# Supplementary Information

## Visible Light-Enabled Synthesis of Phosphorylated Indolizine and Pyridoindole Derivatives via HAT-Mediated Radical Cascade Cyclization

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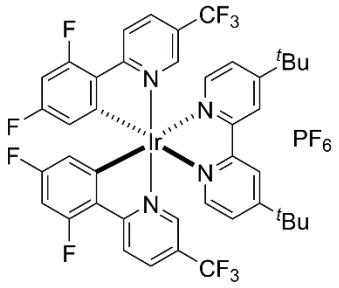
## Contents

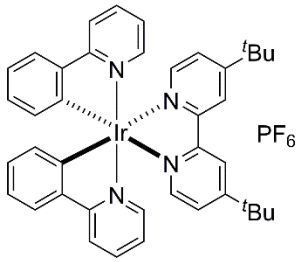
## 1. General information

All reagents and starting materials, unless otherwise noted, were purchased from Bidepharm, Innochem, J&K Scientific, Macklin, Leyan, Aladdin and Adamas-beta® Chemical companies as reagent grade and used without further purification. Anhydrous solvents (including MeCN, $CH_2Cl_2$, DCE, DMF, THF, Water < 0.005%) were purchased from Innochem and J&K Scientific, and used as received. $^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR, and $^{31}P$ NMR spectra were obtained with a Bruker AV II-400 spectrometer ($^{1}H$: 400 MHz, $^{13}C$: 101 MHz, $^{19}F$: 376 MHz, $^{31}P$: 162 MHz). The chemical shifts of $^{1}H$ NMR spectra were reported using either tetramethylsilane (δ = 0.00 ppm) or residual solvent signal of $CD_3OD$ (δ = 3.31 ppm) as internal reference. The chemical shifts of $^{13}C$ NMR spectra were reported using solvent signal of $CDCl_3$ (δ = 77.16 ppm) or $CD_3OD$ (δ = 49.00 ppm) as internal reference. The chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, and br = broad. TLC was performed using commercially prepared silica gel plates (GF254) and visualized under UV light 254 nm. Flash column chromatography was performed on silica gel (100-200 mesh). All mixed solvent eluents are reported as v/v solutions. The blue LEDs (460 nm) were purchased from LY&OY' STAR. Mass analysis data were acquired on a SCIEX UPLC (EXion) – QTOF (X500R) and Agilent Technologies UPLC (1290)-QTOF (6550). Melting points were measured using a Hanon MP470 apparatus.



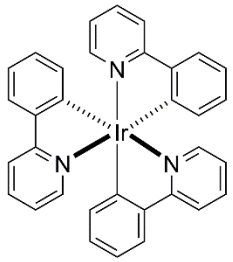

$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$

**PC-1**

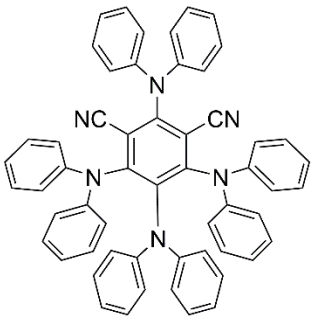



$Ir[(ppy)_2(dtbbpy)]PF_6$

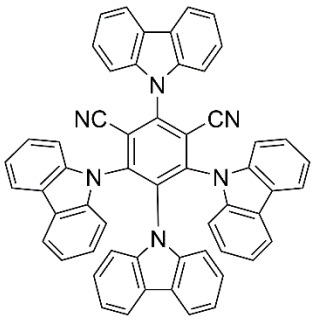
**PC-2**




*fac*-$Ir(ppy)_3$




4DPAIPN

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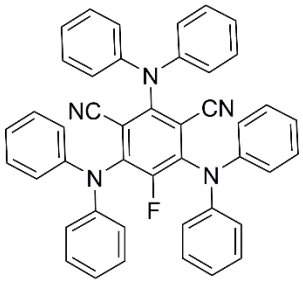


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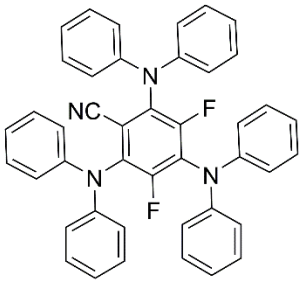


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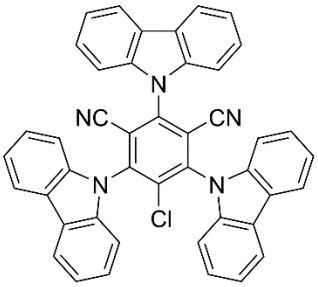


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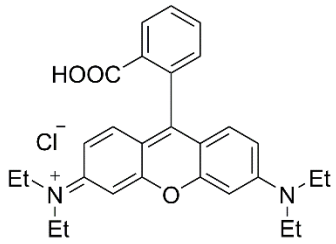
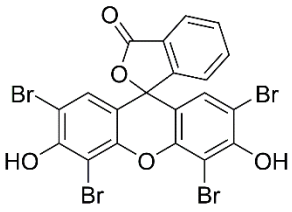


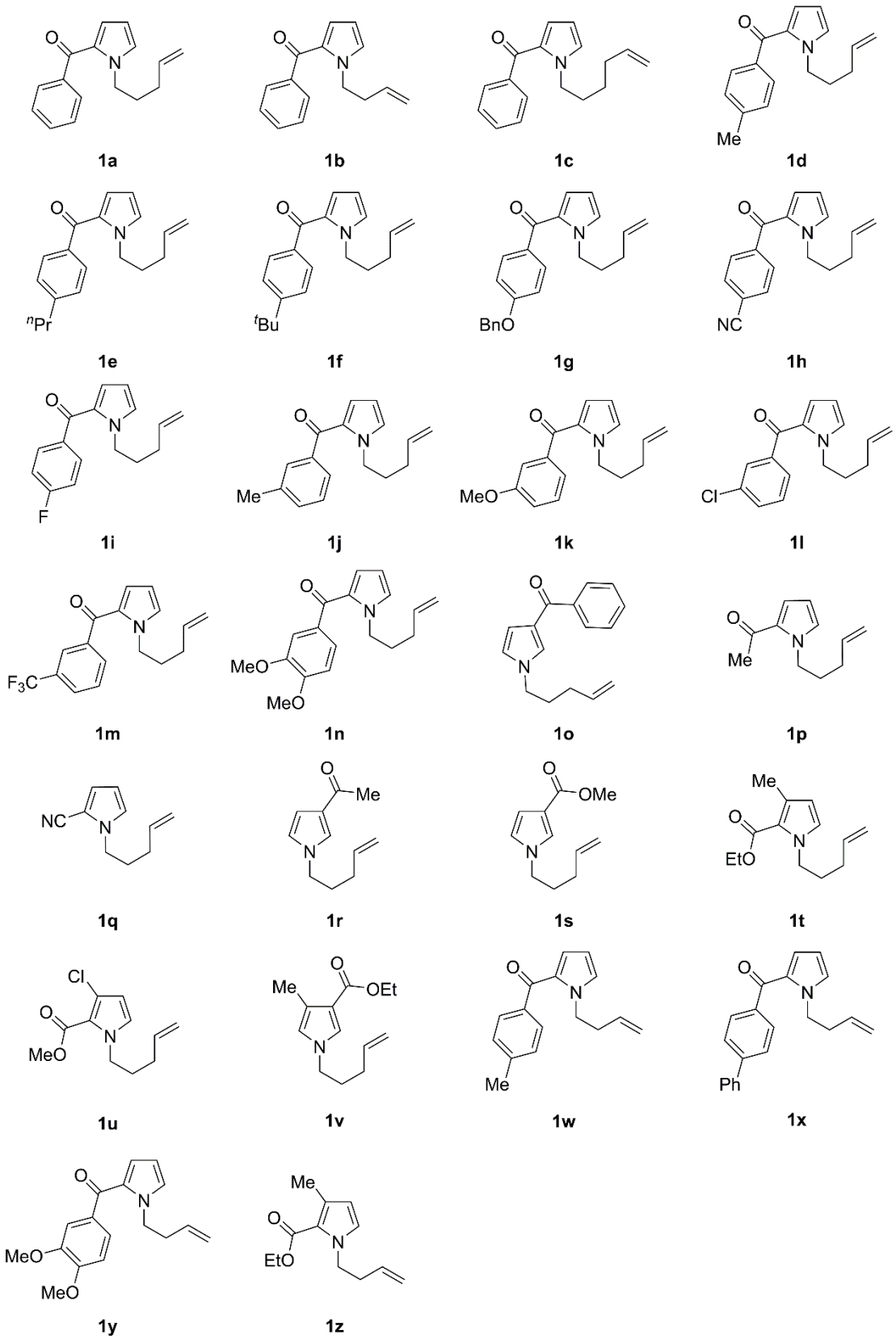

Rhodamine B



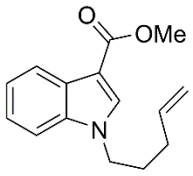

Eosin Y

**Figure S1.** The structures of photocatalysts in reaction conditions optimization

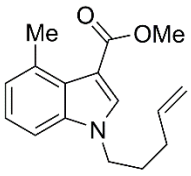
## 2. Synthesis of starting materials



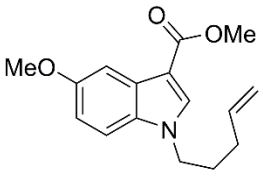

The starting materials **1a**-**1z** were synthesized following the reported procedures.[1, 2]



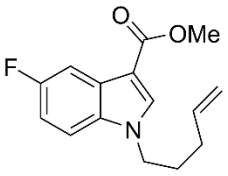
**4a**



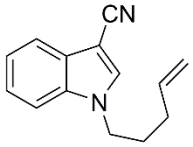
**4b**



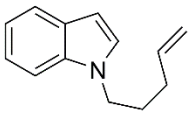
**4c**



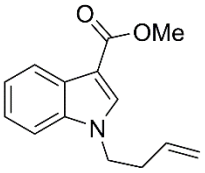
**4d**



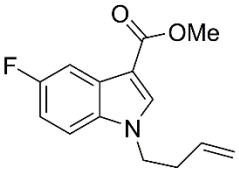
**4e**



**4f**



**4g**

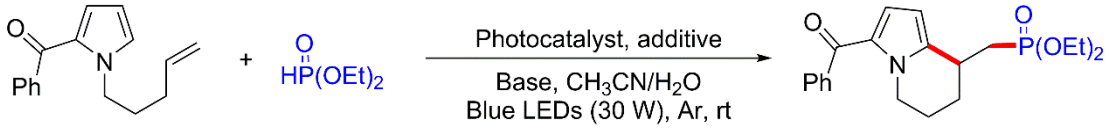


**4h**

The starting materials **4a**-**4h** were synthesized following the reported procedures.[2]

## 3. Reaction optimization

**Table S1.** Optimization of the Reaction Conditions.[a]



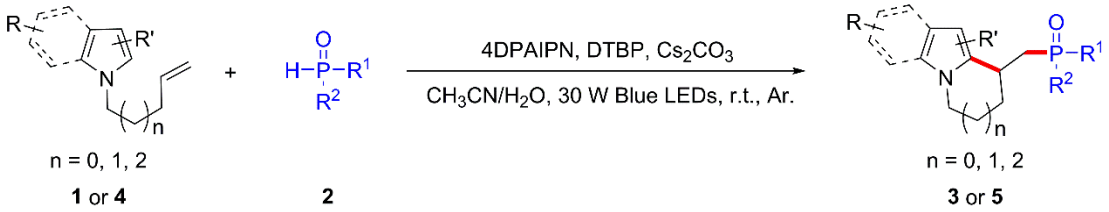

**1a** **2a** **3aa**

| Entry | Photocatalyst | Additive | Base | Yield (%) |
|---|---|---|---|---|
| 1 | 4DPAIPN | TBHP | $Cs_2CO_3$ | 48 |
| 2 | 4DPAIPN | BPO | $Cs_2CO_3$ | ND |
| 3 | 4DPAIPN | LPO | $Cs_2CO_3$ | 28 |
| 4 | 4DPAIPN | DCP | $Cs_2CO_3$ | 57 |
| 5 | 4DPAIPN | DTBP | $NaHCO_3$ | 22 |
| 6 | 4DPAIPN | DTBP | DABCO | ND |
| 7[b] | 4DPAIPN | DTBP | $Cs_2CO_3$ | 41 |

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), photocatalyst (2 mol%), additive (0.3 mmol), base (0.4 mmol), $CH_3CN$ (2 mL), $H_2O$ (10 μL), blue LEDs (30 W), argon atmosphere, rt, 12 h. ND: Not detected. The yield was determined by $^1H$ NMR spectroscopy using dibromomethane as an internal standard. Isolated yield is based on **1a**. [b] $H_2O$ (0 μL).

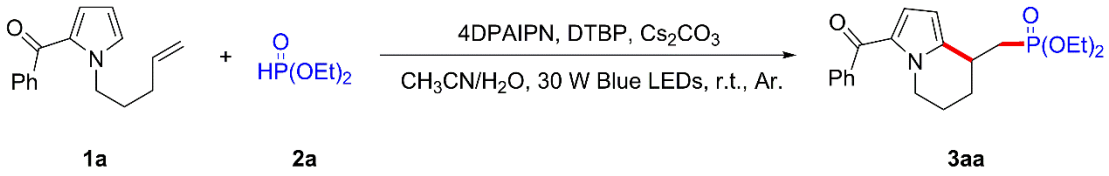
## 4. Experimental procedures

### 4.1 Typical experimental procedures



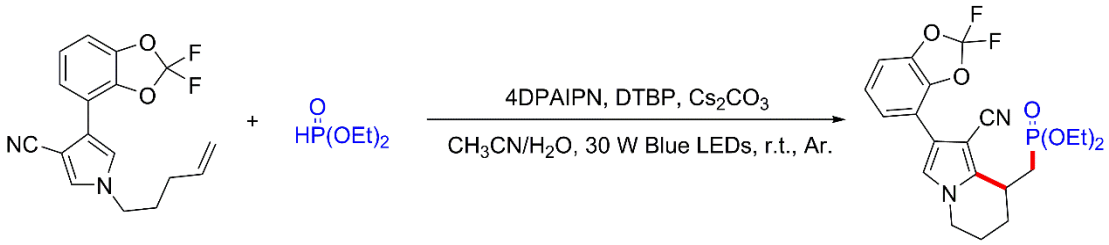

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (2 mol%) and $Cs_2CO_3$ (0.4 mmol, 2.0 eq.). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **1** or **4** (0.2 mmol, 1.0 eq.), **2** (0.4 mmol, 2 eq.) and DTBP (0.3 mmol, 1.5 eq.) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc as eluent to afford the desired product **3** or **5**.

### 4.2 Scaled up reaction




An oven-dried Schlenk tube (100 mL) equipped with a stirring bar was charged with 4DPAIPN (70.1 mg, 0.088 mmol) and $Cs_2CO_3$ (2.87 g, 8.8 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (44 mL), $H_2O$ (220 μL), the substrate **1**a (1.06 g, 4.4 mmol), **2a** (1.13 g, 8.8 mmol) and DTBP (965.1 mg, 6.6 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc (1:2) as eluent to afford the desired product **3aa** (888.2 mg, 54% yield).

### 4.3 The application of the reaction in structural modification



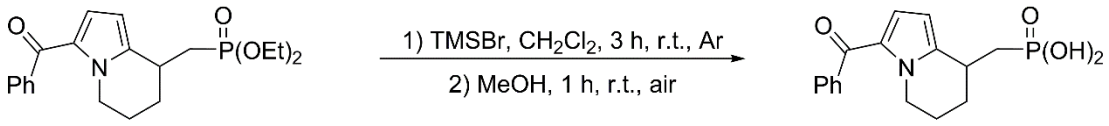

**6a**
from *Fludioxonil*

**2a**

**7aa**, 54%

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 2 mol%) and $Cs_2CO_3$ (130.3 mg, 0.4 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **6a** (47.9 mg, 0.2 mmol), diethyl phosphite **2** (55.2 mg, 0.4 mmol) and DTBP (43.9 mg, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc (1:2) as eluent to afford the desired product **7aa** (49.6 mg, 54% yield).

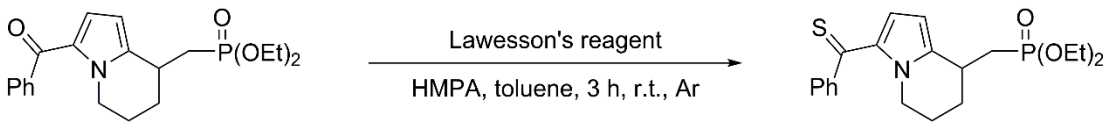
### 4.4 The derivatization of products




**3aa**

**8aa**, 29%

An oven-dried two-necked flask (25 mL) equipped with a stirring bar was charged with **3aa** (187.9 mg, 0.5 mmol). The flask was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry $CH_2Cl_2$ (1.8 mL), TMSBr (225.6 mg, 1.5 mmol) were added under Ar flow. The resulting mixture was stirred at room temperature under Ar atmosphere for 3 h. Then, the mixture was concentrated *in vacuo*. The resulting residue was dissolved in MeOH and stirred at room temperature for 1 h. After completion, the mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel with $CH_2Cl_2$/MeOH (20:1) as eluent to afford the desired product **8aa** (45.9 mg, 29% yield).

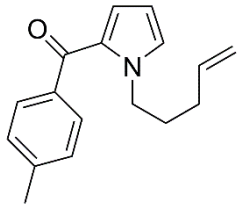



**3aa** **9aa**, 73%

An oven-dried two-necked flask (50 mL) equipped with a stirring bar was charged with **3aa** (187.9 mg, 0.5 mmol) and Lawesson's reagent (409.1 mg, 1.0 mmol). The flask was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, toluene (22.7 mL), HMPA (0.2 mL) were added under Ar flow. The resulting mixture was refluxed under Ar atmosphere for 2.5 h. After completion, the mixture was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc as eluent to afford the desired product **9aa** (131.9 mg, 73% yield).

## 5. Characterization data for substrates and products

**(1-(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)(*p*-tolyl) methanone (1d)**



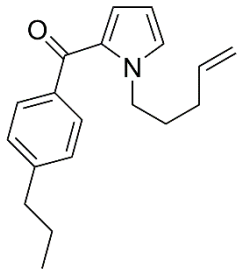
Yellow liquid, 158.9 mg, 45% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 2H), 7.28 – 7.21 (m, 2H), 6.99 – 6.93 (m, 1H), 6.73 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.15 (dd, *J* = 4.0, 2.5 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.97 (m, 2H), 4.43 – 4.37 (m, 2H), 2.42 (s, 3H), 2.14 – 2.06 (m, 2H), 1.97 – 1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 186.1, 142.0, 137.8, 137.5, 130.6, 130.0, 129.5, 128.8, 123.2, 115.4, 108.1, 49.0, 30.9, 30.9, 21.7.

**HRMS** (ESI) calcd for $C_{17}H_{20}NO[M+H]^+$: 254.1539. Found: 254.1544.

**(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)(4-propylphenyl)methanone (1e)**



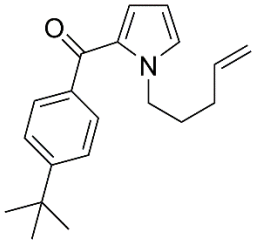
Yellow liquid, 522.6 mg, 93% yield.

1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.70 (m, 2H), 7.28 – 7.22 (m, 2H), 6.95 (t, *J* = 2.1 Hz, 1H), 6.74 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.15 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.08 – 4.96 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.14 – 2.06 (m, 2H), 1.97 – 1.88 (m, 2H), 1.73 – 1.61 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 186.1, 146.7, 137.8, 137.8, 130.5, 130.0, 129.5, 128.2, 123.2, 115.4, 108.1, 49.0, 38.1, 30.88, 30.86, 24.5, 13.9.

**HRMS** (ESI) calcd for $C_{19}H_{24}NO[M+H]^+$: 282.1852. Found: 282.1859.

**(4-(*tert*-butyl) phenyl)(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1f)**



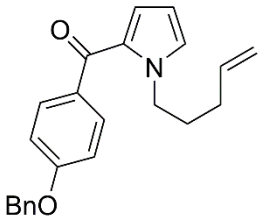
Yellow liquid, 156.1mg, 26% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.48 – 7.43 (m, 2H), 6.96 (t, *J* = 2.1 Hz, 1H), 6.76 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.15 (dd, *J* = 4.0, 2.5 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.08 – 4.96 (m, 2H), 4.40 (t, *J* = 7.2 Hz, 2H), 2.14 – 2.05 (m, 2H), 1.97 – 1.87 (m, 2H), 1.36 (s, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 186.0, 155.0, 137.8, 137.4, 130.5, 130.0, 129.3, 125.1, 123.3, 115.4, 108.1, 49.0, 35.1, 31.3, 30.9, 30.8.

**HRMS** (ESI) calcd for $C_{20}H_{25}NNaO[M+Na]^+$: 318.1828. Found: 318.1834.

**(4-(benzyloxy) phenyl)(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1g)**



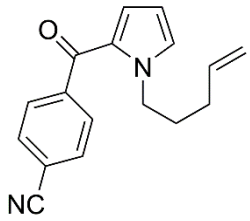
Yellow liquid, 240.8 mg, 99% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 2H), 7.46 – 7.36 (m, 4H), 7.36 – 7.30 (m, 1H), 7.04 – 6.98 (m, 2H), 6.94 (t, *J* = 2.1 Hz, 1H), 6.72 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.14 (dd, *J* = 4.0, 2.5 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.12 (s, 2H), 5.07 – 4.96 (m, 2H), 4.41 – 4.35 (m, 2H), 2.12 – 2.05 (m, 2H), 1.95 – 1.87 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.1, 161.7, 137.8, 136.5, 133.0, 131.6, 130.3, 130.0, 128.8, 128.3, 127.6, 122.7, 115.4, 114.3, 108.0, 70.2, 48.9, 30.9 (overlap).

**HRMS** (ESI) calcd for $C_{23}H_{24}NO_2[M+H]^+$: 346.1802. Found: 346.1801.

**4-(1-(pent-4-en-1-yl)-1*H*-pyrrole-2-carbonyl)benzonitrile (1h)**



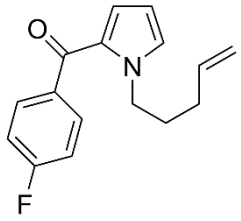
Yellow liquid, 158.8 mg, 60% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.77 – 7.72 (m, 2H), 7.06 – 7.01 (m, 1H), 6.68 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.19 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.10 – 4.99 (m, 2H), 4.45 – 4.37 (m, 2H), 2.15 – 2.08 (m, 2H), 1.98 – 1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 183.9, 144.1, 137.6, 132.07, 132.06, 129.6, 129.1, 124.3, 118.4, 115.6, 114.7, 108.9, 49.3, 30.8, 30.7.

**HRMS** (ESI) calcd for $C_{17}H_{17}N_2O[M+H]^+$: 265.1335. Found: 265.1339.

**(4-fluorophenyl) (1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1i)**



Yellow liquid, 96.7 mg, 38% yield.

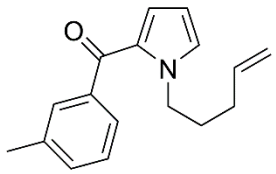
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 2H), 7.16 – 7.09 (m, 2H), 7.01 – 6.96 (m, 1H), 6.71 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.17 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08 – 4.98 (m, 2H), 4.44 – 4.36 (m, 2H), 2.14 – 2.07 (m, 2H), 1.97 – 1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.7, 164.9 (d, *J* = 252.0 Hz), 137.7, 136.5 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 8.8 Hz), 131.0, 129.7, 123.4, 115.5, 115.2 (d, *J* = 21.7 Hz), 108.4, 49.1, 30.9, 30.8.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −108.2.

**HRMS** (ESI) calcd for $C_{16}H_{17}FNO[M+H]^+$: 258.1289. Found: 258.1297.

**(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl) (*m*-tolyl)methanone (1j)**



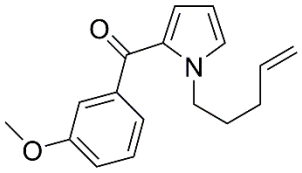
Yellow liquid, 308.6 mg, 61% yield.

**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.63 – 7.53 (m, 2H), 7.36 – 7.27 (m, 2H), 6.96 (t, J = 2.1 Hz, 1H), 6.73 (dd, J = 4.0, 1.7 Hz, 1H), 6.15 (dd, J = 4.1, 2.5 Hz, 1H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.97 (m, 2H), 4.44 – 4.37 (m, 2H), 2.41 (s, 3H), 2.14 – 2.06 (m, 2H), 1.97 – 1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 186.4, 140.3, 137.9, 137.8, 132.2, 130.7, 130.0, 129.8, 127.9, 126.5, 123.5, 115.4, 108.1, 49.1, 30.85, 30.82, 21.5.

**HRMS** (ESI) calcd for $C_{17}H_{19}NNaO[M+Na]^+$: 276.1359. Found: 276.1361.

**(3-methoxyphenyl)(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1k)**



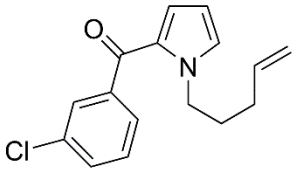
Yellow liquid, 102.2 mg, 76% yield.

**$^1$H NMR** (400 MHz, Chloroform-d) δ 7.39 – 7.31 (m, 3H), 7.09 – 7.05 (m, 1H), 7.00 – 6.95 (m, 1H), 6.77 (dd, J = 4.1, 1.7 Hz, 1H), 6.16 (dd, J = 4.0, 2.5 Hz, 1H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.98 (m, 2H), 4.45 – 4.36 (m, 2H), 3.85 (s, 3H), 2.15 – 2.08 (m, 2H), 1.97 – 1.89 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.9, 159.5, 141.6, 137.8, 131.0, 129.8, 129.1, 123.7, 122.0, 117.9, 115.5, 113.8, 108.3, 55.5, 49.1, 30.9, 30.8.

**HRMS** (ESI) calcd for $C_{17}H_{20}NO_2[M+H]^+$: 270.1489. Found: 270.1495.

**(3-chlorophenyl)(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1l)**



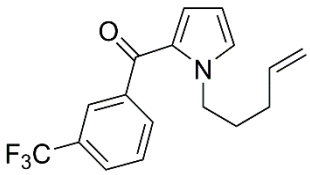
Yellow liquid, 130.9 mg, 48% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (t, *J* = 1.9 Hz, 1H), 7.68 – 7.63 (m, 1H), 7.52 – 7.46 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.17 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.09 – 4.98 (m, 2H), 4.44 – 4.36 (m, 2H), 2.14 – 2.07 (m, 2H), 1.96 – 1.88 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.4, 141.9, 137.7, 134.3, 131.4, 131.3, 129.5, 129.4, 129.3, 127.3, 123.9, 115.5, 108.6, 49.2, 30.82, 30.76.

**HRMS** (ESI) calcd for $C_{16}H_{17}ClNO[M+H]^+$: 274.0993. Found: 274.0992.

**(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)(3-(trifluoromethyl)phenyl)methanone (1m)**



Yellow liquid, 612.3 mg, 99% yield.

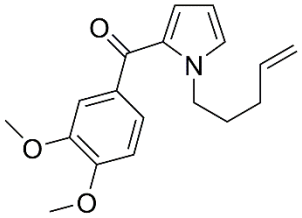
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 2.1 Hz, 1H), 6.71 (dd, *J* = 4.1, 1.7 Hz, 1H), 6.19 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.10 – 4.99 (m, 2H), 4.45 – 4.39 (m, 2H), 2.16 – 2.09 (m, 2H), 1.99 – 1.90 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.3, 140.9, 137.6, 132.4 (m), 131.7, 130.7 (q, *J* = 32.7 Hz), 129.3, 128.7, 127.8 (q, *J* = 3.7 Hz), 126.0 (q, *J* = 3.9 Hz), 124.01, 123.95 (q, *J* = 272.5 Hz), 115.5, 108.7, 49.2, 30.8, 30.7.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −62.7.

**HRMS** (ESI) calcd for $C_{17}H_{17}F_3NO[M+H]^+$: 308.1257. Found: 308.1260.

**(3,4-dimethoxyphenyl)(1-(pent-4-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1n)**



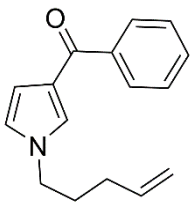
Yellow liquid, 167.4 mg, 56% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.97 (dd, *J* = 2.5, 1.7 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.76 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.16 (dd, *J* = 4.0, 2.5 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08 – 4.97 (m, 2H), 4.42 – 4.36 (m, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 2.14 – 2.07 (m, 2H), 1.97 – 1.89 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.0, 152.2, 148.8, 137.7, 132.8, 130.3, 129.9, 123.8, 122.6, 115.4, 111.9, 109.8, 108.0, 56.1, 56.0, 48.9, 30.9 (overlap).

**HRMS** (ESI) calcd for $C_{18}H_{22}NO_3[M+H]^+$: 300.1594. Found: 300.1600.

**(1-(pent-4-en-1-yl)-1*H*-pyrrol-3-yl)(phenyl)methanone (1o)**



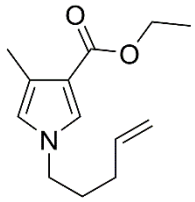
Yellow liquid, 225.7 mg, 94% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 7.19 (t, *J* = 2.0 Hz, 1H), 6.67 (dd, *J* = 3.0, 1.7 Hz, 1H), 6.65 (t, *J* = 2.5 Hz, 1H), 5.74 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.06 – 4.97 (m, 2H), 3.87 (t, *J* = 7.1 Hz, 2H), 2.07 – 1.99 (m, 2H), 1.89 – 1.80 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 190.4, 140.1, 136.8, 131.1, 128.7, 128.0, 127.8, 124.2, 122.1, 115.9, 110.8, 49.2, 30.3, 30.0.

**HRMS** (ESI) calcd for $C_{16}H_{17}NNaO[M+Na]^+$: 262.1202. Found: 262.1207.

**ethyl 4-methyl-1-(pent-4-en-1-yl)-1*H*-pyrrole-3-carboxylate (1v)**



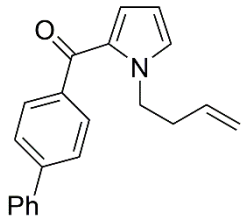
Yellow liquid, 367.3 mg, 83% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.21 (d, *J* = 2.5 Hz, 1H), 6.37 (dd, *J* = 2.4, 1.1 Hz, 1H), 5.76 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.79 (t, *J* = 7.0 Hz, 2H), 2.25 (d, *J* = 1.1 Hz, 3H), 2.07 – 1.99 (m, 2H), 1.87 – 1.79 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.4, 137.0, 126.6, 121.5, 120.2, 115.8, 114.1, 59.2, 49.1, 30.5, 30.1, 14.6, 11.8.

**HRMS** (ESI) calcd for $C_{13}H_{20}NO_2[M+H]^+$: 222.1489. Found: 222.1497.

**[1,1'-biphenyl]-4-yl(1-(but-3-en-1-yl)-1*H*-pyrrol-2-yl)methanone (1x)**



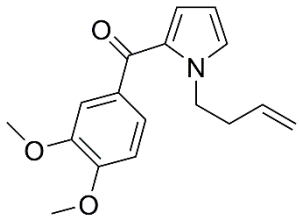
Yellow liquid, 189.9 mg, 63% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.69 – 7.61 (m, 4H), 7.49 – 7.43 (m, 2H), 7.40 – 7.34 (m, 1H), 6.96 (t, *J* = 2.1 Hz, 1H), 6.79 (dd, *J* = 4.0, 1.7 Hz, 1H), 6.16 (dd, *J* = 4.0, 2.5 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.10 – 5.01 (m, 2H), 4.48 (t, *J* = 7.1 Hz, 2H), 2.62 – 2.54 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 144.2, 140.3, 138.9, 134.7, 130.8, 129.91, 129.87, 129.0, 128.0, 127.3, 126.8, 123.4, 117.4, 108.2, 49.1, 36.1.

**HRMS** (ESI) calcd for $C_{21}H_{20}NO[M+H]^+$: 302.1539. Found: 302.1549.

**(1-(but-3-en-1-yl)-1*H*-pyrrol-2-yl) (3,4-dimethoxyphenyl) methanone (1y)**



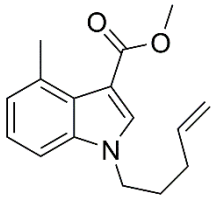
Yellow liquid, 112.7 mg, 56% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.48 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.95 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.18 – 6.12 (m, 1H), 5.86 – 5.74 (m, 1H), 5.10 – 5.00 (m, 2H), 4.44 (t, *J* = 7.2 Hz, 2H), 3.95 (d, *J* = 1.7 Hz, 3H), 3.94 (d, *J* = 1.3 Hz, 3H), 2.61 – 2.53 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.1, 152.1, 148.7, 134.7, 132.7, 130.3, 129.9, 123.8, 122.5, 117.3, 111.8, 109.8, 107.9, 56.1, 56.0, 48.9, 36.1.

**HRMS** (ESI) calcd for $C_{17}H_{19}NNaO_3[M+Na]^+$: 308.1257. Found: 308.1265.

**methyl 4-methyl-1-(pent-4-en-1-yl)-1*H*-indole-3-carboxylate (4b)**



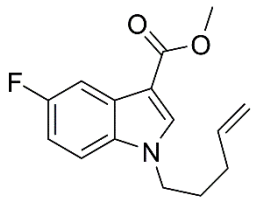
Green liquid, 106.7 mg, 69% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.22 – 7.12 (m, 2H), 7.05 – 7.00 (m, 1H), 5.79 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.09 – 5.03 (m, 2H), 4.12 (t, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 2.86 (s, 3H), 2.12 – 2.05 (m, 2H), 2.01 – 1.89 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 137.3, 137.0, 135.5, 132.9, 125.6, 124.0, 123.0, 116.2, 107.8, 107.7, 51.2, 46.3, 30.8, 28.8, 22.6.

**HRMS** (ESI) calcd for $C_{16}H_{19}NNaO_2[M+Na]^+$: 280.1308. Found: 280.1316.

**methyl 5-fluoro-1-(pent-4-en-1-yl)-1*H*-indole-3-carboxylate (4d)**



Green liquid, 127.3 mg, 97% yield.

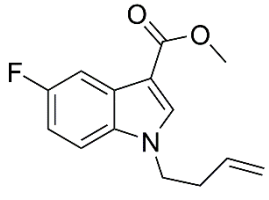
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.78 (m, 2H), 7.27 (dd, *J* = 8.5, 4.7 Hz, 1H), 7.01 (td, *J* = 9.0, 2.6 Hz, 1H), 5.78 (ddt, *J* = 17.6, 9.8, 6.5 Hz, 1H), 5.09 – 5.02 (m, 2H), 4.13 (t, *J* = 7.0 Hz, 2H), 3.90 (s, 3H), 2.11 – 2.03 (m, 2H), 2.00 – 1.92 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.3, 159.3 (d, *J* = 237.2 Hz), 136.8, 135.4, 133.1, 127.5 (d, *J* = 11.0 Hz), 116.3, 111.3 (d, *J* = 26.5 Hz), 110.9 (d, *J* = 9.9 Hz), 107.14 (d, *J* = 4.5 Hz), 107.13 (d, *J* = 24.9 Hz), 51.2, 46.5, 30.7, 28.9.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −121.8.

**HRMS** (ESI) calcd for $C_{15}H_{17}FNO_2[M+H]^+$: 262.1238. Found: 262.1239.

**methyl 1-(but-3-en-1-yl)-5-fluoro-1*H*-indole-3-carboxylate (4g)**



Yellow solid, 131.6 mg, 53% yield, m.p. = 68.8 – 69.4 ℃.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 2H), 7.16 (dd, *J* = 9.0, 4.2 Hz, 1H), 6.91 (td, *J* = 9.0, 2.6 Hz, 1H), 5.63 (ddt, *J* = 17.1, 10.4,

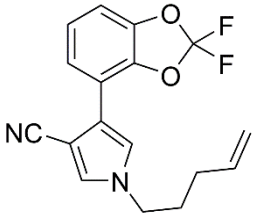
6.8 Hz, 1H), 4.99 – 4.90 (m, 2H), 4.06 (t, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.51 – 2.43 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 159.3 (d, *J* = 237.0 Hz), 135.4, 133.6, 132.9, 127.4 (d, *J* = 11.1 Hz), 118.4, 111.2 (d, *J* = 26.6 Hz), 110.8 (d, *J* = 9.8 Hz), 107.02 (d, *J* = 24.9 Hz), 106.97 (d, *J* = 4.5 Hz), 51.1, 46.8, 34.1.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −121.8.

**HRMS** (ESI) calcd for $C_{14}H_{15}FNO_2[M+H]^+$: 248.1081. Found: 248.1085.

**4-(2,2-difluorobenzo[*d*][1,3]dioxol-4-yl)-1-(pent-4-en-1-yl)-1*H*-pyrrole-3-carbonitrile (6a)**




White solid, 631.3 mg, 99% yield, m.p. = 58.2 – 59.2 ℃.

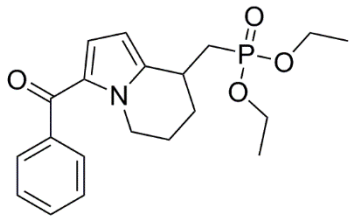
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.96 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.78 (ddt, *J* = 17.9, 9.6, 6.6 Hz, 1H), 5.13 – 5.03 (m, 2H), 3.96 (t, *J* = 7.1 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.98 – 1.89 (m, 2H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 143.9, 139.8, 136.5, 131.5 (t, *J* = 254.8 Hz), 129.6, 124.2, 122.5, 121.3, 118.6, 116.64, 116.62, 116.59, 107.8, 91.1, 49.9, 30.4, 30.0.

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −49.4.

**HRMS** (ESI) calcd for $C_{17}H_{14}F_2N_2NaO_2[M+Na]^+$: 339.0916. Found: 339.0917.

**diethyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3aa)**




Yellow liquid, 54.3 mg, 72% yield.

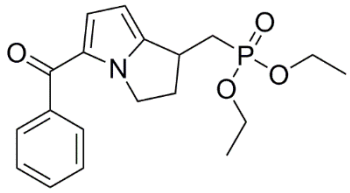
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.72 (m, 2H), 7.54 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.07 (dd, *J* = 4.3, 0.9 Hz, 1H), 4.64 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.34 – 4.25 (m, 1H), 4.20 – 4.09 (m, 4H), 3.39 – 3.27 (m, 1H), 2.41 – 2.28 (m, 2H), 2.18 – 2.08 (m, 1H), 2.04 – 1.93 (m, 2H), 1.70 – 1.60 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.3 (d, *J* = 21.0 Hz), 140.4, 131.2, 129.7, 129.1, 128.1, 123.3, 106.3, 61.9 (d, *J* = 6.5 Hz), 61.7 (d, *J* = 6.7 Hz), 46.2, 31.8 (d, *J* = 139.8 Hz), 30.2 (d, *J* = 2.5 Hz), 26.8 (d, *J* = 3.2 Hz), 22.3, 16.6 (d, *J* = 6.3 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{20}H_{27}NO_4P[M+H]^+$: 376.1672. Found: 376.1672.

**diethyl ((5-benzoyl-2,3-dihydro-1*H*-pyrrolizin-1-yl) methyl) phosphonate (3ba)**



Yellow liquid, 55.7 mg, 77% yield.

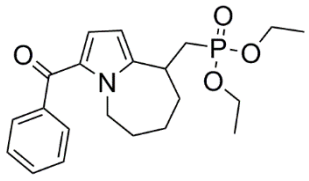
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.77 (m, 2H), 7.56 – 7.48 (m, 1H), 7.49 – 7.41 (m, 2H), 6.81 (d, *J* = 4.0 Hz, 1H), 6.02 (d, *J* = 4.0 Hz, 1H), 4.60 (ddd, *J* = 12.4, 8.7, 3.7 Hz, 1H), 4.30 (dt, *J* = 12.2, 7.8 Hz, 1H), 4.23 – 4.08 (m, 4H), 3.61 – 3.49 (m, 1H), 2.94 – 2.81 (m, 1H), 2.46 – 2.23 (m, 2H), 2.05 – 1.91 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.0, 148.5 (d, *J* = 18.9 Hz), 139.5, 131.4, 128.9, 128.2, 126.8, 125.1, 101.9, 62.0 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.6 Hz), 47.7, 35.5 (d, *J* = 5.3 Hz), 32.3 (d, *J* = 3.9 Hz), 30.5 (d, *J* = 140.9 Hz), 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.8.

**HRMS (ESI)** calcd for $C_{19}H_{25}NO_4P$ $[M+H]^+$: 362.1516. Found: 362.1521.

**diethyl ((3-benzoyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepin-9-yl)methyl) phosphonate (3ca)**



Yellow liquid, 26.7 mg, 34% yield.

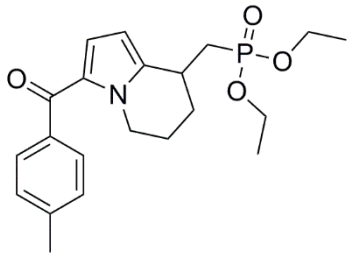
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.56 – 7.47 (m, 1H), 7.45 – 7.40 (m, 2H), 6.57 (d, *J* = 4.1 Hz, 1H), 5.96 (d, *J* = 4.1 Hz, 1H), 4.16 – 4.06 (m, 4H), 3.38 – 3.24 (m, 1H), 2.41 – 2.28 (m, 1H), 2.27 – 2.06 (m, 2H), 2.04 – 1.89 (m, 2H), 1.85 – 1.72 (m, 2H), 1.69 – 1.56 (m, 1H), 1.57 – 1.39 (m, 2H), 1.36 – 1.30 (m, 6H) .

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 186.2, 148.4 (d, *J* = 18.8 Hz), 140.4, 131.4, 130.8, 129.5, 128.1, 123.0, 105.7, 61.9 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.6 Hz), 46.2, 33.4 (d, *J* = 2.6 Hz), 31.1 (d, *J* = 129.5 Hz), 29.4, 28.5, 22.8, 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 30.0.

**HRMS** (ESI) calcd for $C_{21}H_{28}NNaO_4P$$[M+Na]^+$: 412.1648. Found: 412.1655.

**diethyl ((3-(4-methylbenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3da)**



Brown liquid, 58.7 mg, 75% yield.

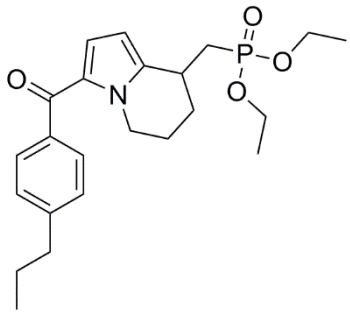
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.06 (d, *J* = 4.2 Hz, 1H), 4.61 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 4.19 – 4.08 (m, 4H), 3.38 – 3.25 (m, 1H), 2.42 (s, 3H), 2.39 – 2.28 (m, 2H), 2.17 – 2.07 (m, 1H), 2.04 – 1.92 (m, 2H), 1.70 – 1.60 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.6, 142.0 (d, *J* = 21.1 Hz), 141.7, 137.7, 129.8, 129.4, 128.8, 122.9, 106.2, 61.9 (d, *J* = 6.7 Hz), 61.8 (d, *J* = 6.6 Hz), 46.2, 31.9 (d, *J* = 139.8 Hz), 30.3 (d, *J* = 2.5 Hz), 26.9 (d, *J* = 3.2 Hz), 22.3, 21.6, 16.6 (d, *J* = 6.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{21}H_{28}NNaO_4P[M+Na]^+$: 412.1648. Found: 412.1653.

**diethyl ((3-(4-propylbenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ea)**



Yellow liquid, 56.2 mg, 58% yield.

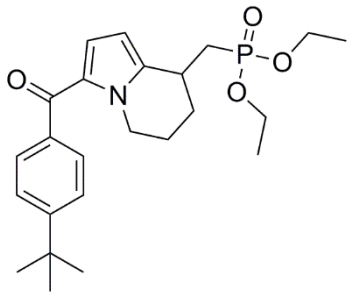
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.66 (m, 2H), 7.27 – 7.20 (m, 2H), 6.72 (d, *J* = 4.2 Hz, 1H), 6.06 (d, *J* = 4.2 Hz, 1H), 4.61 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 4.19 – 4.08 (m, 4H), 3.40 – 3.25 (m, 1H), 2.69 – 2.60 (m, 2H), 2.40 – 2.28 (m, 2H), 2.18 – 2.06 (m, 1H), 2.04 – 1.90 (m, 2H), 1.71 – 1.62 (m, 3H), 1.35 (t, *J* = 7.1 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 146.5, 142.0 (d, *J* = 21.1 Hz), 137.9, 129.9, 129.4, 128.2, 123.0, 106.2, 61.9 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.6 Hz), 46.2, 38.1, 31.9 (d, *J* = 139.7 Hz), 30.3 (d, *J* = 2.5 Hz), 27.0 (d, *J* = 3.3 Hz), 24.5, 22.3, 16.6 (d, *J* = 6.2 Hz), 13.9.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{23}H_{32}NNaO_4P[M+Na]^+$: 440.1961. Found: 440.1964.

**diethyl ((3-(4-(tert-butyl) benzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3fa)**



Yellow liquid, 51.8 mg, 57% yield.

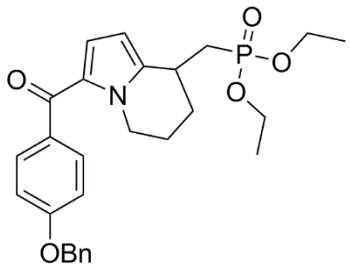
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.76 – 7.68 (m, 2H), 7.48 – 7.42 (m, 2H), 6.74 (d, *J* = 4.2 Hz, 1H), 6.06 (d, *J* = 4.2 Hz, 1H), 4.62 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.0, 4.9 Hz, 1H), 4.20 – 4.08 (m, 4H), 3.40 – 3.25 (m, 1H), 2.41 – 2.28 (m, 2H), 2.17 – 2.08 (m, 1H), 2.05 – 1.87 (m, 2H), 1.70 – 1.60 (m, 1H), 1.39 – 1.31 (m, 15H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.6, 154.8, 142.0 (d, *J* = 21.2 Hz), 137.7, 129.9, 129.2, 125.1, 123.0, 106.2, 61.9 (d, *J* = 6.4 Hz), 61.8 (d, *J* = 6.6 Hz), 46.2, 35.1, 31.9 (d, *J* = 139.8 Hz), 31.4, 30.3 (d, *J* = 2.4 Hz), 27.0 (d, *J* = 3.0 Hz), 22.4, 16.6 (d, *J* = 5.9 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{24}H_{34}NNaO_4P[M+Na]^+$: 454.2118. Found: 454.2119.

**diethyl ((3-(4-(benzyloxy) benzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) Phosphonate (3ga)**



Yellow liquid, 68.4 mg, 67% yield.

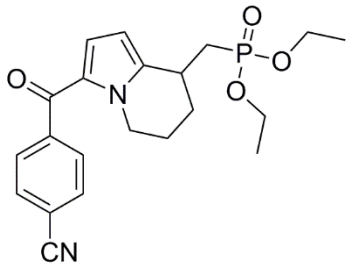
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.46 – 7.38 (m, 4H), 7.37 – 7.32 (m, 1H), 7.04 – 6.98 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.06 (dd, *J* = 4.2, 0.9 Hz, 1H), 5.13 (s, 2H), 4.59 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.27 (ddd, *J* = 14.4, 10.1, 4.9 Hz, 1H), 4.20 – 4.09 (m, 4H), 3.39 – 3.25 (m, 1H), 2.40 – 2.28 (m, 2H), 2.16 – 2.07 (m, 1H), 2.04 – 1.86 (m, 2H), 1.69 – 1.59 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.7, 161.5, 141.8 (d, *J* = 21.3 Hz), 136.6, 133.2, 131.4, 129.8, 128.8, 128.3, 127.6, 122.4, 114.2, 106.0, 70.2, 61.9 (d, *J* = 6.5 Hz), 61.7 (d, *J* = 6.6 Hz), 46.1, 31.9 (d, *J* = 139.7 Hz), 30.3 (d, *J* = 2.5 Hz), 27.0 (d, *J* = 2.8 Hz), 22.4, 16.6 (d, *J* = 6.2 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.5.

**HRMS** (ESI) calcd for $C_{27}H_{32}NNaO_5P[M+Na]^+$: 504.1910. Found: 504.1912.

**diethyl ((3-(4-cyanobenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ha)**



Yellow liquid, 33.5mg, 42% yield.

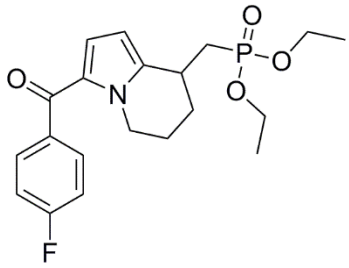
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 2H), 7.77 – 7.70 (m, 2H), 6.64 (d, *J* = 4.2 Hz, 1H), 6.10 (d, *J* = 4.3 Hz, 1H), 4.63 (dt, *J* = 14.2, 4.9 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.0, 5.0 Hz, 1H), 4.20 – 4.08 (m, 4H), 3.38 – 3.27 (m, 1H), 2.38 – 2.27 (m, 2H), 2.19 – 2.10 (m, 1H), 2.04 – 1.88 (m, 2H), 1.72 – 1.63 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 183.4, 144.4, 143.7 (d, *J* = 20.7 Hz), 132.1, 129.5, 129.1, 124.0, 118.5, 114.5, 107.2, 62.0 (d, *J* = 6.7 Hz), 61.8 (d, *J* = 6.6 Hz), 46.4, 31.8 (d, *J* = 140.2 Hz), 30.3 (d, *J* = 2.4 Hz), 26.7 (d, *J* = 3.4 Hz), 22.2, 16.6 (d, *J* = 5.9 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{21}H_{25}N_2NaO_4P$[M+Na]+ :423.1444. Found: 423.1451.

**diethyl ((3-(4-fluorobenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ia)**



Yellow liquid, 43.9 mg, 56% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 2H), 7.15 – 7.07 (m, 2H), 6.68 (d, *J* = 4.2 Hz, 1H), 6.08 (d, *J* = 4.2 Hz, 1H), 4.61 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.28 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 4.20 – 4.09 (m, 4H), 3.40 – 3.25 (m, 1H), 2.40 – 2.27 (m, 2H), 2.17 – 2.09 (m, 1H), 2.05 – 1.91 (m, 2H), 1.71 – 1.60 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

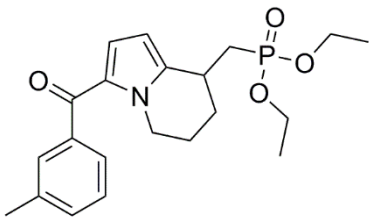
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.2, 164.7 (d, *J* = 251.6 Hz), 142.5 (d, *J* = 21.1 Hz), 136.6 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 8.8 Hz), 129.5, 123.1, 115.1 (d, *J* = 21.6 Hz), 106.4, 61.9 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.7 Hz), 46.2, 31.9 (d, *J* = 139.9 Hz), 30.3 (d, *J* = 2.5 Hz), 26.9 (d, *J* = 3.3 Hz), 22.3, 16.6 (d, *J* = 6.0 Hz).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −108.6.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.3.

**HRMS** (ESI) calcd for $C_{20}H_{25}FNNaO_4P$[M+Na]$^{+}$: 416.1397. Found: 416.1400.

**diethyl ((3-(3-methylbenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ja)**



Yellow liquid, 63.0 mg, 71% yield.

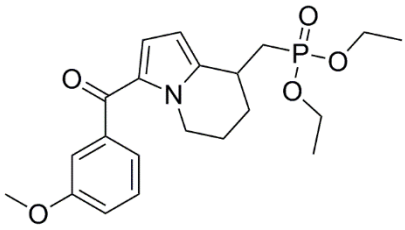
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.51 (m, 2H), 7.35 – 7.27 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.06 (d, *J* = 4.2 Hz, 1H), 4.63 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 4.20 – 4.09 (m, 4H), 3.40 – 3.25 (m, 1H), 2.40 (s, 3H), 2.39 – 2.29 (m, 2H), 2.17 – 2.08 (m, 1H), 2.06 – 1.92 (m, 2H), 1.71 – 1.60 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.9, 142.2 (d, *J* = 21.1 Hz), 140.5, 137.8, 131.9, 129.8, 129.7, 127.9, 126.4, 123.2, 106.2, 61.9 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.6 Hz), 46.2, 31.9 (d, *J* = 139.8 Hz), 30.3 (d, *J* = 2.5 Hz), 26.9 (d, *J* = 3.2 Hz), 22.3, 21.5, 16.6 (d, *J* = 5.6 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{21}H_{28}NNaO_4P[M+Na]^+$ : 412.1648. Found: 412.1651.

**diethyl ((3-(3-methoxybenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ka)**



Yellow liquid, 52.5 mg, 65% yield.

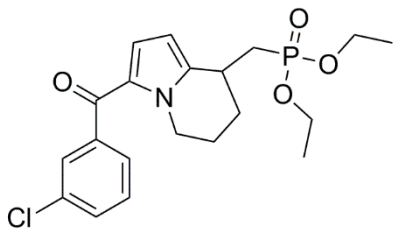
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 7.09 – 7.02 (m, 1H), 6.74 (d, *J* = 4.2 Hz, 1H), 6.07 (d, *J* = 4.2 Hz, 1H), 4.63 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.29 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 4.20 – 4.09 (m, 4H), 3.84 (s, 3H), 3.40 – 3.25 (m, 1H), 2.40 – 2.28 (m, 2H), 2.17 – 2.09 (m, 1H), 2.05 – 1.87 (m, 2H), 1.71 – 1.60 (m, 1H), 1.35 (t, *J* = 7.0 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.4, 159.4, 142.4 (d, *J* = 21.0 Hz), 141.8, 129.7, 129.0, 123.3, 121.8, 117.5, 113.8, 106.4, 62.0 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.5 Hz), 55.5, 46.2, 31.9 (d, *J* = 139.8 Hz), 30.3 (d, *J* = 2.4 Hz), 26.9 (d, *J* = 3.1 Hz), 22.3, 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{21}H_{28}NNaO_5P[M+Na]^+$ : 428.1597. Found: 428.1601.

**diethyl ((3-(3-chlorobenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3la)**



Brown liquid, 30.9 mg, 38% yield.

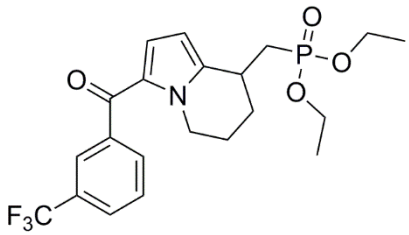
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.77 – 7.71 (m, 1H), 7.70 – 7.56 (m, 1H), 7.51 – 7.42 (m, 1H), 7.41 – 7.34 (m, 1H), 6.70 (d, *J* = 4.1 Hz, 1H), 6.09 (d, *J* = 4.2 Hz, 1H), 4.62 (ddt, *J* = 14.0, 9.7, 4.9 Hz, 1H), 4.28 (ddd, *J* = 14.4, 10.0, 5.1 Hz, 1H), 4.19 – 4.08 (m, 4H), 3.39 – 3.27 (m, 1H), 2.39 – 2.27 (m, 2H), 2.17 – 2.08 (m, 1H), 2.04 – 1.88 (m, 2H), 1.72 – 1.61 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 183.9, 143.0 (d, *J* = 20.9 Hz), 142.2, 134.2, 131.1, 129.5, 129.2, 128.1, 127.2, 123.6, 106.7, 62.0 (d, *J* = 6.4 Hz), 61.8 (d, *J* = 6.7 Hz), 46.3, 31.9 (d, *J* = 140.1 Hz), 30.3 (d, *J* = 2.6 Hz), 26.8 (d, *J* = 3.2 Hz), 22.2, 16.6 (d, *J* = 6.0 Hz)..

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.2.

**HRMS** (ESI) calcd for $C_{20}H_{25}ClNNaO_4P[M+Na]^+$: 432.1102. Found: 432.1103.

**diethyl ((3-(3-(trifluoromethyl)benzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ma)**



Brown liquid, 36.7 mg, 41% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 8.06 – 7.98 (m, 1H), 7.96 – 7.89 (m, 1H), 7.82 – 7.73 (m, 1H), 7.60 – 7.54 (m, 1H), 6.67 (d, *J* = 4.2 Hz, 1H), 6.10 (d, *J* = 4.2 Hz, 1H), 4.63 (dt, *J* = 14.2, 4.9 Hz, 1H), 4.30 (ddd, *J* = 14.5, 10.0, 5.0 Hz, 1H), 4.20 – 4.08 (m, 4H), 3.42 – 3.27 (m, 1H), 2.39 – 2.28 (m, 2H), 2.19 – 2.08 (m, 1H), 2.05 – 1.93 (m, 2H), 1.72 – 1.62 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

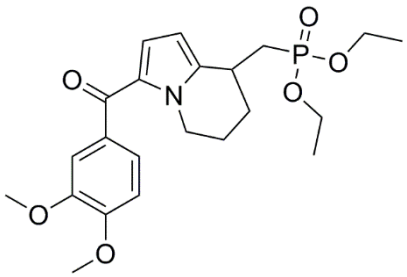
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 183.9, 143.2 (d, *J* = 20.9 Hz), 141.1, 132.3, 130.6 (q, *J* = 32.5 Hz), 129.2, 128.8, 127.7 (q, *J* = 3.5 Hz), 126.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 298.5 Hz), 123.7, 106.9, 62.0 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.7 Hz), 46.3, 31.8 (d, *J* = 140.1 Hz), 30.3 (d, *J* = 2.4 Hz), 26.8 (d, *J* = 3.1 Hz), 22.2, 16.6 (d, *J* = 5.8 Hz).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −62.7.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.2.

**HRMS** (ESI) calcd for $C_{21}H_{25}F_3NNaO_4P[M+Na]^+$: 466.1366. Found: 466.1363.

**diethyl ((3-(3,4-dimethoxybenzoyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3na)**



Yellow liquid, 60.0 mg, 67% yield.

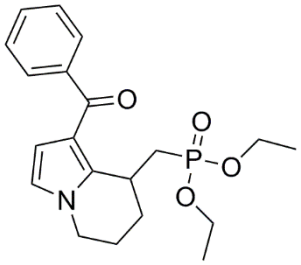
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 4.1 Hz, 1H), 6.08 (d, *J* = 4.1 Hz, 1H), 4.58 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.28 (ddd, *J* = 14.4, 10.1, 4.9 Hz, 1H), 4.20 – 4.09 (m, 4H), 3.95 (s, 3H), 3.93 (s, 3H), 3.40 – 3.26 (m, 1H), 2.41 – 2.30 (m, 2H), 2.17 – 2.08 (m, 1H), 2.05 – 1.86 (m, 2H), 1.71 – 1.60 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.5, 151.9, 148.6, 141.8 (d, *J* = 21.2 Hz), 132.9, 129.6, 123.5, 122.3, 111.9, 109.8, 106.0, 61.8 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.6 Hz), 56.04, 55.98, 46.0, 31.8 (d, *J* = 139.6 Hz), 30.2 (d, *J* = 2.5 Hz), 26.9 (d, *J* = 3.1 Hz), 22.3, 16.5 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{22}H_{30}NNaO_6P[M+Na]^+$ : 458.1703. Found: 458.1711.

**diethyl ((1-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3oa)**



Yellow liquid, 61.8 mg, 82% yield.

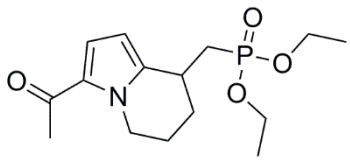
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.70 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 6.46 (d, *J* = 3.1 Hz, 1H), 6.37 (d, *J* = 3.1 Hz, 1H), 4.29 – 4.10 (m, 4H), 4.09 – 4.02 (m, 1H), 4.02 – 3.84 (m, 2H), 2.68 (ddd, *J* = 19.1, 15.2, 3.0 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.18 – 2.09 (m, 1H), 2.08 – 1.99 (m, 1H), 1.98 – 1.89 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 191.6, 141.1, 140.6 (d, *J* = 23.1 Hz), 130.9, 128.9, 128.0, 119.4, 118.4, 113.2, 62.0 (d, *J* = 6.6 Hz), 61.6 (d, *J* = 6.3 Hz), 46.0, 29.0 (d, *J* = 134.4 Hz), 28.6 (d, *J* = 1.5 Hz) 24.4, 18.9, 16.63 (d, *J* = 6.0 Hz), 16.55 (d, *J* = 6.3 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.5.

**HRMS** (ESI) calcd for $C_{20}H_{26}NNaO_4P[M+Na]^+$: 398.1492. Found: 398.1490.

**diethyl ((3-acetyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3pa)**



Yellow liquid, 36.3 mg, 56% yield.

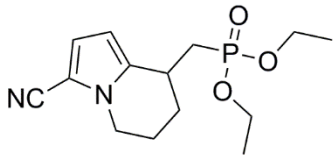
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 4.2 Hz, 1H), 6.04 (d, *J* = 4.2 Hz, 1H), 4.57 (dt, *J* = 14.2, 4.9 Hz, 1H), 4.20 – 4.06 (m, 5H), 3.33 – 3.19 (m, 1H), 2.39 (s, 3H), 2.36 – 2.22 (m, 2H), 2.12 – 2.01 (m, 1H), 2.00 – 1.81 (m, 2H), 1.66 – 1.52 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 188.0, 141.5 (d, *J* = 21.0 Hz), 130.0, 119.9, 106.0, 61.9 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.7 Hz), 46.3, 31.8 (d, *J* = 140.0 Hz), 30.2 (d, *J* = 2.5 Hz), 27.2, 26.7 (d, *J* = 3.0 Hz), 22.1, 16.6 (d, *J* = 5.8 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.4.

**HRMS** (ESI) calcd for $C_{15}H_{24}NNaO_4P[M+Na]^+$: 336.1335. Found: 336.1344.

**diethyl ((3-cyano-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3qa)**



Yellow liquid, 14.2 mg, 22% yield.

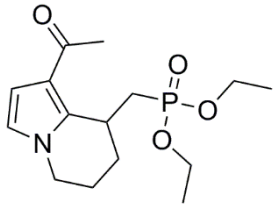
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.76 (d, *J* = 4.1 Hz, 1H), 6.02 (d, *J* = 4.1 Hz, 1H), 4.19 – 4.09 (m, 5H), 3.92 (ddd, *J* = 12.4, 10.1, 4.9 Hz, 1H), 3.30 – 3.16 (m, 1H), 2.37 – 2.23 (m, 2H), 2.18 – 2.10 (m, 1H), 2.02 – 1.87 (m, 2H), 1.67 – 1.57 (m, 1H), 1.34 (t, *J* = 7.0 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 139.0 (d, *J* = 21.0 Hz), 119.7, 114.2, 106.3, 102.3, 62.0 (d, *J* = 6.7 Hz), 61.8 (d, *J* = 6.7 Hz), 44.6, 31.6 (d, *J* = 140.4 Hz), 29.9 (d, *J* = 2.6 Hz), 27.3 (d, *J* = 3.5 Hz), 21.8, 16.6 (d, *J* = 6.2 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.0.

**HRMS** (ESI) calcd for $C_{14}H_{21}N_2NaO_3P[M+Na]^+$: 319.1182. Found: 319.1187.

**diethyl ((1-acetyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)phosphonate (3ra)**



Yellow liquid, 46.6 mg, 73% yield.

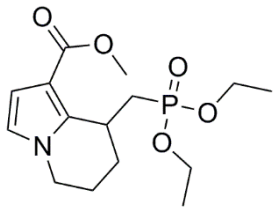
$^1$H NMR (400 MHz, Chloroform-*d*) δ 6.51 (d, *J* = 3.1 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 4.29 – 4.07 (m, 4H), 4.05 – 3.99 (m, 1H), 3.89 – 3.79 (m, 2H), 2.57 – 2.41 (m, 2H), 2.39 (s, 3H), 2.16 – 2.00 (m, 1H), 1.96 – 1.86 (m, 2H), 1.86 – 1.77 (m, 1H), 1.38 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 194.2, 139.0 (d, *J* = 23.2 Hz), 119.6, 119.5, 111.0, 62.0 (d, *J* = 6.6 Hz), 61.6 (d, *J* = 6.3 Hz), 46.0, 28.5 (d, *J* = 134.4 Hz), 28.4, 28.2, 24.0, 18.6, 16.7 (d, *J* = 6.2 Hz), 16.6 (d, *J* = 6.2 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.5.

**HRMS** (ESI) calcd for $C_{15}H_{24}NNaO_4P[M+Na]^+$: 336.1335. Found: 336.1338.

**methyl 8-((diethoxyphosphoryl)methyl)-5,6,7,8-tetrahydroindolizine-1- carboxylate (3sa)**



Yellow liquid, 45.3 mg, 67% yield.

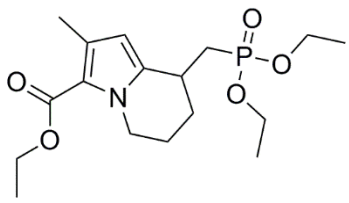
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.56 (d, *J* = 3.0 Hz, 1H), 6.44 (d, *J* = 3.0 Hz, 1H), 4.23 – 4.09 (m, 4H), 4.01 (ddd, *J* = 12.6, 5.7, 2.6 Hz, 1H), 3.87 – 3.82 (m, 1H), 3.79 (s, 3H), 2.51 – 2.37 (m, 2H), 2.06 – 1.97 (m, 1H), 1.95 – 1.79 (m, 4H), 1.37 (t, *J* = 7.3 Hz, 3H), 1.33 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 139.2 (d, *J* = 23.0 Hz), 119.8, 110.5, 110.3, 61.8 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 50.9, 45.9, 29.7 (d, *J* = 134.9 Hz), 27.9 (d, *J* = 1.6 Hz), 24.2, 18.7, 16.65 (d, *J* = 6.5 Hz), 16.58 (d, *J* = 6.6 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.6.

**HRMS** (ESI) calcd for $C_{15}H_{24}NNaO_5P[M+Na]^+$: 352.1284. Found: 352.1290.

**ethyl 8-((diethoxyphosphoryl)methyl)-2-methyl-5,6,7,8-tetrahydroindolizine-3-carboxylate (3ta)**



Yellow liquid, 45.5 mg, 62% yield.

**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 5.86 (s, 1H), 4.47 (dt, *J* = 13.8, 4.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 4.18 – 4.01 (m, 5H),

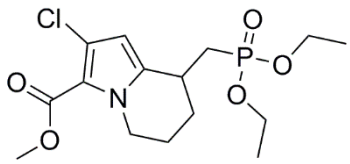
3.21 (qd, *J* = 10.7, 9.6, 4.4 Hz, 1H), 2.30 (s, 3H), 2.37 – 2.20 (m, 2H), 2.10 – 2.02 (m, 1H), 1.97 – 1.80 (m, 2H), 1.61 – 1.50 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 162.2, 138.7 (d, *J* = 21.7 Hz), 129.8, 118.6, 108.4, 61.8 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.7 Hz), 59.4, 45.8, 31.8 (d, *J* = 139.3 Hz), 30.0 (d, *J* = 2.4 Hz), 27.0 (d, *J* = 3.0 Hz), 22.4, 16.6 (d, *J* = 6.0 Hz), 14.6, 14.5.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.7.

**HRMS** (ESI) calcd for $C_{17}H_{28}NNaO_5P[M+Na]^+$: 380.1597. Found: 380.1599.

**methyl 2-chloro-8-((diethoxyphosphoryl)methyl)-5,6,7,8-tetrahydroindolizine-3-carboxylate (3ua)**



Yellow liquid, 43.5 mg, 60% yield.

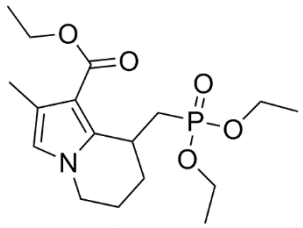
$^1$H NMR (400 MHz, Chloroform-*d*) δ 6.05 (d, *J* = 1.0 Hz, 1H), 4.45 (dt, *J* = 13.8, 4.9 Hz, 1H), 4.20 – 4.01 (m, 5H), 3.85 (s, 3H), 3.27 – 3.13 (m, 1H), 2.30 – 2.18 (m, 2H), 2.12 – 2.03 (m, 1H), 1.98 – 1.85 (m, 2H), 1.64 – 1.54 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 161.2, 138.8 (d, *J* = 21.2 Hz), 120.8, 117.4, 107.9, 61.9 (d, *J* = 6.5 Hz), 61.8 (d, *J* = 6.6 Hz), 51.2, 46.2, 31.7 (d, *J* = 140.2 Hz), 29.9 (d, *J* = 2.4 Hz), 26.6 (d, *J* = 3.4 Hz), 22.1, 16.6 (d, *J* = 6.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.0.

**HRMS** (ESI) calcd for $C_{15}H_{23}ClNNaO_5P[M+Na]^+$: 386.0895. Found: 386.0895.

**ethyl 8-((diethoxyphosphoryl)methyl)-2-methyl-5,6,7,8-tetrahydroindolizine-1-carboxylate (3va)**



Yellow liquid, 40.1 mg, 53% yield.

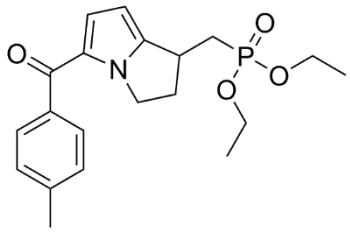
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 6.25 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.21 – 4.01 (m, 5H), 3.97 – 3.82 (m, 2H), 3.75 (td, *J* = 12.0, 5.0 Hz, 1H), 2.50 – 2.35 (m, 2H), 2.21 (s, 3H), 2.09 – 1.93 (m, 1H), 1.92 – 1.74 (m, 2H), 1.38 – 1.31 (m, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.4, 139.5 (d, *J* = 23.1 Hz), 121.8, 118.8, 109.3, 61.7 (d, *J* = 6.6 Hz), 61.5 (d, *J* = 6.5 Hz), 59.2, 45.5, 29.7 (d, *J* = 134.3 Hz), 28.2, 24.1, 18.4, 16.61 (d, *J* = 5.5 Hz), 16.55 (d, *J* = 5.7 Hz), 14.7, 12.6.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.6.

**HRMS** (ESI) calcd for $C_{17}H_{28}NNaO_5P[M+Na]^+$: 380.1597. Found: 380.1600.

**diethyl ((5-(4-methylbenzoyl)-2,3-dihydro-1*H*-pyrrolizin-1-yl)methyl) phosphonate (3wa)**



Yellow liquid, 37.5 mg, 62% yield.

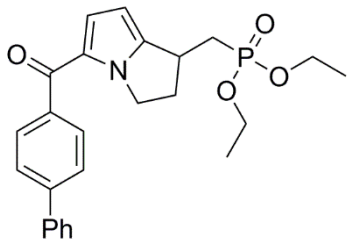
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.70 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 4.0 Hz, 1H), 6.01 (d, *J* = 4.3 Hz, 1H), 4.58 (ddd, *J* = 12.4, 8.6, 3.7 Hz, 1H), 4.28 (dt, *J* = 12.2, 7.8 Hz, 1H), 4.22 – 4.08 (m, 4H), 3.62 – 3.47 (m, 1H), 2.93 – 2.79 (m, 1H), 2.42 (s, 3H), 2.40 – 2.23 (m, 2H), 2.02 – 1.90 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.9, 148.3 (d, *J* = 18.8 Hz), 141.9, 136.8, 129.1, 128.9, 126.9, 124.7, 101.7, 62.0 (d, *J* = 6.6 Hz), 61.9 (d, *J* = 6.7 Hz), 47.7, 35.5 (d, *J* = 5.3 Hz), 32.3 (d, *J* = 4.0 Hz), 30.6 (d, *J* = 140.8 Hz), 21.6, 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.8.

**HRMS** (ESI) calcd for $C_{20}H_{26}NNaO_4P[M+Na]^+$: 398.1492. Found: 398.1493.

**diethyl ((5-([1,1'-biphenyl]-4-carbonyl)-2,3-dihydro-1*H*-pyrrolizin-1-yl) methyl) phosphonate (3xa)**



Brown liquid, 52.7 mg, 60% yield.

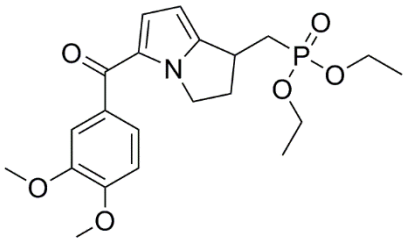
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.92 – 7.85 (m, 2H), 7.69 – 7.62 (m, 4H), 7.50 – 7.44 (m, 2H), 7.41 – 7.36 (m, 1H), 6.87 (d, *J* = 4.0 Hz, 1H), 6.04 (d, *J* = 4.0 Hz, 1H), 4.61 (ddd, *J* = 12.3, 8.7, 3.7 Hz, 1H), 4.31 (dt, *J* = 12.2, 7.8 Hz, 1H), 4.22 – 4.10 (m, 4H), 3.63 – 3.49 (m, 1H), 2.93 – 2.83 (m, 1H), 2.45 – 2.25 (m, 2H), 2.03 – 1.92 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 184.5, 148.6 (d, *J* = 18.7 Hz), 144.2, 140.4, 138.3, 129.6, 129.0, 128.0, 127.4, 127.0, 126.9, 125.0, 101.9, 62.0 (d, *J* = 6.6 Hz), 61.9 (d, *J* = 6.7 Hz), 47.8, 35.5 (d, *J* = 5.5 Hz), 32.4 (d, *J* = 3.9 Hz), 30.6 (d, *J* = 140.9 Hz), 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.8.

**HRMS** (ESI) calcd for $C_{25}H_{28}NNaO_4P[M+Na]^+$: 460.1648. Found: 460.1650.

**diethyl ((5-(3,4-dimethoxybenzoyl)-2,3-dihydro-1*H*-pyrrolizin-1-yl)methyl) phosphonate (3ya)**



Yellow liquid, 52.7 mg, 63% yield.

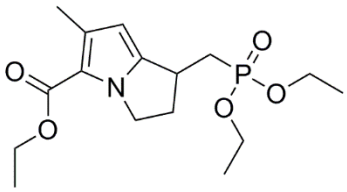
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 3.9 Hz, 1H), 6.03 (d, *J* = 3.9 Hz, 1H), 4.57 (ddd, *J* = 12.3, 8.7, 3.7 Hz, 1H), 4.28 (dt, *J* = 12.2, 7.8 Hz, 1H), 4.21 – 4.10 (m, 4H), 3.95 (s, 3H), 3.93 (s, 3H), 3.62 – 3.48 (m, 1H), 2.92 – 2.81 (m, 1H), 2.43 – 2.24 (m, 2H), 2.02 – 1.91 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 183.9, 152.1, 148.8, 148.1 (d, *J* = 18.6 Hz), 132.1, 126.8, 124.3, 123.2, 111.8, 110.1, 101.7, 61.9 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.6 Hz), 56.1, 56.0, 47.6, 35.5 (d, *J* = 5.4 Hz), 32.3 (d, *J* = 4.0 Hz), 30.6 (d, *J* = 140.9 Hz), 16.6 (d, *J* = 6.0 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.8.

**HRMS** (ESI) calcd for $C_{21}H_{28}NNaO_6P[M+Na]^+$: 444.1546. Found: 444.1553.

**ethyl 1-((diethoxyphosphoryl) methyl)-6-methyl-2,3-dihydro-1*H*-pyrrolizine-5-carboxylate (3za)**



Yellow liquid, 34.1 mg, 50% yield.

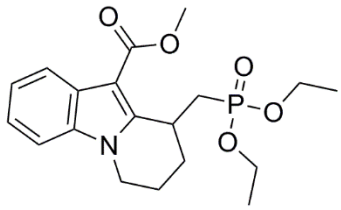
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 5.80 (s, 1H), 4.37 (ddd, *J* = 12.2, 8.6, 3.7 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.19 – 4.05 (m, 5H), 3.51 – 3.39 (m, 1H), 2.81 – 2.71 (m, 1H), 2.33 (s, 3H), 2.32 – 2.16 (m, 2H), 1.94 – 1.83 (m, 1H), 1.37 – 1.32 (m, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 161.9, 144.5 (d, *J* = 19.3 Hz), 133.5, 115.7, 103.4, 61.9 (d, *J* = 6.3 Hz), 61.8 (d, *J* = 6.5 Hz), 59.5, 47.9, 34.9 (d, *J* = 4.8 Hz), 32.5 (d, *J* = 3.7 Hz), 30.8 (d, *J* = 140.4 Hz), 16.6 (d, *J* = 5.7 Hz), 14.7, 14.2.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{16}H_{26}NNaO_5P[M+Na]^+$: 366.1441. Found: 366.1444.

**diethyl ((10-acetyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-9-yl) methyl) phosphonate (5aa)**



Yellow liquid, 49.8 mg, 60% yield.

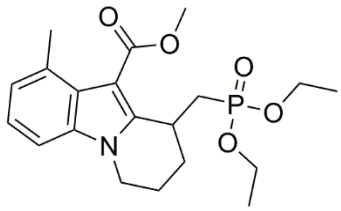
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 8.19 – 8.08 (m, 1H), 7.32 – 7.22 (m, 3H), 4.29 (ddd, *J* = 12.2, 5.7, 1.3 Hz, 1H), 4.26 – 4.09 (m, 5H), 3.93 (s, 3H), 3.87 (td, *J* = 12.0, 5.6 Hz, 1H), 2.60 – 2.46 (m, 2H), 2.31 – 2.15 (m, 1H), 2.16 – 2.04 (m, 2H), 1.94 – 1.84 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 148.4 (d, *J* = 22.7 Hz), 135.9, 126.7, 122.4, 122.3, 121.6, 109.3, 102.3, 62.0 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.4 Hz), 50.9, 42.7, 29.9, 28.5 (d, *J* = 1.7 Hz), 23.6, 17.7, 16.7 (d, *J* = 6.1 Hz), 16.6 (d, *J* = 6.2 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.0.

**HRMS** (ESI) calcd for $C_{19}H_{26}NNaO_5P[M+Na]^+$: 402.1441. Found: 402.1430.

**methyl 9-((diethoxyphosphoryl)methyl)-1-methyl-6,7,8,9-tetrahydropyrido [1,2-*a*]indole-10-carboxylate (5ba)**



Yellow liquid, 52.0 mg, 52% yield.

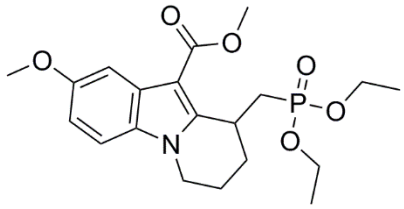
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 2H), 7.06 – 6.98 (m, 1H), 4.30 – 4.04 (m, 6H), 3.91 (s, 3H), 3.82 (td, *J* = 12.0, 5.8 Hz, 1H), 2.69 (s, 3H), 2.55 – 2.42 (m, 2H), 2.30 – 2.05 (m, 3H), 1.94 – 1.82 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.9, 146.8 (d, *J* = 22.6 Hz), 136.6, 131.8, 125.1, 124.7, 122.4, 107.1, 103.9, 61.9 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.6 Hz), 51.0, 42.7, 30.0 (d, *J* = 136.1 Hz), 28.5, 23.8, 22.5, 17.5, 16.7 (d, *J* = 6.5 Hz), 16.6 (d, *J* = 6.5 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{20}H_{28}NNaO_5P[M+Na]^+$: 416.1597. Found: 416.1602.

**methyl 9-((diethoxyphosphoryl)methyl)-2-methoxy-6,7,8,9-tetrahydro pyrido[1,2-*a*]indole-10-Carboxylate (5ca)**



Yellow liquid, 34.2 mg, 41% yield.

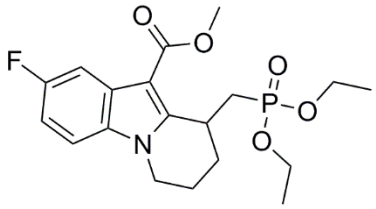
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.5 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.27 – 4.08 (m, 6H), 3.93 (s, 3H), 3.89 (s, 3H), 3.84 (td, *J* = 12.0, 5.6 Hz, 1H), 2.58 – 2.43 (m, 2H), 2.27 – 2.15 (m, 1H), 2.14 – 2.02 (m, 2H), 1.93 – 1.82 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.7, 156.2, 148.3 (d, *J* = 22.4 Hz), 131.0, 127.6, 112.2, 110.0, 103.5, 101.9, 61.9 (d, *J* = 6.8 Hz), 61.7 (d, *J* = 6.5 Hz), 55.9, 50.9, 42.7, 29.3 (d, *J* = 136.2 Hz), 28.6 (d, *J* = 1.2 Hz), 23.5, 17.7, 16.7 (d, *J* = 6.4 Hz), 16.6 (d, *J* = 6.4 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{20}H_{28}NNaO_6P[M+Na]^+$: 432.1546. Found: 432.1552.

**Methyl 9-((diethoxyphosphoryl)methyl)-2-fluoro-6,7,8,9-tetrahydropyrido [1,2-*a*]indole-10-carboxylate (5da)**



Yellow liquid, 52.1 mg, 66% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 10.0, 2.6 Hz, 1H), 7.19 (dd, *J* = 8.9, 4.3 Hz, 1H), 6.96 (td, *J* = 9.0, 2.6 Hz, 1H), 4.28 – 4.08 (m, 6H), 3.92 (s, 3H), 3.85 (td, *J* = 11.9, 5.5 Hz, 1H), 2.58 – 2.46 (m, 2H), 2.28 – 2.16 (m, 1H), 2.15 – 2.03 (m, 2H), 1.93 – 1.83 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

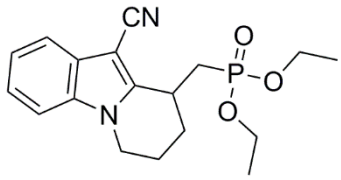
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.3, 159.6 (d, *J* = 236.6 Hz), 149.5 (d, *J* = 22.5 Hz), 132.4, 127.4 (d, *J* = 11.2 Hz), 110.5 (d, *J* = 26.3 Hz), 110.0 (d, *J* = 9.9 Hz), 107.0 (d, *J* = 25.3 Hz), 102.4 (d, *J* = 4.3 Hz), 62.0 (d, *J* = 6.5 Hz), 61.7 (d, *J* = 6.5 Hz), 50.9, 42.8, 29.1 (d, *J* = 136.5 Hz), 28.5 (d, *J* = 1.5 Hz), 23.4, 17.6, 16.6 (d, *J* = 6.0 Hz), 16.5 (d, *J* = 6.2 Hz).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −121.2.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.8.

**HRMS** (ESI) calcd for $C_{19}H_{25}FNNaO_5P[M+Na]^+$: 420.1347. Found: 420.1349.

**diethyl ((10-cyano-6,7,8,9-tetrahydropyrido[1,2-*a*]indol-9-yl)methyl) phosphonate (5ea)**




Yellow liquid, 34.0 mg, 47% yield.

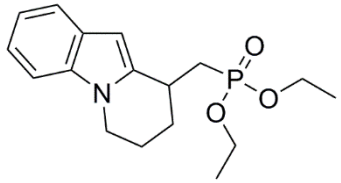
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 1H), 7.35 – 7.30 (m, 1H), 7.31 – 7.22 (m, 2H), 4.25 – 4.09 (m, 5H), 4.07 – 4.00 (m, 1H), 3.79 – 3.65 (m, 1H), 2.74 – 2.63 (m, 1H), 2.30 – 2.14 (m, 4H), 2.12 – 2.02 (m, 1H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 148.2 (d, *J* = 21.5 Hz), 135.2, 127.6, 123.2, 122.5, 119.1, 116.4, 109.9, 82.5, 62.2 (d, *J* = 6.7 Hz), 62.0 (d, *J* = 6.5 Hz), 42.8, 30.1 (d, *J* = 138.5 Hz), 29.3 (d, *J* = 2.1 Hz), 25.3 (d, *J* = 1.6 Hz), 19.8, 16.6 (d, *J* = 6.1 Hz), 16.5 (d, *J* = 6.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 27.4.

**HRMS** (ESI) calcd for $C_{18}H_{23}N_2NaO_3P[M+Na]^+$: 369.1339. Found: 369.1343.

**diethyl ((6,7,8,9-tetrahydropyrido[1,2-*a*]indol-9-yl)methyl)phosphonate (5fa)**




Yellow liquid, 38.0 mg, 59% yield.

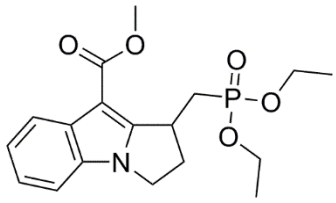
**$^1$H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.50 (m, 1H), 7.29 – 7.23 (m, 1H), 7.19 – 7.13 (m, 1H), 7.12 – 7.06 (m, 1H), 6.31 (s, 1H), 4.24 – 4.07 (m, 5H), 3.88 (td, *J* = 11.1, 5.1 Hz, 1H), 3.47 – 3.34 (m, 1H), 2.56 – 2.38 (m, 2H), 2.27 – 2.17 (m, 1H), 2.10 – 1.97 (m, 2H), 1.69 – 1.57 (m, 1H), 1.36 (td, *J* = 7.1, 1.8 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 140.6 (d, *J* = 21.7 Hz), 136.5, 128.0, 120.9, 120.0, 119.9, 109.0, 97.4, 61.9 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.6 Hz), 42.3, 31.6 (d, *J* = 139.7 Hz), 30.5 (d, *J* = 2.5 Hz), 28.1 (d, *J* = 3.0 Hz), 22.3, 16.64 (d, *J* = 6.1 Hz), 16.63 (d, *J* = 6.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.9.

**HRMS** (ESI) calcd for $C_{17}H_{24}NNaO_3P[M+Na]^+$: 344.1386. Found: 344.1393.

**methyl 1-((diethoxyphosphoryl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*] indole-9-carboxylate (5ga)**



Yellow liquid, 58.3 mg, 80% yield.

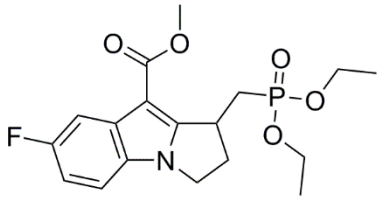
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 8.14 – 8.05 (m, 1H), 7.29 – 7.17 (m, 3H), 4.25 – 4.02 (m, 6H), 4.02 – 3.91 (m, 1H), 3.91 (s, 3H), 2.98 – 2.75 (m, 3H), 2.03 – 1.90 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.6, 154.4 (d, *J* = 20.7 Hz), 132.4, 130.9, 122.3, 122.0, 121.8, 110.1, 99.2, 61.9 (d, *J* = 6.5 Hz), 61.8 (d, *J* = 6.4 Hz), 50.9, 43.7, 33.8 (d, *J* = 3.2 Hz), 32.9, 28.6 (d, *J* = 138.7 Hz), 16.6 (d, *J* = 6.1 Hz), 16.5 (d, *J* = 6.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{18}H_{24}NNaO_5P[M+Na]^+$: 388.1284. Found: 388.1286.

**methyl 1-((diethoxyphosphoryl)methyl)-7-fluoro-2,3-dihydro-1*H*-pyrrolo [1,2-*a*]indole-9-carboxylate (5ha)**



Yellow liquid, 78.5 mg, 71% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 10.1, 2.6 Hz, 1H), 7.17 (dd, *J* = 8.8, 4.4 Hz, 1H), 7.03 – 6.90 (m, 1H), 4.23 – 4.04 (m, 7H), 3.91 (s, 3H), 3.07 – 2.76 (m, 3H), 2.00 (td, *J* = 15.8, 10.8 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H).

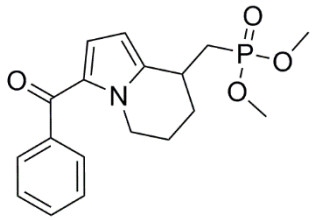
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 165.3, 159.4 (d, *J* = 236.7 Hz), 155.7 (d, *J* = 20.9 Hz), 131.6 (d, *J* = 11.0 Hz), 129.0, 113.1 (d, *J* = 24.3 Hz), 110.8 (d, *J* = 9.8 Hz), 110.6 (d, *J* = 26.4 Hz), 107.4 (d, *J* = 25.2 Hz), 62.0 (d, *J* = 6.8 Hz), 61.8 (d, *J* = 6.3 Hz), 51.0, 44.1, 34.1 (d, *J* = 3.2 Hz), 32.9, 28.6 (d, *J* = 139.4 Hz), 16.6 (d, *J* = 5.9 Hz), 16.5 (d, *J* = 6.2 Hz).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −121.4.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.0.

**HRMS** (ESI) calcd for $C_{18}H_{23}FNNaO_5P[M+Na]^+$: 406.1190. Found: 406.1194.

**dimethyl((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)phosphonate (3ab)**



White solid, 37.7 mg, 54% yield, m.p. = 90.7 – 91.2 ℃.

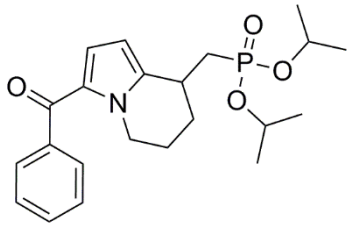
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.54 – 7.49 (m, 1H), 7.46 – 7.41 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.06 (dd, *J* = 4.2, 0.9 Hz, 1H), 4.64 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.30 (ddd, *J* = 14.5, 10.1, 4.9 Hz, 1H), 3.80 (d, *J* = 1.8 Hz, 3H), 3.77 (d, *J* = 1.9 Hz, 3H), 3.38 – 3.27 (m, 1H), 2.42 – 2.28 (m, 2H), 2.18 – 2.09 (m, 1H), 2.06 – 1.88 (m, 2H), 1.71 – 1.57 (m, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.8, 142.1 (d, *J* = 21.5 Hz), 140.5, 131.3, 129.8, 129.2, 128.1, 123.3, 106.3, 52.7 (d, *J* = 6.6 Hz), 52.5 (d, *J* = 6.8 Hz), 46.3, 31.9 (d, *J* = 142.2 Hz), 30.2, 26.9 (d, *J* = 3.2 Hz), 22.3.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 32.0.

**HRMS** (ESI) calcd for $C_{18}H_{23}NO_4P[M+H]^+$: 348.1359. Found: 348.1359.

**diisopropyl((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl) phosphonate (3ac)**



Yellow liquid, 60.7 mg, 75% yield.

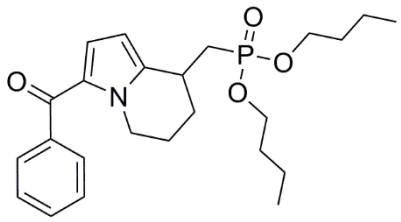
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 2H), 7.54 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.07 (d, *J* = 4.2 Hz, 1H), 4.82 – 4.71 (m, 2H), 4.63 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.30 (ddd, *J* = 14.5, 10.0, 5.0 Hz, 1H), 3.36 – 3.24 (m, 1H), 2.38 – 2.25 (m, 2H), 2.18 – 2.09 (m, 1H), 2.00 – 1.88 (m, 2H), 1.71 – 1.61 (m, 1H), 1.40 – 1.31 (m, 12H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.7 (d, *J* = 21.3 Hz), 140.5, 131.2, 129.7, 129.2, 128.1, 123.4, 106.3, 70.5 (d, *J* = 6.8 Hz), 70.4 (d, *J* = 6.9 Hz), 46.3, 33.3 (d, *J* = 141.0 Hz), 30.5 (d, *J* = 2.7 Hz), 26.9 (d, *J* = 3.0 Hz), 24.3 – 24.2 (m), 22.3.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 27.2.

**HRMS** (ESI) calcd for $C_{22}H_{31}NO_4P[M+H]^+$: 404.1985. Found: 404.1989.

**dibutyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)phosphonate (3ad)**



Yellow solid, 65.7 mg, 76% yield, m.p. = 57.2 – 57.9 ℃.

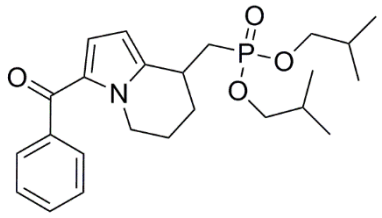
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.54 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.06 (dd, *J* = 4.2, 0.9 Hz, 1H), 4.63 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.30 (ddd, *J* = 14.5, 10.1, 5.0 Hz, 1H), 4.12 – 4.02 (m, 4H), 3.38 – 3.26 (m, 1H), 2.40 – 2.28 (m, 2H), 2.18 – 2.09 (m, 1H), 2.05 – 1.93 (m, 1H), 1.71 – 1.63 (m, 6H), 1.47 – 1.37 (m, 4H), 0.95 (t, *J* = 7.4 Hz, 6H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.4 (d, *J* = 21.3 Hz), 140.5, 131.2, 129.7, 129.2, 128.1, 123.3, 106.3, 65.7 (d, *J* = 6.7 Hz), 65.5 (d, *J* = 6.9 Hz), 46.3, 32.8 (d, *J* = 1.7 Hz), 32.7 (d, *J* = 1.7 Hz), 31.7 (d, *J* = 139.8 Hz), 30.3 (d, *J* = 2.6 Hz), 26.9 (d, *J* = 2.9 Hz), 22.3, 18.9, 13.8.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.3.

**HRMS** (ESI) calcd for $C_{24}H_{34}NNaO_4P[M+Na]^+$: 454.2118. Found: 454.2103.

**diisobutyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ae)**



Yellow liquid, 53.6 mg, 62% yield.

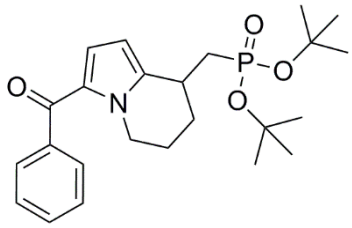
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 6.71 (d, *J* = 4.2 Hz, 1H), 6.07 (d, *J* = 4.2 Hz, 1H), 4.63 (dt, *J* = 14.1, 4.9 Hz, 1H), 4.31 (ddd, *J* = 14.5, 10.0, 4.9 Hz, 1H), 3.90 – 3.78 (m, 4H), 3.40 – 3.28 (m, 1H), 2.44 – 2.29 (m, 2H), 2.18 – 2.09 (m, 1H), 2.07 – 1.90 (m, 4H), 1.73 – 1.62 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 12H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.4 (d, *J* = 21.1 Hz), 140.5, 131.2, 129.7, 129.1, 128.1, 123.3, 106.3, 71.9 (d, *J* = 7.0 Hz), 71.7 (d, *J* = 7.2 Hz), 46.2, 31.6 (d, *J* = 140.1 Hz), 30.3 (d, *J* = 2.7 Hz), 29.4 (d, *J* = 2.4 Hz), 29.3 (d, *J* = 2.3 Hz), 26.9 (d, *J* = 2.9 Hz), 22.3, 18.9.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 29.1.

**HRMS** (ESI) calcd for $C_{24}H_{34}NNaO_4P[M+Na]^+$: 454.2118. Found: 454.2122.

**di-tert-butyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3af)**



Yellow liquid, 55.5 mg, 64% yield.

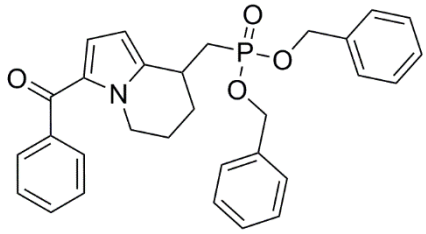
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.55 – 7.46 (m, 1H), 7.47 – 7.38 (m, 2H), 6.71 (d, *J* = 4.1 Hz, 1H), 6.06 (d, *J* = 4.2 Hz, 1H), 4.64 (dt, *J* = 14.1, 4.9 Hz, 1H), 4.30 (ddd, *J* = 14.4, 10.0, 4.9 Hz, 1H), 3.34 – 3.21 (m, 1H), 2.39 – 2.31 (m, 1H), 2.32 – 2.18 (m, 1H), 2.17 – 2.08 (m, 1H), 1.95 – 1.84 (m, 2H), 1.71 – 1.61 (m, 1H), 1.53 (s, 9H), 1.53 (s, 9H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.6, 143.3 (d, *J* = 21.2 Hz), 140.6, 131.1, 129.6, 129.1, 128.1, 123.4, 106.3, 82.3 (d, *J* = 9.0 Hz), 82.2 (d, *J* = 8.6 Hz), 46.3, 36.3 (d, *J* = 144.2 Hz), 31.1 (d, *J* = 3.8 Hz), 30.63 (d, *J* = 1.7 Hz), 30.59 (d, *J* = 1.7 Hz), 26.7 (d, *J* = 3.0 Hz), 22.4.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 20.7.

**HRMS** (ESI) calcd for $C_{24}H_{34}NNaO_4P[M+Na]^+$: 454.2118. Found: 454.2124.

**dibenzyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (3ag)**



Green liquid, 45.3 mg, 45% yield.

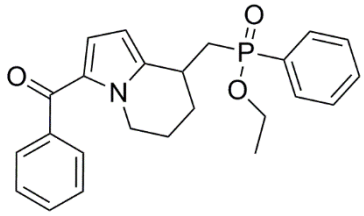
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.75 – 7.71 (m, 2H), 7.52 – 7.47 (m, 1H), 7.44 – 7.39 (m, 2H), 7.38 – 7.31 (m, 10H), 6.66 (d, *J* = 4.2 Hz, 1H), 5.94 (dd, *J* = 4.2, 0.8 Hz, 1H), 5.13 – 5.05 (m, 2H), 5.02 – 4.95 (m, 2H), 4.58 (dt, *J* = 14.0, 4.8 Hz, 1H), 4.24 (ddd, *J* = 14.4, 10.0, 4.9 Hz, 1H), 3.33 – 3.18 (m, 1H), 2.32 (ddd, *J* = 19.5, 15.5, 3.6 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.08 – 1.93 (m, 2H), 1.89 – 1.77 (m, 1H), 1.64 – 1.54 (m, 1H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.1 (d, *J* = 21.3 Hz), 140.4, 136.3 (d, *J* = 5.8 Hz), 131.2, 129.7, 129.1, 128.8, 128.7 (d, *J* = 1.8 Hz), 128.2 (d, *J* = 2.3 Hz), 128.1, 123.3, 106.3, 67.6 (d, *J* = 6.5 Hz), 67.4 (d, *J* = 6.6 Hz), 46.2, 32.3 (d, *J* = 139.4 Hz), 30.1 (d, *J* = 2.5 Hz), 26.8 (d, *J* = 3.3 Hz), 22.2.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 30.6.

**HRMS** (ESI) calcd for $C_{30}H_{30}NNaO_4P[M+Na]^+$: 522.1805. Found: 522.1821.

**ethyl ((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl) methyl) (phenyl) phosphinate (3aj)**



Yellow liquid, 39.8 mg, 47% yield, dr = 1:1.

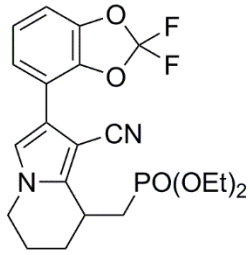
**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.93 – 7.67 (m, 4H), 7.65 – 7.36 (m, 6H), 6.69 (d, *J* = 4.2 Hz, 0.5H), 6.64 (d, *J* = 4.1 Hz, 0.5H), 6.08 (d, *J* = 4.2 Hz, 0.5H), 5.90 (d, *J* = 4.2 Hz, 0.5H), 4.79 – 4.42 (m, 1H), 4.37 – 4.18 (m, 1H), 4.17 – 4.04 (m, 1H), 3.93 – 3.78 (m, 1H), 3.52 – 3.20 (m, 1H), 2.61 – 1.68 (m, 6H), 1.33 – 1.29 (m, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 185.7, 142.6, 142.4, 140.50, 140.47, 132.61, 132.59, 132.6, 131.7, 131.6, 131.2, 129.7, 129.1, 129.02, 128.99, 128.89, 128.87, 128.1, 123.33, 123.27, 106.5, 106.2, 60.91, 60.85, 46.3, 46.2, 36.3, 35.4, 29.9, 29.8, 29.7, 29.6, 27.3, 27.1, 22.24, 22.21, 16.63, 16.61, 16.56, 16.5.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 42.7, 42.0.

