Supporting Information

Metal- and Oxidant-Free S–P(O) Bond Construction via Direct Coupling of P(O)H with Sulfinic Acids

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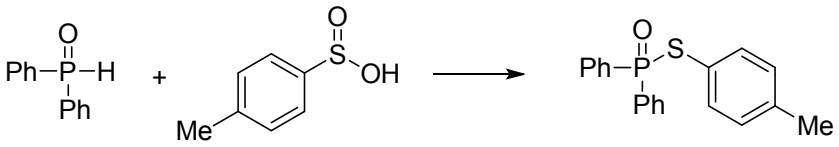
I. Optimization Study

Table S1. Optimization study of diphenylphosphine oxide with 4-methylbenzene sulfinic acid.[a]

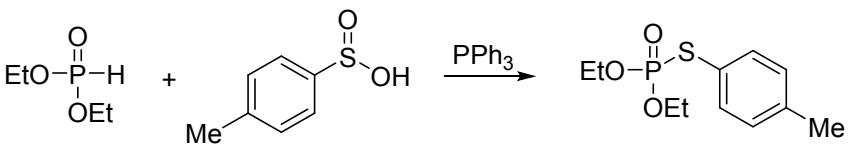


Entry	Additive	Solvent	Yield(%)[b]
1[c]	pyridine	PhMe	40
2[c]	pyridine	MeCN	28
3[c]	pyridine	DCE	21
4	pyridine	PhMe	42
5	-	PhMe	44
6	Cy_3P	PhMe	trace
7	$(C_6F_5)_3P$	PhMe	51
8	$(4\text{-MeOPh})_3P$	PhMe	69
9	Ph_3P	PhMe	72
10	$(4\text{-FPh})_3P$	PhMe	56
11	$(2\text{-furyl})_3P$	PhMe	33
12	$(2\text{-pyridyl})Ph_2P$	PhMe	N.R.
13	$(benzyl)_3P$	PhMe	N.R.
14	Ph_2CyP	PhMe	trace
15	$(o\text{-tolyl})_3P$	PhMe	53
16	$(t\text{-Bu})_3P$	PhMe	29
17[d]	Ph_3P	PhMe	56
18	Ph_3P	DMF	trace

19	Ph_3P	DMSO	20
20	Ph_3P	EtOH	57
21	Ph_3P	EtOAc	57
22	Ph_3P	MeCN	62
23	Ph_3P	H_2O	trace
24	Ph_3P	THF	trace
25	Ph_3P	Acetone	12
26	**Ph_3P**	***i*PrOAc**	**86**
27	Ph_3P	*t*BuOAc	82
28[e]	Ph_3P	*i*PrOAc	83
29[f]	Ph_3P	*i*PrOAc	trace
30[f]	Ph_3P	*i*PrOAc/H_2O(9:1)	N.R.
31[f]	Ph_3P	*i*PrOAc/TFA(9:1)	N.R.
32[f]	Ph_3P	*i*PrOAc/AcOH(9:1)	N.R.
33	Ph_3P/TFA	*i*PrOAc	trace
34	Ph_3P/AcOH	*i*PrOAc	trace

[a] Reaction conditions: diphenylphosphine oxide (0.17 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), additive (1.0 equiv), and solvent (1.0 mL) at room temperature under N_2 for 24 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] under O_2. [d] 4-methylbenzenesulfinic acid (1.5 equiv). [e] 40 °C [f] sodium 4-methylbenzenesulfinate was used. N.R. = no reaction.

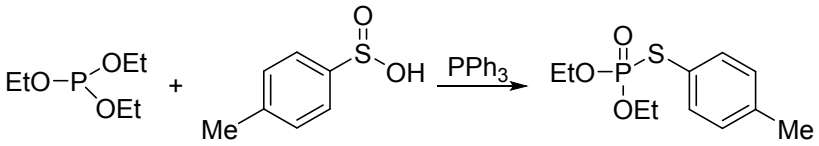
Table S2. Optimization study of diethyl phosphite with 4-methylbenzene sulfinic acid.[a]



Entry	Additive	Solvent	Temp.	Yield(%)[b]
1	-	PhMe	R.T.	N.R.
2	-	*i*PrOAc	R.T.	N.R.
3	-	MeCN	R.T.	N.R.
4	-	*t*BuOAc	R.T.	N.R.
5	-	DMF	R.T.	N.R.
6	DBU (1equiv)	PhMe	R.T.	trace
7	TMG (1equiv)	PhMe	R.T.	trace
8	TEA (1equiv)	PhMe	R.T.	N.R.
9	pyridine (1equiv)	PhMe	R.T.	N.R.
10	DBU (1equiv)	MeCN	R.T.	7
11	DBU (1equiv)	DMF	R.T.	N.R.
12	DBU (1equiv)	*i*PrOAc	R.T.	N.R.
13	DBU (1equiv)	THF	R.T.	N.R.
14	Na_2CO_3 (1equiv)	MeCN	R.T.	N.R.
15	$NaHCO_3$ (1equiv)	MeCN	R.T.	N.R.
16	DIPEA (1equiv)	MeCN	R.T.	trace
17	DABCO (1equiv)	MeCN	R.T.	N.R.
18	DBU (1equiv)	MeCN	40	11
19	**DBU (1equiv)**	**MeCN**	**60**	**54**
20	DBU (1equiv)	MeCN	80	45
21[c]	DBU (1equiv)	MeCN	60	11
22	-	MeCN	60	6

[a] Reaction conditions: diethylphosphite (0.10 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), triphenylphosphine (1.0 equiv), additive, and solvent (1.0 mL) at room temperature under N_2 for 13 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] no triphenylphophine. N.R. = no reaction. R.T. = room temperature

Table S3. Optimization study of triethyl phosphite with 4-methylbenzene sulfinic acid.[a]



Entry	Additive	Solvent	Temp	Yield(%)[b]
1	-	MeCN	R.T.	17
2	-	PhMe	R.T.	15
3	-	DMF	R.T.	13
4	-	THF	R.T.	10
5	-	*i*PrOAc	R.T.	14
6	-	DMF	60	20
7	-	DMF	80	50
8	-	DMF	100	33
9	-	DMF	120	19
10	-	PhMe	80	28
11	-	DME	80	N.R.
12	-	Dioxane	80	22
13	-	MeCN	80	41
14	-	*i*PrOAc	80	20
15	-	EtOH	80	trace

16	**-**	**DMSO**	**80**	**61**
17	aectic acid (10%)	DMSO	80	24
18	Water (3equiv)	DMSO	80	26
19	DMSO (10%)	MeCN	80	42
20	DMSO (10%)	DME	80	N.R.
21	DMSO (10%)	*i*PrOAc	80	29
22	DMSO (10%)	THF	80	40
23	DMSO (10%)	PhMe	80	55
24[c]	-	DMSO	80	33

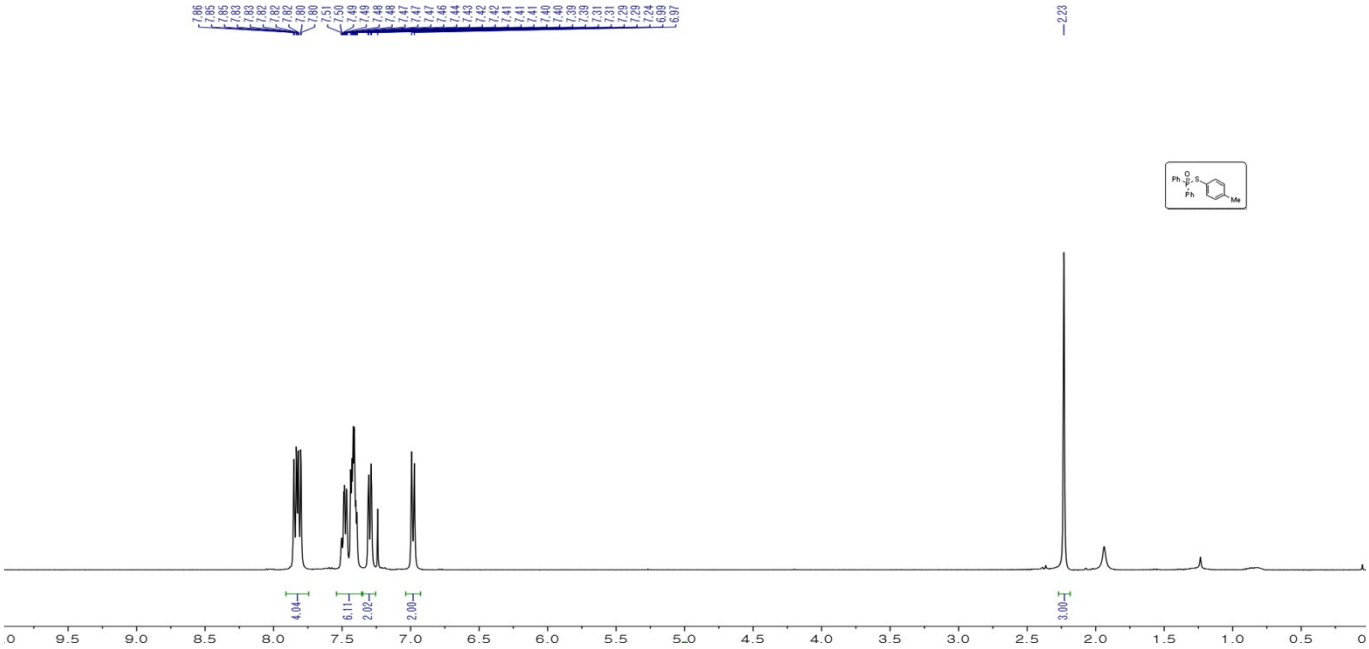
[a] Reaction conditions: triethyl phosphite (0.10 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), triphenylphosphine (1.0 equiv), additive, and solvent (1.0 mL) at room temperature under N_2 for 13 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] no triphenylphosphine. N.R. = no reaction. R.T. = room temperature.

Appendix I

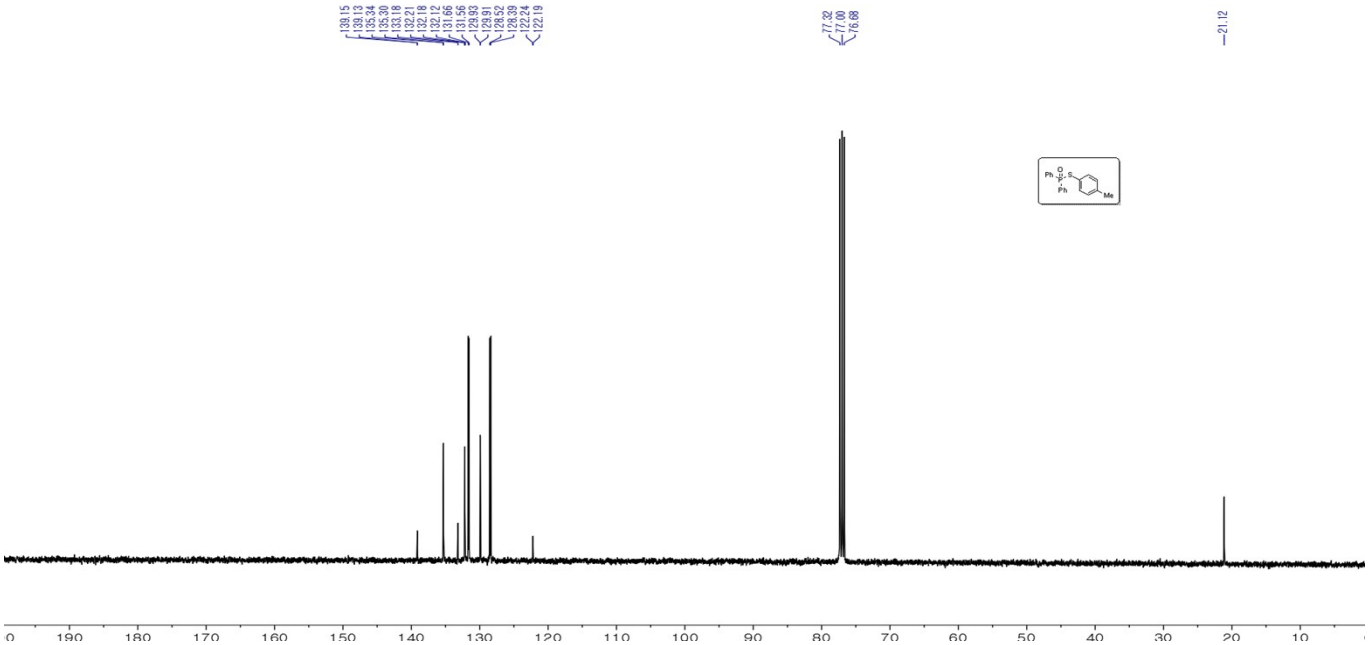
Spectral Copies of ^{1}H, ^{13}C, and ^{31}P NMR Data

Obtained in this Study

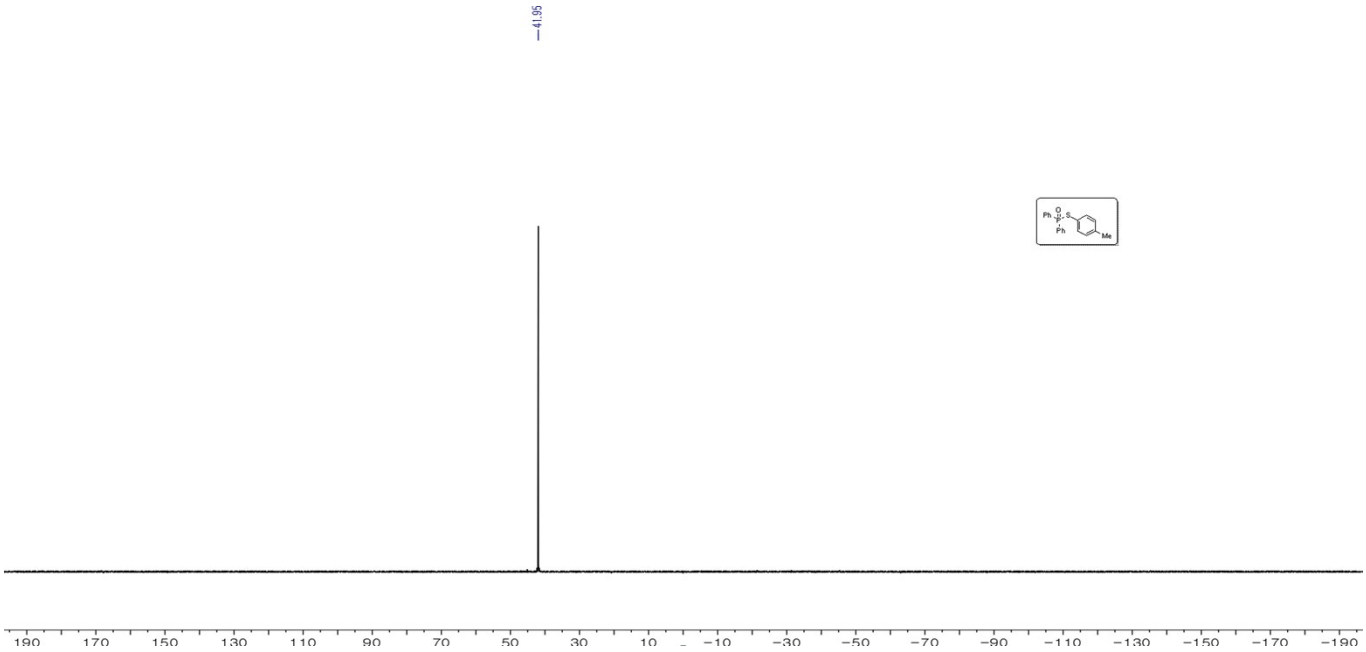
S-p-tolyl diphenylphosphinothioate (3a)



400 MHz, ^{1}H NMR in $CDCl_3$

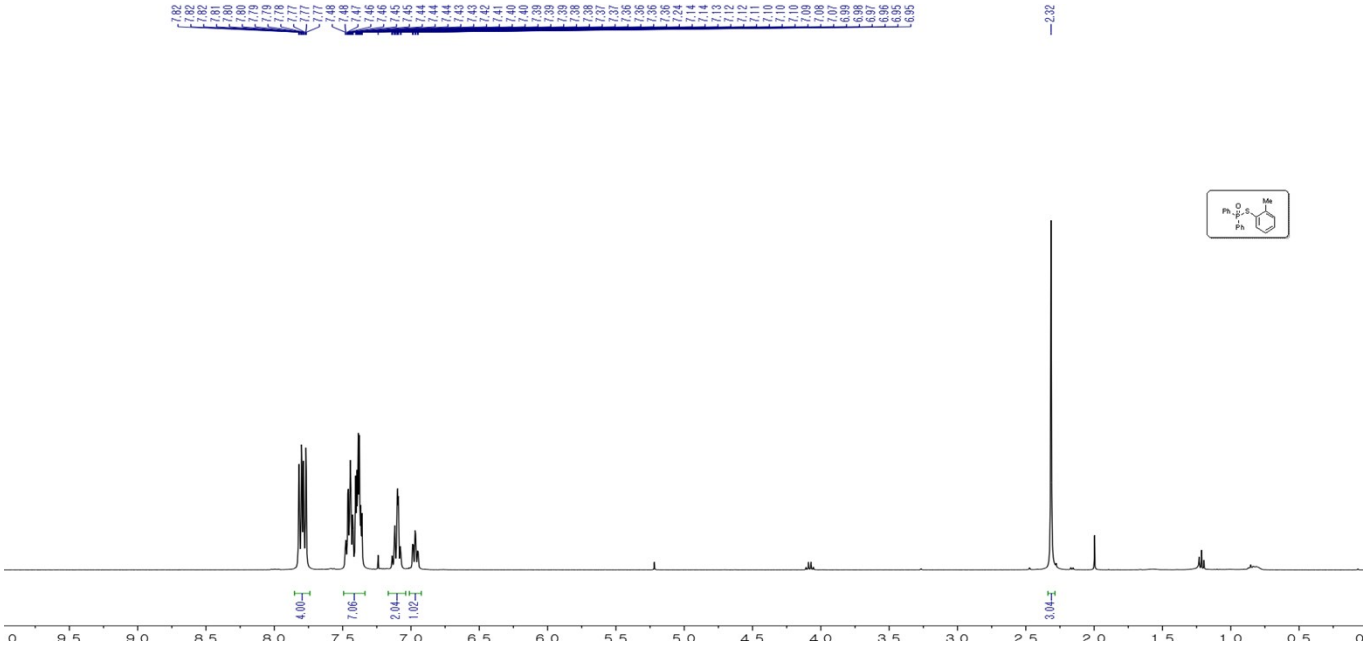


100 MHz, ^{13}C NMR in $CDCl_3$

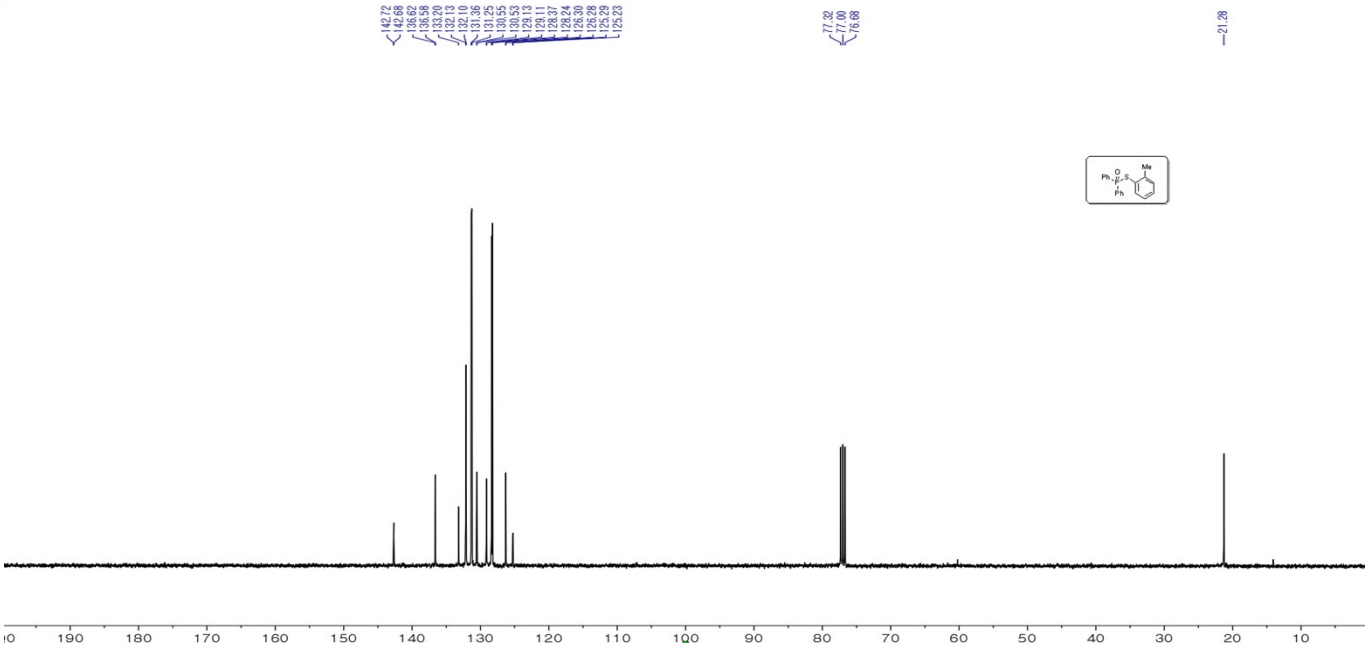


162 MHz, ^{31}P NMR in $CDCl_3$

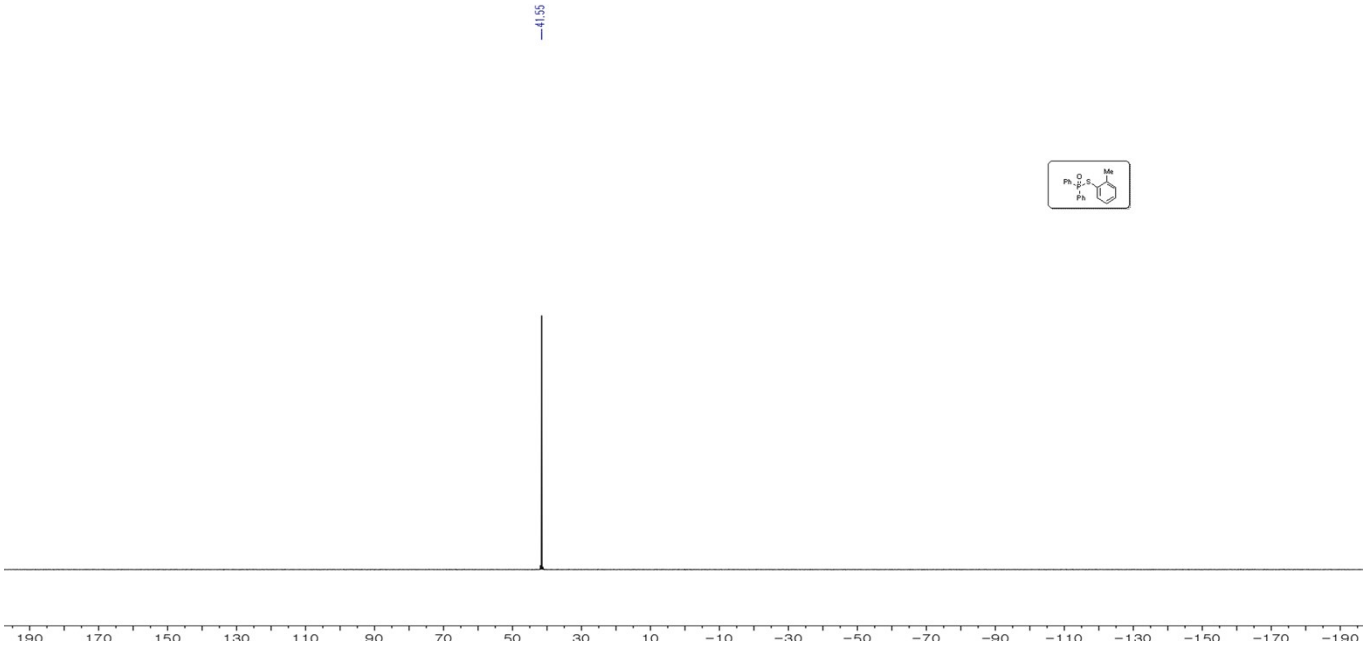
S-o-tolyl diphenylphosphinothioate (3b)



400 MHz, ^{1}H NMR in $CDCl_3$

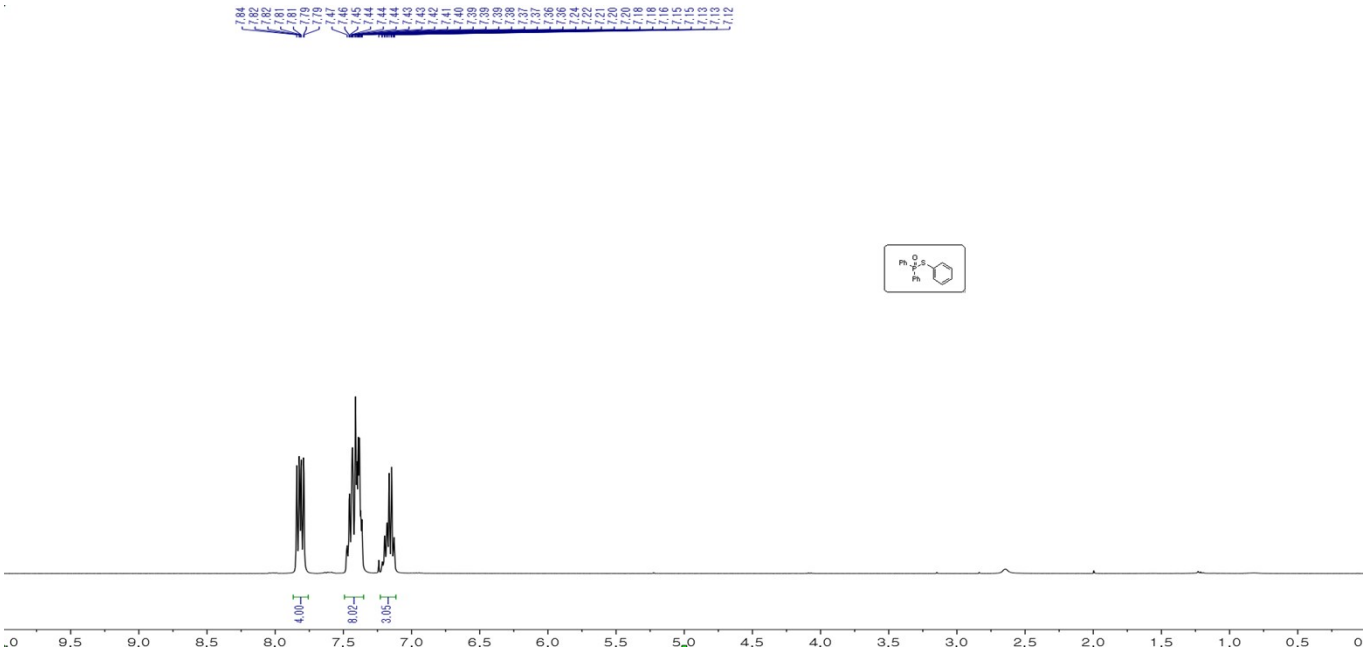


100 MHz, ^{13}C NMR in $CDCl_3$

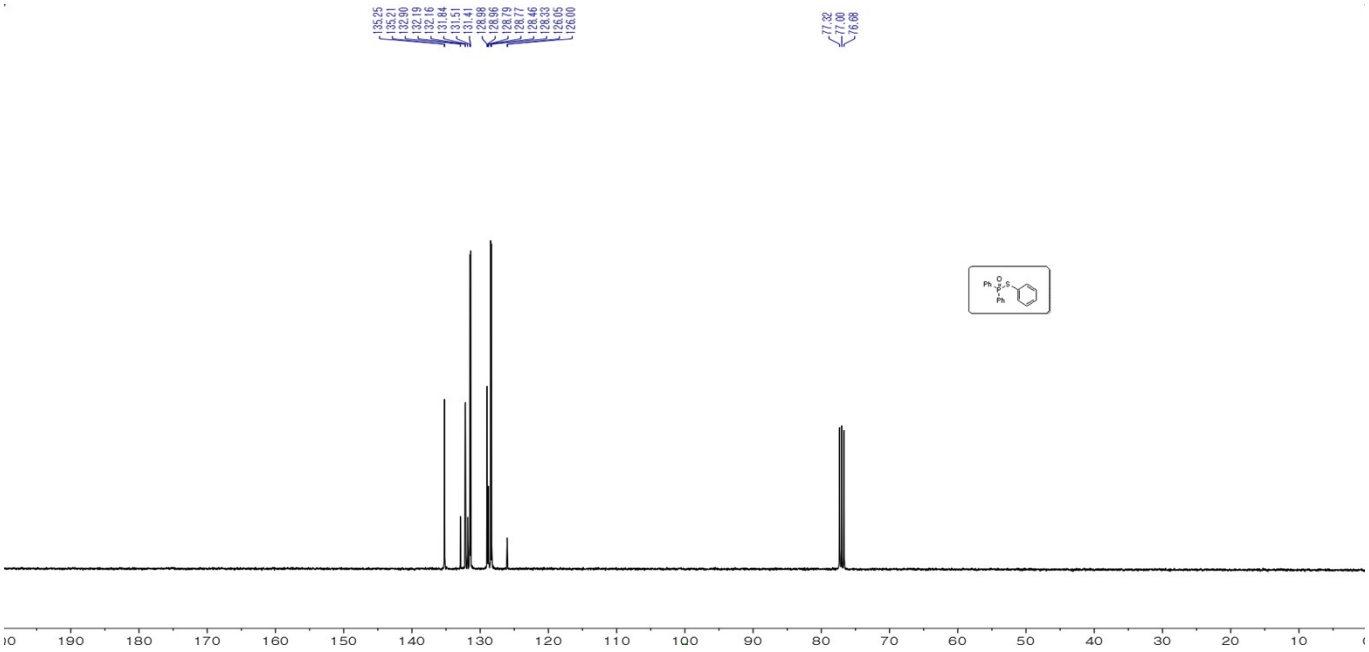


162 MHz, ^{31}P NMR in $CDCl_3$

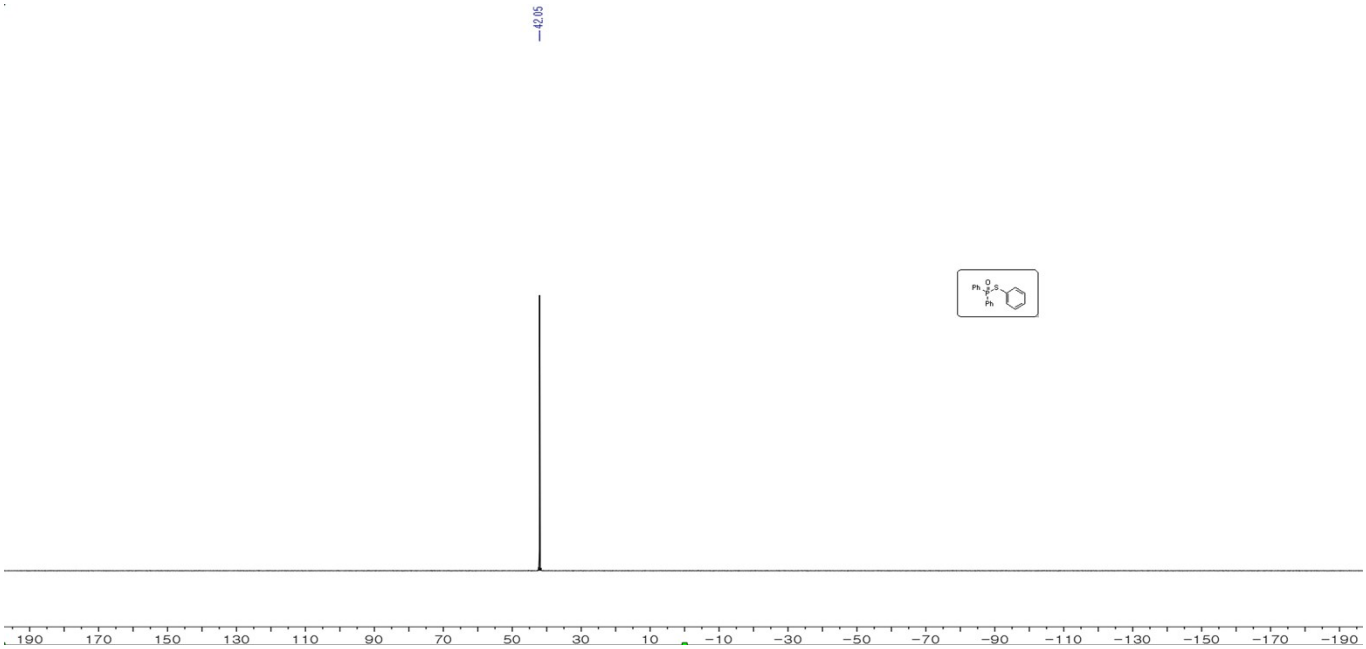
S-phenyl diphenylphosphinothioate (3c)



400 MHz, ^{1}H NMR in $CDCl_3$

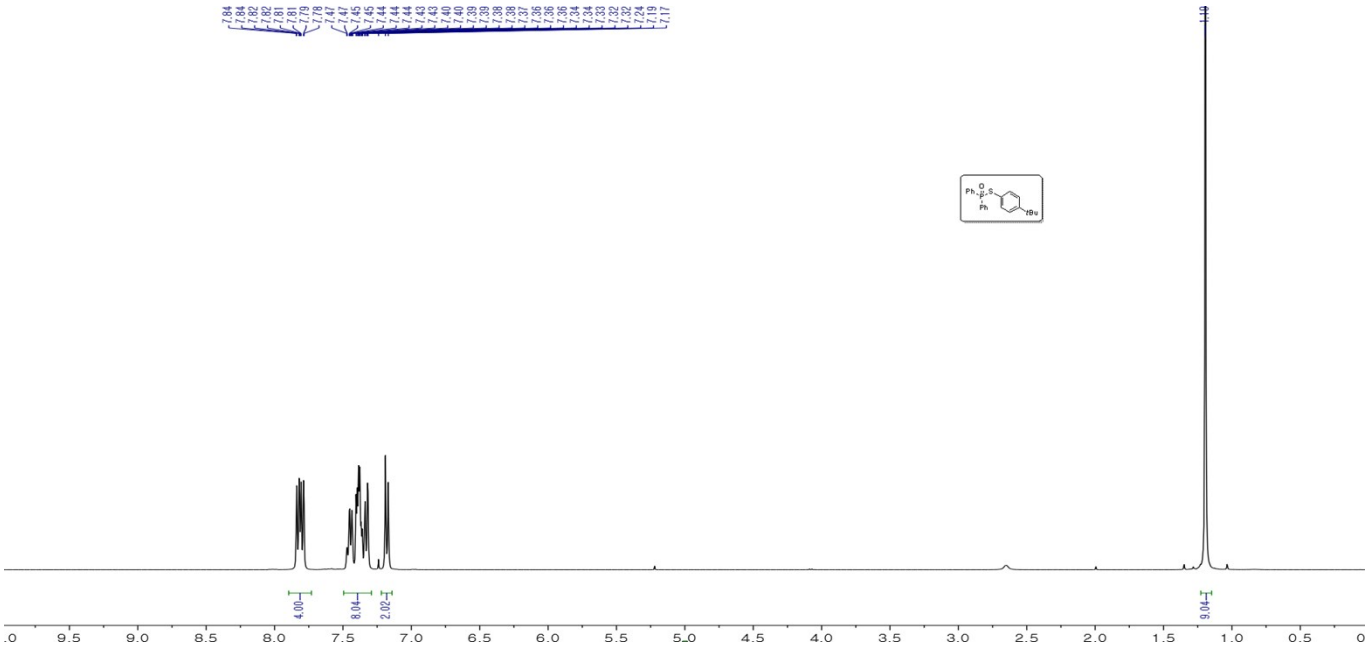


100 MHz, ^{13}C NMR in $CDCl_3$



162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (3d)



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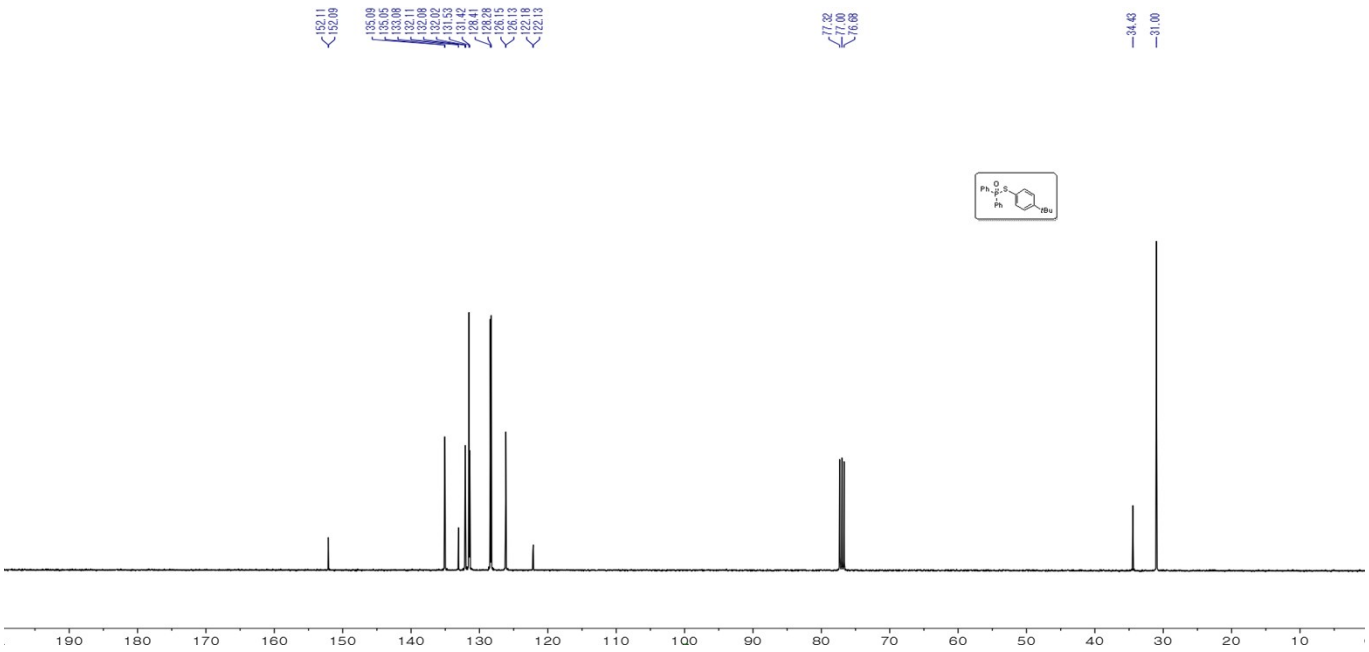
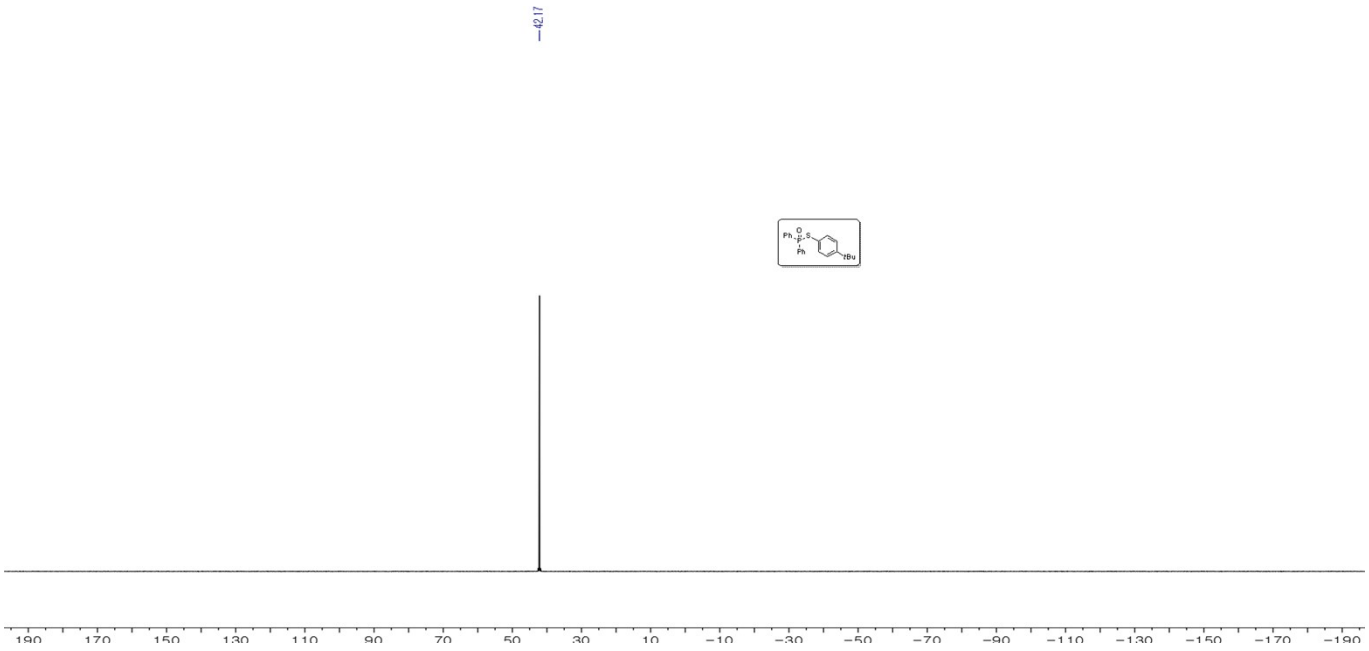
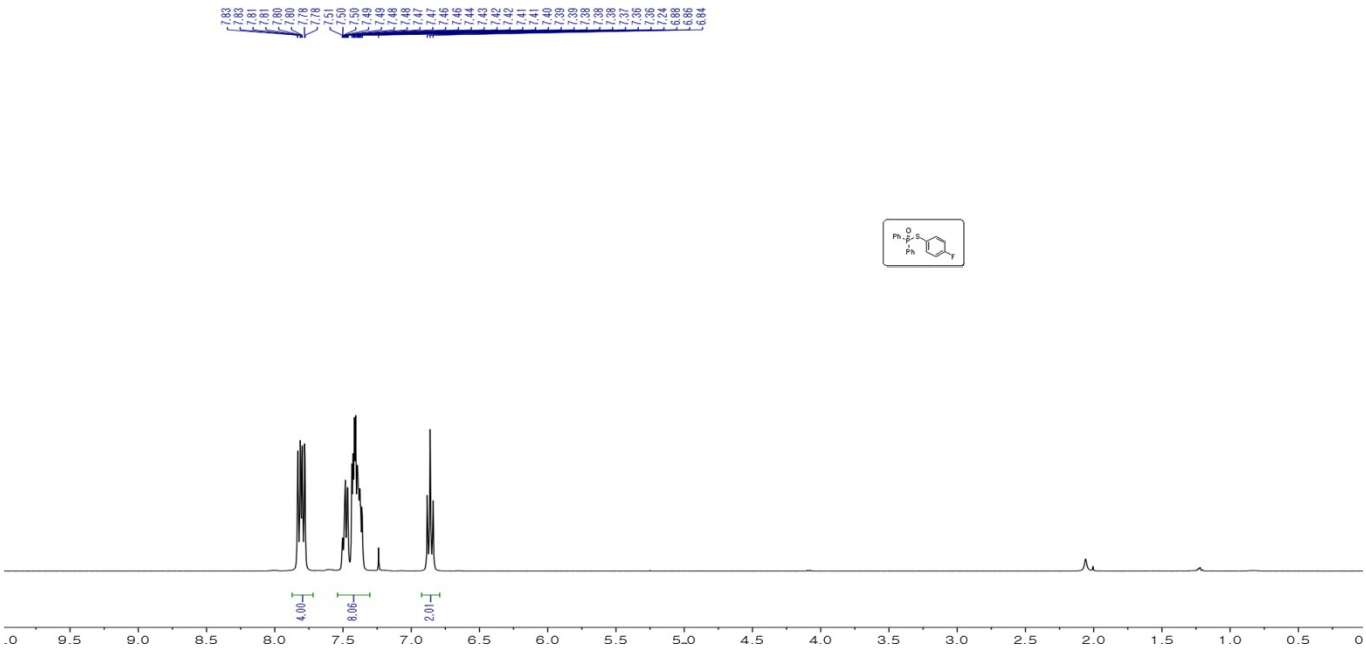


