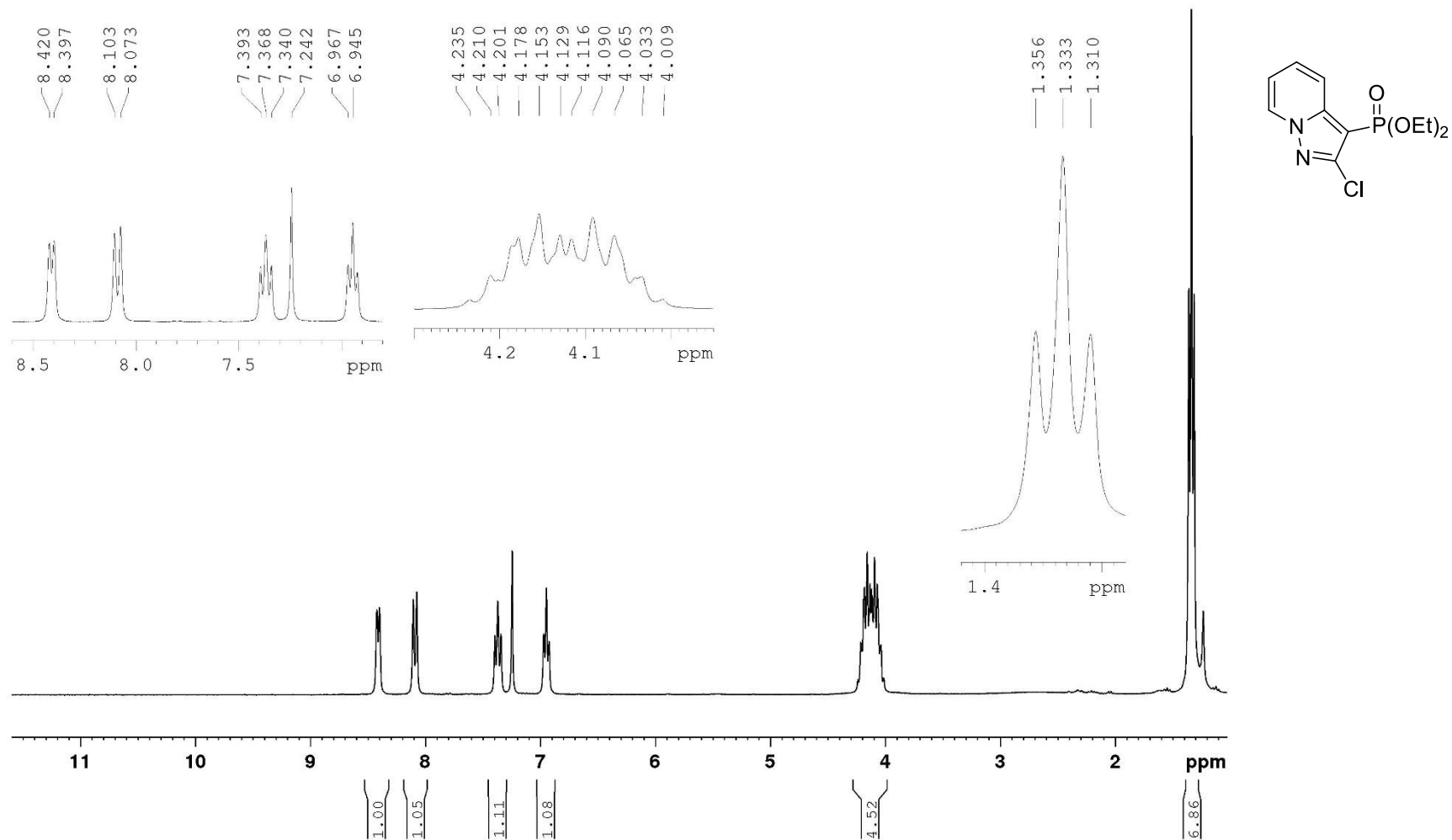
Diethyl (pyrazolo[1,5-a][1,10]phenantroline-3-yl)phosphonate (5q) ^{13}C NMR.



