Supporting Information

Concise Synthesis of *N*-Phosphorylated Amides through Three-Component Reactions

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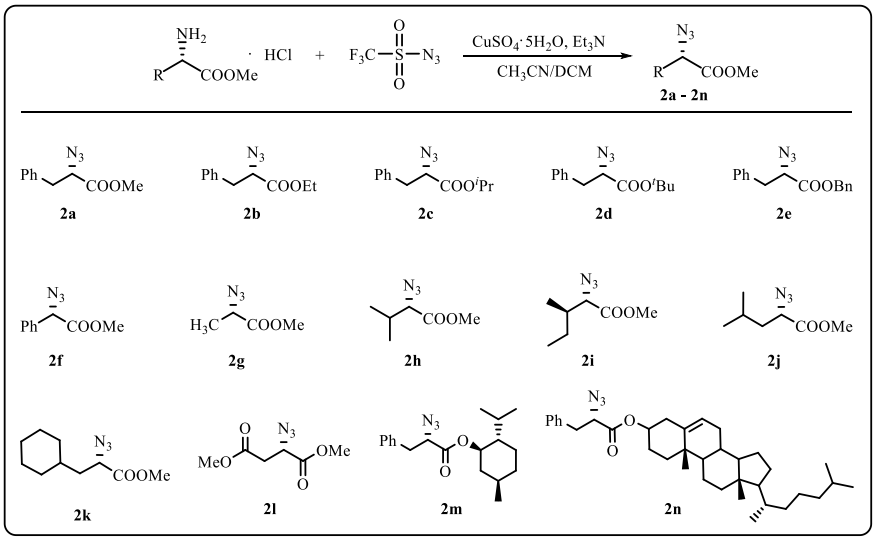
1. General Information.

Reactions were monitored by TLC on silica gel GF_{254} (0.25 mm). Column chromatography purifications were carried out using chromatography neutral Al_2O_3 (200-300 mesh). ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker advance III 400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant in Hertz (Hz). HRMS spectra were recorded using Bruker micro TOF-Q II mass spectrometer. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Chiracel OD-H column.

All solvents were obtained from commercial sources and were purified according to standard procedures.

2. Preparation of Azides 2a-v.

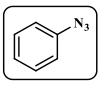
2a-n was prepared according to literature procedure. [1]



Scheme S1. Synthesis of substrates 2a - 2n.

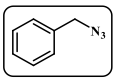
Amino acid methyl ester hydrochloride (5 mmol) was dissolved in 10 mL of acetonitrile. Then 0.01 equiv of $CuSO_4$ and 2 equiv of NEt_3 per substrate amine were added into the mixture at 0 °C, followed by the addition of an acetonitrile solution of triflyl azide (1.2 equiv per amino group) dropwise. The mixture was stirred for 16 hours at room temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to gain the corresponding products. Spectral datas were consistent with the results reported in the literature.

azidobenzene (2o)



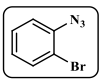
Compound **2o** was prepared according to literature procedure.[2] To an ice-cooled mixture of concentrated HCl (1.9 mL) and water (12 mL) was added aniline (0.53 g, 5.74 mmol), followed by the addition of $NaNO_2$ (0.74 g in 2 mL water) dropwise, the mixture was stirred for 30 minutes. The solution of NaN_3 (0.7 g in 3 mL water) was addition at 0 °C, and the mixture was stirred at room temperature for one hour, and extracted with diethyl ether (3×20mL), the combined organic layers were washed with brine and dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography (petroleum ether) to obtain the pure compound **2o** (0.62 g, 5.2 mmol, 90%) as a yellow liquid. This compound is known and matches the reported spectroscopic data.

(azidomethyl)benzene (2p)



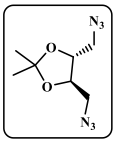
Benzyl azides **2p** was prepared according to literature procedure.[3] To a solution of benzyl bromide (3.6 mL, 30.0 mmol) in tetrahydrofuran (50 mL) was added a solution of sodium azide (3.9 g, 60.0 mmol) in water (50 mL), then the mixture was stirred at 80 °C overnight. Ethyl acetate (50 mL) was added, and the organic layer separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (6 × 20 mL), dried over anhydrous Na_2SO_4 and filtered. Solvent was removed in vacuo, purification by flash chromatography (petroleum ether /ethyl acetate = 50:1) gave the pure product **2p** (3.9 g, 98% yield) as a colorless oil. Spectral data was consistent with previously reported results.

1-azido-2-bromobenzene (2q)



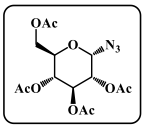
Compound **2q** was prepared according to literature procedure.[2] To an ice-cooled mixture of concentrated HCl (1.9 mL) and water (12 mL) was added 2-Bromoaniline (0.99 g, 5.74 mmol), followed by the addition of $NaNO_2$ (0.74 g in 2 mL water) dropwise, the mixture was stirred for 30 minutes. The solution of NaN_3 (0.7 g in 3 mL water) was addition at 0 °C, and the mixture was stirred at room temperature for one hour, and extracted with diethyl ether (3×20mL), the combined organic layers were washed with brine and dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography (petroleum ether) to obtain the pure compound **2q** (1.03 g, 5.2 mmol, 90%) as a yellow liquid. This compound is known and matches the reported spectroscopic data.

(4*R*,5*R*)-4,5-bis(azidomethyl)-2,2-dimethyl-1,3-dioxolane (2r)



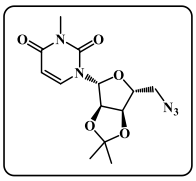
Compound **2r** was prepared according to literature procedure.[4] To an ice-cooled solution of dimethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (20 mmol, 1.0 equiv) in dry methanol (40 mL) was added sodium borohydride (100 mmol, 5.0 equiv) in small portions under Ar atmosphere, and the mixture was stirred at room temperature for 4 h, then was concentrated under reduced pressure. Water (30 mL) was added to the residue, and the aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product in 89% yield, which was used directly without further purification. To an ice-cooled solution of ((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (17.8 mmol, 1.0 equiv) in DCM (30 mL) was added NEt_3 (2.1 equiv) and MsCl (2.1 equiv), the resulting cloudy white mixture was stirred at 0 °C for 1.5 h. The reaction mixture was washed sequentially with water 5% $CuSO_4$, saturated $NaHCO_3$ and brine, then dried over anhydrous Na_2SO_4 and concentrated to give a white solid. The solution of the white solid and NaN_3 (3.0 equiv) in DMF (20 mL) was stirred at 80 °C overnight. The reaction mixture was diluted with 30 mL of water. The aqueous layer was extracted with 100 mL of ethyl acetate. The organic layers were washed with water and brine, dried over Na_2SO_4 and concentrated to give a yellowish soild. The residue was crystallized from ethanol to give compound **2r** as a white soild.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate (2s)



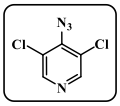
Compound **2s** was prepared according to literature procedure.[5] The mixture of 2,3,4,6-Tetra-O-acetyl-alpha-*D*-glucopyranosyl bromide (2.1 g, 5.0 mmol) and sodium azide (0.65 g, 10.0 mmol) in DMF (5 mL) was stirred at 80 °C overnight. Ethyl acetate (50 mL) was added, and the organic layer separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (6 × 20 mL), dried over anhydrous Na_2SO_4 and filtered. Solvent was removed in vacuo, purification by flash chromatography (petroleum ether /ethyl acetate = 30:1) gave the pure product **2s** (1.8 g, 98% yield) as a white solid. Spectral data was consistent with previously reported results.

1-((3a*R*,4*R*,6*R*,6a*R*)-6-(azidomethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)-3-methylpyrimidine-2,4(1H,3H)-dion e (2t)



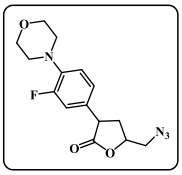
Compound **2t** was prepared according to literature procedure.[6] To an ice-cooled solution of 1-((3a*R*,4*R*,6*R*,6a*R*)-6-(hydroxy-methyl)- 2,2-dimethyltetrahydrofuro[3,4-*d*] [1,3]dioxol-4-yl)-3-methylpyrimidine-2,4(1H,3H)-dione (10 mmol) and triethylamine (36 mmol, 3.6 equiv,) in dry DCM (20 mL) was added methanesulfonyl chloride (18 mmol, 1.8 equiv.) dropwise. The mixture was stirred for 3 hours at room temperature. DCM was removed in vacuo, purification by flash chromatography (petroleum ether /ethyl acetate = 1:1) gave the hydroxyl protected product as a white solid. The solution of the hydroxyl protected product (9.4 mmol, 1 equiv) and NaN_3 (18.8 mmol, 2 equiv) in DMF (10 mL) was stirred at 90 °C for 8 h. The reaction was quenched with water (10 mL) and then ethyl acetate (30 mL) was added. The organic layer was separated and washed with water and saturated NaCl, dried over Na_2SO_4, filtered and evaporated under reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 2:1) to afford product **2t** (2.65 g, 82% yield).

4-azido-3,5-dichloropyridine (2u)



Compound **2u** was prepared according to literature procedure.[7] The mixture of 3,4,5-Trichloropyridine (0.91 g, 5.0 mmol) and sodium azide (0.65 g, 10.0 mmol) in DMSO (5 mL) was stirred at 25 °C overnight. Ethyl acetate (50 mL) was added, and the organic layer separated. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (6 × 20 mL), dried over anhydrous Na_2SO_4 and filtered. Solvent was removed in vacuo, purification by flash chromatography (petroleum ether /ethyl acetate = 10:1) gave the pure product **2u** (0.85 g, 90% yield) as a white solid. Spectral data was consistent with previously reported results.

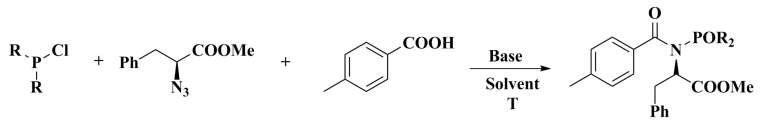
5-(azidomethyl)-3-(3-fluoro-4-morpholinophenyl)dihydrofuran-2(3H)-one (2v)



Compound **2v** was prepared according to literature procedure.[8] To an ice-cooled solution of (5*R*)-3-(3-Fluoro-4-(4-morpholinyl)phenyl)-5-hydroxymethyl-2-oxazo- lidione (10 mmol) and triethylamine (36 mmol, 3.6 equiv,) in dry DCM (20 mL) was added methanesulfonyl chloride (18 mmol, 1.8 equiv.) dropwise. The mixture was stirred for 3 hours at room temperature. DCM was removed in vacuo, purification by flash chromatography (petroleum ether /ethyl acetate = 4:1) gave the hydroxyl protected product as a white solid. The solution of the hydroxyl protected product (9.4 mmol, 1 equiv) and NaN_3 (18.8 mmol, 2 equiv) in DMF (10 mL) was stirred at 80 °C for 6 h. The reaction was quenched with water (10 mL) and then ethyl acetate (30 mL) was added. The organic layer was separated and washed with water and saturated NaCl, dried over Na_2SO_4, filtered and evaporated under reduced pressure, the residue was purified by column chromatography (silica gel, petroleum ether : ethyl acetate = 4:1) to afford product **2v** (2.56 g, 80% yield).

3. Optimization of Reaction Conditions A, B and C.

Table S1. Optimization of Reaction Conditions A and B.



1a: R = Ph
1b: R = OEt

2a

3a

4a: R = Ph
4b: R = OEt

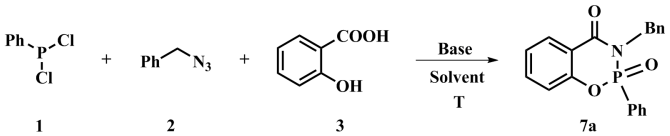
Entry	Solvent	T (°C)	Base	2a/1a/3a/Base 2a/1b/3a/Base	Conv. (mol/L)	t (h) 1a / 1b	Yield (%)[b] 4a / 4b
1	toluene	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	91 / 53
2	C_6H_5Cl	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	87 / 51
3	DCM	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	80 / 48
4	EA	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	5 / 0
5	MeCN	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	80 / 42
6	Et_2O	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	88 / 49
	DMF	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	7 / 3
8	THF	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	5 / 0
9	MeOH	25	Et_3N	1.0/1.2/1.2/1.2	0.10	6 / 36	8 / 0
10	toluene	0	Et_3N	1.0/1.2/1.2/1.2	0.10	18 / 72	88 / 48
11	toluene	15	Et_3N	1.0/1.2/1.2/1.2	0.10	10 / 40	90 / 49
12	toluene	30	Et_3N	1.0/1.2/1.2/1.2	0.10	5 / 30	91 / 51
13	toluene	40	Et_3N	1.0/1.2/1.2/1.2	0.10	2 / 12	87 / 62
14	toluene	50	Et_3N	1.0/1.2/1.2/1.2	0.10	2 / 8	86 / 71
15[c]	toluene	T	DIPEA	1.0/1.2/1.2/1.2	0.10	6 / 8	10 / 6
16[c]	toluene	T	DABCO	1.0/1.2/1.2/1.2	0.10	6 / 8	6 / 3
17[c]	toluene	T	Et_2NH	1.0/1.2/1.2/1.2	0.10	6 / 8	6 / 0
18[c]	toluene	T	DBU	1.0/1.2/1.2/1.2	0.10	6 / 8	3 / 0
19[c]	toluene	T	DMAP	1.0/1.2/1.2/1.2	0.10	6 / 8	11 / 7
20[c]	toluene	T	TMG	1.0/1.2/1.2/1.2	0.10	6 / 8	8 / 3
21[c]	toluene	T	K_2CO_3	1.0/1.2/1.2/1.2	0.10	6 / 8	0 / 0
22[c]	toluene	T	$NaHCO_3$	1.0/1.2/1.2/1.2	0.10	6 / 8	0 / 0
23[c]	toluene	T	NaH_2PO_4	1.0/1.2/1.2/1.2	0.10	6 / 8	0 / 0
24[c]	toluene	T	AcOK	1.0/1.2/1.2/1.2	0.10	6 / 8	0 / 0
25[c]	toluene	T	NaOH	1.0/1.2/1.2/1.2	0.10	6 / 8	0 / 0
26[c]	toluene	T	Et_3N	1.0/1.1/1.1/1.1	0.10	8 / 9	88 / 69
27[c]	toluene	T	Et_3N	1.0/1.3/1.3/1.3	0.10	6 / 6	92 / 69
28[c]	toluene	T	Et_3N	1.0/1.2/1.2/1.3	0.10	6 / 6	92 / 76
29[c]	toluene	T	Et_3N	1.0/1.2/1.2/1.4	0.10	6 / 6	92 / 79
30[c]	toluene	T	Et_3N	1.0/1.2/1.2/1.5	0.10	6 / 6	92 / 79
31[c,d]	toluene	T	Et_3N	1.0/1.2/1.2/ X	0.05	8 / 7	91 / 76
32[c,d]	**toluene**	**T**	**Et_3N**	**1.0/1.2/1.2/ X**	**0.20**	**4 / 6**	**96 / 82**
33[c,d]	toluene	T	Et_3N	1.0/1.2/1.2/ X	0.40	4 / 6	95 / 82

[a] Reaction conditions: **2a** (0.2 mmol). [b] Isolated yields. [c] T = 25 (use **1a** as substrate); T = 50 (use **1b** as substrate); [d] X = 1.2 (use **1a** as substrate); X = 1.4 (use **1b** as substrate).

Optimization of Reaction Conditions A: To a solution of carboxylic acid **3a** in ultra-dry toluene was added chlorodiphenylphosphine **1a** and Et_3N under Ar atmosphere at room temperature, after stirred at 25 ºC for 10 minutes, azide **2a** (0.2 mmol) in ultra-dry toluene was added. The mixture was stirred at 25 ºC for 2-18 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the product **4a**.

Optimization of Reaction Conditions B: To a solution of carboxylic acid **3a** in ultra-dry toluene was added diethyl chlorophosphite **1b** and Et_3N under Ar atmosphere at room temperature, after stirred at 25 ºC for 30 minutes, azide **2a** (0.2 mmol) in ultra-dry toluene was added. The mixture was stirred at 50 ºC for 6-72 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the corresponding product **4b**.

Table S2. Optimization of Reaction Conditions C.



1 2 3 7a

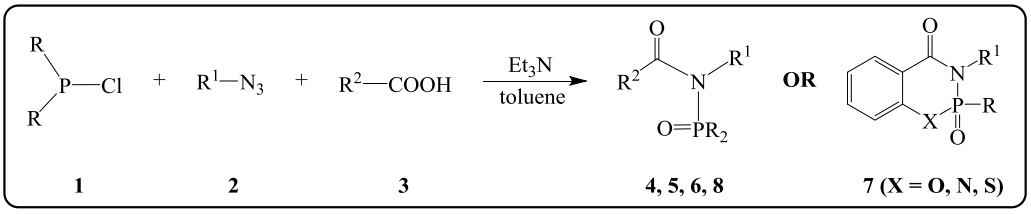
Entry	Solvent	T (°C)	Base	2/1/3/Base	Conv. (mol/L)	t (h)	Yield (%)[b] 7a
1	toluene	25	Et_3N	1.0/1.0/1.0/2.0	0.10	30	trace
2	toluene	30	Et_3N	1.0/1.0/1.0/2.0	0.10	30	22
3	toluene	40	Et_3N	1.0/1.0/1.0/2.0	0.10	26	29
4	toluene	50	Et_3N	1.0/1.0/1.0/2.0	0.10	24	50
5	toluene	60	Et_3N	1.0/1.0/1.0/2.0	0.10	18	54
6	toluene	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	63
7	toluene	80	Et_3N	1.0/1.0/1.0/2.0	0.10	15	61
8	C_6H_5Cl	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	63
9	DCM	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	62
10	EA	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	48
11	MeCN	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	trace
12	Et_2O	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	63
13	DMF	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	trace
14	THF	70	Et_3N	1.0/1.0/1.0/2.0	0.10	16	51
15	toluene	70	DIPEA	1.0/1.0/1.0/2.0	0.10	30	15
16	toluene	70	DABCO	1.0/1.0/1.0/2.0	0.10	30	trace
17	toluene	70	Et_2NH	1.0/1.0/1.0/2.0	0.10	30	trace
18	toluene	70	DBU	1.0/1.0/1.0/2.0	0.10	30	21
19	toluene	70	DMAP	1.0/1.0/1.0/2.0	0.10	30	27
20	toluene	70	K_2CO_3	1.0/1.0/1.0/2.0	0.10	30	0
21	toluene	70	$NaHCO_3$	1.0/1.0/1.0/2.0	0.10	30	0
22	toluene	70	NaH_2PO_4	1.0/1.0/1.0/2.0	0.10	30	0
23	toluene	70	AcOK	1.0/1.0/1.0/2.0	0.10	30	0
24	toluene	70	NaOH	1.0/1.0/1.0/2.0	0.10	30	0
25	toluene	70	Et_3N	1.0/1.0/1.0/2.1	0.10	16	62
26	toluene	70	Et_3N	1.0/1.0/1.0/2.2	0.10	16	63
27	toluene	70	Et_3N	1.0/1.0/1.0/2.3	0.10	16	63
28	toluene	70	Et_3N	1.0/1.1/1.1/2.2	0.10	16	69
29	**toluene**	**70**	**Et_3N**	**1.0/1.2/1.2/2.4**	**0.10**	**16**	**77**
30	toluene	70	Et_3N	1.0/1.3/1.3/2.6	0.10	16	76
31	toluene	70	Et_3N	1.0/1.4/1.4/2.8	0.10	16	77
32	toluene	70	Et_3N	1.0/1.2/1.2/2.4	0.05	16	63
33	toluene	70	Et_3N	1.0/1.2/1.2/2.4	0.20	16	73
34	toluene	70	Et_3N	1.0/1.2/1.2/2.4	0.40	16	71

[a] Reaction conditions: **2** (0.2 mmol). [b] Isolated yields.

Optimization of Reaction Conditions C: To a solution of carboxylic acid **3** in ultra-dry toluene was added dichlorophenylphosphine **1** and Et_3N under Ar atmosphere at room temperature, after stirred at 25 ºC for 10 minutes, azide **2** (0.2 mmol) in ultra-dry toluene was added. The mixture was stirred at 70 ºC for 15-30 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent

to give the product **7a**.

4. Representative Procedure for the Synthesis of Products 4-8.



Scheme S2. Synthesis of products.

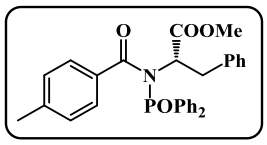
Procedure A: To a solution of carboxylic acid **3** (0.24 mmol) in ultra-dry toluene (0.5 mL) was added chlorodiphenylphosphine **1** (0.24 mmol) and Et_3N (0.24 mmol) under Ar atmosphere at room temperature, after stirred at 25 °C for 10 minutes, azide **2** (0.2 mmol) in ultra-dry toluene (0.5 mL) was added. The mixture was stirred at 25 °C for 4 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the corresponding products **4a**, **5a-x**.

Procedure B: To a solution of carboxylic acid **3** (0.24 mmol) in ultra-dry toluene (0.5 mL) was added diethyl chlorophosphite **1** (0.24 mmol) and Et_3N (0.28 mmol) under Ar atmosphere at room temperature, after stirred at 25 °C for 30 minutes, azide **2** (0.2 mmol) in ultra-dry toluene (0.5 mL) was added. The mixture was stirred at 50 °C for 6 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the corresponding products **4b-e**, **6a-n**, **8a-l**.

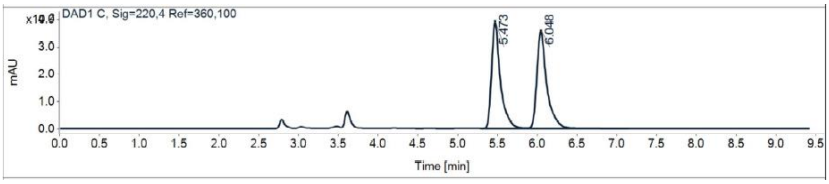
Procedure C: To a solution of carboxylic acid **3** (0.24 mmol) in ultra-dry toluene (0.5 mL) was added dichlorophenylphosphine **1** (0.24 mmol) and Et_3N (0.48 mmol) under Ar atmosphere at room temperature, after stirred at 25 °C for 10 minutes, azide **2** (0.2 mmol) in ultra-dry toluene (0.5 mL) was added. The mixture was stirred at 70 °C for 16 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the corresponding products **7a-j**.

5. Characterization Data of Products.

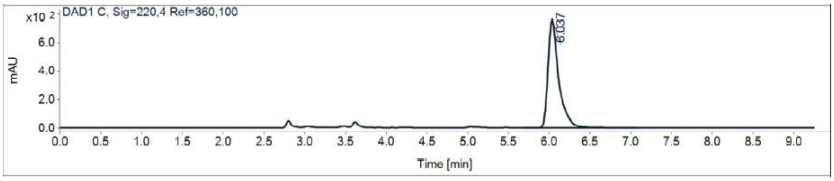
Methyl *N*-(diphenylphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (4a)



Colorless oil, 96% yield (95.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). >99% ee was determined by HPLC analysis (Daicel Chiralcel OD-H column, hexane/2-propanol 9:1, 1.0 mL/min). Retention time: t_{major} = 6.0 min. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 12.4, 7.6 Hz, 2H), 7.85 (dd, *J* = 13.6, 7.2 Hz, 2H), 7.61 - 7.57 (m, 1H), 7.51 - 7.46 (m, 2H), 7.40 - 7.36 (m, 1H), 7.33 - 7.29 (m, 2H), 7.17 - 7.12 (m, 3H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 7.2 Hz, 2H), 4.76 - 4.68 (m, 1H), 3.92 (s, 3H), 3.52 (dd, *J* = 14.8, 4.0 Hz, 1H), 3.24 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8 (d, *J* = 4.0 Hz), 171.3, 141.1, 137.1, 133.8, 133.7, 132.8 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 3.0 Hz), 132.2, 131.6, 131.5, 129.4, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 126.6, 62.8 (d, *J* = 2.0 Hz), 52.8, 36.9, 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.63. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{29}NO_4P$ $[M+H]^+$: 498.1829, found 498.1833.

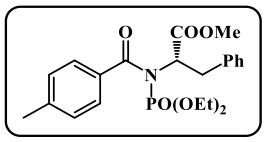


RT [min]	Height	Symm.	Width (50%)	Area	Area%
5.473	388.90823	0.59	0.1089	3027.67896	49.34
6.048	353.94995	0.59	0.1220	3109.24487	50.66



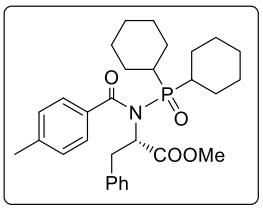
RT [min]	Height	Symm.	Width (50%)	Area	Area%
6.037	755.73755	0.56	0.1278	6919.20166	100.00

Methyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (4b)



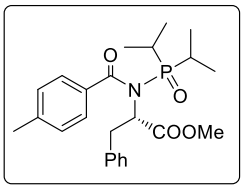
Colorless oil, 82% yield (71.1 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 - 7.26 (m, 2H), 7.22 (q, *J* = 7.5 Hz, 5H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.08 - 5.01 (m, 1H), 4.04 - 3.92 (m, 2H), 3.82 (s, 3H), 3.76 - 3.70 (m, 1H), 3.56 (dd, *J* = 14.4, 4.4 Hz, 1H), 3.50 - 3.43 (m, 1H), 3.41 - 3.34 (m, 1H), 2.35 (s, 3H), 1.11 - 1.03 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8 (d, *J* = 6.0 Hz), 171.0 (d, *J* = 1.0 Hz), 141.3, 138.1, 133.2, 129.8, 128.5, 128.3, 127.7, 126.7, 64.0 (d, *J* = 6.0 Hz), 63.5 (d, *J* = 6.0 Hz), 61.4 (d, *J* = 4.0 Hz), 52.5, 35.2, 21.6, 15.8 (d, *J* = 8.0 Hz), 15.7 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.12. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{29}NO_6P$ $[M+H]^+$: 434.1727, found 434.1730.

Methyl *N*-(dicyclohexylphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (4c)



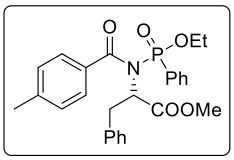
Colorless oil, 81% yield (82.5 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.16 - 7.14 (m, 3H), 6.98 (d, *J* = 6.0 Hz, 2H), 4.98 - 4.91 (m, 1H), 3.66 (s, 3H), 3.55 (dd, J = 14.2, 7.8 Hz, 1H), 3.04 (dd, J = 14.2, 5.0 Hz, 1H), 2.40 - 2.30 (m, 5H), 2.14 - 2.07 (m, 3H), 1.88 - 1.82 (m, 5H), 1.69 - 1.69 (m, 2H), 1.55 - 1.55 (m, 4H), 1.26 - 1.26 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 170.7, 141.1, 138.1, 132.6, 129.2, 128.2, 127.0, 126.4, 60.8, 52.2, 39.8, 39.4, 39.1, 38.4, 37.7, 27.0, 27.0, 26.8, 26.7, 26.6, 26.6, 26.5, 26.1 (d, *J* = 5.0 Hz), 25.9 (d, *J* = 5.0 Hz), 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 64.54. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{41}NO_4P$ $[M+H]^+$: 510.2768, found 510.2772.

Methyl *N*-(diisopropylphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (4d)



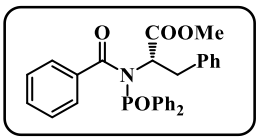
Colorless oil, 83% yield (71.3 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 - 7.12 (m, 3H), 7.00 (d, *J* = 6.0 Hz, 2H), 4.99 - 4.92 (m, 1H), 3.64 (s, 3H), 3.56 (dd, J = 14.4, 8.0 Hz, 1H), 3.03 (dd, J = 14.2, 5.0 Hz, 1H), 2.72 - 2.63 (m, 2H), 2.40 (s, 3H), 1.38 - 1.23 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.6, 170.6, 141.1, 138.1, 132.5 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 3.0 Hz), 128.2, 126.9, 126.4, 60.9, 52.2, 39.5, 29.84, 29.1029.5 (d, *J* = 74.0 Hz), 28.0 (d, *J* = 74.0 Hz), 21.5, 17.3 (d, *J* = 5.0 Hz), 17.1, 17.0, 16.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 70.22. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{33}NO_4P$ $[M+H]^+$: 430.2142, found 430.2147.

Methyl *N*-(ethoxy(phenyl)phosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (4e)



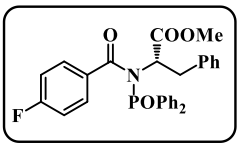
Colorless oil, 63% yield (58.7 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 - 7.54 (m, 0.85H), 7.39 - 7.20 (m, 7.59H), 7.12 - 7.07 (m, 1.31H), 7.00 - 6.94 (m, 1.21H), 6.87 - 6.74 (m, 4.13H), 5.29 - 5.23 (m, 1H), 4.33 - 4.22 (m, 1.25H), 3.91 (s, 1.2H), 3.88 (s, 1.8H), 3.70 - 3.61 (m, 1.06H), 3.49 - 3.36 (m, 1.41H), 2.28 (s, 1.24H), 2.26 (s, 1.78H), 1.34 (t, *J* = 7.0 Hz, 1.96H), 1.15 (t, *J* = 7.0 Hz, 1.3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (d, *J* = 7.0 Hz), 171.3, 171.3, 140.9, 140.5, 138.2, 138.2, 132.8, 132.7, 132.1, 132.0, 131.9 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 11.0 Hz), 129.9, 129.9, 128.8, 128.6, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.8, 127.5, 126.8, 126.7, 62.8 (d, *J* = 7.0 Hz), 61.7 (d, *J* = 6.0 Hz), 61.0, 60.9, 52.6, 52.5, 36.0, 35.8, 21.5, 21.4, 16.3 (d, *J* = 7.0 Hz), 16.0 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.91, 18.48. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{29}NO_5P$ $[M+H]^+$: 466.1778, found 466.1783.

Methyl *N*-benzoyl-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5a)



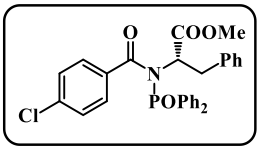
Colorless oil, 96% yield (92.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.87 (dd, *J* = 13.6, 6.8 Hz, 2H), 7.62 - 7.58 (m, 1H), 7.52 - 7.48 (m, 2H), 7.38 - 7.36 (m, 1H), 7.34 - 7.25 (m, 3H), 7.20 - 7.14 (m, 5H), 7.10 - 7.06 (m, 2H), 6.55 (d, *J* = 7.2 Hz, 2H), 4.71 - 4.64 (m, 1H), 3.92 (s, 3H), 3.53 (dd, *J* = 14.8, 3.6 Hz, 1H), 3.26 (dd, *J* = 14.8, 10.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6 (d, *J* = 3.0 Hz), 171.1, 137.1, 135.0, 133.7, 133.6, 132.9 (d, *J* = 2.0 Hz), 132.0 (d, *J* = 3.0 Hz), 131.7, 131.6, 130.7, 129.4, 128.6, 128.5, 128.4, 128.2, 128.0, 127.7, 126.7, 62.9, 52.9, 36.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.59. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{27}NO_4P$ $[M+H]^+$: 484.1672, found 484.1677.

Methyl *N*-(diphenylphosphoryl)-*N*-(4-fluorobenzoyl)-*L*-phenylalaninate (5b)



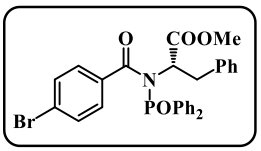
Colorless oil, 93% yield (93.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 11.6, 8.0 Hz, 2H), 7.86 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.60 - 7.57 (m, 1H), 7.49 - 7.48 (m, 2H), 7.37 - 7.35 (m, 1H), 7.31 - 7.30 (m, 2H), 7.26 - 7.21 (m, 3H), 7.18 - 7.14 (m, 2H), 6.81 (t, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 4.8 Hz, 2H), 4.56 - 4.51 (m, 1H), 3.91 (s, 3H), 3.50 (dd, *J* = 14.6, 3.4 Hz, 1H), 3.27 (dd, *J* = 14.2, 10.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (d, *J* = 5.0 Hz), 171.0, 163.9 (d, *J* = 251.0 Hz), 137.1, 133.5, 133.4, 132.9 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 3.0 Hz), 131.7, 131.5, 131.4, 130.6, 130.5, 129.4, 128.6, 128.5, 128.5, 128.4, 128.3, 126.9, 114.9 (d, *J* = 22.0 Hz), 62.7, 52.8, 36.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.17. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.52. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}FNO_4P$ $[M+H]^+$: 502.1578, found 502.1582.

Methyl *N*-(4-chlorobenzoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5c)



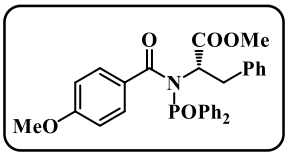
Colorless oil, 93% yield (96.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 12.0, 8.0 Hz, 2H), 7.85 (dd, *J* = 13.4, 7.4 Hz, 2H), 7.60 - 7.56 (m, 1H), 7.51 - 7.46 (m, 2H), 7.39 - 7.35 (m, 1H), 7.33 - 7.28 (m, 2H), 7.23 - 7.19 (m, 1H), 7.16 - 7.09 (m, 6H), 6.63 (d, *J* = 4.8 Hz, 2H), 4.56 - 4.49 (m, 1H), 3.90 (s, 3H), 3.50 (dd, *J* = 14.6, 3.8 Hz, 1H), 3.27 (dd, *J* = 14.6, 10.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5 (d, *J* = 5.0 Hz), 170.9, 137.0, 136.8, 133.6, 133.5, 133.4, 132.9 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 3.0 Hz), 131.7, 131.6, 129.4, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 126.9, 62.8, 52.9, 36.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.38. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}ClNO_4P$ $[M+H]^+$: 518.1282, found 518.1287.

Methyl *N*-(4-bromobenzoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5d)



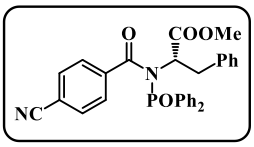
Colorless oil, 94% yield (105.7 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 11.8, 7.8 Hz, 2H), 7.85 (dd, *J* = 13.4, 7.4 Hz, 2H), 7.61 - 7.58 (m, 1H), 7.51 - 7.47 (m, 2H), 7.41 - 7.37 (m, 1H), 7.34 - 7.26 (m, 4H), 7.22 - 7.20 (m, 1H), 7.16 - 7.12 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 4.8 Hz, 2H), 4.55 - 4.49 (m, 1H), 3.91 (s, 3H), 3.50 (dd, *J* = 14.4, 3.6 Hz, 1H), 3.27 (dd, *J* = 14.6, 10.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6 (d, *J* = 4.0 Hz), 170.9, 137.0, 134.1, 133.5, 133.4, 132.9 (d, *J* = 2.0 Hz), 132.1 (d, *J* = 3.0 Hz), 131.7, 131.6, 131.0, 129.5, 129.4, 128.7, 128.6, 128.5, 128.4, 128.3, 126.9, 125.3, 62.8, 52.9, 36.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.32. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}BrNO_4P$ $[M+H]^+$: 562.0777, found 562.0779.

Methyl *N*-(diphenylphosphoryl)-*N*-(4-methoxybenzoyl)-*L*-phenylalaninate (5e)



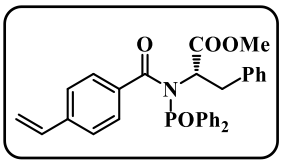
Colorless oil, 96% yield (98.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 12.2, 7.8 Hz, 2H), 7.84 (dd, *J* = 13.4, 7.4 Hz, 2H), 7.60 - 7.57 (m, 1H), 7.50 - 7.46 (m, 2H), 7.38 - 7.35 (m, 1H), 7.32 - 7.30 (m, 2H), 7.26 - 7.24 (m, 2H), 7.21 - 7.17 (m, 1H), 7.13 - 7.09 (m, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 6.8 Hz, 2H), 4.71 - 4.65 (m, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 3.51 (dd, *J* = 14.4, 3.6 Hz, 1H), 3.24 (dd, *J* = 14.8, 10.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.2 (d, *J* = 4.0 Hz), 171.3, 161.5, 137.1, 133.7, 133.6, 132.7, 131.9 (d, *J* = 3.0 Hz), 131.6, 131.5, 130.1, 129.3, 128.5, 128.4, 128.4, 128.3, 128.2, 127.4, 126.7, 113.2, 62.6 (d, *J* = 3.0 Hz), 55.3, 52.8, 36.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.87. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{29}NO_5P$ $[M+H]^+$: 514.1778, found 514.1779.

Methyl *N*-(4-cyanobenzoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5f)



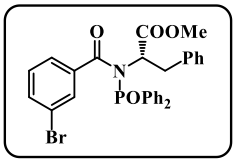
Colorless oil, 91% yield (92.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 - 8.00 (m, 2H), 7.86 - 7.82 (m, 2H), 7.61 - 7.61 (m, 1H), 7.50 - 7.50 (m, 2H), 7.38 - 7.37 (m, 3H), 7.31 - 7.22 (m, 7H), 6.71 (s, 2H), 4.42 - 4.36 (m, 1H), 3.90 (s, 3H), 3.49 (d, *J* = 14.4 Hz, 1H), 3.32 - 3.26 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 5.0 Hz), 170.6, 139.3, 136.9, 133.2, 133.1, 132.3, 131.8, 131.7, 131.4, 129.5, 128.8, 128.7, 128.6, 128.4, 127.1, 118.0, 113.9, 62.7, 53.0, 36.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.50. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{26}N_2O_4P$ $[M+H]^+$: 509.1625, found 509.1630.

Methyl *N*-(diphenylphosphoryl)-*N*-(4-vinylbenzoyl)-*L*-phenylalaninate (5g)



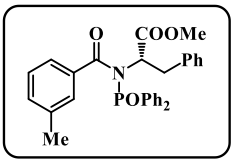
Colorless oil, 88% yield (89.7 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 16.6, 10.2 Hz, 2H), 6.59 (dd, *J* = 18.0, 9.6 Hz, 2H), 6.37 - 6.33 (m, 1H), 6.27 - 6.22 (m, 2H), 6.12 - 6.05 (m, 3H), 5.93 - 5.90 (m, 5H), 5.86 - 5.81 (m, 2H), 5.40 - 5.29 (m, 3H), 4.47 (d, *J* = 23.6 Hz, 1H), 4.02 (d, *J* = 14.8 Hz, 1H), 3.46 - 3.36 (m, 1H), 2.67 (s, 3H), 2.26 (dd, *J* = 19.6, 4.8 Hz, 1H), 1.99 (dd, *J* = 19.6, 14.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.3 (d, *J* = 5.0 Hz), 170.1, 138.7, 136.0, 134.9, 133.1, 132.7, 132.6, 131.8, 130.9 (d, *J* = 4.0 Hz),, 130.6, 129.5, 128.3, 127.5, 127.4, 127.4, 127.3, 127.1, 127.1, 125.7, 124.6, 114.8, 61.7, 51.8, 35.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.24. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{29}NO_4P$ $[M+H]^+$: 510.1829, found 510.1833.

Methyl *N*-(3-bromobenzoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5h)



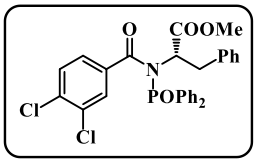
Colorless oil, 88% yield (99.0 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 12.0, 8.0 Hz, 2H), 7.85 (dd, *J* = 13.6, 7.2 Hz, 2H), 7.64 - 7.61 (m, 1H), 7.54 - 7.50 (m, 2H), 7.44 - 7.32 (m, 4H), 7.24 - 7.20 (m, 2H), 7.17 - 7.13 (m, 2H), 7.06 - 7.02 (m, 2H), 6.59 (s, 2H), 4.57 - 4.50 (m, 1H), 3.92 (s, 3H), 3.50 (dd, *J* = 14.4, 3.6 Hz, 1H), 3.26 (dd, *J* = 14.4, 10.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0 (d, *J* = 4.0 Hz), 170.8, 136.9, 133.6, 133.5, 133.1, 132.2 (d, *J* = 3.0 Hz), 131.7, 131.5, 130.9, 130.7, 129.4, 129.3, 128.7, 128.6, 128.6, 128.5, 128.4, 127.0, 126.0, 122.1, 62.9, 52.9, 36.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.32. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}BrNO_4P$ $[M+H]^+$: 562.0777, found 562.0780.

Methyl *N*-(diphenylphosphoryl)-*N*-(3-methylbenzoyl)-*L*-phenylalaninate (5i)



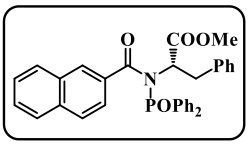
Colorless oil, 86% yield (85.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.86 (dd, *J* = 13.6, 7.2 Hz, 2H), 7.63 - 7.60 (m, 1H), 7.54 - 7.49 (m, 2H), 7.42 - 7.38 (m, 1H), 7.35 - 7.31 (m, 2H), 7.19 - 7.15 (m, 1H), 7.08 - 7.05 (m, 5H), 6.77 (s, 1H), 6.52 (d, *J* = 6.8 Hz, 2H), 4.72 - 4.65 (m, 1H), 3.92 (s, 3H), 3.53 (dd, *J* = 14.8, 3.6 Hz, 1H), 3.25 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9 (d, *J* = 4.0 Hz), 171.2, 137.9, 137.1, 134.9, 133.8, 133.7, 132.8 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 3.0 Hz), 131.6, 131.5, 131.3, 129.5, 128.6, 128.4, 128.4, 128.3, 128.3, 128.2, 127.8, 126.6, 124.2, 62.9, 52.8, 36.9, 21.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.63. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{29}NO_4P$ $[M+H]^+$: 498.1829, found 498.1830.

Methyl-*N*-(3,4-dichlorobenzoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5j)



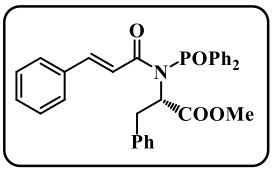
Colorless oil, 81% yield (89.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (t, *J* = 9.0 Hz, 2H), 7.84 (dd, *J* = 13.0, 7.4 Hz, 2H), 7.62 - 7.58 (m, 1H), 7.51 - 7.50 (m, 2H), 7.43 - 7.39 (m, 1H), 7.34 - 7.32 (m, 2H), 7.26 - 7.25 (m, 1H), 7.21 - 7.19 (m, 3H), 7.09 - 7.04 (m, 2H), 6.66 (s, 2H), 4.45 (t, *J* = 10.6 Hz, 1H), 3.90 (s, 3H), 3.48 (dd, *J* = 14.6, 3.4 Hz, 1H), 3.27 (dd, *J* = 14.4, 10.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1 (d, *J* = 5.0 Hz), 170.7, 136.9, 135.0, 133.4, 133.3, 133.1 (d, *J* = 2.0 Hz), 132.3 (d, *J* = 3.0 Hz), 131.7, 131.6, 130.2, 129.7, 129.5, 128.7, 128.7, 128.6, 128.5, 128.4, 127.1, 127.0, 62.8, 52.9, 36.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.81. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{25}Cl_2NO_4P$ $[M+H]^+$: 552.0893, found 552.0898.

Methyl *N*-(2-naphthoyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5k)



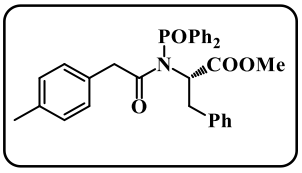
Colorless oil, 91% yield (97.1 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 16.6, 10.2 Hz, 2H), 7.61 (dd, *J* = 18.0, 9.2 Hz, 2H), 7.47 - 7.42 (m, 3H), 7.33 - 7.16 (m, 7H), 7.05 - 6.92 (m, 4H), 6.81 (t, *J* = 10.0 Hz, 2H), 6.28 (d, *J* = 9.6 Hz, 2H), 4.52 - 4.42 (m, 1H), 3.67 (s, 3H), 3.27 (dd, *J* = 19.6, 5.2 Hz, 1H), 3.06 (dd, *J* = 19.4, 14.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.6 (d, *J* = 4.8 Hz), 171.1, 137.0, 133.8, 133.7, 133.6, 132.8, 132.5, 132.2, 131.9, 131.8, 131.6, 131.4, 130.8, 130.8, 129.4, 128.9, 128.6, 128.4, 128.3, 128.1, 127.8, 127.6, 126.7, 126.6, 123.9, 62.7 (d, *J* = 3.3 Hz), 52.8, 36.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.37. **HRMS** (ESI) *m/z* calcd for $C_{33}H_{29}NO_4P$ $[M+H]^+$: 534.1829, found 534.1833.

Methyl *N*-cinnamoyl-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5l)



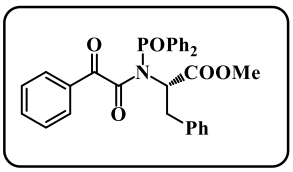
Colorless oil, 80% yield (81.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 16.0, 10.0 Hz, 2H), 7.59 - 7.53 (m, 2H), 7.48 - 7.45 (m, 1H), 7.43 - 7.35 (m, 5H), 7.27 - 7.22 (m, 9H), 7.04 - 7.02 (m, 2H), 6.90 (d, *J* = 20.4 Hz, 1H), 4.57 - 4.37 (m, 1H), 3.83 (s, 3H), 3.54 (dd, *J* = 19.0, 6.2 Hz, 1H), 3.30 (dd, *J* = 19.0, 12.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 168.9 (d, *J* = 5.6 Hz), 144.3, 137.4, 134.3, 132.6, 132.3, 132.2, 132.1, 130.3, 129.9, 128.7, 128.6, 128.2, 126.9, 120.1, 60.7, 52.6, 36.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.61. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{29}NO_4P$ $[M+H]^+$: 510.1829, found 510.1832.

Methyl *N*-(diphenylphosphoryl)-*N*-(2-(*p*-tolyl)acetyl)-*L*-phenylalaninate (5m)



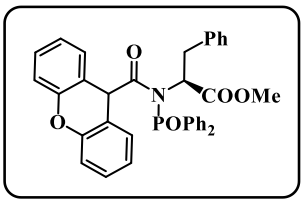
Colorless oil, 80% yield (81.9 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 - 7.99 (m, 2H), 7.51 - 7.44 (m, 6H), 7.35 - 7.32 (m, 2H), 7.25 - 7.22 (m, 3H), 7.04 (d, *J* = 10.4 Hz, 2H), 6.93 (d, *J* = 10.4 Hz, 2H), 6.79 (d, *J* = 9.6 Hz, 2H), 4.22 (s, 1H), 3.74 (s, 4H), 3.48 - 3.40 (m, 2H), 3.14 (dd, *J* = 19.0, 12.6 Hz, 1H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.4 (d, *J* = 7.2 Hz), 171.3 (d, *J* = 4.8 Hz), 137.9, 136.9, 133.5, 133.1, 133.0, 133.0, 132.8, 132.6, 132.5, 131.8, 131.1, 130.3, 130.0, 129.4, 129.2, 129.0, 129.0, 127.3, 62.1, 52.9, 43.9, 36.3, 21.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.37. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{31}NO_4P$ $[M+H]^+$: 512.1985, found 512.1989.

Methyl-*N*-(diphenylphosphoryl)-*N*-(2-oxo-2-phenylacetyl)-*L*-phenylalaninate (5n)



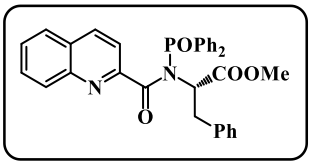
Colorless oil, 71% yield (72.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 - 7.74 (m, 2H), 7.64 (dd, *J* = 12.6, 7.8 Hz, 2H), 7.57 - 7.55 (m, 2H), 7.50 - 7.42 (m, 3H), 7.30 - 7.26 (m, 6H), 7.11 - 7.04 (m, 5H), 5.23 - 5.16 (m, 1H), 7.77 - 7.72 (m, 4H), 3.39 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.8, 170.4 (d, *J* = 2.0 Hz), 169.5 (d, *J* = 5.0 Hz), 137.4, 134.3, 133.4, 133.3, 133.0 (d, *J* = 2.0 Hz), 132.7, 132.4, 130.1, 129.5, 128.5, 128.4, 128.3, 128.3, 128.2, 126.9, 59.4, 52.7, 36.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.90. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{27}NO_5P$ $[M+H]^+$: 512.1621, found 512.1626.

Methyl *N*-(diphenylphosphoryl)-*N*-(9*H*-xanthene-9-carbonyl)-*L*-phenylalaninate (5o)



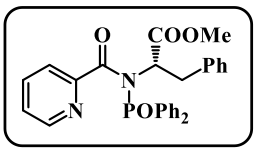
Colorless oil, 81% yield (95.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 - 8.40 (m, 4H), 8.35 - 7.95 (m, 4H), 7.93 - 7.62 (m, 4H), 7.52 - 7.47 (m, 4H), 7.47 - 7.25 (m, 3H), 7.26 - 7.20 (m, 2H), 7.16 - 7.12 (m, 3H), 6.73 - 6.73 (m, 1H), 6.66 (d, *J* = 9.6 Hz, 2H), 5.70 (s, 1H), 5.61 - 5.61 (m, 1H), 4.00 - 3.91 (m, 1H), 3.58 (s, 3H), 3.24 (dd, *J* = 19.6, 7.6 Hz, 1H), 2.62 (dd, *J* = 21.2, 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.0 (d, *J* = 10.6 Hz), 171.1, 153.2 (d, *J* = 49.3 Hz), 138.4, 133.8, 133.6, 133.1 (d, *J* = 14.4 Hz), 130.4, 130.1, 130.0, 129.6 (d, *J* = 16.9 Hz), 129.2, 129.1, 128.7, 127.3, 123.6, 123.3, 121.0, 120.7, 117.8, 117.6, 63.4 (d, *J* = 2.3 Hz), 53.1, 47.7, 36.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 30.72. **HRMS** (ESI) *m/z* calcd for $C_{36}H_{31}NO_5P$ $[M+H]^+$: 588.1934, found 588.1940.

Methyl-*N*-(diphenylphosphoryl)-*N*-(quinoline-2-carbonyl)-*L*-phenylalaninate (5p)



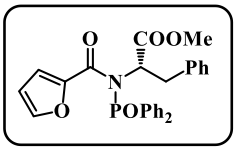
Colorless oil, 95% yield (101.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 13.0, 7.4 Hz, 3H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.53 - 7.43 (m, 3H), 7.40 - 7.32 (m, 3H), 7.24 - 7.19 (m, 2H), 7.12 - 7.03 (m, 3H), 6.93 - 6.92 (m, 2H), 5.93 - 5.82 (m, 1H), 3.84 (s, 3H), 3.79 (dd, *J* = 14.6, 5.0 Hz, 1H), 3.11 (dd, *J* = 13.4, 9.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 170.6 (d, *J* = 3.0 Hz), 151.5, 145.9, 137.8, 137.2, 132.9, 132.7, 132.4, 132.3, 132.1 (d, *J* = 2.0 Hz), 131.7 (d, *J* = 3.0 Hz), 130.4, 129.5, 129.3, 128.6, 128.0, 128.0, 127.9, 127.8, 127.6, 126.7, 121.0, 59.5, 52.5, 37.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 37.36. **HRMS** (ESI) *m/z* calcd for $C_{32}H_{28}N_2O_4P$ $[M+H]^+$: 535.1781, found 535.1786.

Methyl *N*-(diphenylphosphoryl)-*N*-picolinoyl-*L*-phenylalaninate (5q)



Colorless oil, 93% yield (90.1 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.4 Hz, 1H), 8.02 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.65 - 7.57 (m, 3H), 7.54 - 7.50 (m, 1H), 7.45 - 7.39 (m, 4H), 7.30 - 7.24 (m, 3H), 7.08 - 7.04 (m, 1H), 7.01 - 6.98 (m, 2H), 6.76 (d, *J* = 7.2 Hz, 2H), 5.74 - 5.67 (m, 1H), 3.81 (s, 3H), 3.68 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.01 (dd, *J* = 14.4, 10.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4 (d, *J* = 2.0 Hz), 170.6 (d, *J* = 3.0 Hz), 152.0 (d, *J* = 3.0 Hz), 147.6, 137.6, 137.0, 133.2, 133.1, 132.3 (d, *J* = 3.0 Hz), 132.1, 132.0, 131.7 (d, *J* = 3.0 Hz), 129.4, 128.4, 128.2, 128.1, 128.0, 127.9, 126.6, 125.8, 124.8, 60.2, 52.4, 37.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.23. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{26}N_2O_4P$ $[M+H]^+$: 485.1625, found 485.1630.

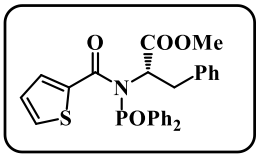
Methyl *N*-(diphenylphosphoryl)-*N*-(furan-2-carbonyl)-*L*-phenylalaninate (5r)



Colorless oil, 88% yield (83.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 17.6, 10.0 Hz, 2H), 7.66 (dd, *J* = 17.2, 9.6 Hz, 2H), 7.52 - 7.47 (m, 3H), 7.42 - 7.40 (m, 1H), 7.39 - 7.35 (m, 4H), 7.30 - 7.25 (m, 3H), 7.16 - 7.13 (m, 1H), 6.91 - 6.88 (m, 2H), 6.34 - 6.33 (m, 2H), 5.19 - 5.10 (m, 1H), 3.84 (s, 3H), 3.64 (dd, *J* = 19.4, 5.8 Hz, 1H), 3.07 (dd, *J* = 19.4, 13.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4, 162.3 (d, *J* = 6.9 Hz), 146.7, 145.6, 137.4, 132.9, 132.8, 132.6,

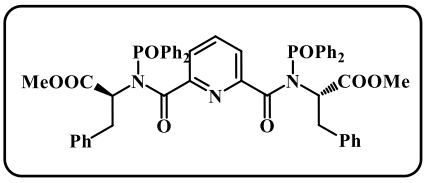
132.6, 132.2, 132.1, 132.0, 132.0, 129.5, 128.7, 128.5, 128.4, 128.3, 128.2, 127.0, 119.8, 60.5, 52.8, 36.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.20. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{25}NO_5P$ $[M+H]^+$: 474.1465, found 474.1469.

Methyl-*N*-(diphenylphosphoryl)-*N*-(thiophene-2-carbonyl)-*L*-phenylalaninate (5s)



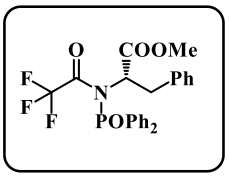
Colorless oil, 88% yield (86.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 - 7.83 (m, 5H), 7.56 - 7.52 (m, 1H), 7.51 - 7.40 (m, 2H), 7.32 - 7.21 (m, 7H), 6.85 - 6.81 (m, 3H), 4.67 - 4.61 (m, 1H), 3.89 (s, 3H), 3.50 (dd, *J* = 19.2, 5.6 Hz, 1H), 3.26 (dd, *J* = 19.6, 14.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.3, 167.6 (d, *J* = 7.4 Hz), 138.1, 137.5, 133.5, 133.4, 133.1, 132.4, 132.4, 132.1, 132.0, 130.8 (d, *J* = 11.6 Hz), 129.7, 128.9, 128.7, 128.6, 127.3, 127.0, 62.9, 53.1, 36.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.28. **HRMS** (ESI) *m/z* calcd for $C_{27}H_{25}NO_4PS$ $[M+H]^+$: 490.1236, found 490.1239.

Dimethyl-2,2'-((pyridine-2,6-dicarbonyl)bis((diphenylphosphoryl)azanediyl))(2*S*,2'*S*)-bis(3-phenylpropanoate) (5t)



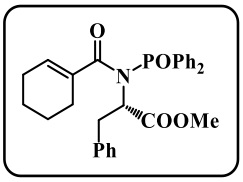
Colorless oil, 84% yield (149.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 - 8.10 (m, 4H), 7.85 - 7.83 (m, 4H), 7.63 - 7.60 (m, 2H), 7.54 - 7.48 (m, 4H), 7.35 - 7.35 (m, 6H), 7.26 - 7.19 (m, 3H), 7.00 - 6.82 (m, 7H), 6.57 (s, 3H), 5.41 (s, 2H), 3.82 (s, 6H), 3.65 (d, *J* = 12.4 Hz, 2H), 3.27 (t, *J* = 12.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 170.1, 150.8, 137.4, 133.7 (d, *J* = 10.0 Hz), 132.9, 132.2, 131.9, 131.8, 131.6, 131.3 (d, *J* = 11.0 Hz), 129.5, 129.3, 128.4, 128.3, 128.2, 126.4, 125.3, 61.3, 52.7, 37.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.68. **HRMS** (ESI) *m/z* calcd for $C_{51}H_{46}N_3O_8P_2$ $[M+H]^+$: 890.2755, found 890.2760.

Methyl-*N*-(diphenylphosphoryl)-*N*-(2,2,2-trifluoroacetyl)-*L*-phenylalaninate (5u)



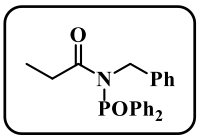
Colorless oil, 32% yield (30.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 12.8, 7.6 Hz, 2H), 7.84 (dd, *J* = 13.2, 7.2 Hz, 1H), 7.73 - 7.66 (m, 2H), 7.57 - 7.54 (m, 3H), 7.45 - 7.43 (m, 2H), 7.15 - 7.14 (m, 3H), 6.92 - 6.92 (m, 2H), 5.07 - 4.99 (m, 1H), 3.89 (dd, *J* = 14.8, 5.6 Hz, 1H), 3.84 (s, 3H), 3.23 (dd, *J* = 14.4, 8.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 136.9, 133.4 (d, *J* = 3.0 Hz), 133.2, 133.1, 132.8 (d, *J* = 3.0 Hz), 132.0, 131.9, 131.5 (d, *J* = 10.0 Hz), 129.4, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 126.9, 60.8, 53.0, 38.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 37.30. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -68.83. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{22}F_3NO_4P$ $[M+H]^+$: 476.1233, found 476.1237.

Methyl-*N*-(cyclohex-1-ene-1-carbonyl)-*N*-(diphenylphosphoryl)-*L*-phenylalaninate (5v)



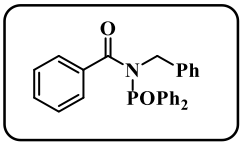
Colorless oil, 79% yield (77.0 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 16.8, 10.4 Hz, 2H), 7.86 (dd, *J* = 16.4, 9.6 Hz, 2H), 7.50 - 7.41 (m, 6H), 7.29 - 7.27 (m, 3H), 6.93 - 6.91 (m, 2H), 6.46 - 6.43 (m, 2H), 4.32 - 4.25 (m, 1H), 3.83 (s, 3H), 3.47 (dd, *J* = 19.0, 5.8 Hz, 1H), 3.16 (dd, *J* = 19.2, 13.2 Hz, 1H), 1.93 - 1.85 (m, 3H), 1.65 - 1.58 (m, 1H), 1.38 - 1.23 (m, 2H), 1.15 - 1.09 (m, 1H), 0.91 - 0.91 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.3 (d, *J* = 6.5 Hz), 171.0, 137.6, 136.9, 133.9, 133.0, 132.9, 132.5, 131.9, 131.7, 131.5, 131.1, 129.6, 128.7, 128.5, 128.4, 127.0, 61.8, 52.6, 36.1, 24.8, 24.7, 21.4, 21.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 27.64. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{31}NO_4P$ $[M+H]^+$: 488.1985, found 488.1990.

***N*-benzyl-*N*-(diphenylphosphoryl)propionamide (5w)**



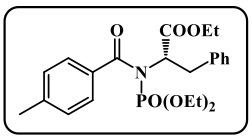
Colorless oil, 96% yield (69.8 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 13.0, 7.8 Hz, 4H), 7.55 - 7.51 (m, 2H), 7.44 - 7.40 (m, 4H), 7.23 - 7.21 (m, 3H), 7.10 - 7.08 (m, 2H), 4.89 (d, *J* = 11.2 Hz, 2H), 2.51 (q, *J* = 10.8 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.3 (d, *J* = 4.0 Hz), 137.9, 132.4, 132.4, 132.1, 132.0, 131.6, 130.3, 128.5, 128.4, 127.2, 126.9, 48.0, 29.9, 8.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 31.75. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{23}NO_2P$ $[M+H]^+$: 364.1461, found 364.1465.

***N*-benzyl-*N*-(diphenylphosphoryl)benzamide (5x)**



Colorless oil, 66% yield (54.3 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 13.0, 7.0 Hz, 4H), 7.49 - 7.45 (m, 2H), 7.41 - 7.32 (m, 7H), 7.27 -7.23 (m, 2H), 7.14 - 7.11 (m, 3H), 7.08 - 7.05 (m, 2H), 4.95 (d, *J* = 10.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2 (d, *J* = 3.0 Hz), 137.7, 135.9, 135.9, 132.1, 132.0, 131.7, 131.0, 130.4, 128.4, 128.3, 128.3, 128.3, 128.1, 127.8, 127.3, 50.2 (d, *J* = 3.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 29.97. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{23}NO_2P$ $[M+H]^+$: 412.1461, found 412.1466.

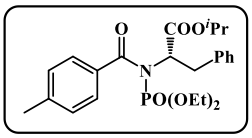
Ethyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (6a)



Colorless oil, 80% yield (71.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 -7.20 (m, 7H), 7.10 (d, *J* = 7.6 Hz, 2H), 5.07 - 5.00 (m, 1H), 4.33 - 4.24 (m, 2H), 4.04 - 3.92 (m, 2H), 3.76 - 3.70 (m, 1H), 3.58 (dd, *J* = 14.0, 4.8 Hz, 1H), 3.51 - 3.45 (m, 1H), 3.40 - 3.34 (m, 1H), 2.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.11 - 1.07 (m, 3H), 1.06 - 1.02 (m, 3H).

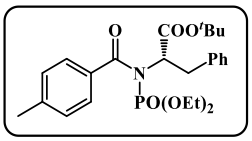
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 7.0 Hz), 170.4 (d, *J* = 2.0 Hz), 141.1, 138.2, 133.3, 129.8, 128.4, 128.2, 127.6, 126.6, 64.0 (d, *J* = 6.0 Hz), 63.5 (d, *J* = 6.0 Hz), 61.5, 61.5, 35.2, 21.5, 15.8 (d, *J* = 8.0 Hz), 15.7 (d, *J* = 8.0 Hz), 14.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.27. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{31}NO_6P$ $[M+H]^+$: 448.1884, found 448.1888.

Isopropyl-*N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (6b)



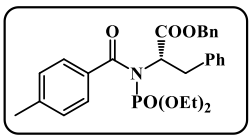
Colorless oil, 79% yield (72.9 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 -7.20 (m, 7H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.19 - 5.13 (m, 1H), 5.02 - 4.95 (m, 1H), 4.02 - 3.93 (m, 2H), 3.73 - 3.67 (m, 1H), 3.57 (dd, *J* = 14.2, 5.0 Hz, 1H), 3.49 - 3.41 (m, 1H), 3.38 - 3.32 (m, 1H), 2.34 (s, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.10 - 1.16 (m, 3H), 1.04 - 1.01 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 6.0 Hz), 169.9 (d, *J* = 2.0 Hz), 140.92, 138.4, 133.4, 129.8, 128.4, 128.2, 127.5, 126.5, 69.0, 63.8 (d, *J* = 6.0 Hz), 63.4 (d, *J* = 6.0 Hz), 61.6 (d, *J* = 4.0 Hz), 35.3, 21.9, 21.8, 21.5, 15.8 (d, *J* = 8.0 Hz), 15.7 (d, *J* = 9.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.30. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{33}NO_6P$ $[M+H]^+$: 462.2040, found 462.2044.

***tert*-butyl-*N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (6c)**



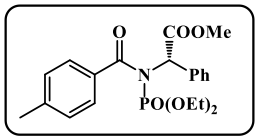
Colorless oil, 80% yield (76.1 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 - 7.23 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.96 - 4.89 (m, 1H), 3.95 - 3.88 (m, 2H), 3.72 - 3.66 (m, 1H), 3.53 (dd, *J* = 14.4, 4.8 Hz, 1H), 3.45 - 3.39 (m, 1H), 3.37 - 3.30 (m, 1H), 2.35 (s, 3H), 1.53 (s, 9H), 1.10 – 1.01 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 7.0 Hz), 169.3, 140.7, 138.6, 133.6, 129.9, 128.4, 128.1, 127.4, 126.5, 81.7, 63.8 (d, *J* = 6.0 Hz), 63.3 (d, *J* = 6.0 Hz), 62.0 (d, *J* = 3.0 Hz), 35.5, 28.0, 21.5, 15.8 (d, *J* = 8.0 Hz), 15.7 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.34. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{35}NO_6P$ $[M+H]^+$: 476.2197, found 476.2199.

Benzyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (6d)



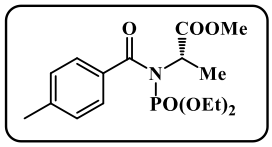
Colorless oil, 77% yield (78.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 - 7.40 (m, 2H), 7.39 - 7.32 (m, 2H), 7.30 - 7.24 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.30 (d, *J* = 12.4 Hz, 1H), 5.19 (d, *J* = 12.4 Hz, 1H), 5.10 (td, *J* = 10.0, 4.8 Hz, 1H), 3.80 - 3.77 (m, 1H), 3.66 - 3.58 (m, 3H), 3.43 - 3.34 (m, 2H), 2.34 (s, 3H), 0.99 - 0.95 (m, 3H), 0.98 - 0.86 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 7.0 Hz), 170.4, 141.1, 138.1, 135.7, 133.2, 129.8, 128.7, 128.5, 128.5, 128.3, 128.2, 127.6, 126.6, 67.4, 63.8 (d, *J* = 6.0 Hz), 63.4 (d, *J* = 6.0 Hz), 61.5, 35.1, 21.5, 15.8 (d, *J* = 8.0 Hz), 15.5 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.20. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{33}NO_6P$ $[M+H]^+$: 510.2040, found 510.2045.

Methyl-(*S*)-2-(*N*-(diethoxyphosphoryl)-4-methylbenzamido)-2-phenylacetate (6e)



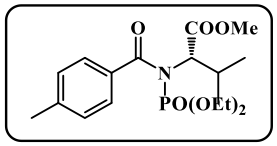
Colorless oil, 84% yield (70.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.8 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.36 -7.29 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.90 (d, *J* = 12.0 Hz, 2H), 4.05 - 3.92 (m, 1H), 3.81 (s, 3H), 3.80 - 3.75 (m, 1H), 2.36 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 7.0 Hz), 169.7 (d, *J* = 3.0 Hz), 141.3, 135.7 (d, *J* = 1.0 Hz), 133.4, 130.0, 128.4, 128.1, 128.0, 127.7, 64.0 (d, *J* = 6.0 Hz), 63.9 (d, *J* = 6.0 Hz), 62.9 (d, *J* = 4.0 Hz), 52.6, 21.5, 15.8 (d, *J* = 7.0 Hz), 15.7 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.18. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{27}NO_6P$ $[M+H]^+$: 420.1571, found 420.1576.

Methyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-alaninate (6f)



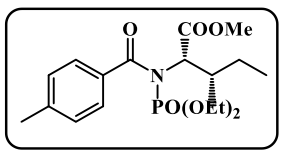
Colorless oil, 80% yield (57.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.78 (td, *J* = 14.0, 6.8 Hz, 1H), 4.13 - 4.03 (m, 4H), 3.77 (s, 3H), 2.38 (s, 3H), 1.66 (d, *J* = 6.8 Hz, 3H), 1.26 - 1.22 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 7.0 Hz), 171.6 (d, *J* = 4.0 Hz), 141.2, 133.5, 128.4, 127.6, 64.0, 63.9, 55.4 (d, *J* = 4.0 Hz), 52.4, 21.6, 16.2, 15.9 (d, *J* = 4.0 Hz), 15.9 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.19. **HRMS** (ESI) *m/z* calcd for $C_{16}H_{25}NO_6P$ $[M+H]^+$: 358.1414, found 358.1419.

Methyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-valinate (6g)



Colorless oil, 78% yield (60.1 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.37 (dd, *J* = 13.2, 8.8 Hz, 1H), 4.13 - 4.02 (m, 4H), 3.77 (s, 3H), 2.71 - 2.64 (m, 1H), 2.39 (s, 3H), 1.26 - 1.19 (m, 9H), 1.02 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 7.0 Hz), 171.2 (d, *J* = 3.0 Hz), 141.2, 133.3, 128.4, 127.8, 65.2 (d, *J* = 3.0 Hz), 64.2 (d, *J* = 6.0 Hz), 63.9 (d, *J* = 5.0 Hz), 52.1, 28.3, 22.4, 21.6, 20.0, 15.9 (d, *J* = 7.0 Hz), 15.8 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.99. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{29}NO_6P$ $[M+H]^+$: 386.1727, found 386.1731.

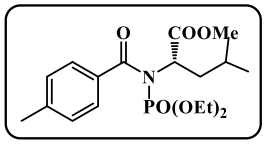
Methyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-isoleucinate (6h)



Colorless oil, 83% yield (66.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 4.45 (dd, *J* = 13.2, 9.2 Hz, 1H), 4.12 - 4.02 (m, 4H), 3.76 (s, 3H), 2.43 - 2.39 (m, 4H), 1.68 - 1.62 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.16 (d, *J* = 6.5 Hz, 3H), 0.98 - 0.88 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8 (d, *J* = 7.0 Hz), 171.3 (d, *J* = 3.0 Hz), 141.3, 133.3, 128.4, 127.8, 64.5 (d, *J* = 3.0 Hz), 64.1 (d, *J* = 6.0 Hz), 63.9 (d, *J*

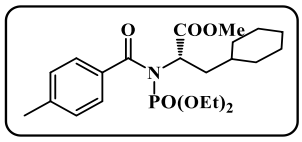
= 6.0 Hz), 52.0, 34.4, 25.6, 21.6, 18.0, 15.9 (d, *J* = 8.0 Hz), 15.8 (d, *J* = 8.0 Hz), 11.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.04. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{31}NO_6P$ $[M+H]^+$: 400.1884, found 400.1889.

Methyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-leucinate (6i)



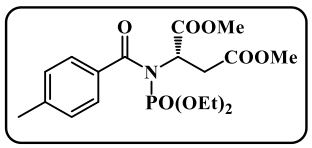
Colorless oil, 83% yield (66.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.84 - 4.77 (m, 1H), 4.15 - 4.06 (m, 4H), 3.78 (s, 3H), 2.39 (s, 3H), 2.09 - 1.92 (m, 2H), 1.84 - 1.74 (m, 1H), 1.23 (q, *J* = 7.6 Hz, 6H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 7.0 Hz), 171.9 (d, *J* = 1.0 Hz), 141.5, 133.4, 128.5, 127.9, 64.0 (d, *J* = 6.0 Hz), 64.0 (d, *J* = 6.0 Hz), 58.0 (d, *J* = 4.0 Hz), 52.3, 38.6, 25.0, 23.4, 21.6, 21.4, 15.9, 15.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.70. **HRMS** (ESI) *m/z* calcd for $C_{19}H_{31}NO_6P$ $[M+H]^+$: 400.1884, found 400.1889.

Methyl-(*S*)-3-cyclohexyl-2-(*N*-(diethoxyphosphoryl)-4-methylbenzamido)propanoate (6j)



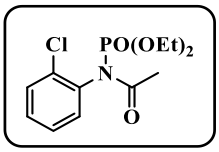
Colorless oil, 81% yield (71.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.87 - 4.17 (m, 1H), 4.17 - 4.03 (m, 4H), 3.77 (s, 3H), 2.39 (s, 3H), 2.20 (t, *J* = 75.6 Hz, 2H), 1.99 - 1.67 (m, 5H), 1.64 - 1.41 (m, 1H), 1.28 - 1.17 (m, 9H), 1.04 - 0.98 (m, 1H), 0.89 - 0.83 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7 (d, *J* = 7.0 Hz), 172.0, 141.5, 133.4, 128.5, 127.8, 64.0 (d, *J* = 6.0 Hz), 64.0 (d, *J* = 6.0 Hz), 57.3 (d, *J* = 3.0 Hz), 52.3, 37.1, 34.4, 33.9, 32.1, 26.5, 26.4, 26.1, 21.5, 15.9 (d, *J* = 5.0 Hz), 15.9 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.77. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{35}NO_6P$ $[M+H]^+$: 440.2197, found 440.2199.

Dimethyl *N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-aspartate (6k)



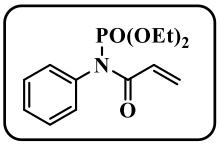
Colorless oil, 86% yield (71.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.25 - 5.18 (m, 1H), 4.14 - 4.06 (m, 4H), 3.78 (s, 3H), 3.73 (s, 3H), 3.39 (dd, *J* = 16.6, 6.2 Hz, 1H), 2.95 (dd, *J* = 16.8, 7.6 Hz, 1H), 2.39 (s, 3H), 1.24 (q, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9 (d, *J* = 6.0 Hz), 171.2, 170.2 (d, *J* = 2.0 Hz), 141.6, 133.0, 128.5, 127.8, 64.3 (d, *J* = 6.0 Hz), 64.2 (d, *J* = 6.0 Hz), 56.2 (d, *J* = 4.0 Hz), 52.7, 51.9, 35.6, 21.5, 15.9, 15.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.78. **HRMS** (ESI) *m/z* calcd for $C_{18}H_{27}NO_8P$ $[M+H]^+$: 416.1469, found 416.1470.

Diethyl acetyl(2-chlorophenyl)phosphoramidate (6l)



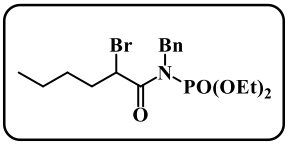
Colorless oil, 71% yield (44.6 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.41 - 7.34 (m, 2H), 7.28 - 7.24 (m, 1H), 4.32 - 4.17 (m, 4H), 2.09 (s, 3H), 1.29 (q, *J* = 7.5 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 5.0 Hz), 138.3, 133.7, 130.9, 130.0, 128.7, 124.4 (d, *J* = 3.0 Hz), 124.3, 64.7 (d, *J* = 6.0 Hz), 64.6 (d, *J* = 7.0 Hz), 24.0 (d, *J* = 4.0 Hz), 16.1, 16.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -0.94. **HRMS** (ESI) *m/z* calcd for $C_{12}H_{18}ClNO_4P$ $[M+H]^+$: 306.0656, found 306.0659.

Diethyl acryloyl(phenyl)phosphoramidate (6m)



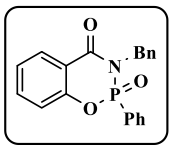
Colorless oil, 66% yield (37.4 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 - 7.38 (m, 3H), 7.27 - 7.24 (m, 2H), 6.46 (dd, *J* = 16.8, 1.6 Hz, 1H), 6.19 (dd, *J* = 16.6, 10.2 Hz, 1H), 5.68 - 5.64 (m, 1H), 4.27 - 4.23 (m, 2H), 4.22 - 4.11 (m, 2H), 1.29 - 1.25 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9 (d, *J* = 5.0 Hz), 138.0, 130.6, 129.5, 129.4 (d, *J* = 2.0 Hz), 128.5, 128.4 (d, *J* = 5.0 Hz), 64.5, 64.5, 16.1, 16.0. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -1.14. **HRMS** (ESI) *m/z* calcd for $C_{13}H_{19}NO_4P$ $[M+H]^+$: 284.1046, found 284.1051.

Diethyl benzyl(2-bromohexanoyl)phosphoramidate (6n)



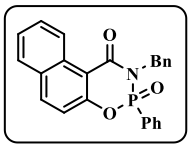
Colorless oil, 53% yield (44.6 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 - 7.22 (m, 5H), 5.30 - 5.17 (m, 3H), 4.24 - 4.10 (m, 4H), 1.42 - 1.27 (m, 11H), 0.95 - 0.91 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 134.3, 128.5, 128.1, 127.6, 64.7 (d, *J* = 4.0 Hz), 64.6 (d, *J* = 3.0 Hz), 43.8, 43.2, 33.7, 29.4, 22.2, 16.3, 16.2, 13.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.54. **HRMS** (ESI) *m/z* calcd for $C_{17}H_{28}BrNO_4P$ $[M+H]^+$: 420.0934, found 420.0936.

3-benzyl-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (7a)



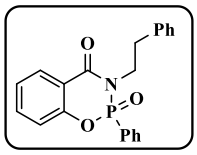
Colorless oil, 77% yield (53.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 6.4, 4.0 Hz, 2H), 7.72 - 7.54 (m, 2H), 7.42 - 7.33 (m, 5H), 7.32 - 7.16 (m, 1H), 7.15 - 7.12 (m, 3H), 4.94 - 4.72 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 5.0 Hz), 150.8 (d, *J* = 10.0 Hz), 136.0, 135.5, 133.8 (d, *J* = 4.0 Hz), 131.9 (d, *J* = 15.0 Hz), 130.2, 128.9 (d, *J* = 12.0 Hz), 128.7, 128.2, 127.6, 124.9, 118.7 (d, *J* = 13.0 Hz), 45.8 (d, *J* = 6.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.59. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{17}NO_3P$ $[M+H]^+$: 350.0941, found 350.0946.

2-benzyl-3-phenyl-2-hydronaphtho[1,2-e][1,3,2]oxazaphosphinin-1-one-3-oxide (7b)



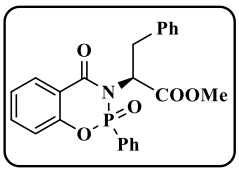
Colorless oil, 72% yield (57.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 - 7.64 (m, 3H), 7.55 - 7.48 (m, 2H), 7.42 - 7.34 (m, 4H), 7.24 - 7.17 (m, 4H), 4.98 - 4.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 4.0 Hz), 151.7 (d, *J* = 8.0 Hz), 137.0, 136.4, 133.8 (d, *J* = 3.0 Hz), 132.1, 132.0, 131.8, 131.2, 129.6, 129.0, 128.8, 128.8, 128.4, 127.6, 126.5, 126.1, 118.3 (d, *J* = 10.0 Hz), 110.8 (d, *J* = 3.0 Hz), 45.9 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.42. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{19}NO_3P$ $[M+H]^+$: 400.1097, found 400.1099.

3-phenethyl-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one-2-oxide (7c)



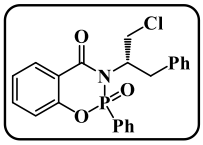
Colorless oil, 79% yield (57.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86 - 7.80 (m, 2H), 7.66 - 7.57 (m, 2H), 7.53 - 7.48 (m, 2H), 7.34 - 7.30 (m, 1H), 7.26 - 7.23 (m, 2H), 7.19 - 7.14 (m, 4H), 4.01 - 3.90 (m, 1H), 3.60 - 3.50 (m, 1H), 3.10 - 3.02 (m, 1H), 2.86 - 2.79 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 4.0 Hz), 150.9 (d, *J* = 8.0 Hz), 138.2, 135.5, 134.1 (d, *J* = 4.0 Hz), 132.1 (d, *J* = 11.0 Hz), 130.0, 129.2, 129.1, 128.9, 128.6, 126.6, 124.9, 118.7 (d, *J* = 9.0 Hz), 117.5 (d, *J* = 2.0 Hz), 44.3 (d, *J* = 5.0 Hz), 35.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 16.68. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{19}NO_3P$ $[M+H]^+$: 364.1097, found 364.1099.

Methyl-(2*S*)-2-(2-oxido-4-oxo-2-phenylbenzo[*e*][1,3,2]oxazaphosphinin-3(4*H*)-yl)-3-phenylpropanoate (7d)



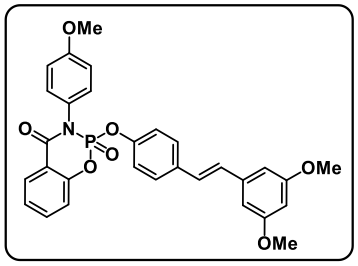
Colorless oil, 74% yield (62.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 - 8.12 (m, 1H), 7.86 (dd, *J* = 14.8, 7.2 Hz, 1H), 7.60 - 7.52 (m, 3H), 7.46 - 7.41 (m, 1H), 7.37 - 7.30 (m, 3H), 7.29 - 7.24 (m, 1H), 7.21 - 7.17 (m, 0.5H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 3.2 Hz, 1.5H), 6.87 - 6.84 (m, 1H), 4.87 - 4.82 (m, 0.5H), 4.52 - 4.46 (m, 0.5H), 3.77 (dd, *J* = 14.0, 8.0 Hz, 0.5H), 3.68 (s, 1.5H), 3.67 (dd, *J* = 14.6, 6.2 Hz, 0.5H), 3.59 (s, 1.5H), 3.31 (dd, *J* = 14.0, 5.2 Hz, 0.5H), 3.19 (dd, *J* = 14.2, 7.4 Hz, 0.5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.6, 169.4 (d, *J* = 5.0 Hz), 162.6 (d, *J* = 4.0 Hz), 162.2, 150.8 (d, *J* = 8.0 Hz), 150.7 (d, *J* = 7.0 Hz), 138.0, 137.4, 135.9, 135.8, 134.0 (d, *J* = 3.0 Hz), 133.6 (d, *J* = 3.0 Hz), 132.4, 132.3, 131.9, 131.8, 130.2, 130.2, 129.7, 129.2, 129.0, 128.8, 128.7, 128.6, 128.3, 126.7, 126.6, 125.0, 118.8, 118.7, 58.3 (d, *J* = 4.0 Hz), 58.1 (d, *J* = 5.0 Hz), 52.8, 52.4, 36.8, 36.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.83, 17.68. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{21}NO_5P$ $[M+H]^+$: 422.1152, found 422.1157.

3-((*S*)-1-chloro-3-phenylpropan-2-yl)-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (7e)



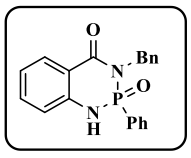
Colorless oil, 71% yield (58.5 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 - 8.15 (m, 1H), 7.77 (dd, *J* = 14.0, 7.6 Hz, 0.87H), 7.59 - 7.51 (m, 3.25H), 7.44 - 7.39 (m, 0.9H), 7.36 - 7.30 (m, 2.27H), 7.28 - 7.20 (m, 2.45H), 7.12 - 7.04 (m, 2.8H), 6.85 (d, *J* = 6.4 Hz, 1.2H), 4.42 (t, *J* = 10.2 Hz, 0.63H), 4.29 (s, 0.57H), 4.21 - 4.17 (m, 0.63H), 3.96 - 3.92 (m, 0.6H), 3.62 - 3.58 (m, 0.43H), 3.40 - 3.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 4.0 Hz), 150.6, 150.5, 137.2, 137.1, 135.7, 135.7, 133.9, 133.7 (d, *J* = 3.0 Hz), 132.1, 132.0, 130.2, 130.1, 129.2, 129.1, 129.0, 128.8, 128.8, 128.7, 128.6, 126.9, 126.7, 125.0, 118.7, 118.6, 60.2, 43.8, 38.0, 36.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 17.68, 17.35. **HRMS** (ESI) *m/z* calcd for $C_{22}H_{20}ClNO_3P$ $[M+H]^+$: 412.0864, found 412.0868.

(*E*)-2-(4-(3,5-dimethoxystyryl)phenoxy)-3-(4-methoxyphenyl)-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (7f)



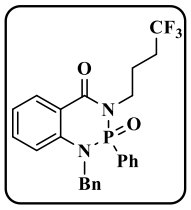
Colorless oil, 43% yield (46.7 mg, Petroleum ether : ethyl acetate = 1 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 3H), 7.18 (d, *J* = 8.4 Hz, 3H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.94 (q, *J* = 17.5 Hz, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 2.0 Hz, 3H), 6.38 - 6.38 (m, 1H), 3.80 (s, 6H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 8.0 Hz), 161.0, 155.5, 149.7 (d, *J* = 7.0 Hz), 139.1, 134.5, 131.6, 128.9, 128.0, 127.8, 120.7 (d, *J* = 5.0 Hz), 120.3 (d, *J* = 7.0 Hz), 114.7, 104.6, 100.1, 55.5, 55.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -3.75. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{27}NO_7P$ $[M+H]^+$: 544.1520, found 544.1525.

3-benzyl-2-phenyl-3-hydrobenzo[*d*][1,3,2]diazaphosphinin-4(1*H*)-one 2-oxide (7g)



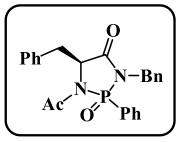
Colorless oil, 47% yield (32.7 mg, Petroleum ether : ethyl acetate = 1 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 14.0, 7.2 Hz, 2H), 7.46 (t, *J* = 6.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 - 7.26 (m, 4H), 7.15 - 7.15 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.76 (dd, *J* = 14.4, 10.0 Hz, 1H), 4.61 (dd, *J* = 14.6, 9.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 140.6, 136.7, 134.7, 133.0, 131.7, 131.6, 130.4, 128.8, 128.6, 128.4, 128.1, 127.2, 121.5, 117.5 (d, *J* = 12.0 Hz), 115.0, 45.1 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 15.69. **HRMS** (ESI) *m/z* calcd for $C_{20}H_{18}N_2O_2P$ $[M+H]^+$: 349.1100, found 349.1104.

1-benzyl-2-phenyl-3-(4,4,4-trifluorobutyl)-3-hydrobenzo[*d*][1,3,2]diazaphosphinin-4(1*H*)-one 2-oxide (7h)



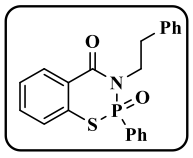
Colorless oil, 62% yield (56.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 14.0, 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 - 7.42 (m, 2H), 7.38 - 7.20 (m, 6H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 4.99 (dd, *J* = 16.8, 10.0 Hz, 1H), 4.62 (dd, *J* = 16.8, 9.2 Hz, 1H), 3.99 - 3.90 (m, 1H), 3.50 - 3.41 (m, 1H), 2.20 - 2.04 (m, 3H), 1.90 - 1.85 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.6 (d, *J* = 3.0 Hz), 141.7 (d, *J* = 4.0 Hz), 135.5, 134.8, 133.4 (d, *J* = 3.0 Hz), 131.5, 131.4, 131.0, 129.4 (q, *J* = 261.7 Hz), 129.2, 129.1, 128.8, 127.6, 126.7, 121.6, 116.7, 115.3 (d, *J* = 8.0 Hz), 47.4 (d, *J* = 6.0 Hz), 41.5 (d, *J* = 5.0 Hz), 31.5 (q, *J* = 29.3 Hz), 21.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.35. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.52. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{23}F_3N_2O_2P$ $[M+H]^+$: 459.1444, found 459.1449.

(5*S*)-1-acetyl-3,5-dibenzyl-2-phenyl-1,3,2-diazaphospholidin-4-one 2-oxide (7i)



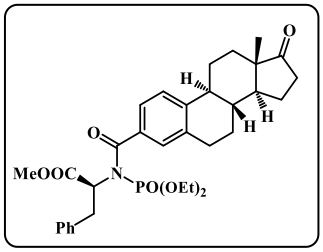
Colorless oil, 53% yield (44.4 mg, Petroleum ether : ethyl acetate = 1 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 - 7.52 (m, 3H), 7.42 - 7.37 (m, 2H), 7.28 - 7.25 (m, 1H), 7.21 - 7.18 (m, 2H), 7.14 - 7.06 (m, 3H), 7.00 - 6.97 (m, 4H), 5.03 - 4.99 (m, 1H), 4.26 (d, *J* = 11.2 Hz, 2H), 3.55 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.35 (dd, *J* = 13.8, 2.2 Hz, 1H), 2.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7 (d, *J* = 17.0 Hz), 169.6 (d, *J* = 9.0 Hz), 134.3, 134.1, 133.8, 132.5 (d, *J* = 11.0 Hz), 130.0, 129.3 (d, *J* = 15.0 Hz), 129.0, 128.6, 128.3, 127.7, 127.4, 62.1, 43.6 (d, *J* = 5.0 Hz), 35.8, 24. 8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 18.58. **HRMS** (ESI) *m/z* calcd for $C_{24}H_{24}N_2O_3P$ $[M+H]^+$: 419.1519, found 419.1522.

3-phenethyl-2-phenyl-3-hydrobenzo[*e*][1,3,2]thiazaphosphinin-4-one-2-oxide (7j)



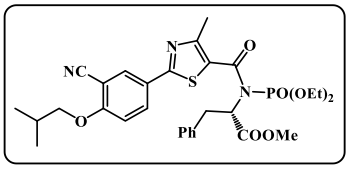
Colorless oil, 69% yield (52.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.82 - 7.76 (m, 2H), 7.58 - 7.54 (m, 1H), 7.47 - 7.39 (m, 4H), 7.35 - 7.33 (m, 1H), 7.26 - 7.23 (m, 2H), 7.20 - 7.16 (m, 3H), 4.16 -4.06 (m, 1H), 3.94 - 3.85 (m, 1H), 3.13 - 3.06 (m, 1H), 2.98 - 2.90 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 6.0 Hz), 138.3, 133.7 (d, *J* = 4.0 Hz), 133.34, 132.4, 131.4, 131.2, 131.1, 130.6 (d, *J* = 3.0 Hz), 129.1, 128.9, 128.9, 128.5, 128.2, 126.6, 126.4 (d, *J* = 3.0 Hz), 45.5, 35.7. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.03. **HRMS** (ESI) *m/z* calcd for $C_{21}H_{19}NO_2PS$ $[M+H]^+$: 380.0869, found 380.0870.

Methyl-*N*-(diethoxyphosphoryl)-*N*-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopent a[*a*]phenanthrene-3-carbonyl)-*L*-phenylalaninate (8a)



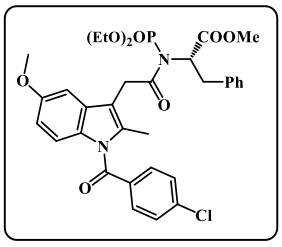
Colorless oil, 69% yield (82.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.12 - 4.02 (m, 4H), 4.45 (dd, *J* = 13.2, 9.2 Hz, 1H), 3.76 (s, 3H),7.52 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 2.43 - 2.39 (m, 4H), 1.68 - 1.62 (m, 1H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.4 Hz, 3H), 1.16 (d, *J* = 6.5 Hz, 3H), 0.98 - 0.88 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 220.6, 172.8 (d, *J* = 7.0 Hz), 171.0, 142.8, 138.1, 135.8, 133.5, 129.9, 128.4, 128.4, 126.7, 125.0, 124.6, 64.0 (d, *J* = 6.0 Hz), 63.5 (d, *J* = 5.0 Hz), 61.4, 52.5, 50.5, 47.9, 44.4, 37.8, 35.8, 35.2, 31.5, 29.2, 26.3, 25.5, 21.6, 15.9 (d, *J* = 8.0 Hz), 15.8 (d, *J* = 8.0 Hz), 13.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.04. **HRMS** (ESI) *m/z* calcd for $C_{33}H_{43}NO_7P$ $[M+H]^+$: 596.2772, found 596.2775.

Methyl-*N*-(2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carbonyl)-*N*-(diethoxyphosphoryl)-*L*-phenylalaninate (8b)



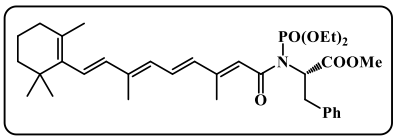
Colorless oil, 80% yield (98.2 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 - 8.05 (m, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.37 - 7.33 (m, 2H), 7.30 - 7.26 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 1H), 5.16 - 5.09 (m, 1H), 4.13 - 4.05 (m, 2H), 3.90 (d, *J* = 6.4 Hz, 2H), 3.85 (s, 3H), 3.80 - 3.74 (m, 1H), 3.61 - 3.51 (m, 2H), 3.43 - 3.37 (m, 1H), 2.36 (s, 3H), 2.36 - 2.17 (m, 1H), 4.45 (td, *J* = 16.0, 6.7 Hz, 3H), 1.14 - 1.09 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5 (d, *J* = 1.0 Hz), 165.0 (d, *J* = 6.0 Hz), 165.0, 162.2, 156.6, 137.7, 132.4, 131.8, 129.7, 128.7, 126.9, 125.9, 124.0, 115.5, 112.7, 102.8, 75.7, 64.6 (d, *J* = 6.0 Hz), 64.0 (d, *J* = 5.0 Hz), 61.7 (d, *J* = 3.0 Hz), 52.6, 35.2, 28.2, 19.1, 16.7, 16.0 (d, *J* = 3.0 Hz), 15.9 (d, *J* = 2.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 0.37. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{37}N_3O_7PS$ $[M+H]^+$: 614.2084, found 614.2088.

Methyl-*N*-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetyl)-*N*-(diethoxyphosphoryl)-*L*-phenylalaninate (8c)



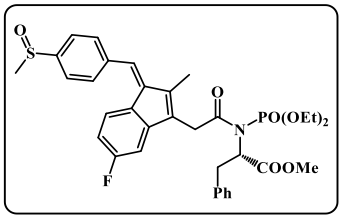
Colorless oil, 67% yield (87.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.32 - 7.29 (m, 2H), 7.24 - 7.21 (m, 3H), 6.85 - 6.82 (m, 2H), 6.66 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.18 (td, *J* = 10.0, 5.3 Hz, 1H), 4.35 - 4.27 (m, 2H), 3.83 - 3.79 (m, 5H), 3.77 - 3.72 (m, 4H), 3.49 - 3.40 (m, 2H), 3.36 - 3.30 (m, 1H), 2.33 (s, 3H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0 (d, *J* = 8.0 Hz), 170.9 (d, *J* = 3.0 Hz), 168.3, 156.0, 139.1, 138.0, 136.2, 134.0, 131.2, 131.1, 130.9, 129.8, 129.1, 128.5, 126.6, 115.0, 113.1, 110.9, 102.0, 64.4 (d, *J* = 5.0 Hz), 63.8 (d, *J* = 5.0 Hz), 60.9 (d, *J* = 4.0 Hz), 55.7, 52.4, 35.3, 31.6, 16.2 (d, *J* = 8.0 Hz), 16.1 (d, *J* = 8.0 Hz), 13.4. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.78. **HRMS** (ESI) *m/z* calcd for $C_{33}H_{37}ClN_2O_8P$ $[M+H]^+$: 655.1971, found 655.1976.

Methyl-*N*-(diethoxyphosphoryl)-*N*-((2*E*,4*E*,6*E*,8*E*)-3,7-dimethyl-9-(2,6,6-trimethylcyclohex-1-en-1-yl)nona-2,4,6,8-tetraenoyl)-*L*-phenylalaninate (8d)



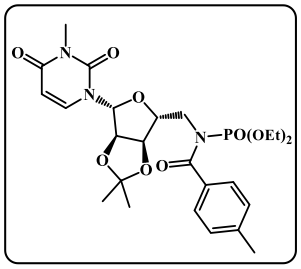
Colorless oil, 81% yield (96.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 - 7.16 (m, 5H), 6.99 (dd, *J* = 15.0, 11.4 Hz, 1H), 6.30 - 6.23 (m, 3H), 6.16 - 6.11 (m, 2H), 5.09 (td, *J* = 10.5, 5.1 Hz, 1H), 4.19 - 4.12 (m, 2H), 3.76 (s, 3H), 3.59 - 3.51 (m, 2H), 3.38 - 3.32 (m, 1H), 3.20 - 3.14 (m, 1H), 2.27 (s, 2H), 2.06 - 2.01 (m, 5H), 1.71 (s, 3H), 1.65 - 1.59 (m, 2H), 1.48 - 1.45 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.07 - 1.03 (m, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4 (d, *J* = 3.0 Hz), 167.9 (d, *J* = 6.0 Hz), 151.3, 139.6, 138.3, 137.7, 137.3, 135.4, 131.0, 130.1, 129.8, 129.5, 128.7, 128.4, 126.4, 120.5, 63.8 (d, *J* = 5.0 Hz), 63.1 (d, *J* = 5.0 Hz), 60.5 (d, *J* = 4.0 Hz), 52.3, 39.6, 35.4, 34.3, 33.1, 29.0, 21.8, 19.2, 16.0 (d, *J* = 8.0 Hz), 16.0 (d, *J* = 7.0 Hz), 14.6, 12.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.22. **HRMS** (ESI) *m/z* calcd for $C_{34}H_{49}NO_6P$ $[M+H]^+$: 598.3292, found 598.3296.

Methyl-*N*-(diethoxyphosphoryl)-*N*-(2-(5-fluoro-2-methyl-1-((*Z*)-4-(methylsulfinyl)benzylidene)-1*H*-inden-3-yl)acetyl)-*L*-phenylalaninate (8e)



Colorless oil, 73% yield (95.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.25 - 7.20 (m, 3H), 7.15 (t, *J* = 6.8 Hz, 2H), 6.65 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.56 (td, *J* = 8.7, 1.9 Hz, 1H), 5.19 (td, *J* = 10.7, 5.3 Hz, 1H), 4.33 - 4.28 (m, 2H), 3.84 - 3.69 (m, 6H), 3.50 - 3.43 (m, 2H), 3.41 - 3.34 (m, 1H), 2.81 (s, 3H), 2.15 (s, 3H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4 (d, *J* = 8.0 Hz), 170.8 (d, *J* = 3.0 Hz), 163.3 (d, *J* = 244.0 Hz), 147.0 (d, *J* = 8.0 Hz), 145.4, 141.8, 139.8, 138.4, 137.9, 132.5 (d, *J* = 2.0 Hz), 130.3, 129.8, 129.6 (d, *J* = 2.0 Hz), 128.5, 128.0, 126.7, 123.8, 123.7 (d, *J* = 9.0 Hz), 110.7 (d, *J* = 23.0 Hz), 105.8 (d, *J* = 24.0 Hz), 64.5 (d, *J* = 6.0 Hz), 63.9 (d, *J* = 5.0 Hz), 60.8, 52.4, 43.9, 35.2, 33.0, 16.2 (d, *J* = 8.0 Hz), 16.1 (d, *J* = 8.0 Hz), 10.6. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.71. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.31. **HRMS** (ESI) *m/z* calcd for $C_{34}H_{38}FNO_7PS$ $[M+H]^+$: 654.2085, found 654.2090.

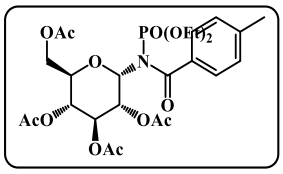
Diethyl-(((3a*R*,4*R*,6*R*,6a*R*)-2,2-dimethyl-6-(3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)tetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl)(4-methylbenzoyl)phosphoramidate (8f)



Colorless oil, 47% yield (51.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* =

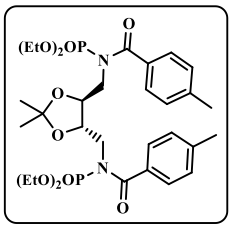
8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J* = 8.0 Hz, 1H), 5.58 (s, 1H), 4.94 - 4.93 (m, 1H), 4.82 - 4.79 (m, 1H), 4.43 - 4.39 (m, 1H), 4.17 - 4.03 (m, 6H), 3.19 (s, 3H), 2.37 (s, 3H), 1.54 (s, 3H), 1.33 (s, 3H), 1.27 - 1.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8 (d, *J* = 5.0 Hz), 162.7, 150.6, 141.5, 140.2, 133.3, 128.5, 128.0, 114.4, 101.9, 95.5, 86.8, 84.8, 82.3, 64.0 (d, *J* = 7.0 Hz), 64.0 (d, *J* = 6.0 Hz), 48.6, 27.4, 27.1, 25.3, 21.5, 16.0, 15.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.19. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{35}N_3O_9P$ $[M+H]^+$: 552.2105, found 552.2110.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(acetoxymethyl)-6-(*N*-(diethoxyphosphoryl)-4-methylbenzamido)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (8g)



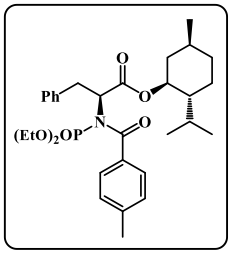
Colorless oil, 61% yield (73.4 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.62 (t, *J* = 9.2 Hz, 1H), 5.13 - 5.02 (m, 3H), 4.24 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.18 - 4.05 (m, 5H), 3.62 - 3.58 (m, 1H), 2.33 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.91 (s, 3H), 1.27 - 1.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.6, 170.4, 170.3, 169.2, 169.0, 142.6, 132.4, 128.9, 128.2, 85.0, 74.3, 74.2, 69.6, 67.7, 64.8 (d, *J* = 6.0 Hz), 64.1 (d, *J* = 6.0 Hz), 62.0, 21.6, 20.7, 20.6, 20.5, 16.1 (d, *J* = 7.0 Hz), 15.9 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.12. **HRMS** (ESI) *m/z* calcd for $C_{26}H_{37}NO_{13}P$ $[M+H]^+$: 602.1997, found 602.2001.

Tetraethyl-(((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene))bis((4-methylbenzoyl)phosphoramidate) (8h)



Colorless oil, 58% yield (77.6 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 4.14 - 4.09 (m, 4H), 4.07 - 4.04 (m, 2H), 4.03 - 3.98 (m, 4H), 3.58 (dd, *J* = 13.2, 3.2 Hz, 2H), 3.33 (dd, *J* = 13.0, 5.0 Hz, 2H), 2.39 (s, 6H), 1.43 (s, 3H), 1.39 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.23 (t, *J* = 7.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.7 (d, *J* = 7.0 Hz), 141.5, 133.4, 128.6, 127.9, 109.9, 78.1, 64.1 (d, *J* = 6.0 Hz), 64.0 (d, *J* = 6.0 Hz), 51.7, 47.9 (d, *J* = 4.0 Hz), 27.0, 26.9, 21.5, 16.0 (d, *J* = 7.0 Hz), 15.9 (d, *J* = 7.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.78. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{47}N_2O_{10}P_2$ $[M+H]^+$: 669.2700, found 669.2706.

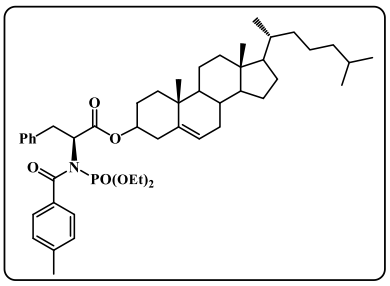
(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-*N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (8i)



Colorless oil, 72% yield (80.3 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 - 7.29 (m,

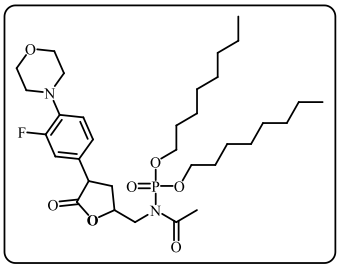
2H), 7.27 - 7.24 (m, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.03 (td, *J* = 12.0, 4.76 Hz, 1H), 7.84 (td, *J* = 13.0, 7.4 Hz, 1H), 3.98 - 3.88 (m, 2H), 3.64 - 3.55 (m, 2H), 3.42 - 3.34 (m, 2H), 2.35 (s, 3H), 2.19 - 2.13 (m, 3H), 1.70 (d, *J* = 12.0 Hz, 2H), 1.38 (s, 1H), 1.38 (t, *J* = 11.6 Hz, 1H), 1.06 (t, *J* = 7.0 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.94 - 0.90 (m, 8H), 0.83 (d, *J* = 6.8 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4 (d, *J* = 6.0 Hz), 170.0, 140.9, 138.5, 133.5, 129.9, 128.4, 128.1, 127.5, 126.5, 75.5, 63.7 (d, *J* = 6.0 Hz), 63.3 (d, *J* = 5.0 Hz), 61.6 (d, *J* = 4.0 Hz), 47.4, 40.8, 35.1, 34.4, 31.5, 25.8, 23.2, 22.1, 21.5, 21.0, 16.0, 15.8 (d, *J* = 7.0 Hz), 15.7 (d, *J* = 8.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.34. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{45}NO_6P$ $[M+H]^+$: 558.2979, found 558.2984.

(10*R*,13*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl-*N*-(diethoxyphosphoryl)-*N*-(4-methylbenzoyl)-*L*-phenylalaninate (8j)



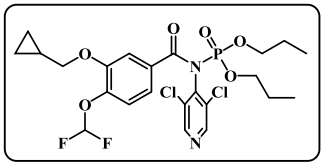
Colorless oil, 69% yield (108.8 mg, Petroleum ether : ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 - 7.21 (m, 2H), 7.19 - 7.17 (m, 3H), 7.15 - 7.13 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 5.35 (s, 1H), 4.92 (td, *J* = 12.0, 4.5 Hz, 1H), 4.74 - 4.66 (m, 1H), 3.96 - 3.85 (m, 2H), 3.67 - 3.61 (m, 1H), 3.53 - 3.48 (m, 1H), 3.43 - 3.37 (m, 1H), 3.32 - 3.23 (m, 1H), 2.42 - 2.32 (m, 2H), 2.29 (s, 3H), 1.97 - 1.89 (m, 3H), 1.84 - 1.75 (m, 2H), 1.54 - 1.37 (m, 8H), 1.32 - 1.19 (m, 4H), 1.10 - 1.02 (m, 10H), 0.99 - 0.96 (m, 8H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.80 (dd, *J* = 6.5, 1.3 Hz, 6H), 0.62 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6 (d, *J* = 6.0 Hz), 169.8, 140.9, 139.5, 138.4, 133.4, 129.9, 128.4, 128.2, 127.5, 126.6, 122.8, 75.2, 63.9 (d, *J* = 6.0 Hz), 63.4 (d, *J* = 6.0 Hz), 61.6, 56.7, 56.2, 50.0, 42.3, 39.7, 39.5, 38.0, 37.0, 36.6, 36.2, 35.8, 35.4, 31.9, 31.9, 28.2, 28.0, 27.8, 24.3, 23.8, 22.8, 22.6, 21.5, 21.1, 19.3, 18.7, 15.8 (d, *J* = 7.0 Hz), 15.7 (d, *J* = 7.0 Hz), 11.9. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 1.21. **HRMS** (ESI) *m/z* calcd for $C_{48}H_{71}NO_6P$ $[M+H]^+$: 788.5014, found 788.5016.