100 MHz, ^{13}C NMR in $CDCl_3$

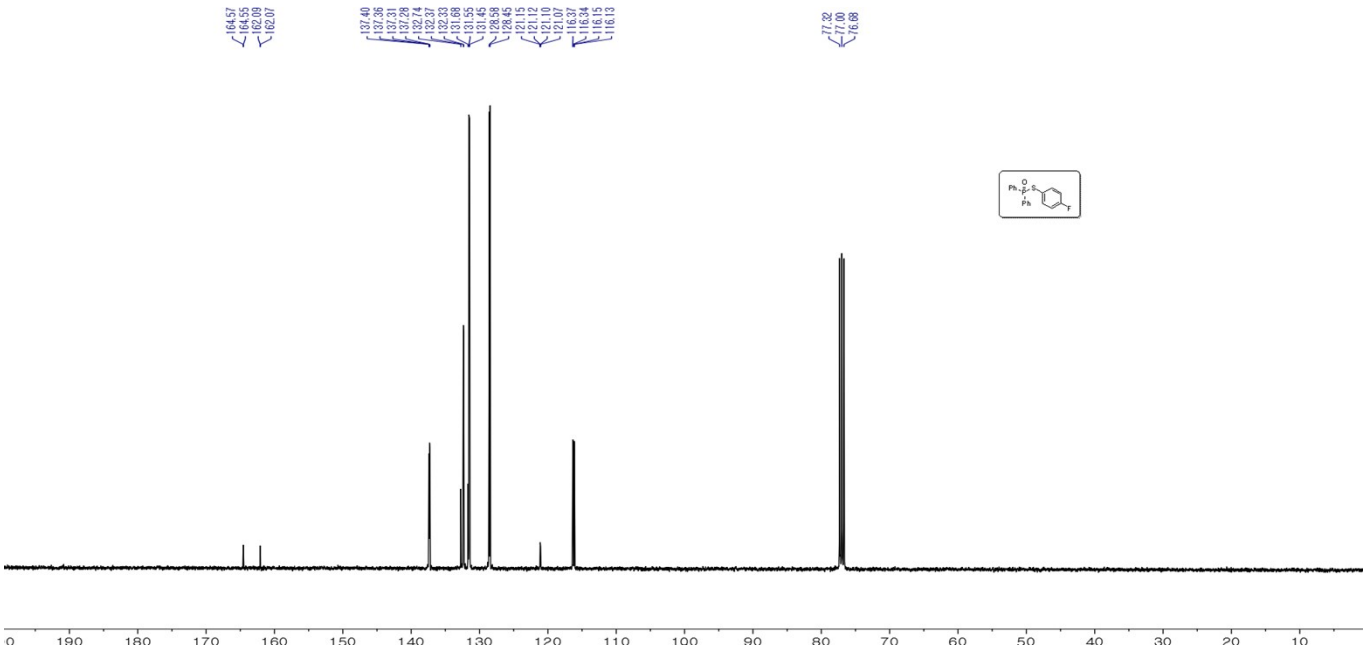


162 MHz, ^{31}P NMR in $CDCl_3$

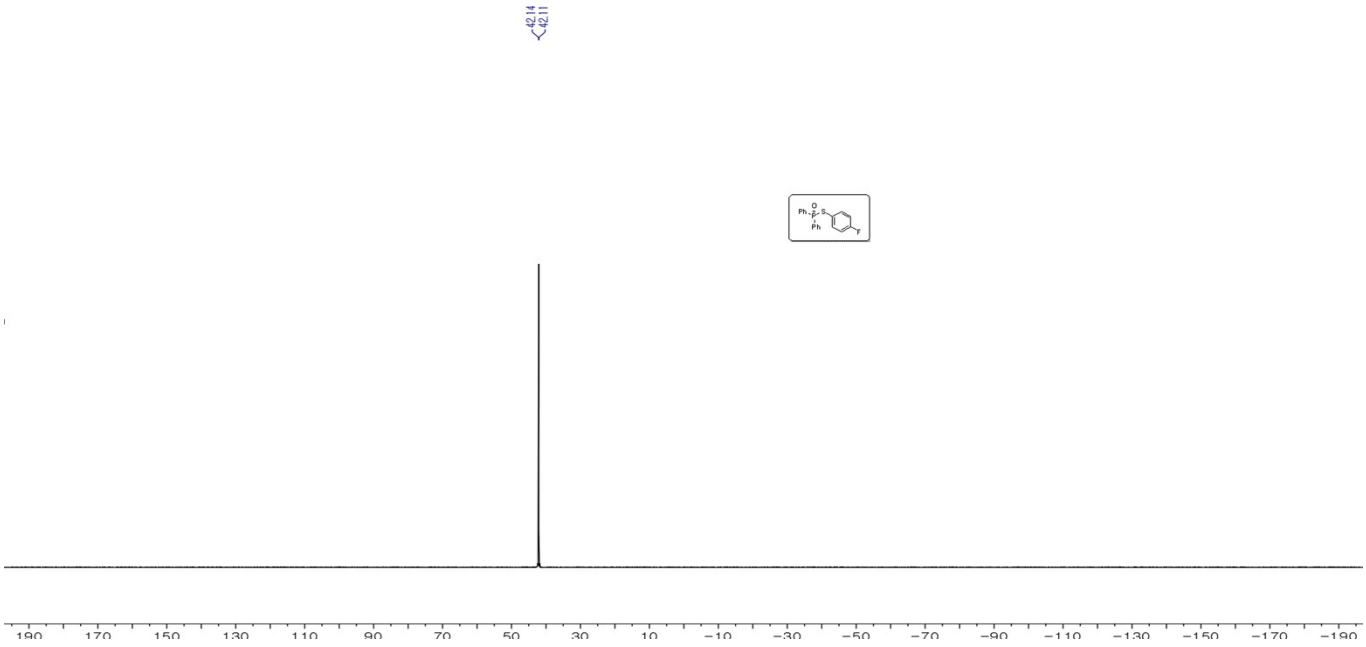
S-(4-fluorophenyl) diphenylphosphinothioate (3e)



400 MHz, ^{1}H NMR in $CDCl_3$

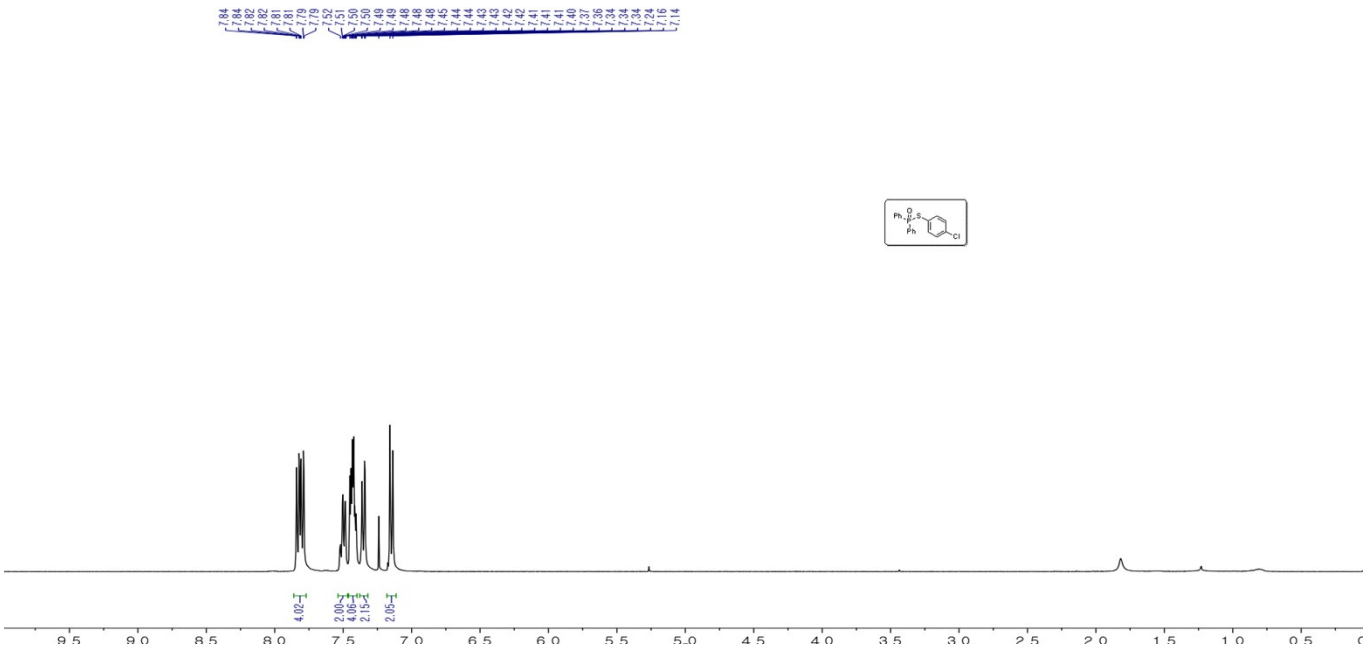


100 MHz, ^{13}C NMR in $CDCl_3$



162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-chlorophenyl) diphenylphosphinothioate (3f)



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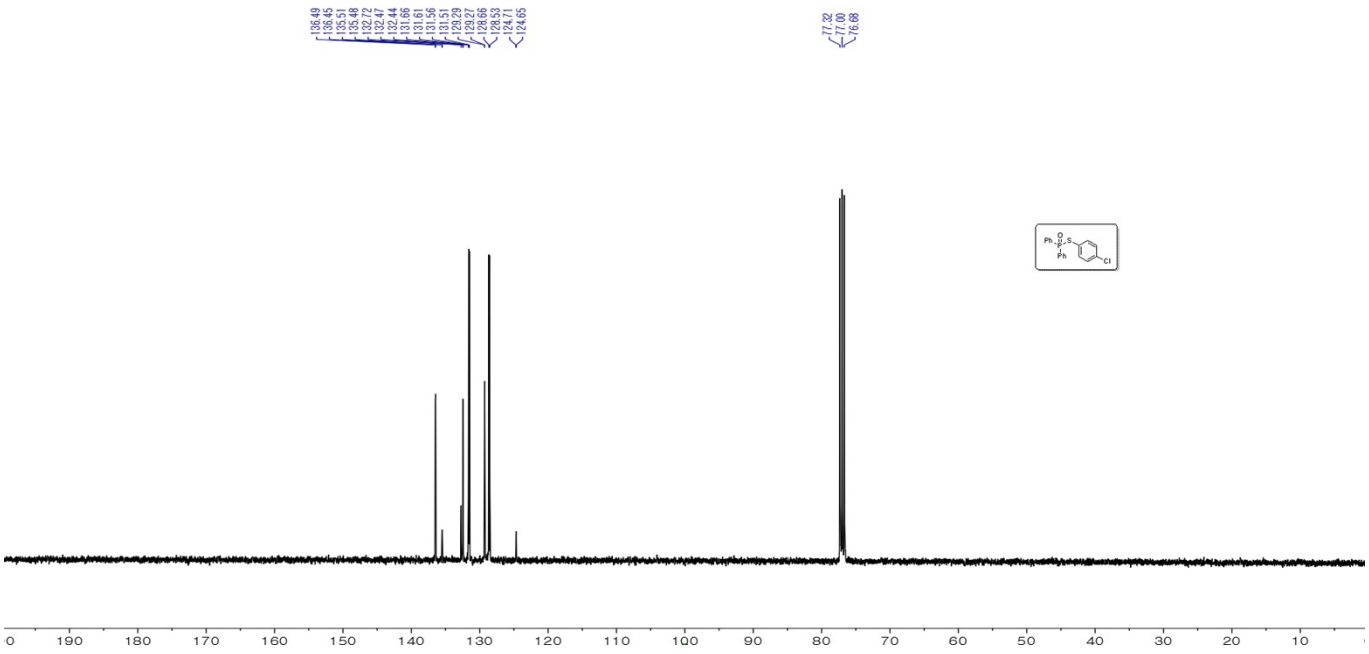
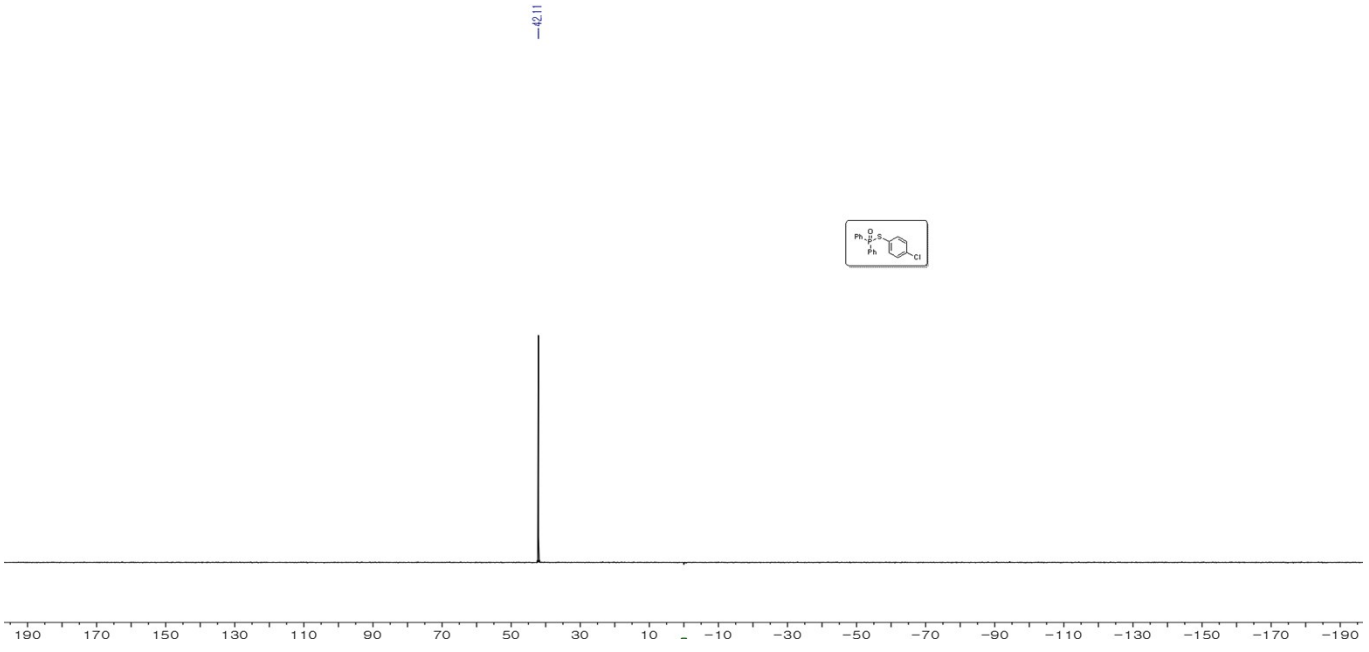
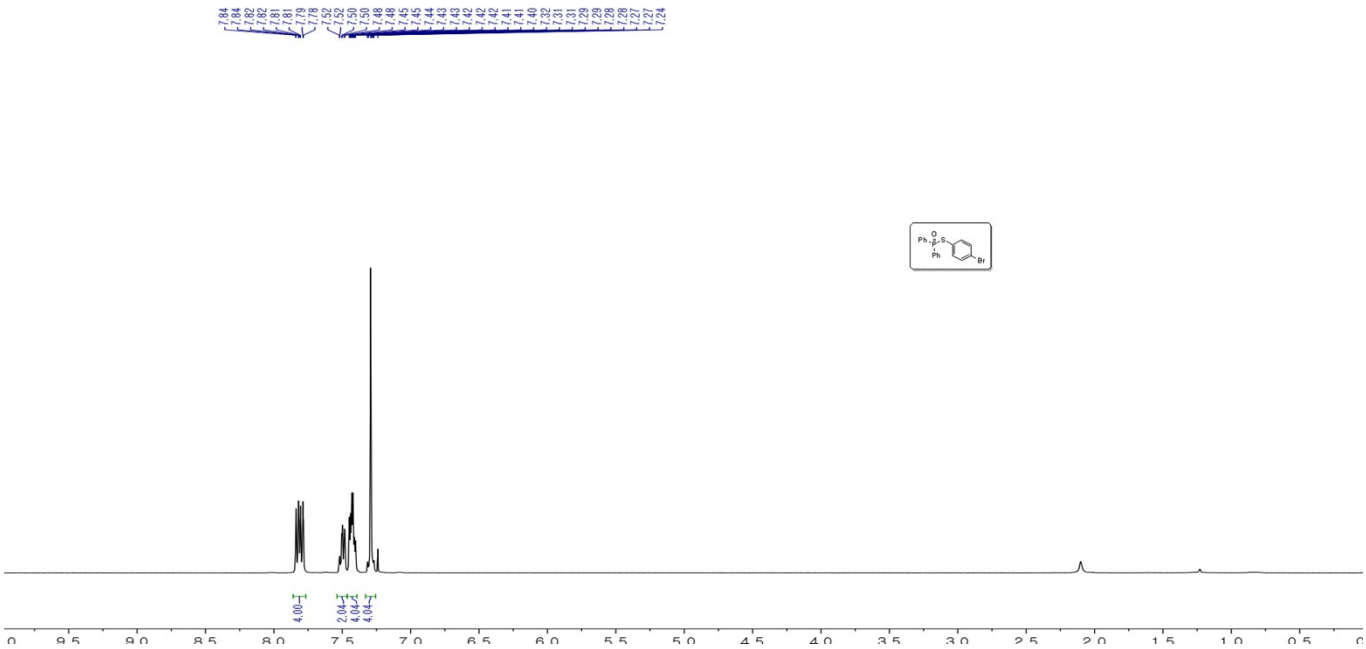


100 MHz, ^{13}C NMR in $CDCl_3$



162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-bromophenyl) diphenylphosphinothioate (3g)



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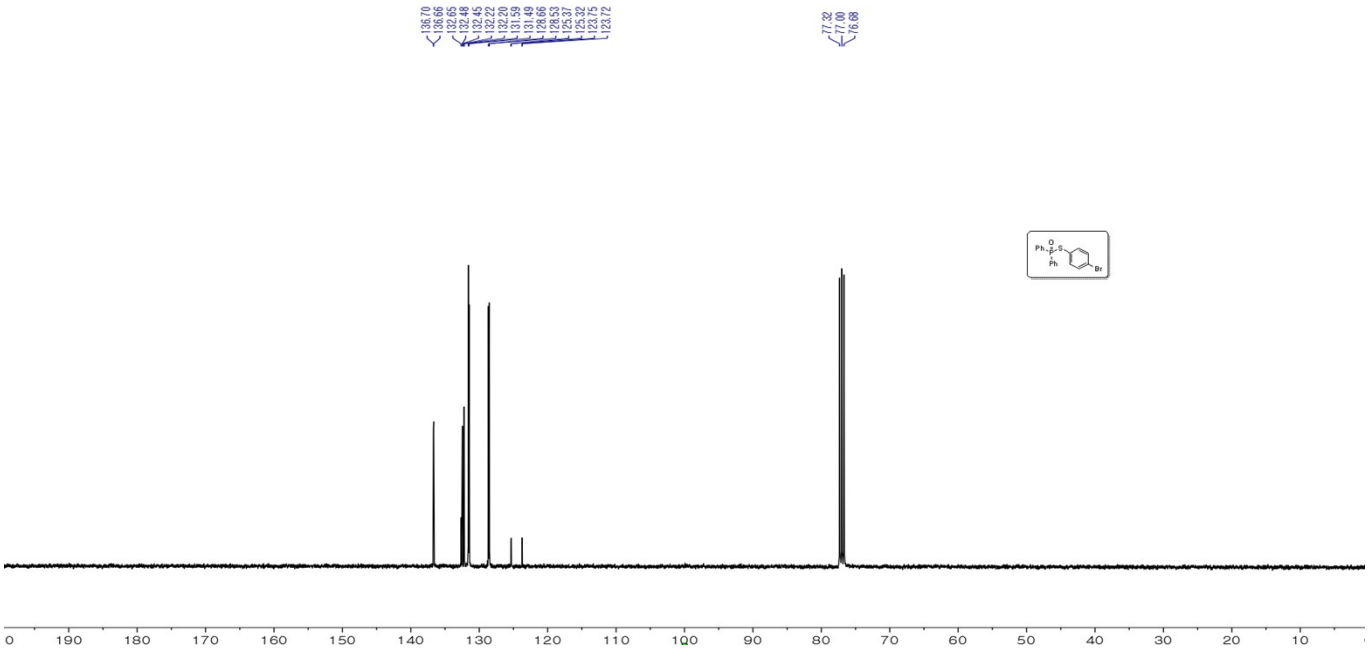

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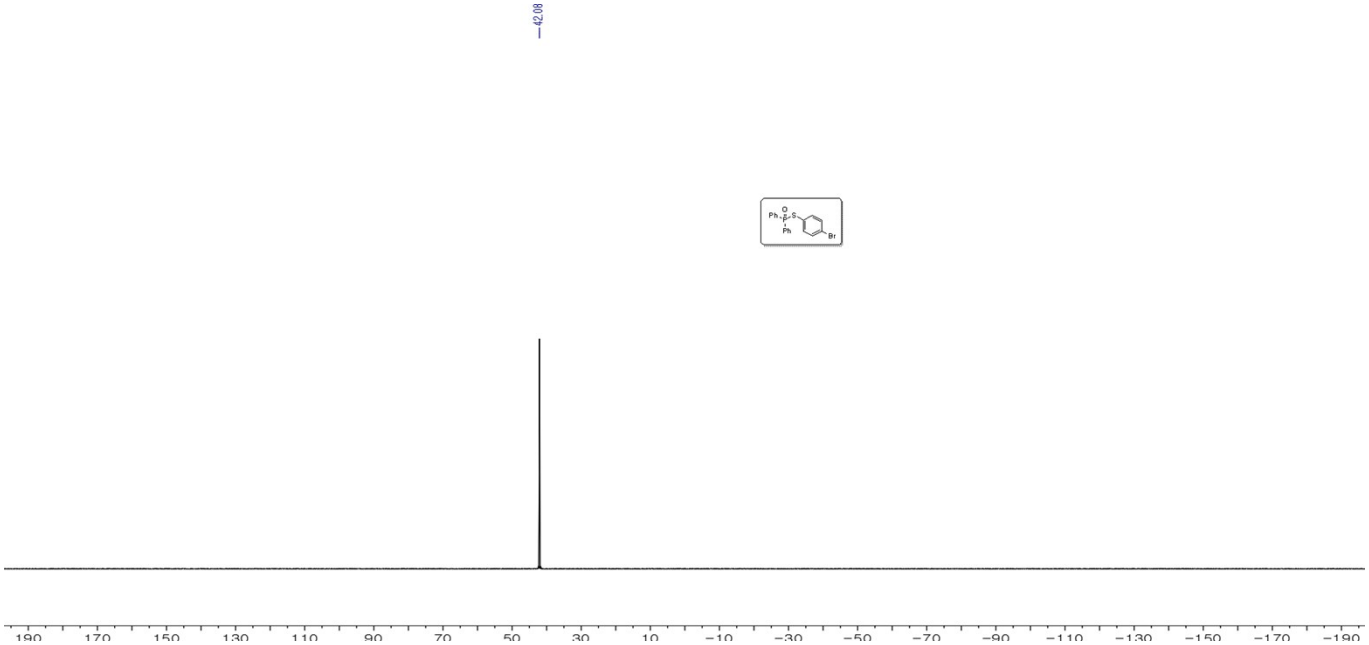
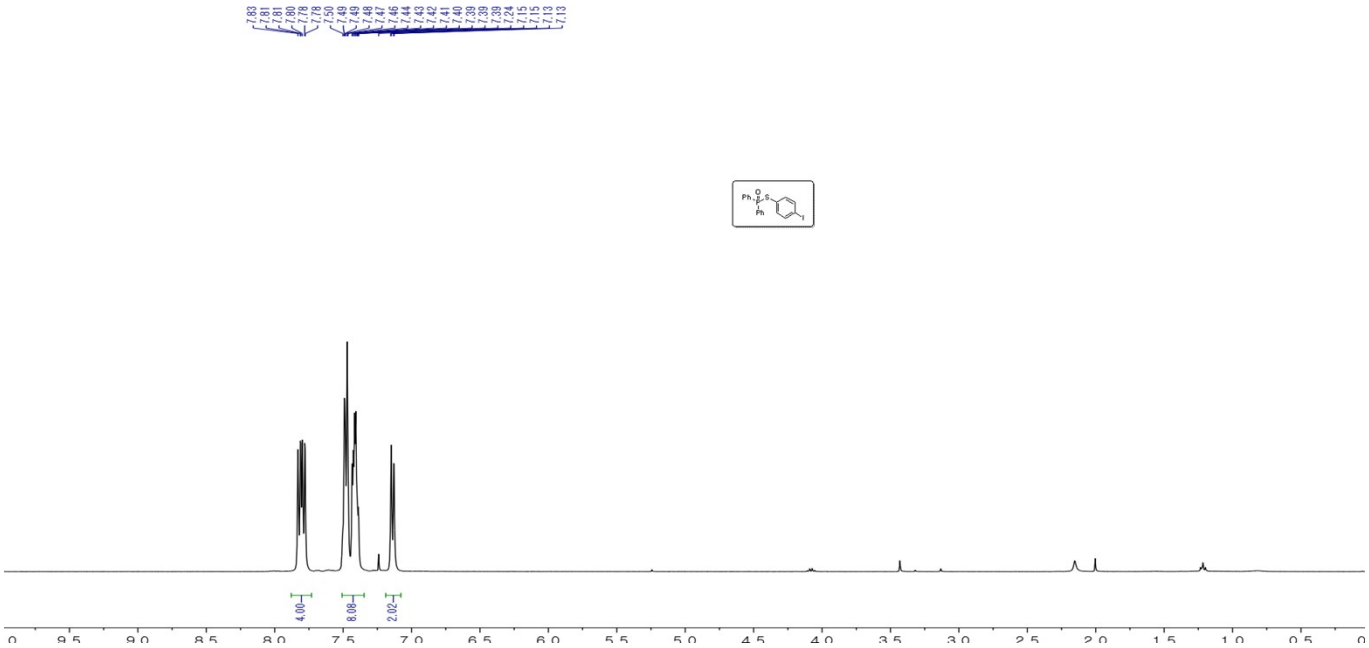


162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-iodophenyl) diphenylphosphinothioate (3h)



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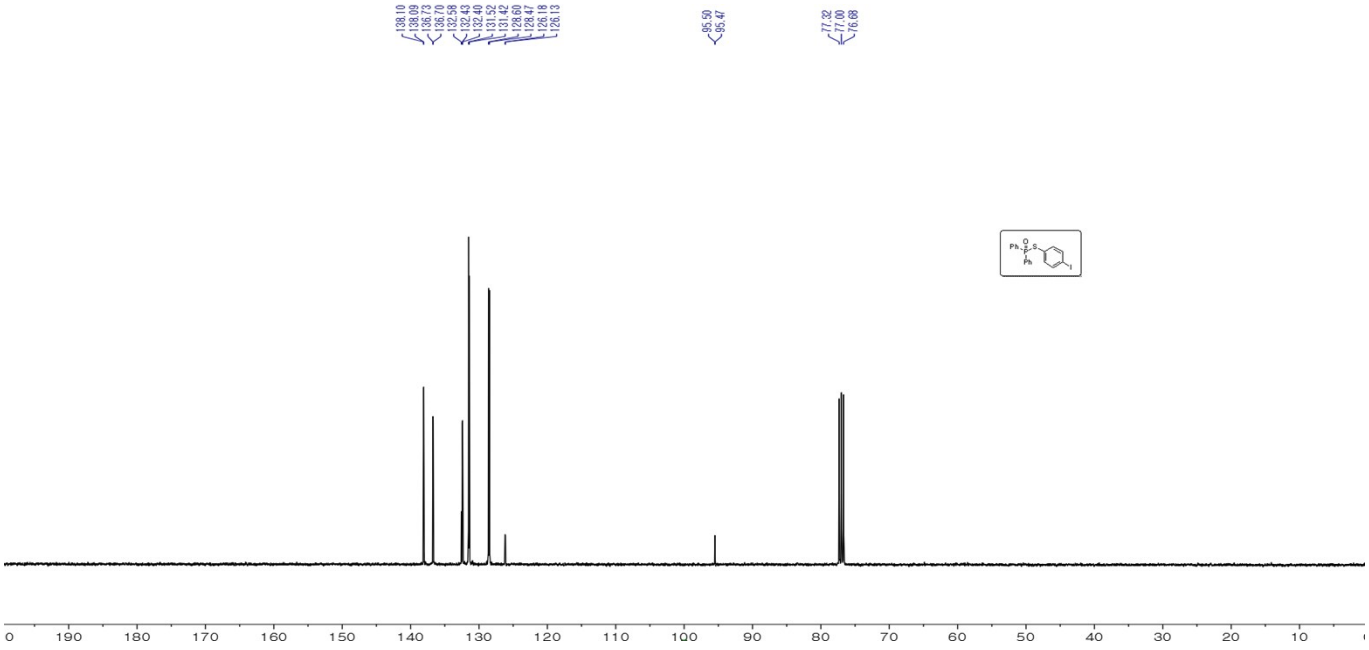

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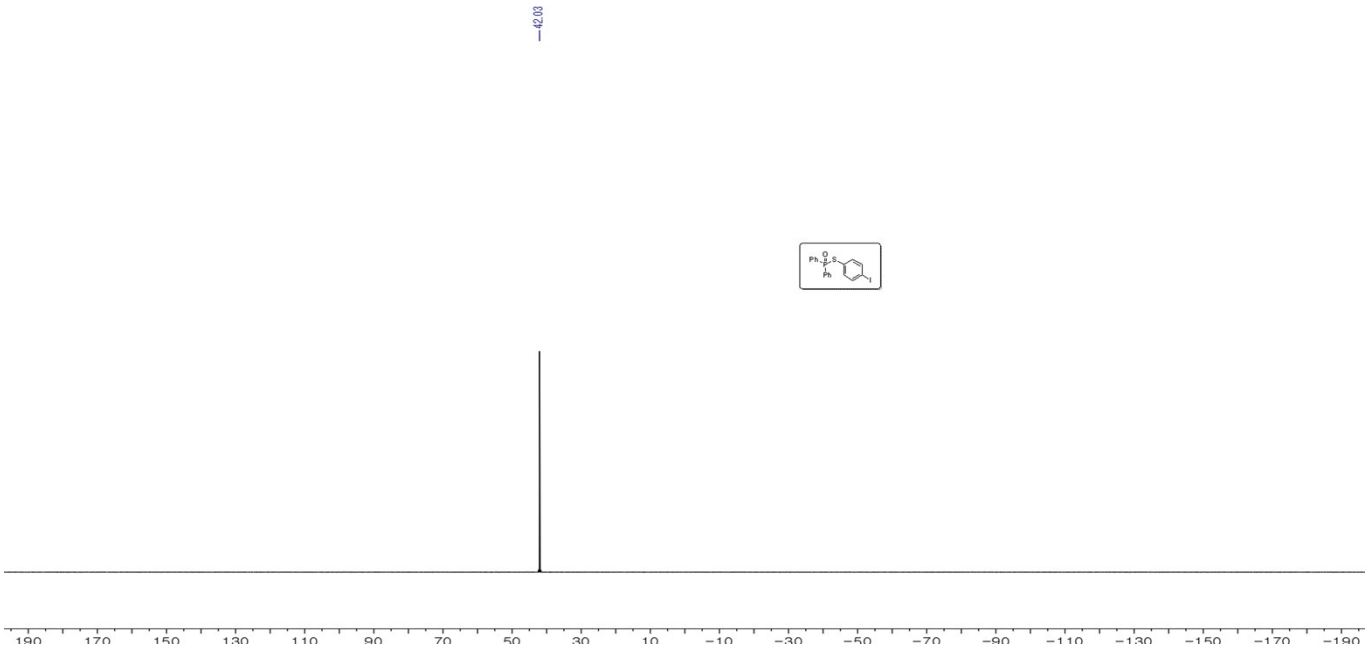
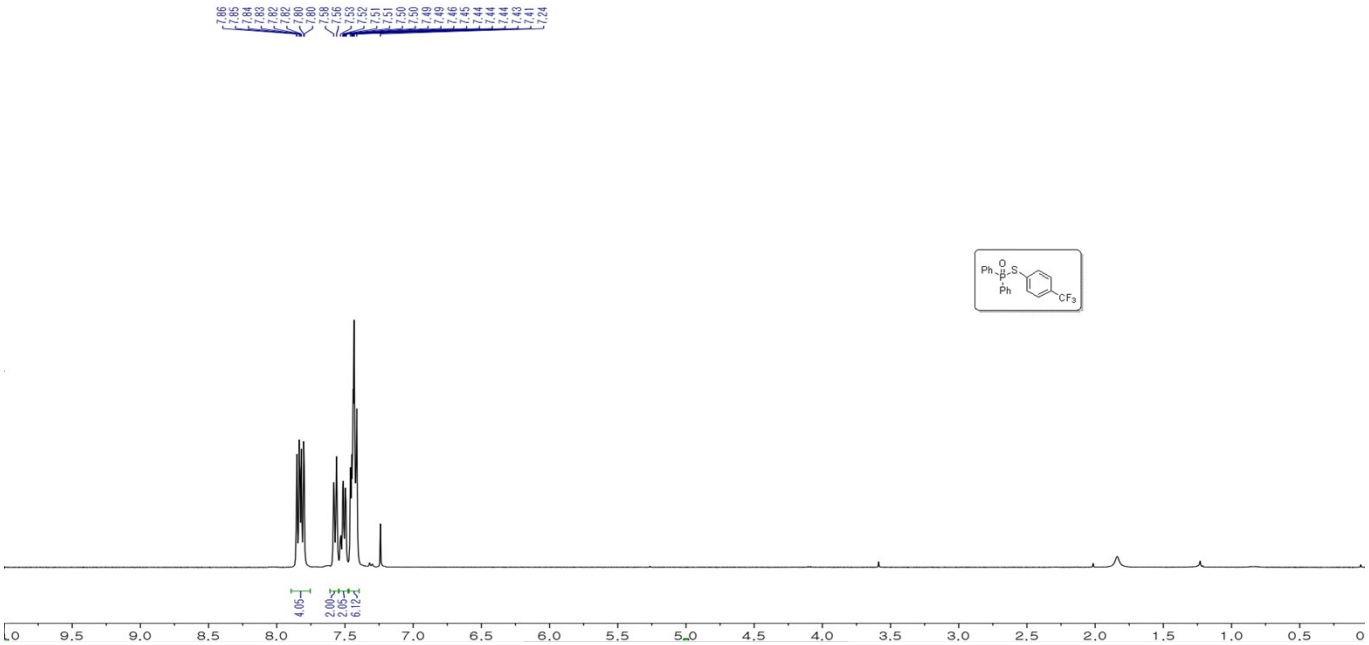


162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (3i)



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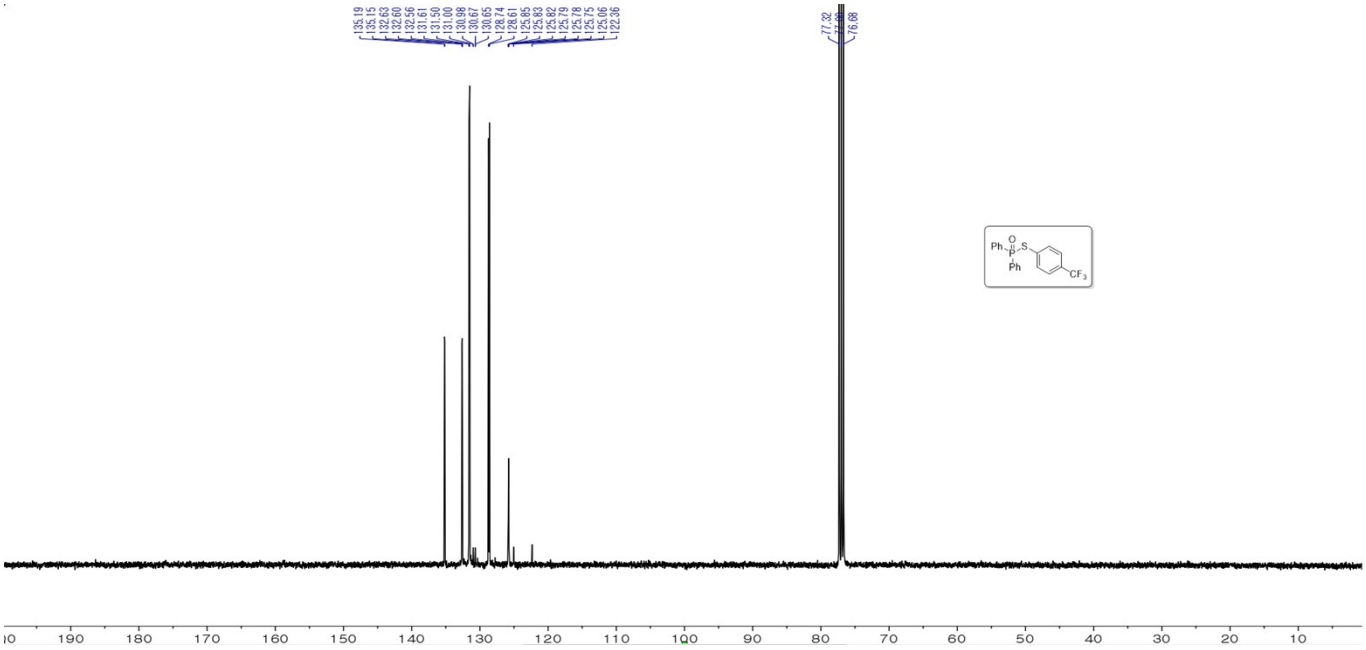

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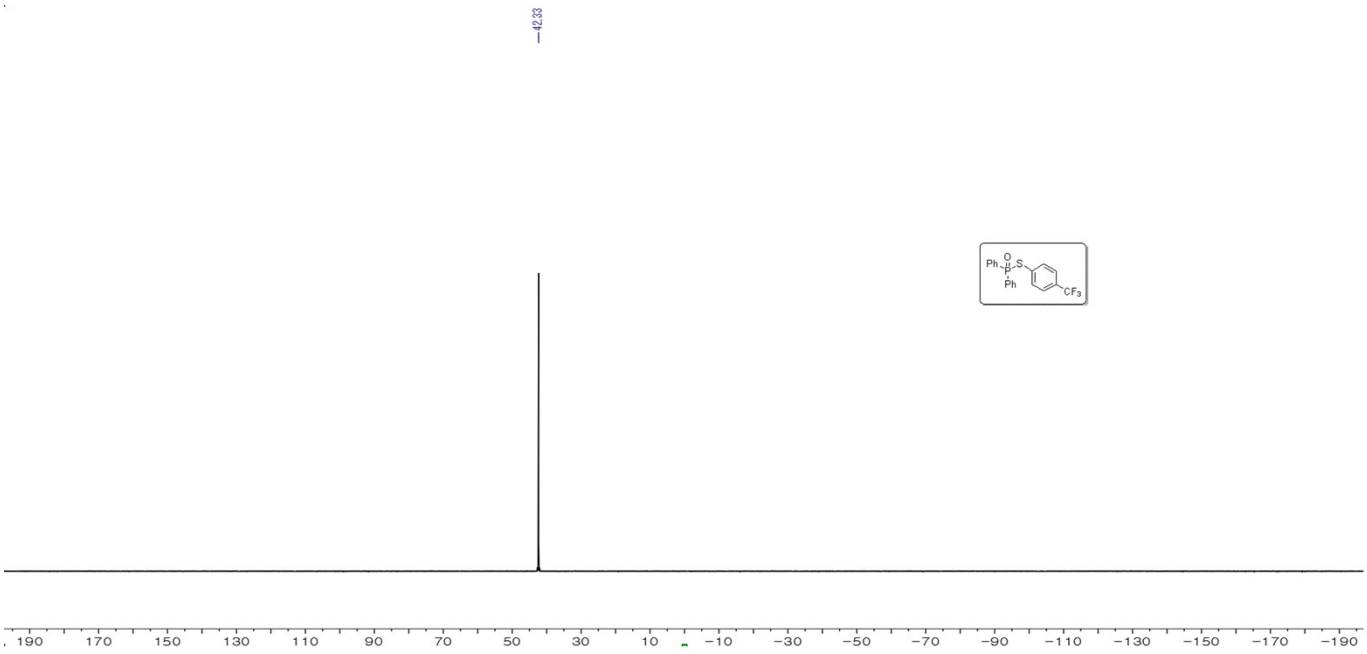
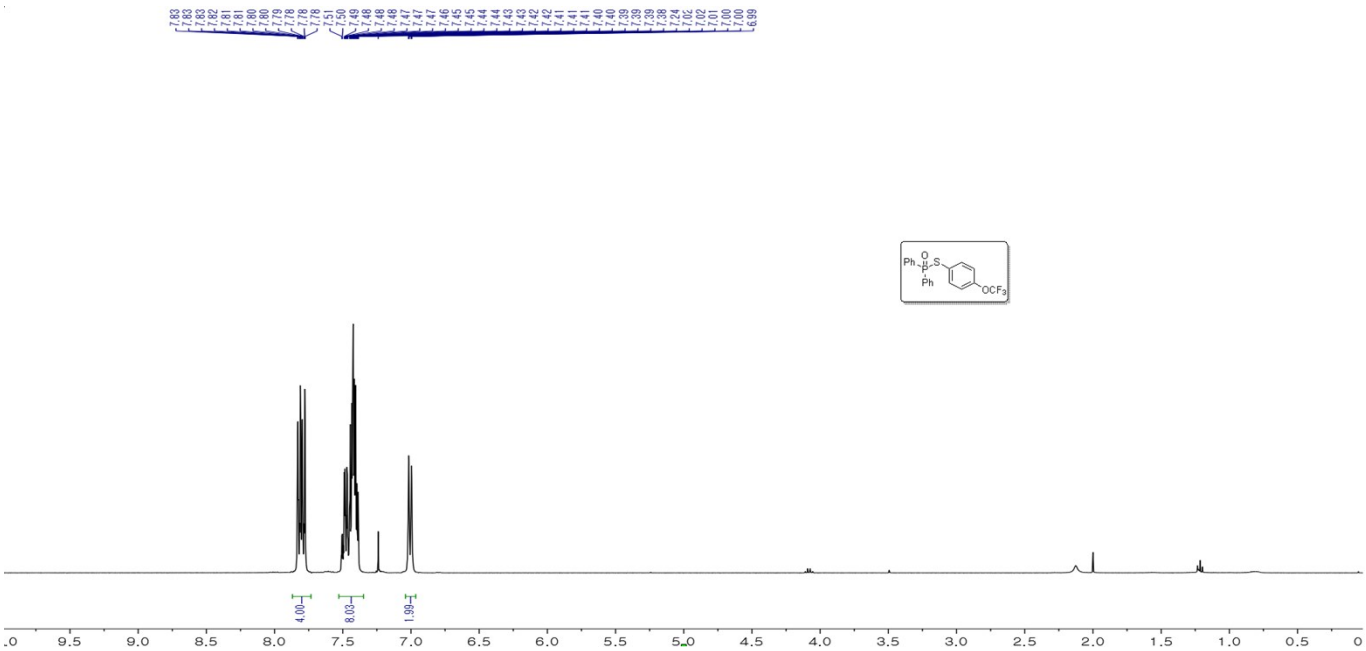
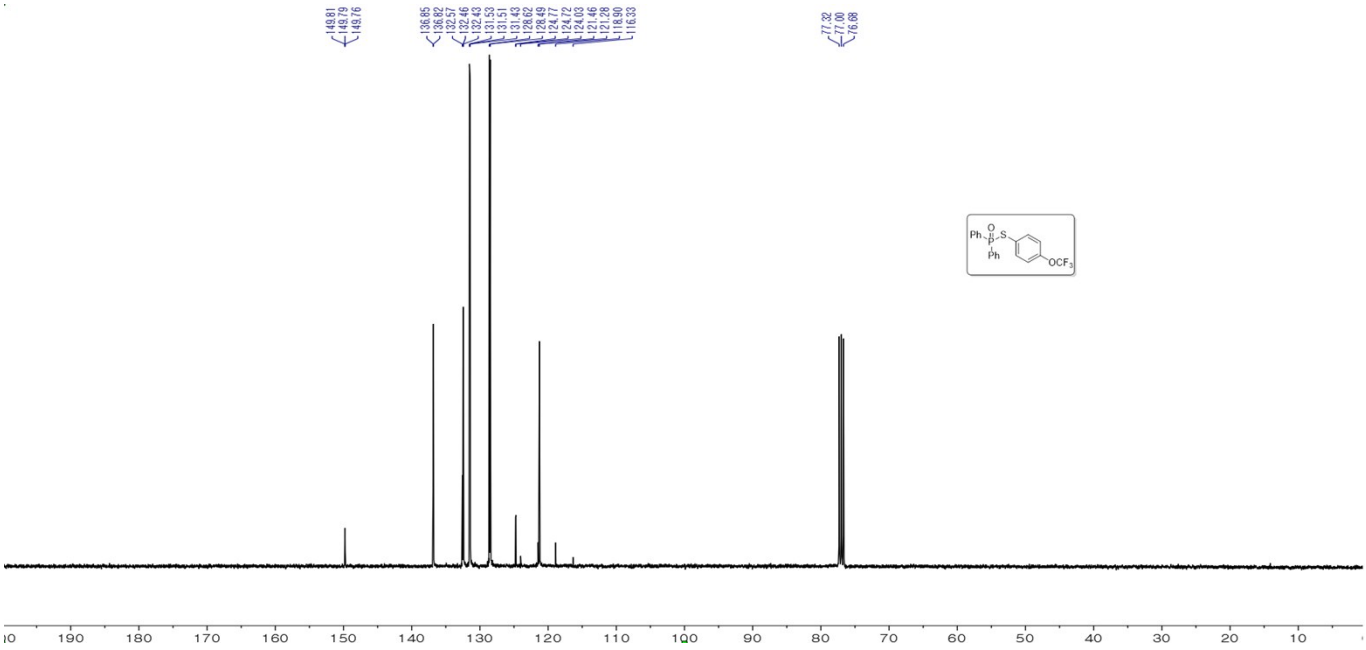


