Supporting Information for

Enantioselective Ni-catalyzed *Syn*-Hydrometalative Cyclization of Alkyne-tethered Ketoamides to α-Hydroxy-γ-Lactams

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I. General Information

Unless otherwise stated, all experiments were carried out in oven-dried glassware using argon manifolds or in a glovebox. Reactions were monitored by thin-layer chromatography (TLC). TLC was performed using Huanghai 8 ± 0.2 μm pre-coated glass plates (0.25 mm) and visualized by UV fluorescence quenching, $KMnO_4$, *p*-anisaldehyde or phosphomolybdic acid staining. Huanghai silica gel (particle size 300 – 400 or 200 – 300 mesh) was used for chromatography. ^1H NMR spectra were recorded at room temperature on a Bruker AVANCE NEO 400 MHz Digital NMR spectrometer and were reported relative to residual $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz Digital NMR spectrometer (100 MHz) and were reported relative to $CDCl_3$ (δ 77.16 ppm). Data for ^1H NMR were reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Data for ^{13}C NMR and ^{31}P NMR were reported in terms of chemical shifts (δ ppm). The regioselectivity was determined by ^1H NMR of the crude mixture, while the relaxation delay (d1) was set as 10 s. High resolution mass spectra (HRMS) were obtained by use of a Bruker Compact TOF mass spectrometer or a Thermo Scientific Quadrupole-Orbitrap Mass Spectrometer in electrospray ionization mode (ESI^+). Single crystal diffraction data were collected using a Rigaku XtaLAB AFC11 diffractometer. Enantiomeric ratio (er) was determined by an Agilent 1260 Series HPLC utilizing DAICEL Chiralpak (AD-H, IB, AS-H or IC) or Chiralcel (OD-H, OJ-H) columns (4.6 mm x 250 mm). Optical rotations were measured with a Perkin Elmer 343 Polarimeter and were reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent).

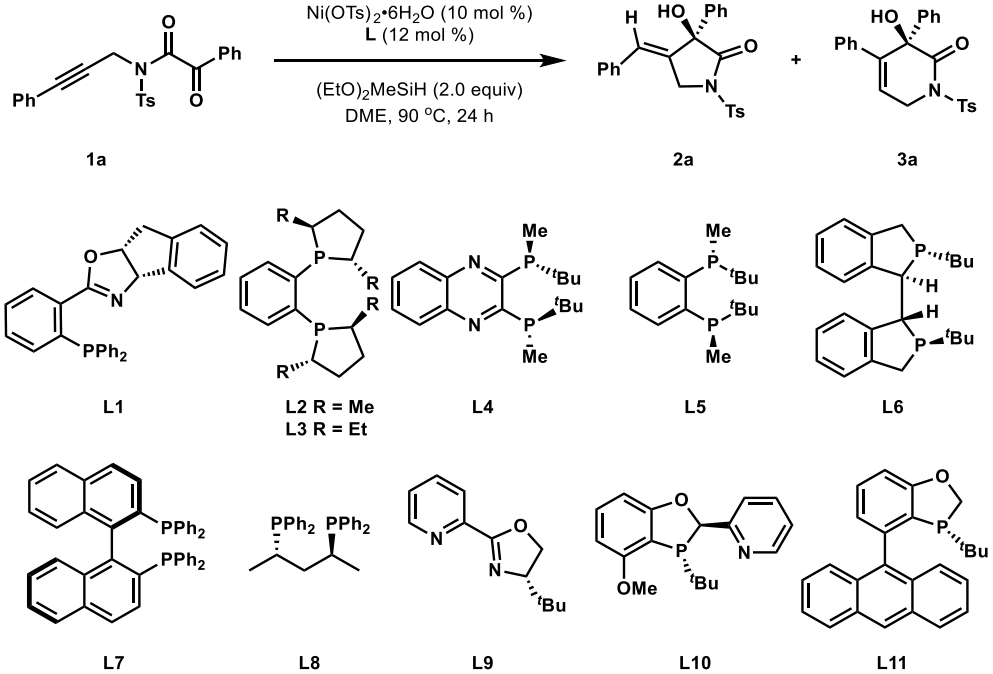
Unless otherwise noted, all chemicals were purchased from Strem, Alfa Aesar, Adamas-beta, TCI, J&K, and Energy, and used as received. Petroleum ether (PE, 60 ~ 90℃) was used as eluent for silica gel chromatography. Dry solvents were purchased commercially or were dried by passage through an activated alumina column under argon.

II. Optimization of Reaction Conditions (Tables S1–S9)

General procedure for condition optimization: To a resealable Schlenk tube equipped with

a magnetic stirring bar were added [Ni] (0.01 mmol, 10 mol %), ligand (0.012 mmol, 12 mol %), and 0.5 mL of solvent in a glovebox. After the resultant mixture was stirred at room temperature for 20 min, $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) was added and the mixture was stirred at room temperature for an additional 10 min. Substrate **1a** (41.7 mg, 0.1 mmol, 1.0 equiv) or substrate **1b** (49.5 mg, 0.1 mmol, 1.0 equiv) and another 0.5 mL of solvent were added. The tube was sealed with a Teflon valve, removed from the glovebox, and stirred at the indicated temperature for the indicated time. Then the resultant mixture was cooled to room temperature, and 1 mL of EtOAc was added. After the catalyst was filtered off by a pad of celite. The celite pad was rinsed with EtOAc (5 mL x 3). The filtrates were collected and the solvents were removed under reduced pressure to give a crude mixture. The yield was determined by ^{1}H NMR analysis of the crude mixture using 1,3,5-trimethoxybenzene as an internal standard. The er of **2a** or **2b** was determined by HPLC analysis (Chiralpak IB) after quick separation of the product using prep TLC.

Table S1. Investigation of ligands

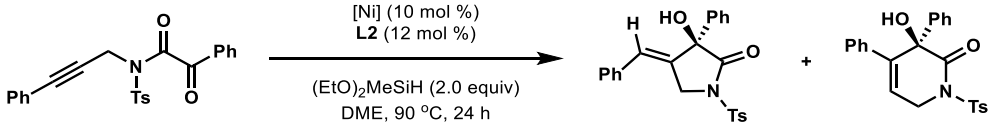


entry[a]	L	yield of **2a** (%)[b]	rr (**2a**:**3a**)[b]	er of **2a**[c]
1[d]	**L1**	24	>20:1	93.5:6.5
2	**L2**	71	>20:1	90:10

3	**L3**	21	>20:1	81.5:18.5
4	**L4**	34	>20:1	15:85
5	**L5**	42	>20:1	85.5:14.5
6	**L6**	29	>20:1	78:22
7	**L7**	<5	–	–
8	**L8**	22	>20:1	64.5:35.5
9	**L9**	<5	–	–
10	**L10**	30	>20:1	38:62
11	**L11**	<5	–	–

[a]Conducted with $Ni(OTs)_2•6H_2O$ (10 mol %), ligand (12 mol %), $(EtO)_2MeSiH$ (0.2 mmol), and **1a** (0.1 mmol) in DME (1.0 mL) at 90 °C for 24 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB). [d]Another product (structure unidentified) also obtained.

Table S2. Screening of nickel precursors

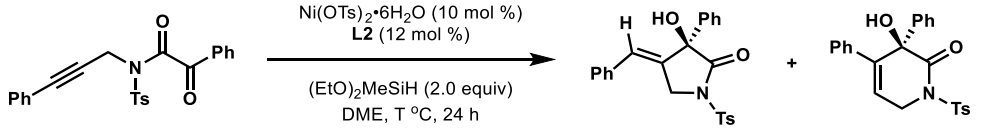


1a 2a 3a

entry[a]	[Ni]	yield of **2a** (%)[b]	rr (**2a**:**3a**)[b]	er of **2a**[c]
1	$Ni(OTs)_2•6H_2O$	71	>20:1	90:10
2	$Ni(BF_4)_2•6H_2O$	13	>20:1	–
3	$Ni(OAc)_2•4H_2O$	24	>20:1	83.5:16.5
4	$Ni(OTf)_2$	<5	–	–
5	$Ni(cod)_2$	19	>20:1	–

[a]Conducted with [Ni] (10 mol %), **L2** (12 mol %), $(EtO)_2MeSiH$ (0.1 mmol), and **1a** (0.05 mmol) in DME (1.0 mL) at 90 °C for 24 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

Table S3. Investigation of the effect of temperature



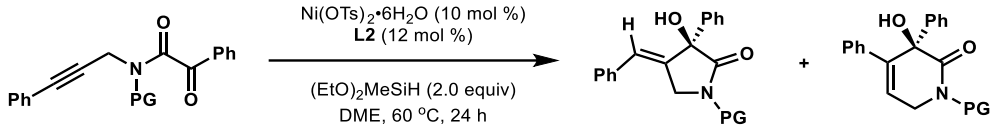
1a 2a 3a

entry[a]	T (°C)	yield of **2a** (%)[b]	rr (**2a**:**3a**)[b]	er of **2a**[c]

1	90	72	>20:1	90:10
2	80	61	>20:1	90.5:9.5
3	70	56	>20:1	91.5:8.5
4	60	42	>20:1	92:8

[a]Conducted with $Ni(OTs)_2$•$6H_2O$ (10 mol %), **L2** (12 mol %), $(EtO)_2MeSiH$ (0.1 mmol), and **1a** (0.05 mmol) in DME at T °C for 24 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

Table S5. Investigation of the effect of *N*-protective groups

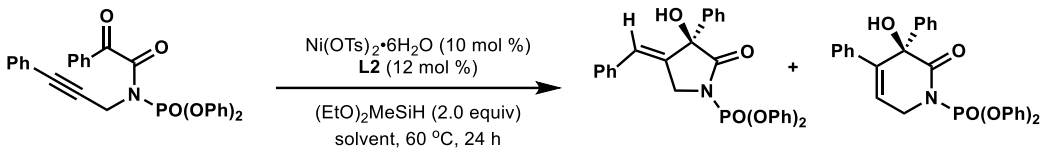


1 2 3

entry[a]	PG	yield of **2** (%)[b]	rr (**2**:**3**)[b]	er of **2**[c]
1	Ts (**1a**)	42 (**2a**)	>20:1	92:8
2	$PO(OPh)_2$ (**1b**)	50 (**2b**)	>20:1	93:7
3	$POPh_2$	17	>20:1	92.5:7.5
4	Ms	30	>20:1	92:8
5	PMP	56	>20:1	91.5:8.5
6	Me	30	>20:1	83.5:16.5
7	Ac	66	>20:1	84:16
8	Bz	48	>20:1	90.5:9.5
9	H	<5	–	–

[a]Conducted with $Ni(OTs)_2$•$6H_2O$ (10 mol %), **L2** (12 mol %), $(EtO)_2MeSiH$ (0.2 mmol), and **1** (0.1 mmol) in DME (1.0 mL) at 60 °C for 24 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

Table S6. Investigation of the effect of solvents



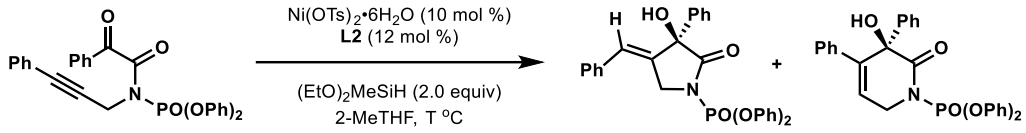
1b 2b 3b

entry[a]	solvent	yield of **2b** (%)[b]	rr (**2b**:**3b**)[b]	er of **2b**[c]
1	DME	50	>20:1	93:7

2	THF	55	>20:1	93.5:6.5
3	2-MeTHF	64	>20:1	93.5:6.5
4	toluene	53	>20:1	86.5:13.5
5	benzene	44	>20:1	93:7

[a]Conducted with $Ni(OTs)_2$•$6H_2O$ (10 mol %), **L2** (12 mol %), $(EtO)_2MeSiH$ (0.1 mmol), and **1** (0.05 mmol) in solvent (0.5 mL) at 60 °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

Table S7. Further Investigation of the effect of temperature and concentration



1b 2b 3b

entry[a]	T (°C)	conc. (M)	time (h)	yield of **2b** (%)[b]	rr (**2b**:**3b**)[b]	er of **2b**[c]
1	60	0.05	24	65	>20:1	93:7
2	50	0.05	24	60	>20:1	93.5:6.5
3	40	0.05	24	51	>20:1	93.5:6.5
4	40	0.1	24	52	>20:1	94:6
5	40	0.1	12	50	>20:1	94.5:5.5

[a]Conducted with $Ni(OTs)_2$•$6H_2O$ (10 mol %), **L2** (12 mol %), $(EtO)_2MeSiH$ (0.1 mmol), and **1b** (0.05 mmol) in 2-MeTHF at T °C. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

Table S8. Investigation of the loading of the ligand

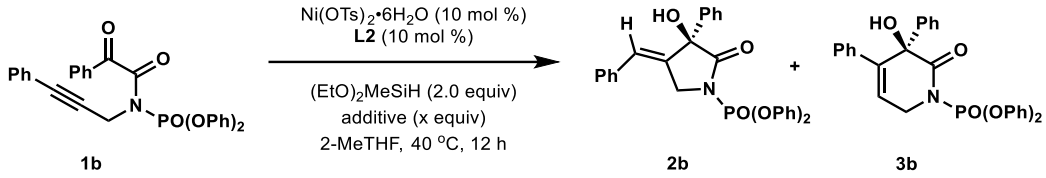
1b 2b 3b

entry[a]	**L2** (x mol %)	yield of **2b** (%)[b]	rr (**2b**:**3b**)[b]	er of **2b**[c]
1	5	33	>20:1	93:7
2	8	47	>20:1	94:6
3	10	57	>20:1	94.5:5.5
4	12	49	>20:1	94.5:5.5
5	15	45	>20:1	94.5:5.5

6	20	38	>20:1	94.5:5.5

[a]Conducted with $Ni(OTs)_2•6H_2O$ (10 mol %), **L2** (x mol %), $(EtO)_2MeSiH$ (0.1 mmol), and **1b** (0.05 mmol) in 2-MeTHF at 40 °C for 12 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB).

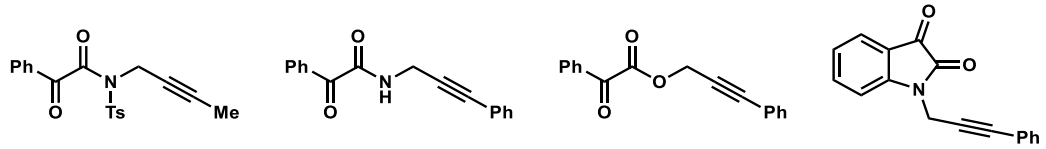
Table S9. Screening of additives



entry[a]	additive (x equiv)	yield of **2b** (%)[b]	rr (**2b**:**3b**)[b]	er of **2b**[c]
1	none	57	>20:1	94.5:5.5
2	Na_2CO_3 (2.0 equiv)	27	>20:1	93.5:6.5
3	$NaHCO_3$ (2.0 equiv)	41	>20:1	83.5:16.5
4	NaOAc (2.0 equiv)	18	–	–
5	NaF (2.0 equiv)	53	>20:1	93.5:6.5
6	K_3PO_4 (2.0 equiv)	–	–	–
7	KPF_6 (2.0 equiv)	–	–	–
8	$K_2HPO_4•3H_2O$ (2.0 equiv)	52	>20:1	90.5:9.5
9	KH_2PO_4 (2.0 equiv)	71	>20:1	94:6
10	NaH_2PO_4 (2.0 equiv)	71	>20:1	94:6
11	NaH_2PO_4 (1.0 equiv)	70	>20:1	94.5:5.5
12	NaH_2PO_4 (0.5 equiv)	77 (73)	>20:1	94.5:5.5
13[d]	NaH_2PO_4 (0.5 equiv)	40	>20:1	94.5:5.5
14	NaH_2PO_4 (0.2 equiv)	74	>20:1	94.5:5.5

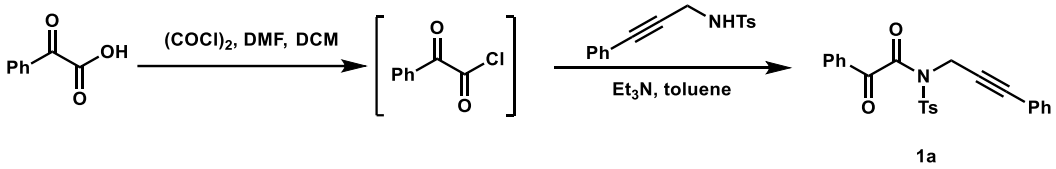
[a]Conducted with $Ni(OTs)_2•6H_2O$ (10 mol %), **L2** (10 mol %), $(EtO)_2MeSiH$ (0.2 mmol), additive, and **1b** (0.1 mmol) in 2-MeTHF (1.0 mL) at 40 °C for 12 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Determined by HPLC analysis (Chiralpak IB). [d]Conducted with $Ni(OTs)_2•6H_2O$ (5 mol %), **L2** (5 mol %).

Scheme S1. Unsuccessful Substrates



III. General Procedures for the Preparation of Substrates 1

α-Ketoacids were prepared following the reported procedures and the spectroscopic data were found consistent with those reported in the literature [1-3].

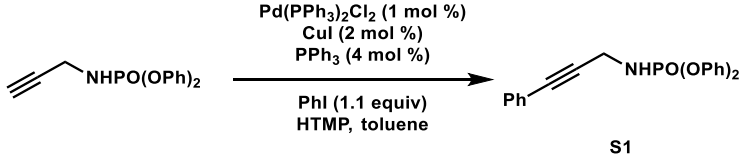


1a

2-Oxo-2-phenyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*-tosylacetamide (1a)

To a solution of phenylglyoxylic acid (1.07 g, 7.1 mmol, 1.2 equiv) in DCM (10 mL) were added 2 drops of DMF followed by the addition of oxalyl chloride (0.70 mL, 9.0 mmol, 1.4 equiv) dropwise by a syringe. The yellow mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure. and the residue was dissolved in toluene (10 mL). The resultant solution was then added dropwise to a flask containing 4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1.69 g, 5.9 mmol, 1.0 equiv), Et_3N (1.6 mL, 20 mmol, 2.0 equiv), and toluene (10 mL) at 0 °C. The mixture was left to stir at room temperature for 15 h. An aqueous solution of HCl (1 M) was added and the mixture was stirred until a clear organic layer was obtained. The aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The desired product **1a** (1.42 g, 58%) was obtained as a yellow solid after purification by silica gel chromatography (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 4H), 7.65 – 7.57 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.18 (m, 3H), 7.14 – 7.03 (m, 2H), 4.82 (s, 2H), 2.33 (s, 3H). These data are in agreement with those reported in the literature.[4]



S1

Diphenyl (3-phenylprop-2-yn-1-yl)phosphoramidate (S1)

General procedure A: To a Schlenk flask equipped with a magnetic stirring bar were added CuI (76.0 mg, 0.4 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol, 1 mol %), PPh_3 (209.6 mg, 0.8 mmol, 4 mol %), iodobenzene (4.49 g, 22 mmol, 1.1 equiv) and diphenyl prop-2-yn-

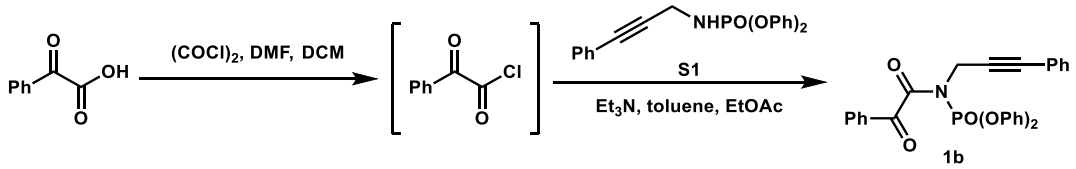
1-ylphosphoramidate (5.74 g, 20 mmol, 1.0 equiv), followed by the addition of 2,2,6,6-tetramethylpiperidine (7 mL) and toluene (28 mL). The flask was sealed and the mixture was stirred at room temperature for 6 h. The mixture was quenched with saturated NH_4Cl (30 mL), diluted with H_2O (20 mL), and extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The desired product **S1** (6.18 g, 85%) was obtained as a white solid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 13H), 7.20 – 7.13 (m, 2H), 4.12 (dd, *J* = 11.7, 6.6 Hz, 2H), 3.43 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, *J* = 6.8 Hz), 131.8, 129.9, 128.6, 128.4, 125.2, 122.6, 120.5 (d, *J* = 5.1 Hz), 85.8 (d, *J* = 6.8 Hz), 84.0, 32.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.0.

HRMS (ESI^+) *m/z* calc'd for $C_{21}H_{18}NO_3PNa$ $[M+Na]^+$: 386.0917, found 386.0912.



Diphenyl (2-oxo-2-phenylacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1b)

General procedure B: To a solution of phenylglyoxylic acid (0.98 g, 6.5 mmol, 1.3 equiv) and 2 drops of DMF in DCM (10 mL) was added oxalyl chloride (0.68 mL, 8.0 mmol, 1.6 equiv) dropwise. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in toluene (10 mL). The resultant solution was then added dropwise to a solution of **S1** (1.81 g, 5.0 mmol, 1.0 equiv) and Et_3N (1.4 mL, 20 mmol, 4.0 equiv) in EtOAc (10 mL) at 0 °C. The mixture was left to stir at room temperature for 18 h. An aqueous solution of HCl (1 M) was added and the mixture was stirred until a clear organic layer was obtained. The aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The desired product **1b** (1.97 g, 80%) was obtained as a brown solid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 5 / 1).

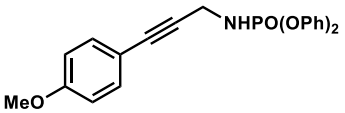
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* =

7.7 Hz, 2H), 7.26 – 7.06 (m, 15H), 4.72 (d, *J* = 10.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.2 (d, *J* = 10.3 Hz), 149.8 (d, *J* = 6.6 Hz), 134.3, 133.0, 131.9, 130.1, 129.6, 128.9, 128.8, 128.3, 126.0, 122.2, 120.2 (d, *J* = 5.1 Hz), 84.6, 83.2, 35.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.3.

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{23}NO_5P$ $[M+H]^+$: 496.1308, found 496.1306.



S2

Diphenyl (3-(4-methoxyphenyl)prop-2-yn-1-yl)phosphoramidate (S2)

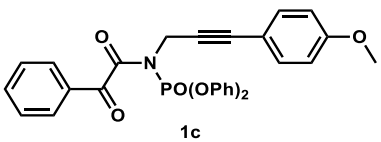
The general procedure A was followed. The reaction was performed with CuI (7.6 mg, 0.04 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (14.1 mg, 0.02 mmol, 1 mol %), PPh_3 (20.9 mg, 0.08 mmol, 4 mol %), 1-iodo-4-methoxybenzene (514.8 mg, 2.2 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (629.4 mg, 2.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (0.5 mL) and toluene (2.5 mL) at room temperature for 10 h. The desired product **S2** (813.2 mg, 94%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 10H), 7.23 – 7.13 (m, 2H), 6.87 – 6.78 (m, 2H), 4.10 (dd, *J* = 11.8, 6.6 Hz, 2H), 3.81 (s, 3H), 3.63 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 150.8 (d, *J* = 6.7 Hz), 133.2, 129.8, 125.2 (d, *J* = 1.2 Hz), 120.5 (d, *J* = 4.8 Hz), 114.7, 114.0, 84.4 (d, *J* = 6.7 Hz), 83.9, 55.4, 32.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ –1.8.

HRMS (ESI^+) *m/z* calc'd for $C_{22}H_{21}NO_4P$ $[M+H]^+$: 394.1208, found 394.1210.



1c

Diphenyl (3-(4-methoxyphenyl)prop-2-yn-1-yl)(2-oxo-2-phenylacetyl)phosphoramidate (1c)

The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.38 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.23 mL, 3.2 mmol, 1.6 equiv), **S2** (786.4 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (5 mL) and toluene (5 mL) at room

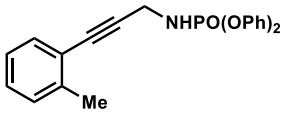
temperature for 14 h. The desired product **1c** (764.2 mg, 73%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.46 – 7.37 (m, 1H), 7.28 – 7.20 (m, 2H), 7.20 – 7.09 (m, 8H), 7.09 – 7.00 (m, 4H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.69 (d, *J* = 10.1 Hz, 2H), 3.66 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.2 (d, *J* = 10.1 Hz), 159.9, 149.7 (d, *J* = 6.6 Hz), 134.2, 133.3, 132.9, 129.7, 129.5, 128.8, 125.9 (d, *J* = 1.3 Hz), 120.1 (d, *J* = 5.1 Hz), 114.1, 113.8, 84.7, 81.8, 55.3, 35.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{24}NO_6PNa$ $[M+Na]^+$: 548.1233, found 548.1235.



S3

Diphenyl (3-(*o*-tolyl)prop-2-yn-1-yl)phosphoramidate (S3)

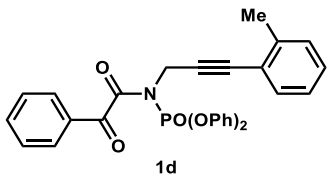
The general procedure A was followed. The reaction was performed with CuI (7.6 mg, 0.04 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (14.1 mg, 0.02 mmol, 1 mol %), PPh_3 (20.9 mg, 0.08 mmol, 4 mol %), 1-iodo-2-methylbenzene (479.6 mg, 2.2 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (572.1 mg, 2.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (0.5 mL) and toluene (2.5 mL) at room temperature for 10 h. The desired product **S3** (748.5 mg, 90%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 8H), 7.25 – 7.07 (m, 6H), 4.17 (dd, *J* = 11.6, 6.7 Hz, 2H), 3.58 (brs, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 6.8 Hz), 140.3, 132.0, 129.7, 129.4, 128.5, 125.5, 125.1, 122.3, 120.4 (d, *J* = 4.9 Hz), 89.5 (d, *J* = 7.0 Hz), 82.8, 32.3, 20.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ –1.9.

HRMS (ESI^+) *m/z* calc'd for $C_{22}H_{21}NO_3P$ $[M+H]^+$: 378.1259, found 378.1259.



1d

Diphenyl (2-oxo-2-phenylacetyl)(3-(*o*-tolyl)prop-2-yn-1-yl)phosphoramidate (1d)

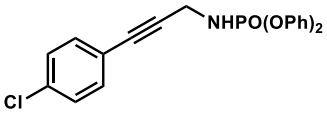
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S3** (717.2 mg, 1.9 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1d** (187.4 mg, 20%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.7 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.50 – 7.40 (m, 1H), 7.33 – 7.23 (m, 3H), 7.22 – 7.15 (m, 5H), 7.15 – 7.05 (m, 7H), 7.01 (d, *J* = 7.7 Hz, 1H), 4.74 (d, *J* = 10.1, 2H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.2 (d, *J* = 10.5 Hz), 149.8 (d, *J* = 6.7 Hz), 140.7, 134.3, 133.0, 132.2, 130.0, 129.6, 129.5, 128.84, 128.76, 126.0, 125.5, 122.0, 120.2 (d, *J* = 5.1 Hz), 86.9, 83.7, 35.2, 20.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{25}NO_5P$ $[M+H]^+$: 510.1465, found 510.1459.



S4

Diphenyl (3-(4-chlorophenyl)prop-2-yn-1-yl)phosphoramidate (S4)

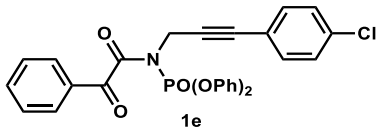
The general procedure A was followed. The reaction was performed with CuI (15.2 mg, 0.08 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (28.0 mg, 0.04 mmol, 1 mol %), PPh_3 (41.8 mg, 0.16 mmol, 4 mol %), 1-chloro-4-iodobenzene (1.05 g, 4.4 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (1.05 g, 2.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (1.0 mL) and toluene (5.0 mL) at room temperature for 24 h. The desired product **S4** (1.38 g, 85%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 6H), 7.26 – 7.21 (m, 4H), 7.20 – 7.12 (m, 2H), 4.10 (dd, *J* = 12.0, 6.7 Hz, 2H), 3.55 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8 (d, *J* = 6.7 Hz), 134.7, 133.0, 129.9, 128.8, 125.3, 121.1, 120.4 (d, *J* = 4.9 Hz), 86.8 (d, *J* = 6.5 Hz), 82.9, 32.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.0.

HRMS (ESI$^+$) *m/z* calc'd for $C_{21}H_{18}NO_3PCl$ $[M+H]^+$: 398.0713, found 398.0710.



1e

Diphenyl (3-(4-chlorophenyl)prop-2-yn-1-yl)(2-oxo-2-phenylacetyl)phosphoramidate (1e)

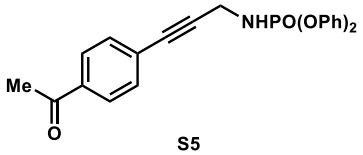
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S4** (795.6 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (5 mL) and toluene (5 mL) at room temperature for 14 h. The desired product **1e** (194.8 mg, 19%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) 7.66 (d, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.05 (m, 10H), 7.04 – 6.94 (m, 4H), 4.67 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 169.0 (d, *J* = 10.2 Hz), 149.6 (d, *J* = 6.5 Hz), 134.6, 134.2, 132.9, 132.7, 129.9, 129.3, 128.7, 128.5, 125.9, 120.0 (d, *J* = 5.1 Hz), 119.9, 84.1, 83.4, 34.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.3.

HRMS (ESI$^+$) *m/z* calc'd for $C_{29}H_{22}NO_5PCl$ $[M+H]^+$: 530.0919, found 530.0919.



S5

Diphenyl (3-(4-acetylphenyl)prop-2-yn-1-yl)phosphoramidate (S5)

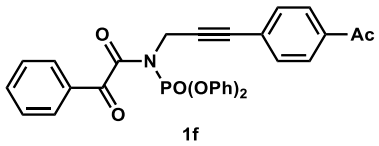
The general procedure A was followed. The reaction was performed with CuI (7.6 mg, 0.04 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (14.1 mg, 0.02 mmol, 1 mol %), PPh_3 (20.9 mg, 0.08 mmol, 4 mol %), 1-(4-iodophenyl)ethan-1-one (541.2 mg, 2.2 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (572.0 mg, 2.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (0.5 mL) and toluene (2.5 mL) at room temperature for 10 h. The desired product **S5** (777.2 mg, 96%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.47 – 7.36 (m, 2H), 7.35 – 7.26 (m, 8H), 7.23 – 7.12 (m, 2H), 4.13 (dd, *J* = 12.3, 6.7 Hz, 2H), 3.77 (brs, 1H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 150.8 (d, *J* = 6.7 Hz), 136.5, 131.9, 129.9, 128.3, 127.5, 125.2 (d, *J* = 1.2 Hz), 120.4 (d, *J* = 5.0 Hz), 89.3 (d, *J* = 6.1 Hz), 83.2, 32.3, 26.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.0.

HRMS (ESI^+) *m/z* calc'd for $C_{23}H_{21}NO_4P$ $[M+H]^+$: 406.1208, found 406.1208.



1f

Diphenyl (3-(4-acetylphenyl)prop-2-yn-1-yl)(2-oxo-2-phenylacetyl)phosphoramidate (1f)

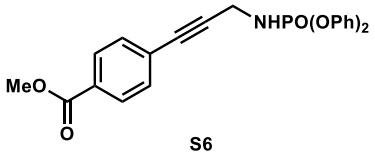
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S5** (770.1 mg, 1.9 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (5 mL) and toluene (5 mL) at room temperature for 14 h. The desired product **1f** (554.0 mg, 52%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.12 – 7.07 (m, 10H), 7.02 (t, *J* = 7.1 Hz, 2H), 4.71 (d, *J* = 9.9 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 187.4, 168.9 (d, *J* = 10.3 Hz), 149.5 (d, *J* = 6.5 Hz), 136.4, 134.2, 132.6, 131.7, 129.9, 129.3, 128.7, 128.0, 126.6, 125.9, 119.9 (d, *J* = 5.1 Hz), 86.3, 83.6, 34.7, 26.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.4.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{25}NO_6P$ $[M+H]^+$: 538.1414, found 538.1413.



S6

Methyl 4-(3-((diphenoxyphosphoryl)amino)prop-1-yn-1-yl)benzoate (S6)

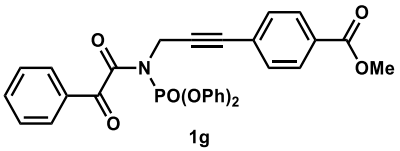
The general procedure A was followed. The reaction was performed with CuI (30.4 mg, 0.04 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (56.0 mg, 0.02 mmol, 1 mol %), PPh_3 (41.8 mg, 0.08 mmol, 4 mol %), methyl 4-iodobenzoate (1.15 g, 4.4 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (1.14 g, 4.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (1.0 mL) and toluene (5.0 mL) at room temperature for 10 h. The desired product **S6** (1.32 g, 78%) was obtained as a white solid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.30 – 7.20 (m, 10H), 7.12 – 7.02 (m, 2H), 4.04 (dd, *J* = 12.3, 6.7 Hz, 2H), 3.83 (s, 3H), 3.70 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 150.6 (d, *J* = 6.6 Hz), 131.6, 129.8, 129.4, 127.2, 125.1 (d, *J* = 1.3 Hz), 120.3 (d, *J* = 4.9 Hz), 88.9 (d, *J* = 6.2 Hz), 83.1, 52.3, 32.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –1.9.

HRMS (ESI^+) *m/z* calc'd for $C_{23}H_{21}NO_5P$ $[M+H]^+$: 422.1157, found 422.1157.



1g

Methyl 4-(3-(*N*-(diphenoxyphosphoryl)-2-oxo-2-phenylacetamido)prop-1-yn-1-yl)benzoate (1g)

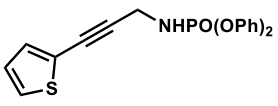
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S6** (842.8 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1g** (798.1 mg, 72%) was obtained as a yellow solid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.71 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.54 – 7.44 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.17 (m, 6H), 7.17 – 7.01 (m, 6H), 4.74 (d, *J* = 10.1 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 187.6, 169.1 (d, *J* = 10.1 Hz), 166.5, 149.8 (d, *J* = 6.6 Hz), 134.4, 132.9, 131.8, 130.1, 129.6, 129.4, 128.9, 126.8, 126.1, 120.2 (d, *J* = 5.1 Hz), 86.2, 84.0, 52.4, 35.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.1.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{25}NO_7P$ $[M+H]^+$: 554.1369, found 554.1369.



S7

Diphenyl (3-(thiophen-2-yl)prop-2-yn-1-yl)phosphoramidate (S7)

The general procedure A was followed. The reaction was performed with CuI (30.4 mg, 0.04 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (56.0 mg, 0.02 mmol, 1 mol %), PPh_3 (41.8 mg, 0.08 mmol, 4 mol %), 2-iodothiophene (0.49 mL, 4.4 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-

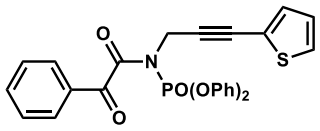
ylphosphoramidate (1.14 g, 4.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (1.0 mL) and toluene (5.0 mL) at room temperature for 10 h. The desired product **S7** (1.07 g, 73%) was obtained as a brown solid after purification by silica gel chromatography. R_f= 0.4 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 8H), 7.19 – 7.15 (m, 2H), 7.13 – 7.06 (m, 2H), 7.05 (d, *J* = 3.6 Hz, 1H), 6.88 (dd, *J* = 5.2, 3.6 Hz, 1H), 4.05 (dd, *J* = 11.9, 6.7 Hz, 2H), 3.38 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 6.8 Hz), 132.4, 129.9, 127.4, 127.1, 125.3 (d, *J* = 1.3 Hz), 122.5, 120.5 (d, *J* = 5.0 Hz), 89.7 (d, *J* = 6.6 Hz), 89.2, 32.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.0.

HRMS (ESI^+) *m/z* calc'd for $C_{19}H_{17}NO_3PS$ $[M+H]^+$: 370.0667, found 370.0667.



1h

Diphenyl (2-oxo-2-phenylacetyl)(3-(thiophen-2-yl)prop-2-yn-1-yl)phosphoramidate (1h)

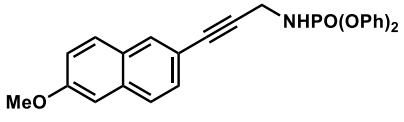
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S7** (0.74 g, 2.0 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1h** (430.2 mg, 43%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f= 0.6 (PE / EtOAc = 1 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.50 – 7.42 (m, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.06 (m, 11H), 6.97 (s, 1H), 6.89 – 6.82 (m, 1H), 4.73 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.2 (d, *J* = 10.1 Hz), 149.8 (d, *J* = 6.8 Hz), 134.3, 133.0, 132.9, 130.1, 129.6, 128.9, 127.8, 127.0, 126.1 (d, *J* = 1.3 Hz), 122.0, 120.2 (d, *J* = 5.3 Hz), 87.2, 35.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –13.0.

HRMS (ESI^+) *m/z* calc'd for $C_{27}H_{21}NO_5PS$ $[M+H]^+$: 502.0878, found 502.0878.



S8

Diphenyl (3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-yl)phosphoramidate (S8)

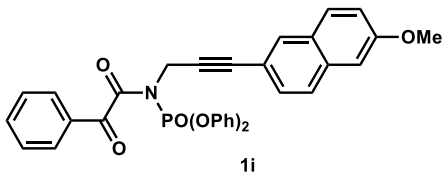
The general procedure A was followed. The reaction was performed with CuI (30.4 mg, 0.08 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (56.0 mg, 0.04 mmol, 1 mol %), PPh_3 (41.8 mg, 0.16 mmol, 4 mol %), 2-iodothiophene (0.49 mL, 4.4 mmol, 1.1 equiv) and diphenyl prop-2-yn-1-ylphosphoramidate (1.14 g, 4.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (1.0 mL) and toluene (5.0 mL) at room temperature for 10 h. The desired product **S8** (1.07 g, 73%) was obtained as a brown solid after purification by silica gel chromatography. R_f = 0.4 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 1.6 Hz, 1H), 7.65 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.38 – 7.29 (m, 9H), 7.23 – 7.12 (m, 3H), 7.10 (d, *J* = 2.5 Hz, 1H), 4.16 (dd, *J* = 11.7, 6.7 Hz, 2H), 3.92 (s, 3H), 3.43 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 150.8 (d, *J* = 6.8 Hz), 134.3, 131.6, 129.9, 129.4, 129.0, 128.5, 126.9, 125.2, 120.5 (d, *J* = 5.0 Hz), 119.6, 117.4, 105.9, 85.4 (d, *J* = 6.7 Hz), 84.6, 55.5, 32.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –2.0.

HRMS (ESI^+) *m/z* calc'd for $C_{26}H_{23}NO_4P$ $[M+H]^+$: 444.1365, found 444.1363.



1i

Diphenyl (3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-yl)(2-oxo-2-phenylacetyl)phosphoramidate (1i)

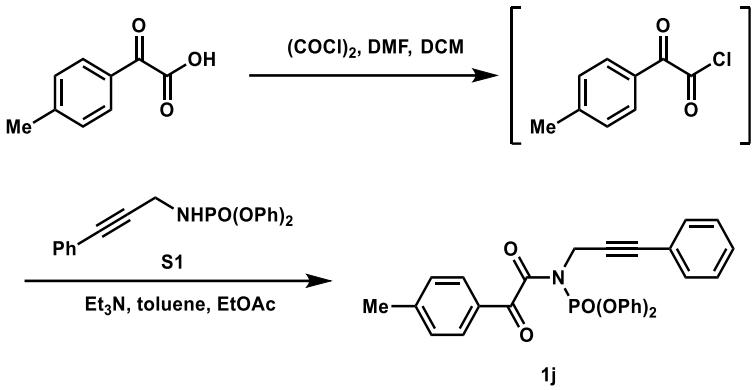
The general procedure B was followed. The reaction was performed with phenylglyoxylic acid (0.39 g, 2.5 mmol, 1.3 equiv), oxalyl chloride (0.25 mL, 3.2 mmol, 1.6 equiv), **S8** (881.5 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.6 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1i** (441.3 mg, 39%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.59 – 7.50 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.14 (m, 10H), 7.14 – 7.04 (m, 3H), 7.01 (d, *J* = 2.5 Hz, 1H), 4.76 (d, *J* = 10.1 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.1 (d, *J* = 9.9 Hz), 158.5, 149.8 (d, *J* = 6.6 Hz), 134.3, 134.2, 132.9, 131.8, 130.0, 129.6, 129.3, 128.9, 128.8, 128.2, 126.7, 125.9, 120.2 (d, *J* = 5.1 Hz), 119.5, 116.9, 105.8, 82.7, 55.4, 35.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI$^+$) *m/z* calc'd for $C_{34}H_{27}NO_6P$ $[M+H]^+$: 576.1571, found 576.1567.



Diphenyl (2-oxo-2-(*p*-tolyl)acetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1j)

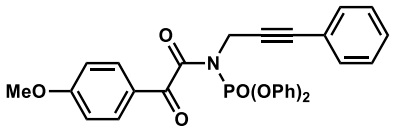
General procedure C: To a solution of 2-oxo-2-(*p*-tolyl)acetic acid (491.7 mg, 3.0 mmol, 1.2 equiv) and 1 drop of DMF in DCM (5 mL) was added oxalyl chloride (0.31 mL, 3.6 mmol, 1.44 equiv) dropwise. The yellow mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum and the residue was dissolved in toluene (5 mL). The resulting solution was then added dropwise to a mixture of **S1** (908.4 mg, 2.5 mmol, 1.0 equiv) and Et_3N (0.51 g, 5 mmol, 2.0 equiv) in EtOAc (5 mL) at 0 °C. The mixture was stirred at room temperature for 12 h. An aqueous solution of HCl (1 M) was added to the mixture until a clear organic layer was obtained. The organic phase was separated and the aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The desired product **1j** (844.3 mg, 66%) was obtained as a white solid after purification by silica gel chromatography (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.10 (m, 13H), 7.09 – 7.00 (m, 4H), 4.69 (d, *J* = 10.1 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 169.2 (d, *J* = 9.6 Hz), 149.8 (d, *J* = 6.5 Hz), 145.5, 131.8, 130.5, 130.0, 129.7, 129.5, 128.7, 128.2, 125.9, 122.1, 120.2 (d, *J* = 5.1 Hz), 84.7, 83.3, 35.1, 21.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI$^+$) *m/z* calc'd for $C_{30}H_{25}NO_5P$ $[M+H]^+$: 510.1465, found 510.1467.



1k

Diphenyl (2-(4-methoxyphenyl)-2-oxoacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1k)

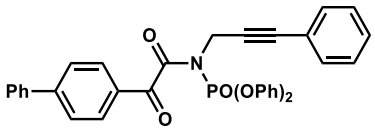
The general procedure C was followed. The reaction was performed with 2-(4-methoxyphenyl)-2-oxoacetic acid (432.4 mg, 2.4 mmol, 1.2 equiv), oxalyl chloride (0.24 mL, 2.9 mmol, 1.44 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1k** (432.3 mg, 43%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.10 (s, 13H), 7.09 – 7.00 (m, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 4.69 (d, *J* = 10.2 Hz, 2H), 3.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 169.3 (d, *J* = 9.1 Hz), 164.5, 149.8 (d, *J* = 6.7 Hz), 131.9, 131.8, 129.89, 129.86, 128.7, 128.2, 125.9, 122.1, 120.2 (d, *J* = 5.2 Hz), 114.2, 84.6, 83.4, 55.6, 35.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI$^+$) *m/z* calc'd for $C_{30}H_{25}NO_6P$ $[M+H]^+$: 526.1414, found 526.1413.



1l

Diphenyl (2-([1,1'-biphenyl]-4-yl)-2-oxoacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1l)

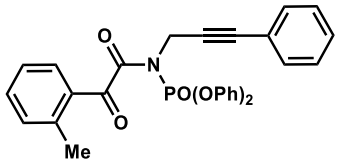
The general procedure C was followed. The reaction was performed with 2-([1,1'-biphenyl]-4-yl)-2-oxoacetic acid (657.2 mg, 3.0 mmol, 1.5 equiv), oxalyl chloride (0.45 mL, 3.6 mmol, 1.8 equiv), **S1** (725.4 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1l** (456.8 mg, 40%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 1H), 7.26 – 7.12 (m, 13H), 7.11 – 7.05 (m, 2H), 4.73 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.3, 169.2 (d, *J* = 9.8 Hz), 149.8 (d, *J* = 6.6 Hz), 147.0, 139.8, 131.9, 131.7, 130.1, 130.0, 129.1, 128.8, 128.6, 128.3, 127.5, 127.4, 126.0, 122.1, 120.2 (d, *J* = 5.1 Hz), 85.5, 83.3, 35.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI^+) *m/z* calc'd for $C_{35}H_{27}NO_5P$ $[M+H]^+$: 572.1621, found 572.1617.



1m

Diphenyl (2-oxo-2-(*o*-tolyl)acetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1m)

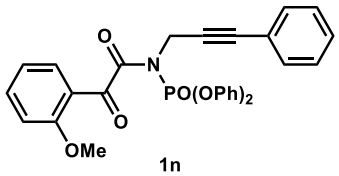
The general procedure C was followed. The reaction was performed with 2-oxo-2-(o-tolyl)acetic acid (492.0 mg, 3.0 mmol, 1.5 equiv), oxalyl chloride (0.48 mL, 5.4 mmol, 2.7 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1m** (771.0 mg, 76%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.7 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.24 – 7.14 (m, 9H), 7.15 – 7.05 (m, 7H), 7.02 – 6.92 (m, 1H), 4.69 (d, *J* = 10.0 Hz, 2H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 169.4 (d, *J* = 10.6 Hz), 149.9 (d, *J* = 6.6 Hz), 141.9, 133.3, 132.5, 132.4, 131.9, 131.2, 130.0, 128.7, 128.3, 126.0 (d, *J* = 1.2 Hz), 125.8, 122.2, 120.2 (d, *J* = 5.2 Hz), 84.6, 83.2, 35.0, 21.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.1.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{25}NO_5P$ $[M+H]^+$: 510.1465, found 510.1465.



1n

Diphenyl (2-(2-methoxyphenyl)-2-oxoacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1n)

The general procedure C was followed. The reaction was performed with 2-oxo-2-(*o*-tolyl)acetic acid (540.1 mg, 3.0 mmol, 1.5 equiv), oxalyl chloride (0.48 mL, 5.4 mmol, 2.7 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene

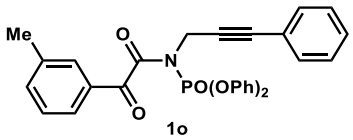
(2 mL) at room temperature for 14 h. The desired product **1n** (750.2 mg, 71%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.7 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.31 – 7.15 (m, 13H), 7.13 – 7.03 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 10.4 Hz, 2H), 3.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 169.8 (d, *J* = 12.6 Hz), 160.0, 150.2 (d, *J* = 6.7 Hz), 136.2, 131.9, 130.7, 129.9, 128.7, 128.4, 125.7, 122.6, 122.5, 121.3, 120.1 (d, *J* = 5.3 Hz), 112.0, 84.1, 83.6, 55.7, 34.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.2.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{25}NO_6P$ $[M+H]^+$: 526.1414, found 526.1413.



1o

Diphenyl (2-oxo-2-(*m*-tolyl)acetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1o)

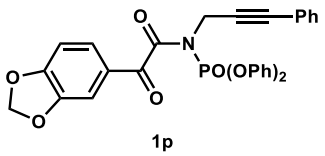
The general procedure C was followed. The reaction was performed with 2-oxo-2-(*m*-tolyl)acetic acid (492.0 mg, 3.0 mmol, 1.5 equiv), oxalyl chloride (0.48 mL, 5.4 mmol, 2.7 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1o** (801.4 mg, 79%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.7 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) 7.55 – 7.48 (m, 2H), 7.29 – 7.05 (m, 17H), 4.71 (d, *J* = 10.0 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 169.1 (d, *J* = 10.2 Hz), 149.6 (d, *J* = 6.5 Hz), 138.5, 135.1, 132.8, 131.7, 129.84, 129.79, 128.62, 128.58, 128.1, 126.7, 125.8, 121.9, 120.0 (d, *J* = 5.1 Hz), 84.5, 83.1, 34.8, 21.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.3.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{25}NO_5P$ $[M+H]^+$: 510.1465, found 510.1458.



1p

Diphenyl (2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetyl)(3-phenylprop-2-yn-1-

yl)phosphoramidate (1p)

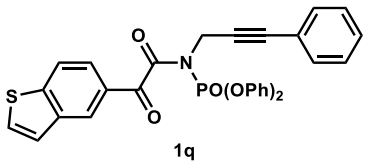
The general procedure C was followed. The reaction was performed with 2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetic acid (510.0 mg, 2.64 mmol, 1.3 equiv), oxalyl chloride (0.45 mL, 5.4 mmol, 2.6 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 14 h. The desired product **1p** (759.9 mg, 70%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f= 0.7 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.14 (m, 17H), 6.70 (d, *J* = 8.1 Hz, 1H), 6.02 (s, 2H), 4.77 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 169.1 (d, *J* = 9.6 Hz), 153.0, 149.9 (d, *J* = 6.7 Hz), 148.5, 131.9, 130.0, 128.7, 128.3, 127.8, 127.1, 126.0 (d, *J* = 1.2 Hz), 122.2, 120.3 (d, *J* = 5.1 Hz), 108.5, 108.3, 102.2, 84.7, 83.3, 35.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –10.3.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{23}NO_7P$ $[M+H]^+$: 540.1207, found 540.1200.



1q

Diphenyl (2-(benzo[*b*]thiophen-5-yl)-2-oxoacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1q)

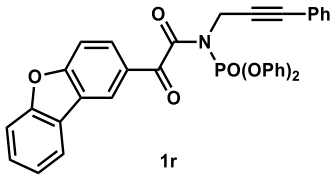
The general procedure C was followed. The reaction was performed with 2-(benzo[*b*]thiophen-5-yl)-2-oxoacetic acid (515.3 mg, 2.5 mmol, 1.25 equiv), oxalyl chloride (0.45 mL, 5.4 mmol, 2.6 equiv), **S1** (726.7 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 13 h. The desired product **1q** (538.3 mg, 48%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f= 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89 – 7.78 (m, 2H), 7.47 (d, *J* = 5.5 Hz, 1H), 7.35 – 7.10 (m, 16H), 4.84 (d, *J* = 10.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.7, 169.3 (d, *J* = 9.7 Hz), 149.8 (d, *J* = 6.6 Hz), 145.6, 139.3, 131.9, 130.0, 129.6, 128.8, 128.3, 128.1, 126.2, 126.0, 124.7, 123.9, 123.0, 122.1, 120.2 (d, *J* = 5.2 Hz), 83.3, 77.4.

^{31}P NMR (162 MHz, $CDCl_3$) –10.3

HRMS (ESI$^+$) *m/z* calc'd for $C_{31}H_{23}NO_7PS$ $[M+H]^+$: 552.1029, found 552.1028.



1r

Diphenyl (2-(dibenzo[*b*,*d*]furan-2-yl)-2-oxoacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1r)

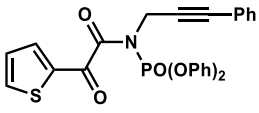
The general procedure C was followed. The reaction was performed with 2-(dibenzo[*b*,*d*]furan-2-yl)-2-oxoacetic acid (721.3 mg, 2.5 mmol, 1.25 equiv), oxalyl chloride (0.45 mL, 5.4 mmol, 2.6 equiv), **S1** (725.2 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 13 h. The desired product **1r** (876.7 mg, 72%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f= 0.4 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 1.8 Hz, 1H), 7.87 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.34 – 7.08 (m, 14H), 7.07 – 6.97 (m, 2H), 4.77 (d, *J* = 9.9 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 169.3, 159.6, 157.0, 149.7 (d, *J* = 6.3 Hz), 132.0, 130.0, 129.0, 128.9, 128.4, 128.3, 126.0, 125.0, 123.5, 123.4, 123.2, 121.3, 120.1 (d, *J* = 5.1 Hz), 112.3, 112.0, 89.2, 83.5, 35.4.

^{31}P NMR (162 MHz, $CDCl_3$) –10.3

HRMS (ESI$^+$) *m/z* calc'd for $C_{35}H_{25}NO_6P$ $[M+H]^+$: 586.1414, found 586.1413.



1s

Diphenyl (2-oxo-2-(thiophen-2-yl)acetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1s)

The general procedure C was followed. The reaction was performed with 2-oxo-2-(thiophen-2-yl)acetic acid (620.1 mg, 4.0 mmol, 2.0 equiv), oxalyl chloride (0.42 mL, 5.0 mmol, 2.5 equiv), **S1** (721.3 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 13 h. The desired product **1s** (487.3 mg, 49%) was obtained as a purple liquid after purification by silica gel chromatography. R_f= 0.4 (PE / EtOAc = 2 / 1).

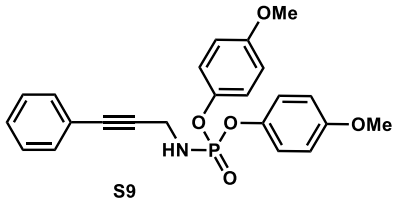
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.42 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.30 – 7.15 (m, 11H), 7.15 – 7.06 (m, 4H), 6.94 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.72 (d, *J* = 10.1 Hz,

2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 167.9, 167.8, 149.9 (d, *J* = 6.7 Hz), 139.8, 136.2, 135.9, 131.9, 130.0, 128.8, 128.5, 128.3, 126.0, 122.1, 120.3 (d, *J* = 5.1 Hz), 84.9, 83.3, 35.7.

^{31}P NMR (162 MHz, $CDCl_3$) –10.2.

HRMS (ESI^+) *m/z* calc'd for $C_{27}H_{21}NO_5PS$ $[M+H]^+$: 502.0878, found 502.0878.



S9

Diphenyl (3-(6-methoxynaphthalen-2-yl)prop-2-yn-1-yl)phosphoramidate (S9)

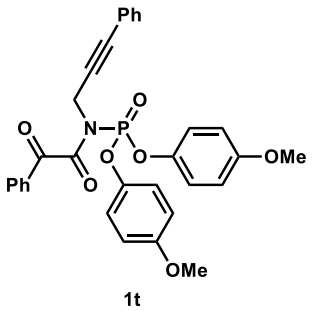
The general procedure A was followed. The reaction was performed with CuI (19.0 mg, 0.10 mmol, 2 mol %), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 1 mol %), PPh_3 (52.5 mg, 0.20 mmol, 4 mol %), iodobenzene (1.12 g, 5.5 mmol, 1.1 equiv) and bis(4-methoxyphenyl) prop-2-yn-1-ylphosphoramidate (1.74 g, 5.0 mmol, 1.0 equiv) in 2,2,6,6-tetramethylpiperidine (1.5 mL) and toluene (7.5 mL) at room temperature for 20 h. The desired product **S9** (1.50 g, 71%) was obtained as a white solid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 1 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 4H), 7.25 – 7.17 (m, 4H), 6.87 – 6.78 (m, 4H), 4.09 (dd, *J* = 11.6, 6.7 Hz, 2H), 3.75 (s, 6H), 3.34 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 144.2 (d, *J* = 6.9 Hz), 131.7, 128.5, 128.3, 122.5, 121.3 (d, *J* = 4.6 Hz), 114.7, 85.8 (d, *J* = 6.8 Hz), 83.9, 55.6, 32.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –1.0.

HRMS (ESI^+) *m/z* calc'd for $C_{23}H_{23}NO_5P$ $[M+H]^+$: 424.1314, found 424.1310.



1t

Bis(4-methoxyphenyl) (2-oxo-2-phenylacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1t)

The general procedure C was followed. The reaction was performed with phenylglyoxylic acid

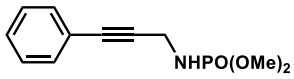
(0.39 g, 2.6 mmol, 1.3 equiv), oxalyl chloride (0.27 mL, 3.2 mmol, 1.6 equiv), **S9** (846.8 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.55 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 12 h. The desired product **1t** (207.2 mg, 19%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.6 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.51 – 7.37 (m, 1H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.11 (m, 4H), 7.10 – 7.00 (m, 5H), 6.68 (d, *J* = 8.7 Hz, 4H), 4.68 (d, *J* = 9.9 Hz, 2H), 3.64 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.6, 169.2 (d, *J* = 9.4 Hz), 157.3, 143.2 (d, *J* = 6.7 Hz), 134.2, 132.9, 131.8, 129.5, 129.0, 128.7, 128.2, 122.1, 121.1 (d, *J* = 5.0 Hz), 114.8, 84.6, 83.2, 55.6, 35.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ –9.7.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{27}NO_7P$ $[M+H]^+$: 556.1520, found 556.1514.



S10

Dimethyl (3-phenylprop-2-yn-1-yl)phosphoramidate (S10)

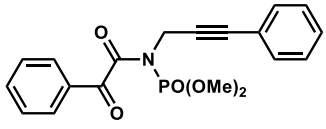
The general procedure A was followed. The reaction was performed with CuI (68.4 mg, 0.36 mmol, 3.6 mol %), $PdCl_2$ (44.0 mg, 0.25 mmol, 2.5 mol %), PPh_3 (131.0 mg, 0.50 mmol, 5 mol %), iodobenzene (2.24 g, 11.0 mmol, 1.1 equiv) and dimethyl prop-2-yn-1-ylphosphoramidate (1.63 g, 10.0 mmol, 1.0 equiv) in Et_3N (10 mL) and THF (10 mL) at room temperature for 20 h. The desired product **S10** (1.10 g, 46%) was obtained as a white solid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 1 / 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.33 – 7.26 (m, 3H), 3.91 (dd, *J* = 11.8, 6.6 Hz, 2H), 3.76 (d, *J* = 11.3 Hz, 6H), 3.25 (brs, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.52, 128.45, 122.7, 86.6 (d, *J* = 5.9 Hz), 83.3 (d, *J* = 5.2 Hz), 53.3, 31.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 10.6.

HRMS (ESI^+) *m/z* calc'd for $C_{11}H_{15}NO_3P$ $[M+H]^+$: 240.0790, found 240.0786.



1u

Dimethyl (2-oxo-2-phenylacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1u)

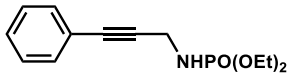
The general procedure C was followed. The reaction was performed with phenylglyoxylic acid (0.30 g, 2.0 mmol, 1.0 equiv), oxalyl chloride (0.20 mL, 2.4 mmol, 1.2 equiv), **S10** (478.4 mg, 2.0 mmol, 1.0 equiv), and Et_3N (0.3 mL) in EtOAc (2 mL) and toluene (2 mL) at room temperature for 12 h. The desired product **1u** (317.2 mg, 43%) was obtained as a colorless liquid after purification by silica gel chromatography. R_f = 0.3 (PE / EtOAc = 1 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.65 – 7.55 (m, 1H), 7.53 – 7.40 (m, 4H), 7.39 – 7.27 (m, 3H), 4.60 (d, *J* = 9.7 Hz, 2H), 3.82 (d, *J* = 11.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 169.5 (d, *J* = 11.4 Hz), 134.2, 133.1, 131.8, 129.4, 128.84, 128.77, 128.4, 122.2, 83.7, 83.5, 54.6 (d, *J* = 4.9 Hz), 34.0.

^{31}P NMR (162 MHz, $CDCl_3$) δ 2.0.

HRMS (ESI^+) *m/z* calc'd for $C_{19}H_{19}NO_5P$ $[M+H]^+$: 372.0995, found 372.0989.



S11

Diethyl (3-phenylprop-2-yn-1-yl)phosphoramidate (S11)

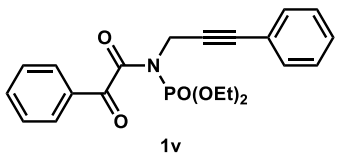
The general procedure A was followed. The reaction was performed with CuI (34.2 mg, 0.18 mmol, 3.6 mol %), $PdCl_2$ (22.0 mg, 0.13 mmol, 2.5 mol %), PPh_3 (65.5 mg, 0.25 mmol, 5 mol %), iodobenzene (1.12 g, 5.5 mmol, 1.1 equiv) and diethyl prop-2-yn-1-ylphosphoramidate (1.46 g, 5.0 mmol, 1.0 equiv) in Et_3N (5 mL) and THF (5 mL) at room temperature for 20 h. The desired product **S11** (1.98 g, 90%) was obtained as a brown liquid after purification by silica gel chromatography. R_f = 0.5 (DCM / EtOAc = 1 / 2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 4.13 (p, *J* = 7.2 Hz, 4H), 3.93 (dd, *J* = 11.4, 6.8 Hz, 2H), 2.95 (brs, 1H), 1.35 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.54, 128.49, 122.8, 86.0, 83.3, 62.7 (d, *J* = 5.0 Hz), 31.6, 16.3 (d, *J* = 7.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 7.8.

HRMS (ESI^+) *m/z* calc'd for $C_{13}H_{19}NO_3P$ $[M+H]^+$: 268.1103, found 268.1103.



1v

Diethyl (2-oxo-2-phenylacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1v)

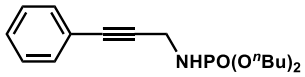
The general procedure C was followed. The reaction was performed with phenylglyoxylic acid (0.60 g, 4.0 mmol, 1.0 equiv), oxalyl chloride (0.4 mL, 4.8 mmol, 1.2 equiv), **S11** (1.07 g, 4.0 mmol, 1.0 equiv), and Et_3N (1.0 mL) in EtOAc (10 mL) and toluene (10 mL) at room temperature for 12 h. The desired product **1v** (660.0 mg, 41%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 2H), 7.66 – 7.55 (m, 1H), 7.55 – 7.40 (m, 4H), 7.38 – 7.28 (m, 3H), 4.60 (d, *J* = 9.5 Hz, 2H), 4.19 (p, *J* = 7.2 Hz, 4H), 1.35 – 1.27 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 169.7 (d, *J* = 11.4 Hz), 134.2, 133.4, 131.9, 129.5, 128.9, 128.8, 128.5, 122.5, 83.7, 83.6, 64.8 (d, *J* = 5.0 Hz), 34.1, 16.0 (d, *J* = 7.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –1.1.

HRMS (ESI^+) *m/z* calc'd for $C_{21}H_{23}NO_5P$ $[M+H]^+$: 400.1308, found 400.1317.



S12

Dibutyl (3-phenylprop-2-yn-1-yl)phosphoramidate (S12)

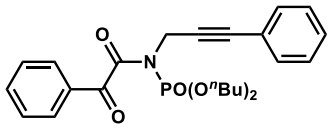
The general procedure A was followed. The reaction was performed with CuI (34.1 mg, 0.18 mmol, 3.6 mol %), $PdCl_2$ (22.0 mg, 0.13 mmol, 2.5 mol %), PPh_3 (65.4 mg, 0.25 mmol, 5 mol %), iodobenzene (1.12 g, 5.5 mmol, 1.1 equiv) and dibutyl prop-2-yn-1-ylphosphoramidate (1.23 g, 5.0 mmol, 1.0 equiv) in Et_3N (5 mL) and THF (5 mL) at room temperature for 20 h. The desired product **S12** (1.25 g, 77%) was obtained as a brown liquid after purification by silica gel chromatography. R_f = 0.5 (DCM / EtOAc = 2 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 4.05 (q, *J* = 6.6 Hz, 4H), 3.91 (dd, *J* = 11.4, 6.9 Hz, 2H), 3.11 (brs, 1H), 1.67 (dq, *J* = 8.7, 6.7 Hz, 4H), 1.47 – 1.33 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ131.7, 128.5, 128.4, 122.8, 86.8 (d, *J* = 6.3 Hz), 83.2, 66.5 (d, *J* = 5.4 Hz), 32.5 (d, *J* = 7.2 Hz), 31.9, 18.9, 13.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ 8.0.

HRMS (ESI^+) *m/z* calc'd for $C_{17}H_{27}NO_3P$ $[M+H]^+$: 324.1729, found 324.1733.



1w

Dibutyl (2-oxo-2-phenylacetyl)(3-phenylprop-2-yn-1-yl)phosphoramidate (1w)

The general procedure C was followed. The reaction was performed with phenylglyoxylic acid (787.5 mg, 5.3 mmol, 1.5 equiv), oxalyl chloride (0.6 mL, 7.0 mmol, 2.0 equiv), **S12** (1.13 g, 3.5 mmol, 1.0 equiv), and Et_3N (3.5 mL) in DCM (15 mL) at room temperature for 12 h. The desired product **1w** (608.6 mg, 42%) was obtained as a yellow liquid after purification by silica gel chromatography. R_f = 0.5 (PE / EtOAc = 5 / 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.62 – 7.55 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.39 (m, 4H), 7.35 – 7.29 (m, 3H), 4.59 (d, *J* = 9.5 Hz, 2H), 4.11 (q, *J* = 6.8 Hz, 4H), 1.62 (dq, *J* = 9.0, 6.4 Hz, 4H), 1.34 (h, *J* = 7.4 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

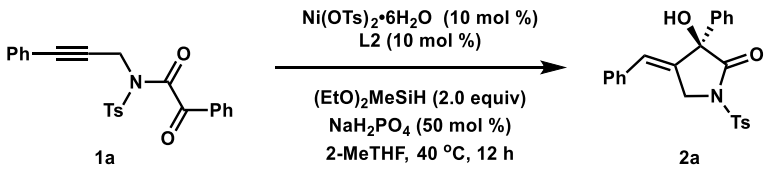
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 169.6 (d, *J* = 11.3 Hz), 134.2, 133.3, 131.8, 129.4, 128.8, 128.7, 128.4, 122.4, 83.7, 83.5, 68.3 (d, *J* = 5.3 Hz), 34.0, 32.0 (d, *J* = 7.1 Hz), 18.6, 13.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –0.8.

HRMS (ESI^+) *m/z* calc'd for $C_{25}H_{31}NO_5P$ $[M+H]^+$: 456.1934, found 456.1928.

IV. General Procedures for Synthesis of α-Hydroxy-γ-Lactams by Ni-catalyzed *Syn*-Hydrometalative Cyclization of Alkyne-tethered Ketoamides and Characterization Data

*Please note that the absolute configuration was determined only for the lactam **2b** via X-ray analysis (vide infra). The absolute configuration for all other products **2** was inferred by analogy.*



(*R*,*E*)-4-Benzylidene-3-hydroxy-3-phenyl-1-tosylpyrrolidin-2-one (2a)

General procedure: To a Schlenk tube were added Ni(OTs)$_2$•6H$_2$O (5.1 mg, 0.01 mmol, 10 mol %), **L2** (3.1 mg, 0.01 mmol, 10 mol %), and 0.5 mL of 2-MeTHF under Ar. The resultant solution was stirred at room temperature for 20 min, then **1a** (41.7 mg, 0.1 mmol, 1.0 equiv),

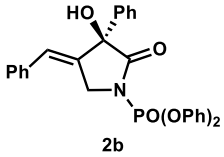
NaH_2PO_4 (6.0 mg, 0.5 equiv), $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) and another 0.5 mL of 2-MeTHF were added. The tube was sealed and the mixture was stirred at 40 °C for 12 h. After the reaction was cooled to room temperature, the mixture was filtered through a celite pad and the solid was washed with EtOAc (5 mL × 3). After the collected solvents were removed under reduced pressure, the reside was purified by silica gel column chromatography to provide **2a** (23.5 mg, 56%) as a white solid. er = 91 : 9. $[\alpha]_D^{25}$ = +7.12 (c 1.6, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 5 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.20 (m, 10H), 7.20 – 7.12 (m, 2H), 6.84 (d, *J* = 2.4 Hz, 1H), 4.68 – 4.56 (m, 2H) 3.13 (brs, 1H), 2.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 145.9, 139.6, 134.69, 134.67, 132.7, 130.0, 129.12, 129.09, 129.0, 128.9, 128.5, 128.3, 127.9, 125.5, 79.7, 48.6, 21.8.

HRMS (ESI^+) *m/z* calc'd for $C_{24}H_{22}O_4NS$ $[M+H]^+$: 420.1264, found 420.1271.

HPLC conditions: hexane/2-propanol 60 : 40, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 7.0 min, t_r (minor) = 10.4 min.



2b

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2b)

Following the general procedure, the reaction was performed with **1b** (49.5 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.01 mmol, 10 mol %), **L2** (3.1 mg, 0.01 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2b** was obtained in 73% yield (36.0 mg) as a white solid. er = 94.5 :5.5. $[\alpha]_D^{25}$ = +56.94 (c 0.2, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

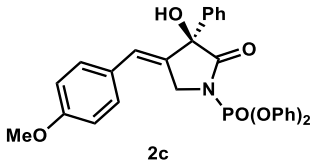
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 12H), 7.25 – 7.15 (m, 6H), 7.13 – 7.08 (m, 2H), 6.86 (dd, *J* = 2.7, 1.6 Hz, 1H), 4.68 (dt, *J* = 14.5, 1.6 Hz, 1H), 4.51 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.28 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 149.9 (d, *J* = 7.2 Hz), 149.6 (d, *J* = 6.7 Hz), 140.0, 134.8, 134.4 (d, *J* = 8.6 Hz), 130.1, 130.0, 129.0, 128.94, 128.92, 128.88, 128.4, 128.0, 126.1 (d, *J* = 1.7 Hz), 126.0 (d, *J* = 1.5 Hz), 125.7, 120.7 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.8 Hz), 79.5 (d, *J* = 8.8 Hz), 49.6 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.5.

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{25}O_5NP$ $[M+H]^+$: 498.1465, found 498.1473.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 6.4 min, t_r (minor) = 7.5 min.



2c

Diphenyl (*R*,*E*)-(3-hydroxy-4-(4-methoxybenzylidene)-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2c)

Following the general procedure, the reaction was performed with **1c** (103.4 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.1 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2c** was obtained in 62% yield (64.1 mg) as a colorless liquid. er = 93 : 7. $[\alpha]_D^{25}$ = +42.20 (c 0.5, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

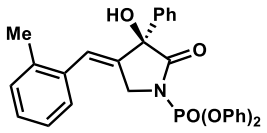
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.16 (m, 9H), 7.14 – 7.07 (m, 3H), 7.07 – 6.96 (m, 5H), 6.78 (d, *J* = 8.6 Hz, 2H), 6.66 (dd, *J* = 1.5, 2.7 Hz, 1H), 4.58 (dt, *J* = 14.4, 1.5 Hz, 1H), 4.40 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.71 (s, 3H), 3.43 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 159.4, 149.7 (d, *J* = 7.0 Hz), 149.5 (d, *J* = 6.6 Hz), 140.1, 131.9 (d, *J* = 8.5 Hz), 130.2, 129.9, 129.8, 128.8, 128.6, 127.5, 127.4, 125.84, 125.76, 125.6, 120.5 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 4.7 Hz), 114.1, 79.3 (d, *J* = 8.8 Hz), 55.3, 49.6 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.6.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_6P$ $[M+H]^+$: 528.1571, found 528.1572.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 10.5 min, t_r (minor) = 12.9 min.



2d

Diphenyl (*R*,*E*)-(3-hydroxy-4-(2-methylbenzylidene)-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2d)

Following the general procedure, the reaction was performed with **1d** (81.5 mg, 0.2 mmol, 1.0

equiv), $Ni(OTs)_2•6H_2O$ (10.1 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2d** was obtained in 75% yield (63.0 mg) as a yellow liquid. er = 92.5 : 7.5. $[\alpha]_D^{25}$ = +44.65 (c 2.7, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

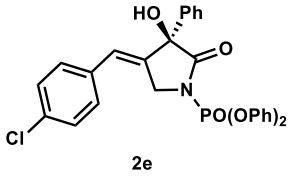
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.25 (m, 7H), 7.25 – 7.14 (m, 7H), 7.13 – 7.06 (m, 2H), 7.04 – 6.97 (m, 2H), 4.49 (d, *J* = 14.3 Hz, 1H), 4.37 (dd, *J* = 14.3, 2.6 Hz, 1H), 3.26 (brs, 1H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5 (d, *J* = 1.8 Hz), 149.9 (d, *J* = 7.0 Hz), 149.6 (d, *J* = 6.7 Hz), 139.7, 136.9, 135.1 (d, *J* = 8.4 Hz), 133.6, 130.5, 130.0, 129.9, 129.0, 128.9, 128.5, 128.2, 126.4, 126.1, 126.0 (d, *J* = 1.5 Hz), 125.9, 125.8, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.7 Hz), 79.4 (d, *J* = 8.8 Hz), 49.2 (d, *J* = 5.2 Hz), 19.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_5P$ $[M+H]^+$: 512.1621, found 512.1622.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 7.5 min, t_r (minor) = 9.1 min.



2e

Diphenyl (*R*,*E*)-(4-(4-chlorobenzylidene)-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2e)

Following the general procedure, the reaction was performed with **1e** (52.5 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2•6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 1.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2e** was obtained in 65% yield (34.2 mg) as a yellow liquid. er = 94 : 6. $[\alpha]_D^{25}$ = +40.82 (c 0.6, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 11H), 7.24 – 7.16 (m, 4H), 7.14 – 7.08 (m, 4H), 6.80 (d, *J* = 2.5 Hz, 1H), 4.62 (d, *J* = 14.5 Hz, 1H), 4.47 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.44 (brs, 1H).

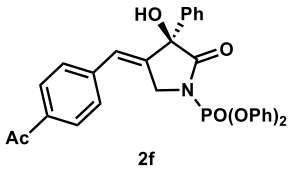
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1 (d, *J* = 1.6 Hz), 149.9 (d, *J* = 7.1 Hz), 149.6 (d, *J* = 6.6 Hz), 139.9, 135.2 (d, *J* = 8.5 Hz), 134.3, 133.2, 130.12, 130.08, 130.0, 129.1, 129.0, 126.8,

126.1 (d, *J* = 1.7 Hz), 126.0, 125.6, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.8 Hz), 79.5 (d, *J* = 9.0 Hz), 49.5 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.6.

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{24}NO_5PCl$ $[M+H]^+$: 532.1075, found 532.1069.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 8.3 min, t_r (minor) = 10.7 min.



2f

Diphenyl (*R*,*E*)-(4-(4-acetylbenzylidene)-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2f)

Following the general procedure, the reaction was performed with **1f** (103.8 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.2 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2f** was obtained in 67% yield (41.8 mg) as a colorless liquid. er = 94.5 : 5.5. $[\alpha]_D^{25}$ = +45.96 (c 1.1, $CHCl_3$). R_f = 0.4 (PE : EtOAc = 2 : 1).

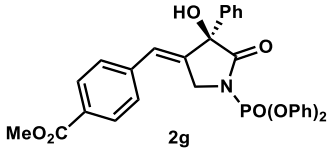
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.30 – 7.17 (m, 11H), 7.16 – 7.13 (m, 2H), 7.13 – 7.08 (m, 2H), 7.07 – 7.03 (m, 2H), 6.83 – 6.80 (m, 1H), 4.58 (dt, *J* = 14.7, 1.6 Hz, 1H), 4.44 (dd, *J* = 14.6, 2.8 Hz, 1H), 2.81 (brs, 1H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 176.0, 149.8 (d, *J* = 7.0 Hz), 149.6 (d, *J* = 6.6 Hz), 139.8, 139.3, 137.3 (d, *J* = 8.6 Hz), 136.4, 130.1, 130.0, 129.14, 129.08, 129.0, 128.9, 126.9, 126.12, 126.06, 125.5, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.8 Hz), 79.5 (d, *J* = 8.9 Hz), 49.5 (d, *J* = 5.5 Hz), 26.8.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.9.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{27}NO_6P$ $[M+H]^+$: 540.1571, found 540.1581.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 19.3 min, t_r (minor) = 24.9 min.



2g

Methyl (*R*,*E*)-4-((1-(diphenoxyphosphoryl)-4-hydroxy-5-oxo-4-phenylpyrrolidin-3-ylidene)methyl)benzoate (2g)

Following the general procedure, the reaction was performed with **1g** (52.3 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2g** was obtained in 32% yield (17.0 mg) as a yellow liquid. er = 91.5 : 8.5. $[\alpha]_D^{25}$ = +37.18 (c 1.0, $CHCl_3$). R_f = 0.7 (PE : EtOAc = 2 : 1).

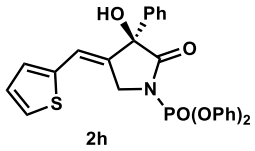
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.25 (m, 12H), 7.25 – 7.17 (m, 3H), 7.16 – 7.08 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 4.66 (dt, *J* = 14.7, 1.6 Hz, 1H), 4.52 (dd, *J* = 14.7, 2.8 Hz, 1H), 3.92 (s, 3H), 3.41 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 166.7, 149.9 (d, *J* = 6.9 Hz), 149.6 (d, *J* = 6.7 Hz), 139.8, 139.1, 137.0 (d, *J* = 8.6 Hz), 130.10, 130.08, 130.0, 129.7, 129.14, 129.07, 128.8, 127.0, 126.1, 126.0, 125.5, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.7 Hz), 79.5 (d, *J* = 9.1 Hz), 52.4, 49.5 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{27}NO_7P$ $[M+H]^+$: 556.1520, found 556.1516.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 12.3 min, t_r (minor) = 15.8 min.



2h

Diphenyl (*R*,*E*)-(3-hydroxy-2-oxo-3-phenyl-4-(thiophen-2-ylmethylene)pyrrolidin-1-yl)phosphonate (2h)

Following the general procedure, the reaction was performed with **1h** (48.7 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.1 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2h** was obtained in 45% yield (21.8 mg) as a yellow liquid. er = 95 : 5. $[\alpha]_D^{25}$ = +42.21 (c 1.0, $CHCl_3$). R_f = 0.7 (PE : EtOAc = 2 : 1).

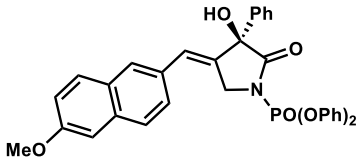
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.25 – 7.15 (m, 9H), 7.14 – 7.09 (m, 2H), 7.06 – 7.02 (m, 1H), 6.99 – 6.96 (m, 1H), 6.00 (s, 1H), 4.53 (AB, *J* = 19.6 Hz 1H), 4.28 (BA, *J* = 19.6 Hz, 1H), 3.22 (brs, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (d, *J* = 2.2 Hz), 157.2 (d, *J* = 8.5 Hz), 150.12 (d, *J* = 4.7 Hz), 150.05 (d, *J* = 4.7 Hz), 144.3, 132.7 (d, *J* = 9.8 Hz), 130.00, 129.98, 129.96, 129.5, 129.2, 129.1, 128.7, 127.2, 126.1, 125.91, 125.87, 125.0, 120.8 (d, *J* = 4.5 Hz), 66.3, 50.1 (d, *J* = 6.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –11.9.

HRMS (ESI^+) *m/z* calc'd for $C_{27}H_{23}NO_5PS$ $[M+H]^+$: 504.1029, found 504.1027.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 8.0 min, t_r (minor) = 11.9 min.



2i

Diphenyl (*R*,*E*)-(3-hydroxy-4-((6-methoxynaphthalen-2-yl)methylene)-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2i)

Following the general procedure, the reaction was performed with **1i** (57.4 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2i** was obtained in 48% yield (27.8 mg) as a yellow liquid. er = 92 : 8. $[\alpha]_D^{25}$ = +57.30 (c 1.4, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 2 : 1).

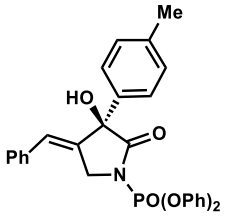
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 3.2 Hz, 1H), 7.60 (d, *J* = 2.7 Hz, 1H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.25 – 7.19 (m, 9H), 7.16 – 7.12 (m, 2H), 7.11 – 7.00 (m, 5H), 6.86 (d, *J* = 2.1 Hz, 1H), 4.69 (dt, *J* = 14.5, 1.6 Hz, 1H), 4.53 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.84 (s, 3H), 3.41 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 158.5, 149.9 (d, *J* = 7.0 Hz), 149.7 (d, *J* = 6.6 Hz), 140.2, 134.2, 133.6 (d, *J* = 8.6 Hz), 130.2, 130.04, 129.98, 129.9, 129.0, 128.9, 128.8, 128.3, 127.3, 126.9, 126.03, 125.96, 125.7, 120.6 (d, *J* = 4.7 Hz), 120.5 (d, *J* = 4.8 Hz), 119.6, 105.8, 79.6 (d, *J* = 9.0 Hz), 55.5, 49.8 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

HRMS (ESI^+) *m/z* calc'd for $C_{34}H_{29}NO_6P$ $[M+H]^+$: 578.1727, found 578.1727.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 12.3 min, t_r (minor) = 14.2 min.



2j

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-(*p*-tolyl)pyrrolidin-1-yl)phosphonate (2j)

Following the general procedure, the reaction was performed with **1j** (101.5 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.1 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2j** was obtained in 74% yield (74.6 mg) as a white liquid. er = 94 : 6. $[\alpha]_D^{25}$ = +66.73 (c 1.0, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

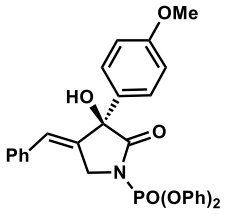
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 2H), 7.23 – 7.16 (m, 6H), 7.16 – 7.06 (m, 7H), 7.04 – 6.94 (m, 4H), 6.79 – 6.72 (m, 1H), 4.58 (d, *J* = 14.4 Hz, 1H), 4.40 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.31 (brs, 1H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 149.9 (d, *J* = 6.9 Hz), 149.7 (d, *J* = 6.7 Hz), 138.8, 137.0, 134.8, 134.6 (d, *J* = 8.1 Hz), 130.0, 129.9, 129.7, 128.9, 128.8, 128.3, 127.7, 126.0 (d, *J* = 1.5 Hz), 125.9 (d, *J* = 1.5 Hz), 125.7, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.7 Hz), 79.3 (d, *J* = 8.9 Hz), 49.5 (d, *J* = 5.3 Hz), 21.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_5P$ $[M+H]^+$: 512.1621, found 512.1623.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 7.4 min, t_r (minor) = 9.2 min.



2k

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-3-(4-methoxyphenyl)-2-oxopyrrolidin-1-yl)phosphonate (2k)

Following the general procedure, the reaction was performed with **1k** (105.4 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.1 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0

mL of 2-MeTHF at 40 °C for 12 h. The desired product **2k** was obtained in 73% yield (76.8 mg) as a white liquid. er = 95.5 : 4.5. $[\alpha]_D^{25}$ = +56.49 (c 1.0, $CHCl_3$). R_f = 0.7 (PE : EtOAc = 2 : 1).

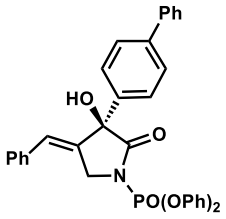
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 9H), 7.14 – 7.04 (m, 6H), 7.03 – 6.93 (m, 2H), 6.78 (s, 1H), 6.76 – 6.69 (m, 2H), 4.56 (dt, *J* = 14.4, 1.5 Hz, 1H), 4.38 (dd, *J* = 14.4, 2.7 Hz, 1H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 160.1, 149.9 (d, *J* = 7.1 Hz), 149.6 (d, *J* = 6.6 Hz), 134.8, 134.5 (d, *J* = 8.4 Hz), 131.8, 130.0, 129.9, 128.91, 128.89, 128.3, 127.7, 127.4, 126.0, 125.9, 120.6 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.7 Hz), 114.3, 79.0 (d, *J* = 9.0 Hz), 55.5, 49.5 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_6P$ $[M+H]^+$: 528.1571, found 528.1566.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 10.6 min, t_r (minor) = 13.2 min.



2l

Diphenyl (*R*,*E*)-(3-([1,1'-biphenyl]-4-yl)-4-benzylidene-3-hydroxy-2-oxopyrrolidin-1-yl)phosphonate (2l)

Following the general procedure, the reaction was performed with **1l** (58.1 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2l** was obtained in 61% yield (35.2 mg) as a colorless liquid. er = 94.5 : 5.5. $[\alpha]_D^{25}$ = +41.85 (c 1.9, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.44 – 7.34 (m, 5H), 7.33 – 7.26 (m, 5H), 7.25 – 7.15 (m, 5H), 7.15 – 7. (m, 3H), 6.90 (s, 1H), 4.71 (d, *J* = 14.5 Hz, 1H), 4.55 (dd, *J* = 14.5, 2.7 Hz, 1H).

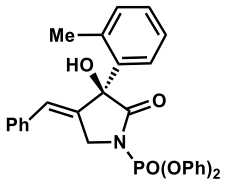
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 149.9 (d, *J* = 7.0 Hz), 149.6 (d, *J* = 6.4 Hz), 141.8, 140.4, 138.9, 134.8, 134.4 (d, *J* = 8.5 Hz), 130.1, 129.9, 129.0, 128.94, 128.89, 128.4, 128.1, 127.8,

127.7, 127.2, 126.2, 126.0, 125.9, 120.7 (d, *J* = 4.6 Hz), 120.5 (d, *J* = 4.8 Hz), 79.3 (d, *J* = 8.8 Hz), 49.7 (d, *J* = 5.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.5.

HRMS (ESI^+) *m/z* calc'd for $C_{35}H_{29}NO_5P$ $[M+H]^+$: 574.1778, found 574.1772.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 11.8 min, t_r (minor) = 21.4 min.



2m

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-(*o*-tolyl)pyrrolidin-1-yl)phosphonate (2m)

Following the general procedure, the reaction was performed with **1m** (49.8 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.1 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2m** was obtained in 84% yield (42.8 mg) as a colorless liquid. er = 89.5 : 10.5. $[\alpha]_D^{25}$ = +46.35 (c 0.7, $CHCl_3$). R_f = 0.7 (PE : EtOAc = 2 : 1).

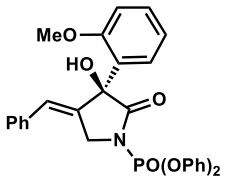
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.29 – 7.21 (m, 10H), 7.20 – 7.09 (m, 5H), 7.06 – 6.99 (m, 3H), 6.20 (dd, *J* = 2.6, 2.3 Hz, 1H), 4.78 (dd, *J* = 14.7, 2.6 Hz, 1H), 4.67 (dd, *J* = 14.8, 2.3 Hz, 1H) 3.12 (brs, 1H), 1.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 150.0 (d, *J* = 6.6 Hz), 149.8 (d, *J* = 7.0 Hz), 136.9, 135.5, 134.8, 134.4 (d, *J* = 9.4 Hz), 131.9, 130.1, 130.0, 129.6, 129.0, 128.8, 128.5, 126.5, 126.1, 126.0, 125.9, 120.8 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 5.0 Hz), 80.7 (d, *J* = 8.5 Hz), 50.6 (d, *J* = 5.8 Hz), 20.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.2.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_5P$ $[M+H]^+$: 512.1621, found 512.1620.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 6.9 min, t_r (minor) = 8.5 min.



2n

Diphenyl (*S*,*E*)-(4-benzylidene-3-hydroxy-3-(2-methoxyphenyl)-2-oxopyrrolidin-1-yl)phosphonate (2n)

Following the general procedure, the reaction was performed with **1n** (53.2 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.3 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2n** was obtained in 70% yield (36.4 mg) as a yellow liquid. er = 97 : 3. $[\alpha]_D^{25}$ = +37.33 (c 0.7, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

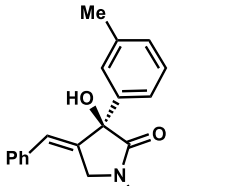
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 – 7.27 (m, 11H), 7.26 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 7.17 – 7.12 (m, 2H), 7.07 – 7.02 (m, 1H), 6.82 (dd, *J* = 8.1, 1.0 Hz, 1H), 6.35 (q, *J* = 2.3 Hz, 1H), 4.83 (d, *J* = 2.6 Hz, 2H), 3.50 (s, 3H), 3.27 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9 (d, *J* = 1.5 Hz), 155.8, 150.3 (d, *J* = 7.0 Hz), 150.0 (d, *J* = 6.9 Hz), 135.8 (d, *J* = 9.8 Hz), 135.3, 130.03, 129.96, 129.9, 129.6, 128.9, 128.8, 128.5, 128.1, 126.3, 126.0 (d, *J* = 1.5 Hz), 125.8 (d, *J* = 1.4 Hz), 121.0, 120.8 (d, *J* = 4.4 Hz), 120.7 (d, *J* = 4.4 Hz), 111.3, 78.7 (d, *J* = 9.1 Hz), 55.6, 50.9 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –11.9.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_6P$ $[M+H]^+$: 528.1571, found 528.1560.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 280 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 10.3 min, t_r (minor) = 8.8 min.



2o

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-(*m*-tolyl)pyrrolidin-1-yl)phosphonate (2o)

Following the general procedure, the reaction was performed with **1o** (50.4 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %),

NaH_2PO_4 (6.3 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2o** was obtained in 71% yield (35.7 mg) as a yellow liquid. er = 94 : 6. $[\alpha]_D^{25}$ = +32.94 (c 0.5, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

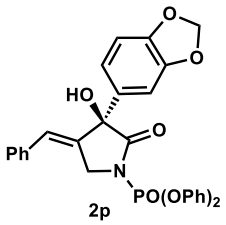
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 8H), 7.13 – 6.96 (m, 11H), 6.75 (s, 1H), 4.58 (d, *J* = 14.4 Hz, 1H), 4.43 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.44 (brs, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3 (d, *J* = 1.5 Hz), 149.9 (d, *J* = 7.0 Hz), 149.6 (d, *J* = 6.7 Hz), 139.9, 138.8, 134.8, 134.6 (d, *J* = 8.5 Hz), 130.0, 129.9, 129.7, 128.91, 128.86, 128.8, 128.3, 127.9, 126.3, 126.0 (d, *J* = 1.6 Hz), 125.9, 122.8, 120.5 (d, *J* = 4.8 Hz), 120.5 (d, *J* = 4.8 Hz), 79.4 (d, *J* = 8.9 Hz), 49.6 (d, *J* = 5.4 Hz), 21.7.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.4.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{27}NO_5P$ $[M+H]^+$: 512.1621, found 512.1623.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 6.6 min, t_r (minor) = 8.5 min.



2p

Diphenyl (*R*,*E*)-(3-(benzo[*d*][1,3]dioxol-5-yl)-4-benzylidene-3-hydroxy-2-oxopyrrolidin-1-yl)phosphonate (2p)

Following the general procedure, the reaction was performed with **1p** (53.8 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2p** was obtained in 66% yield (35.4 mg) as a colorless liquid. er = 93.5 : 6.5. $[\alpha]_D^{25}$ = +36.88 (c 0.5, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.15 (m, 6H), 7.16 – 7.01 (m, 7H), 6.86 (d, *J* = 1.9 Hz, 1H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.66 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.56 (d, *J* = 8.1 Hz, 1H), 5.87 (s, 2H), 4.56 (d, *J* = 14.4 Hz, 1H), 4.39 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.38 (brs, 1H).

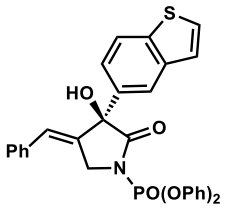
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1 (d, *J* = 1.5 Hz), 149.9 (d, *J* = 7.2 Hz), 149.6 (d, *J* = 6.8 Hz), 148.3, 148.2, 134.7, 134.4 (d, *J* = 8.4 Hz), 133.7, 130.0 (d, *J* = 1.1 Hz), 129.9 (d, *J* = 1.1

Hz), 128.91, 128.87, 128.4, 128.0, 126.0 (d, *J* = 1.5 Hz), 125.9 (d, *J* = 1.6 Hz), 120.6 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 5.0 Hz), 119.6, 108.3, 106.7, 101.5, 79.1 (d, *J* = 8.8 Hz), 49.5 (d, *J* = 5.3 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.5.

HRMS (ESI^+) *m/z* calc'd for $C_{30}H_{24}NO_7PNa$ $[M+Na]^+$: 564.1183, found 564.1181.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 10.4 min, t_r (minor) = 13.2 min.



2q

Diphenyl (*R*,*E*)-(3-(benzo[*b*]thiophen-5-yl)-4-benzylidene-3-hydroxy-2-oxopyrrolidin-1-yl)phosphonate (2q)

Following the general procedure, the reaction was performed with **1q** (55.9 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2q** was obtained in 68% yield (37.9 mg) as a colorless liquid. er = 95.5 : 4.5. $[\alpha]_D^{25}$ = +30.79 (c 1.1, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 2 : 1).

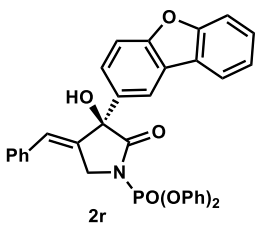
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 5.5 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.22 – 7.15 (m, 5H), 7.14 – 7.08 (m, 3H), 7.08 – 7.03 (m, 1H), 6.97 – 6.87 (m, 5H), 6.79 (s, 1H), 4.61 (d, *J* = 14.5 Hz, 1H), 4.46 (dd, *J* = 14.5, 2.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 149.8 (d, *J* = 7.1 Hz), 149.5 (d, *J* = 6.5 Hz), 140.2, 139.8, 136.3, 134.8, 134.6 (d, *J* = 8.5 Hz), 130.0, 129.8, 128.92, 128.86, 128.3, 128.2, 127.5, 120.6 (d, *J* = 4.5 Hz), 124.3, 123.1, 122.0, 121.0, 120.6 (d, *J* = 4.5 Hz), 120.3 (d, *J* = 4.8 Hz), 79.54 (d, *J* = 8.8 Hz), 49.69 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.5.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{25}NO_5PS$ $[M+H]^+$: 554.1186, found 554.1187.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 9.6 min, t_r (minor) = 12.0 min.



2r

Diphenyl (*R*,*E*)-(4-benzylidene-3-(dibenzo[*b*,*d*]furan-2-yl)-3-hydroxy-2-oxopyrrolidin-1-yl)phosphonate (2r)

Following the general procedure, the reaction was performed with **1r** (57.4 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.1 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2r** was obtained in 52% yield (29.8 mg) as a yellow liquid. er = 95 : 5. $[\alpha]_D^{25}$ = +48.03 (c 1.6, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 2 : 1).

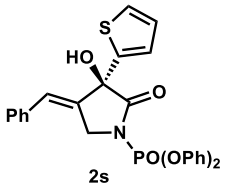
^{1}H NMR (400 MHz, $CDCl_3$) 7.99 (d, *J* = 1.8 Hz, 1H), 7.83 – 7.76 (m, 1H), 7.55 – 7.48 (m, 1H), 7.45 – 7.36 (m, 2H), 7.34 – 7.29 (m, 3H), 7.28 – 7.22 (m, 5H), 7.20 – 7.15 (m, 4H), 7.15 – 7.09 (m, 1H), 7.03 – 6.93 (m, 4H), 6.93 – 6.84 (m, 2H), 4.67 (dt, *J* = 14.7, 1.5 Hz, 1H), 4.52 (dd, *J* = 14.5, 2.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 156.8, 156.3, 149.9 (d, *J* = 7.0 Hz), 149.6 (d, *J* = 6.5 Hz), 134.8, 134.60 (d, *J* = 8.7 Hz), 134.58, 130.1, 129.8, 129.0, 128.9, 128.5, 127.8, 126.1, 125.8, 125.1, 124.9, 123.9, 123.1, 121.1, 120.6 (d, *J* = 4.7 Hz), 120.3 (d, *J* = 4.8 Hz), 118.5, 112.0, 111.9, 79.5 (d, *J* = 9.0 Hz), 49.7 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.6.

HRMS (ESI^+) *m/z* calc'd for $C_{35}H_{27}NO_6P$ $[M+H]^+$: 588.1571, found 588.1566.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 9.1 min, t_r (minor) = 14.7 min.



2s

Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-(thiophen-2-yl)pyrrolidin-1-yl)phosphonate (2s)

Following the general procedure, the reaction was performed with **1s** (55.1 mg, 0.1 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.010 mmol, 10 mol %), **L2** (3.2 mg, 0.010 mmol, 10 mol %), NaH_2PO_4 (6.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) in 1.0 mL of 2-

MeTHF at 40 °C for 12 h. The desired product **2s** was obtained in 69% yield (37.7 mg) as a white solid. er = 87.5 : 12.5. $[\alpha]_D^{25}$ = +38.71 (c 0.8, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 2 : 1).

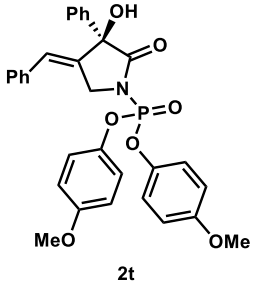
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 8H), 7.24 – 7.09 (m, 6H), 7.10 – 7.05 (m, 2H), 6.99 (s, 1H), 6.96 – 6.88 (m, 2H), 4.74 – 4.60 (m, 1H), 4.52 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.71 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 149.8 (d, *J* = 7.0 Hz), 149.5 (d, *J* = 6.7 Hz), 143.5, 134.6, 133.8 (d, *J* = 8.7 Hz), 130.0, 129.9, 129.0, 128.9, 128.5, 127.9, 127.5, 127.4, 126.3, 126.0, 125.9, 120.6 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 4.7 Hz), 76.7 (d, *J* = 9.3 Hz), 49.3 (d, *J* = 5.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.6.

HRMS (ESI^+) *m/z* calc'd for $C_{27}H_{23}NO_5PS$ $[M+H]^+$: 504.1035, found 504.1035.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 7.5 min, t_r (minor) = 8.4 min.



2t

Bis(4-methoxyphenyl) (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2t)

Following the general procedure, the reaction was performed with **1t** (110.7 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.2 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2t** was obtained in 80% yield (88.1 mg) as a colorless liquid. er = 94 : 6. $[\alpha]_D^{25}$ = +56.61 (c 2.9, $CHCl_3$). R_f = 0.6 (PE : EtOAc = 2 : 1).

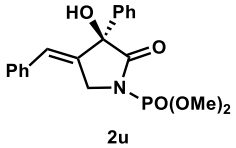
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 8H), 7.22 – 7.14 (m, 4H), 7.03 – 6.95 (m, 2H), 6.82 (s, 1H), 6.81 – 6.74 (m, 2H), 6.71 – 6.63 (m, 2H), 4.67 (d, *J* = 14.5 Hz, 1H), 4.46 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 3.69 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 157.4, 157.3, 143.3 (d, *J* = 7.1 Hz), 143.1 (d, *J* = 6.8 Hz), 140.1, 134.8, 134.6 (d, *J* = 8.3 Hz), 128.91, 128.90, 128.8, 128.3, 128.0, 125.8, 121.6, 121.5 (d, *J* = 4.4 Hz), 121.4 (d, *J* = 4.5 Hz), 114.9, 114.8, 79.4 (d, *J* = 8.8 Hz), 55.7, 49.7 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –11.4.

HRMS (ESI^+) *m/z* calc'd for $C_{31}H_{29}NO_7P$ $[M+H]^+$: 558.1676, found 558.1677.

HPLC conditions: hexane/2-propanol 90 : 10, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 13.8 min, t_r (minor) = 15.4 min.



2u

Dimethyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2u)

Following the general procedure, the reaction was performed with **1u** (74.3 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.2 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2u** was obtained in 50% yield (37.2 mg) as a yellow liquid. er = 94.5 : 5.5. $[\alpha]_D^{25}$ = +44.30 (c 0.6, $CHCl_3$). R_f = 0.6 (DCM : EtOAc = 2 : 1).

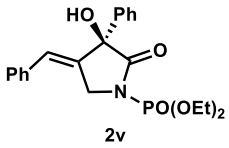
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 2H), 7.33 – 7.21 (m, 5H), 7.19 – 7.13 (m, 3H), 6.83 (d, *J* = 2.0 Hz, 1H), 4.59 (dt, *J* = 14.5, 1.4 Hz, 1H), 4.47 (dd, *J* = 14.5, 2.7 Hz, 1H), 3.88 (brs, 1H), 3.74 (d, *J* = 11.7 Hz, 3H), 3.67 (d, *J* = 11.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 140.3, 135.1, 135.0, 129.0, 128.93, 128.92, 128.85, 128.2, 127.6, 125.7, 79.4 (d, *J* = 8.7 Hz), 54.9 (d, *J* = 6.0 Hz), 54.7 (d, *J* = 6.1 Hz), 49.1 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –0.7.

HRMS (ESI^+) *m/z* calc'd for $C_{19}H_{21}NO_5P$ $[M+H]^+$: 374.1152, found 374.1153.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 10.0 min, t_r (minor) = 15.1 min.



2v

Diethyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2v)

Following the general procedure, the reaction was performed with **1v** (78.9 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.2 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-

MeTHF at 40 °C for 12 h. The desired product **2v** was obtained in 65% yield (51.0 mg) as a yellow liquid. er = 95 : 5. $[\alpha]_D^{25}$ = +29.87 (c 1.0, $CHCl_3$). R_f = 0.5 (DCM : EtOAc = 2 : 1).

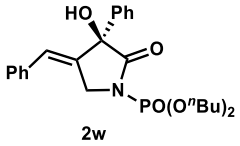
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 2H), 7.33 – 7.23 (m, 5H), 7.26 – 7.13 (m, 3H), 6.83 (s, 1H), 4.59 (d, *J* = 14.6 Hz, 1H), 4.47 (dd, *J* = 14.6, 2.7 Hz, 1H), 4.19 – 4.02 (m, 3H), 4.00 – 3.89 (m, 1H), 3.85 (brs, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 140.4, 135.2 (d, *J* = 8.0 Hz), 135.0, 128.91, 128.89, 128.84, 128.82, 128.2, 127.4, 125.7, 79.4 (d, *J* = 8.6 Hz), 64.7 (d, *J* = 5.9 Hz), 64.6 (d, *J* = 5.9 Hz), 49.0 (d, *J* = 5.2 Hz), 16.1 (d, *J* = 7.5 Hz), 16.0 (d, *J* = 7.5 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –3.7.

HRMS (ESI^+) *m/z* calc'd for $C_{21}H_{25}NO_5P$ $[M+H]^+$: 402.1465, found 402.1462.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 6.3 min, t_r (minor) = 10.0 min.



2w

Dibutyl (*R*,*E*)-(4-benzylidene-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (2w)

Following the general procedure, the reaction was performed with **1w** (91.0 mg, 0.2 mmol, 1.0 equiv), $Ni(OTs)_2$•$6H_2O$ (10.2 mg, 0.020 mmol, 10 mol %), **L2** (6.1 mg, 0.020 mmol, 10 mol %), NaH_2PO_4 (12.0 mg, 0.5 equiv) and $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) in 2.0 mL of 2-MeTHF at 40 °C for 12 h. The desired product **2w** was obtained in 55% yield (50.1 mg) as a yellow liquid. er = 95 : 5. $[\alpha]_D^{25}$ = +29.27 (c 1.0, $CHCl_3$). R_f = 0.4 (DCM : EtOAc = 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 2H), 7.44 – 7.37 (m, 5H), 7.35 – 7.24 (m, 3H), 6.93 (q, *J* = 2.0 Hz, 1H), 4.69 (dt, *J* = 14.6, 1.4 Hz, 1H), 4.56 (dd, *J* = 14.6, 2.7 Hz, 1H), 4.22 – 4.03 (m, 3H), 3.96 (dq, *J* = 9.9, 6.7 Hz, 1H), 3.88 (brs, 1H), 1.72 – 1.62 (m, 2H), 1.62 – 1.53 (m, 2H), 1.46 – 1.35 (m, 2H), 1.35 – 1.24 (m, 2H), 0.89 (dt, *J* = 14.6, 7.4 Hz, 6H).

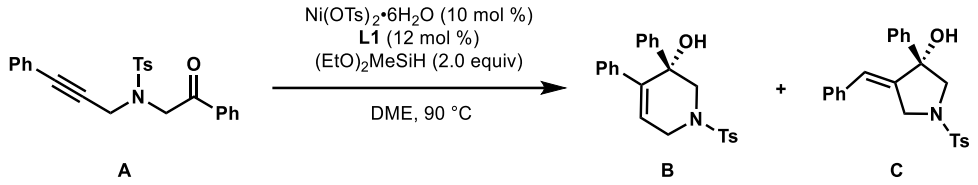
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 140.4, 135.2 (d, *J* = 8.0 Hz), 135.0, 128.90, 128.88, 128.83, 128.80, 128.1, 127.4, 125.8, 79.4 (d, *J* = 8.4 Hz), 68.4 (d, *J* = 6.3 Hz), 68.3 (d, *J* = 6.3 Hz), 49.1 (d, *J* = 5.1 Hz), 32.2 (d, *J* = 7.2 Hz), 32.1 (d, *J* = 7.2 Hz), 18.7, 18.6, 13.61, 13.58.

^{31}P NMR (162 MHz, $CDCl_3$) δ –3.5.

HRMS (ESI^+) *m/z* calc'd for $C_{25}H_{33}NO_5P$ $[M+H]^+$: 458.2091, found 458.2089.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 260 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 4.7 min, t_r (minor) = 7.9 min.

V. Mechanistic Experiments



(*S*)-3,4-Diphenyl-1-tosyl-1,2,3,6-tetrahydropyridin-3-ol (B)

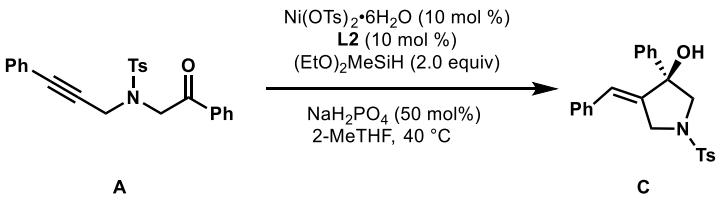
$Ni(OTs)_2•6H_2O$ (10.1 mg, 0.020 mmol, 10 mol %), **L1** (10.2 mg, 0.024 mmol, 12 mol %) and 2.0 mL of DME were added to a Schlenk tube under Ar. The resultant solution was stirred at rt for 20 min, then **A** (81.1 mg, 0.2 mmol, 1.0 equiv), $(EtO)_2MeSiH$ (64 μL, 0.4 mmol, 2.0 equiv) and another 2.0 mL of DME were added. The tube was sealed and the mixture was stirred at 90 °C for 24 h. After the reaction was cooled to rt, the mixture was filtered through a celite pad and the solid was washed with EtOAc (5 mL × 3). After the collected solvents were removed under reduced pressure, the regioselectivity was determined (**B** : **C** = 3.5 : 1) by ^{1}H NMR of the crude mixture. The reside was purified by silica gel column chromatography to provide **B** (33.1 mg, 44%) as a colorless liquid. er = 54 : 46. R_f = 0.2 (PE : DCM = 1 : 4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.23 (m, 2H), 7.23 – 7.16 (m, 3H), 7.14 – 7.06 (m, 3H), 6.14 (dd, *J* = 4.6, 2.5 Hz, 1H), 4.26 – 4.13 (m, 1H), 3.64 (AB, *J* = 11.8 Hz, 1H), 3.52 (dd, *J* = 16.9, 2.6 Hz, 1H), 2.86 (BA, *J* = 11.8 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 142.3, 141.9, 138.3, 132.8, 130.0, 128.15, 128.13, 128.0, 127.5, 127.34, 127.31, 126.3, 124.2, 73.9, 58.6, 46.0, 21.7.

HRMS (ESI^+) *m/z* calc'd for $C_{24}H_{23}NO_3SNa$ $[M+Na]^+$: 428.1291, found 428.1286.

HPLC conditions: hexane/2-propanol 70 : 30, 1.0 mL/min, λ = 254 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_r (major) = 13.4 min, t_r (minor) = 19.2 min.



(*R*,*E*)-4-Denzylidene-3-phenyl-1-tosylpyrrolidin-3-ol (C)

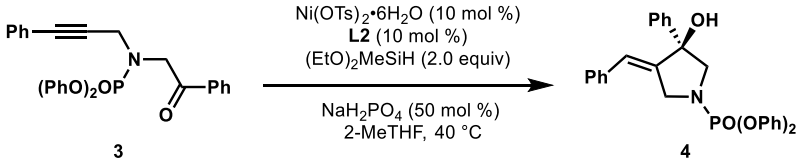
To a Schlenk tube were added $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.01 mmol, 10 mol %), **L2** (3.1 mg, 0.01 mmol, 10 mol %), and 0.5 mL of 2-MeTHF under Ar. The resultant solution was stirred at room temperature for 20 min, then **A** (40.3 mg, 0.1 mmol, 1.0 equiv), NaH_2PO_4 (6.0 mg, 0.5 equiv), $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) and another 0.5 mL of 2-MeTHF were added. The tube was sealed and the mixture was stirred at 40 °C for 12 h. After the reaction was cooled to room temperature, the mixture was filtered through a celite pad and the solid was washed with EtOAc (5 mL × 3). After the collected solvents were removed under reduced pressure, the reside was purified by silica gel column chromatography to provide **C** (13.2 mg, 33%) as a cololess liquid. er = 96 : 4. $[\alpha]_D^{25}$ = +15.9 (c 1.6, $CHCl_3$). R_f = 0.2 (PE : EtOAc = 5 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.40 – 7.24 (m, 8H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.30 (d, *J* = 2.6 Hz, 1H), 4.52 (dd, *J* = 15.0, 2.5 Hz, 1H), 4.27 (dd, *J* = 15.0, 2.6 Hz, 1H), 3.58 (q, *J* = 10.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.6, 141.5, 135.7, 133.0, 130.0, 128.8, 128.7, 128.5, 128.1, 128.04, 127.99, 126.7, 126.3, 82.1, 61.6, 50.8, 21.7

HRMS (ESI^+) *m/z* calc'd for $C_{24}H_{24}O_3NS$ $[M+H]^+$: 406.1477, found 406.1475.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 11.4 min, t_r (minor) = 13.7 min.



Diphenyl (*R*,*E*)-(4-benzylidene-3-hydroxy-3-phenylpyrrolidin-1-yl)phosphonate (4)

To a Schlenk tube were added $Ni(OTs)_2$•$6H_2O$ (5.1 mg, 0.01 mmol, 10 mol %), **L2** (3.1 mg, 0.01 mmol, 10 mol %), and 0.5 mL of 2-MeTHF under Ar. The resultant solution was stirred at room temperature for 20 min, then **3** (48.2 mg, 0.1 mmol, 1.0 equiv), NaH_2PO_4 (6.0 mg, 0.5 equiv), $(EtO)_2MeSiH$ (32 μL, 0.2 mmol, 2.0 equiv) and another 0.5 mL of 2-MeTHF were added. The tube was sealed and the mixture was stirred at 40 °C for 12 h. After the reaction was cooled to room temperature, the mixture was filtered through a celite pad and the solid was washed with EtOAc (5 mL × 3). After the collected solvents were removed under reduced

pressure, the reside was purified by silica gel column chromatography to provide **4** (21.1 mg, 33%) as a cololess liquid. er = 90 : 10. $[\alpha]_D^{25}$ = +9.7 (c 1.4, $CHCl_3$). R_f = 0.5 (PE : EtOAc = 5 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.32 – 7.16 (m, 12H), 7.15 – 7.01 (m, 6H), 6.24 (s, 1H), 4.62 (dt, *J* = 15.3, 3.0 Hz, 1H), 4.46 – 4.31 (m, 1H), 3.73 – 3.60 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (d, *J* = 2.7 Hz), 150.8 (d, *J* = 2.6 Hz), 144.2 (d, *J* = 10.2 Hz), 141.9, 136.0, 129.9, 128.8, 128.4, 127.9, 126.5, 126.0, 125.2 (d, *J* = 3.6 Hz), 120.3 (d, *J* = 5.0 Hz), 120.2 (d, *J* = 5.0 Hz), 82.8 (d, *J* = 8.3 Hz), 61.0 (d, *J* = 2.9 Hz), 50.3 (d, *J* = 5.6 Hz).

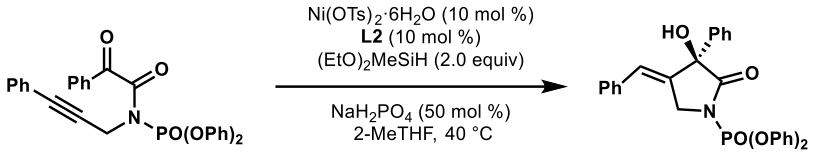
^{31}P NMR (162 MHz, $CDCl_3$) δ –3.4.

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{27}NO_4P$ $[M+H]^+$: 484.1678, found 484.1678.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 210 nm, Chiralpak IB column (4.6 mm x 250 mm), t_r (major) = 7.5 min, t_r (minor) = 9.1 min.

VI. Gram-Scale Synthesis and Procedures of Product Derivatizations

Gram-scale synthesis:

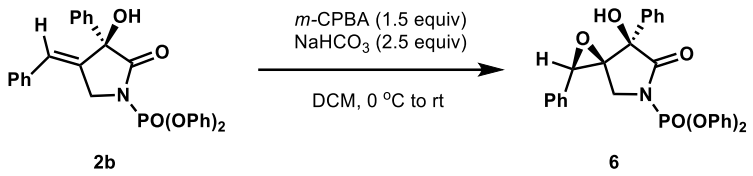


1b
3.4 mmol

2b
1.10 g

To a Schlenk flask under Ar were added $Ni(OTs)_2$•$6H_2O$ (173.1 mg, 0.34 mmol, 10 mol %), **L2** (104.0 mg, 0.34 mmol, 10 mol %), and 17 mL of 2-MeTHF. The resultant solution was stirred at room temperature for 30 min, and then **1b** (1.68 g, 3.4 mmol, 1.0 equiv), $(EtO)_2MeSiH$ (0.88 mL, 6.4 mmol, 2.0 equiv), and 17 mL of 2-MeTHF were added. The flask was sealed and the mixture was stirred at 40 °C for 14 h. After the reaction was cooled to room temperature, the mixture was filtered through a celite pad and the pad was washed with EtOAc (30 mL × 3). After the collected solvents were removed under reduced pressure, the residue was purified by silica gel column chromatography to provide the desired product **2b** (1.10 g, 65%) as a white solid. er = 94 : 6.

Procedures of Product Derivatizations:



2b 6

Diphenyl ((2*R*,3*S*,7*R*)-7-hydroxy-6-oxo-2,7-diphenyl-1-oxa-5-azaspiro[2.4]heptan-5-yl)phosphonate (6)

The reported procedure was followed [2]. To a mixture of **2b** (49.7 mg, 0.10 mmol, 1.0 equiv) and $NaHCO_3$ (21.7 mg, 0.25 mmol, 2.5 equiv) in DCM (2 mL) was added *m*-CPBA (85%, 30.4 mg, 0.15 mmol, 1.5 equiv) at 0 °C. The mixture was stirred at room temperature for 6 h, and then it was quenched by sat. $Na_2S_2O_3$. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrates were removed under reduced pressure and the desired product **6** (45.3 mg, 88%) was obtained as a colorless liquid after purification by silica gel chromatography. er = 96 : 4. $[\alpha]_D^{25}$ = +19.58 (c 4.0, $CHCl_3$). R_f = 0.5 (PE / EtOAc = 2 / 1).