Dioctyl acetyl((4-(3-fluoro-4-morpholinophenyl)-5-oxotetrahydrofuran-2-yl)methyl)phosphoramidate (8k)



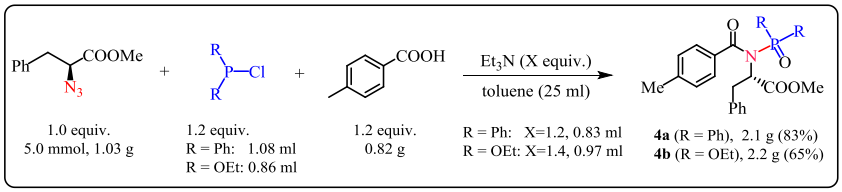
Colorless oil, 47% yield (60.2 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 14.6, 2.6 Hz, 1H), 7.05 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.84 (t, *J* = 9.0 Hz, 1H), 4.67 - 4.61 (m, 1H), 3.92 (d, *J* = 8.0 Hz, 2H), 3.82 - 3.78 (m, 5H), 3.71 - 3.66 (m, 1H), 3.32 - 3.26 (m, 2H), 3.22 - 3.18 (m, 1H), 2.97 (t, *J* = 4.6 Hz, 4H), 1.50 - 1.46 (m, 1H), 1.39 - 1.36 (m, 1H), 1.34 - 1.27 (m, 2H), 1.21 - 1.14 (m, 12H), 0.84 - 0.78 (m, 7H), 0.74 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8 (d, *J* = 9.0 Hz), 155.5 (d, *J* = 245.0 Hz), 154.3, 136.3 (d, *J* = 9.0 Hz), 133.2 (d, *J* = 10.0 Hz), 118.8 (d, *J* = 4.0 Hz), 113.7 (d, *J* = 3.0 Hz), 107.4, 107.1, 72.3 (d, *J* = 5.0 Hz), 68.8 (d, *J* = 5.0 Hz), 66.9, 51.0 (d, *J* = 2.0 Hz), 47.2, 44.1, 40.0 (d, *J* = 7.0 Hz), 39.9 (d, *J* = 7.0 Hz), 29.9 (d, *J* = 3.0 Hz), 29.8, 28.8 (d, *J* = 3.0 Hz), 28.8 (d, *J* = 5.0 Hz), 23.3 (d, *J* = 5.0 Hz), 23.2 (d, *J* = 6.0 Hz), 22.9 (d, *J* = 4.0 Hz), 14.0, 10.9 (d, *J* = 2.0 Hz), 10.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 2.45. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.42. **HRMS** (ESI) *m/z* calcd for $C_{33}H_{55}FN_2O_7P$ $[M+H]^+$: 641.3725, found 641.3729.

Dipropyl (3-(cyclopropylmethoxy)-4-(difluoromethoxy)benzoyl)(3,5-dichloropyridin-4-yl)phosphoramidate (8l)



Colorless oil, 75% yield (85.1 mg, Petroleum ether: ethyl acetate = 2 : 1 as the eluent). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.14 - 7.09 (m, 2H), 7.03 - 7.01 (m, 1H), 6.61 (t, *J* = 74.6 Hz, 1H), 4.27 - 4.17 (m, 4H), 3.78 (d, *J* = 7.2 Hz, 2H), 1.74 - 1.65 (m, 5H), 0.93 (t, *J* = 7.4 Hz, 6H), 0.67 - 0.63 (m, 2H), 0.36 - 0.32 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 149.8, 148.8, 142.8 (q, *J* = 3.0 Hz), 132.7, 132.7, 131.8, 121.4, 120.4, 118.2, 115.6, 113.5, 113.0, 74.0, 65.6, 65.5, 16.1, 16.0, 9.9, 3.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ -4.42. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -82.00. **HRMS** (ESI) *m/z* calcd for $C_{23}H_{28}Cl_2F_2N_2O_6P$ $[M+H]^+$: 567.1025, found 567.1029.

6. The Scaled-up Synthesis of Product 4a and 4b.

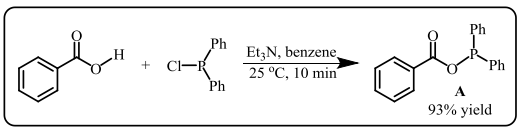


Scheme S3. Scaled-up synthesis of products.

The procedure for the scaled-up synthesis of product 4a: To a solution of *p*-toluic acid (0.82 g, 6.0 mmol) in ultra-dry toluene (12.5 ml) was added chlorodiphenylphosphine (1.08 ml, 6.0 mmol) and Et_3N (0.83 ml, 6.0 mmol) under Ar atmosphere at room temperature, after stirred at 25 °C for 10 minutes, azide **2a** (1.03 g, 5.0 mmol) in ultra-dry toluene (12.5 ml) was added. The mixture was stirred at 25 °C for 6 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the product **4a** (2.1 g, 4.15 mmol, 83%) as a colorless oil.

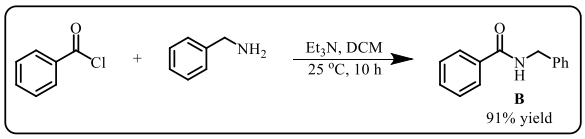
The procedure for the scaled-up synthesis of product 4b: To a solution of *p*-toluic acid (0.82 g, 6.0 mmol) in ultra-dry toluene (12.5 ml) was added diethyl chlorophosphite (0.86 ml, 6.0 mmol) and Et_3N (0.97 ml, 7.0 mmol) under Ar atmosphere at room temperature, after stirred at 25 °C for 30 minutes, azide **2a** (1.03 g, 5.0 mmol) in ultra-dry toluene (12.5 ml) was added. The mixture was stirred at 50 °C for 6 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the product **4b** (2.2 g, 3.25 mmol, 65%) as a colorless oil.

7. The Investigation of the Reaction Mechanism.



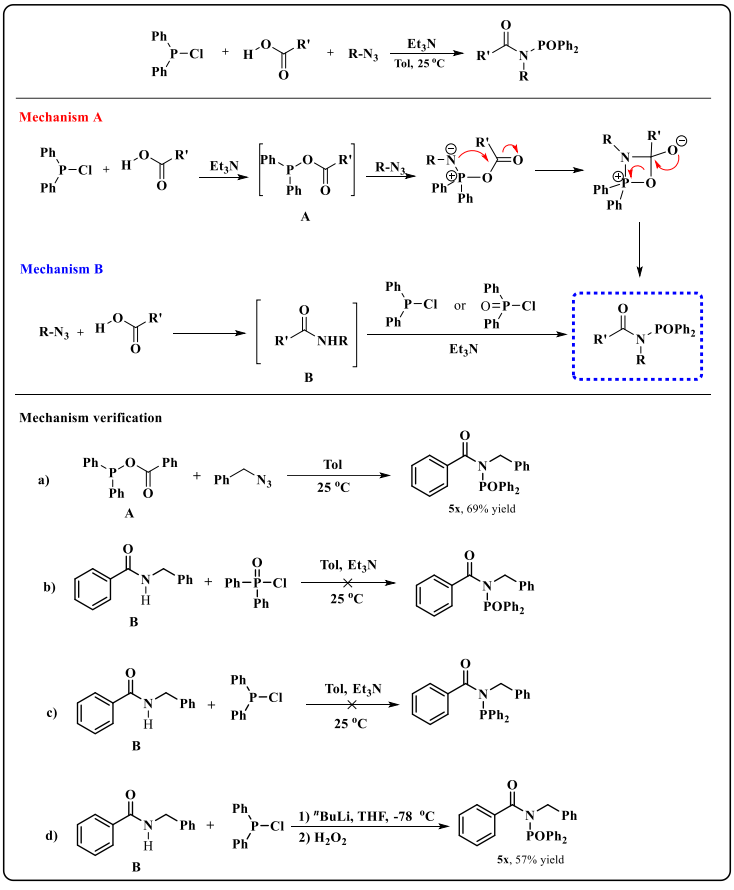
Scheme S4. Synthesis of the intermediate A.

The intermediate **A** was prepared according to literature procedure.[9] To a solution of benzoic acid (122 mg, 1.0 mmol, 1.0 equiv.) in benzene (5.0 ml) was added chlorodiphenylphosphine (221 mg, 1.0 mmol, 1.0 equiv.) and Et_3N (0.14 ml, 1.0 mmol, 1.0 equiv.) under Ar atmosphere at room temperature, after stirred at 25 °C for 10 minutes, the salt was removed by suction filtration, the filtrate was concentrated to give the residue **A** (0.28 g, 93% yield) as a colorless oil, which was used in the next step without further purification. Spectral data was consistent with previously reported results.



Scheme S5. Synthesis of the intermediate B.

The intermediate **B** was prepared according to literature procedure.[10] To a solution of benzoyl chloride (0.116 ml, 1.0 mmol, 1.0 equiv.) and benzylamine (0.109 ml, 1.0 mmol, 1.0 equiv.) in DCM (5.0 ml) was added Et_3N (0.14 ml, 1.0 mmol, 1.0 equiv.) at 0 °C, the mixture was stirred at 25 °C for 10 h, the solvent was evaporated under reduced pressure and the crude residue was purified by flash chromatography (petroleum ether /ethyl acetate = 4:1) to give the pure product **B** (0.19 g, 91% yield) as a colorless oil. Spectral data was consistent with previously reported results.



Scheme S6. The reaction mechanism research.

Procedure for the reaction a: The solution of benzyl azide **2p** (26.6 mg, 0.2 mmol, 1.0 equiv.) and **A** (73.5 mg, 0.24 mmol, 1.2 equiv.) in ultra-dry toluene (1.0 ml) was stirred at 25 °C for 6 h. The solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the product **5x** (56.8 mg, 69%) as a colorless oil.

Procedure for the reaction b and c: Benzoyl benzylamine **B** could not react with $Ph_2P(O)Cl$ or Ph_2PCl under the standard conditions on a 0.2 mmol scall.

Procedure for the reaction d: According to literature procedure[10]: To a solution of benzoyl benzylamine **B** (42.3 mg, 0.2 mmol, 1.0 equiv.) in THF (1.0 ml) was added ^{n}BuLi (0.2 mmol, 1.0 equiv.) under Ar atmosphere at -78 ^{o}C, after stirred at -78 ^{o}C for 30 min, chlorodiphenylphosphine (44.2 mg, 0.2 mmol, 1.0 equiv.) was added. Then the mixture was stirred at 25 ^{o}C for 2 h, followed by the addition of H_2O_2 (0.2 mmol, 1.0 equiv.), the mixture was stirred at 25 ^{o}C for 1 h. The reaction was quenched with sodium thiosulfate solution, extracted with DCM, the organic phase was washed with water and saturated brine, dried with anhydrous sodium sulfate, the solvent was evaporated under reduced pressure and the crude residue was purified on silica gel flash column chromatography using ethyl acetate/petroleum ether eluent to give the product **5x** (46.9 mg, 57%) as a colorless oil.

8. References.

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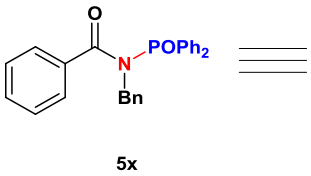
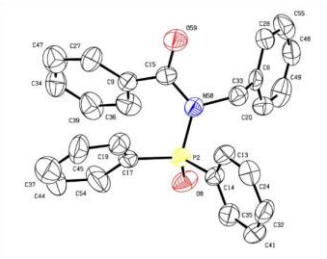
9. X-ray Crystallographic Data of Compound 5x and 7c.



5x

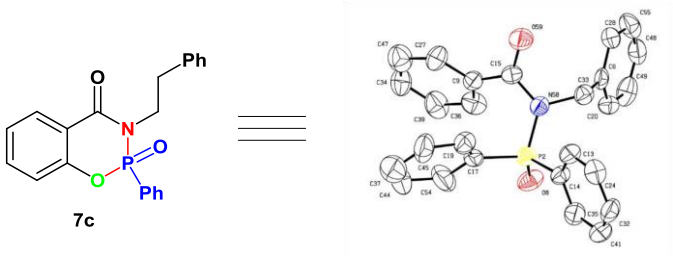


CCDC : 2015301

Table S3. Crystal data and structure refinement for **5x**.

Identification code	5x
Empirical formula	$C_{26}H_{22}NO_2P$
Formula weight	411.41
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.6285(3)
b/Å	9.3057(2)
c/Å	14.6152(2)
α/°	90.00
β/°	95.164(2)
γ/°	90.00
Volume/Å^3	2116.92(7)
Z	4
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	1.325
F(000)	864.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.078 to 133.174
Index ranges	-18 ⩽ h ⩽ 13, -11 ⩽ k ⩽ 9, -16 ⩽ l ⩽ 17
Reflections collected	7576
Independent reflections	3736
Data/restraints/parameters	3736/0/271
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.1060
Final R indexes [all data]	R_1 = 0.0486, wR_2 = 0.1137
Largest diff. peak/hole / e Å^{-3}	0.18/-0.35

Single crystals of $C_{26}H_{22}NO_2P$ (zhuyy_0414) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Scheme S2 and Table S3. CCDC 2015301 contains the supplementary crystallographic data for **5x**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.



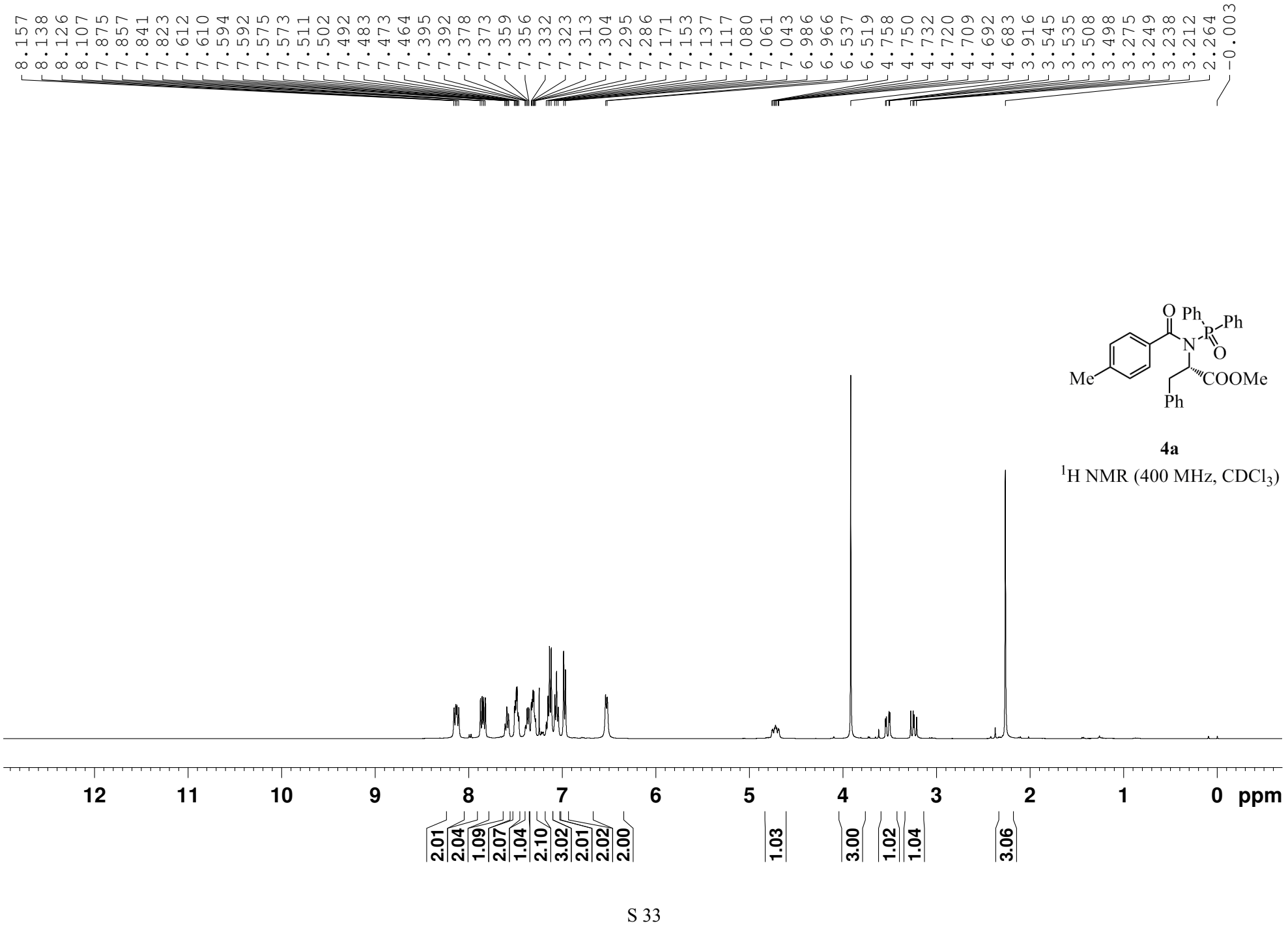
CCDC : 2074478

Table S4. Crystal data and structure refinement for **7c**.

Identification code	7c
Empirical formula	$C_{21}H_{18}NO_3P$
Formula weight	363.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.52643(9)
b/Å	14.88162(13)
c/Å	12.71774(11)
α/°	90.00
β/°	90.7242(8)
γ/°	90.00
Volume/Å^3	1802.83(3)
Z	4
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	1.523
F(000)	760.0
Crystal size/mm^3	0.15 × 0.13 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.028 to 152.098
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	11200
Independent reflections	3586
Data/restraints/parameters	3586/0/235
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.1057
Final R indexes [all data]	R_1 = 0.0387, wR_2 = 0.1077
Largest diff. peak/hole / e Å^{-3}	0.20/-0.31

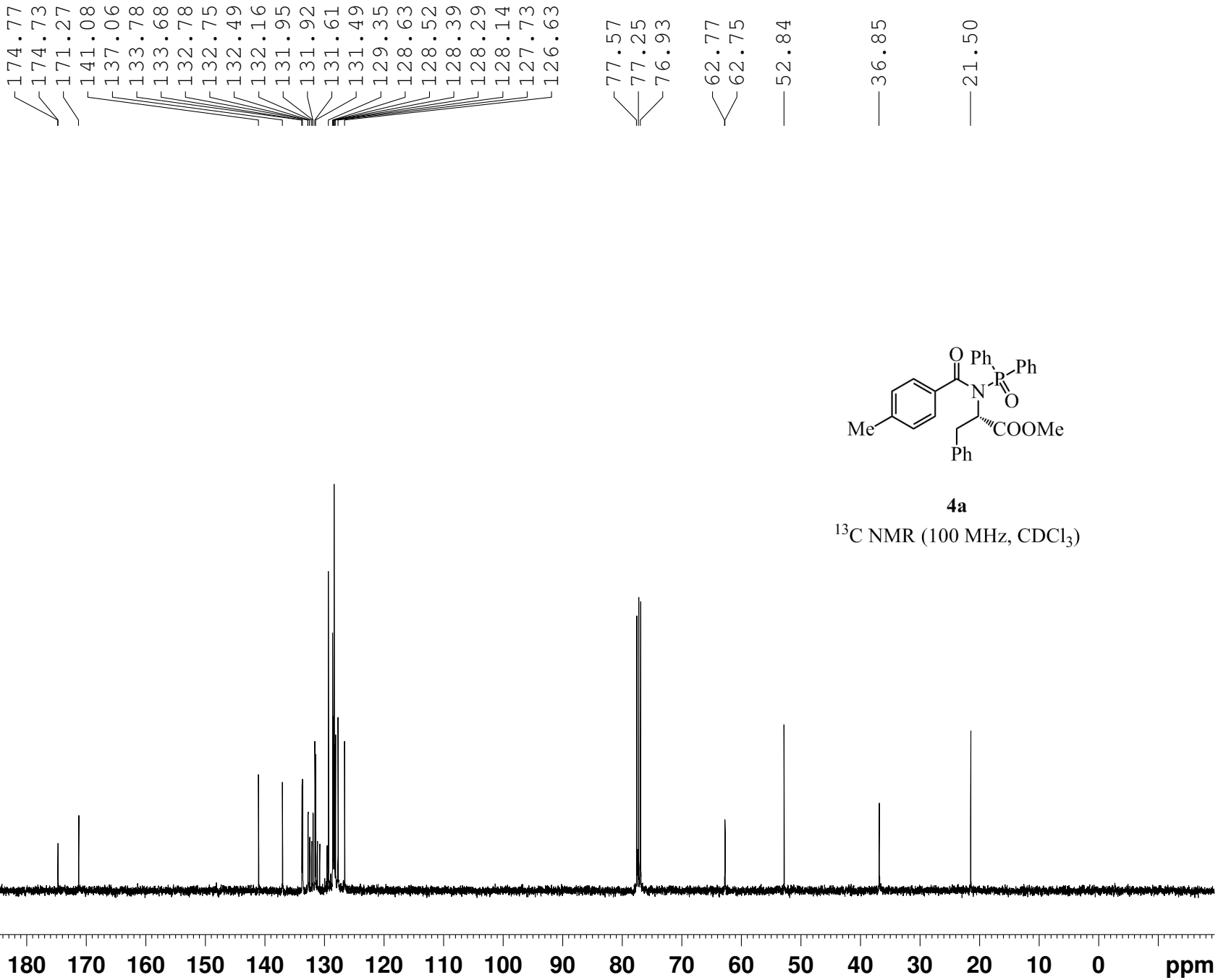
Single crystals of $C_{21}H_{18}NO_3P$ (ZHUYY_0316) was collected. A suitable crystal was selected and collected on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Refined structure and crystallographic parameters are summarized in Scheme S2 and Table S4. CCDC 2074478 contains the supplementary crystallographic data for **7c**. The crystallographic data of the compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

10. Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR Spectra.



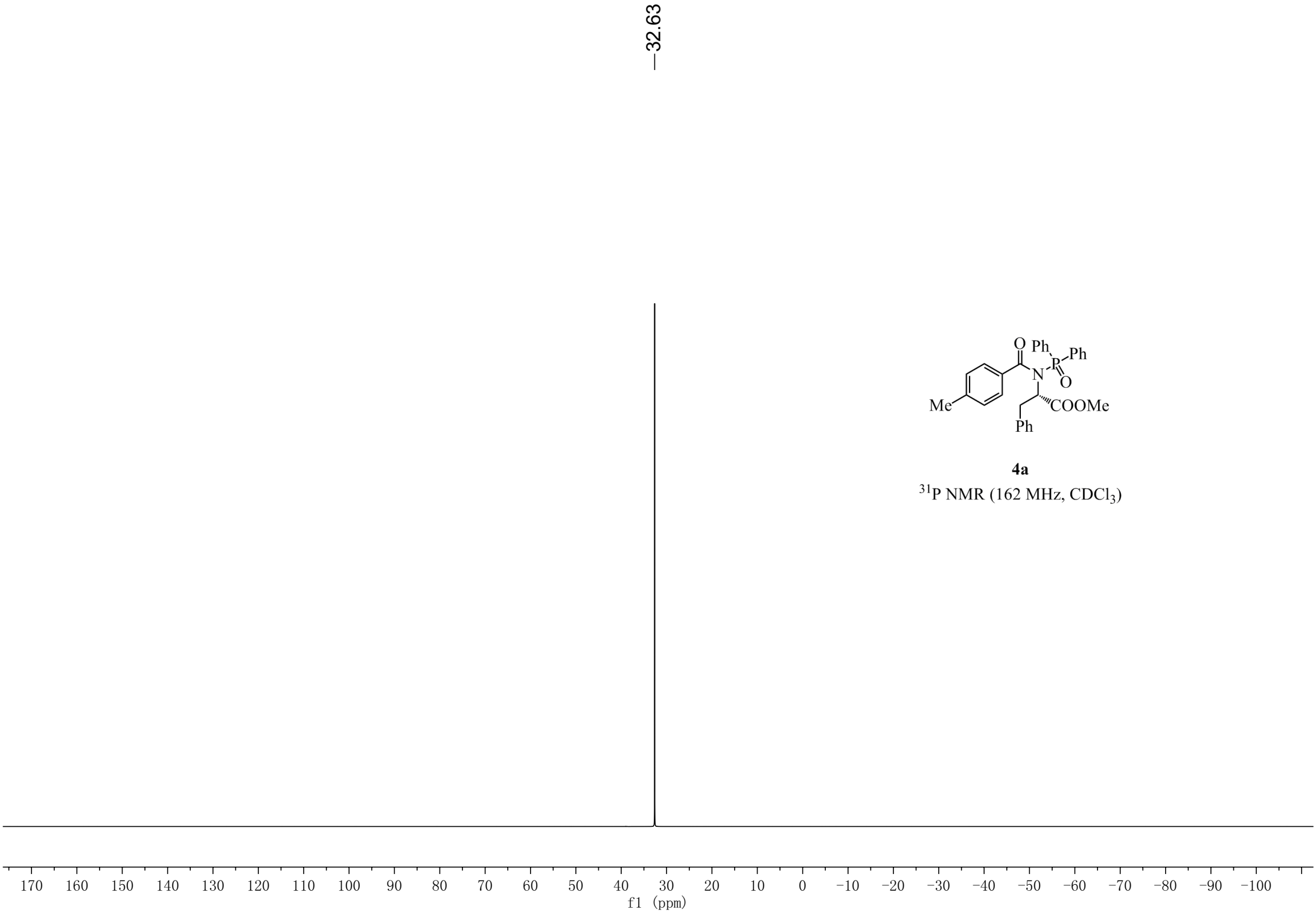
4a

^{1}H NMR (400 MHz, $CDCl_3$)



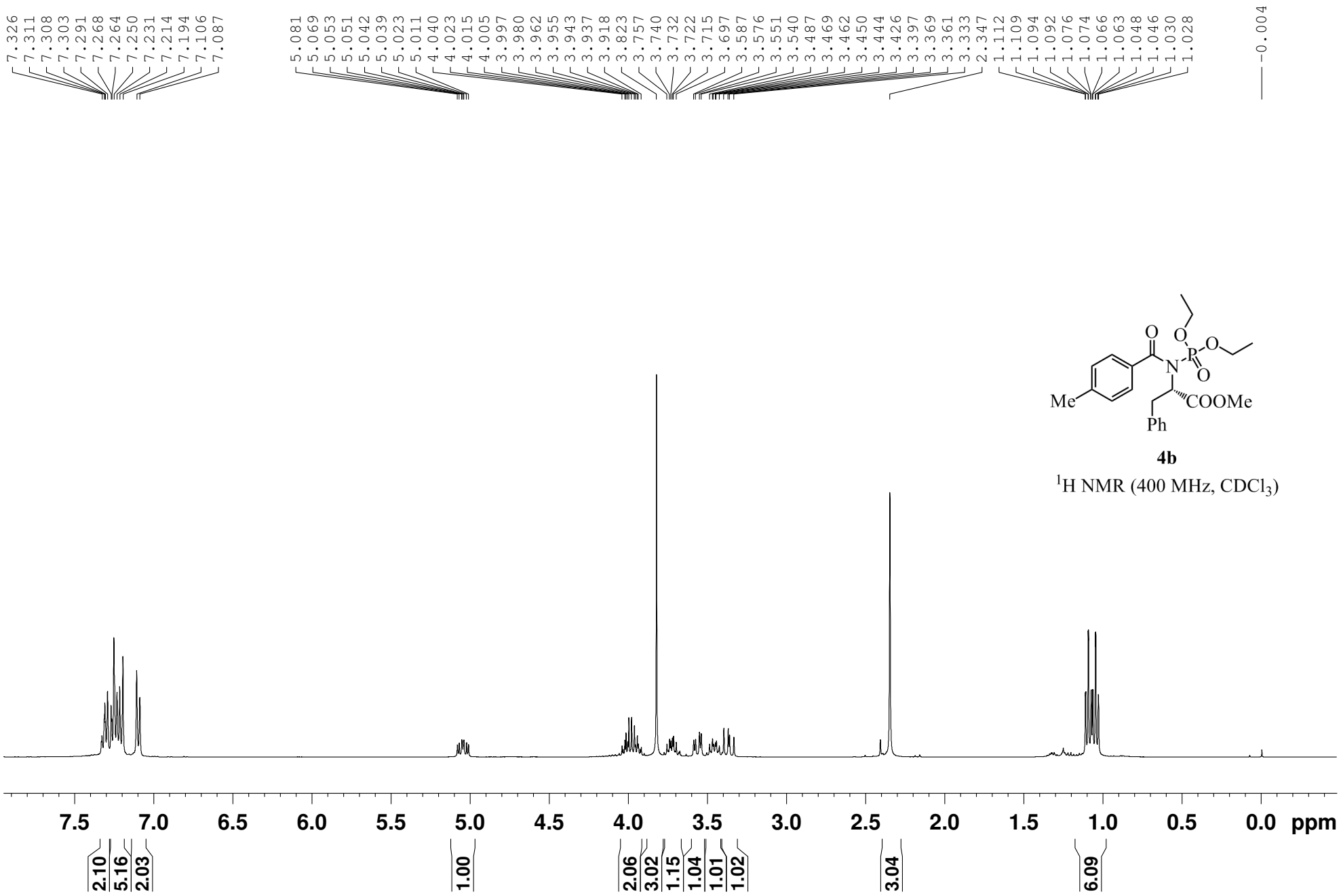
4a

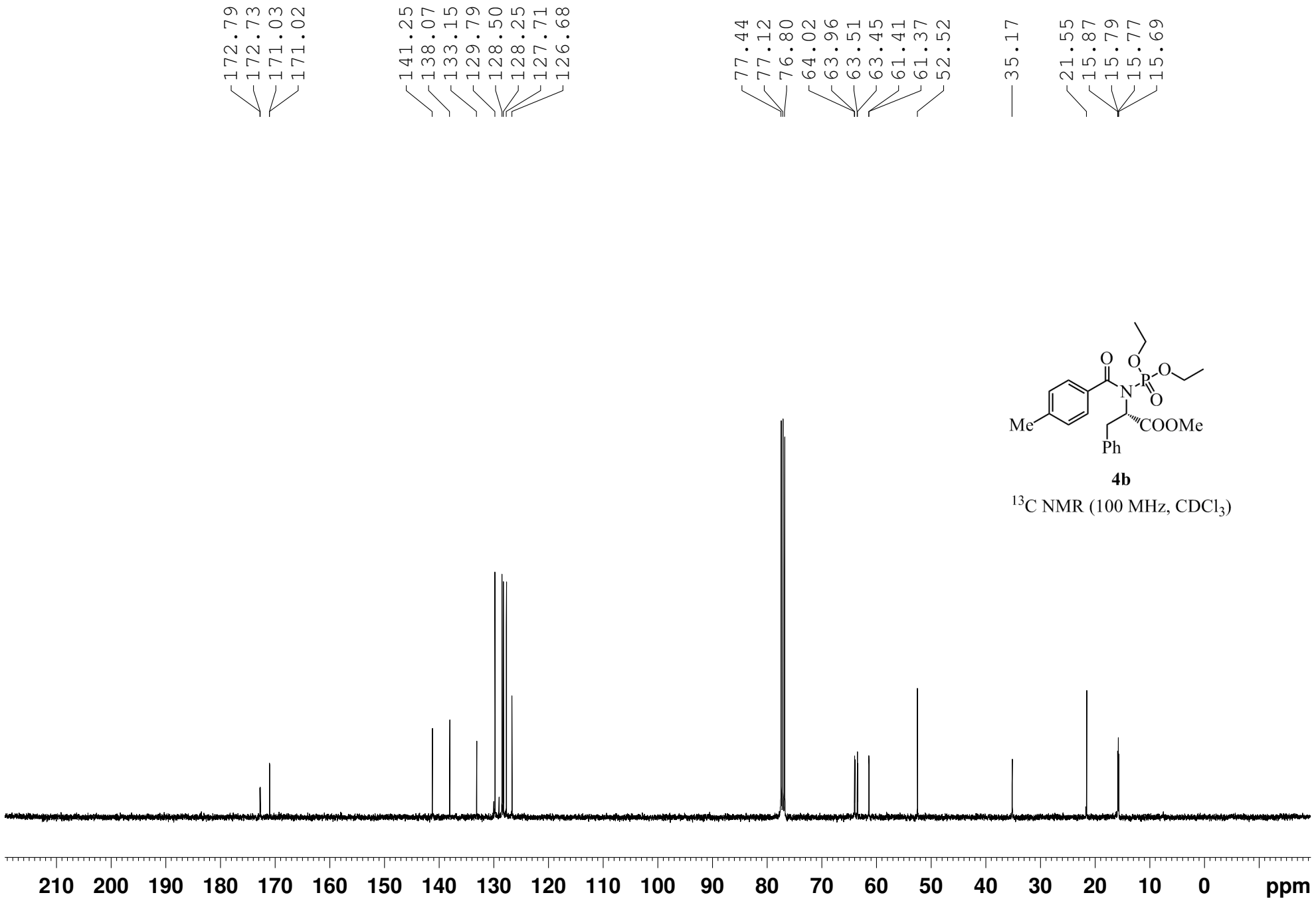
^{13}C NMR (100 MHz, $CDCl_3$)



4a

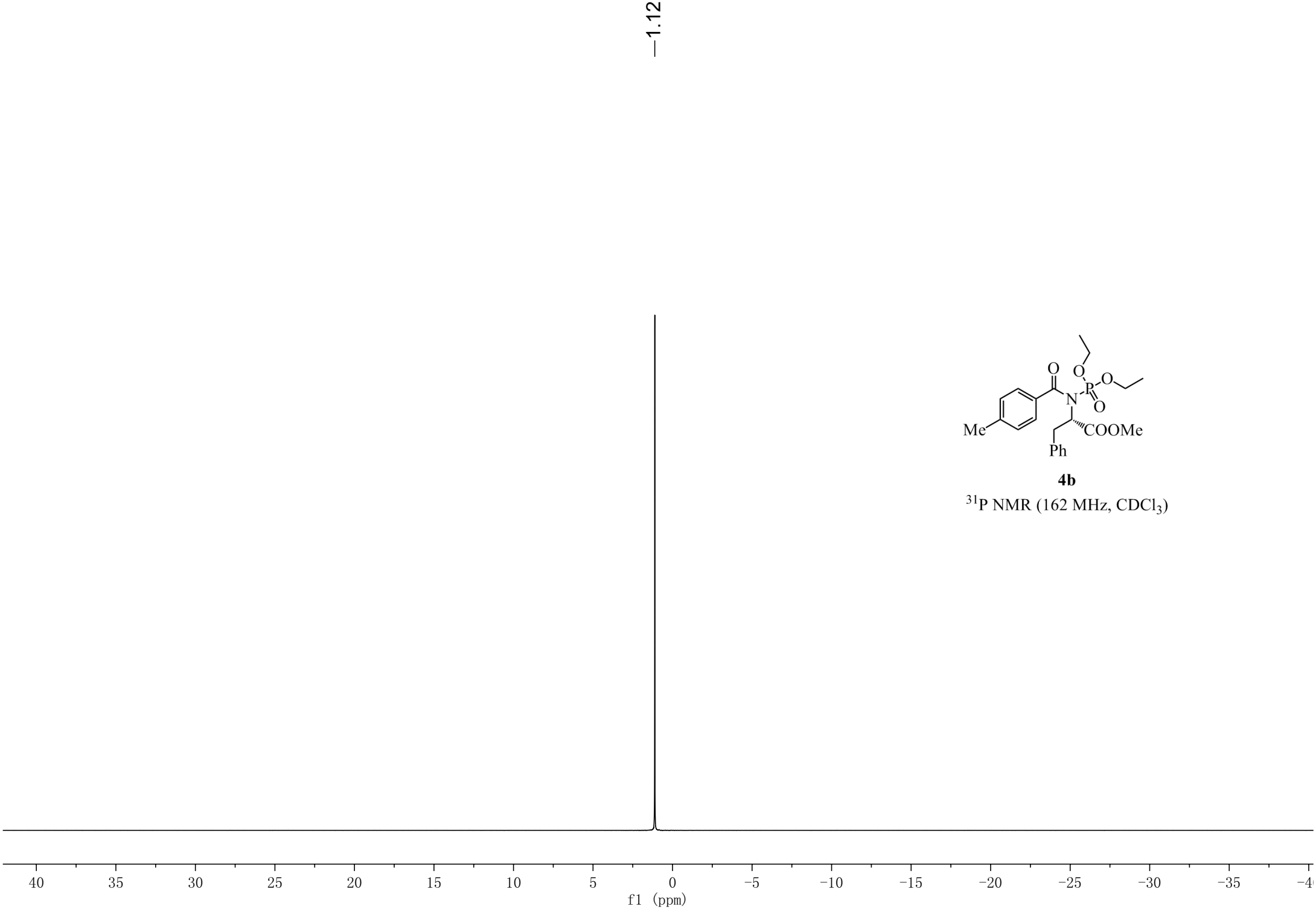
^{31}P NMR (162 MHz, $CDCl_3$)


7.326
7.311
7.308
7.303
7.291
7.268
7.264
7.250
7.231
7.214
7.194
7.106
7.087
5.081
5.069
5.053
5.051
5.042
5.039
5.023
5.011
4.040
4.023
4.015
4.005
3.997
3.980
3.962
3.955
3.943
3.937
3.918
3.823
3.757
3.740
3.732
3.722
3.715
3.697
3.587
3.576
3.551
3.540
3.487
3.469
3.462
3.450
3.444
3.426
3.397
3.369
3.361
3.333
2.347
1.112
1.109
1.094
1.092
1.076
1.074
1.066
1.063
1.048
1.046
1.030
1.028
-0.004
Me
COOMe
Ph
4b
1H NMR (400 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.10
5.16
2.03
1.00
2.06
3.02
1.15
1.04
1.01
1.02
3.04
6.09



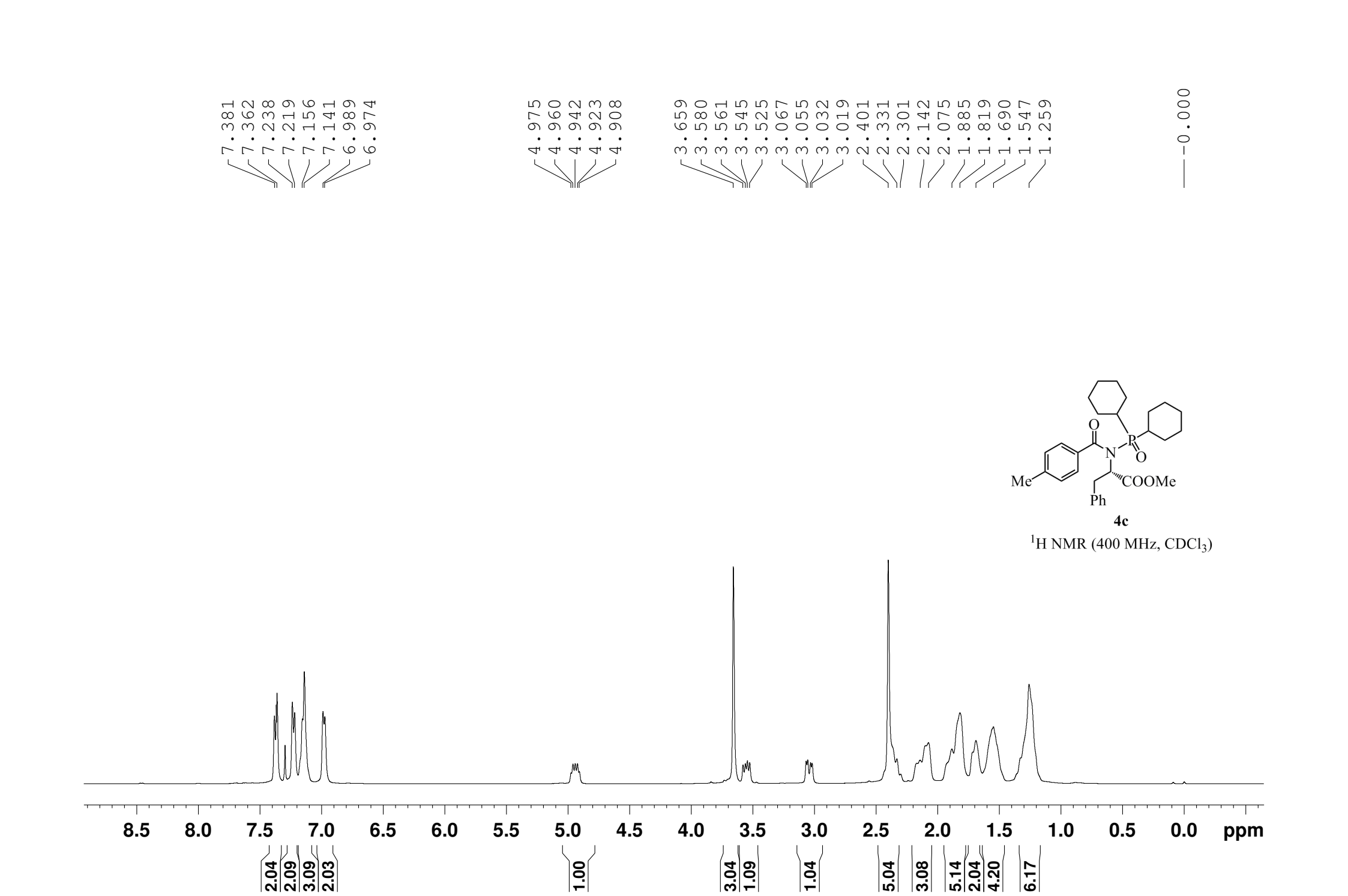
4b

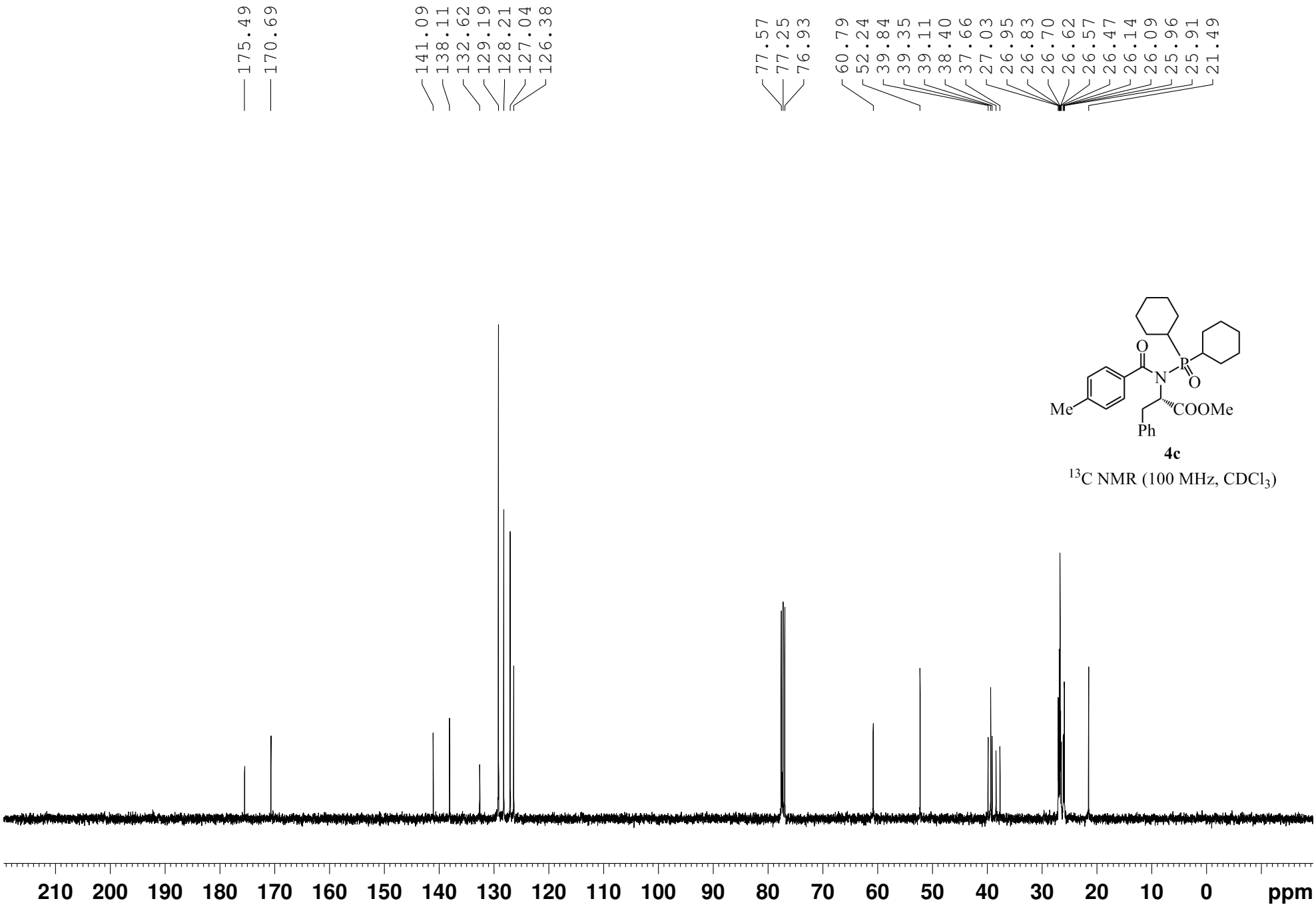
^{13}C NMR (100 MHz, $CDCl_3$)

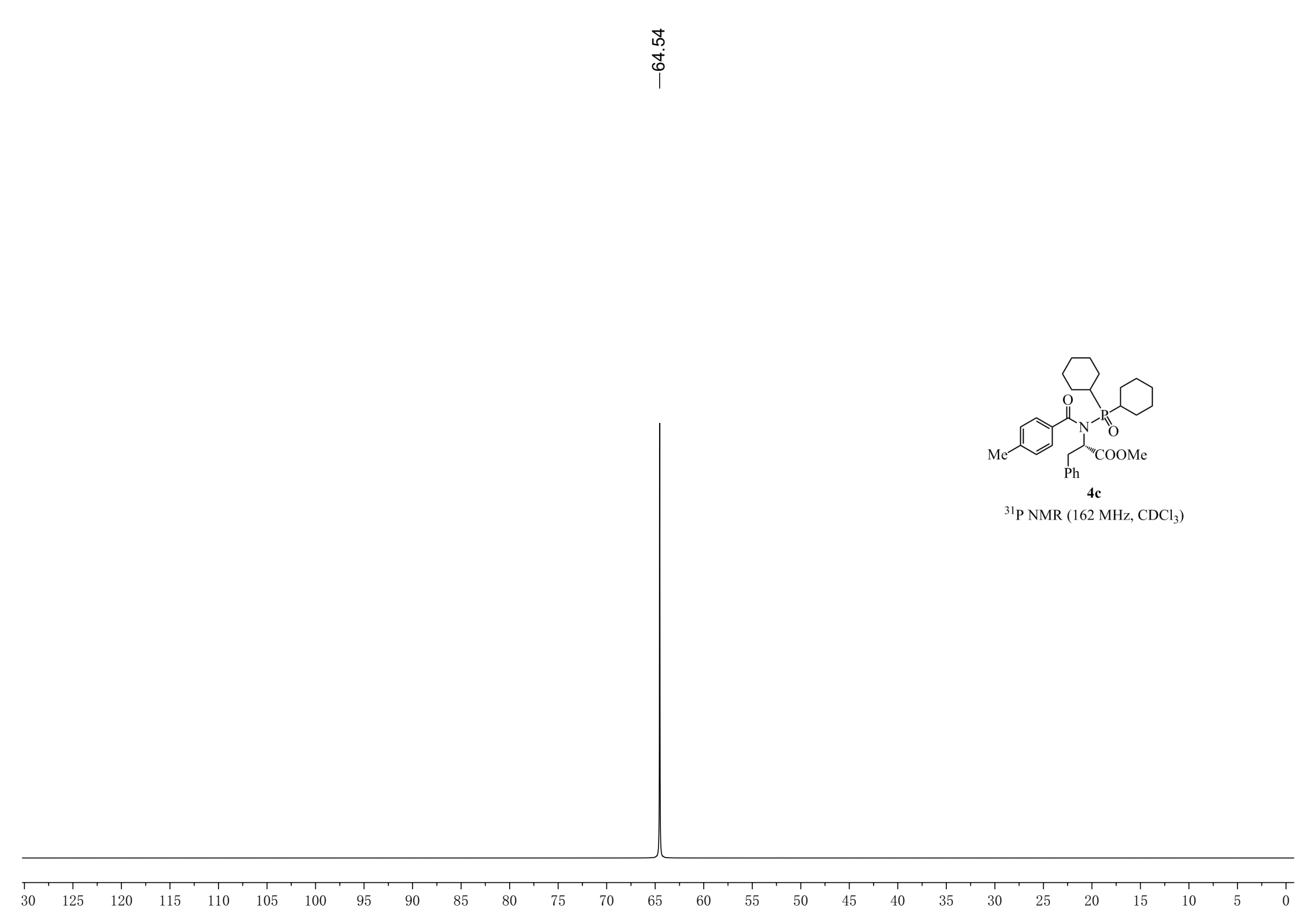


4b

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

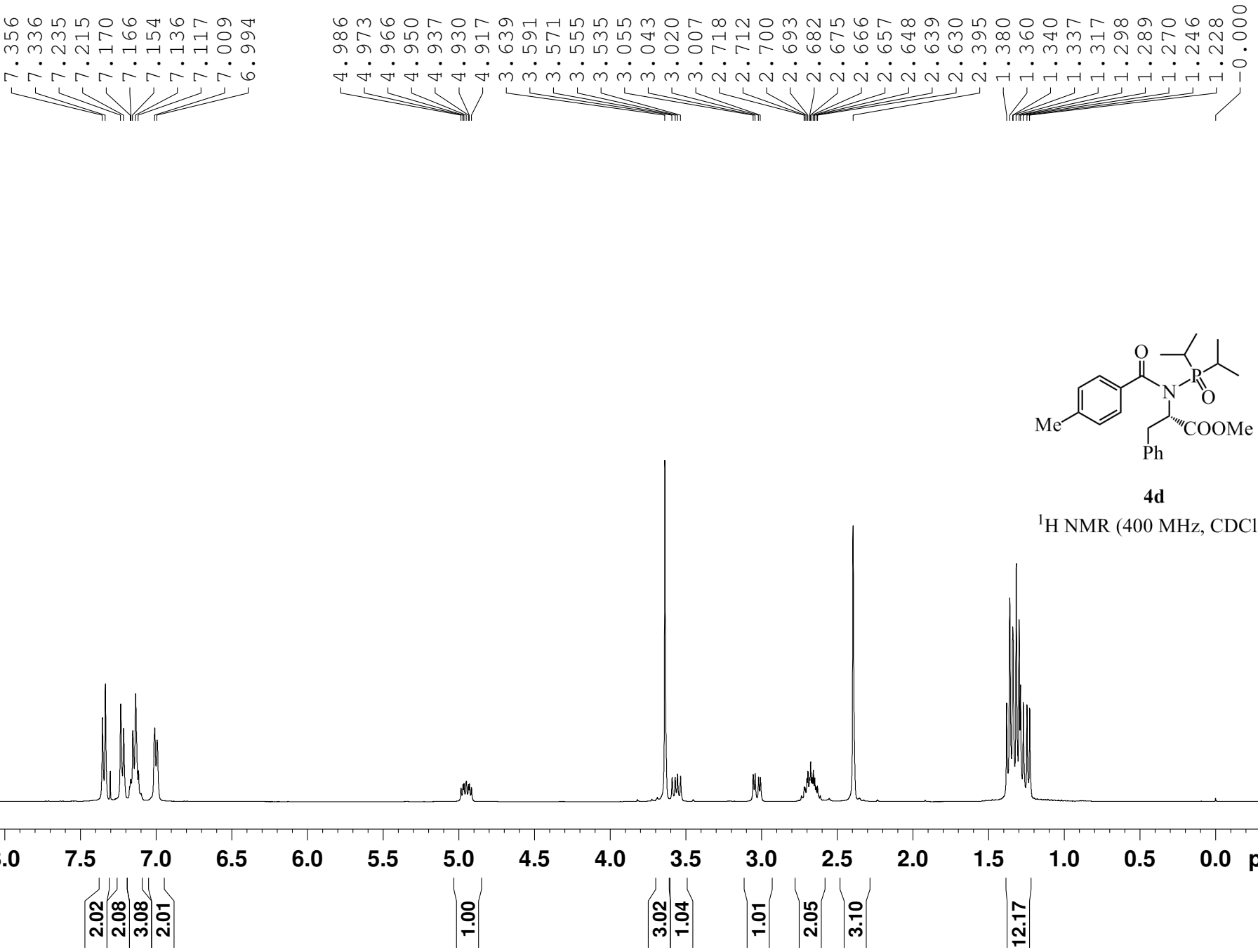

7.381
7.362
7.238
7.219
7.156
7.141
6.989
6.974
4.975
4.960
4.942
4.923
4.908
3.659
3.580
3.561
3.545
3.525
3.067
3.055
3.032
3.019
2.401
2.331
2.301
2.142
2.075
1.885
1.819
1.690
1.547
1.259
0.000
O
P
O
N
Me
COOMe
Ph
4c
1H NMR (400 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.04
2.09
3.09
2.03
1.00
3.04
1.09
1.04
5.04
3.08
5.14
2.04
4.20
6.17


175.49
170.69
141.09
138.11
132.62
129.19
128.21
127.04
126.38
77.57
77.25
76.93
60.79
52.24
39.84
39.35
39.11
38.40
37.66
27.03
26.95
26.83
26.70
26.62
26.57
26.47
26.14
26.09
25.96
25.91
21.49
O
P
O
N
Me
COOMe
Ph
4c
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



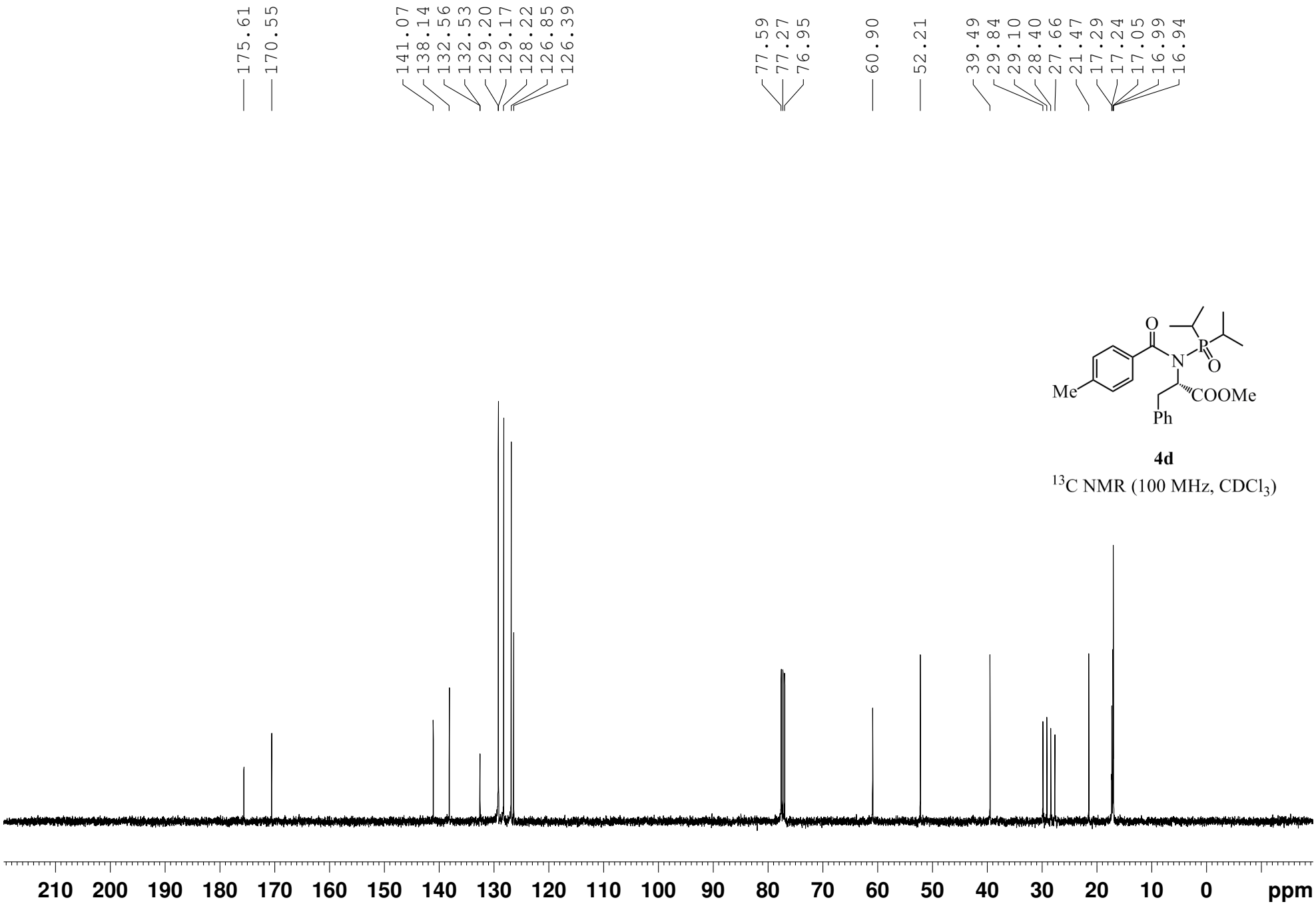
4c

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



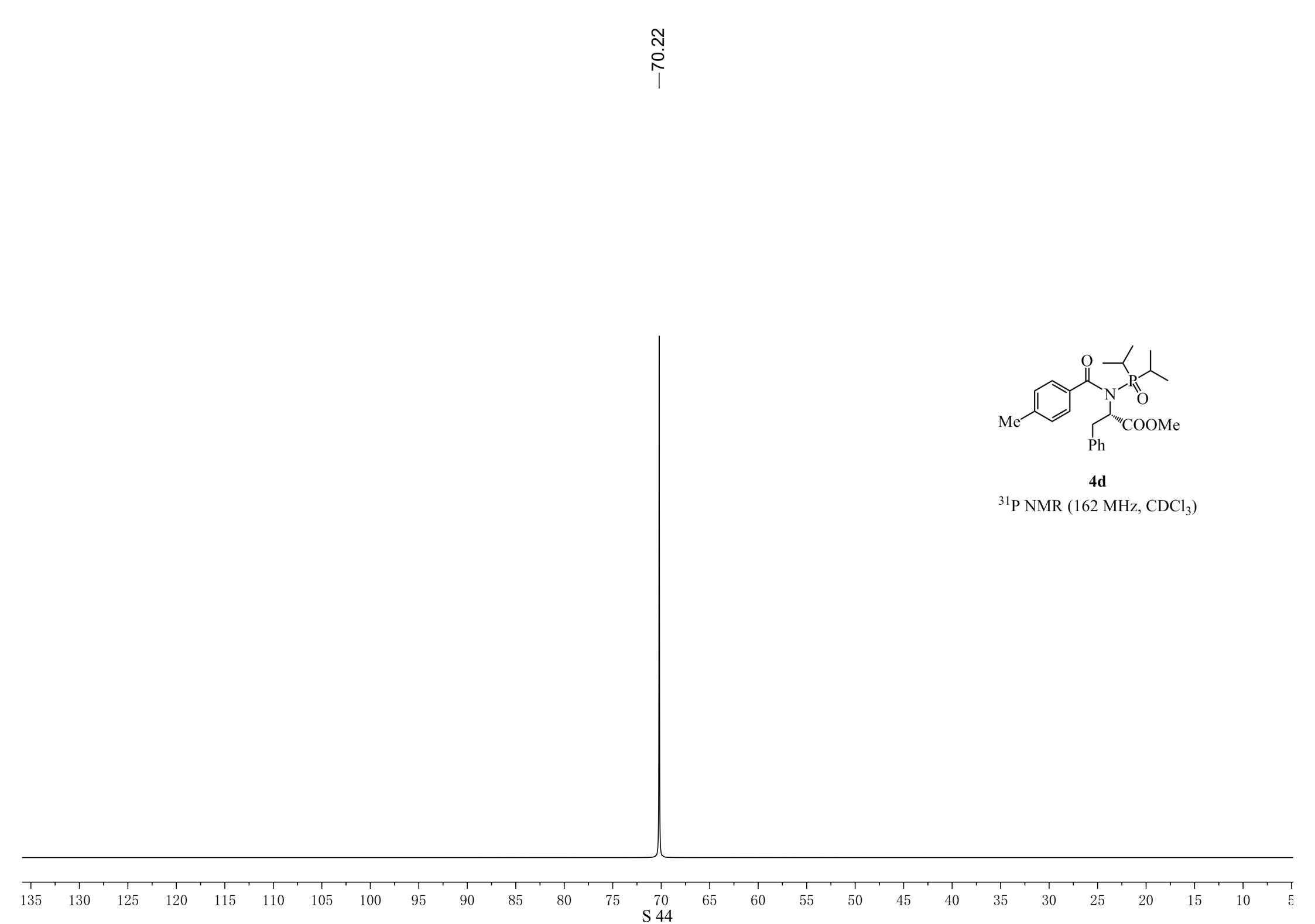
4d

^{1}H NMR (400 MHz, $CDCl_3$)



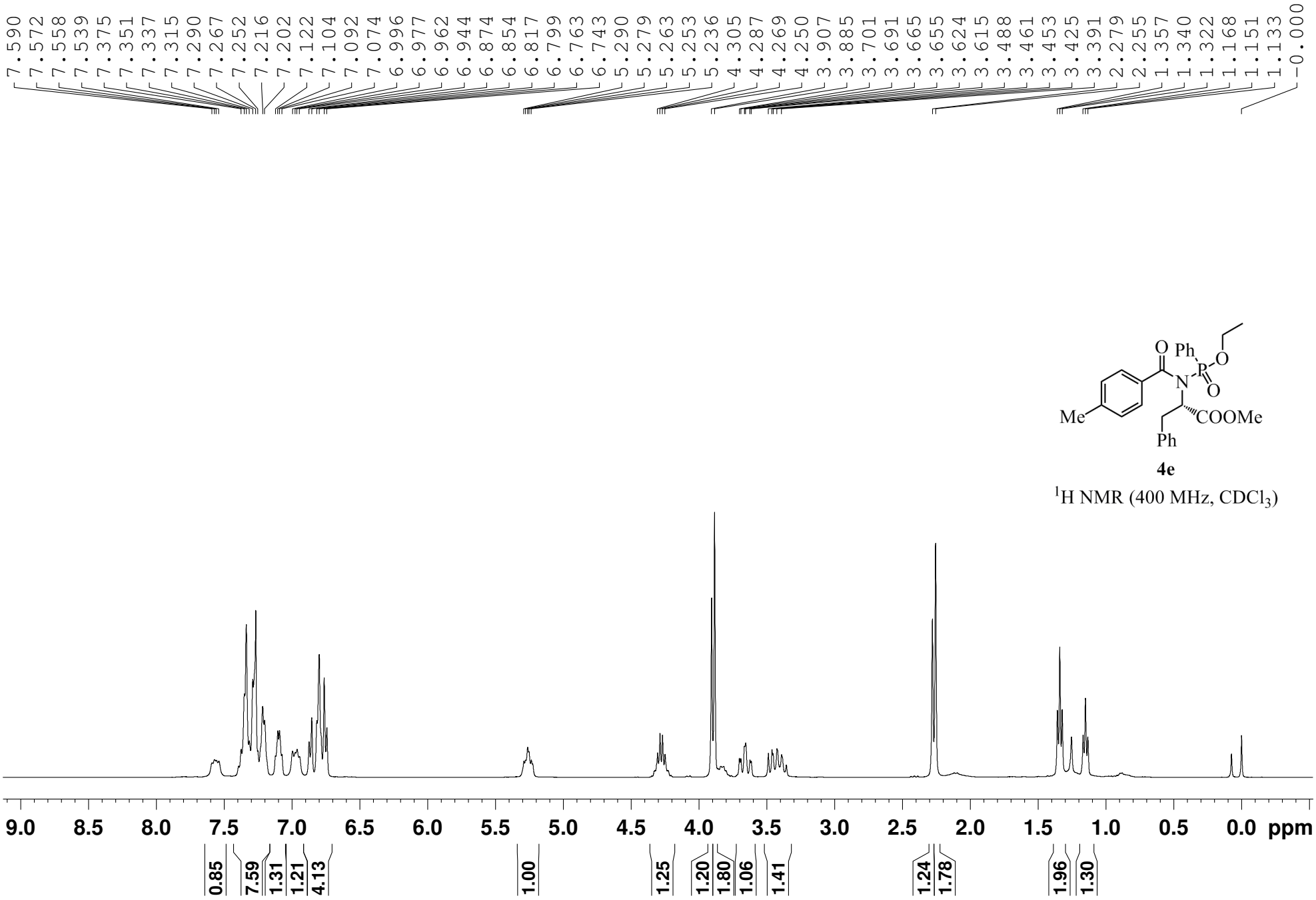
4d

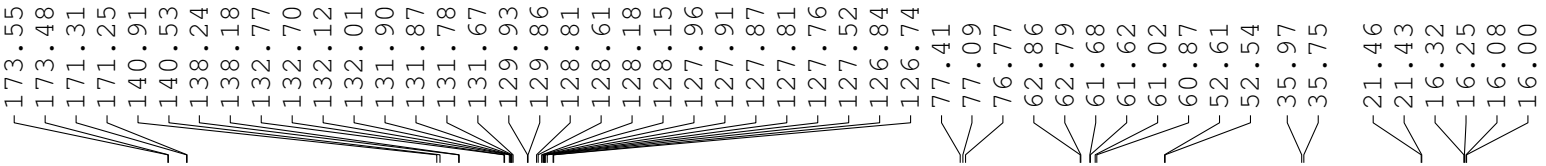
^{13}C NMR (100 MHz, $CDCl_3$)

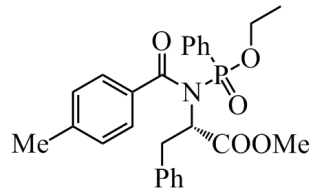


4d

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

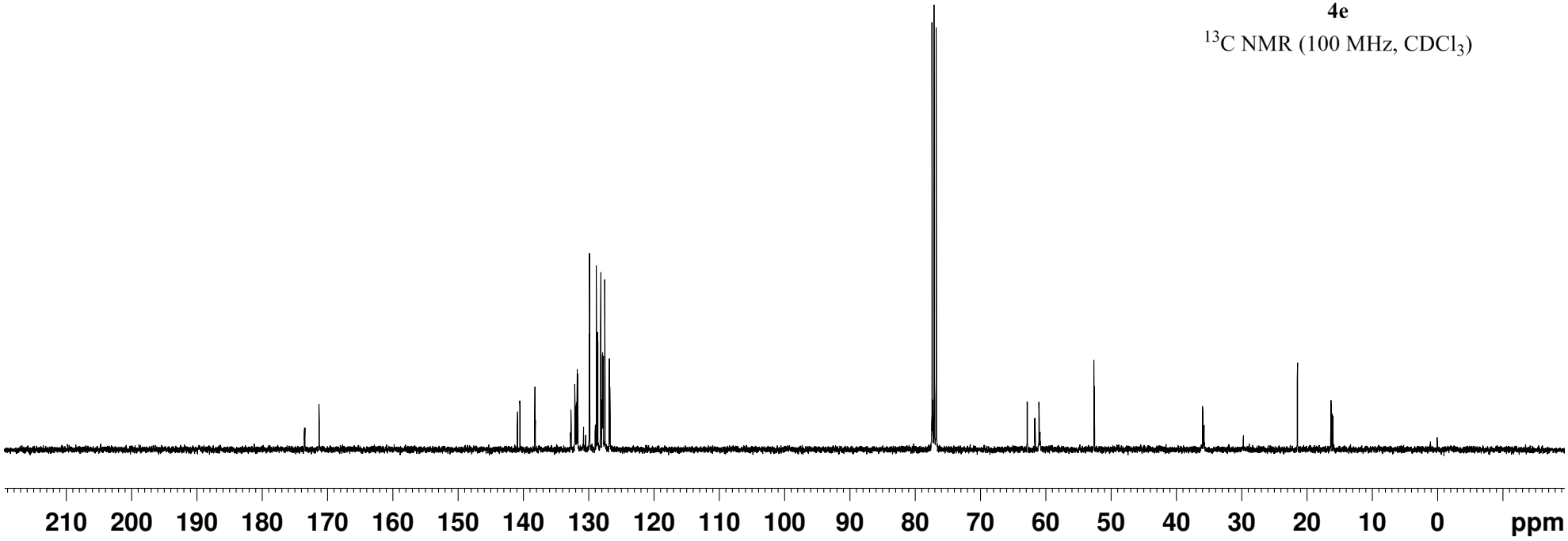

7.590
7.572
7.558
7.539
7.375
7.351
7.337
7.315
7.290
7.267
7.252
7.216
7.202
7.122
7.104
7.092
7.074
6.996
6.977
6.962
6.944
6.874
6.854
6.817
6.799
6.763
6.743
5.290
5.279
5.263
5.253
5.236
4.305
4.287
4.269
4.250
3.907
3.885
3.701
3.691
3.665
3.655
3.624
3.615
3.488
3.461
3.453
3.425
3.391
2.279
2.255
1.357
1.340
1.322
1.168
1.151
1.133
-0.000
Me
COOMe
Ph
4e
^{1}H NMR (400 MHz, $CDCl_3$)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.85
7.59
1.31
1.21
4.13
1.00
1.25
1.20
1.80
1.06
1.41
1.24
1.78
1.96
1.30

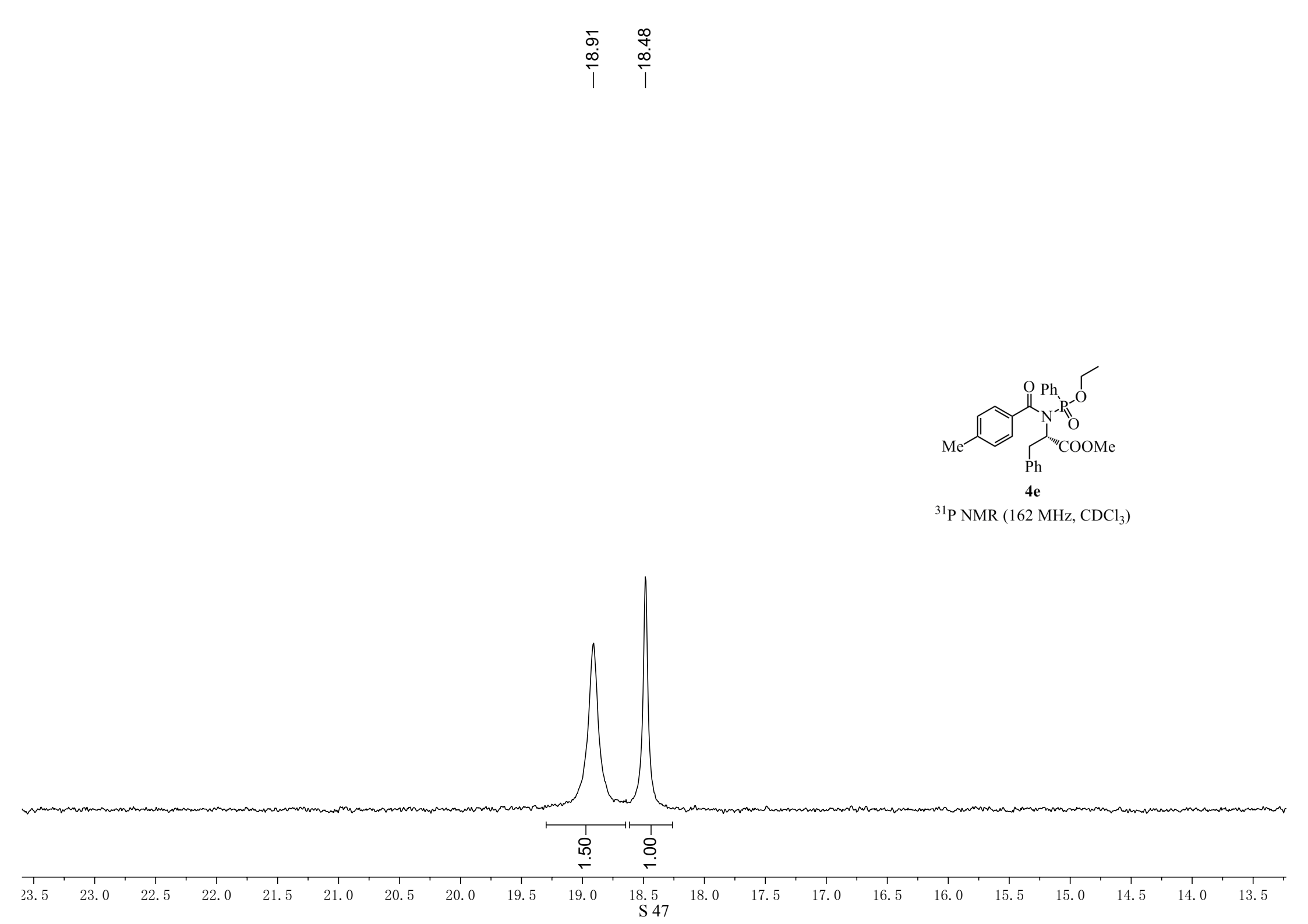




4e

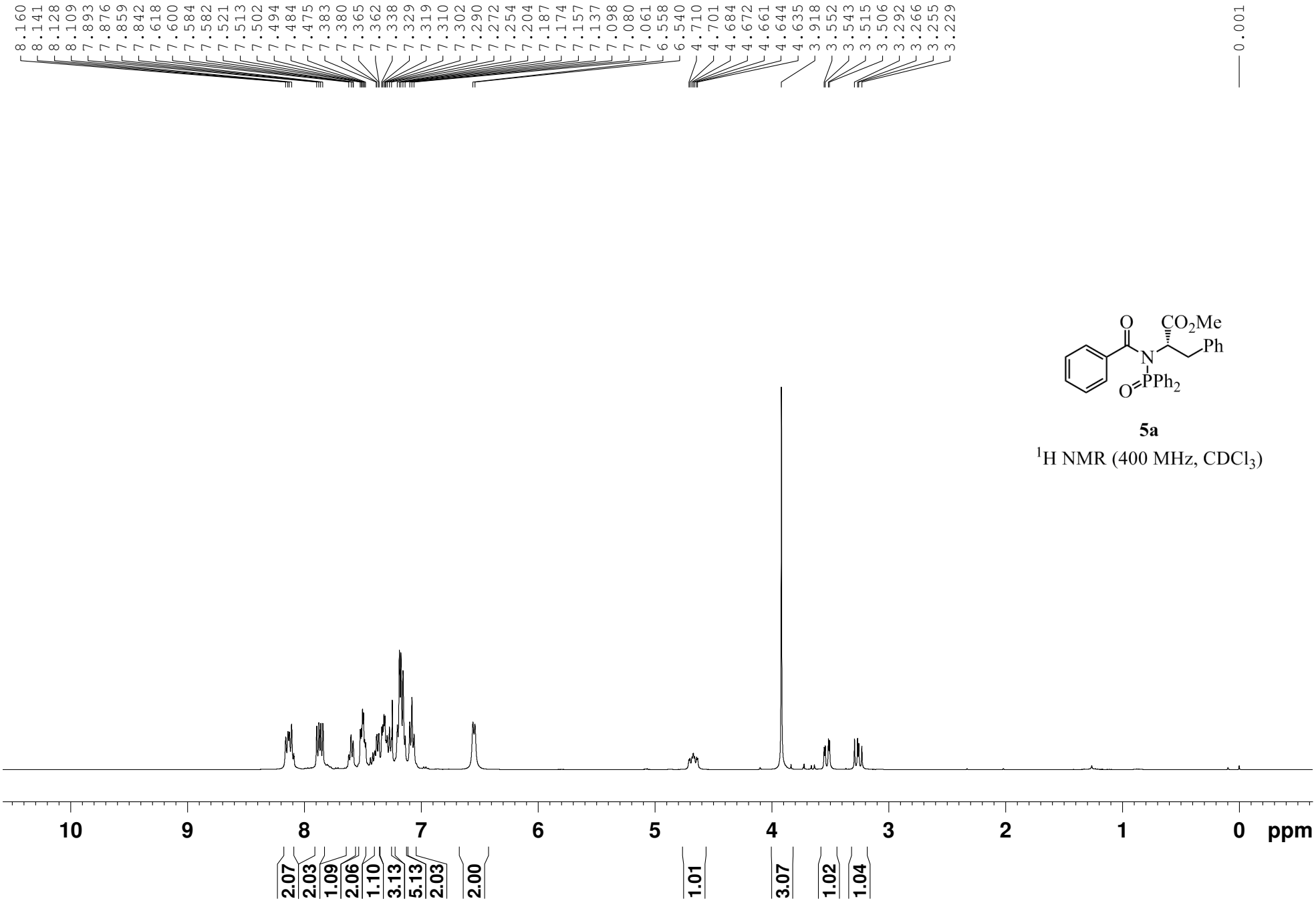
^{13}C NMR (100 MHz, $CDCl_3$)





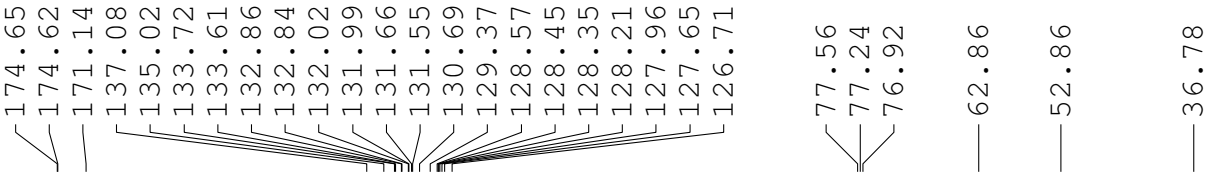
4e

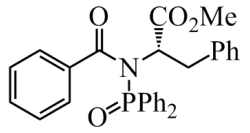
^{31}P NMR (162 MHz, $CDCl_3$)



5a

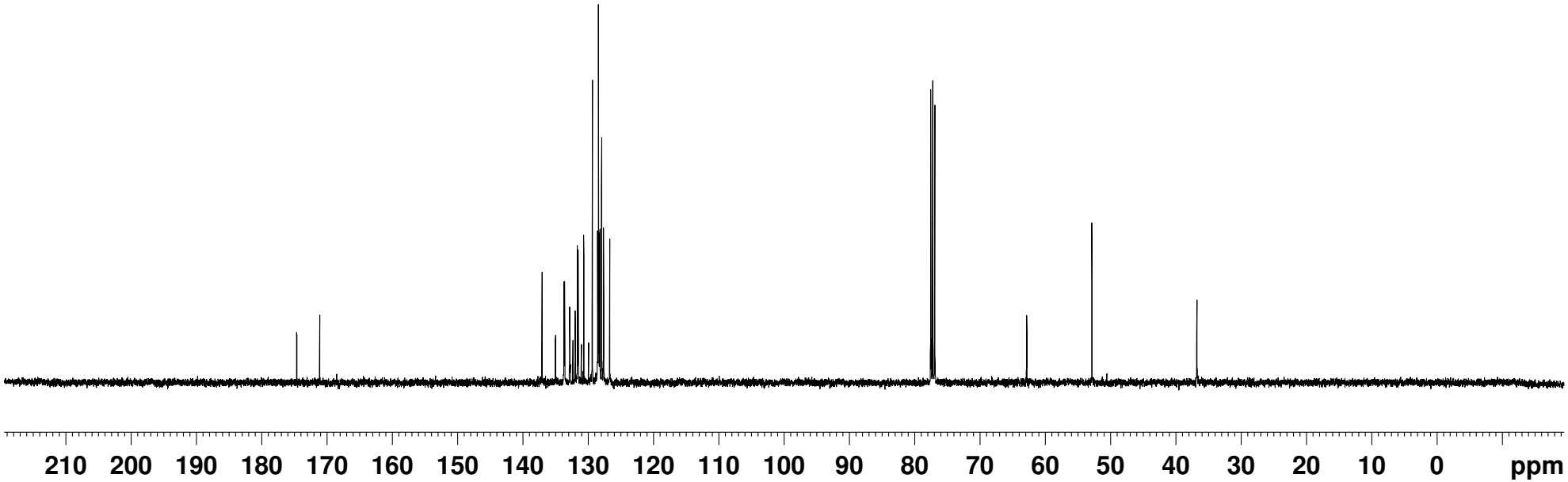
^{1}H NMR (400 MHz, $CDCl_3$)

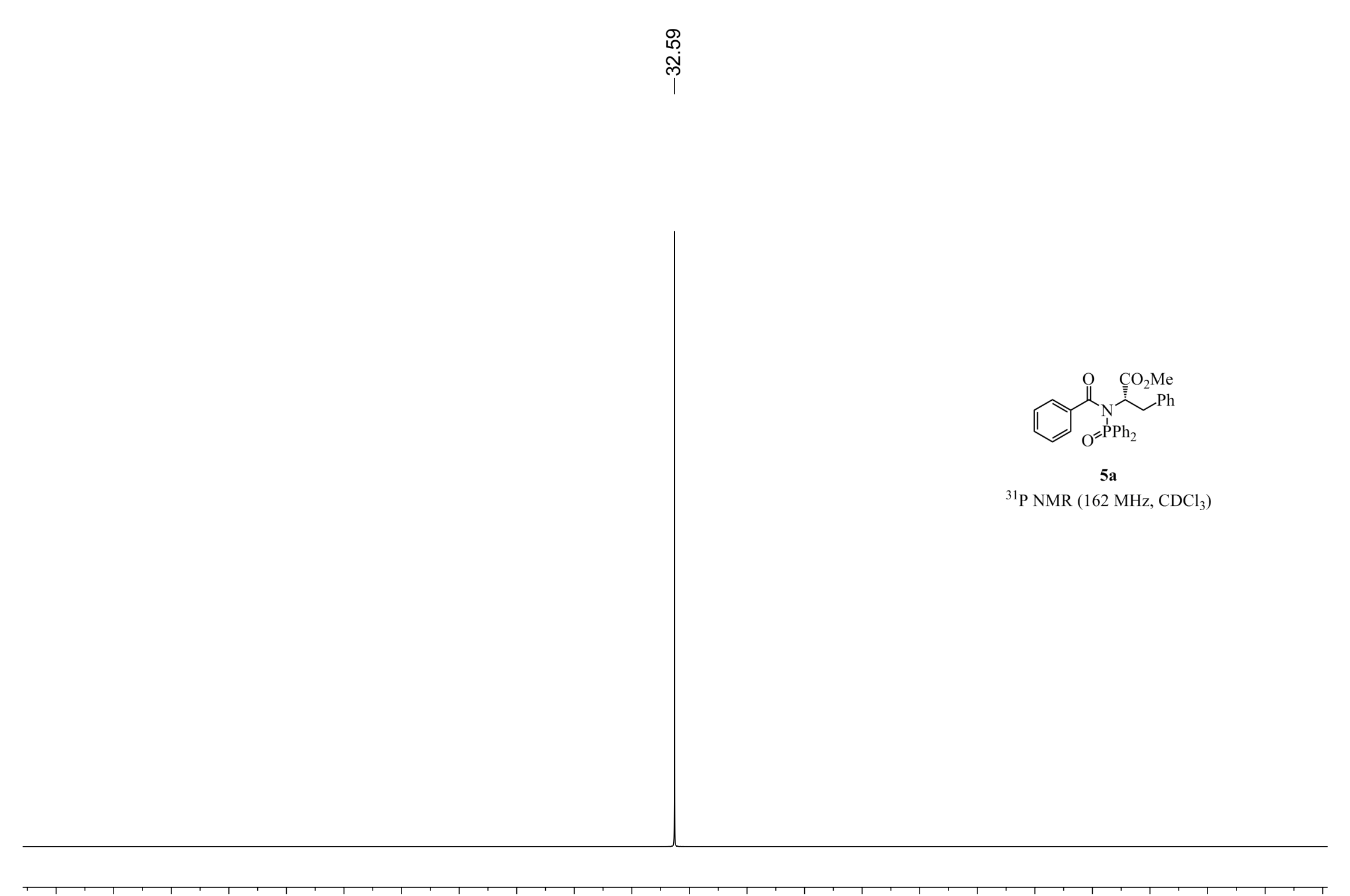




5a

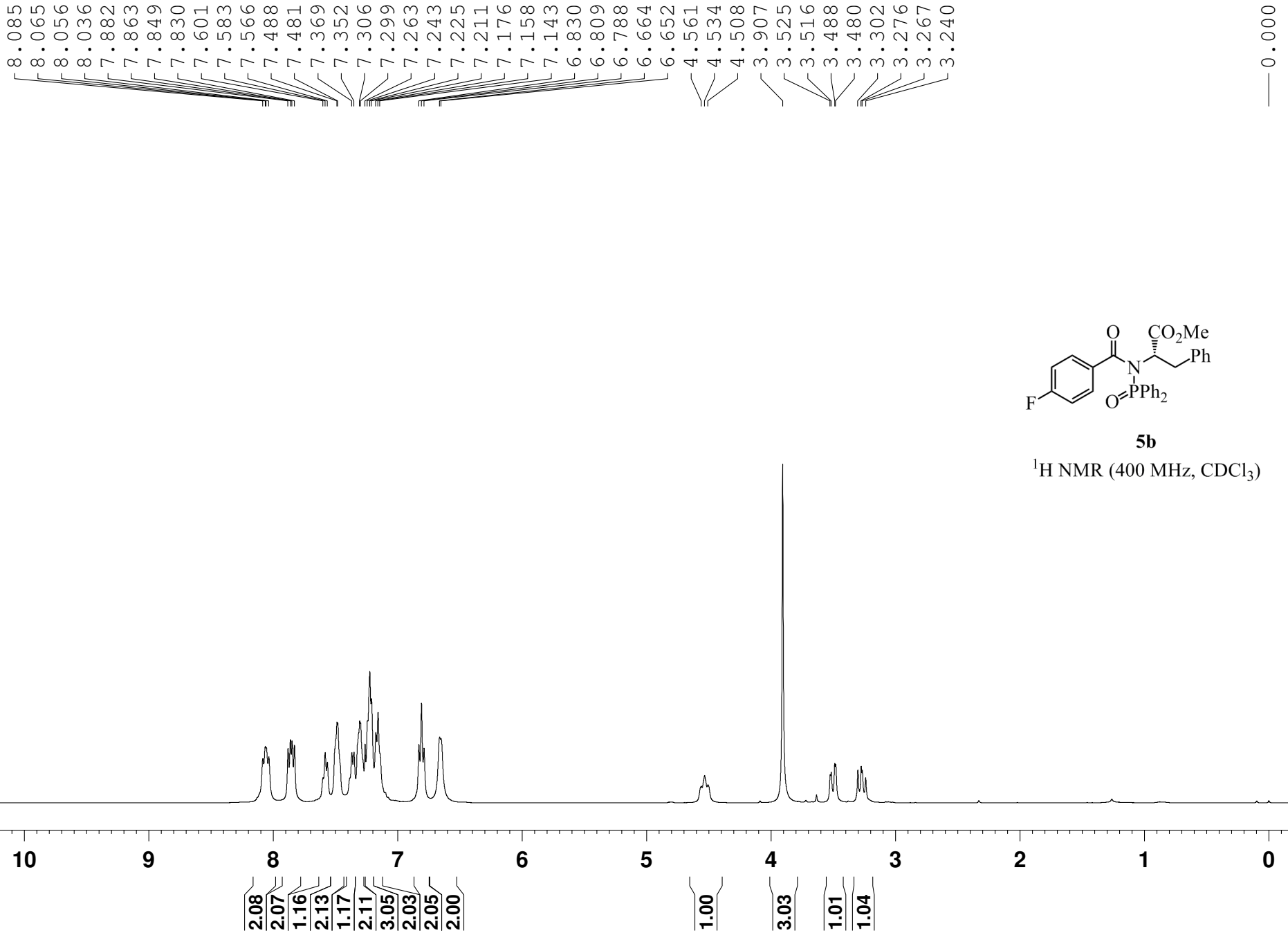
^{13}C NMR (100 MHz, $CDCl_3$)





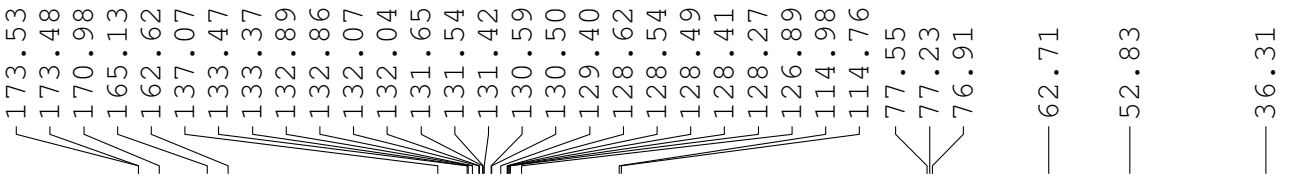
5a

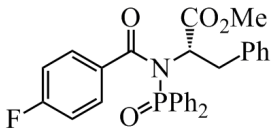
^{31}P NMR (162 MHz, $CDCl_3$)



5b

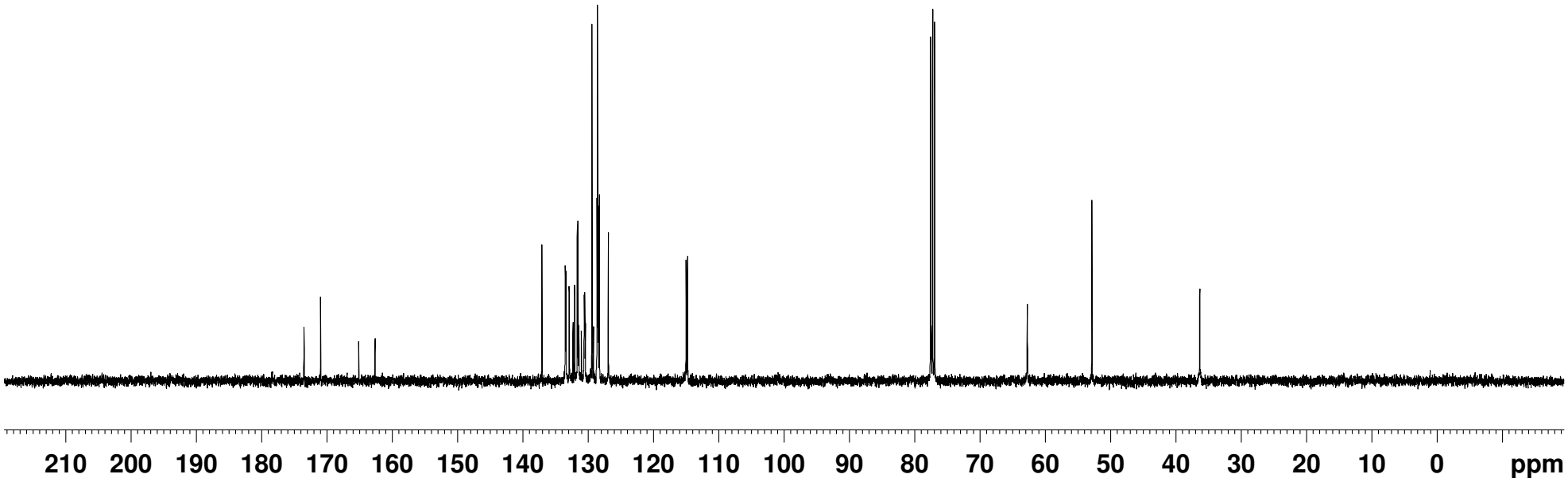
^{1}H NMR (400 MHz, $CDCl_3$)

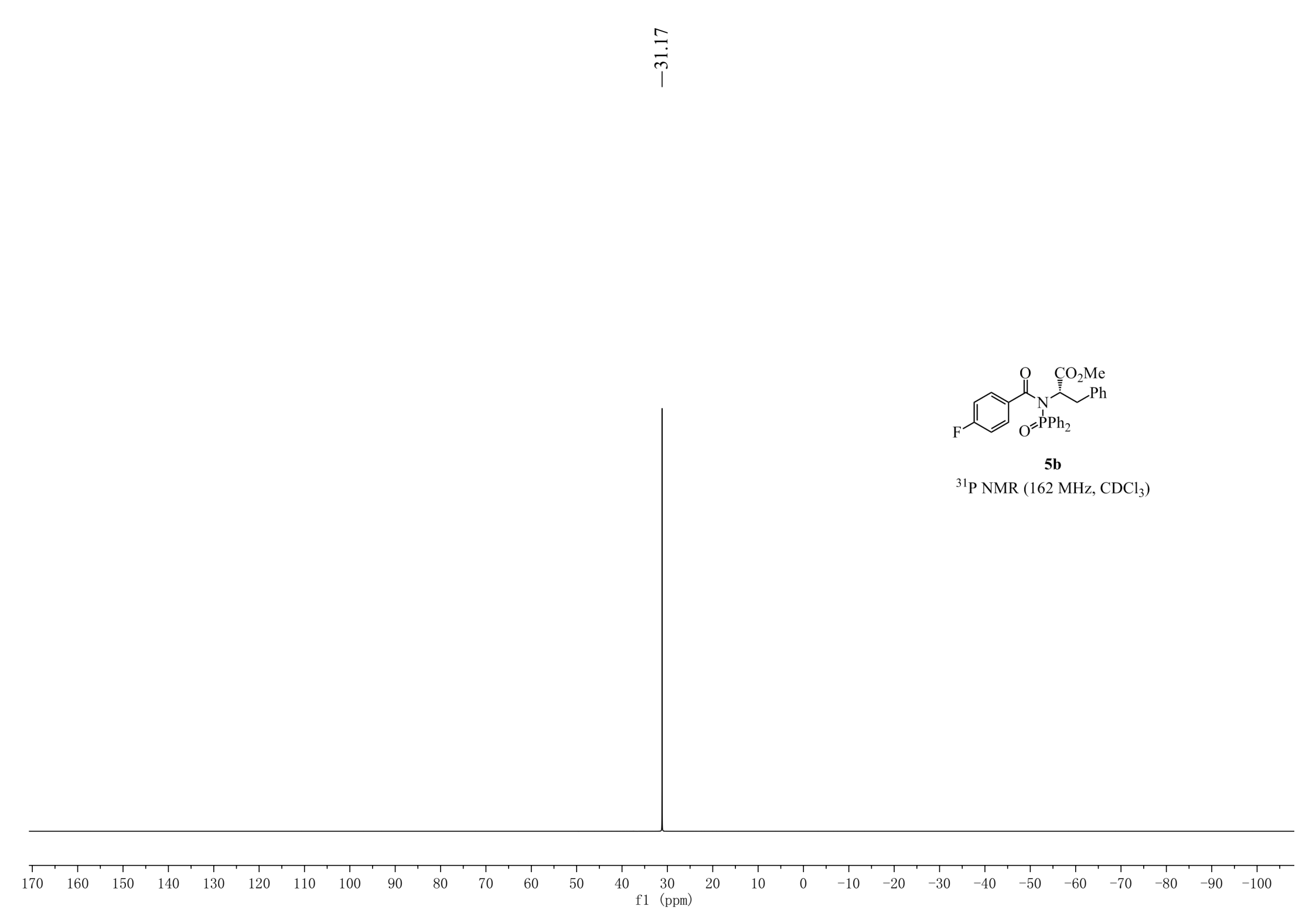




5b

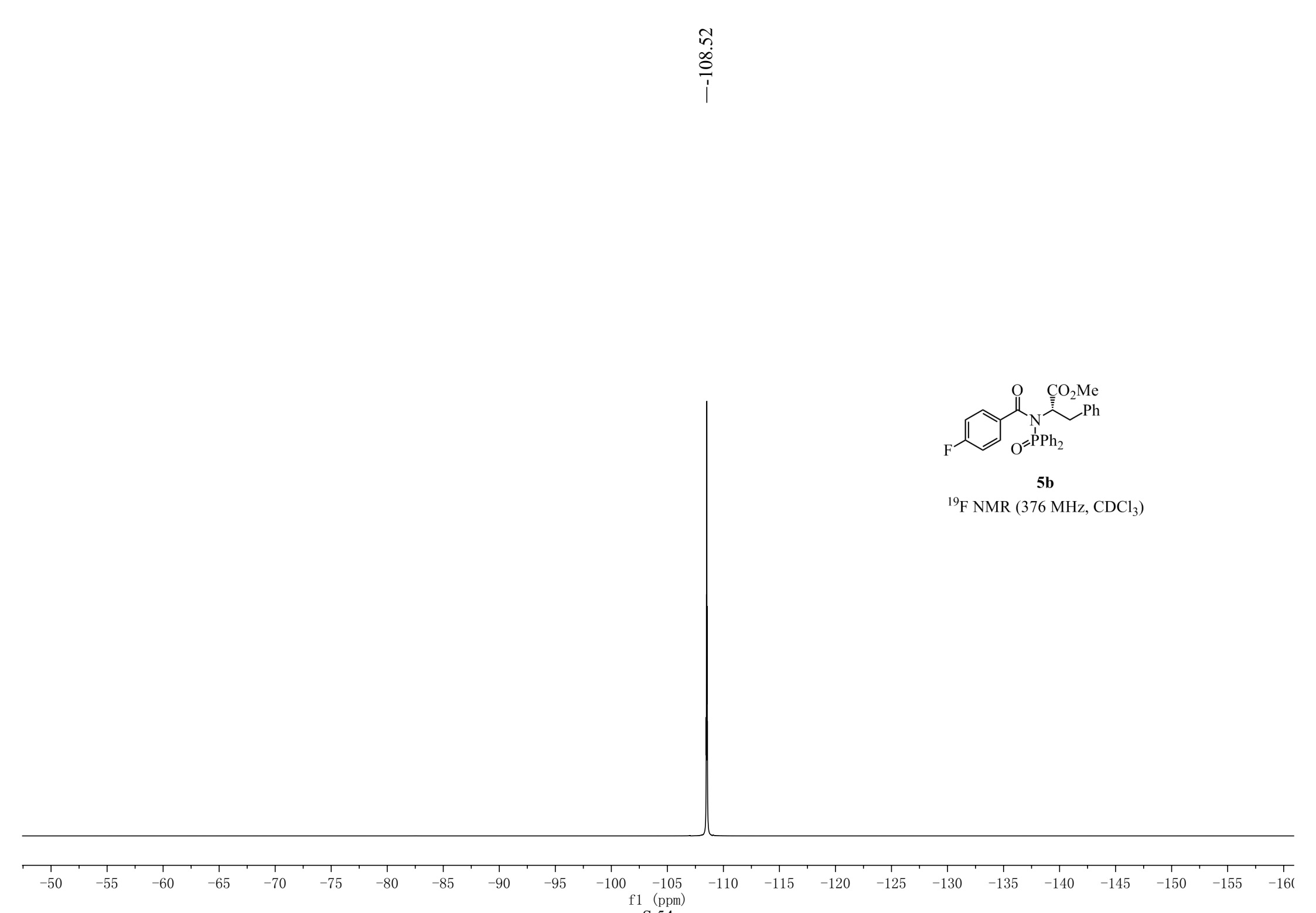
^{13}C NMR (100 MHz, $CDCl_3$)





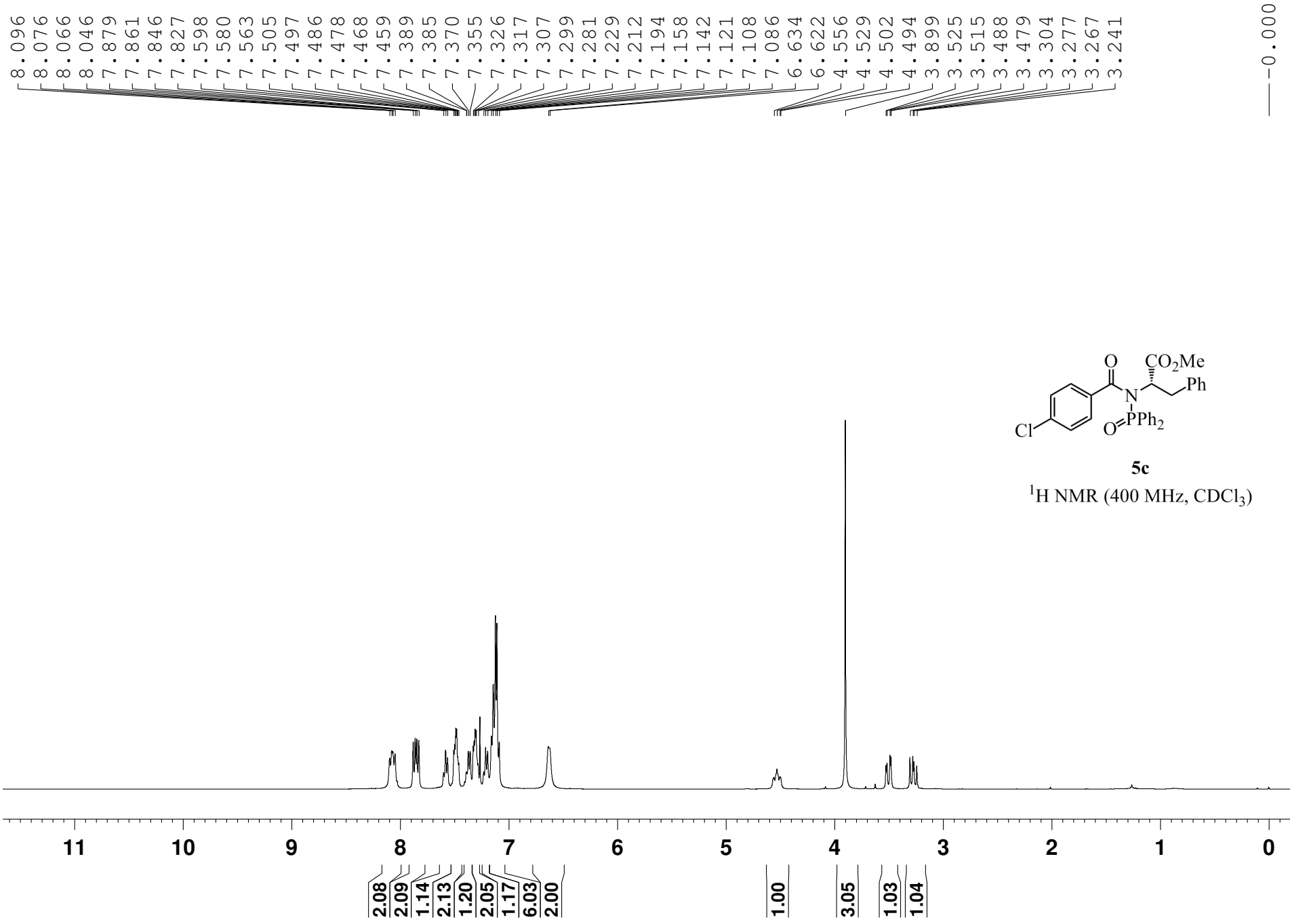
5b

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



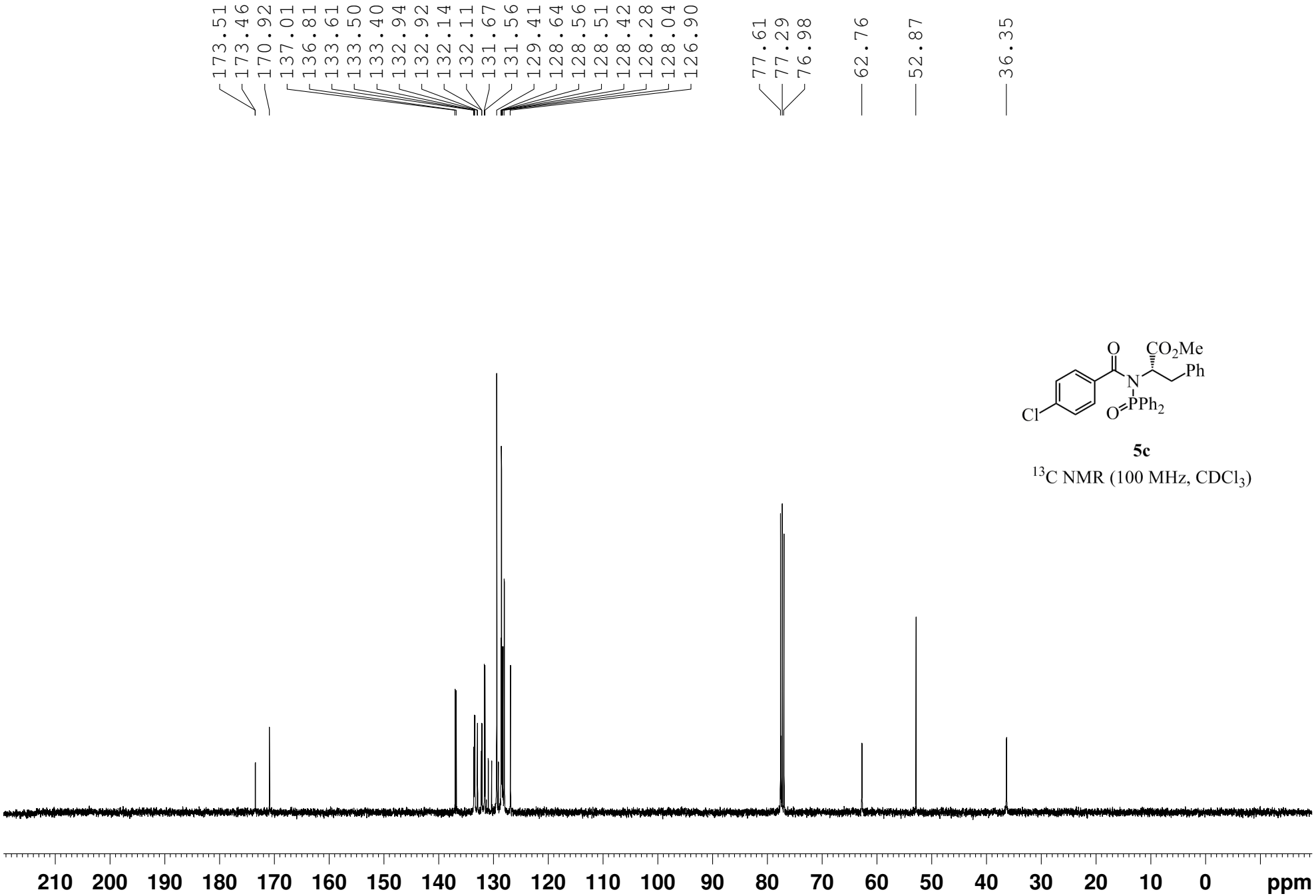
5b

^{19}F NMR (376 MHz, $CDCl_3$)