162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-(trifluoromethoxy)phenyl) diphenylphosphinothioate (3j)



400 MHz, ^{1}H NMR in $CDCl_3$



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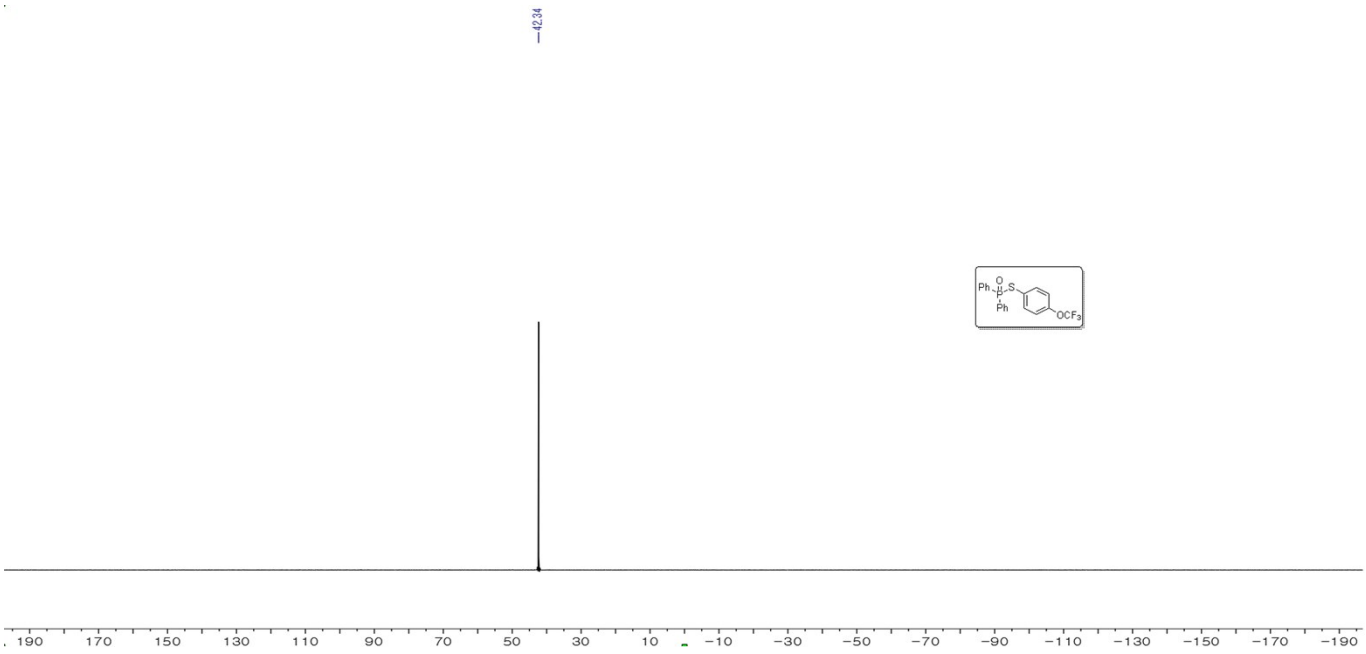
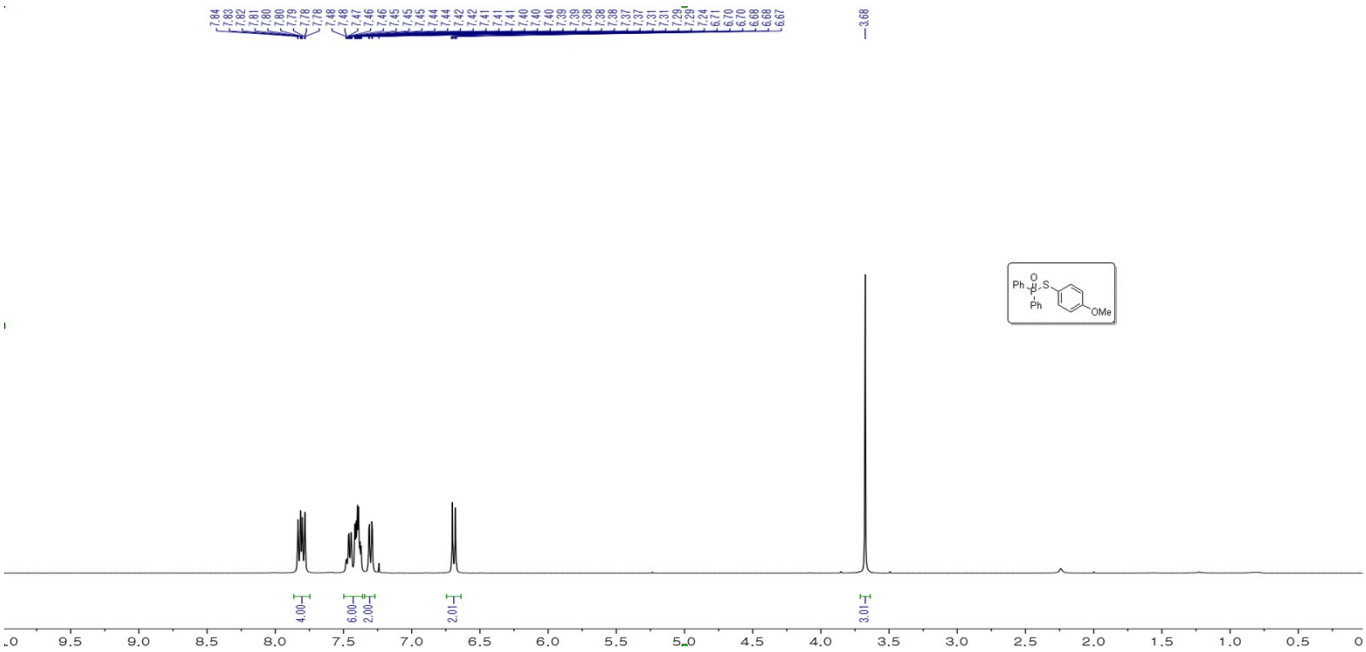


162 MHz, ^{31}P NMR in $CDCl_3$

S-(4-methoxyphenyl) diphenylphosphinothioate (3k)



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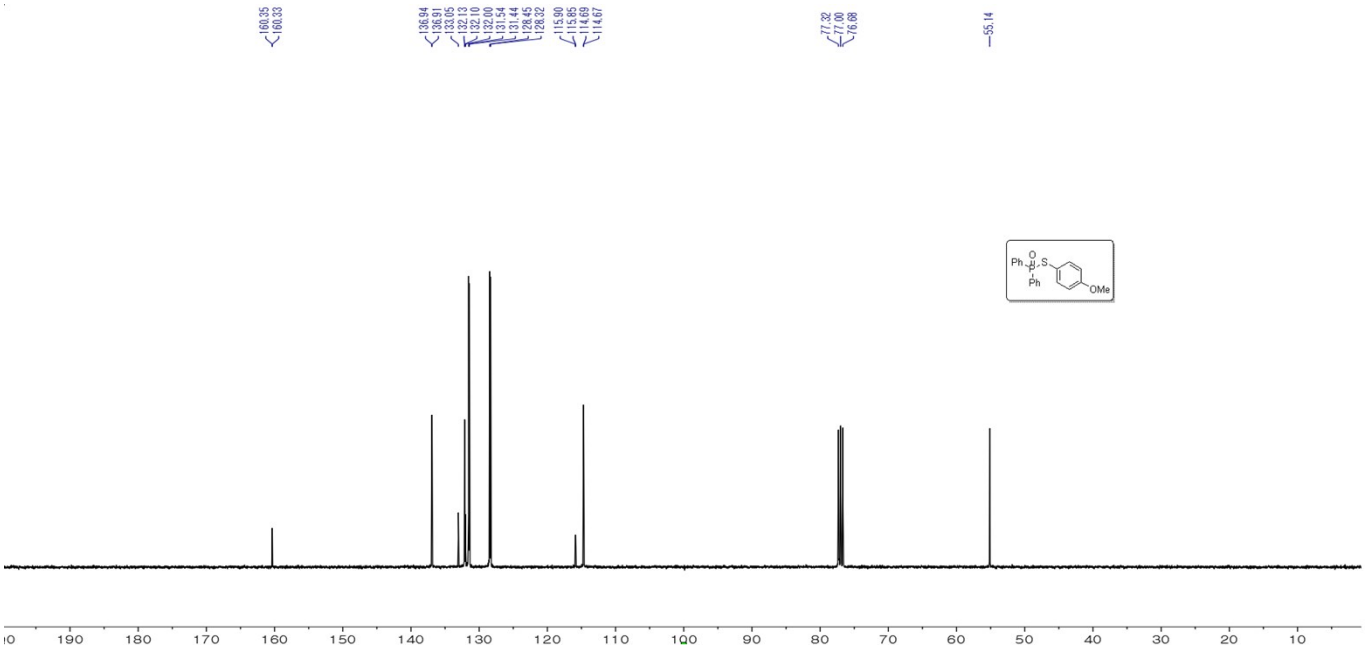

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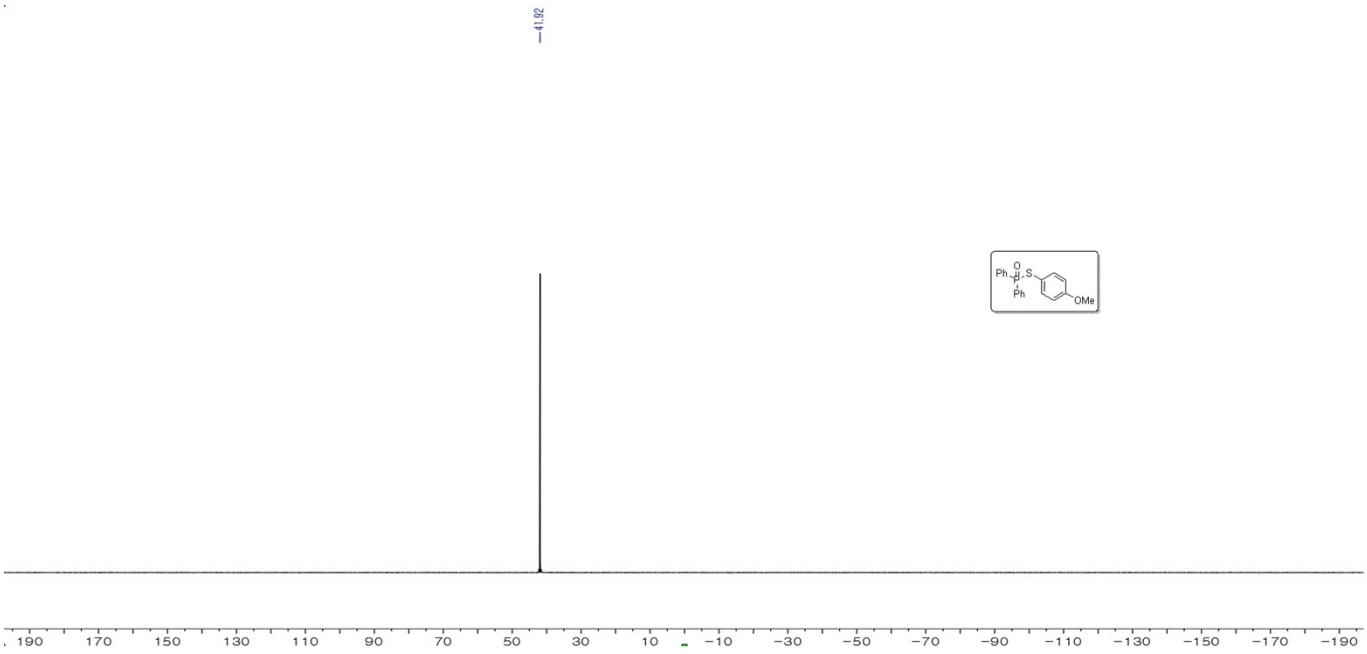
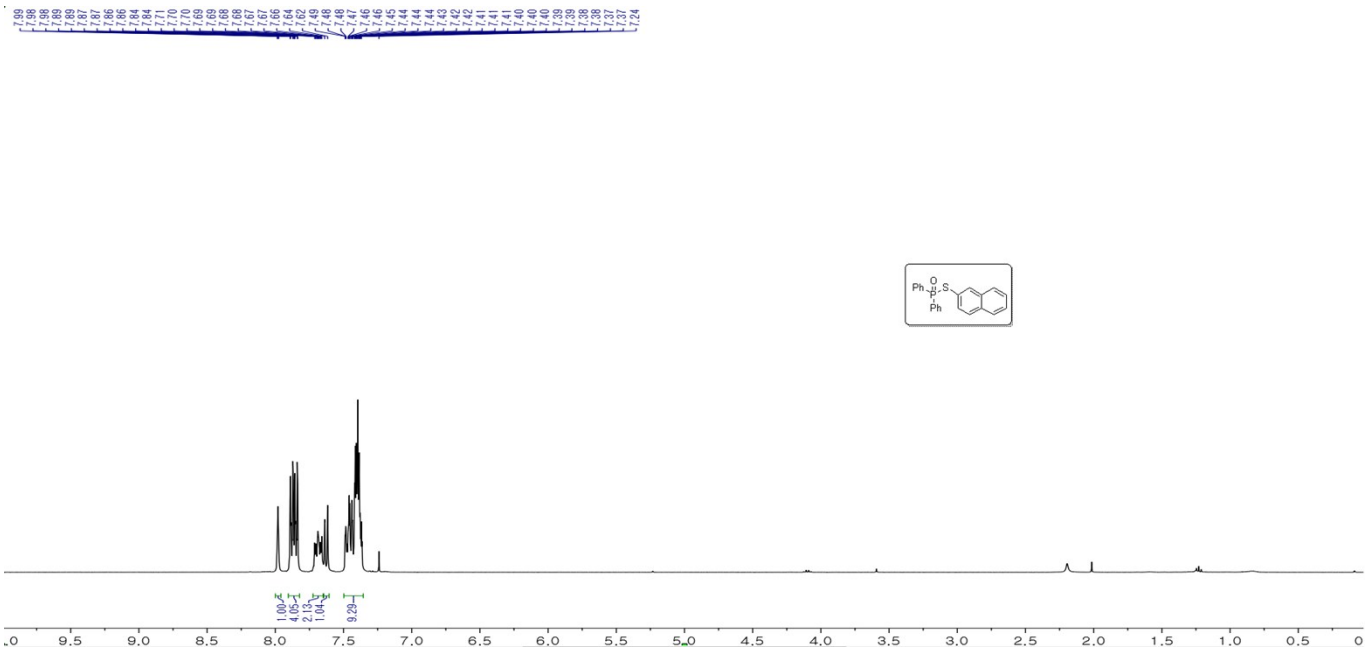
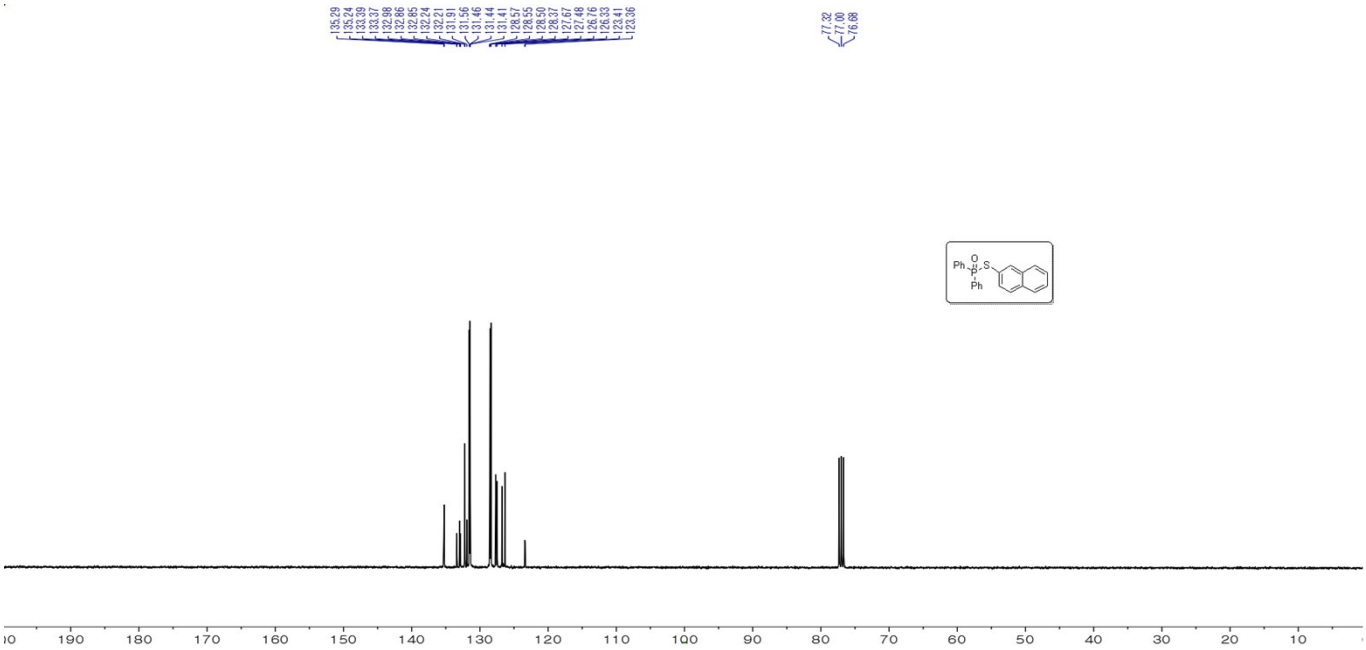


162 MHz, ^{31}P NMR in $CDCl_3$

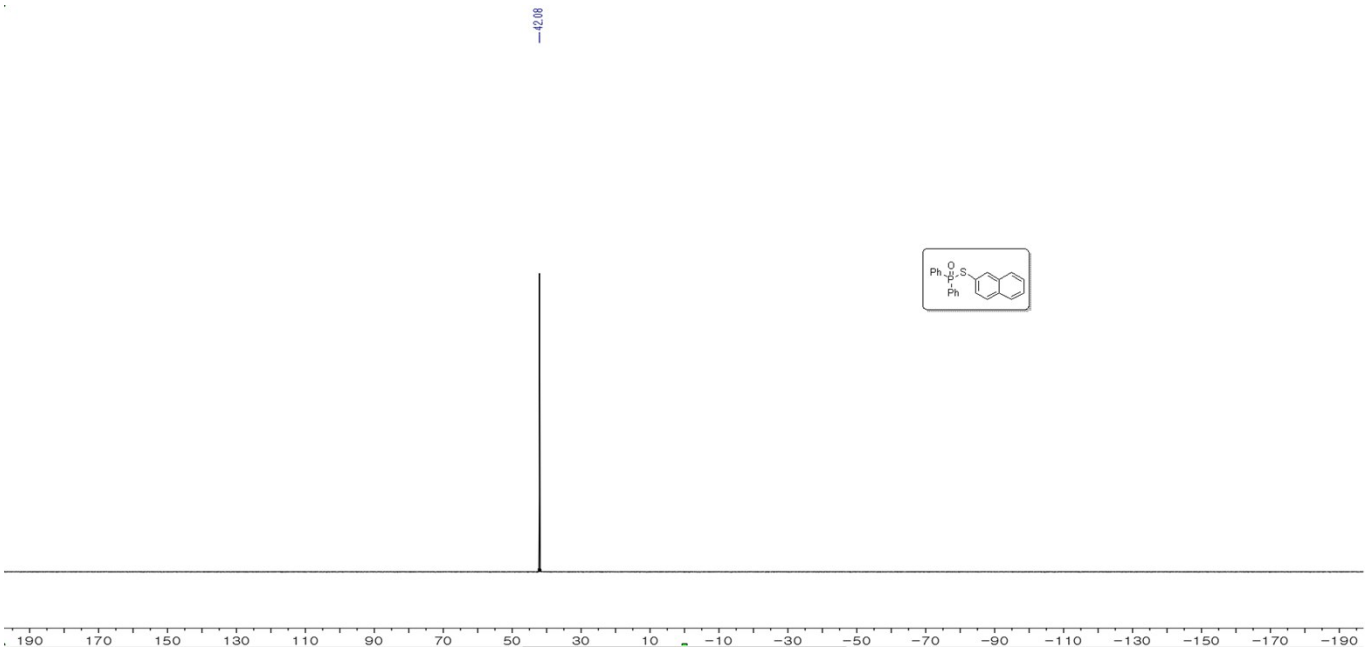
S-(naphthalen-2-yl) diphenylphosphinothioate (3l)



400 MHz, ^{1}H NMR in $CDCl_3$

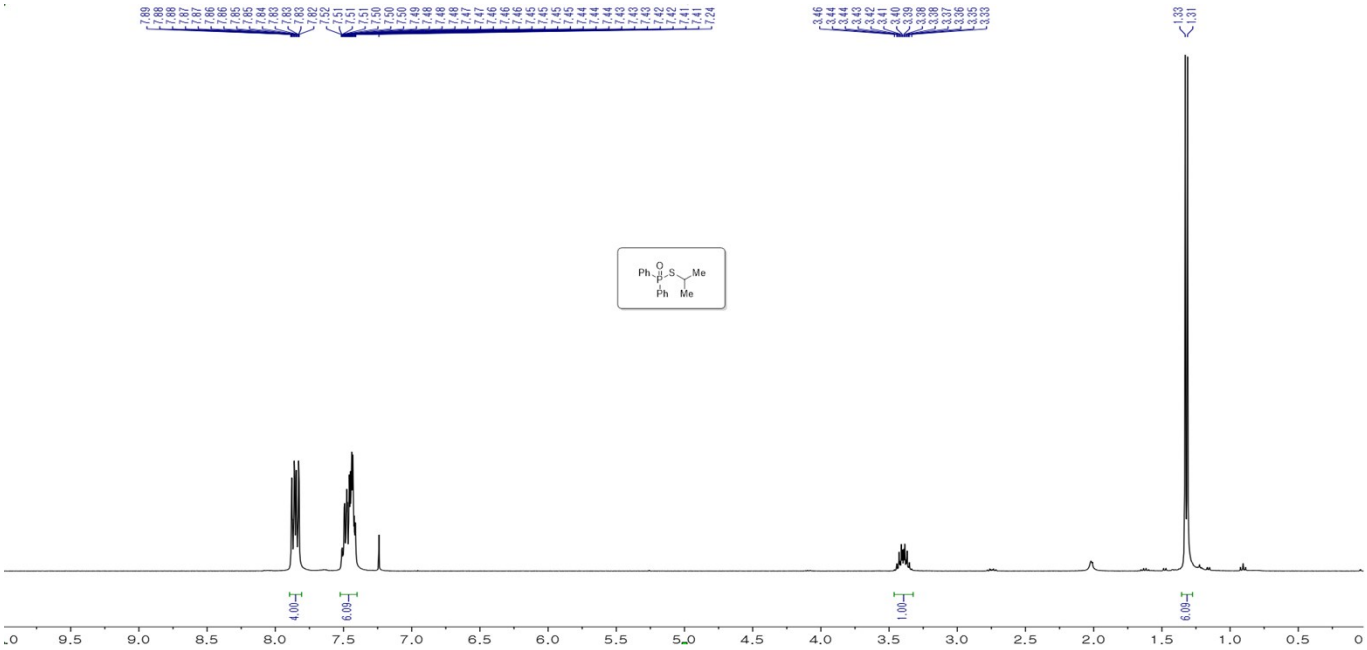


100 MHz, ^{13}C NMR in $CDCl_3$

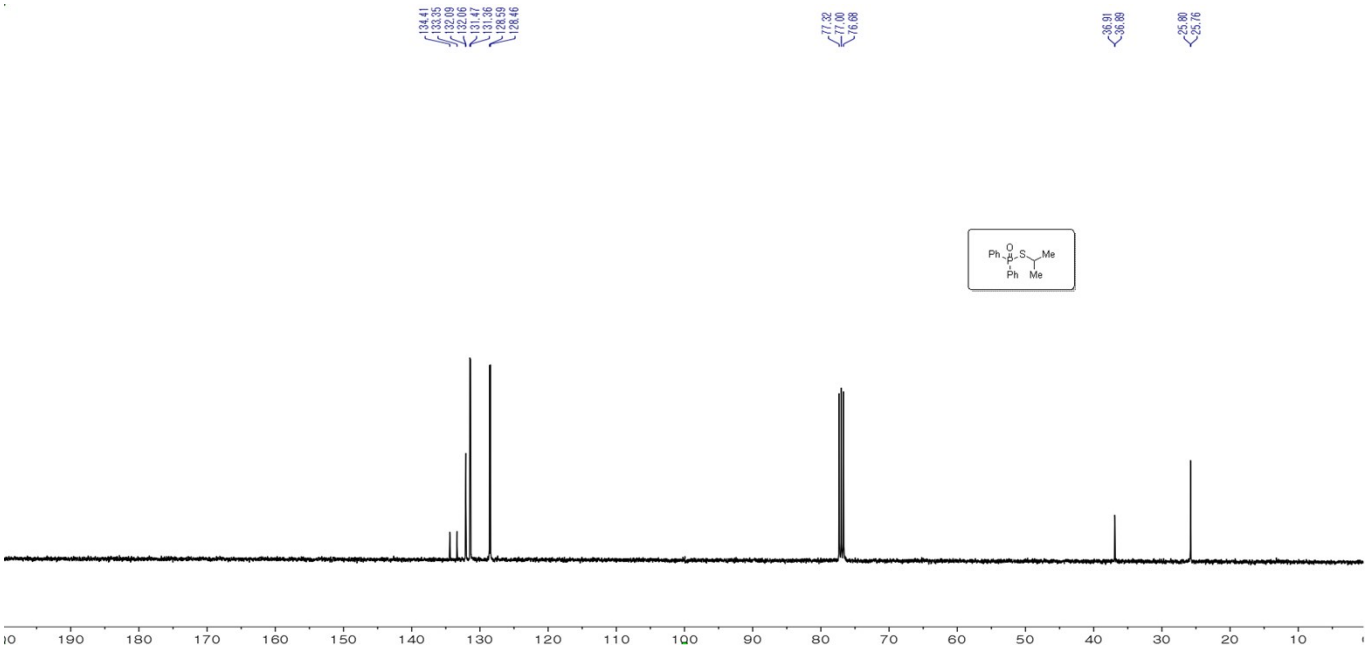


162 MHz, ^{31}P NMR in $CDCl_3$

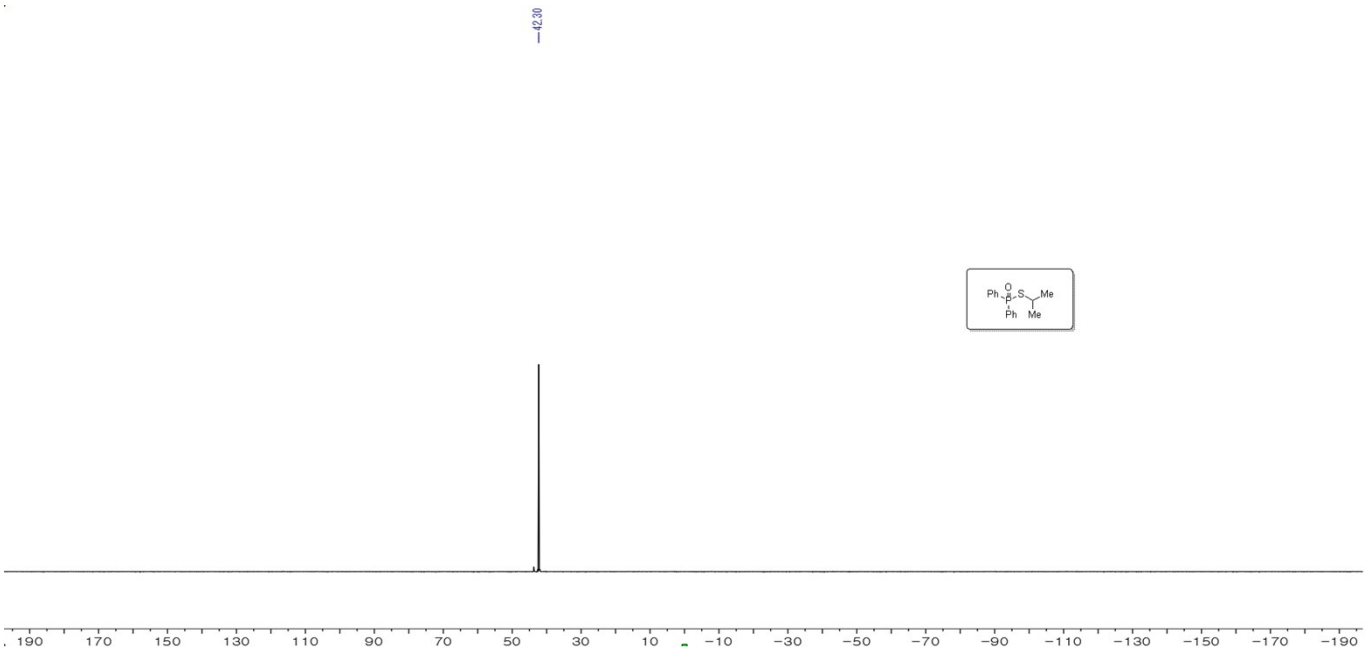
S-isopropyl diphenylphosphinothioate (3m)



400 MHz, ^{1}H NMR in $CDCl_3$

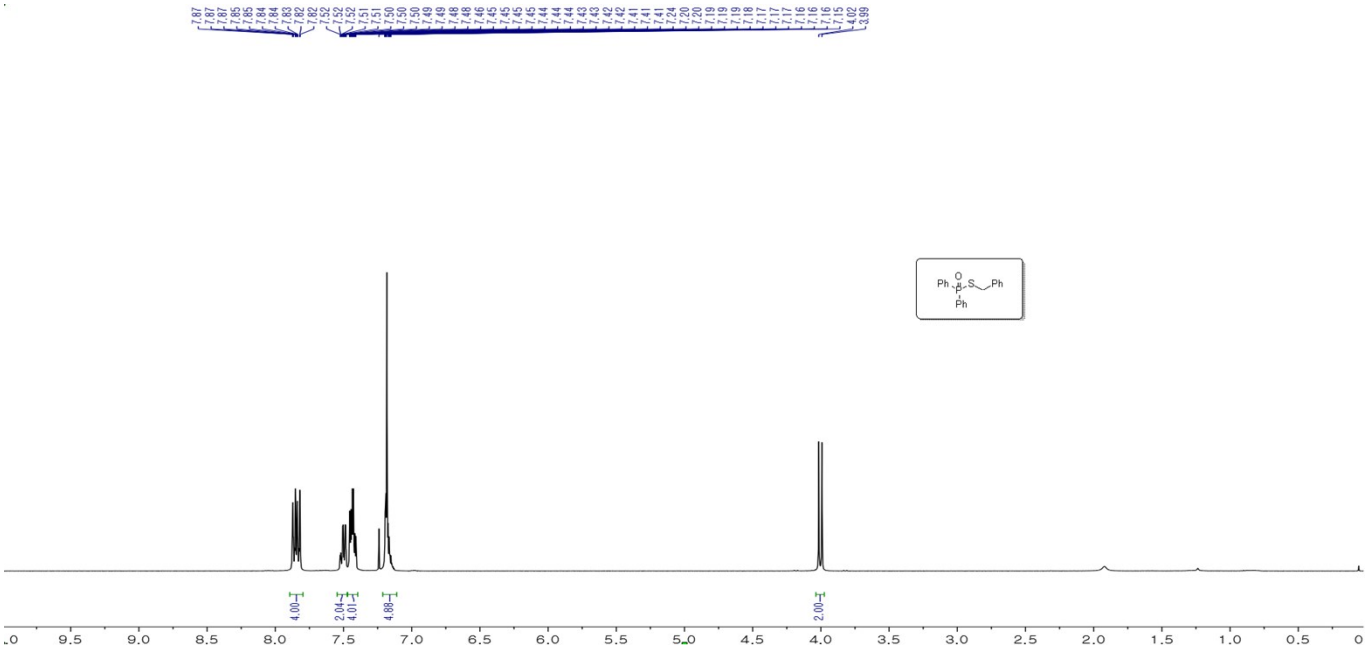


100 MHz, ^{13}C NMR in $CDCl_3$

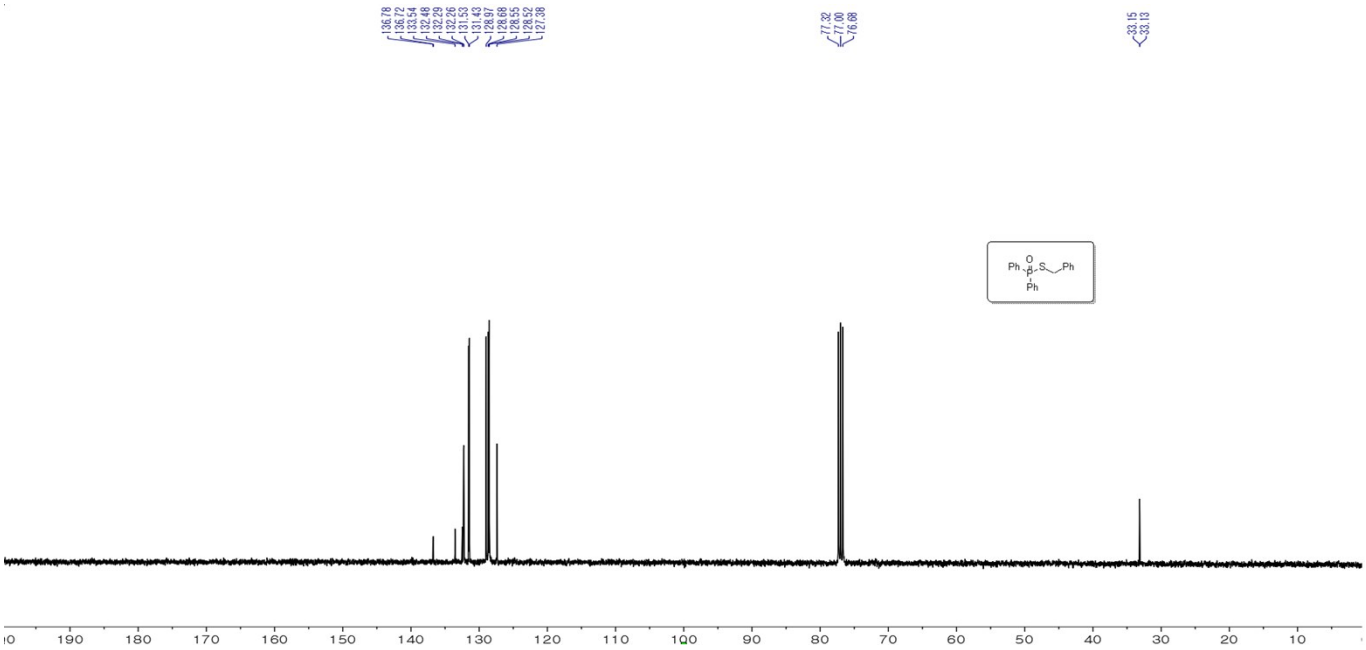


162 MHz, ^{31}P NMR in $CDCl_3$

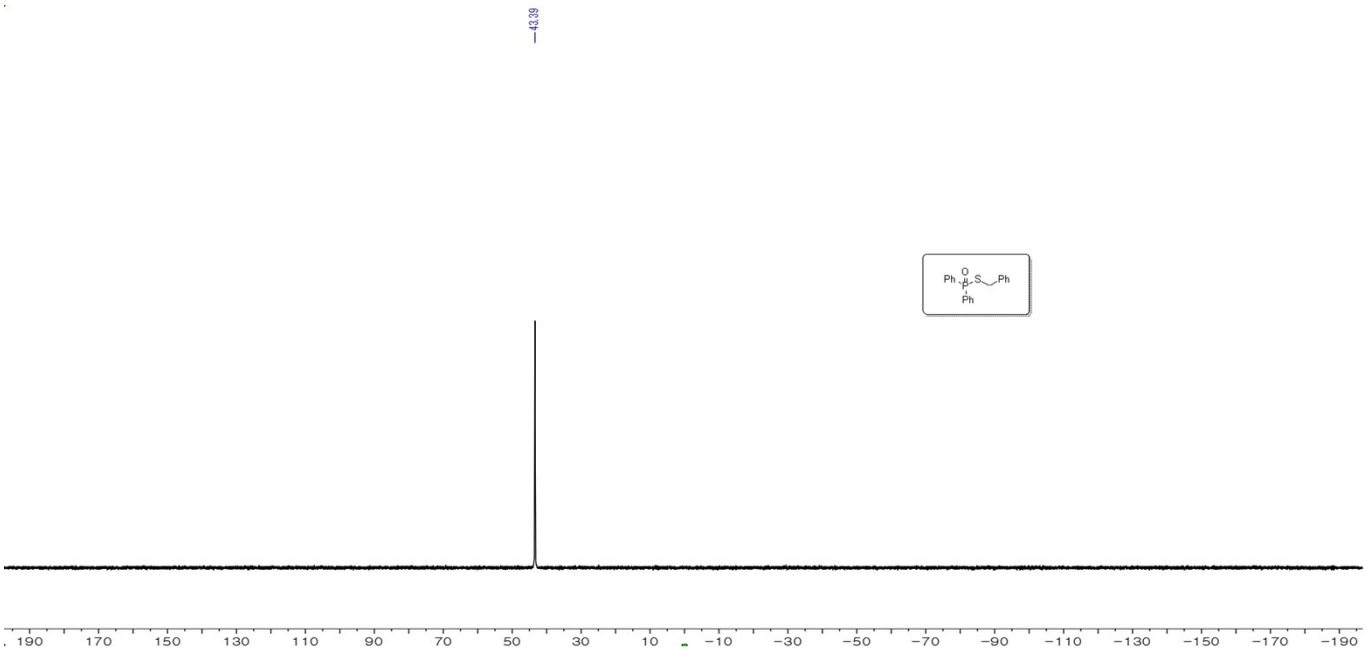
S-benzyl diphenylphosphinothioate (3n)