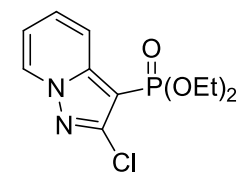
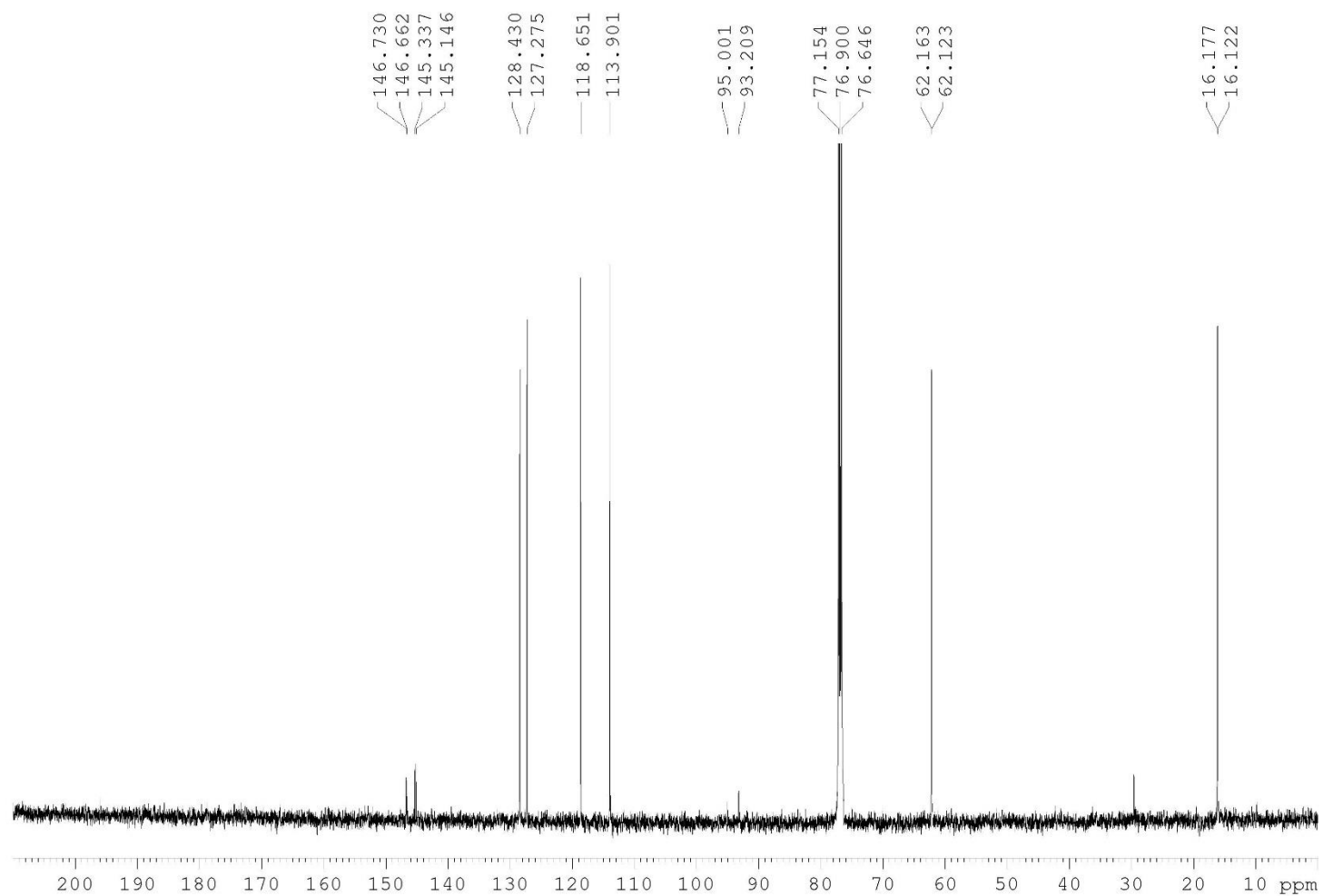
Diethyl (pyrazolo[1,5-a][1,10]phenantroline-3-yl)phosphonate (5q) ^{31}P NMR.