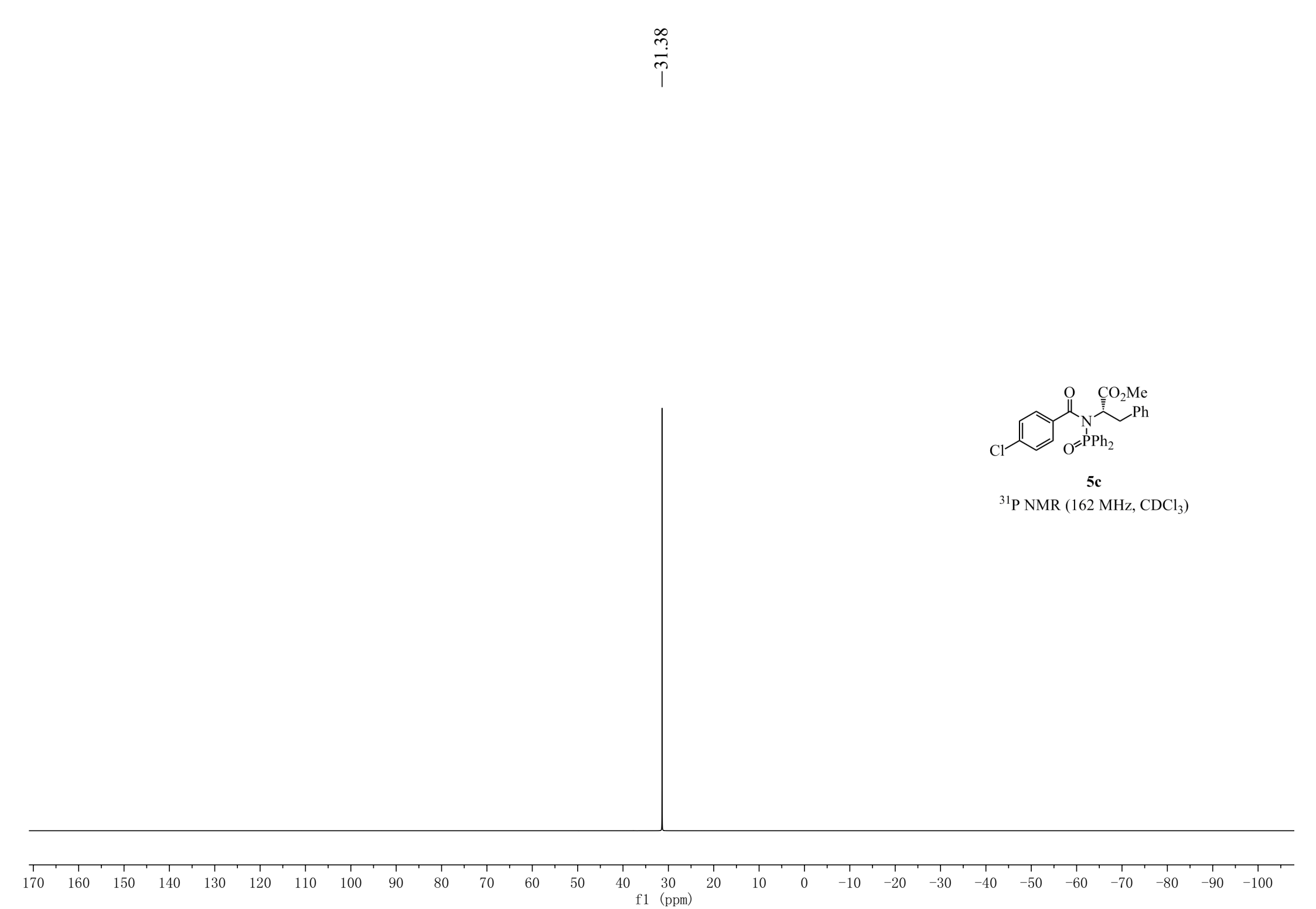
5c

^{1}H NMR (400 MHz, $CDCl_3$)



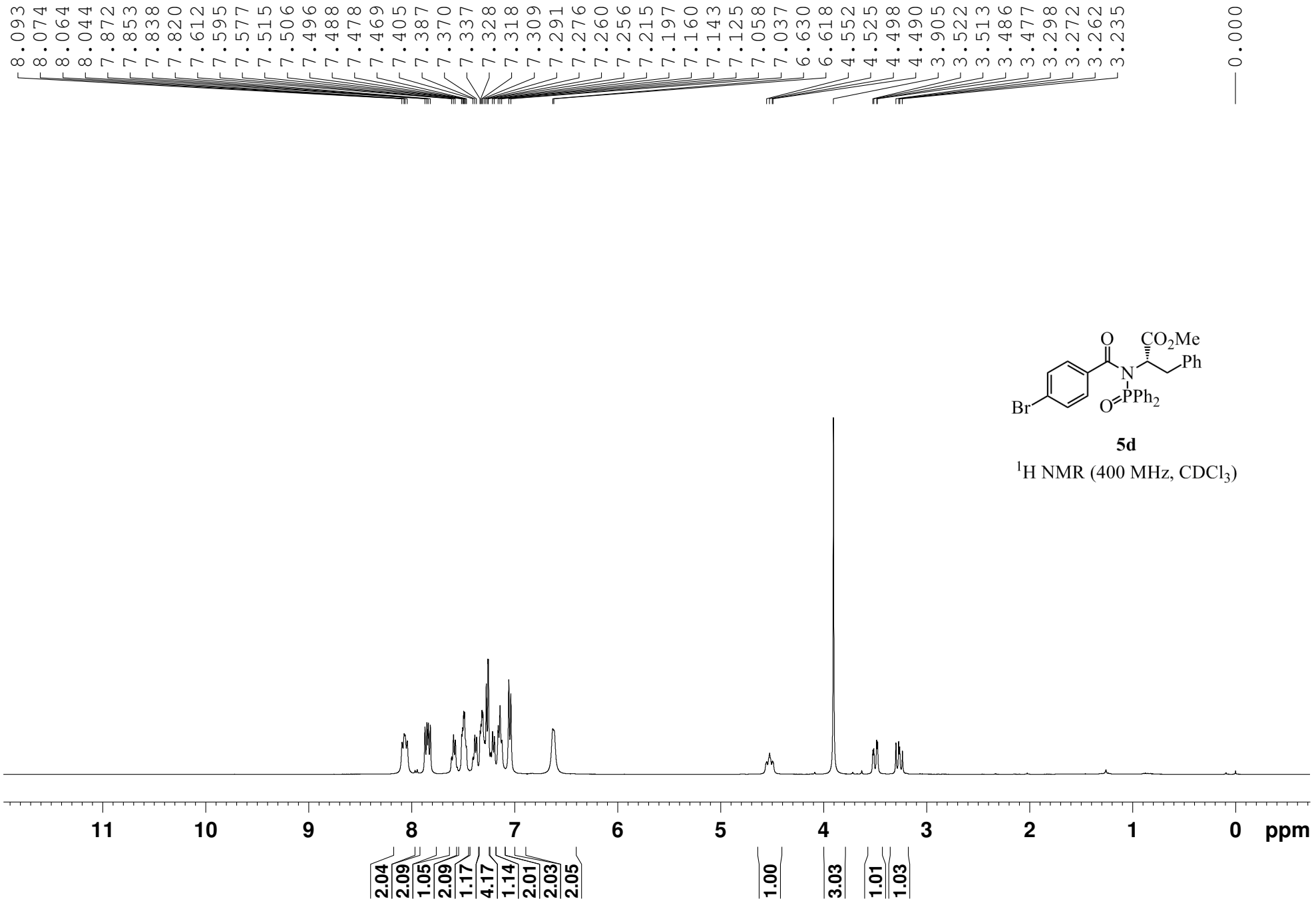
5c

^{13}C NMR (100 MHz, $CDCl_3$)



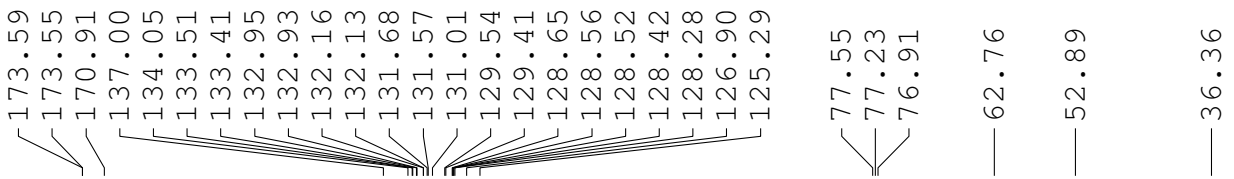
5c

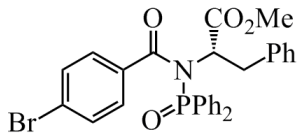
^{31}P NMR (162 MHz, $CDCl_3$)



5d

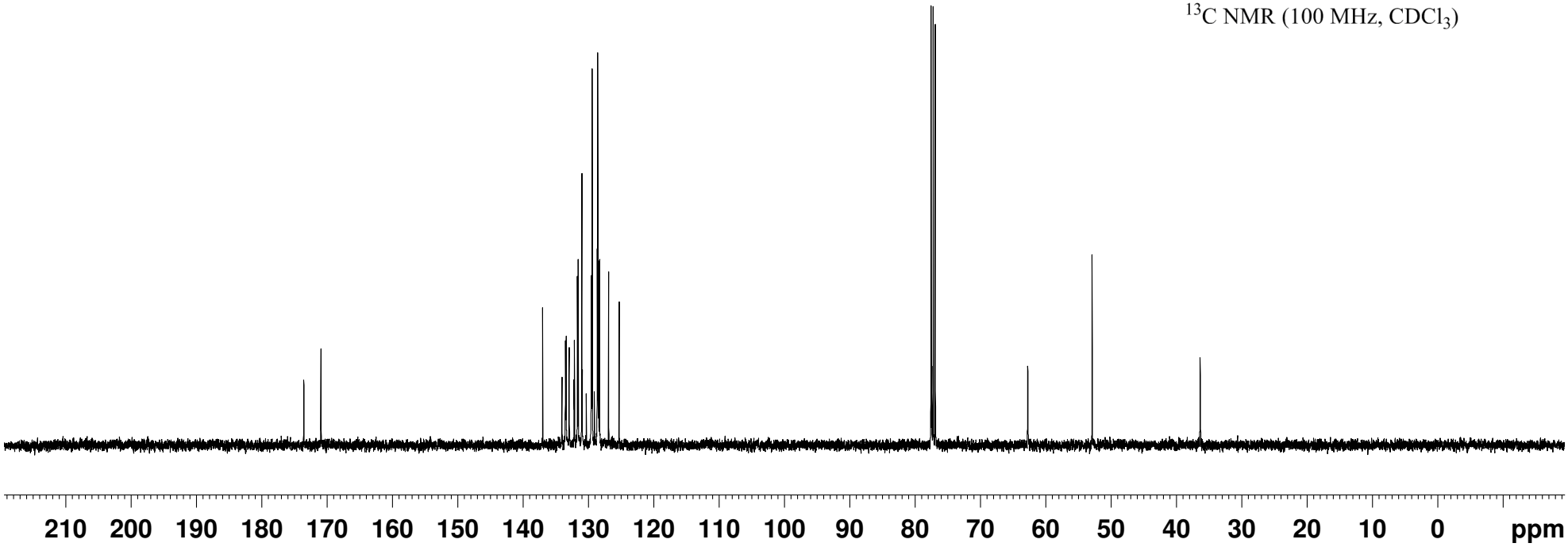
^{1}H NMR (400 MHz, $CDCl_3$)

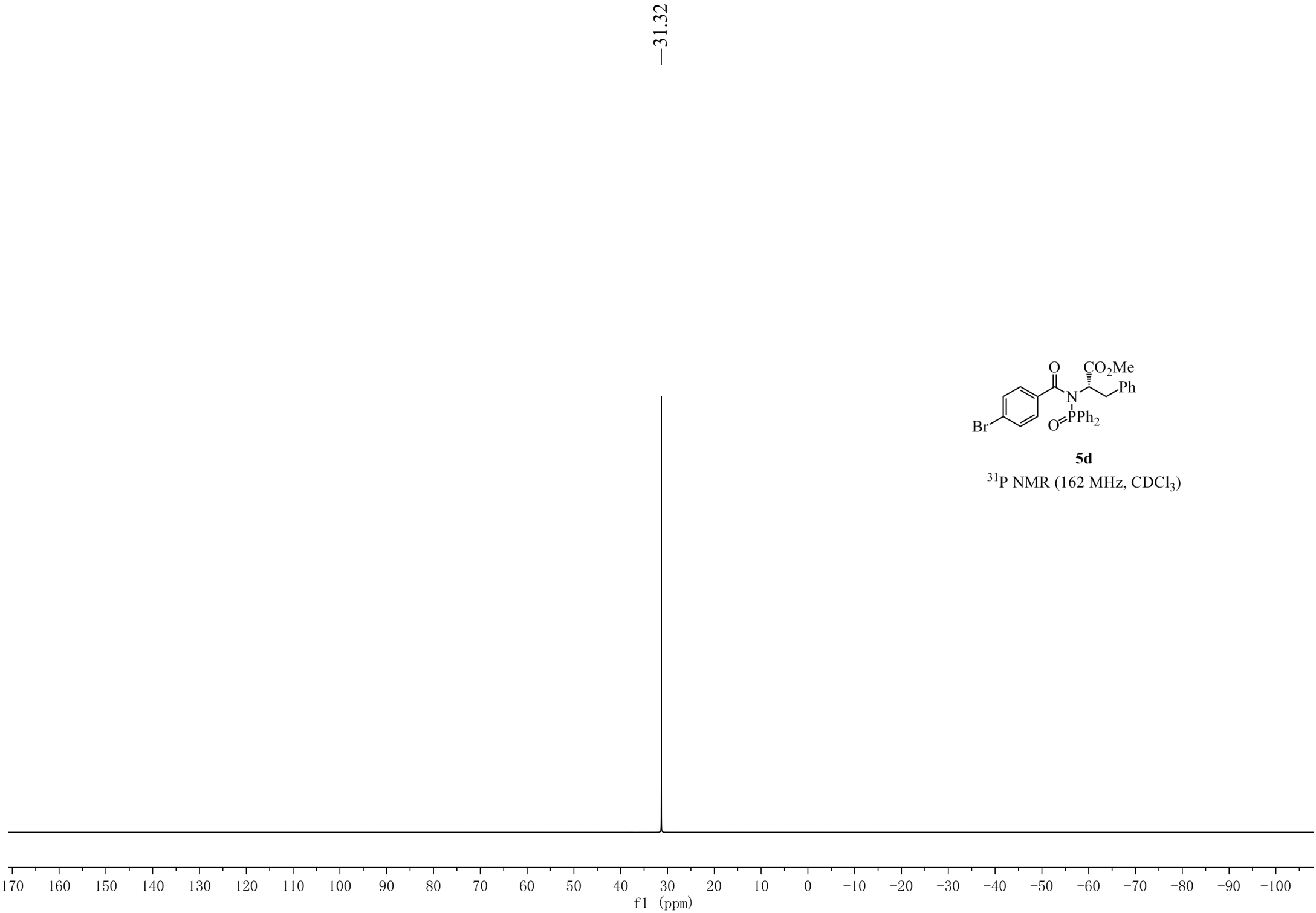




5d

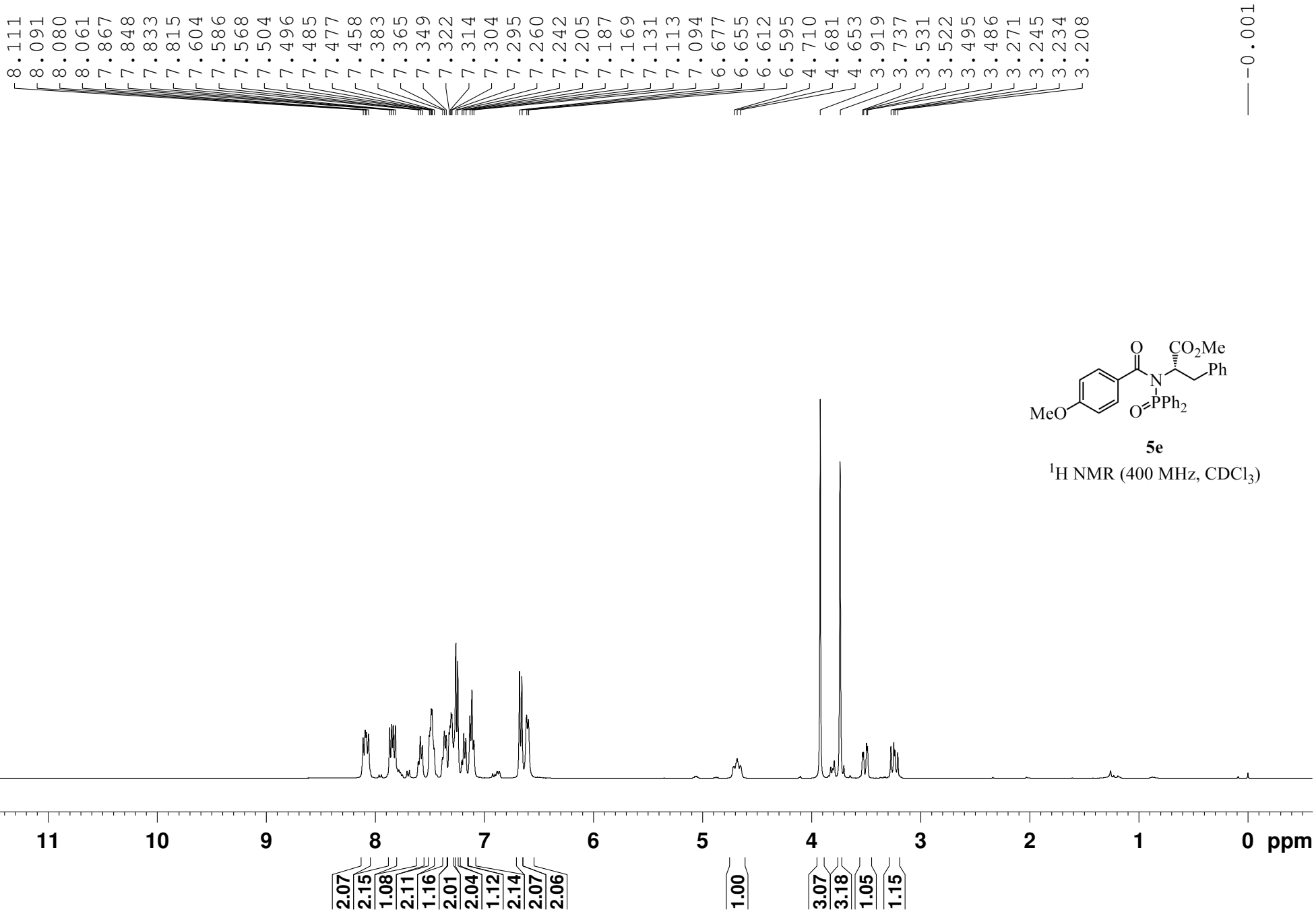
^{13}C NMR (100 MHz, $CDCl_3$)





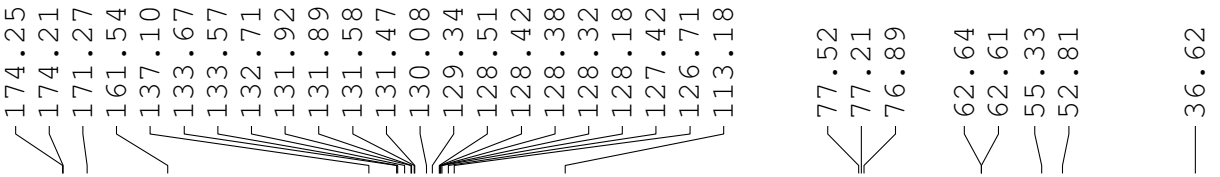
5d

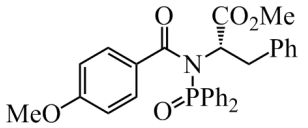
^{31}P NMR (162 MHz, $CDCl_3$)



5e

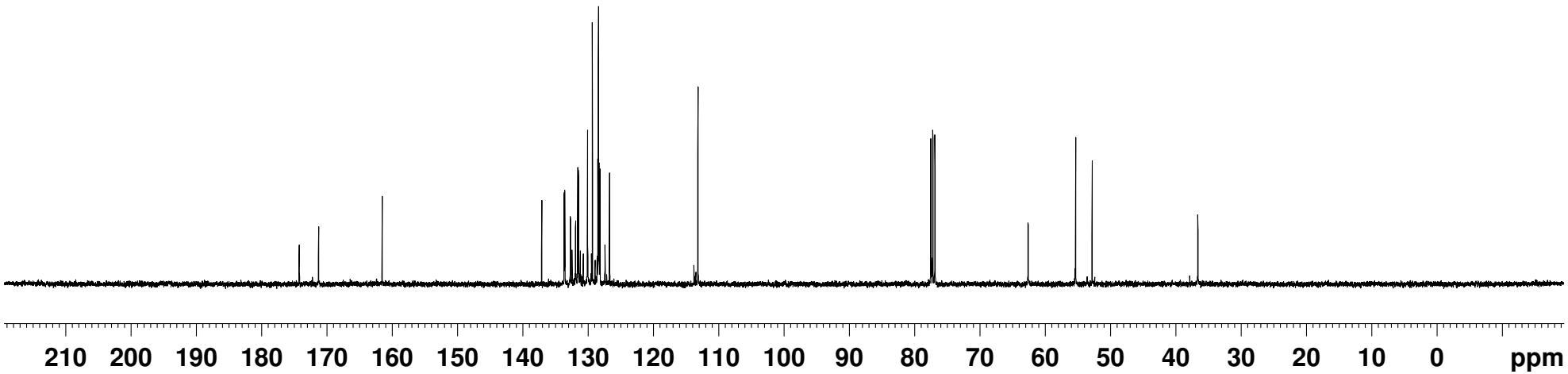
^{1}H NMR (400 MHz, $CDCl_3$)

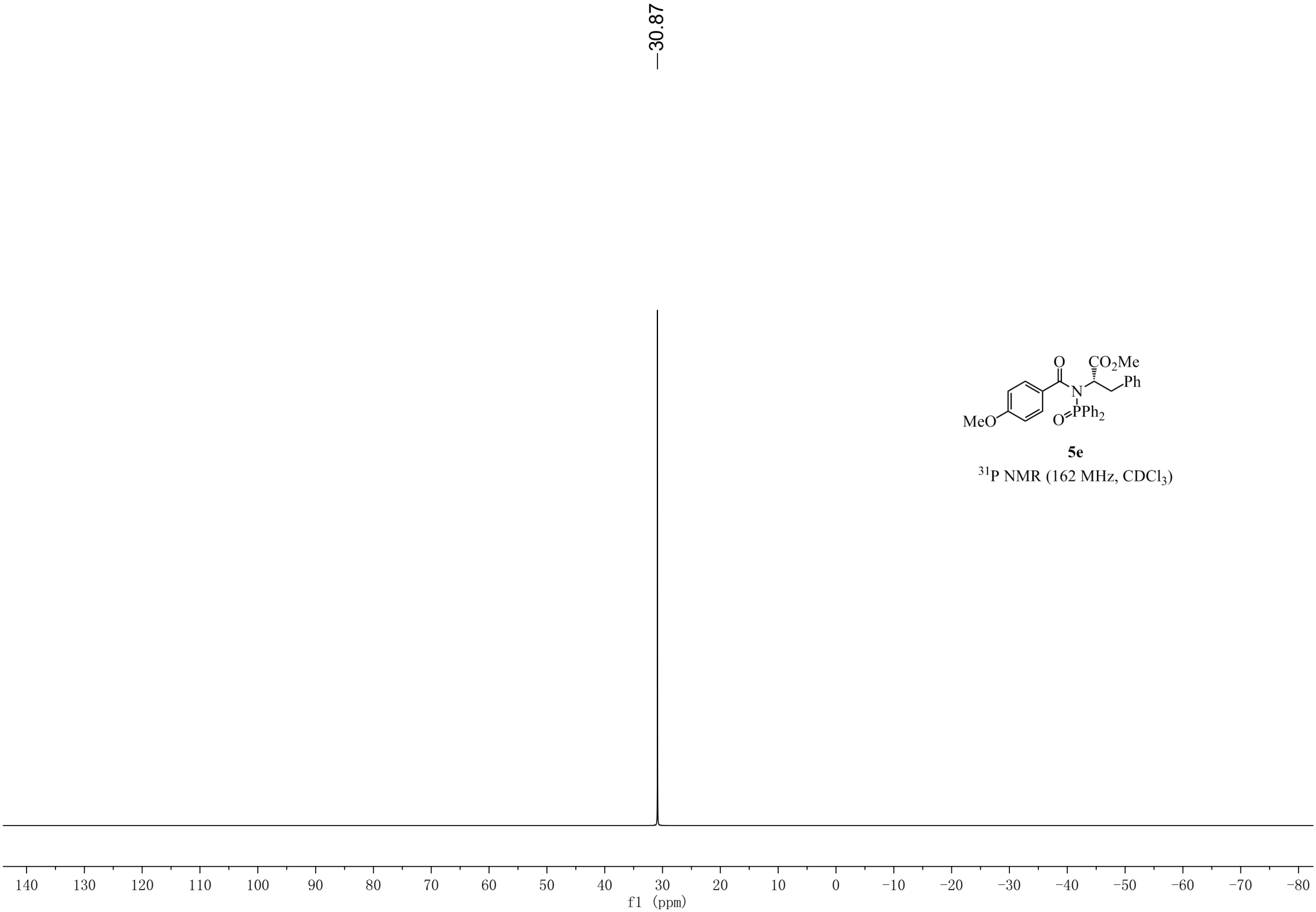




5e

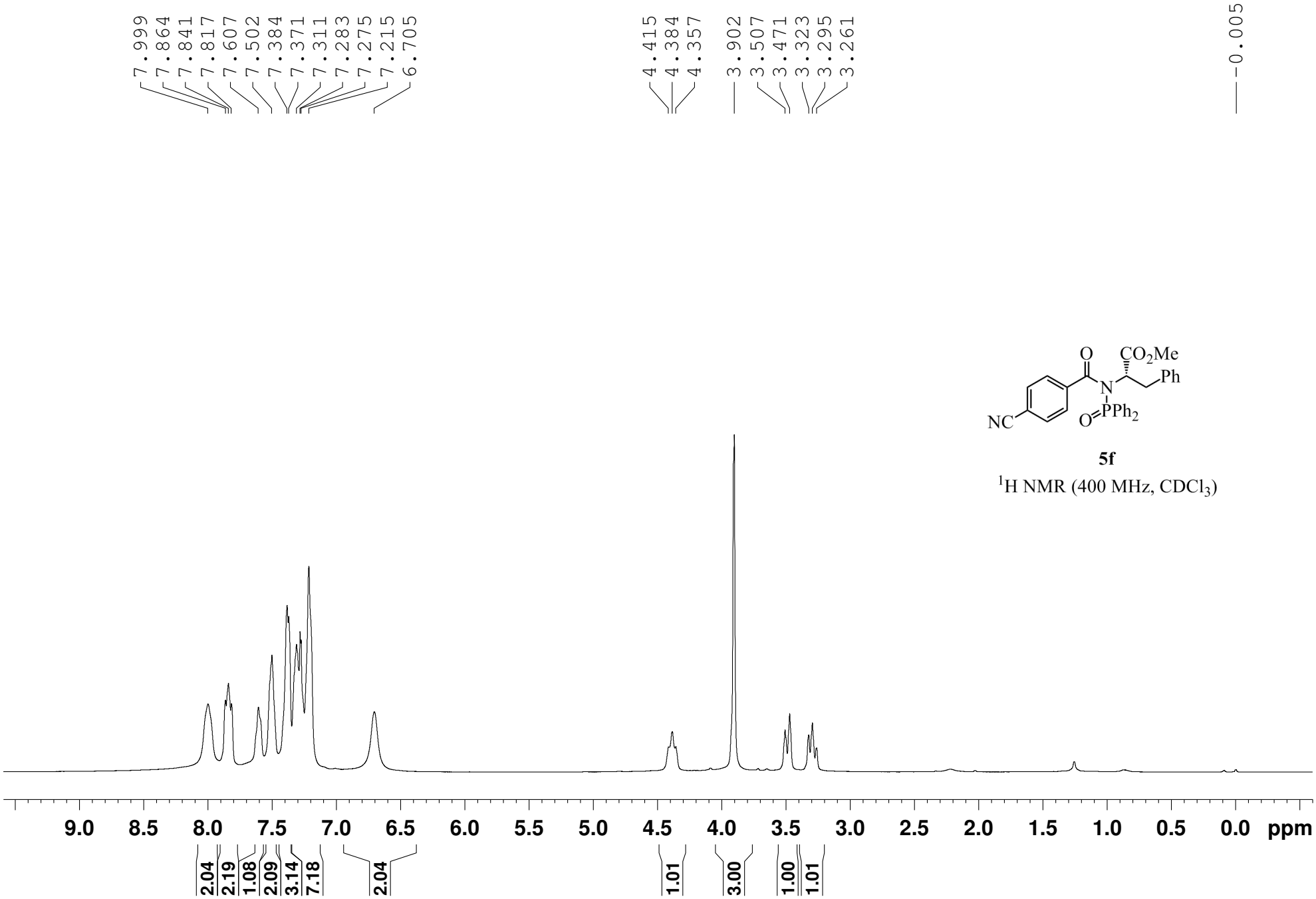
^{13}C NMR (100 MHz, $CDCl_3$)





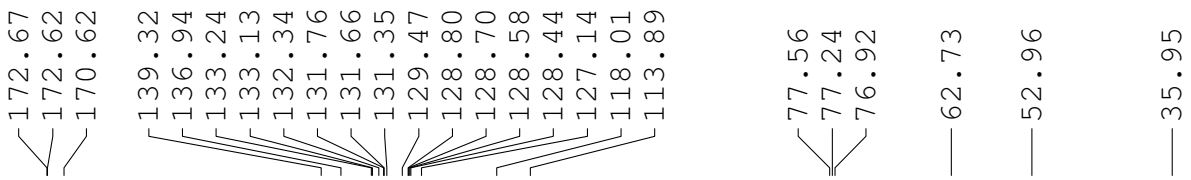
5e

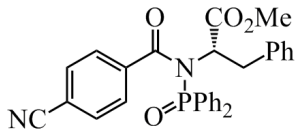
^{31}P NMR (162 MHz, $CDCl_3$)



5f

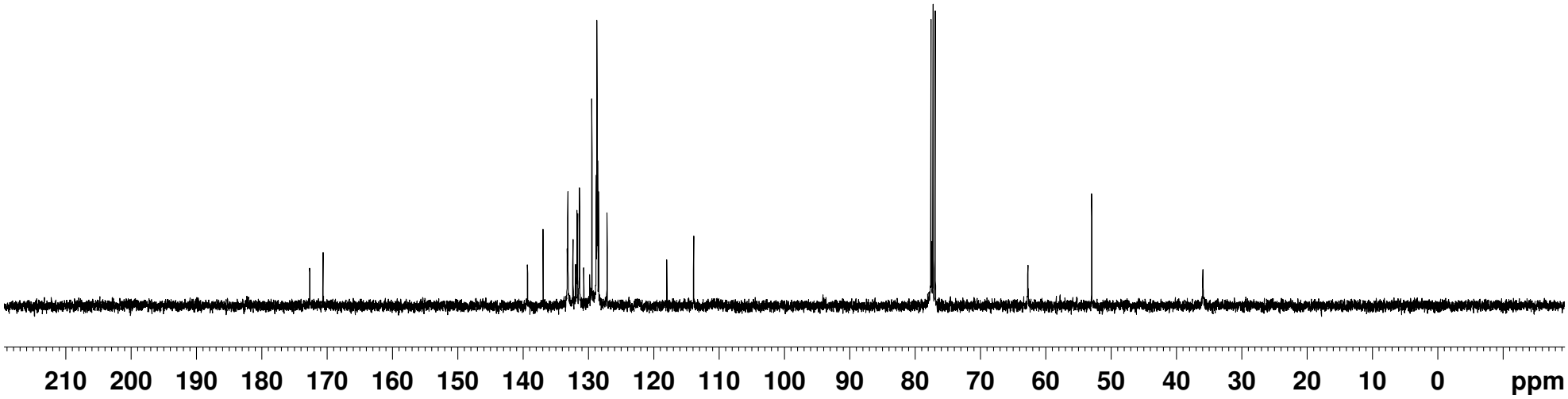
^{1}H NMR (400 MHz, $CDCl_3$)

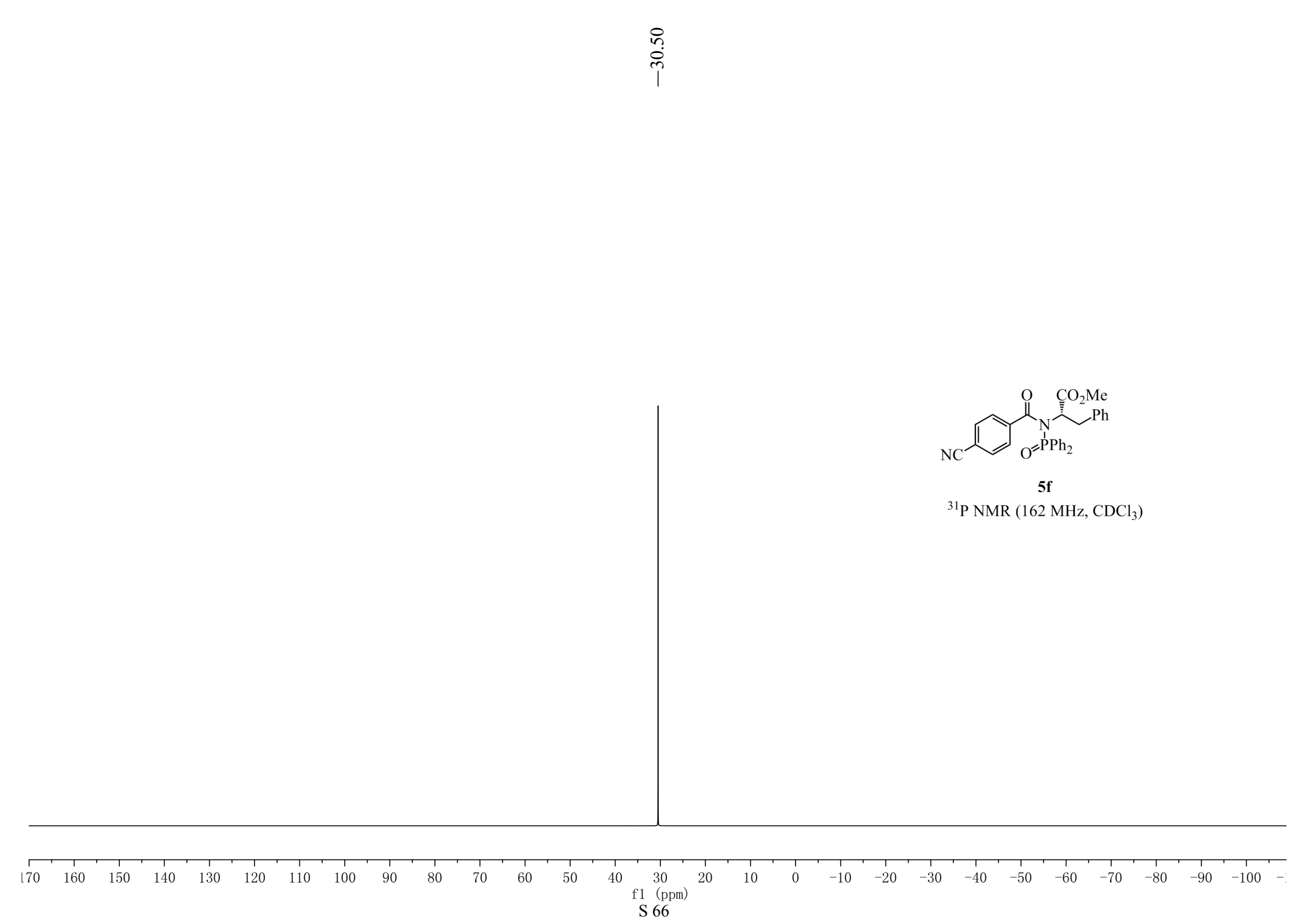




5f

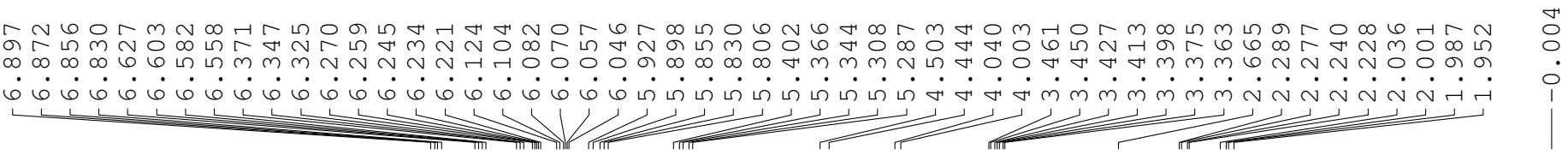
^{13}C NMR (100 MHz, $CDCl_3$)

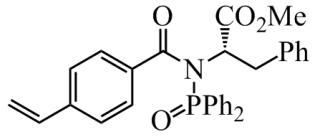




5f

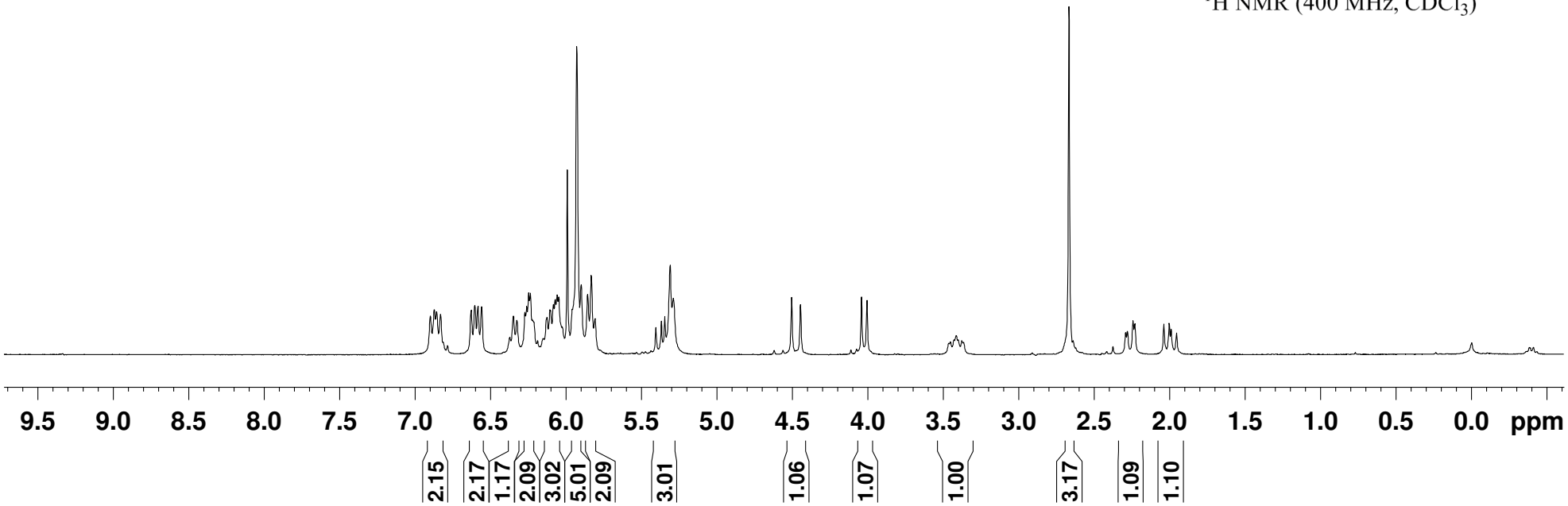
^{31}P NMR (162 MHz, $CDCl_3$)

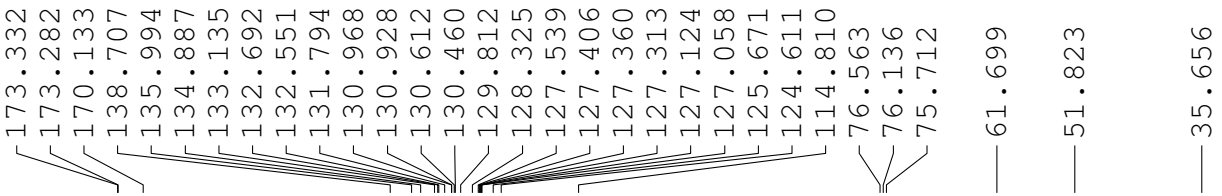


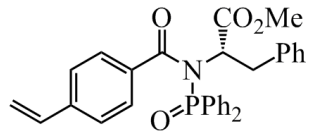


5g

^{1}H NMR (400 MHz, $CDCl_3$)

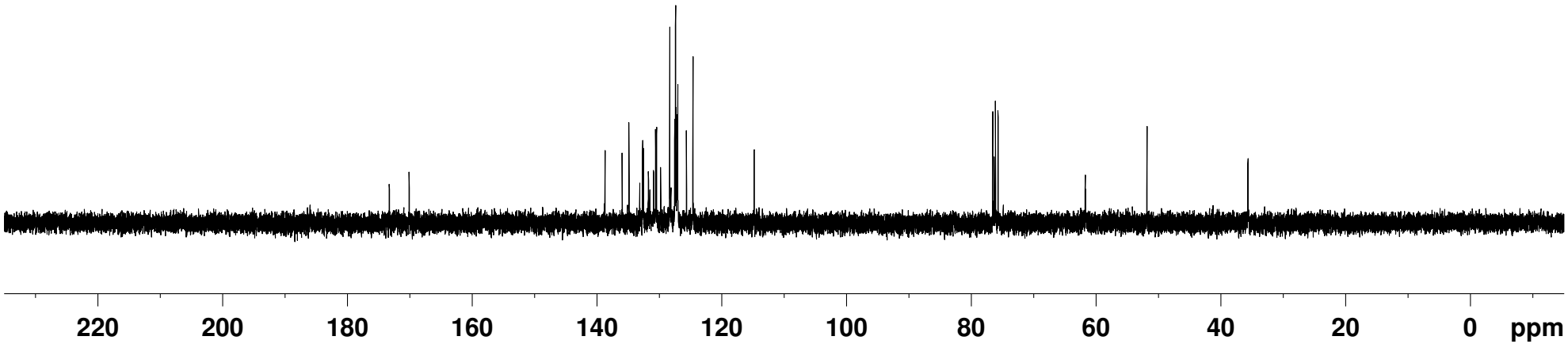


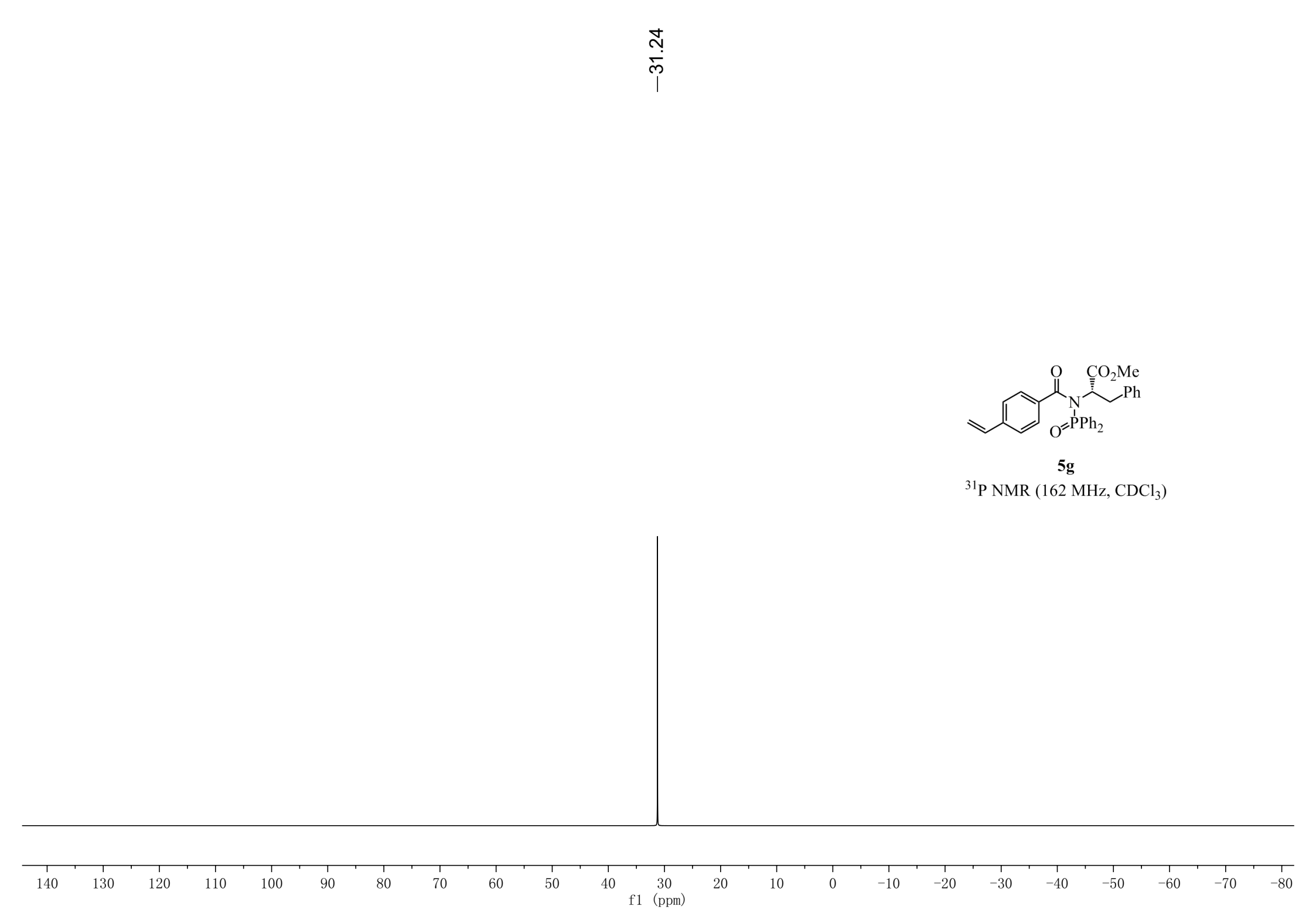




5g

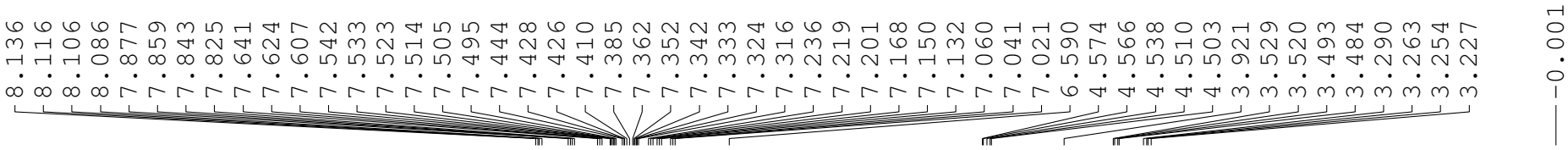
^{13}C NMR (100 MHz, $CDCl_3$)

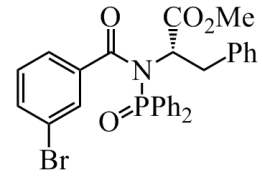




5g

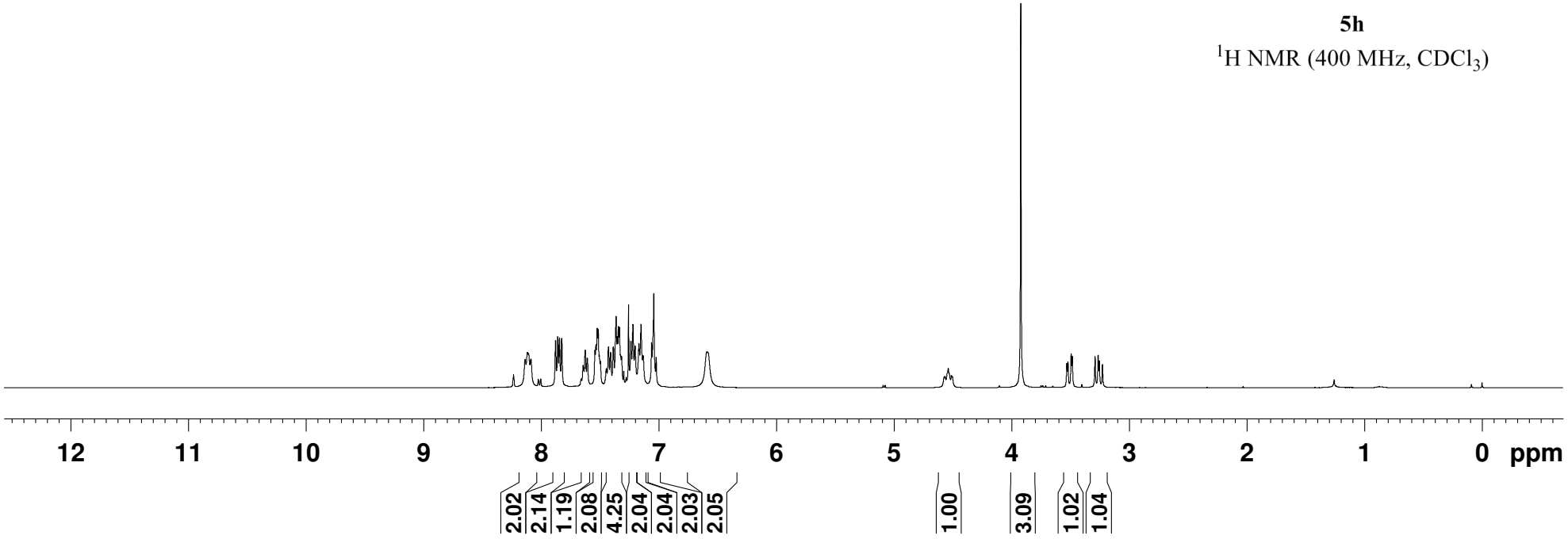
^{31}P NMR (162 MHz, $CDCl_3$)

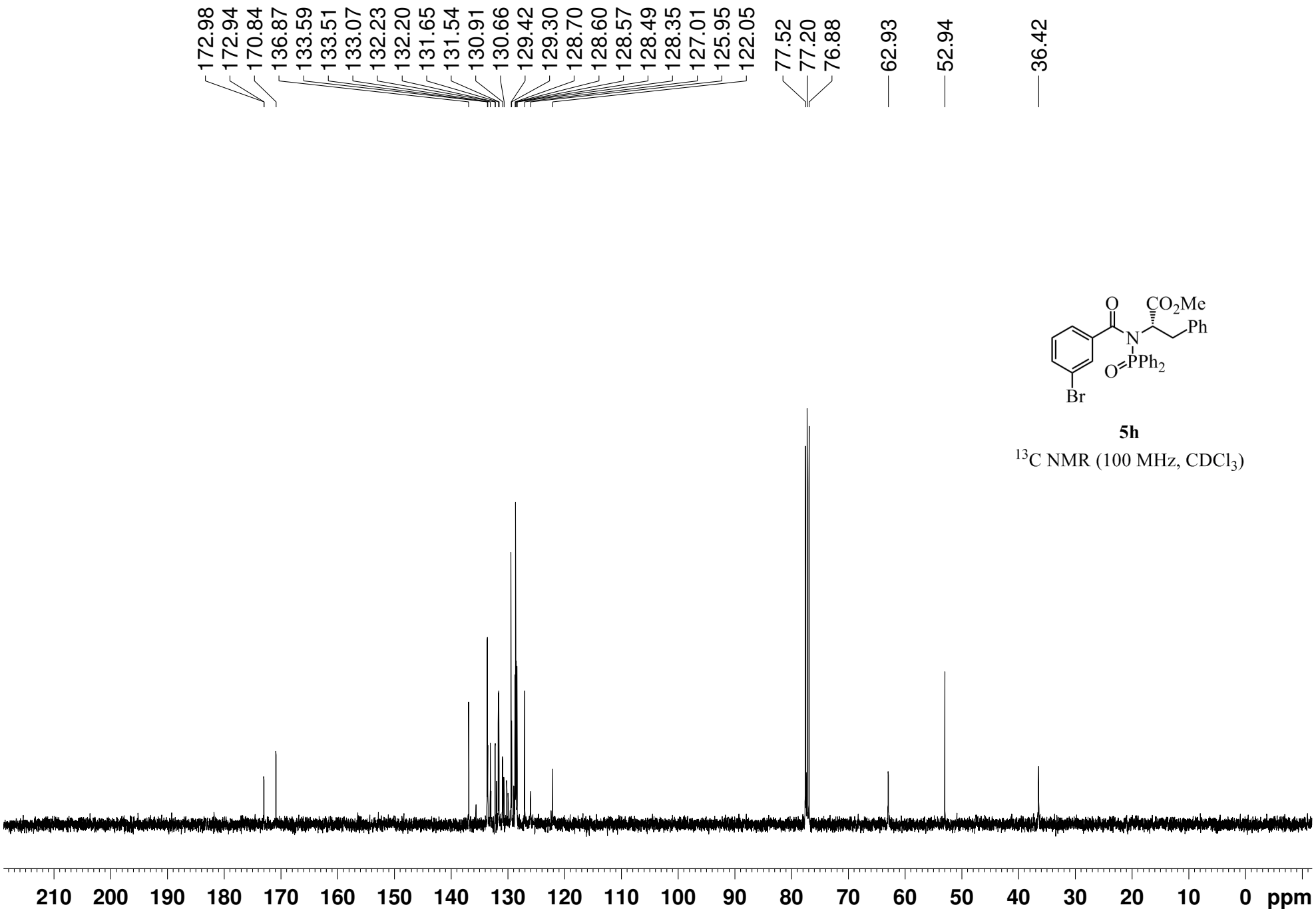




5h

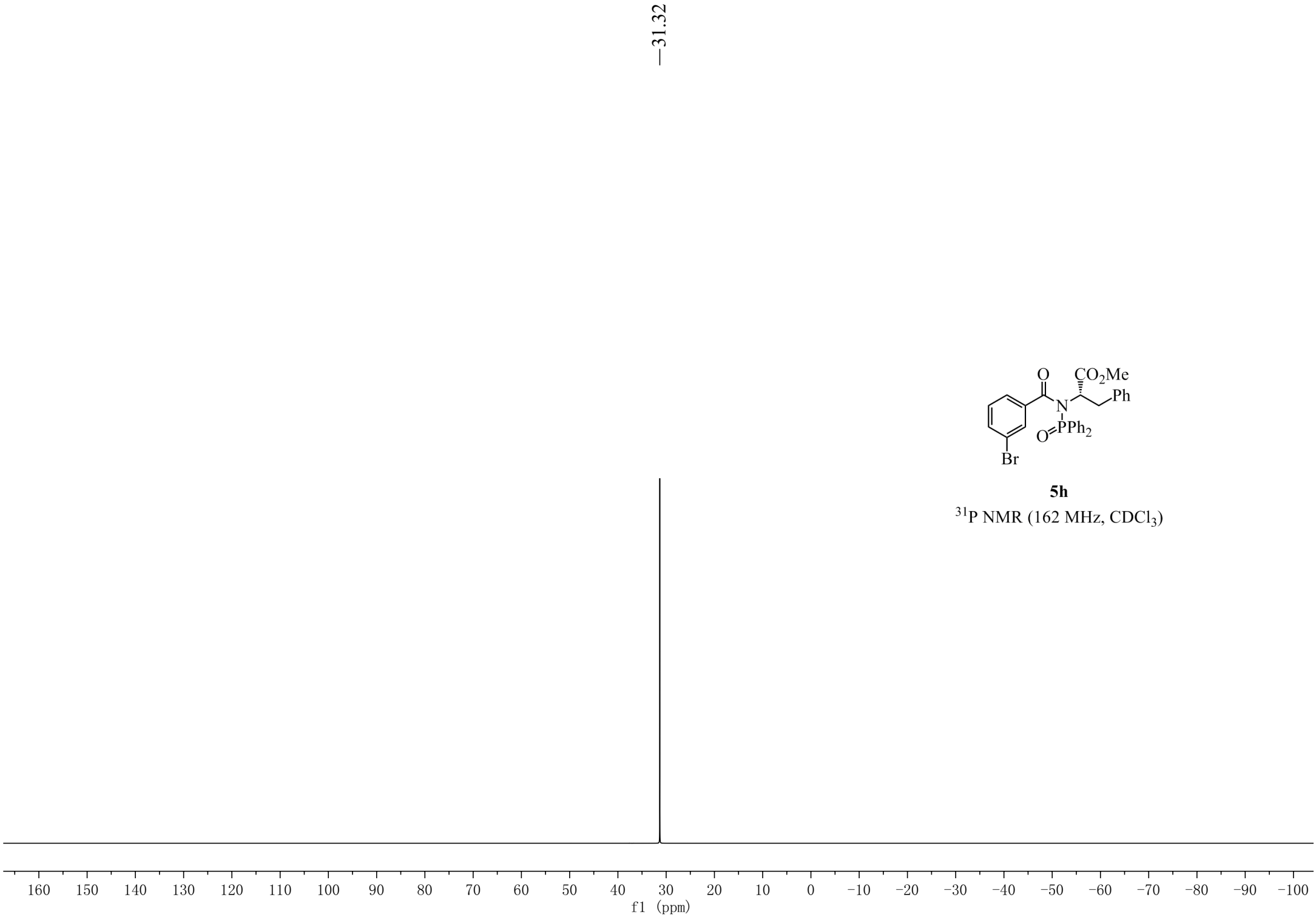
^{1}H NMR (400 MHz, $CDCl_3$)





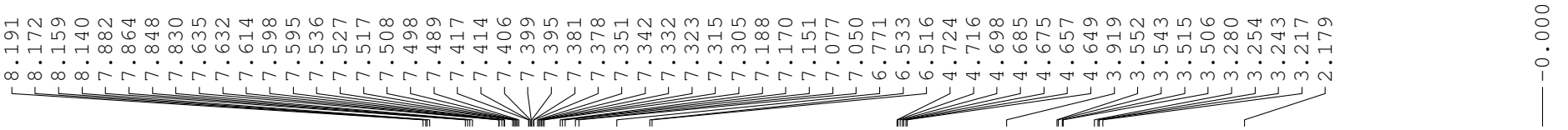
5h

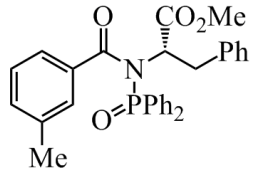
^{13}C NMR (100 MHz, $CDCl_3$)



5h

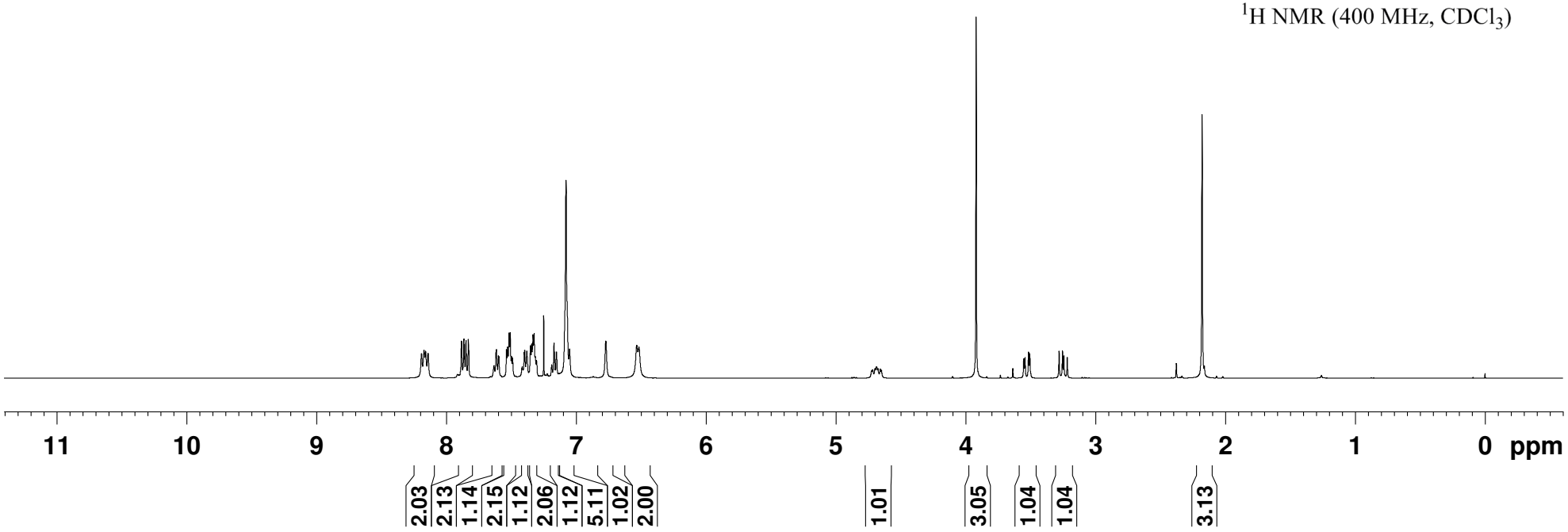
^{31}P NMR (162 MHz, $CDCl_3$)

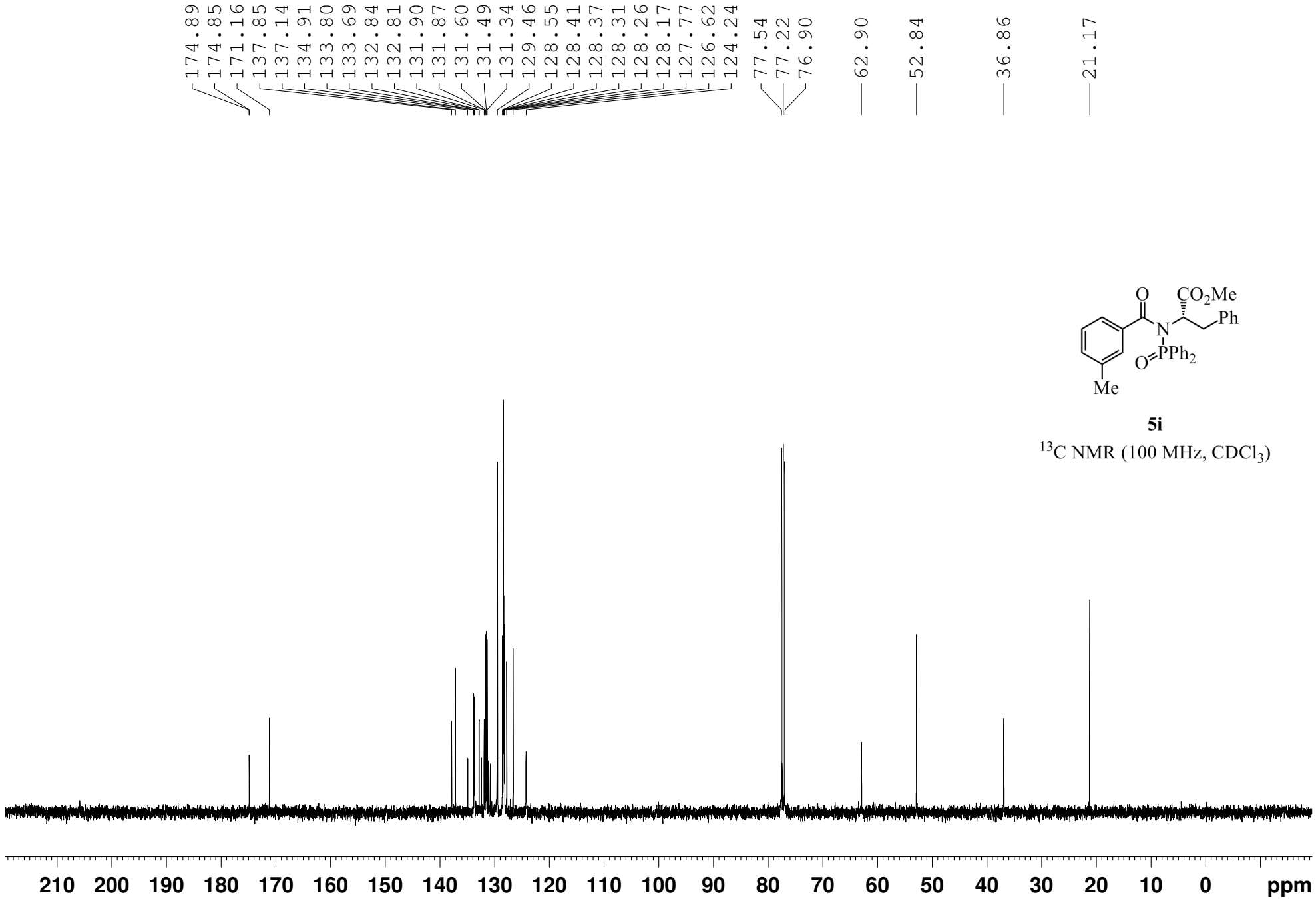


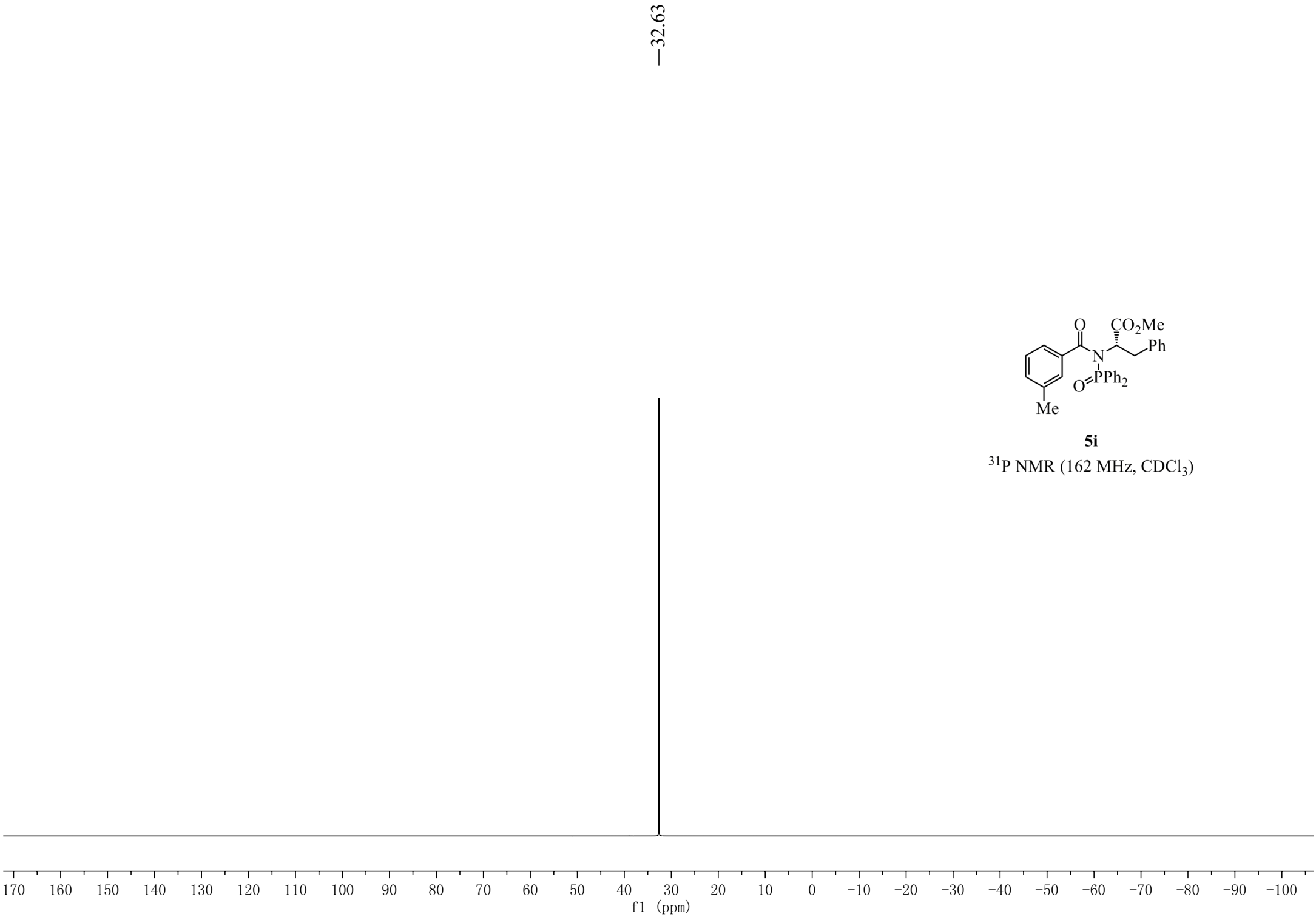


5i

^{1}H NMR (400 MHz, $CDCl_3$)

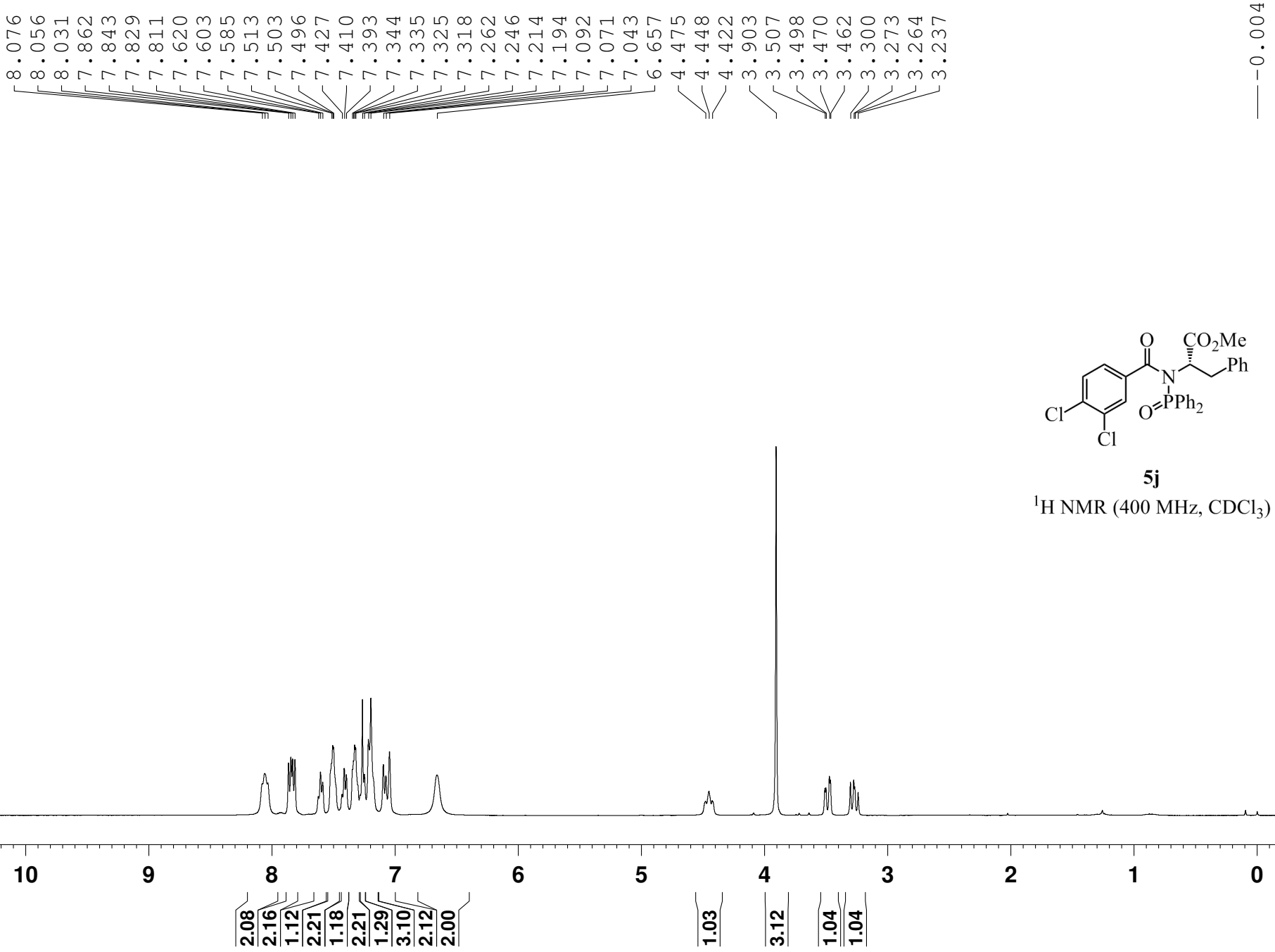



174.89
174.85
171.16
137.85
137.14
134.91
133.80
133.69
132.84
132.81
131.90
131.87
131.60
131.49
131.34
129.46
128.55
128.41
128.37
128.31
128.26
128.17
127.77
126.62
124.24
77.54
77.22
76.90
62.90
52.84
36.86
21.17
O
CO2Me
Ph
N
PPh2
O
Me
5i
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



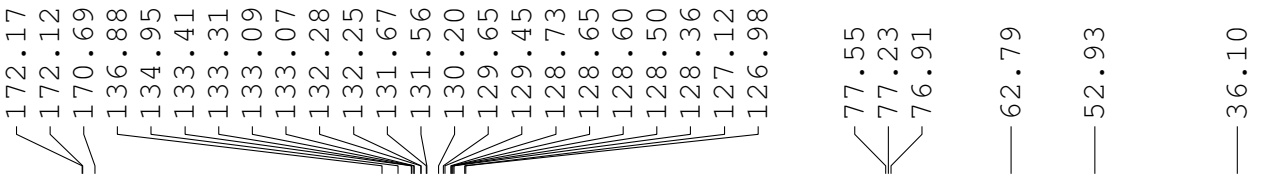
5i

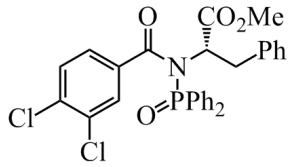
^{31}P NMR (162 MHz, $CDCl_3$)



5j

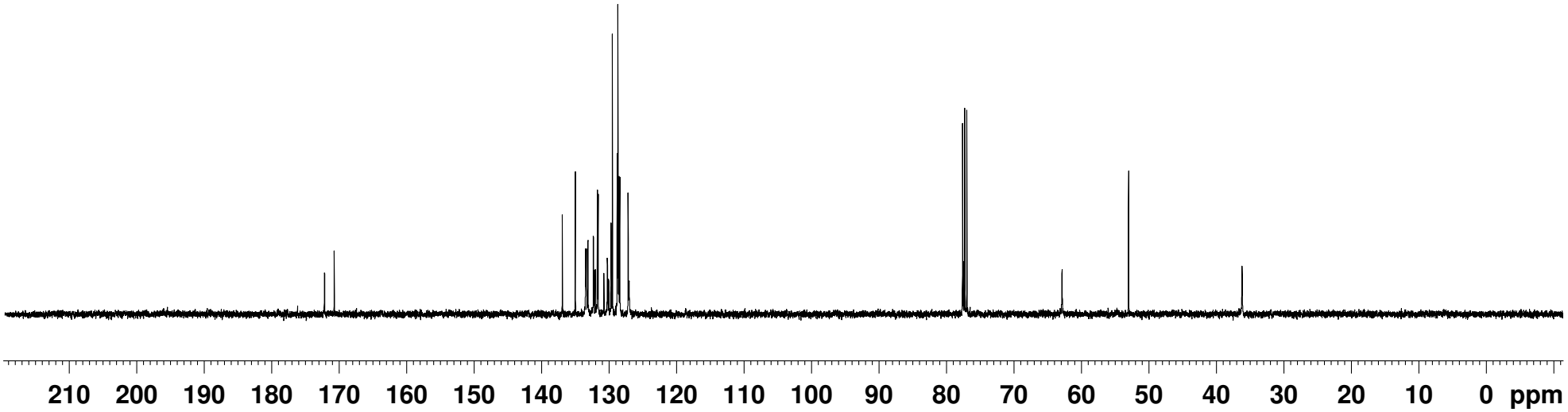
^{1}H NMR (400 MHz, $CDCl_3$)

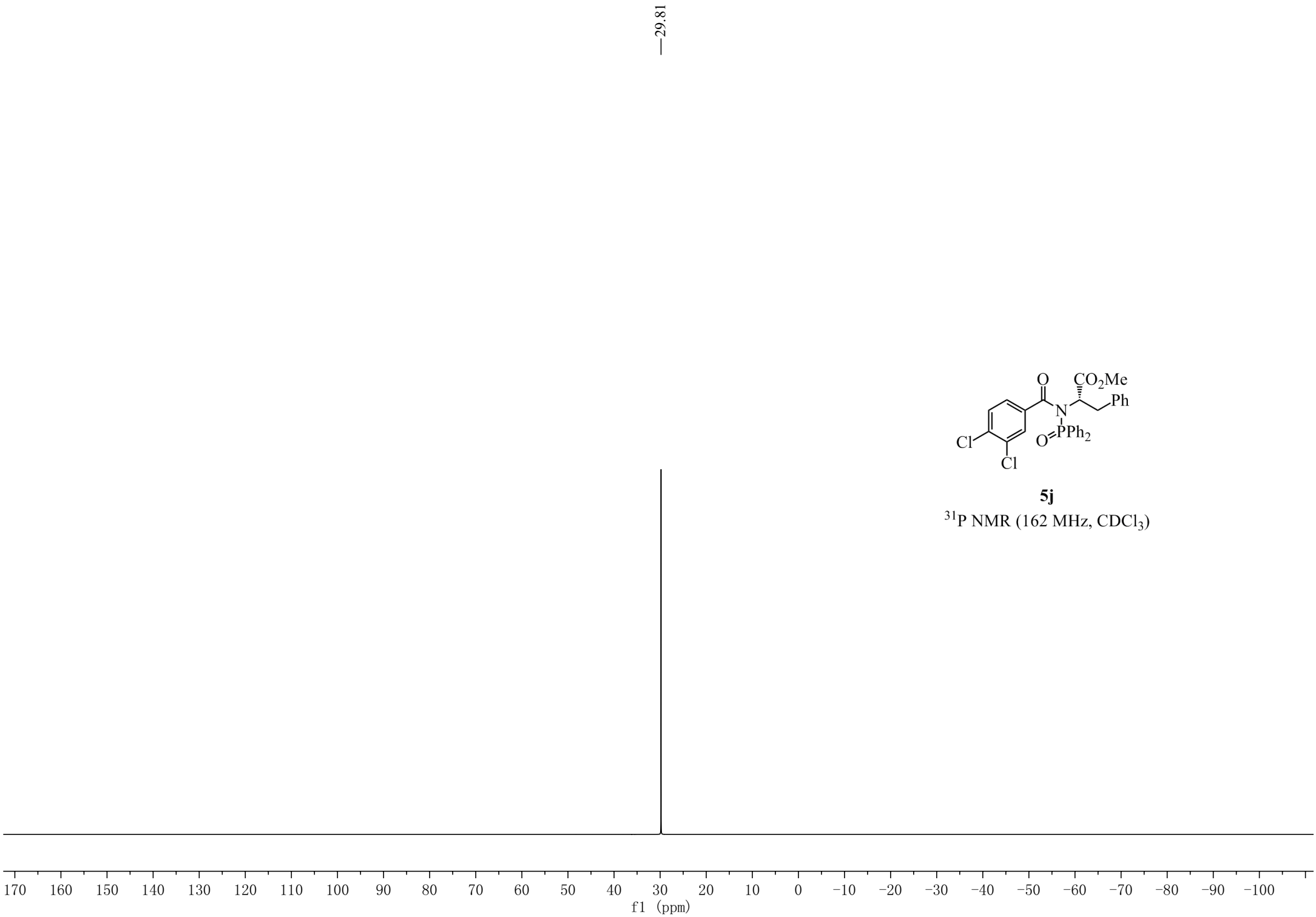




5j

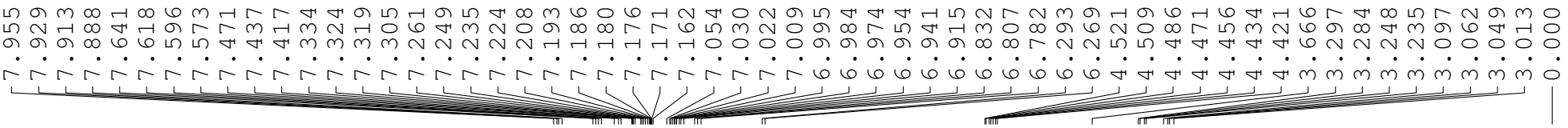
^{13}C NMR (100 MHz, $CDCl_3$)

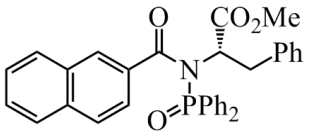




5j

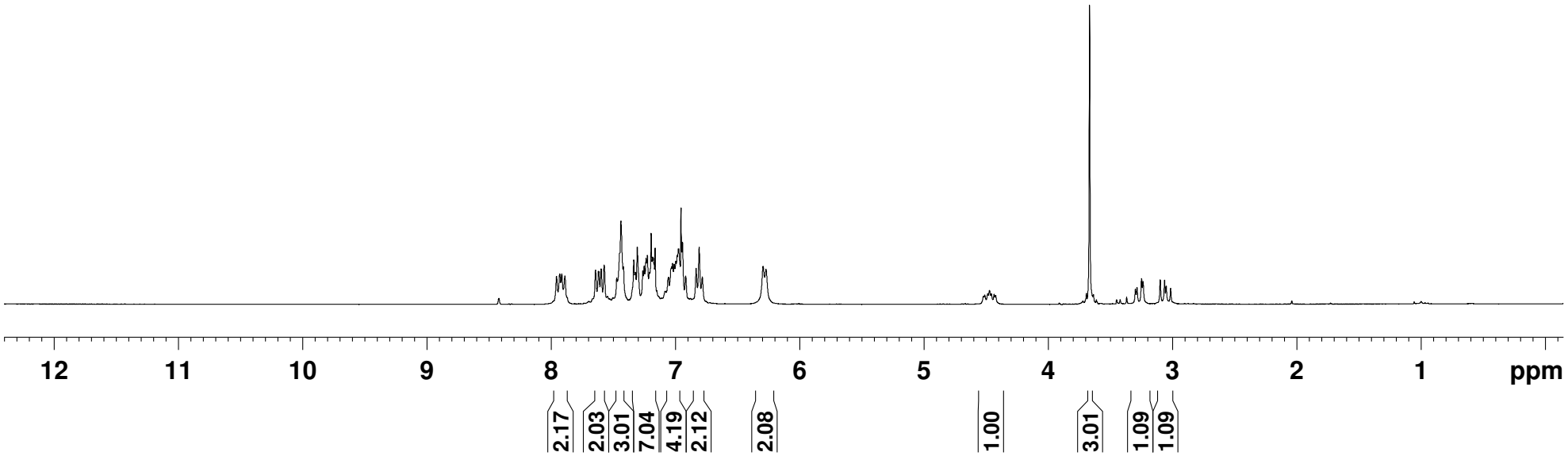
^{31}P NMR (162 MHz, $CDCl_3$)

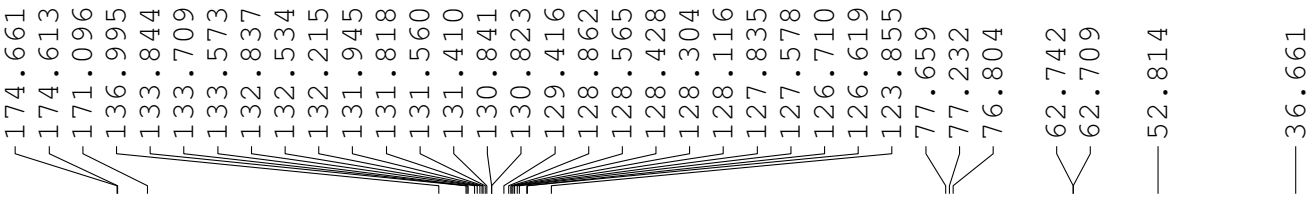


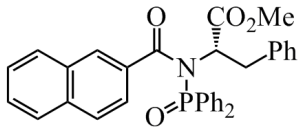


5k

^{1}H NMR (400 MHz, $CDCl_3$)

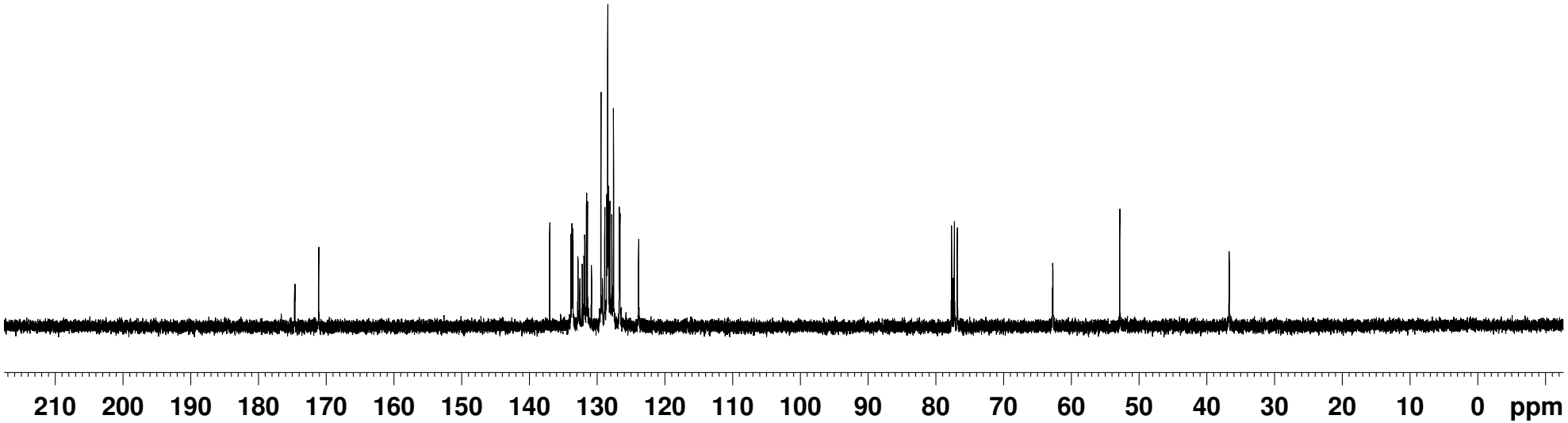


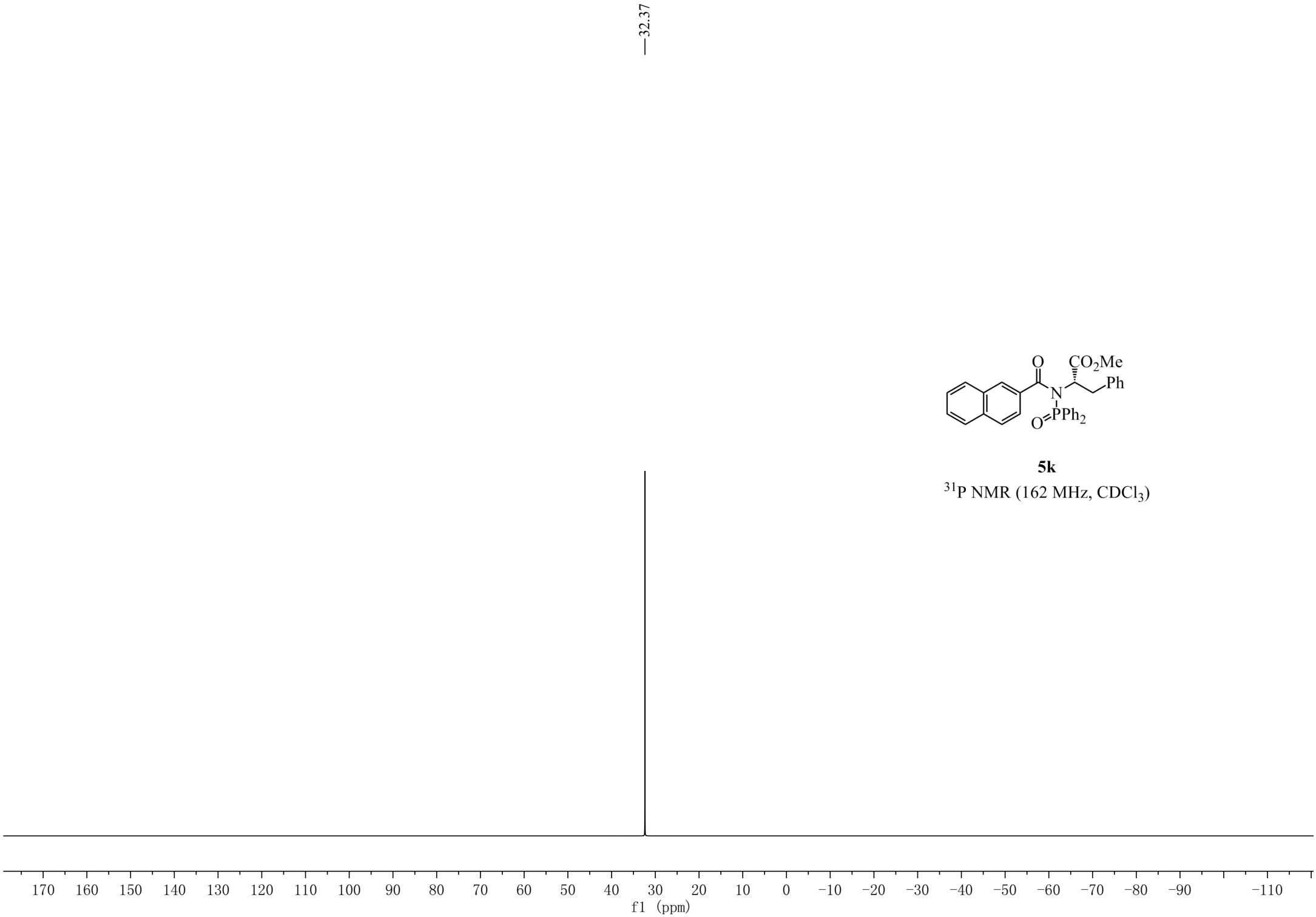




5k

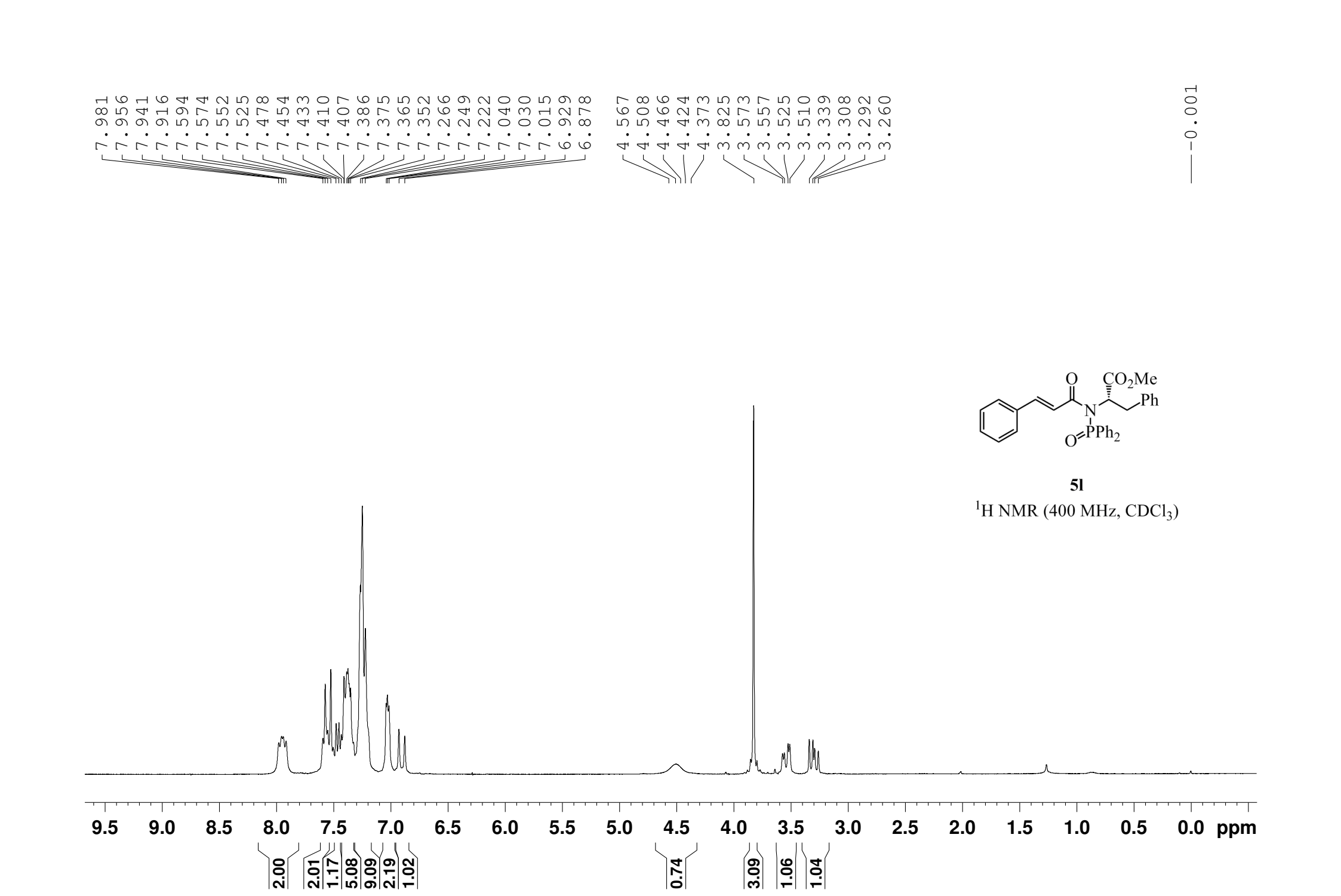
^{13}C NMR (100 MHz, $CDCl_3$)





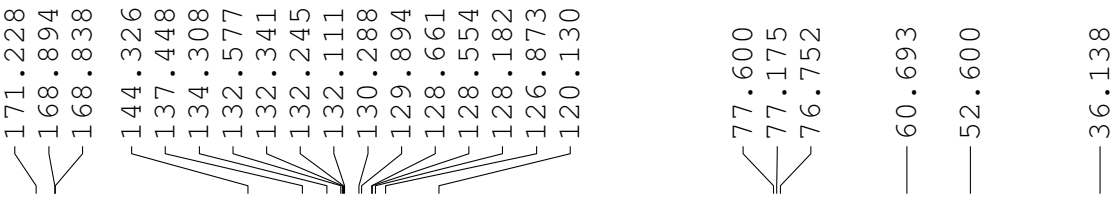
5k

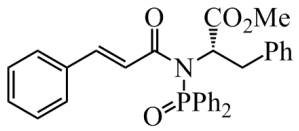
^{31}P NMR (162 MHz, $CDCl_3$)



5l

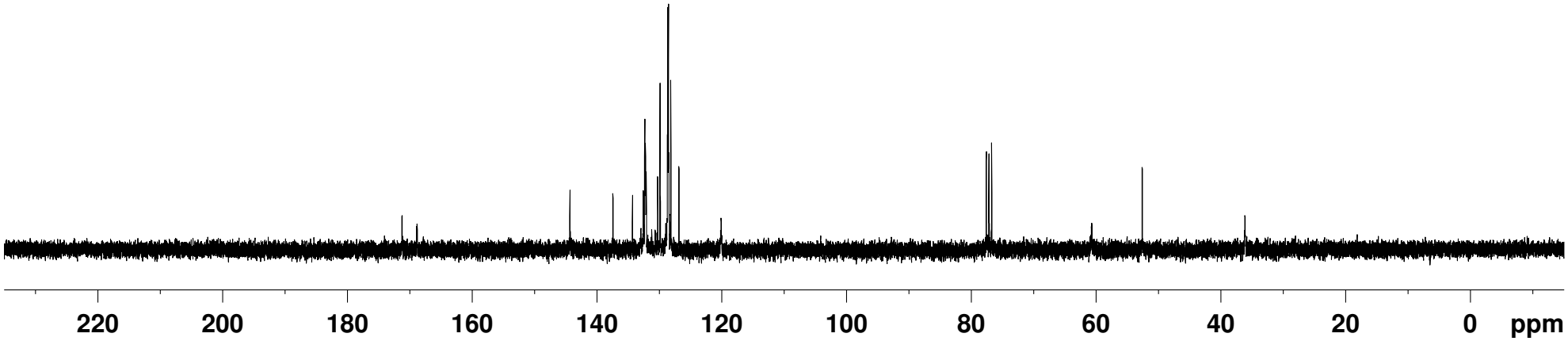
^{1}H NMR (400 MHz, $CDCl_3$)

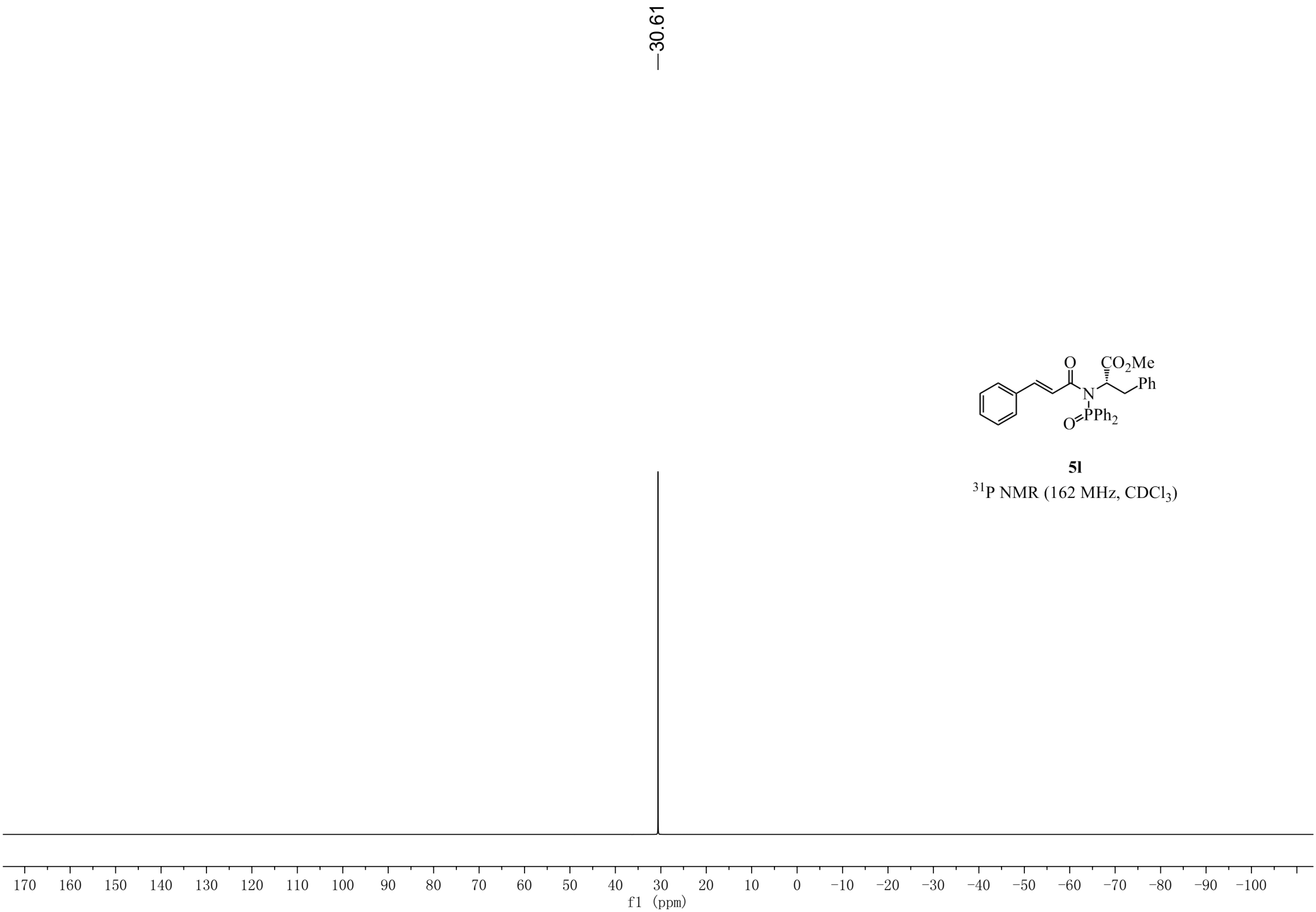




5l

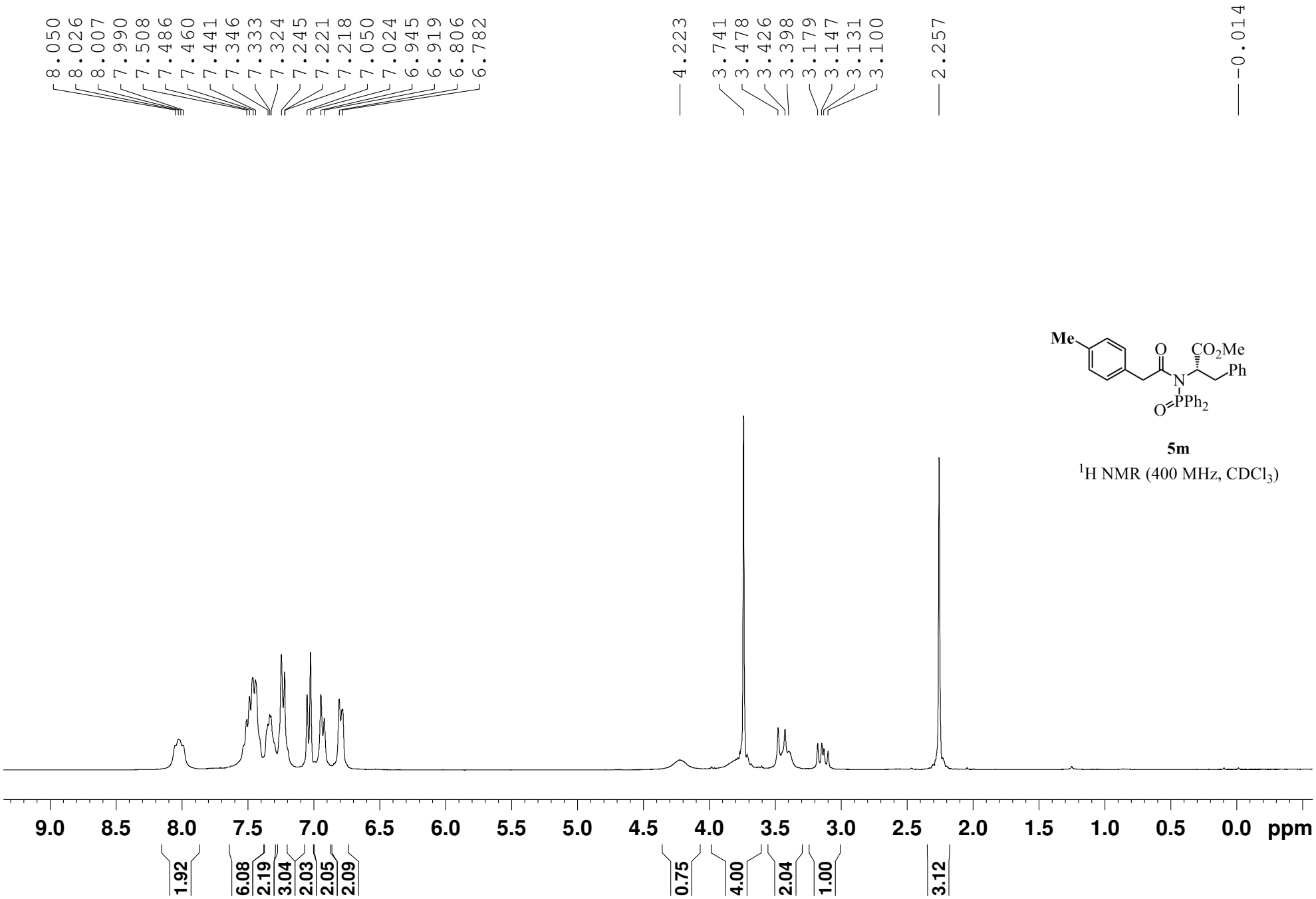
^{13}C NMR (100 MHz, $CDCl_3$)

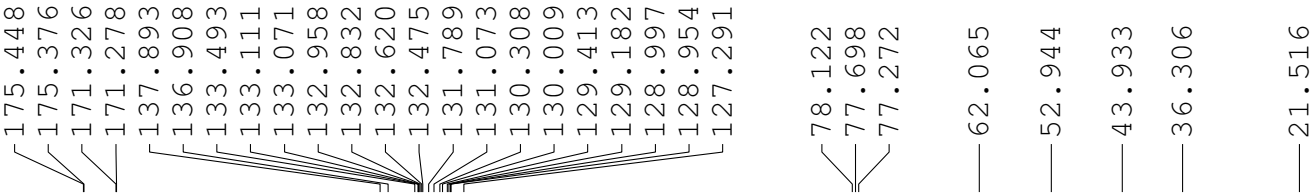


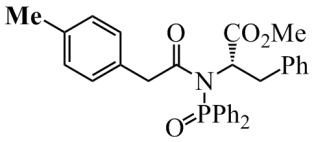


5l

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

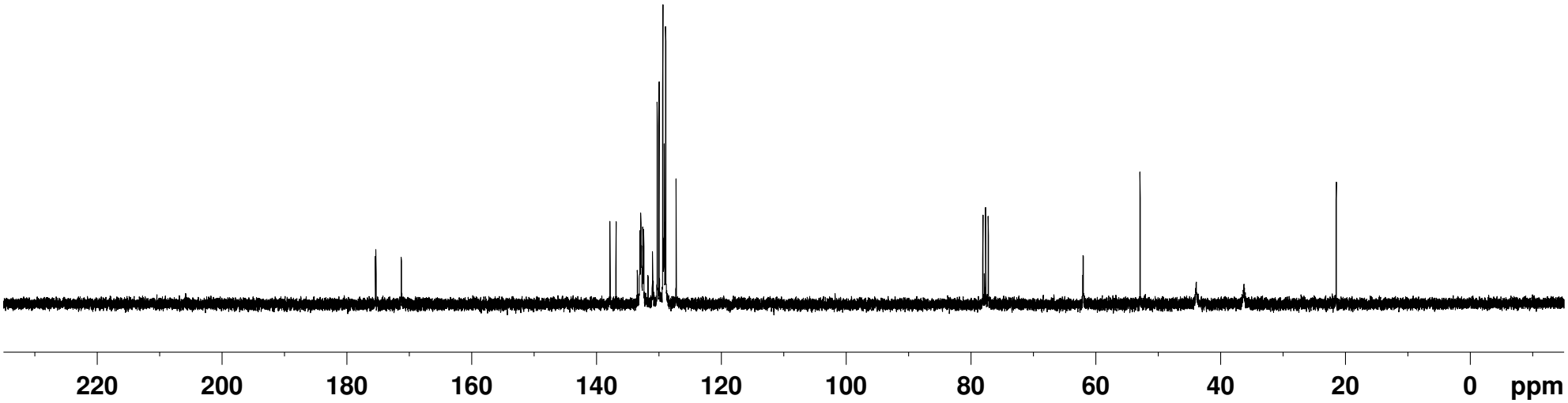

8.050
8.026
8.007
7.990
7.508
7.486
7.460
7.441
7.346
7.333
7.324
7.245
7.221
7.218
7.050
7.024
6.945
6.919
6.806
6.782
4.223
3.741
3.478
3.426
3.398
3.179
3.147
3.131
3.100
2.257
0.014
Me
O
CO2Me
Ph
N
O
PPh2
5m
1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.92
6.08
2.19
3.04
2.03
2.05
2.09
0.75
4.00
2.04
1.00
3.12