**HRMS** (ESI) calcd for $C_{24}H_{26}NNaO_3P[M+Na]^+$: 430.1543. Found: 430.1548.

**diethyl((1-cyano-2-(2,2-difluorobenzo[*d*][1,3]dioxol-4-yl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (7aa)**



Yellow solid, 49.6 mg, 54% yield, m.p. = 119.6 – 120.1 ℃

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.12 (t, *J* = 8.1 Hz, 1H), 7.00 (s, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.24 – 4.08 (m, 4H), 4.06 – 3.92 (m, 2H), 3.63 – 3.53 (m, 1H), 2.65 – 2.53 (m, 1H), 2.21 – 2.06 (m, 4H), 2.00 – 1.92 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H).

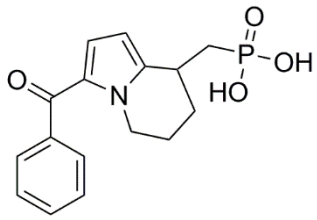
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 143.9, 142.3 (d, *J* = 21.5 Hz), 139.9, 131.5 (t, *J* = 254.7 Hz), 124.1, 121.4, 120.9, 118.2, 116.8, 116.7, 107.8, 87.8, 62.2 (d, *J* = 6.8 Hz), 62.0 (d, *J* = 6.6 Hz), 46.2, 30.1 (d, *J* = 137.8 Hz), 28.3 (d, *J* = 2.1 Hz), 25.4, 20.1, 16.6 (d, *J* = 4.3 Hz), 16.5 (d, *J* = 4.2 Hz).

**$^{19}$F NMR** (376 MHz, Chloroform-*d*) δ −49.5.

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 27.6.

**HRMS** (ESI) calcd for $C_{21}H_{23}F_2N_2NaO_5P[M+Na]^+$: 475.1205. Found: 475.1206.

**((3-benzoyl-5,6,7,8-tetrahydroindolizin-8-yl)methyl)phosphonic acid (8aa)**



Grey solid, 45.9 mg, 29% yield, m.p. = 79.2 – 80.0 ℃.

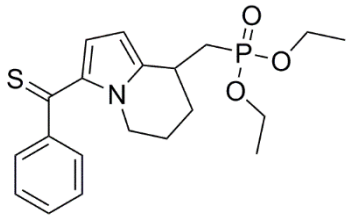
**$^{1}$H NMR** (400 MHz, Methanol-$d_4$) δ 7.72 – 7.64 (m, 2H), 7.56 – 7.51 (m, 1H), 7.48 – 7.41 (m, 2H), 6.68 (d, *J* = 4.1 Hz, 1H), 6.16 (d, *J* = 4.2 Hz, 1H), 4.57 (dt, *J* = 14.1, 4.8 Hz, 1H), 4.25 (ddd, *J* = 14.3, 9.8, 4.8 Hz, 1H), 3.36 – 3.24 (m, 1H), 2.44 – 2.25 (m, 2H), 2.18 – 2.08 (m, 1H), 2.02 – 1.84 (m, 2H), 1.74 – 1.62 (m, 1H).

**$^{13}$C NMR** (101 MHz, Methanol-$d_4$) δ 187.4, 145.3 (d, *J* = 20.6 Hz), 141.7, 132.3, 130.6, 129.9, 129.1, 125.4, 107.9, 47.4, 34.1 (d, *J* = 137.2 Hz), 31.8, 27.8, 23.1.

**$^{31}$P NMR** (162 MHz, Methanol-$d_4$) δ 26.8.

**HRMS** (ESI) calcd for $C_{16}H_{19}NO_4P[M+H]^+$: 320.1046. Found: 320.1048.

**diethyl ((3-(phenylcarbonothioyl)-5,6,7,8-tetrahydroindolizin-8-yl) methyl) phosphonate (9aa)**



Yellow liquid, 131.9 mg, 73% yield.

**$^{1}$H NMR** (400 MHz, Chloroform-*d*) δ 7.52 – 7.43 (m, 2H), 7.36 – 7.30 (m, 1H), 7.26 – 7.19 (m, 2H), 6.49 (d, *J* = 4.3 Hz, 1H), 6.03 (d, *J* = 4.4 Hz, 1H), 4.61 (dt, *J* = 14.1, 4.7 Hz, 1H), 4.34 (ddd, *J* = 14.4, 9.9, 4.8 Hz, 1H), 4.13 – 3.98 (m, 4H), 3.30 – 3.14 (m, 1H), 2.33 – 2.19 (m, 2H), 2.03 (ddt, *J* = 9.5, 6.6, 2.7 Hz, 1H), 1.97 – 1.85 (m, 1H), 1.84 – 1.73 (m, 1H), 1.65 – 1.51 (m, 1H), 1.27 (t, *J* = 7.0 Hz, 6H).

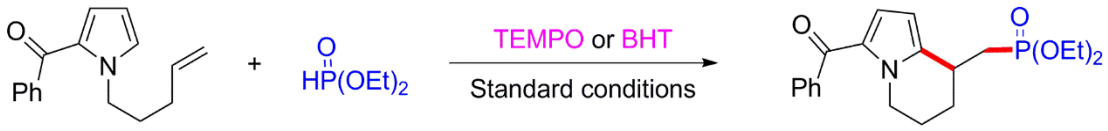
**$^{13}$C NMR** (101 MHz, Chloroform-*d*) δ 212.6, 149.7, 147.2 (d, *J* = 20.2 Hz), 142.9, 129.8, 129.0, 127.5, 123.4, 107.7, 61.9 (d, *J* = 5.2 Hz), 61.7 (d, *J* = 5.6 Hz), 47.8, 31.7 (d, *J* = 138.0 Hz), 30.8, 26.2, 22.2, 16.5 (d, *J* = 4.1 Hz).

**$^{31}$P NMR** (162 MHz, Chloroform-*d*) δ 28.9.

**HRMS** (ESI) calcd for $C_{20}H_{26}NNaO_3PS[M+Na]^+$: 414.1263. Found: 414.1268.

## 6. Mechanistic studies

### 6.1 Radical inhibition experiments




**1a** **2a** **3aa** (ND)

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 0.004 mmol), $Cs_2CO_3$ (130.3 mg, 0.4 mmol) and TEMPO (93.8 mg, 0.6 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **1a** (47.9 mg, 0.2 mmol), **2a** (52 μL, 0.4 mmol) and DTBP (55 μL, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the desired product **3aa** was not detected.

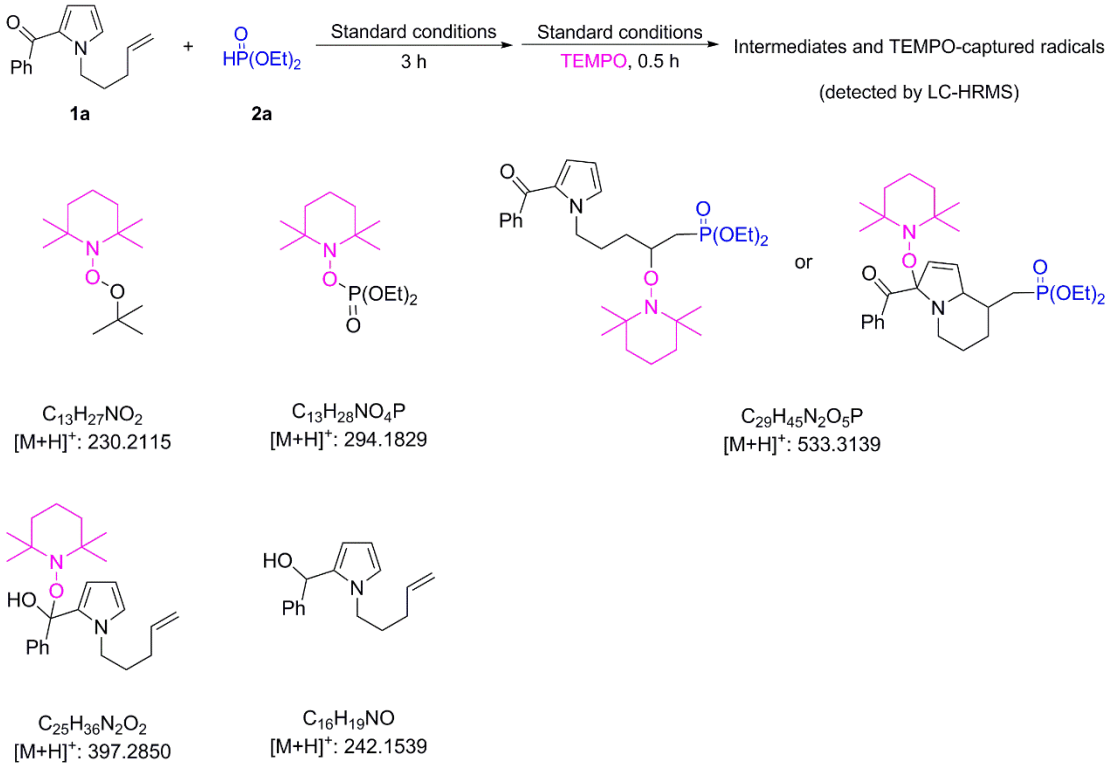
An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 0.004 mmol), $Cs_2CO_3$ (130.3 mg, 0.4 mmol) and BHT (88.1 mg, 0.4 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **1a** (47.9 mg, 0.2 mmol), **2a** (52 μL, 0.4 mmol) and DTBP (55 μL, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the desired product **3aa** was not detected.

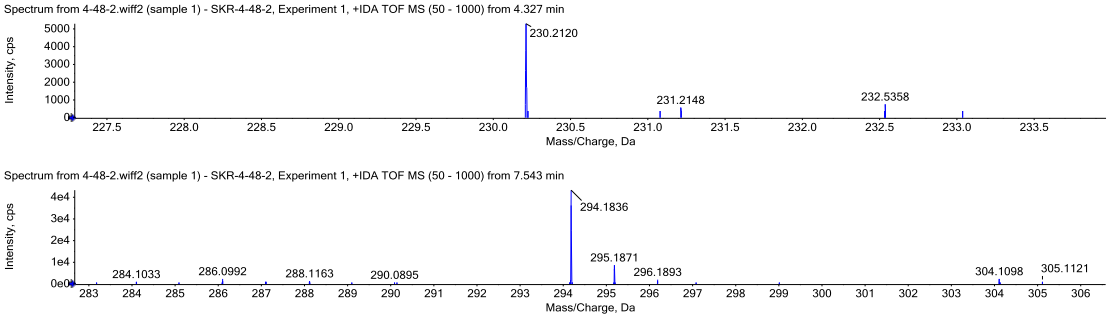
### 6.2 The detection of intermediates with LC-HRMS analysis

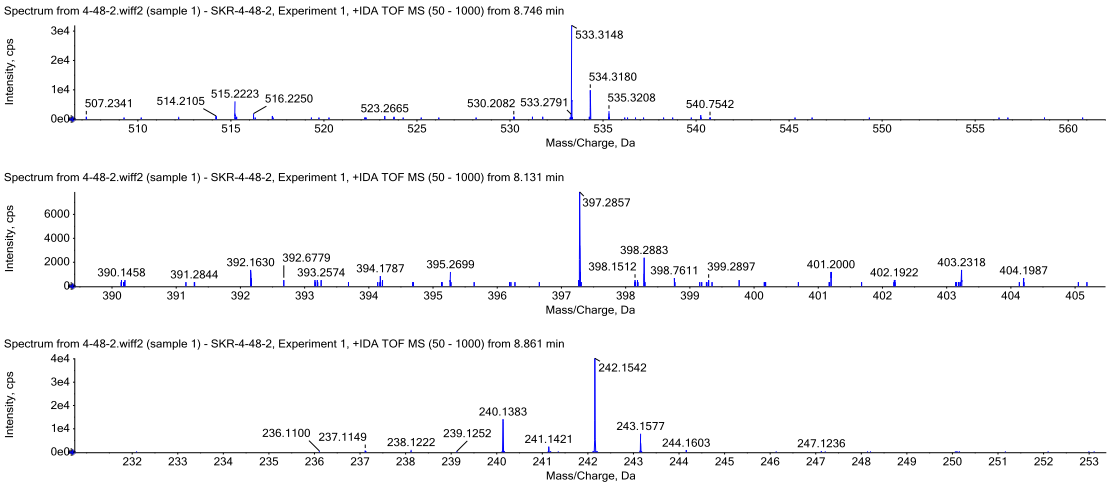
An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 0.004 mmol) and $Cs_2CO_3$ (130.3 mg, 0.4 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **1a** (47.9 mg, 0.2 mmol), **2a** (52 μL, 0.4 mmol) and DTBP (55 μL, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from 30 W blue LEDs and stirred at room temperature for 3 h. Then, TEMPO (31.3 mg, 0.2 mmol) was added under Ar flow. The tube

was placed approximately 2 cm from 30 W blue LEDs and stirred at room temperature for 0.5 h. After completion, the mixture was filtered and analyzed by LC-HRMS.

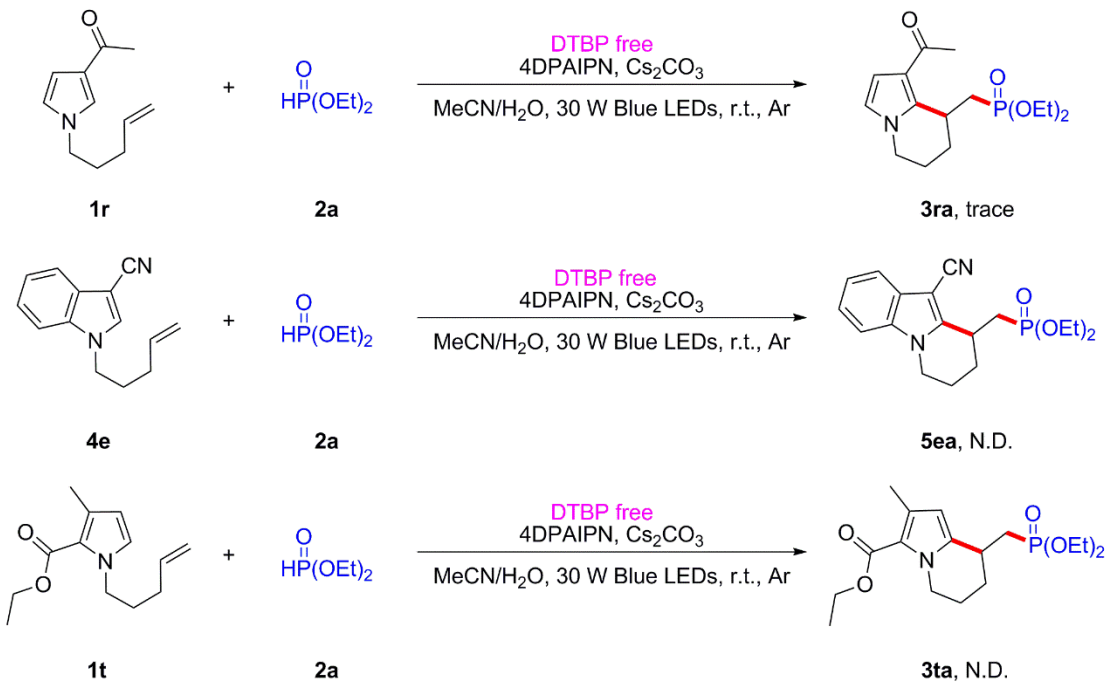
The reaction was analyzed using UPLC (ExionLC$^{TM}$) coupled with QTOF/MS (SCIEX X500R). The mobile phases consisted of (A) 1:1000 (v/v) formic acid: water and (B) acetonitrile. The separation was conducted under the following gradient at a flow rate of 0.3 mL/min: 0 min 5% (B), 1 min 5% (B), 9 min 95% (B), 12 min 95% (B), 12.1 min 5% (B) and 13 min 5% (B). LC-MS analyses were carried out by using the HALO column (C18, 2.1*100 mm, 2.1 μm). The QTOF/MS settings were as follows: sample size, 5 μL; ionization mode, electrospray ionization 4000 V; MS1 scan range, 50-1000 m/z. Proposed structures are shown below.






## 6.3 Control experiments




An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (2 mol%) and $Cs_2CO_3$ (0.4 mmol, 2.0 eq.). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), the substrate **1r**, **4e** or **1t** (0.2 mmol, 1.0 eq.) and **2a** (0.4 mmol, 2 eq.) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was detected by TLC, the desired product **3ra** was detected in trace, **5ea** and **3ta** were not detected in the conditions without DTBP.


**1t** **2a** **3ta**, 60%

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 0.004 mmol) and $Cs_2CO_3$ (130.3 mg, 0.4 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), **1t** (47.9 mg, 0.2 mmol), **2a** (52 μL, 0.4 mmol) and 2-benzoylpyrrole (51.4 mg, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc (1:2) as eluent to afford the desired product **3ta** (42.9 mg, 60% yield).


**1t** **2a** **3ta**, 43% 87%

An oven-dried Schlenk tube (10 mL) equipped with a stirring bar was charged with 4DPAIPN (3.2 mg, 0.004 mmol) and $Cs_2CO_3$ (130.3 mg, 0.4 mmol). The tube was connected to a vacuum line where it was evacuated and back-filled with Ar for three times. Then, dry MeCN (2 mL), $H_2O$ (10 μL), **1t** (47.9 mg, 0.2 mmol), **2a** (52 μL, 0.4 mmol) and benzophenone (54.7 mg, 0.3 mmol) were added under Ar flow. The tube was placed approximately 2 cm from blue LEDs and stirred at room temperature for 12 h. After completion, the mixture was filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel to afford the desired product **3ta** (31.0 mg, 43% yield) and byproduct diphenylmethanol (47.9 mg, 87% yield).

### 6.4 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell under argon at room temperature. All cyclic voltammograms were measured using $Ag/Ag^+$ (0.01 M $AgNO_3$ in MeCN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M

tetrabutylammonium tetrafluoroborate ($^{n}Bu_4NBF_4$) in $CH_3CN$ at a scan rate of 2 V/s or 0.2 V/s; Prior to each measurement, solutions were purged with Ar for 10 minutes to ensure the oxygen-free conditions.

Measuring the $Fc/Fc^+$ redox couple afforded $E_{1/2}$ = +0.07 V vs $Ag/Ag^+$ under our experimental conditions. The obtained value was referenced to $Ag/Ag^+$ and converted to SCE by adding 0.35 V, providing a value of +0.42 V for the $Fc/Fc^+$ couple.[3] The reduction half-peak potential of DTBP in MeCN was measured as −1.33 V (vs $Ag/Ag^+$), and calculated to −0.98 V (vs SCE). The oxidative peak of **2a** was not observed.

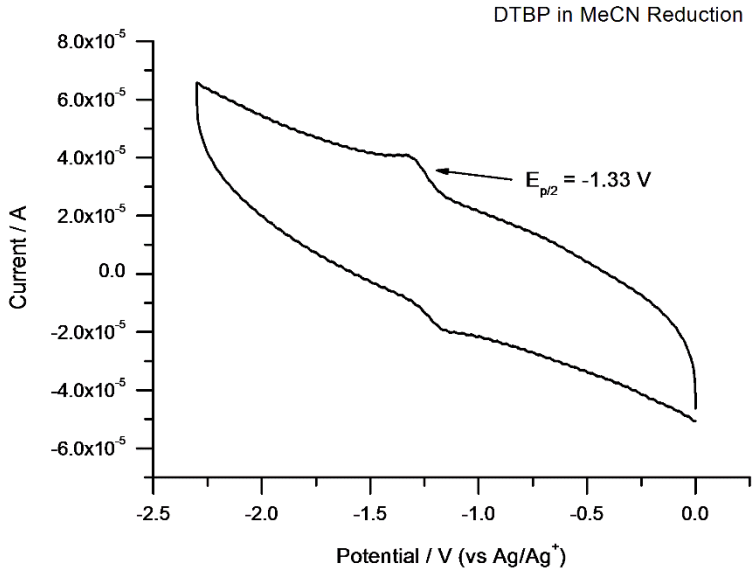



**Figure S2**. Cyclic voltammetry of DTBP (0.05 M) in $CH_3CN$ (vs $Ag/Ag^+$) with $^{n}Bu_4NBF_4$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 2 V/s.

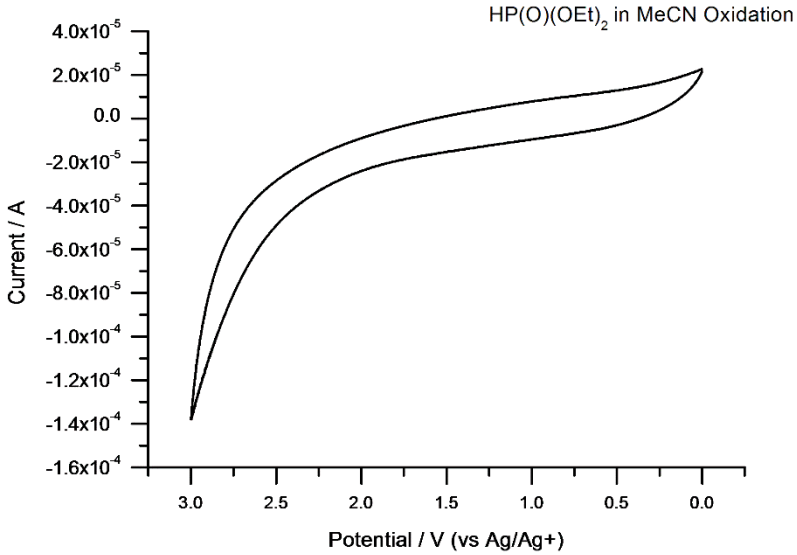



**Figure S3**. Cyclic voltammetry of **2a** (0.05 M) in $CH_3CN$ (vs $Ag/Ag^+$) with $^nBu_4NBF_4$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 0.2 V/s.

## 6.5 The plausible reaction pathway

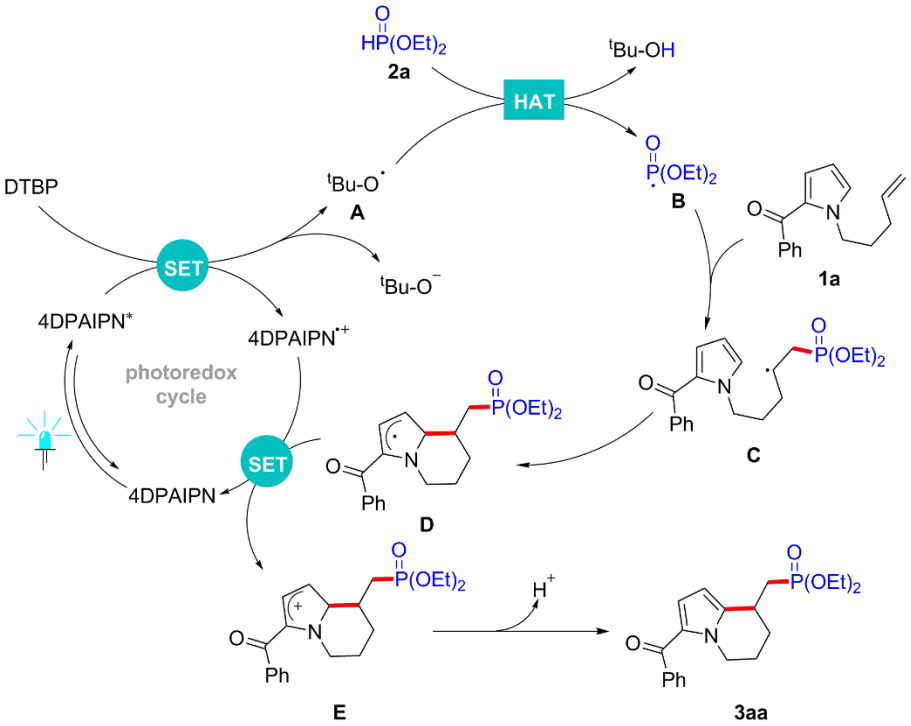



**Figure S4**. The proposed major reaction pathway.

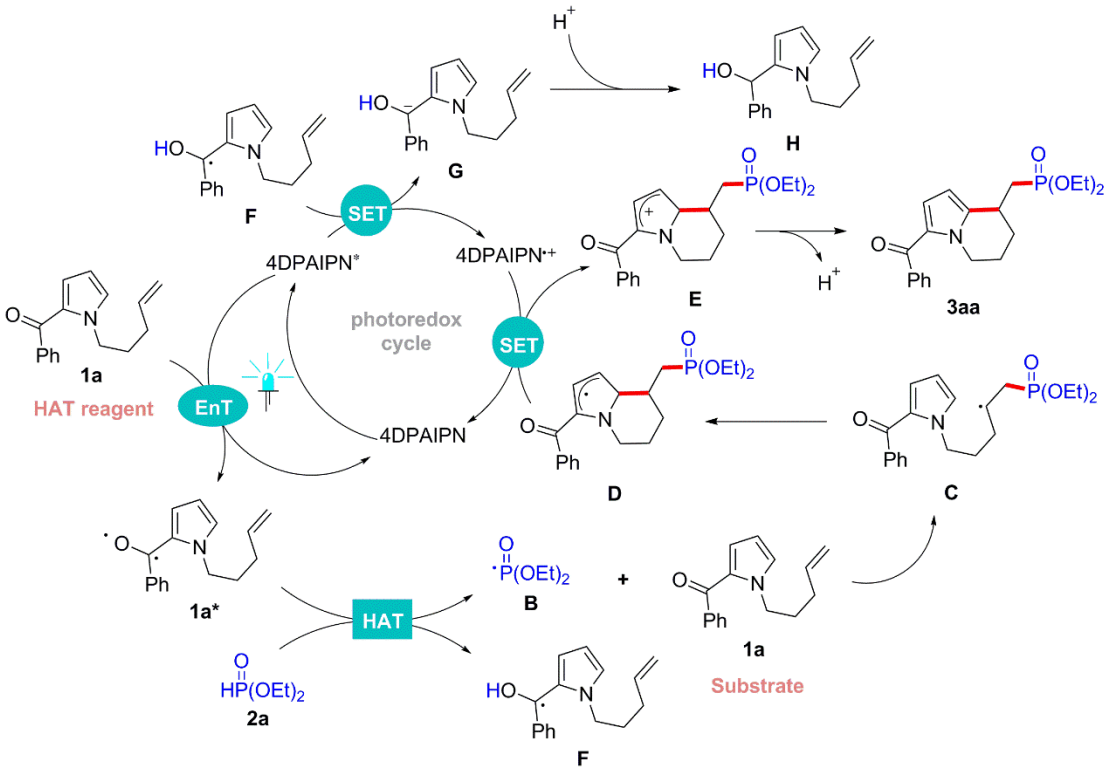


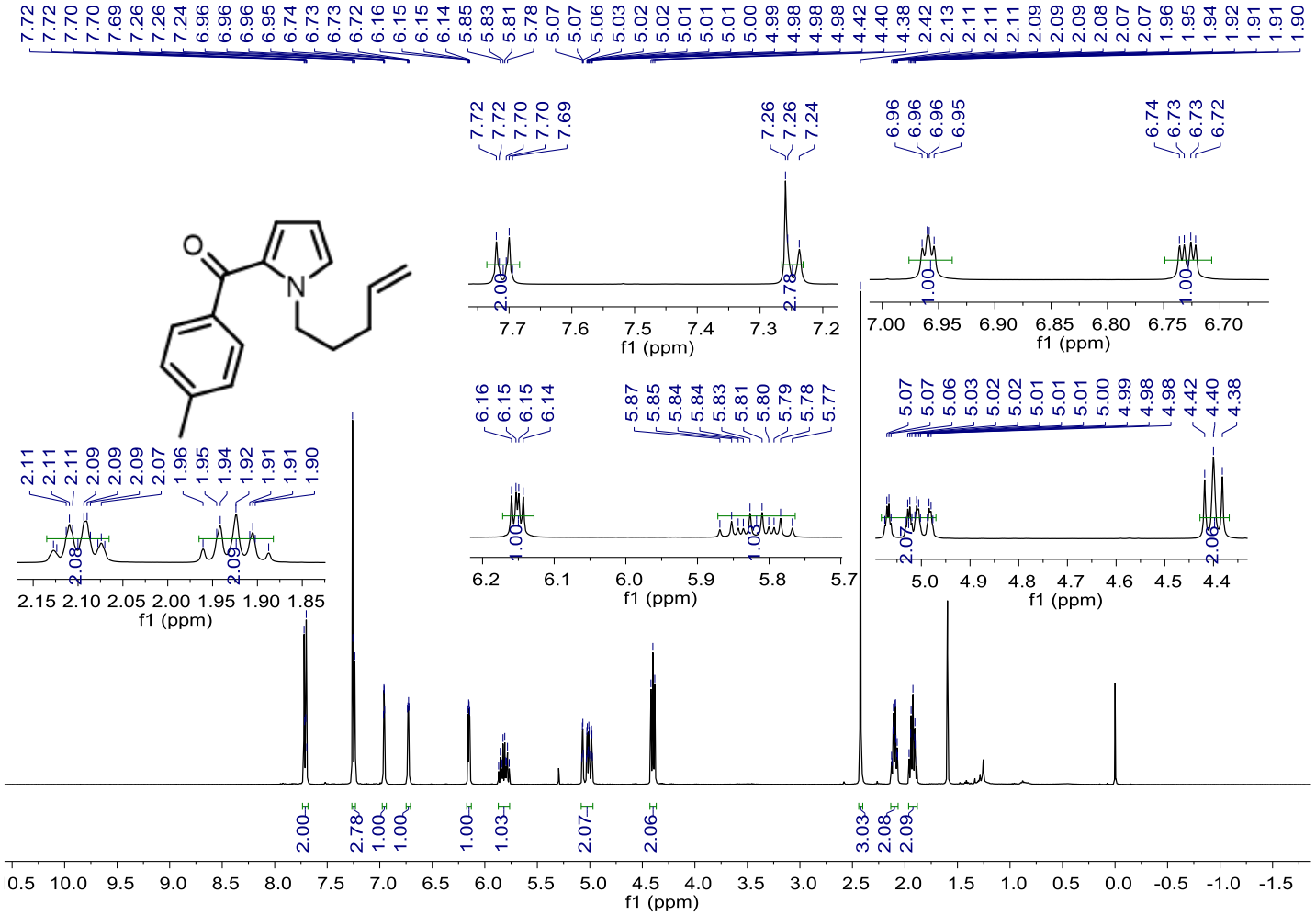

**Figure S5**. The proposed minor reaction pathway.

## 7. Supplementary references

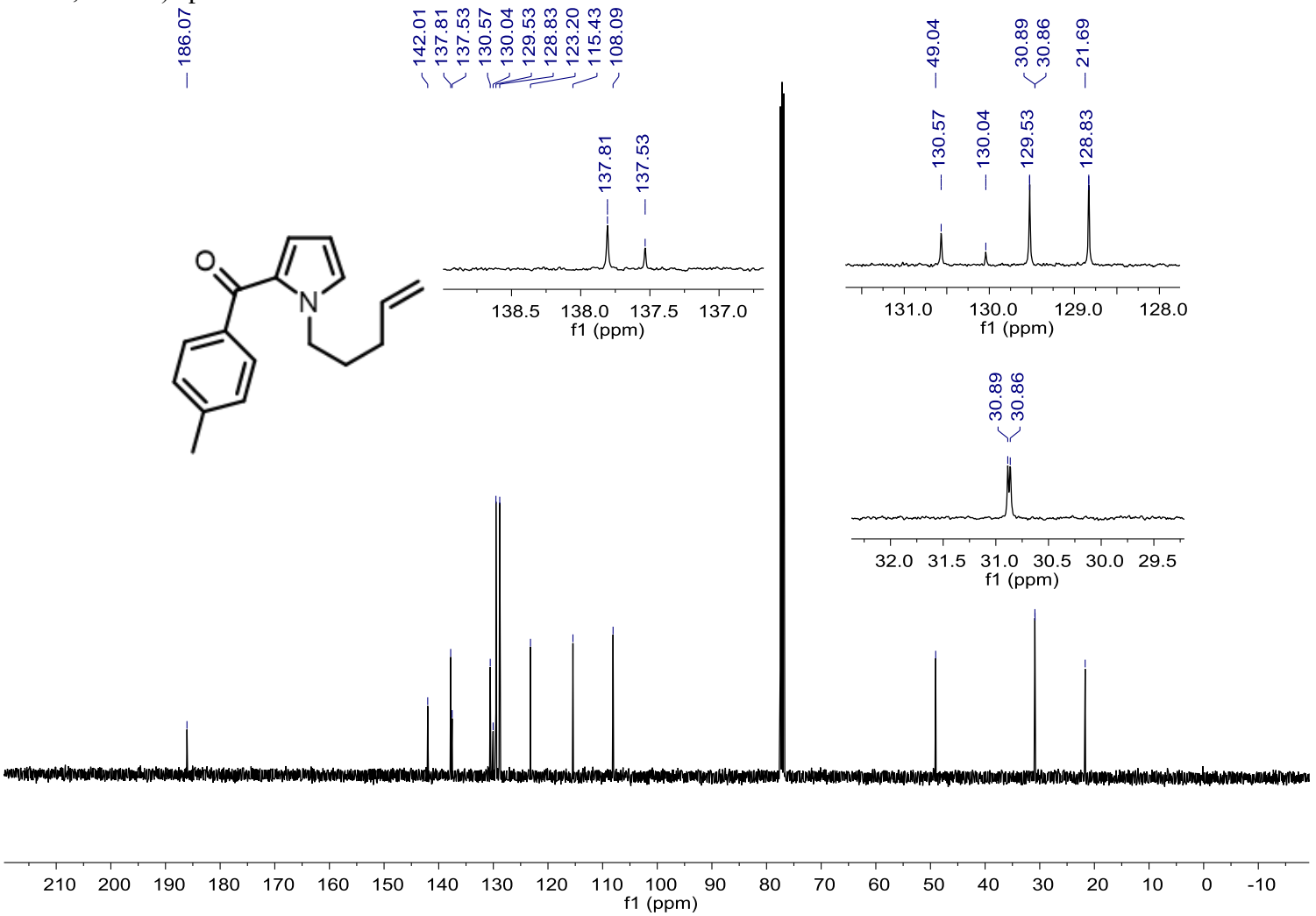

1. M. Milen, T. Foldesi, A. Dancso, G. Simig and B. Volk, *Synlett*, 2015, **26**, 2418-2424.
2. R. Yang, D. Yi, K. R. Shen, Q. Fu, J. Wei, J. Lu, L. Yang, L. Wang, S. P. Wei and Z. J. Zhang, *Org Lett*, 2022, **24**, 2014-2019.
3. H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett*, 2016, **27**, 714-723.

## 8. Copies of NMR spectra for synthesized compounds

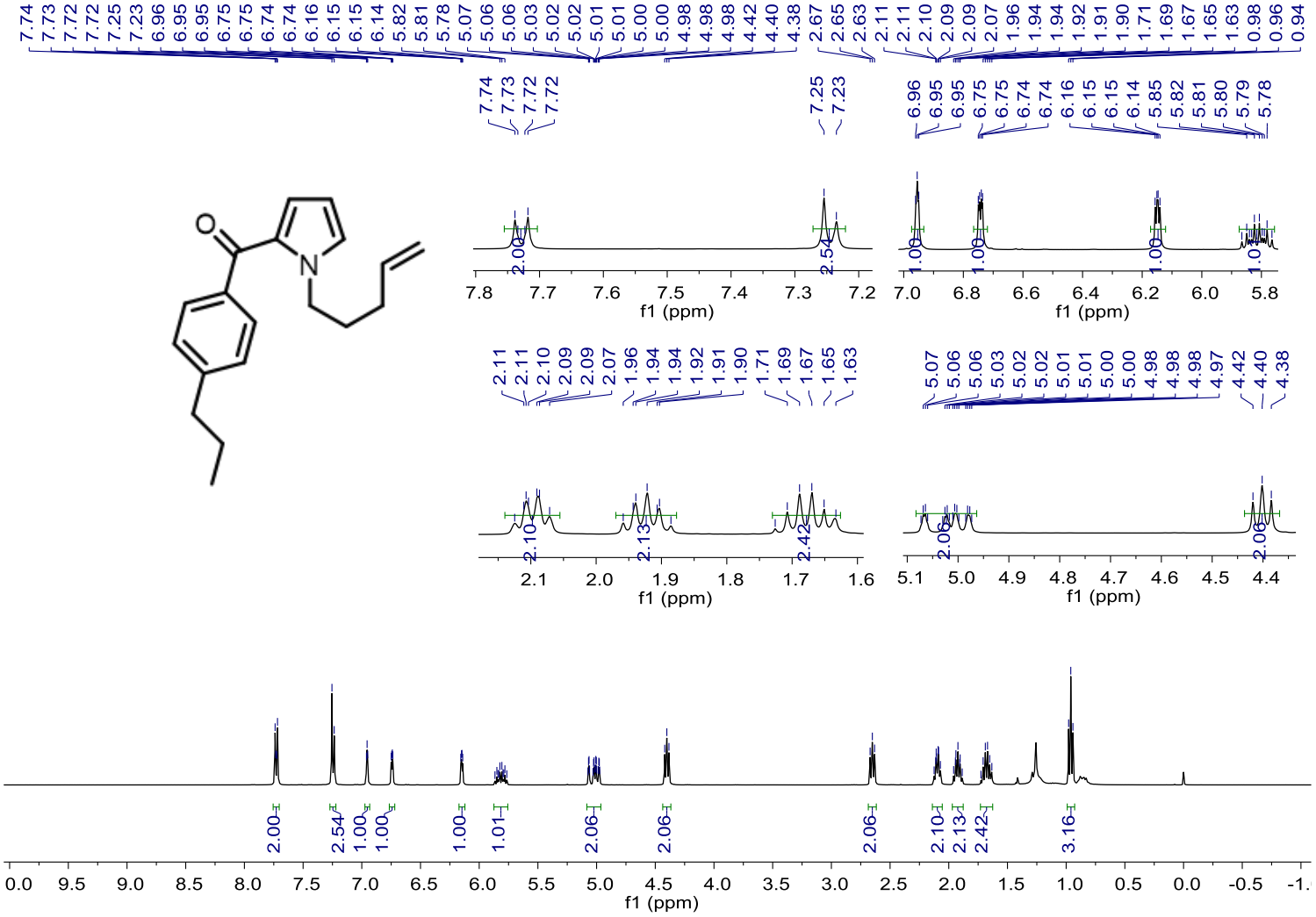
$^1$H NMR (400 MHz, $CDCl_3$) spectrum of **1d**



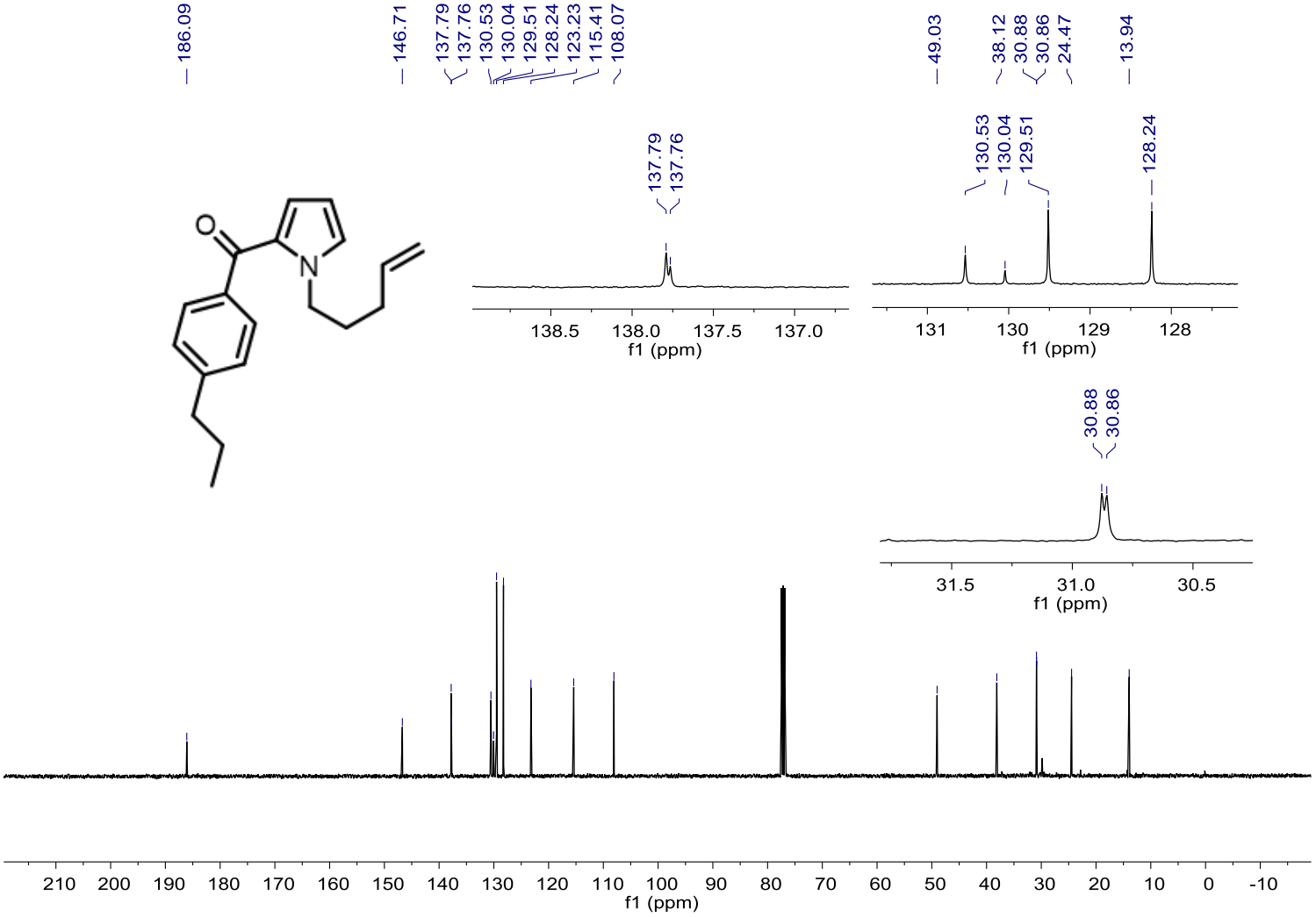
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1d**



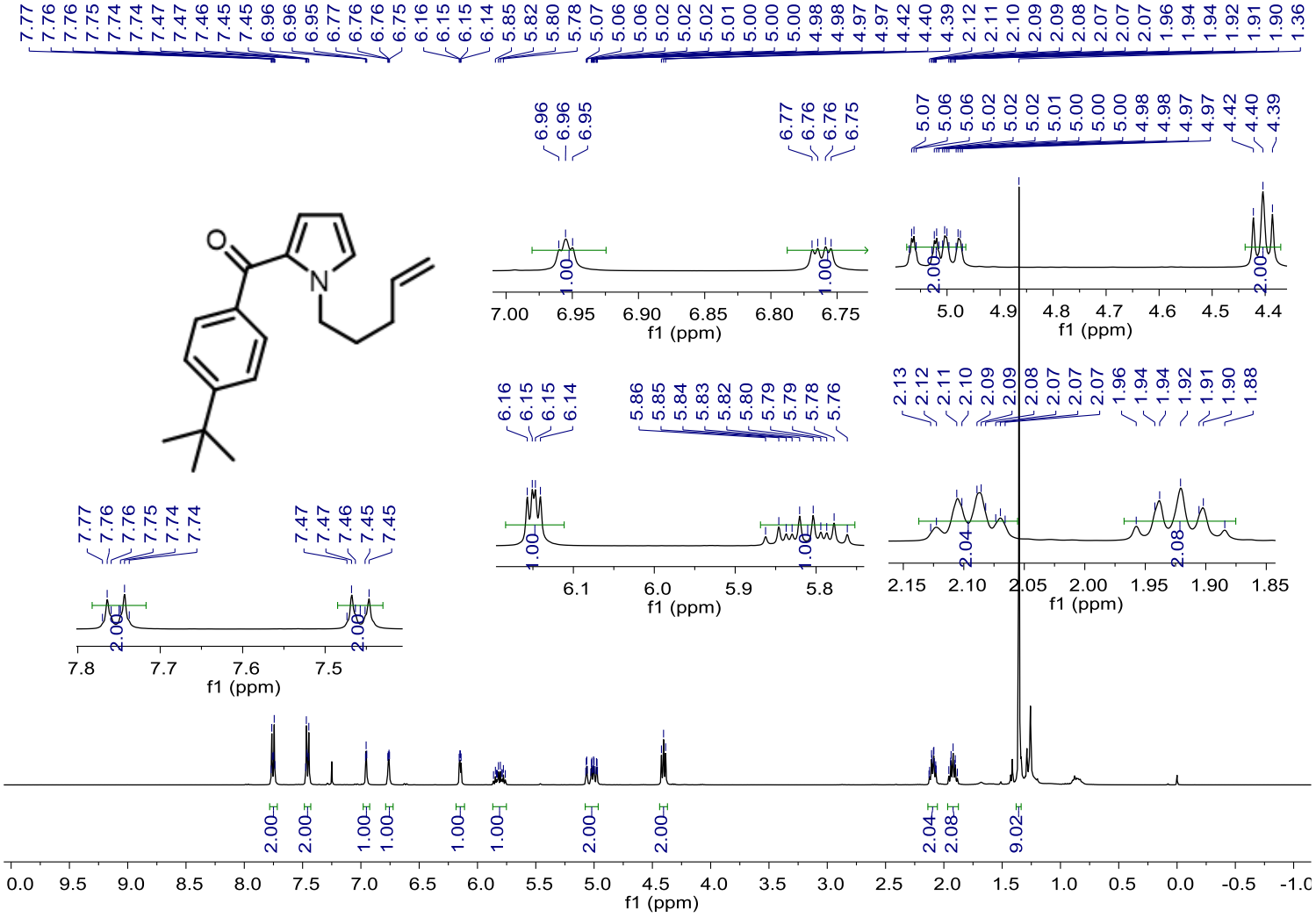
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1e**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1e**



$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1f**



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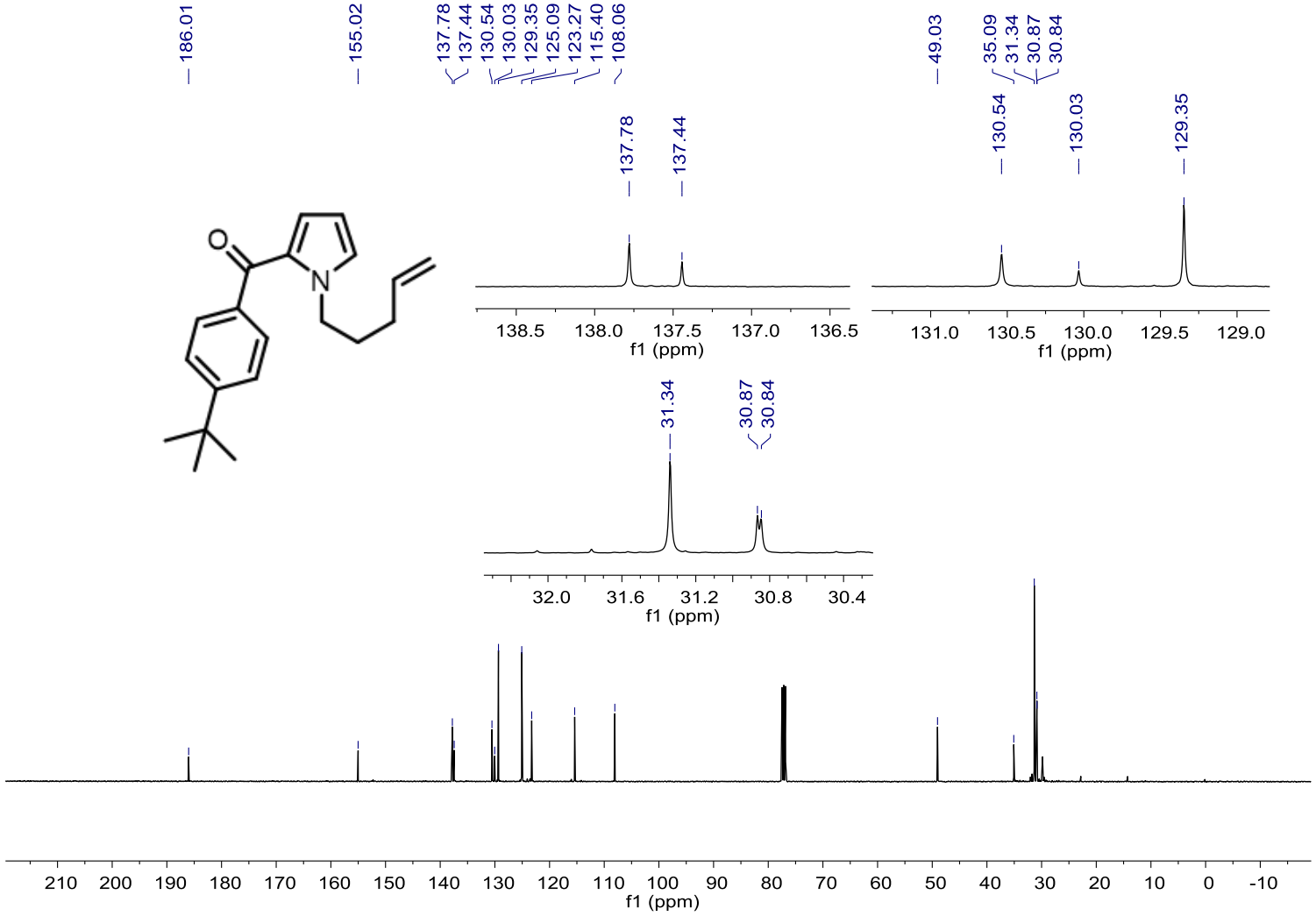
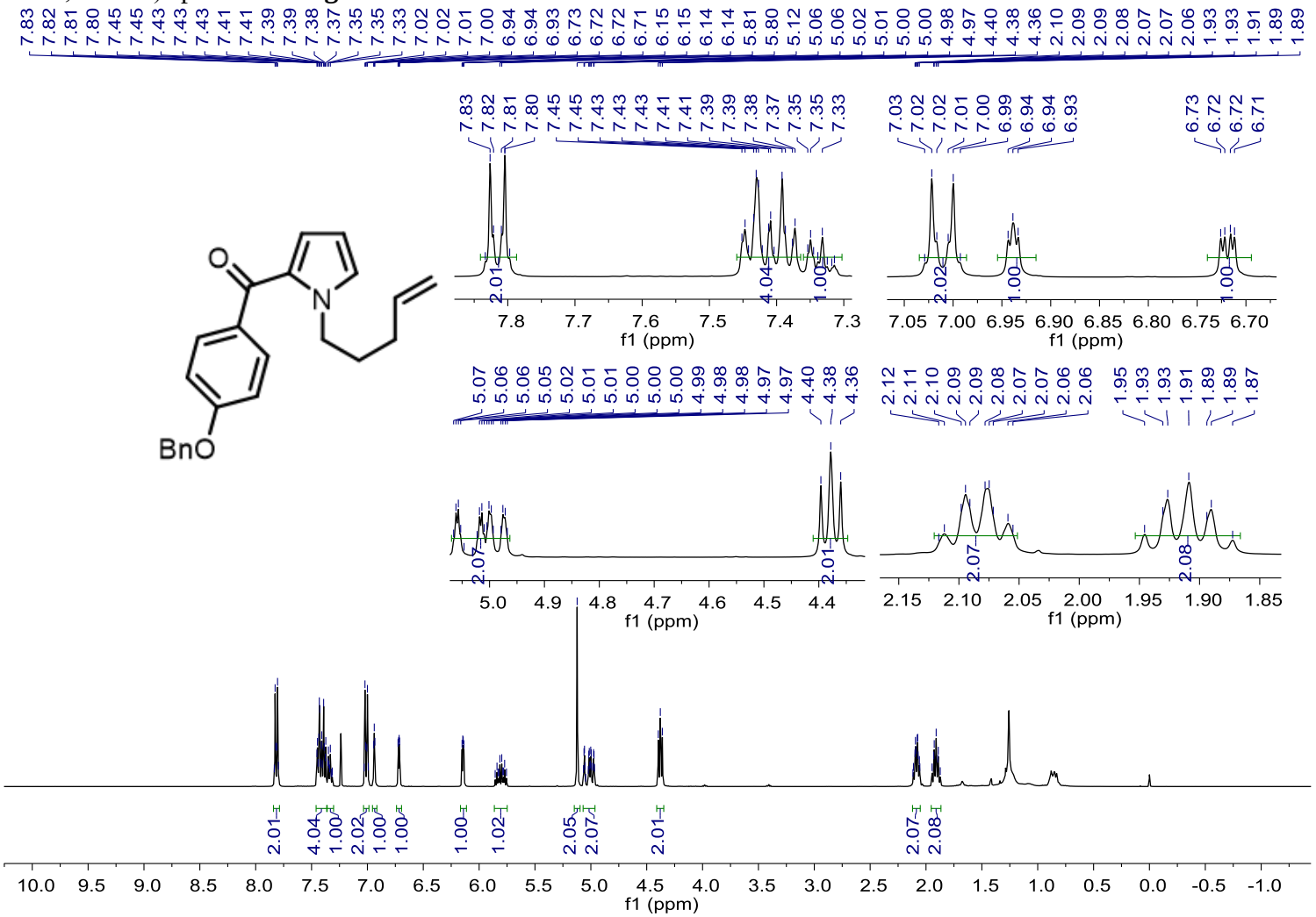
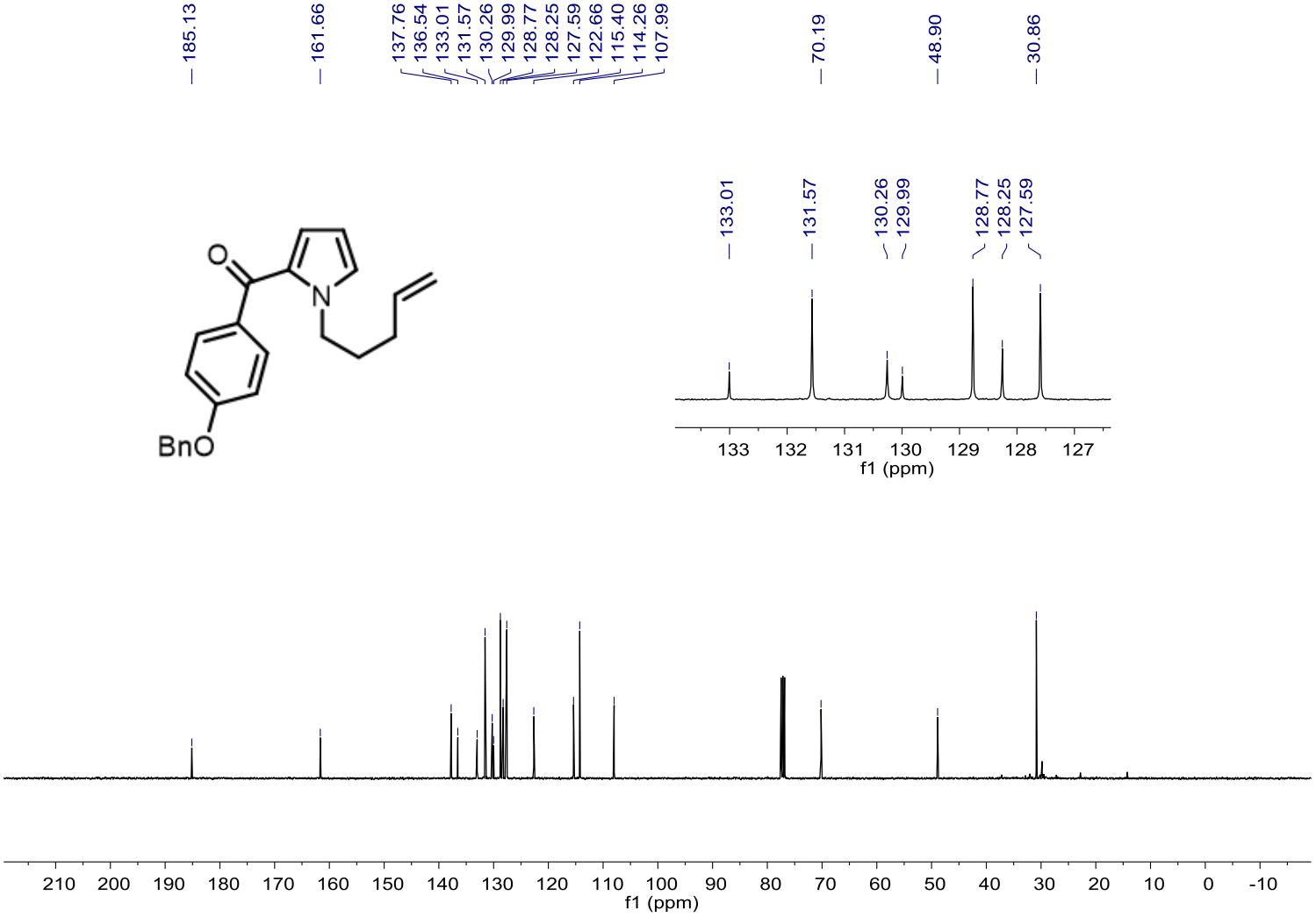


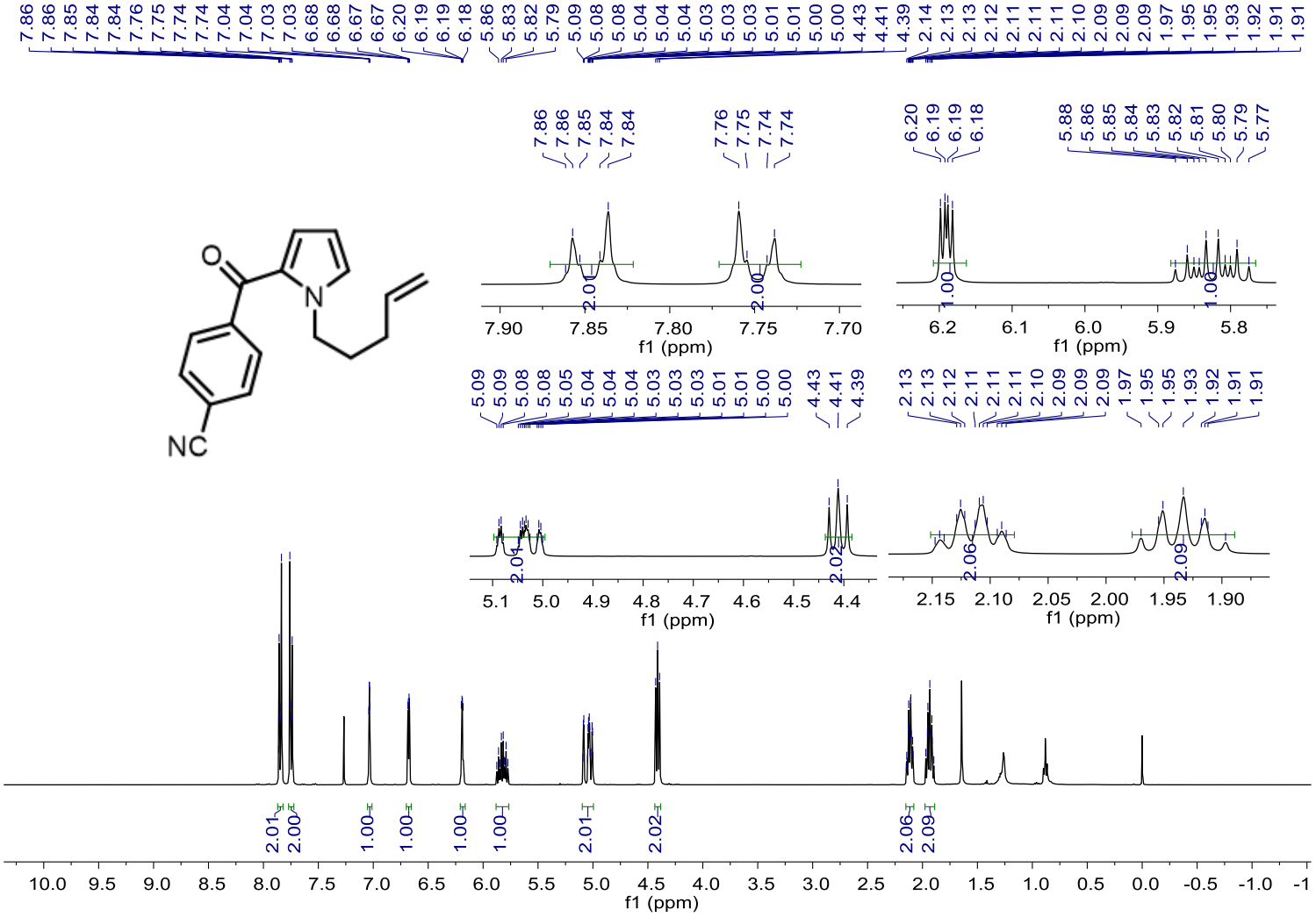
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1g**



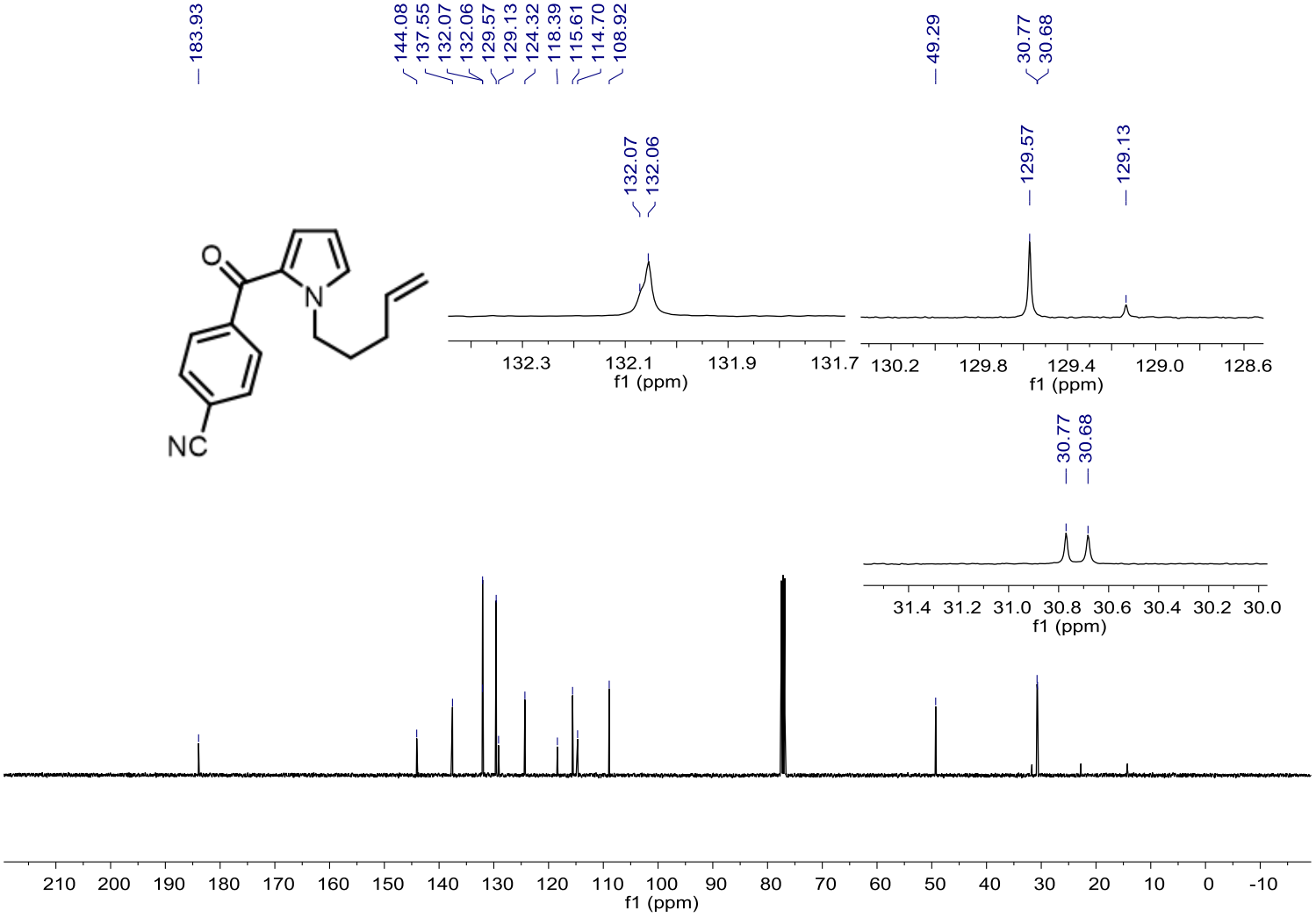
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1g**



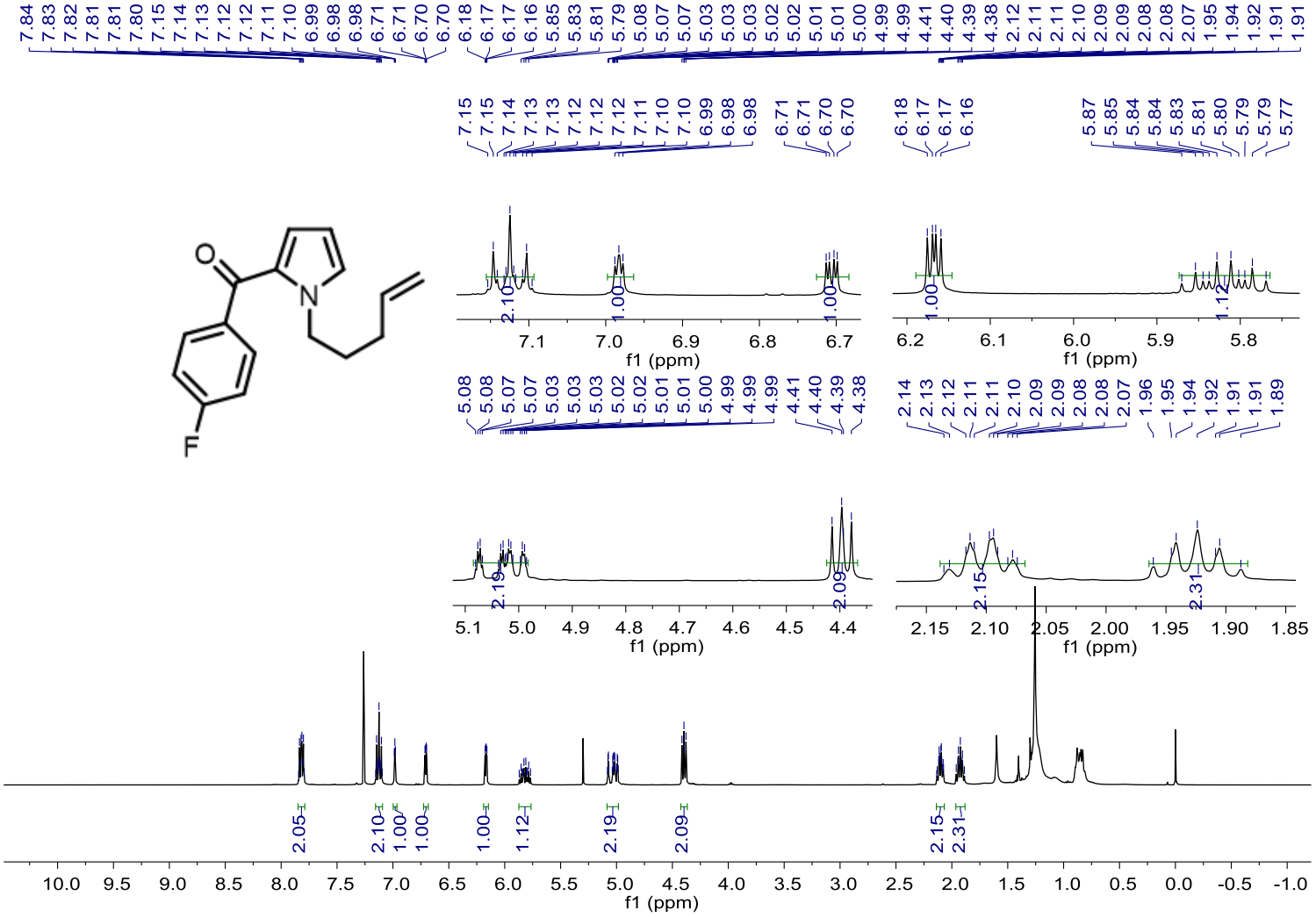
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1h**



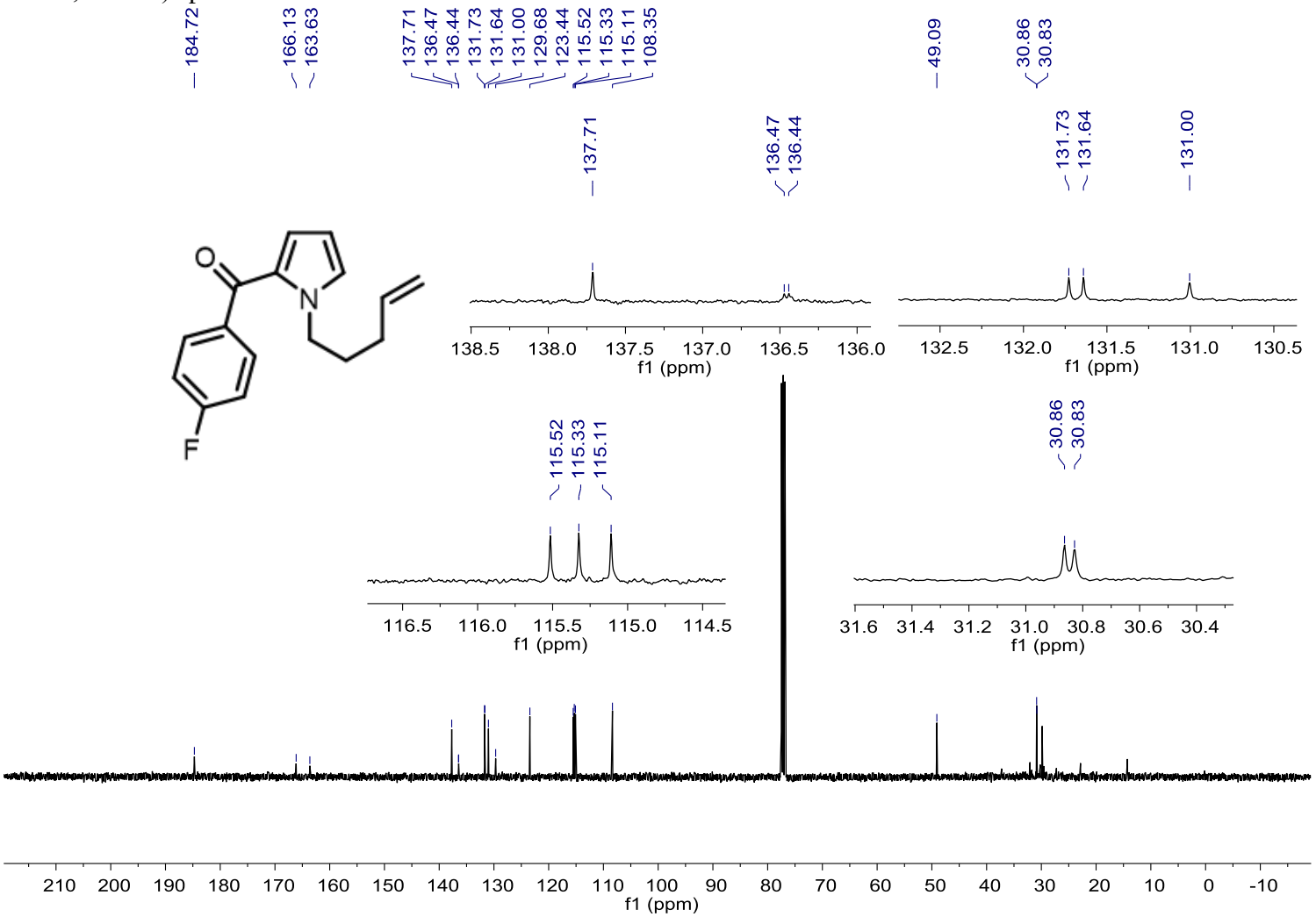
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1h**



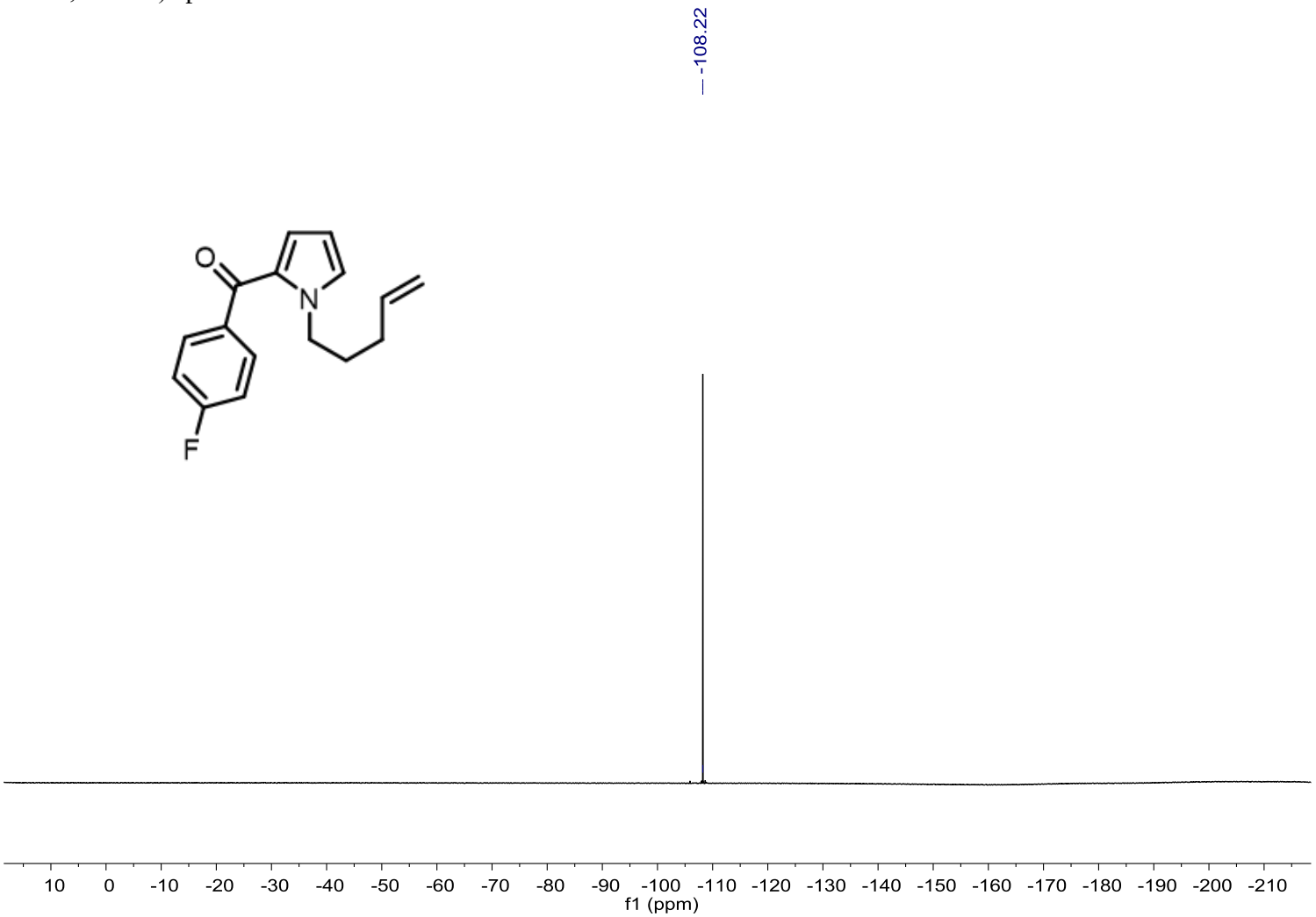
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1i**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1i**



$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **1i**



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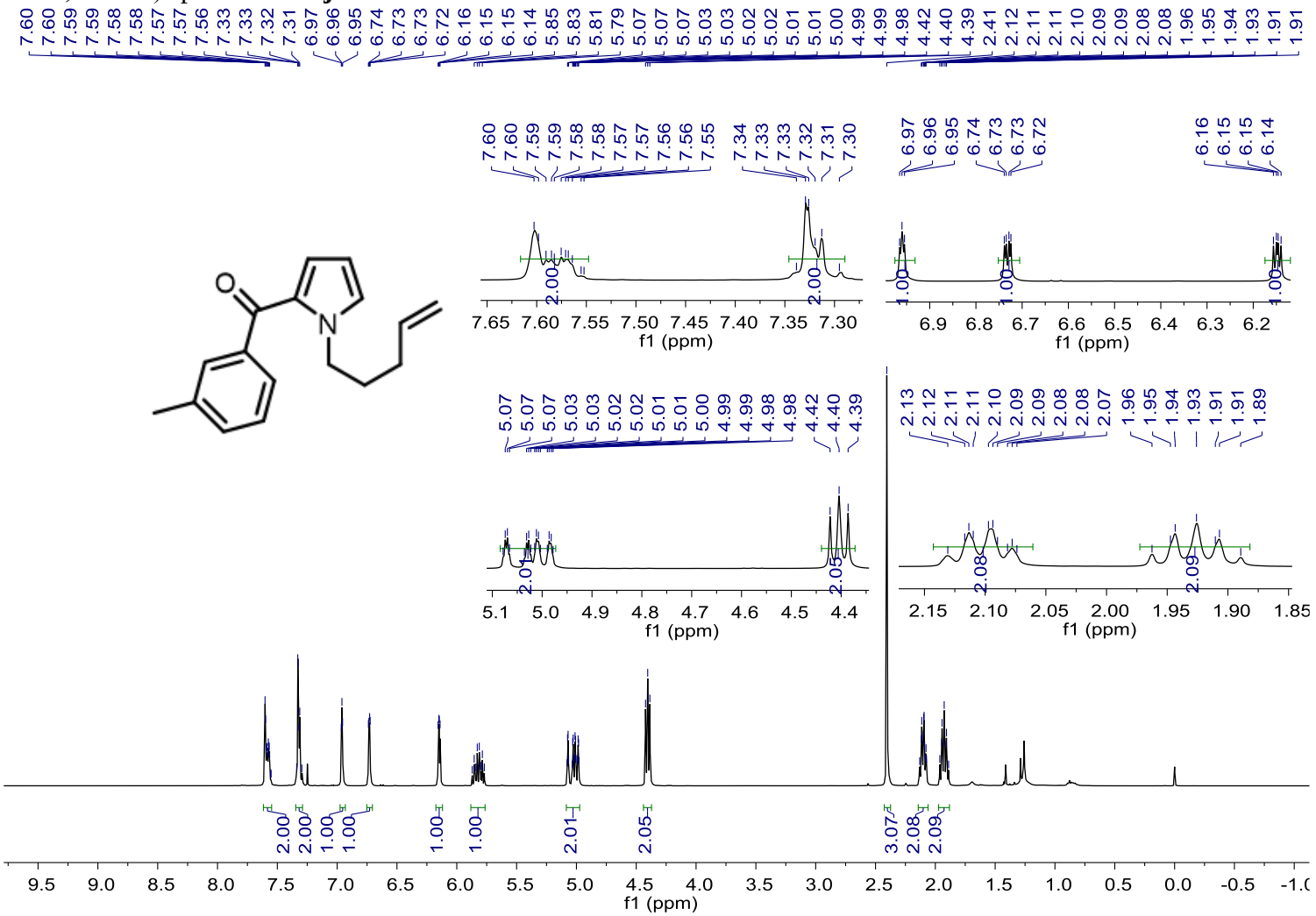
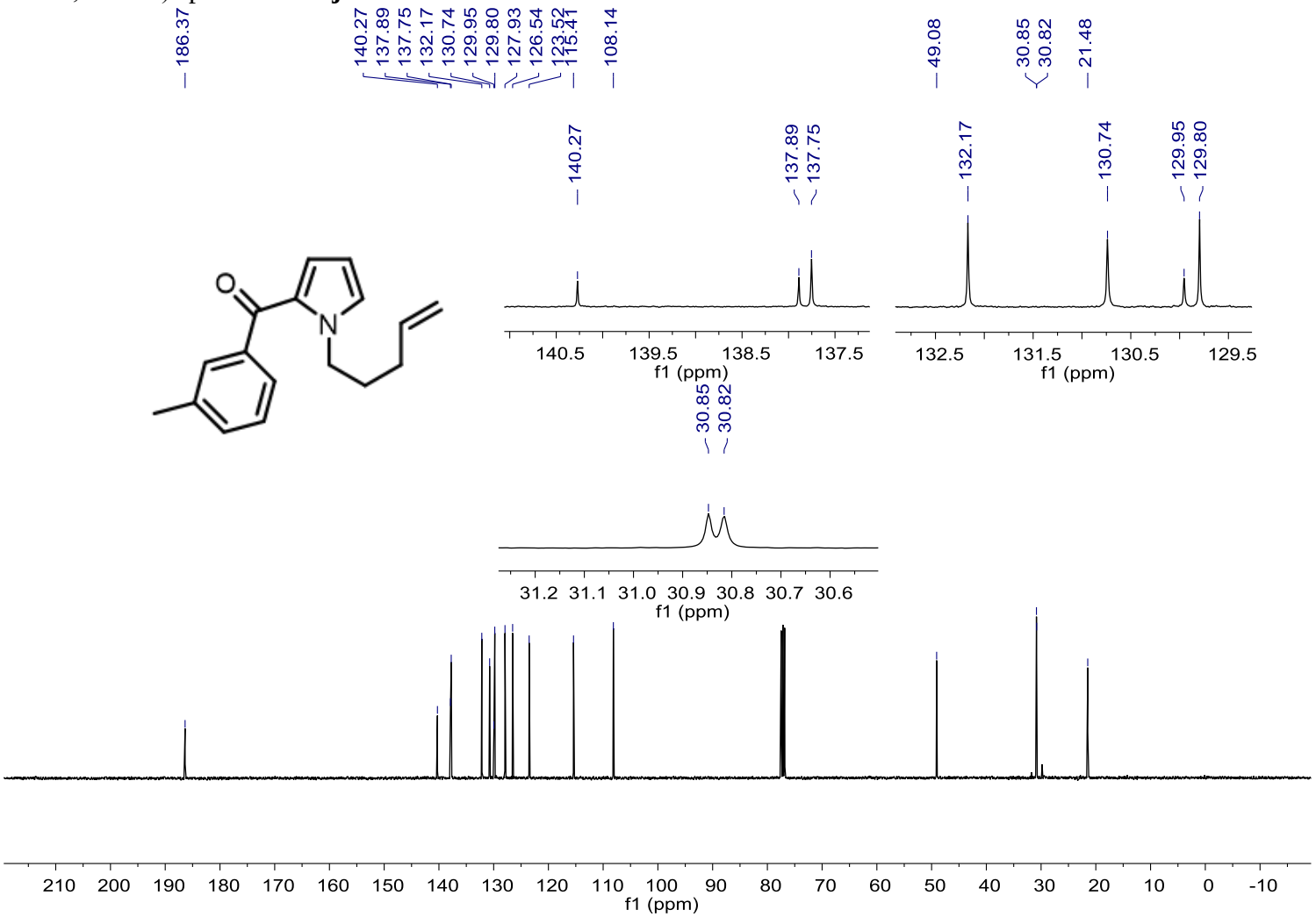
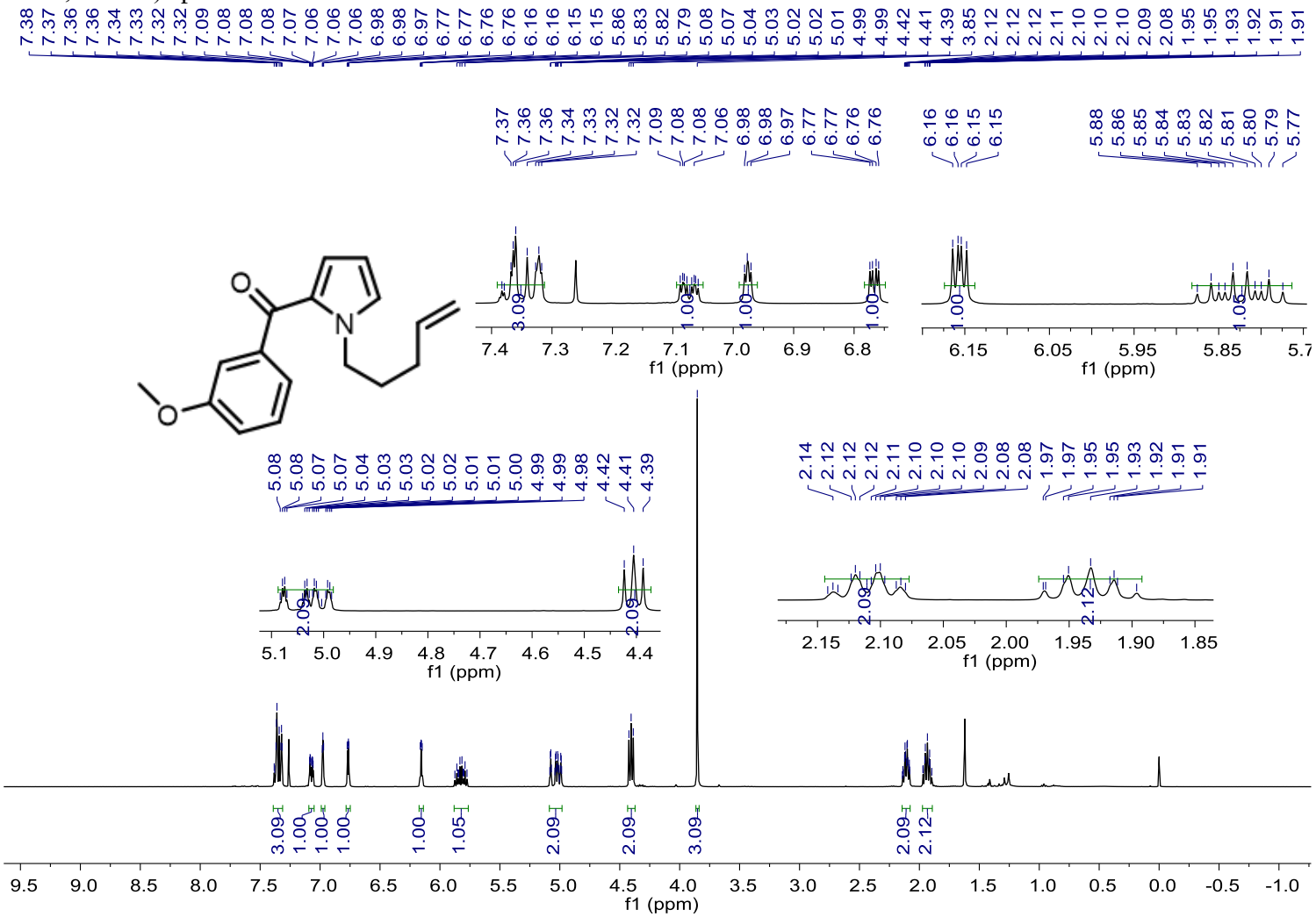


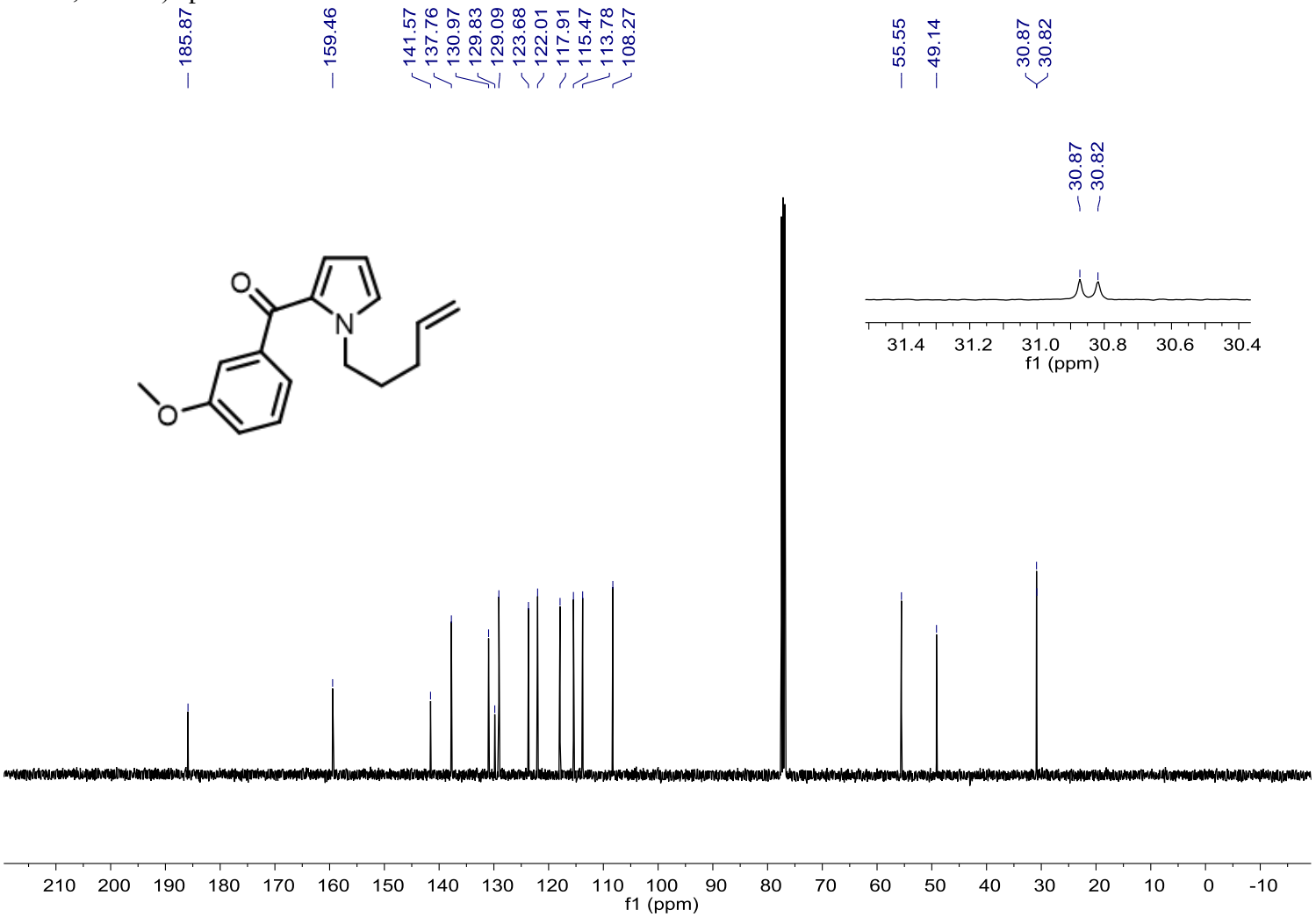
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1j**



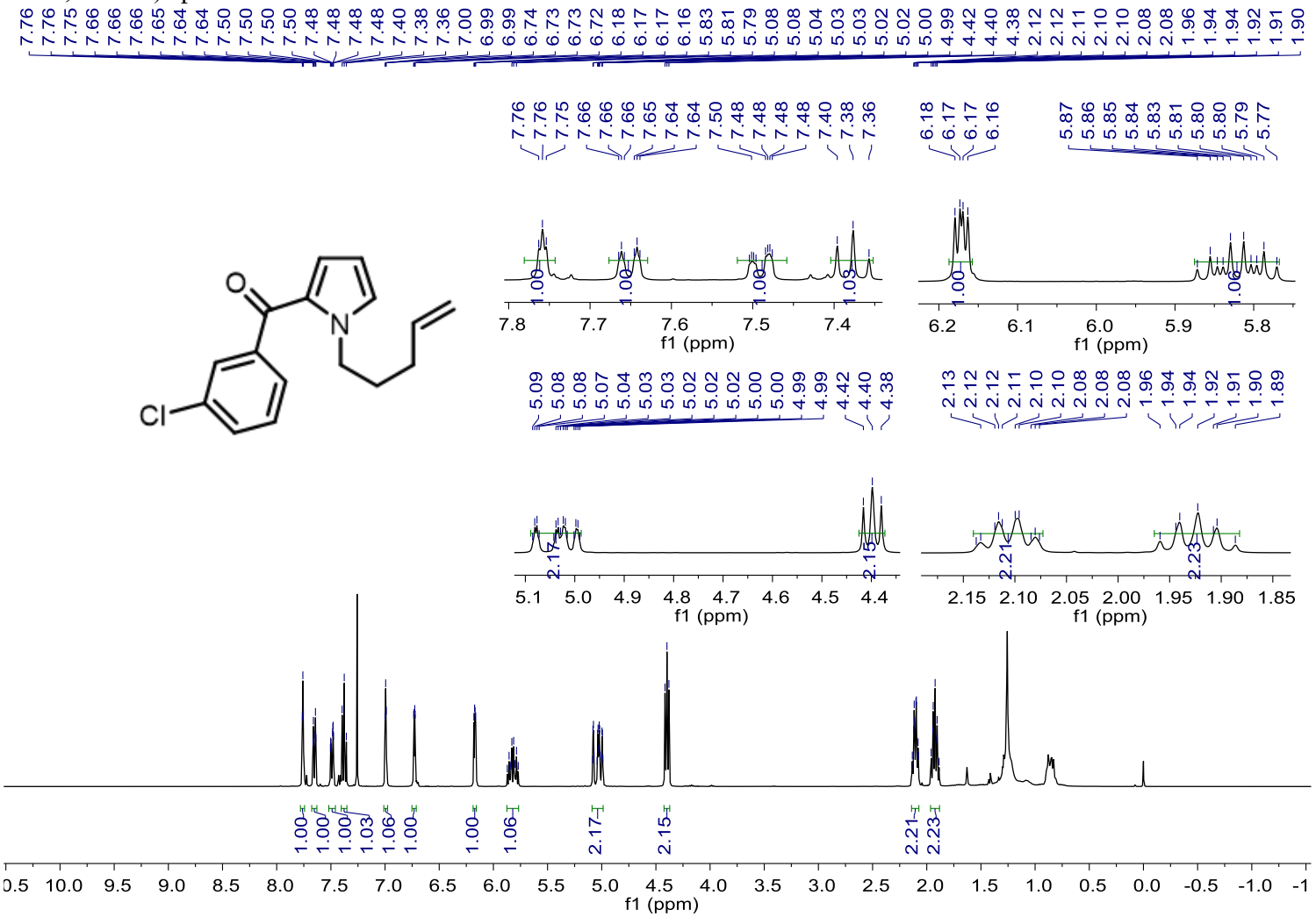
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1k**



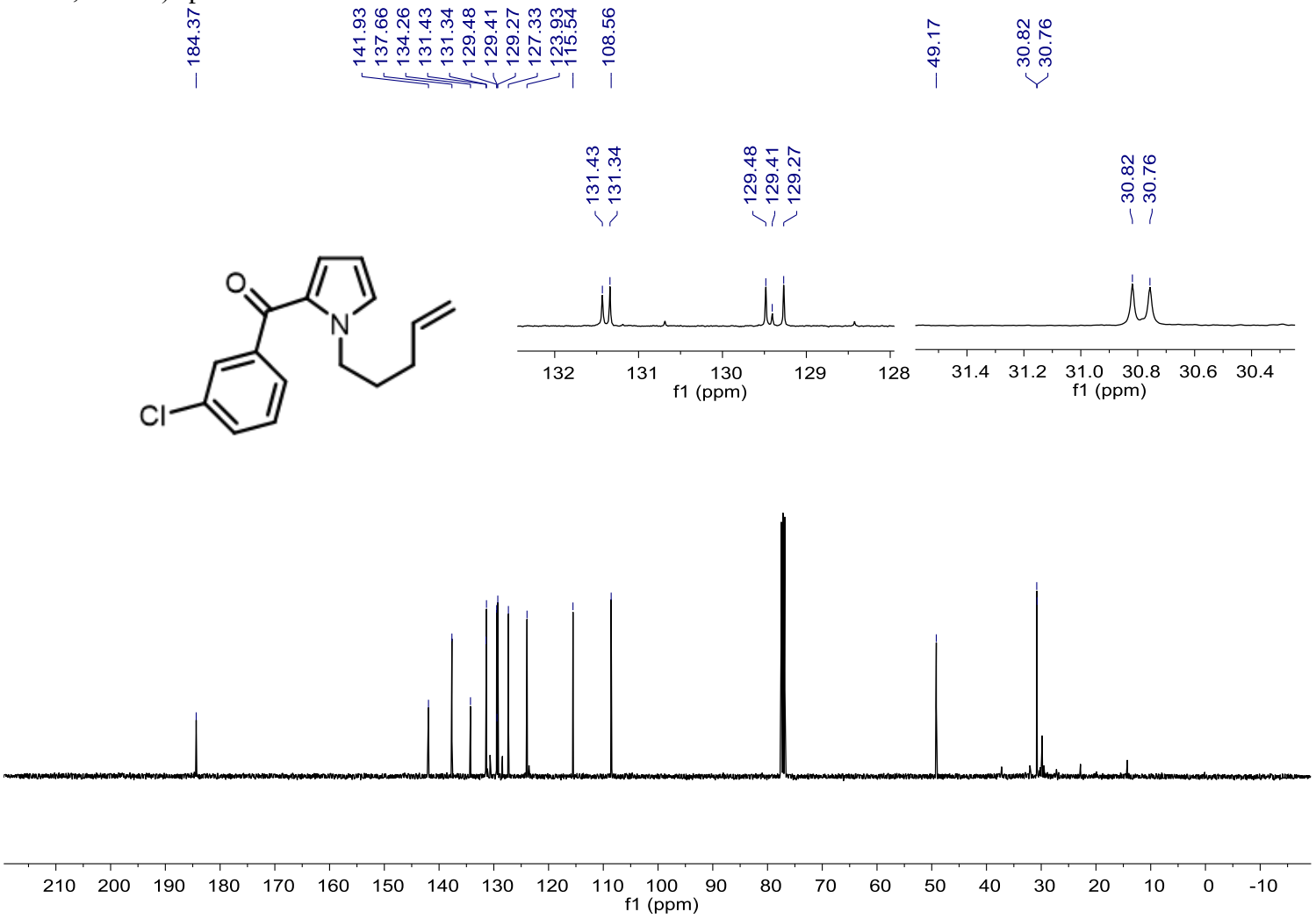
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1k**