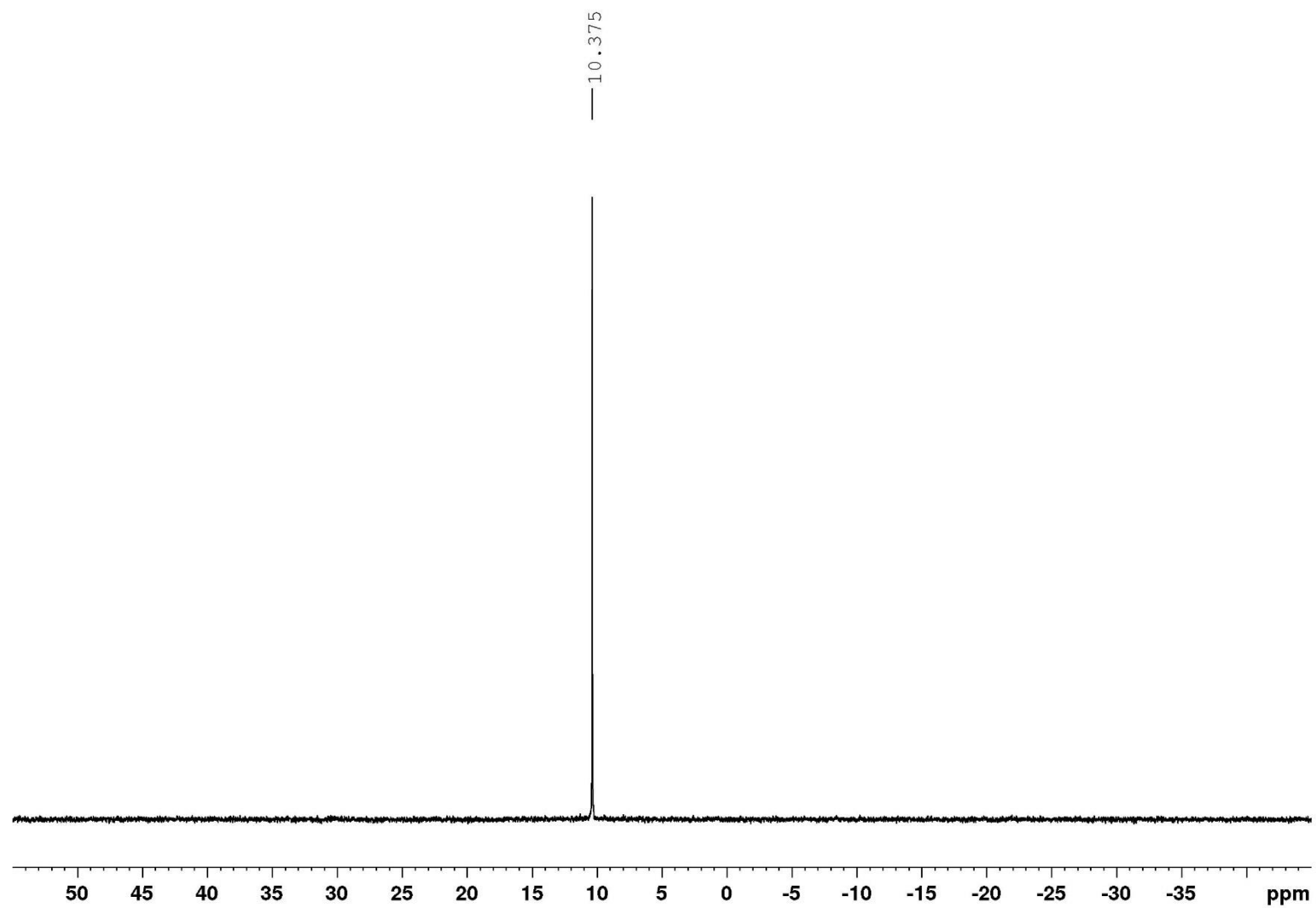
Diethyl (2-chloro[1,5-a]pyridin-3-yl)phosphonate ¹H NMR(5r).



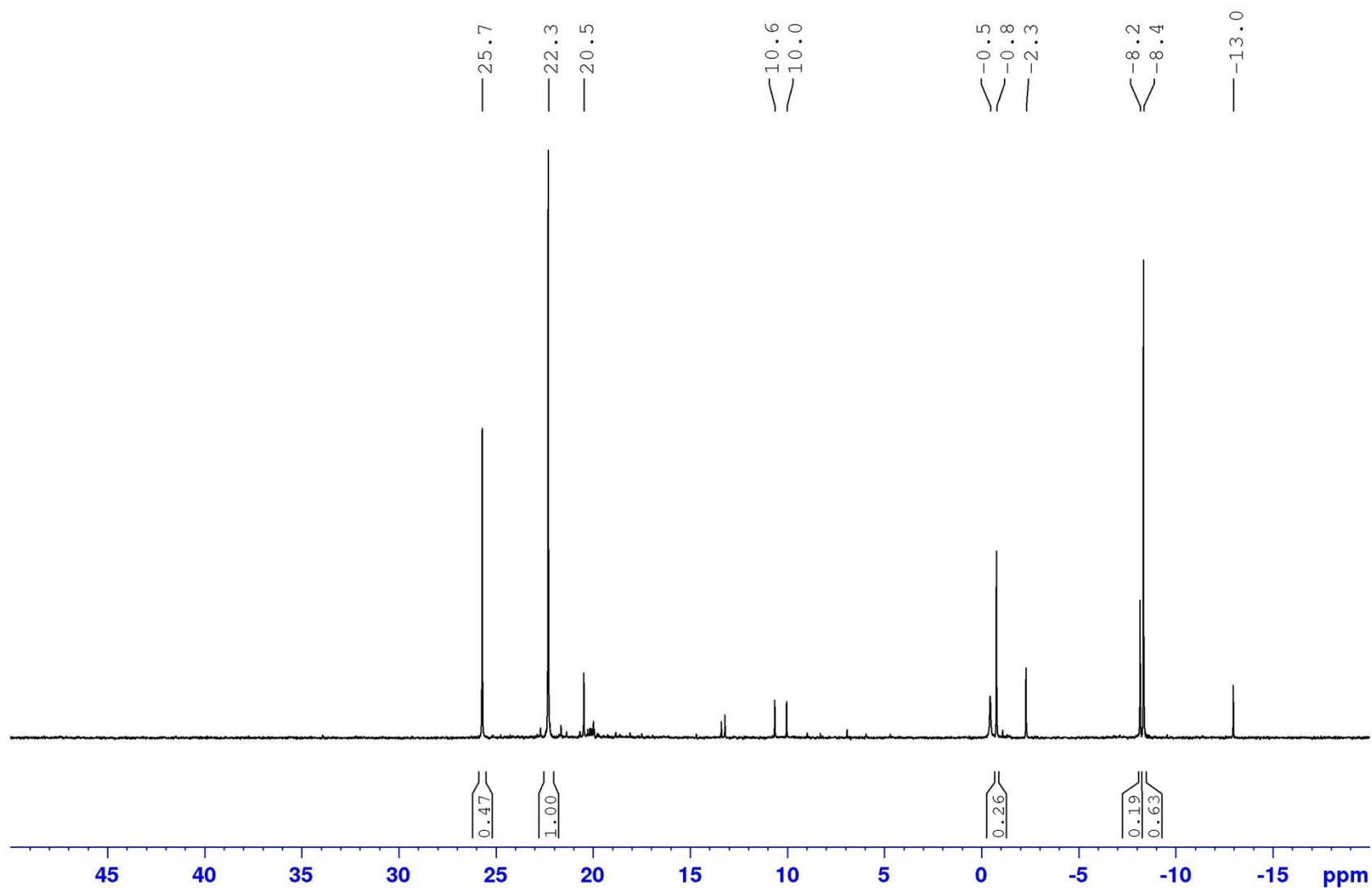