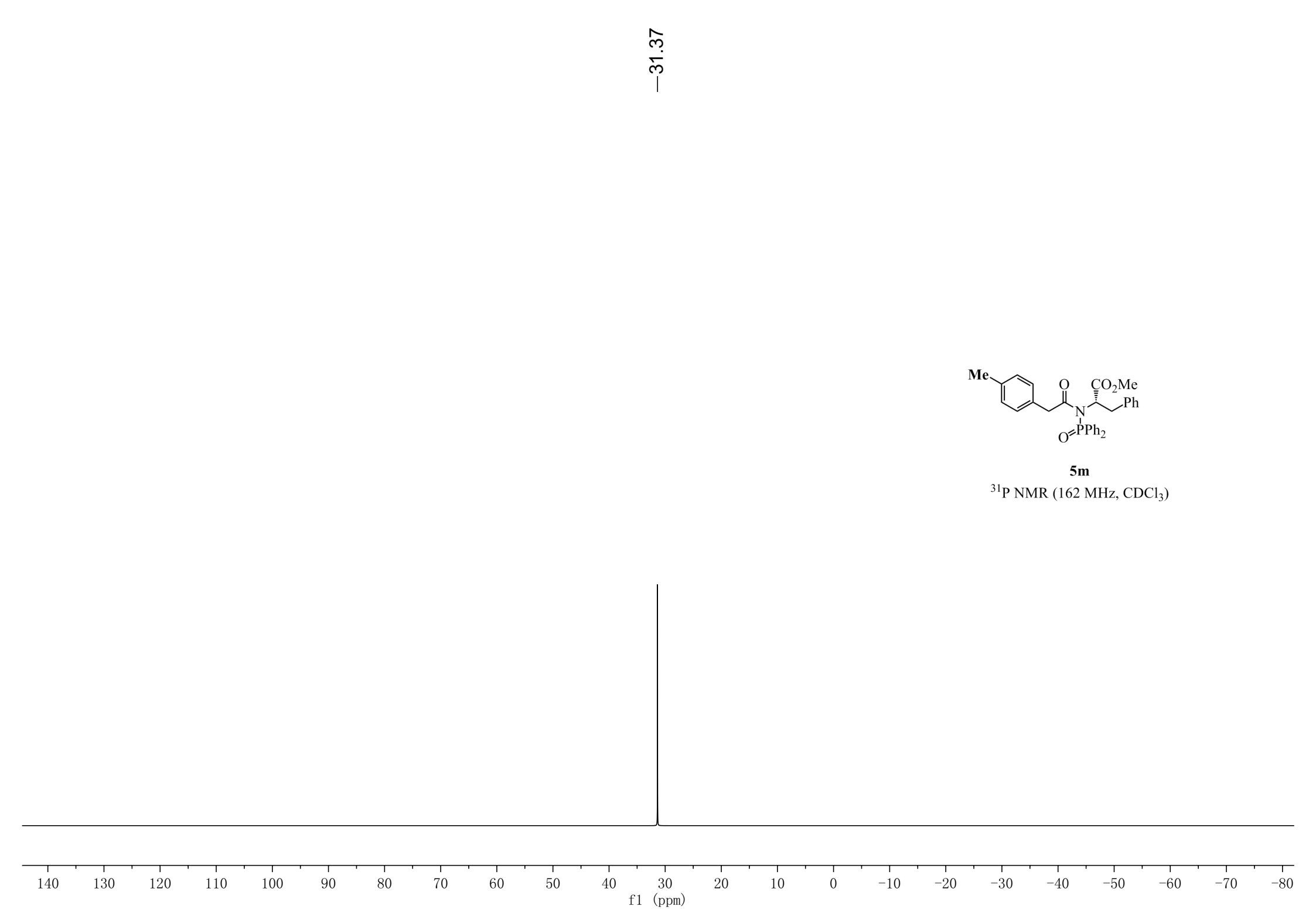




5m

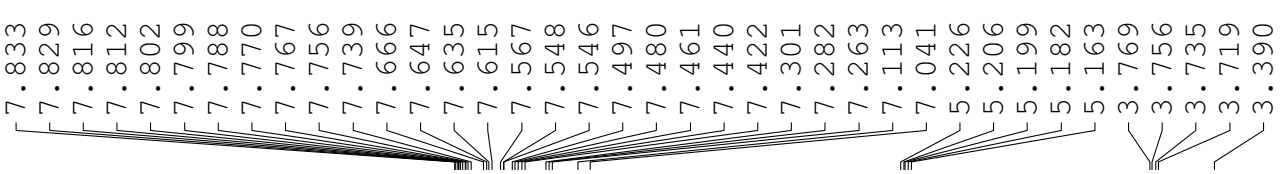
^{13}C NMR (100 MHz, $CDCl_3$)

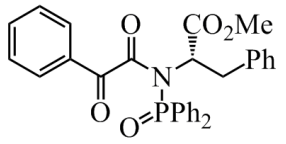




5m

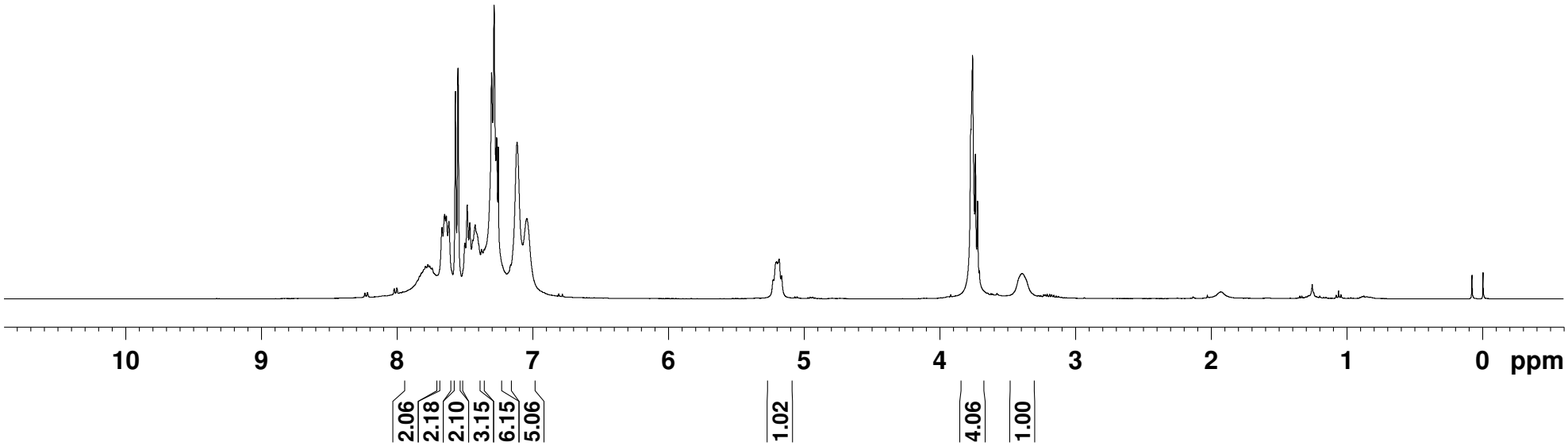
^{31}P NMR (162 MHz, $CDCl_3$)

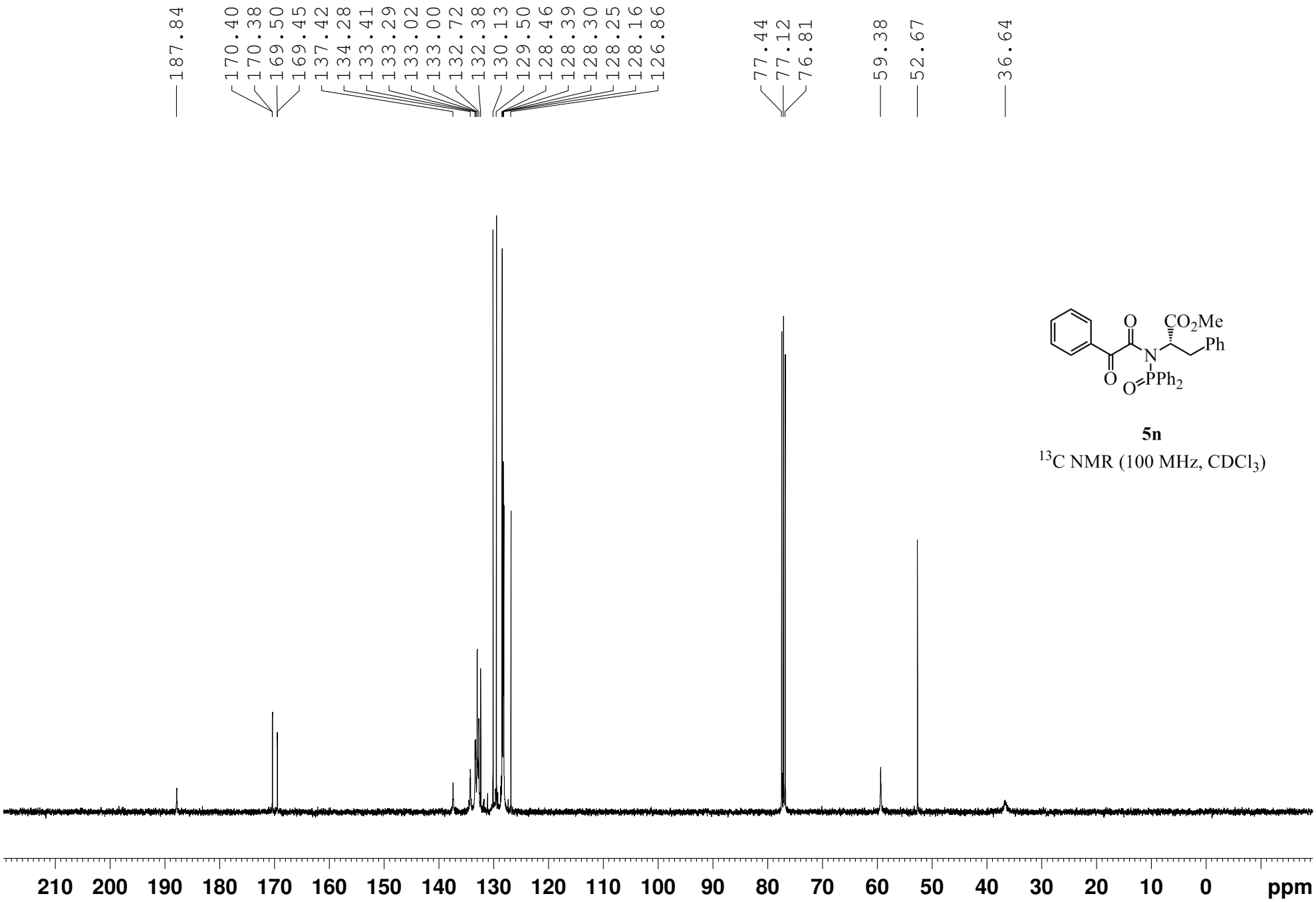




5n

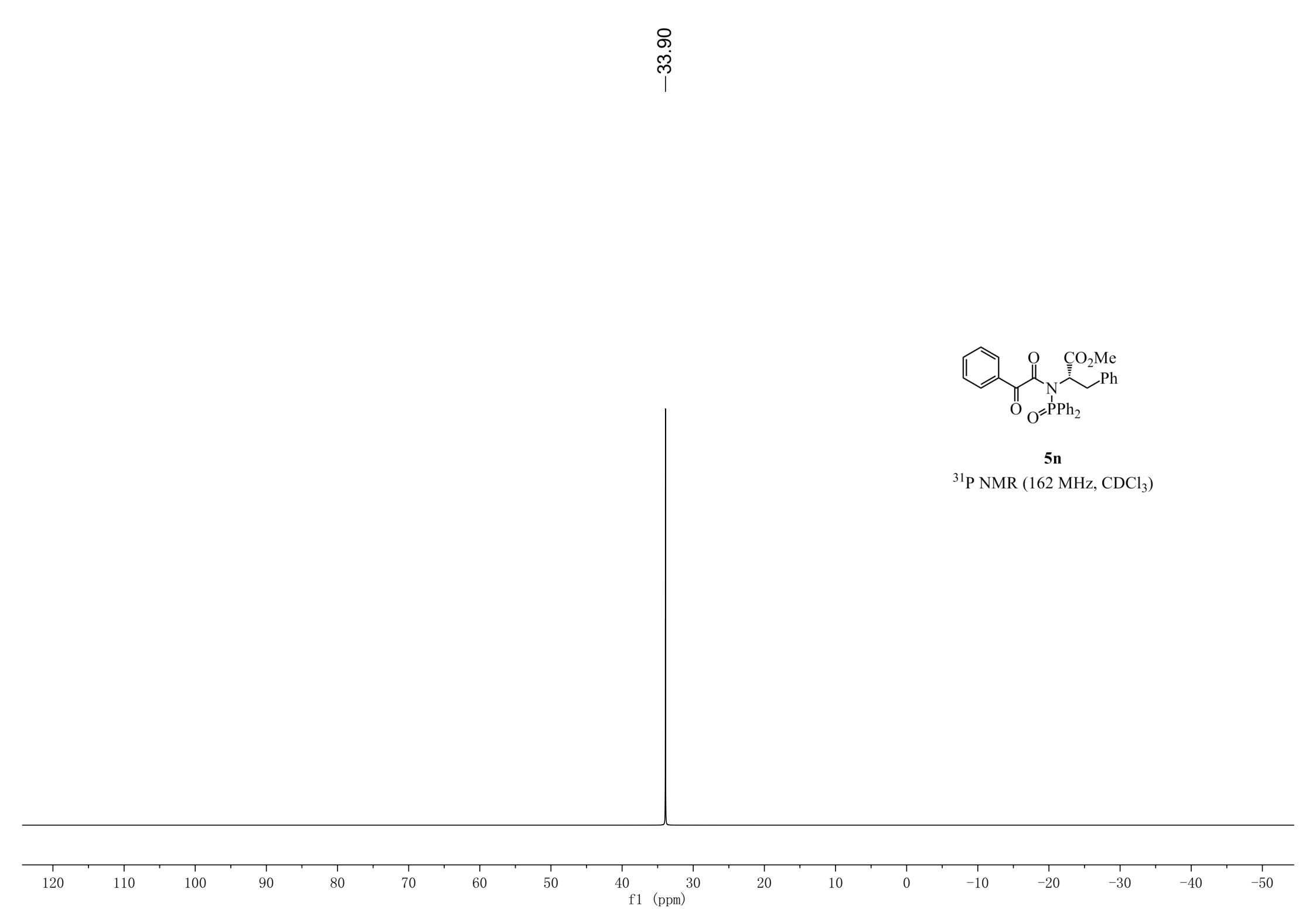
^{1}H NMR (400 MHz, $CDCl_3$)





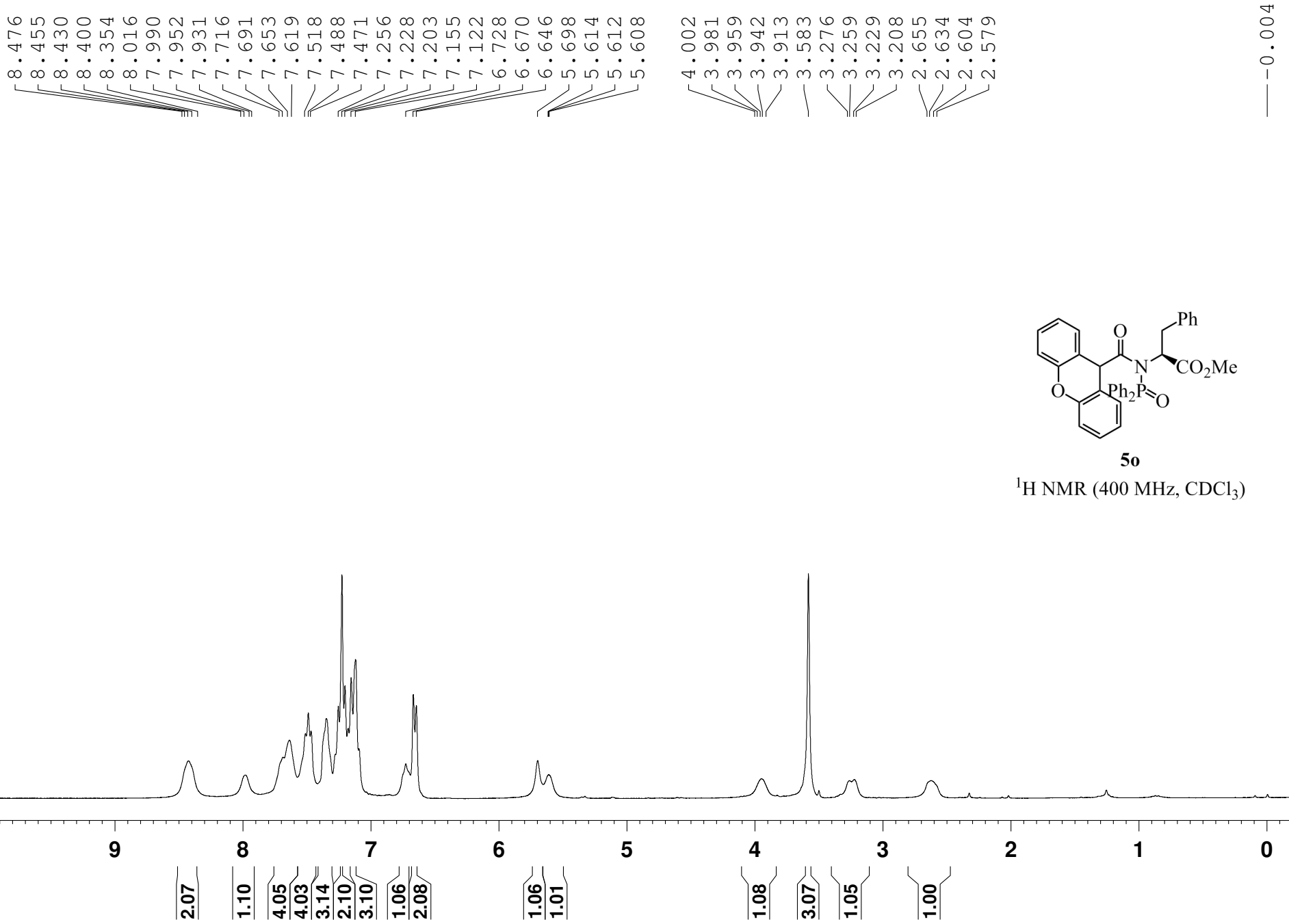
5n

^{13}C NMR (100 MHz, $CDCl_3$)



5n

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



5o

^{1}H NMR (400 MHz, $CDCl_3$)

177.023
176.917
171.099
153.427
152.934
138.376
133.787
133.558
133.186
133.042
130.418
130.149
130.034
129.673
129.504
129.202
129.051
128.730
127.280
123.613
123.285
120.994
120.664
117.771
117.576
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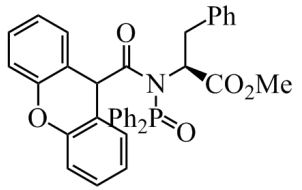
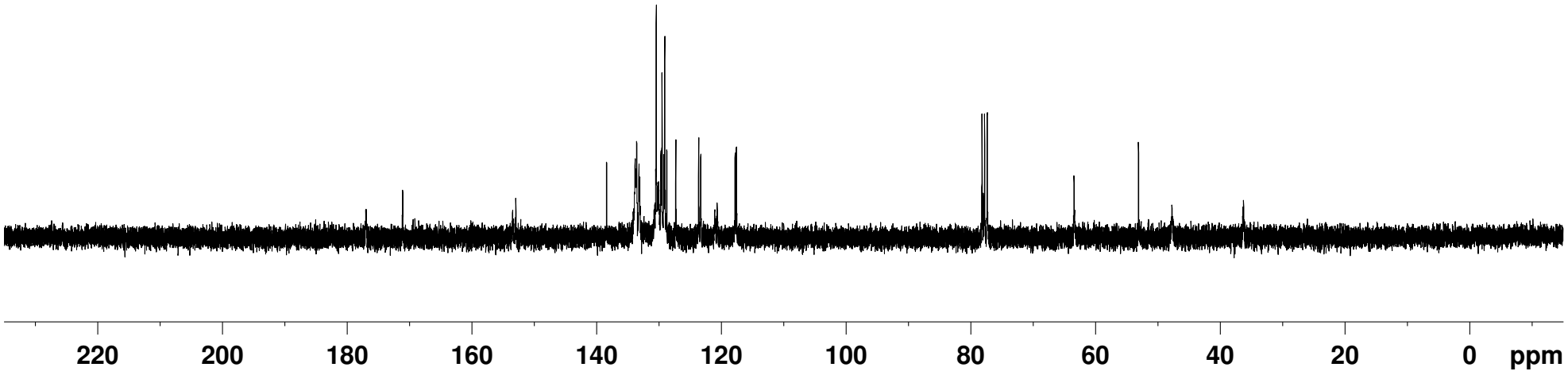
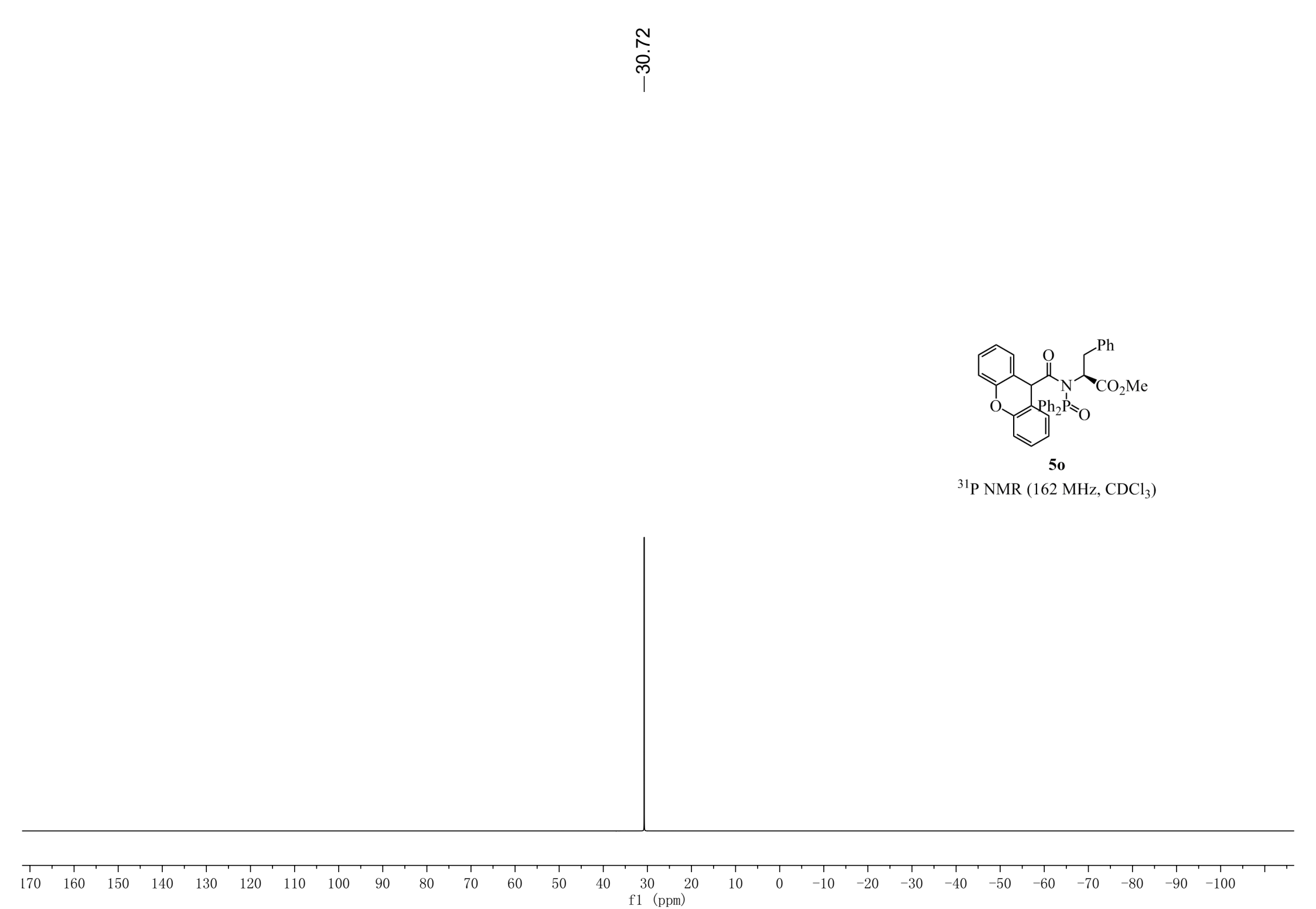
77.337
63.438
63.415
53.087
47.713
36.231



5o

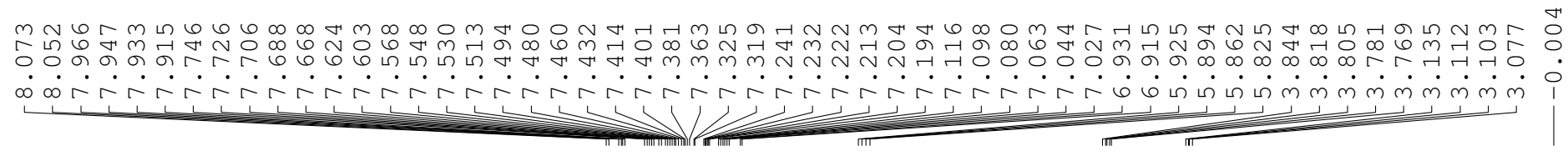
^{13}C NMR (100 MHz, $CDCl_3$)

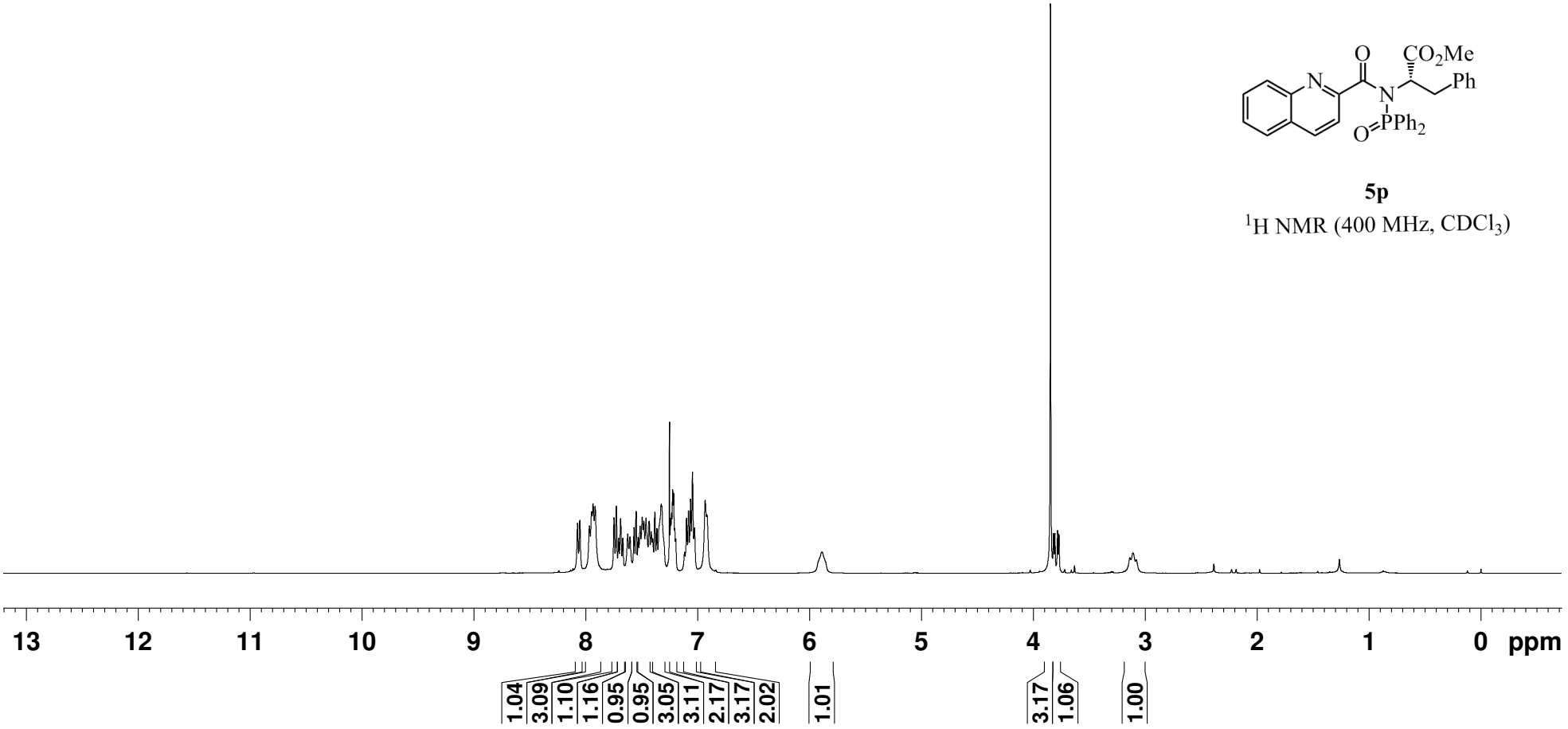




5o

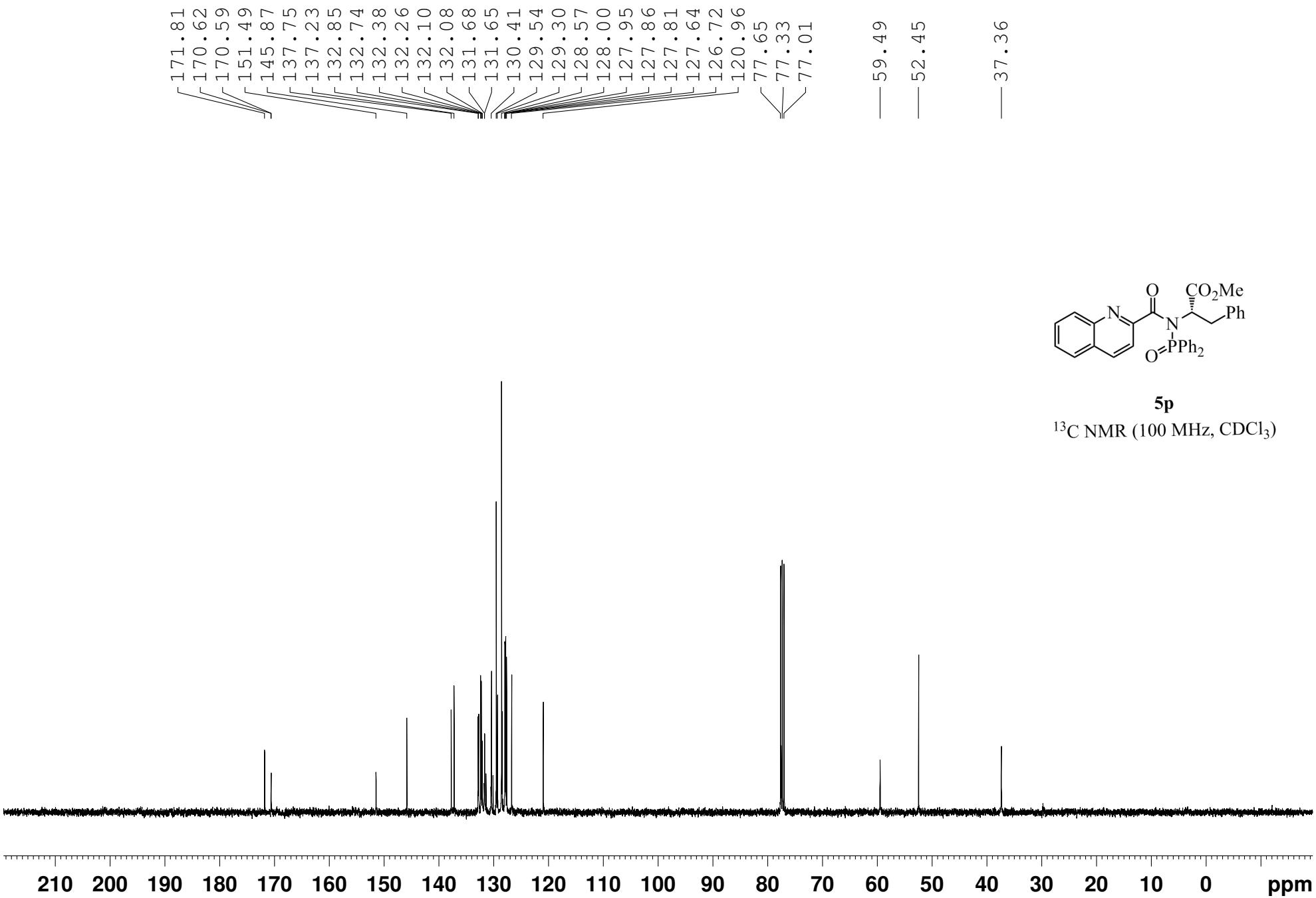
^{31}P NMR (162 MHz, $CDCl_3$)





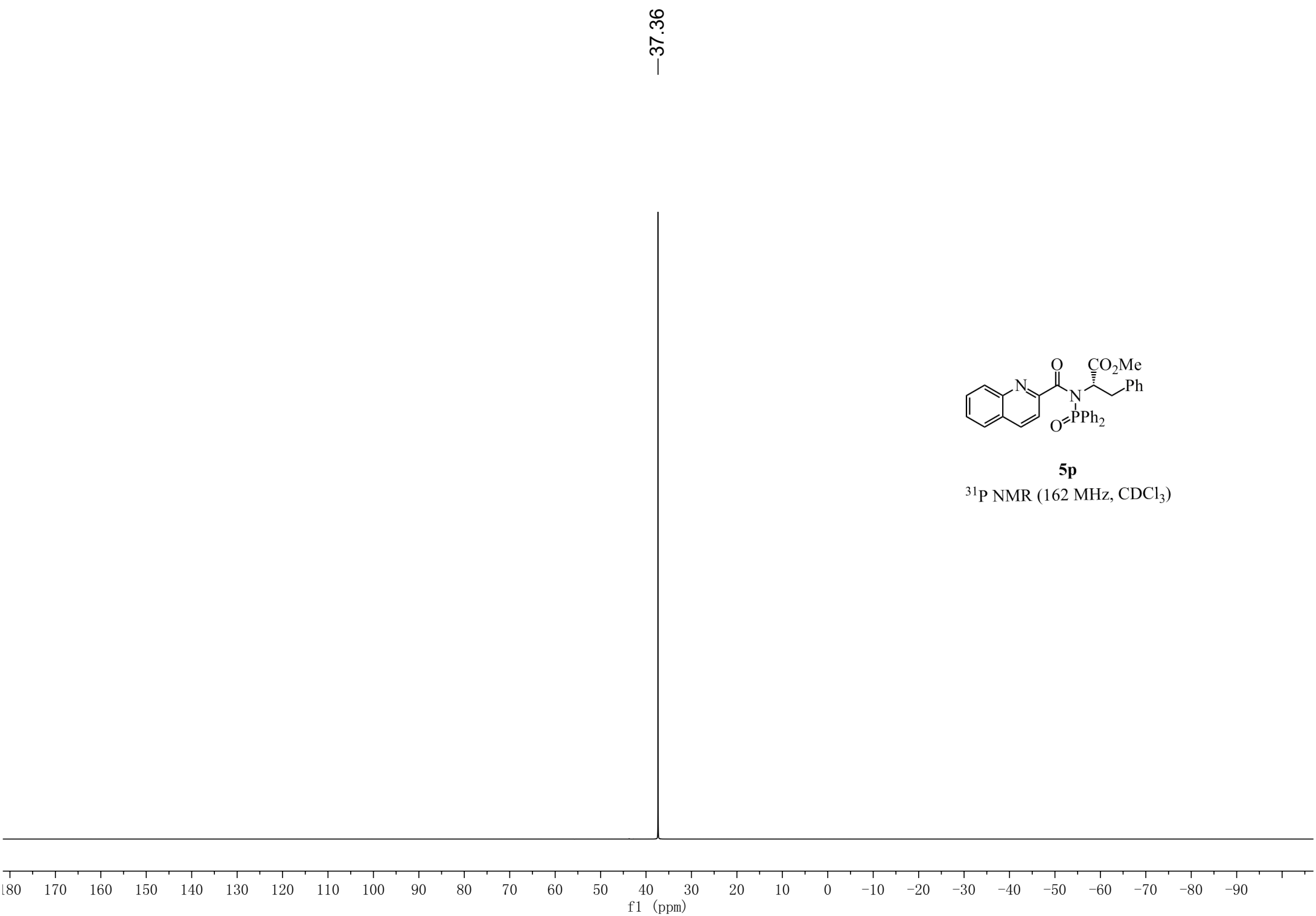
5p

^{1}H NMR (400 MHz, $CDCl_3$)



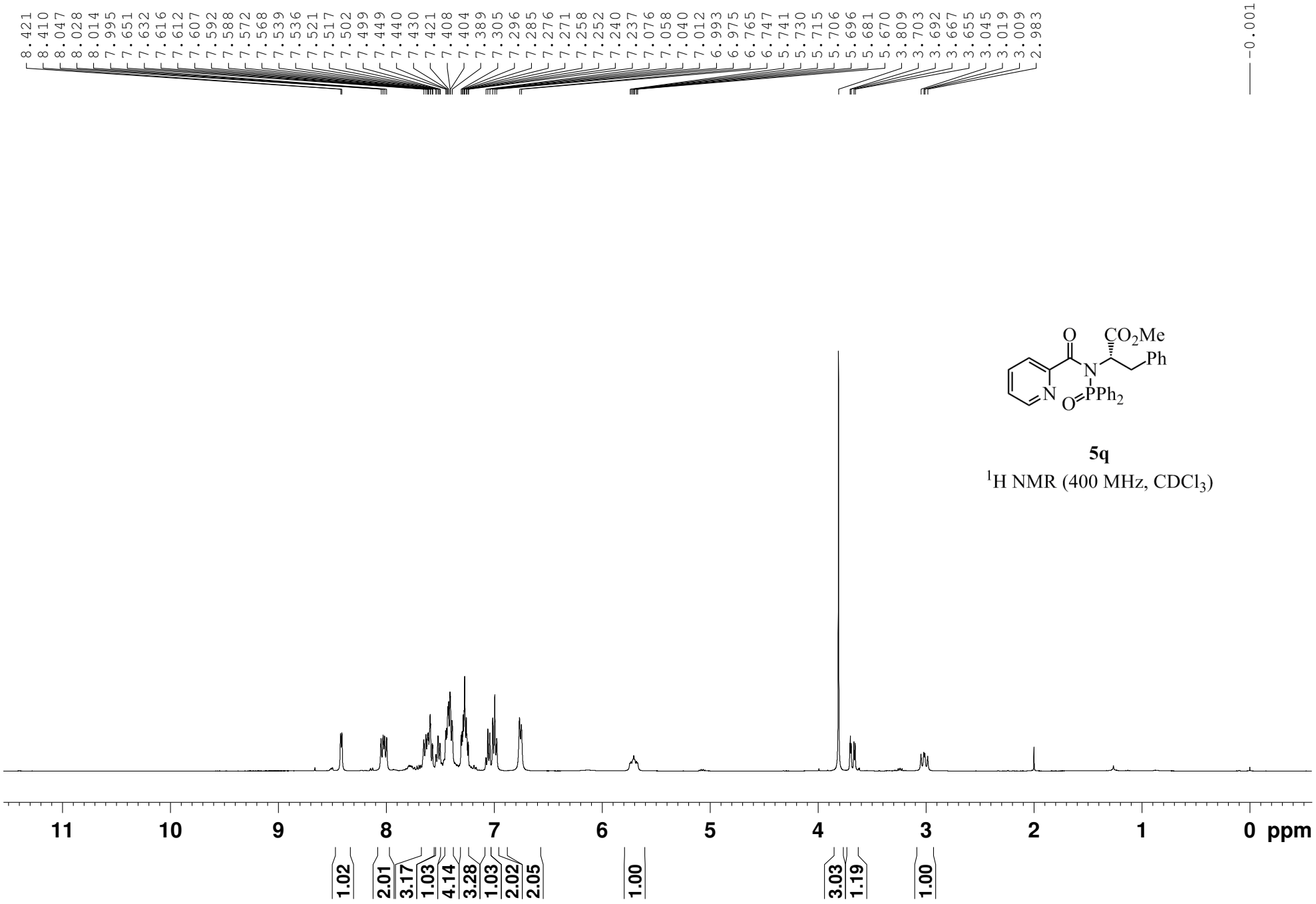
5p

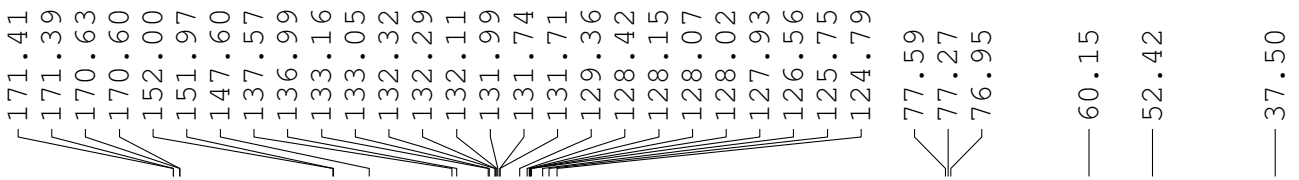
^{13}C NMR (100 MHz, $CDCl_3$)

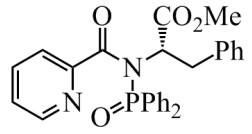


5p

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

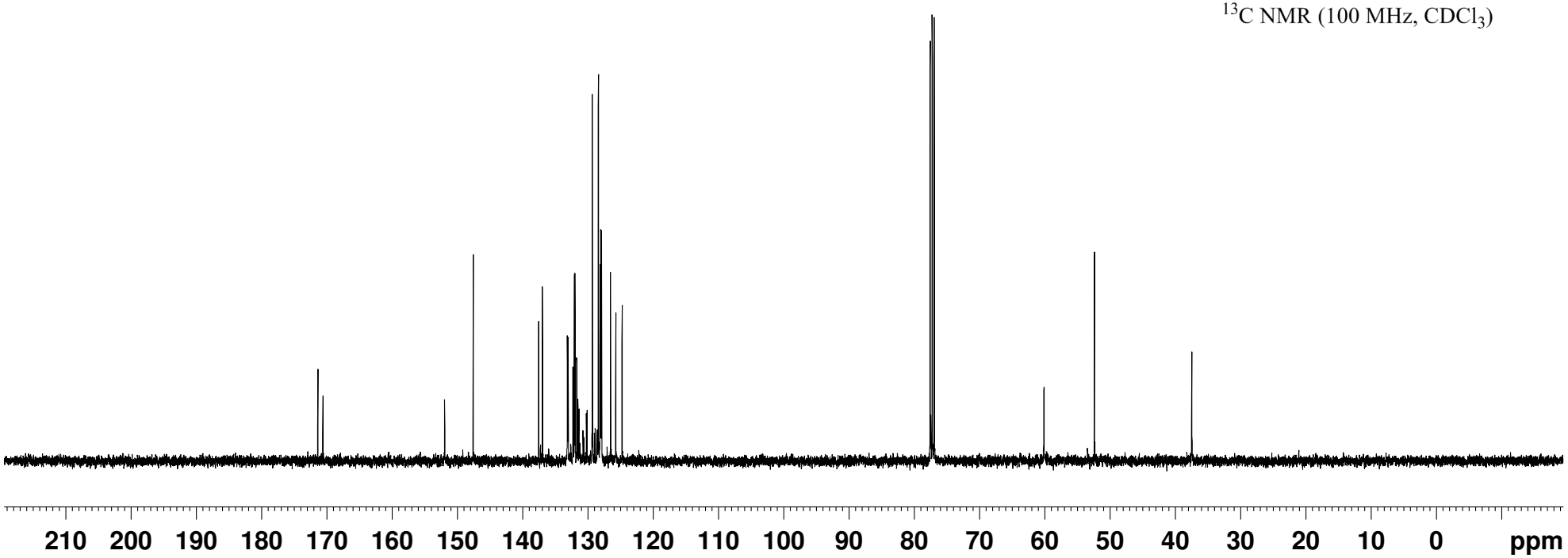

8.421
8.410
8.047
8.028
8.014
7.995
7.651
7.632
7.616
7.612
7.607
7.592
7.588
7.572
7.568
7.539
7.536
7.521
7.517
7.502
7.499
7.449
7.440
7.430
7.421
7.408
7.404
7.389
7.305
7.296
7.285
7.276
7.271
7.258
7.252
7.240
7.237
7.076
7.058
7.040
7.012
6.993
6.975
6.765
6.747
5.741
5.730
5.715
5.706
5.696
5.681
5.670
3.809
3.703
3.692
3.667
3.655
3.045
3.019
3.009
2.983
0.001
O
CO2Me
Ph
N
N
O
PPh2
5q
1H NMR (400 MHz, CDCl3)
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.02
2.01
3.17
1.03
4.14
3.28
1.03
2.02
2.05
1.00
3.03
1.19
1.00

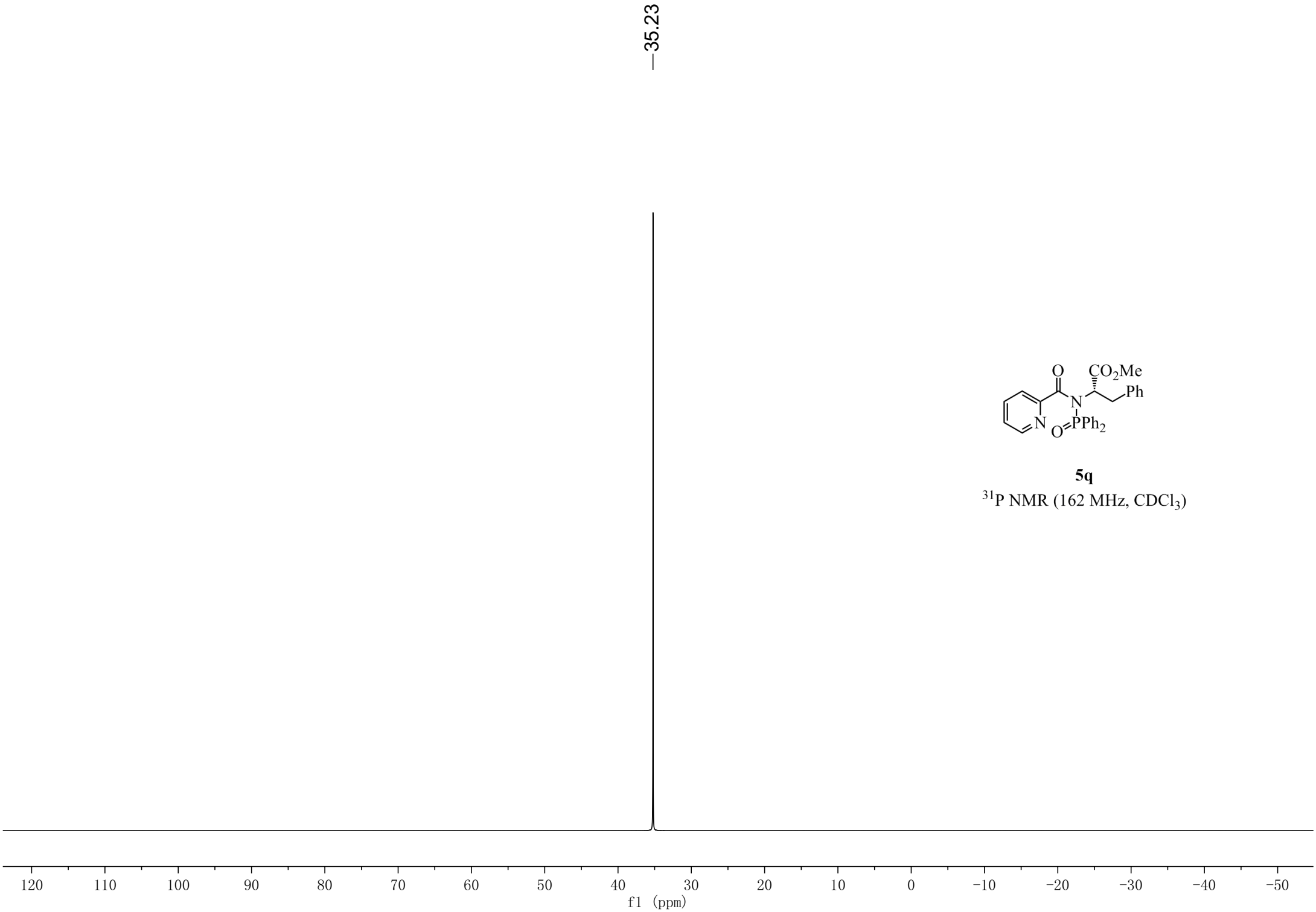




5q

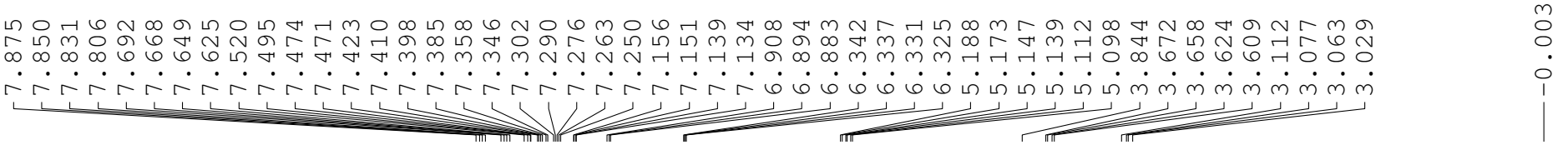
^{13}C NMR (100 MHz, $CDCl_3$)

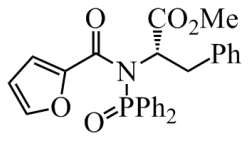




5q

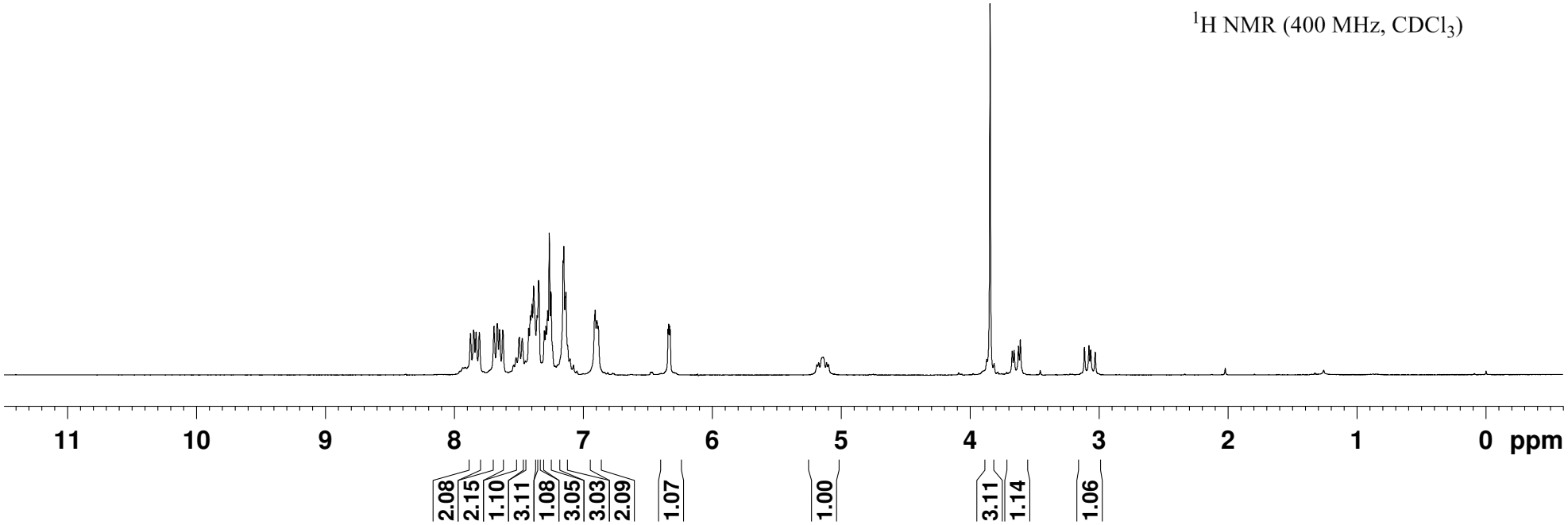
^{31}P NMR (162 MHz, $CDCl_3$)

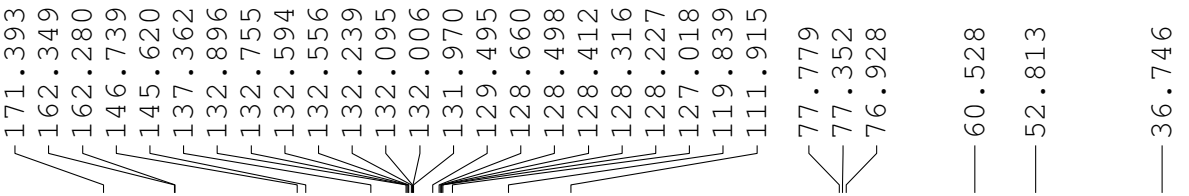


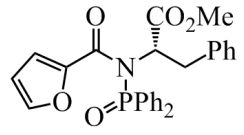


5r

^{1}H NMR (400 MHz, $CDCl_3$)

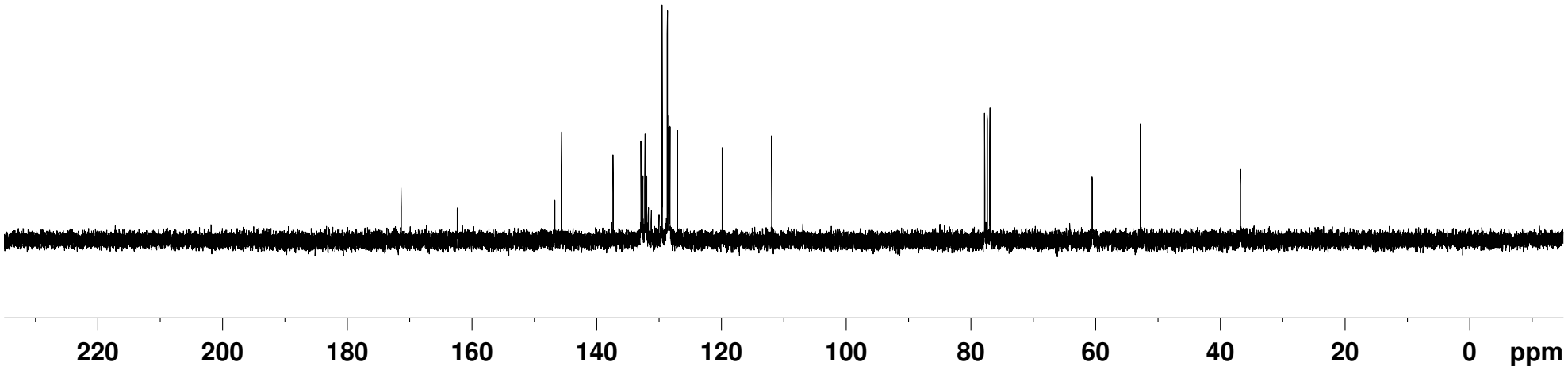


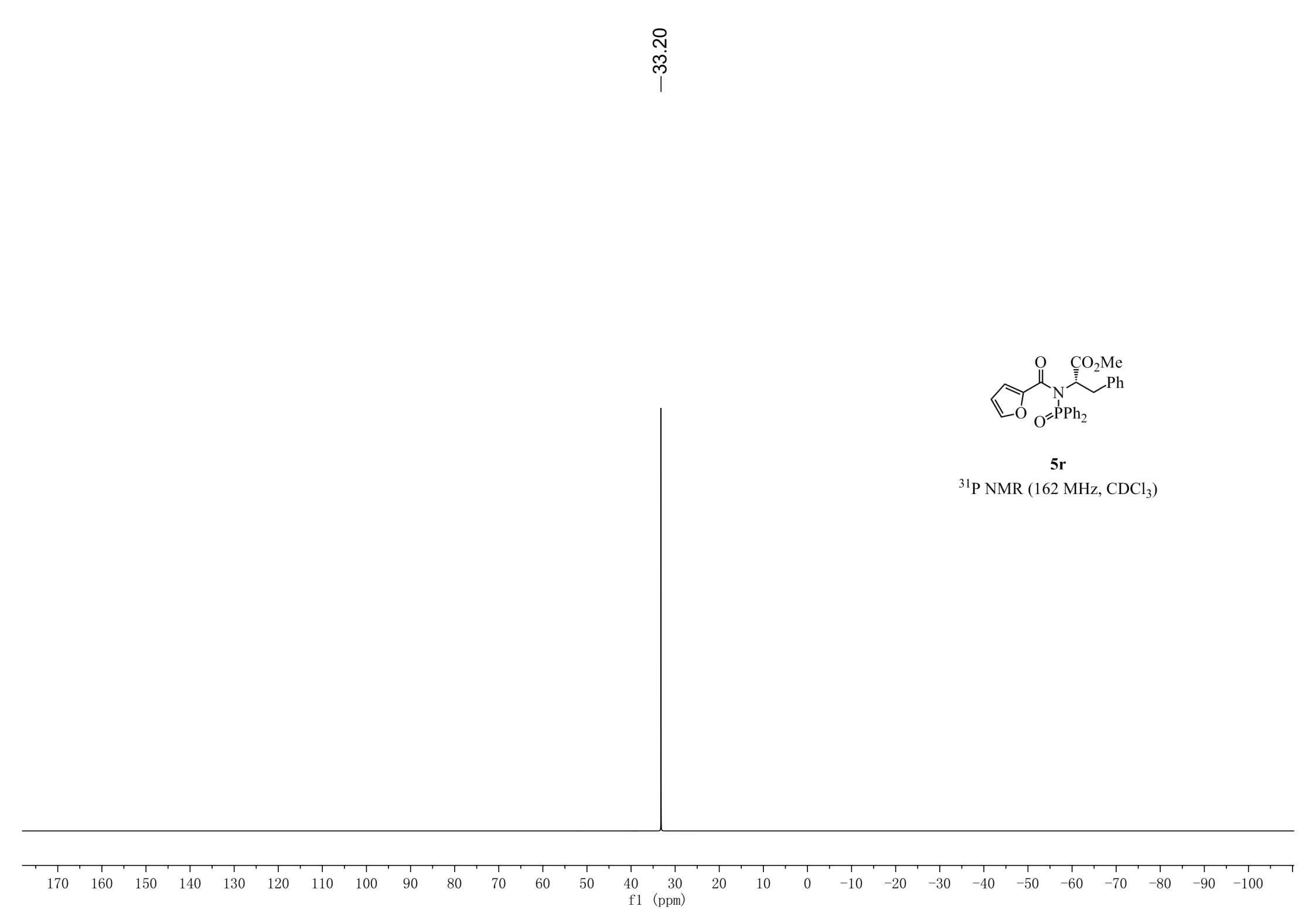




5r

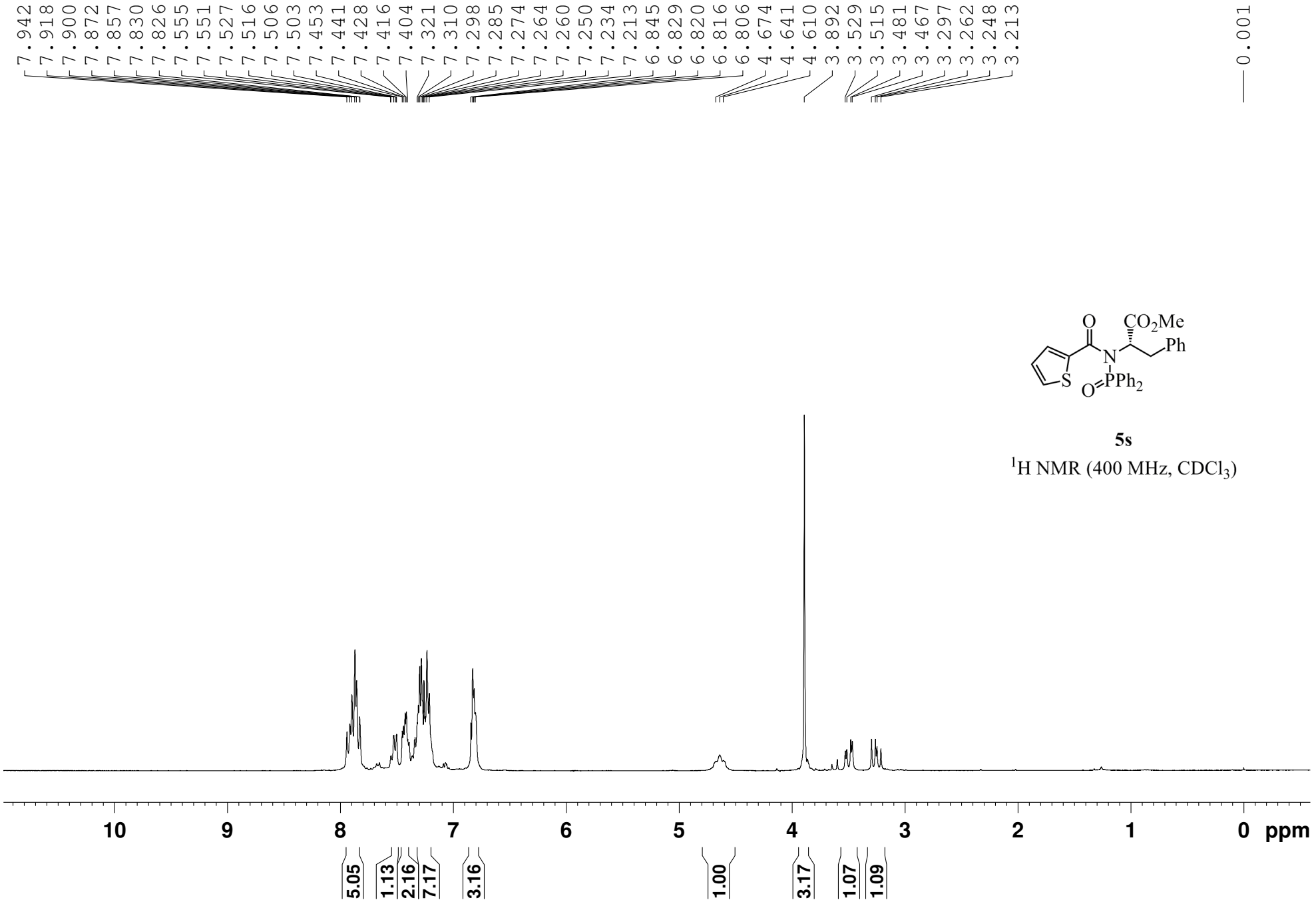
^{13}C NMR (100 MHz, $CDCl_3$)





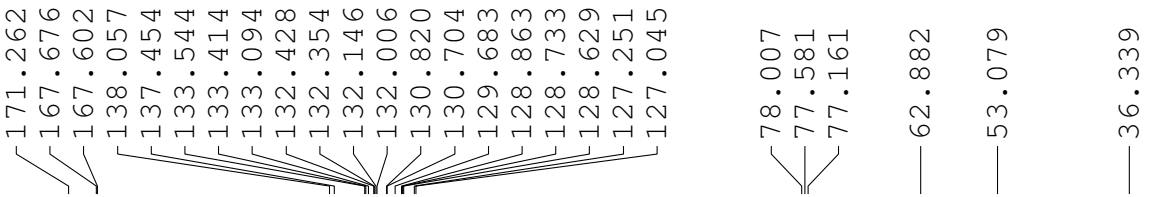
5r

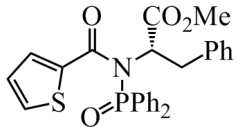
^{31}P NMR (162 MHz, $CDCl_3$)



5s

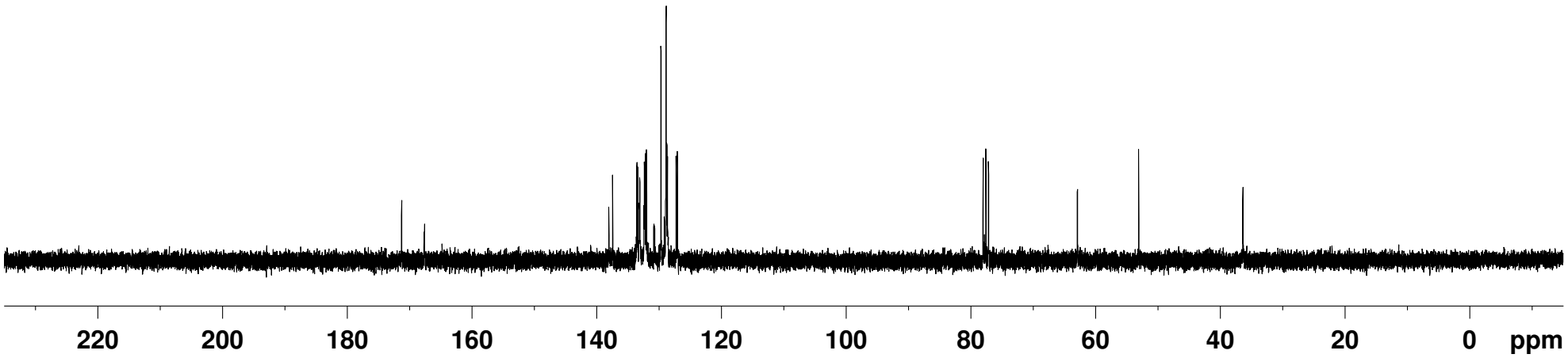
^{1}H NMR (400 MHz, $CDCl_3$)

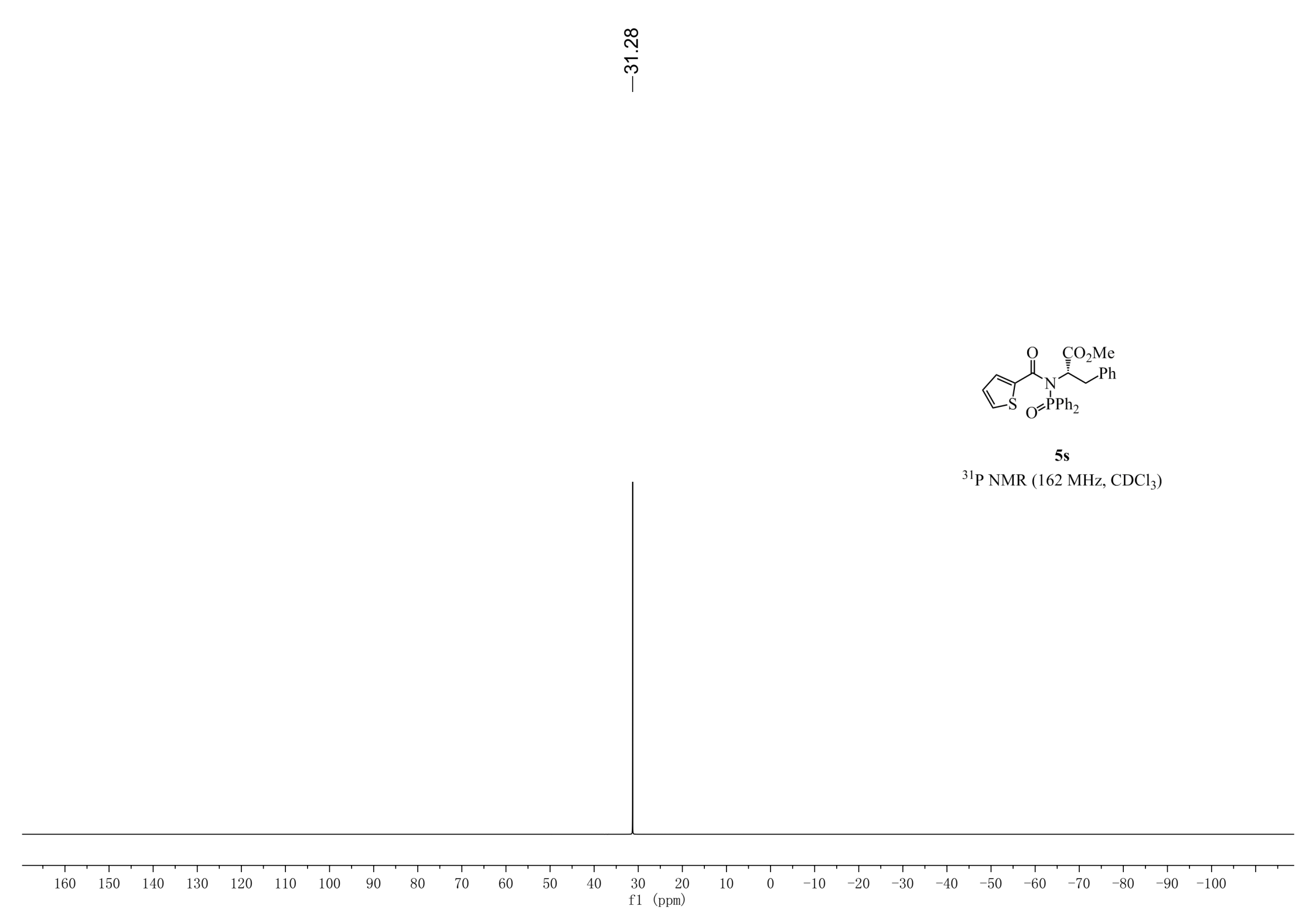




5s

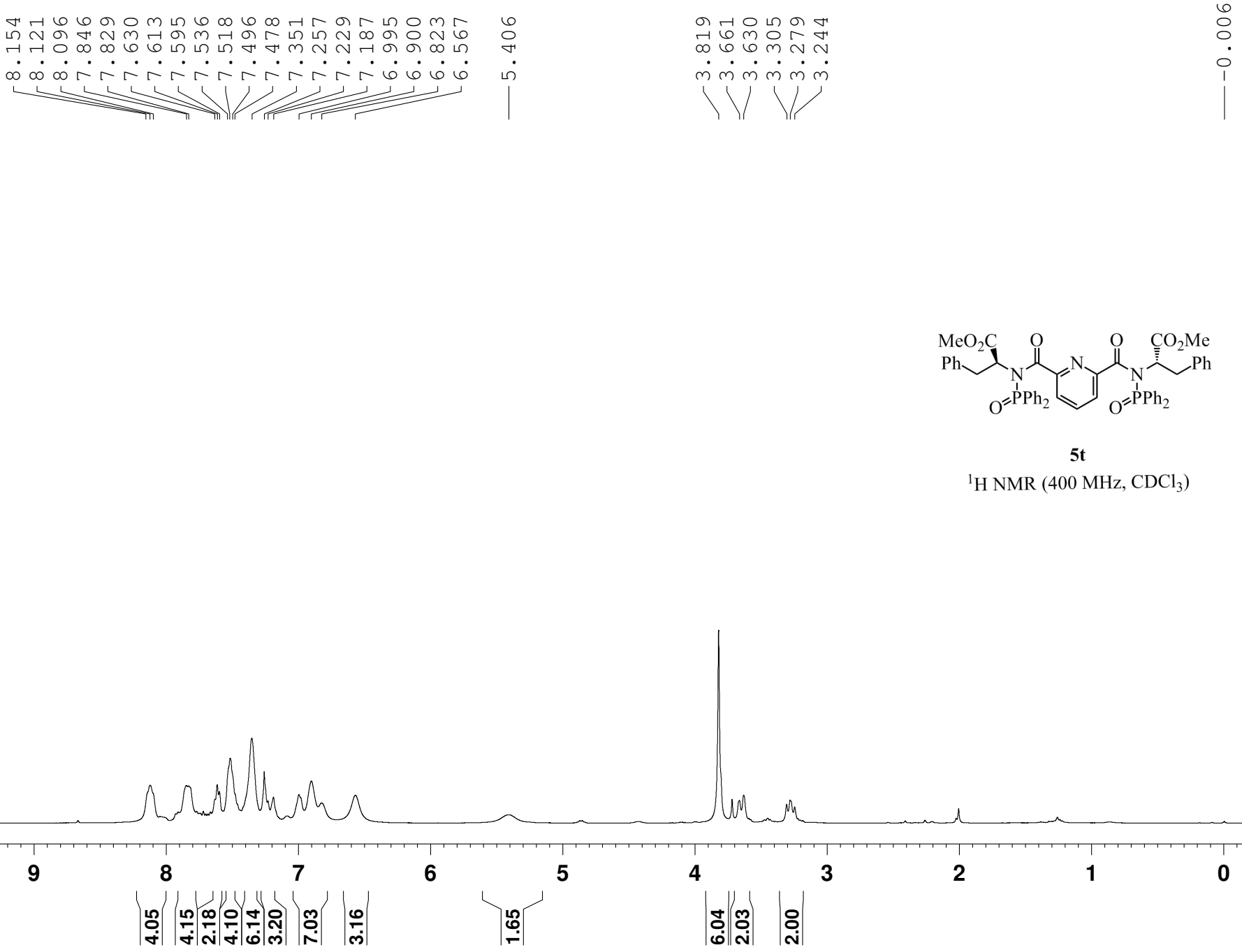
^{13}C NMR (100 MHz, $CDCl_3$)





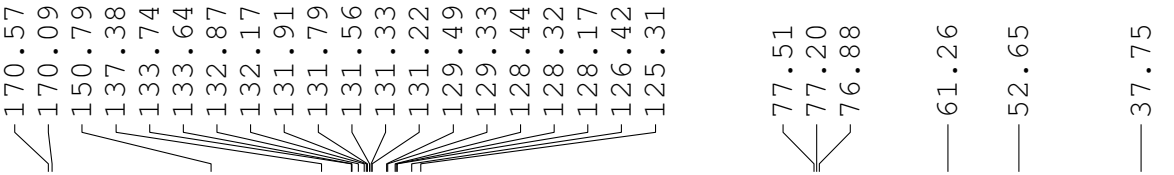
5s

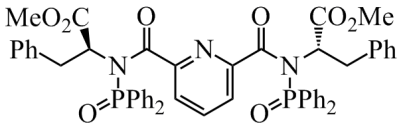
^{31}P NMR (162 MHz, $CDCl_3$)



5t

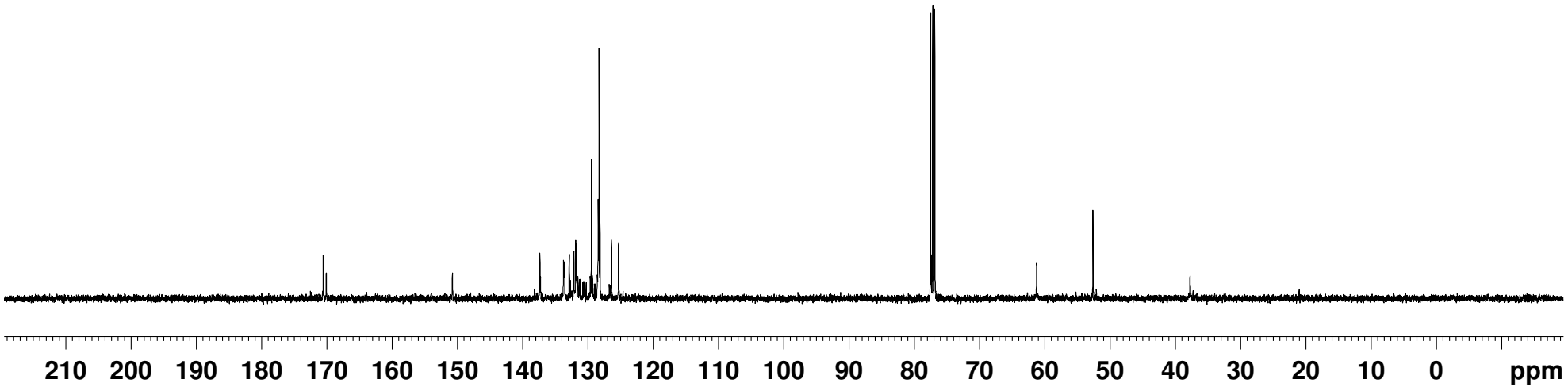
^{1}H NMR (400 MHz, $CDCl_3$)

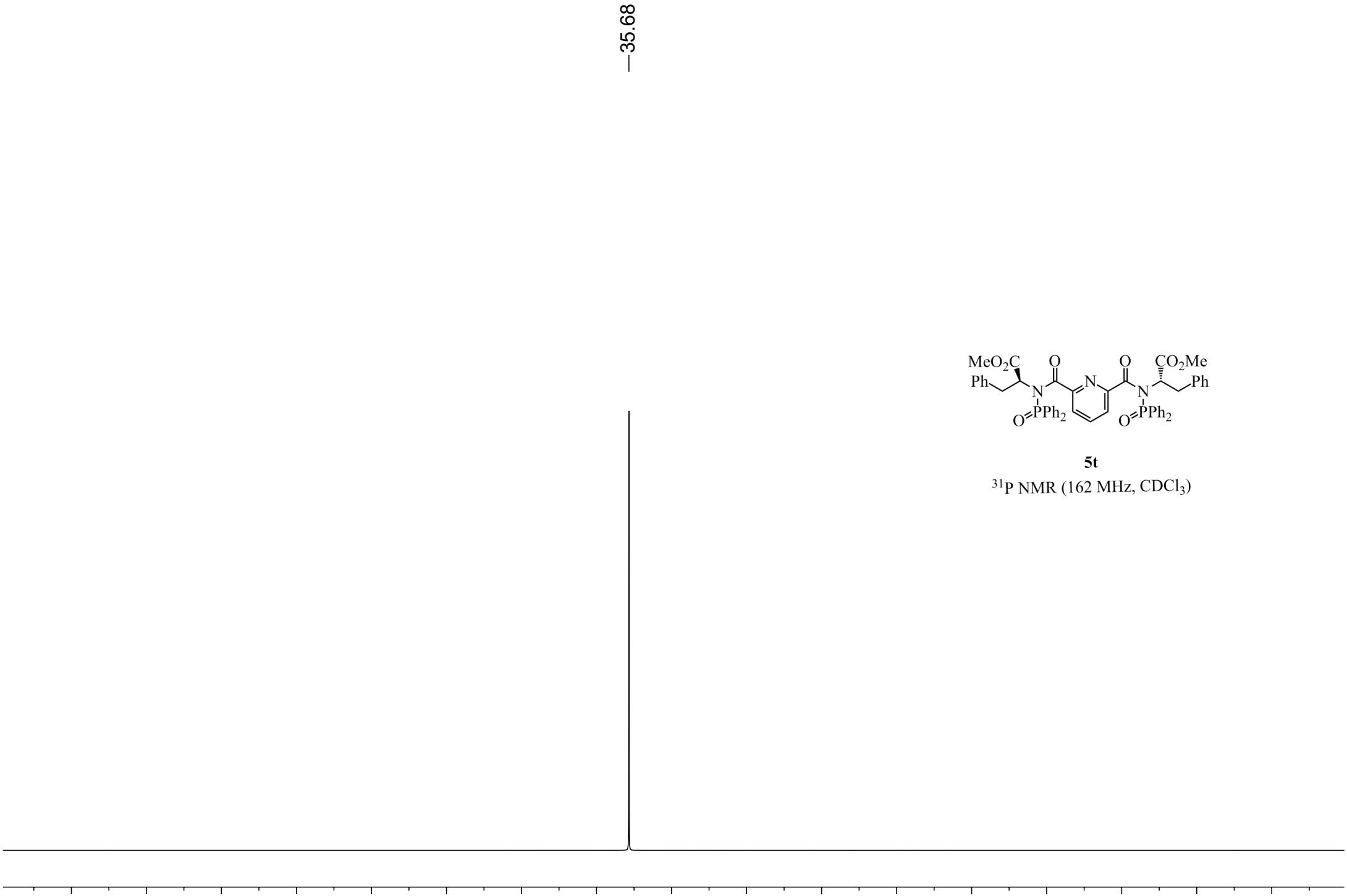




5t

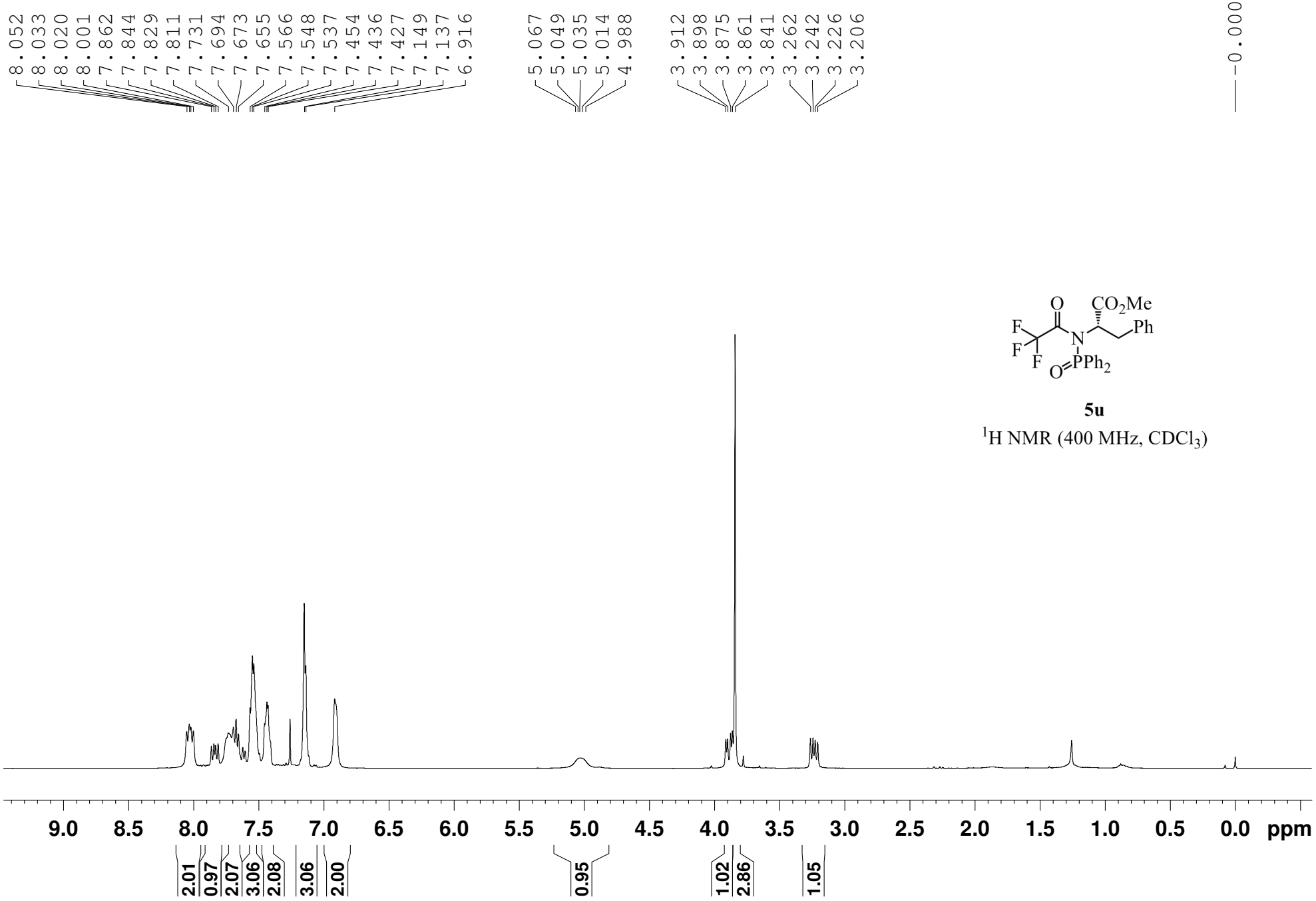
^{13}C NMR (100 MHz, $CDCl_3$)

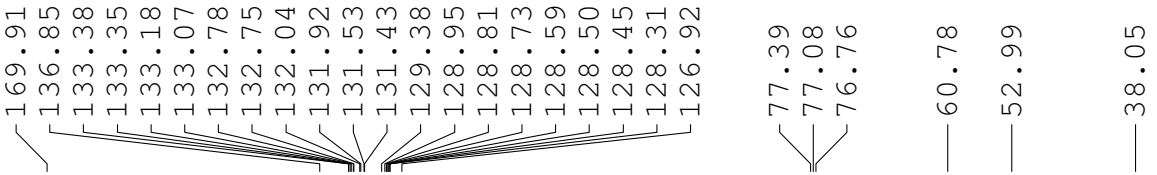


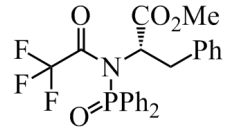


5t

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

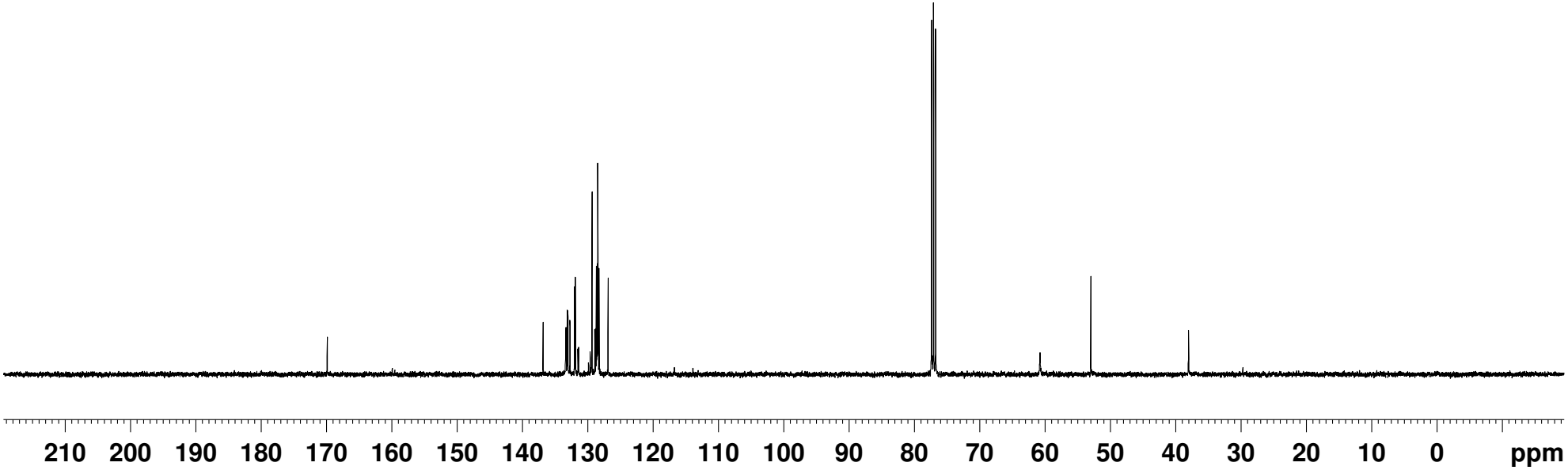

8.052
8.033
8.020
8.001
7.862
7.844
7.829
7.811
7.731
7.694
7.673
7.655
7.566
7.548
7.537
7.454
7.436
7.427
7.149
7.137
6.916
5.067
5.049
5.035
5.014
4.988
3.912
3.898
3.875
3.861
3.841
3.262
3.242
3.226
3.206
0.000
O
CO2Me
F
F
F
N
Ph
O
PPh2
5u
1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
0.97
2.07
3.06
2.08
3.06
2.00
0.95
1.02
2.86
1.05

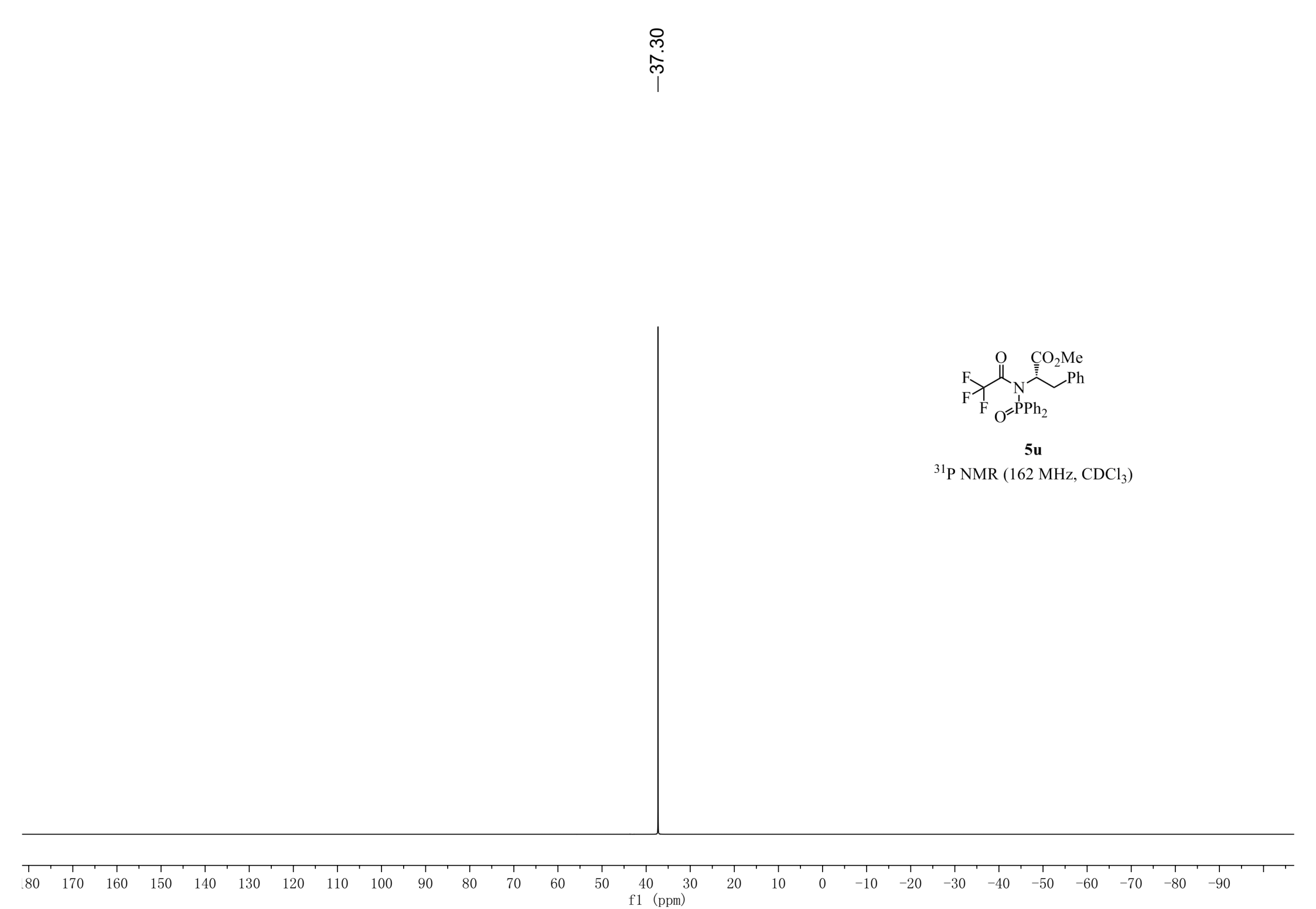




5u

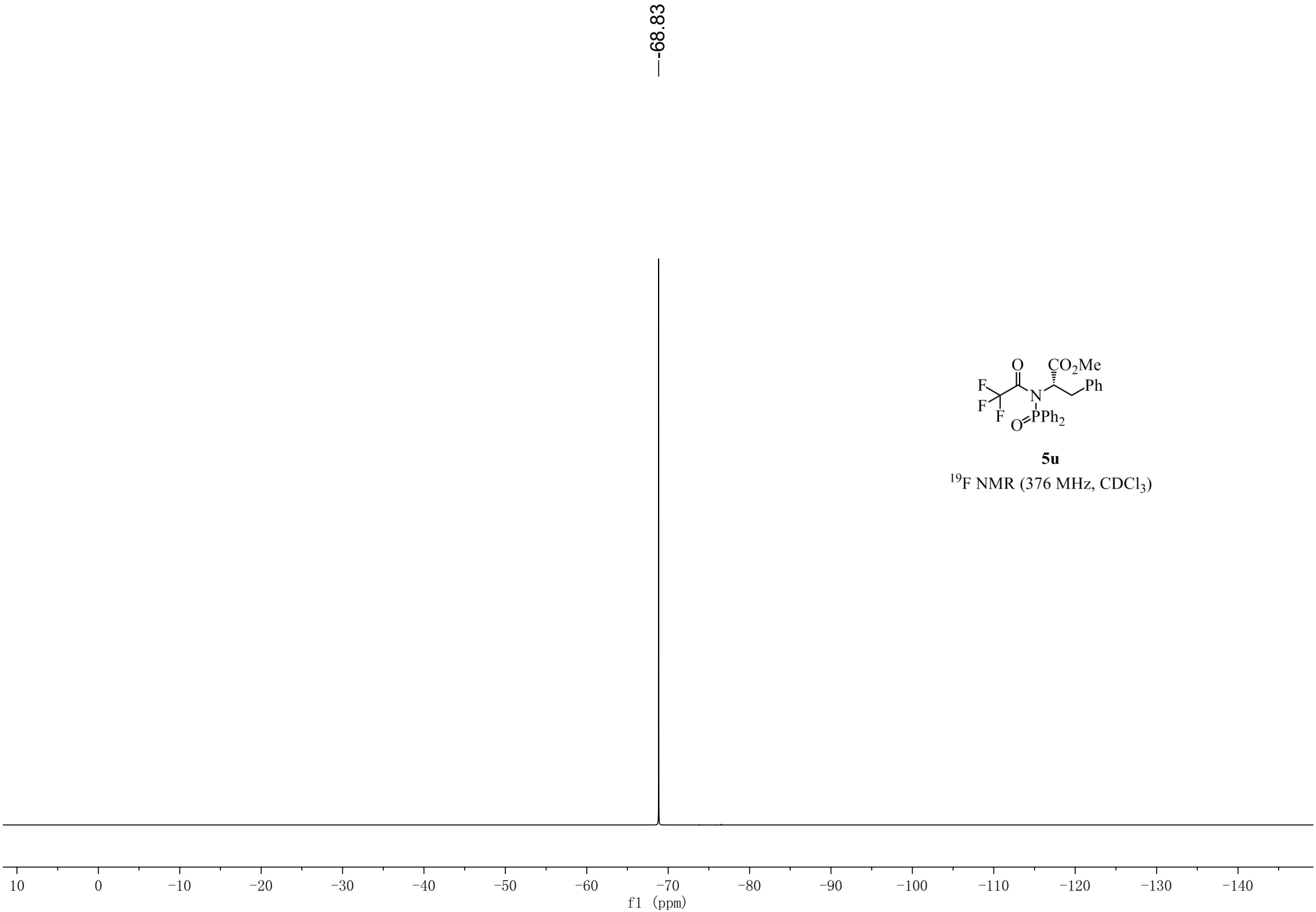
^{13}C NMR (100 MHz, $CDCl_3$)





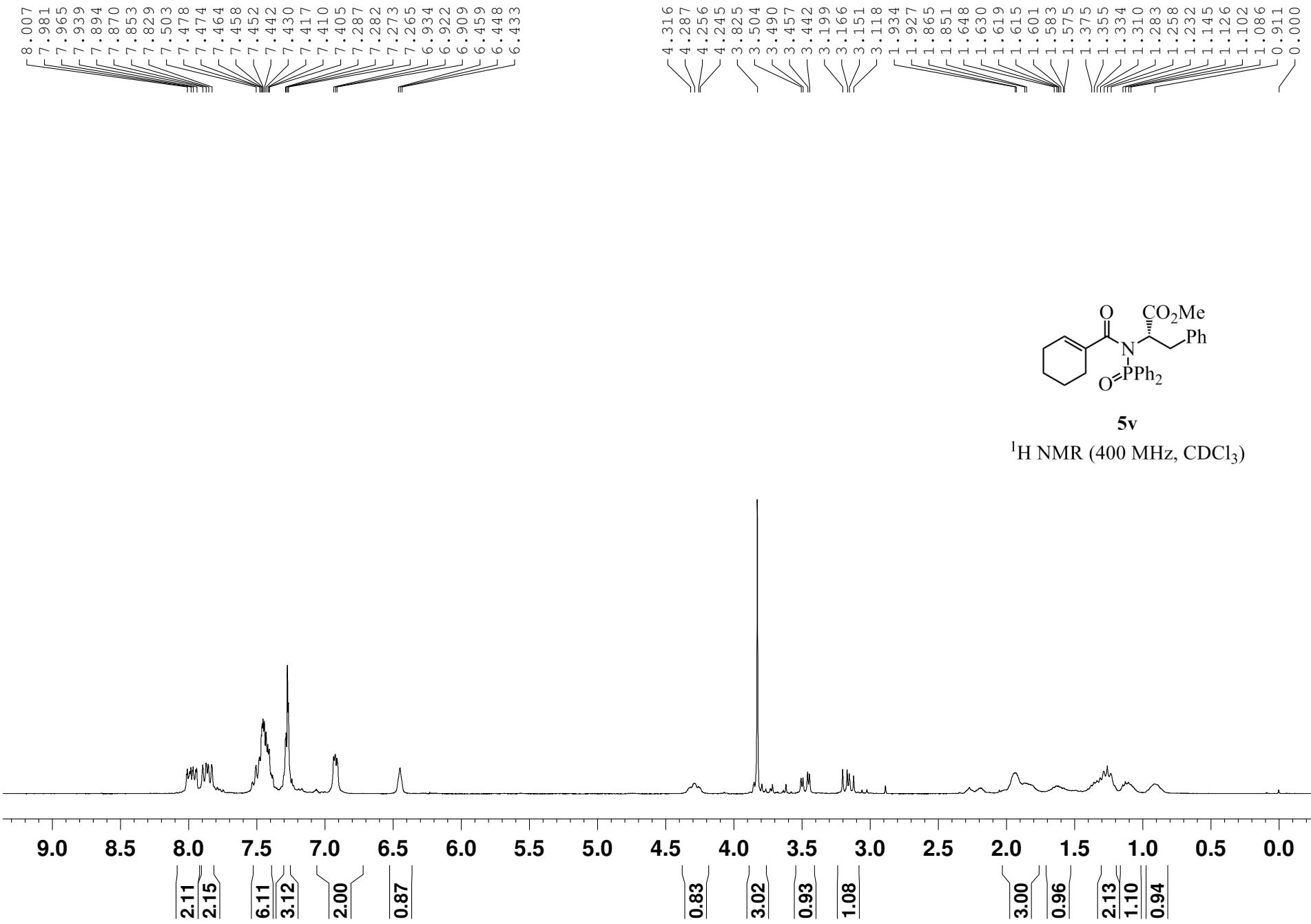
5u

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



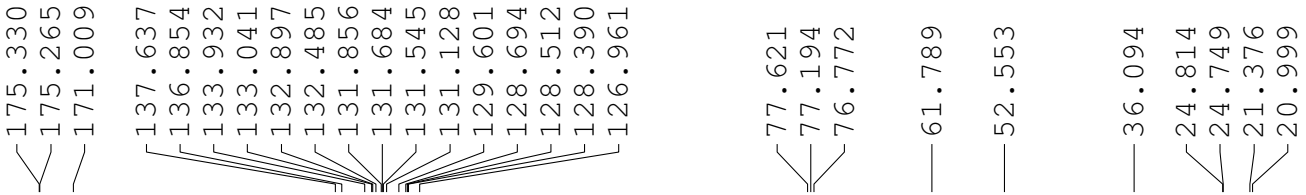
5u

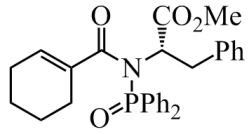
^{19}F NMR (376 MHz, $CDCl_3$)



5v

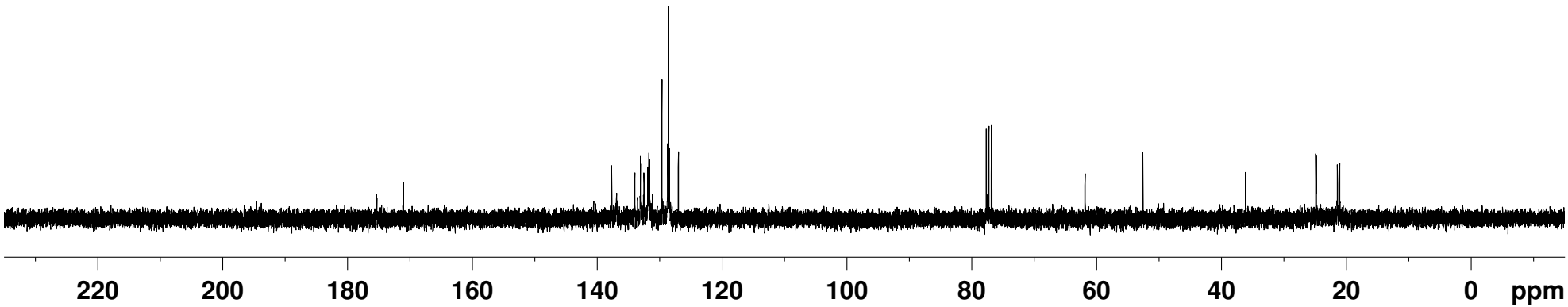
^{1}H NMR (400 MHz, $CDCl_3$)

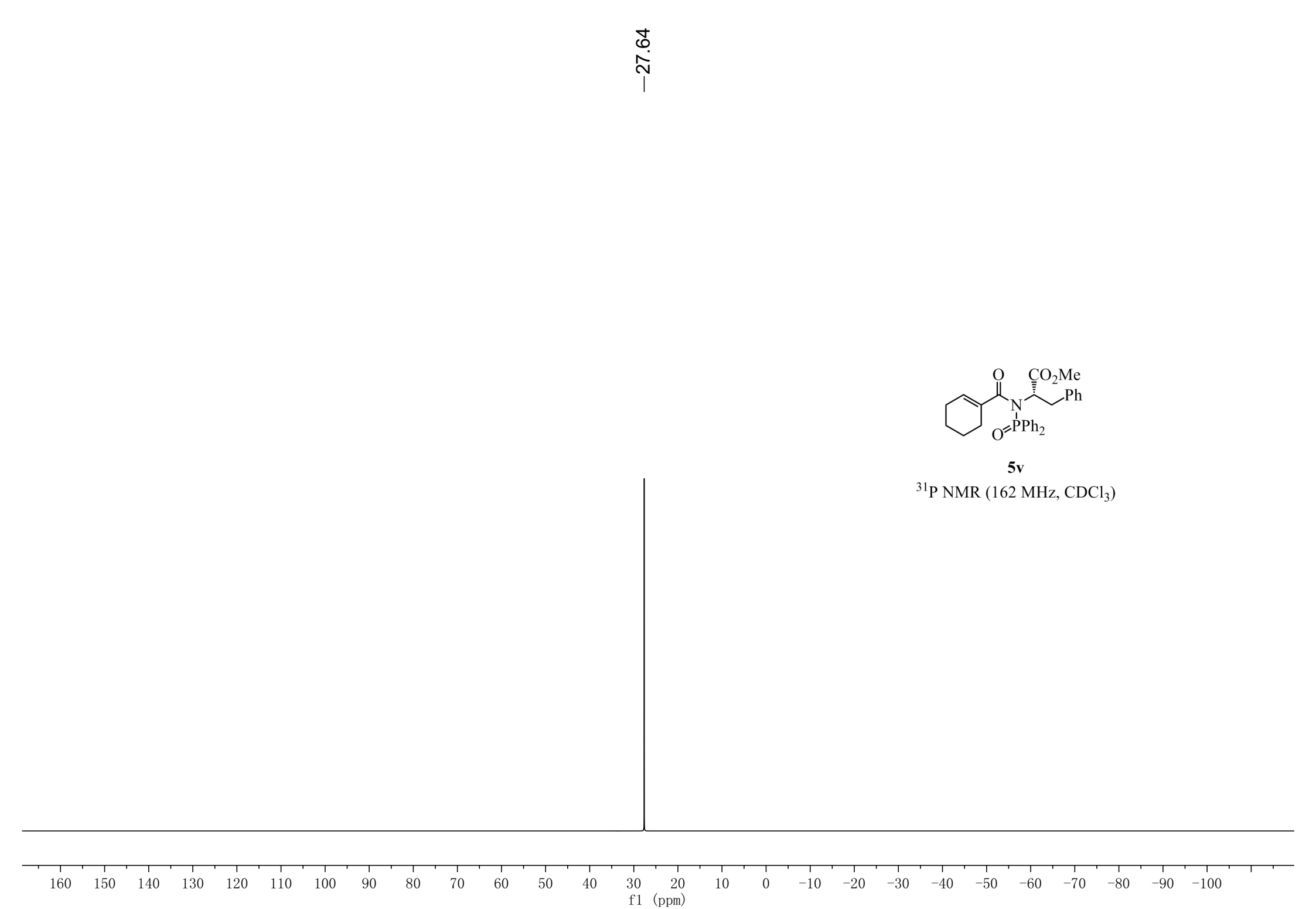




5v

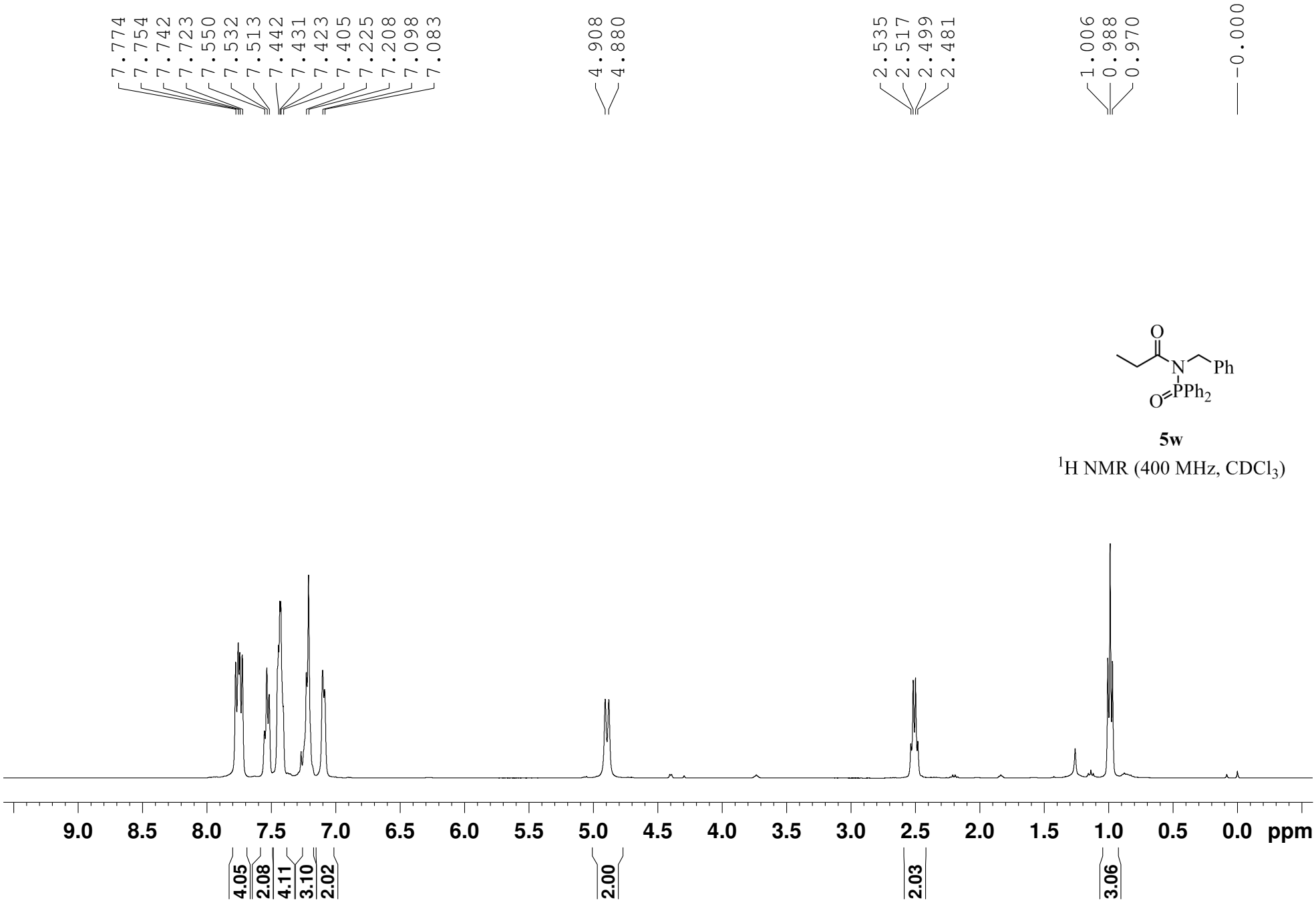
^{13}C NMR (100 MHz, $CDCl_3$)





