Supporting Information

The selenium-assisted copper-catalyzed synthesis of phosphoramide from secondary phosphine oxide involves the construction of N-P bonds

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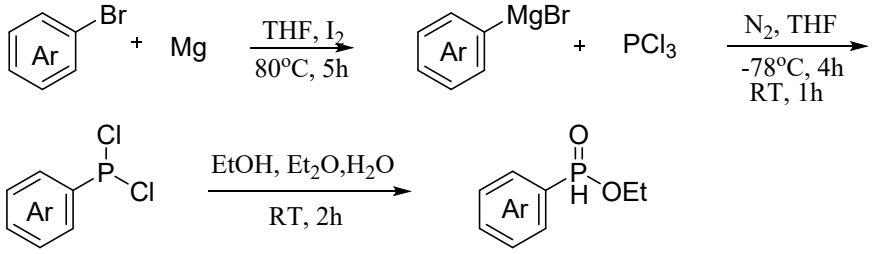
Table of Contents

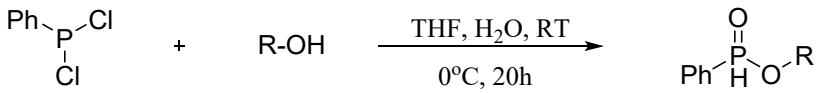
1. General information:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance III 600 spectrometer (600 MHz for ^{1}H and 150 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS $\delta = 0$ for ^{1}H, or to chloroform $\delta = 77.0$ for ^{13}C as internal tandard. ^{31}P and ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) and mass spectra were measured using Bruker micro TOF-Q mass spectrometer and Thermo Scientific DS II mass spectrometer. Analytical thin layer chromatography (TLC) was carried out using commercial silicagel plates, spots were detected with UV light (254 nm) and revealed with phosphomolybdic acid solutions. The starting materials were purchased from Aldrich, Across Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM).

2. General Procedures for the Synthesis of Substrates

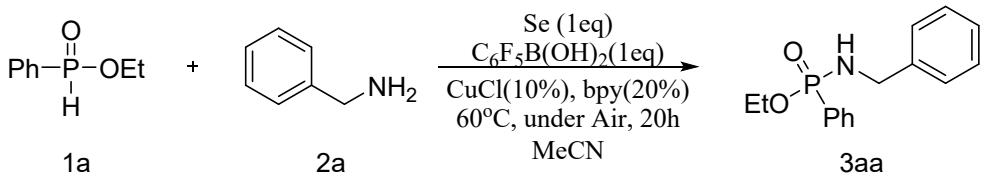


Mg (15 mmol), I_2 (two pieces), and a stirrer add to a dry three necked flask. Under N_2 condtions, add THF (20.0 mL) and halogenated reagent (10 mmol). Use a hair dryer to initiate the format reagent and reflux the reaction at 80 ℃ for 5 h. Take another dry three necked bottle and add THF (5.0 mL) and PCl_3 (10 mmol) under N_2 and -78 ℃ conditions. Drop the supernatant of Grignard reagent into a syringe and react for 4 h. Then, react at room temperature for 1 h and concentrate under vacuum to obtain a yellow oily substance. Then add Et_2O (15.0 mL) to the mixture at 0 ℃, add EtOH (20 mmol) dropwise, and react for 30 min before turning to room temperature for 2h. Quench with water. Until the disappearance of the raw material is determined by TLC. Add the reaction mixture to water (40.0 mL) and EtOAc (20.0 mL). Separate each layer and extract the water layer with EtOAc (3 x 20.0 mL). Eluting the merged organic layers with salt water, dry with magnesium sulfate, filter, and evaporate under vacuum to obtain a white oily substance. Further purify it using column chromatography on silica gel (eluent: 30% EtOAc in PE). Separate the target compound as a white oily substance (65%).



THF (10 mL) add to a dry flask under N_2 conditions, cool at 0 ℃, and then add $PhPCl_2$ (5 mmol). Then, add hydroxyl containing compounds (55 mmol) dropwise with an in Jection, stir at room temperature for 20 h, and quench with water. Until the disappearance of the raw material is determined by TLC. Add the reaction mixture to water (40.0 mL) and EtOAc (20.0 mL). Separate each layer and extract the water layer with EtOAc (3 x 20.0 mL). Eluting the merged organic layers with salt water, dry with magnesium sulfate, filter, and evaporate under vacuum to obtain a white oily substance. Further purify it using column chromatography on silica gel (eluent: 30% EtOAc in PE). Separate the target compound as a white oily substance .

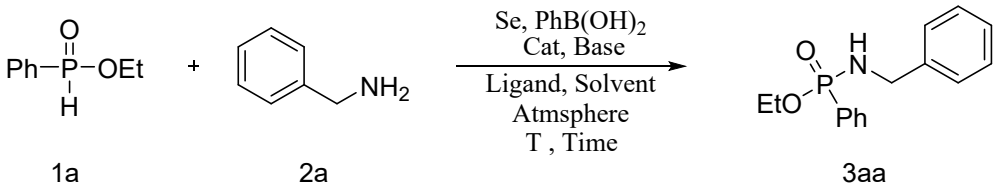
3. General Procedures for the Synthesis Products



Ethyl phenylphosphite (**1a**) (51 mg, 0.30 mmol, 1.0 equiv), Se (23.7 mg, 0.30 mmol, 1.0 equiv), $C_6F_5B(OH)_2$ (63.6 mg, 0.30 mmol, 1.0 equiv), bpy (9.4 mg, 0.06 mmol, 0.2 equiv), CuCl (3 mg, 0.03 mmol, 0.1 equiv), $BnNH_2$ (**2a**) (80.3 mg, 0.75 mmol, 2.5 equiv), and MeCN (2mL) add to a tube containing a magnetic stirring rod in an air atmosphere. Stir the mixture in an oil bath at 60 ℃ until the substrate disappears as determined by TLC. After cooling to room tempeture, the solution was vacuum removed to obtain the residue, which was purified using silica gel (10:1 = PE: IPA) to obtain pure **3aa** as an oily substance (60 mg, 90%).

4.Optimization of Reaction Conditions

Table SI Optimization of Reaction Conditions



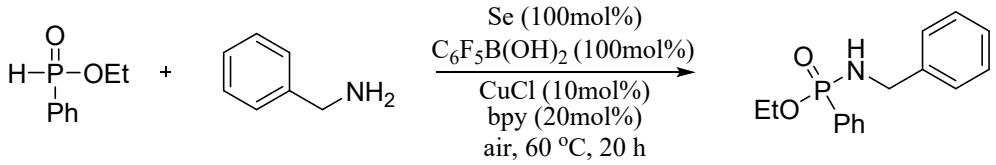
entry	cat	ligand	solvent	Boronic acid	Time	T (℃)	Atm	yield (%)
1	$Cu(OTf)_2$	bpy	MeCN	$PhB(OH)_2$	24	60	Air	75
2	$Cu(OTf)_2$	bpy	MeCN	$PhB(OH)_2$	24	60	Air	81
3	$Cu(OTf)_2$	bpy	DMSO	$PhB(OH)_2$	24	60	Air	69
4	$Cu(OTf)_2$	bpy	Toluene	$PhB(OH)_2$	24	60	Air	64
5	$Cu(OTf)_2$	bpy	MeOH	$PhB(OH)_2$	24	60	Air	23
6	$Cu(OTf)_2$	bpy	DCE	$PhB(OH)_2$	24	60	Air	35
7	$Cu(OTf)_2$	bpy	1, 4-dioxane	$PhB(OH)_2$	24	60	Air	40

8	$Cu(OTf)_2$	bpy	THF	$PhB(OH)_2$	24	60	Air	52
9	$Cu(OTf)_2$	bpy	DMF	$PhB(OH)_2$	24	60	Air	37
10	$Cu(OTf)_2$	bpy	MeCN	$PhB(OH)_2F$	24	60	Air	60
11	$Cu(OTf)_2$	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	82
12	$Cu(OTf)_2$	bpy	MeCN	$PhB(OH)_2CF_3$	24	60	Air	55
13	$Cu(OTf)_2$	bpy	MeCN	$PhB(OH)_2(CF_3)_2$	24	60	Air	48
14	CuI	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	60
15	CuBr	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	55
16	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	85
17	CuO	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	0
18	$Cu(OAc)_2$	bpy	MeCN	$C_6F_5B(OH)_2$	24	60	Air	59
19	CuCl	1,10-phen	MeCN	$C_6F_5B(OH)_2$	24	60	Air	77
20	CuCl	TERPY	MeCN	$C_6F_5B(OH)_2$	24	60	Air	70
21	CuCl	quinoxaline-5,6-dione	MeCN	$C_6F_5B(OH)_2$	24	60	Air	40
22	CuCl	4,5-Diazafluoren-9-one	MeCN	$C_6F_5B(OH)_2$	24	60	Air	34
23	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	24	23	Air	65
24	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	24	40	Air	70
25	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	24	80	Air	66
26	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	24	100	Air	40
27	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	15	60	Air	75
28	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	Air	87
29	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	N_2	69
30	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	Ar	71
31[b]	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	Air	80
32[c]	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	Air	88
33[d]	CuCl	bpy	MeCN	$C_6F_5B(OH)_2$	20	60	Air	89
34[e]	**CuCl**	**bpy**	**MeCN**	**$C_6F_5B(OH)_2$**	**20**	**60**	**Air**	**90**

[a]Reaction Condition. [b]add to Et_3N. [c]Se (0.3 mmol), $C_6F_5B(OH)_2$ (0.3 mmol). [d]CuCl (0.03 mmol), bpy (0.06 mmol). [e]$BnNH_2$ (0.75 mmol).

Optimization of Reaction Conditions: 1a 0.3 mmol, Se 0.15 mmol, $C_6F_5B(OH)_2$ 0.15 mmol add to the reactor CuCl 0.06 mmol, bpy 0.12 mmol, $BnNH_2$ (**2a**) 0.6 mmol, Then 2 mL of MeCN was added to the air environment at 60 ℃ and stirred continuously for 24 h. The reaction was stopped and cooled to room temperature. The solvent was removed by vacuum distillation. The crude product was separated by column chromatography and eluted with isopropanol/petroleum ether to obtain the target product **3aa**.

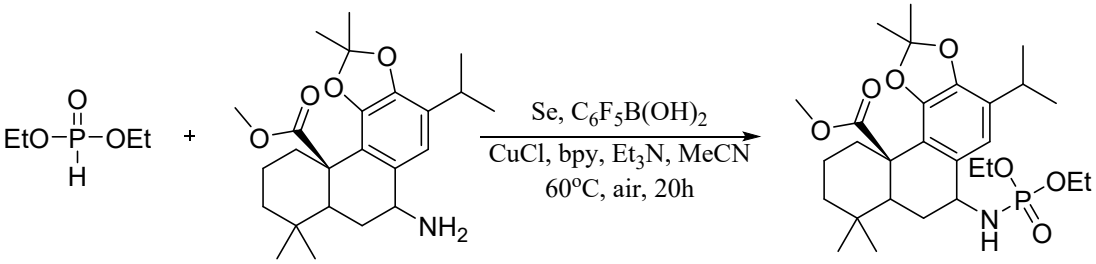
5. Gram-scale Experiment



1a, 5mmol 2a 3aa,1.1g, 80%

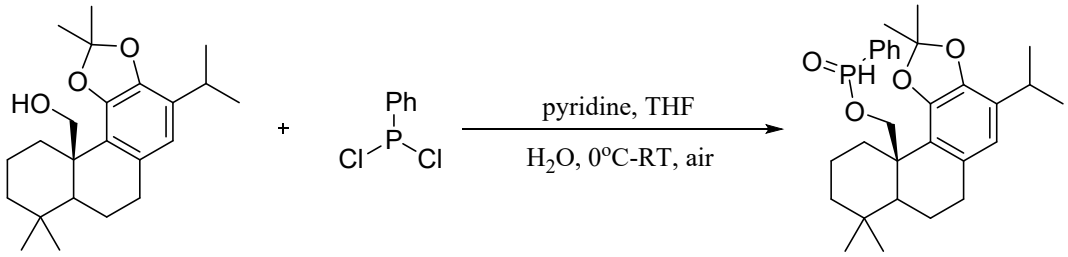
Ethyl phenylphosphite (**1a**) (5 mmol), Se (100 mol%), $C_6F_5B(OH)_2$ (100 mol%), CuCl (10.0 mol%), bpy (20.0 mol%), $BnNH_2$ (**2a**) (250 mol%) and DMSO (60 mL) add to the reaction mixture in a 100 mL Schlenk tube containing a magnetic stirring rod. Stir the reaction mixture in an air atmosphere at 60 ℃ for 20 h and monitor it through TLC. Then cool the solution to room tempeature and remove the solvent directly under vacuum. The crude product was purified by silica gel column chromatography (10:1 = PE: IPA) to obtain pure product **3aa** (1.1 g, 80%).

6. Synthetic Application.



1b **2z** **3bz**

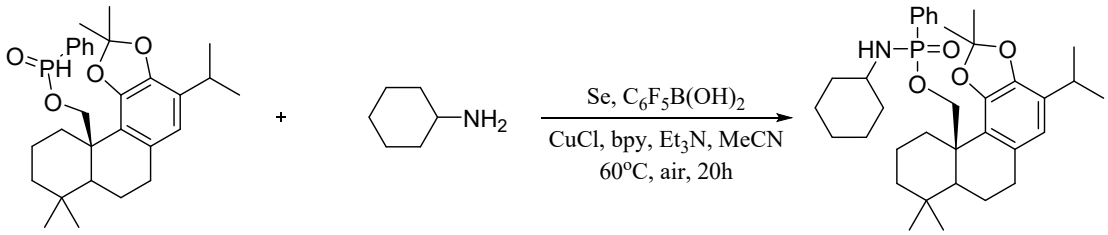
1b (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and **2z** (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile to the air environment and stir continuously for 20 hours at 60 ℃. React and cool to room temperature. Solvents were removed by vacuum distillation and purified by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (**3bz**, 60%).



1h

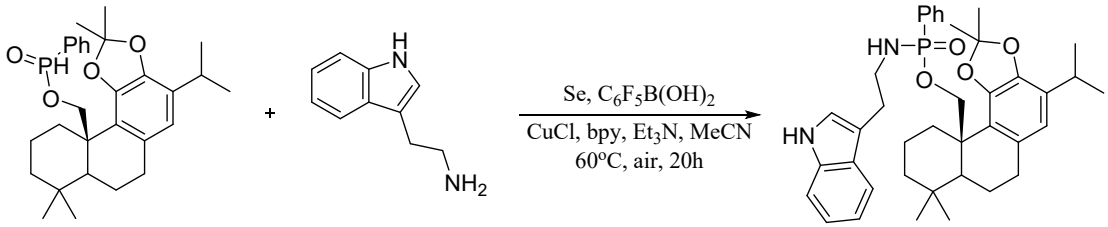
At 0 °C, a THF solution of ((11aR)-4-isopropyl-2,2,8,8-tetramethyl-7,7a,8,9,10,11-hexahy drophenanthro [3,4-d][1,3] dioxol-11a(6H)-yl) methanol and pyridine (1.5 eq) was added dropwise

to thesolution of $PhPCl_2$ in THF. Slowly stir and white precipitate was observed. The reaction was vigorously stirred to room temperature for 12 hours. Excess water (10 mL) wasadded and stirred for 30 minutes before extraction (EA and saturated salt water). The plate was prepared with PE: IPA = 10:1. (**1h**, 50%).



1h **2t** **3ht**

1h (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and **2t** (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile to the air environment and stir continuously for 20 hours at 60 ℃. Stop the reaction and cool to room temperature. Solvents are removed by vacuum distillation and purified by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (**3ht**, 93%).

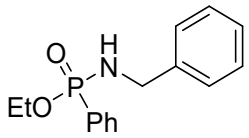


1h **2y** **3hy**

1h (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and **2y** (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile to the air environment and stir continuously for 20 hours at 60 ℃. Stop the reaction and cool to room temperature. Remove the solvent using vacuum distillation and purify it using silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (**3hy**, 70%).

7. Characterization Data of New Product

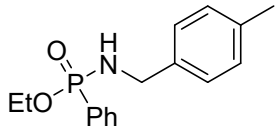
ethyl N-benzyl-P-phenylphosphonamidate **(3aa)**



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at

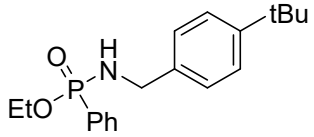
60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (90%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (dd, J = 12.9, 7.6 Hz, 2H), 7.52-7.46 (m, 1H), 7.45-7.38 (m, 2H), 7.30-7.17 (m, 5H), 4.18-3.93 (m, 4H), 3.65-3.53 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 139.71 (d, J = 6.4 Hz), 131.75 (d, J = 2.9 Hz), 131.43 (d, J = 9.8 Hz), 130.01 (t), 60.60 (d, J = 5.6 Hz), 44.81 (s), 16.35 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.20. HRMS(ESI): $C_{15}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 298.0973, found 298.0982.

ethyl N-(4-methylbenzyl)-P-phenylphosphonamidate（**3ab**）



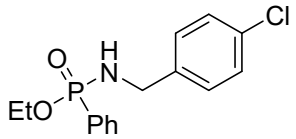
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-methylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (82%). ^{1}H NMR (600 MHz, Chlorofo-rmd) δ7.81 (dd, J = 12.9, 7.6 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46 - 7.41 (m, 2H), 7.13 (d, J = 7.7 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 4.14 - 4.06 (m, 2H), 4.04 - 3.97 (m, 2H), 3.15 (d, J = 7.5 Hz, 1H), 2.31 (s, 3H), 1.31 (t, J = 7.0 Hz, 3H).^{13}C NMR (150 MHz, Chloroform-d) δ 135.92 (s),135.55 (d, J = 6.8 Hz), 130.79 (d, J = 2.9 Hz), 130.45 (d, J = 9.7 Hz), 129.24 (s),128.17 (s),127.40 (d, J = 14.4 Hz), 126.32(s),59.68 (d, J = 5.2 Hz), 43.59(s),20.03(s),15.36 (d, J = 6.7 Hz).^{31}P NMR (243 MHz, Chloroform-d) δ 23.02. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1316.

ethyl N-(4-(tert-butyl)benzyl)-P-phenylphosphonamidate**(3ac)**



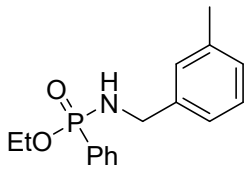
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-tert butylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (42%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.86-7.78 (m, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.48-7.42 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.15-4.07 (m, 2H), 4.07-4.01 (m, 2H), 3.10-3.01 (m, 1H), 1.35-1.28 (m, 12H). ^{13}C NMR (150 MHz, Chloroform-d) δ 150.45 (s), 136.65 (d, J = 7.0 Hz), 131.94 (d, J = 2.9 Hz), 131.79 (s), 131.60 (d, J = 9.7 Hz), 128.54 (d, J = 14.2 Hz), 127.26 (s), 125.58 (s), 80.73-74.78 (m), 60.84 (d, J = 5.6 Hz), 44.66 (s), 34.60 (s), 31.45 (s), 16.51 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.24. HRMS(ESI): $C_{19}H_{26}NO_2NaP$ for $[M+Na]^+$, calculated 354.1599, found 354.1587.

ethyl N-(4-chlorobenzyl)-P-phenylphosphonamidate（**3ad**）



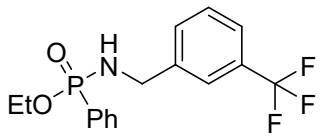
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-chlorobenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Distillunder reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (80%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (dd, J = 12.6,7.6 Hz, 2H), 7.49 (t, J = 7.4Hz, 1H), 7.44-7.38 (m, 2H),7.21 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 4.10-3.94 (m, 4H), 3.63-3.55 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 138.42 (d, J = 6.2 Hz), 133.00 (s), 131.94 (d, J = 2.9 Hz), 131.50 (d, J = 9.7 Hz), 128.83 (s), 128.63 (s), 128.56 (s), 128.46 (s), 77.17 (t), 60.83 (d, J = 5.6 Hz), 44.26 (s), 16.44 (d, J = 6.7 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.20. HRMS(ESI): $C_{15}H_{18}NO_2ClP$ for $[M+H]^+$, calculated 310.0764, found 310.0752.

ethyl N-(3-methylbenzyl)-P-phenylphosphonamidate（**3ae**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 3-methylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature.Remove the solvent by vacuum distillation, purify it by silica gel chromatography, wash itwith PE: IPA (10:1), and obtain a yellow oily substance (43%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (dd, J = 12.9, 7.1 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46-7.40 (m, 2H), 7.19-7.15 (m, 1H), 7.04 (d, J = 6.1 Hz, 3H), 4.15-4.07 (m, 2H), 4.05-3.99 (m, 2H), 3.15 (d, J = 7.7Hz, 1H), 2.29 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 138.44 (d, J = 7.0 Hz), 137.21 (s), 130.83 (d, J = 2.8 Hz), 130.47 (d, J = 9.7 Hz), 129.23 (s), 127.45 (d, J = 3.1 Hz), 127.37 (s), 127.13 (s), 127.03 (s),123.36 (s), 59.74 (d, J = 5.9 Hz), 43.84 (s), 20.32 (s), 15.37 (d, J = 7.1 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.98. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1308.

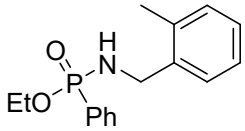
ethyl P-phenyl-N-(3-(trifluoromethyl)benzyl)phosphonamidate（**3af**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 3-trifluoromethylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60

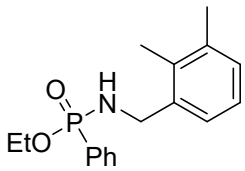
℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (43%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.80 (dd, J = 13.0, 7.0 Hz, 2H), 7.50 (dd, J = 16.8, 8.5 Hz, 3H), 7.46-7.42(m, 3H), 7.40 (t, J = 7.6Hz, 1H), 4.17-4.05(m, 4H), 3.25 (d, 1H), 1.32 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 132.18 (s), 132.16 (s), 131.61 (s), 131.54 (s), 130.84 (s), 129.12 (s), 128.71 (s), 128.62 (s), 124.27 (d, J = 3.7 Hz), 124.22 (d, J = 2.6 Hz), 61.09 (s), 44.57 (s), 16.52 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.25. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.56. HRMS(ESI): $C_{16}H_{18}NO_2PF_3$ for$[M+H]^+$, calculated 344.1027, found 344.1025.

ethyl N-(2-methylbenzyl)-P-phenylphosphonamidate（**3ag**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2-methylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (91%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 (dd, J =12.9, 7.4 Hz, 2H), 7.52 (t, J =7.4 Hz, 1H), 7.48 -7.43 (m, 2H), 7.27 (s, 1H), 7.18 - 7.10 (m, 3H), 4.29 - 3.92 (m, 4H), 3.06 (d, J =7.7 Hz, 1H), 2.26 (s, 3H), 1.32 (t, J = 7.1 Hz, 31H). ^{13}C NMR (150 MHz, Chloroform-d) δ137.28 (d, J = 7.2 Hz), 135.89 (s), 131.84 (s), 131.47 (d, J = 9.8 Hz), 130.74 (d, J = 172.1 Hz), 130.33 (s), 128.43 (d, J = 13.8 Hz), 127.78 (s), 127.42 (s), 126.10 (s), 60.77 (d, J = 5.4 Hz), 42.65 (s), 18.85 (s), 16.38 (d, J = 6.3 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.99. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1302.

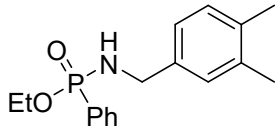
ethyl N-(2, 3-dimethylbenzyl)-P-phenylphosphonamidate（**3ah**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2,3-dimethylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (45%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.84-7.79 (m, 2H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 2H), 7.10-7.03 (m, 3H), 4.14-4.04 (m, 4H), 2.85 (d, J = 7.8 Hz, 1H), 2.26 (s, 3H), 2.17 (s, 3H), 1.33 (t, J = 7.1Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 137.32 (s), 134.76 (s), 131.98 (d, J = 3.0 Hz), 131.64 (s), 131.57 (s), 129.39 (s), 128.59 (s), 128.50 (s), 126.16 (s), 125.71 (s), 60.95 (s), 43.51 (s), 20.55 (s), 16.53 (d, J = 6.8 Hz), 14.84 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.20. HRMS(ESI): $C_{17}H_{23}NO_2P$ for $[M+H]^+$, calculated 304.1466, found

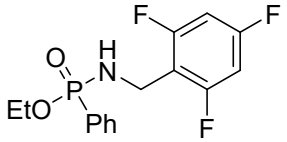
304.1457.

ethyl N-(3, 4-dimethylbenzyl)-P-phenylphosphonamidate（**3ai**）



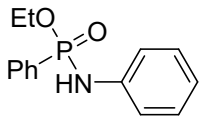
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 3,4-dimethylbenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment andstir continuously at 60 ℃ for 20 h. Stop the reaction and cool toroom temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (33%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 (dd, J = 12.9, 7.0 Hz, 2H), 7.56 - 7.49 (m, 1H), 7.50 - 7.42 (m, 2H), 7.05 (d, J = 7.6 Hz, 1H), 7.01 - 6.95 (m, 2H), 4.18 - 4.05 (m, 2H), 4.03 - 3.94 (m, 2H), 3.01 (d, J = 7.8 Hz, 1H), 2.21 (d, J = 8.5 Hz, 6H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 136.96 (d, J = 6.7 Hz), 136.75 (s), 135.61 (s), 131.81 (d, J = 3.3 Hz), 131.49 (d, J = 9.7 Hz), 130.33 (s), 129.76 (s), 128.77 (s), 128.42 (d, J = 14.4 Hz), 124.77 (s), 60.70 (d, J = 5.7 Hz), 44.62 (s), 19.70 (s), 19.38 (s), 16.40 (d, J = 7.0 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.15. HRMS(ESI): $C_{17}H_{23}NO_2P$ for $[M+H]^+$, calculated 304.1466, found 304.1462.

ethyl P-phenyl-N-(2, 4, 6-trifluorobenzyl)phosphonamidate（**3aj**）



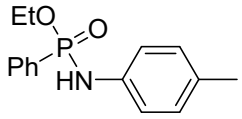
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2,4,6-trifluorobenzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (21%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.74 (dd, J = 13.0, 7.1 Hz, 2H), 7.48 (t, J = 6.9 Hz, 1H), 7.43 -7.36 (m, 2H), 6.57 (t, J = 8.1 Hz, 2H), 4.21- 3.88 (m, 4H), 3.30 (q, J = 7.7 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 162.92 (t), 162.15 (dd, J = 14.7, 11.0 Hz), 161.27 (t, J = 15.7 Hz), 160.50 (dd, J = 14.7, 11.0 Hz), 131.88 (d, J = 2.5 Hz), 131.41 (d, J = 9.9 Hz), 130.42 (d, J = 173.4 Hz), 128.36 (d, J = 14.5 Hz), 112.22 - 111.51 (m), 100.54-99.79 (m), 60.69 (d, J = 5.7 Hz), 32.36 (t, J = 2.7 Hz), 16.29 (d, J = 6.4 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 21.78. ^{19}F NMR (376 MHz, Chloroform-d) δ -108.22 (t, J = 9.3 Hz), -112.35 (t, J = 7.6 Hz). HRMS(ESI): $C_{15}H_{16}NO_2PF_3$ for $[M+H]^+$, calculated 330.0871, found 330.0874.

ethyl N,P-diphenylphosphonamidate（**3ak**）



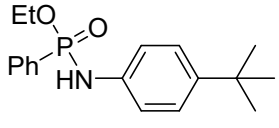
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and aniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stopthe reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (67%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 (dd, J = 13.6, 7.3 Hz,2H), 7.50 (t, J = 7.4 Hz, 1H), 7.45-7.39 (m, 2H), 7.14 (t, J = 7.8 Hz, 2H), 6.92 (s, 2H), 6.87 (t, J = 7.4 Hz, 1H), 6.34 (d, J = 5.6 Hz, 1H), 4.41-4.11 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 140.39, 132.25 (d, J = 3.0 Hz), 131.50 (d, J = 10.3 Hz), 130.26 (d, J = 177.7 Hz), 129.31 (s), 128.65 (d, J = 14.8 Hz), 121.41 (s), 117.53 (d, J = 6.7Hz), 77.16 (t), 61.03 (d, J = 6.1 Hz), 16.40 (d, J = 6.9 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.03. HRMS(ESI): $C_{14}H_{16}NO_2NaP$ for $[M+Na]^+$, calculated 284.0816, found 284.0809.

ethyl P-phenyl-N-(p-tolyl)phosphonamidate（**3al**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-methylaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), andobtain a yellow oily substance (66%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.84 (dd, J = 13.4, 7.9 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.45-7.36 (m, 2H), 7.05-6.88 (m, 3H), 6.82 (d, J = 8.1 Hz, 1H), 6.44 (d, J = 5.2 Hz, 1H), 4.35-4.24 (m, 1H), 4.21-4.09 (m, 1H), 2.21 (d, J = 3.8 Hz, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 137.69, 132.18 (t, J = 3.4 Hz), 131.50 (d, J = 10.2 Hz), 130.80 (s), 129.84 (d, J = 4.9 Hz), 129.30 (d, J = 39.0 Hz), 128.60 (d, J = 14.8 Hz), 117.60 (d, J = 6.5 Hz), 78.00-76.17 (m), 61.11-60.83 (m), 20.68 (d, J = 6.5 Hz), 16.40 (d, J = 6.9 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 20.96. HRMS(ESI): $C_{15}H_{19}NO_2P$ for $[M+H]^+$, calculated 276.1153, found 276.1145.

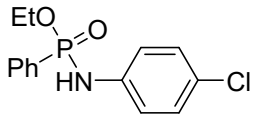
ethyl N-(4-(tert-butyl)phenyl)-P-phenylphosphonamidate（**3am**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-tertbutylaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and

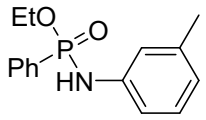
obtain a yellow oily substance (55%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.86 (dd, J = 13.5, 7.4 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.44-7.37 (m, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.12 (d, J = 5.9 Hz, 1H), 4.33-4.26 (m, 1H), 4.18-4.13 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.23 (s, 9H). ^{13}C NMR (150 MHz, Chloroform-d) δ 144.29, 137.48 (s), 132.18 (d, J = 3.0 Hz), 131.55 (d, J = 10.2 Hz), 130.48 (d, J = 177.4 Hz), 128.62 (d, J = 14.8 Hz), 126.14 (s), 117.24 (d, J = 6.5 Hz), 61.04 (s), 61.00 (s), 34.15 (s), 31.49 (s), 16.45 (s), 16.40 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 16.88. HRMS(ESI): $C_{18}H_{25}NO_2P$ for $[M+H]^+$, calculated 318.1623, found 318.1619.

ethyl N-(4-chlorophenyl)-P-phenylphosphonamidate（**3an**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-chloroaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuoussly at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (17%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.83 (dd, J = 13.5, 7.8 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.46-7.37 (m, 2H), 7.19 (d, J = 5.5 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.37-4.25 (m, 1H), 4.23-4.10 (m, 1H), 1.38 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 139.09 (s), 132.35 (d, J = 3.1 Hz), 131.32 (d, J = 10.3Hz), 130.64 (s), 129.13 (s), 128.65 (d, J = 14.9 Hz), 126.30 (s), 118.66 (d, J = 6.8 Hz), 61.03 (d, J = 6.2 Hz), 16.29 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.12. HRMS(ESI): $C_{14}H_{15}NO_2NaPCl$ for $[M+Na]^+$, calculated 318.0427, found 318.0431.

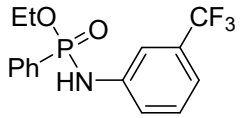
ethyl P-phenyl-N-(m-tolyl)phosphonamidate（**3ao**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 4-chloroaniline (0.75 mmol) add to the reactor Add 0.3 mmol of ethyl phenylphosphite, 0.3 mmol of pentafluorophenylboronic acid, 0.03 mmol of cuprous chloride, 0.06 mmol of bipyridine, and 0.75 mmol of 3-methylaniline to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (53%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 (dd, J = 13.5, 7.8 Hz, 2H), 7.52-7.45 (m, 1H), 7.46-7.38 (m, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.79-6.66 (m, 3H), 6.59 (s, 1H), 4.35-4.24 (m, 1H), 4.22-4.10 (m, 1H), 2.21 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 140.28 (s), 139.16 (s), 132.18 (d, J = 3.0 Hz), 131.47 (d, J = 10.3 Hz), 130.34 (d, J = 177.5 Hz), 129.08 (s), 128.59 (d, J = 14.8 Hz), 122.28 (s), 118.35 (d, J = 7.2 Hz), 114.49 (d, J = 6.1 Hz), 60.99 (d, J = 6.1 Hz), 21.53 (d, J = 2.5 Hz), 16.39 (d, J = 6.9 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.14. HRMS(ESI): $C_{15}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 298.0973, found

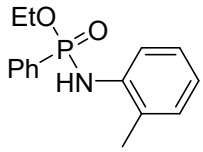
298.0983.

ethyl P-phenyl-N-(3-(trifluoromethyl)phenyl)phosphonamidate（**3ap**）



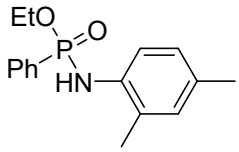
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 3-trifluoromethylaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperaturee. Distill under reduced pressure to remove the solvent, purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (26%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85 (dd, J = 13.5, 7.7 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.45-7.41 (m, 2H), 7.30 (d, J = 5.7 Hz, 1H), 7.22 (dd, J = 16.1, 8.1 Hz, 2H), 7.11 (t, J = 8.8 Hz, 1H), 4.37- 4.16 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 141.16 (s), 132.60 (d, J = 2.9 Hz), 131.49 (s), 131.43 (s), 129.82 (s), 128.86 (s), 128.76 (s), 120.66 (s), 120.62 (s), 118.00 (s), 114.12 (h), 61.42 (s), 61.38 (s), 16.36 (s), 16.32 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 16.80. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.86. HRMS(ESI): $C_{15}H_{16}NO_2PF_3$ for $[M+H]^+$, calculated 330.0871, found 330.0866.

ethyl P-phenyl-N-(o-tolyl)phosphonamidate（**3aq**）



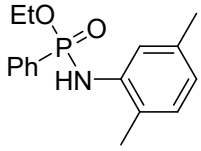
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2-methylaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (51%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.82 (dd, J = 13.5, 7.7 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.42 (d, J = 4.1 Hz, 2H), 7.09 (d, J = 7.4 Hz, 1H), 7.00 (dt, J = 15.2, 8.0 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H), 5.09 (d, J = 4.6 Hz, 1H), 4.48-3.99 (m, 2H), 2.25 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 137.03 (s), 131.20 (d, J = 3.2 Hz), 130.42, 130.35 (s), 129.60 (s), 127.59 (s), 127.49 (s), 125.96 (s), 120.79 (s), 116.19 (s), 60.08 (d, J = 6.0 Hz), 16.79 (s), 15.26 (d, J = 6.4 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 23.69. HRMS(ESI): $C_{15}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 298.0973, found 298.0982.

ethyl N-(2, 4-dimethylphenyl)-P-phenylphosphonamidate（**3ar**）



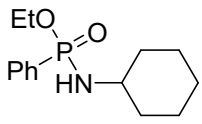
Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2,4-dimethylaniline (0.75 mmol) add to the reactor. Then, add 2 mLof solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pres-sure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (18%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (dd, J = 13.5, 7.1 Hz, 2H), 7.55 -7.46 (m, 1H), 7.46-7.37 (m, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.1 Hz,1H), 4.96 (d, J = 5.2 Hz, 1H), 4.35-4.09 (m, 2H), 2.20 (d, J = 8.2 Hz, 6H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 137.96 (s), 136.80 (s), 132.31 (d, J = 3.1 Hz), 131.57 (s), 131.51 (s), 130.49 (s), 128.70 (s), 128.60 (s), 122.72 (s), 118.19 (s), 61.27 (d, J = 5.9 Hz), 21.32 (s), 17.48 (s), 16.43 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.48. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1299.

ethyl N-(2, 5-dimethylphenyl)-P-phenylphosphonamidate**(3as)**



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2,5-dimethylaniline (0.75 mmol) add to the reactor. Then, add 2 mL of solventacetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent. Purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtaina yellow oily substance (20%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.85-7.78 (m, 2H), 7.52-7.48 (m, 1H), 7.45-7.40 (m, 2H), 6.97 (d, J = 7.6 Hz, 1H), 6.89 (s, 1H), 6.65 (d, J = 7.5 Hz, 1H), 4.99 (d, J = 5.1 Hz, 1H), 4.31-4.22 (m, 1H), 4.20-4.14 (m, 1H), 2.18 (d, J = 19.7 Hz, 6H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 137.97 (s), 136.79 (s), 132.29 (d, J = 3.0 Hz), 131.59 (s), 131.52 (s), 130.49 (s), 128.69 (s), 128.59 (s), 122.75 (s), 118.29 (d, J = 1.8 Hz), 61.27 (d, J = 5.9 Hz), 21.30 (s), 17.47 (s), 16.43 (d, J = 6.7 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.35. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1308.

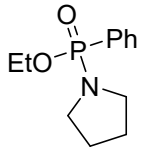
ethyl N-cyclohexyl-P-phenylphosphonamidate（**3at**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and cyclohexylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow

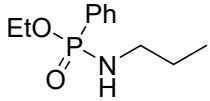
oily substance (67%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 (dd, J = 12.9, 7.6 Hz, 2H), 7.51-7.45 (m, 1H), 7.45-7.38 (m, 2H), 4.06 (p, J = 7.2 Hz, 2H), 3.03-2.87 (m, 1H), 2.66 (t, 1H), 1.81 (t, J = 12.2 Hz, 2H), 1.68-1.57 (m, 2H), 1.50 (d, J = 12.6 Hz, 1H), 1.31 (t, J = 7.0 Hz, 3H), 1.28-1.16 (m, 2H), 1.17-1.03 (m, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 131.93 (d, J = 172.2 Hz), 131.69 (d, J = 2.9 Hz), 131.53 (d, J = 9.7 Hz), 128.39 (d, J = 14.2 Hz), 60.50 (d, J = 5.5 Hz), 49.99 (s), 36.05 (dd, J = 14.0, 4.3 Hz), 25.46 (s), 25.10 (s), 16.53 (d, J = 6.9 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 21.29. HRMS(ESI): $C_{14}H_{22}NO_2NaP$ for $[M+Na]^+$, calculated 290.1286, found 290.1280.

ethyl phenyl(pyrrolidin-1-yl)phosphinate（**3au**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and tetrahydropyrrole (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (45%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.72 (dd, J = 12.5, 7.1 Hz, 2H), 7.47 (t, J = 6.9 Hz, 1H), 7.42 (dd, J = 7.5, 3.7 Hz, 2H), 4.09 (d, J = 16.3 Hz, 2H), 3.16 (d, J = 12.6 Hz, 4H), 1.78 (t, J = 6.4 Hz, 4H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 131.66-131.51 (m), 131.32 (d, J = 9.3 Hz), 129.91 (s), 128.41 (d, J = 13.9 Hz), 77.16 (t), 60.42 (d, J = 5.7 Hz), 46.59 (d, J = 4.8 Hz), 26.35 (d, J = 8.2 Hz), 16.55 (d, J = 6.7 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 21.73. HRMS(ESI): $C_{12}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 262.0973, found 262.0977.

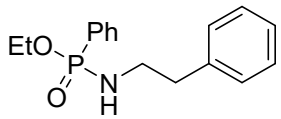
ethyl P-phenyl-N-propylphosphonamidate（**3av**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and npropylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent, purify it by silica gel chromatography, elute with PE: IPA (10:1), and obtain a yellow oily substance (64%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.78 (dd, J = 12.9, 6.9 Hz, 2H), 7.52-7.46 (m, 1H), 7.45-7.39 (m, 2H), 4.09 (p, J = 7.1 Hz, 2H), 2.87-2.68 (m, 3H), 1.44 (h, J = 6.5 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H).^{13}C NMR (150 MHz, Chloroform-d) δ 131.70 (s), 131.40 (d, J = 9.7 Hz), 130.56 (s), 128.37 (d, J = 14.3 Hz), 60.44 (d, J = 5.1 Hz), 42.73 (s), 24.98 (d, J = 6.5 Hz), 16.43 (d, J = 6.8 Hz), 11.17 . ^{31}P NMR (243 MHz, Chloroform-d) δ 22.56. HRMS(ESI): $C_{11}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 250.0973, found 250.0973.

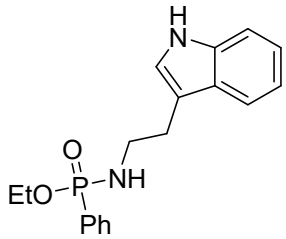
ethyl N-phenethyl-P-phenylphosphonamidate（**3aw**）

Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3



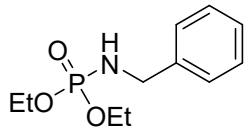
mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and 2-phenylethane-1-amine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent, purify by silica gel chromatography, Eluting with PE: IPA (10:1), and obtain a yellow oily substance (89%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (dd, J = 12.9, 7.1 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.47-7.40 (m, 2H), 7.27 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.12 (d, J = 7.2 Hz, 2H), 4.05 (dt, J = 14.2, 7.2 Hz, 2H), 3.14 (p, J = 6.9 Hz, 2H), 2.92-2.81 (m, 1H), 2.72 (t, J = 6.9 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 138.63 (s), 131.78 (d, J = 2.9 Hz), 131.40 (s), 131.33 (s), 130.97 (d, J = 172.7 Hz), 128.85 (s), 128.60 (s), 128.46 (s), 128.37 (s), 126.52 (s), 60.53 (d, J = 5.6 Hz), 42.18 (s), 37.98 (d, J = 5.9 Hz), 16.44 (d, J = 6.7 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 17.11. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1316.

ethyl N-(2-(1H-indol-3-yl)ethyl)-P-phenylphosphonamidate（**3ax**）



Ethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and tryptamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify itby silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (69%). ^{1}H NMR (600 MHz, Chloroform-d) δ 9.09 (d, J = 13.8 Hz, 1H), 7.81-7.73 (m, 2H), 7.52-7.45 (m, 2H), 7.43-7.37 (m, 2H), 7.32 (d, J = 8.2 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.90 (s, 1H), 4.13-4.01 (m, 2H), 3.26-3.13 (m, 2H), 2.95 (s, 1H), 2.88 (t, J = 6.6 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 136.72 (s), 131.88 (d, J = 3.0 Hz), 131.46 (d, J = 9.7 Hz), 131.10 (d, J = 172.8 Hz), 128.54 (d, J = 14.3 Hz), 127.26 (s), 122.78 (s), 121.92 (s), 119.18 (s), 118.56 (s), 112.04 (s), 111.60 (s), 77.21 (t), 60.66 (d, J = 5.7 Hz), 41.18 (s), 27.69 (d, J = 6.2 Hz), 16.50 (d, J = 6.8 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.59. HRMS(ESI): $C_{19}H_{21}NO_2NaP$ for $[M+Na]^+$, calculated 350.1286, found 350.1294.

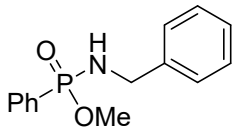
diethyl benzylphosphoramidate（**3ba**）



Diethyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at

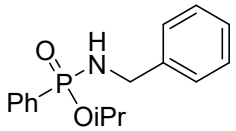
60 ℃ for 20 h. Stop the reaction and cool to room temperature. Distill under reduced pressure to remove the solvent, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (94%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.33 (d, J = 4.2 Hz, 4H), 7.28-7.24 (m, 1H), 4.11-3.98 (m, 6H), 3.22 (s, 1H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-d) δ 138.70 (d, J = 6.3 Hz), 127.49 (s), 126.28 (s), 76.27 (s), 76.07 (t), 61.30 (d, J = 5.3 Hz), 44.28 (s), 15.15 (d, J = 7.1 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 8.41. HRMS(ESI): $C_{11}H_{18}NO_2NaP$ for $[M+Na]^+$, calculated 250.0973, found 250.0973.

methyl N-benzyl-P-phenylphosphonamidate（**3ca**）



Methyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (51%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.86-7.75 (m, 2H), 7.51 (t, J = 8.1 Hz, 1H), 7.44 (dd, J = 7.7, 3.9 Hz, 2H), 7.30-7.19 (m, 5H), 4.14-3.94 (m, 2H), 3.69 (d, J = 11.1 Hz, 3H), 3.43 (d, J = 8.1 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 139.63 (d, J = 6.5 Hz), 132.07 (d, J = 2.5 Hz), 131.60 (d, J = 9.7 Hz), 131.21 (s), 129.49 (s), 128.67 (s), 128.53 (s), 127.74-127.25 (m), 77.16 (t), 51.43 (d, J = 5.9 Hz), 44.99 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 23.81. HRMS(ESI): $C_{14}H_{17}NO_2P$ for $[M+H]^+$, calculated 262.0997, found 262.0989.

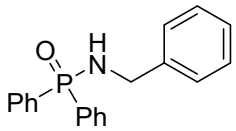
isopropyl N-benzyl-P-phenylphosphonamidate（**3da**）



Isopropyl phenylphosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (51%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 (dd, J = 12.8, 8.0 Hz, 2H), 7.49-7.44 (m, 1H), 7.43-7.37 (m, 2H), 7.27-7.21 (m, 4H), 7.21-7.17 (m, 1H), 4.78-4.68 (m, 1H), 4.03 (s, 2H), 3.37 (s, 1H), 1.29 (dd, J = 10.8, 6.3 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-d) δ 139.85 (d, J = 7.0 Hz), 131.71 (d, J = 2.9 Hz), 131.56(d, J = 9.8 Hz), 128.54 (s), 128.44 (s), 128.34 (s), 127.43 (s), 127.25 (s), 79.23-73.56 (m), 69.57 (d, J = 5.7 Hz), 44.95 (s), 24.24 (dd, J = 4.2, 1.9 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.17. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1302.

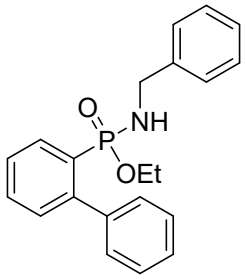
N-benzyl-P,P-diphenylphosphinic amide（**3ea**）

Diphenyl oxyphosphate (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3



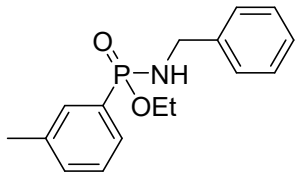
mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment andstir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation and purify it by silica gel chromatography. Eluting with PE: IPA (10:1) to obtain a yellow oily substance (60%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.93 (dd, J =11.9, 7.1 Hz,4H), 7.49 (t, J = 7.3 Hz, 2H), 7.43 (td, J = 7.4, 3.2 Hz, 4H), 7.35 (d, J =7.4 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (d, J = 4.6 Hz, 1H), 4.12 (t, J=7.4 Hz, 2H), 3.15 (d, J =5.7 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ 132.17 (d, J = 9.5 Hz), 132.15 (d, J =129.4 Hz), 131.99 (d, J = 2.3 Hz), 128.63 (d, J = 13.3 Hz), 127.73 (s), 127.47 (s), 44.70 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 24.30. HRMS(ESI): $C_{19}H_{19}NO_2P$ for $[M+H]^+$, calculated 324.1153, found 324.1141.

ethyl P-([1, 1'-biphenyl]-2-yl)-N-benzylphosphonamidate（**3fa**）



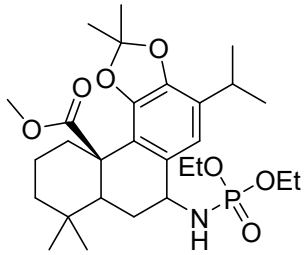
[1,1'-biphenyl]-2-ylphosphonate ethyl ester (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment at 60 ℃ and stir continuously for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (33%). ^{1}H NMR (600 MHz, Chloroform-d) δ 8.03 (dd, J = 13.7, 7.7 Hz, 1H), 7.46 (t, J = 7.2 Hz, 1H), 7.40-7.31 (m, 3H), 7.27 (d, J = 4.8 Hz, 3H), 7.22 (t, 1H), 7.19-7.08 (m, 3H), 6.96 (d, J = 7.3 Hz, 2H), 4.00-3.89 (m, 1H), 3.89-3.78 (m, 1H), 3.66 (qt, J = 14.8, 7.8 Hz, 2H), 2.08-1.99 (m, 1H), 1.09 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 145.19 (d, J = 10.7 Hz), 141.60 (d, J = 4.4 Hz), 139.66 (d, J = 6.8 Hz), 133.50 (d, J = 8.6 Hz), 131.52 (d, J = 2.8 Hz), 131.14 (d, J = 13.3 Hz), 130.64 (s), 129.39 (s), 128.95 (s), 128.48 (s), 127.85 (d, J = 6.1 Hz), 127.44 (s), 127.21 (d, J = 2.2 Hz), 127.07 (s), 77.16 (t), 60.30 (d, J = 6.1 Hz), 44.97 (s), 16.27 (d, J =7.0 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 29.37. HRMS(ESI): $C_{21}H_{22}NO_2NaP$ for $[M+Na]^+$, calculated 374.1286, found 374.1290.

ethyl N-benzyl-P-(m-tolyl)phosphonamidate（**3ga**）



3-methylphenylethyl phosphite (0.3 mmol), selenium (0.3 mmol), pentafluorophenylboronic acid (0.3 mmol), cuprous chloride (0.03 mmol), bipyridine (0.06 mmol), and benzylamine (0.75 mmol) add to the reactor. Then, add 2 mL of solvent acetonitrile in an air environment and stir continuously at 60 ℃ for 20 h. Stop the reaction and cool to room temperature. Remove the solvent by vacuum distillation, purify it by silica gel chromatography, Eluting it with PE: IPA (10:1), and obtain a yellow oily substance (66%). ^{1}H NMR (600 MHz, Chloroform-d) δ 7.79 (dd, J = 13.7, 7.8 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.25 - 7.21 (m, 2H), 7.18 (d, J = 6.3 Hz, 5H), 4.17 - 3.89 (m, 4H), 3.03 (d, J = 7.5 Hz, 1H), 2.55 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 141.71 (d, J = 10.8 Hz), 139.68 (d, J = 6.6 Hz), 133.22 (d, J = 9.6 Hz), 131.96 (d, J = 2.4 Hz), 131.40 (d, J = 14.0 Hz), 129.53 (s), 128.56 (s), 128.40 (s), 127.38 (d, J = 20.4 Hz), 125.37 (d, J = 13.8 Hz), 60.50 (d, J = 5.4 Hz), 44.91 (s), 21.31 (d, J = 3.7 Hz), 16.36 (d, J = 6.6 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.37. HRMS(ESI): $C_{16}H_{21}NO_2P$ for $[M+H]^+$, calculated 290.1310, found 290.1316.

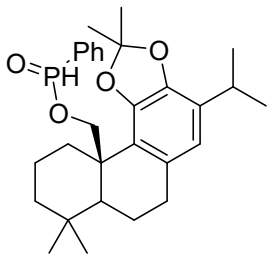
methyl (11aR)-6-((diethoxyphosphoryl)amino)-4-isopropyl-2, 2, 8, 8-tetramethyl-7, 7a, 8, 9, 10, 11-hexahydrophenanthro[3, 4-d][1, 3]dioxole-11a(6H)-carboxylate（**3bz**）



^{1}H NMR (600 MHz, Chloroform-d) δ 7.07 (s, 1H), 4.29 (p, J = 10.4 Hz, 1H), 4.20-4.12 (m, 4H), 3.60 (s, 3H), 3.34 (d, J = 13.5 Hz, 1H), 2.92 (p, J = 6.9 Hz, 1H), 2.80 (t, J = 11.6 Hz, 1H), 2.37 (q, J = 12.8 Hz, 1H), 2.22 (dd, J = 12.1, 6.2 Hz, 1H), 2.06-1.99 (m, 1H), 1.79 (s, 1H), 1.64 (s, 3H), 1.54 (s, 3H), 1.46 (d, J = 13.2 Hz, 1H), 1.36 (td, J = 7.0, 2.5 Hz, 6H), 1.28-1.23 (m, 3H), 1.20 (t, 6H), 0.96 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 174.88 (s), 144.15 (s), 143.65 (s), 132.08 (d, J = 8.2 Hz), 128.62 (s), 121.66 (s), 118.55 (s), 116.76 (s), 62.46 (dd, J = 7.9, 5.7 Hz), 52.53 (s), 52.09 (s), 51.56 (s), 47.05 (s), 41.52 (s), 33.86 (s), 33.60 (s), 32.16 (s), 29.68 (d, J = 5.5 Hz), 28.56 (s), 25.69 (s), 25.63 (s), 22.08 (s), 21.99 (s), 19.98 (s), 19.86 (s), 16.35 (dd, J = 7.3, 3.7 Hz). ^{31}P NMR (243 MHz, Chloroform-d) δ 8.43. HRMS(ESI): $C_{28}H_{44}NO_7NaP$ for $[M+Na]^+$, calculated 560.2753, found 560.2758.

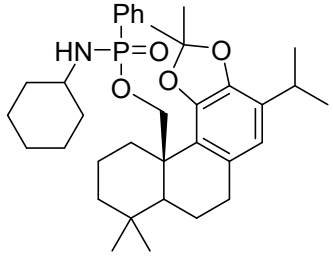
((11aR)-4-isopropyl-2,2,8,8-tetramethyl-7,7a,8,9,10,11-hexahydrophenanthro[3,4-d][1,3]dioxol-11a(6H)-yl)methyl phenylphosphinate **(1h)**

^{1}H NMR (600 MHz, Chloroform-d) δ 7.66 (d, J = 69.3 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.51 – 7.41 (m, 1H), 7.42 – 7.32 (m, 2H), 7.32 – 7.28 (m, 1H), 6.72 (d, J = 63.3 Hz, 1H), 6.45 (d, J = 4.2 Hz, 1H), 4.55 – 4.36 (m, 2H), 3.03 – 2.92 (m, 2H), 2.91 – 2.76 (m, 1H), 2.76 – 2.63 (m, 1H), 1.87 (s, 1H), 1.73 – 1.70 (m, 1H), 1.65 – 1.56 (m, 3H), 1.55 – 1.48 (m, 5H), 1.47 – 1.37 (m, 1H), 1.35 – 1.26



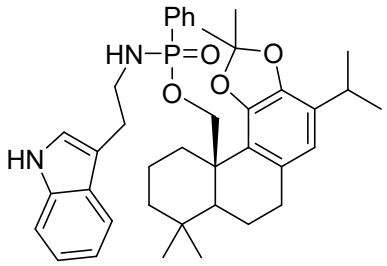
(m, 1H), 1.26 – 1.19 (m, 7H), 1.09 – 0.79 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-d) δ 144.78 (s), 144.39 (s), 144.00 (s), 132.97 (d, J = 2.8 Hz), 132.87 (d, J = 2.7 Hz), 131.21 (s), 131.08 (s), 131.00 (s), 128.77 (s), 128.64 (d, J = 11.8 Hz), 128.51 (s), 127.59 (s), 126.46 (s), 125.18 (d, J = 27.5 Hz), 123.67 (s), 118.81 (s), 116.17 (d, J = 4.4 Hz), 51.39 (s), 50.47 (s), 41.34 (s), 34.05 (s), 33.64 (d, J = 2.3 Hz), 33.56 (s), 33.46 (s), 30.39 (s), 29.78 (s), 29.42 (s), 28.45 (s), 26.03 (s), 25.86 (s), 25.44 (d, J = 9.9 Hz), 22.43 (s), 22.18 (d, J = 6.2 Hz), 20.57 (d, J = 8.8 Hz), 19.11 (s), 19.01 (d, J = 1.9 Hz), 18.74 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 26.20 , 24.84 . HRMS(ESI): $C_{29}H_{39}O_4NaP$ for $[M+Na]^+$, calculated 505.2484, found 505.2488.