Diethyl (2-chloro[1,5-a]pyridin-3-yl)phosphonate ¹³C NMR(5r).



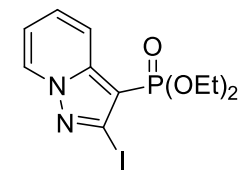
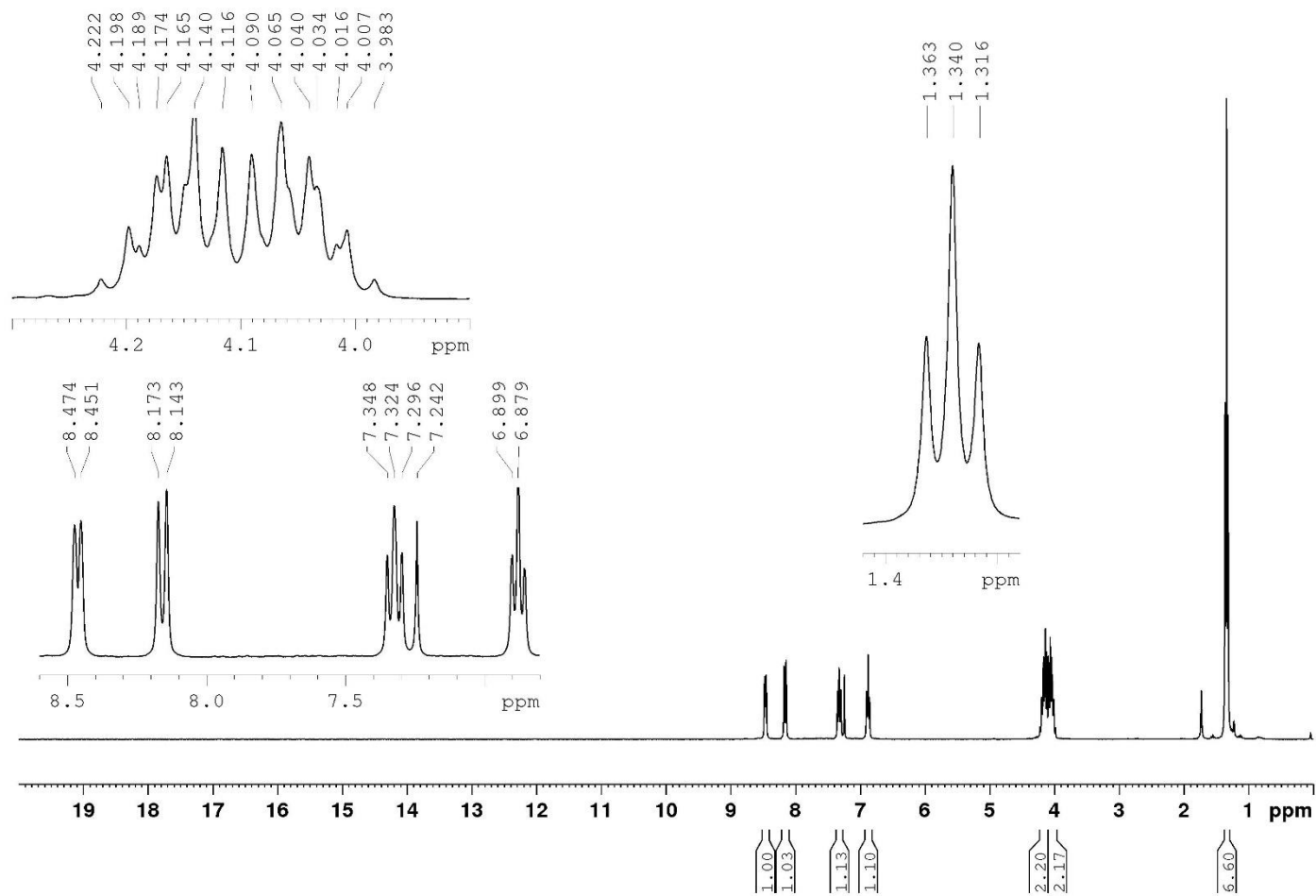
Diethyl (2-chloro[1,5-a]pyridin-3-yl)phosphonate ^{31}P NMR(5r).