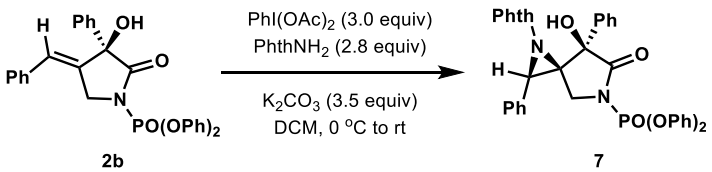
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 9H), 7.23 – 7.17 (m, 4H), 7.11 – 7.00 (m, 5H), 6.99 – 6.87 (m, 2H), 4.00 (s, 1H), 3.67 (dd, *J* = 12.8, 1.6 Hz, 1H), 3.59 (d, *J* = 12.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7 (d, *J* = 2.1 Hz), 149.9 (d, *J* = 6.9 Hz), 149.5 (d, *J* = 6.6 Hz), 136.9, 132.4, 130.1 (d, *J* = 1.3 Hz), 129.9 (d, *J* = 1.2 Hz), 129.21, 129.20, 129.04, 129.01, 126.2 (d, *J* = 1.7 Hz), 126.0 (d, *J* = 1.6 Hz), 125.7, 125.4, 120.7 (d, *J* = 4.5 Hz), 120.5 (d, *J* = 4.6 Hz), 76.1 (d, *J* = 8.8 Hz), 68.3 (d, *J* = 9.3 Hz), 60.1, 48.8 (d, *J* = 5.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.6

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{25}NO_6P$ $[M+H]^+$: 514.1414, found 514.1413.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 280 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 6.4 min, t_r (minor) = 9.1 min.



2b 7

Diphenyl ((2*R*,3*S*,7*R*)-1-(1,3-dioxoisoindolin-2-yl)-7-hydroxy-6-oxo-2,7-diphenyl-1,5-diazaspiro[2.4]heptan-5-yl)phosphonate (7)

The reported procedure was followed [5]. To a mixture of **2b** (49.5 mg, 0.10 mmol, 1.0 equiv), K_2CO_3 (48.4 mg, 0.35 mmol, 3.5 equiv) and *N*-aminophthalimide (45.4 mg, 0.28 mmol, 2.8

equiv) in DCM (1 mL) was added (diacetoxyiodo)benzene (96.6 mg, 0.30 mmol, 3.0 equiv) at 0 °C. The mixture was stirred at room temperature for 12 h, and then it was quenched by aqueous NH_4Cl. The mixture was extracted with DCM (5 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. The filtrates were removed under reduced pressure and the desired product **7** (57.2 mg, 87%) was obtained as a yellow liquid after purification by silica gel chromatography. $[\alpha]_D^{25}$ = –136.42 (c 0.4, $CHCl_3$). R_f = 0.4 (PE / EtOAc = 2 / 1).

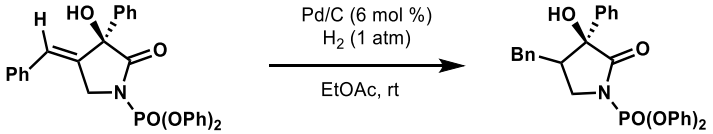
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.63 – 7.57 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.13 (m, 12H), 7.17 – 7.05 (m, 2H), 6.99 – 6.94 (m, 2H), 4.50 (s, 1H), 3.81 (AB, *J* = 11.7 Hz, 1H), 3.45 (brs, 1H), 3.37 (BA, *J* = 11.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 165.5, 150.1 (d, *J* = 7.1 Hz), 149.9 (d, *J* = 6.8 Hz), 138.9, 134.2, 132.9, 130.7, 130.03, 130.00, 129.2, 129.1, 128.8, 128.3, 126.9, 126.0, 125.5, 123.4, 121.1 (d, *J* = 4.5 Hz), 120.7 (d, *J* = 4.9 Hz), 79.3 (d, *J* = 9.3 Hz), 55.9 (d, *J* = 9.1 Hz), 49.7, 49.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.2

HRMS (ESI^+) *m/z* calc'd for $C_{37}H_{29}N_3O_7P$ $[M+H]^+$: 658.1738, found 658.1732.

HPLC conditions: hexane/2-propanol 80 : 20, 1.0 mL/min, λ = 254 nm, Chiralcel OD-H column (4.6 mm x 250 mm), t_r (major) = 6.4 min, t_r (minor) = 11.2 min.



2b **8**

Diphenyl ((3*S*)-4-benzyl-3-hydroxy-2-oxo-3-phenylpyrrolidin-1-yl)phosphonate (8)

To a Schlenk tube were added **2b** (49.5 mg, 0.10 mmol, 1.0 equiv), Pd/C (5.8 mg, 0.06 mmol, with H_2. The reaction was stirred at room temperature for 3 h, the mixture was filtered through a celite pad and the solid was washed with EtOAc (5 mL × 3). After the collected solvents were removed under reduced pressure and the desired product **8** (46.6 mg, 94%) was obtained as a colorless liquid after purification by silica gel chromatography. $[\alpha]_D^{25}$ = +46.62 (c 2.1, $CHCl_3$). R_f = 0.6 (PE / EtOAc = 2 / 1).

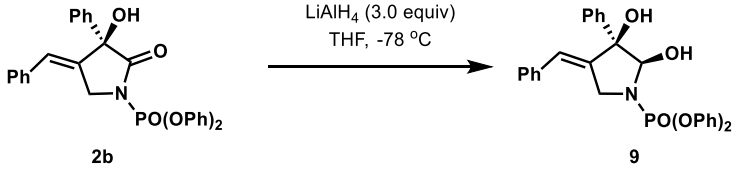
For the major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.28 – 7.24 (m, 3H), 7.23 – 7.17 (m, 4H), 7.18 – 7.12 (m, 3H), 7.10 – 7.05 (m, 2H), 6.96 – 6.92 (m, 2H), 6.90 – 6.85

(m, 2H), 3.54 (ddd, *J* = 10.4, 7.4, 2.6 Hz, 1H), 3.07 (t, *J* = 10.5 Hz, 1H), 2.71 – 2.57 (m, 2H), 1.63 – 1.52 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 150.0 (d, *J* = 6.5 Hz), 149.9 (d, *J* = 6.9 Hz), 140.1, 138.6, 138.0, 137.2, 130.2, 130.1, 128.8, 128.7, 128.6, 126.7, 126.1, 125.5, 120.8 (d, *J* = 4.9 Hz), 120.7 (d, *J* = 4.9 Hz), 81.4 (d, *J* = 9.8 Hz), 49.1 (d, *J* = 3.8 Hz), 48.2 (d, *J* = 6.0 Hz), 34.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ –12.3.

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{27}NO_5P$ $[M+H]^+$: 500.1621, found 500.1616.



2b 9

Diphenyl ((2*R*,3*R*)-4-((*E*)-benzylidene)-2,3-dihydroxy-3-phenylpyrrolidin-1-yl)phosphonate (9)

A solution of **2b** (25.1 mg, 0.05 mmol, 1.0 equiv) in THF (1 mL) was cooled to –78 °C, and $LiAlH_4$ (1.0 M in THF, 0.15 mL, 0.15 mmol, 0.15 equiv) was added. The mixture was stirred at –78 °C for 1h, The solution was quenched with vigorous stirring by the addition of aqueous potassium sodium tartrate solution (2 mL) until the solution was stratified. The mixture was extracted with EtOAc (3 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. The filtrates were removed under reduced pressure and the desired product **9** (16.8 mg, 68%) was obtained as a white solid after purification by silica gel chromatography. $[\alpha]_D^{25}$ = +106.54 (c 1.3, $CHCl_3$). R_f = 0.3 (PE : EtOAc = 2 : 1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 4H), 7.29 – 7.19 (m, 9H), 7.16 – 7.06 (m, 5H), 6.94 – 6.90 (m, 2H), 6.84 (d, *J* = 2.3 Hz, 1H), 5.44 (d, *J* = 2.1 Hz, 1H), 5.32 (brs, 1H), 4.47 (dt, *J* = 14.5, 1.9 Hz, 1H), 4.34 – 4.26 (m, 1H), 3.34 (brs, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, *J* = 6.9 Hz), 150.3(d, *J* = 6.9 Hz), 142.0, 140.4 (d, *J* = 9.8 Hz), 136.2, 129.89, 129.86, 128.84, 128.77, 128.6, 128.2, 127.6, 126.6, 126.3, 125.4, 125.3, 120.4 (d, *J* = 4.8 Hz), 119.9 (d, *J* = 5.0 Hz), 86.6 (d, *J* = 4.3 Hz), 82.7 (d, *J* = 11.4 Hz), 48.2 (d, *J* = 4.7 Hz).

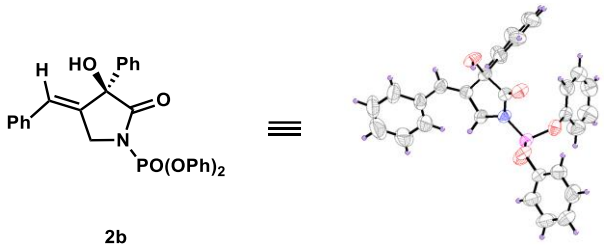
^{31}P NMR (162 MHz, $CDCl_3$) δ –4.3

HRMS (ESI^+) *m/z* calc'd for $C_{29}H_{26}NO_5PNa$ $[M+Na]^+$: 522.1441, found 522.1433.

HPLC conditions: hexane/2-propanol 85 : 15, 1.0 mL/min, λ = 254 nm, Chiralpak AD-H column (4.6 mm x 250 mm), t_r (major) = 24.8 min, t_r (minor) = 20.6 min.

VII. X-ray Crystallography Data of 2b

The crystals of **2b** (>99.5:0.5 er) were grown by vapor diffusion method (DCM and EtOAc) at 25 ºC. Data were collected on Rigaku XtaLAB AFC11 kappa diffractometer equipped with a CCD area detector and operated (45kV, 0.65mA) to generate Cu Kα radiation (λ = 1.5418 Å).



2b

Table S10. Crystal data and structure refinement for 2b.

Identification code	CCDC 2246876	
Empirical formula	$C_{29}H_{24}NO_5P$	
Formula weight	497.46	
Temperature	293.15 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.5892(2) Å	α= 90°.
	b = 11.5377(2) Å	β= 90°.
	c = 23.4103(4) Å	γ = 90°.
Volume	2590.05(8) $Å^3$	
Z	4	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	1.266 mm^{-1}	
F(000)	1040	
Crystal size	0.04 x 0.04 x 0.01 mm^3	
Theta range for data collection	3.776 to 71.683°.	
Index ranges	-11<=h<=11, -14<=k<=14, -28<=l<=28	
Reflections collected	53502	

Independent reflections	5021 [R(int) = 0.0576]
Completeness to theta = 67.684°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89259
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5021 / 0 / 326
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0858
R indices (all data)	R1 = 0.0396, wR2 = 0.0889
Absolute structure parameter	-0.008(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.141 and -0.232 e.$Å^{-3}$

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 2b. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	4575(1)	3445(1)	1788(1)	48(1)
O(3)	5770(2)	3453(2)	1330(1)	56(1)
O(4)	6723(2)	1625(2)	2197(1)	60(1)
O(1)	3786(2)	2299(1)	1637(1)	55(1)
O(2)	3728(2)	4486(2)	1823(1)	63(1)
O(5)	7329(2)	1607(2)	3417(1)	62(1)
N(1)	5306(2)	3170(2)	2414(1)	48(1)
C(11)	6935(3)	2622(2)	3123(1)	46(1)
C(10)	6343(3)	2368(2)	2524(1)	45(1)
C(12)	8266(2)	3334(2)	3036(1)	46(1)
C(24)	2982(3)	2199(2)	1127(1)	51(1)
C(18)	6752(3)	4375(2)	1302(1)	53(1)
C(8)	5761(2)	3303(2)	3396(1)	48(1)
C(7)	5548(3)	3362(2)	3958(1)	57(1)
C(13)	9419(3)	2799(2)	2798(1)	60(1)
C(9)	4874(3)	3821(2)	2933(1)	56(1)
C(15)	10735(3)	4550(3)	2849(1)	74(1)
C(17)	8369(3)	4498(2)	3174(1)	66(1)
C(6)	4426(3)	3929(3)	4282(1)	65(1)
C(23)	8068(3)	4170(3)	1490(1)	70(1)
C(29)	3467(3)	1514(3)	700(1)	67(1)
C(14)	10647(3)	3399(3)	2707(1)	70(1)
C(16)	9608(4)	5087(3)	3082(2)	81(1)
C(1)	3500(4)	4721(4)	4062(1)	85(1)
C(19)	6382(4)	5407(3)	1064(2)	78(1)
C(28)	2662(4)	1359(3)	221(1)	83(1)
C(25)	1716(3)	2720(3)	1097(1)	77(1)
C(22)	9061(4)	5030(3)	1447(2)	79(1)
C(21)	8707(4)	6081(3)	1214(2)	79(1)
C(27)	1384(4)	1878(4)	180(1)	88(1)
C(20)	7370(4)	6266(3)	1020(2)	93(1)
C(26)	917(4)	2543(4)	613(2)	99(1)

C(5)	4289(4)	3641(4)	4859(1)	97(1)
C(4)	3241(6)	4111(5)	5191(2)	122(2)
C(3)	2325(6)	4872(6)	4958(2)	138(2)
C(2)	2435(5)	5186(5)	4394(2)	119(2)

Table S12. Bond lengths [Å] and angles [°] for 2b.

P(1)-O(3)	1.5703(18)
P(1)-O(1)	1.5642(18)
P(1)-O(2)	1.4531(18)
P(1)-N(1)	1.6547(19)
O(3)-C(18)	1.422(3)
O(4)-C(10)	1.207(3)
O(1)-C(24)	1.424(3)
O(5)-H(5)	0.8200
O(5)-C(11)	1.410(3)
N(1)-C(10)	1.382(3)
N(1)-C(9)	1.488(3)
C(11)-C(10)	1.539(3)
C(11)-C(12)	1.531(3)
C(11)-C(8)	1.514(3)
C(12)-C(13)	1.383(4)
C(12)-C(17)	1.384(4)
C(24)-C(29)	1.356(4)
C(24)-C(25)	1.357(4)
C(18)-C(23)	1.358(4)
C(18)-C(19)	1.362(4)
C(8)-C(7)	1.334(3)
C(8)-C(9)	1.502(3)
C(7)-H(7)	0.9300
C(7)-C(6)	1.470(4)
C(13)-H(13)	0.9300
C(13)-C(14)	1.384(4)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(15)-H(15)	0.9300
C(15)-C(14)	1.372(4)
C(15)-C(16)	1.360(5)
C(17)-H(17)	0.9300
C(17)-C(16)	1.386(4)
C(6)-C(1)	1.375(5)
C(6)-C(5)	1.397(4)
C(23)-H(23)	0.9300

C(23)-C(22)	1.379(4)
C(29)-H(29)	0.9300
C(29)-C(28)	1.373(4)
C(14)-H(14)	0.9300
C(16)-H(16)	0.9300
C(1)-H(1)	0.9300
C(1)-C(2)	1.392(5)
C(19)-H(19)	0.9300
C(19)-C(20)	1.375(5)
C(28)-H(28)	0.9300
C(28)-C(27)	1.367(5)
C(25)-H(25)	0.9300
C(25)-C(26)	1.384(4)
C(22)-H(22)	0.9300
C(22)-C(21)	1.373(5)
C(21)-H(21)	0.9300
C(21)-C(20)	1.377(5)
C(27)-H(27)	0.9300
C(27)-C(26)	1.348(5)
C(20)-H(20)	0.9300
C(26)-H(26)	0.9300
C(5)-H(5A)	0.9300
C(5)-C(4)	1.381(6)
C(4)-H(4)	0.9300
C(4)-C(3)	1.357(8)
C(3)-H(3)	0.9300
C(3)-C(2)	1.372(7)
C(2)-H(2)	0.9300

O(3)-P(1)-N(1)	107.28(10)
O(1)-P(1)-O(3)	101.71(10)
O(1)-P(1)-N(1)	104.12(9)
O(2)-P(1)-O(3)	116.23(11)
O(2)-P(1)-O(1)	116.21(11)
O(2)-P(1)-N(1)	110.17(10)
C(18)-O(3)-P(1)	121.26(15)
C(24)-O(1)-P(1)	121.30(15)
C(11)-O(5)-H(5)	109.5

C(10)-N(1)-P(1)	126.78(16)
C(10)-N(1)-C(9)	112.65(19)
C(9)-N(1)-P(1)	120.57(16)
O(5)-C(11)-C(10)	112.64(18)
O(5)-C(11)-C(12)	106.64(19)
O(5)-C(11)-C(8)	115.1(2)
C(12)-C(11)-C(10)	106.78(18)
C(8)-C(11)-C(10)	102.09(19)
C(8)-C(11)-C(12)	113.36(18)
O(4)-C(10)-N(1)	125.0(2)
O(4)-C(10)-C(11)	127.0(2)
N(1)-C(10)-C(11)	107.95(19)
C(13)-C(12)-C(11)	118.7(2)
C(13)-C(12)-C(17)	118.0(2)
C(17)-C(12)-C(11)	123.3(2)
C(29)-C(24)-O(1)	118.6(2)
C(29)-C(24)-C(25)	121.8(3)
C(25)-C(24)-O(1)	119.5(2)
C(23)-C(18)-O(3)	118.0(2)
C(23)-C(18)-C(19)	121.8(3)
C(19)-C(18)-O(3)	120.1(3)
C(7)-C(8)-C(11)	123.9(2)
C(7)-C(8)-C(9)	127.3(2)
C(9)-C(8)-C(11)	108.81(19)
C(8)-C(7)-H(7)	115.0
C(8)-C(7)-C(6)	130.1(3)
C(6)-C(7)-H(7)	115.0
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-C(12)	121.3(3)
C(14)-C(13)-H(13)	119.3
N(1)-C(9)-C(8)	103.4(2)
N(1)-C(9)-H(9A)	111.1
N(1)-C(9)-H(9B)	111.1
C(8)-C(9)-H(9A)	111.1
C(8)-C(9)-H(9B)	111.1
H(9A)-C(9)-H(9B)	109.1
C(14)-C(15)-H(15)	120.3
C(16)-C(15)-H(15)	120.3

C(16)-C(15)-C(14)	119.3(3)
C(12)-C(17)-H(17)	120.0
C(12)-C(17)-C(16)	120.1(3)
C(16)-C(17)-H(17)	120.0
C(1)-C(6)-C(7)	125.1(3)
C(1)-C(6)-C(5)	117.4(3)
C(5)-C(6)-C(7)	117.5(3)
C(18)-C(23)-H(23)	120.2
C(18)-C(23)-C(22)	119.5(3)
C(22)-C(23)-H(23)	120.2
C(24)-C(29)-H(29)	120.5
C(24)-C(29)-C(28)	119.0(3)
C(28)-C(29)-H(29)	120.5
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-C(13)	119.9(3)
C(15)-C(14)-H(14)	120.0
C(15)-C(16)-C(17)	121.3(3)
C(15)-C(16)-H(16)	119.3
C(17)-C(16)-H(16)	119.3
C(6)-C(1)-H(1)	119.3
C(6)-C(1)-C(2)	121.4(4)
C(2)-C(1)-H(1)	119.3
C(18)-C(19)-H(19)	120.6
C(18)-C(19)-C(20)	118.8(3)
C(20)-C(19)-H(19)	120.6
C(29)-C(28)-H(28)	119.8
C(27)-C(28)-C(29)	120.3(3)
C(27)-C(28)-H(28)	119.8
C(24)-C(25)-H(25)	120.9
C(24)-C(25)-C(26)	118.2(3)
C(26)-C(25)-H(25)	120.9
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-C(23)	119.6(3)
C(21)-C(22)-H(22)	120.2
C(22)-C(21)-H(21)	120.1
C(22)-C(21)-C(20)	119.9(3)
C(20)-C(21)-H(21)	120.1
C(28)-C(27)-H(27)	120.2

C(26)-C(27)-C(28)	119.5(3)
C(26)-C(27)-H(27)	120.2
C(19)-C(20)-C(21)	120.4(3)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(25)-C(26)-H(26)	119.4
C(27)-C(26)-C(25)	121.1(3)
C(27)-C(26)-H(26)	119.4
C(6)-C(5)-H(5A)	119.4
C(4)-C(5)-C(6)	121.3(4)
C(4)-C(5)-H(5A)	119.4
C(5)-C(4)-H(4)	120.1
C(3)-C(4)-C(5)	119.9(4)
C(3)-C(4)-H(4)	120.1
C(4)-C(3)-H(3)	119.7
C(4)-C(3)-C(2)	120.6(5)
C(2)-C(3)-H(3)	119.7
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-C(1)	119.5(5)
C(3)-C(2)-H(2)	120.3

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 2b. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	58(1)	45(1)	41(1)	-1(1)	-6(1)	9(1)
O(3)	70(1)	53(1)	44(1)	-5(1)	3(1)	1(1)
O(4)	74(1)	48(1)	58(1)	-11(1)	-15(1)	16(1)
O(1)	64(1)	53(1)	50(1)	2(1)	-18(1)	4(1)
O(2)	78(1)	53(1)	60(1)	0(1)	-6(1)	21(1)
O(5)	80(1)	43(1)	62(1)	10(1)	-28(1)	-10(1)
N(1)	53(1)	52(1)	40(1)	-6(1)	-5(1)	10(1)
C(11)	53(1)	40(1)	44(1)	3(1)	-10(1)	-6(1)
C(10)	50(1)	38(1)	48(1)	1(1)	-7(1)	-2(1)
C(12)	49(1)	43(1)	47(1)	0(1)	-7(1)	-2(1)
C(24)	54(2)	53(1)	44(1)	1(1)	-10(1)	2(1)
C(18)	64(2)	54(1)	41(1)	0(1)	2(1)	5(1)
C(8)	46(1)	52(1)	45(1)	0(1)	-3(1)	-10(1)
C(7)	60(2)	69(2)	43(1)	0(1)	-3(1)	-17(2)
C(13)	53(2)	51(1)	74(2)	-5(1)	-7(1)	4(1)
C(9)	57(2)	68(2)	42(1)	-8(1)	0(1)	8(1)
C(15)	59(2)	76(2)	88(2)	5(2)	-3(2)	-19(2)
C(17)	66(2)	47(1)	85(2)	-11(1)	14(2)	-10(1)
C(6)	65(2)	88(2)	42(1)	-11(1)	6(1)	-29(2)
C(23)	70(2)	74(2)	65(2)	14(1)	7(2)	12(2)
C(29)	63(2)	72(2)	67(2)	-15(2)	-3(1)	7(2)
C(14)	48(2)	79(2)	82(2)	4(2)	-1(1)	2(2)
C(16)	83(2)	54(2)	105(2)	-10(2)	10(2)	-23(2)
C(1)	76(2)	122(3)	57(2)	-22(2)	4(2)	1(2)
C(19)	74(2)	69(2)	91(2)	18(2)	-9(2)	9(2)
C(28)	96(3)	97(3)	57(2)	-22(2)	-1(2)	-7(2)
C(25)	68(2)	99(2)	64(2)	-18(2)	-15(2)	24(2)
C(22)	63(2)	100(2)	75(2)	11(2)	1(2)	1(2)
C(21)	82(2)	73(2)	83(2)	-5(2)	9(2)	-8(2)

C(27)	85(2)	120(3)	58(2)	-6(2)	-24(2)	-5(2)
C(20)	93(3)	62(2)	123(3)	21(2)	1(2)	7(2)
C(26)	75(2)	142(4)	81(2)	-17(2)	-28(2)	31(2)
C(5)	107(3)	137(3)	46(2)	-3(2)	12(2)	-33(3)
C(4)	116(4)	194(5)	56(2)	-10(3)	31(2)	-38(4)
C(3)	96(3)	233(7)	84(3)	-53(4)	32(3)	-24(4)
C(2)	89(3)	184(5)	86(3)	-46(3)	11(2)	23(3)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 2b.

	x	y	z	U(eq)
H(5)	6893	1052	3289	93
H(7)	6213	2985	4180	69
H(13)	9367	2020	2698	71
H(9A)	3891	3710	3012	67
H(9B)	5058	4644	2891	67
H(15)	11557	4959	2787	89
H(17)	7605	4885	3327	79
H(23)	8298	3454	1647	84
H(29)	4332	1155	732	81
H(14)	11413	3022	2549	84
H(16)	9671	5865	3183	97
H(1)	3586	4950	3683	102
H(19)	5477	5530	935	94
H(28)	2988	899	-76	100
H(25)	1393	3183	1394	93
H(22)	9965	4898	1575	95
H(21)	9370	6667	1187	95
H(27)	840	1772	-145	106
H(20)	7134	6976	858	111
H(26)	44	2889	585	119
H(5A)	4915	3123	5023	116
H(4)	3164	3906	5574	146
H(3)	1617	5184	5182	165
H(2)	1803	5706	4236	143

Table S15. Torsion angles [°] for 2b.

P(1)-O(3)-C(18)-C(23)	106.3(3)
P(1)-O(3)-C(18)-C(19)	-77.0(3)
P(1)-O(1)-C(24)-C(29)	109.1(3)
P(1)-O(1)-C(24)-C(25)	-75.6(3)
P(1)-N(1)-C(10)-O(4)	-11.9(4)
P(1)-N(1)-C(10)-C(11)	166.48(17)
P(1)-N(1)-C(9)-C(8)	179.31(16)
O(3)-P(1)-O(1)-C(24)	-70.24(19)
O(3)-P(1)-N(1)-C(10)	-41.7(2)
O(3)-P(1)-N(1)-C(9)	137.7(2)
O(3)-C(18)-C(23)-C(22)	177.3(3)
O(3)-C(18)-C(19)-C(20)	-177.1(3)
O(1)-P(1)-O(3)-C(18)	178.91(17)
O(1)-P(1)-N(1)-C(10)	65.6(2)
O(1)-P(1)-N(1)-C(9)	-115.0(2)
O(1)-C(24)-C(29)-C(28)	176.2(3)
O(1)-C(24)-C(25)-C(26)	-175.6(3)
O(2)-P(1)-O(3)-C(18)	51.7(2)
O(2)-P(1)-O(1)-C(24)	57.0(2)
O(2)-P(1)-N(1)-C(10)	-169.1(2)
O(2)-P(1)-N(1)-C(9)	10.2(2)
O(5)-C(11)-C(10)-O(4)	-36.4(3)
O(5)-C(11)-C(10)-N(1)	145.3(2)
O(5)-C(11)-C(12)-C(13)	51.2(3)
O(5)-C(11)-C(12)-C(17)	-130.2(3)
O(5)-C(11)-C(8)-C(7)	32.4(3)
O(5)-C(11)-C(8)-C(9)	-144.5(2)
N(1)-P(1)-O(3)-C(18)	-72.10(19)
N(1)-P(1)-O(1)-C(24)	178.35(18)
C(11)-C(12)-C(13)-C(14)	179.6(2)
C(11)-C(12)-C(17)-C(16)	-179.9(3)
C(11)-C(8)-C(7)-C(6)	-176.4(2)
C(11)-C(8)-C(9)-N(1)	15.2(3)
C(10)-N(1)-C(9)-C(8)	-1.2(3)
C(10)-C(11)-C(12)-C(13)	-69.4(3)
C(10)-C(11)-C(12)-C(17)	109.2(3)

C(10)-C(11)-C(8)-C(7)	154.8(2)
C(10)-C(11)-C(8)-C(9)	-22.1(2)
C(12)-C(11)-C(10)-O(4)	80.3(3)
C(12)-C(11)-C(10)-N(1)	-98.0(2)
C(12)-C(11)-C(8)-C(7)	-90.8(3)
C(12)-C(11)-C(8)-C(9)	92.3(2)
C(12)-C(13)-C(14)-C(15)	-0.4(5)
C(12)-C(17)-C(16)-C(15)	1.2(5)
C(24)-C(29)-C(28)-C(27)	-0.8(5)
C(24)-C(25)-C(26)-C(27)	-0.4(6)
C(18)-C(23)-C(22)-C(21)	-0.1(5)
C(18)-C(19)-C(20)-C(21)	-0.1(6)
C(8)-C(11)-C(10)-O(4)	-160.4(2)
C(8)-C(11)-C(10)-N(1)	21.2(2)
C(8)-C(11)-C(12)-C(13)	178.9(2)
C(8)-C(11)-C(12)-C(17)	-2.4(3)
C(8)-C(7)-C(6)-C(1)	-13.7(5)
C(8)-C(7)-C(6)-C(5)	166.2(3)
C(7)-C(8)-C(9)-N(1)	-161.6(2)
C(7)-C(6)-C(1)-C(2)	177.7(3)
C(7)-C(6)-C(5)-C(4)	-178.3(4)
C(13)-C(12)-C(17)-C(16)	-1.3(4)
C(9)-N(1)-C(10)-O(4)	168.7(2)
C(9)-N(1)-C(10)-C(11)	-12.9(3)
C(9)-C(8)-C(7)-C(6)	-0.1(5)
C(17)-C(12)-C(13)-C(14)	0.9(4)
C(6)-C(1)-C(2)-C(3)	1.6(7)
C(6)-C(5)-C(4)-C(3)	-0.3(7)
C(23)-C(18)-C(19)-C(20)	-0.6(5)
C(23)-C(22)-C(21)-C(20)	-0.6(5)
C(29)-C(24)-C(25)-C(26)	-0.5(5)
C(29)-C(28)-C(27)-C(26)	0.0(6)
C(14)-C(15)-C(16)-C(17)	-0.7(5)
C(16)-C(15)-C(14)-C(13)	0.3(5)
C(1)-C(6)-C(5)-C(4)	1.6(5)
C(19)-C(18)-C(23)-C(22)	0.7(5)
C(28)-C(27)-C(26)-C(25)	0.6(7)
C(25)-C(24)-C(29)-C(28)	1.0(5)

C(22)-C(21)-C(20)-C(19)	0.7(6)
C(5)-C(6)-C(1)-C(2)	-2.2(5)
C(5)-C(4)-C(3)-C(2)	-0.4(9)
C(4)-C(3)-C(2)-C(1)	-0.2(8)

Symmetry transformations used to generate equivalent atoms:

VIII. References

1 R. Shruti, K. Ramandeep and J. Nidhi, *Org. Biomol. Chem.*, 2022, **20**, 1453.

2 S. Xie, D Li, H. Huang, F. Zhang and Y. Chen, *J. Am. Chem. Soc*., 2019, **141**, 16237.

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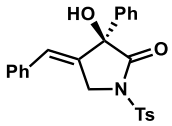
4 Y. Zheng, T. Zhang and W. Shen, *Org. Biomol. Chem.*, 2021, **19**, 9688.

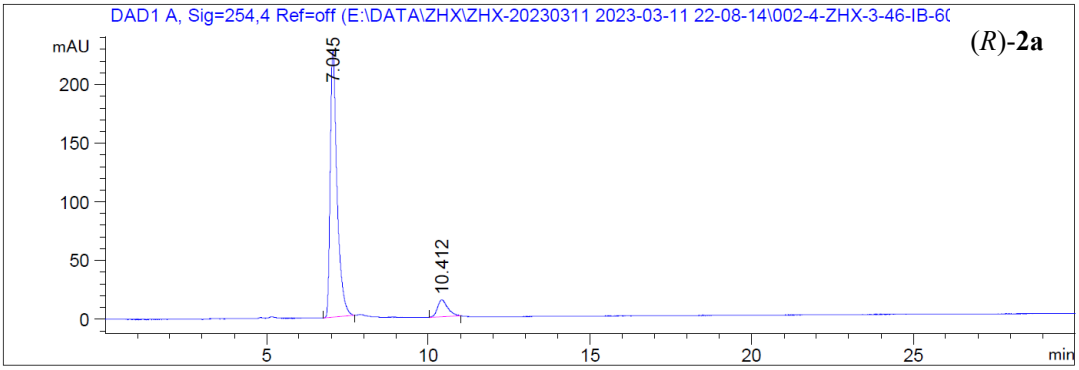
5 Y. Li and M. Xu, *Org. Lett.*, 2014, **16**, 2712

6 J. Hernández-T, M. M. Hussain and P. J. Walsh., *Org. Lett.*, 2011, **13**, 6094

IX. HPLC Spectra

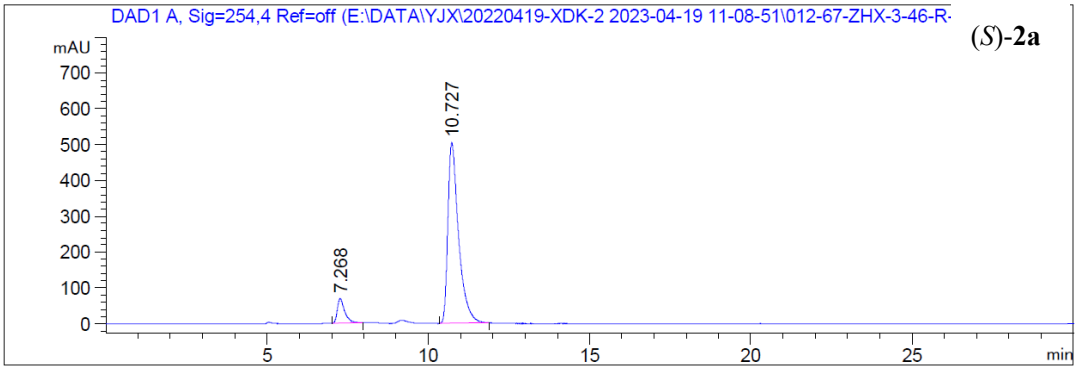


2a



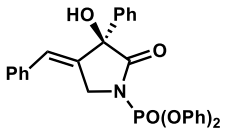
Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.045	VV R	0.2152	3331.77124	227.69815	91.2302
2	10.412	BV R	0.2589	320.27921	14.60144	8.7698



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.268	VV R	0.1978	1100.06995	68.89561	8.6483
2	10.727	VV R	0.3157	1.16200e4	504.46481	91.3517



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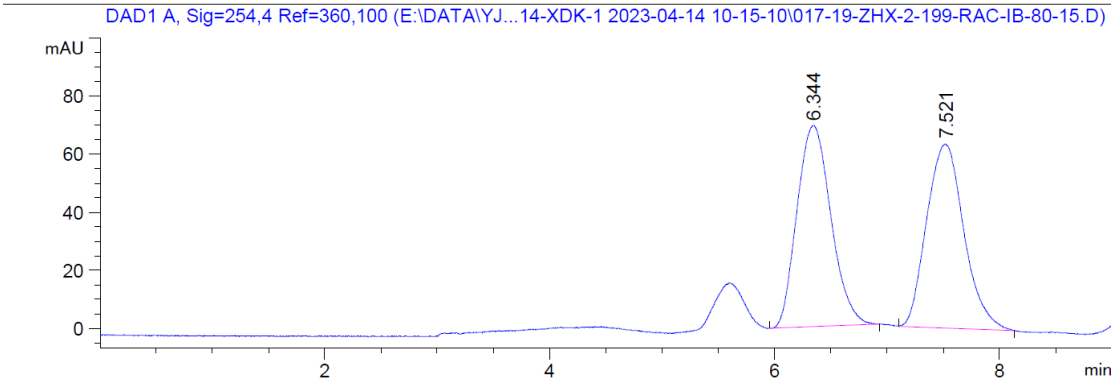
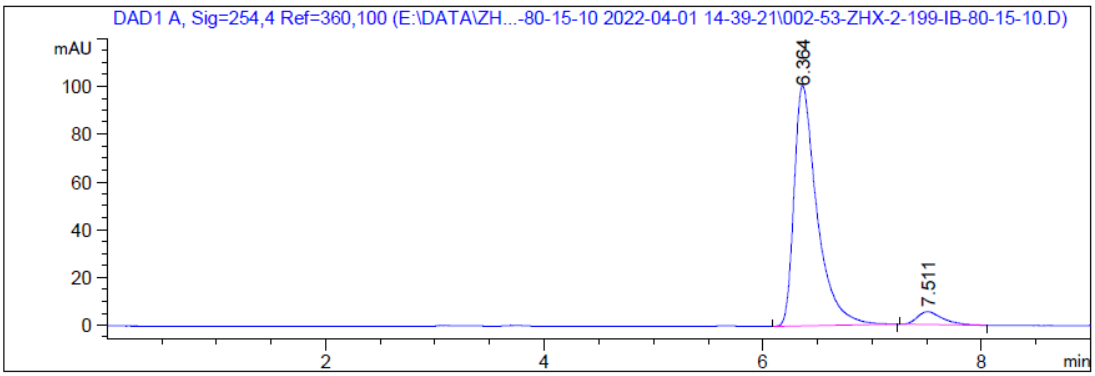


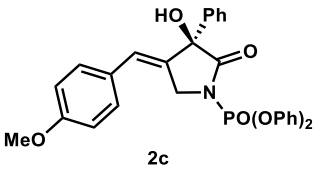
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.344	VV R	0.2487	1455.15222	69.22610	49.9526
2	7.521	BV R	0.2754	1457.91296	63.25254	50.0474



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.364	BB	0.2127	1471.99194	100.59951	94.3238
2	7.511	BB	0.1923	88.58142	5.46068	5.6762



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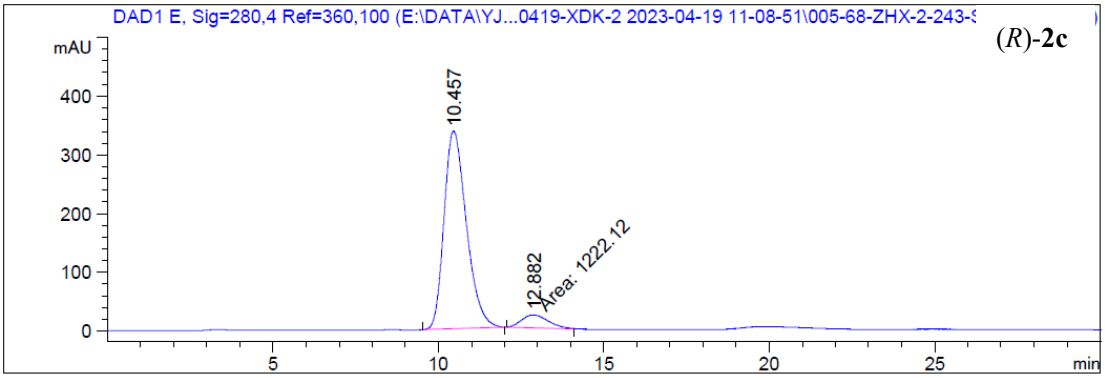
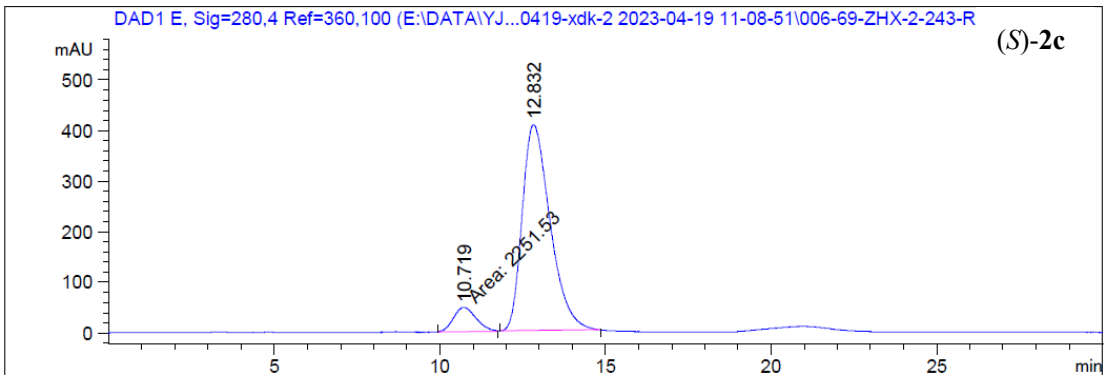


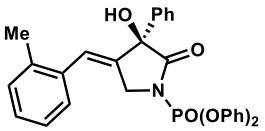
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.457	BV R	0.5522	1.58232e4	337.33197	92.8302
2	12.882	MM	0.9188	1222.12036	22.16956	7.1698



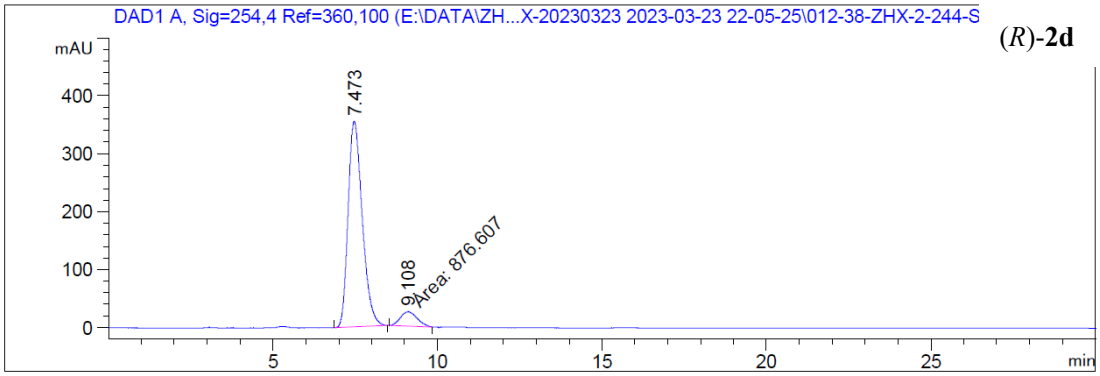
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.719	MM	0.7834	2251.53320	47.89946	8.6065
2	12.832	BV R	0.6889	2.39092e4	406.95715	91.3935



2d

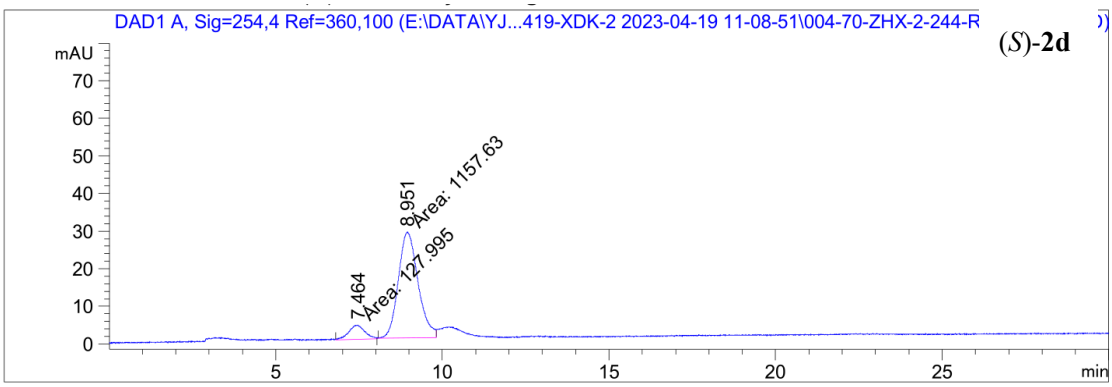
(*R*)-**2d**



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

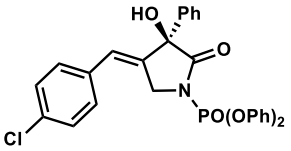
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.473	BV R	0.3726	1.06446e4	355.17755	92.3914
2	9.108	MM	0.5896	876.60706	24.78147	7.6086

(*S*)-**2d**

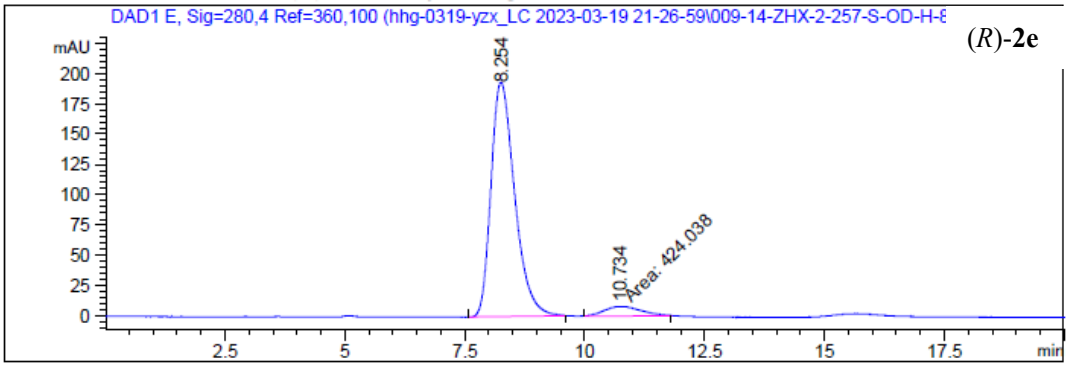


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.464	MM	0.5525	127.99550	3.86116	9.9559
2	8.951	MF	0.6853	1157.62988	28.15346	90.0441

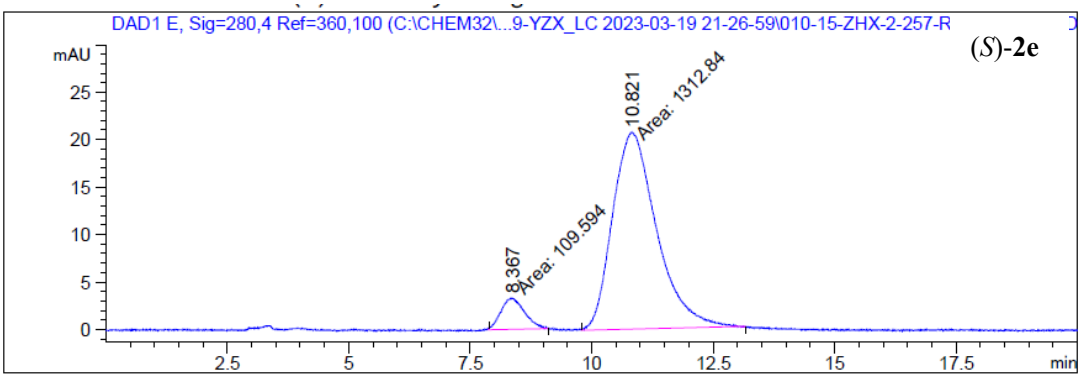


2e



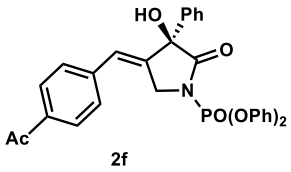
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.254	VV R	0.4075	6646.92480	193.37662	94.0031
2	10.734	MM	0.9034	424.03769	7.82281	5.9969



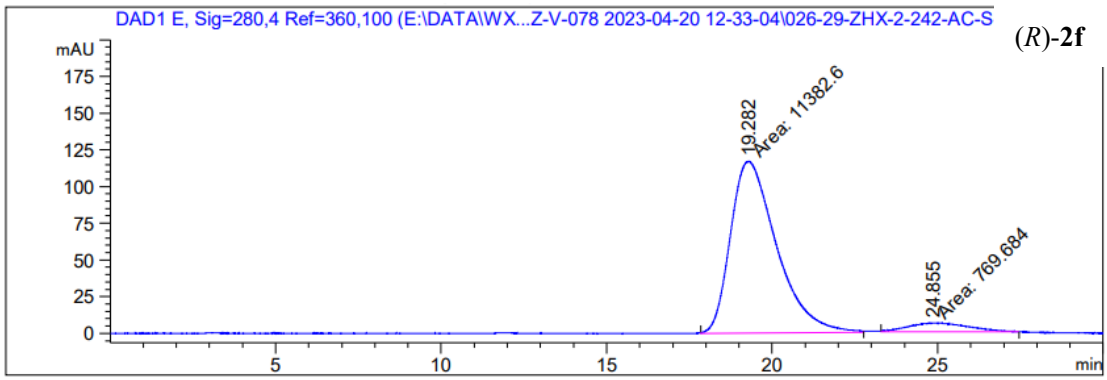
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.367	MM	0.5570	109.59396	3.27942	7.7047
2	10.821	MM	1.0551	1312.83972	20.73817	92.2953



2f

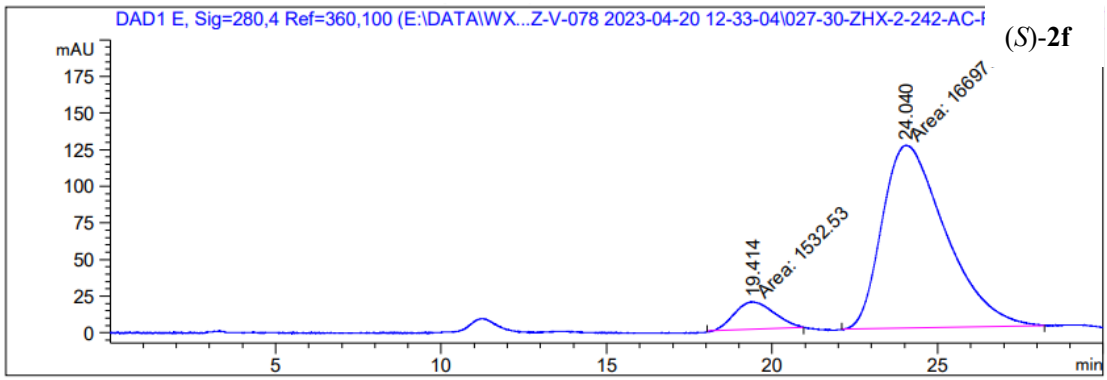
(*R*)-**2f**



Signal 1: DAD1 E, Sig=280,4 Ref=360,100

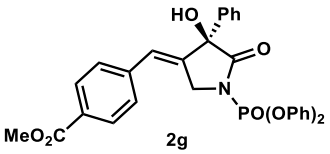
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.282	MM	1.6183	1.13826e4	117.22636	93.6663
2	24.855	MM	2.1248	769.68439	6.03732	6.3337

(*S*)-**2f**

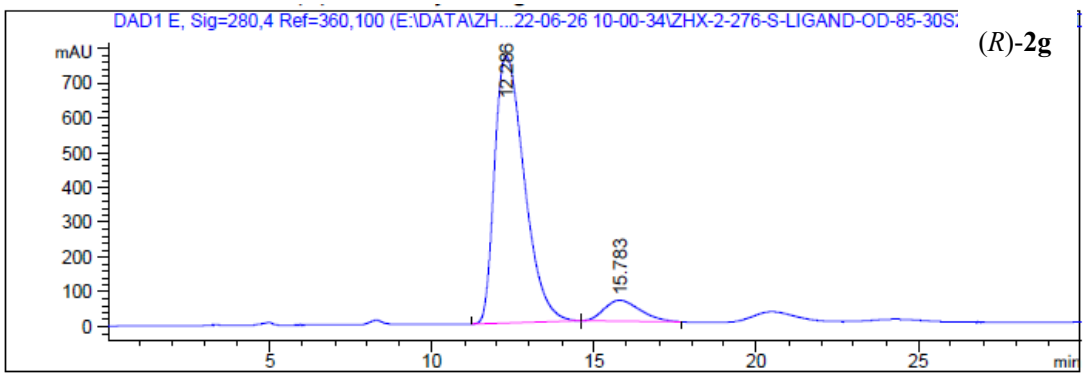


Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.414	MM	1.3761	1532.52966	18.56092	8.4065
2	24.040	MM	2.2296	1.66979e4	124.82070	91.5935



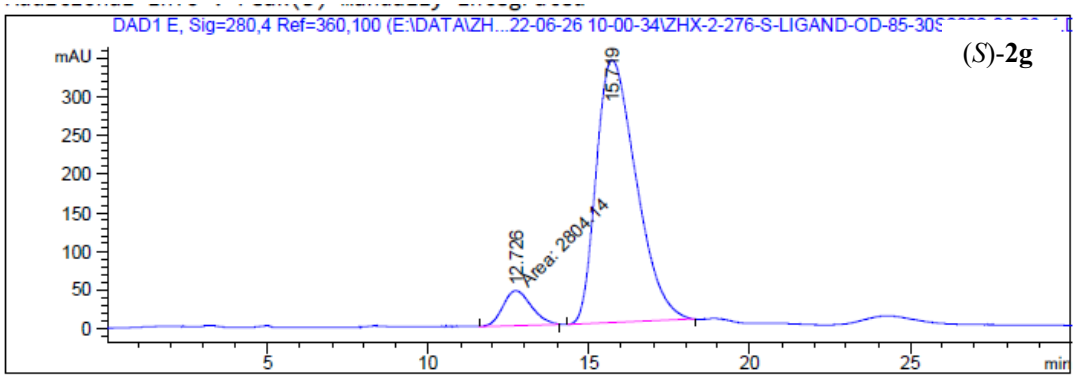
2g



(*R*)-**2g**

Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.286	BV R	0.7474	4.89709e4	768.01099	91.3186
2	15.783	BV R	0.9077	4655.54443	60.03323	8.6814

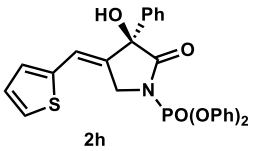


(*S*)-**2g**

Signal 1: DAD1 E, Sig=280,4 Ref=360,100

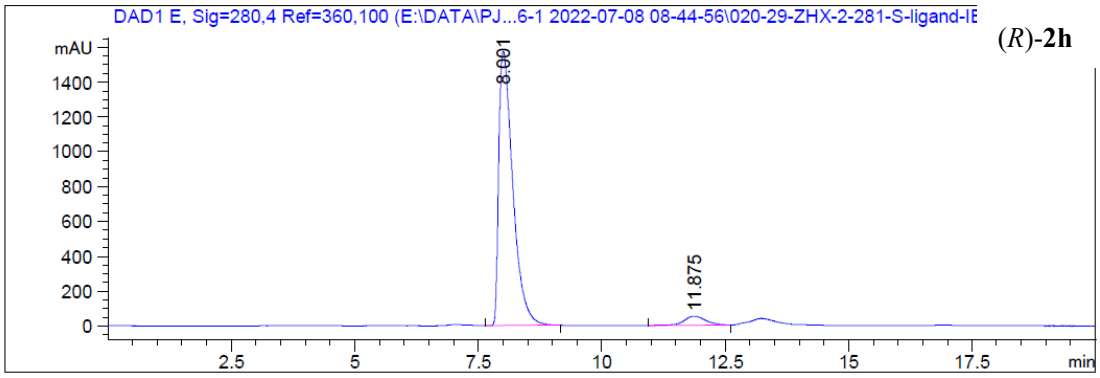
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.726	MM	1.0288	2804.14185	45.42743	8.6837
2	15.719	VV R	1.0127	2.94879e4	340.73651	91.3163

Totals :



2h

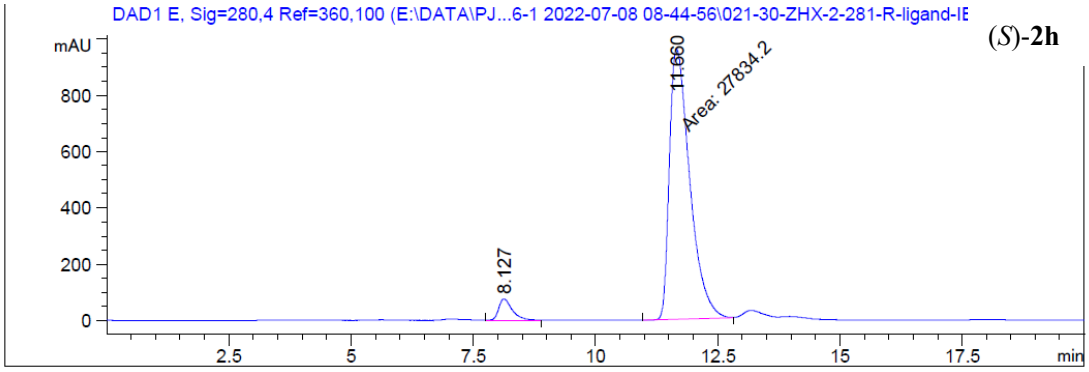
(*R*)-**2h**



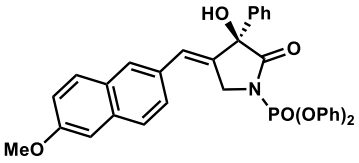
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.001	VV R	0.2339	3.11606e4	1574.20496	95.0971
2	11.875	VV R	0.3608	1606.55029	52.38714	4.9029

(*S*)-**2h**

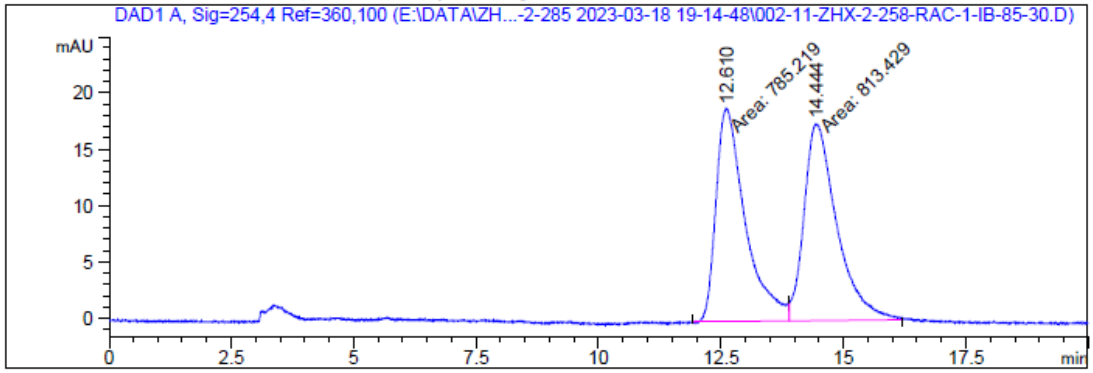


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.127	VV R	0.2289	1434.59998	75.58652	4.9015
2	11.660	MF	0.4827	2.78342e4	961.01709	95.0985



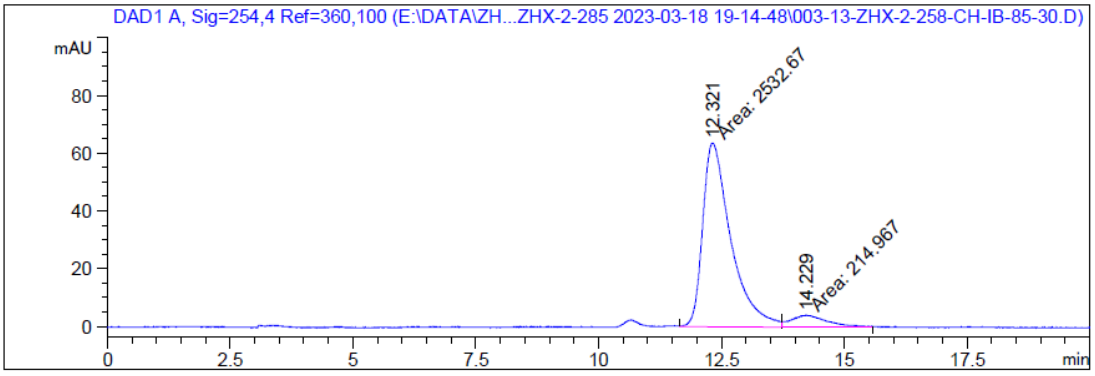
2i

Additional info : Peak(s) manually integrated



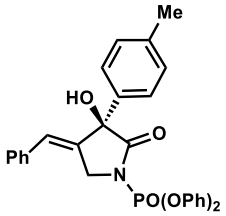
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.610	MF	0.6922	785.21936	18.90717	49.1177
2	14.444	FM	0.7757	813.42896	17.47756	50.8823

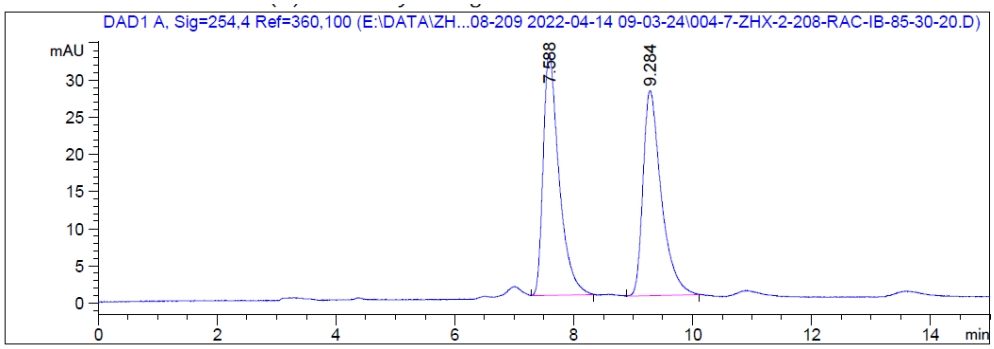


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.321	MF	0.6641	2532.67212	63.56120	92.1763
2	14.229	FM	0.8773	214.96744	4.08410	7.8237

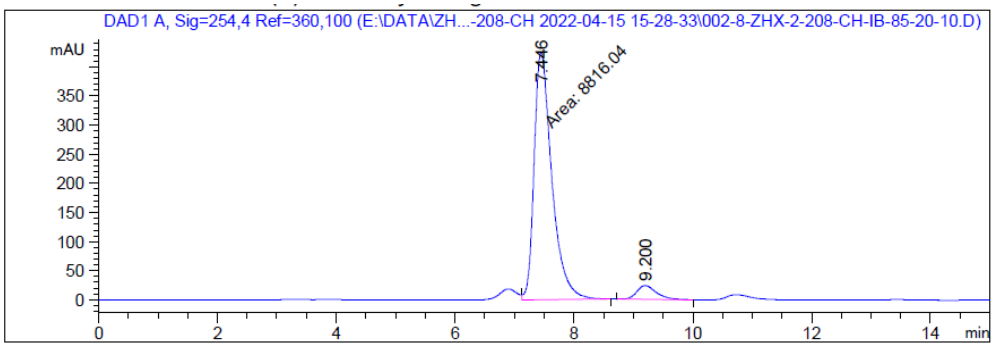


2j

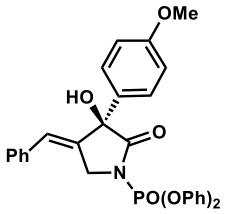


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.588	BB	0.2542	603.46094	32.48744	50.5808
2	9.284	BB	0.2742	589.60199	27.60595	49.4192



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.446	FM	0.3463	8816.04199	424.33841	94.1097
2	9.200	VB R	0.2745	551.79193	23.89024	5.8903



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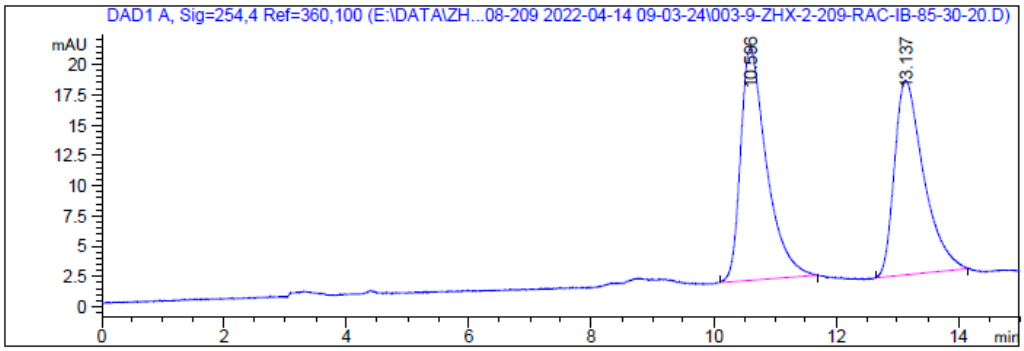
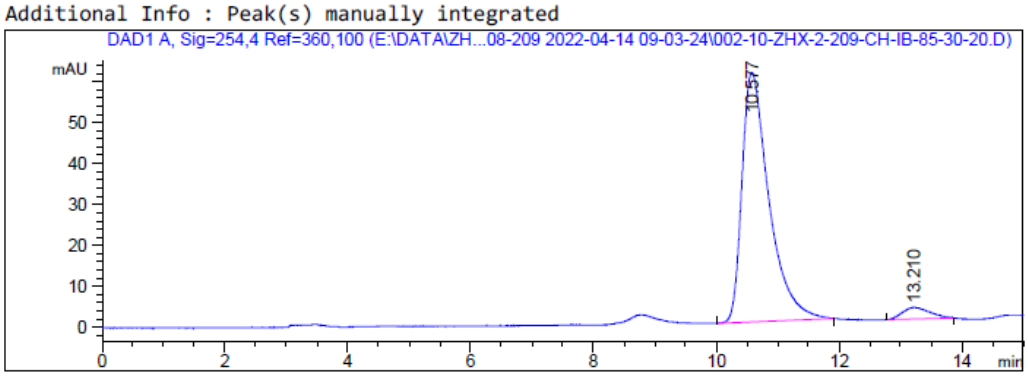


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

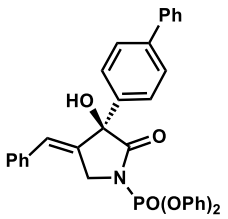
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.596	BB	0.3468	565.01715	19.14369	51.5227
2	13.137	BB	0.3891	531.61926	16.08514	48.4773

Additional Info : Peak(s) manually integrated

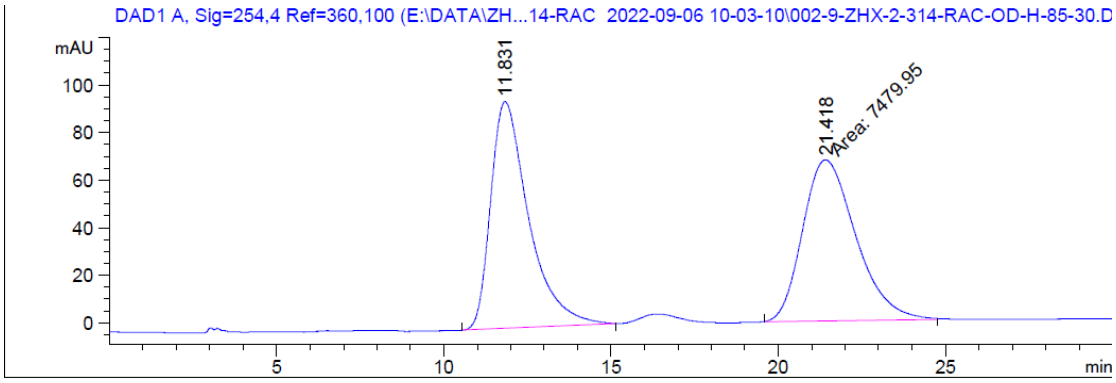


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.577	BB	0.3680	1862.24414	60.85852	95.3839
2	13.210	BB	0.3682	90.12354	2.89102	4.6161

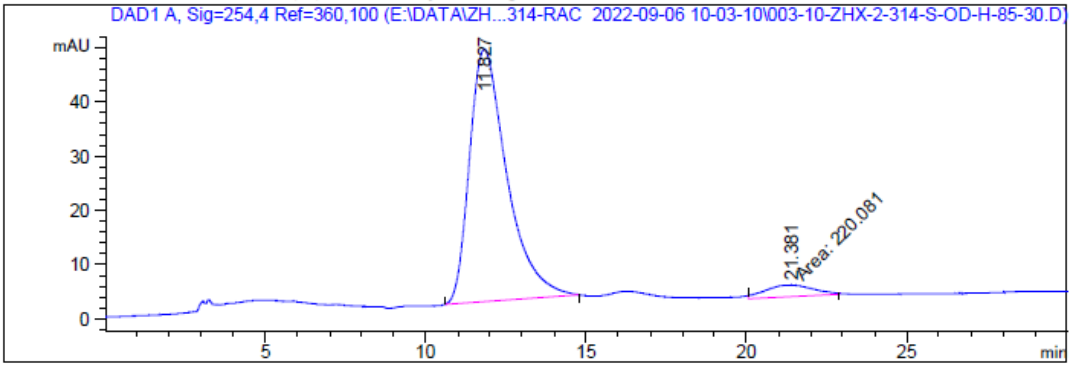


2l



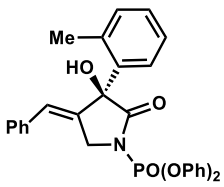
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.831	BB	0.9276	7516.10352	95.19493	50.1205
2	21.418	MM	1.8414	7479.95361	67.70033	49.8795

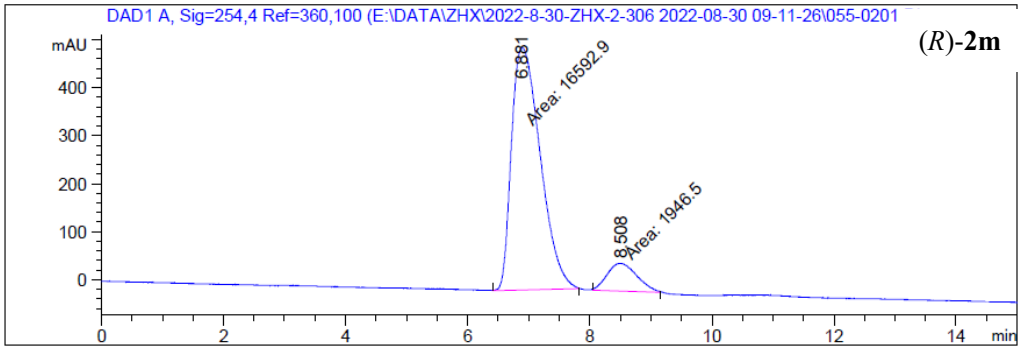


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.827	BB	0.9524	3774.10425	46.49958	94.4900
2	21.381	MM	1.7247	220.08112	2.12675	5.5100

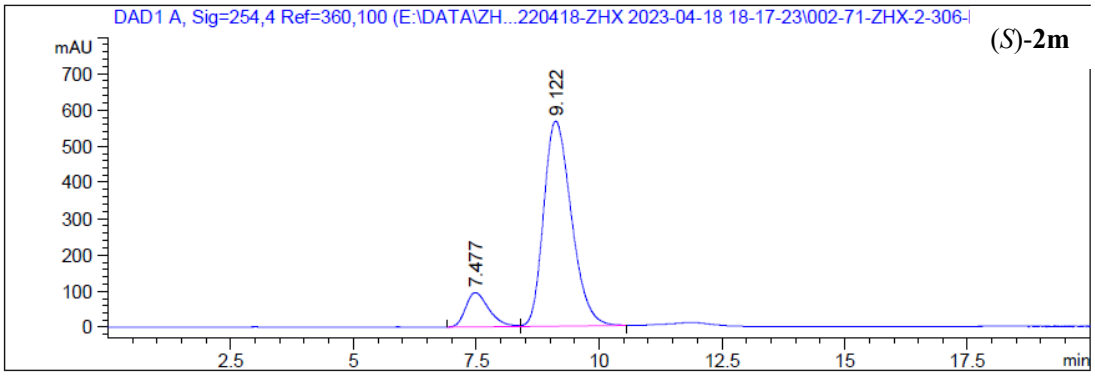


2m



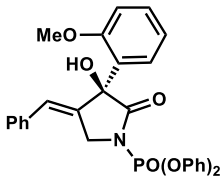
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.881	MM	0.5474	1.65929e4	505.20212	89.5007
2	8.508	MM	0.5614	1946.50195	57.78852	10.4993

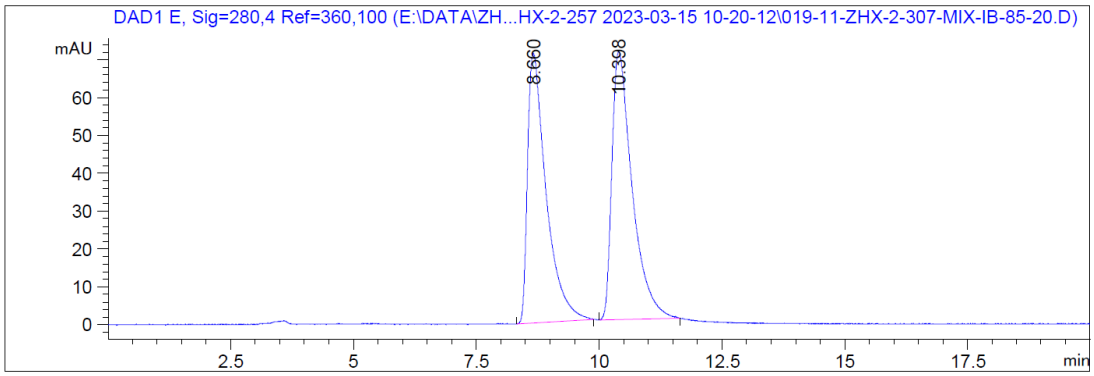


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.477	VV R	0.3835	3088.53711	94.57771	12.1936
2	9.122	VV R	0.4615	2.22406e4	565.91272	87.8064

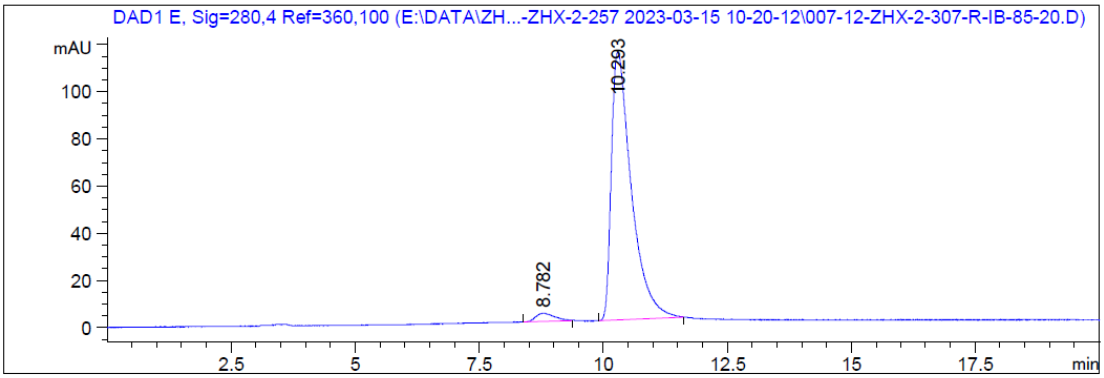


2n



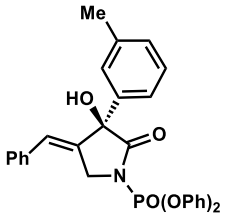
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.660	BV R	0.3145	1877.95691	71.24891	48.0755
2	10.398	BV R	0.3400	2028.30872	70.75235	51.9245

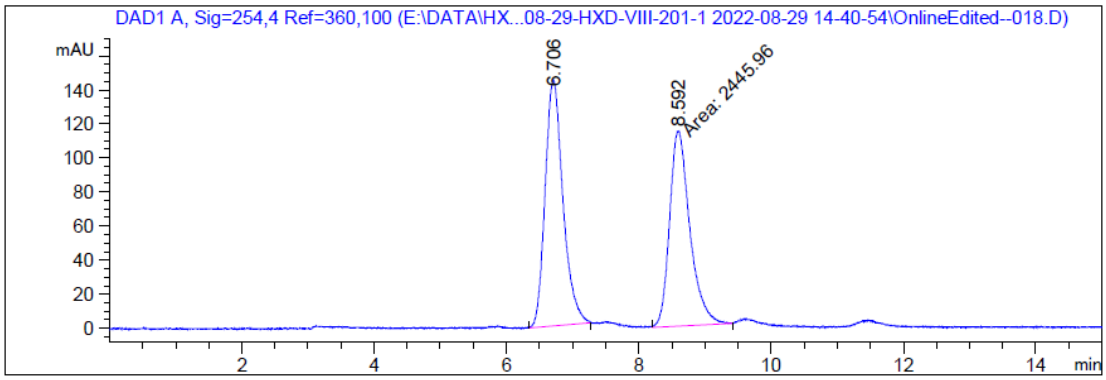


Signal 1: DAD1 E, Sig=280,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.782	BV R	0.3040	90.65819	3.51372	2.7694
2	10.293	BV R	0.3401	3182.91821	113.53058	97.2306

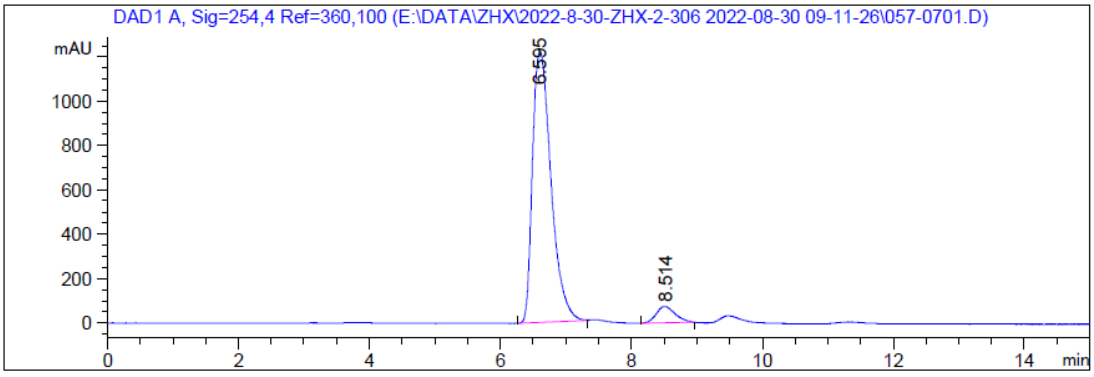


2o



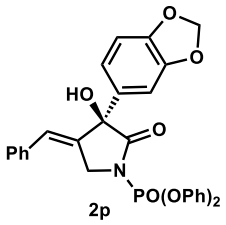
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.706	VV R	0.2235	2711.19629	144.45935	52.5715
2	8.592	MM	0.3555	2445.96118	114.66341	47.4285

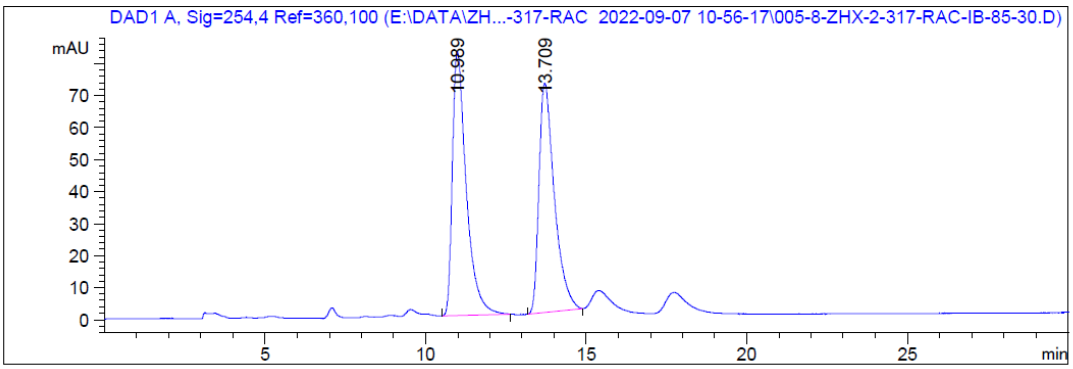


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.595	VV R	0.2317	2.40421e4	1223.74805	94.2014
2	8.514	VV R	0.2371	1479.91357	73.74467	5.7986

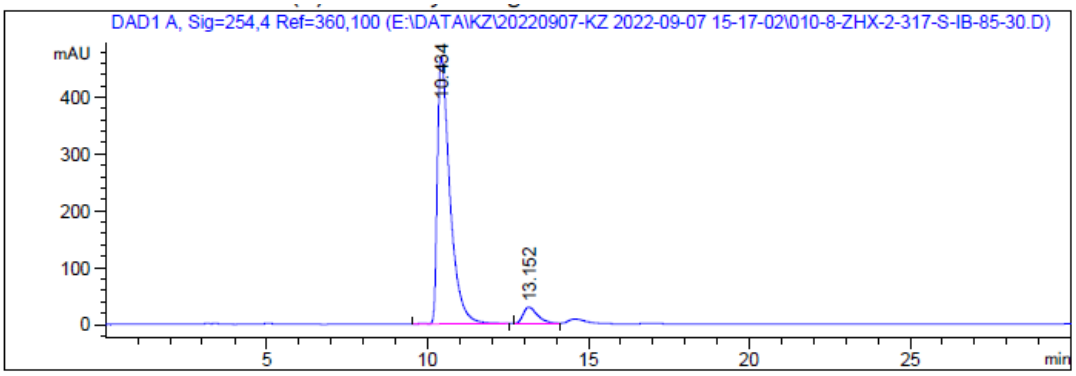


2p



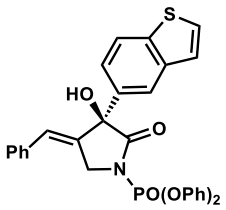
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.989	BB	0.4296	2483.10938	82.61861	50.9151
2	13.709	BB	0.4527	2393.85400	71.67513	49.0849

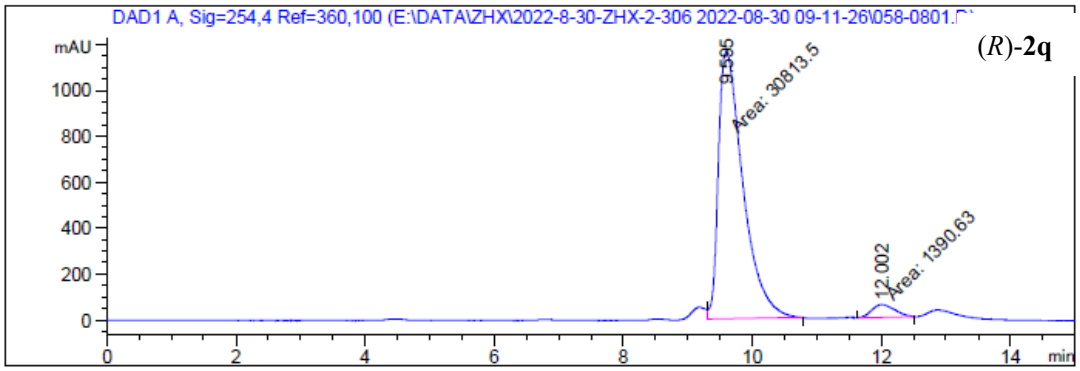


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.434	VB R	0.3973	1.27867e4	470.80933	93.4929
2	13.152	BB	0.3808	889.95807	28.93553	6.5071



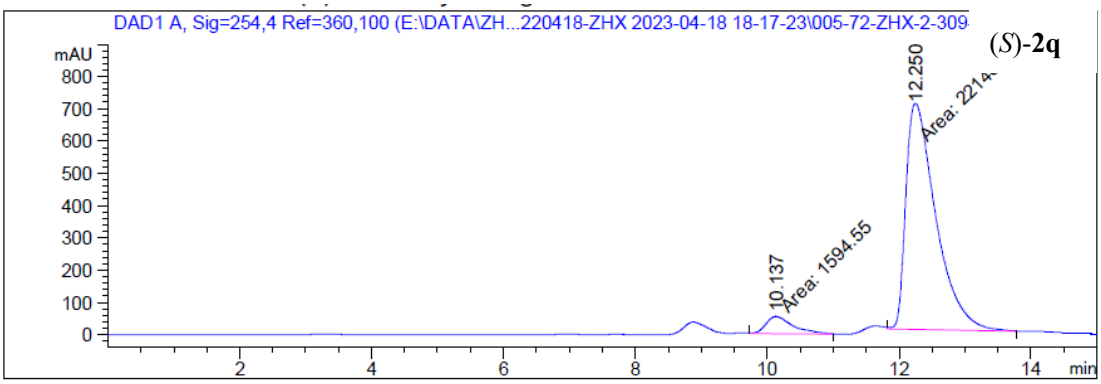
2q



(*R*)-**2q**

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

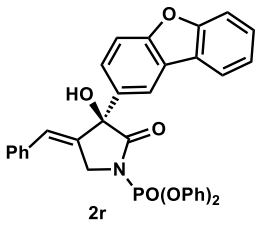
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.595	FM	0.4405	3.08135e4	1165.90186	95.6818
2	12.002	MM	0.4116	1390.62781	56.31136	4.3182



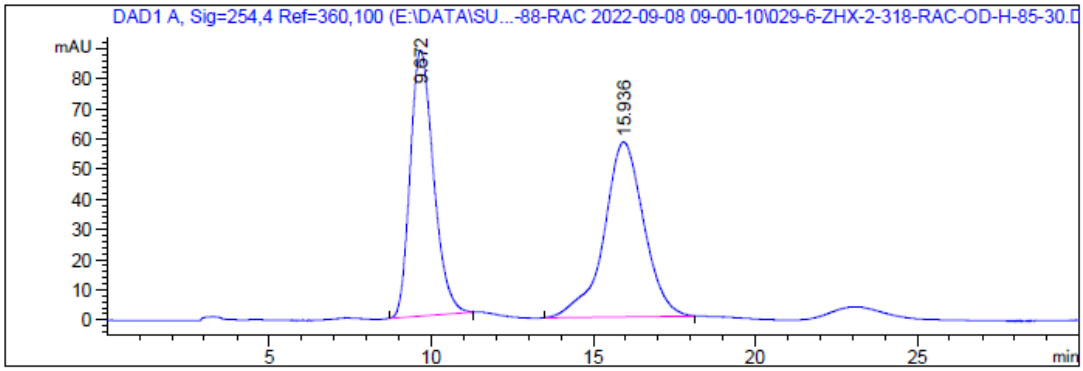
(*S*)-**2q**

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.137	MM	0.4914	1594.55457	54.08352	6.7159
2	12.250	MM	0.5262	2.21484e4	701.45410	93.2841

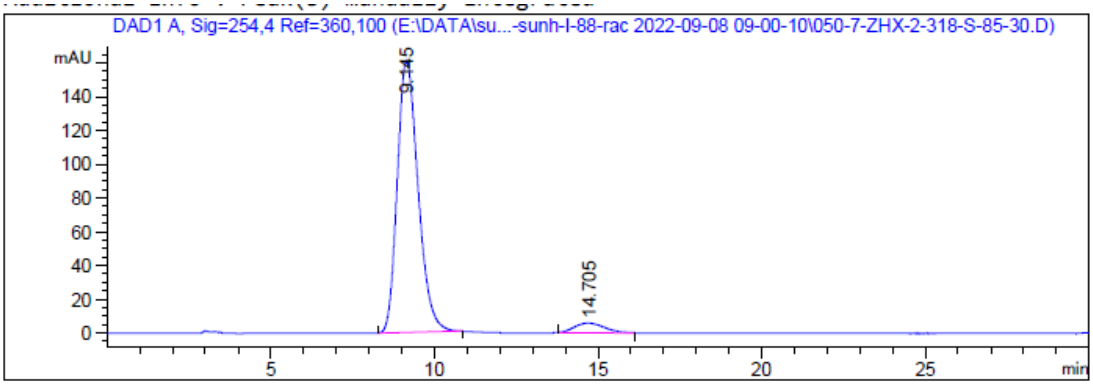


2r



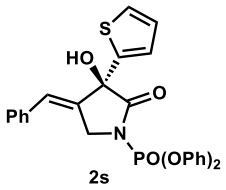
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.672	BB	0.6001	4406.70410	87.94814	47.0429
2	15.936	BB	1.0022	4960.70605	57.95118	52.9571

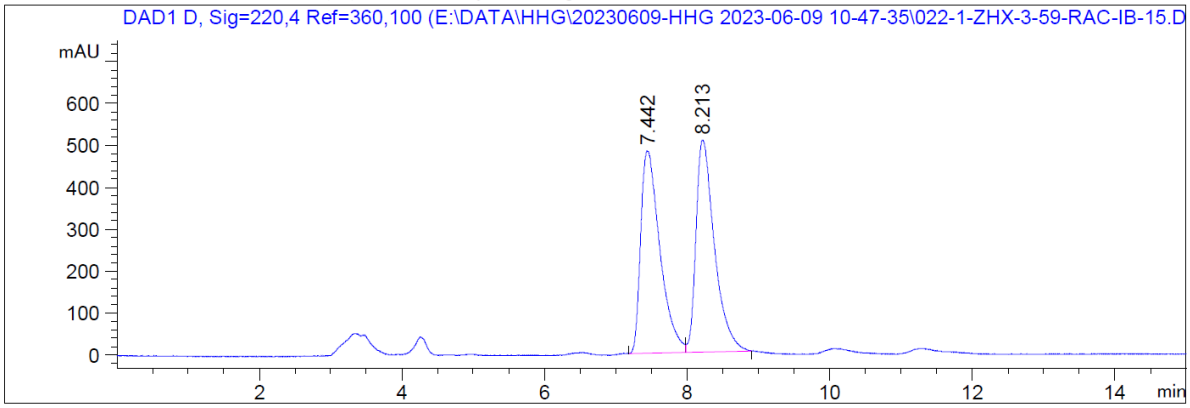


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.145	BB	0.6338	7111.06543	160.83282	95.1745
2	14.705	BB	0.7350	360.54550	5.74233	4.8255

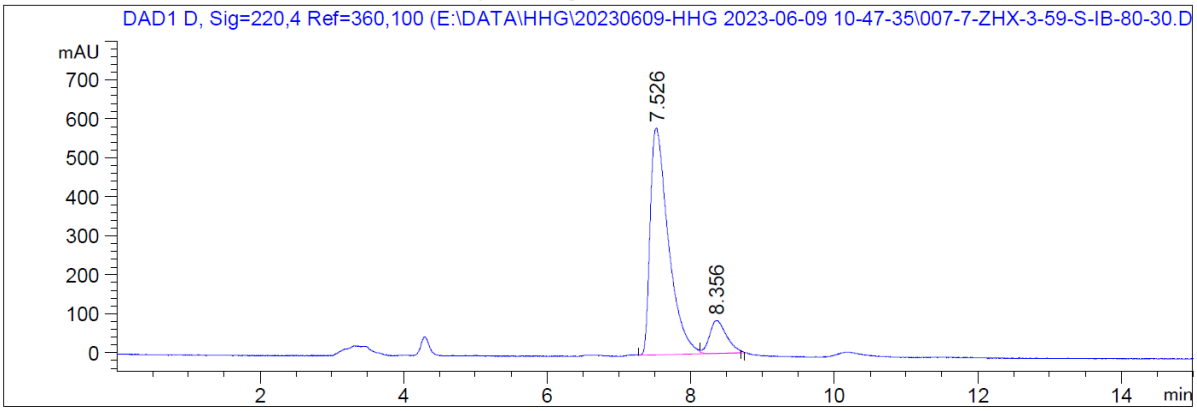


2s



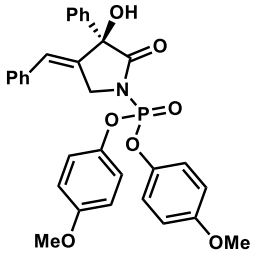
Signal 1: DAD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.442	VV R	0.2248	9075.09961	482.80521	49.8252
2	8.213	VV R	0.2172	9138.77539	505.98129	50.1748

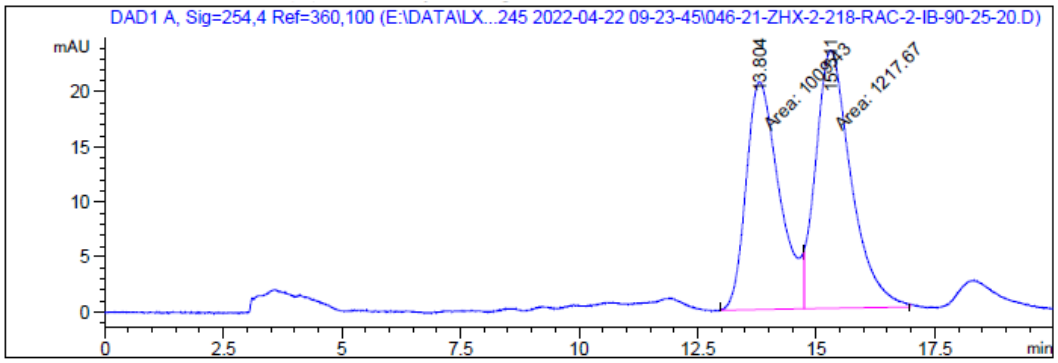


Signal 1: DAD1 D, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.526	BV R	0.2103	1.02888e4	582.96527	88.2516
2	8.356	VV E	0.1935	1369.68396	84.10990	11.7484

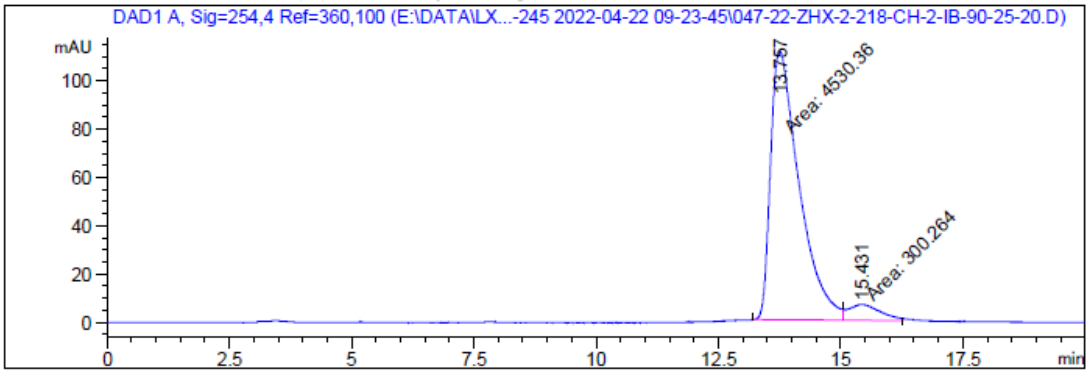


2t



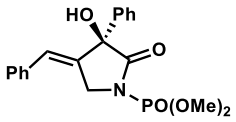
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.804	MF	0.8135	1009.43231	20.68173	45.3249
2	15.311	FM	0.8665	1217.66870	23.42100	54.6751

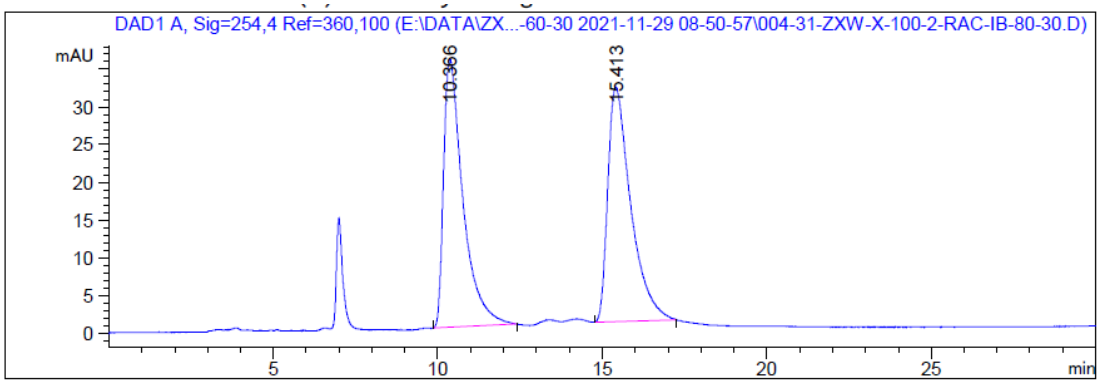


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.757	MF	0.6789	4530.35889	111.21449	93.7842
2	15.431	FM	0.7685	300.26407	6.51173	6.2158

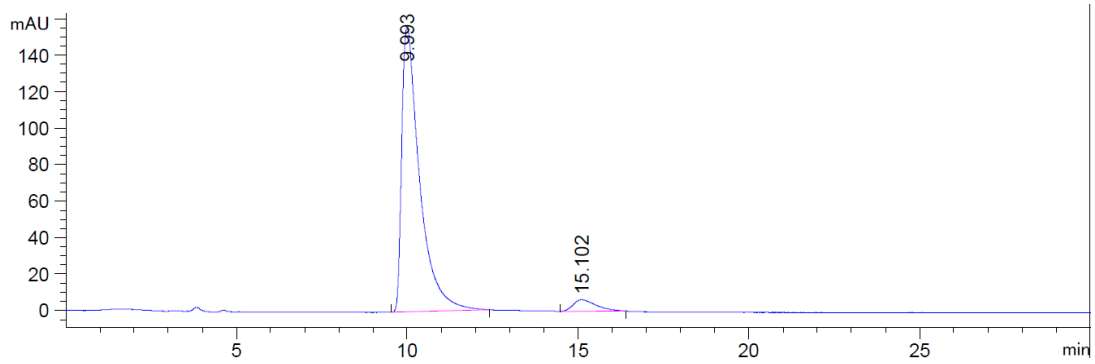


2u



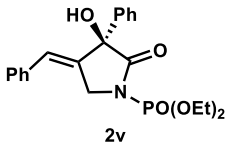
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.366	BB	0.5229	1458.55713	35.57013	49.1428
2	15.413	BB	0.5692	1509.44324	31.07320	50.8572

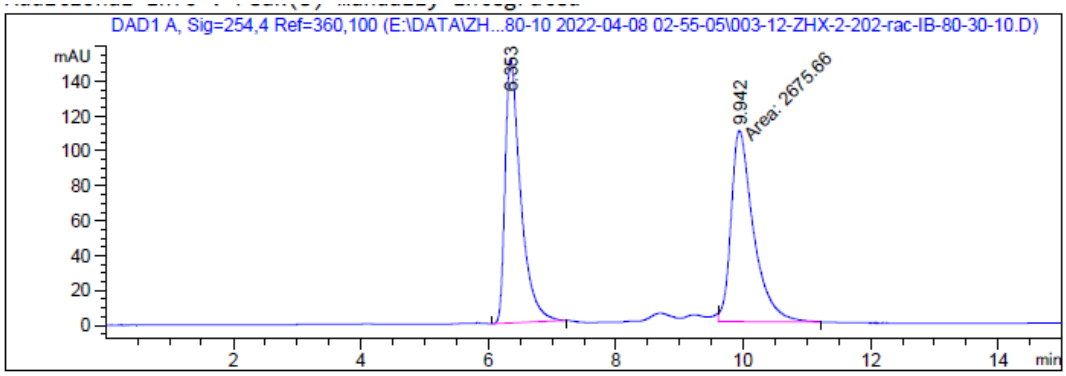


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.993	BB	0.5192	5689.43896	155.92778	95.0575
2	15.102	BB	0.5505	295.81943	6.29795	4.9425

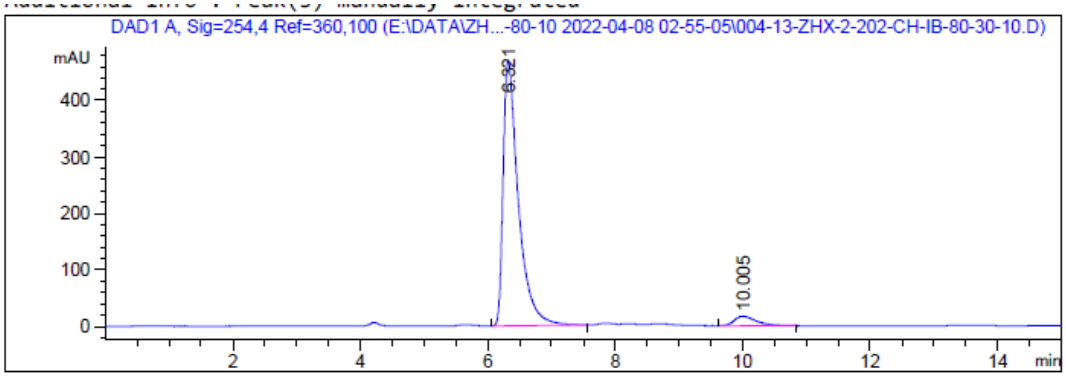


2v

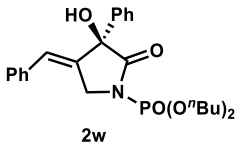


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

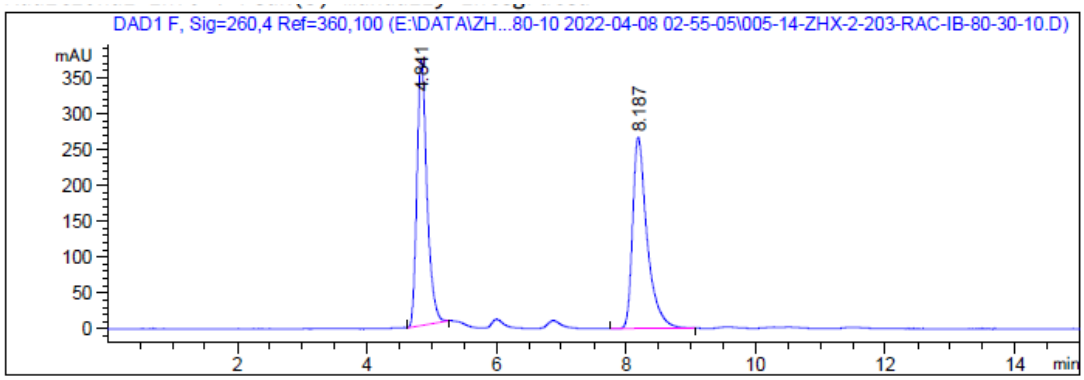
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.353	BB	0.2482	2558.74438	151.01503	48.8832
2	9.942	FM	0.4075	2675.66162	109.42923	51.1168



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.321	BB	0.2433	7772.64551	469.12244	95.0444
2	10.005	BB	0.2842	405.26199	16.84375	4.9556

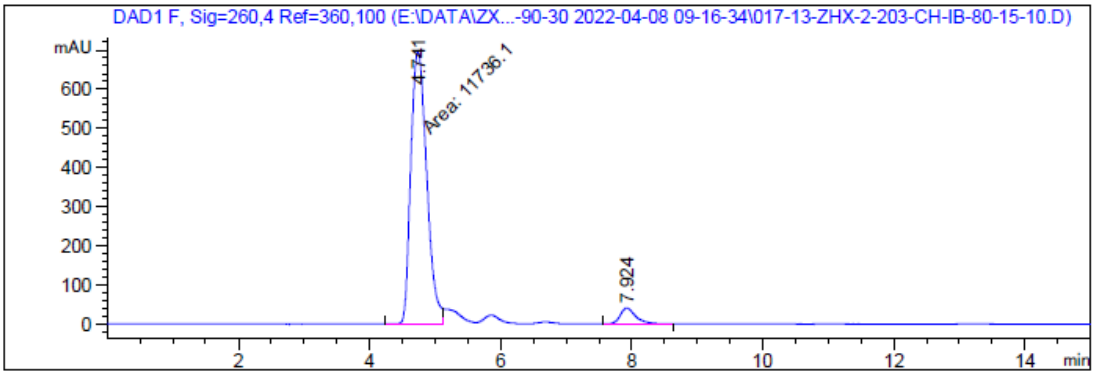


2w



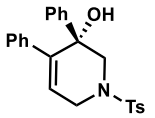
Signal 1: DAD1 F, Sig=260,4 Ref=360,100

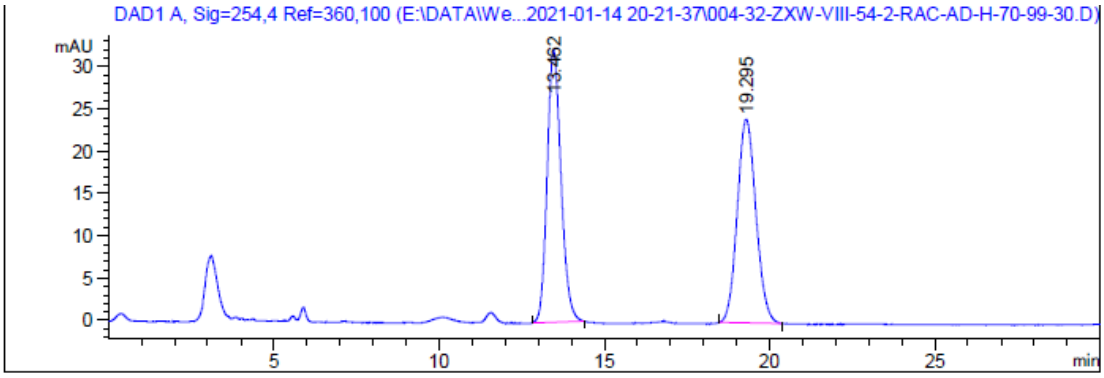
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.841	BB	0.1633	3992.69263	371.82065	49.0168
2	8.187	VB R	0.2296	4152.86865	266.75391	50.9832



Signal 1: DAD1 F, Sig=260,4 Ref=360,100

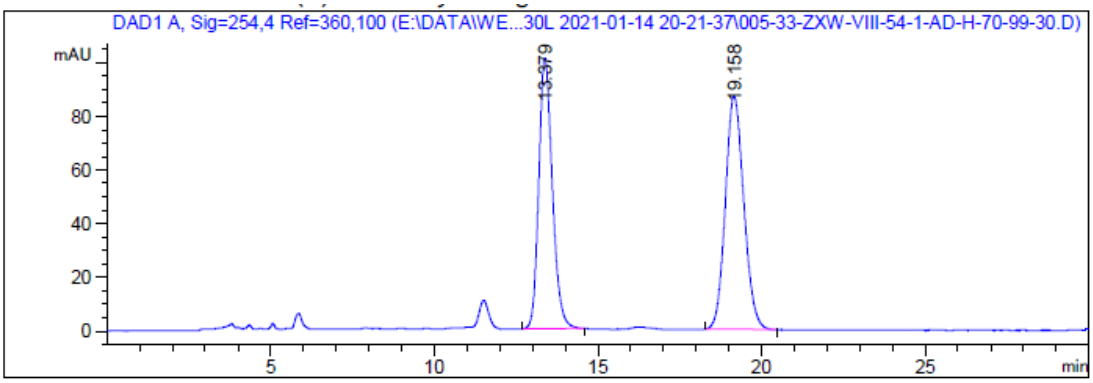
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.741	MF	0.2804	1.17361e4	697.62030	94.5899
2	7.924	BB	0.2299	671.25037	40.70617	5.4101





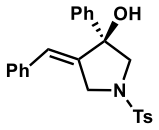
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

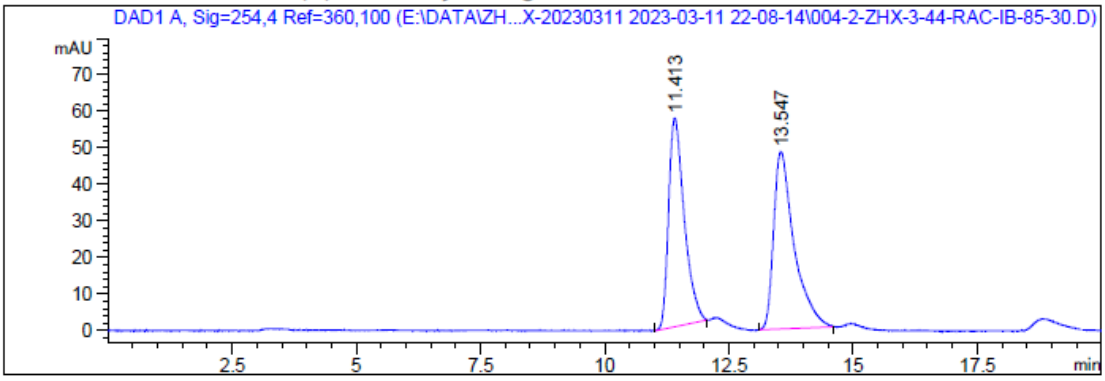
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.462	BB	0.3551	938.94525	32.25625	49.8454
2	19.295	BB	0.4604	944.76868	24.10011	50.1546



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

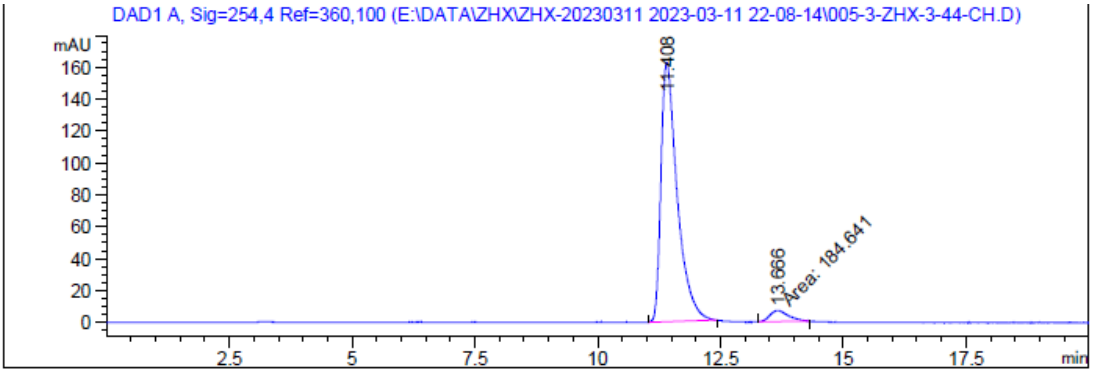
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.379	BB	0.4186	2902.73413	100.89861	45.9885
2	19.158	BB	0.5044	3409.12891	86.85380	54.0115





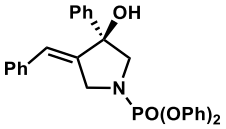
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

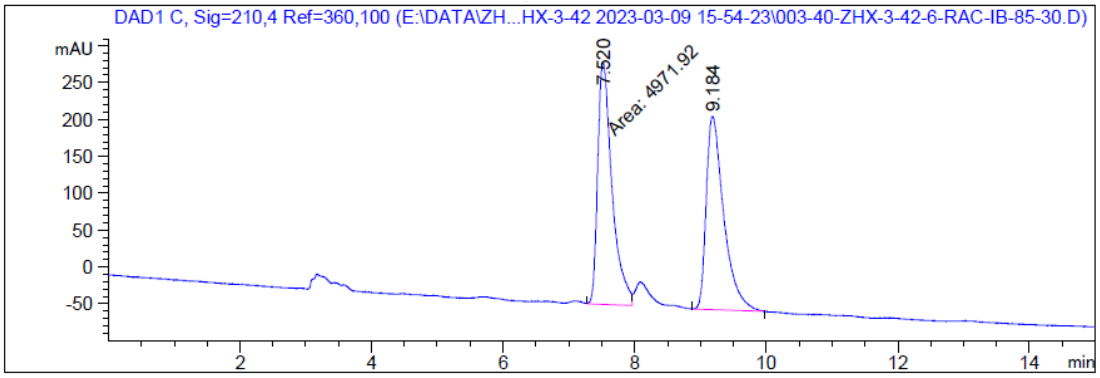
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.413	VV R	0.2592	1254.55286	57.12785	47.3720
2	13.547	VV R	0.3389	1393.74829	48.48606	52.6280



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

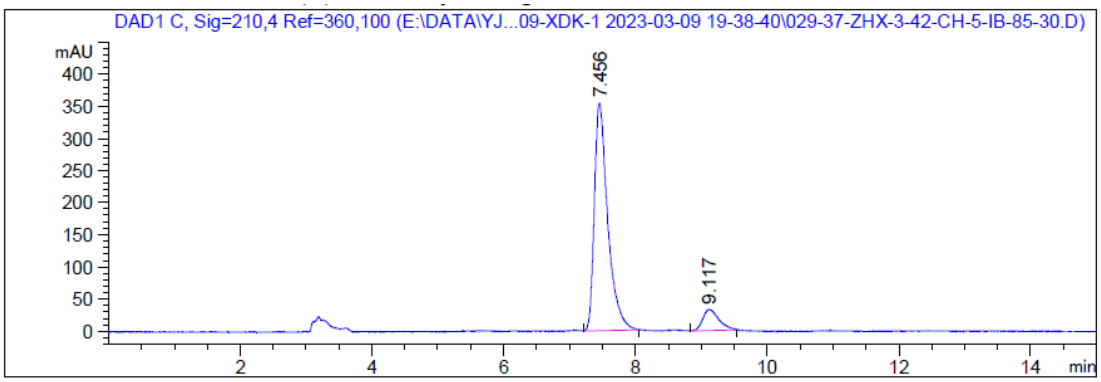
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.408	BV R	0.3161	3749.28003	162.57106	95.3064
2	13.666	MM	0.4417	184.64084	6.96734	4.6936





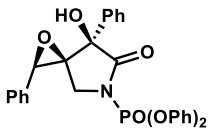
Signal 1: DAD1 C, Sig=210,4 Ref=360,100

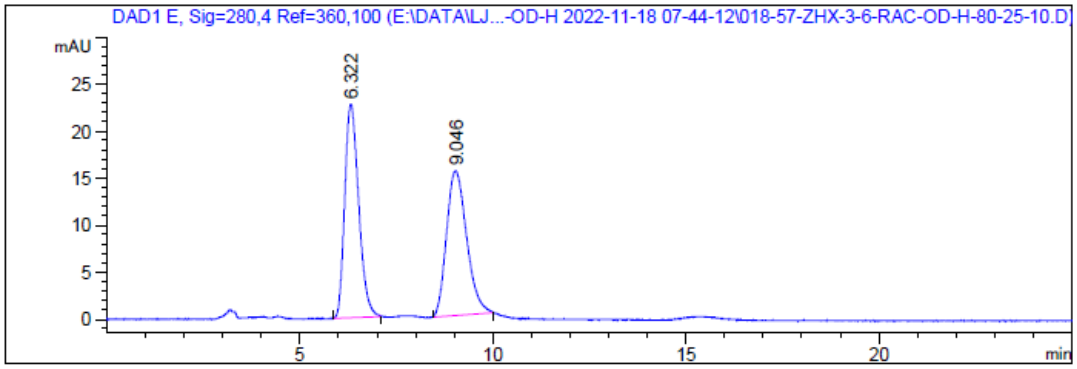
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.520	MF	0.2524	4971.91650	328.36710	50.5474
2	9.184	VV R	0.2234	4864.22412	262.21100	49.4526



Signal 1: DAD1 C, Sig=210,4 Ref=360,100

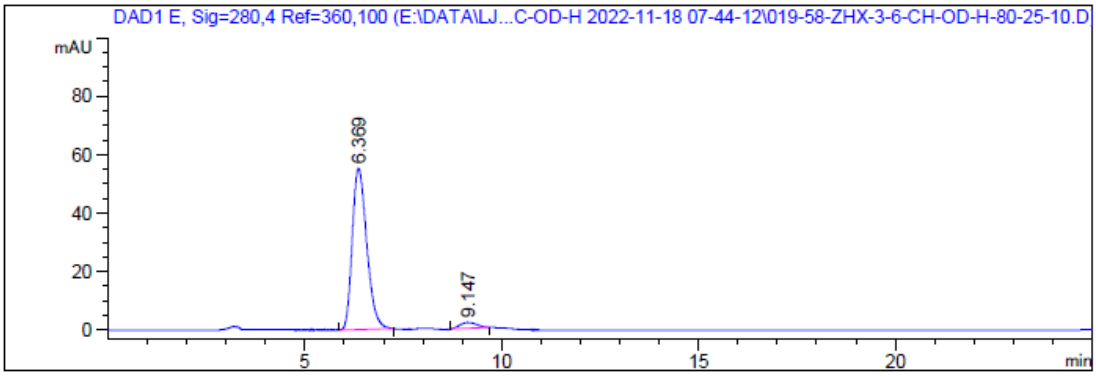
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.456	VV R	0.1686	5013.73096	354.22839	90.1594
2	9.117	VV R	0.1987	547.23175	32.87066	9.8406