((11aR)-4-isopropyl-2, 2, 8, 8-tetramethyl-7, 7a, 8, 9, 10, 11-hexahydrophenanthro[3, 4-d][1, 3]diox-ol-11a(6H)-yl)methyl N-cyclohexyl-P-phenylphosphonamidate（**3ht**）



^{1}H NMR (600 MHz, Chloroform-d) δ 7.57-7.54 (m, 1H), 7.49-7.36 (m, 2H), 7.34-7.28 (m, 2H), 6.45 (d, J = 16.4 Hz, 1H), 4.44-4.36 (m, 1H), 4.34-4.24 (m, 1H), 3.02-2.89 (m, 3H), 2.85-2.74 (m, 2H), 1.94-1.73 (m, 4H), 1.66 (d, J = 12.6 Hz, 2H), 1.60-1.50 (m, 6H), 1.49-1.46 (m, 4H), 1.37-1.29 (m, 3H), 1.28-1.21 (m, 7H), 1.21-0.98 (m, 3H), 0.95 (d, J = 7.1 Hz, 4H), 0.92-0.81 (m, 4H). ^{13}C NMR (150 MHz, Chloroform-d) δ 144.92 (s), 144.74 (s), 142.54 (s), 131.45 (d, J = 2.3 Hz), 131.39 (d, J = 2.3 Hz), 131.23 (t, J = 3.0 Hz), 129.67 (s), 128.07 (d, J = 4.3 Hz), 128.02-127.85 (m), 124.78 (s), 118.69 (d, J = 11.9 Hz), 115.57 (s), 66.89 (d, J = 6.1 Hz), 66.36 (d), 51.00 (s), 50.86 (s), 49.66 (s), 42.13 (d, J = 7.3 Hz), 41.92 (d, J = 7.5 Hz), 41.59 (d, J = 2.8 Hz), 36.06 (s), 35.92 (d, J = 3.8 Hz), 33.78 (s), 33.53 (d, J = 6.4 Hz), 33.38 (d, J = 4.4 Hz), 33.23 (s), 29.70 (d, J = 3.6 Hz), 29.60 (s), 28.42 (s), 28.34 (s), 25.89 (s), 25.57 (s), 25.40 (s), 25.36 (d, J = 2.3 Hz), 25.32 (s), 25.07 (s), 22.44 (s), 22.31 (s), 22.13 (s), 22.10 (s), 22.03 (s), 19.05 (s), 18.78 (s), 18.72 (s). ^{31}P NMR (243 MHz, Chloroform-d) δ 21.25, 20.83. HRMS(ESI): $C_{35}H_{50}NO_4NaP$ for $[M+Na]^+$, calculated 602.3375, found 602.3380.

((11aR)-4-isopropyl-2, 2, 8, 8-tetramethyl-7, 7a, 8, 9, 10, 11-hexahydrophenanthro[3,4-d][1, 3]diox--ol-11a(6H)-yl)methyl N-(2-(3a, 7a-dihydro-1H-indol-3-yl)ethyl)-P-phenylph-osphonamidate（**3hy**）

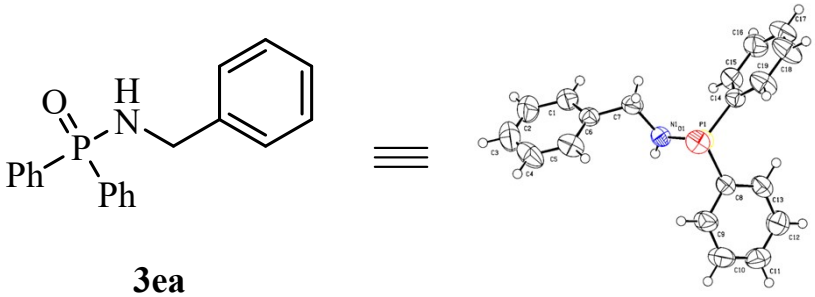


3hy

^{1}H NMR (600 MHz, Chloroform-d) δ 8.60 (d, J = 11.6 Hz, 1H), 7.48 (dd, J = 13.6, 7.5 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.35 – 7.27 (m, 3H), 7.18 – 7.13 (m, 1H), 7.06 (dd, J = 7.1 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.46 (d, J = 11.8 Hz, 1H), 4.49 – 4.33 (m, 2H), 3.04 – 2.77 (m, 6H), 2.68 (d, J = 7.1 Hz, 2H), 2.47 (d, J = 69.7 Hz, 1H), 1.92 – 1.58 (m, 4H), 1.51 (d, J = 12.1 Hz, 5H), 1.41 (s, 2H), 1.25 (dd, J = 12.6, 7.1 Hz, 9H), 0.94 (d, J = 8.9 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-d) δ 145.02 (s), 144.86 (s), 142.64 (d, J = 4.8 Hz), 136.57 (s), 131.62-131.45 (m), 131.41 (s), 131.35 (s), 130.26 (s), 129.90 (s), 128.31 (s), 128.22 (s), 128.14 (s), 128.05 (s), 127.25 (s), 124.76 (s), 124.53 (s), 122.44 (s), 122.05 (d, J = 3.1 Hz), 119.29 (s), 118.90-118.58 (m), 115.74 (d, J = 2.0 Hz), 112.40 (s), 111.41 (s), 66.88 (d, J = 6.2 Hz), 66.68 (d, J = 6.2 Hz), 51.18 (s), 51.07 (s), 42.08 (dd, J = 12.7, 7.7 Hz), 41.67 (d, J = 2.3 Hz), 40.76 (s), 40.48 (s), 34.00 (s), 33.65 (d, J = 4.4 Hz), 33.51 (t, J = 3.0 Hz), 29.95 (s), 29.81 (d, J = 6.0 Hz), 28.62-28.44 (m), 27.72 (d, J = 5.9 Hz), 27.62 (d, J = 6.3 Hz), 25.86-25.72 (m), 25.64 (s), 25.50 (d, J = 5.5 Hz), 22.50 (s), 22.36 (d, J = 3.8 Hz), 22.20 (s), 19.18 (s), 19.04-18.88 (m). ^{31}P NMR (243 MHz, Chloroform-d) δ 22.81 (d, J = 5.7 Hz), 22.24 (d, J = 6.5 Hz). HRMS(ESI): $C_{39}H_{52}N_2O_4P$ for $[M+H]^+$, calculated 643.3665, found 643.3664.

8. X-ray Crystallographic Data

The single crystal is obtained by adding dichloromethane and evaporating it statically. A suitable crystal was selectedand collected on a SuperNova, Dual, Cu at zero, Eos difiractometer. The supplementary crystallographic data of CCDC 2344192 can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. Displacement ellipsoids are drawn at the 50% probability level.



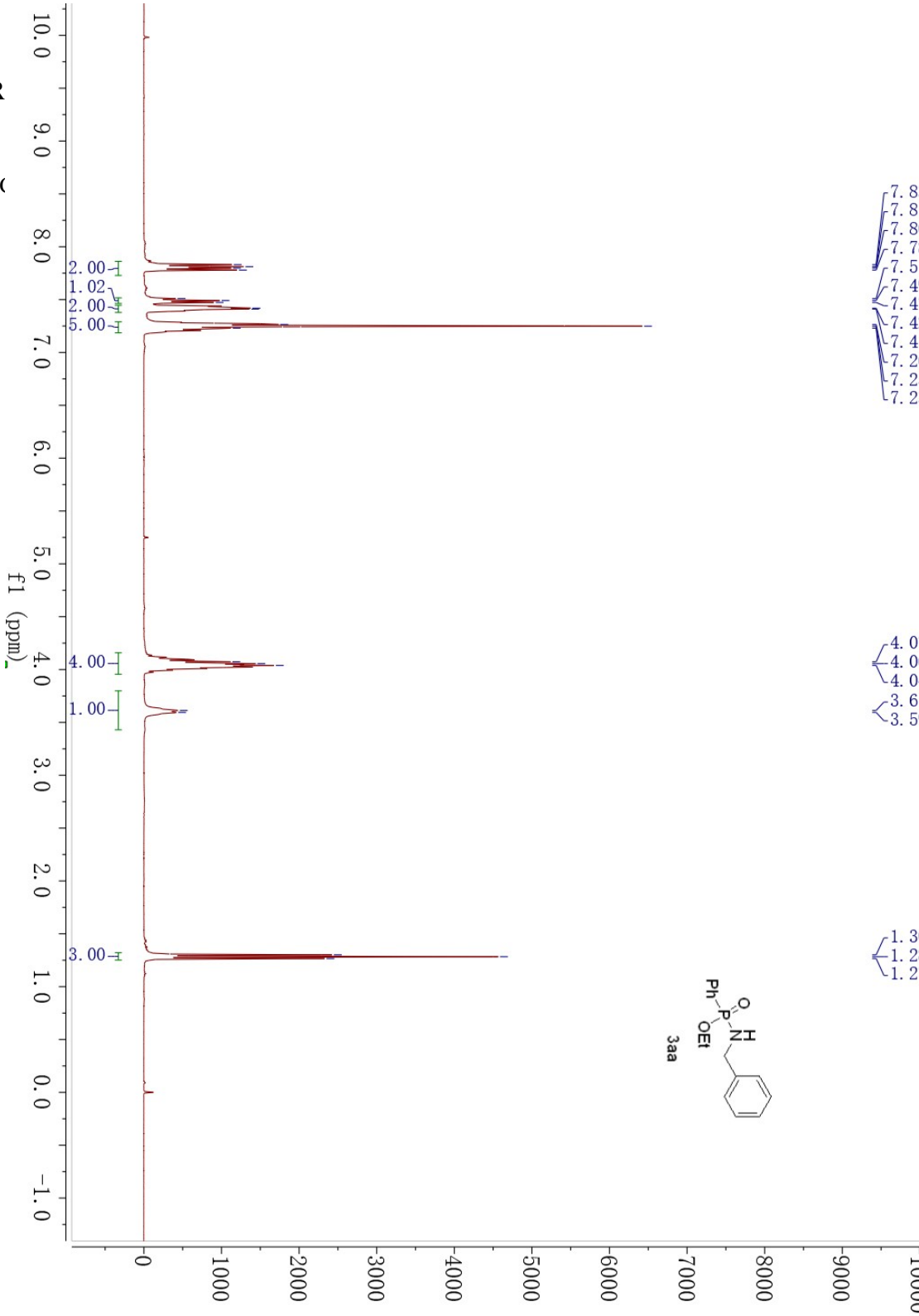
3ea

CCDC: 2344192

Identification code	1_a
Empirical formula	$C_{19}H_{18}NOP$
Formula weight	307.31
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.4323(18)
b/Å	15.080(2)
c/Å	10.6793(16)
α/°	90
β/°	116.703(4)
γ/°	90
Volume/Å^3	1644.8(4)
Z	4
ρcalcg/cm^3	1.241
μ/mm-1	0.168
F(000)	648.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.816 to 50.094
Index ranges	$-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-12 \leq l \leq 12$
Reflections collected	24691
Independent reflections	2898 [R_{int} = 0.0685, R_{sigma} = 0.0484]
Data/restraints/parameters	2898/0/199
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0531, wR_2 = 0.1284
Final R indexes [all data]	R_1 = 0.0948, wR_2 = 0.1625
Largest diff. peak/hole / e Å^{-3}	0.38/-0.51

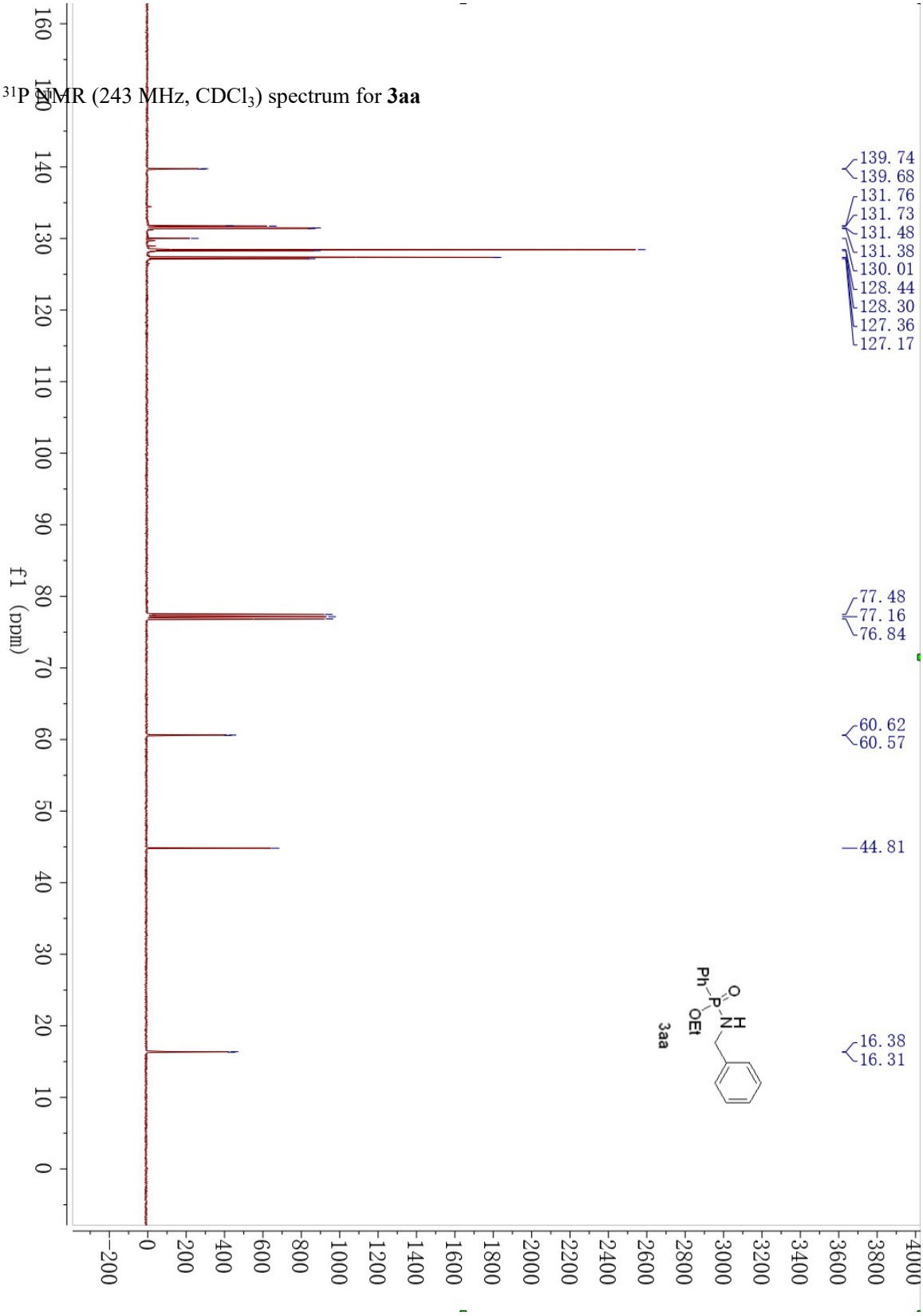
9. Copies of NMR

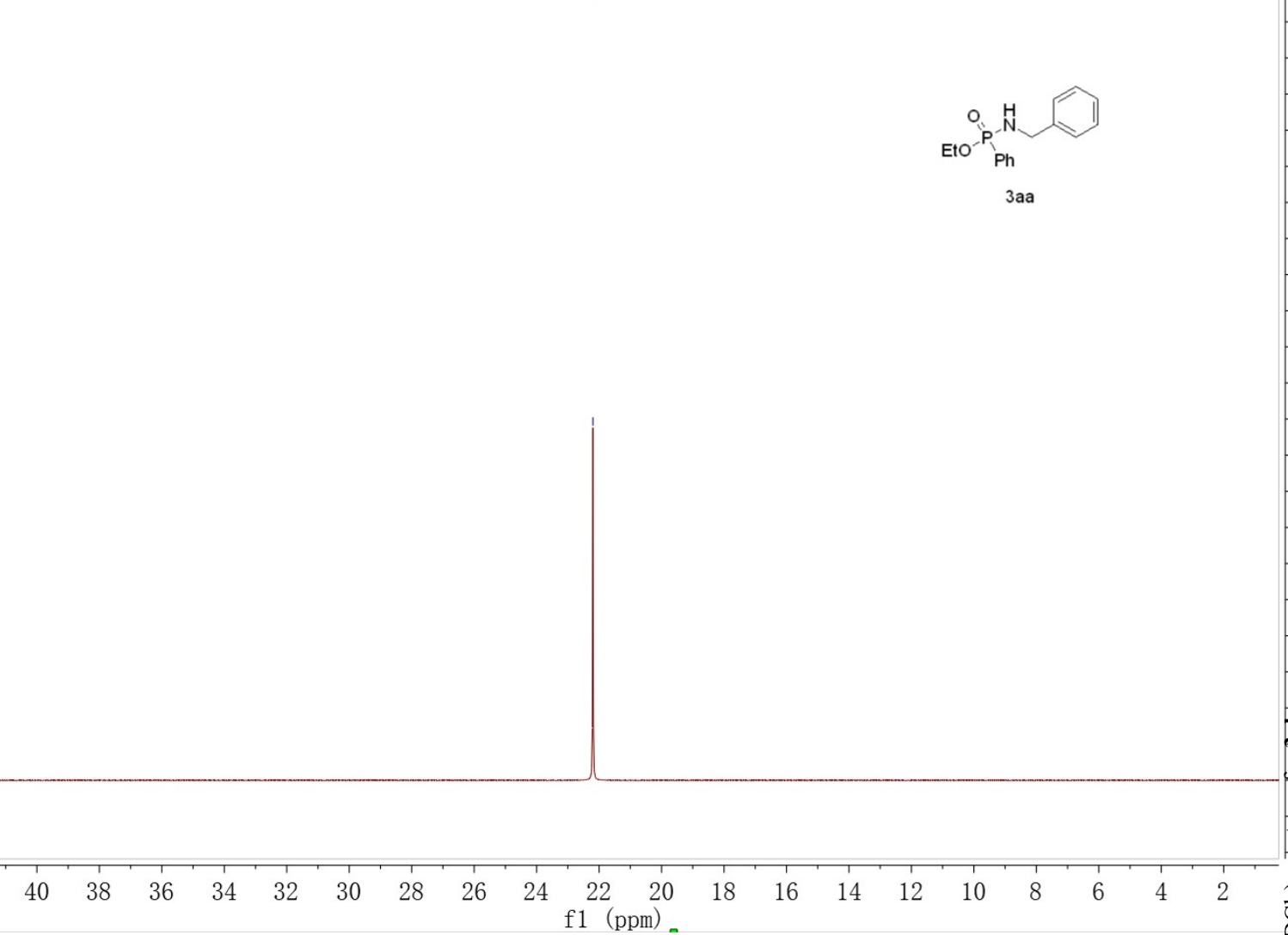
^{1}H NMR (600 MHz, C

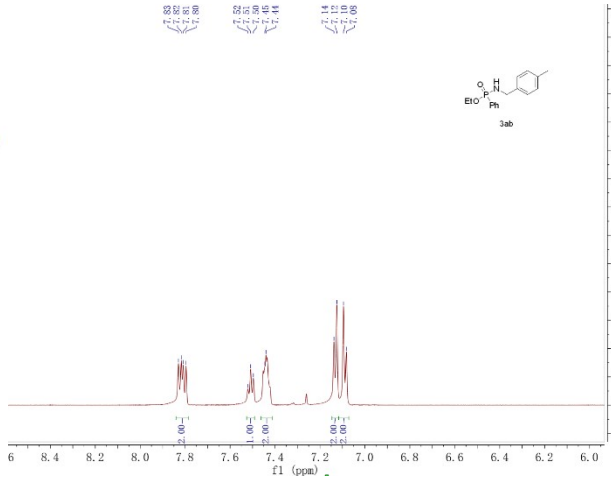


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3aa**

^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3aa**

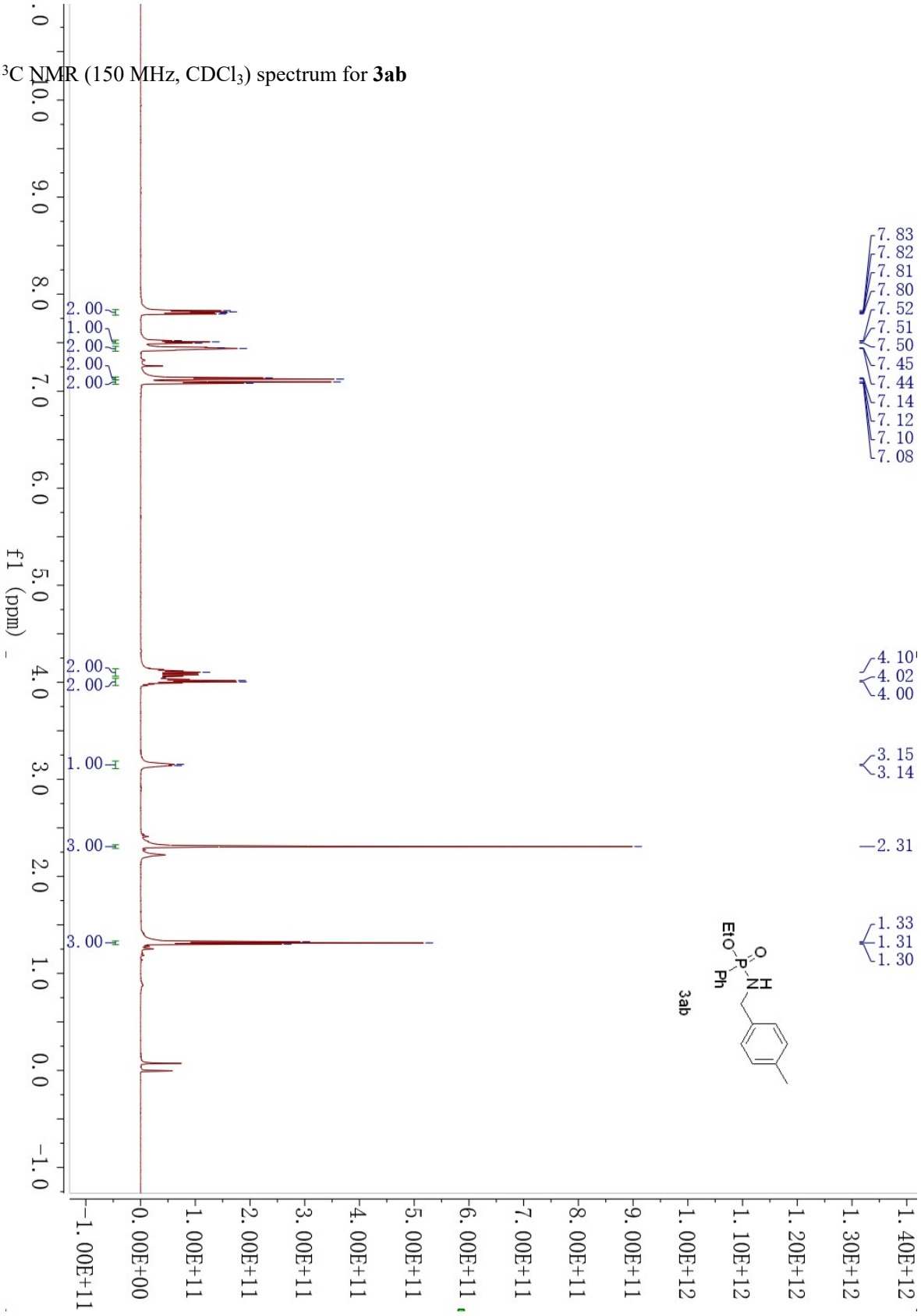


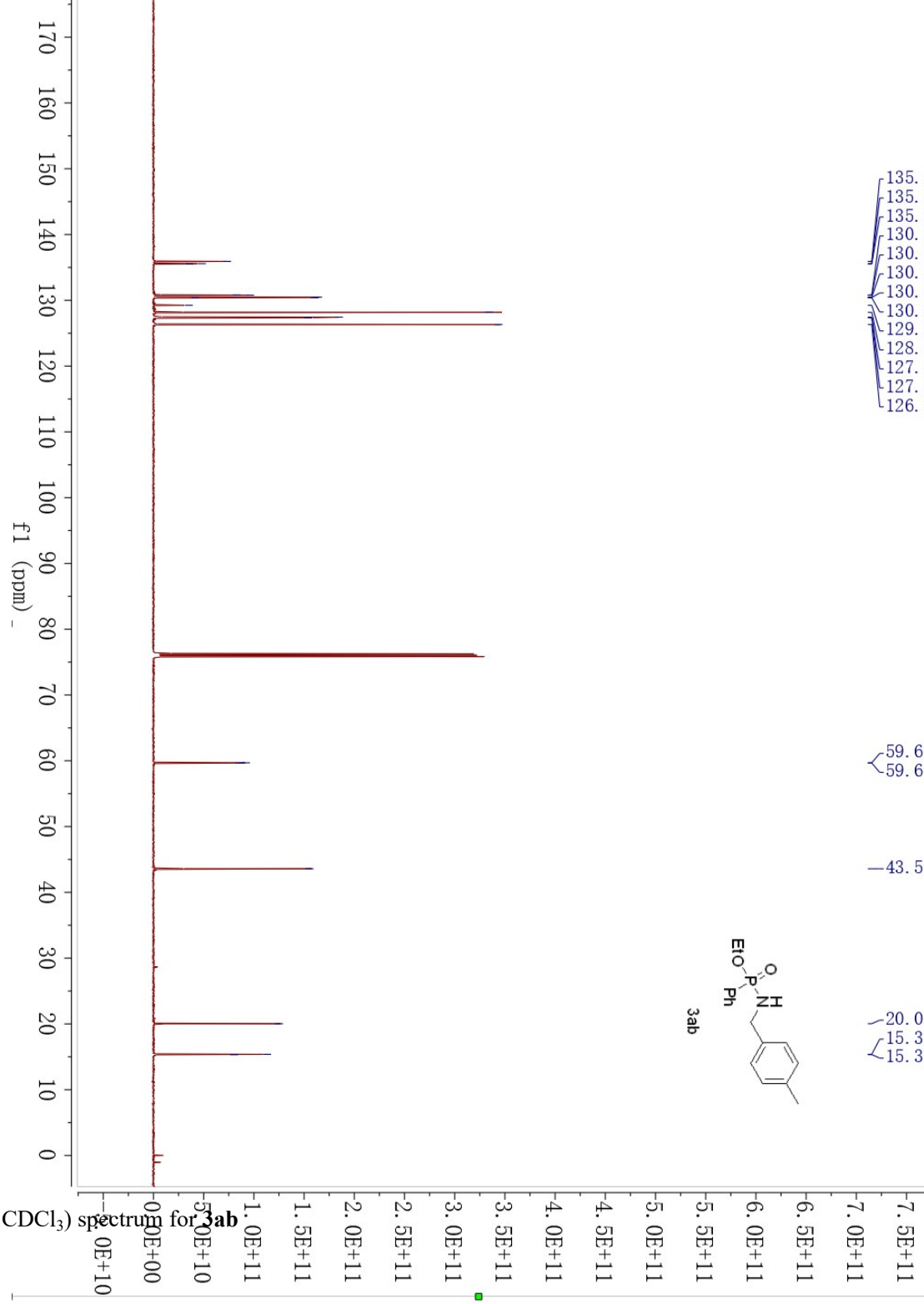




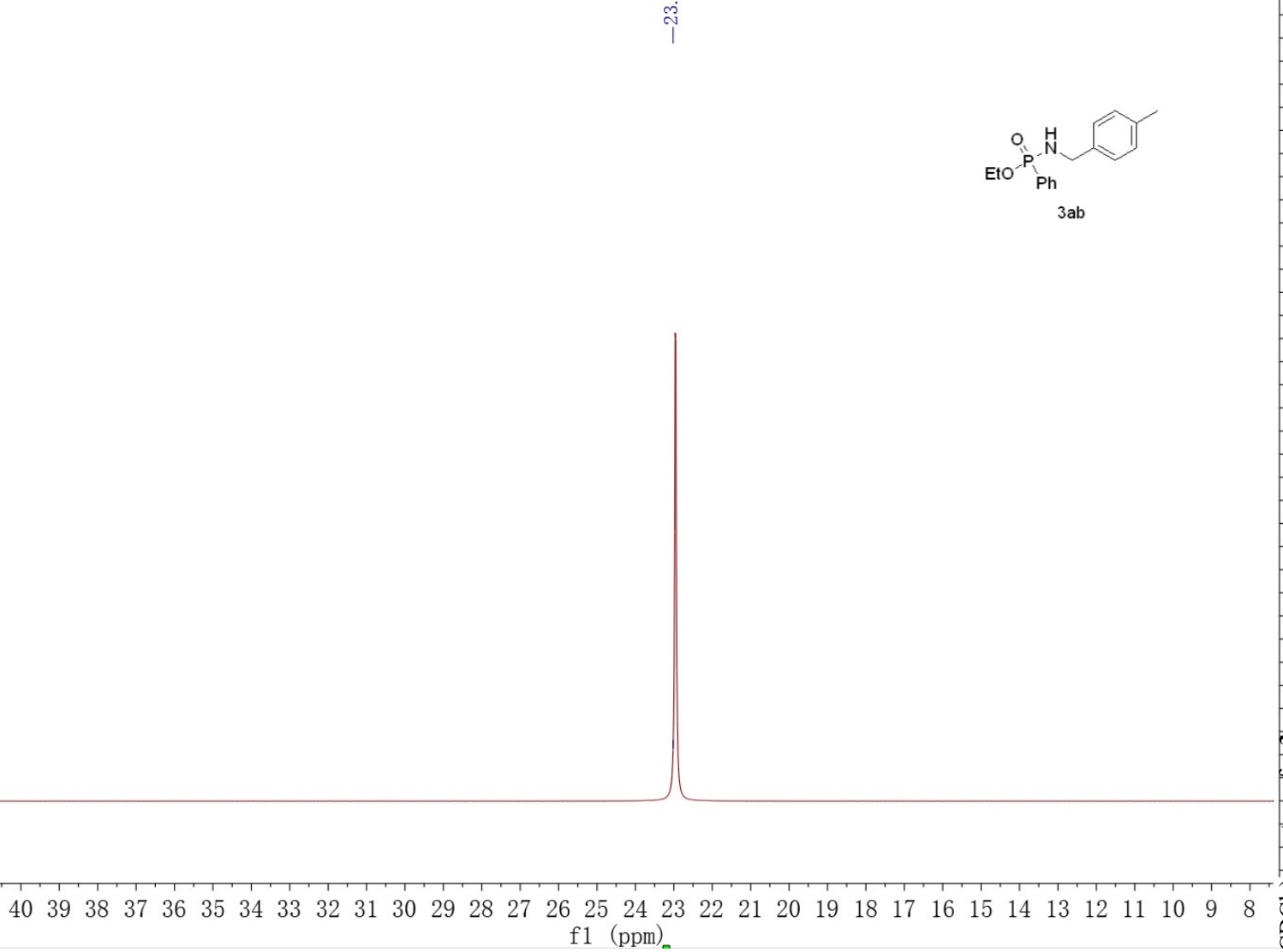
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ab**

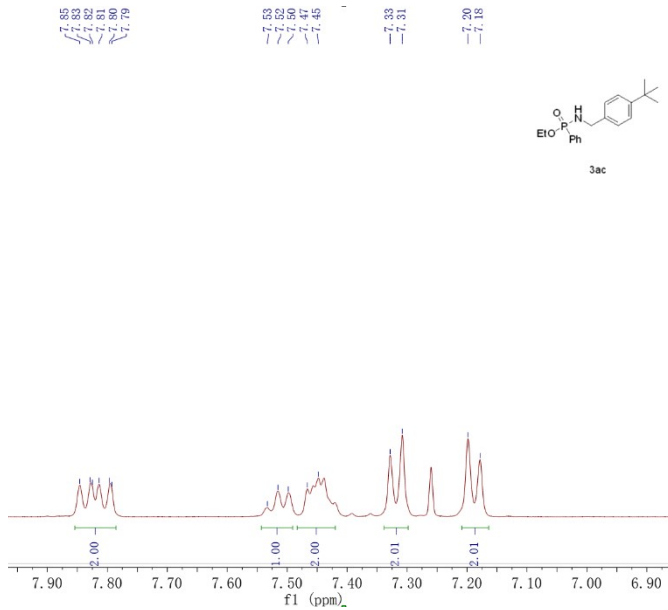
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ab**





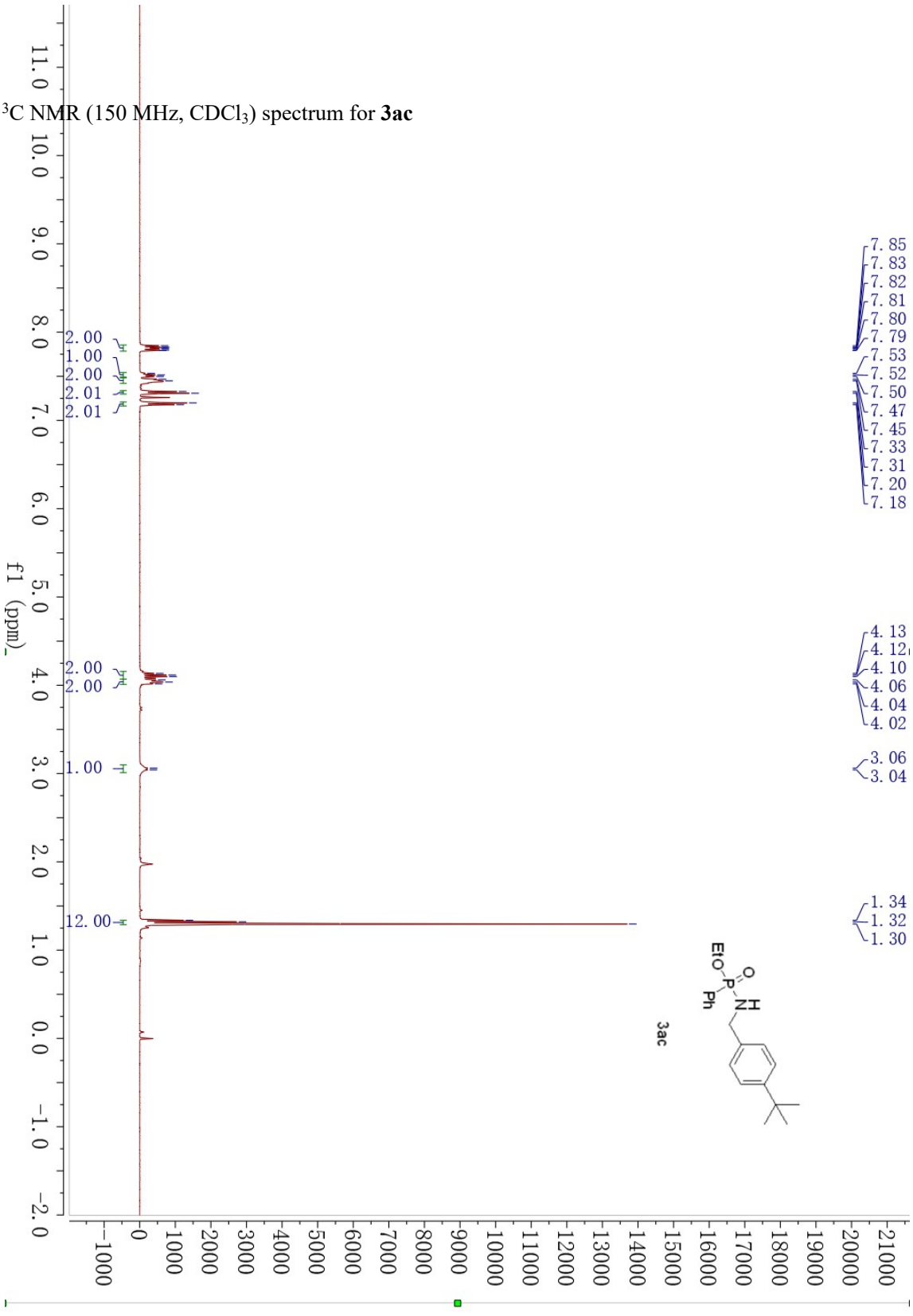
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ab**

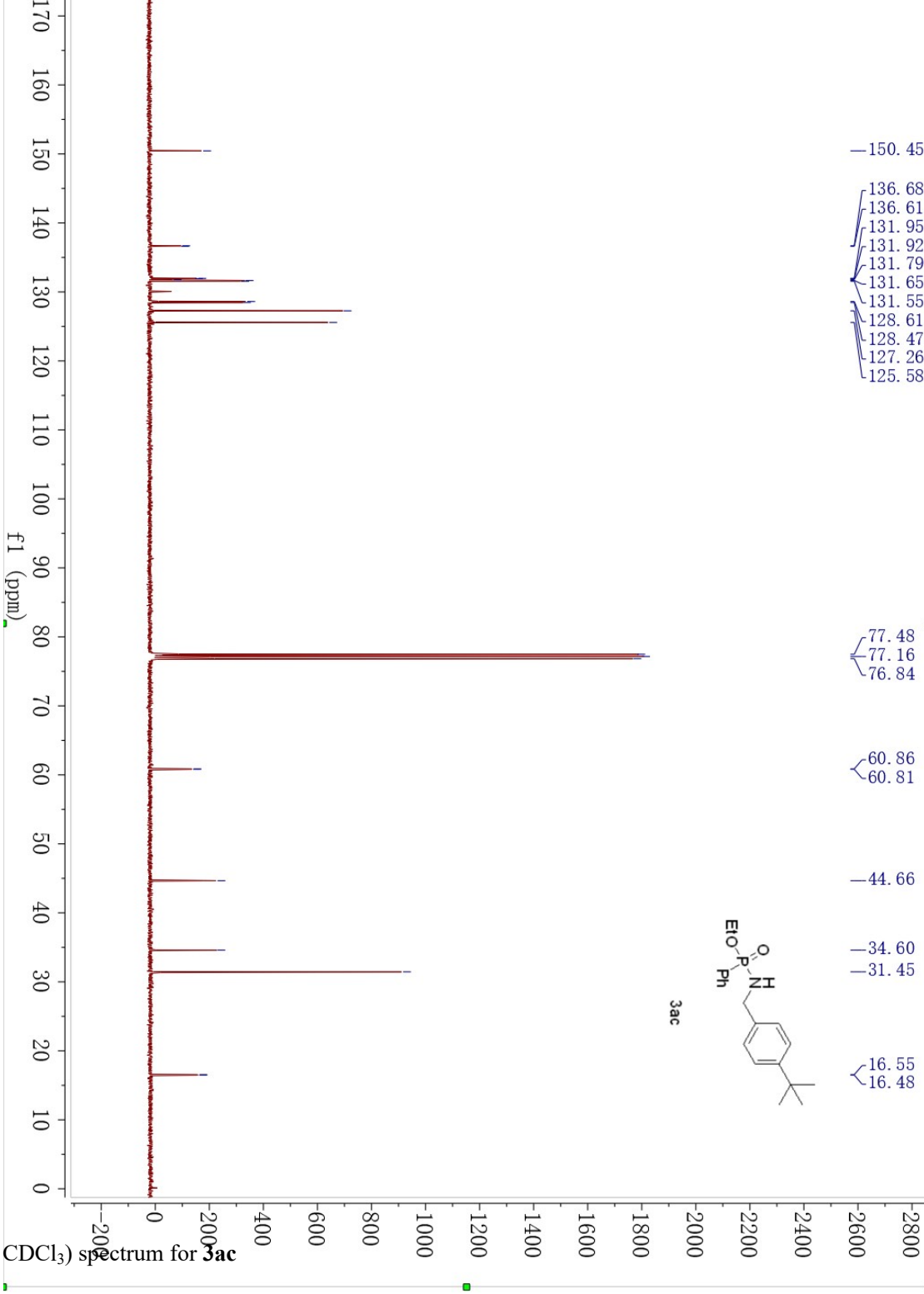




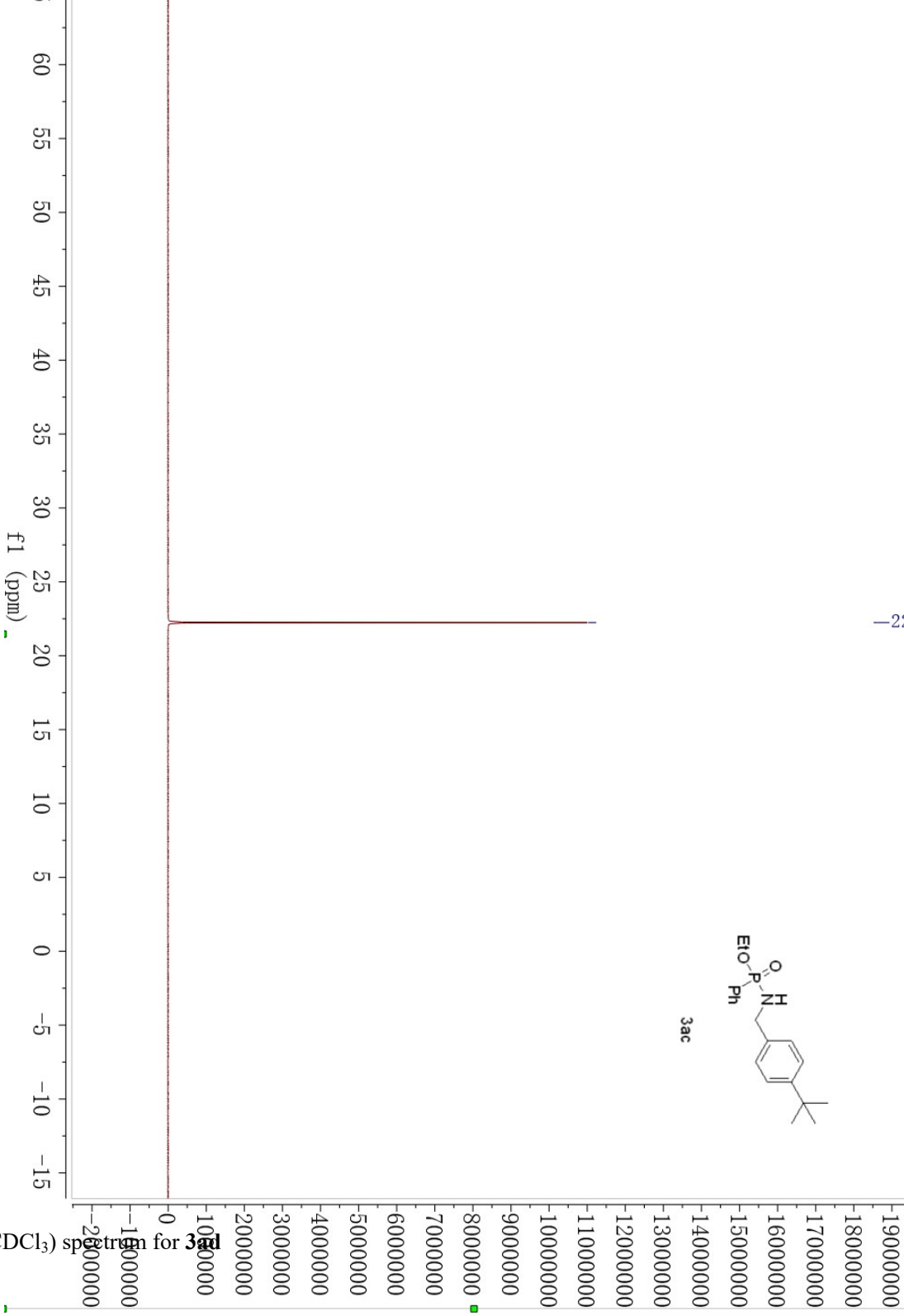
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ac**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ac**

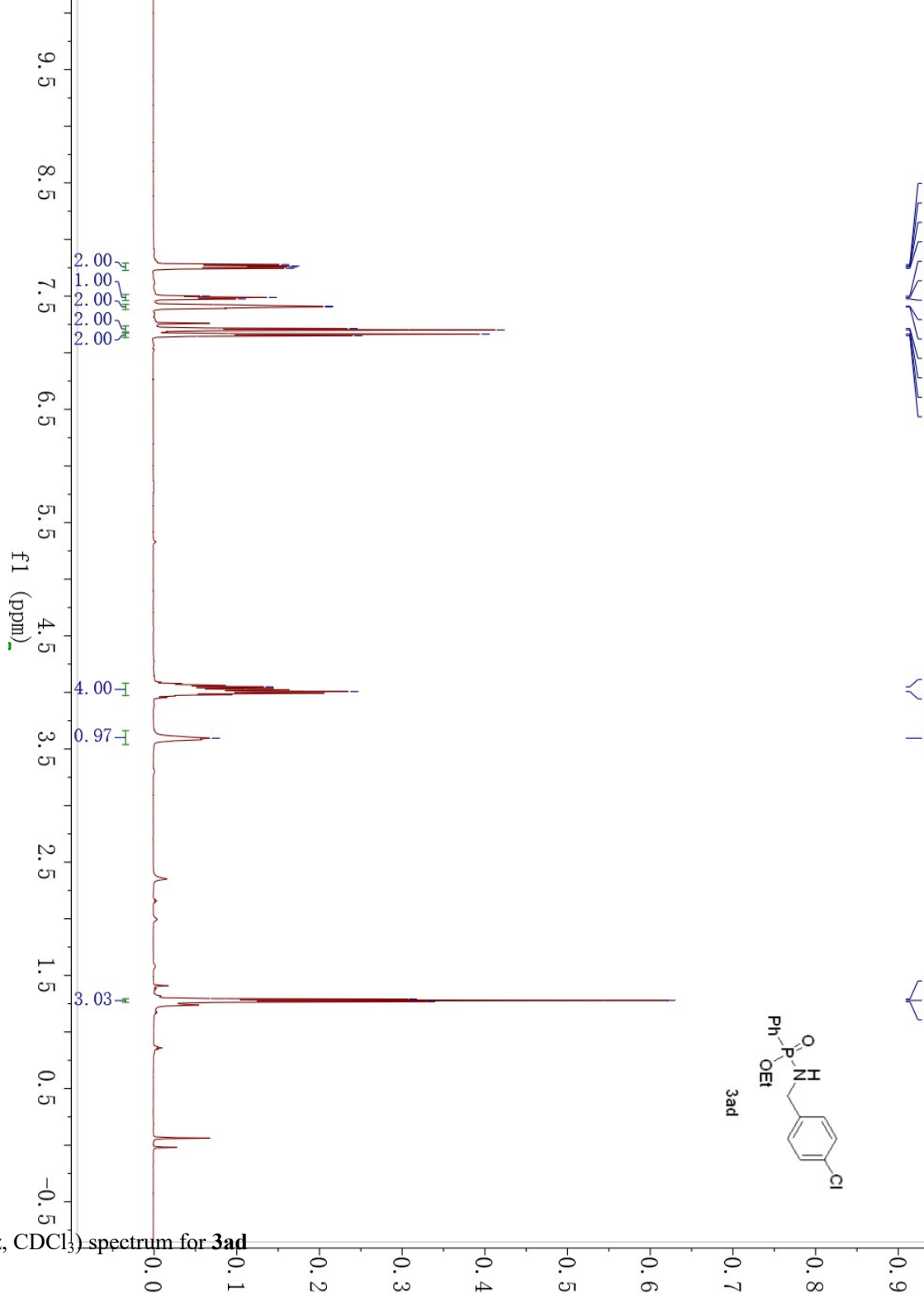




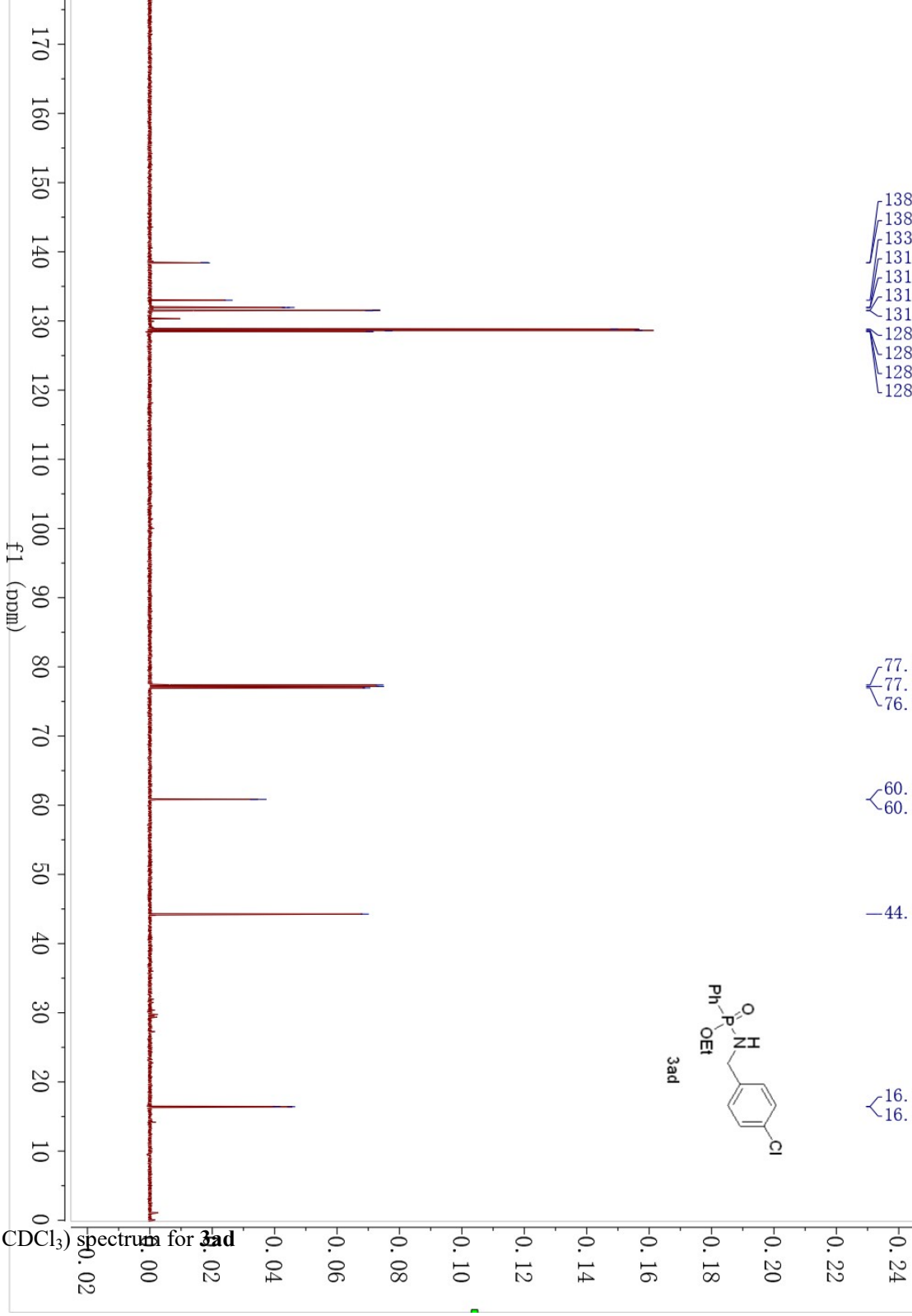
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ac**



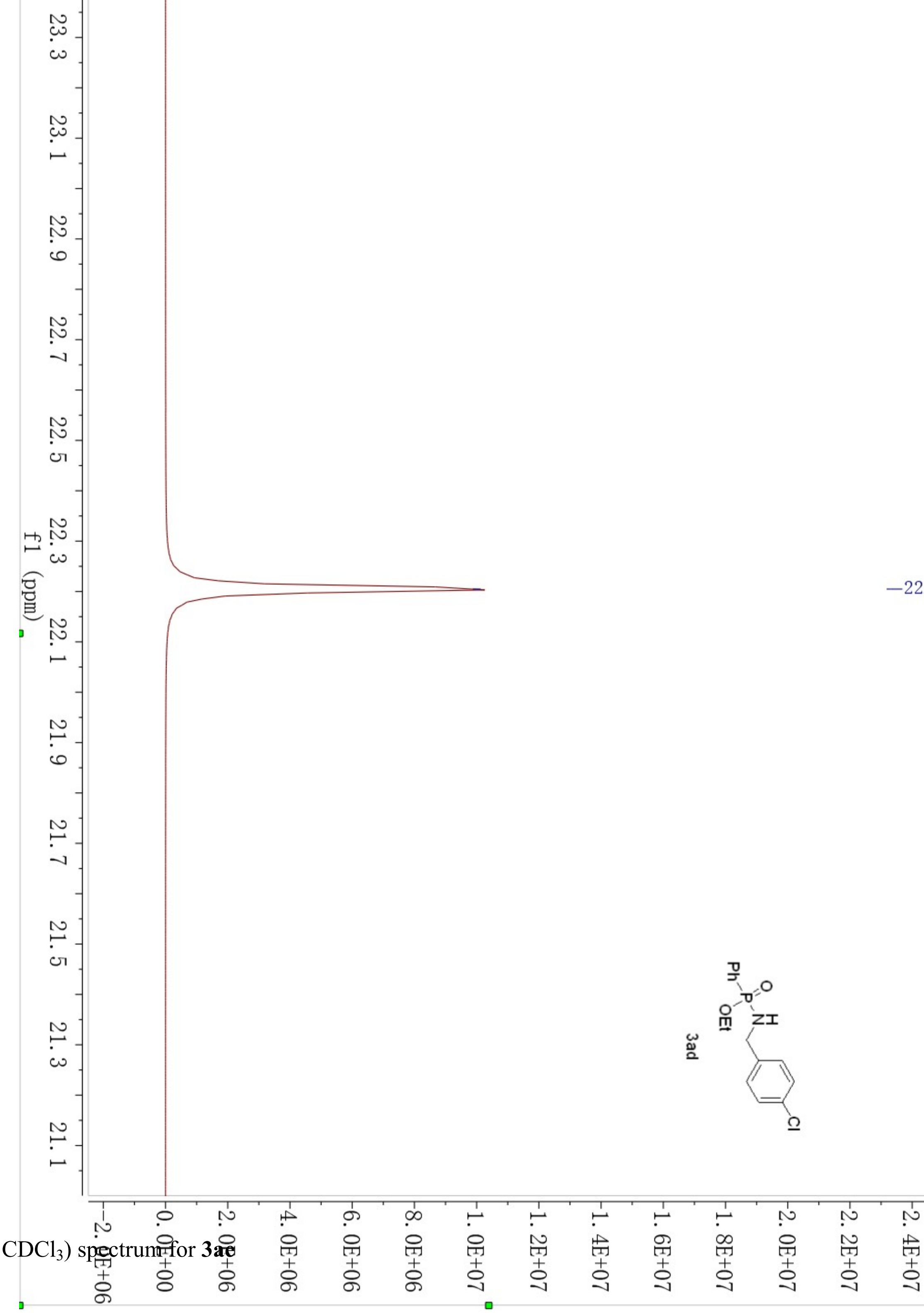
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ad**