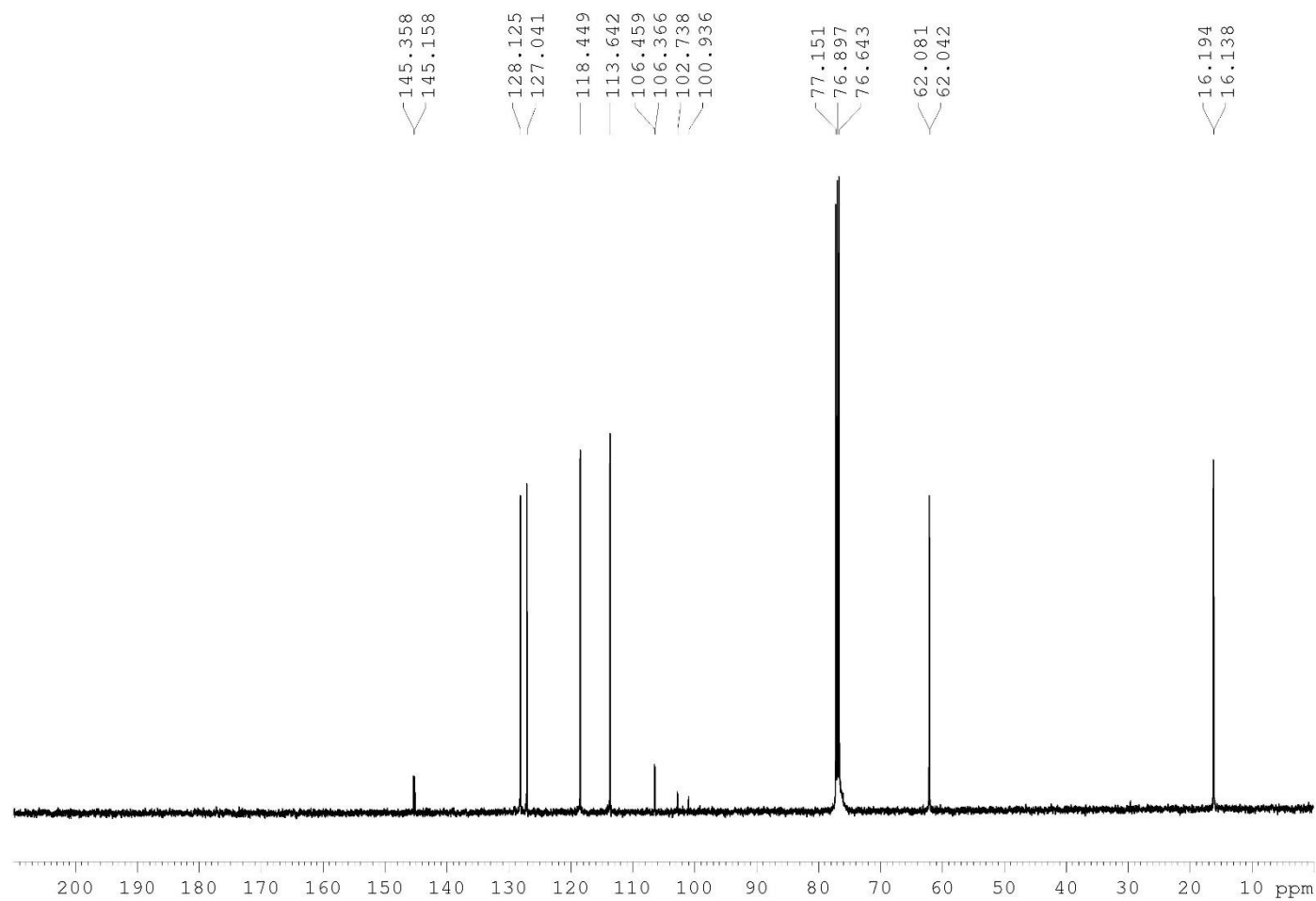
^{31}P NMR spectrum of reaction mixture for diethyl (2-bromo[1,5-a]pyridin-3-yl)phosphonate (5s) preparation.