400 MHz, ^{1}H NMR in $CDCl_3$

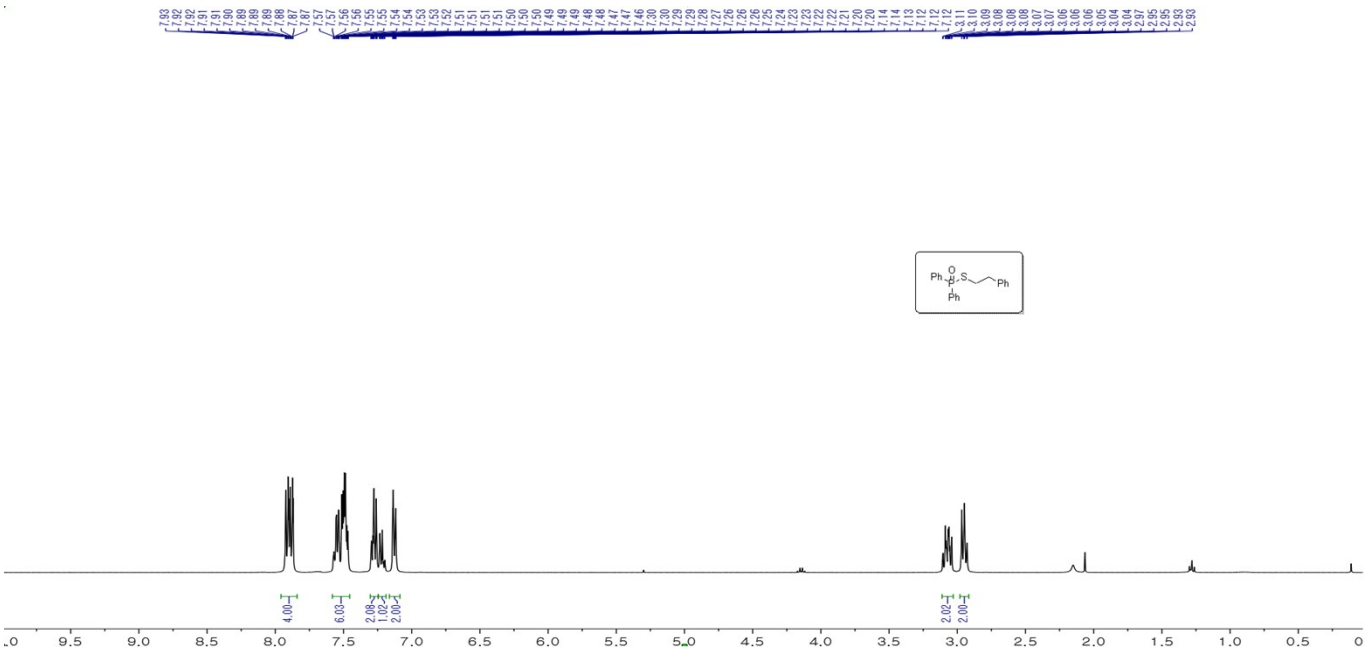


100 MHz, ^{13}C NMR in $CDCl_3$

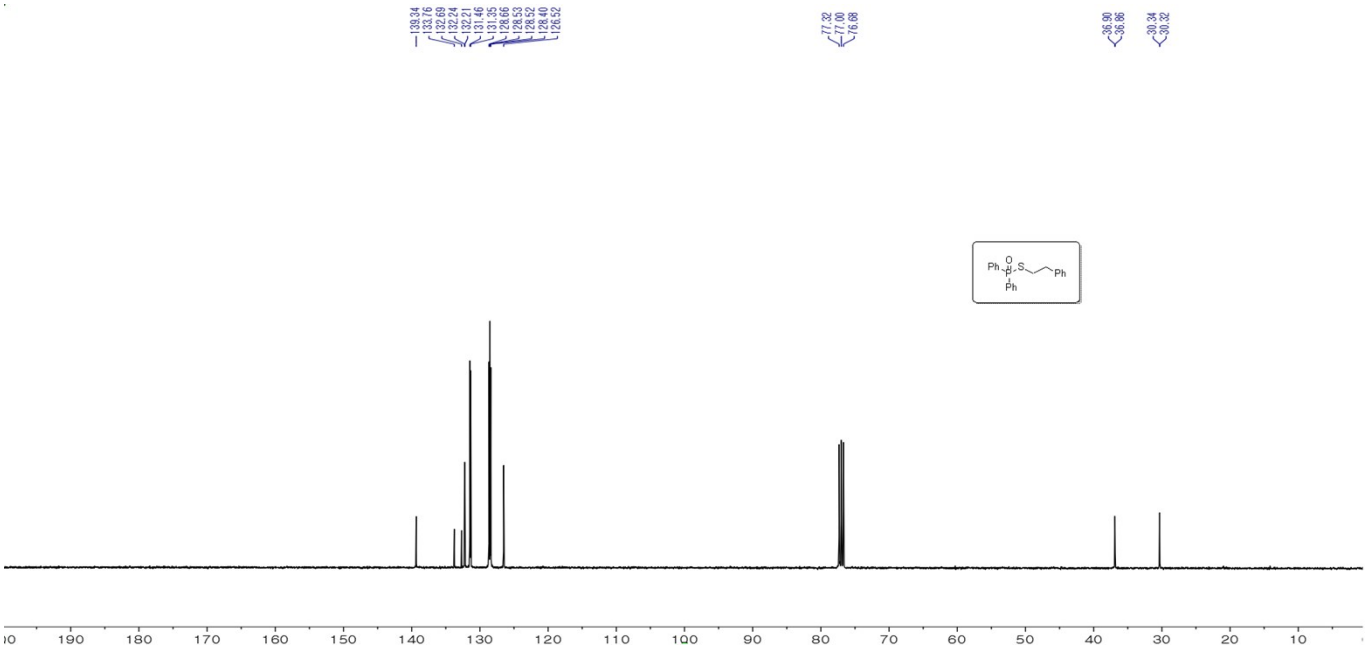


162 MHz, ^{31}P NMR in $CDCl_3$

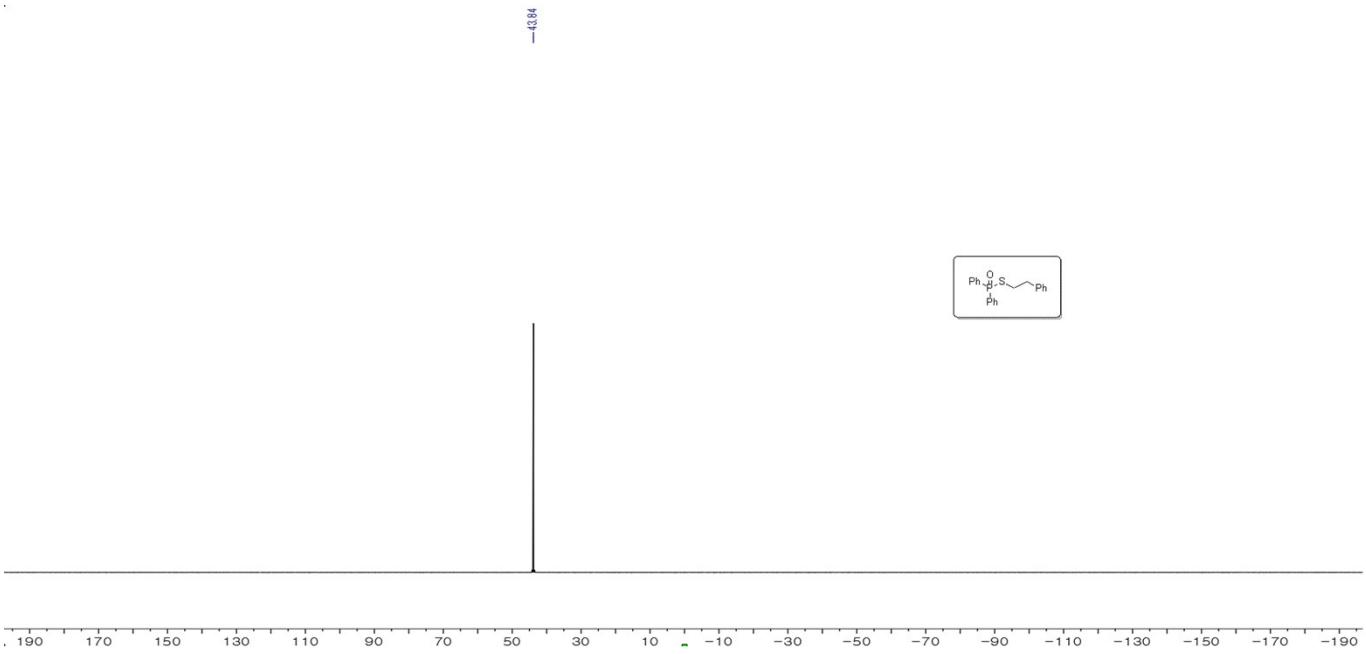
S-phenethyl diphenylphosphinothioate (3o)



400 MHz, ^{1}H NMR in $CDCl_3$

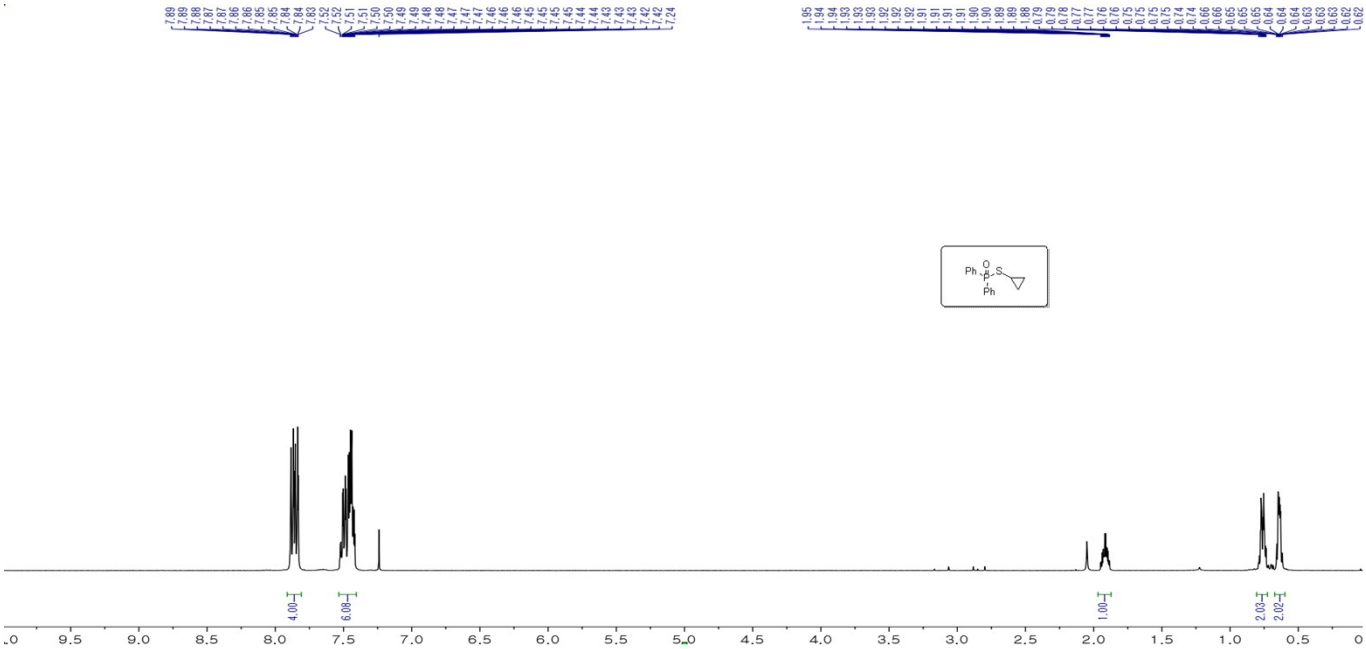


100 MHz, ^{13}C NMR in $CDCl_3$

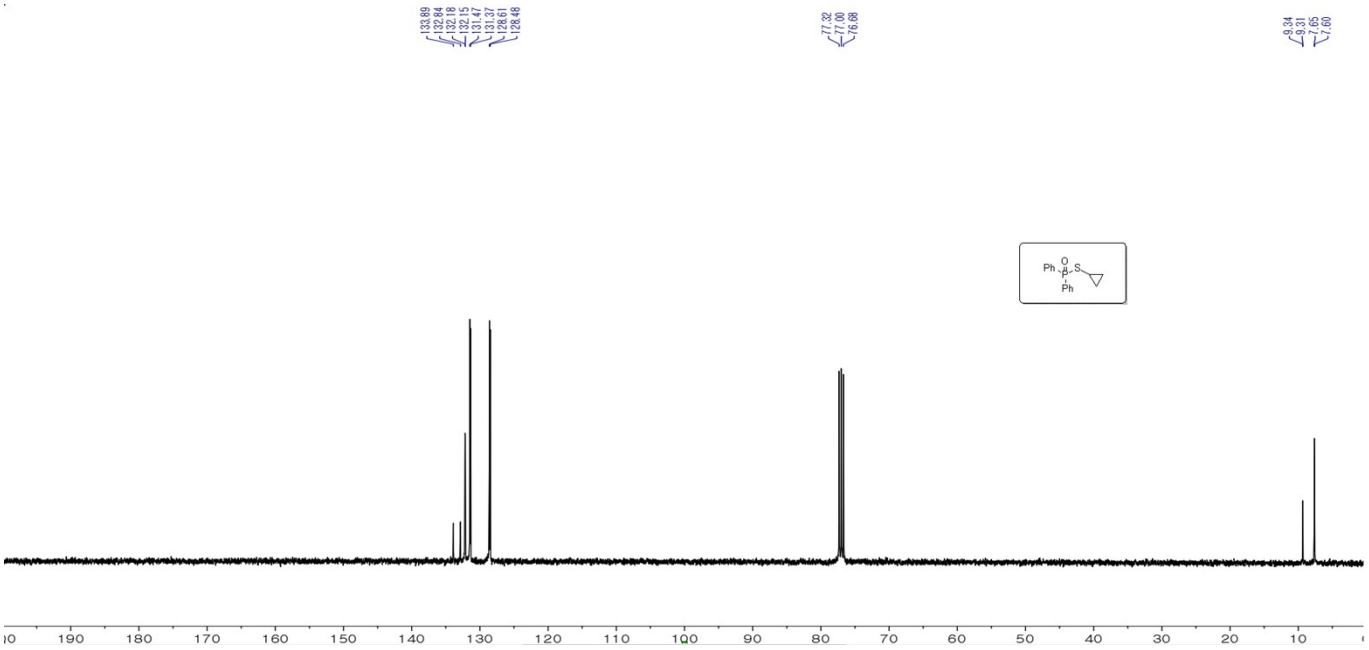


162 MHz, ^{31}P NMR in $CDCl_3$

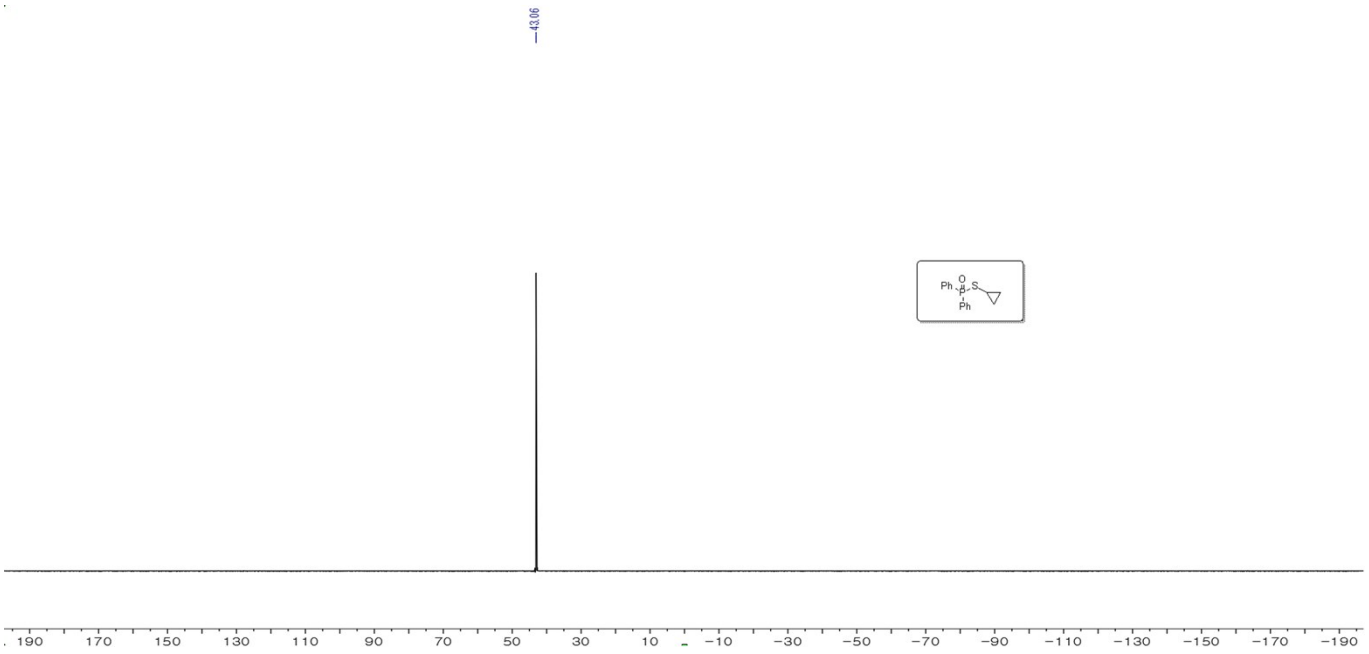
S-cyclopropyl diphenylphosphinothioate (3p)



400 MHz, ^{1}H NMR in $CDCl_3$

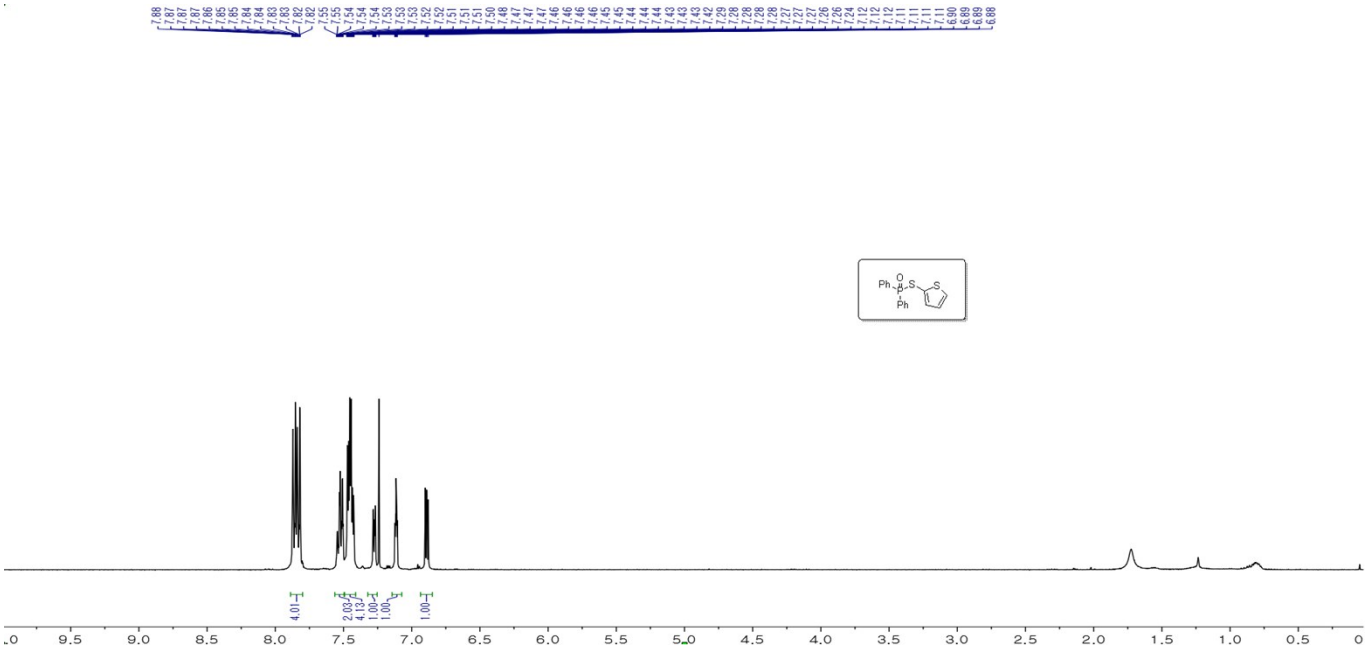


100 MHz, ^{13}C NMR in $CDCl_3$

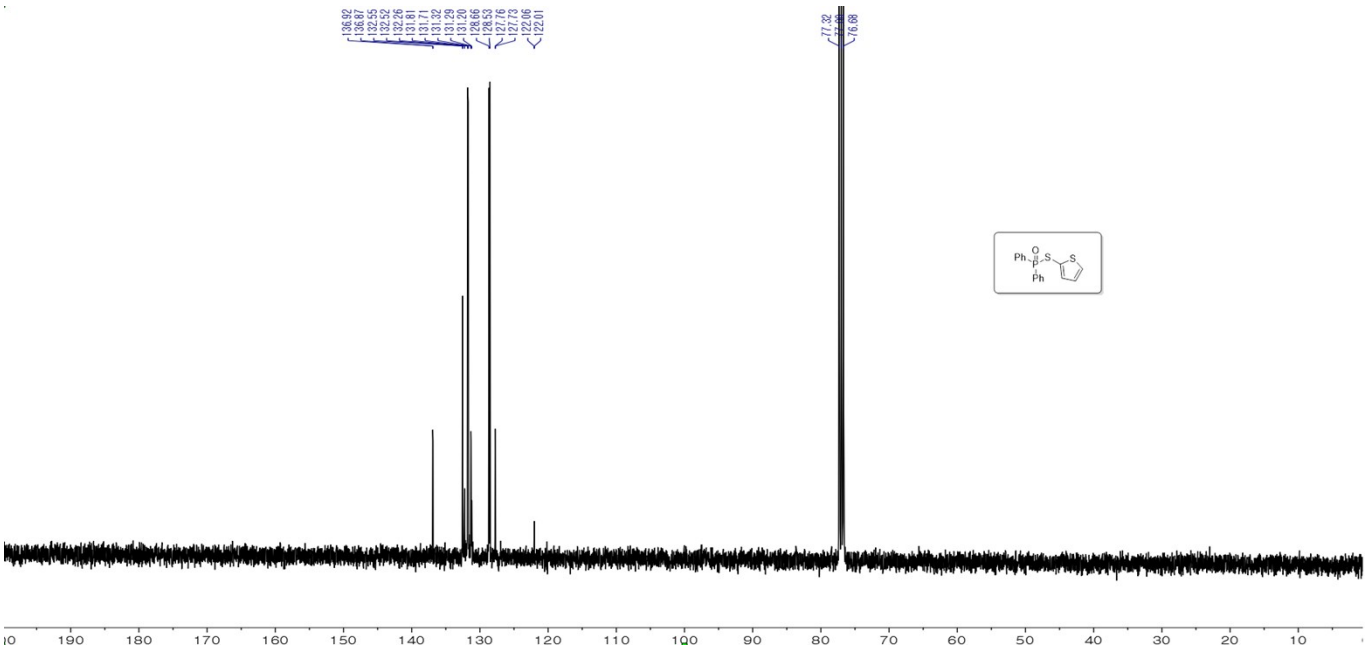


162 MHz, ^{31}P NMR in $CDCl_3$

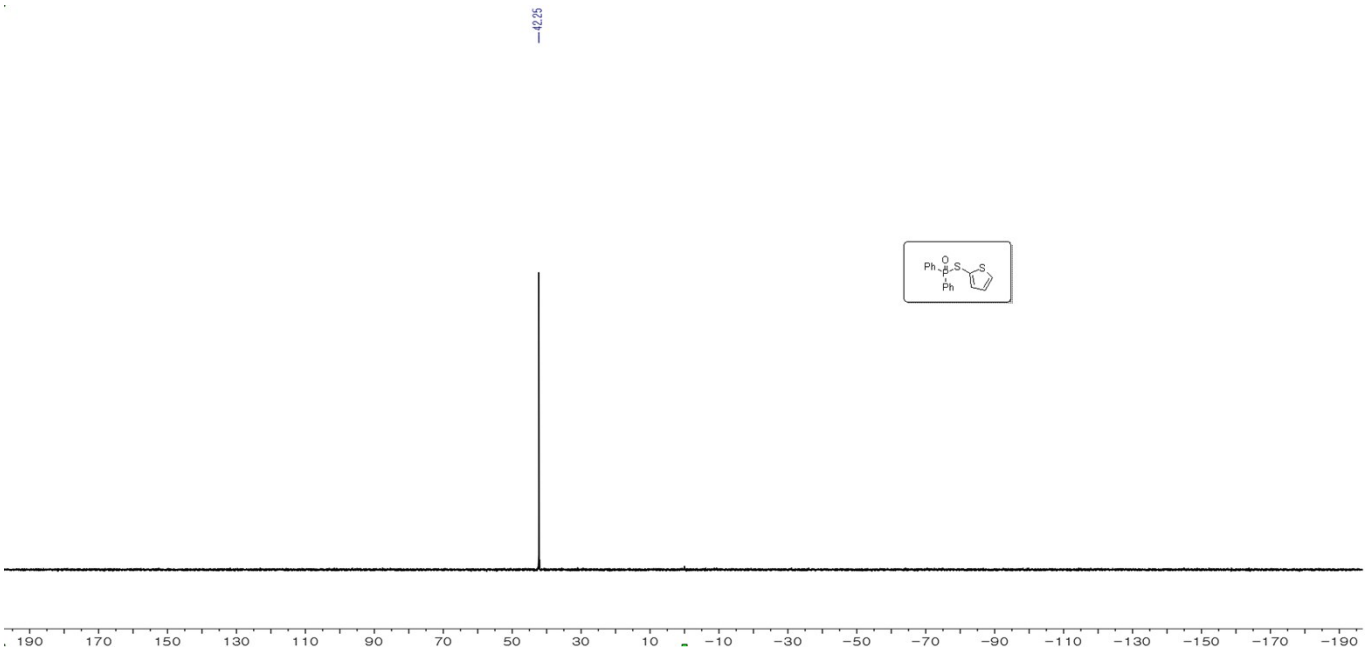
S-(thiophen-2-yl) diphenylphosphinothioate (3q)



400 MHz, ^{1}H NMR in $CDCl_3$

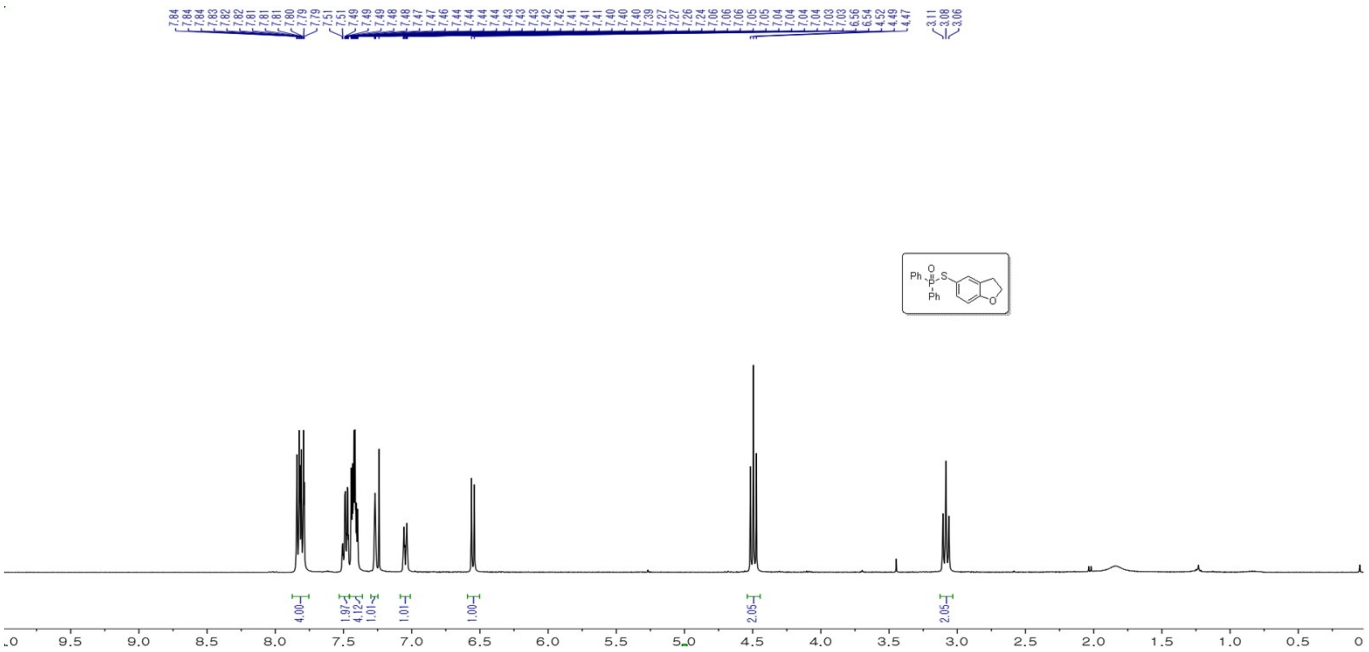


100 MHz, ^{13}C NMR in $CDCl_3$

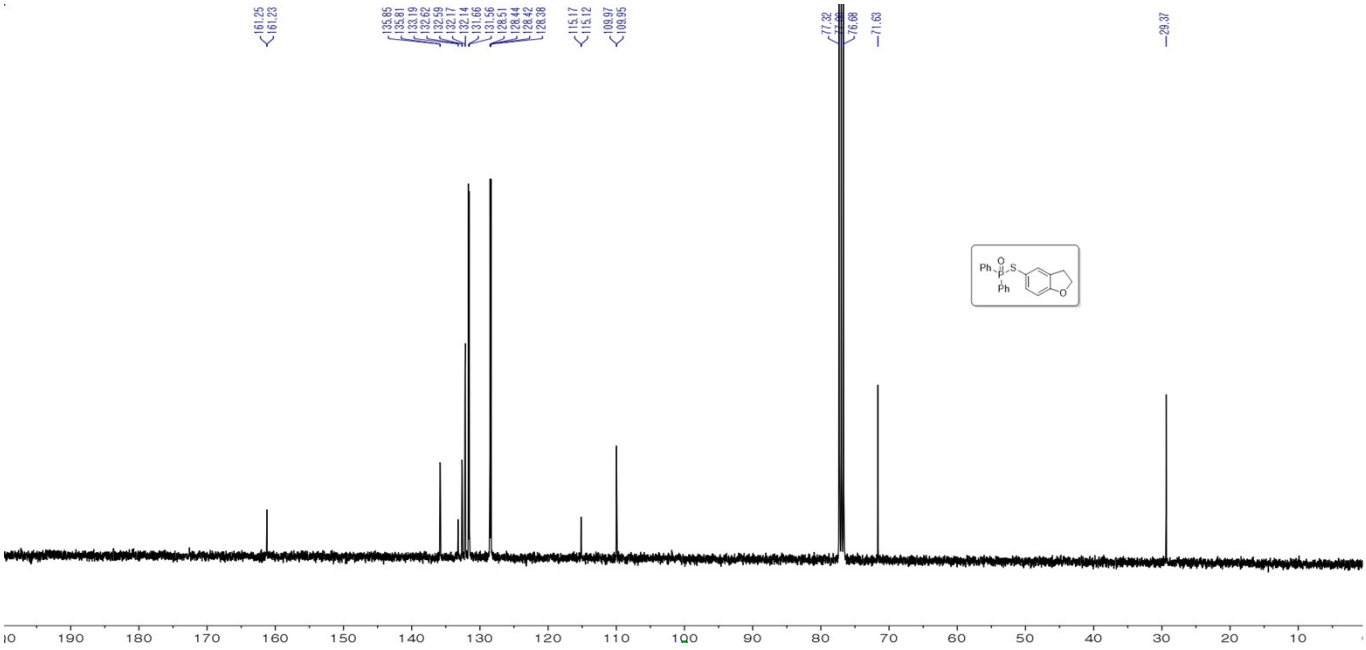


162 MHz, ^{31}P NMR in $CDCl_3$

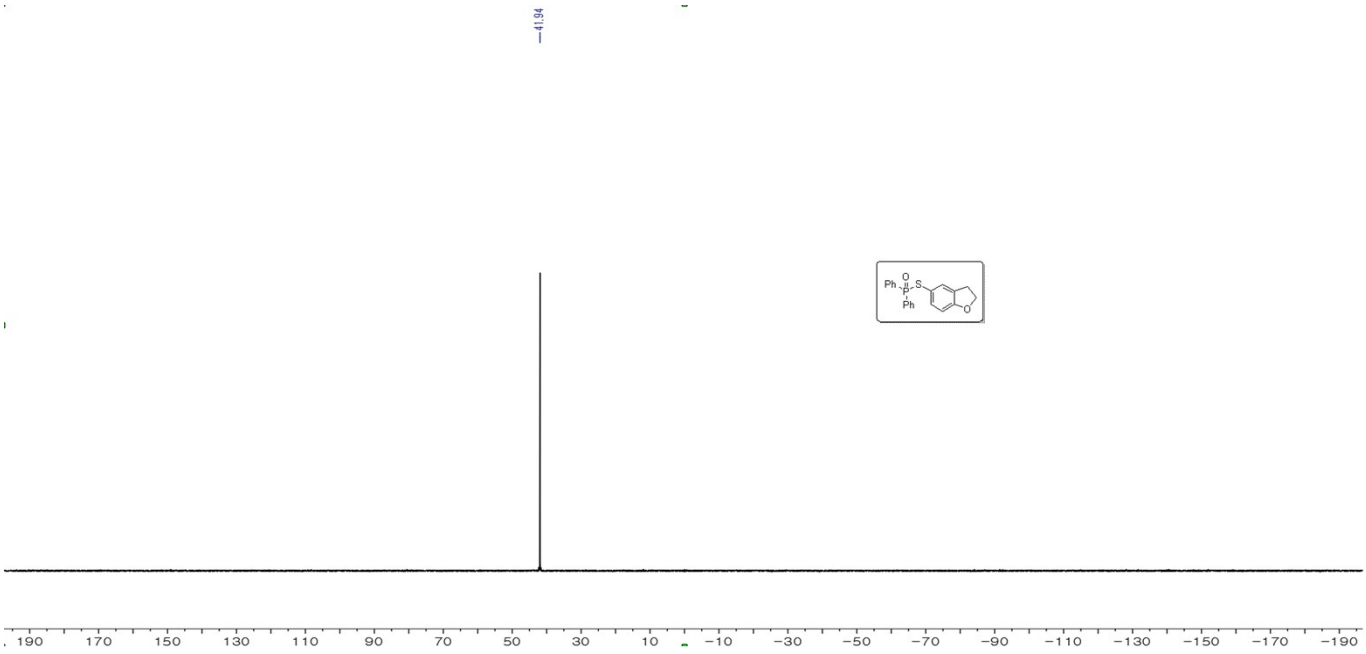
S-(2,3-dihydrobenzofuran-5-yl) diphenylphosphinothioate (3r)



400 MHz, ^{1}H NMR in $CDCl_3$

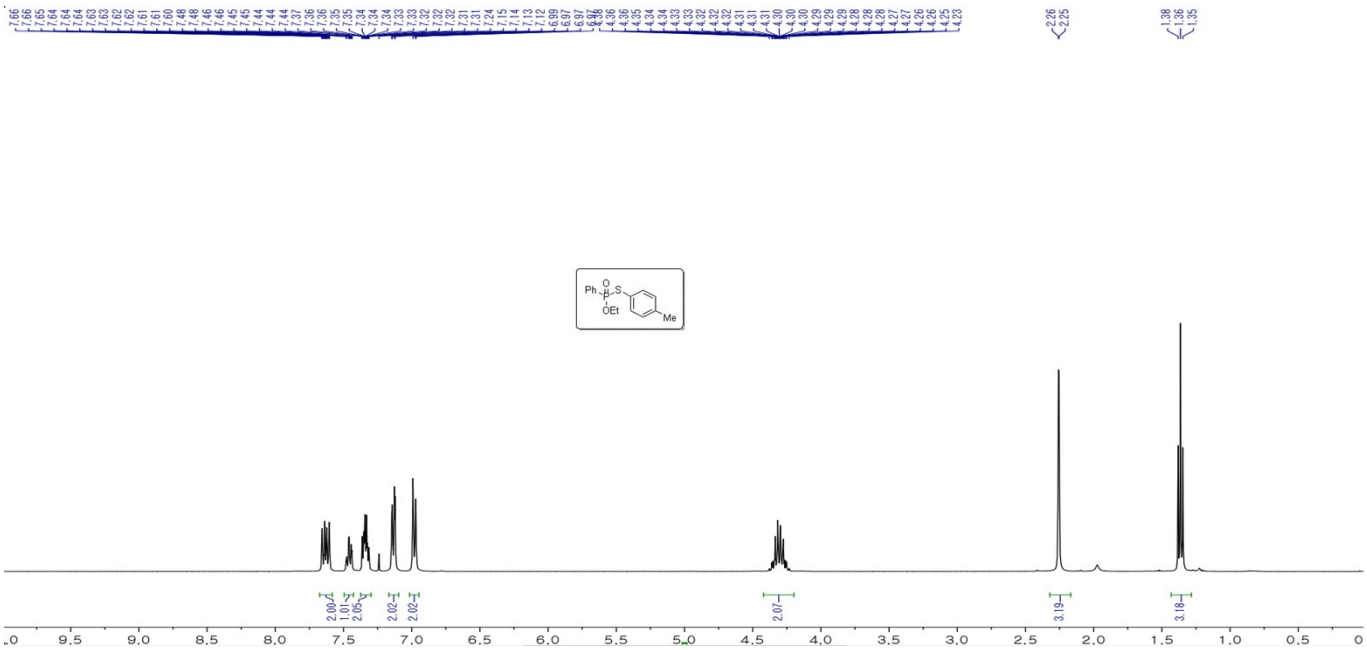


100 MHz, ^{13}C NMR in $CDCl_3$

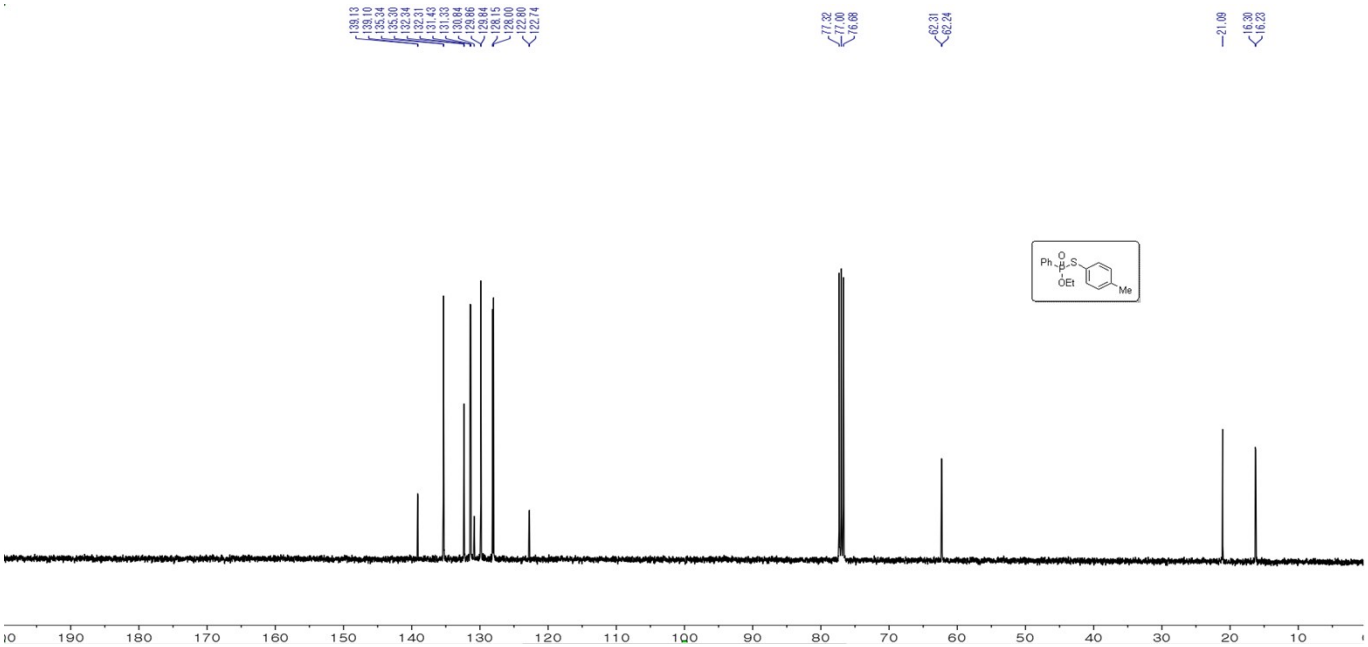


162 MHz, ^{31}P NMR in $CDCl_3$

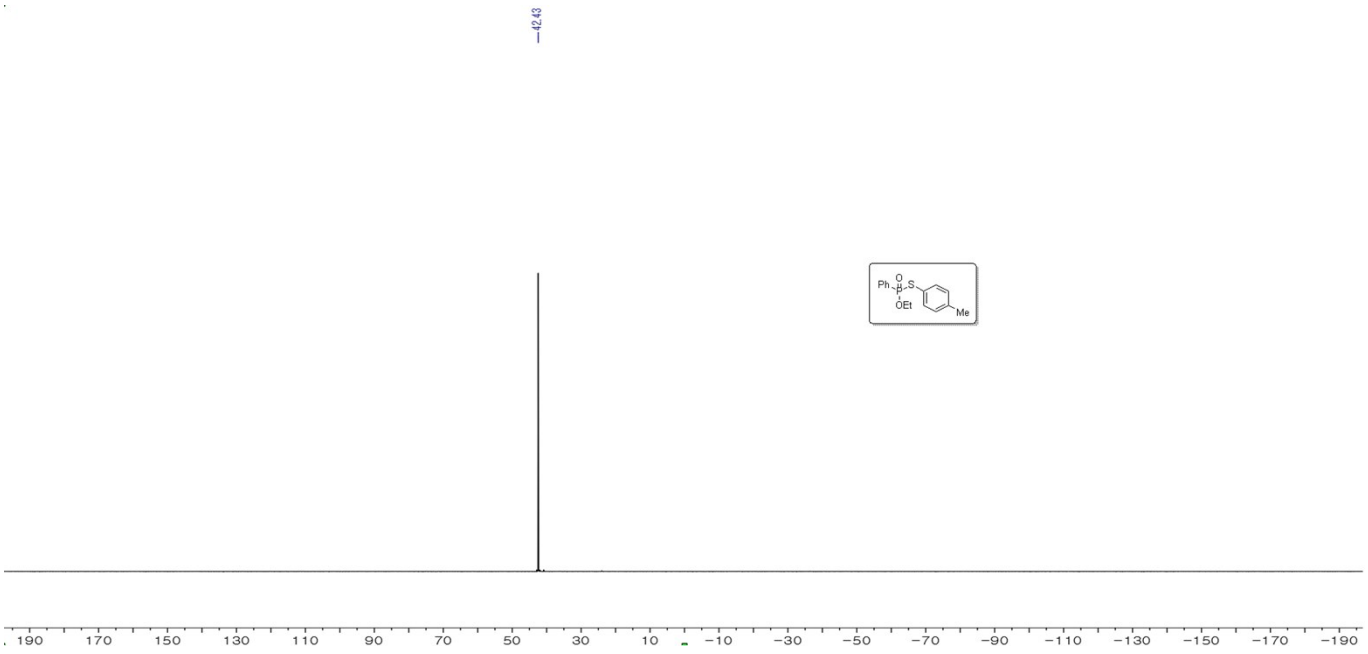
O-ethyl S-(p-tolyl) phenylphosphonothioate (4a)



400 MHz, ^{1}H NMR in $CDCl_3$

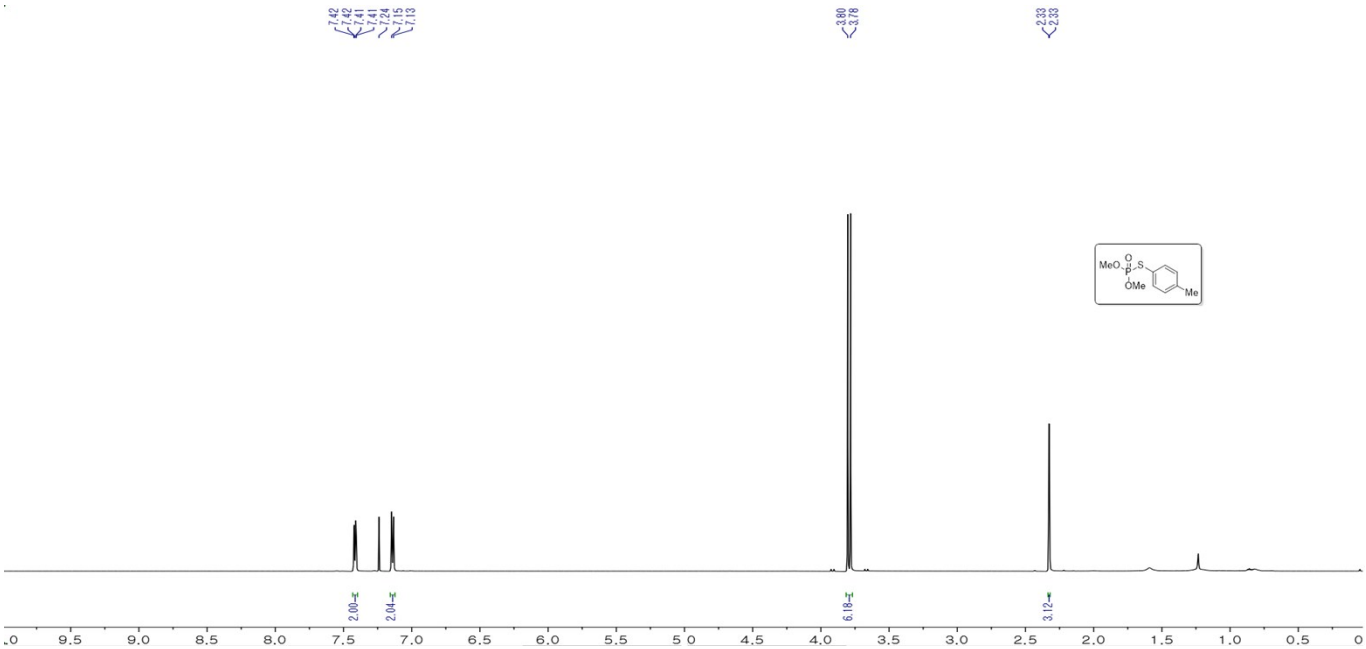


100 MHz, ^{13}C NMR in $CDCl_3$

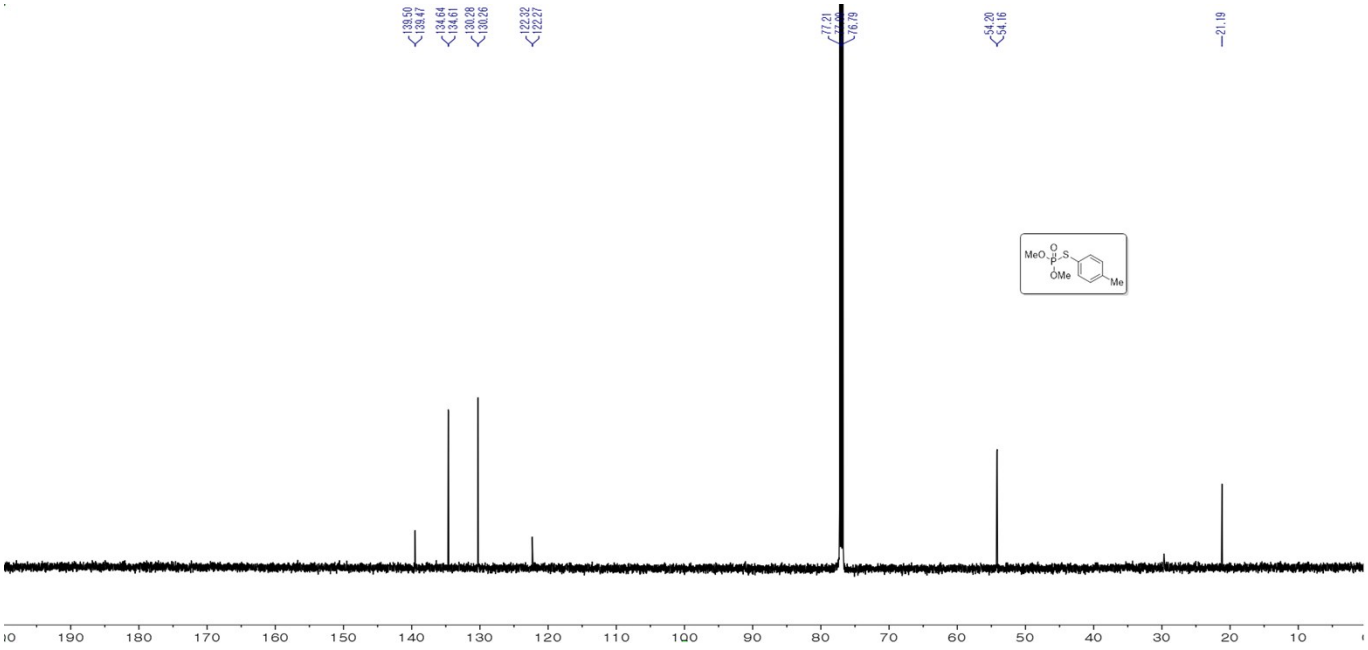


162 MHz, ^{31}P NMR in $CDCl_3$

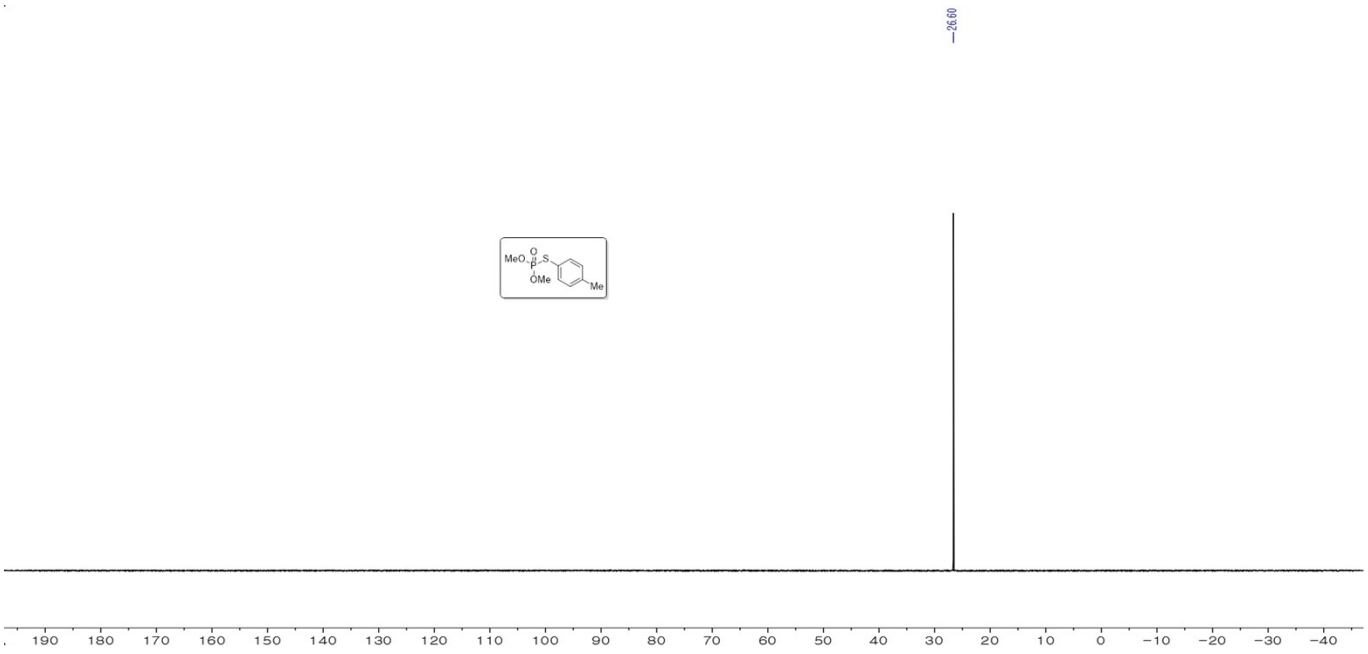
O,O-dimethyl S-p-tolyl phosphorothioate (4b)