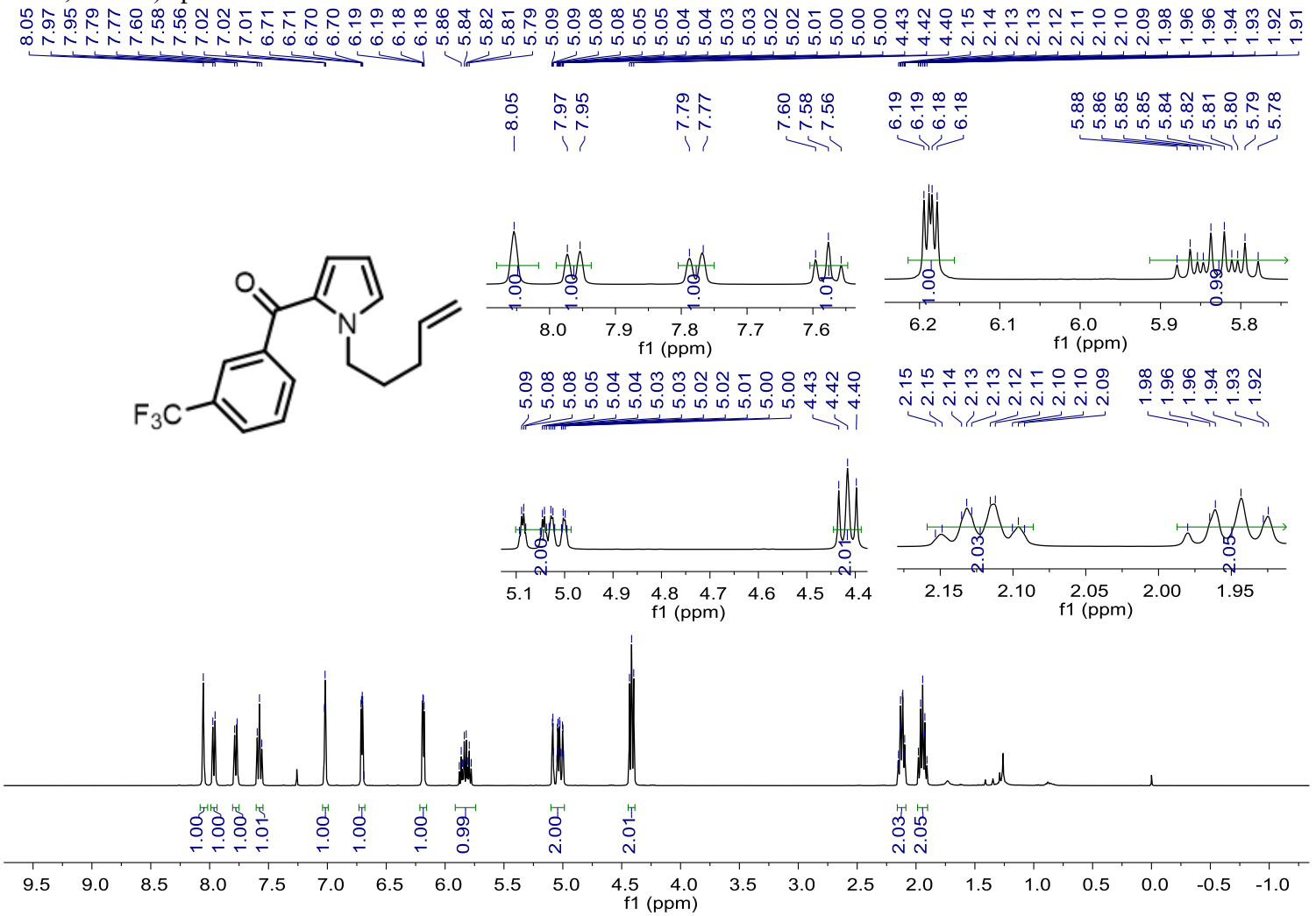
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1l**



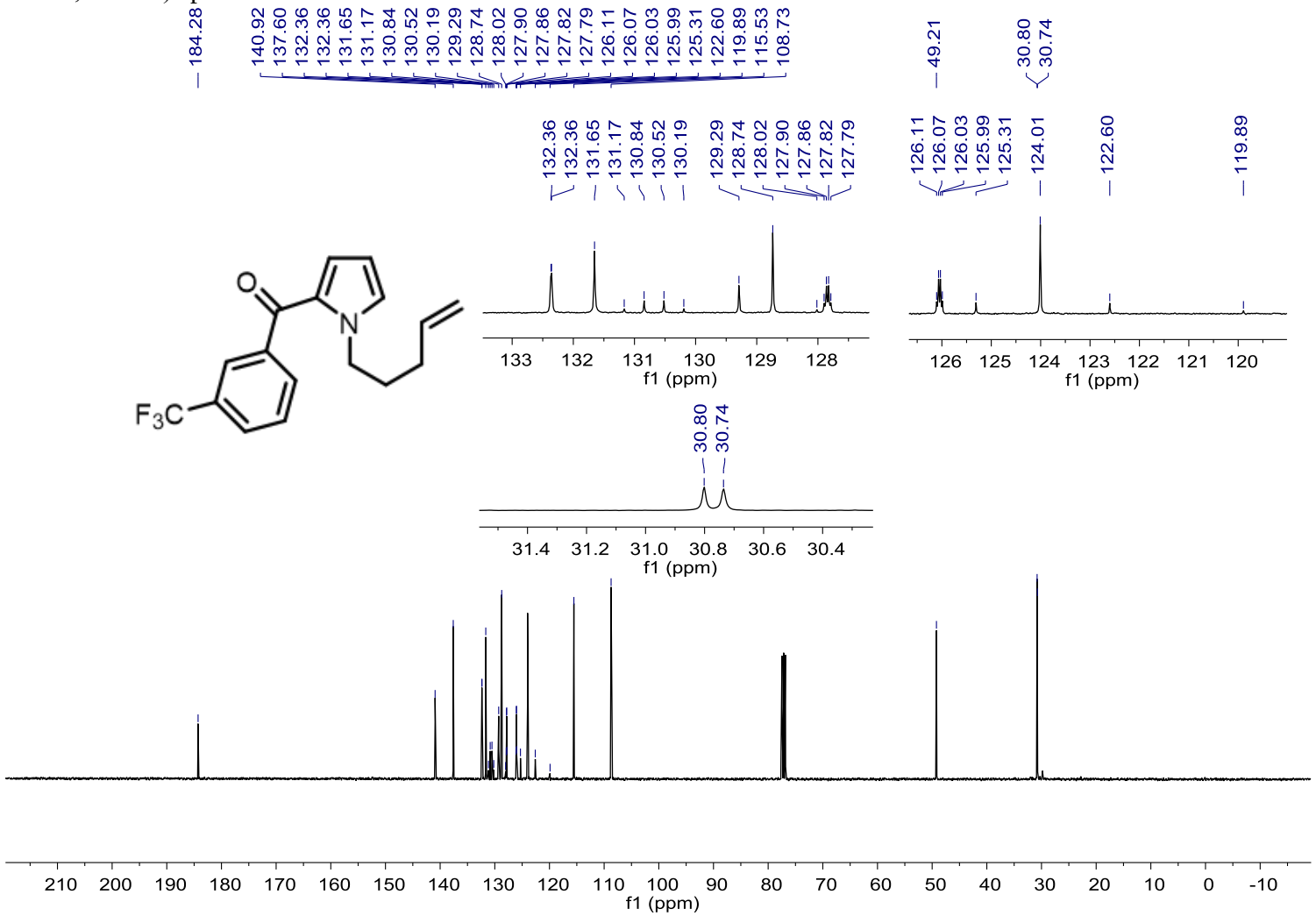
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1l**



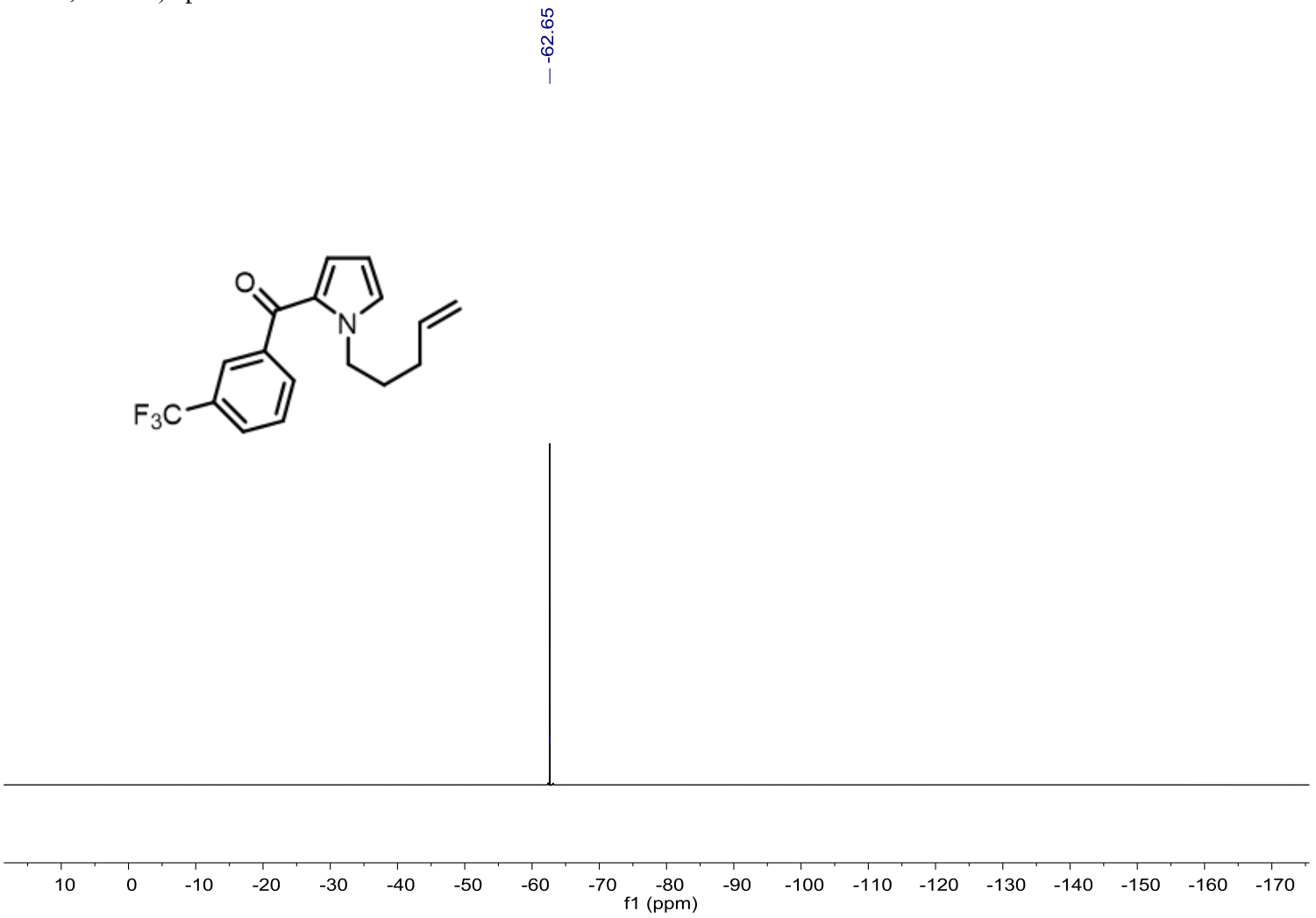
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1m**



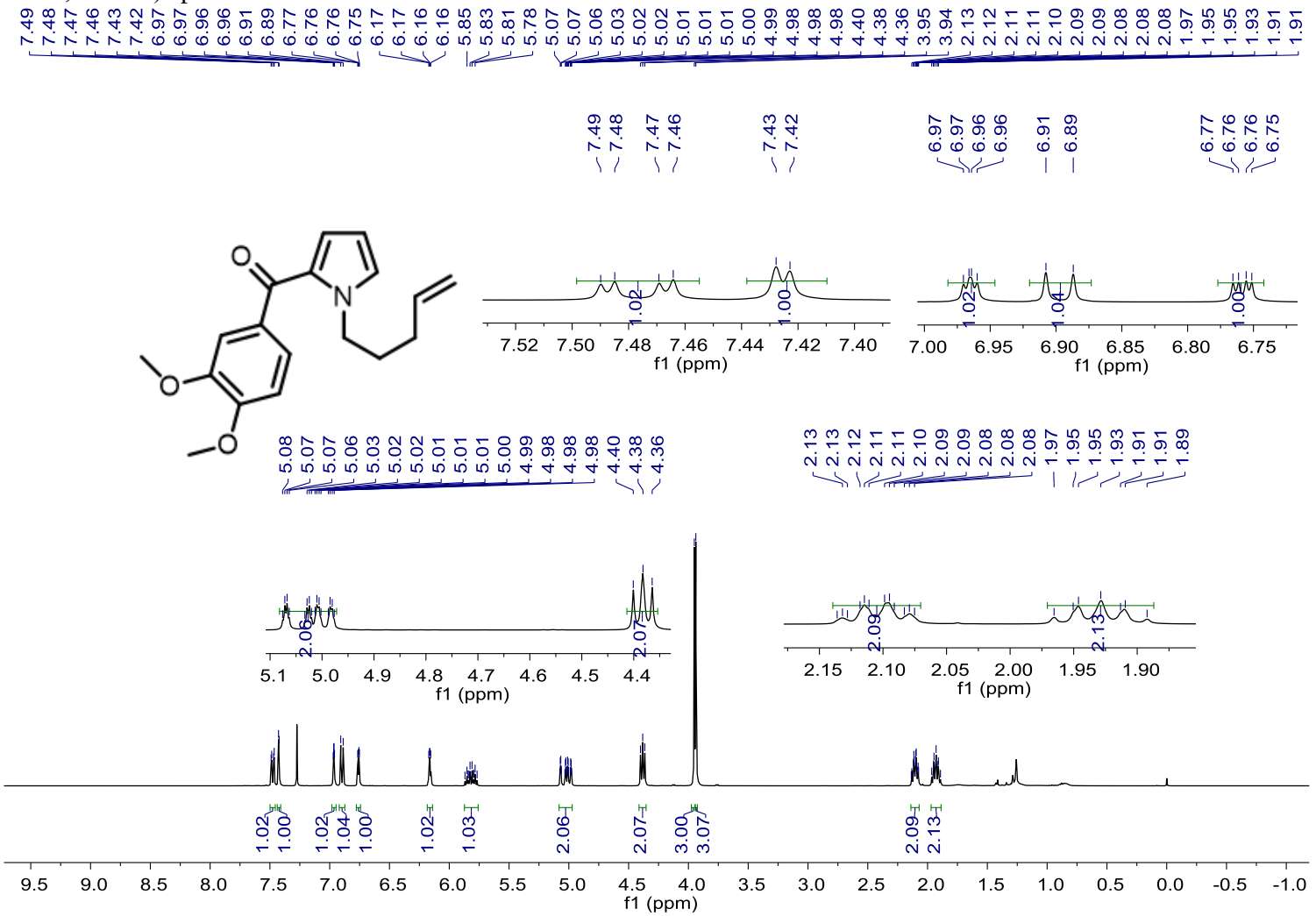
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1m**



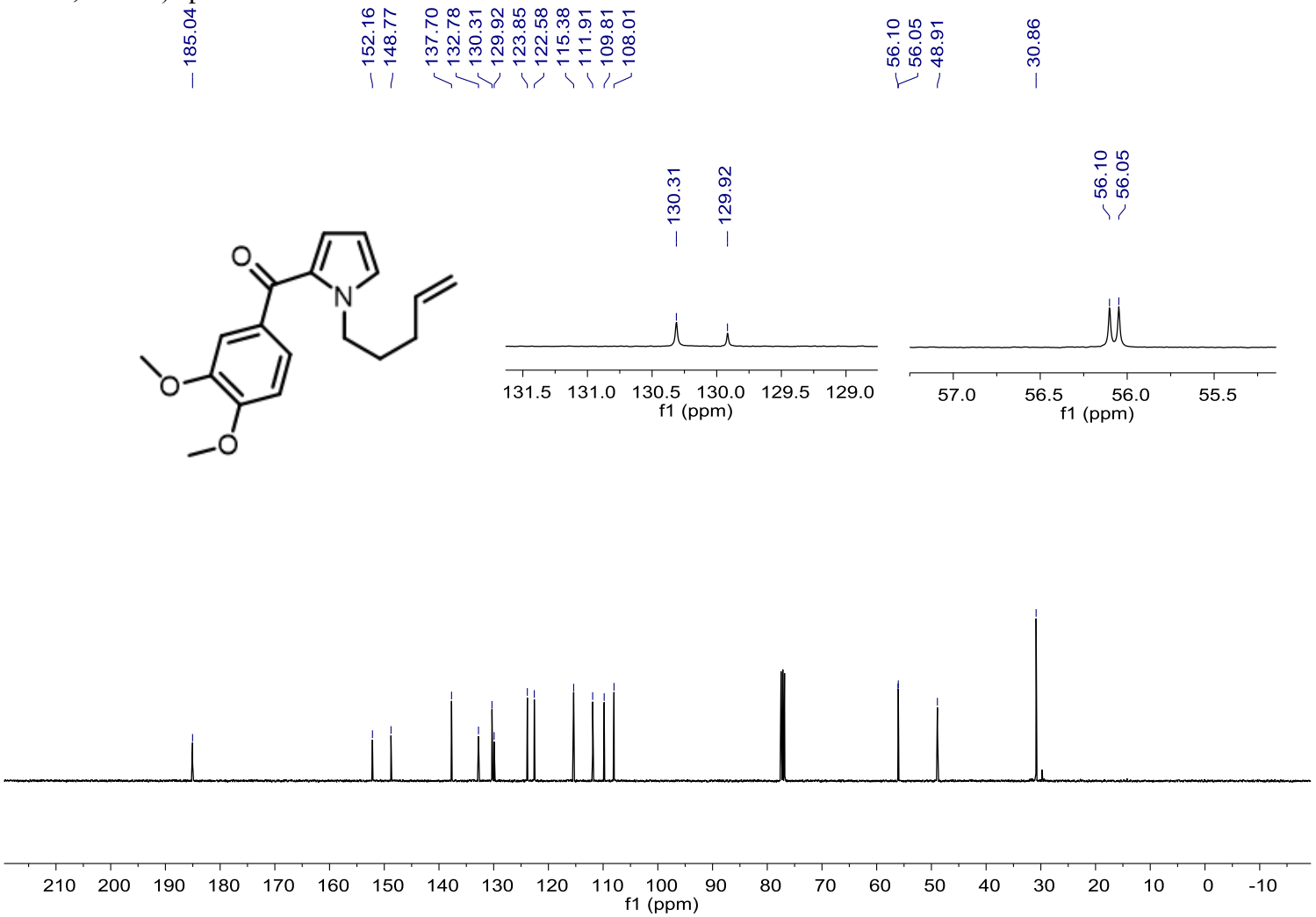
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **1m**



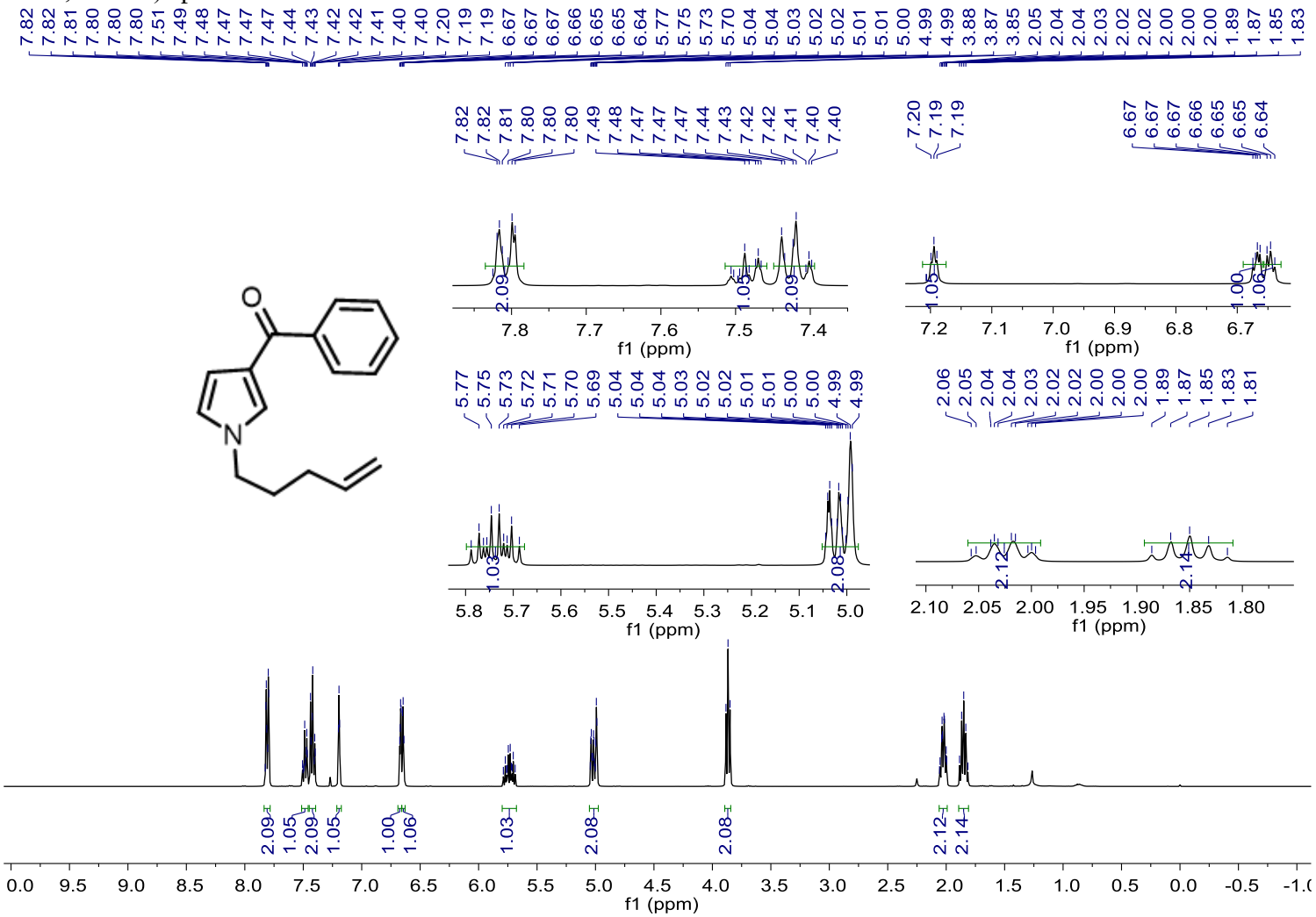
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1n**



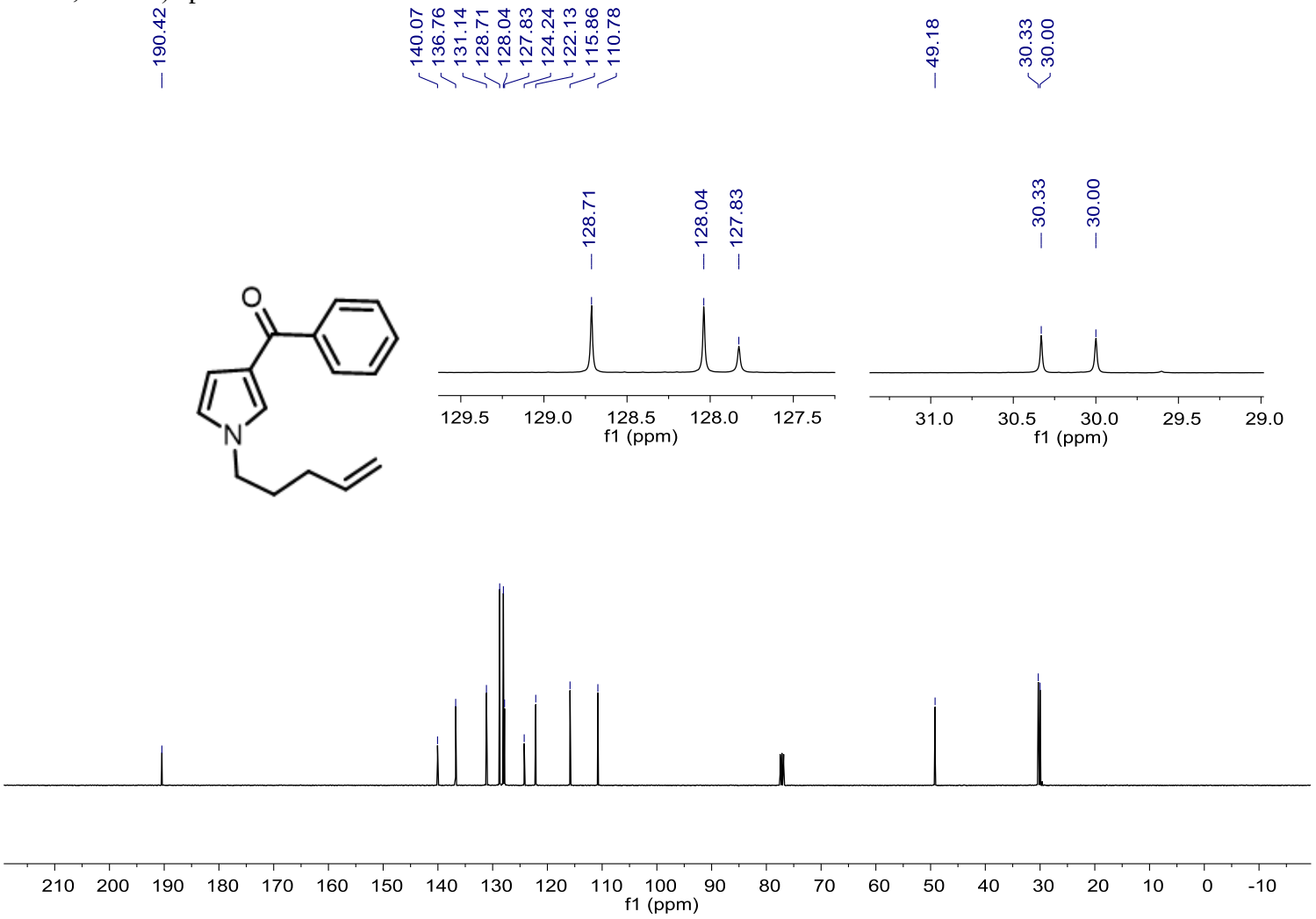
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1n**



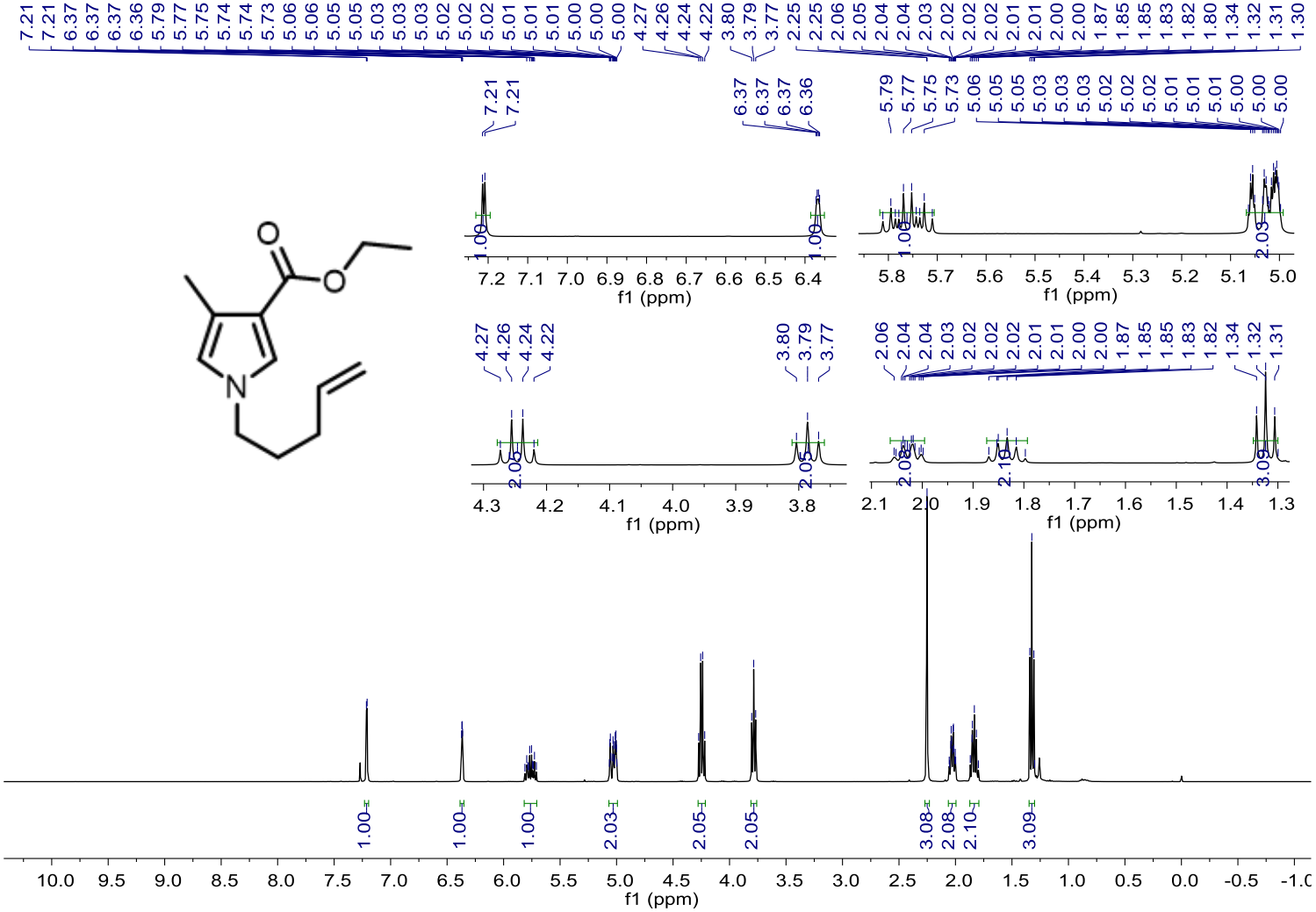
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1o**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1o**



$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **1v**



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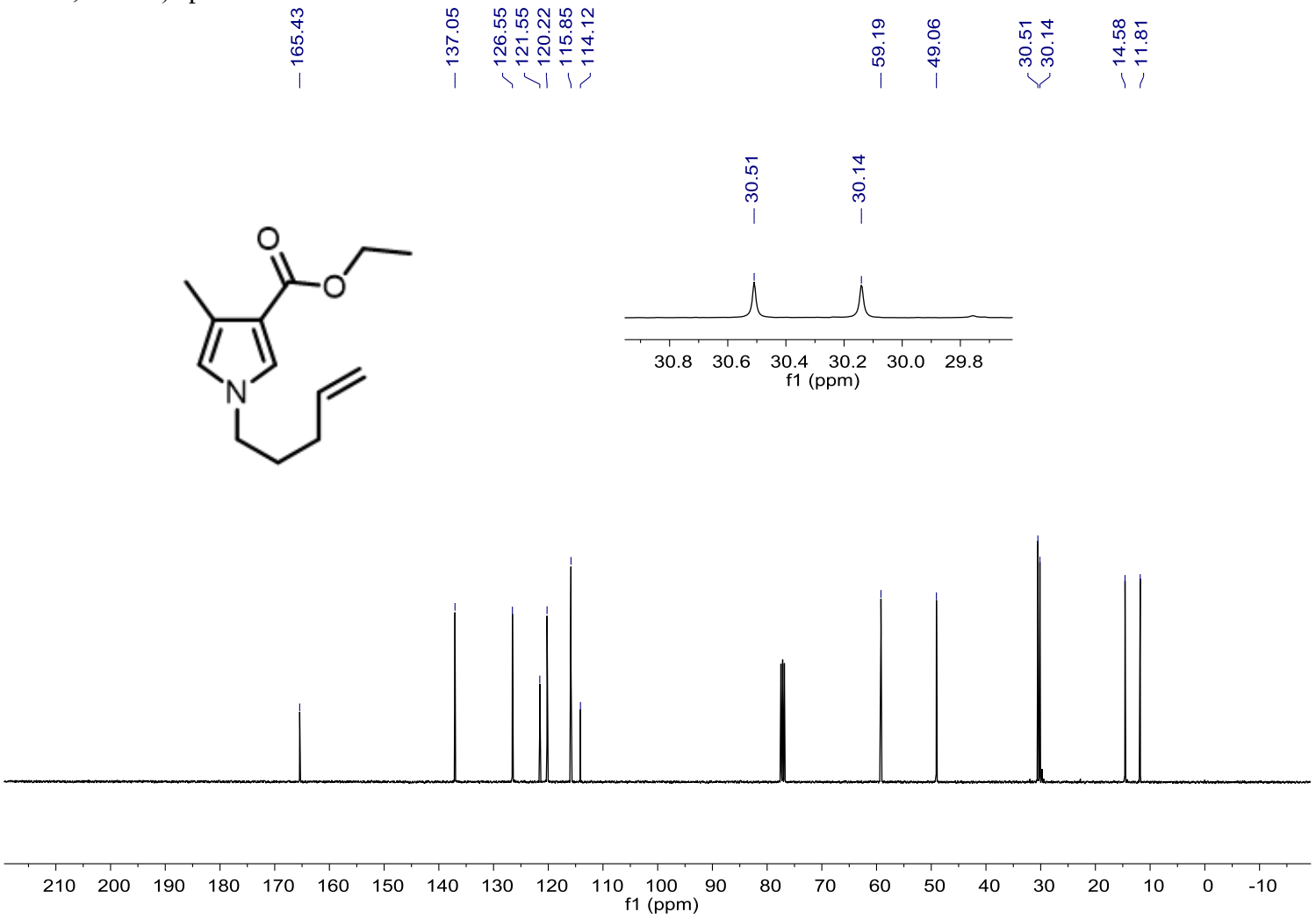

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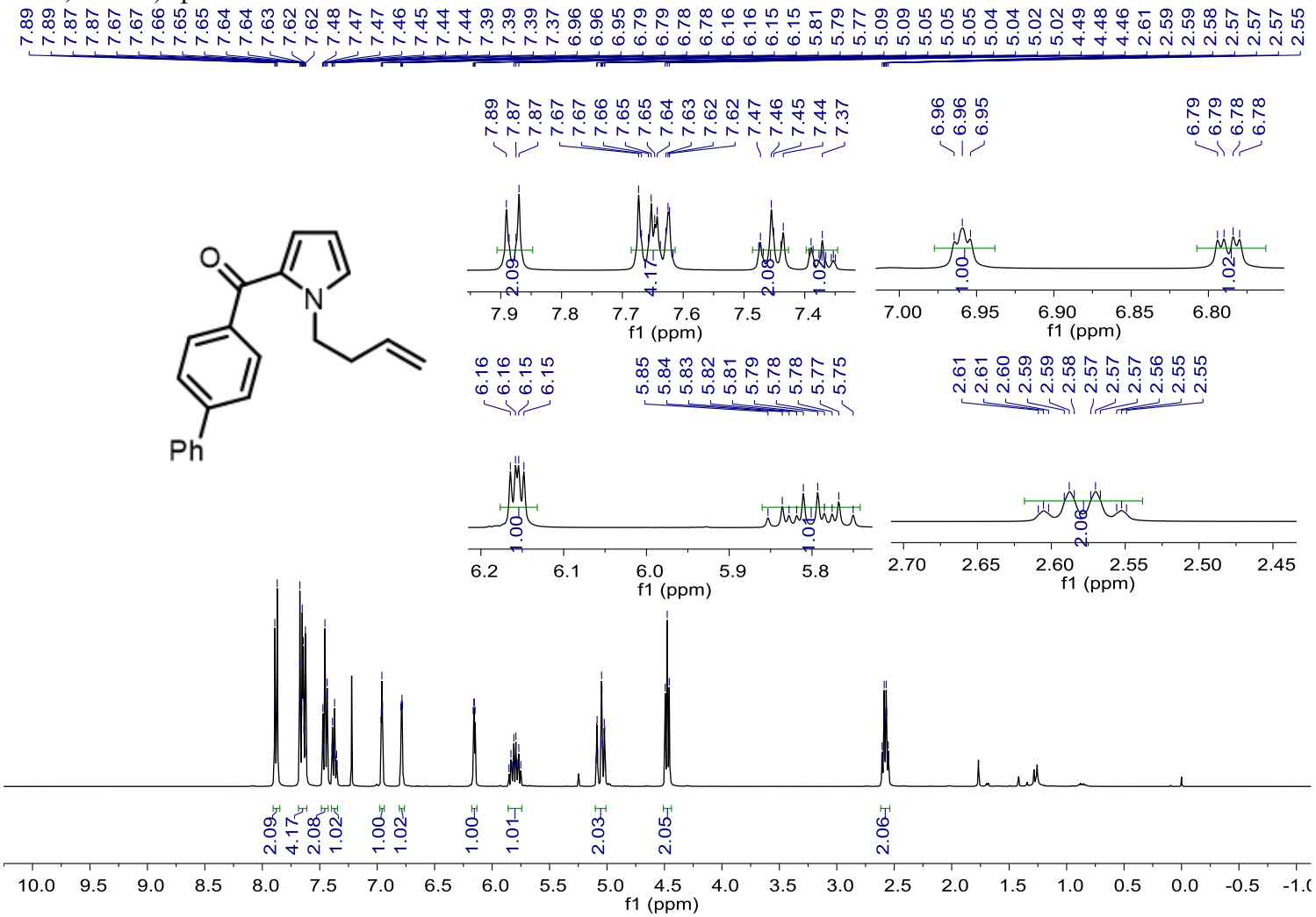
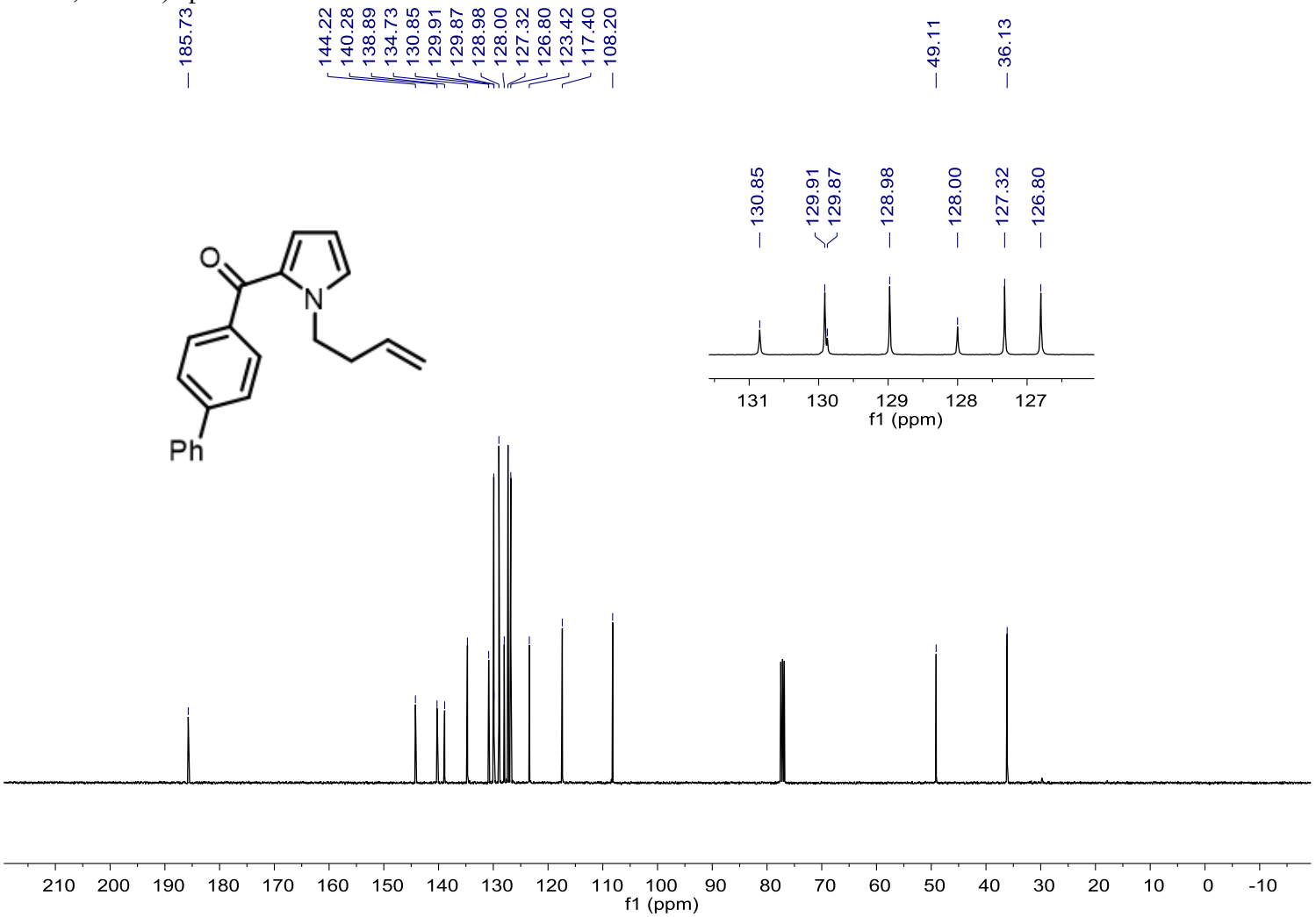


$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1x**



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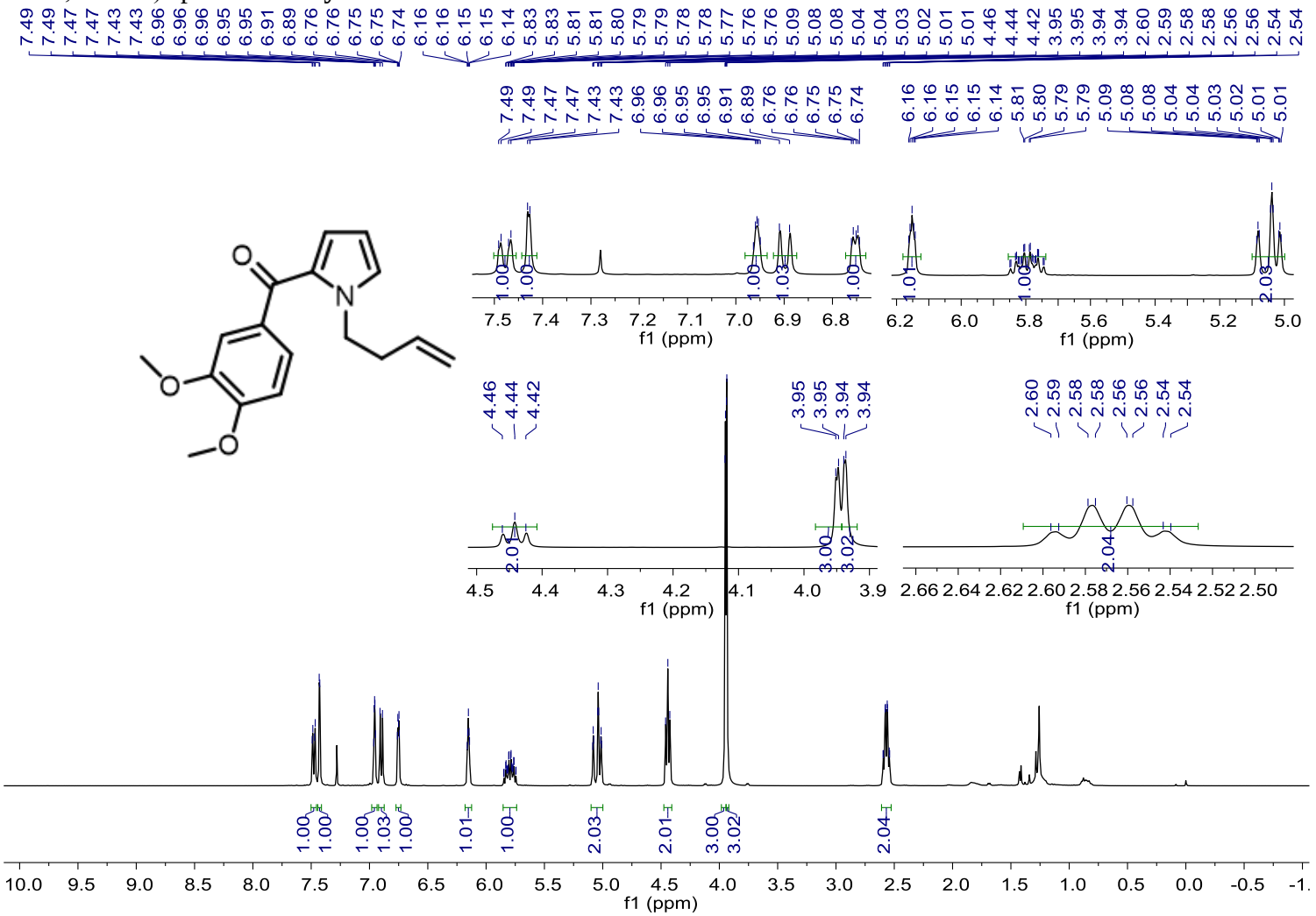
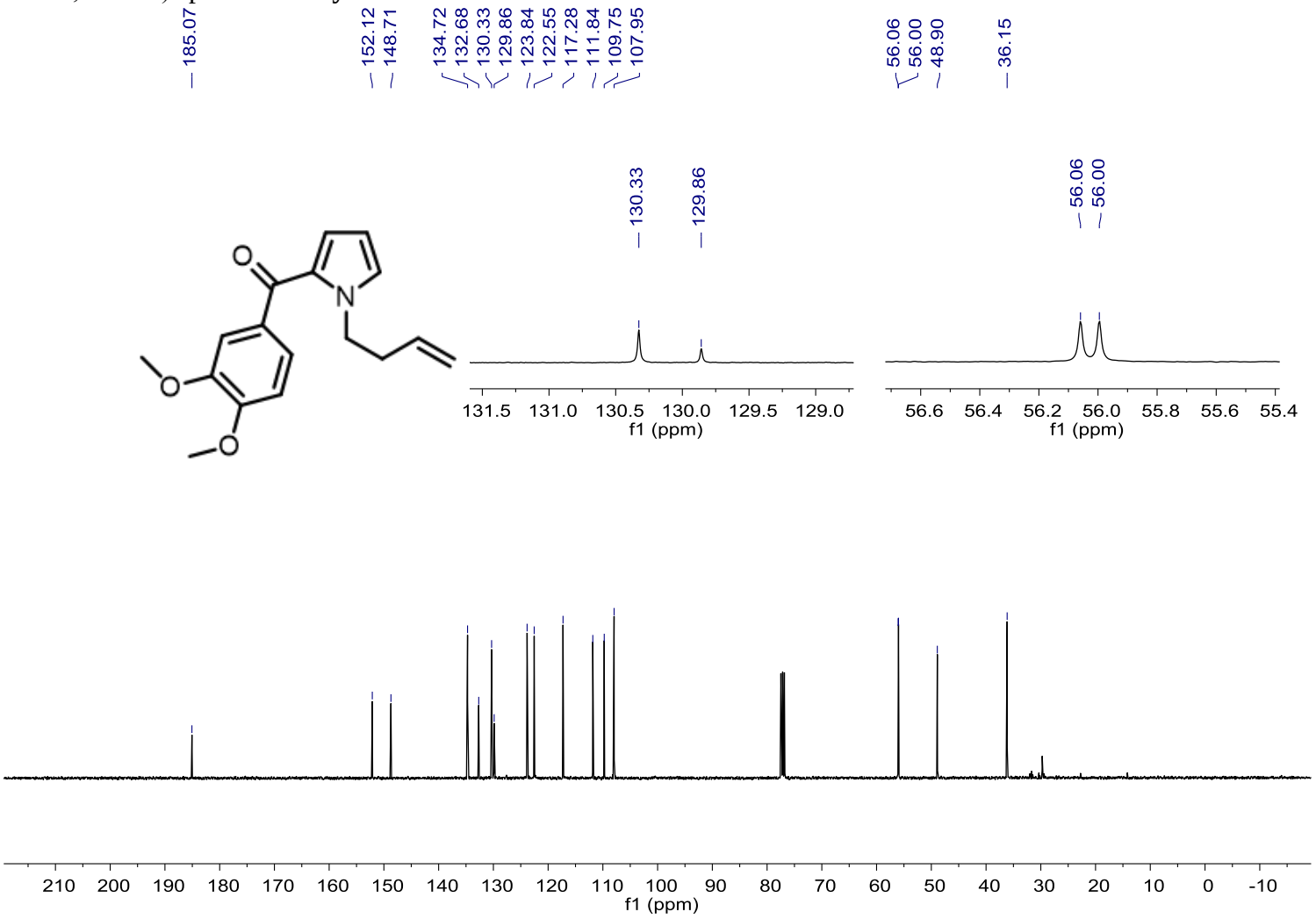
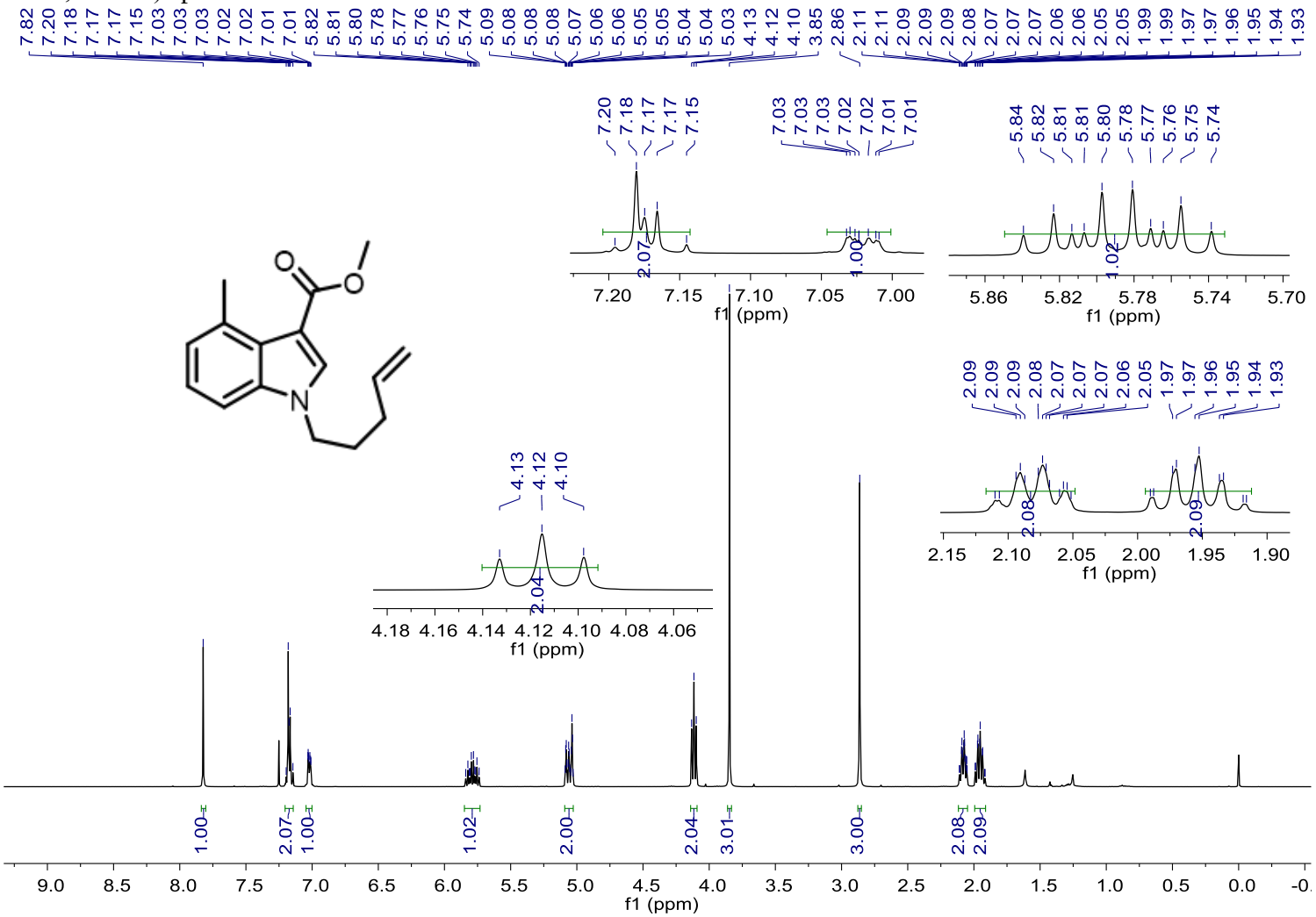


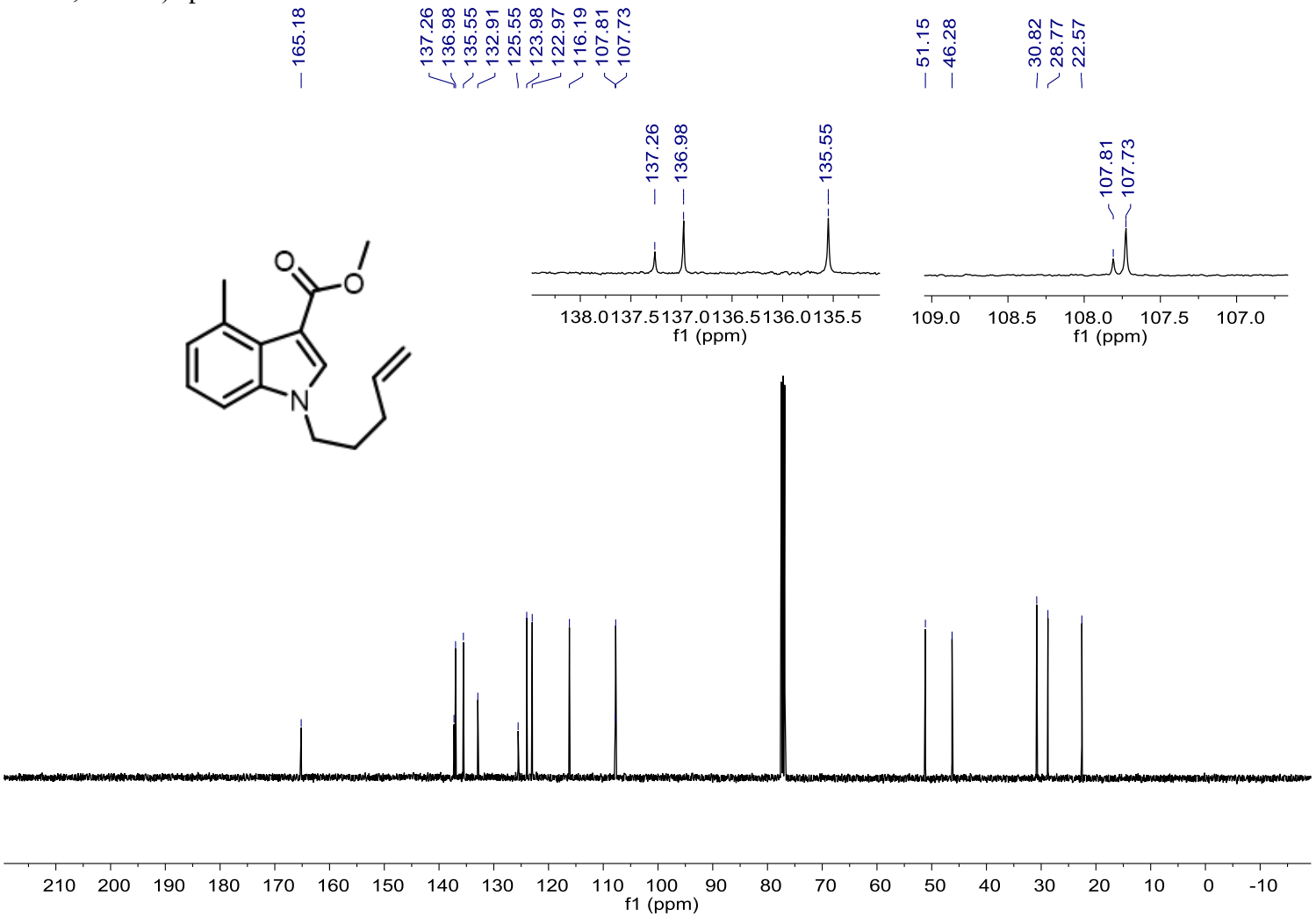
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **1y**



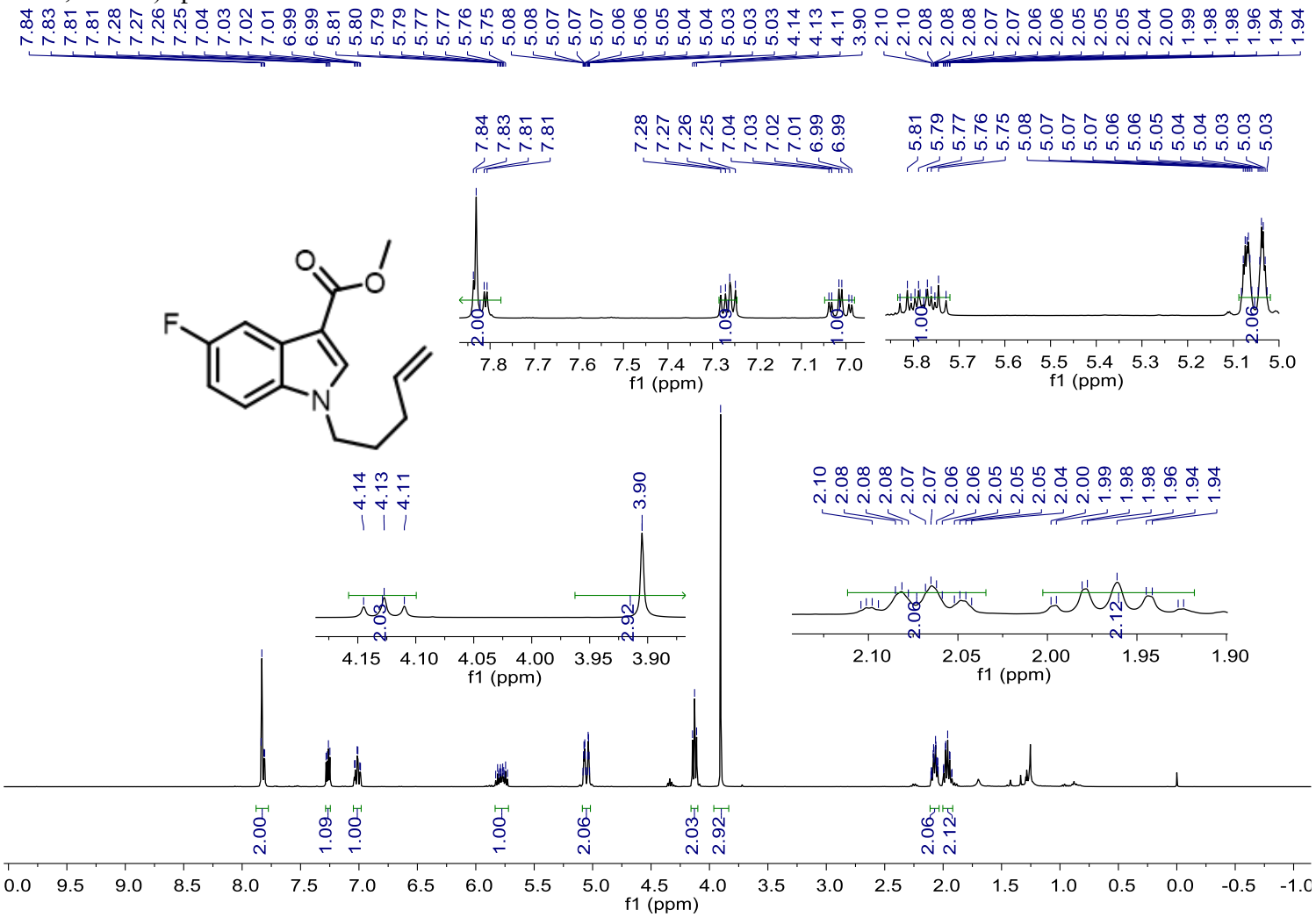
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4b**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **4b**



$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4d**



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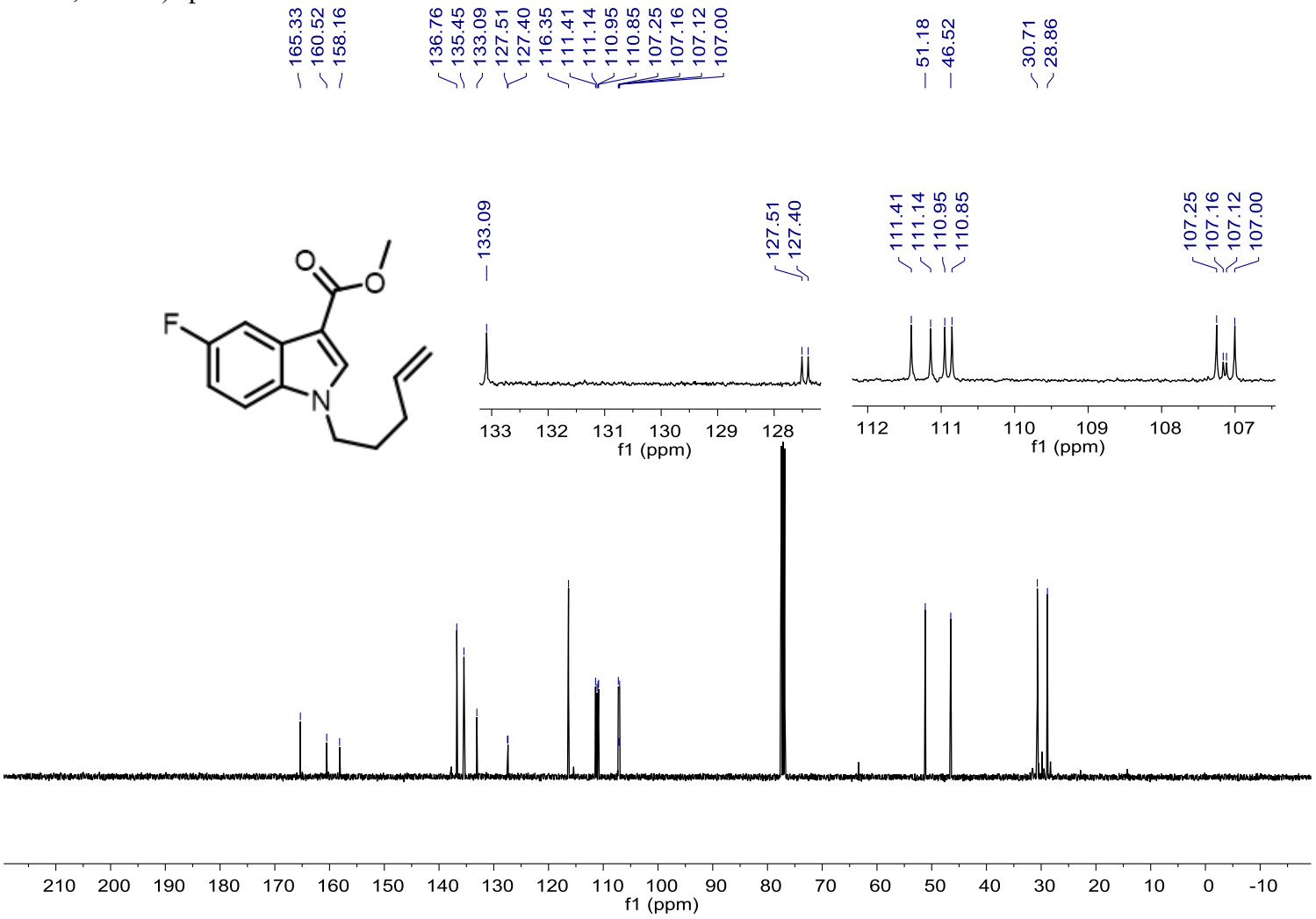
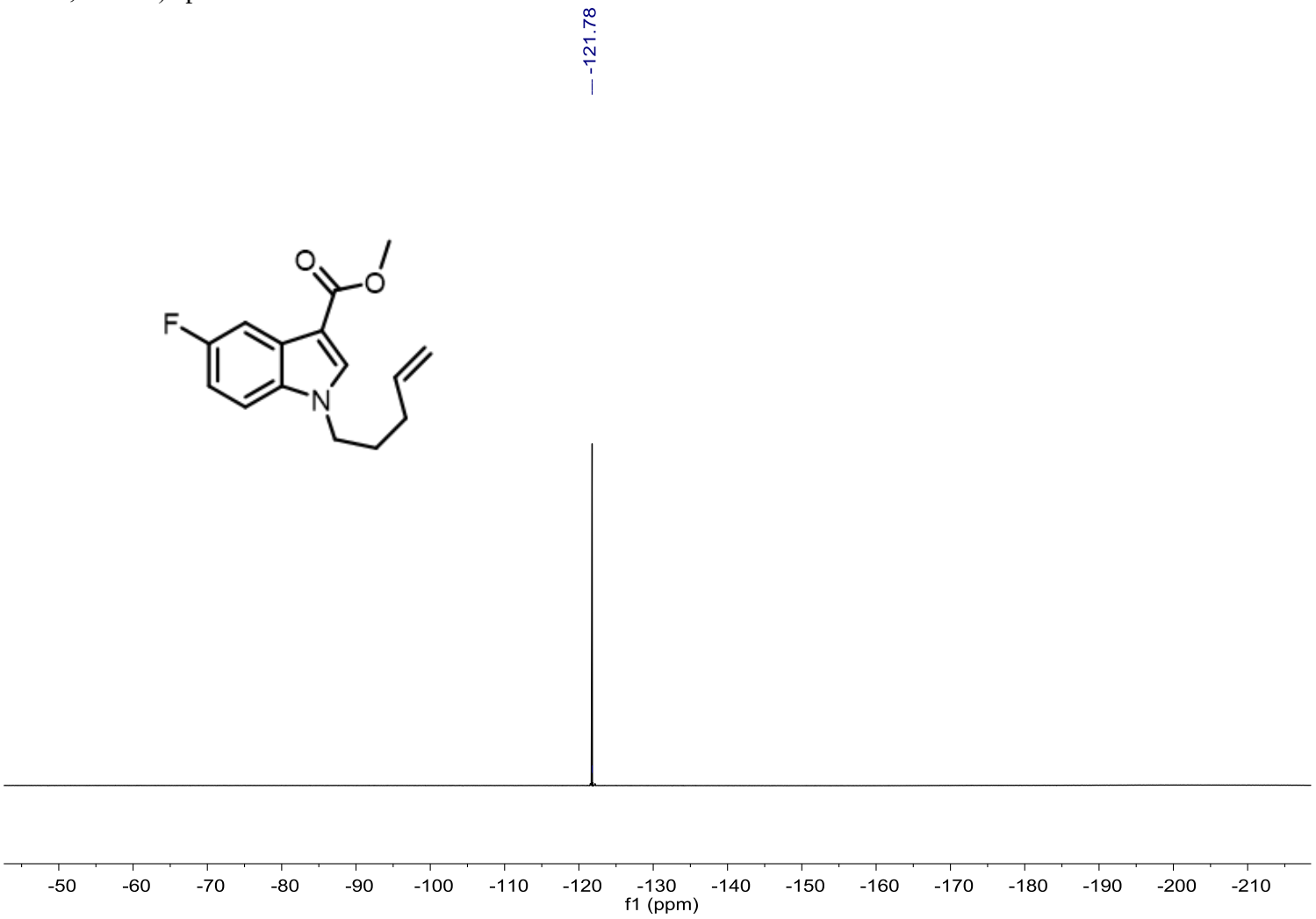


$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **4d**



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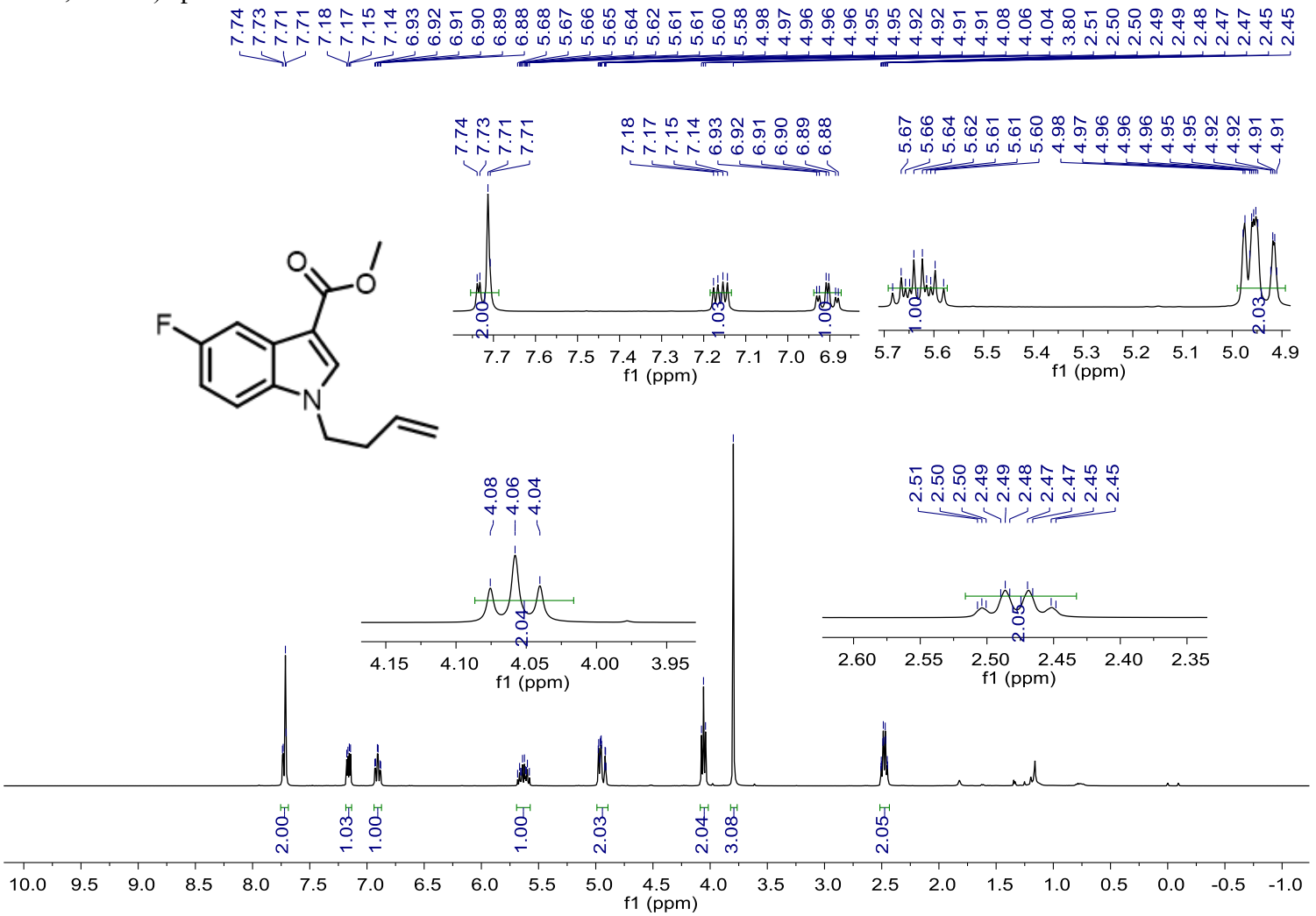

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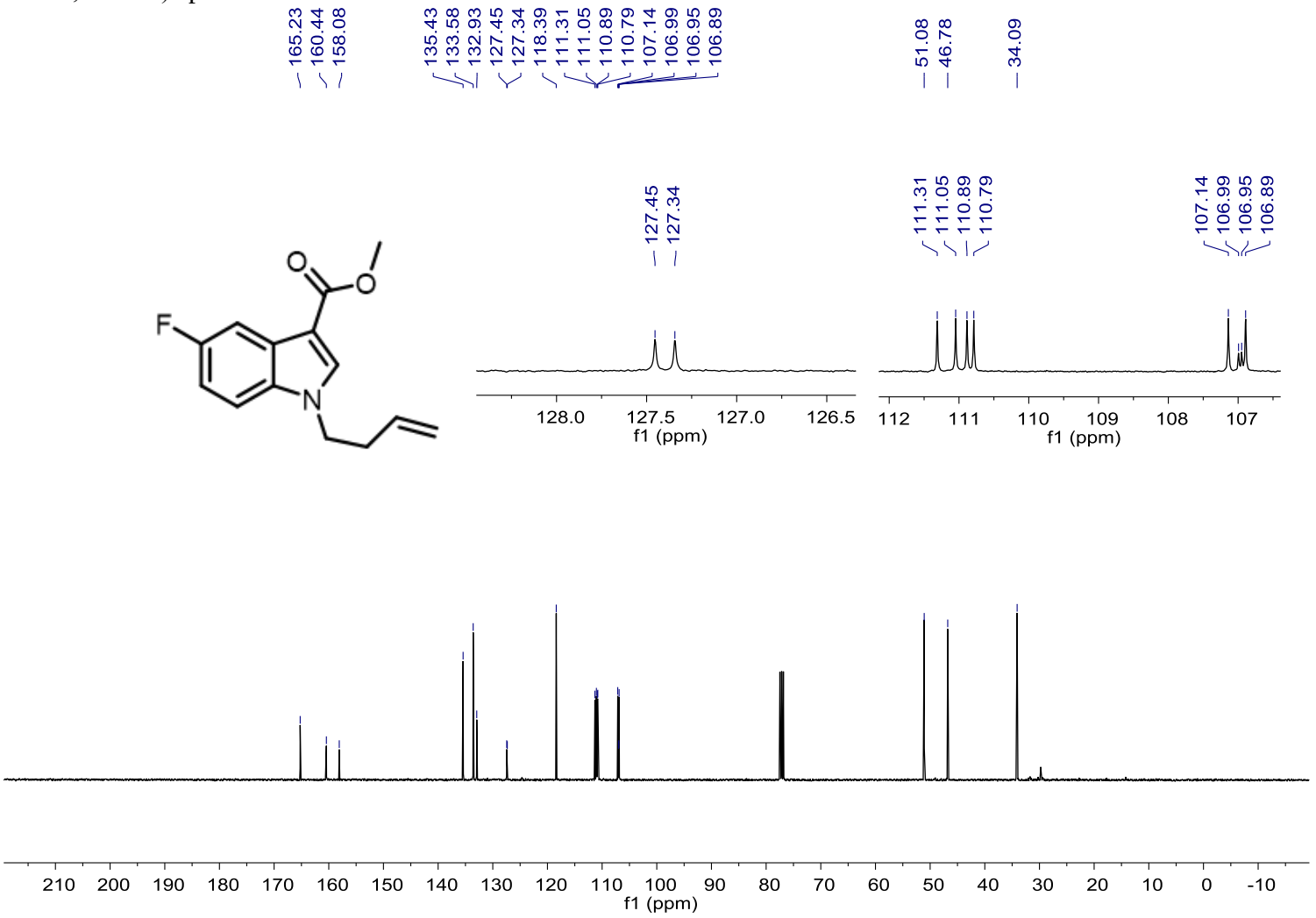
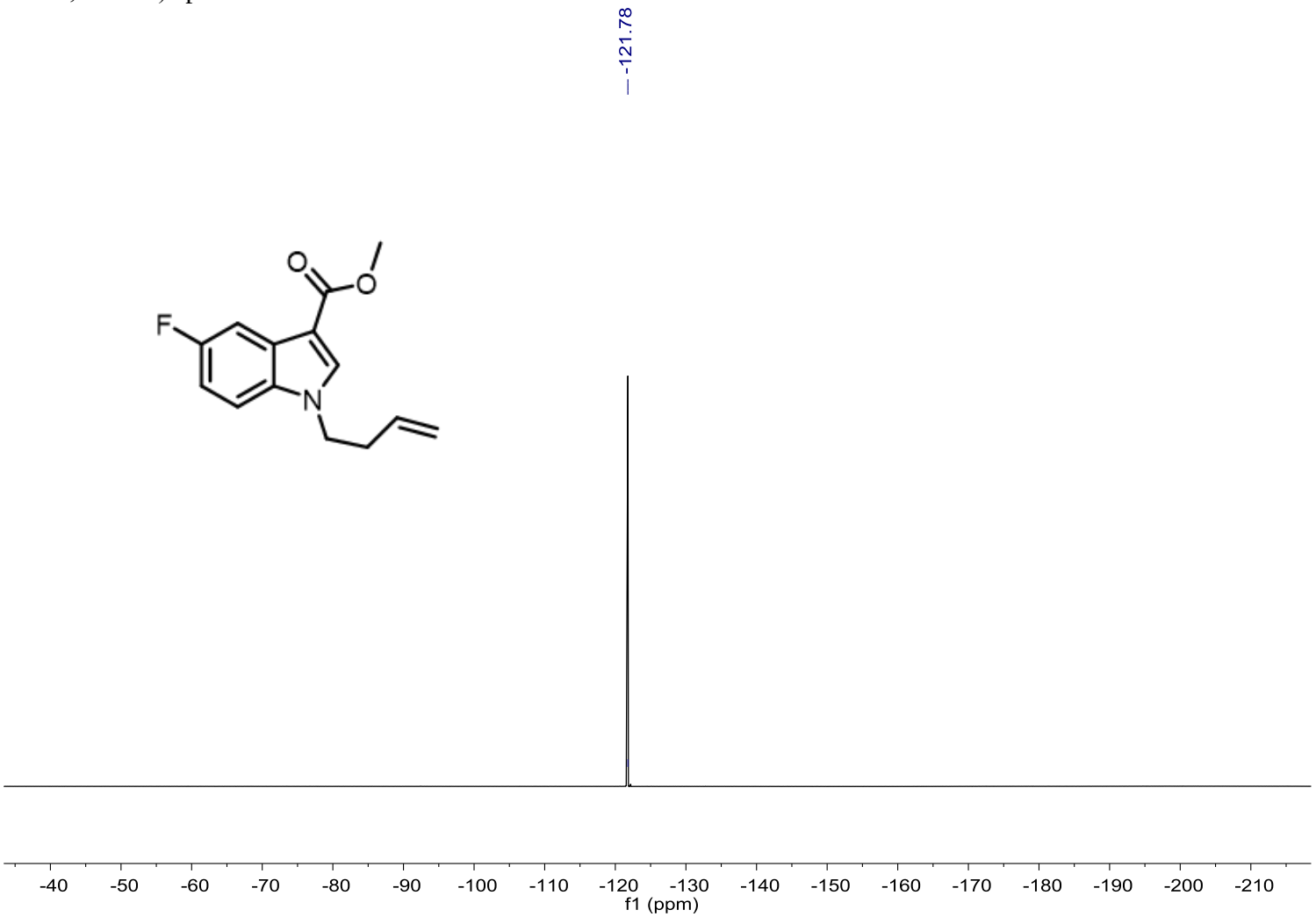
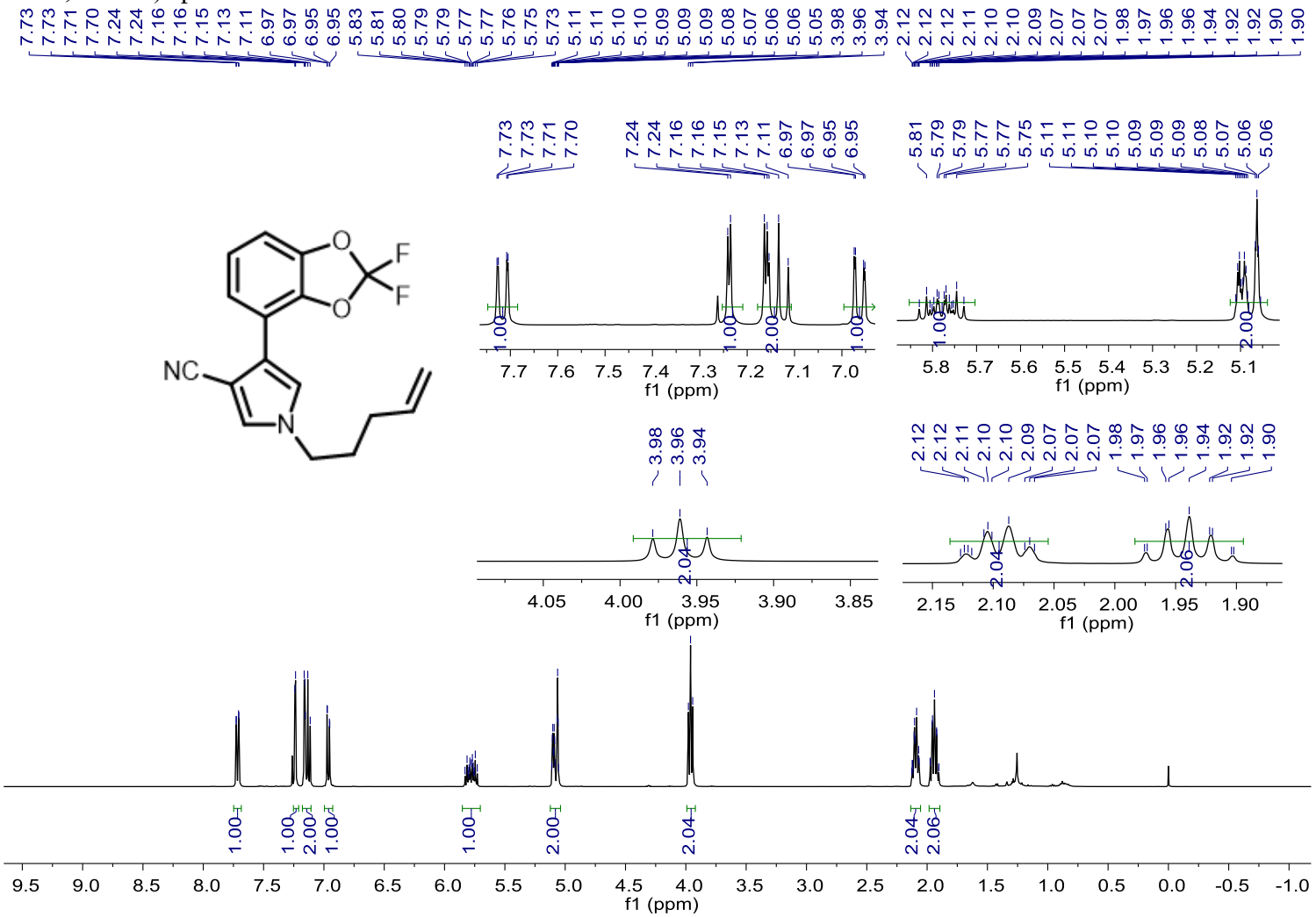


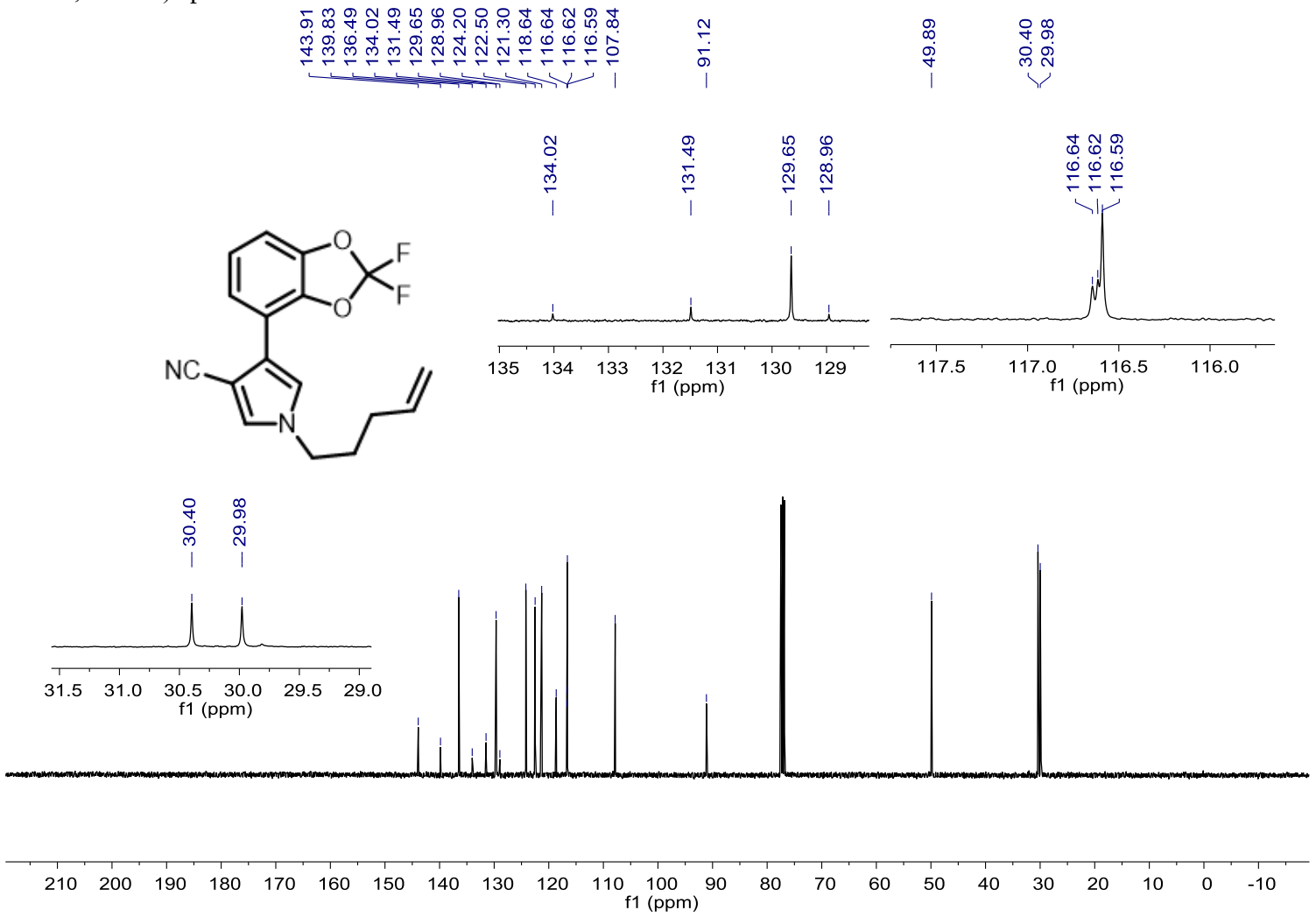
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **4h**



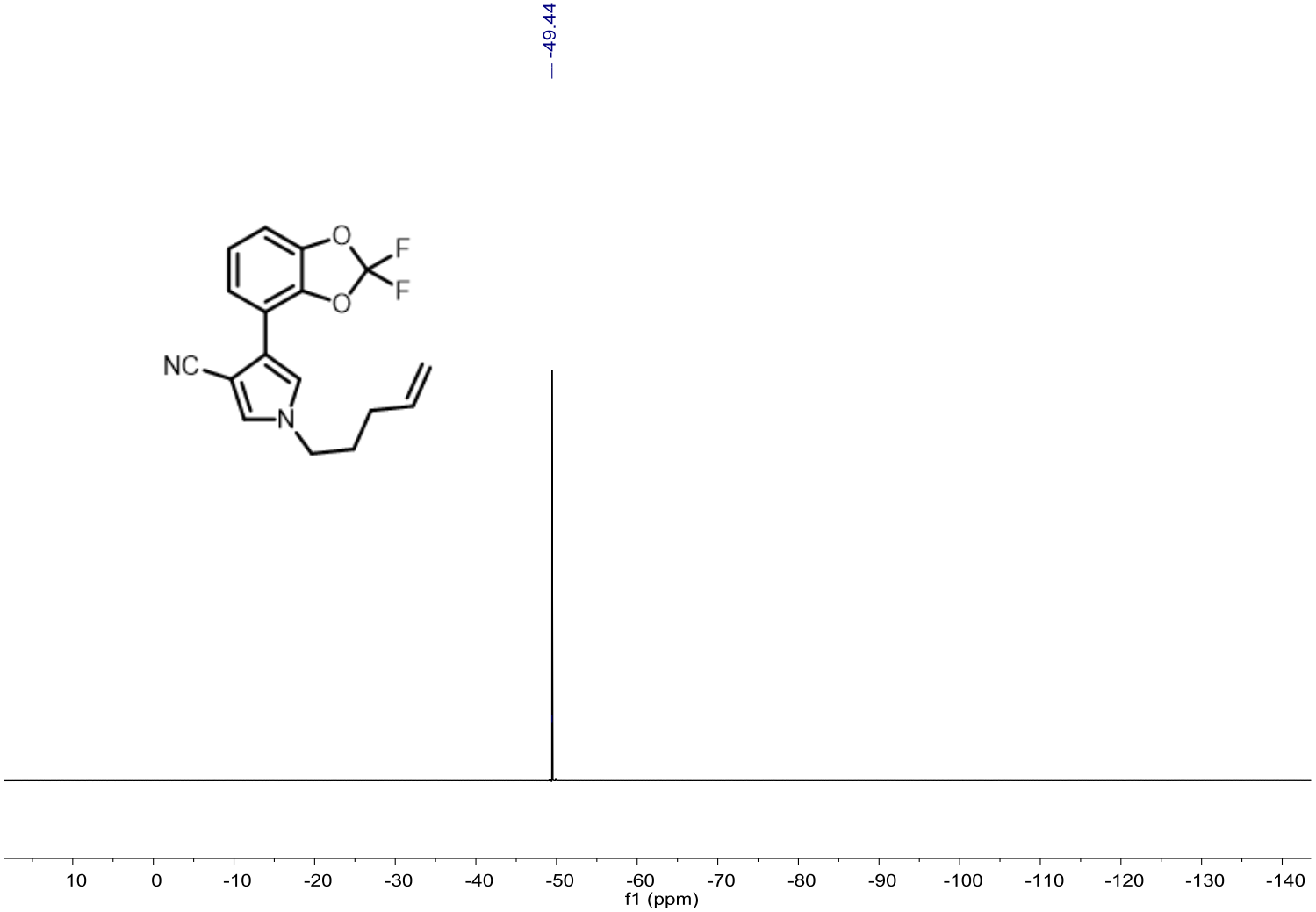
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **6a**



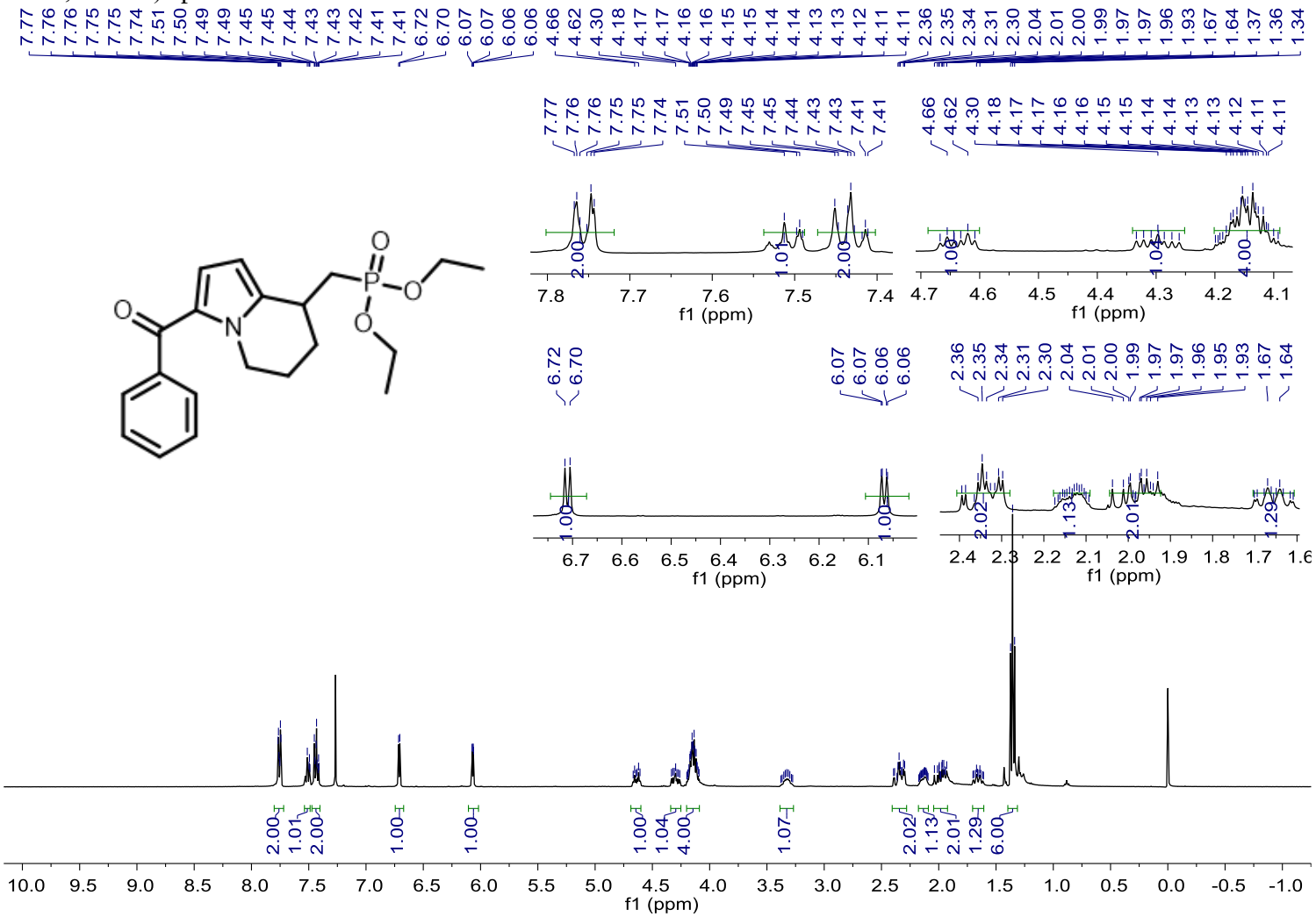
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **6a**



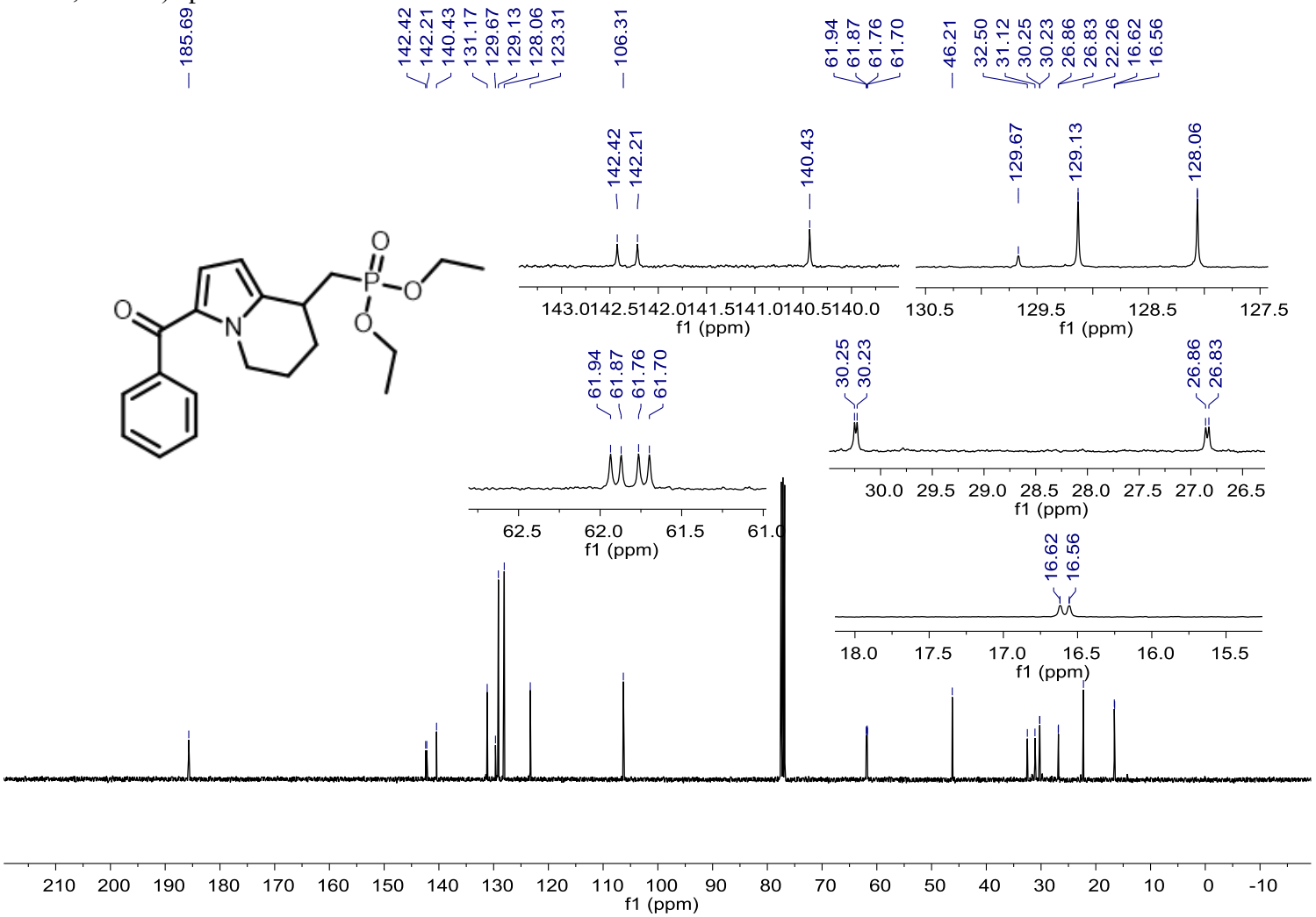
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **6a**



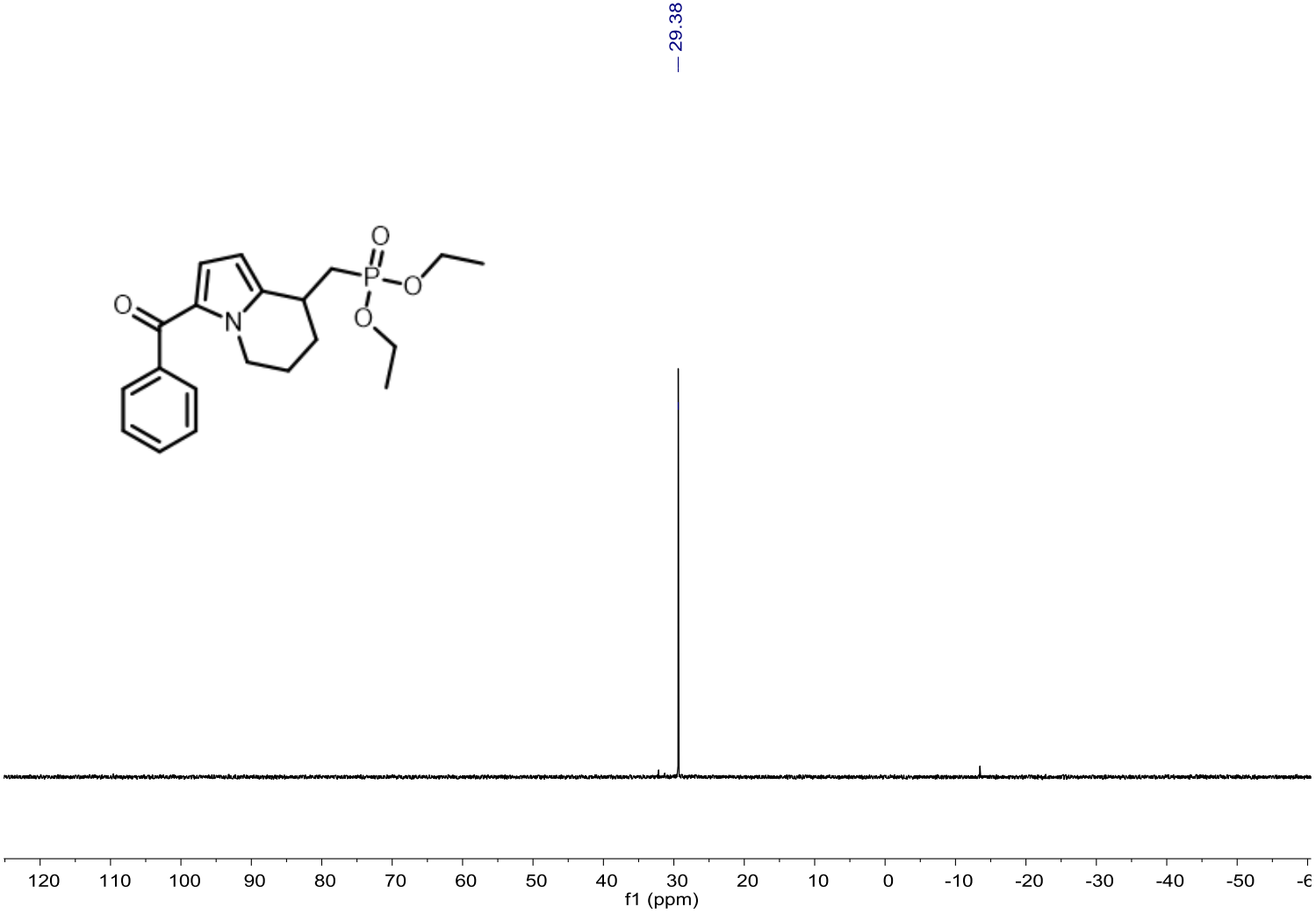
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3aa**