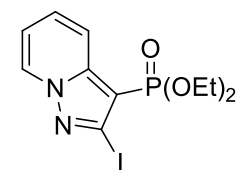
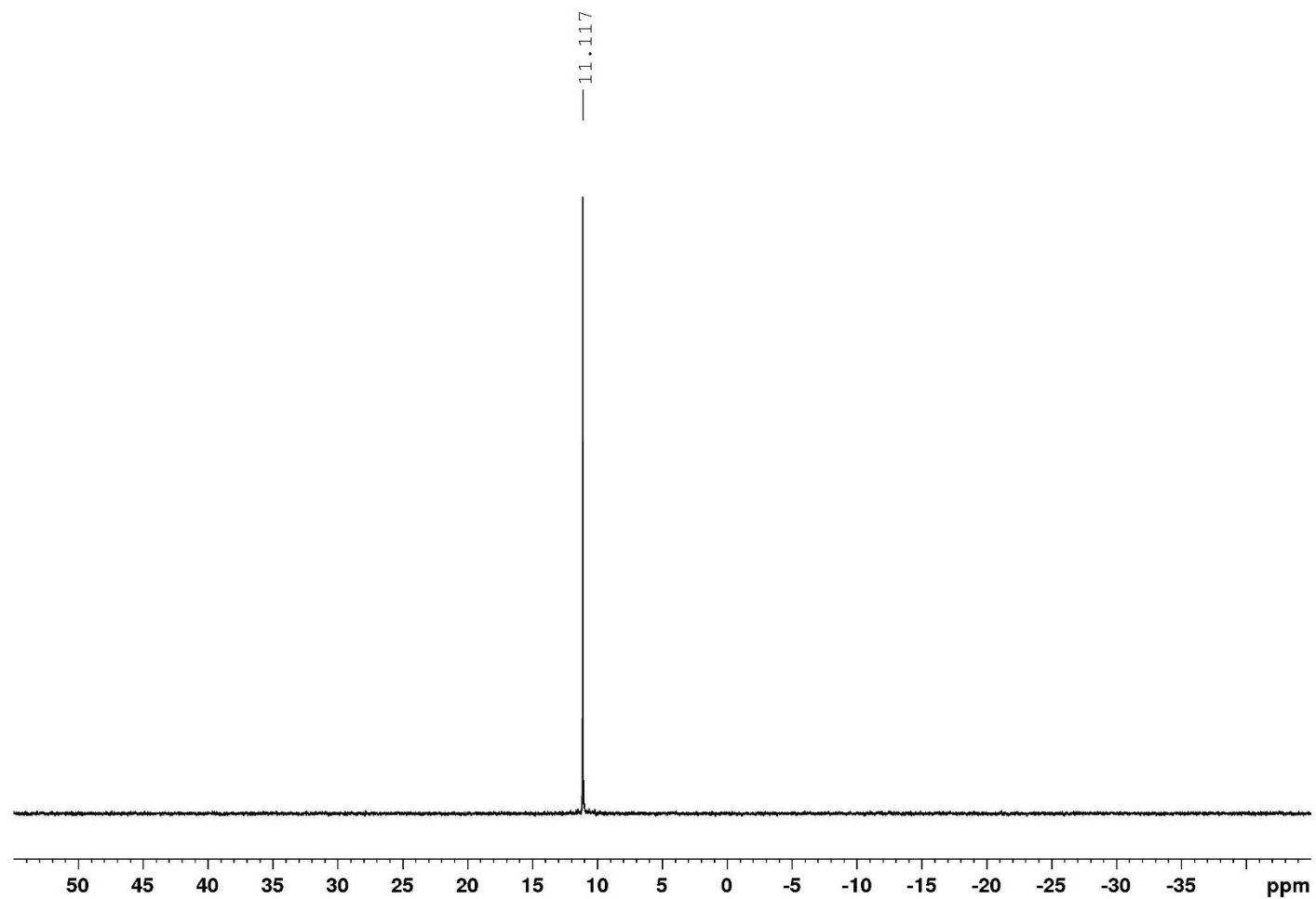
Diethyl (2-iodo[1,5-a]pyridin-3-yl)phosphonate ^1H NMR(5t).



