Electronic Supplementary Information

for

Three-component coupling reaction of white phosphorus, alcohols and diaryl disulfides: A chlorine-free avenue for accessing phosphorothioates

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1. General information.

All reactions were carried out under dry air (unless otherwise noted). All glassware was oven-dried prior to use. The commercially available reagents were purchased from TCI, Energy Chemical and Bide Pharmatech Ltd and used without further purification. Some disulfides were prepared according to literature references.[1,2] Toluene, *N*, *N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, acetonitrile and dichloroethane were purchased from Sinopharm Chemical Reagent Co., Ltd and used as the solvent. petroleum ether and ethyl acetate are all AR grade were obtained commercially and used as eluent without further purification. ^{1}H, ^{13}C, ^{31}P, ^{19}F and spectra were measured on Bruker AV 600M, 500M or 400M spectrometers with $CDCl_3$ as solvent. Data were reported relative to solvent peaks $CDCl_3$ (7.26 ppm) for ^{1}H NMR and $CDCl_3$ (77.26 ppm) for ^{13}C NMR. 85% H_3PO_4 as external standard for $^{31}P\{^{1}H\}$ NMR spectra, $^{19}F\{^{1}H\}$ chemical shifts were un-calibrated. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constants in Hertz (Hz). The products were purified by column chromatography on silica gel 300-400 mesh. The CAS number of the known compound was listed. All products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

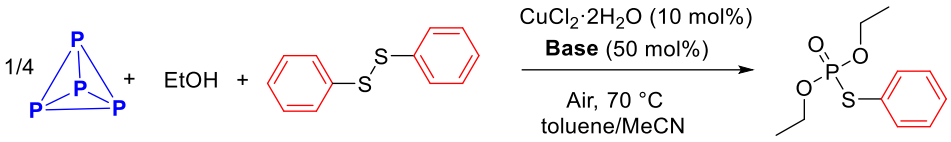
Preparation of P_4-toluene solution A piece of white phosphorus was taken out of water and then put in acetone under argon. One minute later, white phosphorus was taken out and the surface acetone was blowed dry with argon. Then, the dry white phosphorus was put in a conical flask containing toluene. The mixture was stirred intensely with a magnetic stirrer for overnight. White phosphorus-toluene solution prepared with 0.125 mol/L (15.5 g/L, determined by ^{31} P NMR analysis of the solution using $Ph_3P(O)$ as an internal standard. D1 = 20 s, zg30, LB = 1).

Safety note for P_4: White phosphorus is spontaneously flammable; it should be stored in water or glove box. White phosphorus-toluene solution should be sealed in argon and stored away from light.

2. Tables for optimization of the reaction conditions

The yield of product was determined by $^{31}P\{^{1}H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard.

Supplementary Table 1-1 Screening of **bases**.[a]

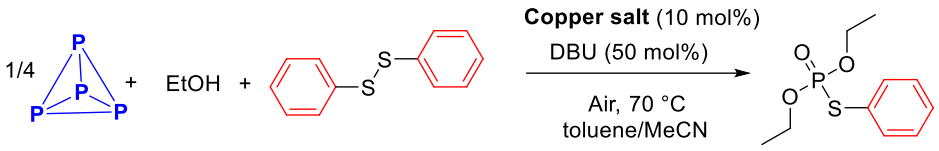


eq. 1 10 1.5 **4a**

Entry	Base	Yield of **4a**[b]
1	K_2CO_3	6%
2	K_3PO_4	Tarce
3	Na_2CO_3	n.d
4	Cs_2CO_3	28%
5	KOH	n.d
6	$NaHCO_3$	n.d
7	*t*-BuONa	10%
8	TEA	6%
9	DIPEA	5%
10	Et_2NH	7%
11	DABCO	15%
12	TMEDA	8%
13	DBU	46%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), $CuCl_2 \cdot H_2O$ (0.02 mmol,) **base (0.10 mmol, 50 mol %)** in solvent (acetonitrile, 2.00 mL), react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^{1}H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard. TEA = Triethylamine, DIPEA = *N*, *N*-Diisopropylethylamine, DABCO = Triethylenediamine, TMEDA = Tetramethylenediamine, DBU = 1,8-Diazabicyclo[5.4.0]undecane-7-ene.

Supplementary Table 1-2 Screening of **copper salt**.[a]

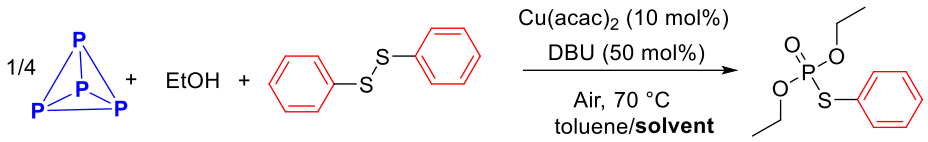


eq. 1 10 1.5 **4a**

Entry	Copper salt	Yield of **4a**[b]
1	$Cu(OAc)_2$	26%
2	CuI	37%
3	$Cu(OTf)_2$	18%
4	CuCl	37%
5	$Cu(CH_3CN)_4PF_6$	41%
6	$Cu(CH_3CN)_4BF_4$	58%
7	$Cu(acac)_2$	70%
8	CuBr	18%
9	$Cu(TFA)_2$	45%
10	$CuSO_4 \cdot 5H_2O$	65%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), DBU (0.10 mmol, 50 mol %) and **copper salt (0.02 mmol)** in solvent (acetonitrile, 2.00 mL) , react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard. $Cu(OAc)_2$ = Copper(II) acetate, $Cu(OTf)_2$ = Copper(II) trifluoromethanesulfonate, $Cu(acac)_2$ = Cupric acetylacetonate, $Cu(TFA)_2$ = Copper (II) trifluoroacetate

Supplementary Table 1-3 Screening of **solvent**.[a]

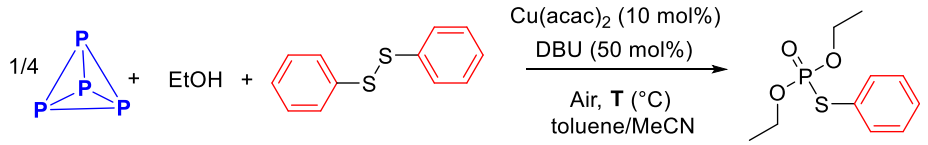


eq. 1 10 1.5 **4a**

Entry	Solvent	Yield of **4a**[b]
1	toluene (1.4 mL) : CH_3CN (1.0 mL)	40%
2	toluene (1.1 mL) : CH_3CN (1.4 mL)	54%
3	toluene (0.4 mL) : CH_3CN (2.0 mL)	70%
4	toluene (0.4 mL) : DMSO (2.0 mL)	23%
5	toluene (0.4 mL) : DMF (2.0 mL)	10%
6	toluene (0.4 mL) : DCE (2.0 mL)	13%
7	toluene (2.4 mL)	18%
8	toluene (0.4 mL) : THF (2.0 mL)	trace

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.30 mmol of P atom, a 0.125 M solution of P_4 **in toluene, 0.40 mL**), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), DBU (0.10 mmol, 50 mol %) and $Cu(acac)_2$ (0.02 mmol) in **solvent (2.00 mL)**, react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard. DMSO = Dimethyl sulfoxide, DMF = N,N-Dimethylformamide, DCE = 1,2-Dichloroethane, THF = Tetrahydrofuran.

Supplementary Table 1-4 Screening of **reaction temperature**.[a]

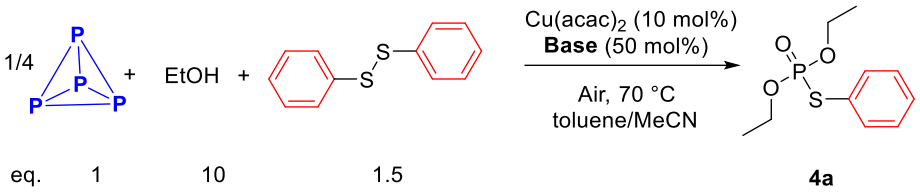


eq. 1 10 1.5 **4a**

Entry	T	Yield of **4a**[b]
1	60	46%
2	70	70%
3	80	65%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, a 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), DBU (0.10 mmol, 50 mol %) and $Cu(acac)_2$ (0.02 mmol) in CH_3CN (2.00 mL), react at T °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard.

Supplementary Table 1-5 Screening of **other organic bases**.[a]

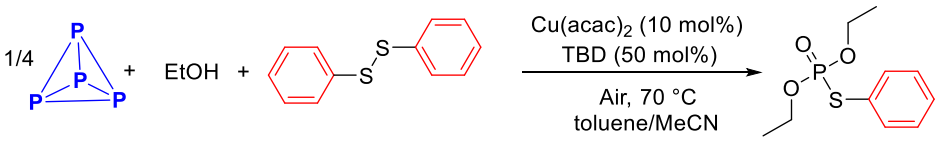


eq. 1 10 1.5 **4a**

Entry	Base	Yield of **4a**[b]
1	TMG	37%
2	DBN	80%
3	MTBD	80%
4	TBD	94%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), $Cu(acac)_2$ (0.02 mmol,) **base (0.10 mmol, 50 mol %)** in CH_3CN (2.00 mL), react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard. TMG = Tetramethylguanidine, DBN = 1,5-Diazabicyclo[4.3.0]non-5-ene, MTBD = 1,3,4,6,7,8-hexahydro-1-methyl-2h-pyrimidol[1,2-a]pyrimidine, TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.

Supplementary Table 1-6 Screening of **loading amount of disulfide and alcohol**.[a]

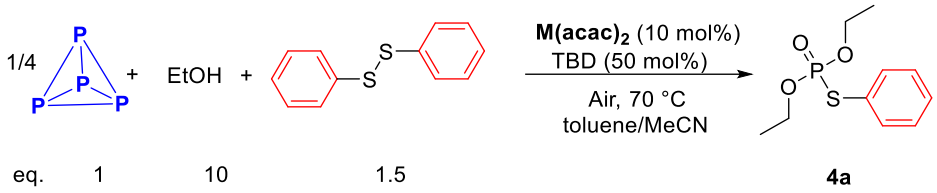


eq. 1 **x** **y** **4a**

Entry	x : y	Yield of **4a**[b]
1	10:0.5	44%
2	10:1.0	74%
3	10:1.5	94%
3	7.5:1.5	74%
4	5.0:1.5	50%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, a 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (x eq.), diphenyl disulfide (y eq.), TBD (0.10 mmol, 50 mol %) and $Cu(acac)_2$ (0.02 mmol) in solvent (2.00 mL), react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard.

Supplementary Table 1-7 Investigation of other **metal salts**[a]

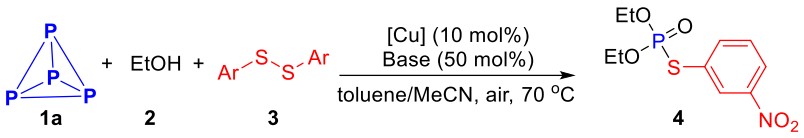


eq. 1 10 1.5 **4a**

Entry	M	Yield of **4a**[b]
1	Fe	20%
2	Co	13%
3	Ni	17%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, a 0.125M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), TBD (0.10 mmol, 50 mol %) and metal salt (0.02 mmol) in CH_3CN (2.00 mL), react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard.

Supplementary Table 1-8 Optimization of the reaction conditions for substrates bearing the **strong electron-withdrawing group** [a]



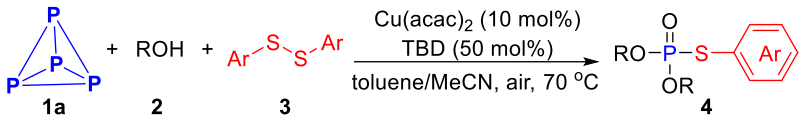
1a **2** **3** **4**

Entry	deviation	Yield
1	[Cu] 50 mol%	17%
2	TBD 1 eq.	31%
3	[Cu]50 mol% and TBD 1 eq.	22%
4	**3** 2 eq.	45%
5	**3** 3 eq.	51%
6	**3** 4 eq.	58%
7	$CuCl_2$	24%
8	$Cu(OAc)_2$	20%
9	$CuSO_4$	27%
10	MTBD	40%
11	DBN	31%
12	80 °C	28%

[a] Standard conditions (unless otherwise specified): P_4 (6.20 mg, 0.20 mmol of P atom, a 0.125 M solution of P_4 in toluene, 0.40 mL), ethanol (2.00 mmol, 10.0 eq.), diphenyl disulfide (0.30 mmol, 1.5 eq.), Base (0.10 mmol, 50 mol %) and metal salt (0.02 mmol) in solvent (2.00 mL), react at 70 °C (oil bath) for 16 h under an air atmosphere [b] Yield of product was determined by $^{31}P\{^1H\}$ NMR analysis of the crude reaction mixture using $(C_6H_5O)_3P(O)$ as an internal standard.