$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3aa**



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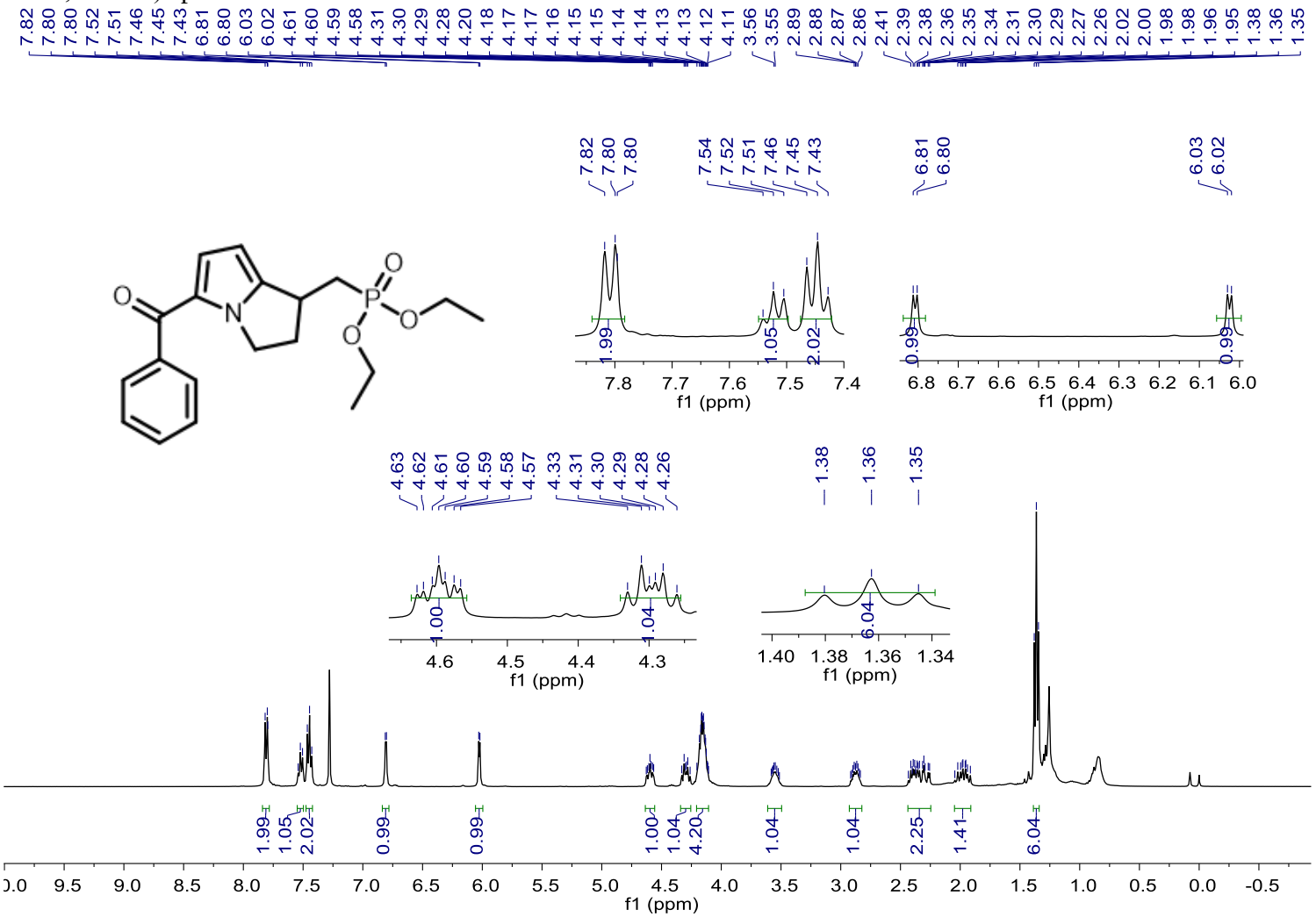
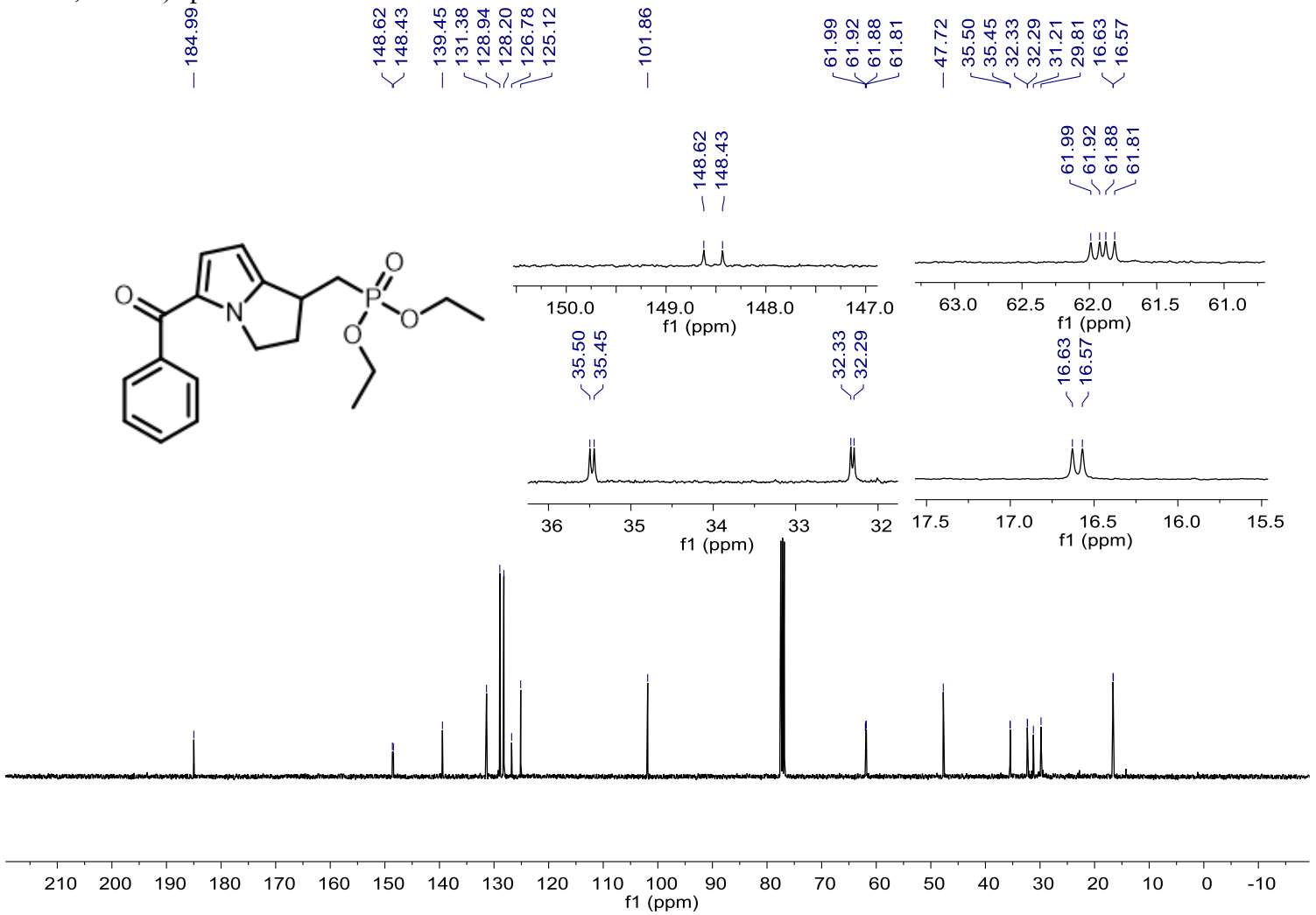
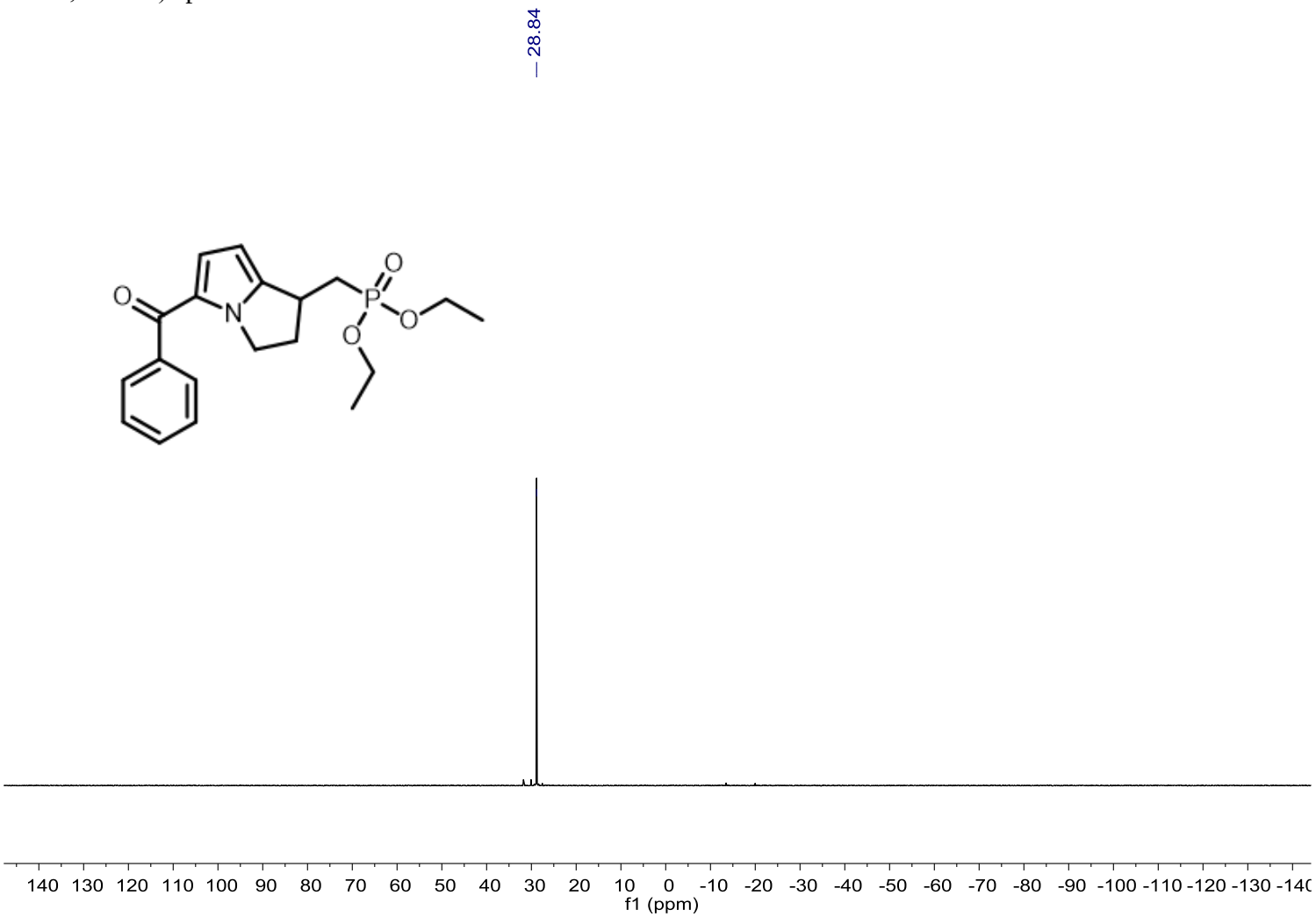


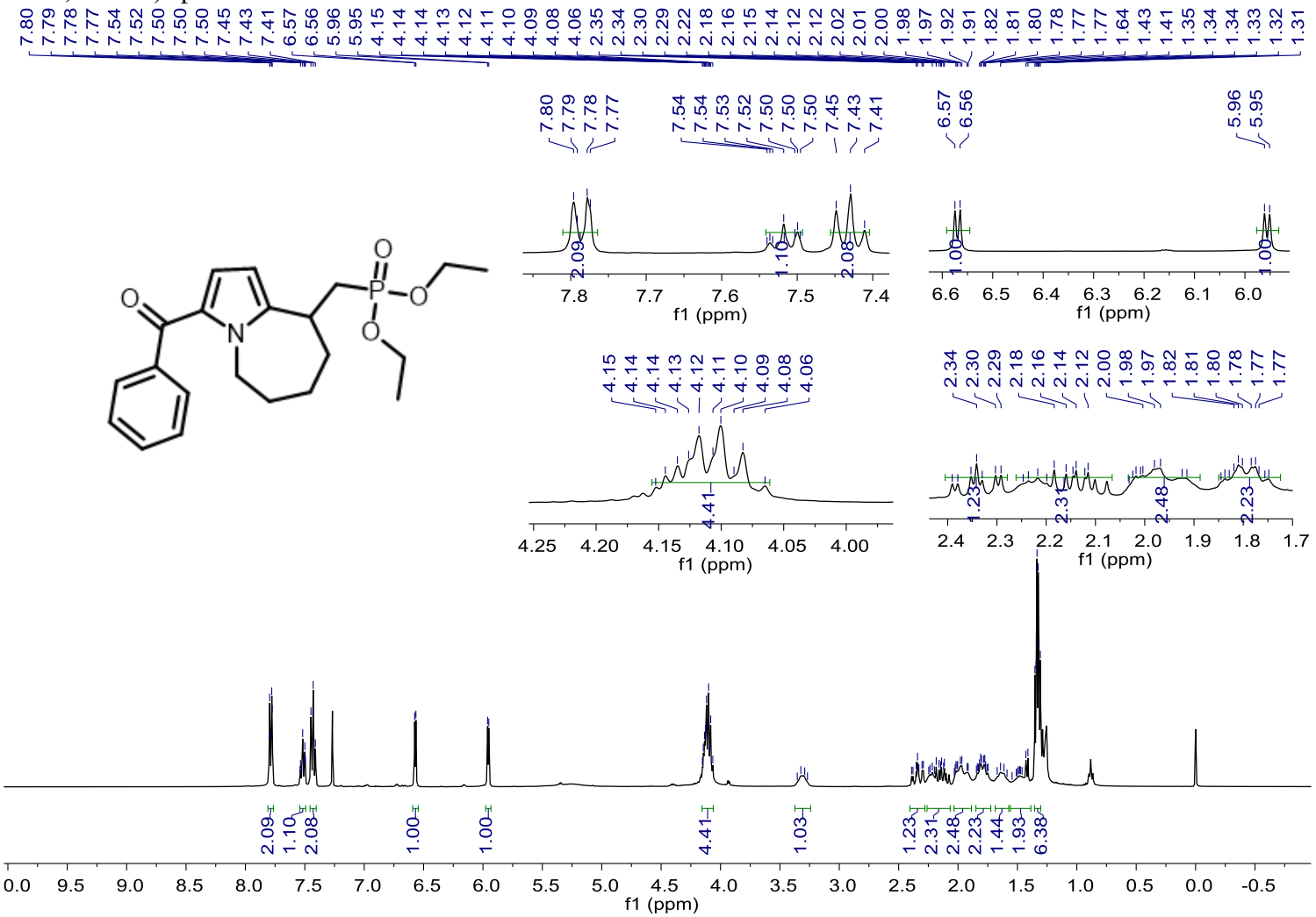
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ba**



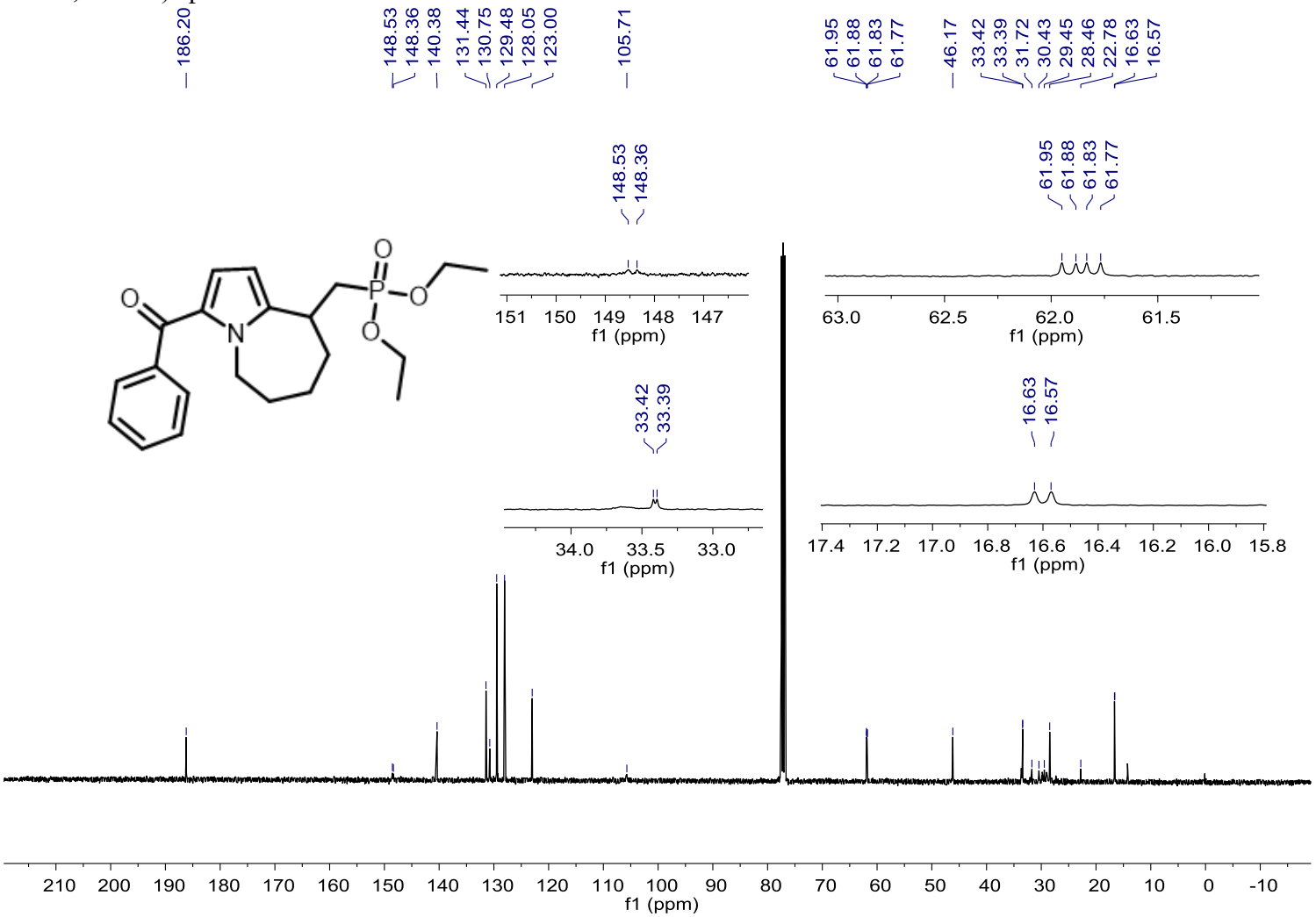
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ba**



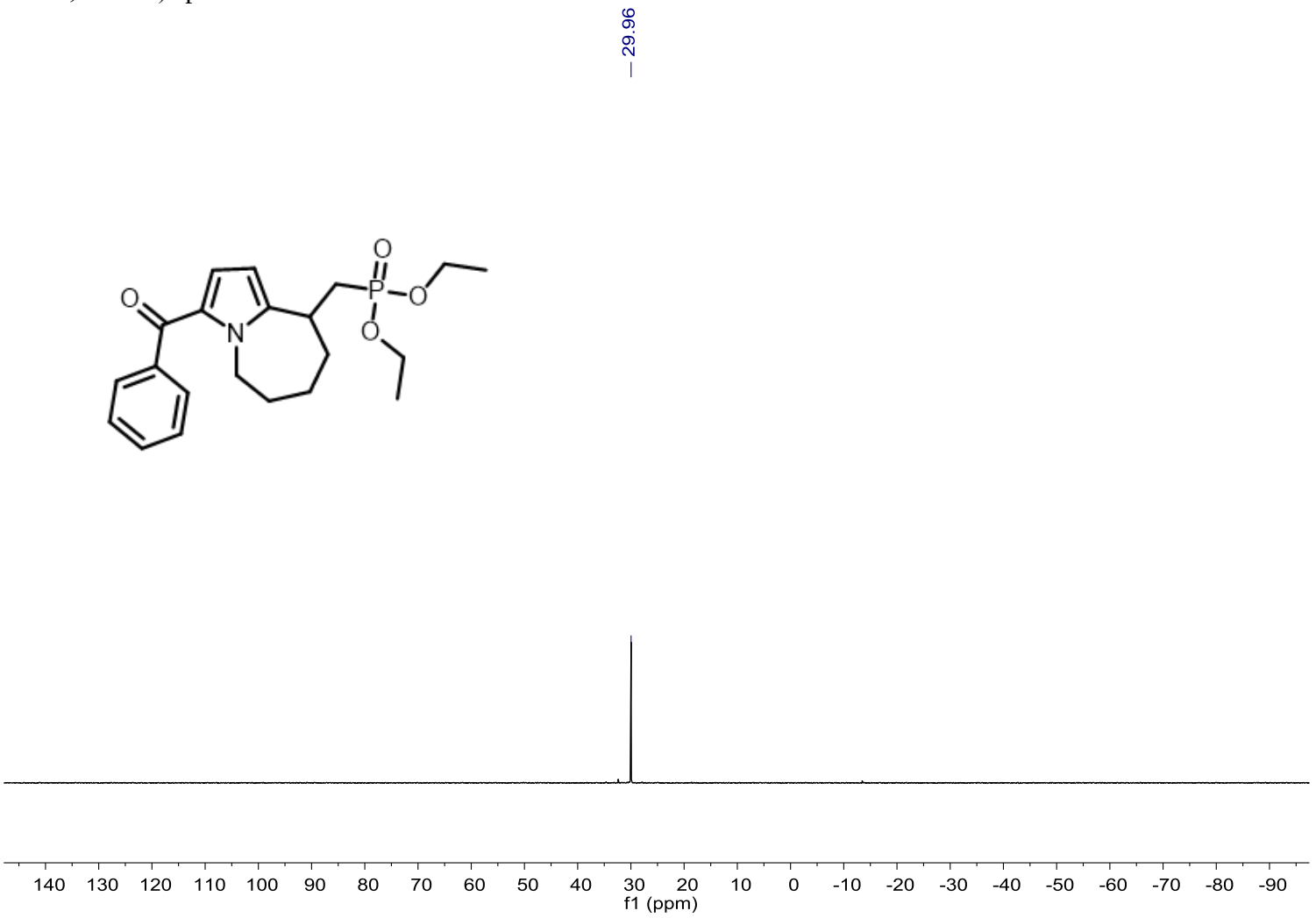
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ca**



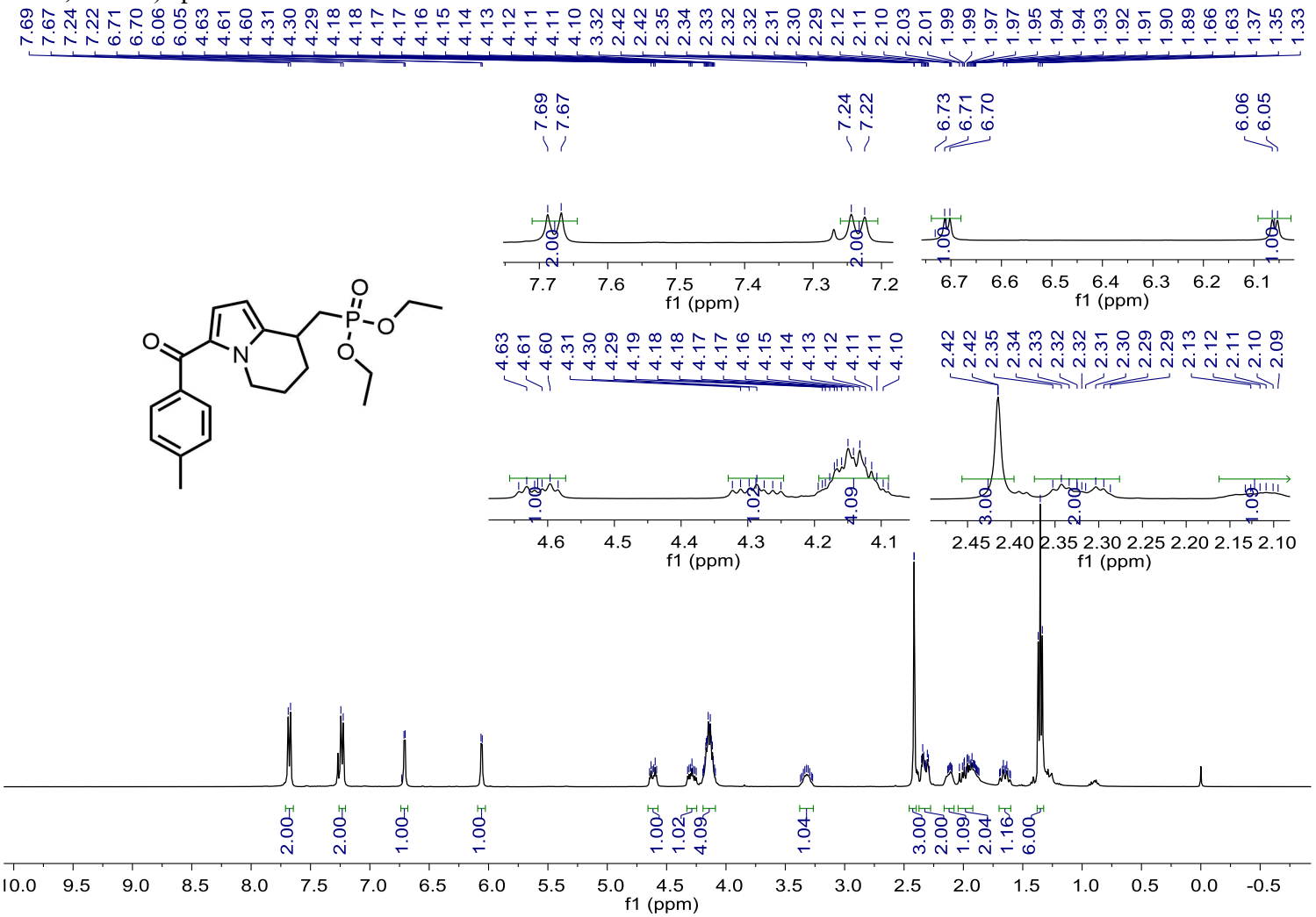
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ca**



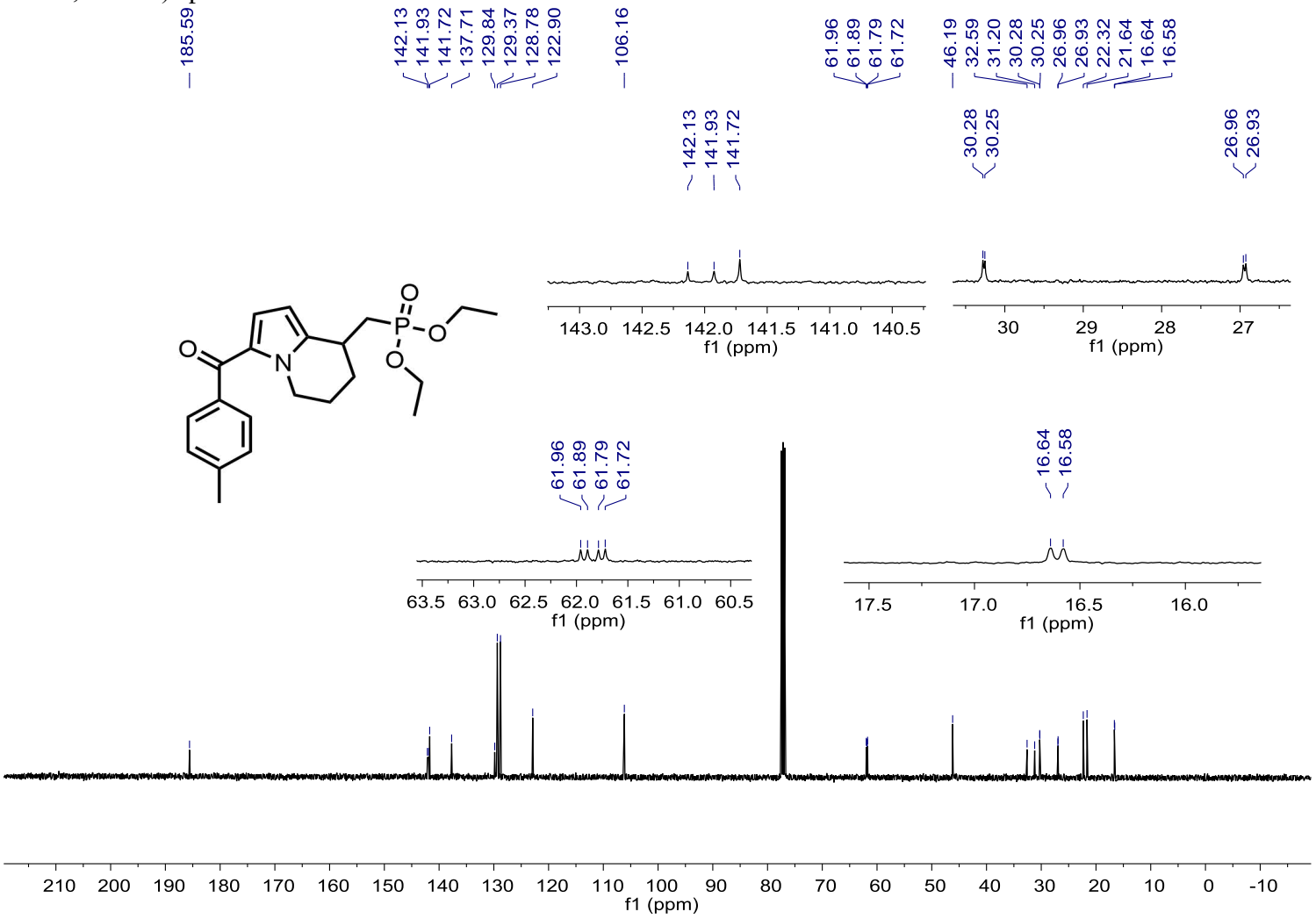
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ca**



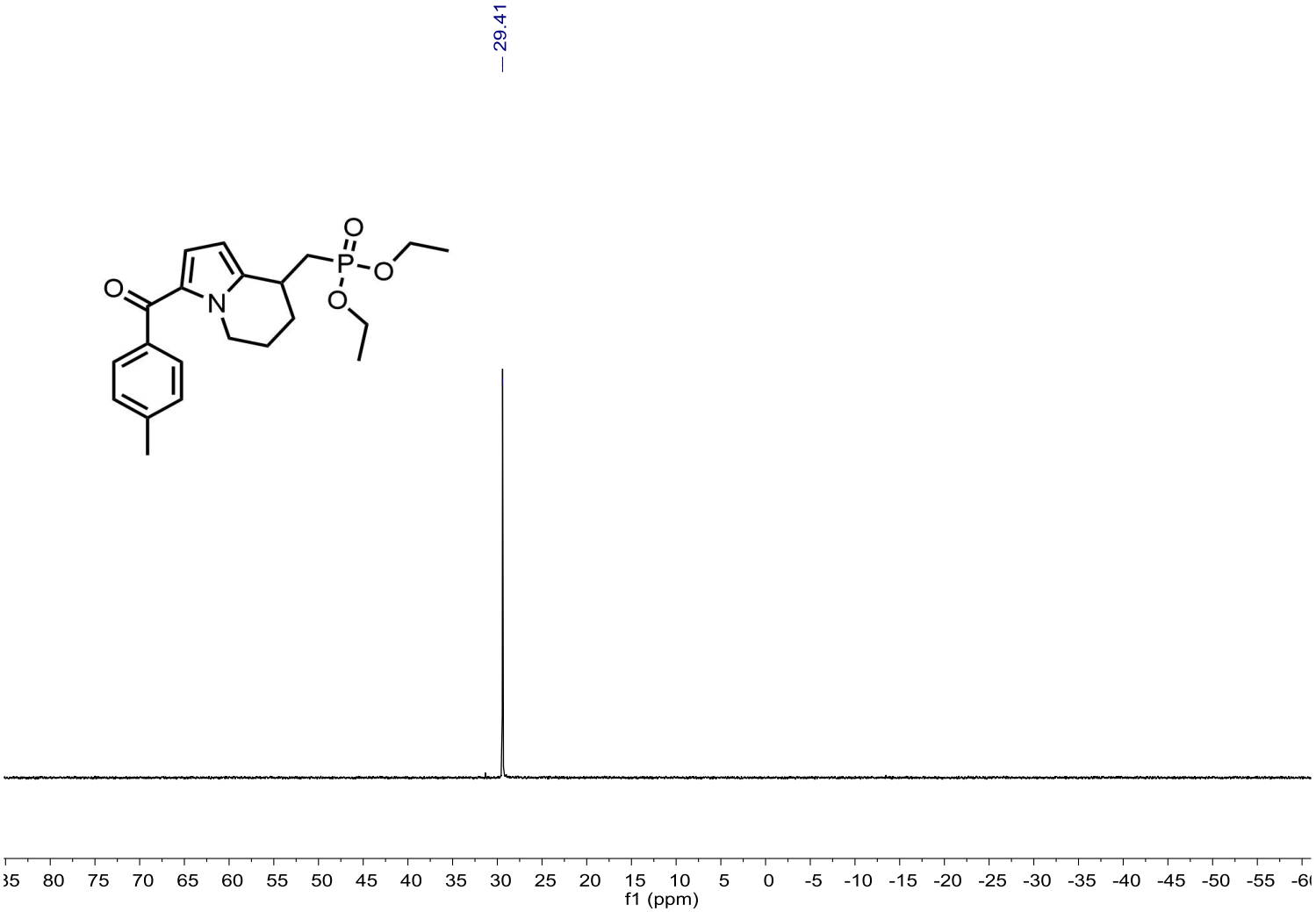
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



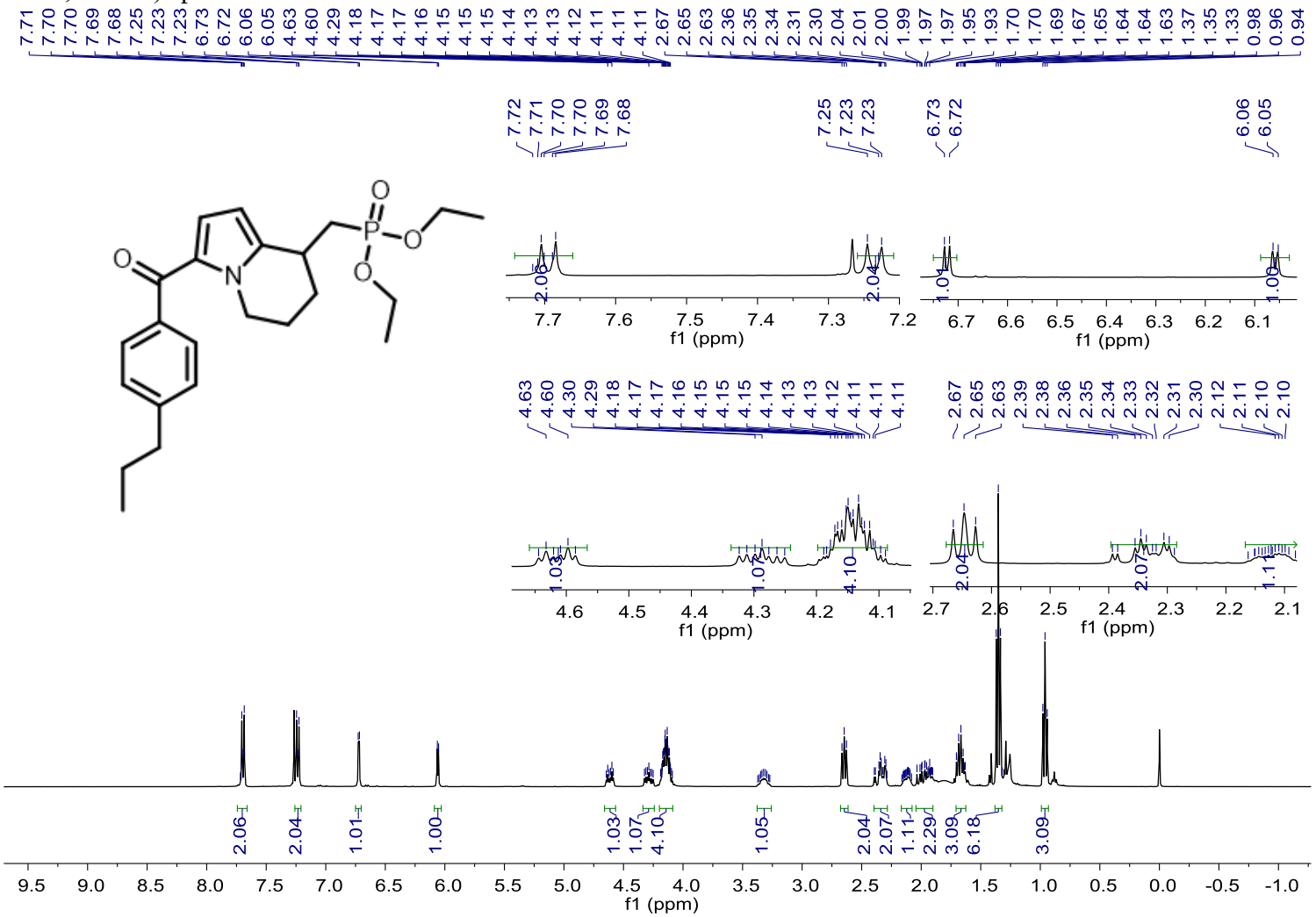
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3da**



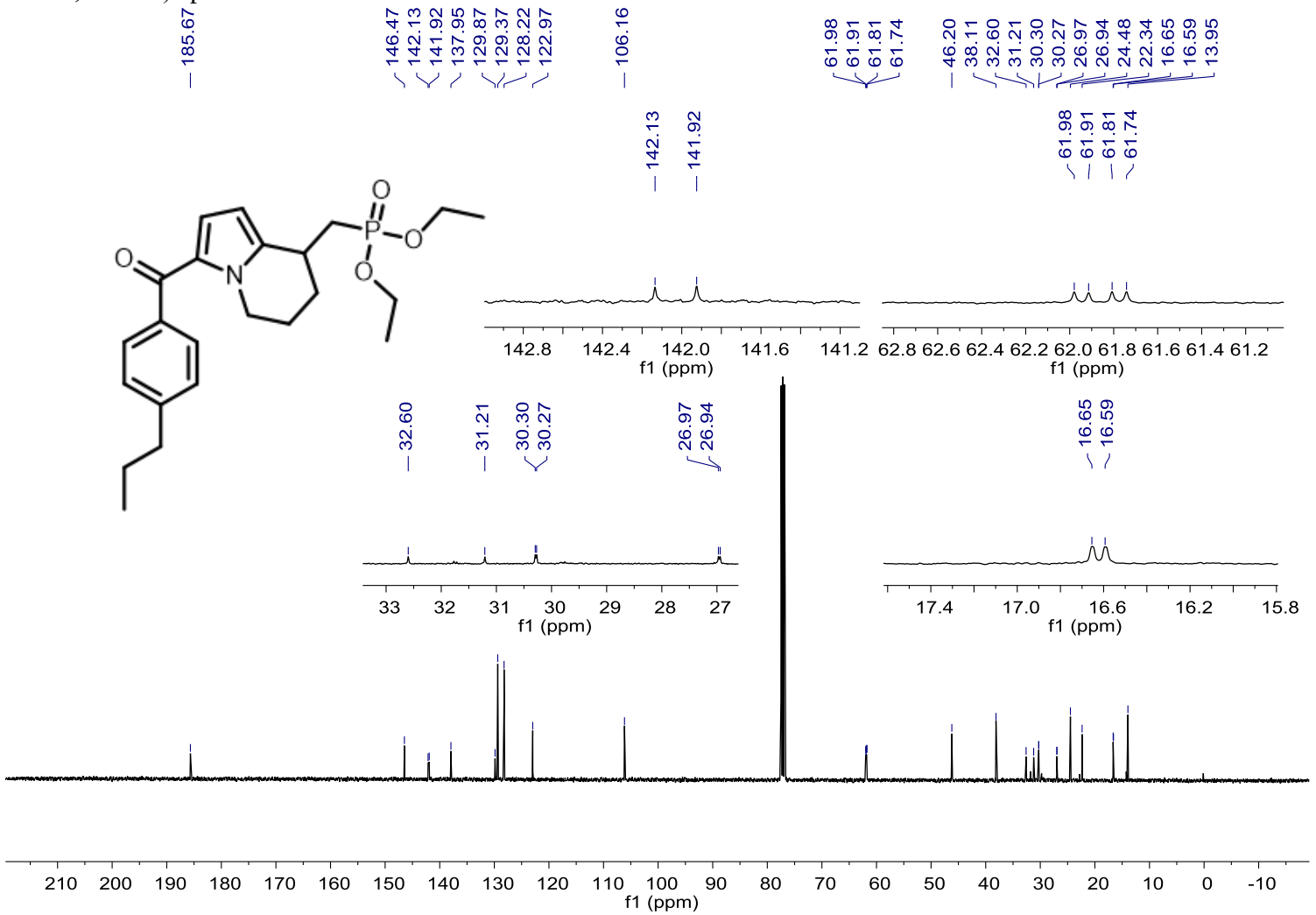
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3da**



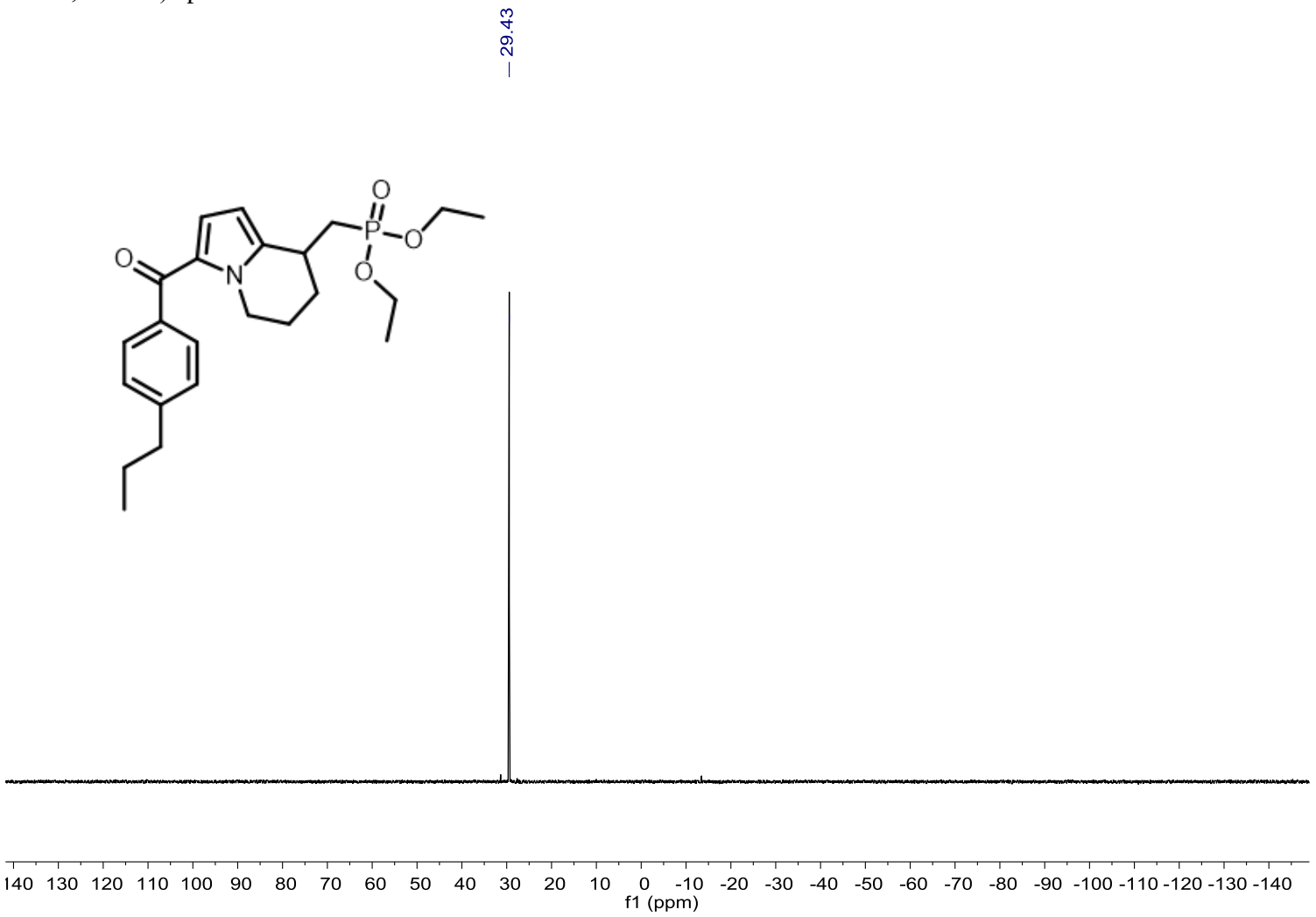
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**



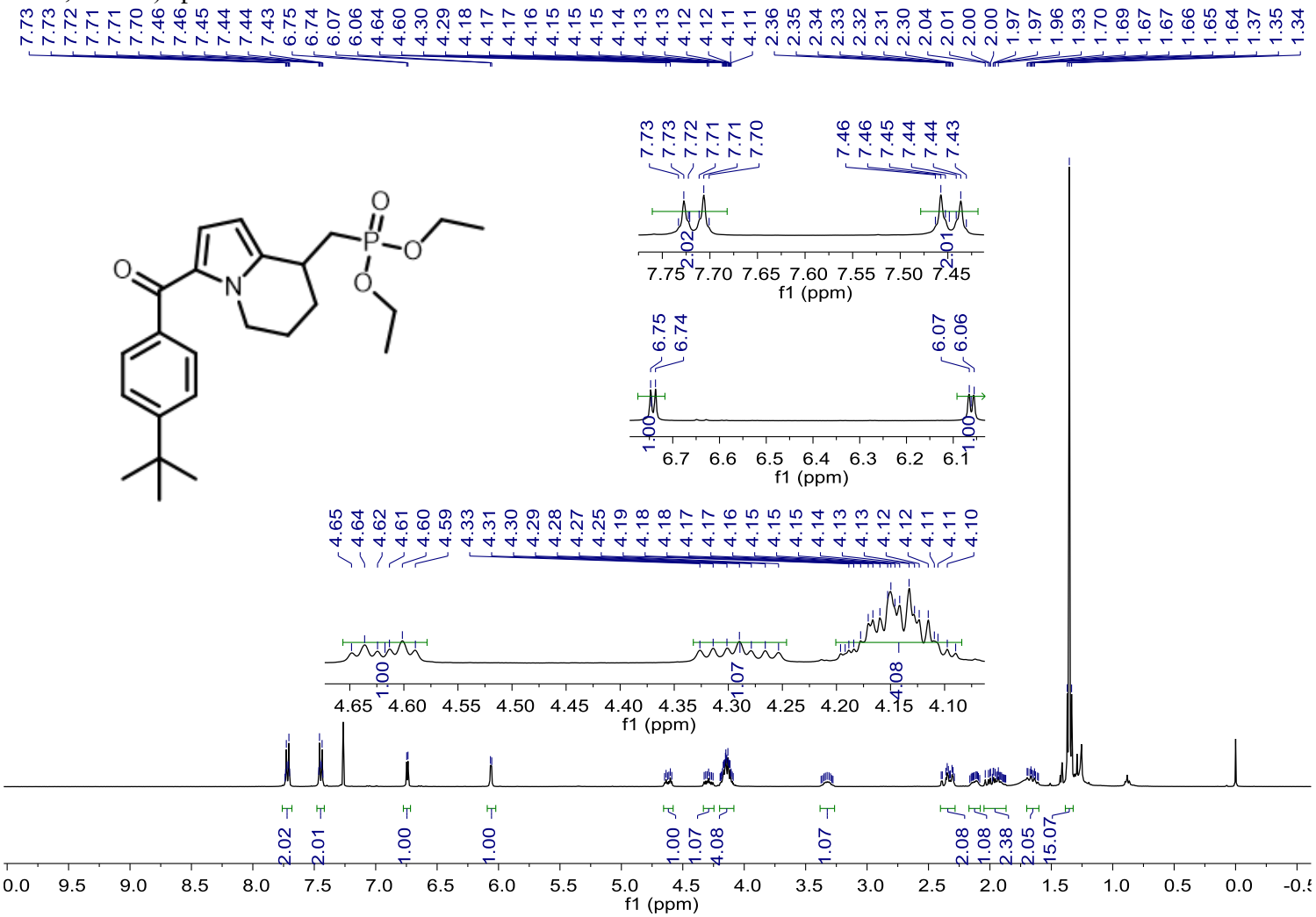
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ea**



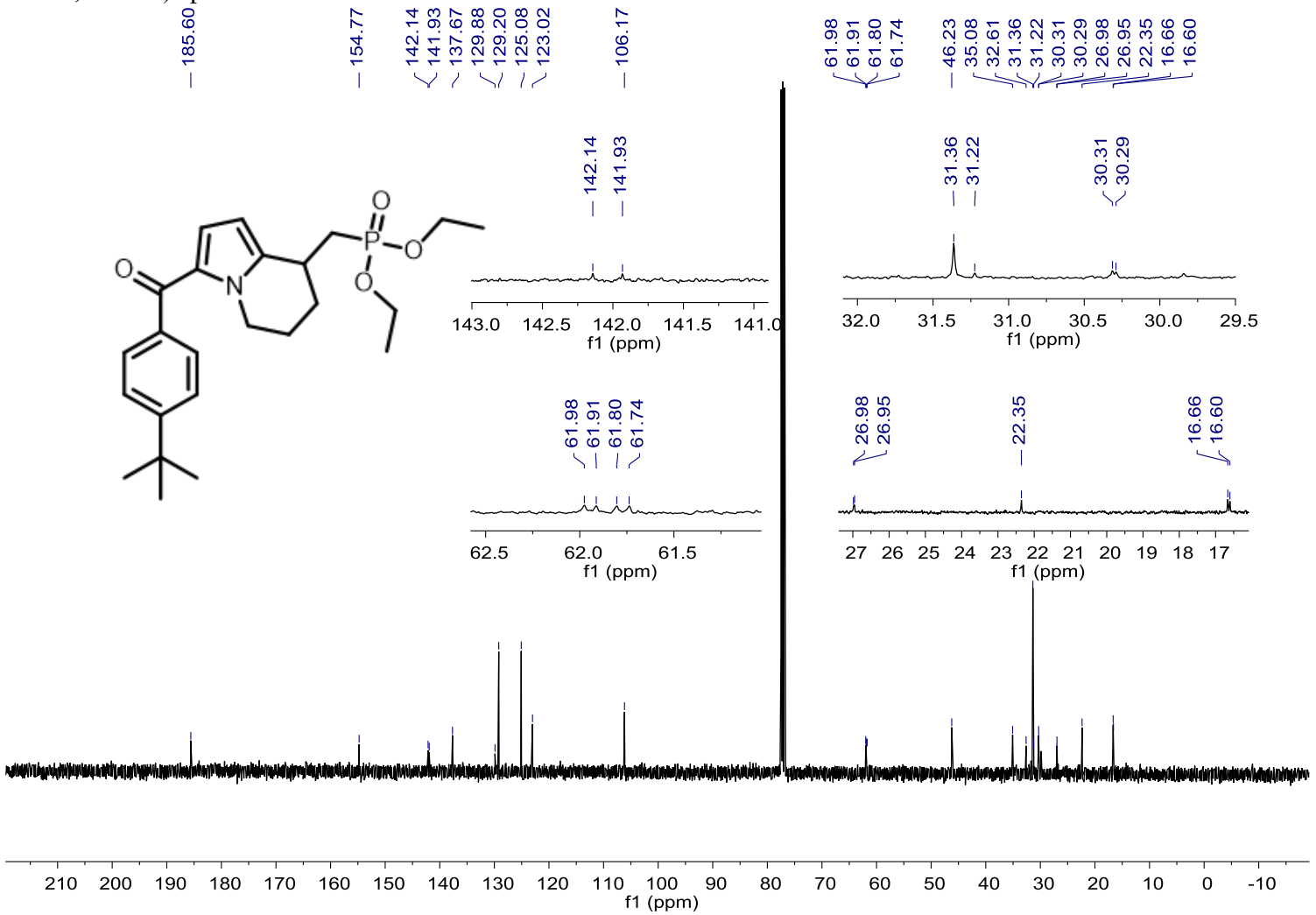
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ea**



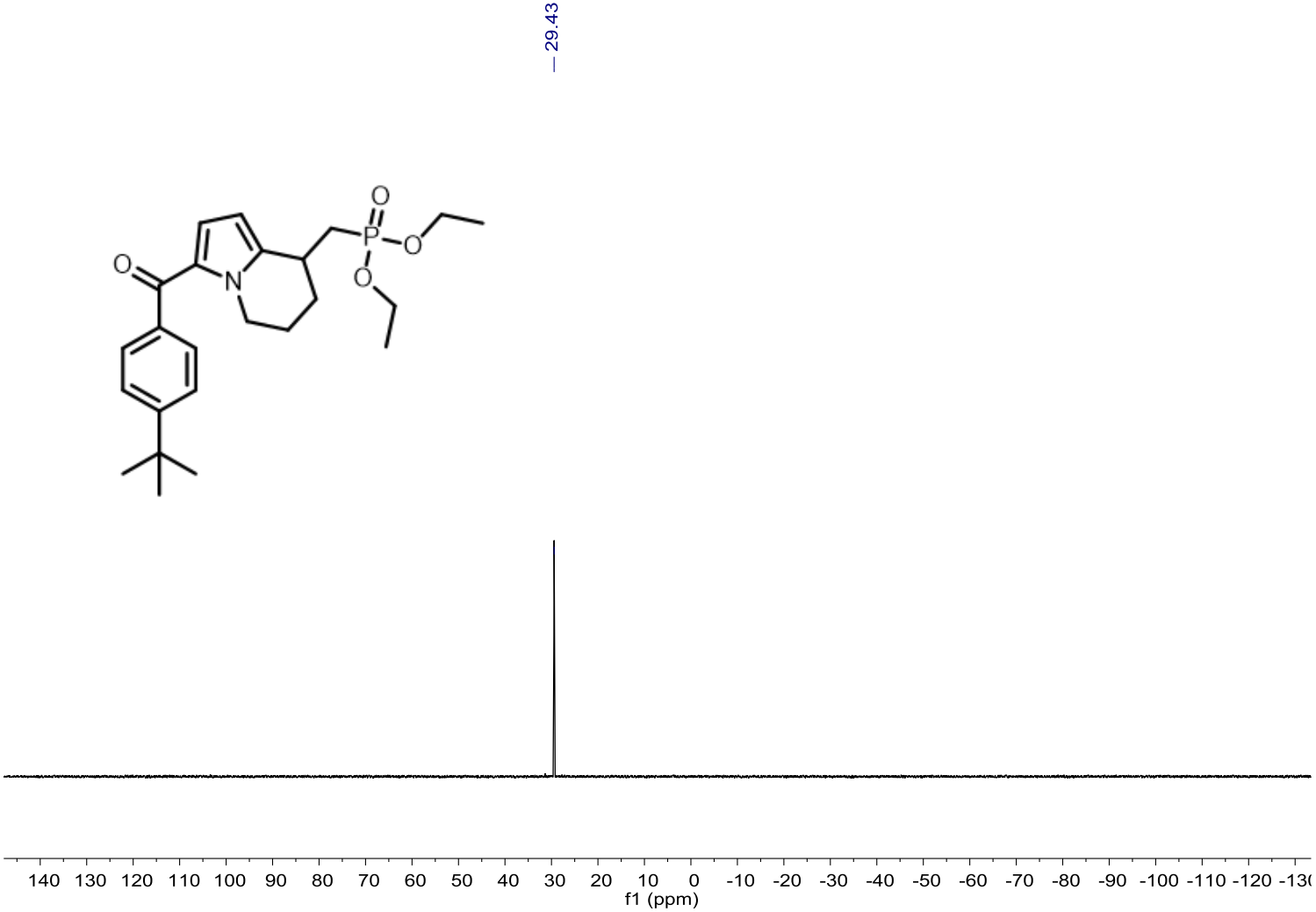
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**



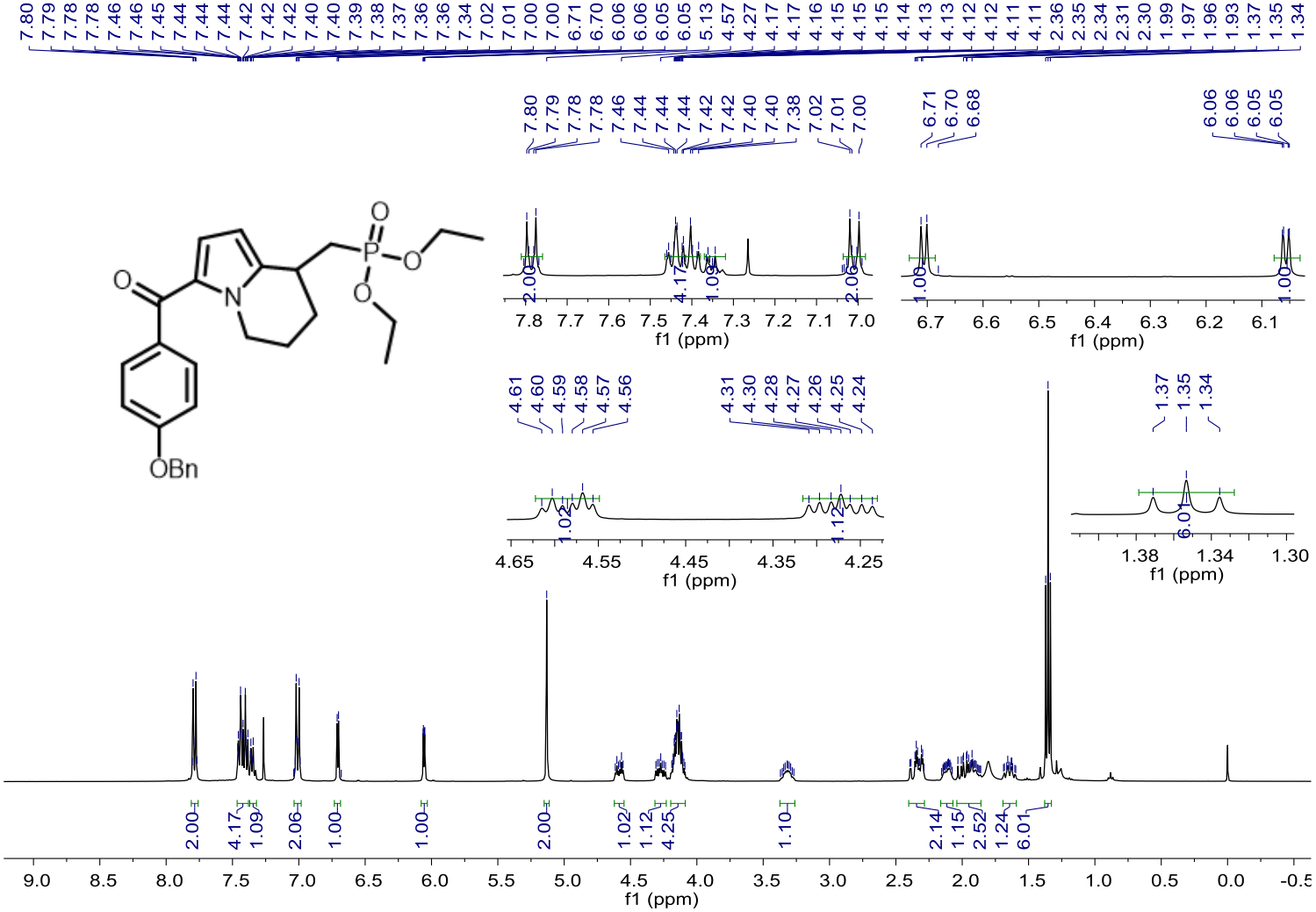
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3fa**



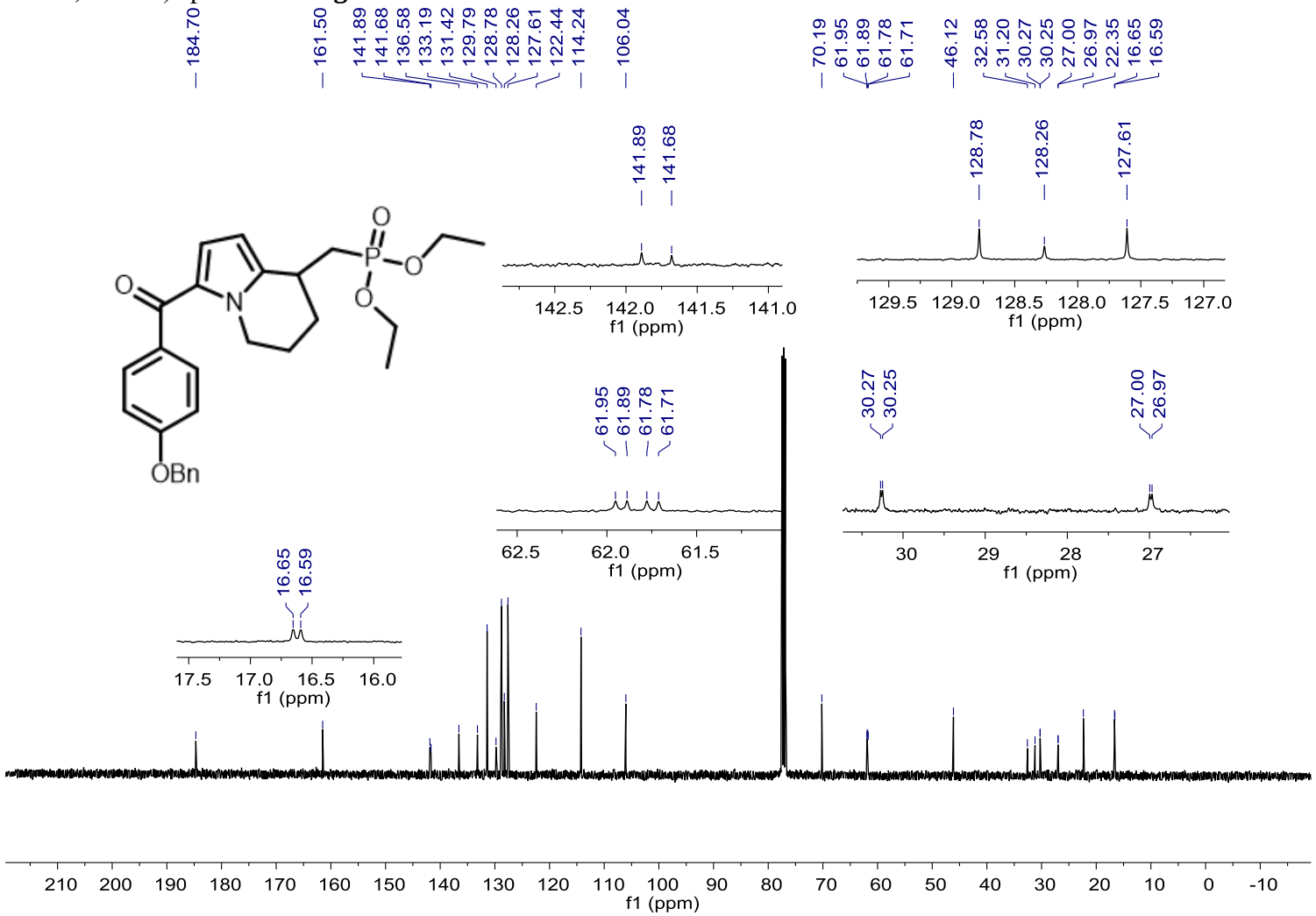
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3fa**



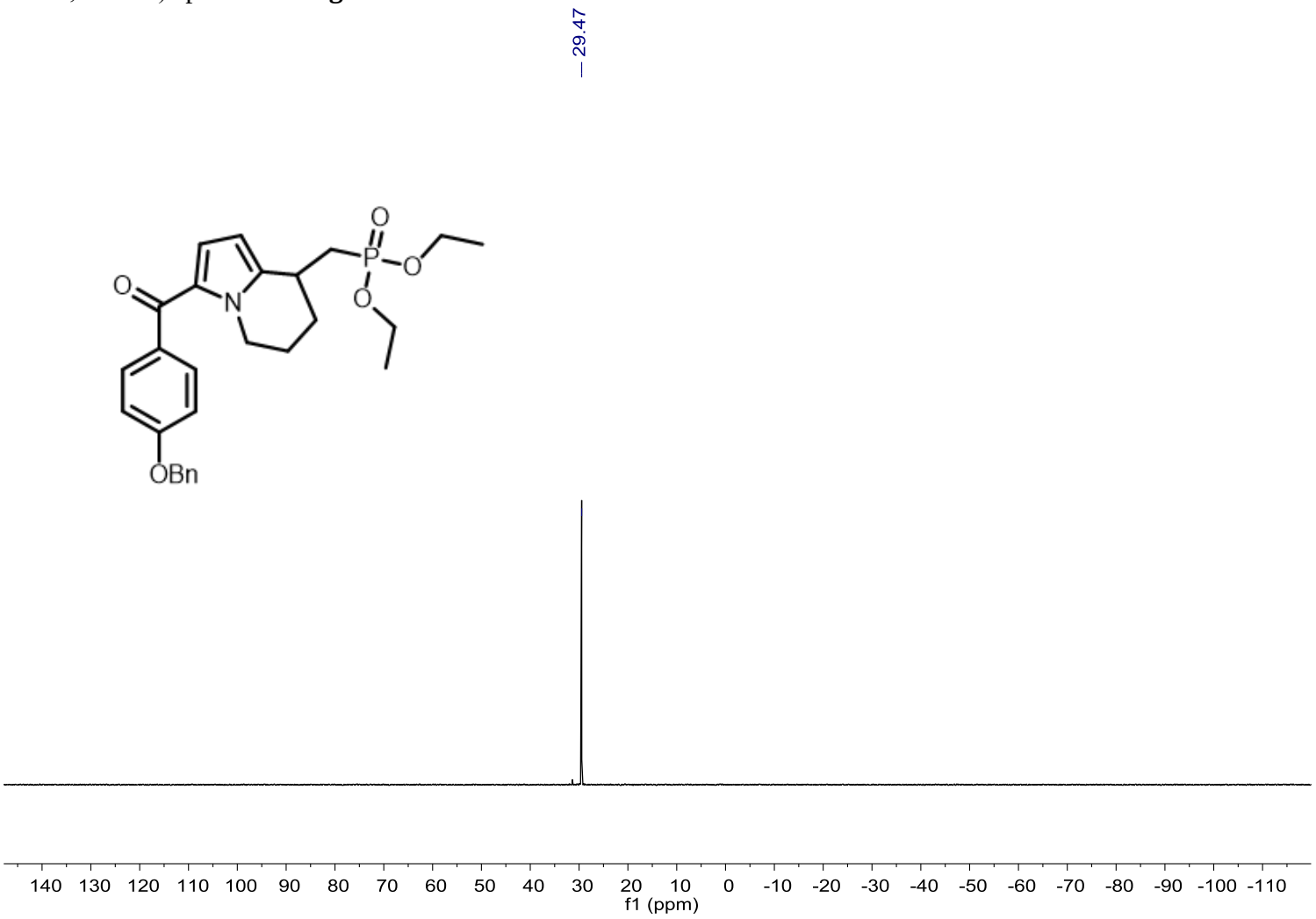
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



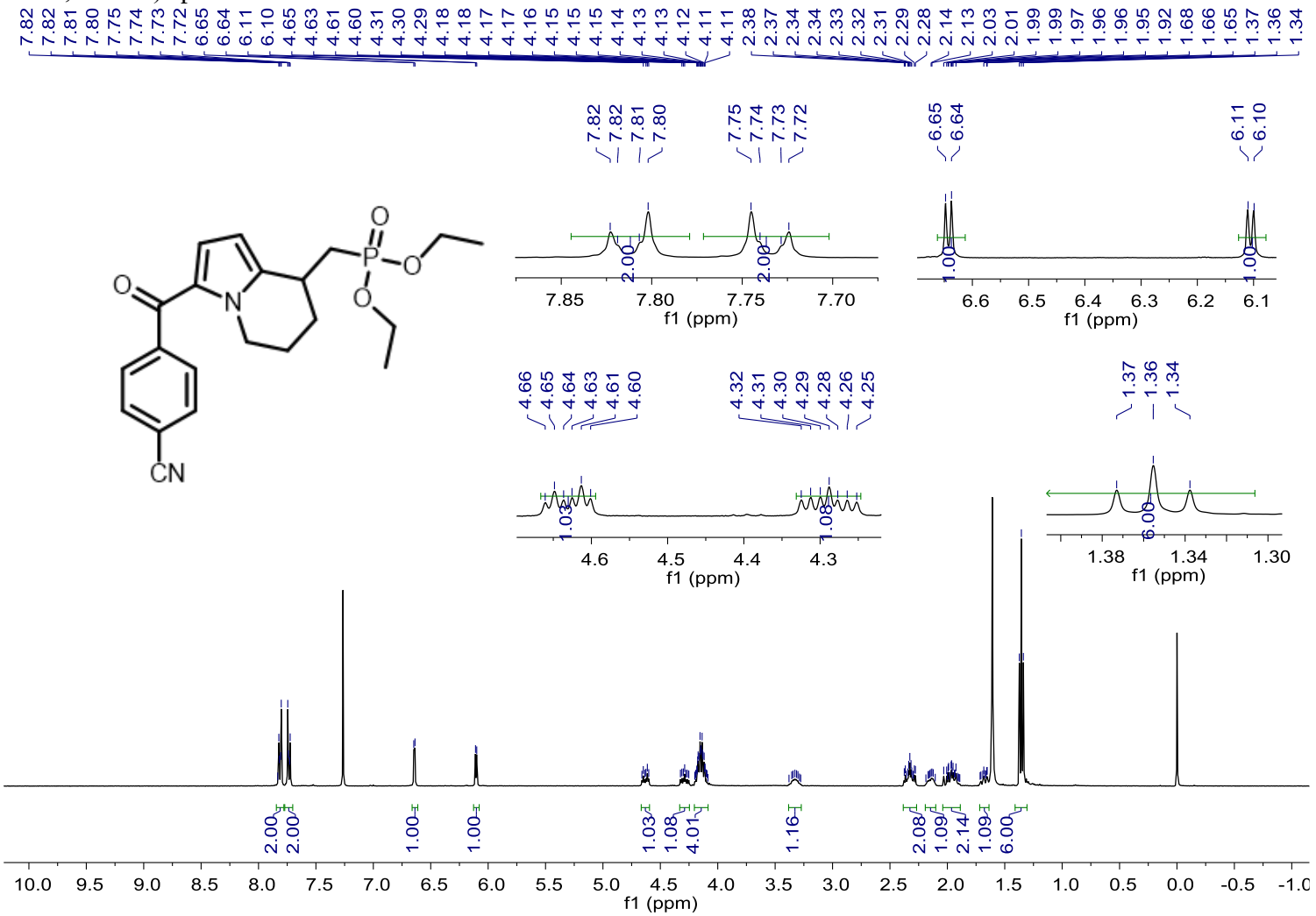
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ga**



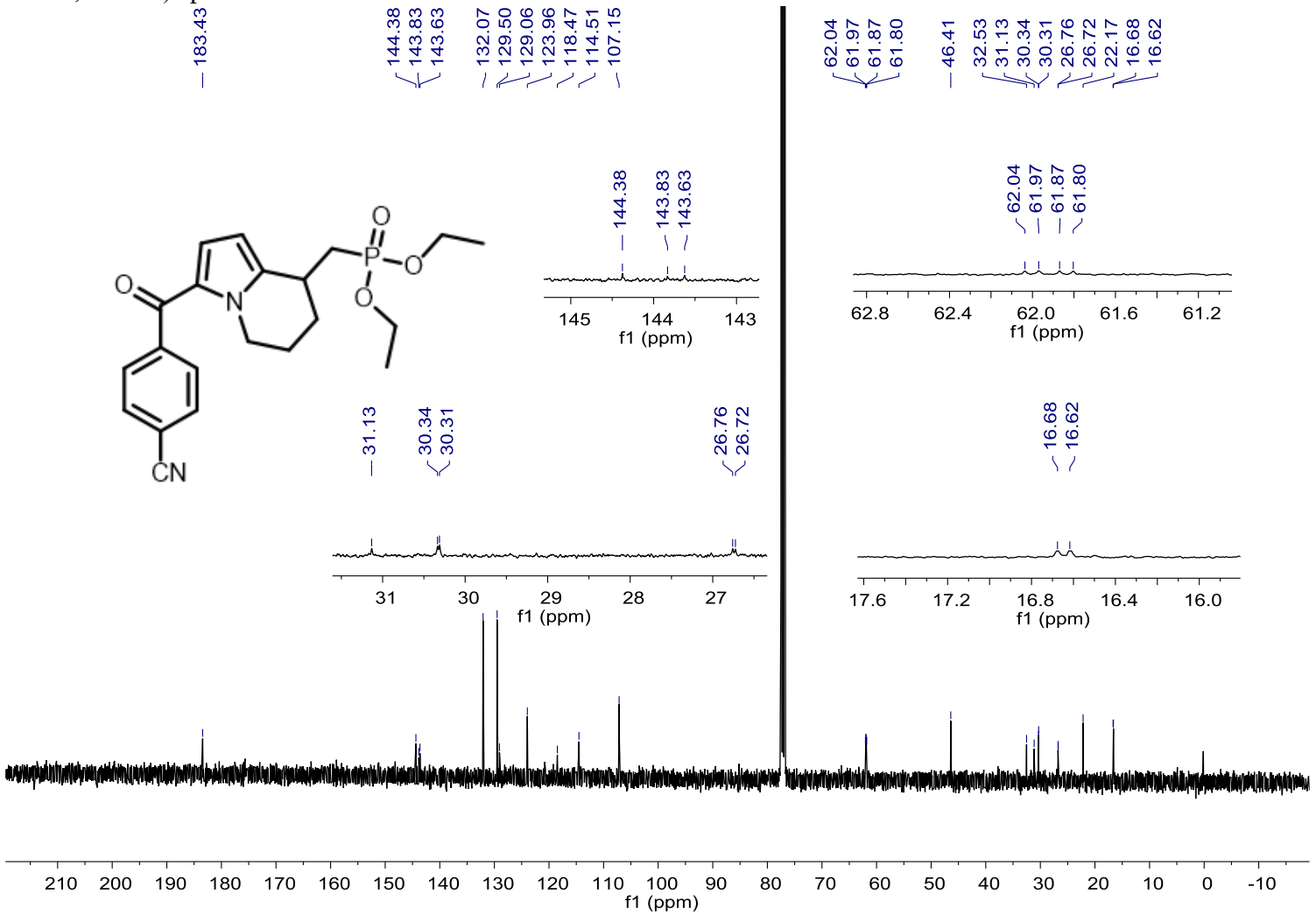
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ga**



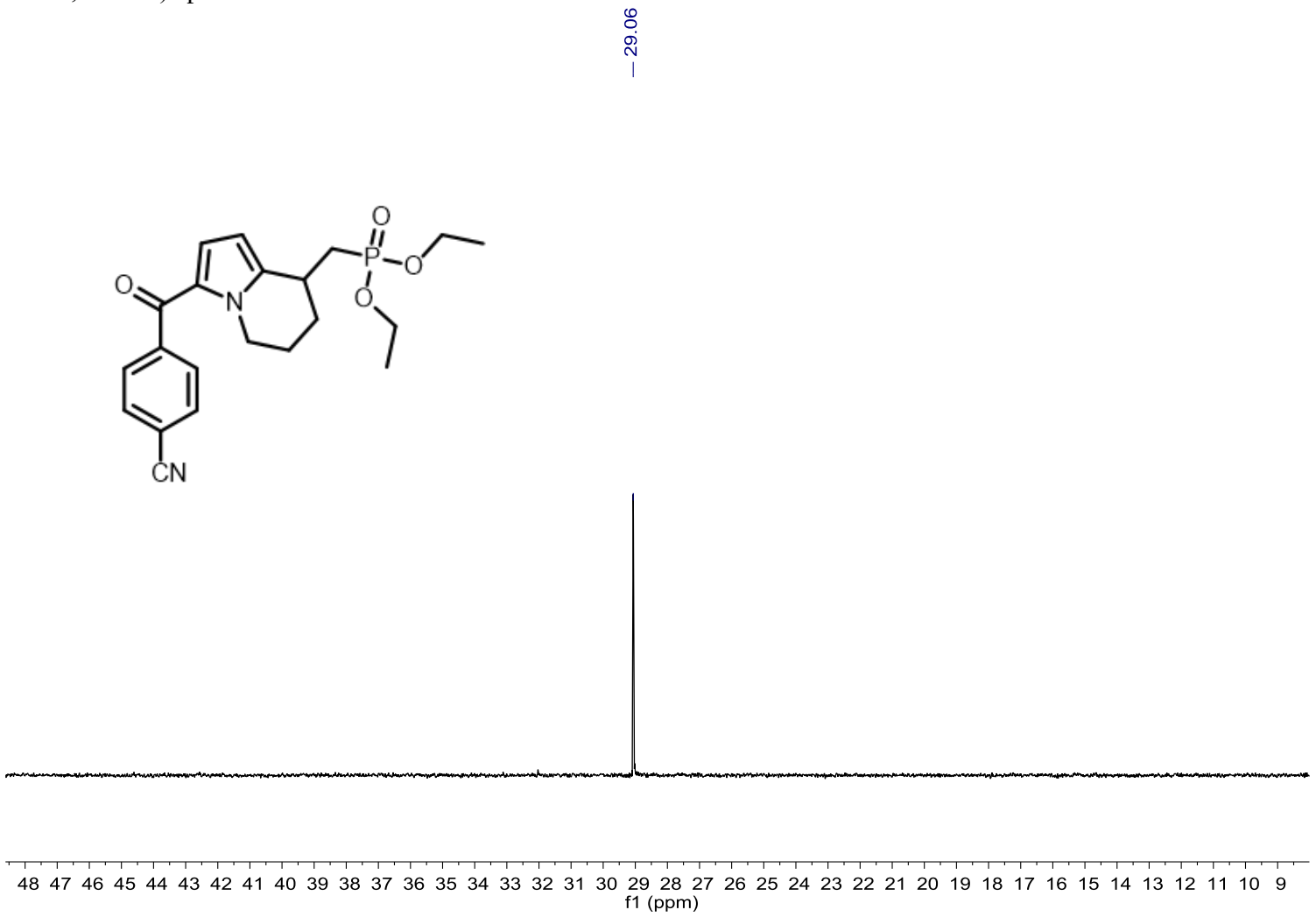
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



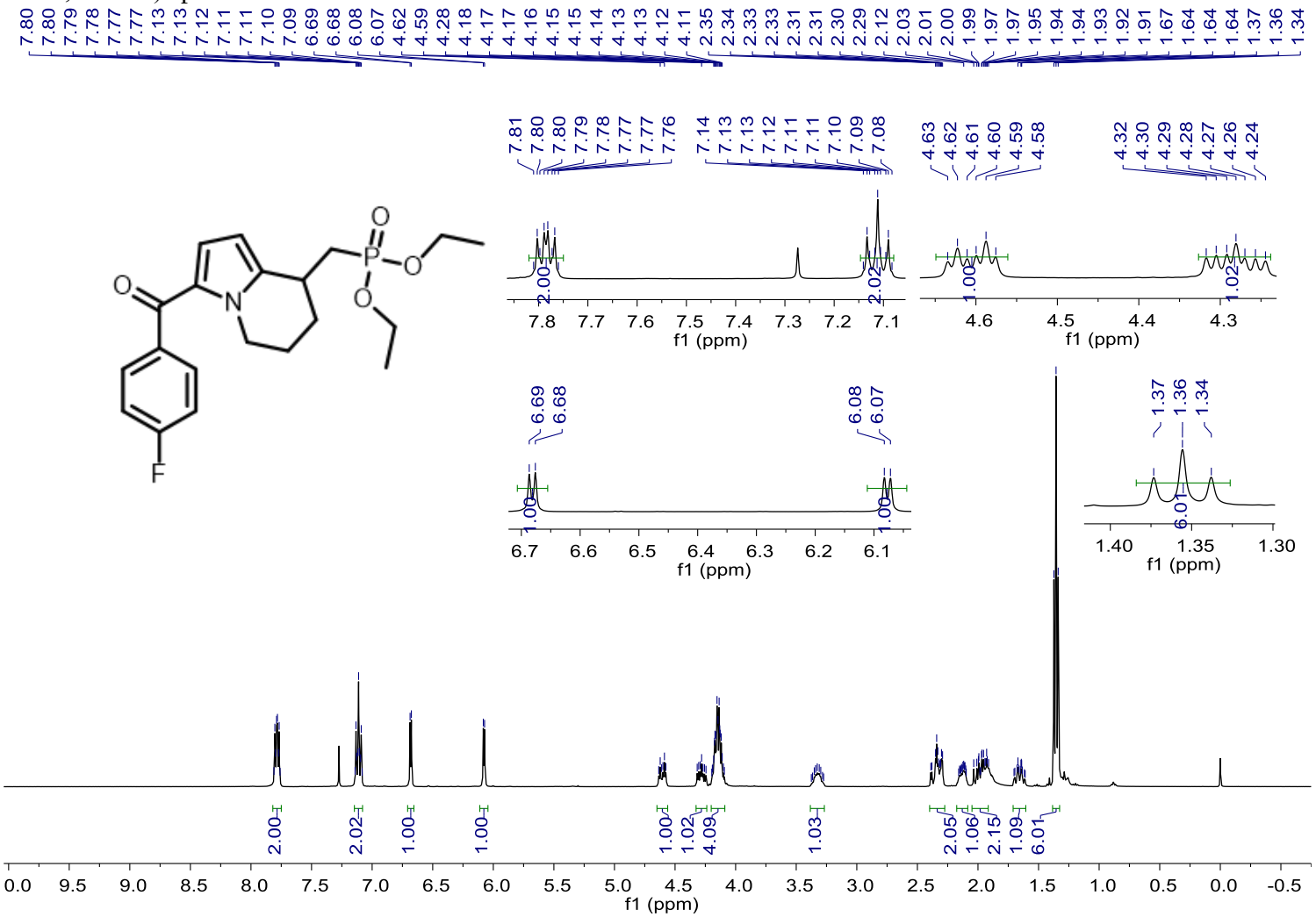
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ha**



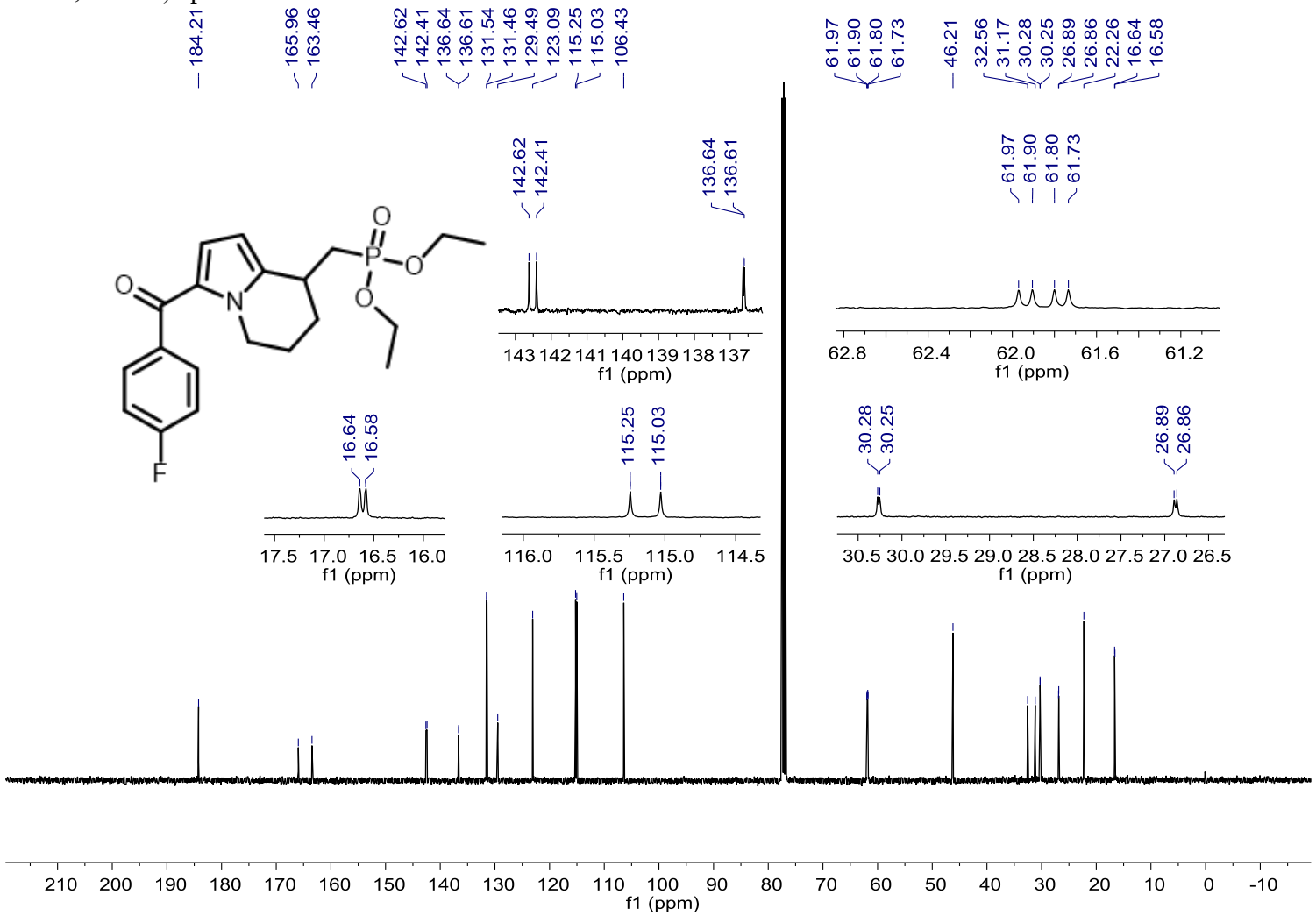
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ha**



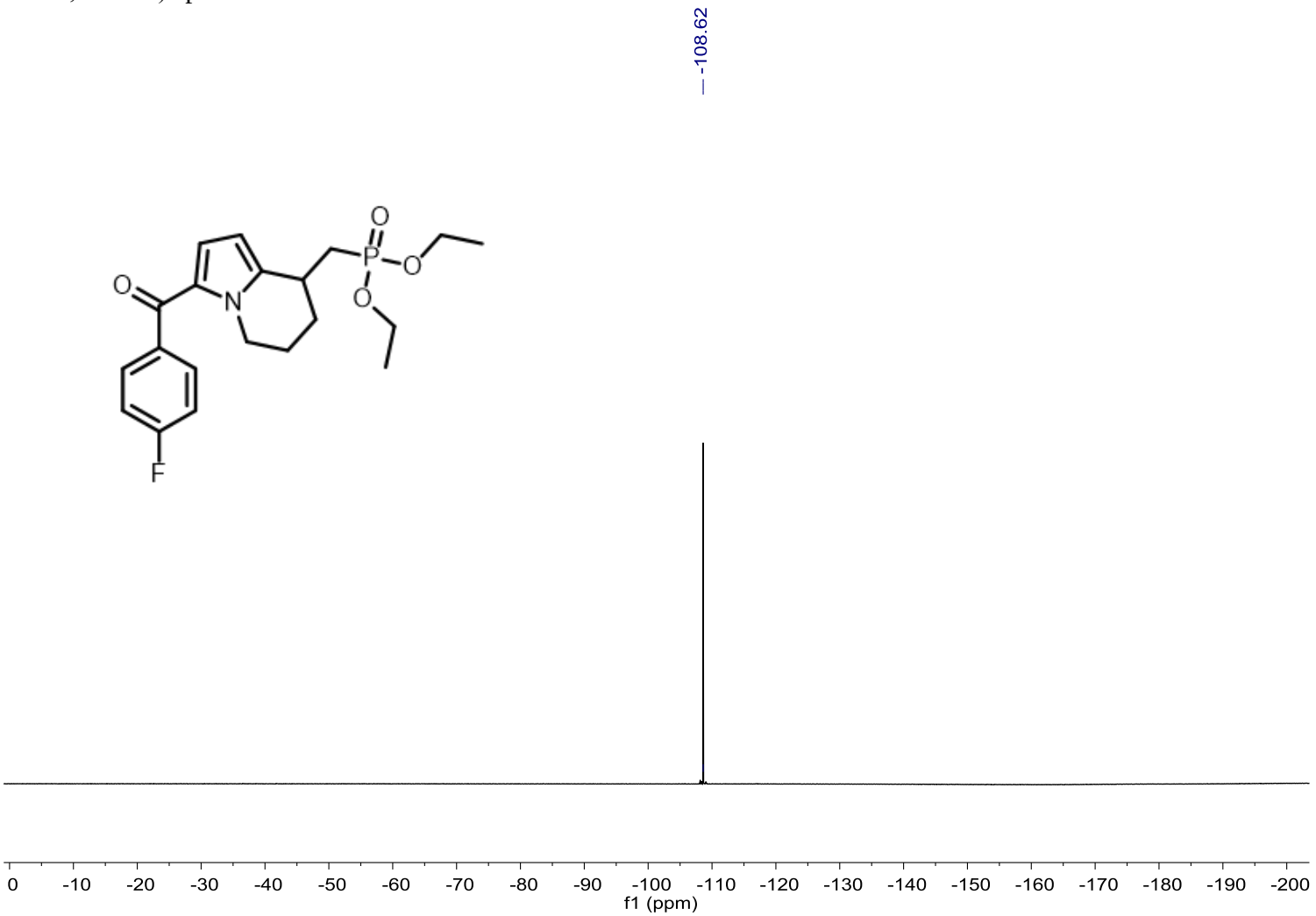
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ia**



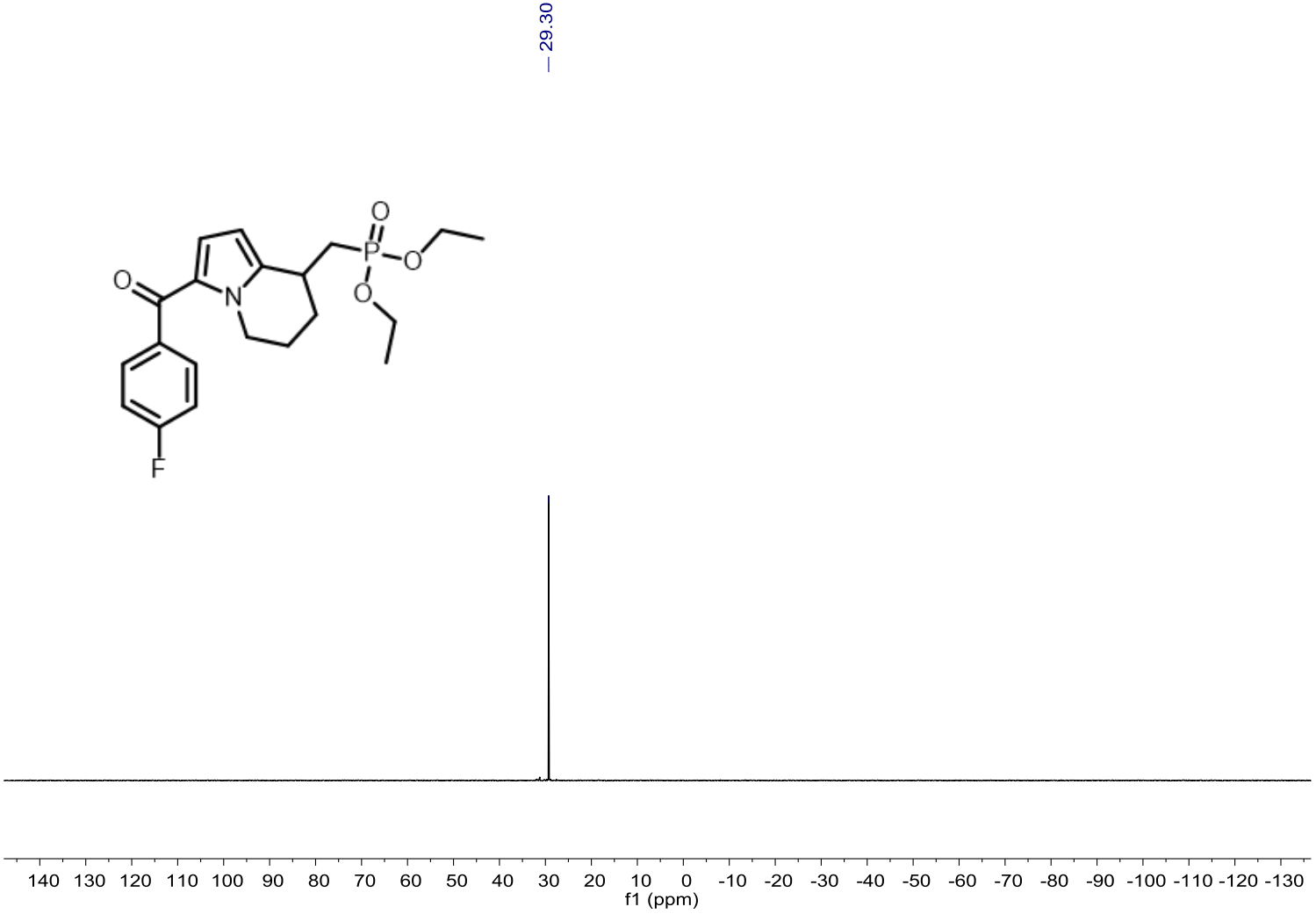
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ia**



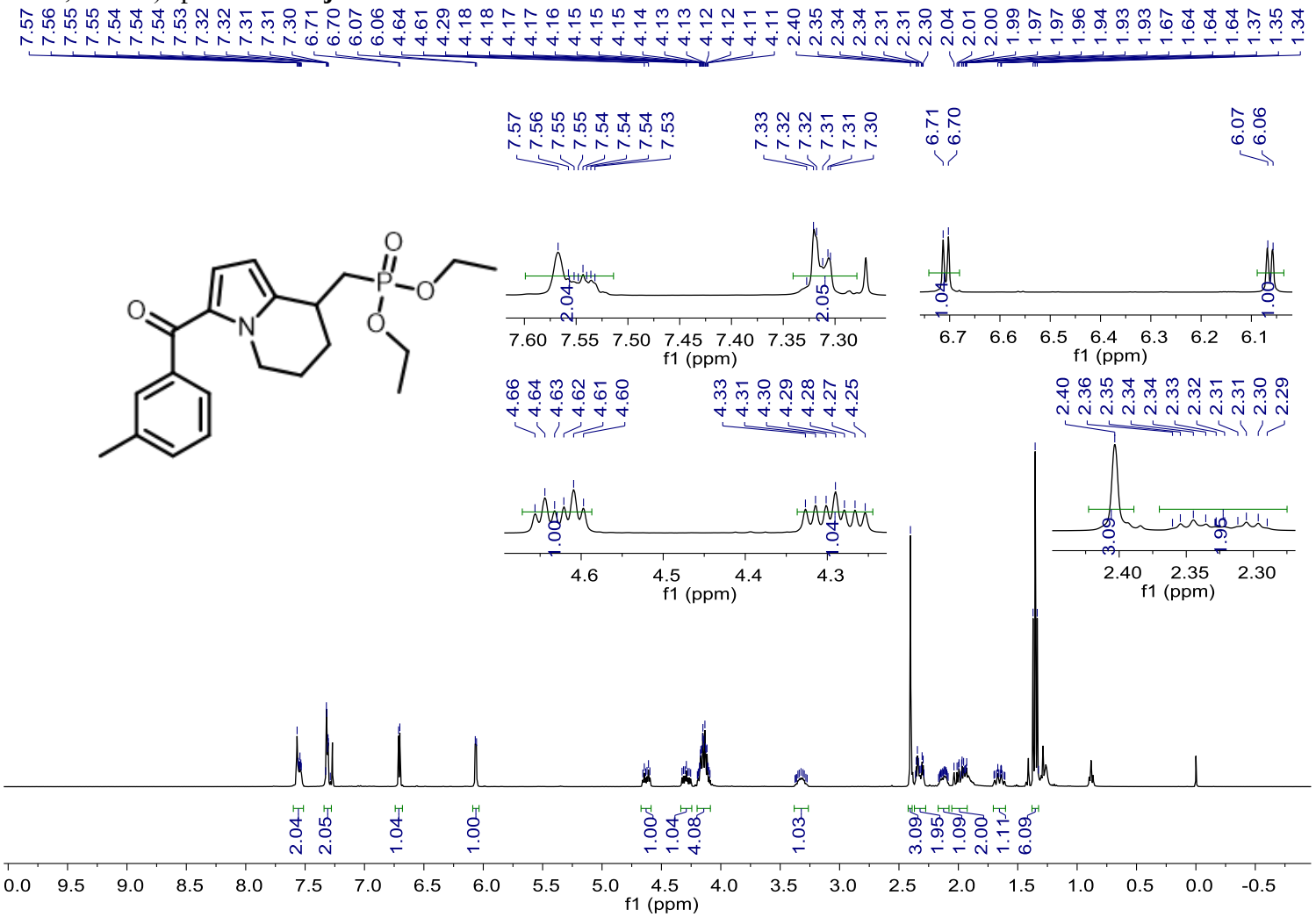
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **3ia**



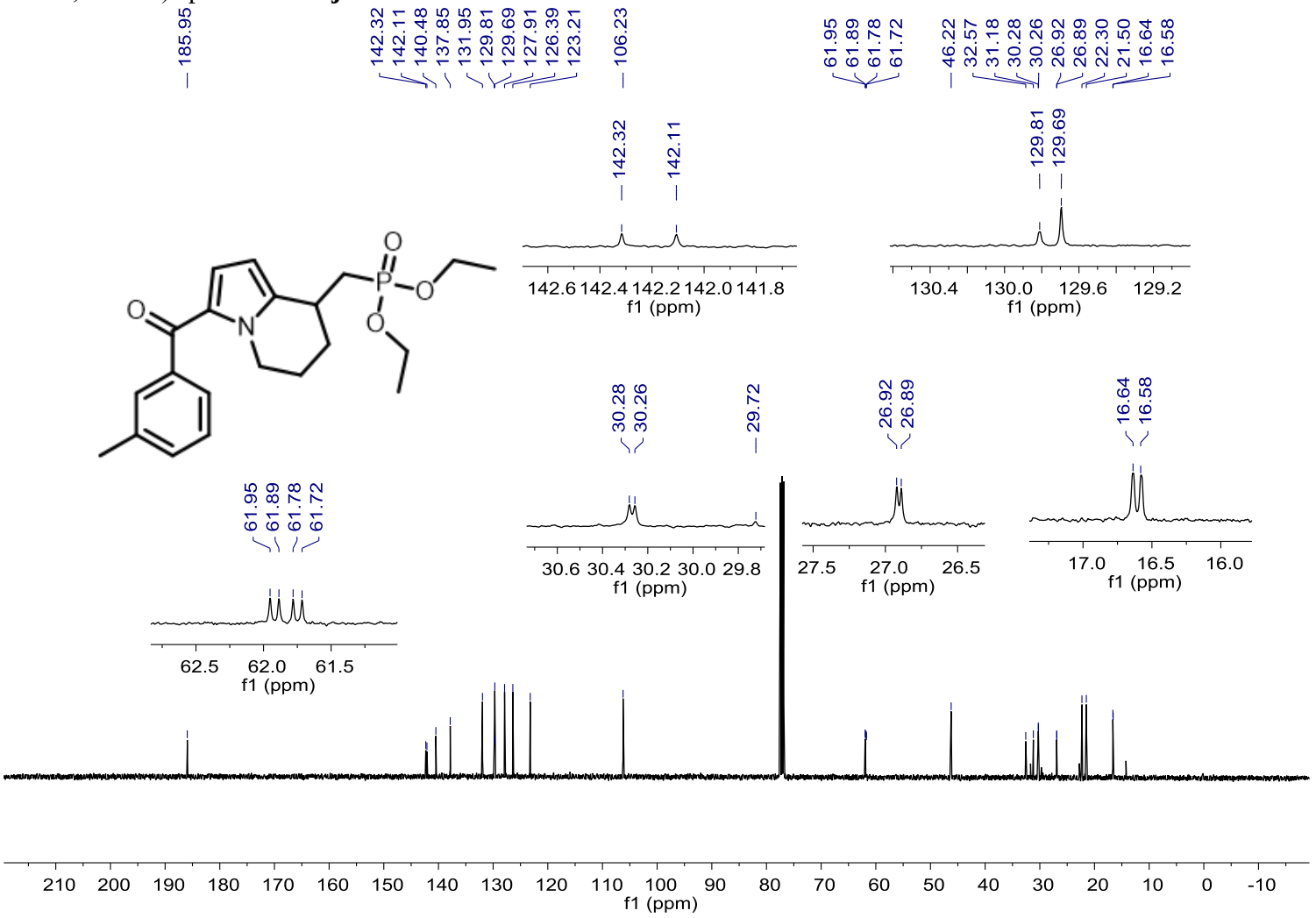
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ia**