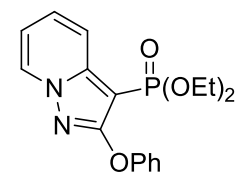
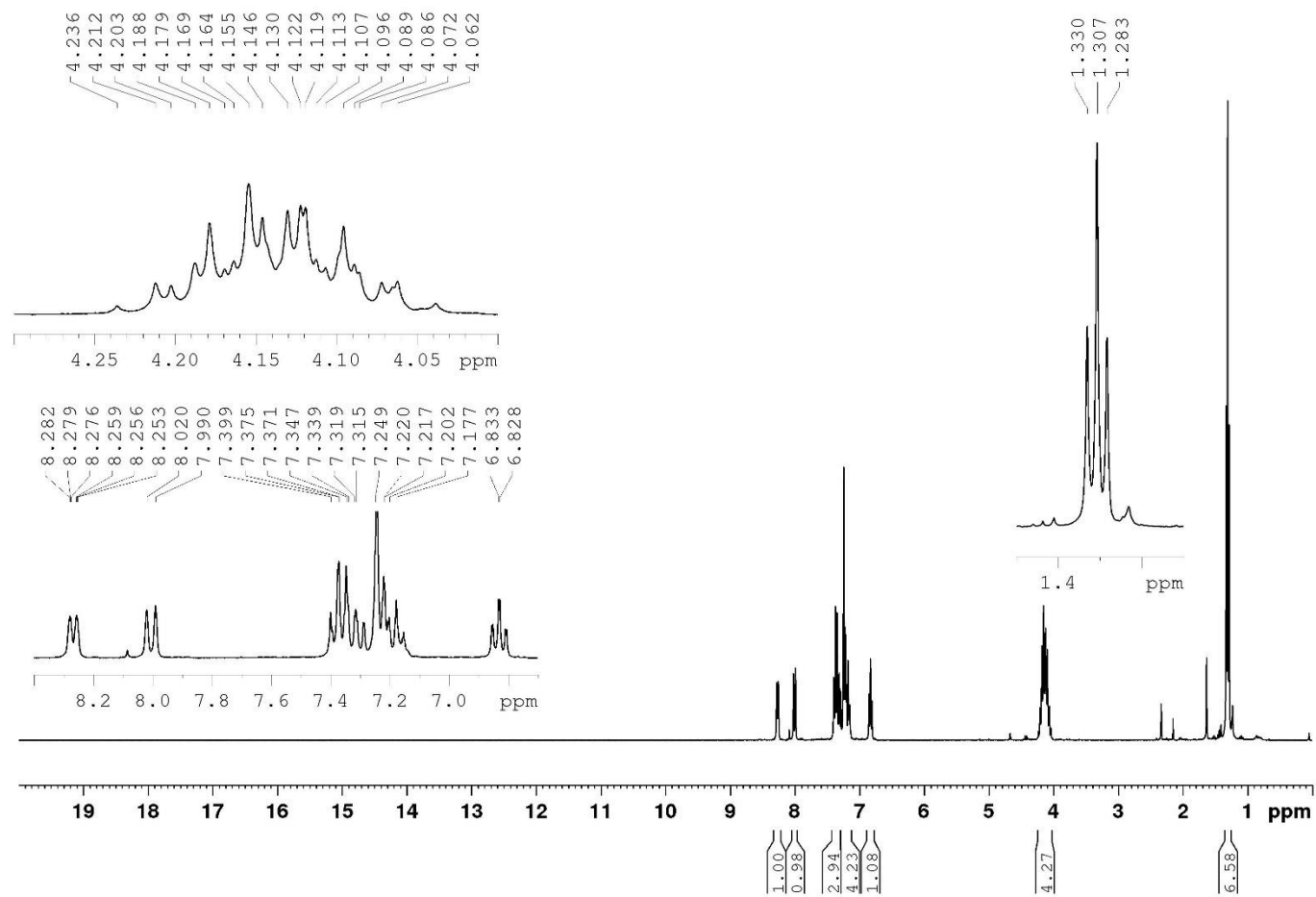
Diethyl (2-iodo[1,5-a]pyridin-3-yl)phosphonate ^{13}C NMR(5t).