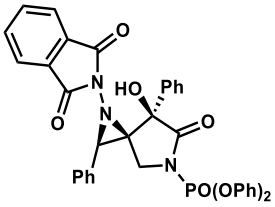
Signal 1: DAD1 E, Sig=280,4 Ref=360,100

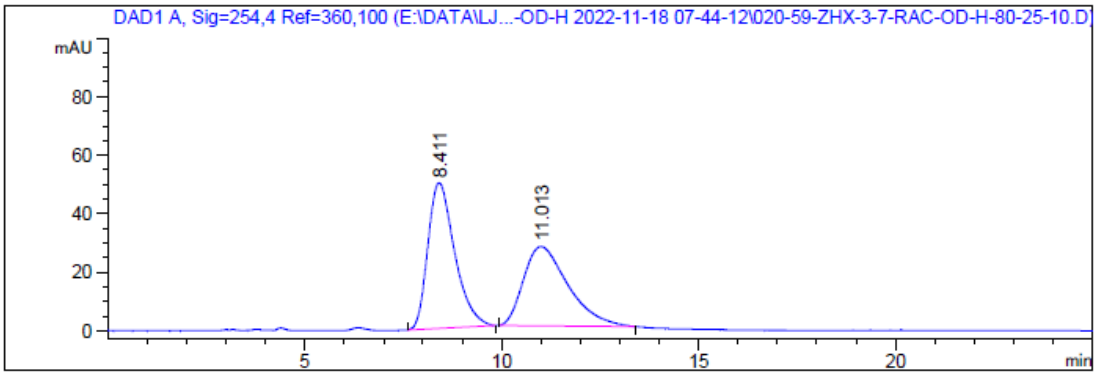
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.322	BB	0.3010	568.62793	22.67685	50.4775
2	9.046	BB	0.4259	557.86908	15.37144	49.5225



Signal 1: DAD1 E, Sig=280,4 Ref=360,100

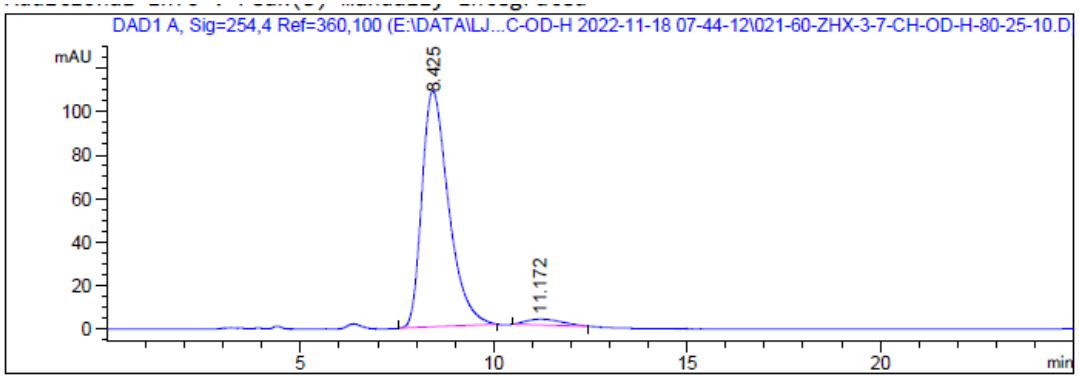
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.369	BB	0.3531	1412.99707	55.20432	95.7163
2	9.147	BB	0.3625	63.23706	2.05235	4.2837





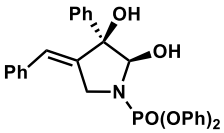
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

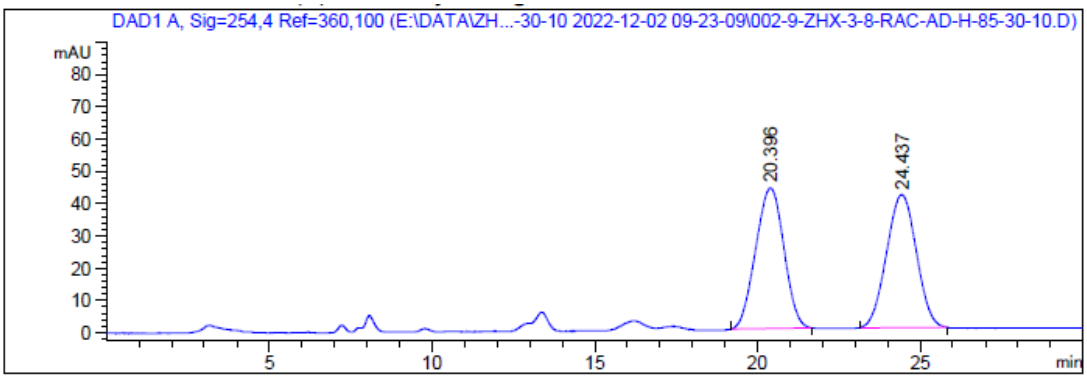
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.411	BB	0.5586	2354.98145	49.72205	52.4672
2	11.013	BB	0.9223	2133.50269	27.07479	47.5328



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

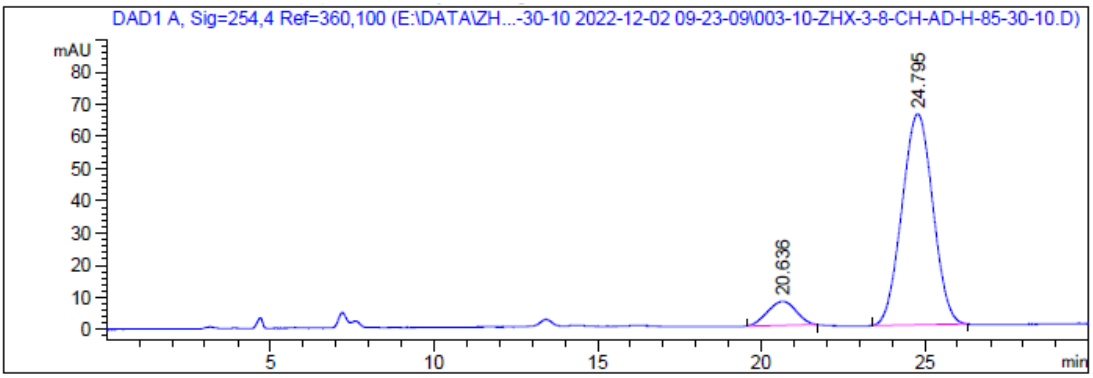
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.425	BB	0.5672	5213.52295	108.58469	96.7646
2	11.172	BB	0.7597	174.31798	2.68769	3.2354





Signal 1: DAD1 A, Sig=254,4 Ref=360,100

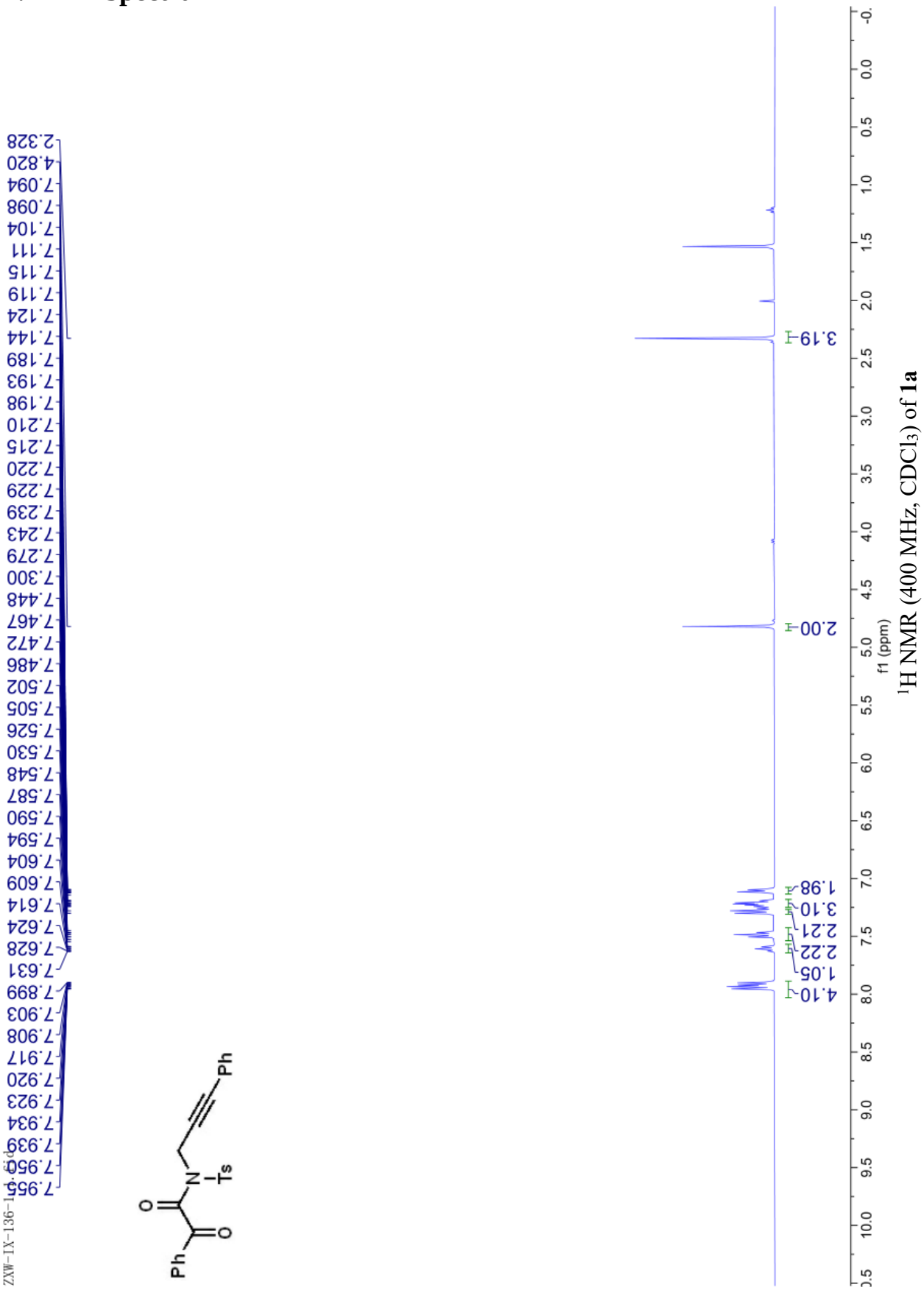
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.396	BB	0.7081	2631.04004	43.53609	50.0574
2	24.437	BB	0.7473	2625.00928	41.14862	49.9426



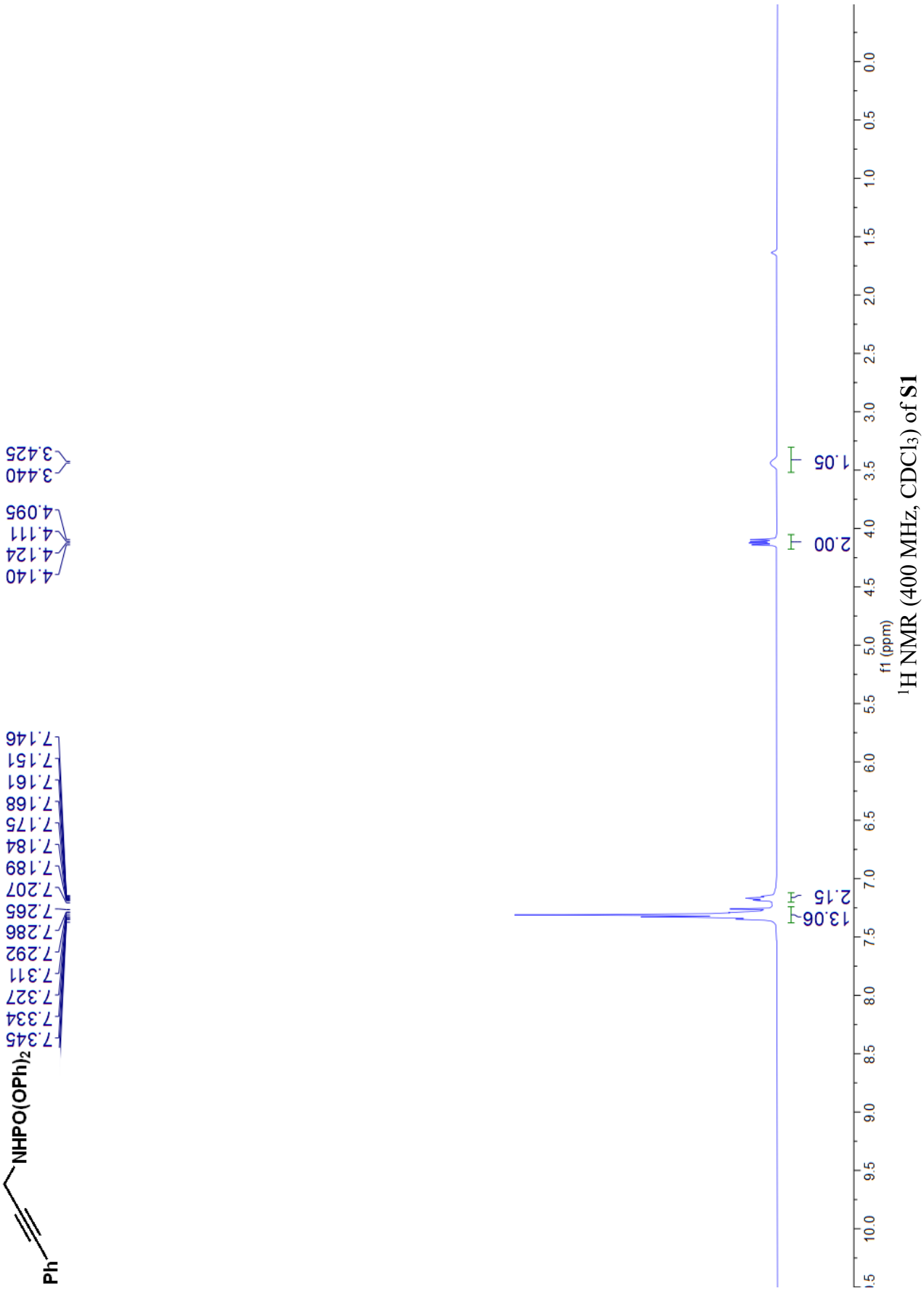
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.636	BB	0.7046	450.69247	7.49477	9.4662
2	24.795	BB	0.7702	4310.37695	65.54405	90.5338

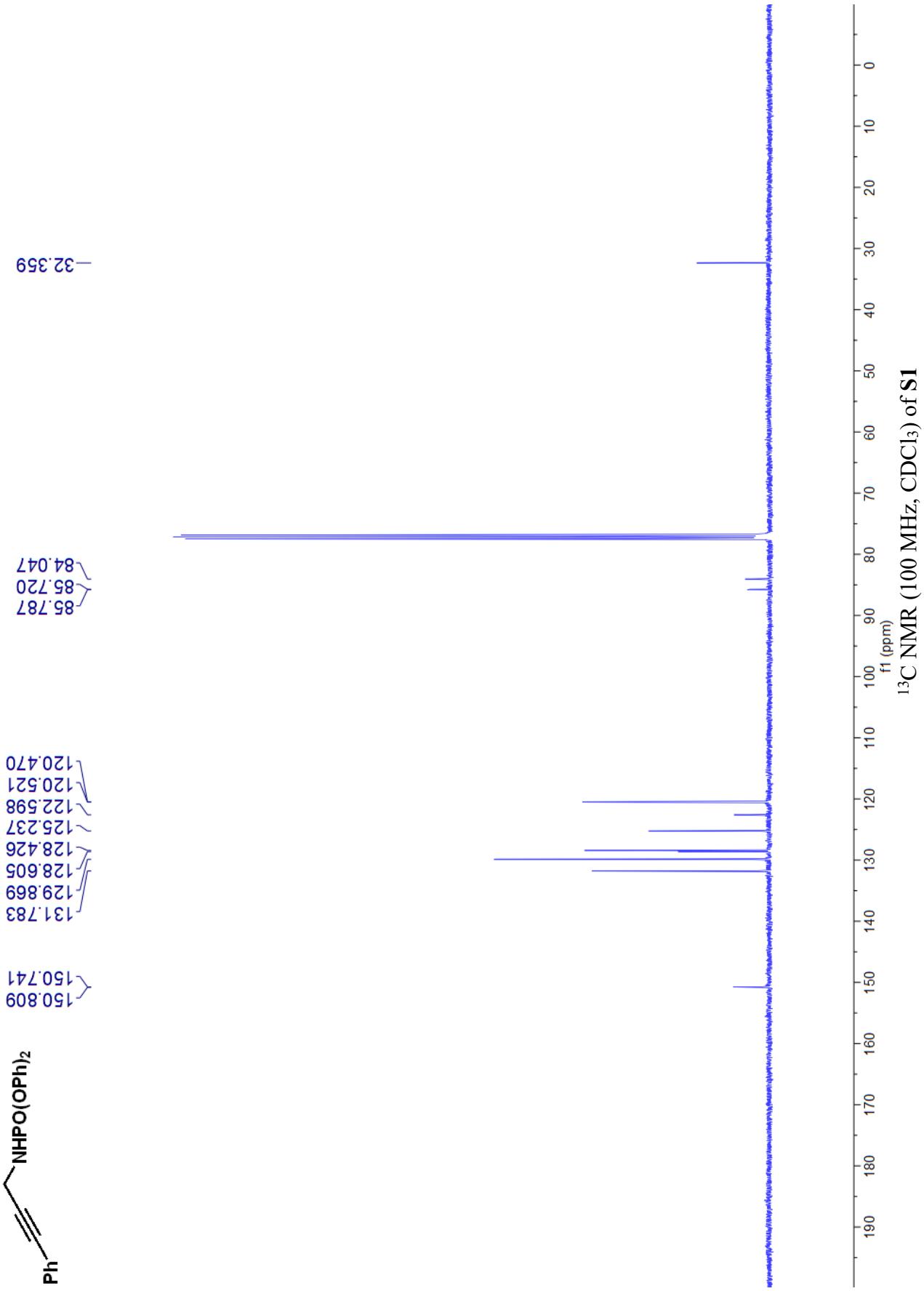
X. NMR Spectra



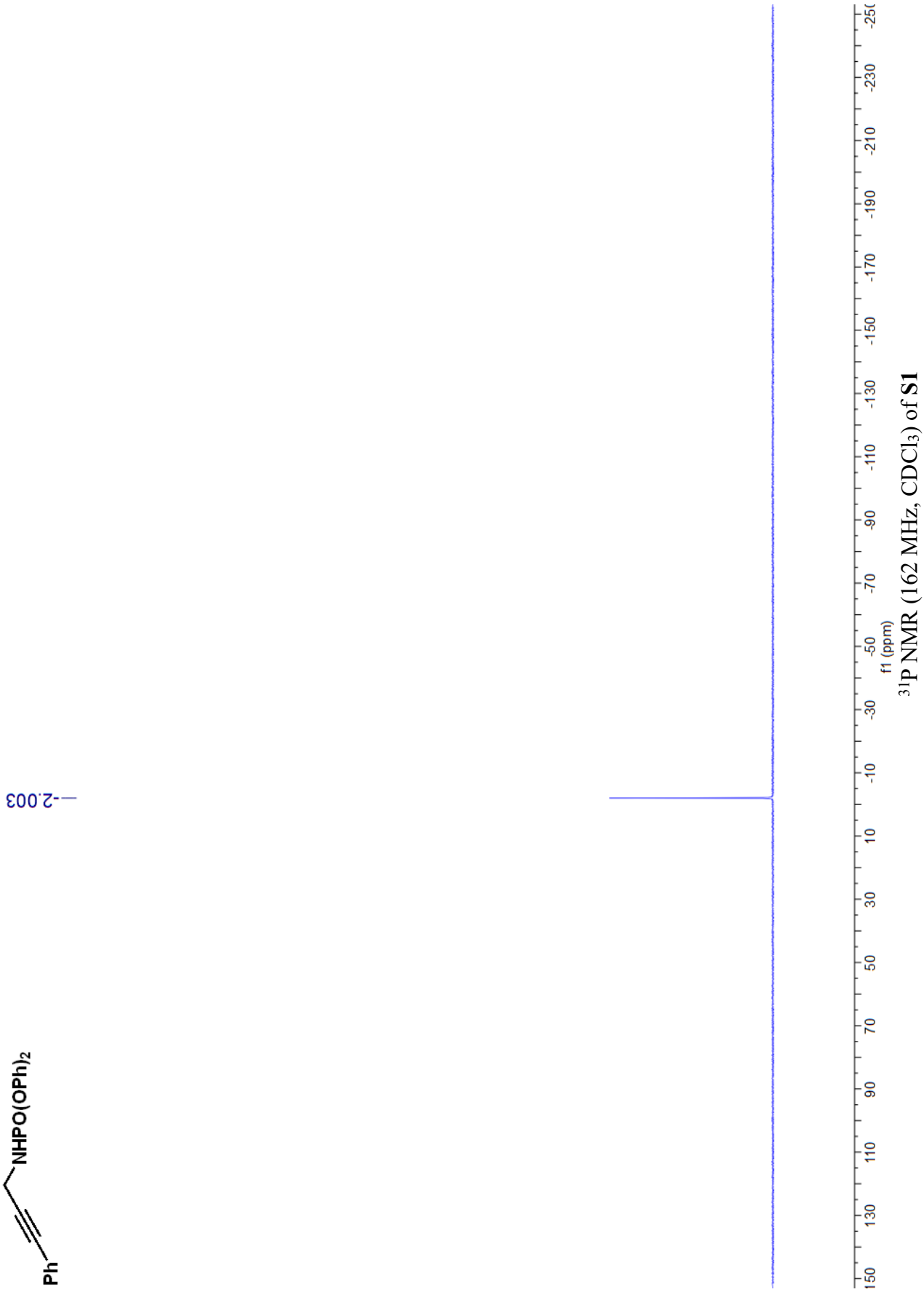
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



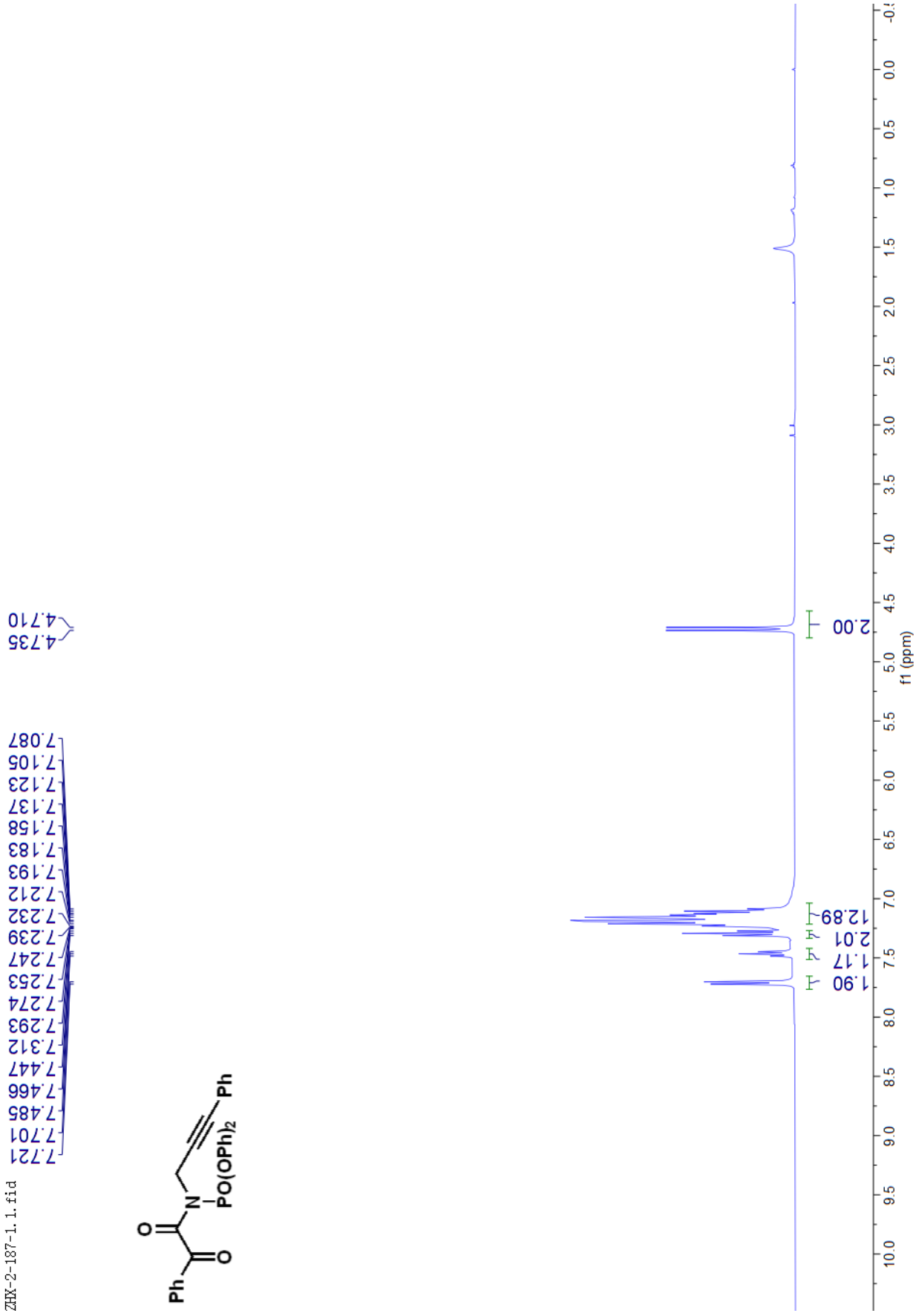
^{1}H NMR (400 MHz, $CDCl_3$) of **S1**



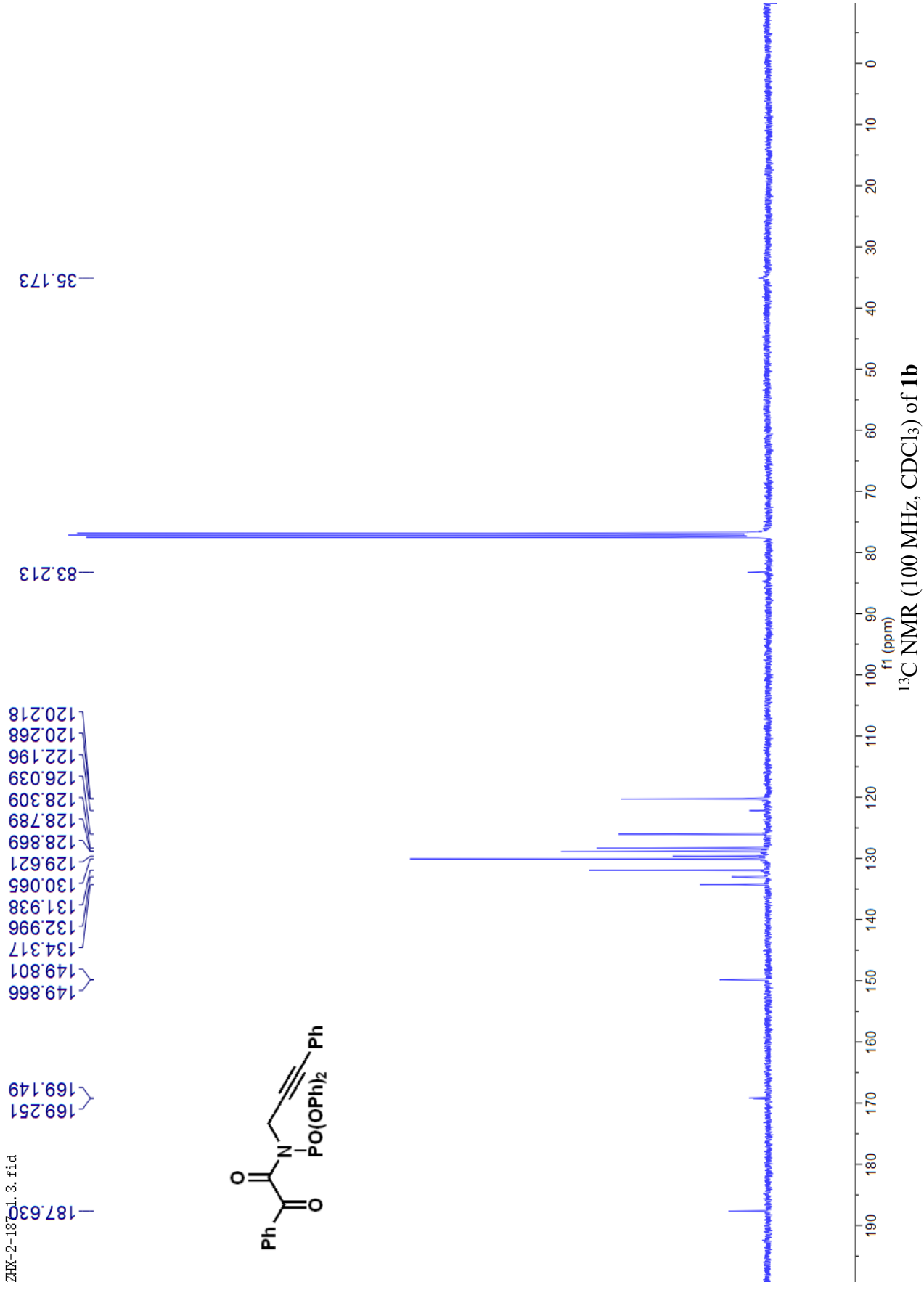
^{13}C NMR (100 MHz, $CDCl_3$) of **S1**



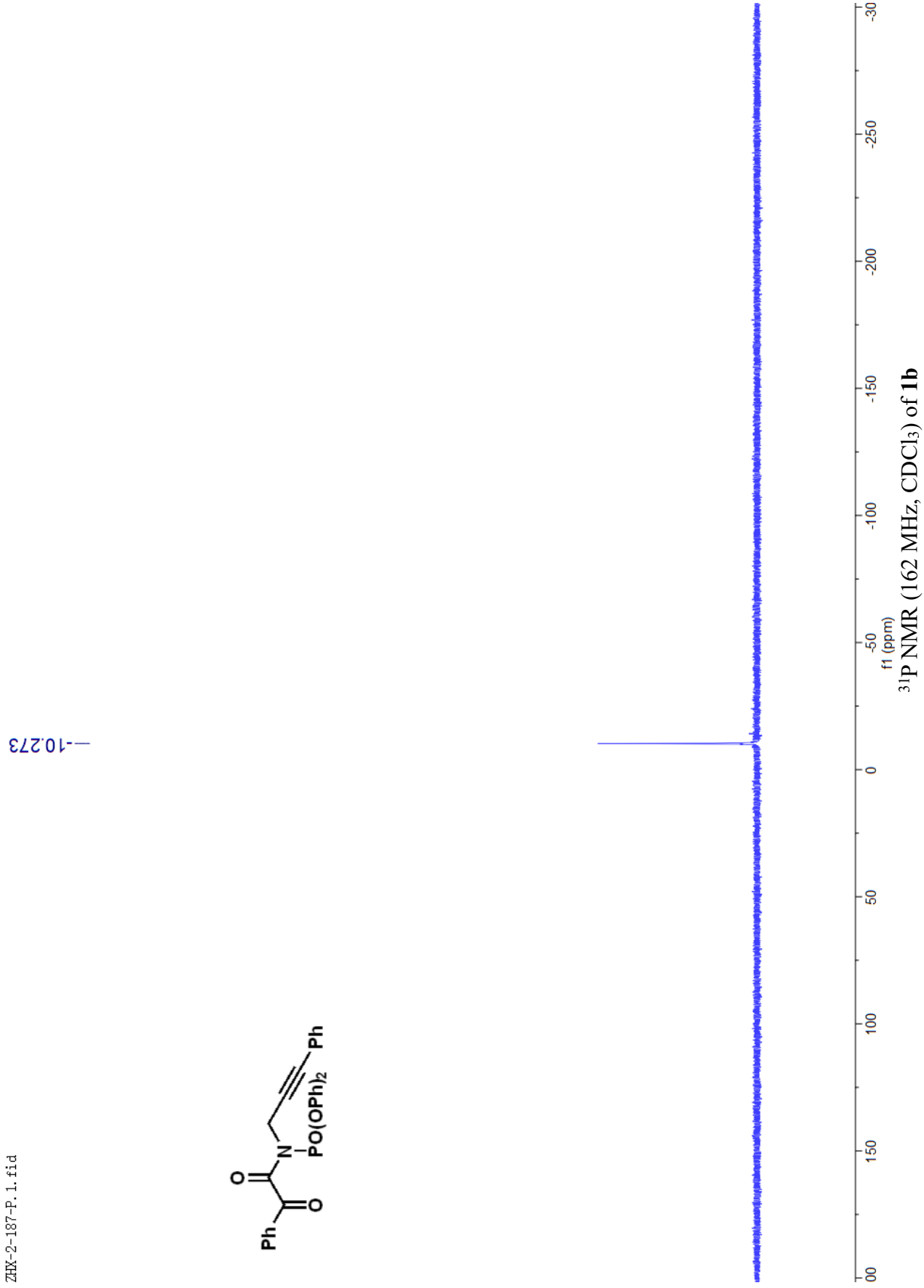
^{31}P NMR (162 MHz, $CDCl_3$) of **S1**



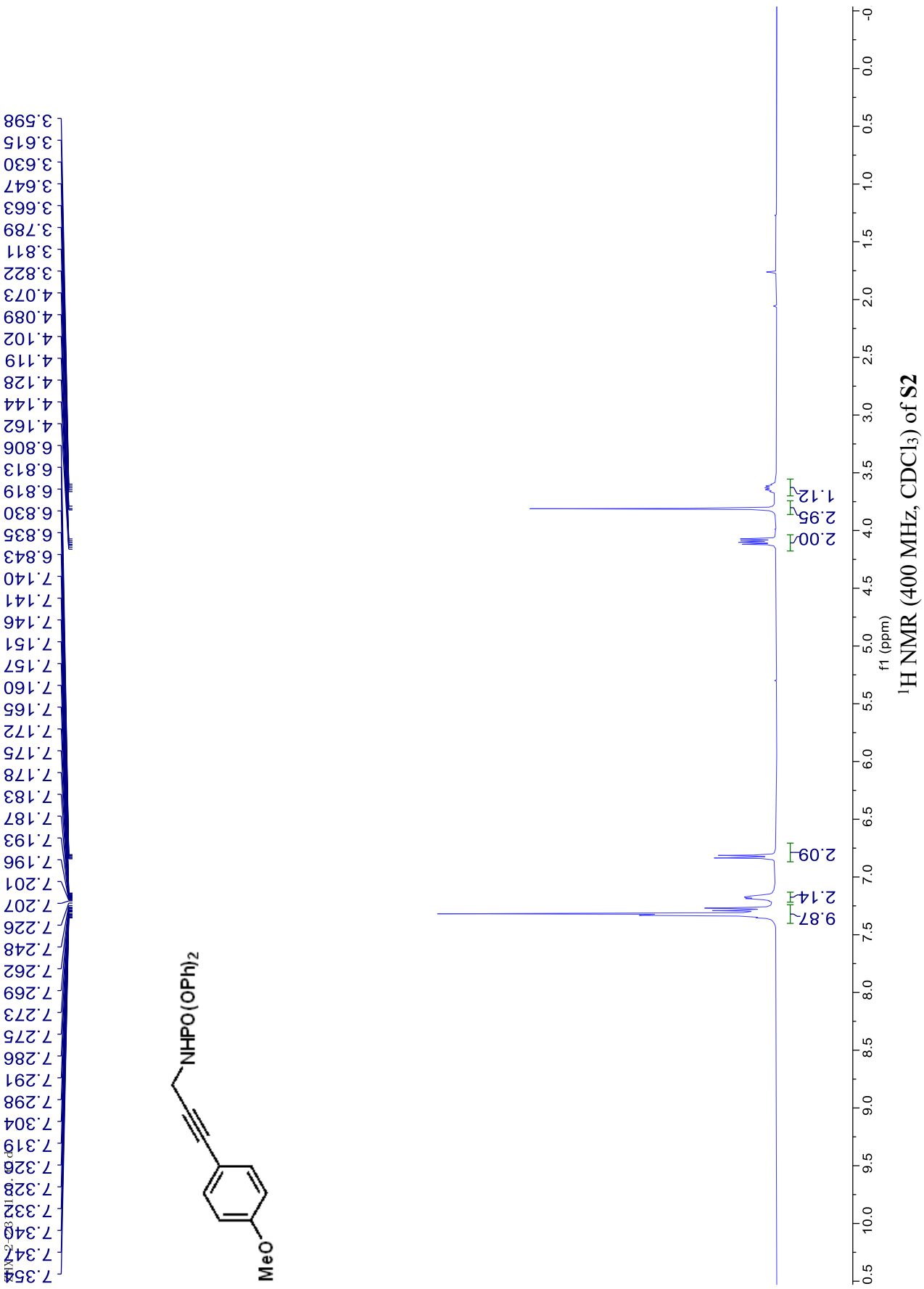
^{1}H NMR (400 MHz, $CDCl_3$) of **1b**



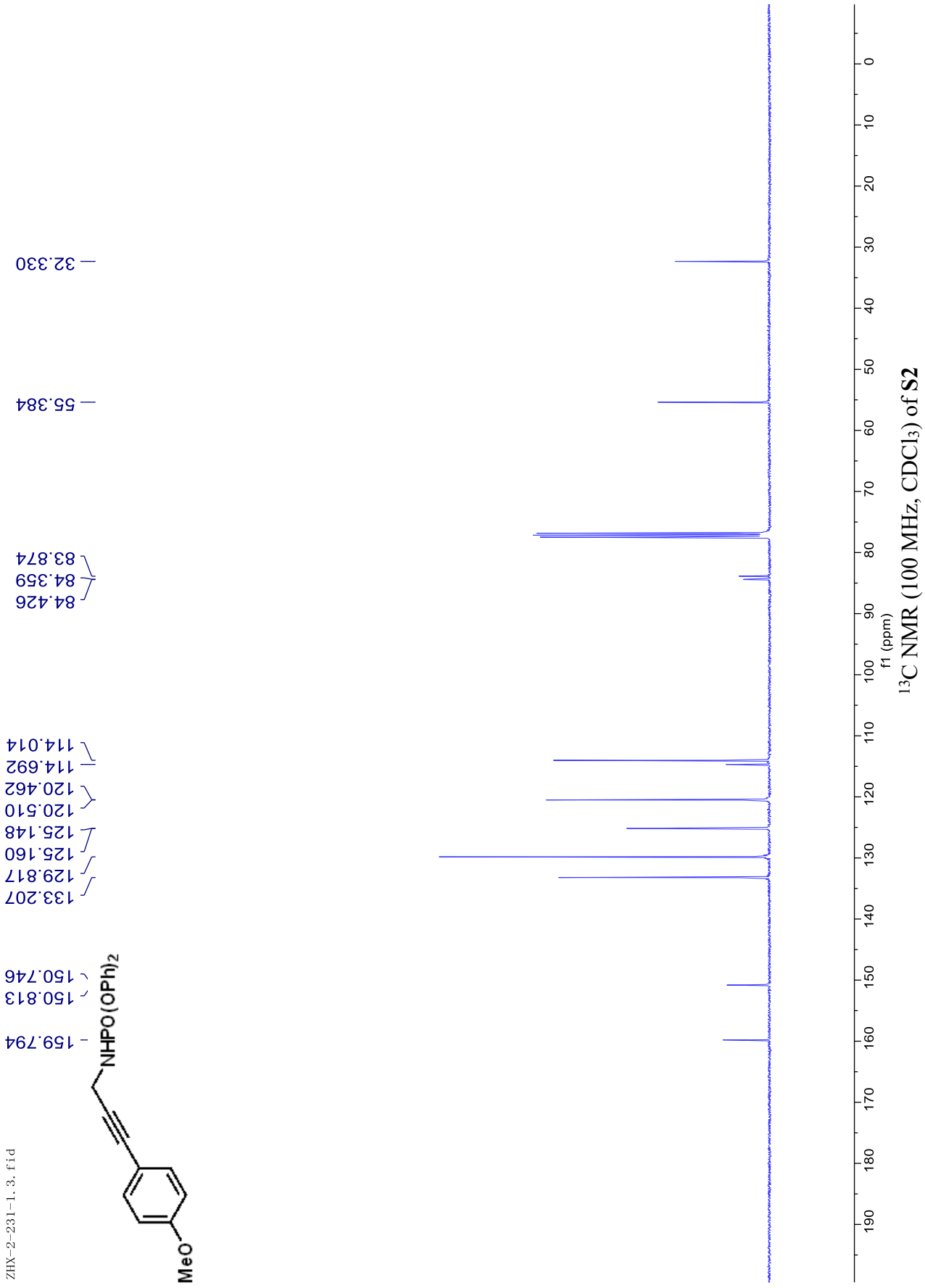
^{13}C NMR (100 MHz, $CDCl_3$) of **1b**



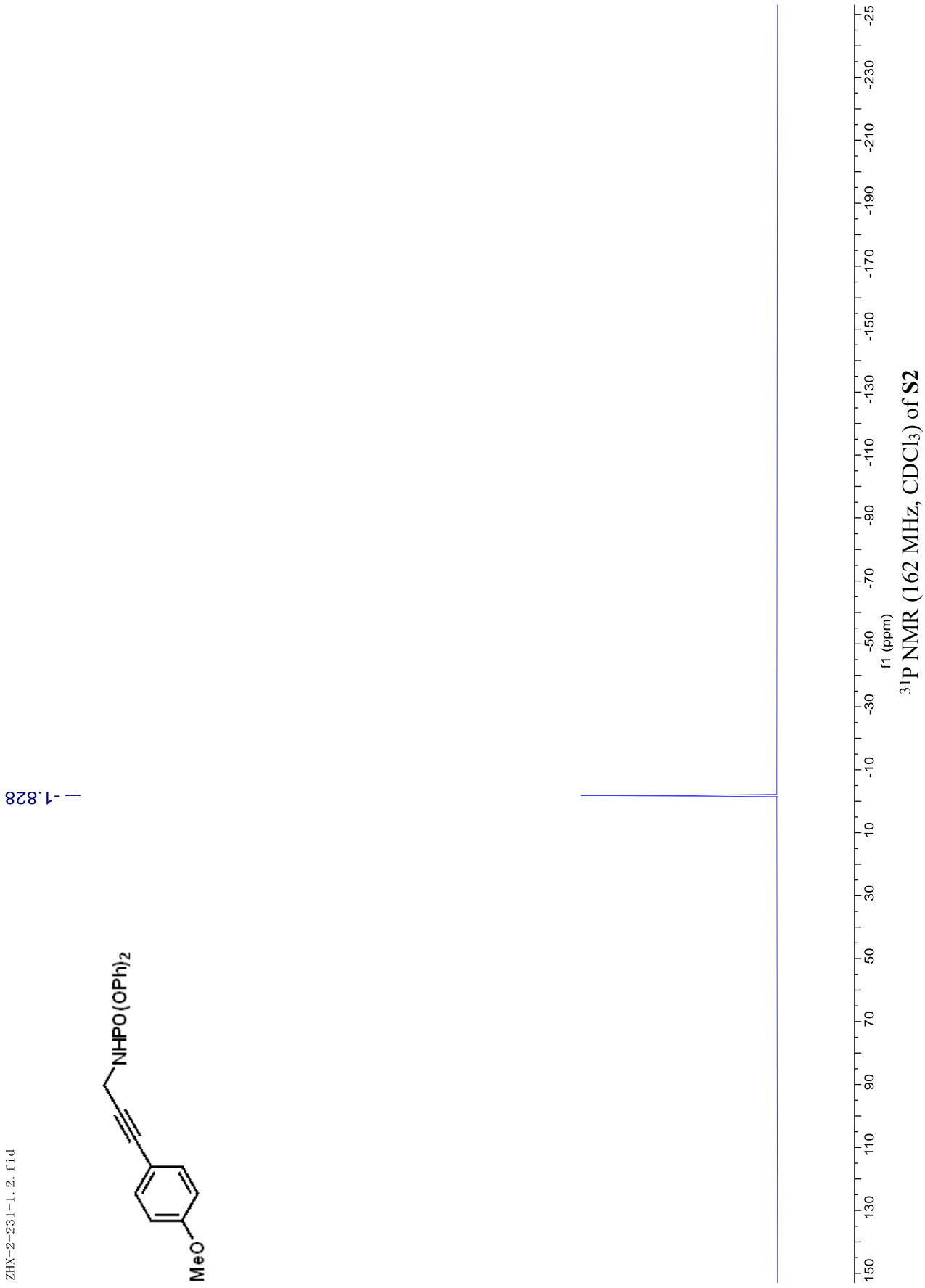
^{31}P NMR (162 MHz, $CDCl_3$) of **1b**



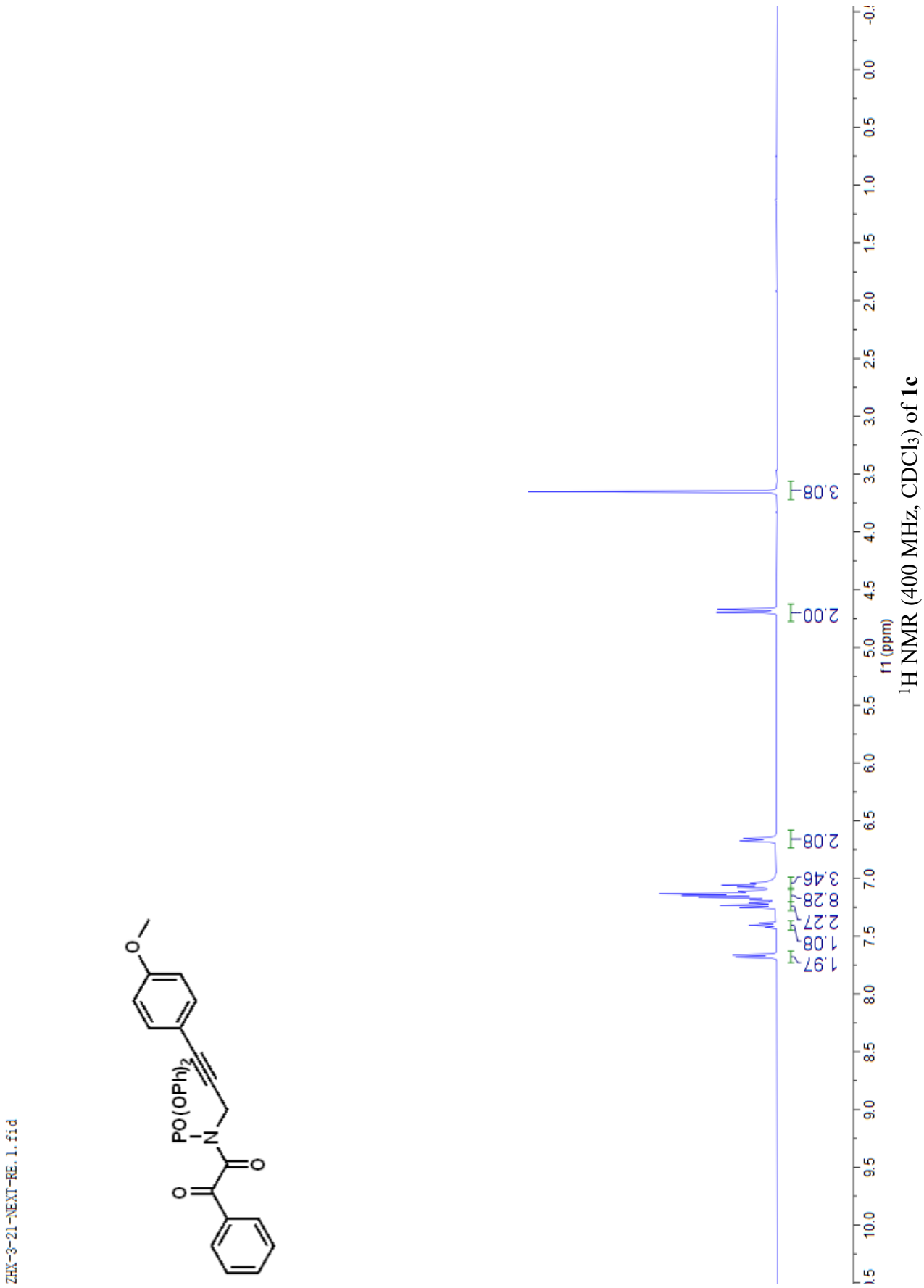
^{1}H NMR (400 MHz, $CDCl_3$) of **S2**



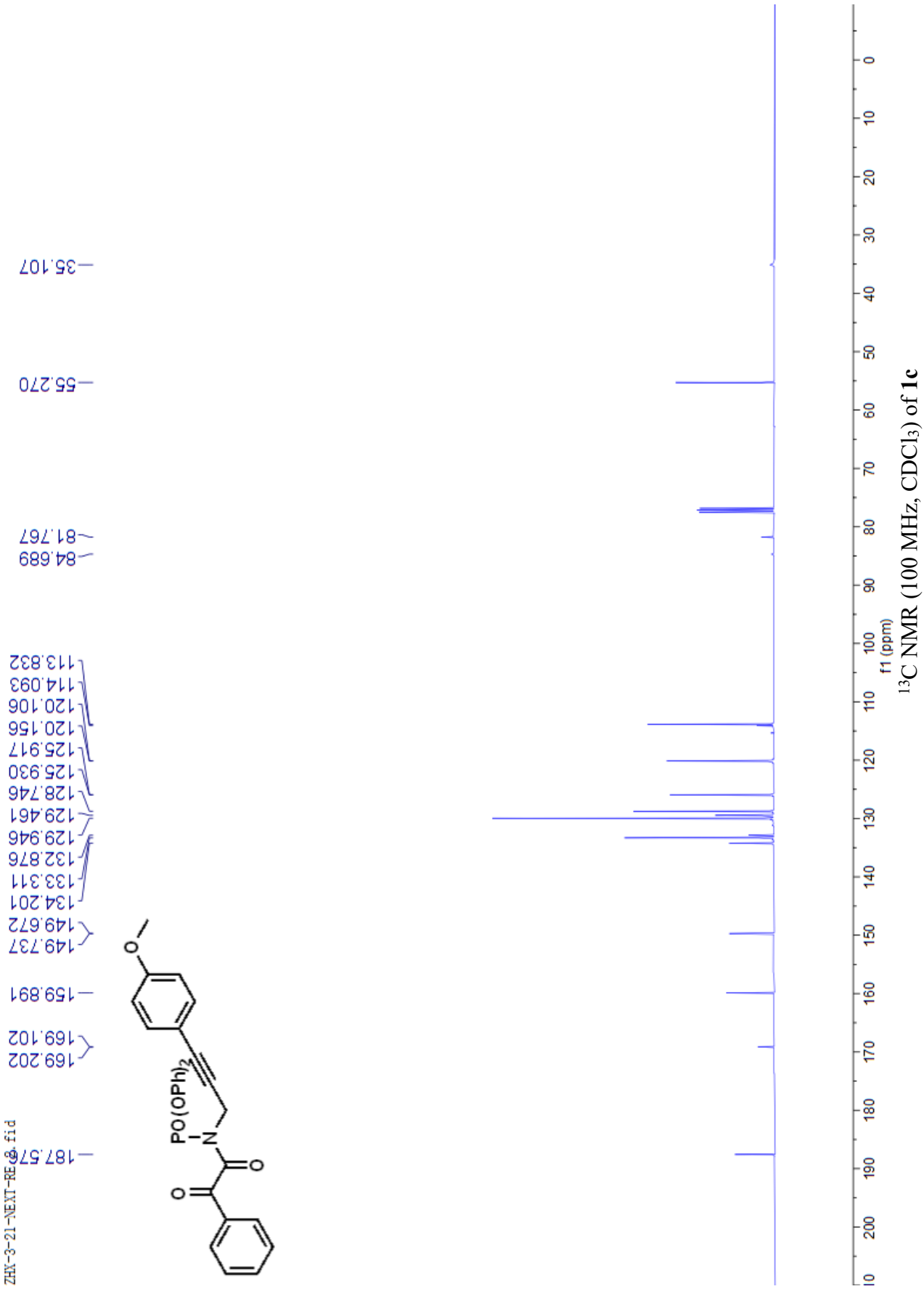
^{13}C NMR (100 MHz, $CDCl_3$) of **S2**



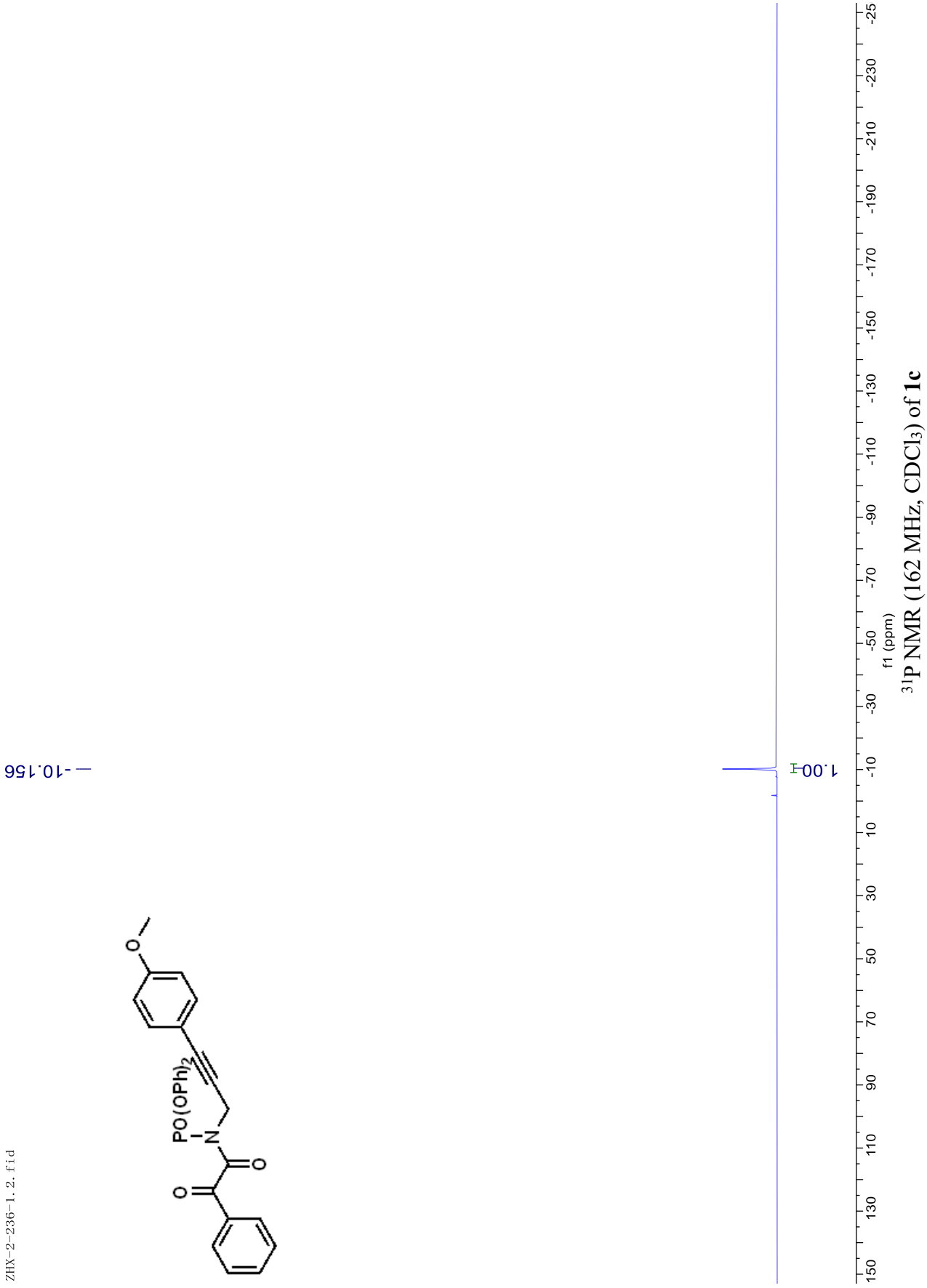
^{31}P NMR (162 MHz, $CDCl_3$) of **S2**



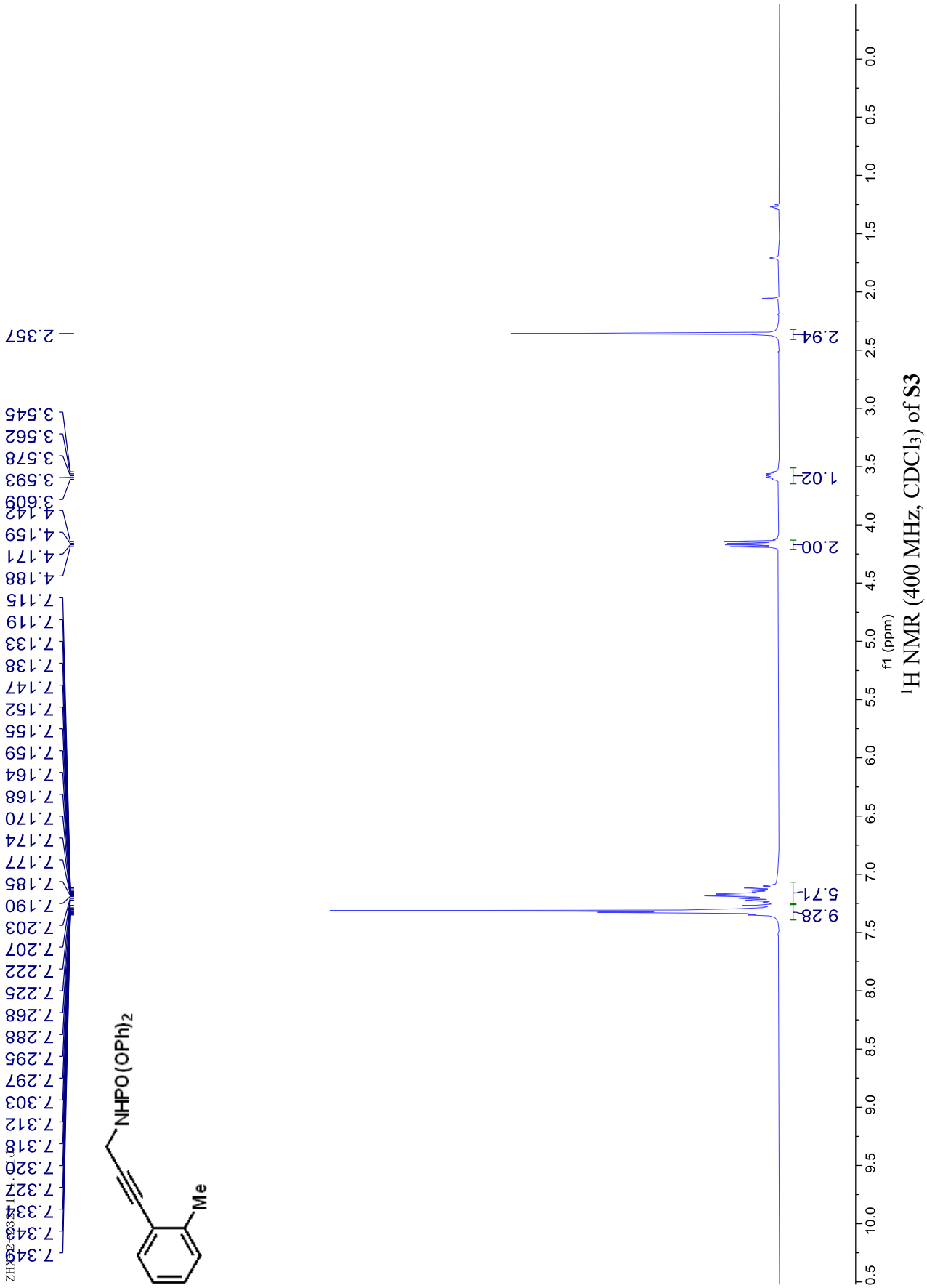
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



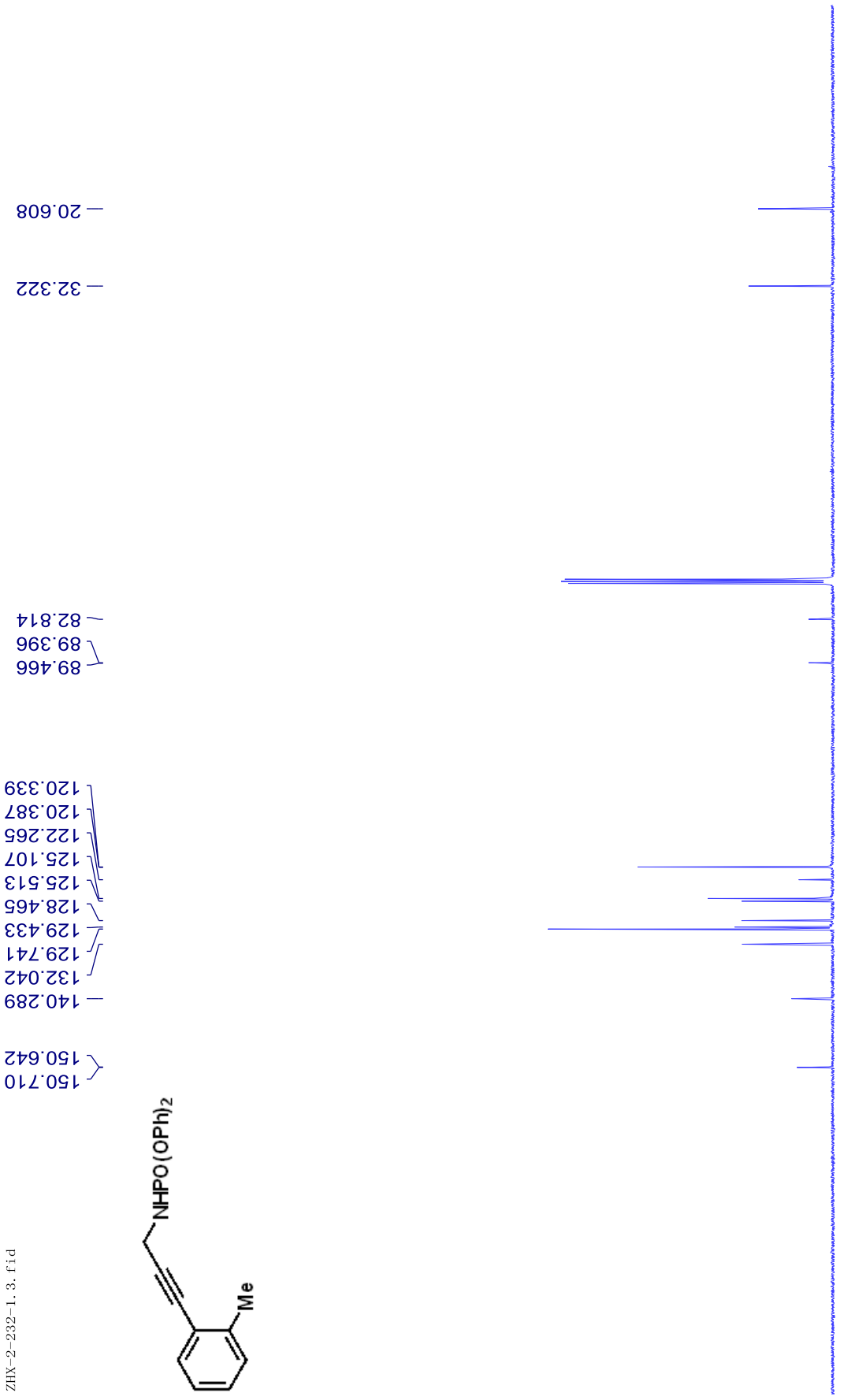
^{13}C NMR (100 MHz, $CDCl_3$) of **1c**



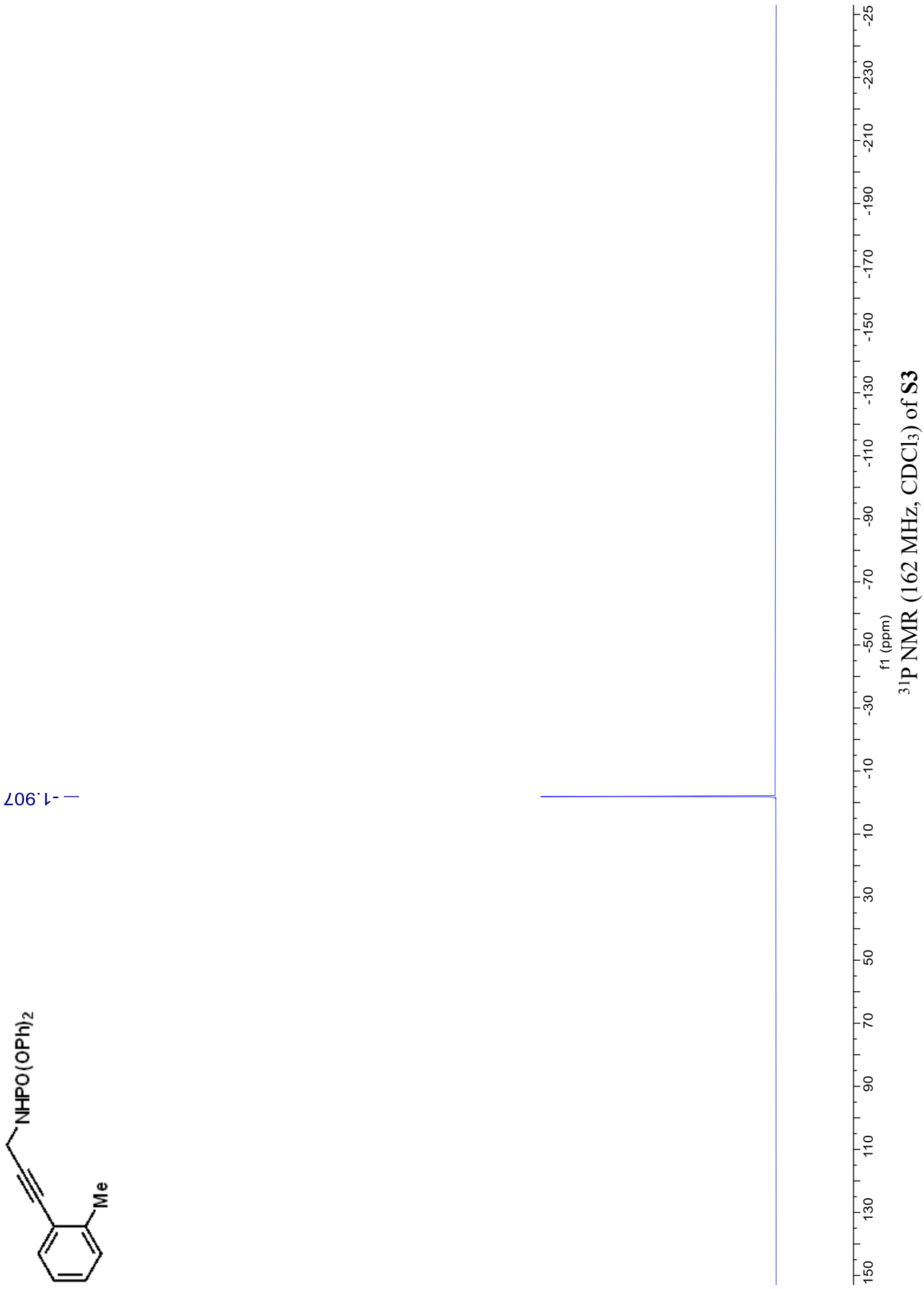
^{31}P NMR (162 MHz, $CDCl_3$) of **1c**



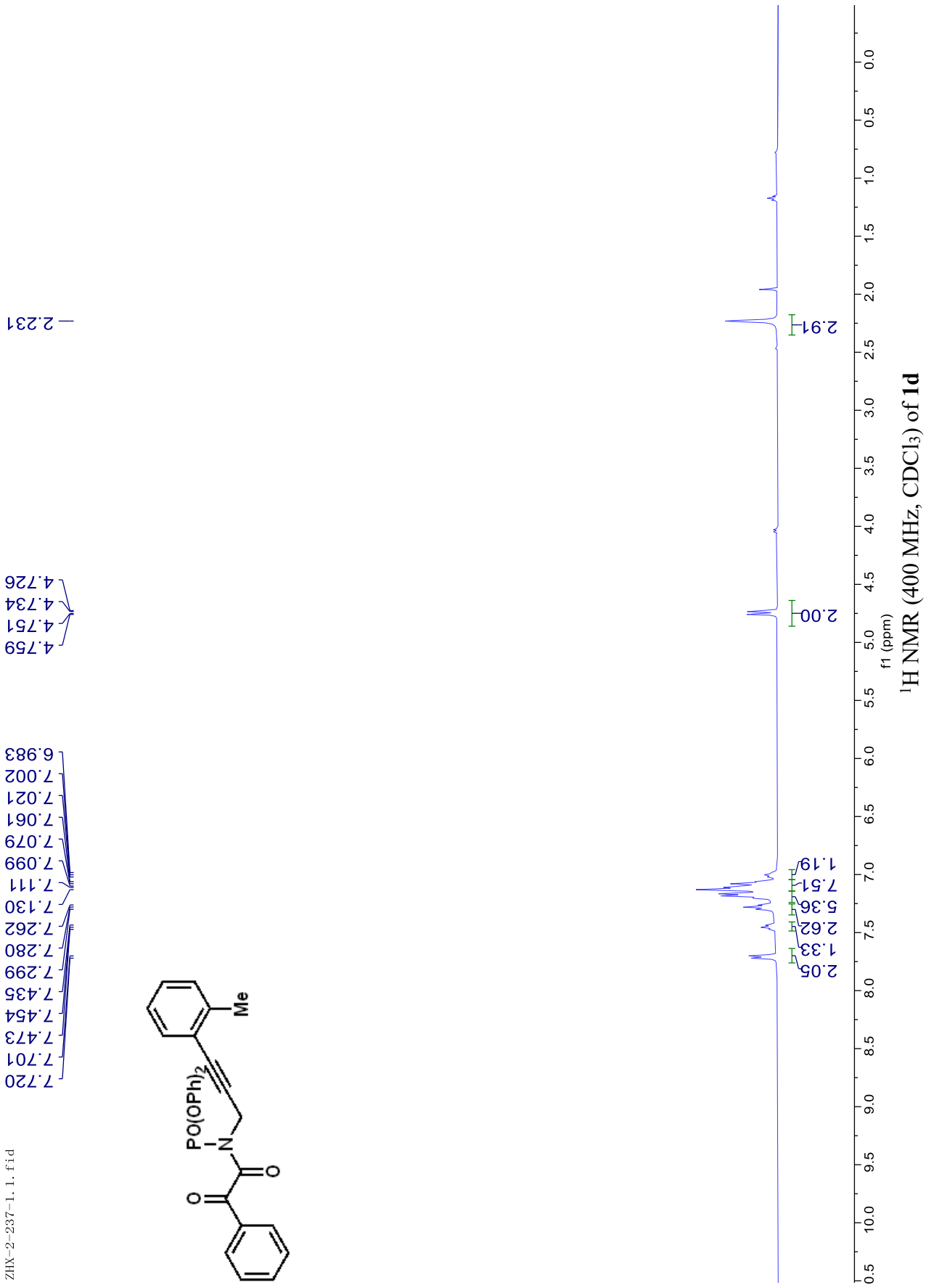
^{1}H NMR (400 MHz, $CDCl_3$) of **S3**



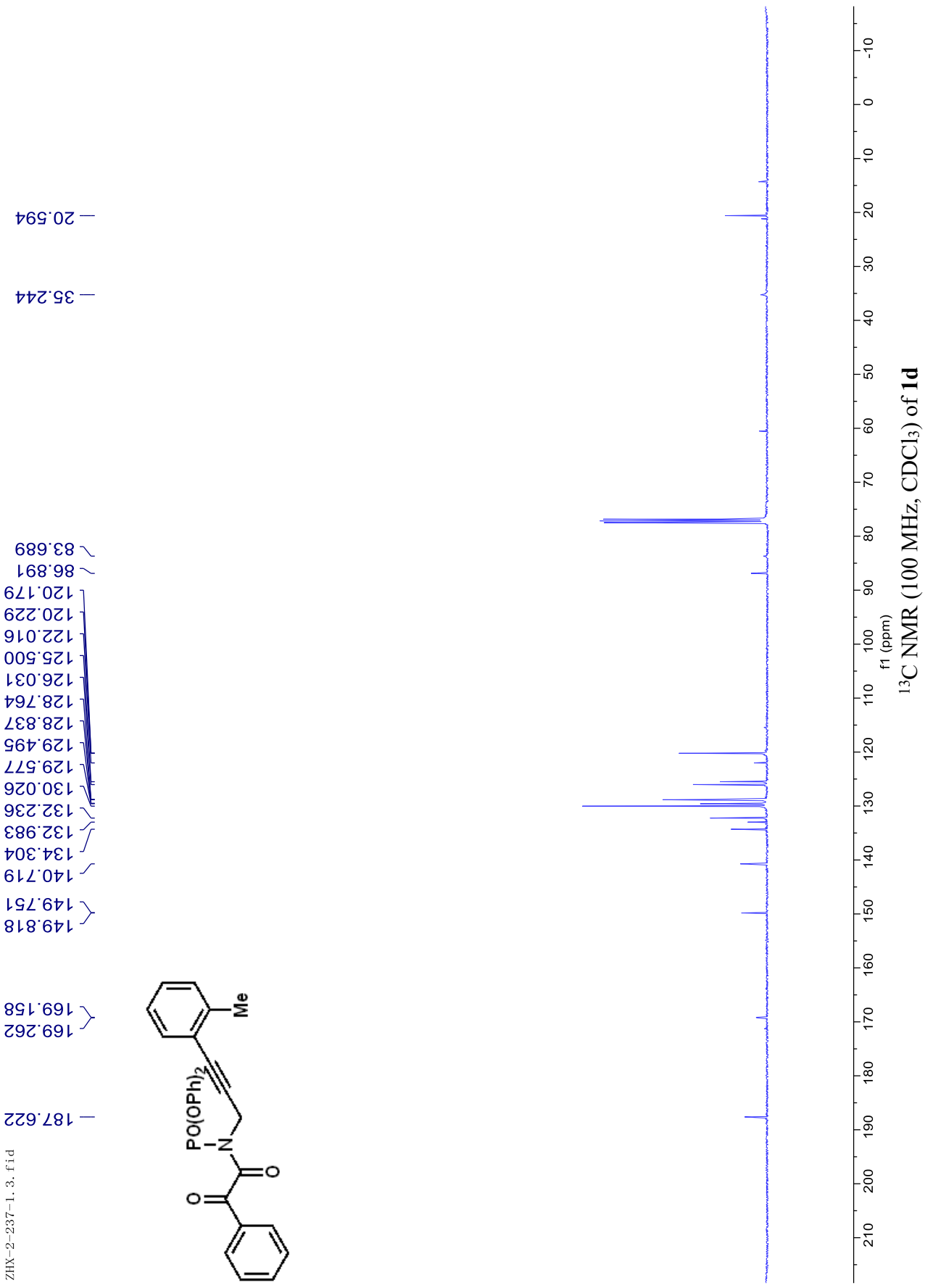
^{13}C NMR (100 MHz, $CDCl_3$) of **S3**



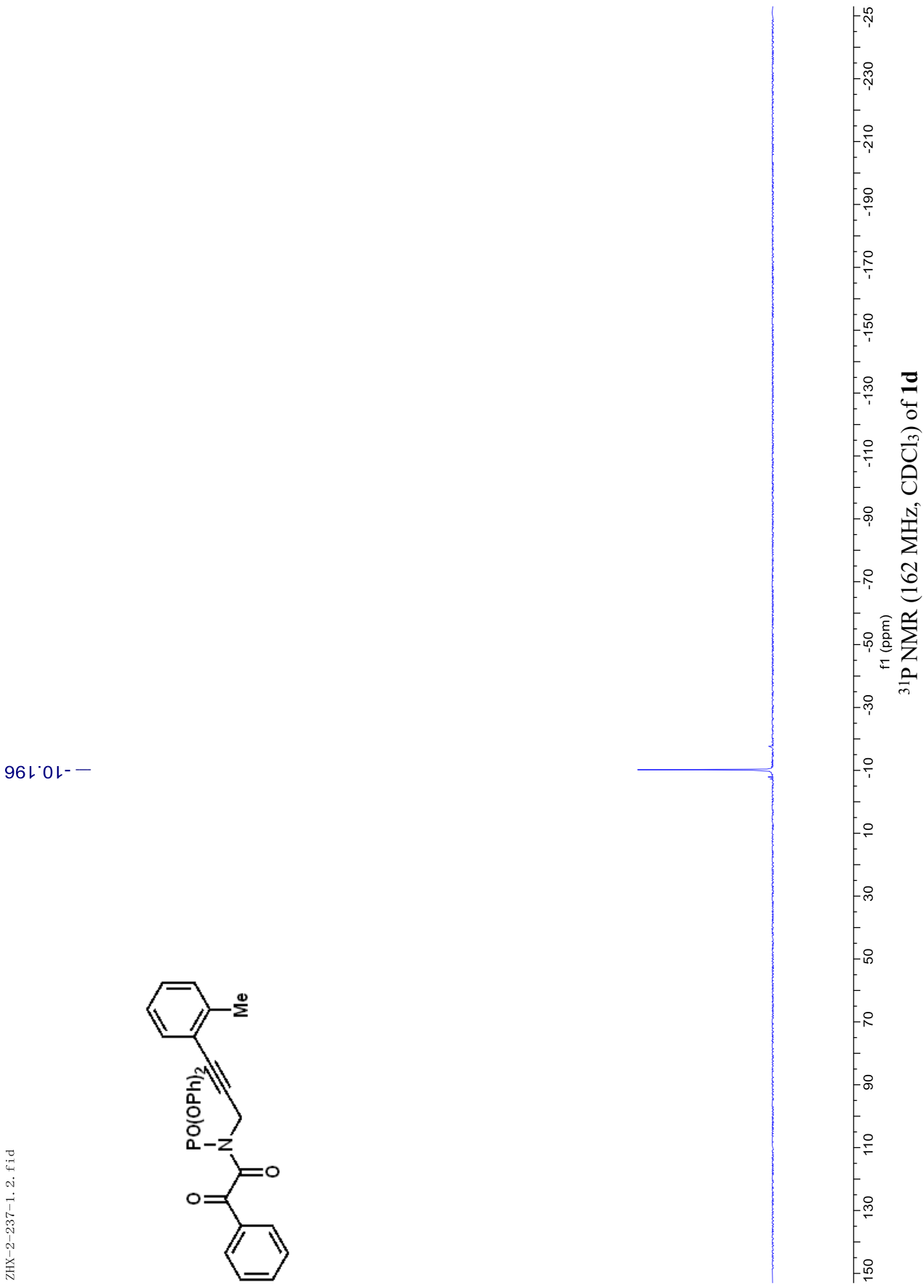
^{31}P NMR (162 MHz, $CDCl_3$) of **S3**



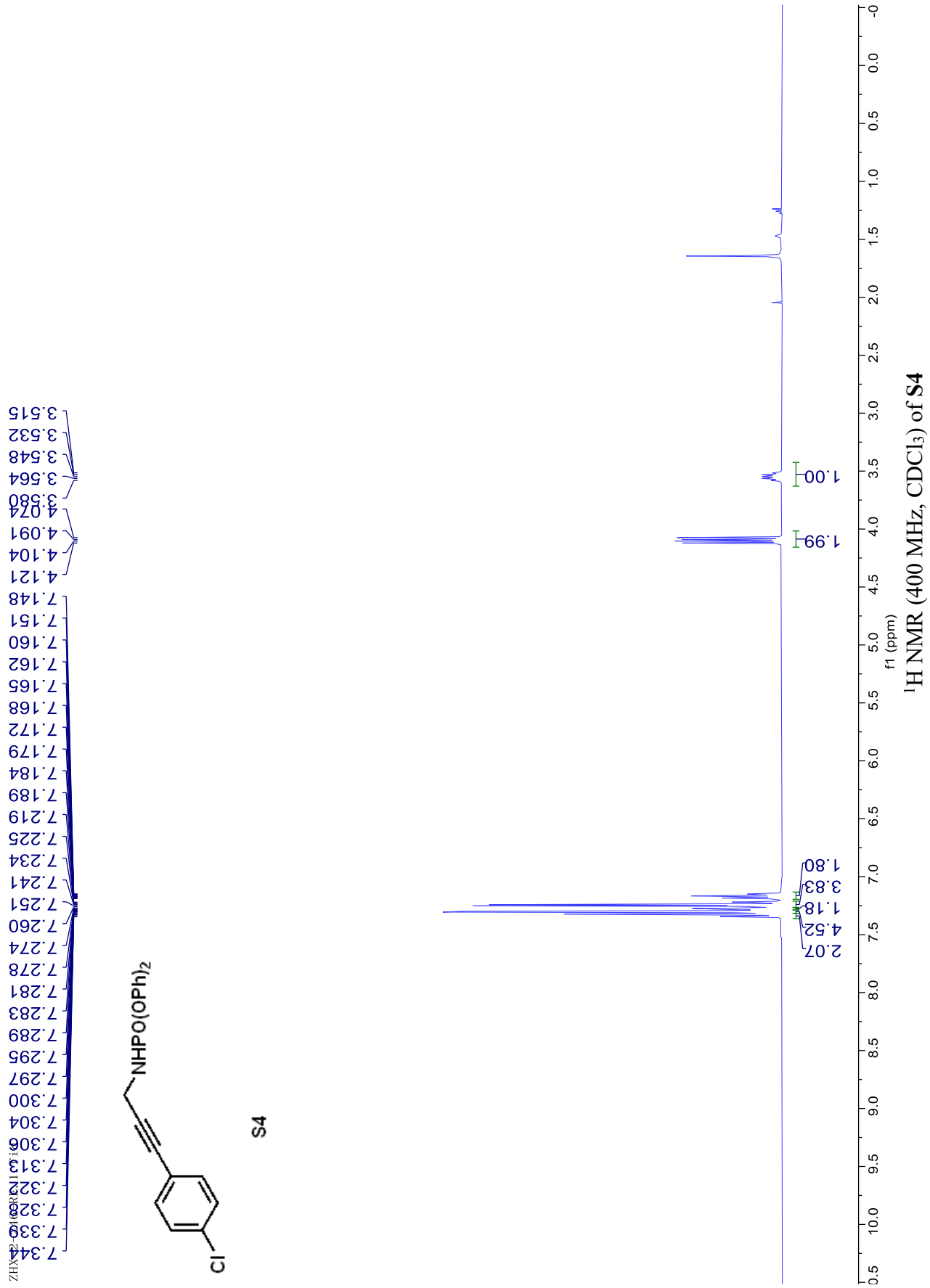
^{1}H NMR (400 MHz, $CDCl_3$) of **1d**



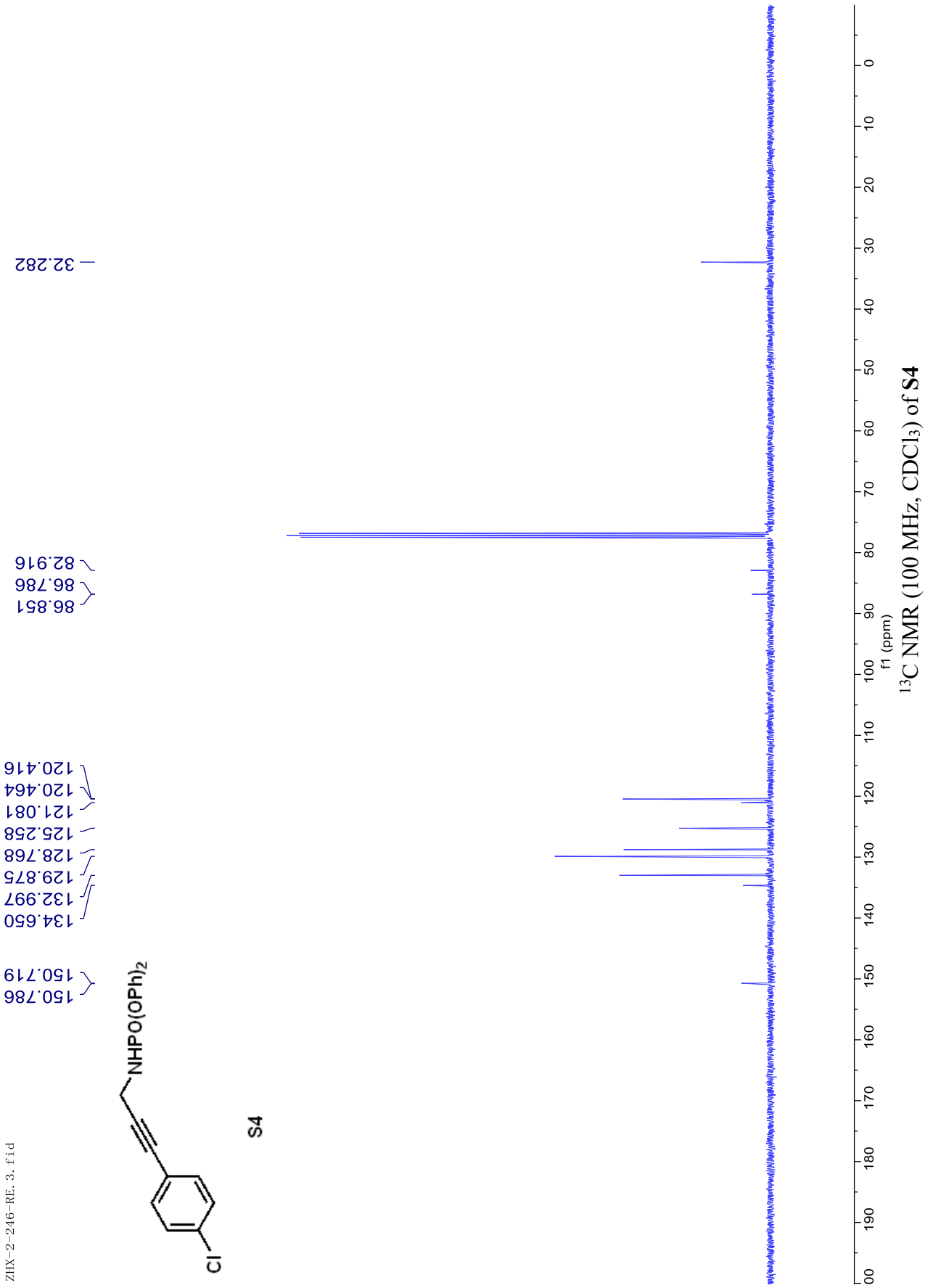
^{13}C NMR (100 MHz, $CDCl_3$) of **1d**



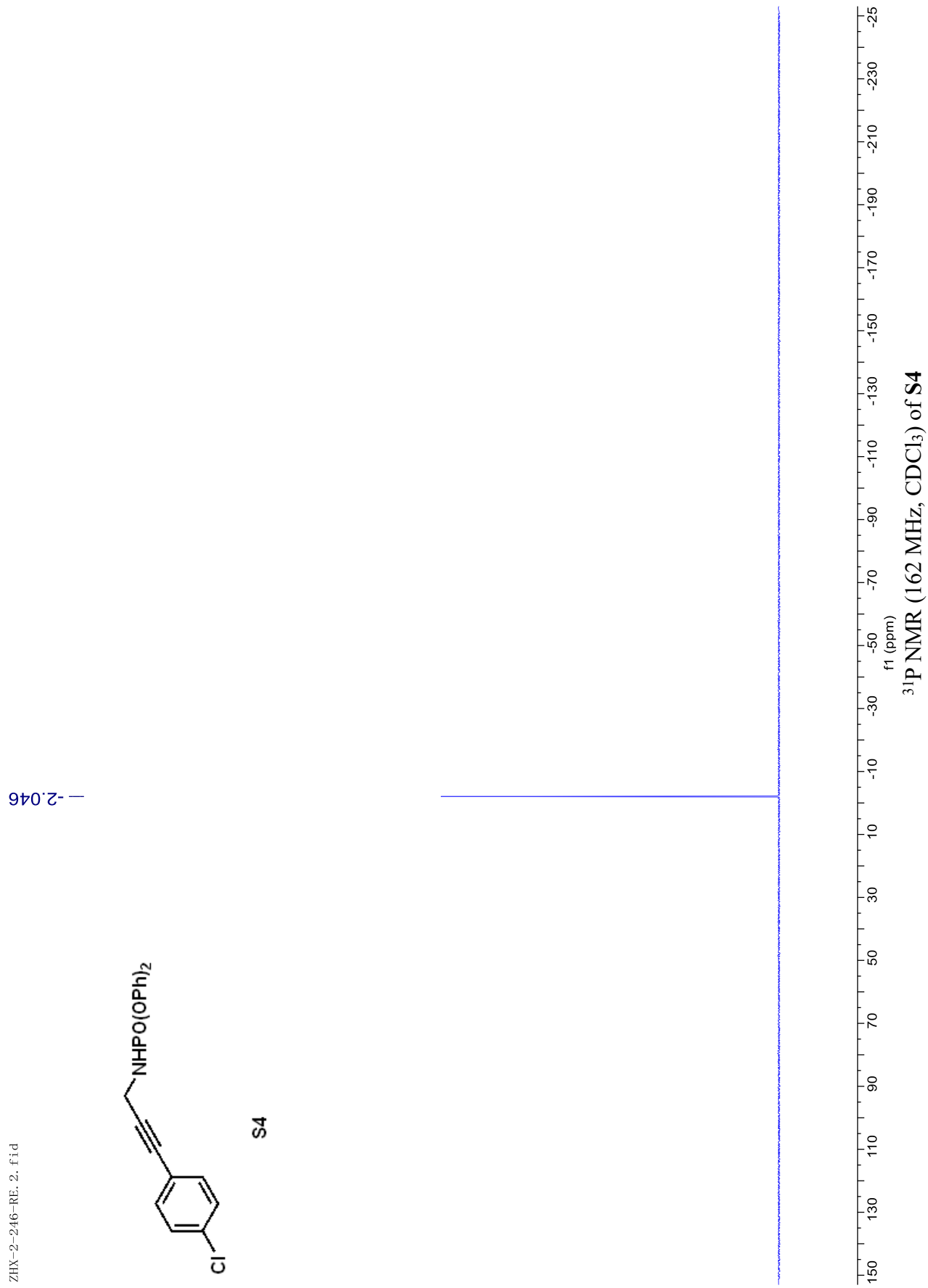
^{31}P NMR (162 MHz, $CDCl_3$) of **1d**



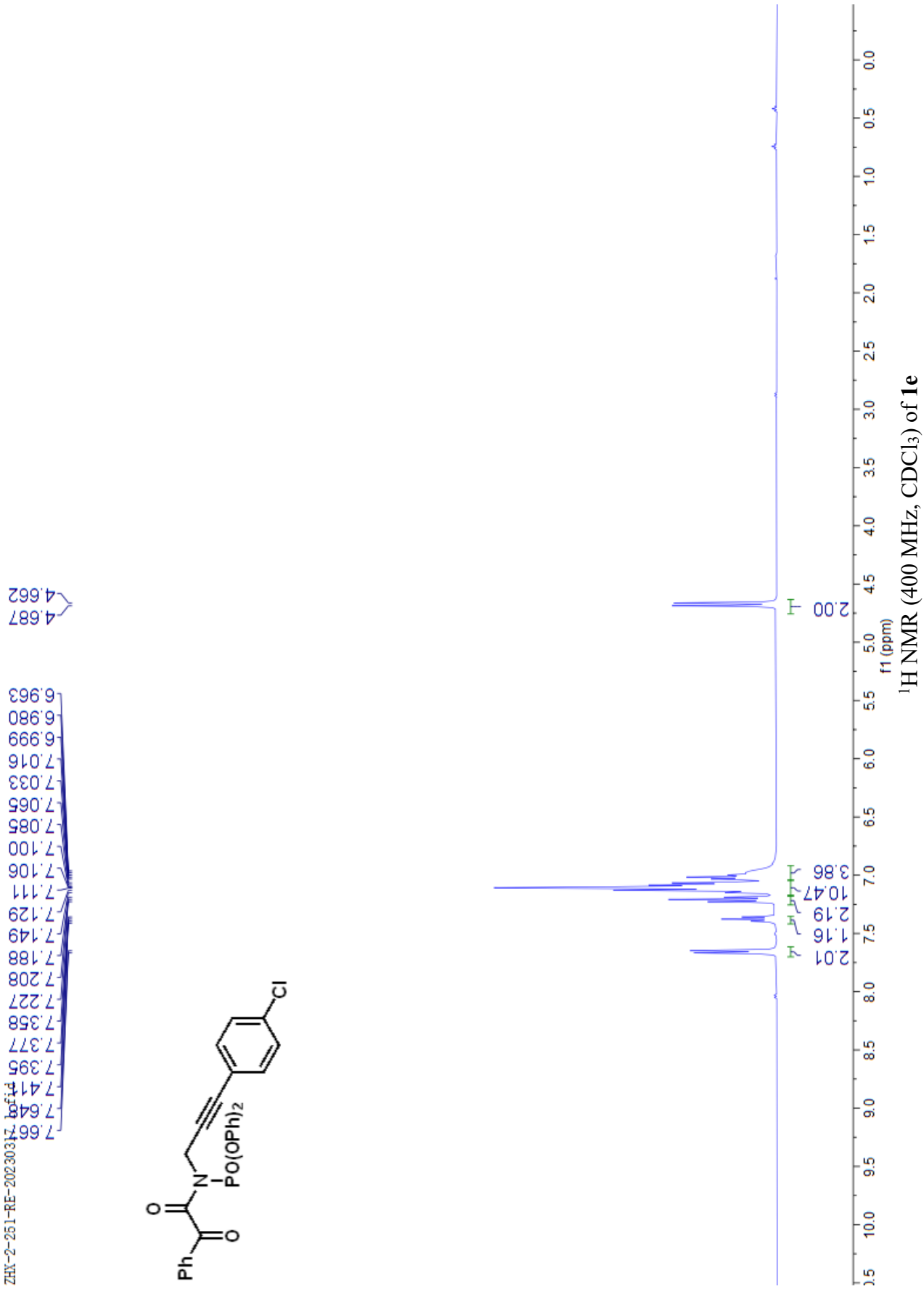
^{1}H NMR (400 MHz, $CDCl_3$) of **S4**



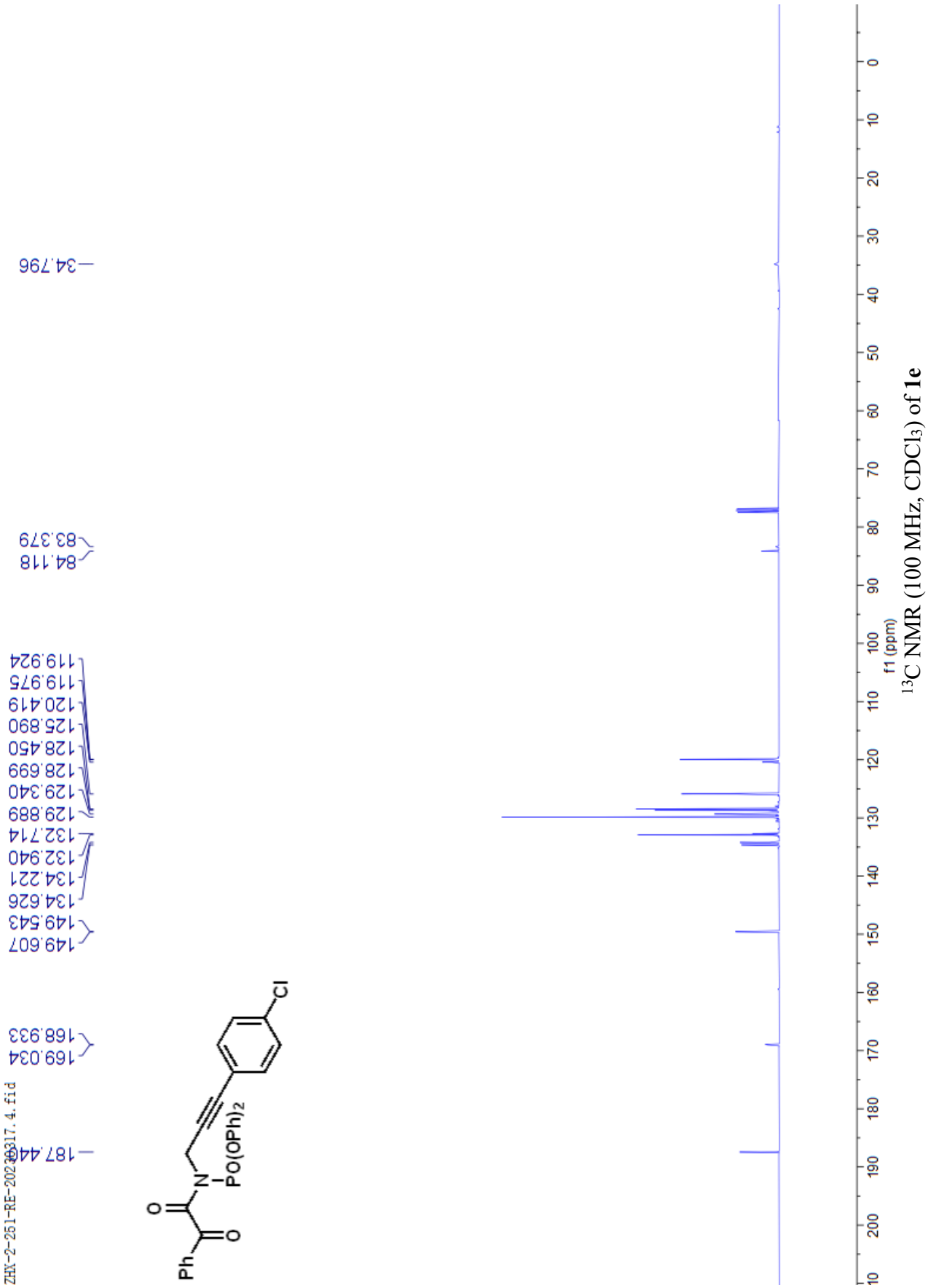
^{13}C NMR (100 MHz, $CDCl_3$) of **S4**



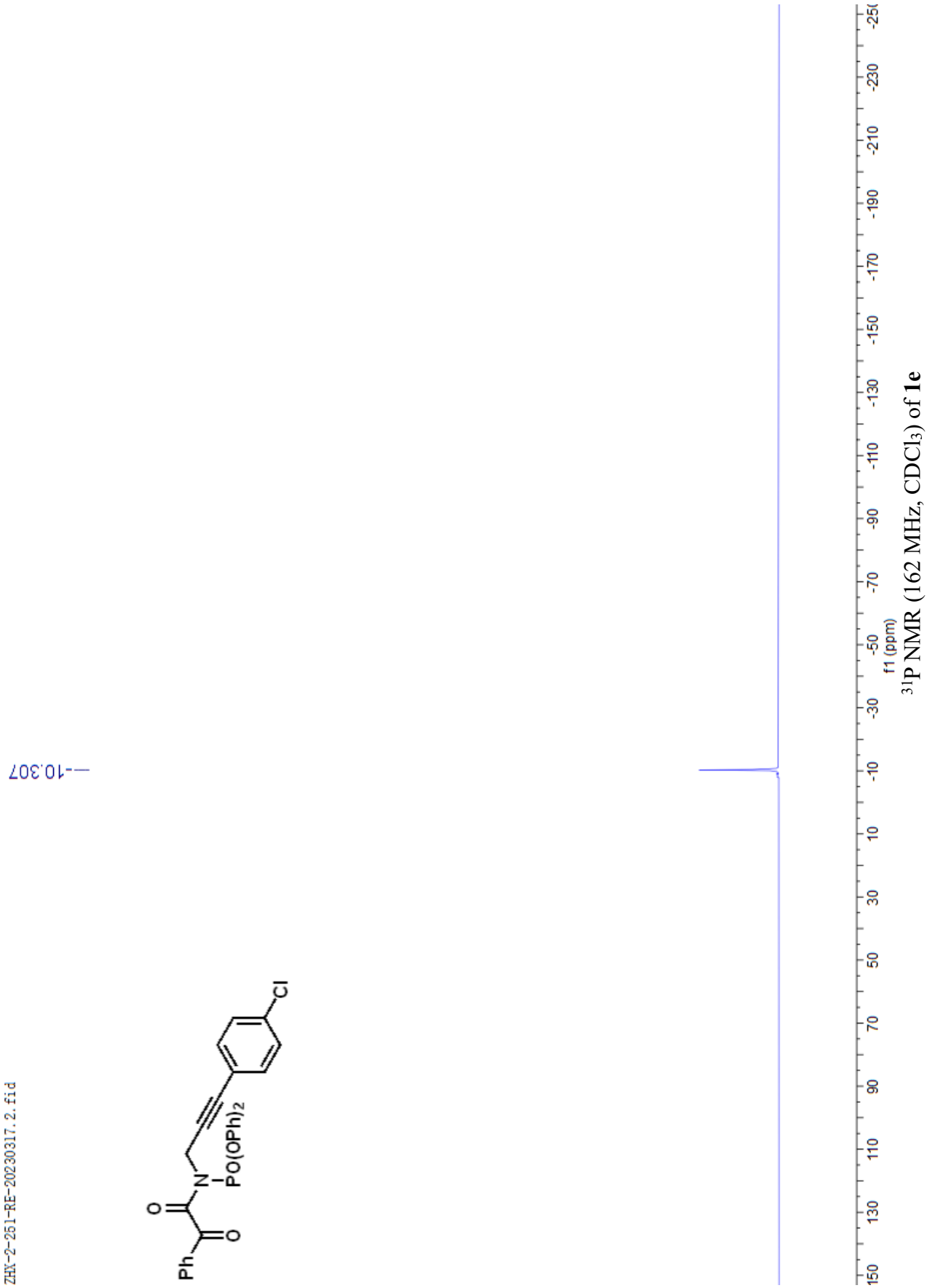
^{31}P NMR (162 MHz, $CDCl_3$) of **S4**



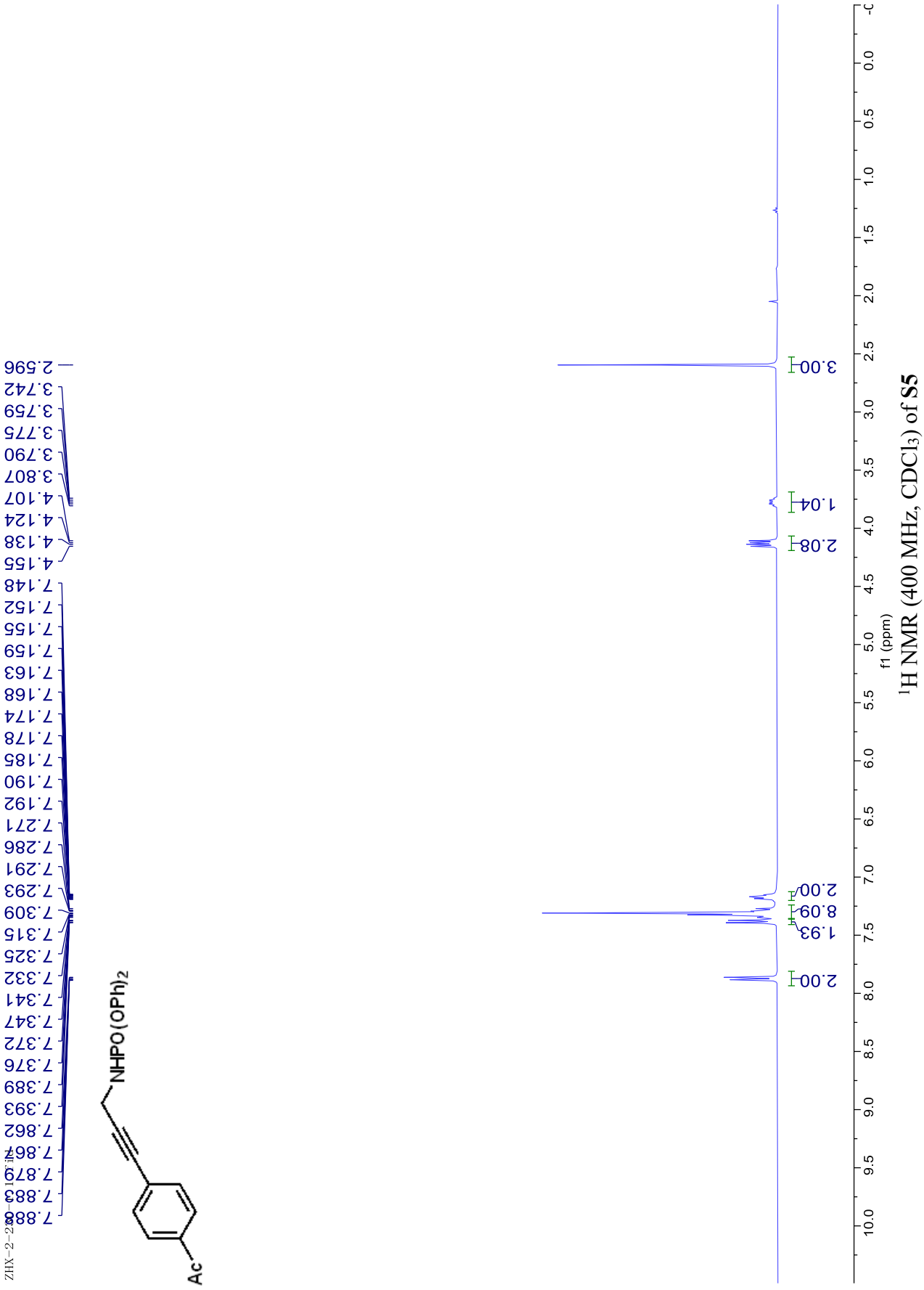
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



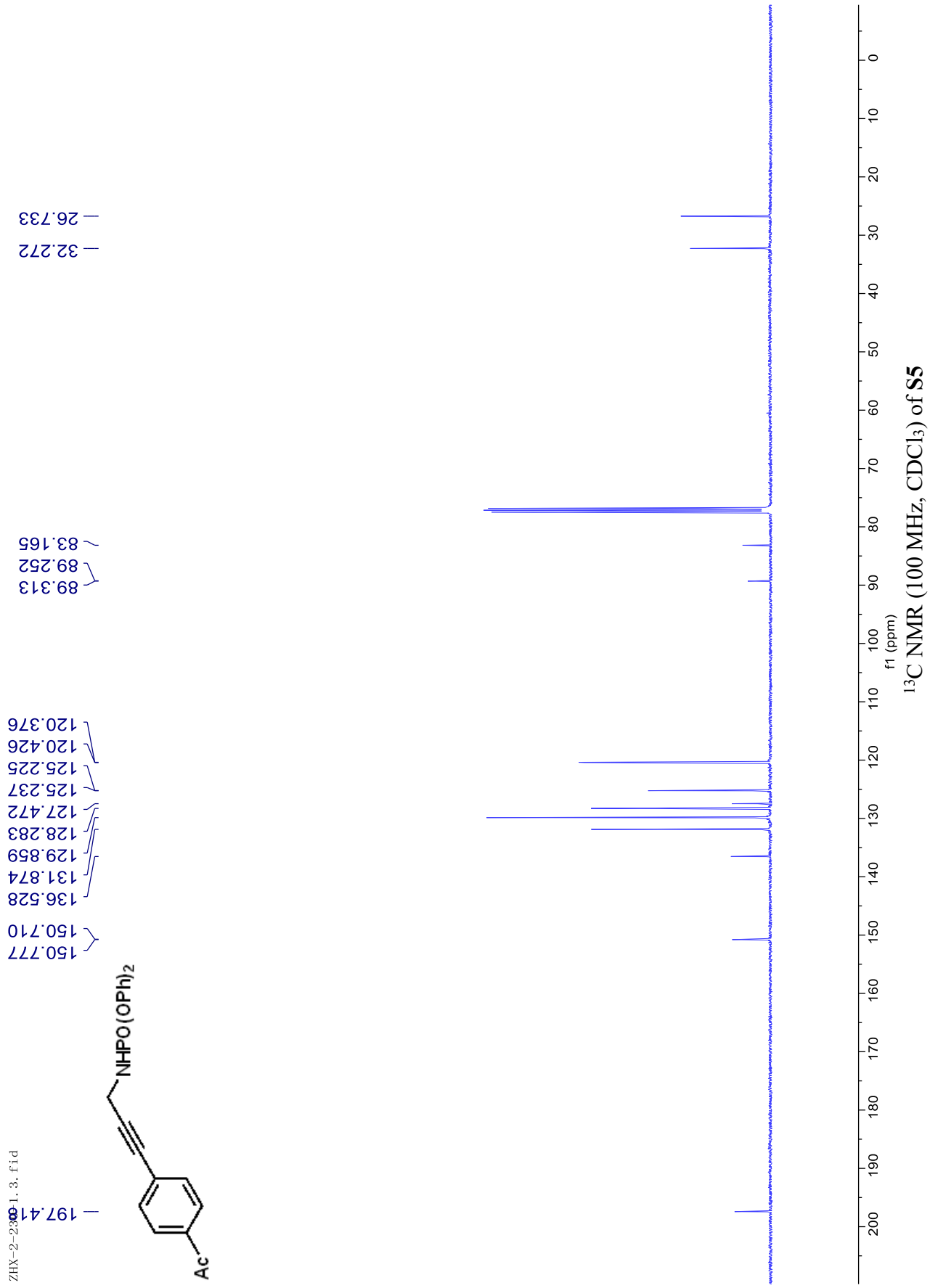
^{13}C NMR (100 MHz, $CDCl_3$) of **1e**



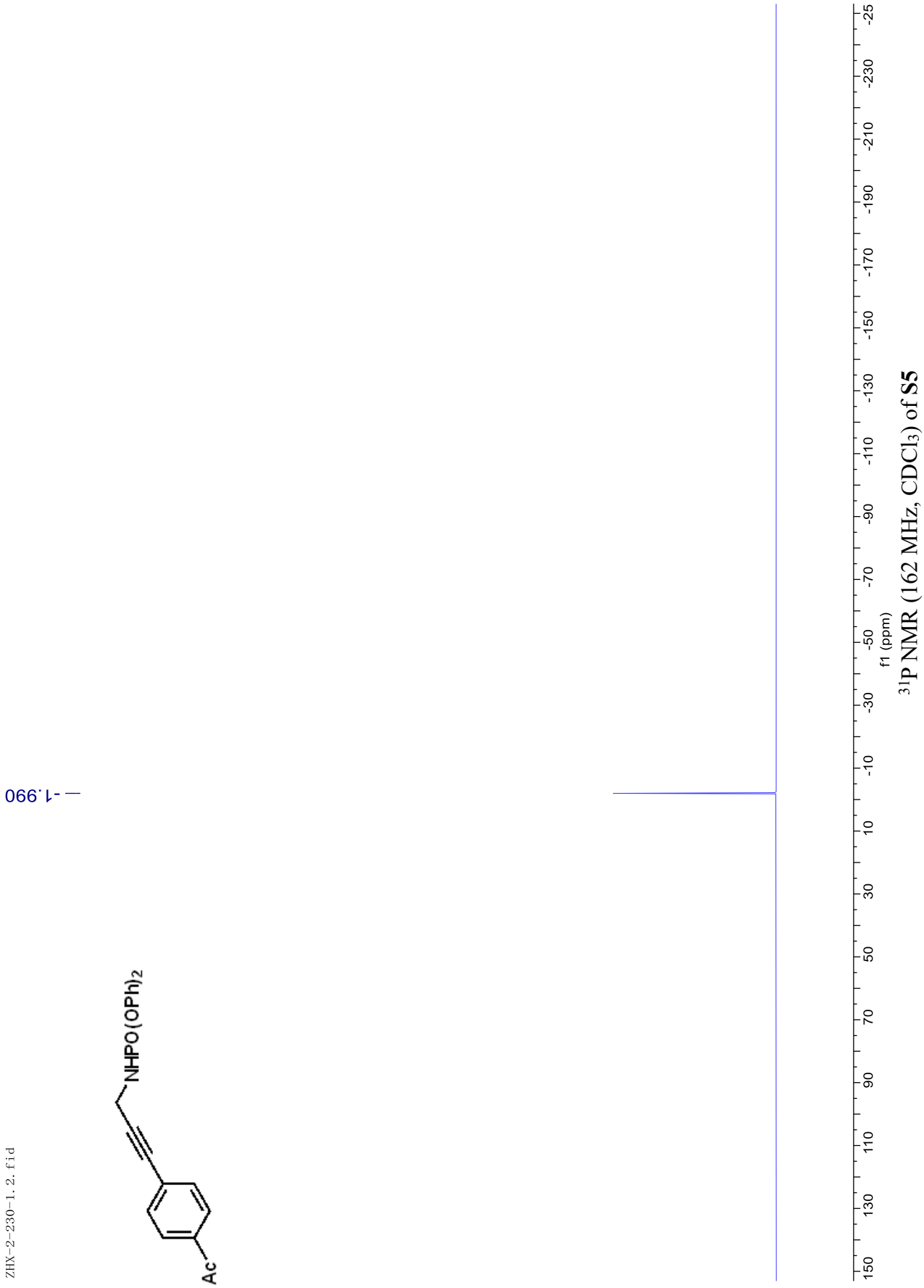
^{31}P NMR (162 MHz, $CDCl_3$) of **1e**