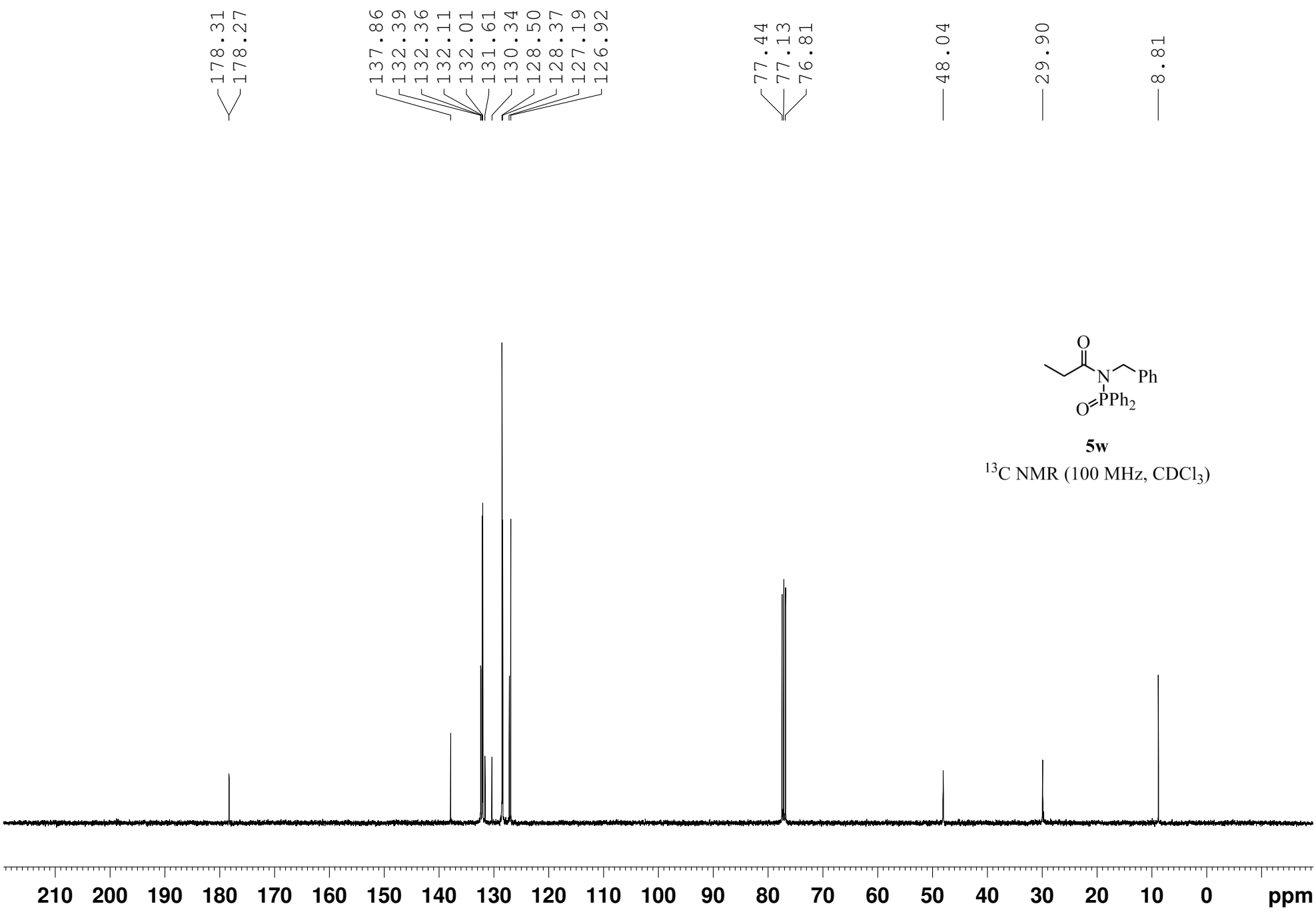
5v

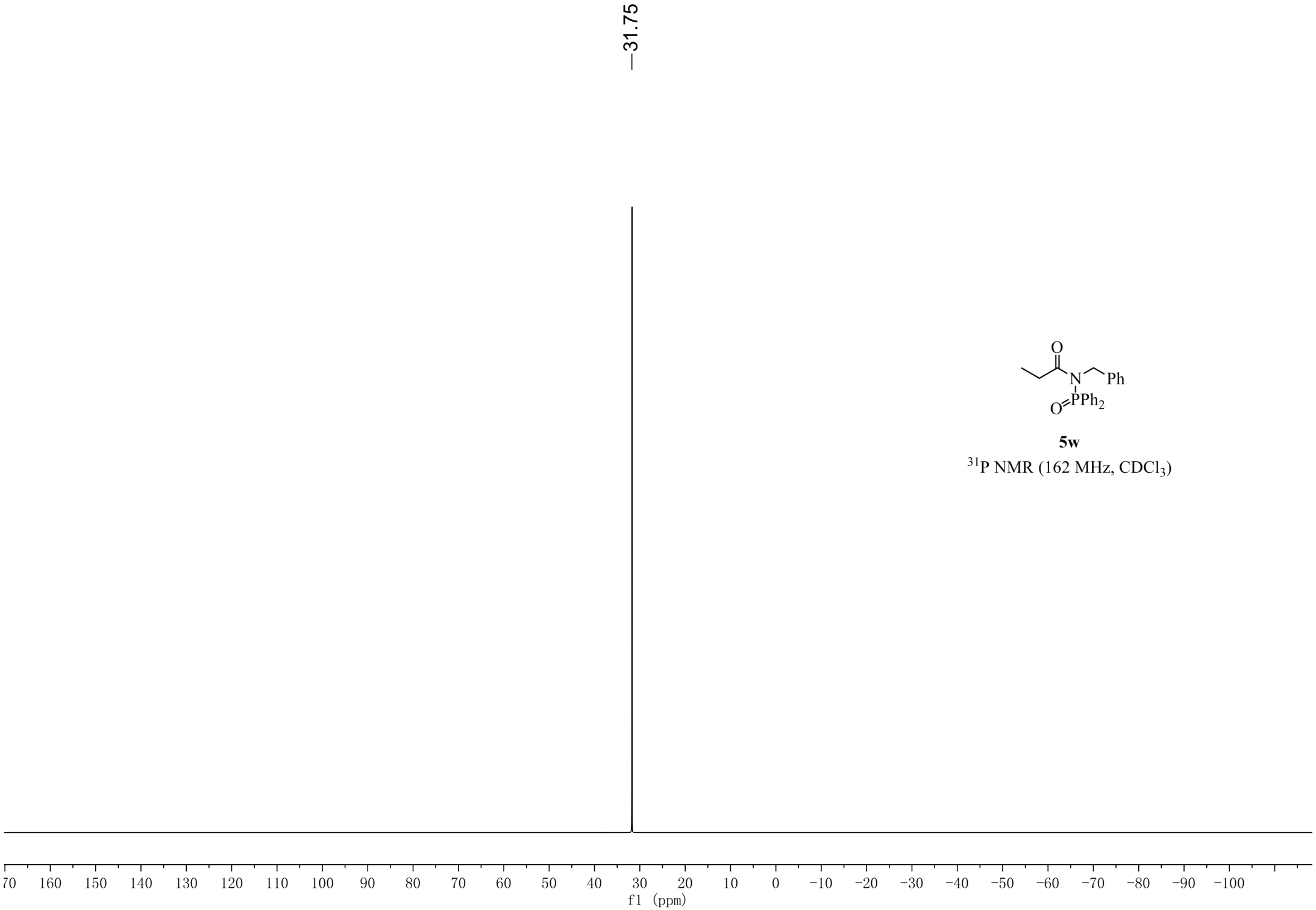
^{31}P NMR (162 MHz, $CDCl_3$)



5w

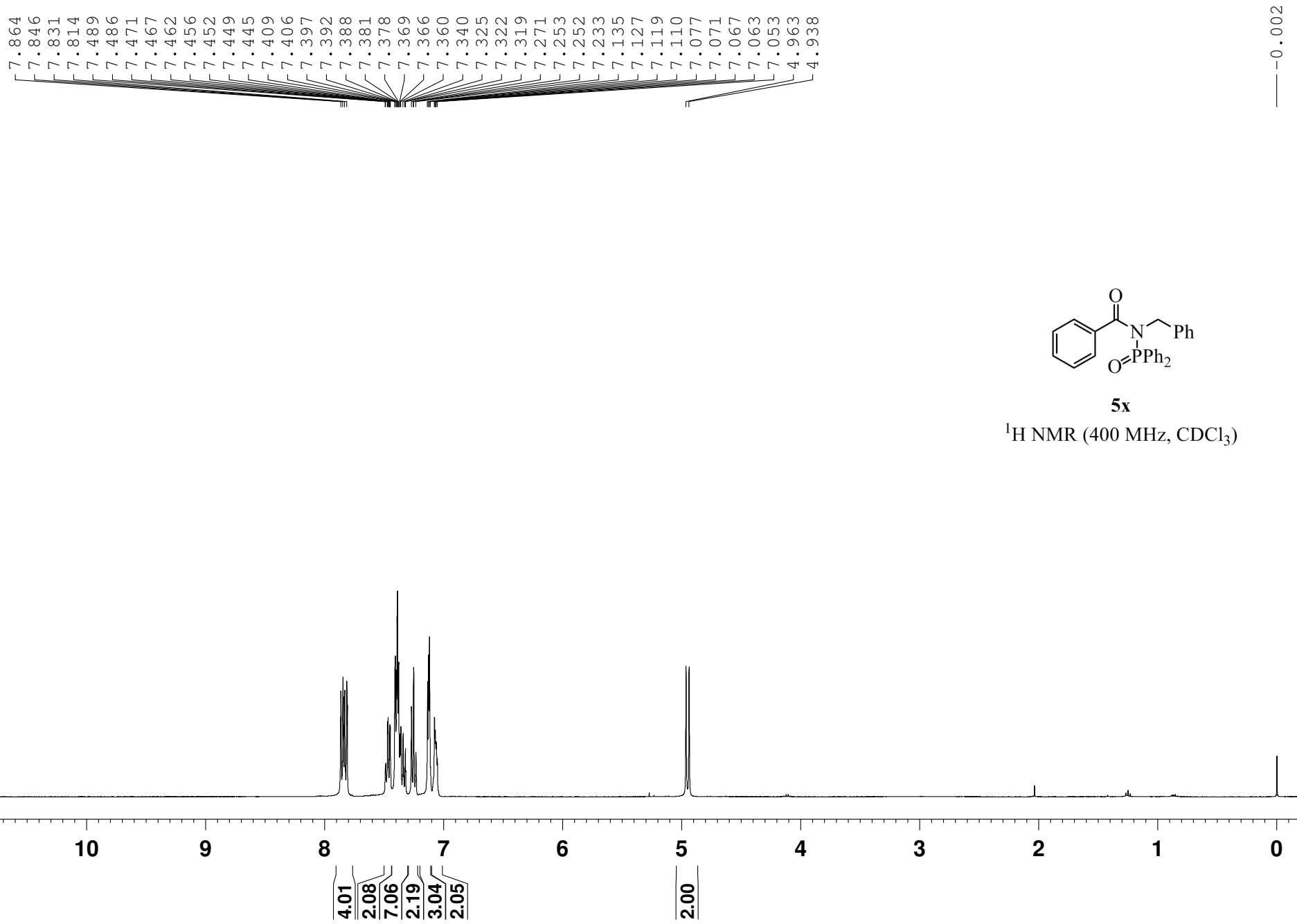
^{1}H NMR (400 MHz, $CDCl_3$)


178.31
178.27
137.86
132.39
132.36
132.11
132.01
131.61
130.34
128.50
128.37
127.19
126.92
77.44
77.13
76.81
48.04
29.90
8.81
O
N
Ph
O
PPh2
5w
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



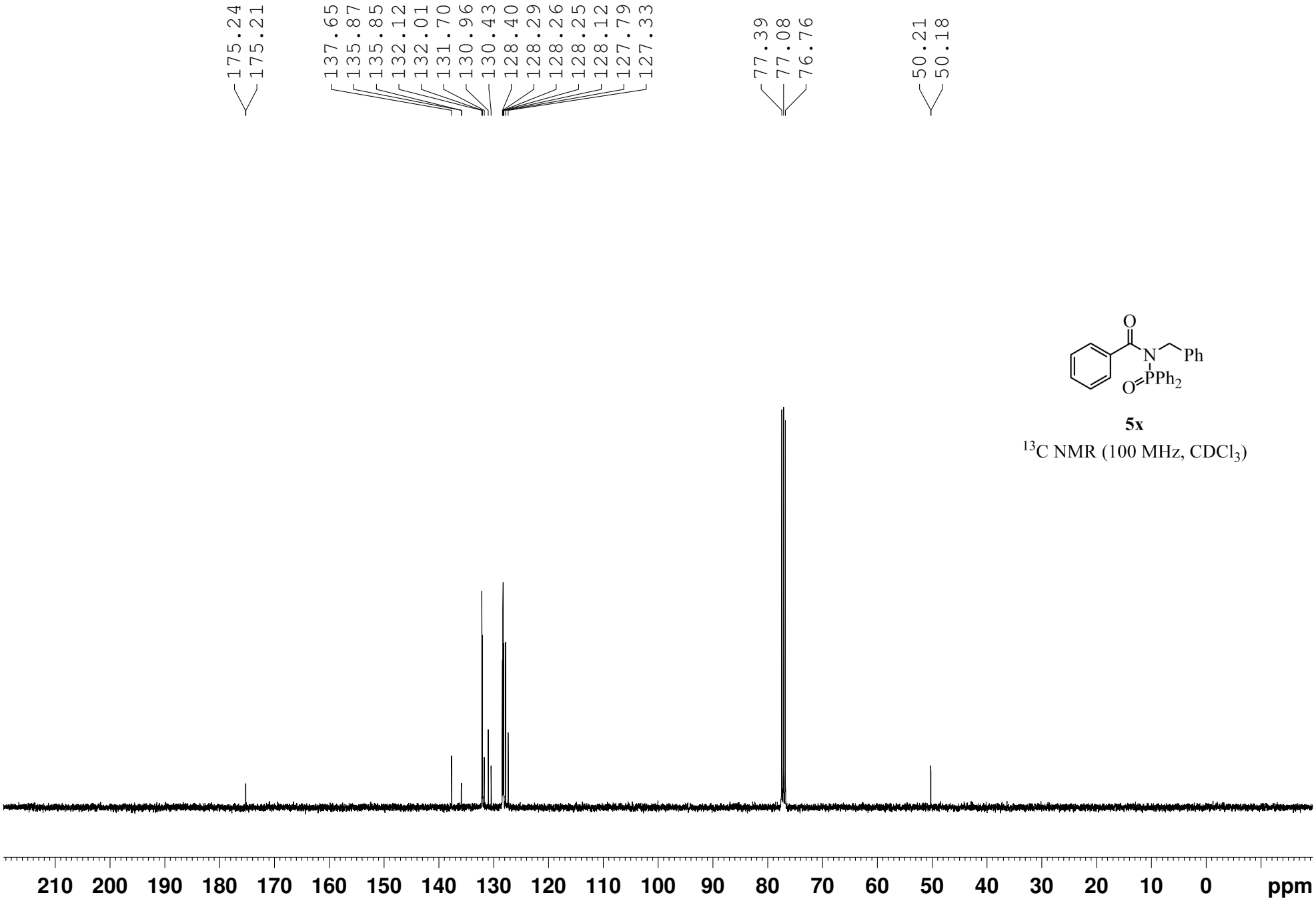
5w

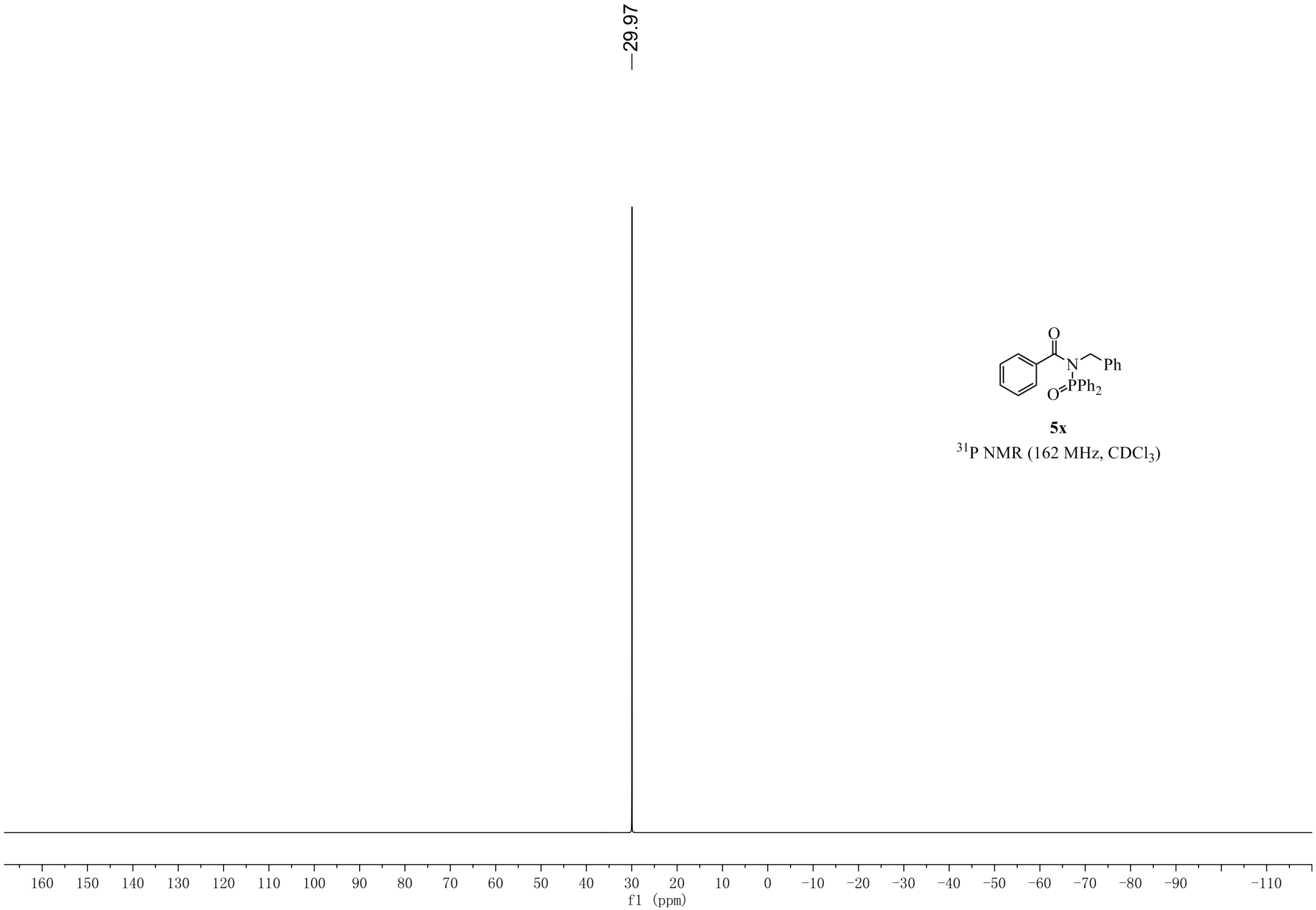
^{31}P NMR (162 MHz, $CDCl_3$)



5x

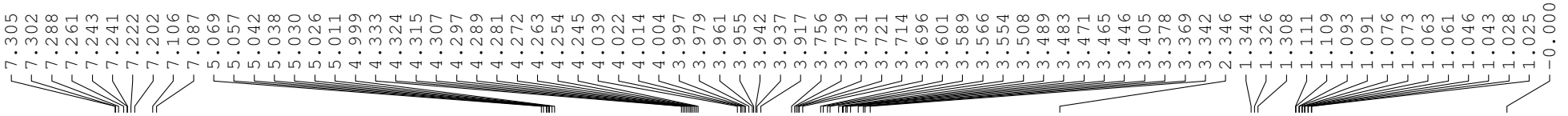
^{1}H NMR (400 MHz, $CDCl_3$)

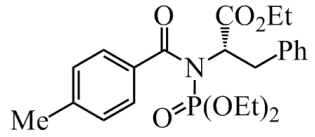

175.24
175.21
137.65
135.87
135.85
132.12
132.01
131.70
130.96
130.43
128.40
128.29
128.26
128.25
128.12
127.79
127.33
77.39
77.08
76.76
50.21
50.18
O
N
Ph
O=PPh2
5x
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



5x

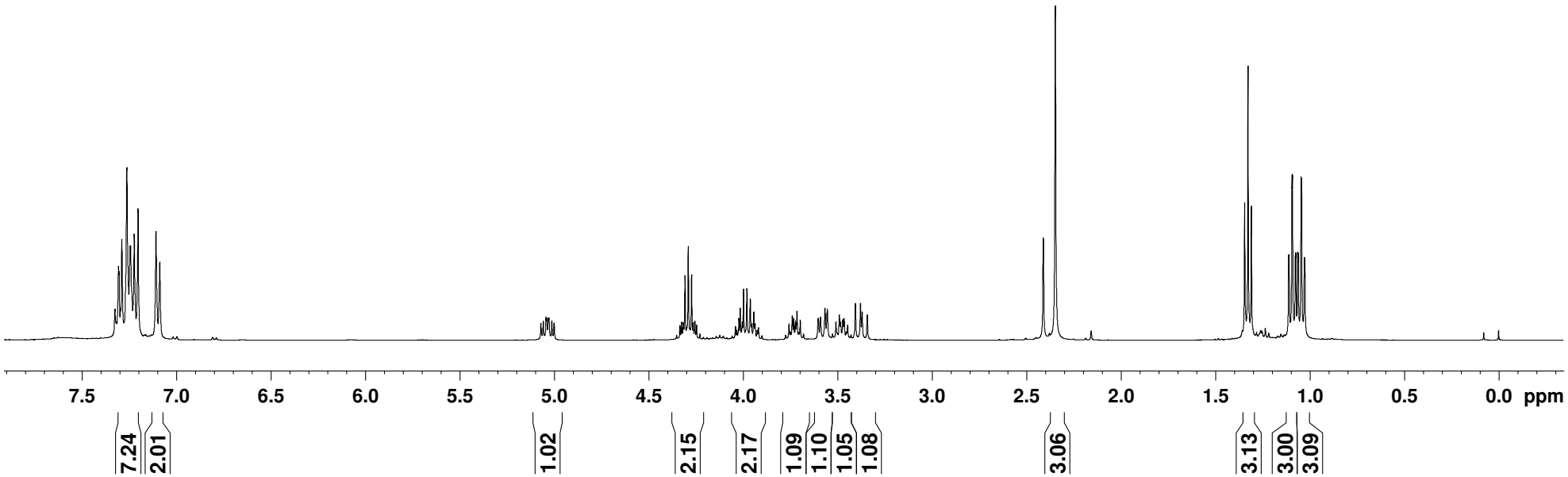
^{31}P NMR (162 MHz, $CDCl_3$)

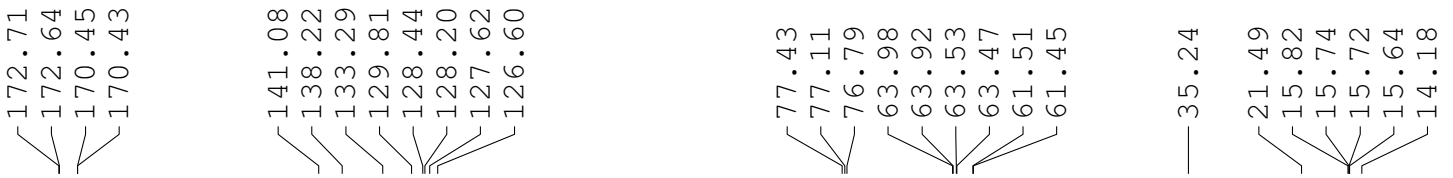


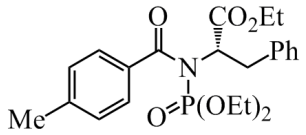


6a

^{1}H NMR (400 MHz, $CDCl_3$)

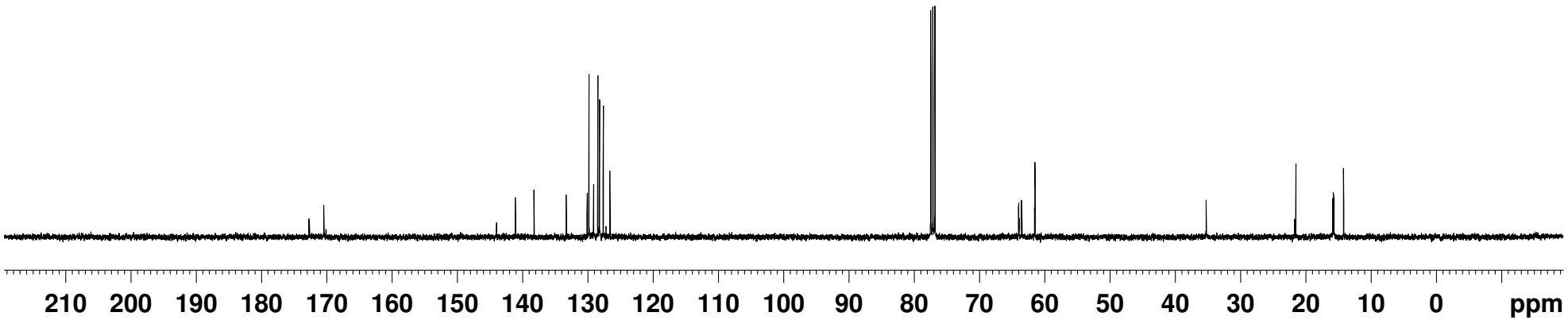


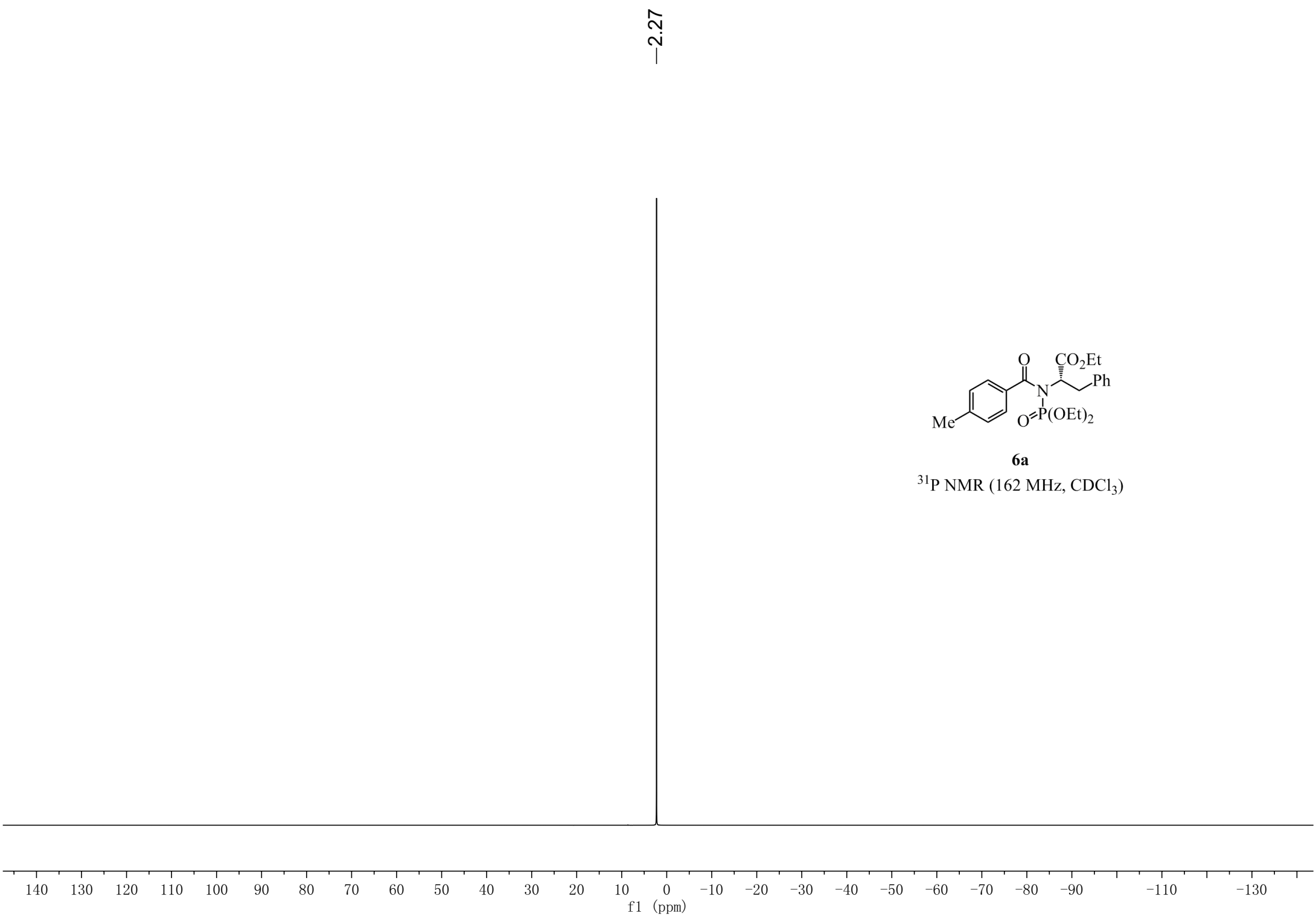




6a

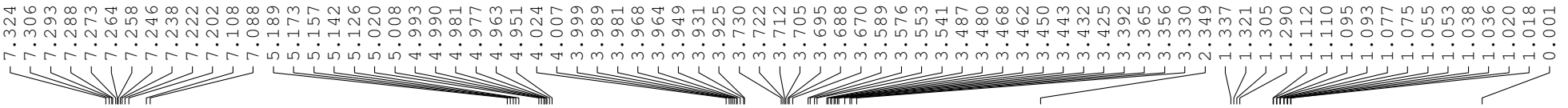
^{13}C NMR (100 MHz, $CDCl_3$)

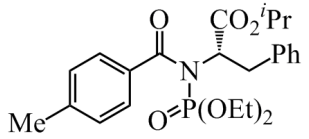




6a

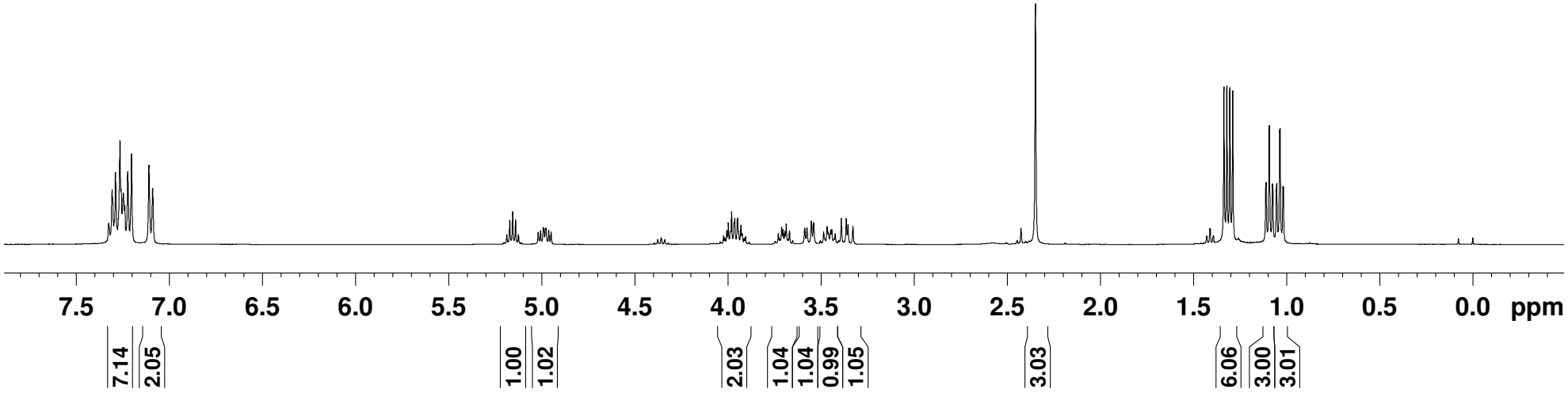
^{31}P NMR (162 MHz, $CDCl_3$)

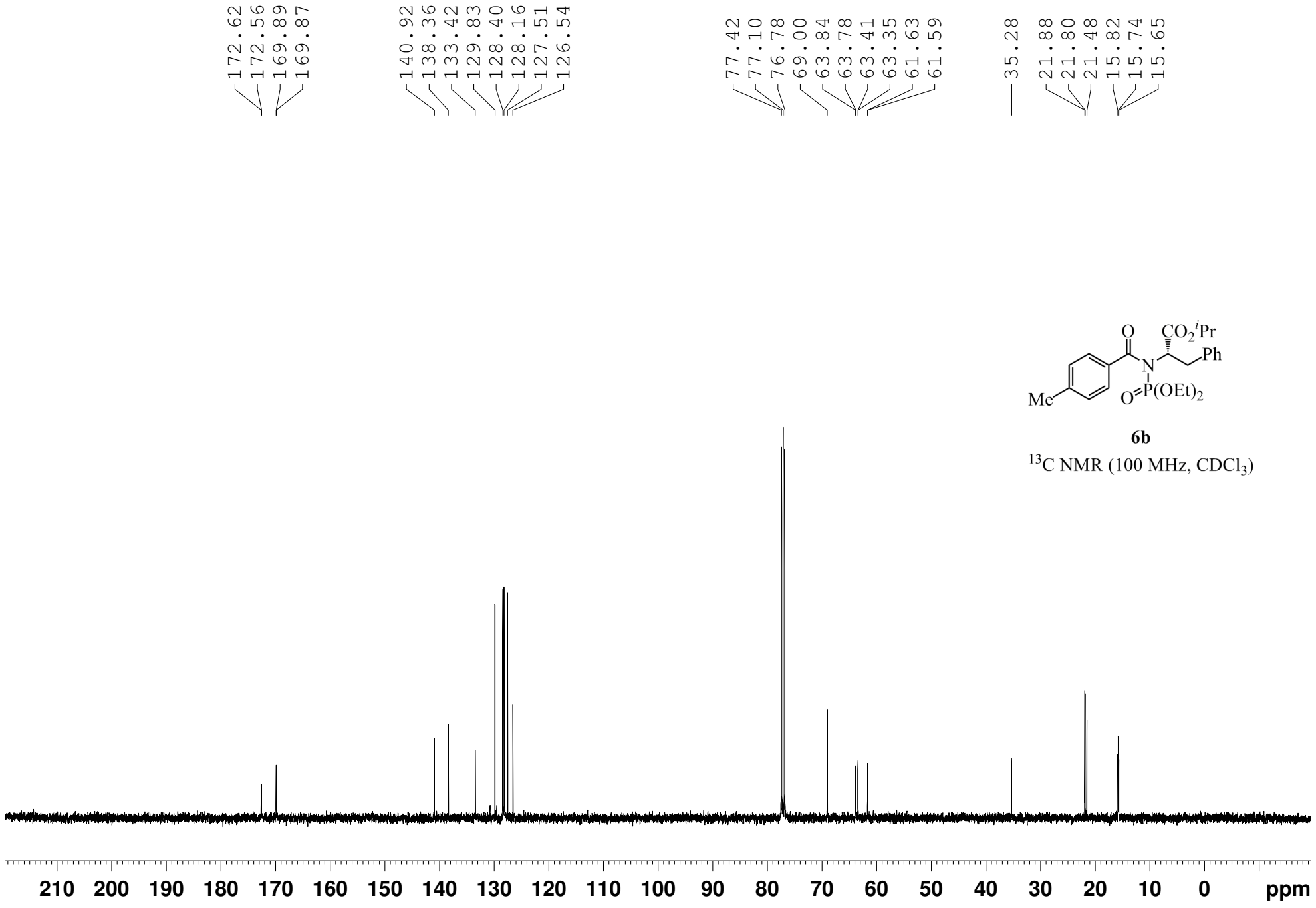




6b

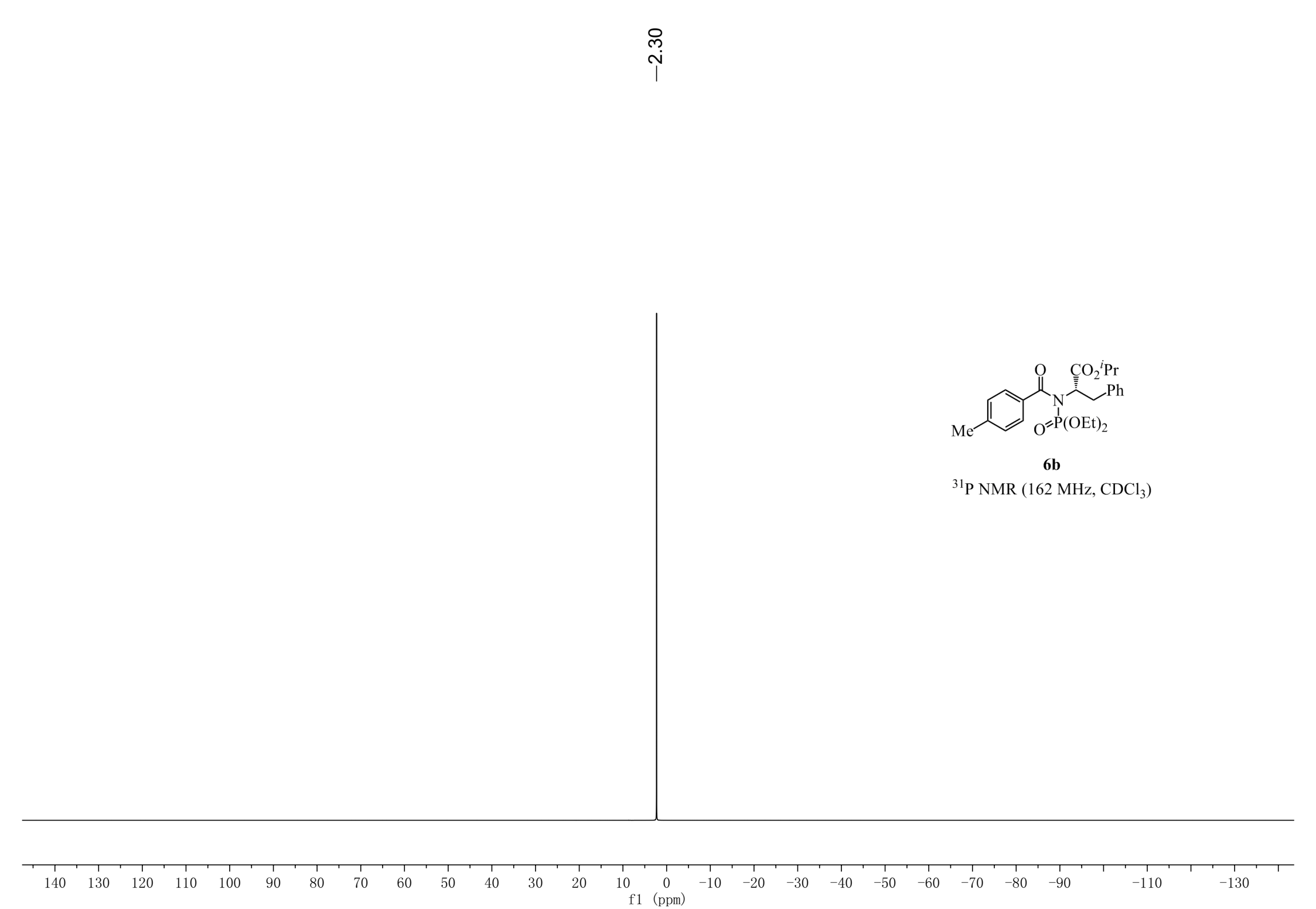
^{1}H NMR (400 MHz, $CDCl_3$)





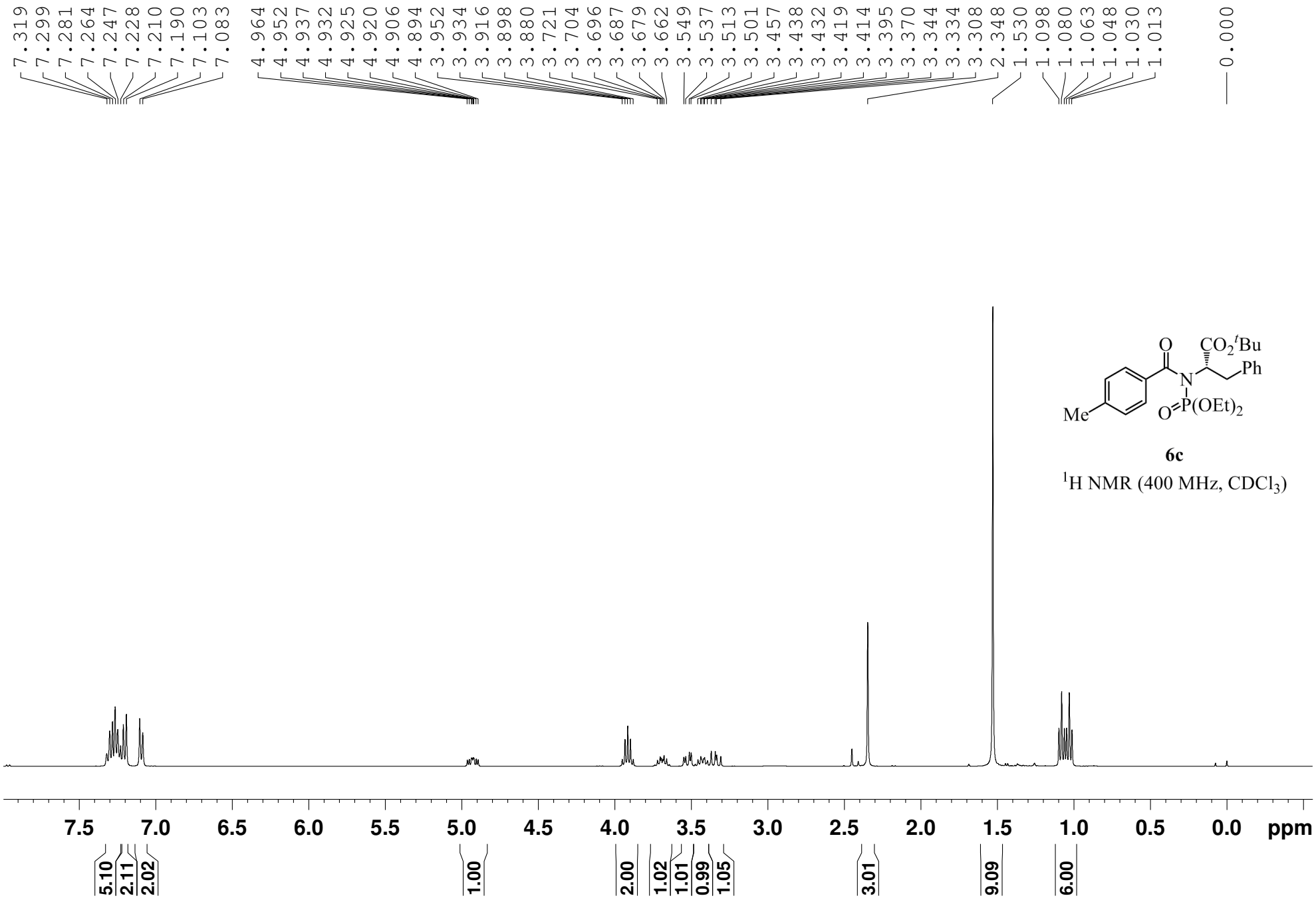
6b

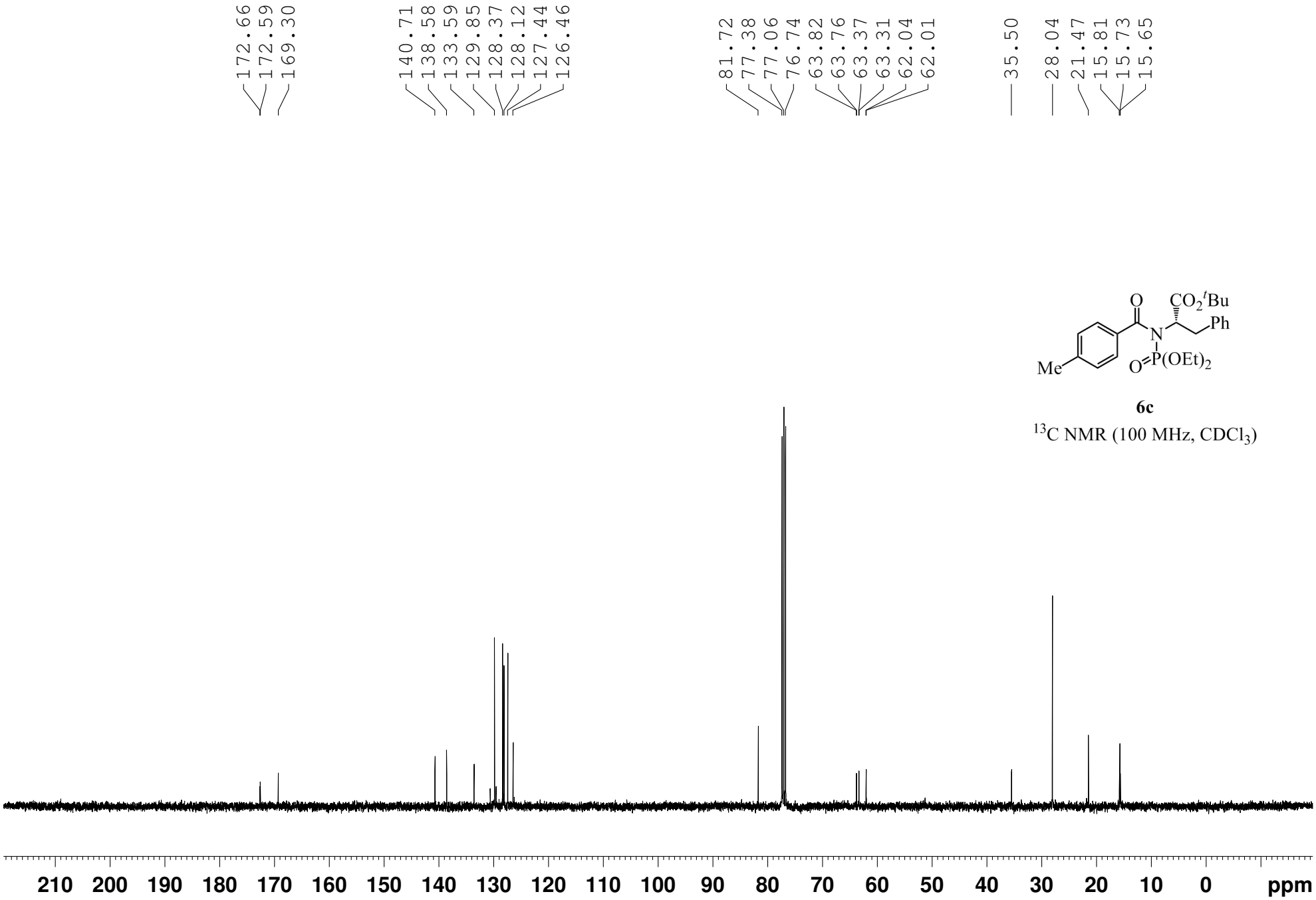
^{13}C NMR (100 MHz, $CDCl_3$)



6b

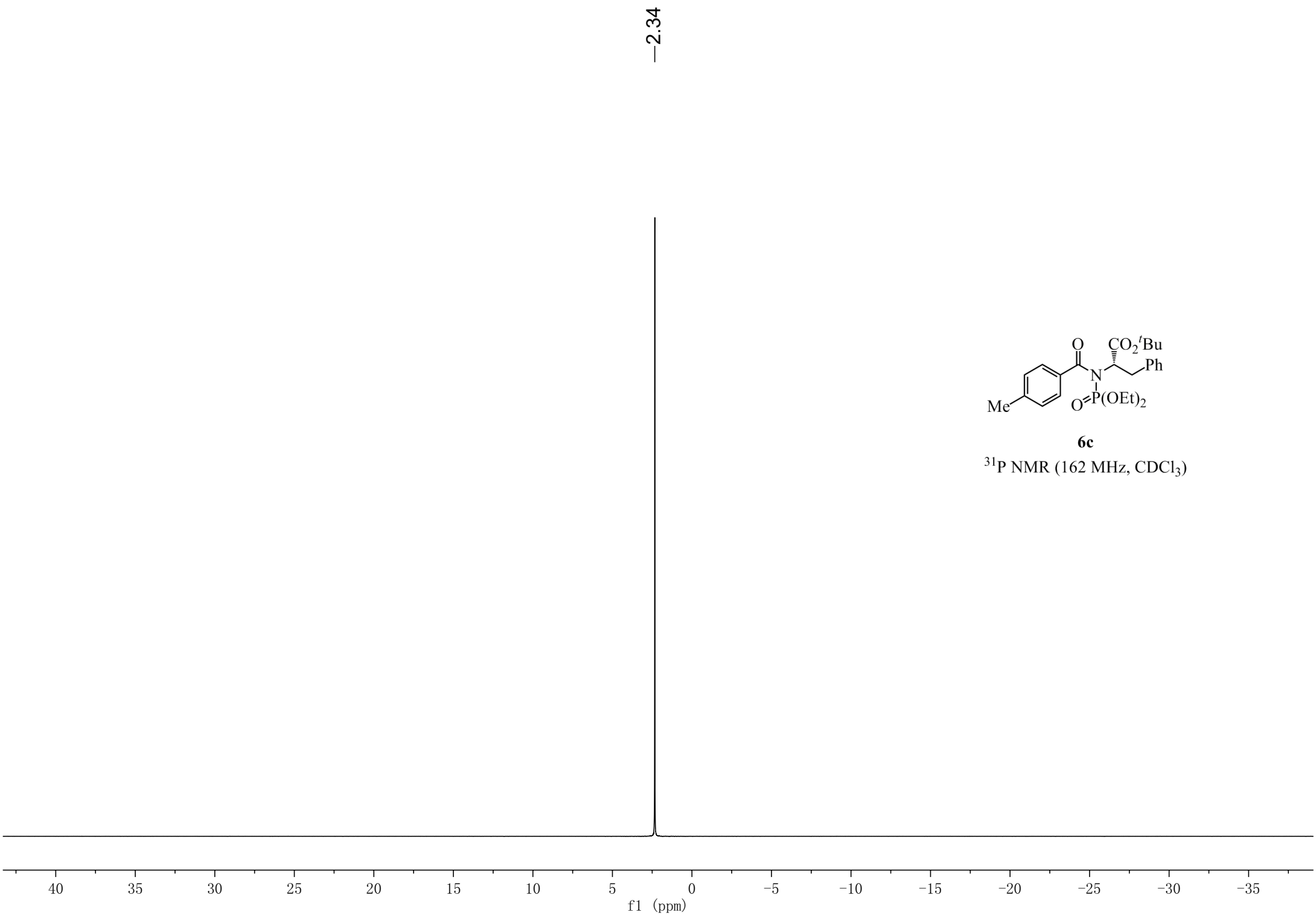
^{31}P NMR (162 MHz, $CDCl_3$)


7.319
7.299
7.281
7.264
7.247
7.228
7.210
7.190
7.103
7.083
4.964
4.952
4.937
4.932
4.925
4.920
4.906
4.894
3.952
3.934
3.916
3.898
3.880
3.721
3.704
3.696
3.687
3.679
3.662
3.549
3.537
3.513
3.501
3.457
3.438
3.432
3.419
3.414
3.395
3.370
3.344
3.334
3.308
2.348
1.530
1.098
1.080
1.063
1.048
1.030
1.013
0.000
O
CO2tBu
Ph
N
O=P(OEt)2
Me
6c
1H NMR (400 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.10
2.11
2.02
1.00
2.00
1.02
1.01
0.99
1.05
3.01
9.09
6.00



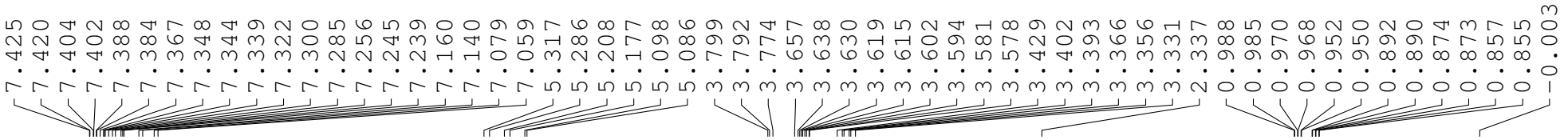
6c

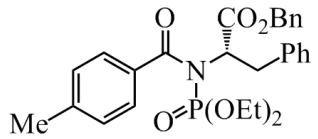
^{13}C NMR (100 MHz, $CDCl_3$)



6c

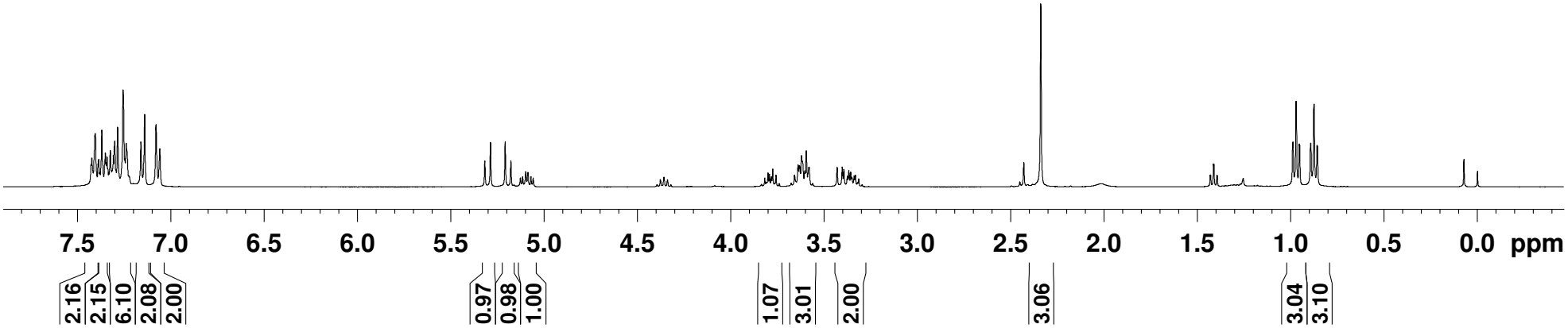
^{31}P NMR (162 MHz, $CDCl_3$)

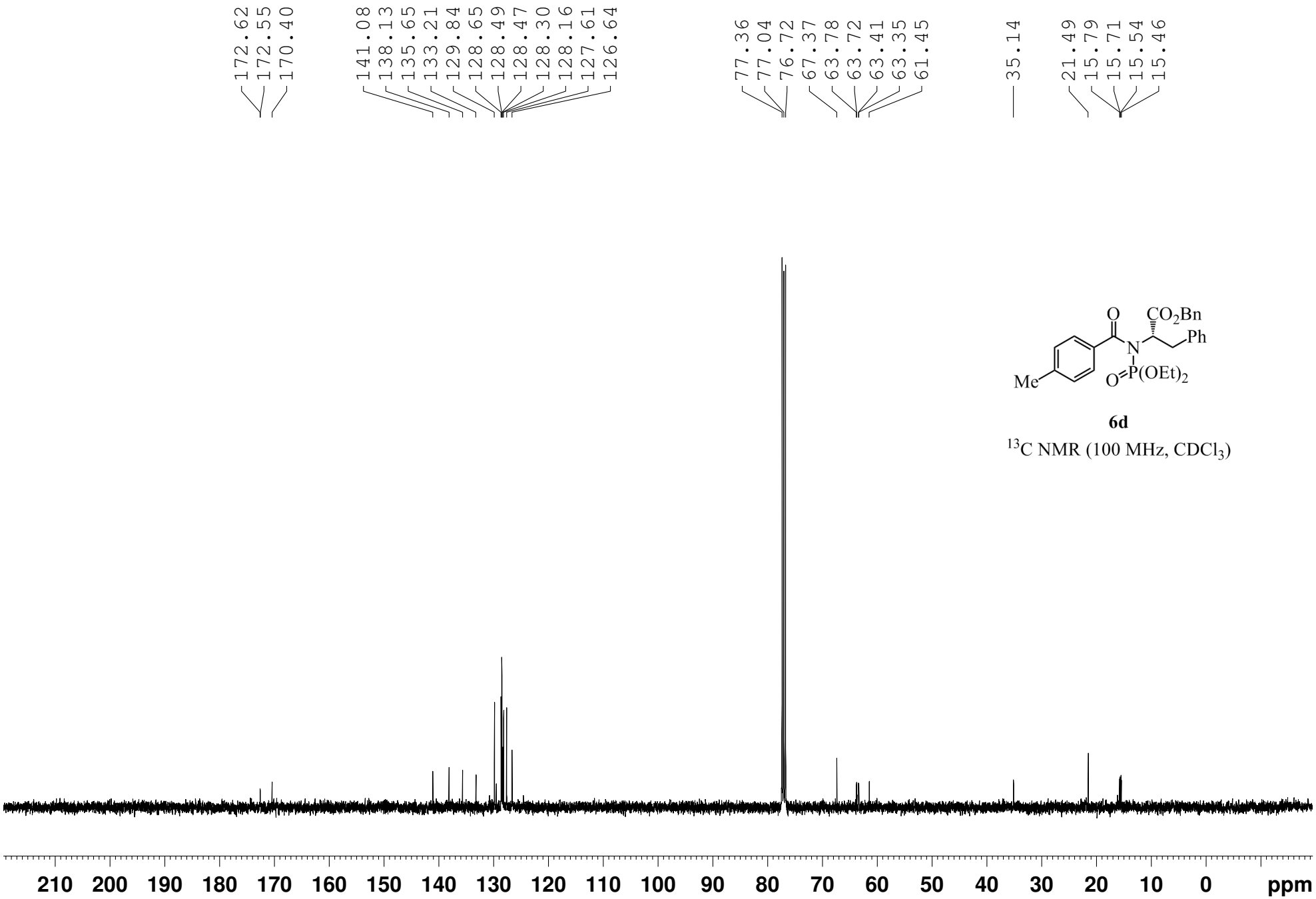




6d

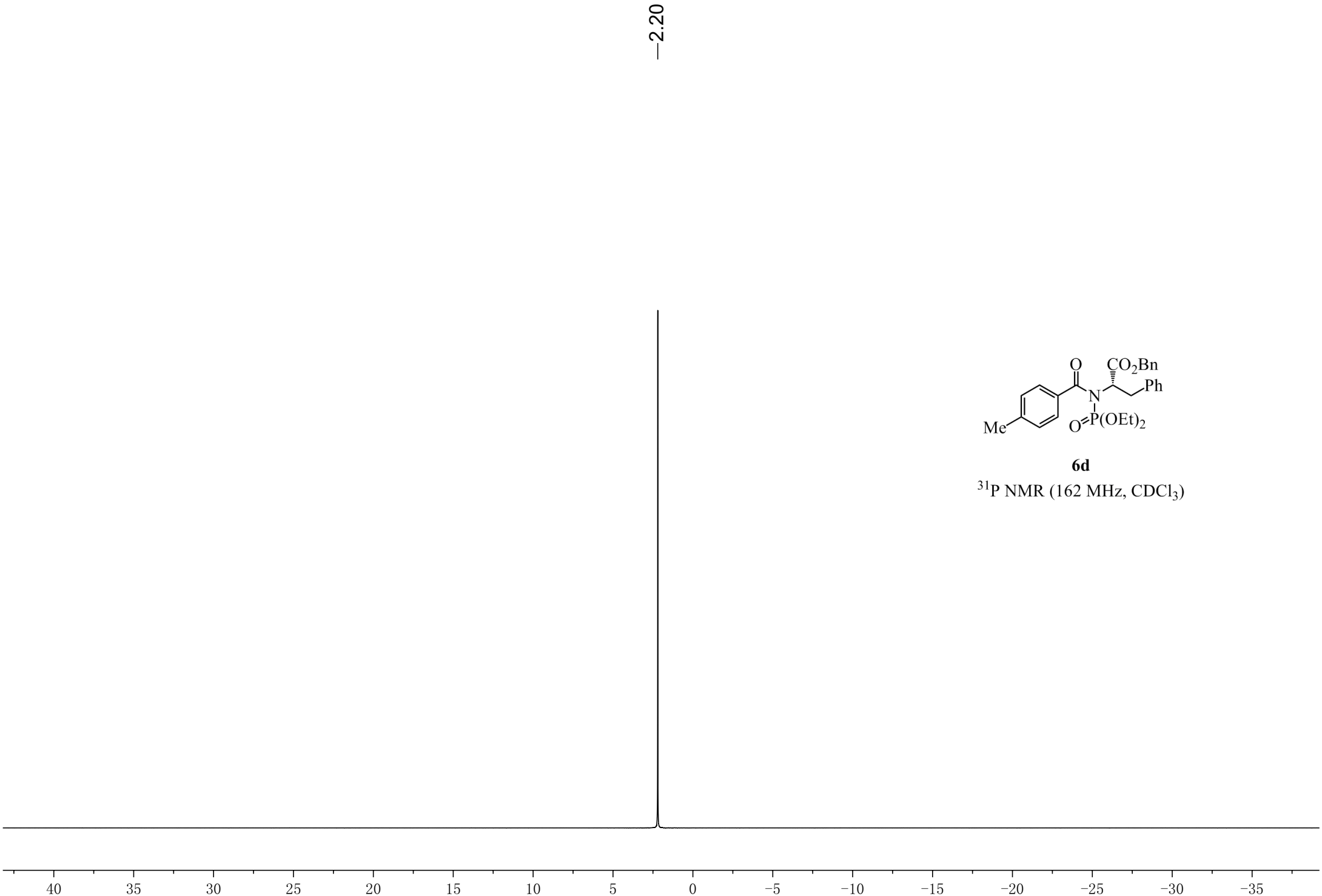
^{1}H NMR (400 MHz, $CDCl_3$)





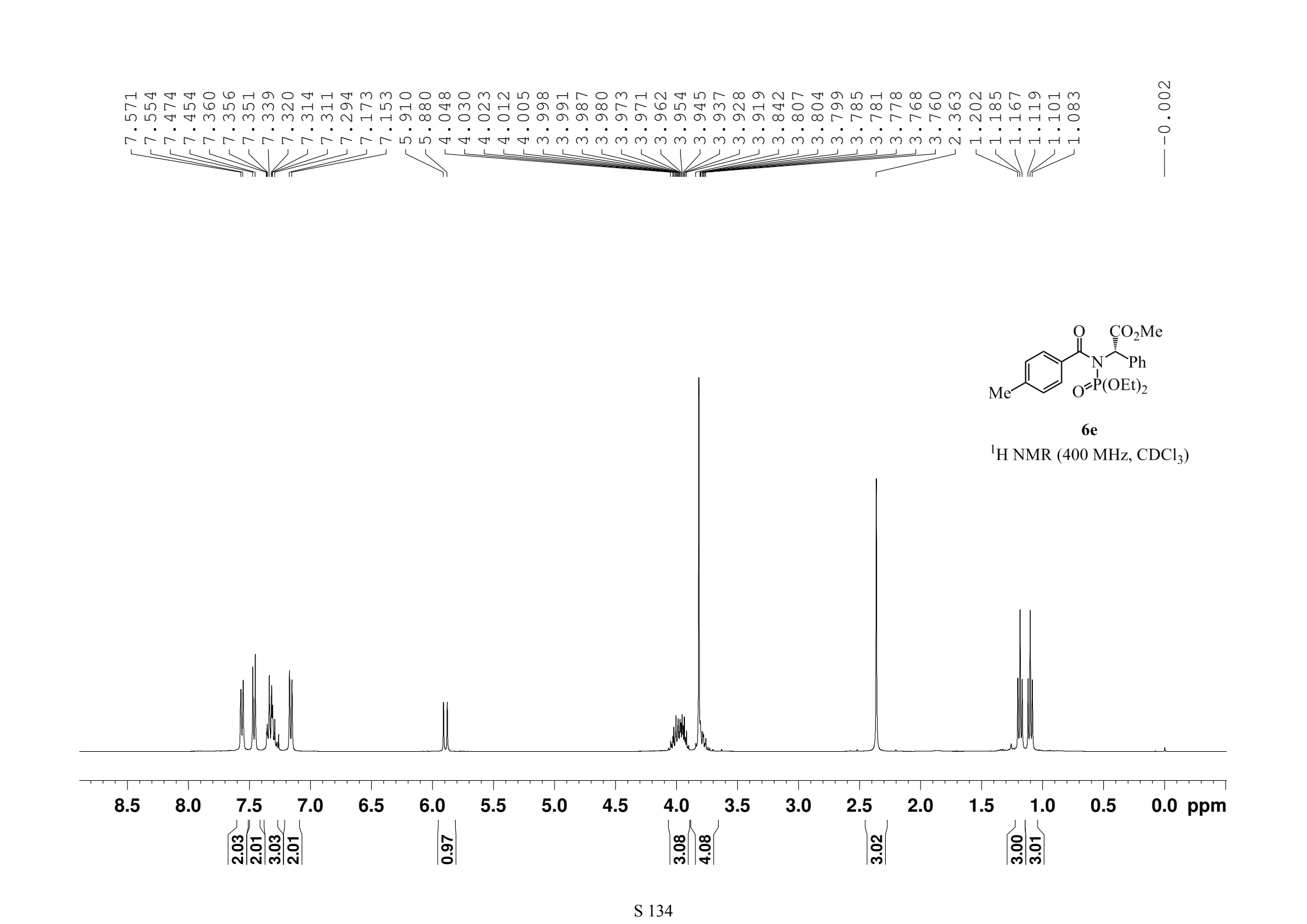
6d

^{13}C NMR (100 MHz, $CDCl_3$)



6d

^{31}P NMR (162 MHz, $CDCl_3$)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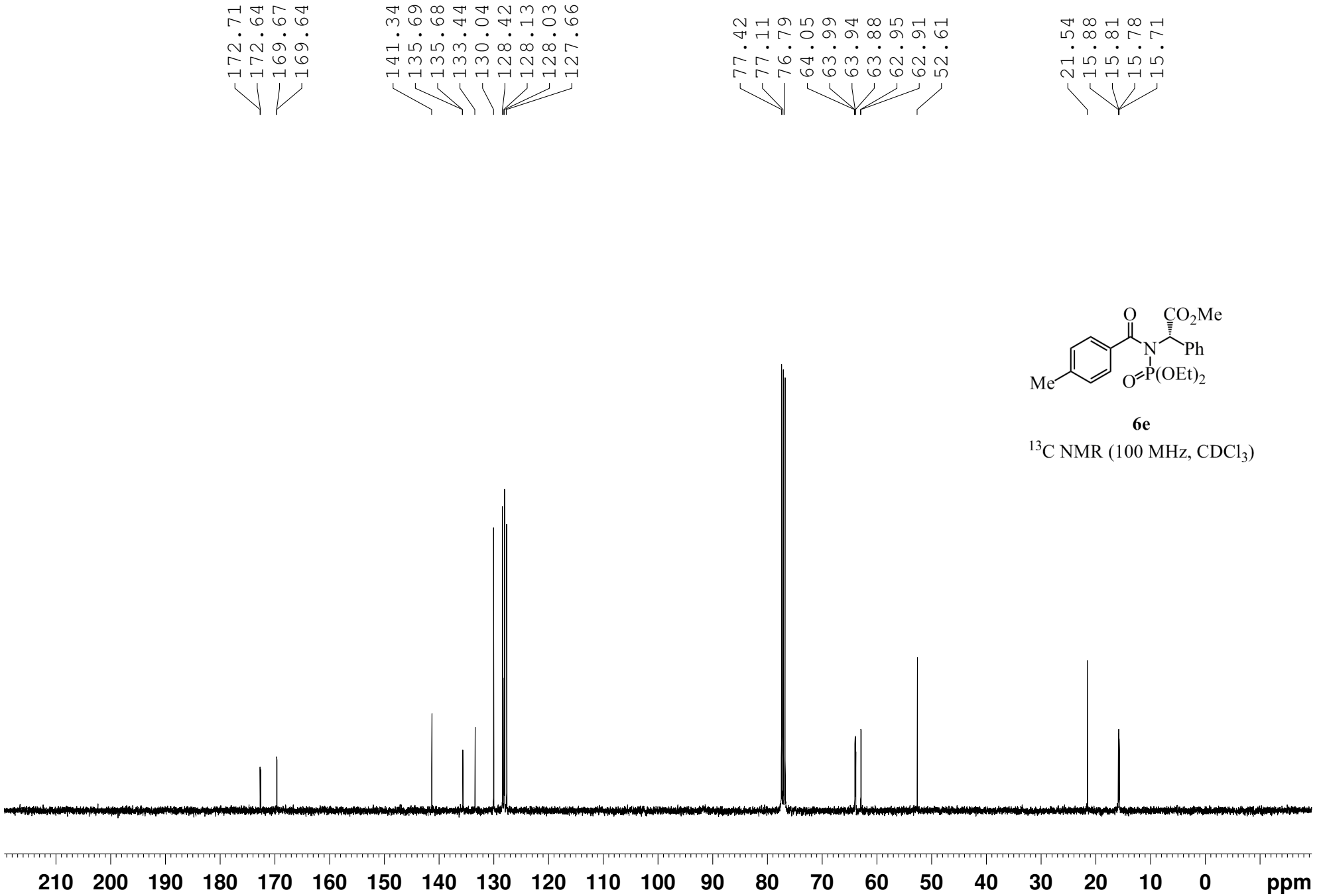
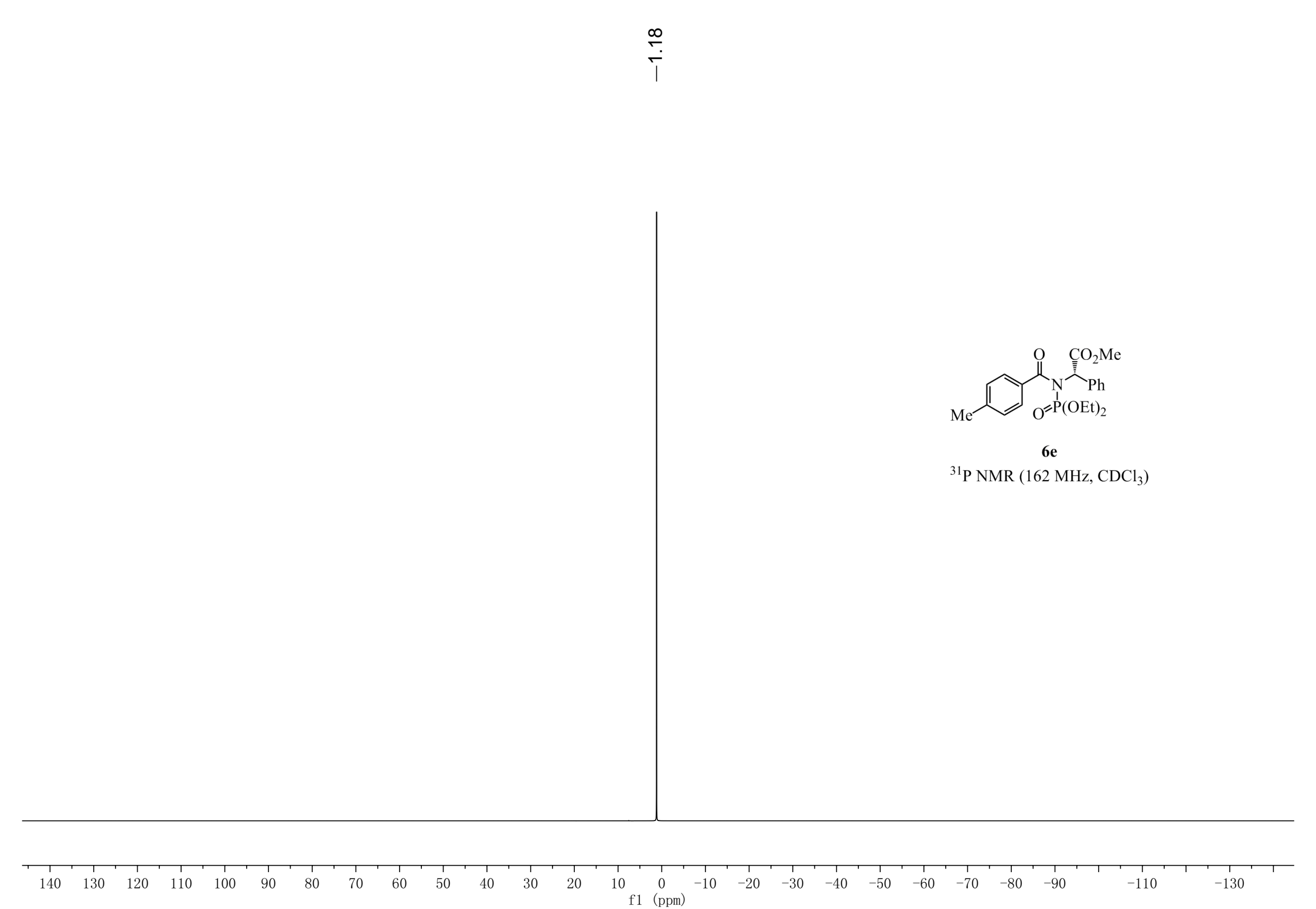
7.554
7.474
7.454
7.360
7.356
7.351
7.339
7.320
7.314
7.311
7.294
7.173
7.153
5.910
5.880
4.048
4.030
4.023
4.012
4.005
3.998
3.991
3.987
3.980
3.973
3.971
3.962
3.954
3.945
3.937
3.928
3.919
3.842
3.807
3.804
3.799
3.785
3.781
3.778
3.768
3.760
2.363
1.202
1.185
1.167
1.119
1.101
1.083
-0.002
O
CO2Me
N
Ph
O
P(OEt)2
Me
6e
1H NMR (400 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.03
2.01
3.03
2.01
0.97
3.08
4.08
3.02
3.00
3.01



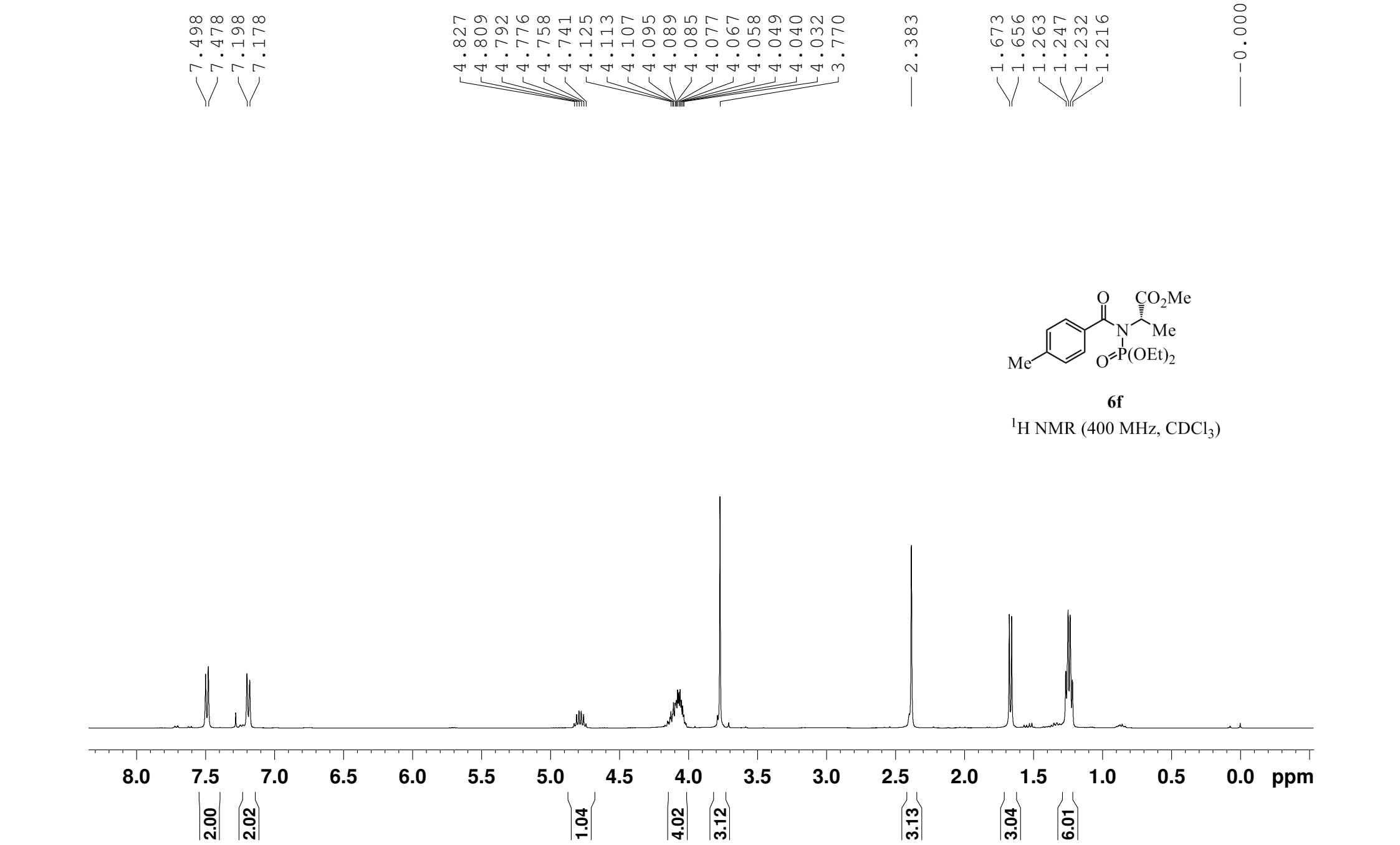
6e

^{13}C NMR (100 MHz, $CDCl_3$)



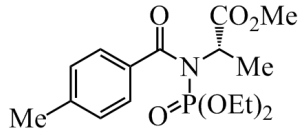
6e

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



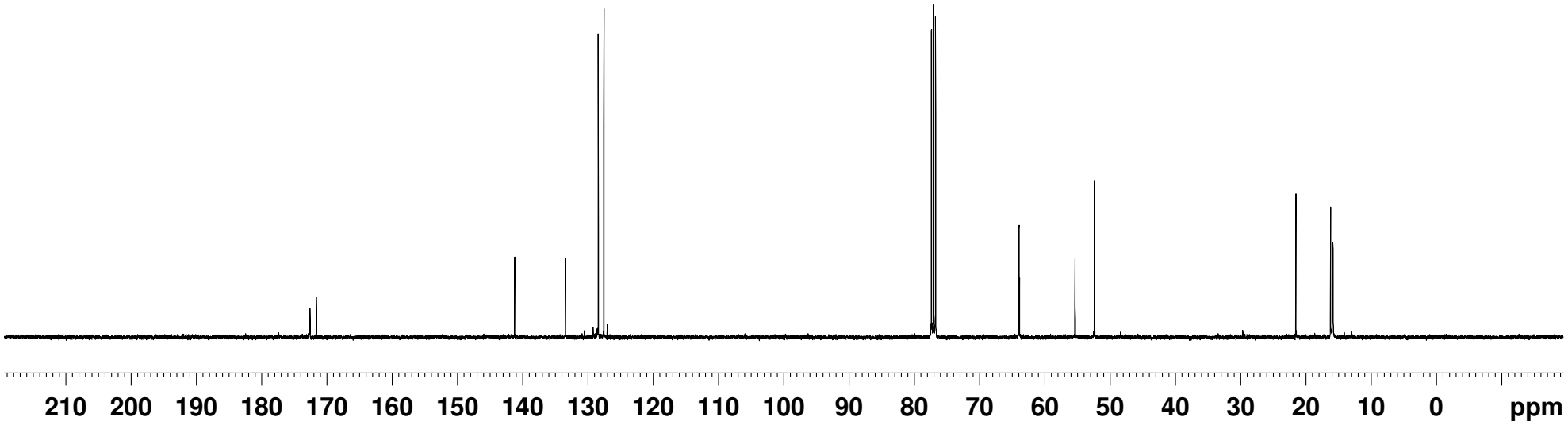
6f

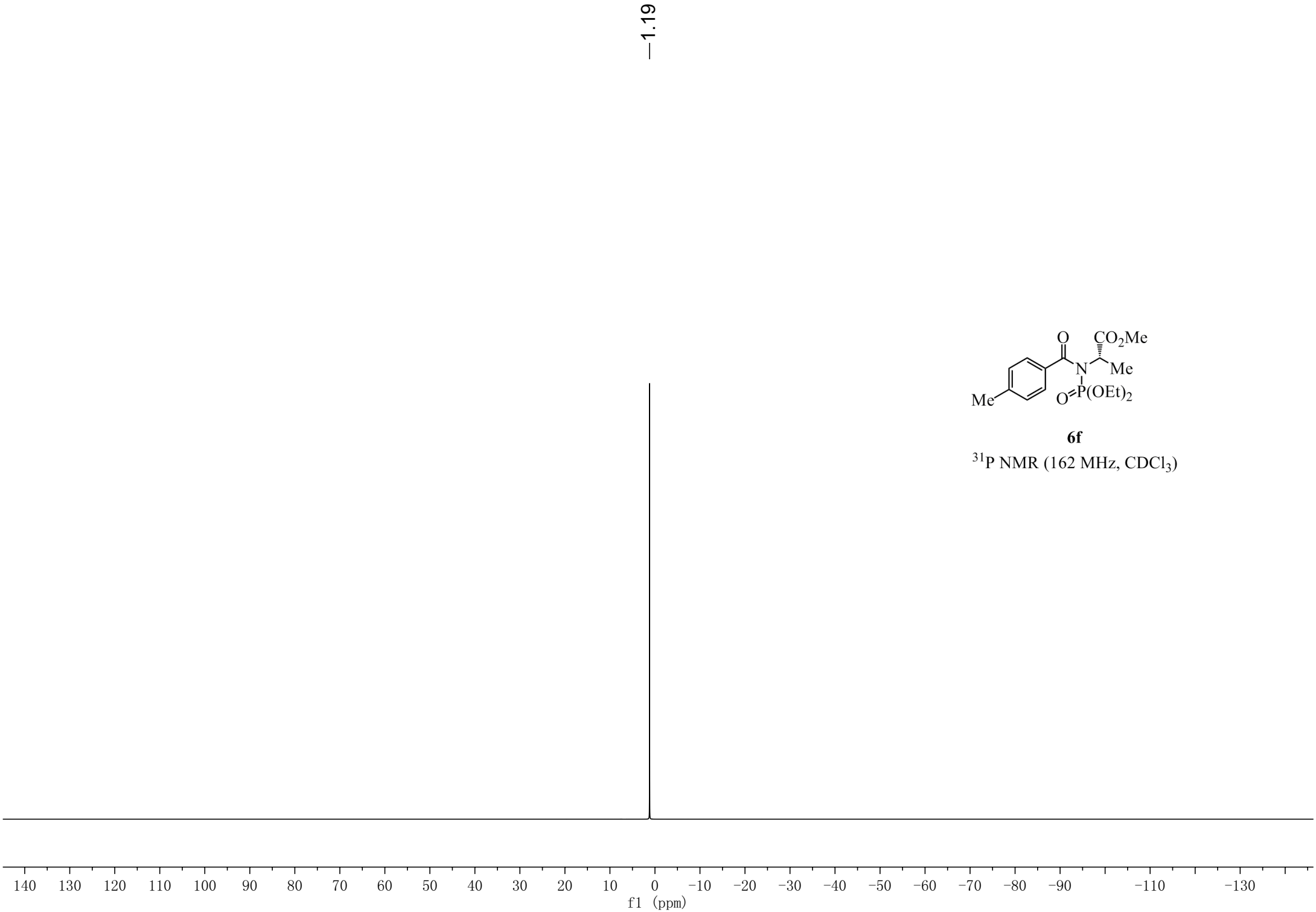
^{1}H NMR (400 MHz, $CDCl_3$)



6f

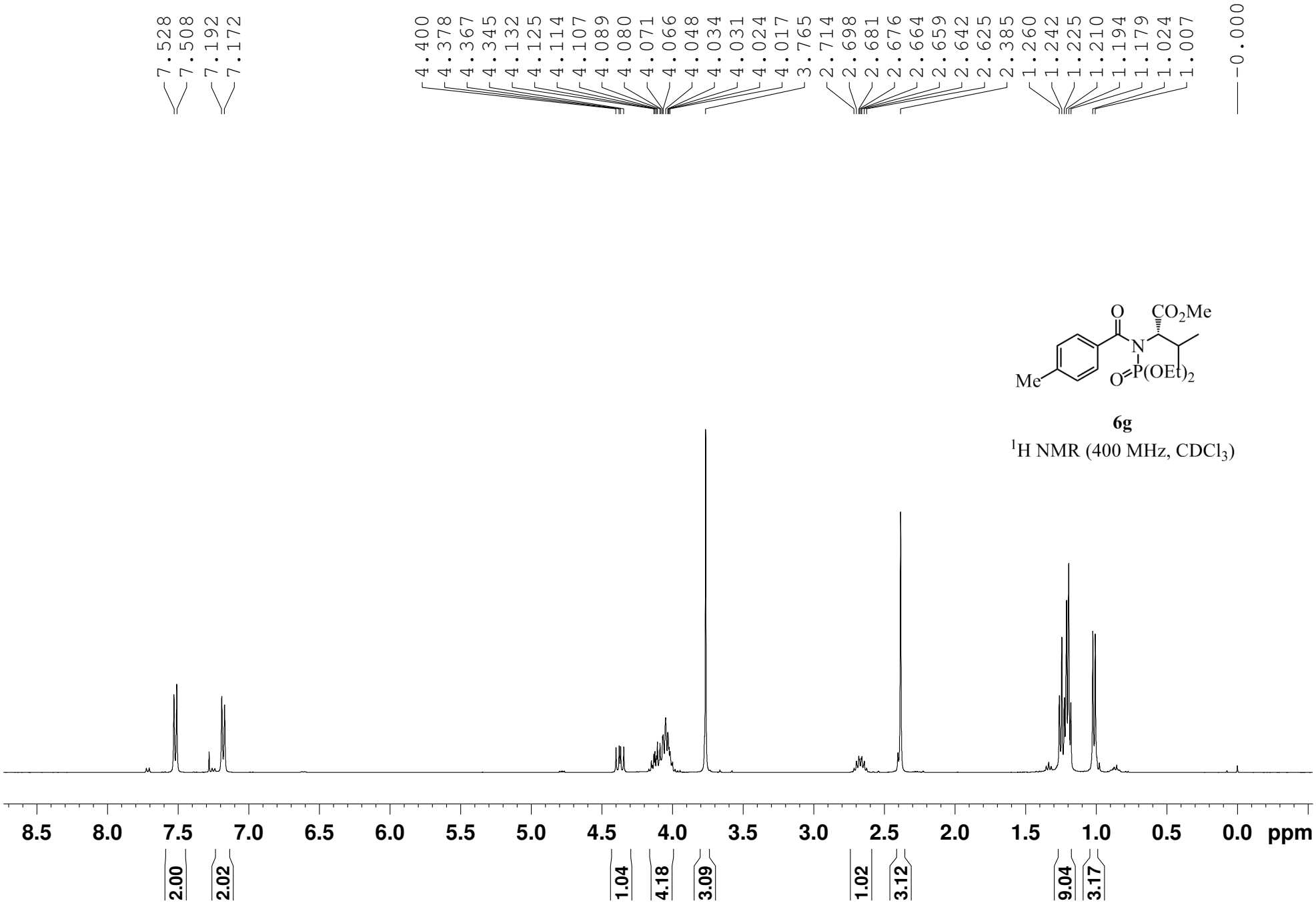
^{13}C NMR (100 MHz, $CDCl_3$)





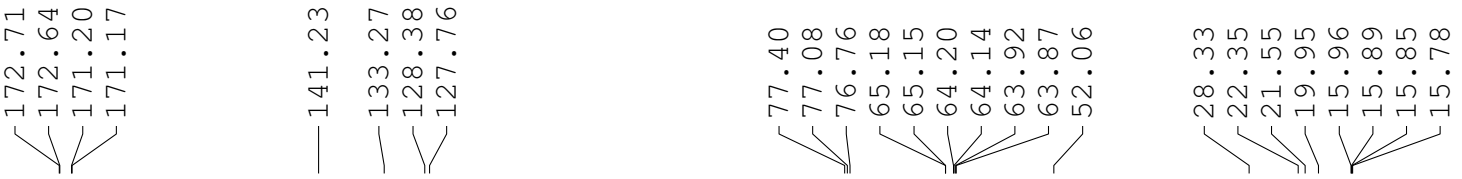
6f

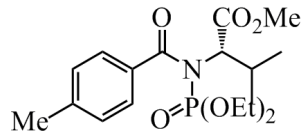
^{31}P NMR (162 MHz, $CDCl_3$)



6g

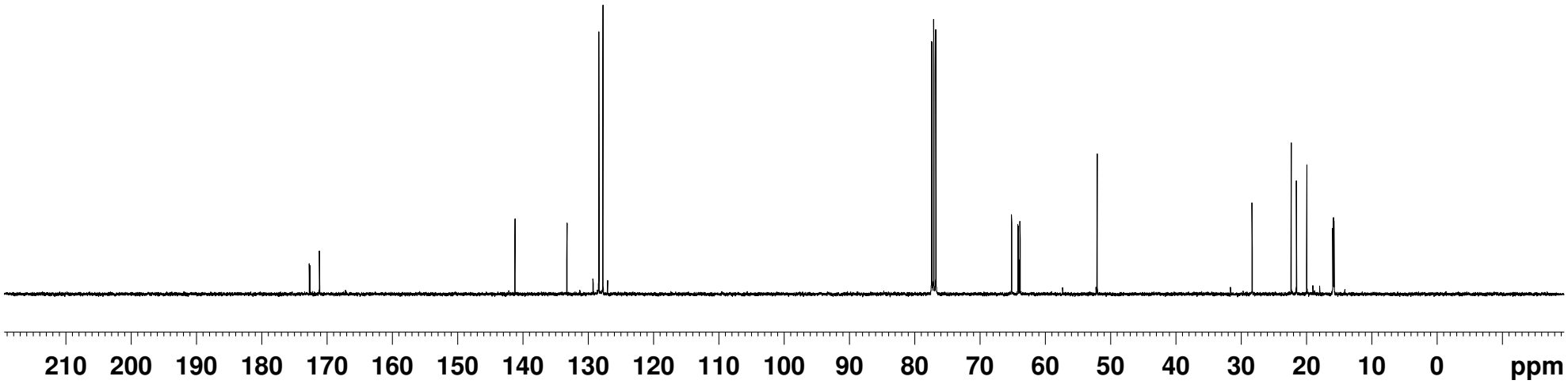
^{1}H NMR (400 MHz, $CDCl_3$)

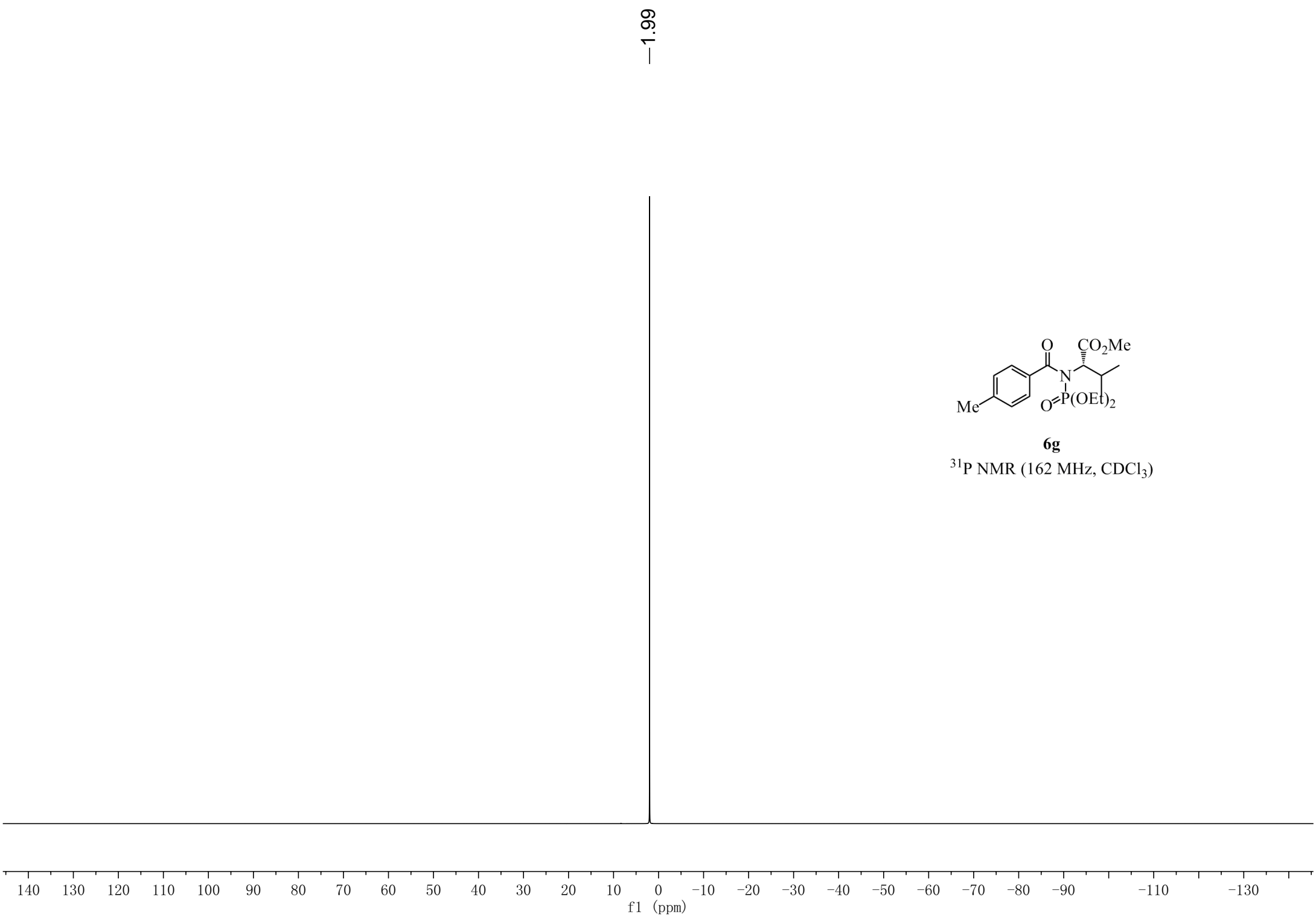




6g

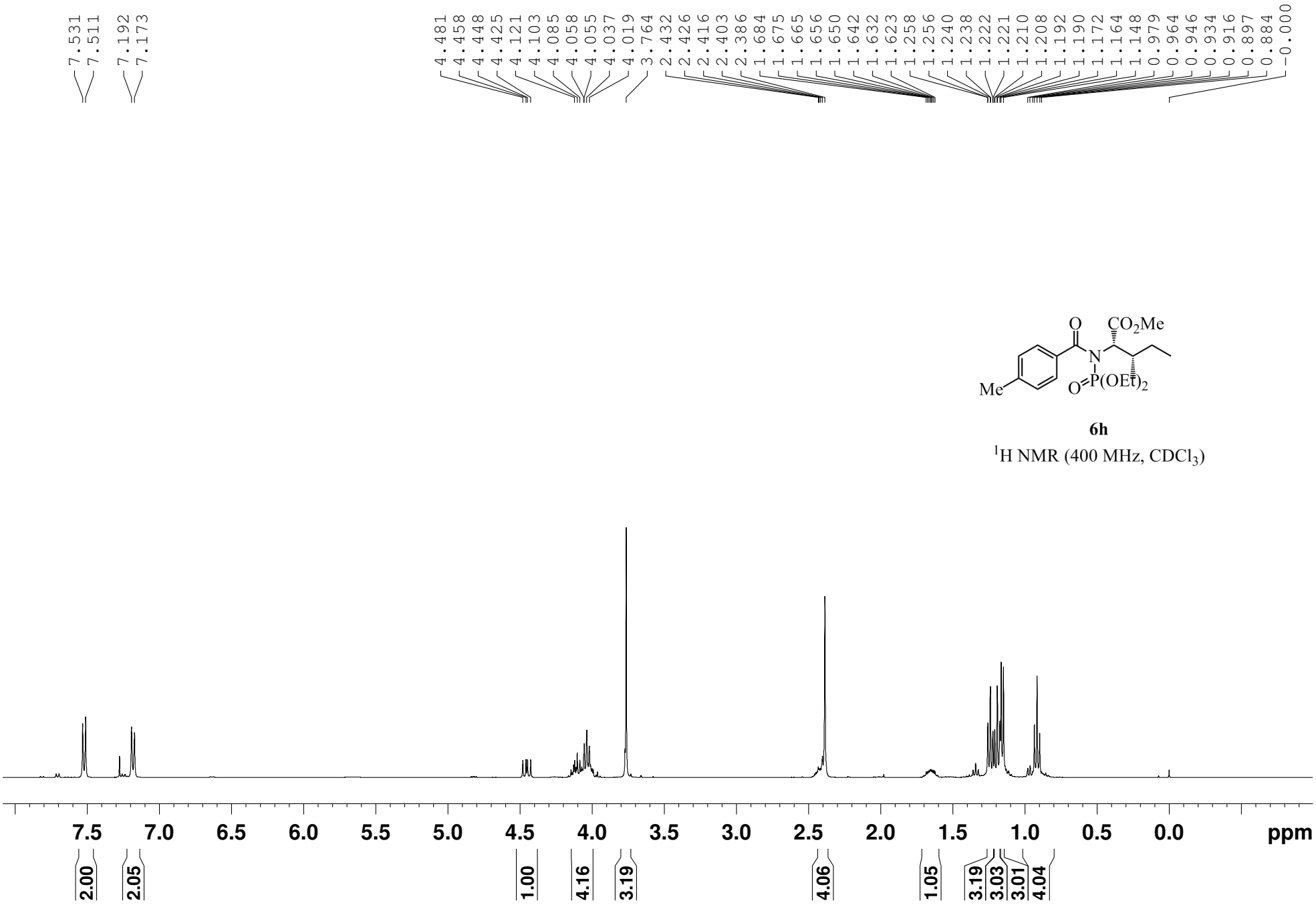
^{13}C NMR (100 MHz, $CDCl_3$)





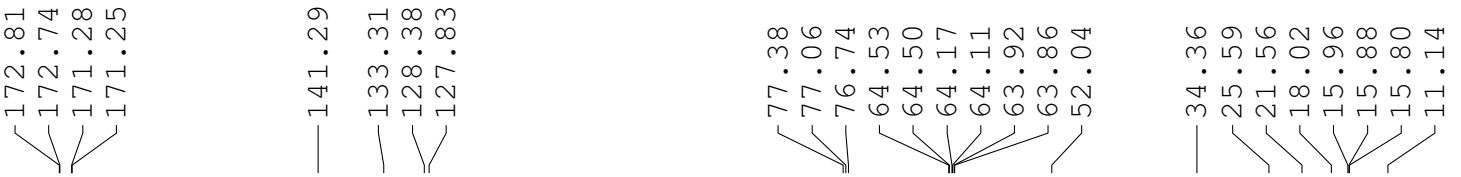
6g

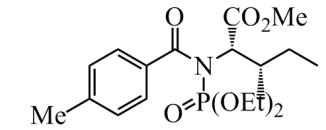
^{31}P NMR (162 MHz, $CDCl_3$)



6h

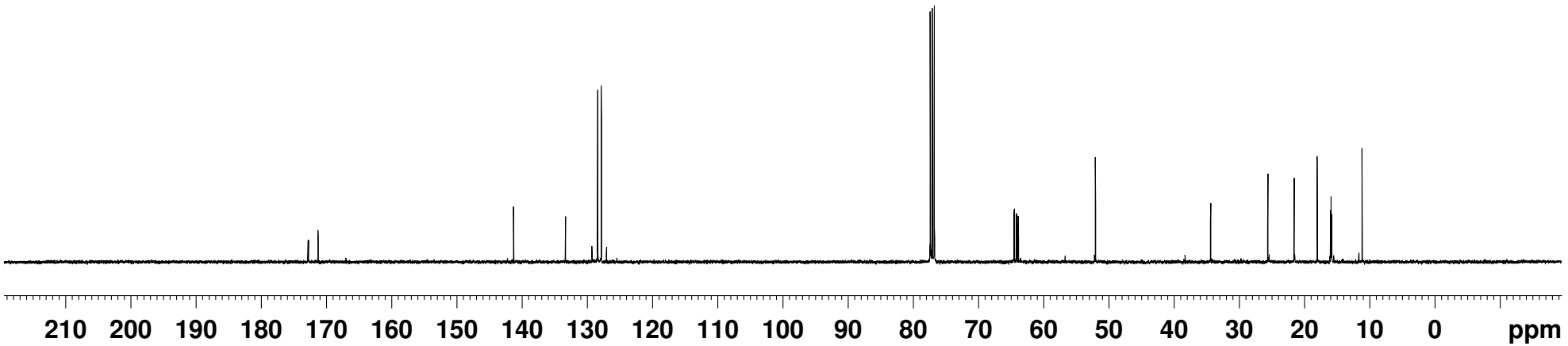
^{1}H NMR (400 MHz, $CDCl_3$)