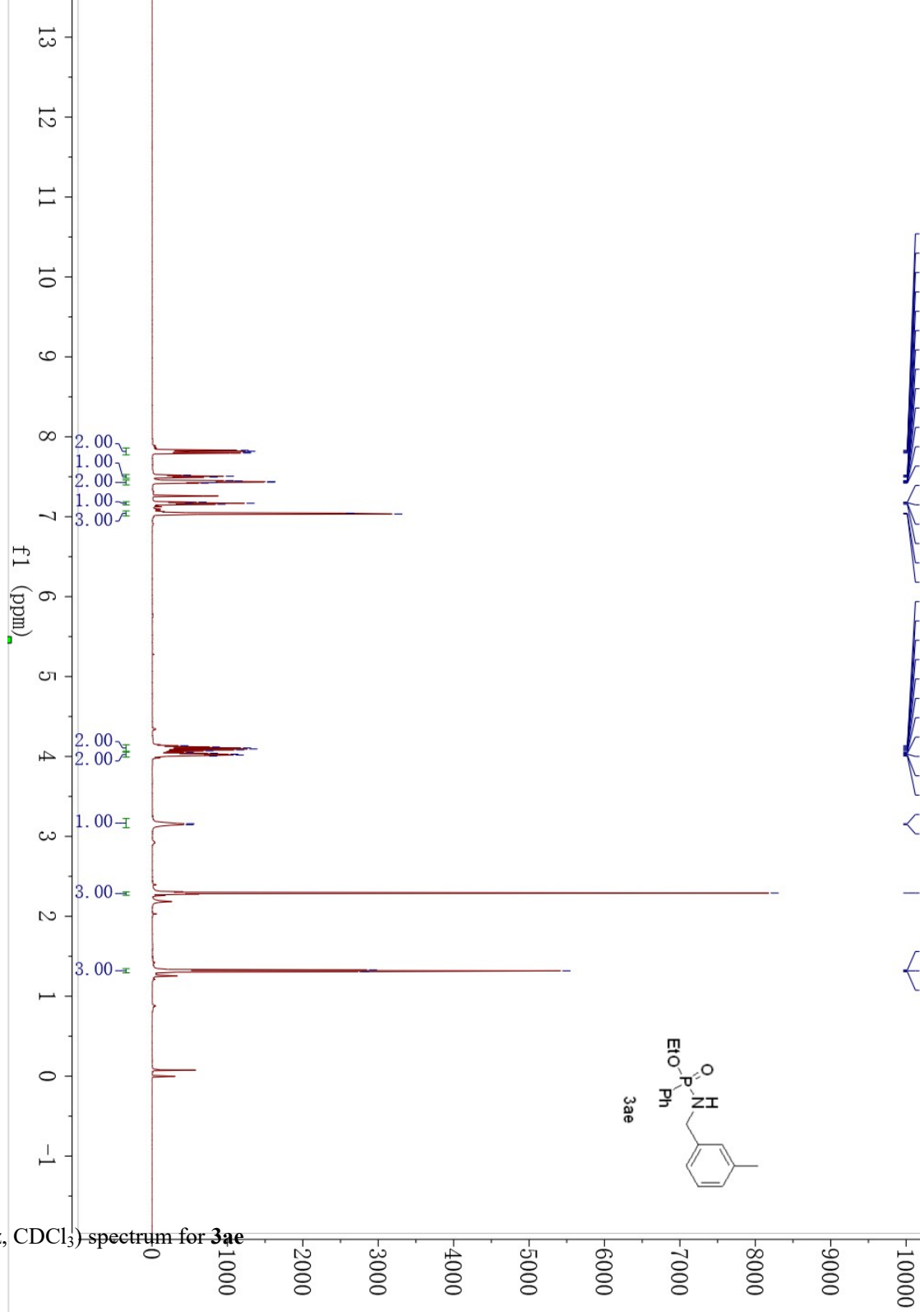
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ad**



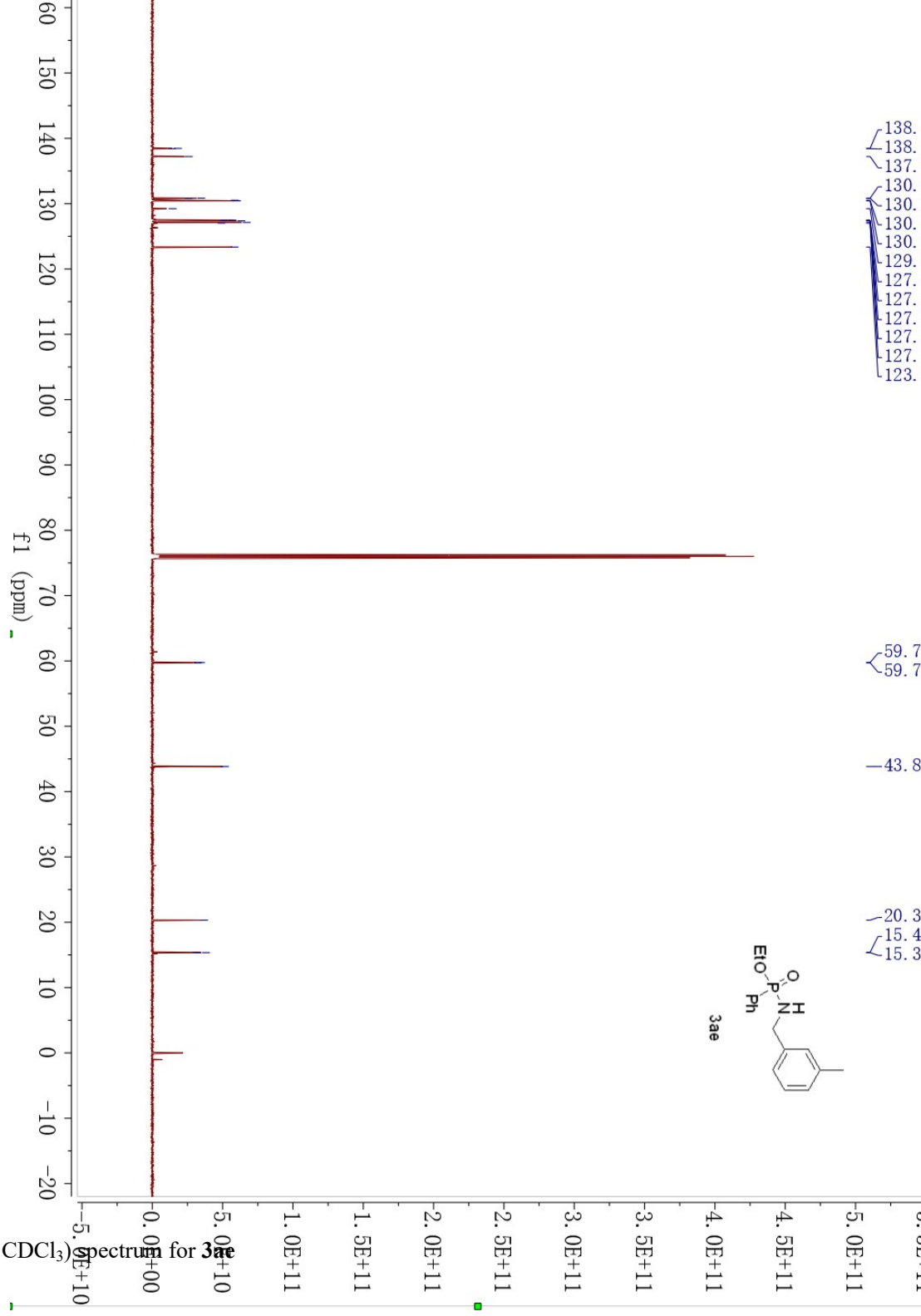
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ad**



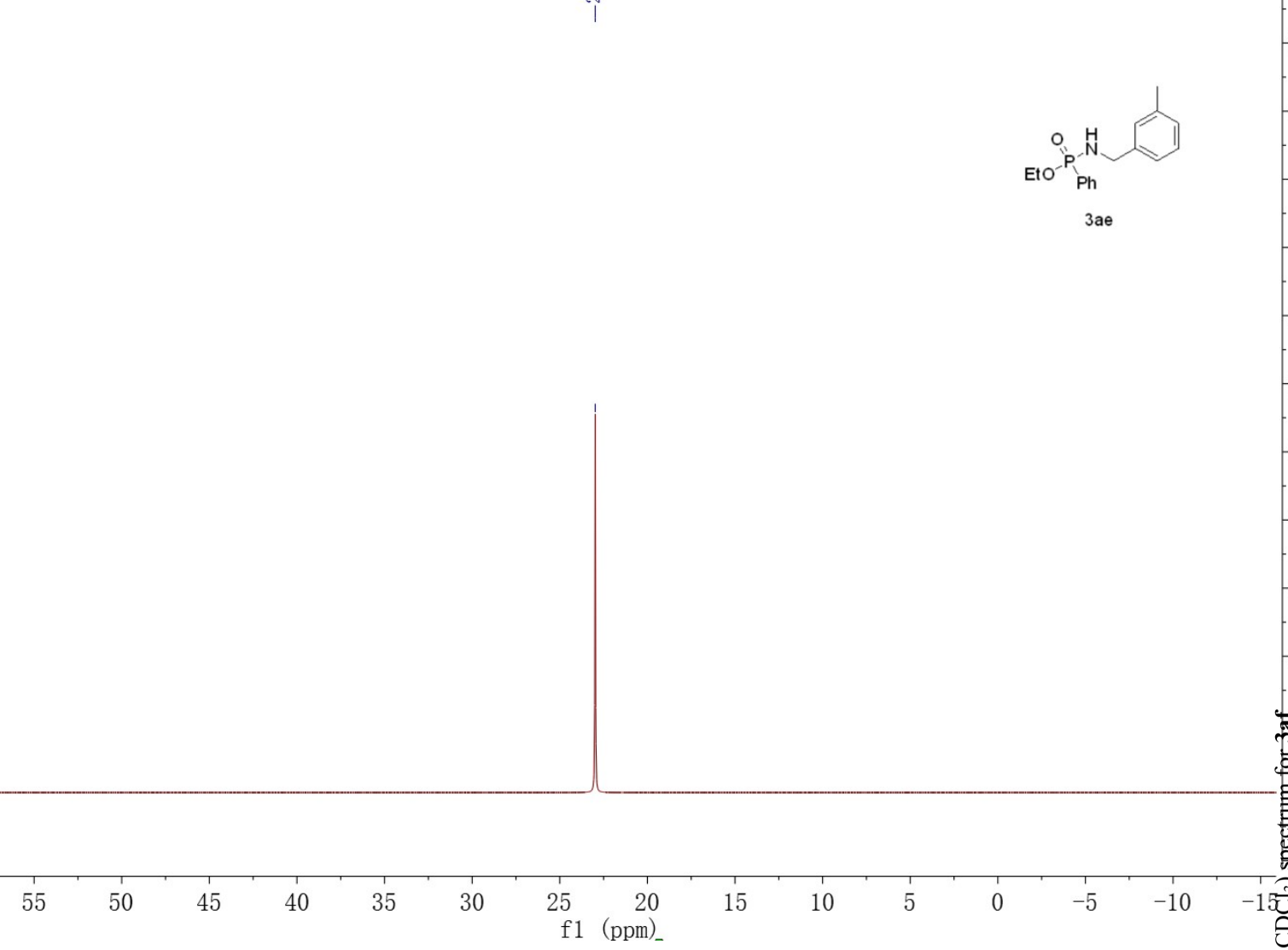
[1]H NMR (600 MHz, $CDCl_3$) spectrum for **3ae**

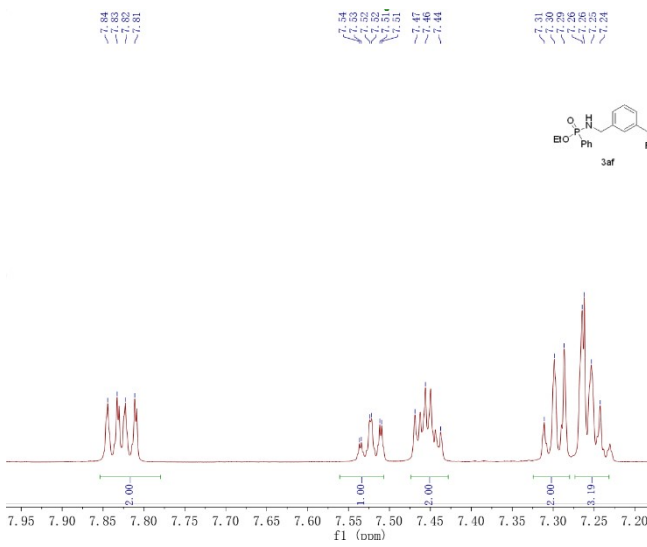


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ae**



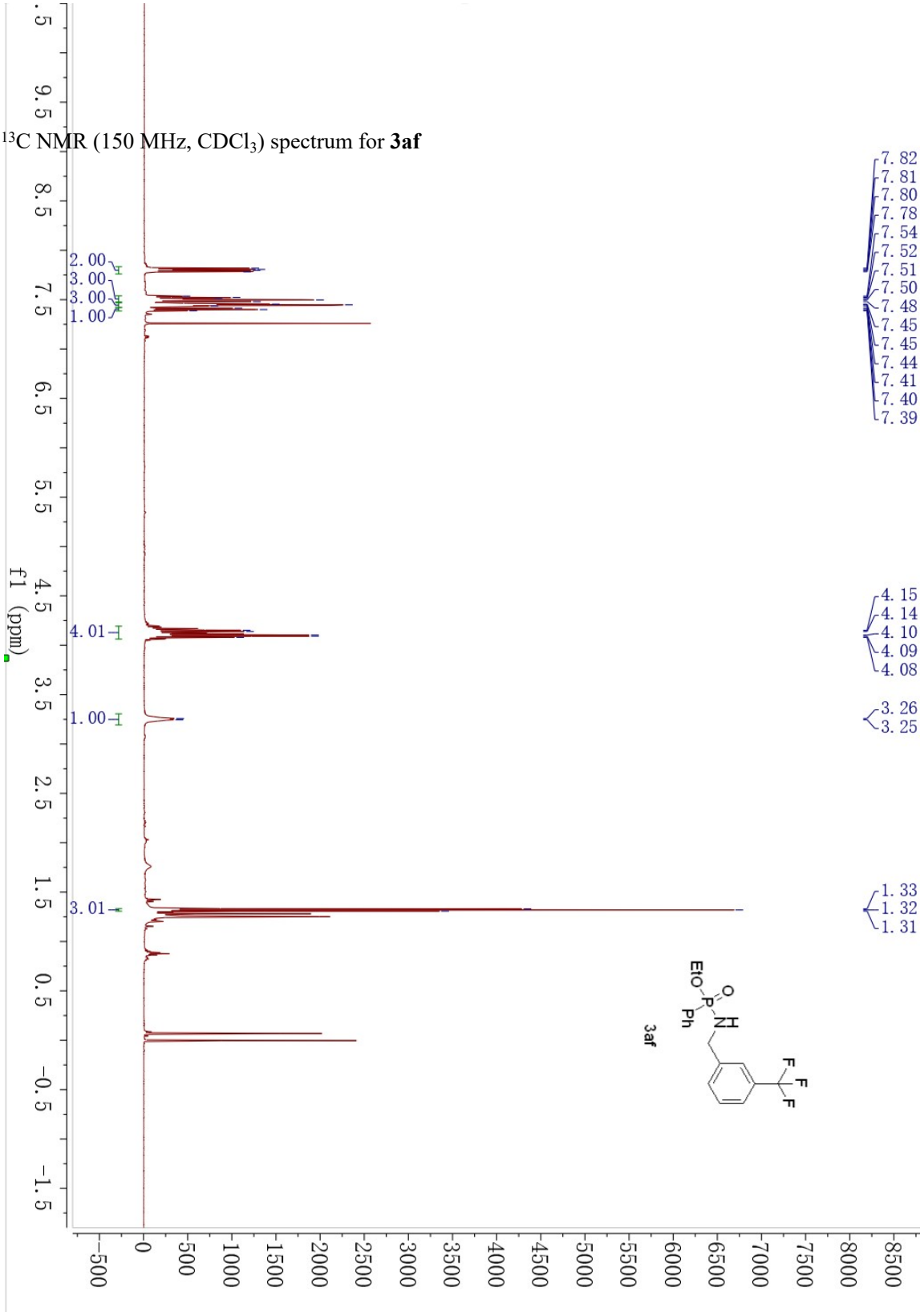
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ae**

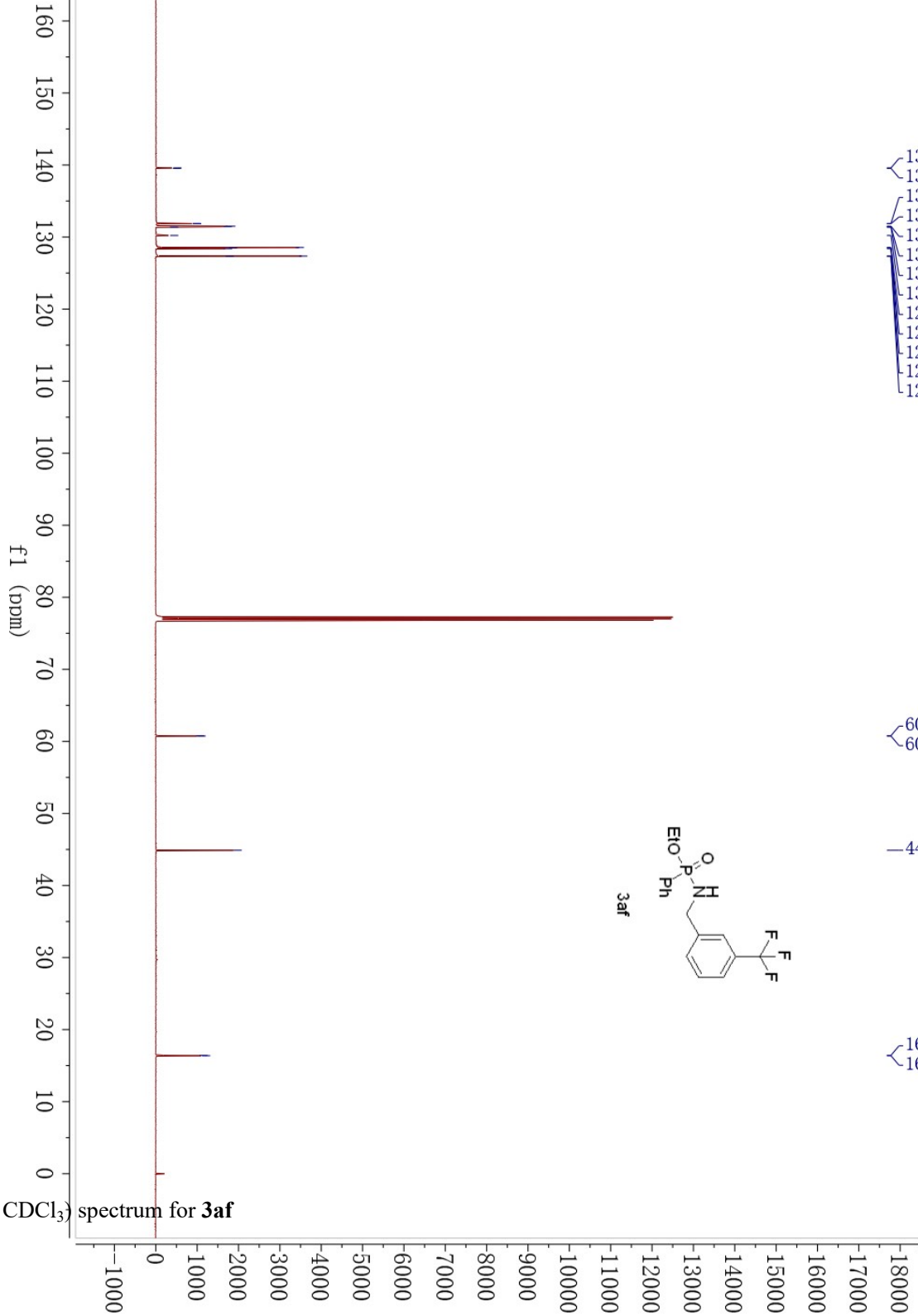




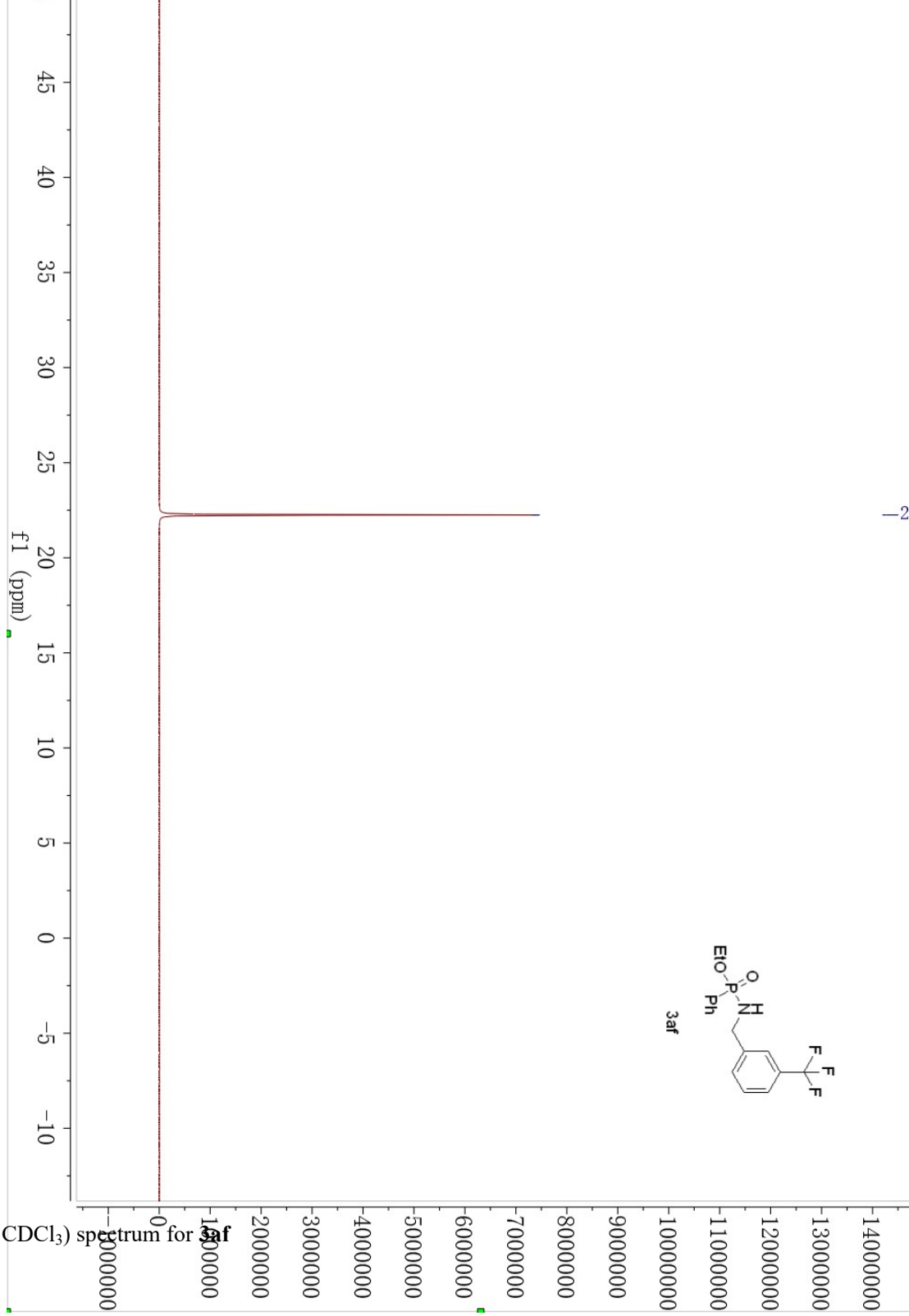
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3af**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3af**

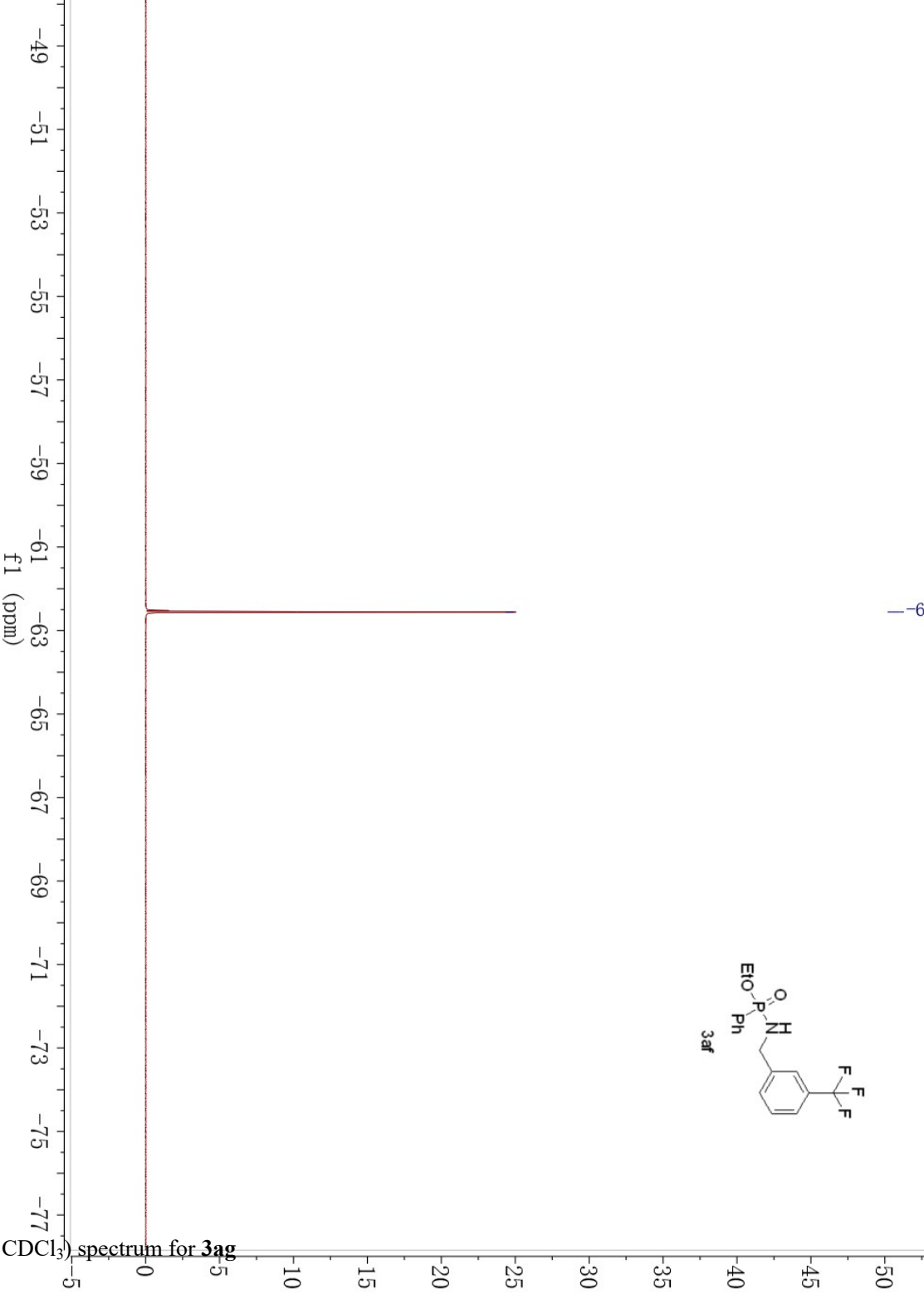




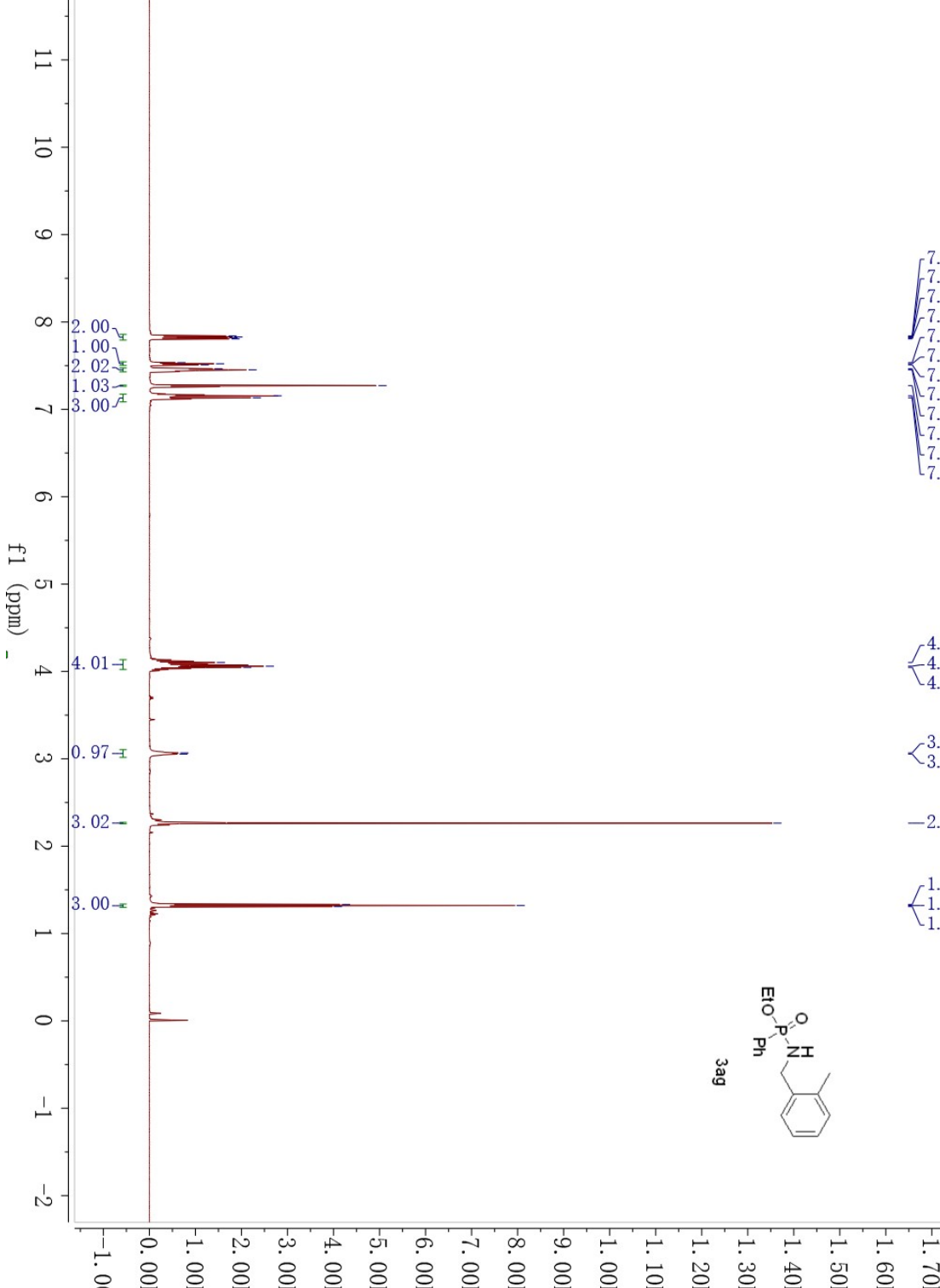
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3af**



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

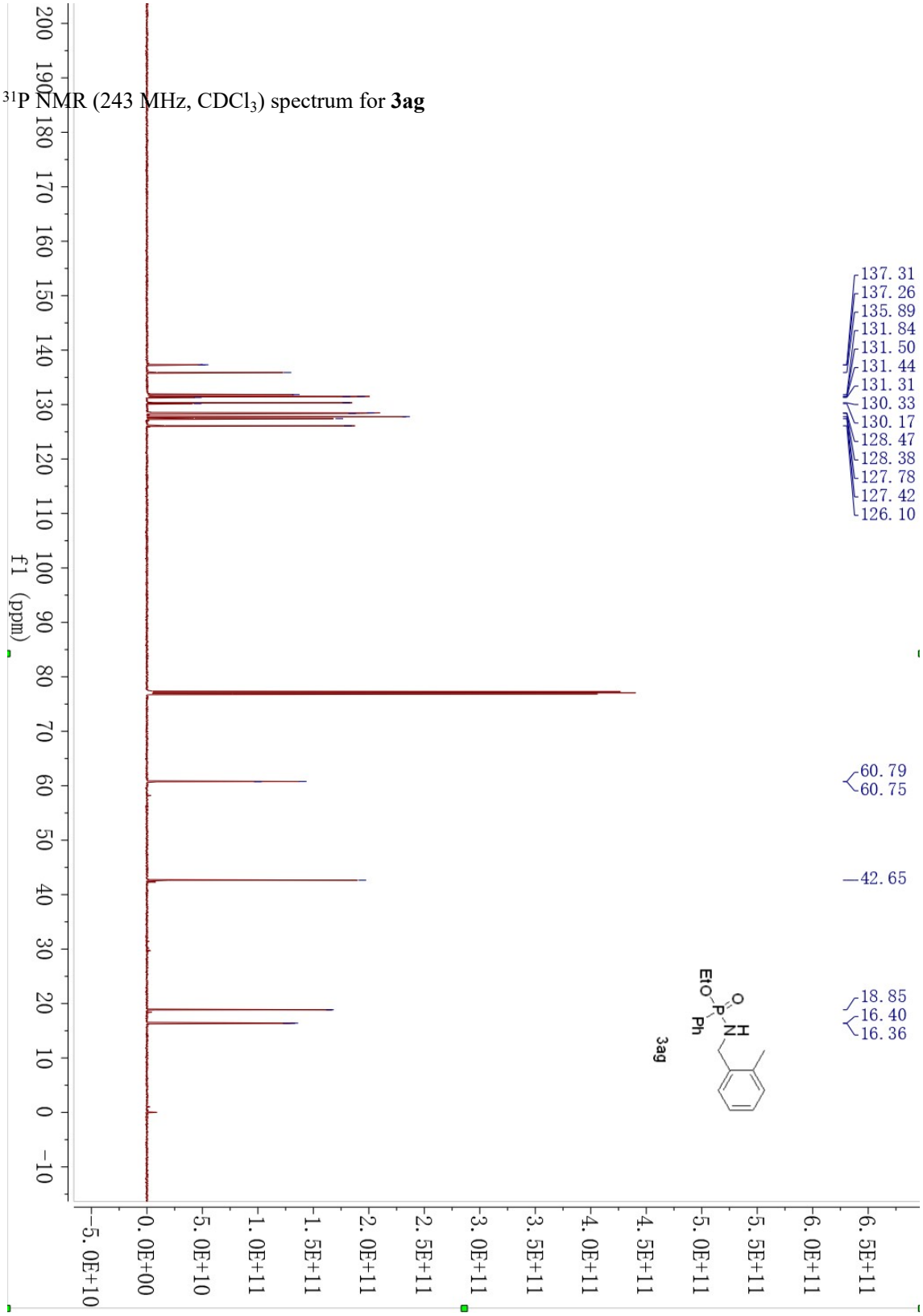


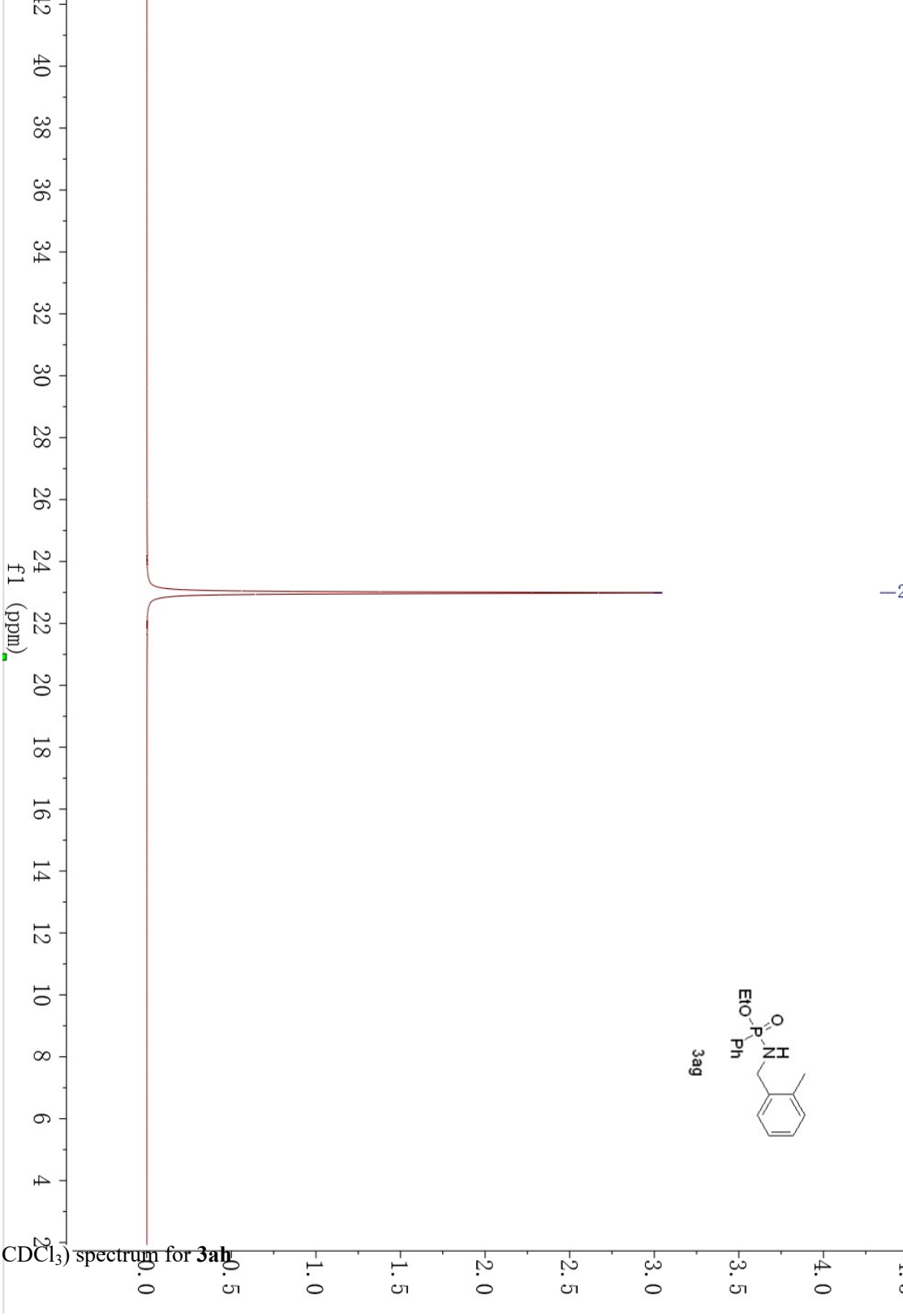
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ag**


f1 (ppm)
2.00
1.00
2.02
1.03
3.00
4.01
0.97
3.02
3.00
3ag

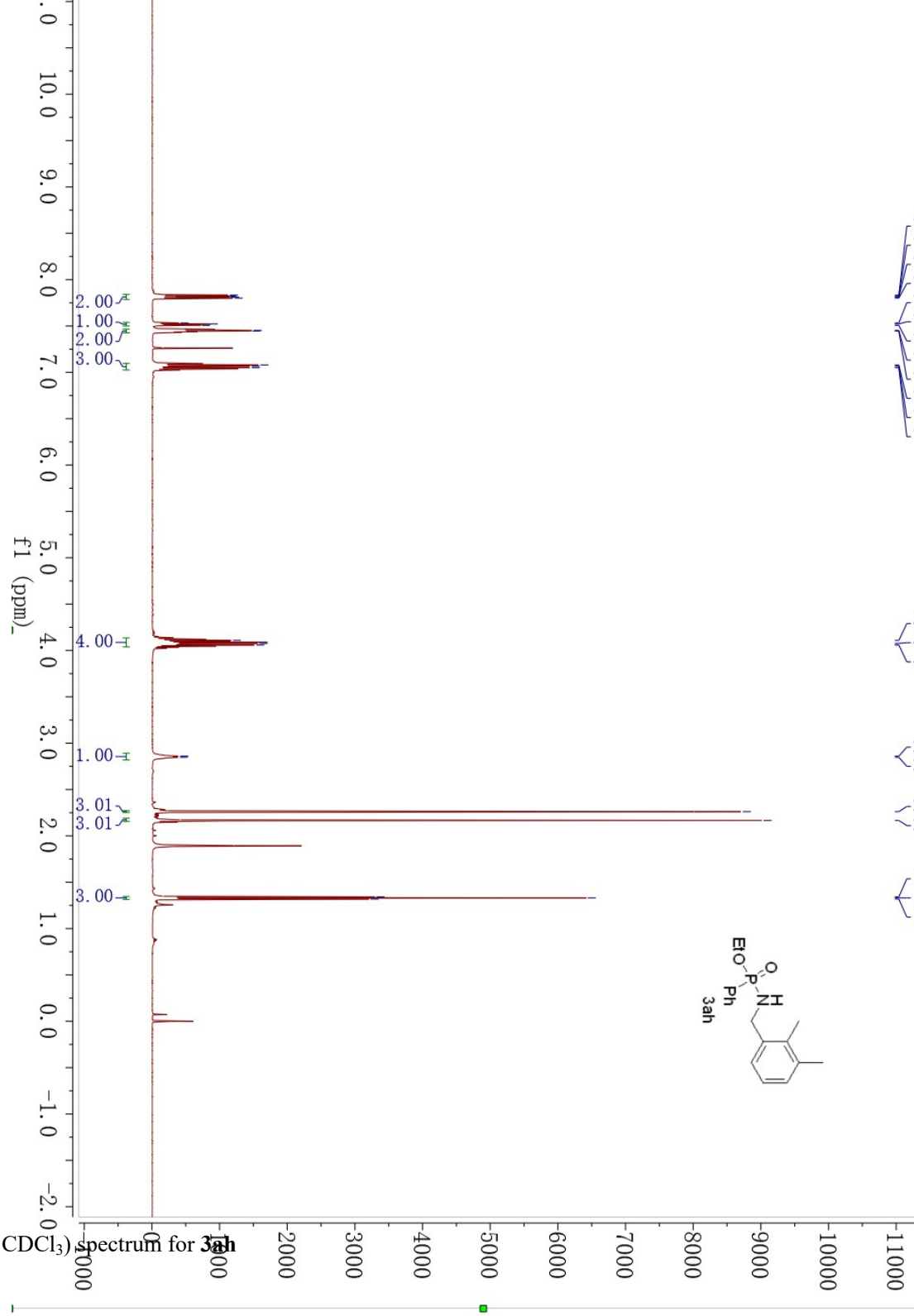
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ag**

^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ag**

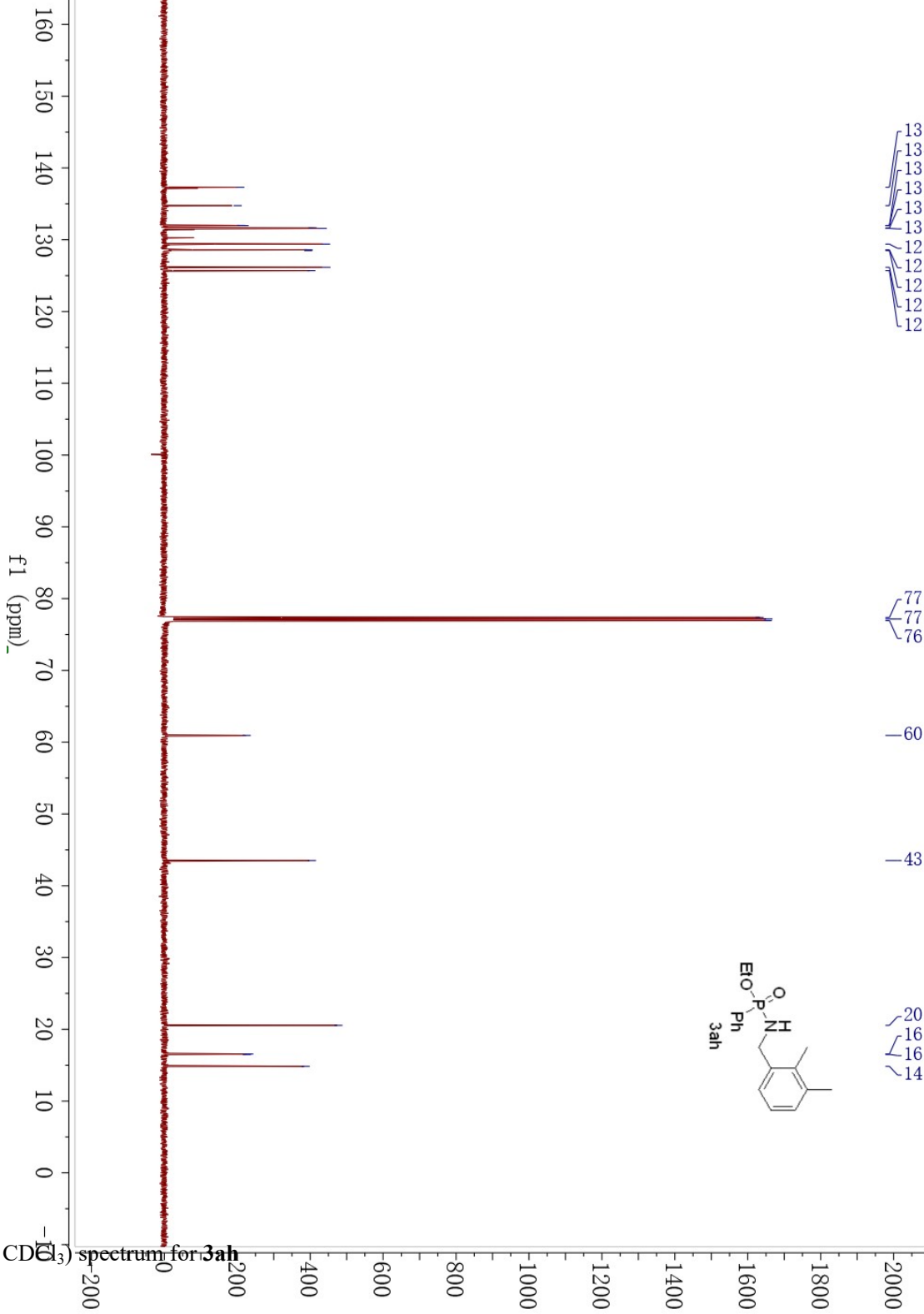




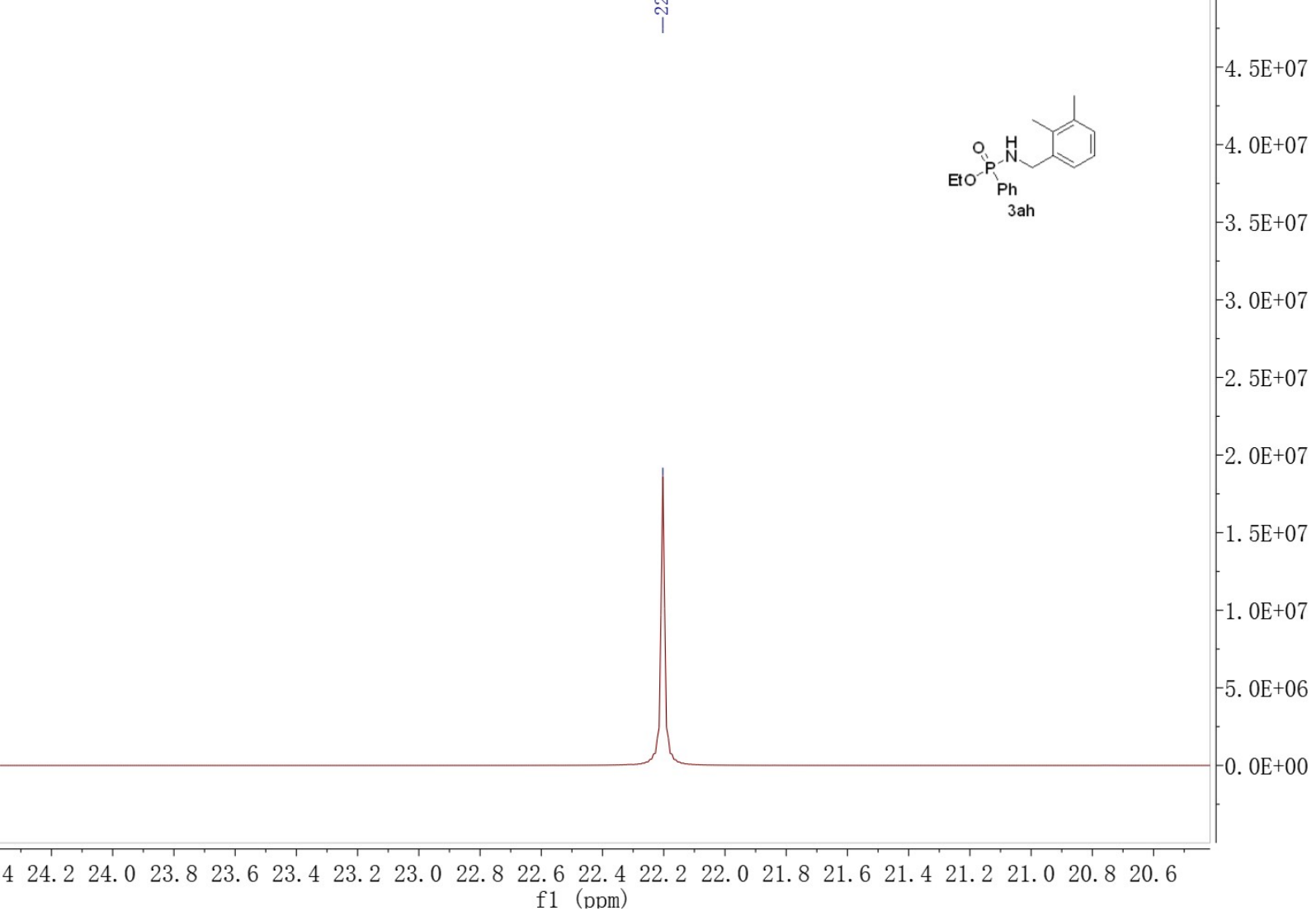
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ah**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ah**

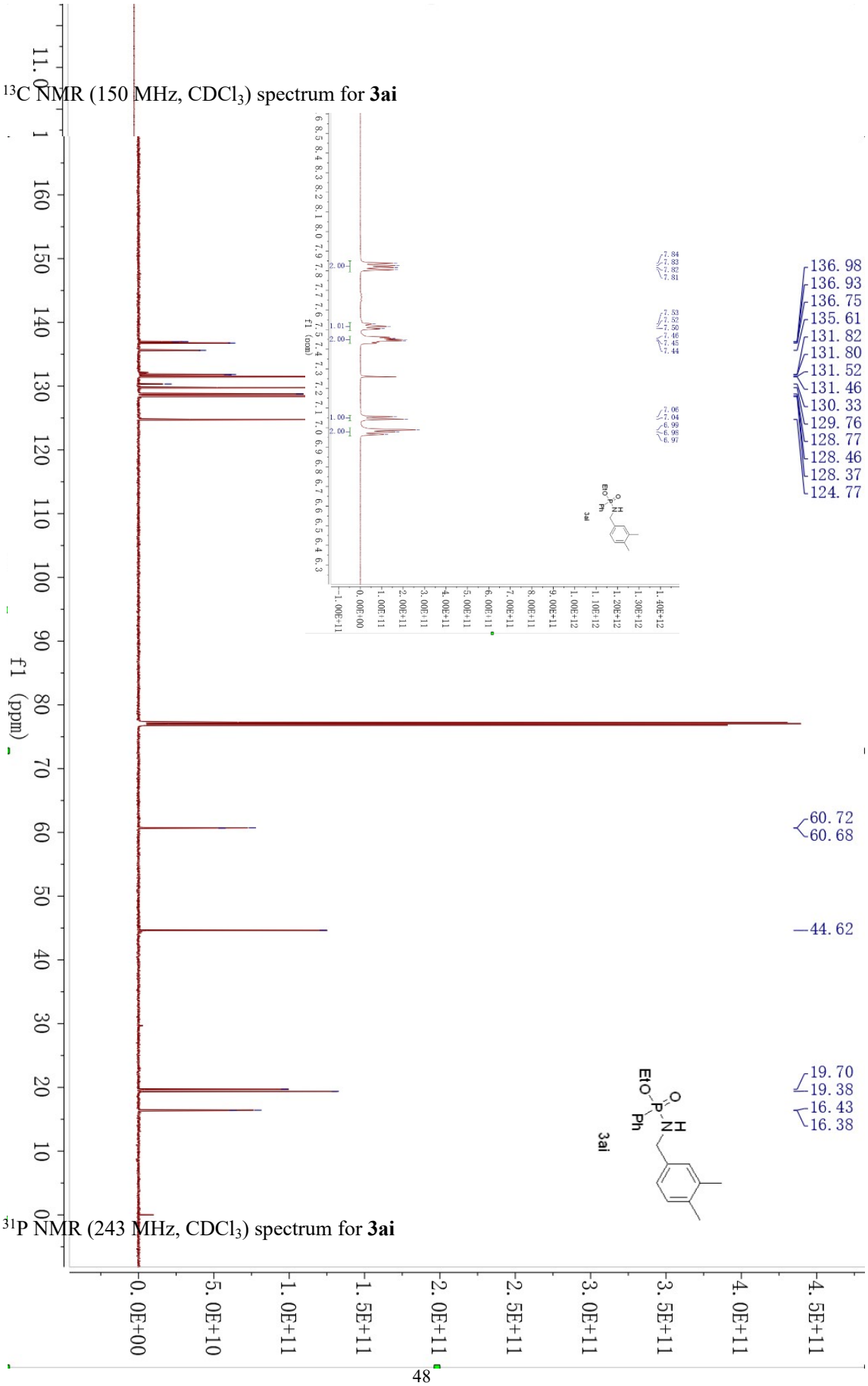


^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ah**

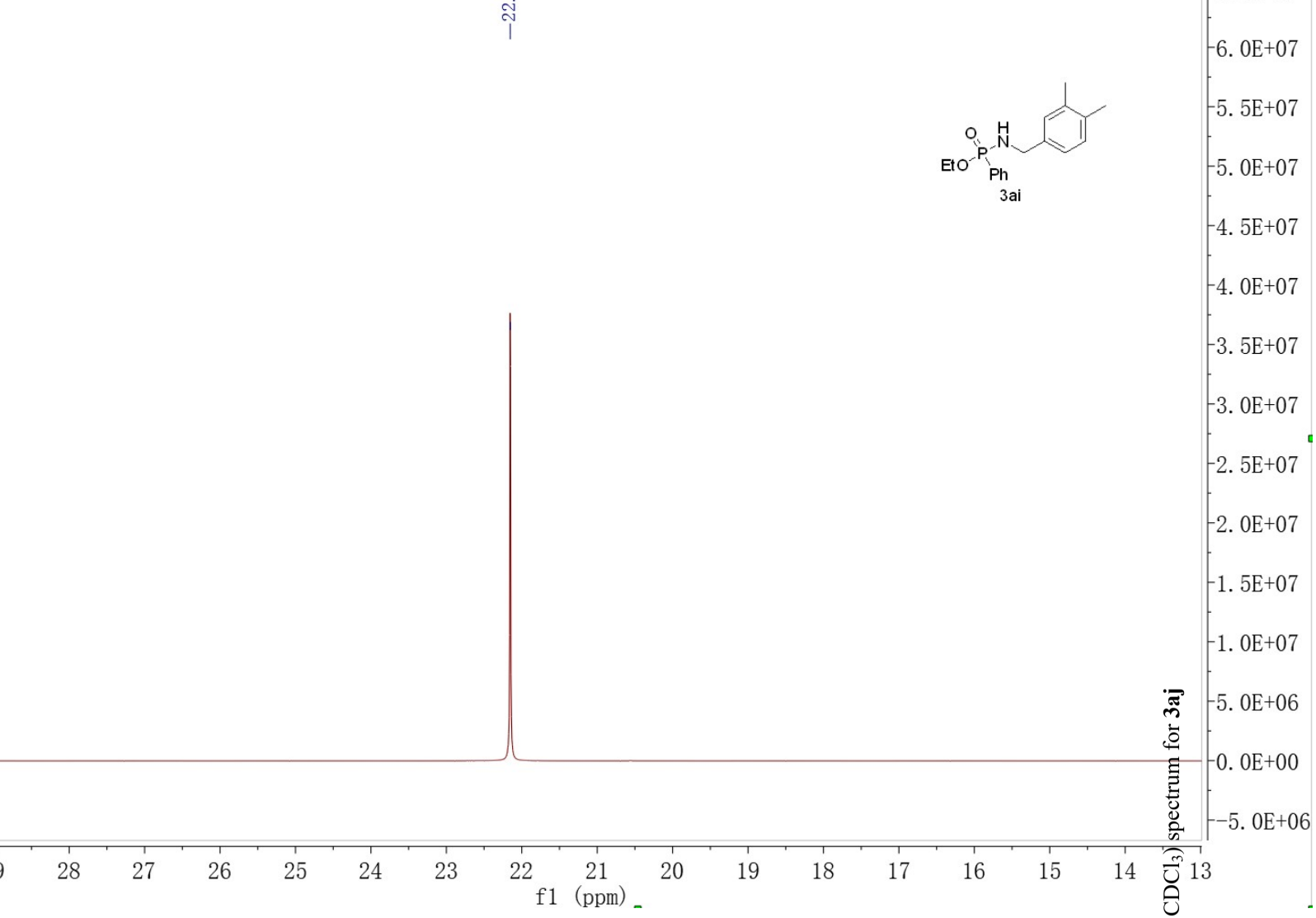

22.19
4.5E+07
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
24.2 24.0 23.8 23.6 23.4 23.2 23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6
f1 (ppm)
EtO
O
P
H
N
Ph
3ah