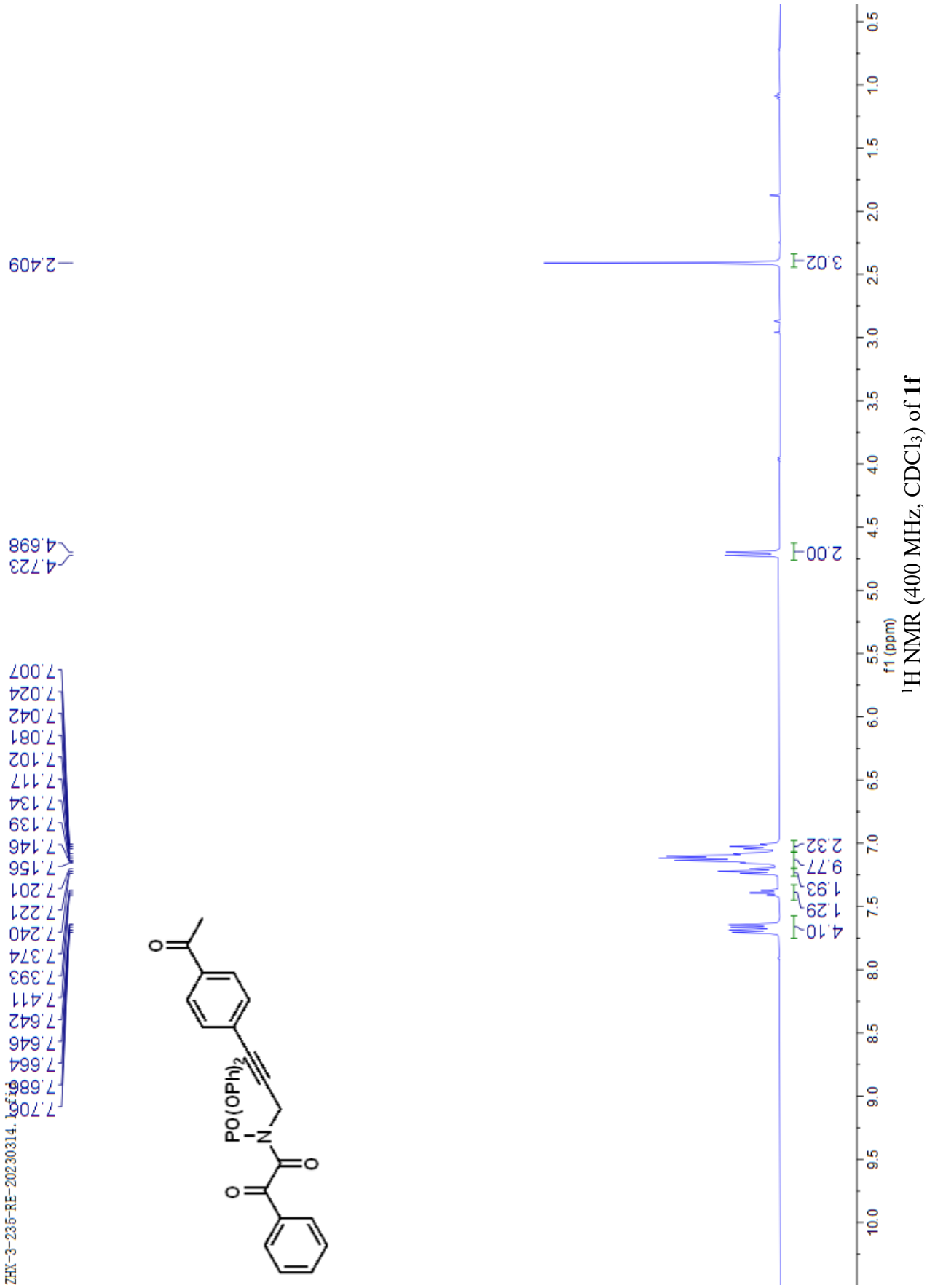
^{1}H NMR (400 MHz, $CDCl_3$) of **S5**



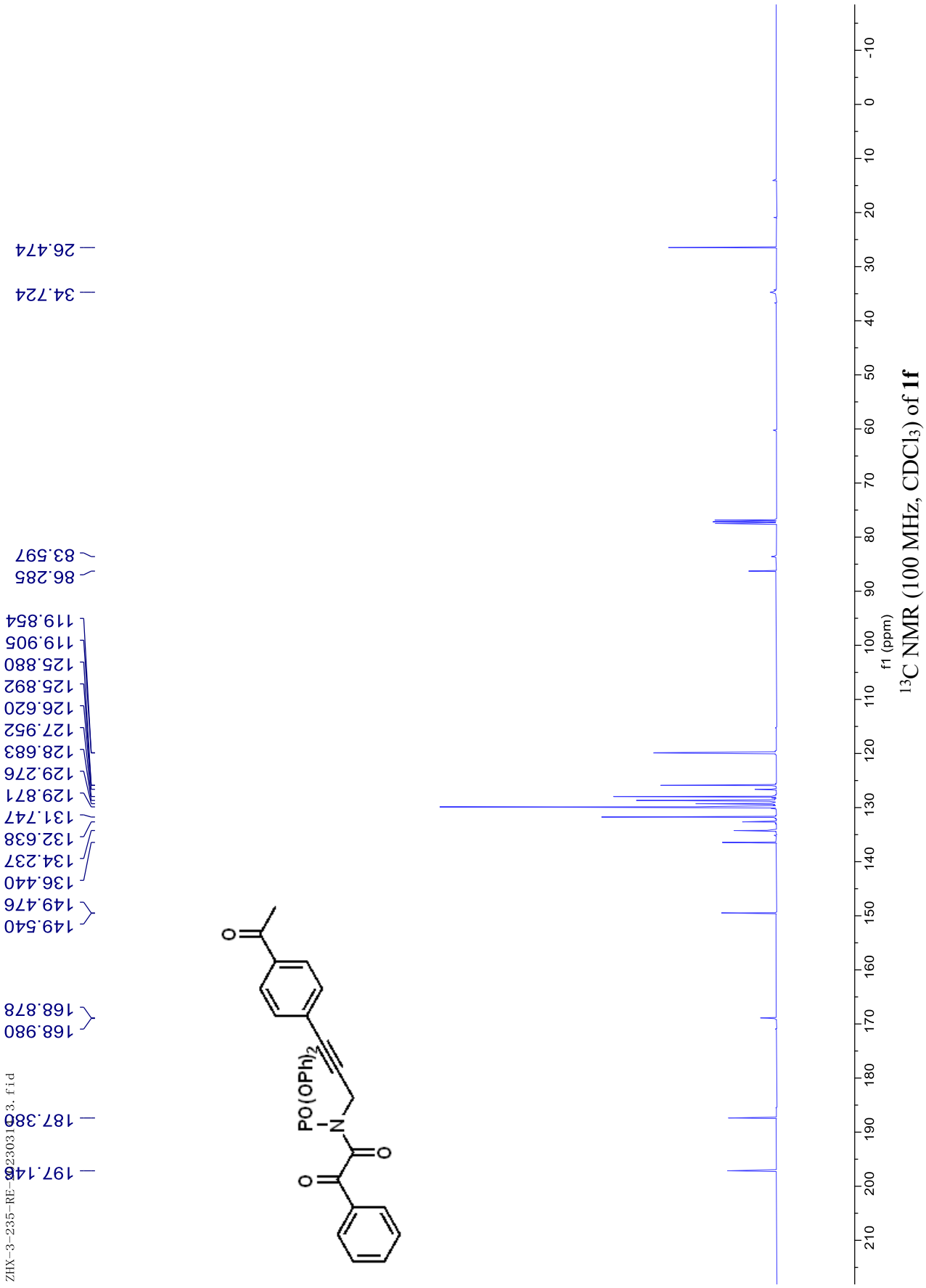
^{13}C NMR (100 MHz, $CDCl_3$) of **S5**



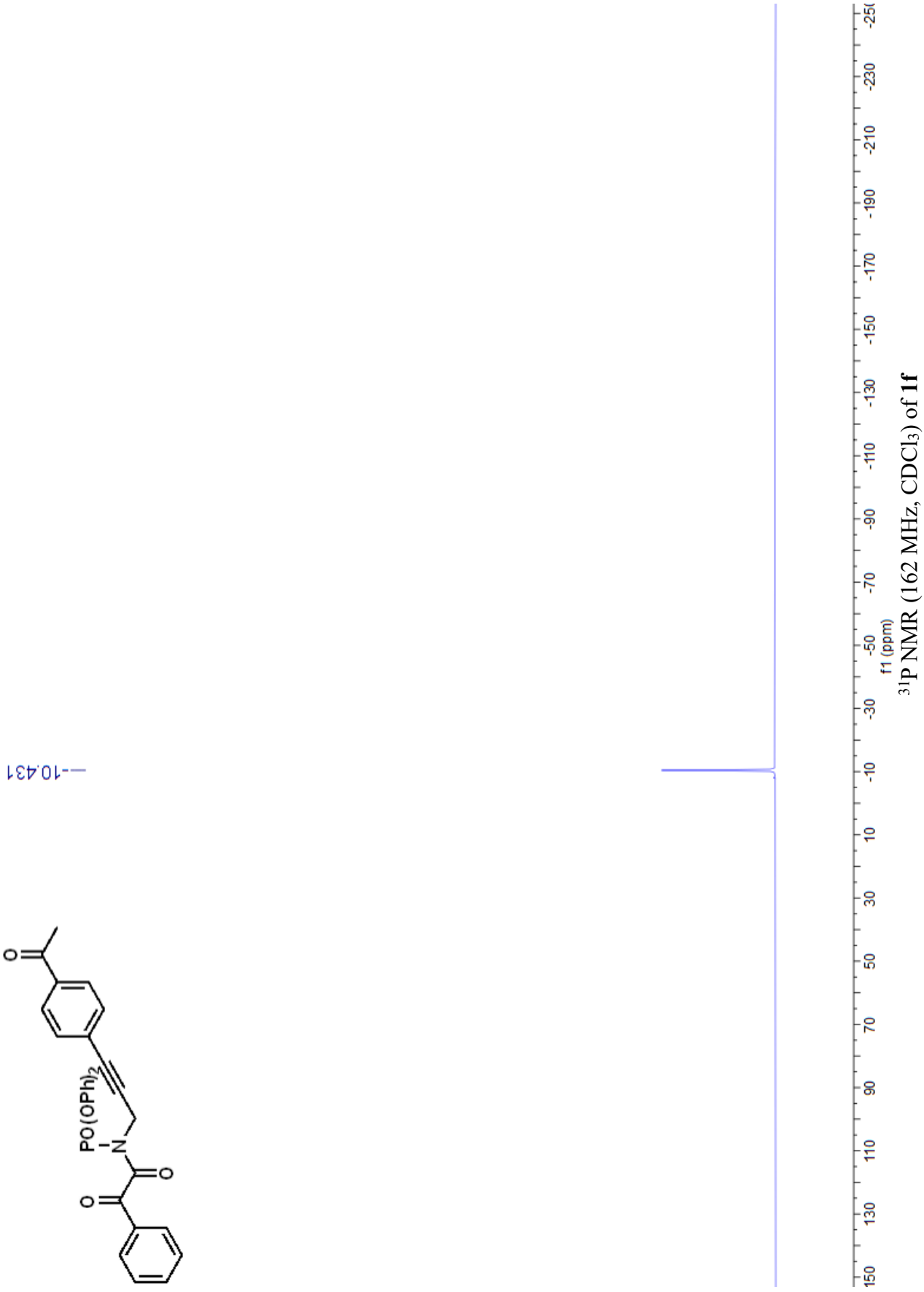
^{31}P NMR (162 MHz, $CDCl_3$) of **S5**



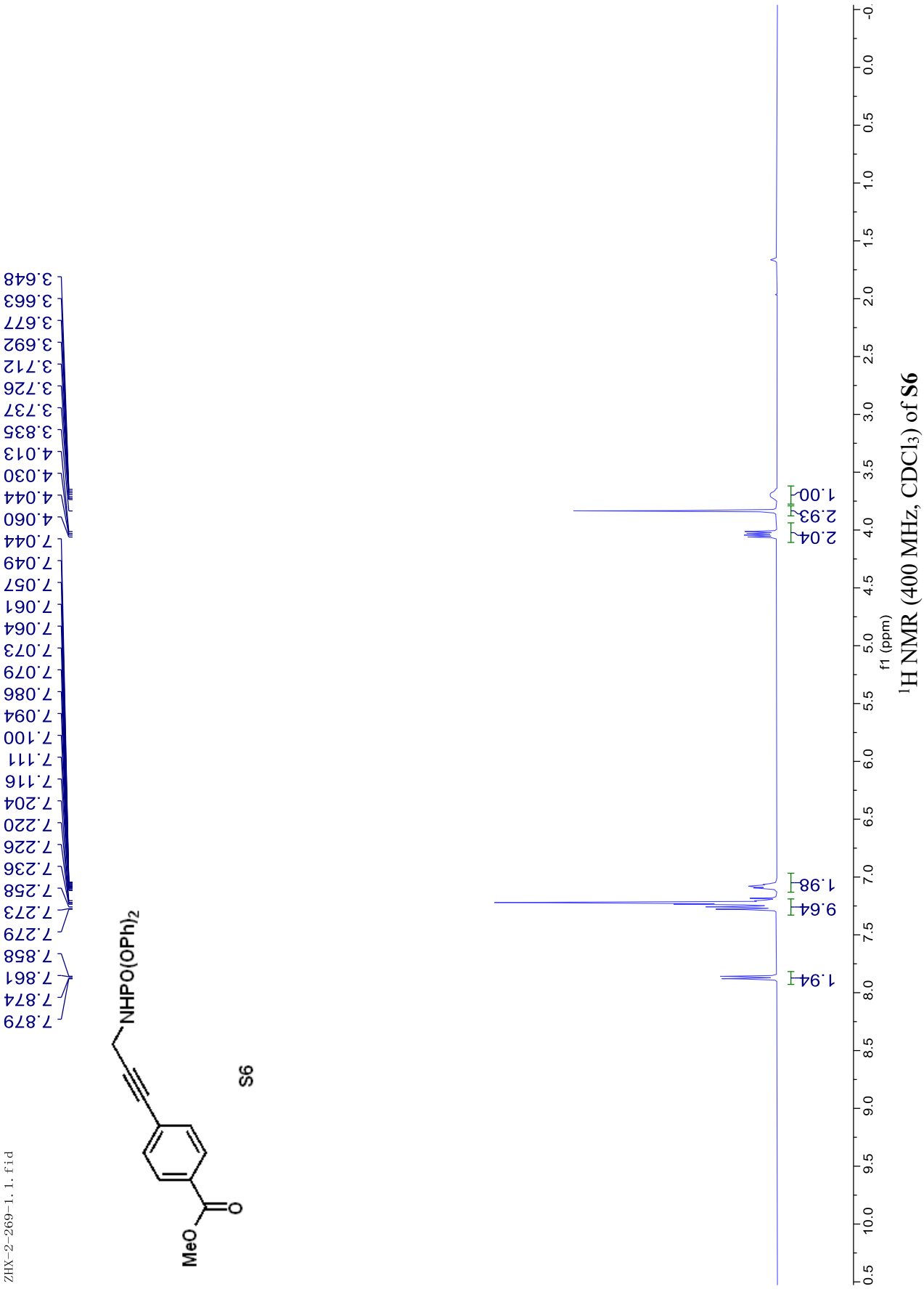
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



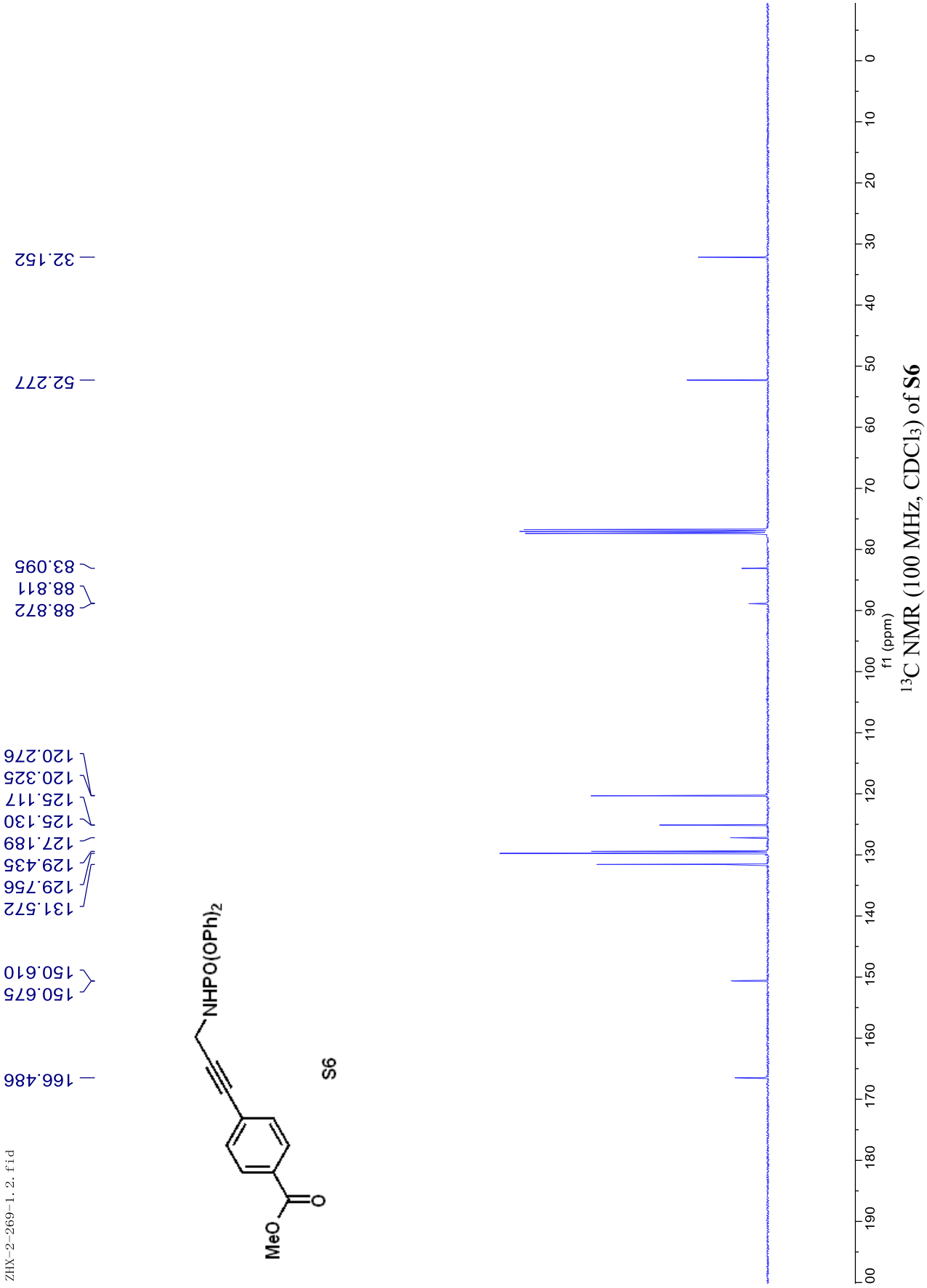
^{13}C NMR (100 MHz, $CDCl_3$) of **1f**



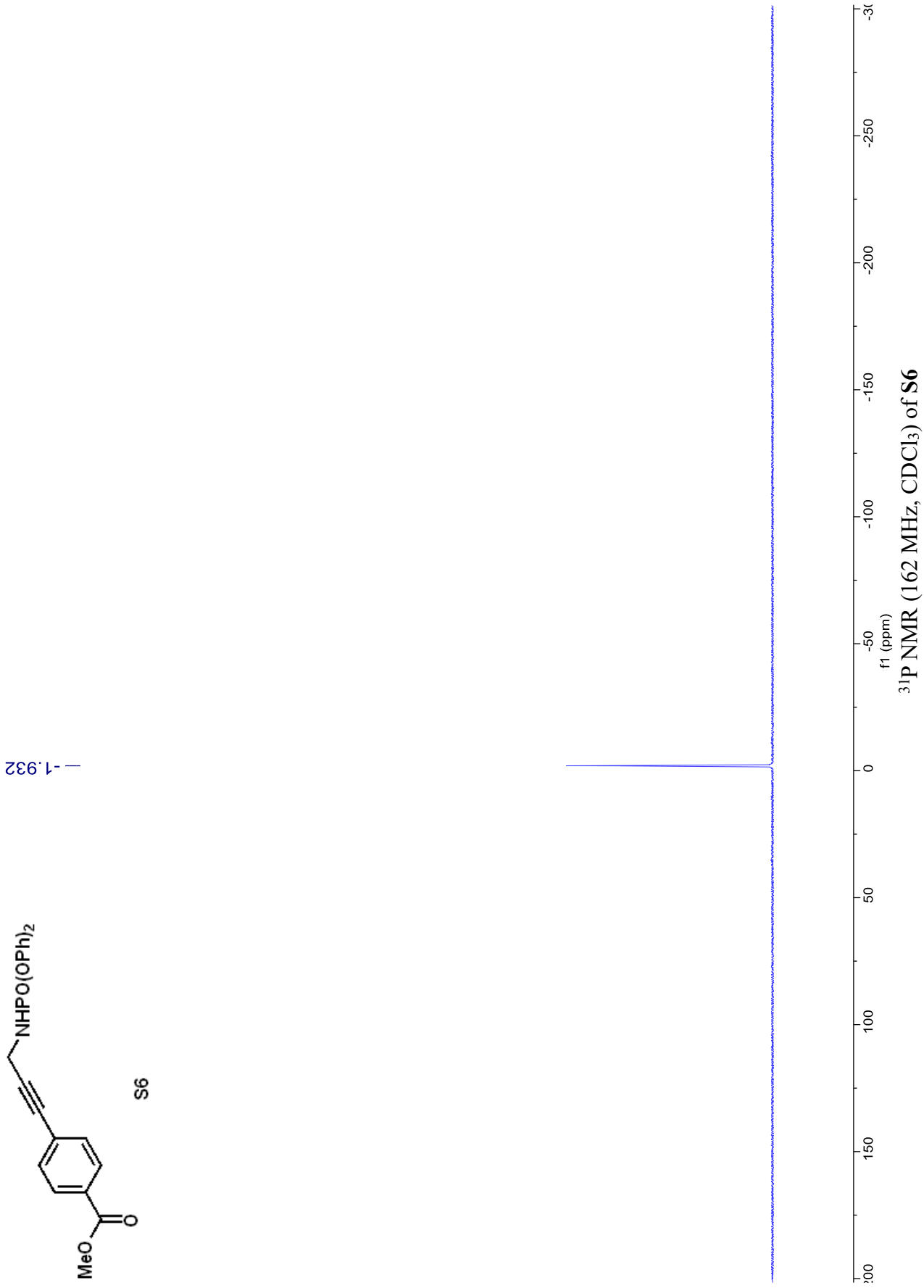
^{31}P NMR (162 MHz, $CDCl_3$) of **1f**



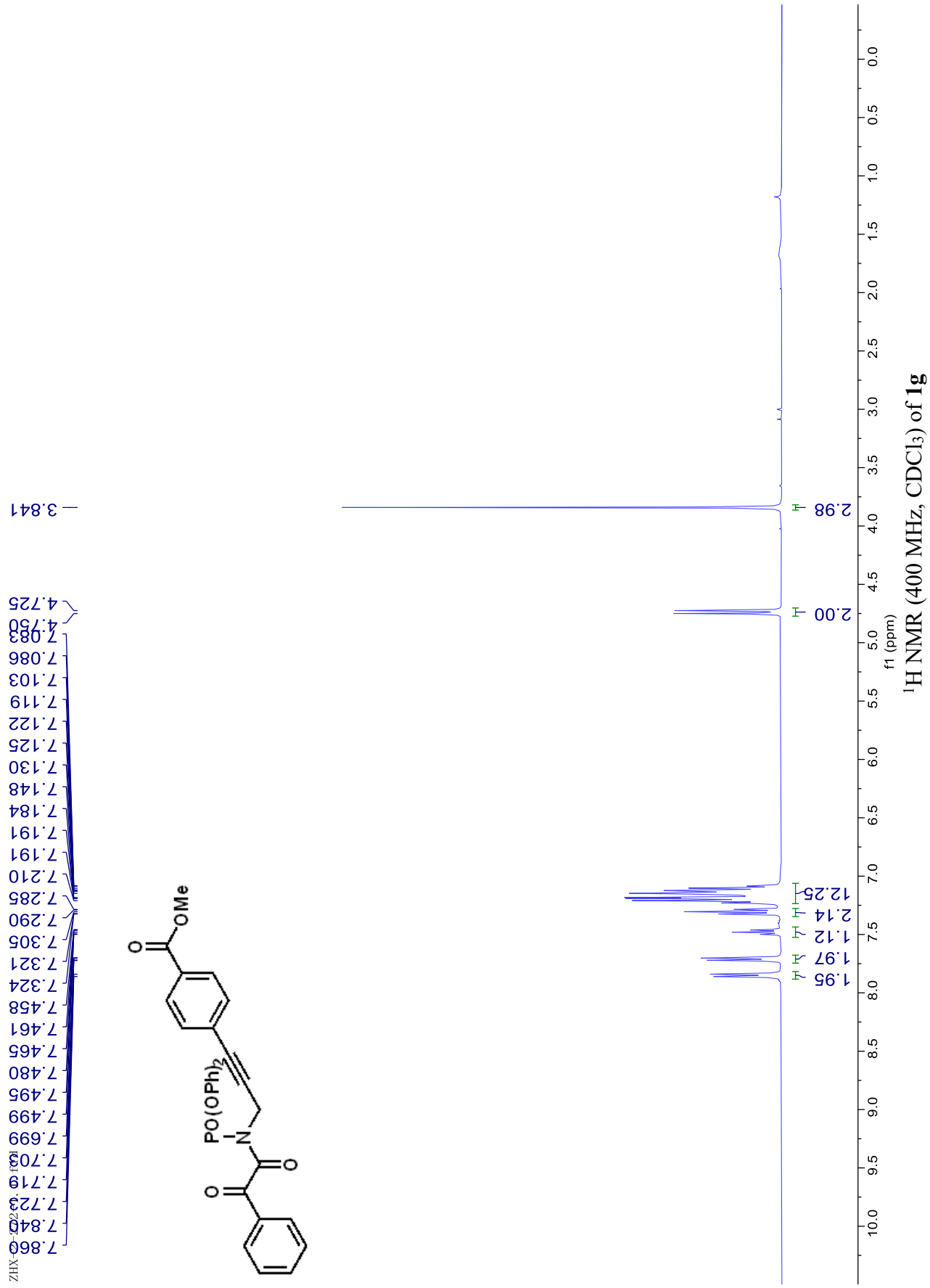
^{1}H NMR (400 MHz, $CDCl_3$) of **S6**



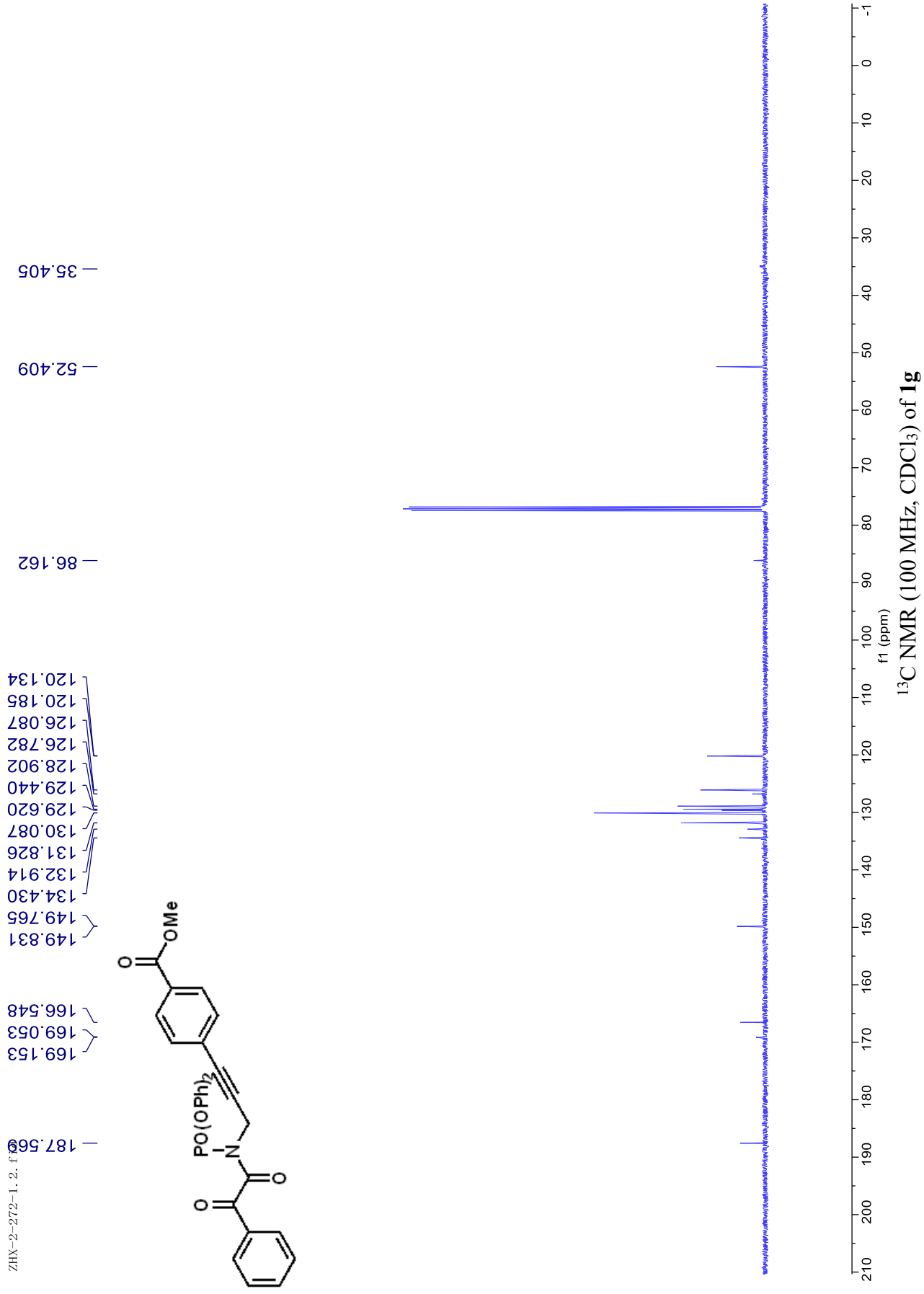
^{13}C NMR (100 MHz, $CDCl_3$) of **S6**



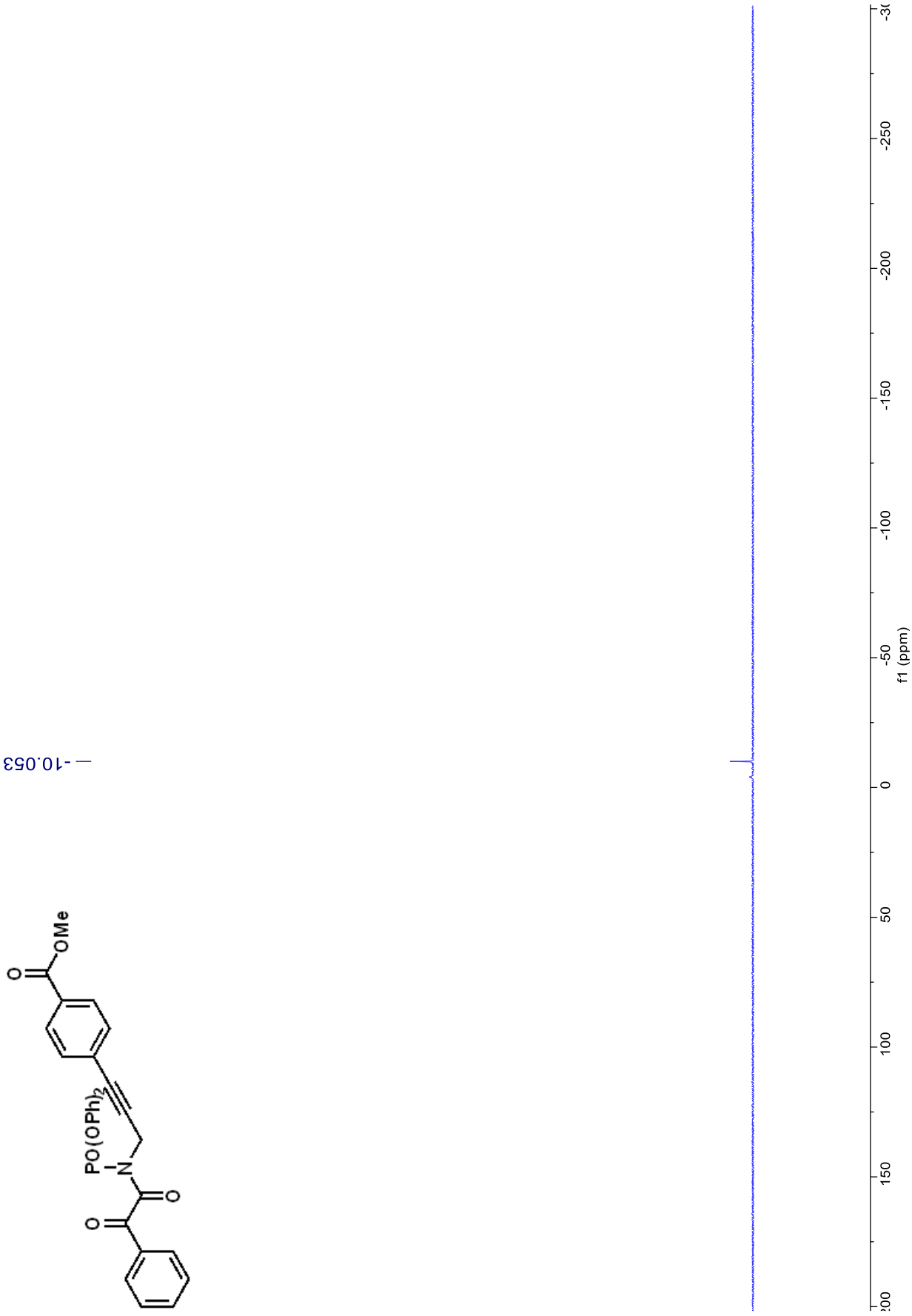
^{31}P NMR (162 MHz, $CDCl_3$) of **S6**



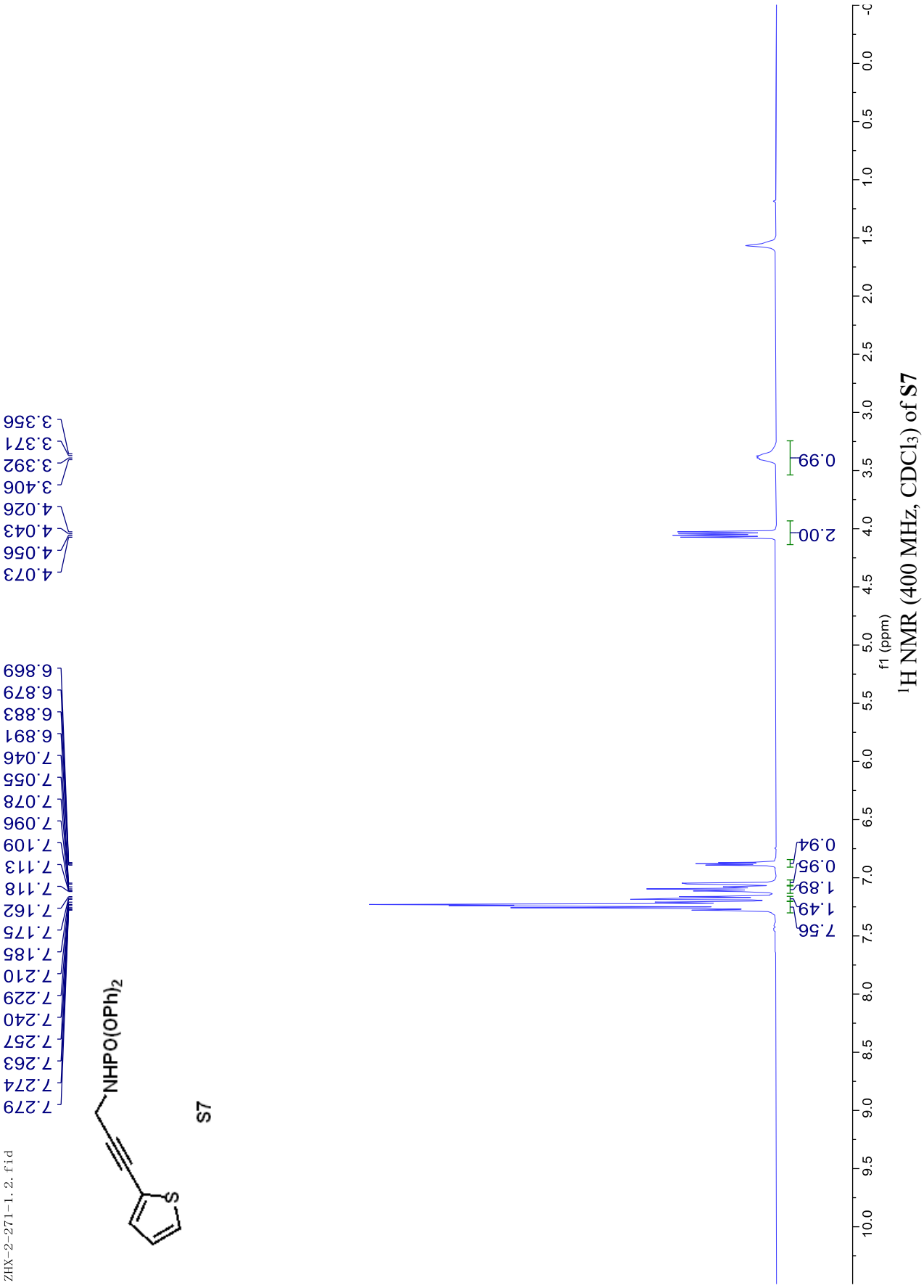
^{1}H NMR (400 MHz, $CDCl_3$) of **1g**

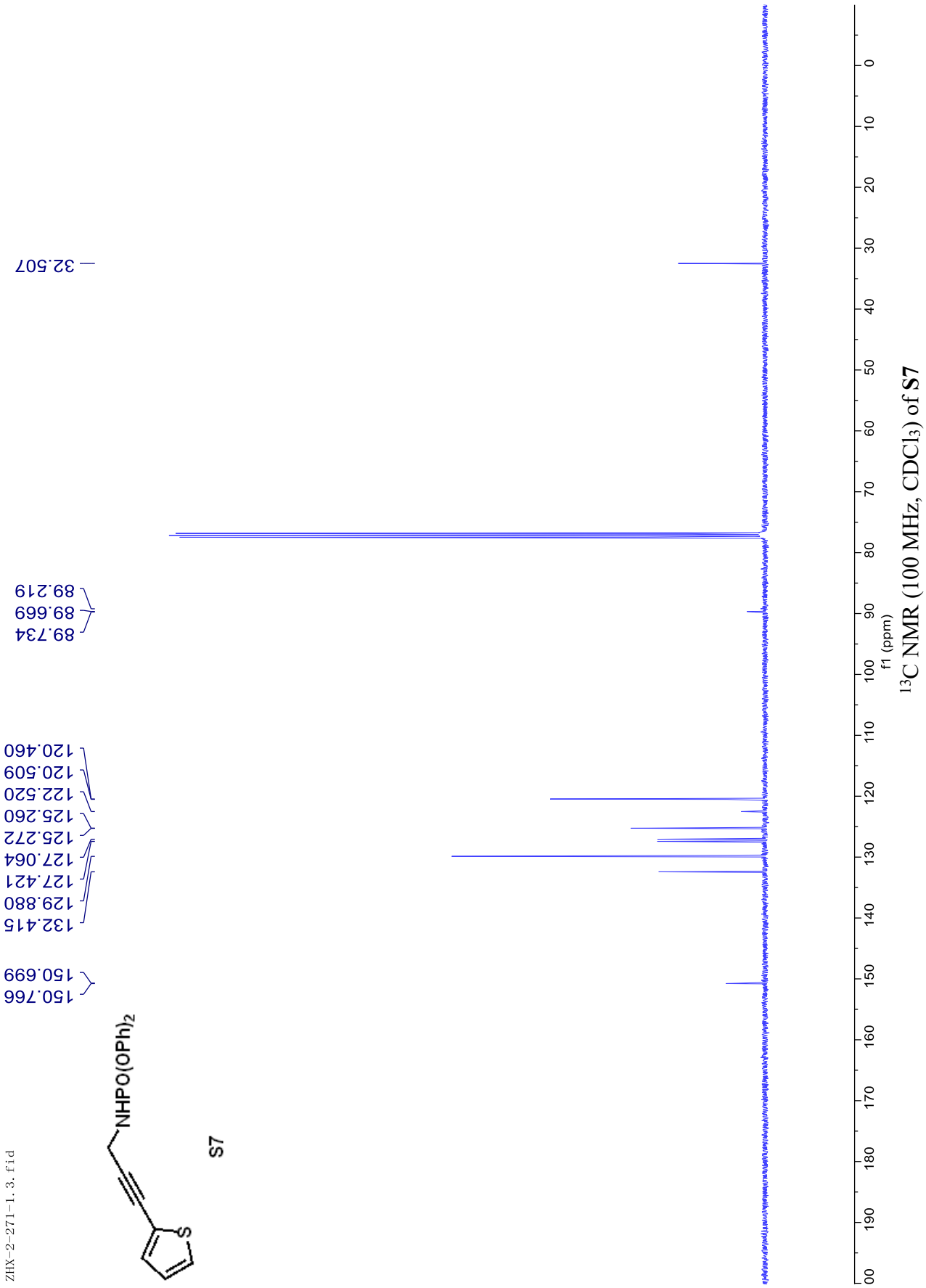


^{13}C NMR (100 MHz, $CDCl_3$) of **1g**



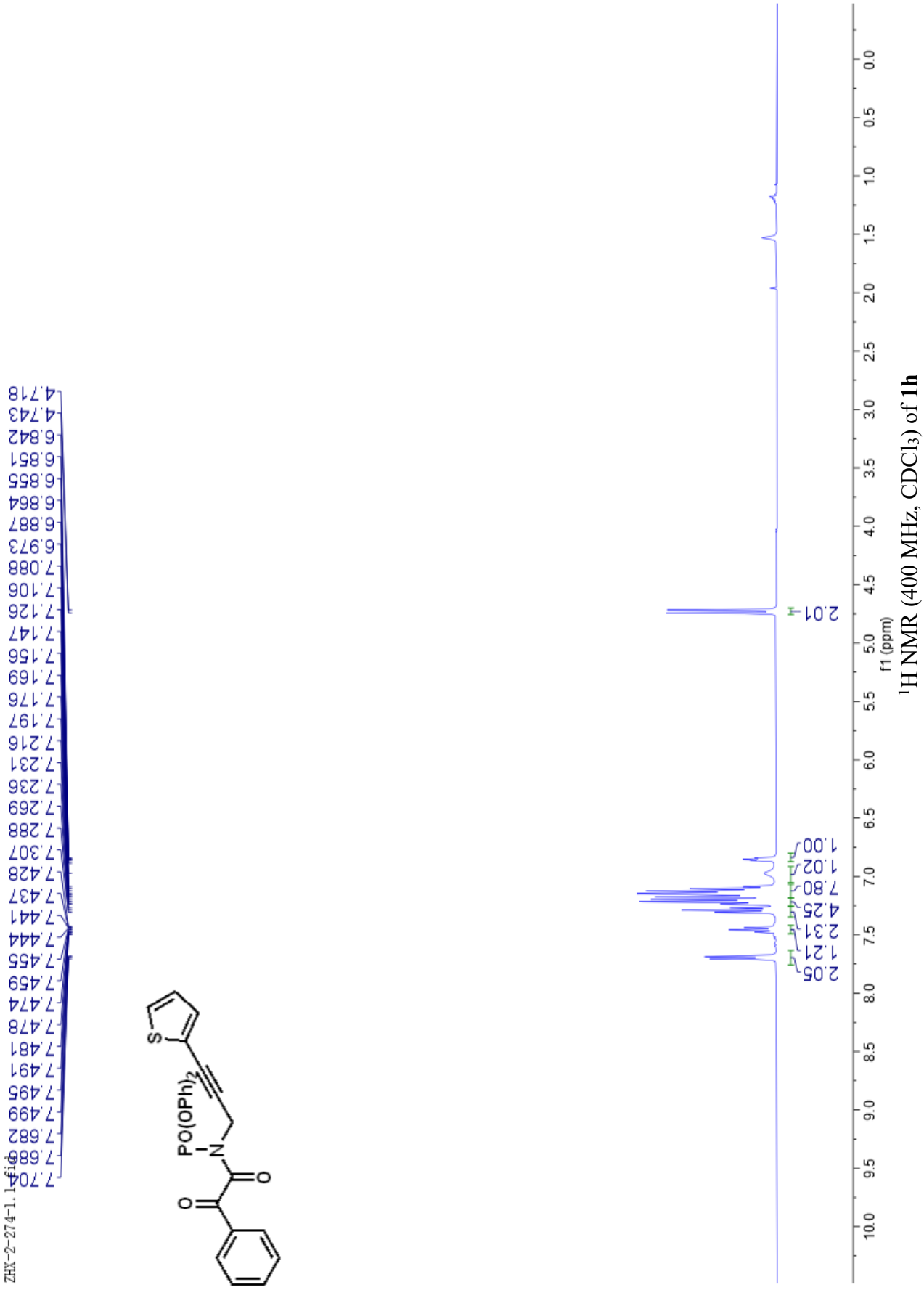
^{31}P NMR (162 MHz, $CDCl_3$) of **1g**


^{1}H NMR (400 MHz, $CDCl_3$) of **S7**
f1 (ppm)
7.279
7.274
7.263
7.257
7.240
7.229
7.210
7.185
7.175
7.162
7.118
7.113
7.109
7.096
7.078
7.055
7.046
6.891
6.883
6.879
6.869
4.073
4.056
4.043
4.026
3.406
3.392
3.371
3.356
7.56
1.49
1.89
0.95
0.94
2.00
0.99
NHPO(OPh)$_2$
S
S7
ZHX-2-271-1.2.fid

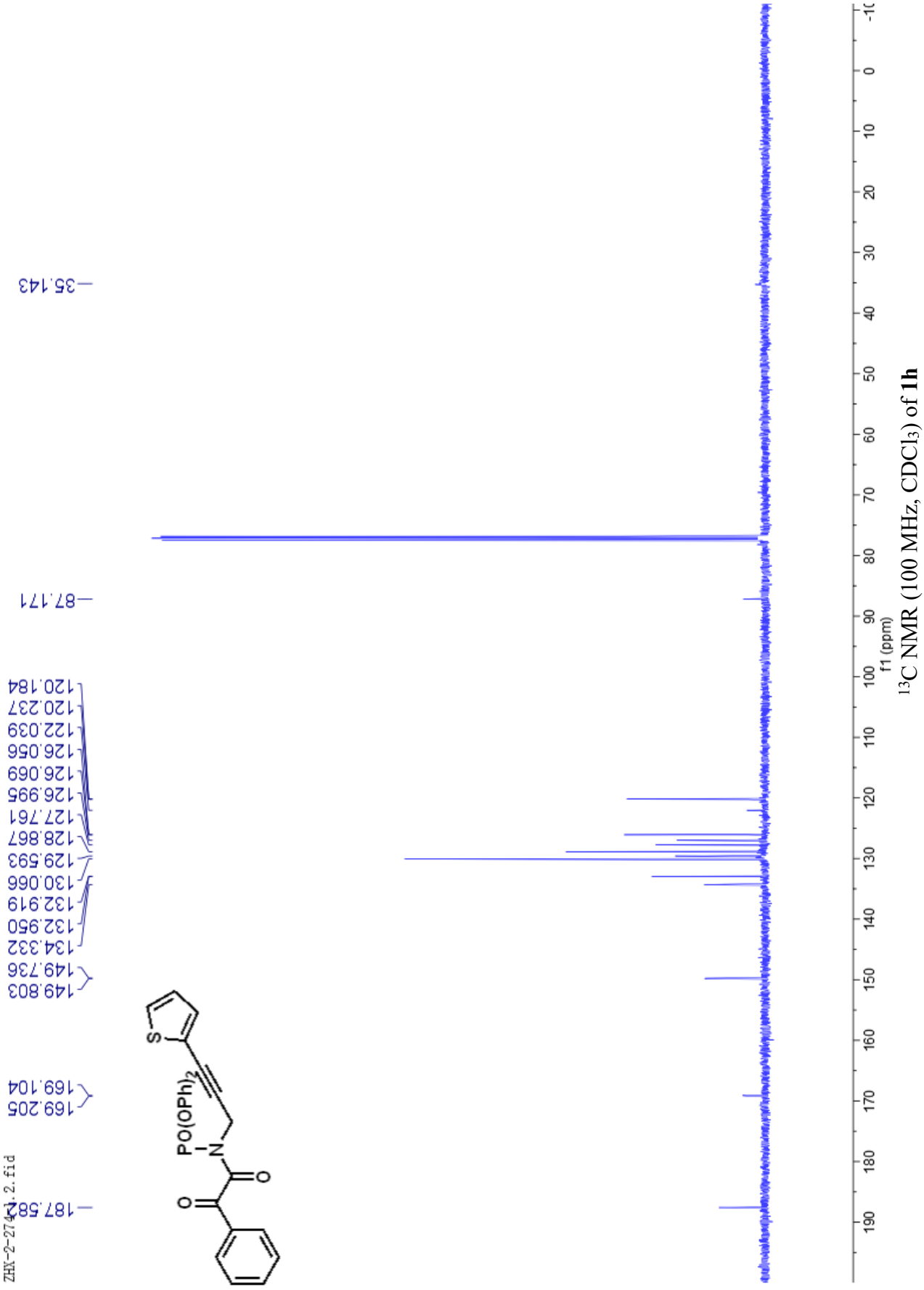


^{13}C NMR (100 MHz, $CDCl_3$) of **S7**

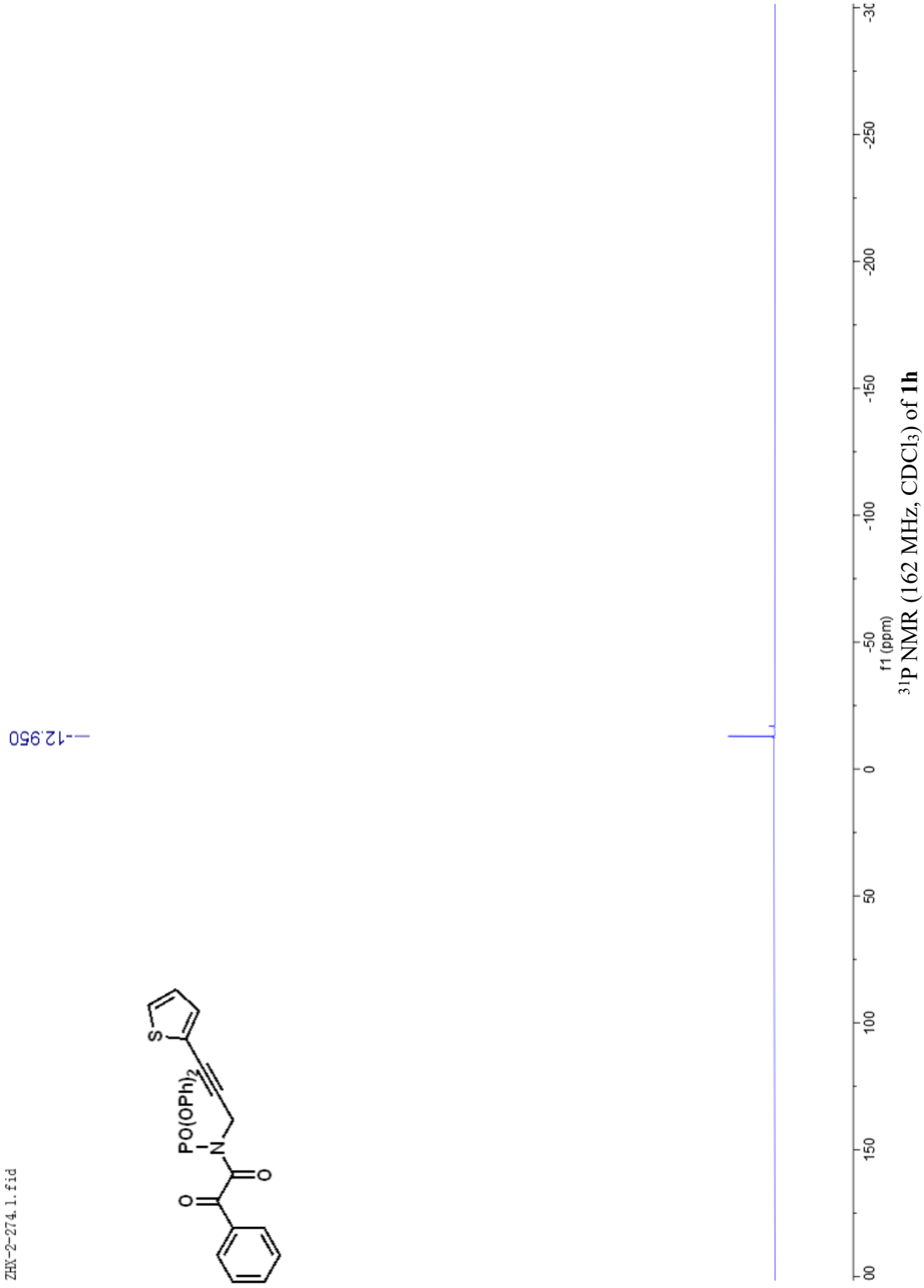
^{31}P NMR (162 MHz, $CDCl_3$) of **S7**



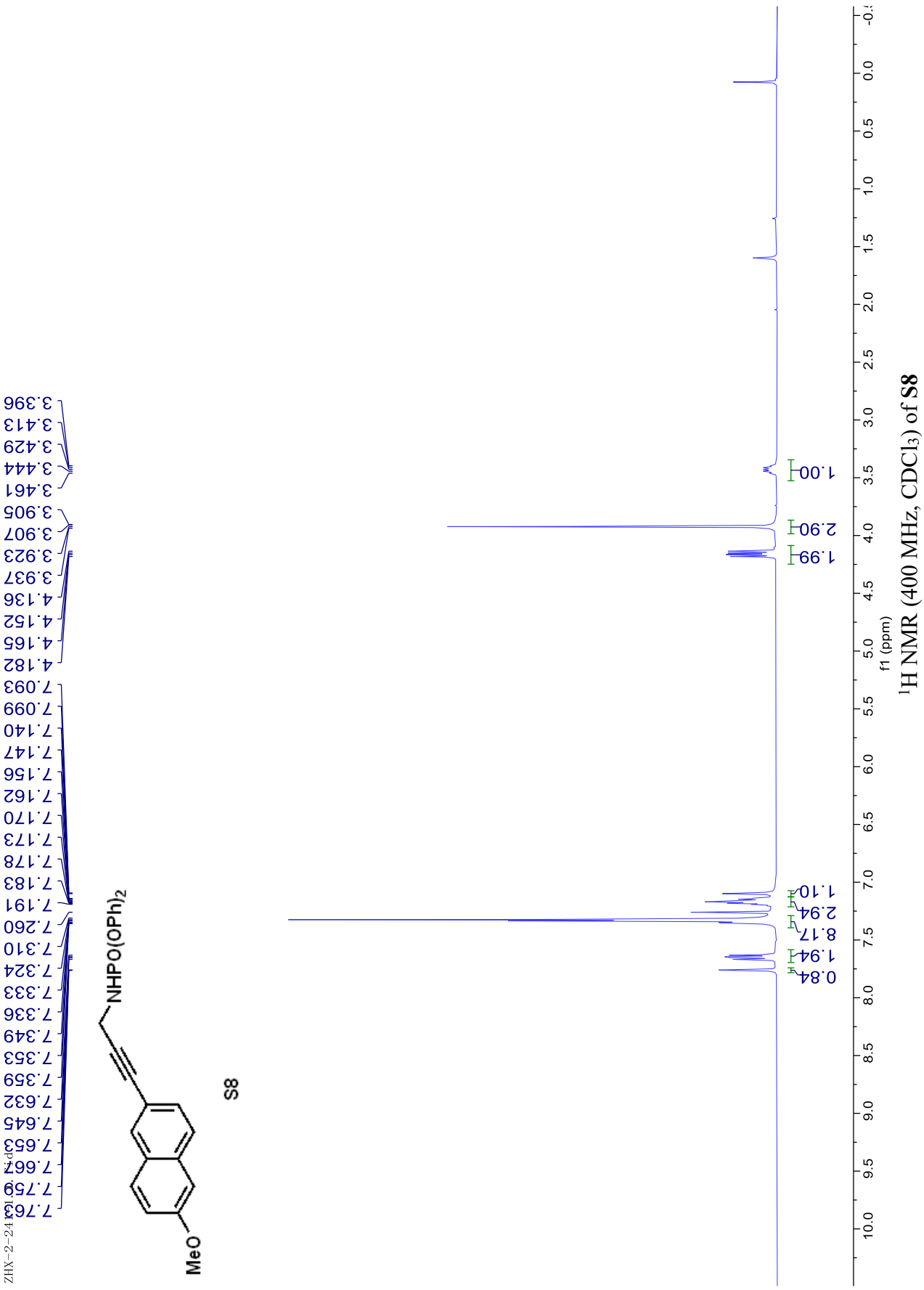
^{1}H NMR (400 MHz, $CDCl_3$) of **1h**



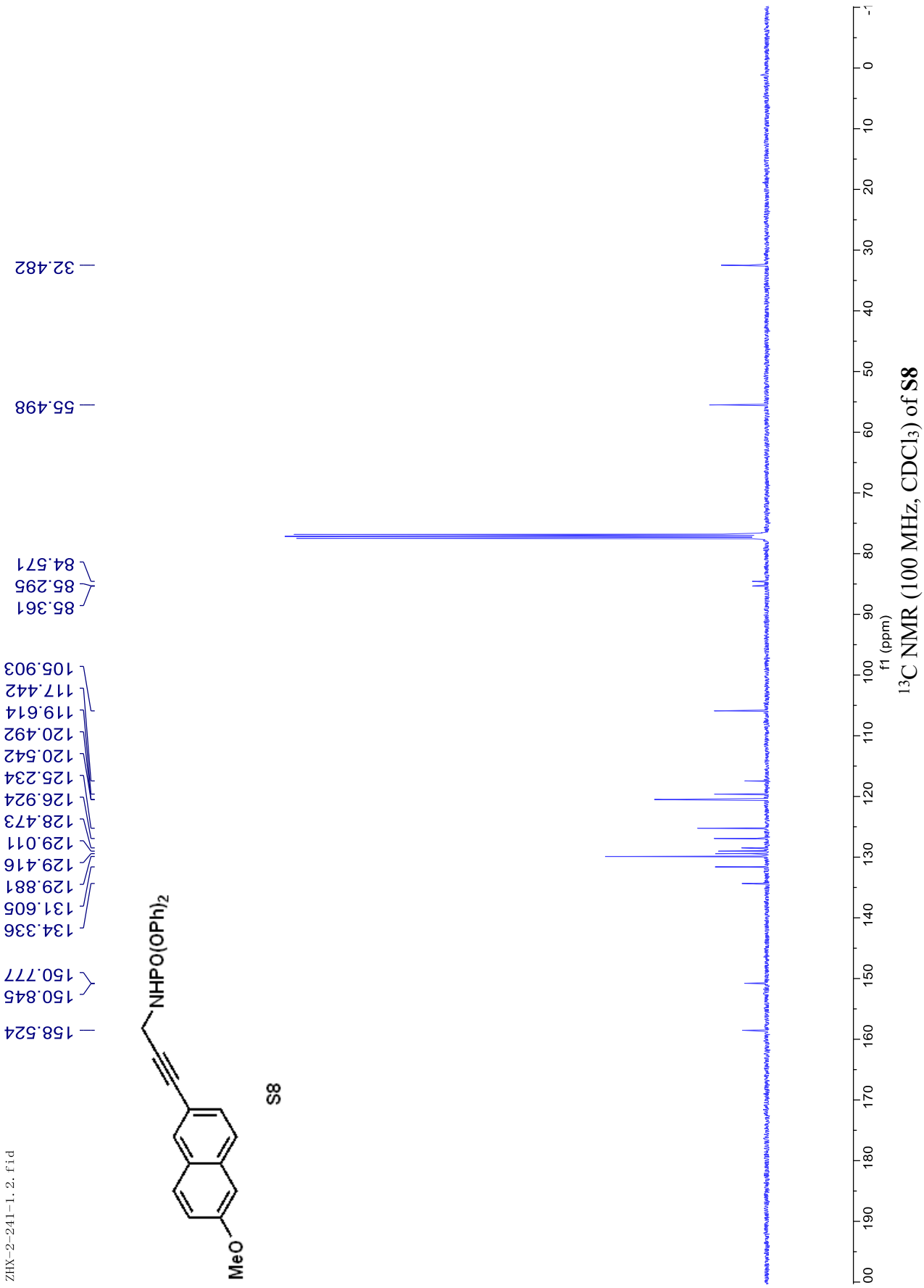
^{13}C NMR (100 MHz, $CDCl_3$) of **1h**



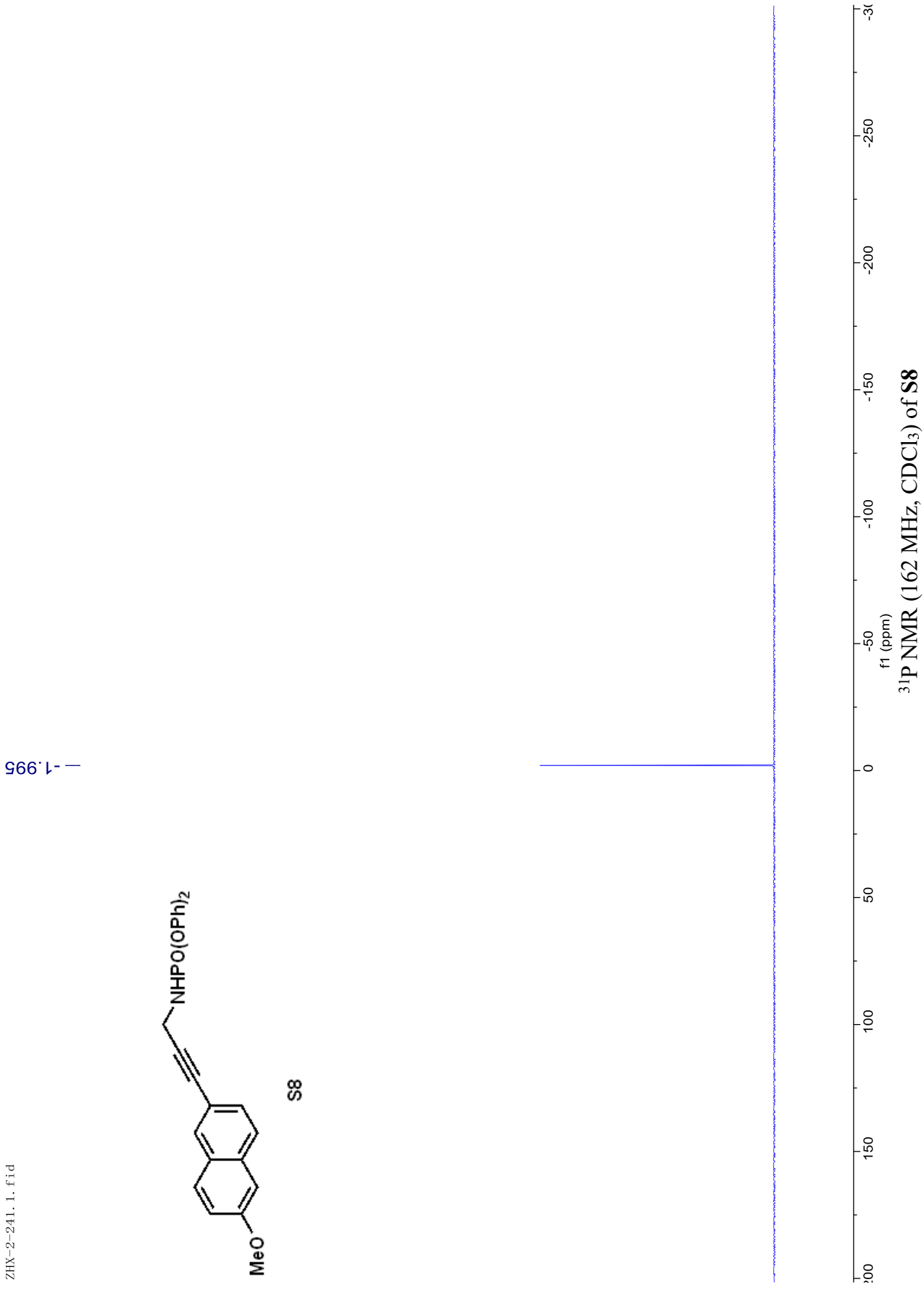
^{31}P NMR (162 MHz, $CDCl_3$) of **1h**



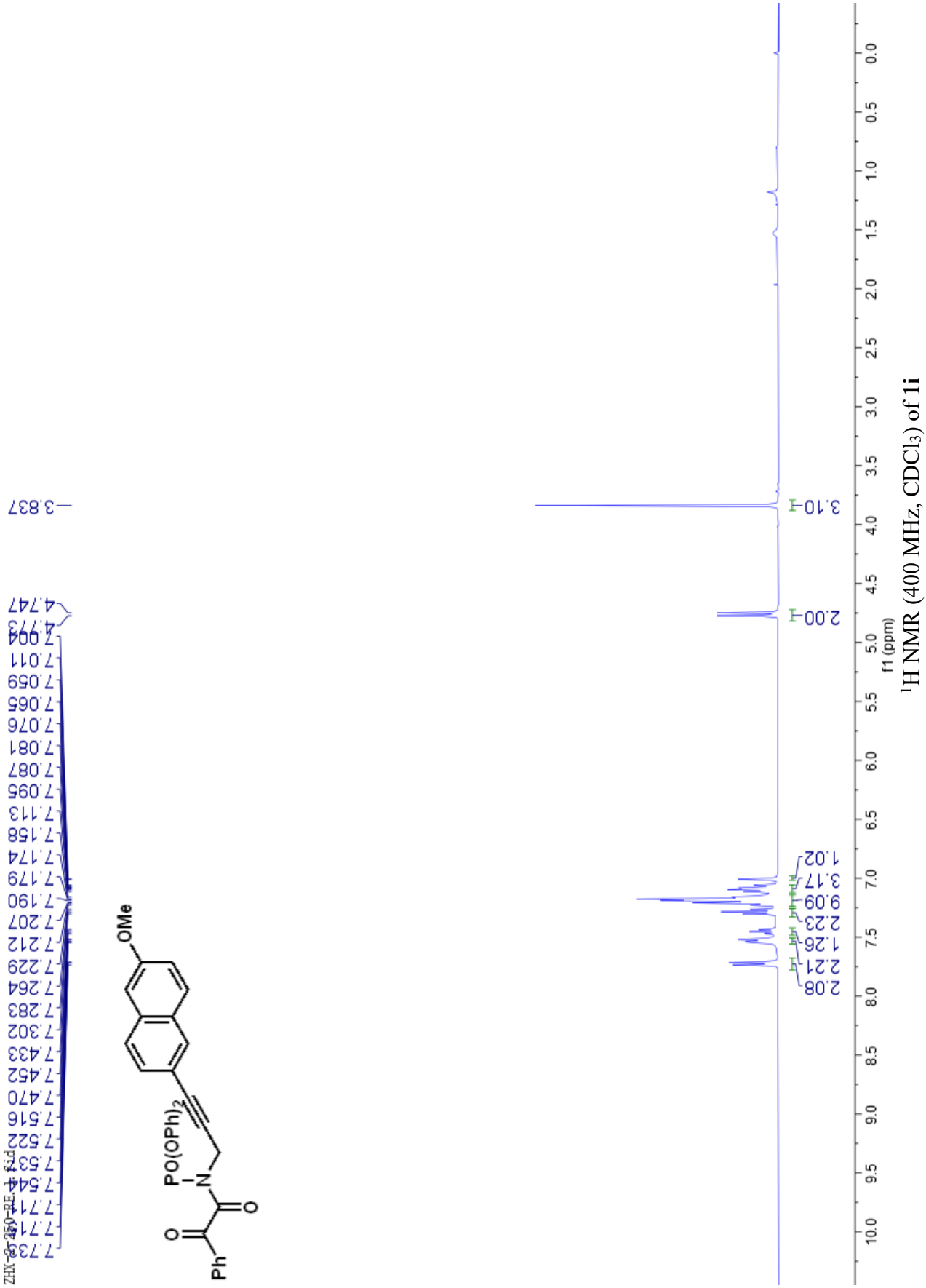
^{1}H NMR (400 MHz, $CDCl_3$) of **S8**



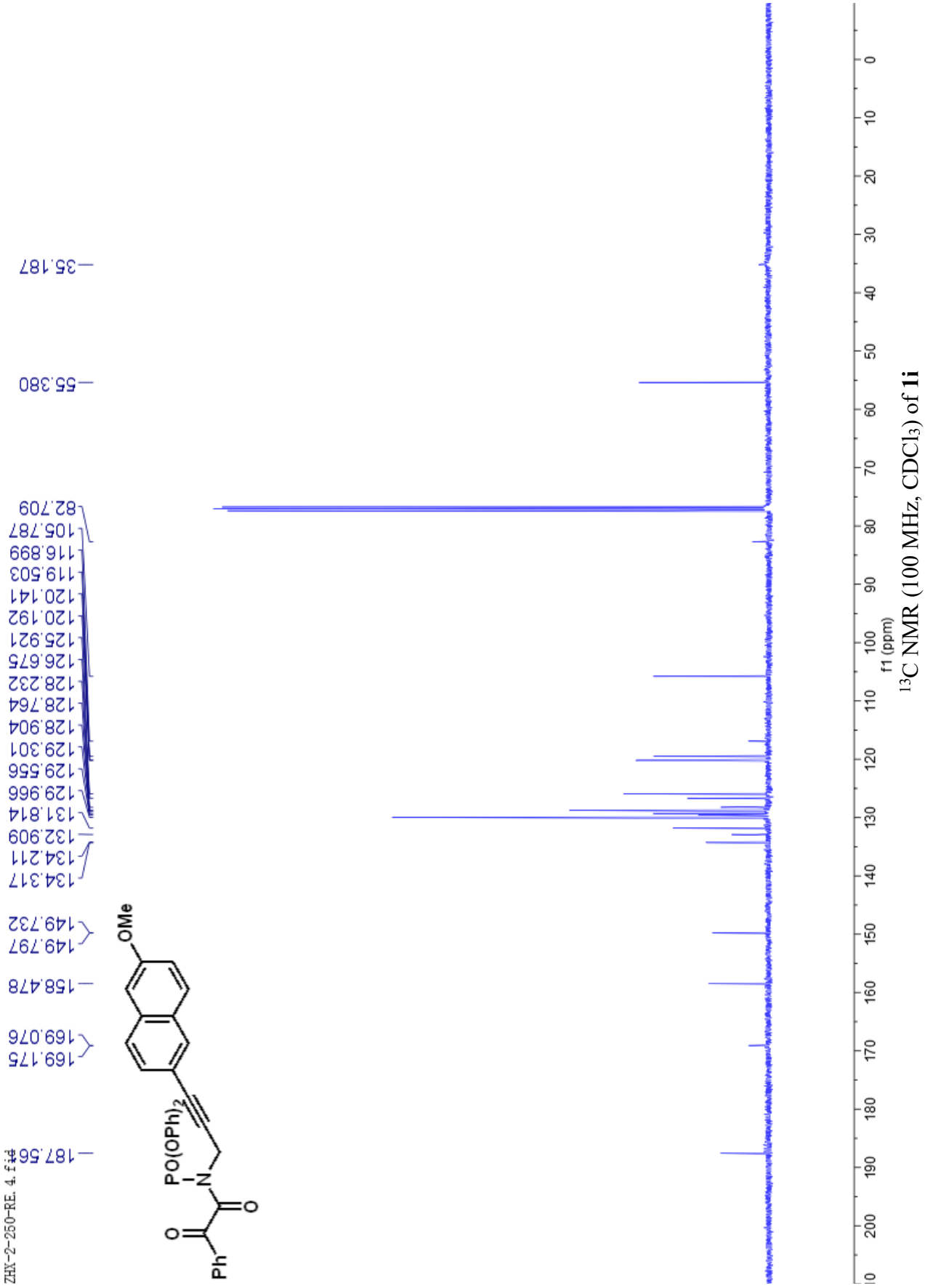
^{13}C NMR (100 MHz, $CDCl_3$) of **S8**



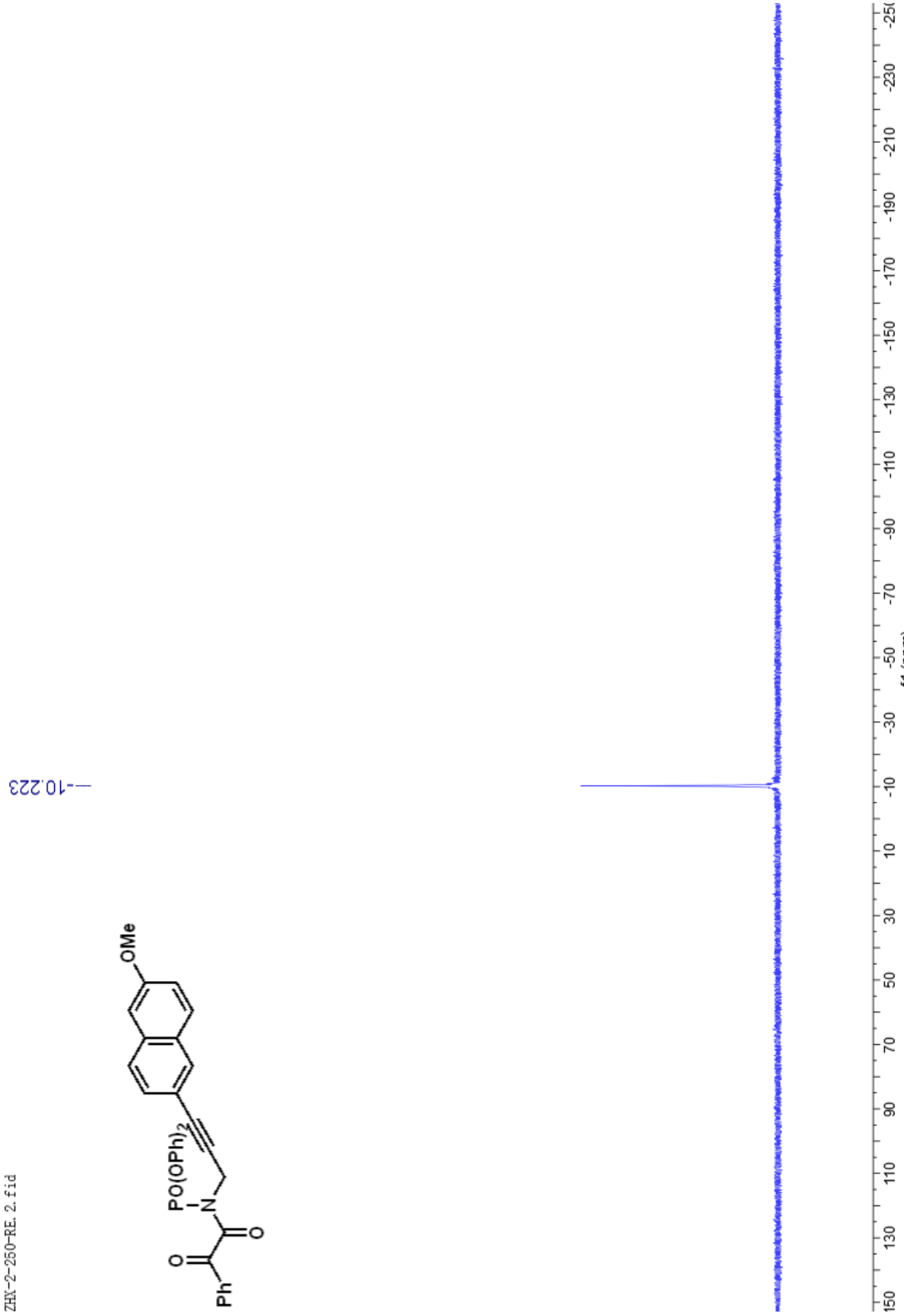
^{31}P NMR (162 MHz, $CDCl_3$) of **S8**



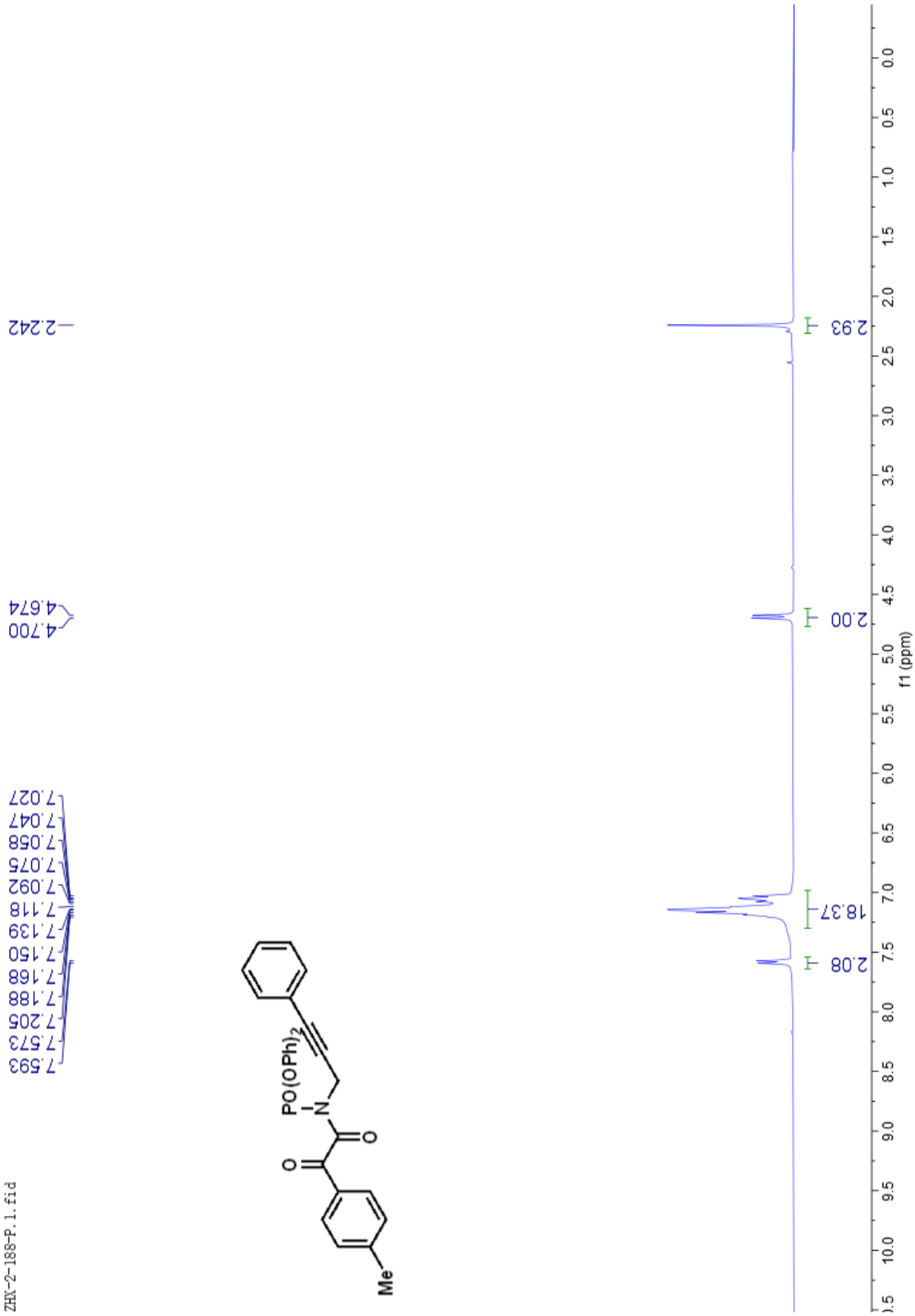
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



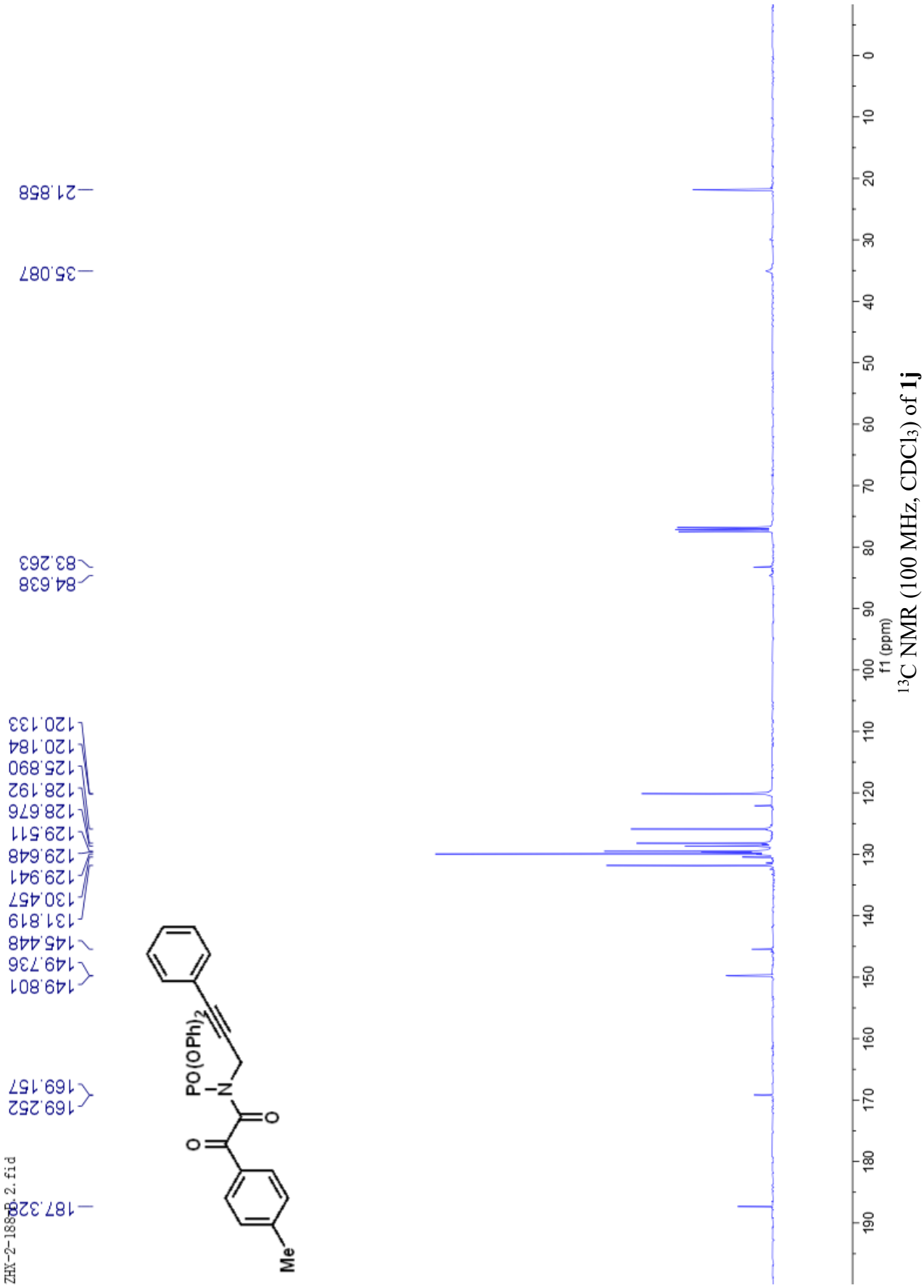
^{13}C NMR (100 MHz, $CDCl_3$) of **1i**



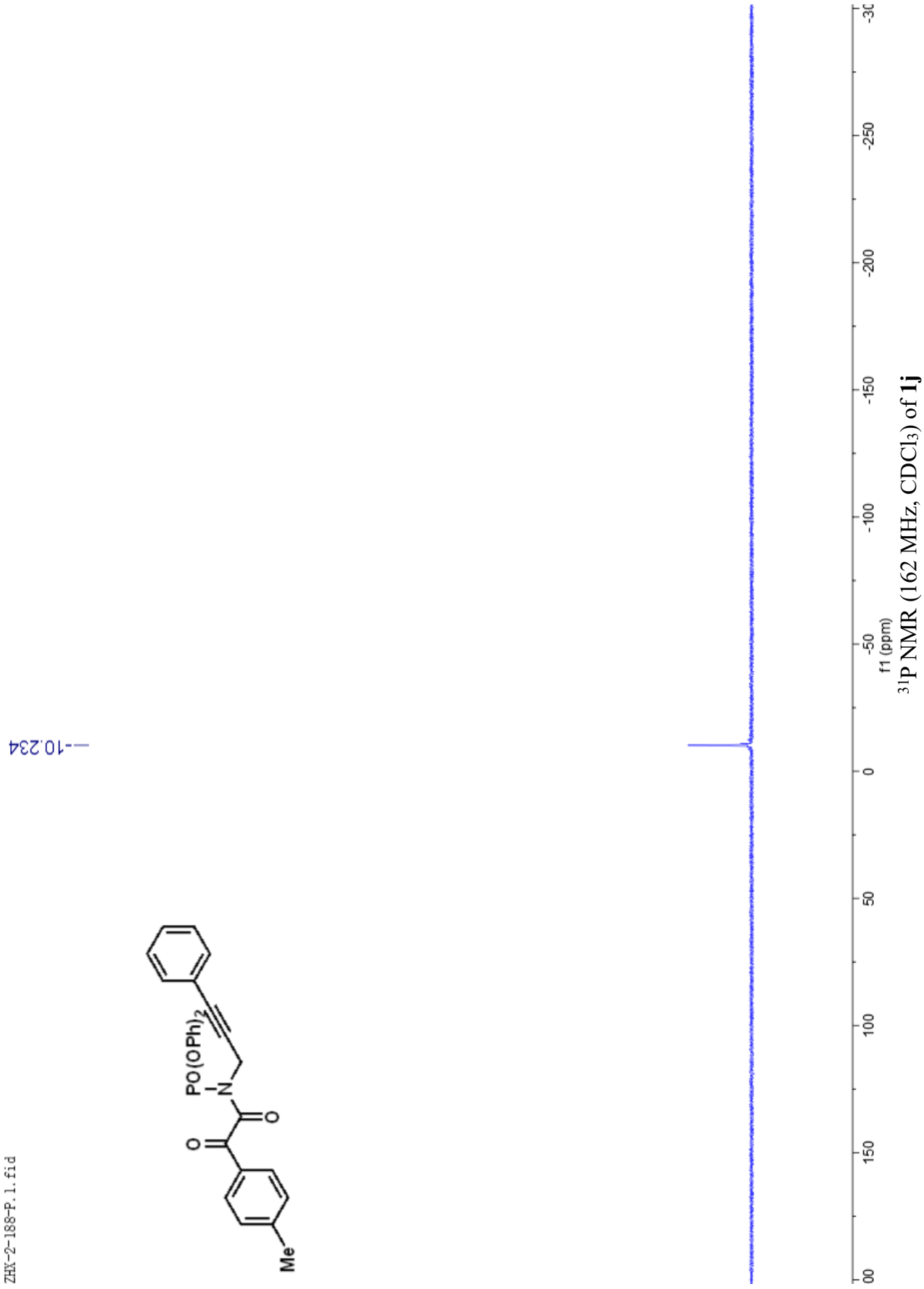
^{31}P NMR (162 MHz, $CDCl_3$) of **1i**



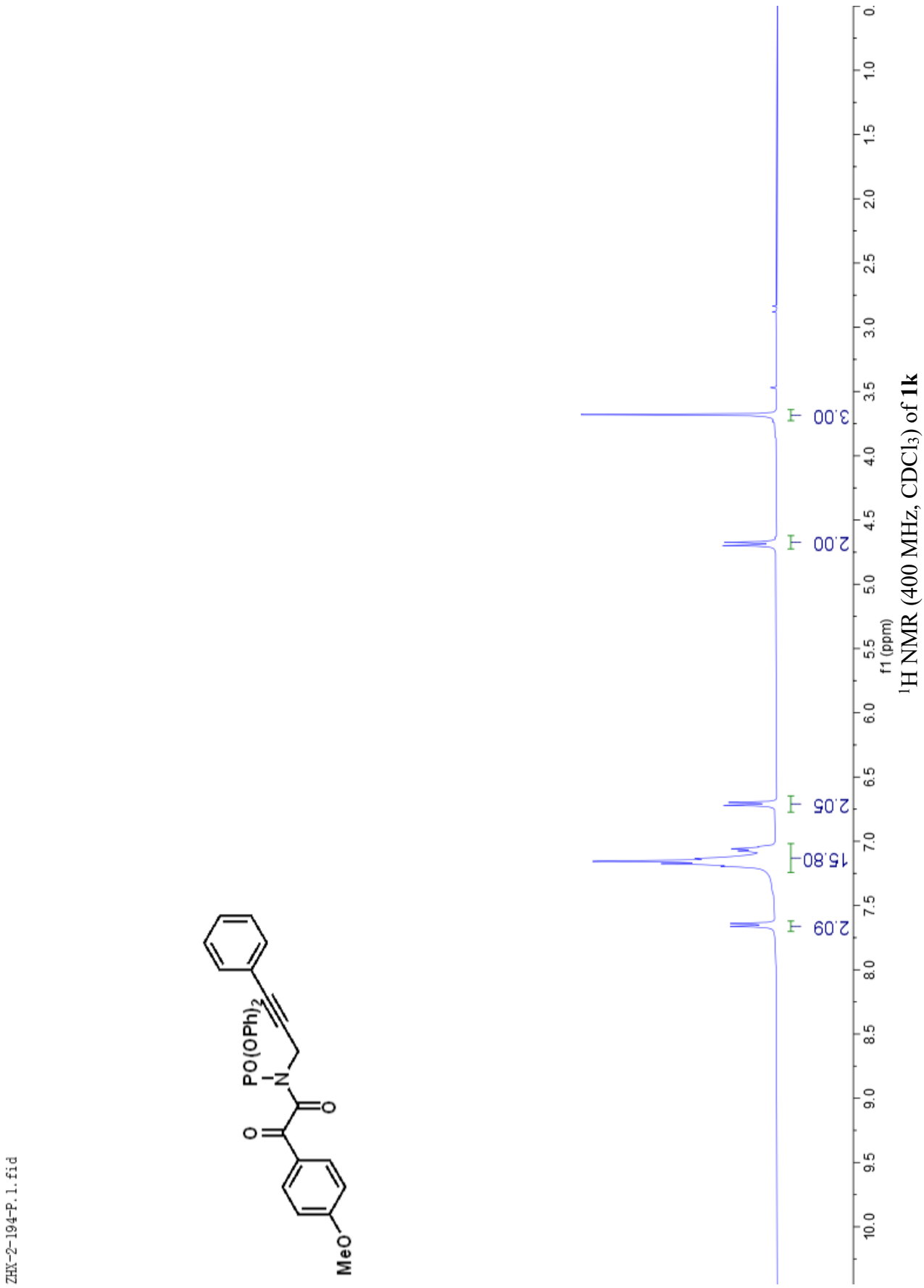
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**



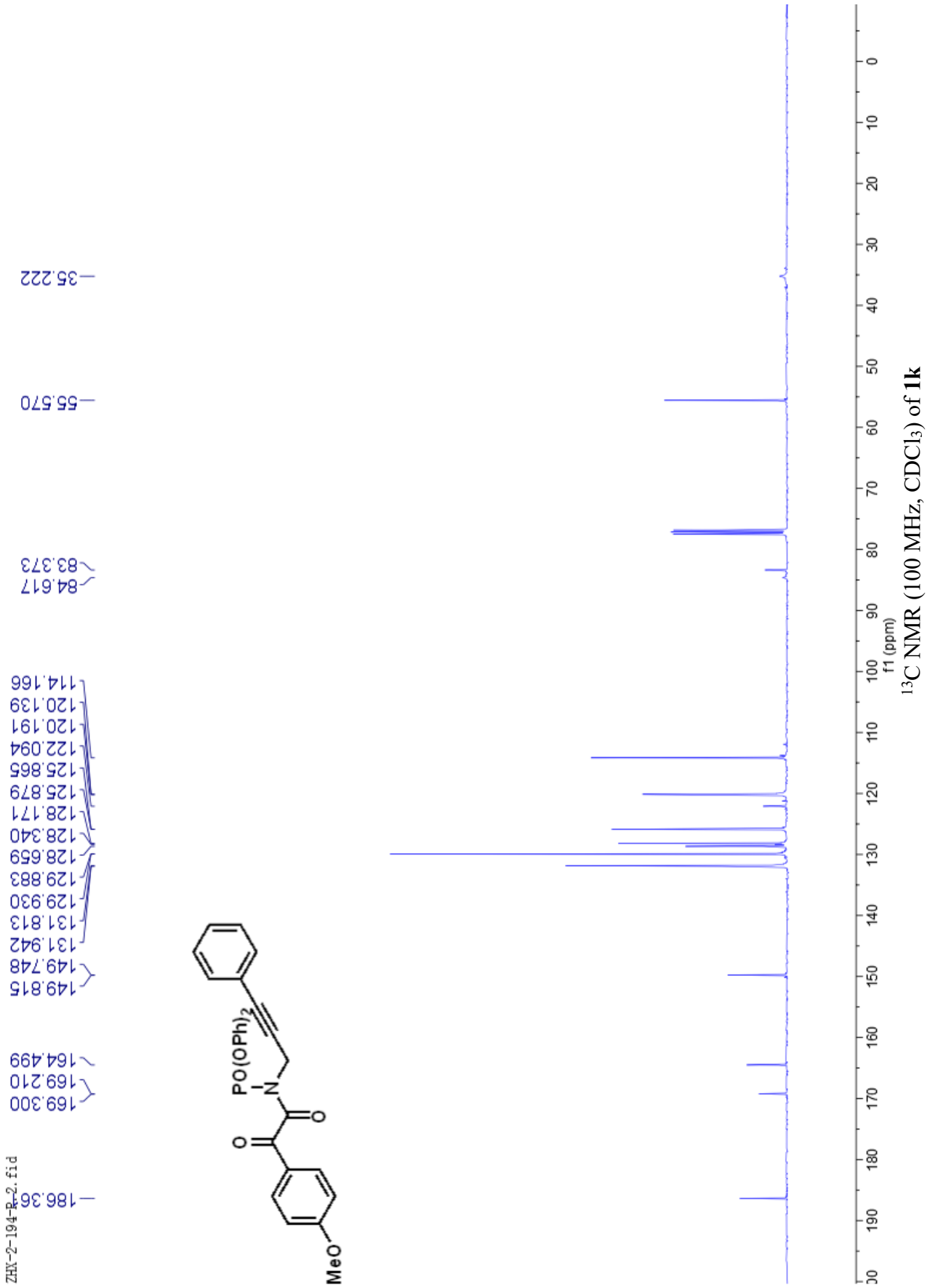
^{13}C NMR (100 MHz, $CDCl_3$) of **1j**



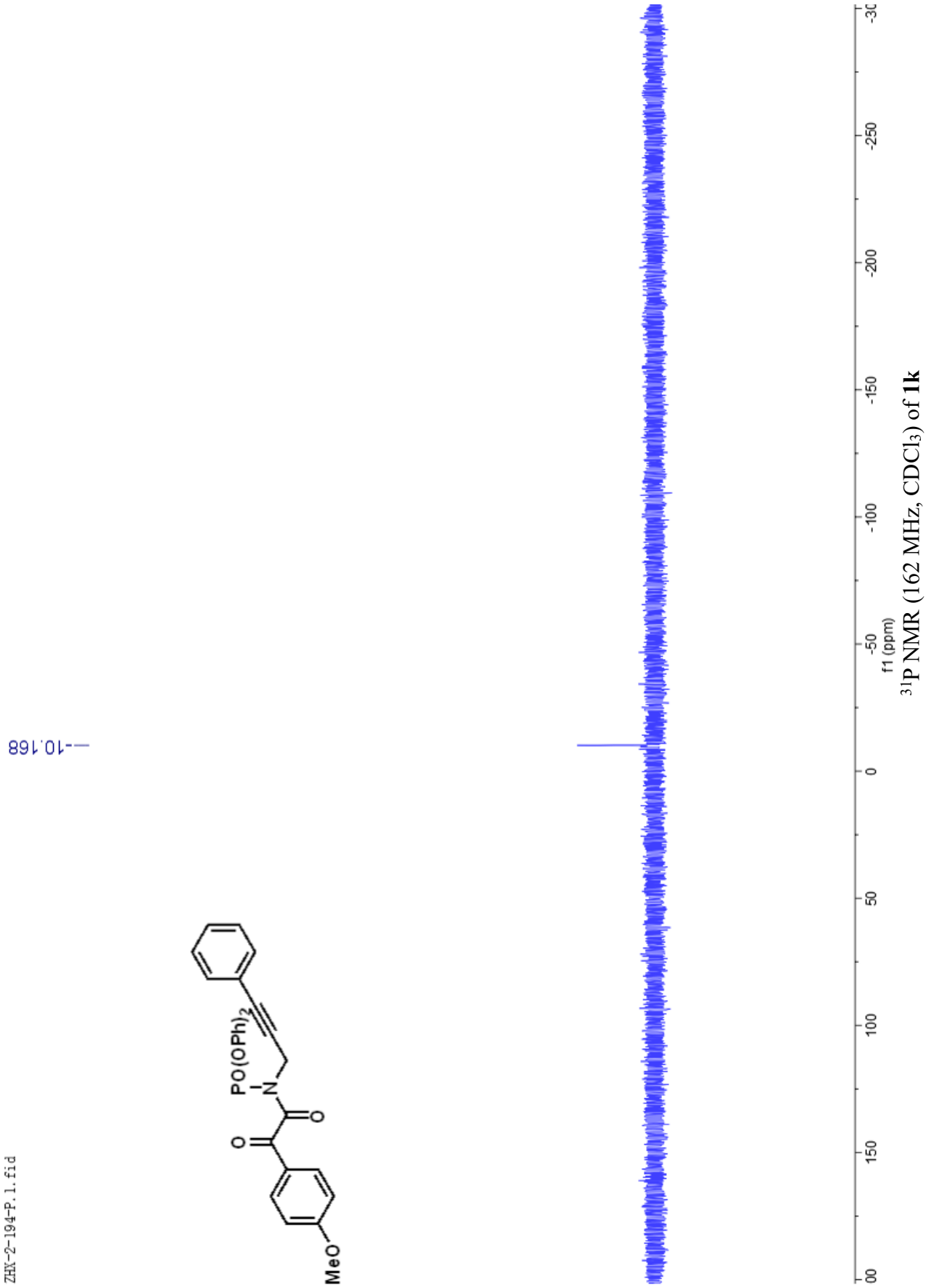
^{31}P NMR (162 MHz, $CDCl_3$) of **1j**



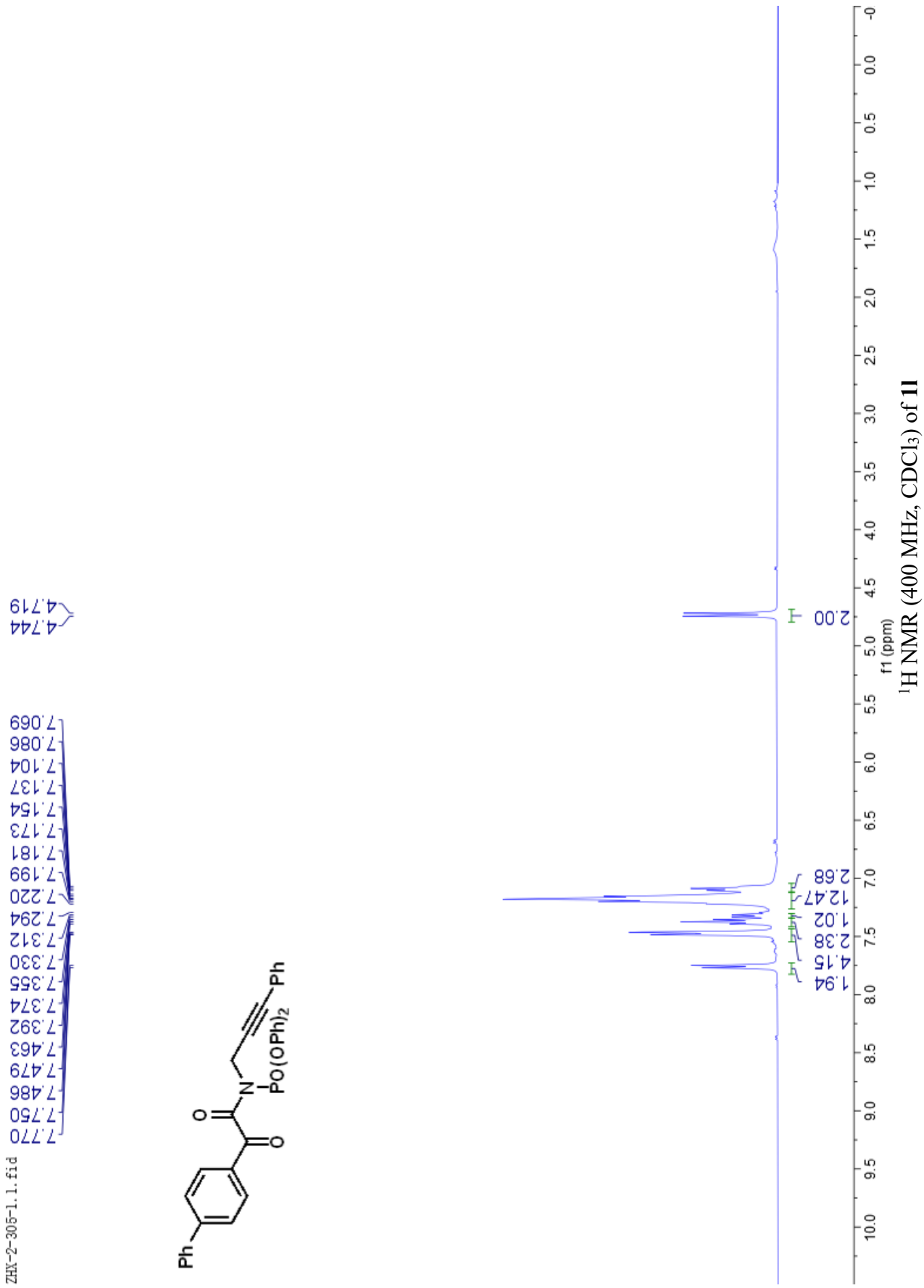
^{1}H NMR (400 MHz, $CDCl_3$) of **1k**



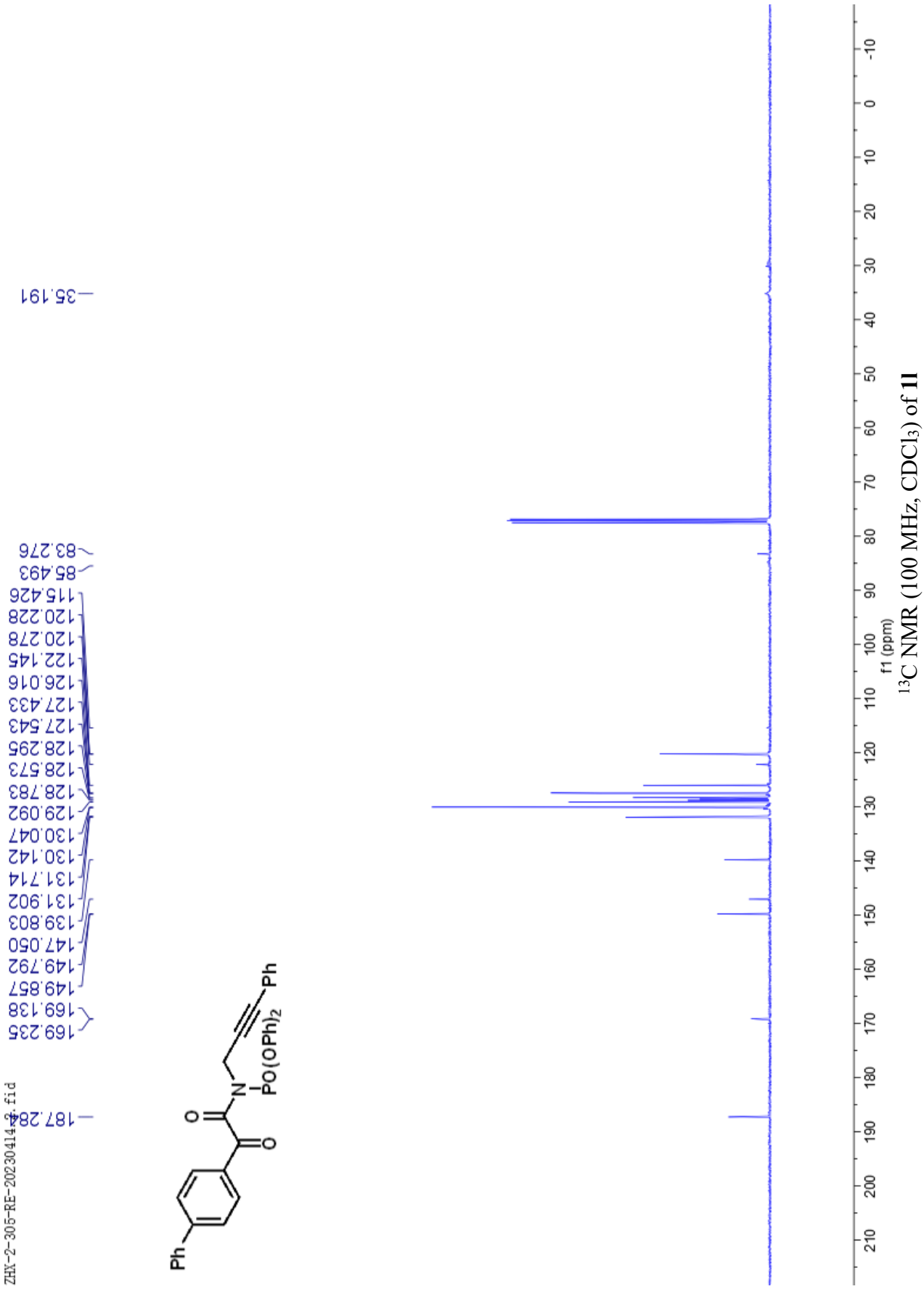
^{13}C NMR (100 MHz, $CDCl_3$) of **1k**



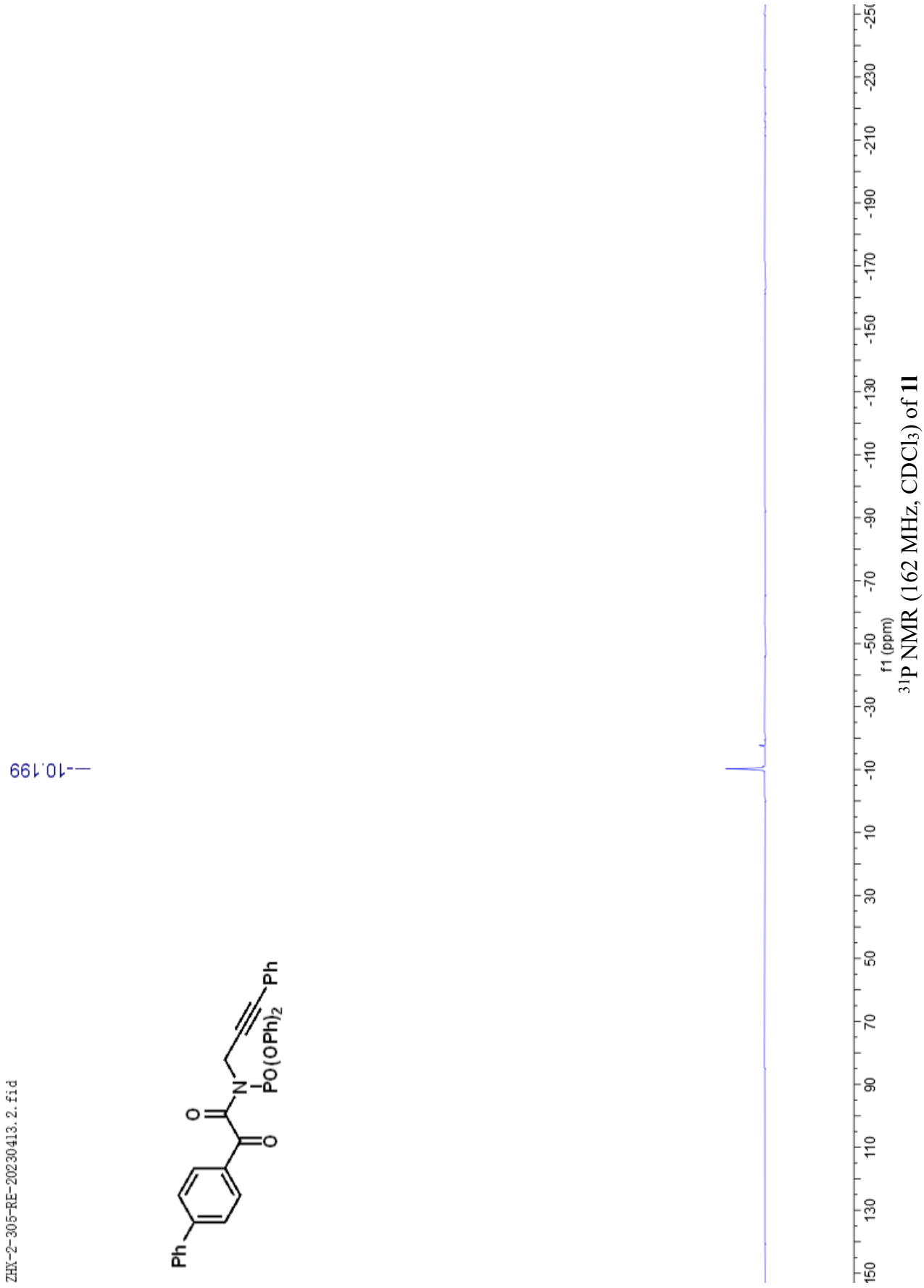
^{31}P NMR (162 MHz, $CDCl_3$) of **1k**



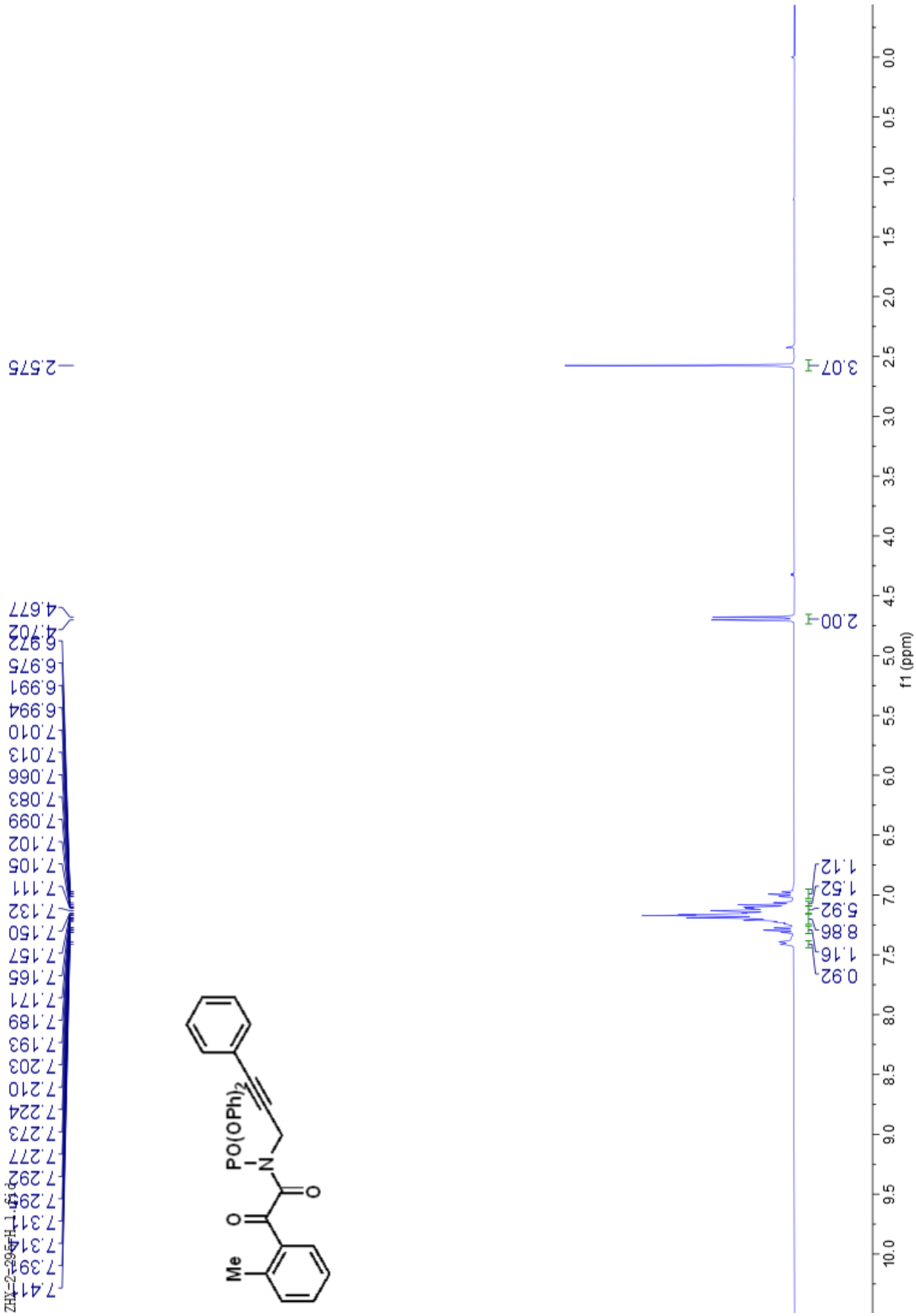
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