3. General experimental procedures

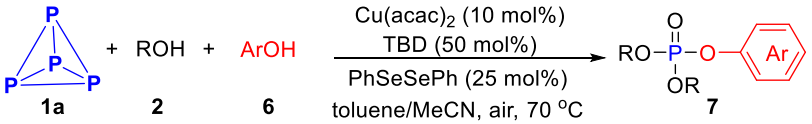
General procedure 1: Synthesis of phosphorothioates (4a-5l)



Supplementary Scheme 1-1

To an oven-dried schlenk tube with a magnetic stir bar was added $Cu(acac)_2$ (0.02 mmol, 5.3 mg), TBD(1,5,7-Triazabicyclo[4.4.0]dec-5-ene) (0.1 mmol, 13.9 mg) and disulfide (0.3 mmol).. Then alcohol (2 mmol), acetonitrile (2.00 mL) and P_4 (6.2 mg total of P_4, a 0.125 M solution of P_4 in toluene, 0.40 mL) were sequentially added to the system. Then the system was stirred at 70 °C (oil bath) for 16 h. After competition, the solvent was evaporated by rotary evaporation, the crude reaction mixture was purified by flash chromatography using petroleum-AcOEt [4:1 (v/v)] as the eluent to give the product.

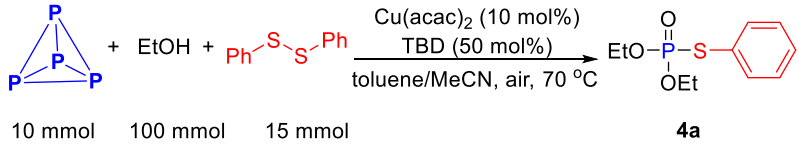
General procedure 2: Synthesis of phosphates (7a-7i)



Supplementary Scheme 1-2

To an oven-dried schlenk tube with a magnetic stir bar was added $Cu(acac)_2$ (0.02 mmol, 5.3 mg), TBD(1,5,7-Triazabicyclo[4.4.0]dec-5-ene) (0.1 mmol, 13.9 mg) , diselenide (0.05 mmol) and phenol (0.4 mmol). Then alcohol (2 mmol), acetonitrile (2.00 mL) and P_4 (6.2 mg total of P_4, a 0.125 M solution of P_4 in toluene, 0.40 mL) were sequentially added to the system. Then the system was stirred at 70 °C (oil bath) for 16 h. After competition, the solvent was evaporated by rotary evaporation, the crude reaction mixture was purified by flash chromatography using petroleum-AcOEt [4:1 (v/v)] as the eluent to give the product.

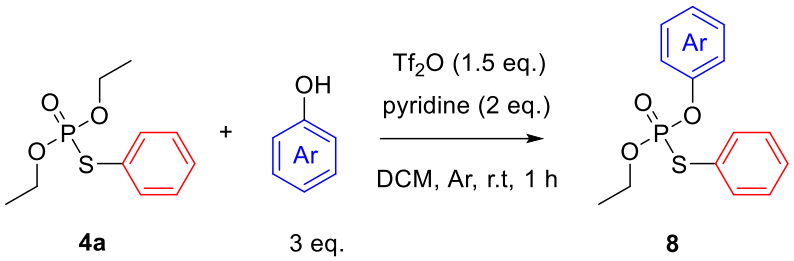
General procedure 3: Gram-scale synthesis of *O,O*-diethyl *S*-phenyl phosphorothioate (4a)



Supplementary Scheme 1-3

To an oven-dried schlenk bottle with a magnetic stir bar was added $Cu(acac)_2$ (1 mmol, 261 mg), TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) (5 mmol, 696 mg) and diphenyl disulfide (15 mmol, 3.275g). Then ethanol (100 mmol), acetonitrile (100 mL) and P_4 (310 mg total of P_4, a 0.125 M solution of P_4 in toluene, 20 mL) were sequentially added to the system. Then the system was stirred at 70 °C (oil bath) for 72 h. After competition, the solvent was evaporated by rotary evaporation, the crude reaction mixture was purified by flash chromatography using petroleum-AcOEt [4:1 (v/v)] as the eluent to give the product **4a** (1.771 g, 72%).

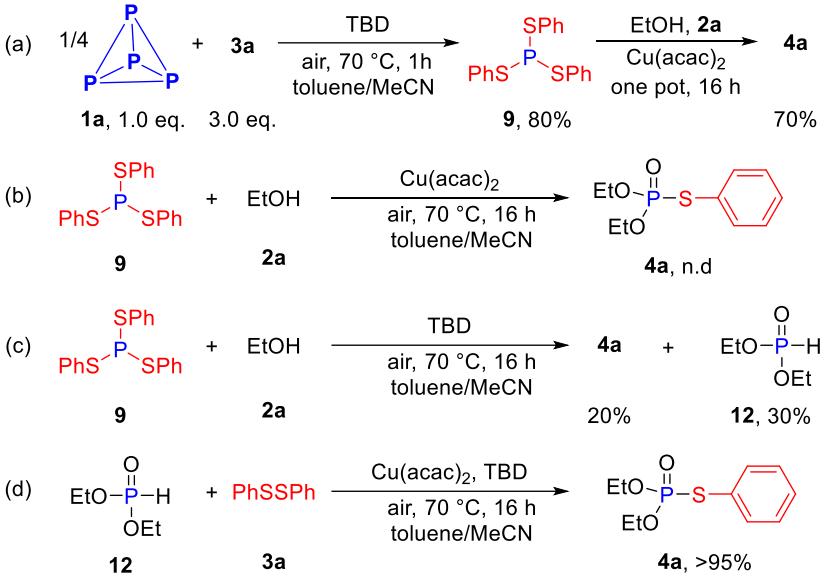
General procedure 4: Transformation of *O,O*-diethyl *S*-phenyl phosphorothioate (4a)



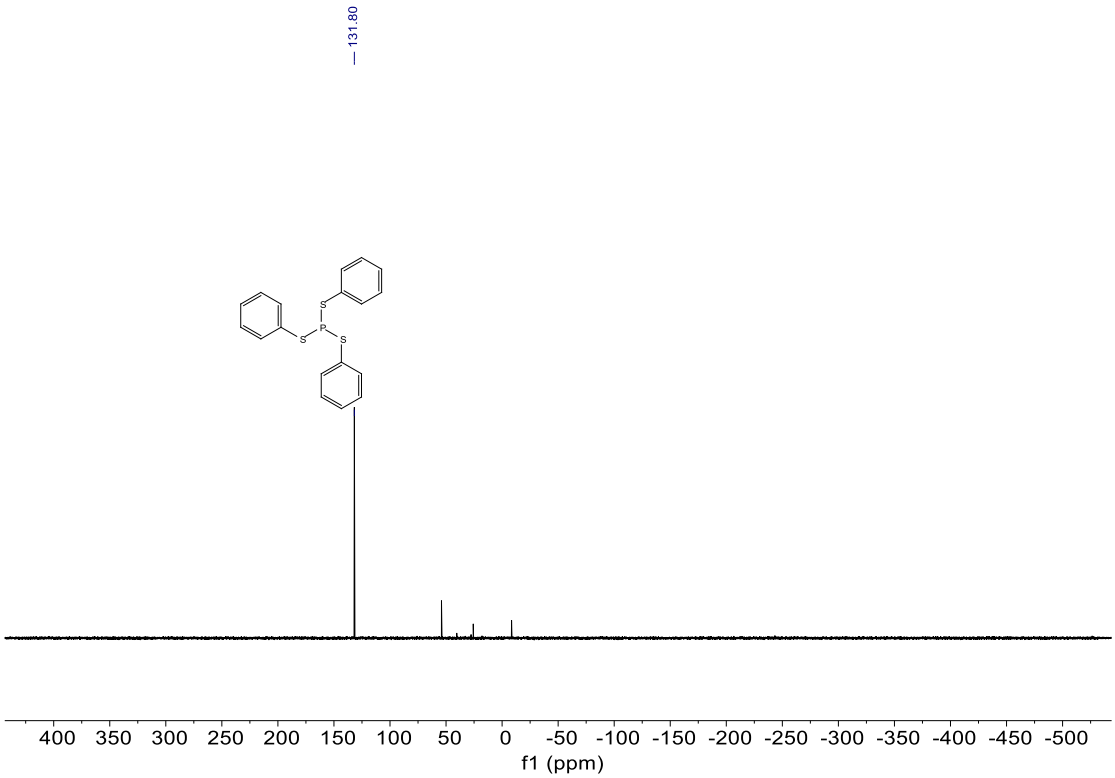
Supplementary Scheme 1-4

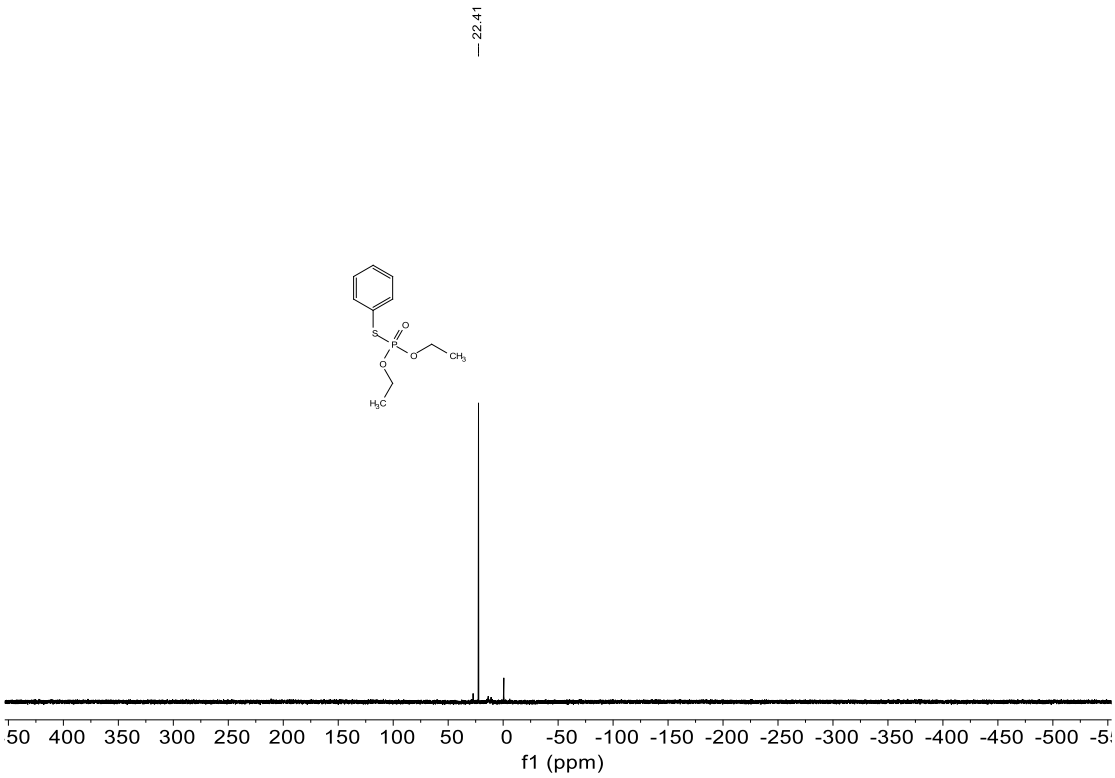
To an oven-dried schlenk tube with a magnetic stir bar containing O,O-diethyl S-phenyl phosphorothioate **(4a)** (0.2 mmol, 49.2 mg) was evacuated and purged with argon three times. Then Tf_2O (0.3 mmol, 51μL) and pyridine (0.4 mmol, 33 μL) were added. The mixture was stirred at room temperature for 15 mins. Then phenol (0.6 mmol) was added under argon atmosphere, the reaction mixture was stirred at room temperature for 1 h. After completion, the solvent was evaporated by rotary evaporation, the crude reaction mixture was purified by flash chromatography using petroleum-AcOEt [3:1 (v/v)] as the eluent to give the products **8a** and **8b**.