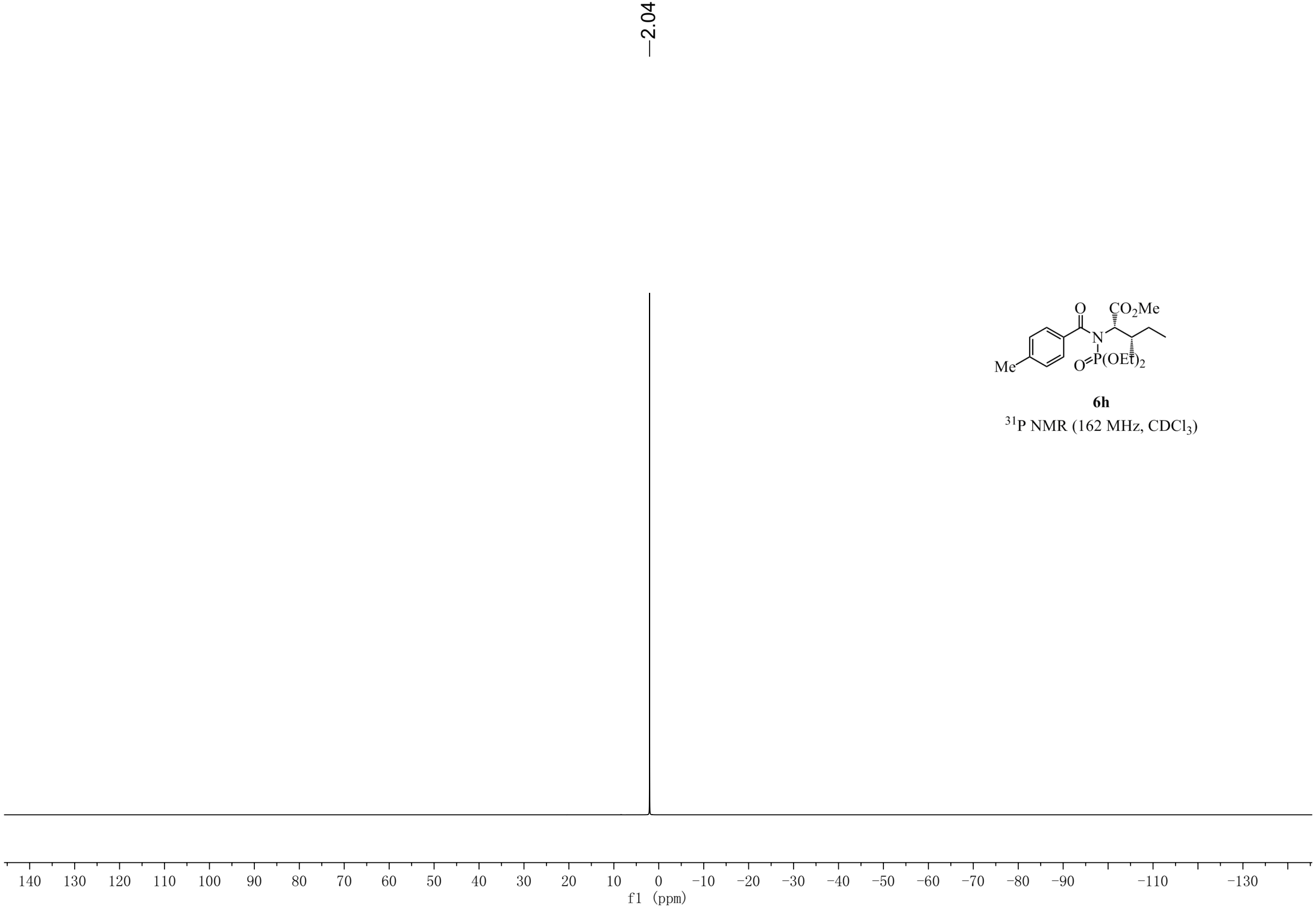




6h

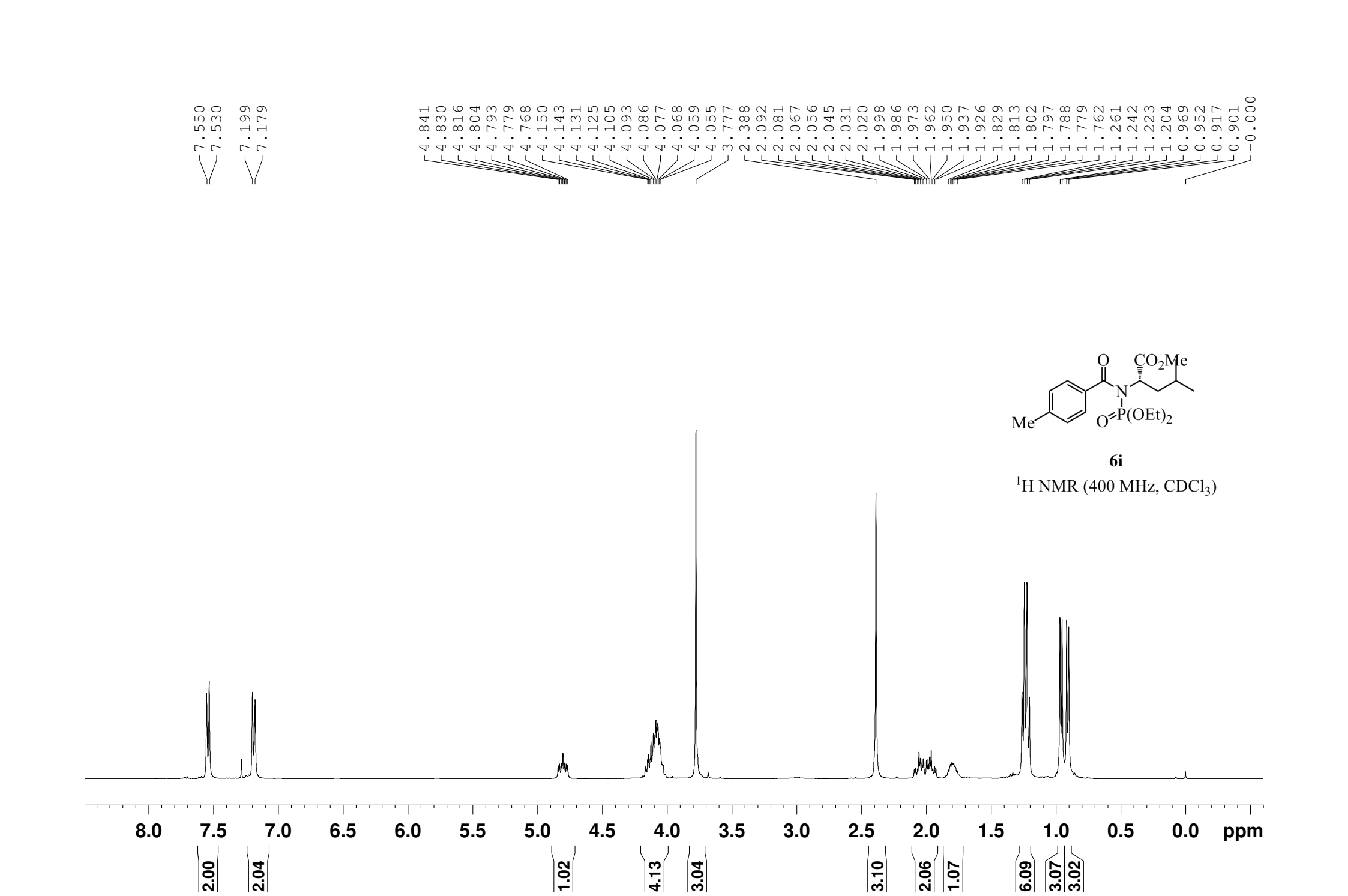
^{13}C NMR (100 MHz, $CDCl_3$)





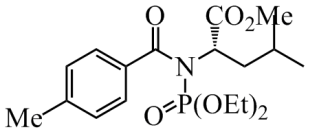
6h

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



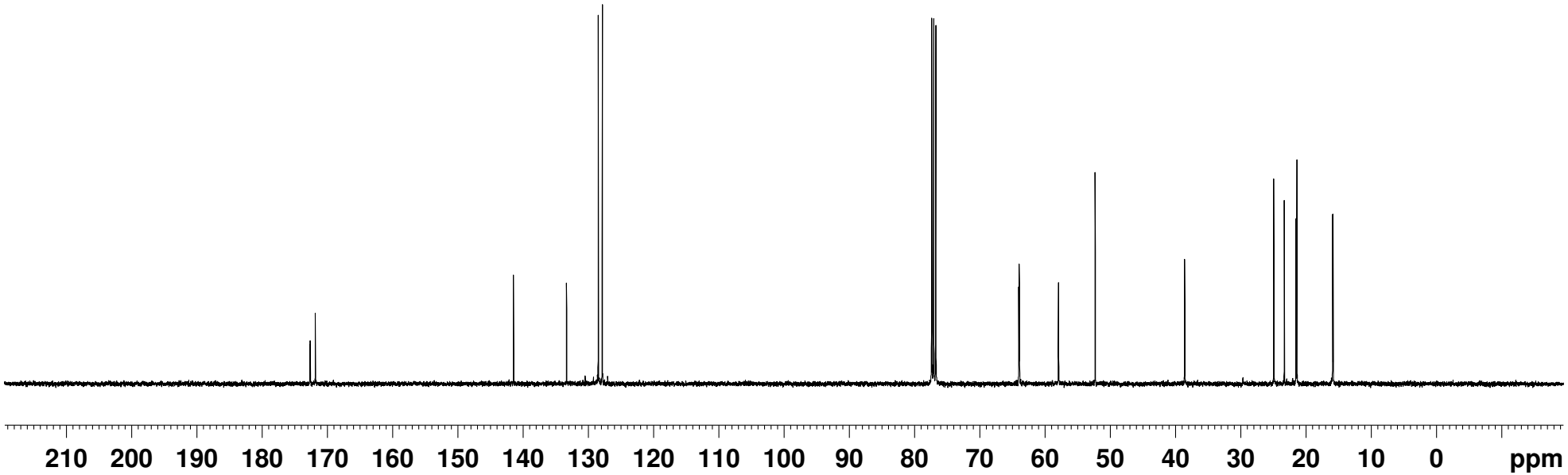
6i

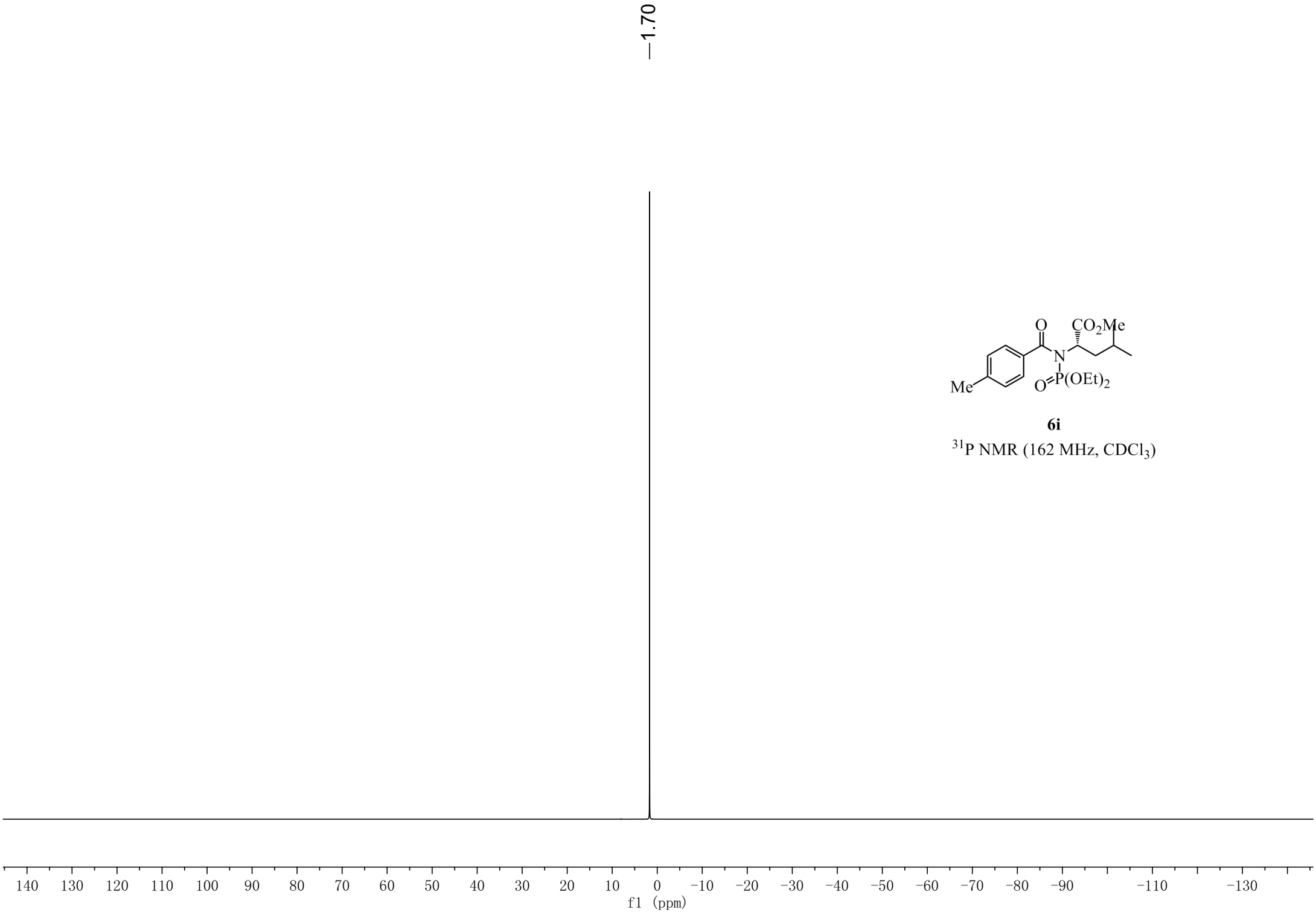
^{1}H NMR (400 MHz, $CDCl_3$)



6i

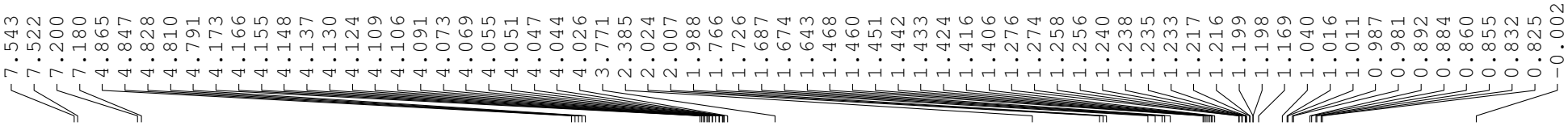
^{13}C NMR (100 MHz, $CDCl_3$)

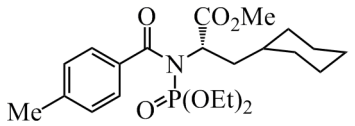




6i

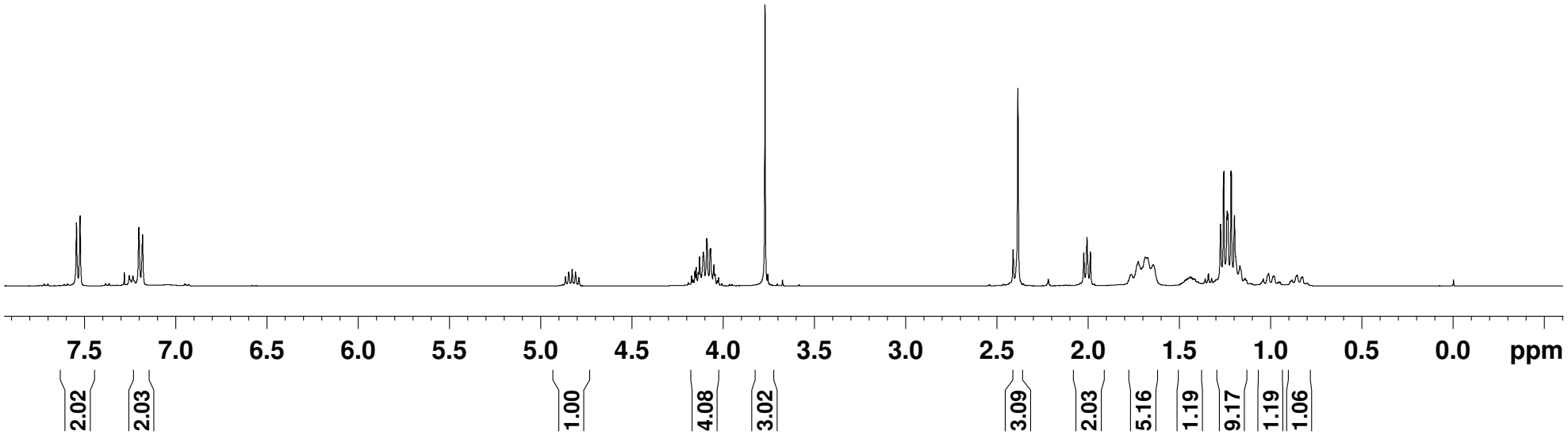
^{31}P NMR (162 MHz, $CDCl_3$)

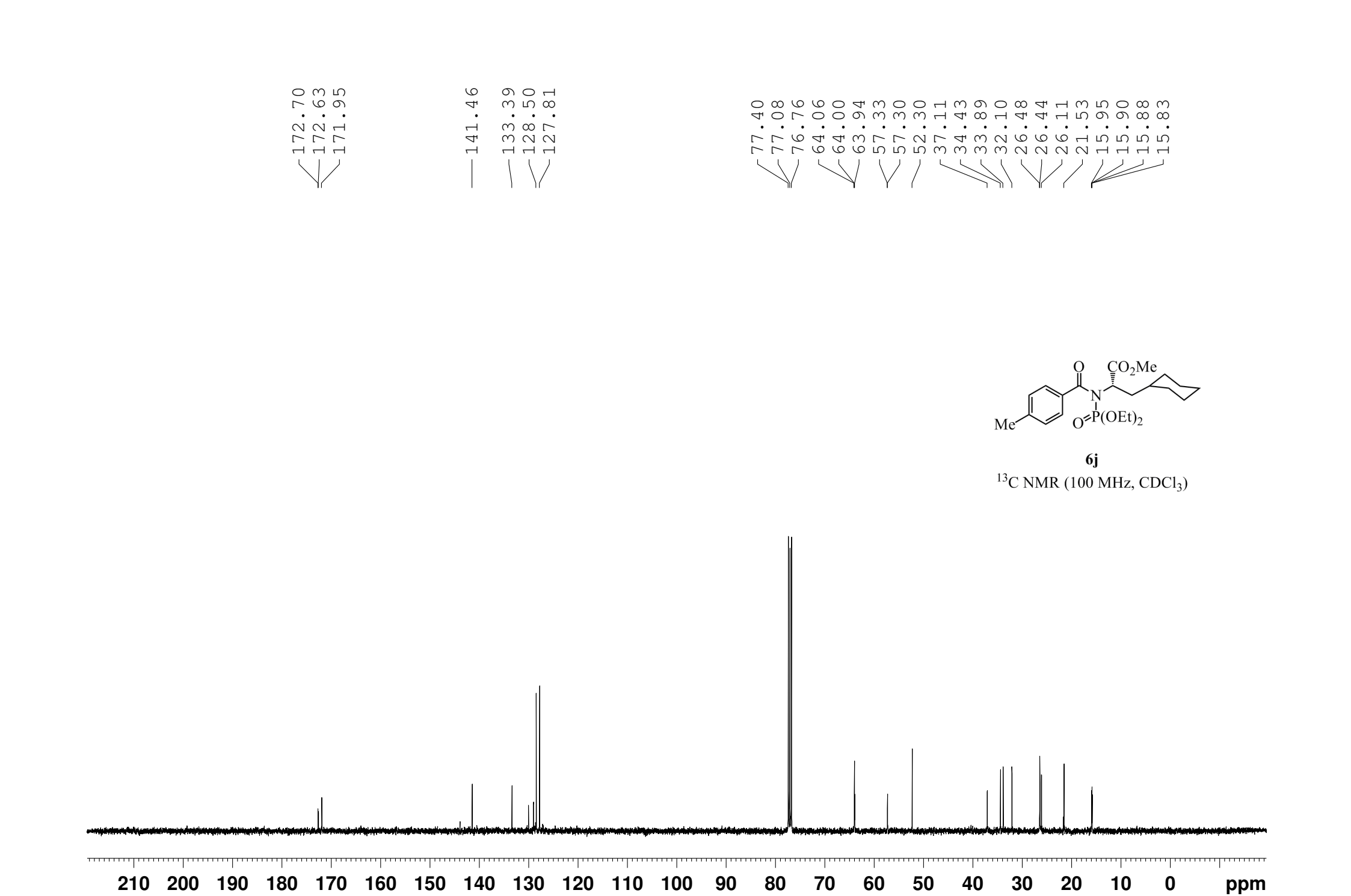




6j

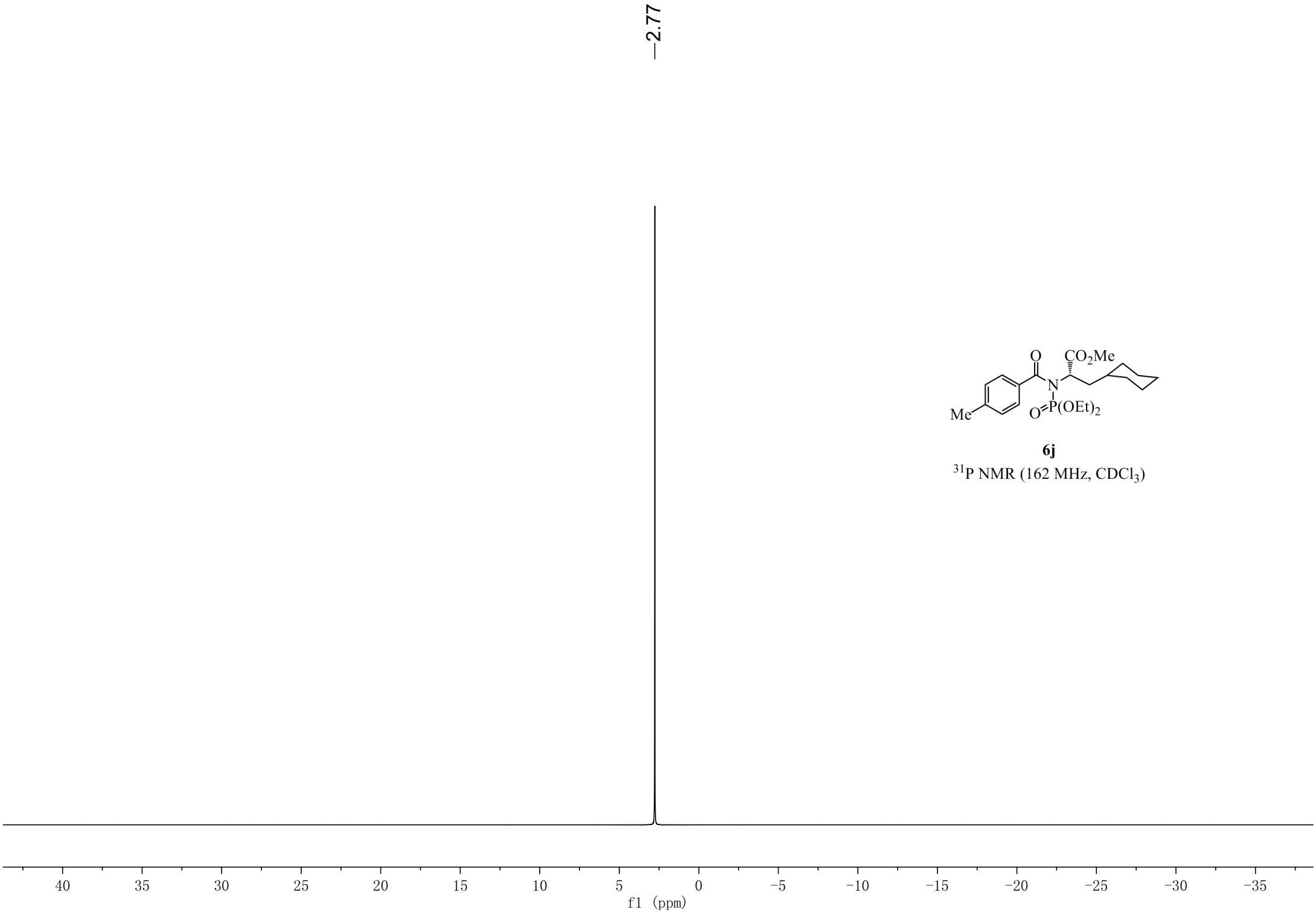
^{1}H NMR (400 MHz, $CDCl_3$)





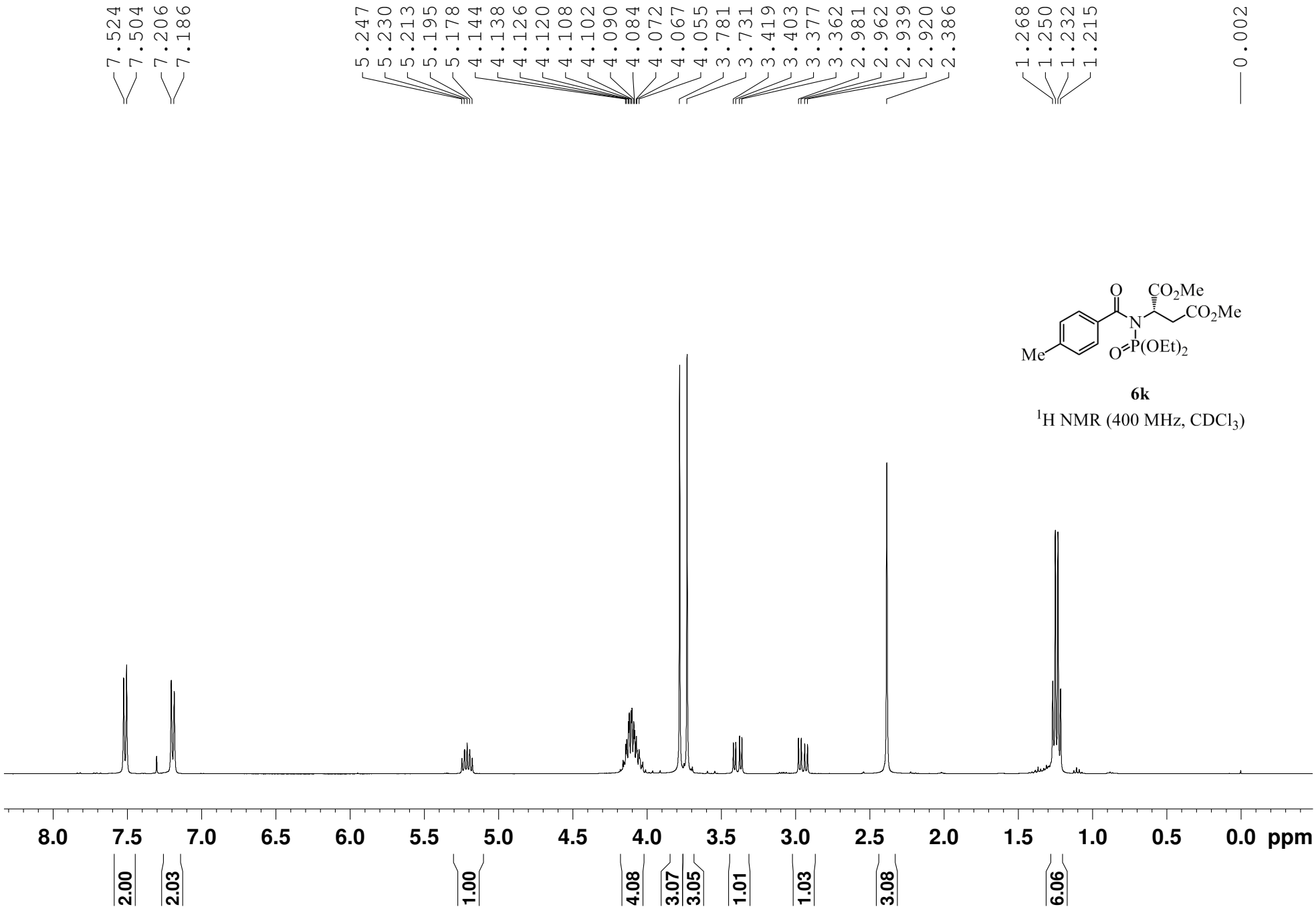
6j

^{13}C NMR (100 MHz, $CDCl_3$)



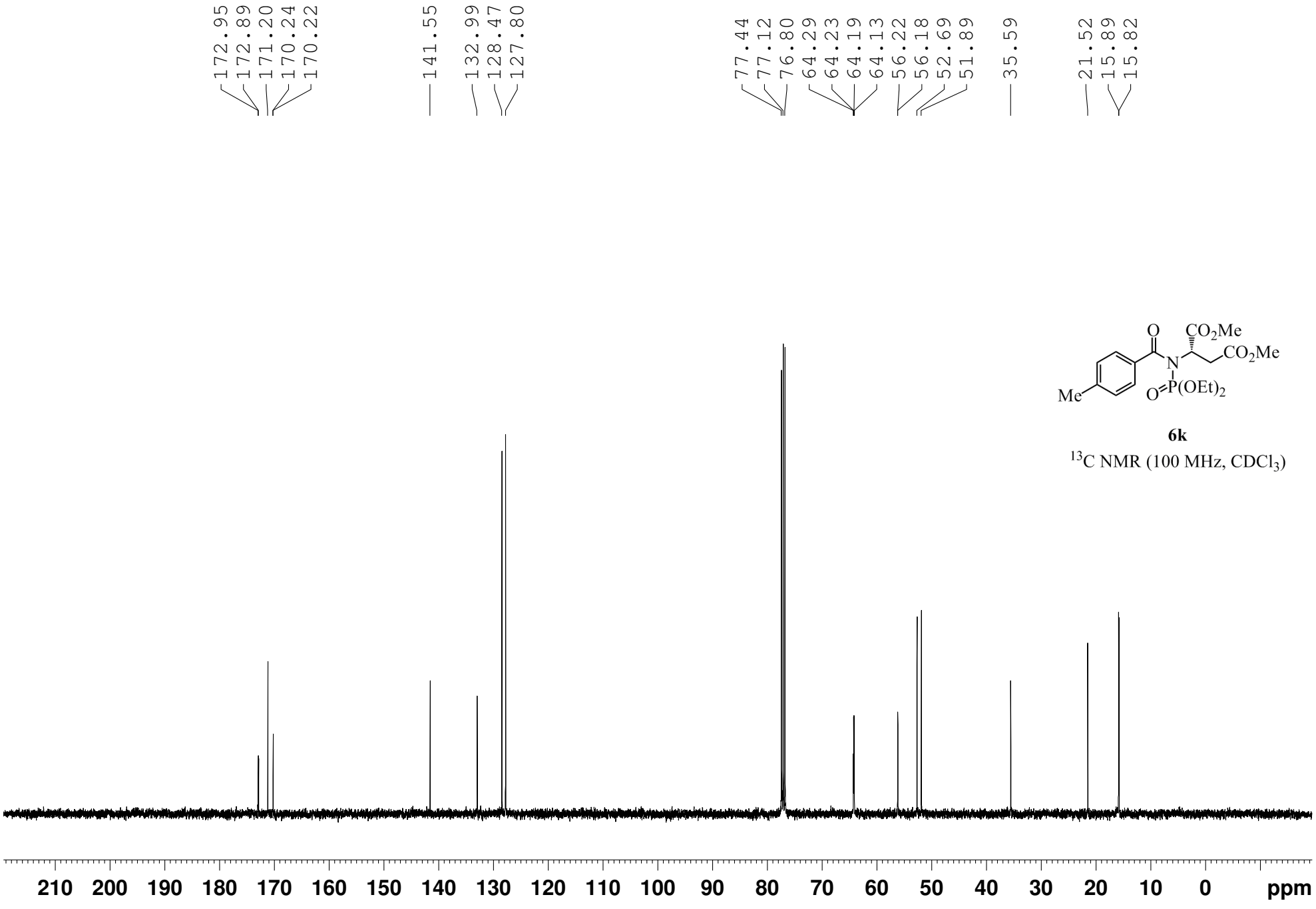
6j

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



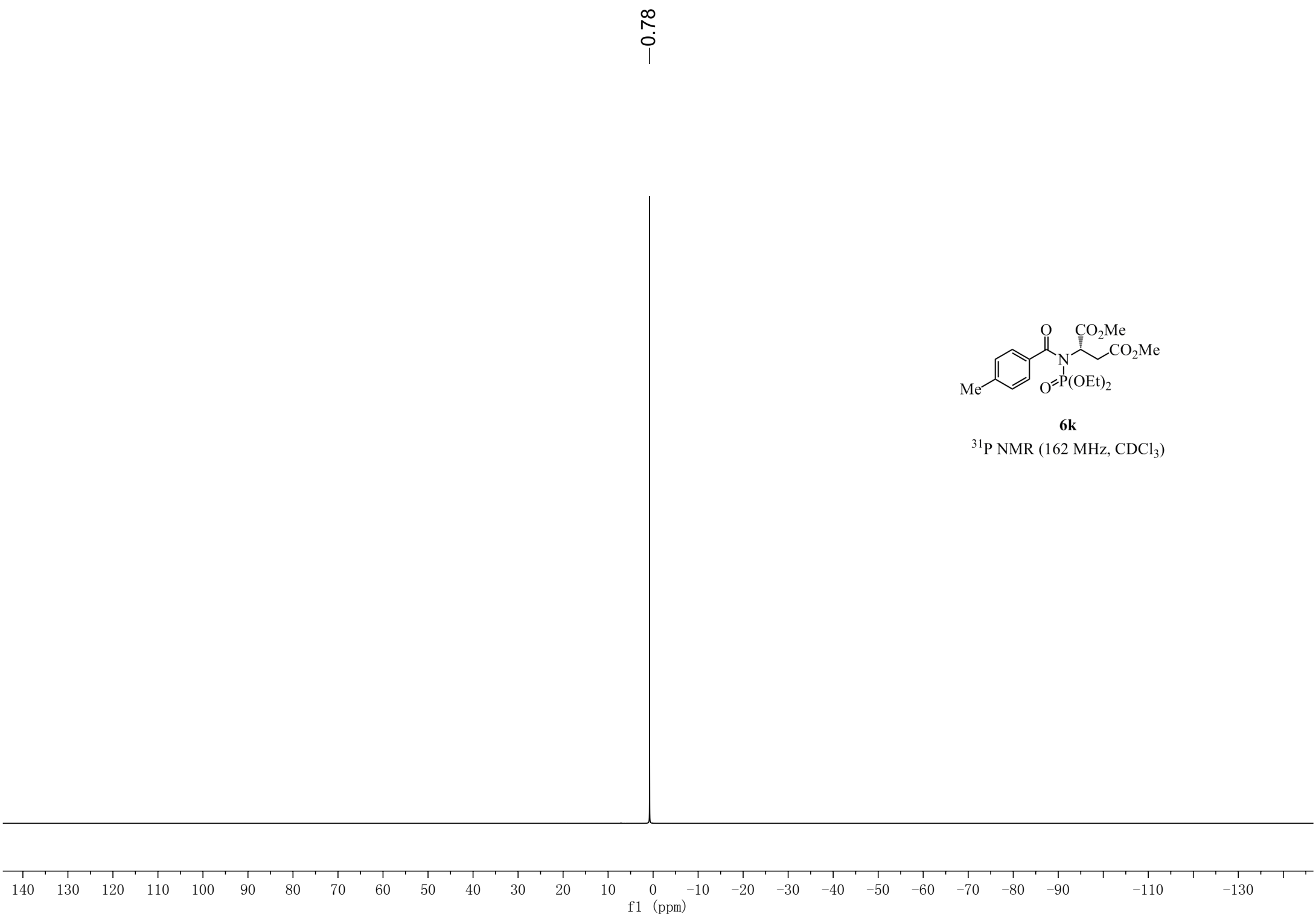
6k

^{1}H NMR (400 MHz, $CDCl_3$)



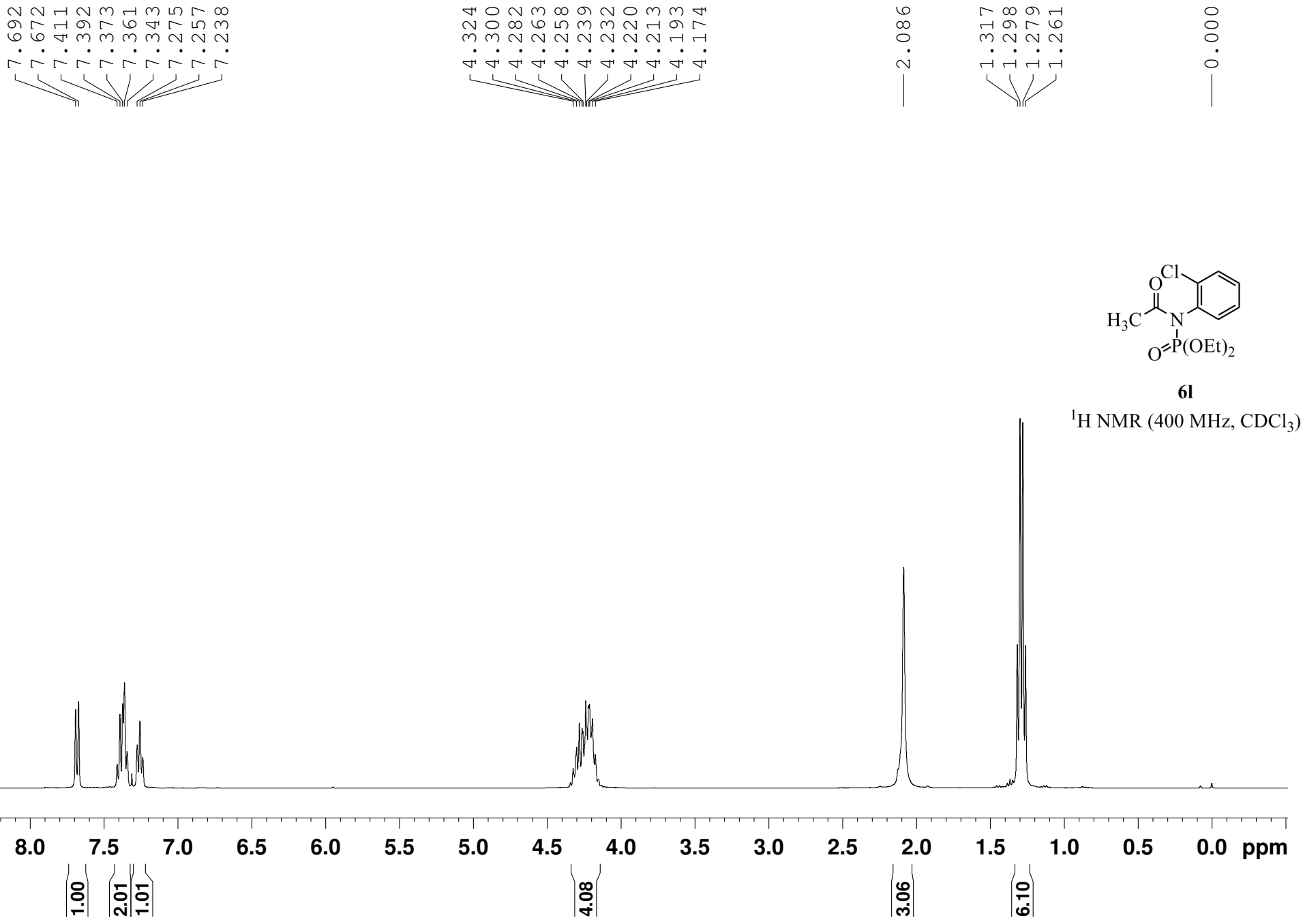
6k

^{13}C NMR (100 MHz, $CDCl_3$)



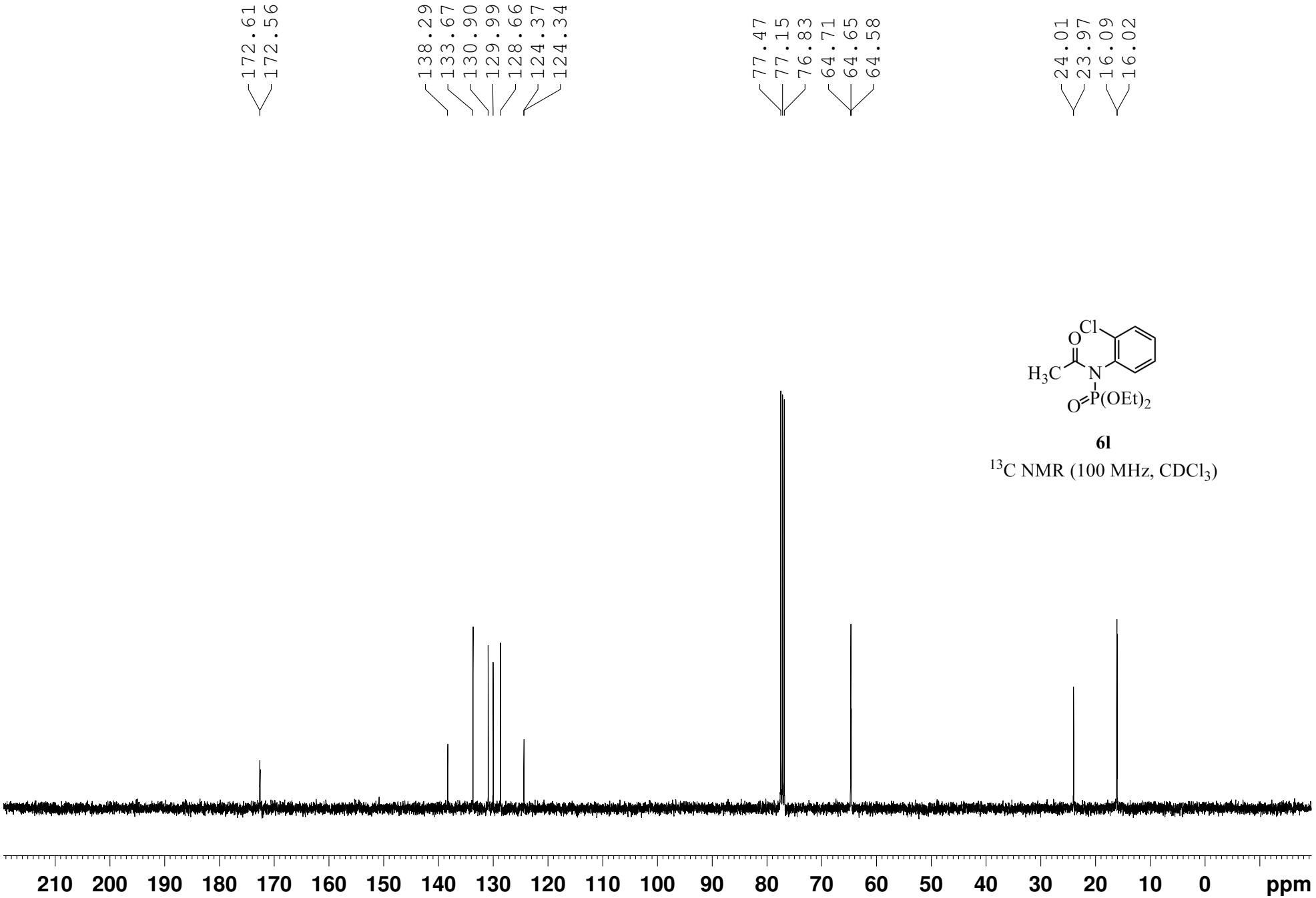
6k

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



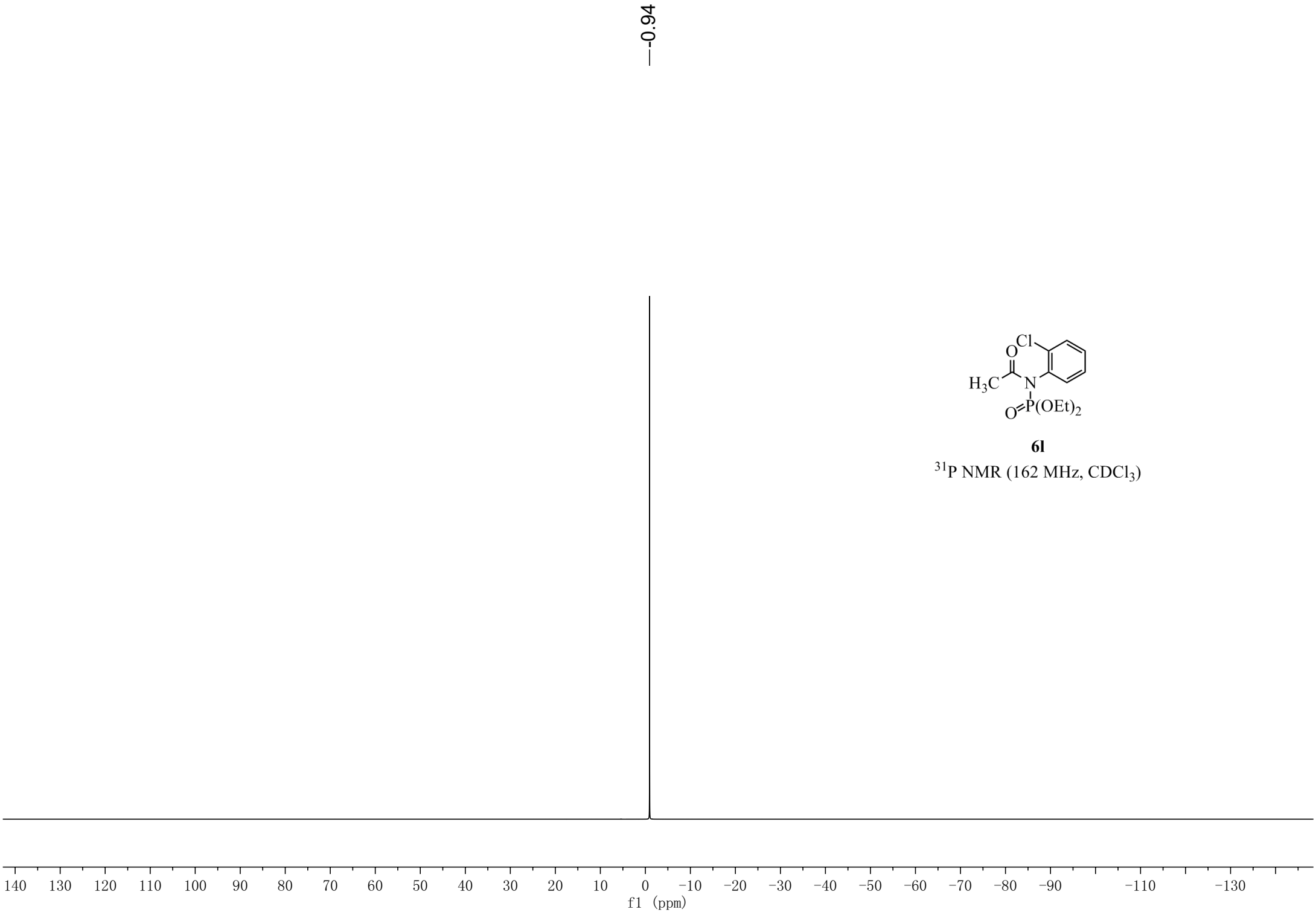
6l

^{1}H NMR (400 MHz, $CDCl_3$)



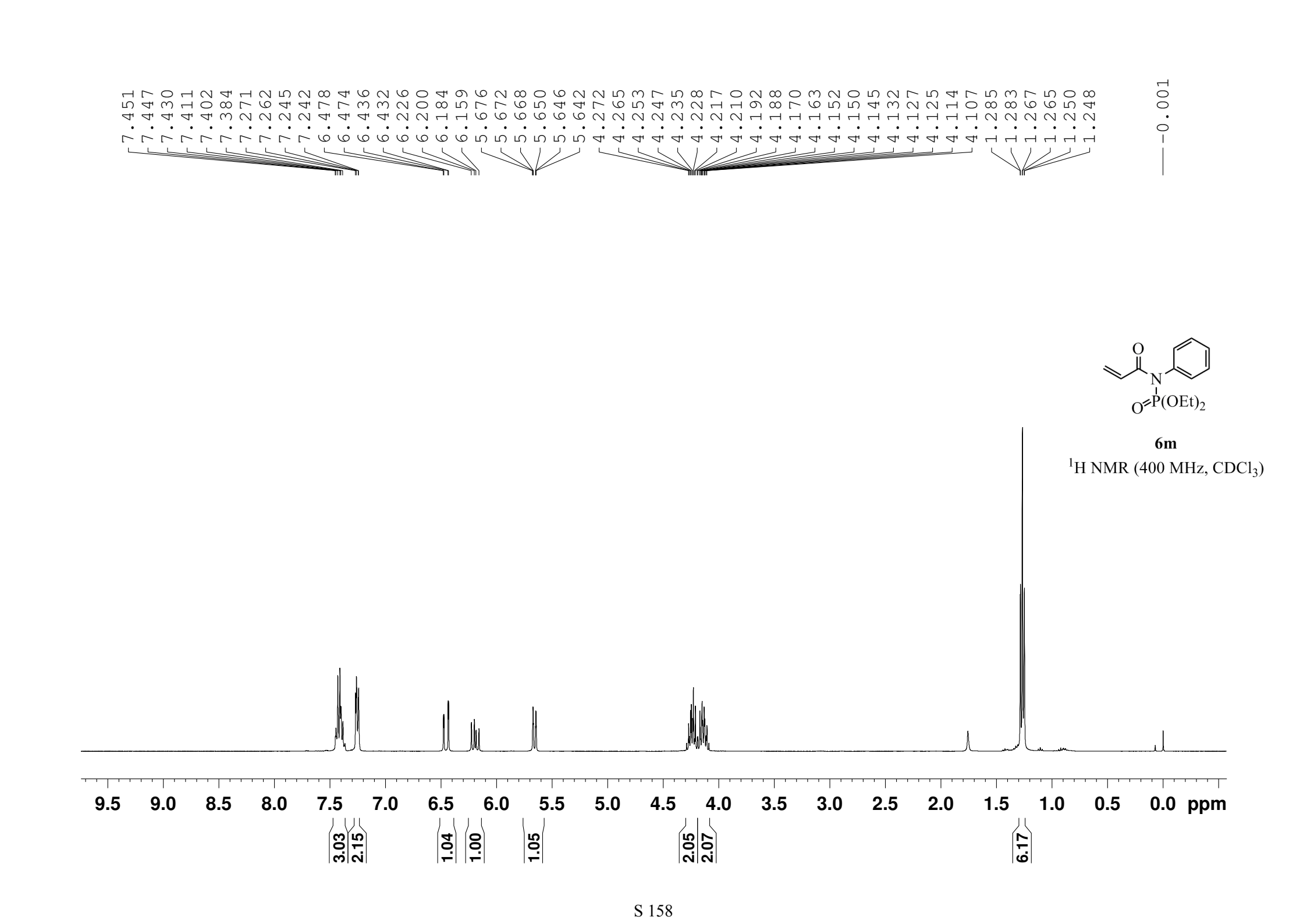
6l

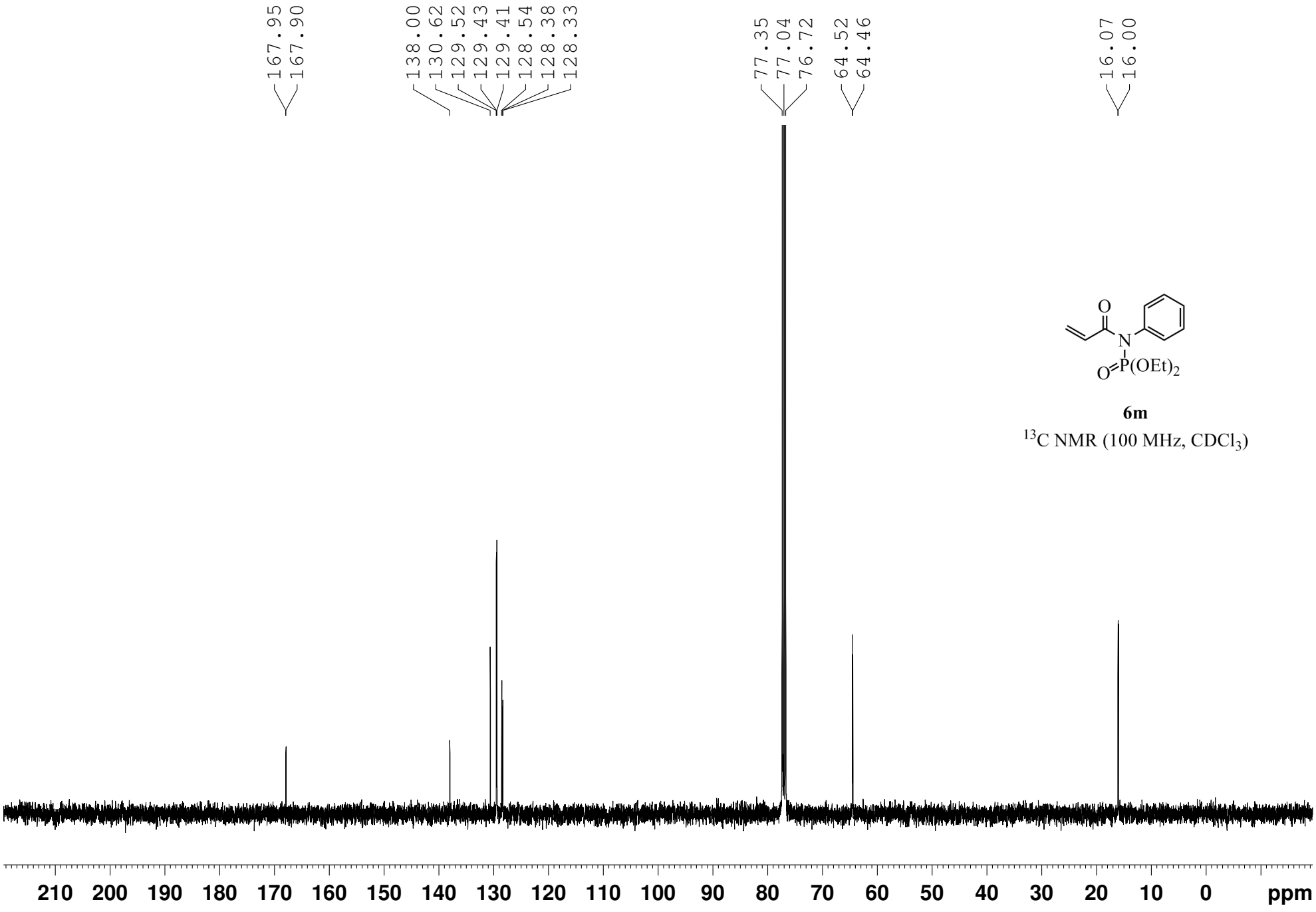
^{13}C NMR (100 MHz, $CDCl_3$)



6l

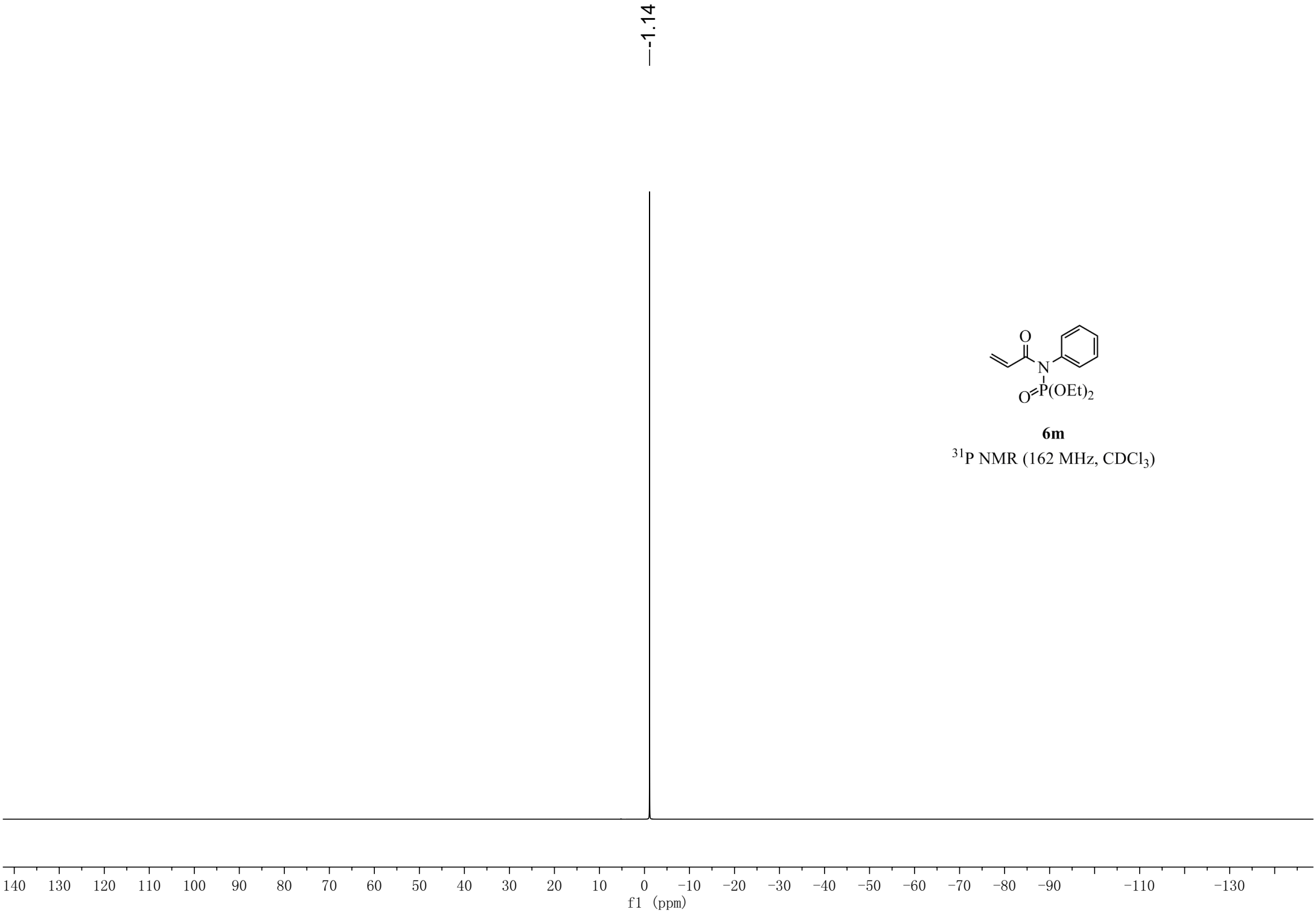
^{31}P NMR (162 MHz, $CDCl_3$)


7.451
7.447
7.430
7.411
7.402
7.384
7.271
7.262
7.245
7.242
6.478
6.474
6.436
6.432
6.226
6.200
6.184
6.159
5.676
5.672
5.668
5.650
5.646
5.642
4.272
4.265
4.253
4.247
4.235
4.228
4.217
4.210
4.192
4.188
4.170
4.163
4.152
4.150
4.145
4.132
4.127
4.125
4.114
4.107
1.285
1.283
1.267
1.265
1.250
1.248
0.001
O
N
O=P(OEt)2
6m
1H NMR (400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.03
2.15
1.04
1.00
1.05
2.05
2.07
6.17



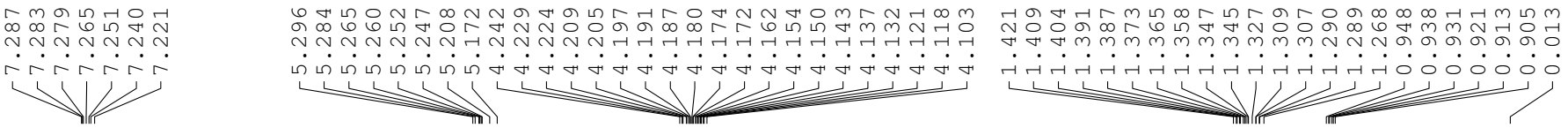
6m

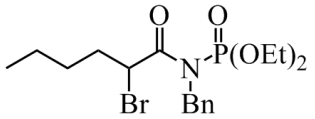
^{13}C NMR (100 MHz, $CDCl_3$)



6m

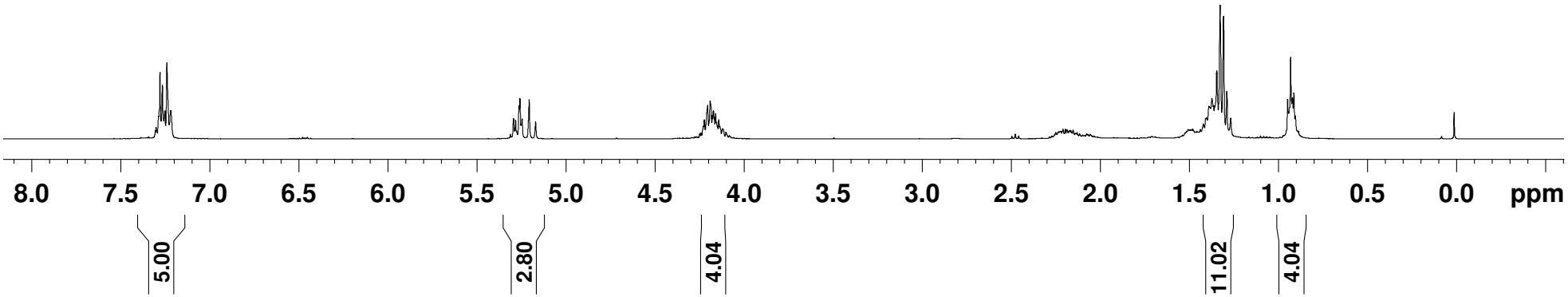
^{31}P NMR (162 MHz, $CDCl_3$)

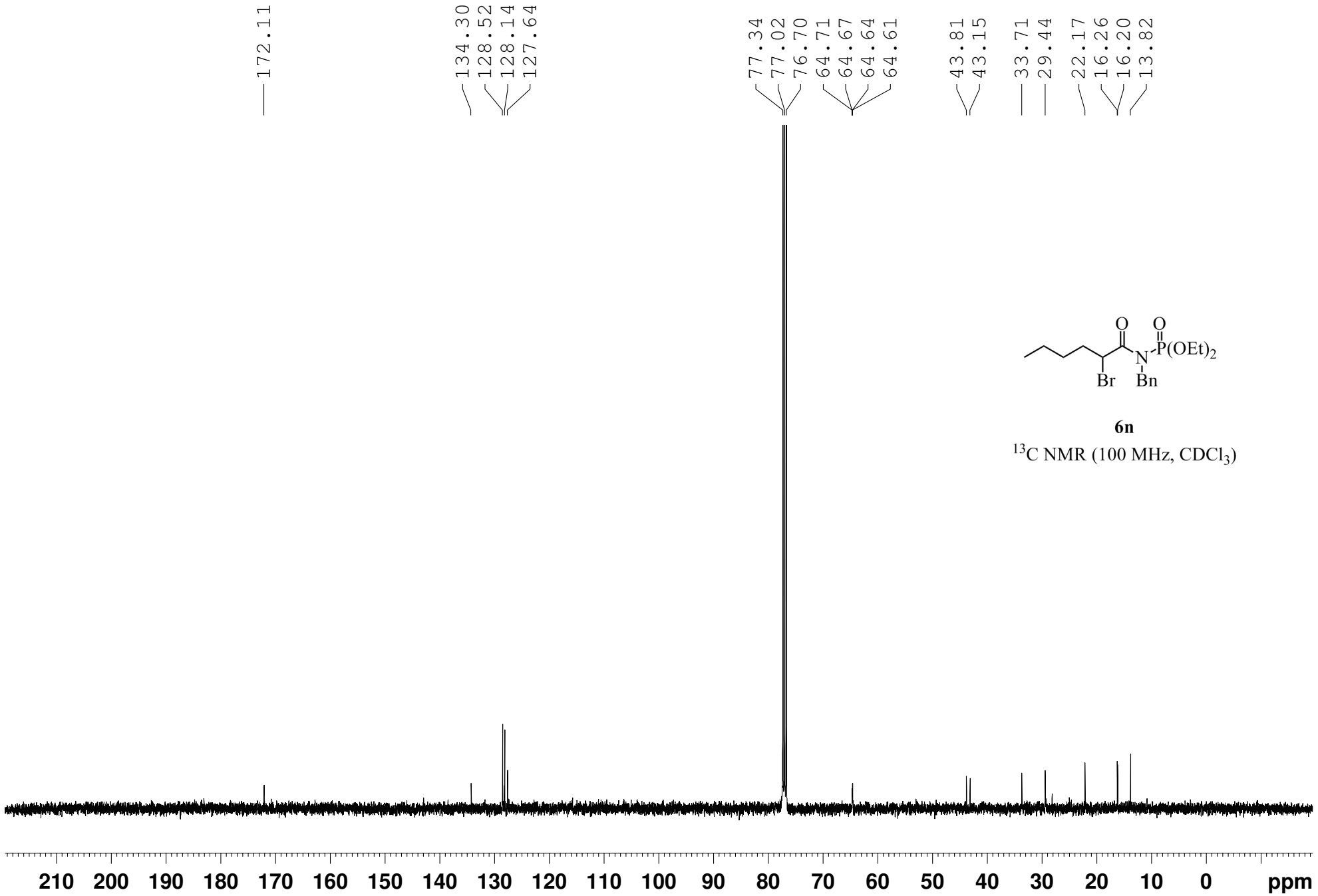




6n

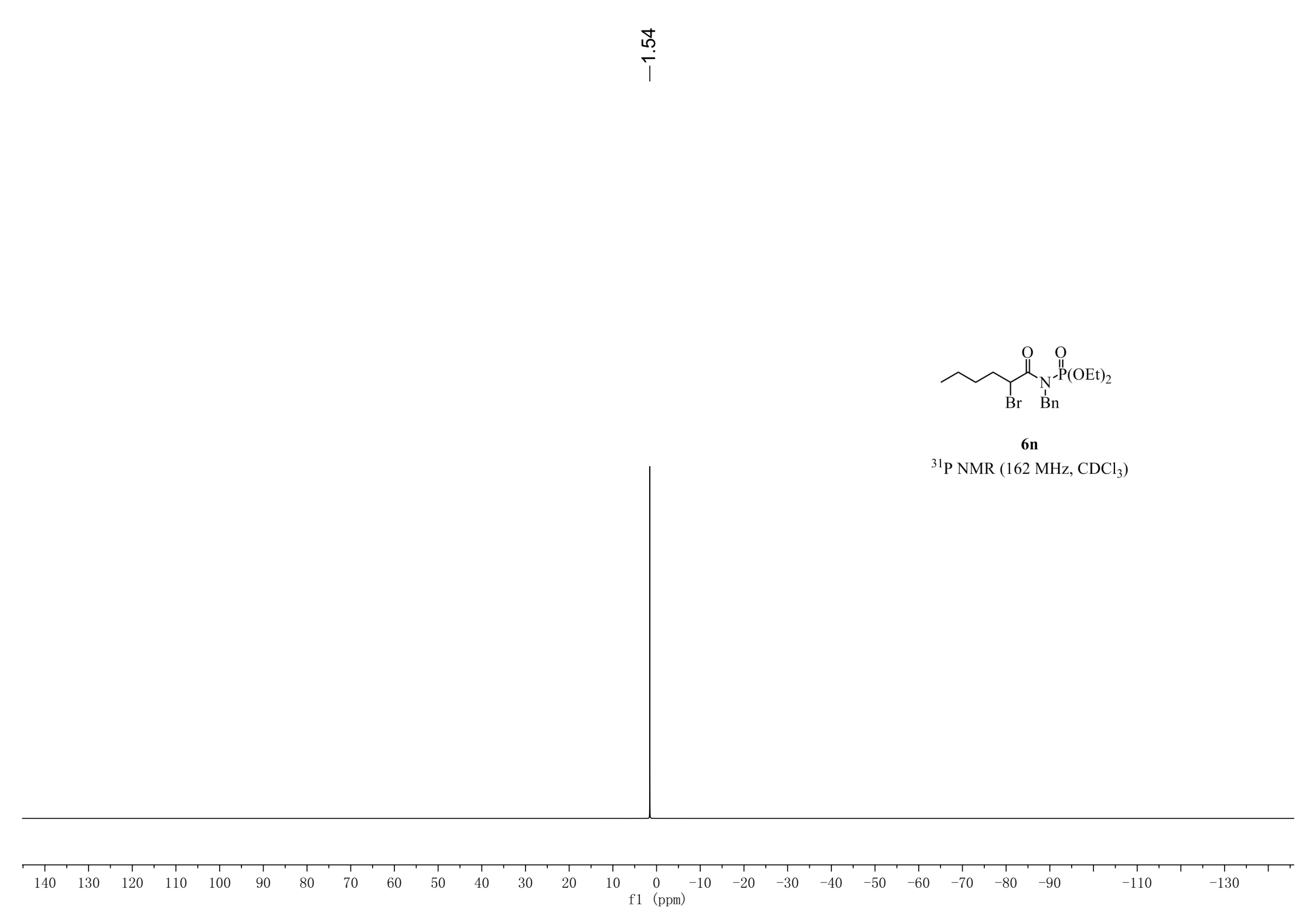
^{1}H NMR (400 MHz, $CDCl_3$)





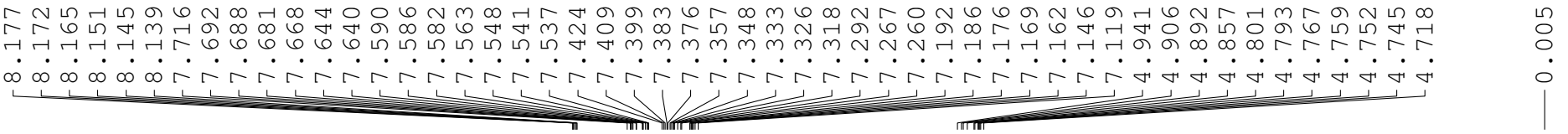
6n

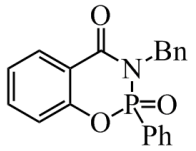
^{13}C NMR (100 MHz, $CDCl_3$)



6n

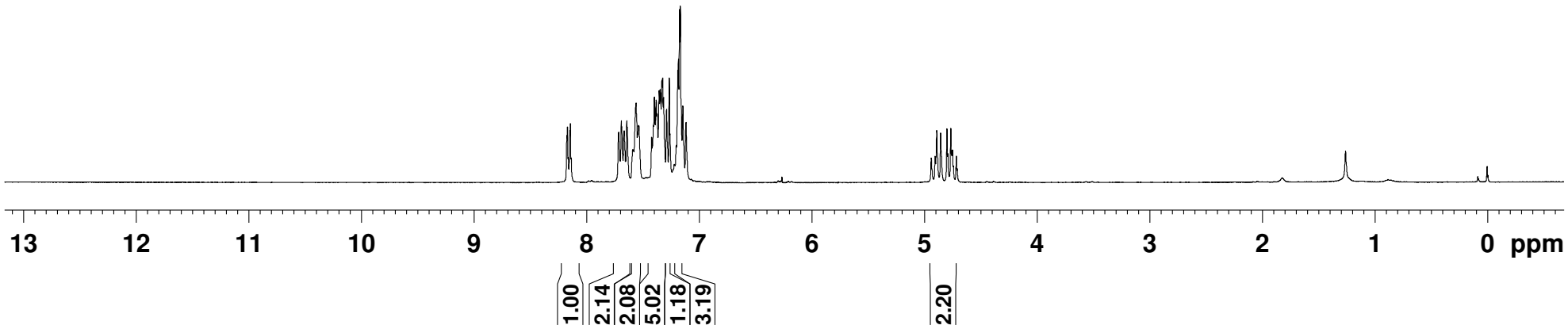
^{31}P NMR (162 MHz, $CDCl_3$)

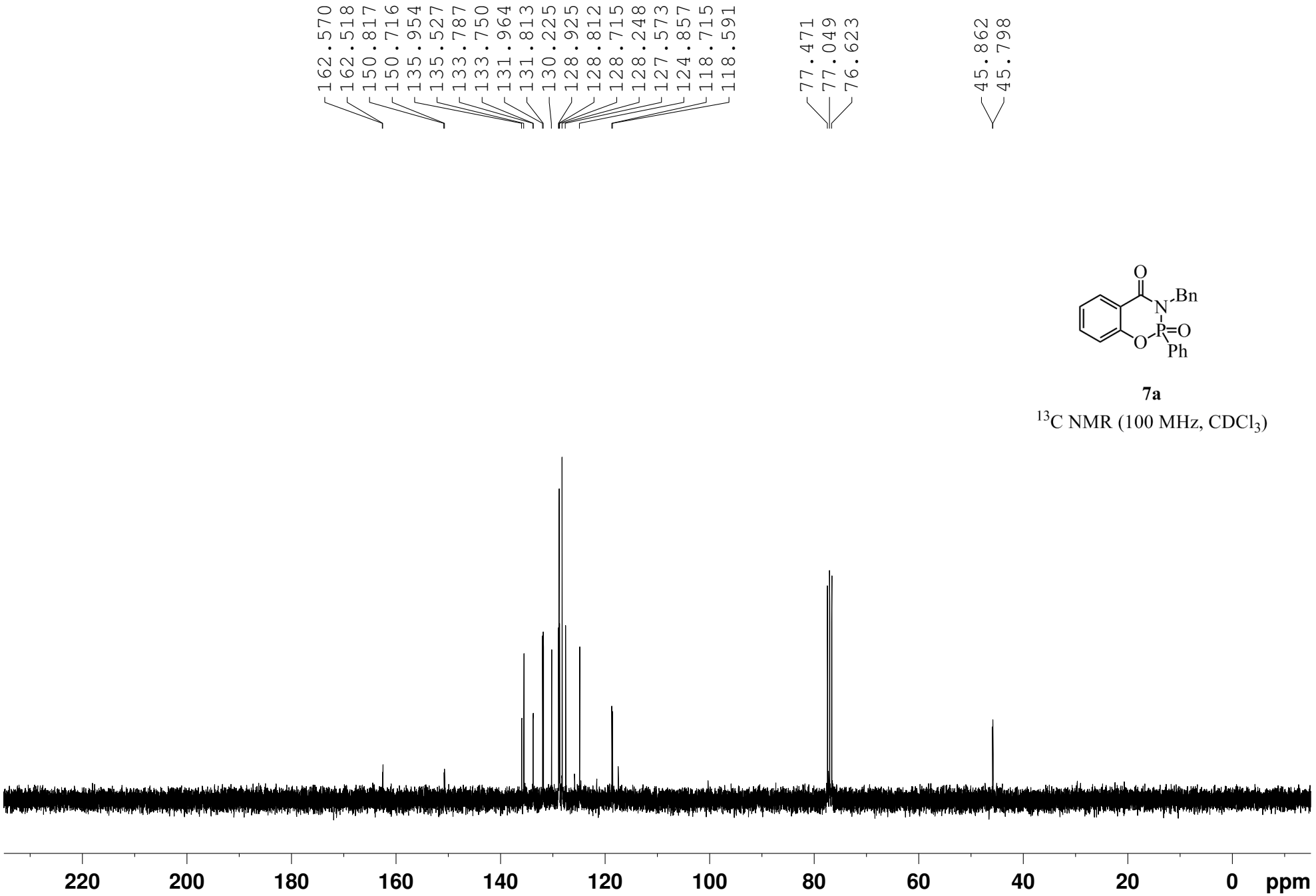




7a

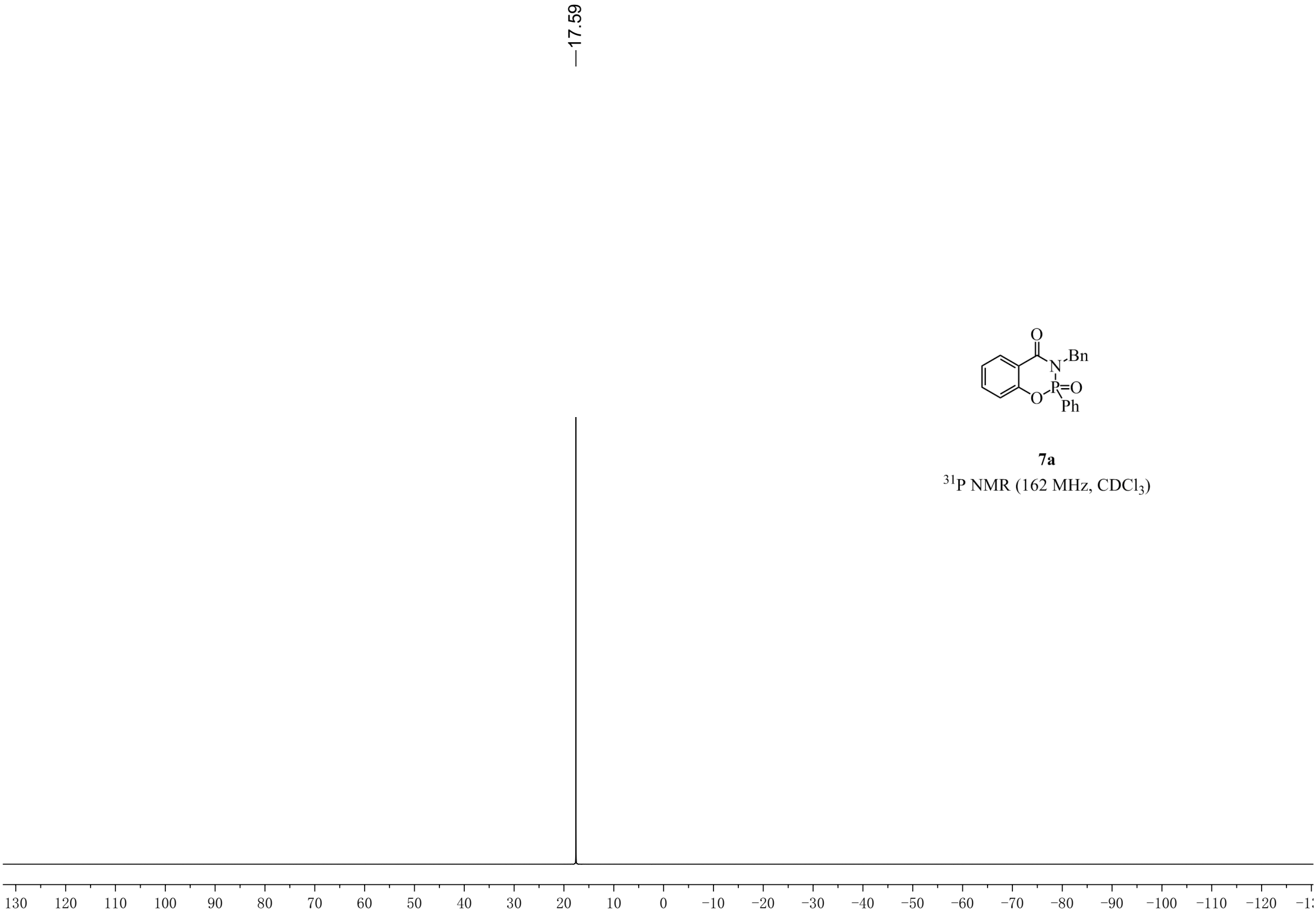
^{1}H NMR (400 MHz, $CDCl_3$)





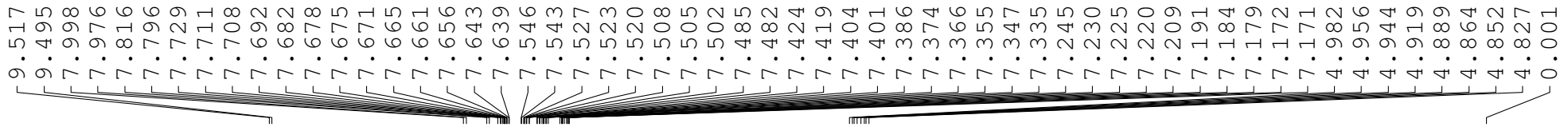
7a

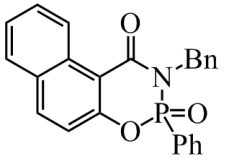
^{13}C NMR (100 MHz, $CDCl_3$)



7a

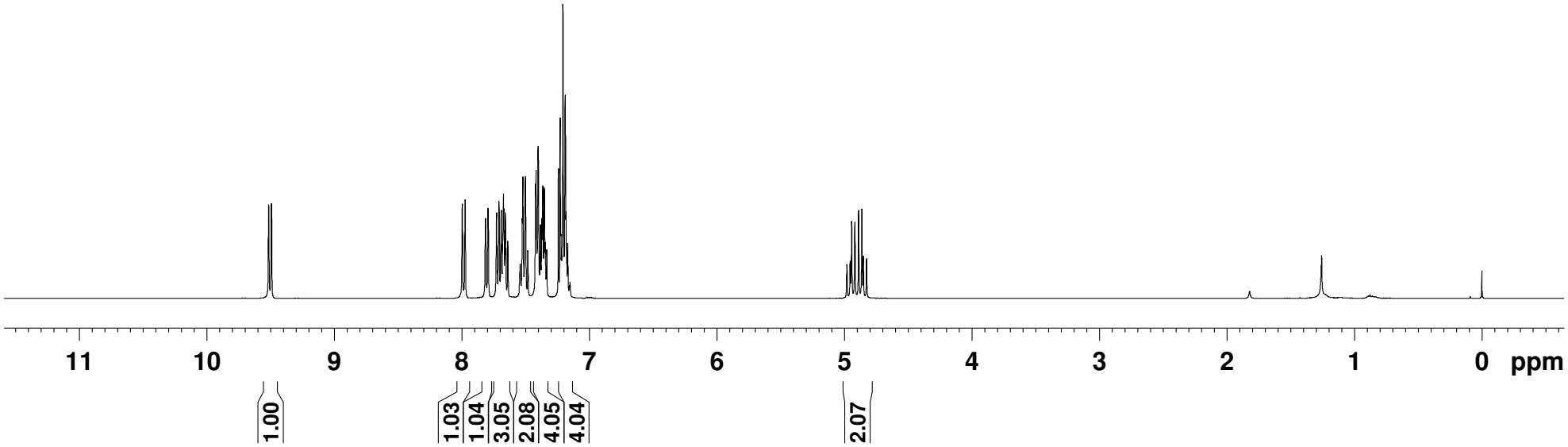
^{31}P NMR (162 MHz, $CDCl_3$)

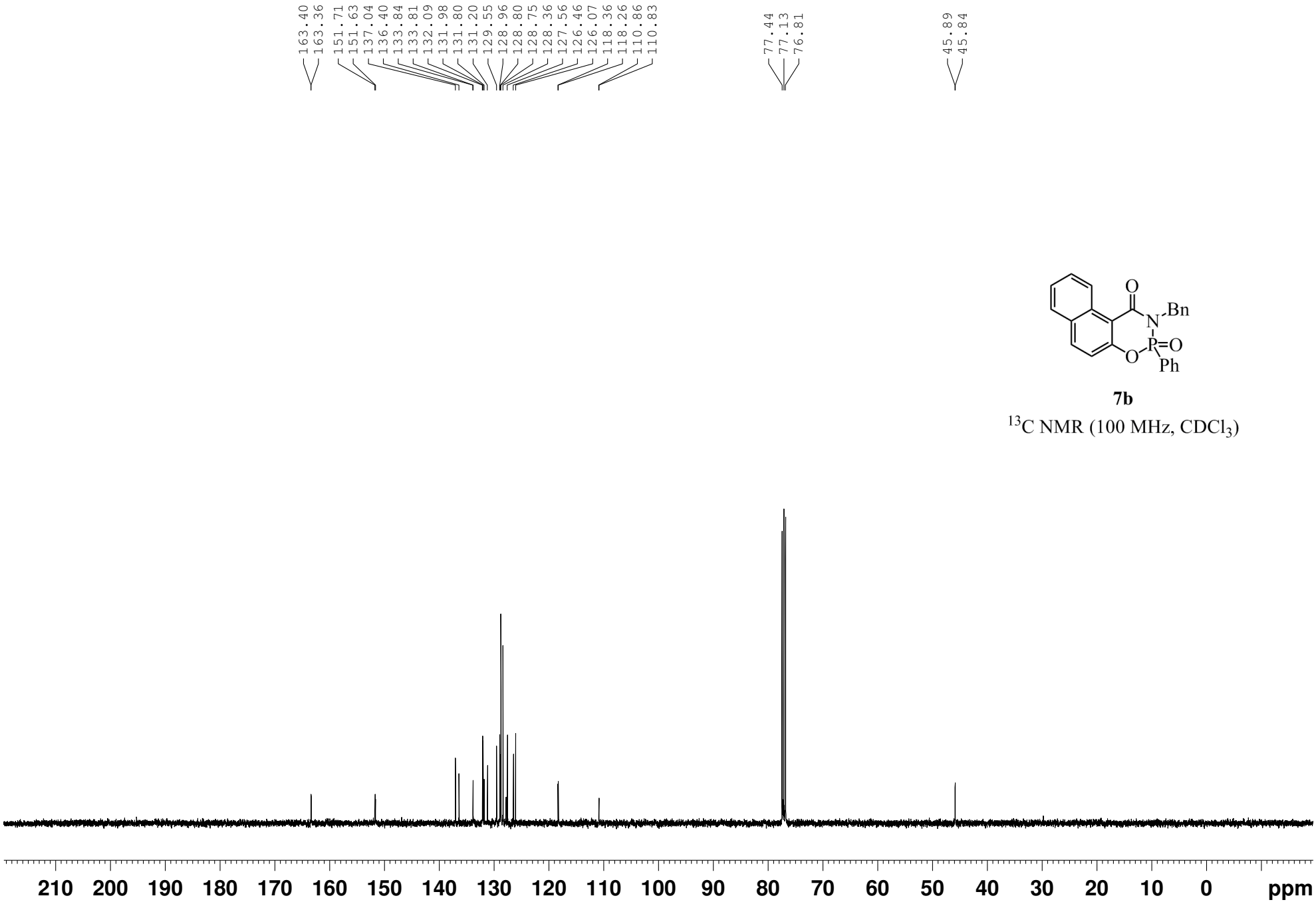




7b

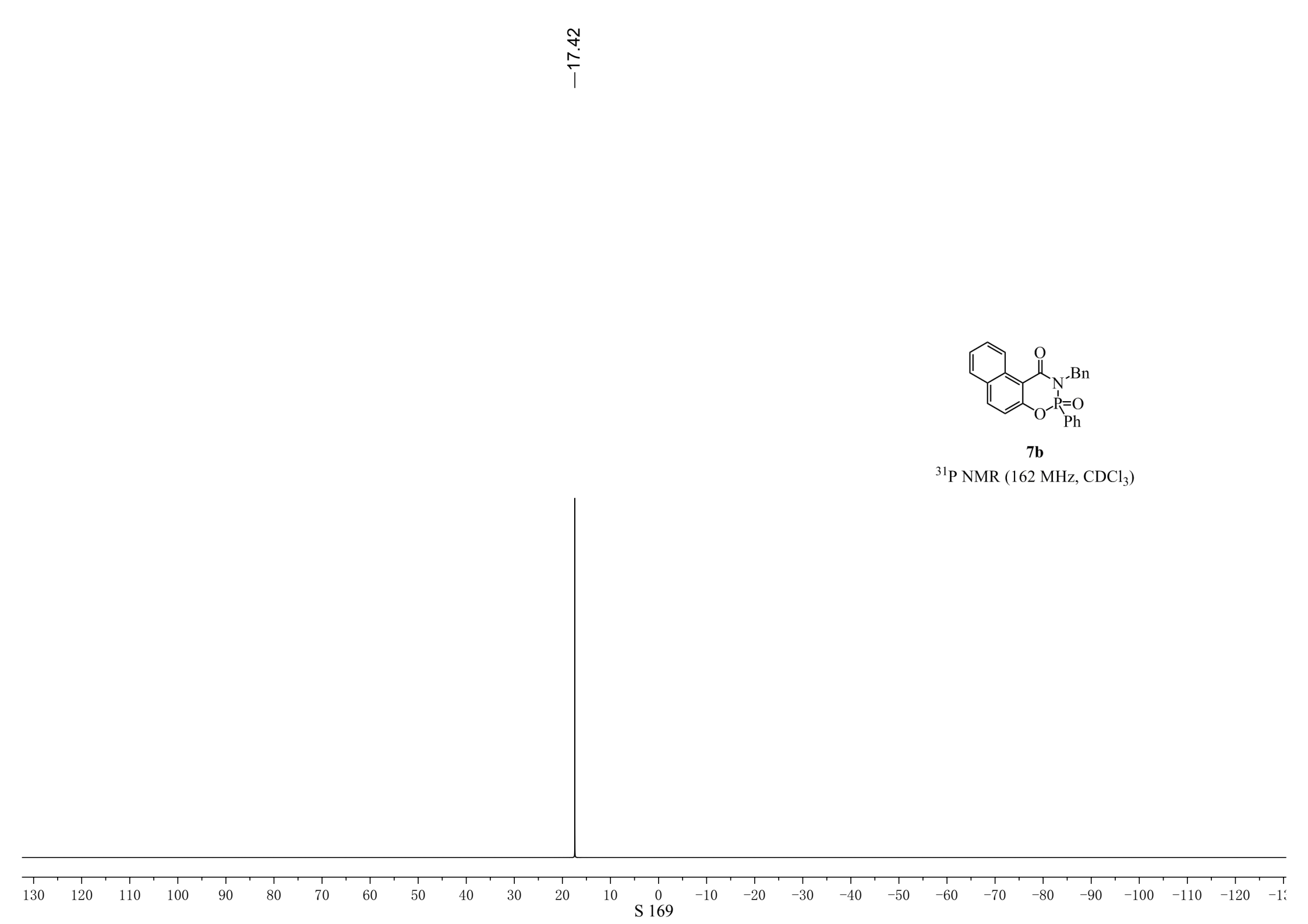
^{1}H NMR (400 MHz, $CDCl_3$)





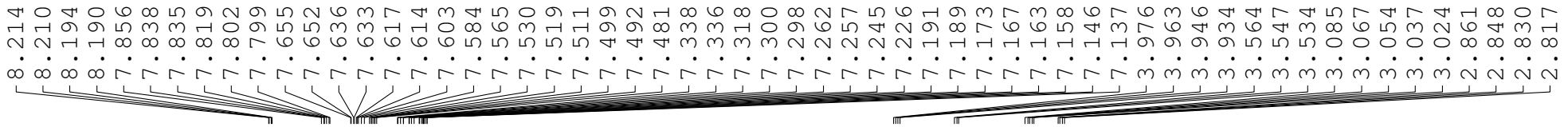
7b

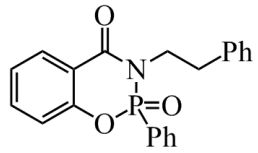
^{13}C NMR (100 MHz, $CDCl_3$)



7b

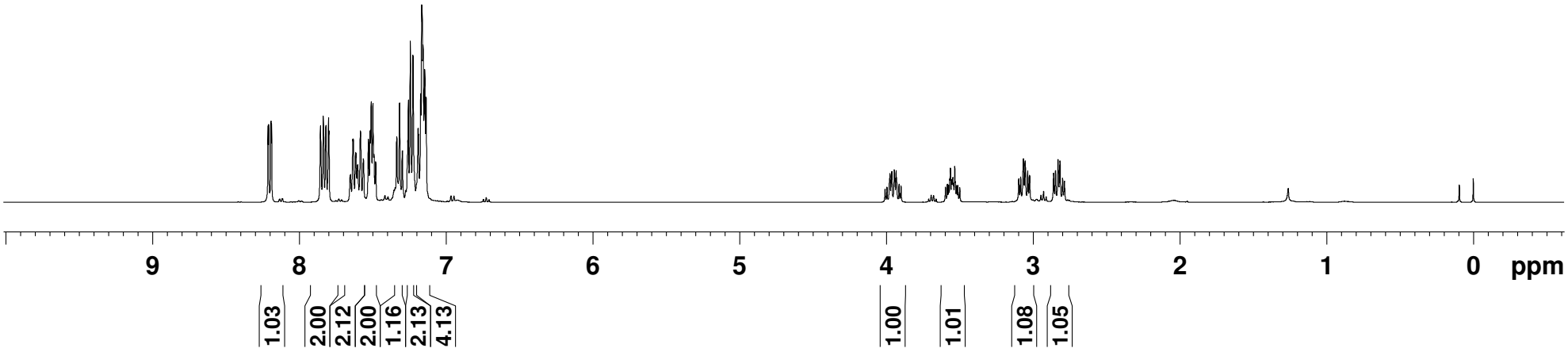
^{31}P NMR (162 MHz, $CDCl_3$)

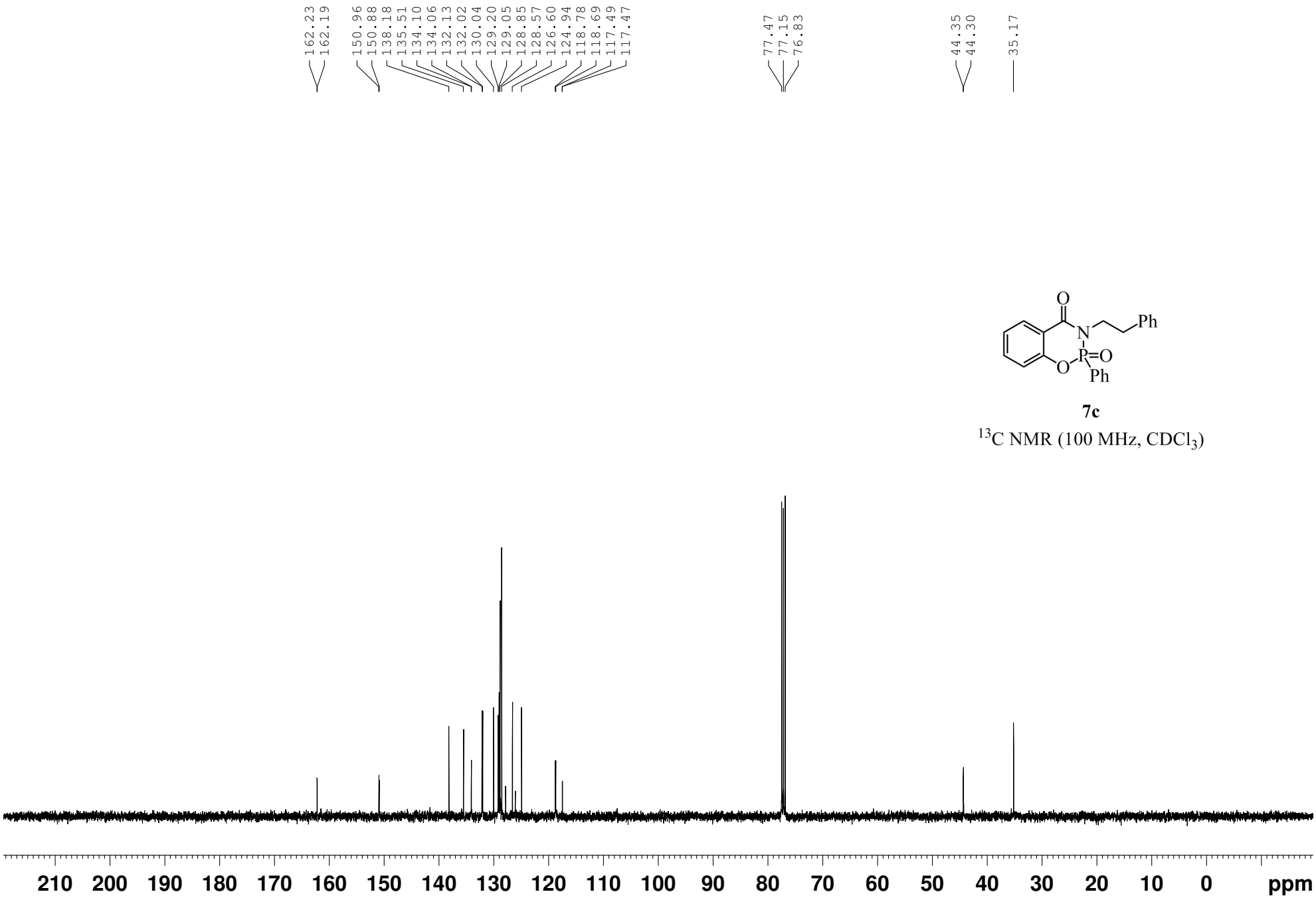




7c

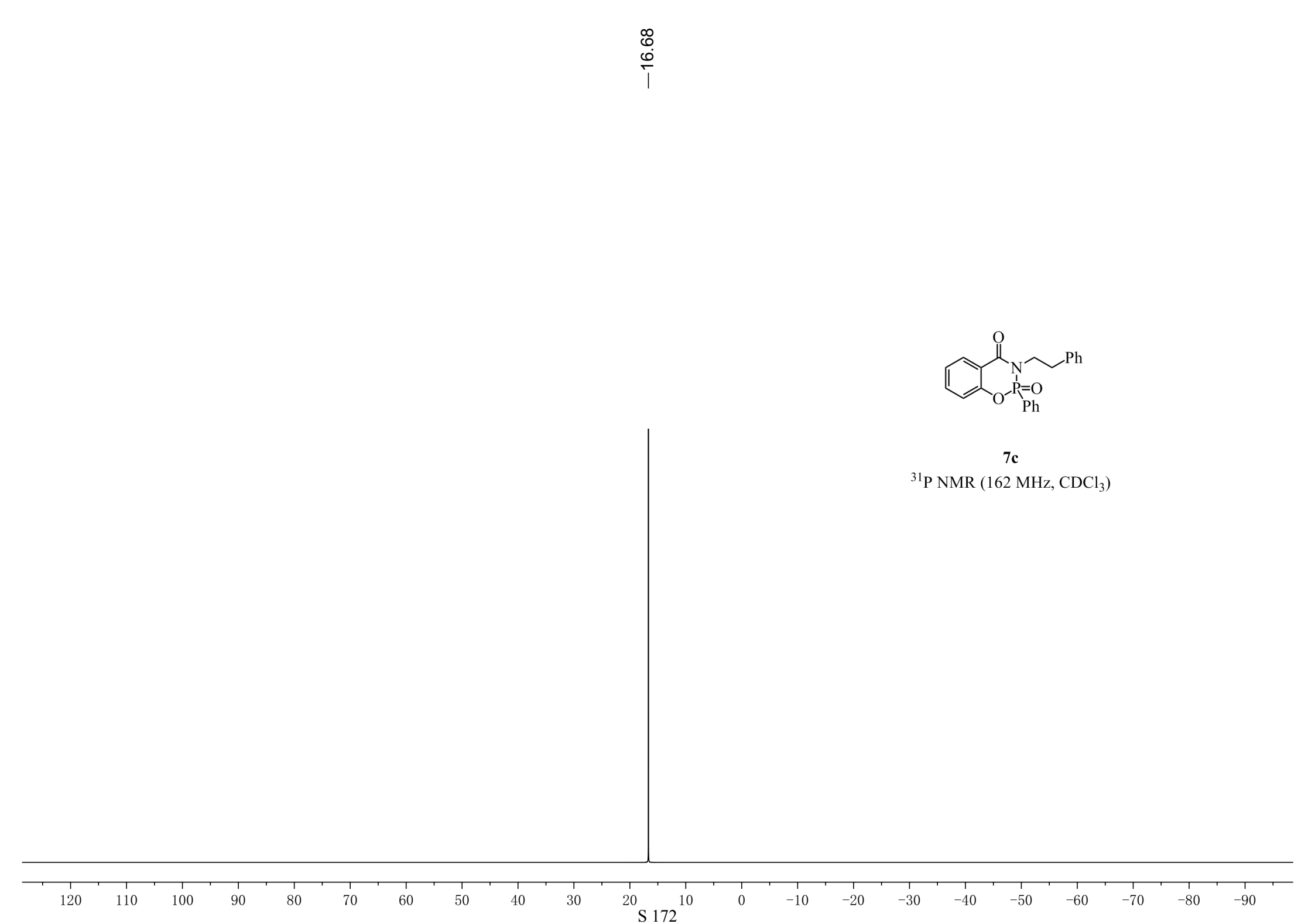
^{1}H NMR (400 MHz, $CDCl_3$)





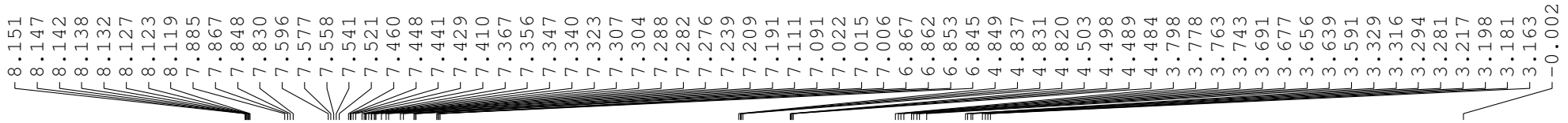
7c

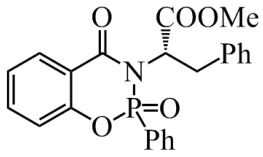
^{13}C NMR (100 MHz, $CDCl_3$)



7c

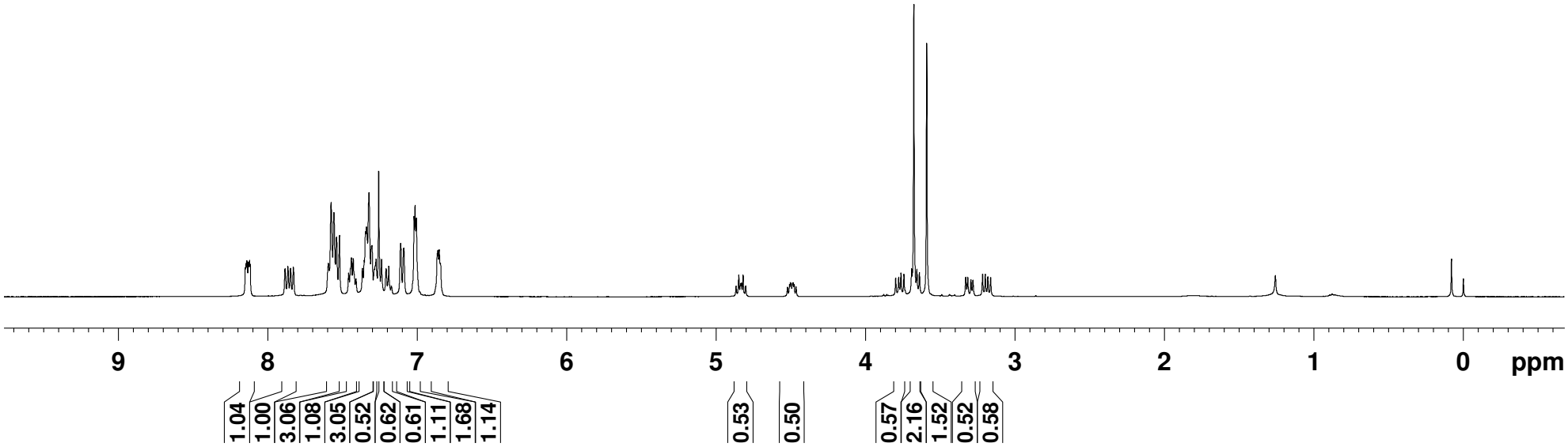
^{31}P NMR (162 MHz, $CDCl_3$)

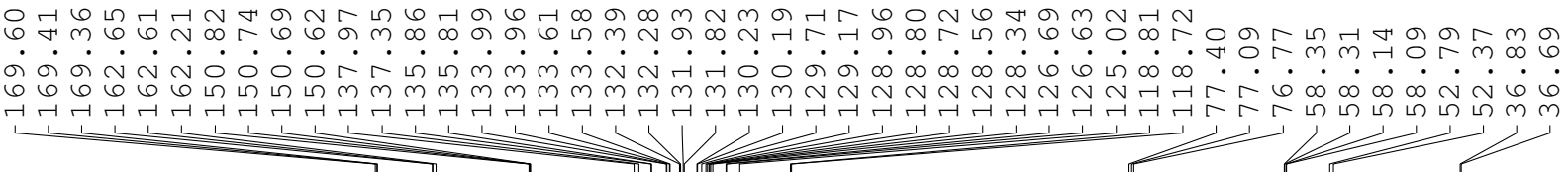


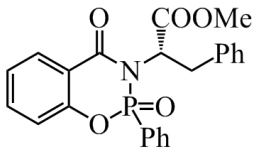


7d

^{1}H NMR (400 MHz, $CDCl_3$)

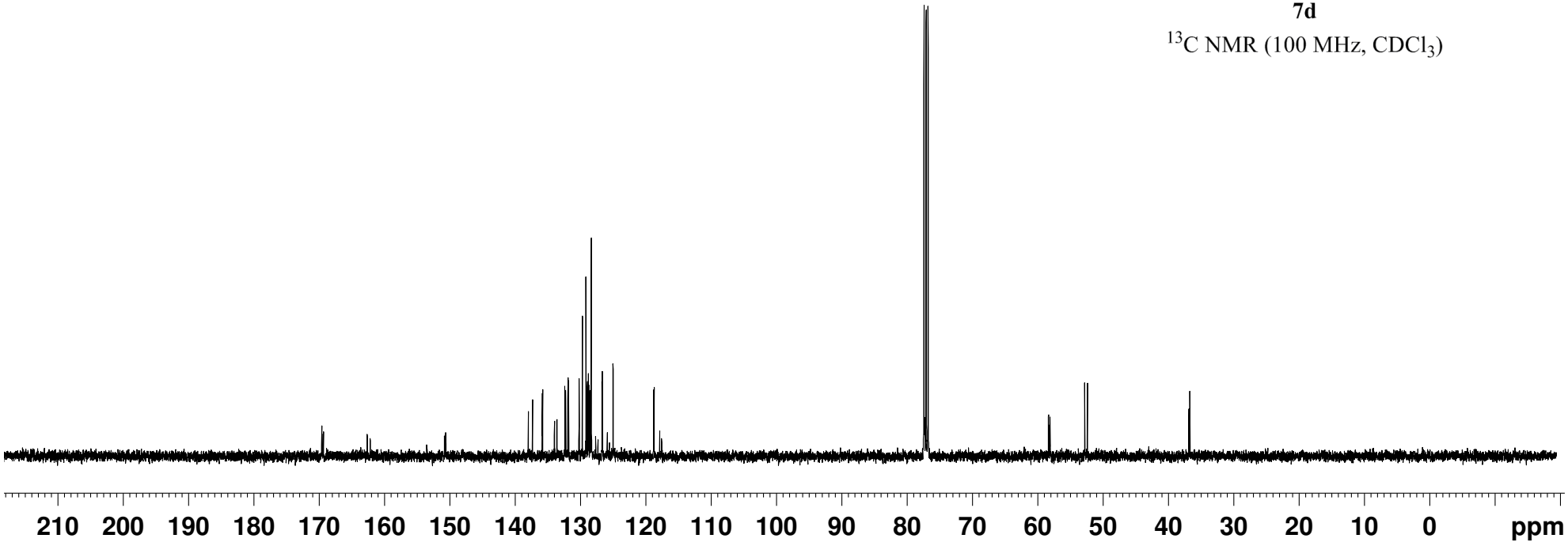


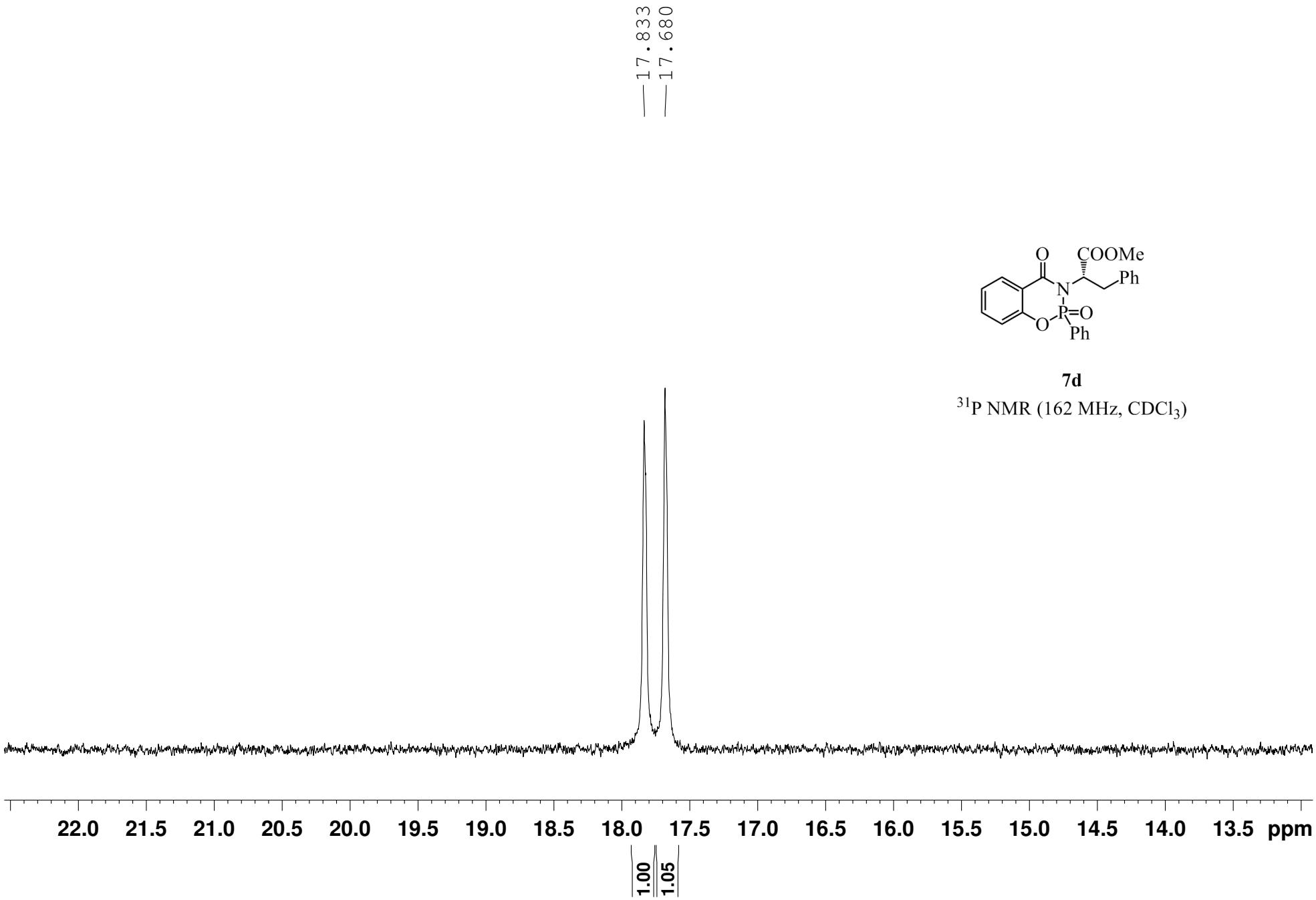




7d

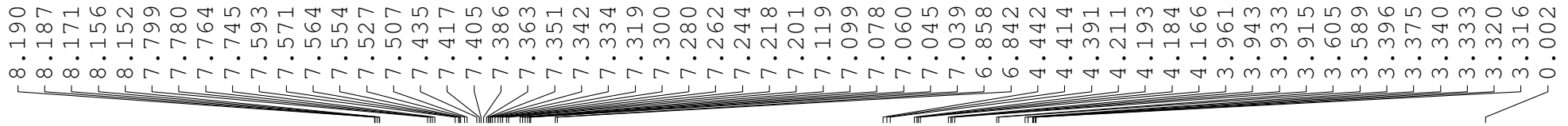
^{13}C NMR (100 MHz, $CDCl_3$)