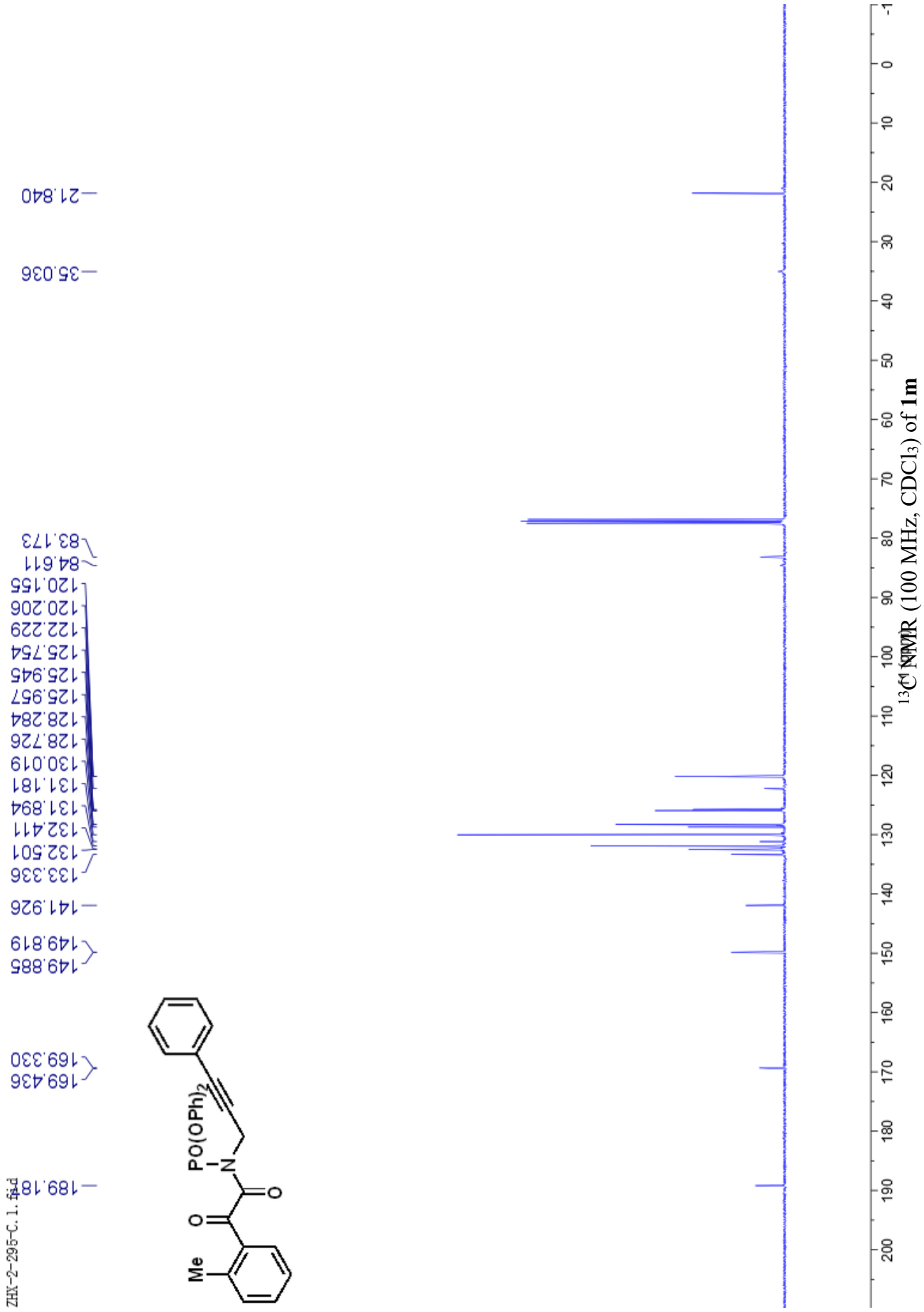
^{13}C NMR (100 MHz, $CDCl_3$) of **11**



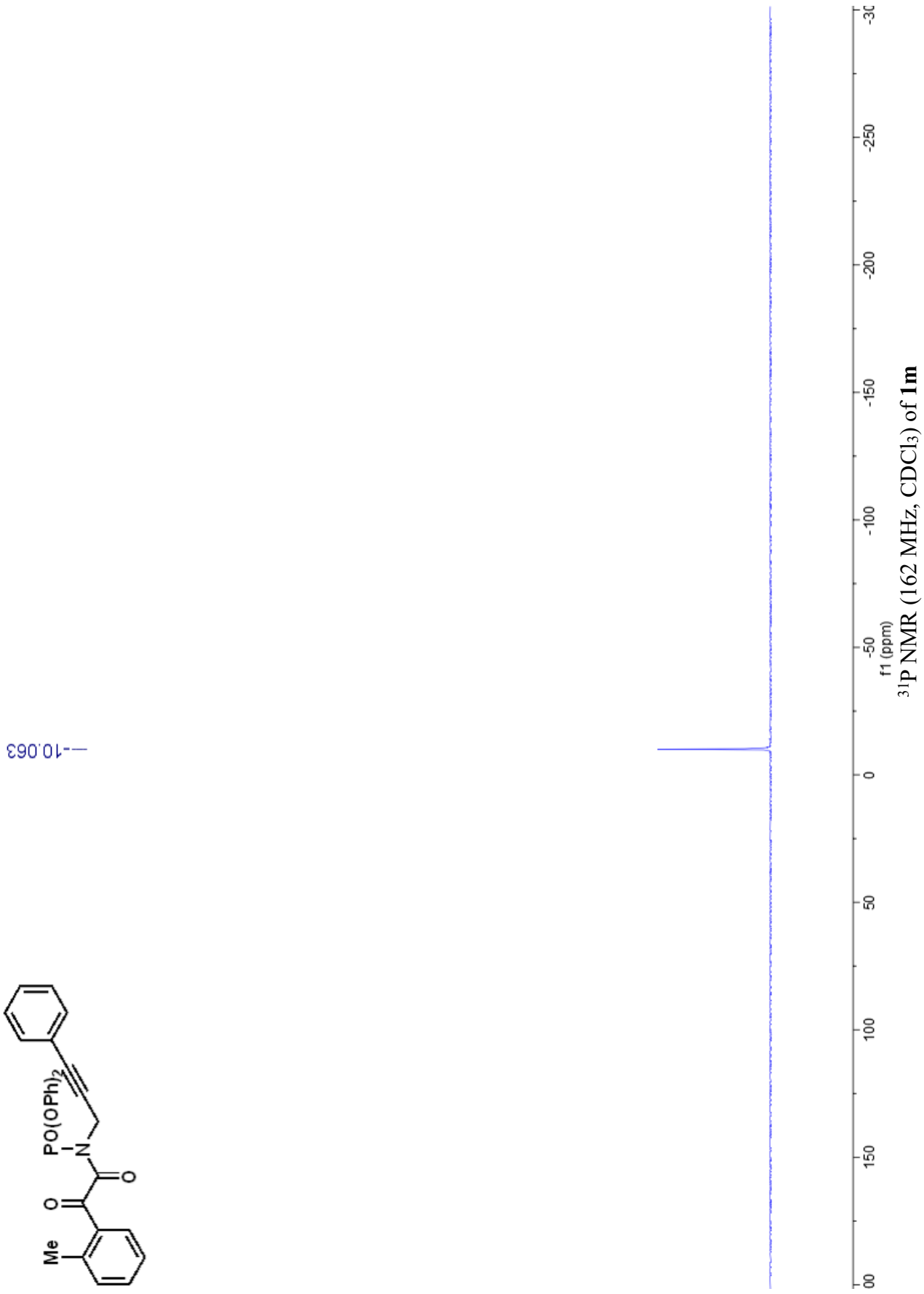
^{31}P NMR (162 MHz, $CDCl_3$) of **11**



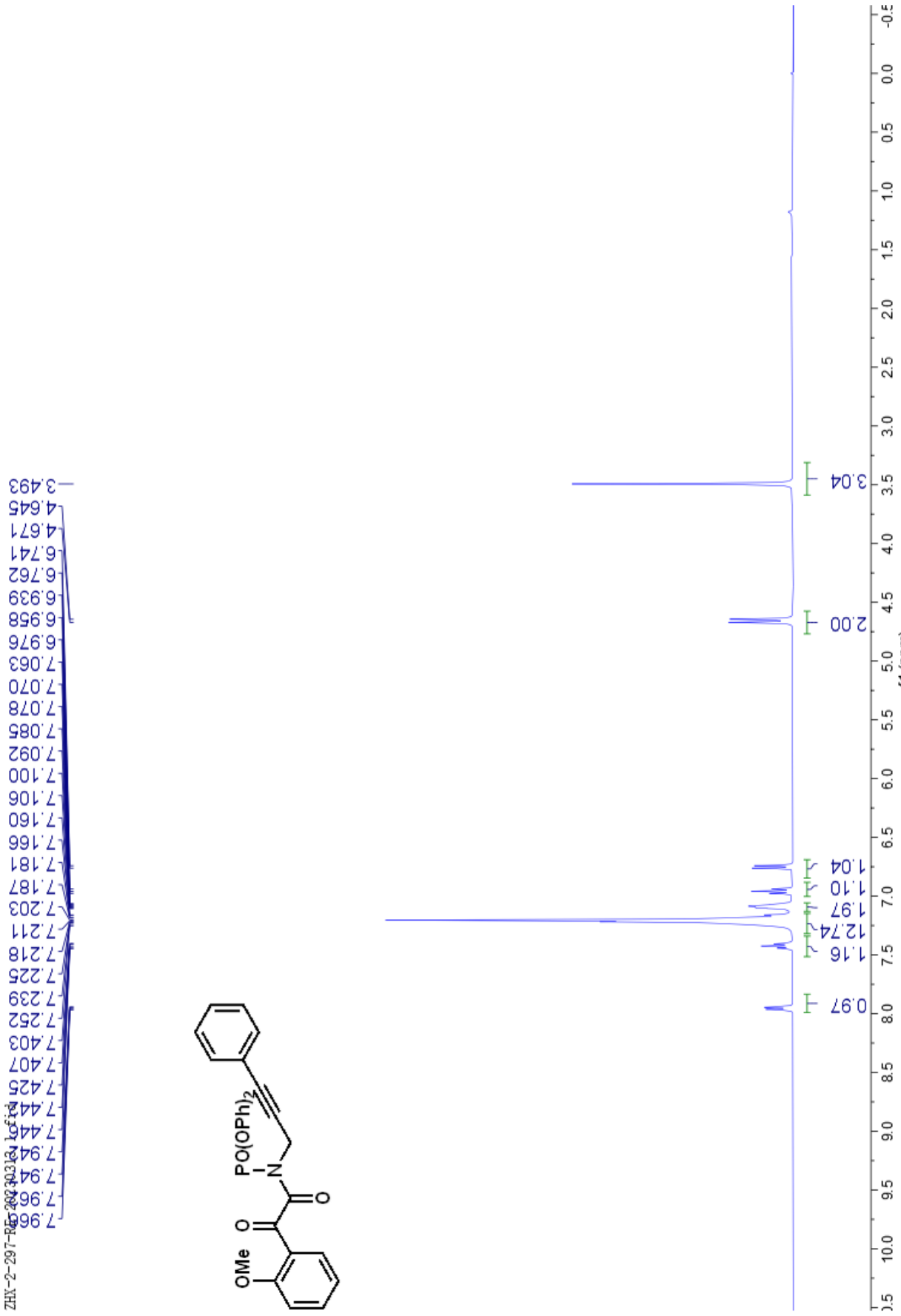
^{1}H NMR (400 MHz, $CDCl_3$) of **1m**



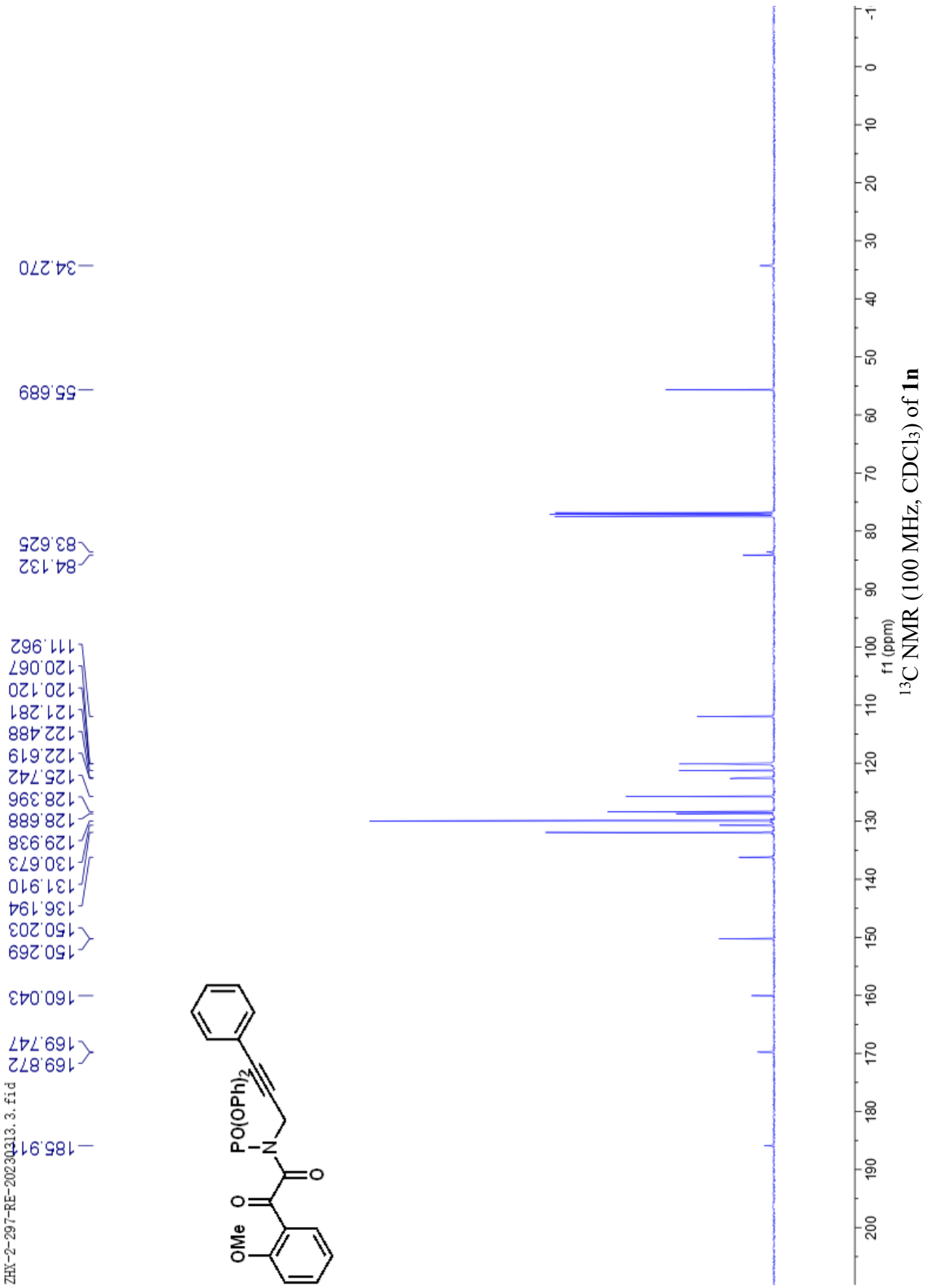
^{13}C NMR (100 MHz, $CDCl_3$) of **1m**



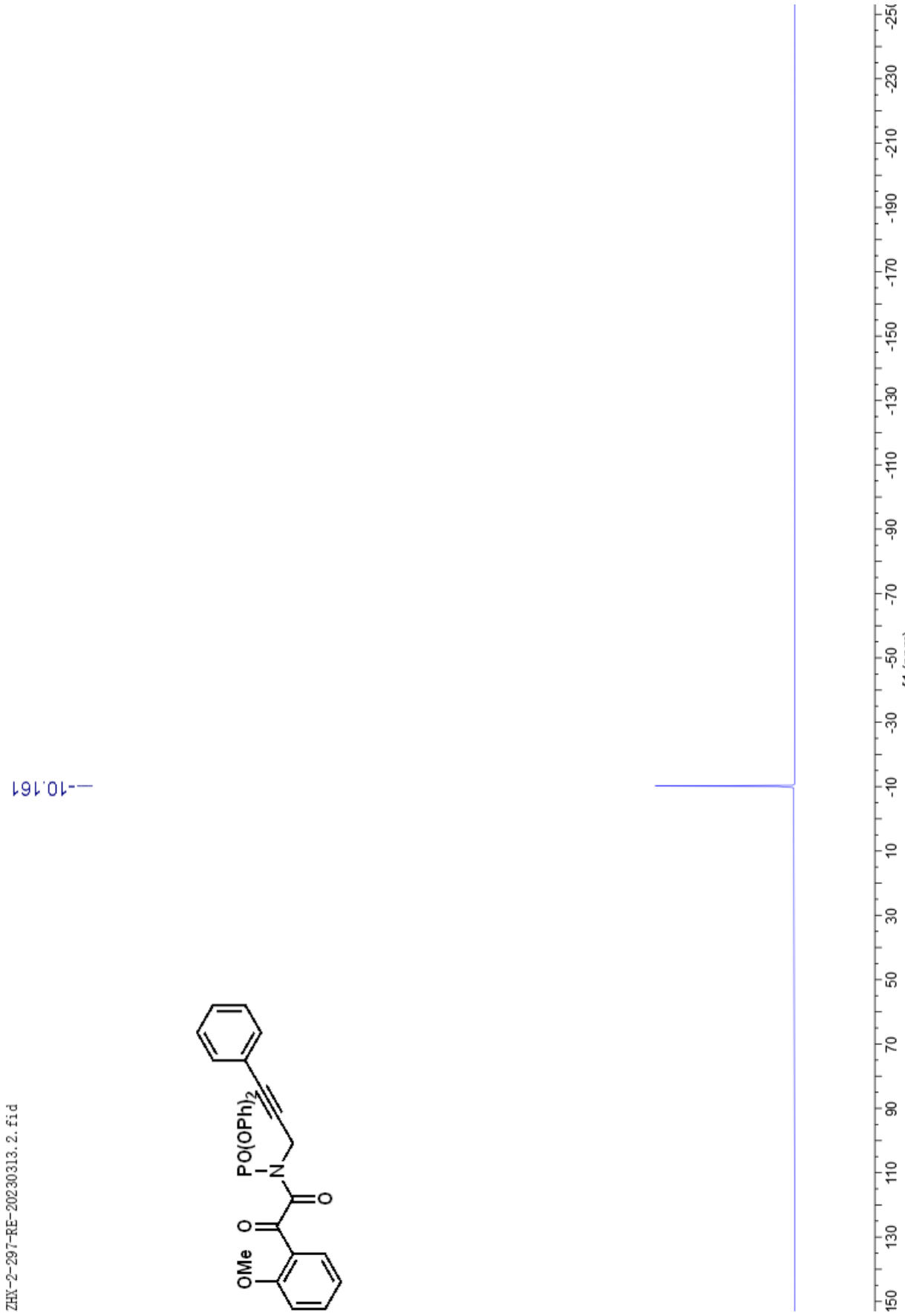
^{31}P NMR (162 MHz, $CDCl_3$) of **1m**



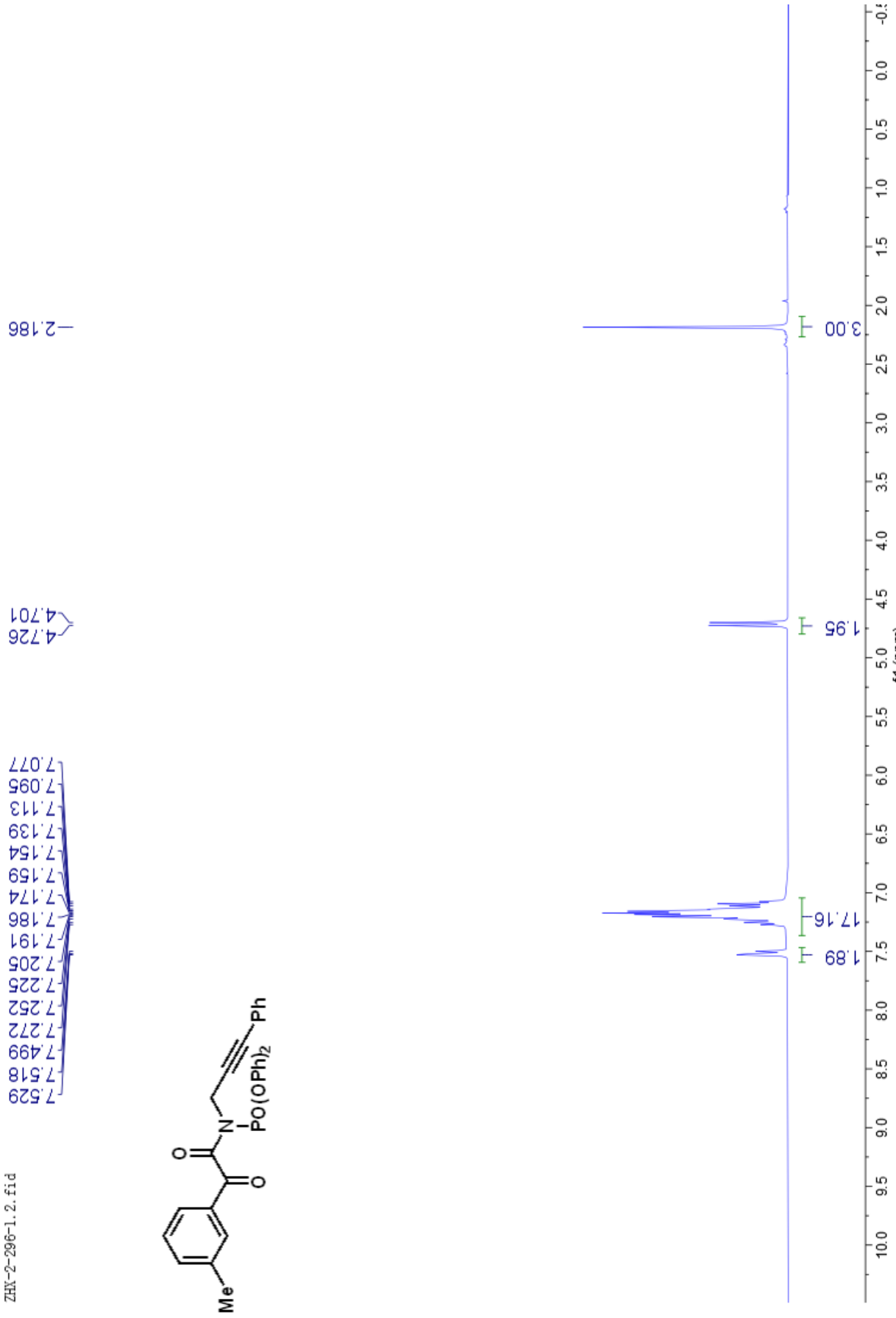
^{1}H NMR (400 MHz, $CDCl_3$) of **1n**



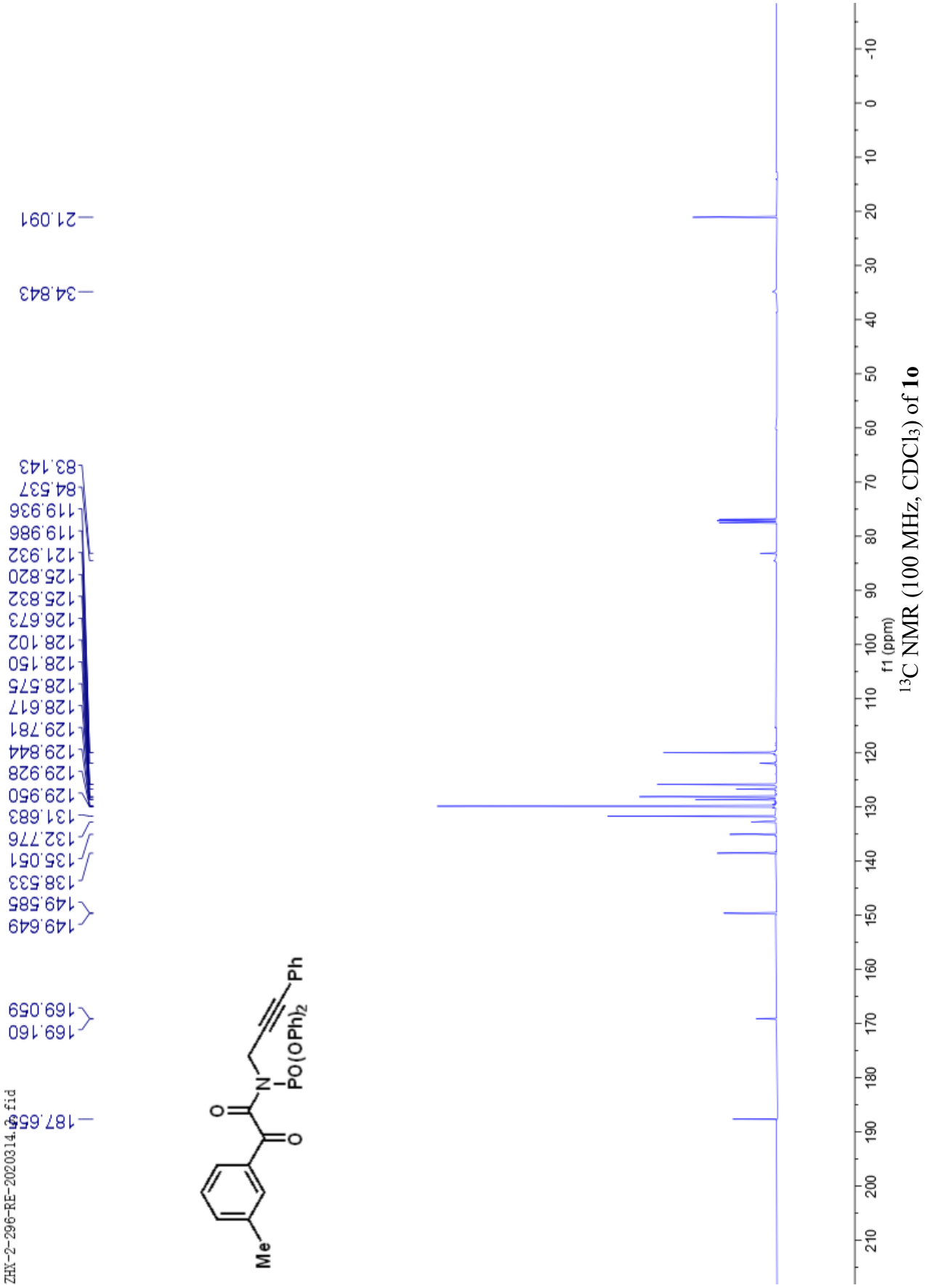
^{13}C NMR (100 MHz, $CDCl_3$) of **1n**



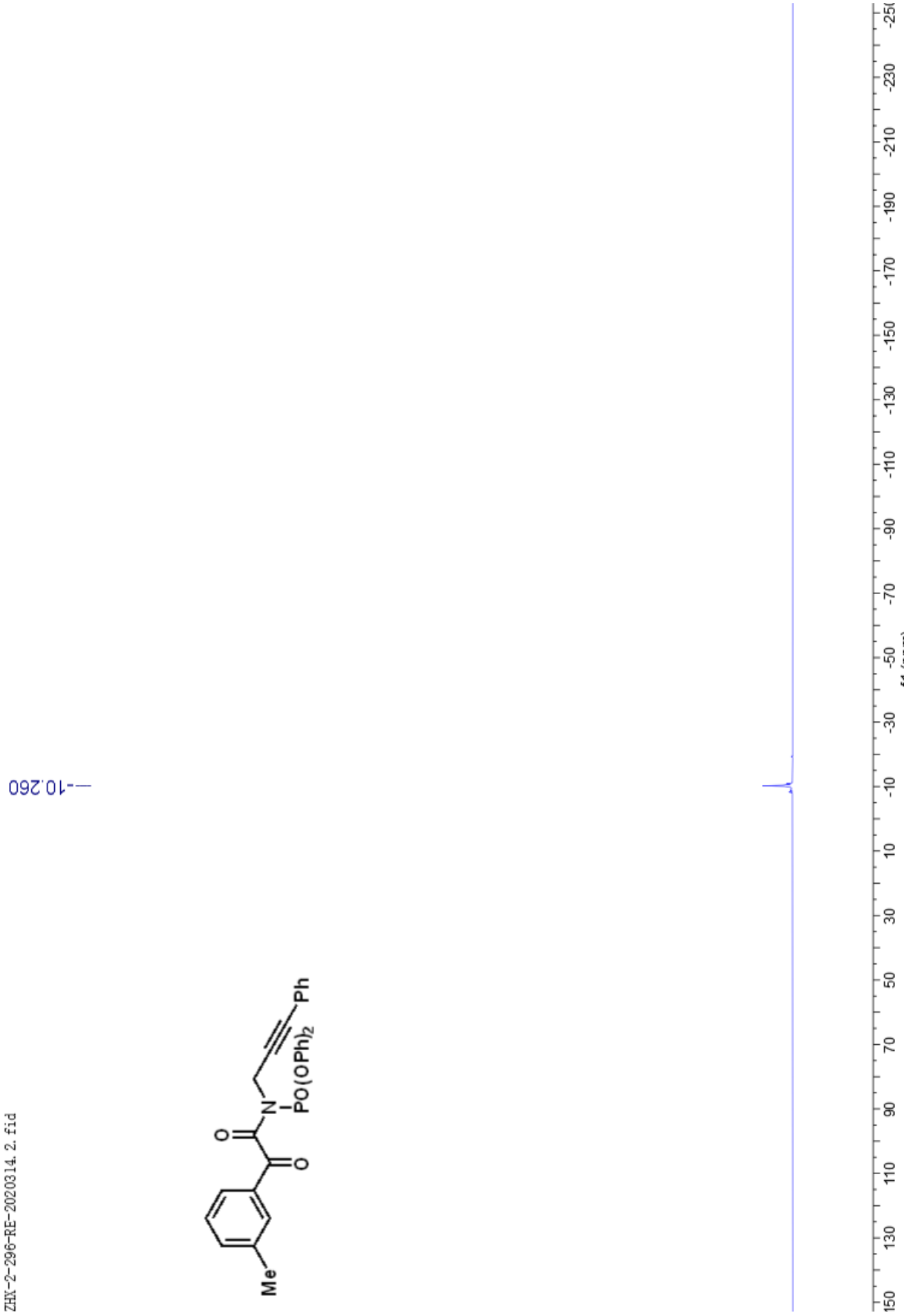
^{31}P NMR (162 MHz, $CDCl_3$) of **1n**



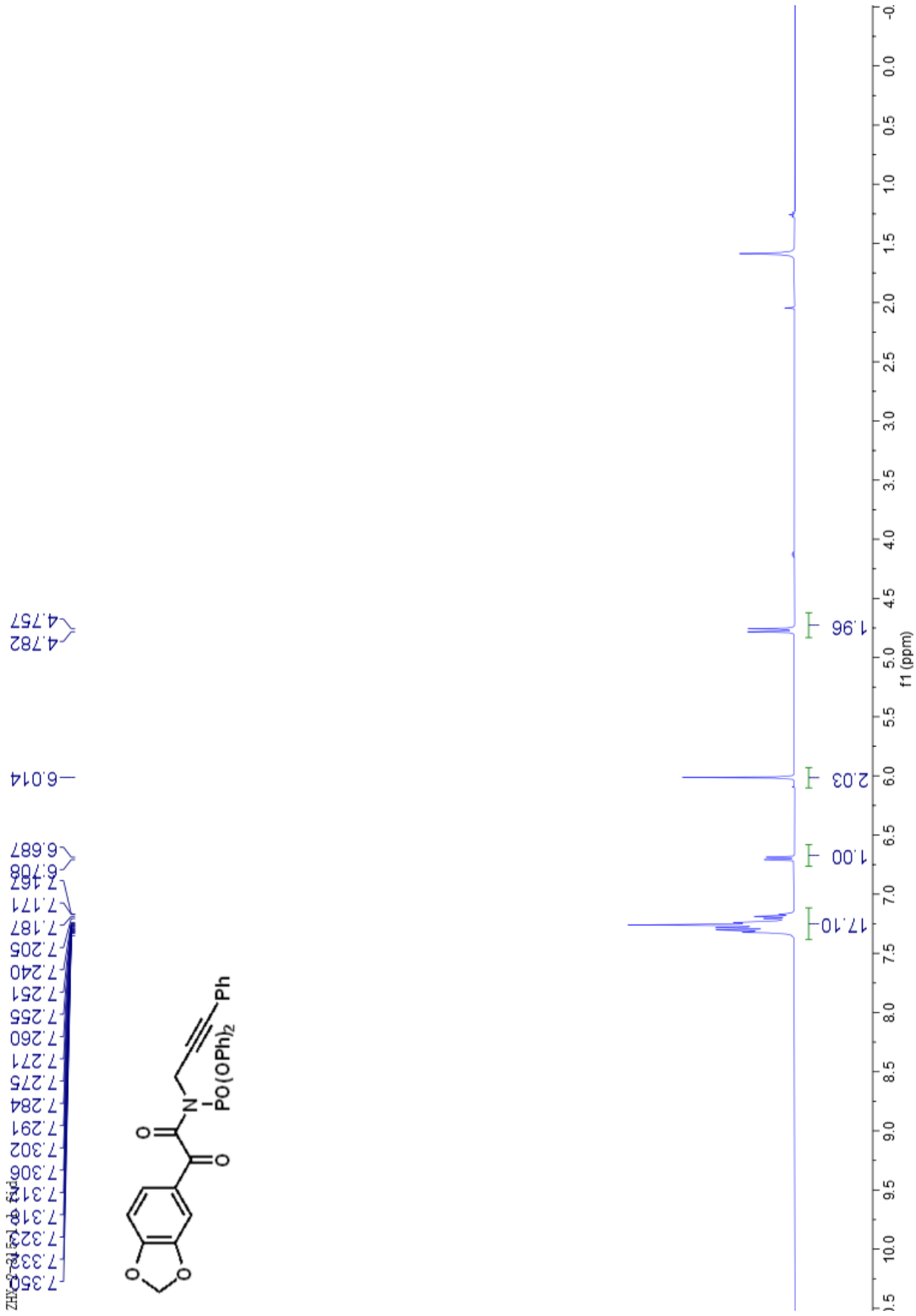
^{1}H NMR (400 MHz, $CDCl_3$) of **1o**



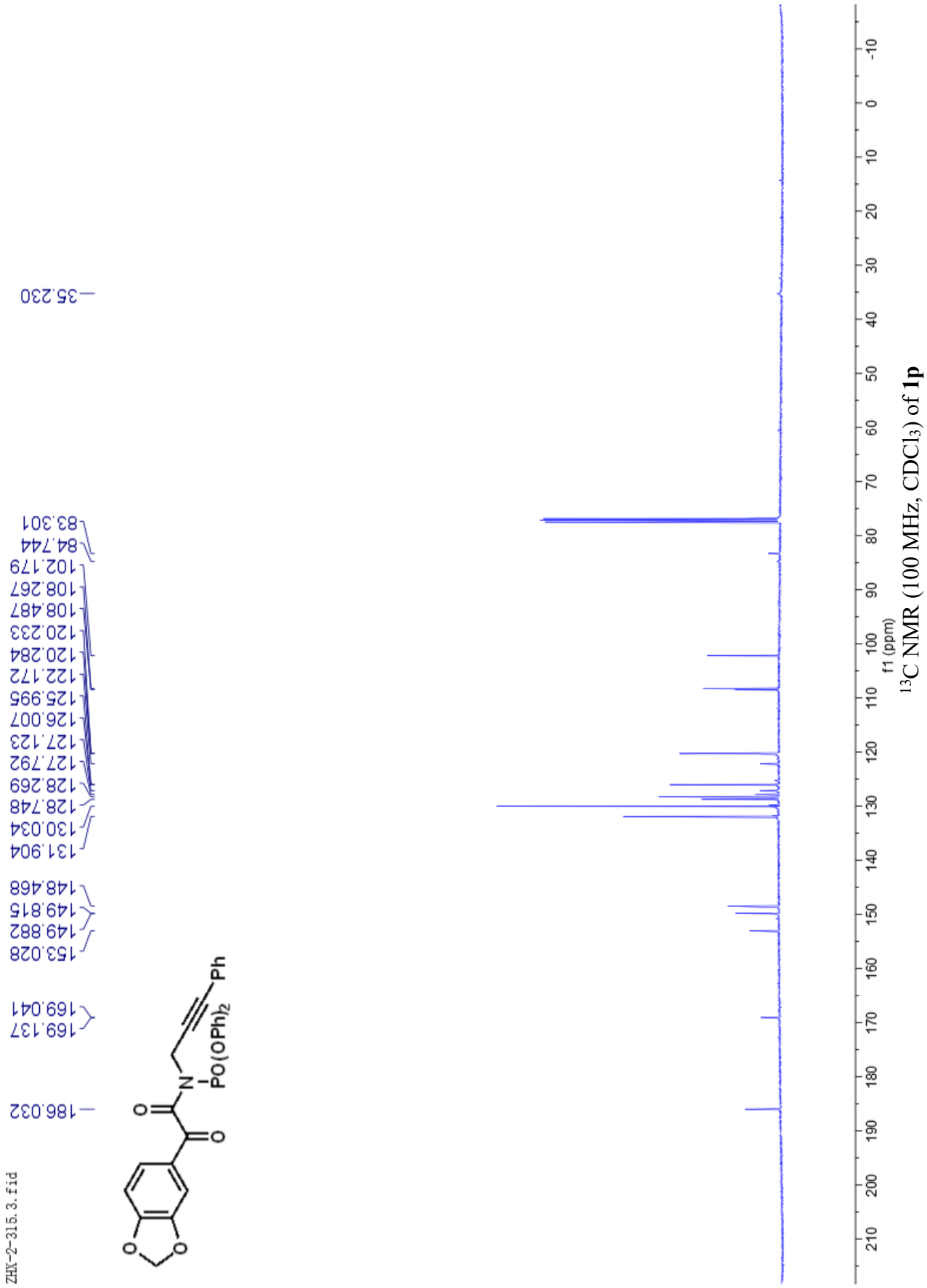
^{13}C NMR (100 MHz, $CDCl_3$) of **1o**



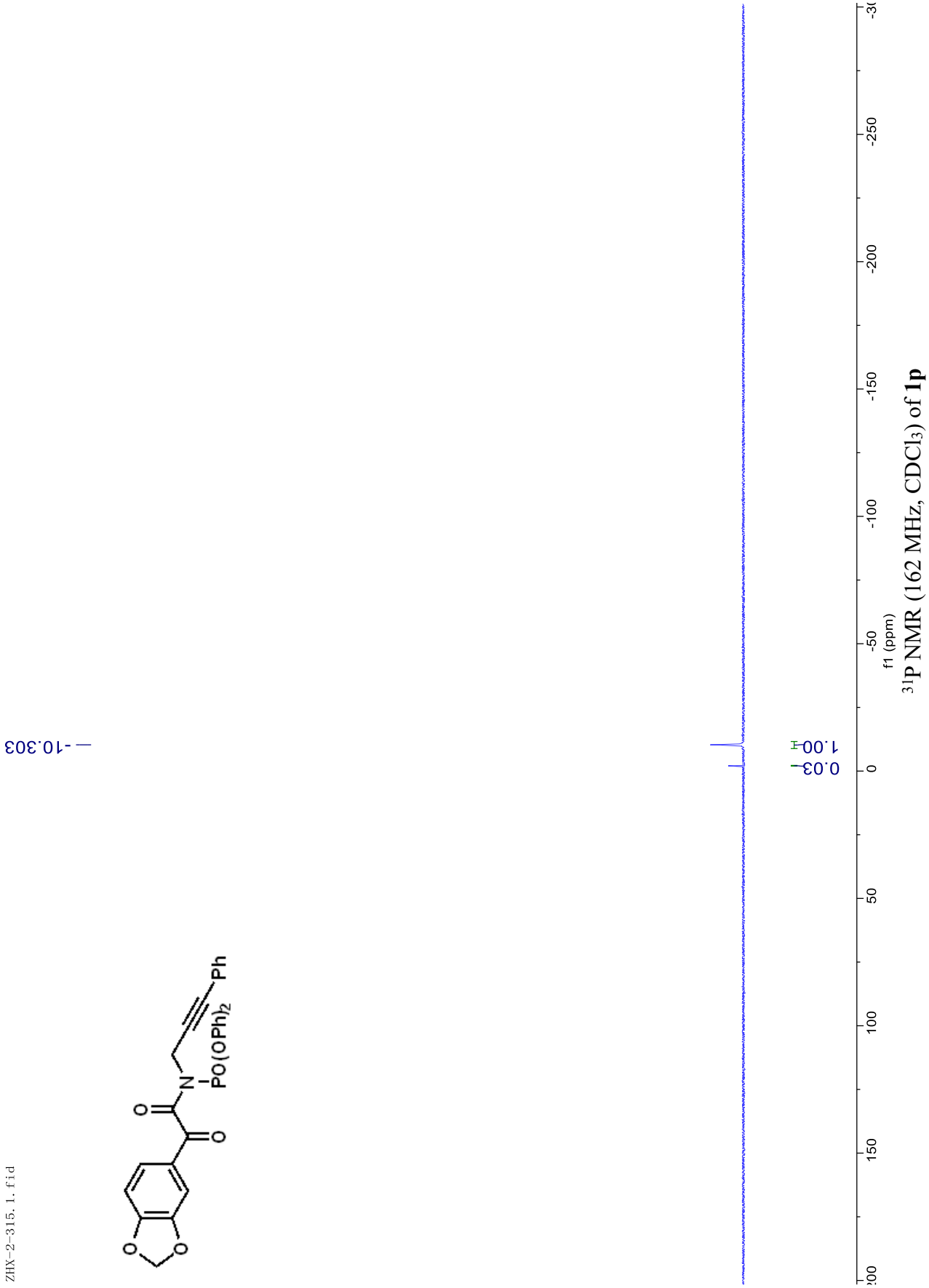
^{31}P NMR (162 MHz, $CDCl_3$) of **1o**



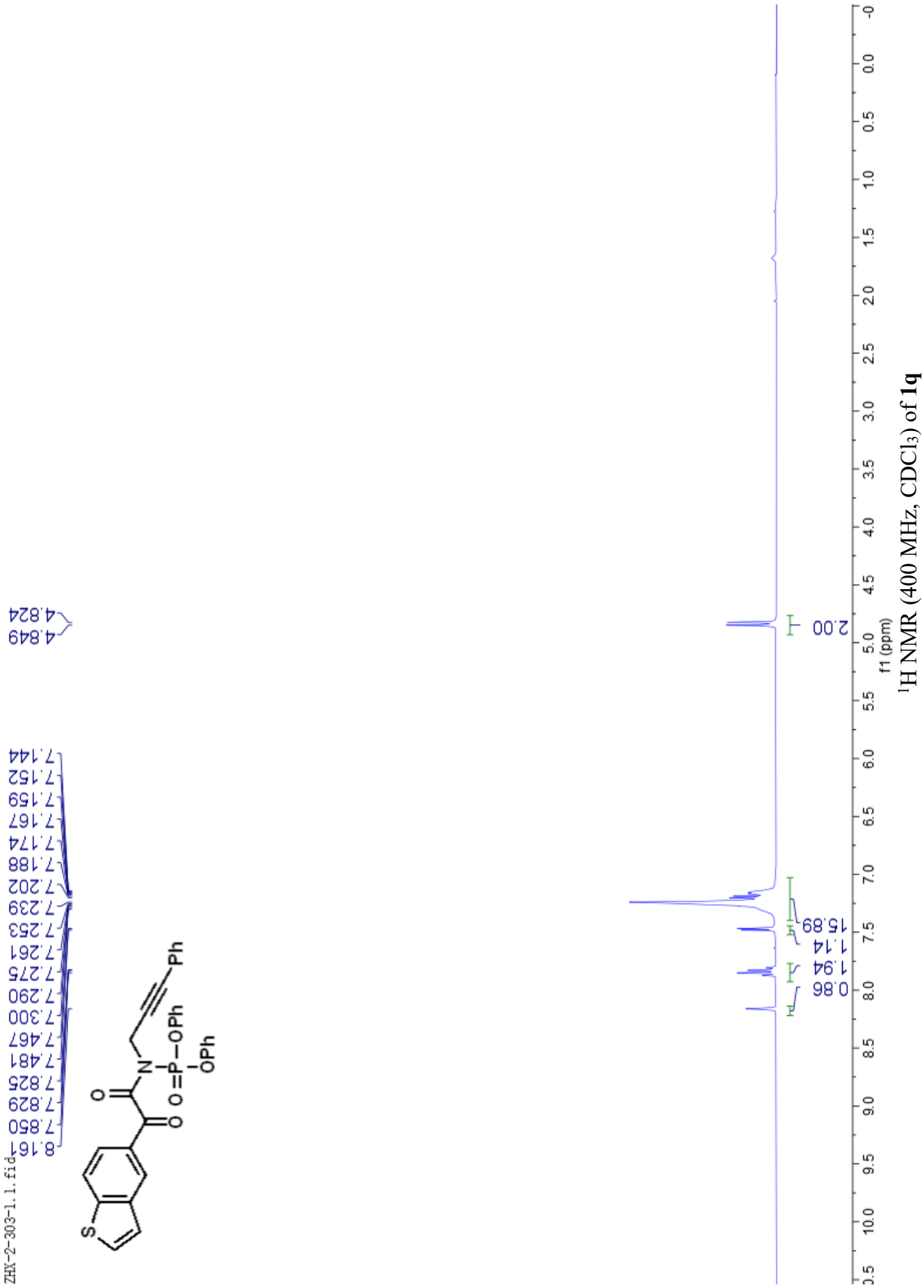
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



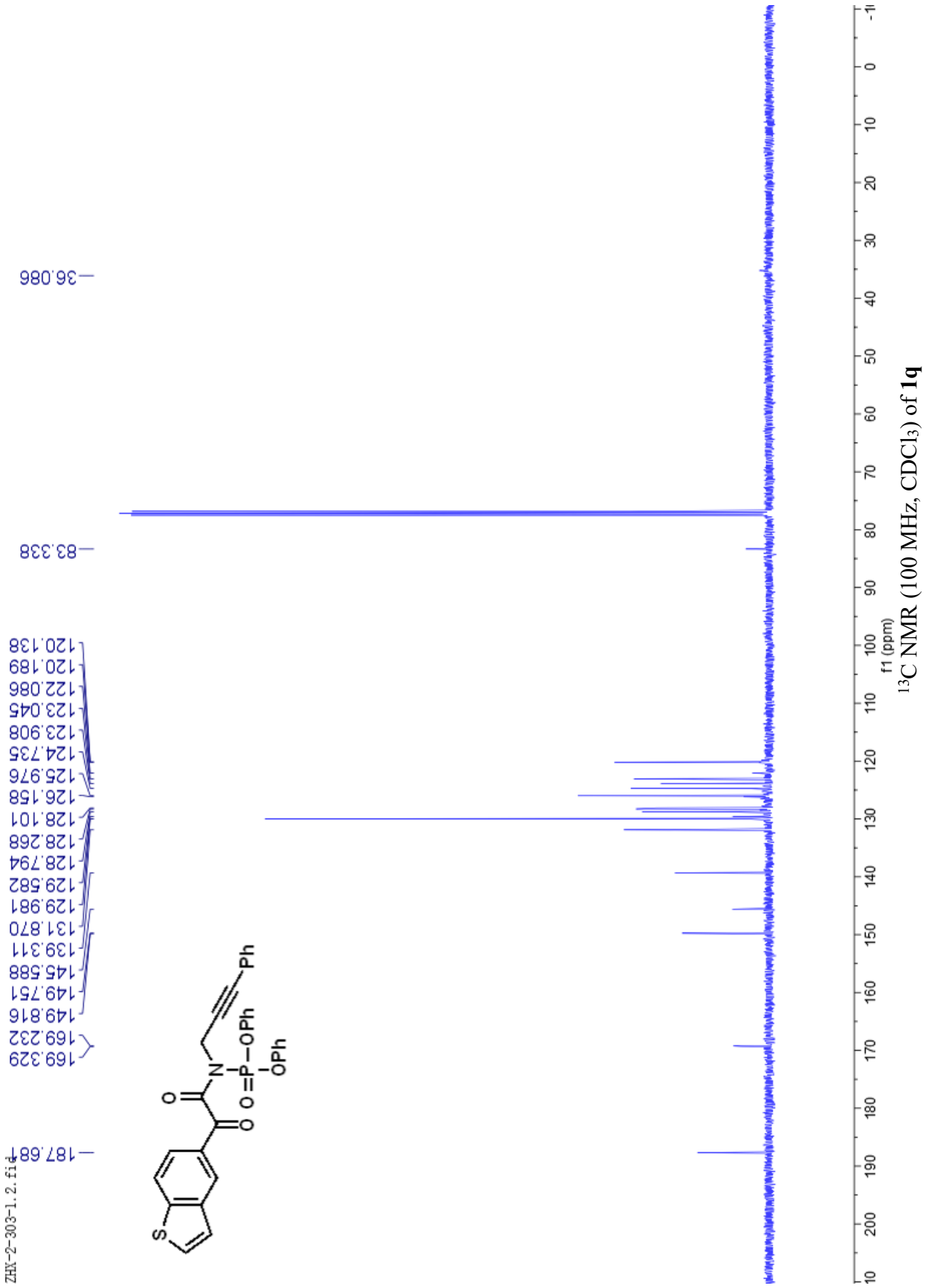
^{13}C NMR (100 MHz, $CDCl_3$) of **1p**



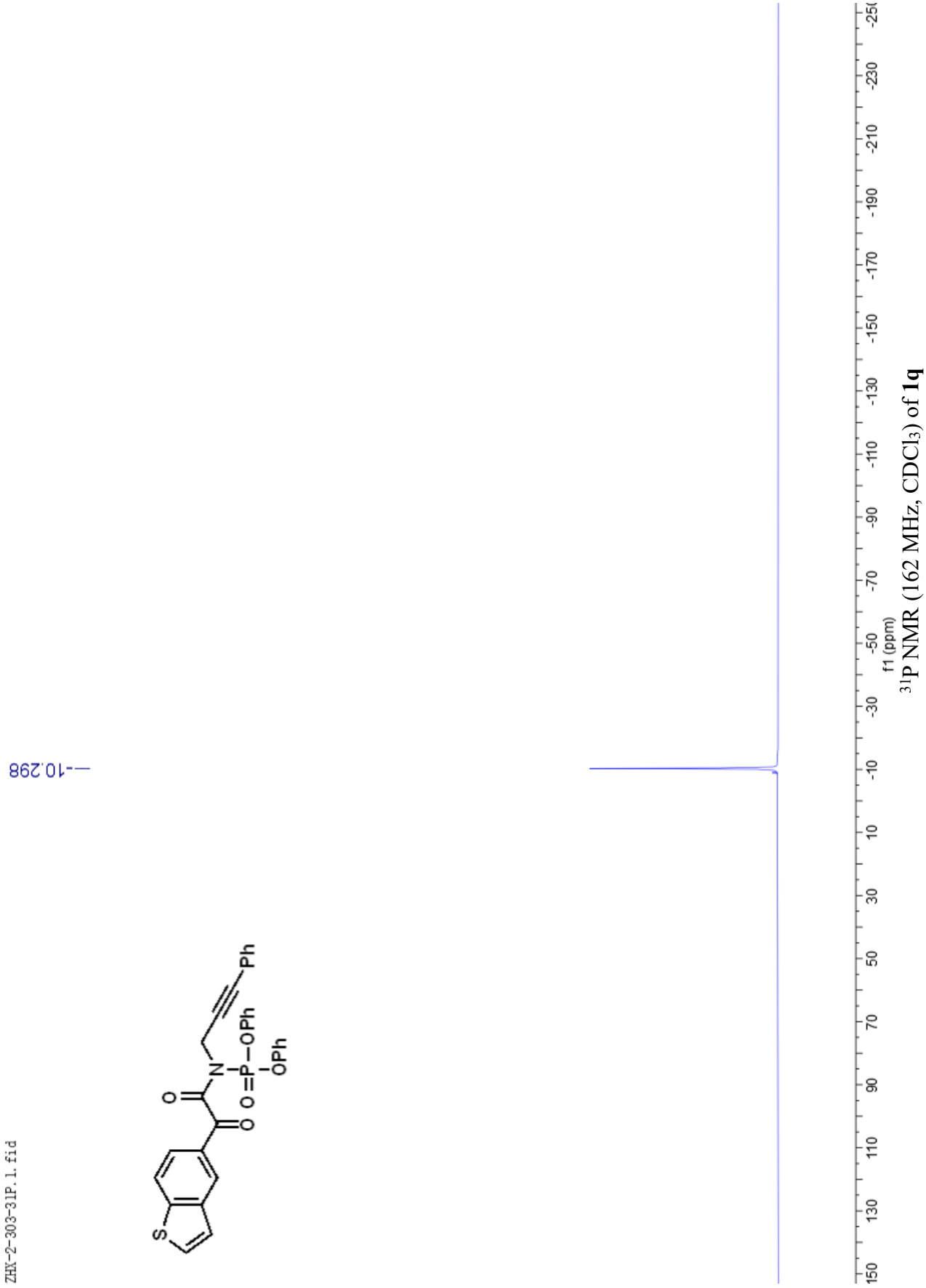
^{31}P NMR (162 MHz, $CDCl_3$) of **1p**



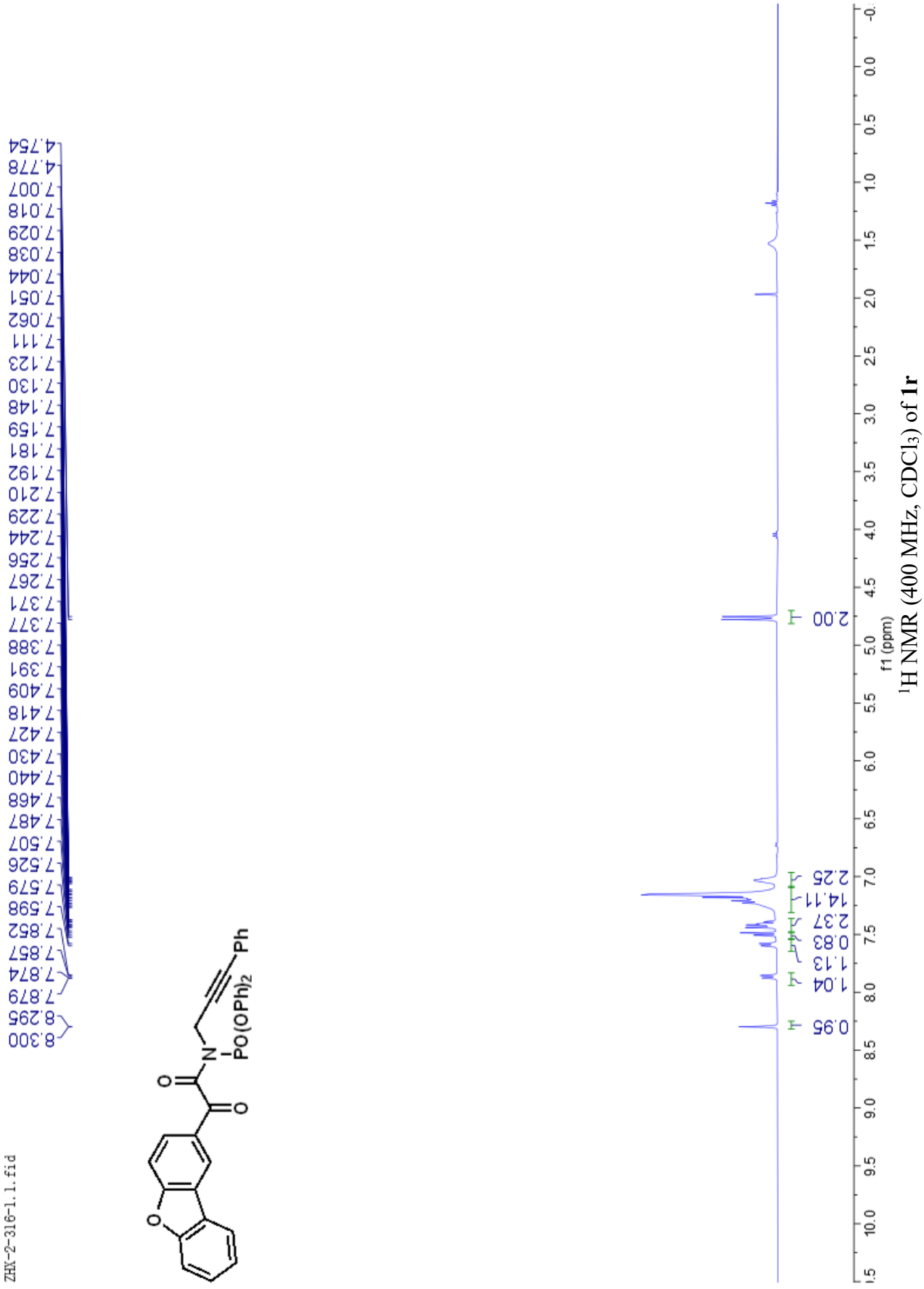
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



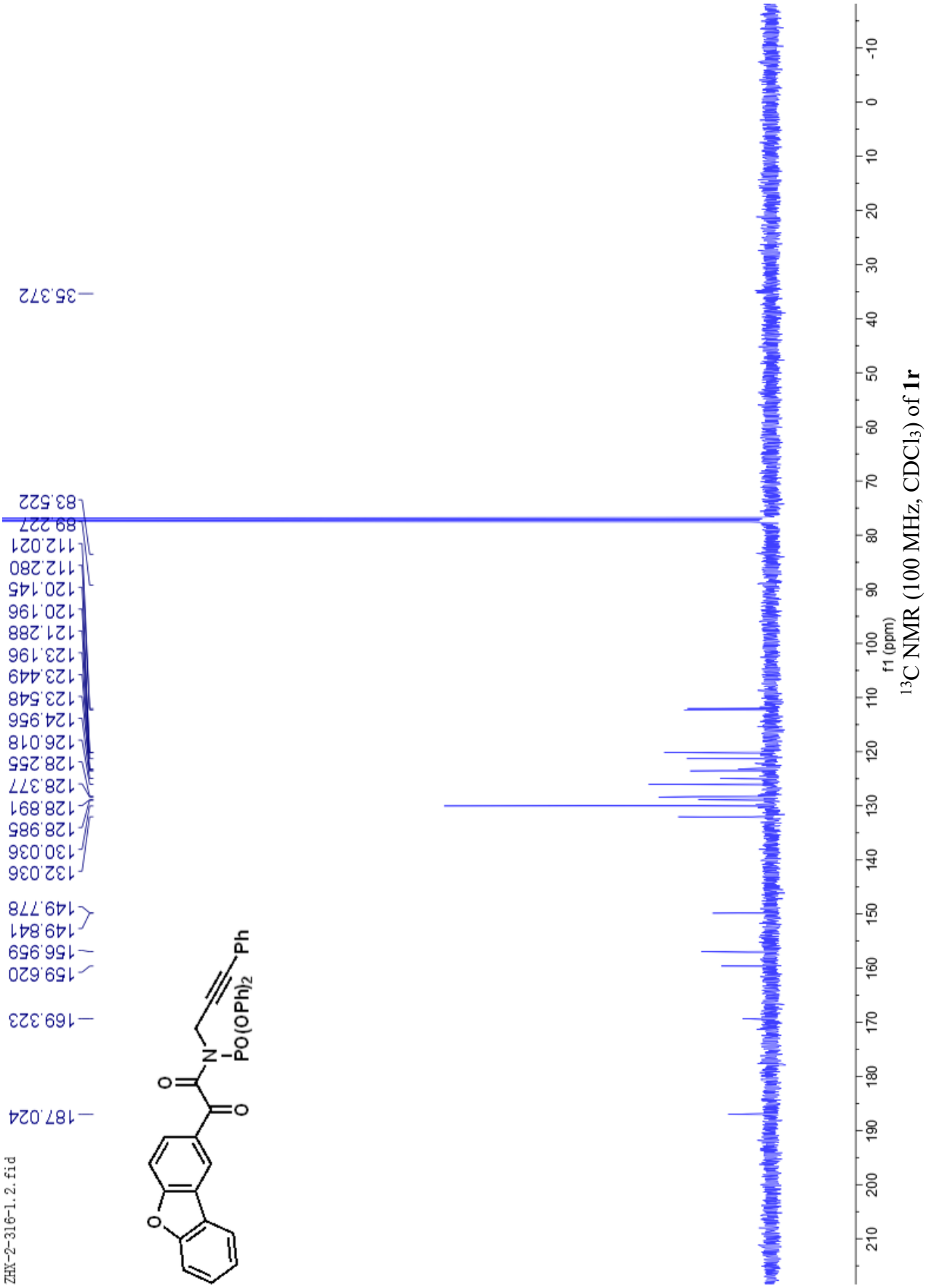
^{13}C NMR (100 MHz, $CDCl_3$) of **1q**



^{31}P NMR (162 MHz, $CDCl_3$) of **1q**

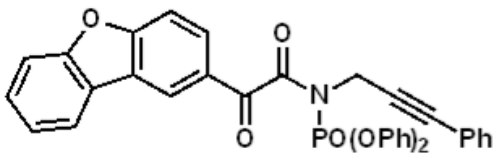


^{1}H NMR (400 MHz, $CDCl_3$) of **1r**

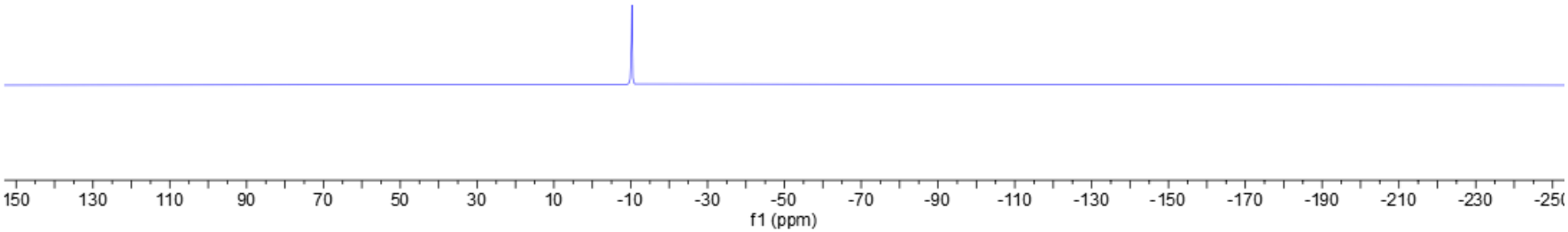


^{13}C NMR (100 MHz, $CDCl_3$) of **1r**

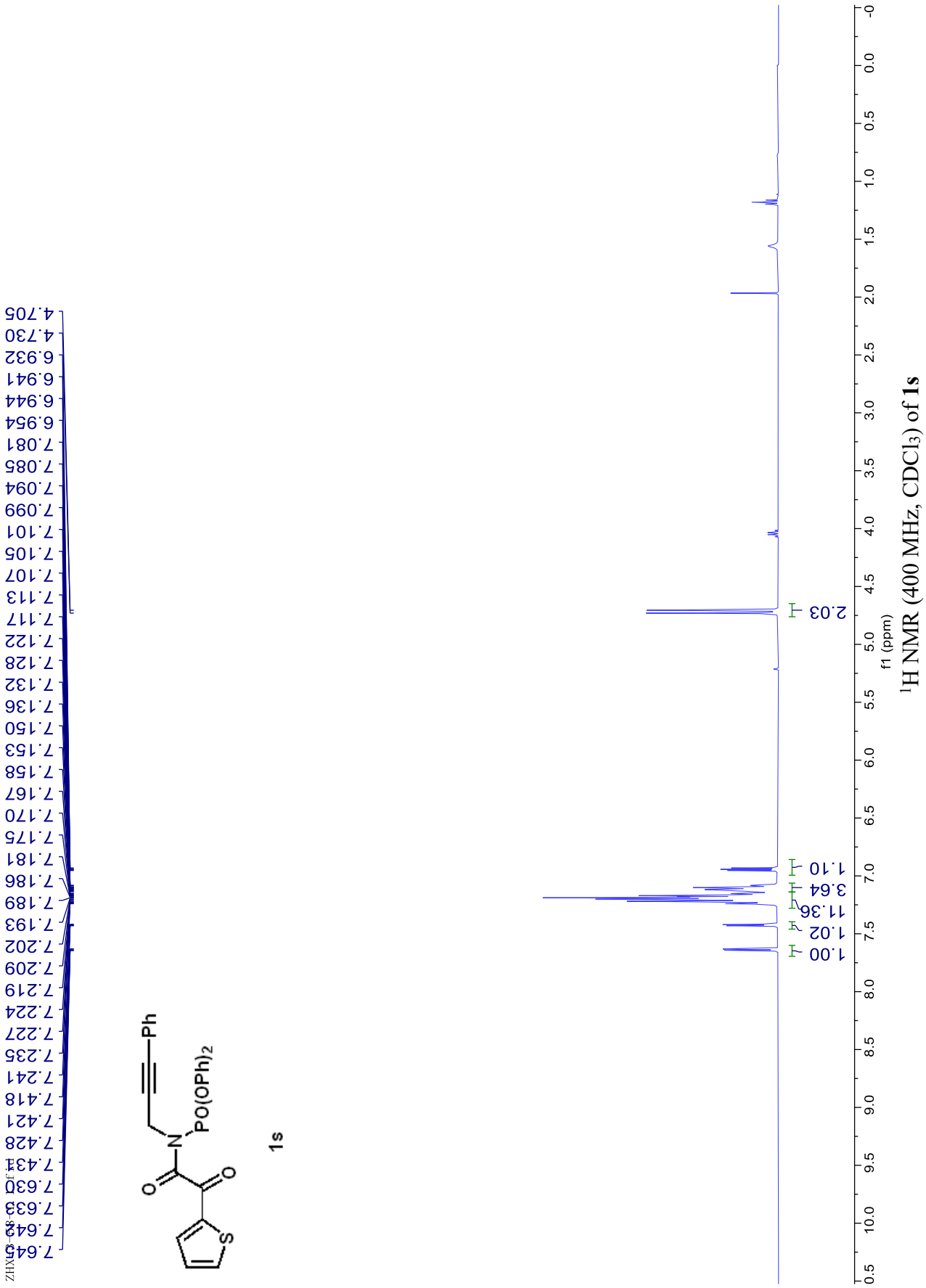
ZHX-2-316-P.1.fid

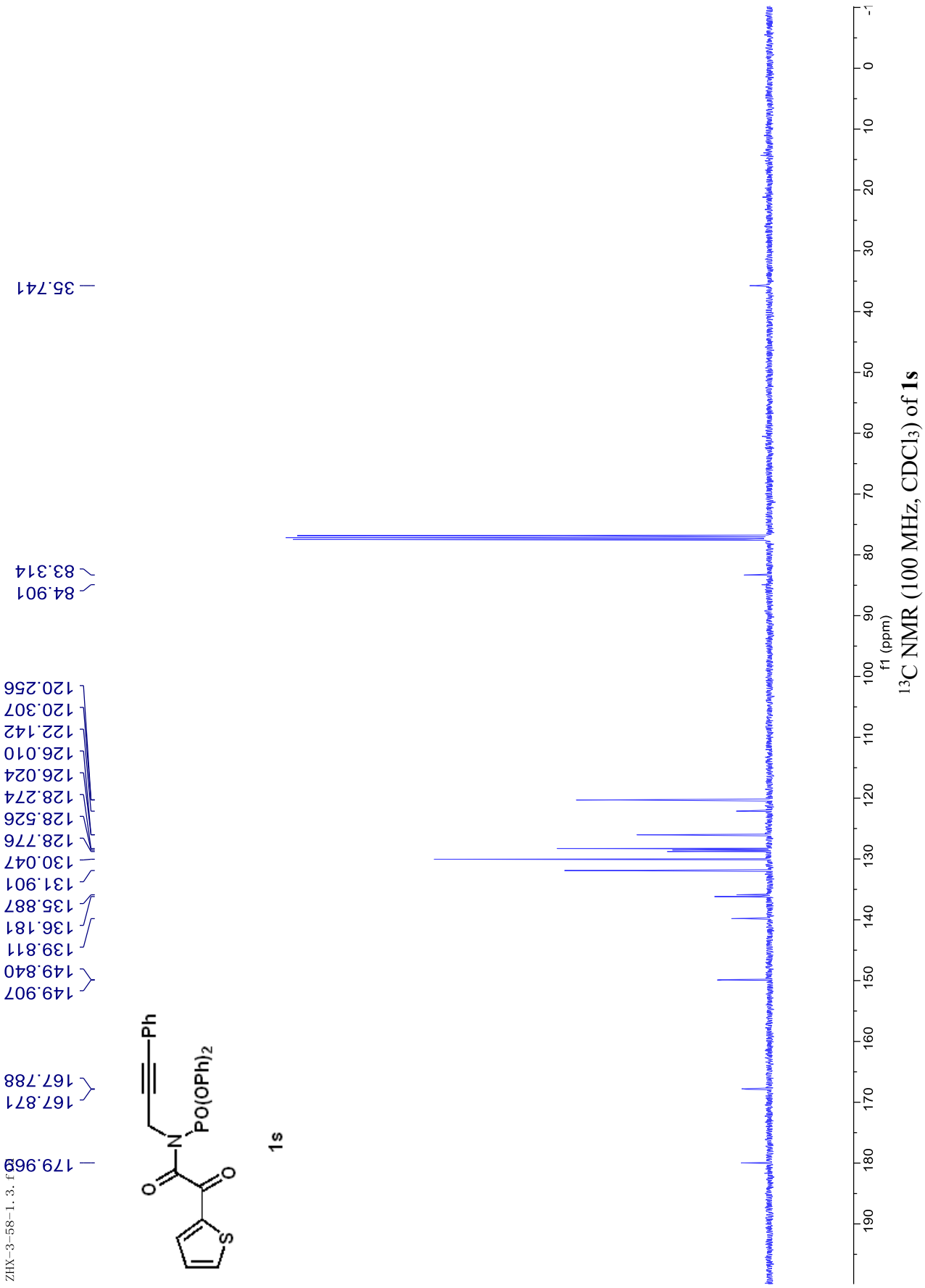


-10.323

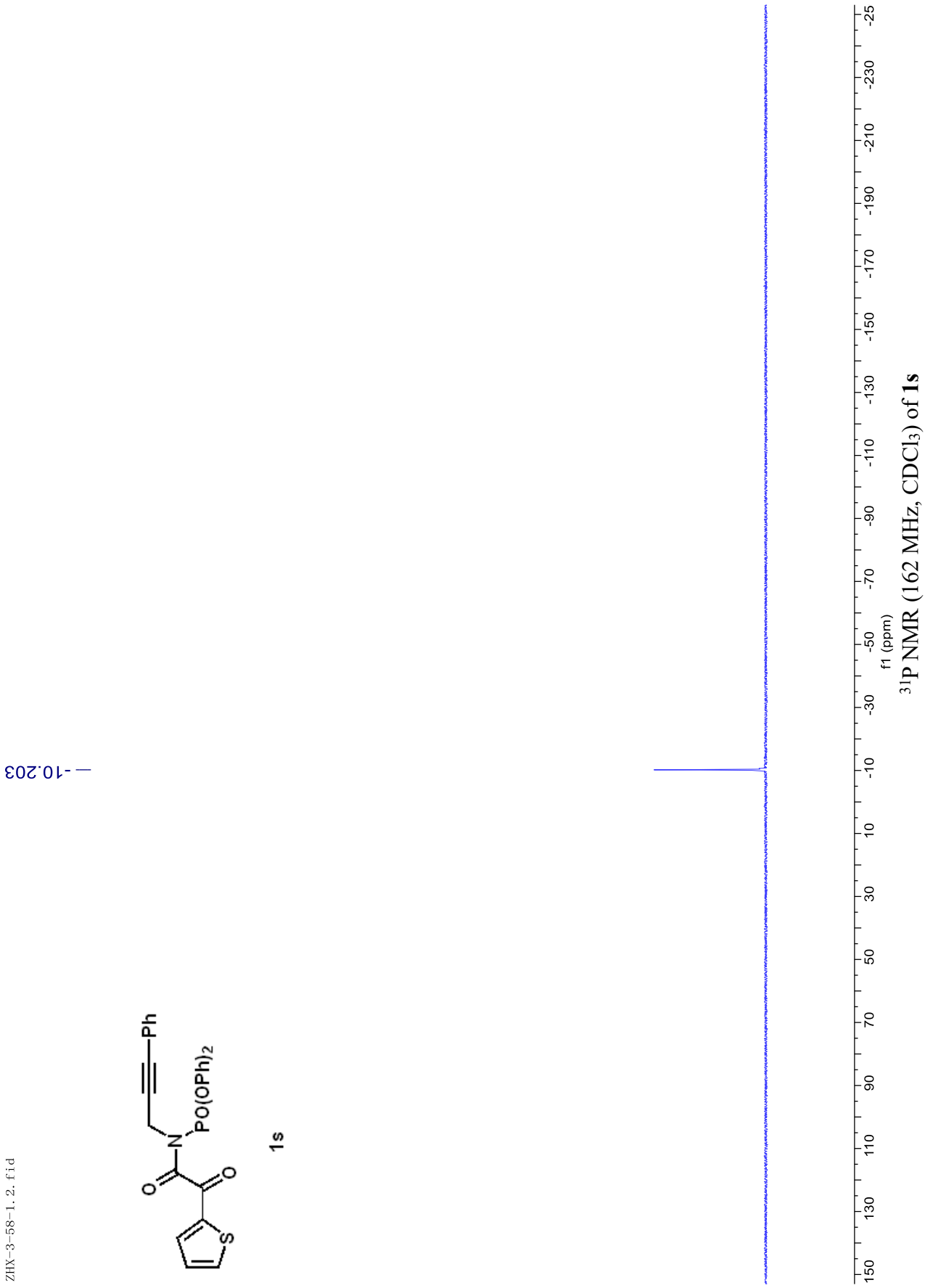


^{31}P NMR (162 MHz, $CDCl_3$) of **1r**

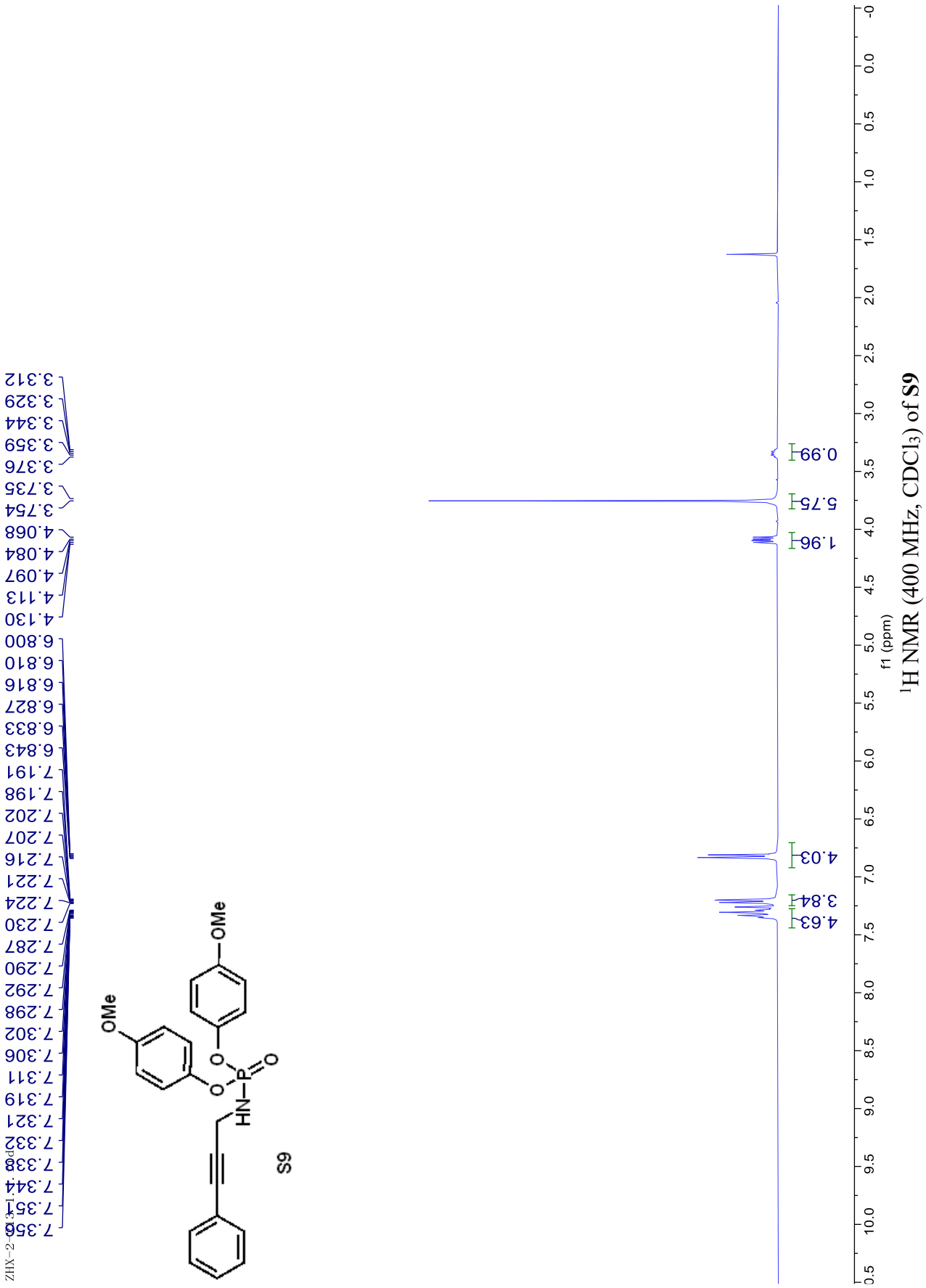

Ph
PO(OPh)2
N
O
O
S
1s
2.03
1.10
3.64
11.36
1.02
1.00
f1 (ppm)
^{1}H NMR (400 MHz, CDCl$_3$) of **1s**



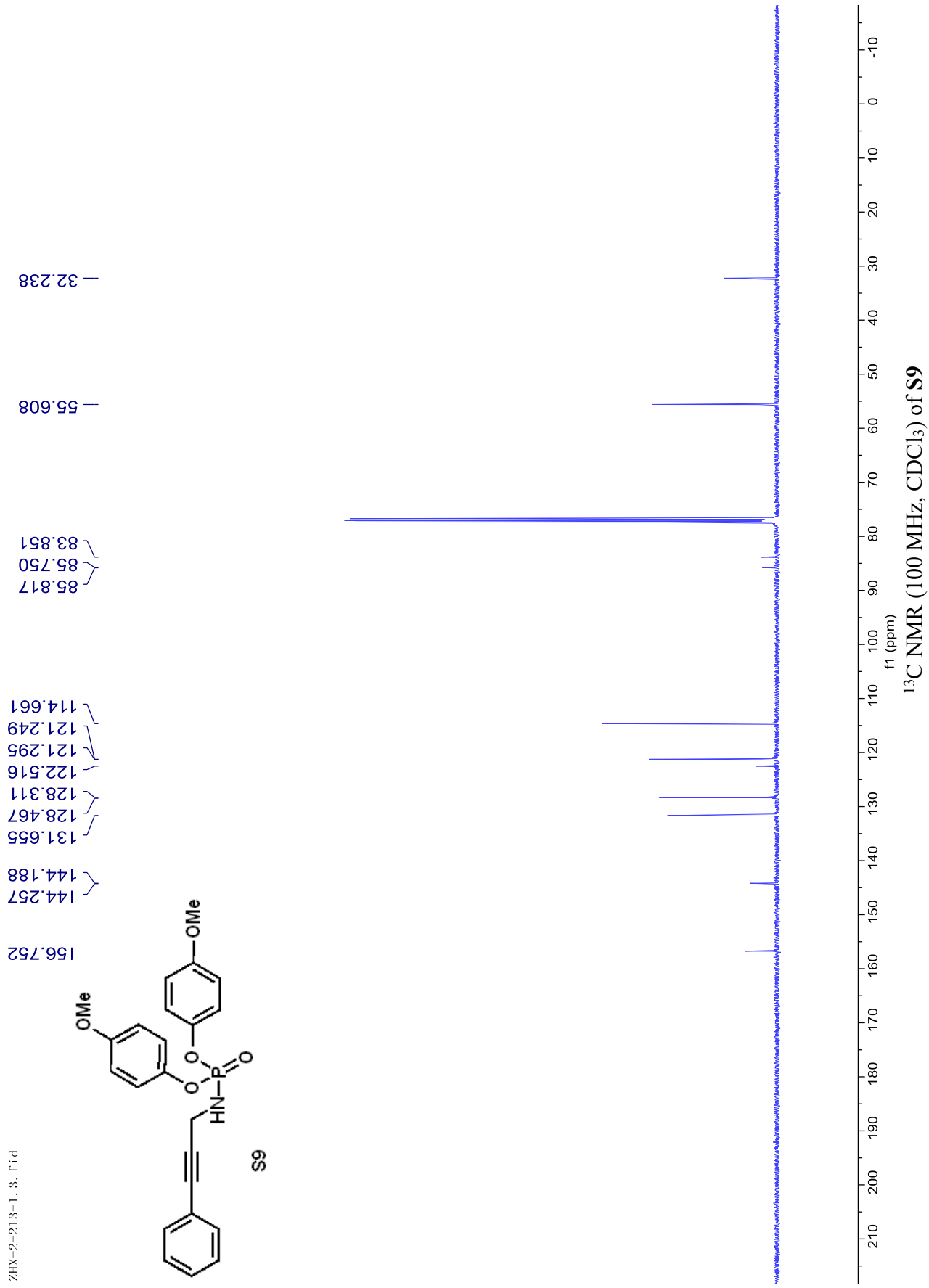
^{13}C NMR (100 MHz, $CDCl_3$) of **1s**



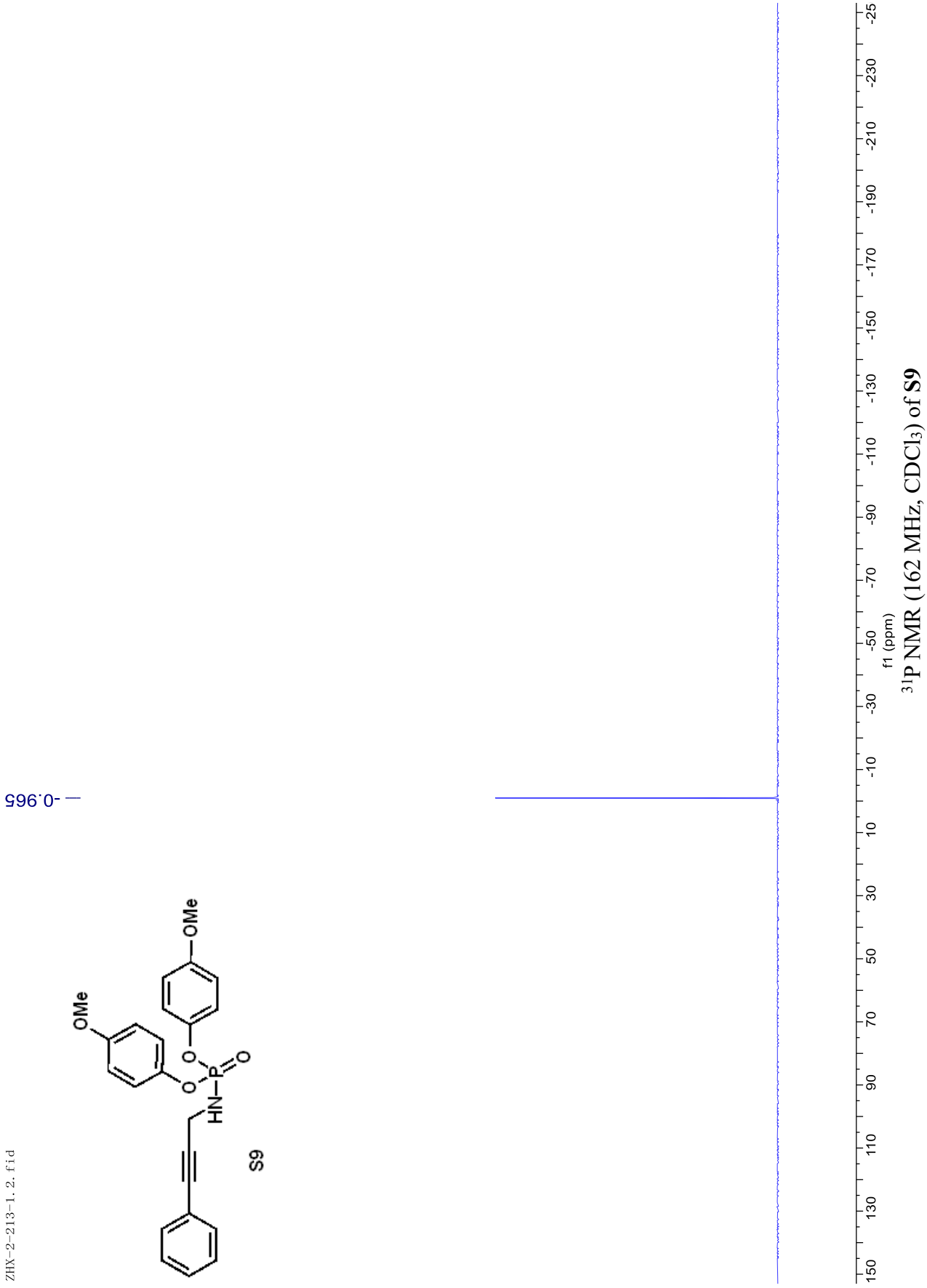
^{31}P NMR (162 MHz, $CDCl_3$) of **1s**



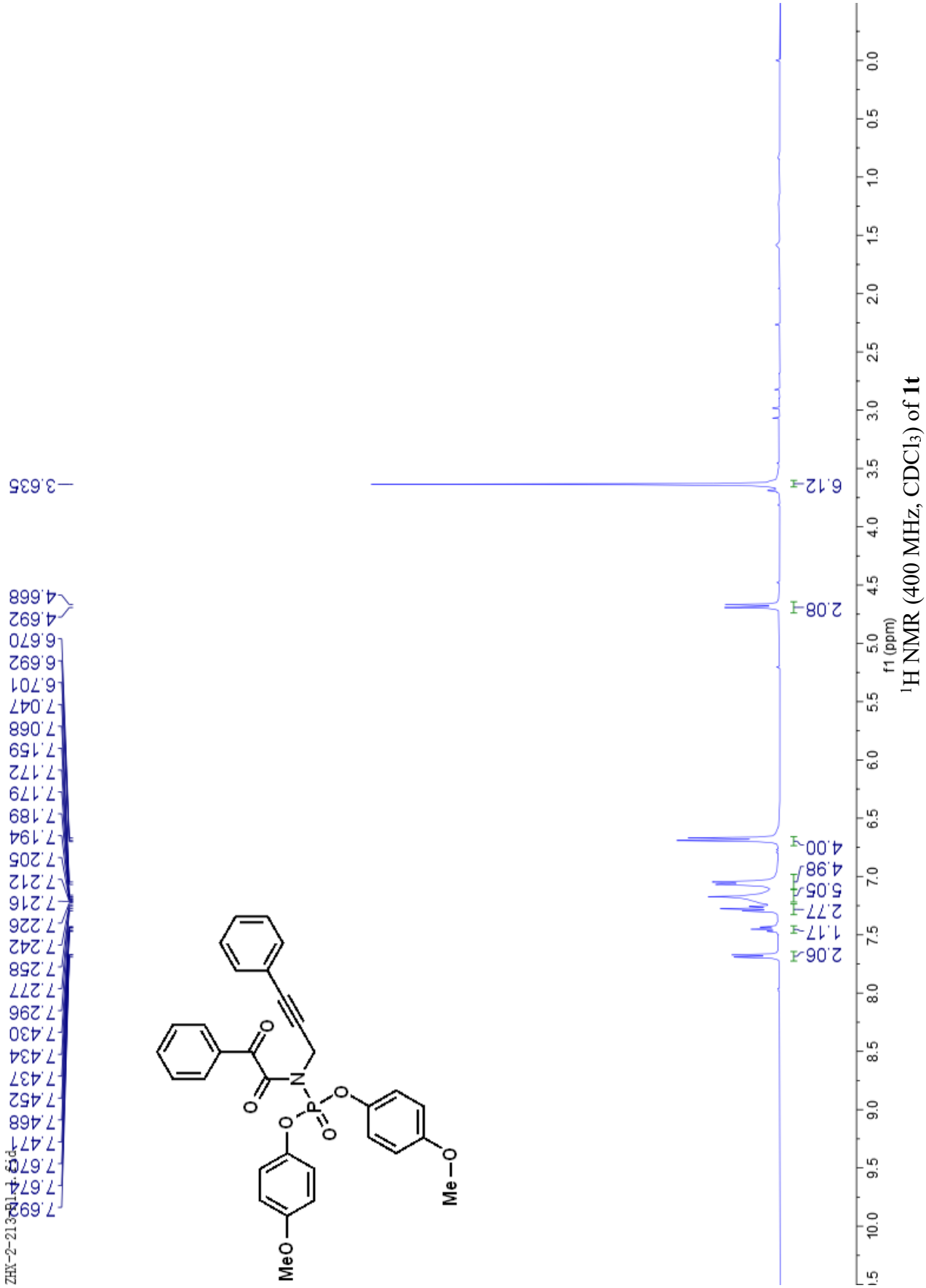
^{1}H NMR (400 MHz, $CDCl_3$) of **S9**



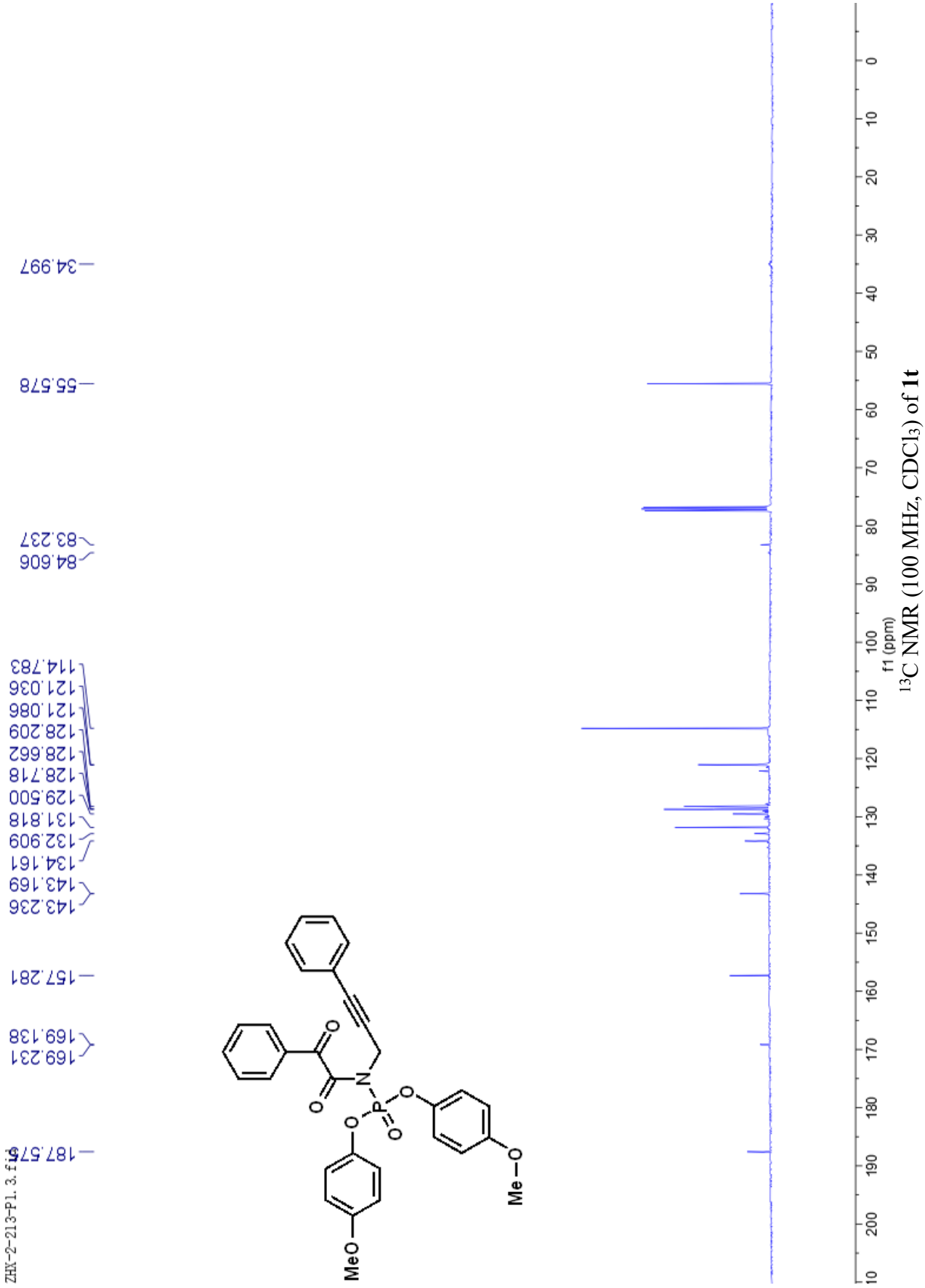
^{13}C NMR (100 MHz, $CDCl_3$) of **S9**



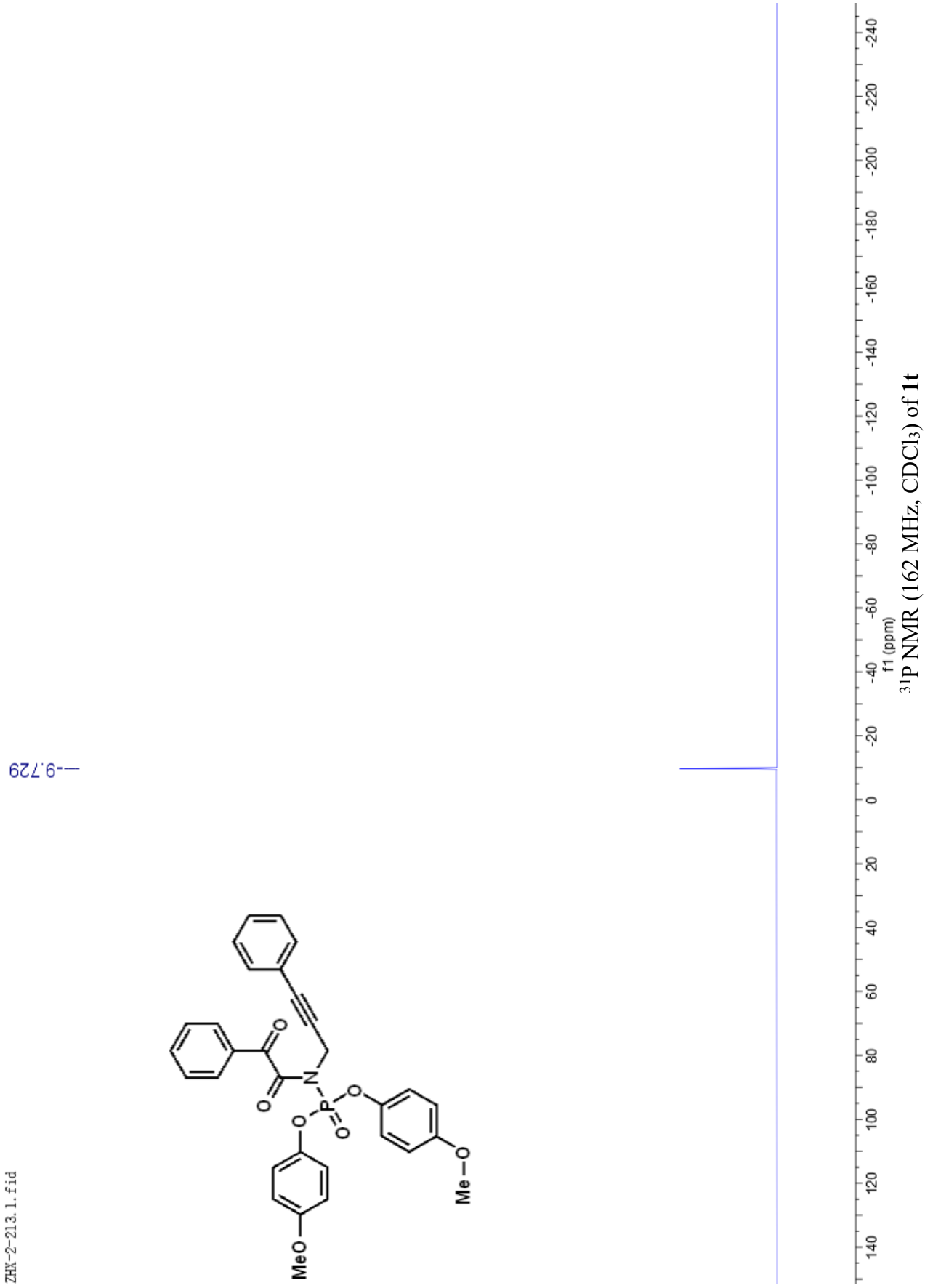
^{31}P NMR (162 MHz, $CDCl_3$) of **S9**



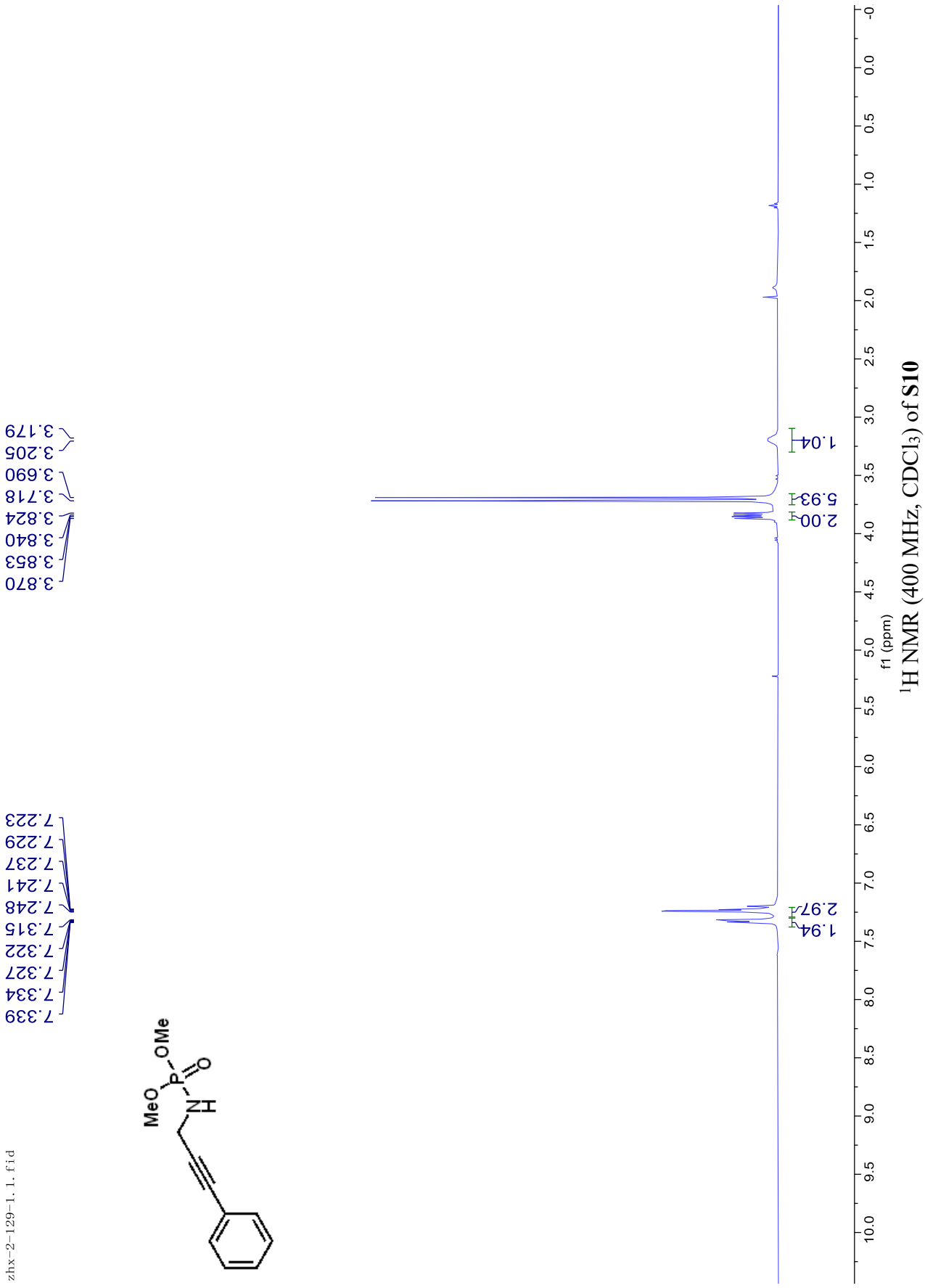
^{1}H NMR (400 MHz, $CDCl_3$) of **1t**



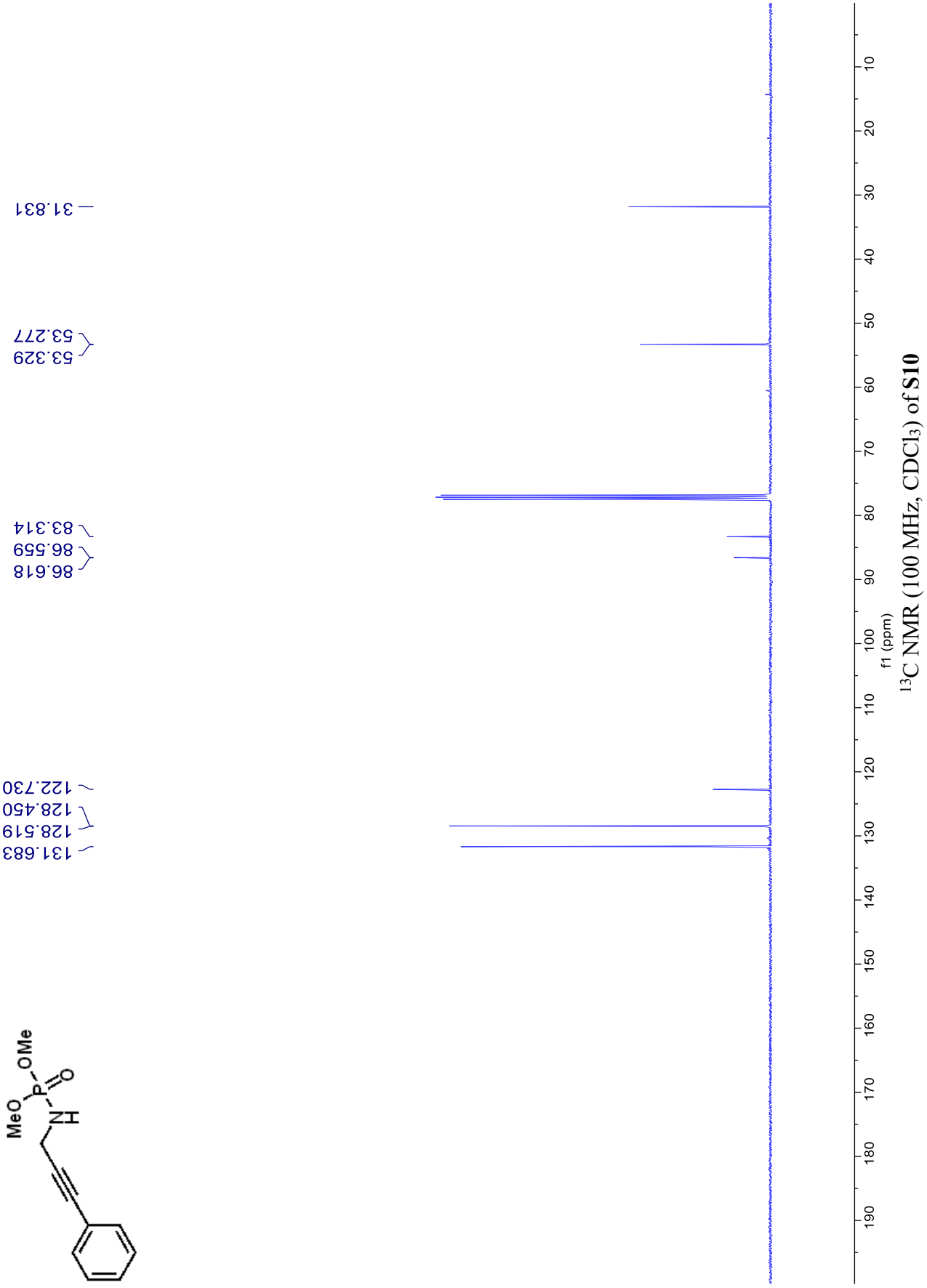
^{13}C NMR (100 MHz, $CDCl_3$) of **1t**



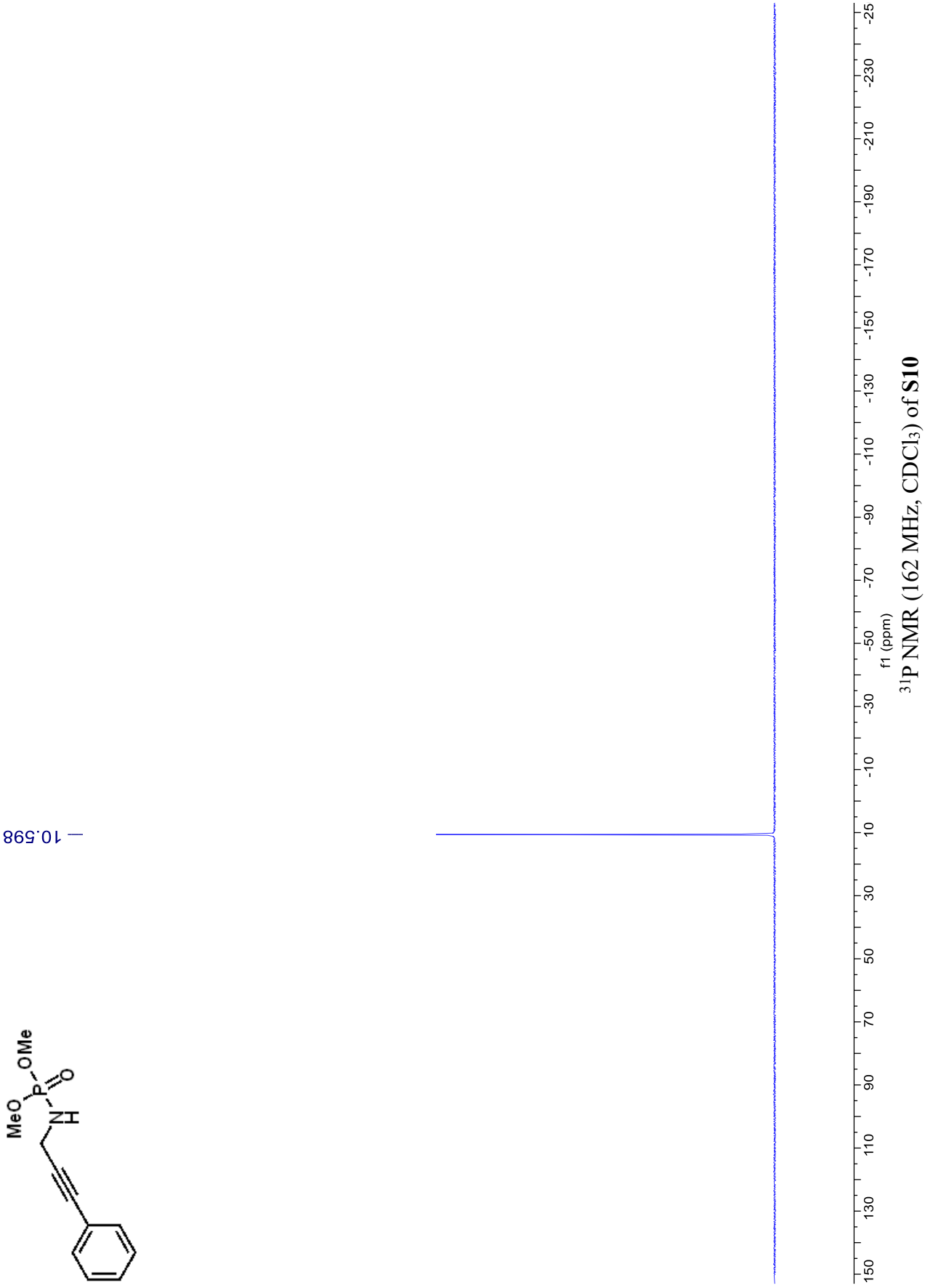
^{31}P NMR (162 MHz, $CDCl_3$) of **1t**



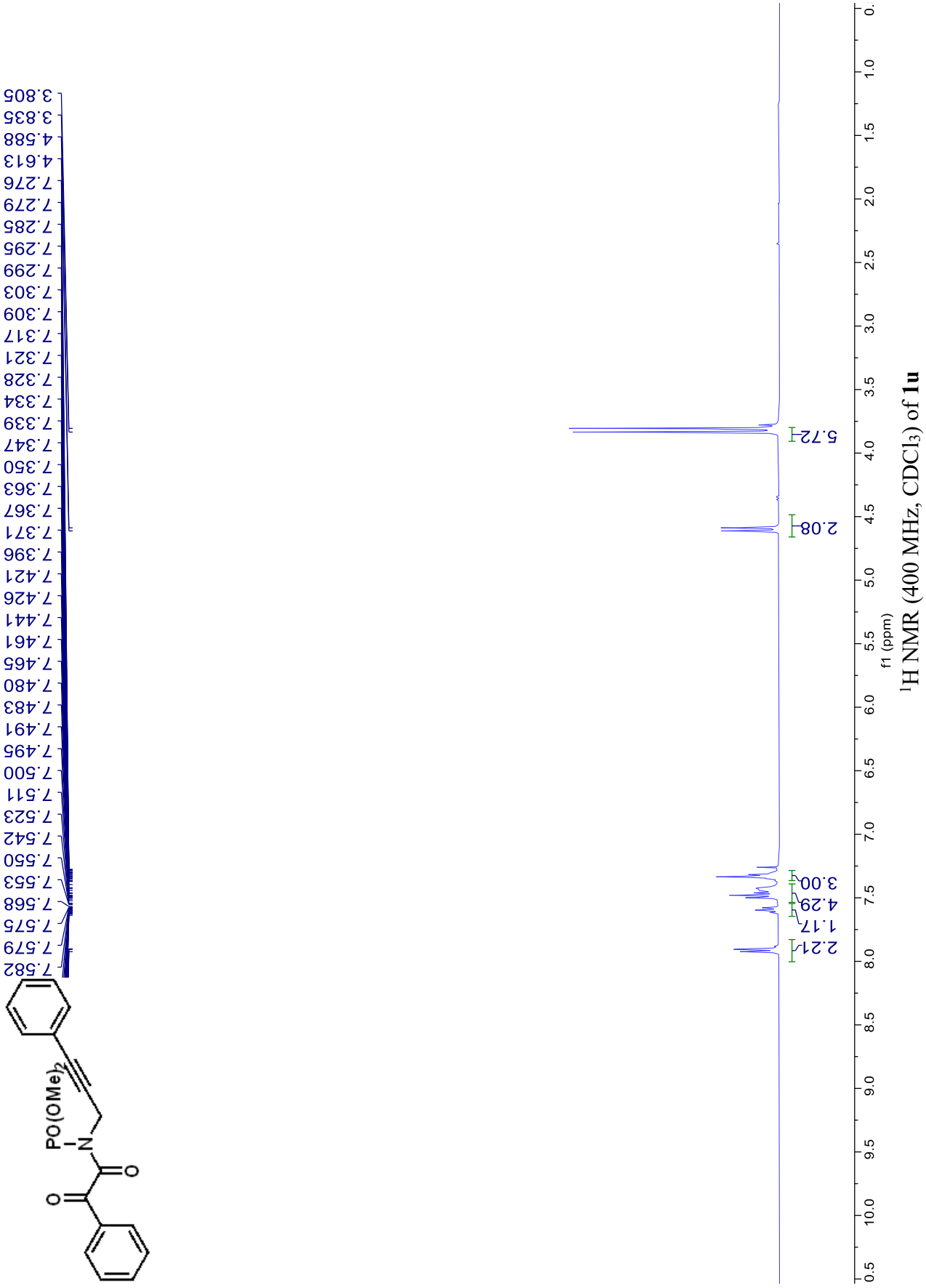
^{1}H NMR (400 MHz, $CDCl_3$) of **S10**



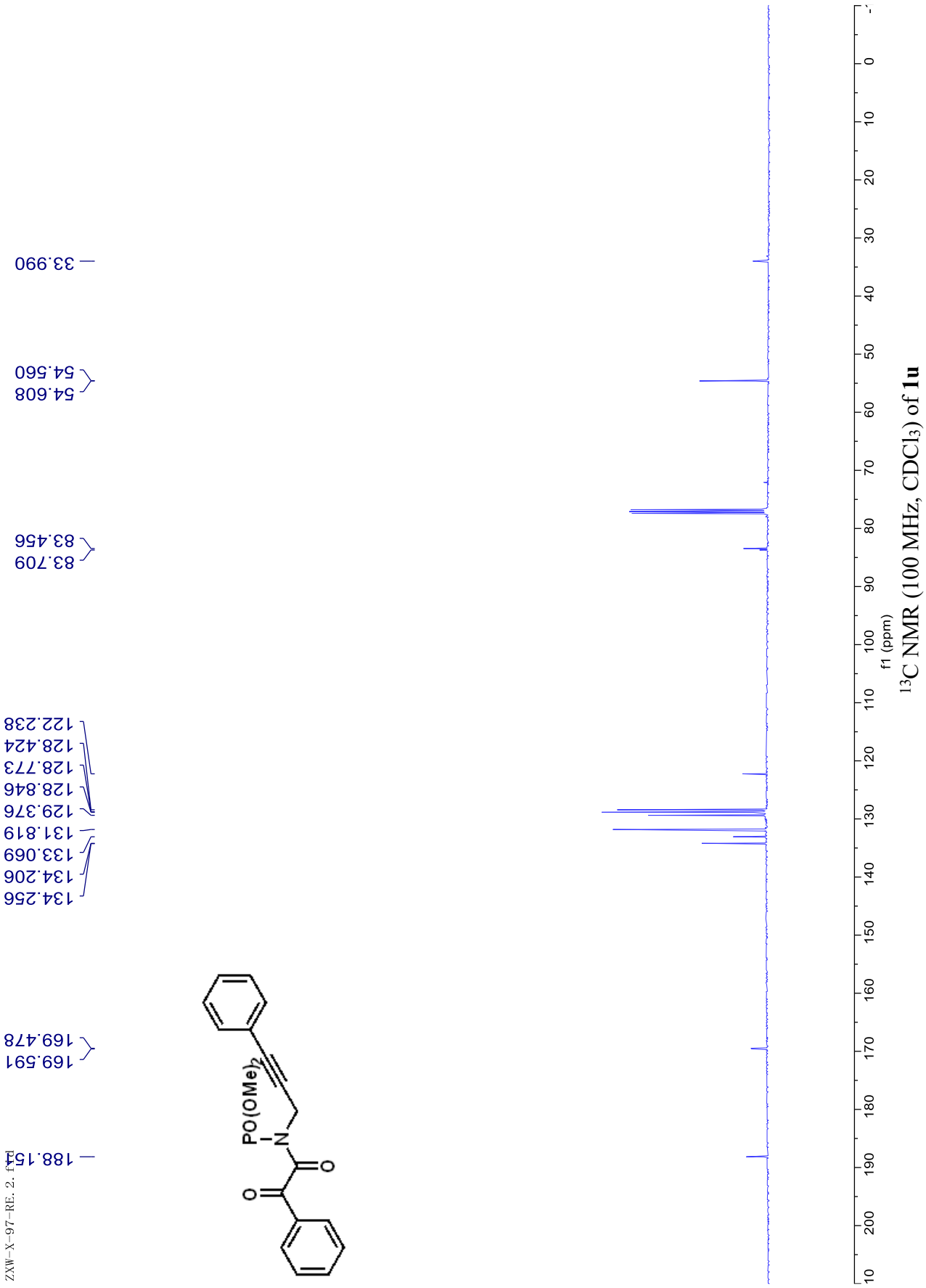
^{13}C NMR (100 MHz, $CDCl_3$) of **S10**