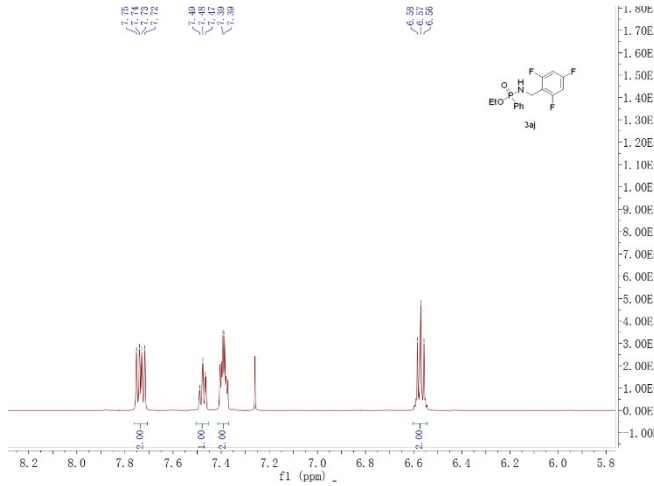
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ai**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ai**



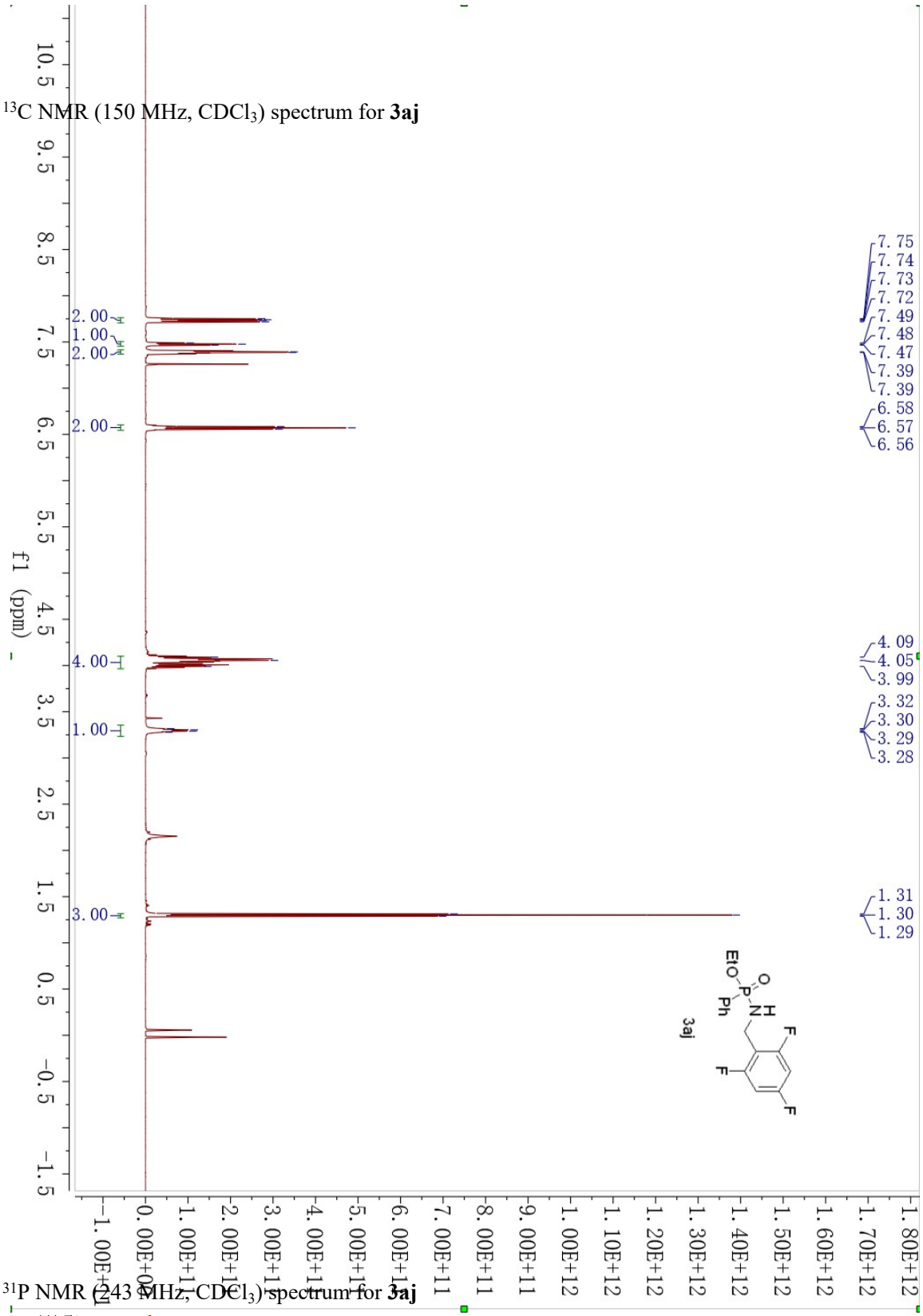
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ai**



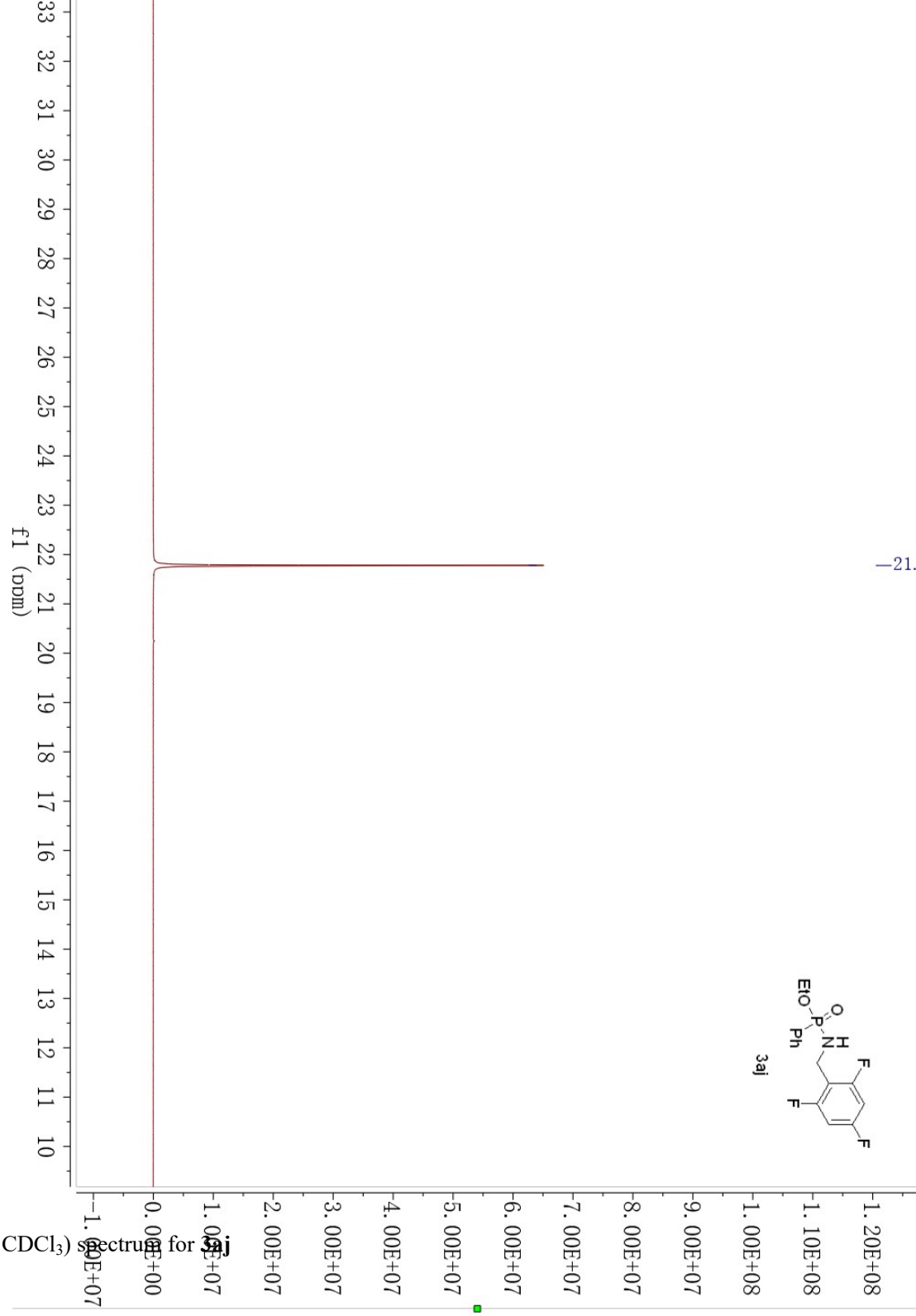


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3aj**

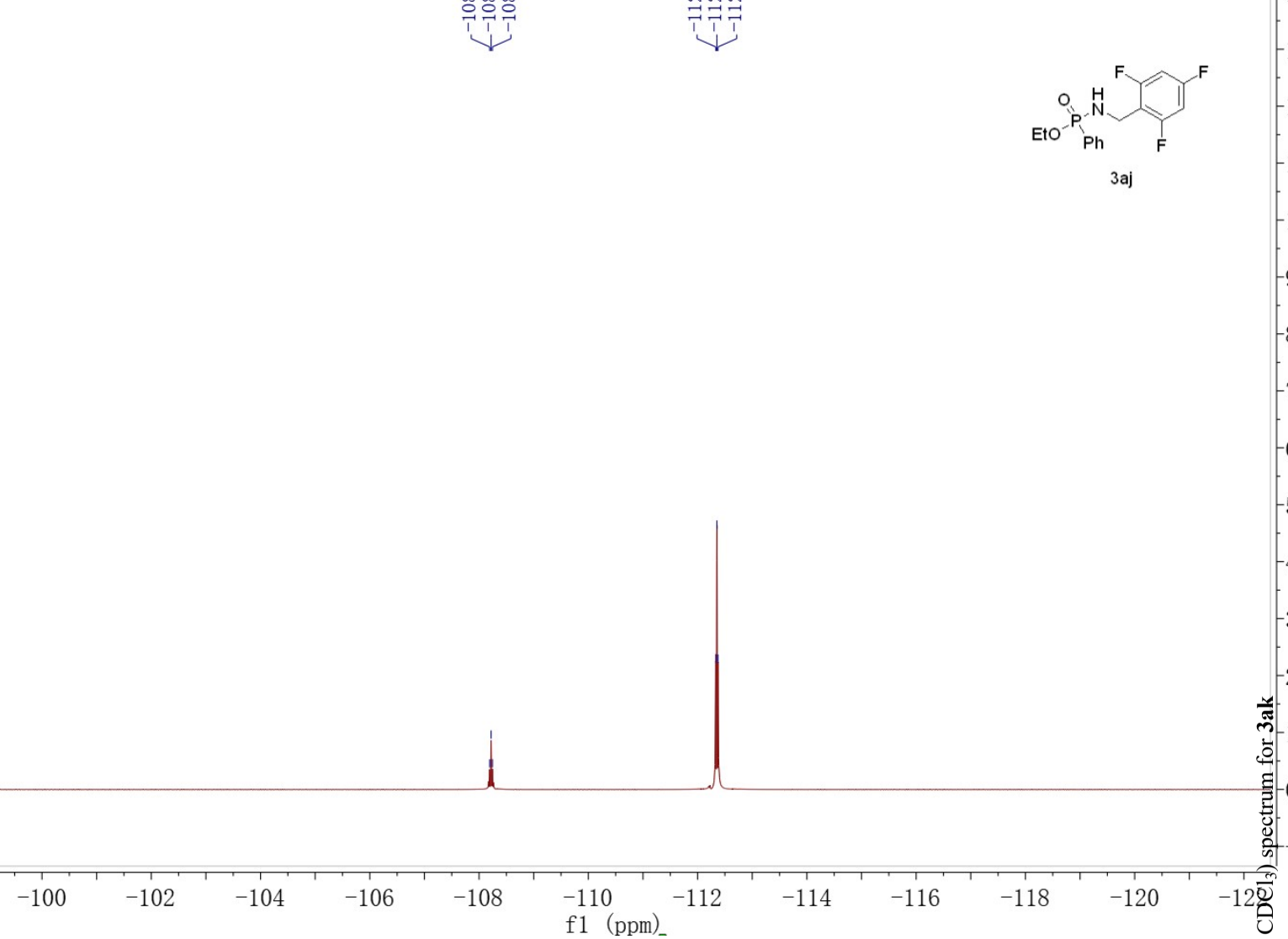
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3aj**



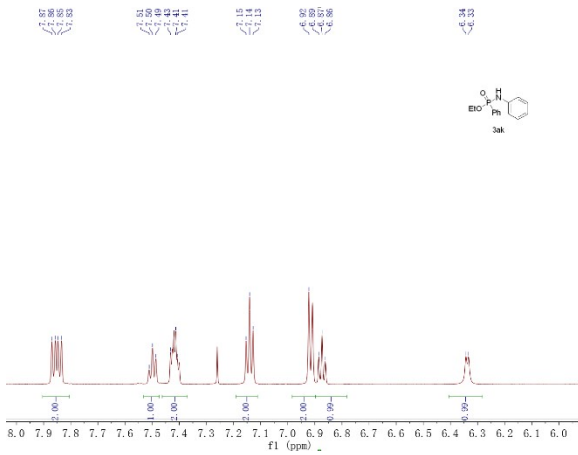
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3aj**



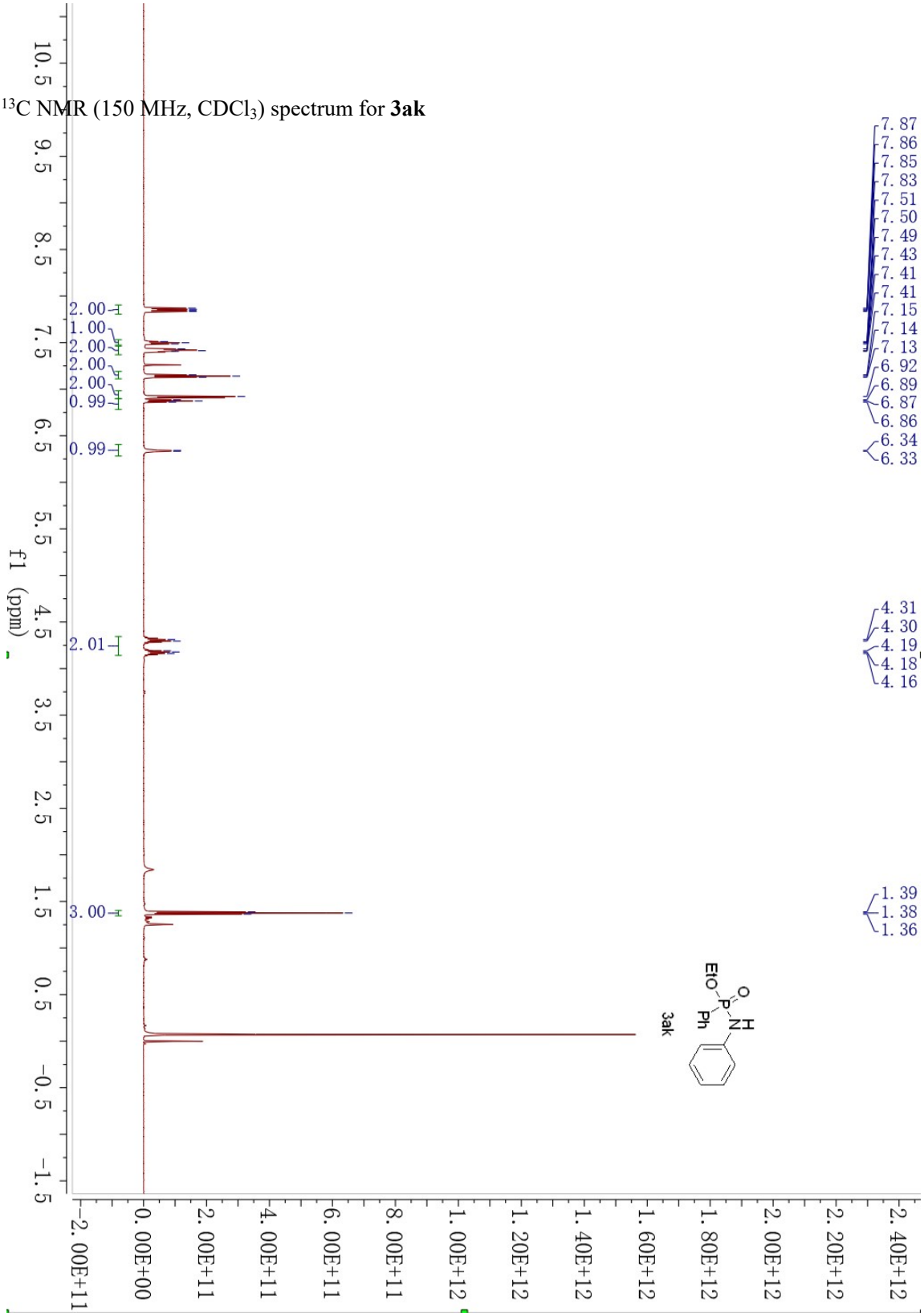
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3aj**

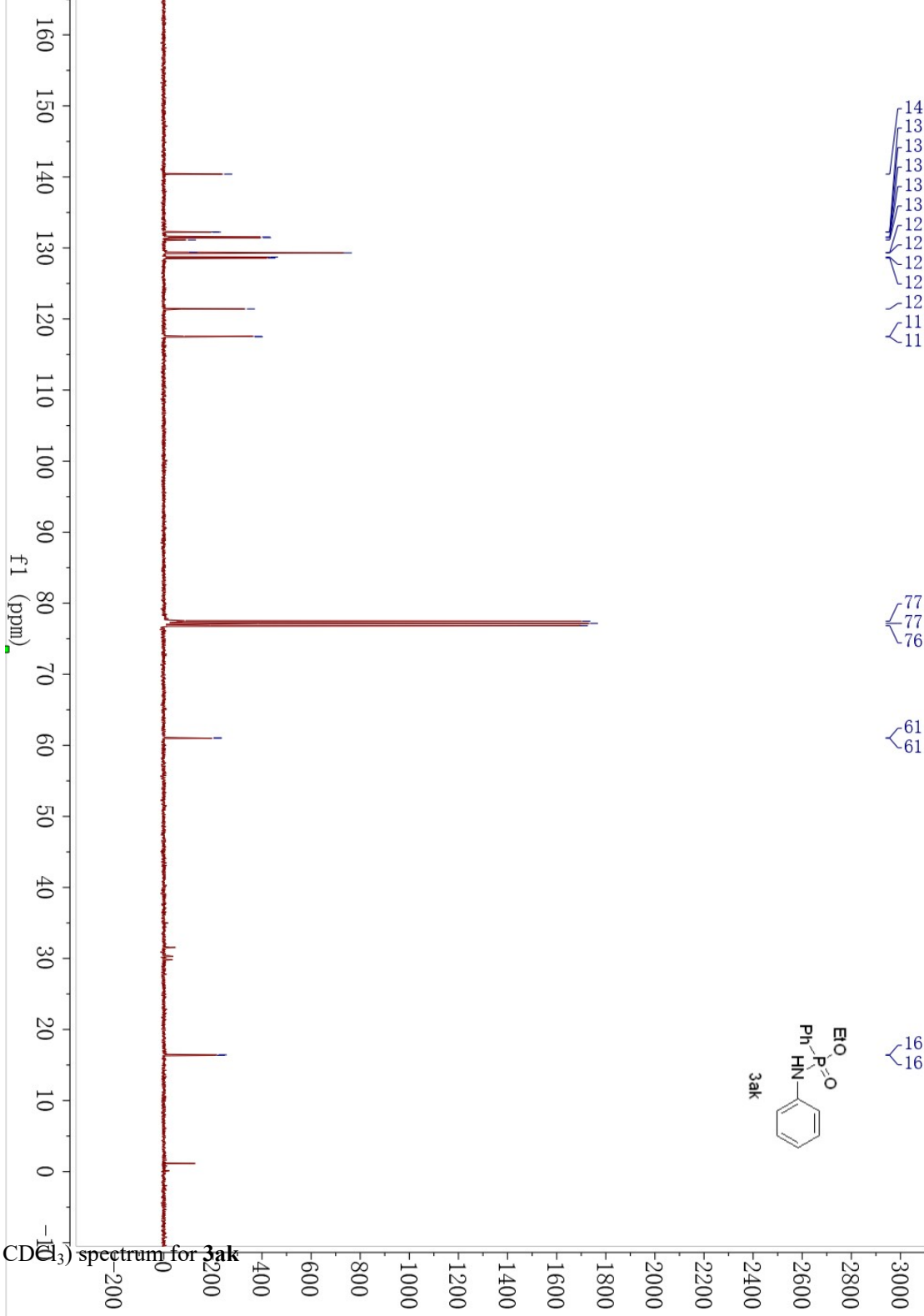


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ak**

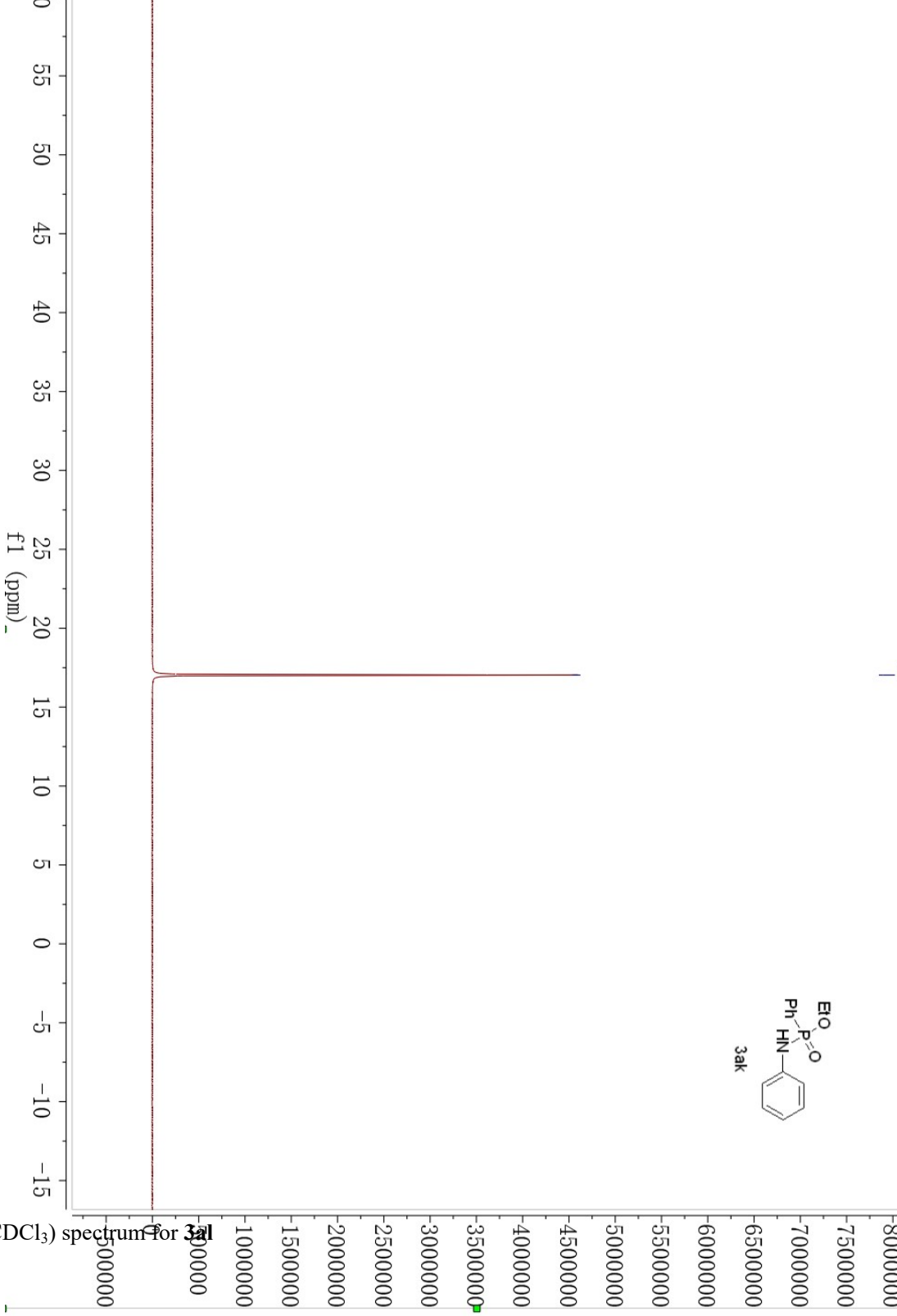


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ak**

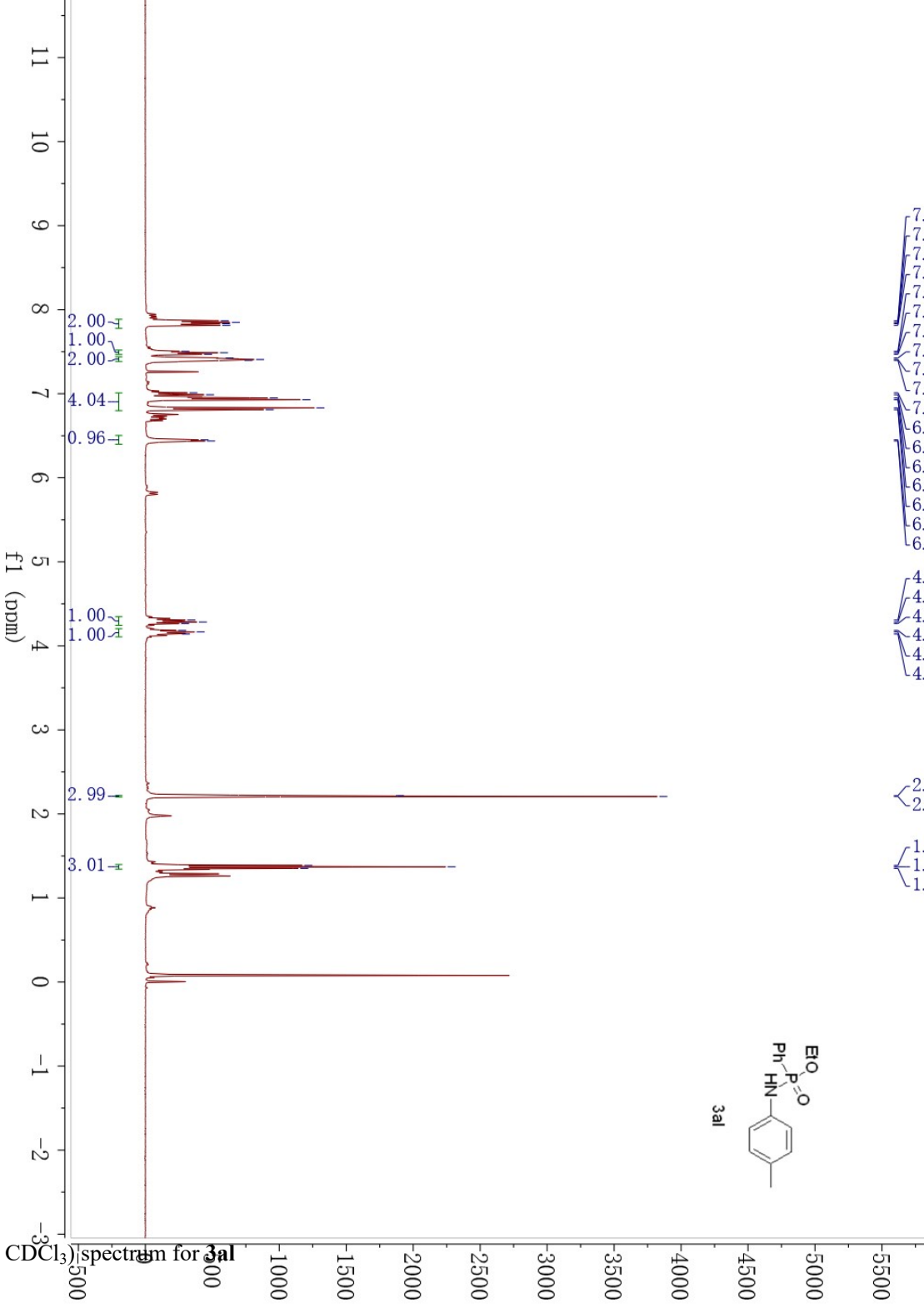




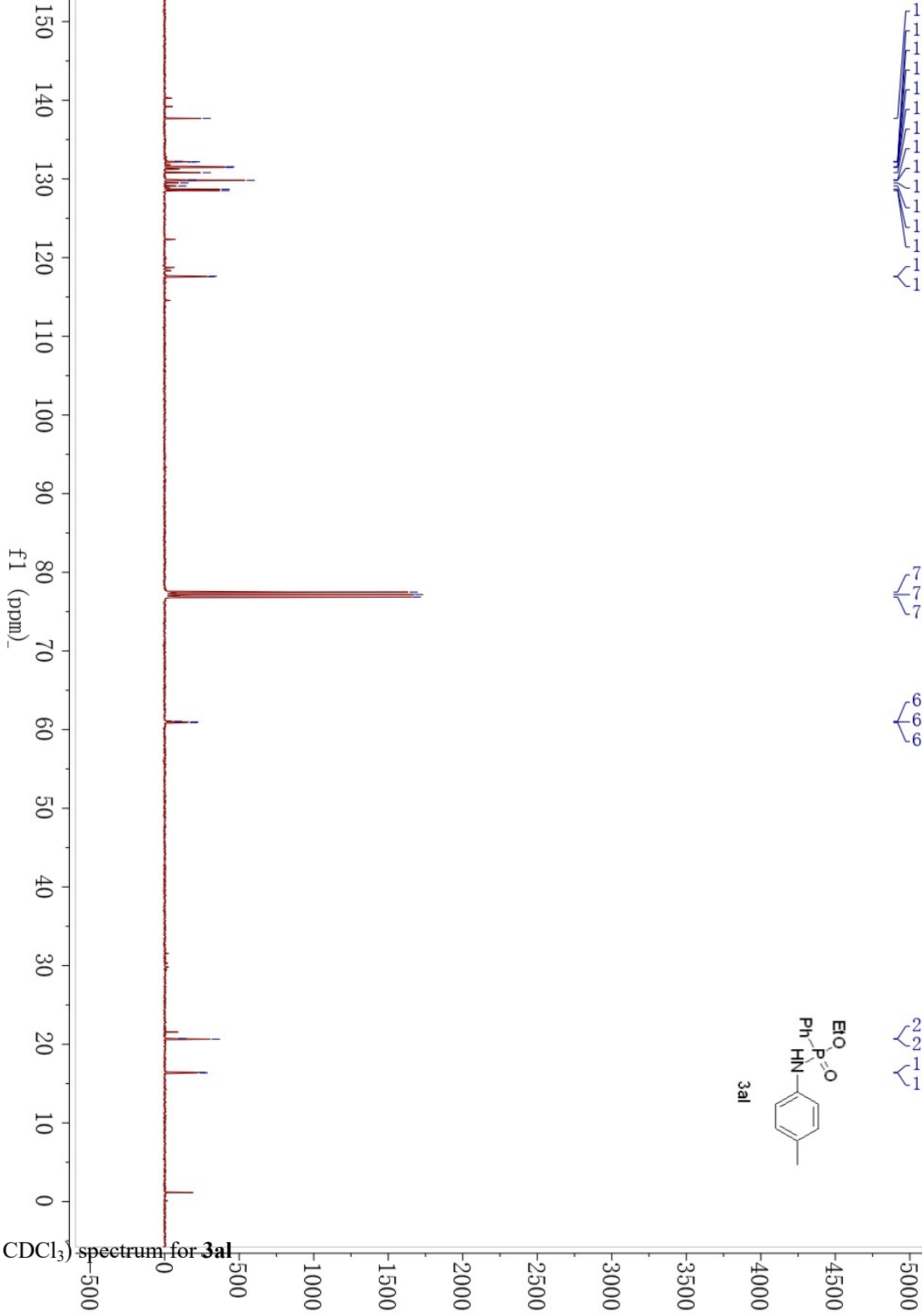
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ak**



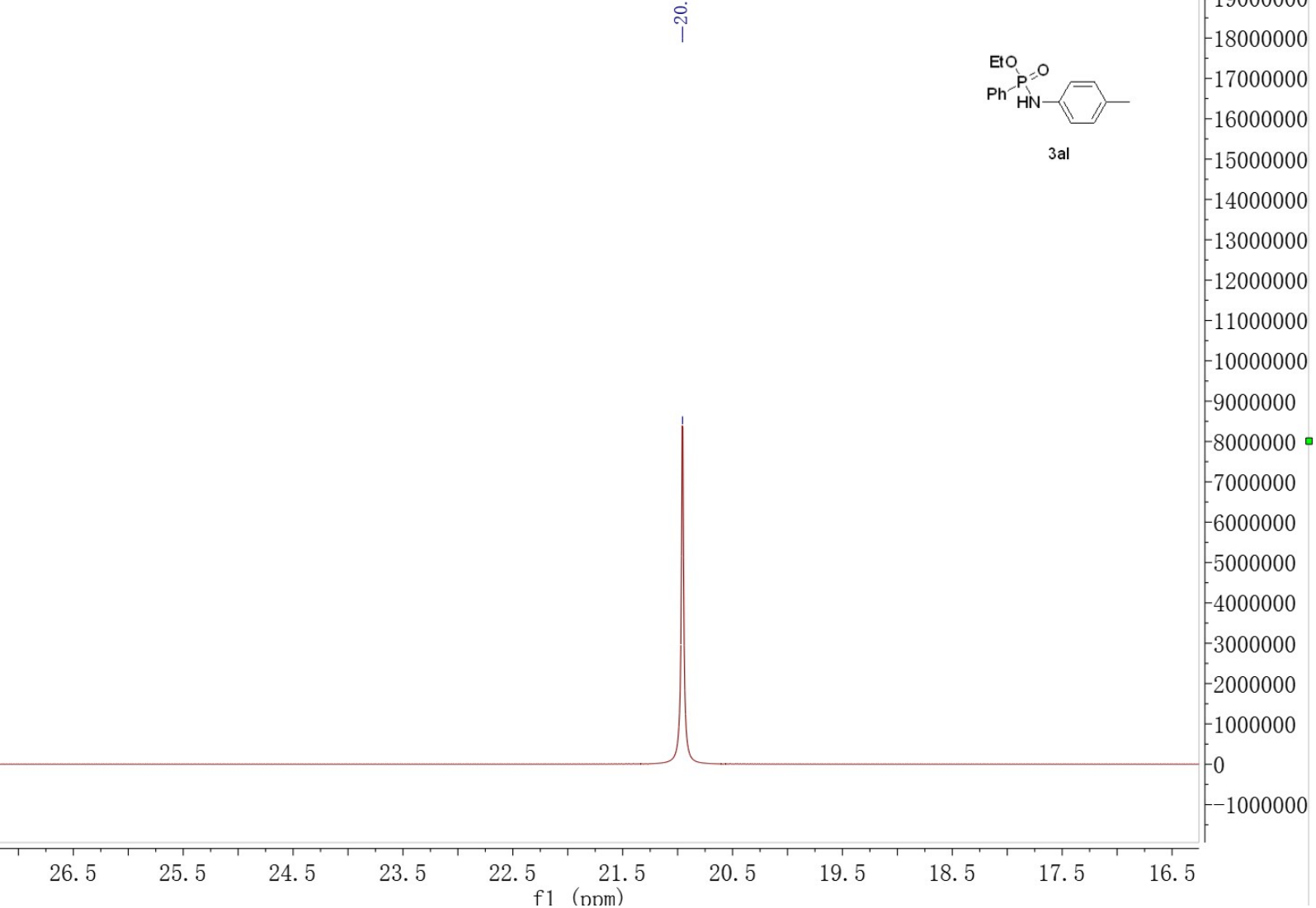
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3al**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3al**

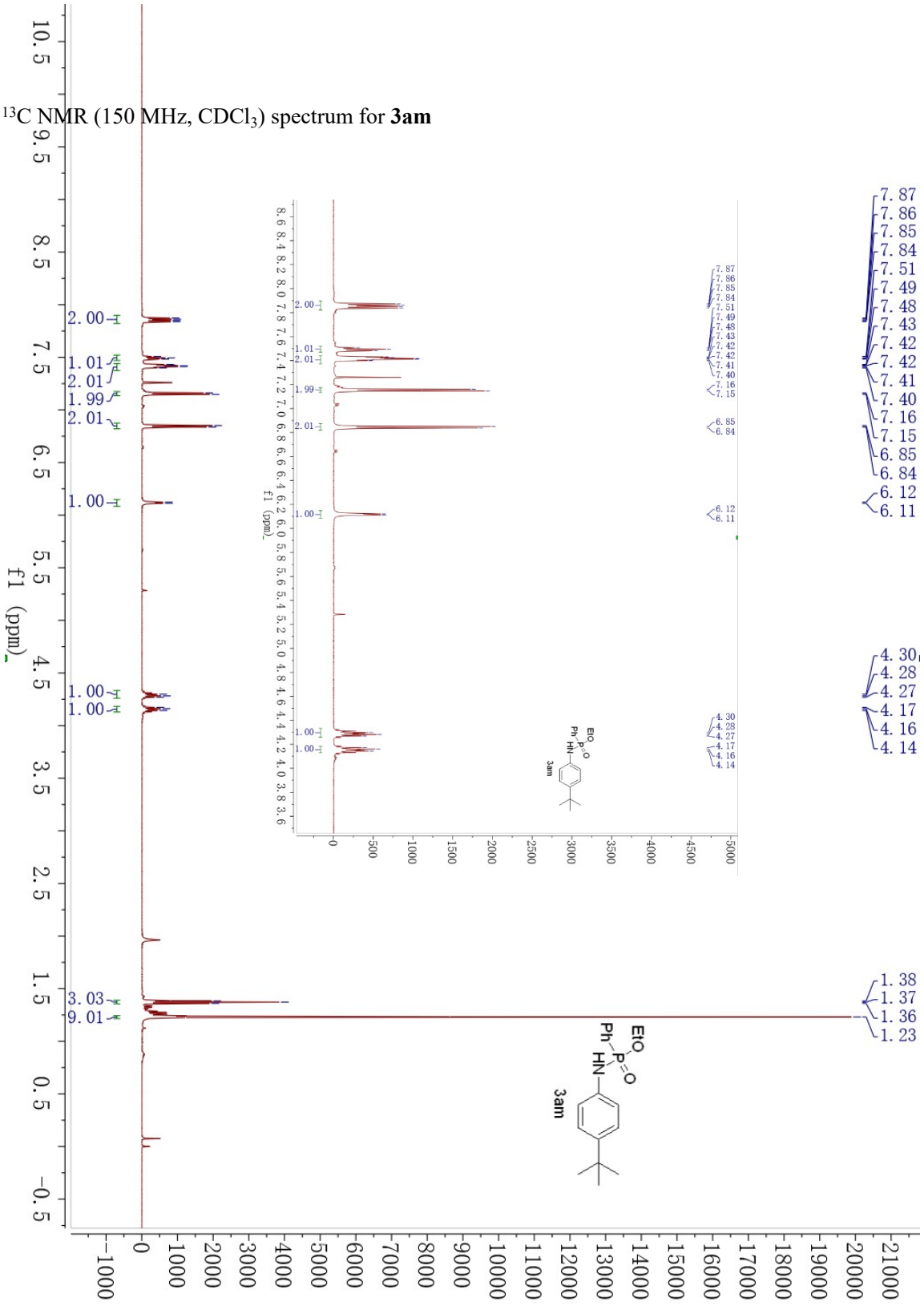


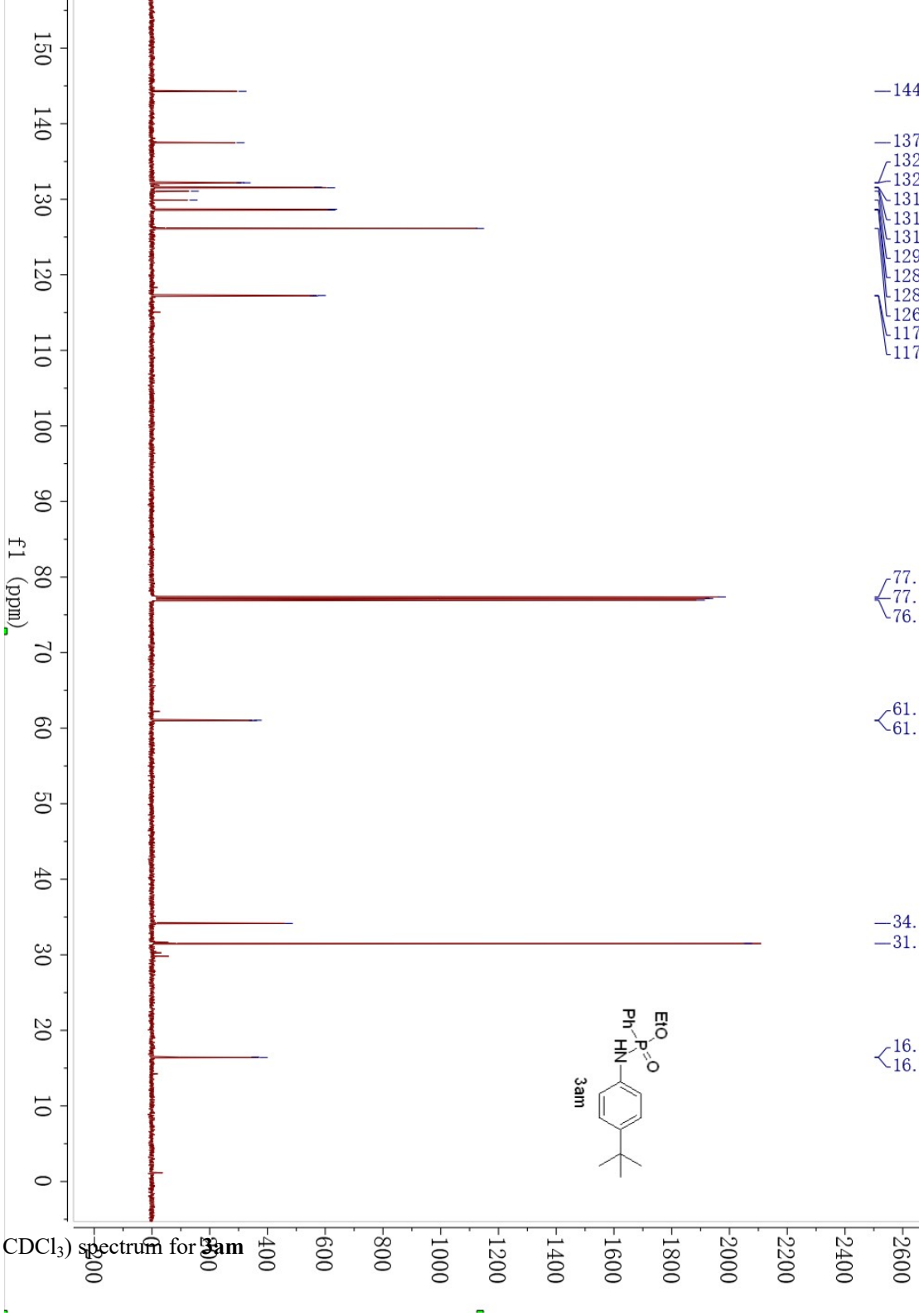
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3al**


20.
EtO
O
P
Ph
HN
3al
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
26.5
25.5
24.5
23.5
22.5
21.5
20.5
19.5
18.5
17.5
16.5
f1 (ppm)

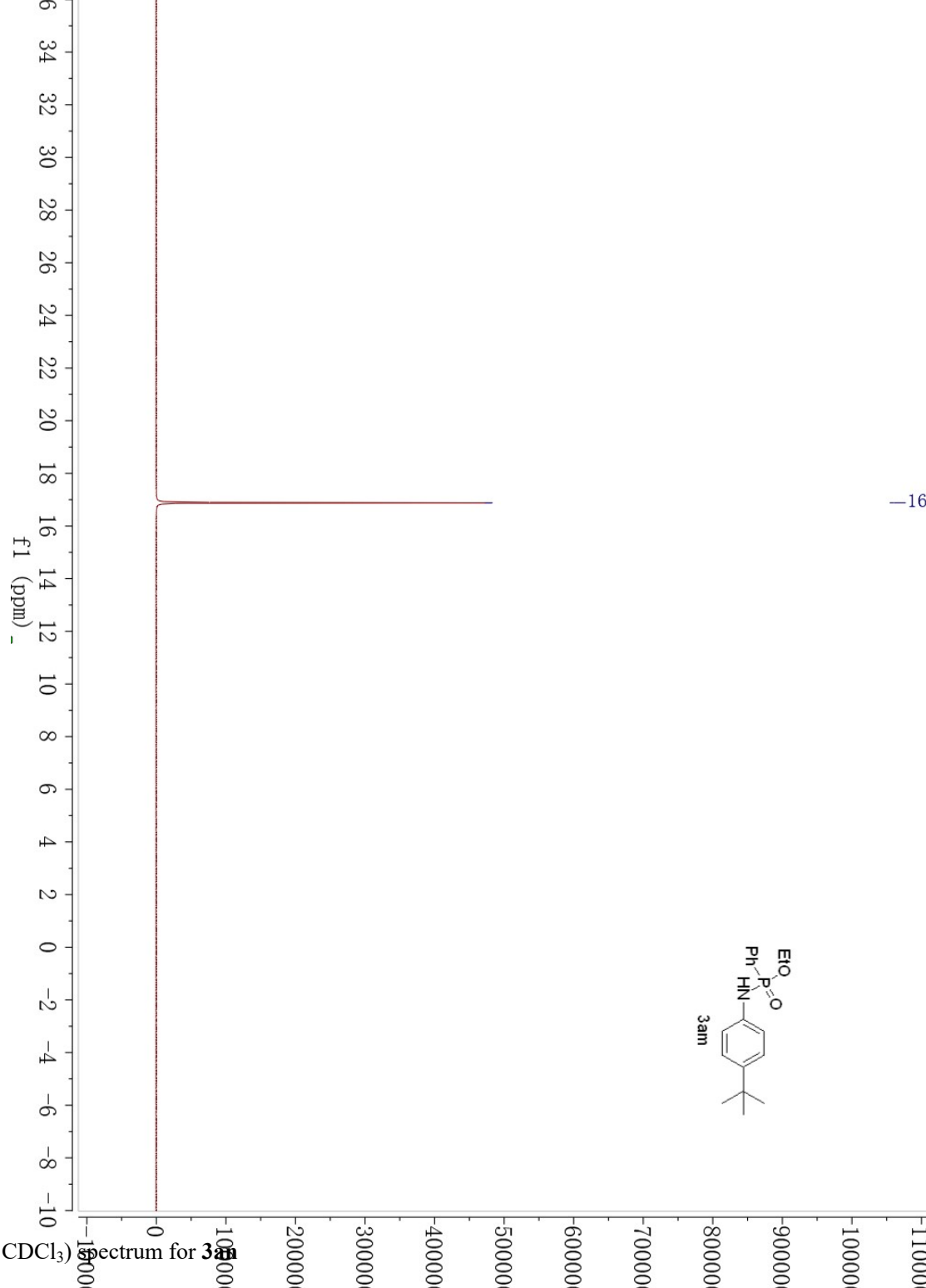
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3am**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3am**

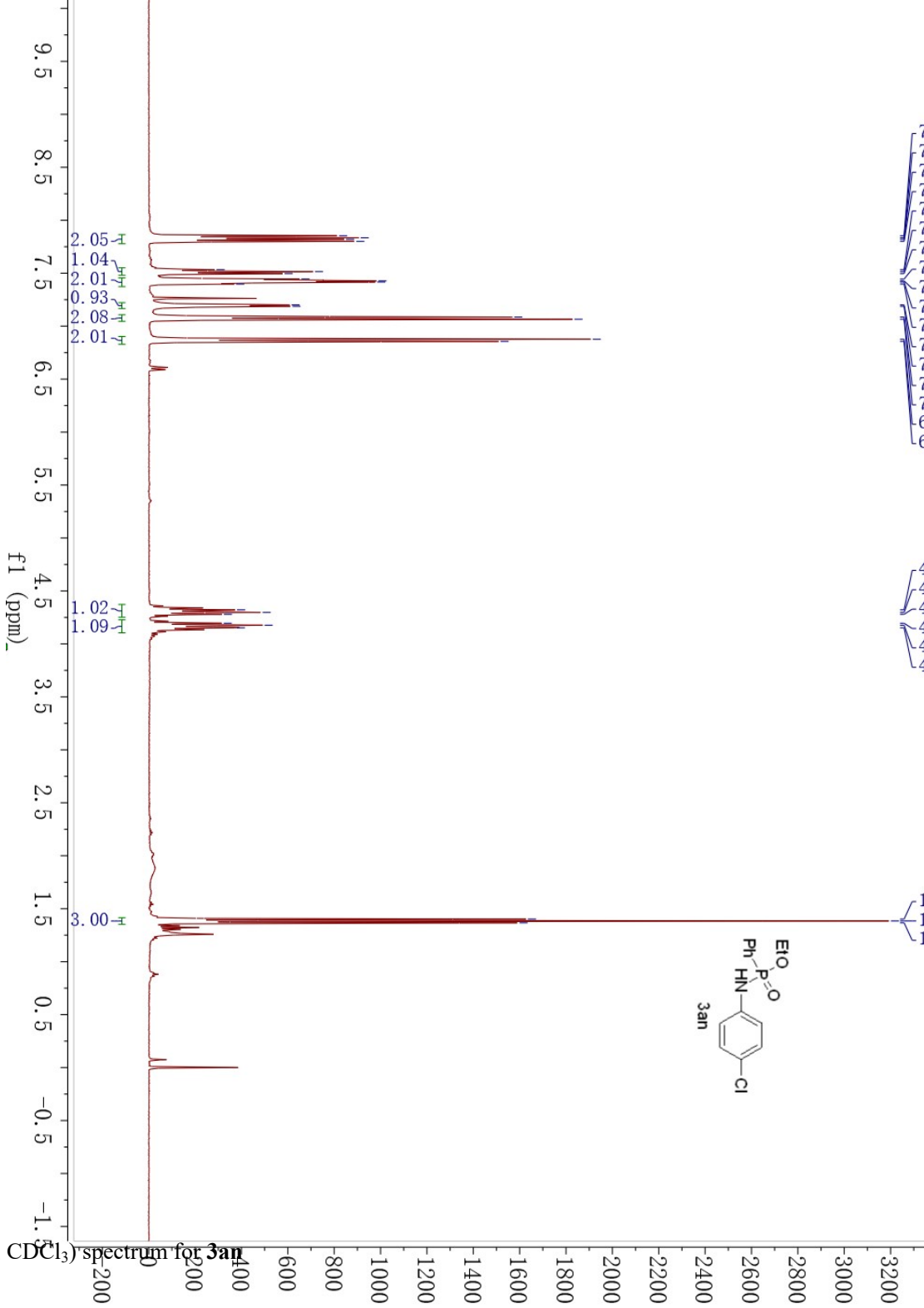




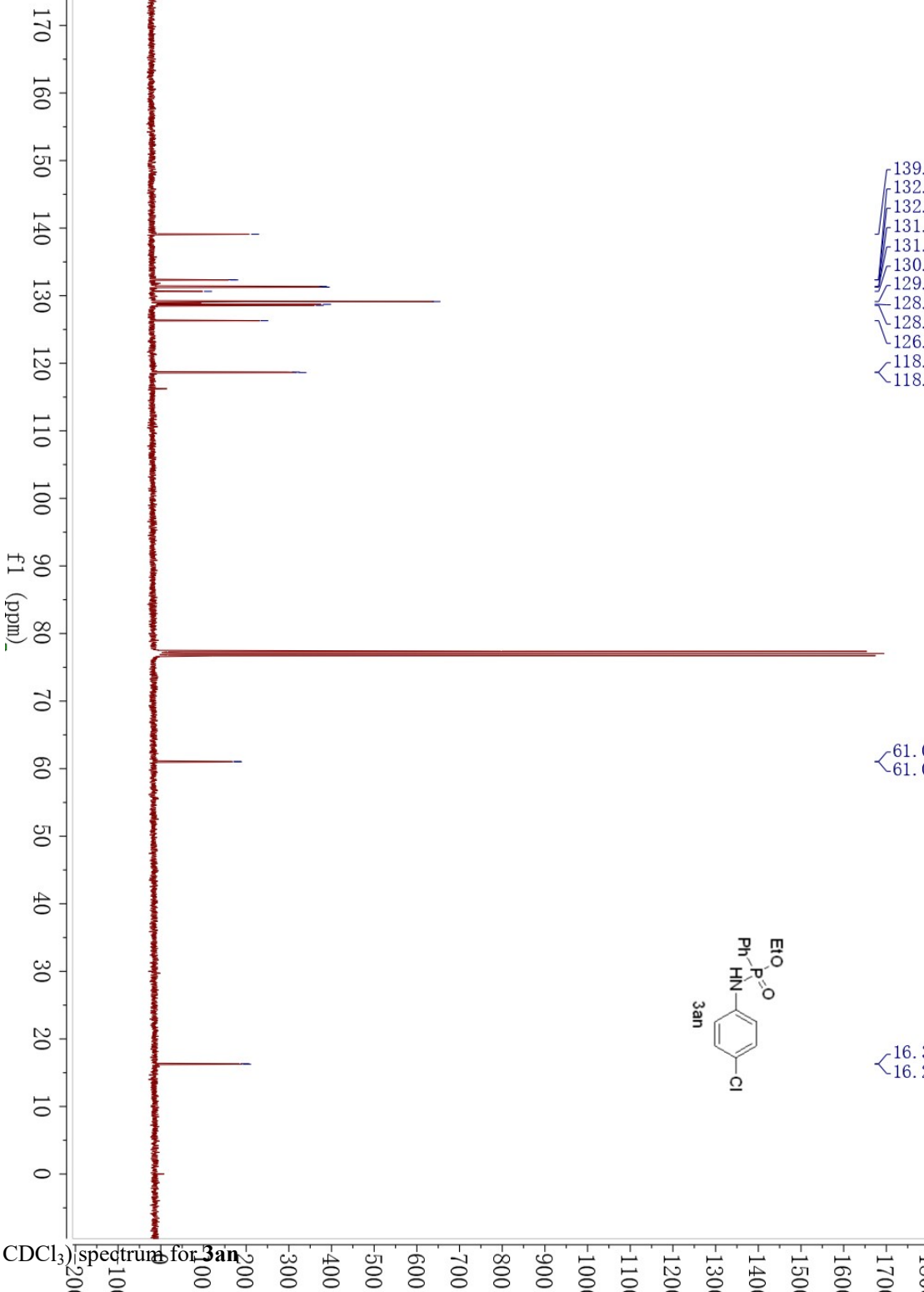
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3am**