4. Control experiments and ^{31}P NMR spectra for the synthesis of phosphorothioates.

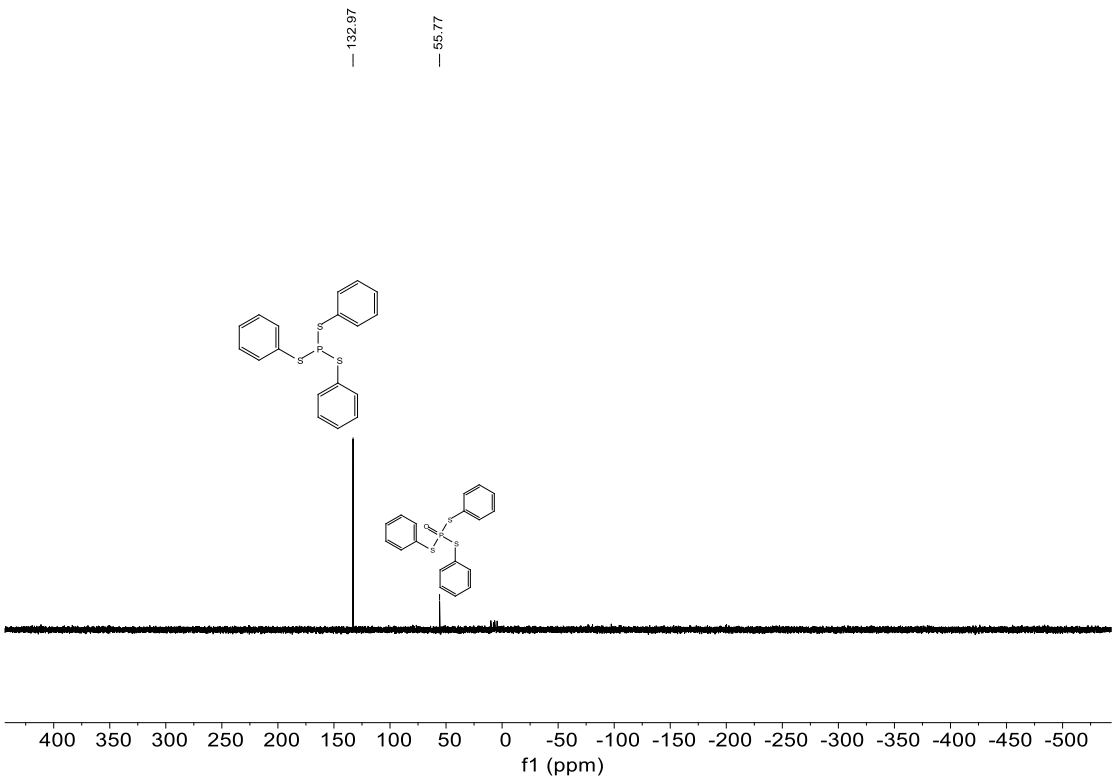


Supplementary Scheme 2-1. Control experiments A.

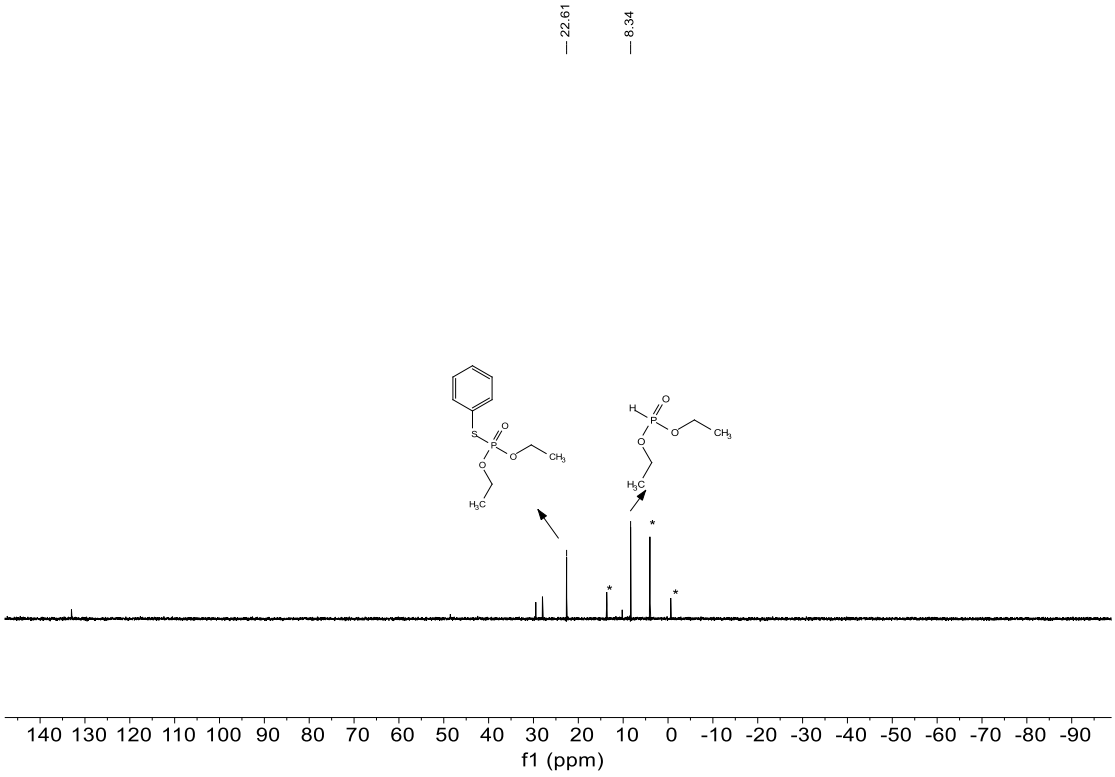




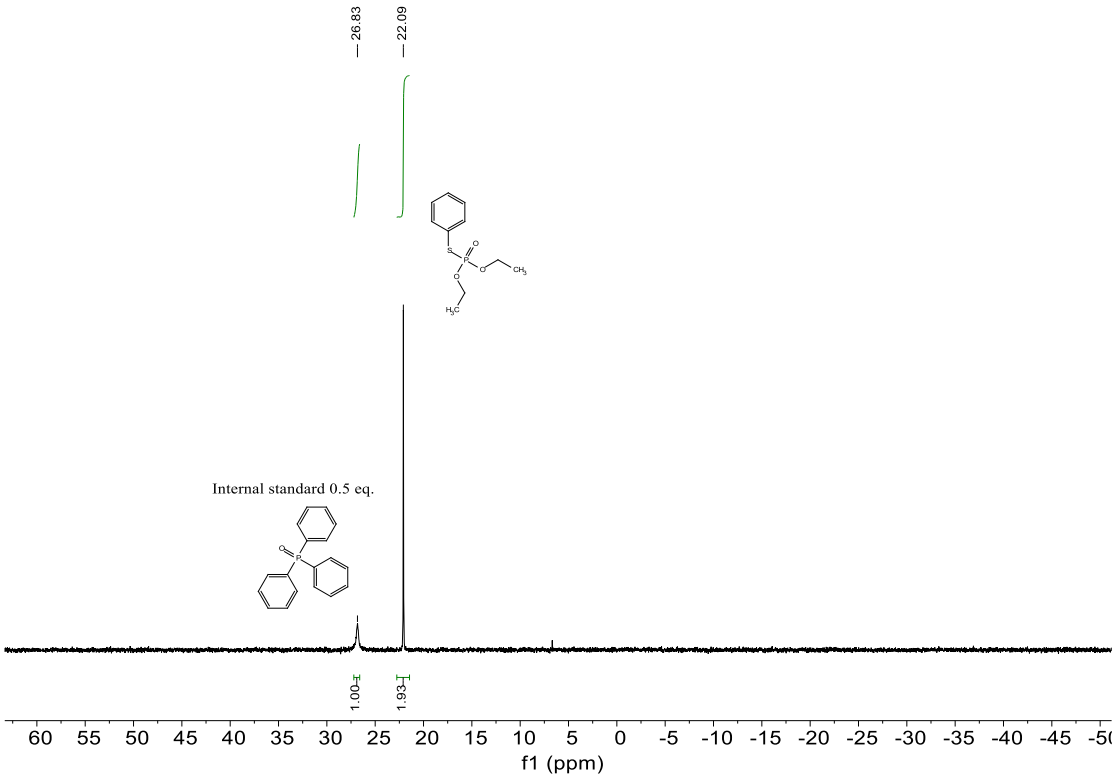
Supplementary figure 1-1. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 2-1 (a).



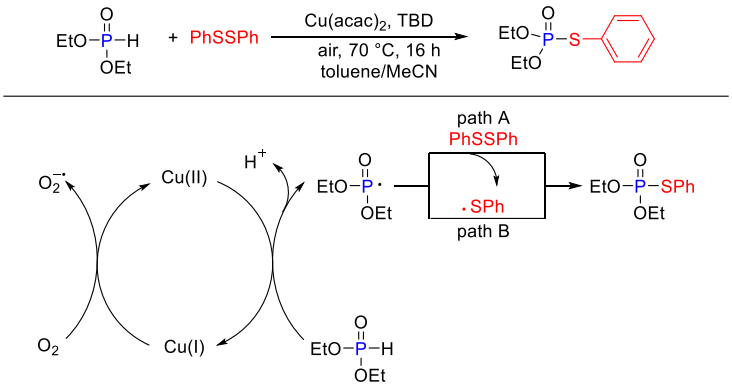
Supplementary figure 1-2. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 2-1 (b).



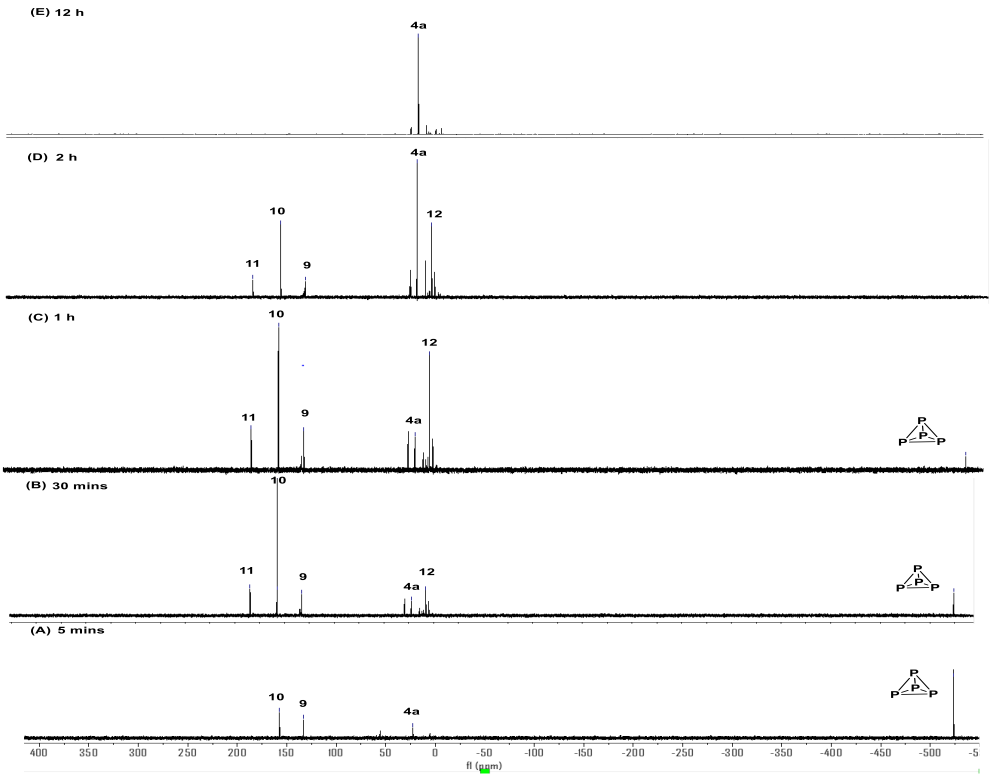
Supplementary figure 1-3. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 2-1 (c).



Supplementary figure 1-4. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 2-1 (d).

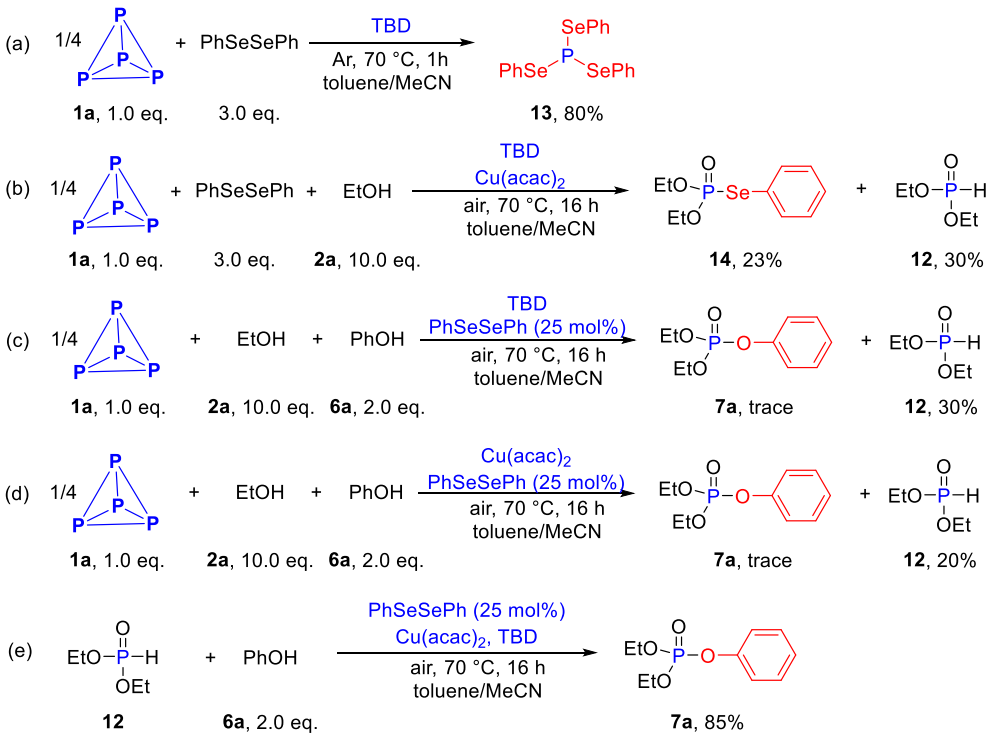


Supplementary Scheme 2-2. The propose mechanism for the copper-catalyzed cross-coupling reaction of *H*-phosphonates and disulfide (Supplementary Scheme 2-1 d).