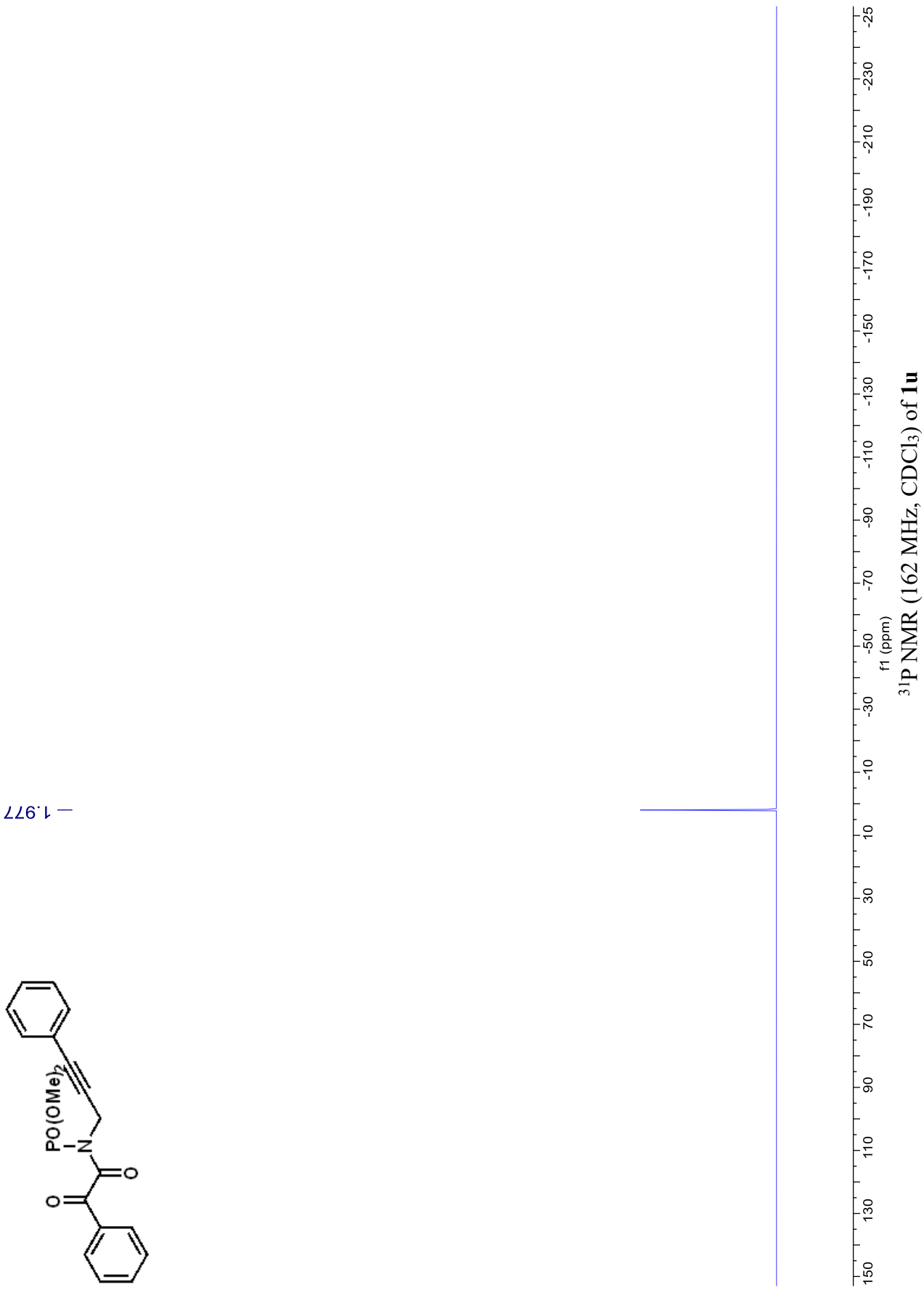
^{31}P NMR (162 MHz, $CDCl_3$) of **S10**



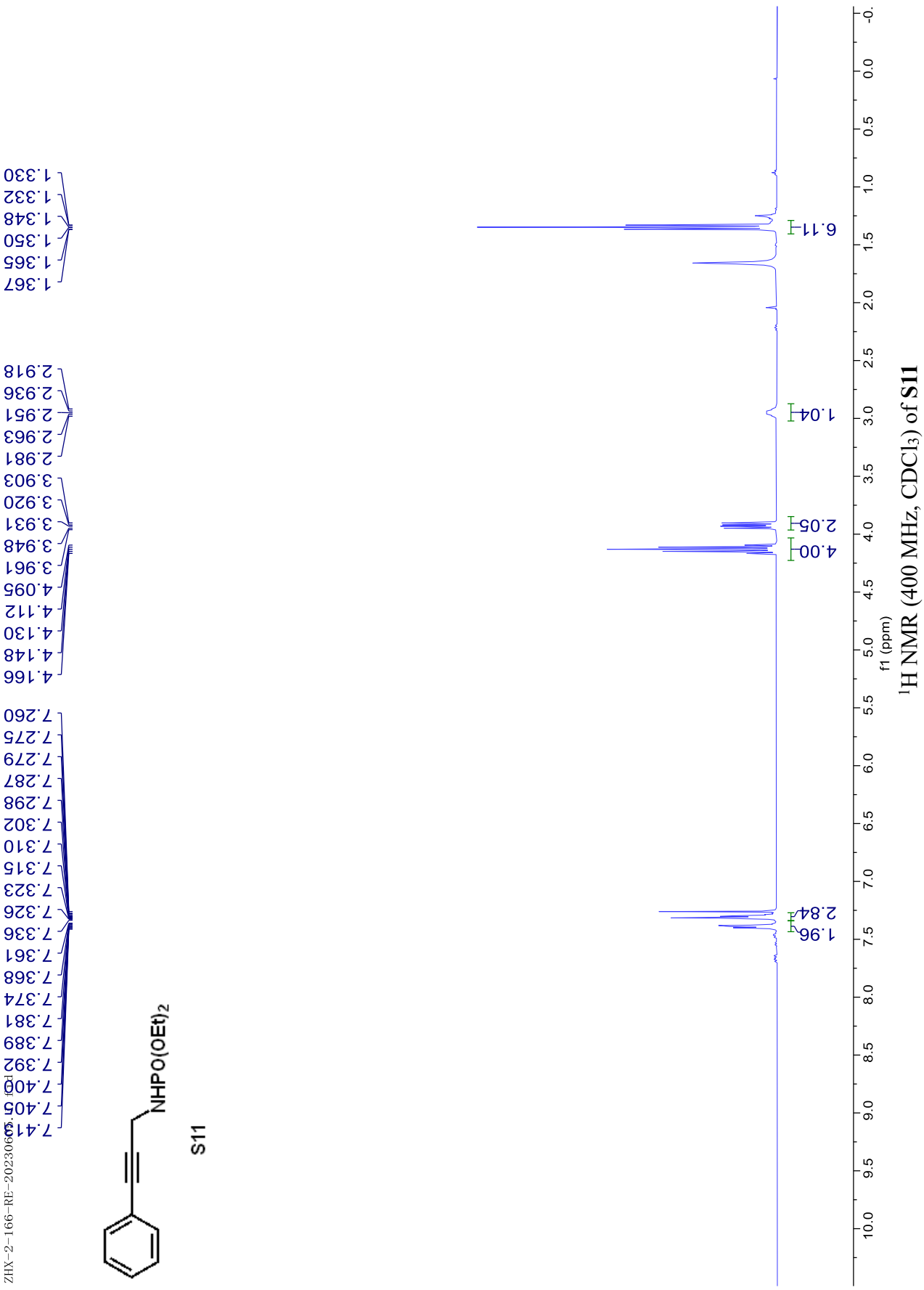
^{1}H NMR (400 MHz, $CDCl_3$) of **1u**



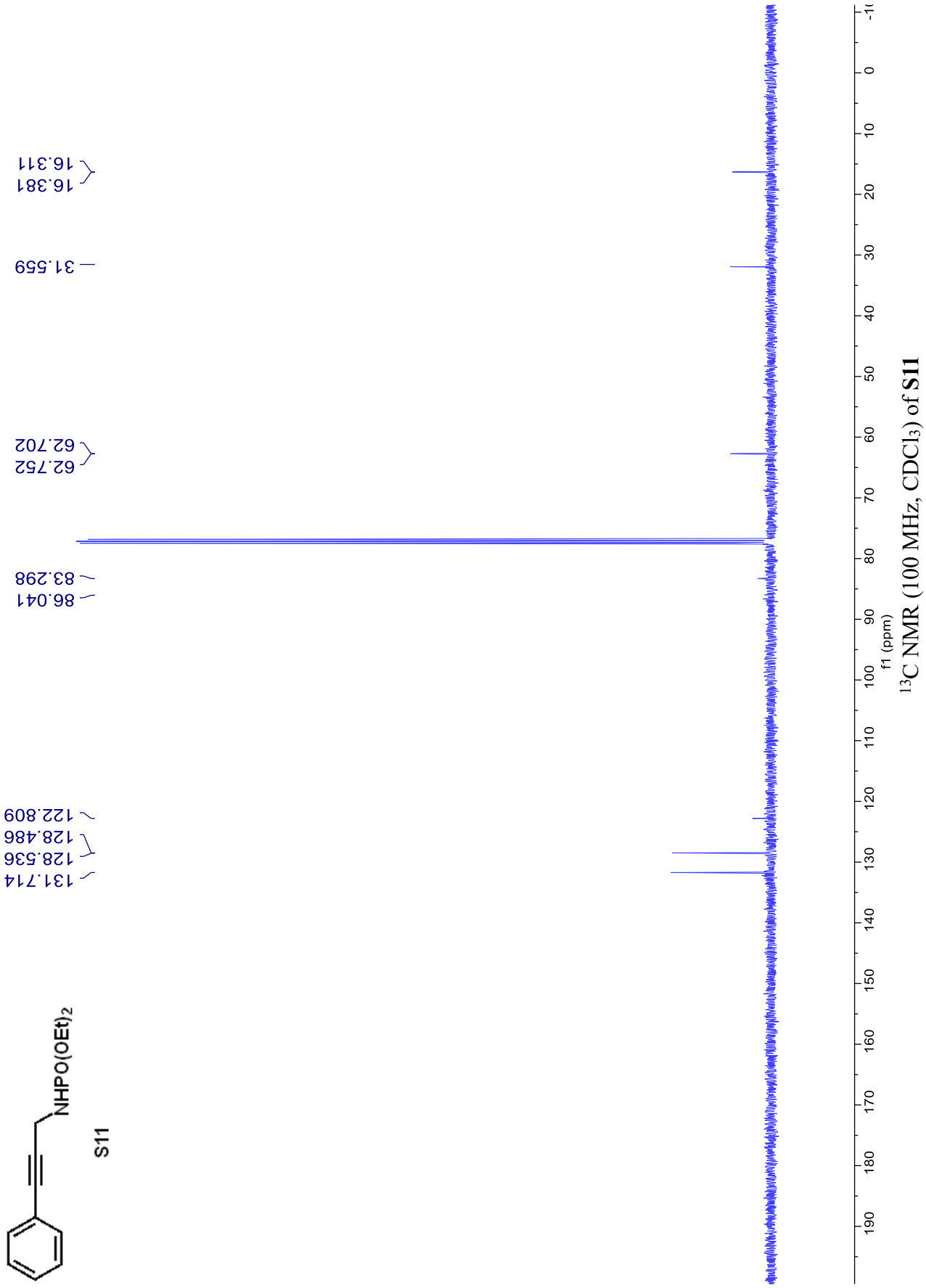
^{13}C NMR (100 MHz, $CDCl_3$) of **1u**



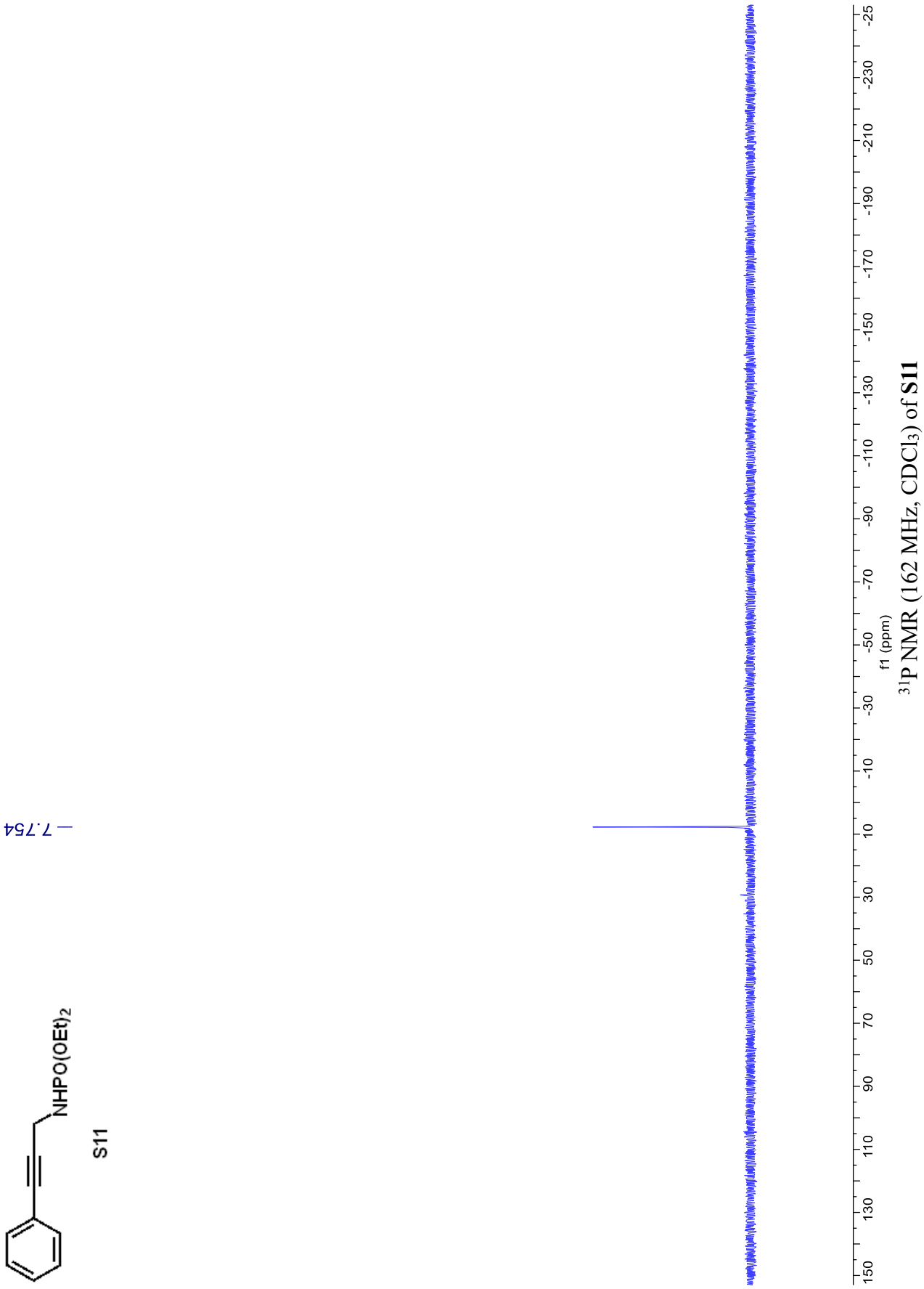
^{31}P NMR (162 MHz, $CDCl_3$) of **1u**



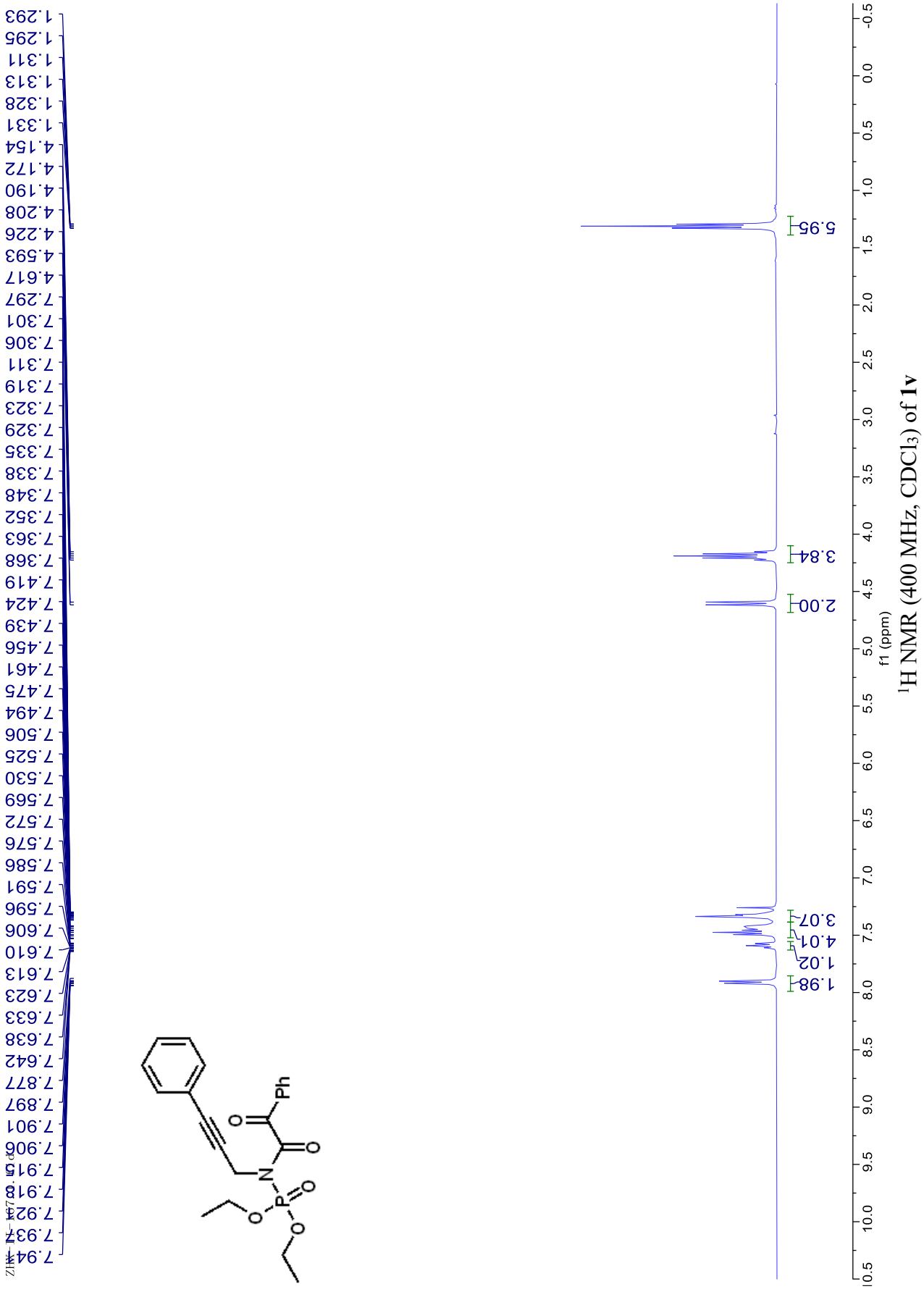
^{1}H NMR (400 MHz, $CDCl_3$) of **S11**



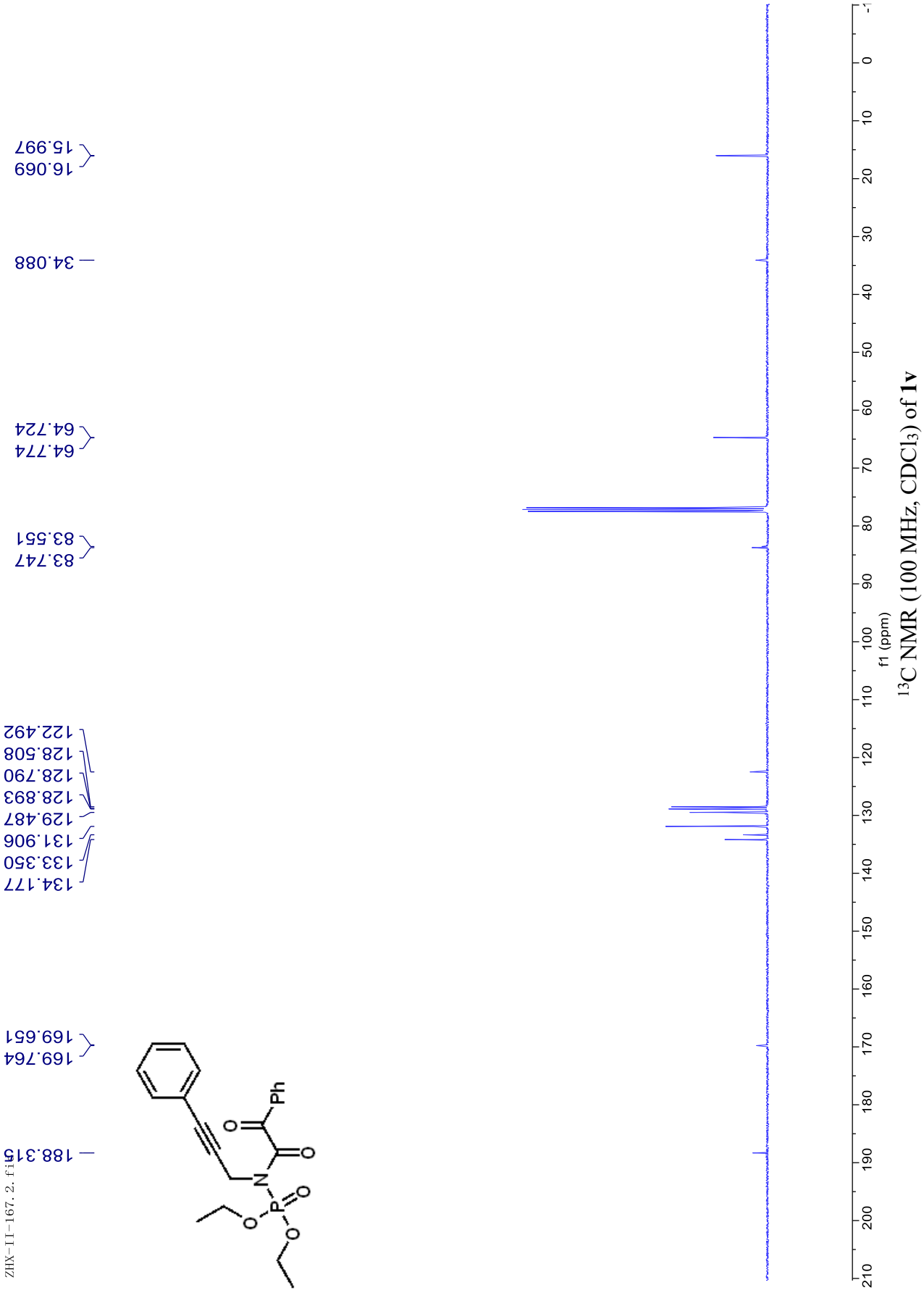
^{13}C NMR (100 MHz, $CDCl_3$) of **S11**



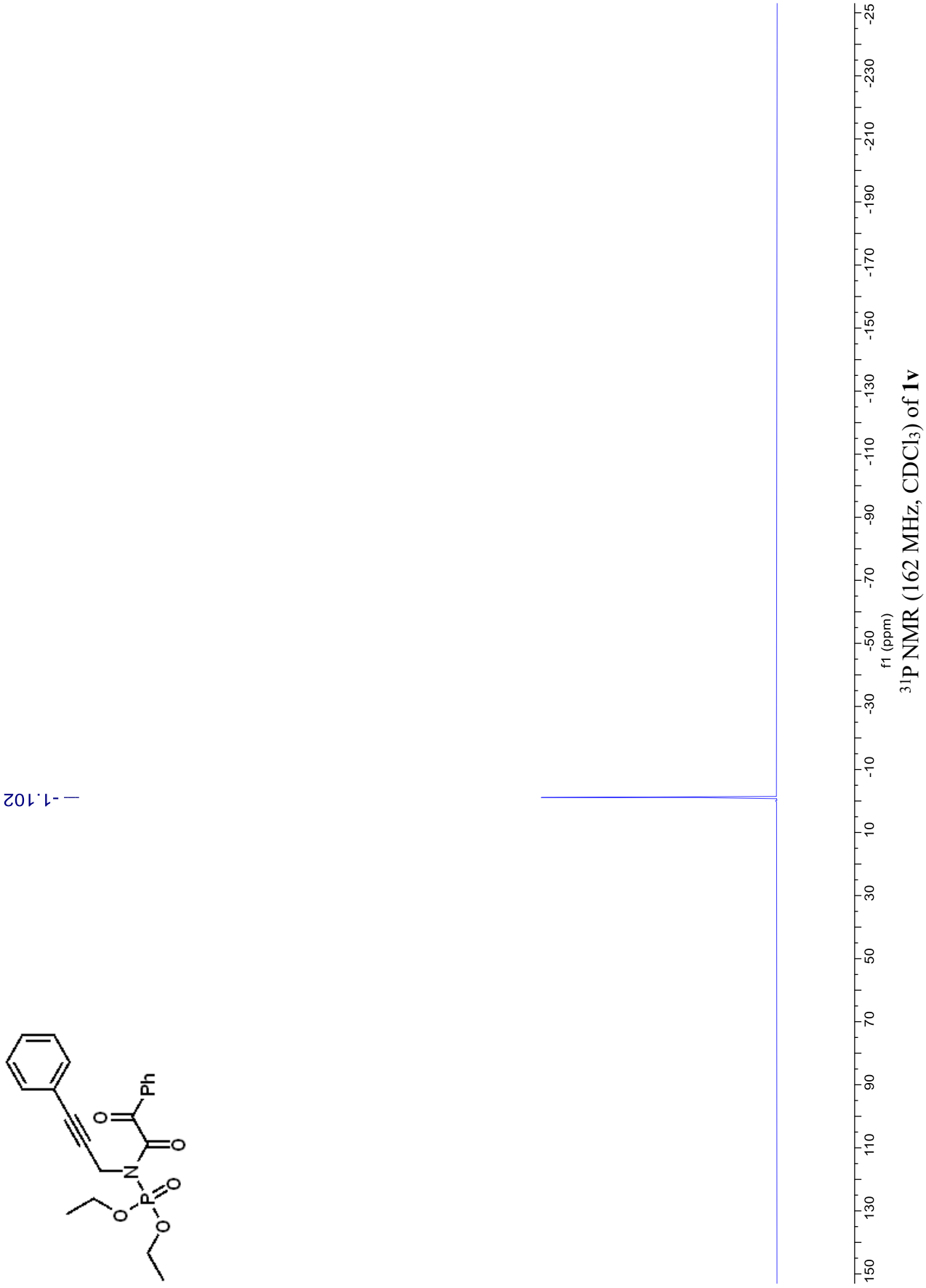
^{31}P NMR (162 MHz, $CDCl_3$) of **S11**



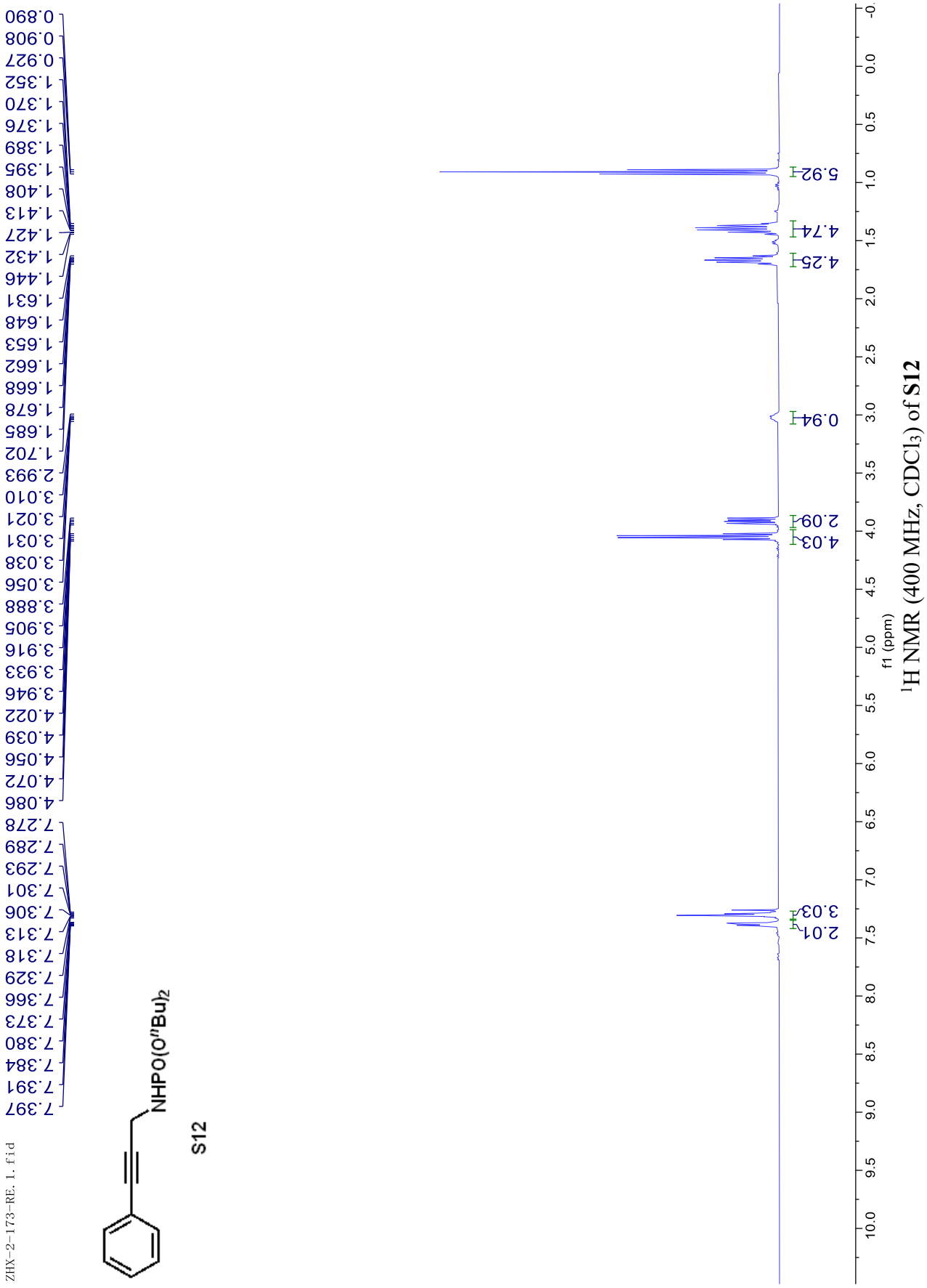
^{1}H NMR (400 MHz, $CDCl_3$) of **1v**



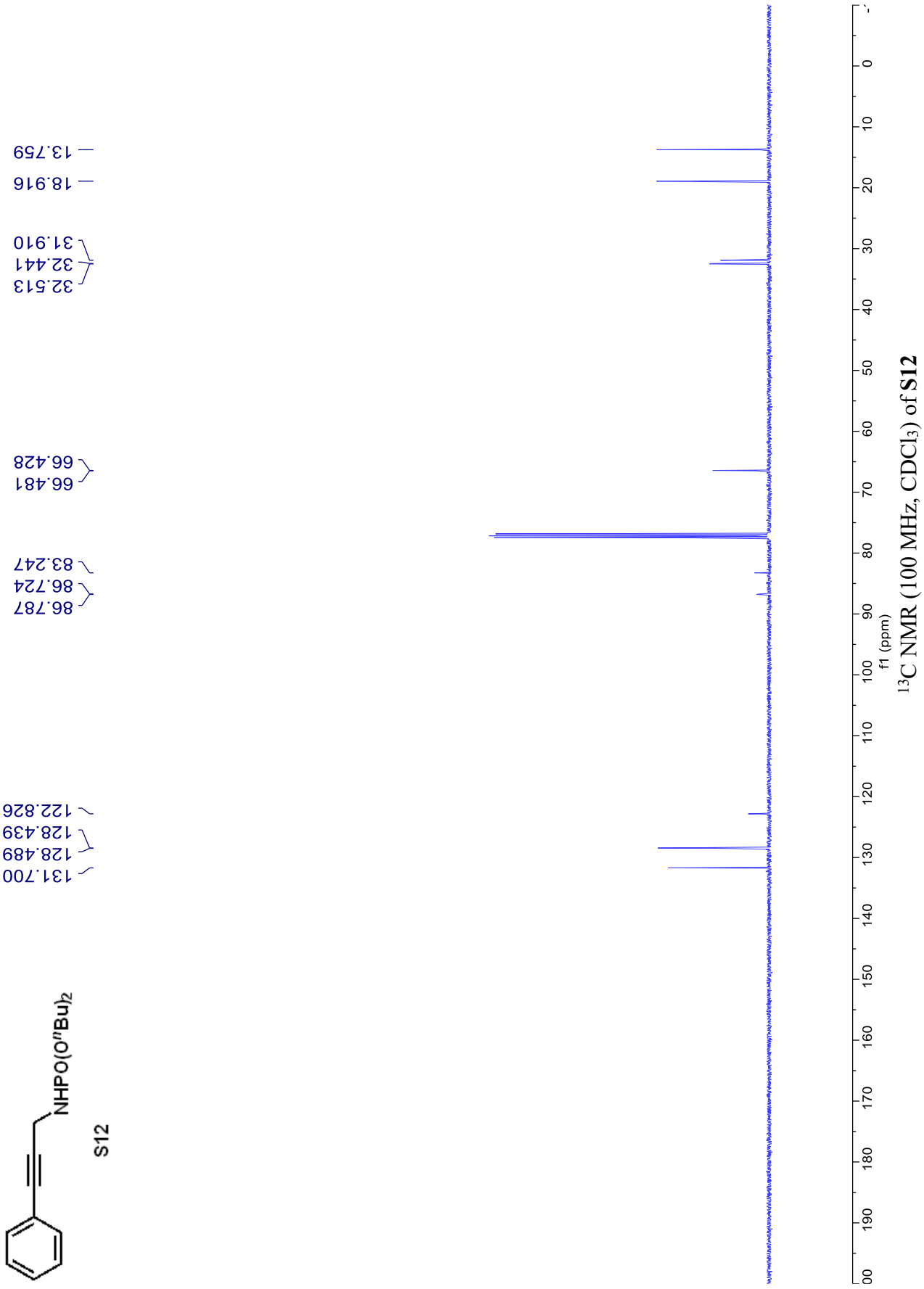
^{13}C NMR (100 MHz, $CDCl_3$) of **1v**



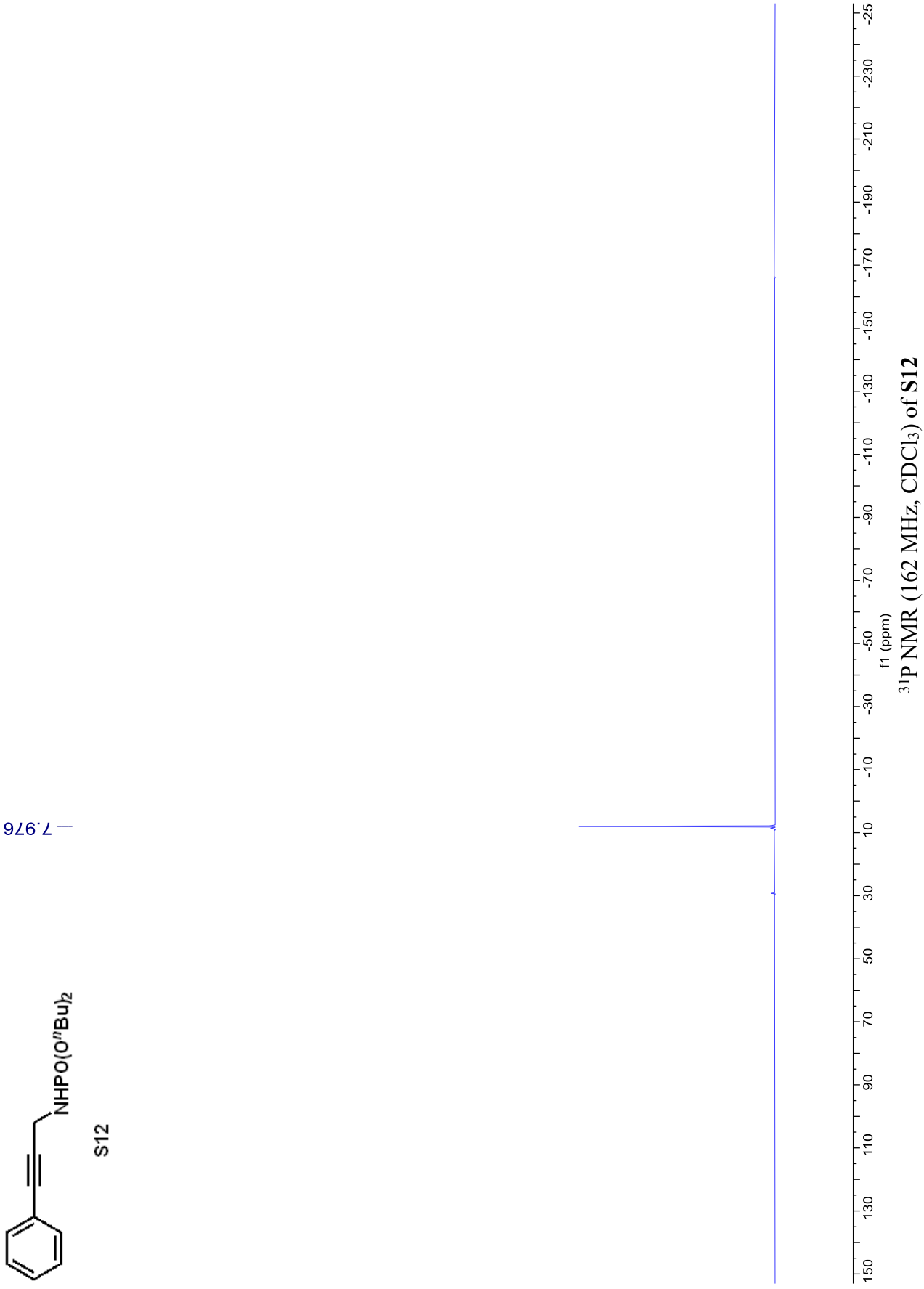
^{31}P NMR (162 MHz, $CDCl_3$) of **1v**



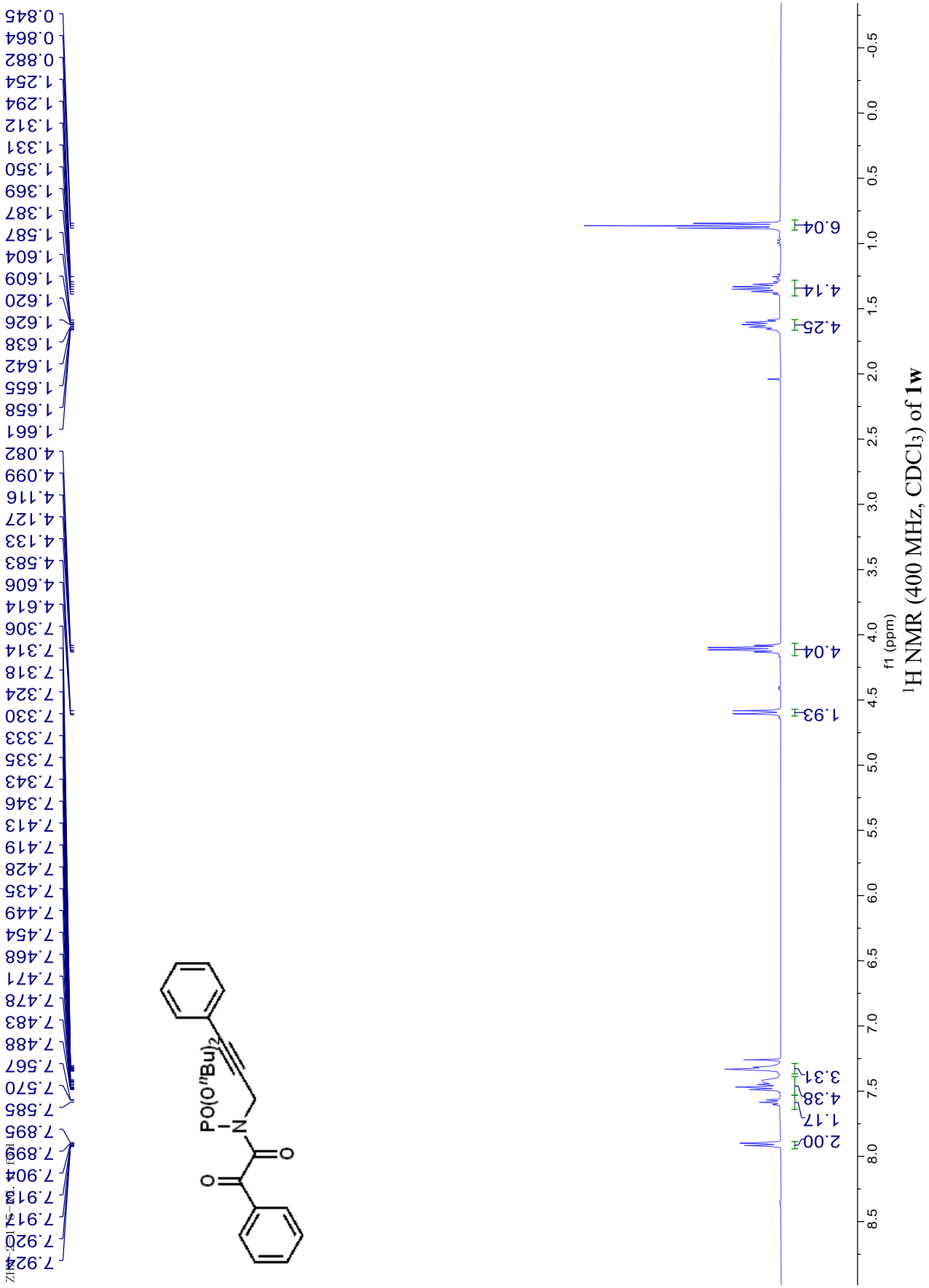
^{1}H NMR (400 MHz, $CDCl_3$) of **S12**



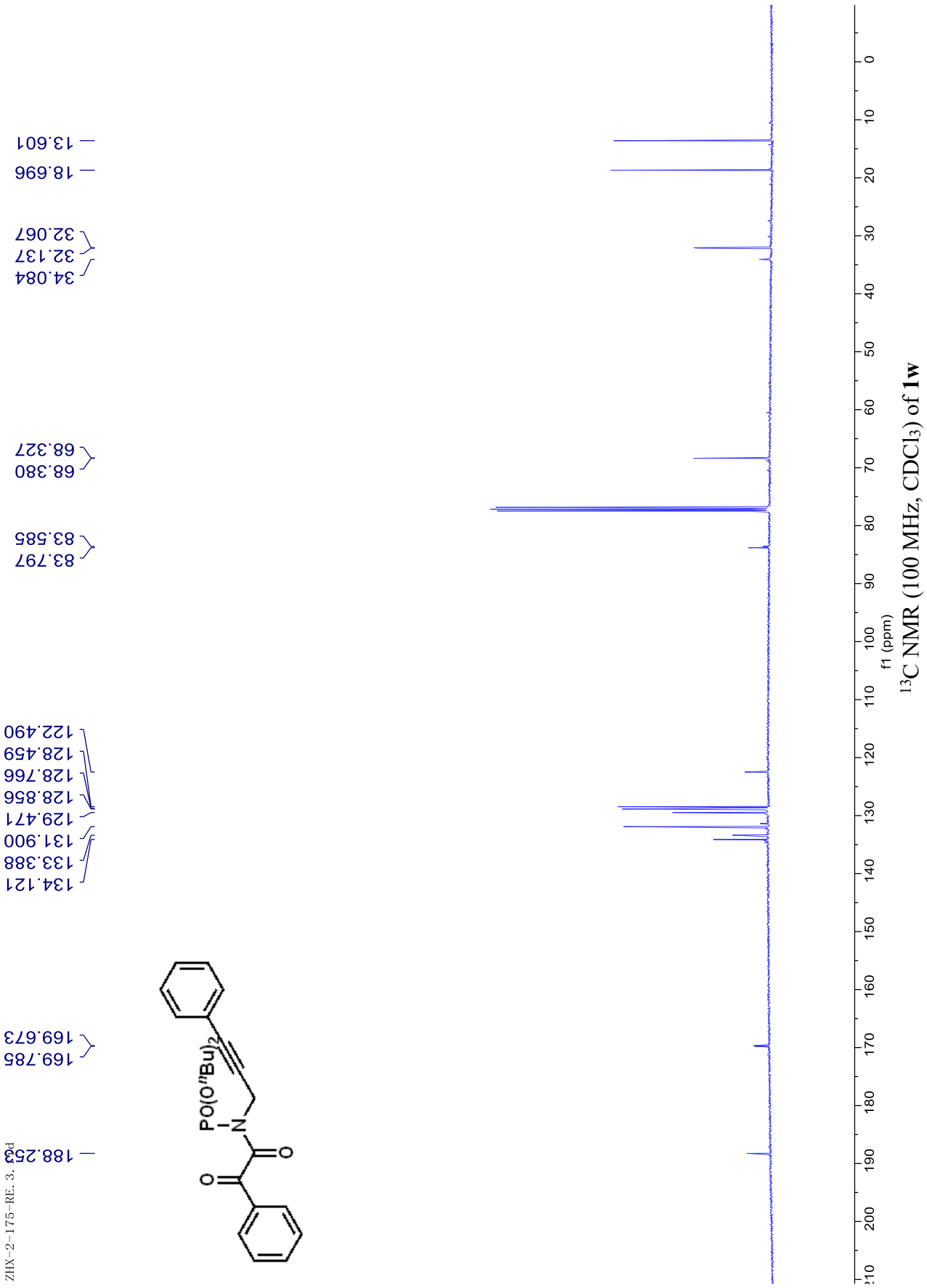
^{13}C NMR (100 MHz, $CDCl_3$) of **S12**



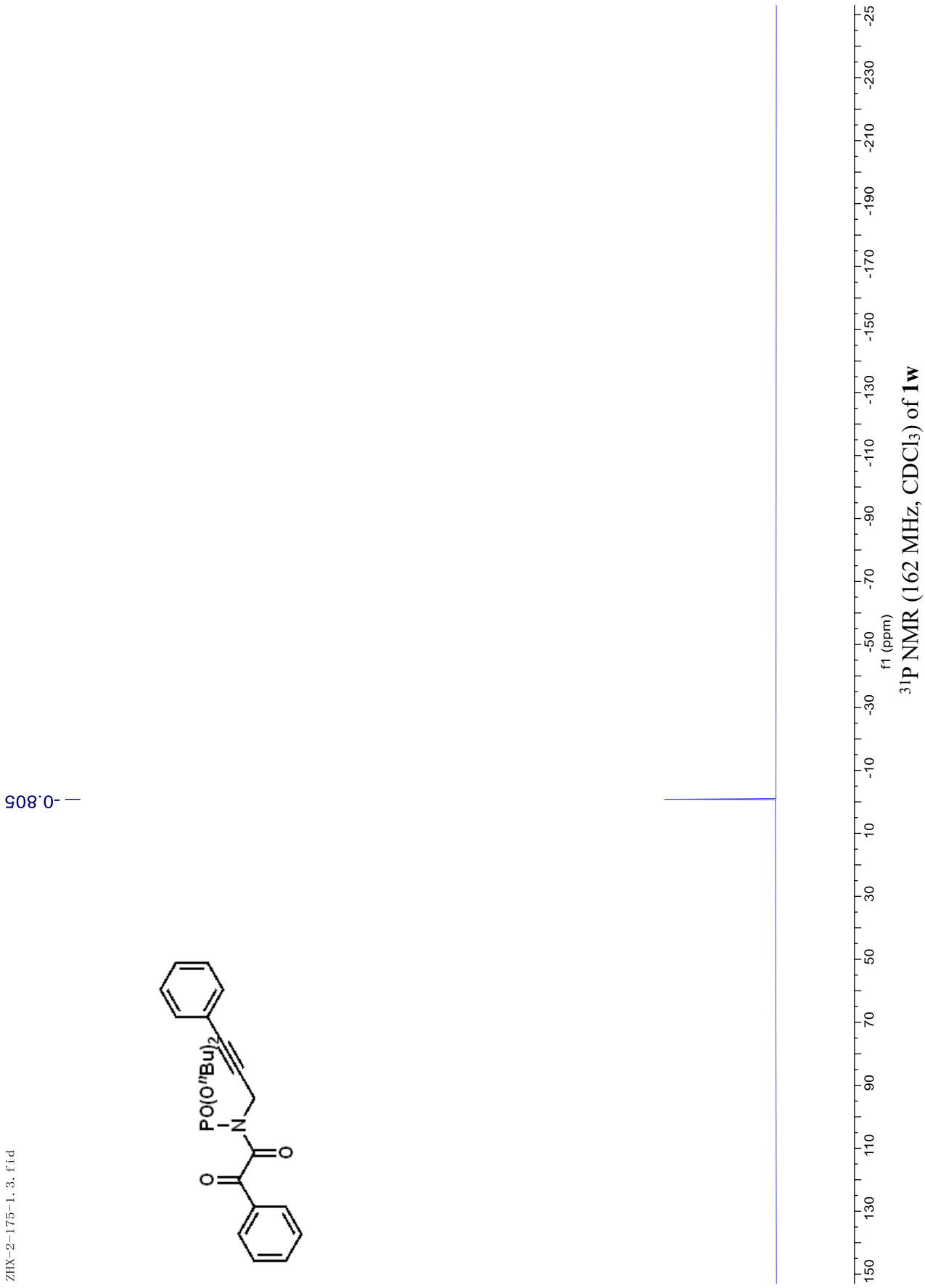
^{31}P NMR (162 MHz, $CDCl_3$) of **S12**



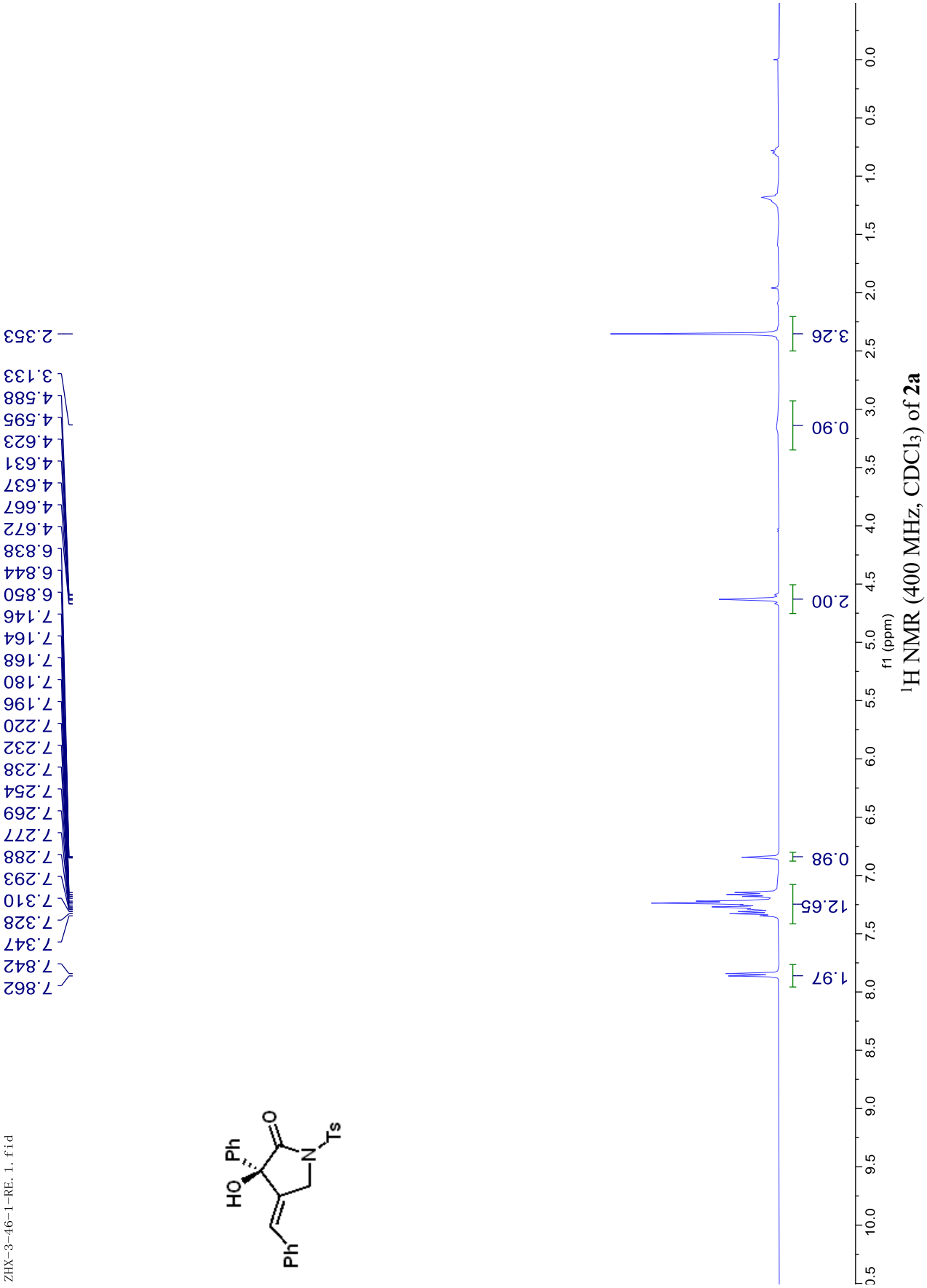
^{1}H NMR (400 MHz, $CDCl_3$) of **1w**



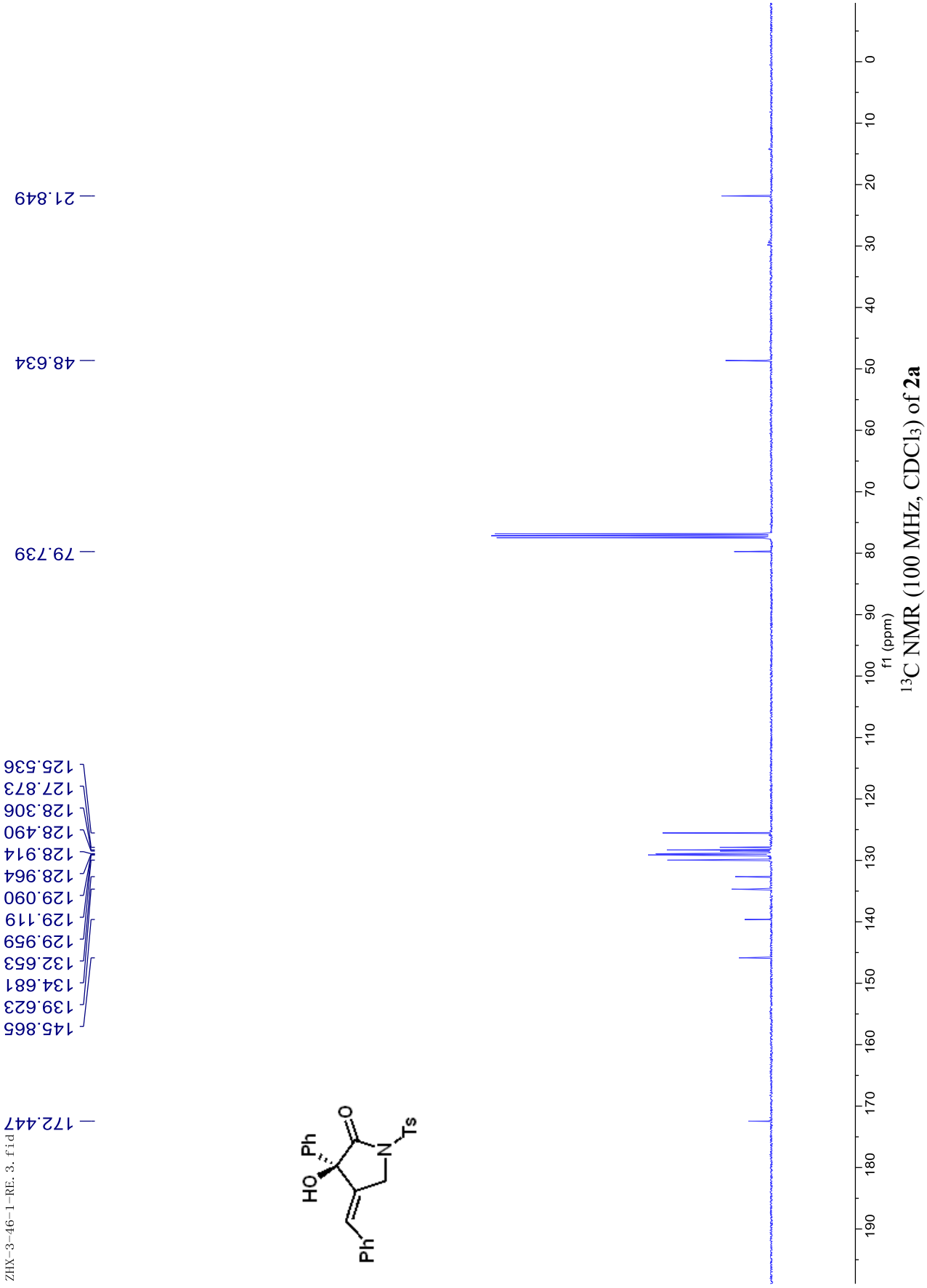
^{13}C NMR (100 MHz, $CDCl_3$) of **1w**



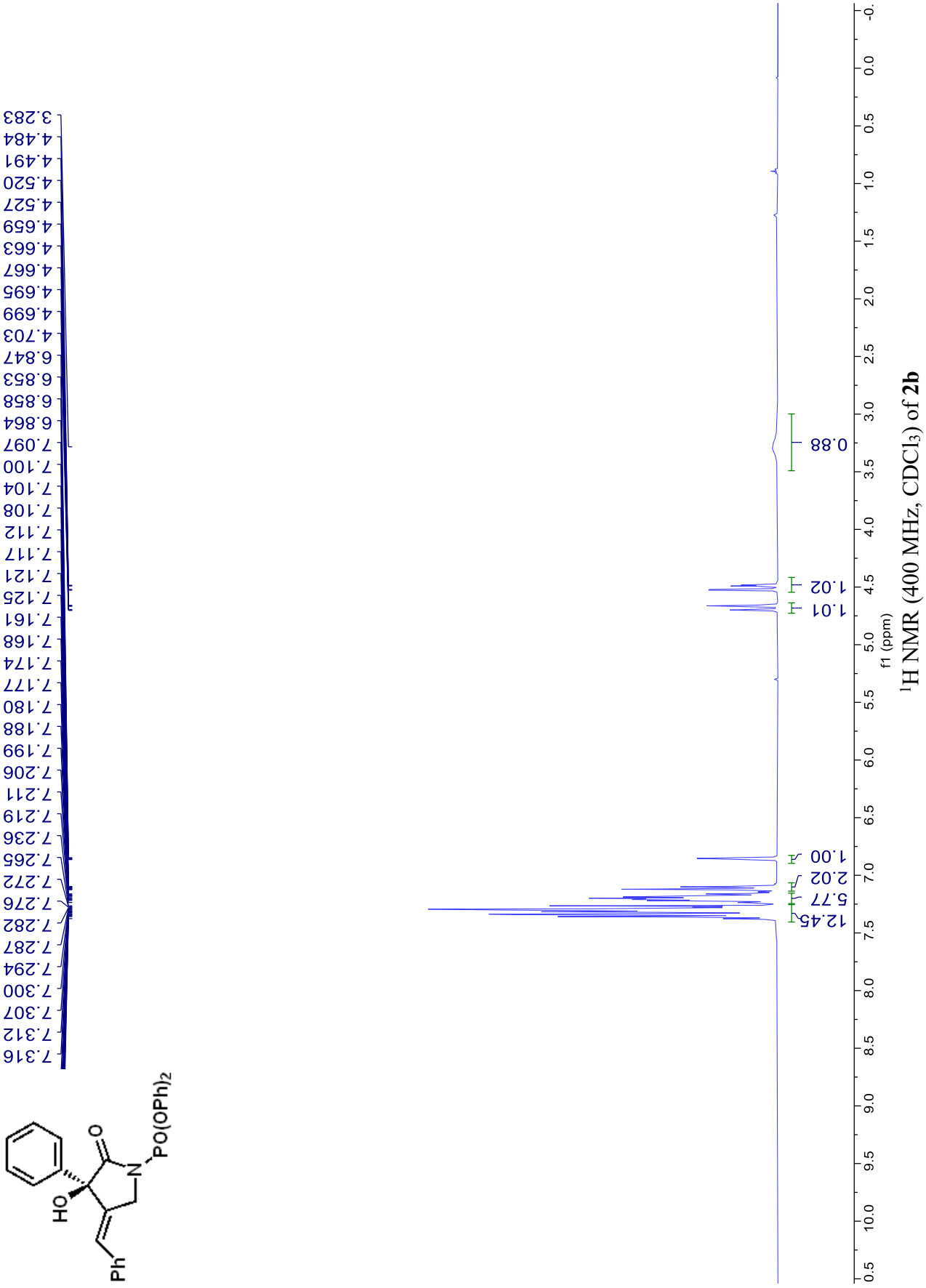
^{31}P NMR (162 MHz, $CDCl_3$) of **1w**



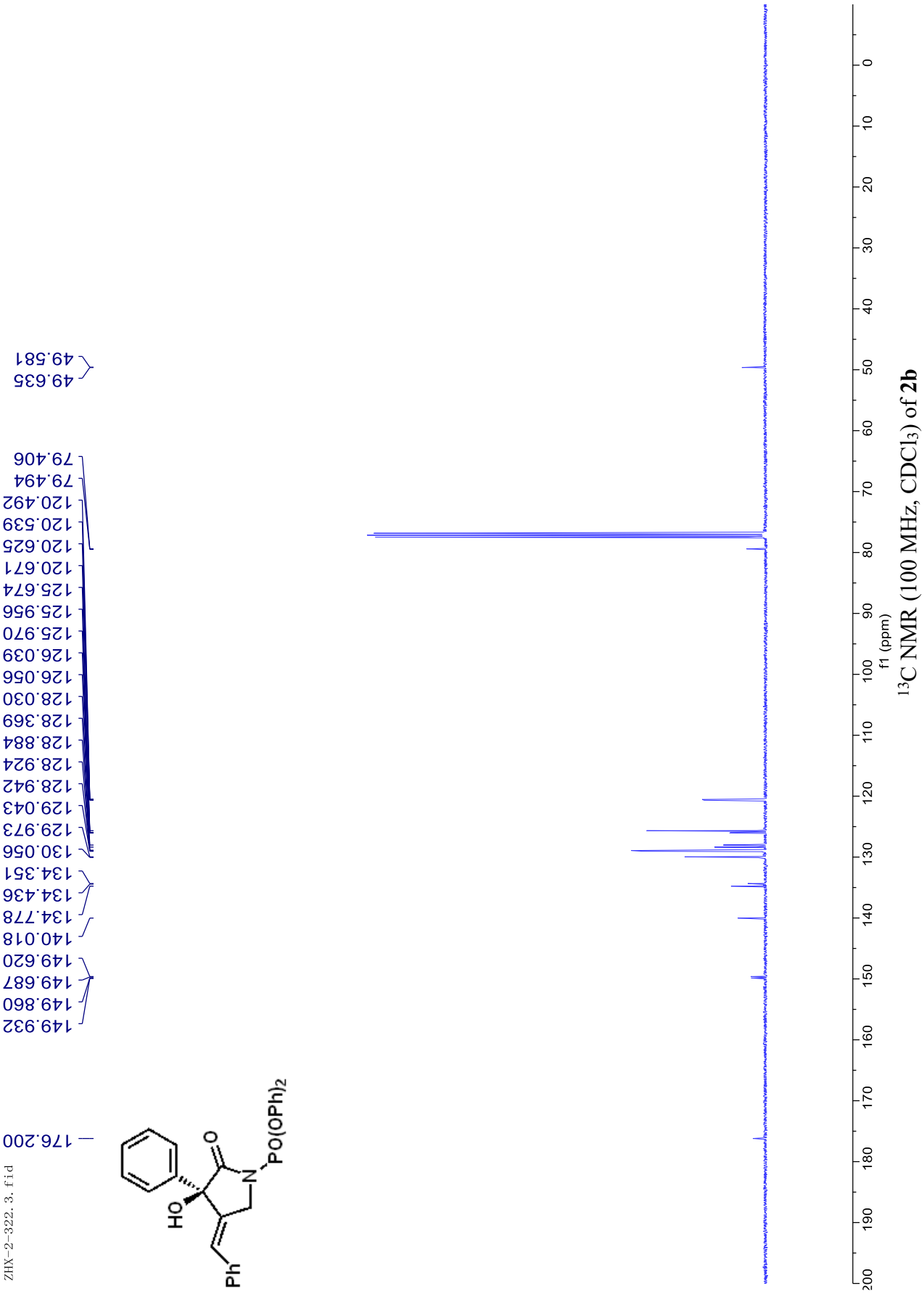
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



^{13}C NMR (100 MHz, $CDCl_3$) of **2a**

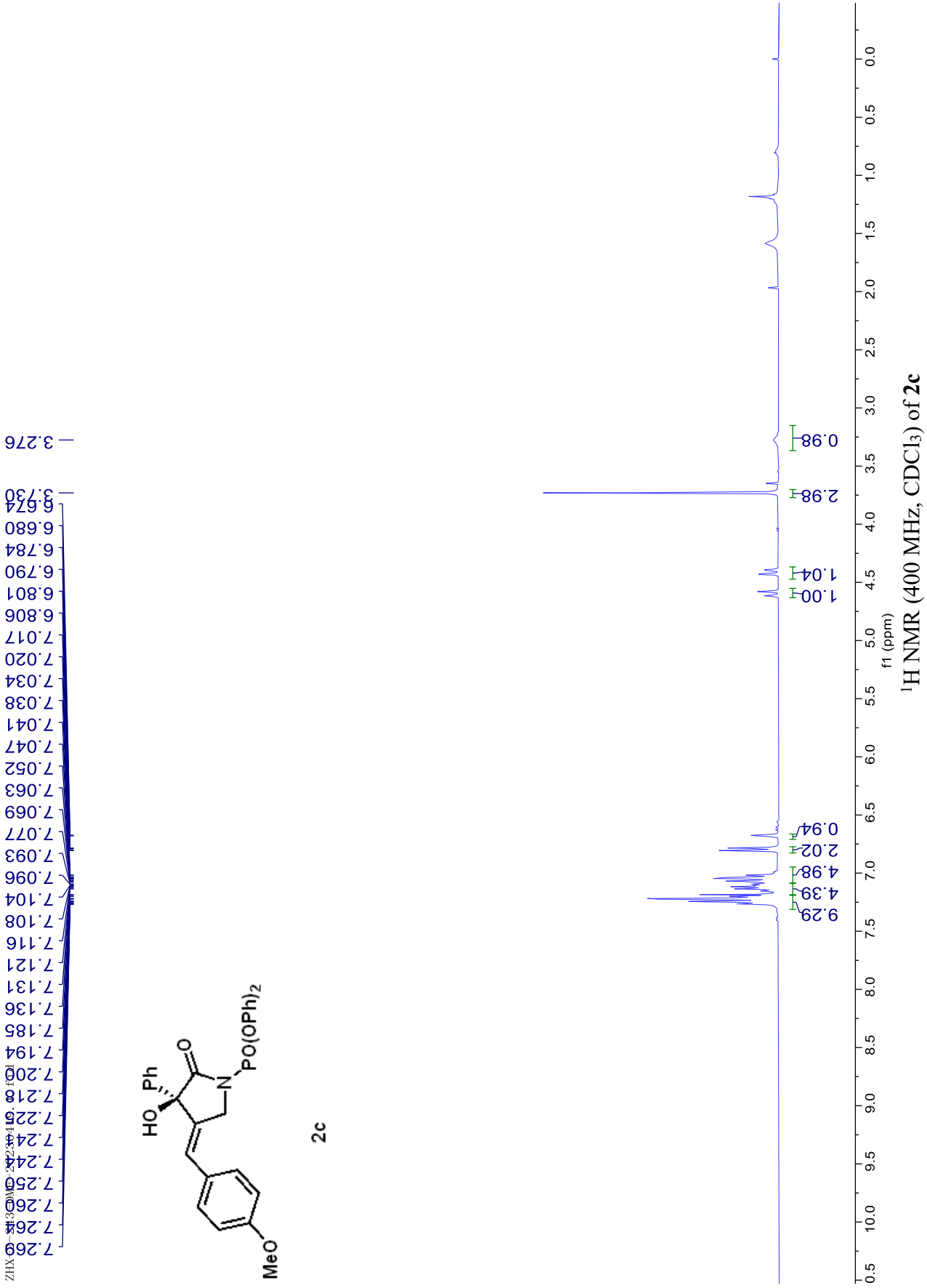


^{1}H NMR (400 MHz, $CDCl_3$) of **2b**

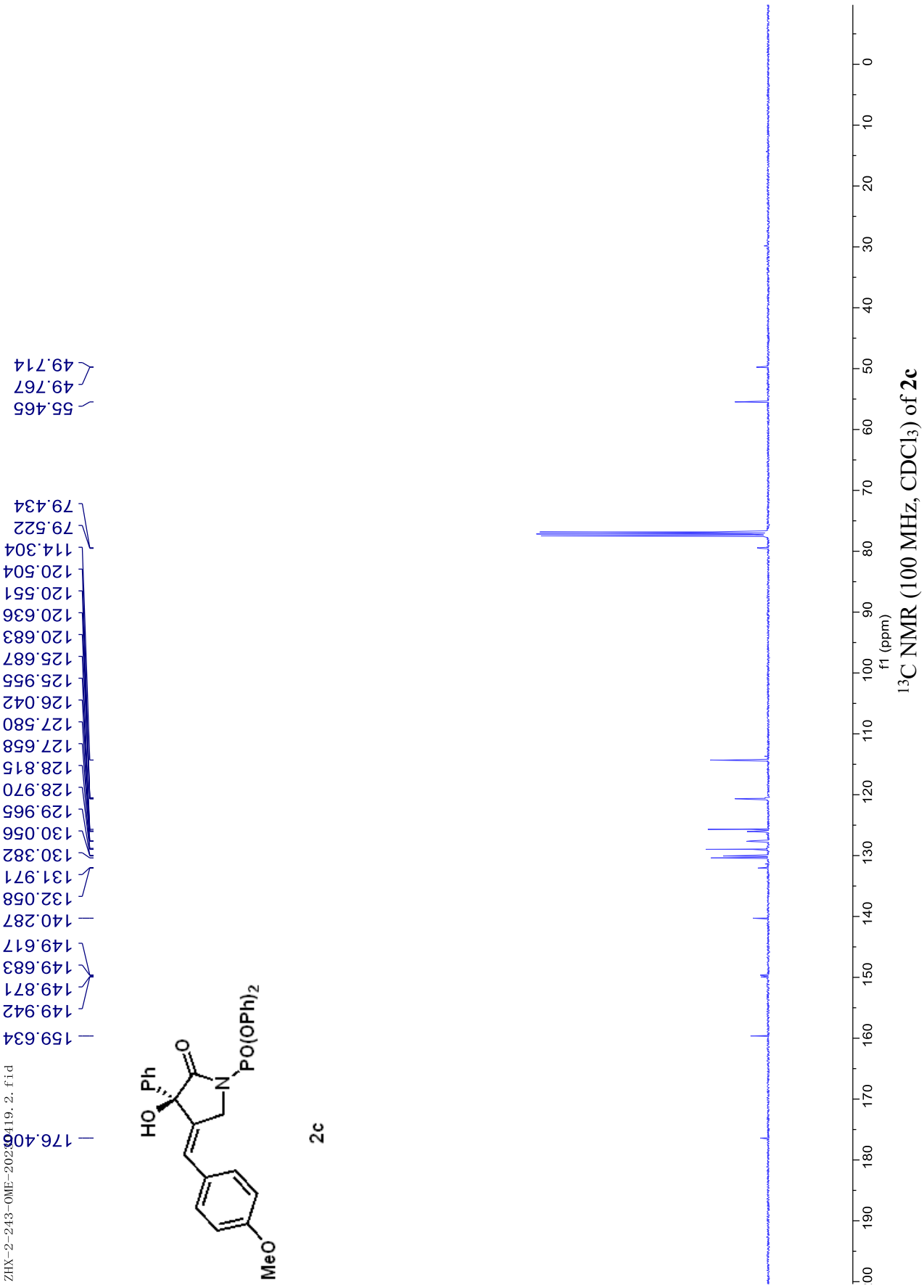


^{13}C NMR (100 MHz, $CDCl_3$) of **2b**

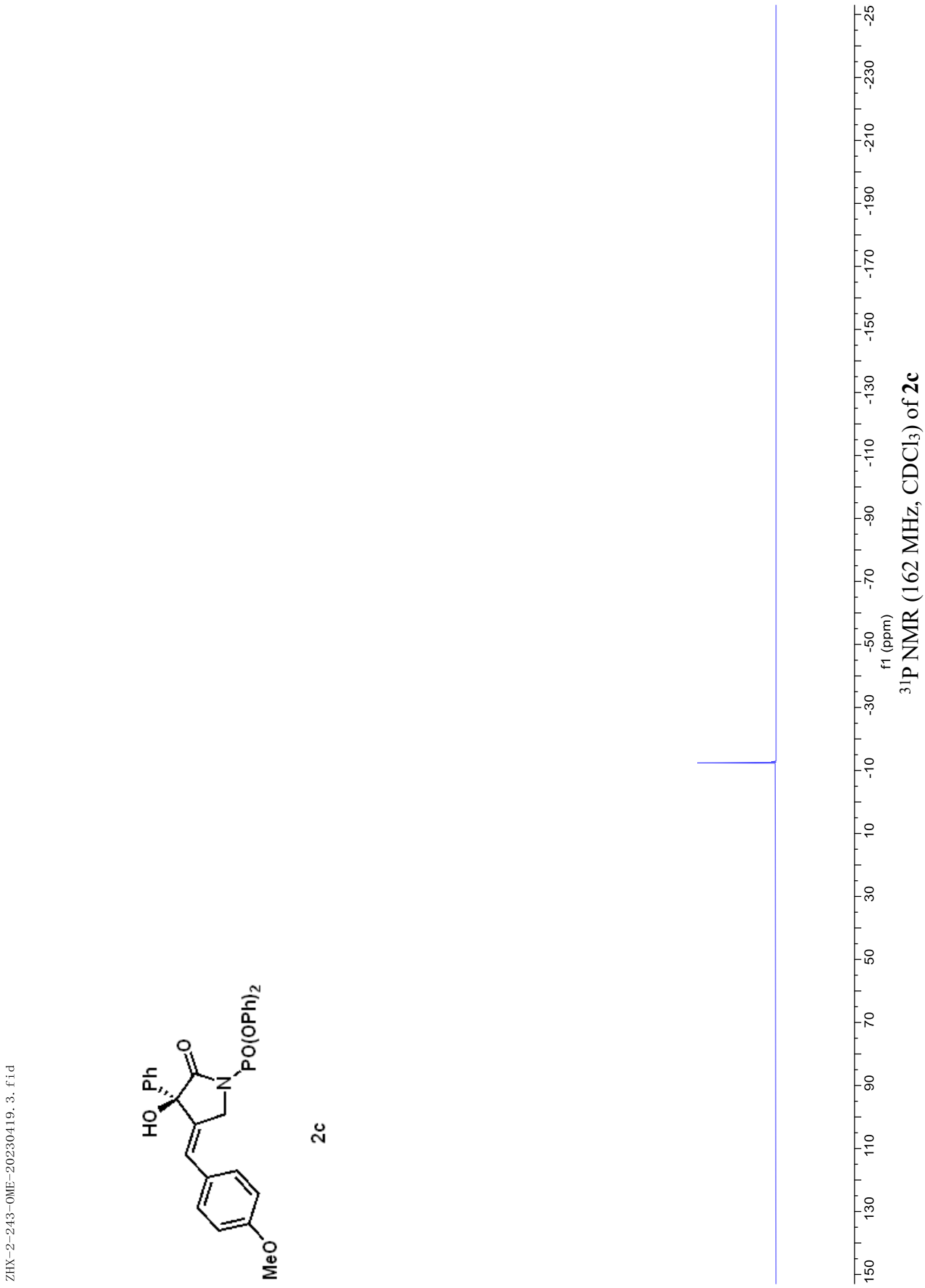
^{31}P NMR (162 MHz, $CDCl_3$) of **2b**



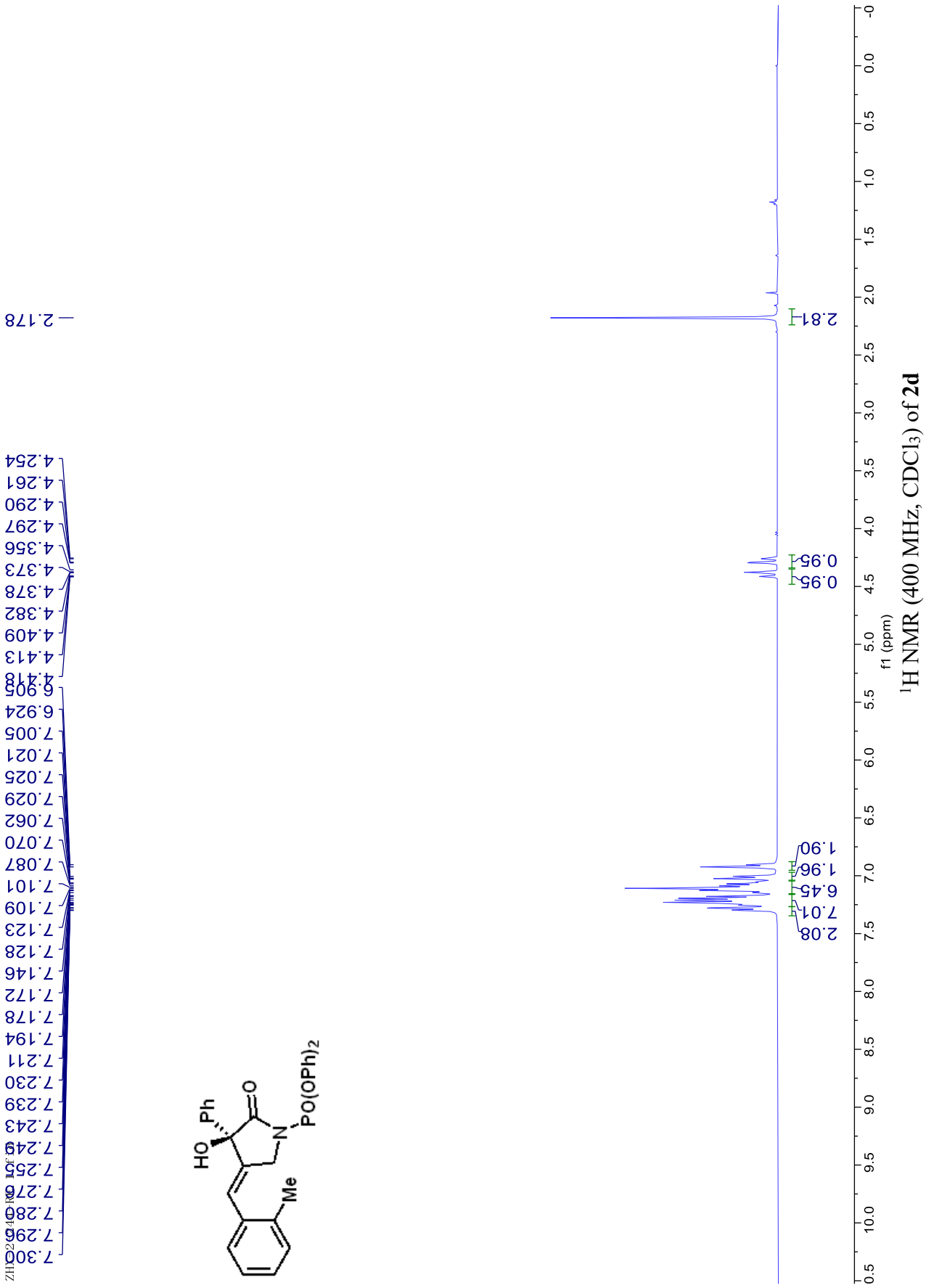
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



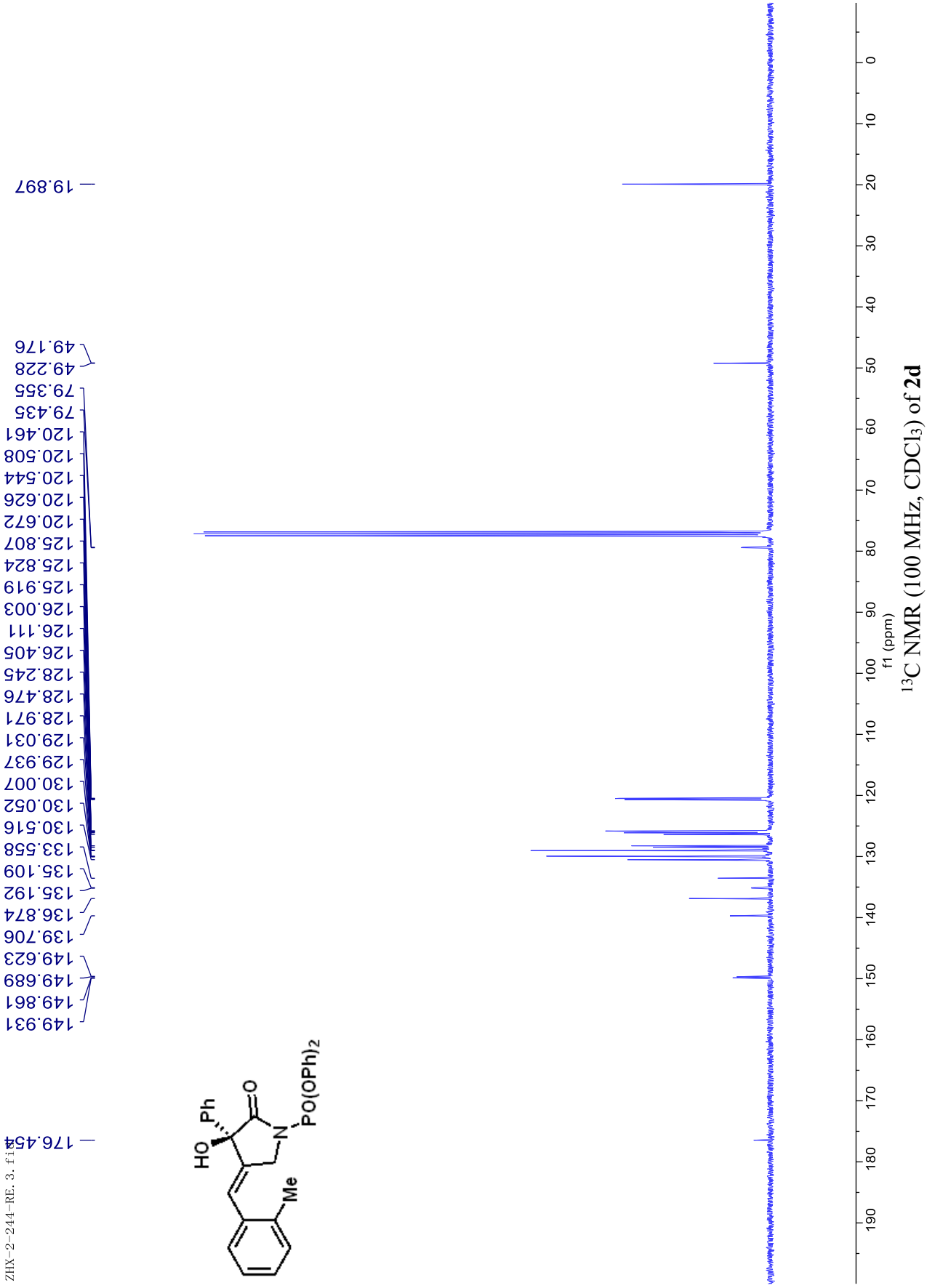
^{13}C NMR (100 MHz, $CDCl_3$) of **2c**



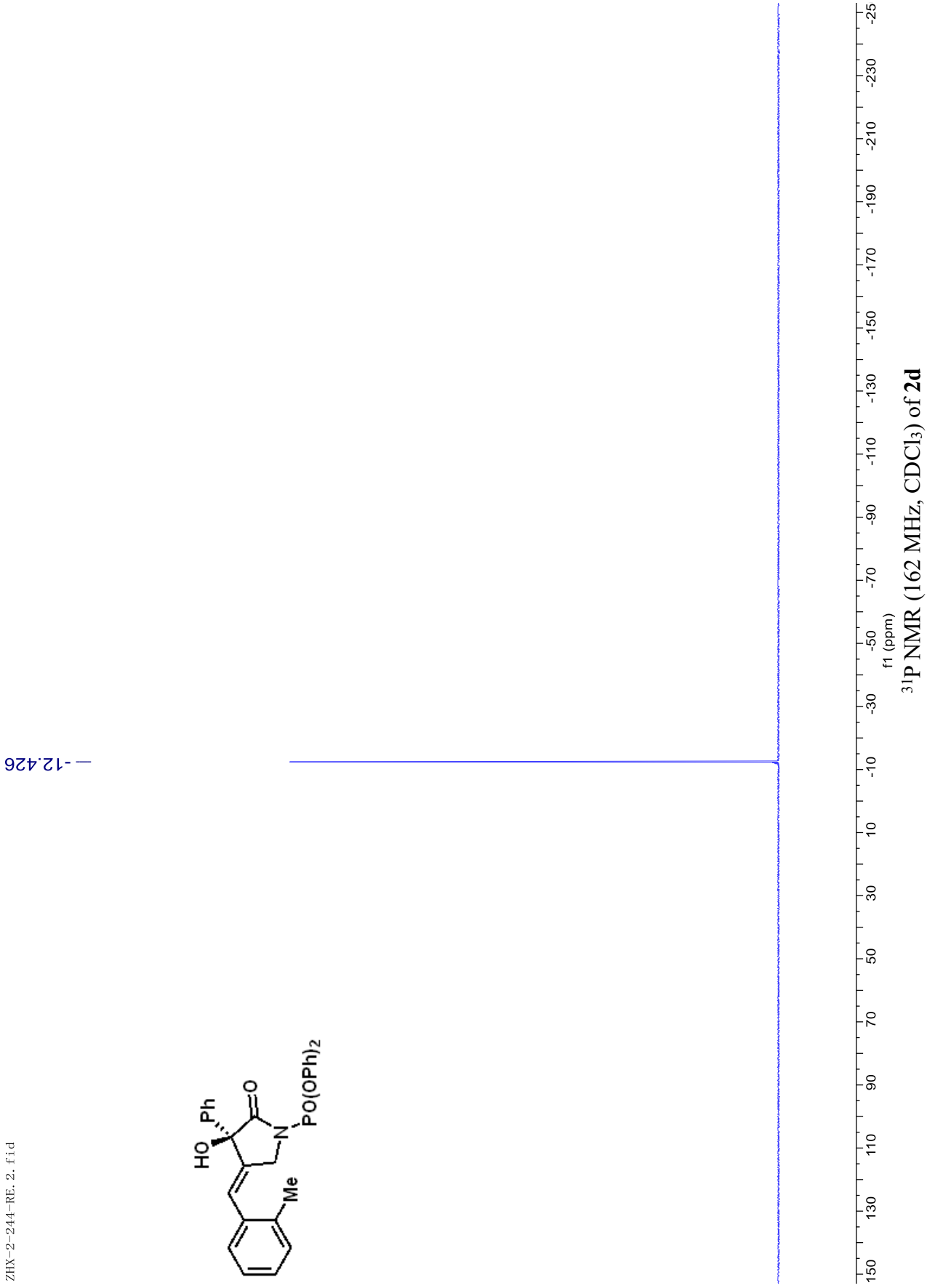
^{31}P NMR (162 MHz, $CDCl_3$) of **2c**



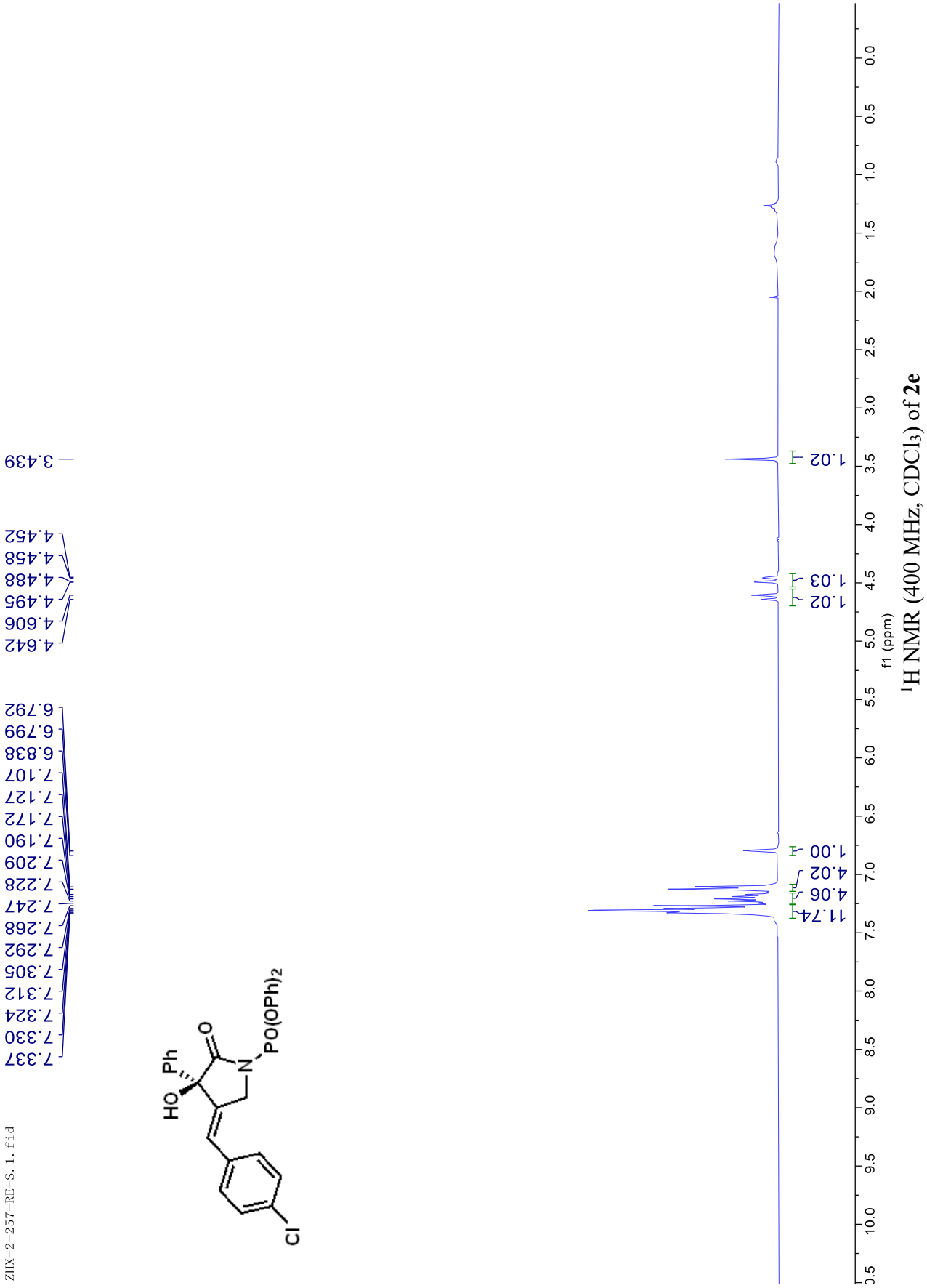
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



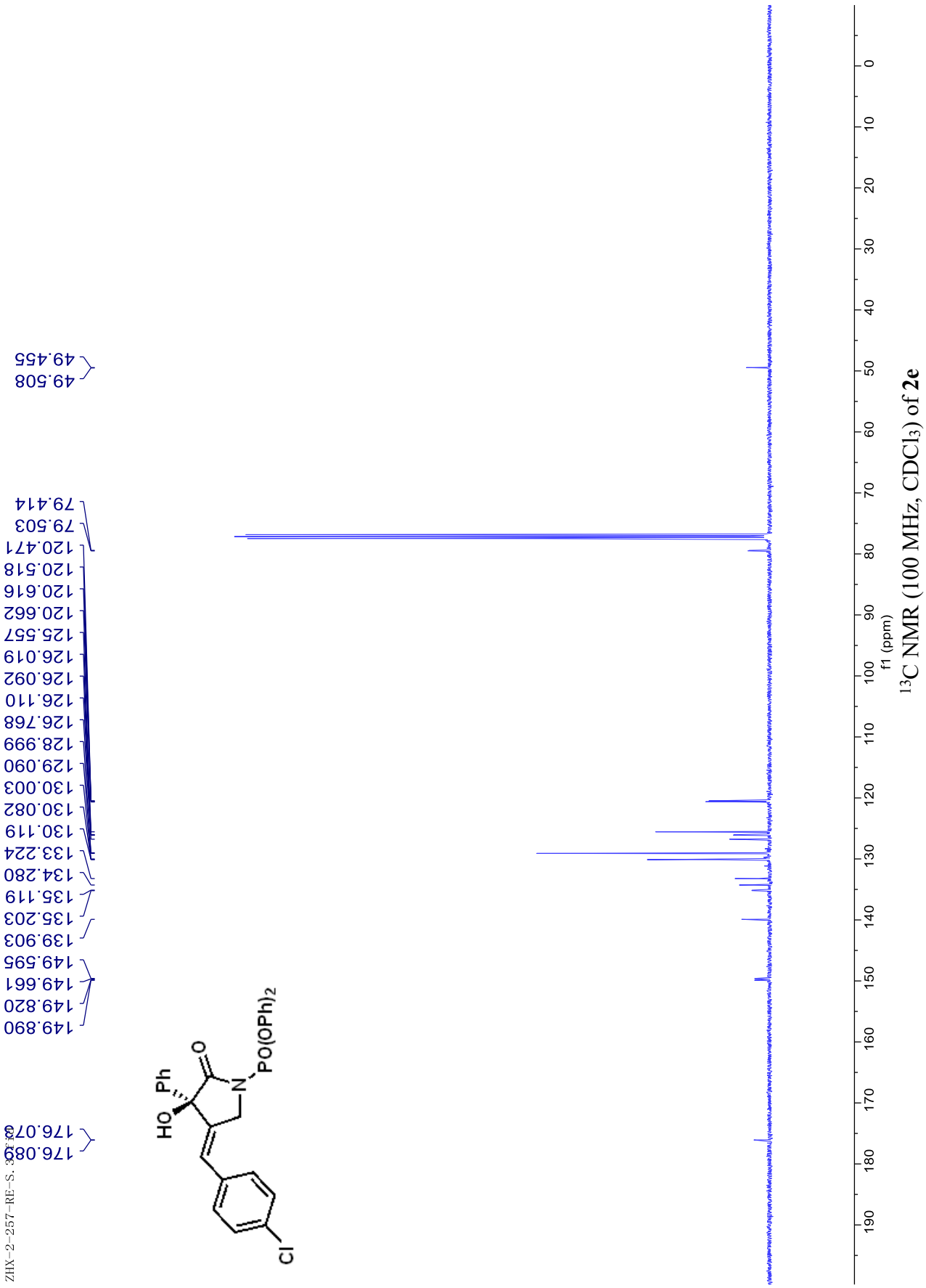
^{13}C NMR (100 MHz, $CDCl_3$) of **2d**



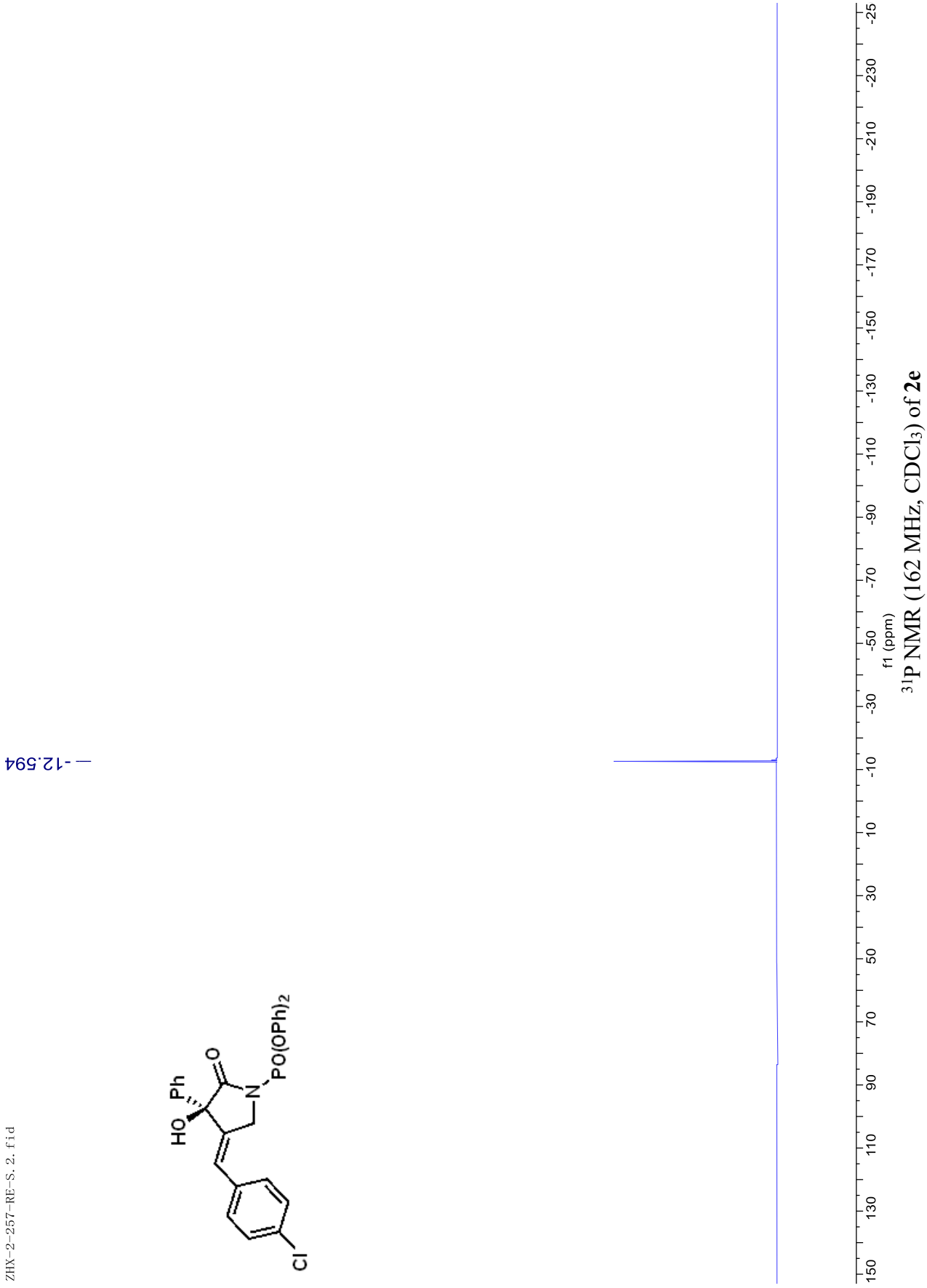
^{31}P NMR (162 MHz, $CDCl_3$) of **2d**



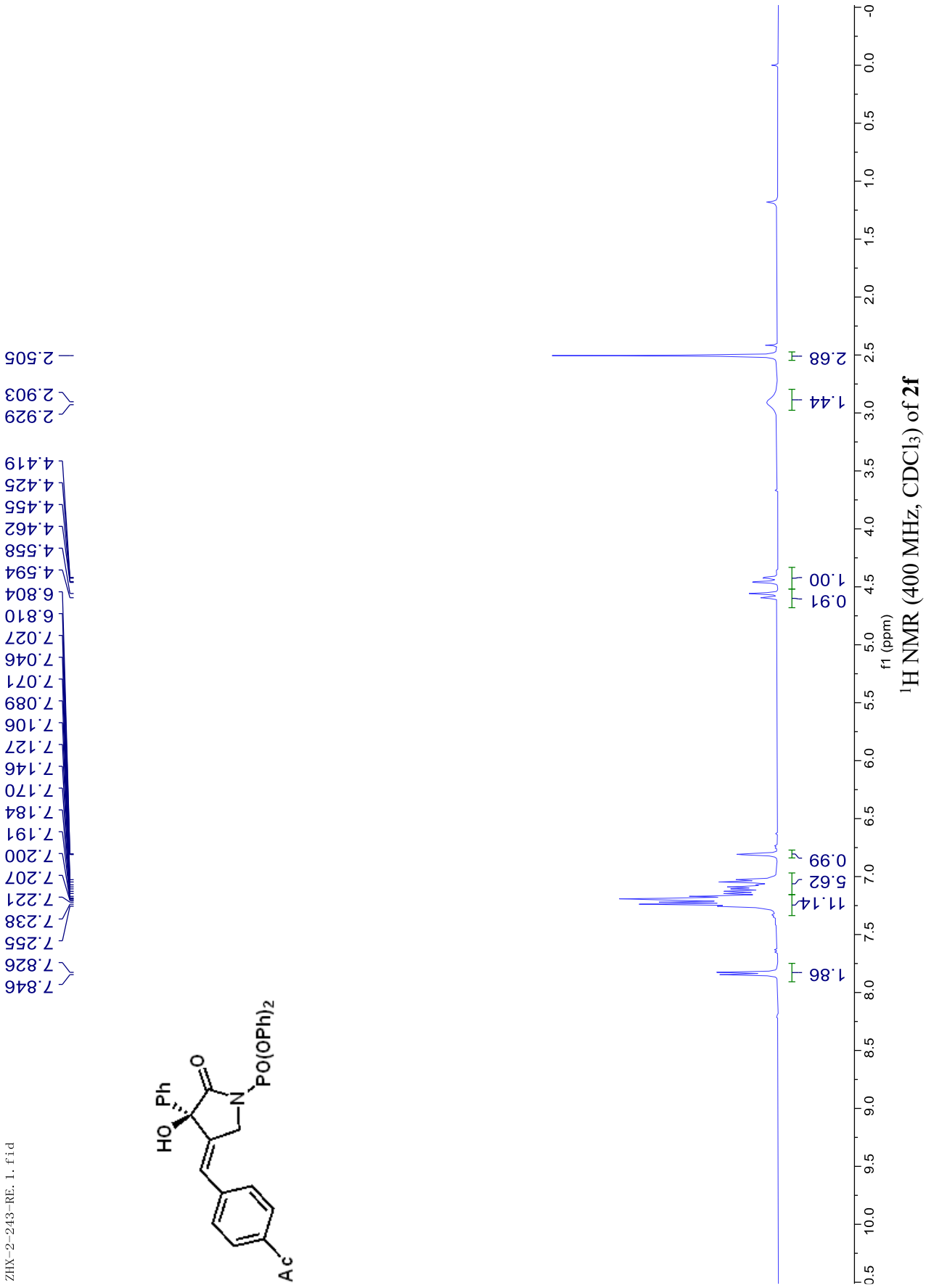
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



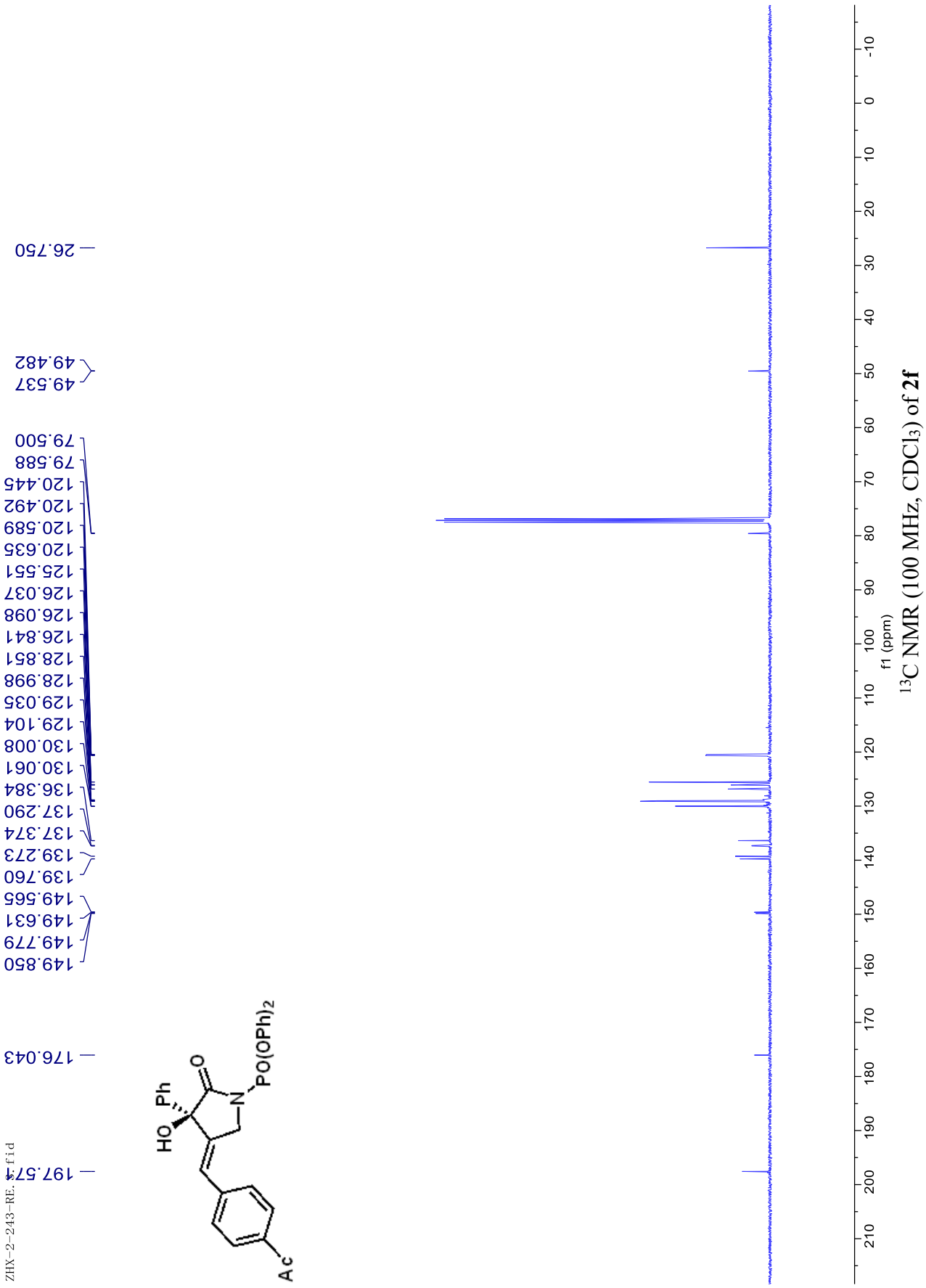
^{13}C NMR (100 MHz, $CDCl_3$) of **2e**



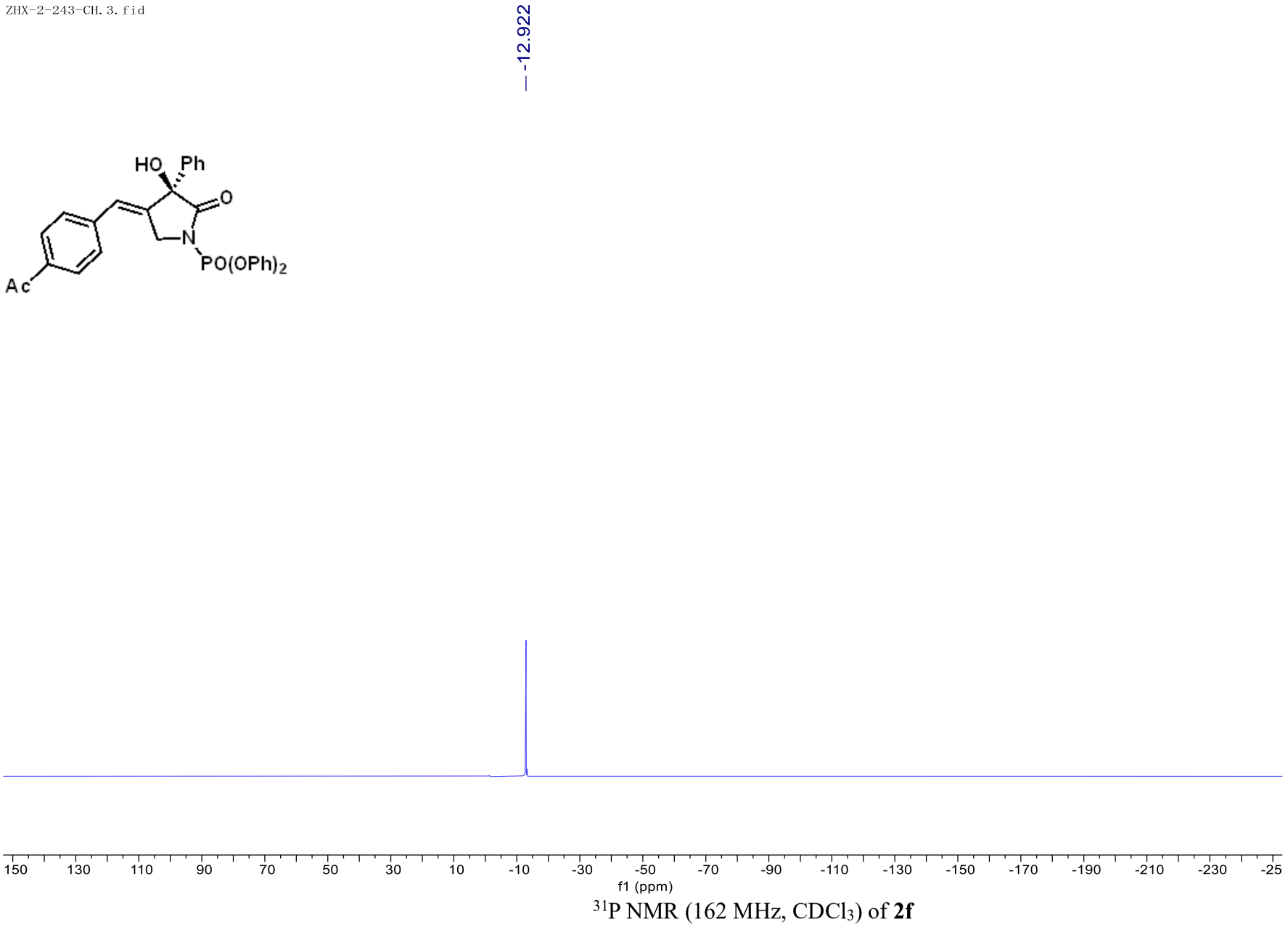
^{31}P NMR (162 MHz, $CDCl_3$) of **2e**



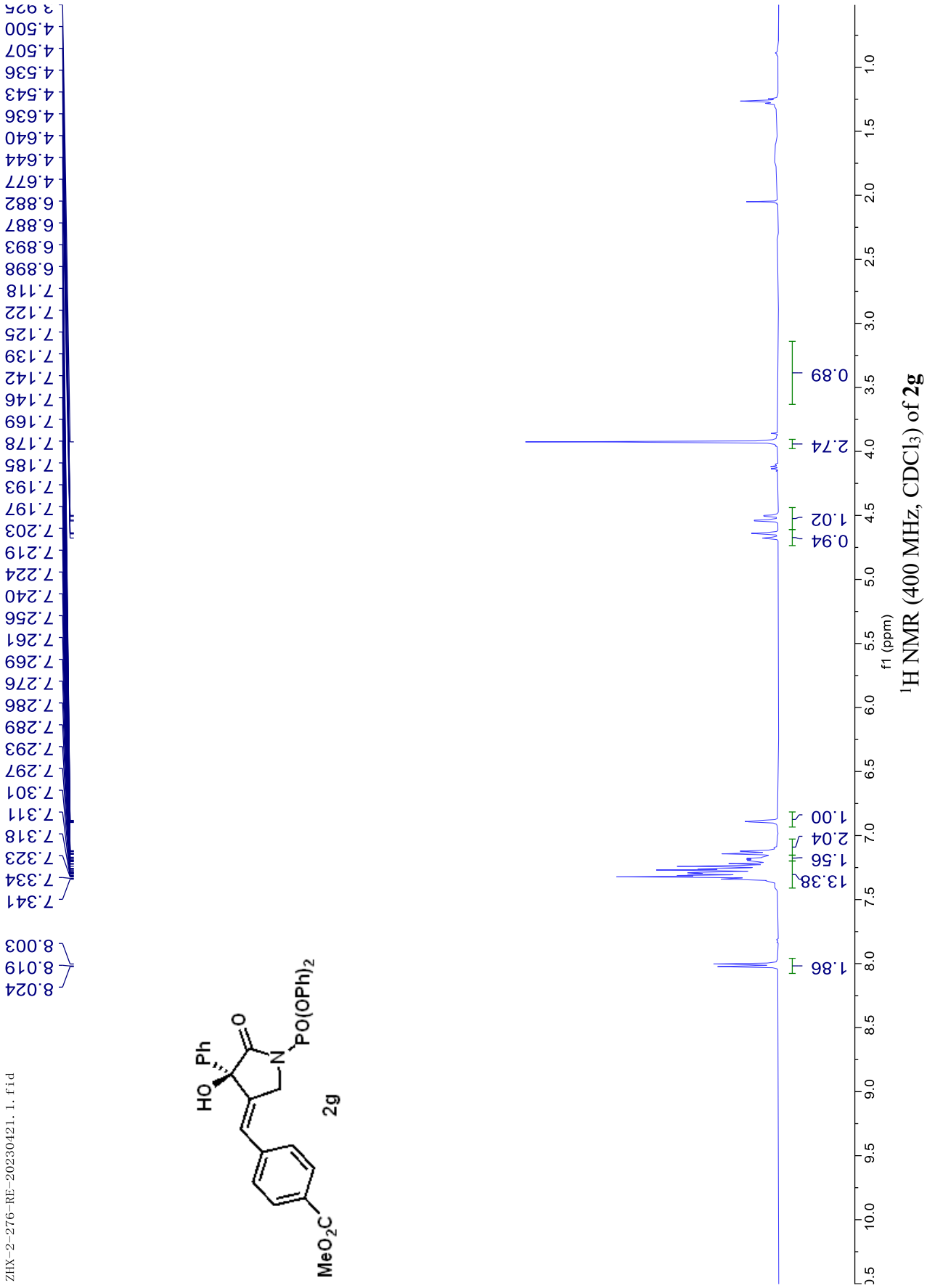
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