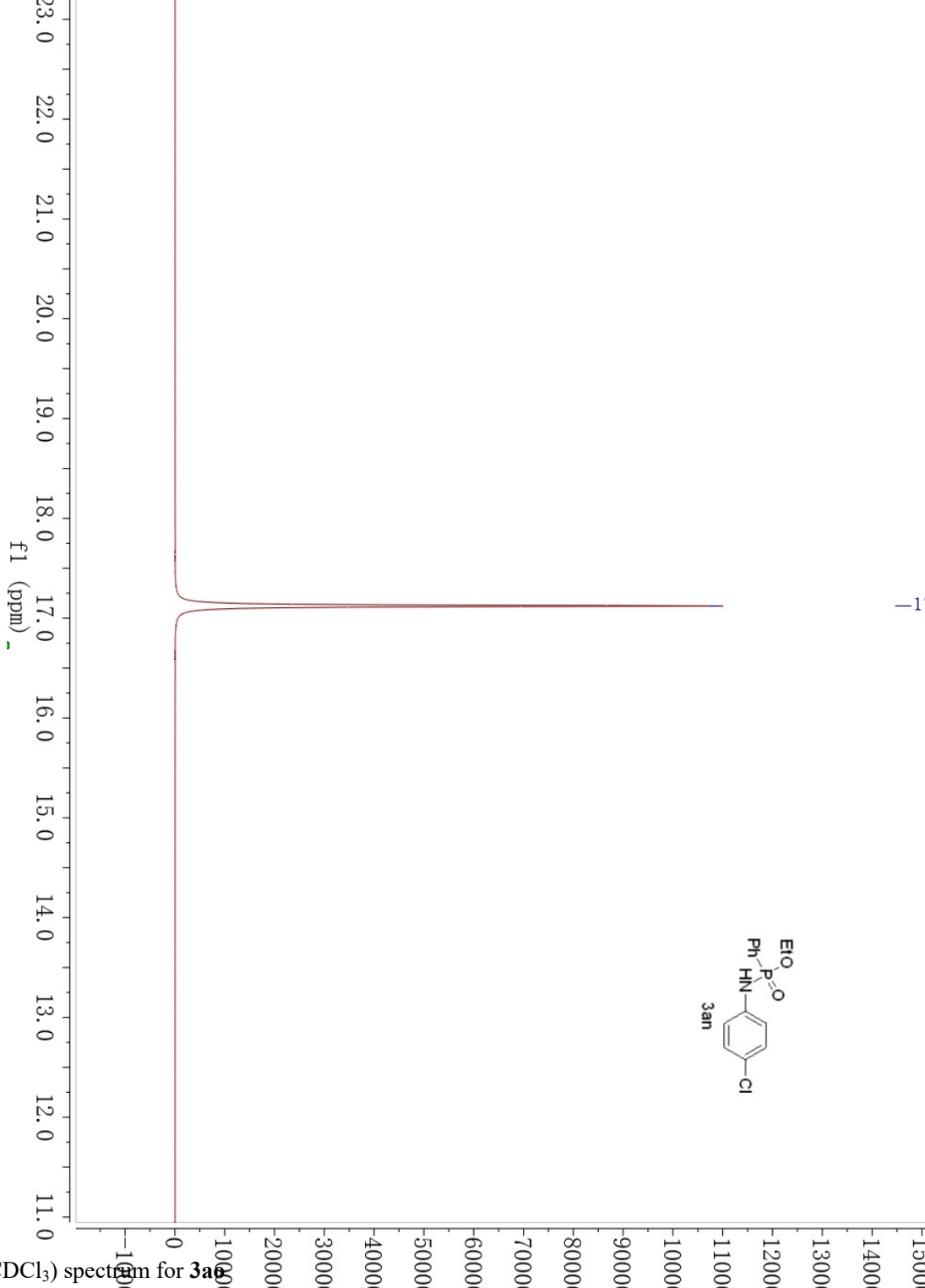
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3am**



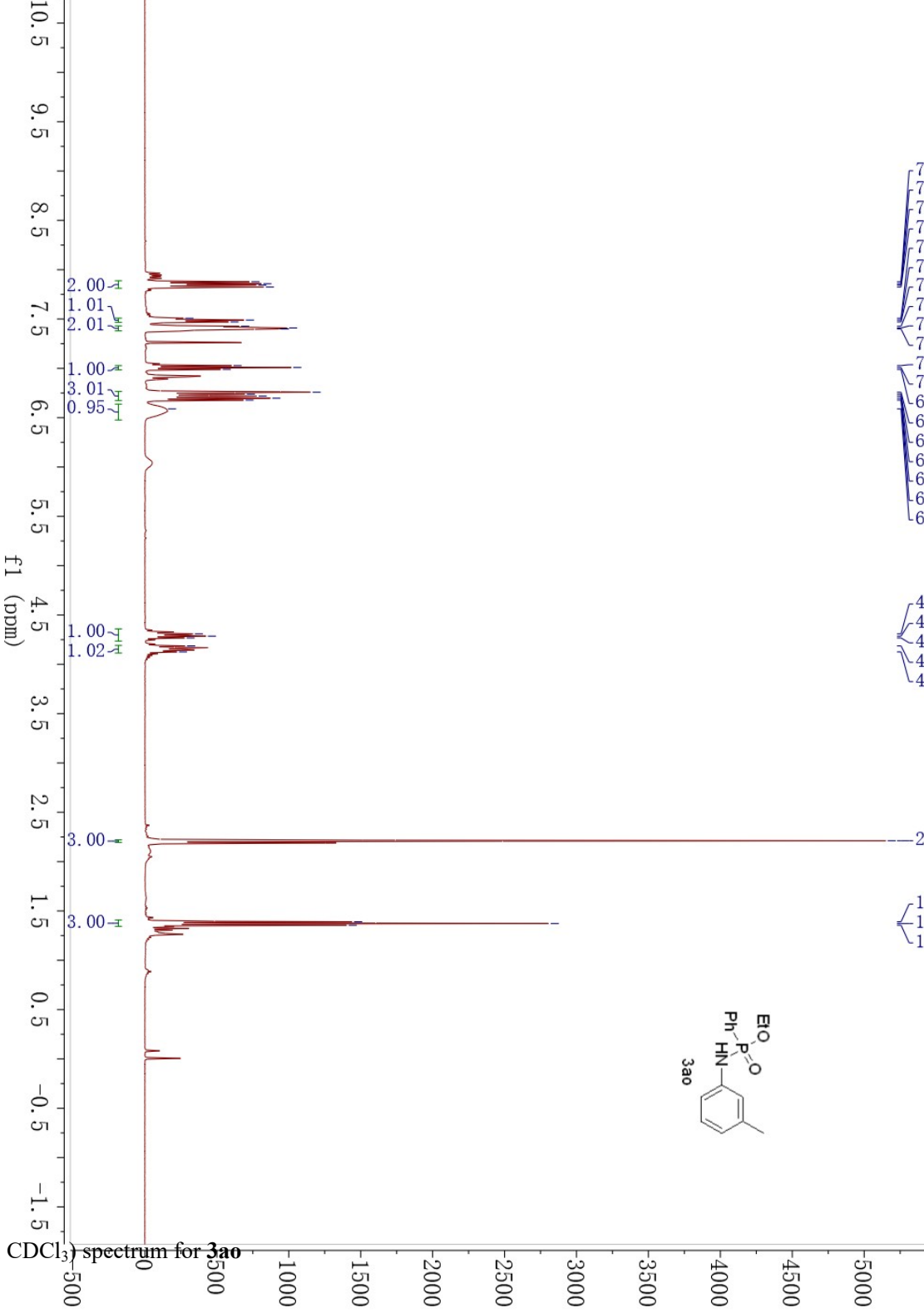
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3an**



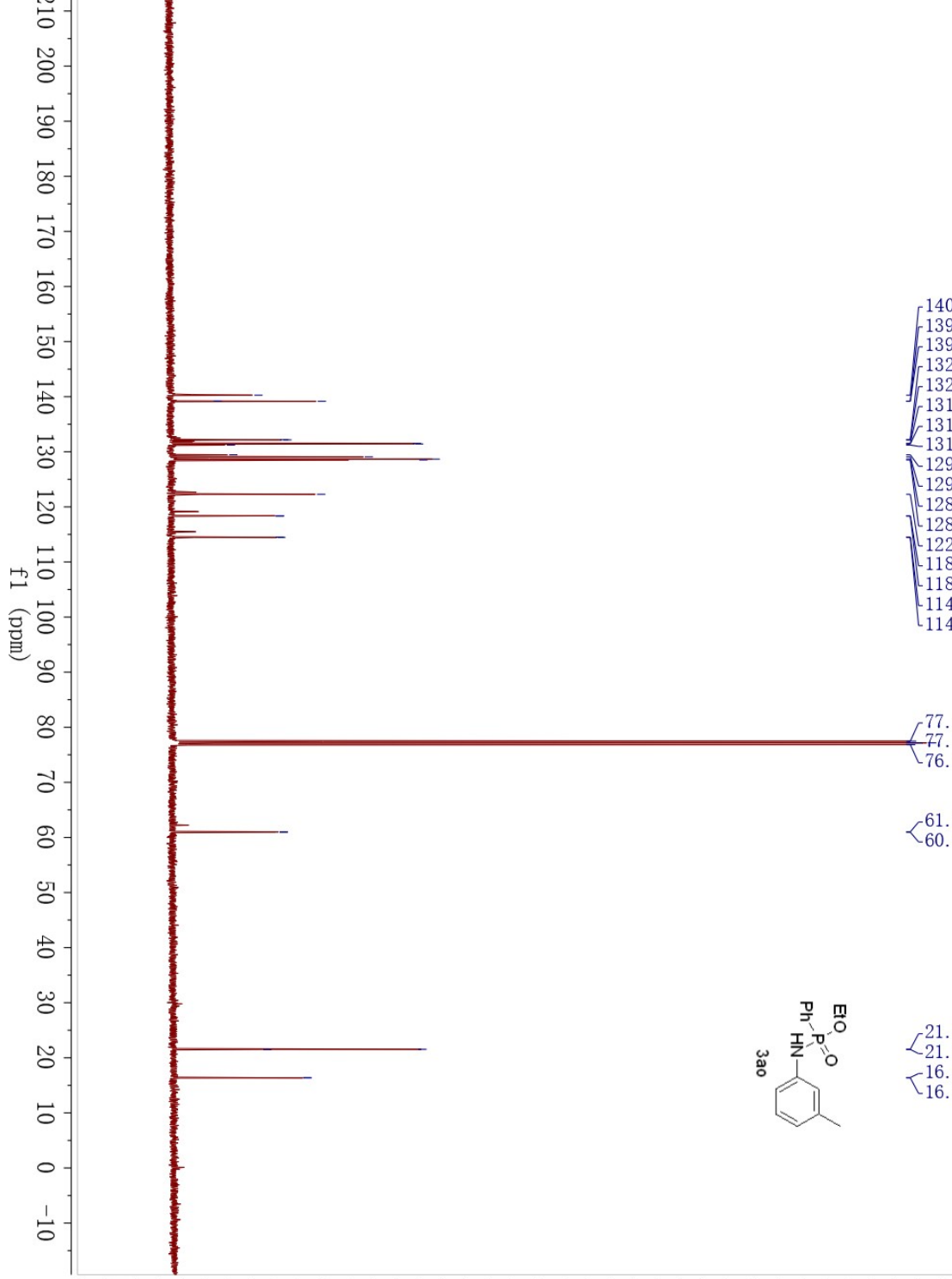
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3an**



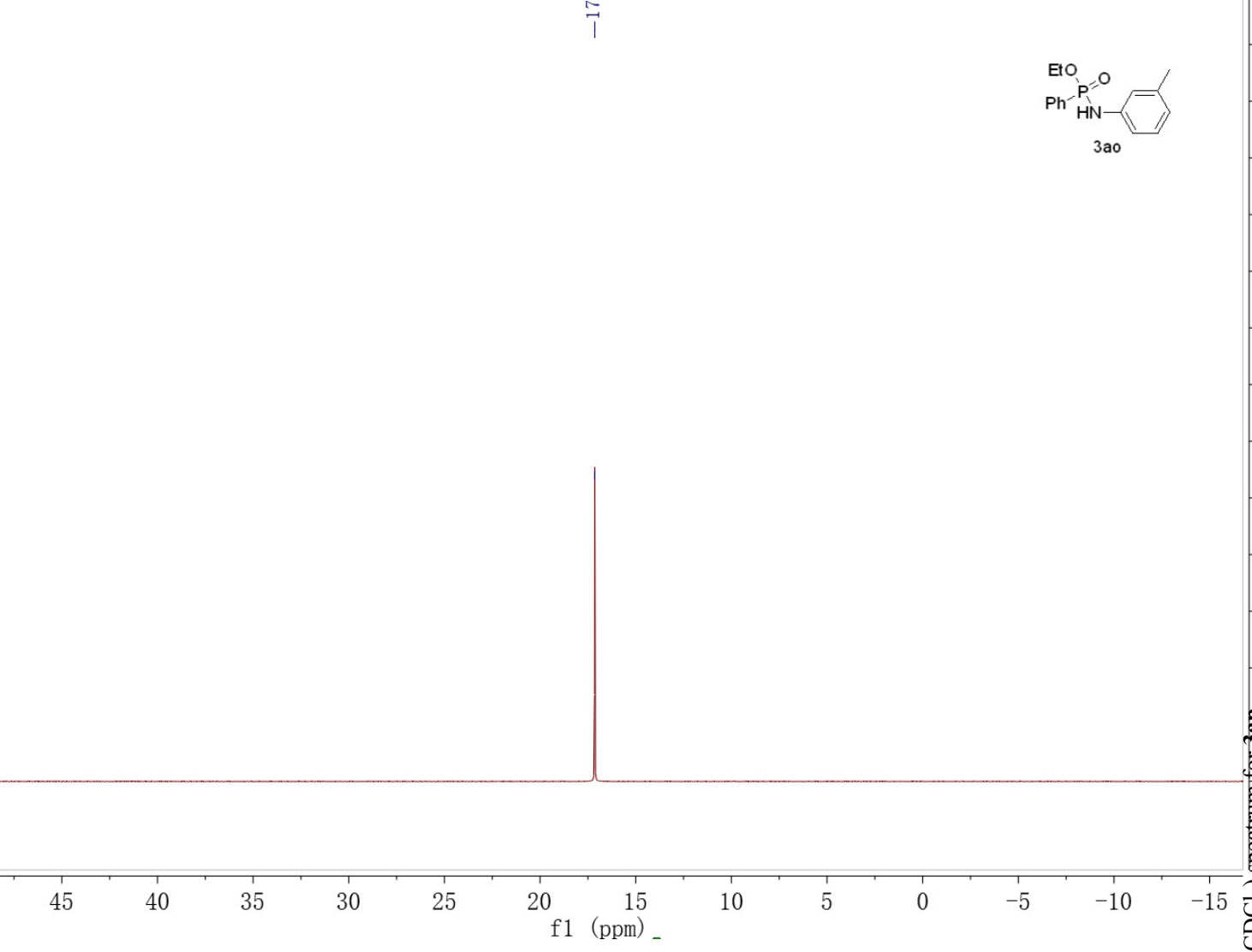
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3an**

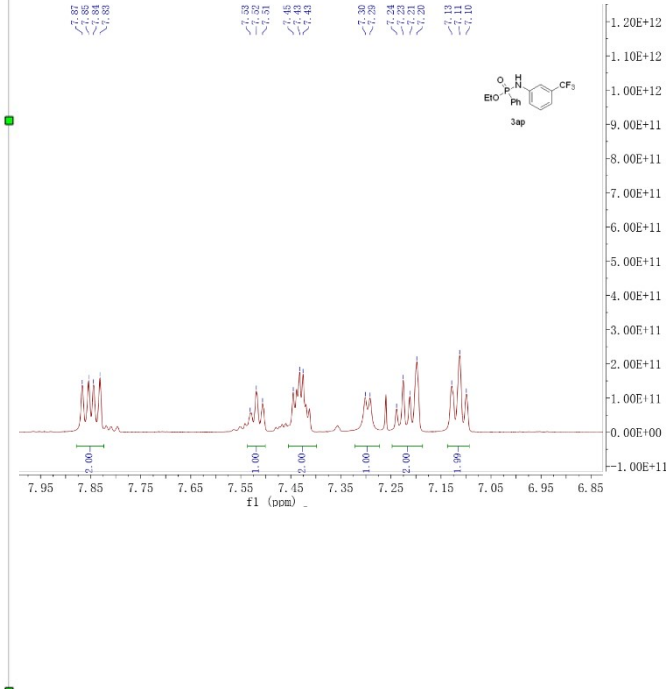


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ao**



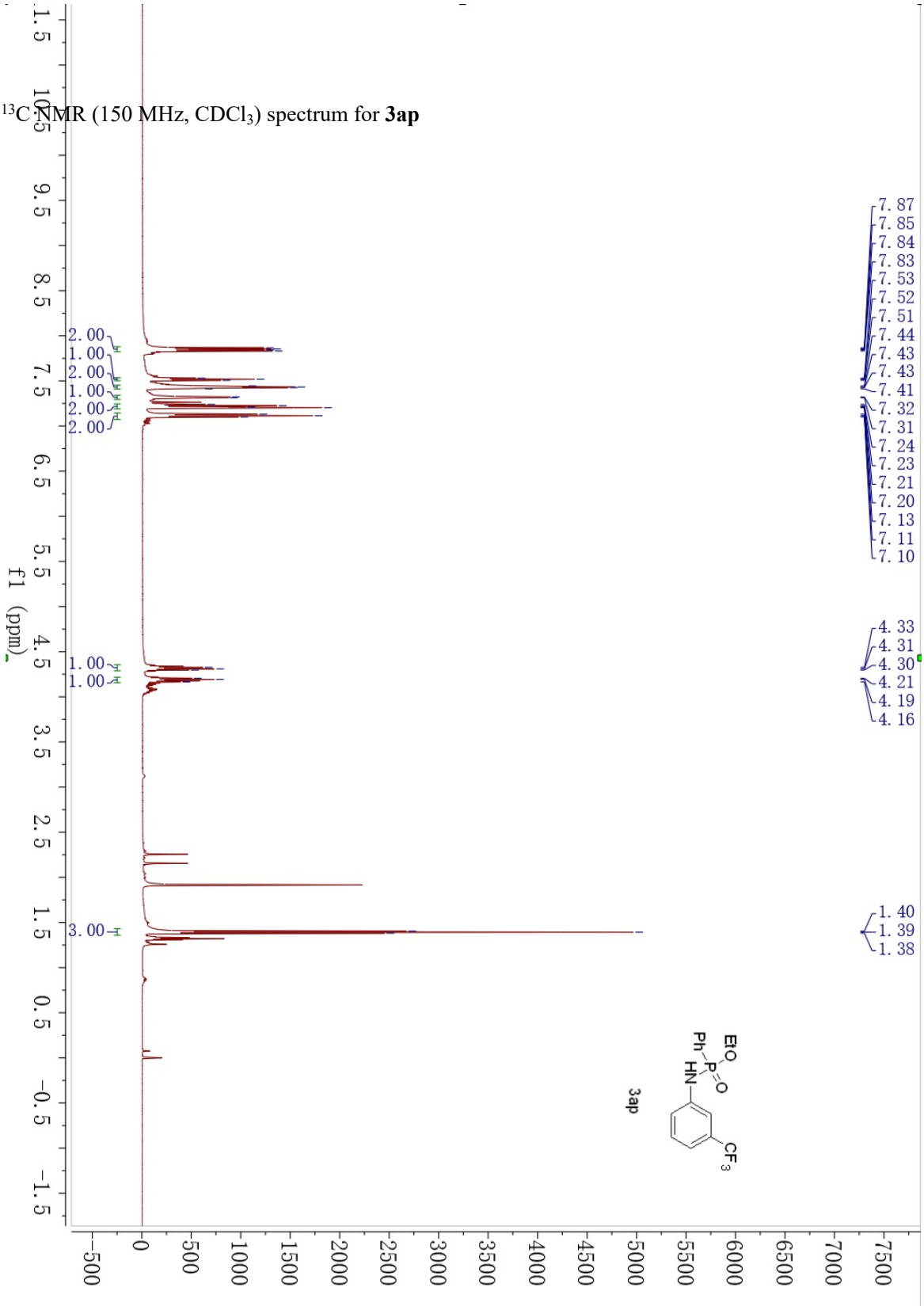
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ao**

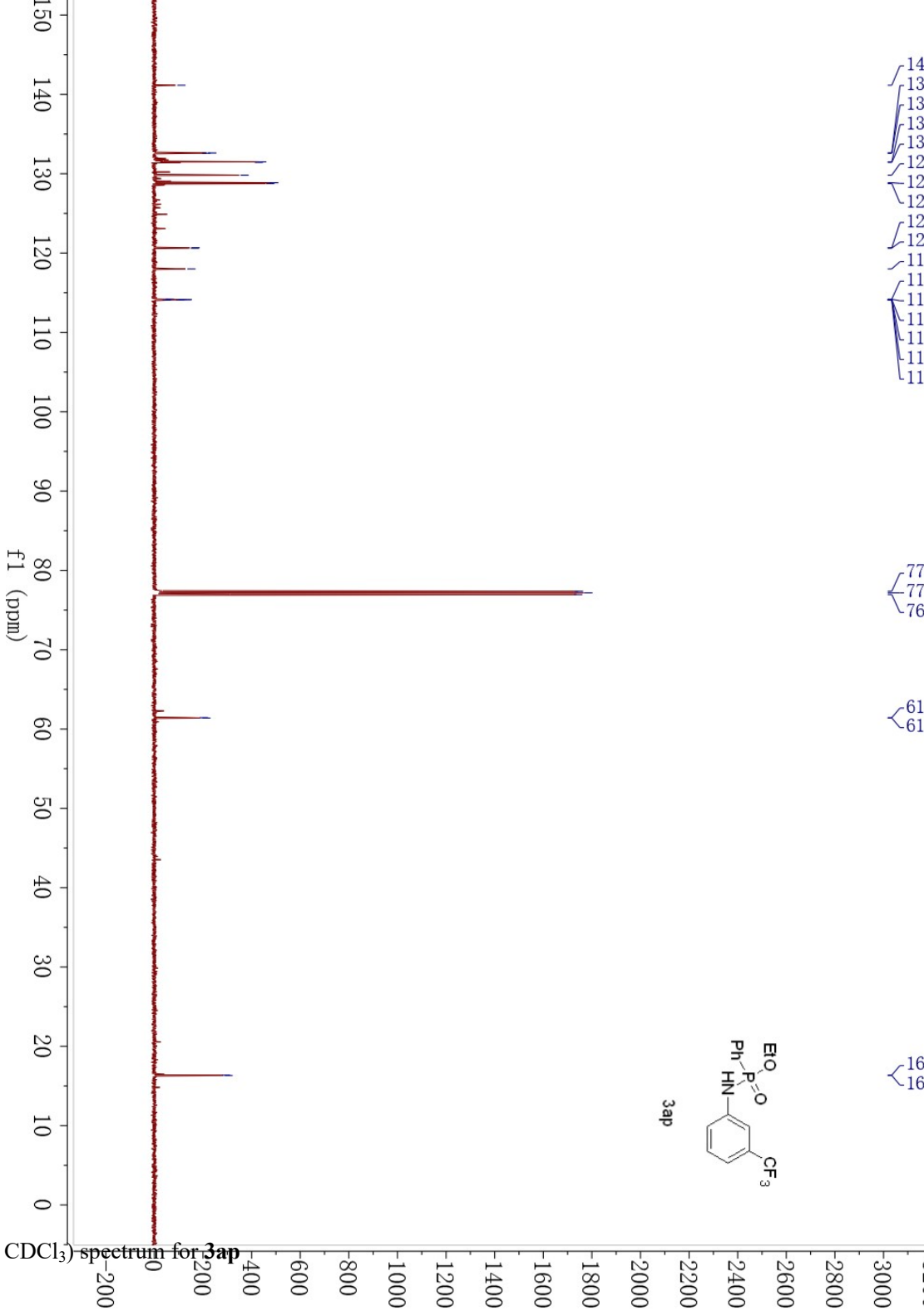




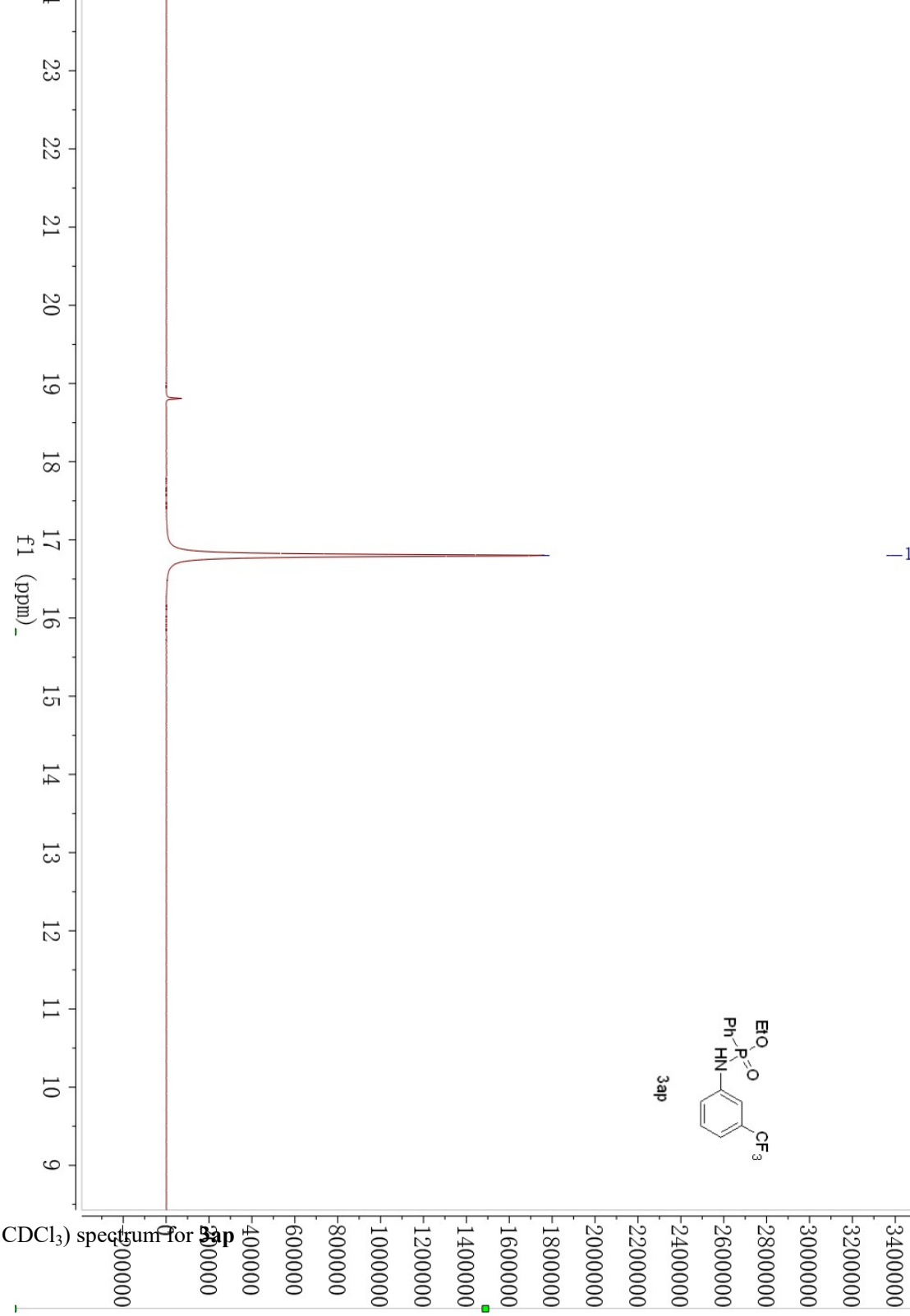
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ap**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ap**

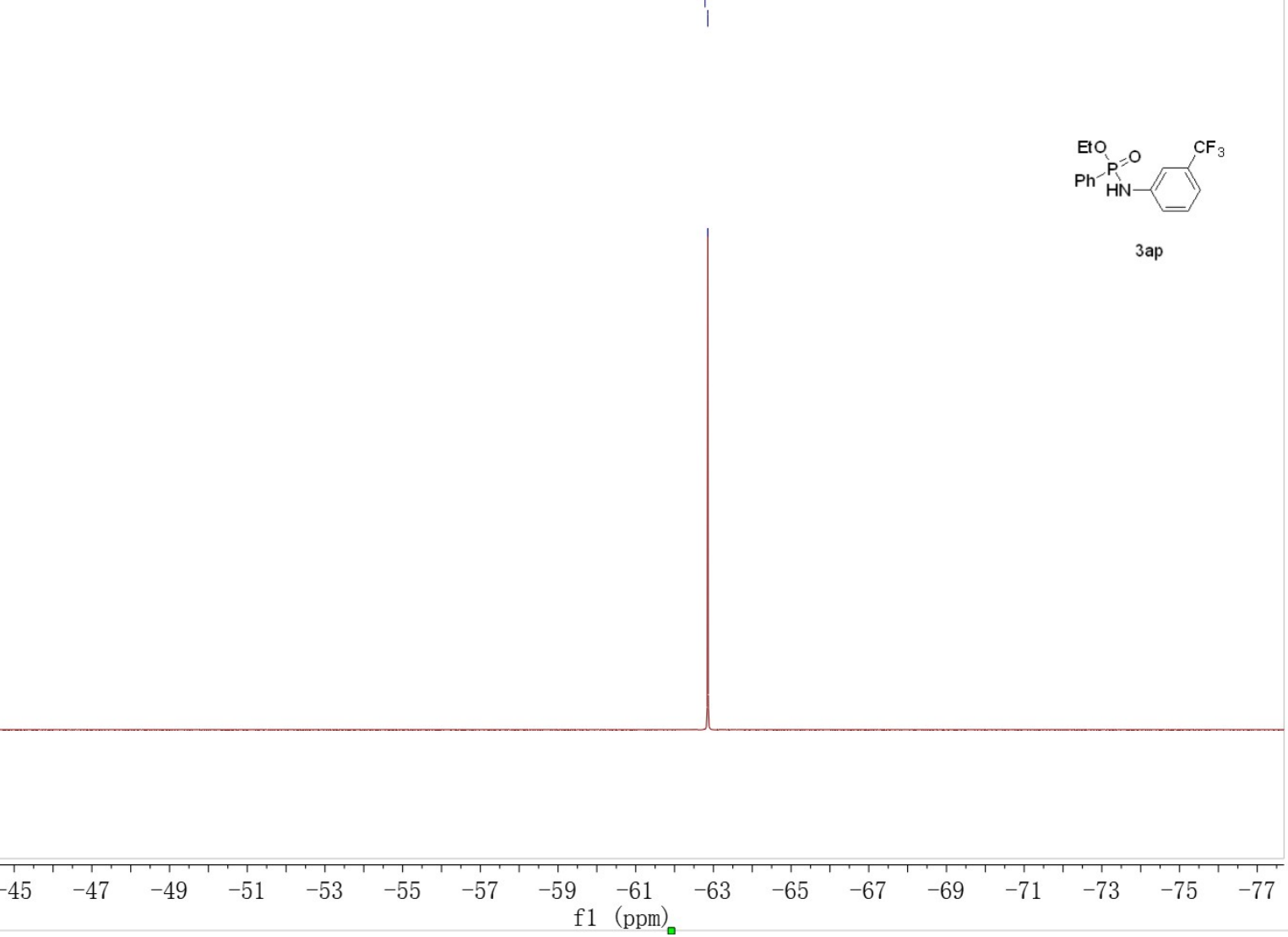




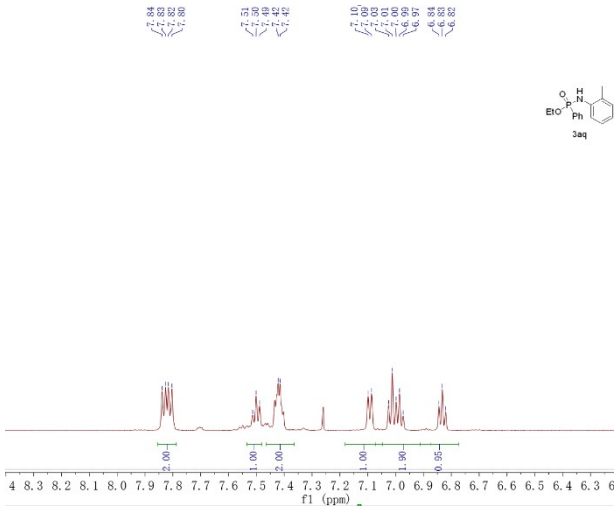
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ap**



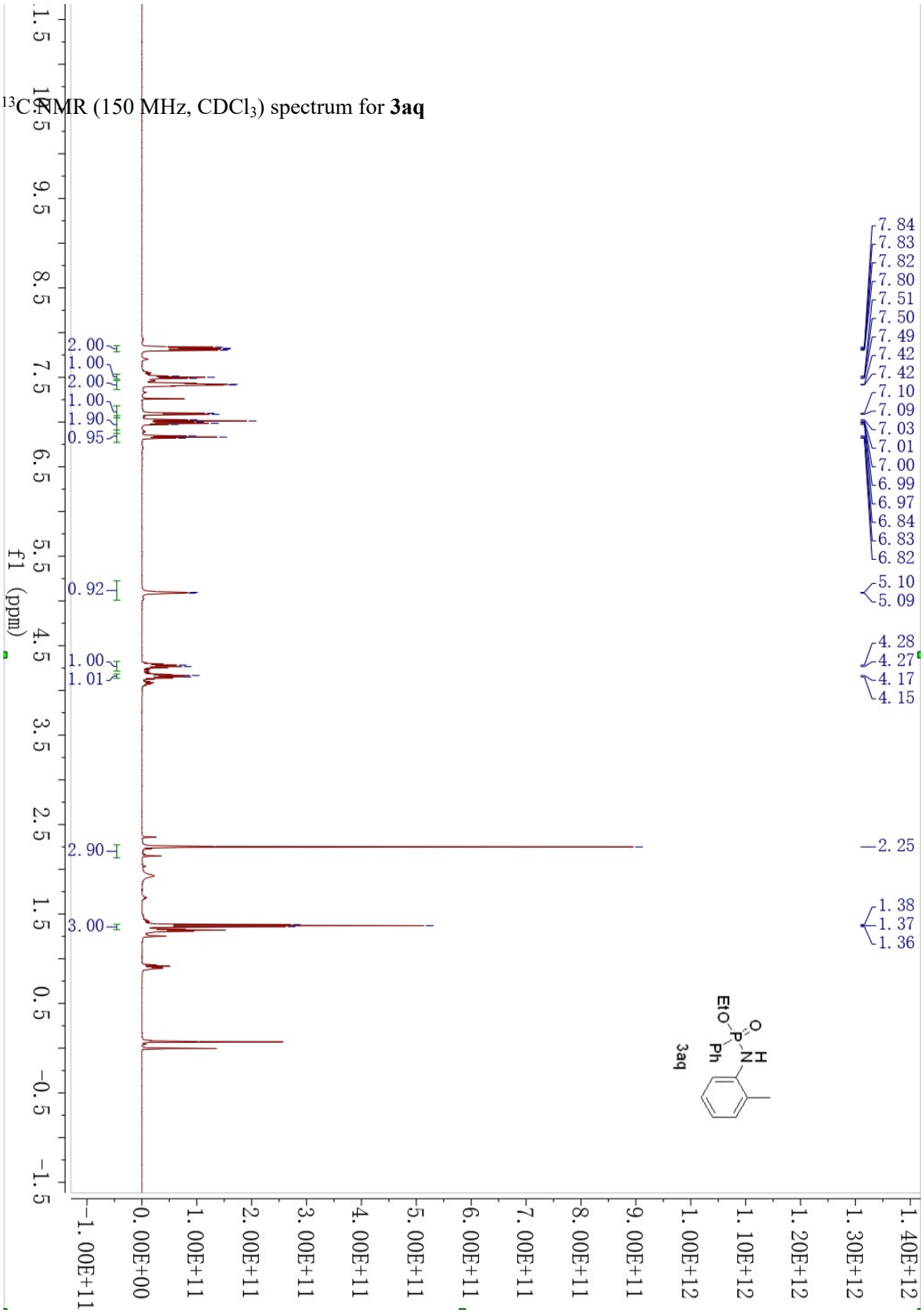
^{19}F NMR (376 MHz, $CDCl_3$) spectrum for **3ap**

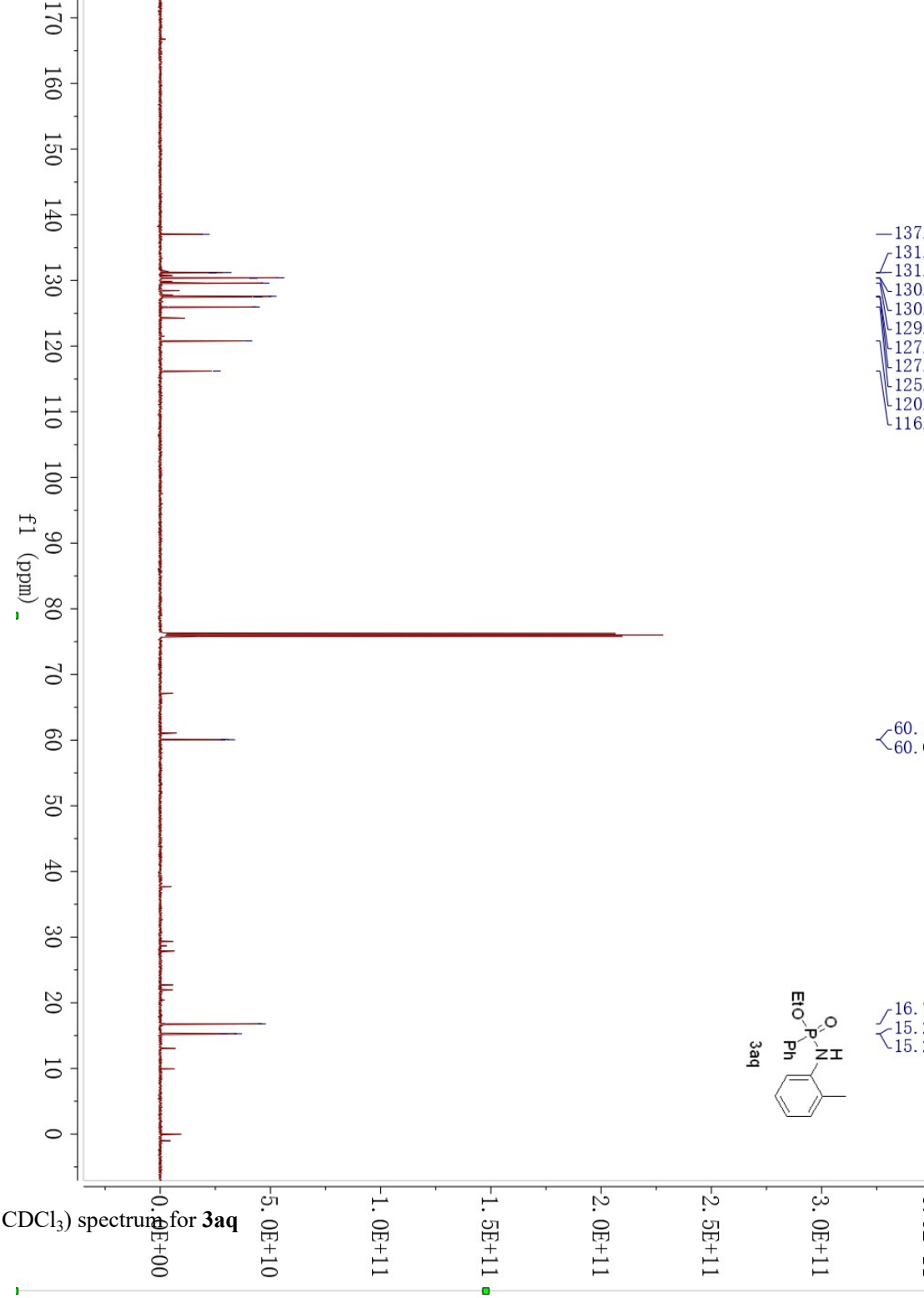


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3aq**

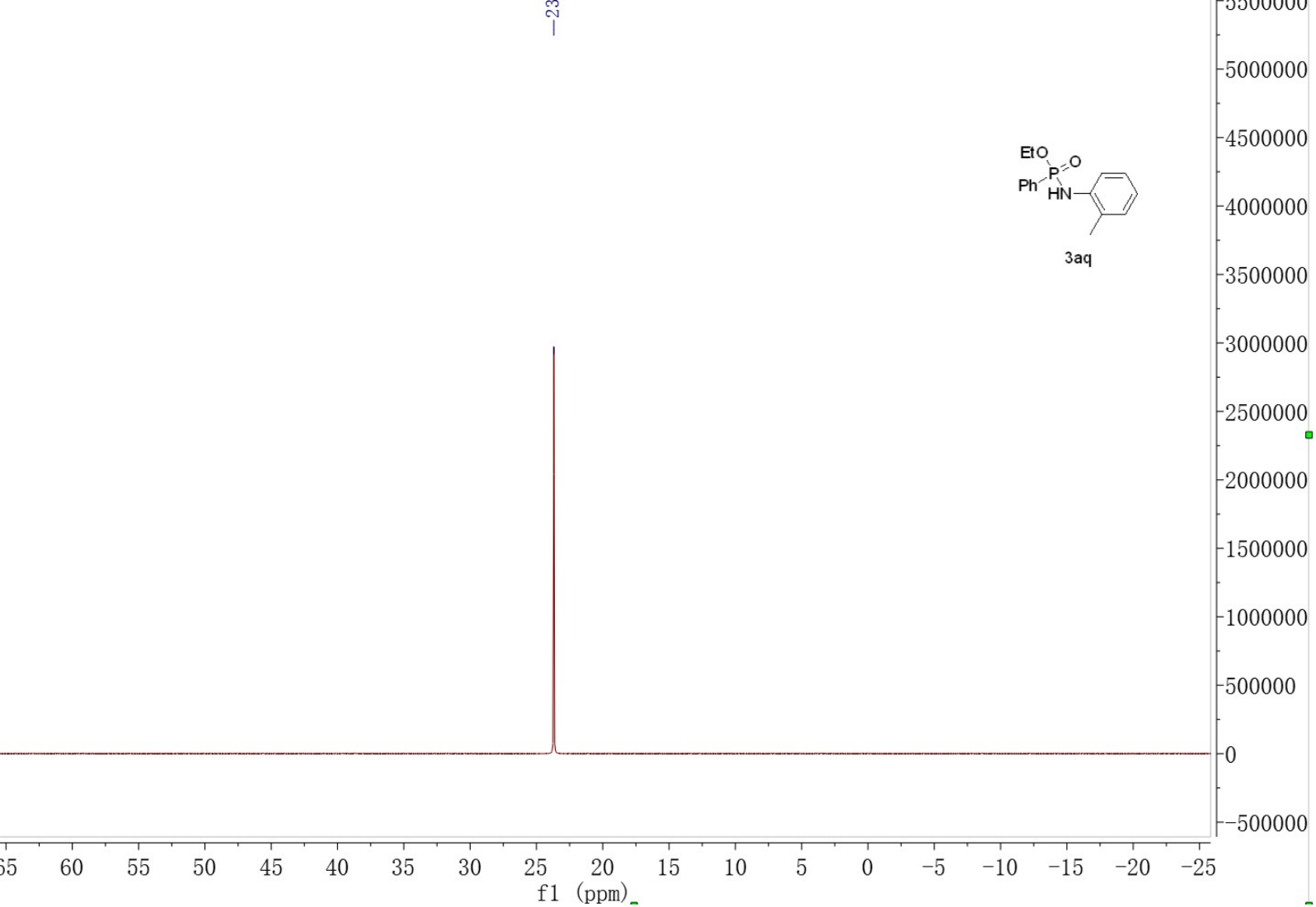


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3aq**



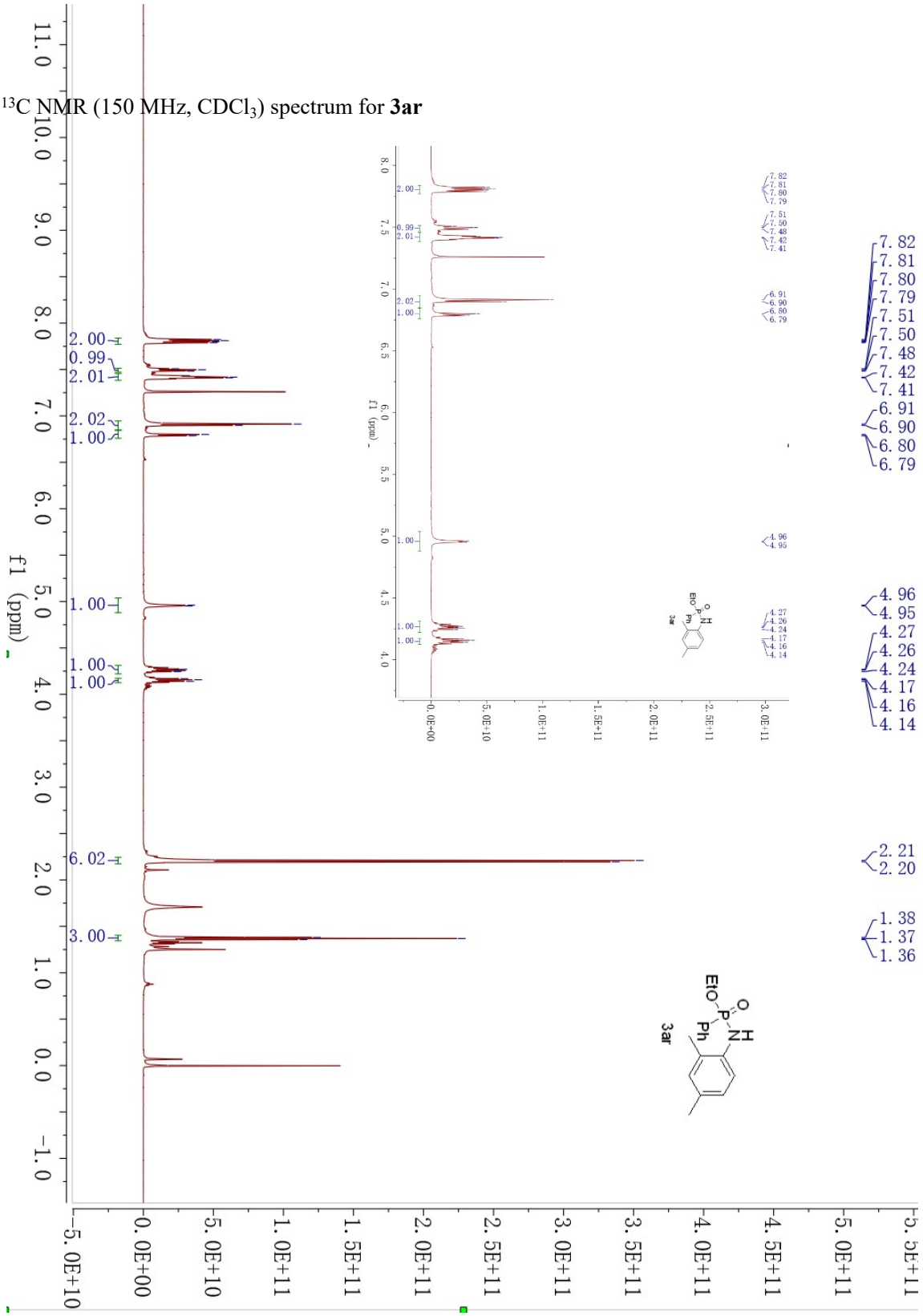


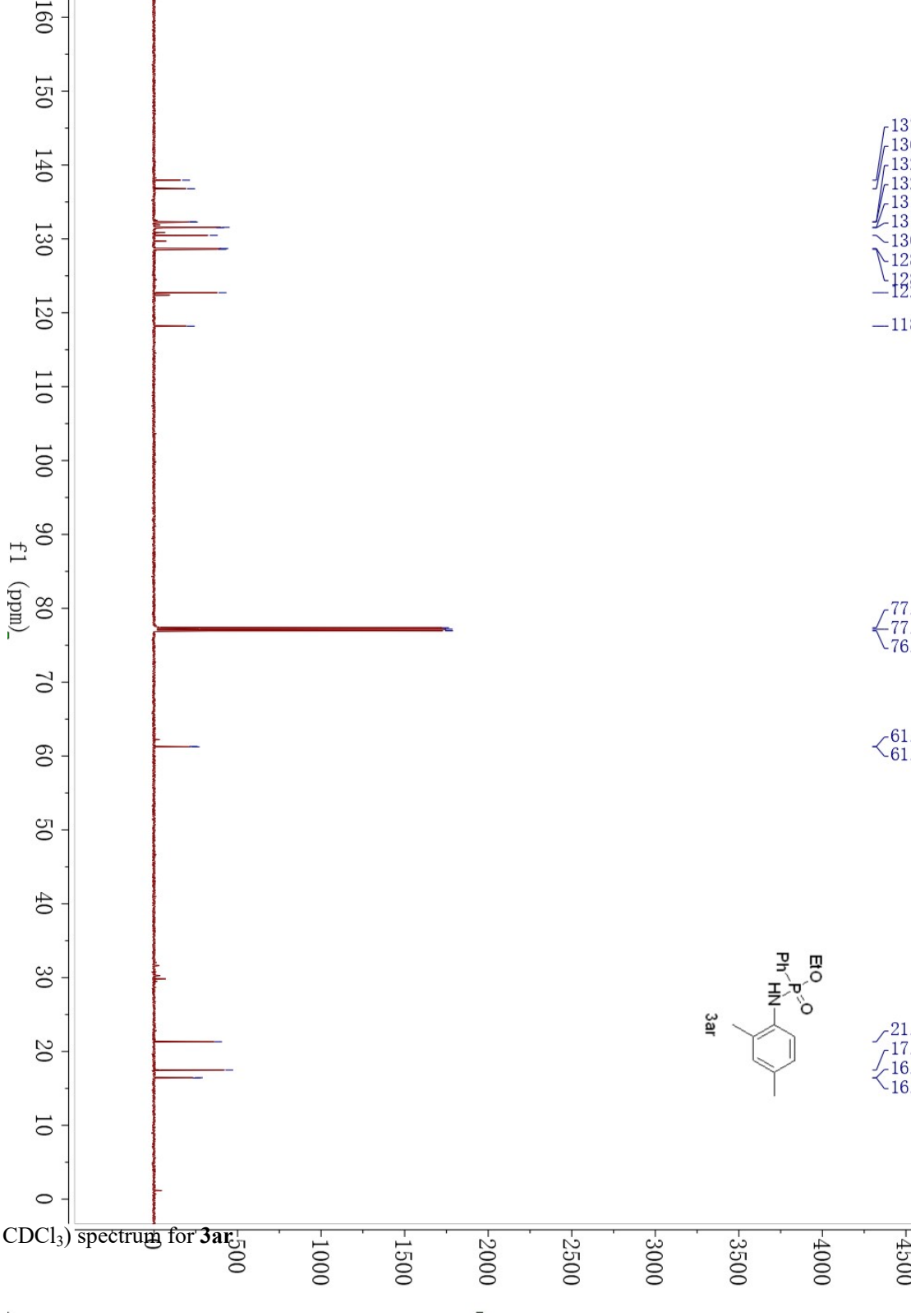
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3aq**


23.
EtO
O
P
Ph
HN
3aq
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ar**

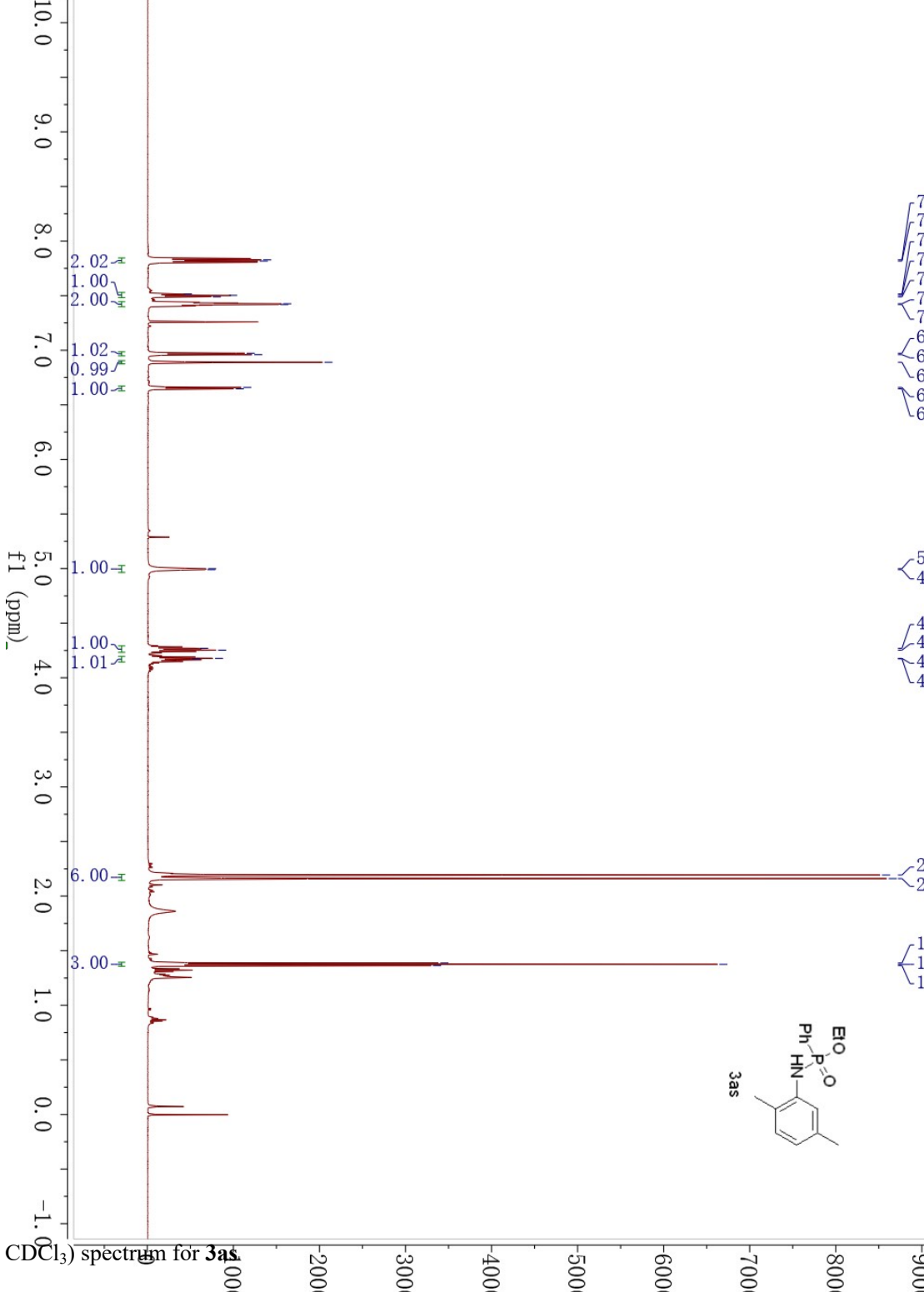
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ar**



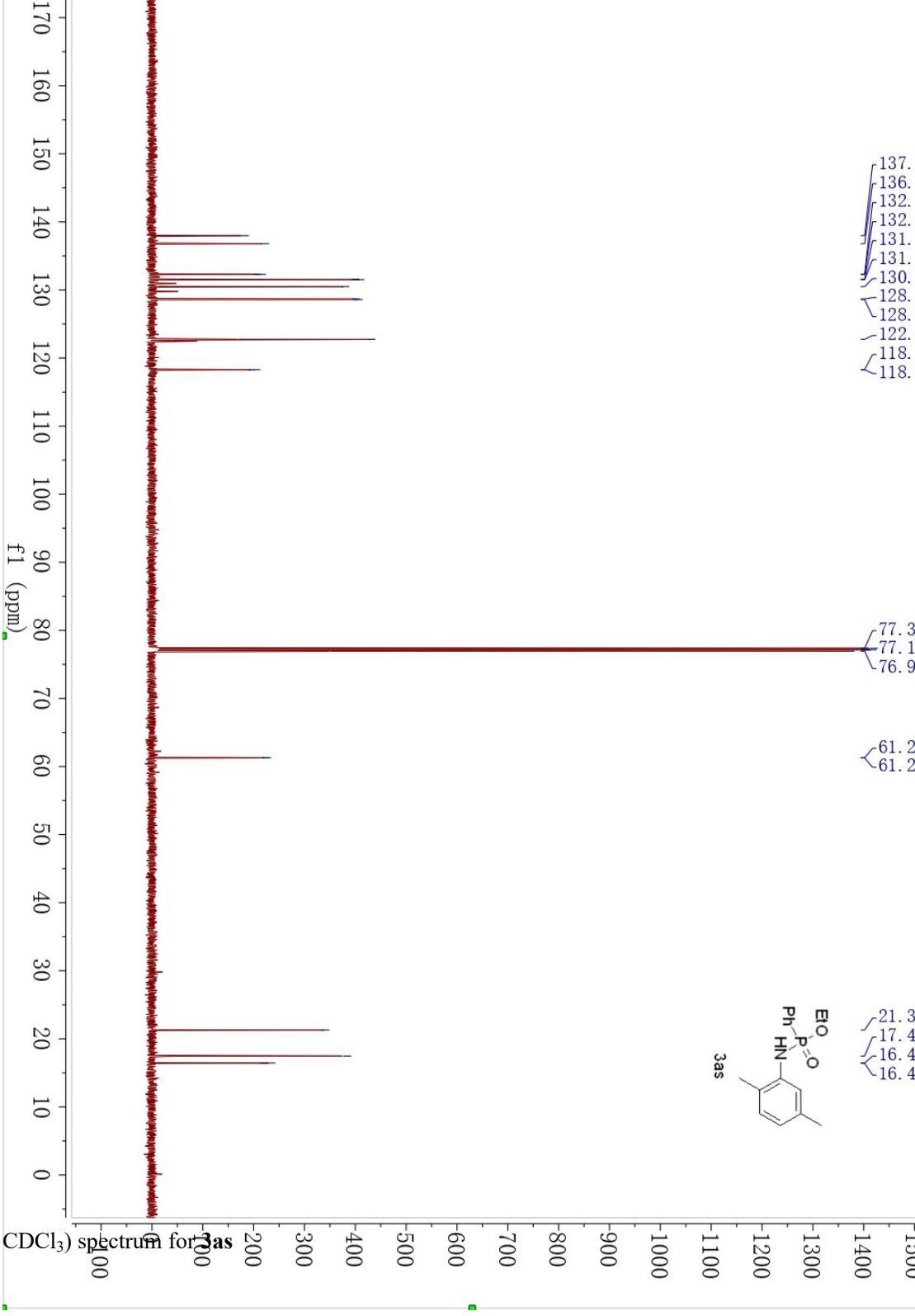


^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ar**.