600 MHz, ^{1}H NMR in $CDCl_3$

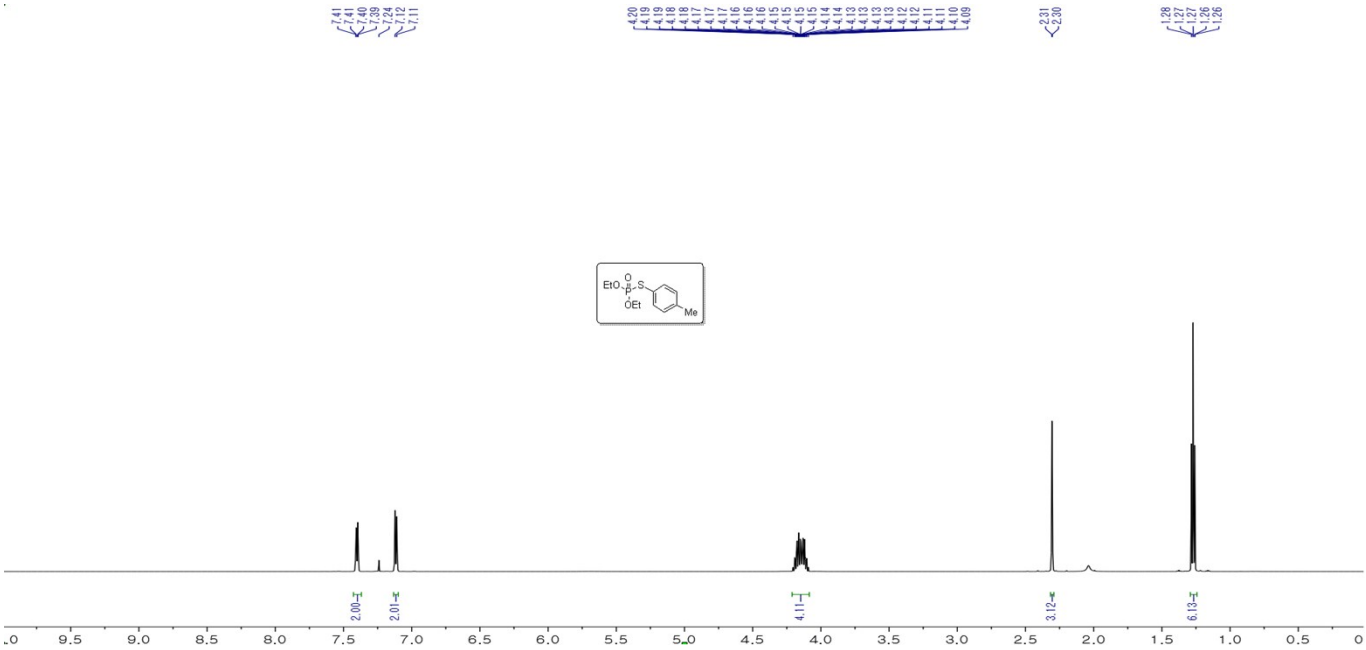


150 MHz, ^{13}C NMR in $CDCl_3$

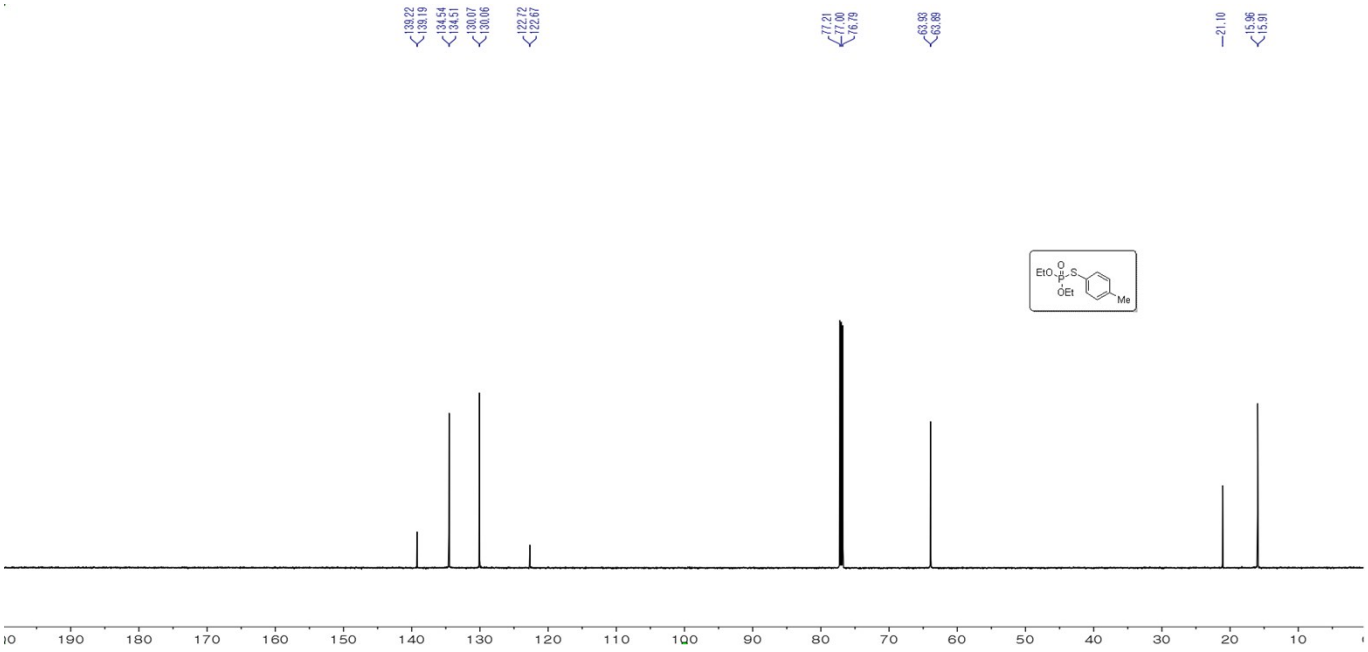


243 MHz, ^{31}P NMR in $CDCl_3$

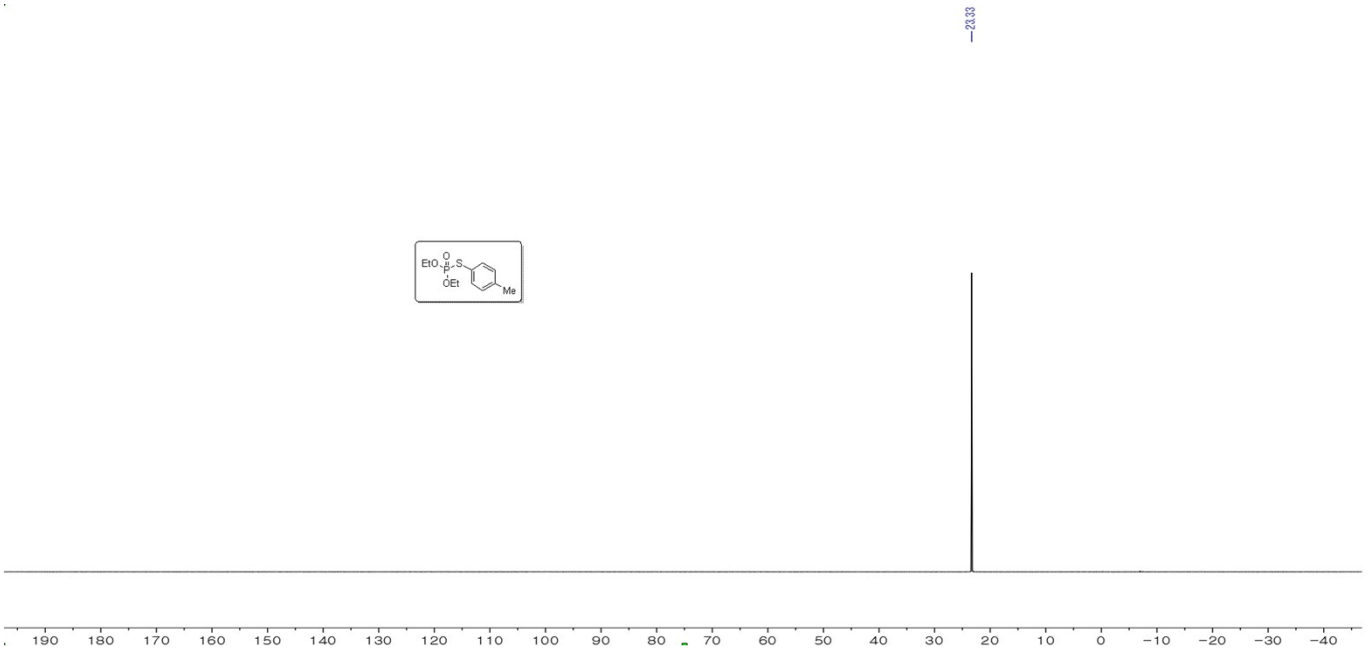
O,O-diethyl S-(p-tolyl) phosphorothioate (4c)



600 MHz, ^{1}H NMR in $CDCl_3$

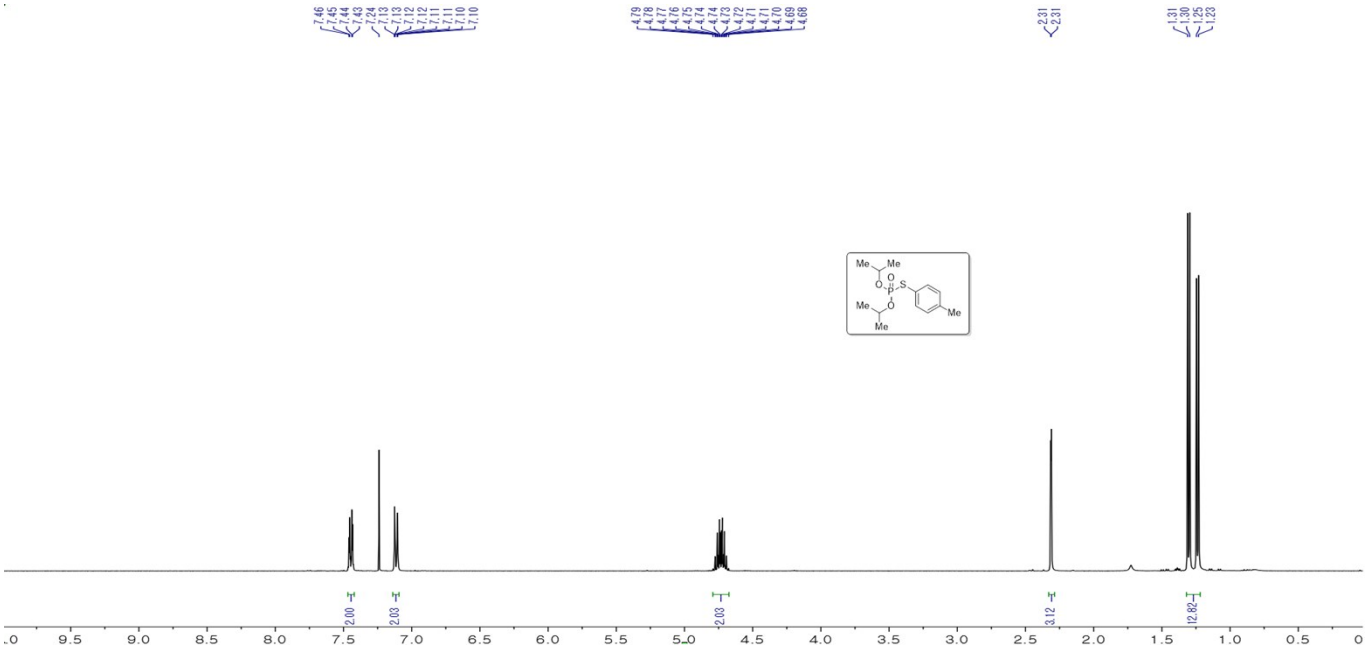


150 MHz, ^{13}C NMR in $CDCl_3$

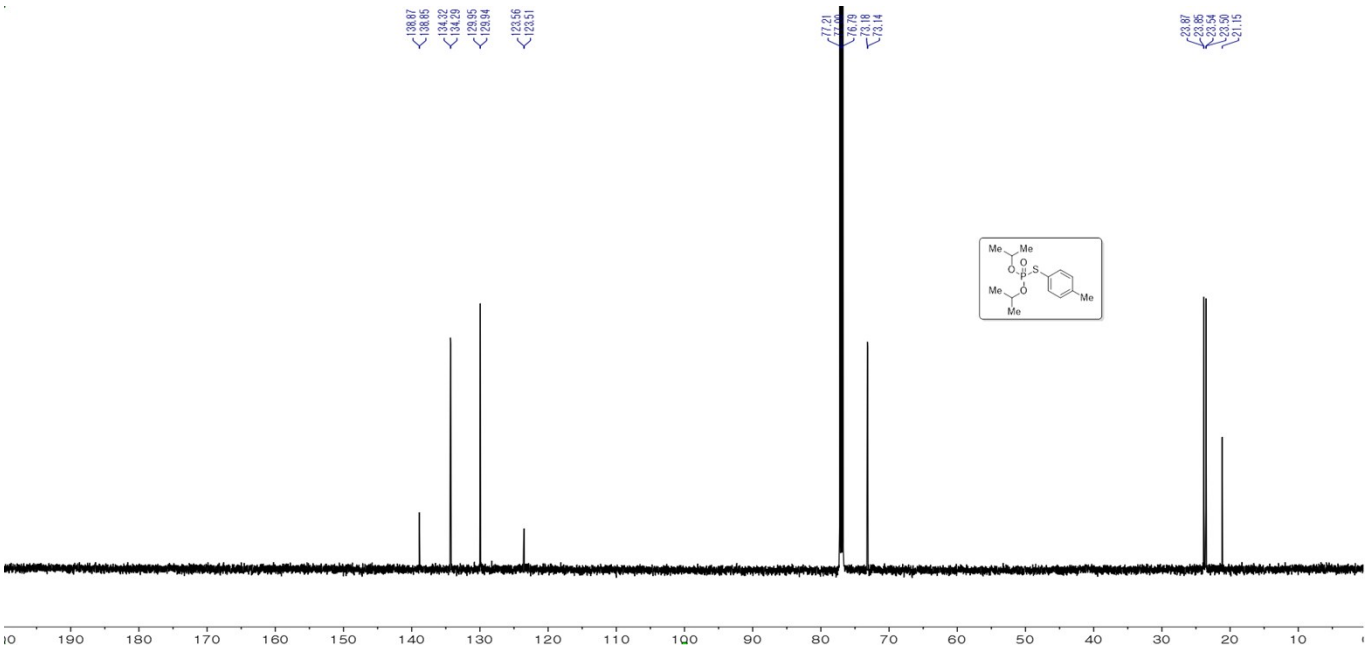


243 MHz, ^{31}P NMR in $CDCl_3$

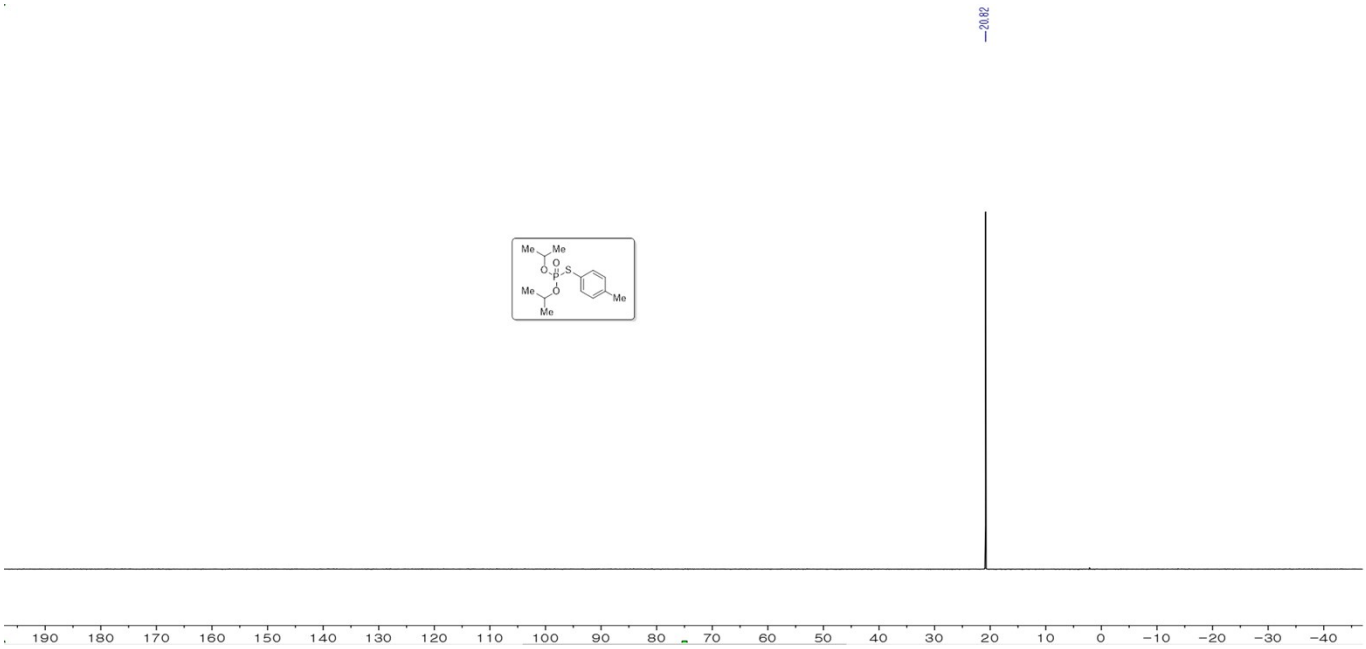
O,O-diisopropyl S-p-tolyl phosphorothioate (4d)



400 MHz, ^{1}H NMR in $CDCl_3$

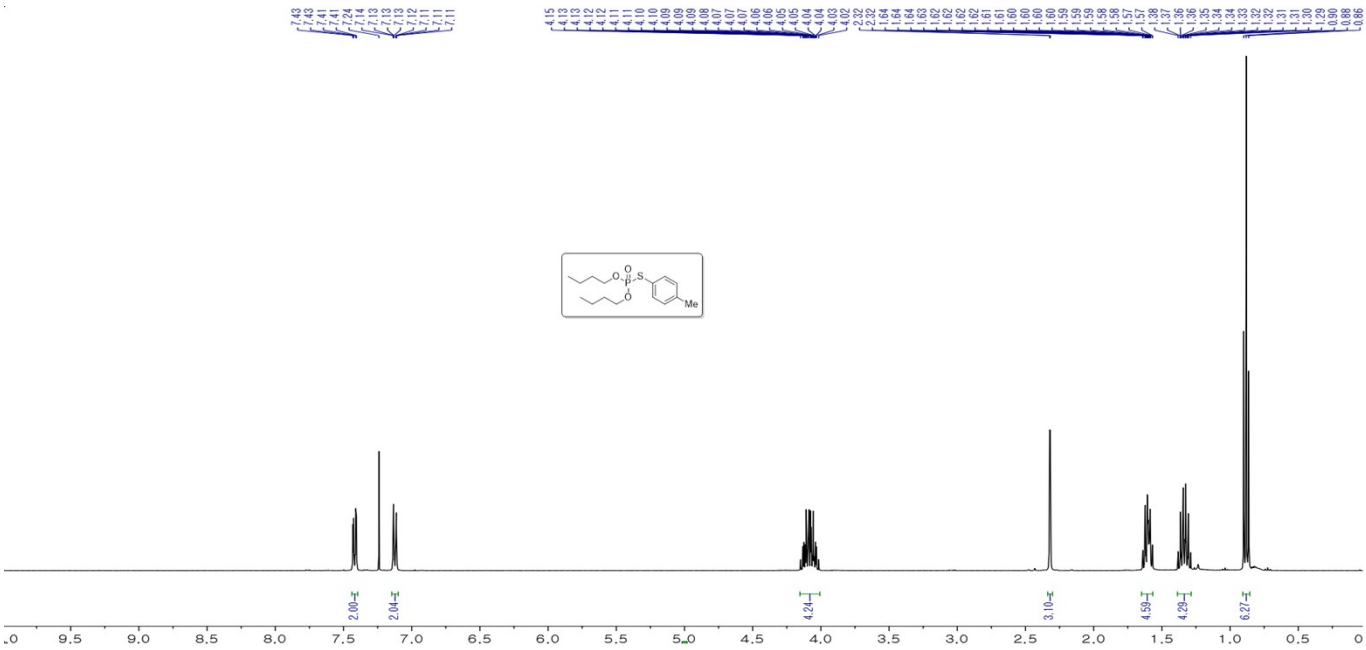


150 MHz, ^{13}C NMR in $CDCl_3$

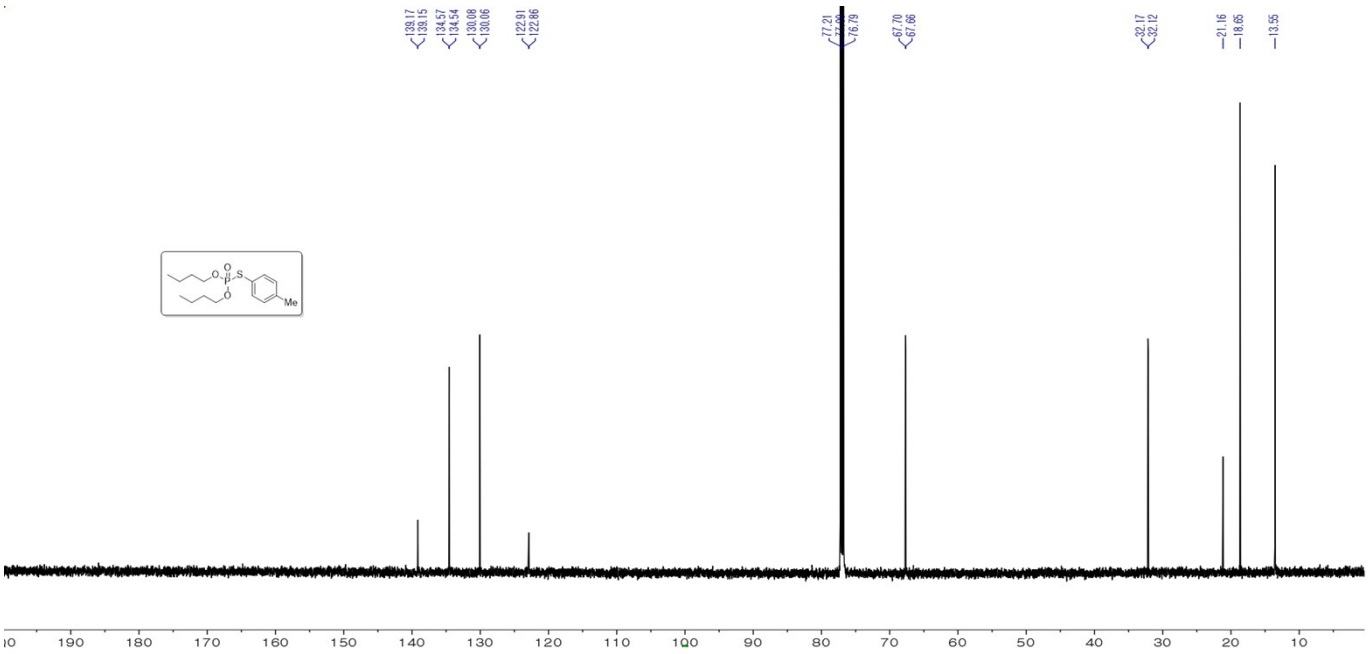


243 MHz, ^{31}P NMR in $CDCl_3$

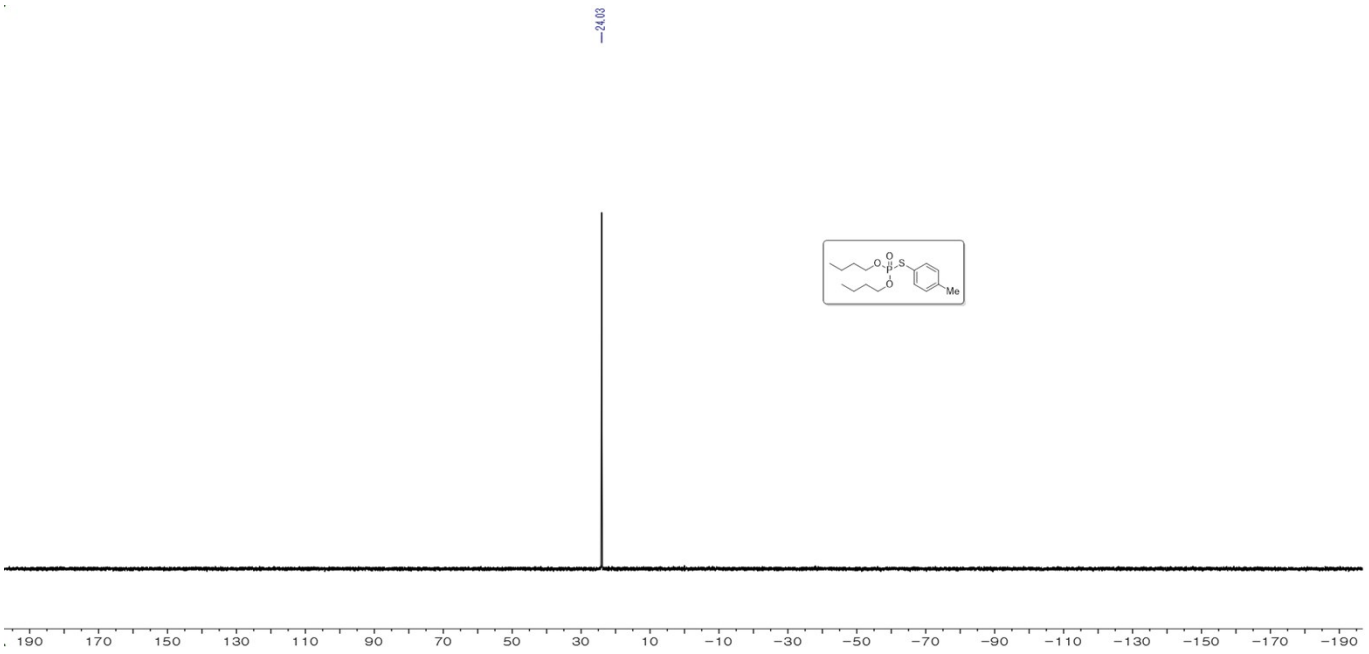
O,O-dibutyl S-p-tolyl phosphorothioate (4e)



400 MHz, ^{1}H NMR in $CDCl_3$

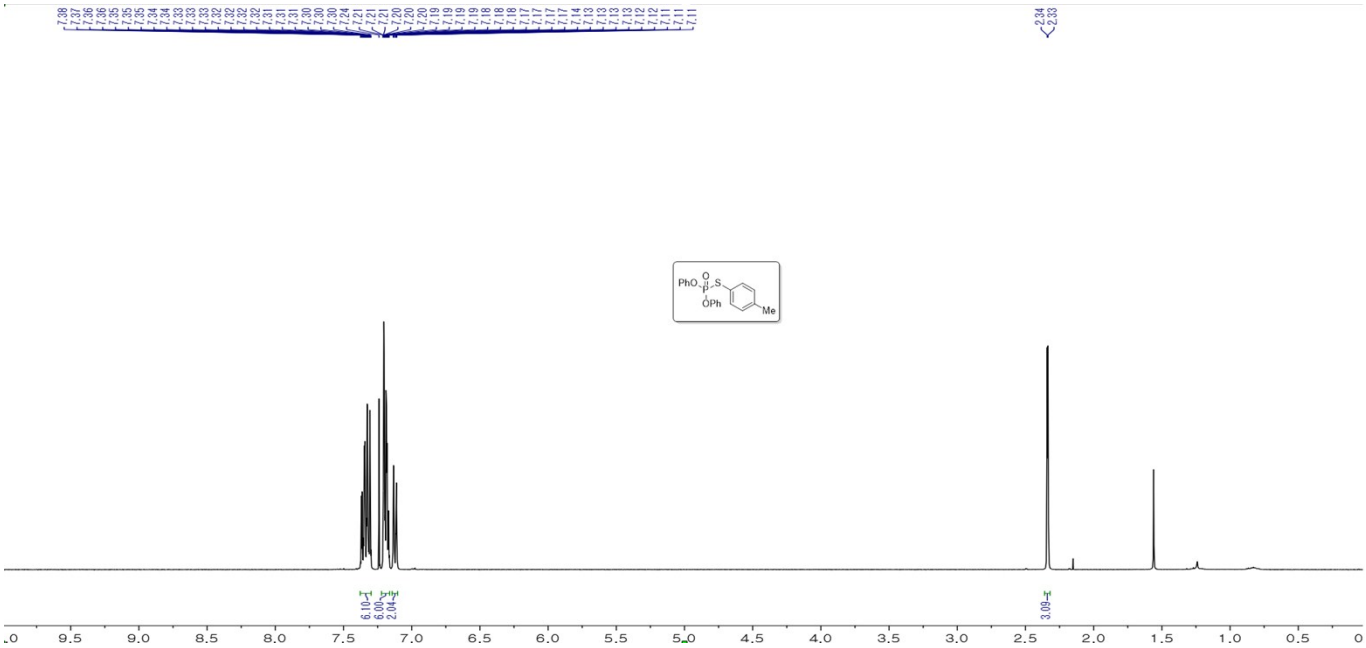


150 MHz, ^{13}C NMR in $CDCl_3$

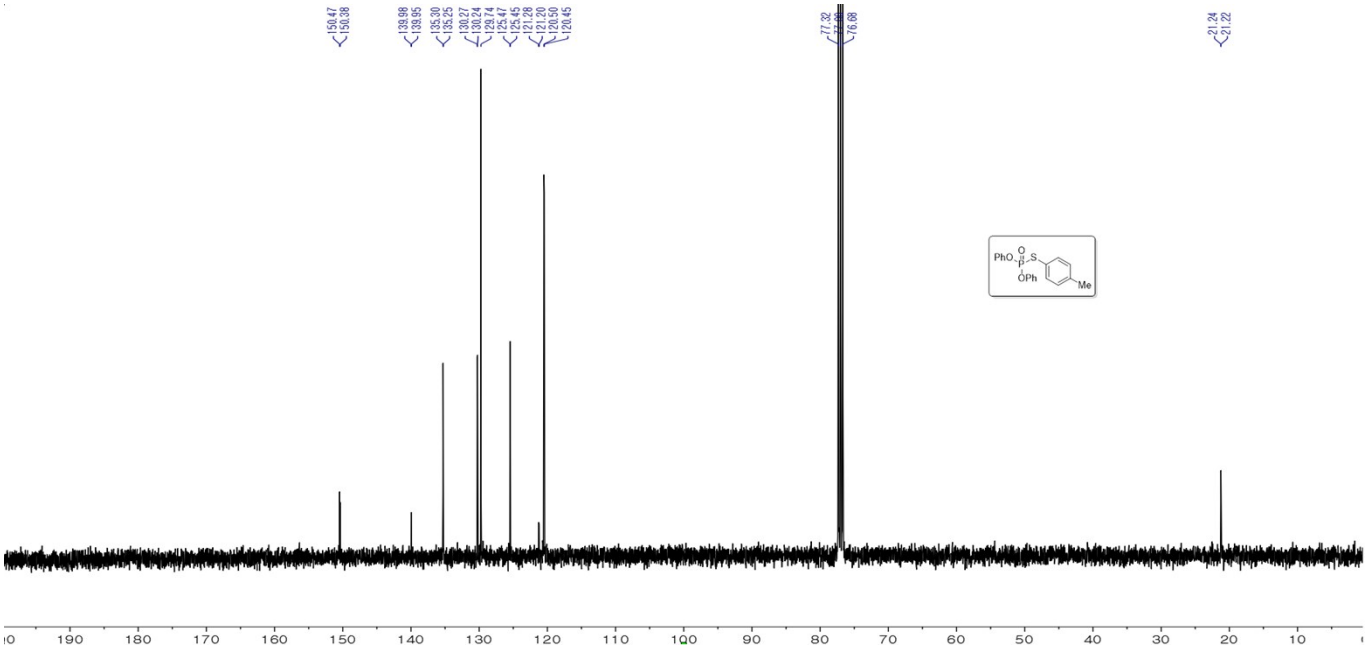


162 MHz, ^{31}P NMR in $CDCl_3$

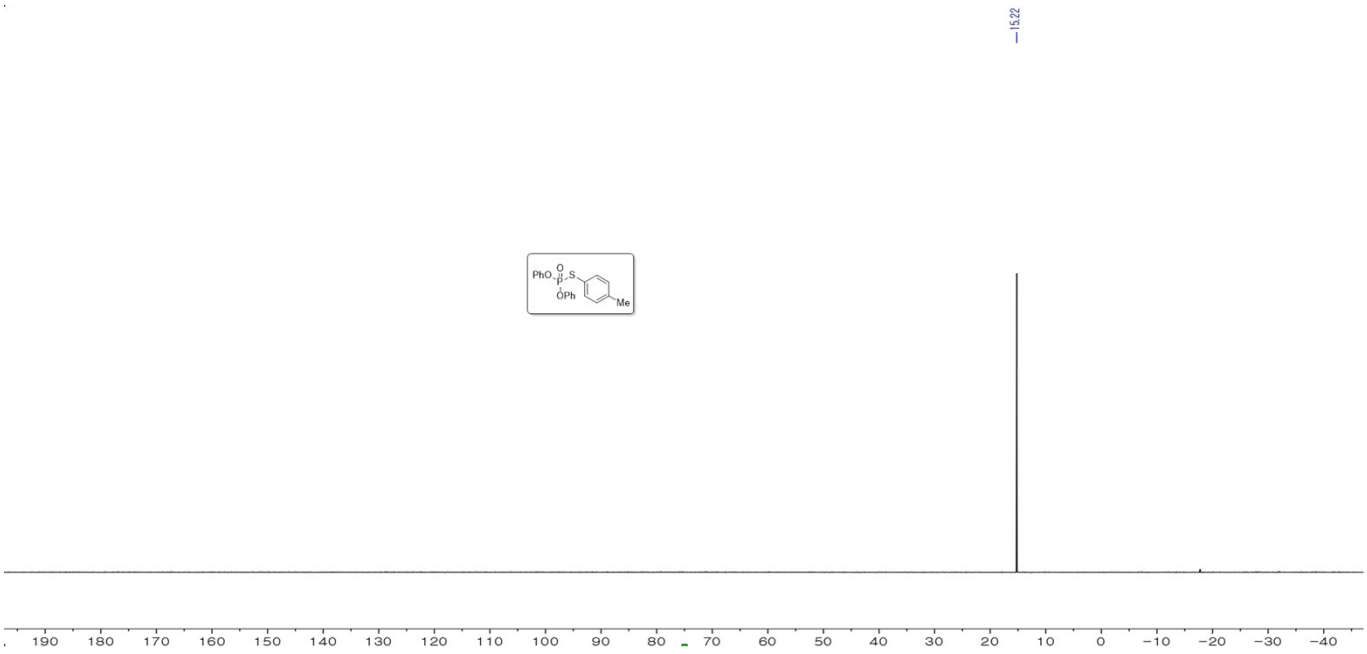
O,O-diphenyl S-p-tolyl phosphorothioate (4f)



400 MHz, ^{1}H NMR in $CDCl_3$

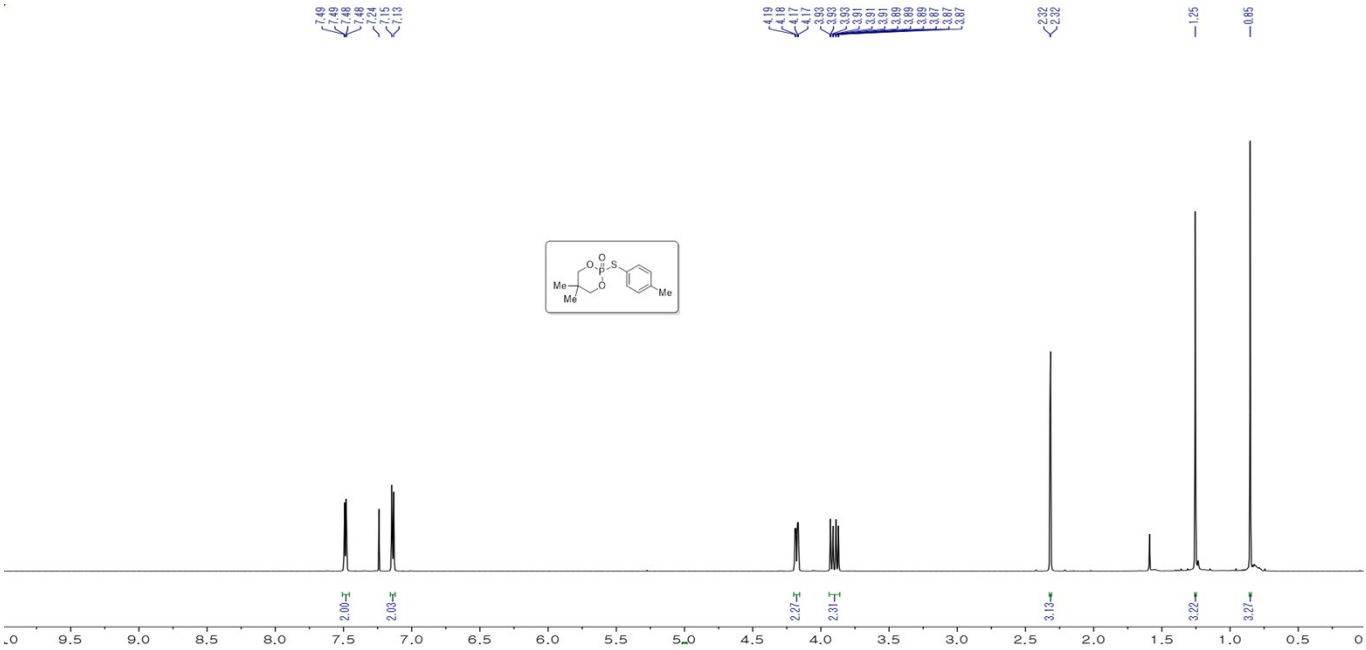


100 MHz, ^{13}C NMR in $CDCl_3$

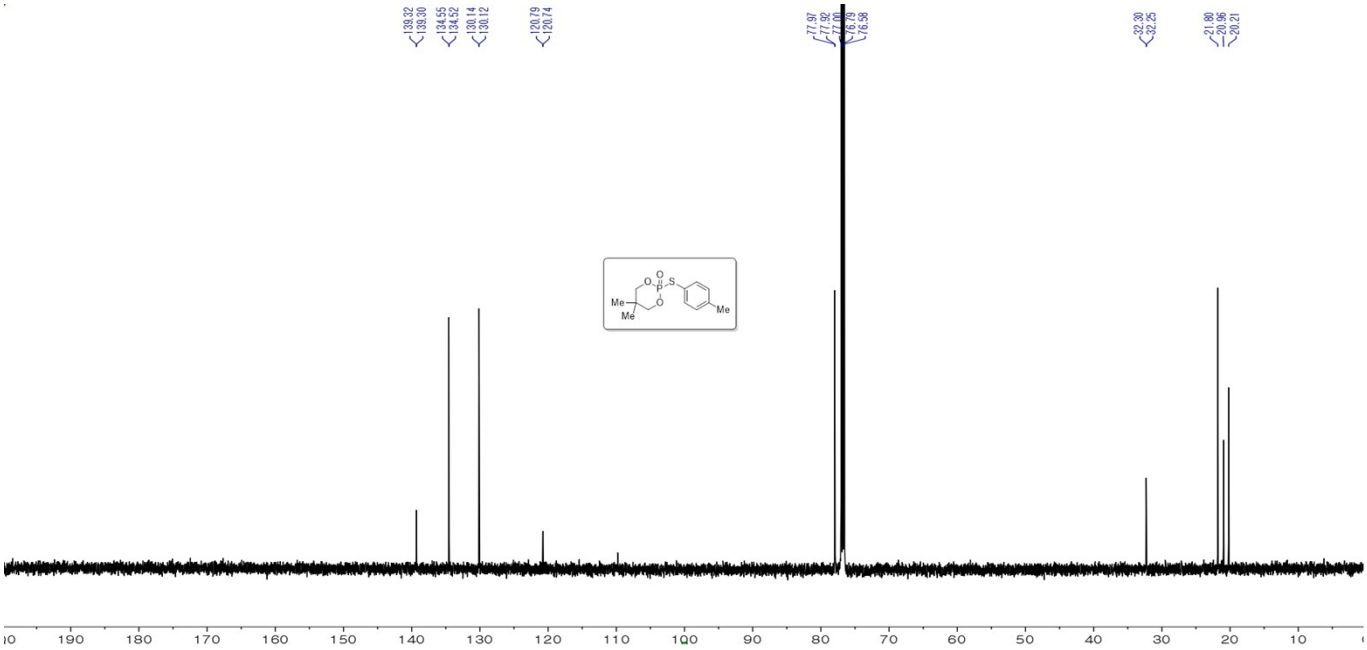


243 MHz, ^{31}P NMR in $CDCl_3$

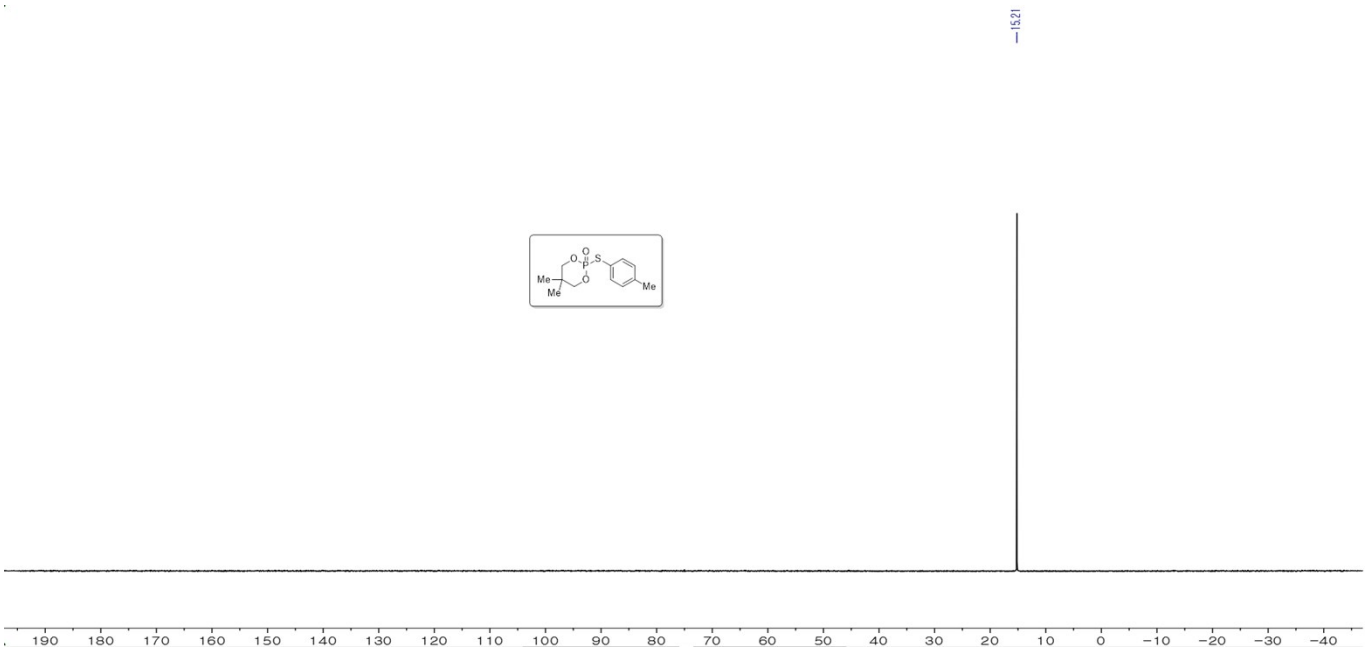
5,5-dimethyl-2-(p-tolylthio)-1,3,2-dioxaphosphinane 2-oxide (4g)