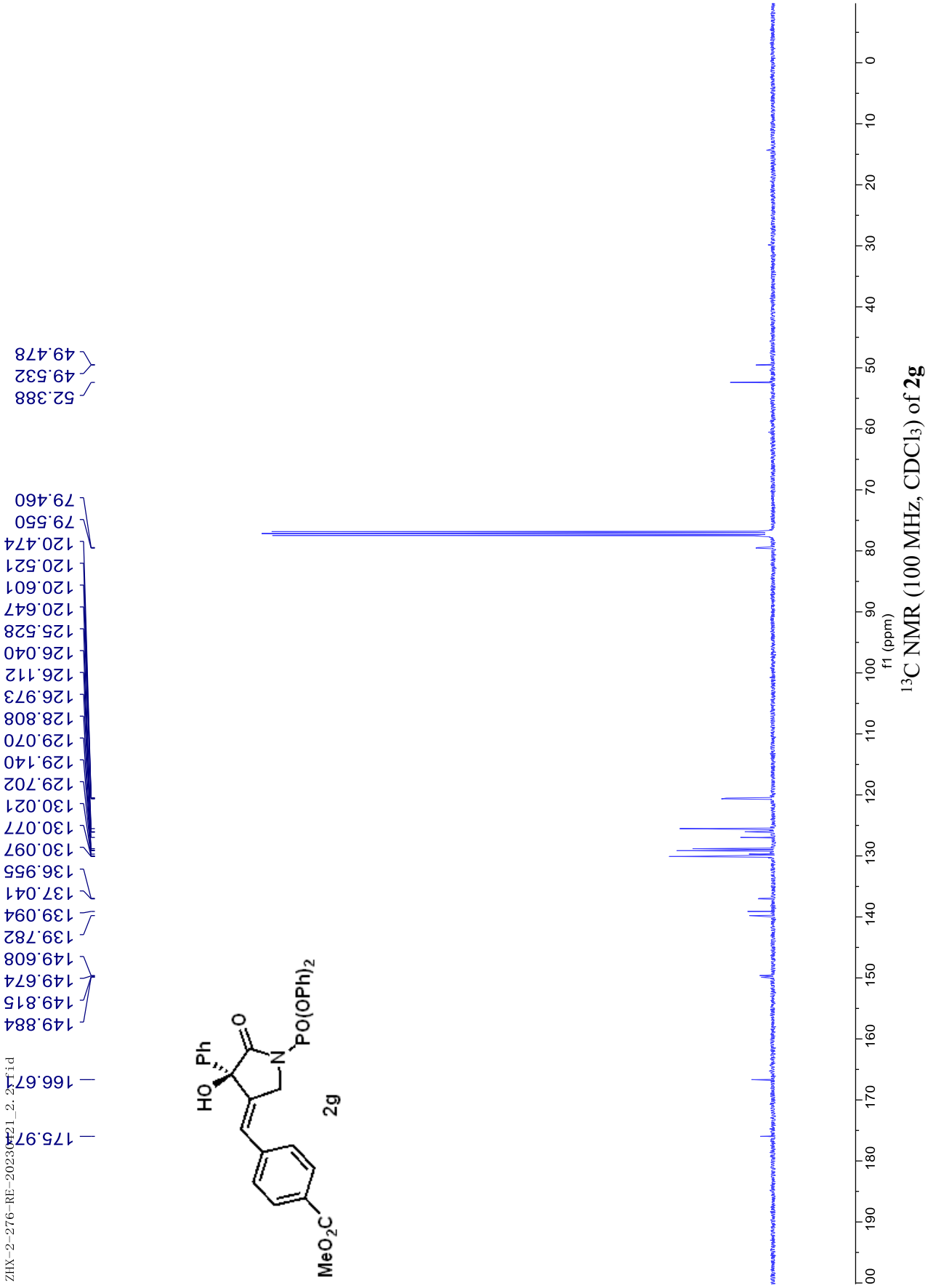
^{13}C NMR (100 MHz, $CDCl_3$) of **2f**



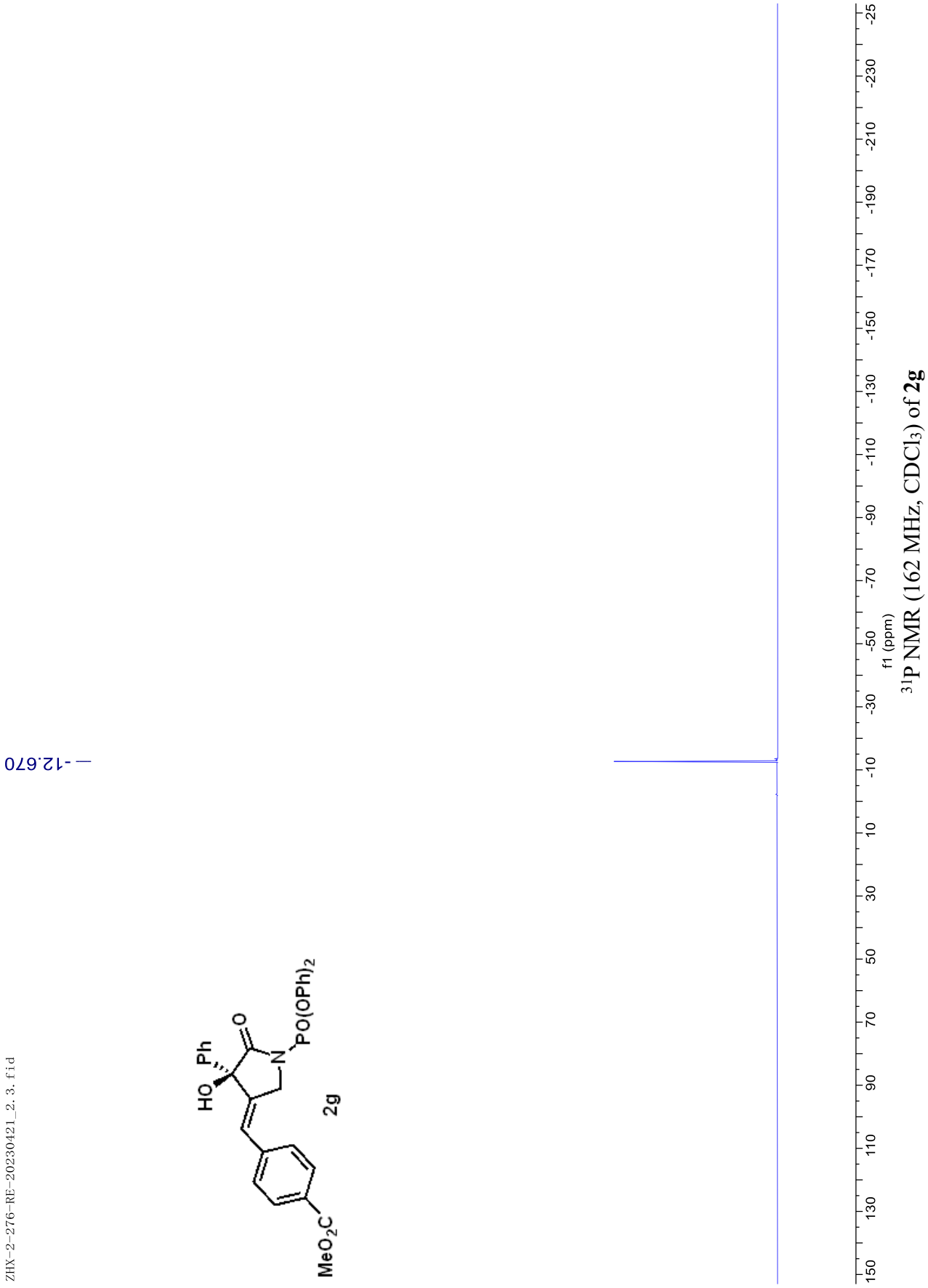
^{31}P NMR (162 MHz, $CDCl_3$) of **2f**



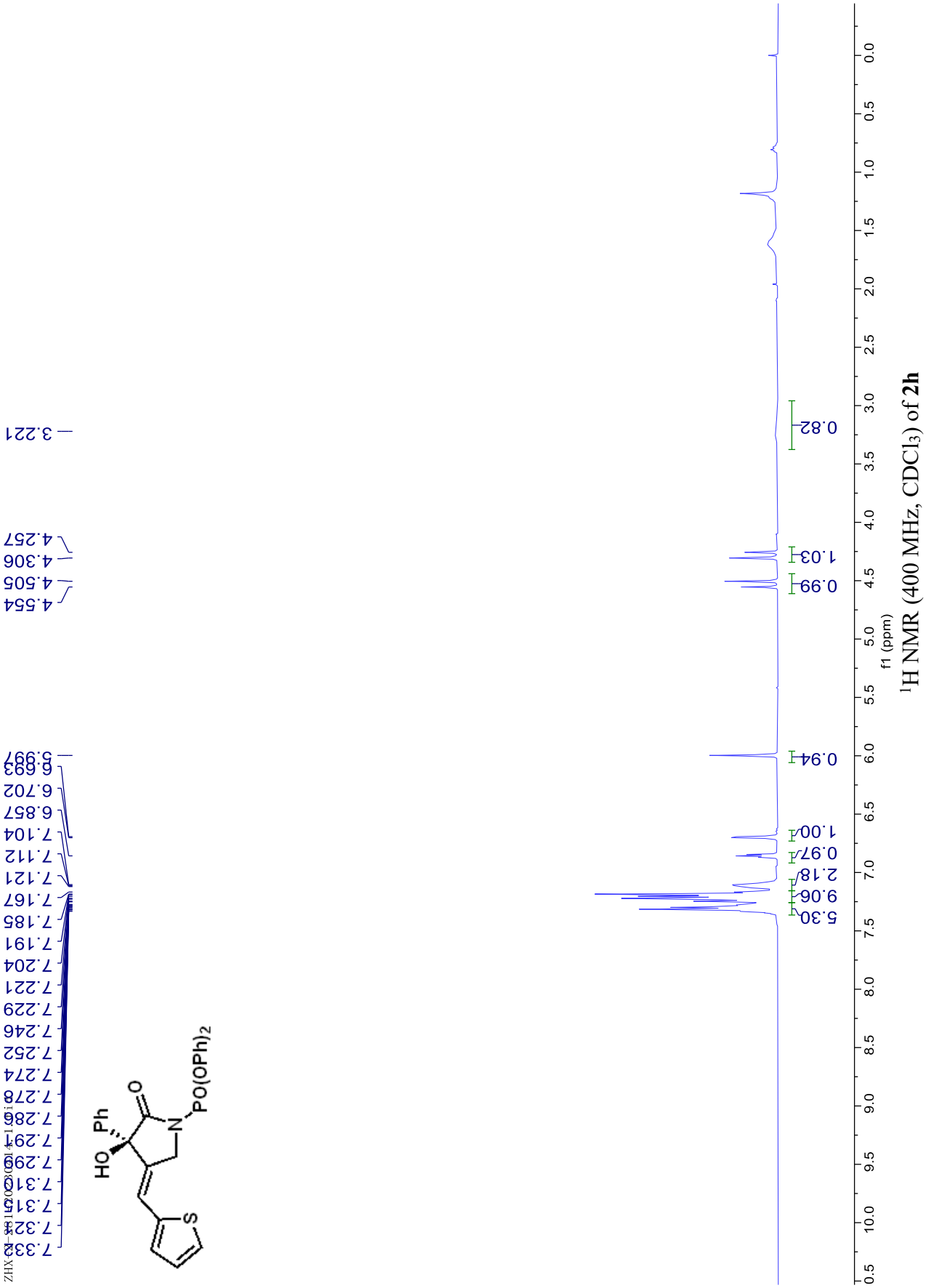
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**

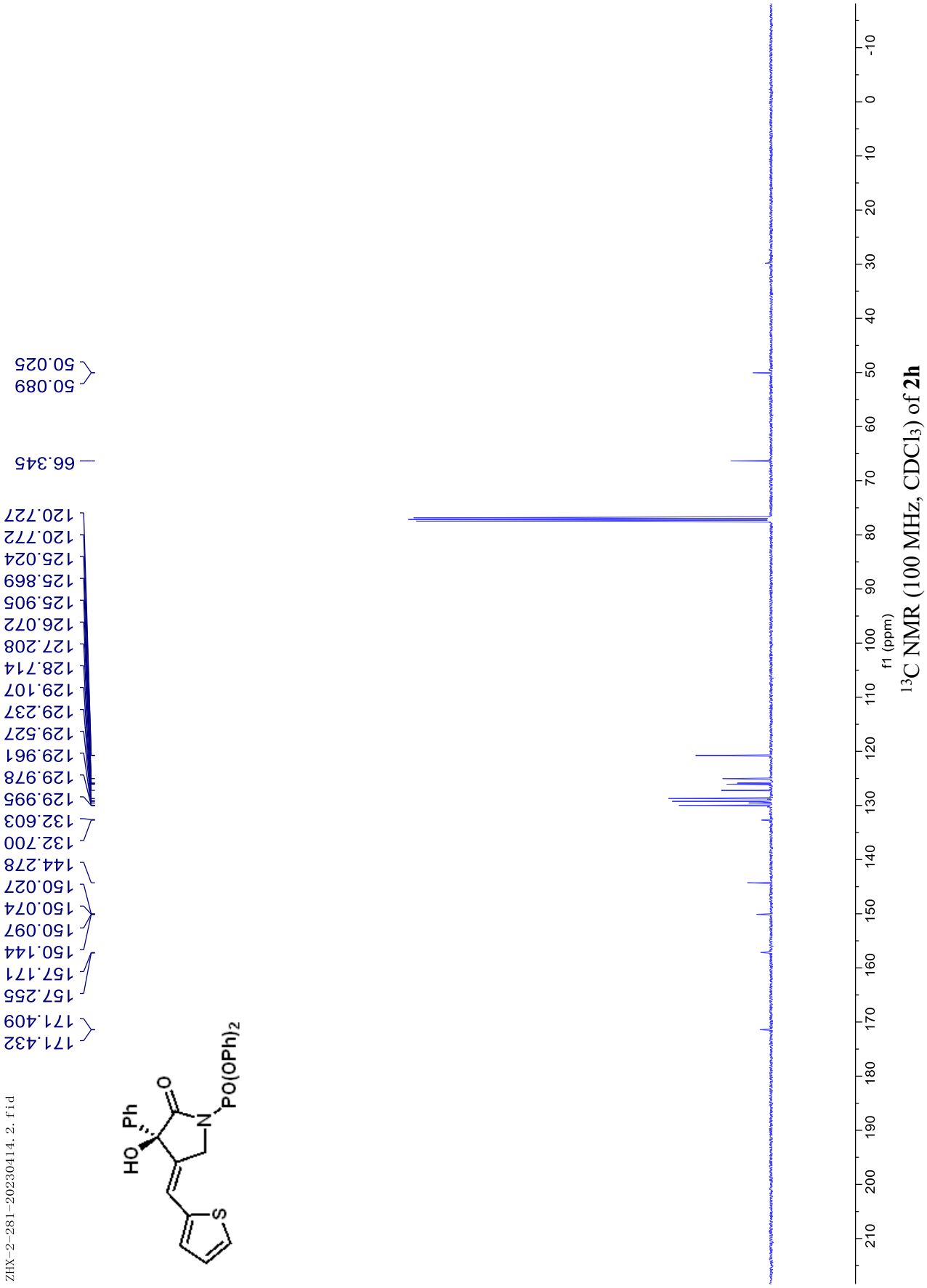


^{13}C NMR (100 MHz, $CDCl_3$) of **2g**

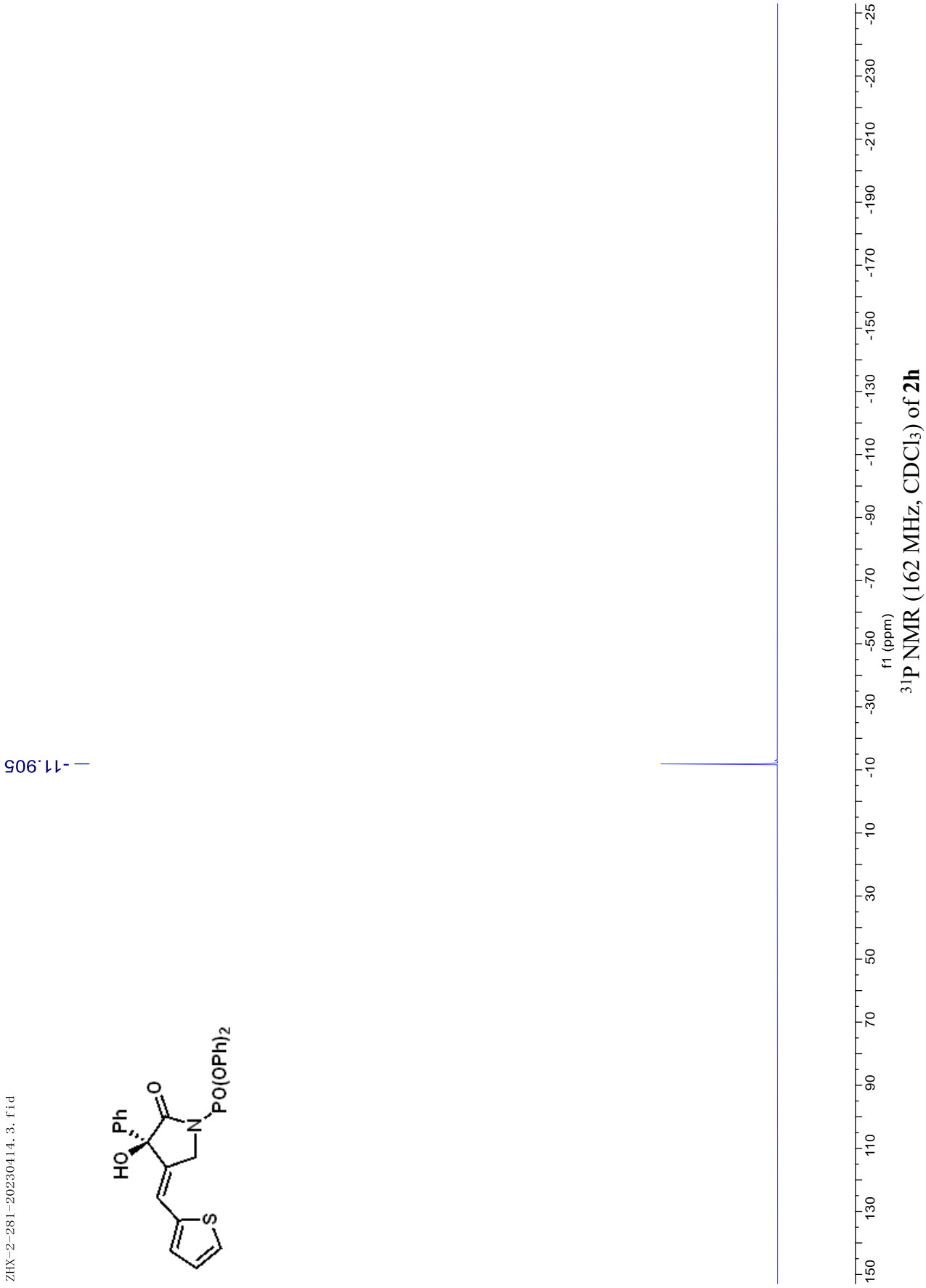


^{31}P NMR (162 MHz, $CDCl_3$) of **2g**

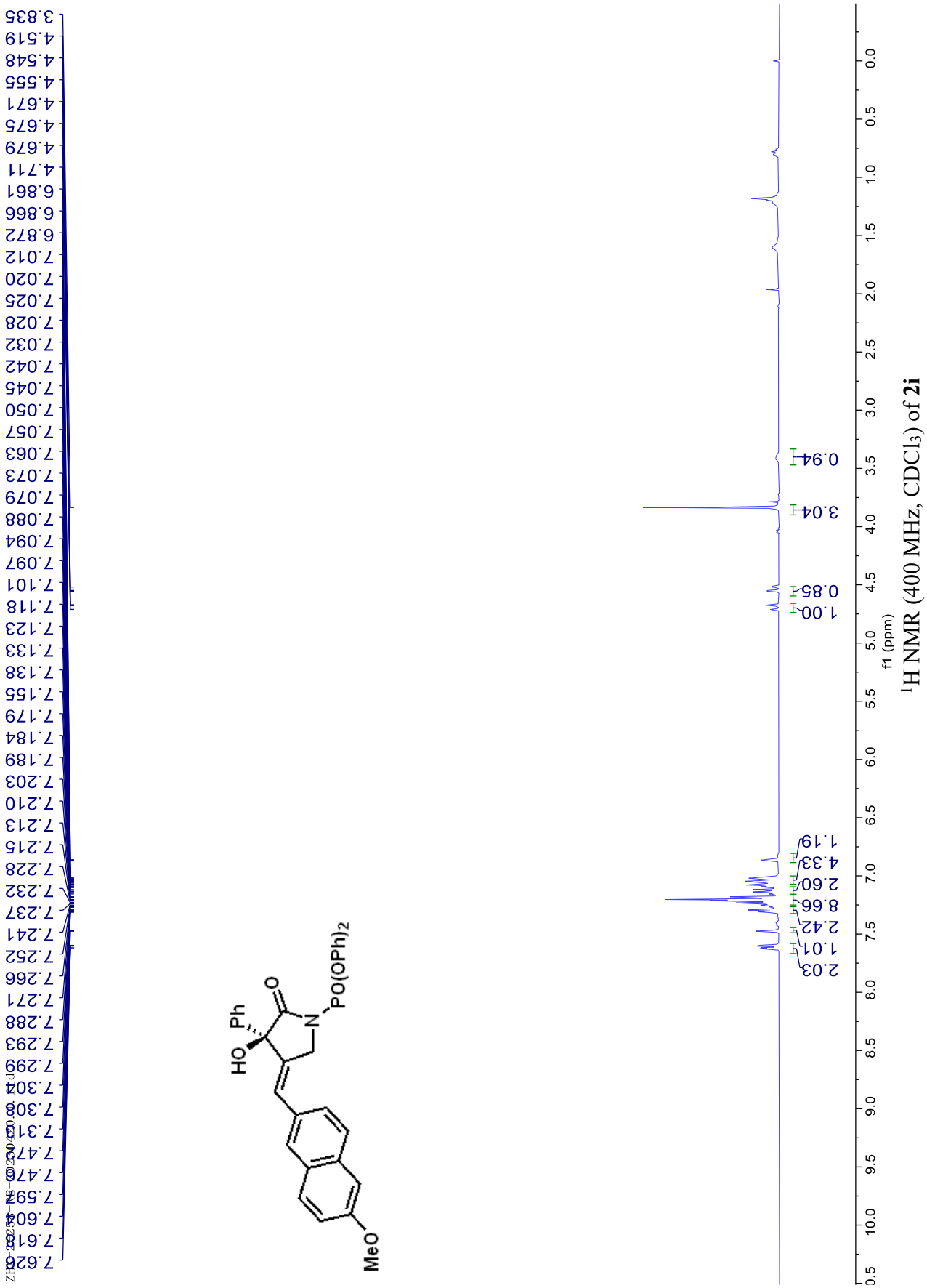

^{1}H NMR (400 MHz, CDCl$_3$) of **2h**
f1 (ppm)
HO
Ph
O
N
PO(OPh)$_2$
S



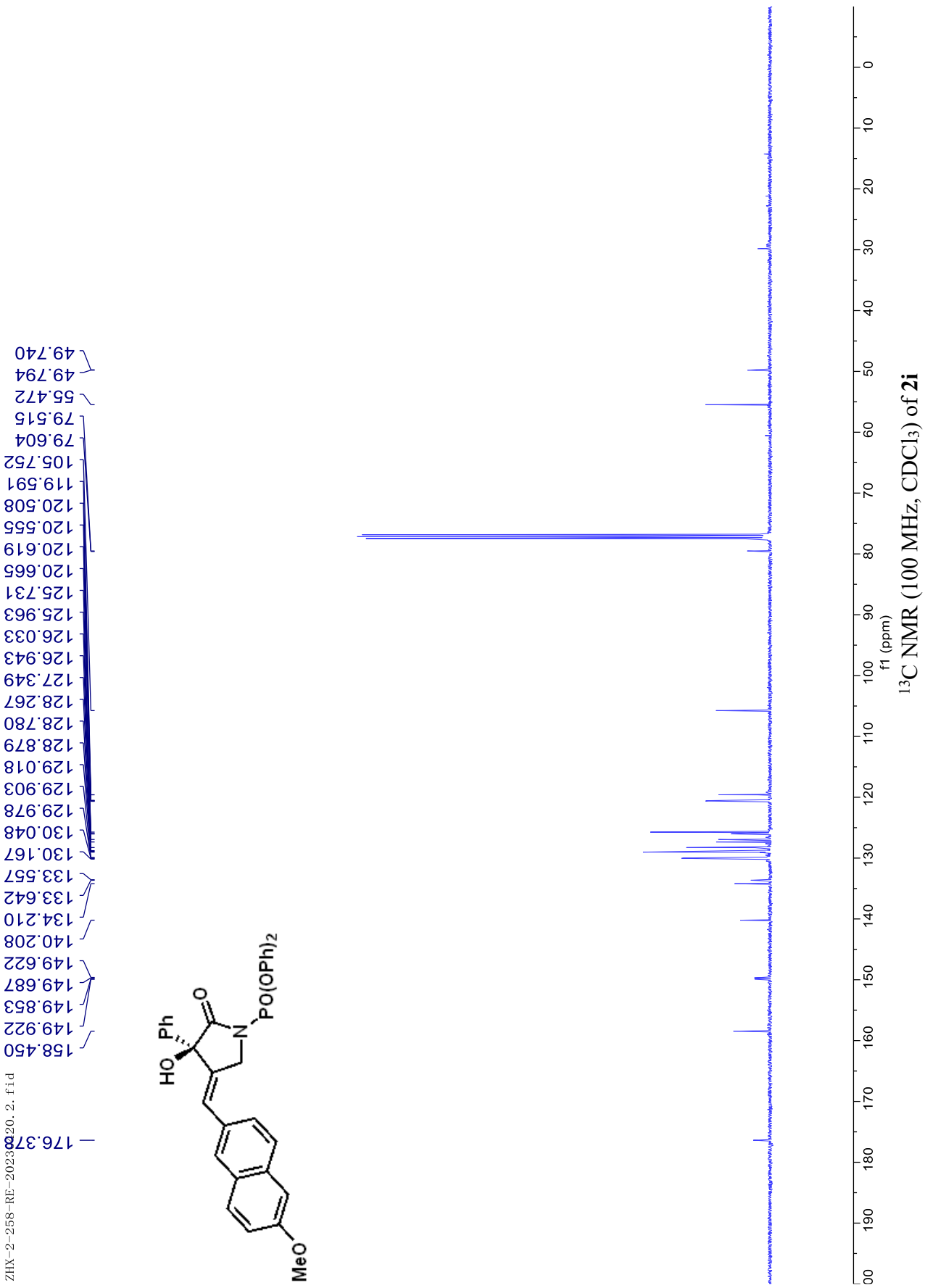
^{13}C NMR (100 MHz, $CDCl_3$) of **2h**



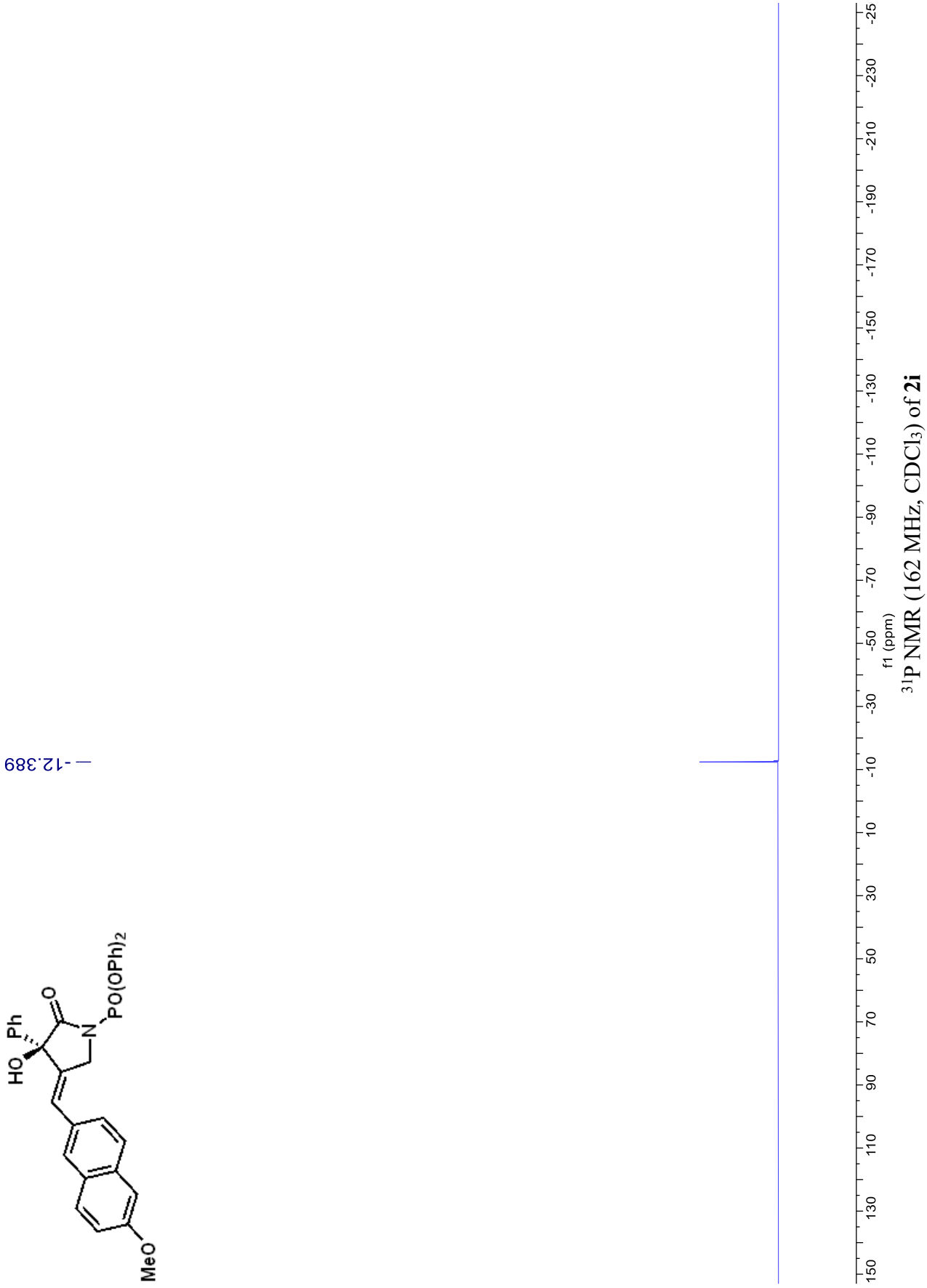
^{31}P NMR (162 MHz, $CDCl_3$) of **2h**



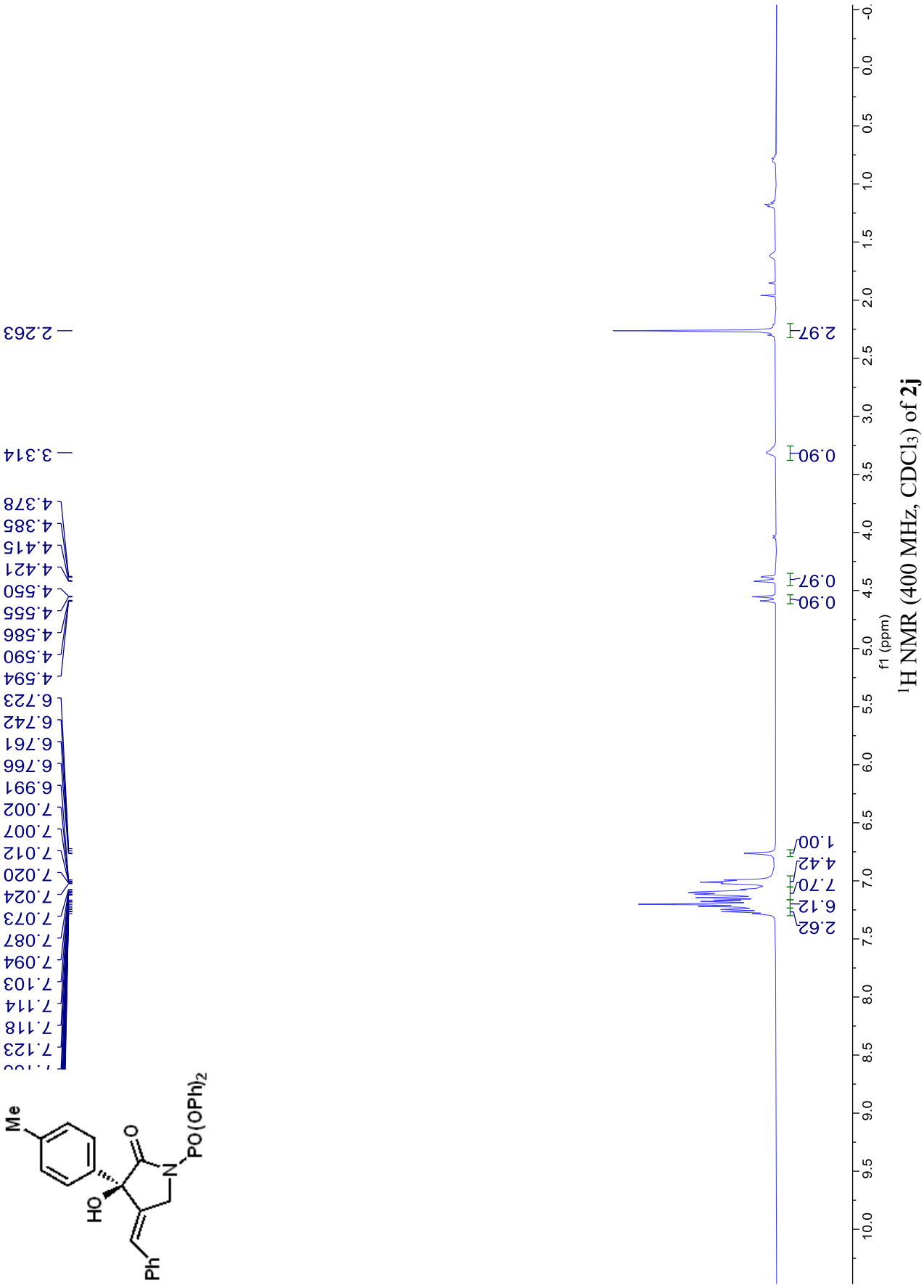
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



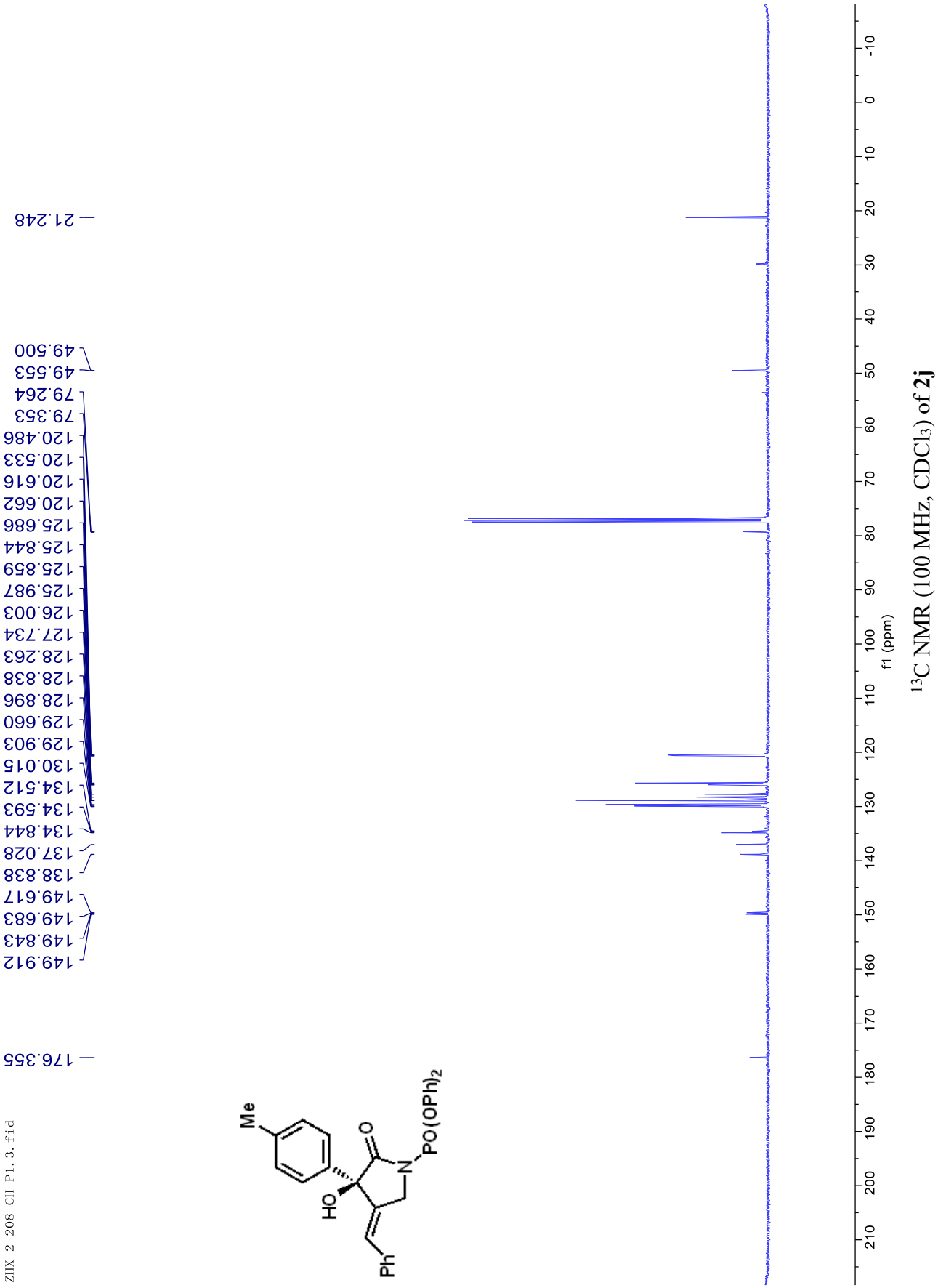
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



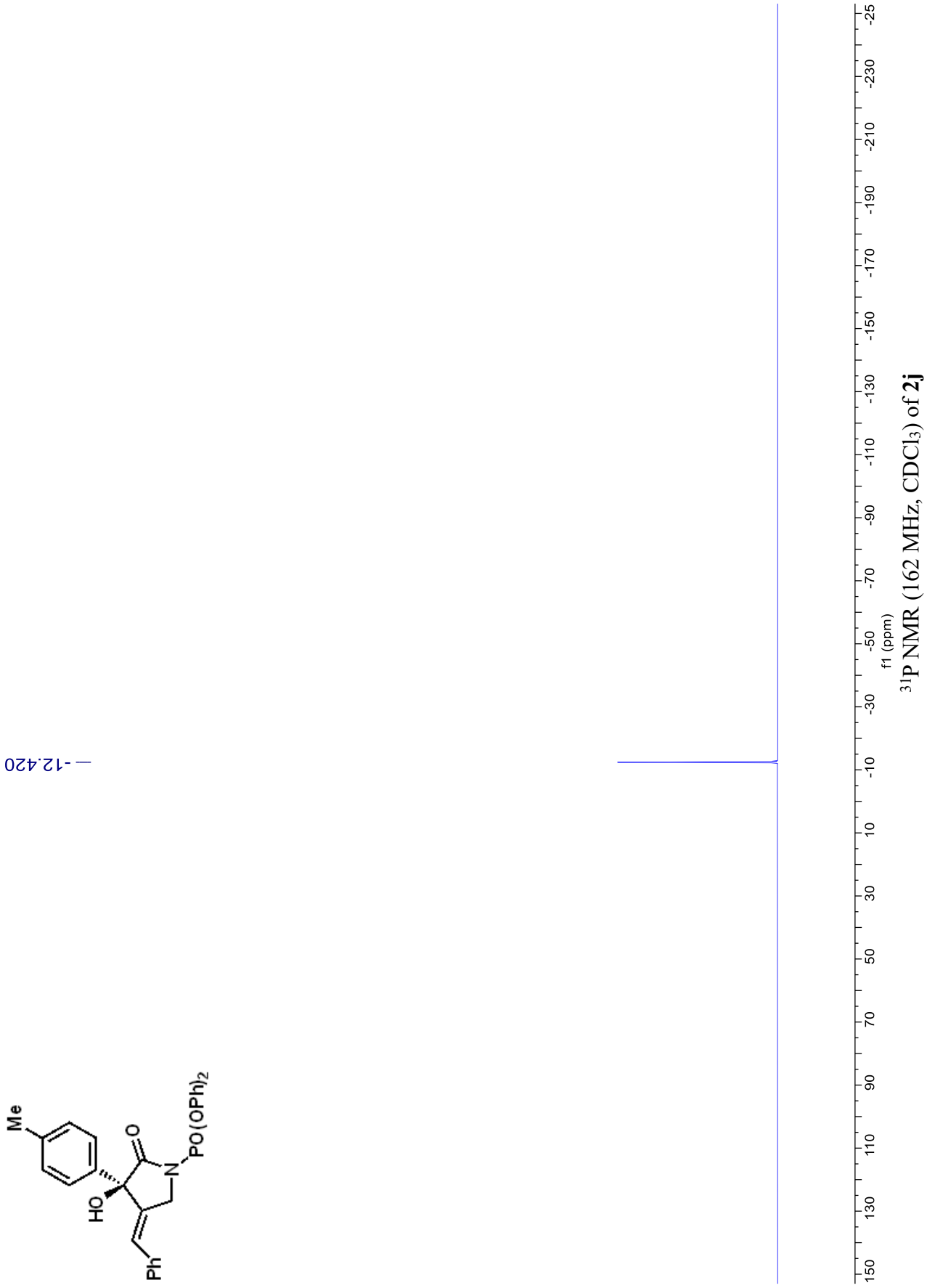
^{31}P NMR (162 MHz, $CDCl_3$) of **2i**



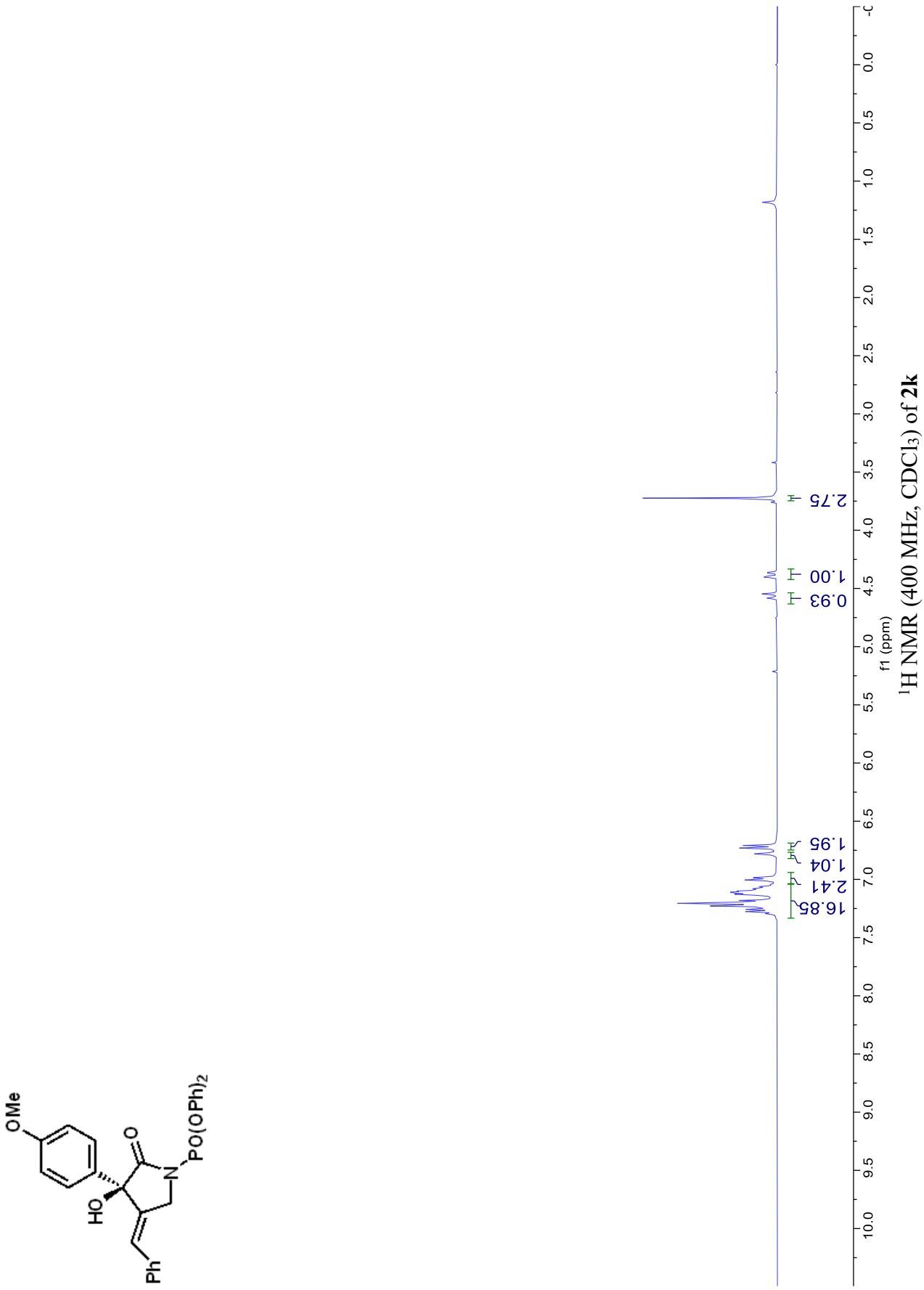
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



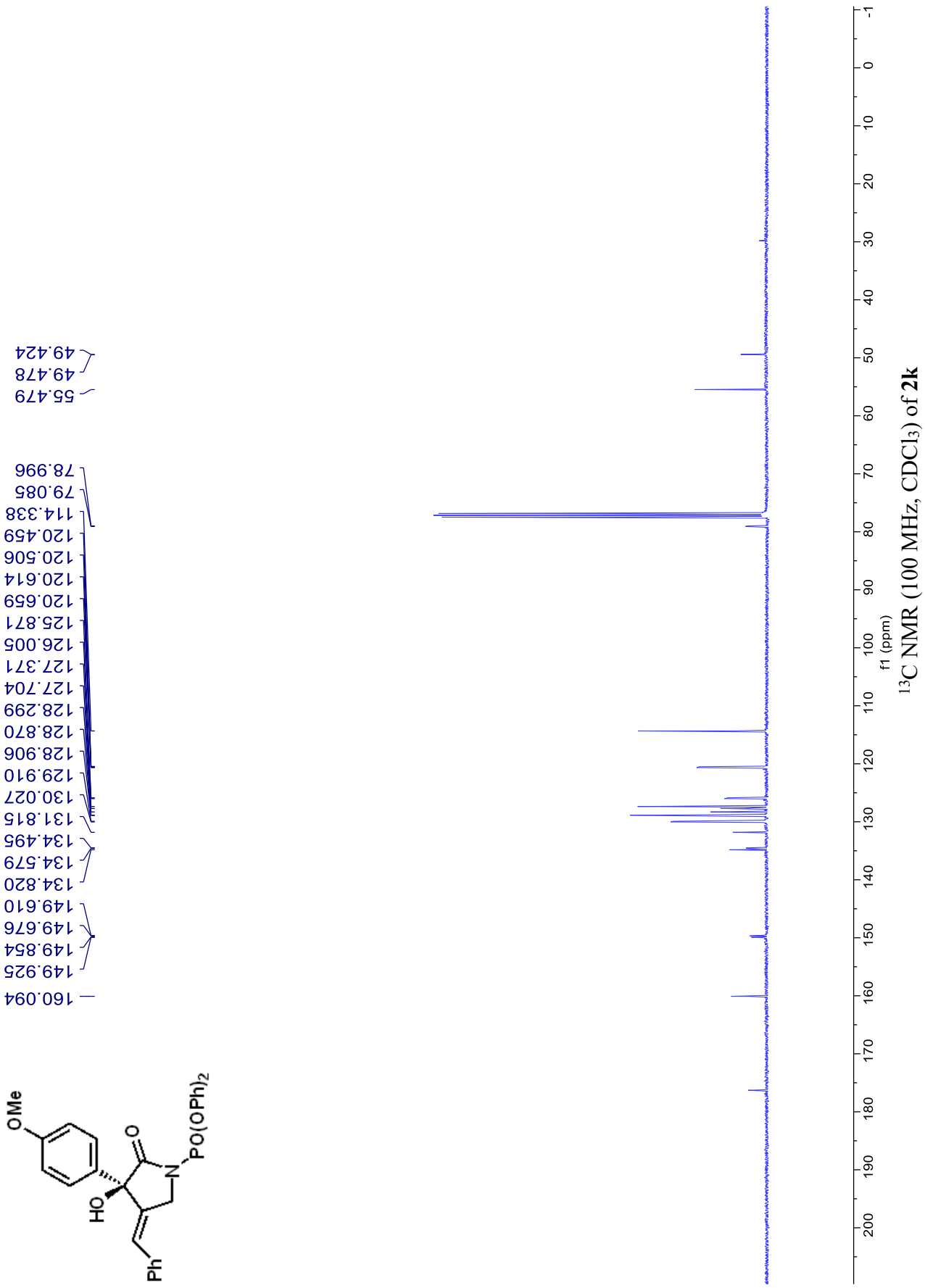
^{13}C NMR (100 MHz, $CDCl_3$) of **2j**



^{31}P NMR (162 MHz, $CDCl_3$) of **2j**

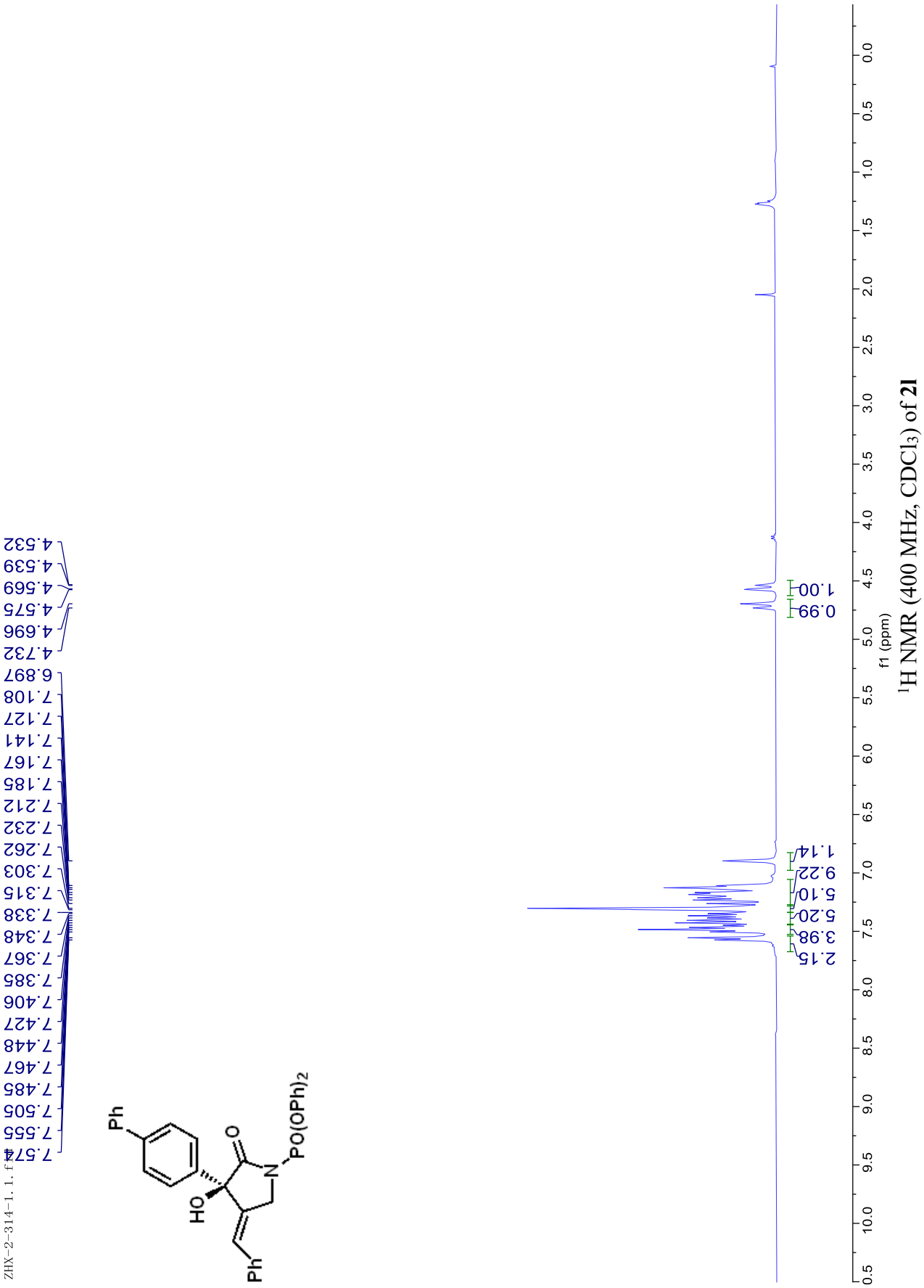


^{1}H NMR (400 MHz, $CDCl_3$) of **2k**

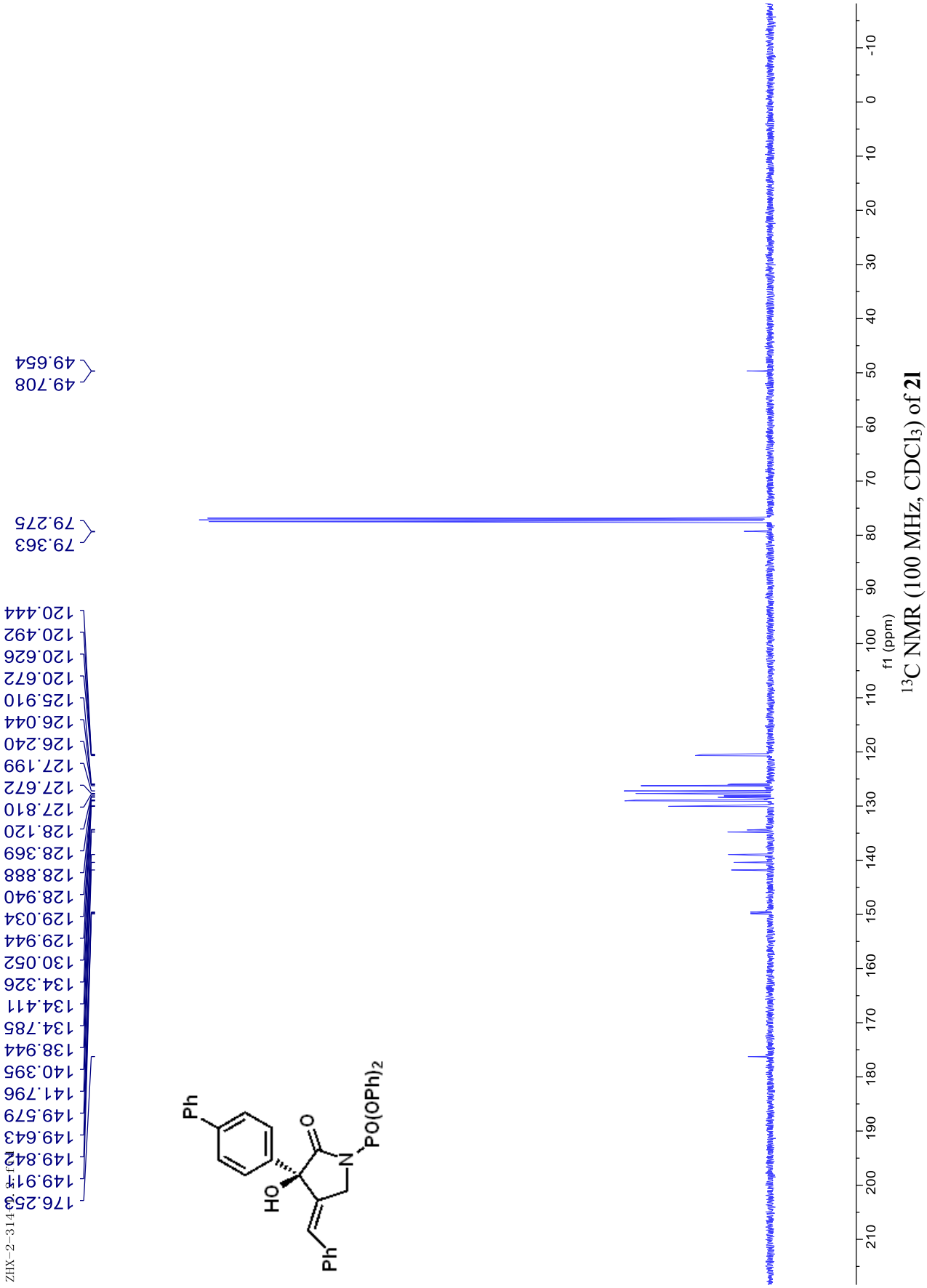


^{13}C NMR (100 MHz, $CDCl_3$) of **2k**

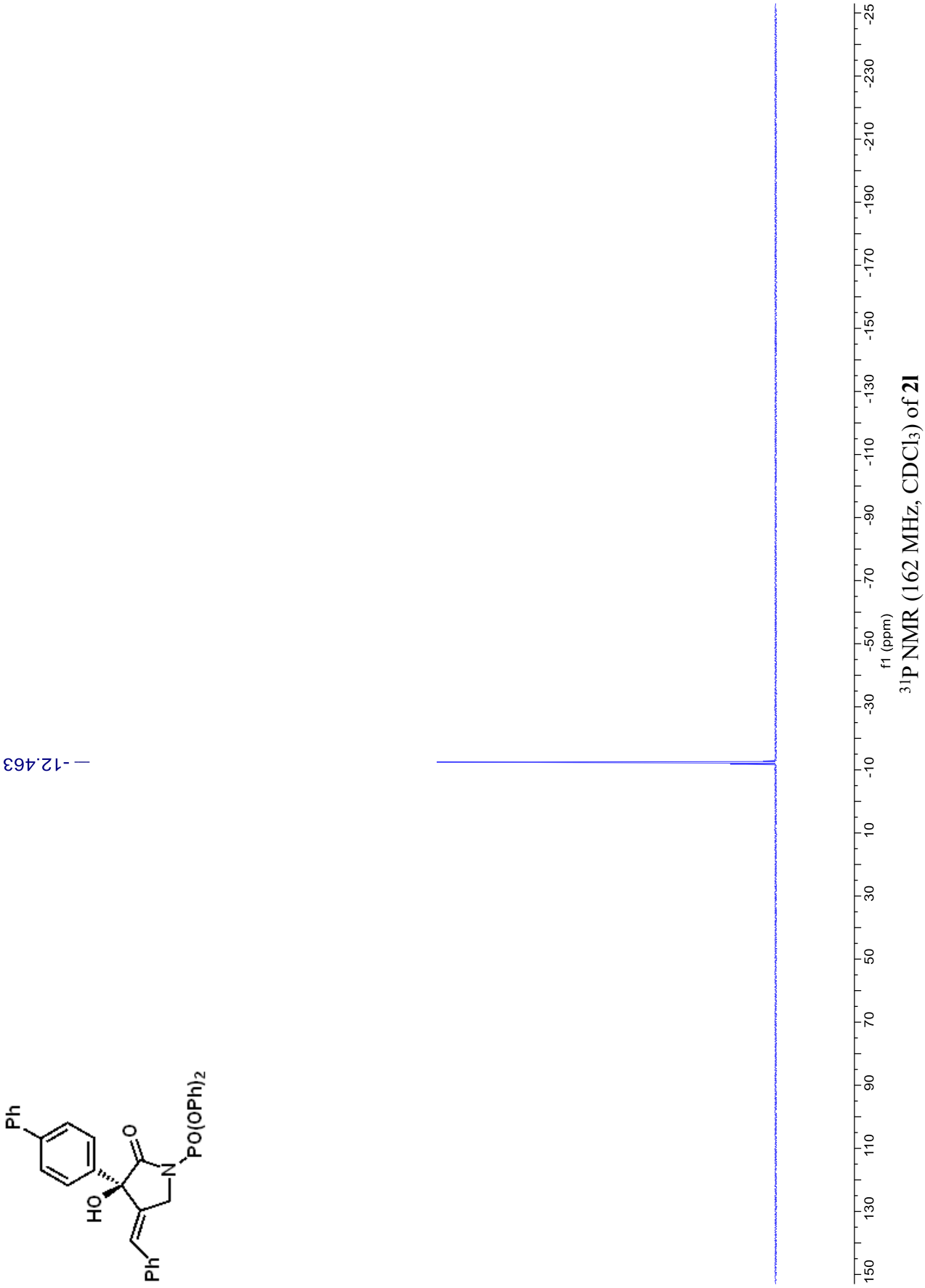
^{31}P NMR (162 MHz, $CDCl_3$) of **2k**



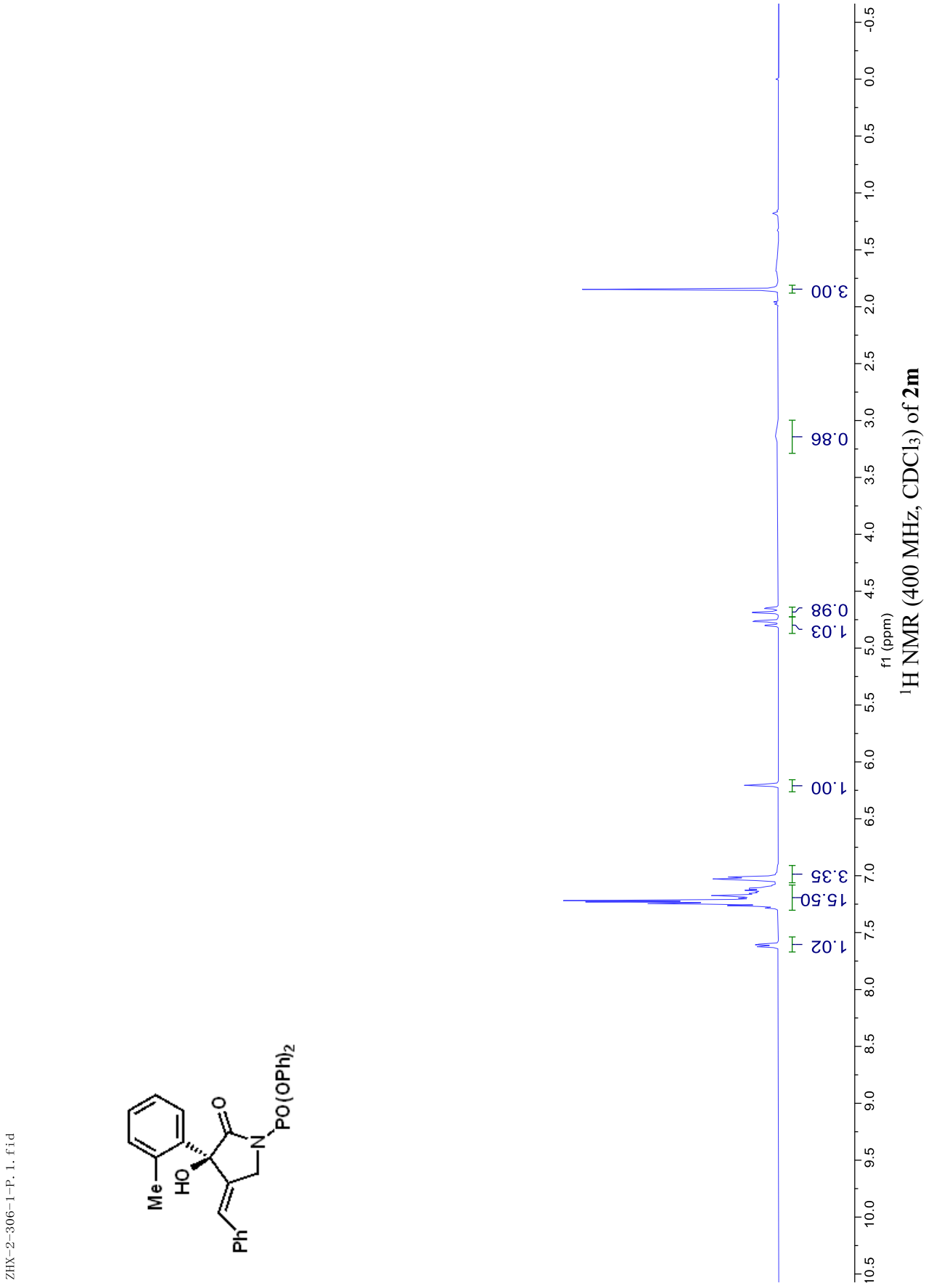
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



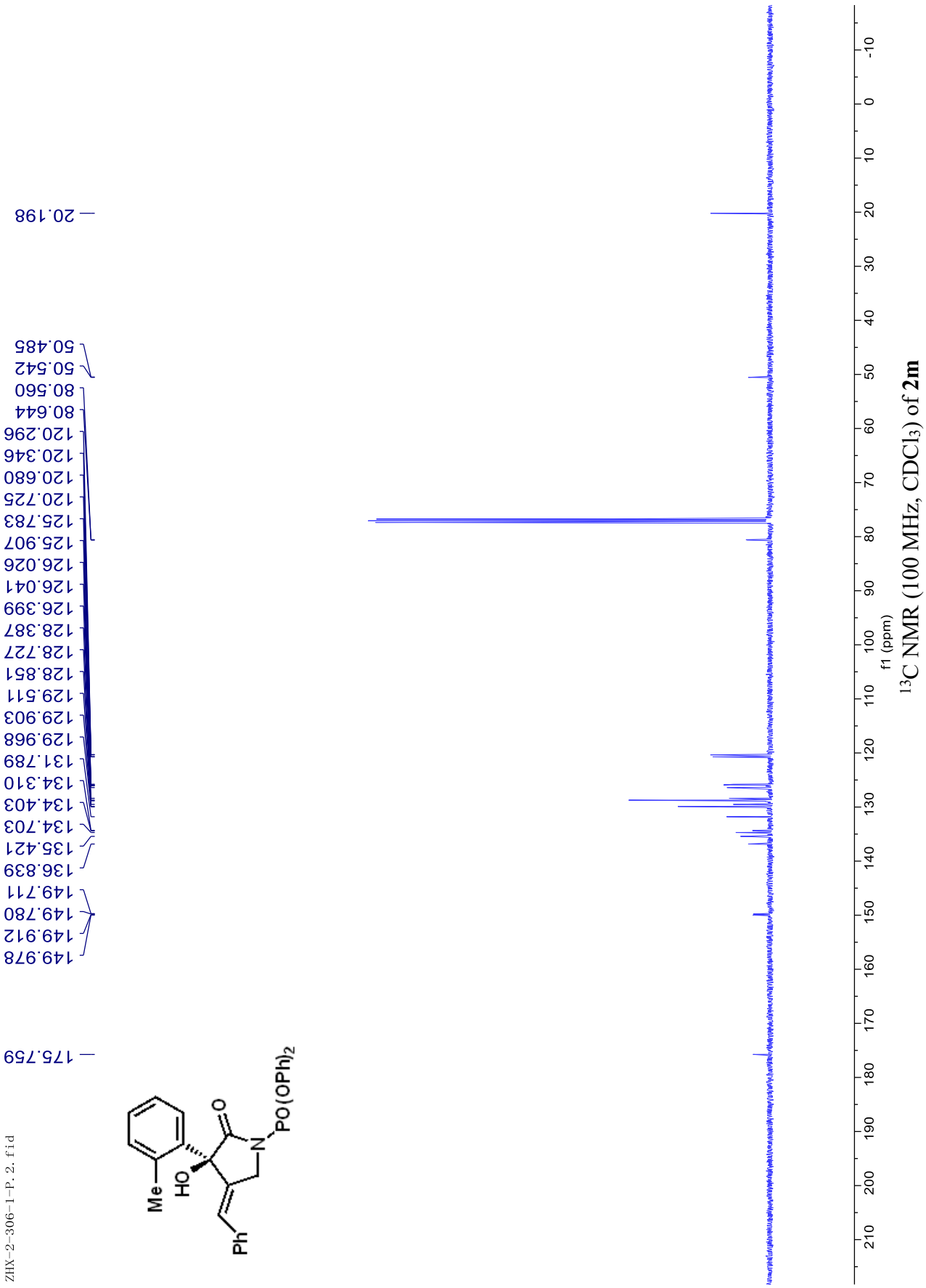
^{13}C NMR (100 MHz, $CDCl_3$) of **21**



^{31}P NMR (162 MHz, $CDCl_3$) of **21**

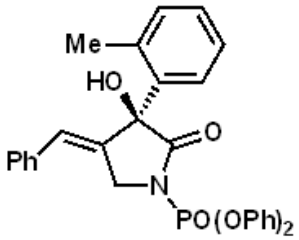


^{1}H NMR (400 MHz, $CDCl_3$) of **2m**

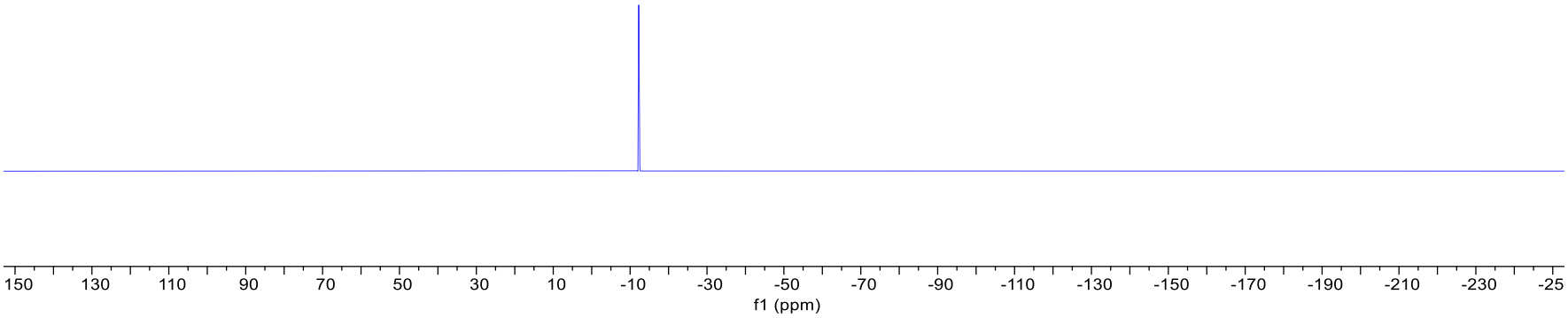


^{13}C NMR (100 MHz, $CDCl_3$) of **2m**

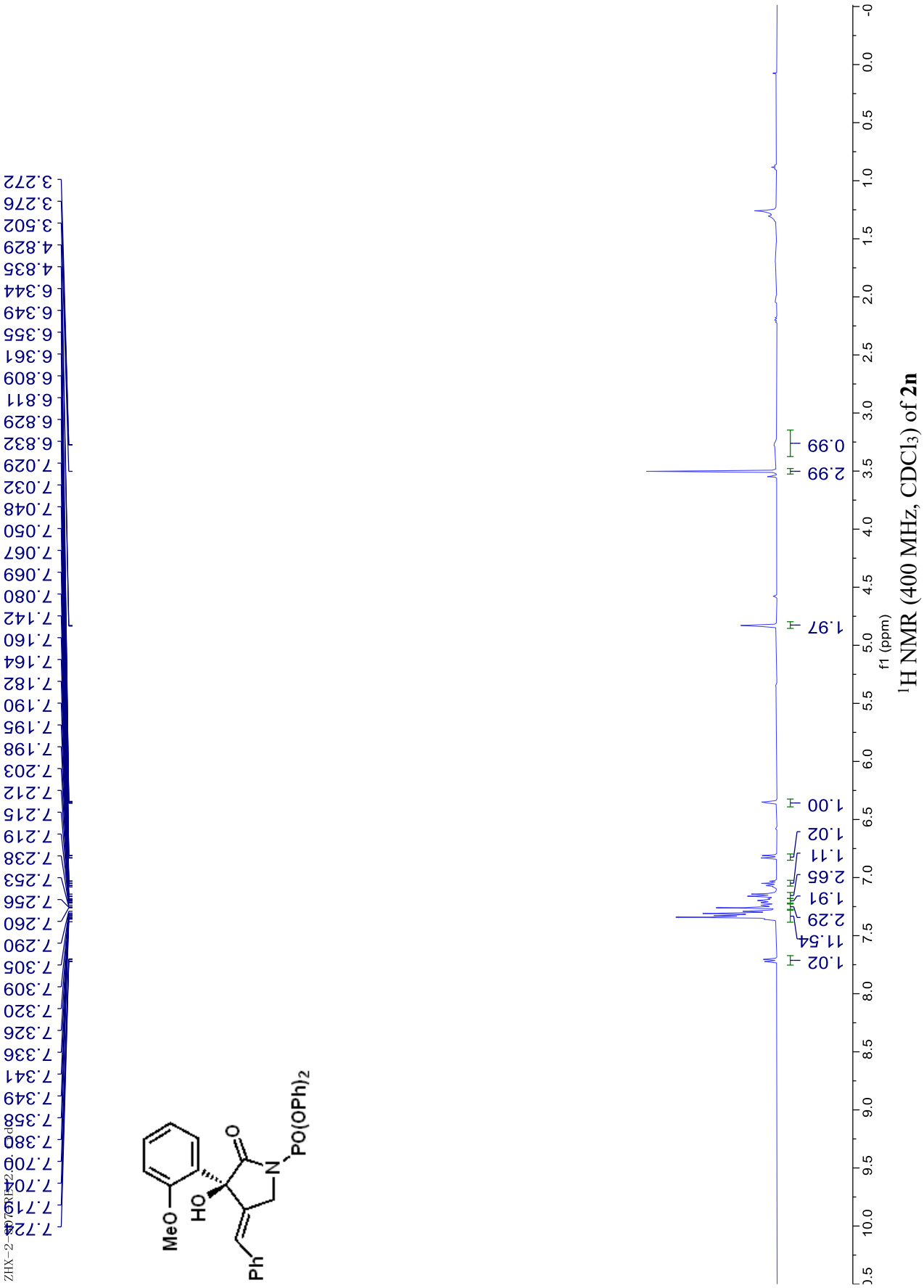
ZHX-2-306-2.1.fid



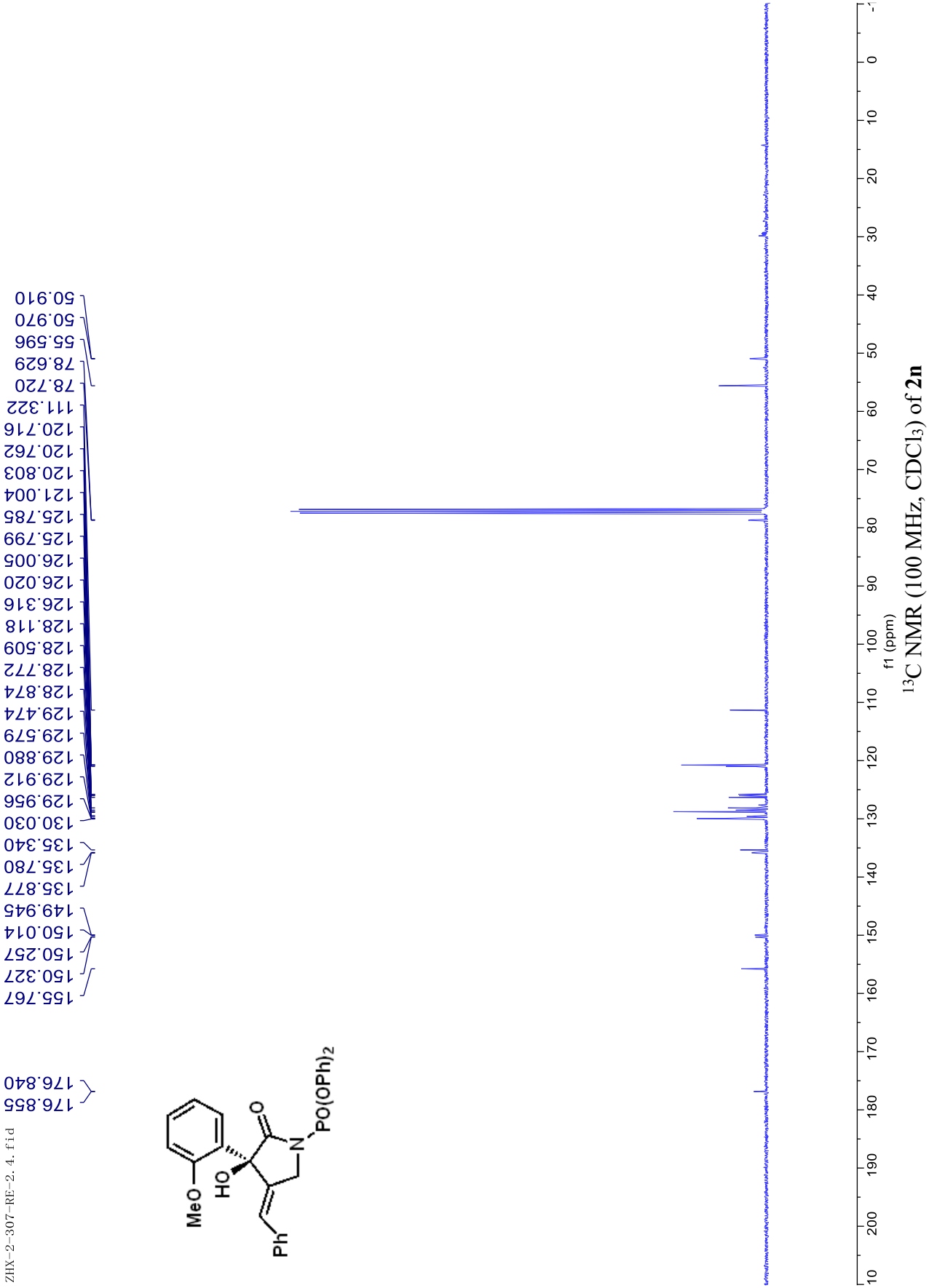
-12.225



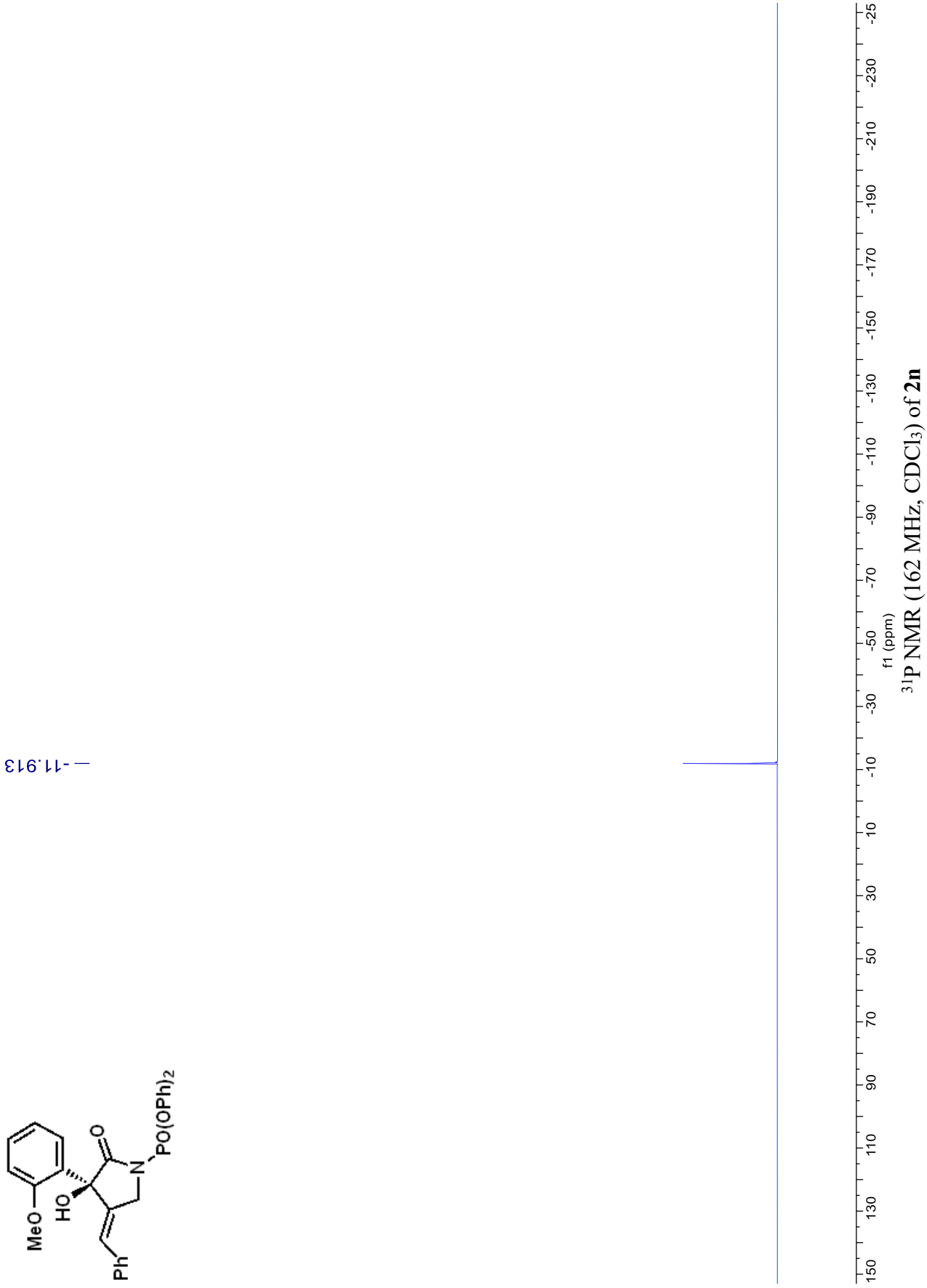
^{31}P NMR (162 MHz, $CDCl_3$) of **2m**



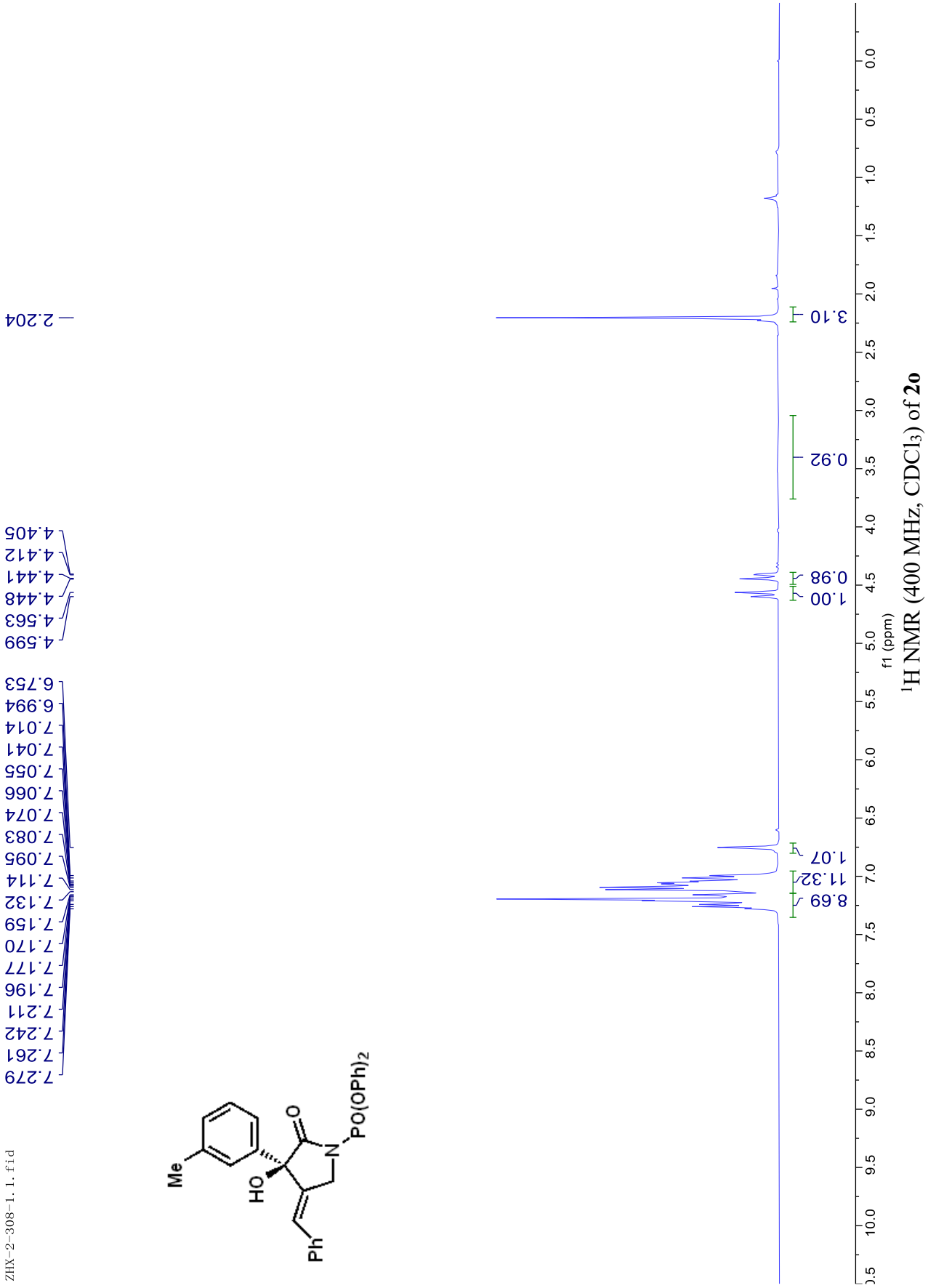
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



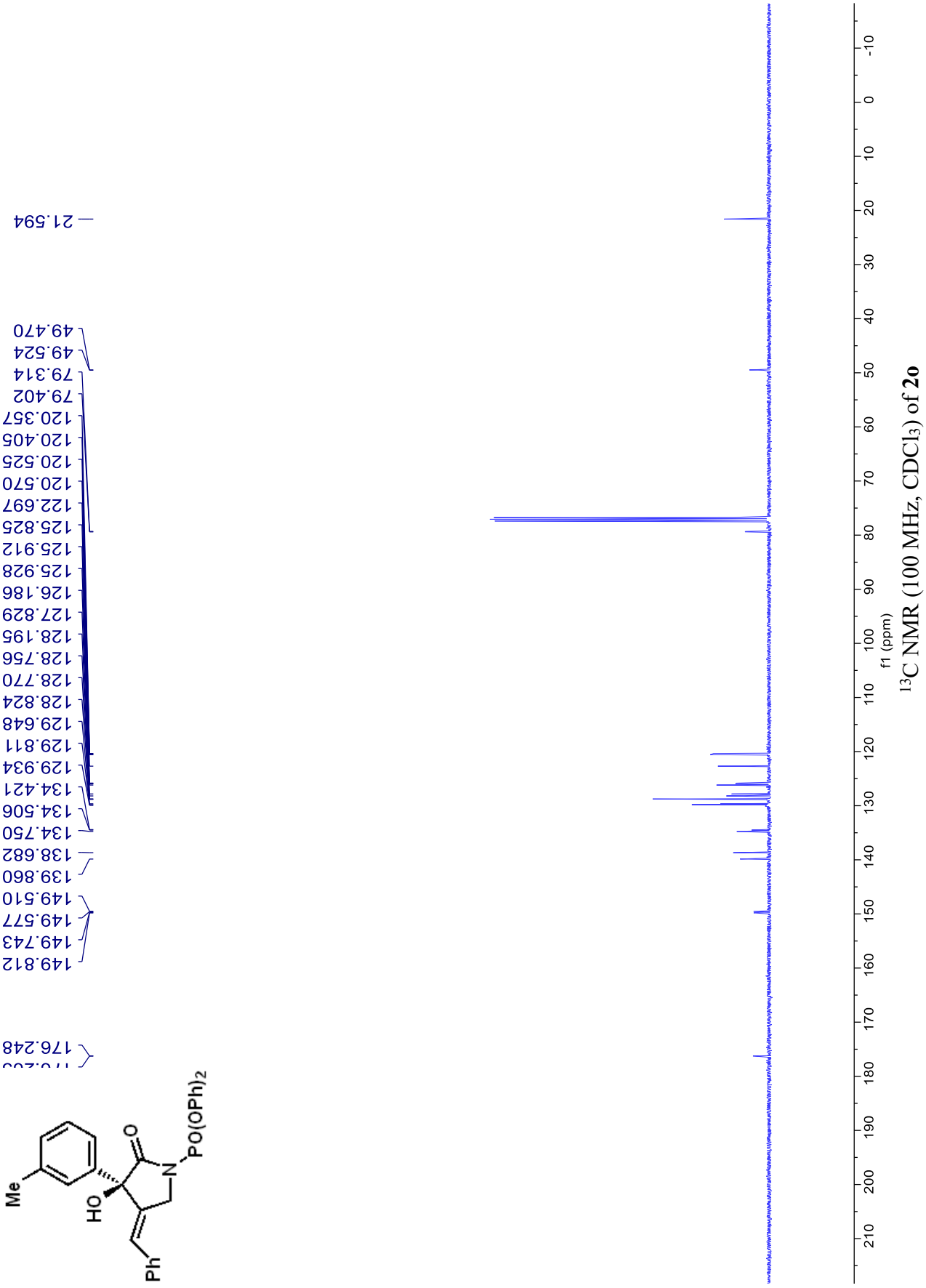
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



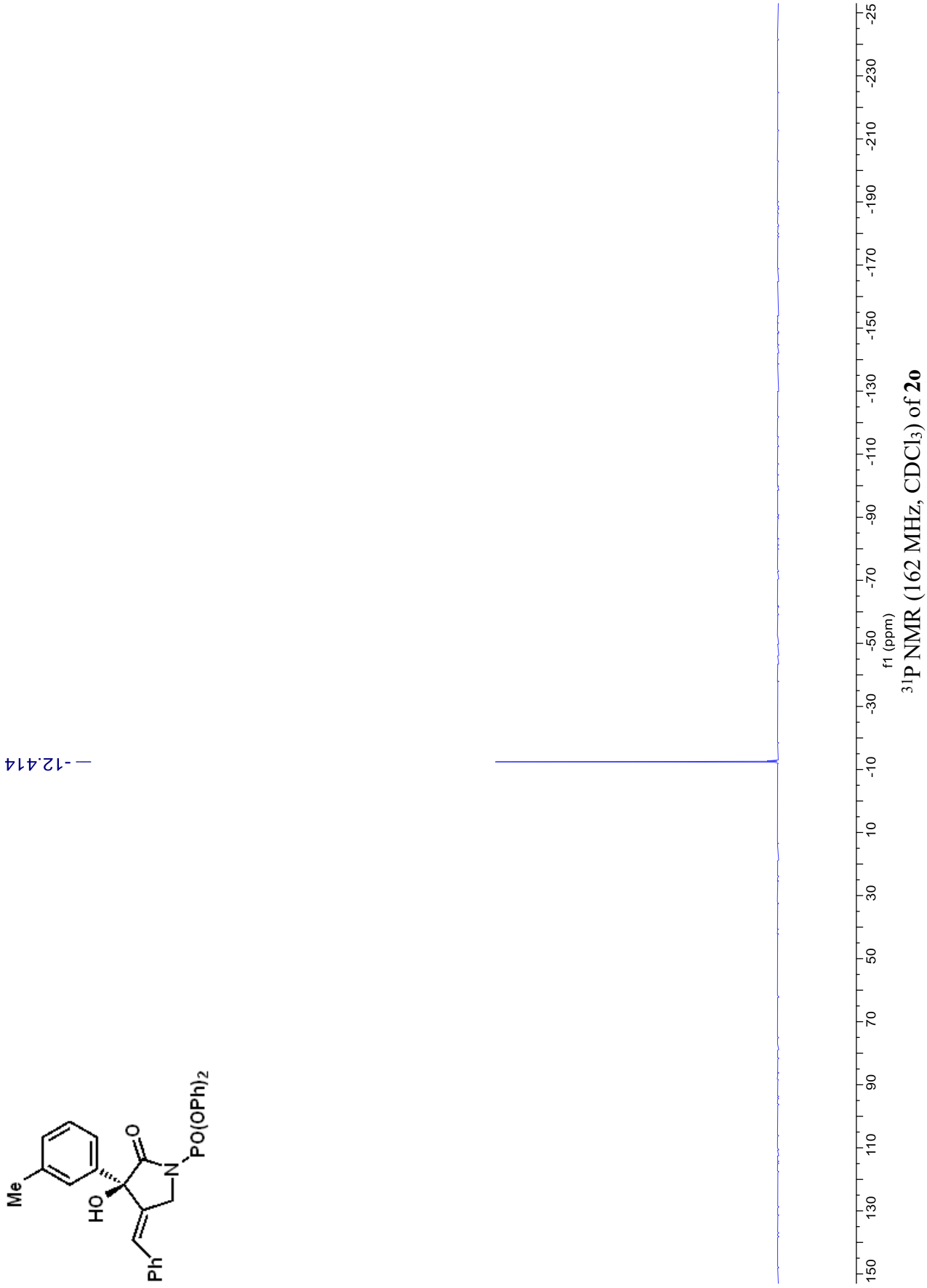
^{31}P NMR (162 MHz, $CDCl_3$) of **2n**



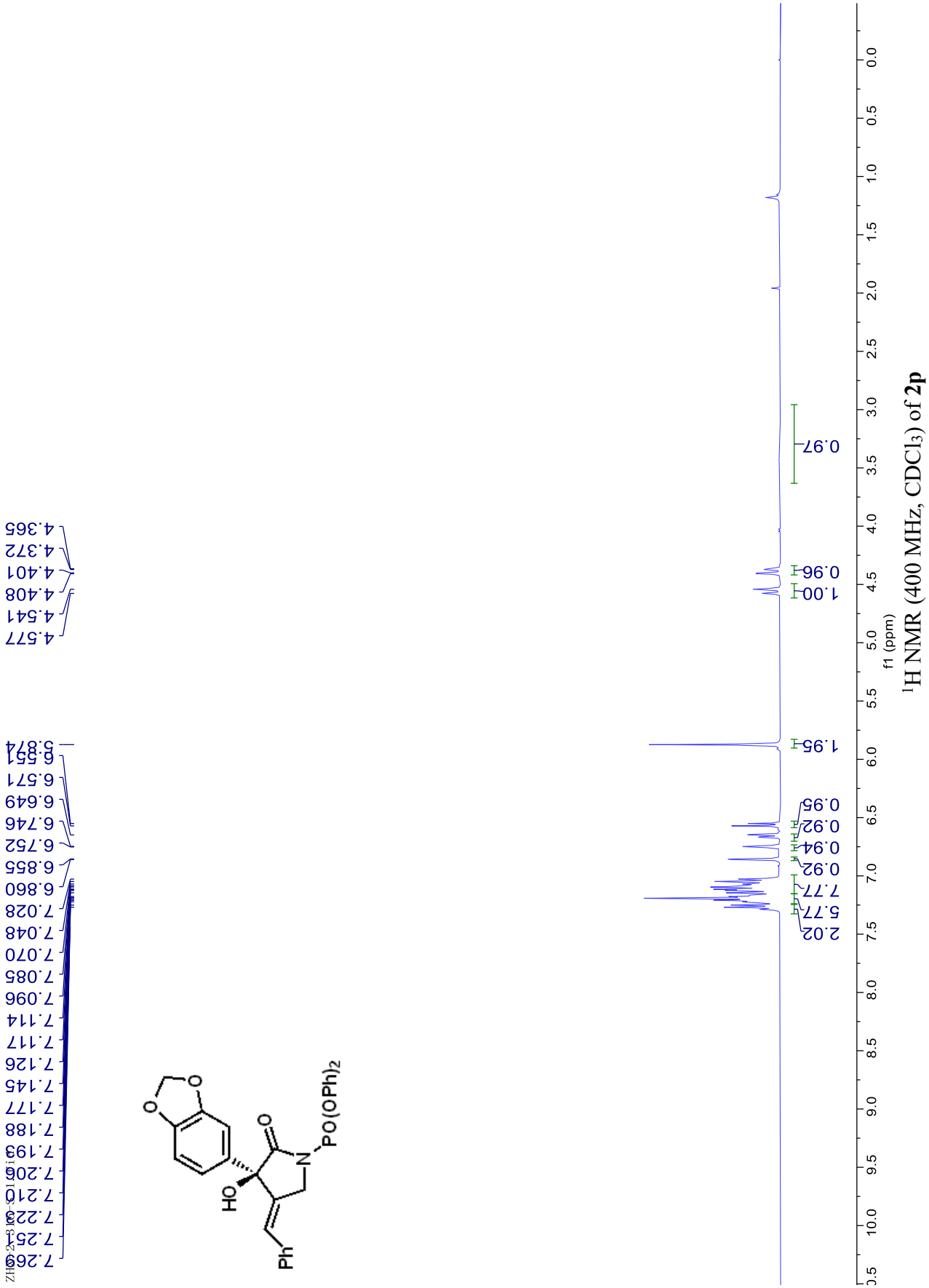
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



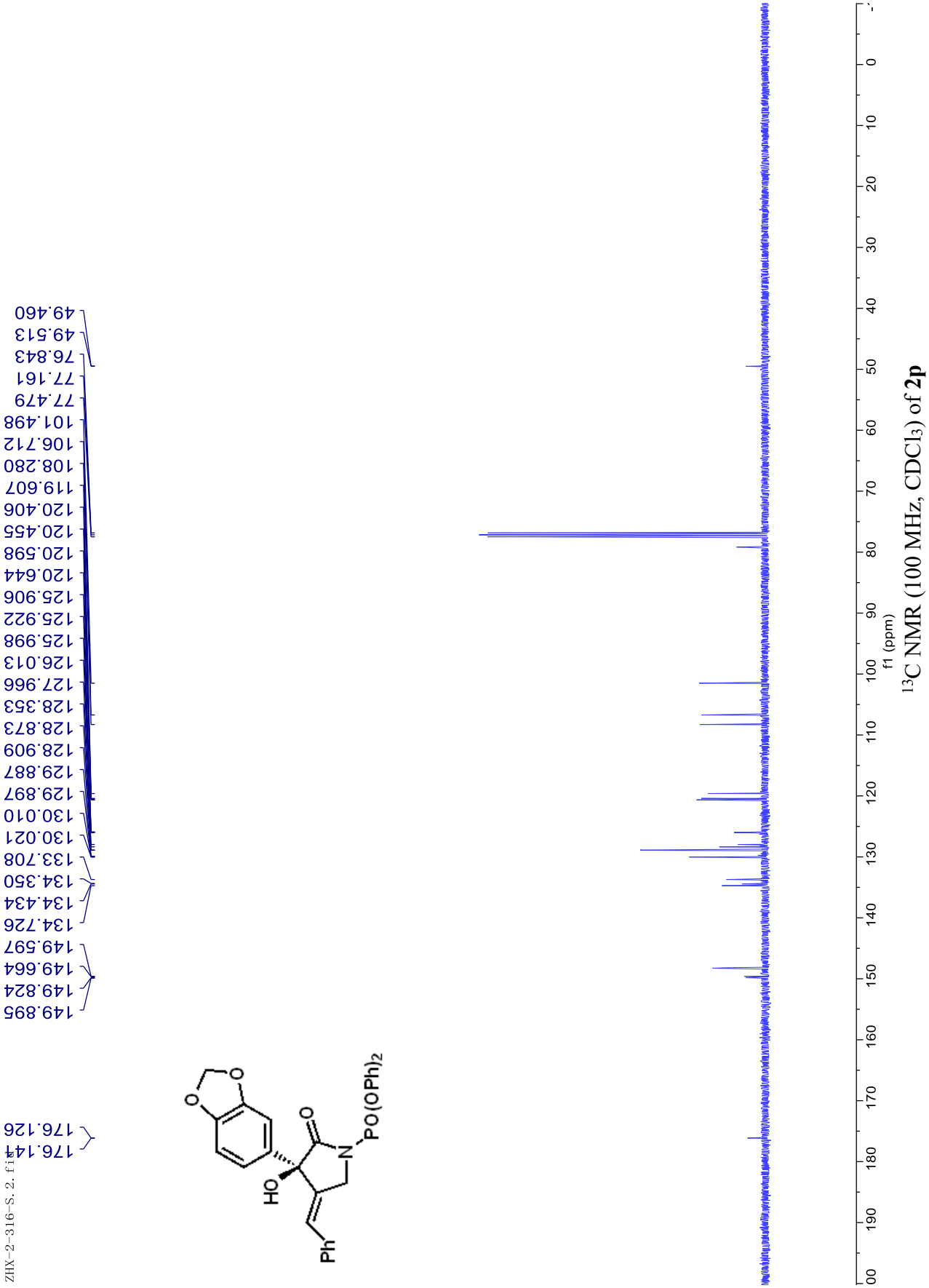
^{13}C NMR (100 MHz, $CDCl_3$) of **2o**