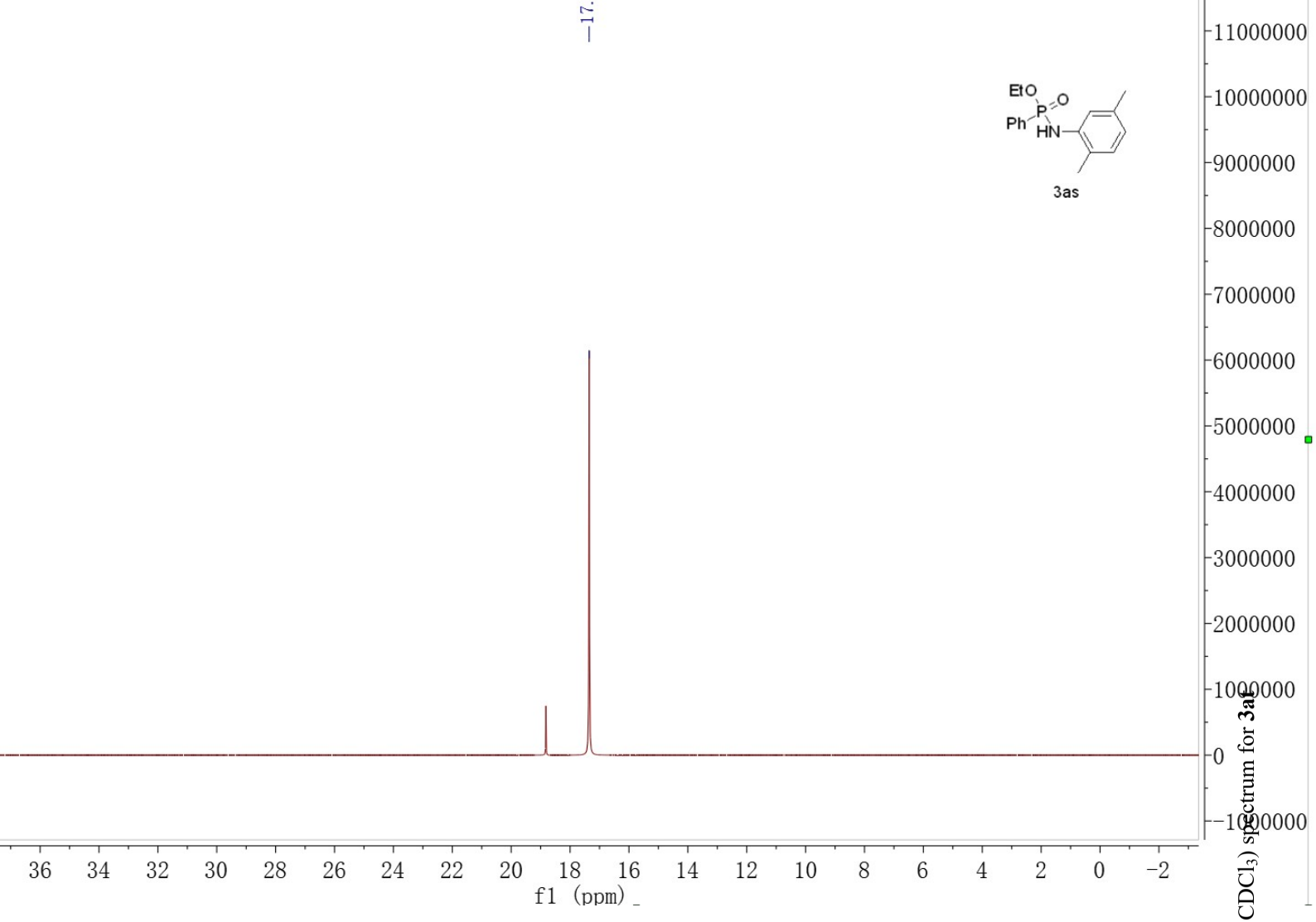
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3as**

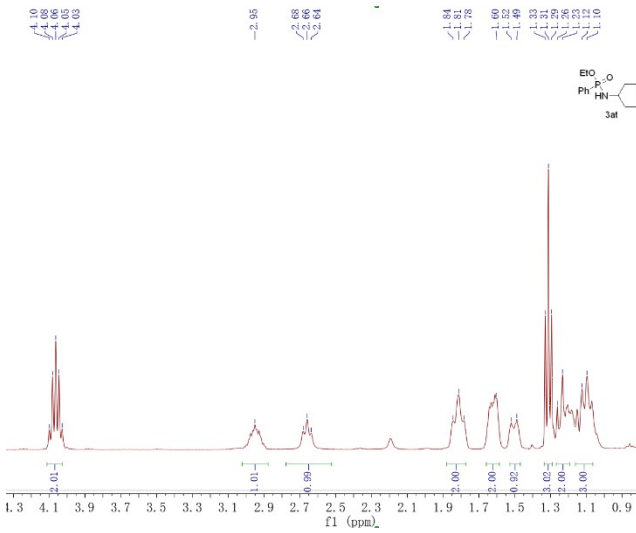


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3as**.



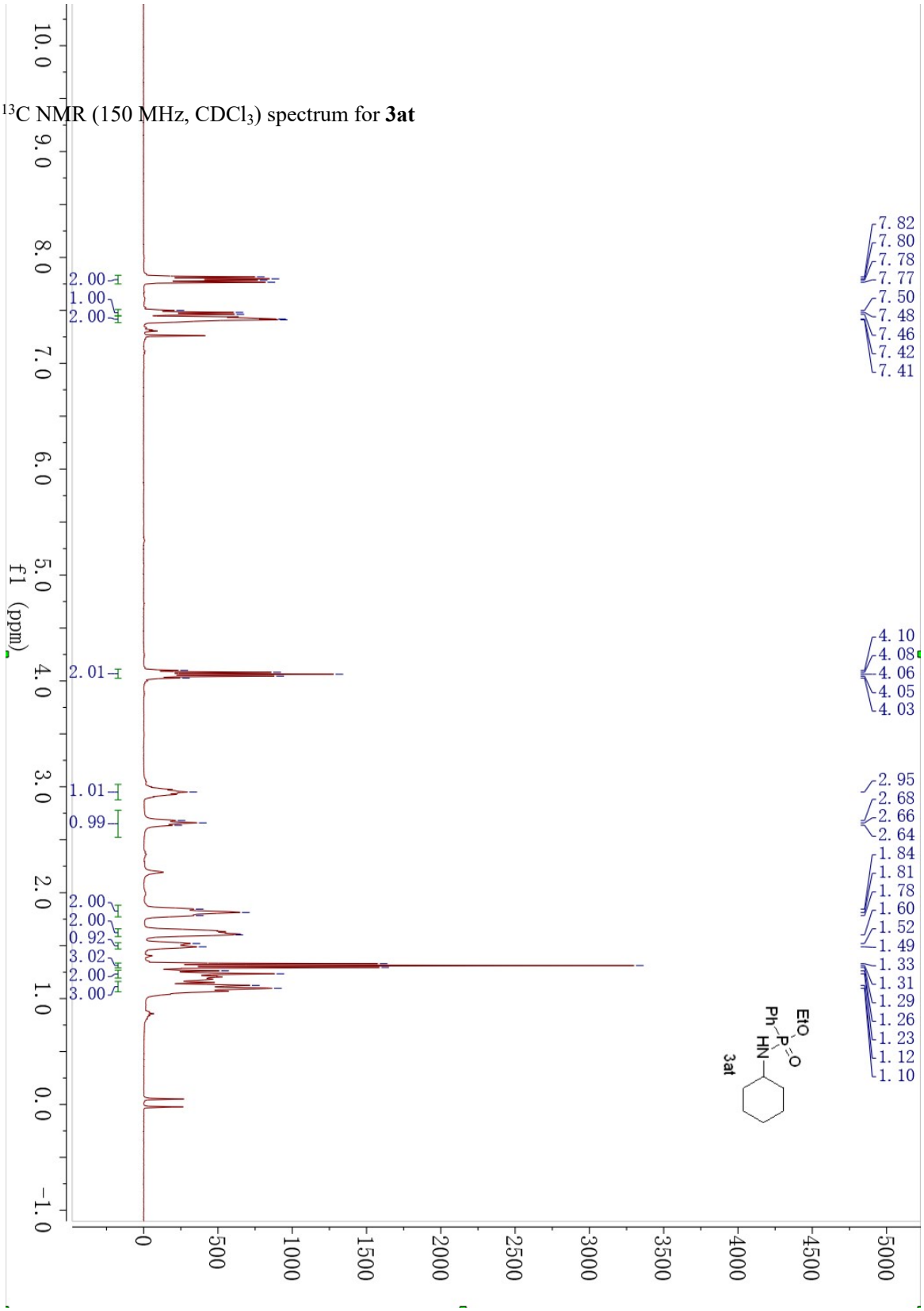
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3as**

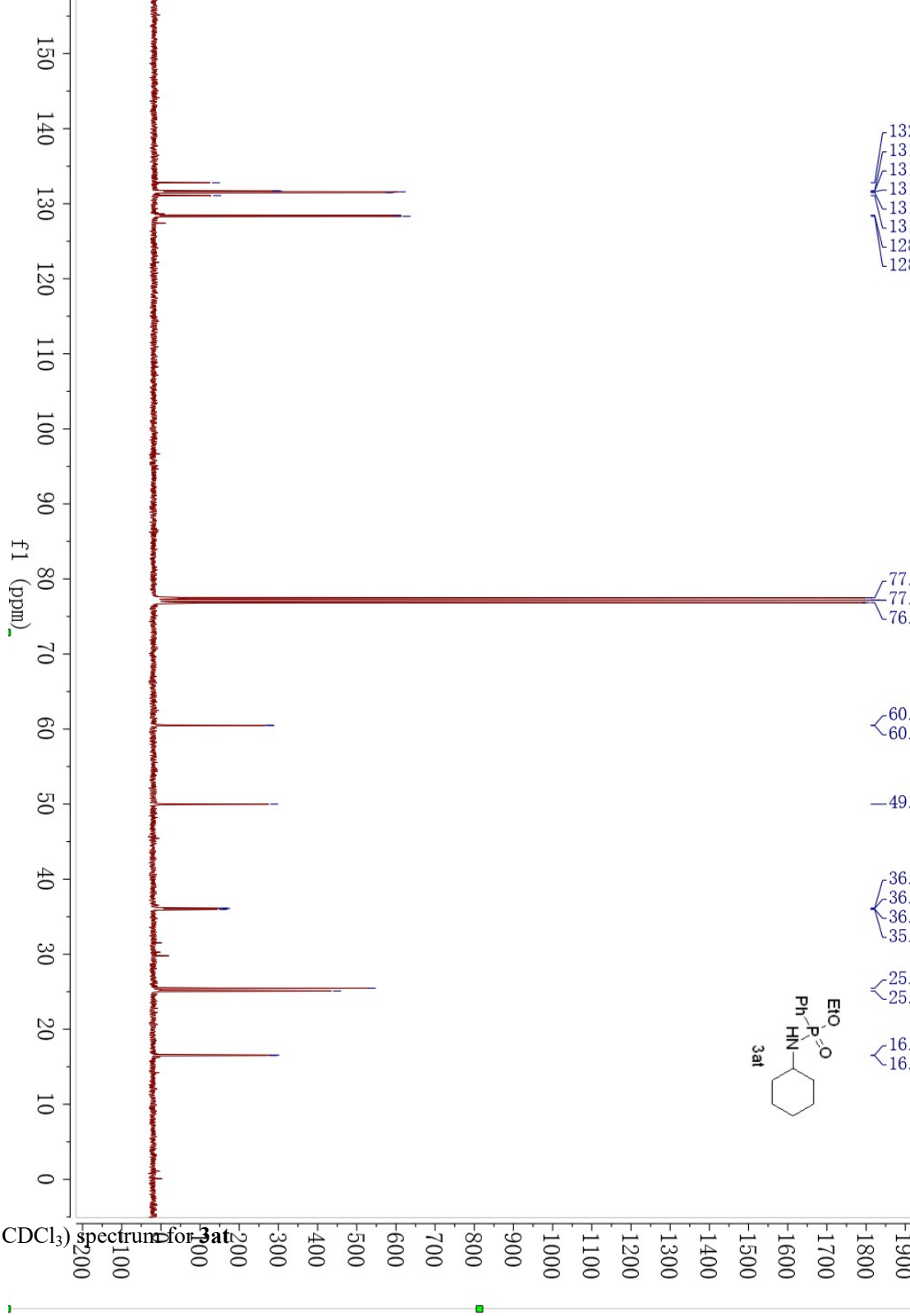




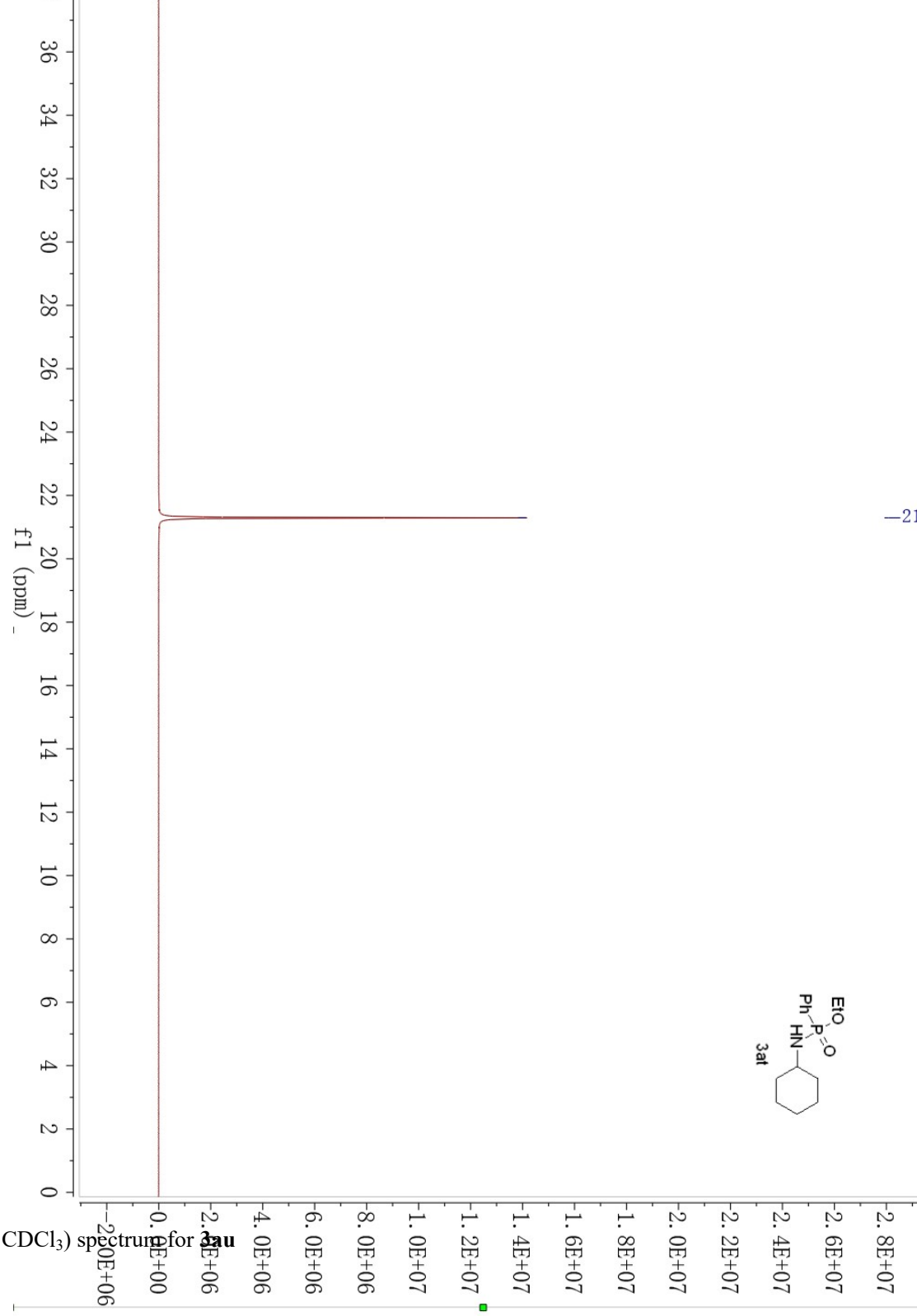
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3at**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3at**

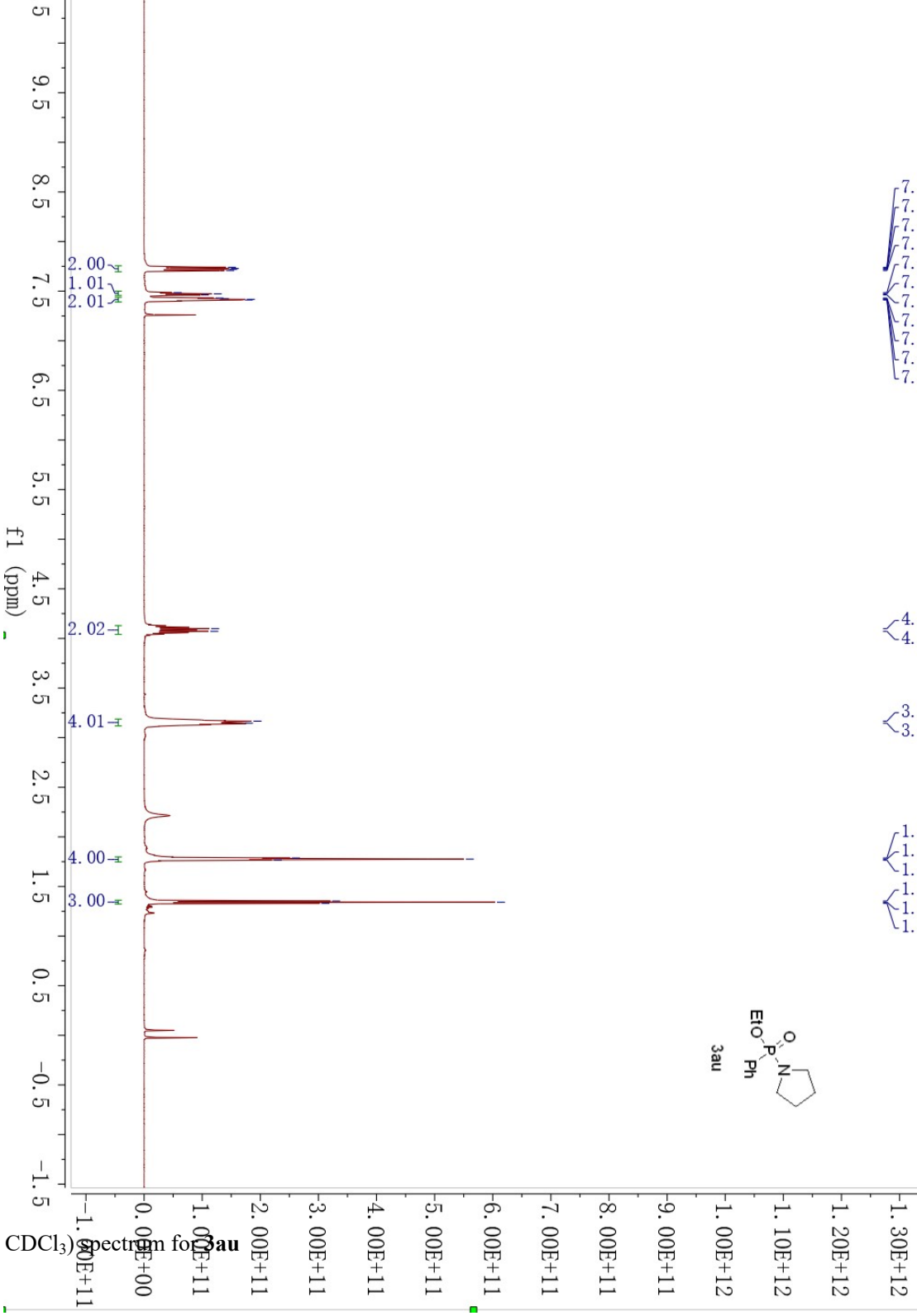




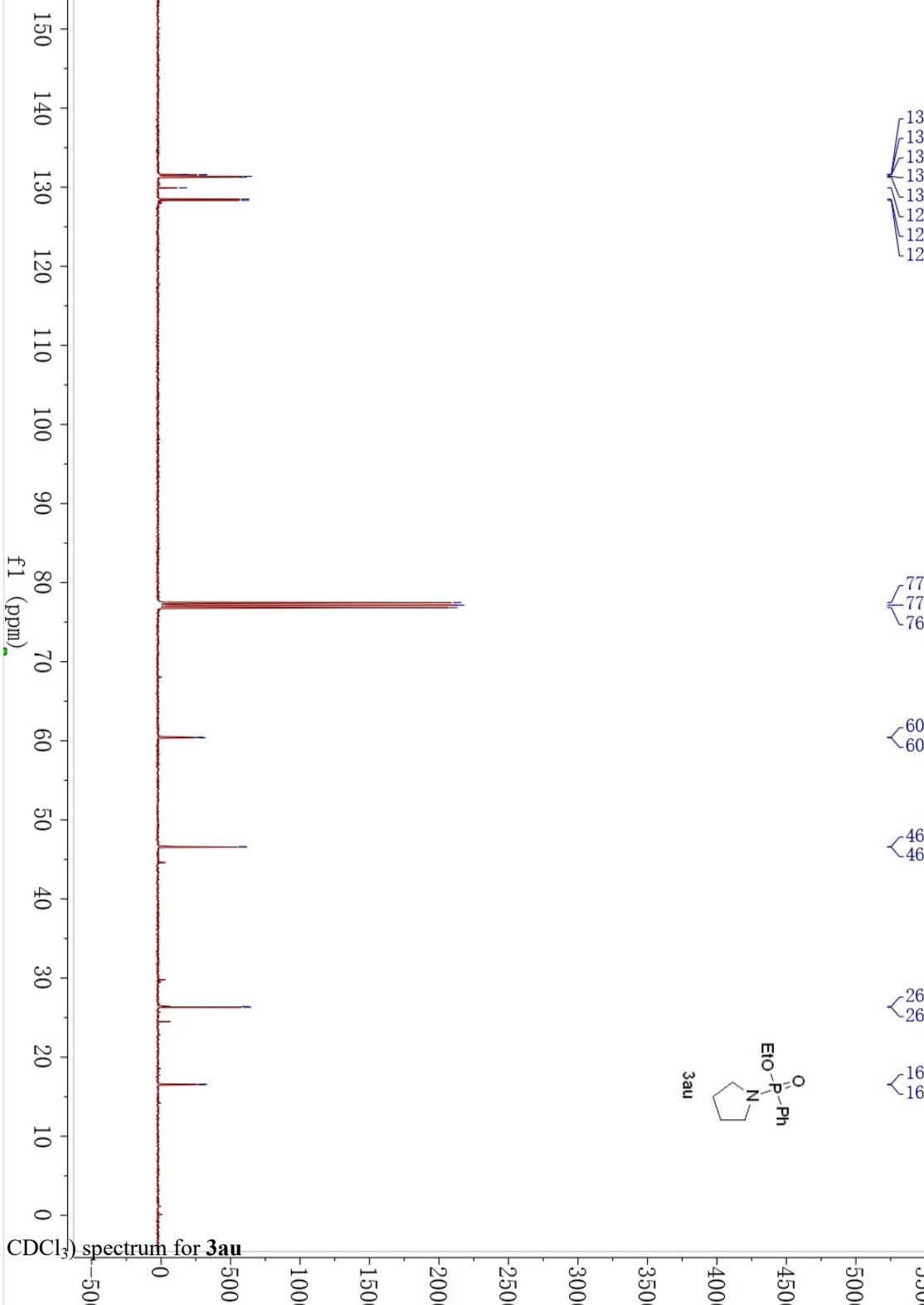
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3at**



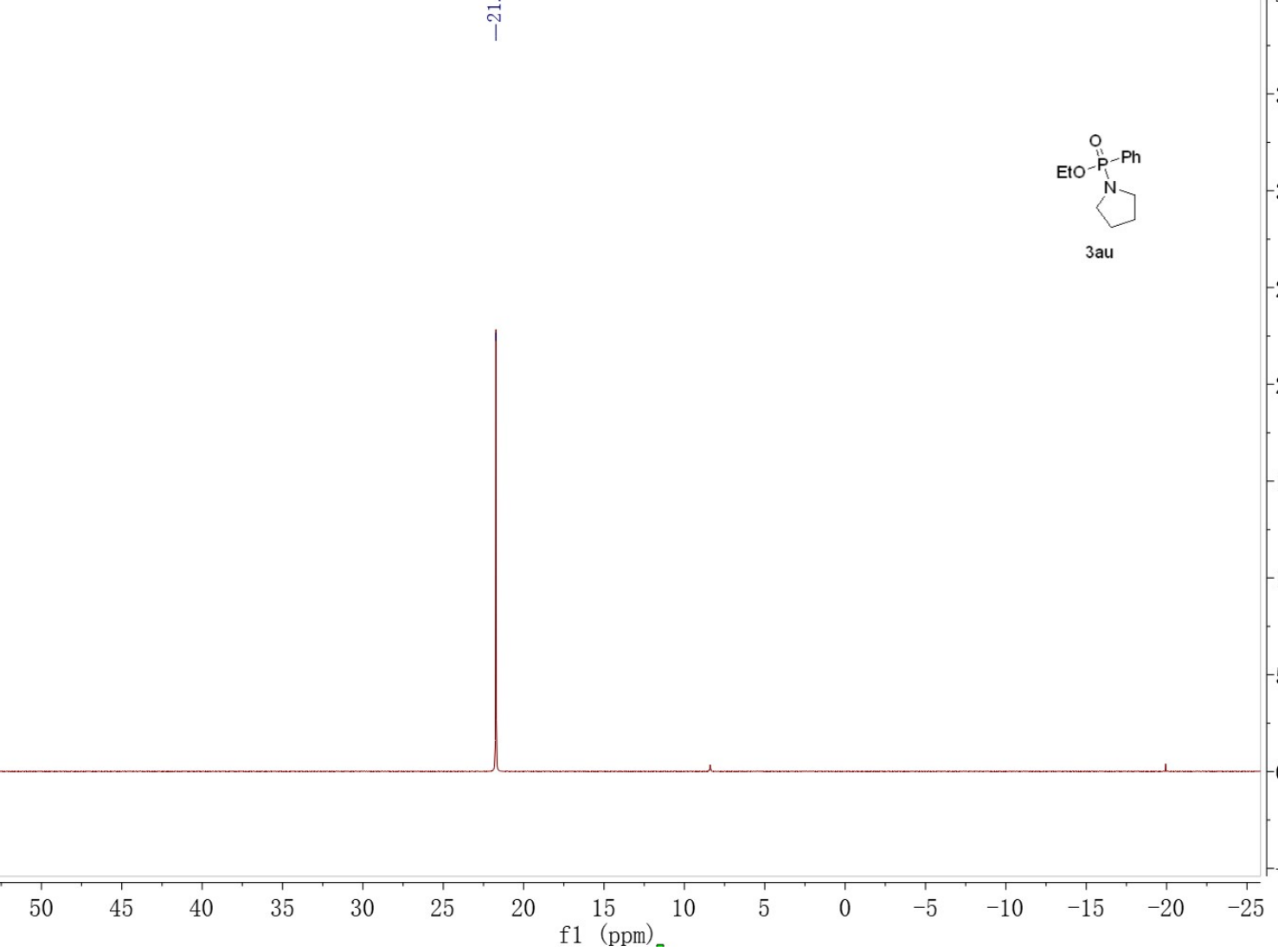
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3au**

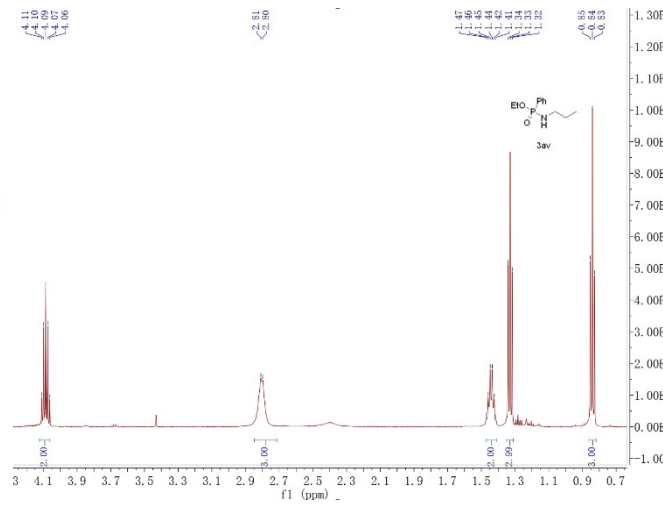


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3au**



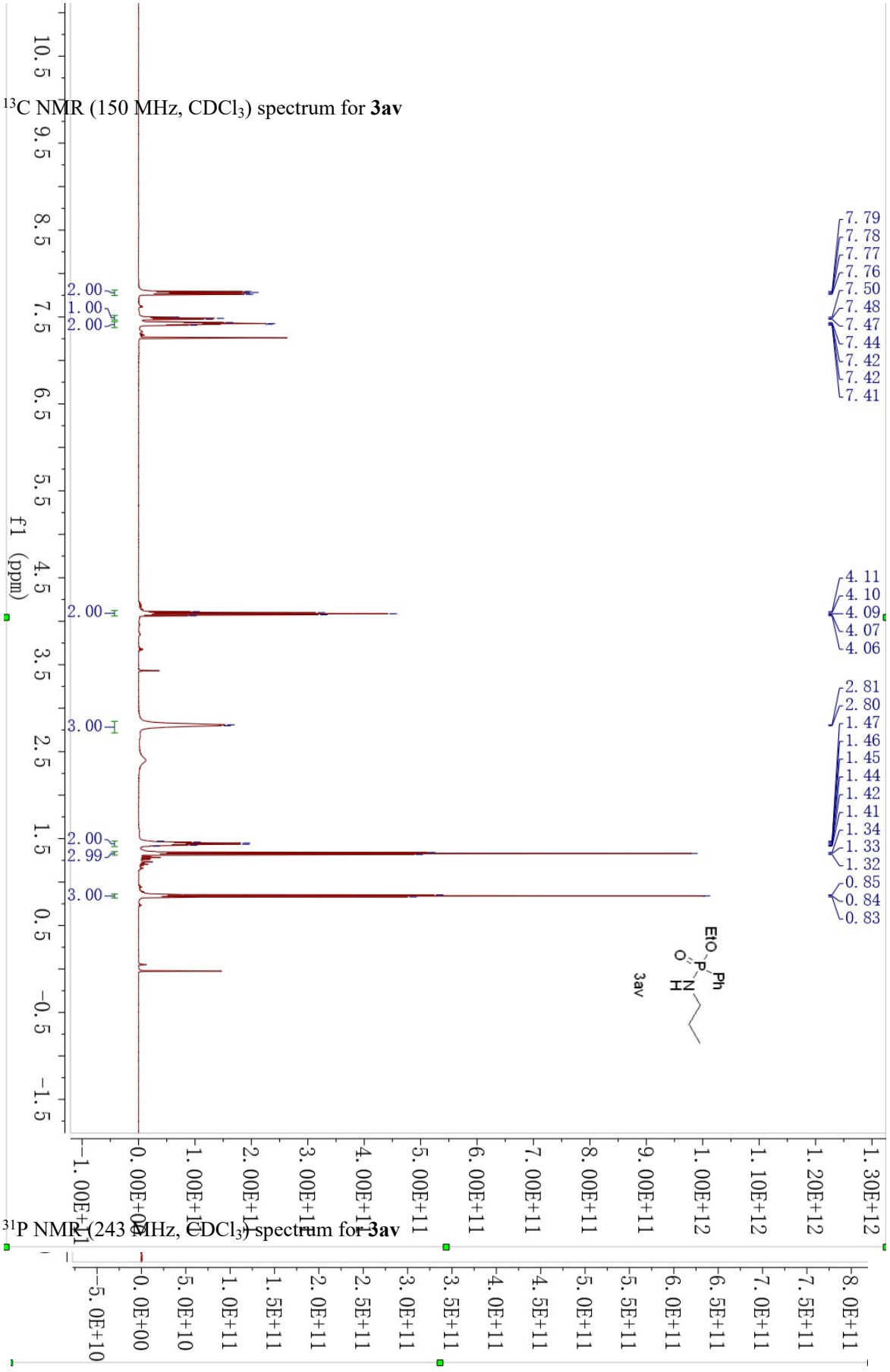
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3au**



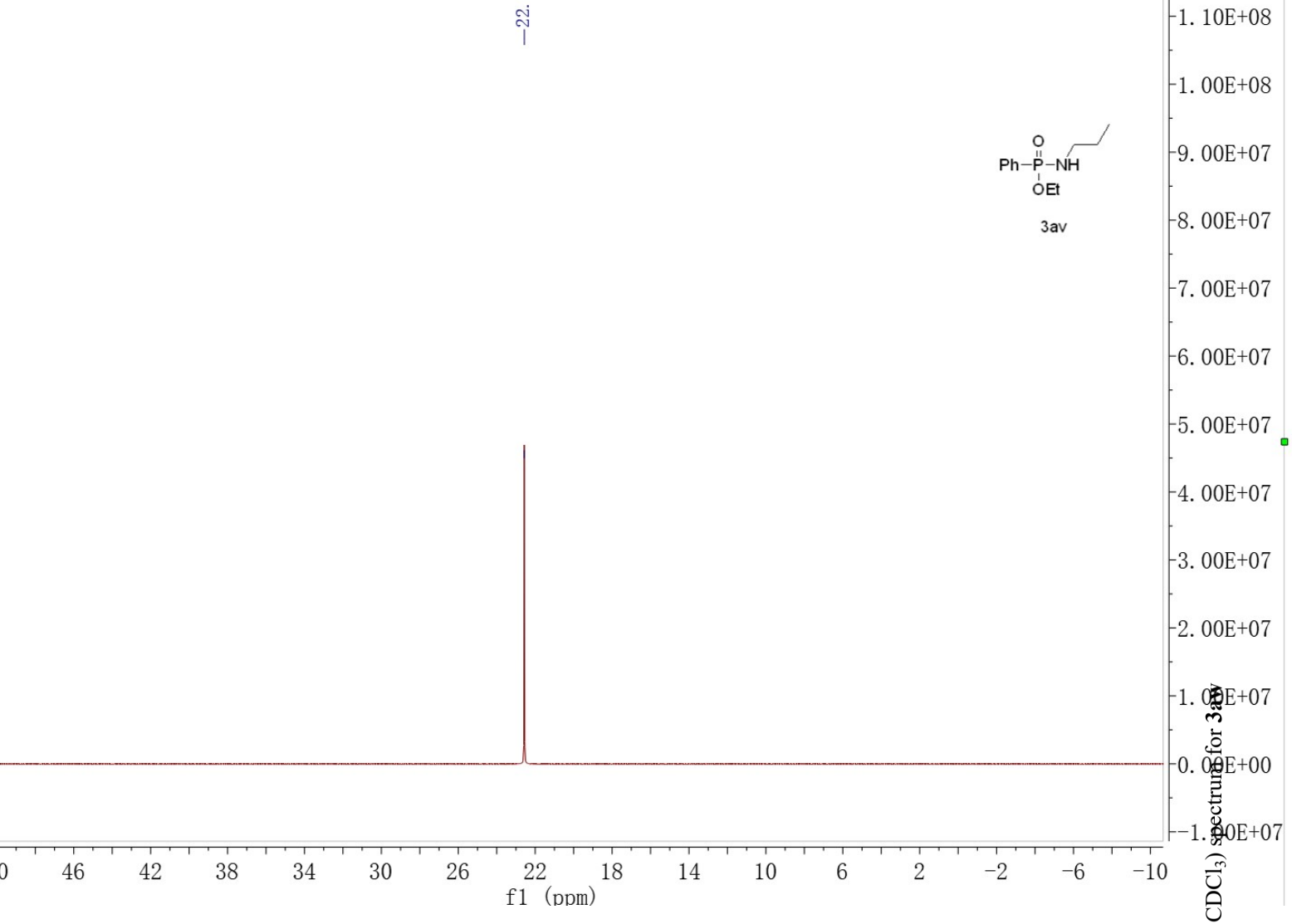


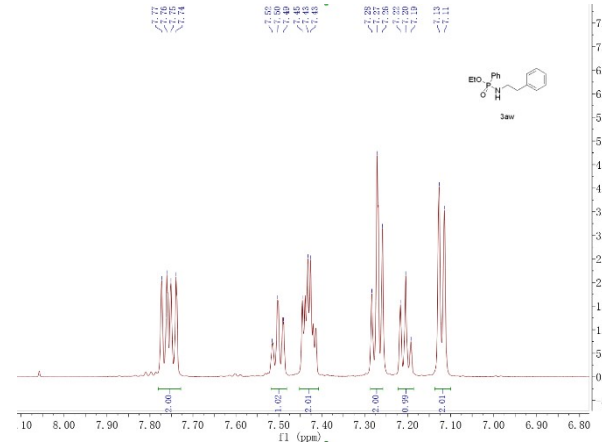
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3av**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3av**



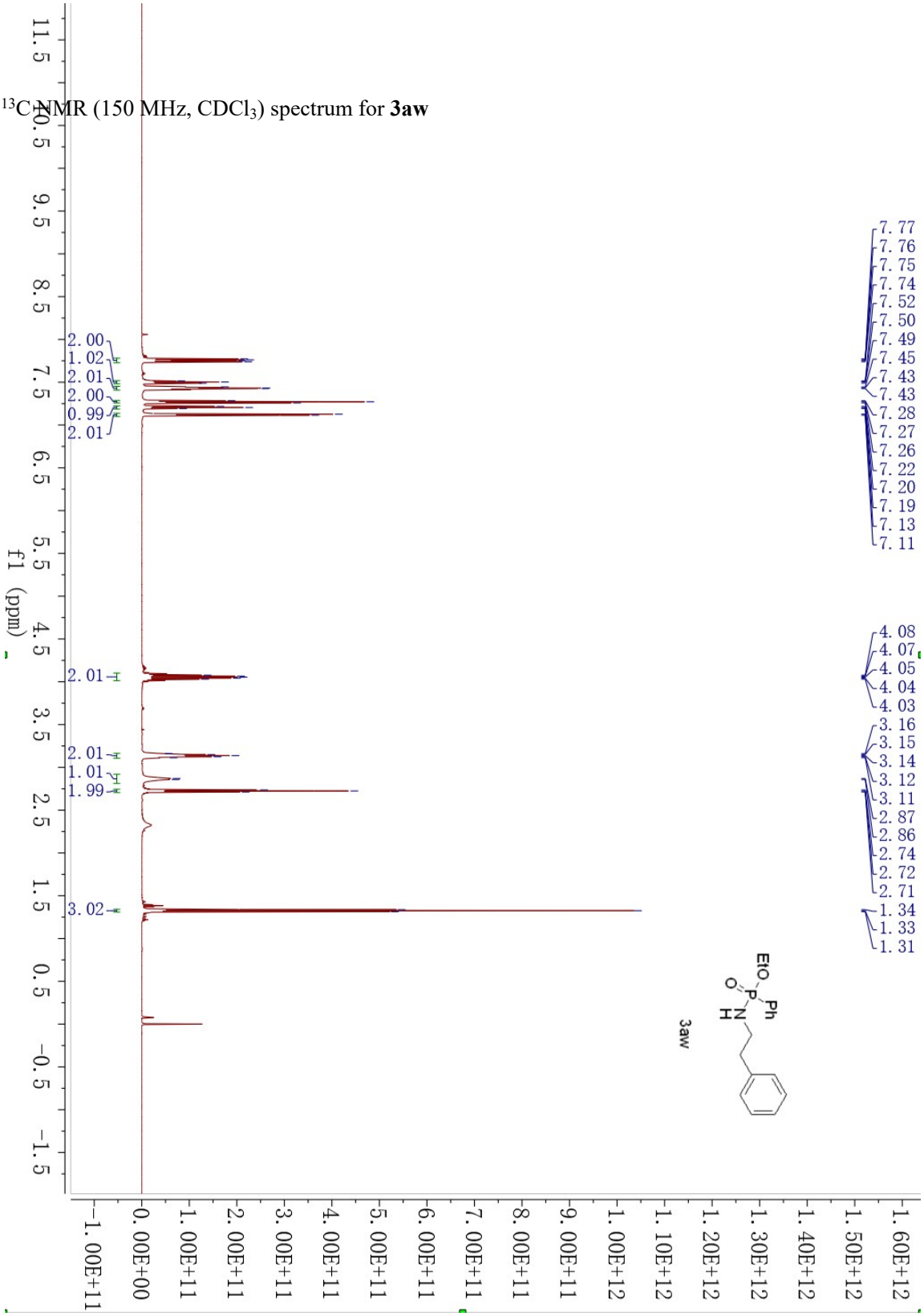
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3av**

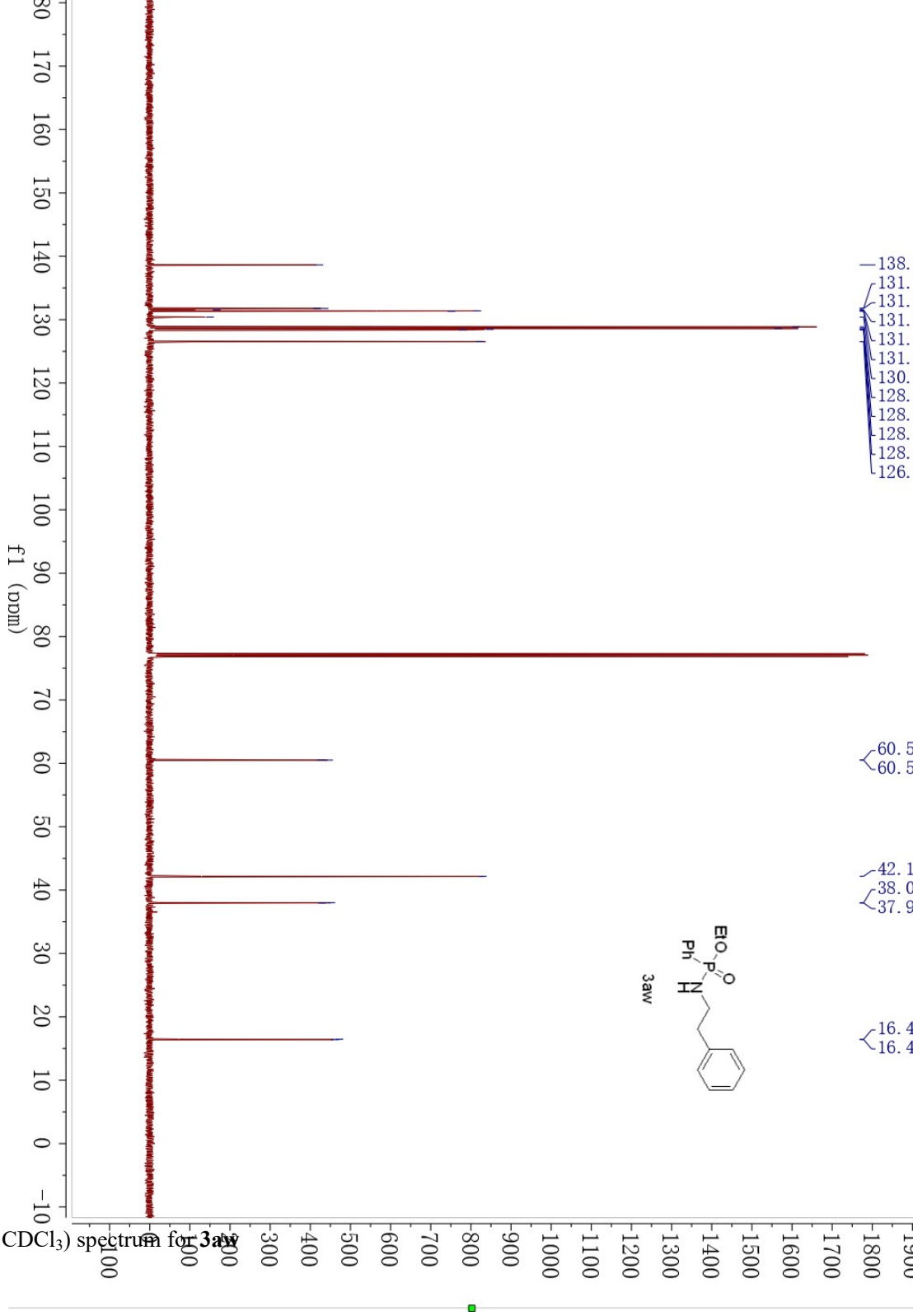




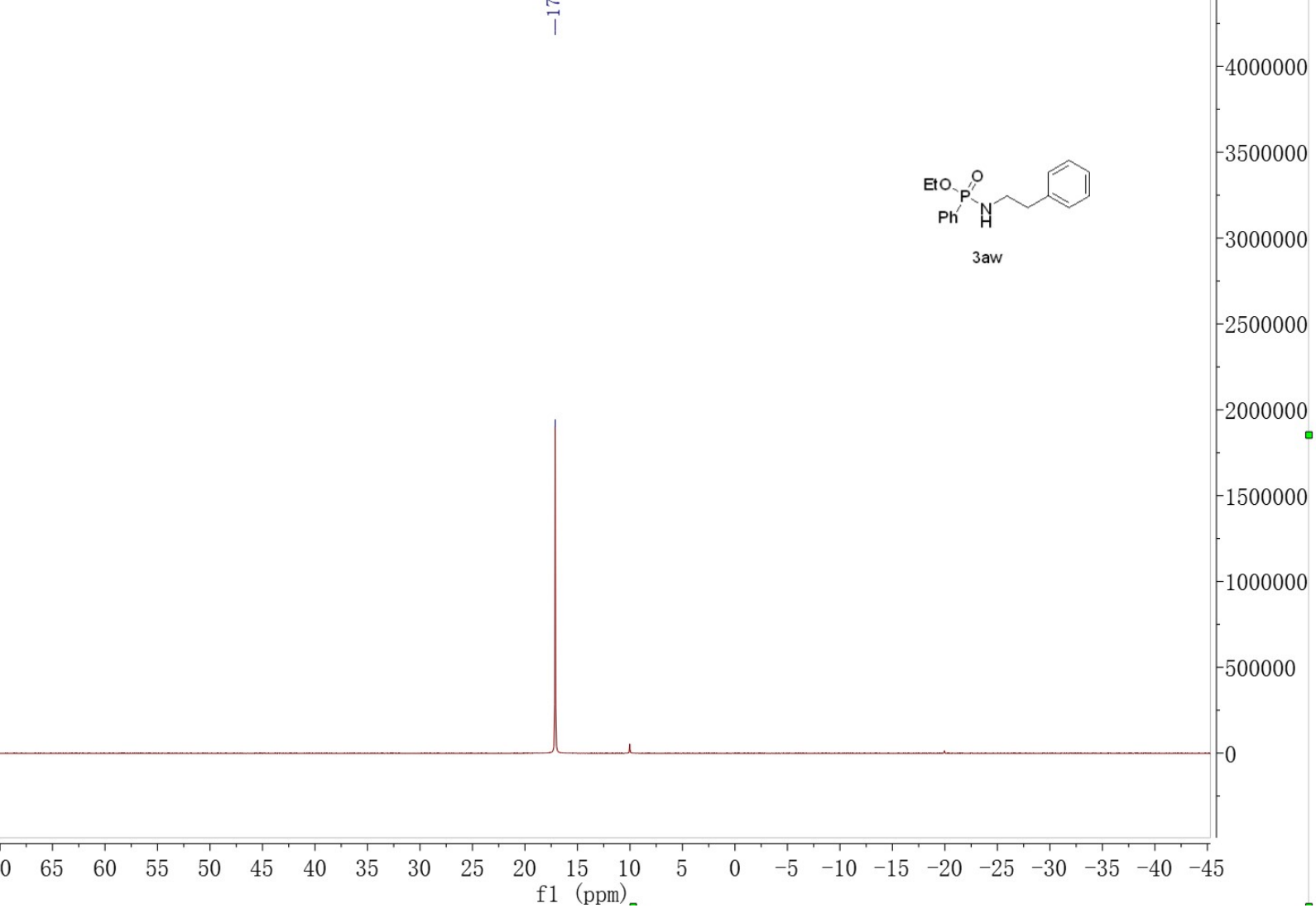
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3av**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3aw**





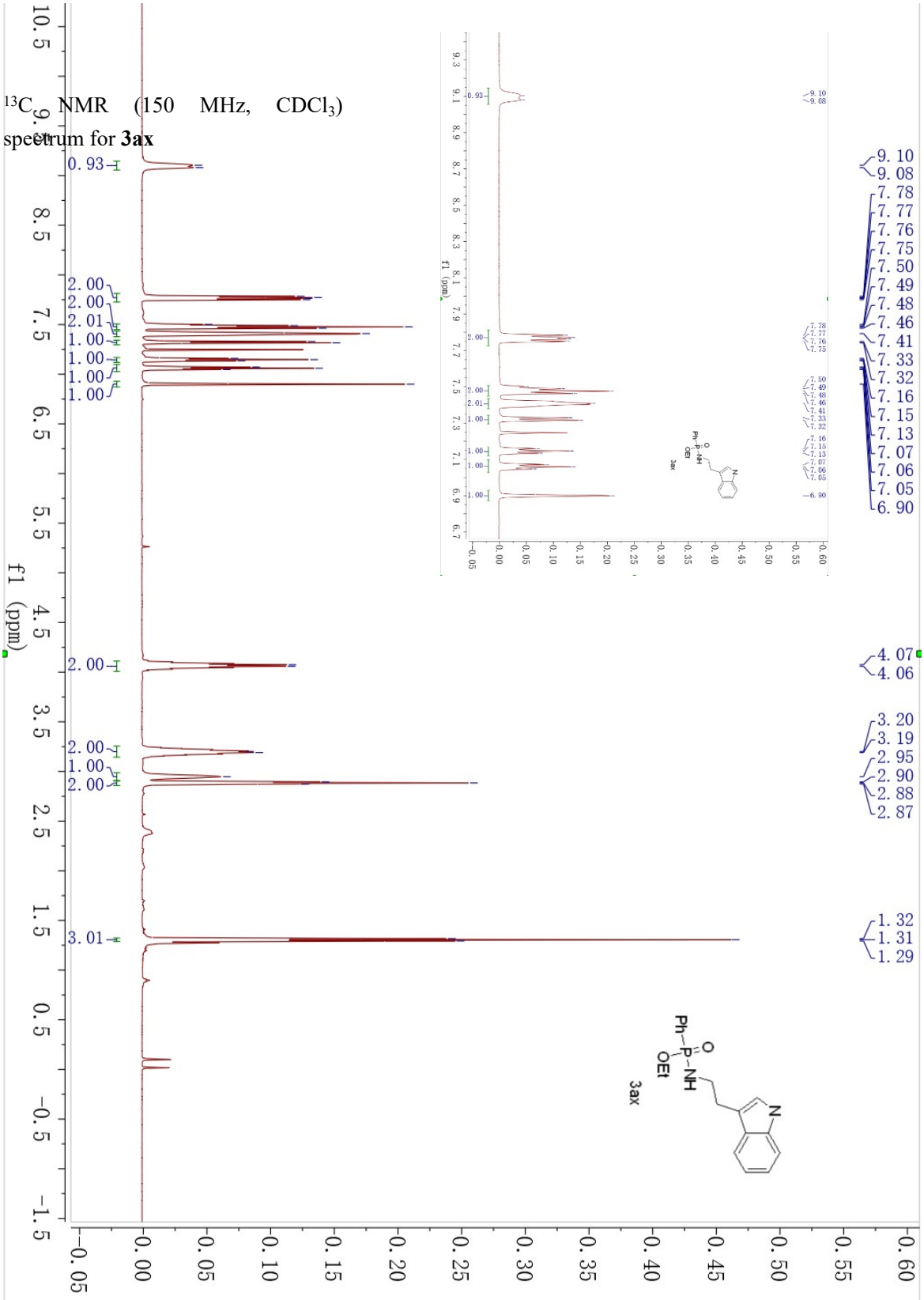
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3aw**


4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)