600 MHz, ^{1}H NMR in $CDCl_3$

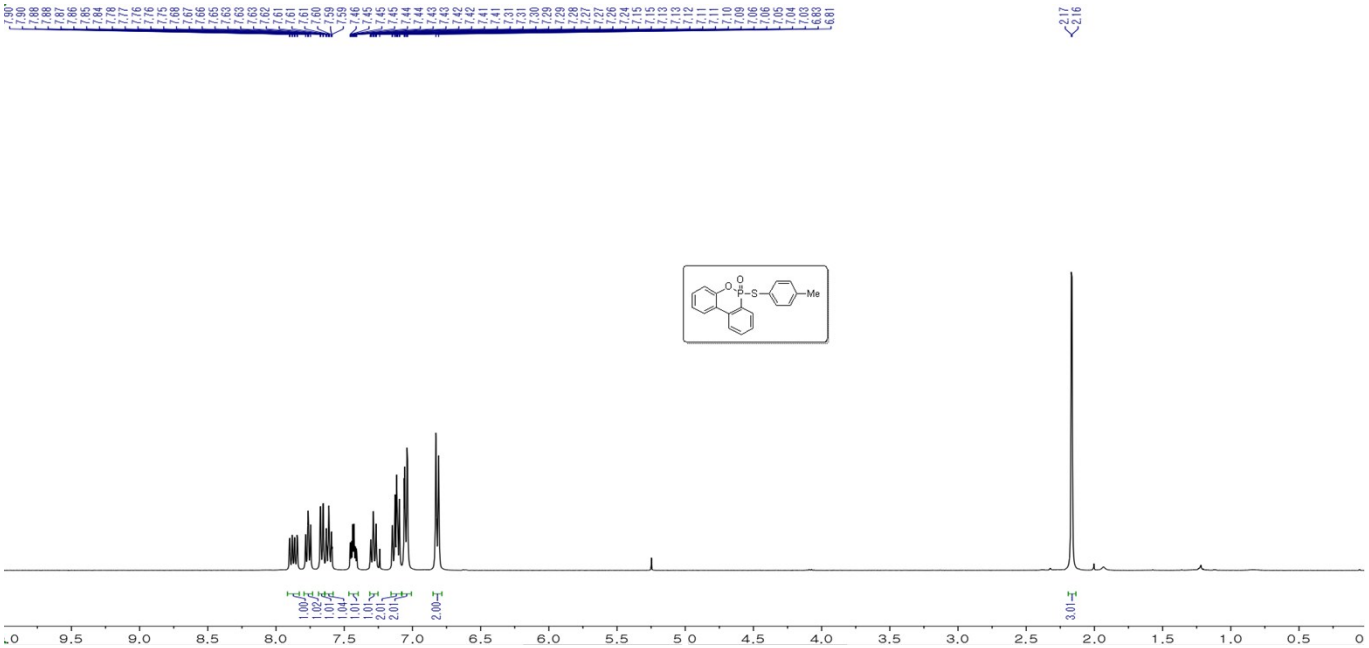


150 MHz, ^{13}C NMR in $CDCl_3$

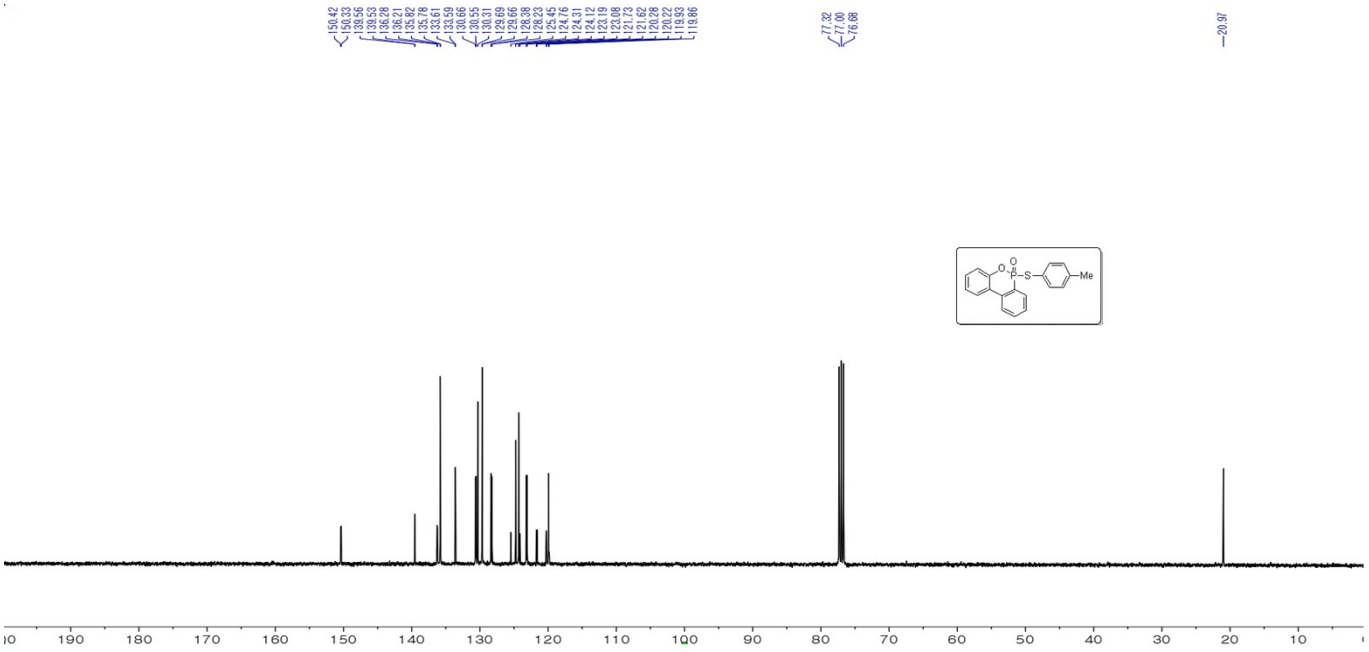


243 MHz, ^{31}P NMR in $CDCl_3$

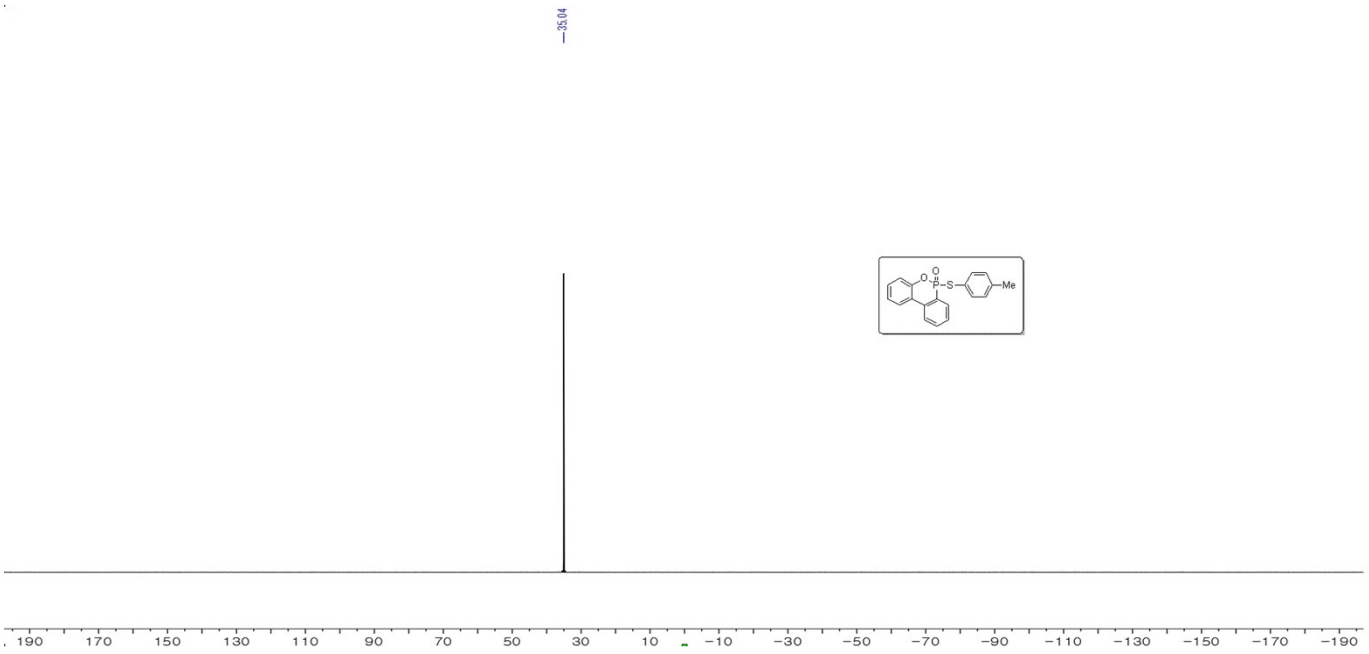
6-(p-tolylthio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4h)



400 MHz, ^{1}H NMR in $CDCl_3$

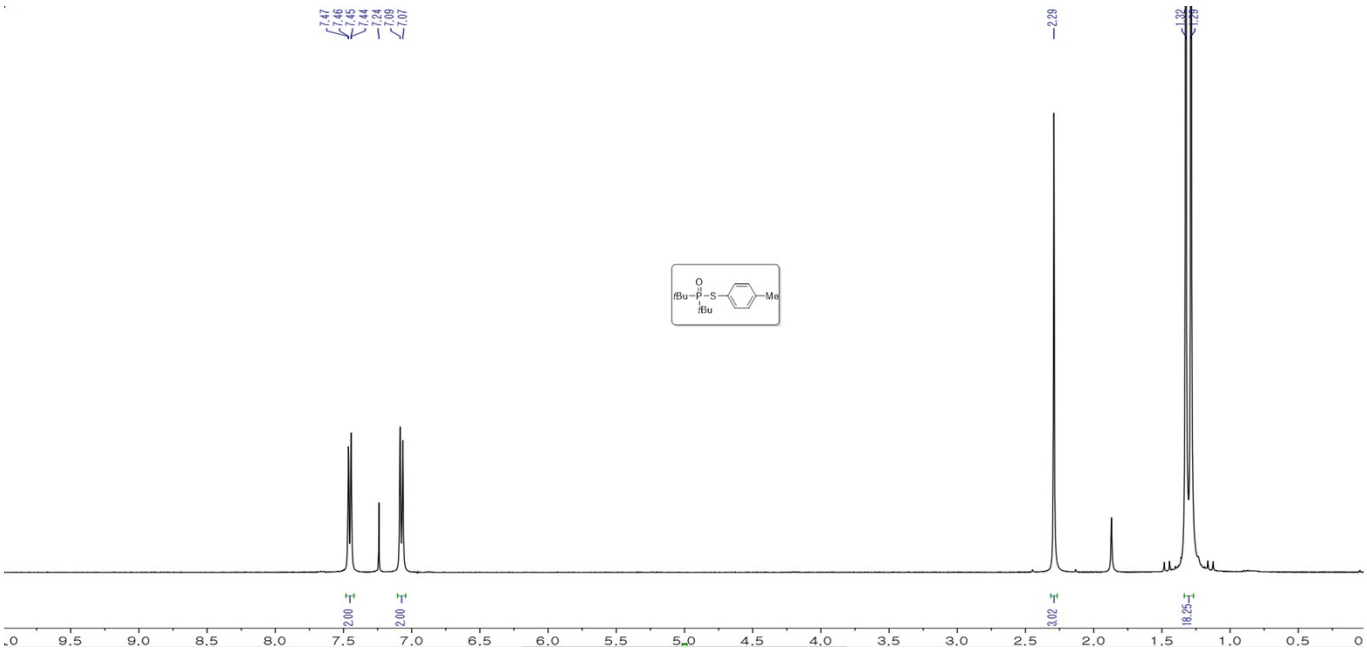


100 MHz, ^{13}C NMR in $CDCl_3$

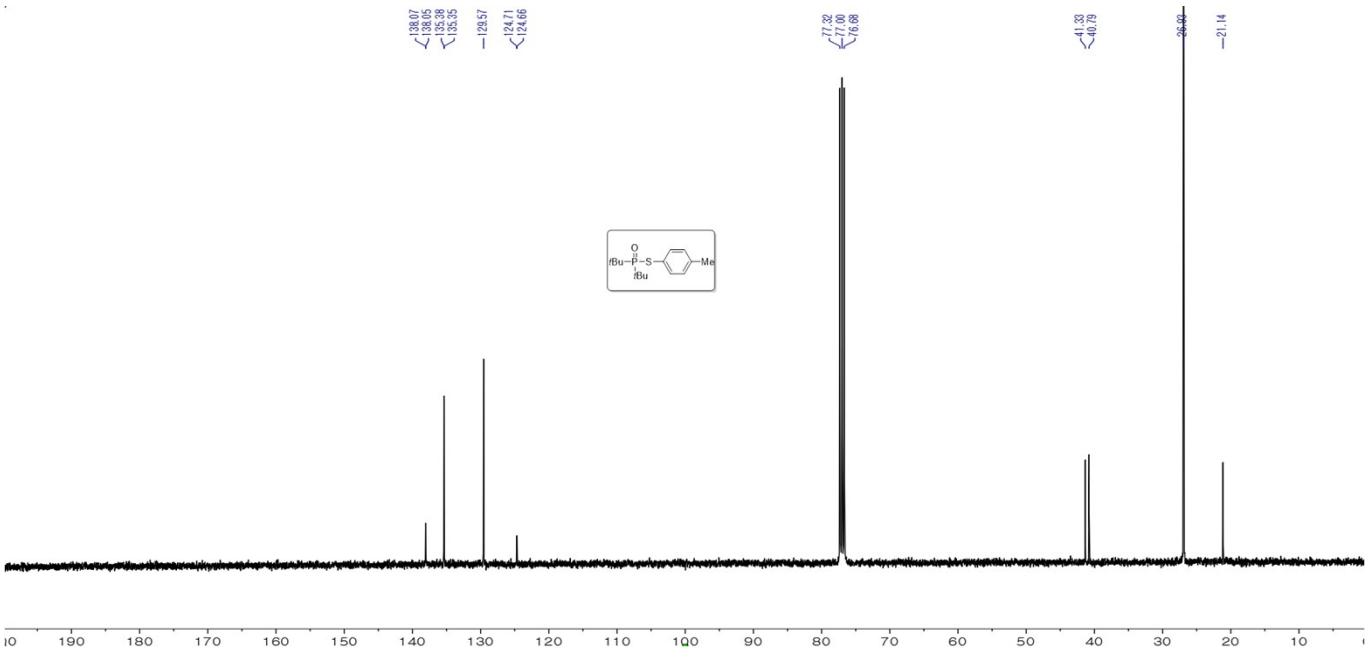


162 MHz, ^{31}P NMR in $CDCl_3$

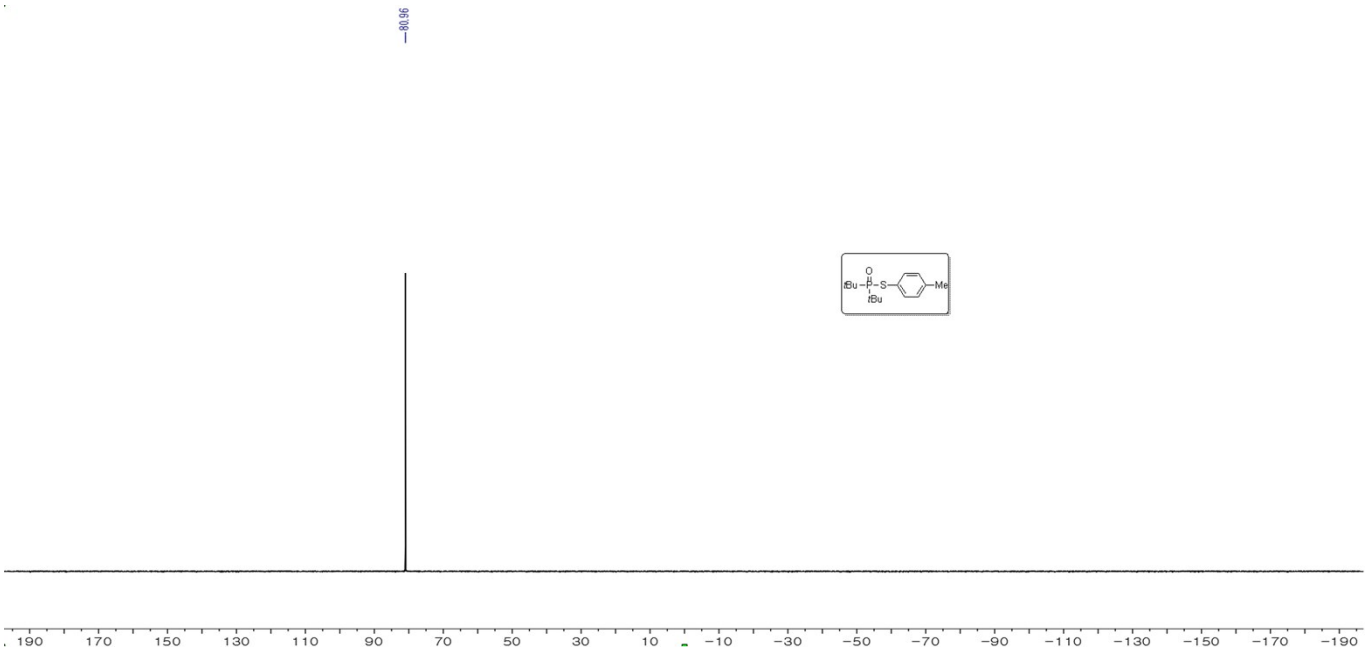
S-(p-tolyl) di-tert-butylphosphinothioate (4i)



400 MHz, ^{1}H NMR in $CDCl_3$

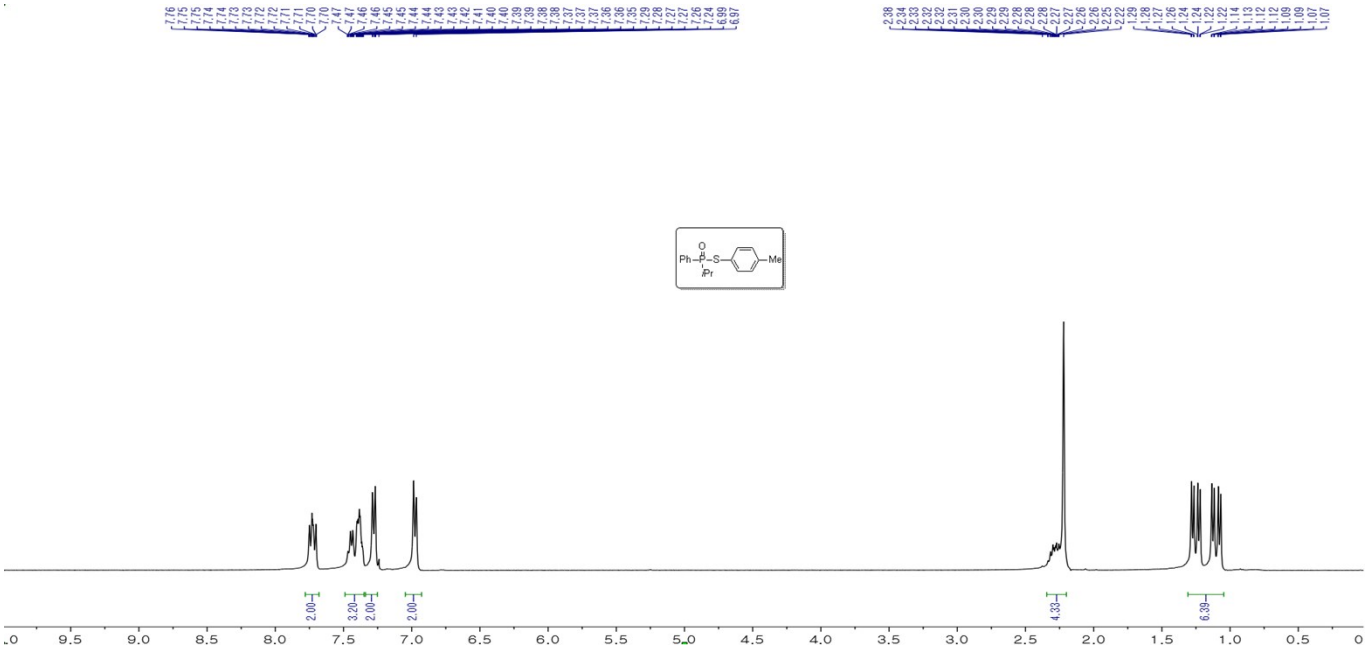


100 MHz, ^{13}C NMR in $CDCl_3$

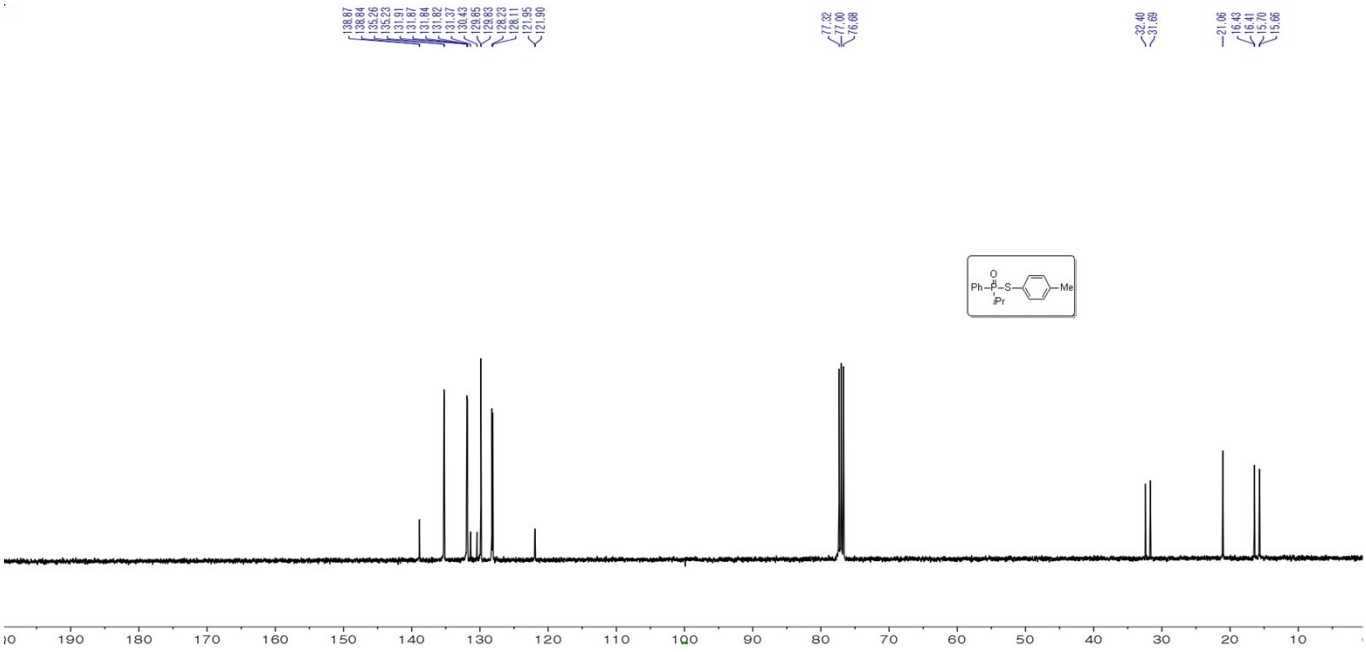


162 MHz, ^{31}P NMR in $CDCl_3$

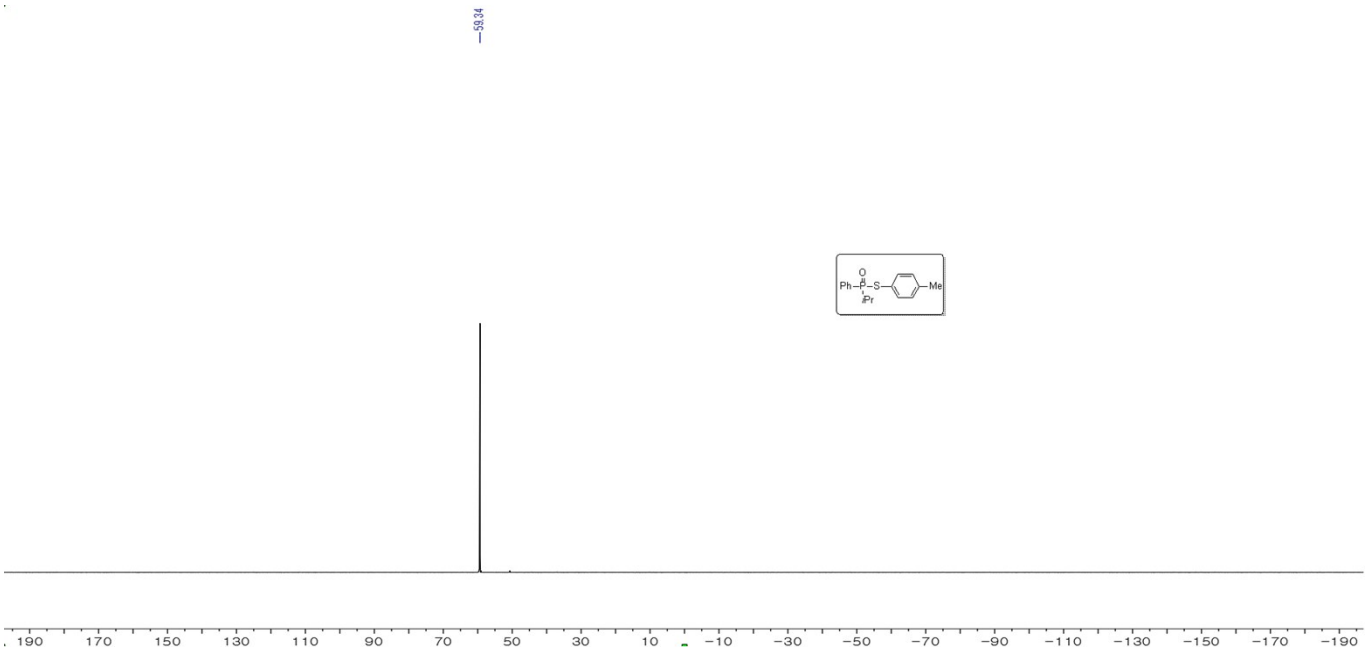
S-(p-tolyl) isopropyl(phenyl)phosphinothioate (4j)



400 MHz, ^{1}H NMR in $CDCl_3$

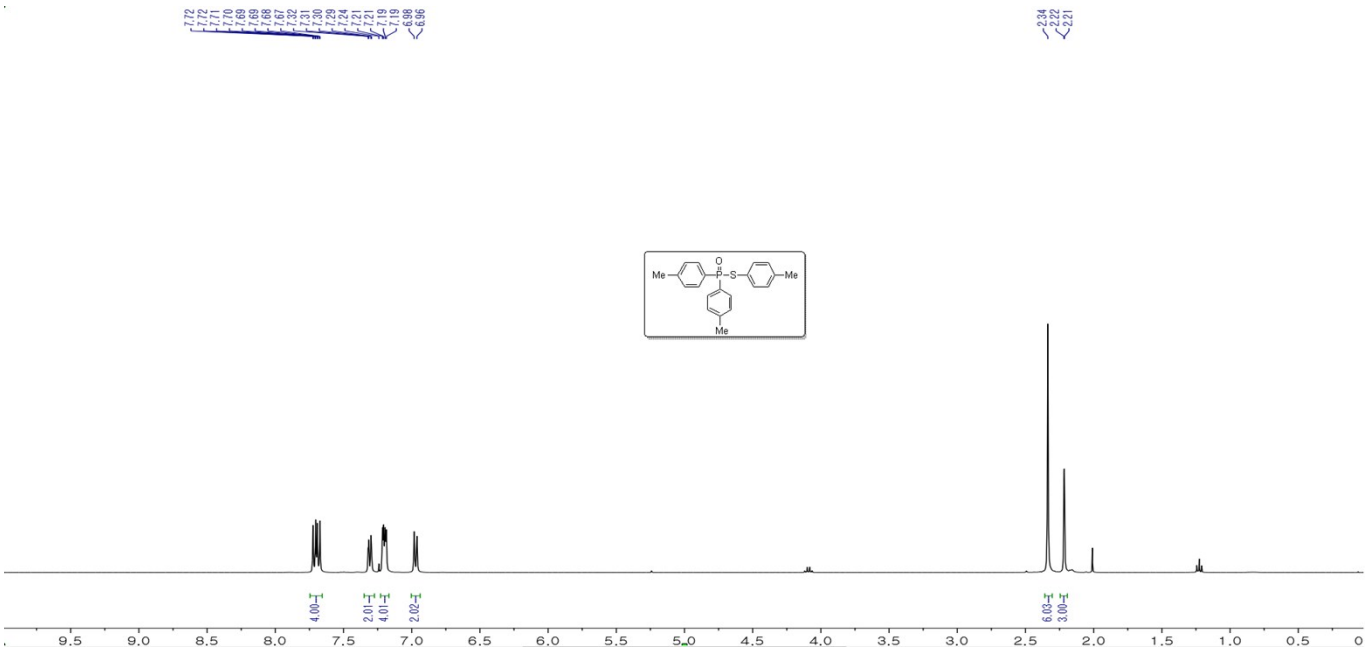


100 MHz, ^{13}C NMR in $CDCl_3$

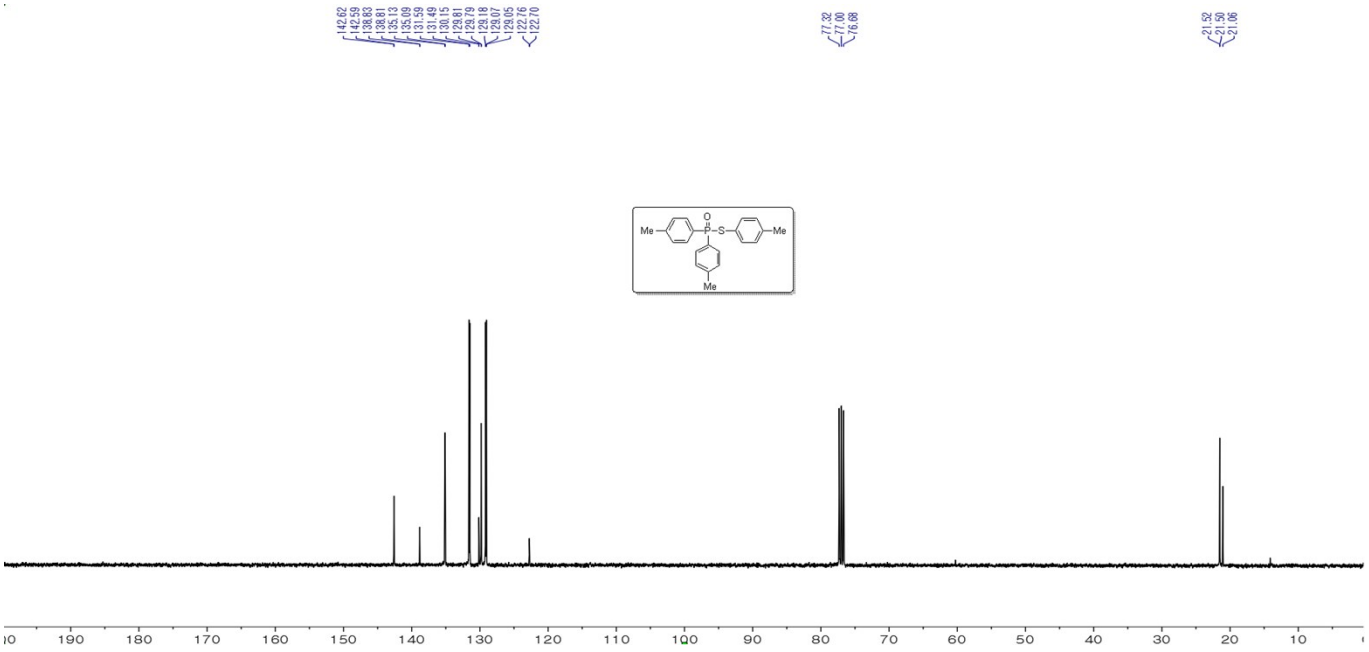


162 MHz, ^{31}P NMR in $CDCl_3$

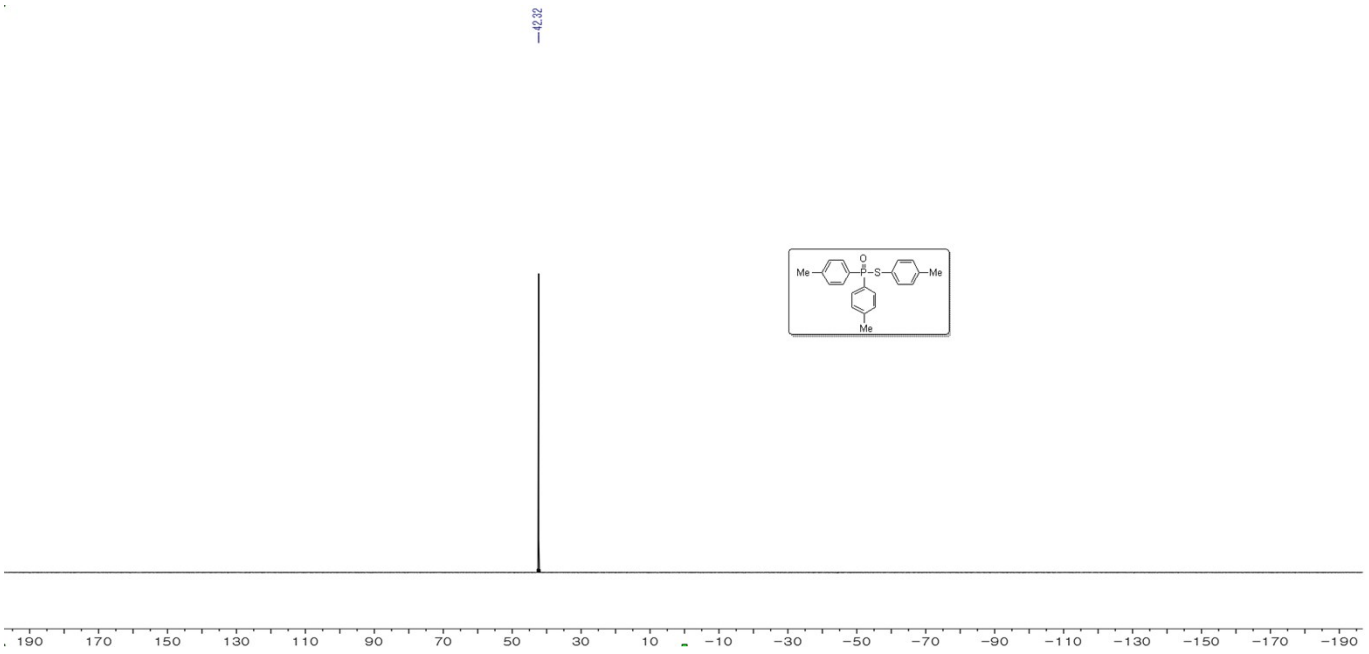
S-(p-tolyl) di-p-tolylphosphinothioate (4k)



400 MHz, ^{1}H NMR in $CDCl_3$

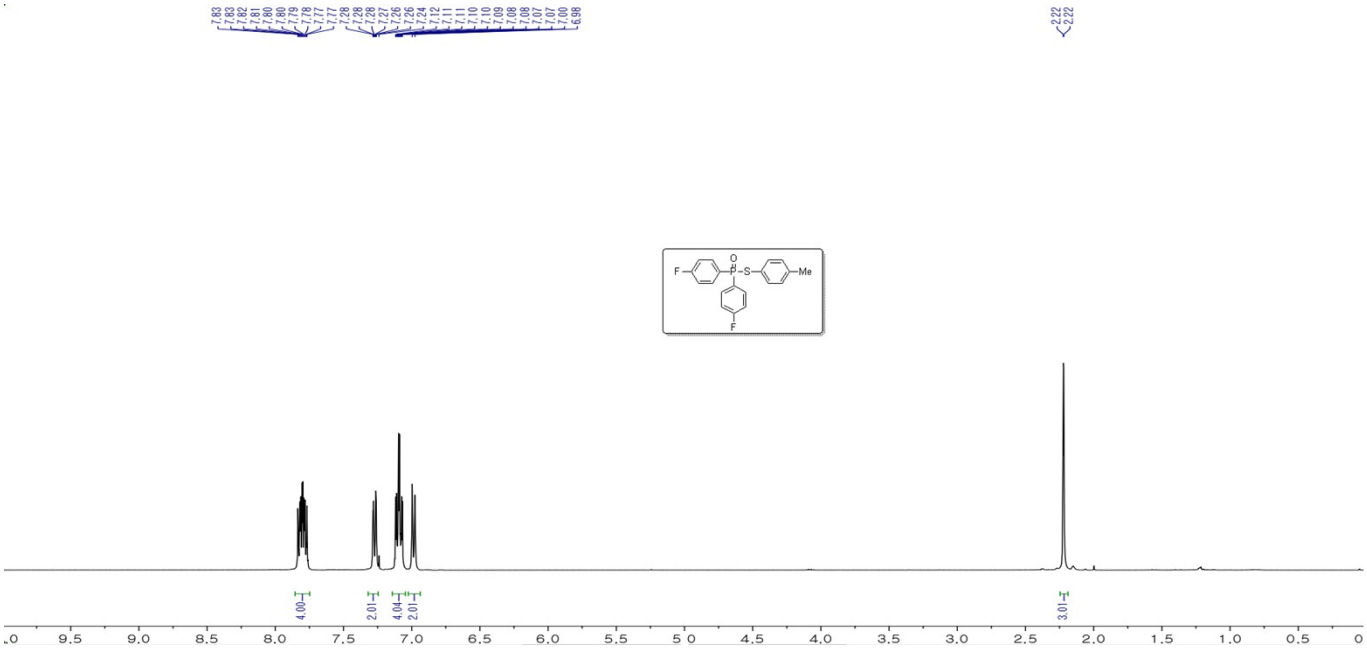


100 MHz, ^{13}C NMR in $CDCl_3$

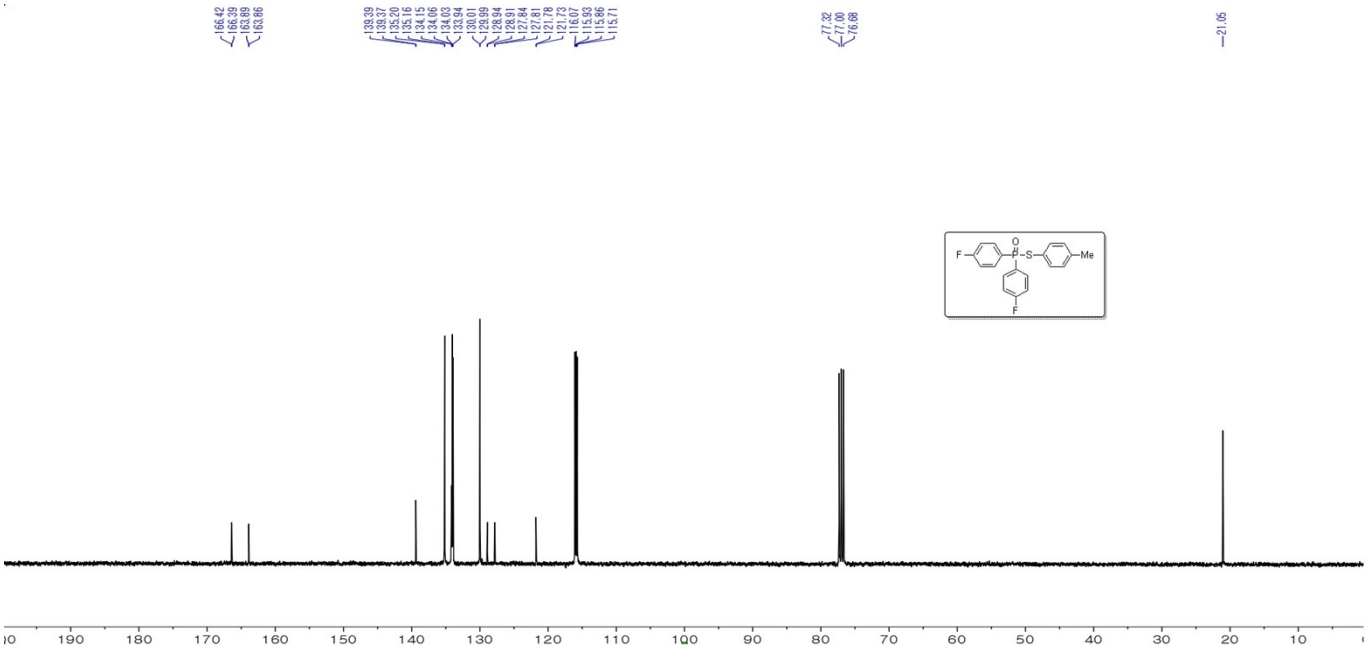


162 MHz, ^{31}P NMR in $CDCl_3$

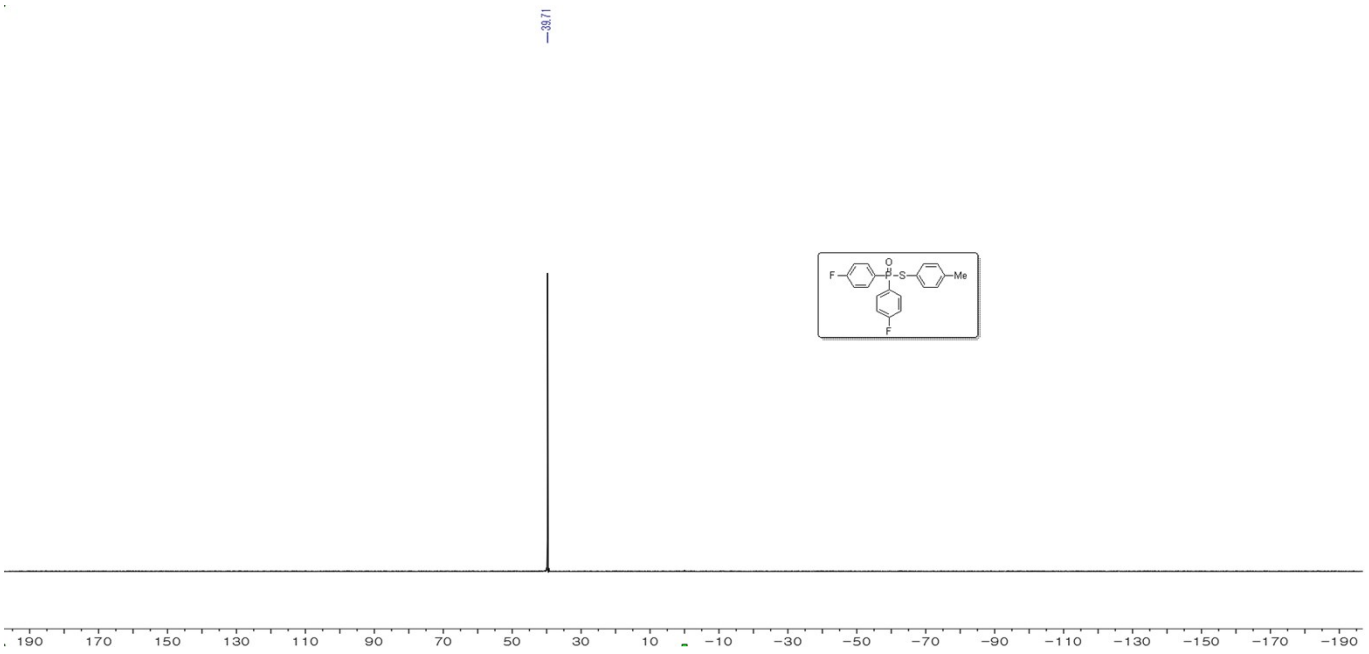
S-(p-tolyl) bis(4-fluorophenyl)phosphinothioate (4l)