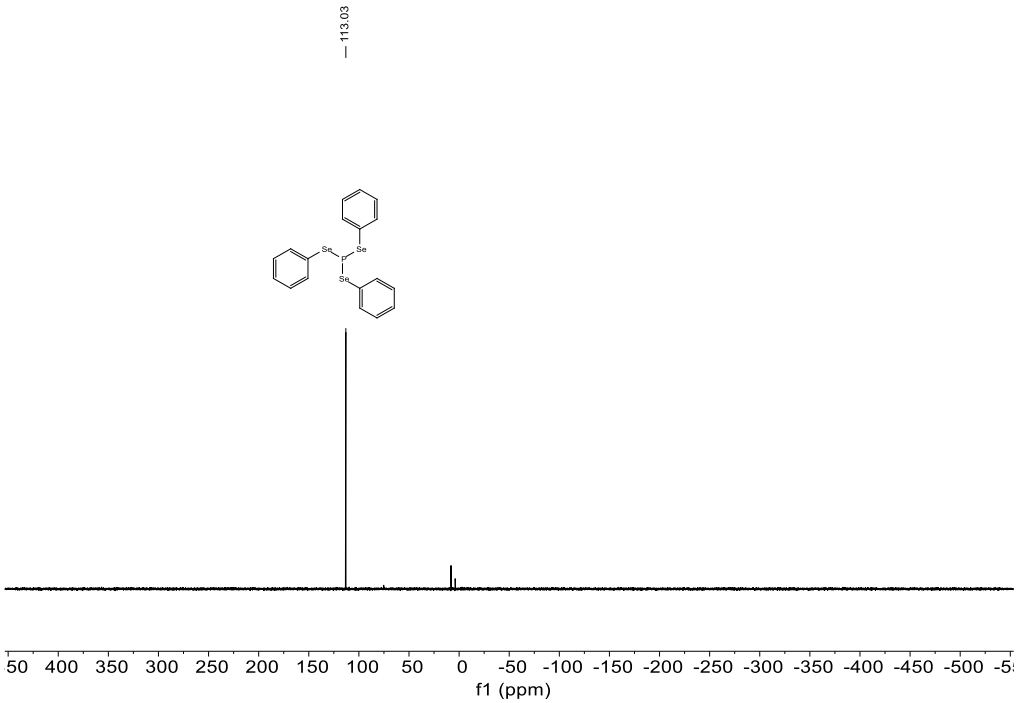


Supplementary Scheme 2-3. In situ NMR study on the mechanism of reaction A.

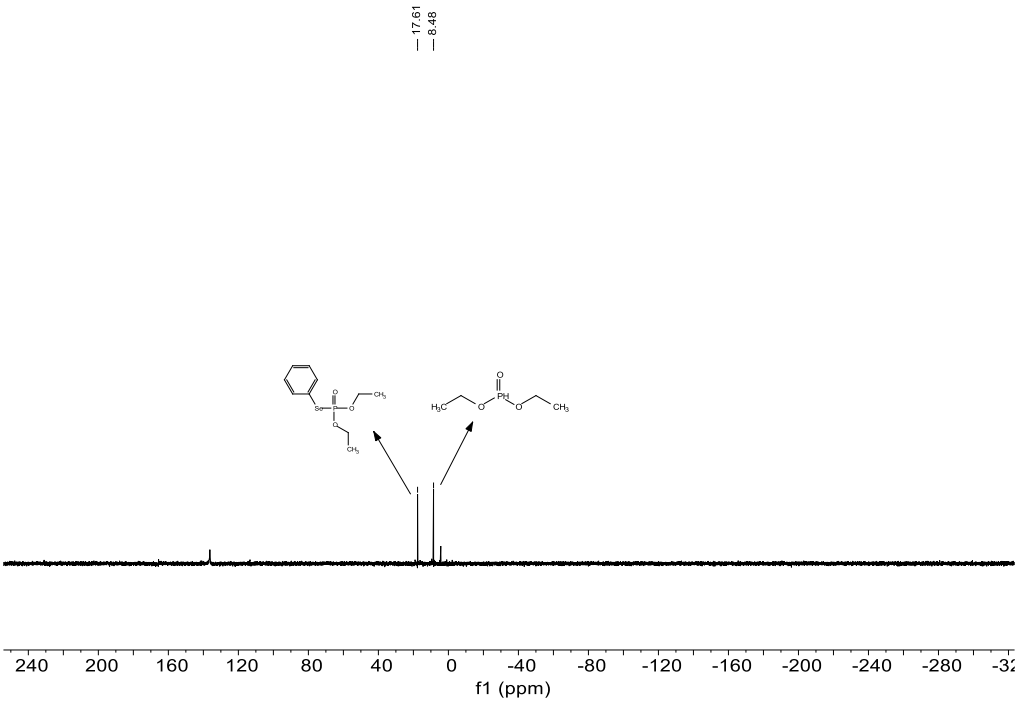
5. Control experiments and ^{31}P NMR spectra for the synthesis of mixed phosphates.



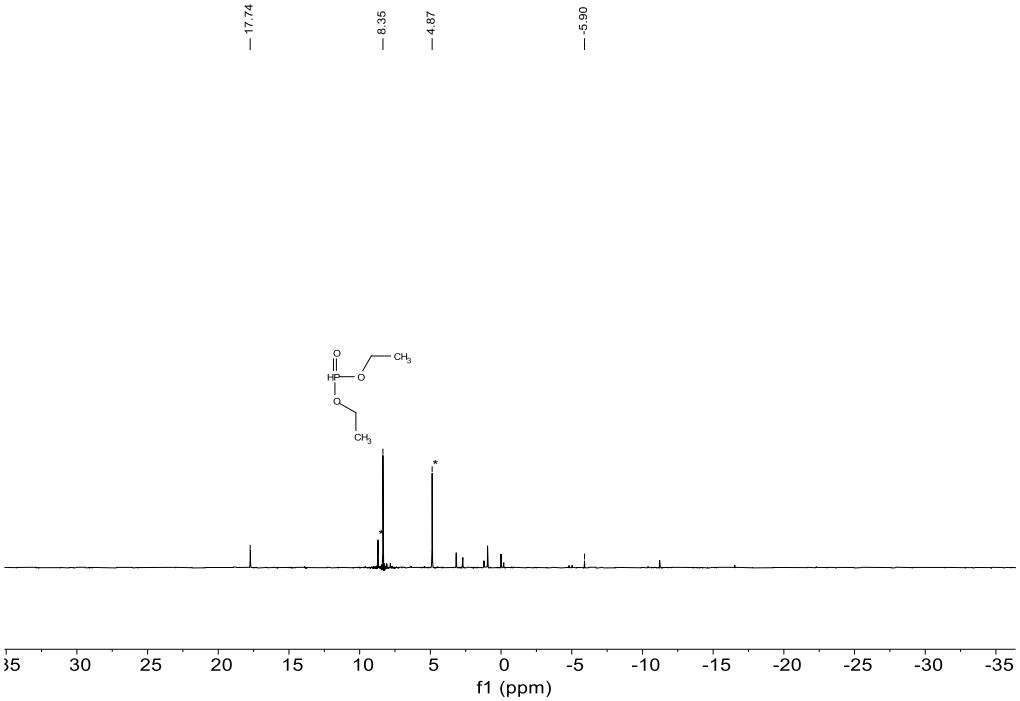
Supplementary Scheme 3-1. Control experiments B.



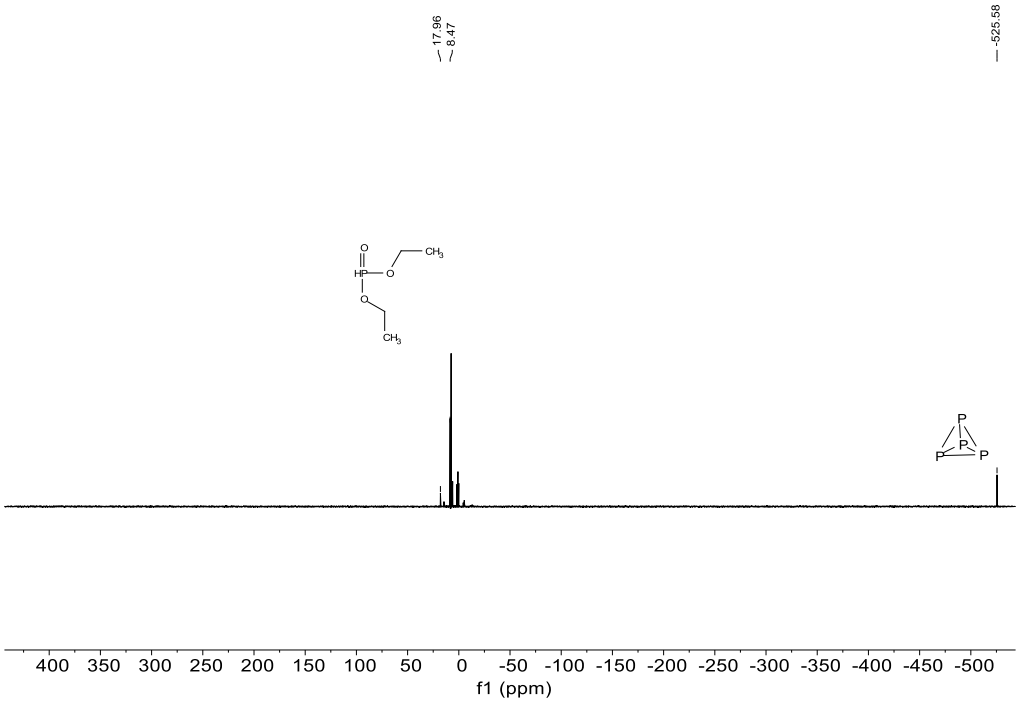
Supplementary figure 2-1. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 3-1 (a).



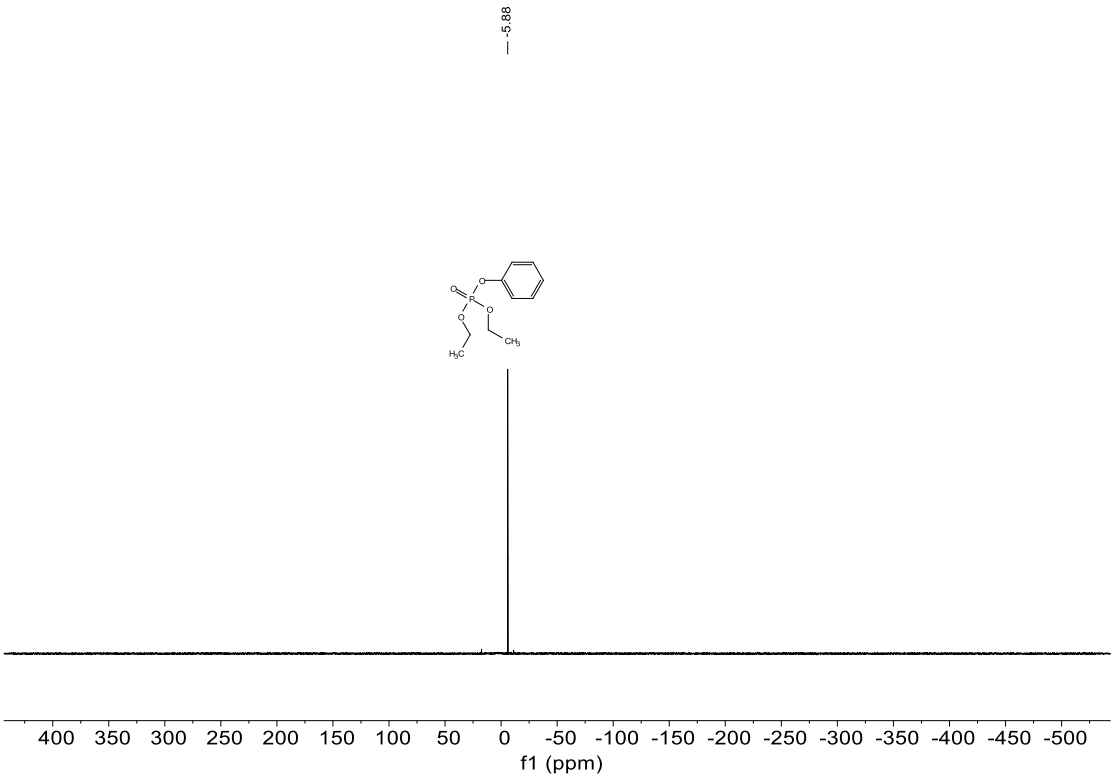
Supplementary figure 2-2. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 3-1 (b).