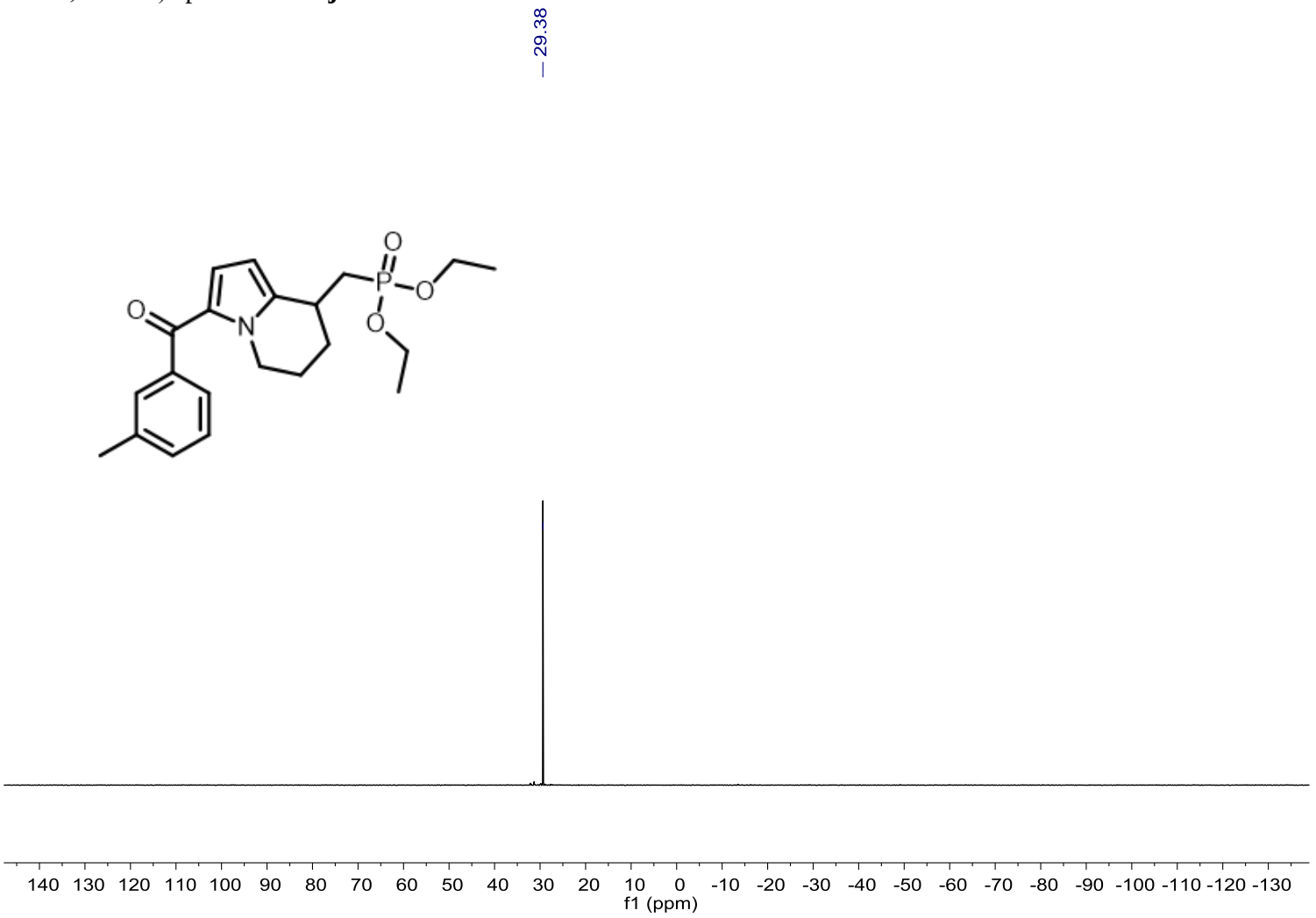
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ja**



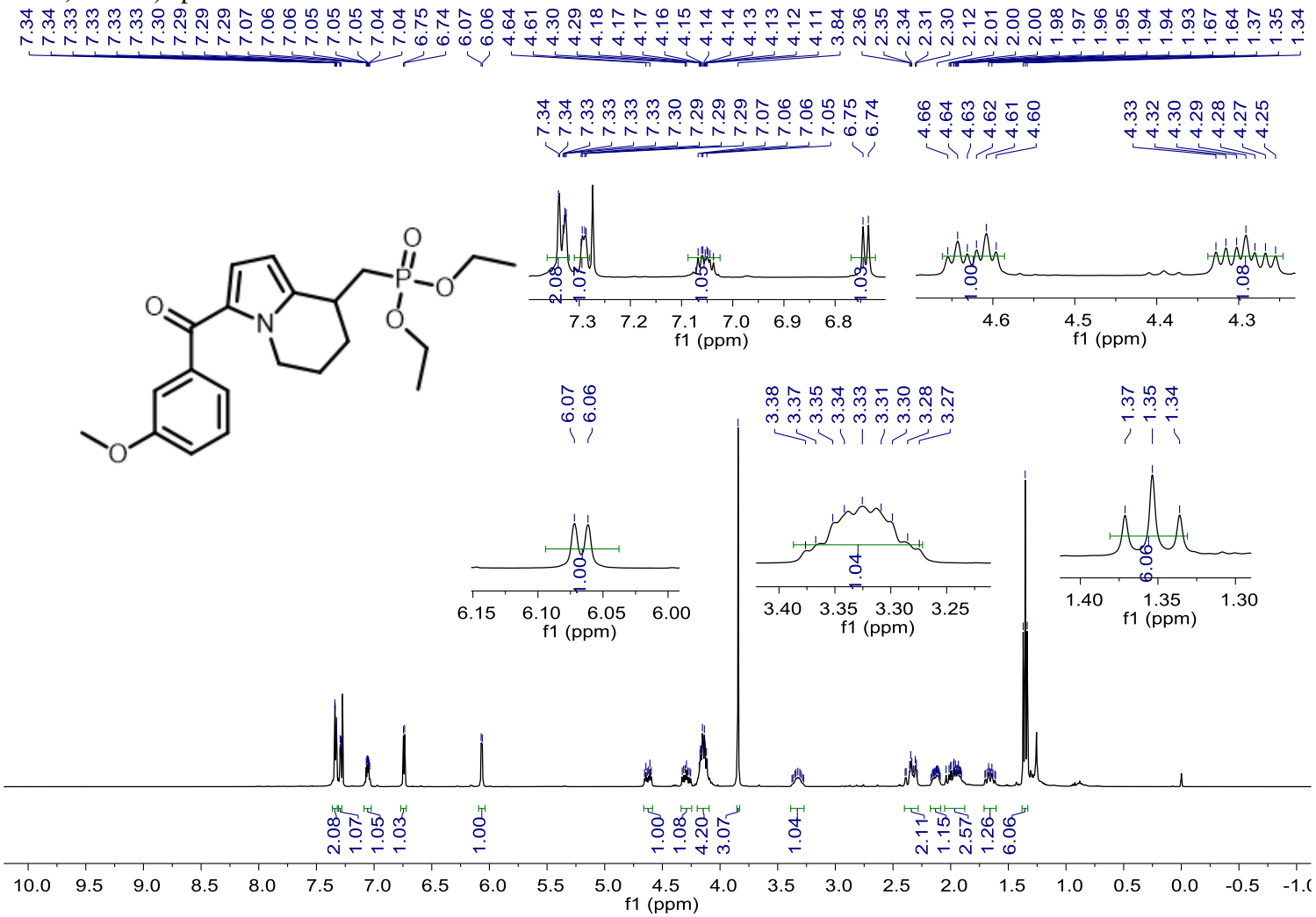
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ja**



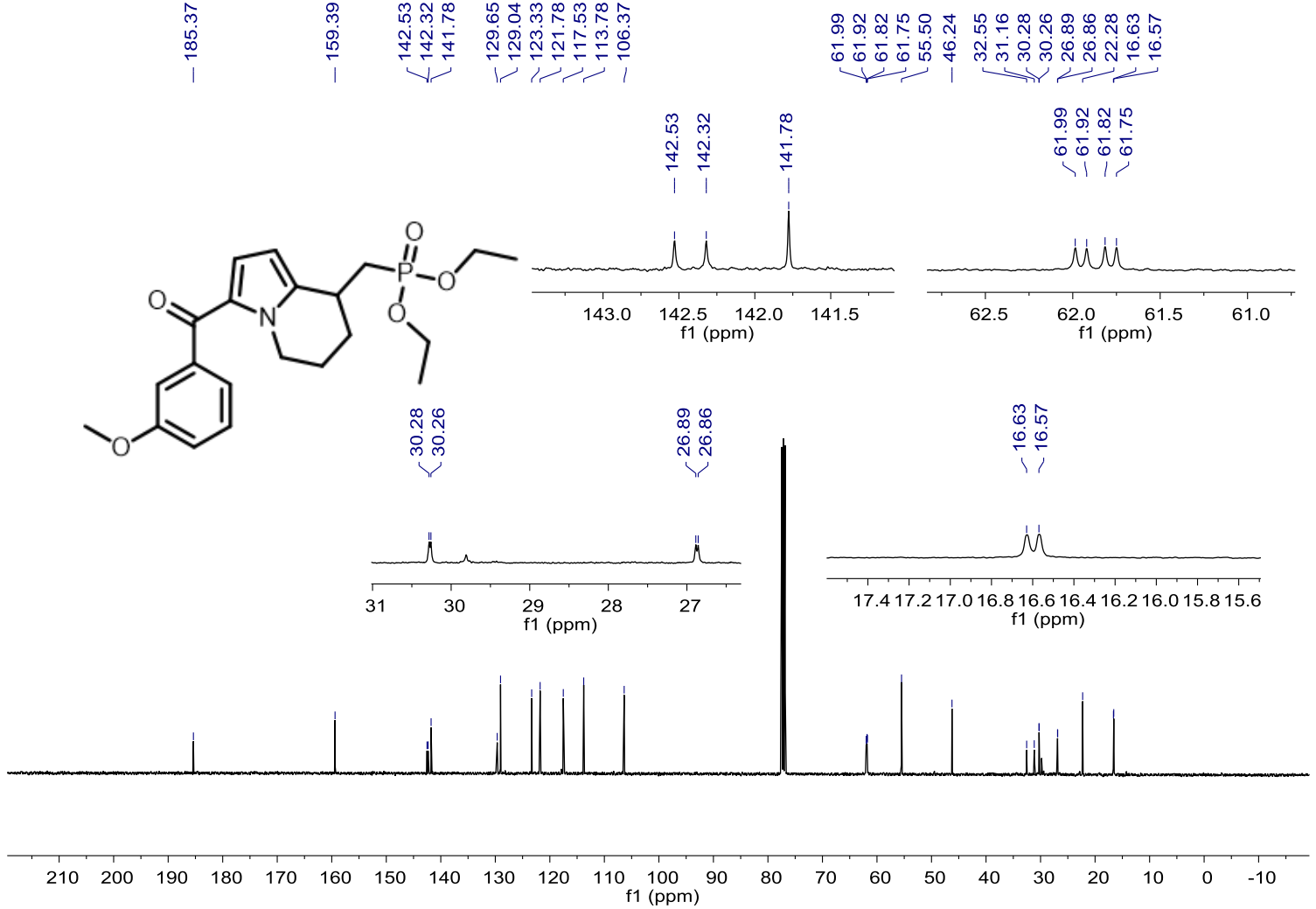
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ja**



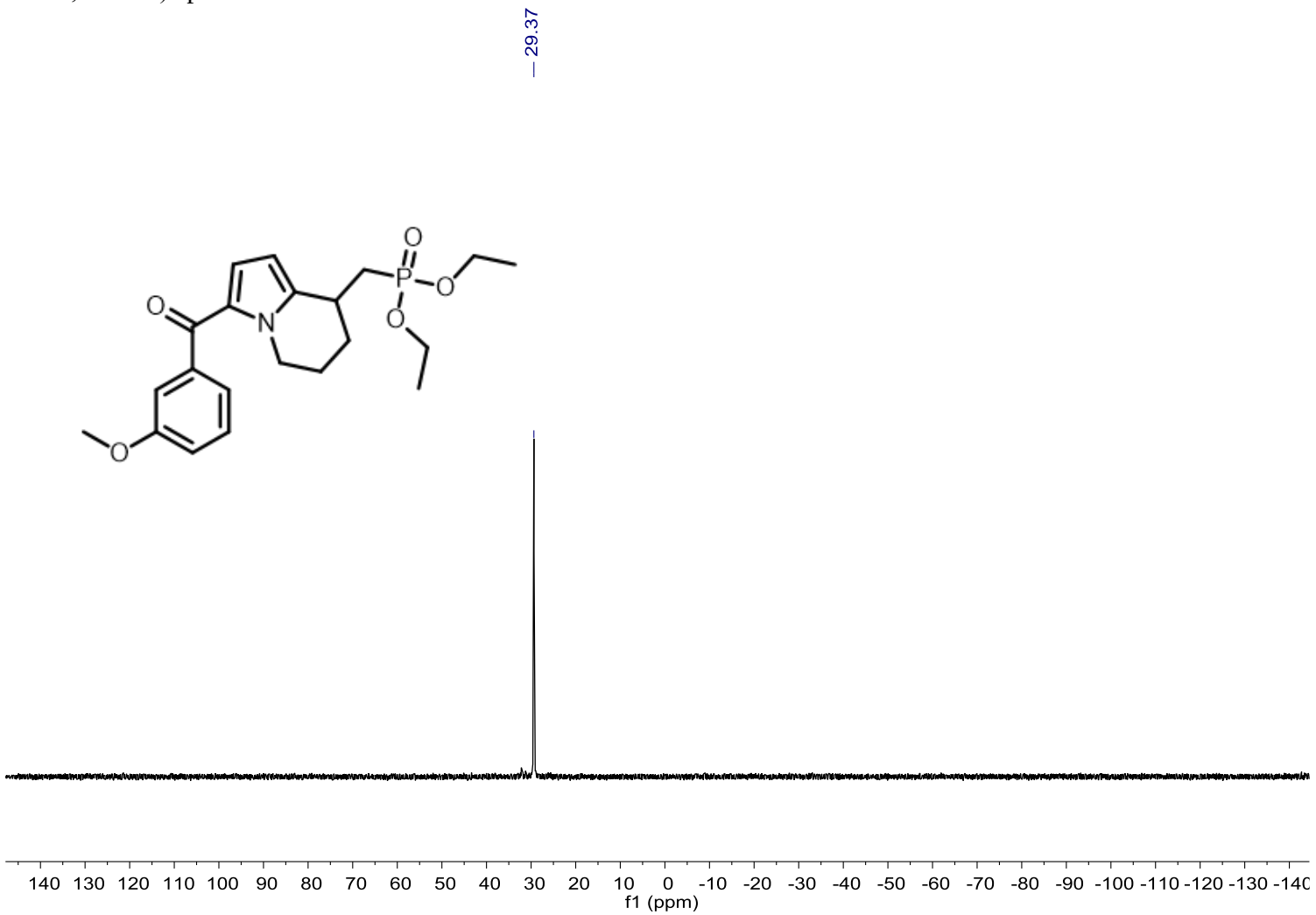
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



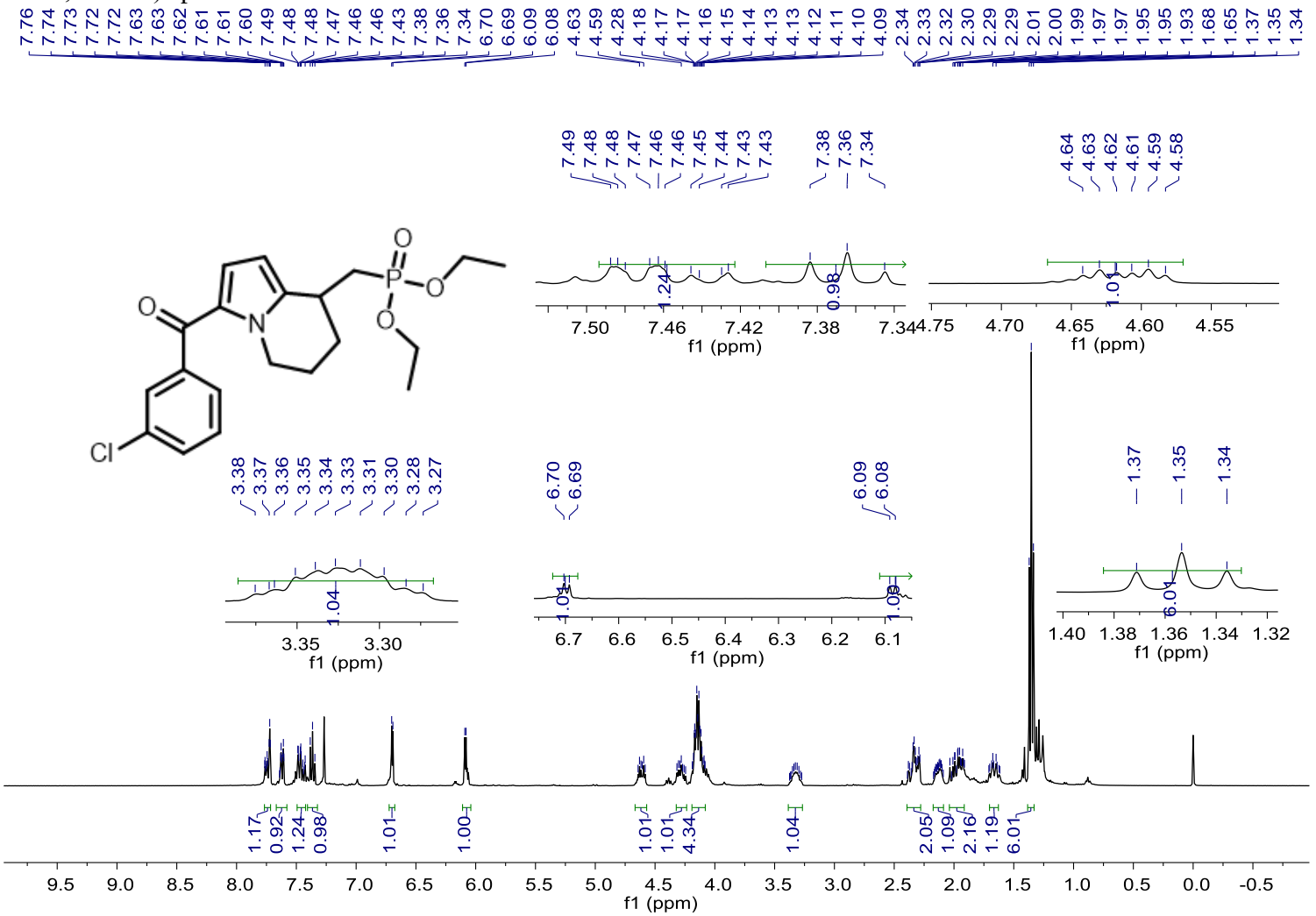
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ka**



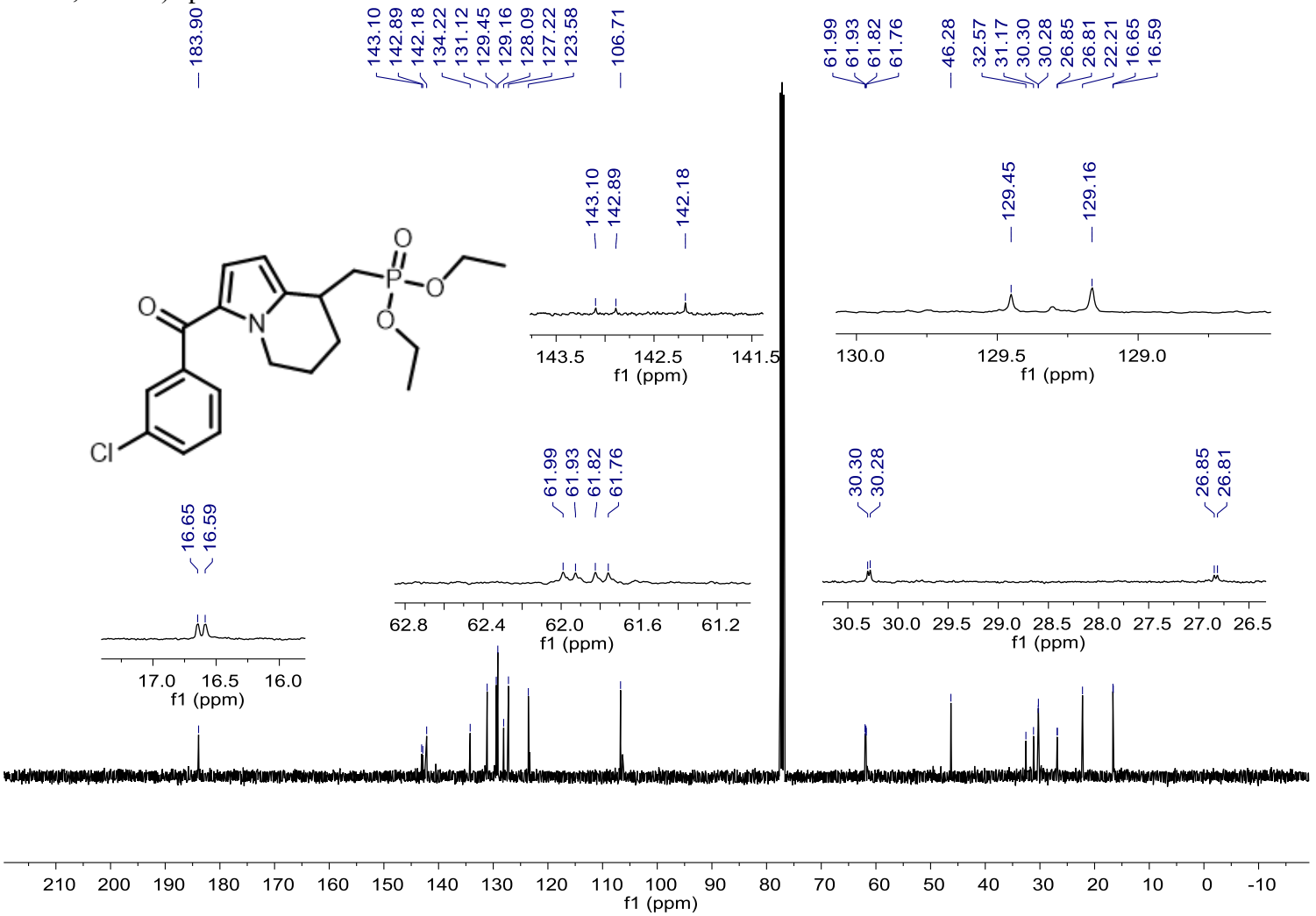
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ka**



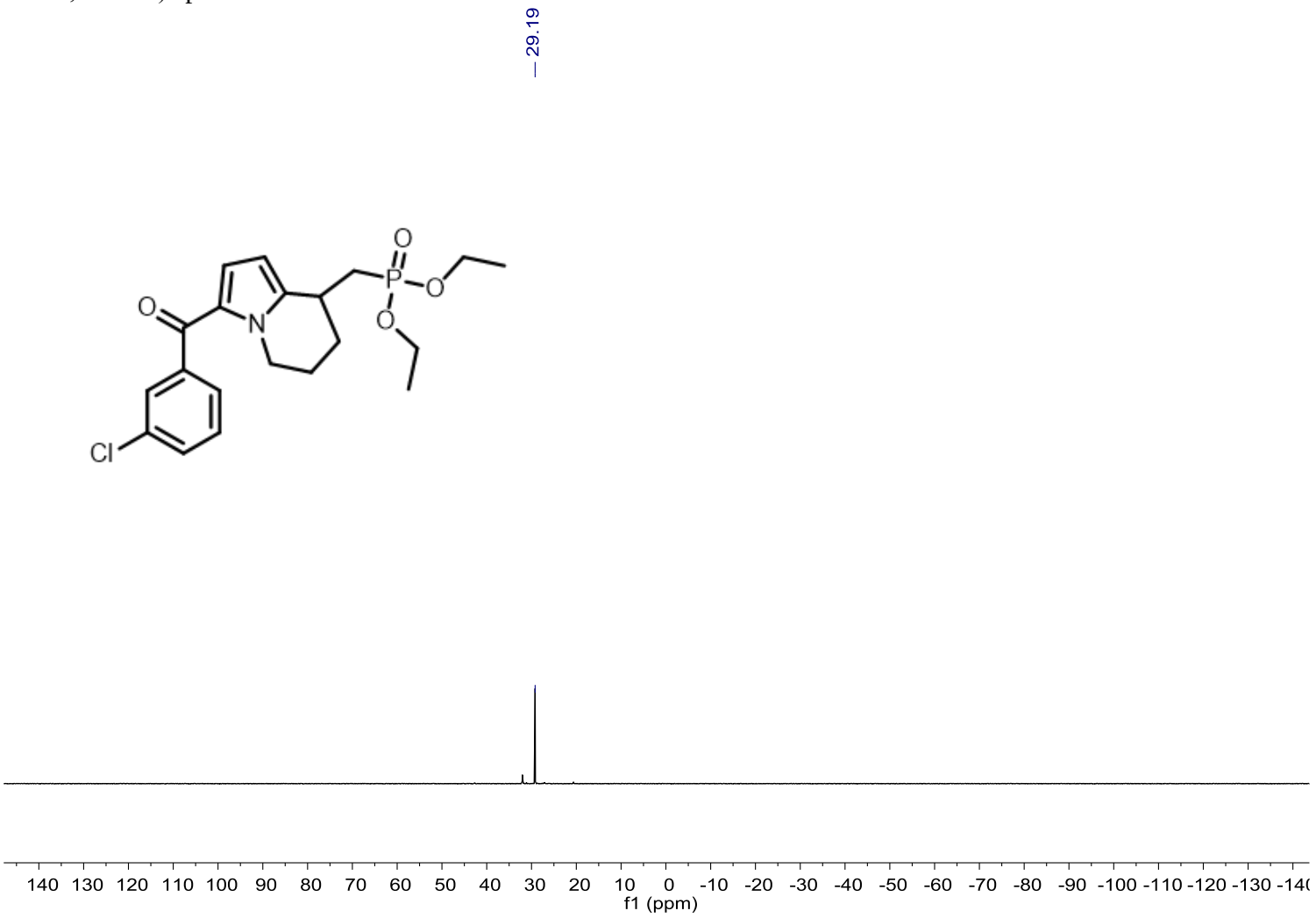
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3la**



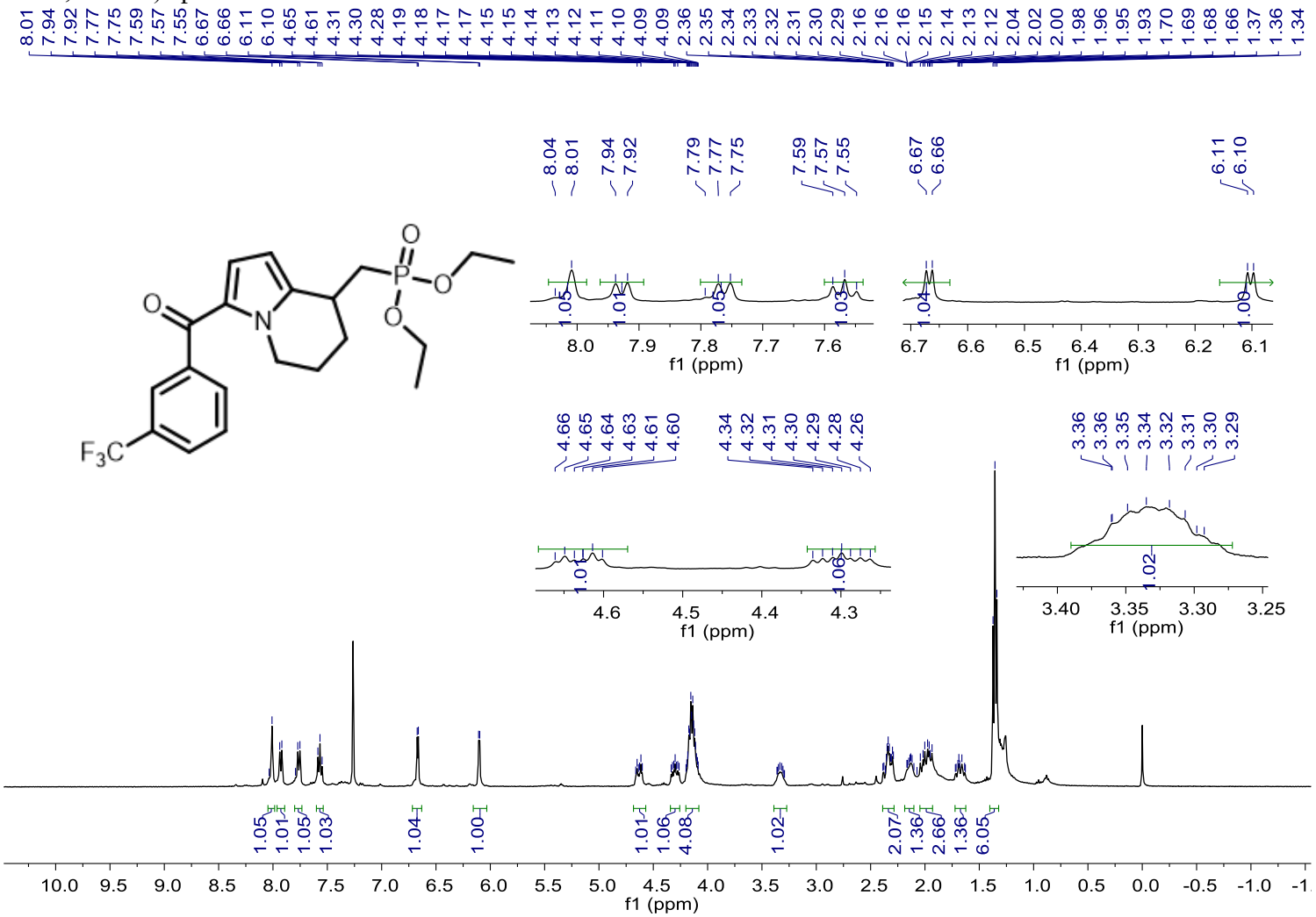
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3la**



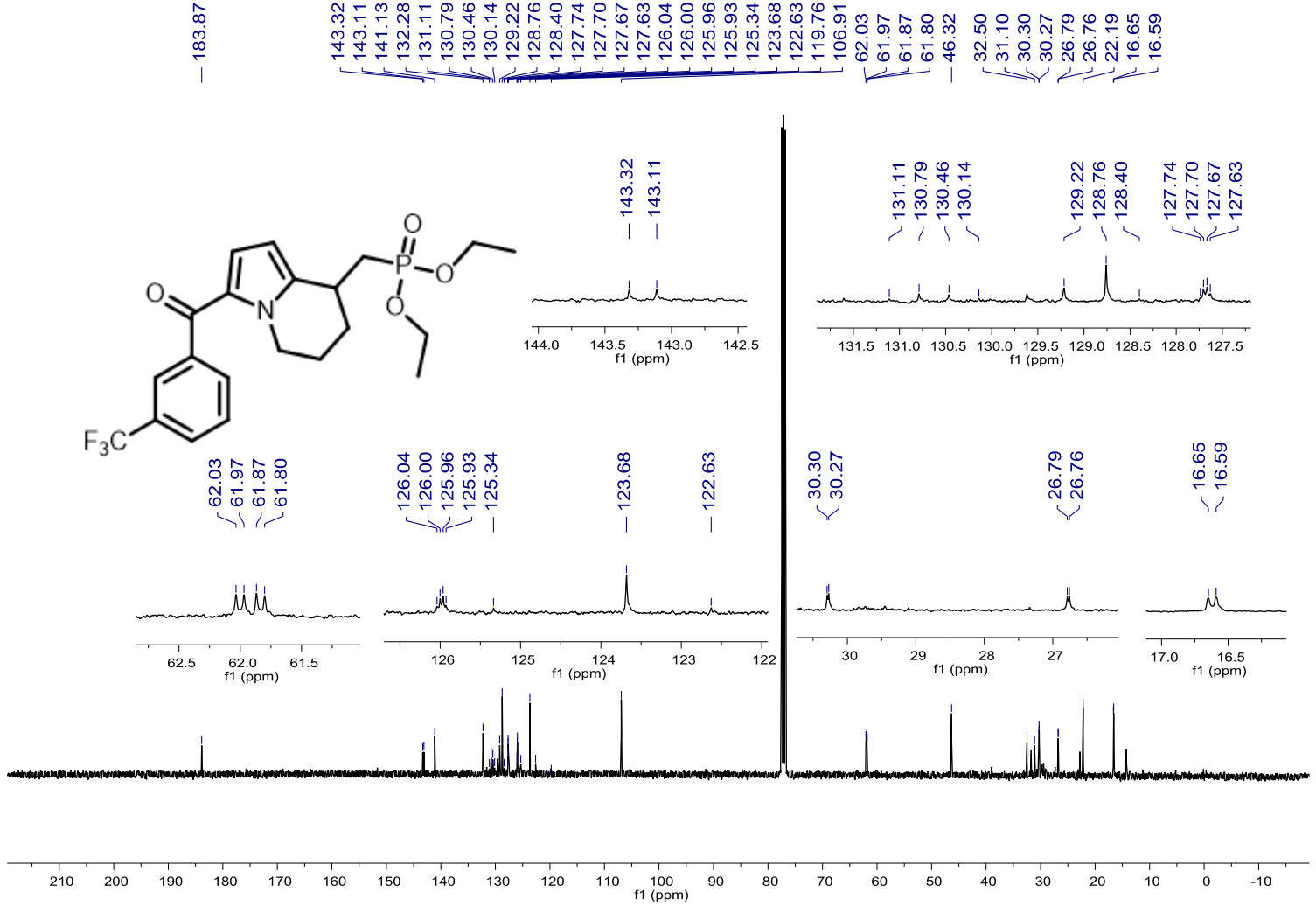
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3la**



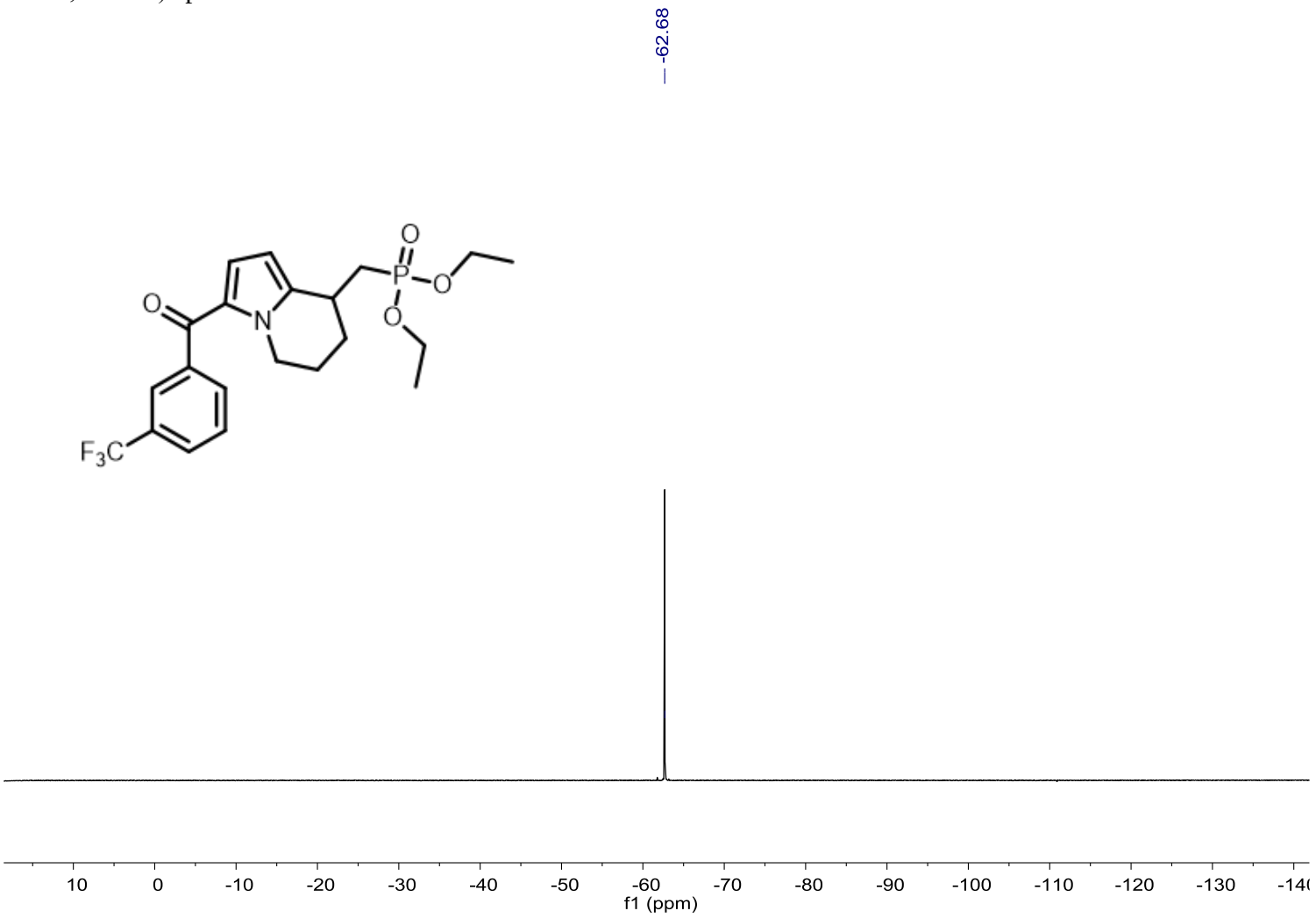
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ma**



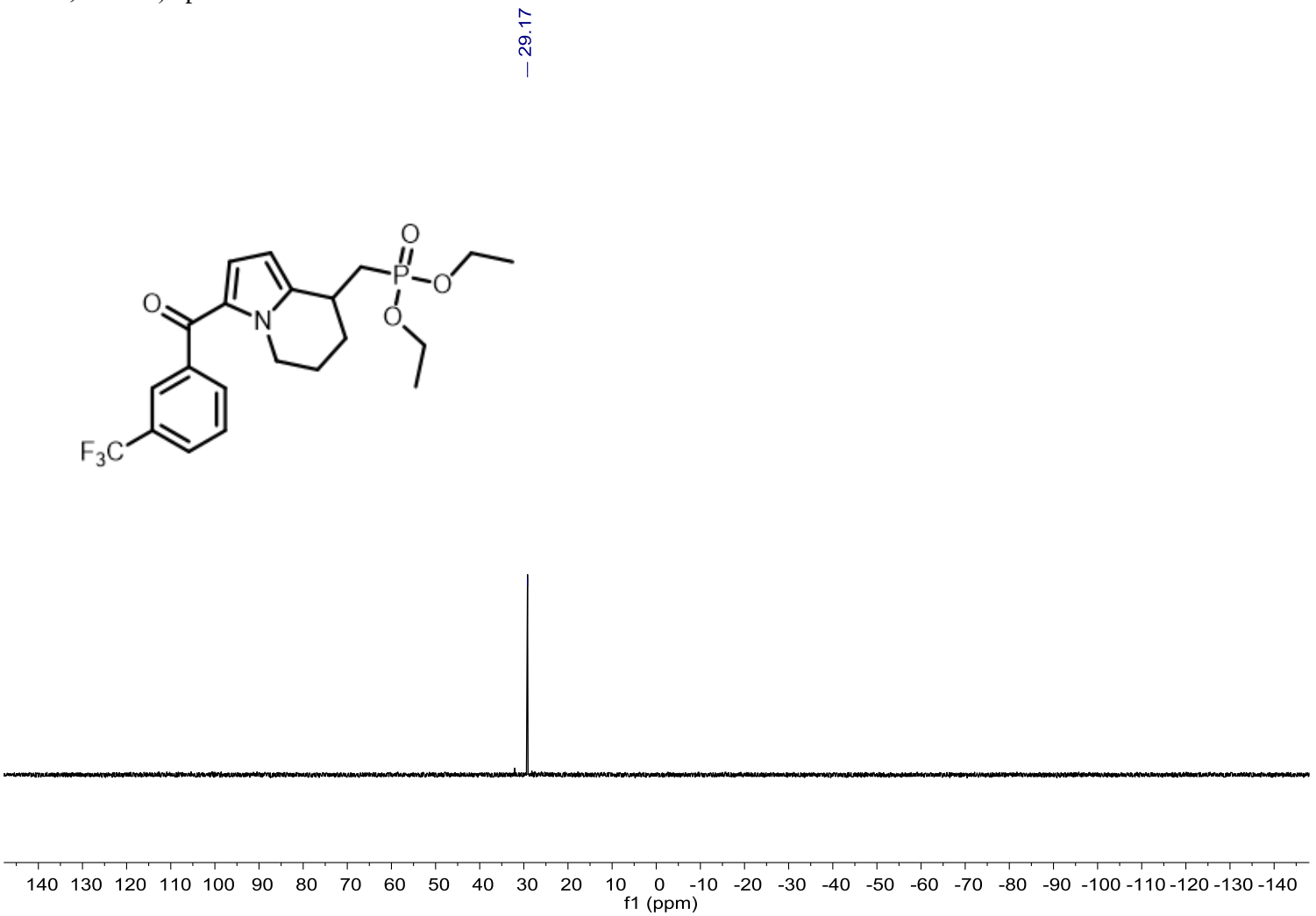
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ma**



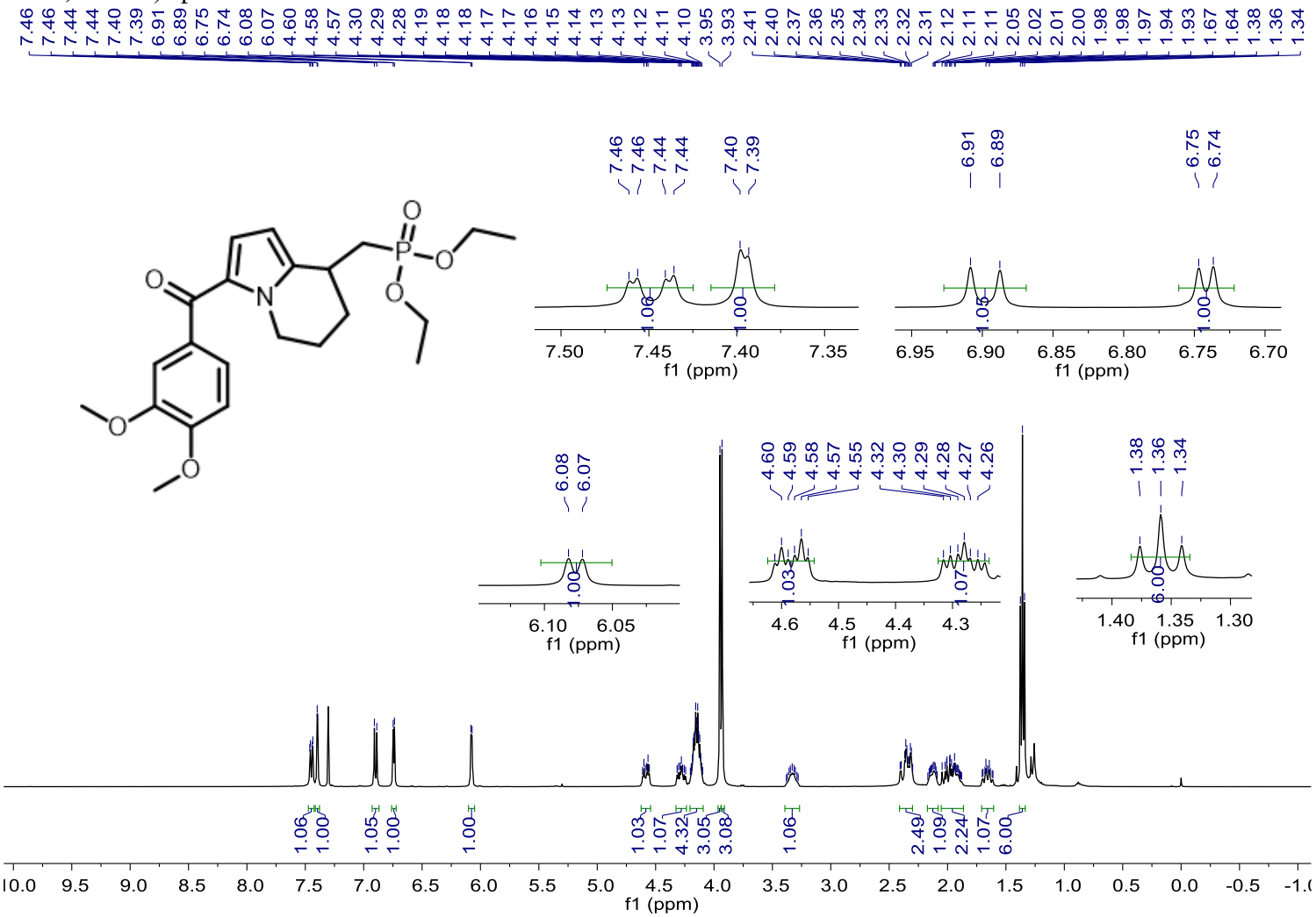
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **3ma**



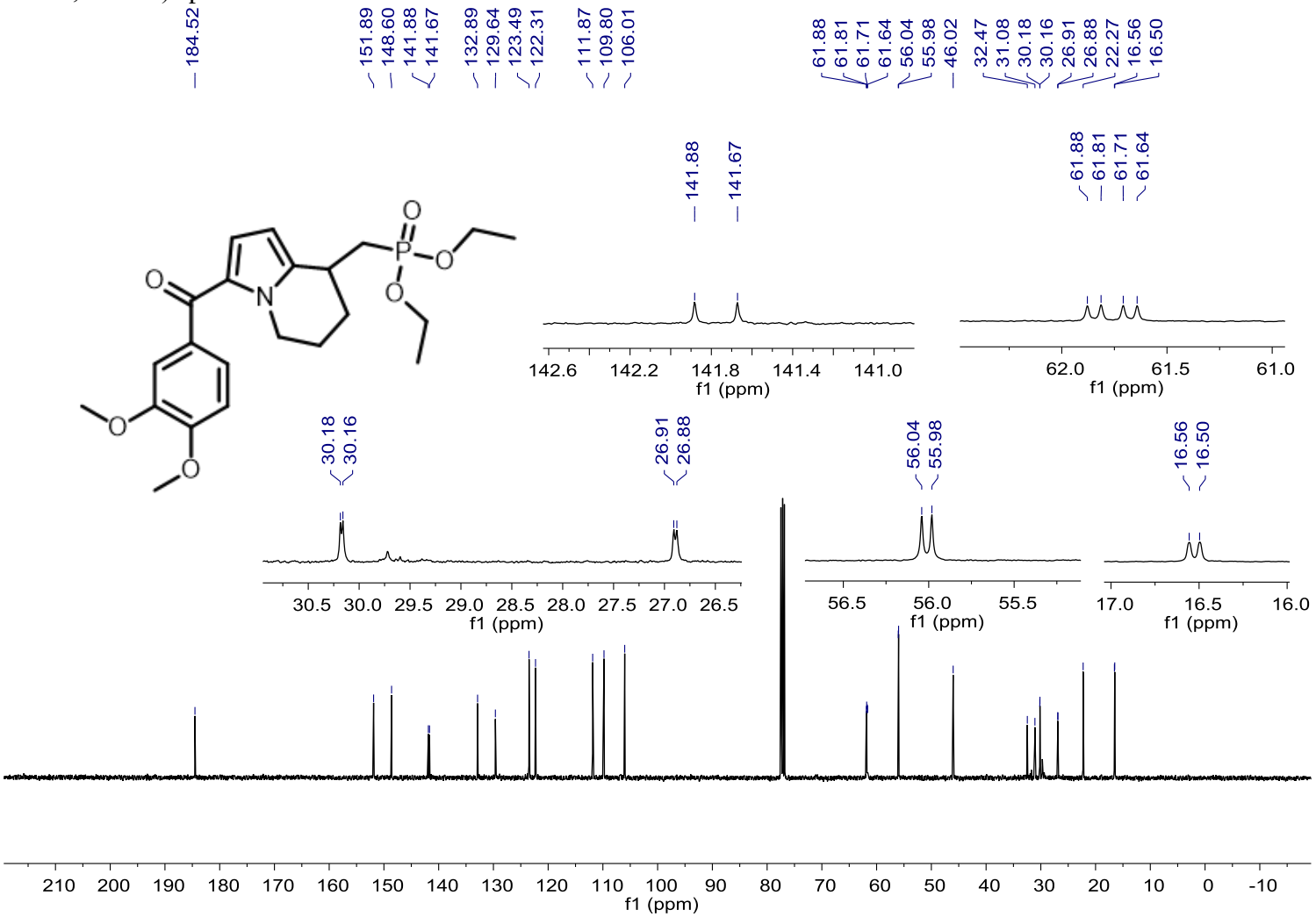
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ma**



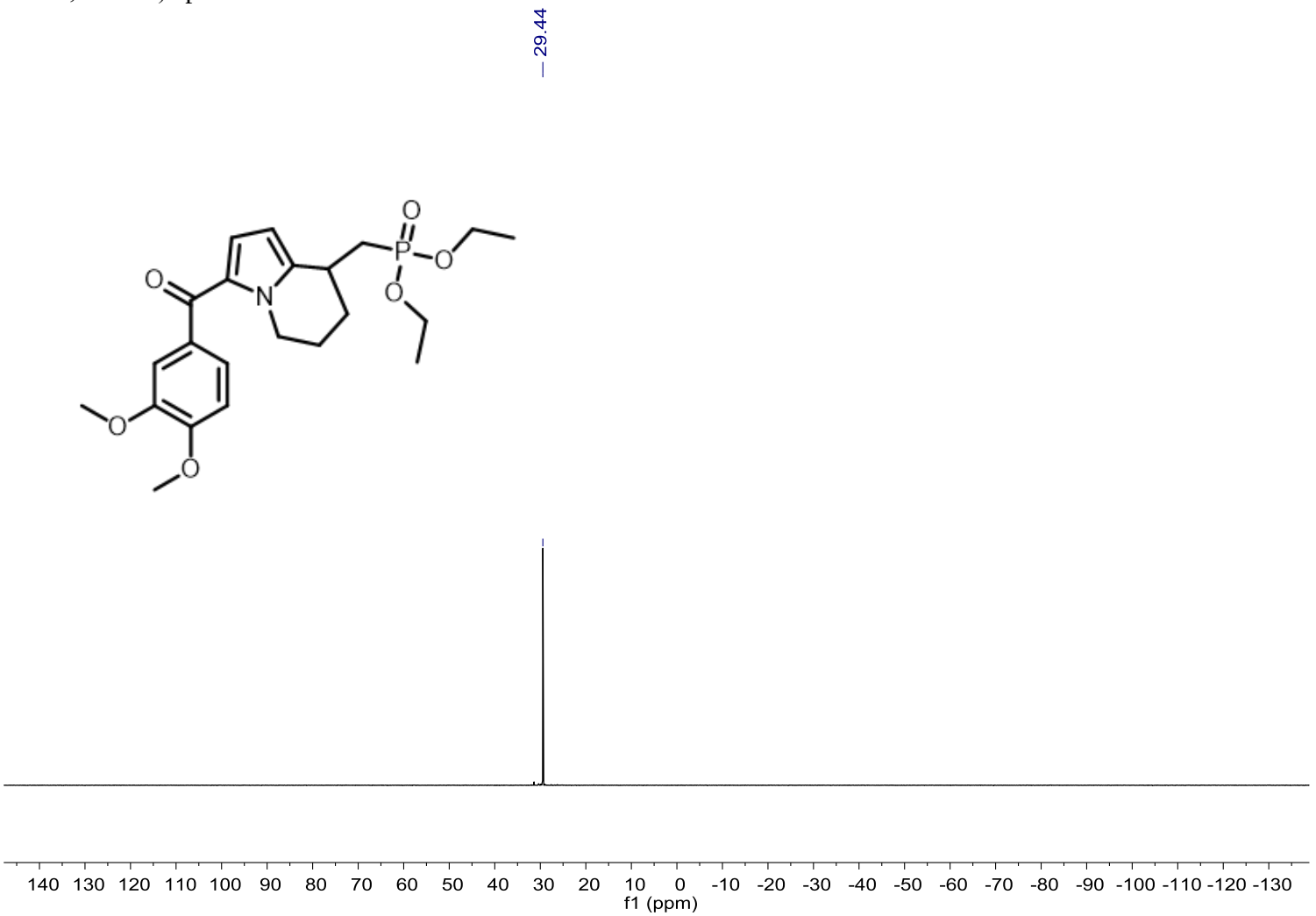
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3na**



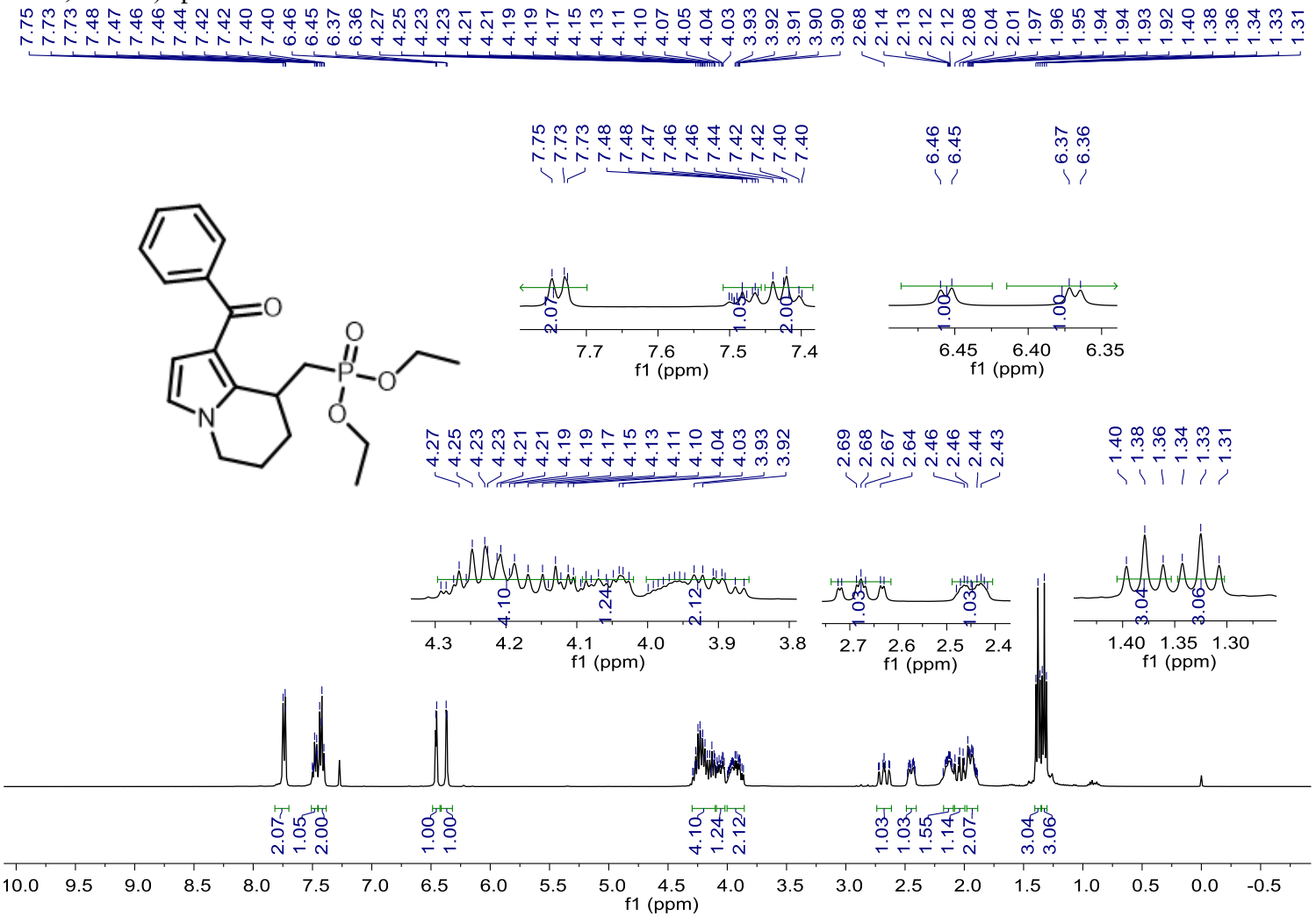
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3na**



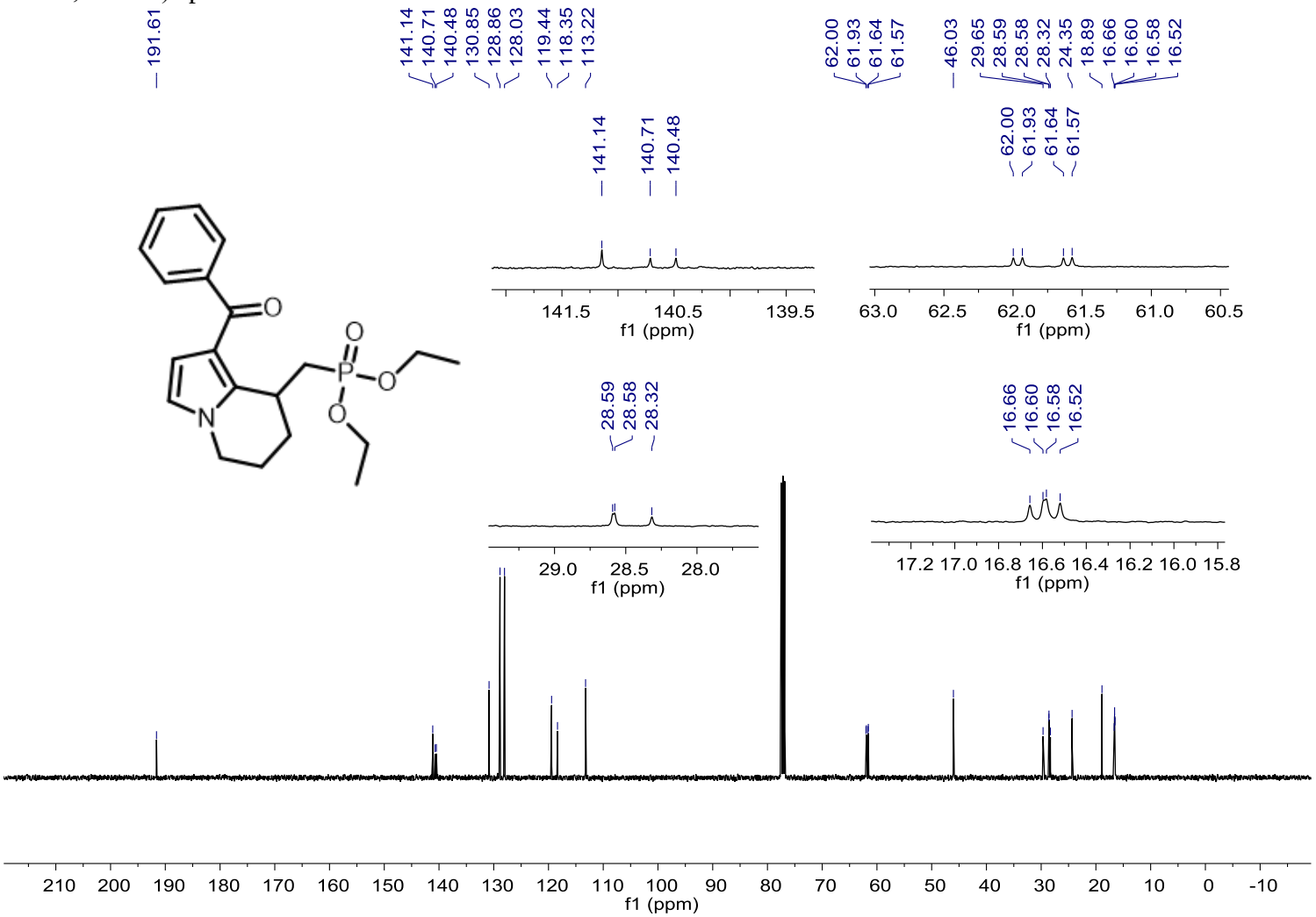
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3na**



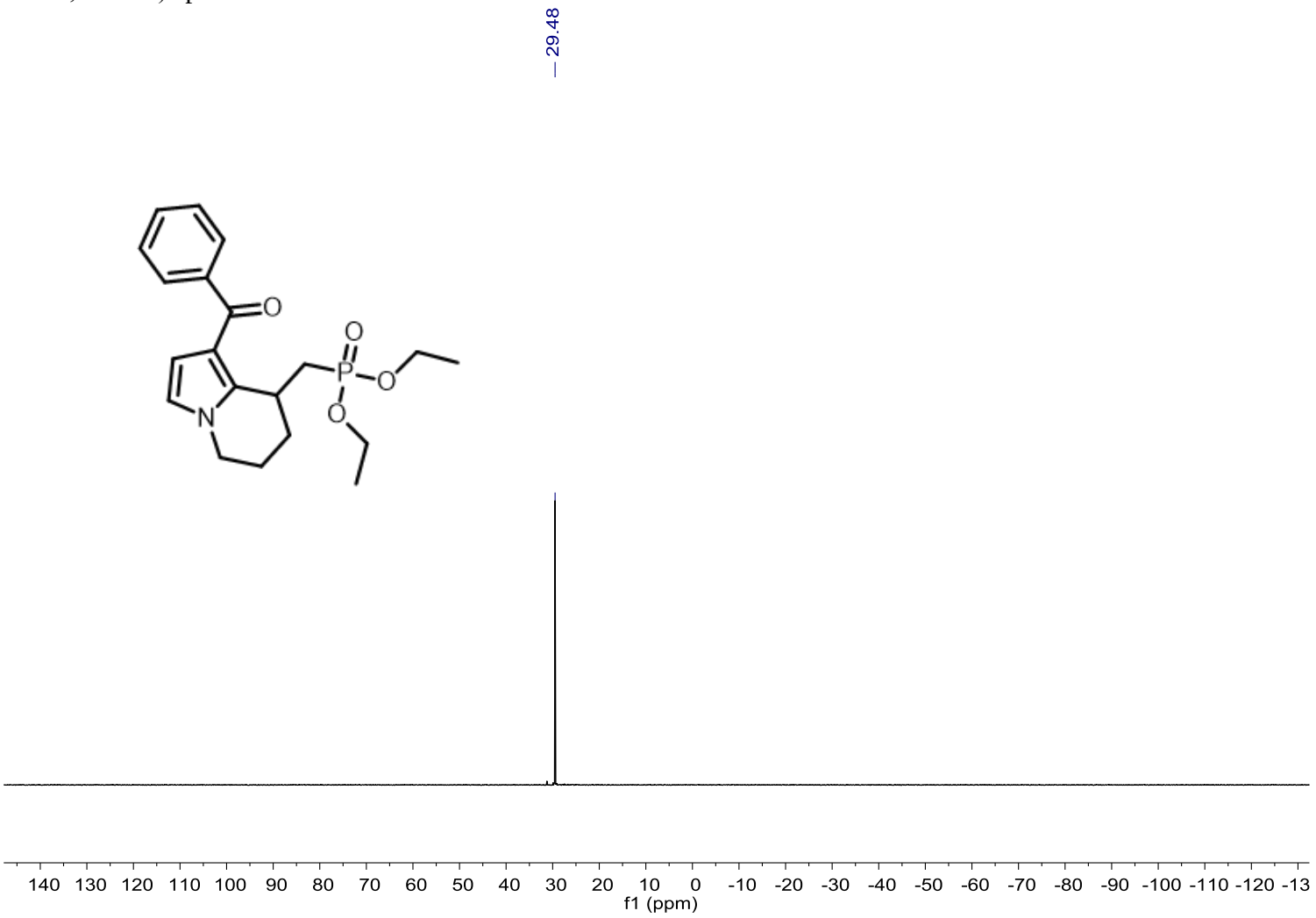
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3oa**



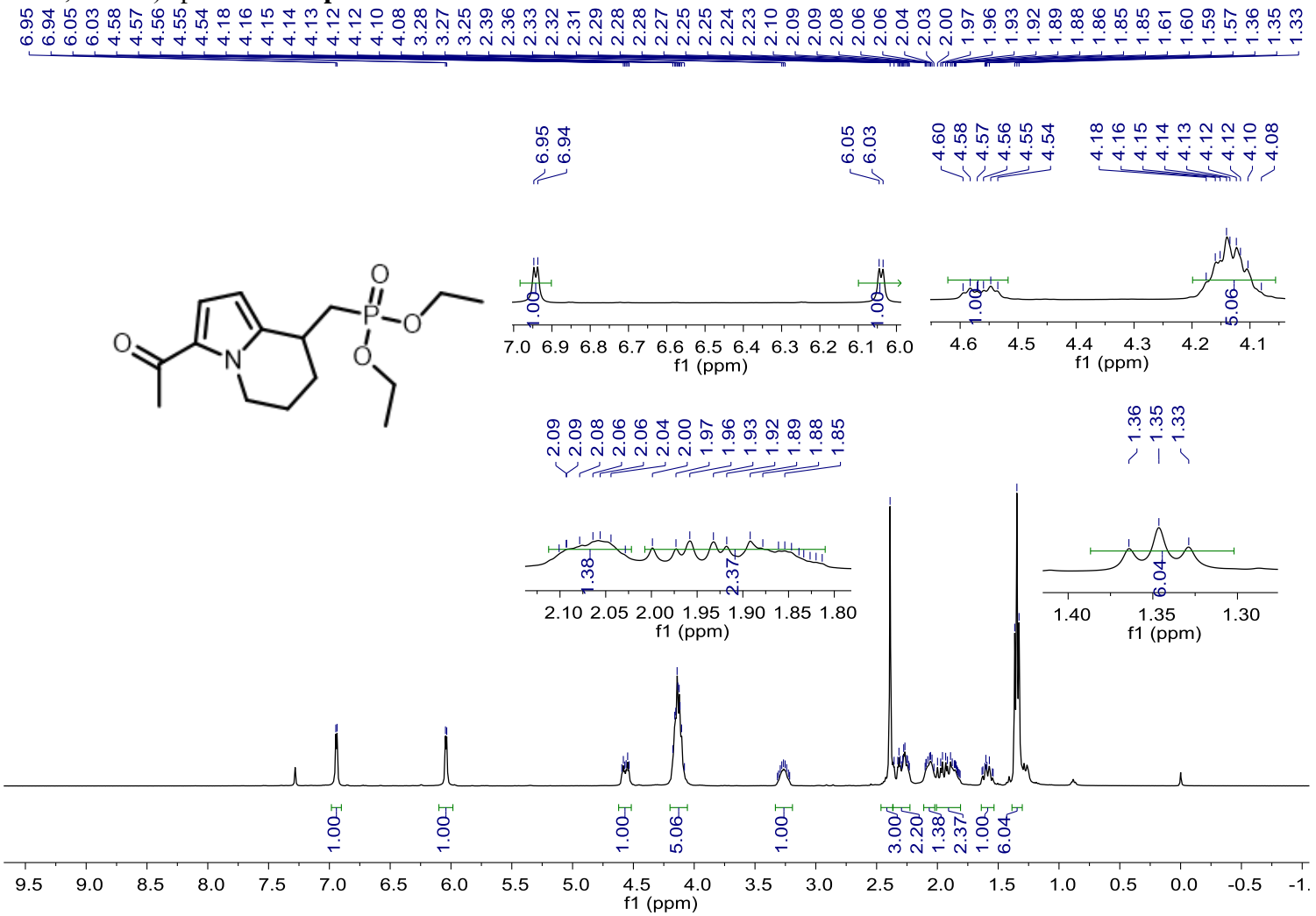
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3oa**



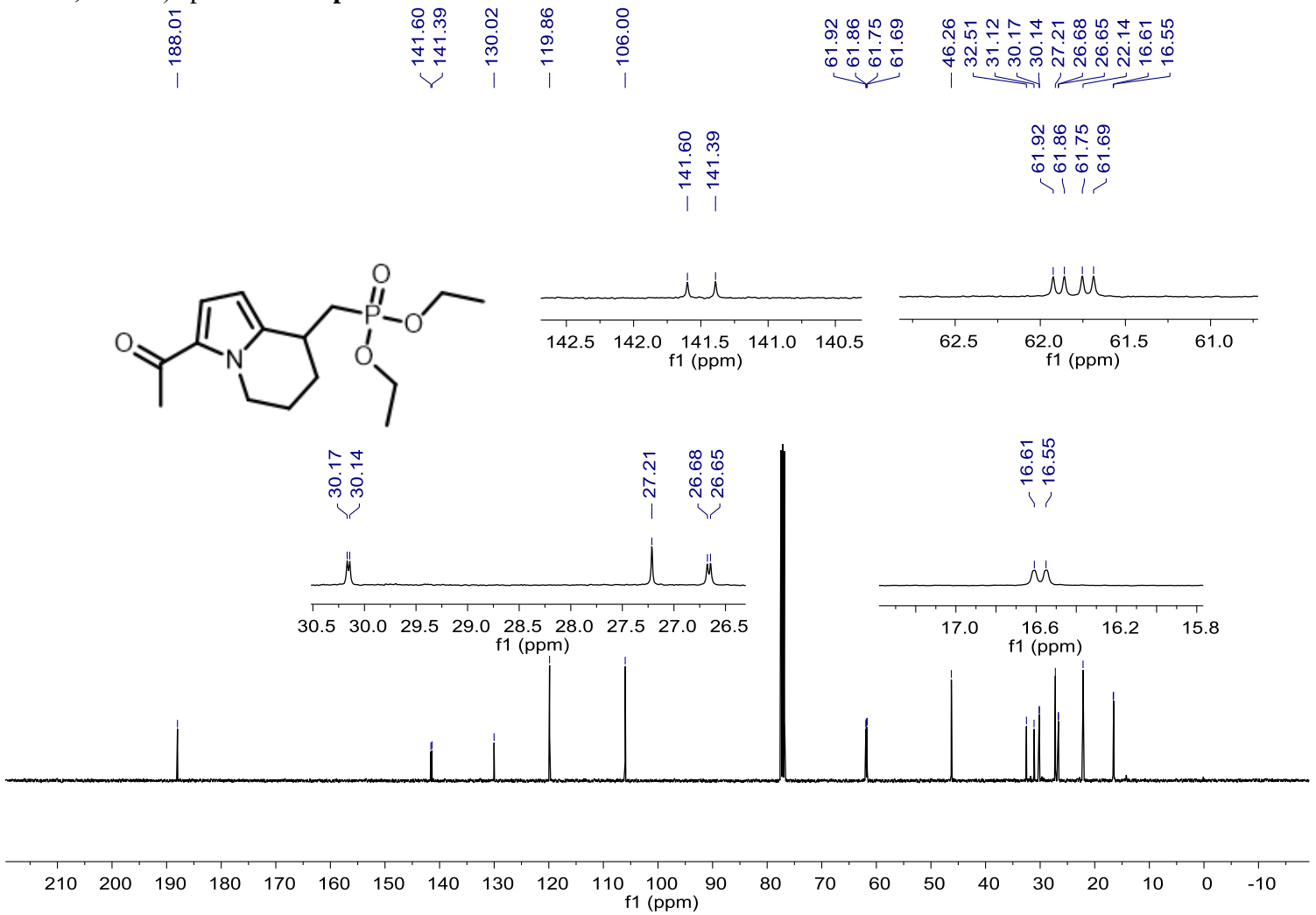
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3oa**



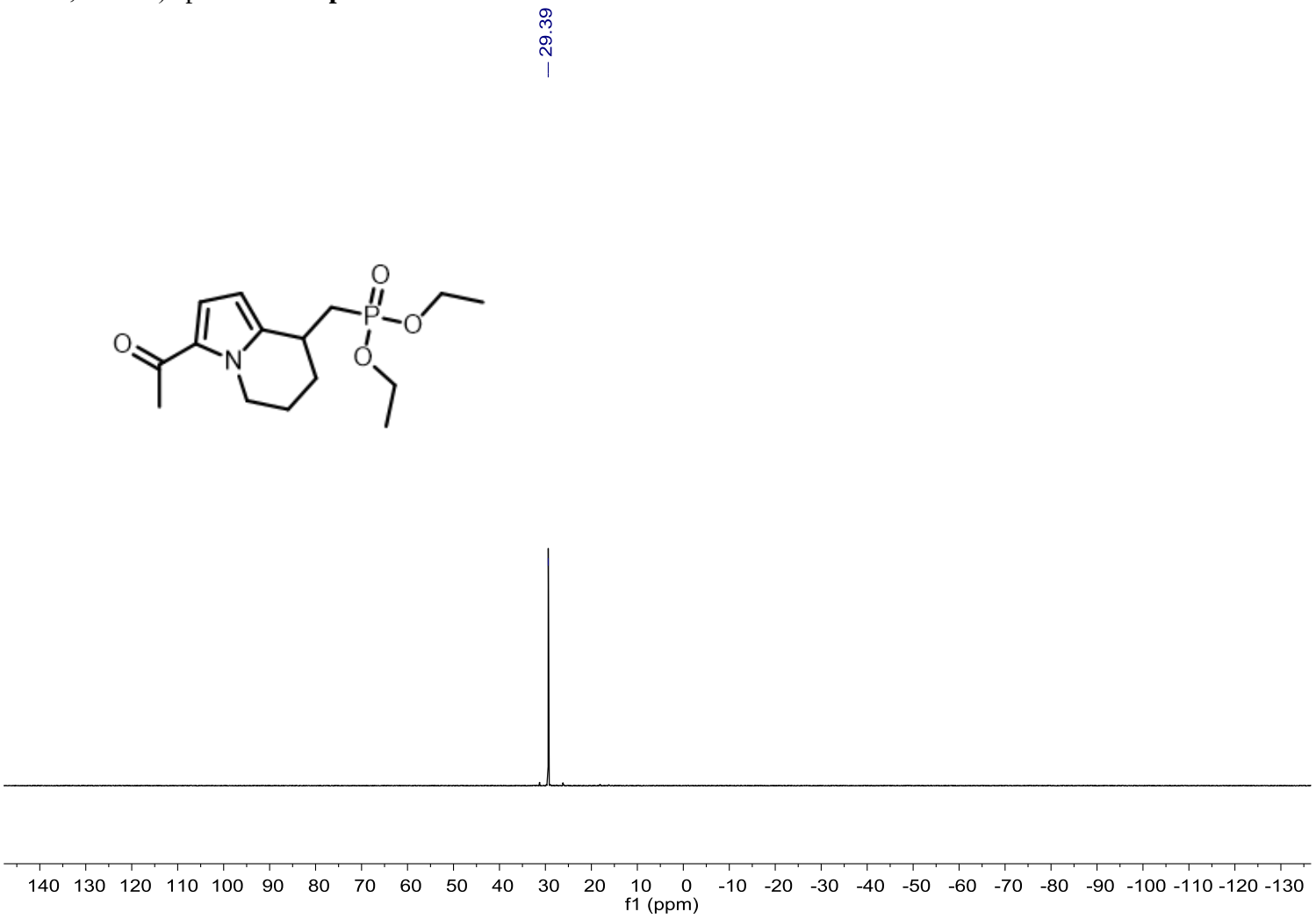
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3pa**



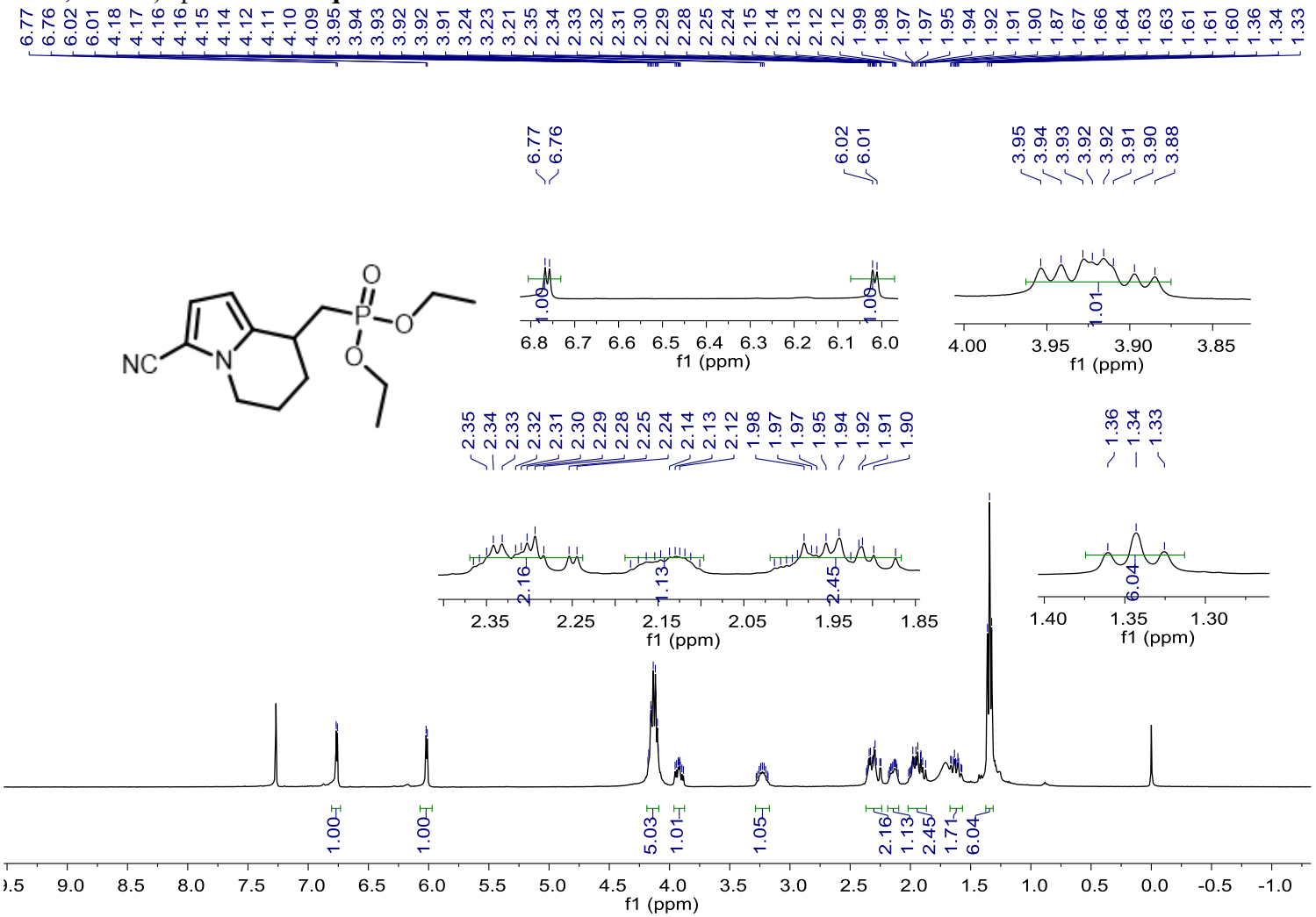
$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **3pa**



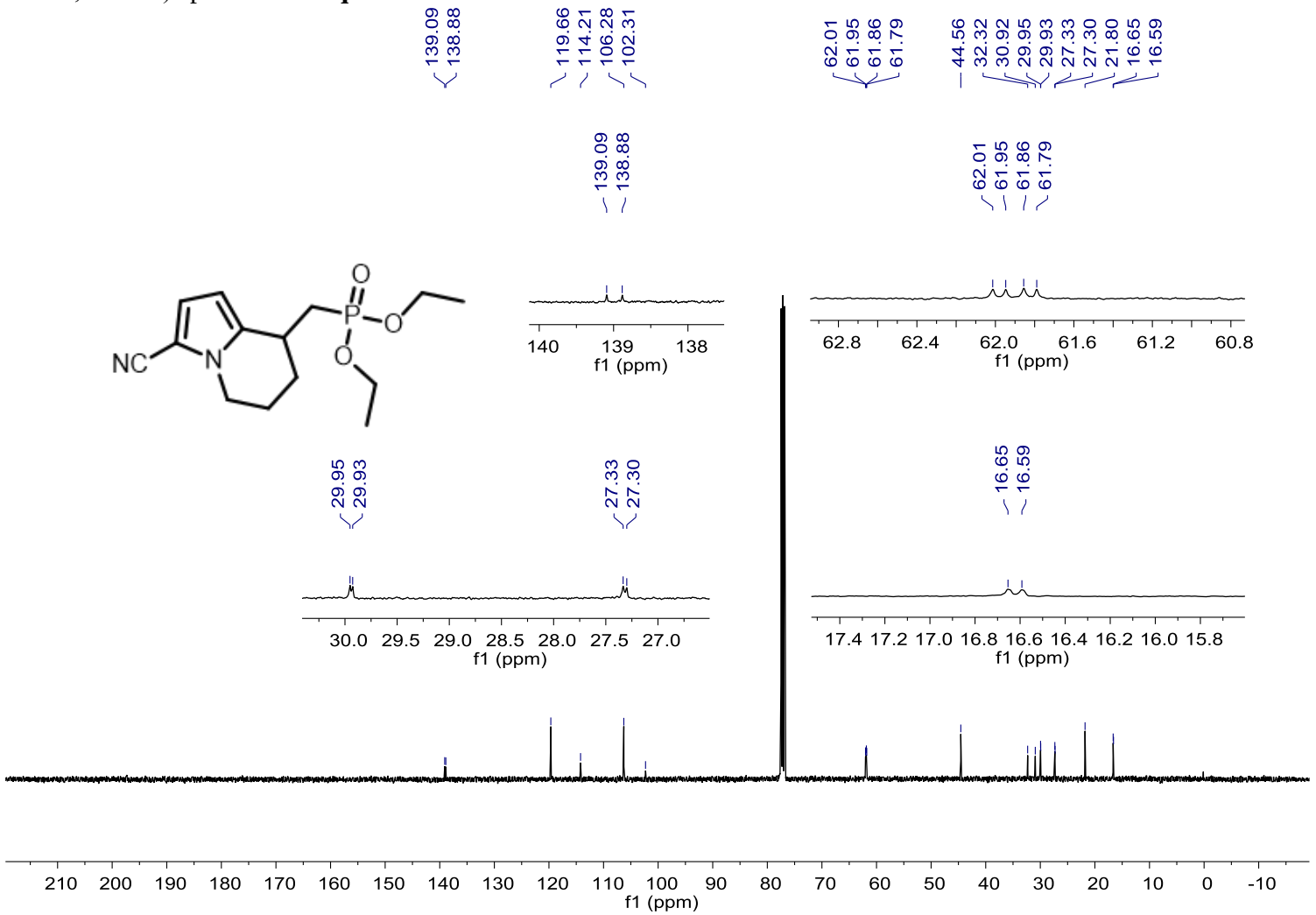
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3pa**



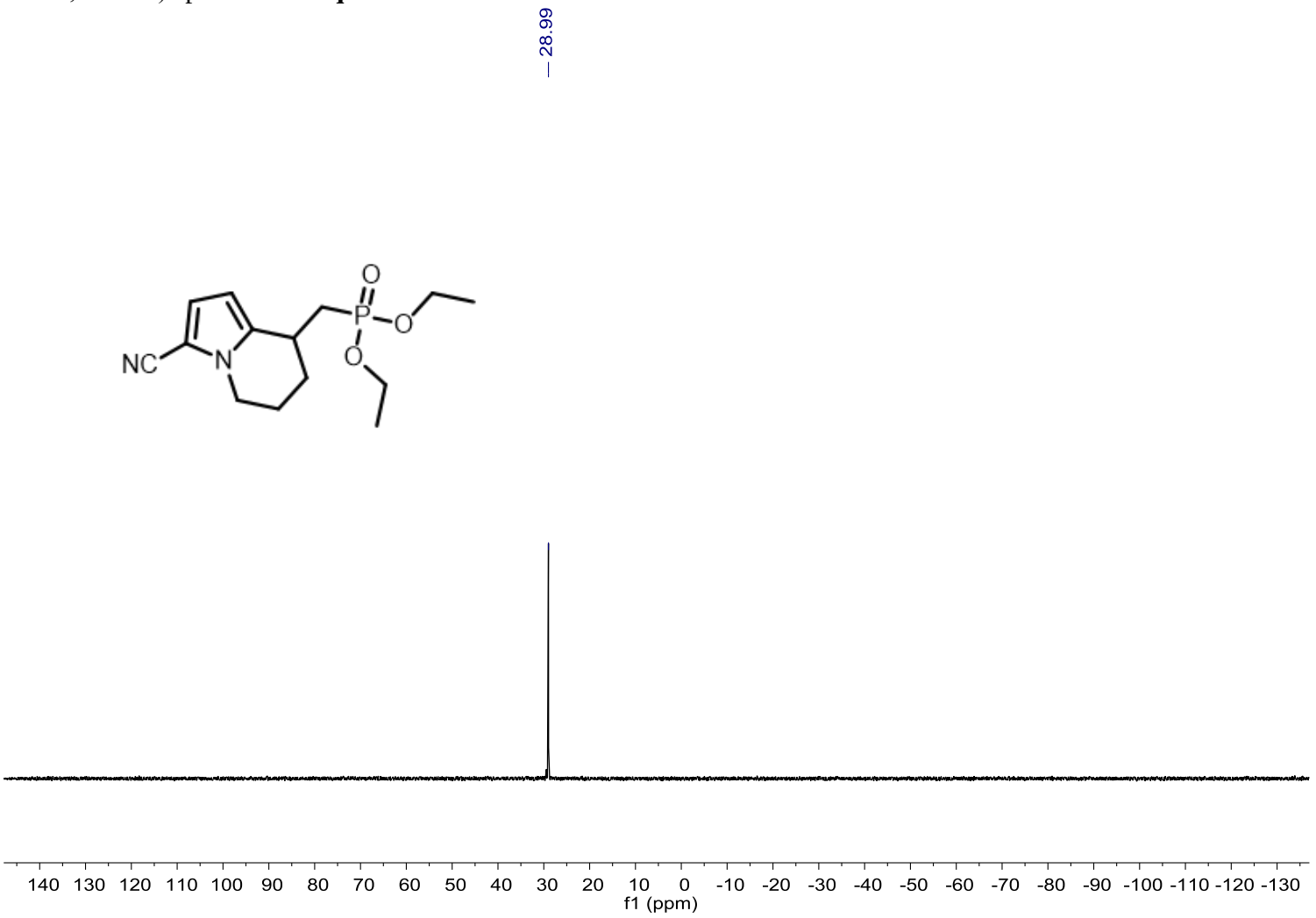
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3qa**



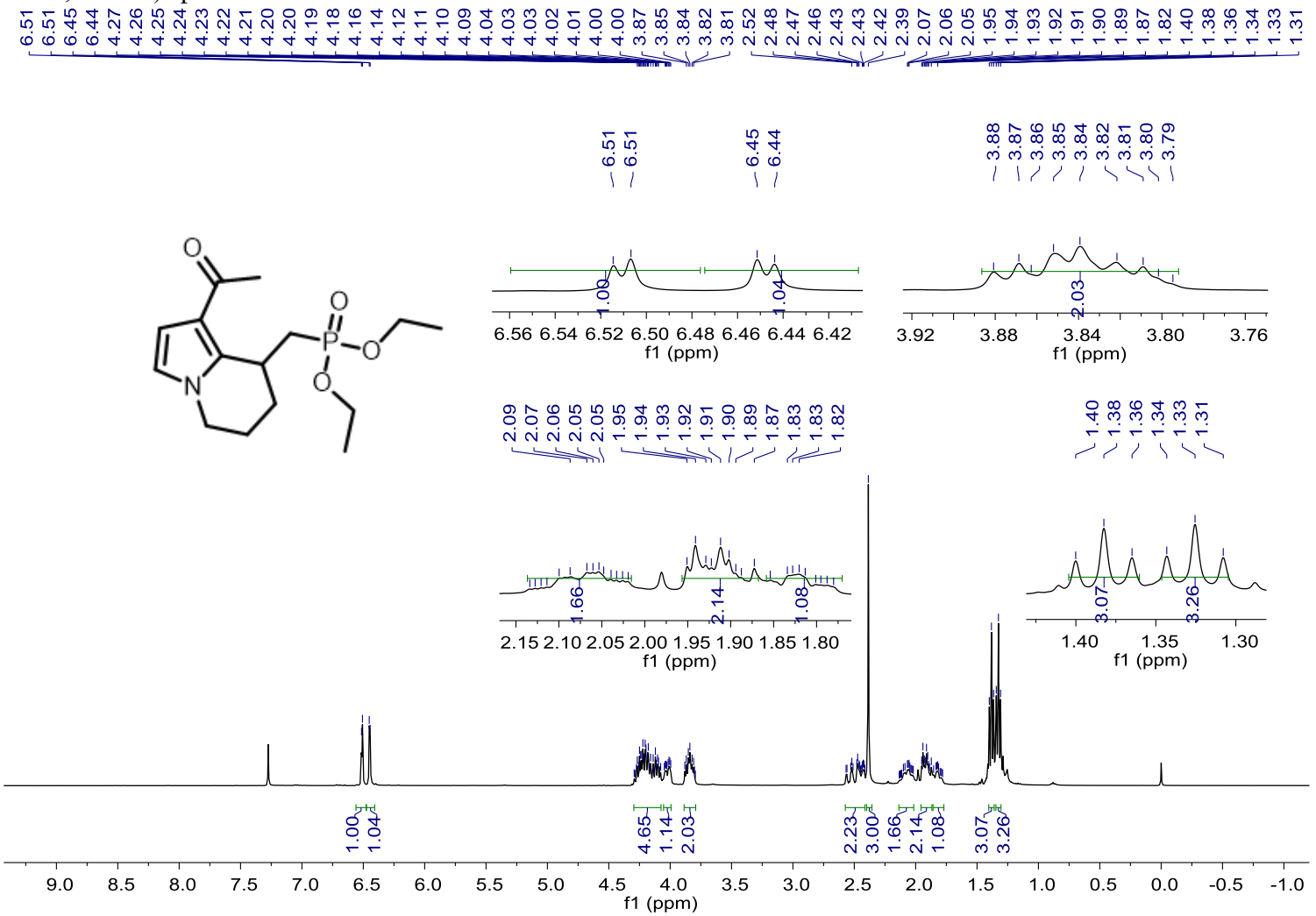
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3qa**



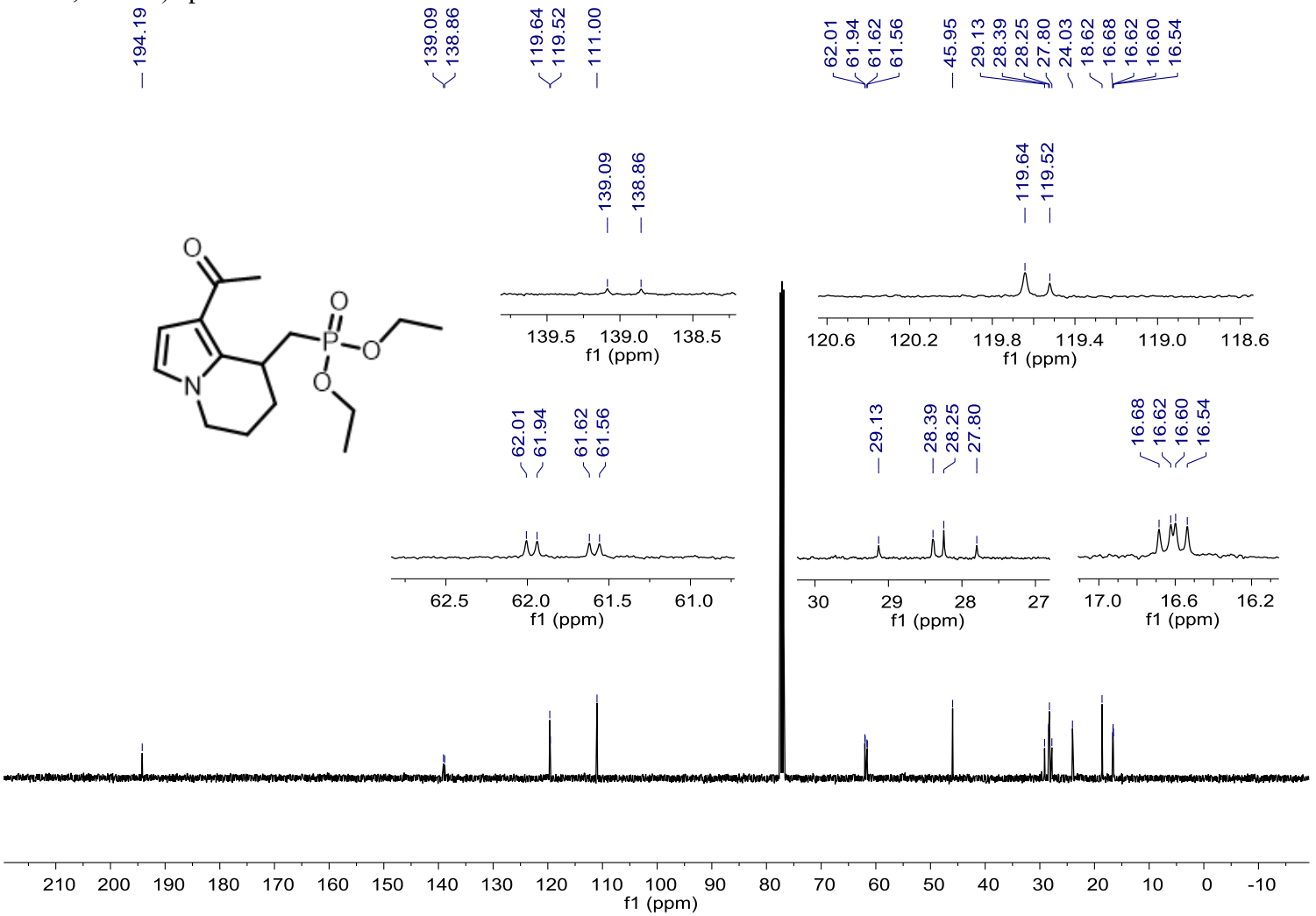
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3qa**



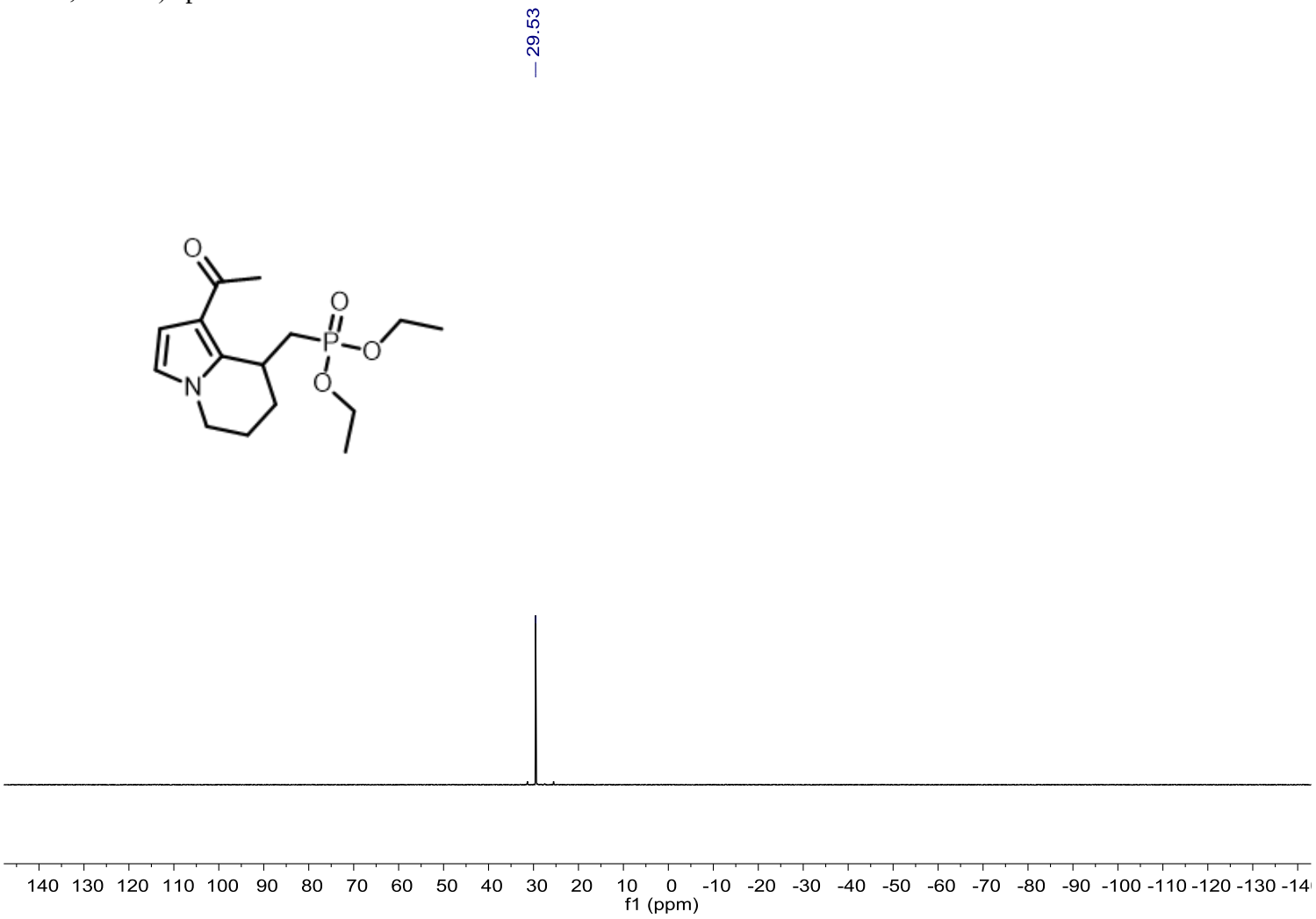
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ra**