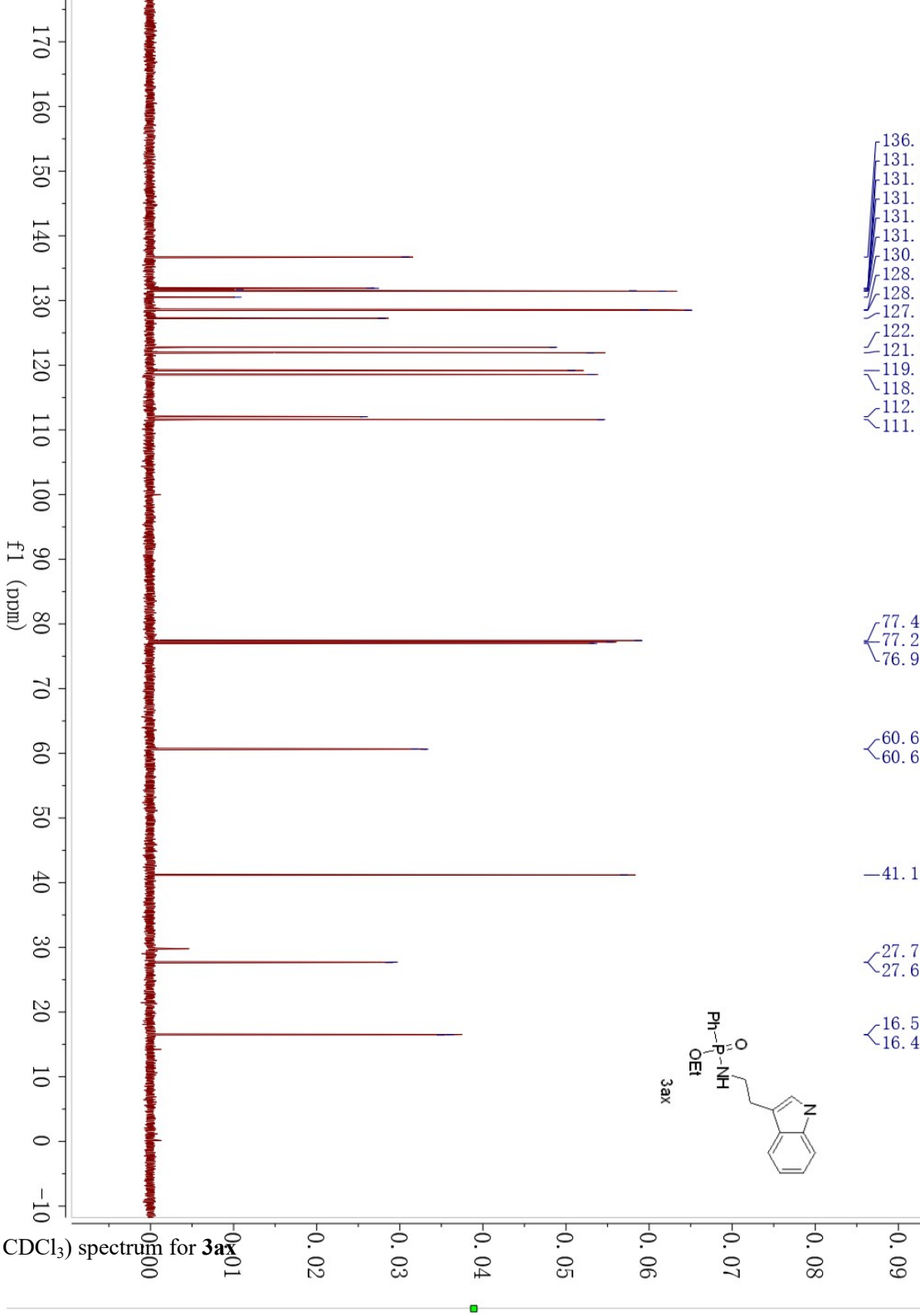
EtO
O
P
Ph
N
H

3aw

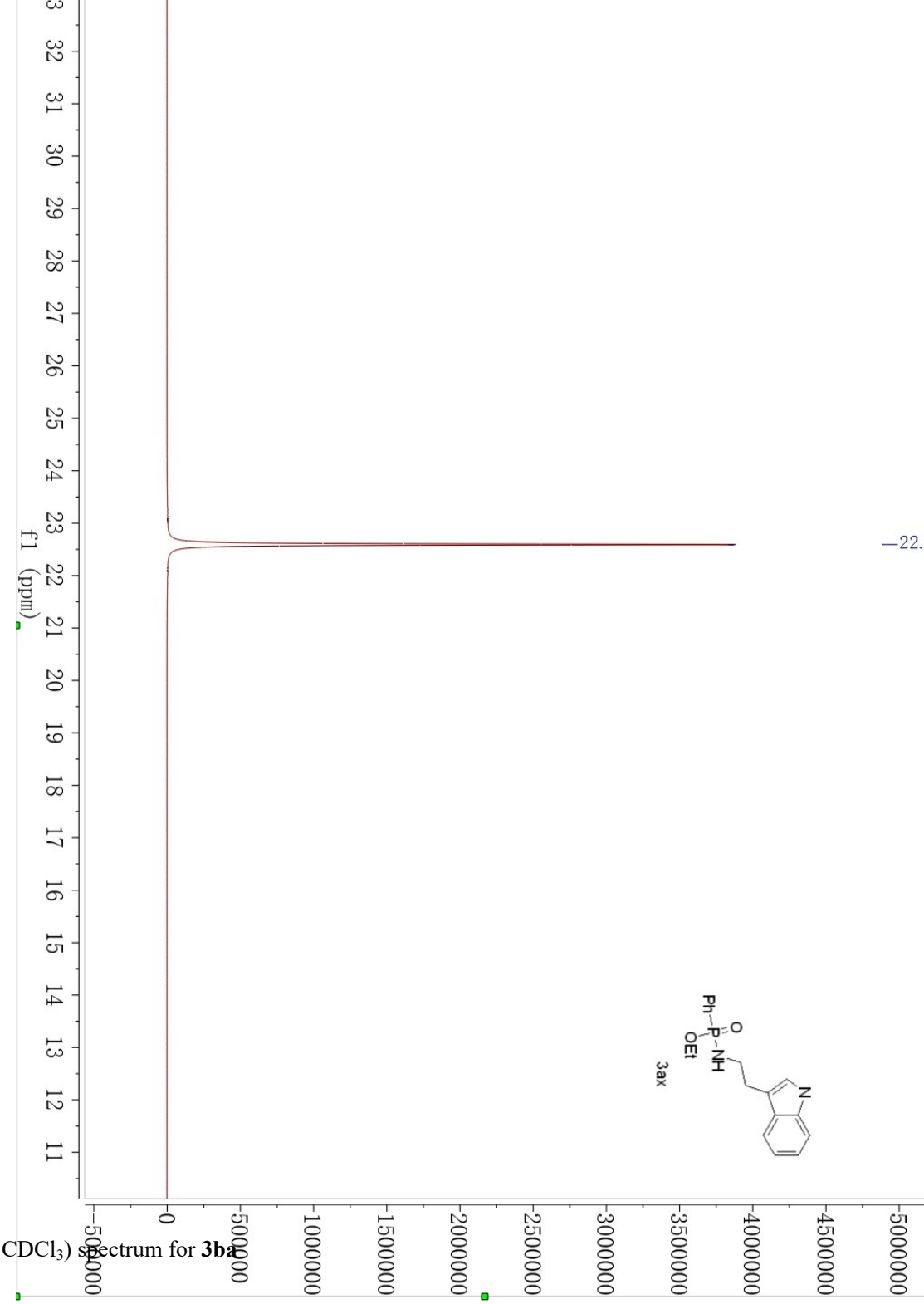
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ax**



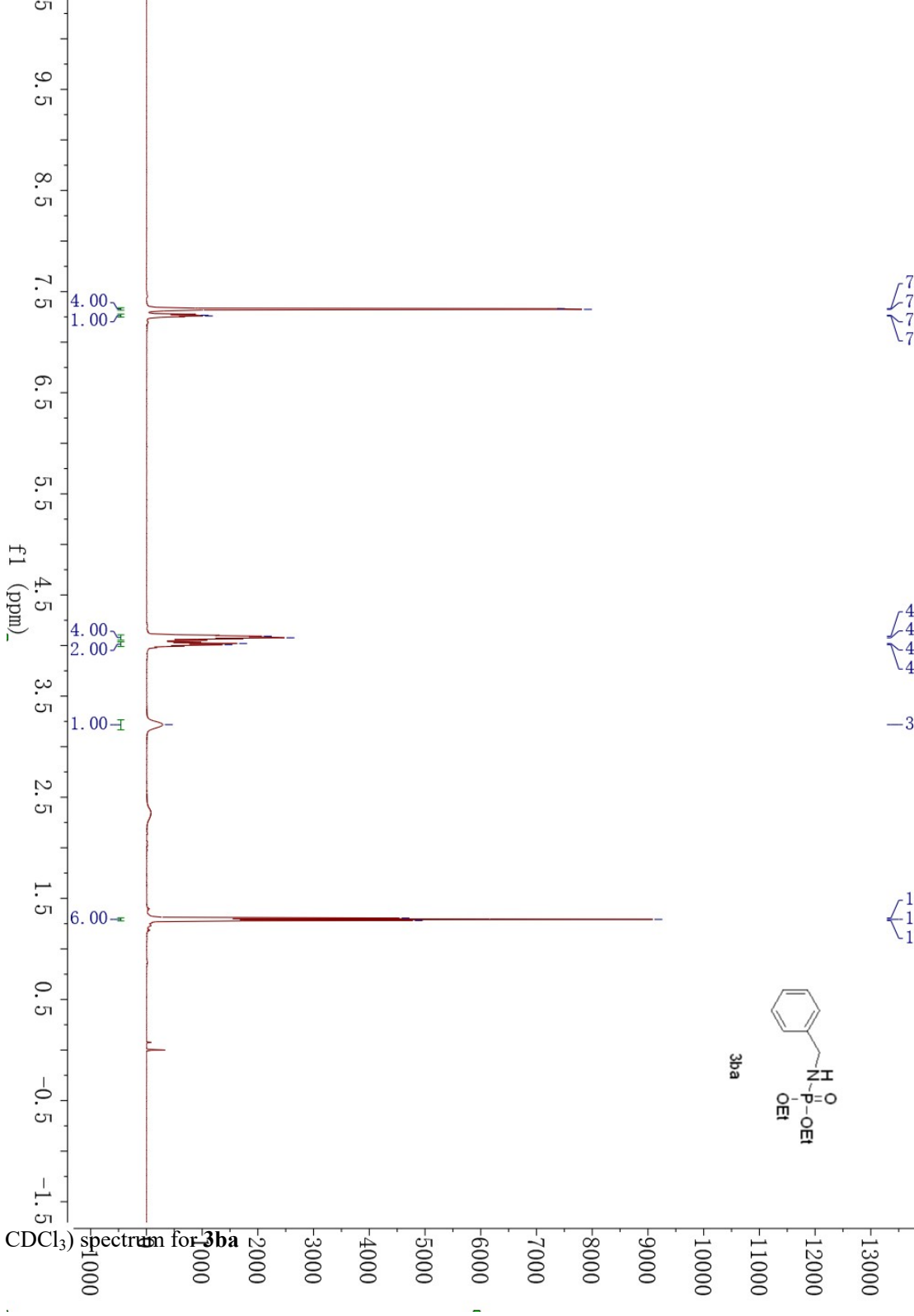
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ax**



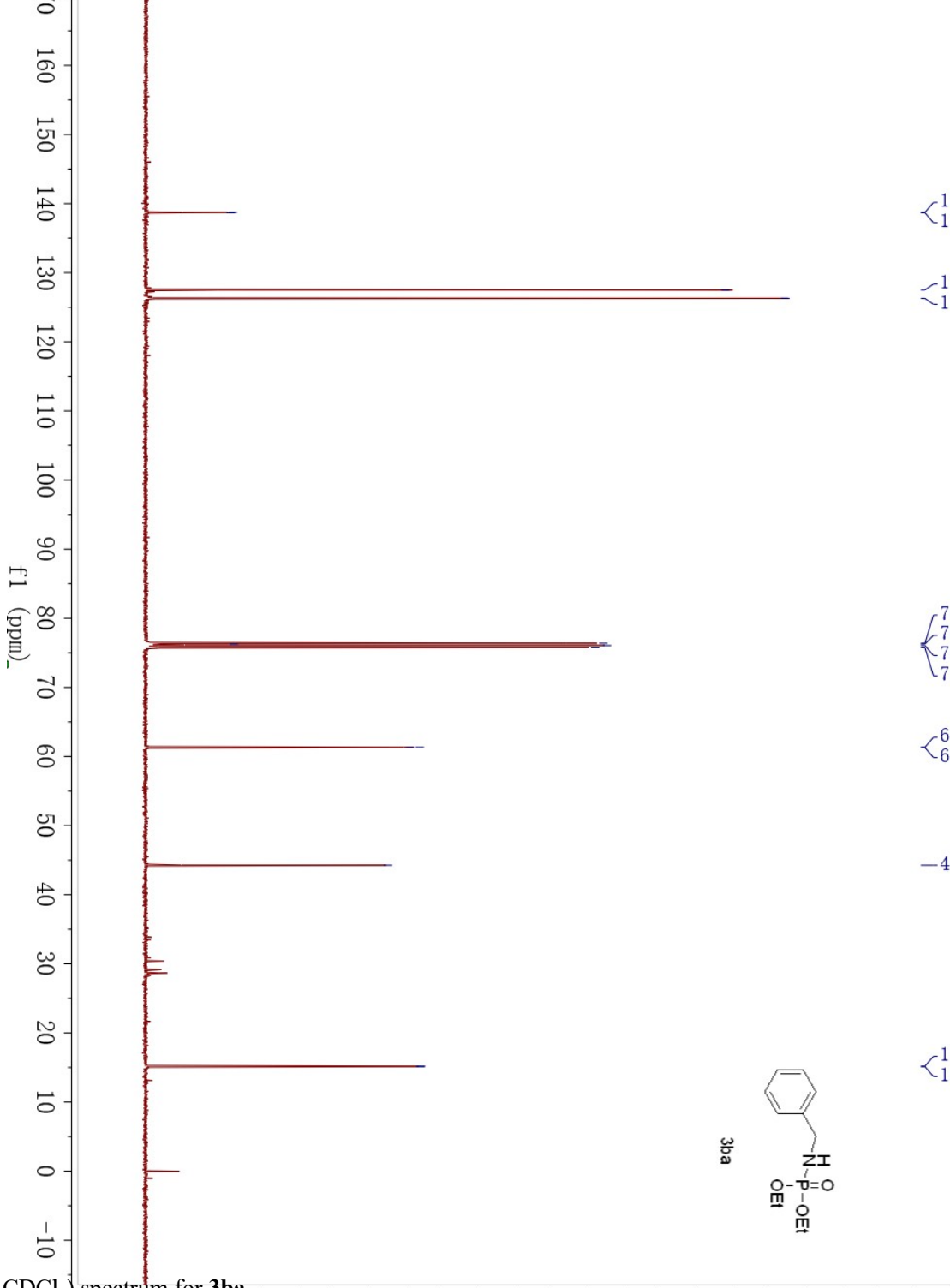
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ax**



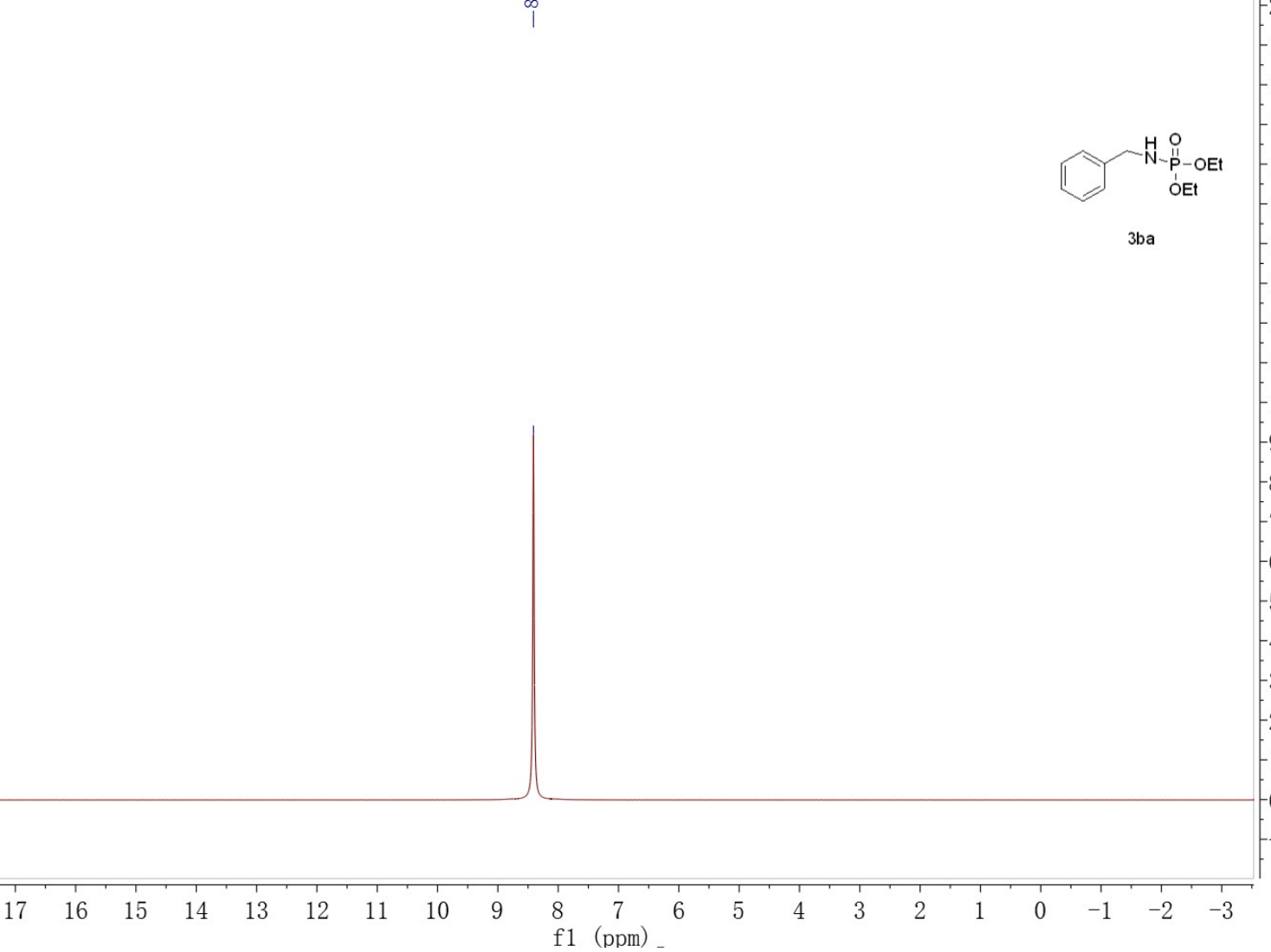
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ba**

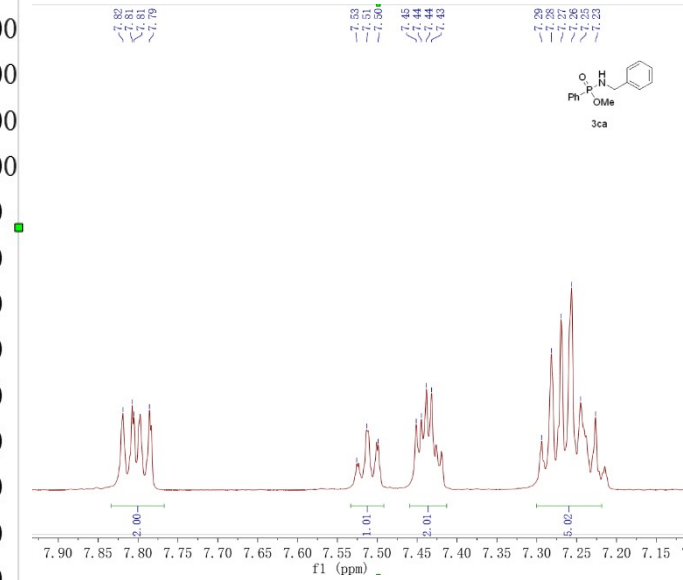


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ba**



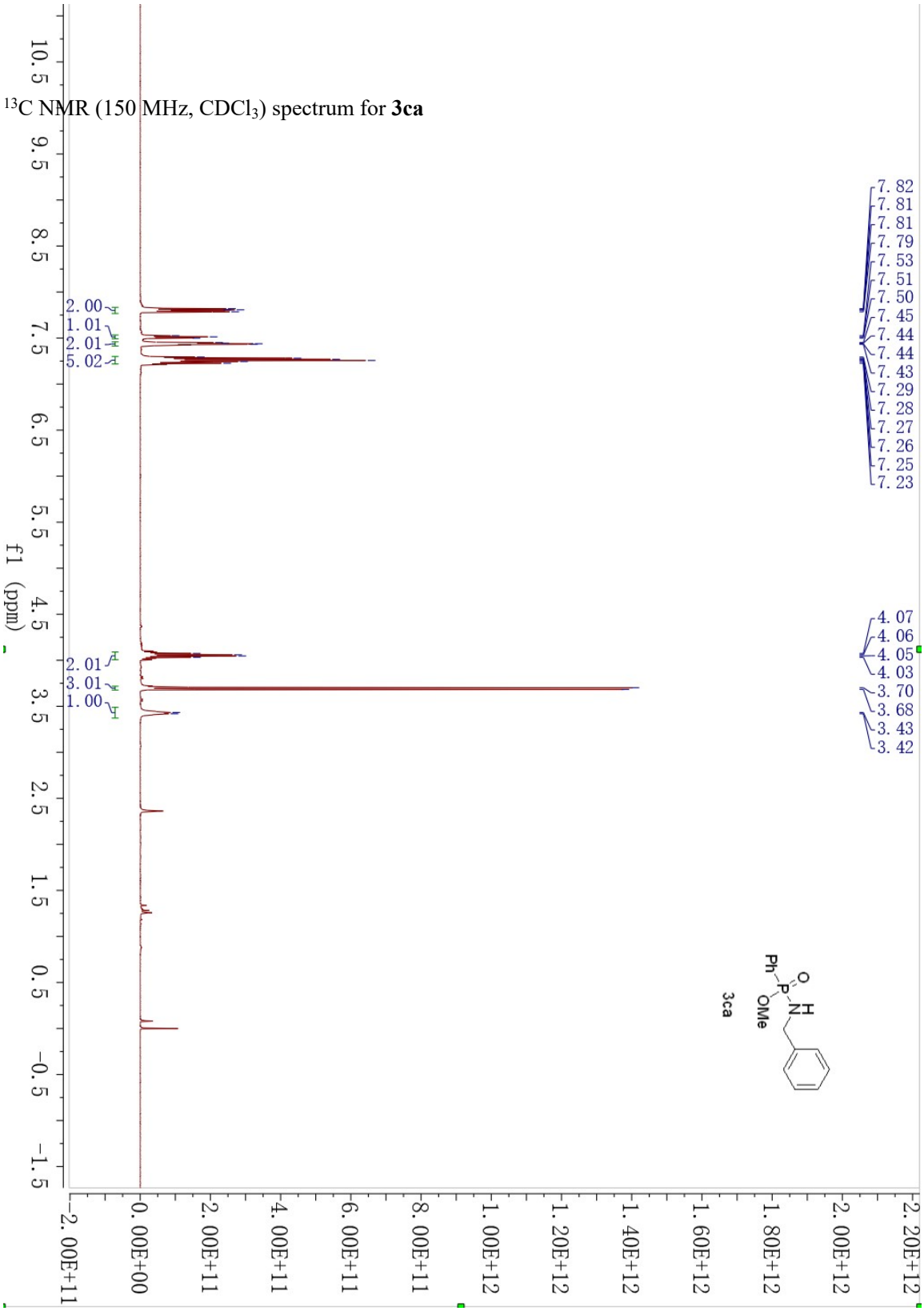
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ba**

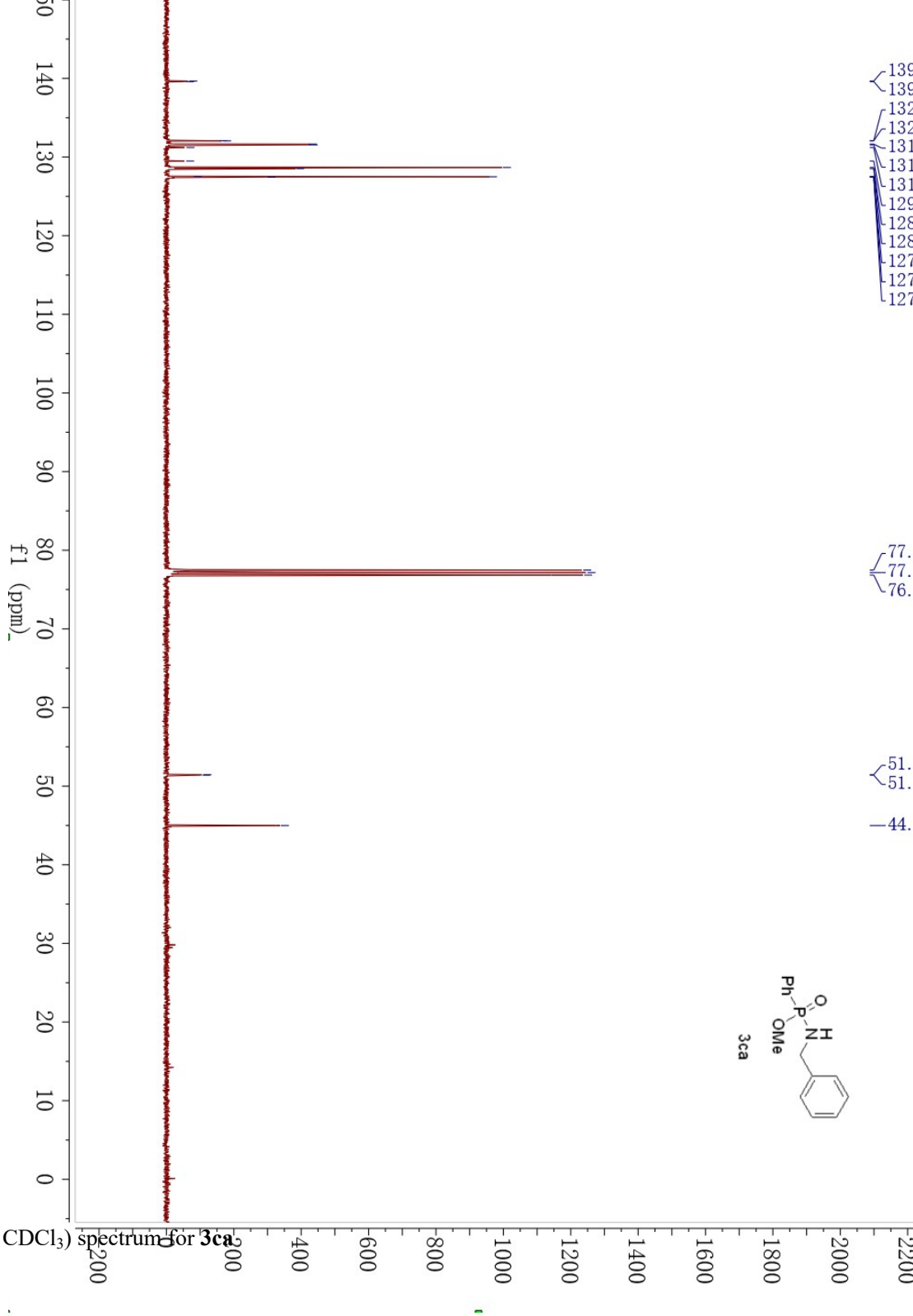




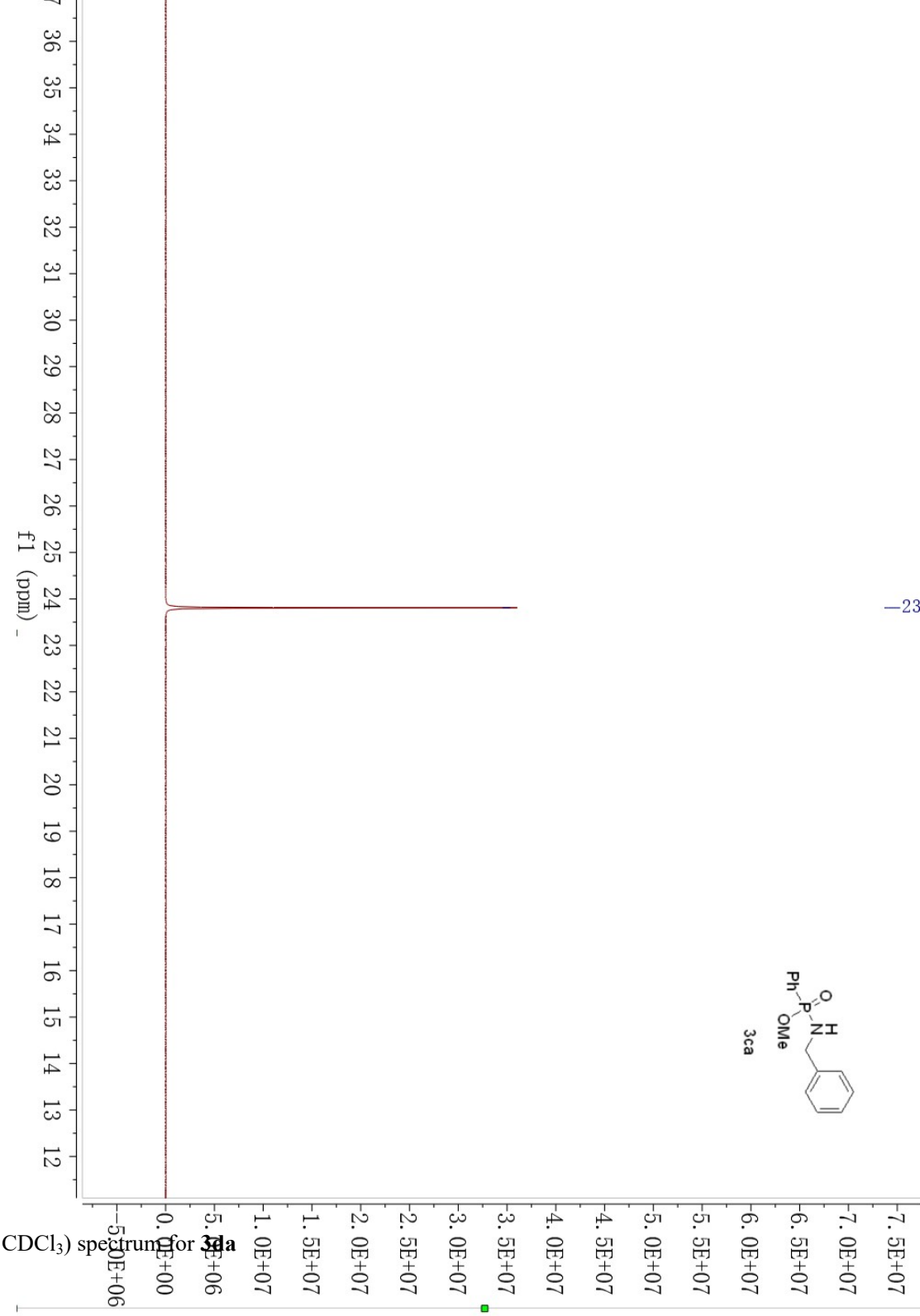
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ca**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ca**

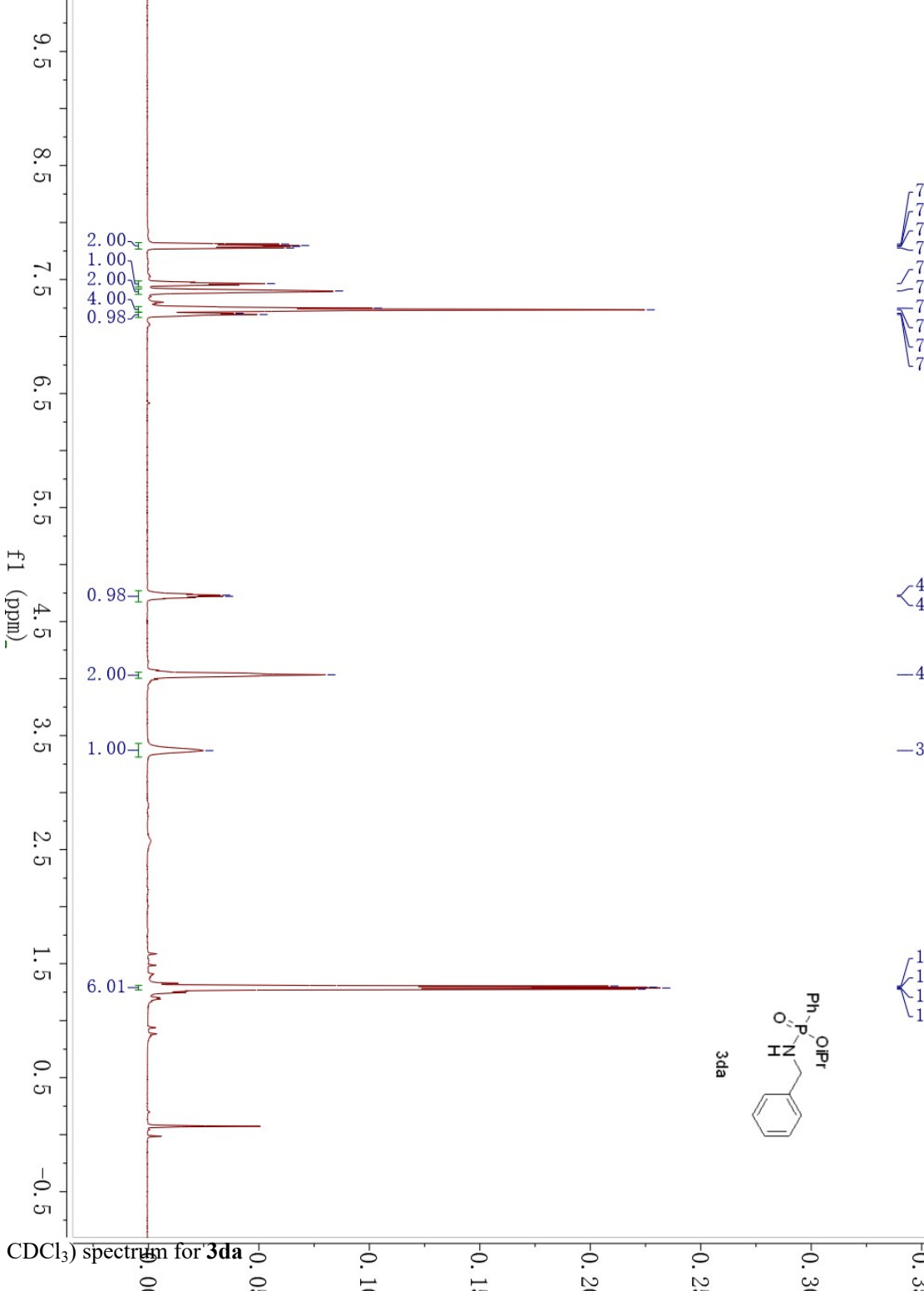




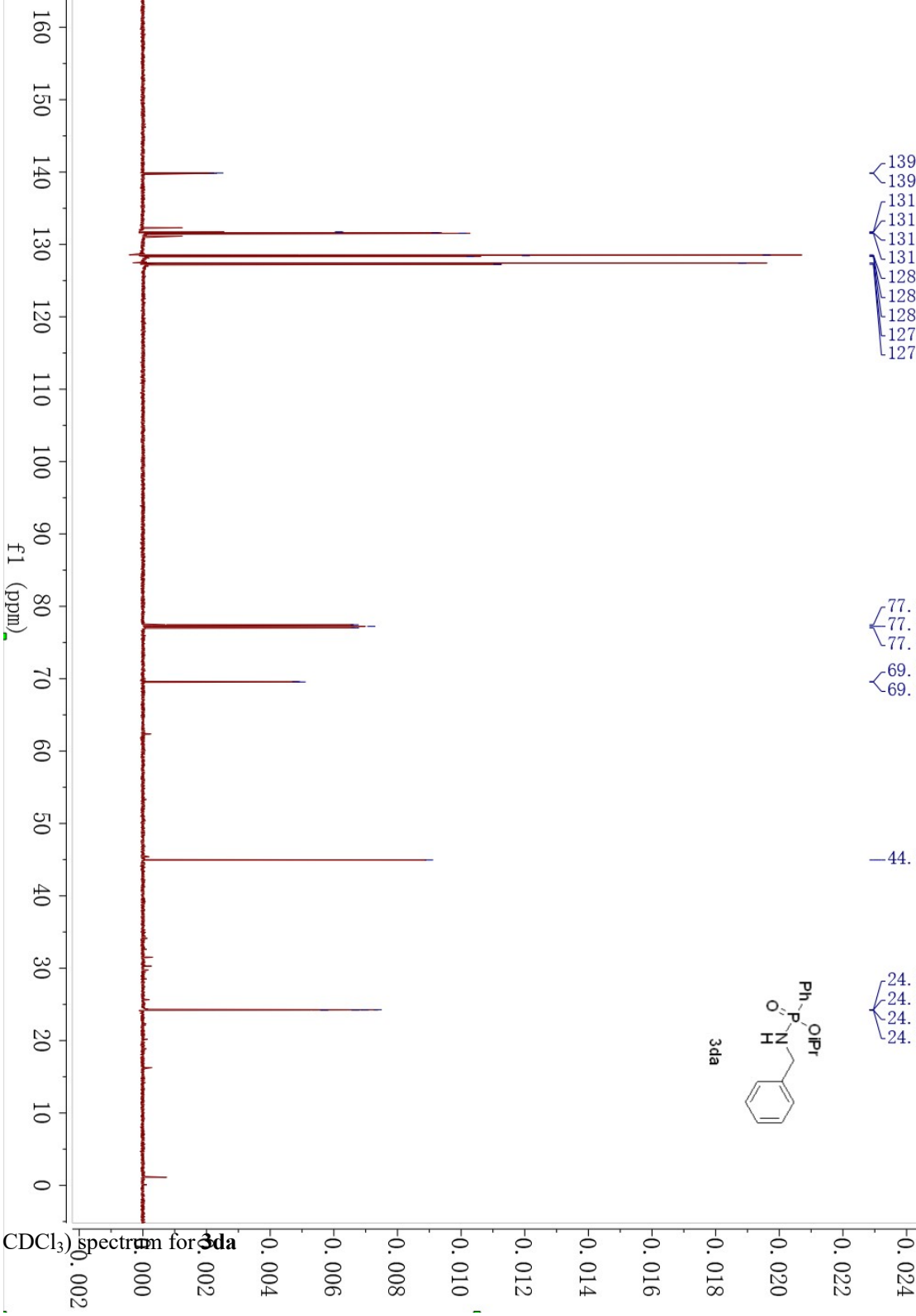
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ca**



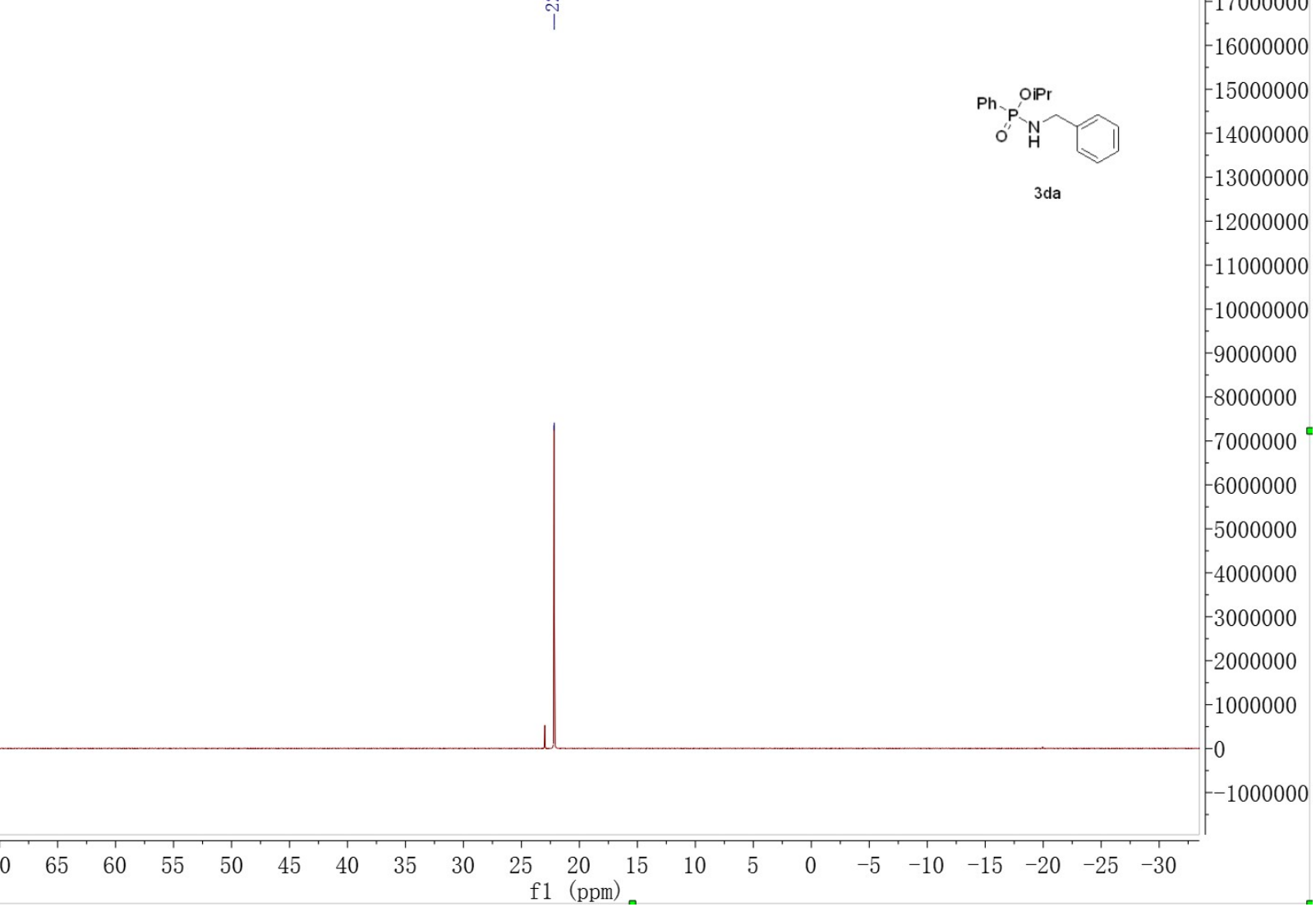
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3da**



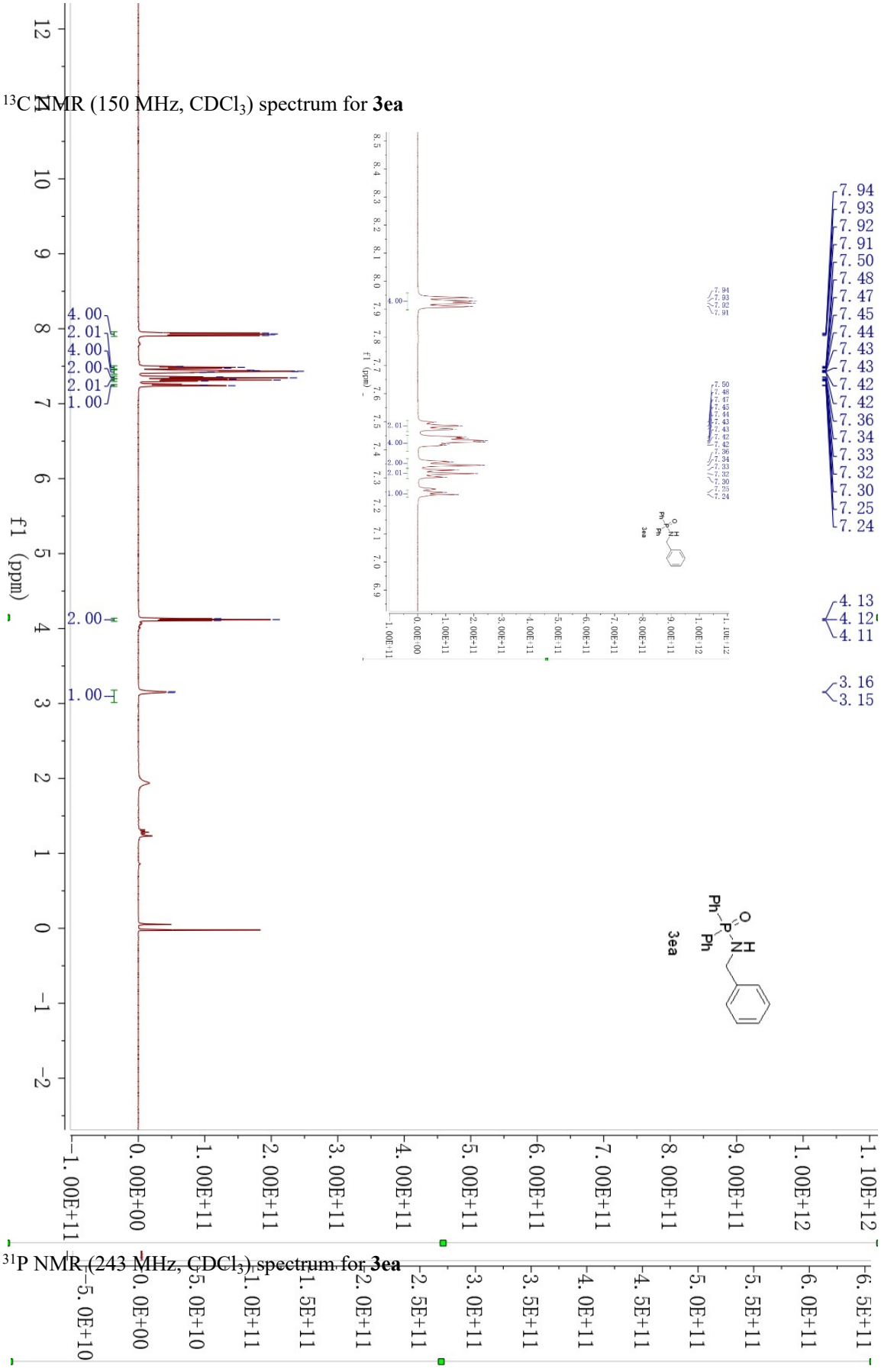
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3da**



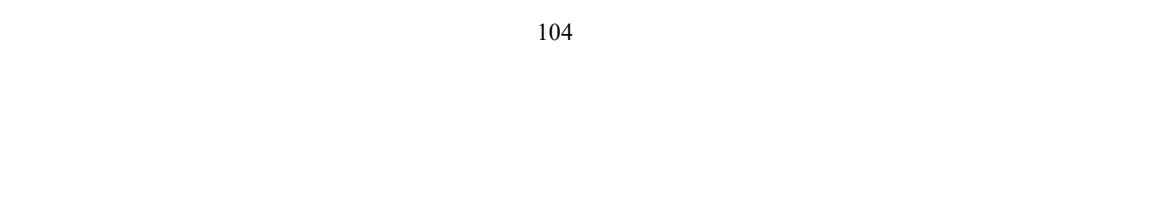
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3da**


Ph
OiPr
O
P
N
H
3da
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
f1 (ppm)

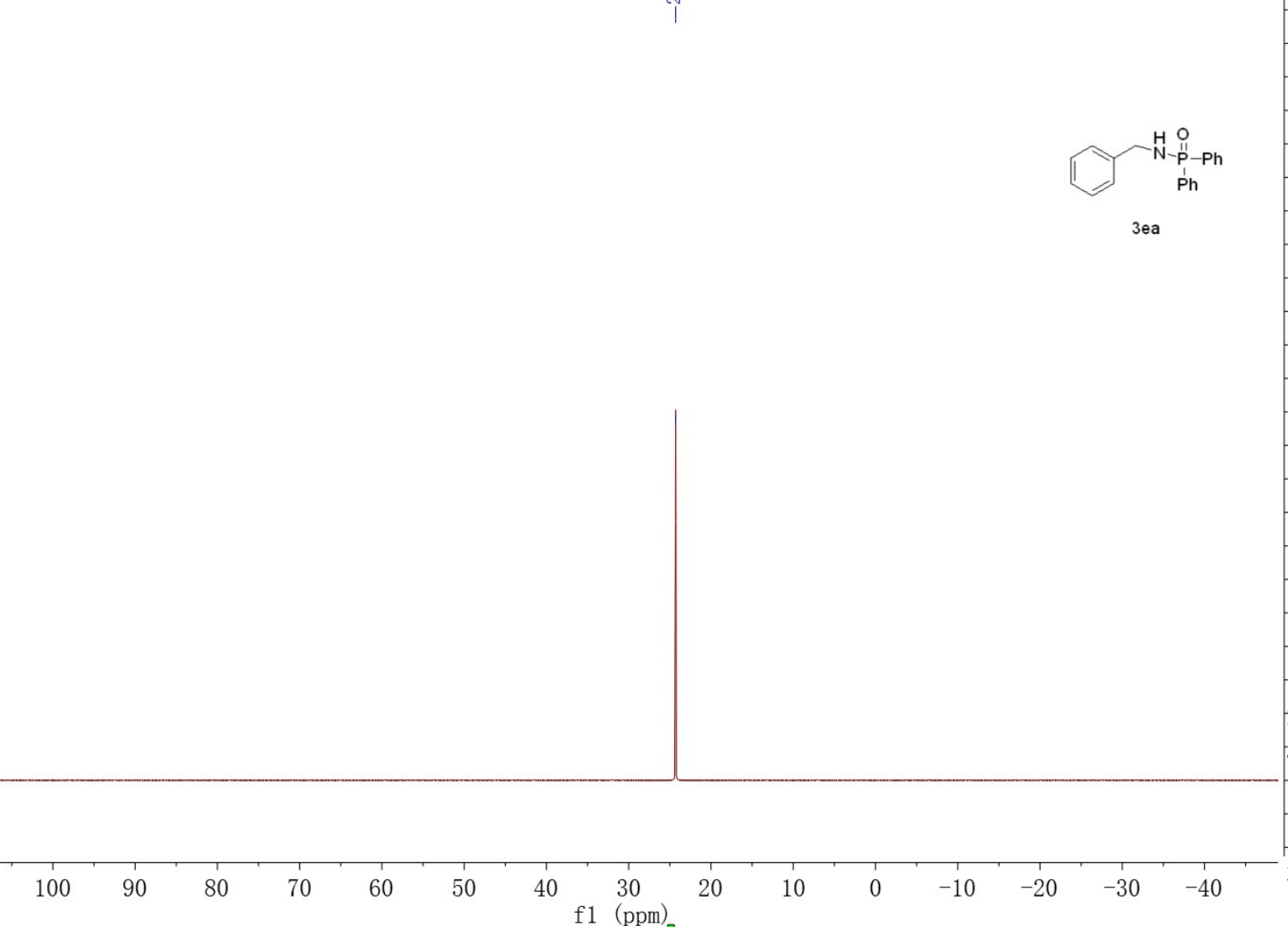
NMR (600 MHz, $CDCl_3$) spectrum for **3ea**



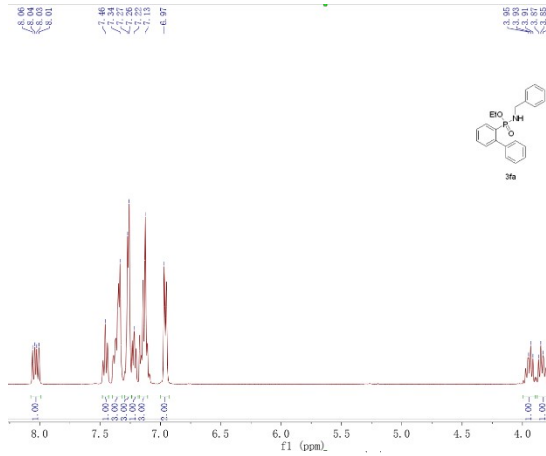
^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ea**