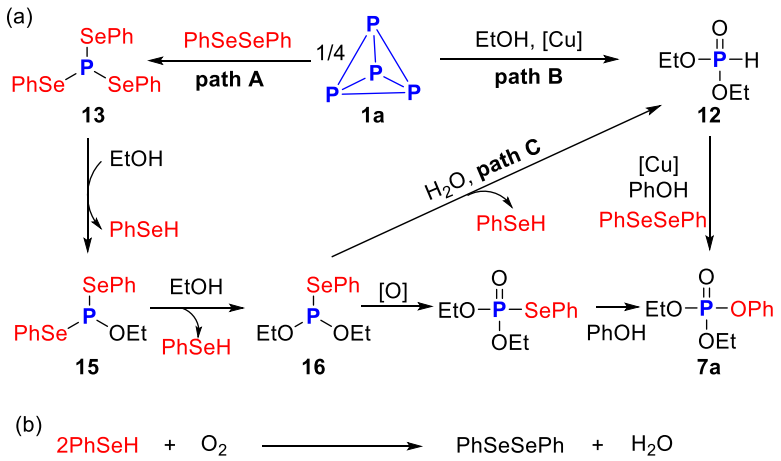
Supplementary figure 2-3. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 3-1 (c).



Supplementary figure 2-4. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 3-1 (d).



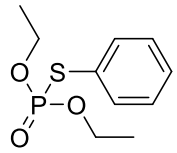
Supplementary figure 2-4. $^{31}P\{^{1}H\}$ spectrum of supplementary scheme 3-1 (e).



Supplementary Scheme 3-2. The propose mechanism for the multicomponent synthesis of mixed phosphonates from P_4.

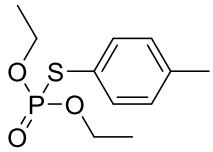
6. Characterization for products.

***O,O*-diethyl *S*-phenyl phosphorothioate (4a, CAS Registry No. 1889-58-3)**



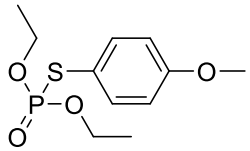
Light yellow oil; 44.2 mg, 90% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.55 (dt, *J* = 7.7, 2.0 Hz, 2H), 7.42-7.27 (m, 3H), 4.26-4.06 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 134.69 (d, *J* = 5.0Hz), 129.47 (d, *J* = 2.1Hz), 129.12(d, *J* = 2.7Hz), 126.76 (d, *J* = 7.3 Hz), 64.23 (d, *J* = 6.3 Hz), 16.12(d, *J* = 7.1Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.86 **HRMS:** $[M+Na]^+$ m/z calcd for $C_{10}H_{15}O_3PSNa^+$ 269.0372, found 269.0370.

***O,O*-diethyl *S*-(p-tolyl) phosphorothioate (4b, CAS Registry No. 4143-38-8)**



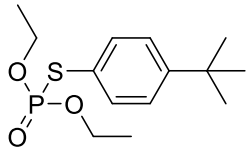
Light yellow oil; 45.2 mg, 87% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.42 (dd, *J*=8.2, 2.2 Hz, 2H), 7.13 (d, *J* =7.9 Hz, 2H), 4.24-4.09 (m, 4H), 2.32 (s, 3H), 1.29 (t, *J* =7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 139.44 (d, *J* = 3.1Hz), 134.77 (d, *J* = 5.2 Hz), 130.31 (d, *J* = 2.4 Hz), 123.01(d, *J* =7.2 Hz), 64.15 (d, *J* = 6.3 Hz), 21.32, 16.17 (d, *J* = 7.1 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.30; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{11}H_{17}O_3PSNa^+$ 283.0528, found 283.0529.

***O,O*-diethyl *S*-(4-methoxyphenyl) phosphorothioate (4c, CAS Registry No. 56809-76-9)**



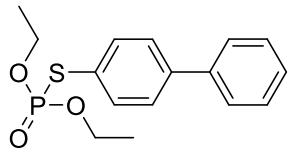
Light yellow oil; 36.5 mg, 66% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.47-7.41 (m, 2H), 6.87-6.81 (m, 2H), 4.22-4.04 (m, 4H), 3.76 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ160.61 (d, *J* = 2.8 Hz), 136.48 (d, *J* = 4.8 Hz), 116.78 (d, *J* = 7.1 Hz), 115.13 (d, *J* = 2.6 Hz), 64.10 (d, *J* = 6.4 Hz), 55.49, 16.17 (d, *J* = 7.0 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.50; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{11}H_{17}O_4PSNa^+$ 299.0477, found 299.0480.

***S*-(4-(tert-butyl)phenyl) *O,O*-diethyl phosphorothioate (4d, CAS Registry No. 4521-71-4)**



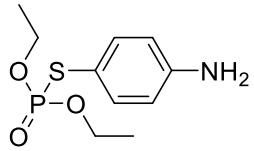
Light yellow oil; 37.8 mg, 67% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.24-4.14 (m, 4H), 1.31-1.28 (m, 15H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 152.55 (d, *J* = 3.3 Hz), 134.52 (d, *J* = 5.1 Hz), 126.65 (d, *J* = 2.3 Hz), 123.06 (d, *J* = 7.2 Hz), 64.18 (d, *J* = 6.1 Hz), 34.85, 31.36, 16.18 (d, *J* = 7.2 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 23.30; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{23}O_3PSNa^+$ 325.0998, found 325.0997.

***S*-([1,1'-biphenyl]-4-yl) *O,O*-diethyl phosphorothioate (4e, CAS Registry No. 1929539-74-1)**



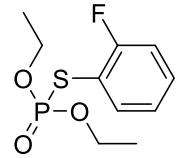
Light yellow oil; 48.3mg, 75% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.63 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.59-7.53 (m, 4H), 7.44 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.38-7.33 (m, 1H), 4.29-4.17 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ142.18 (d, *J* = 2.9 Hz), 140.13, 135.09 (d, *J* = 5.2 Hz), 129.08, 128.20 (d, *J* = 2.3 Hz), 128.01, 127.27, 125.60 (d, *J* = 7.2 Hz), 64.34 (d, *J* = 6.3 Hz), 16.23 (d, *J* = 7.1 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.81; **HRMS:** $[M+H]^+$ m/z calcd for $C_{16}H_{20}O_3PS^+$ 323.0865, found 323.0864.

***S*-(4-aminophenyl) *O,O*-diethyl phosphorothioate (4f, CAS Registry No. 94409-35-5)**



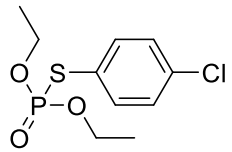
Light yellow oil; 31.9 mg, 61% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.32-7.21 (m, 2H), 6.65-6.57 (m, 2H), 4.20-4.10 (m, 4H), 3.85 (brs, 2H), 1.29 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 147.96, 136.55 (d, *J* = 4.6 Hz), 115.90 (d, *J* = 2.5 Hz), 113.08, 64.08 (d, *J* = 6.3 Hz), 16.26 (d, *J* = 7.2 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 24.10; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{10}H_{16}NO_3PSNa^+$ 284.0481, found 284.0480.

***O,O*-diethyl *S*-(2-fluorophenyl) phosphorothioate (4g, CAS Registry No. 1883501-47-0)**



Light yellow oil; 40.1 mg, 76% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.64-7.58 (m, 1H), 7.37(ddt, *J* = 10.3, 7.6, 3.6 Hz, 1H), 7.15-7.10 (m, 2H), 4.28-4.15 (m, 4H), 1.31(t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 162.29 (dd, *J* = 248.8, 5.6 Hz), 137.71 (d, *J* = 4.2 Hz), 131.82 (dd, *J* = 8.1, 3.2 Hz), 116.51 (dd, *J* =23.1, 2.7 Hz), 114.05 (dd, *J* =19.3, 7.6 Hz), 64.46 (d, *J* = 6.1 Hz), 16.15 (d, *J* = 7.4 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 21.36 (d, *J* = 4.0 Hz); **^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz):** δ -106.23 (d, *J* = 4.0 Hz); **HRMS:** $[M+Na]^+$ m/z calcd for $C_{10}H_{14}FO_3PSNa^+$ 287.0278, found 287.0277.

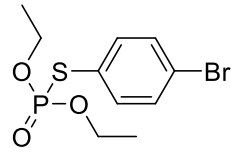
***S*-(4-chlorophenyl) *O,O*-diethyl phosphorothioate (4k, CAS Registry No. 4524-70-3)**



Light yellow oil; 48.3 mg, 86% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.51-7.46(m, 2H), 7.34-7.28(m, 2H), 4.24-4.10 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 135.95 (d, *J* = 5.1 Hz), 135.69 (d, *J* = 3.3 Hz), 129.74 (d, *J* = 2.4 Hz), 125.38 (d, *J* = 7.4 Hz), 64.46

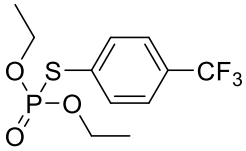
(d, J = 6.4 Hz), 16.21 (d, J = 7.0 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ 22.13; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{10}H_{14}ClO_3PSNa^+$ 302.9982, found 302.9985.

***S*-(4-bromophenyl) *O,O*-diethyl phosphorothioate (4i, CAS Registry No. 15224-36-9)**



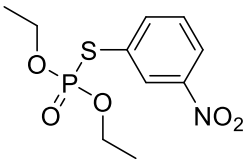
Light yellow oil; 52.7 mg, 81% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.47-7.45 (m, 2H), 7.42-7.40 (m, 2H), 4.24-4.09 (m, 4H), 1.30 (t, J = 7.1 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz):** δ 136.15 (d, J = 5.3 Hz), 132.69 (d, J = 2.1 Hz), 126.04 (d, J = 7.3 Hz), 123.83 (d, J = 3.6 Hz), 64.46 (d, J = 6.4 Hz), 16.21 (d, J = 7.2 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ 21.91; **HRMS:** $[M+H]^+$ m/z calcd for $C_{10}H_{15}BrO_3PS^+$ 324.9657, found 324.9658.

***O,O*-diethyl *S*-(4-(trifluoromethyl)phenyl) phosphorothioate (4j, CAS Registry No. 1883501-42-5)**



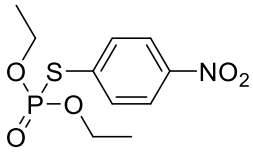
Light yellow oil; 25.7 mg, 41% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.70 (dd, J = 8.4, 2.0 Hz, 2H), 7.59 (d, J = 8.2 Hz, 2H), 4.27-4.13 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz):** δ 134.50 (d, J = 5.5 Hz), 132.20 (d, J = 6.6 Hz), 130.97 (dq, J = 2.2, 33.0 Hz), 126.12 (m), 123.74 (q, J = 272.0 Hz), 64.46 (d, J = 6.4 Hz), 16.01 (d, J = 7.0 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ 21.29; **$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 471MHz):** δ -62.92; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{11}H_{14}F_3O_3PSNa^+$ 337.0245, found 337.0244.

***O,O*-diethyl *S*-(3-nitrophenyl) phosphorothioate (4k, CAS Registry No. 4184-51-4)**



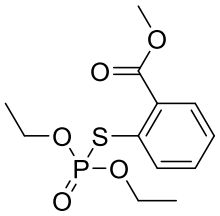
Yellow oil; 33.9 mg, 58% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.42 (d, J = 2.3 Hz, 1H), 8.20 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 4.28-4.15 (m, 4H), 1.33 (t, J = 7.0 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz):** δ 148.64, 140.39 (d, J = 5.1 Hz), 130.28 (d, J = 2.0 Hz), 129.84 (d, J = 6.9 Hz), 129.24 (d, J = 5.5 Hz), 124.01 (d, J = 2.5 Hz), 64.83 (d, J = 6.5 Hz), 16.19 (d, J = 6.9 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 242 MHz):** δ 20.71; **HRMS:** $[M+H]^+$ m/z calcd for $C_{10}H_{15}NO_5PS^+$ 292.0402, found 292.0402.