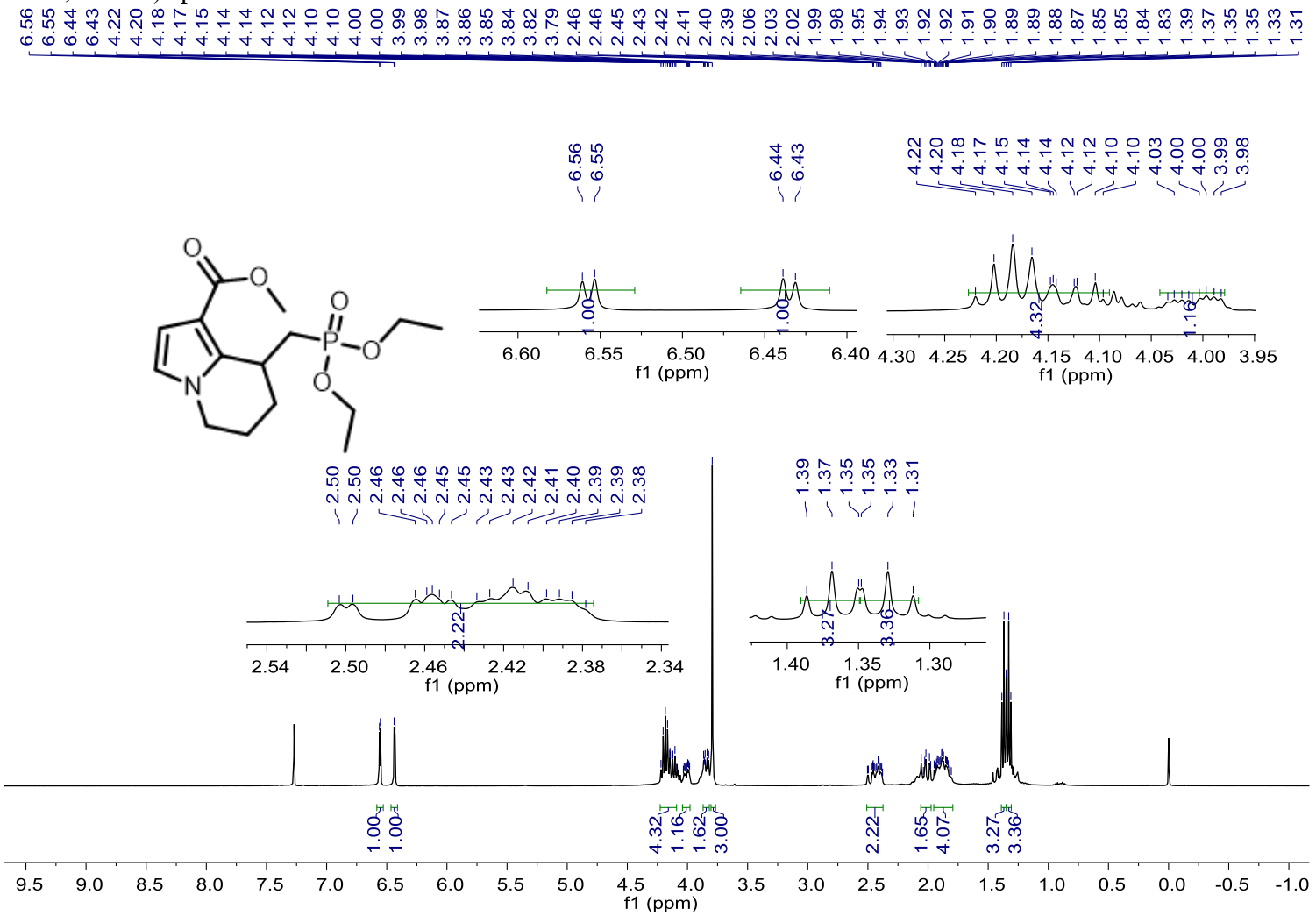
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ra**



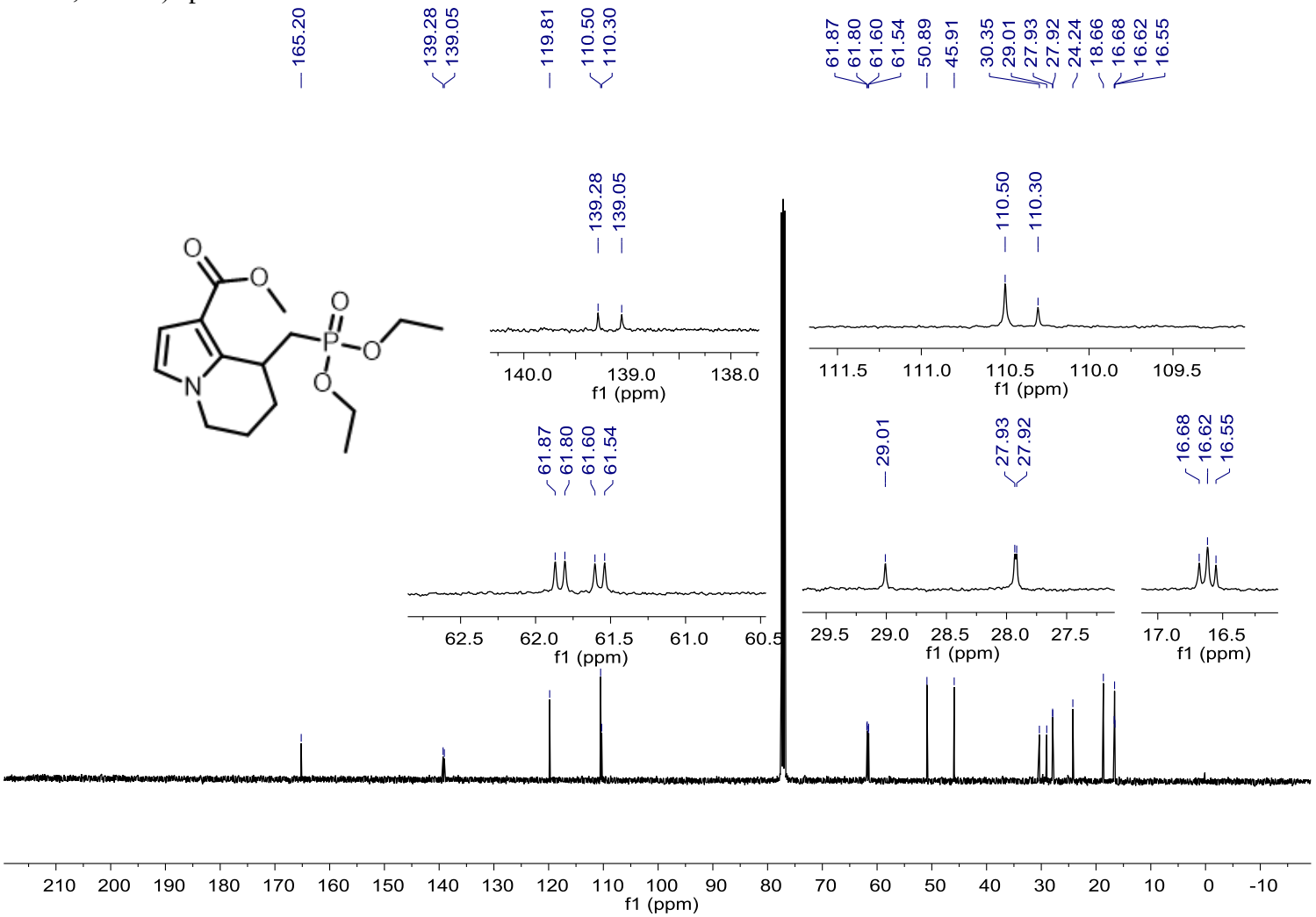
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ra**



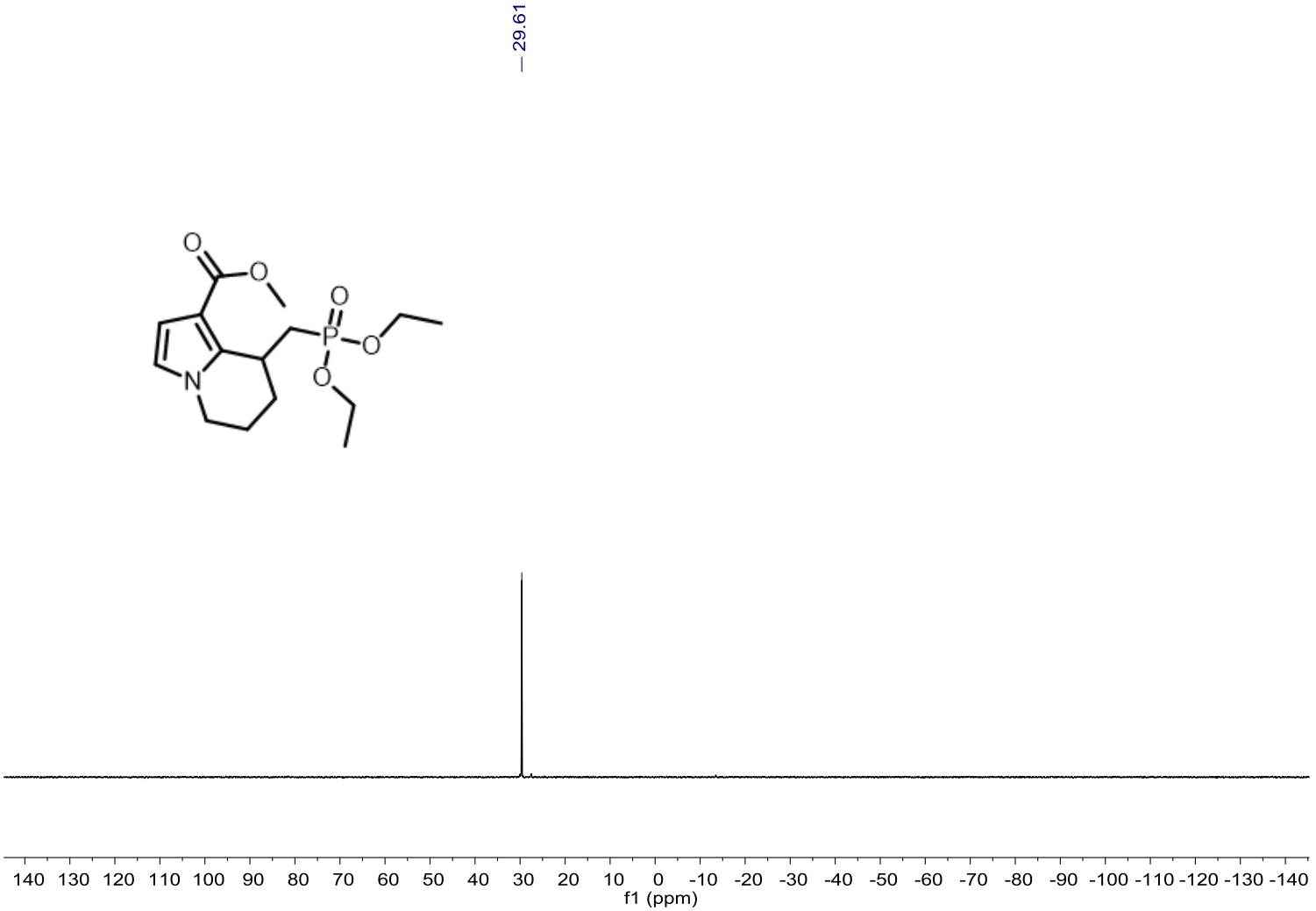
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3sa**



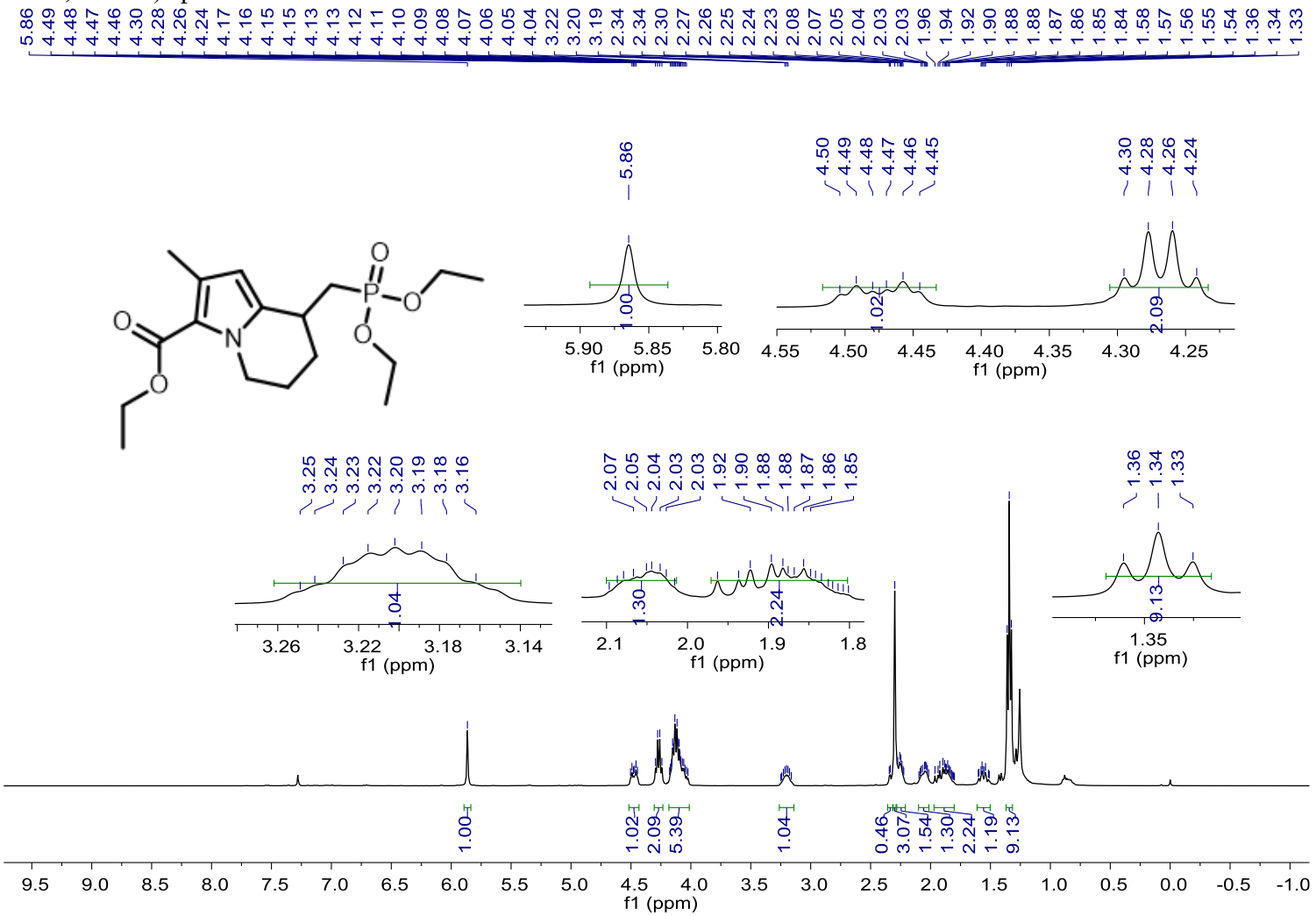
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3sa**



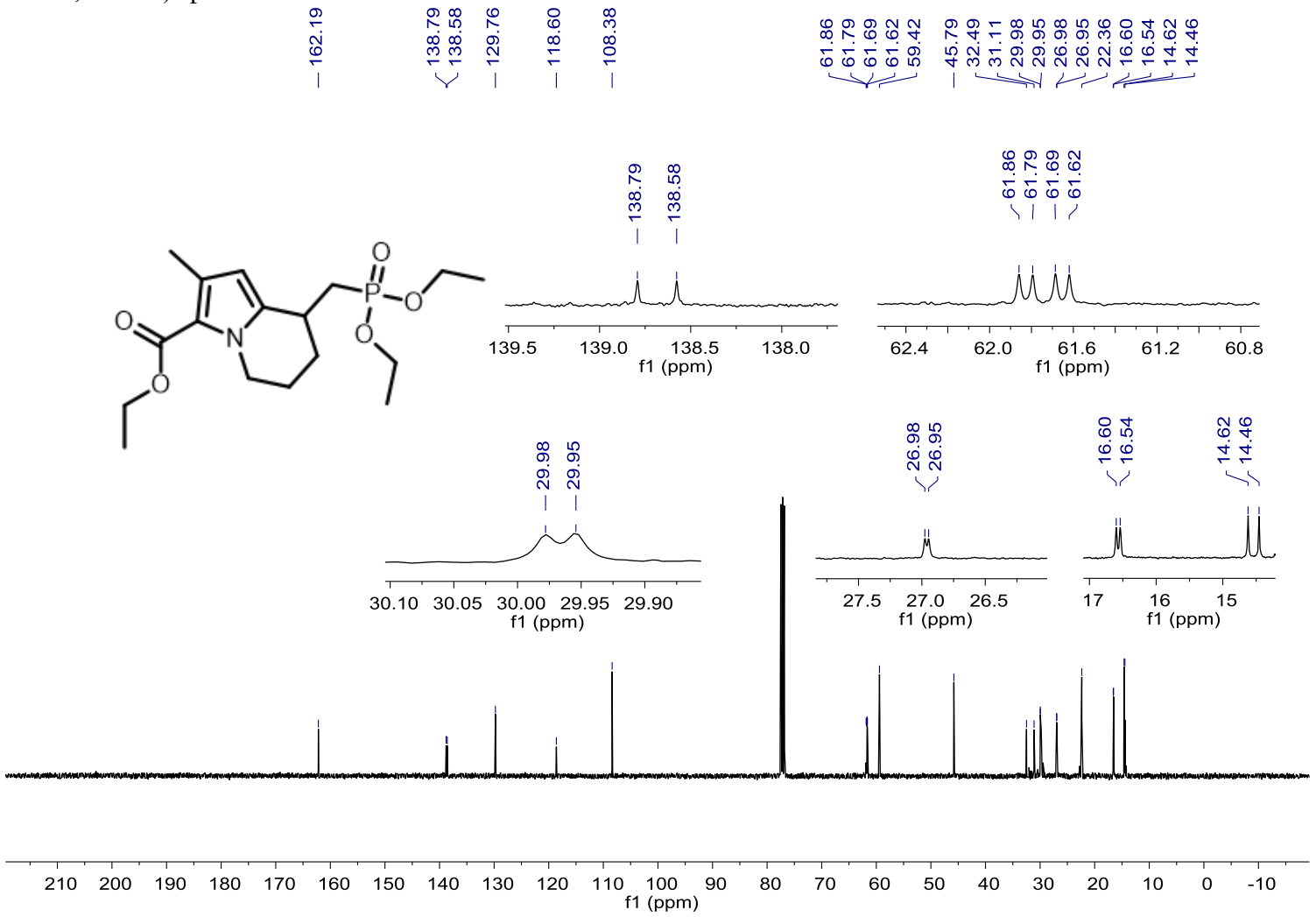
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3sa**



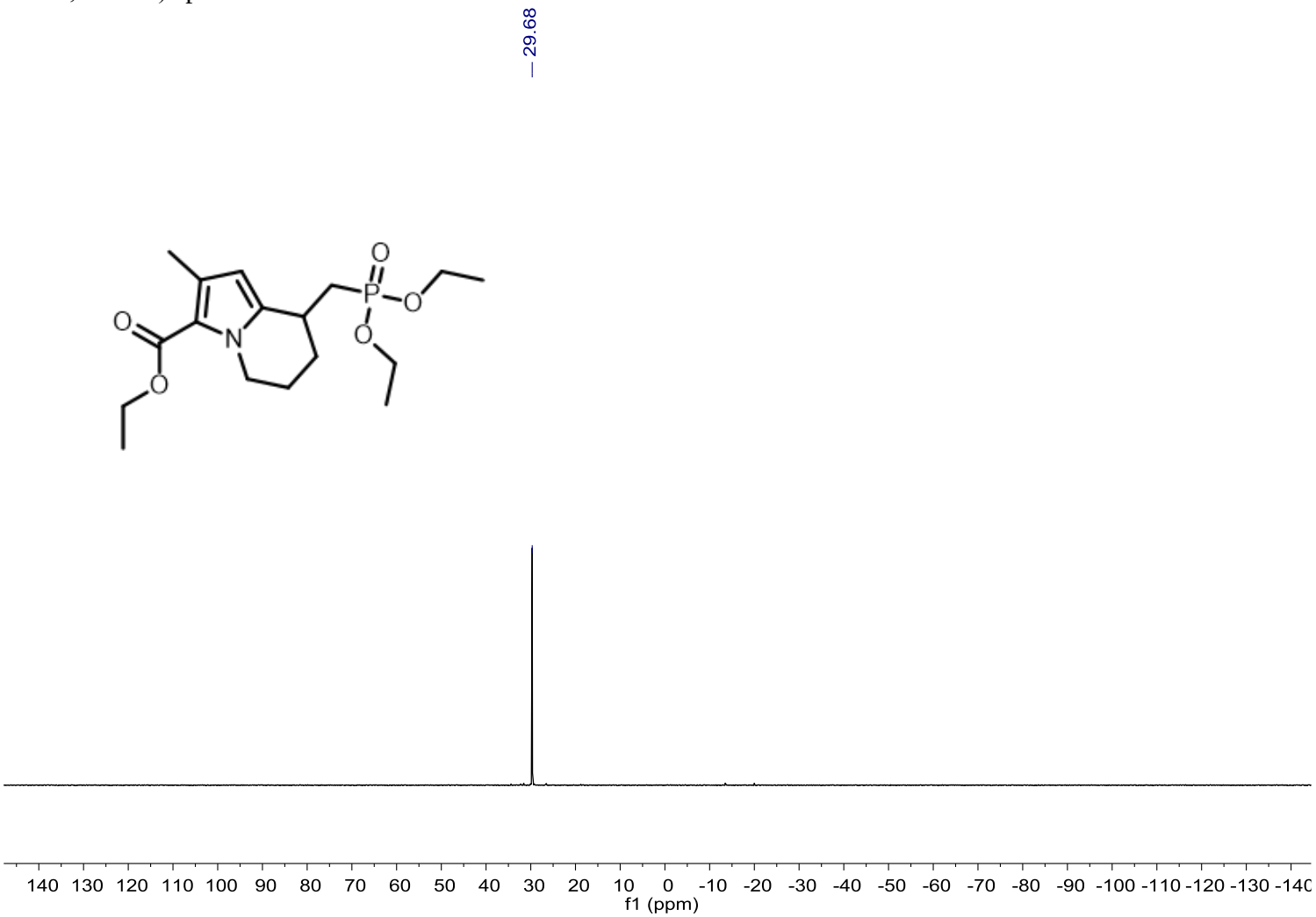
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ta**



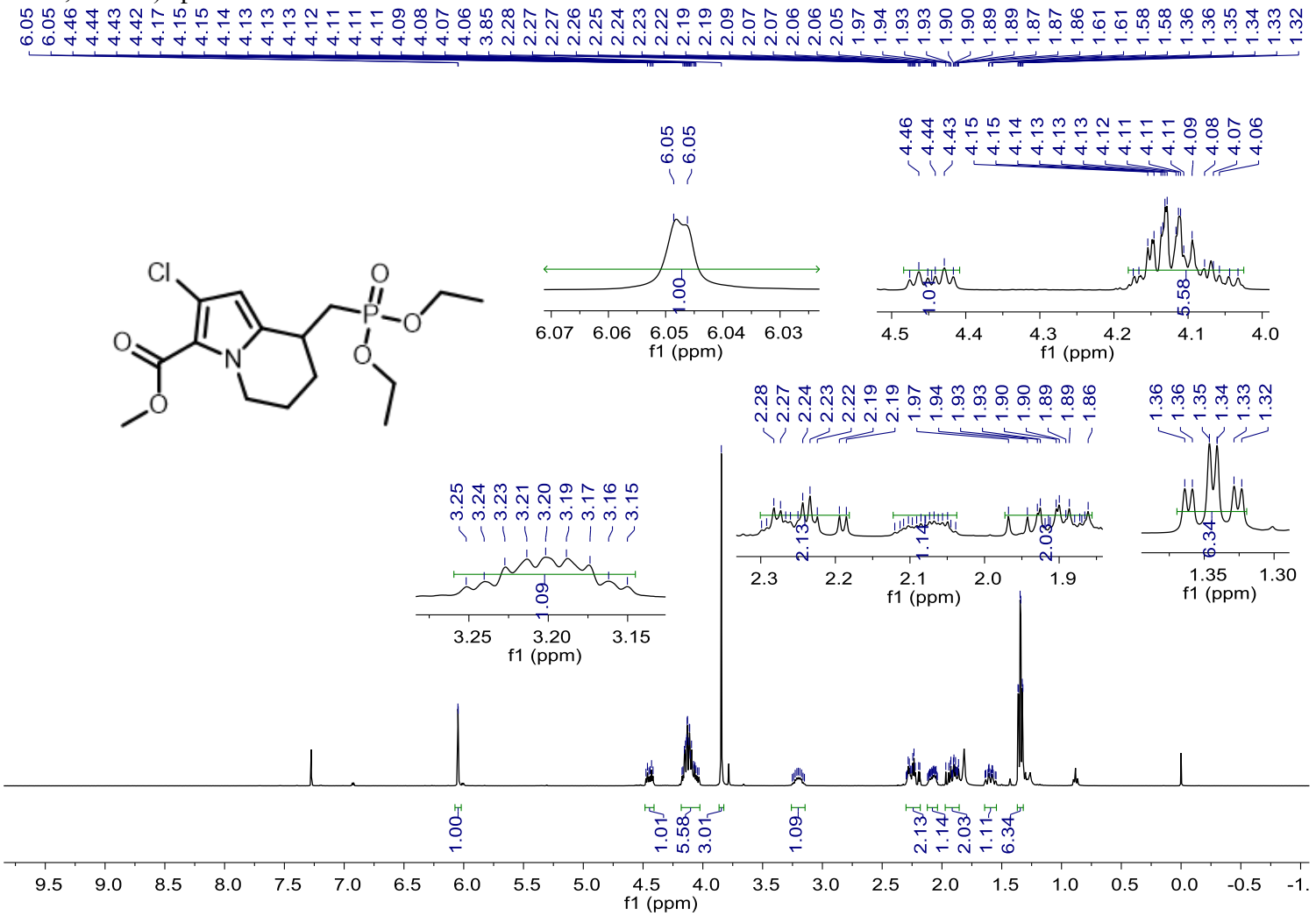
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ta**



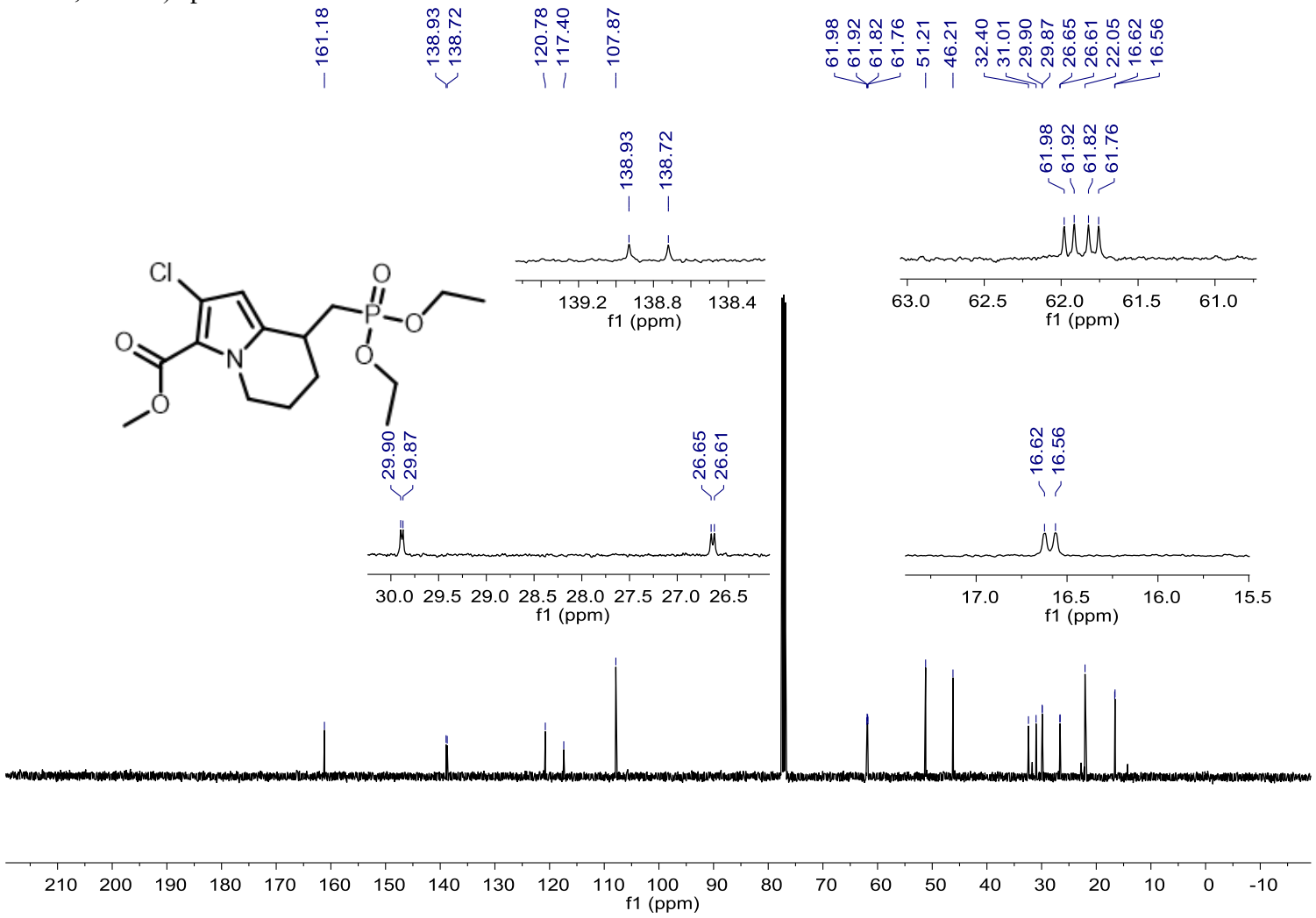
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ta**



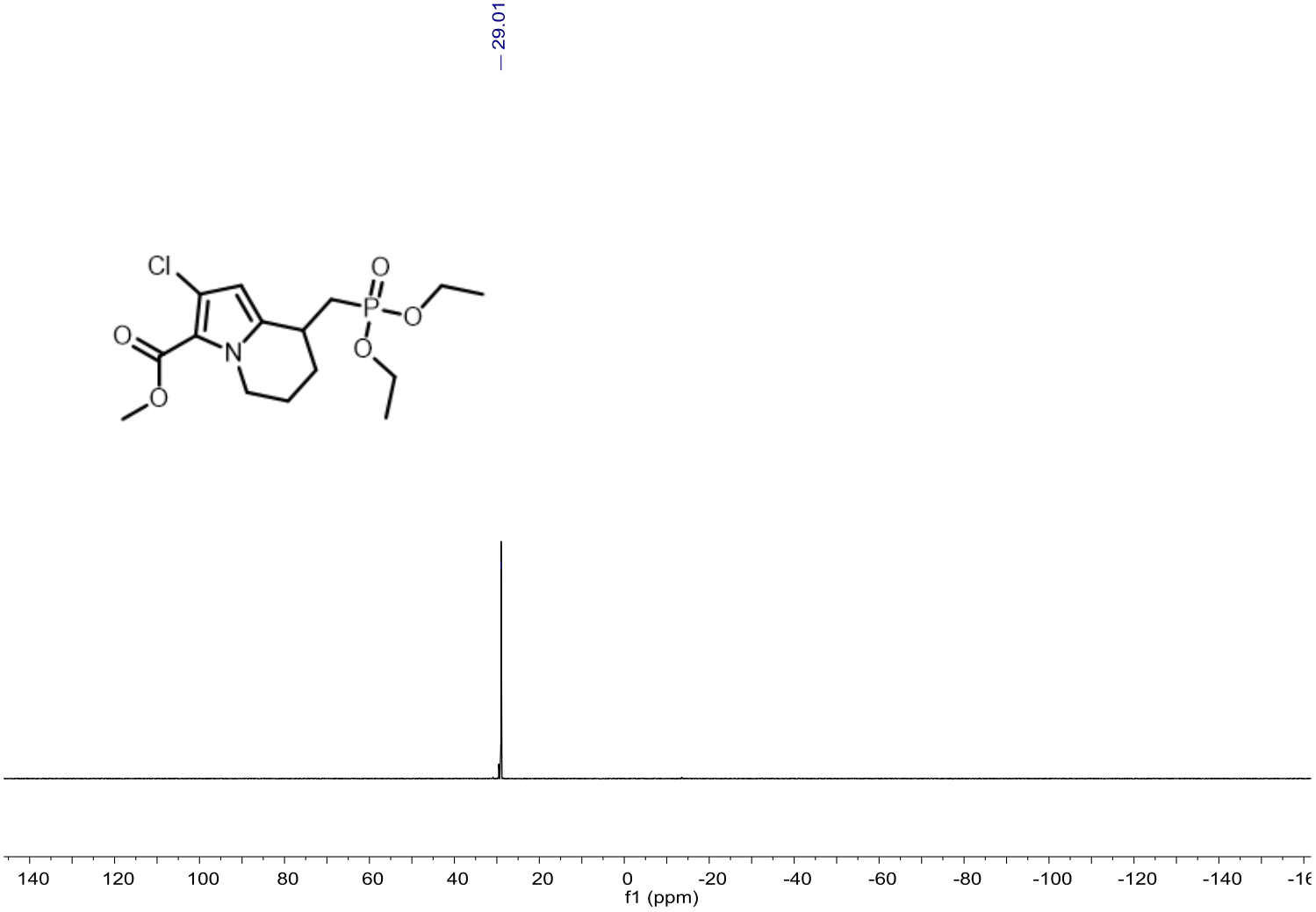
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ua**



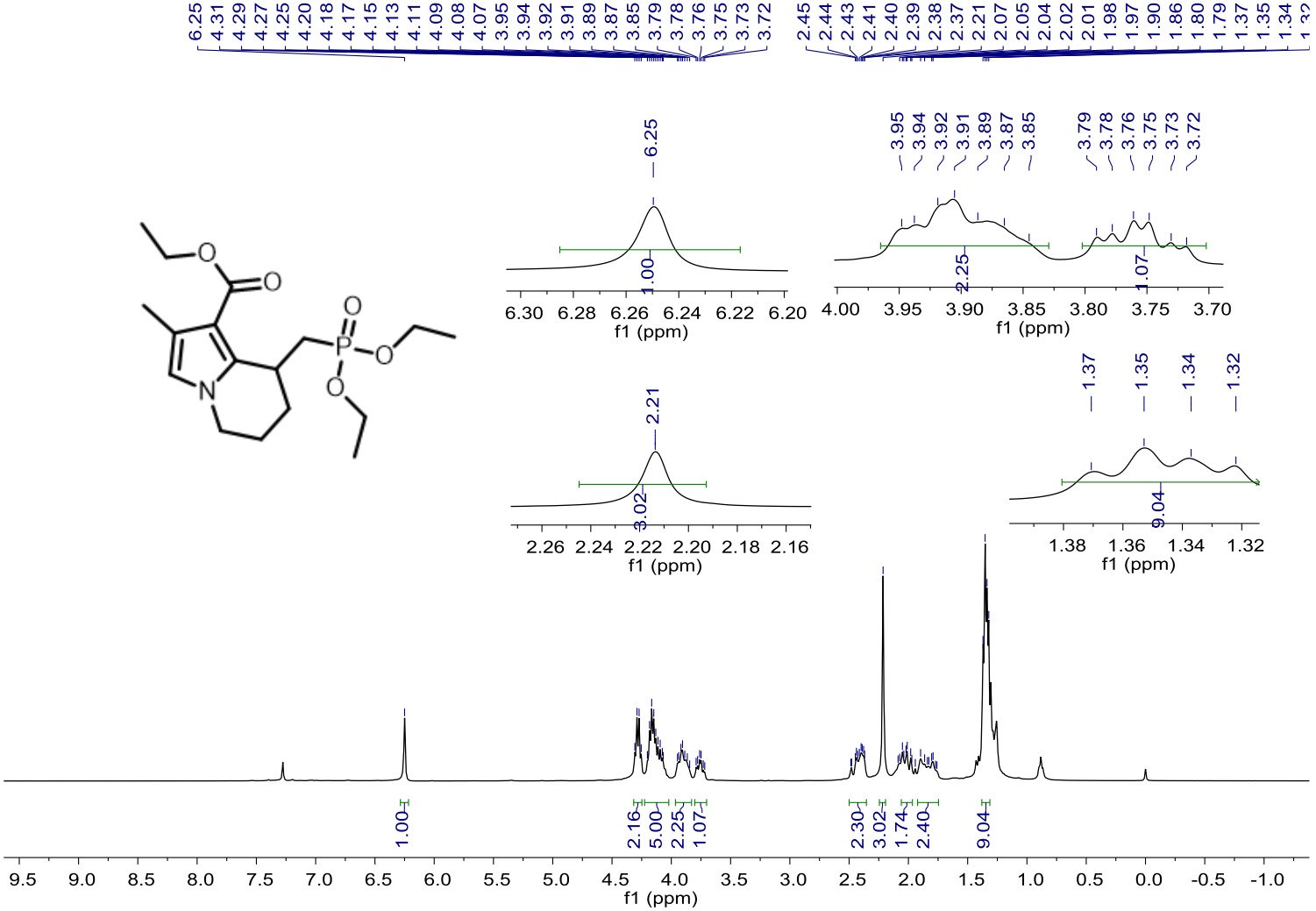
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ua**



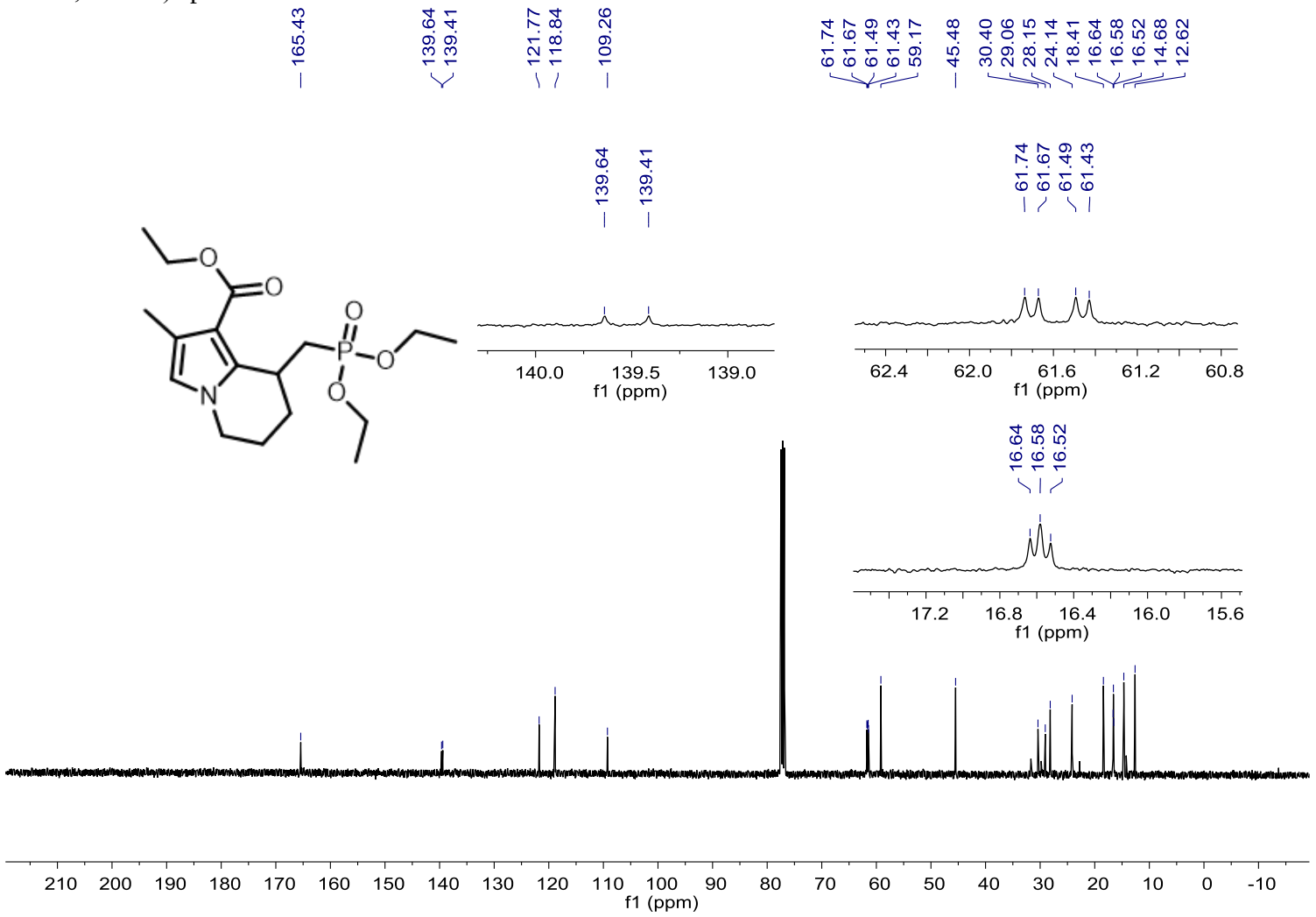
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ua**



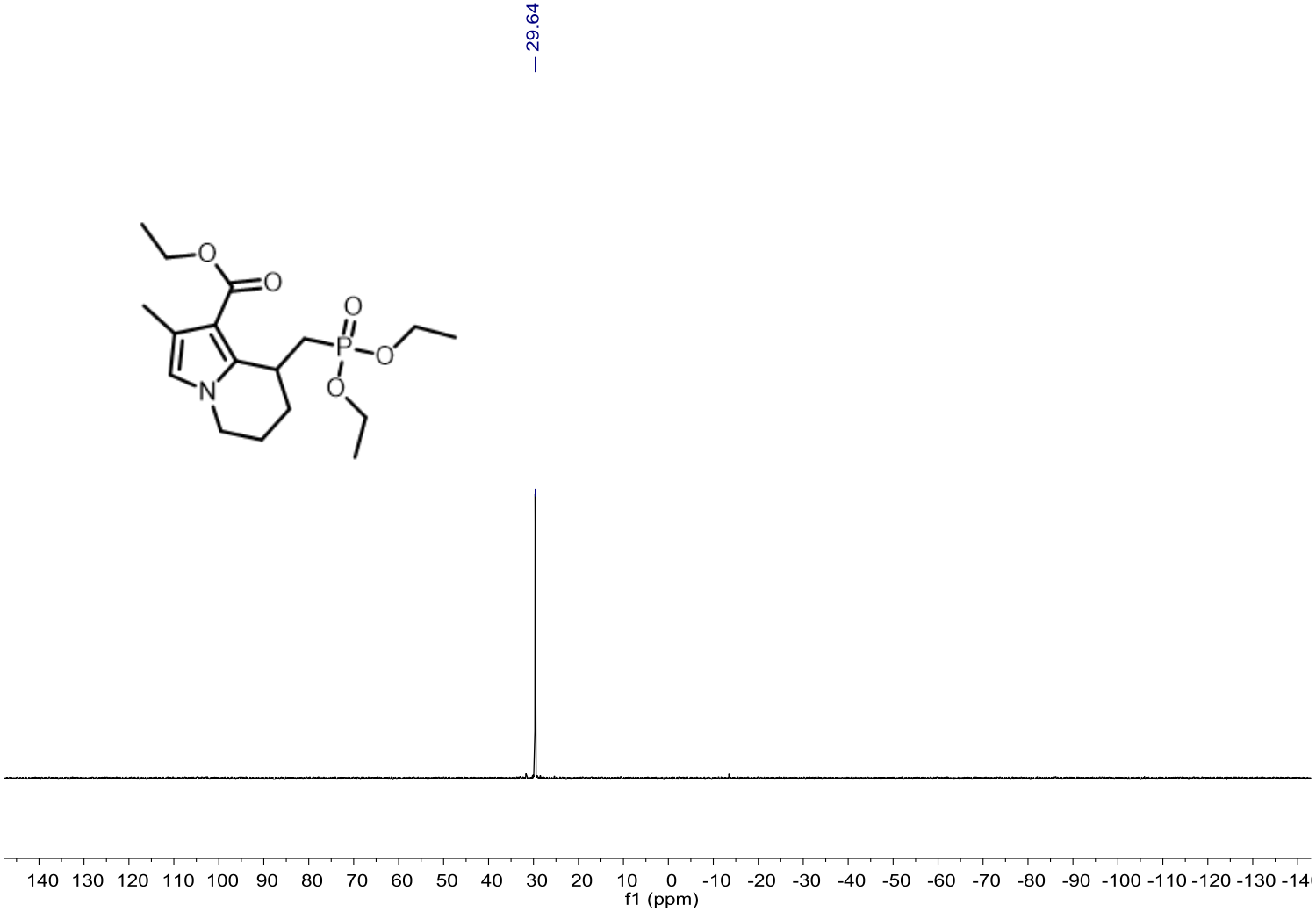
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3va**



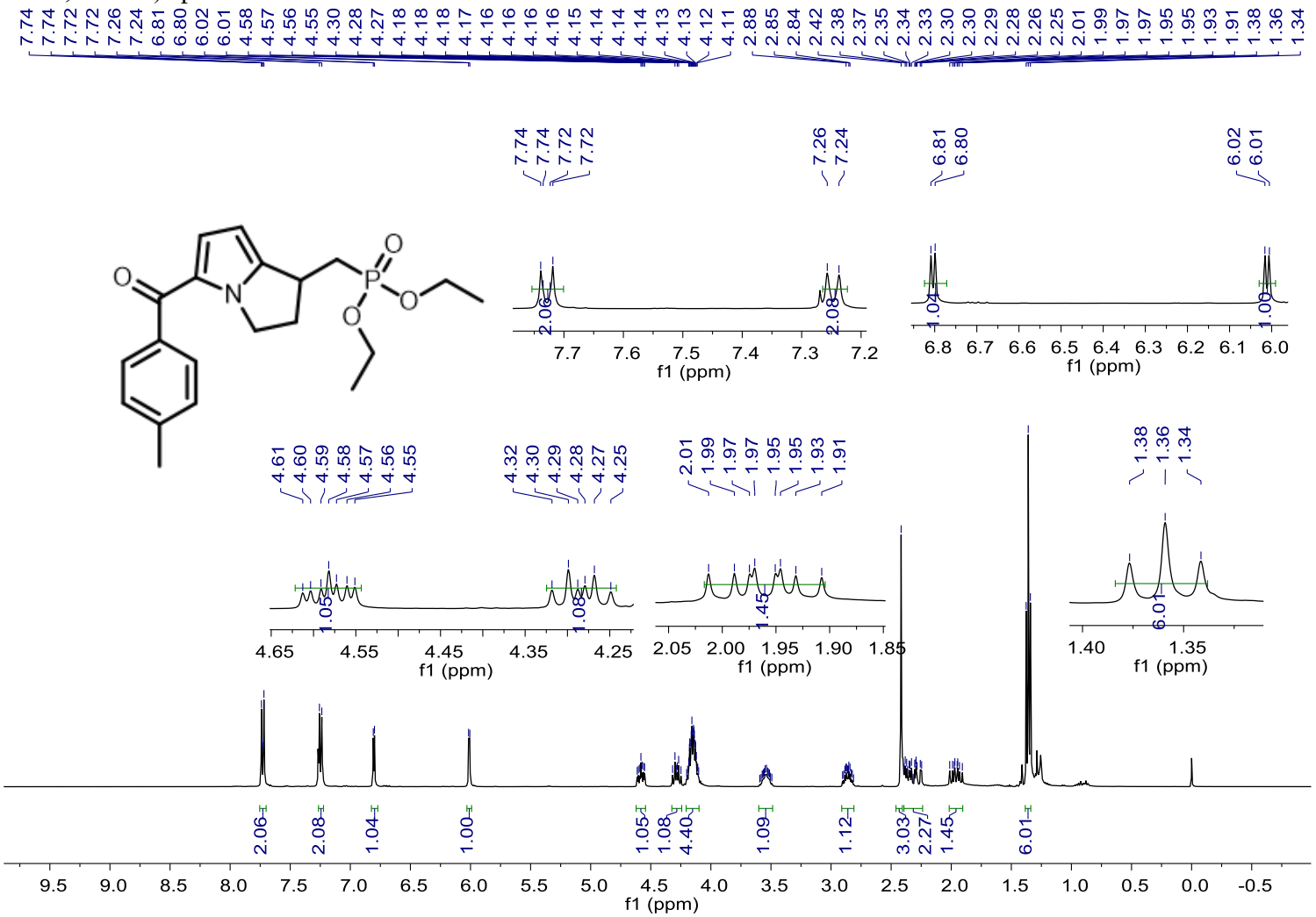
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3va**



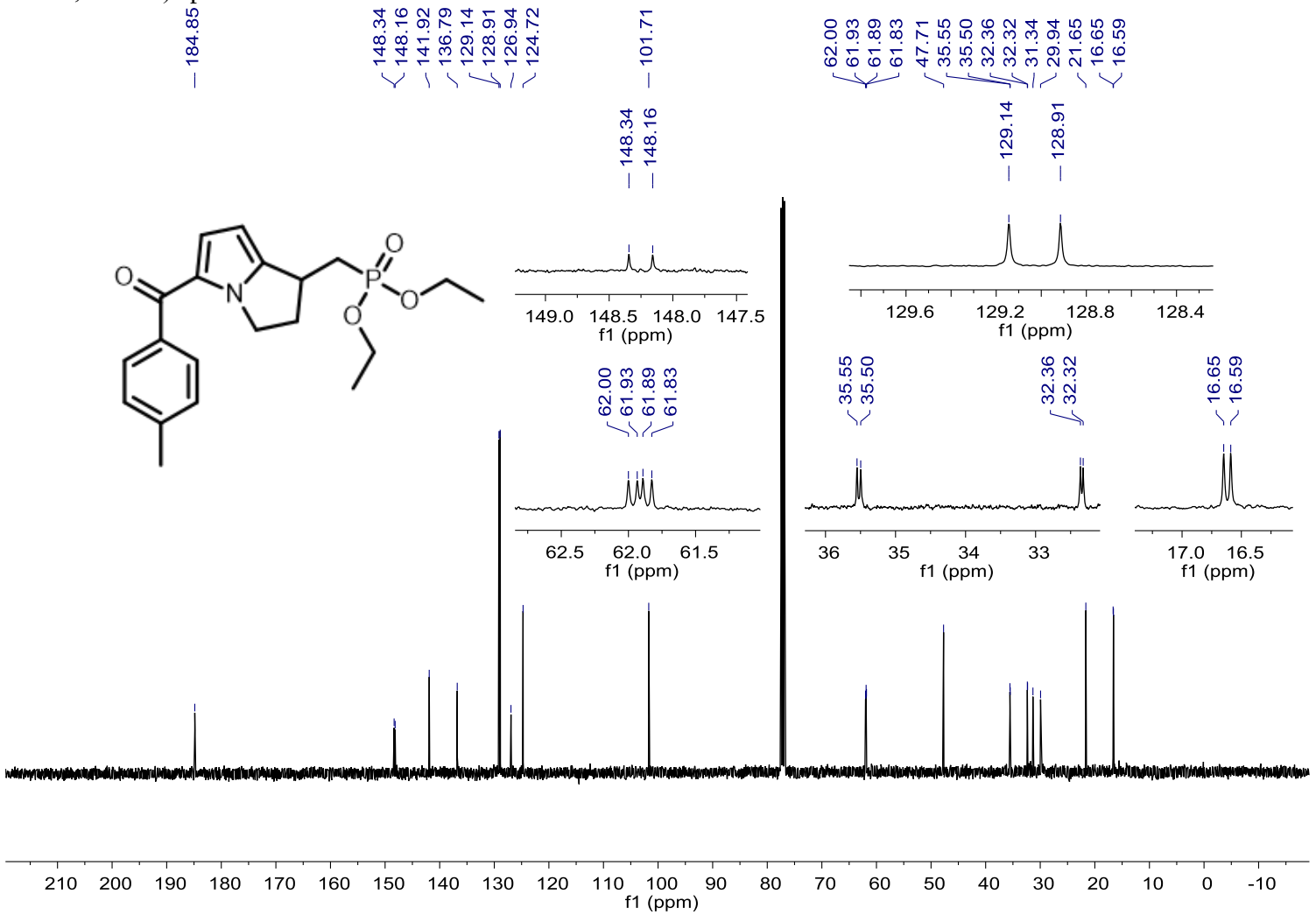
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3va**



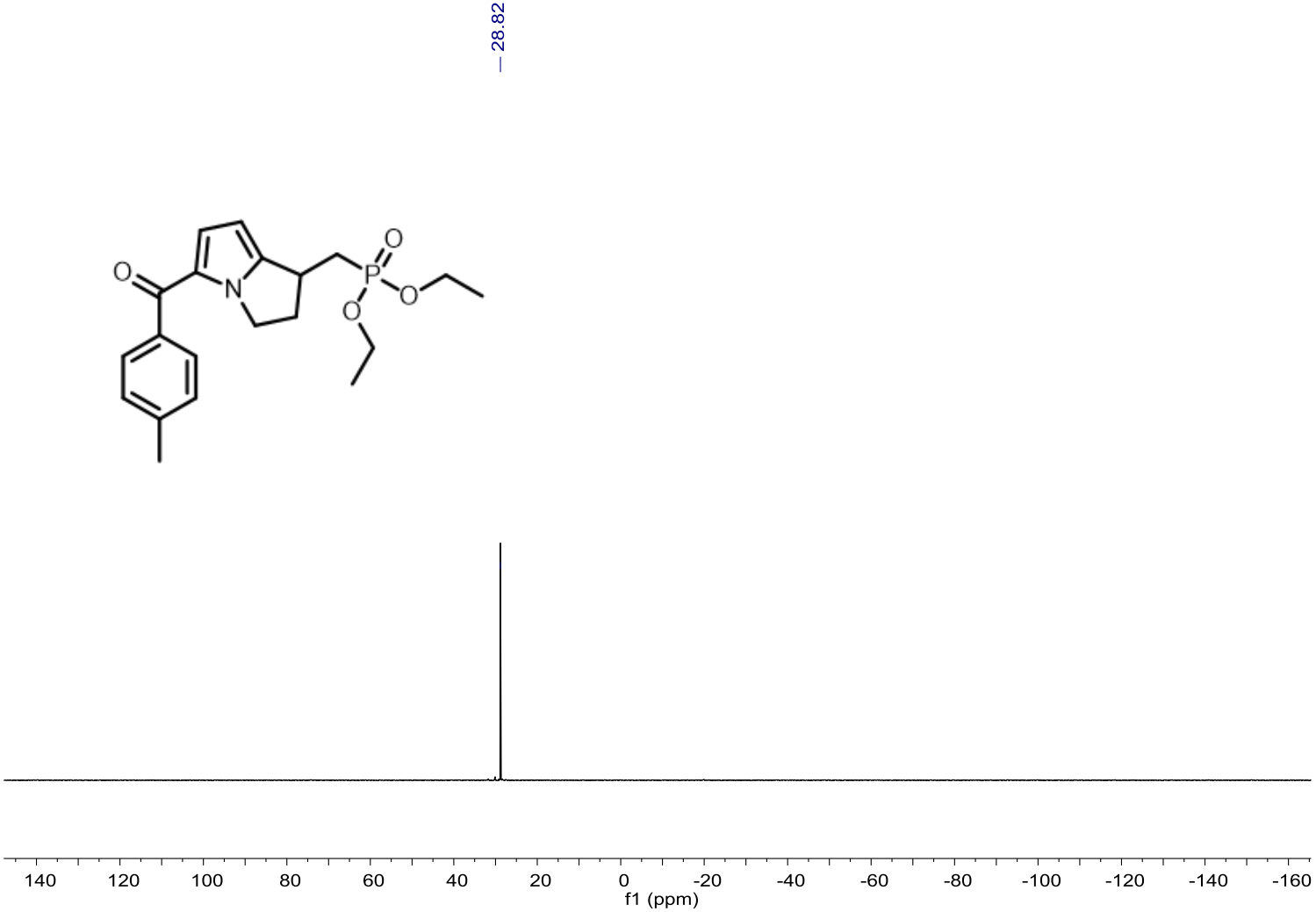
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3wa**



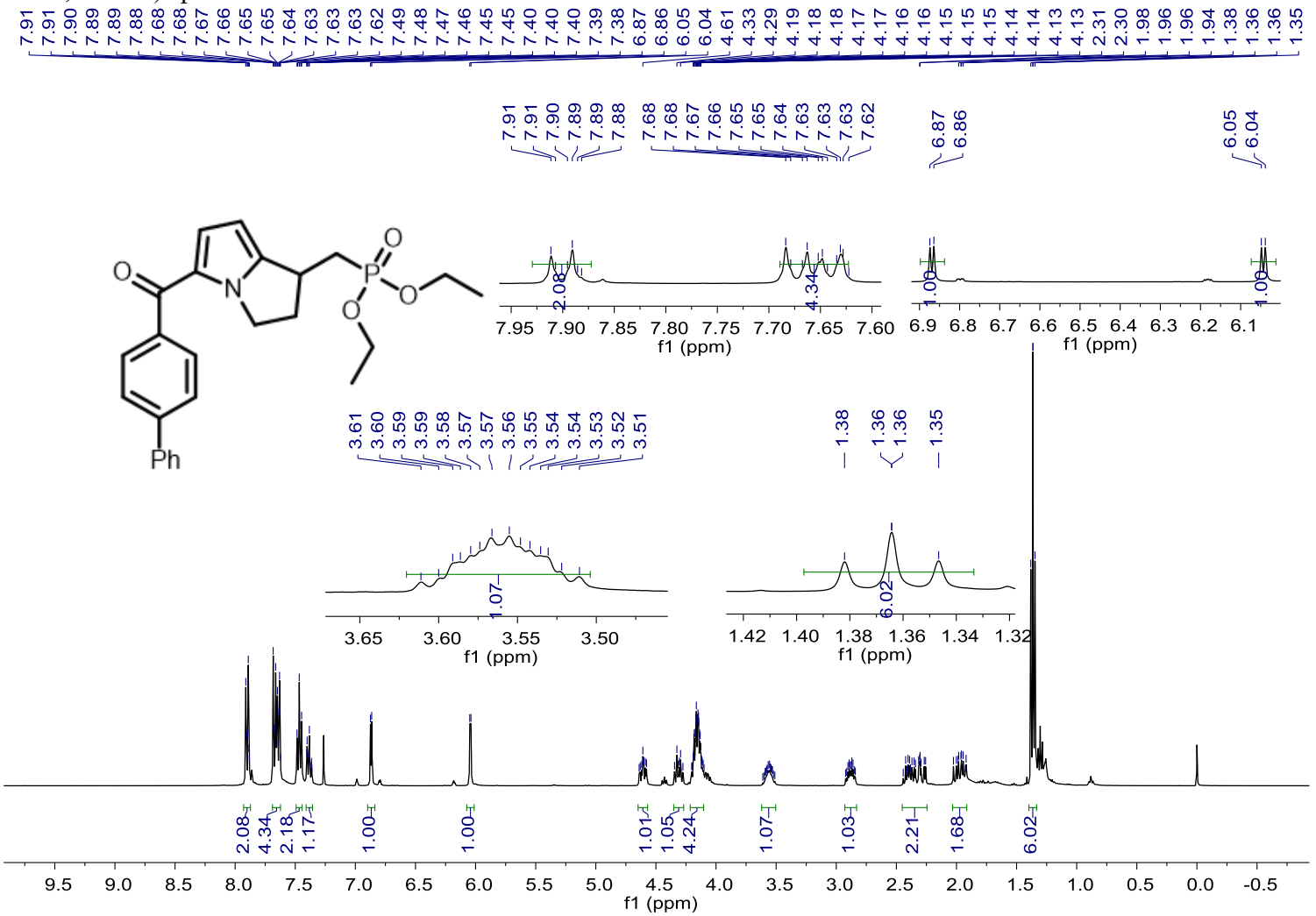
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3wa**



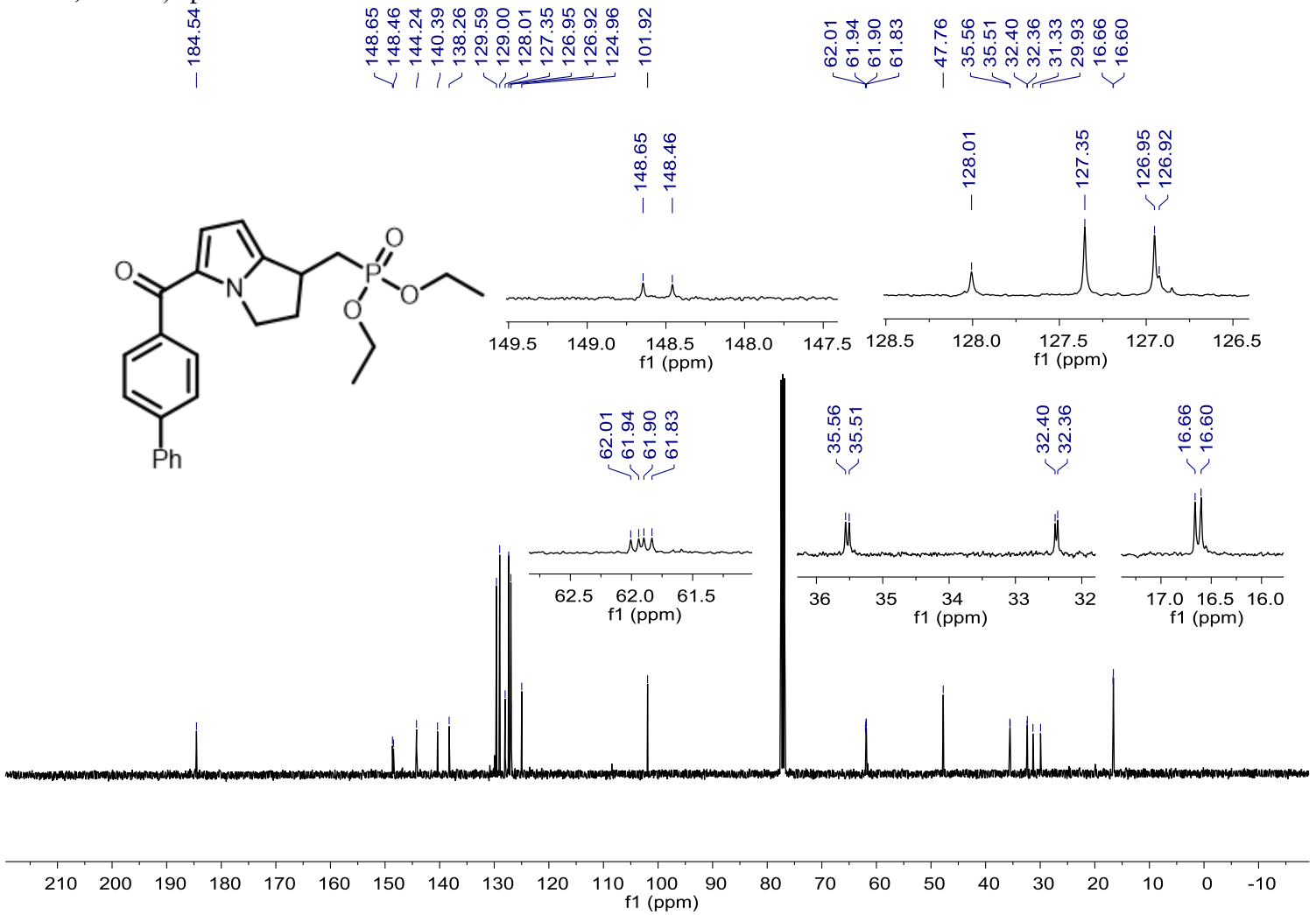
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3wa**



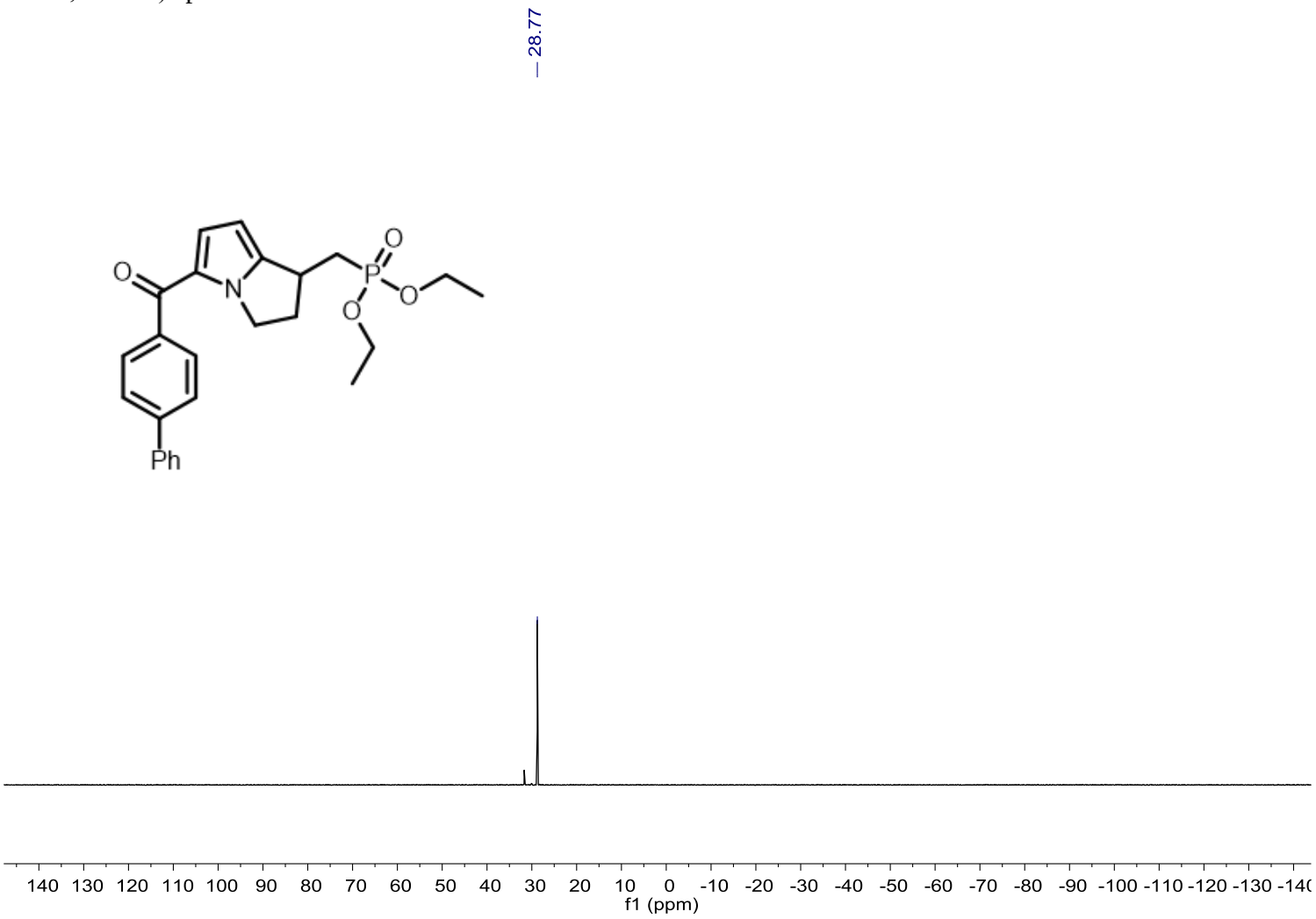
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3xa**



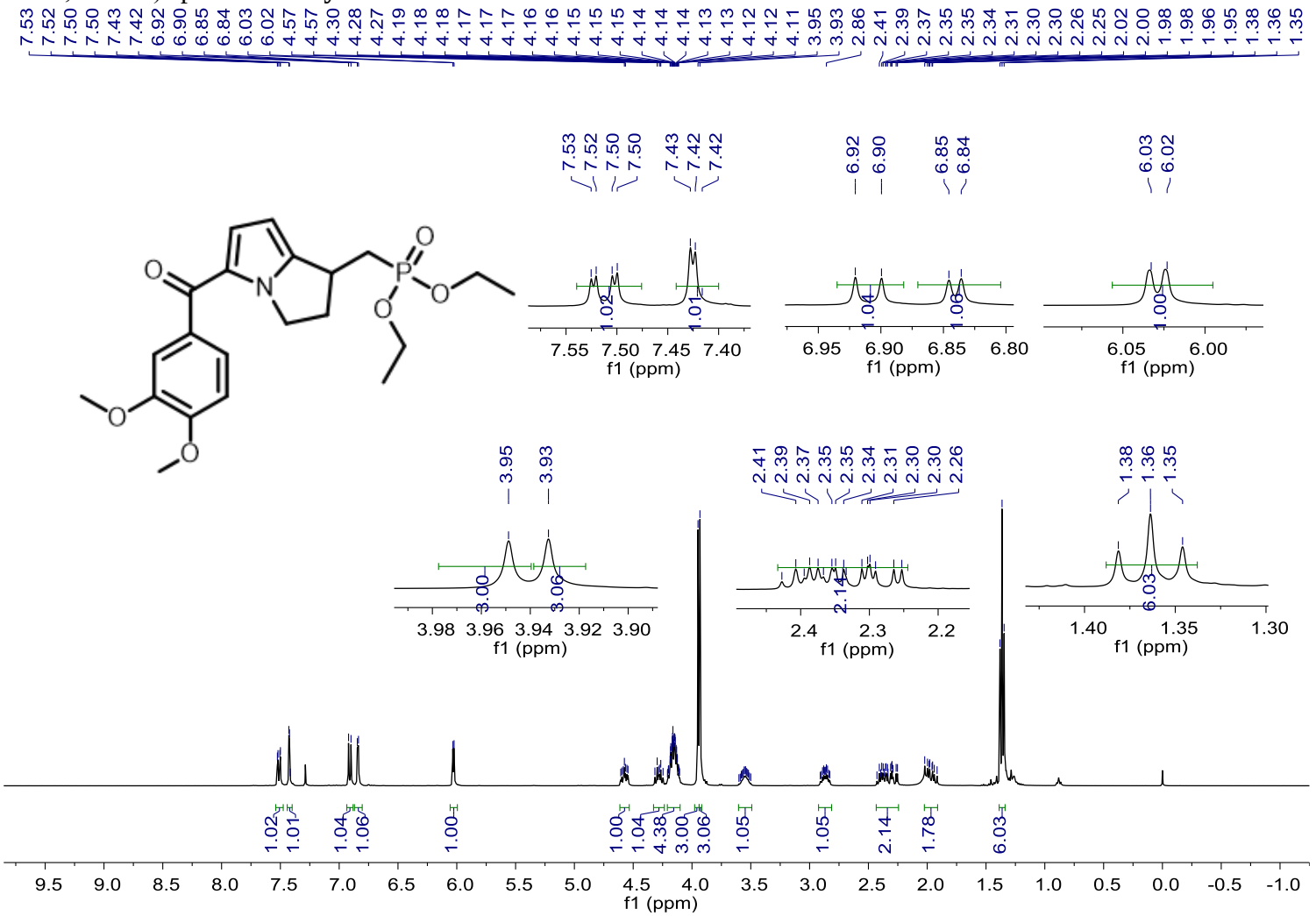
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3xa**



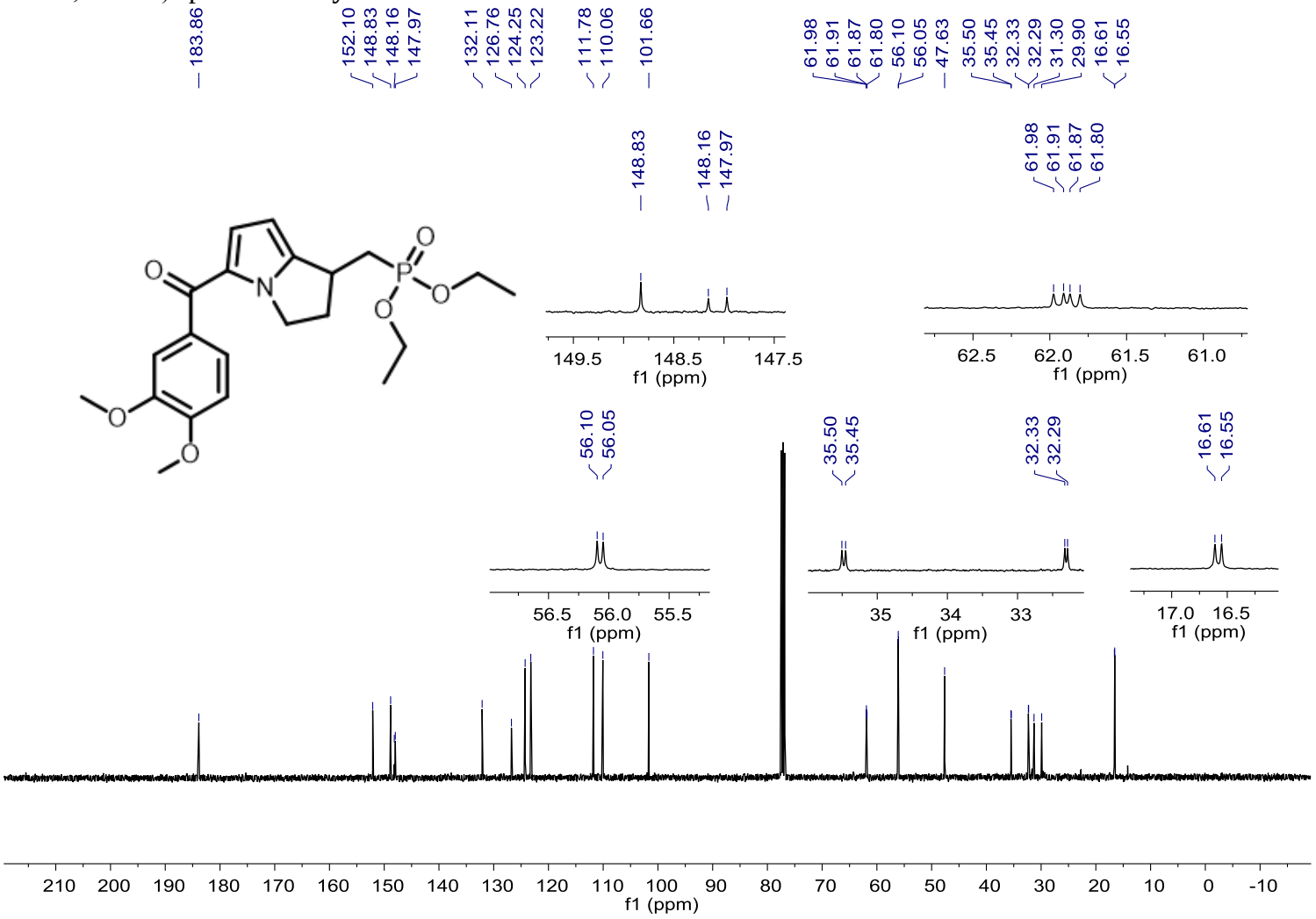
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3xa**



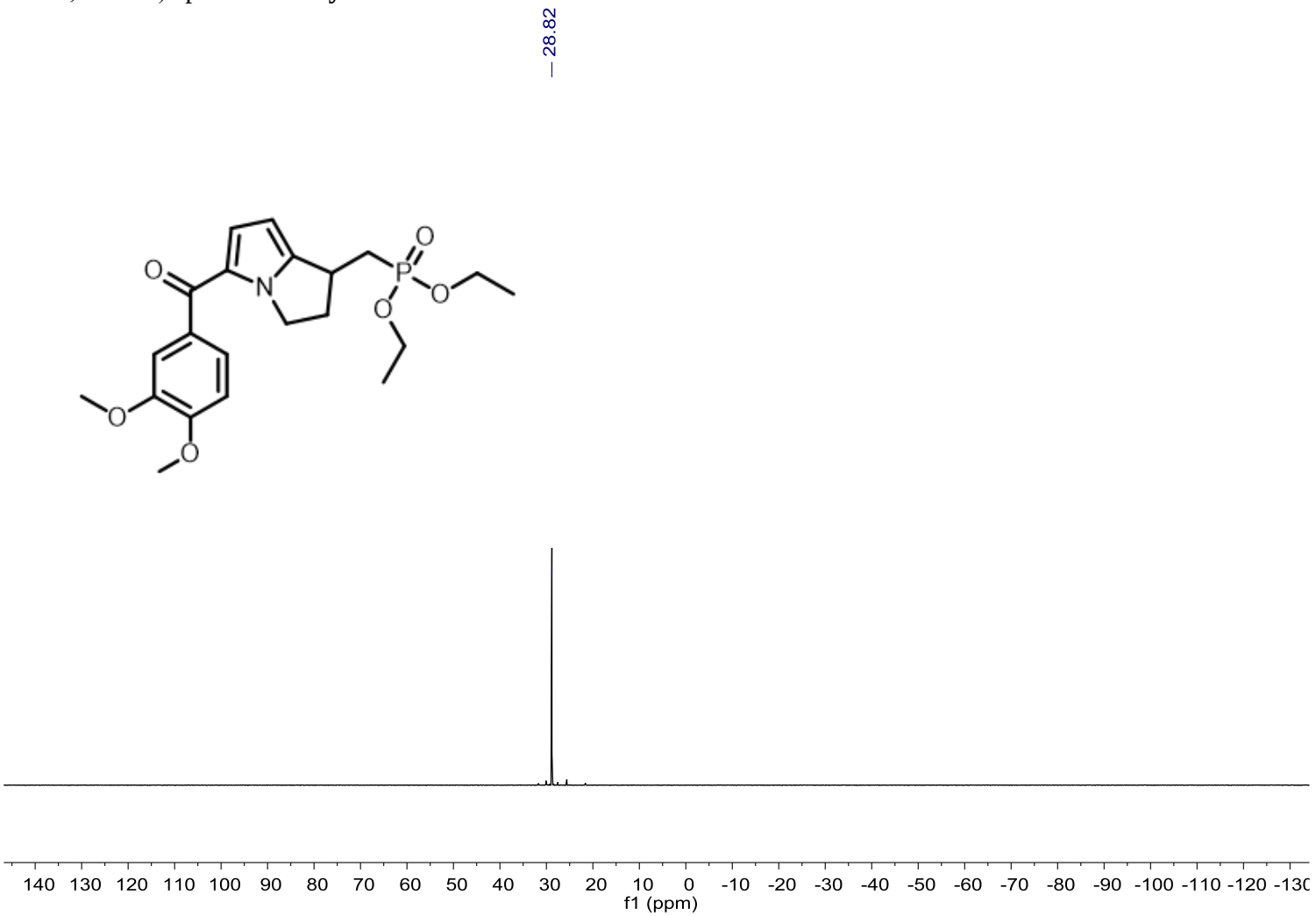
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ya**



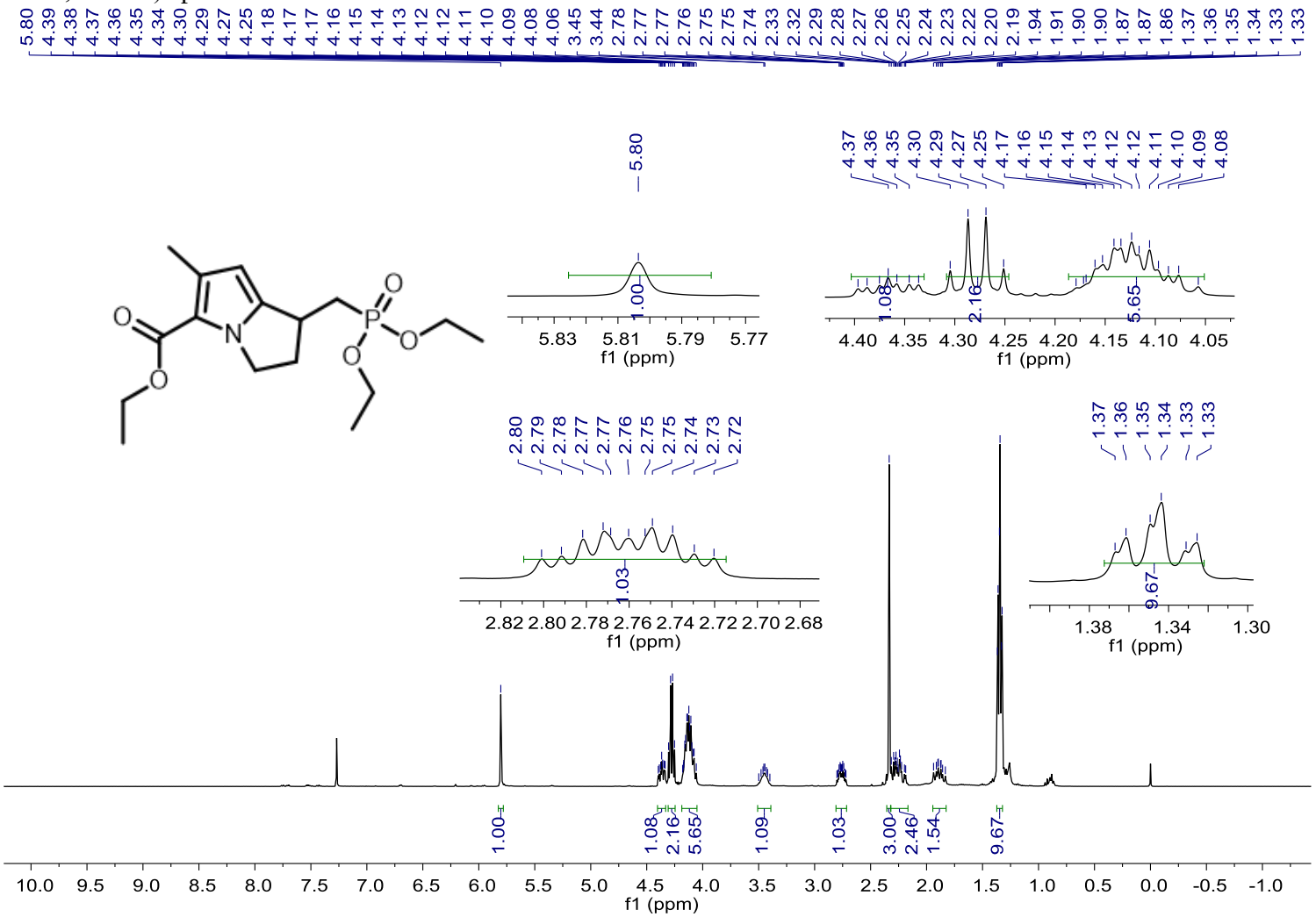
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ya**



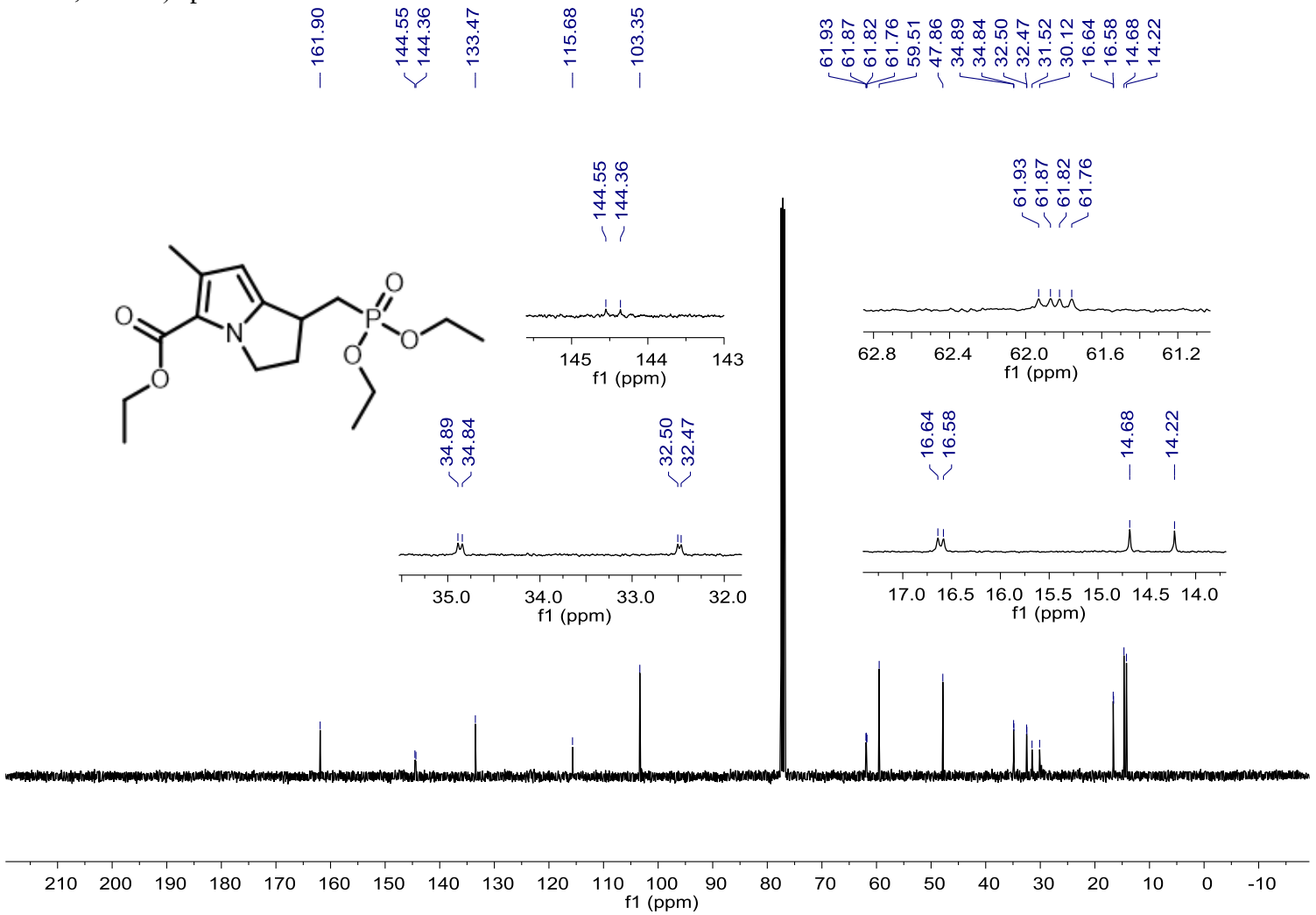
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ya**



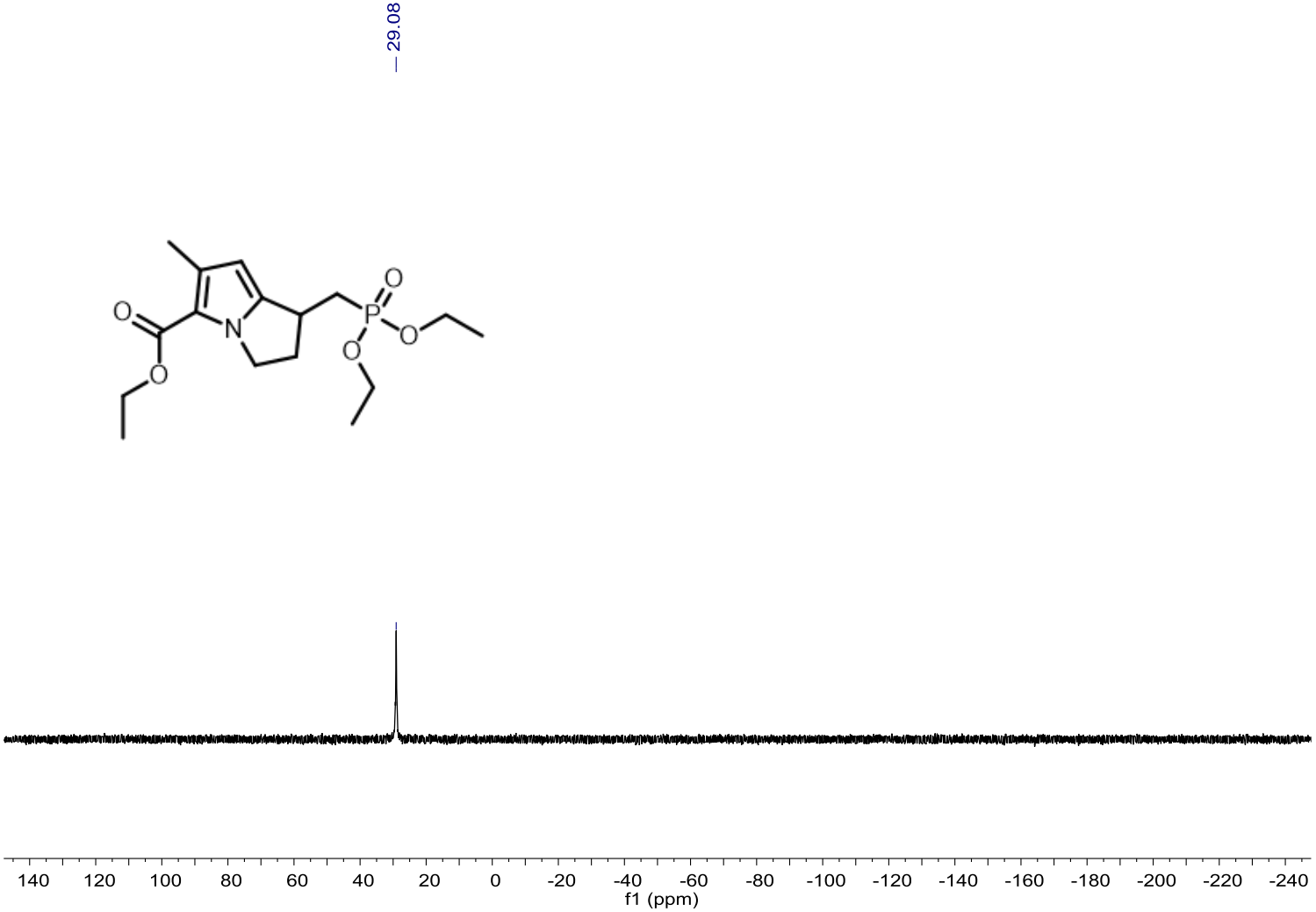
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3za**



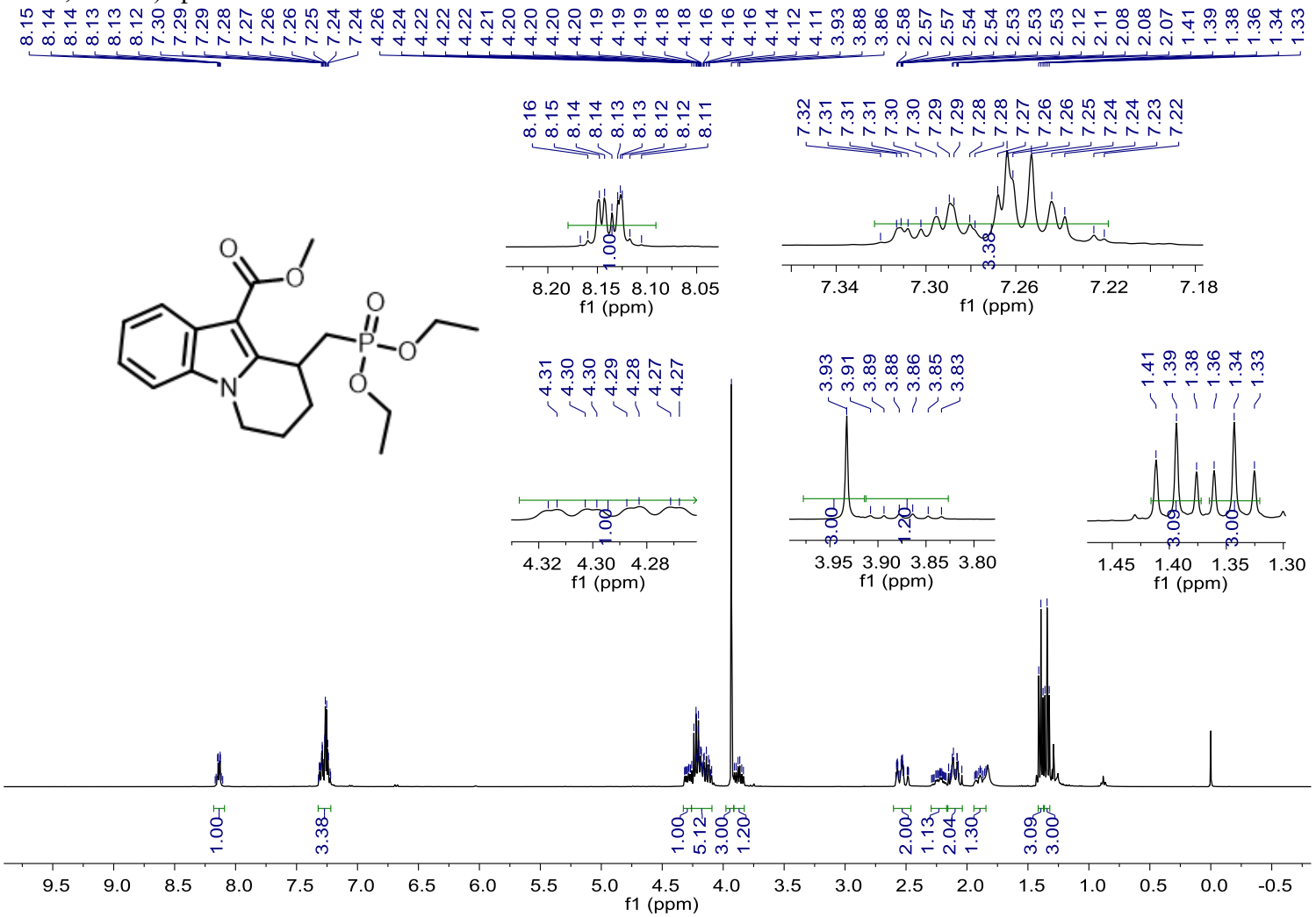
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3za**



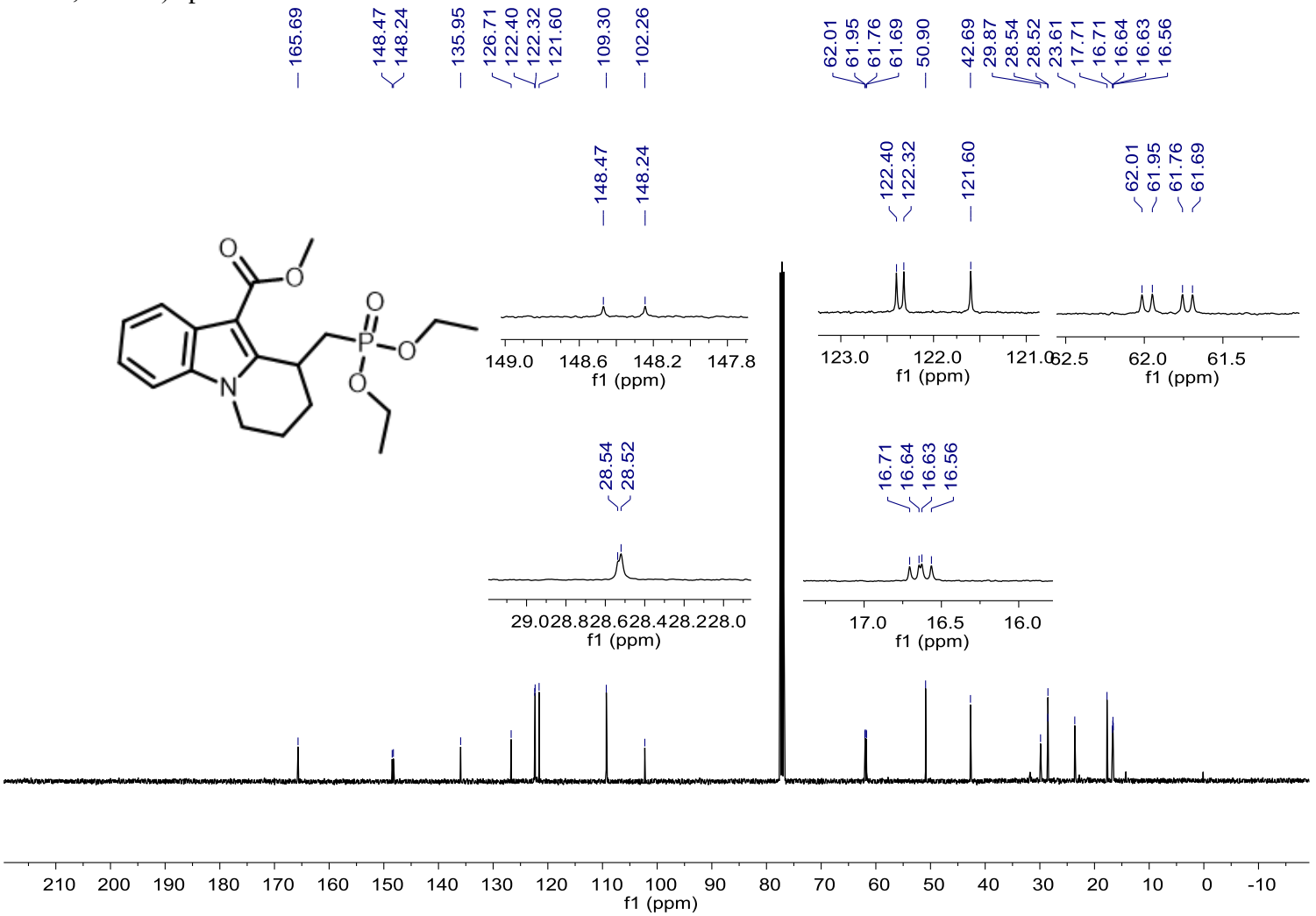
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3za**



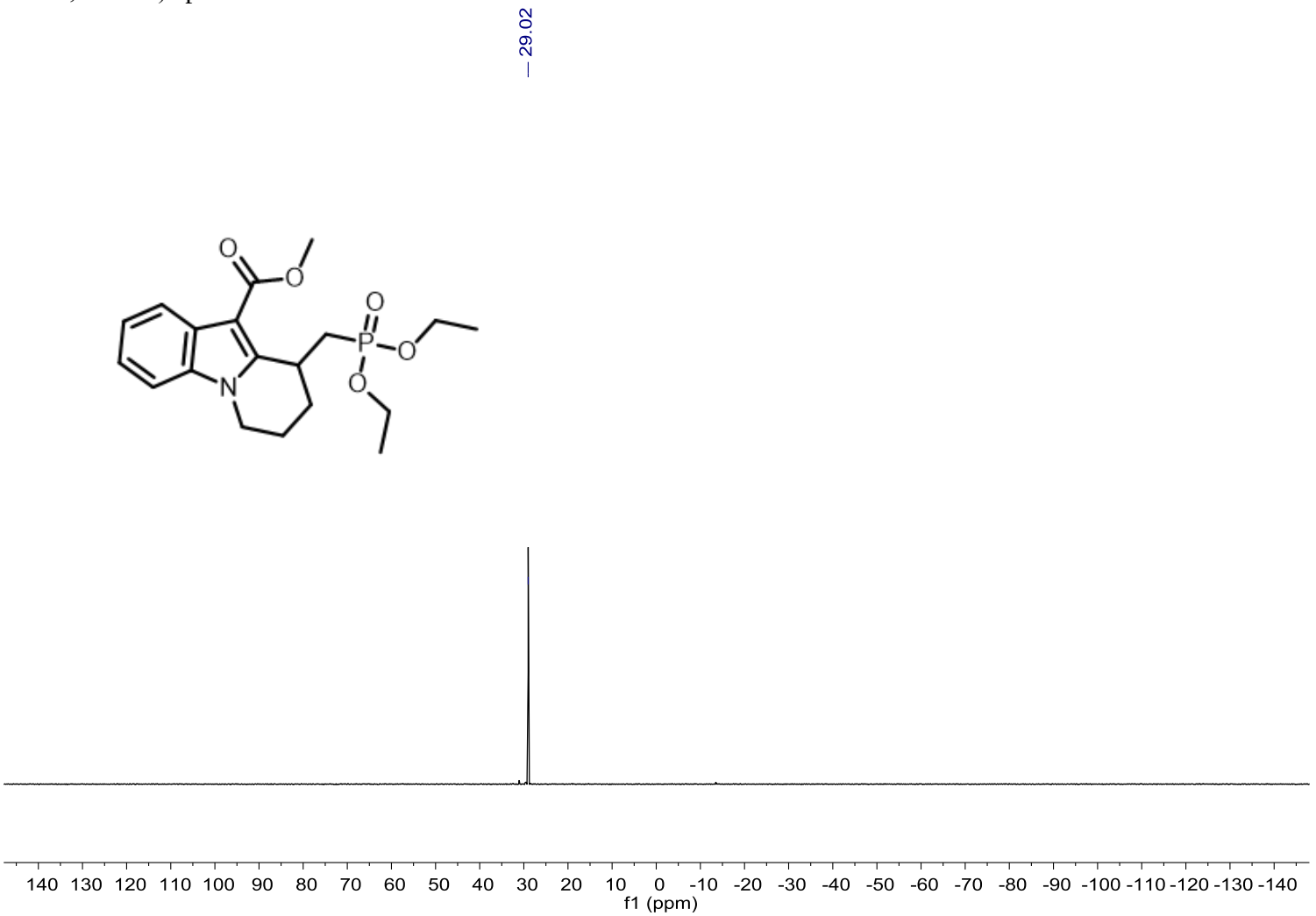
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5aa**