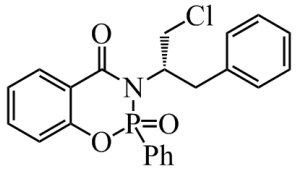




7d

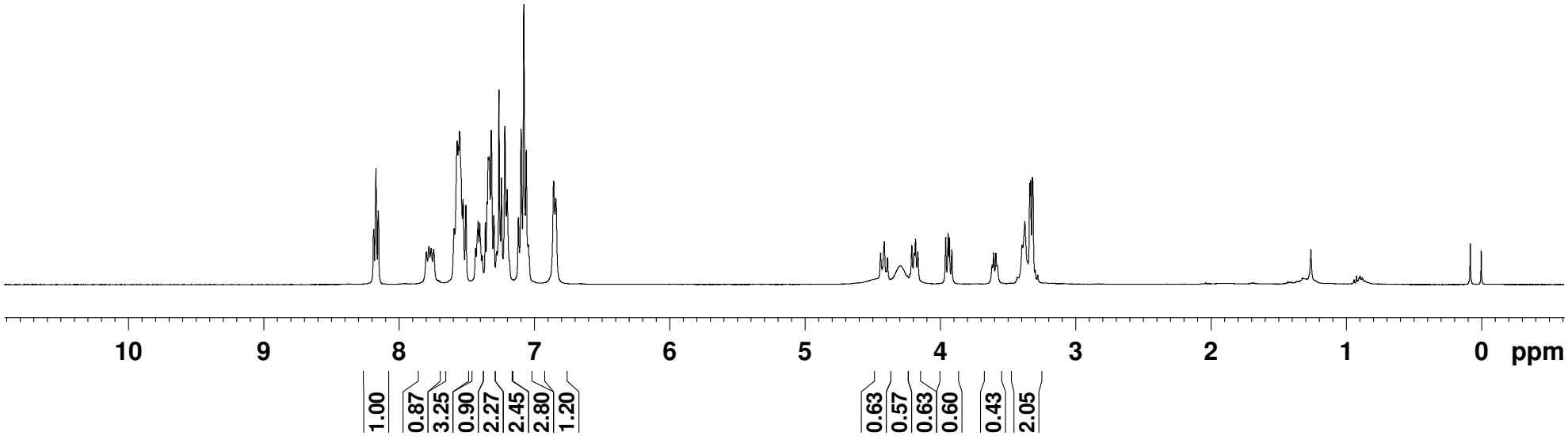
^{31}P NMR (162 MHz, $CDCl_3$)

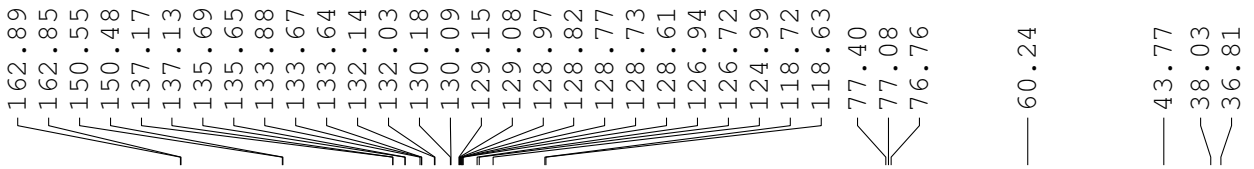


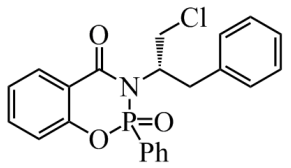


7e

^{1}H NMR (400 MHz, $CDCl_3$)

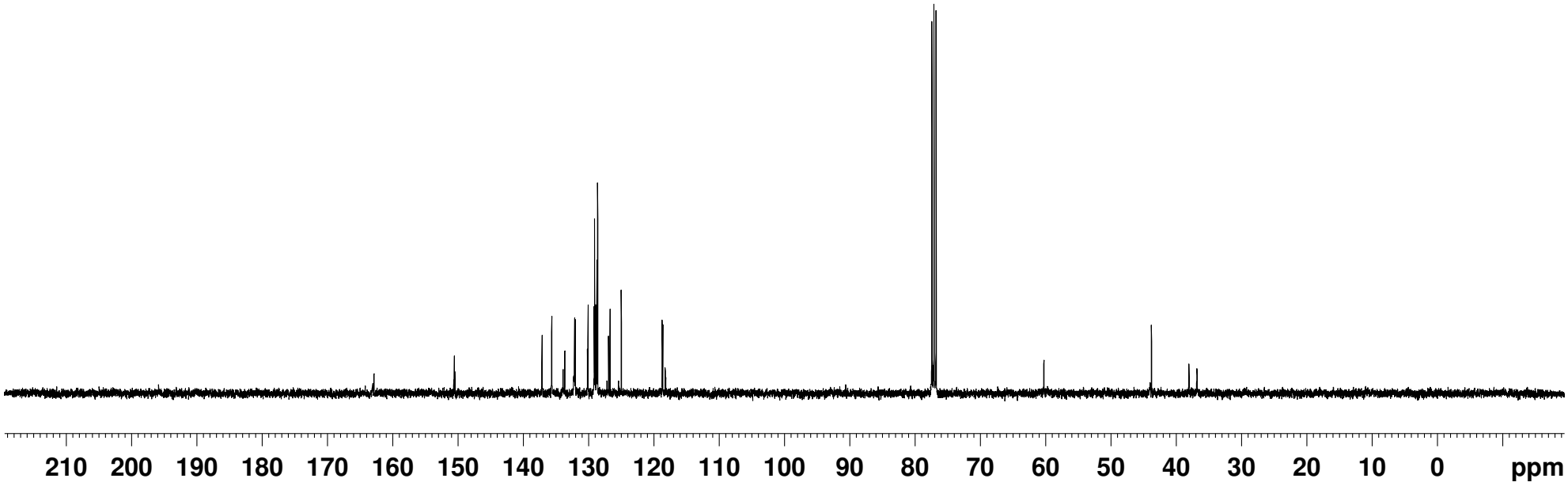


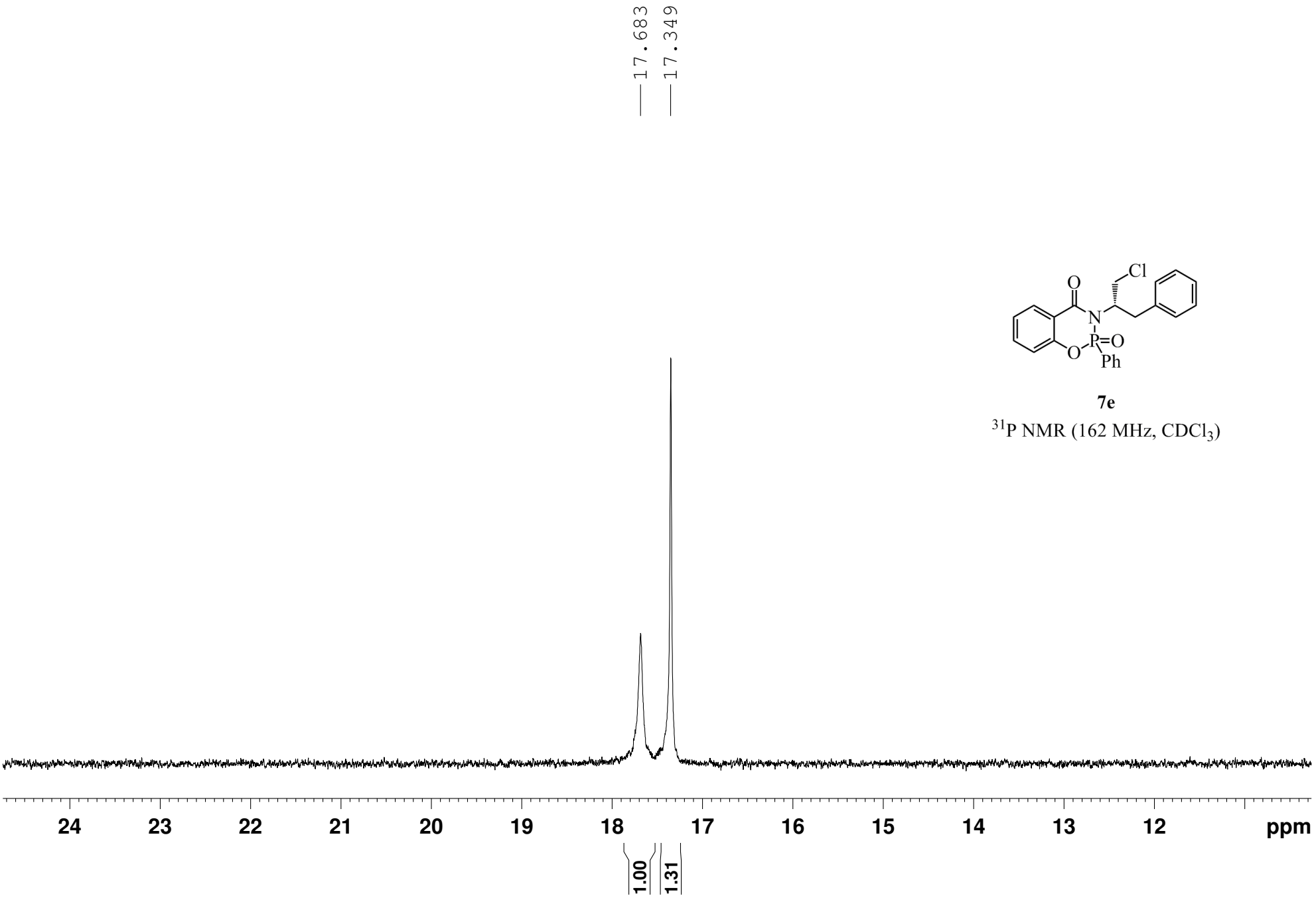




7e

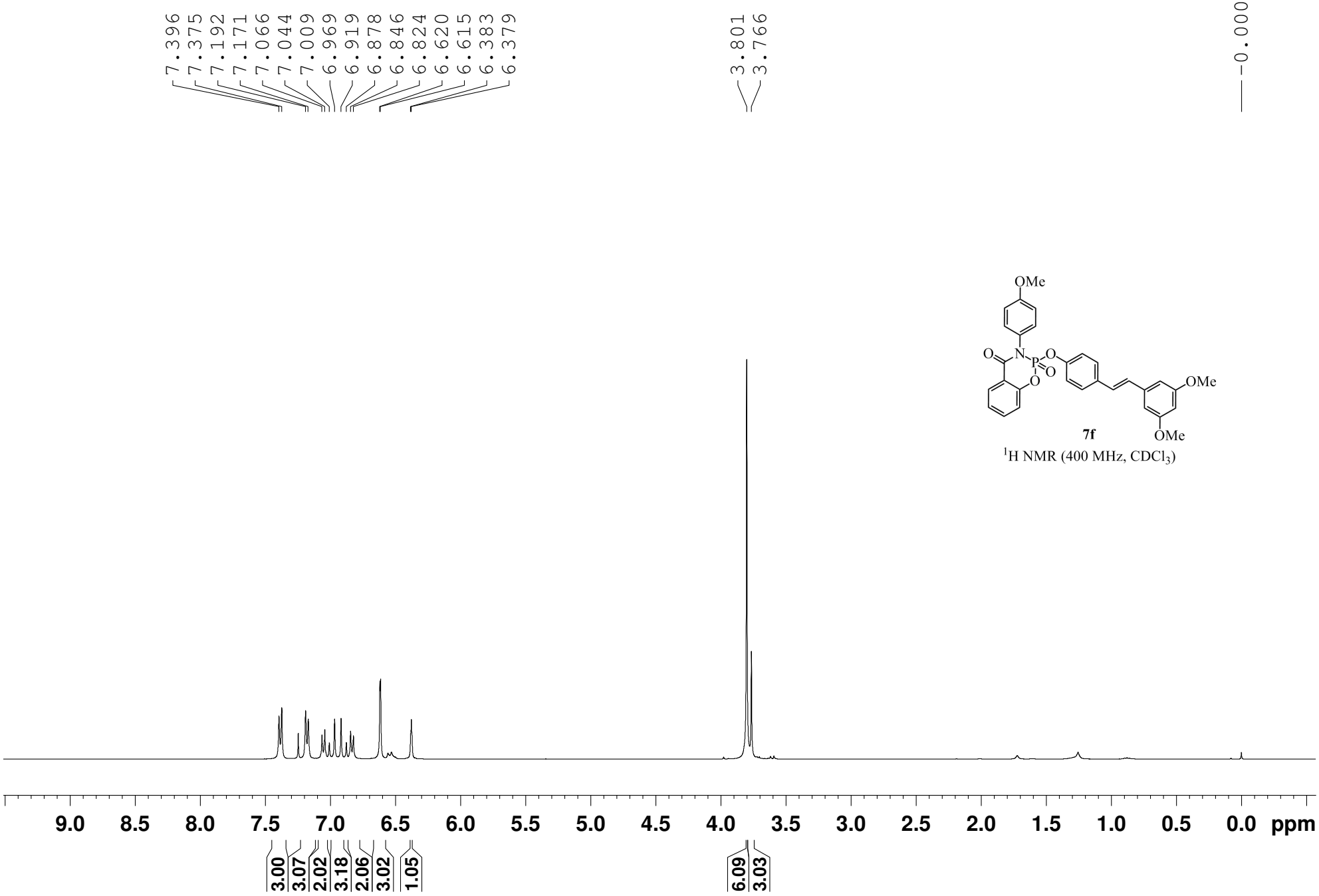
^{13}C NMR (100 MHz, $CDCl_3$)





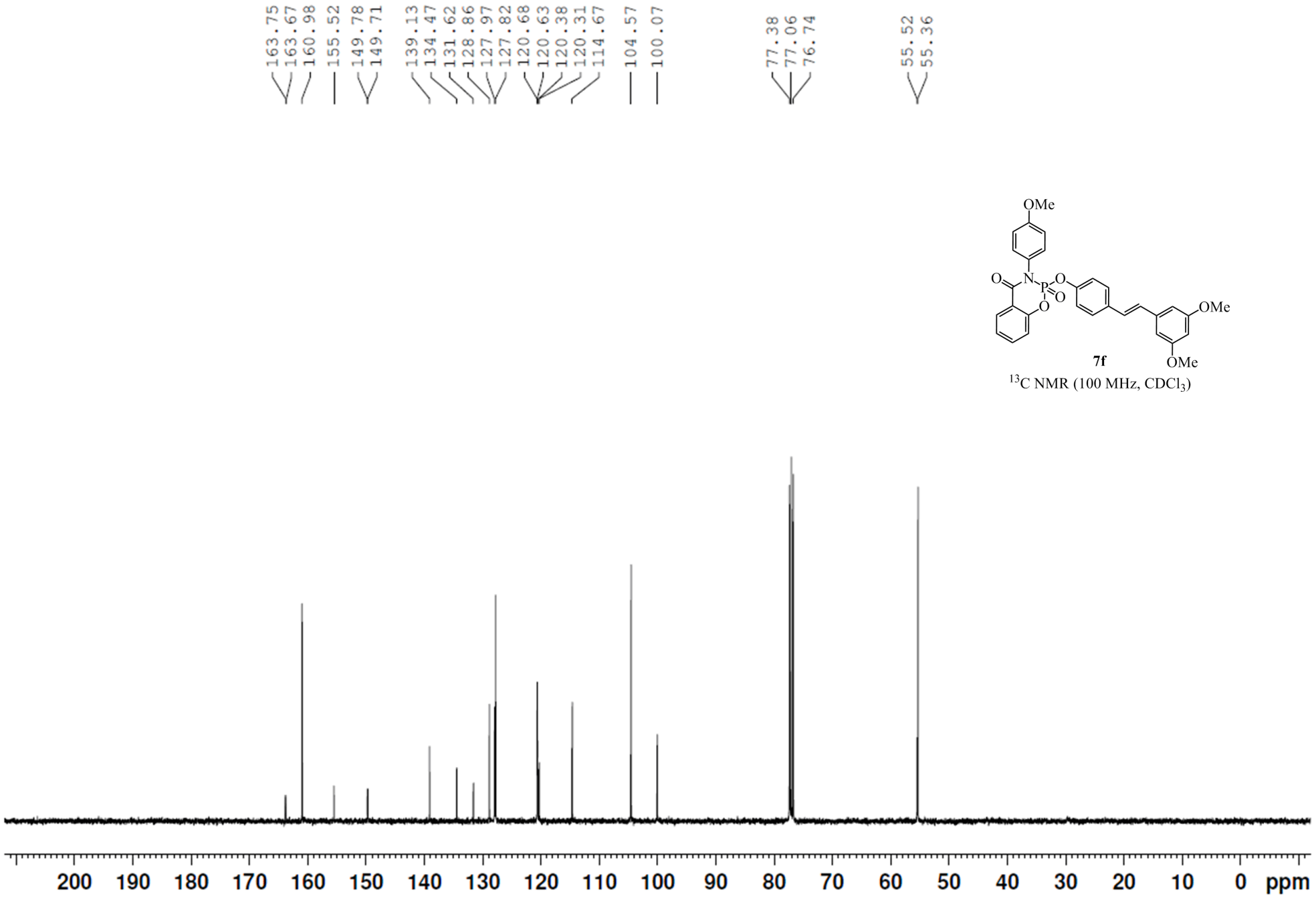
7e

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



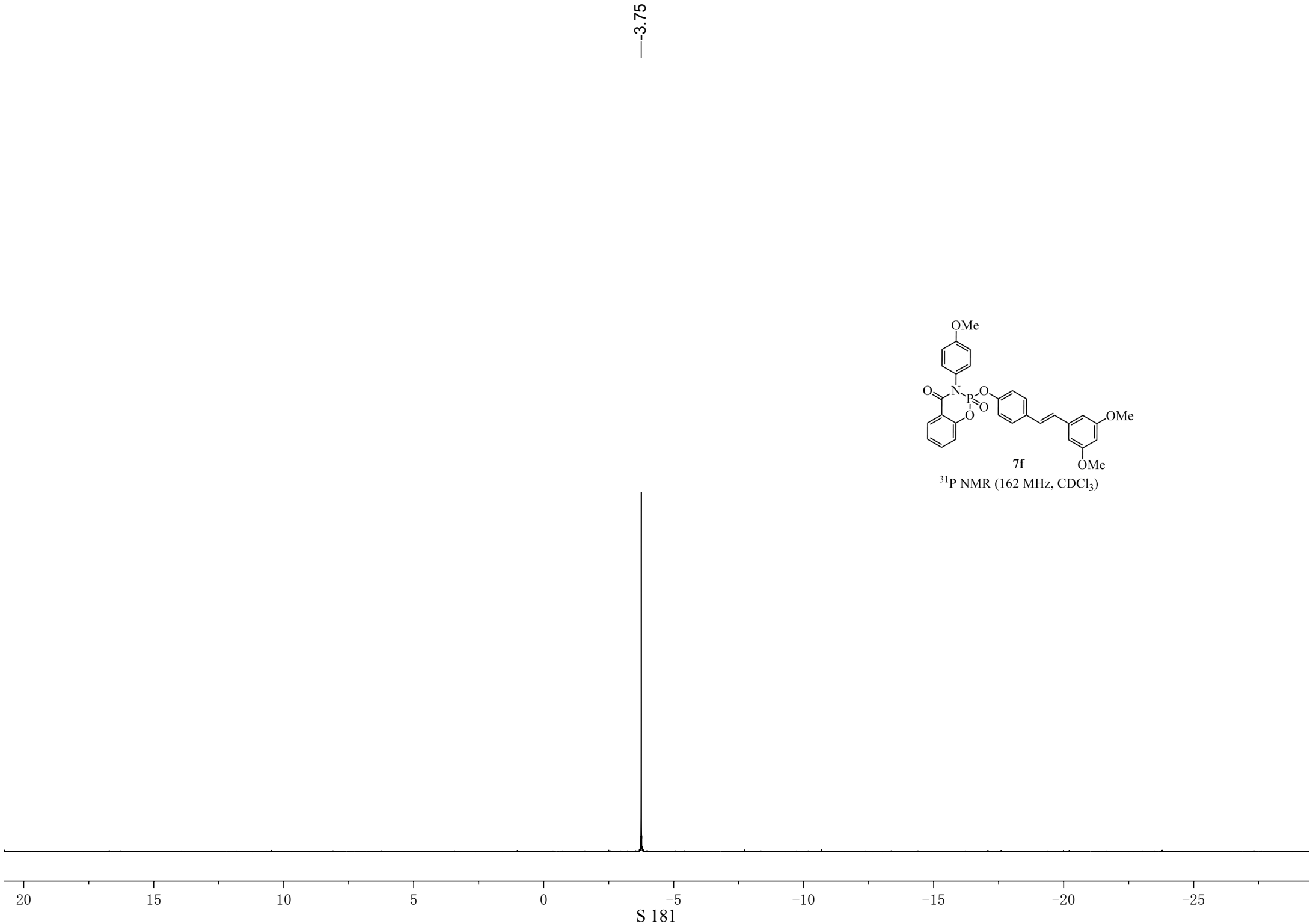
7f

^{1}H NMR (400 MHz, $CDCl_3$)

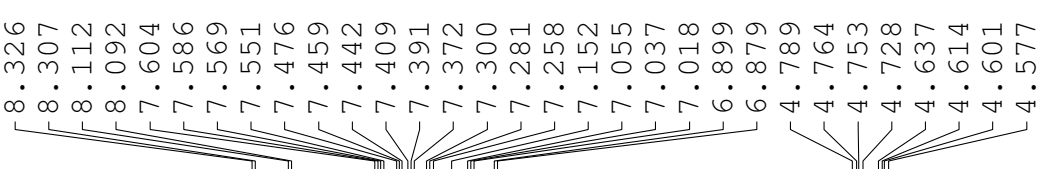


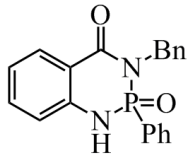
7f

^{13}C NMR (100 MHz, $CDCl_3$)



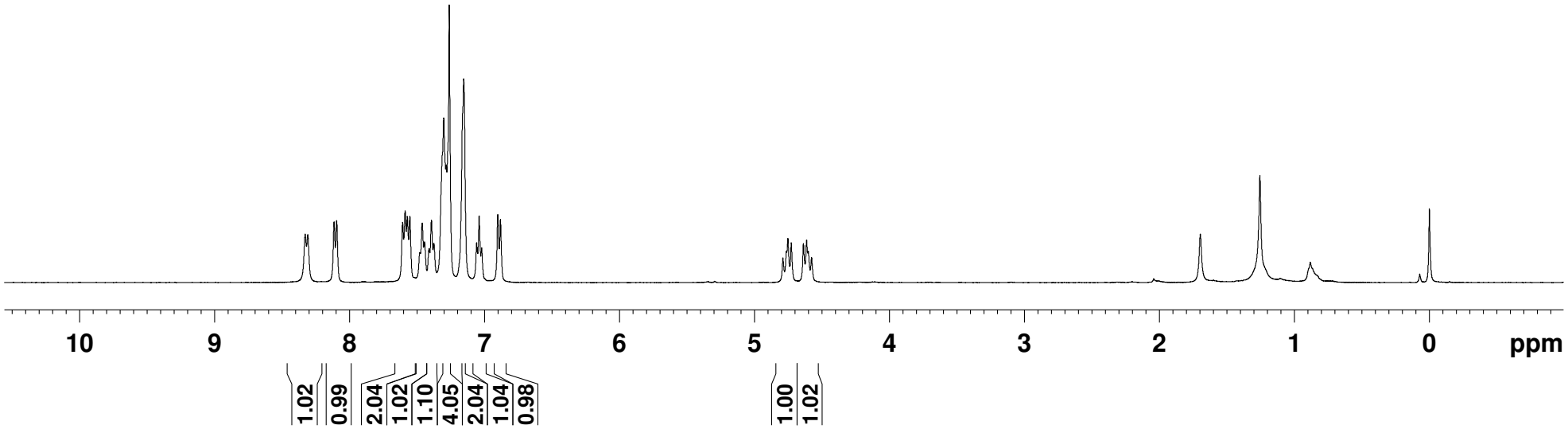
^{31}P NMR (162 MHz, $CDCl_3$)

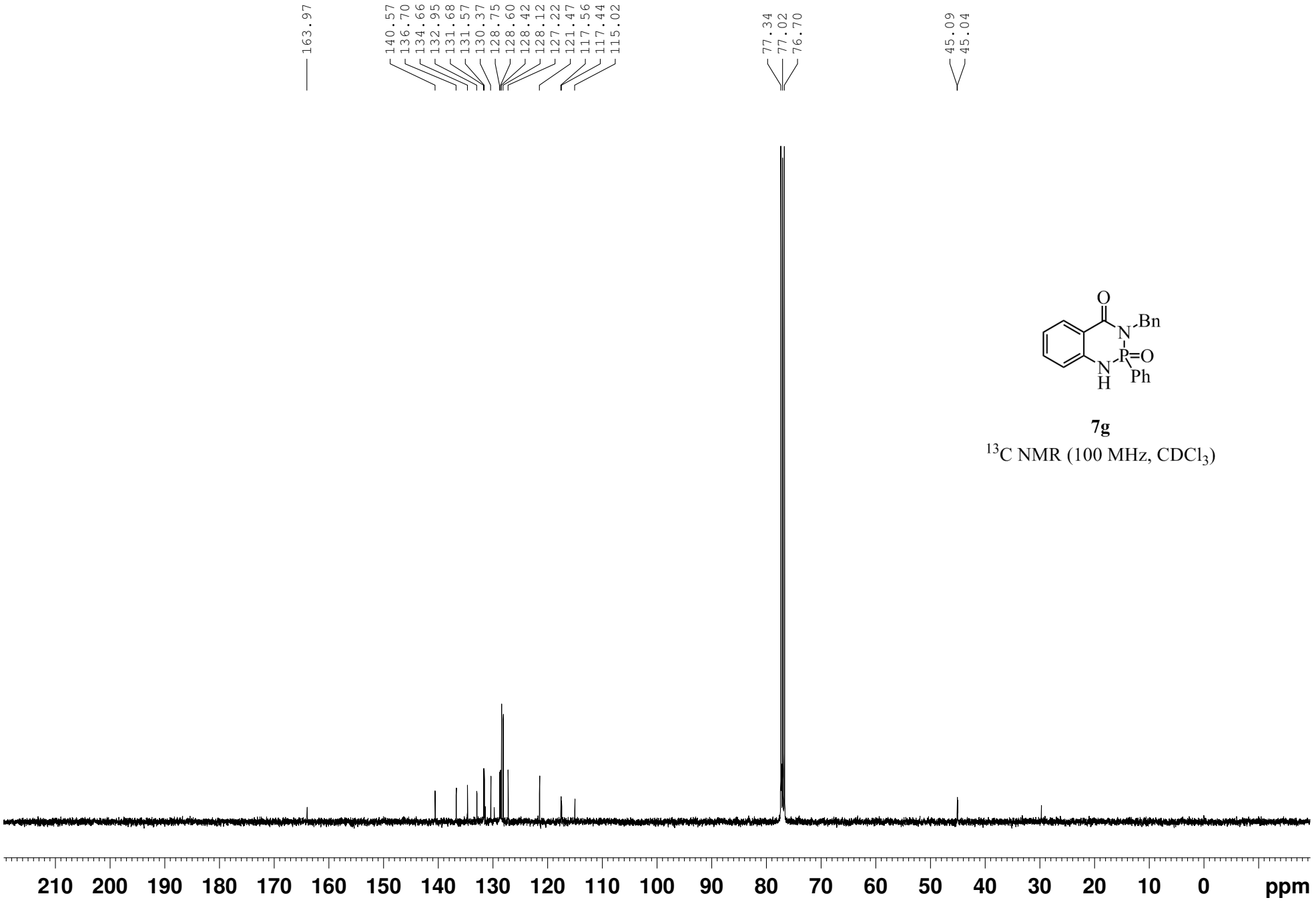




7g

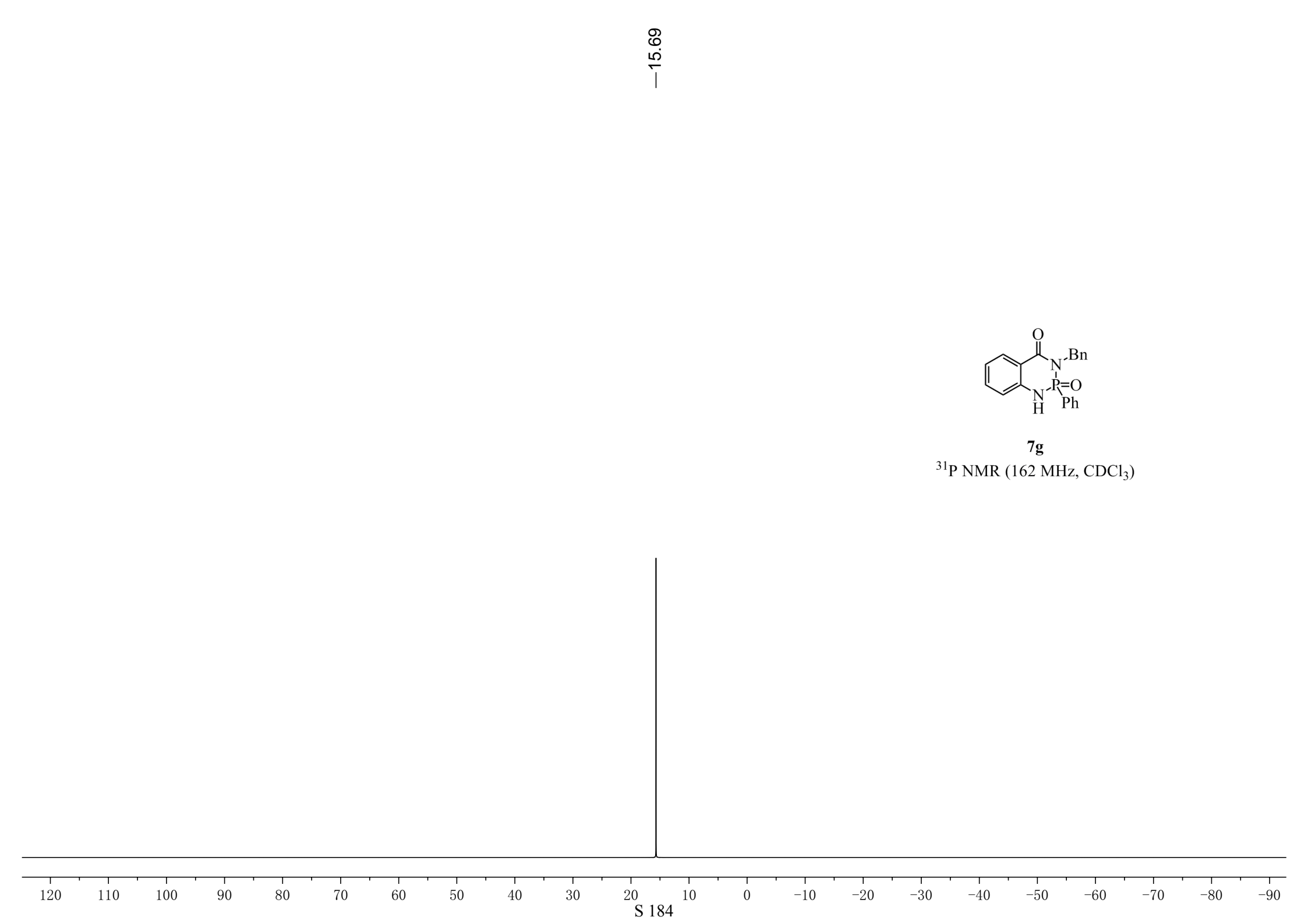
^{1}H NMR (400 MHz, $CDCl_3$)





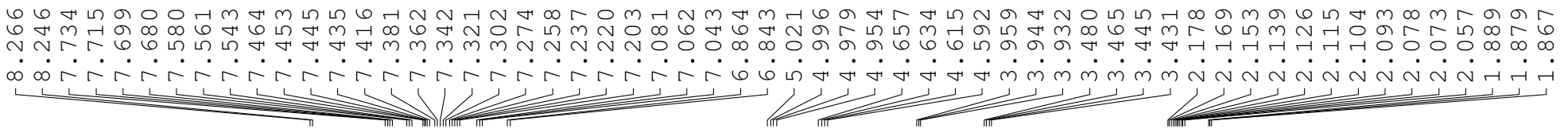
7g

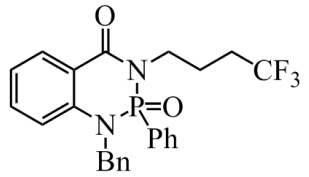
^{13}C NMR (100 MHz, $CDCl_3$)



7g

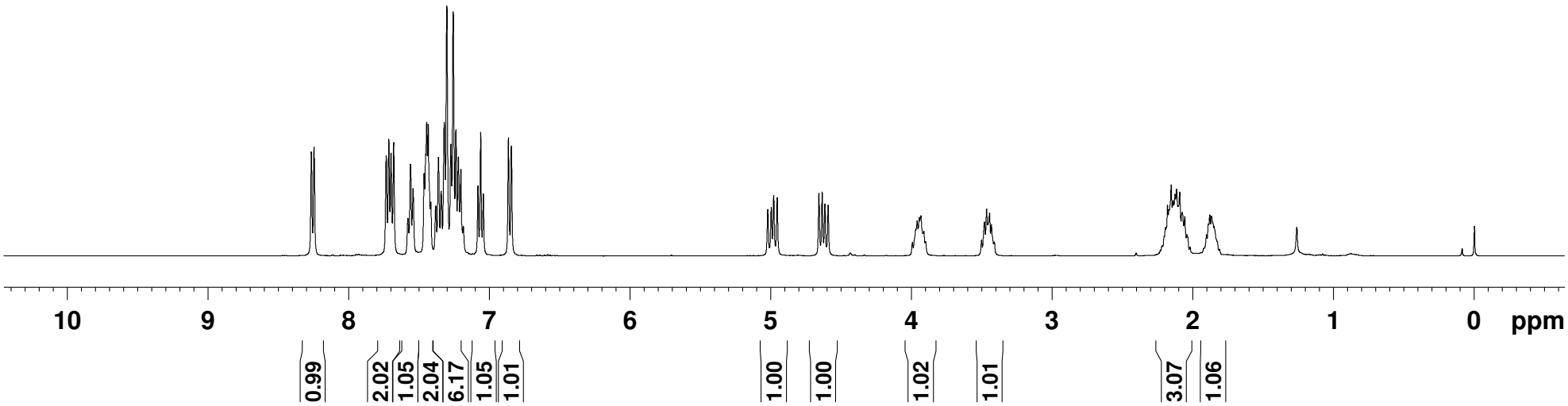
^{31}P NMR (162 MHz, $CDCl_3$)

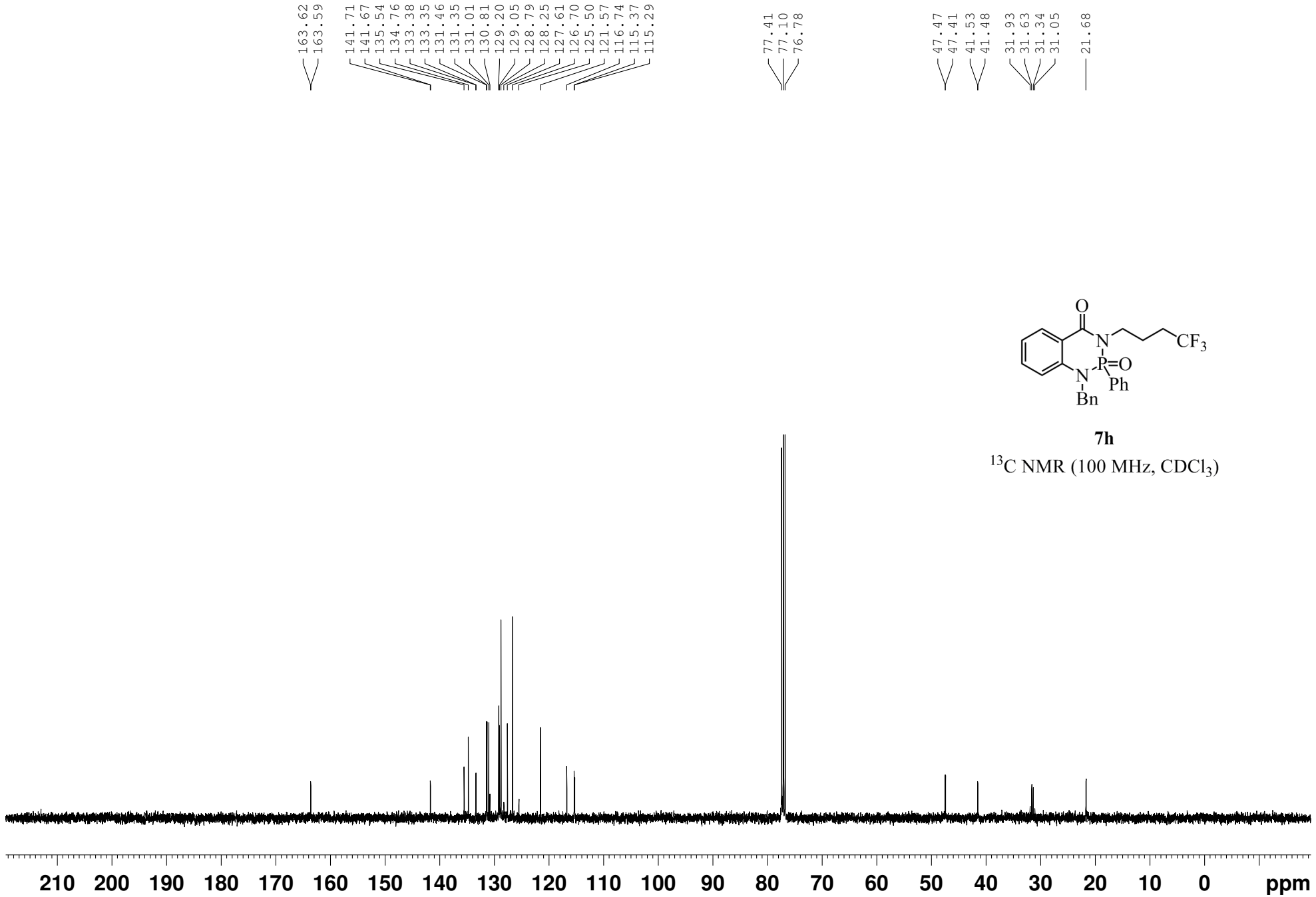




7h

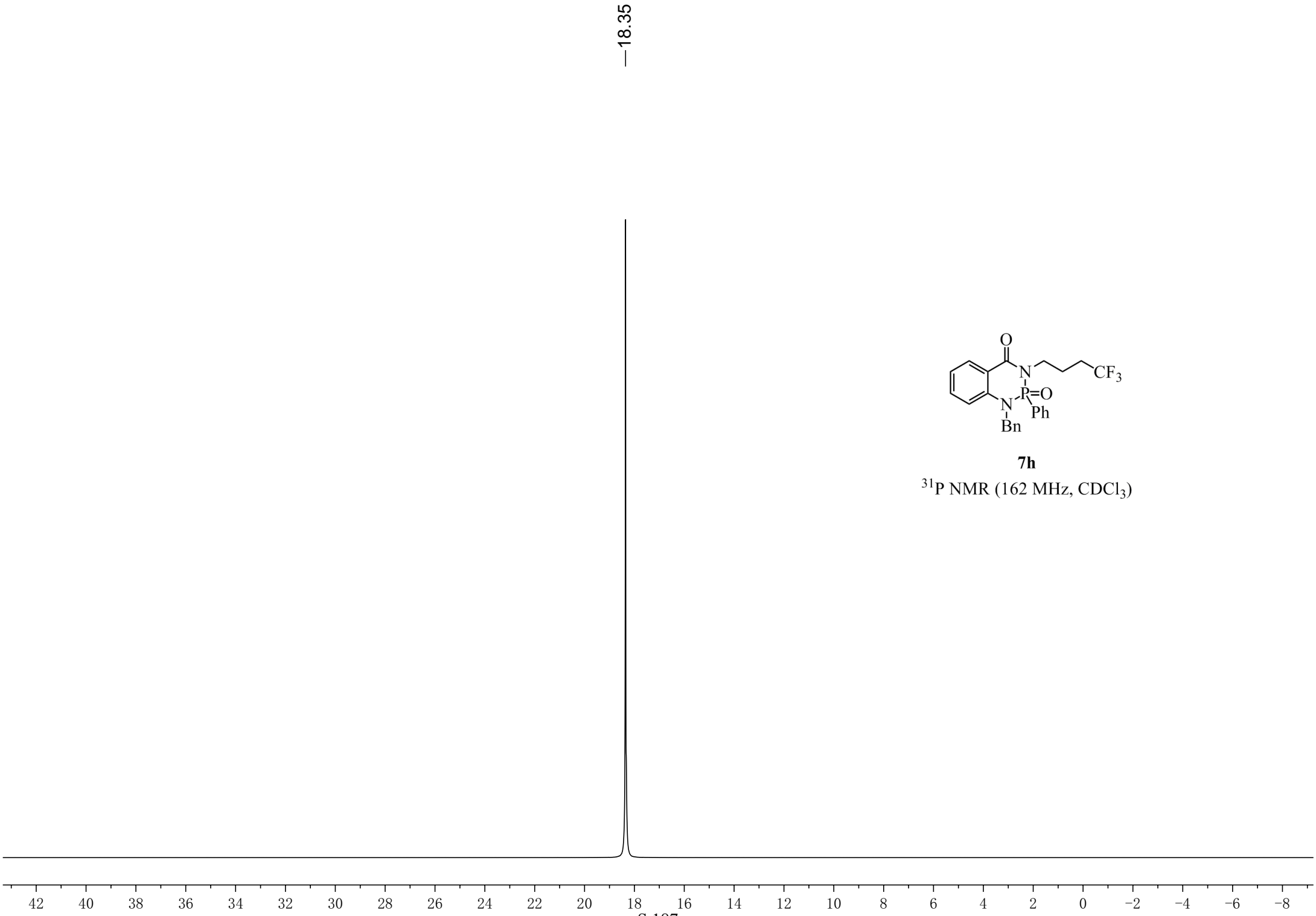
^{1}H NMR (400 MHz, $CDCl_3$)





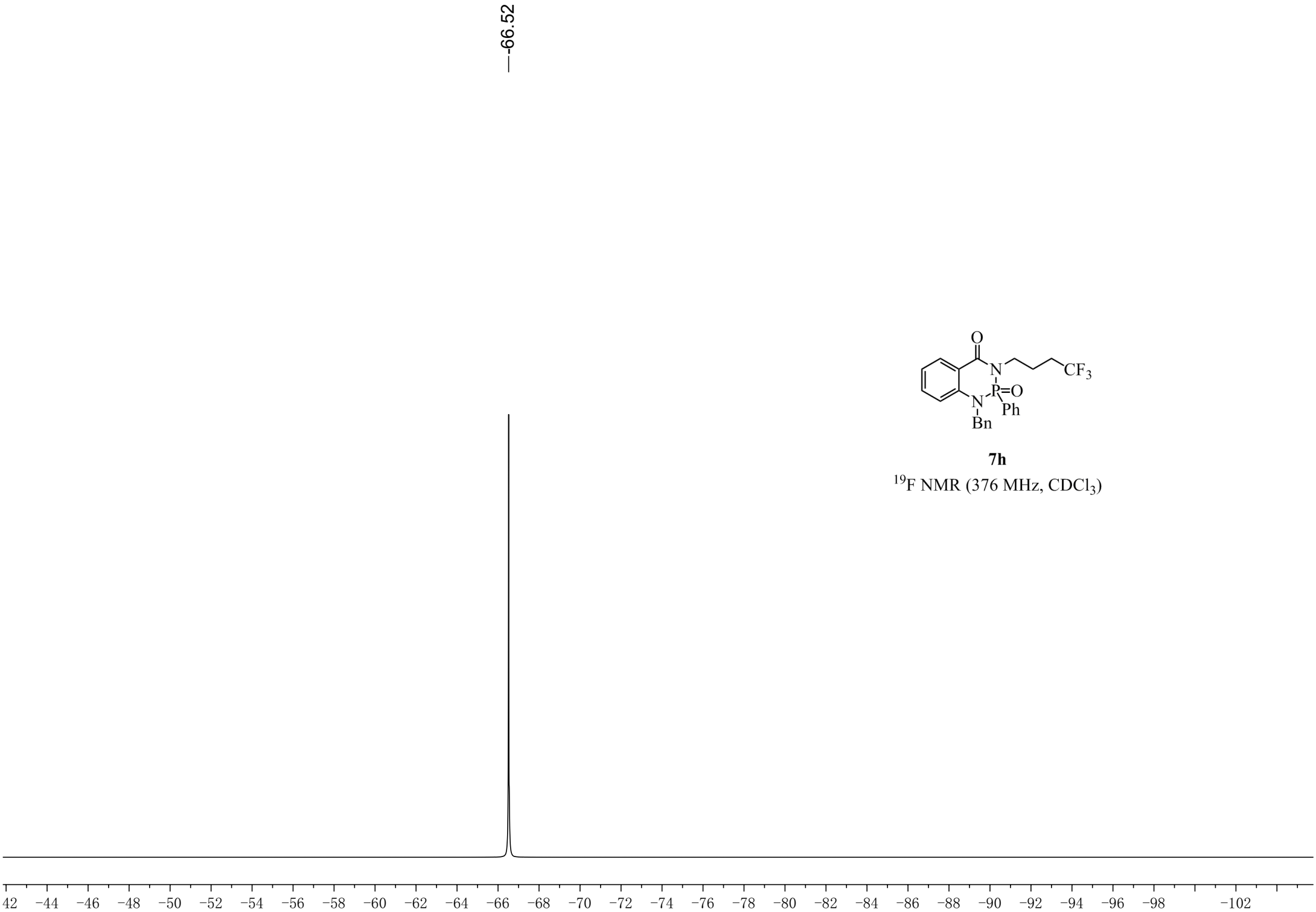
7h

^{13}C NMR (100 MHz, $CDCl_3$)



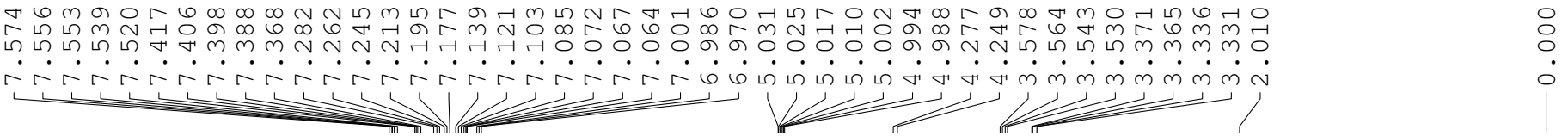
7h

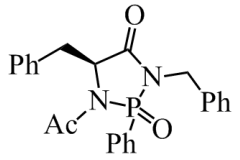
^{31}P NMR (162 MHz, $CDCl_3$)



7h

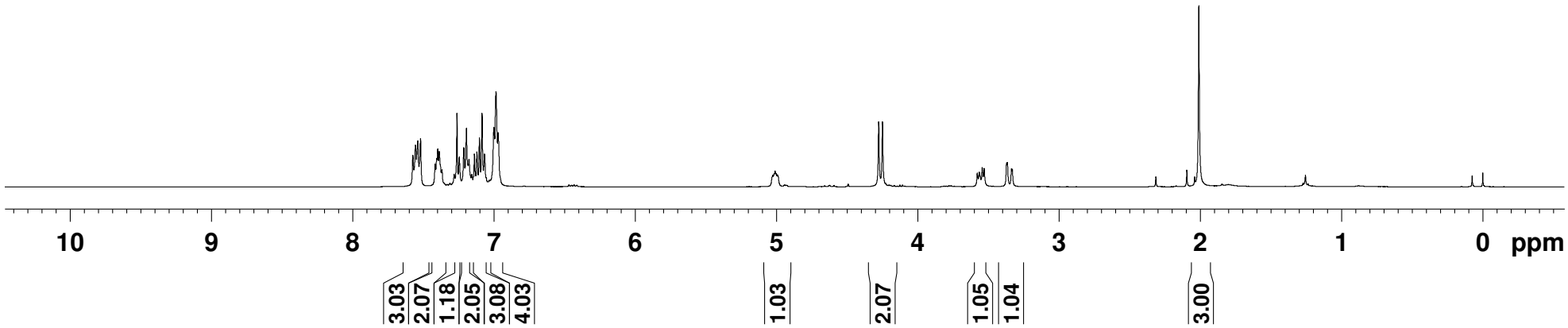
^{19}F NMR (376 MHz, $CDCl_3$)

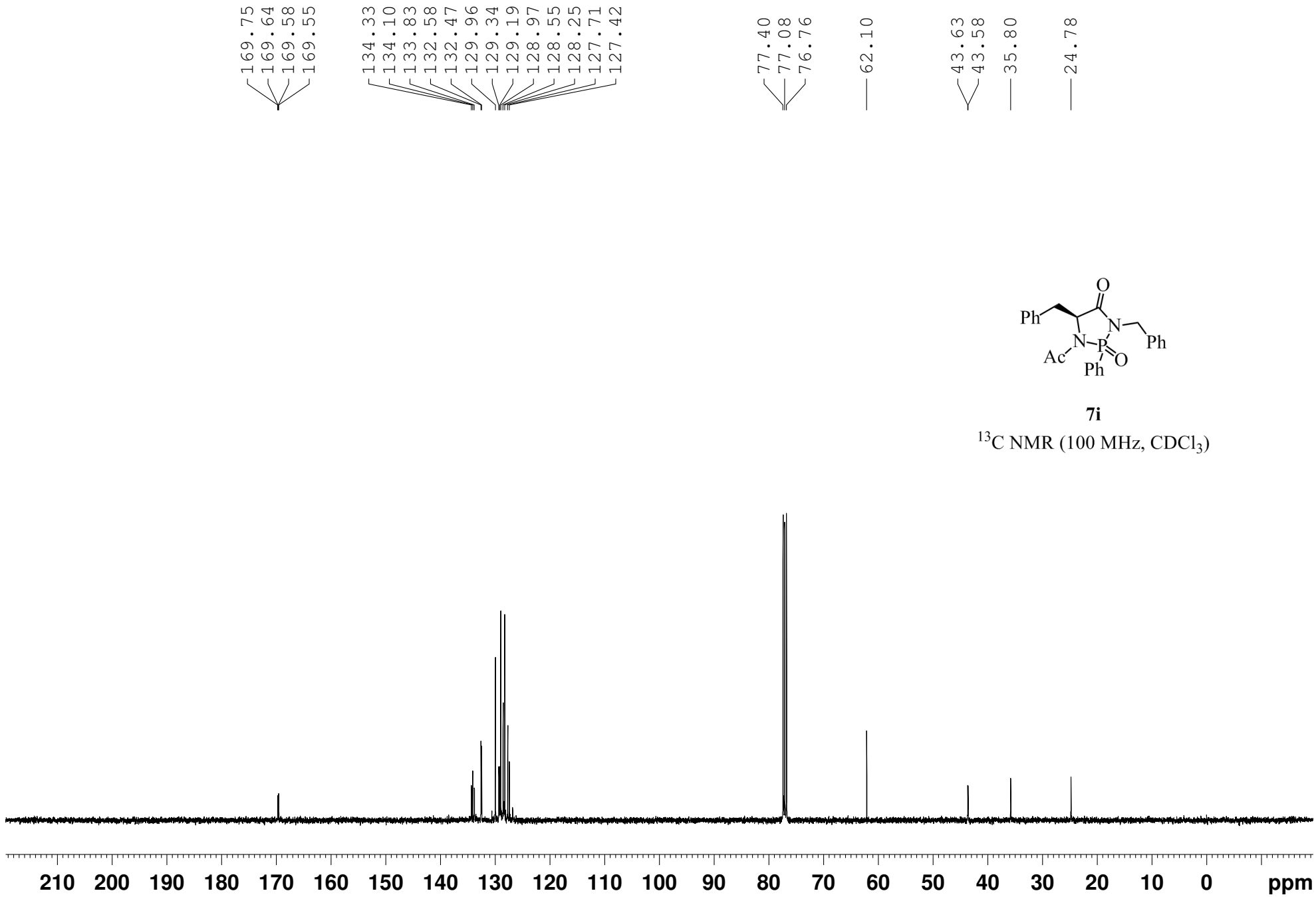




7i

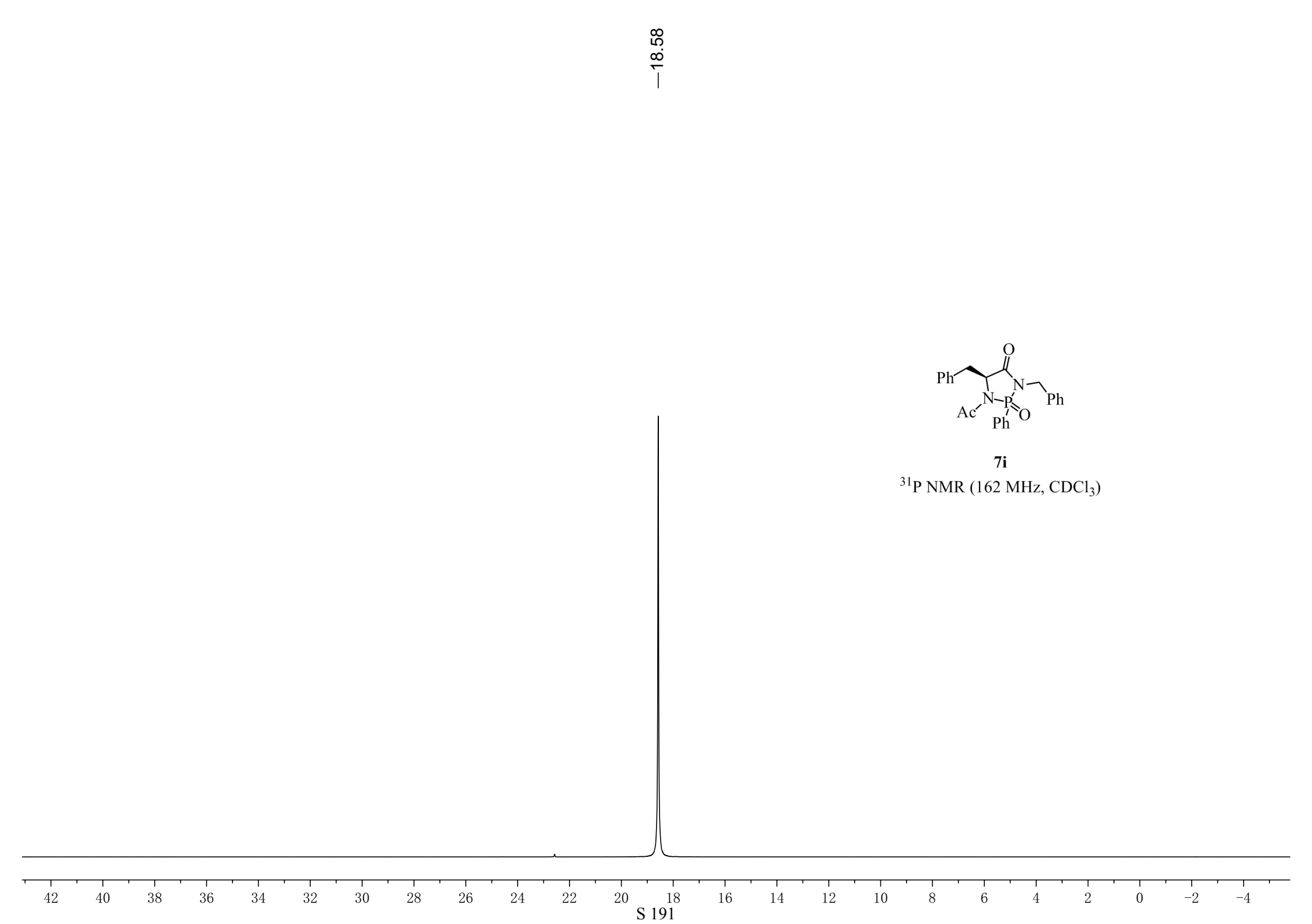
^{1}H NMR (400 MHz, $CDCl_3$)





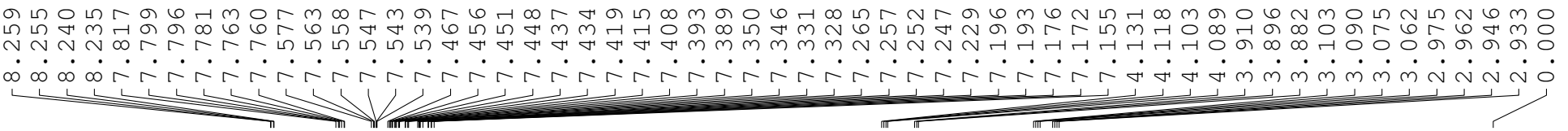
7i

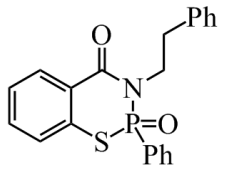
^{13}C NMR (100 MHz, $CDCl_3$)



7i

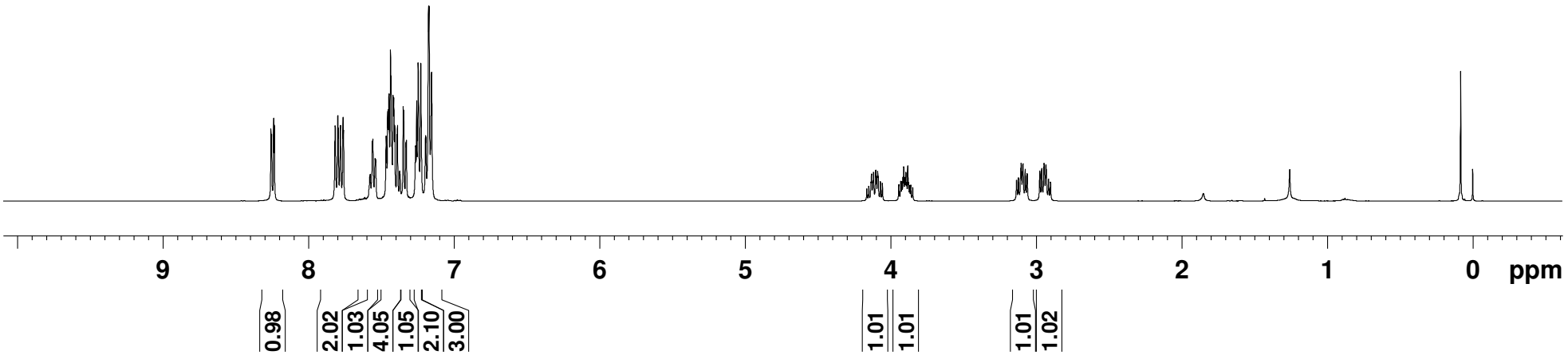
^{31}P NMR (162 MHz, $CDCl_3$)

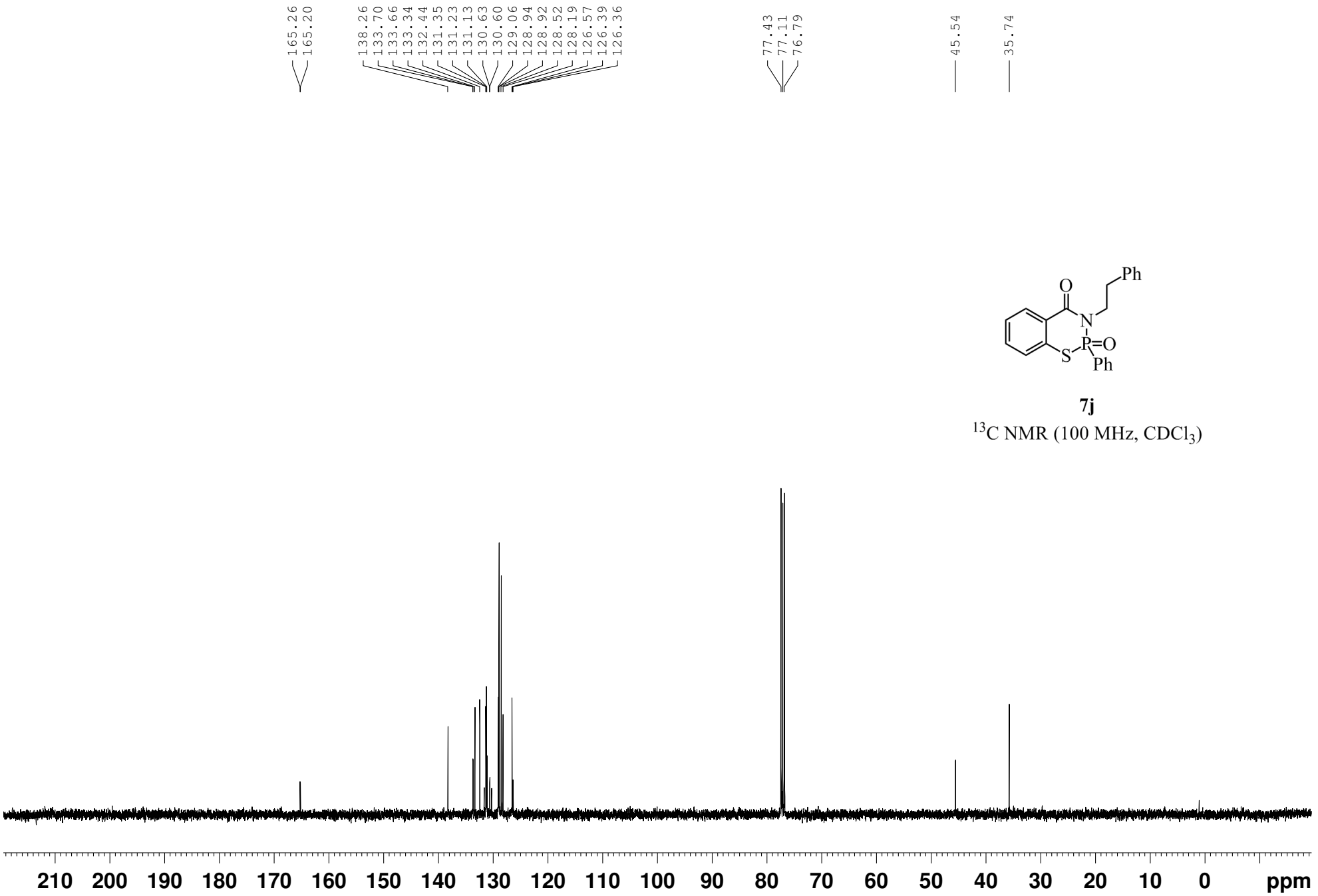




7j

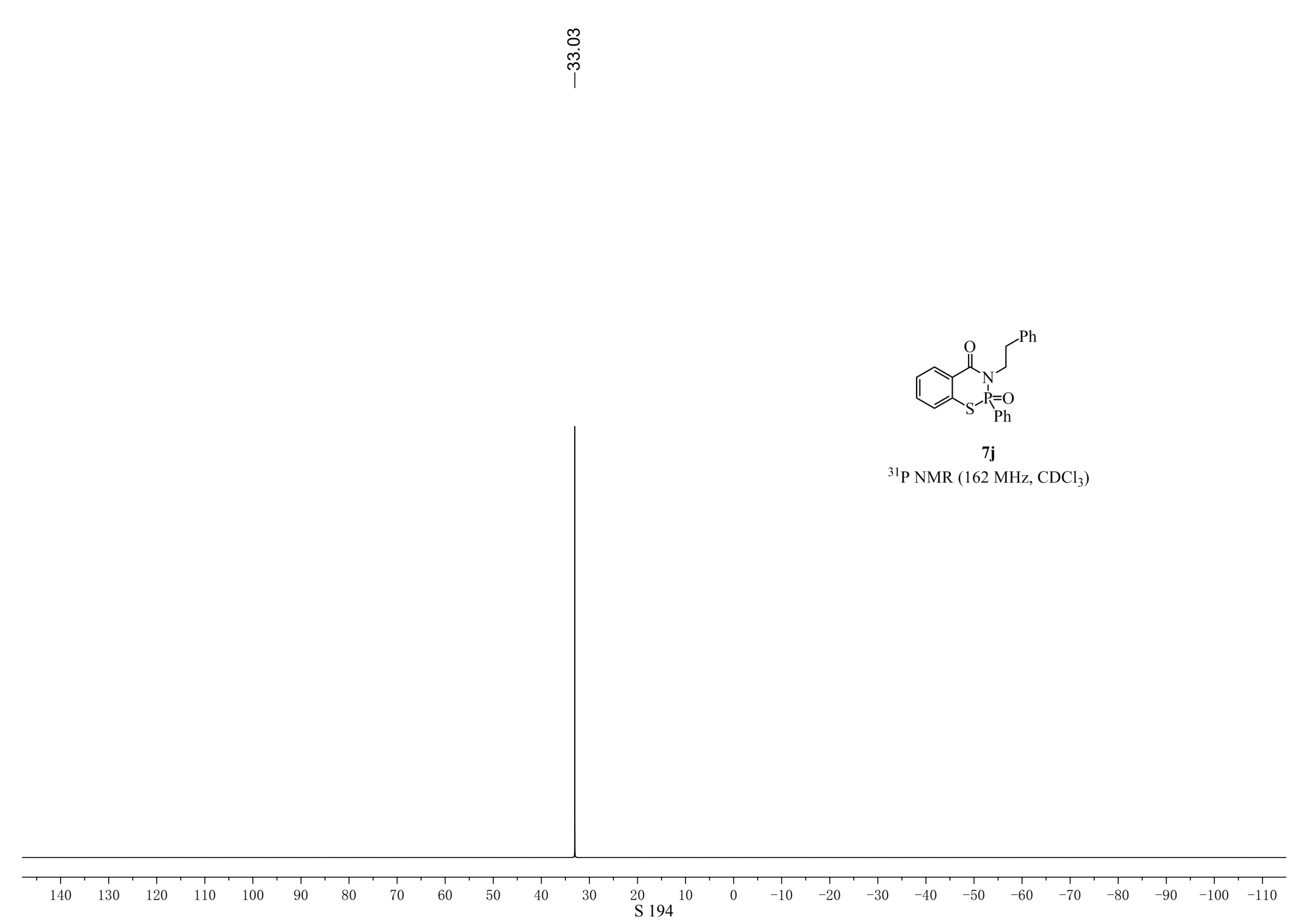
^{1}H NMR (400 MHz, $CDCl_3$)





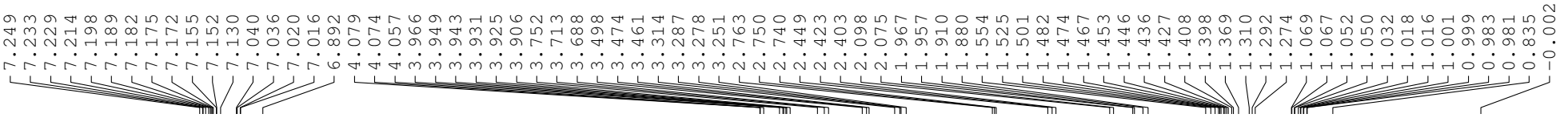
7j

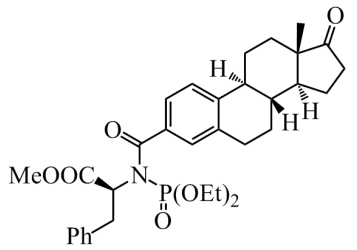
^{13}C NMR (100 MHz, $CDCl_3$)



7j

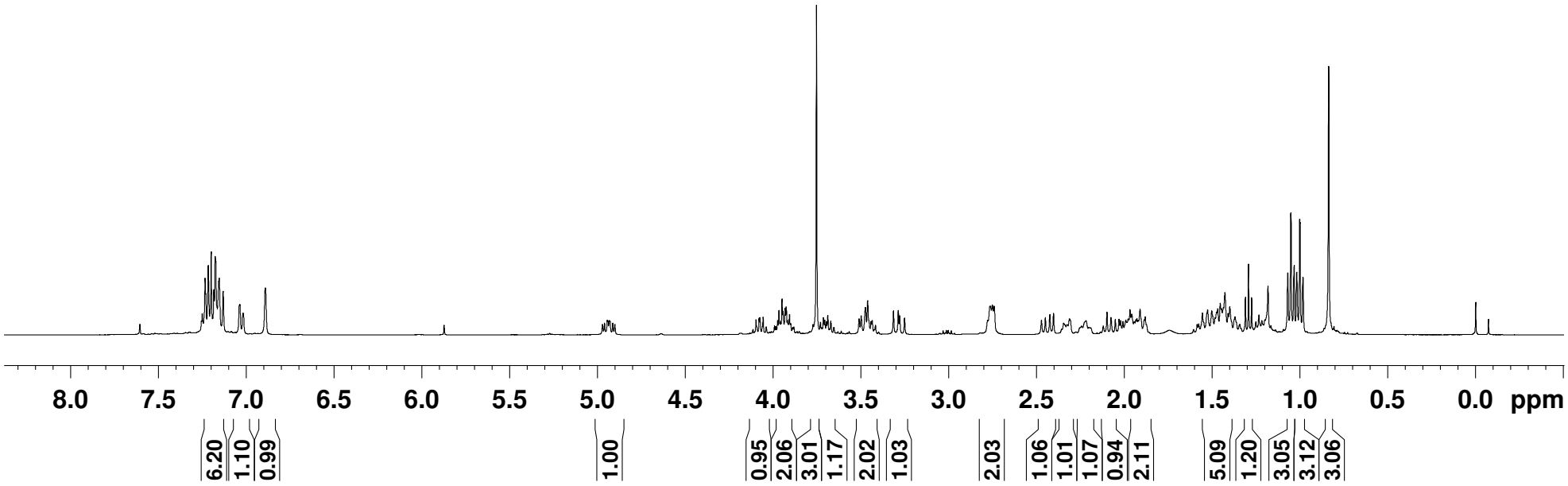
^{31}P NMR (162 MHz, $CDCl_3$)

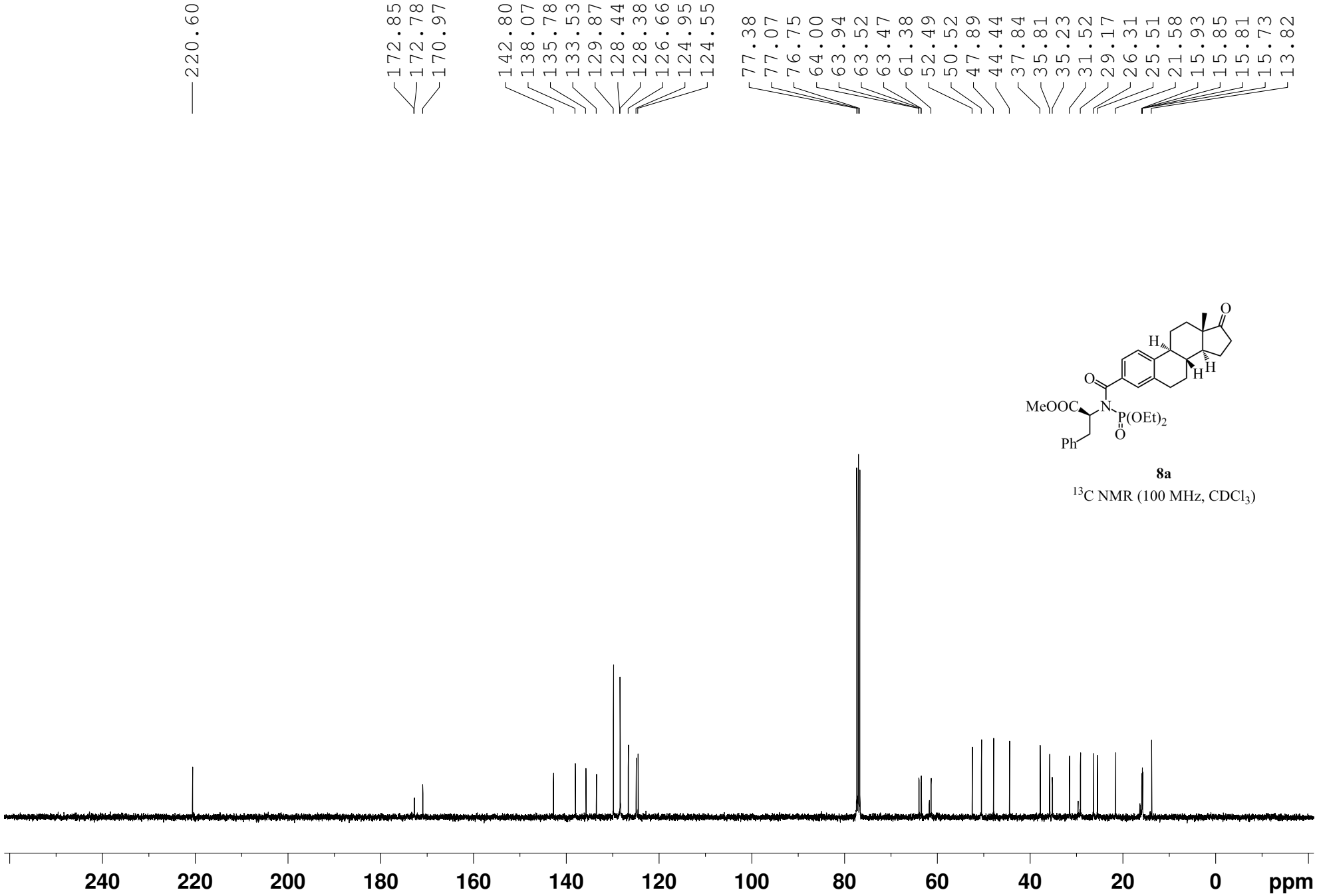




8a

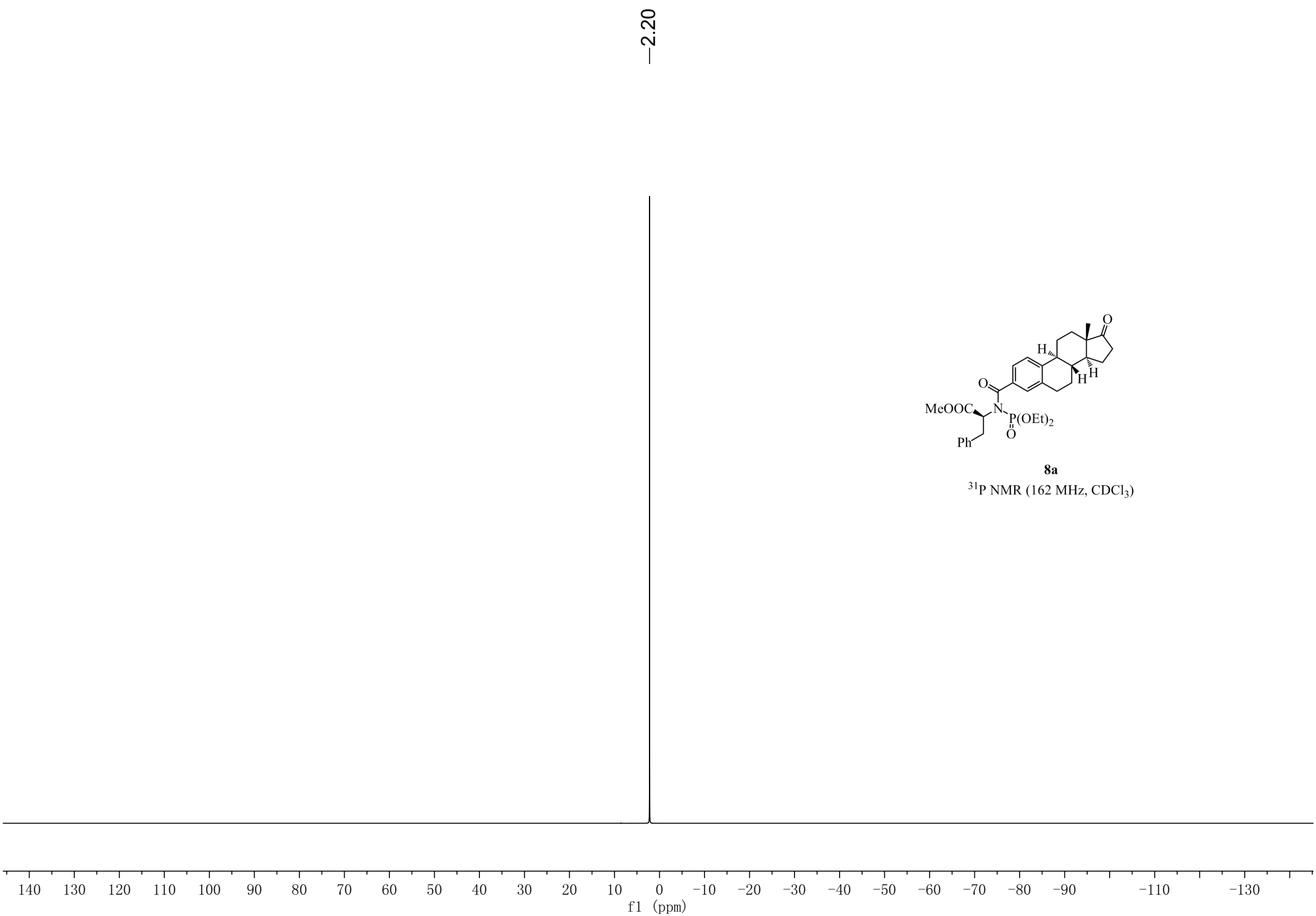
^{1}H NMR (400 MHz, $CDCl_3$)





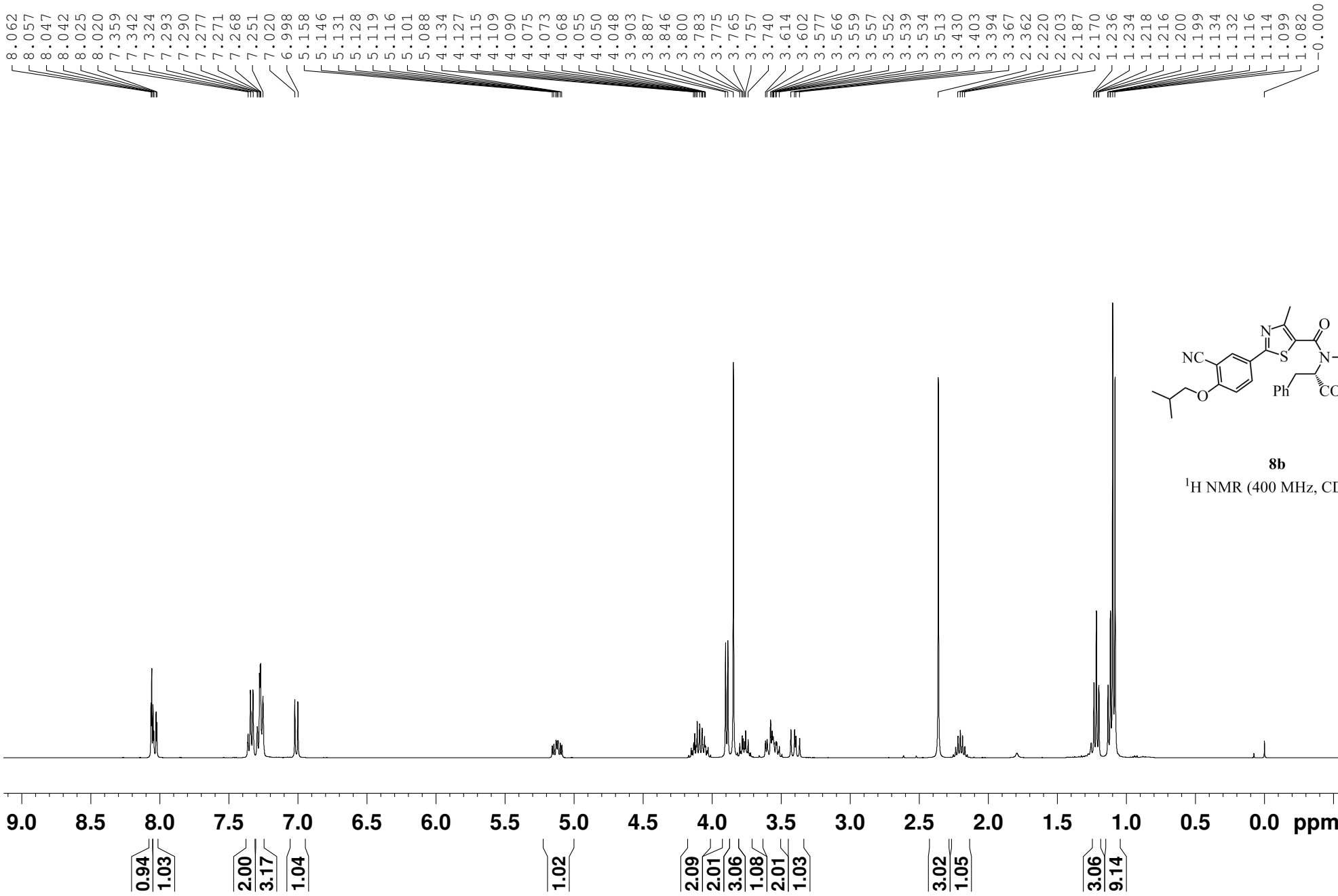
8a

^{13}C NMR (100 MHz, $CDCl_3$)



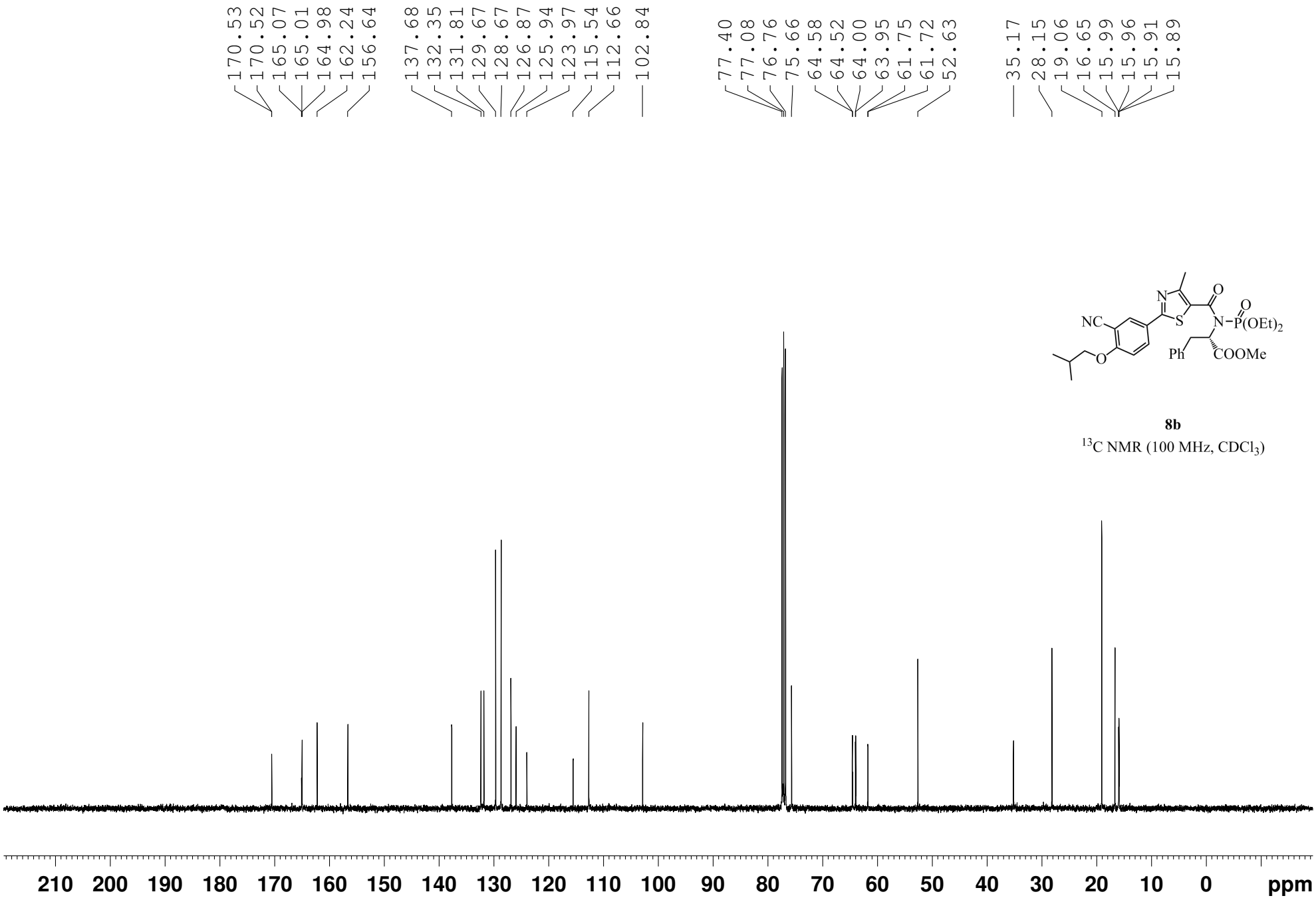
8a

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



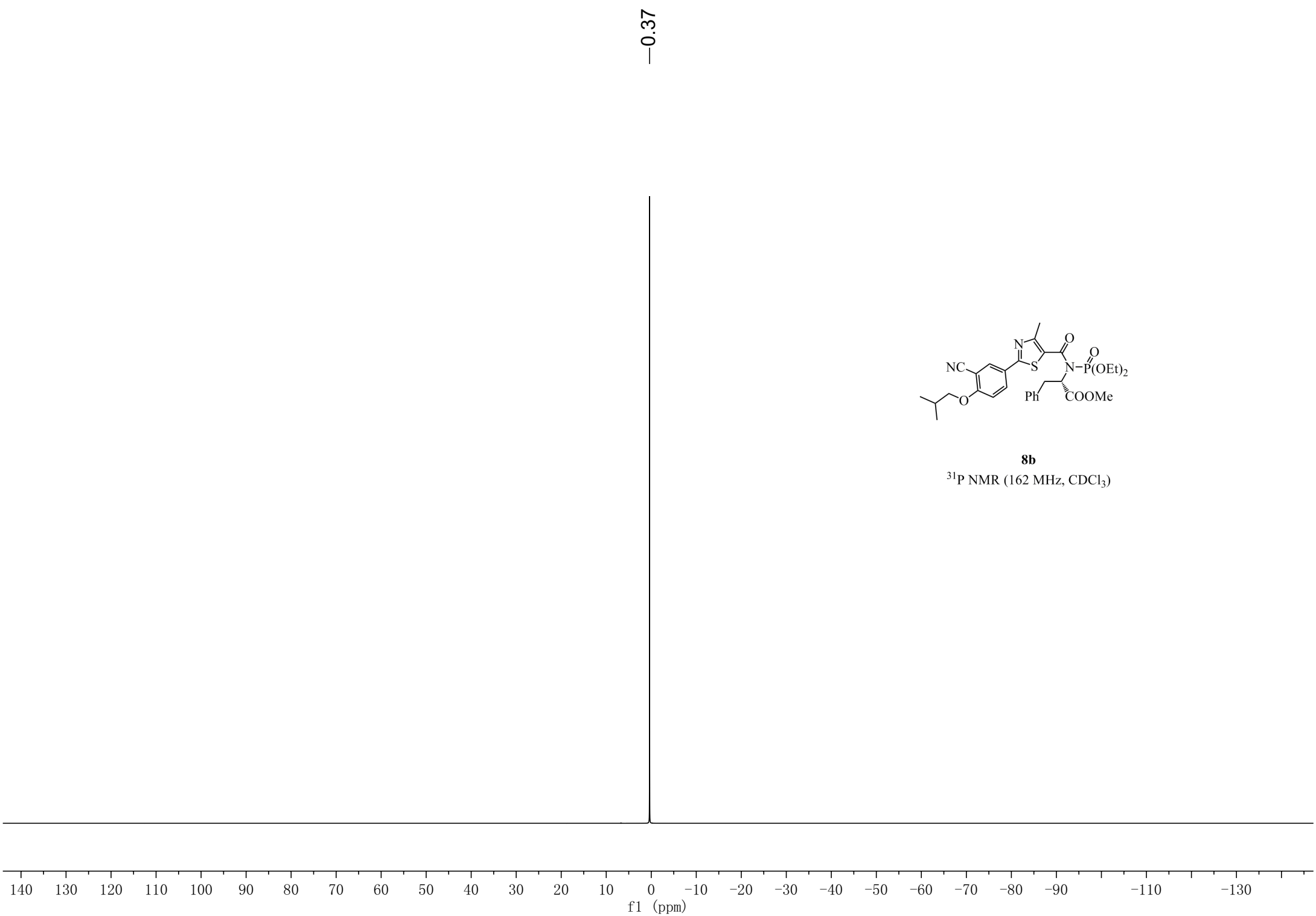
8b

^{1}H NMR (400 MHz, $CDCl_3$)



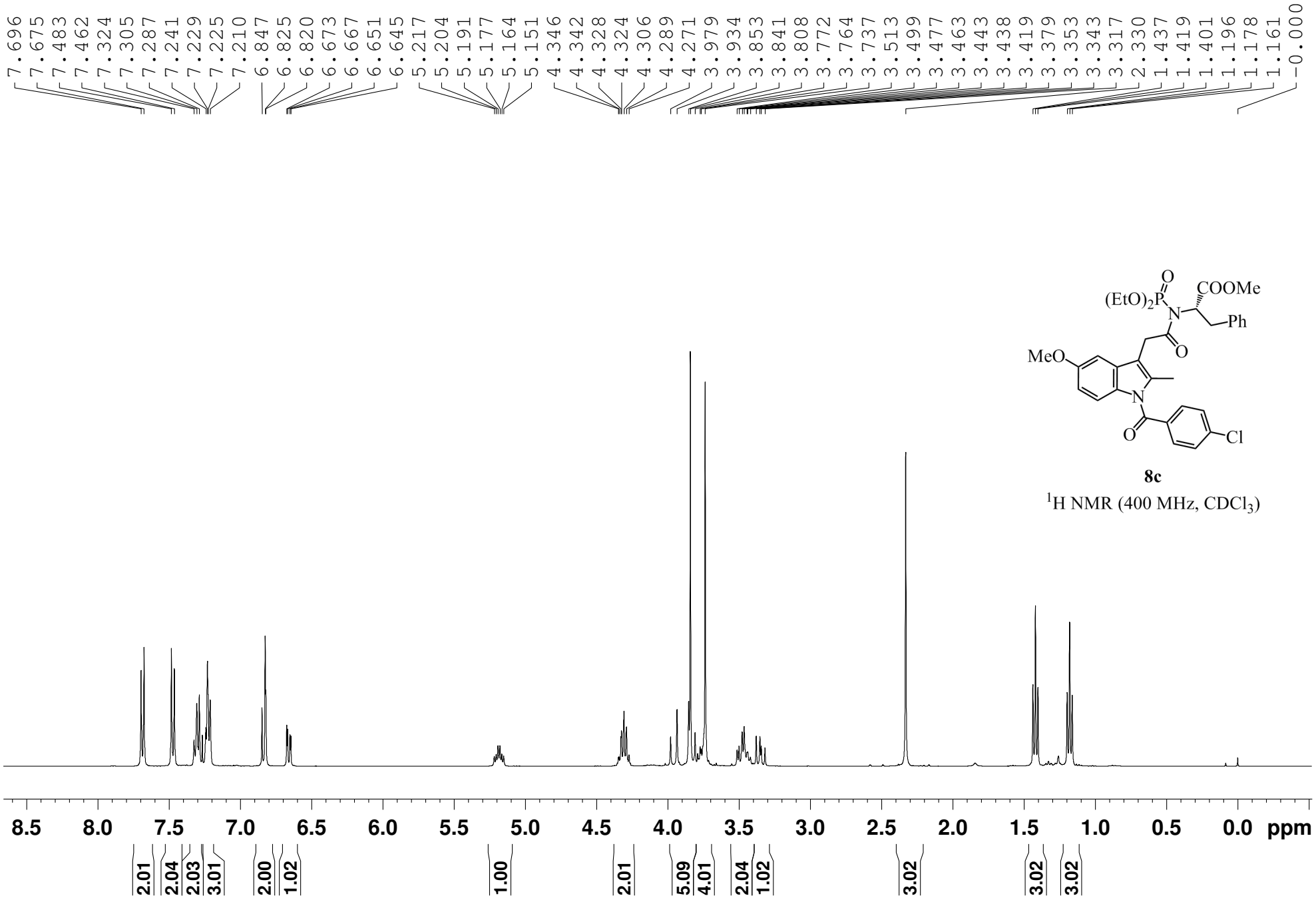
8b

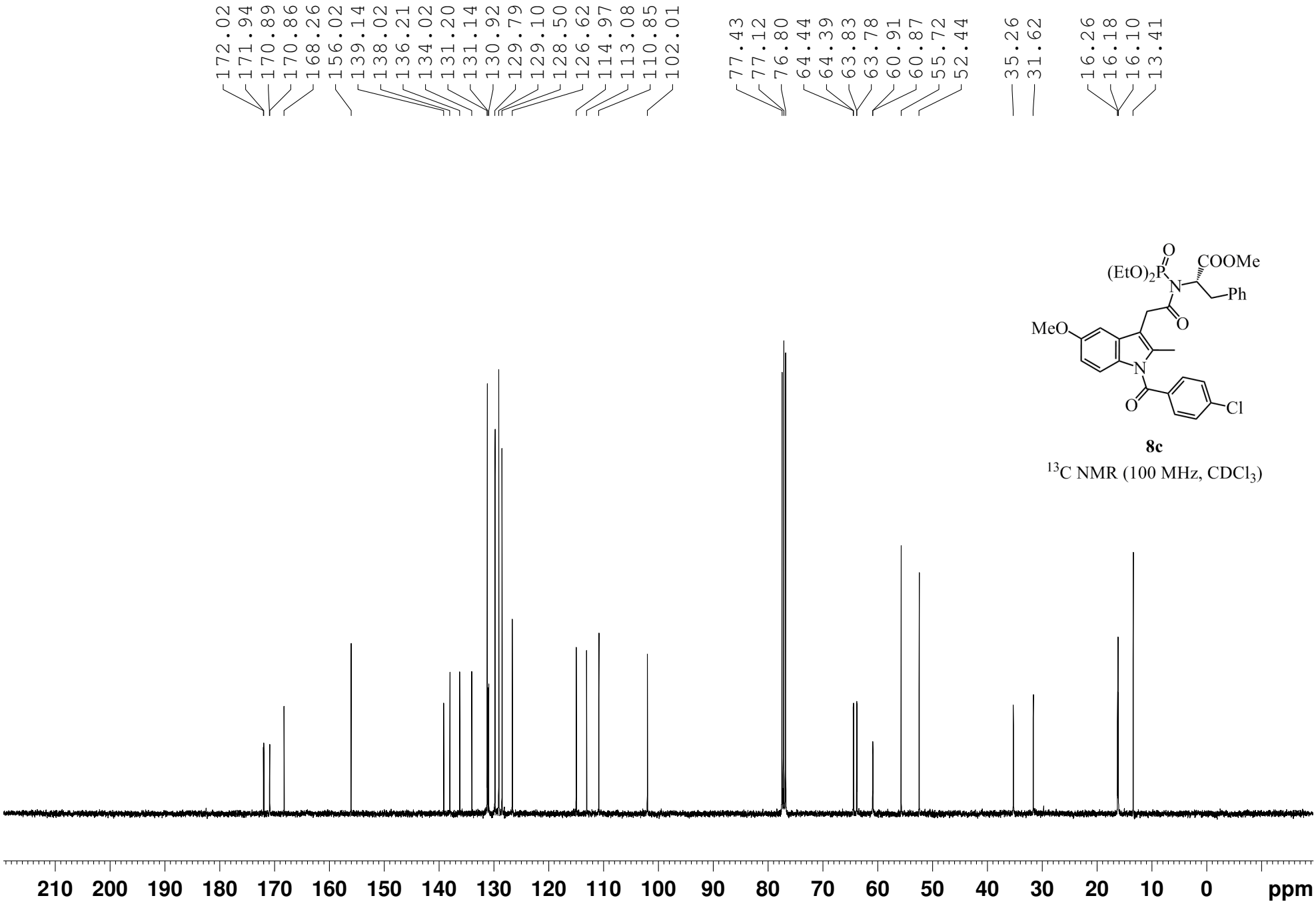
^{13}C NMR (100 MHz, $CDCl_3$)



8b

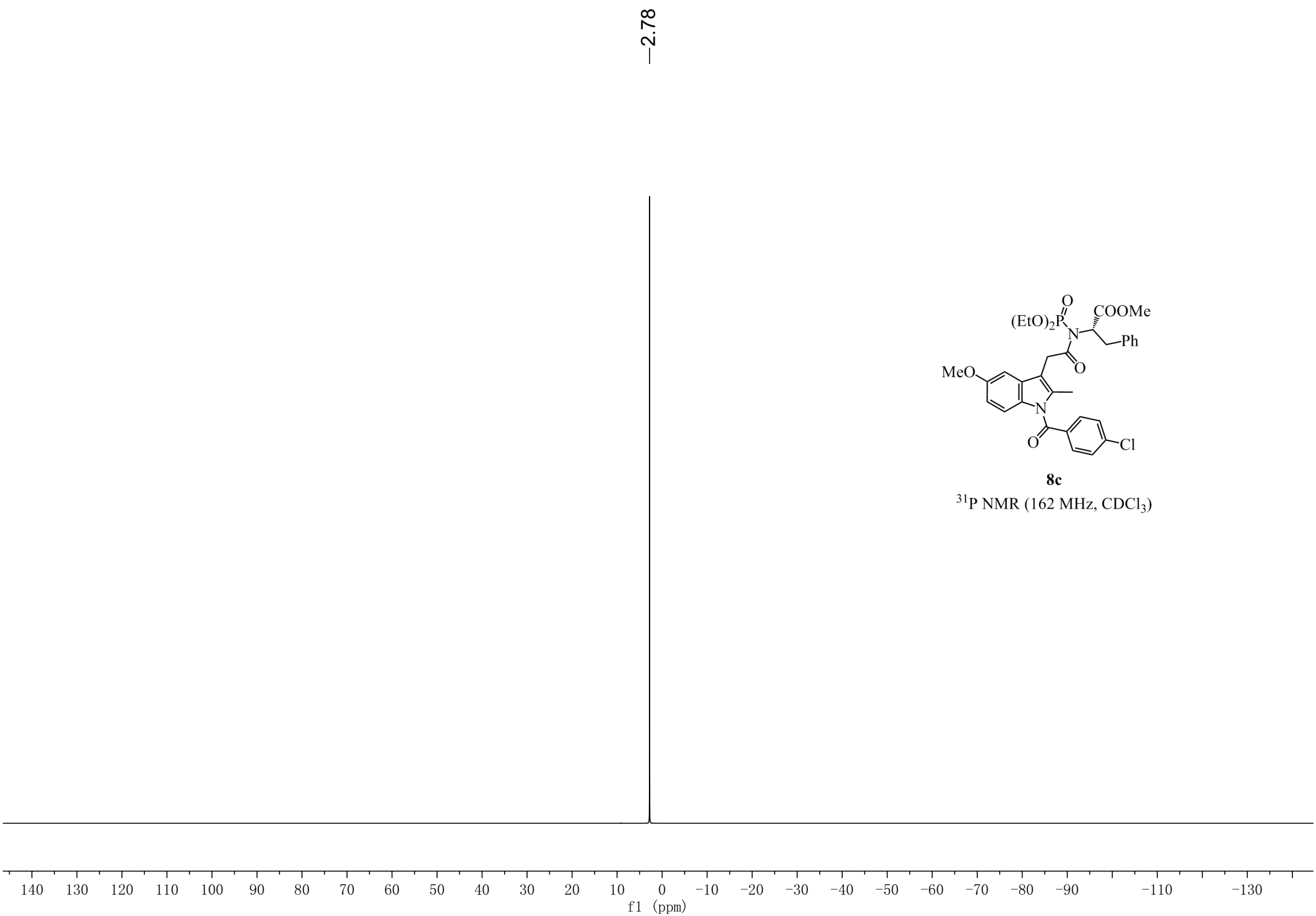
^{31}P NMR (162 MHz, $CDCl_3$)


7.696
7.675
7.483
7.462
7.324
7.305
7.287
7.241
7.229
7.225
7.210
6.847
6.825
6.820
6.673
6.667
6.651
6.645
5.217
5.204
5.191
5.177
5.164
5.151
4.346
4.342
4.328
4.324
4.306
4.289
4.271
3.979
3.934
3.853
3.841
3.808
3.772
3.764
3.737
3.513
3.499
3.477
3.463
3.443
3.438
3.419
3.379
3.353
3.343
3.317
2.330
1.437
1.419
1.401
1.196
1.178
1.161
-0.000
O
(EtO)2P
N
COOMe
Ph
O
MeO
N
O
Cl
8c
1H NMR (400 MHz, CDCl3)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.01
2.04
2.03
3.01
2.00
1.02
1.00
2.01
5.09
4.01
2.04
1.02
3.02
3.02
3.02



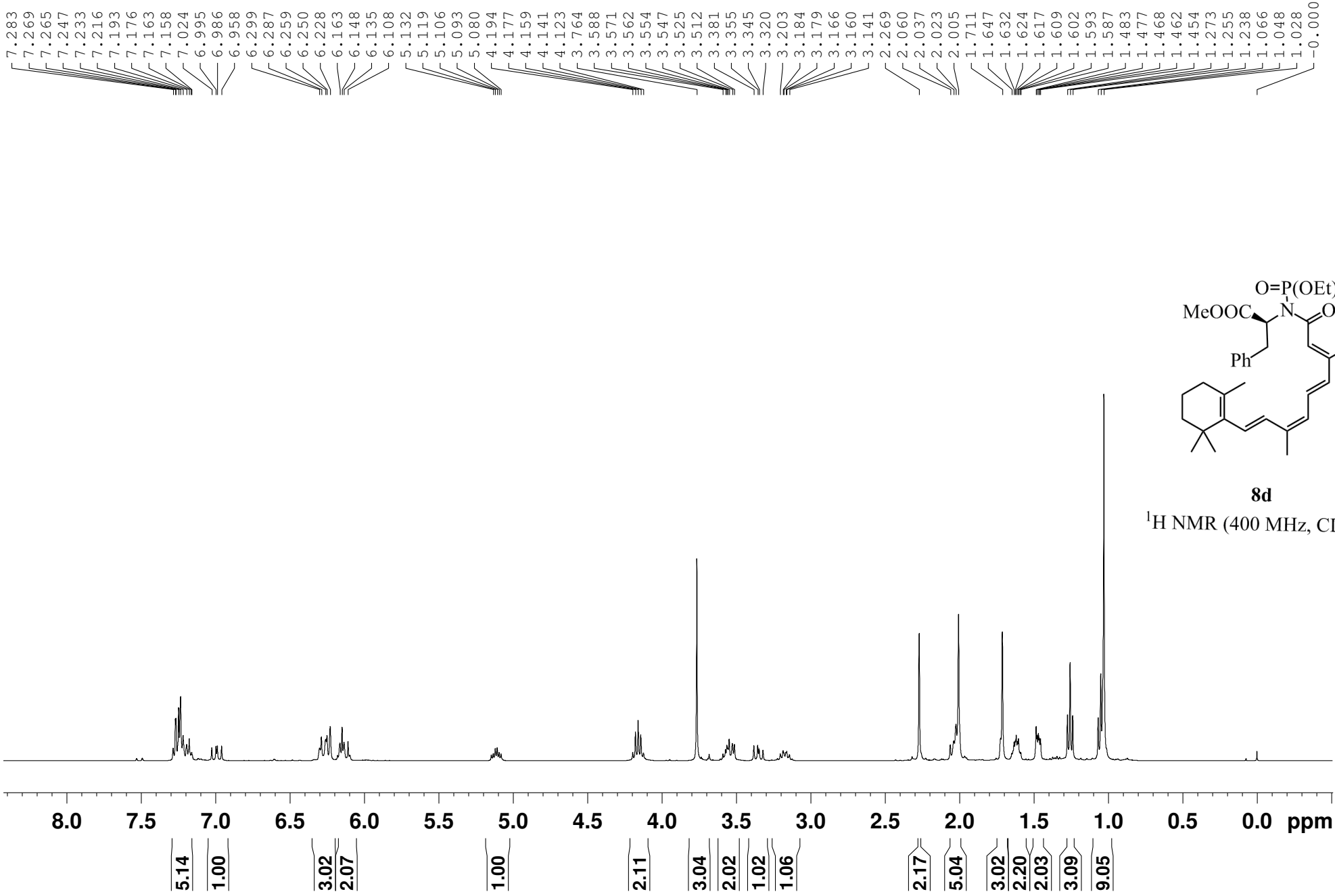
8c

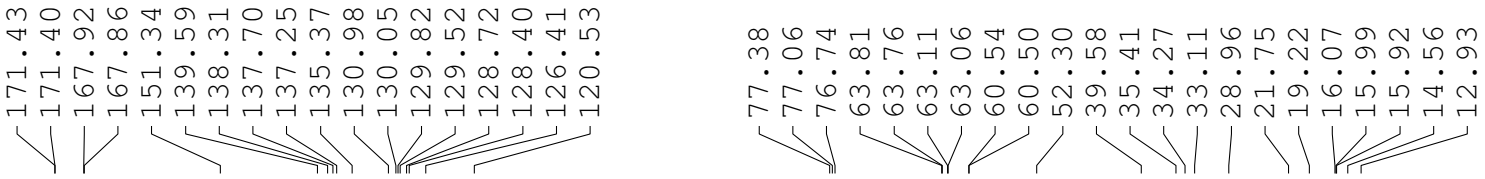
^{13}C NMR (100 MHz, $CDCl_3$)