^{31}P NMR (162 MHz, $CDCl_3$) of **2o**

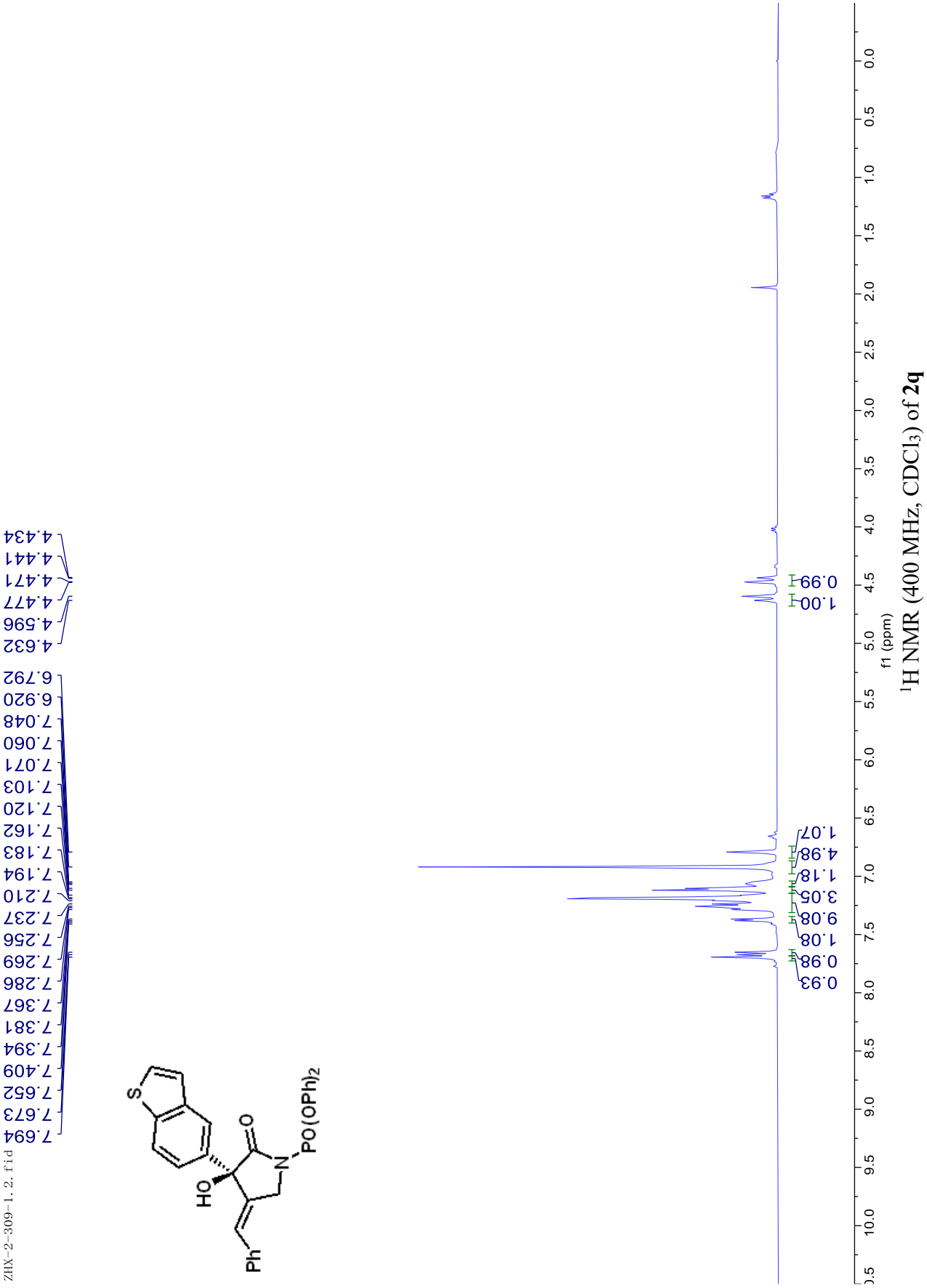


^{1}H NMR (400 MHz, $CDCl_3$) of **2p**

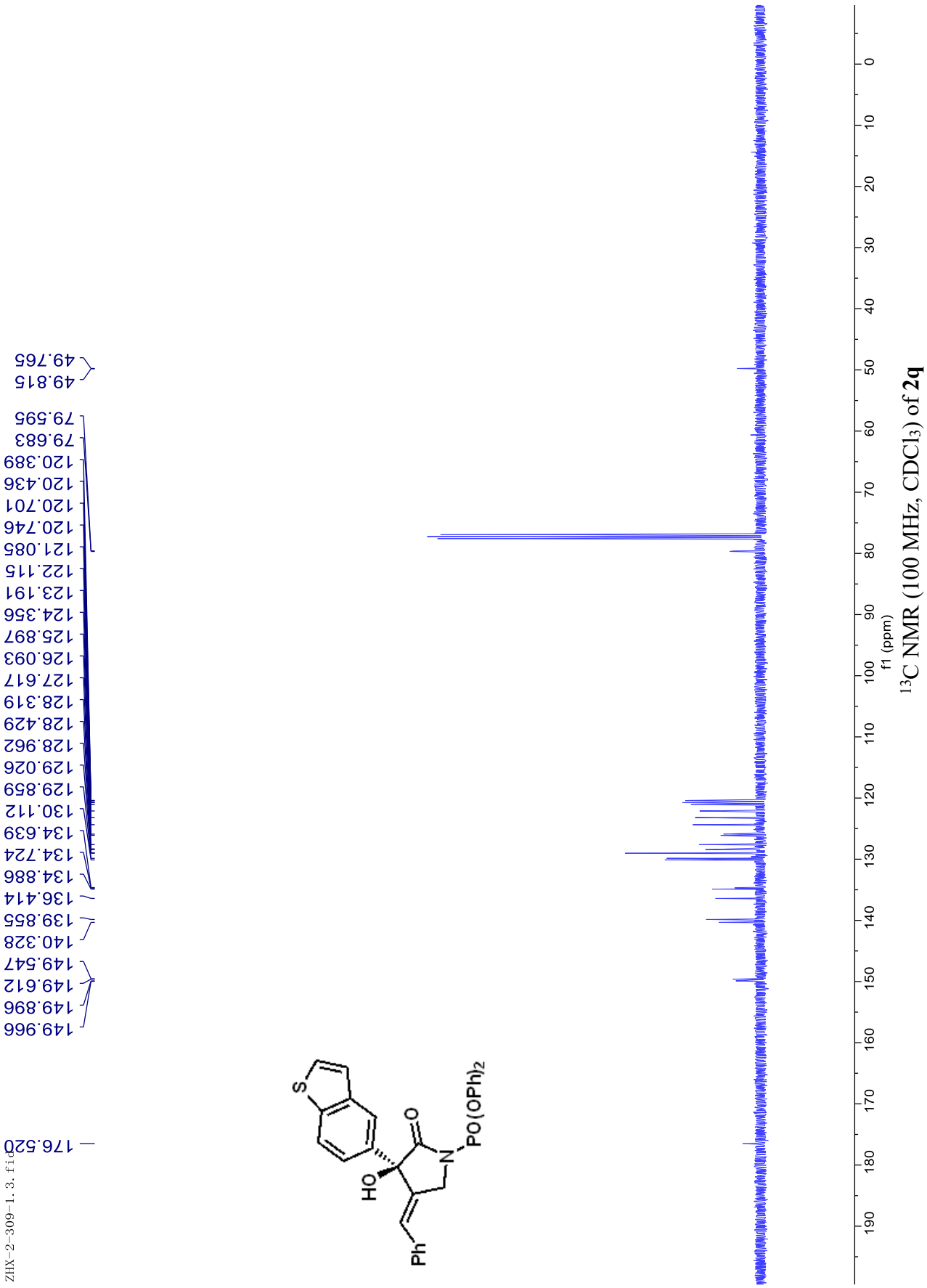


^{13}C NMR (100 MHz, $CDCl_3$) of **2p**

^{31}P NMR (162 MHz, $CDCl_3$) of **2p**

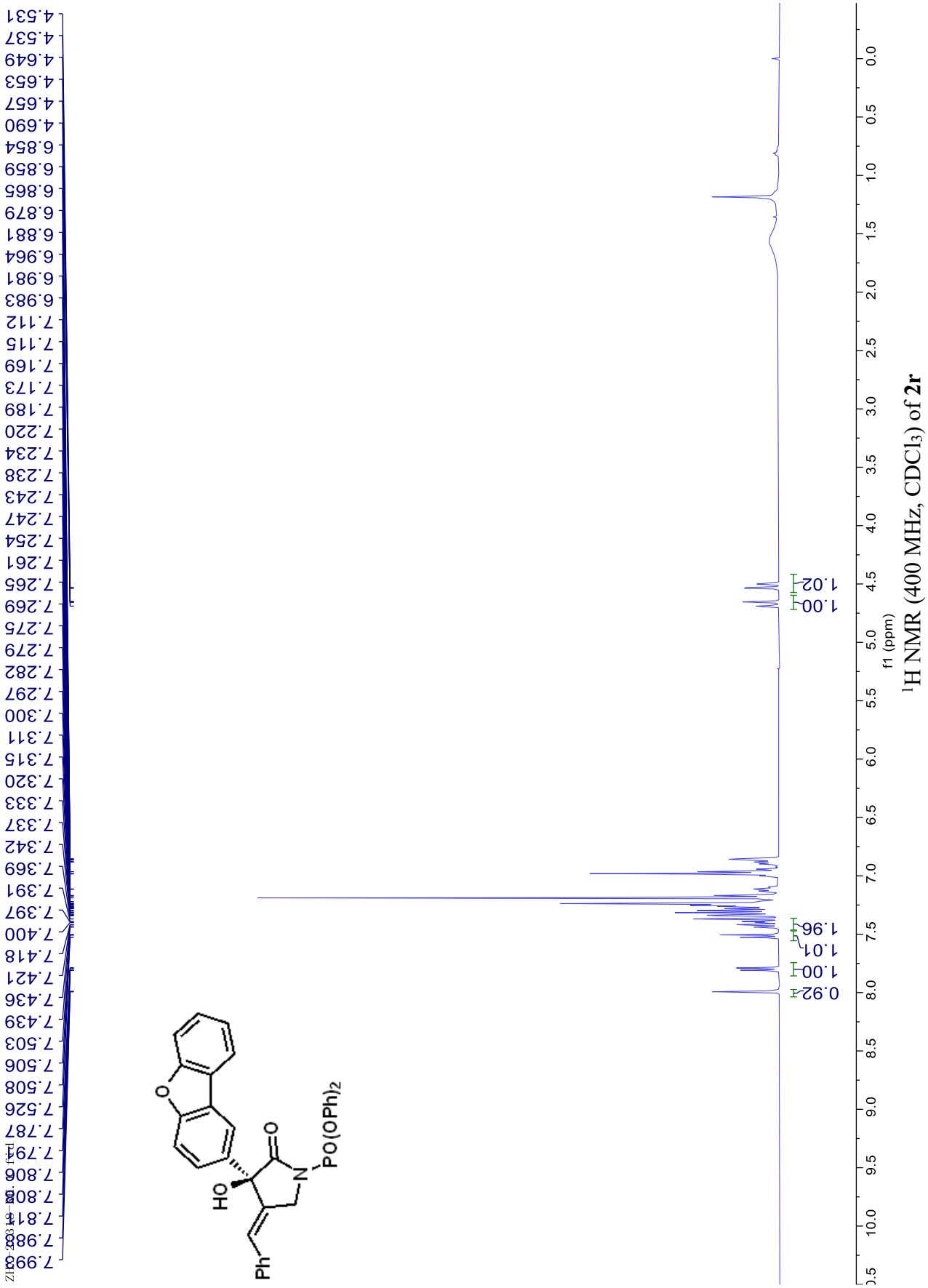


^{1}H NMR (400 MHz, $CDCl_3$) of **2q**

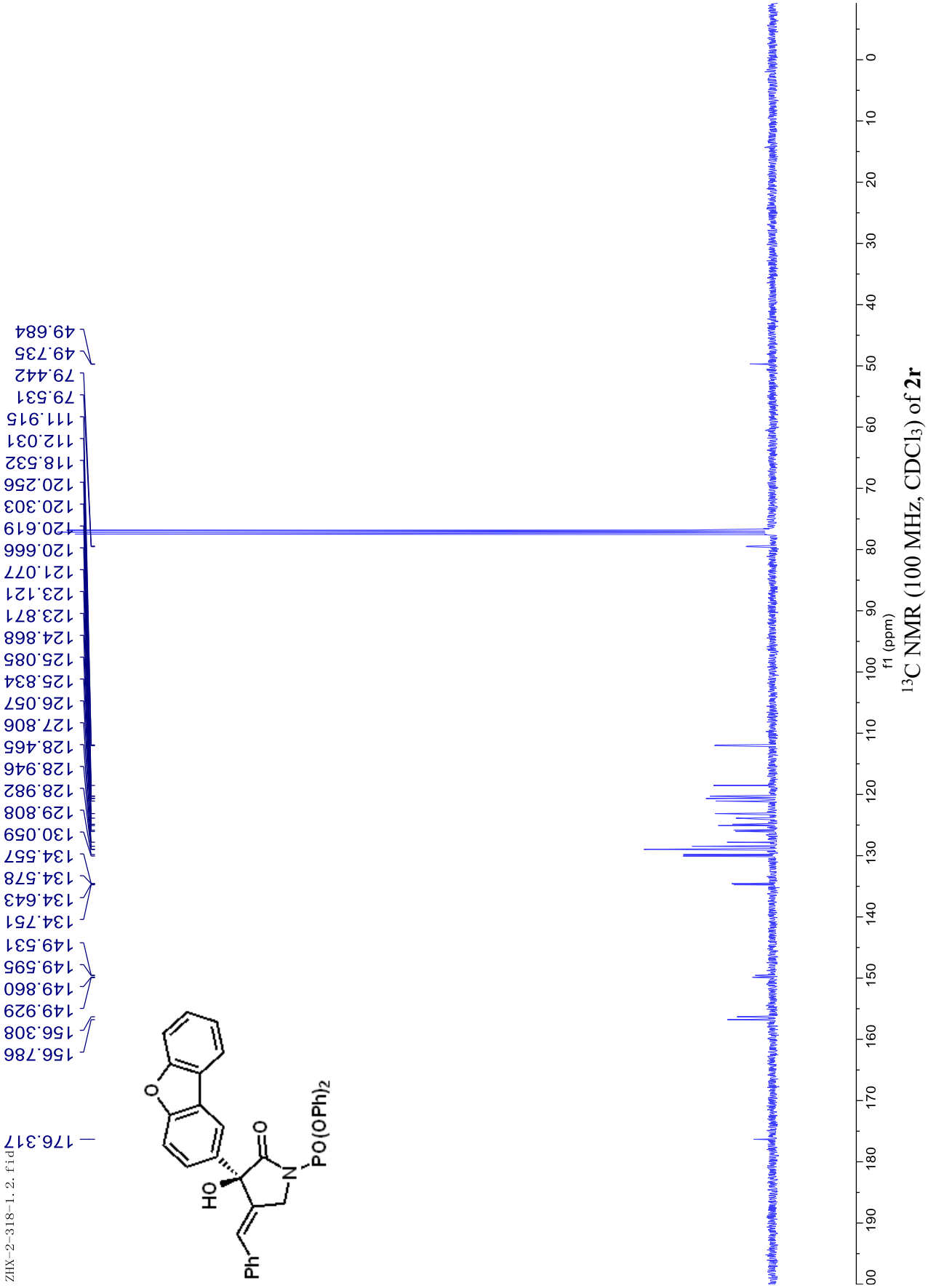


^{13}C NMR (100 MHz, $CDCl_3$) of **2q**

^{31}P NMR (162 MHz, $CDCl_3$) of **2q**

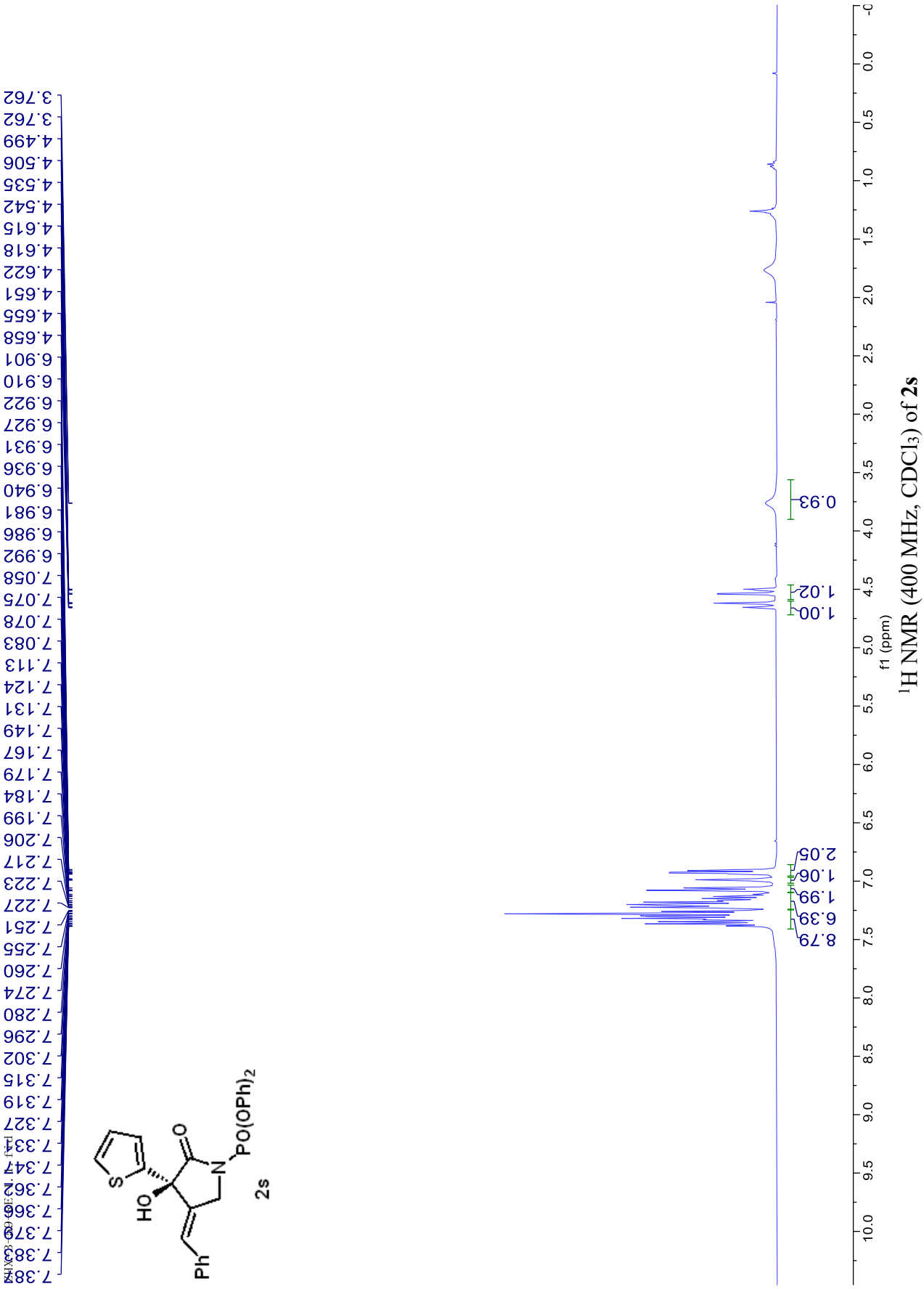


^{1}H NMR (400 MHz, $CDCl_3$) of **2r**

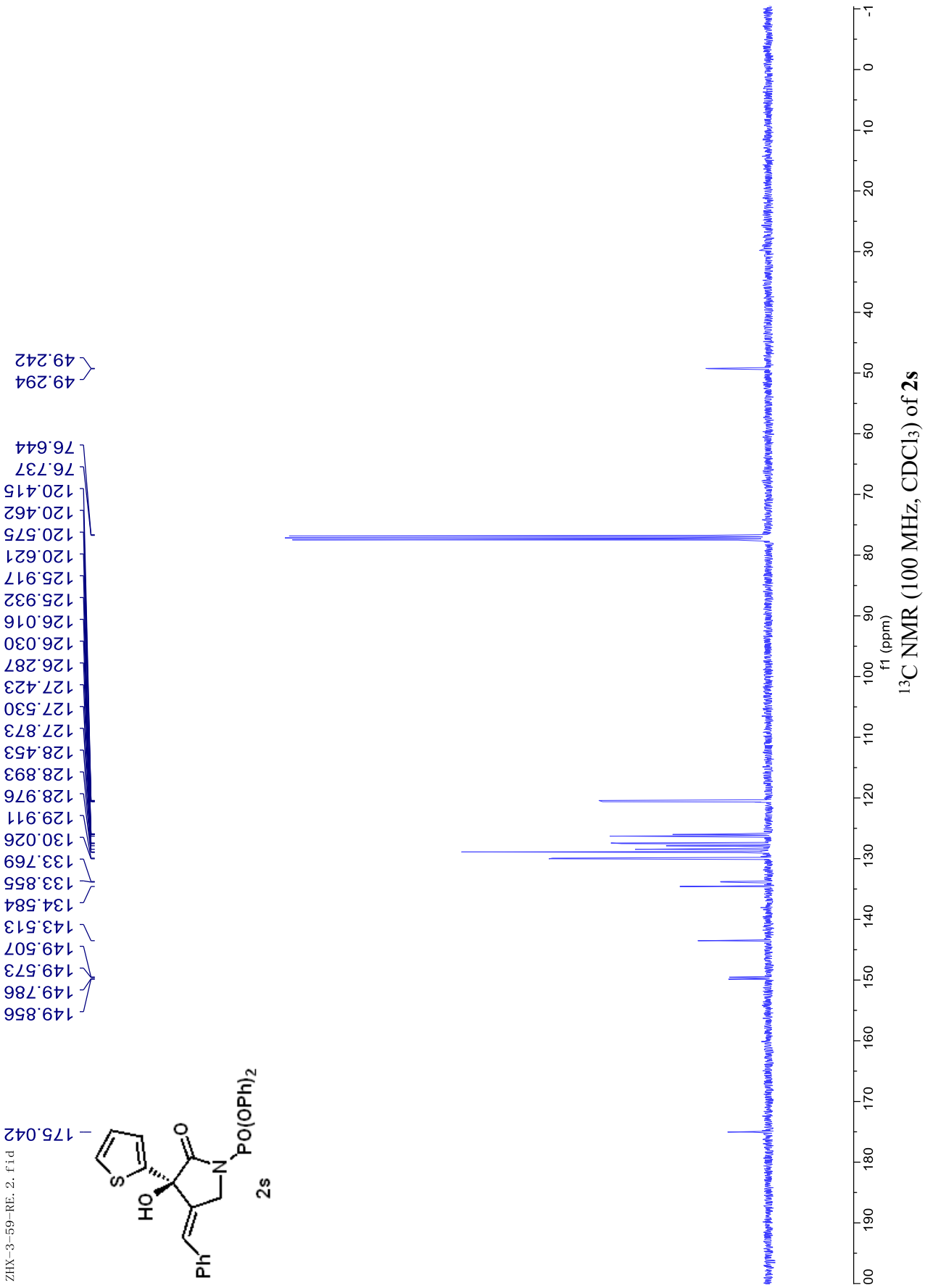


^{13}C NMR (100 MHz, $CDCl_3$) of **2r**

^{31}P NMR (162 MHz, $CDCl_3$) of **2r**

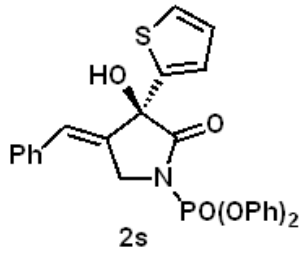


^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



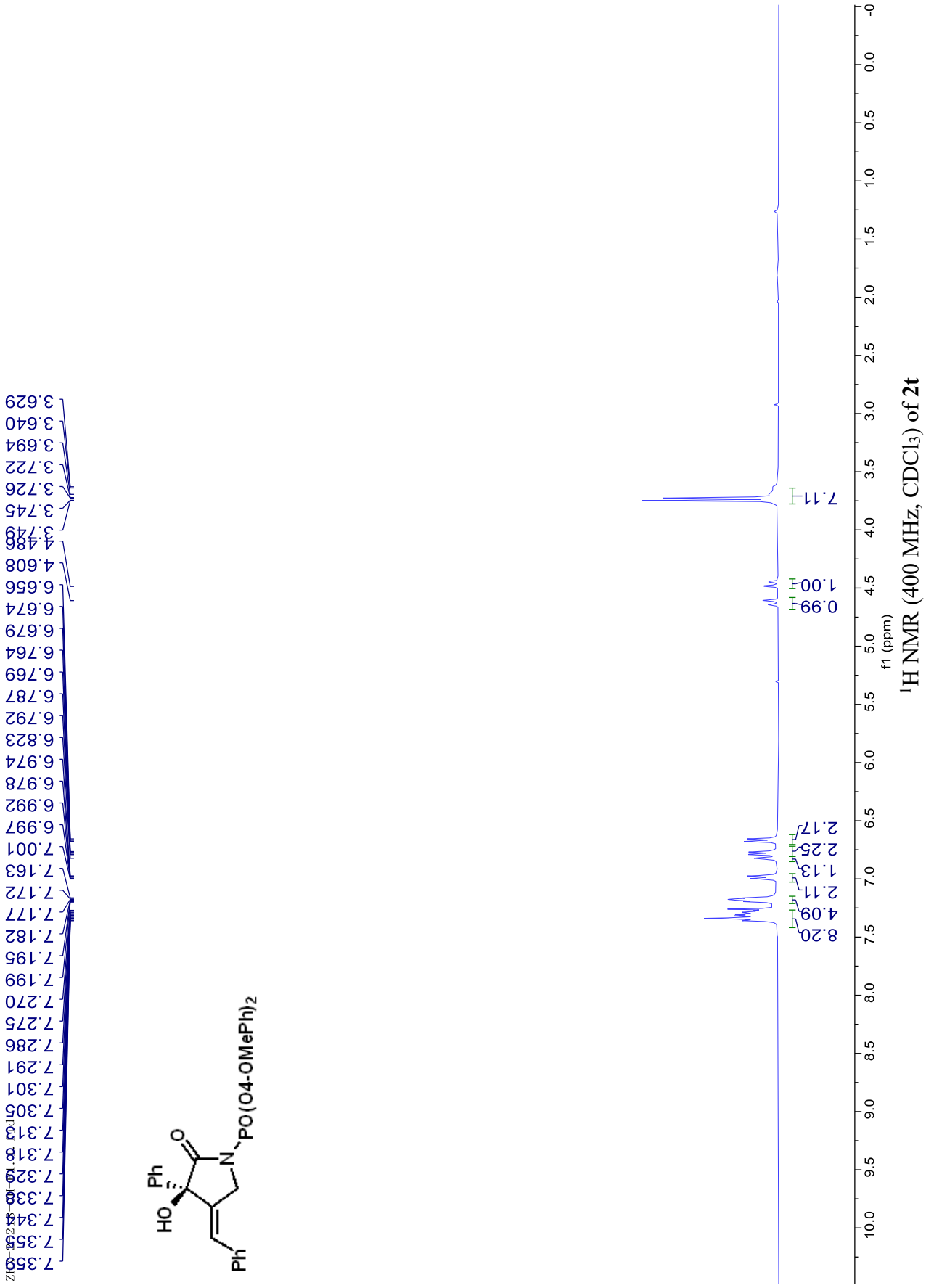
^{13}C NMR (100 MHz, $CDCl_3$) of **2s**

ZHX-3-59-1.2.fid

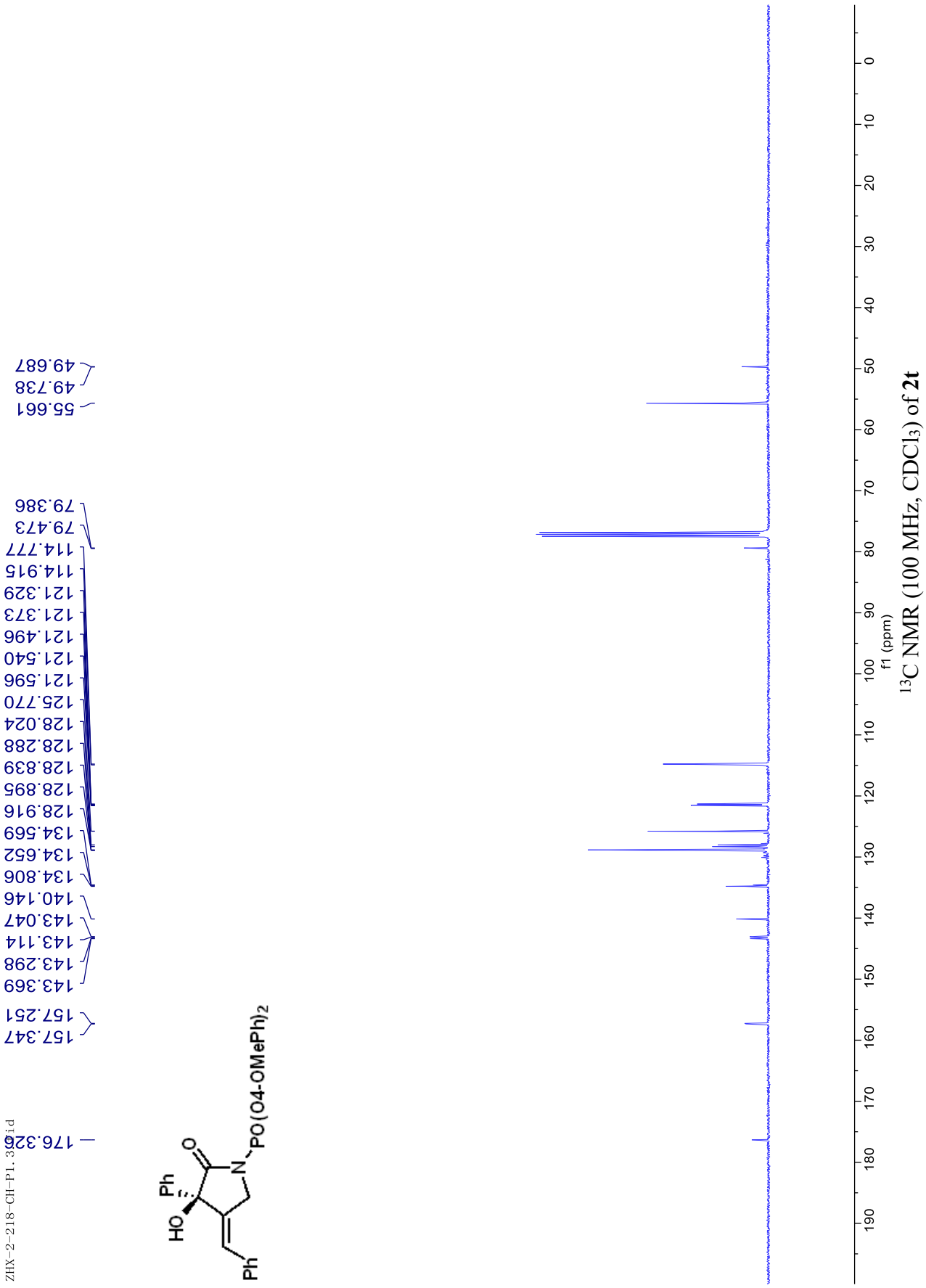


2s

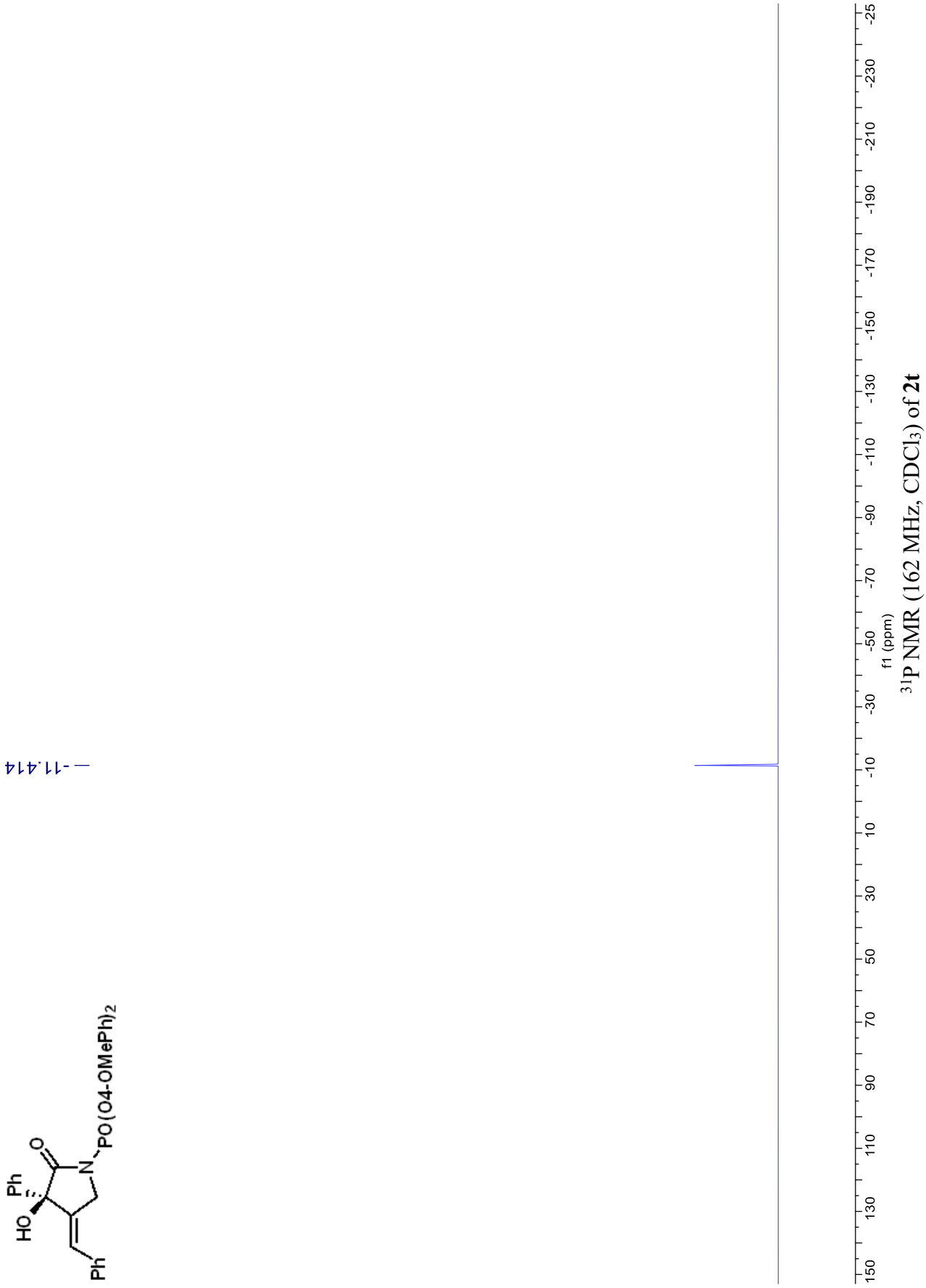
^{31}P NMR (162 MHz, $CDCl_3$) of **2s**



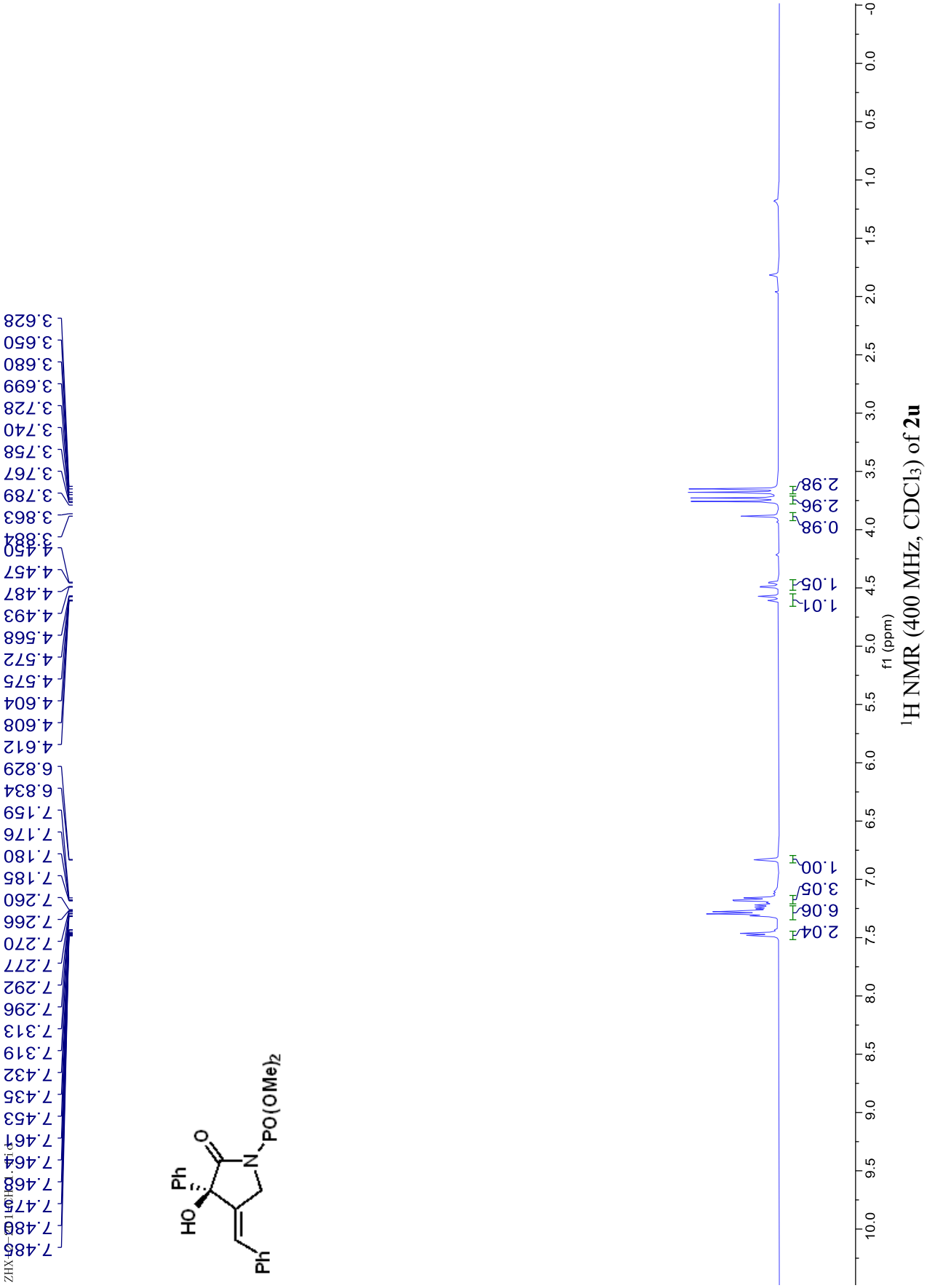
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



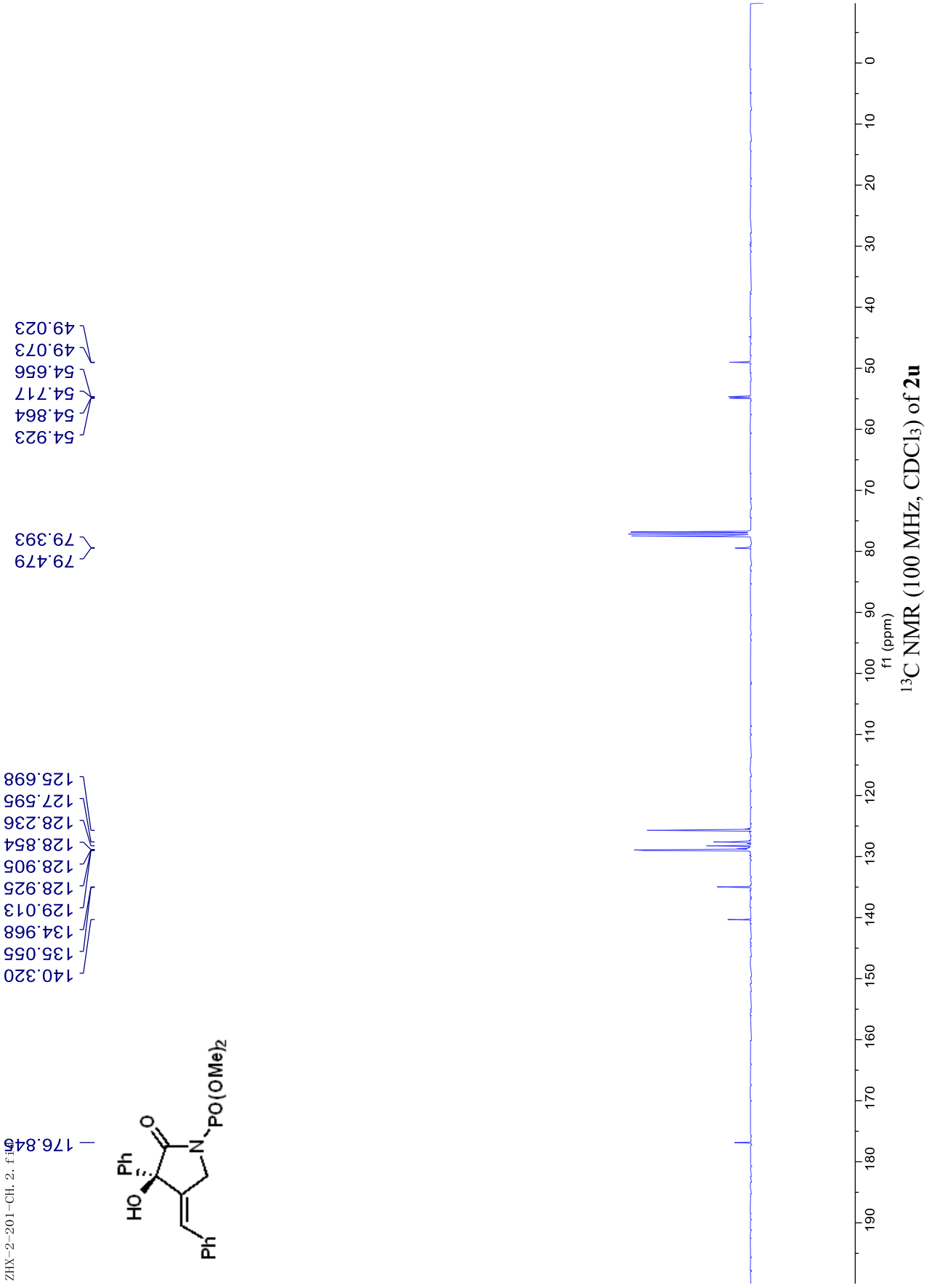
^{13}C NMR (100 MHz, $CDCl_3$) of **2t**



^{31}P NMR (162 MHz, $CDCl_3$) of **2t**

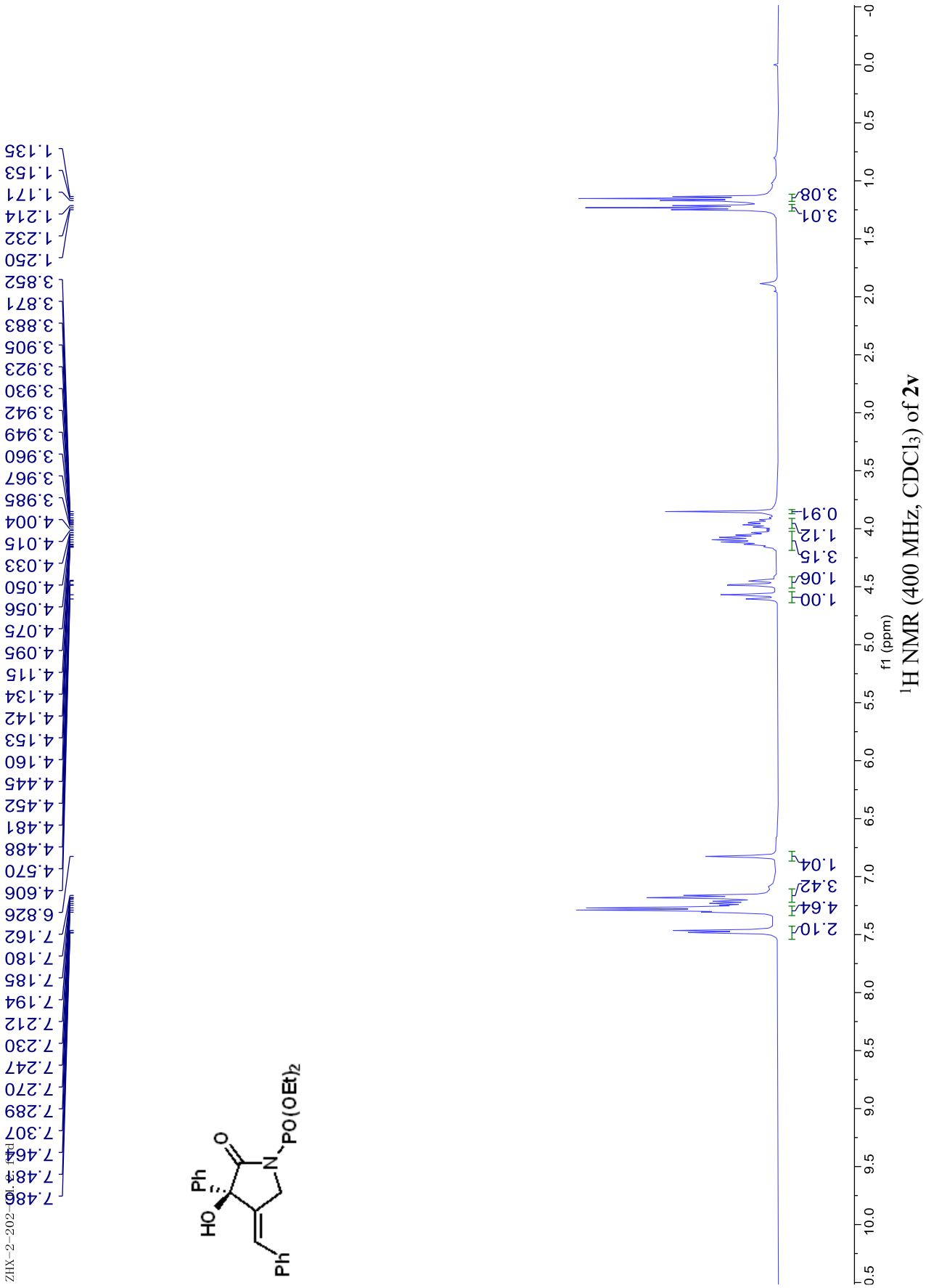


^{1}H NMR (400 MHz, $CDCl_3$) of **2u**

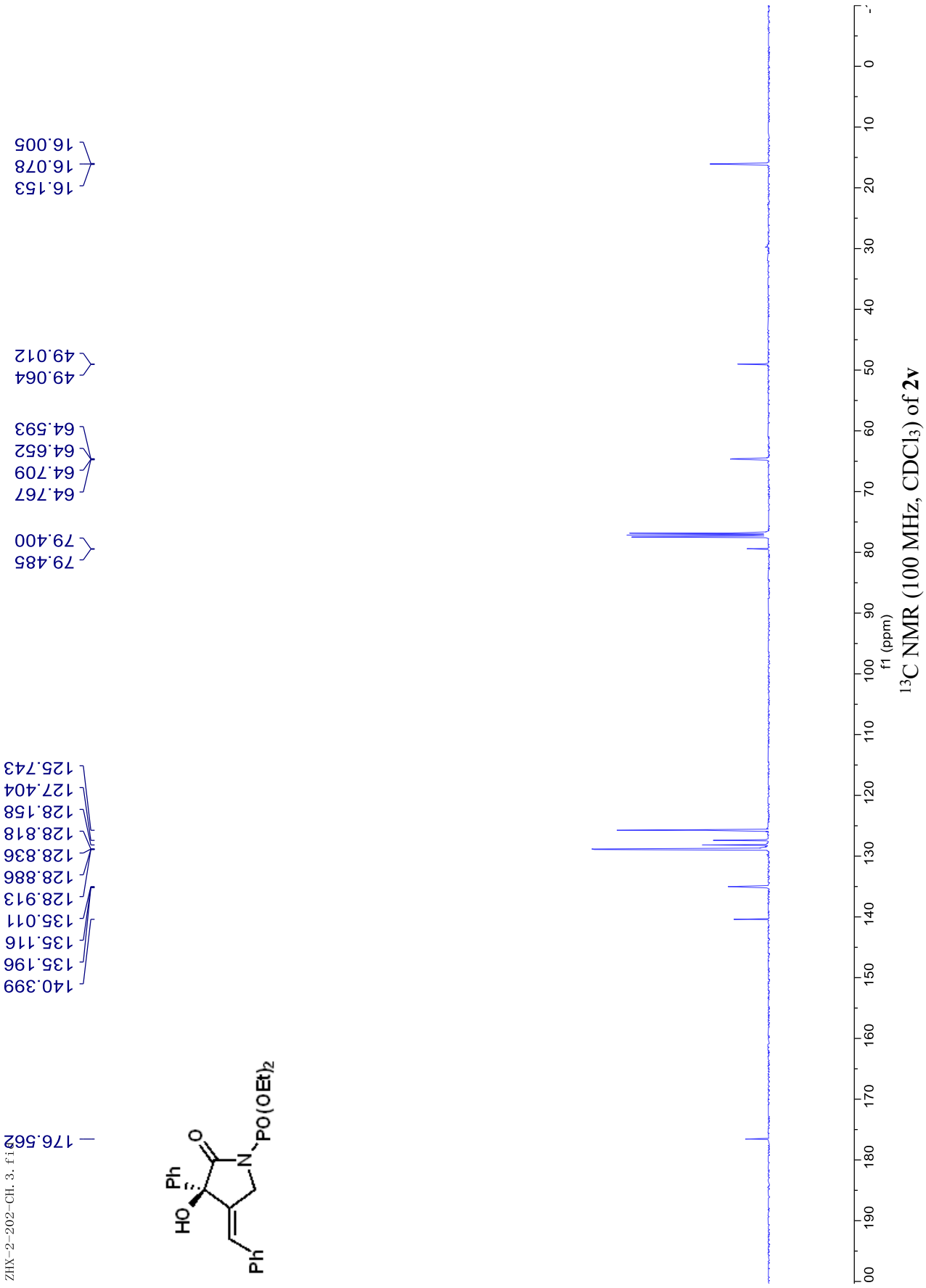


^{13}C NMR (100 MHz, $CDCl_3$) of **2u**

^{31}P NMR (162 MHz, $CDCl_3$) of **2u**

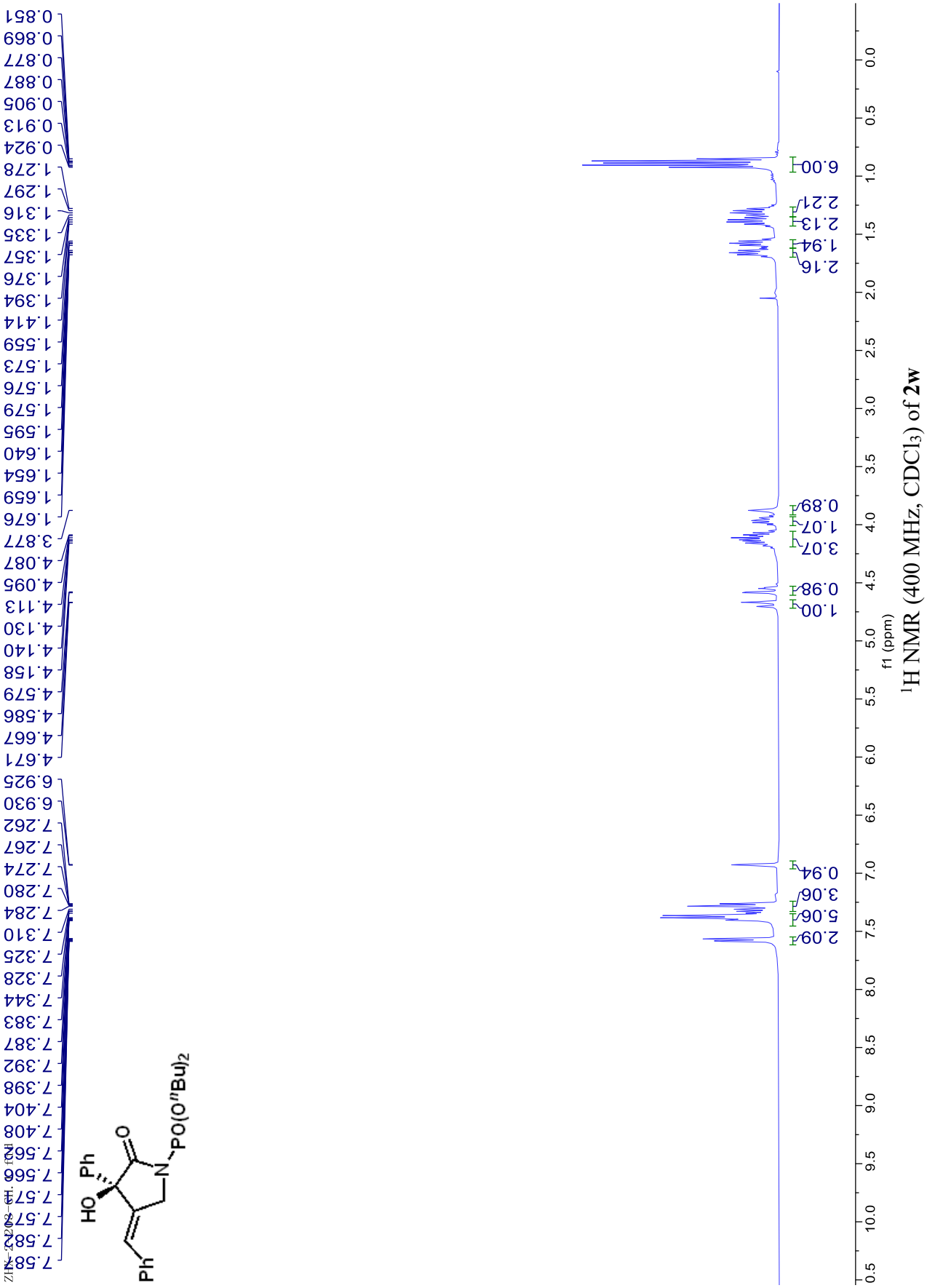


^{1}H NMR (400 MHz, $CDCl_3$) of **2v**

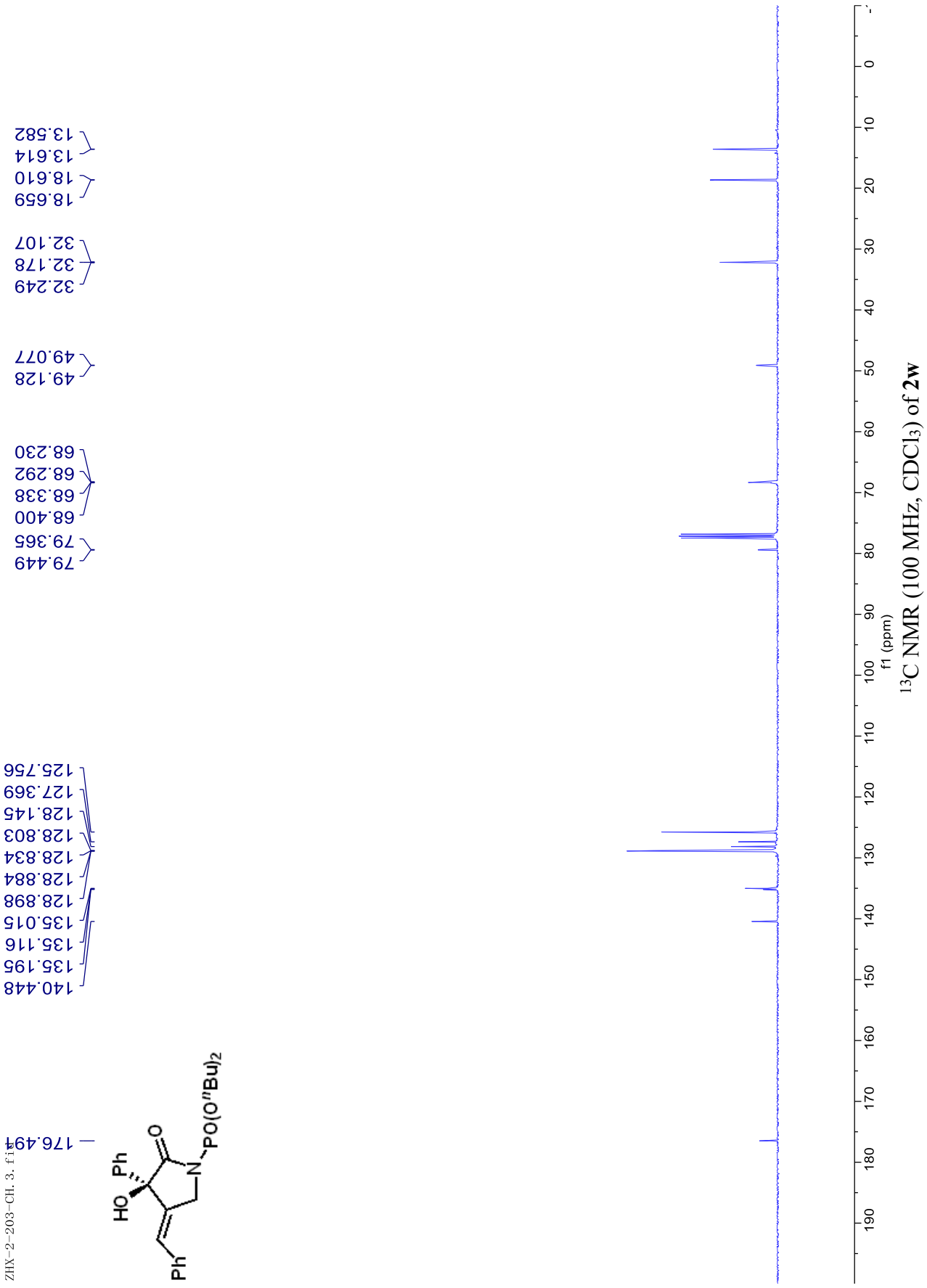


^{13}C NMR (100 MHz, $CDCl_3$) of **2v**

^{31}P NMR (162 MHz, $CDCl_3$) of **2v**

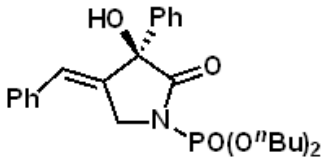


^{1}H NMR (400 MHz, $CDCl_3$) of **2w**

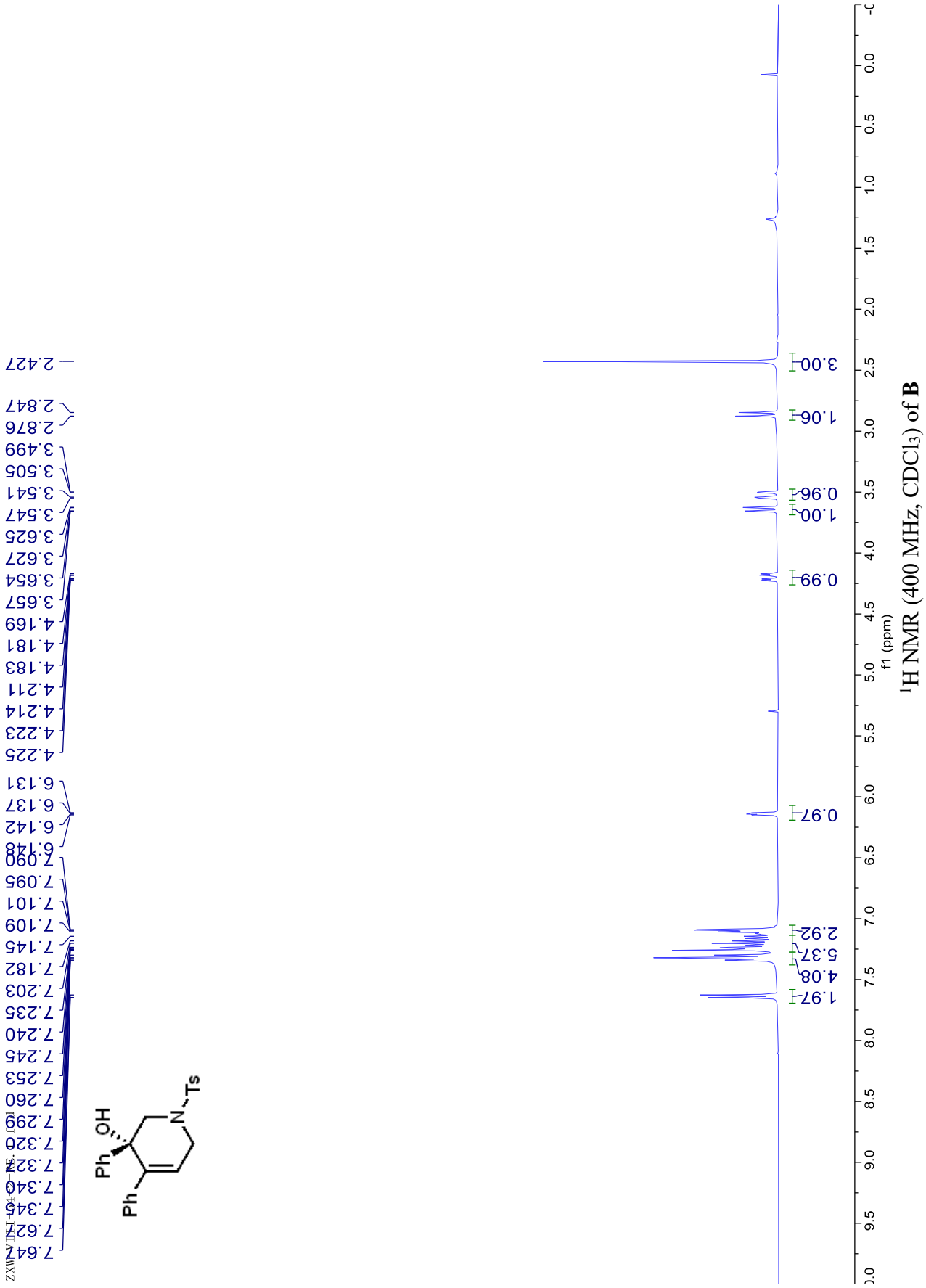


^{13}C NMR (100 MHz, $CDCl_3$) of **2w**

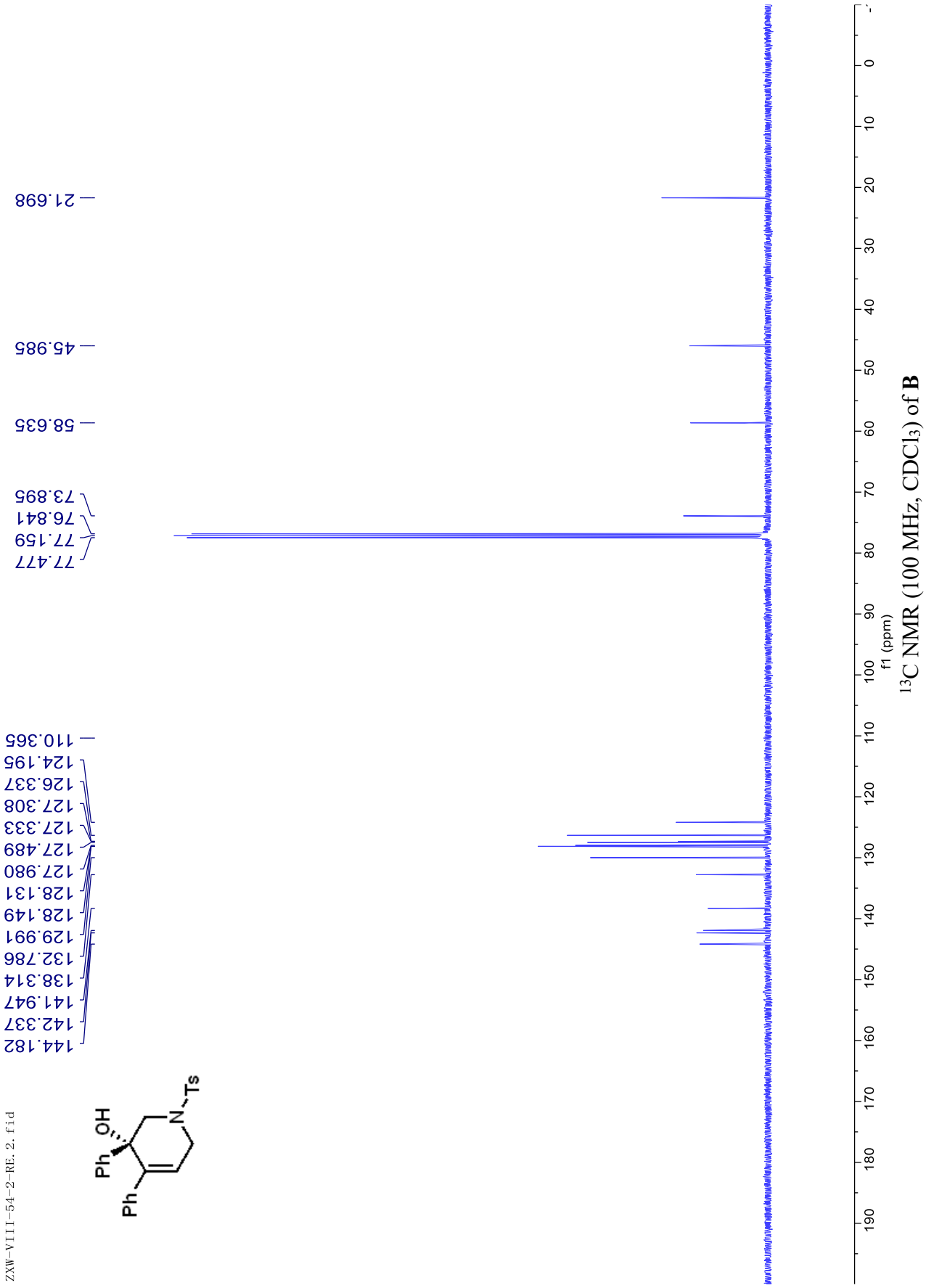
ZHX-2-203-31P.1.fid



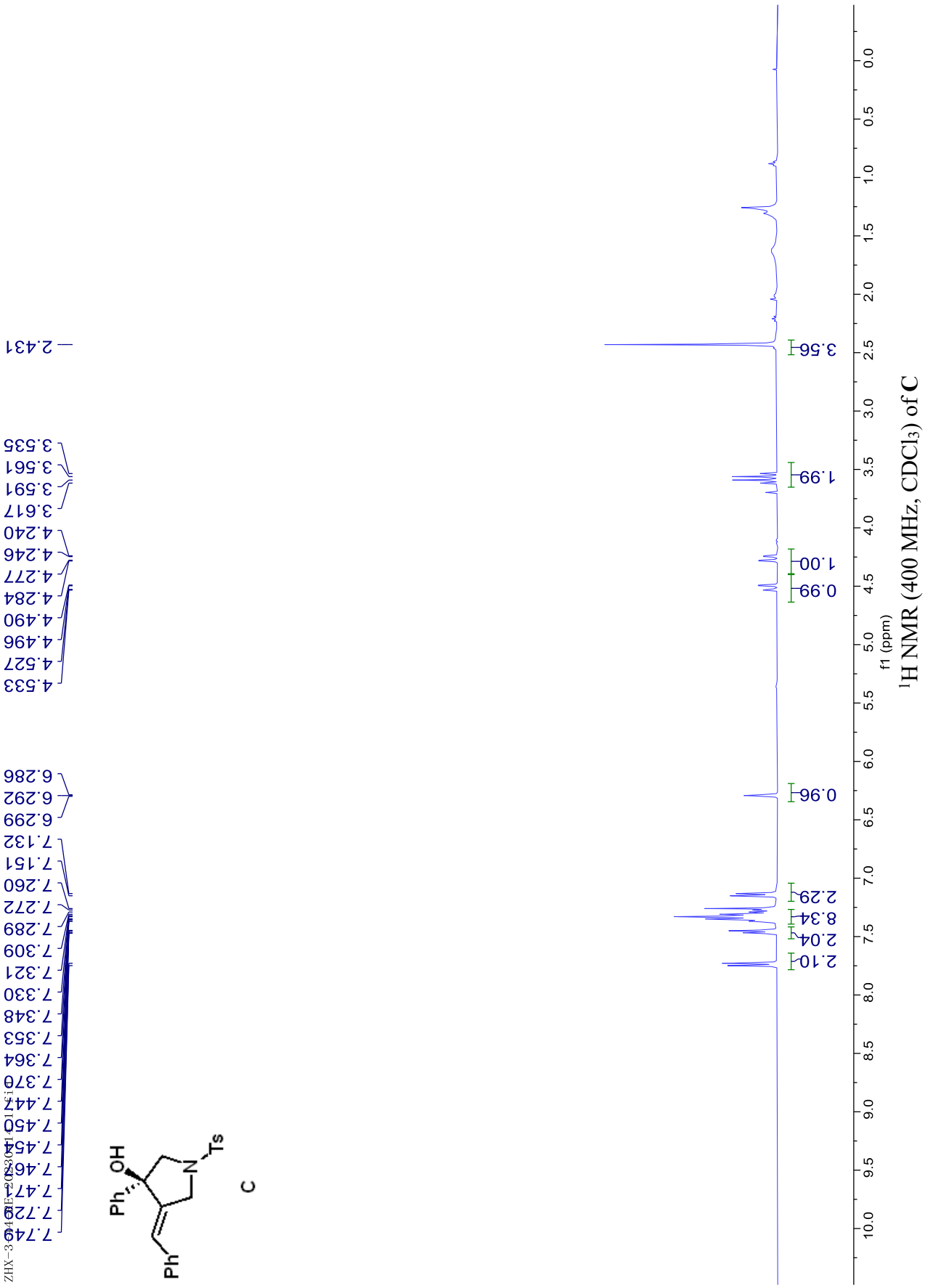
^{31}P NMR (162 MHz, $CDCl_3$) of **2w**

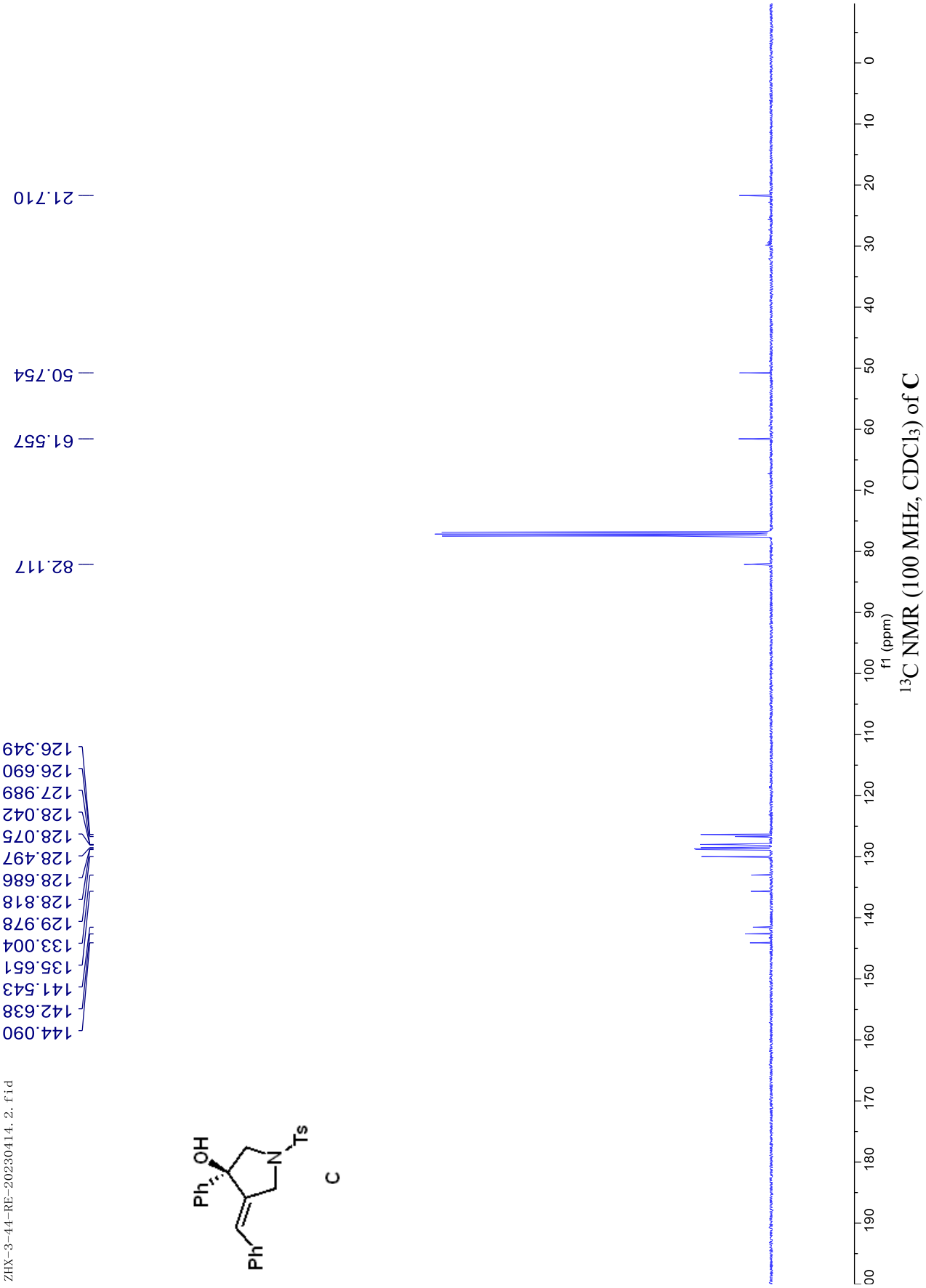


^{1}H NMR (400 MHz, $CDCl_3$) of **B**

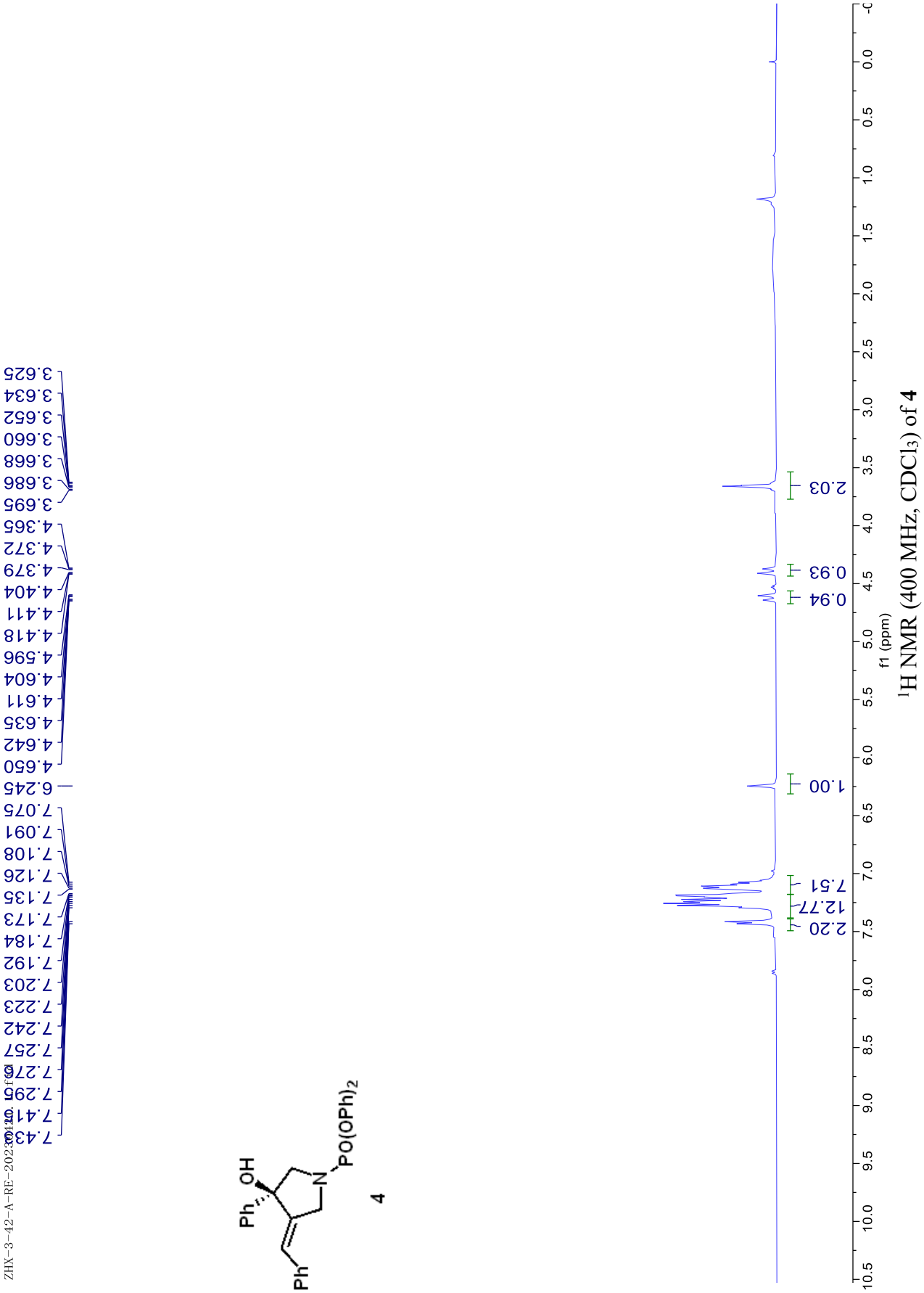


^{13}C NMR (100 MHz, $CDCl_3$) of **B**

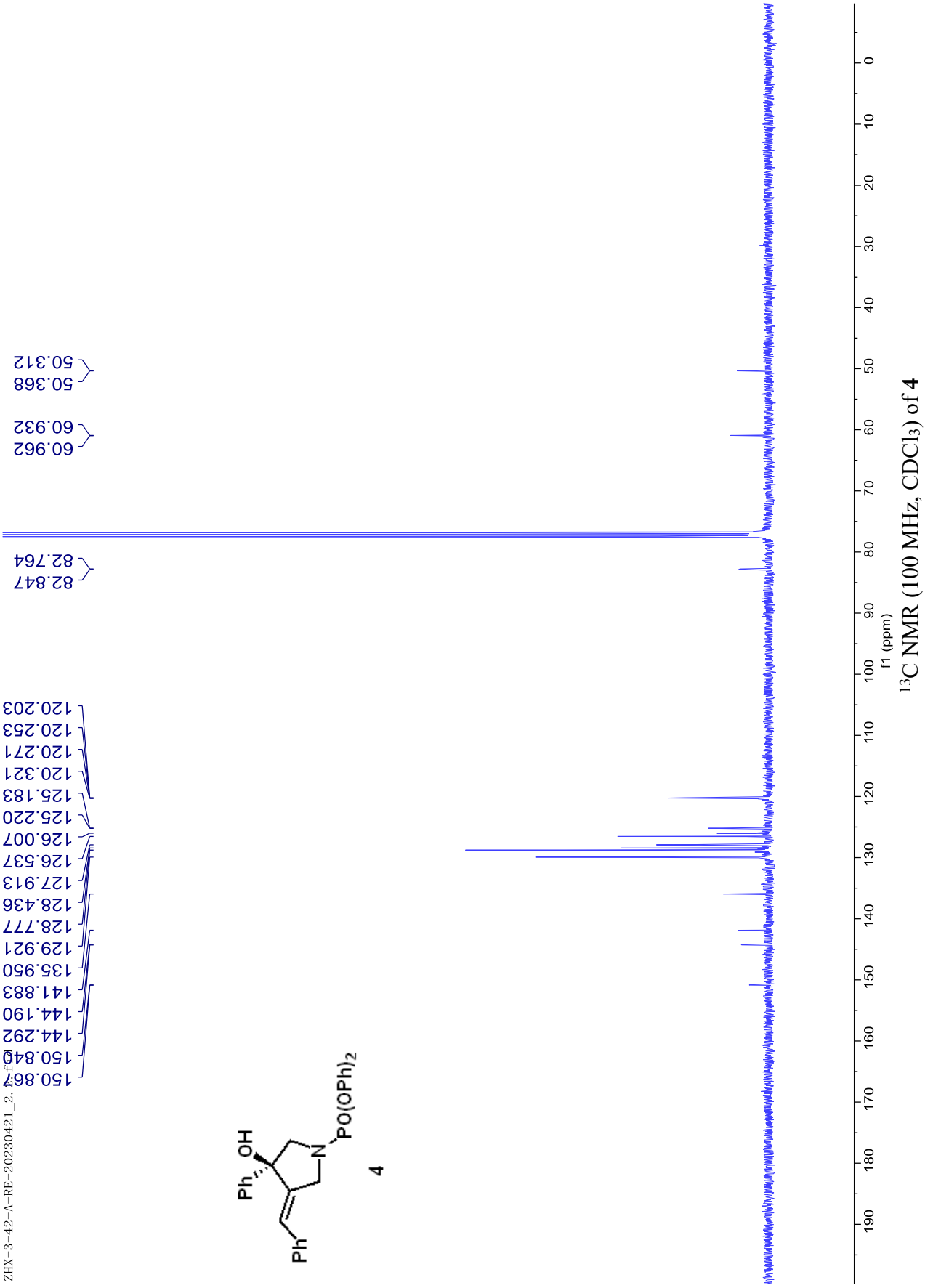

^{1}H NMR (400 MHz, CDCl$_3$) of C
f1 (ppm)
3.56
1.99
1.00
0.99
0.96
2.29
8.34
2.04
2.10
Ph
OH
N
Ts
Ph
C



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

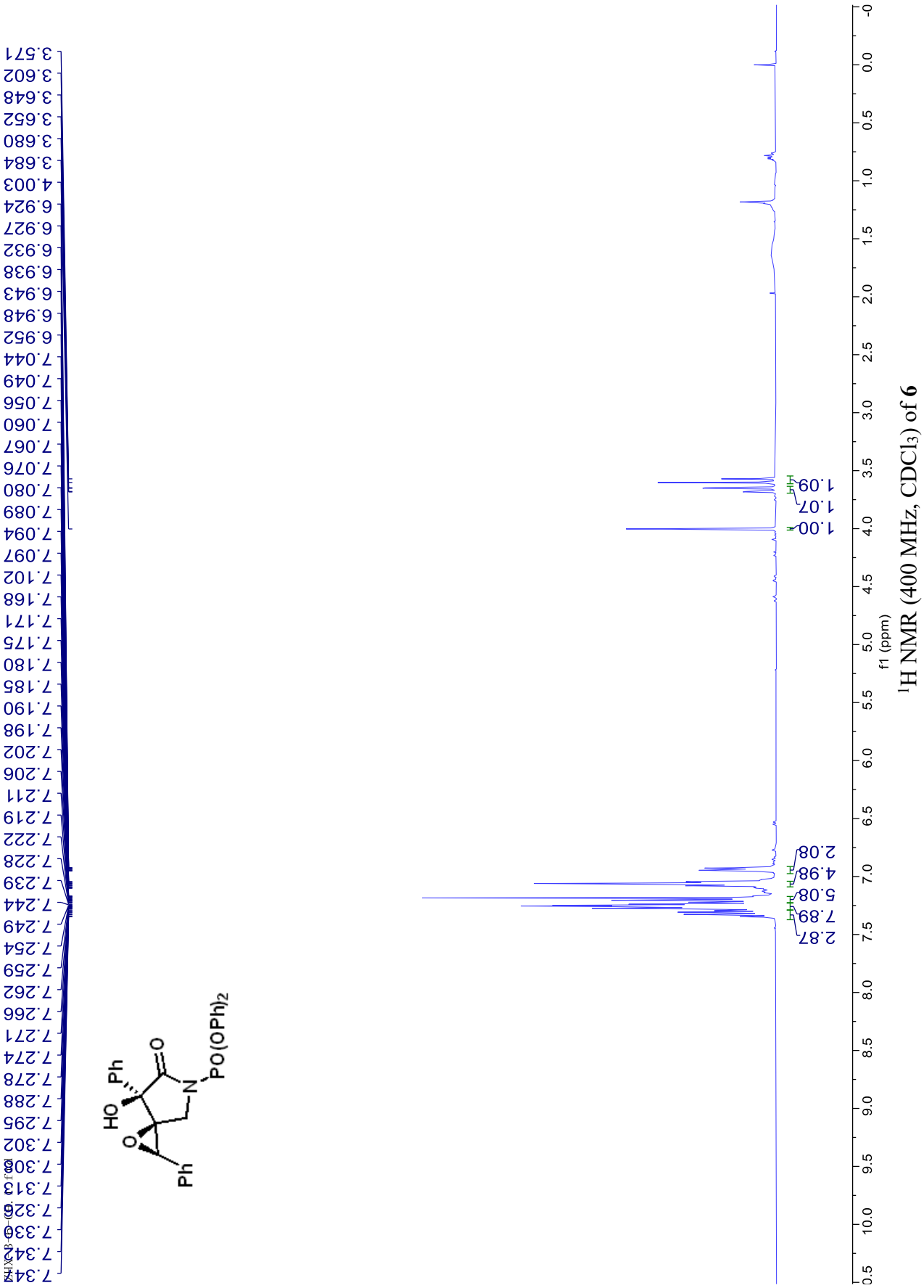


^{1}H NMR (400 MHz, $CDCl_3$) of **4**

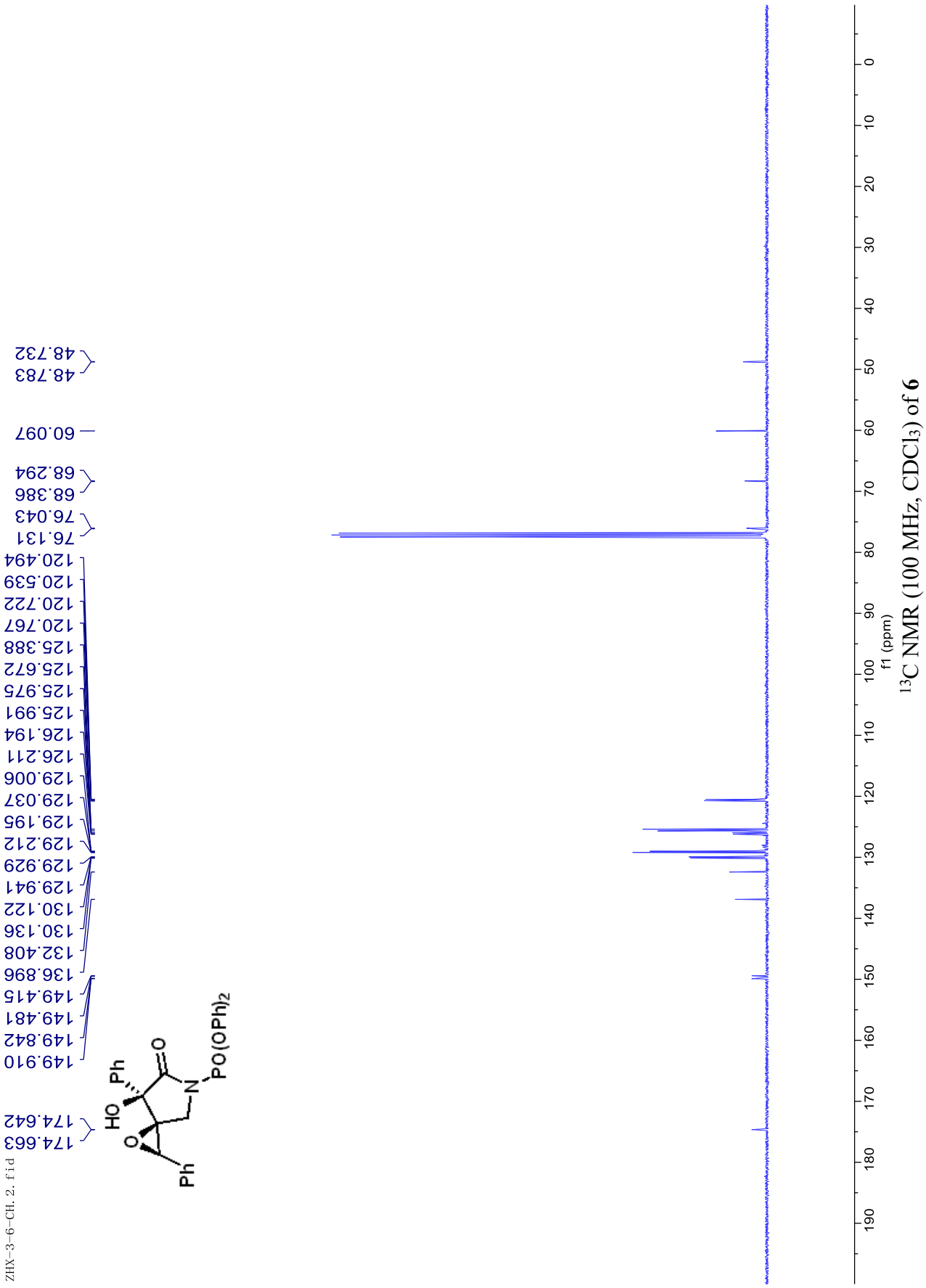


^{13}C NMR (100 MHz, $CDCl_3$) of **4**

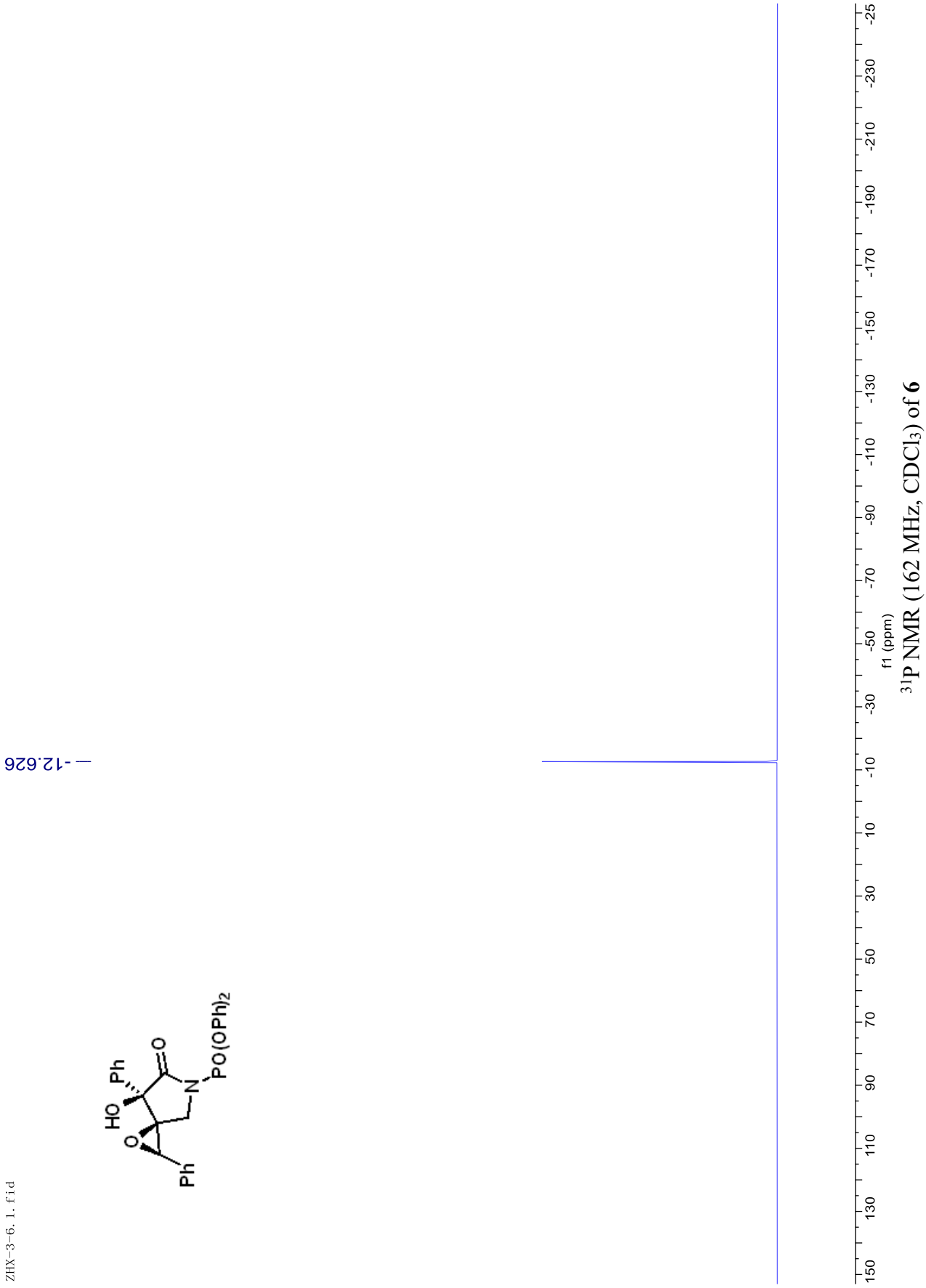
^{31}P NMR (162 MHz, $CDCl_3$) of **4**



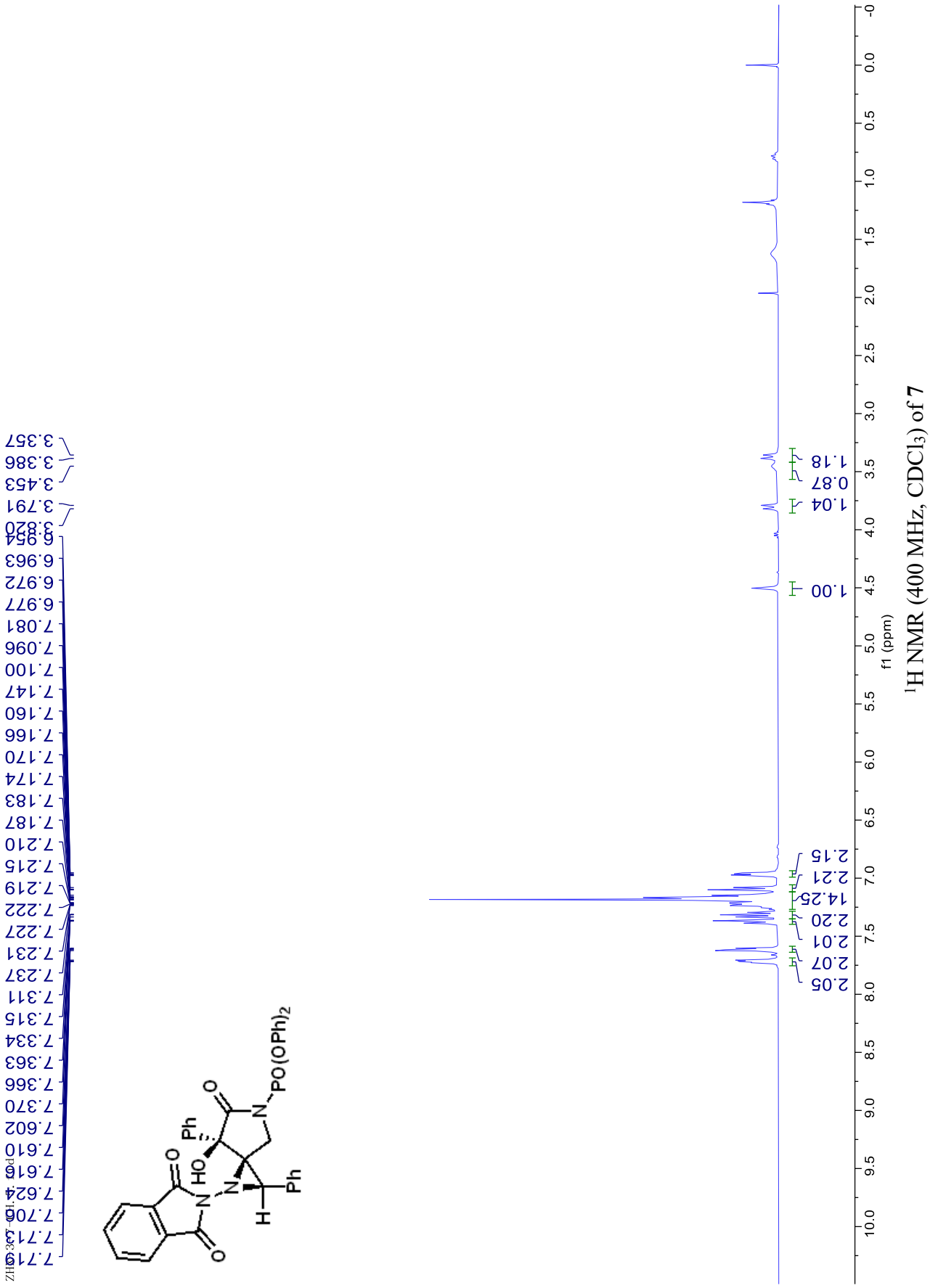
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



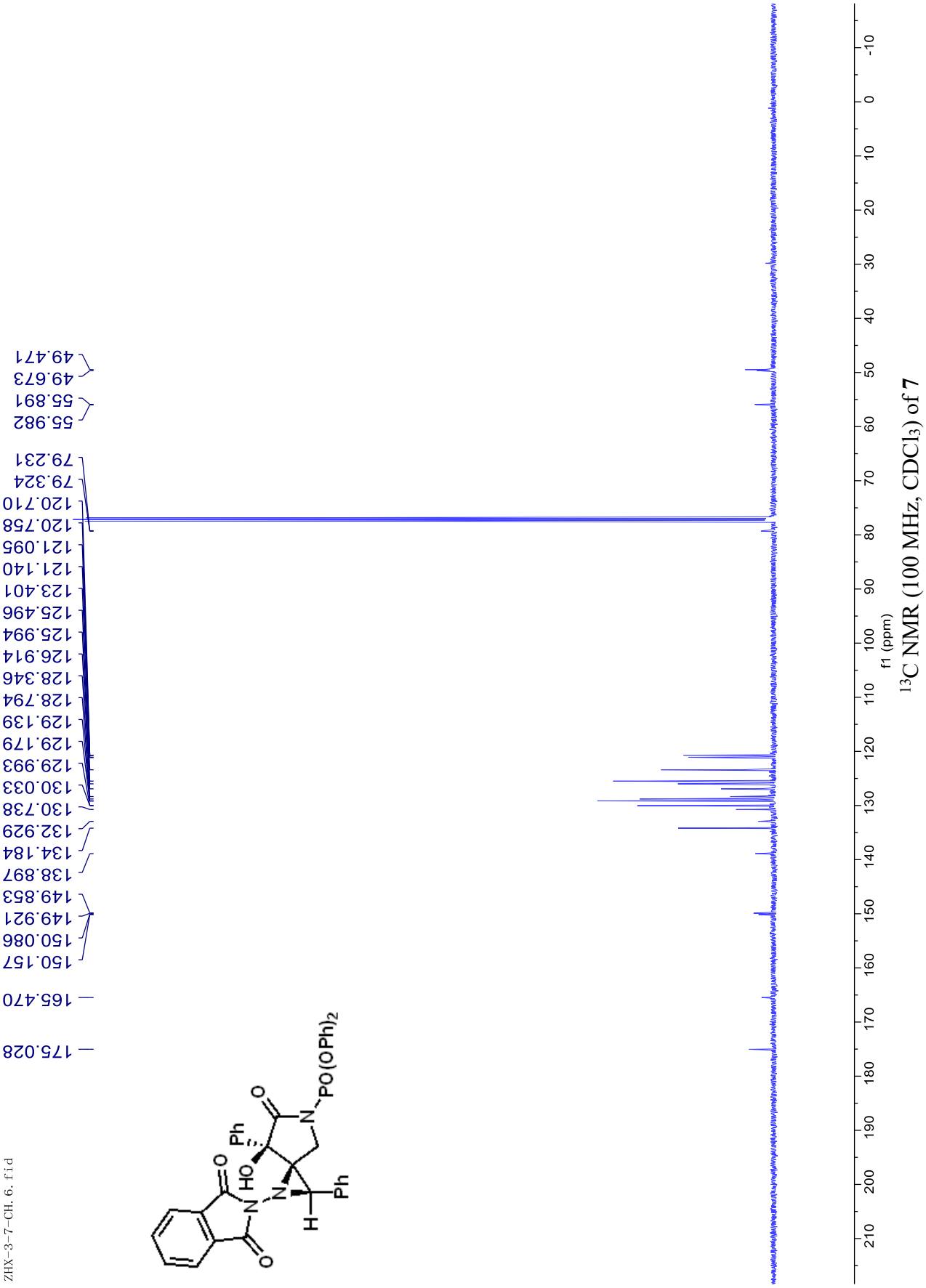
^{13}C NMR (100 MHz, $CDCl_3$) of **6**

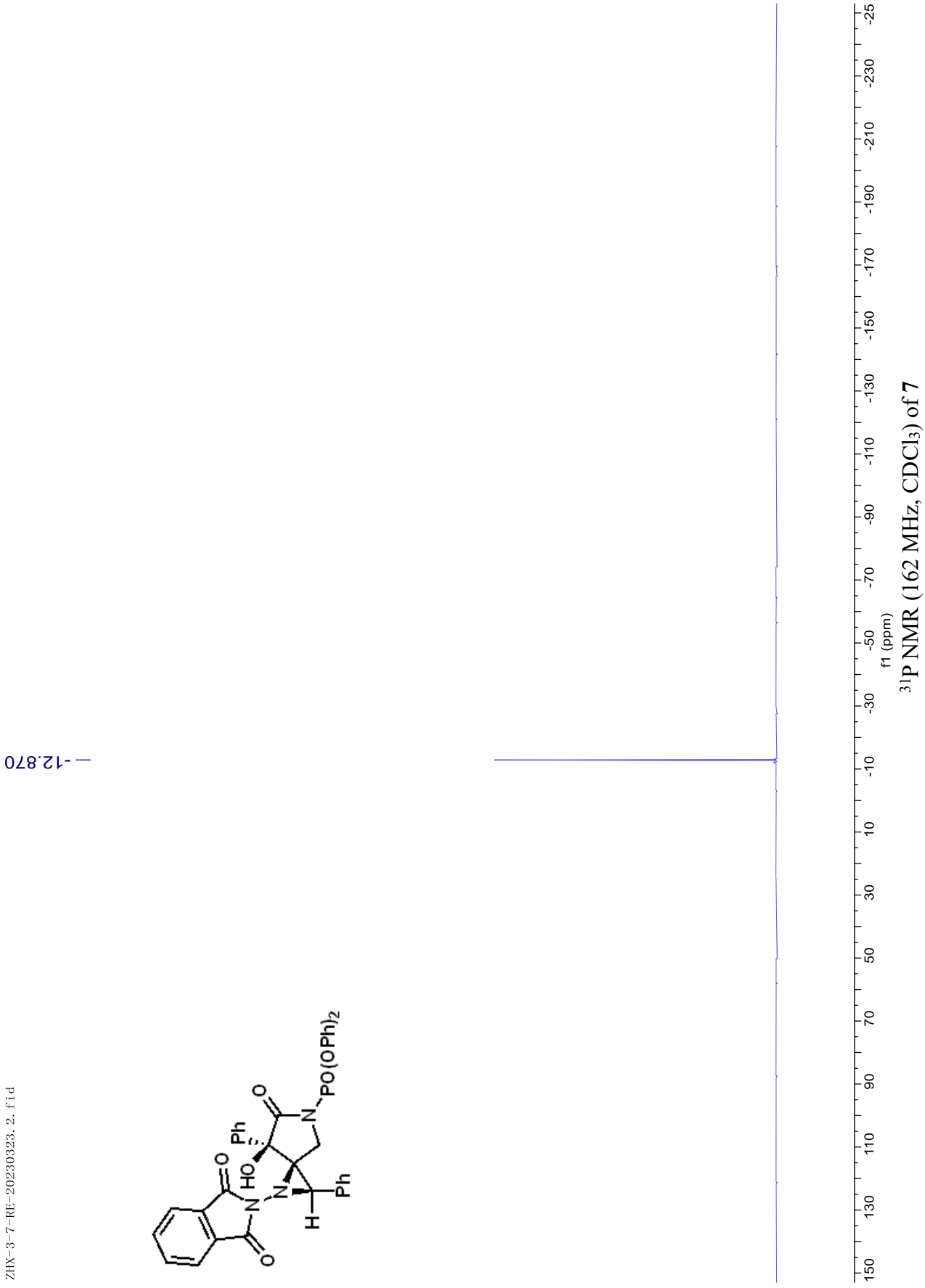


^{31}P NMR (162 MHz, $CDCl_3$) of **6**

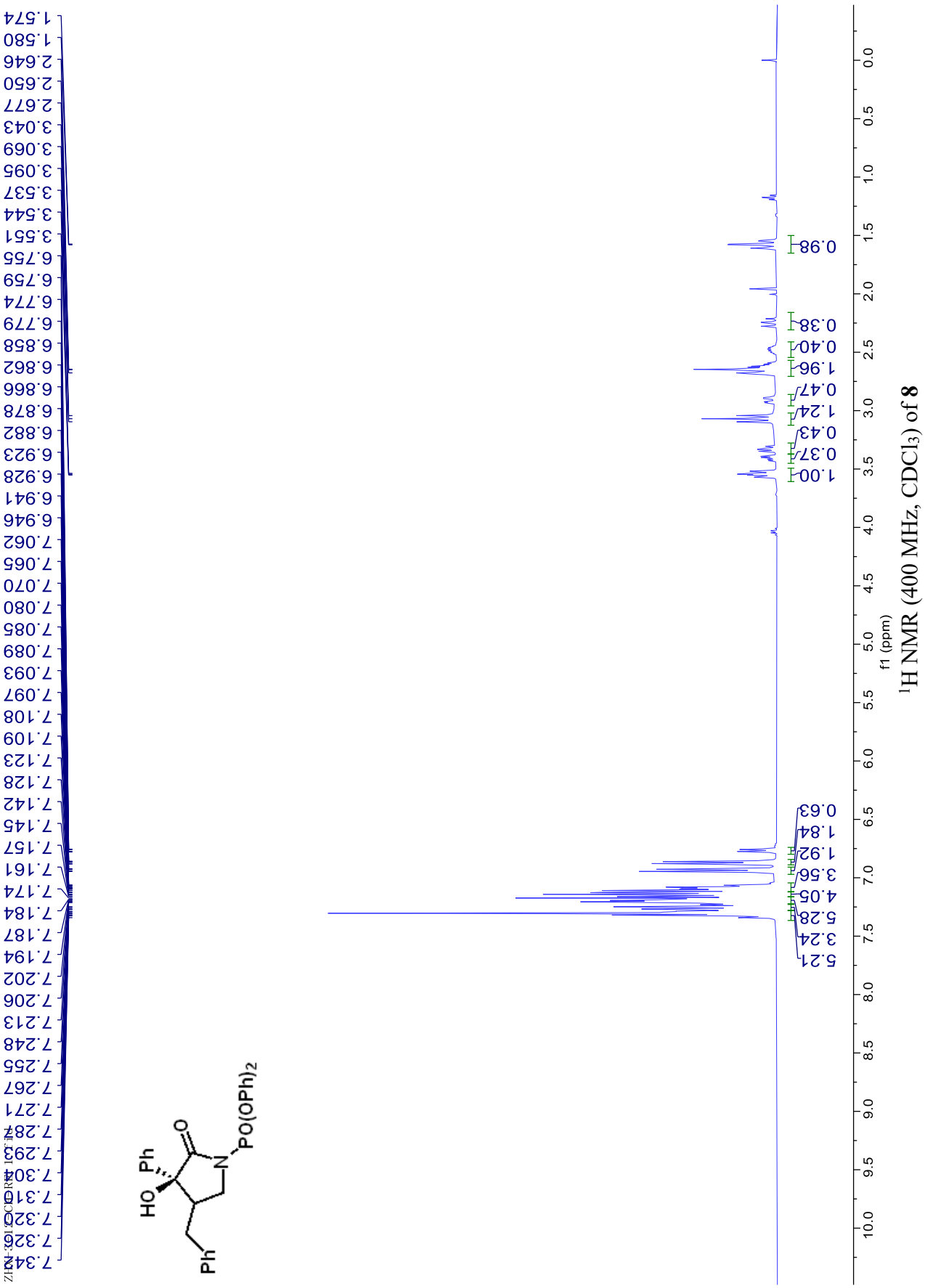


^{1}H NMR (400 MHz, $CDCl_3$) of **7**

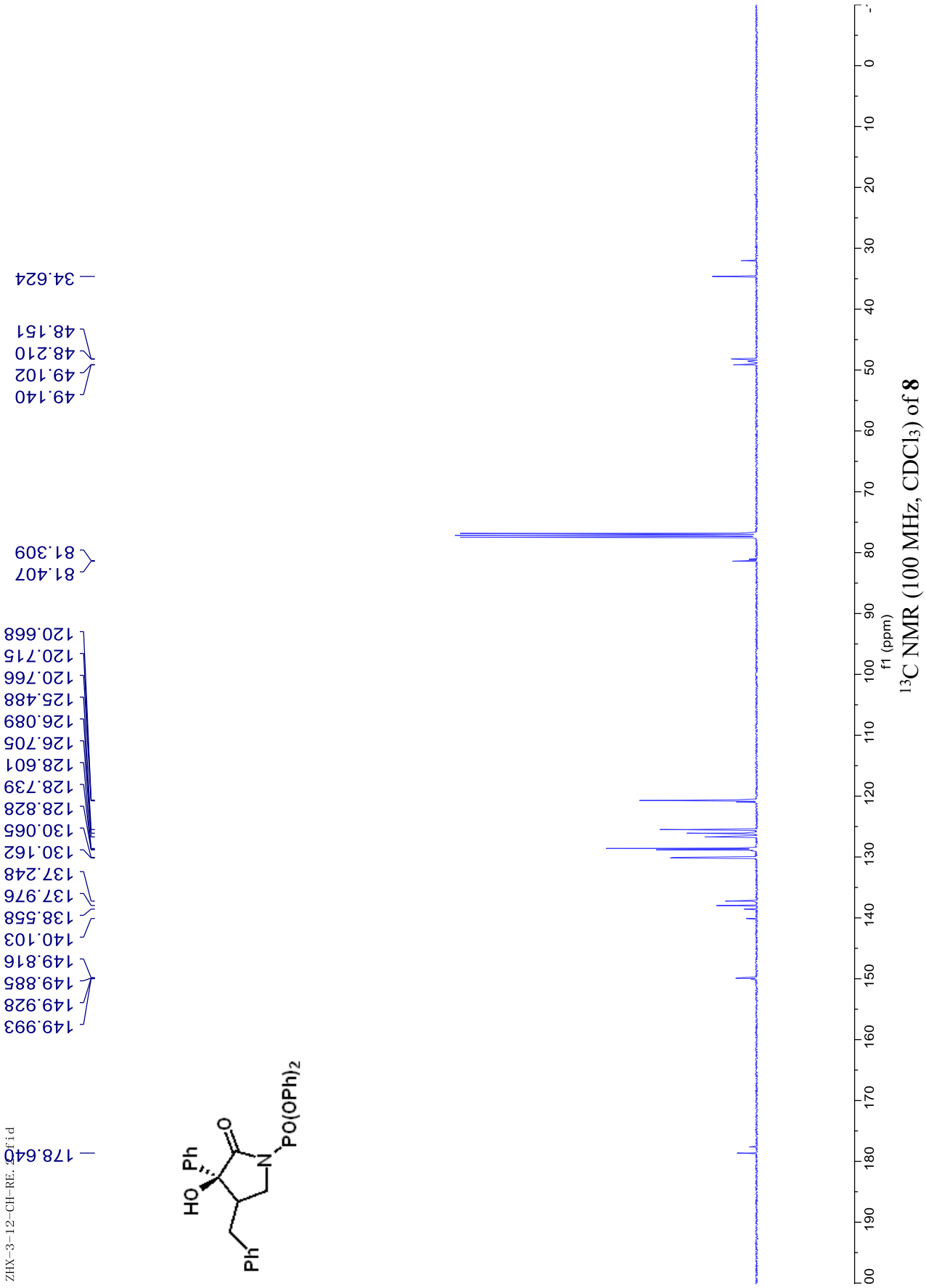

ZHX-3-7-CH.6.fid
175.028
165.470
150.157
150.086
149.921
149.853
138.897
134.184
132.929
130.738
130.033
129.993
129.179
129.139
128.794
128.346
126.914
125.994
125.496
123.401
121.140
121.095
120.758
120.710
79.324
79.231
55.982
55.891
49.673
49.471
f1 (ppm)
^{13}C NMR (100 MHz, CDCl$_3$) of **7**



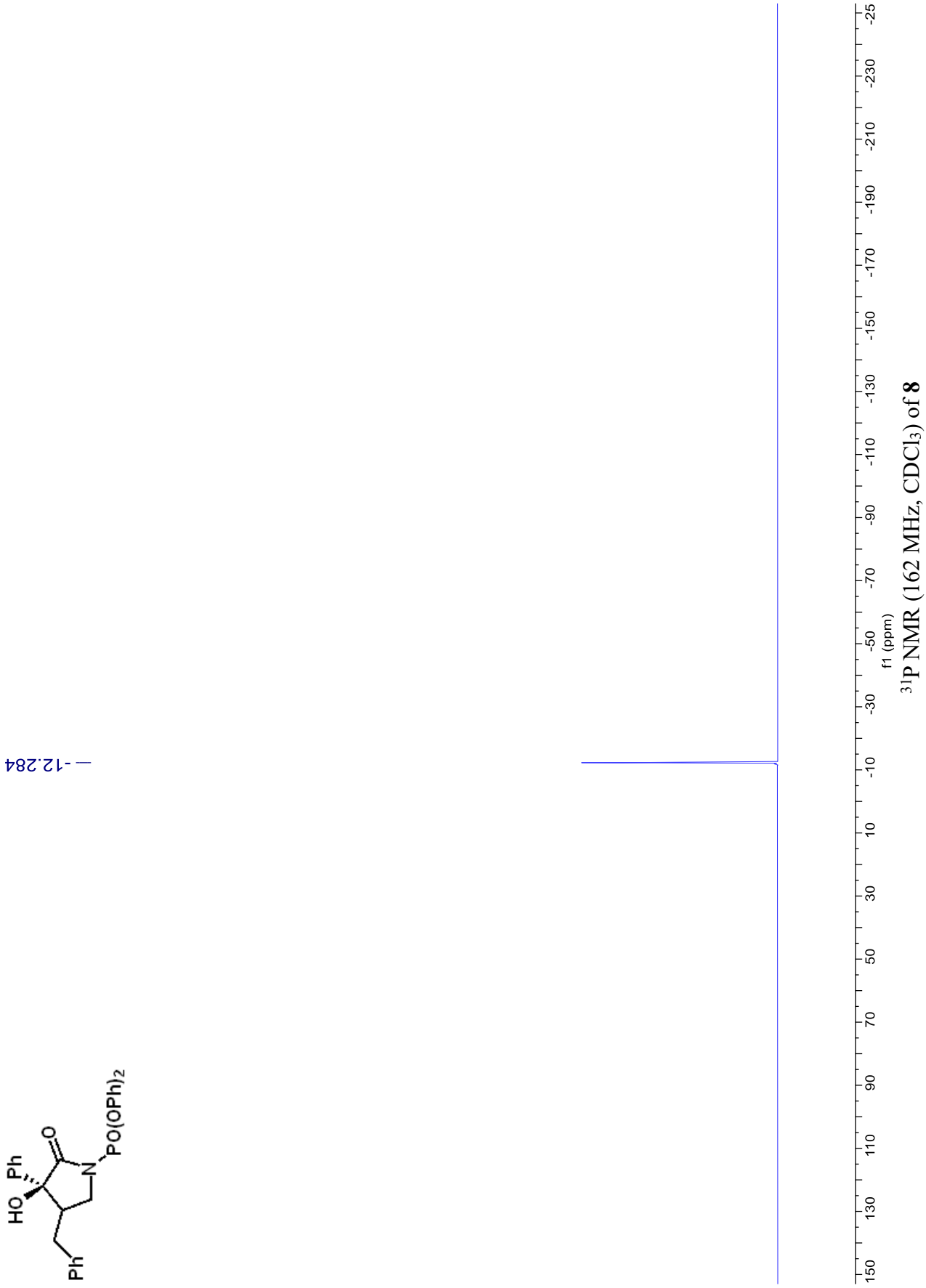
^{31}P NMR (162 MHz, $CDCl_3$) of **7**



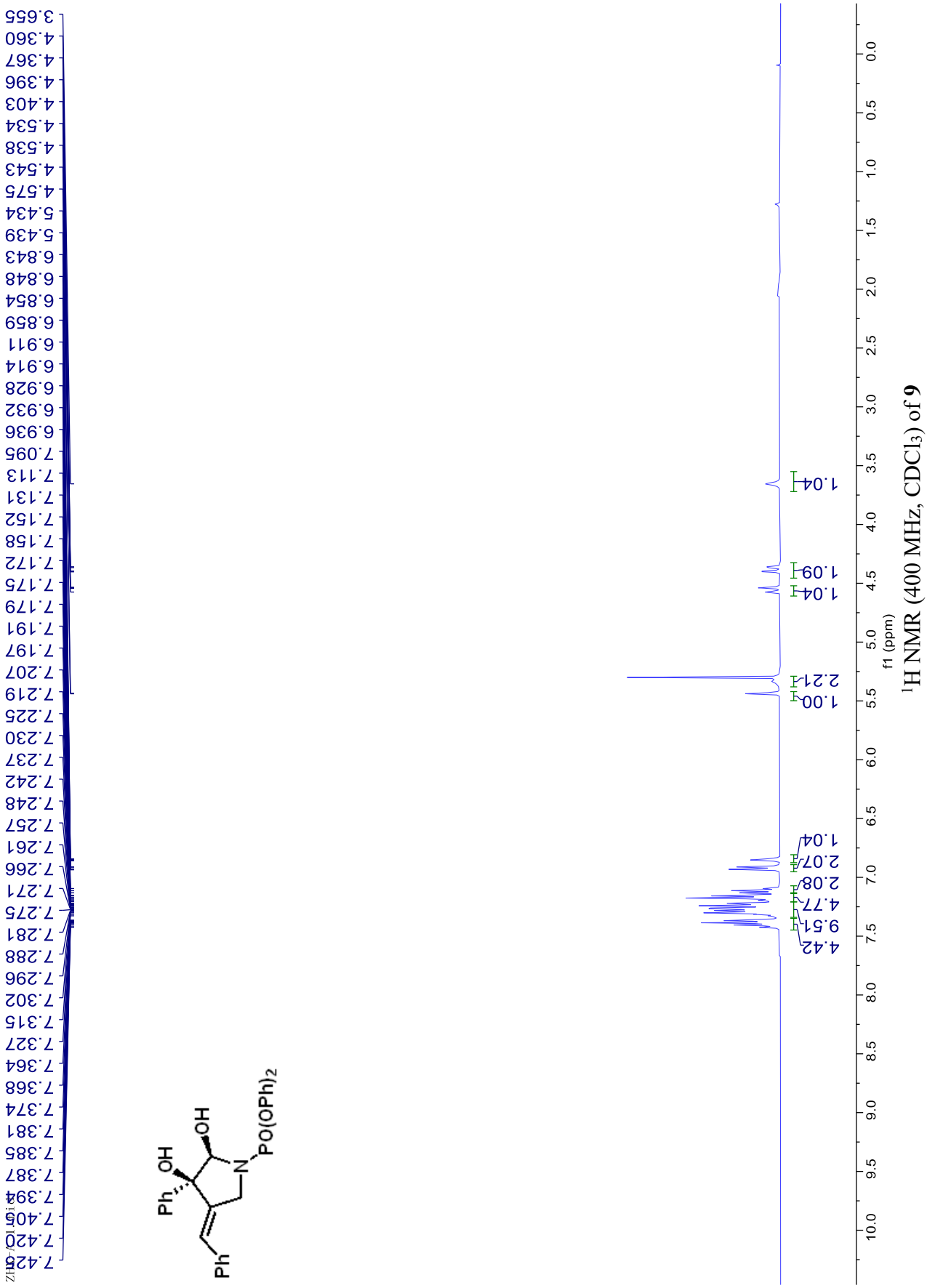
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



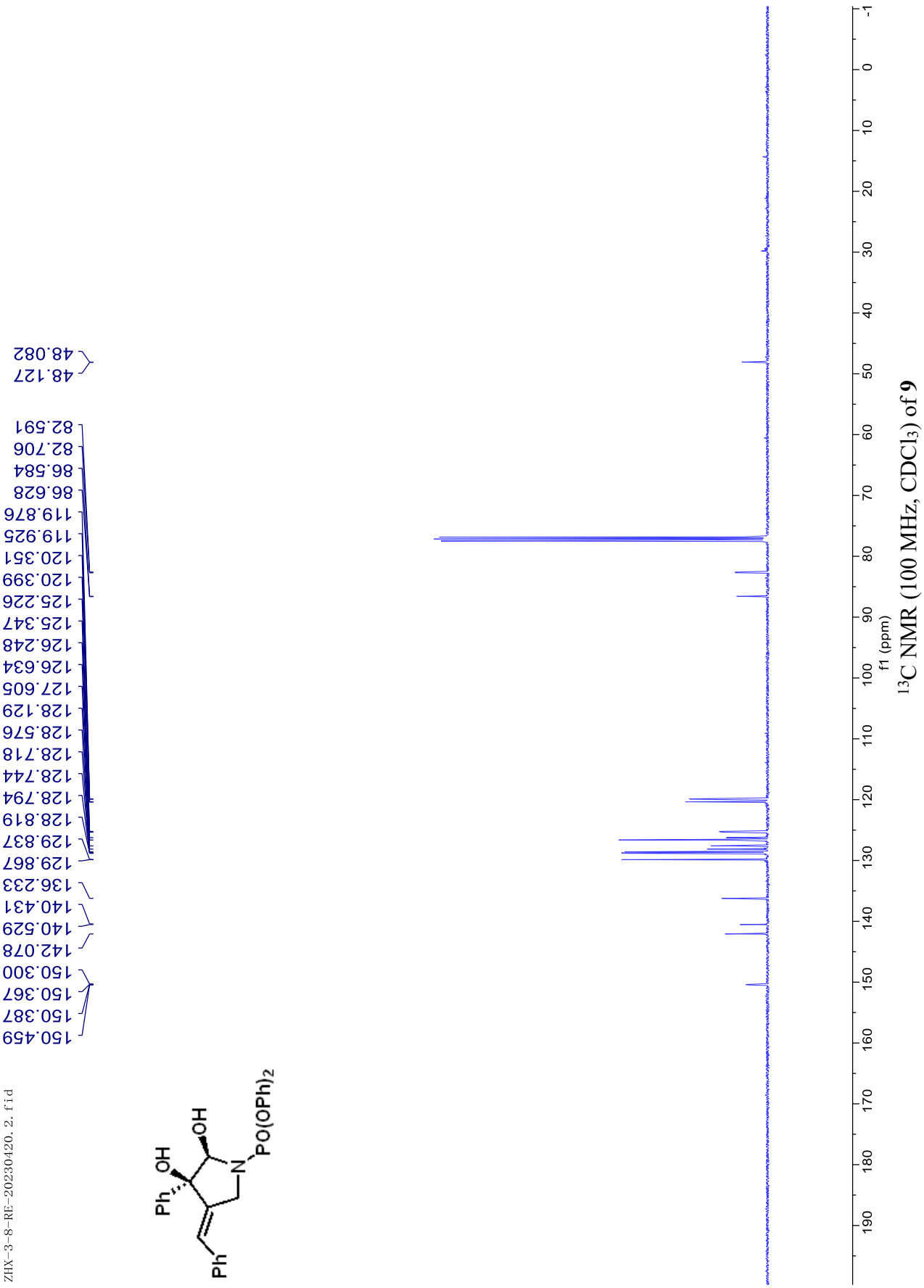
^{13}C NMR (100 MHz, $CDCl_3$) of **8**



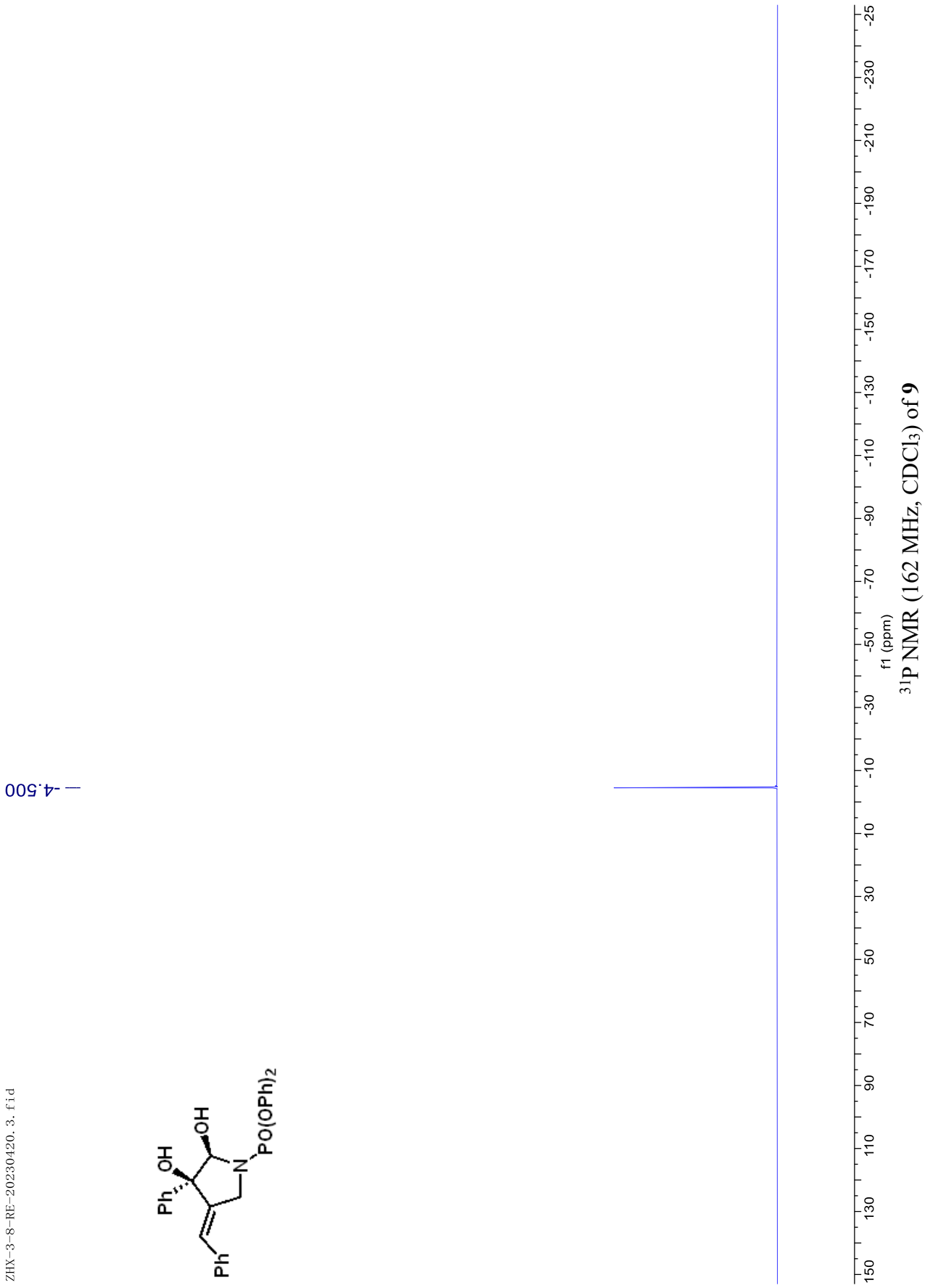
^{31}P NMR (162 MHz, $CDCl_3$) of **8**



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



^{13}C NMR (100 MHz, $CDCl_3$) of **9**



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