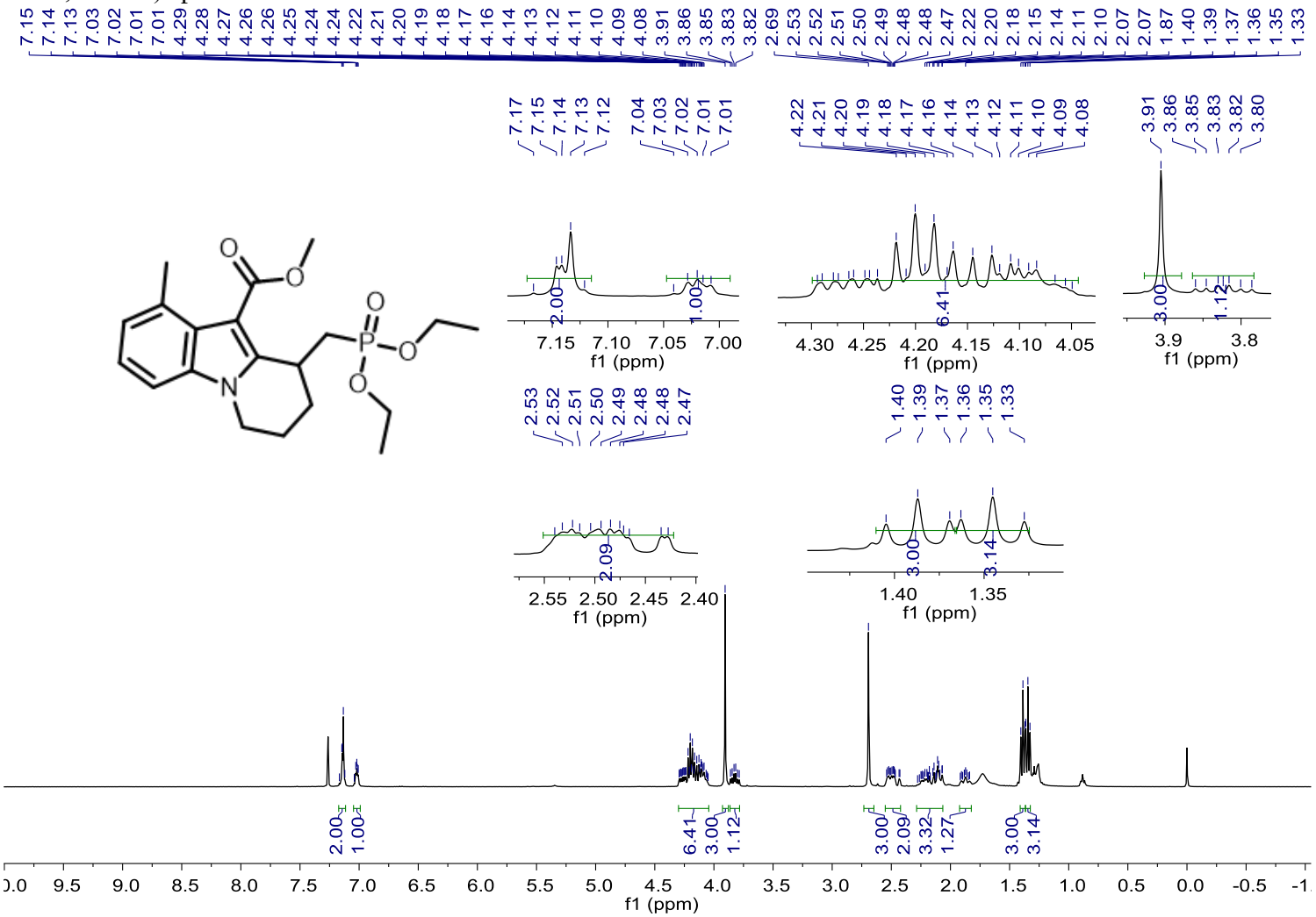
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5aa**



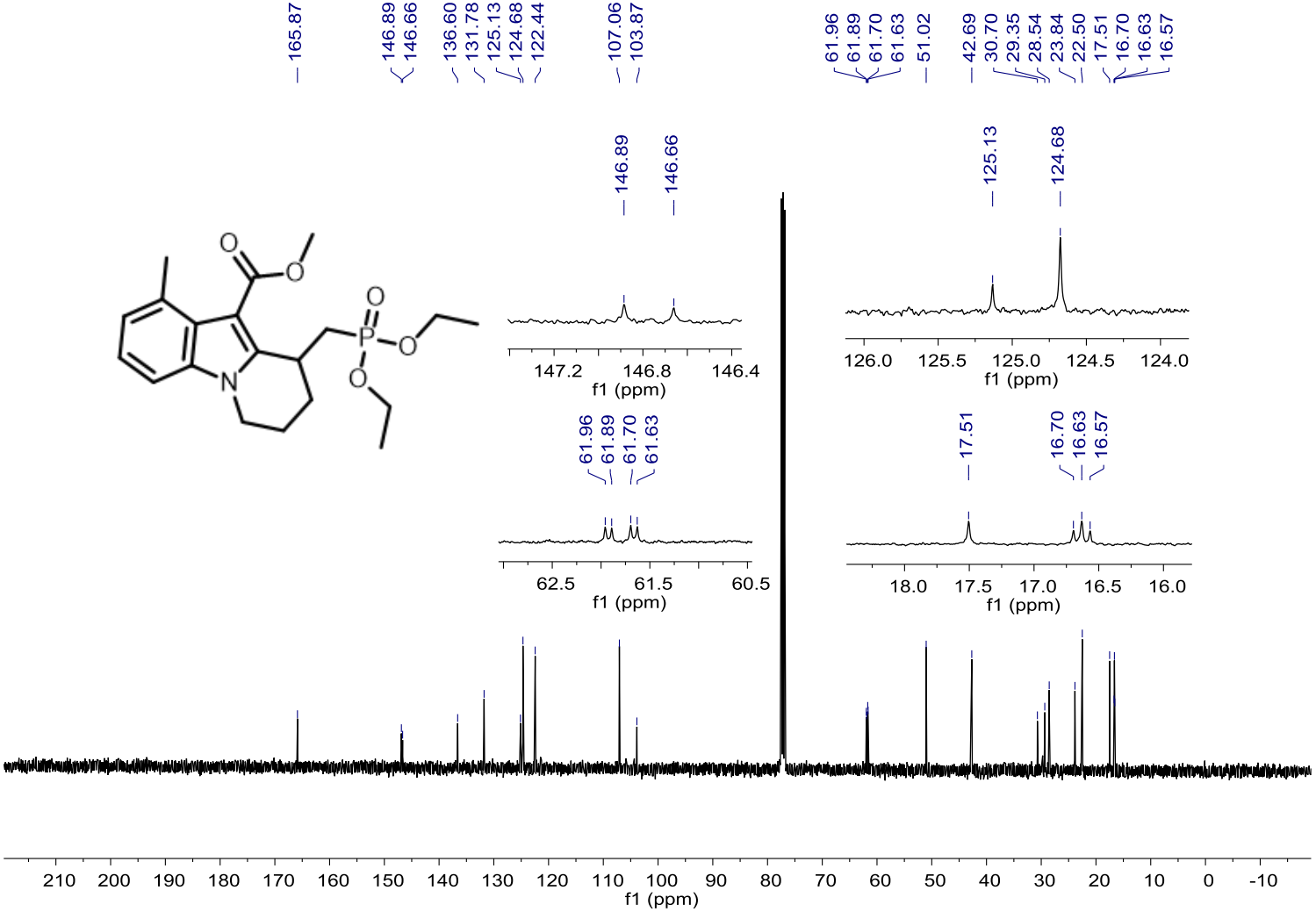
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **5aa**



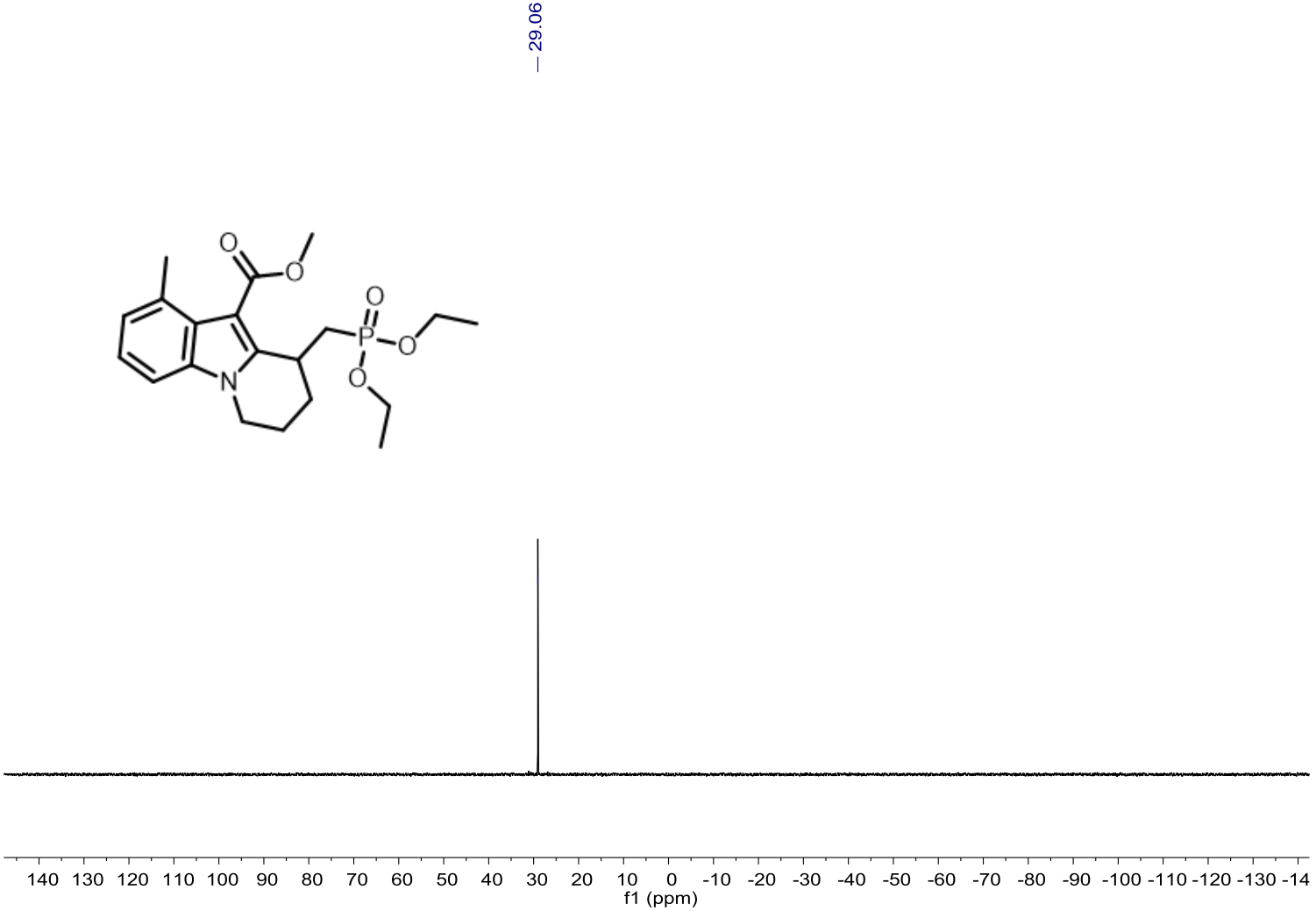
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5ba**



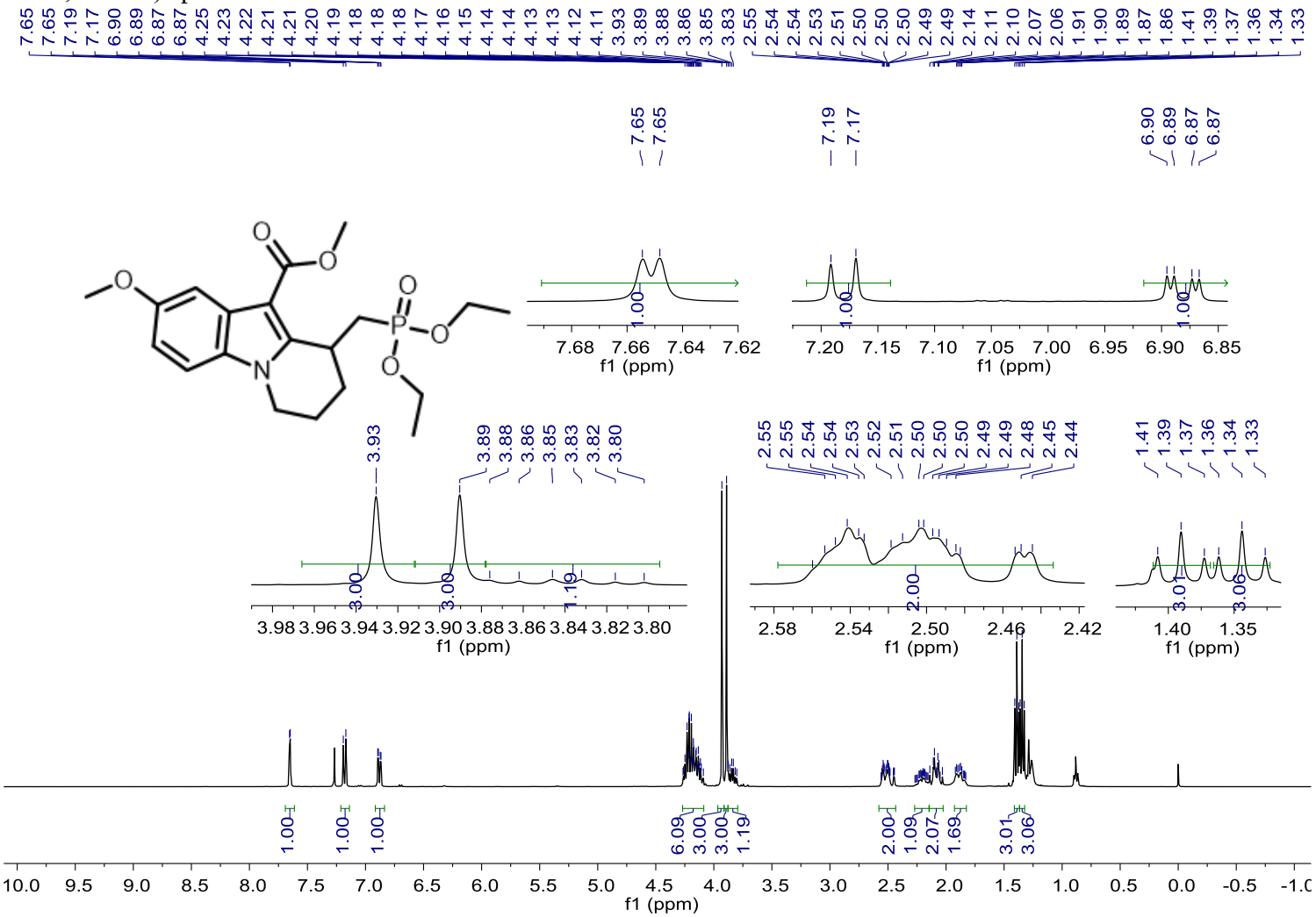
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5ba**



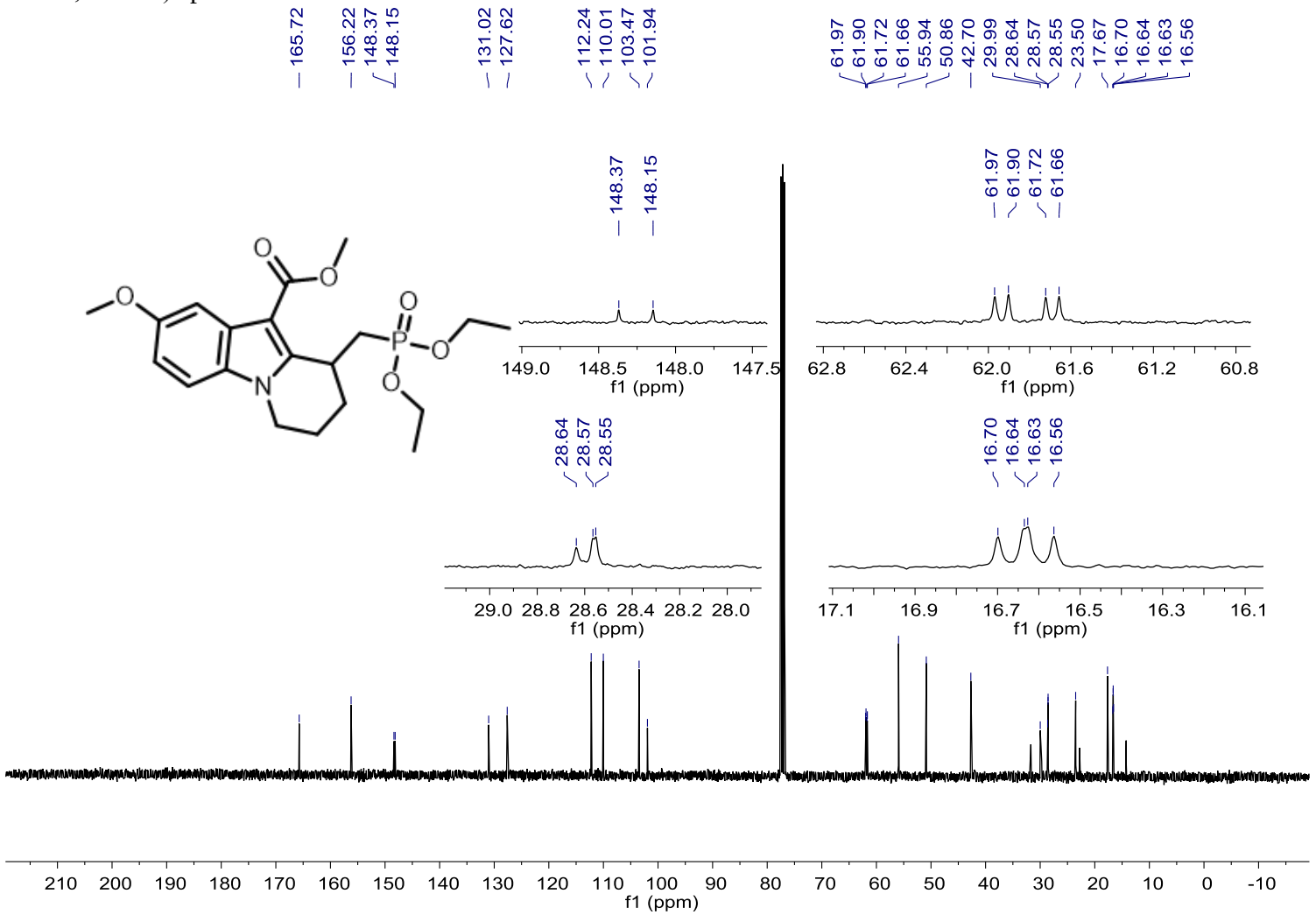
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **5ba**



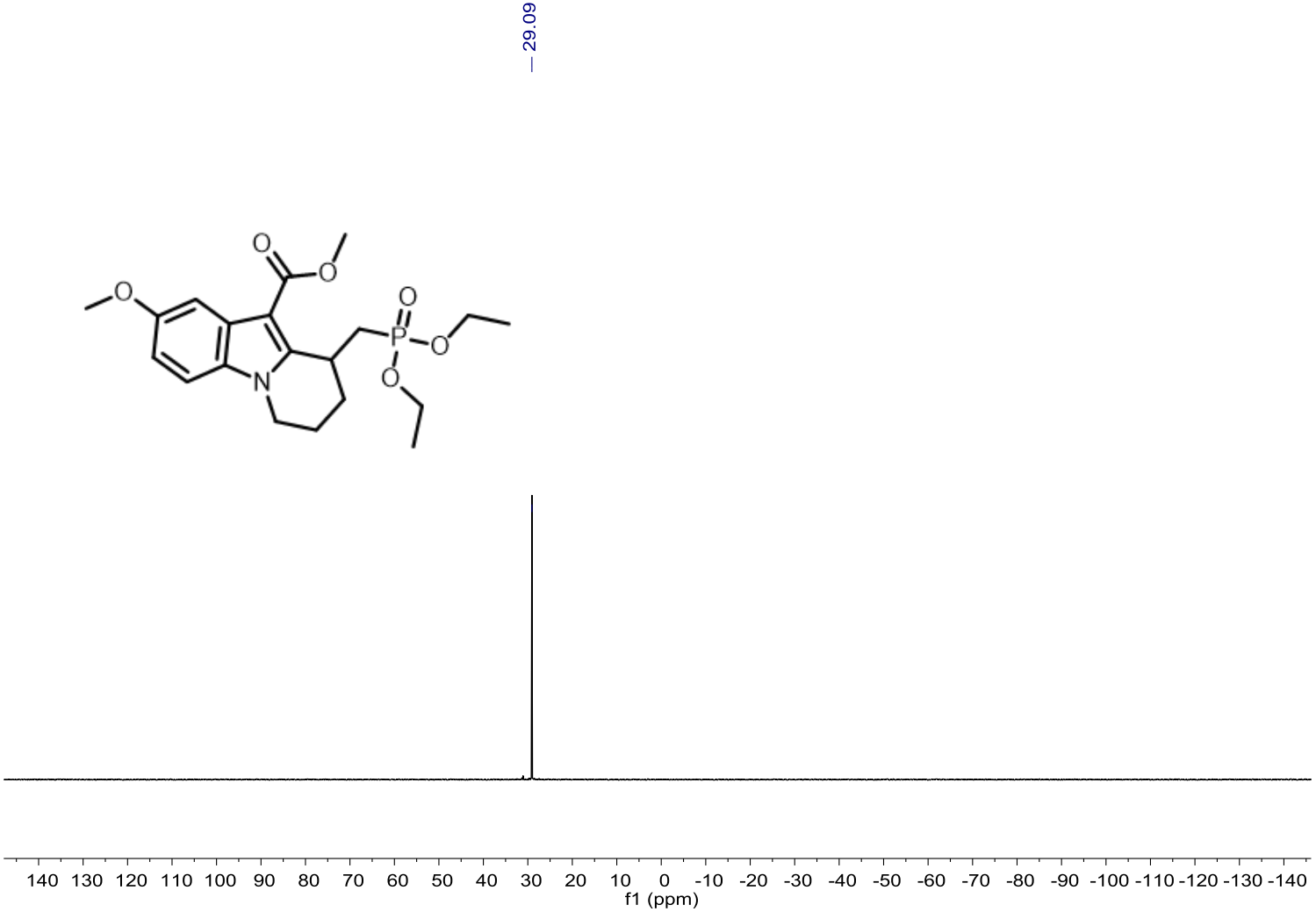
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5ca**



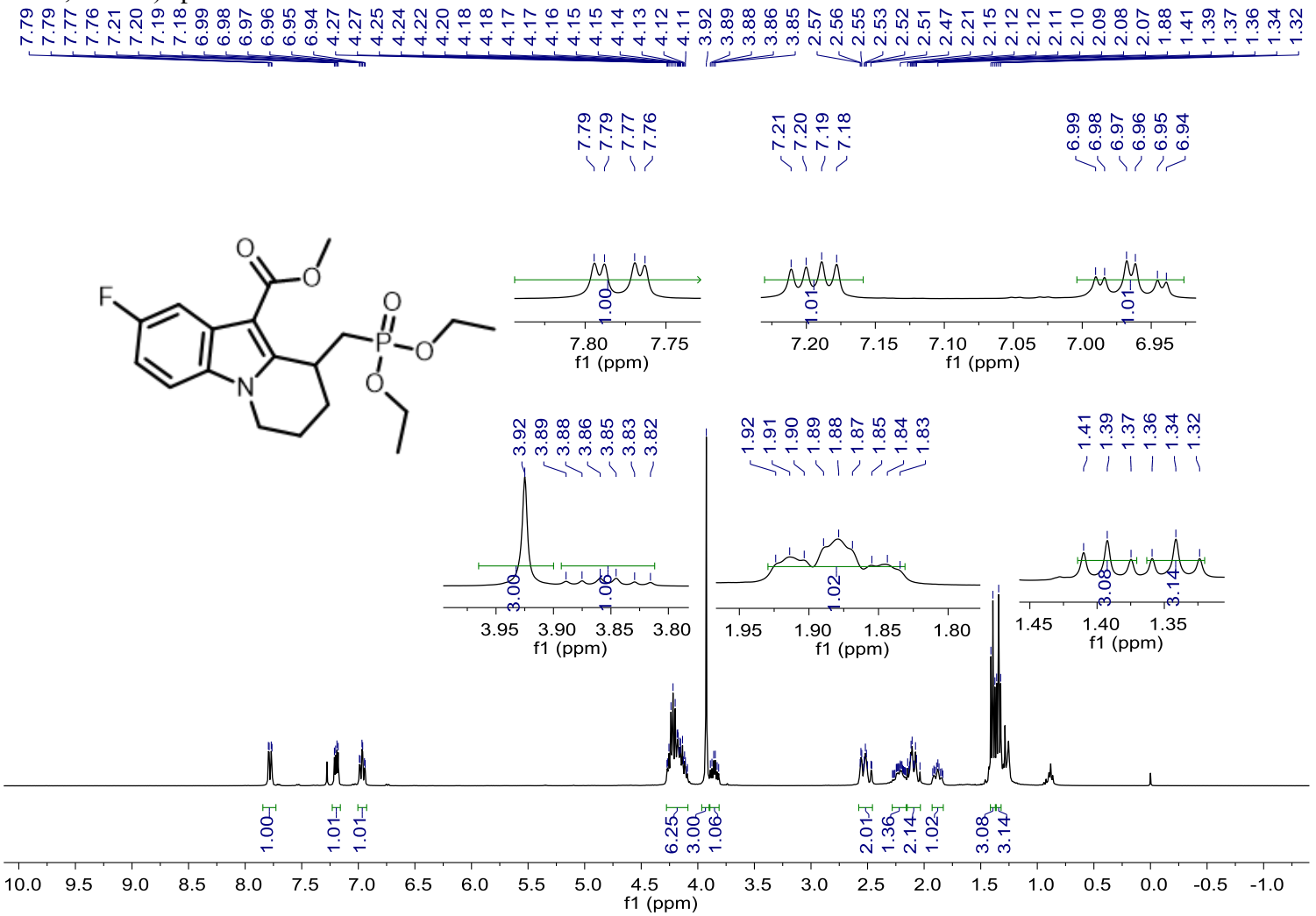
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5ca**



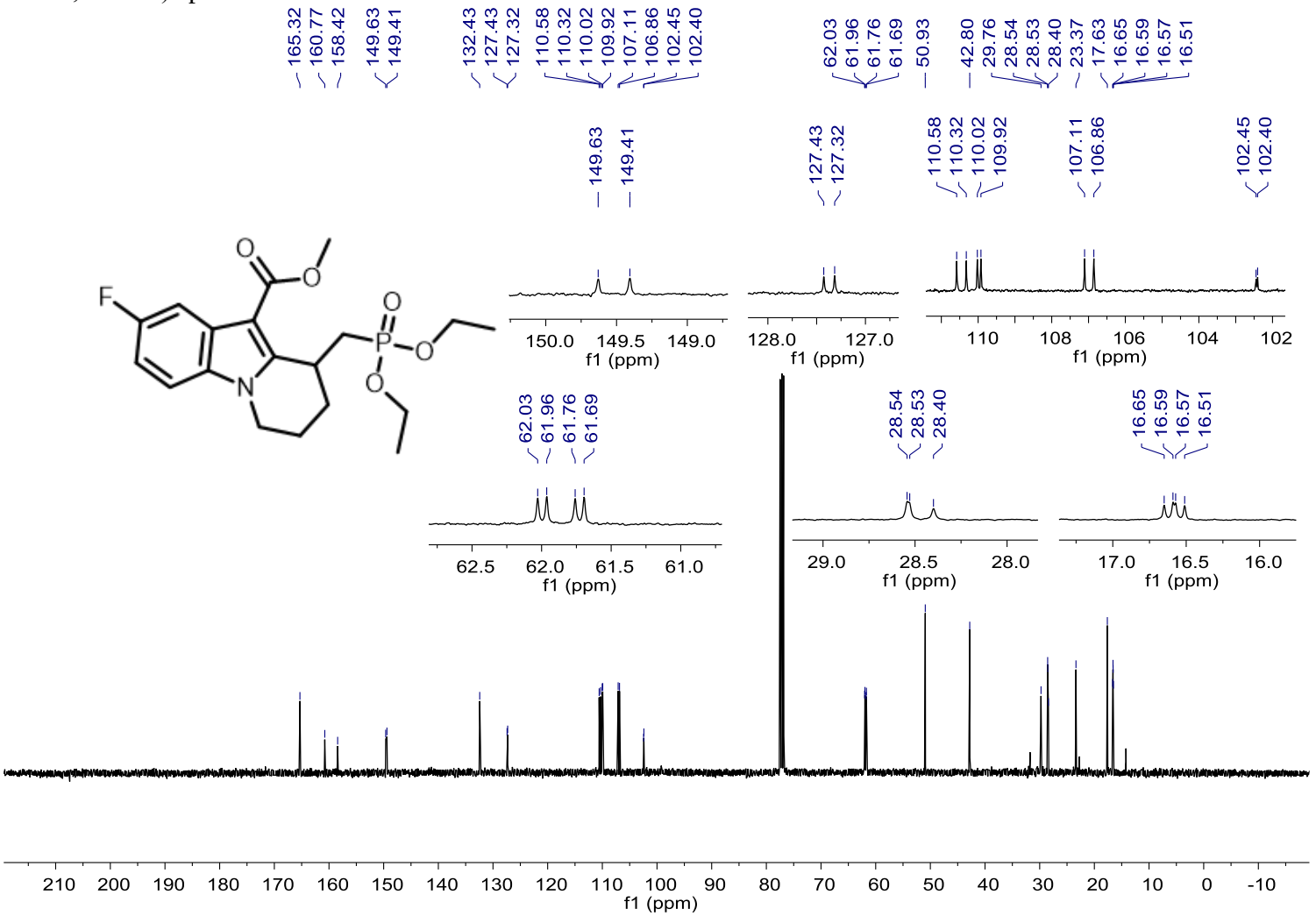
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **5ca**



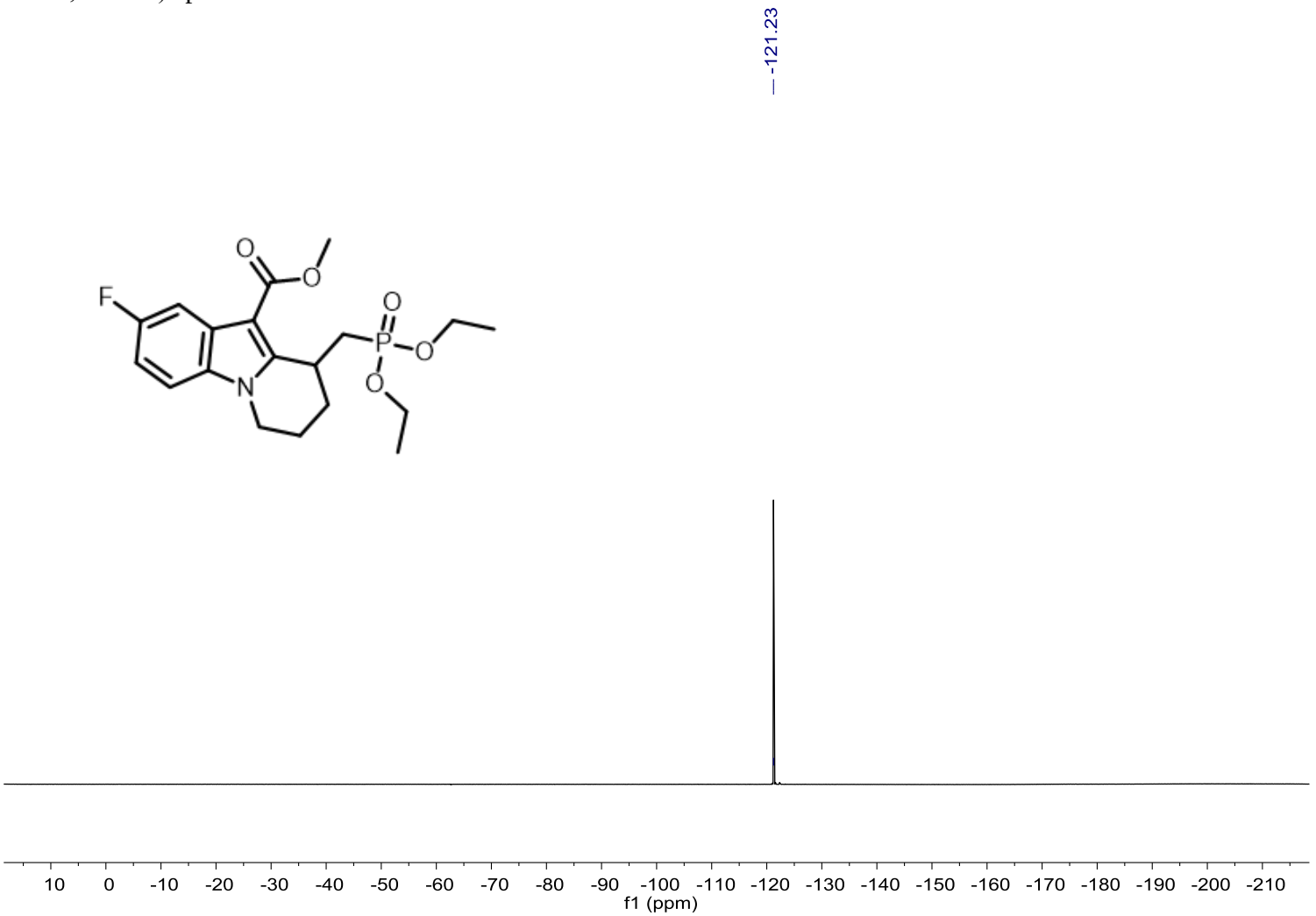
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5da**



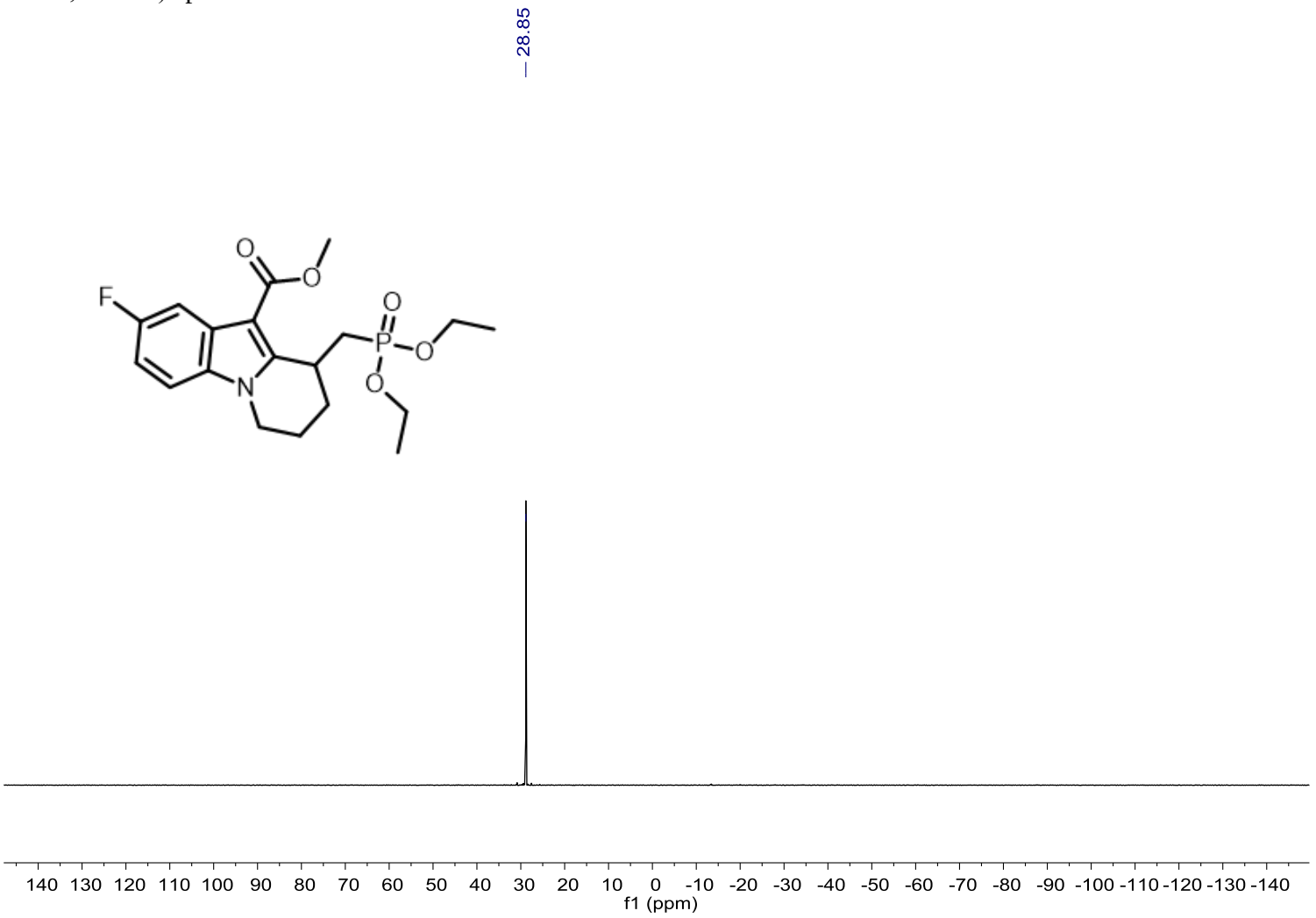
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5da**



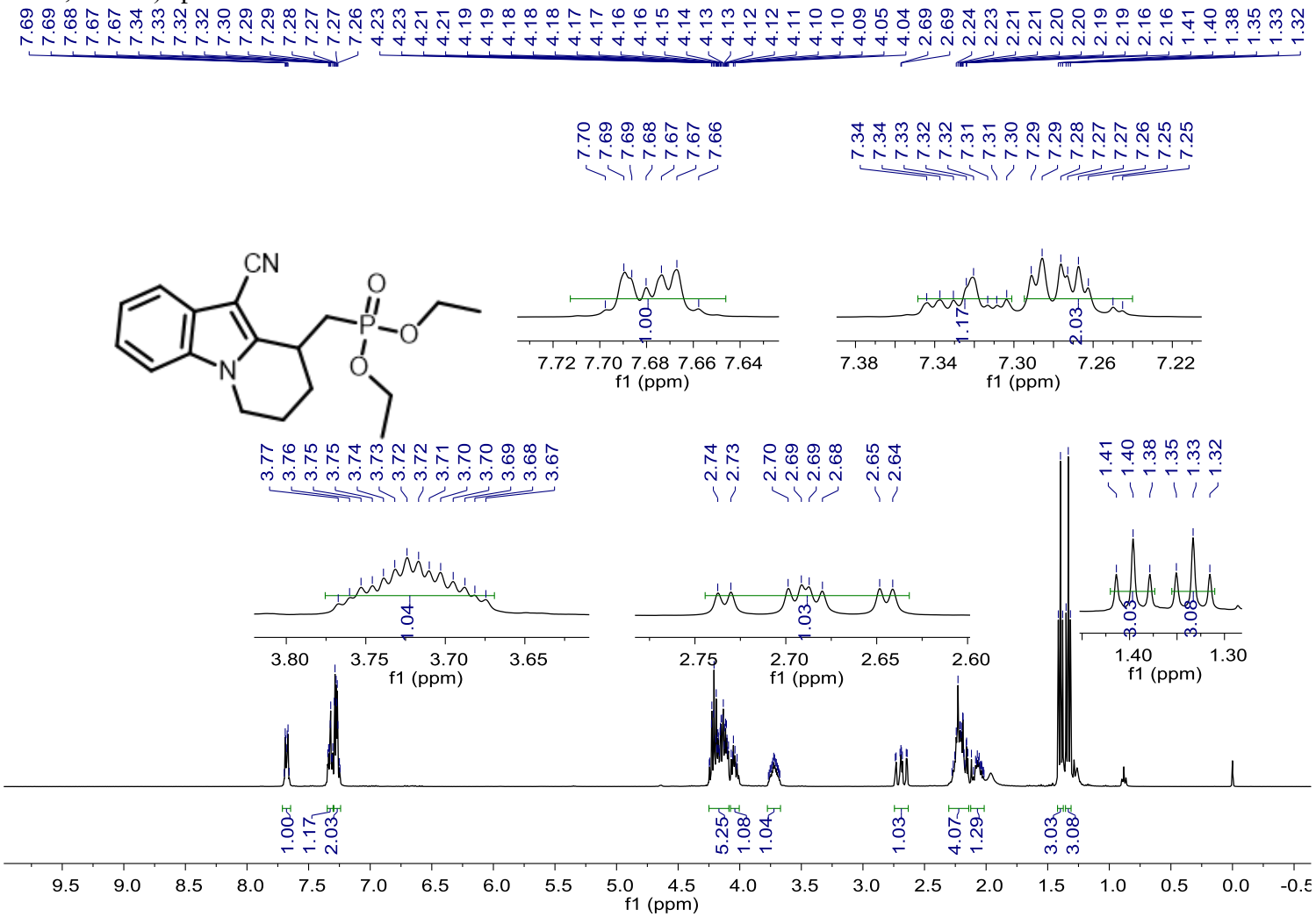
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **5da**



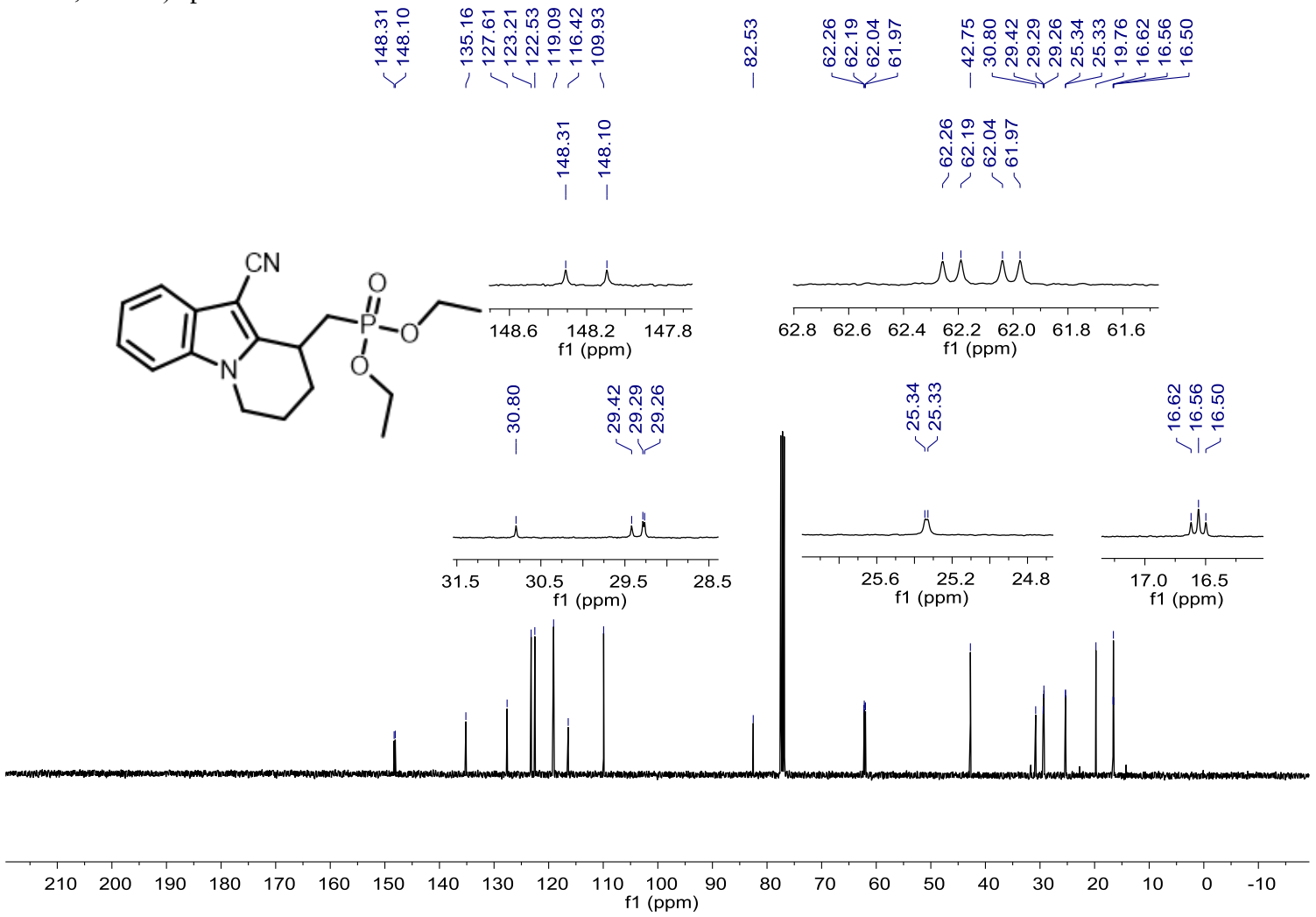
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **5da**



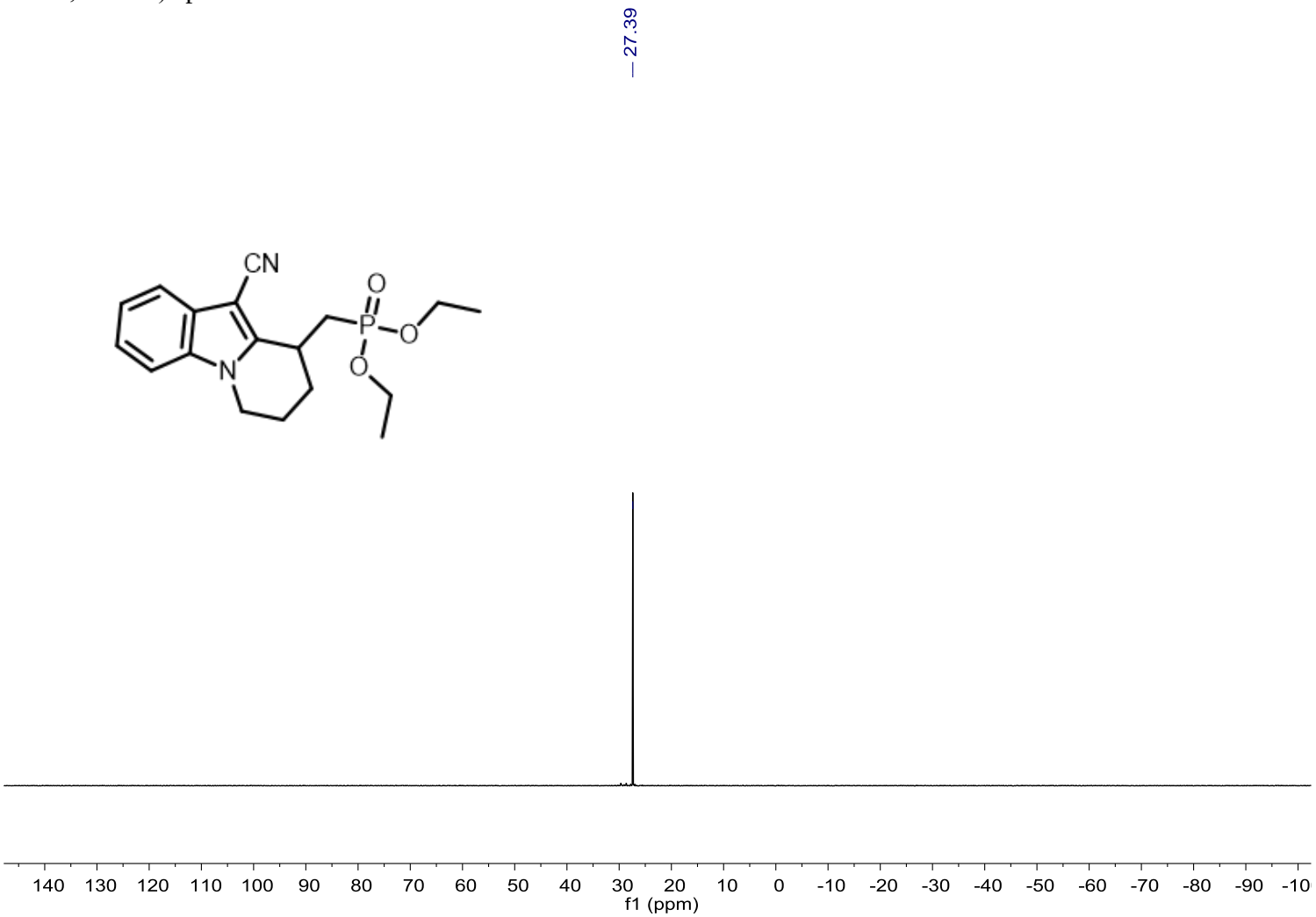
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5ea**



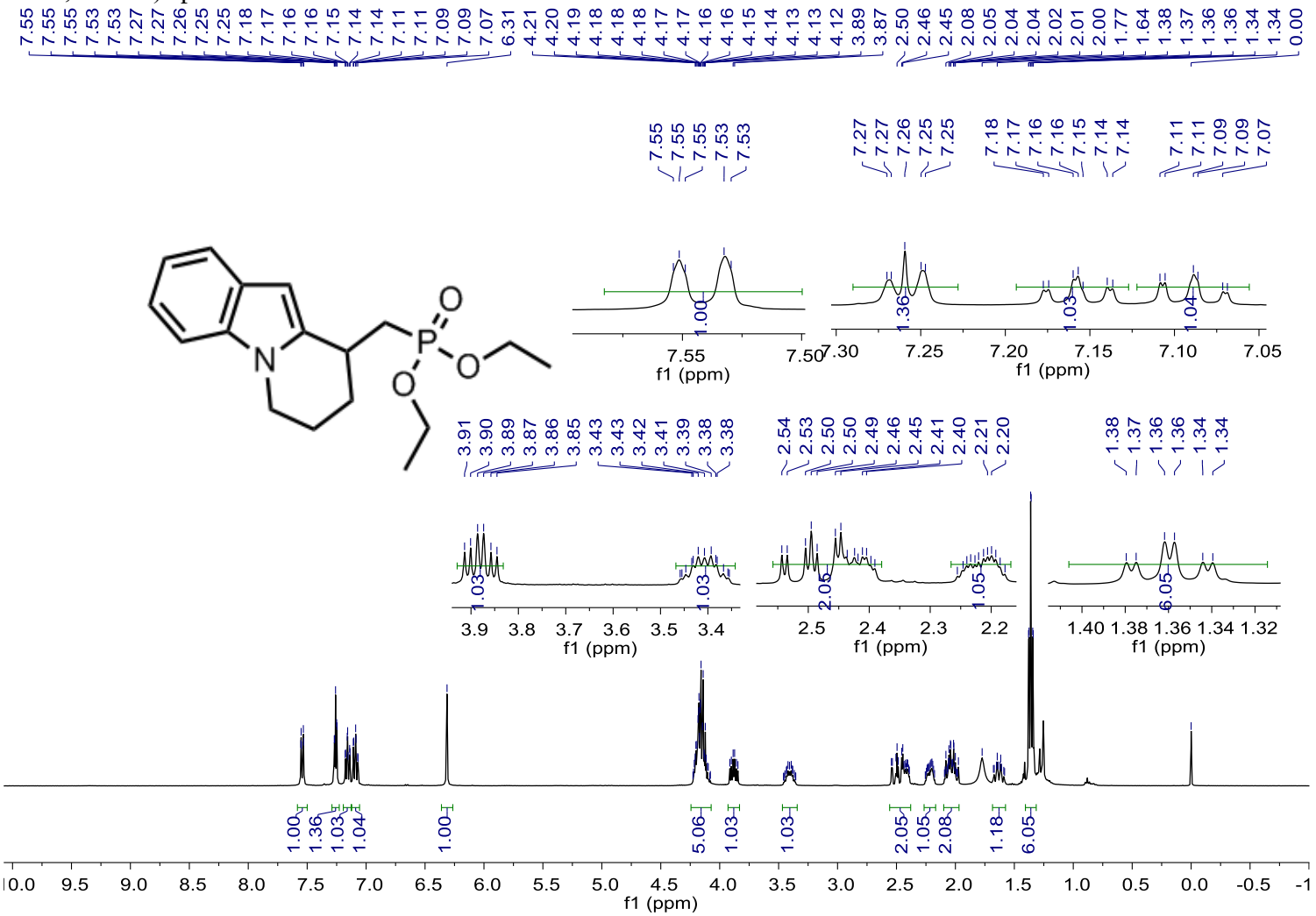
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5ea**



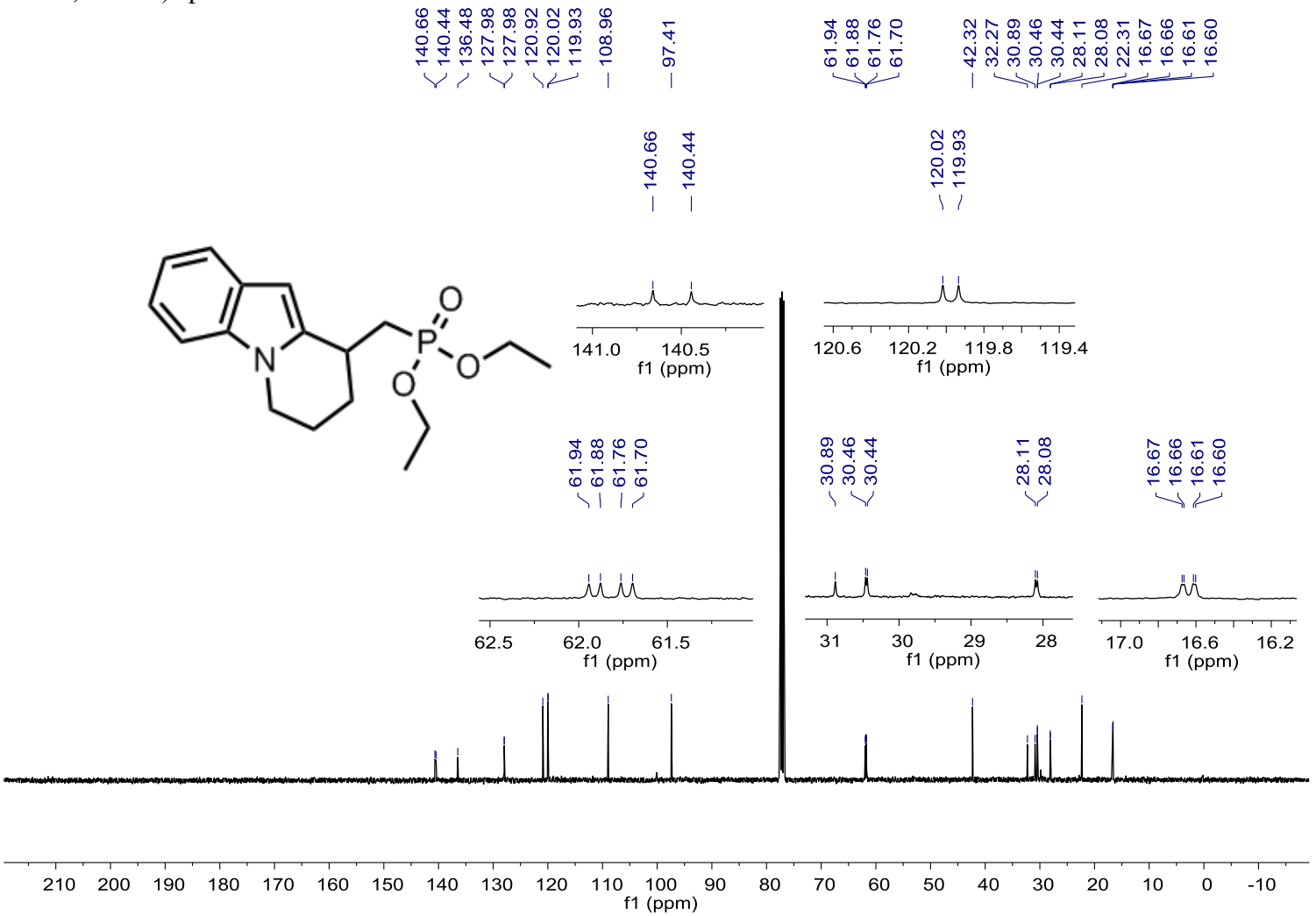
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **5ea**



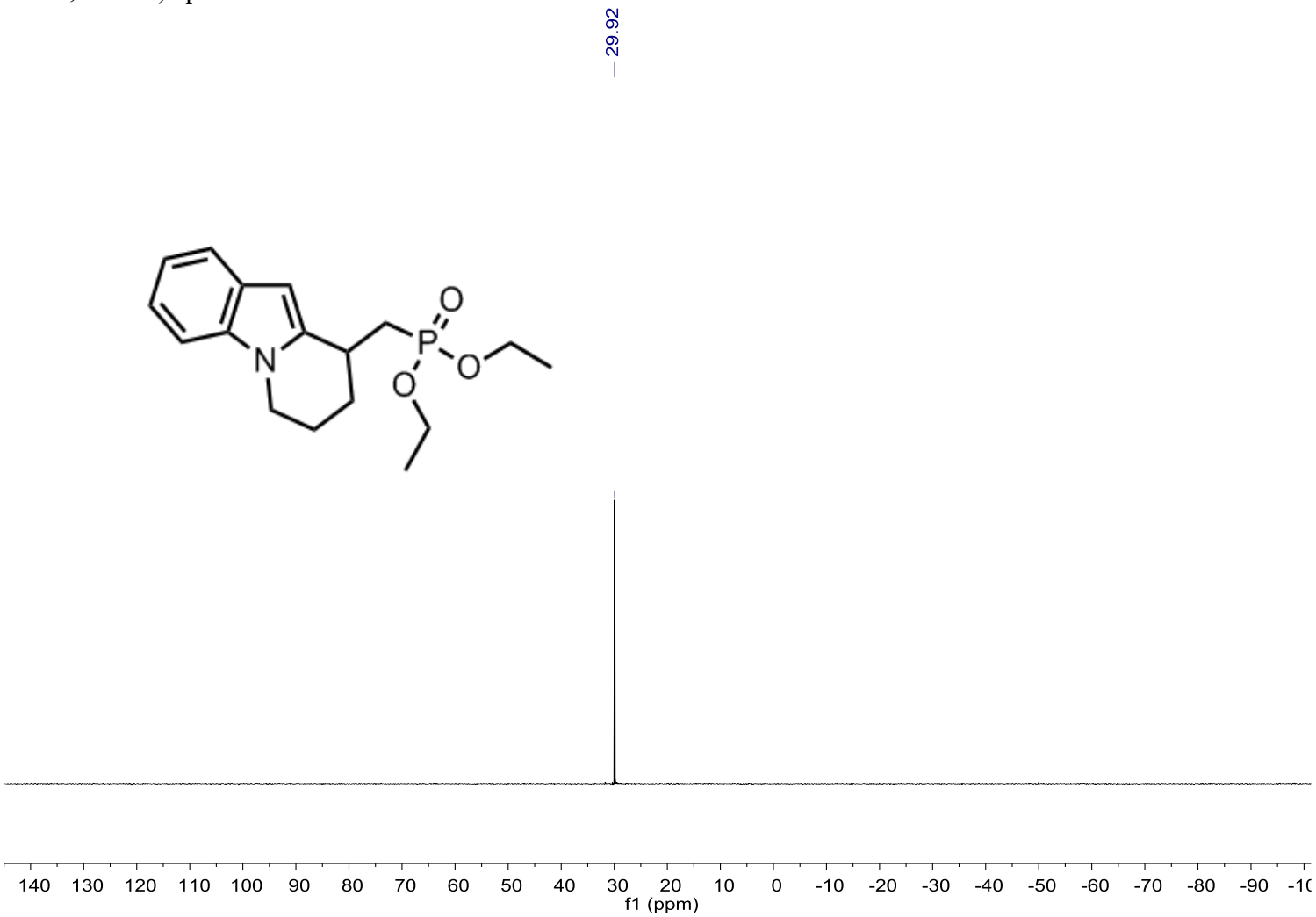
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5fa**



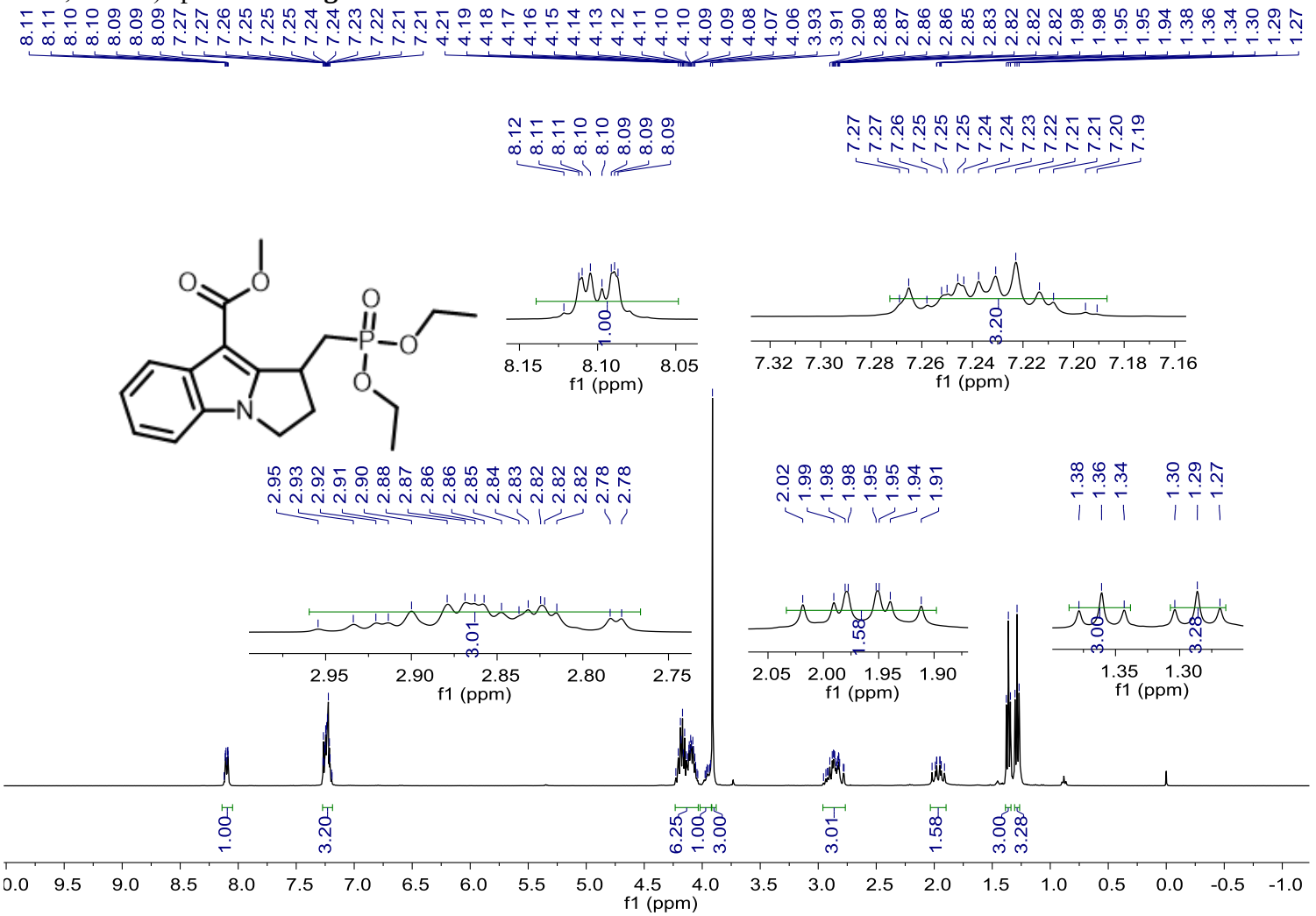
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5fa**



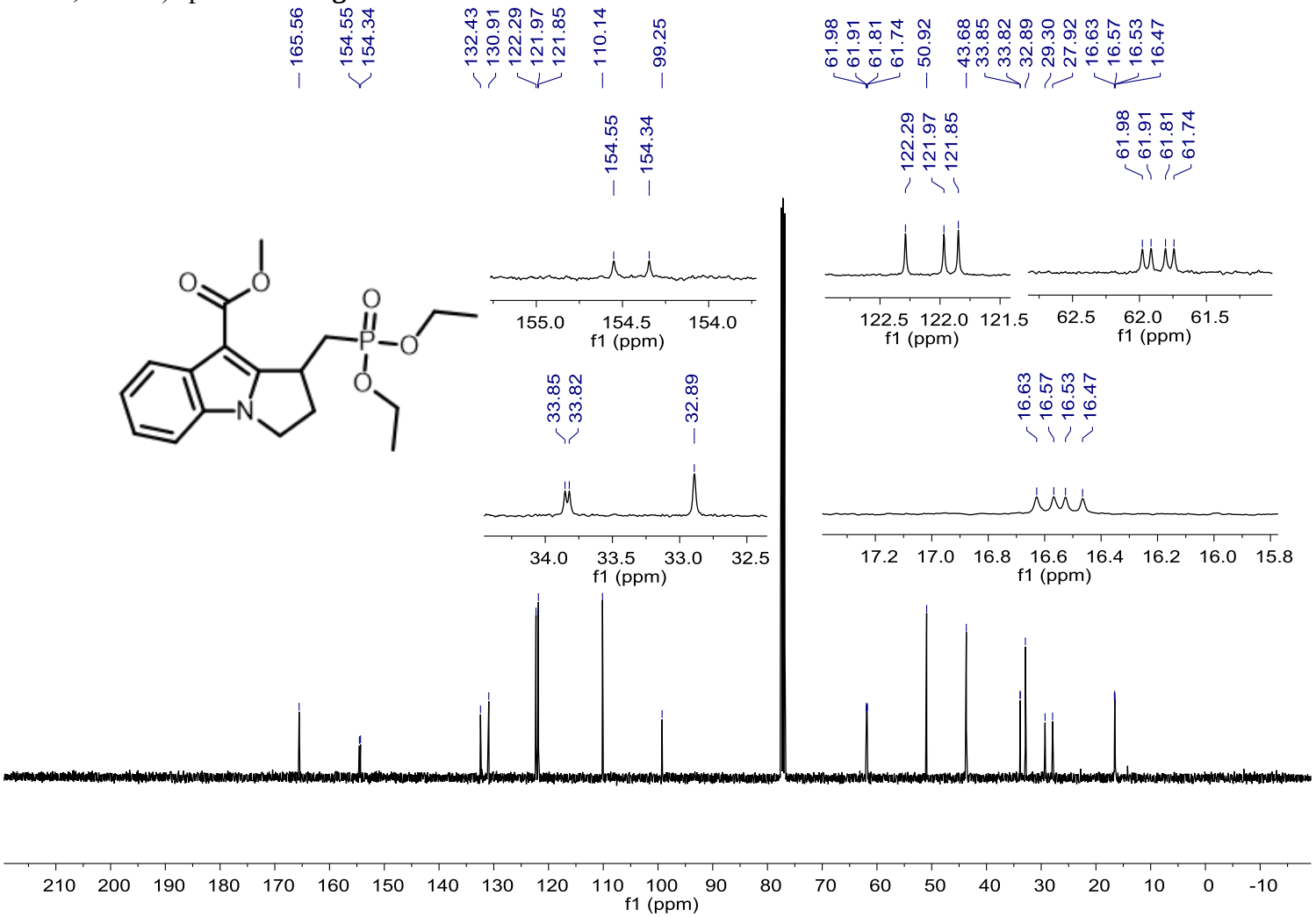
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **5fa**



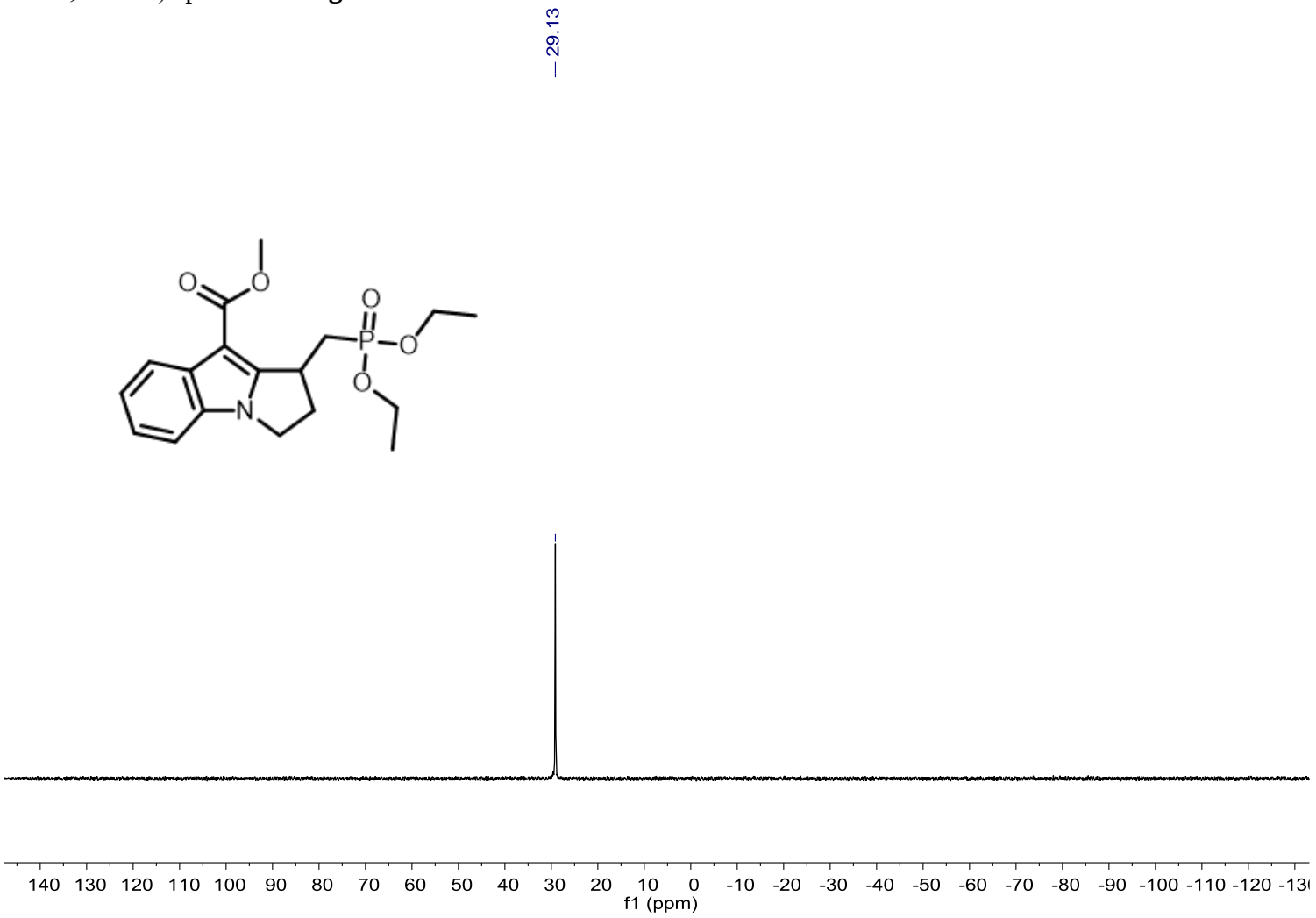
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5ga**



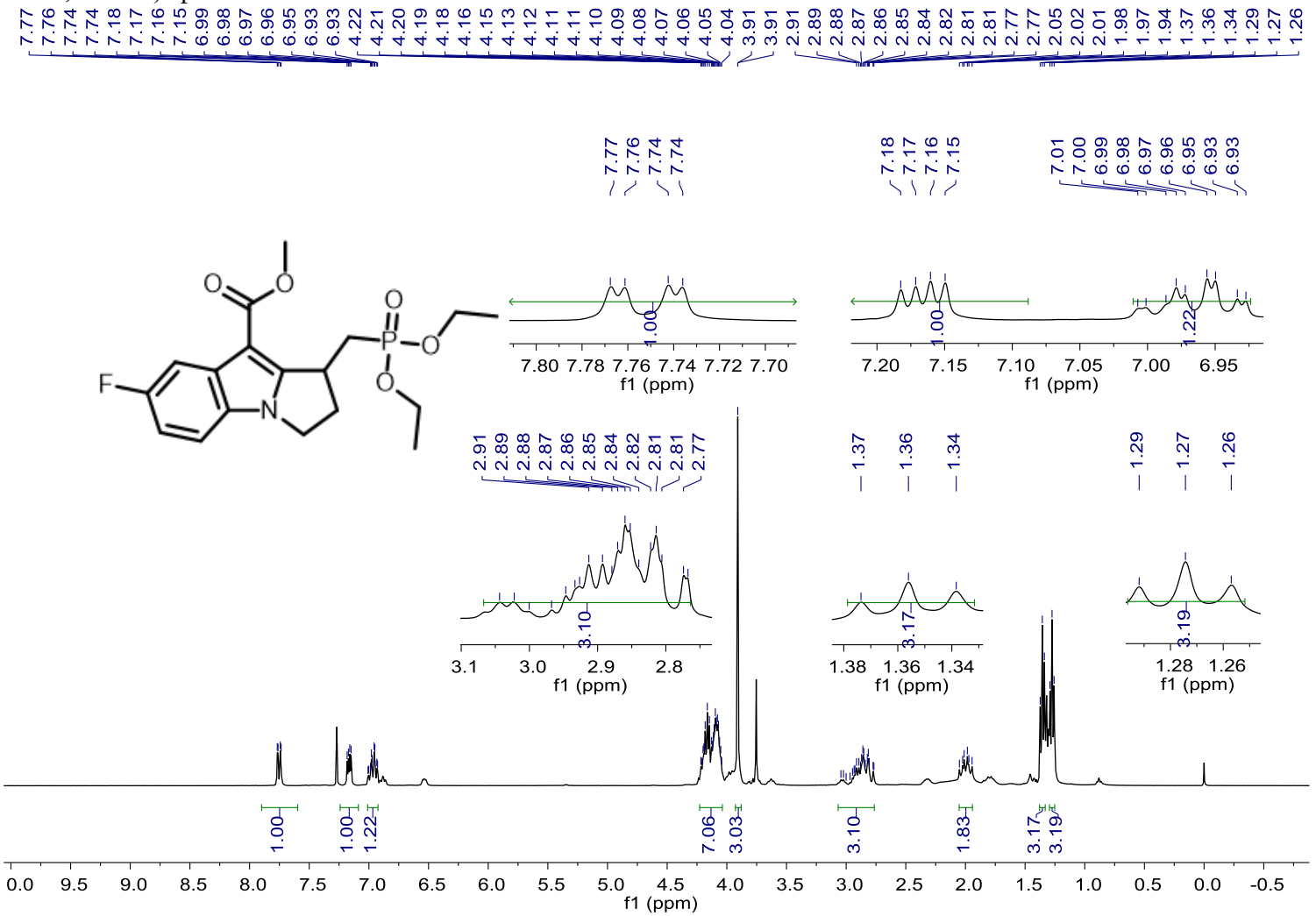
$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **5ga**



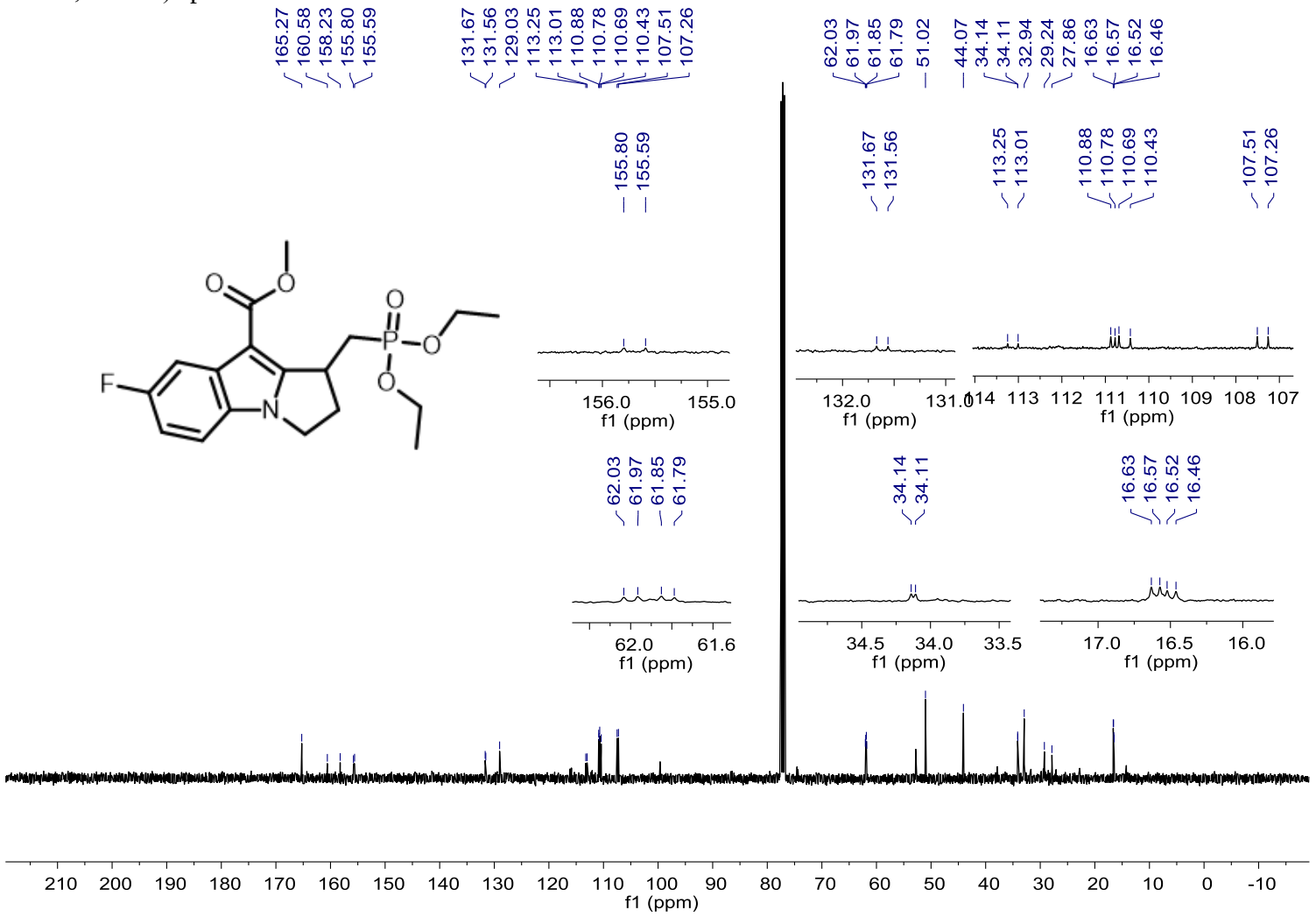
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **5ga**



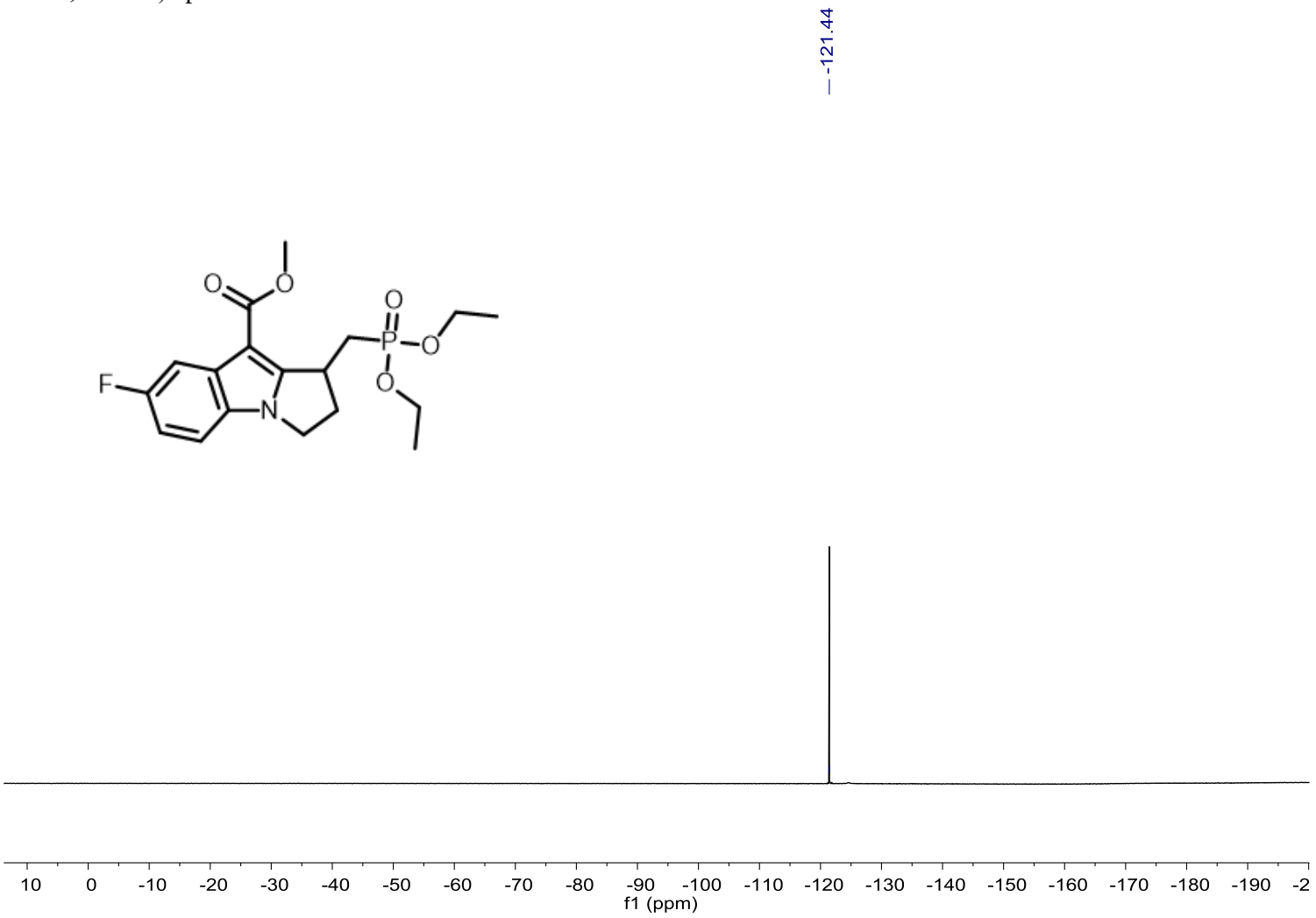
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **5ha**



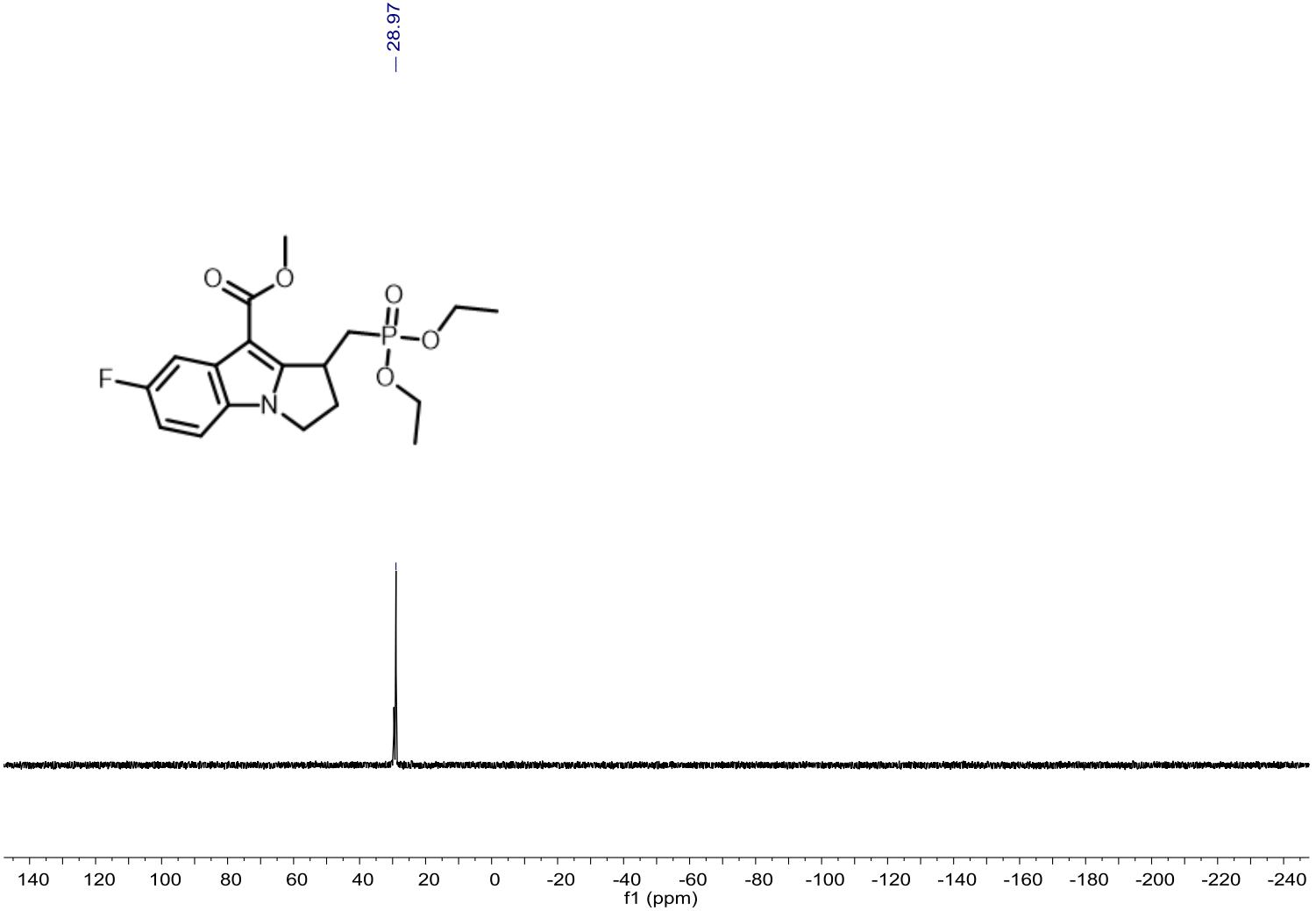
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **5ha**



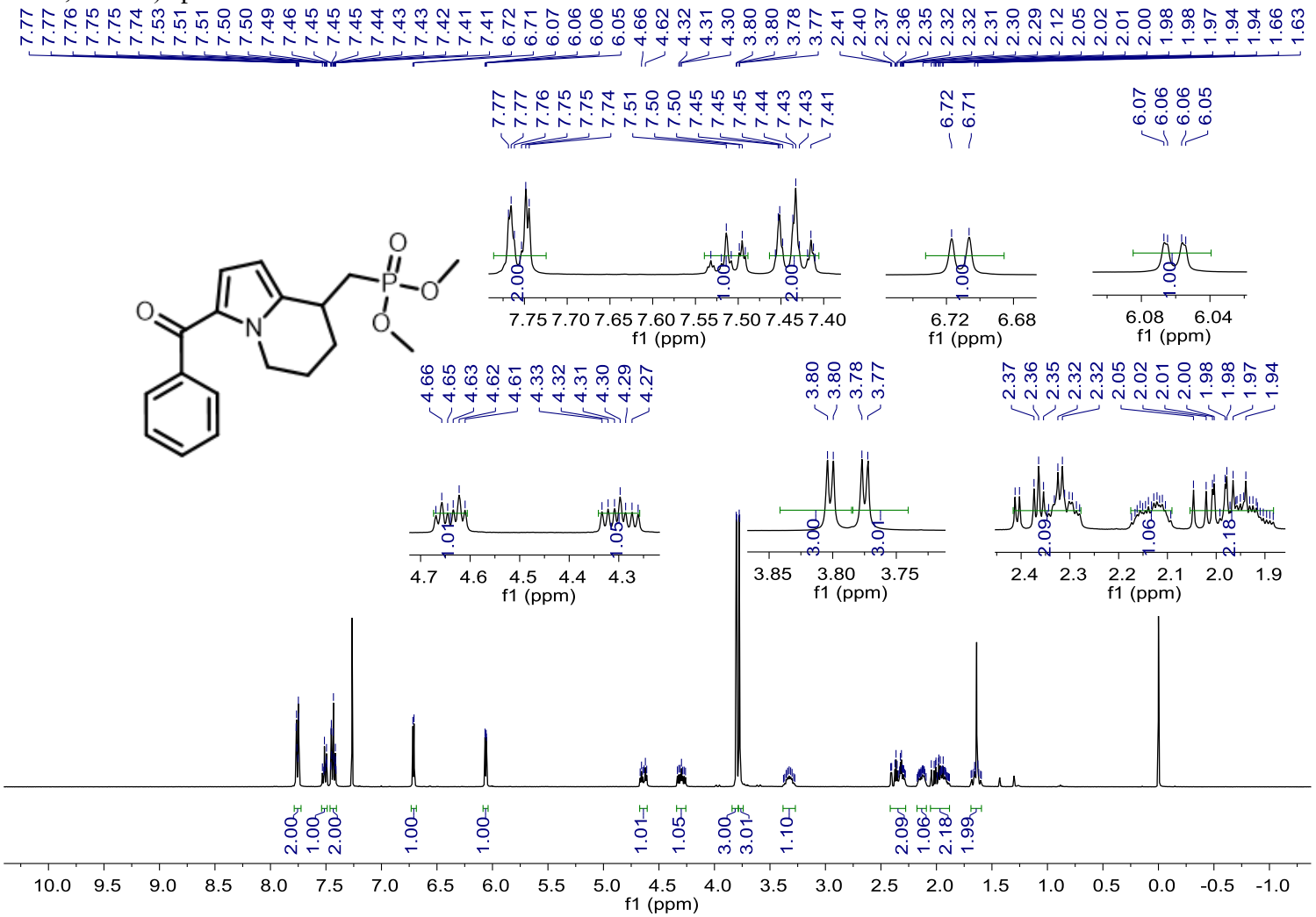
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **5ha**



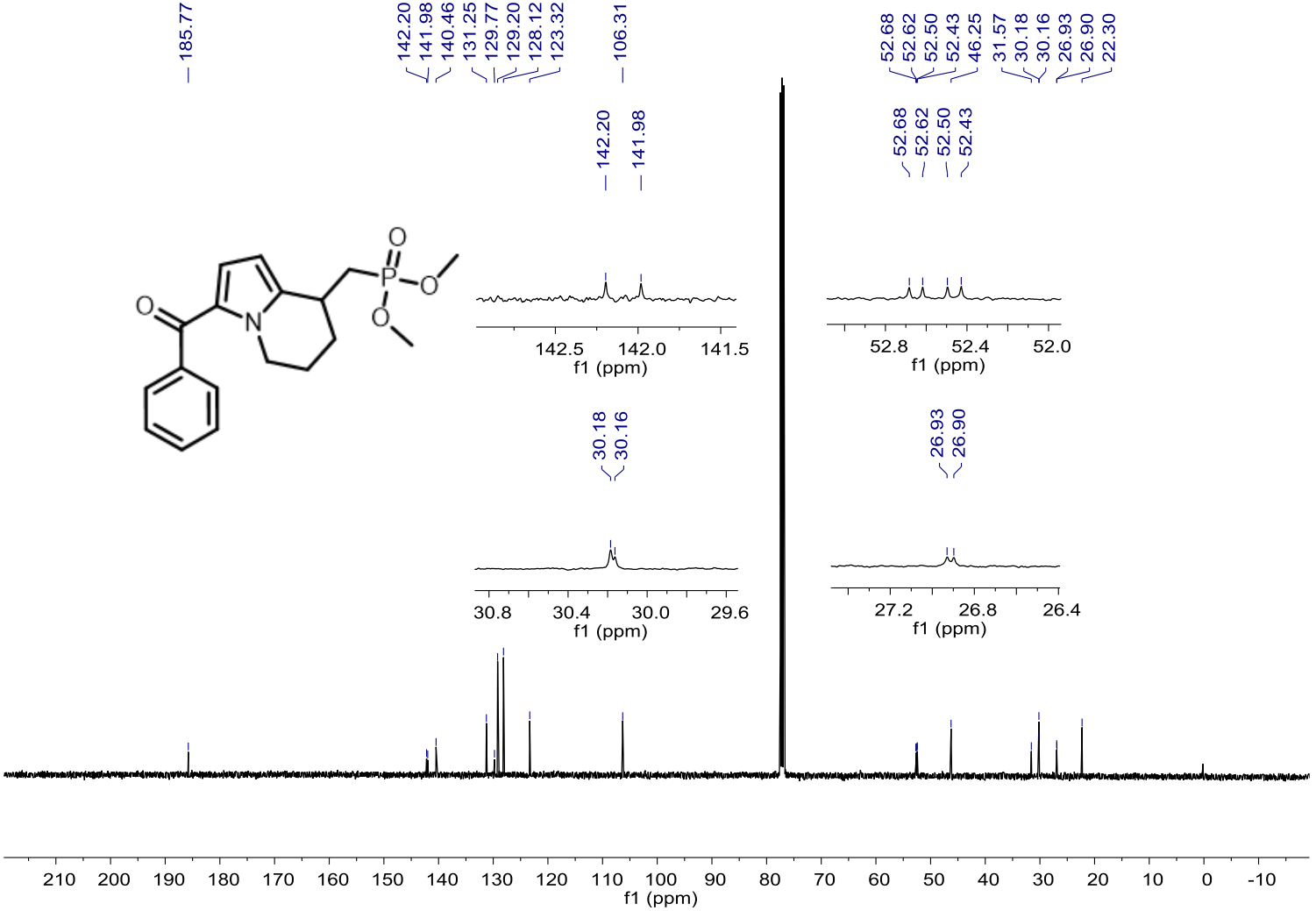
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **5ha**



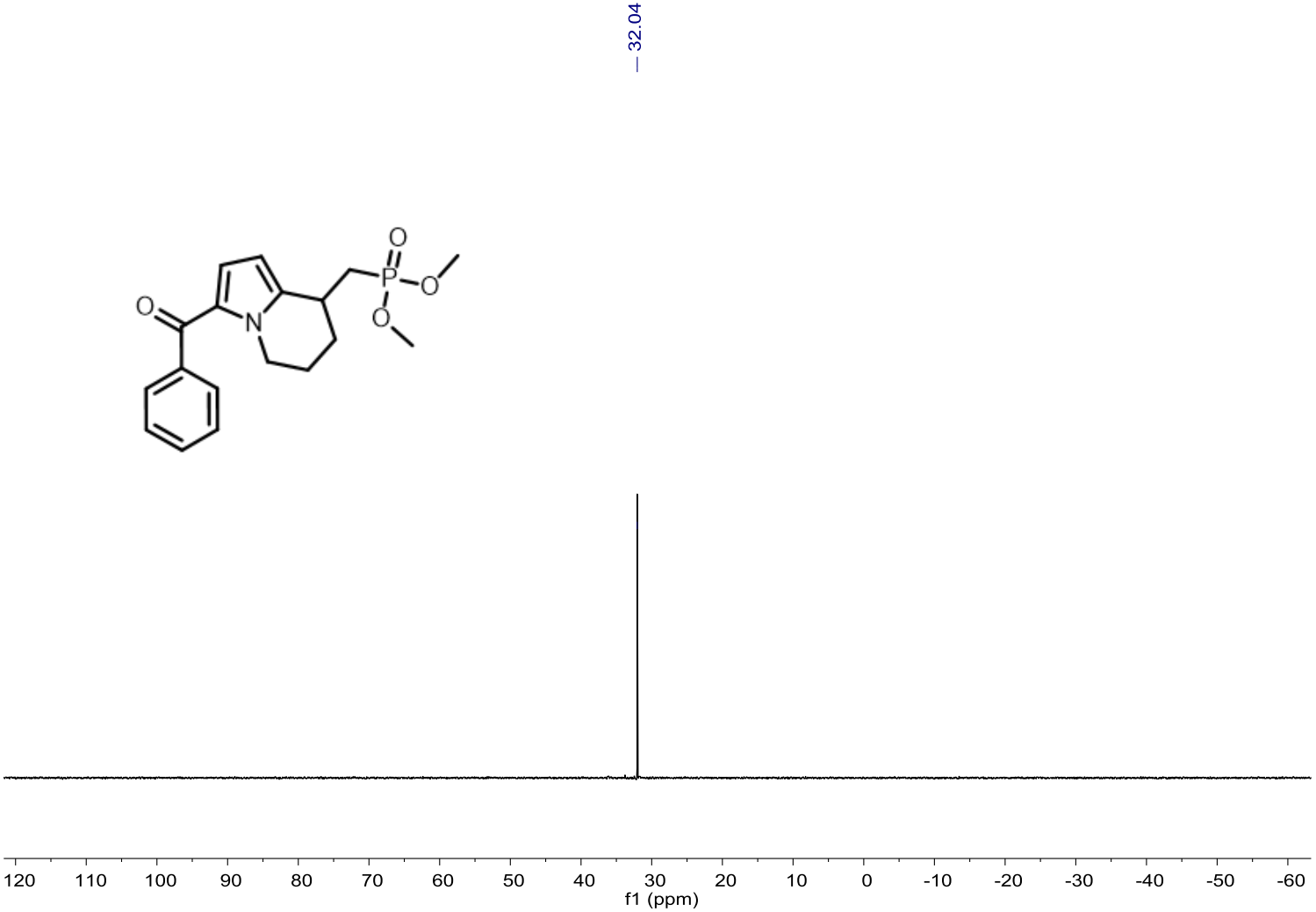
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



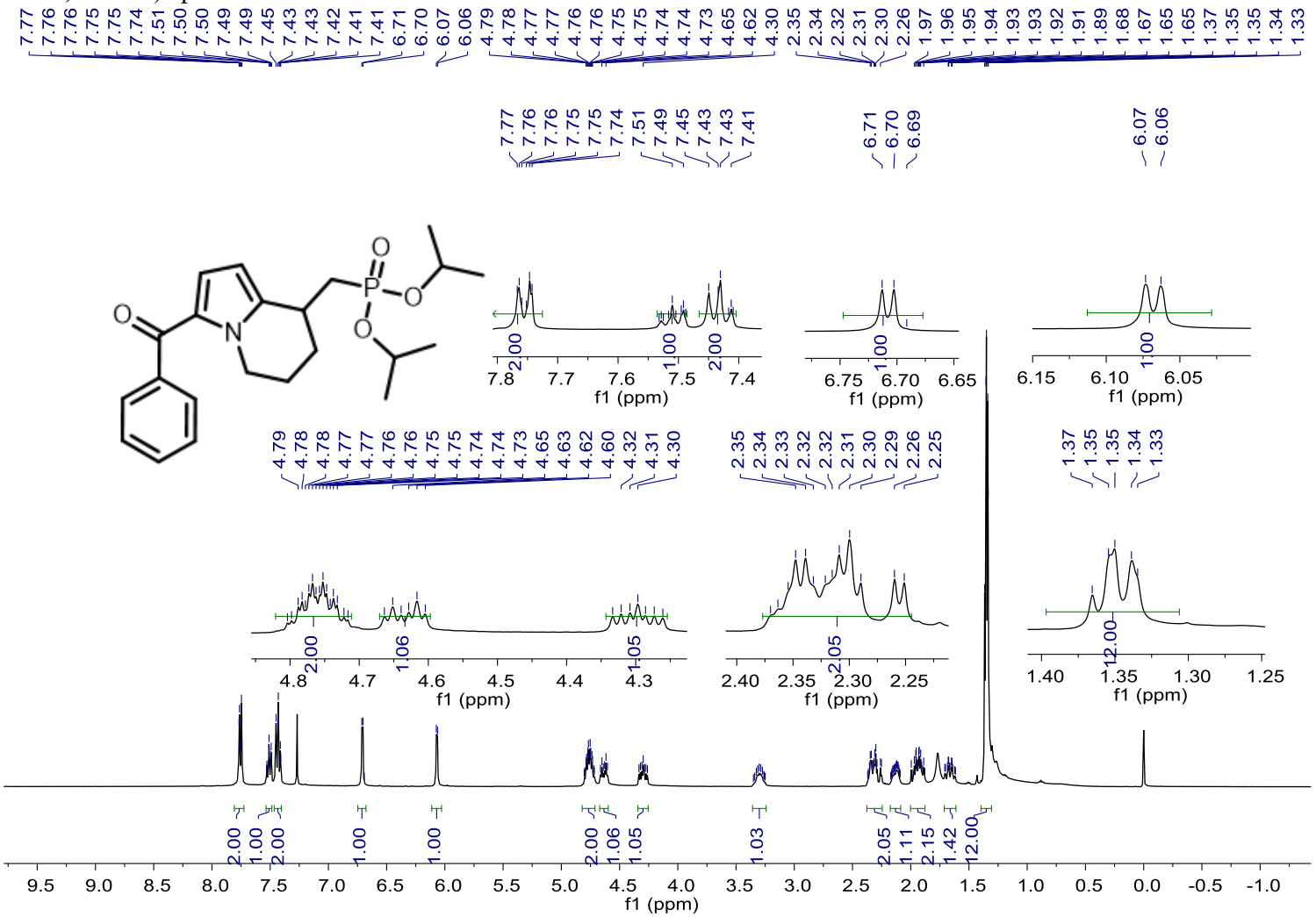
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ab**