***O,O*-diethyl *S*-(4-nitrophenyl) phosphorothioate (4l, CAS Registry No. 3270-82-8)**



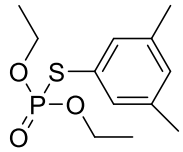
Yellow oil; 34.4 mg, 59% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.75 (dd, *J* = 8.8, 1.7 Hz, 2H), 4.29-4.14 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 148.04, 136.47 (d, *J* = 6.6 Hz), 134.31 (d, *J* = 1.7 Hz), 124.31 (d, *J* = 1.7 Hz), 64.94 (d, *J* =6.5 Hz), 16.22 (d, *J* = 6.9 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 20.08; **HRMS:** $[M+H]^+$ m/z calcd for $C_{10}H_{15}NO_5PS^+$ 292.0402, found 292.0404.

methyl 2-((diethoxyphosphoryl)thio)benzoate (4m, CAS Registry No. 2222022-82-2)



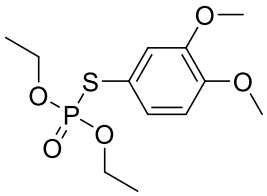
Brown oil; 20.7 mg, 34% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.88 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.81 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.39-7.33 (m, 1H), 4.23-4.10(m, 4H), 3.92 (s,3H), 1.28 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 157.25, 135.35 (d, *J* = 5.0 Hz), 134.43 (d, *J* = 5.6 Hz), 132.16 (d, *J* = 1.8 Hz), 130.99, 128.53 (d, *J* = 6.8 Hz), 128.40 (d, *J* = 2.2 Hz), 64.55 (d, *J* = 6.5 Hz), 52.61, 16.19 (d, *J* = 7.0 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.03; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{12}H_{17}O_5PSNa^+$ 327.0426, found 327.0425.

***S*-(3,5-dimethylphenyl) *O,O*-diethyl phosphorothioate (4n, CAS Registry No. 1883501-37-8)**



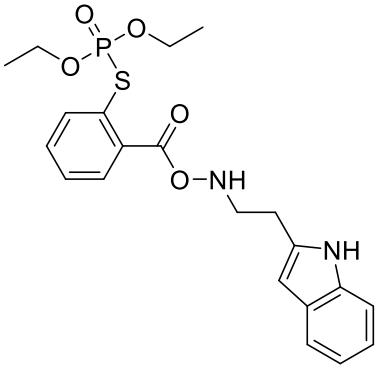
Light yellow oil; 45.5mg, 89% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ7.17 (s, 2H), 6.96 (s, 1H), 4.24-4.11 (m, 4H), 2.28(s, 6H), 1.30 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz):** δ139.12 (d, *J* = 2.4 Hz),132.39 (d, *J* = 5.3 Hz), 131.00 (d, *J* = 3.0 Hz), 125.90 (d, *J* = 7.1 Hz), 64.14 (d, *J* = 6.2 Hz), 21.30, 16.15 (d, *J* = 7.2 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.29; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{12}H_{19}O_3PSNa^+$ 297.0685, found 297.0683.

***S*-(3,4-dimethoxyphenyl) *O,O*-diethyl phosphorothioate (4o, CAS Registry No. 2376402-64-9)**



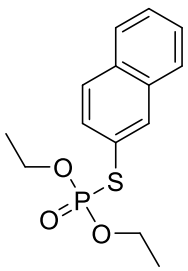
Light yellow oil; 36.0mg, 56% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.10 (dt, *J* = 8.4, 2.5 Hz, 1H), 7.06 (q, *J* = 2.3 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.22-4.11 (m, 4H), 3.85 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 150.35 (d, *J* = 3.2 Hz), 149.43 (d, *J* = 2.3 Hz), 128.06 (d, *J* = 5.7 Hz), 117.88 (d, *J* = 4.1 Hz), 117.03 (d, *J* = 7.4 Hz), 111.86 (d, *J* = 2.6 Hz), 64.23 (d, *J* = 6.6 Hz), 56.21, 56.11, 16.27 (d, *J* = 7.0 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ23.44; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{12}H_{19}O_5PSNa^+$ 329.0583, found 329.0583.

***S*-(2-((((2-(1H-indol-2-yl)ethyl)amino)oxy)carbonyl)phenyl) *O,O*-diethyl phosphorothioate (4p, new compound)**



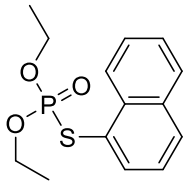
Brown oil; 26.0 mg, 29% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.33 (s, 1H), 7.68 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.59 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 (tt, *J* = 7.6, 1.7 Hz, 1H), 7.38-7.31 (m, 2H), 7.19-7.15 (m, 1H), 7.12-7.07 (m, 2H), 4.15-4.02 (m, 4H), 3.80 (dt, *J* = 7.3, 5.7 Hz, 2H), 3.13 (t, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 158.53, 143.58 (d, *J* = 5.3 Hz), 137.35 (d, *J* = 4.1 Hz), 136.63, 130.29 (d, *J* = 2.5 Hz), 130.26 (d, *J* = 2.8 Hz), 130.04 (d, *J* = 2.9 Hz), 127.64, 122.45, 122.15, 121.73 (d, *J* = 7.1Hz), 119.47, 118.91, 113.18, 111.44, 65.08 (d, *J* = 7.2 Hz), 40.66, 25.45, 16.25 (d, *J* = 7.0 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.83; **HRMS:** $[M+H]^+$ m/z calcd for $C_{21}H_{26}N_2O_5PS^+$ 449.1295, found 449.1296.

***O,O*-diethyl *S*-(naphthalen-2-yl) phosphorothioate (4q, CAS Registry No. 109161-61-7)**



Light yellow oil; 46.2 mg, 78% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.08 (s, 1H), 7.80 (ddt, *J* = 7.0, 3.9, 3.5 Hz, 3H), 7.61 (dt, *J* = 8.6, 1.6 Hz, 1H), 7.54-7.46 (m, 2H), 4.30-4.14 (m, 4H), 1.30 (t, *J* = 7.1 Hz ,6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.55 (d, *J* = 7.0 Hz), 133.78 (d, *J* = 2.3 Hz), 133.21 (d, *J* = 2.0 Hz), 131.09 (d, *J* = 4.1 Hz), 129.16 (d, *J* = 1.8 Hz), 127.24, 125.93, 123.96 (d, *J* = 7.2 Hz), 64.35 (d, *J* = 6.3 Hz), 16.20 (d, *J* = 7.3 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.85; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{17}O_3PSNa^+$ 319.0528, found 319.0526.

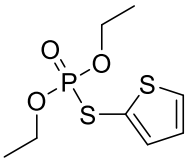
***O,O*-diethyl *S*-(naphthalen-1-yl) phosphorothioate (4r, CAS Registry No. 1883501-39-0)**



Light yellow oil; 38.8mg, 69% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 8.53 (d, *J* = 8.5 Hz, 1H),

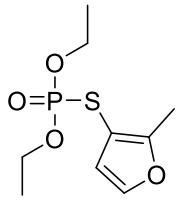
7.94-7.83 (m, 3H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 4.20-4.04 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 101MHz):** δ 135.45 (d, *J* = 5.6 Hz), 134.94 (d, *J* = 4.1 Hz), 134.50 (d, *J* = 2.3 Hz), 130.51(d, *J* = 3.5 Hz), 128.74, 127.26, 126.67, 126.15, 125.88 (d, *J* = 3.4 Hz), 123.97 (d, *J* = 8.1Hz), 64.44 (d, *J* = 6.6 Hz), 16.15 (d, *J* = 7.2 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.61; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{17}O_3PSNa^+$ 319.0528, found 319.0530.

***O,O*-diethyl *S*-(thiophen-2-yl) phosphorothioate (4s, CAS Registry No. 2085285-68-1)**



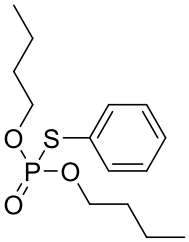
Brown oil; 29.3 mg, 58% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.41 (dd, *J* = 5.7, 2.7 Hz, 1H), 7.21 (d, *J* = 3.7 Hz, 1H), 7.00 (dd, *J* = 5.4, 3.6 Hz, 1H), 4.26-4.15 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 136.27 (d, *J* = 6.7 Hz), 131.21 (d, *J* = 4.4 Hz), 127.99 (d, *J* = 3.4 Hz), 123.34 (d, *J* = 8.5 Hz), 64.55 (d, *J* = 6.1 Hz), 16.17 (d, *J* = 7.1 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 20.71; **HRMS:** $[M+Na]^+$ m/z calcd for $C_8H_{13}O_3PS_2Na^+$ 274.9936, found 274.9927.

***O,O*-diethyl *S*-(2-methylfuran-3-yl) phosphorothioate (4t, new compound)**



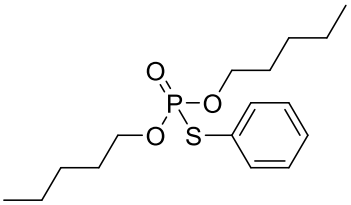
Brown oil; 25.1 mg, 50% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.27 (d, *J* =2.0 Hz, 1H), 6.36 (d, *J* = 2.0 Hz, 1H), 4.22-4.10 (m, 4H), 2.34 (d, *J* =3.5 Hz, 3H), 1.31 (t, *J* =7.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 156.65 (d, *J* = 8.7 Hz), 141.13, 115.41, 101.99 (d, *J* = 7.6 Hz), 64.22 (d, *J* = 6.4 Hz), 16.25 (d, *J* =7.1Hz), 12.09 (d, *J* =2.3 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.88; **HRMS:** $[M+Na]^+$ m/z calcd for $C_9H_{15}O_4PSNa^+$ 273.0321, found 273.0320.

***O,O*-dibutyl *S*-phenyl phosphorothioate (5a, CAS Registry No. 22946-78-7)**



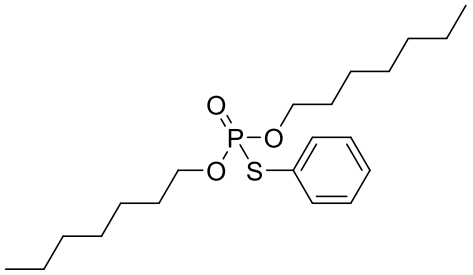
Light yellow oil; 54.4mg, 92% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.59-7.52(m, 2H), 7.32(dt, *J* = 5.3, 2.6 Hz 3H), 4.16-4.02 (m, 4H), 1.65-1.55 (m, 4H), 1.36-1.28 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.66 (d, *J* = 5.3 Hz), 129.44 (d, *J* = 2.1 Hz), 129.06 (d, *J* = 2.8 Hz) 126.85 (d, *J* = 7.1 Hz), 67.96 (d, *J* = 7.1 Hz), 32.28(d, *J* = 6.9 Hz), 18.80, 13.68; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.95; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{23}O_3PSNa^+$ 325.0998, found 325.1000.

***O,O*-dipentyl *S*-phenyl phosphorothioate(5b, CAS Registry No. 195209-86-0)**



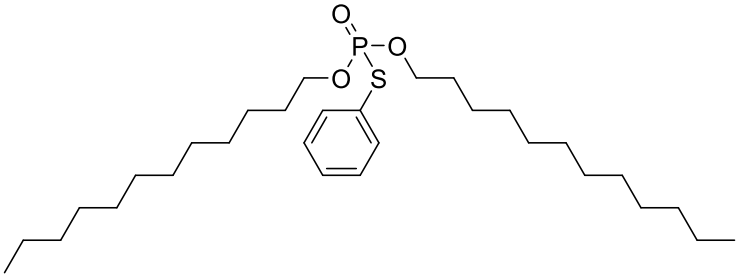
Light yellow oil; 59.4 mg, 86% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.55 (dt, *J* = 7.6, 2.0 Hz, 2H), 7.32 (dd, *J*=5.3, 2.0 Hz, 3H), 4.21-3.94 (m, 4H), 1.65-1.60 (m, 4H), 1.30-1.26 (m, 8H), 0.98-0.76 (m, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 134.66 (d, *J* = 5.2 Hz), 129.46 (d, *J* = 2.2 Hz), 129.07 (d, *J* = 3.0 Hz), 126.90 (d, *J* = 7.0 Hz), 68.27(d, *J*=6.8 Hz), 30.00 (d, *J* = 6.8 Hz), 27.73, 22.33, 14.06; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.92; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{16}H_{27}O_3PSNa^+$ 353.1311, found 353.1308.