400 MHz, ^{1}H NMR in $CDCl_3$

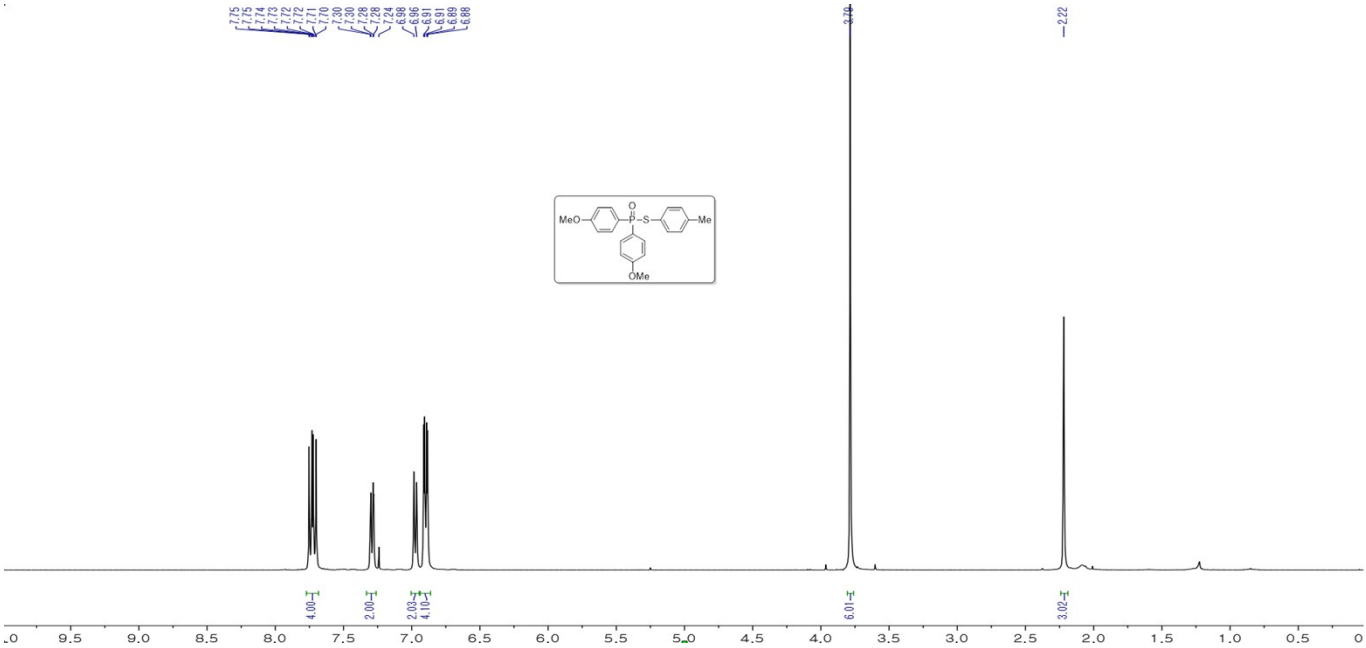


100 MHz, ^{13}C NMR in $CDCl_3$

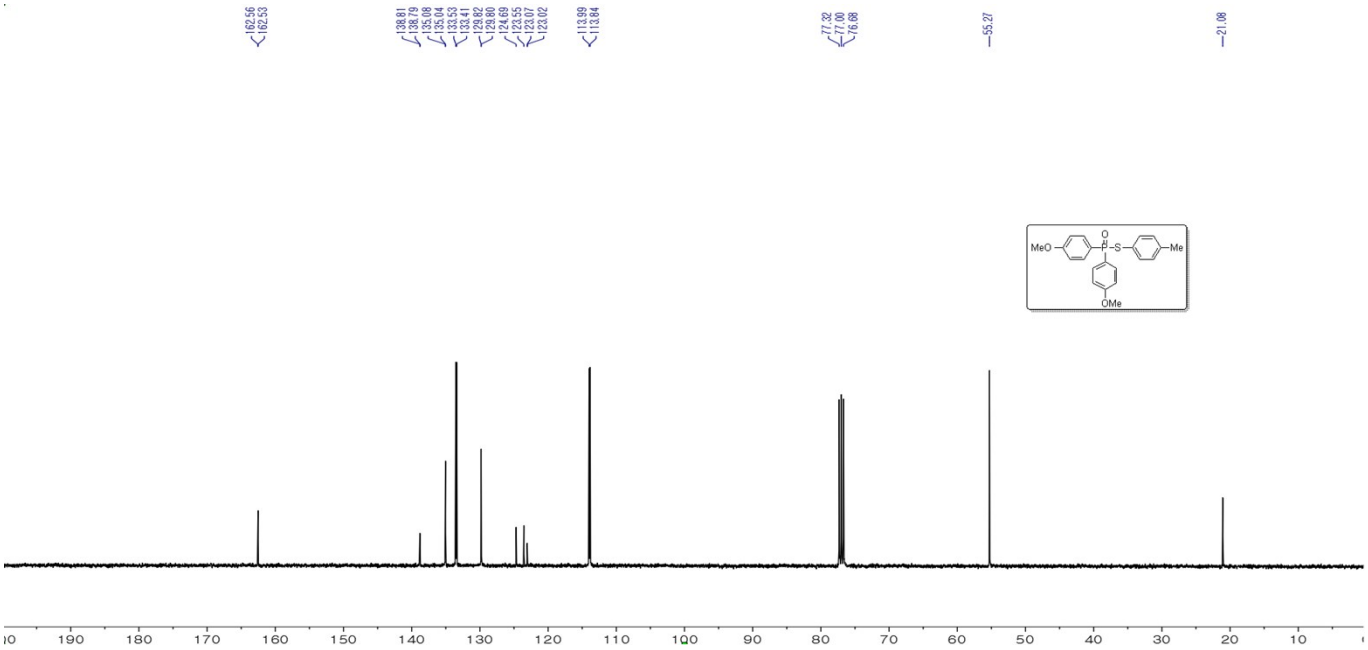


162 MHz, ^{31}P NMR in $CDCl_3$

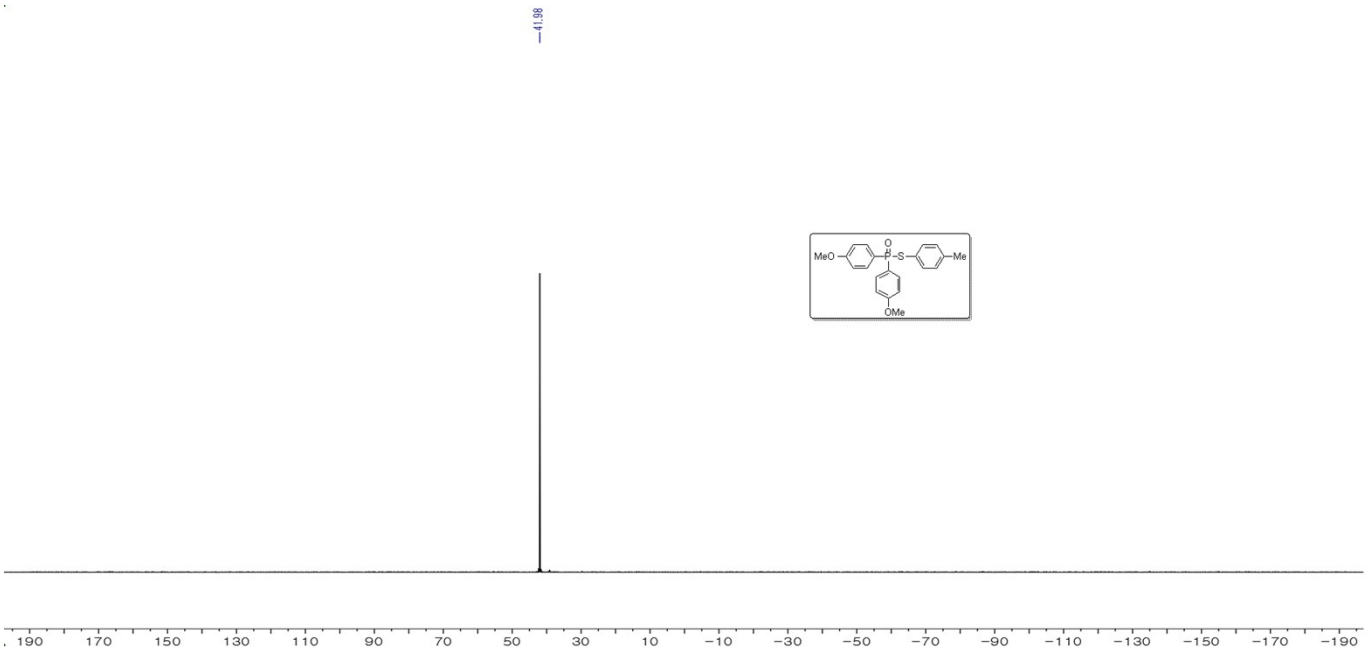
S-(p-tolyl) bis(4-methoxyphenyl)phosphinothioate (4m)



400 MHz, ^{1}H NMR in $CDCl_3$

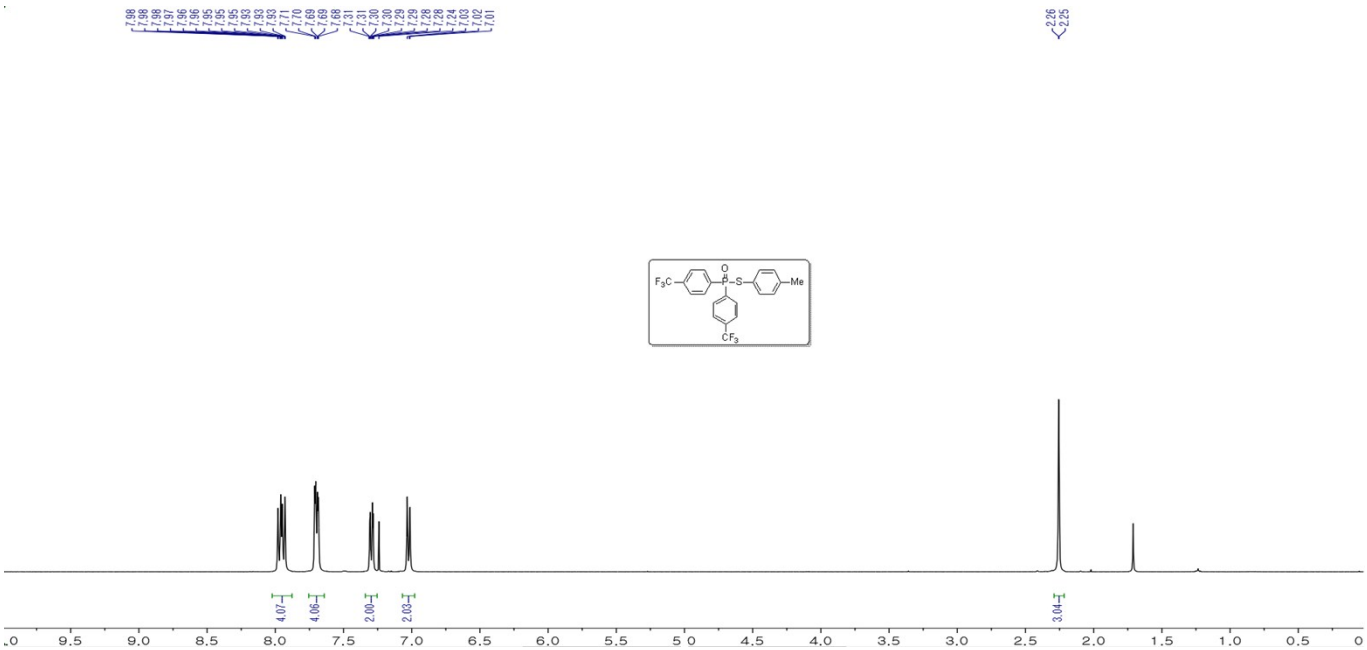


100 MHz, ^{13}C NMR in $CDCl_3$

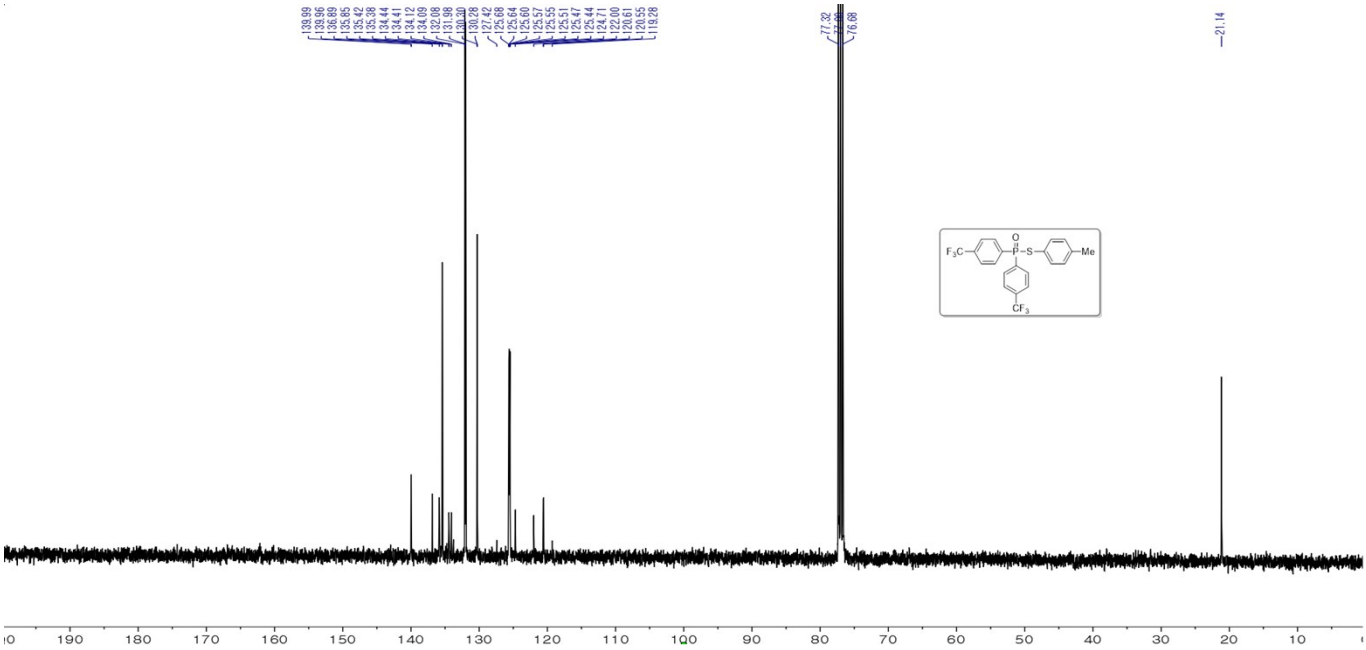


162 MHz, ^{31}P NMR in $CDCl_3$

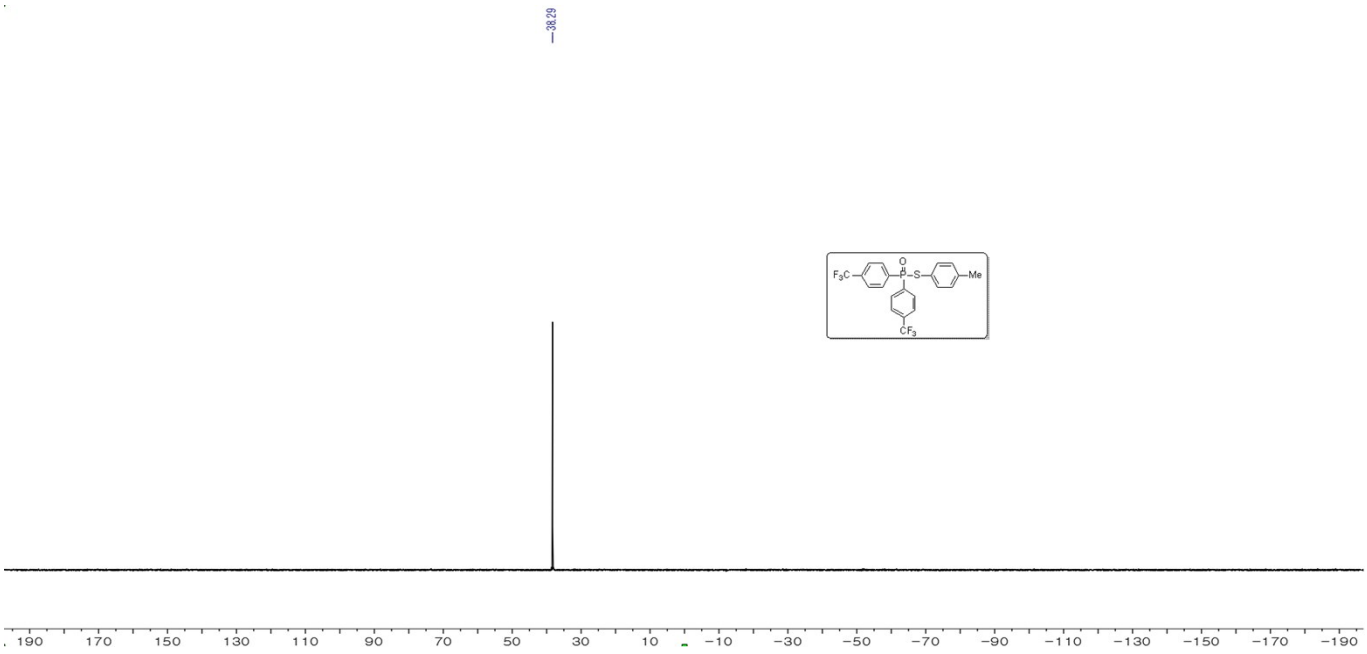
S-(p-tolyl) bis(4-(trifluoromethyl)phenyl)phosphinothioate (4n)



400 MHz, ^{1}H NMR in $CDCl_3$

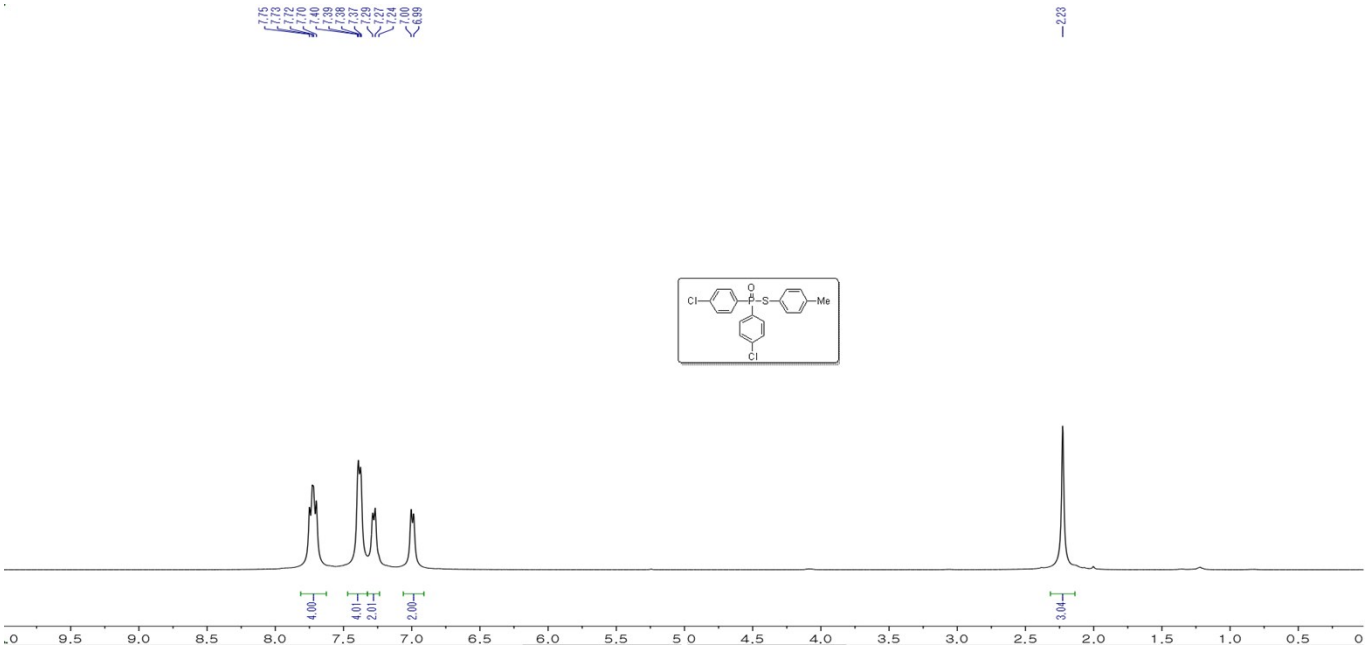


100 MHz, ^{13}C NMR in $CDCl_3$

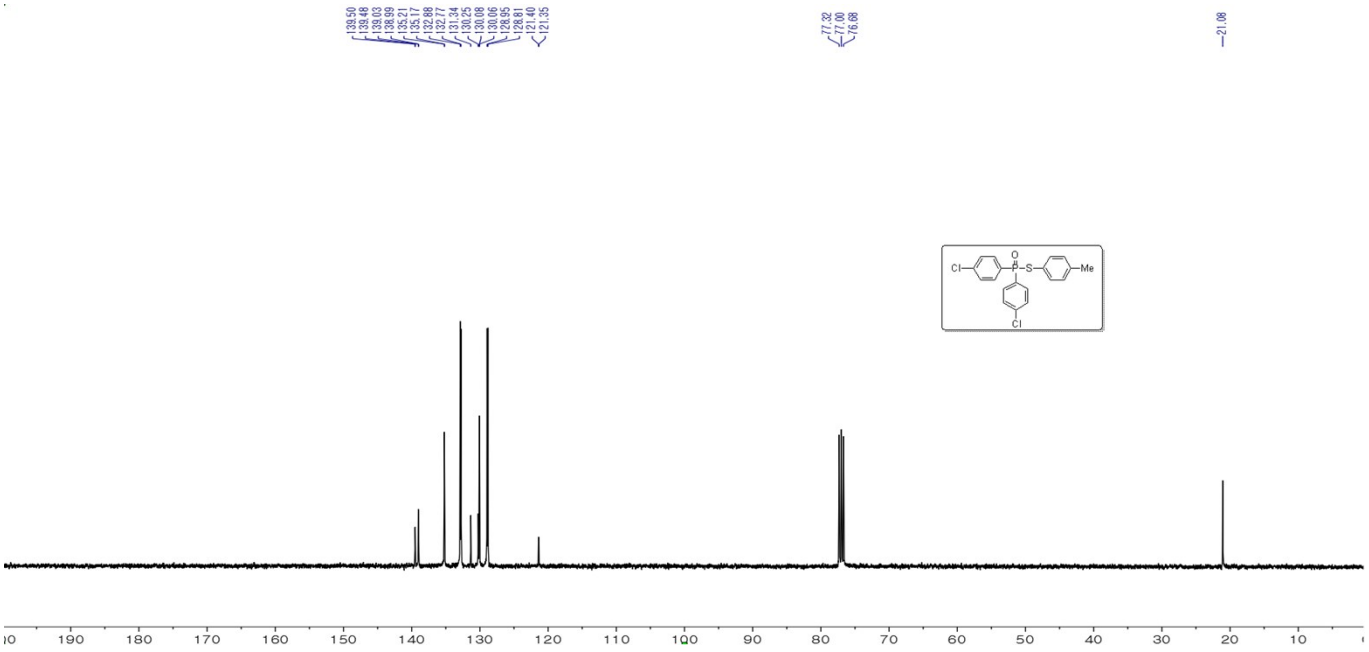


162 MHz, ^{31}P NMR in $CDCl_3$

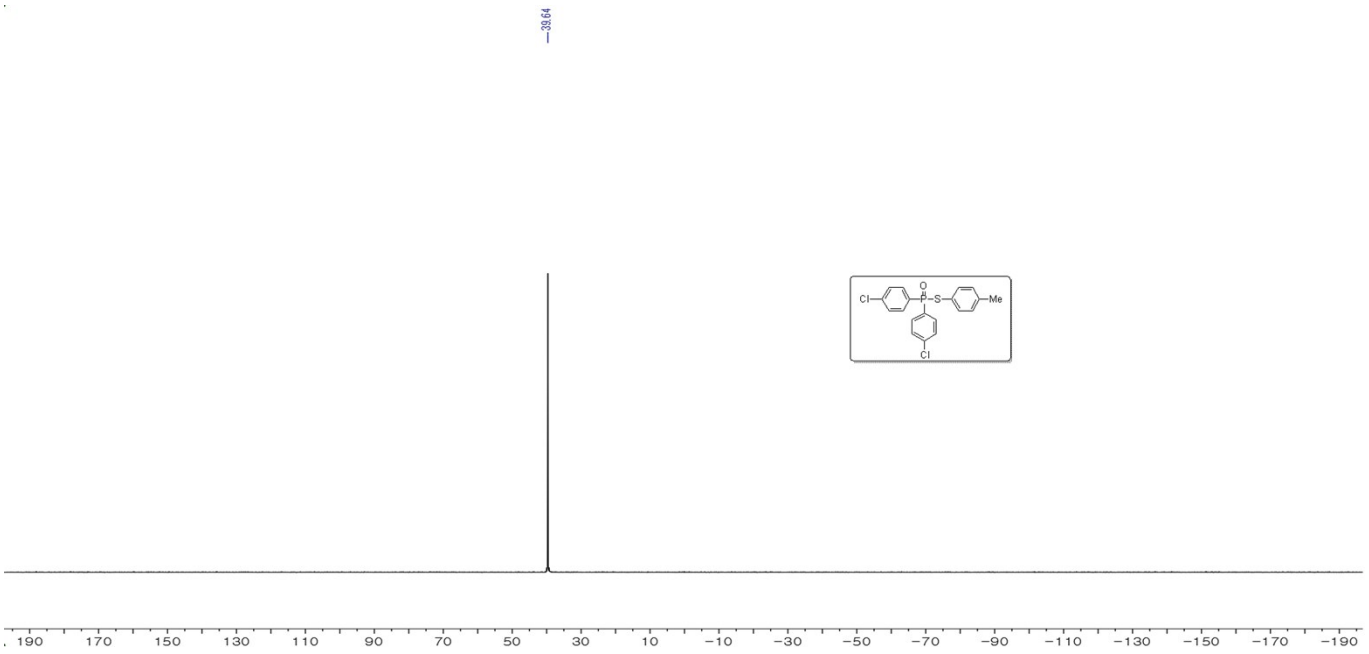
S-(p-tolyl) bis(4-chlorophenyl)phosphinothioate (4o)



400 MHz, ^{1}H NMR in $CDCl_3$

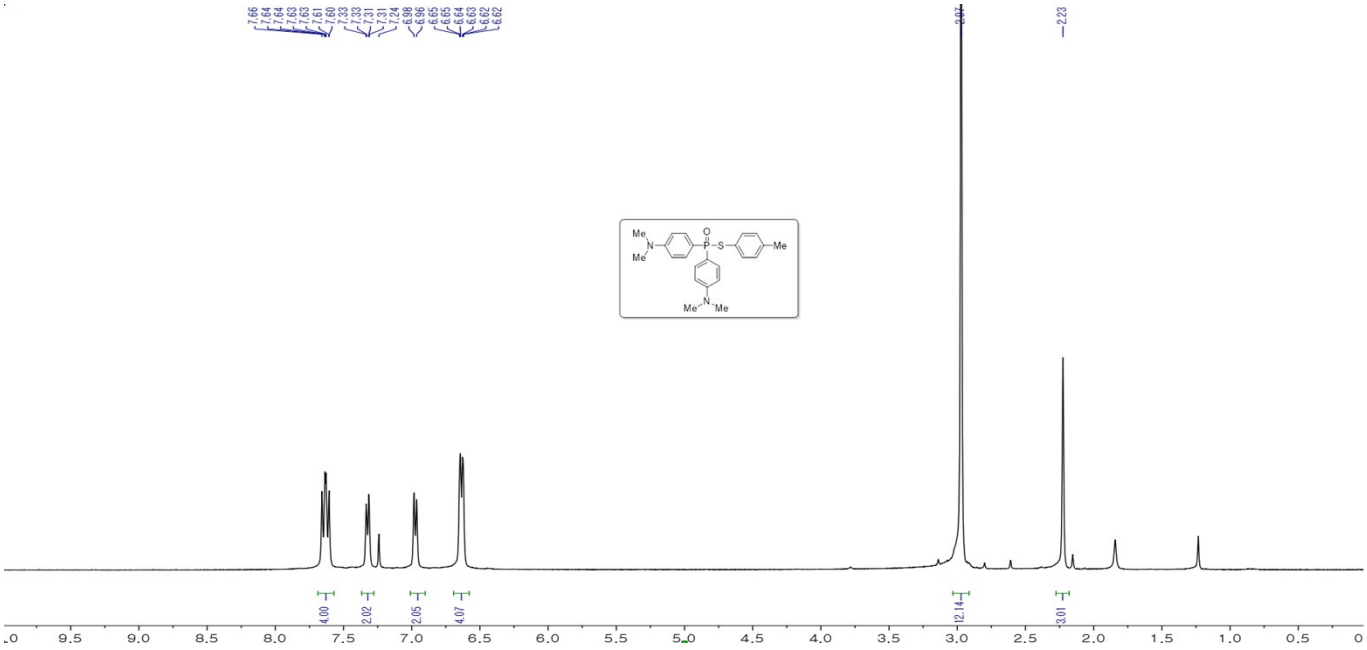


100 MHz, ^{13}C NMR in $CDCl_3$

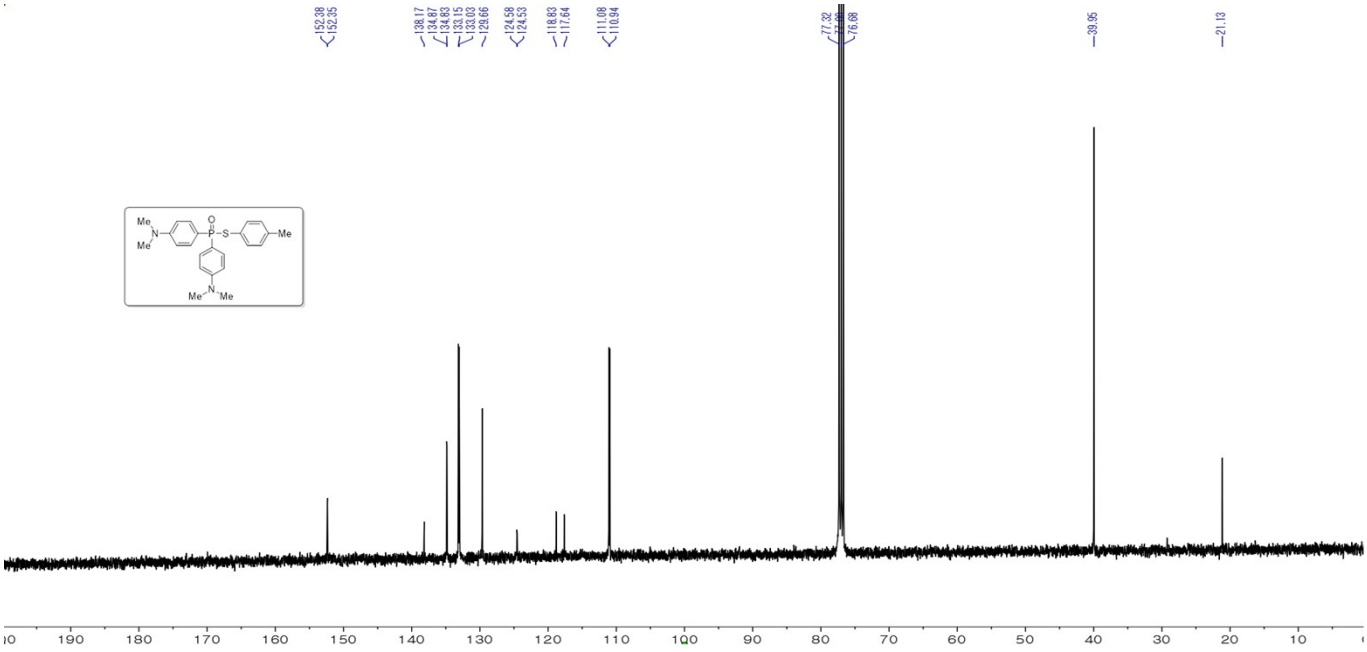


162 MHz, ^{31}P NMR in $CDCl_3$

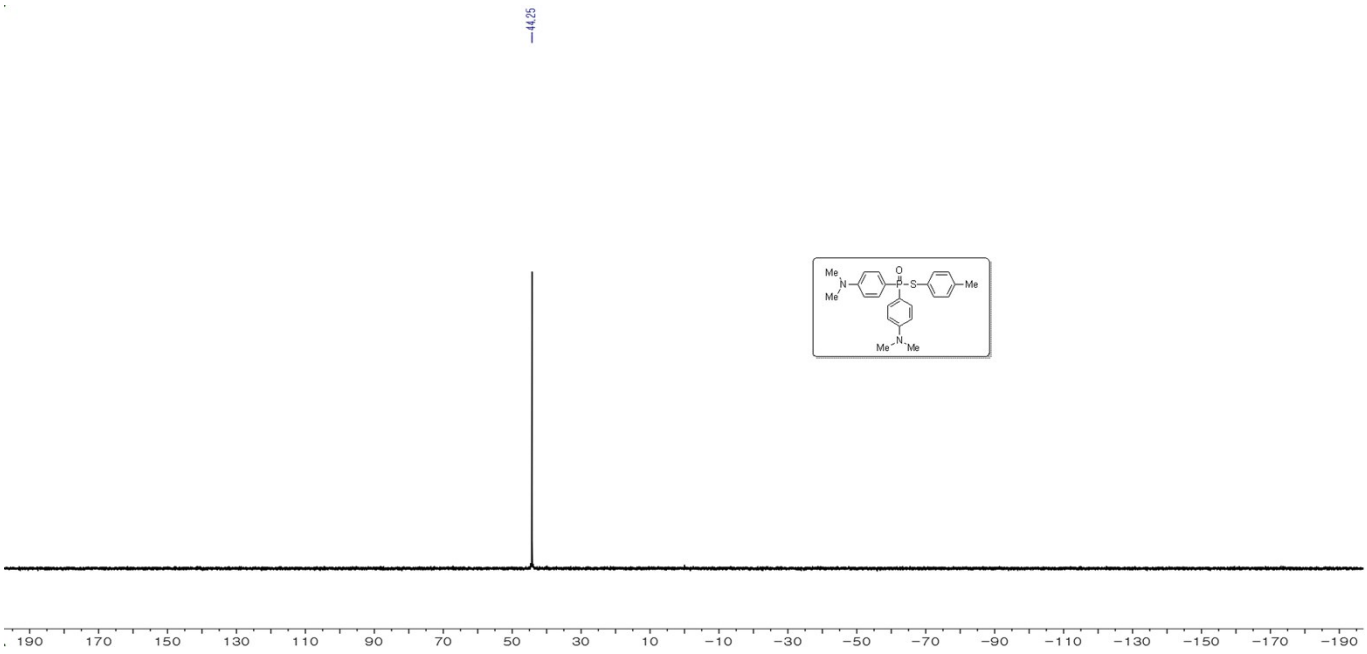
S-(p-tolyl) bis(4-(dimethylamino)phenyl)phosphinothioate (4p)



400 MHz, ^{1}H NMR in $CDCl_3$

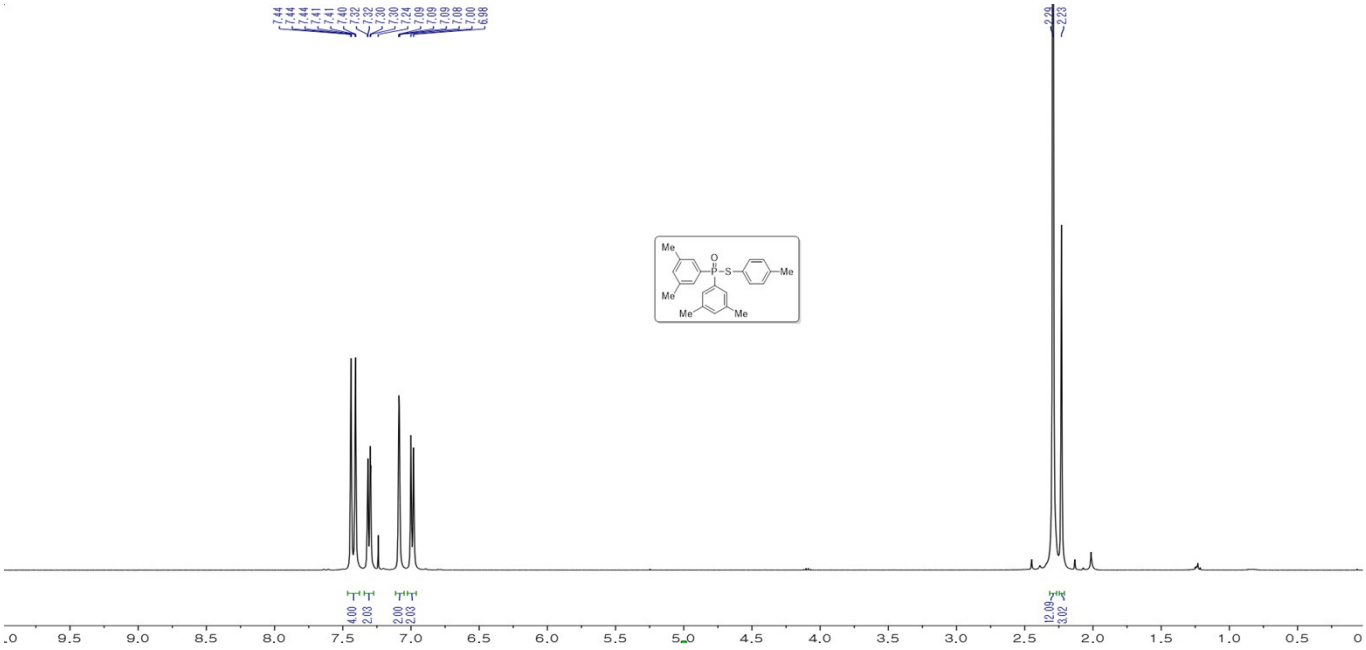


100 MHz, ^{13}C NMR in $CDCl_3$

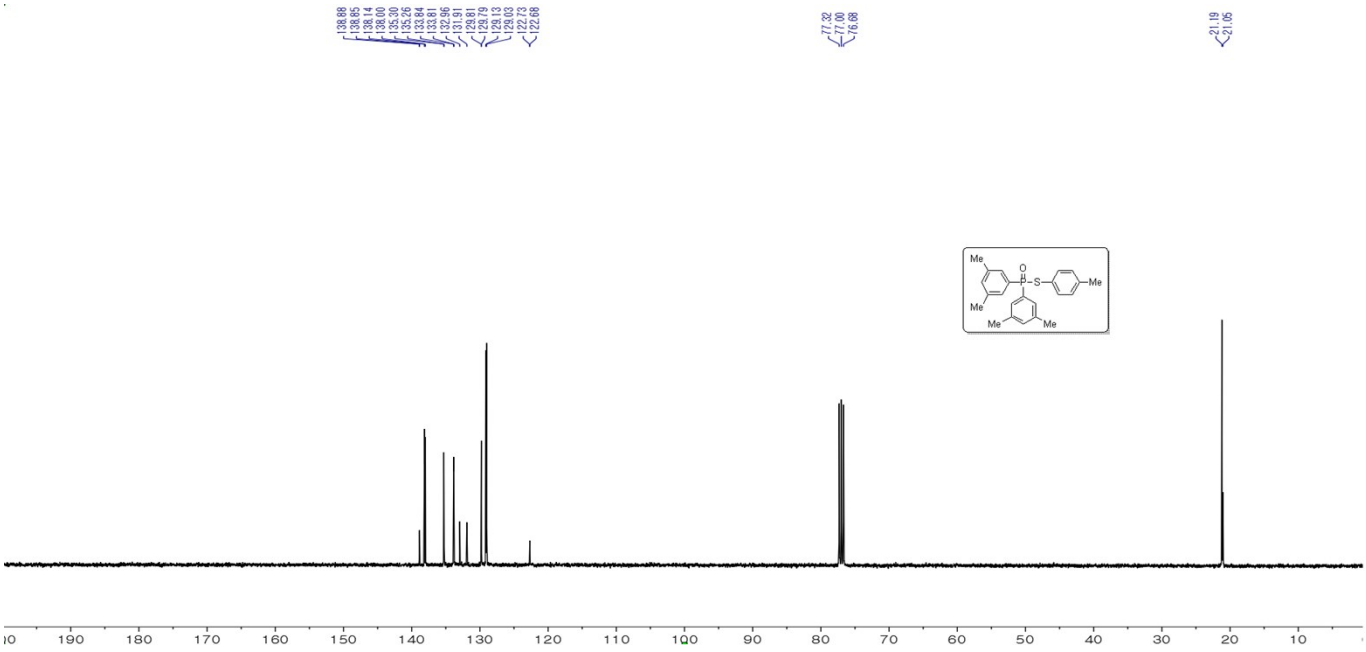


162 MHz, ^{31}P NMR in $CDCl_3$

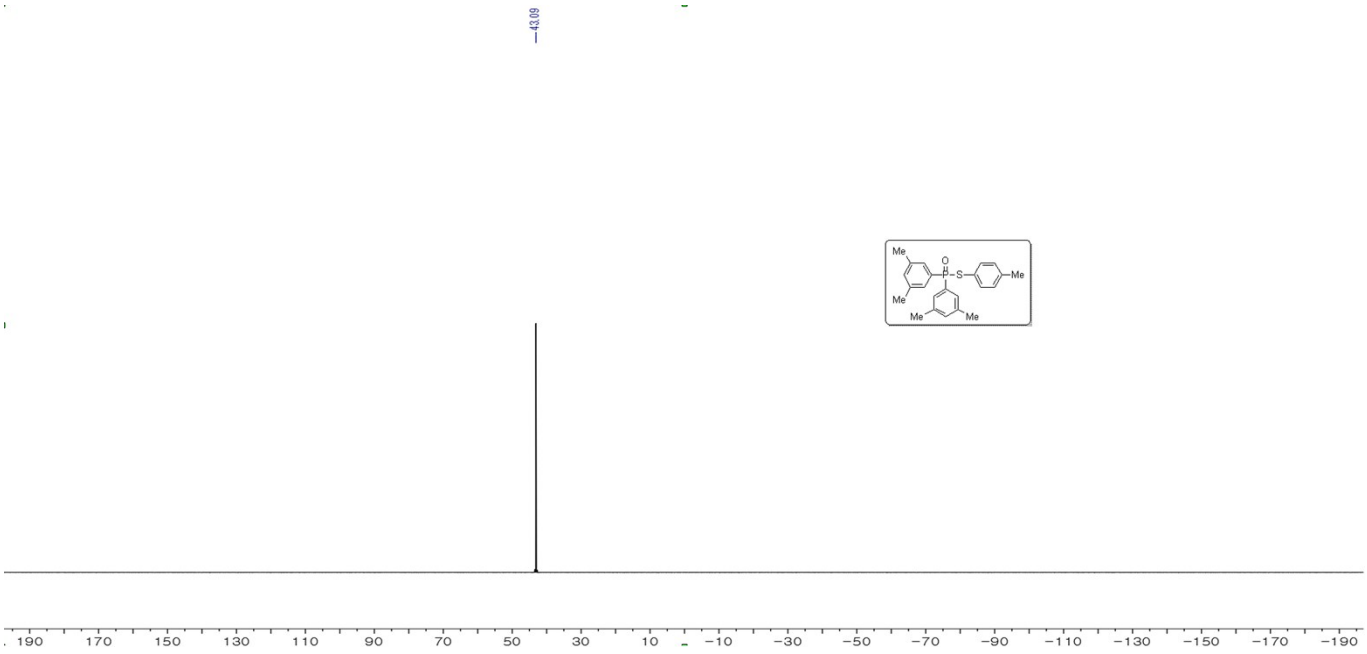
S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate (4q)