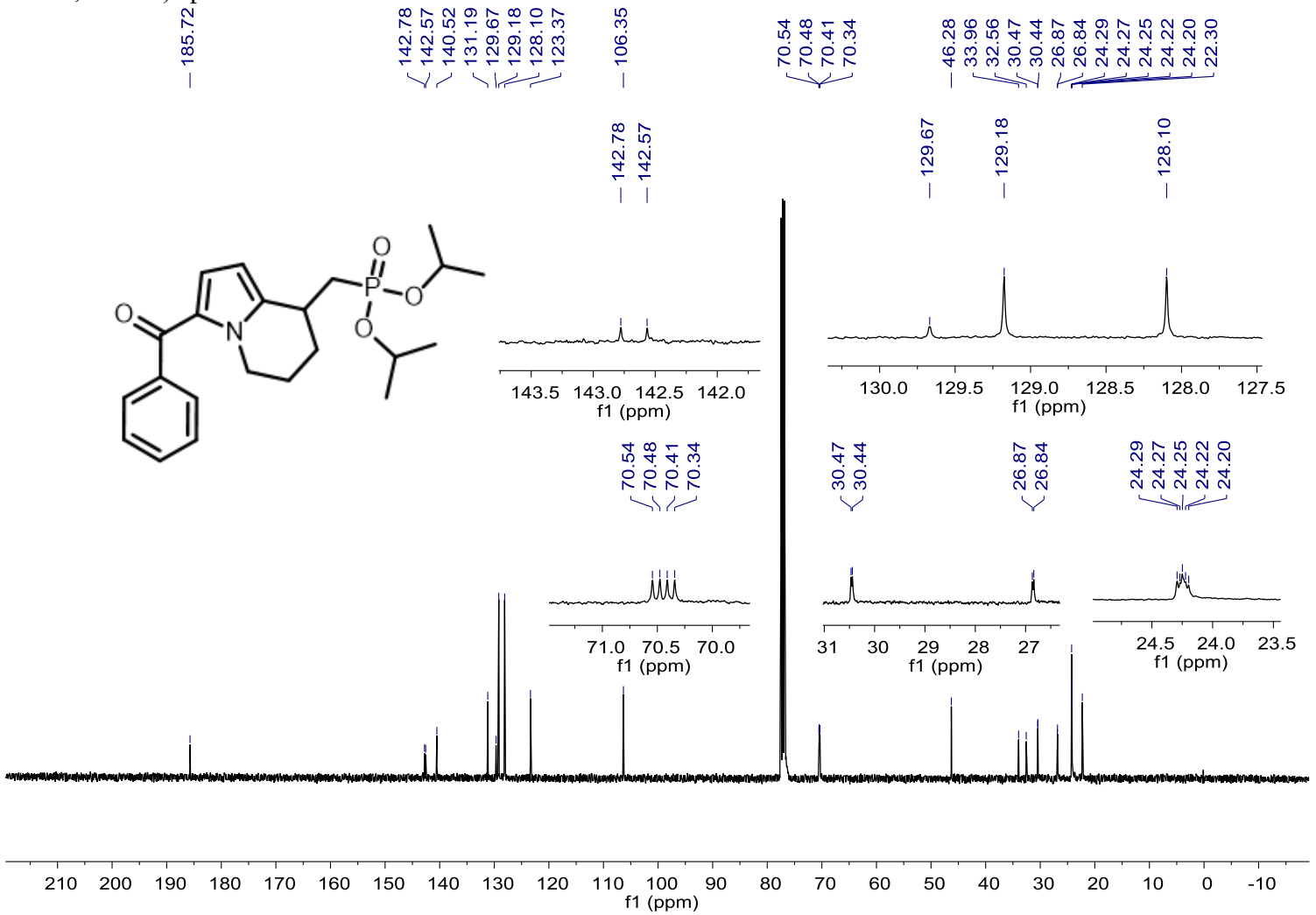
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ab**



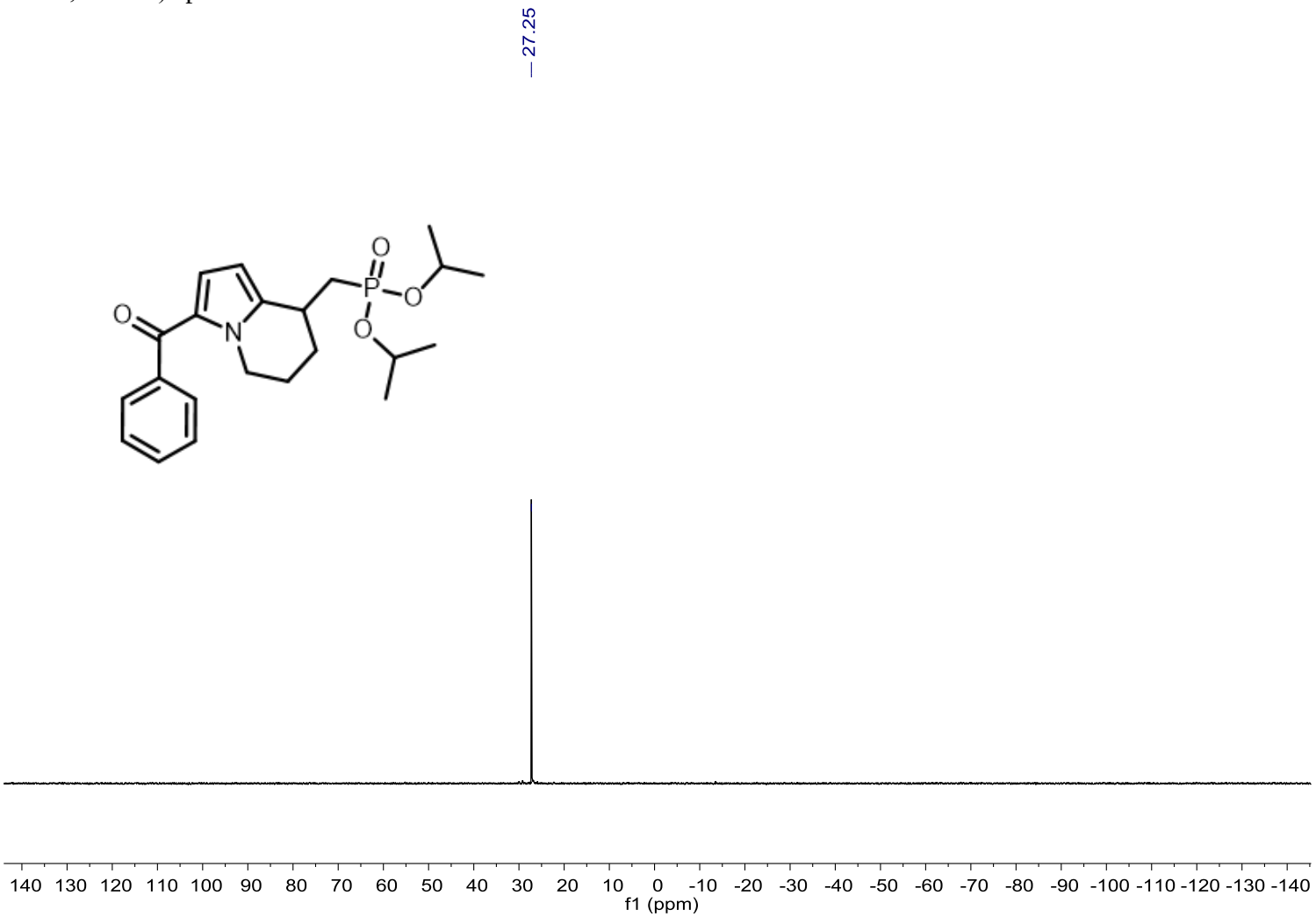
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



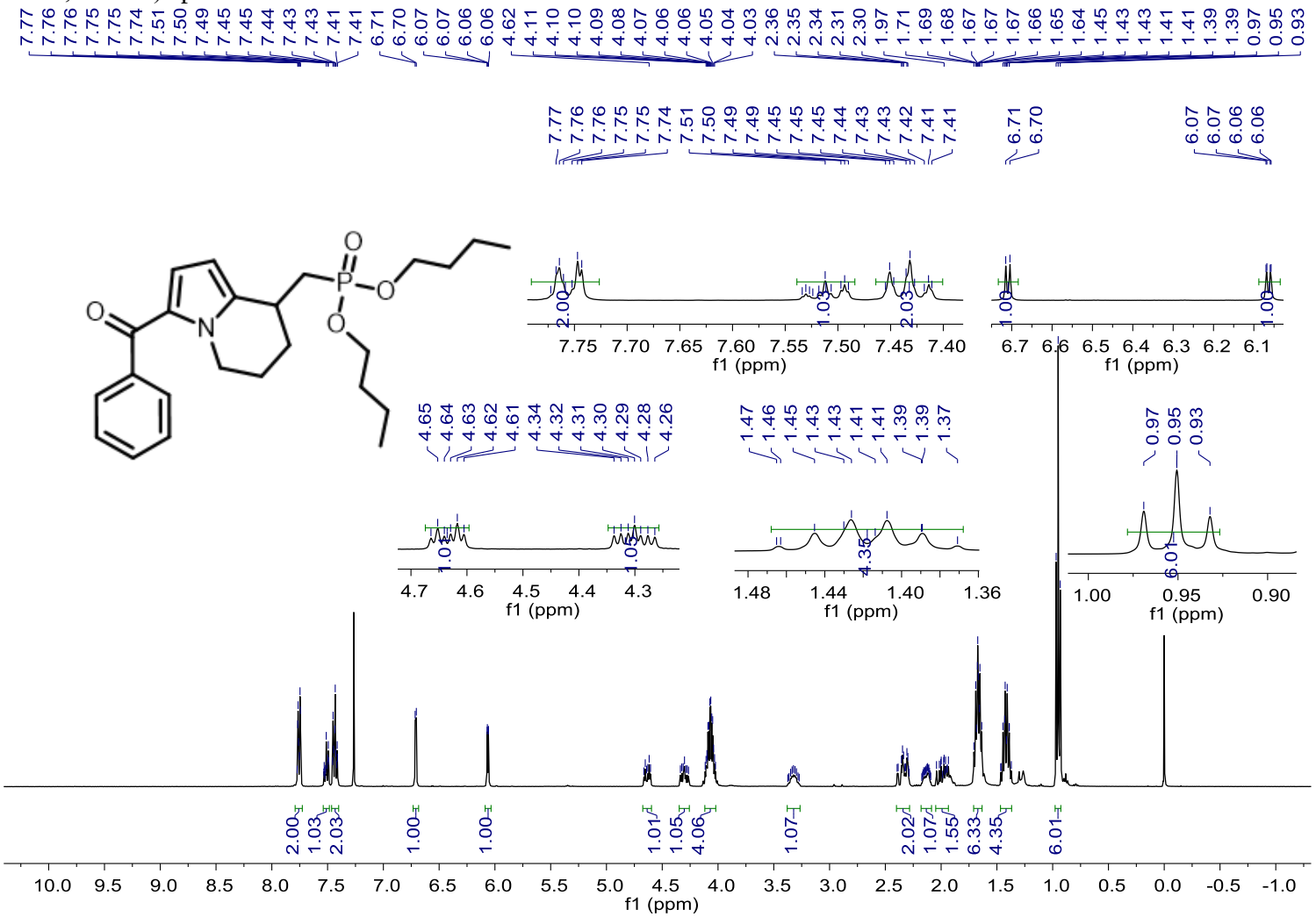
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ac**



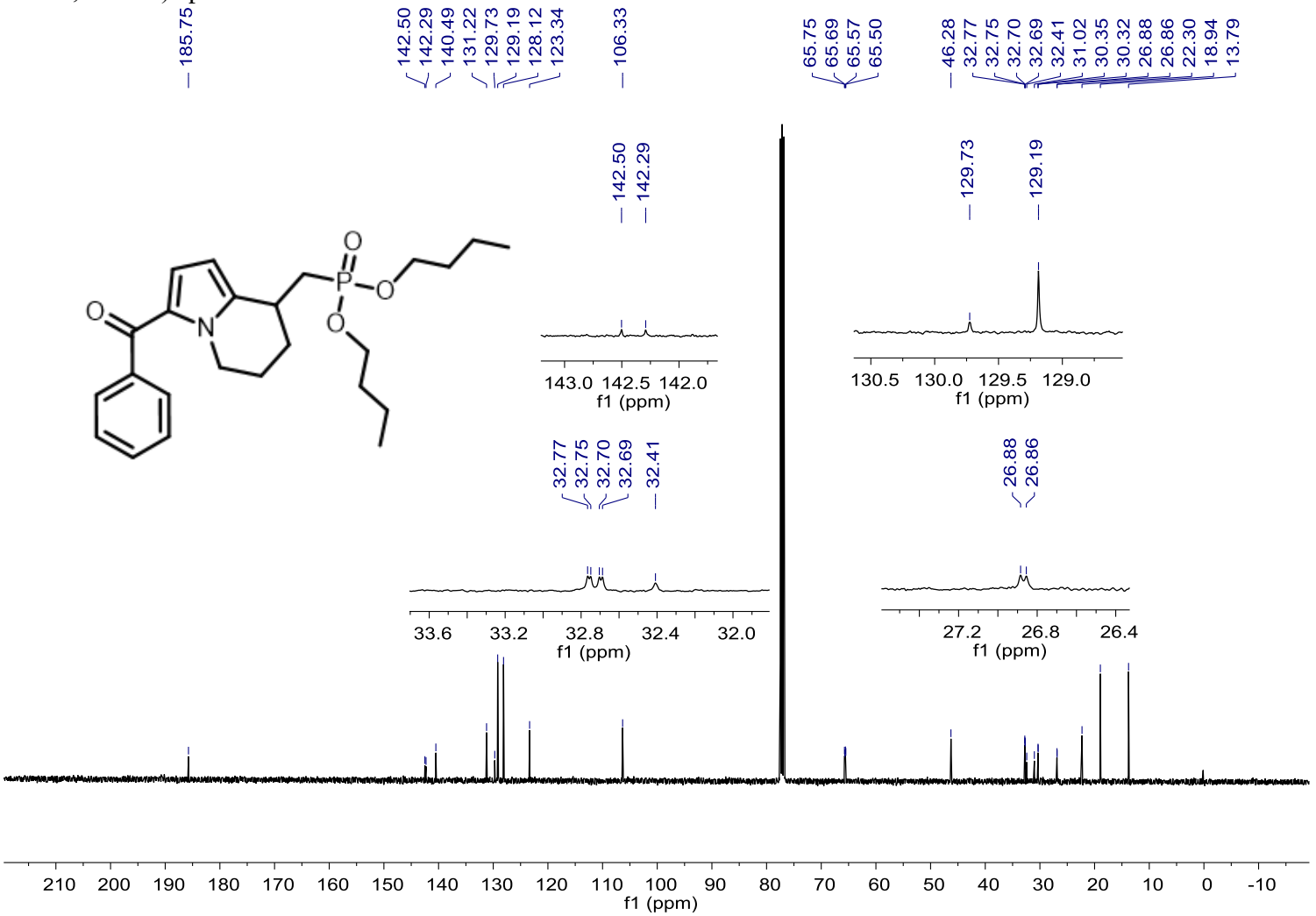
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ac**



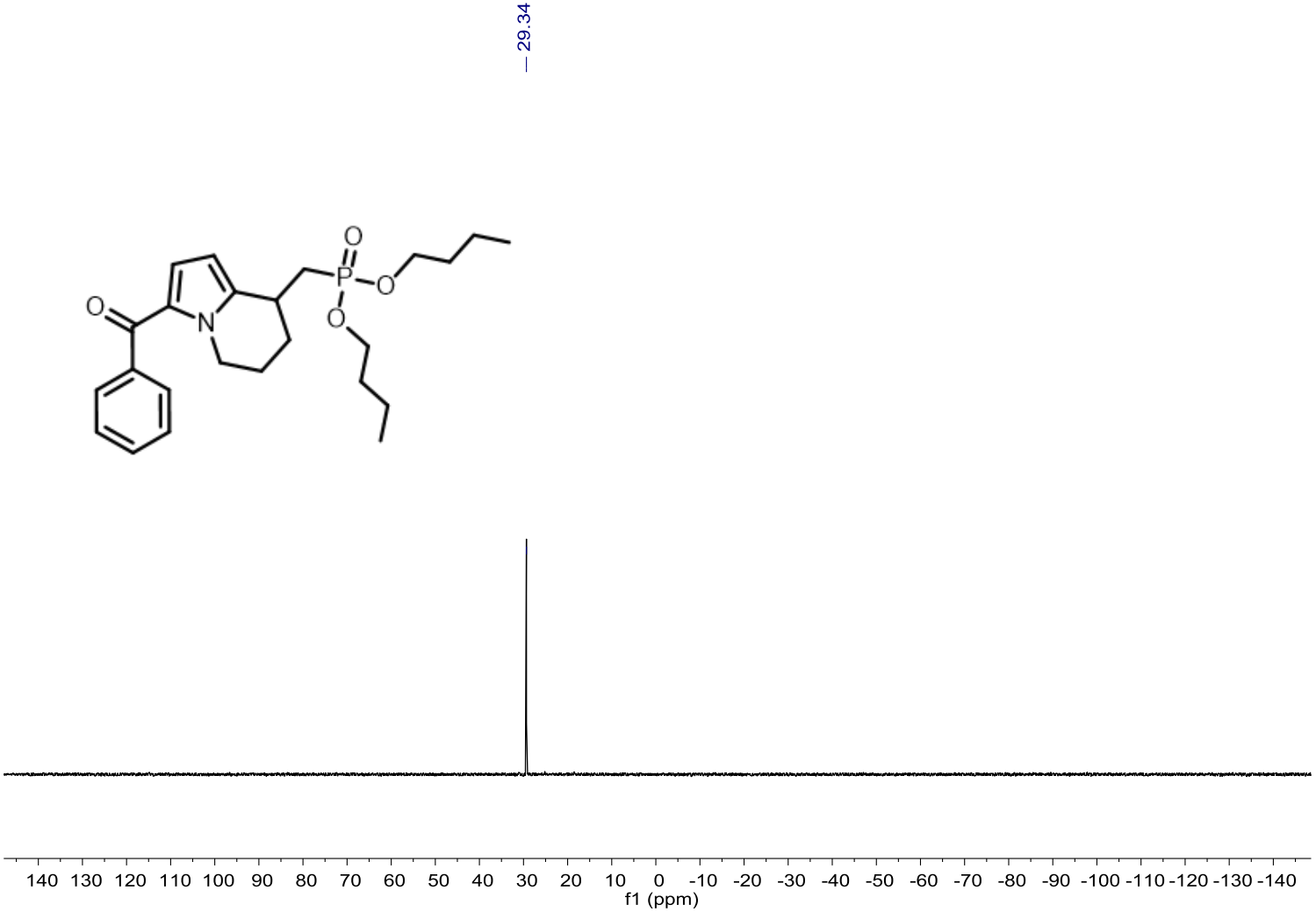
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



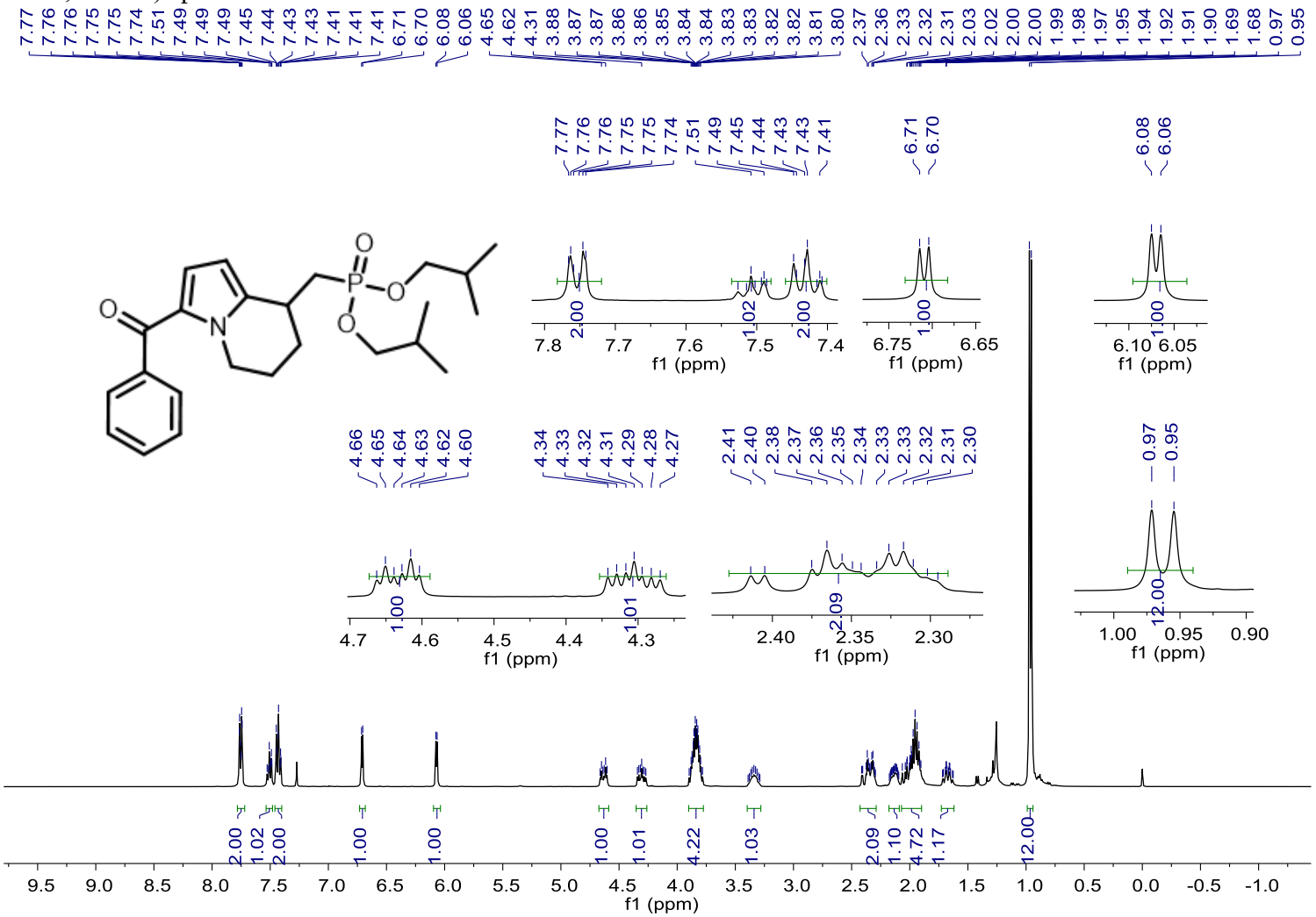
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ad**



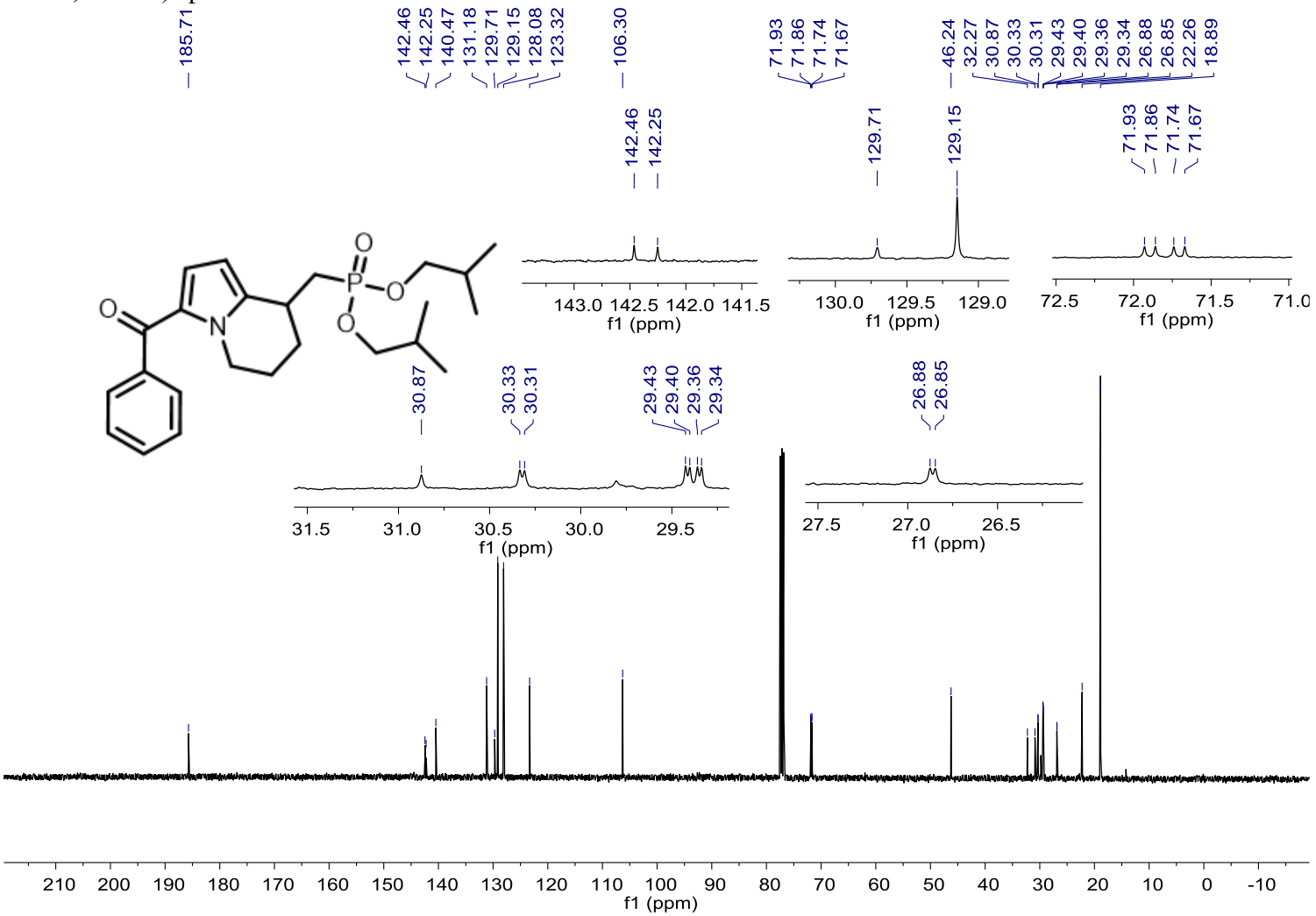
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ad**



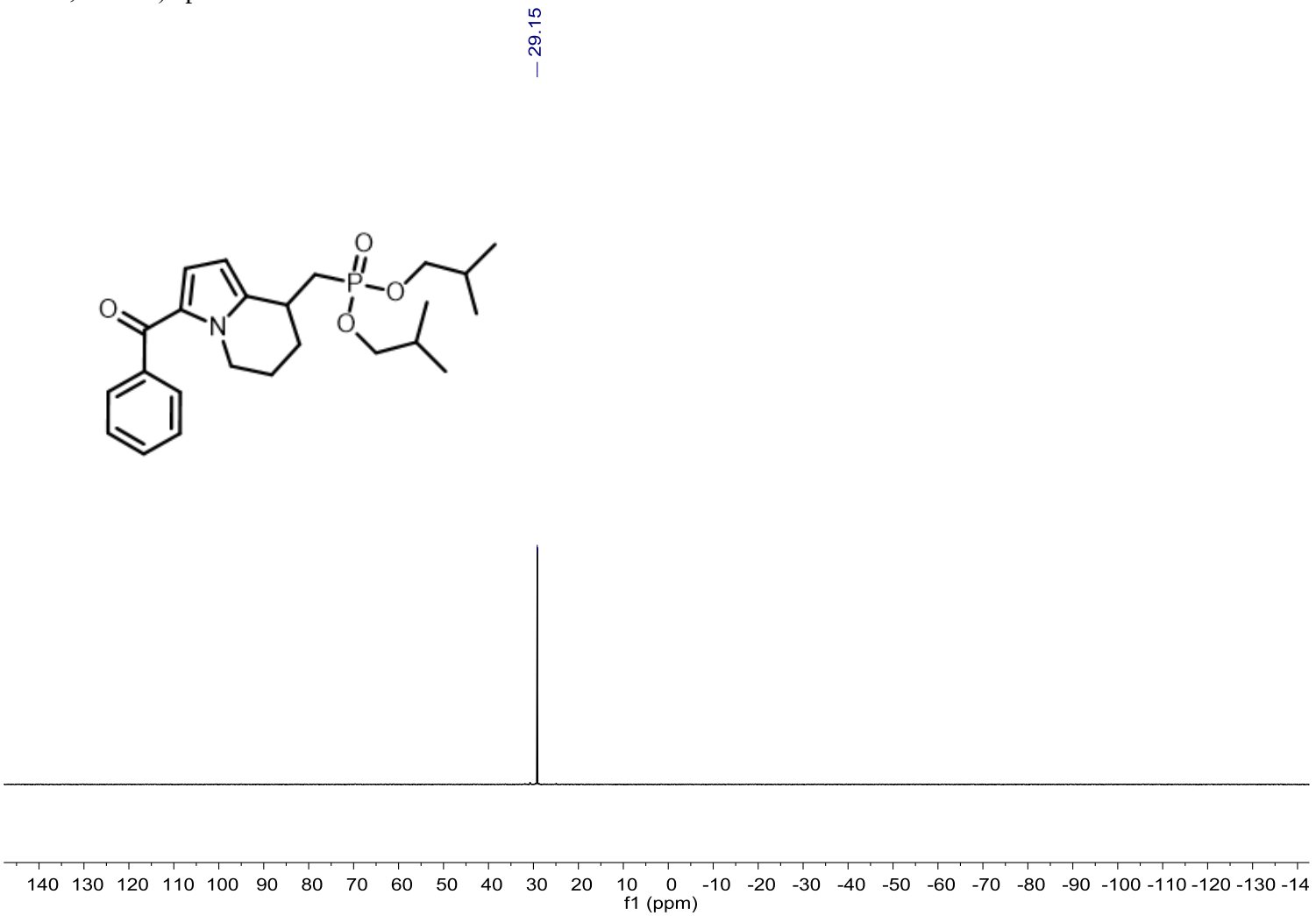
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



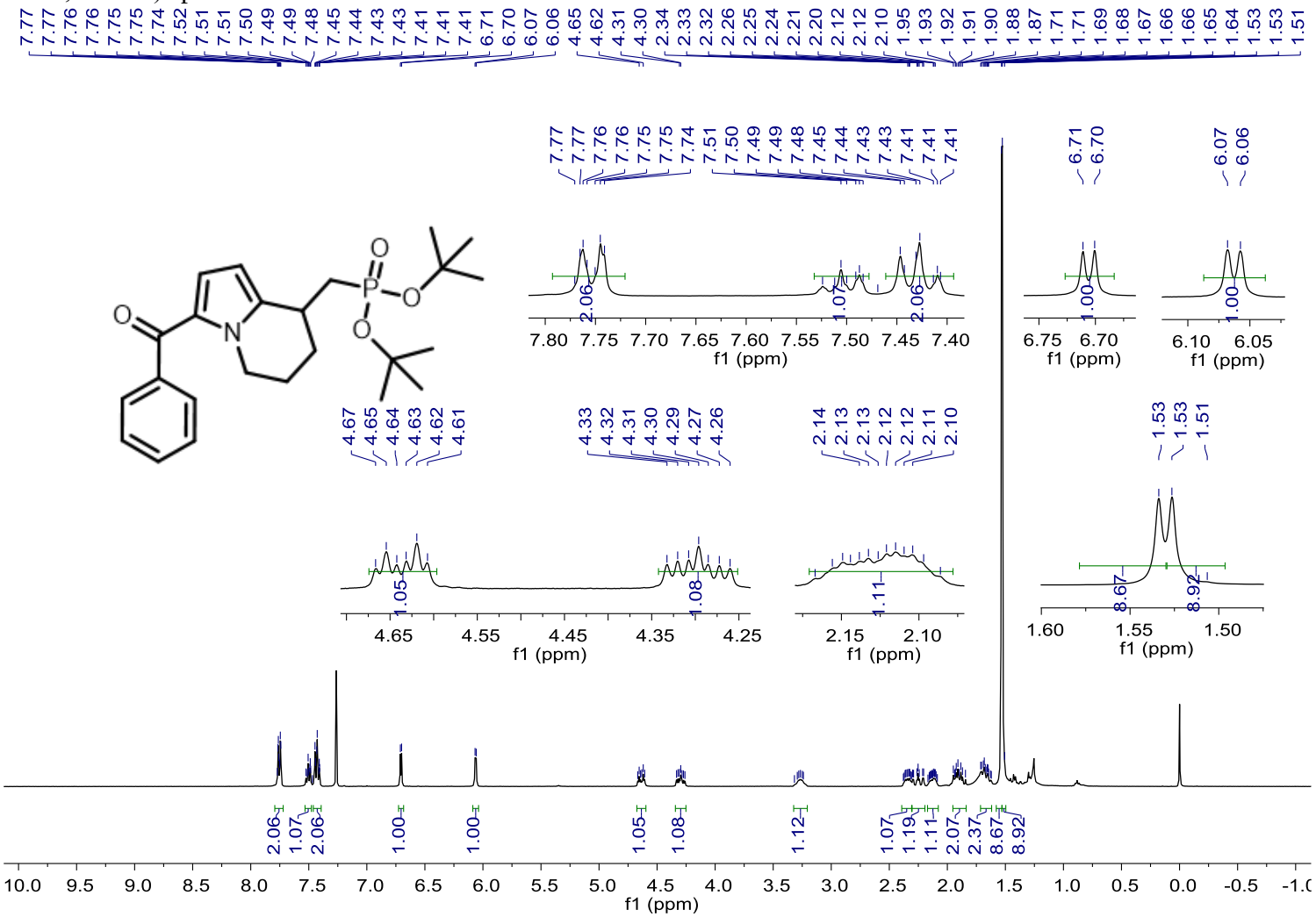
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ae**



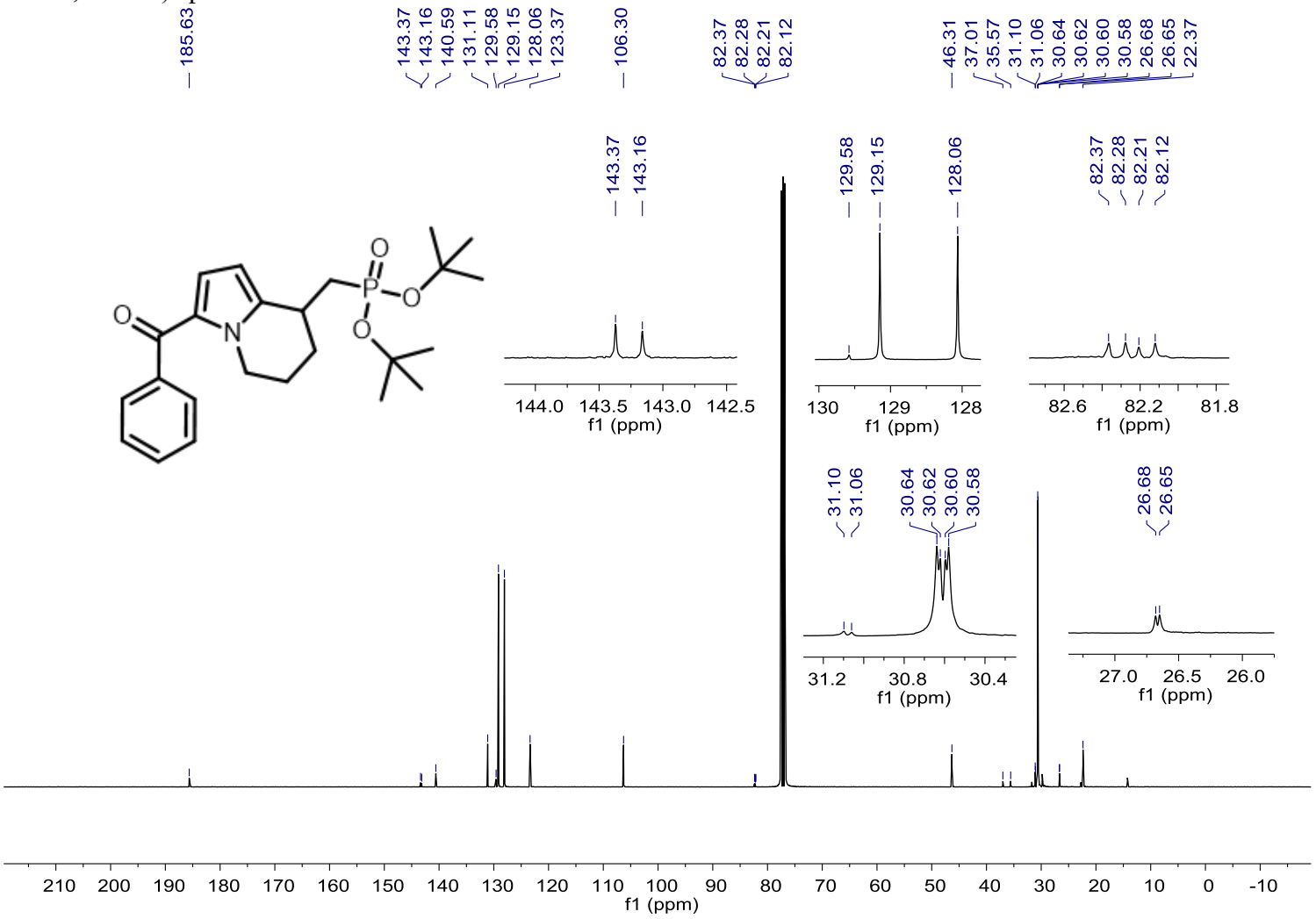
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3ae**



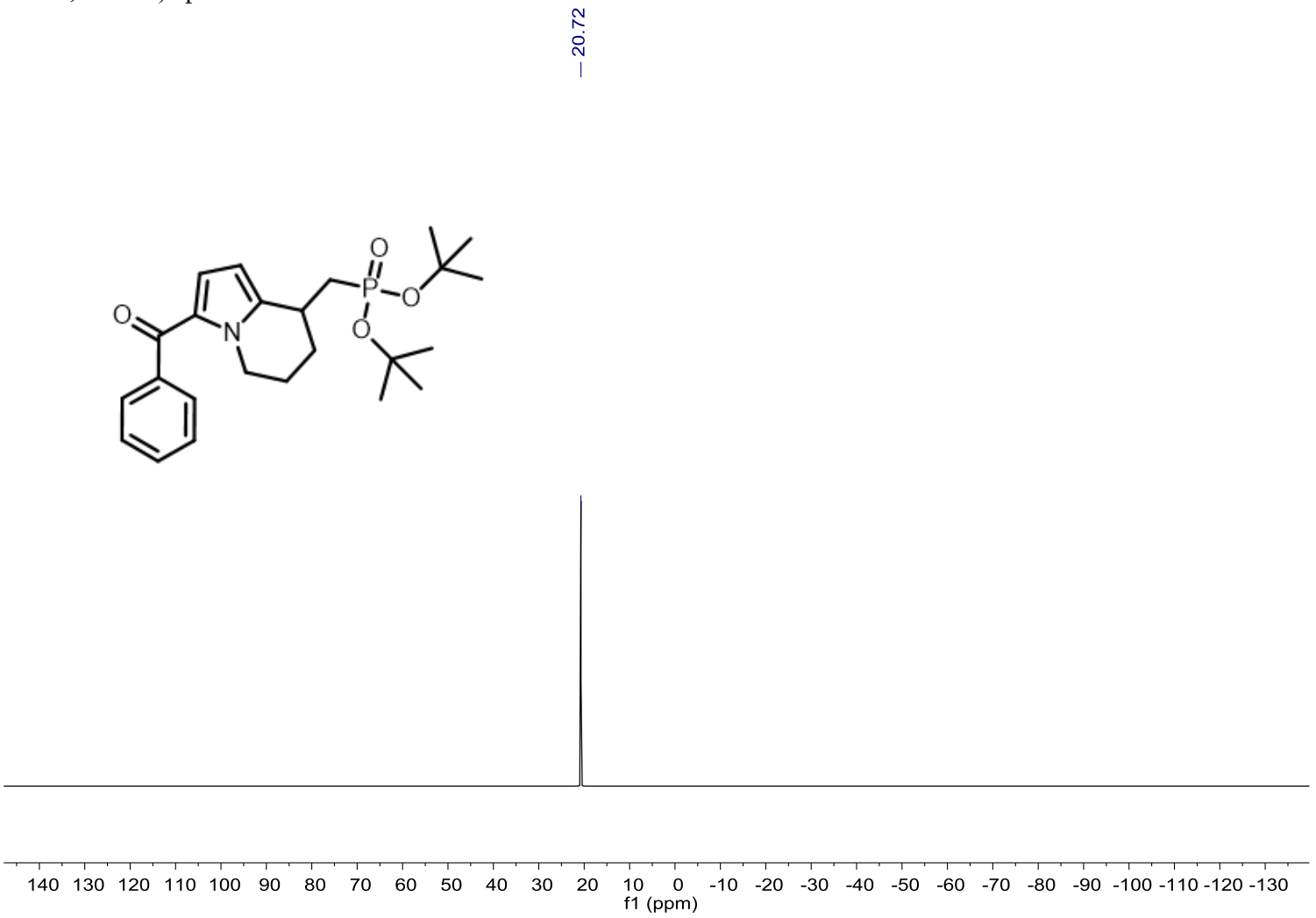
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



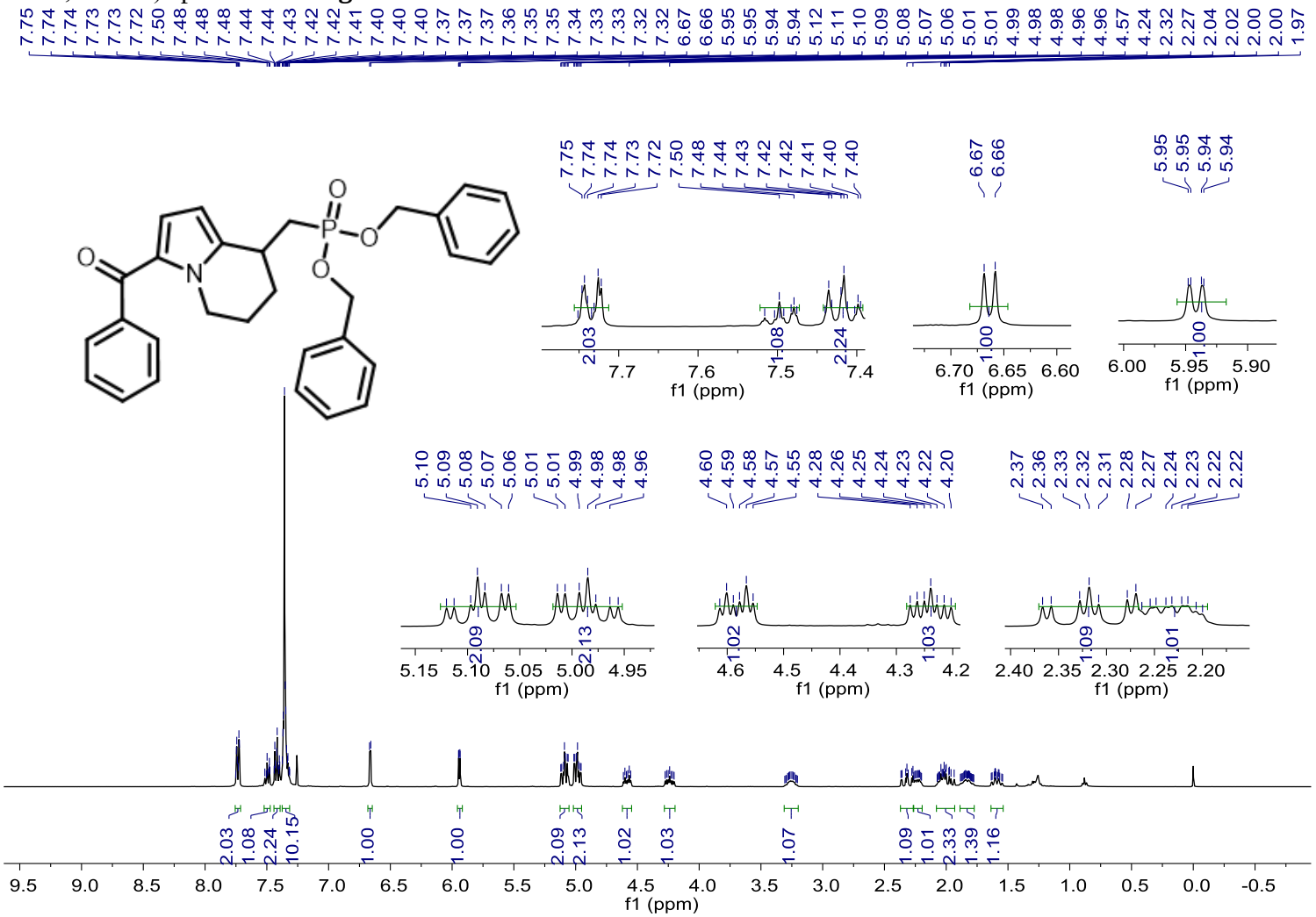
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3af**



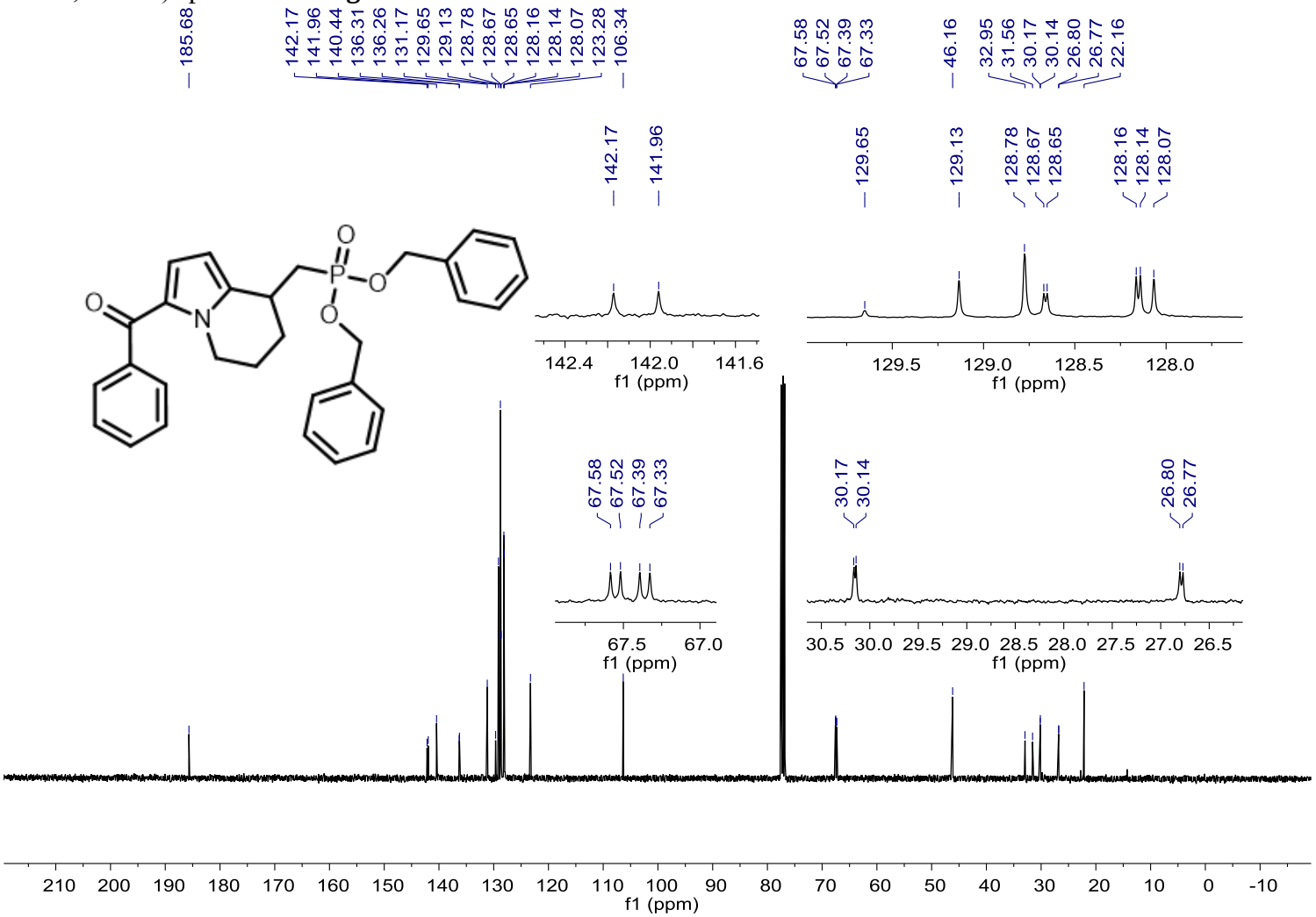
$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **3af**



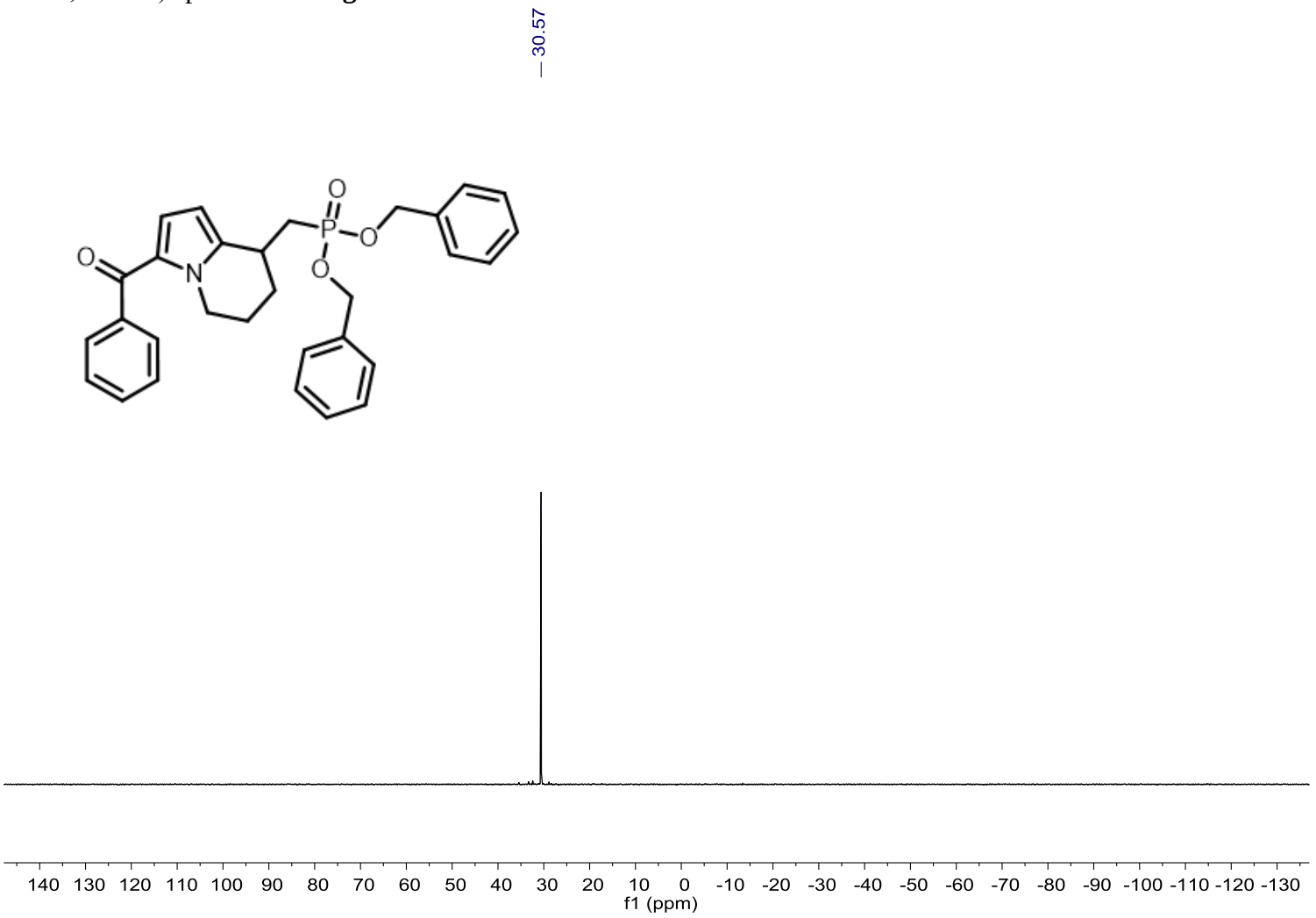
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**



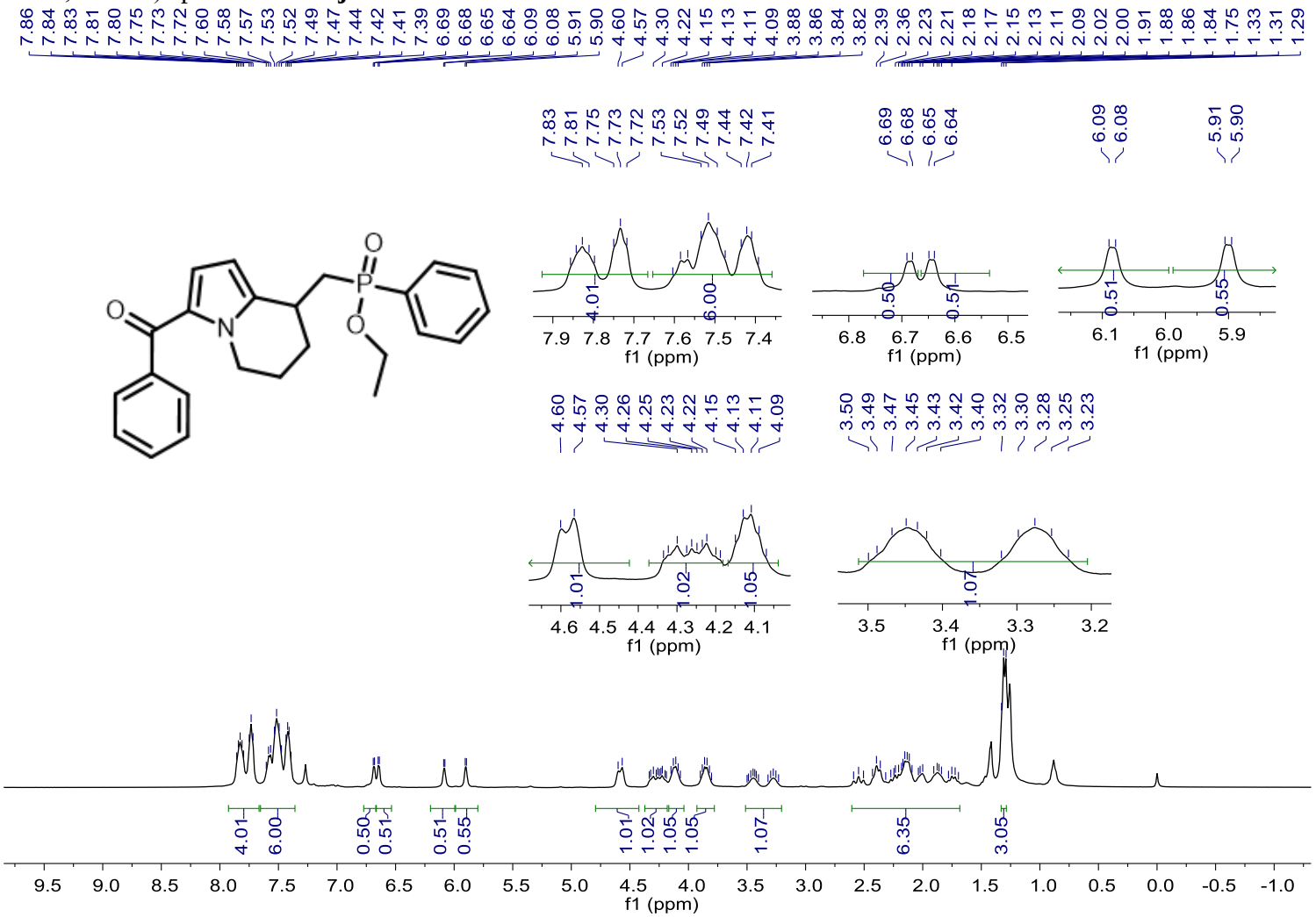
$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **3ag**



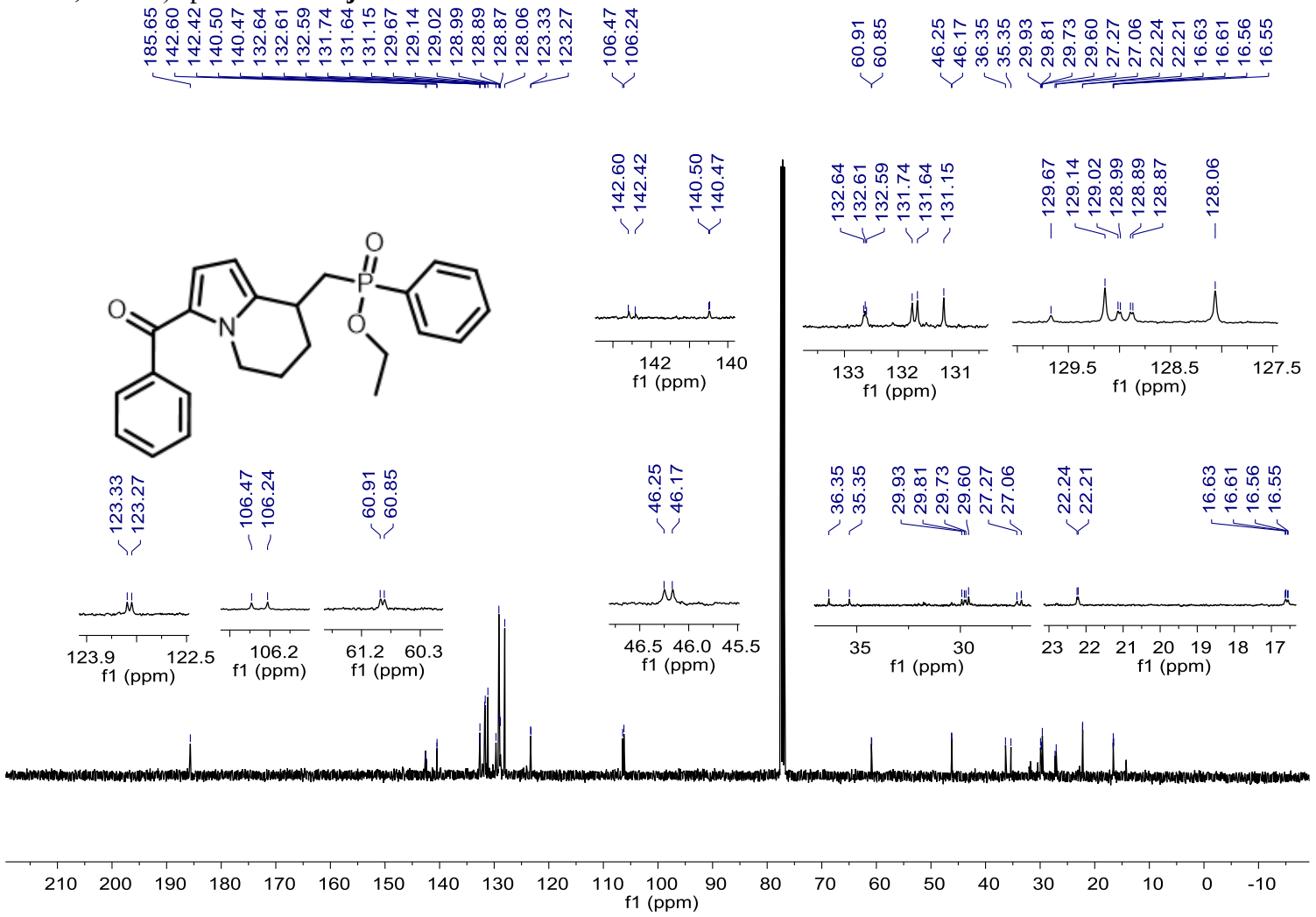
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3ag**



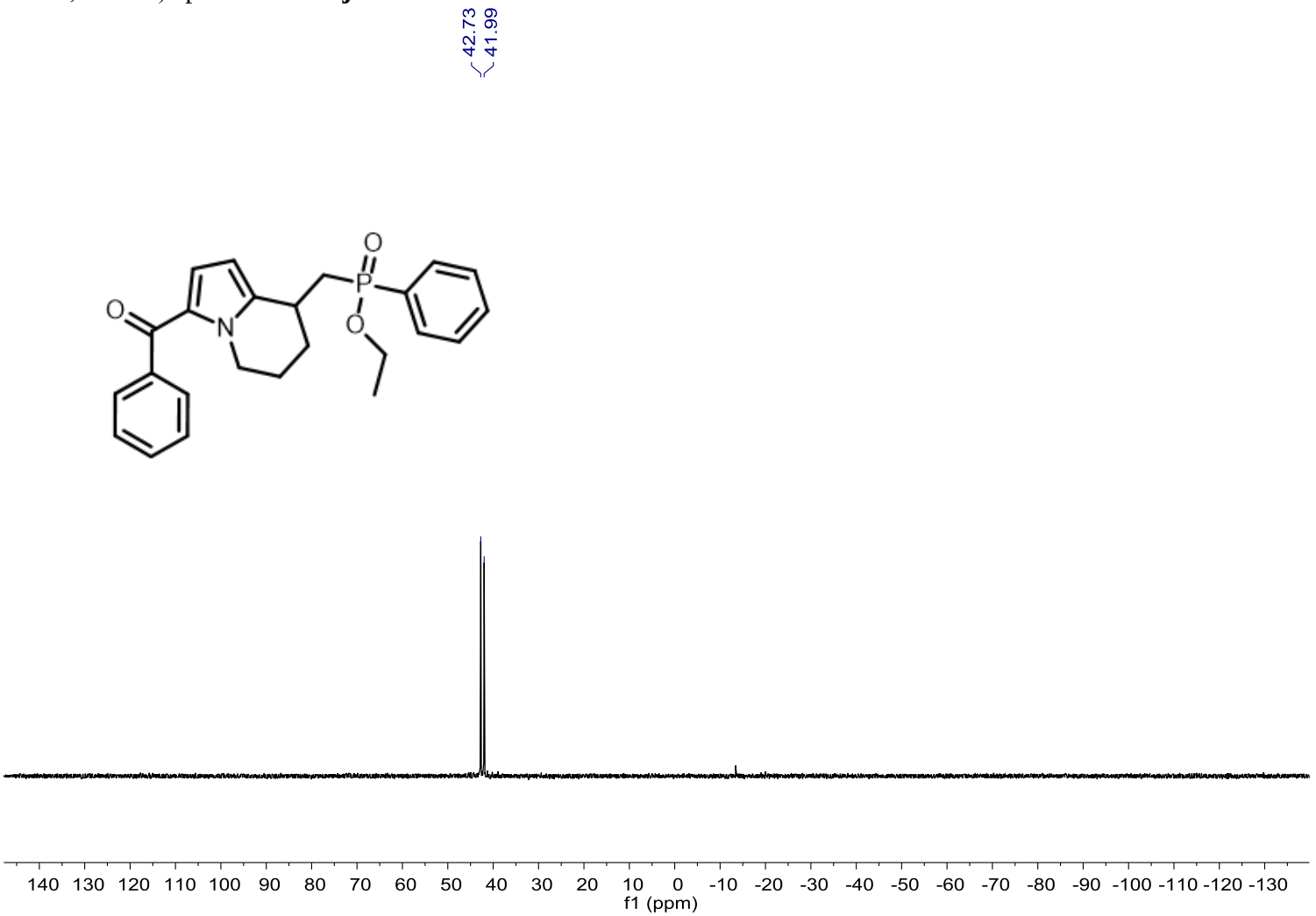
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3aj**



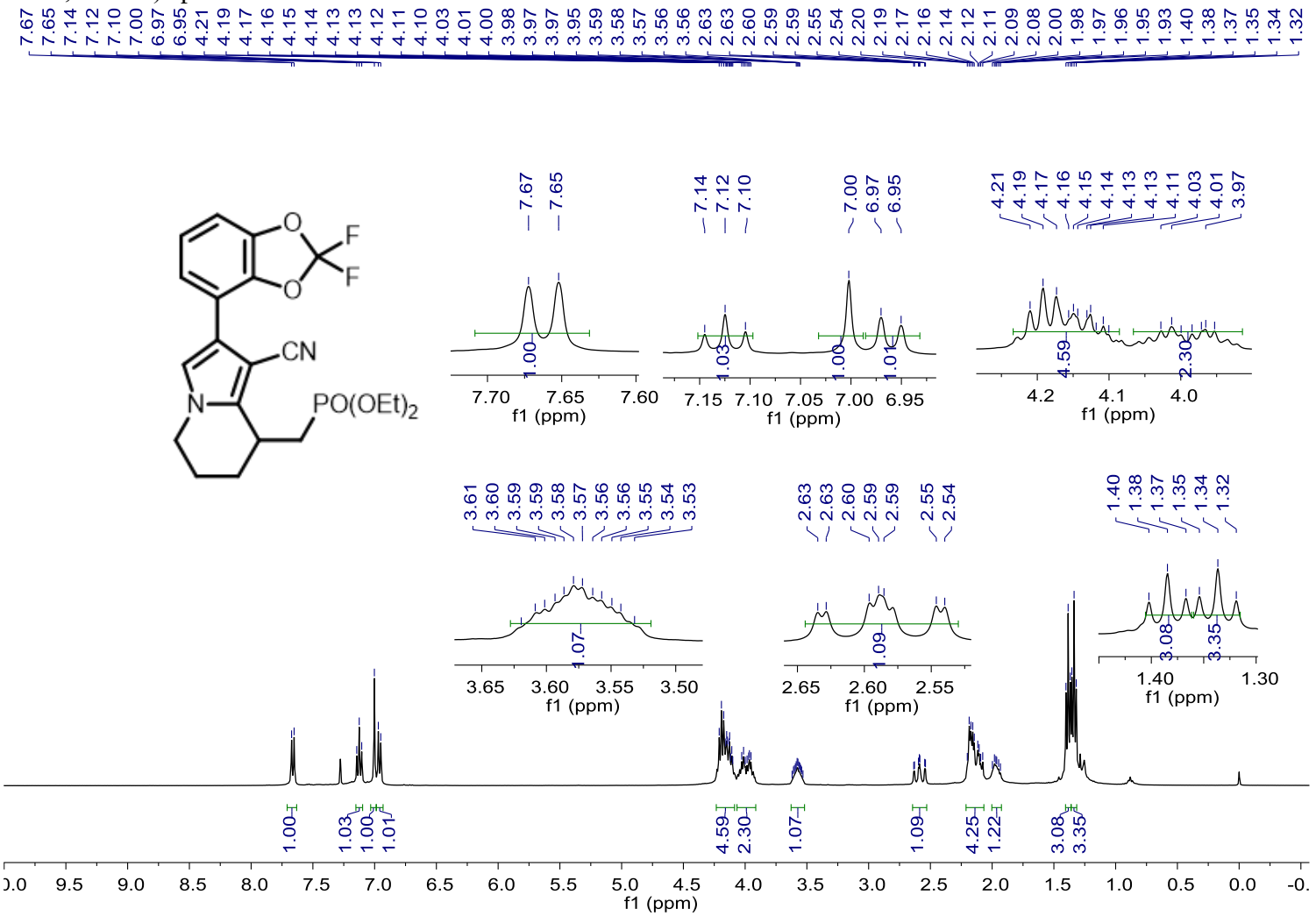
$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **3aj**



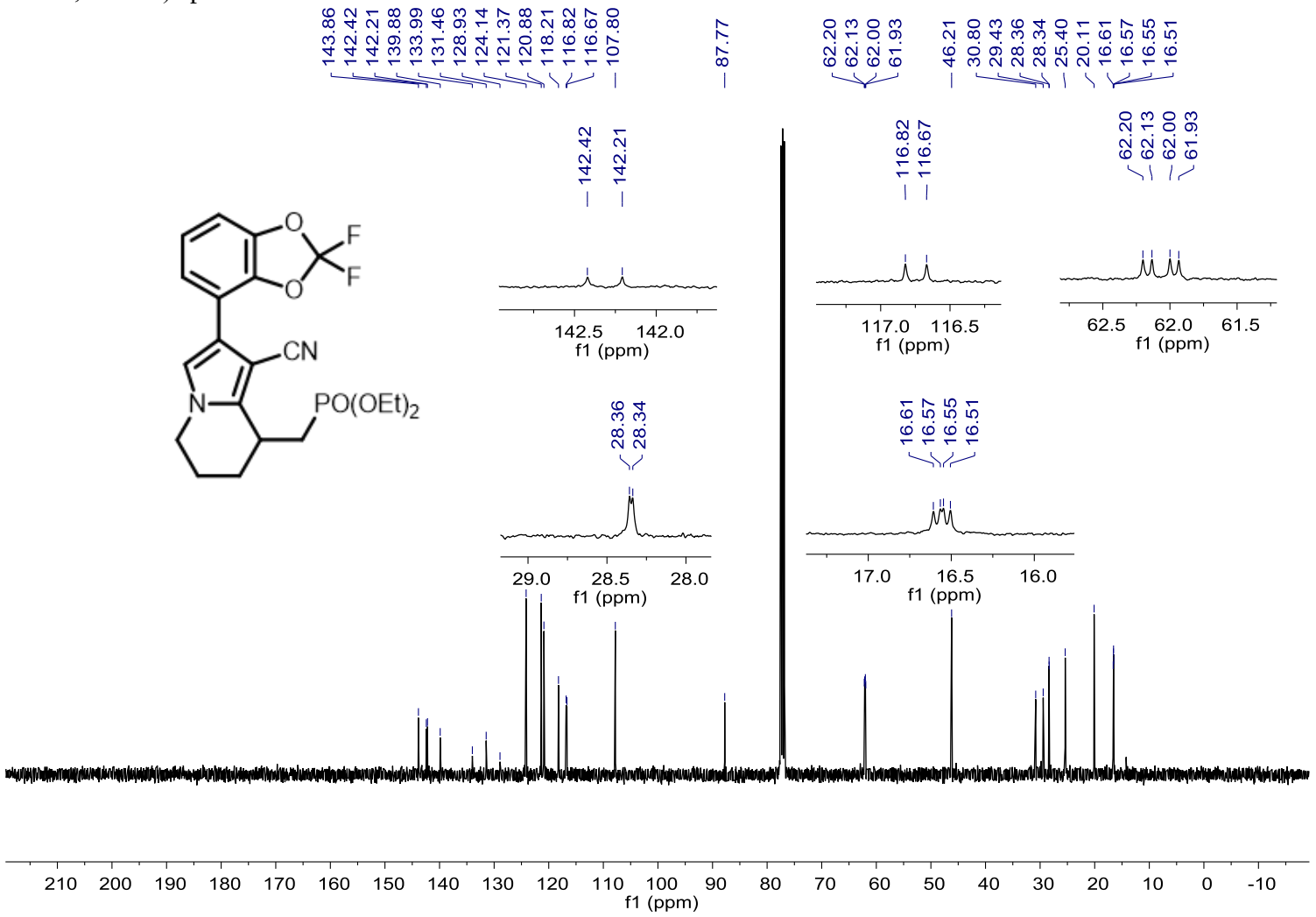
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **3aj**



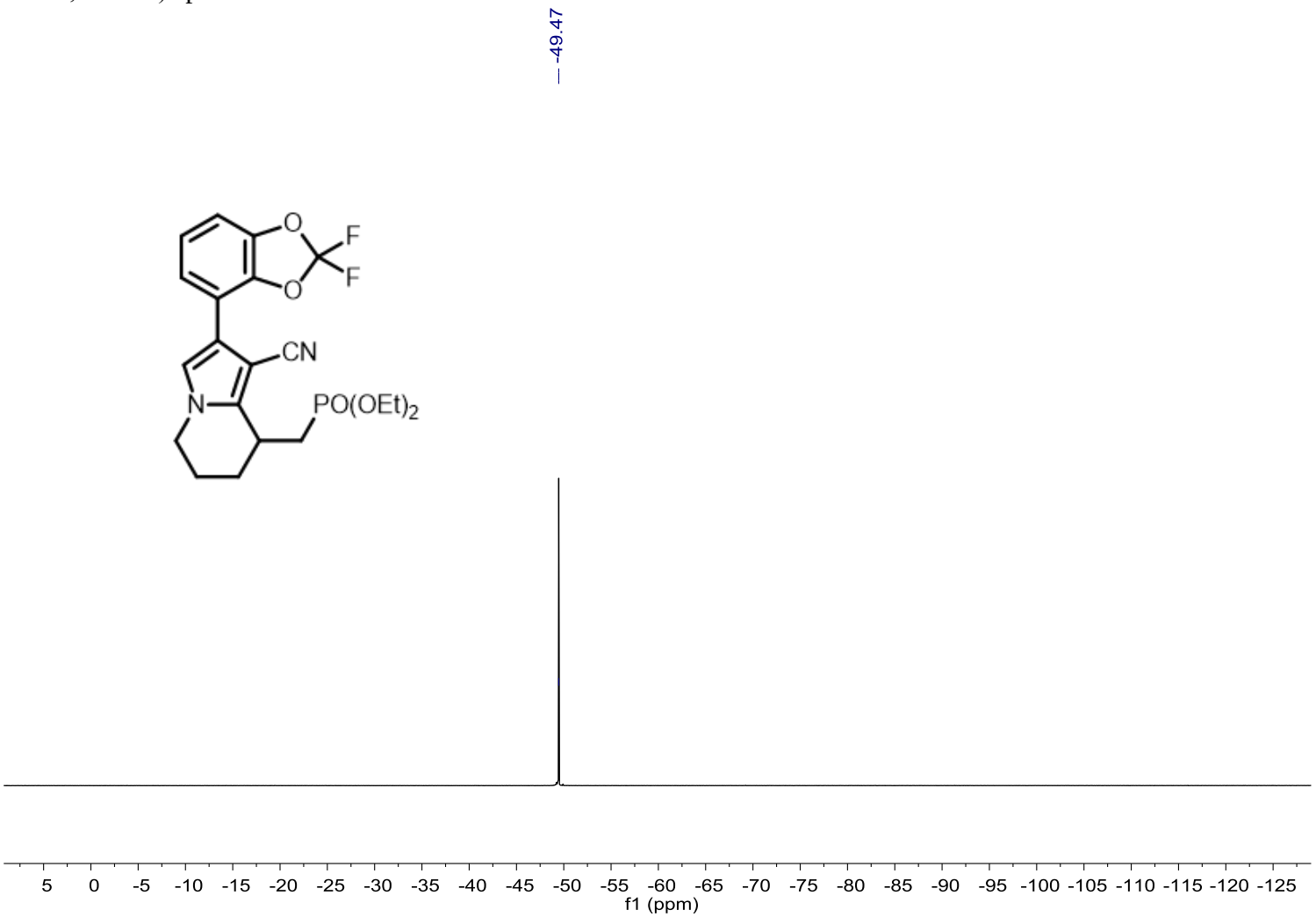
$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **7aa**



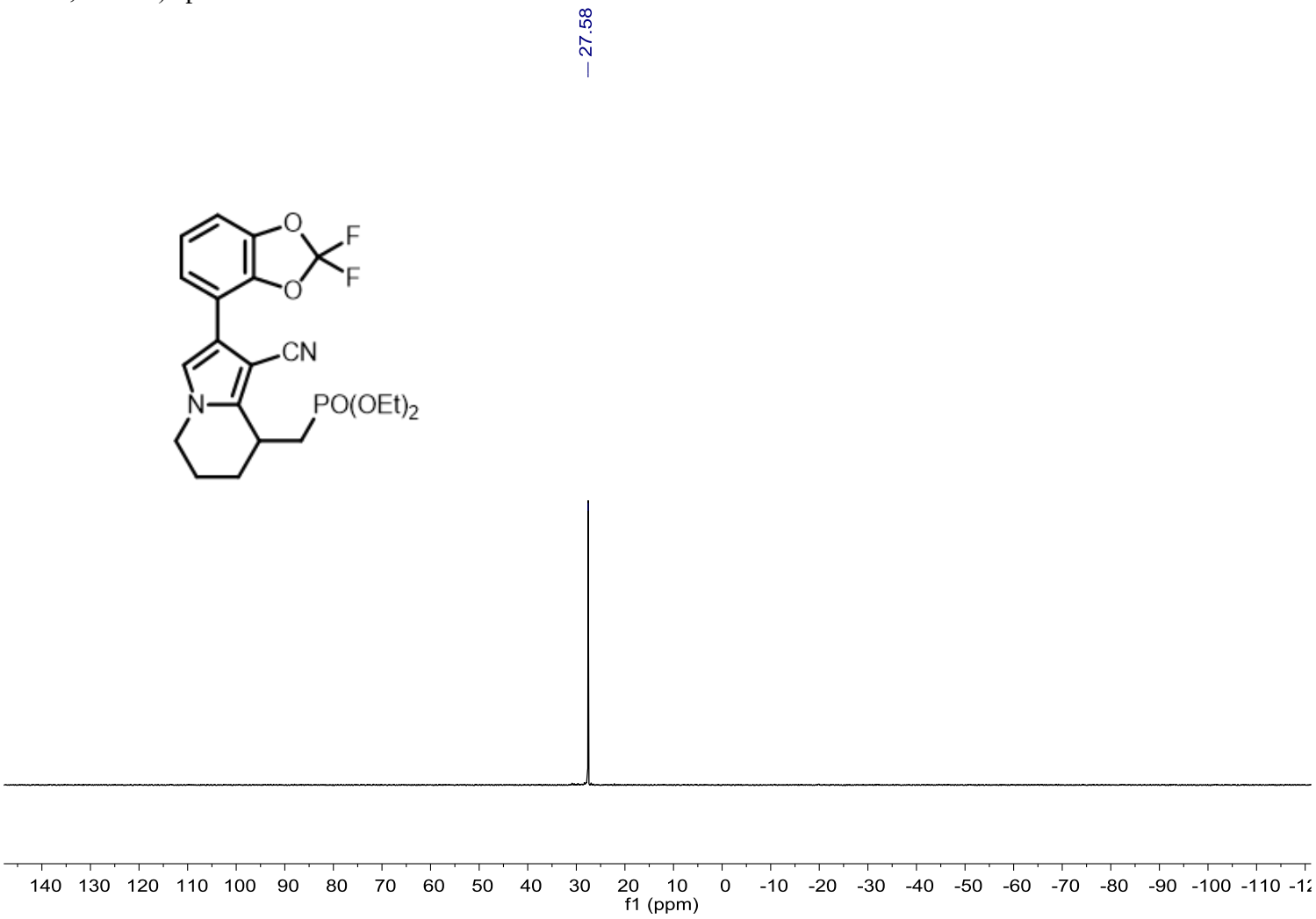
$^{13}$C NMR (101 MHz, $CDCl_3$) spectrum of **7aa**



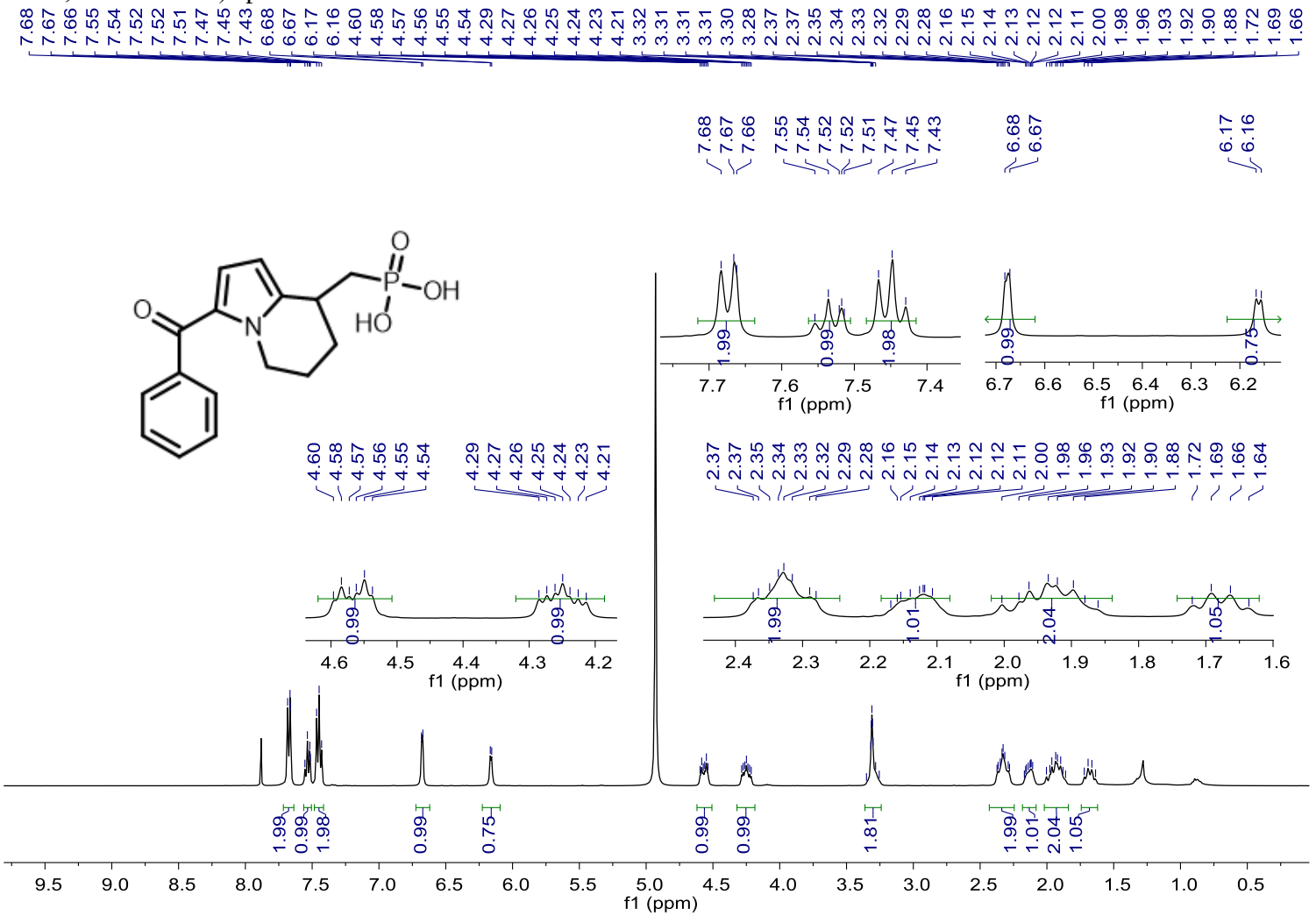
$^{19}F$ NMR (376 MHz, $CDCl_3$) spectrum of **7aa**



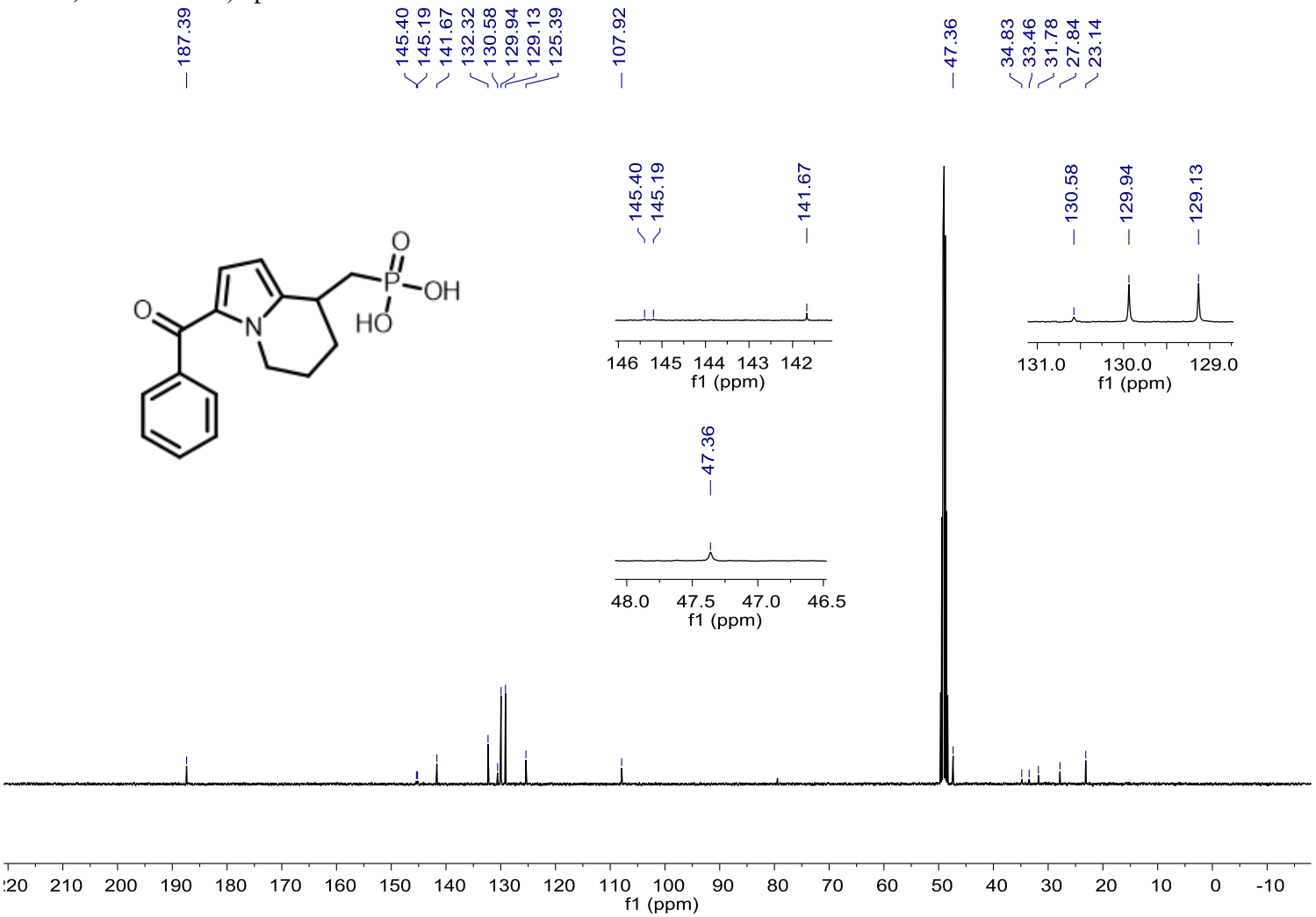
$^{31}P$ NMR (162 MHz, $CDCl_3$) spectrum of **7aa**



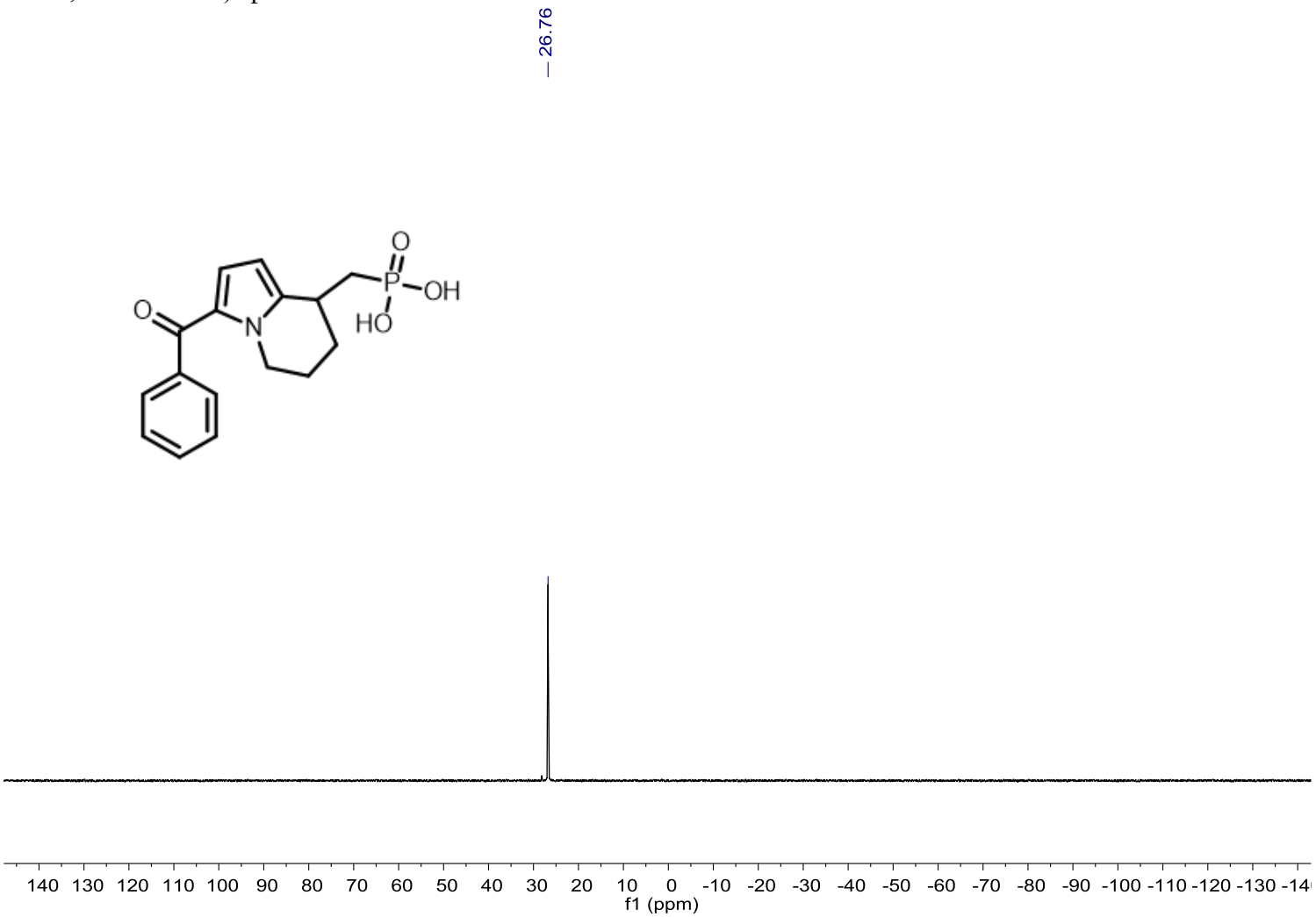
$^{1}$H NMR (400 MHz, Methanol-$d_4$) spectrum of **8aa**



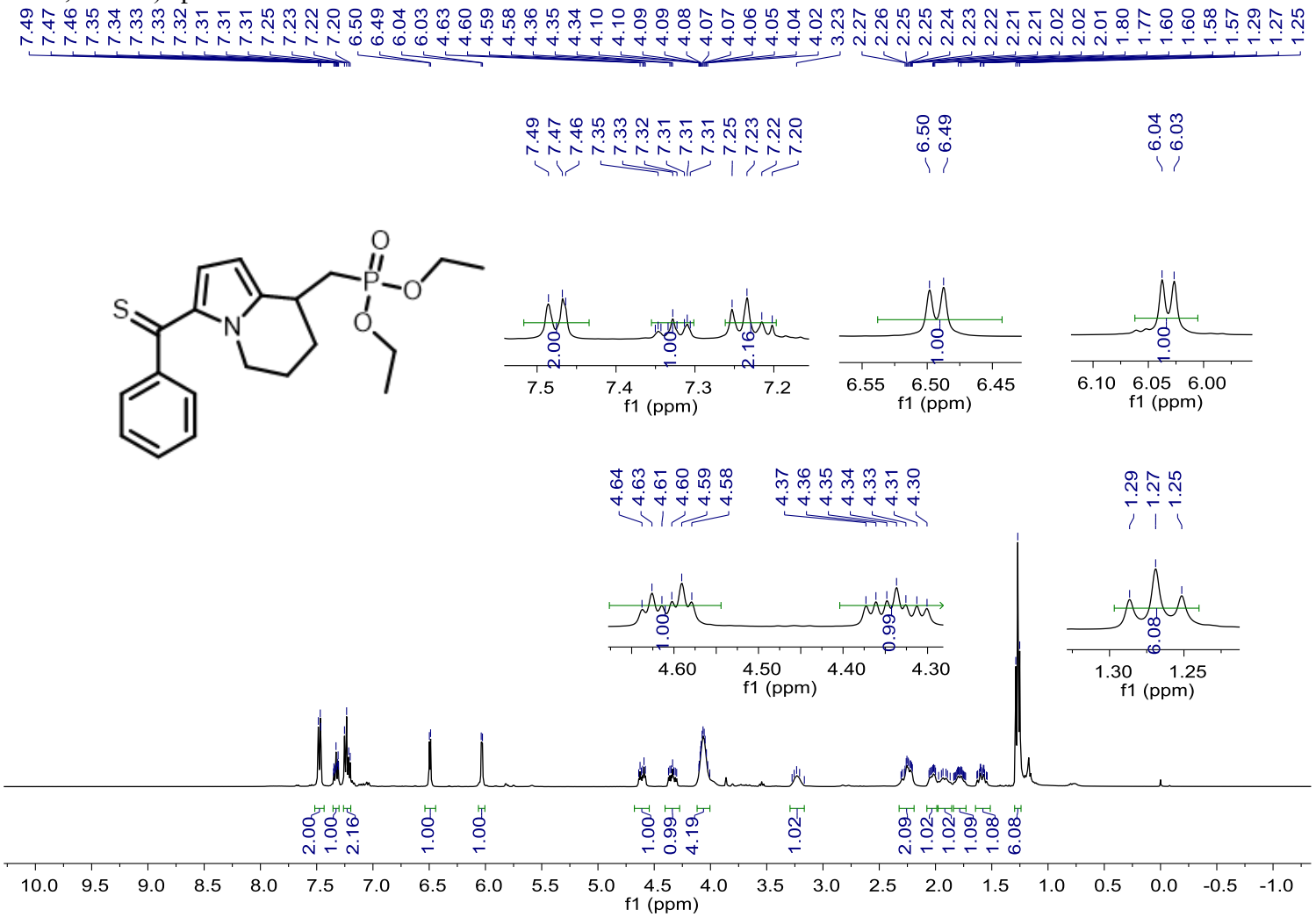
$^{13}$C NMR (101 MHz, Methanol-$d_4$) spectrum of **8aa**



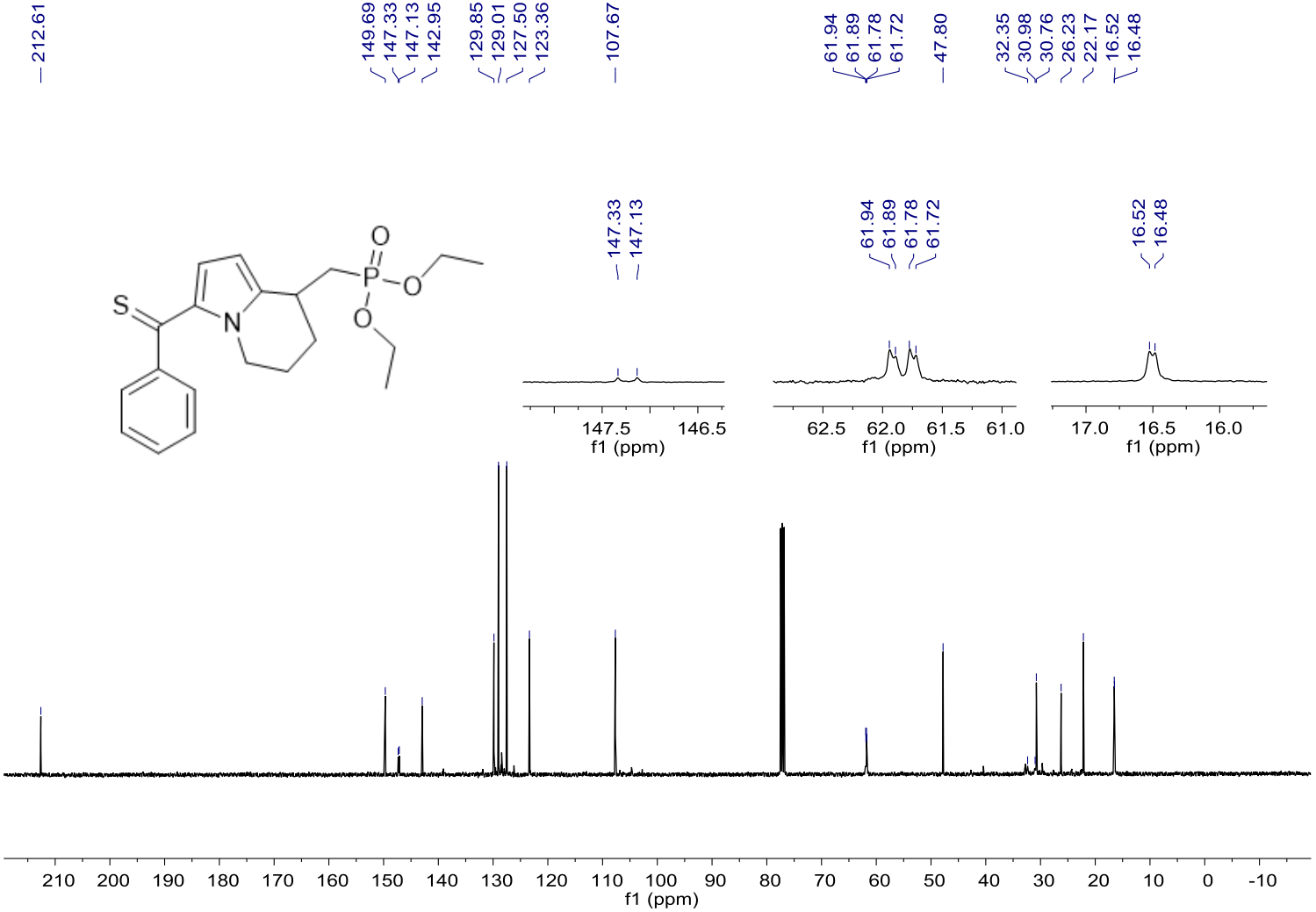
$^{31}$P NMR (162 MHz, Methanol-$d_4$) spectrum of **8aa**



$^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **9aa**



$^{13}C$ NMR (101 MHz, $CDCl_3$) spectrum of **9aa**



$^{31}$P NMR (162 MHz, $CDCl_3$) spectrum of **9aa**