***O,O*-diheptyl *S*-phenyl phosphorothioate (5c, CAS Registry No. 2217636-00-3)**



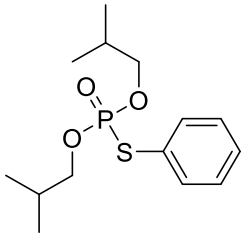
Light yellow oil; 70.5 mg, 87% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ7.55(dt, *J* = 7.6, 2.1 Hz, 2H), 7.35-7.29 (m, 3H), 4.14-4.03 (m, 4H), 1.65-1.59 (m, 4H), 1.31-1.21 (m, 16H), 0.86 (t, *J* = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** 134.66 (d, *J* = 5.4 Hz), 129.46 (d, *J* = 2.3 Hz), 129.06 (d, *J* = 2.7 Hz), 126.93 (d, *J* = 7.1 Hz), 68.30 (d, *J* = 6.7 Hz) 31.85, 30.33 (d, *J* = 7.1 Hz), 28.94, 25.57, 22.71; **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 37.01 (d, *J* = 446.7 Hz); **HRMS:** $[M+H]^+$ m/z calcd for $C_{20}H_{35}O_3PS^+$ 387.2117, found 387.2118.

***O,O*-didodecyl *S*-phenyl phosphorothioate (5d, new compound)**



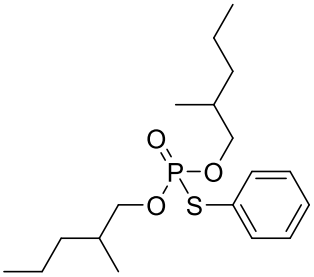
Light yellow oil; 94.8 mg, 90% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.58-7.54 (m, 2H), 7.34-7.30 (m, 3H), 4.13-4.12 (m, 4H), 1.64-1.60 (m, 4H),1.31-1.24 (m, 36H), 0.87 (t, *J* = 6.9 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.69 (d, *J* = 5.4 Hz), 129.48 (d, *J* = 2.8 Hz), 129.08 (d, *J* = 2.8 Hz), 126.97 (d, *J* = 7.2 Hz), 68.33 (d, *J* = 6.7 Hz), 30.39, 30.34, 29.85, 29.84, 29.75, 29.69, 29.55, 29.32, 25.65, 22.89, 14.30; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.92; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{30}H_{55}O_3PNa^+$ 549.3502, found 549.3502.

(2-isobutoxy-5-methyl-2l5-hex-1-en-2-yl)(phenyl)sulfane (5e, CAS Registry No. 195209-88-2)



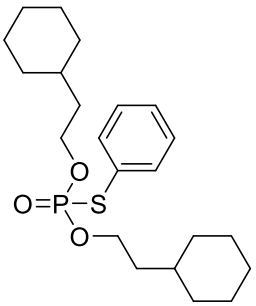
Light yellow oil; 38.7 mg, 64% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.60-7.51 (m, 2H), 7.32 (d, *J* = 6.0 Hz, 3H), 3.91-3.87 (m, 2H), 3.84-3.80 (m, 2H), 1.94-1.86 (m, 2H), 0.88 (d, *J* = 6.8 Hz, 12H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.76 (d, *J* = 5.4 Hz), 129.45 (d, *J* = 2.3 Hz), 129.10 (d, *J* = 2.9 Hz), 126.75 (d, *J* = 7.1 Hz), 74.08 (d, *J* = 7.2 Hz), 29.17 (d, *J* = 7.1 Hz), 18.81; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.83; **HRMS:** $[M+H]^+$ m/z calcd for $C_{14}H_{23}O_3PSNa^+$ 325.0998, found 325.0998.

***O,O*-bis(2-methylpentyl) *S*-phenyl phosphorothioate (5f, new compound)**



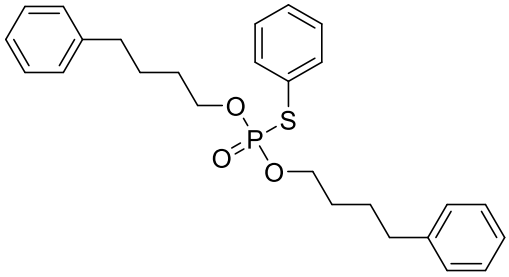
Light yellow oil; 60.9mg, 85% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.58-7.55 (m,2H), 7.34-7.29 (m, 3H), 4.02-3.81 (m, 4H), 1.76 (dt, *J* = 12.6, 6.2 Hz, 2H), 1.37-1.21 (m, 6H), 1.12-1.04 (m, 2H), 0.91-0.83 (m, 12H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 134.71, (dt, *J* = 5.5, 2.8 Hz), 129.43 (d, *J* = 2.2 Hz), 129.05 (d, *J* = 3.1 Hz), 126.88 (d, *J* = 7.0 Hz), 72.91 (dd, *J* = 7.2, 1.9 Hz), 35.19, 33.75 (d, *J* = 7.4 Hz), 20.01, 16.59 (d, *J* = 3.5 Hz), 14.36; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.84; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{18}H_{31}O_3PSNa^+$ 381.1624, found 381.1631.

***O,O*-bis(2-cyclohexylethyl) *S*-phenyl phosphorothioate (5g, new compound)**



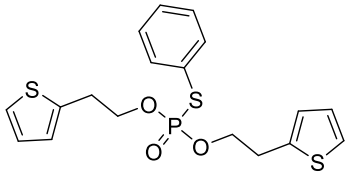
Light yellow oil; 63,2 mg, 77% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.54 (dt, *J* = 7.5, 2.1 Hz, 2H), 7.32 (dd, *J* = 5.2, 1.9 Hz, 3H), 4.18-4.06 (m, 4H), 1.69-1.60 (m, 10H), 1.54-1.49 (m, 4H), 1.37-1.29 (m, 2H), 1.21-1.09 (m, 6H), 0.91-0.82 (m, 4H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.57 (d, *J* = 5.3 Hz), 129.44 (d, *J* = 2.3 Hz), 129.01 (d, *J* = 2.7 Hz), 126.94 (d, *J* = 7.2 Hz), 66.32 (d, *J* = 7.0 Hz), 37.61 (d, *J* = 7.1 Hz), 34.02, 33.16, 26.60, 26.28; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.88; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{22}H_{35}O_3PSNa^+$ 433.1937 found 433.1938.

***S*-phenyl *O,O*-bis(4-phenylbutyl) phosphorothioate (5h, new compound)**



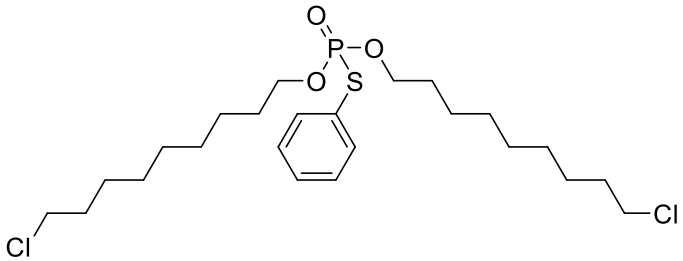
Light yellow oil; 81.6 mg, 89% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.53 (dt, *J* = 8.1, 2.0 Hz, 2H), 7.27(dt, *J* = 13.1, 5.3 Hz, 7H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 4H), 4.17-4.04 (m, 4H), 2.59 (t, *J* = 7.0 Hz, 4H), 1.66 (dq, *J* = 7.9, 4.6 Hz, 8H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 142.06, 134.70 (d, *J* = 5.4 Hz), 129.53 (d, *J* = 2.3 Hz), 129.16 (d, *J* = 2.8 Hz), 128.60, 128.55, 128.53 (d, *J* = 4.5 Hz), 126.80, 68.06 (d, *J* = 6.7 Hz), 35.45, 29.87 (d, *J* = 7.2 Hz), 27.38; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.10; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{26}H_{31}O_3PSNa^+$ 477.1624, found 477.1625.

***S*-phenyl *O,O*-bis(2-(thiophen-2-yl)ethyl) phosphorothioate (5i, new compound)**



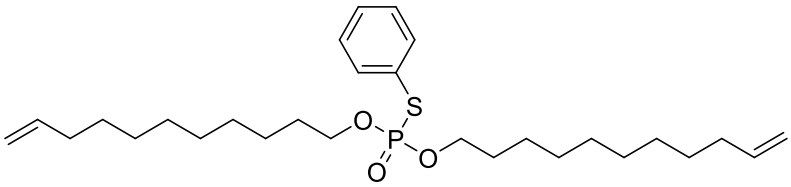
Light brown oil; 57.4 mg, 70% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51-7.45 (m, 2H), 7.38-7.28 (m, 3H), 7.16 (dd, *J* = 5.1, 1.2 Hz, 2H), 6.94 (dd, *J* = 5.2, 3.4 Hz, 2H), 6.83 (dd, *J* = 3.5, 1.1 Hz, 2H), 4.36-4.22 (m, 4H), 3.14 (t, *J* = 6.8 Hz, 4H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 138.91, 134.87 (d, *J* = 5.3 Hz), 129.61 (d, *J* = 2.4 Hz), 129.30 (d, *J* = 2.9 Hz), 127.13, 126.11, 124.37, 68.13 (d, *J* = 6.8 Hz), 30.90 (d, *J* = 7.6 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 23.24; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{18}H_{19}O_3PS_3Na^+$ 433.0126, found 433.0130.

***O,O*-bis(9-chlorononyl) *S*-phenyl phosphorothioate (5j, new compound)**



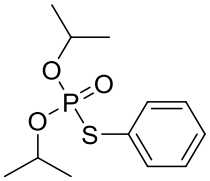
Light yellow oil; 70.3 mg, 66% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.58-7.53 (m, 2H), 7.33 (d, *J* = 6.1 Hz, 3H), 4.15-4.03 (m, 4H), 3.52 (d, *J* = 6.7 Hz, 4H), 1.77-1.73 (m, 4H), 1.66-1.60 (m, 4H), 1.32-1.25 (m, 20H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.67 (d, *J* = 5.2 Hz), 129.51 (d, *J* = 2.2 Hz), 129.12 (d, *J* = 2.7 Hz), 126.13 (d, *J* = 7.0 Hz), 68.29 (d, *J* = 6.7 Hz), 45.32, 32.82, 30.39 (d, *J* = 7.0 Hz), 29.48, 29.18, 28.97, 27.04, 25.60; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 22.98; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{24}H_{41}Cl_2O_3PSNa^+$ 533.1783, found 533.1780.

***S*-phenyl *O,O*-di(undec-10-en-1-yl) phosphorothioate (5k, new compound)**



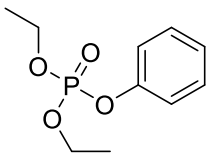
Light yellow oil; 41.3 mg, 40% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.59-7.55 (m, 2H), 7.33 (d, *J* = 5.9 Hz, 3H), 5.82-5.79 (m, 2H), 5.00-4.92 (m, 4H), 3.63(t, *J* = 5.9 Hz 4H), 2.06-2.01 (m, 4H), 1.69-1.60 (m, 2H), 1.60-1.53 (m, 2H), 1.38-1.26 (m, 24H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 139.42 (d, *J* = 5.6 Hz), 134.71 (d, *J* = 5.3 Hz), 129.52 (d, *J* = 2.1 Hz), 129.11 (d, *J* = 3.2 Hz), 127.01 (d, *J* = 6.7 Hz), 114.36 (d, *J* = 4.5 Hz), 68.37 (d, *J* = 6.7 Hz), 63.30, 34.02, 33.06, 30.39 (d, *J* = 6.9 Hz), 29.65, 29.32, 25.98, 25.67; **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 22.94; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{28}H_{47}O_3PNa^+$ 517.2876, found 517.2875.

***O,O*-diisopropyl *S*-phenyl phosphorothioate (5l, CAS Registry No. 15267-38-6)**



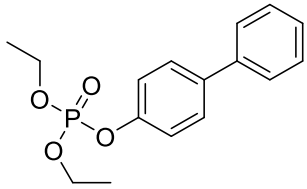
Light yellow oil; 48.3mg, 88% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.61-7.56 (m, 2H), 7.35-7.32 (m, 3H), 4.82-4.72 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.23 (d, *J* = 6.2 Hz, 6H), **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.39 (d, *J* = 5.6 Hz), 129.32 (d, *J* = 1.8 Hz), 128.82 (d, *J* =2.7 Hz), 127.50 (d, *J* = 7.2 Hz), 73.48 (d, *J* =6.8 Hz), 23.64 (d, *J* =5.7 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 20.42; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{12}H_{19}O_3PSNa^+$ 297.0685, found 297.0684.

diethyl phenyl phosphate (7a, CAS Registry No. 2510-86-3)



Light yellow oil; 31.3 mg, 68% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.35-7.27 (m, 2H), 7.20 (dt, *J* = 8.7, 1.2 Hz, 2H), 7.17-7.11(m, 1H), 4.21-4.14 (m, 4H), 1.33 (dt, *J* = 7.1, 1.1 Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126MHz):** δ 150.96 (d, *J* = 6.9 Hz), 129.85, 125.12, 120.15 (d, *J* = 4.8 Hz), 64.73 (d, *J* = 6.1 Hz), 16.25 (d, *J* = 6.7 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ -6.31; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{10}H_{15}O_4PNa^+$ 253.0600, found 253.0599.