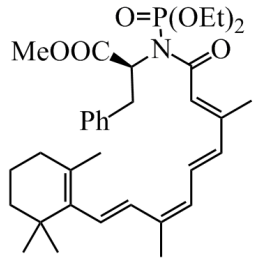


8c

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

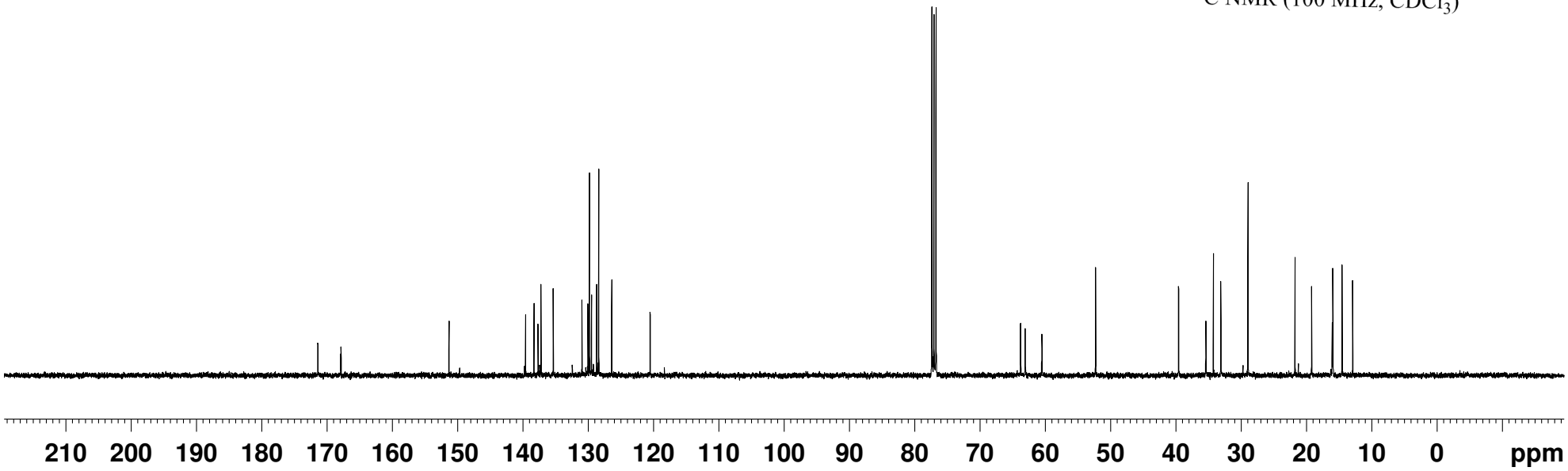

7.283
7.269
7.265
7.247
7.233
7.216
7.193
7.176
7.163
7.158
7.024
6.995
6.986
6.958
6.299
6.287
6.259
6.250
6.228
6.163
6.148
6.135
6.108
5.132
5.119
5.106
5.093
5.080
4.194
4.177
4.159
4.141
4.123
3.764
3.588
3.571
3.562
3.554
3.547
3.525
3.512
3.381
3.355
3.345
3.320
3.203
3.184
3.179
3.166
3.160
3.141
2.269
2.060
2.037
2.023
2.005
1.711
1.647
1.632
1.624
1.617
1.609
1.602
1.593
1.587
1.483
1.477
1.468
1.462
1.454
1.273
1.255
1.238
1.066
1.048
1.028
-0.000
O=P(OEt)2
MeOOC
N
O
Ph
8d
1H NMR (400 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.14
1.00
3.02
2.07
1.00
2.11
3.04
2.02
1.02
1.06
2.17
5.04
3.02
2.20
2.03
3.09
9.05

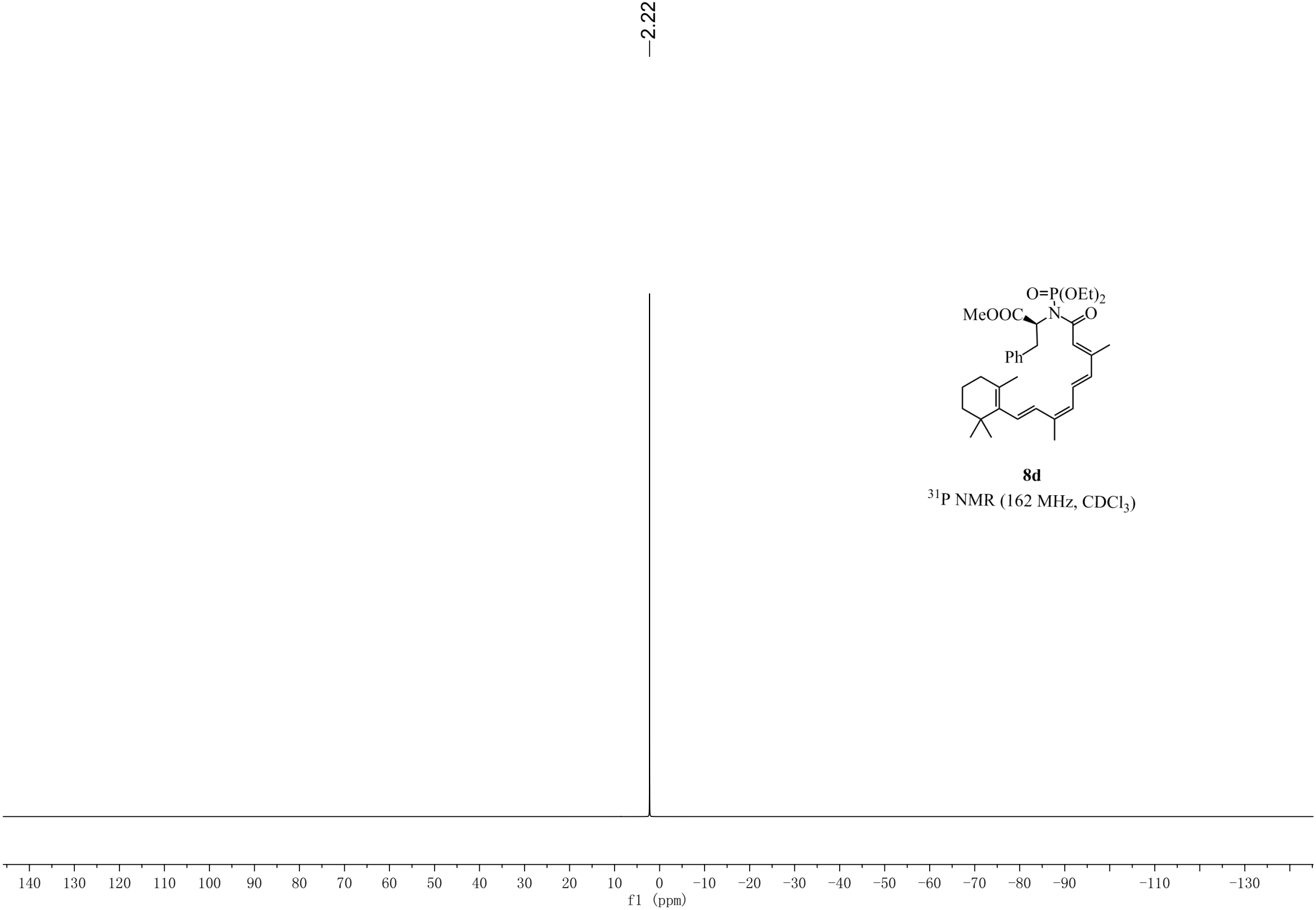




8d

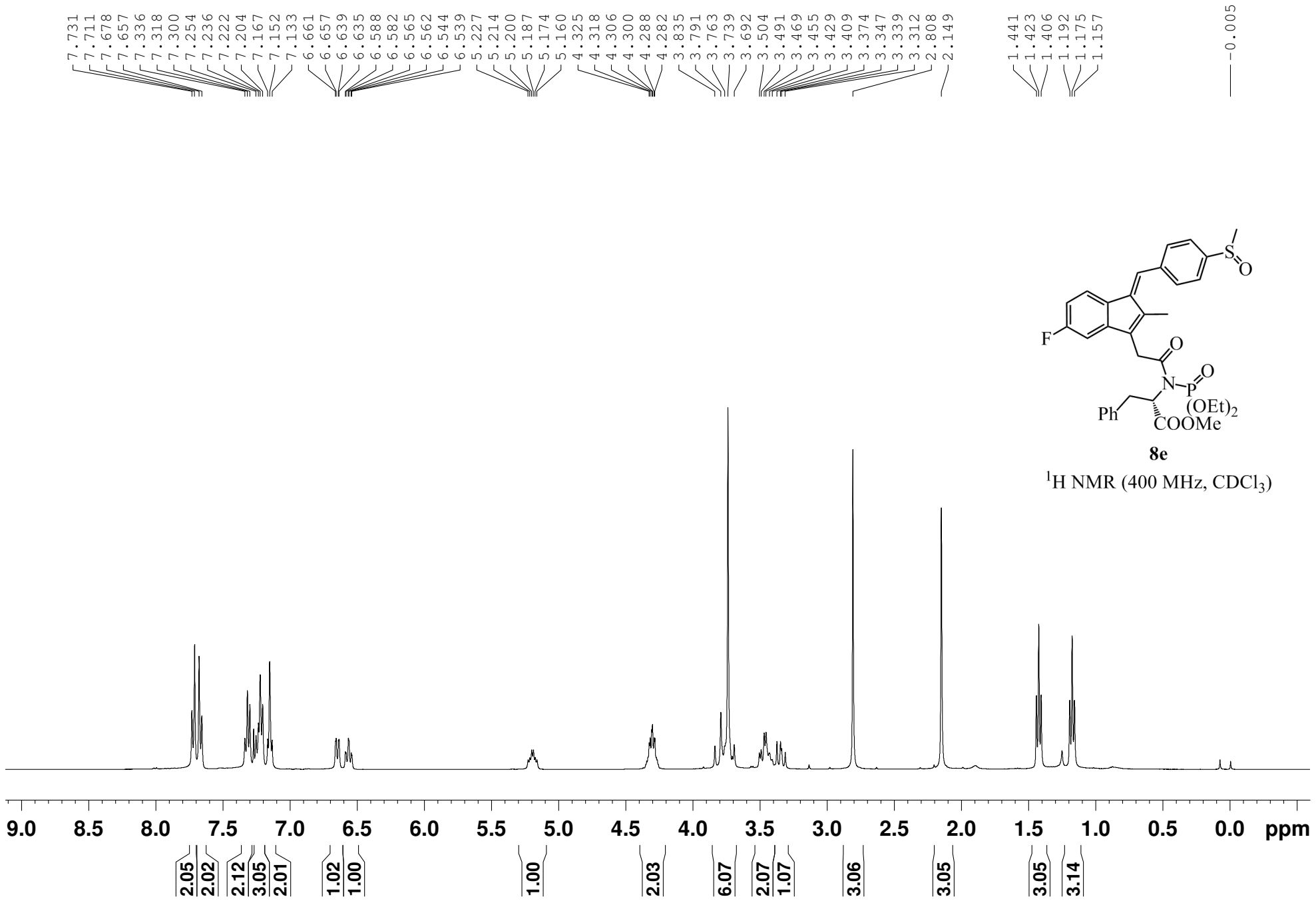
^{13}C NMR (100 MHz, $CDCl_3$)





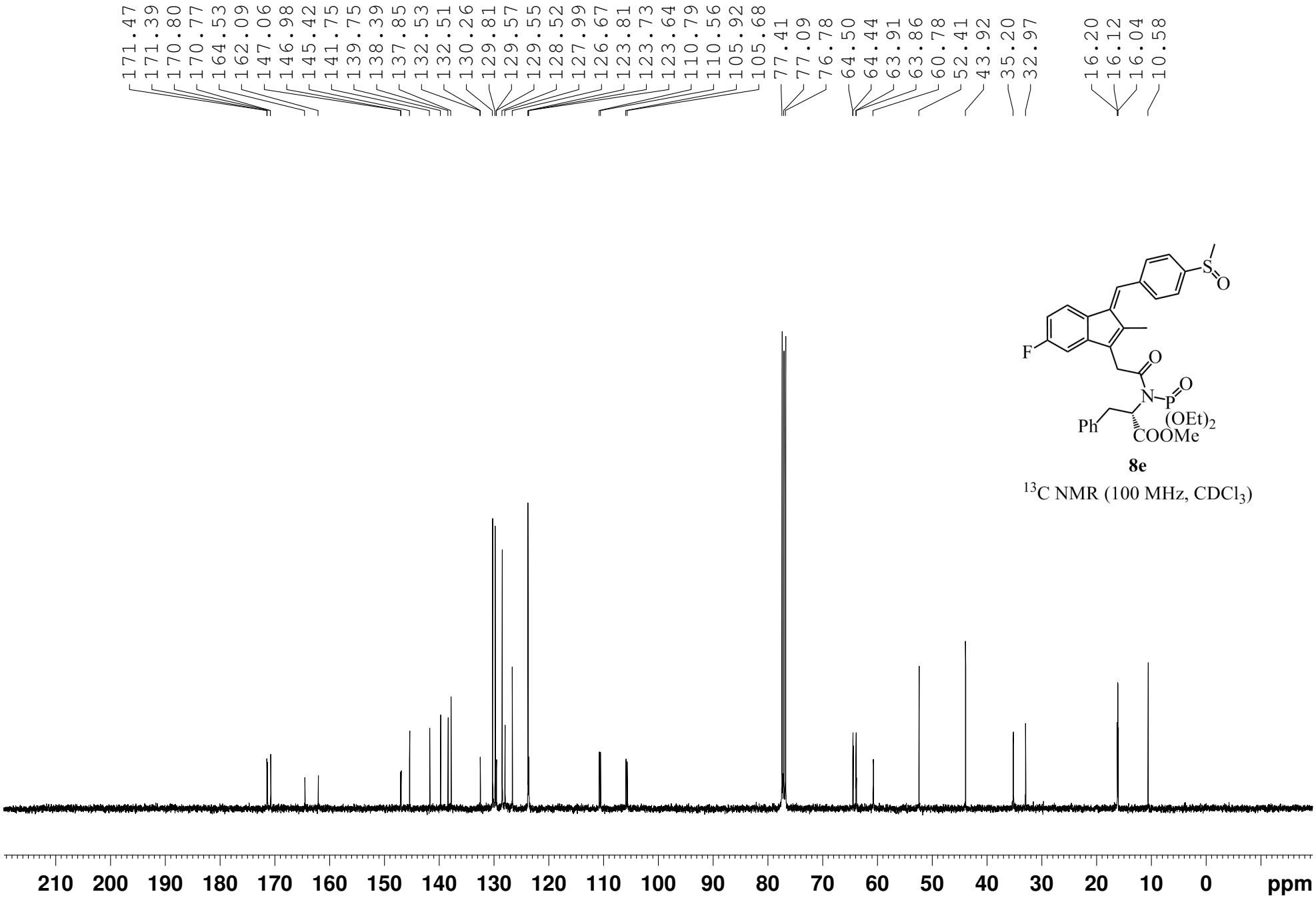
8d

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



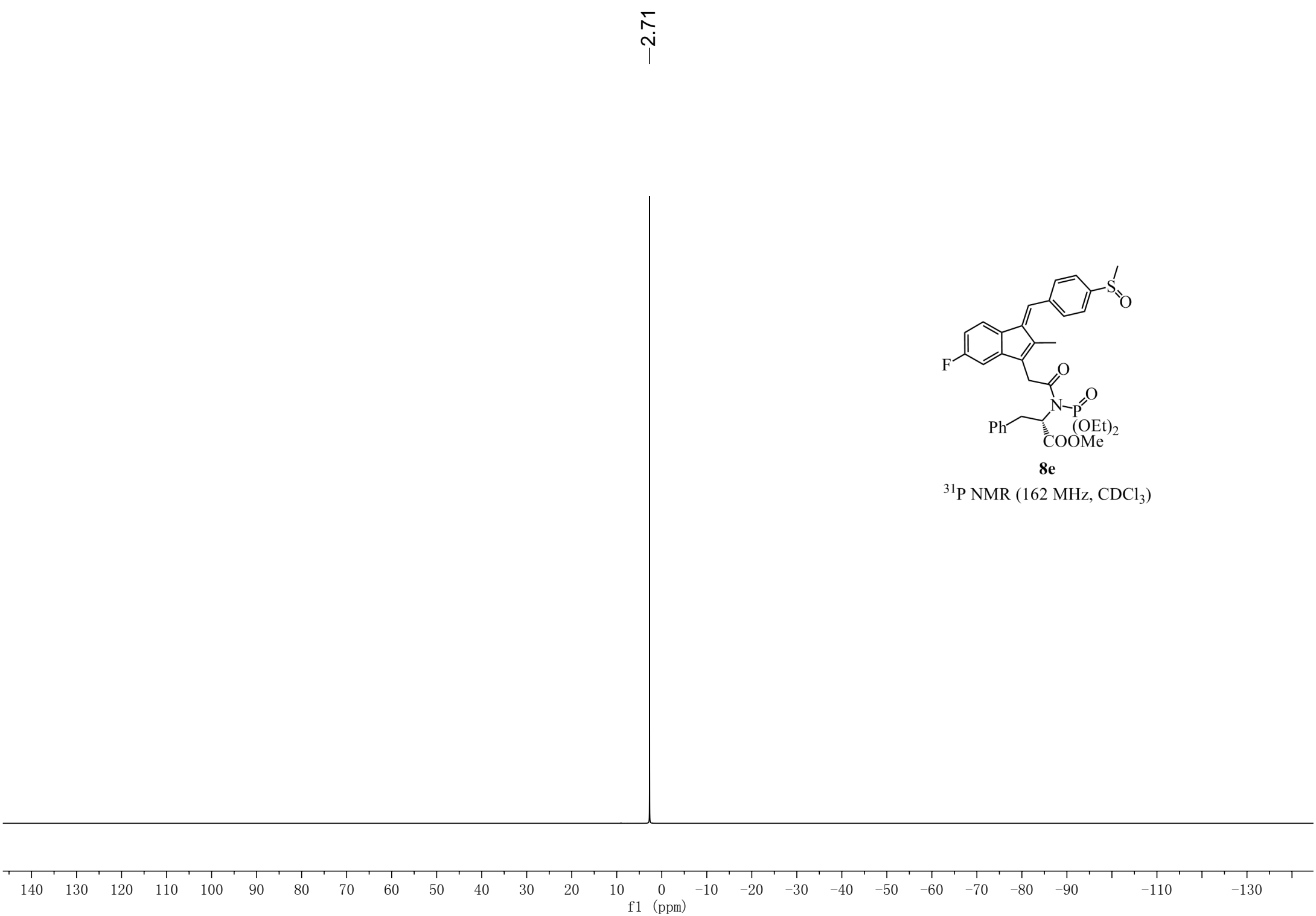
8e

^{1}H NMR (400 MHz, $CDCl_3$)



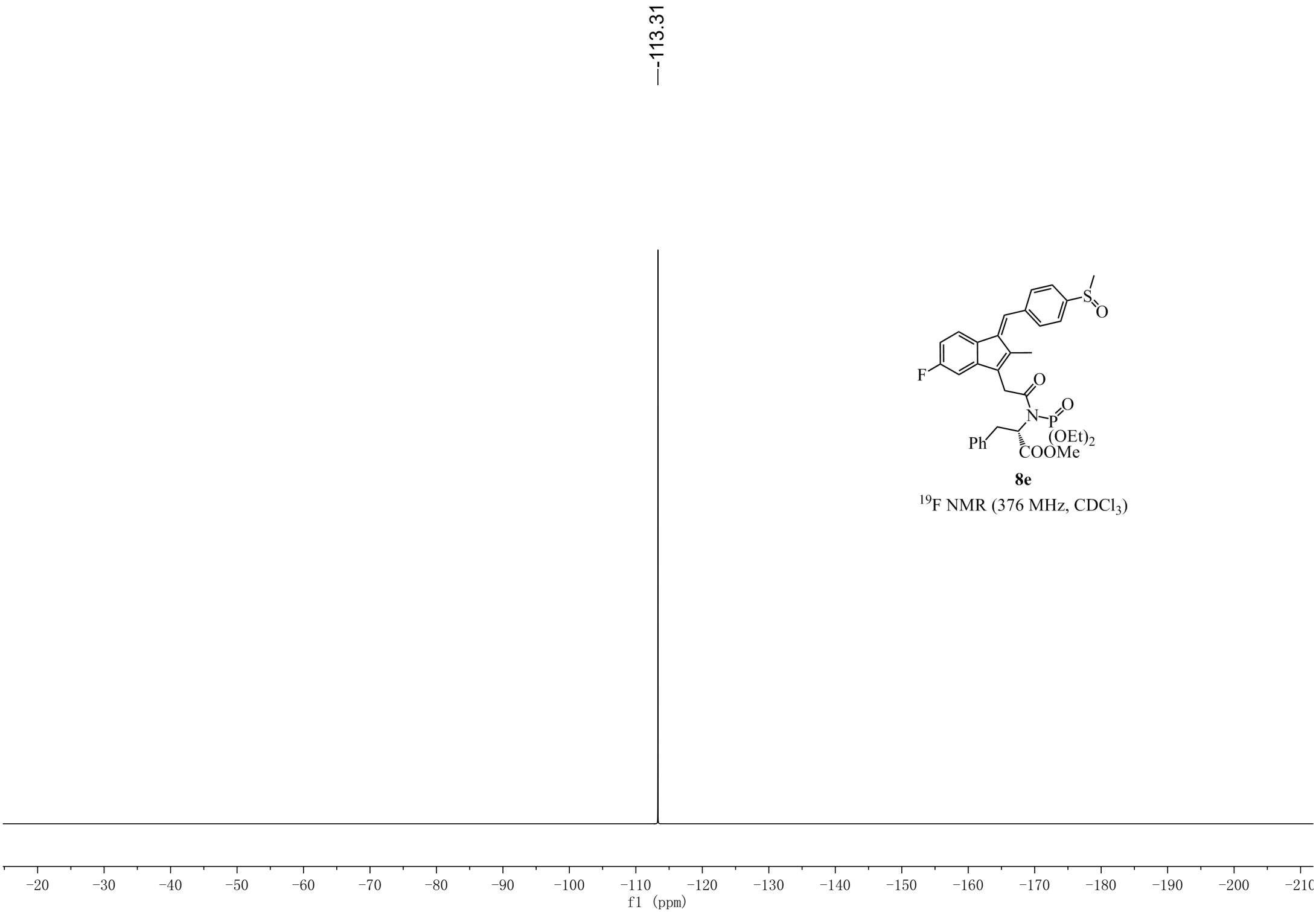
8e

^{13}C NMR (100 MHz, $CDCl_3$)



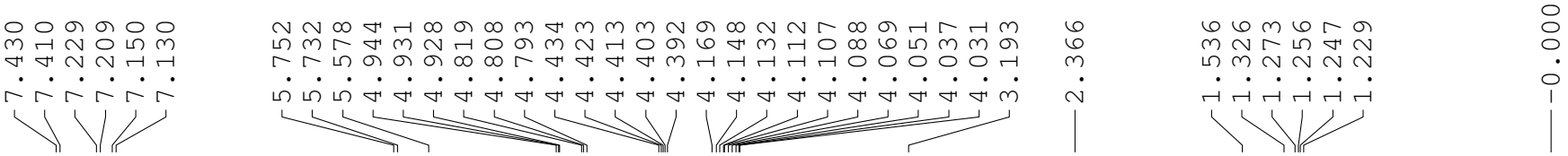
8e

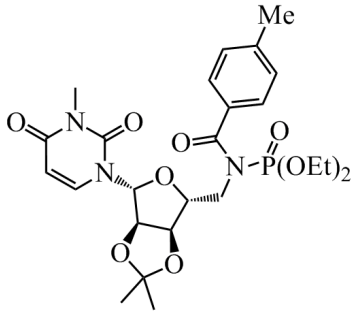
^{31}P NMR (162 MHz, $CDCl_3$)



8e

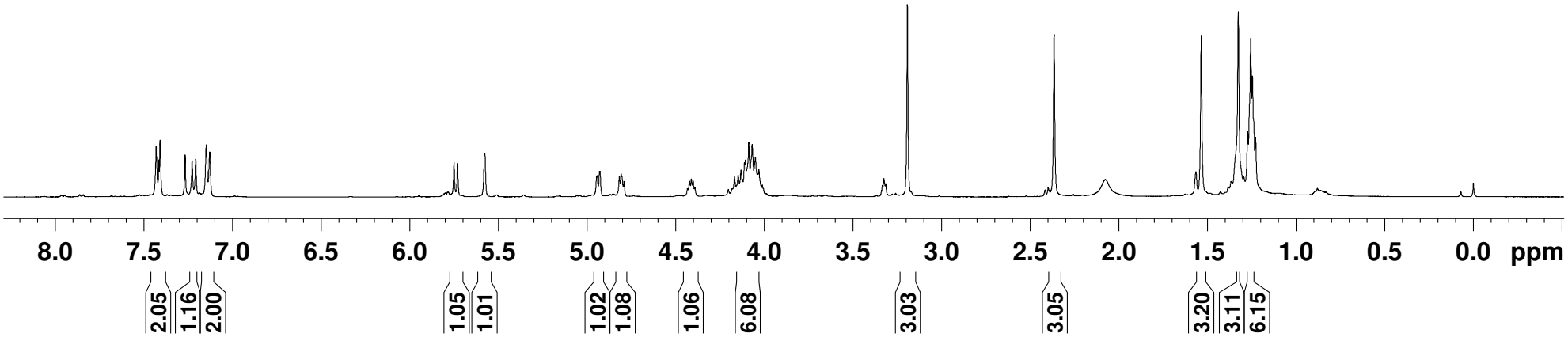
^{19}F NMR (376 MHz, $CDCl_3$)

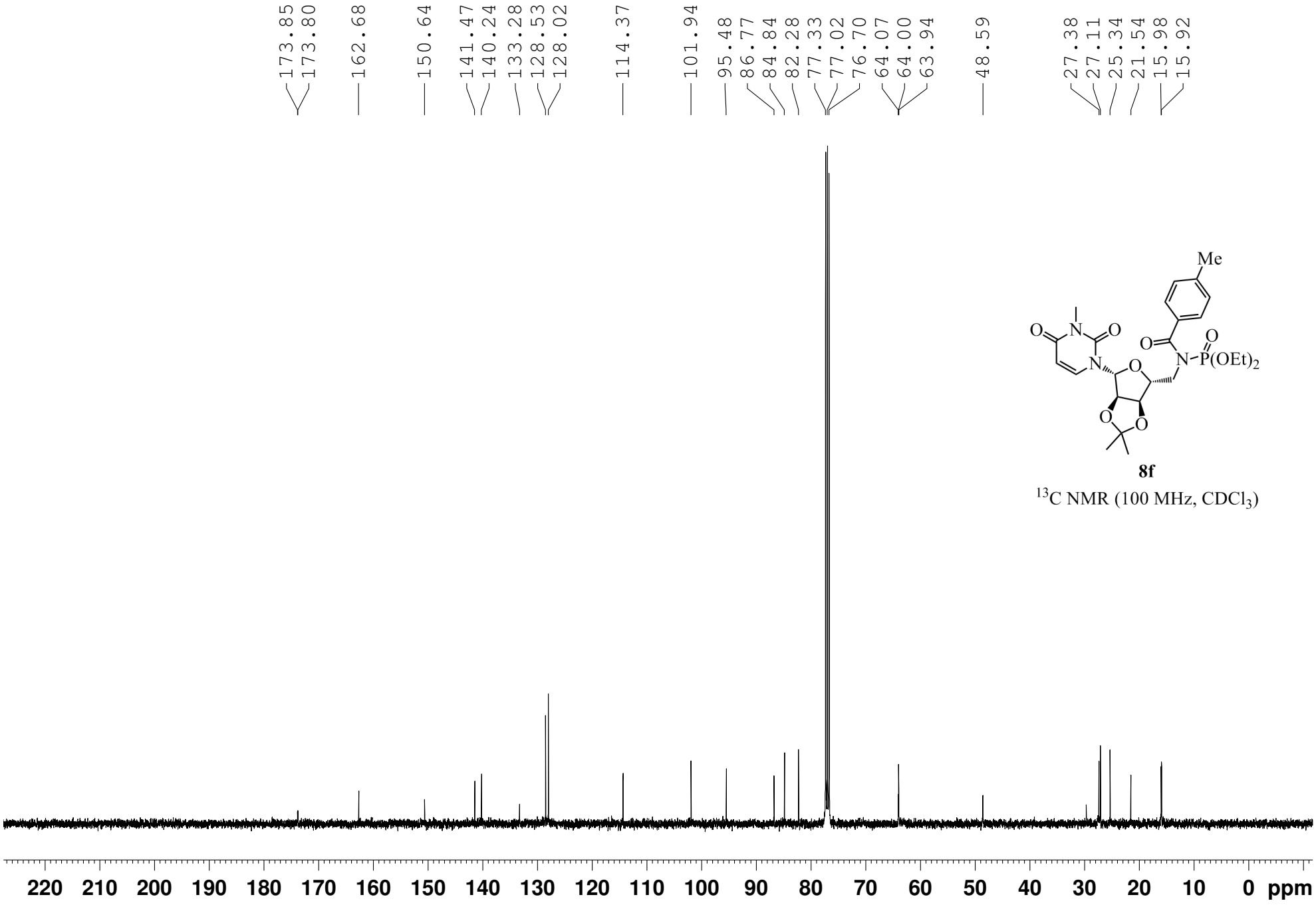




8f

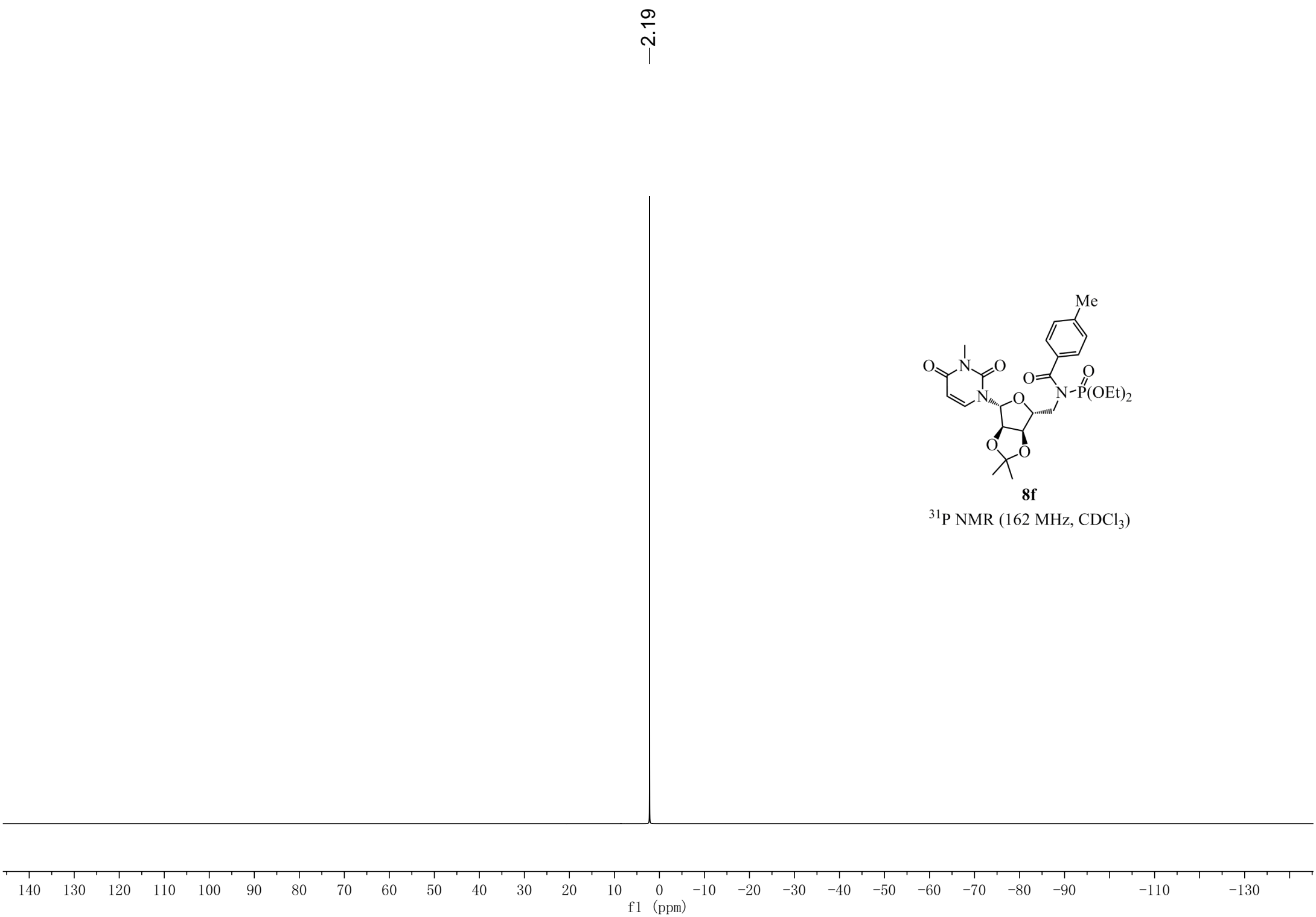
^{1}H NMR (400 MHz, $CDCl_3$)





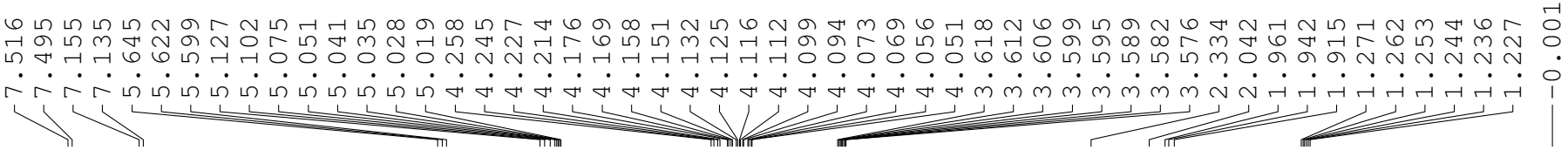
8f

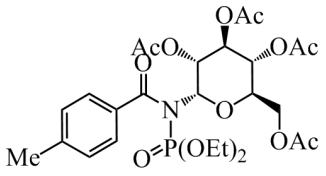
^{13}C NMR (100 MHz, $CDCl_3$)



8f

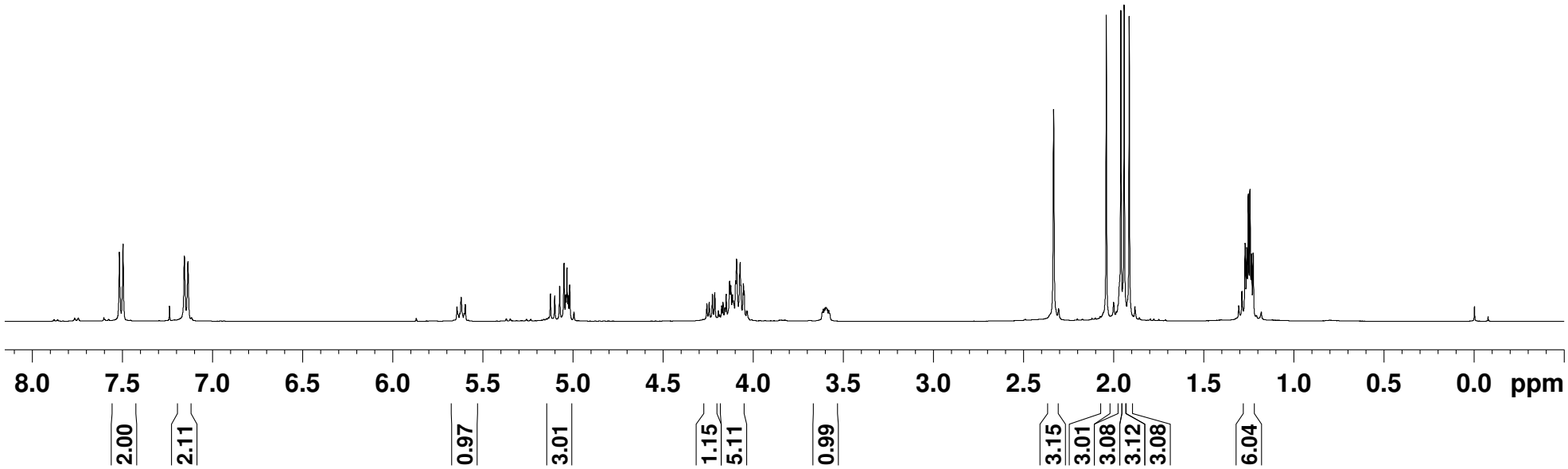
^{31}P NMR (162 MHz, $CDCl_3$)

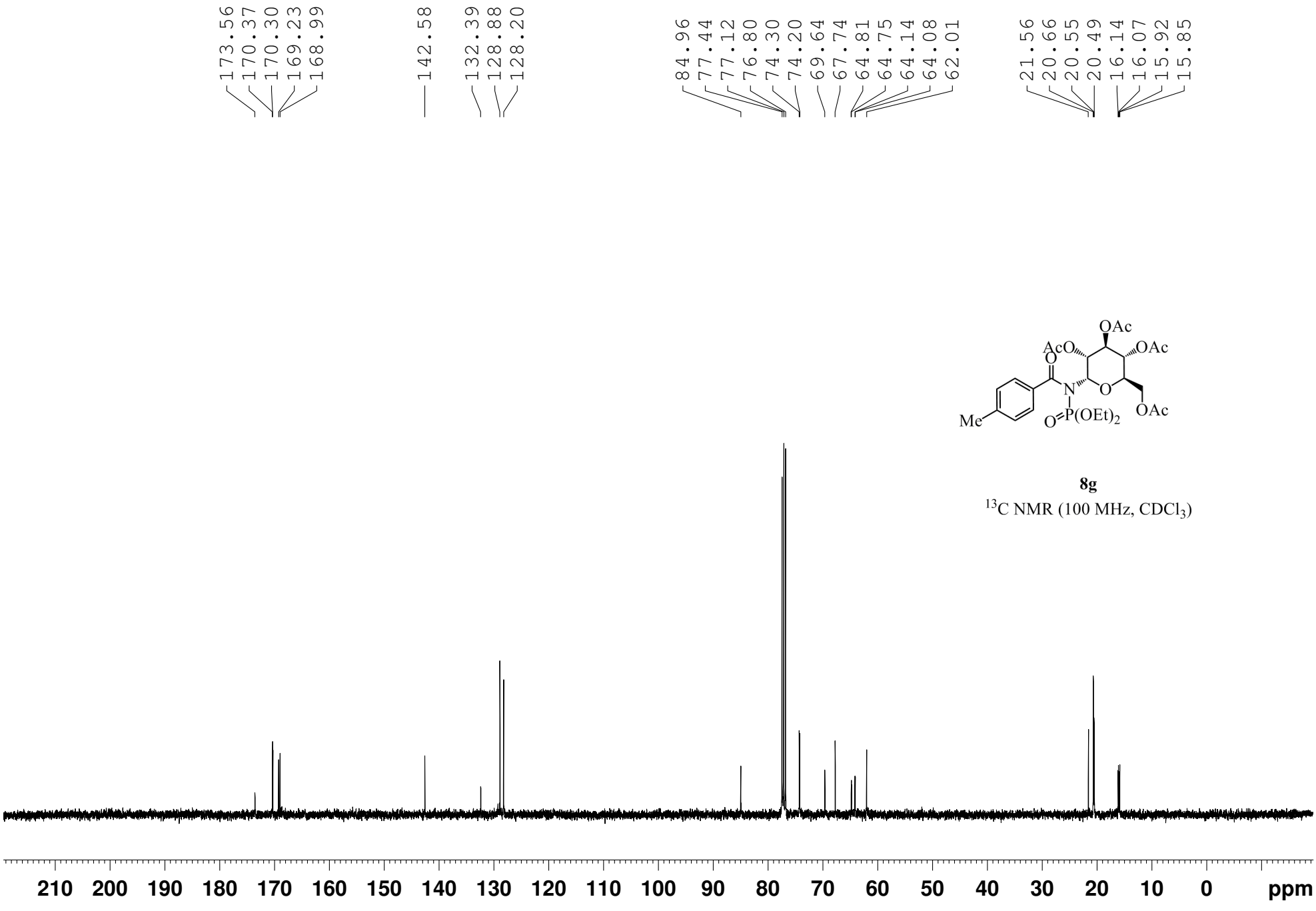




8g

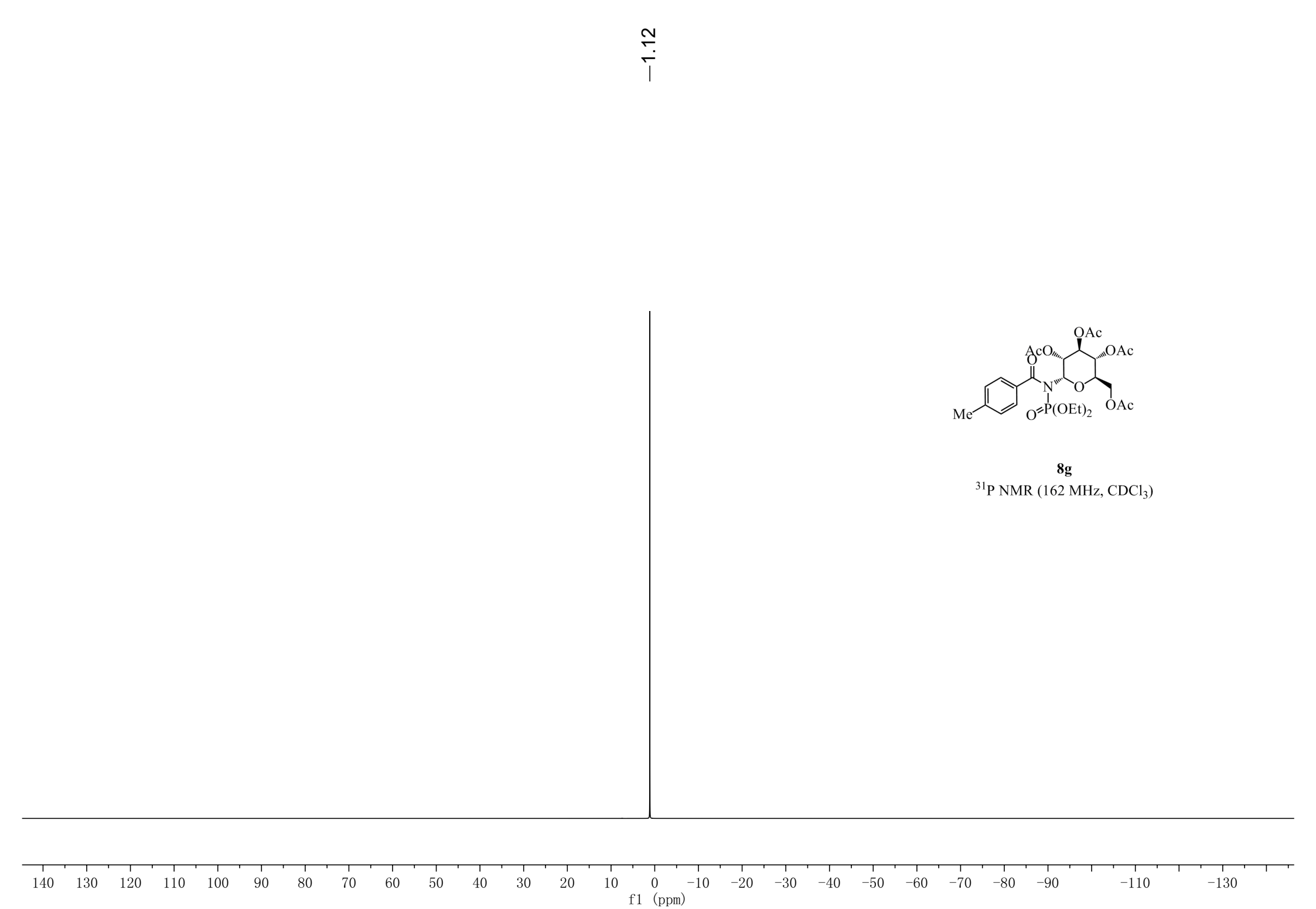
^{1}H NMR (400 MHz, $CDCl_3$)





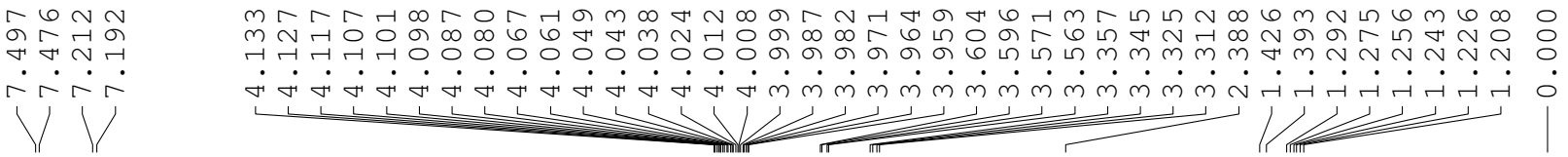
8g

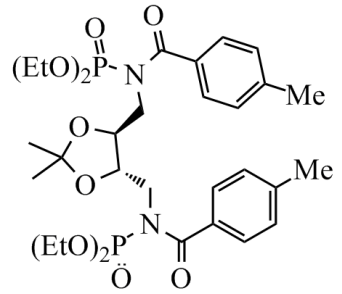
^{13}C NMR (100 MHz, $CDCl_3$)



8g

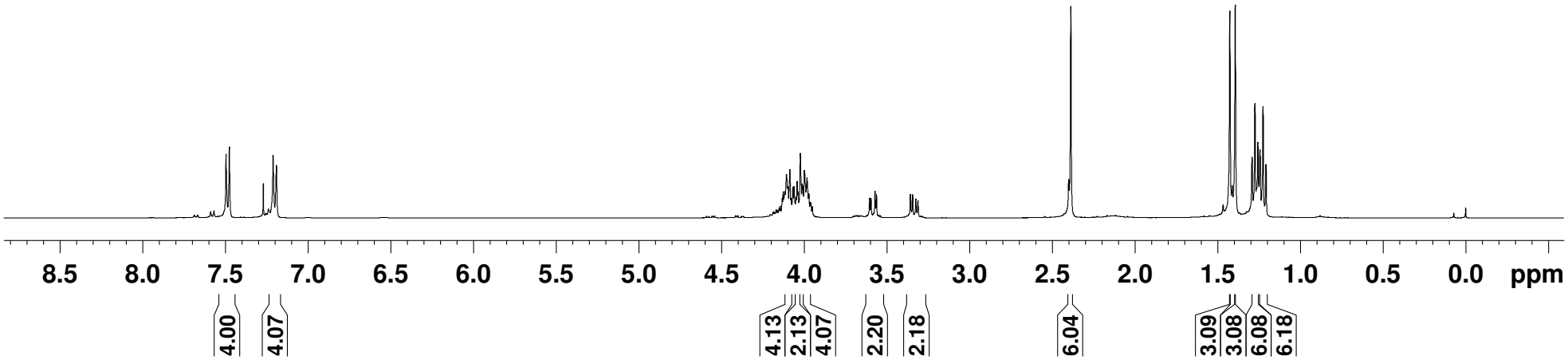
^{31}P NMR (162 MHz, $CDCl_3$)

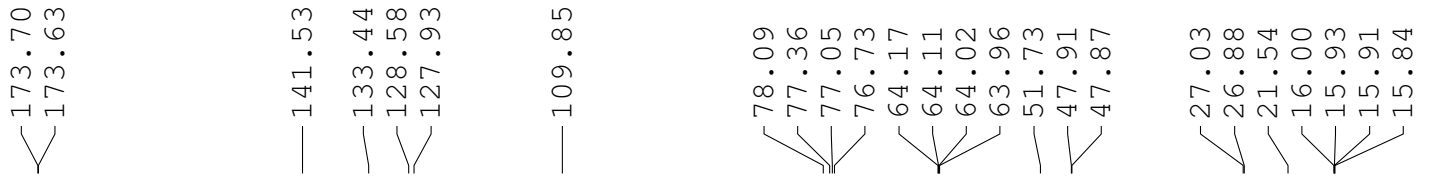


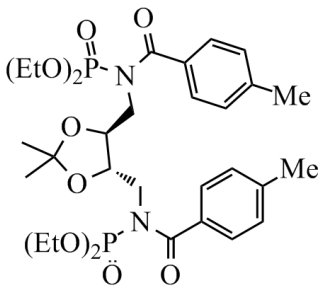


8h

^{1}H NMR (400 MHz, $CDCl_3$)

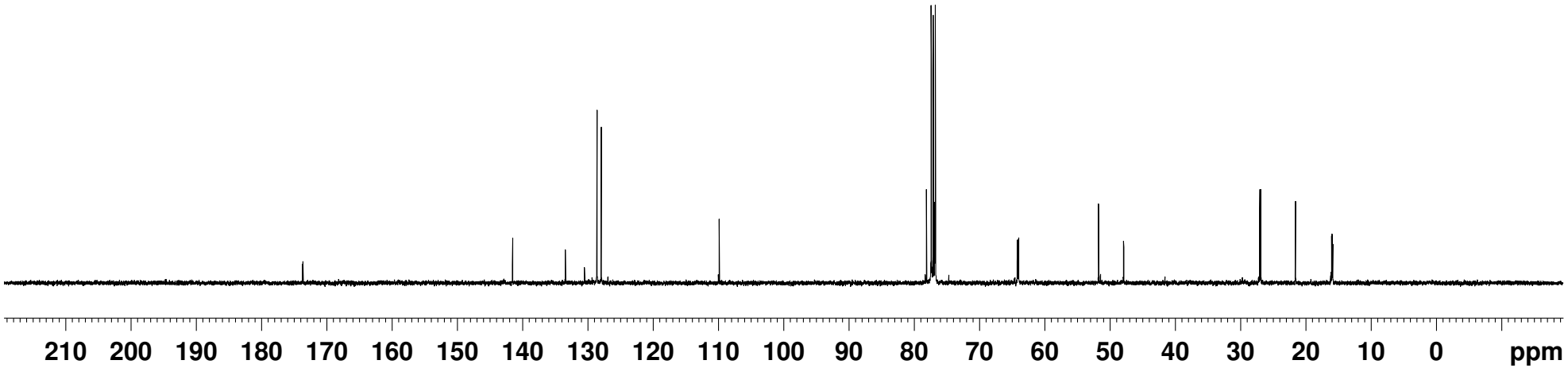


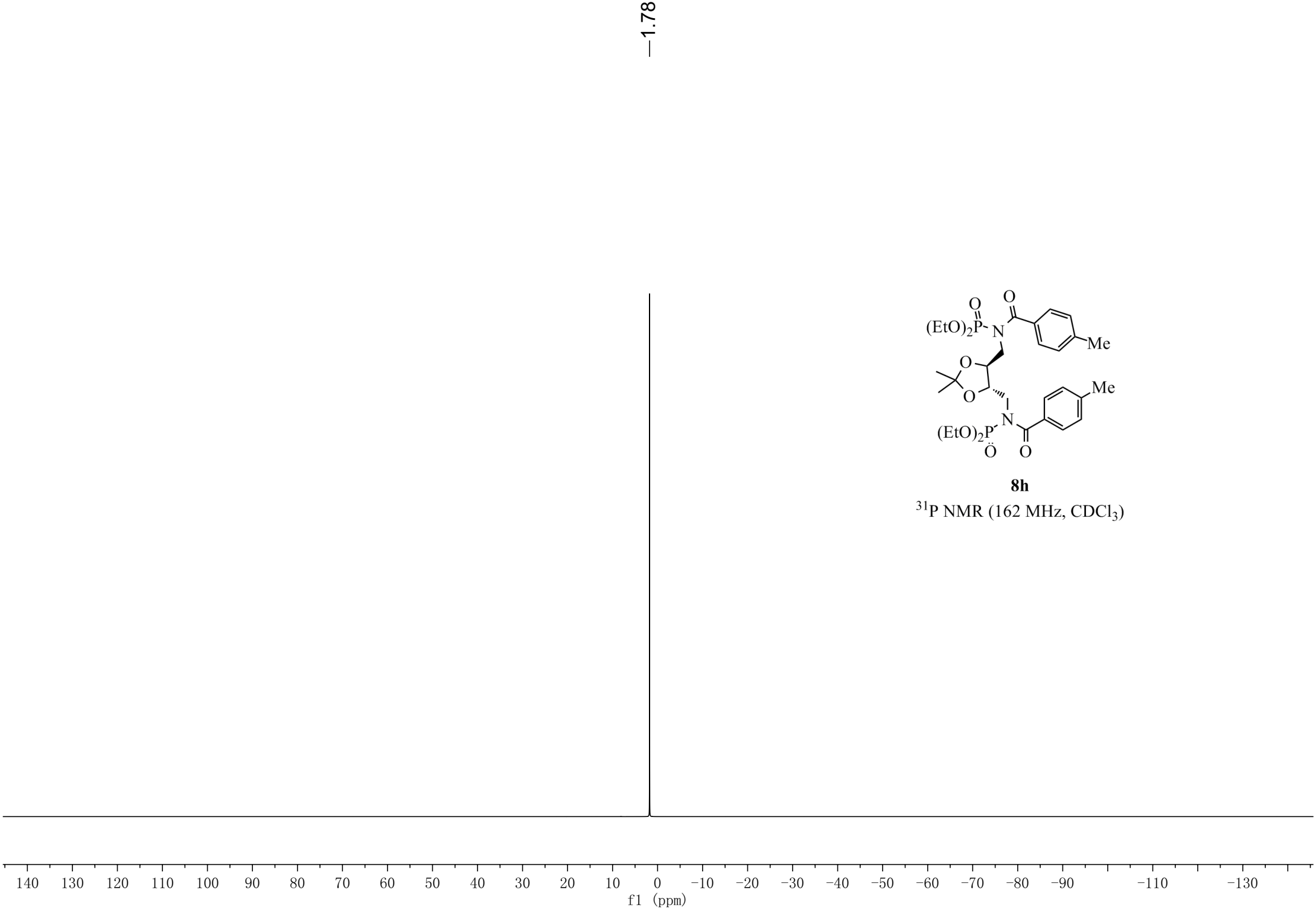


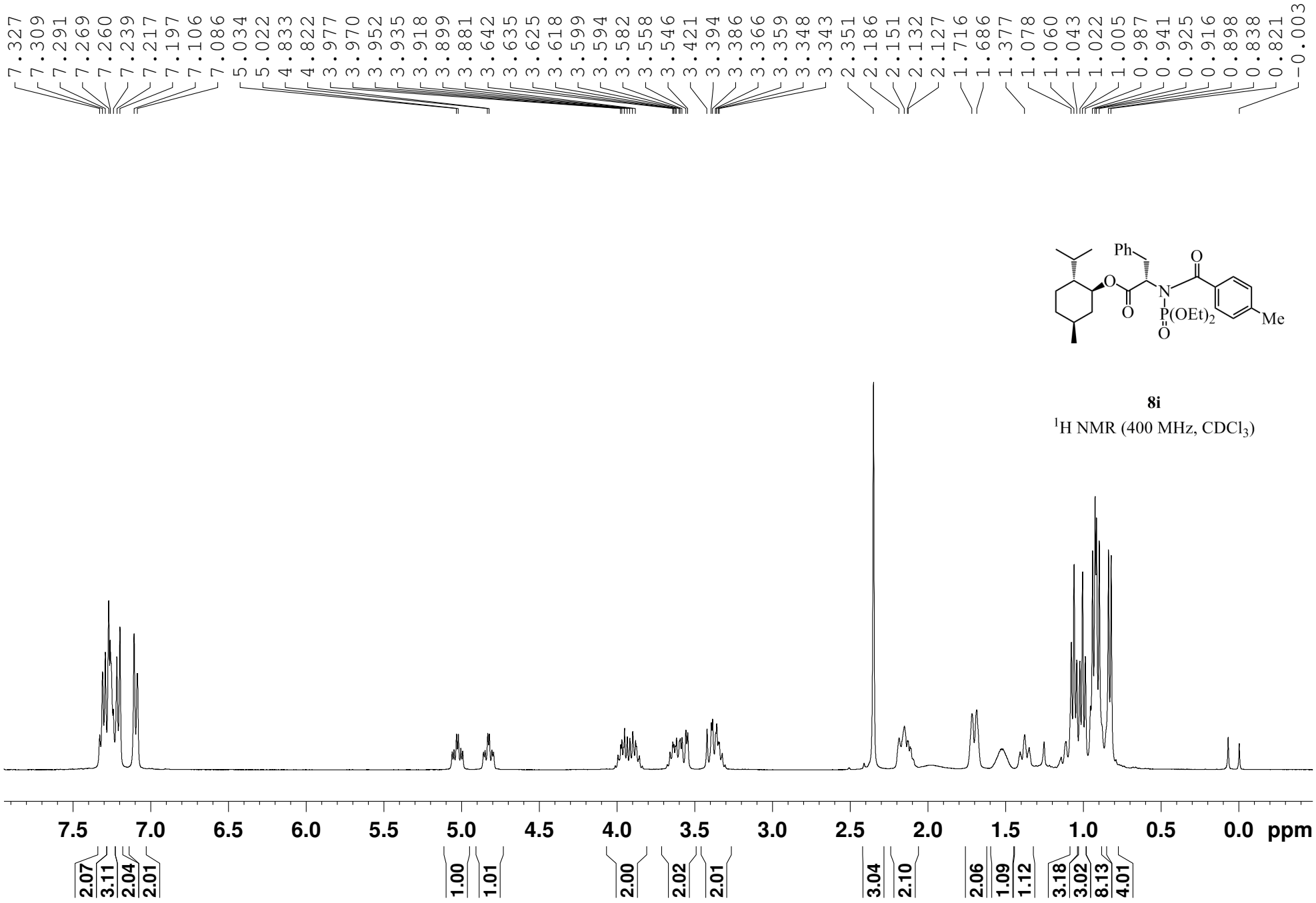


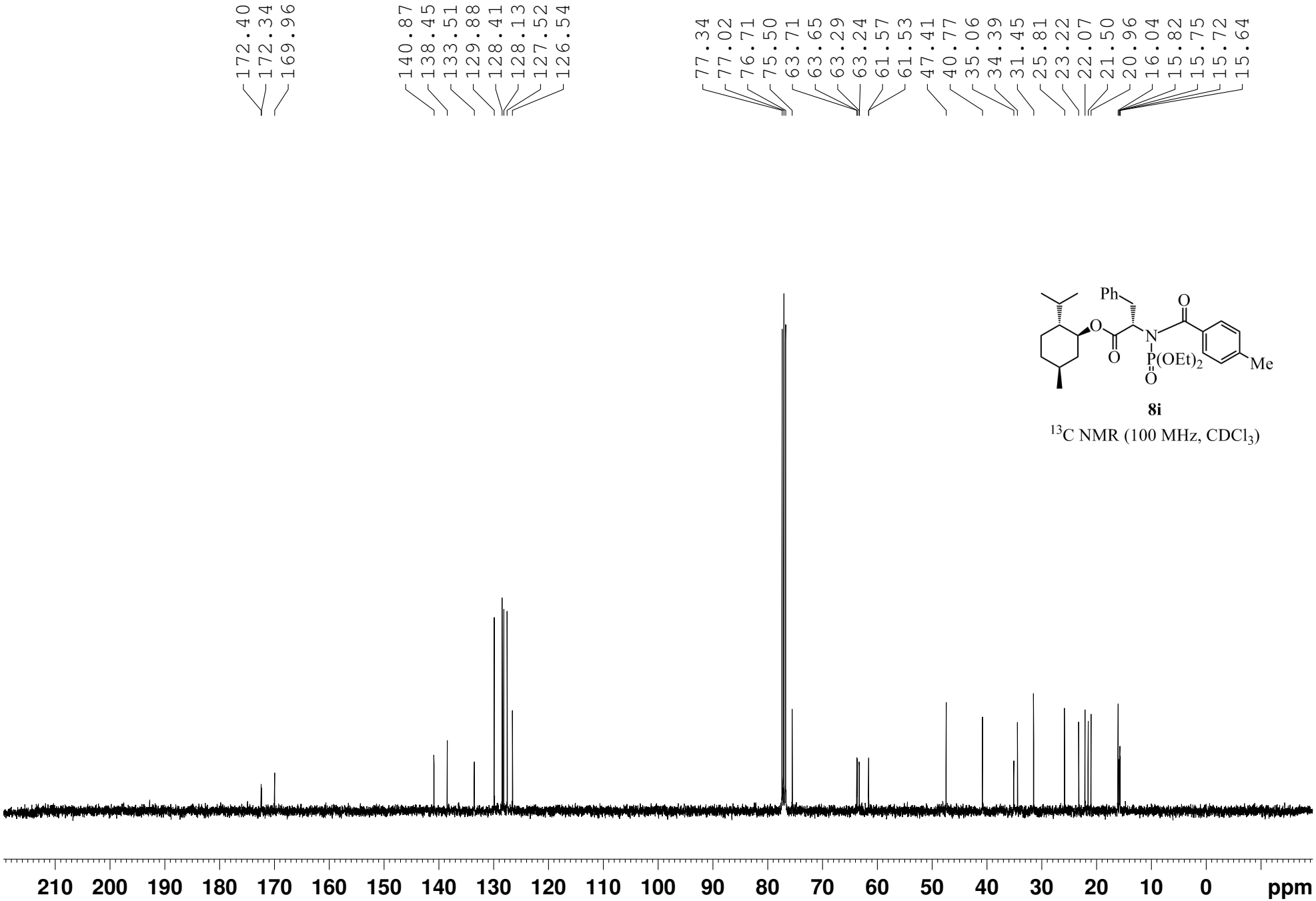
8h

^{13}C NMR (100 MHz, $CDCl_3$)



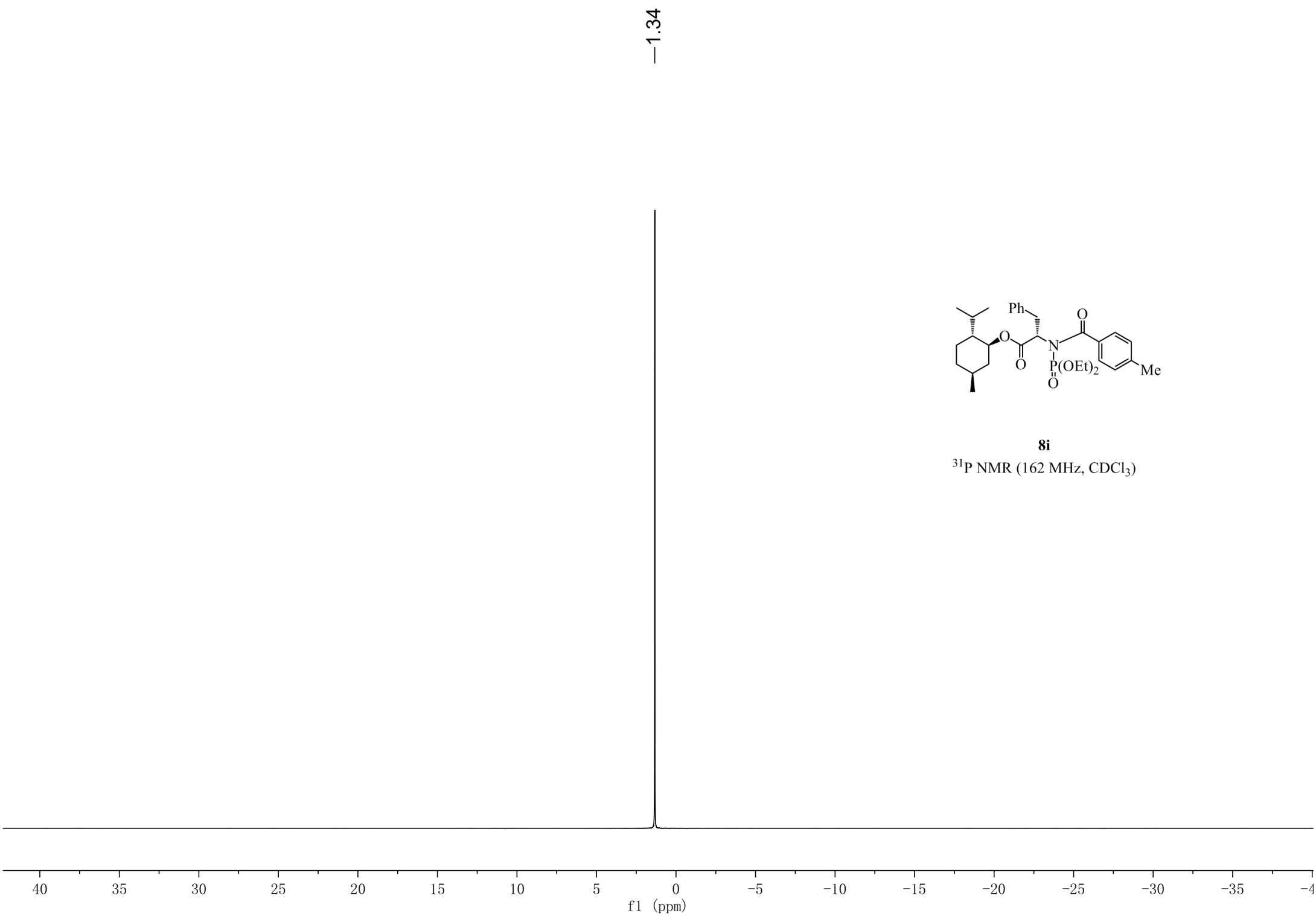

1.78
Me
Me
8h
31P NMR (162 MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130
f1 (ppm)


7.327
7.309
7.291
7.269
7.260
7.239
7.217
7.197
7.106
7.086
5.034
5.022
4.833
4.822
3.977
3.970
3.952
3.935
3.918
3.899
3.881
3.642
3.635
3.625
3.618
3.599
3.594
3.582
3.558
3.546
3.421
3.394
3.386
3.366
3.359
3.348
3.343
2.351
2.186
2.151
2.132
2.127
1.716
1.686
1.377
1.078
1.060
1.043
1.022
1.005
0.987
0.941
0.925
0.916
0.898
0.838
0.821
-0.003
Ph
O
O
N
O
P(OEt)2
O
Me
8i
1H NMR (400 MHz, CDCl3)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.07
3.11
2.04
2.01
1.00
1.01
2.00
2.02
2.01
3.04
2.10
2.06
1.09
1.12
3.18
3.02
8.13
4.01



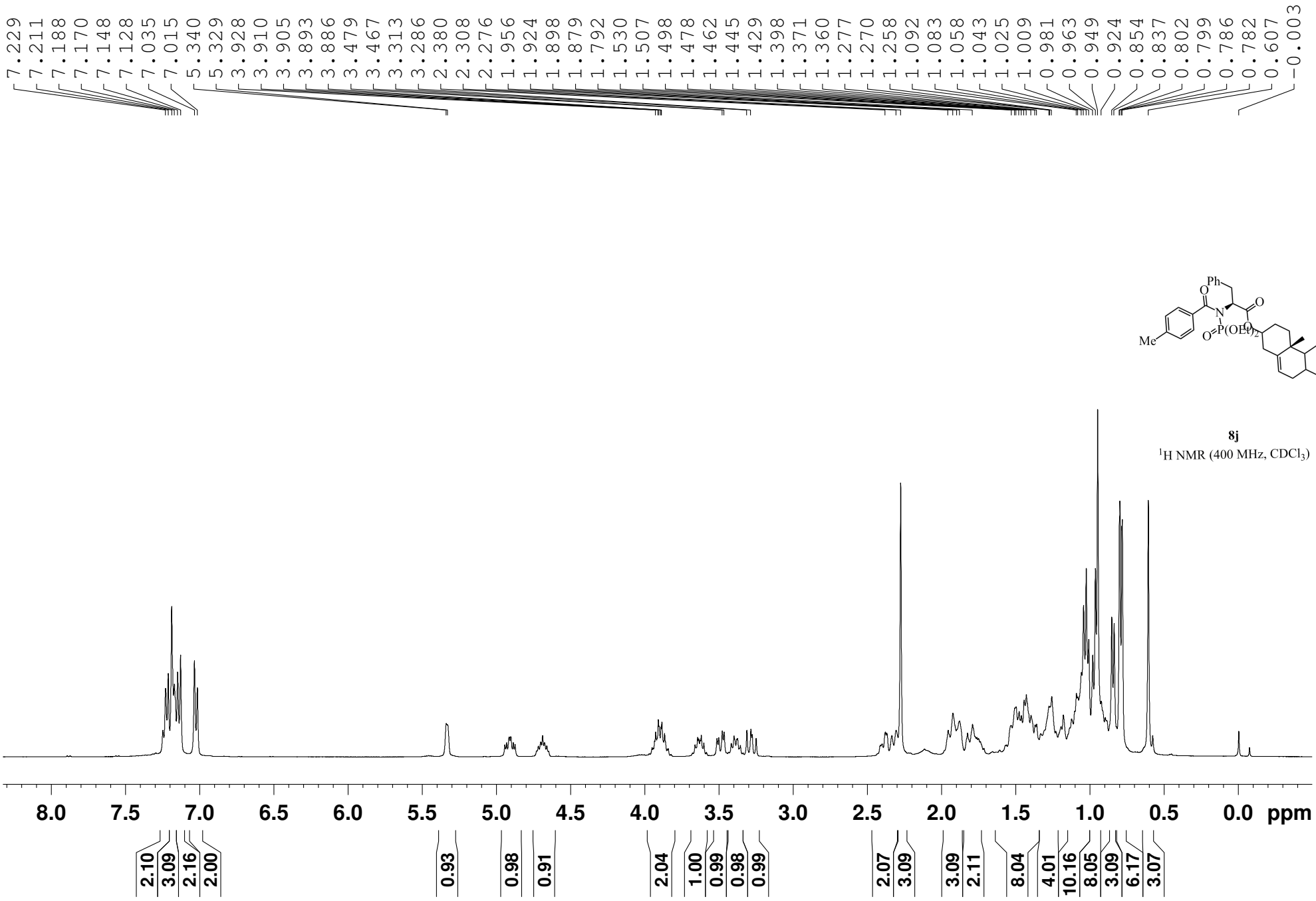
8i

^{13}C NMR (100 MHz, $CDCl_3$)



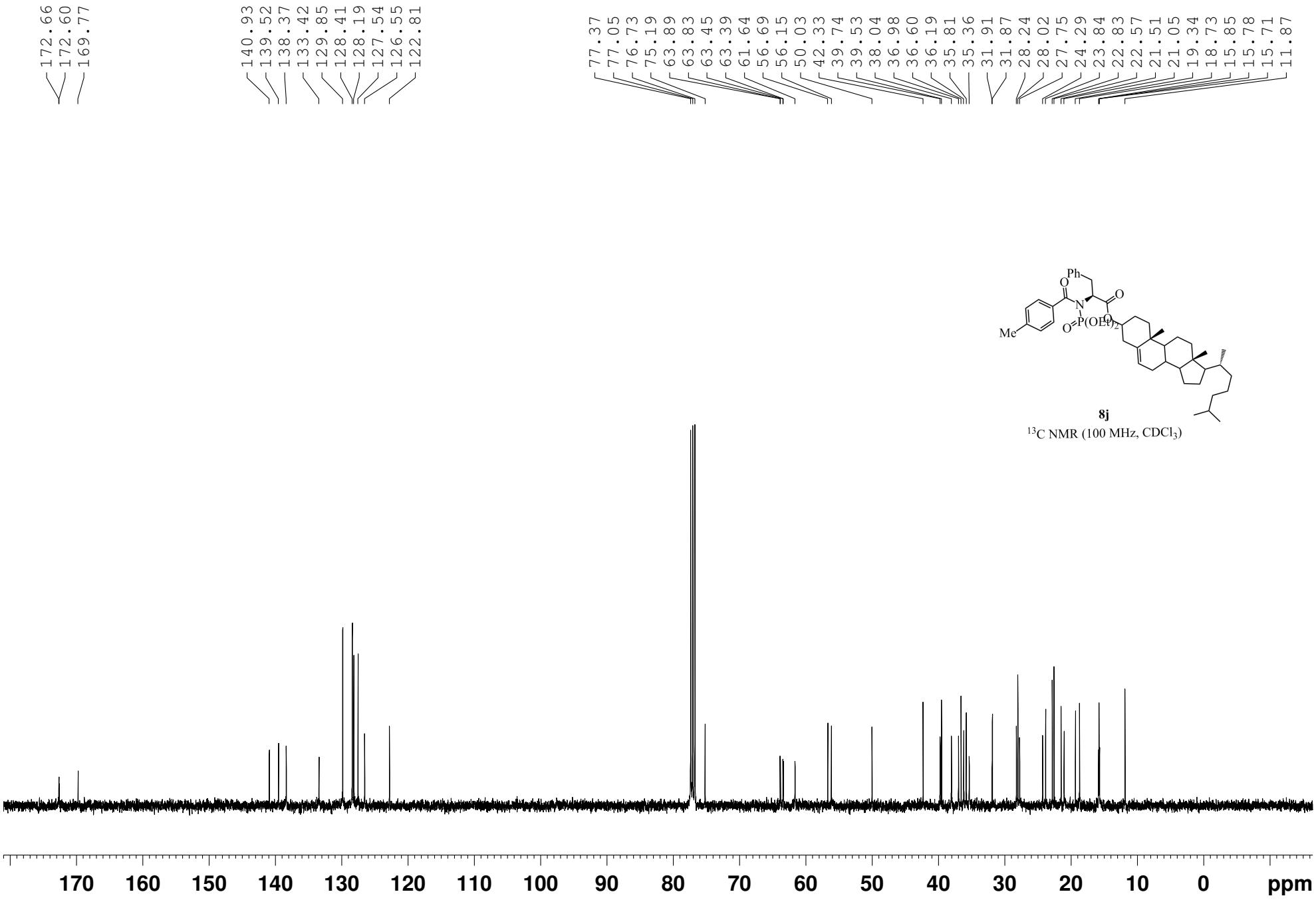
8i

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



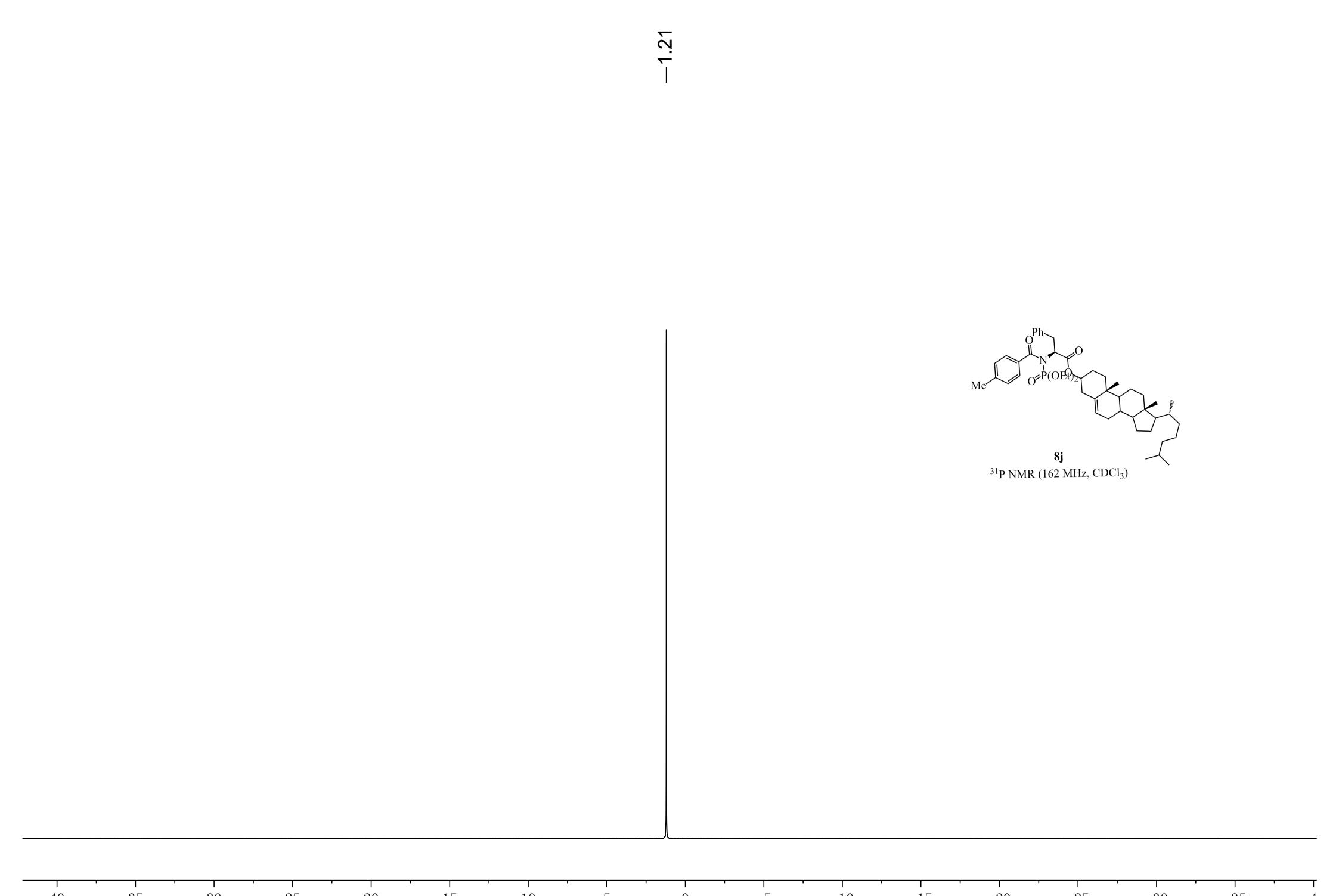
8j

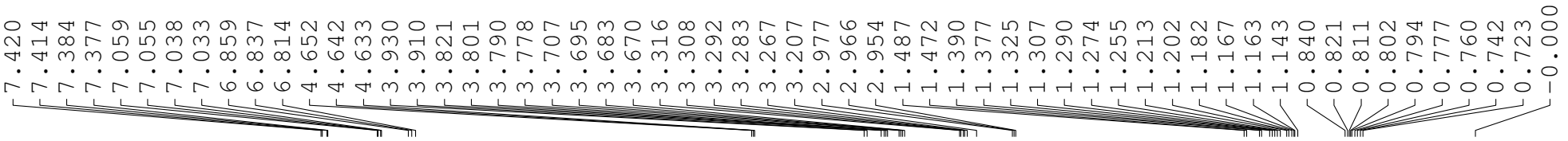
^{1}H NMR (400 MHz, $CDCl_3$)

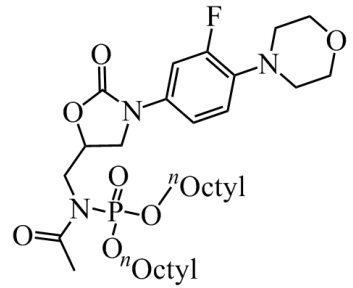


8j

^{13}C NMR (100 MHz, $CDCl_3$)

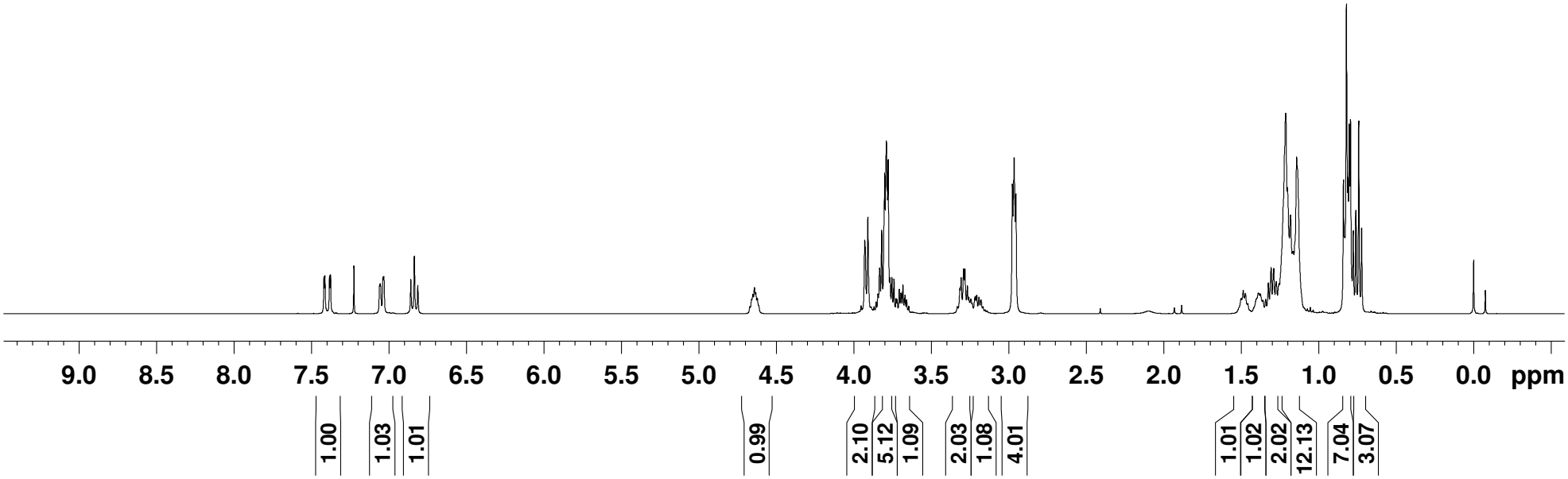

1.21
Ph
O
N
O
O
O
O
P(OEt)2
Me
8j
31P NMR (162 MHz, CDCl3)
40
35
30
25
20
15
10
5
0
−5
−10
−15
−20
−25
−30
−35
−4
f1 (ppm)

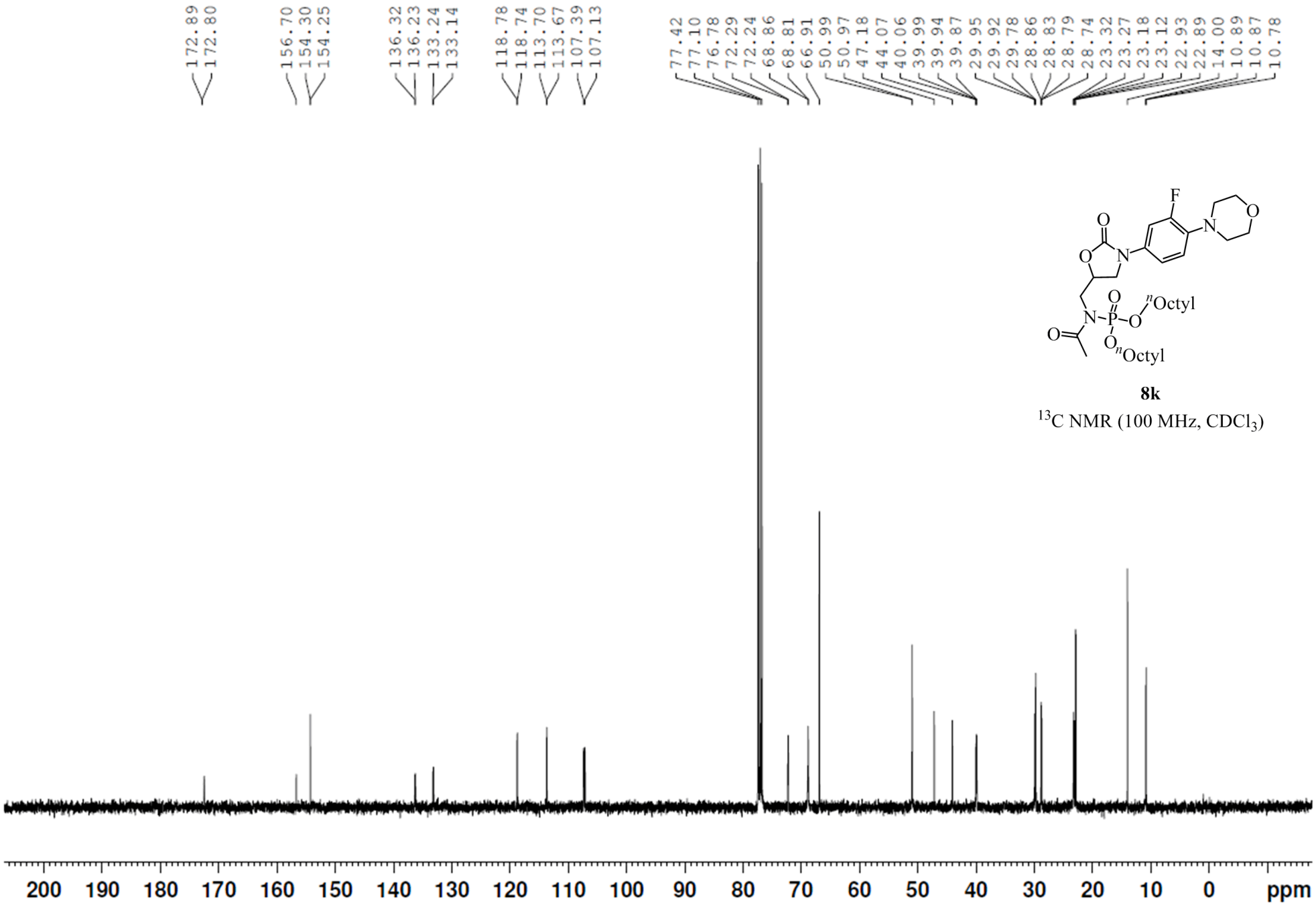




8k

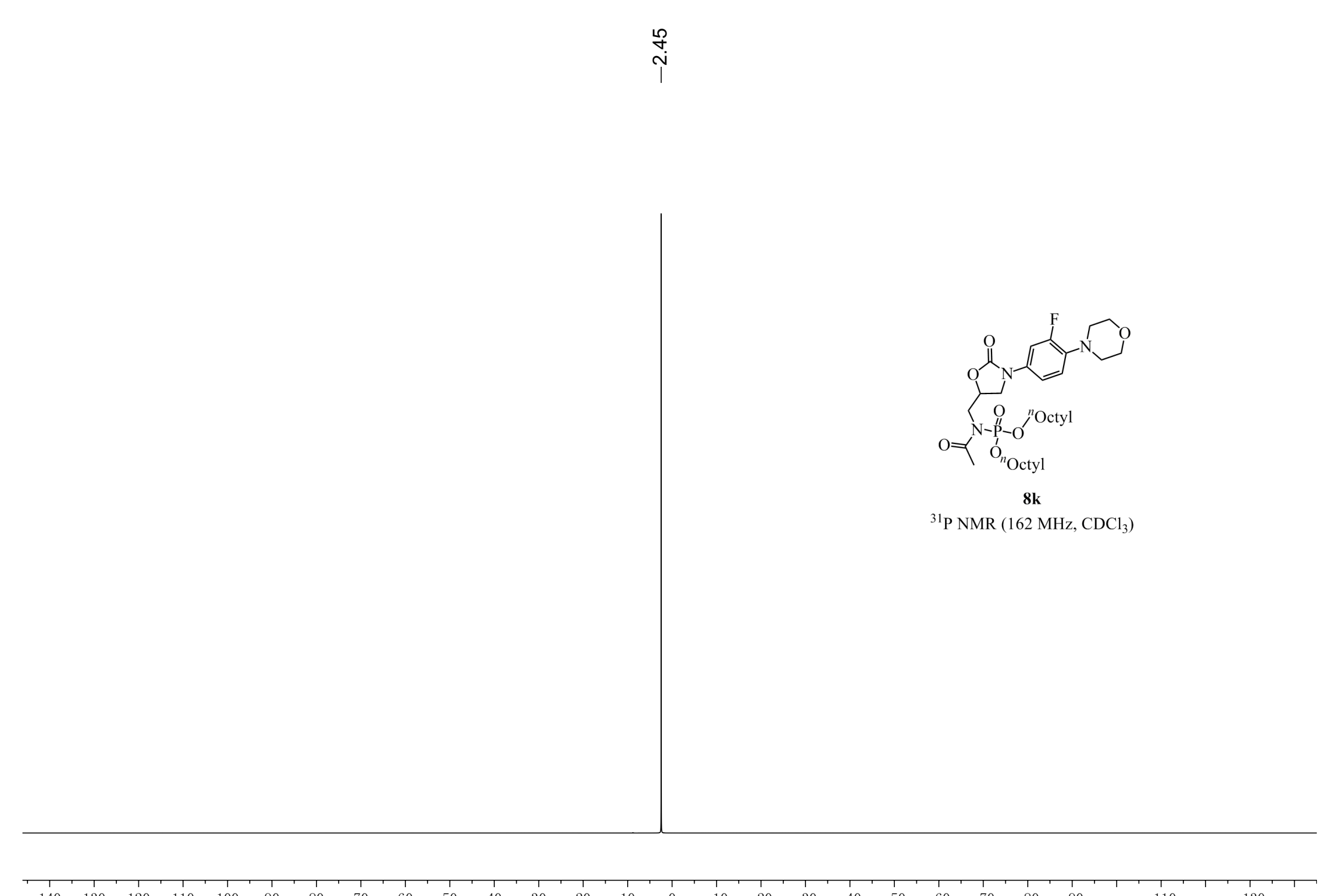
^{1}H NMR (400 MHz, $CDCl_3$)





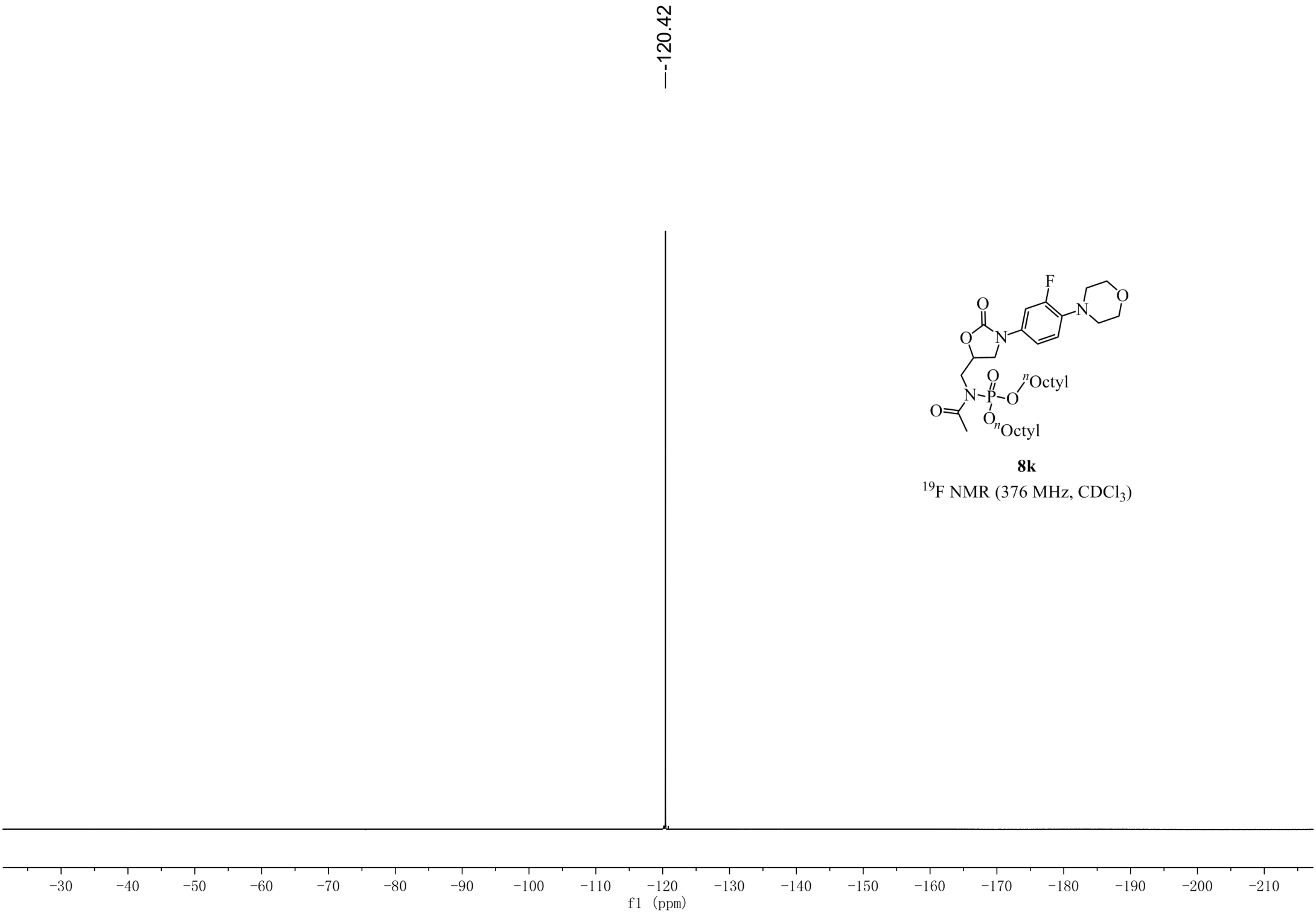
8k

^{13}C NMR (100 MHz, $CDCl_3$)



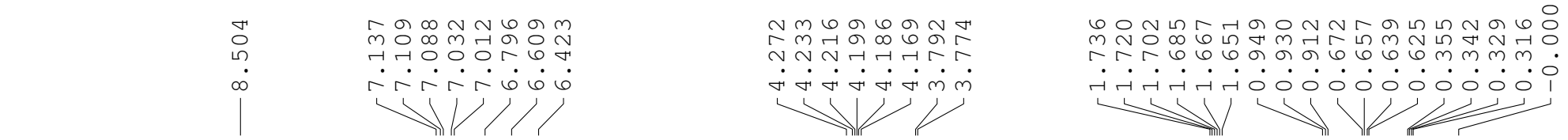
8k

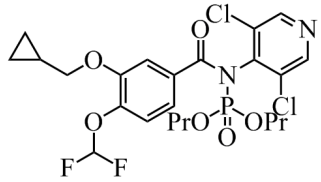
^{31}P NMR (162 MHz, $CDCl_3$)



8k

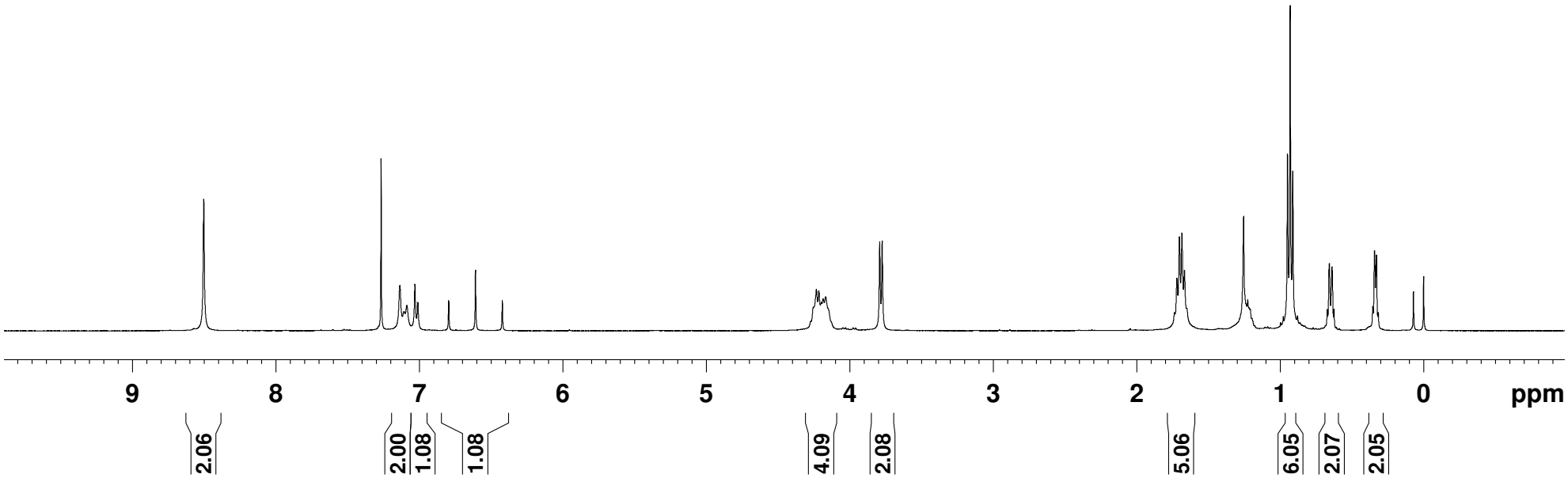
^{19}F NMR (376 MHz, $CDCl_3$)

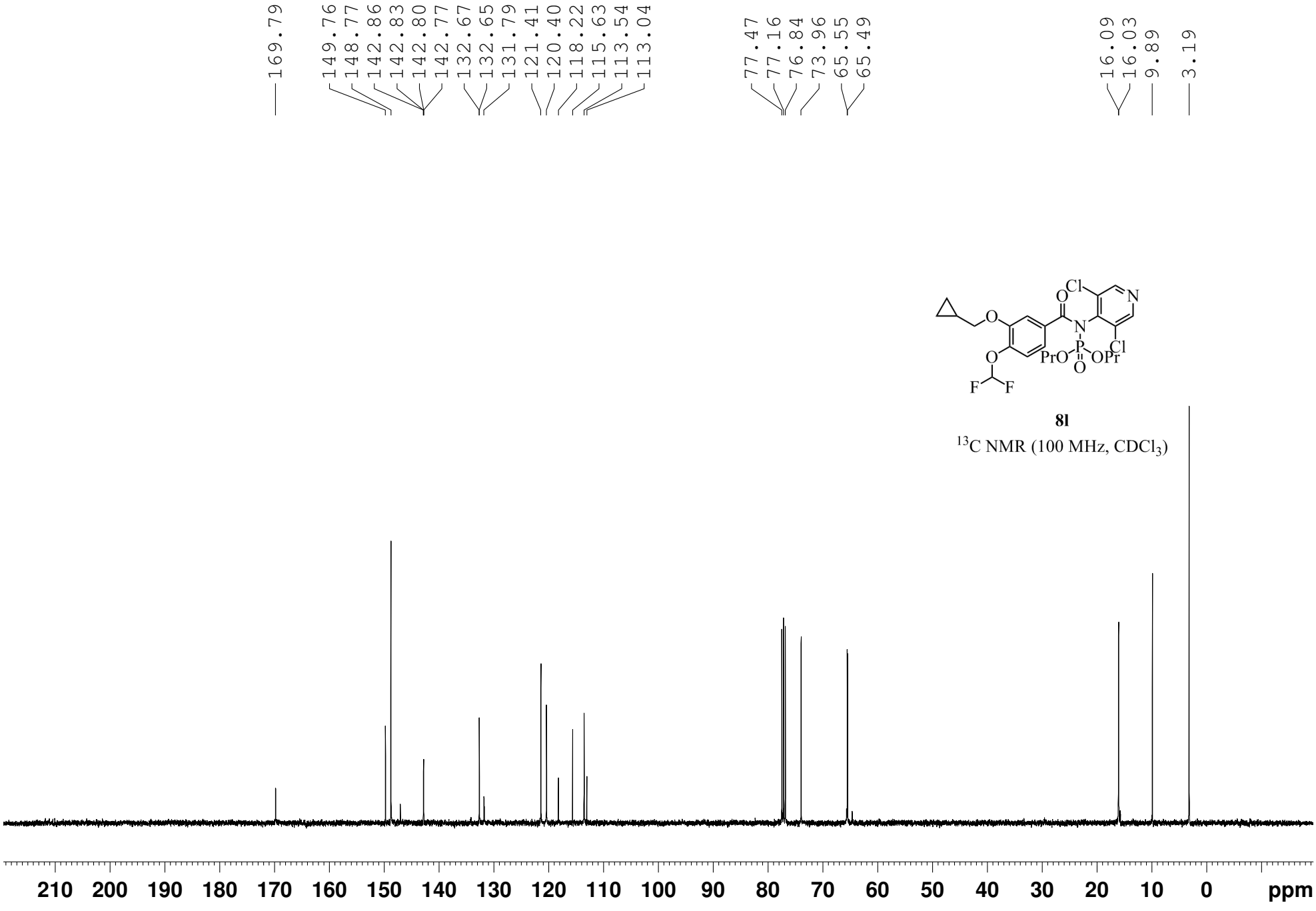


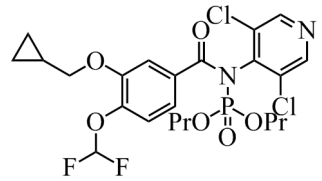


8l

^{1}H NMR (400 MHz, $CDCl_3$)

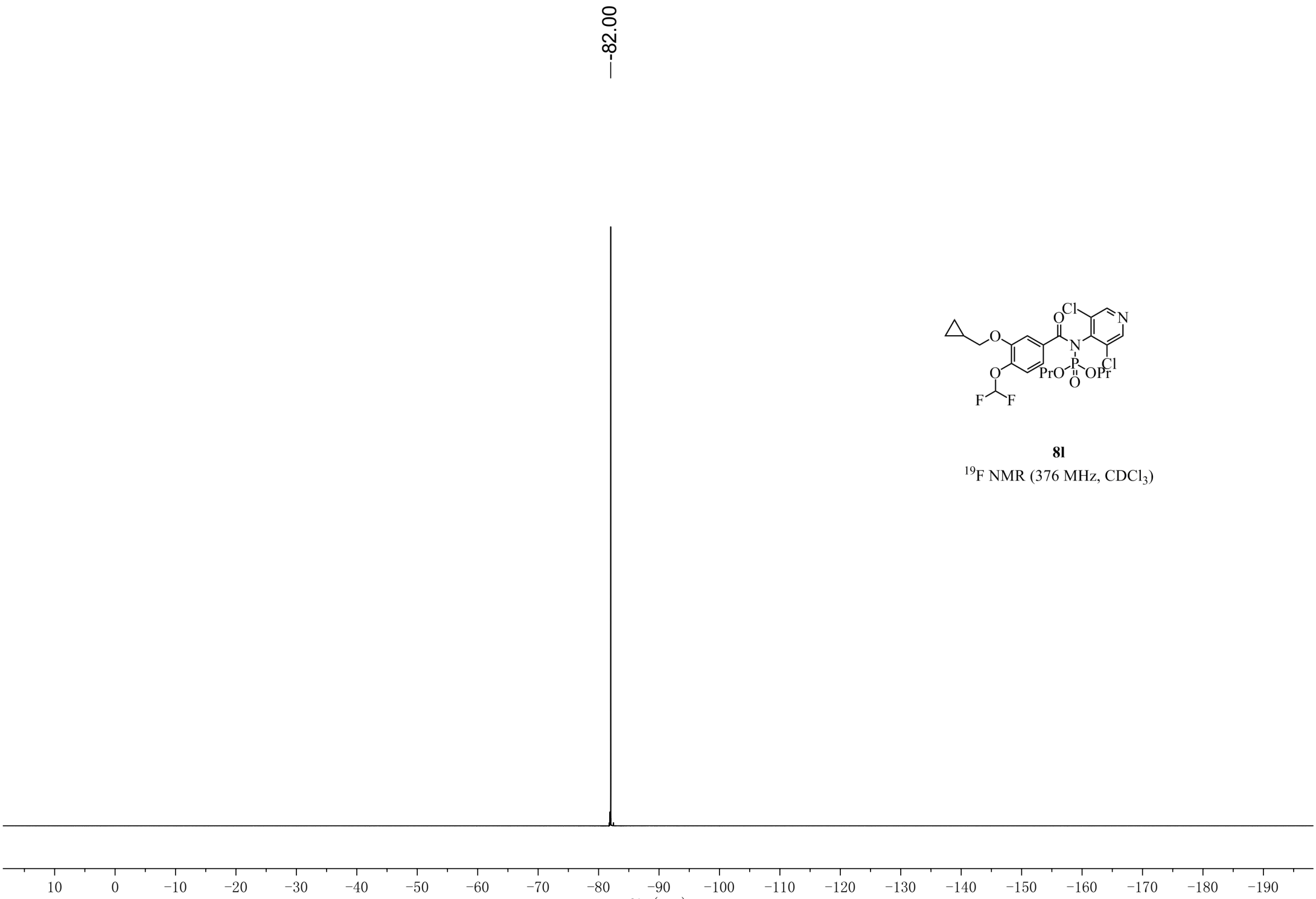



169.79
149.76
148.77
142.86
142.83
142.80
142.77
132.67
132.65
131.79
121.41
120.40
118.22
115.63
113.54
113.04
77.47
77.16
76.84
73.96
65.55
65.49
16.09
16.03
9.89
3.19
Cl
O
N
O
N
P
O
PrO
OPr
Cl
O
F
F
81
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



8l

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



8l

^{19}F NMR (376 MHz, $CDCl_3$)