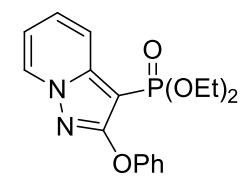
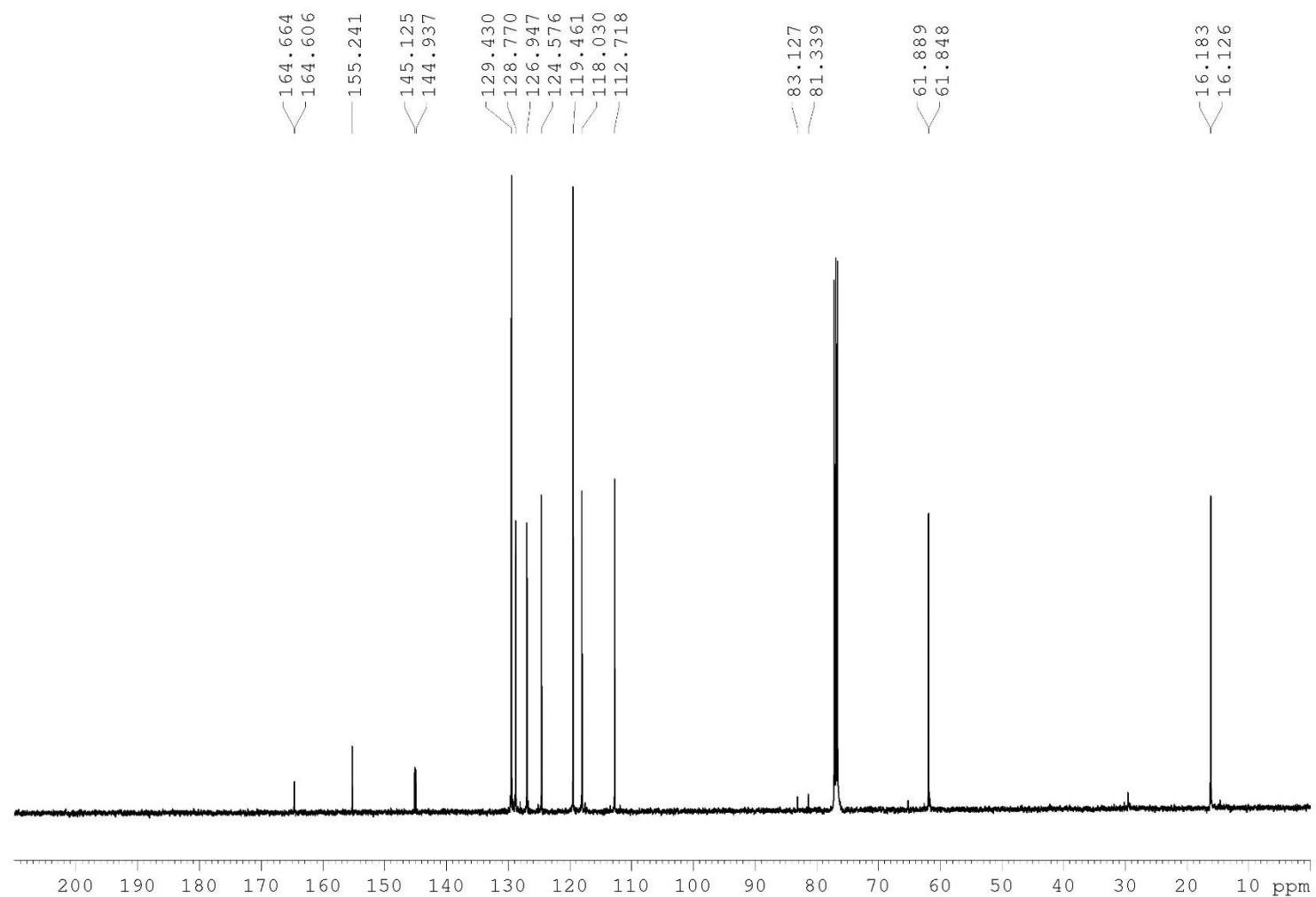
Diethyl (2-iodo[1,5-a]pyridin-3-yl)phosphonate ^{31}P NMR(5t).



Diethyl (2-phenoxy[1,5-a]pyridin-3-yl)phosphonate ¹H NMR(5u).



Diethyl (2-phenoxy[1,5-a]pyridin-3-yl)phosphonate ¹³C NMR(5u).



Diethyl (2-phenoxy[1,5-a]pyridin-3-yl)phosphonate ^{31}P NMR(5u).