^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ea**

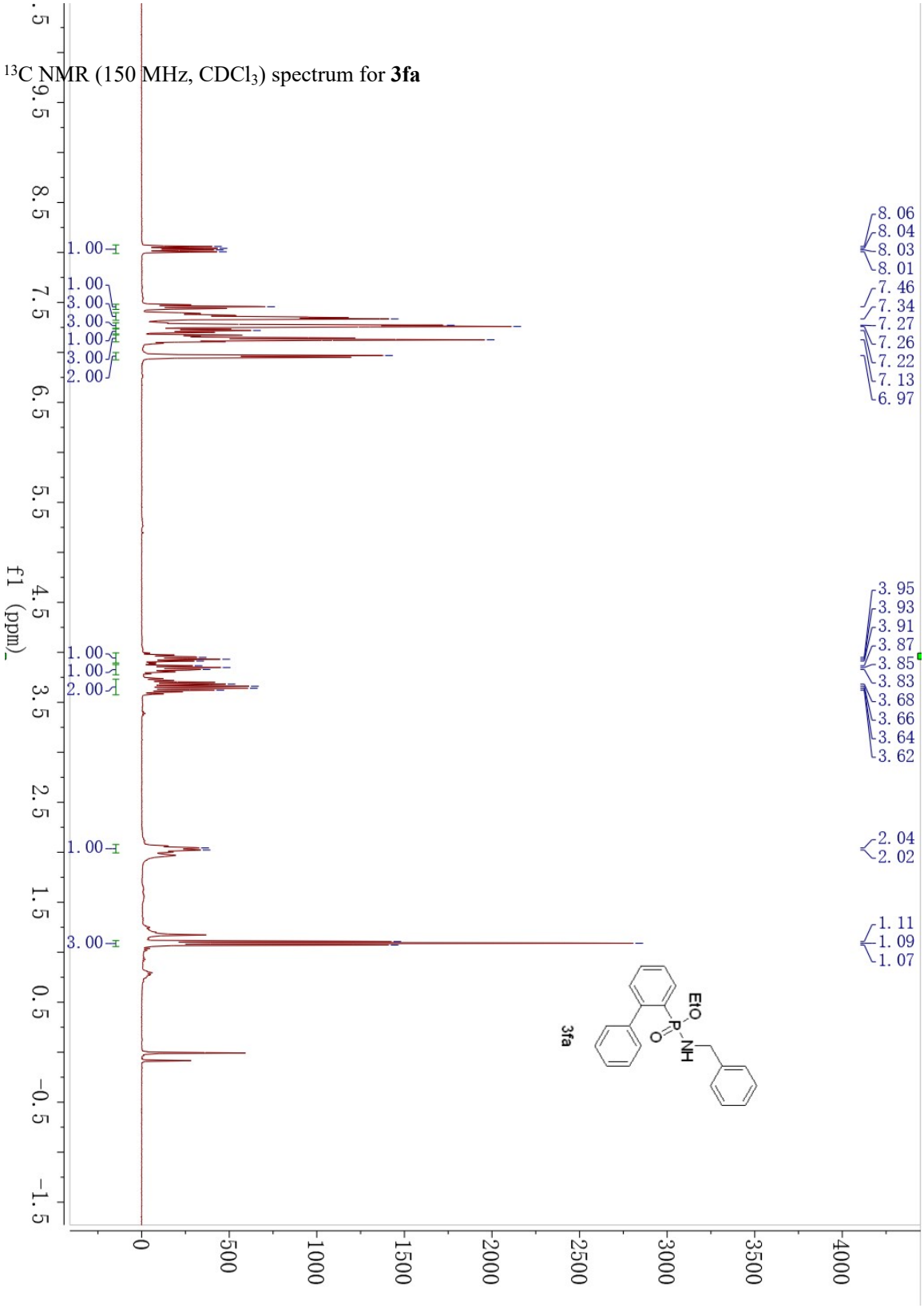


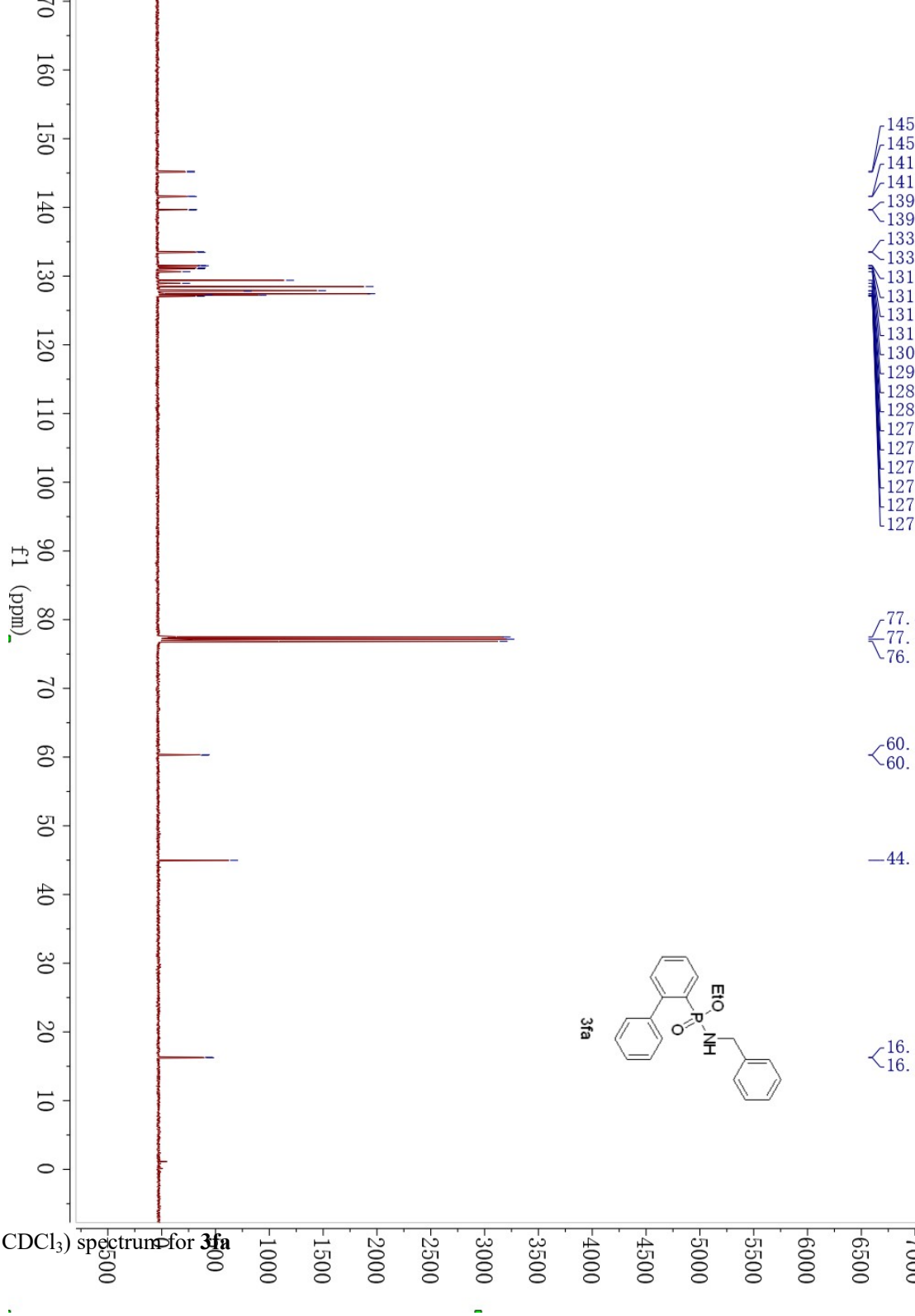
3ea



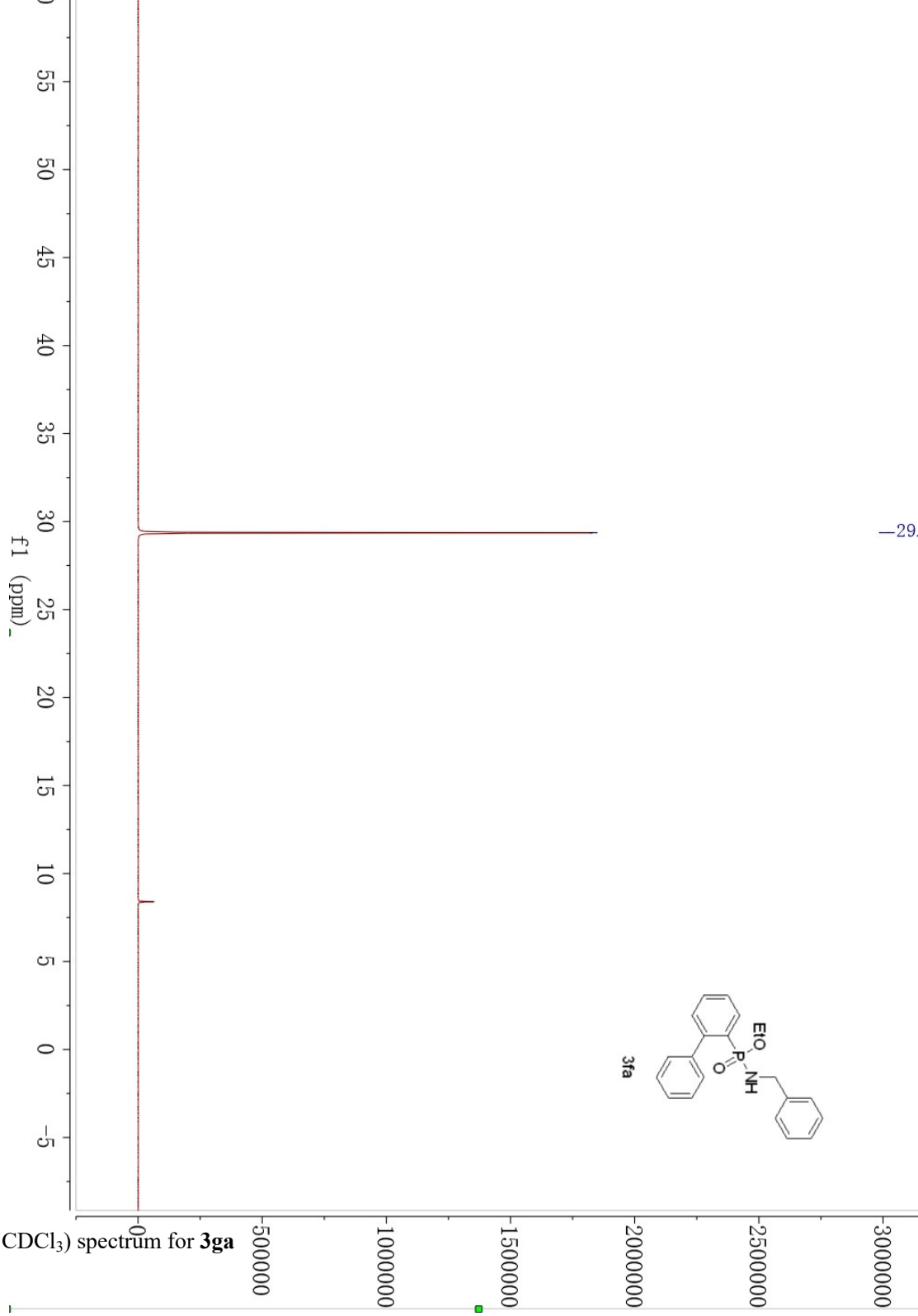
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3fa**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3fa**

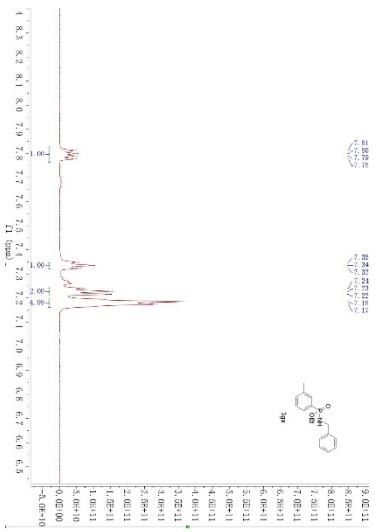




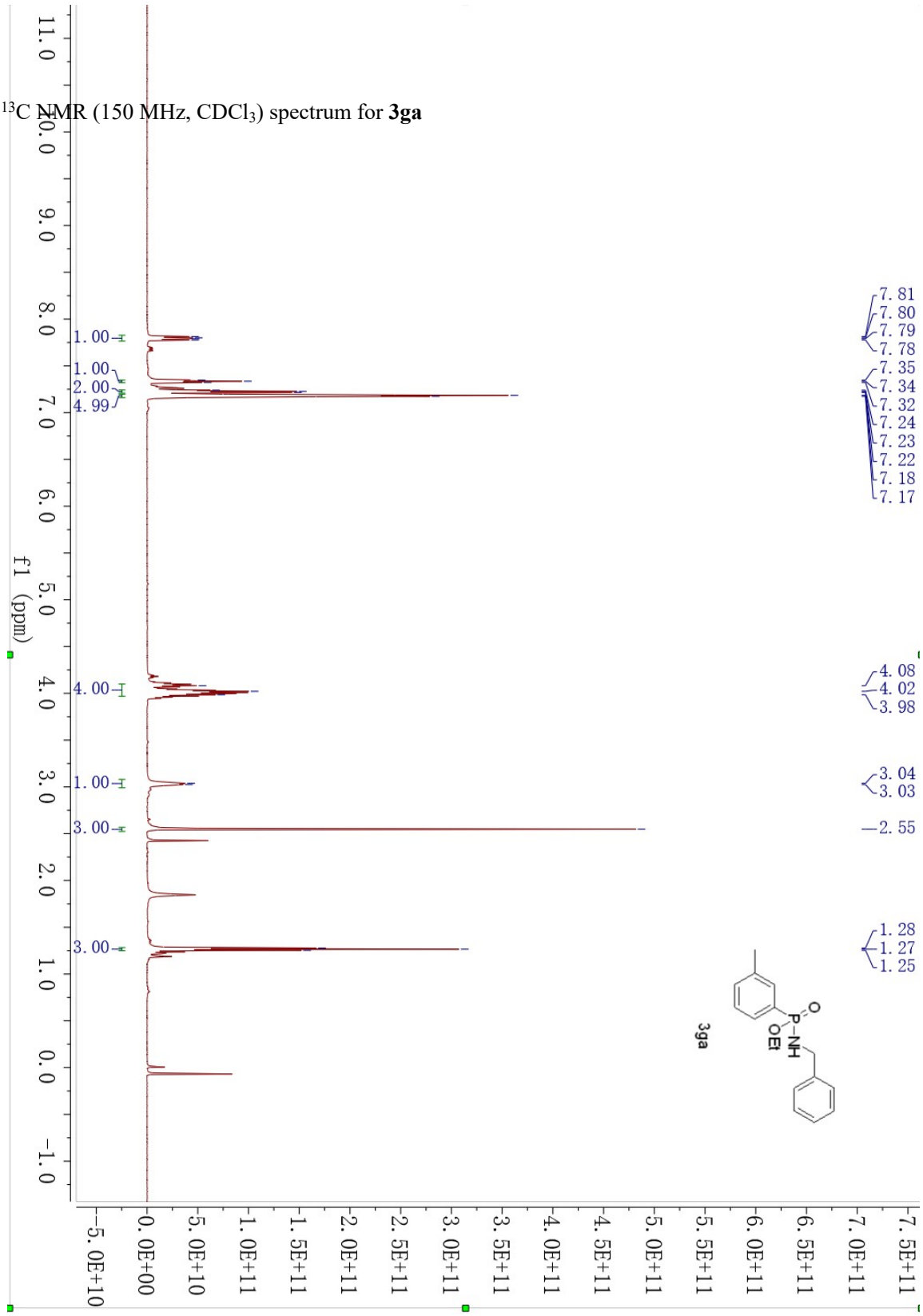
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3fa**

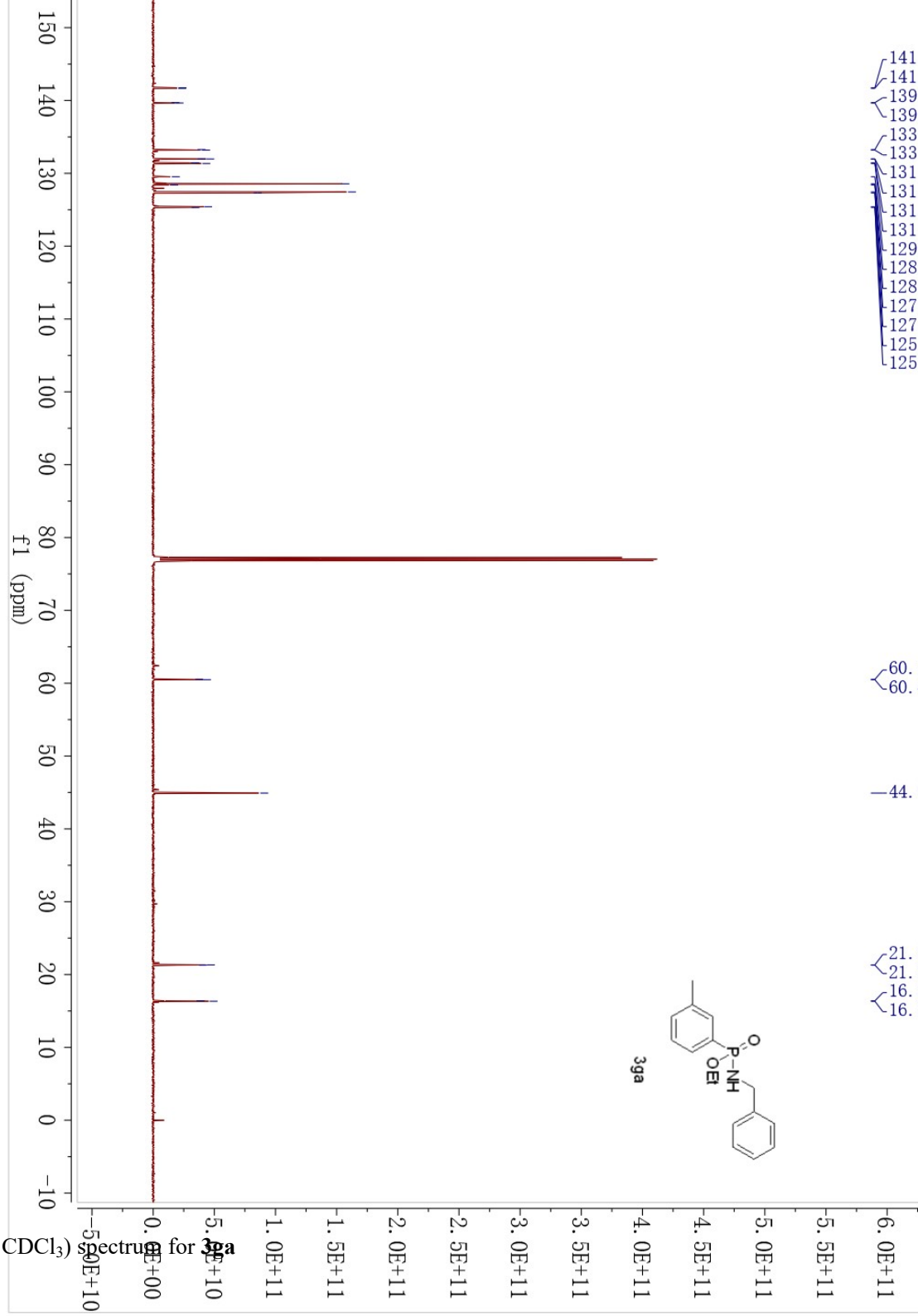


^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3ga**

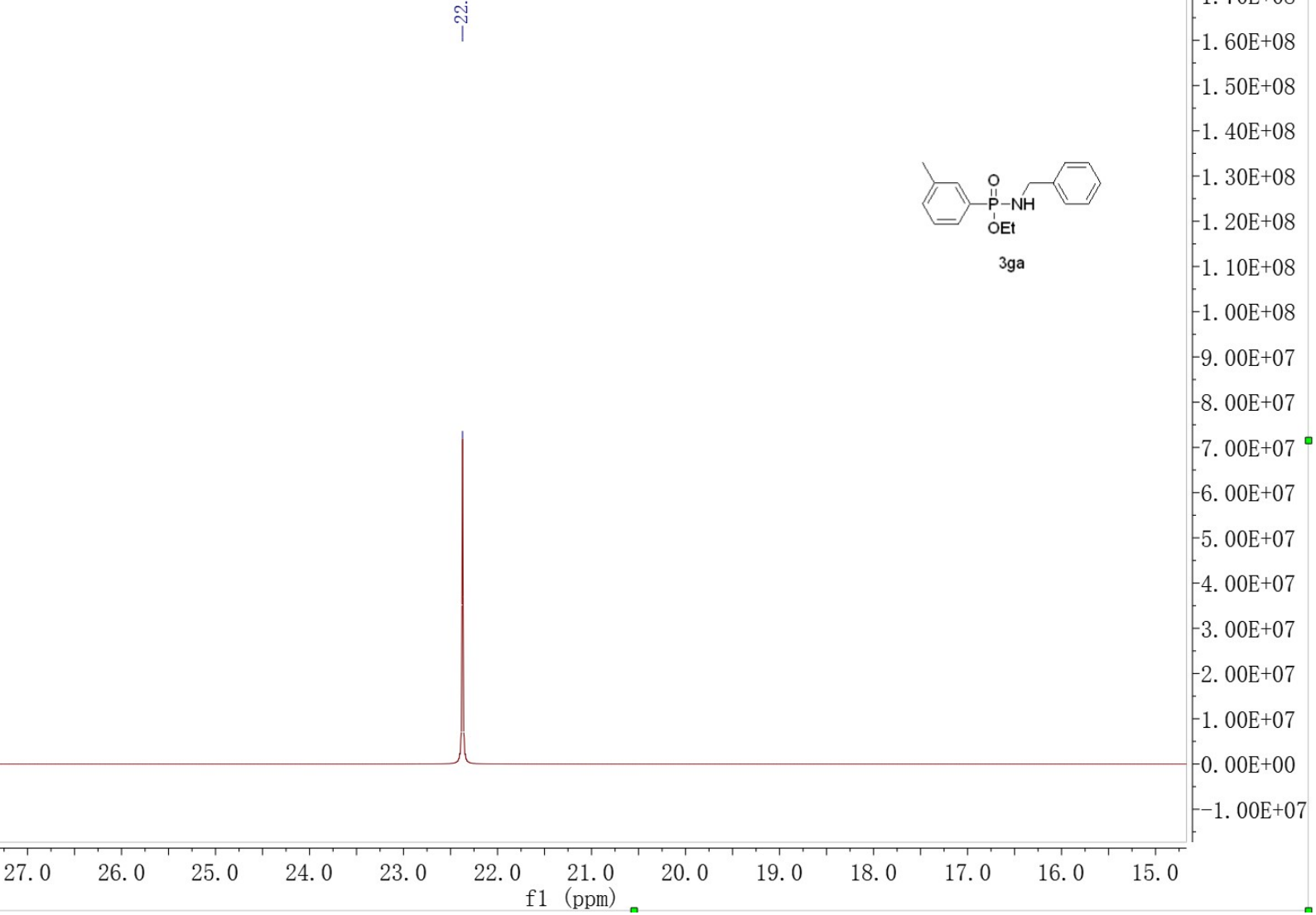


^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ga**

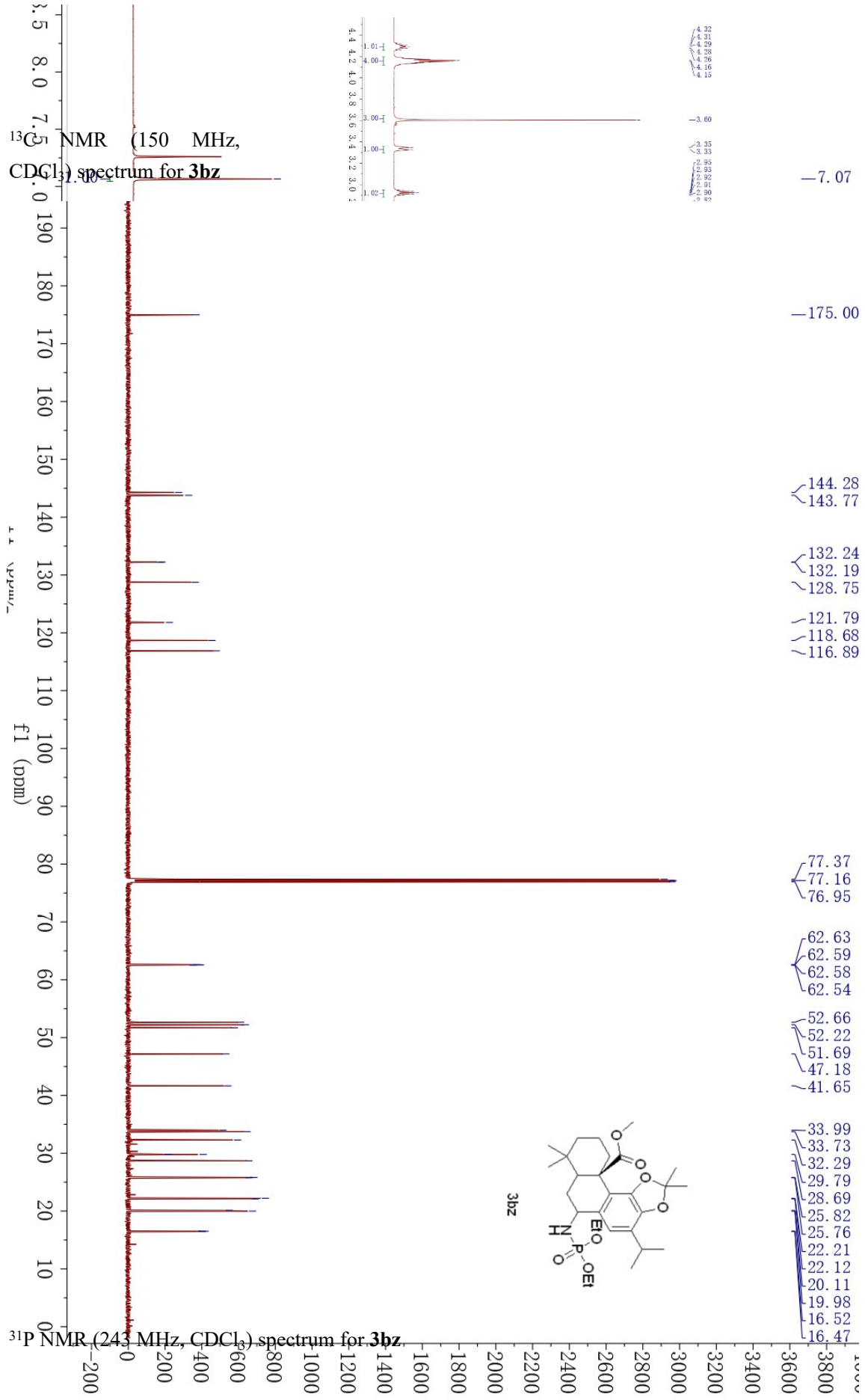




^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ga**

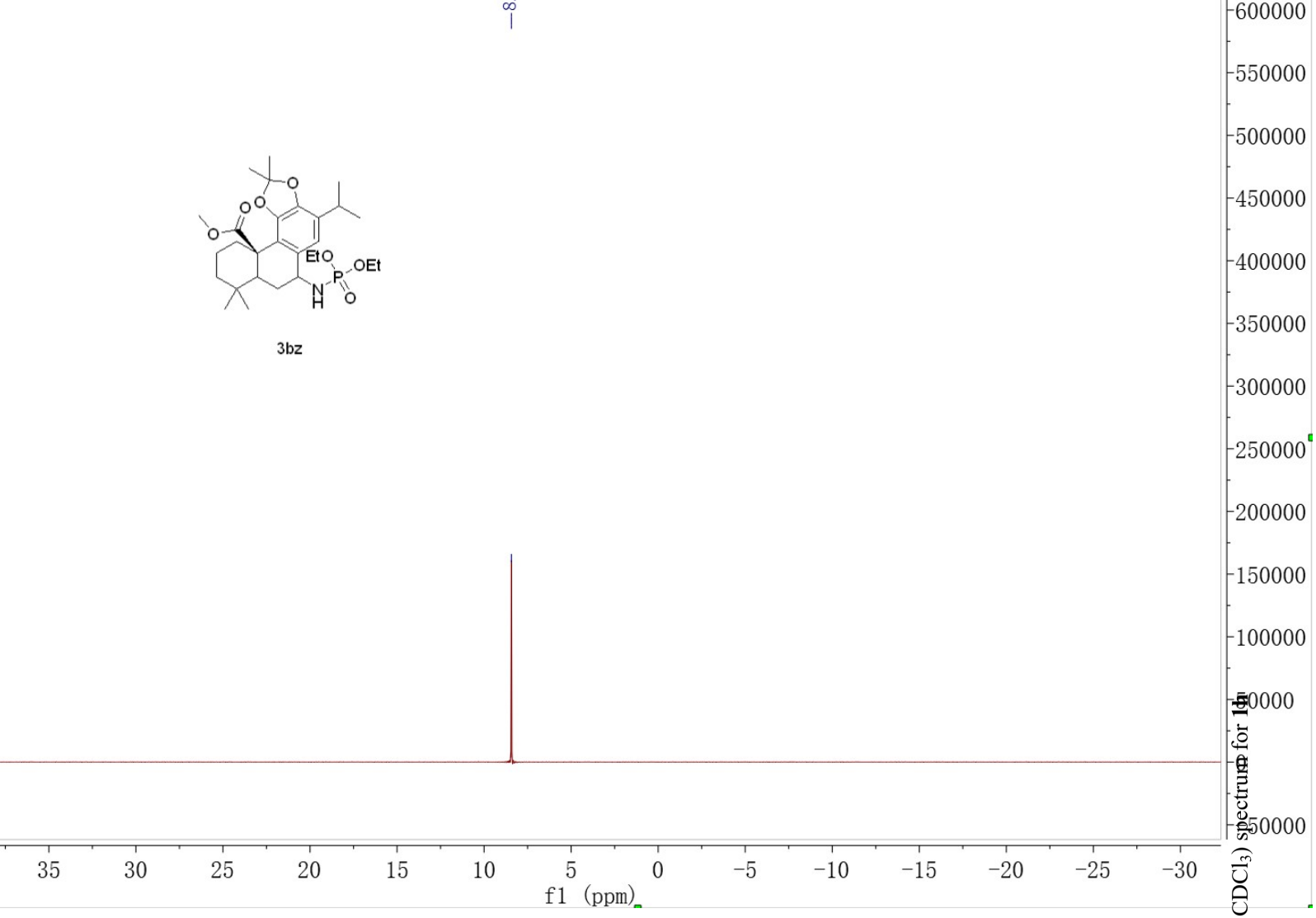

22.
O
P
NH
OEt
3ga
1.60E+08
1.50E+08
1.40E+08
1.30E+08
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
27.0
26.0
25.0
24.0
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
f1 (ppm)

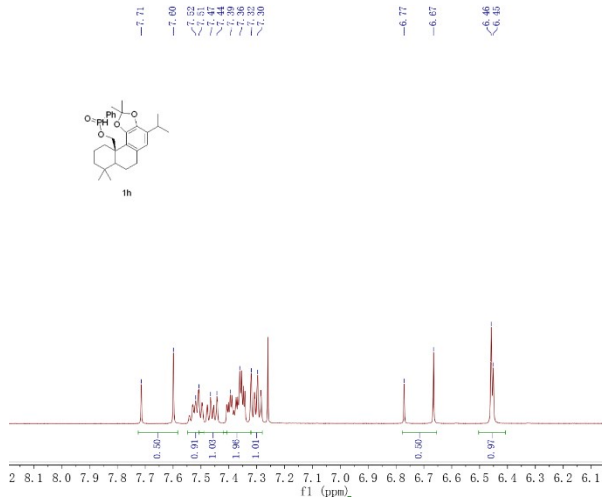
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3bz**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3bz**

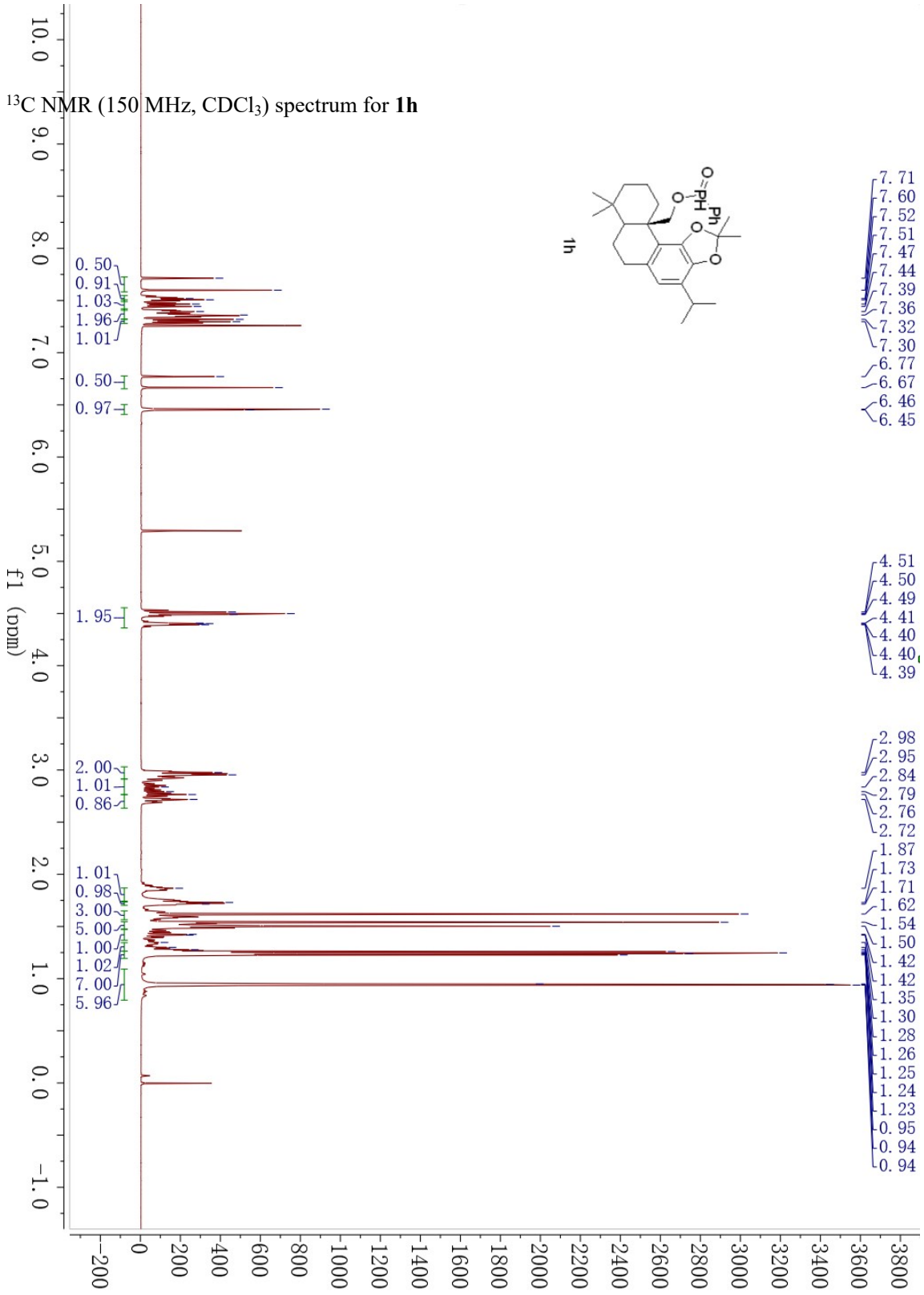
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3bz**.

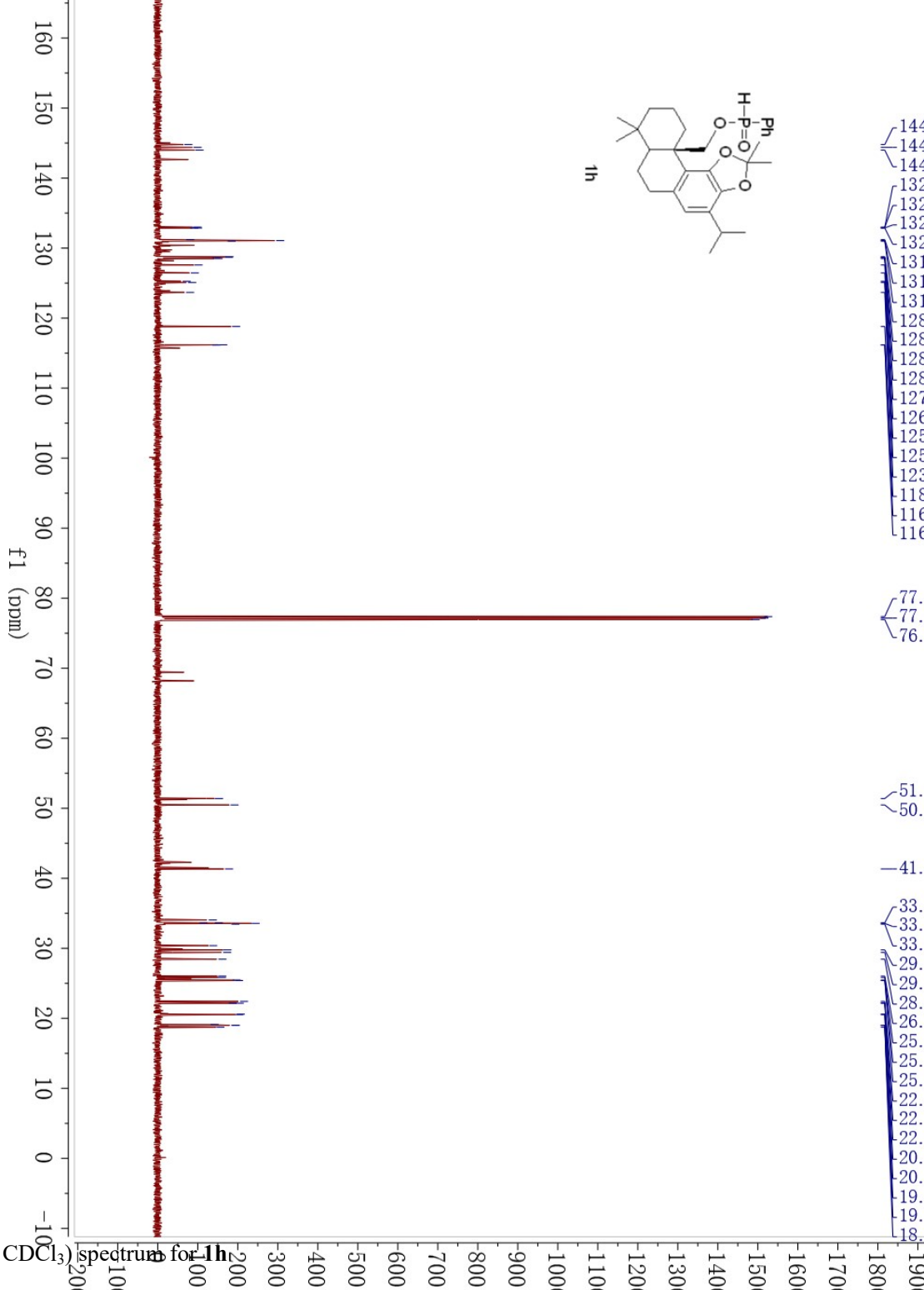




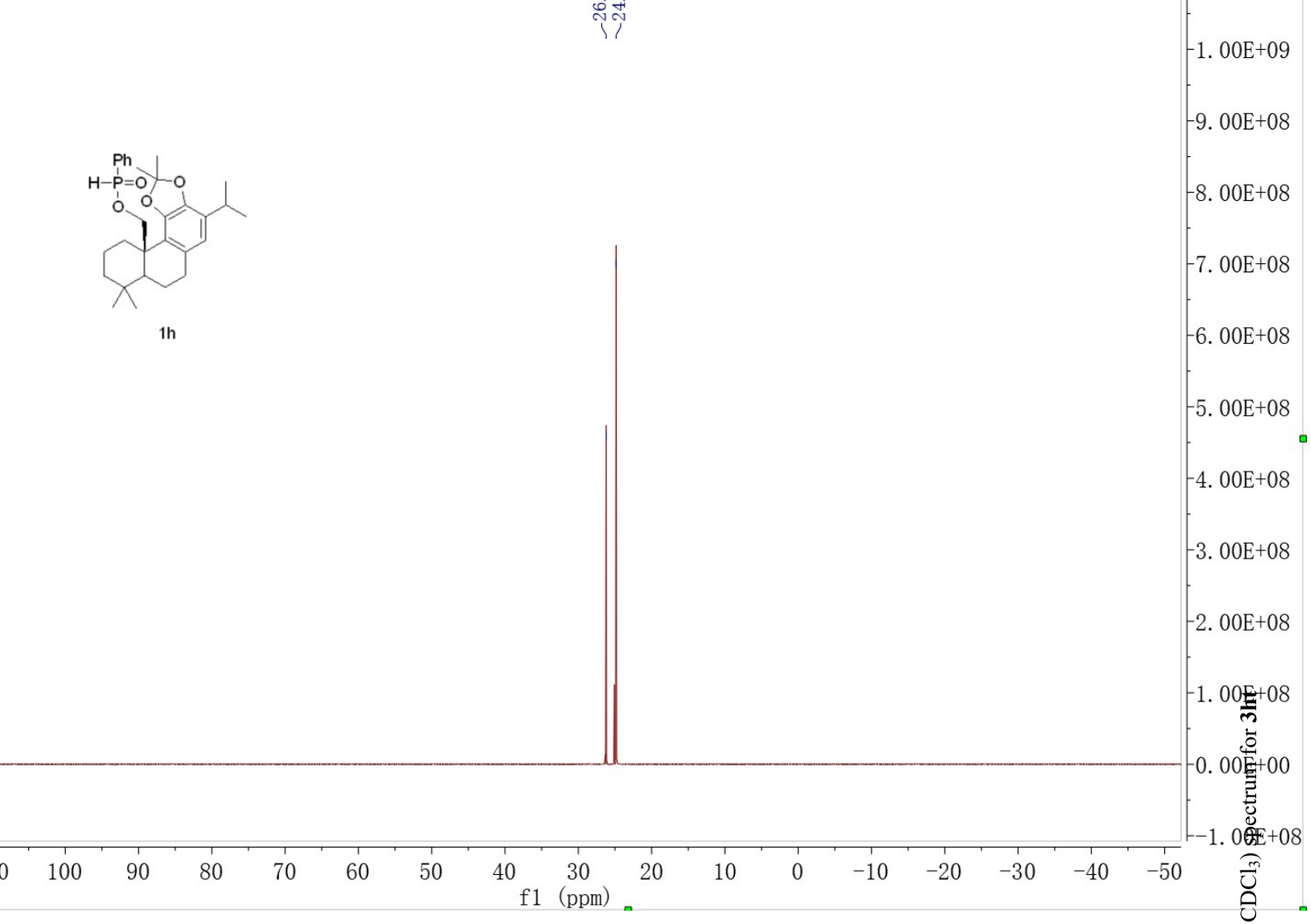
^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **1h**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **1h**

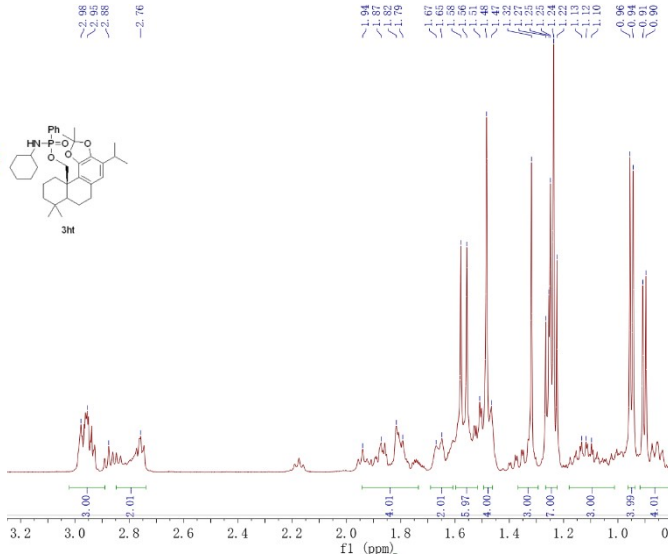




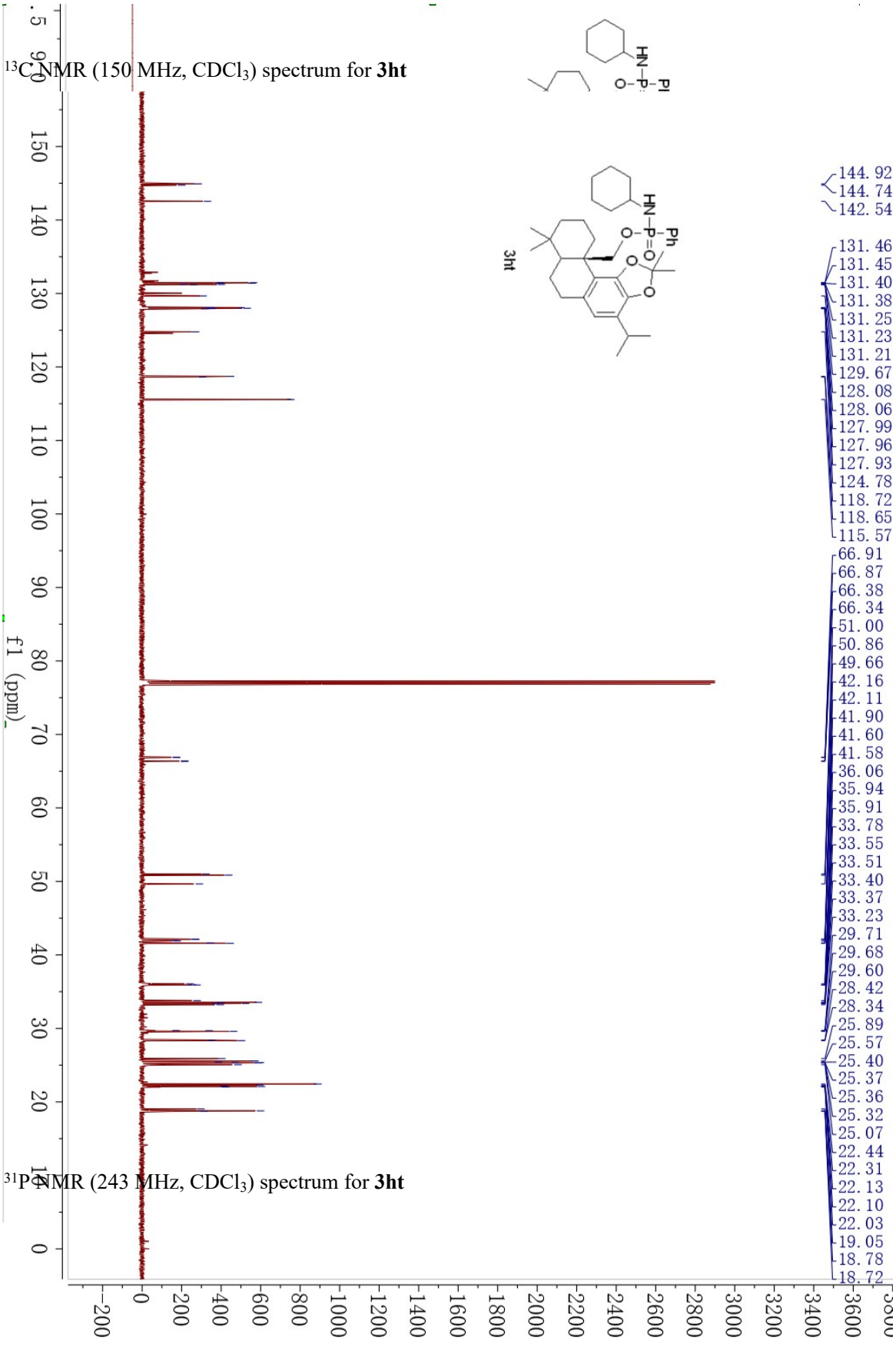
^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **1h**



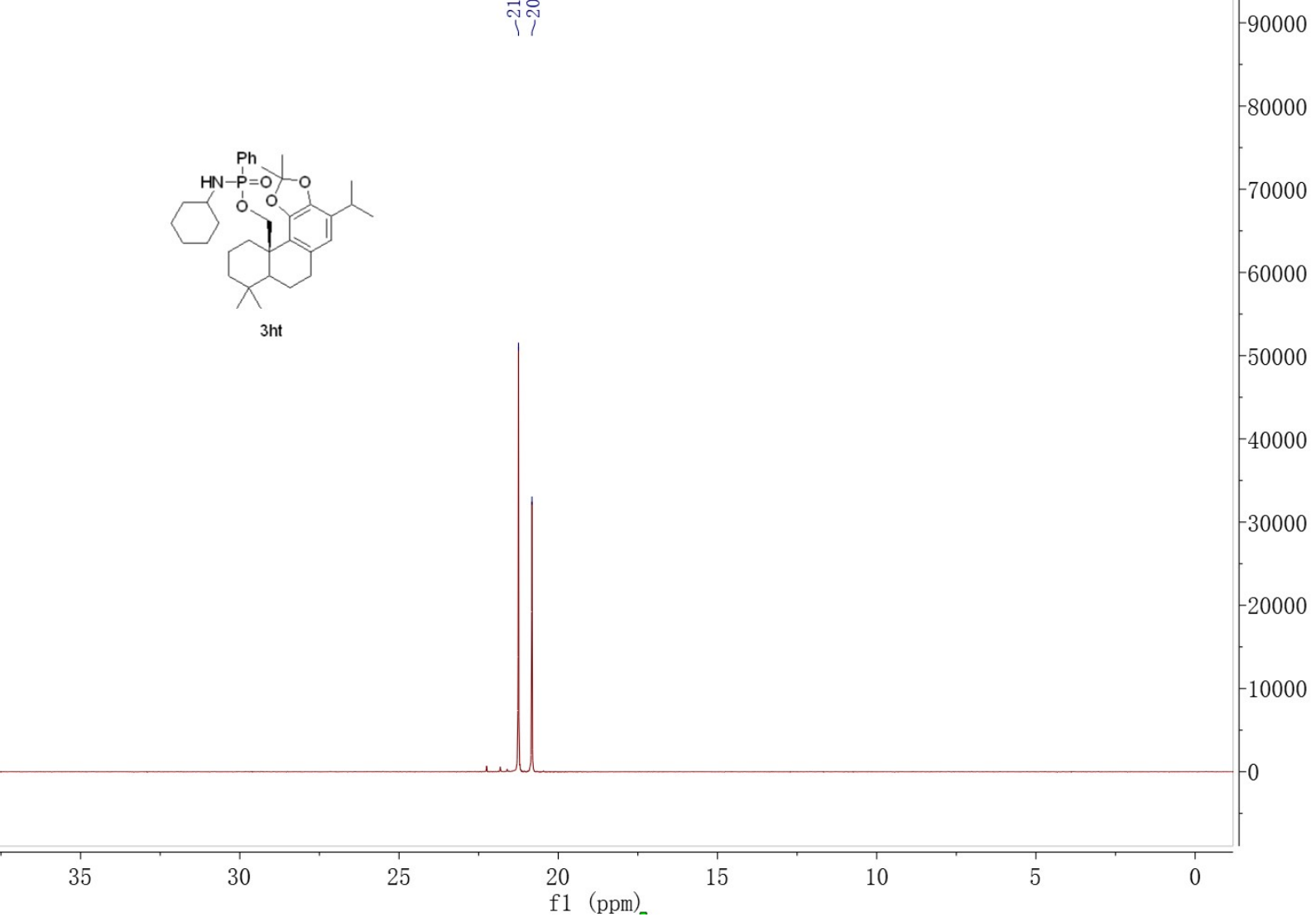
^{1}H NMR (600 MHz, $CDCl_3$) Spectrum for **3ht**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3ht**

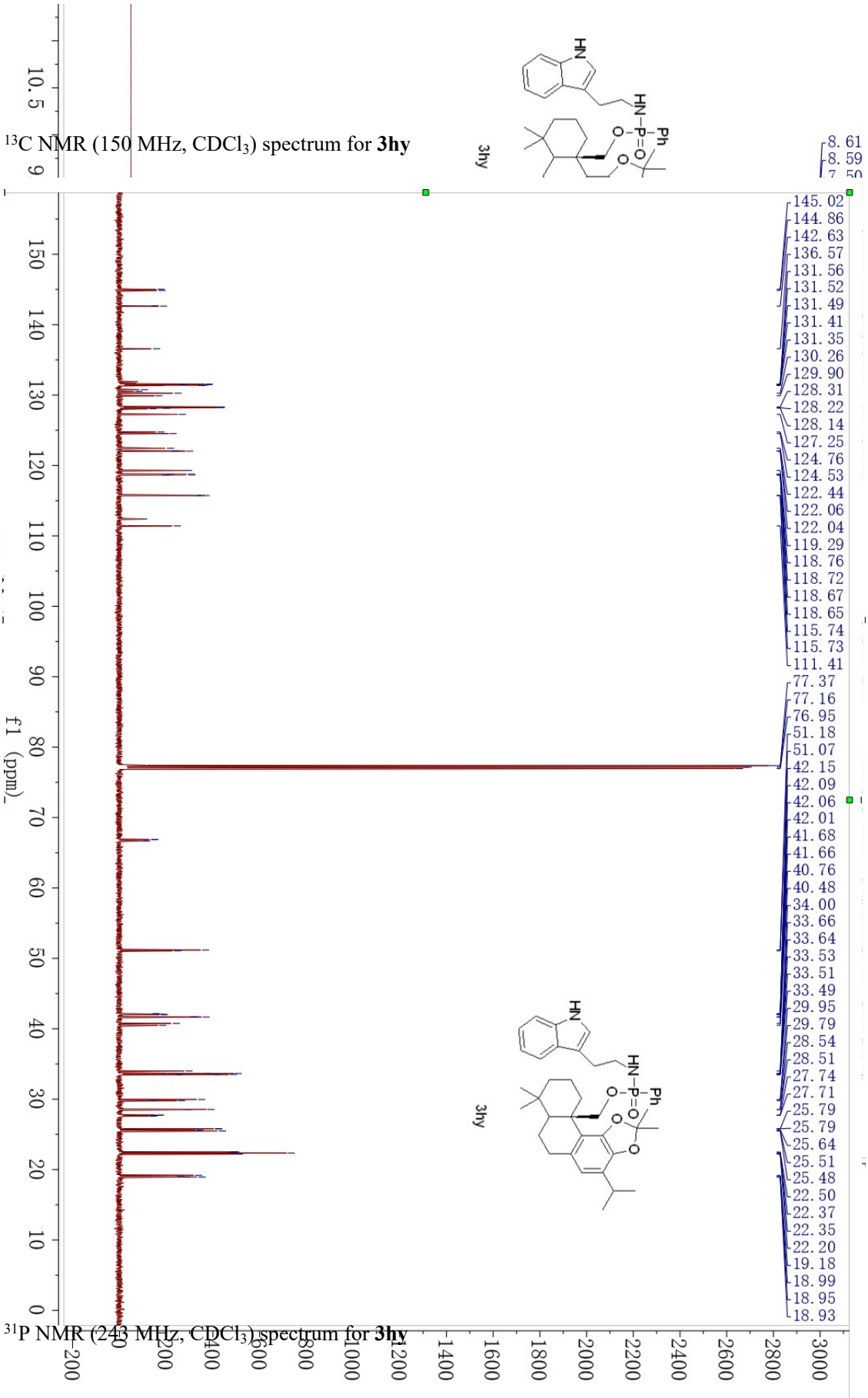


^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3ht**

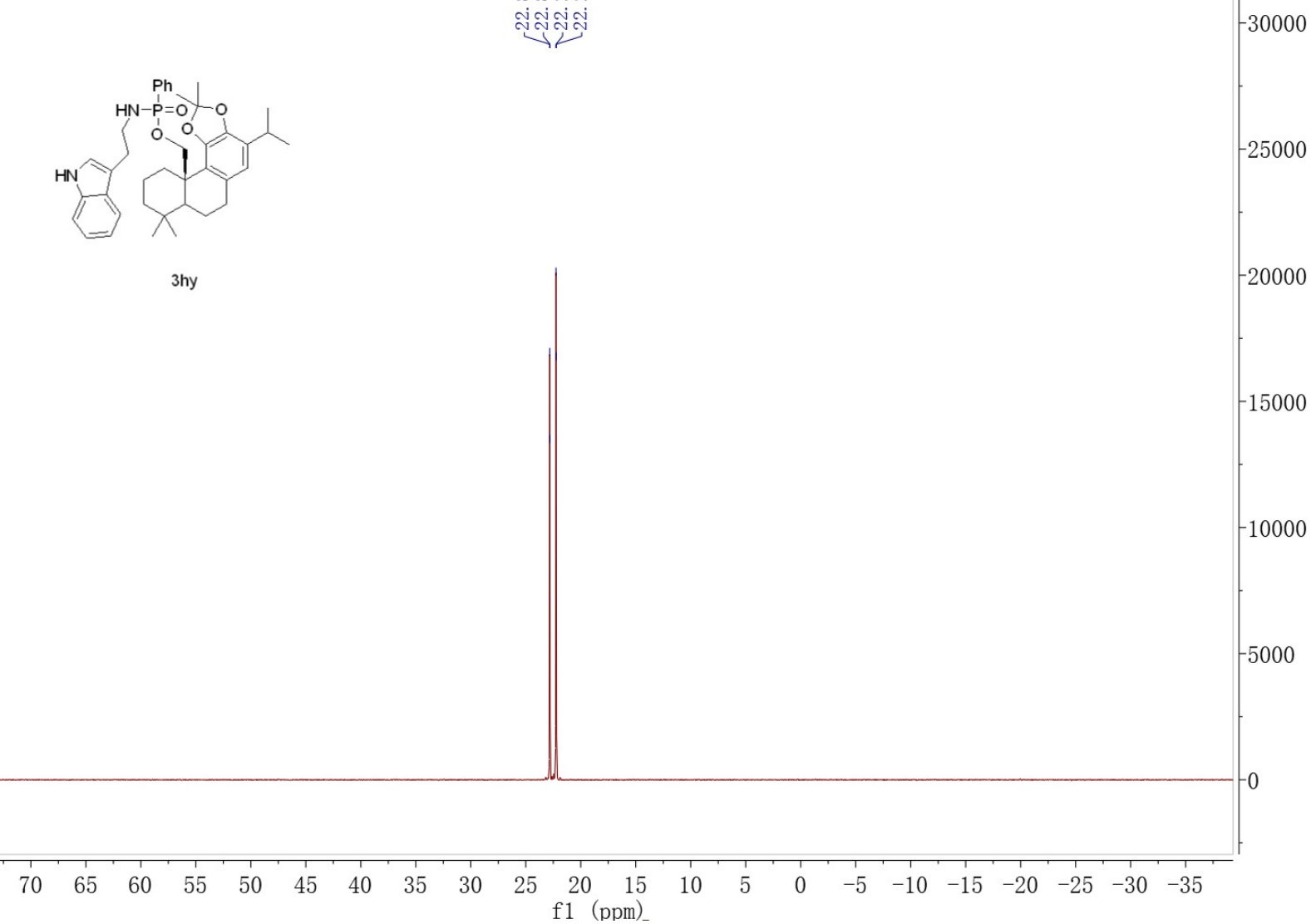

Ph
HN
P
O
O
O
O
3ht
21.
20.
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
35
30
25
20
15
10
5
0
f1 (ppm)

^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **3hy**

^{13}C NMR (150 MHz, $CDCl_3$) spectrum for **3hy**



^{31}P NMR (243 MHz, $CDCl_3$) spectrum for **3hy**


Ph
HN
P
O
O
O
O
HN
3hy
22.
22.
22.
22.
30000
25000
20000
15000
10000
5000
0
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)