400 MHz, ^{1}H NMR in $CDCl_3$

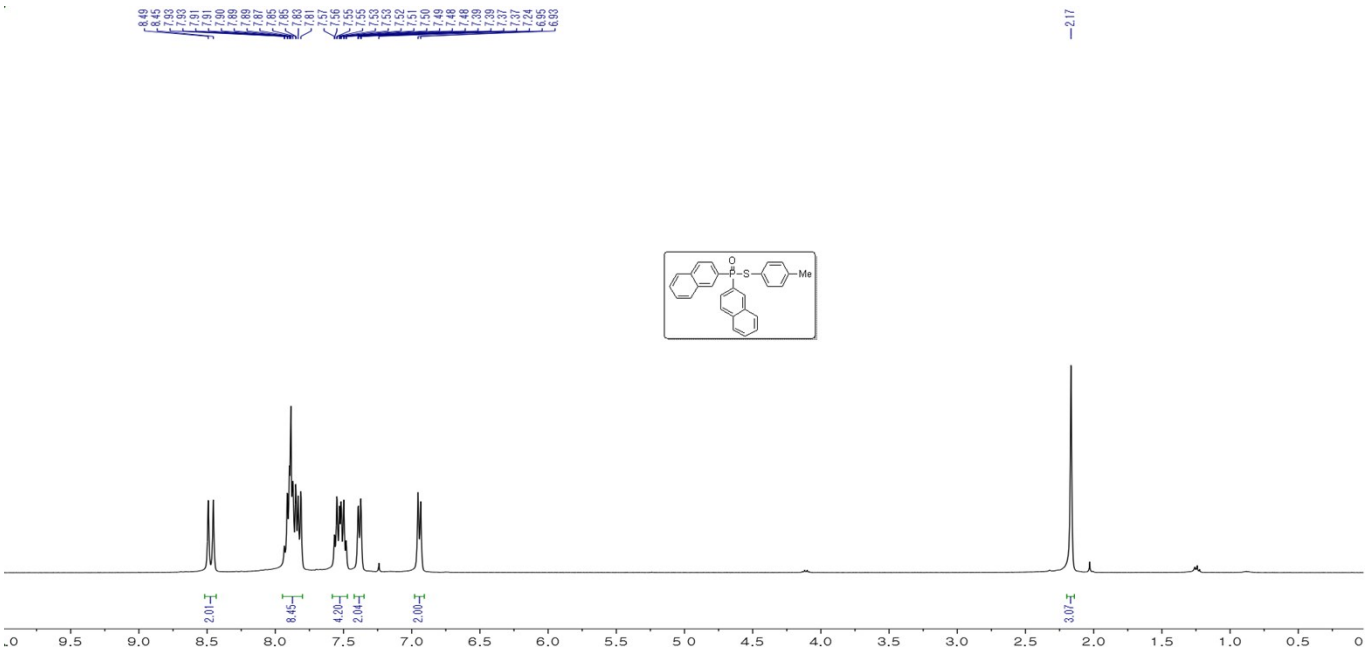


100 MHz, ^{13}C NMR in $CDCl_3$

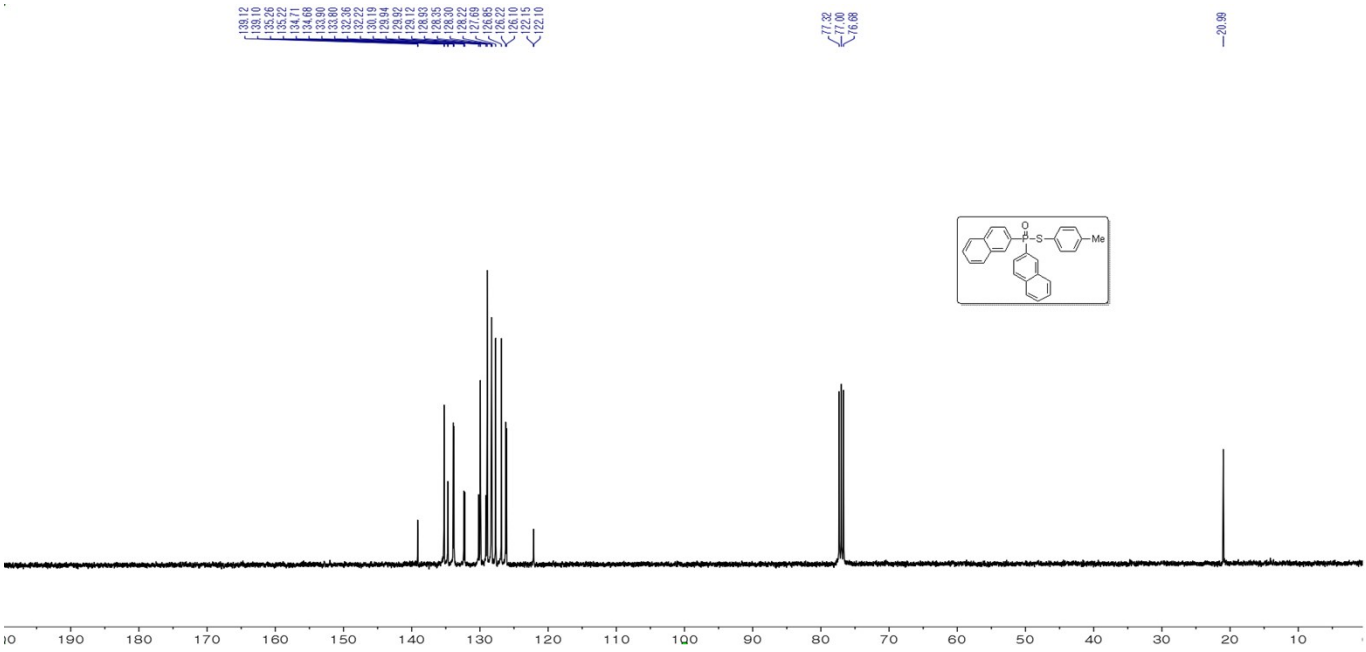


162 MHz, ^{31}P NMR in $CDCl_3$

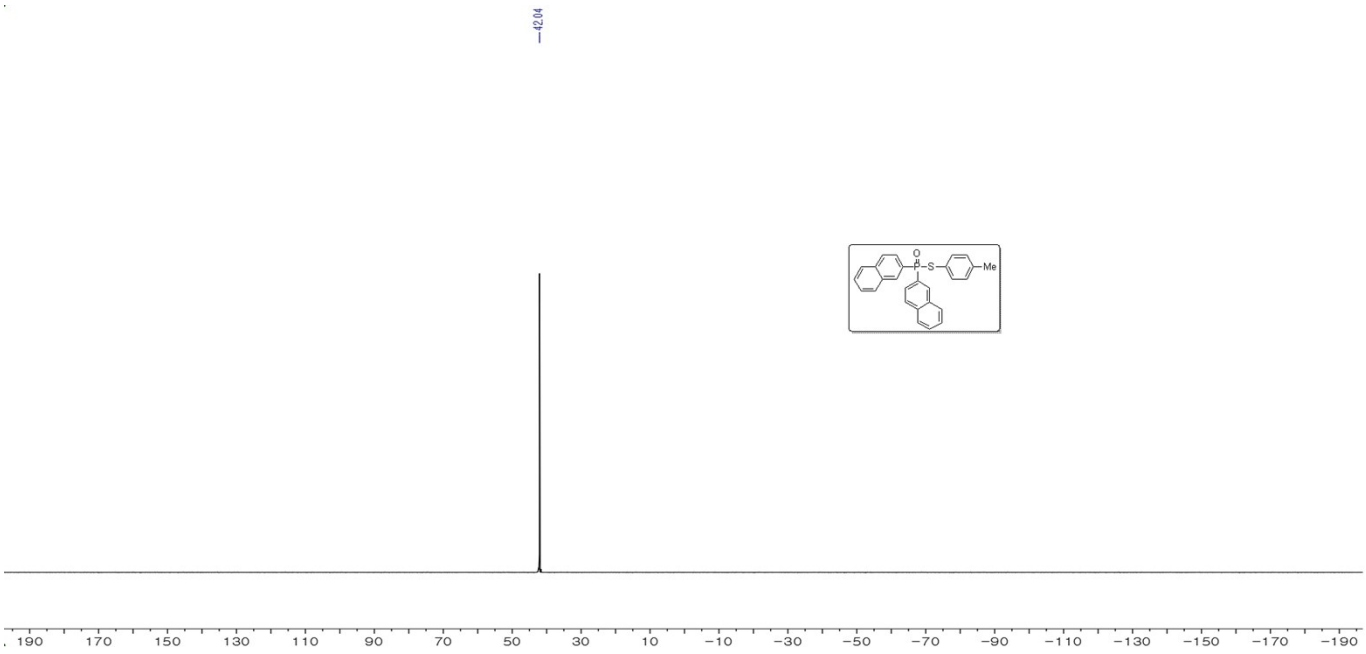
S-(p-tolyl) di(naphthalen-2-yl)phosphinothioate (4r)



400 MHz, ^{1}H NMR in $CDCl_3$

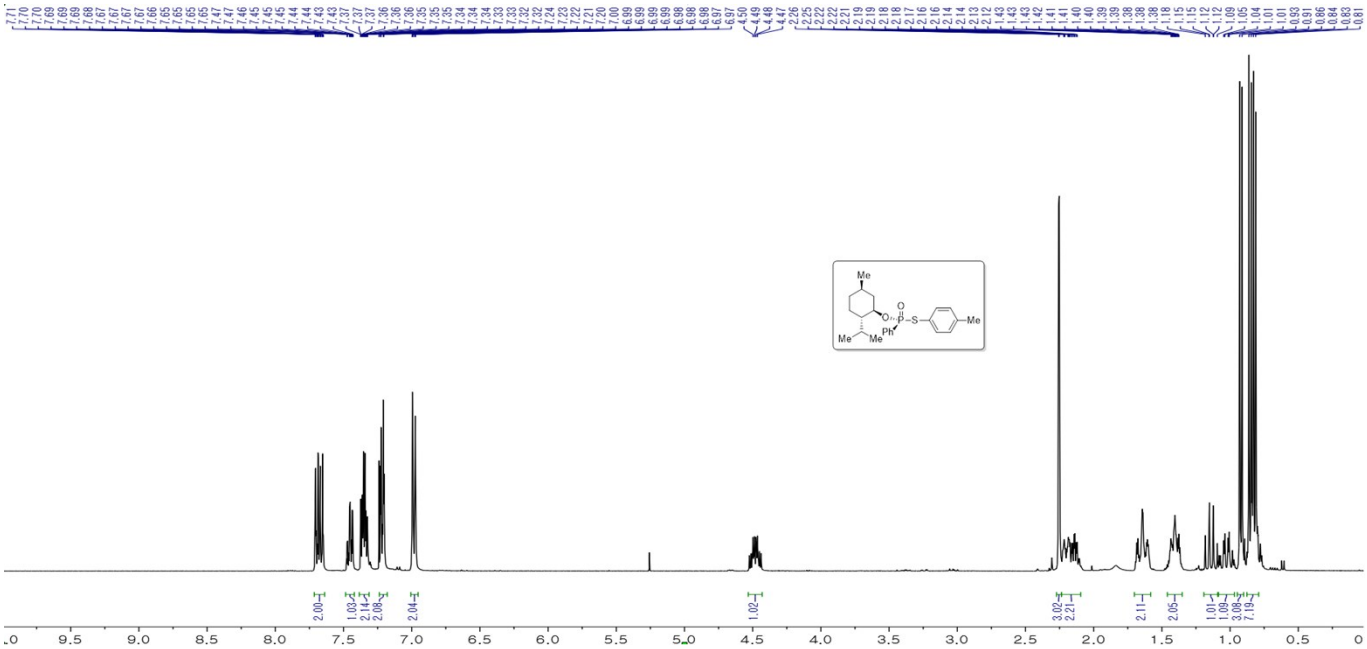


100 MHz, ^{13}C NMR in $CDCl_3$

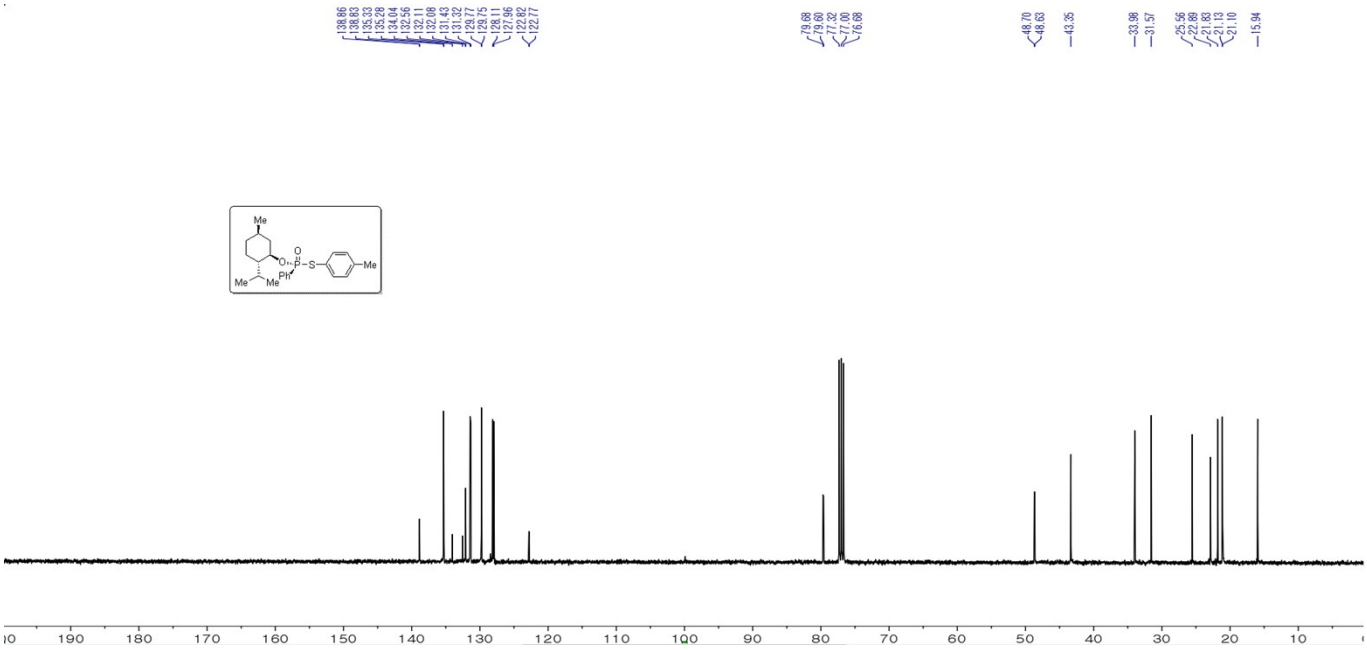


162 MHz, ^{31}P NMR in $CDCl_3$

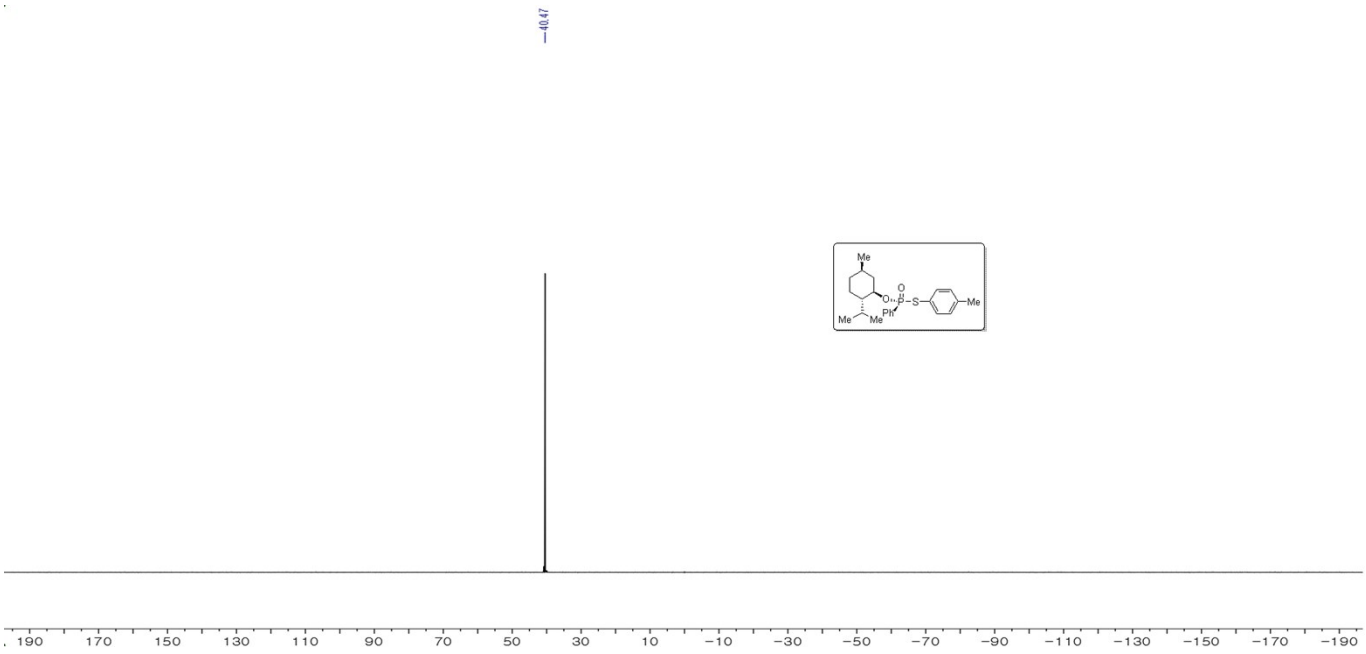
O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-(p-tolyl) (S)-phenylphosphonothioate (5a)



400 MHz, ^{1}H NMR in $CDCl_3$

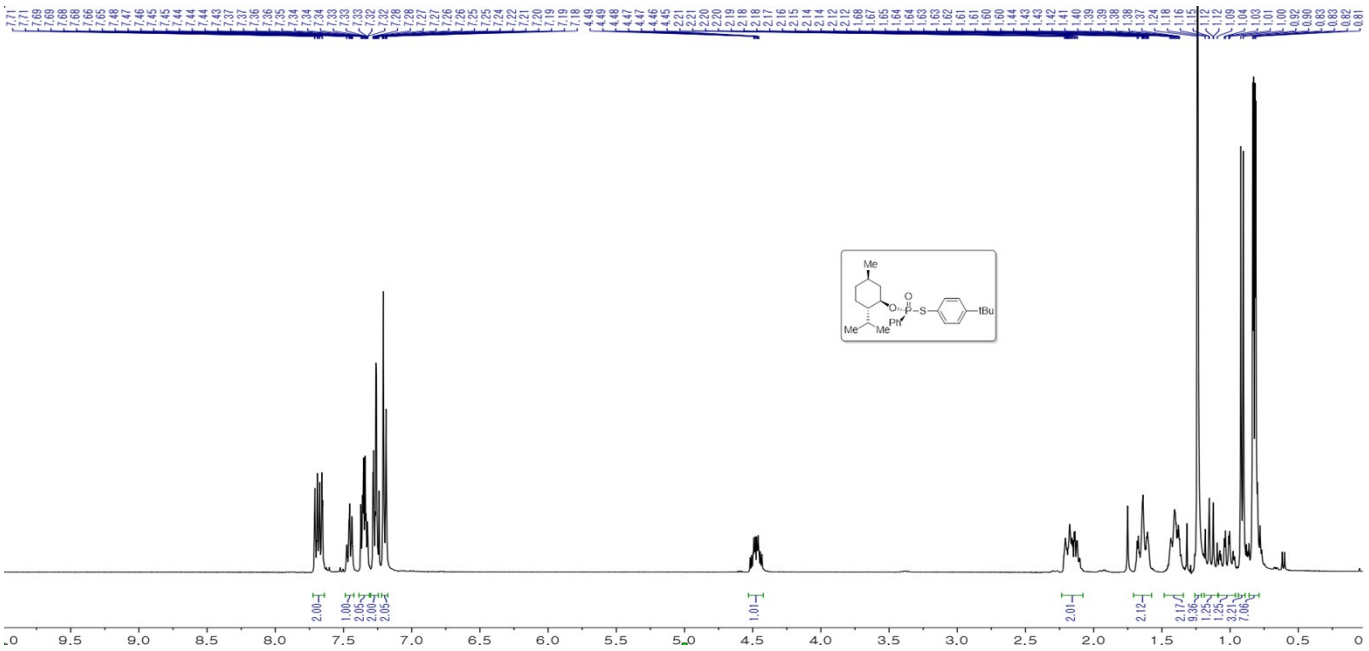


100 MHz, ^{13}C NMR in $CDCl_3$

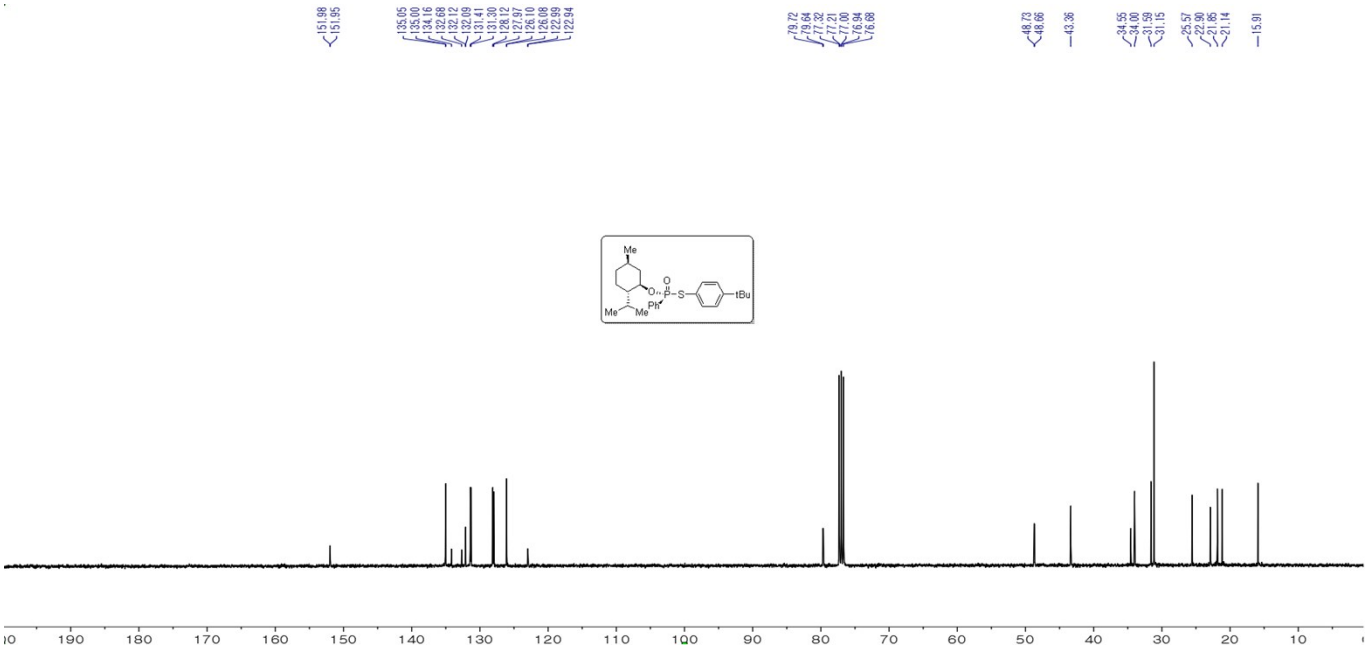


162 MHz, ^{31}P NMR in $CDCl_3$

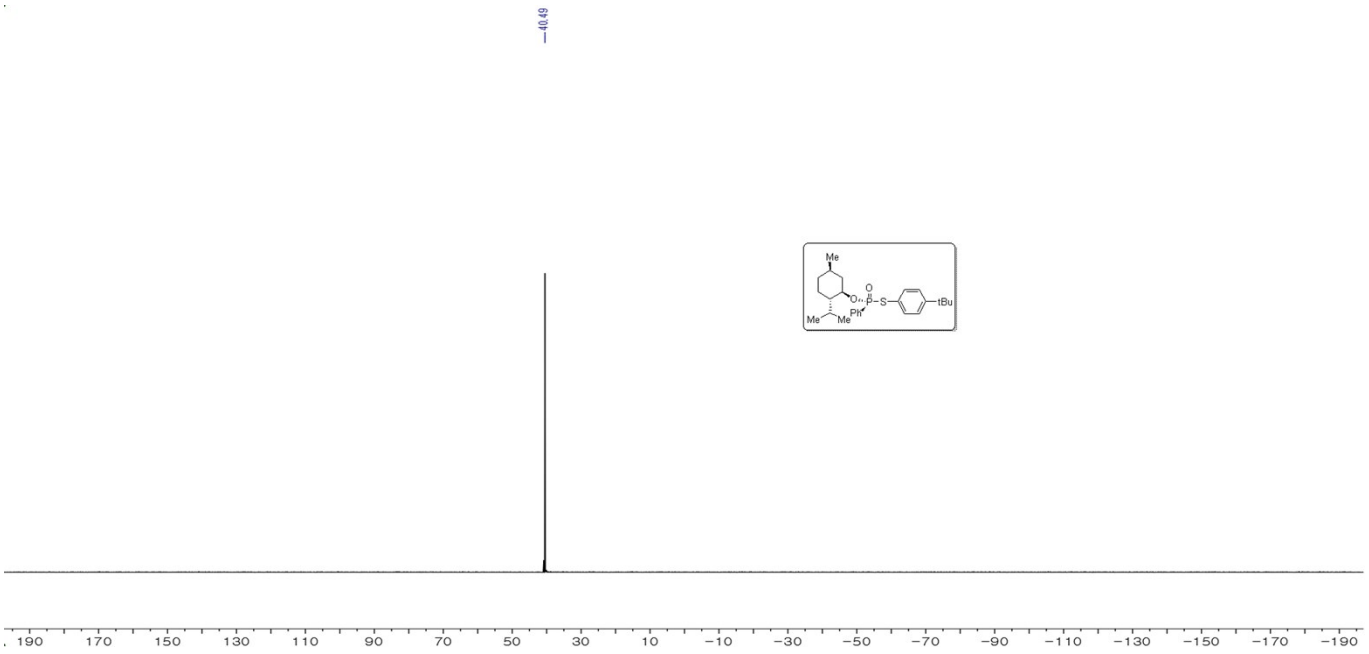
S-(4-(tert-butyl)phenyl) O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) (S)-phenylphosphonothioate (5b)



400 MHz, ^{1}H NMR in $CDCl_3$

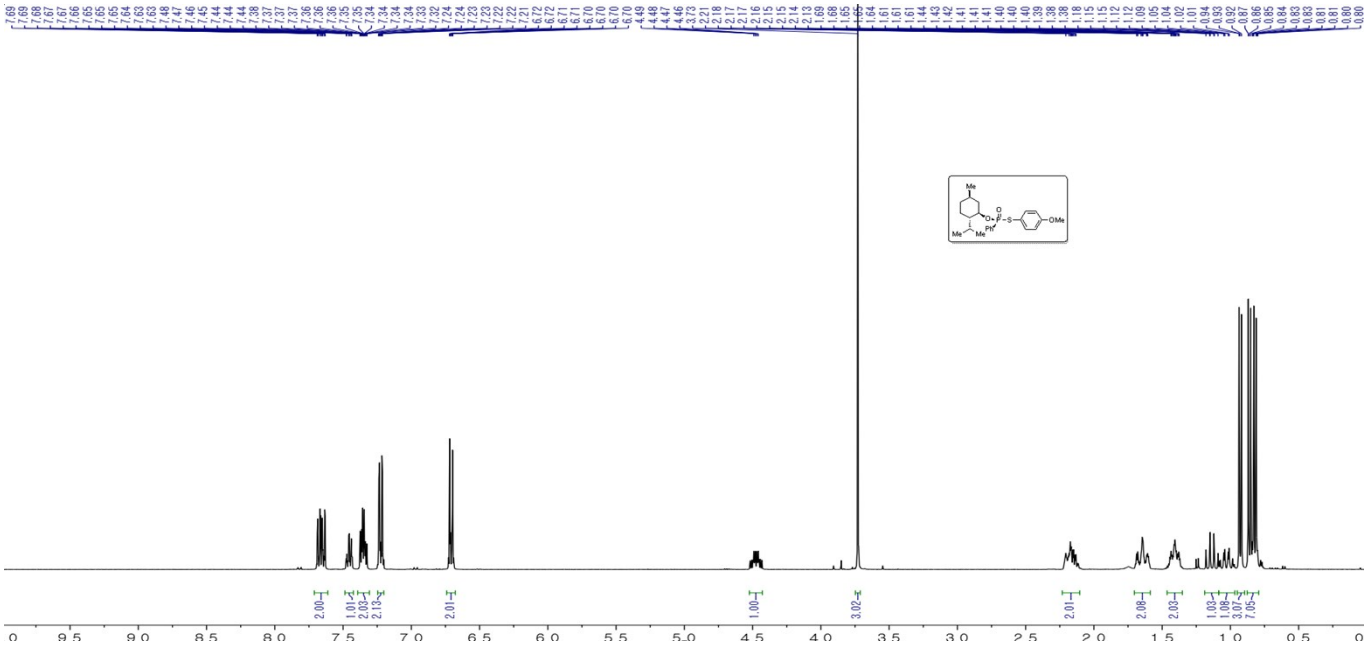


100 MHz, ^{13}C NMR in $CDCl_3$

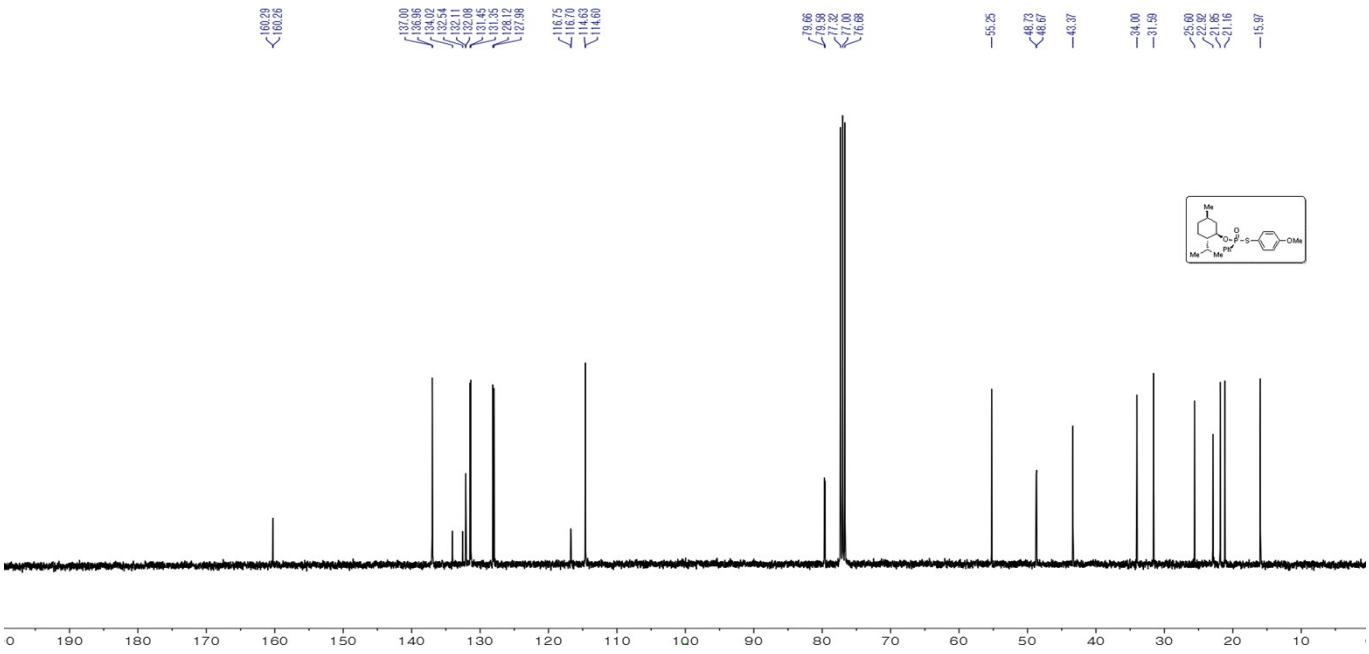


162 MHz, ^{31}P NMR in $CDCl_3$

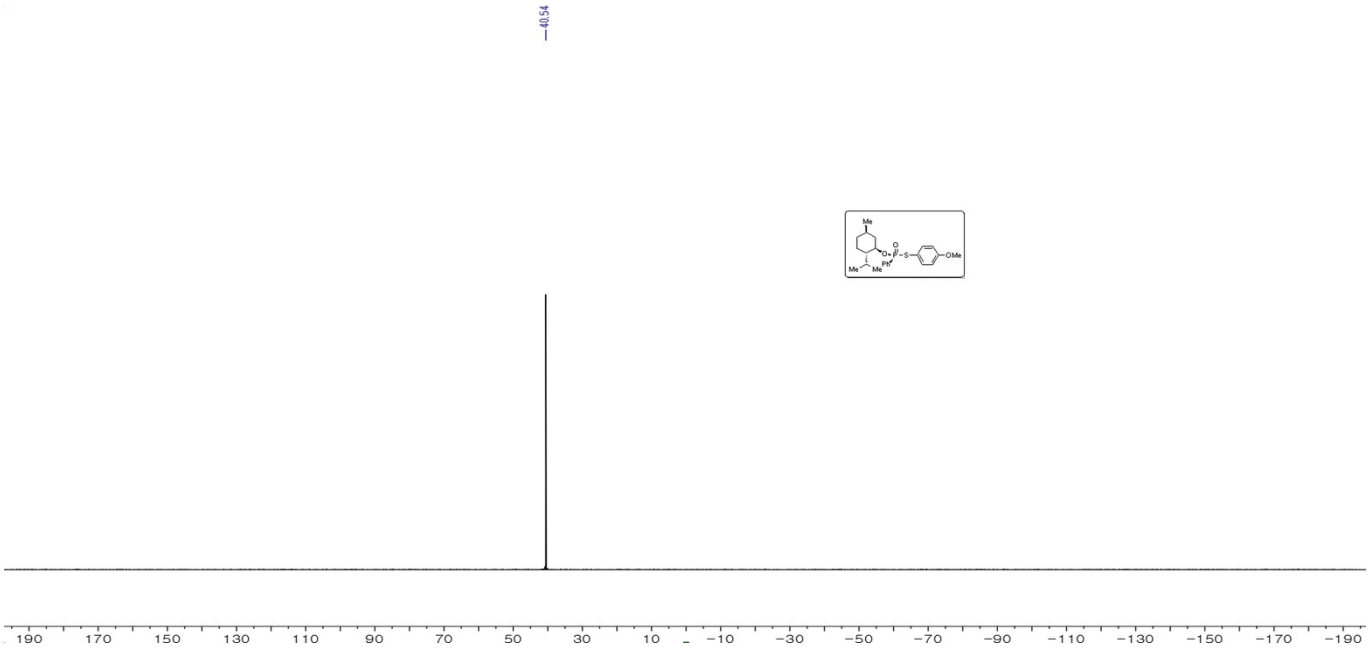
(S)-O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-(4-methoxyphenyl) phenylphosphonothioate (5c)



400 MHz, ^{1}H NMR in $CDCl_3$

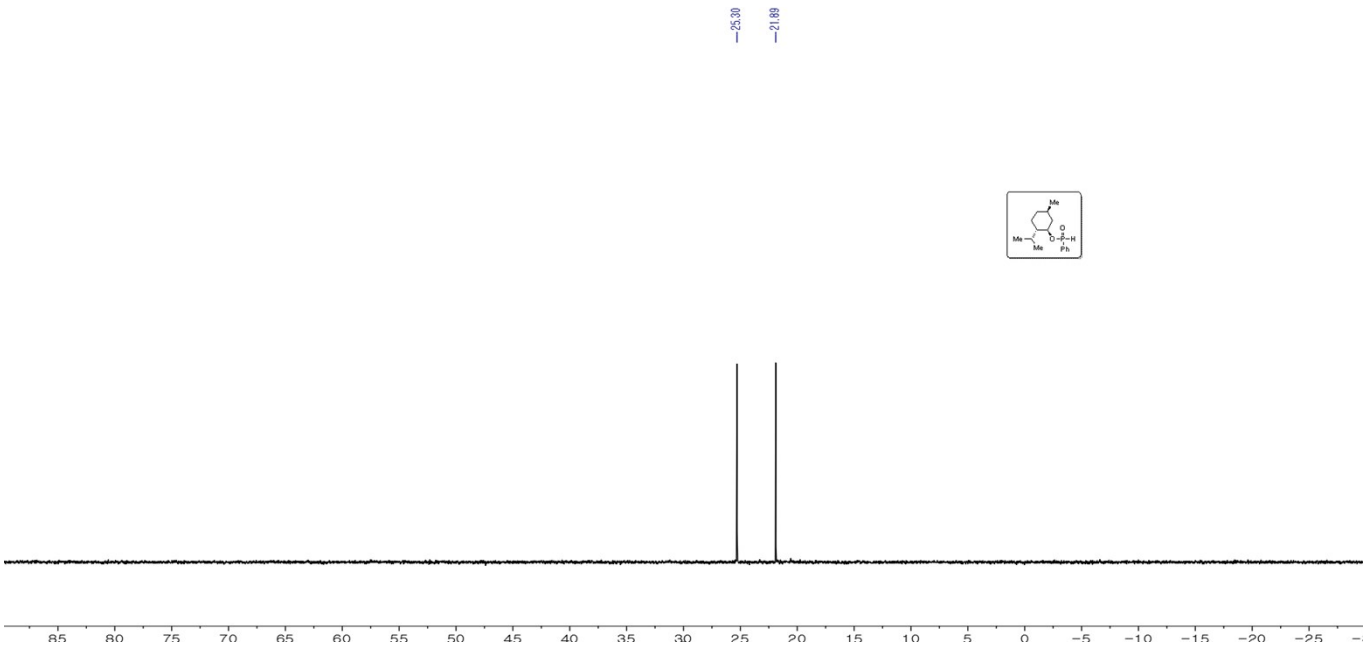


100 MHz, ^{13}C NMR in $CDCl_3$



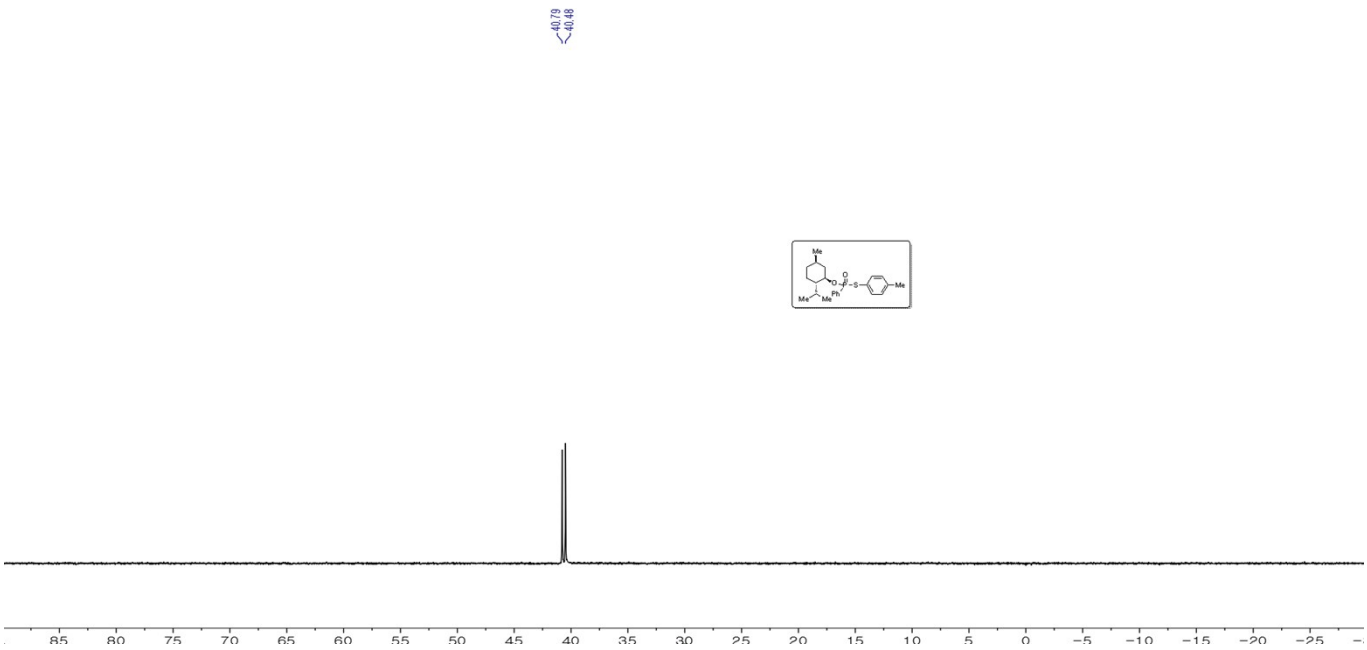
162 MHz, ^{31}P NMR in $CDCl_3$

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl phenylphosphinate (1c)



162 MHz, ^{31}P NMR in $CDCl_3$

O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-p-tolyl phenylphosphonothioate (6a)



162 MHz, ^{31}P NMR in $CDCl_3$