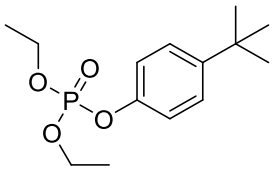
[1,1'-biphenyl]-4-yl diethyl phosphate (7b, CAS Registry No. 37782-03-9)



Light yellow oil; 36.1 mg, 59% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57-7.51 (m, 4H), 7.44-7.38

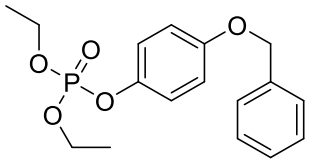
(m, 2H), 7.36-7.31 (m, 1H), 7.31-7.27 (m, 2H), 4.29-4.18 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101MHz):** δ 150.40 (d, *J* = 7.0 Hz), 140.36, 138.25, 128.94, 128.51, 127.45, 127.13, 120.40 (d, *J* = 5.1 Hz), 64.77 (d, *J* = 6.1 Hz), 16.25 (d, *J* = 6.7 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ -6.28; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{16}H_{19}O_4PNa^+$ 329.0913, found 329.0907.

4-(*tert*-butyl)phenyl diethyl phosphate (7c, CAS Registry No. 13538-40-4)



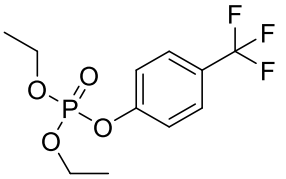
Light yellow oil; 40.5 mg, 66% yield; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.36-7.28 (m, 2H), 7.14-7.07 (m, 2H), 4.24-4.15 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.28 (s, 9H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz):** δ 148.63 (d, *J* = 7.0 Hz), 147.96, 126.70, 119.50 (d, *J*= 4.8 Hz), 64.64 (d, *J* = 6.0 Hz), 34.54, 31.58, 16.27 (d, *J* = 6.7 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ -6.05; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{23}O_4PNa^+$ 309.1226, found 309.1226.

4-(benzyloxy)phenyl diethyl phosphate (7d, CAS Registry No. 57991-82-9)



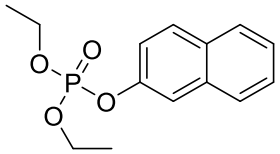
Pale yellow oil; 28.3 mg, 42% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.43-7.35 (m, 4H), 7.34-7.31 (m, 1H), 7.16-7.10 (m, 2H), 6.94-6.89 (m, 2H), 5.02 (s, 2H), 4.25-4.15(m, 4H) 1.34 (t, *J* = 7.0 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101MHz):** δ 156.05, 144.76 (d, *J* = 7.1 Hz), 137.01, 128.77, 128.20, 127.63, 121.09 (d, *J* = 4.6 Hz), 115.88, 70.66, 64.68 (d, *J* = 6.1 Hz), 16.28 (d, *J* = 6.7 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ -5.97; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{17}H_{21}O_5PNa^+$ 359.1019, found 359.1021.

diethyl (4-(trifluoromethyl)phenyl) phosphate (7e, CAS Registry No.1454305-46-4)



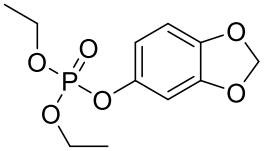
Pale yellow oil; 20.3 mg, 34% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, *J*= 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.27-4.17 (m, 4H), 1.35 (t, *J*= 7.1 Hz, 6H); **$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126MHz):** δ 153.51 (d, *J* = 6.2 Hz), 127.23 (q, *J* = 32.0 Hz), 127.11 (dq, *J* = 3.8, 1.1 Hz), 123.85 (q, *J* = 271.6 Hz), 120.30 (d, *J* = 5.2 Hz), 64.89 (d, *J* = 6.4 Hz), 16.04 (d, *J* = 6.7 Hz); **$^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz):** δ -6.72; **$^{19}F\{^{1}H\}$ NMR ($CDCl_3$, 377 MHz):** δ -62.34; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{27}H_{33}OPNa^+$ 427.2161, found 427.2154.

diethyl naphthalen-2-yl phosphate (7f, CAS Registry No. 16519-26-9)



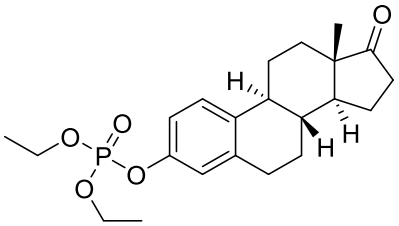
Pale yellow oil; 32.0 mg, 57% yield; **^{1}H NMR ($CDCl_3$, 600 MHz):** δ 7.85-7.76 (m, 3H), 7.69 (s, 1H), 7.50-7.41 (m, 2H), 7.39-7.34 (m, 1H), 4.30-4.20 (m, 4H), 1.36 (t, *J* = 7.1Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 148.55 (d, *J* = 7.0 Hz), 134.06, 131.06, 130.00, 127.87, 127.70, 126.87, 125.62, 120.21 (d, *J* = 7.0 Hz), 116.55 (d, *J* = 4.9 Hz), 64.86 (d, *J* = 6.0 Hz), 16.29 (d, *J* = 6.7 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ -6.25; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{17}O_4PNa^+$ 303.0756, found 303.0757.

benzo[d][1,3]dioxol-5-yl diethyl phosphate (7g, CAS Registry No. 5460-52-6)



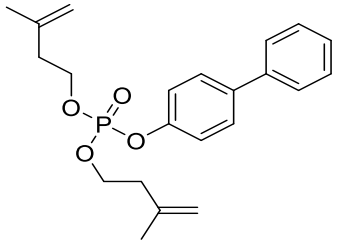
Yellow oil; 34.0 mg, 62% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 6.67-6.63 (m, 3H), 5.93 (s, 2H), 4.23-4.13 (m, 4H), 1.33 (t, *J* = 7.1Hz, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz):** δ 148.28, 145.35 (d, *J* = 7.1 Hz), 144.90, 112.56 (d, *J* = 5.0 Hz), 108.16, 102.68 (d, *J* = 4.7 Hz), 101.86, 64.75 (d, *J* = 6.1 Hz), 16.27 (d, *J* = 6.7 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ -5.90; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{11}H_{15}O_6PNa^+$ 297.0498, found 297.0496.

diethyl ((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl) phosphate (7h, CAS Registry No. 2529-44-4)



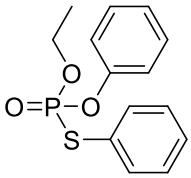
Light yellow oil; 46.3 mg, 57% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.21 (d, *J* = 8.4 Hz, 1H), 7.00-6.91 (m, 2H), 4.26-4.13 (m, 4H), 2.88 (dd, *J* = 9.1, 4.3 Hz, 2H), 2.52-2.45 (m, 1H), 2.40-2.33 (m, 1H), 2.27-2.20 (m, 1H), 2.17-1.92 (m, 4H), 1.66-1.41 (m, 6H), 1.35 (t, *J* = 7.1 Hz, 6H), 0.89 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 220.93, 148.84 (d, *J* = 7.1 Hz), 138.46, 136.65, 126.74, 120.11(d, *J* = 4.6 Hz), 117.34 (d, *J* = 4.8 Hz), 64.66 (d, *J* = 6.1 Hz), 50.60, 48.12, 44.23, 38.23, 36.03, 31.72, 29.60, 26.51, 25.97, 21.76, 16.30 (d, *J* = 6.6 Hz), 14.01; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ -6.07; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{22}H_{31}O_5PNa^+$ 429.1801, found 429.1801.

[1,1'-biphenyl]-4-yl bis(3-methylbut-3-en-1-yl) phosphate (7i, new compound)



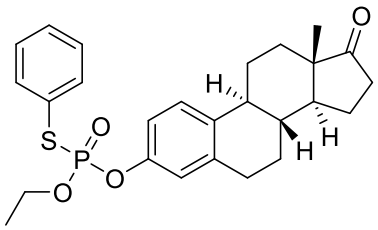
Light yellow oil; 49.4 mg, 64% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.55 (dt, *J* = 7.1, 1.3 Hz, 4H), 7.46-7.40 (m, 2H), 7.37-7.32 (m, 1H), 7.31-7.27 (m, 2H), 4.84 (s, 2H), 4.77 (s, 2H), 4.31-4.22 (m, 4H), 2.43 (t, *J* = 6.9 Hz, 4H), 1.75 (s, 6H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 150.39 (d, *J* = 6.9 Hz), 140.98, 140.45, 138.40, 129.02, 128.57, 127.53, 127.22, 120.51 (d, *J* = 4.9 Hz), 113.09, 66.85 (d, *J* = 6.3 Hz), 38.40 (d, *J* = 7.0 Hz), 22.64; **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ -6.24; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{22}H_{27}O_4PNa^+$ 409.1539, found 409.1539.

***O*-ethyl *O, S*-diphenyl phosphorothioate (8a, CAS Registry No. 51350-42-6)**



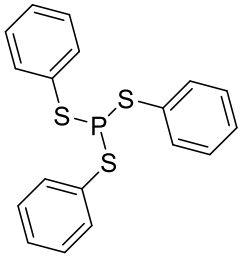
Pale yellow oil; 47.0 mg, 80% yield; **^{1}H NMR ($CDCl_3$, 600 MHz):** δ 7.56-7.48 (m, 2H), 7.41-7.28 (m, 5H), 7.21-7.13 (m, 3H), 4.31-4.26 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 150 MHz):** δ 150.62 (d, *J* = 7.9 Hz), 135.17 (d, *J* = 5.6 Hz), 129.89, 129.61 (d, *J* = 2.4 Hz), 129.53 (d, *J* = 2.9 Hz), 125.90 (d, *J* = 7.3 Hz), 125.50, 120.62 (d, *J* = 5.1 Hz), 65.05 (d, *J* = 5.8 Hz), 16.22 (d, *J* = 7.2 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 19.13; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{15}O_3PSNa^+$ 317.0372, found 317.0371.

***O*-ethyl *O*-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl) *S*-phenyl phosphorothioate (8b, new compound)**



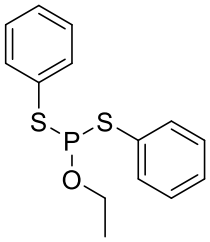
Pale yellow oil; 65.9 mg, 70% yield; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56-7.53 (m, 2H), 7.40-7.30 (m, 3H), 7.21 (d, *J* = 8.5 Hz, 1H), 6.93-6.89 (m, 2H), 4.34-4.24 (m, 2H), 2.88-2.84 (m, 2H), 2.55-2.47 (m, 1H), 2.41-2.36 (m, 1H), 2.19-1.95 (m, 5H), 1.61-1.44 (m, 6H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 3H) ; **^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz):** δ 220.97, 148.42 (d, *J* = 8.3 Hz), 138.47, 137.02, 135.07 (d, *J* = 5.4 Hz), 129.52 (d, *J* = 2.5 Hz), 129.42 (d, *J* = 3.1 Hz), 126.70, 126.00 (d, *J* = 7.5 Hz), 120.52 (d, *J* = 4.8 Hz), 117.76 (d, *J* = 4.9 Hz), 65.00 (d, *J* = 6.6 Hz), 50.57, 48.09, 44.20, 38.16, 36.00, 31.69, 29.54, 26.45, 25.90, 21.73, 16.17 (d, *J* = 7.1 Hz), 13.99; **^{31}P{^{1}H} NMR ($CDCl_3$, 242 MHz):** δ 18.57; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{26}H_{31}O_4PSNa^+$ 493.1573, found 493.1575.

triphenyl phosphorotrithioite (9，CAS Registry No. 1095-04-1)



White solid; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.49-7.46 (m, 6H), 7.31-7.28 (m,9H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 134.41 (d, *J* = 4.6 Hz) ,132.31 (d, *J* = 12.7 Hz), 129.36, 128.69 (d, *J* = 2.1 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 132.31; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{18}H_{15}O_3PS_3Na^+$ 380.9965, found 380.9965.

***O*-ethyl *S, S*-diphenyl phosphorodithioite (10, CAS Registry No. 28204-36-6)**

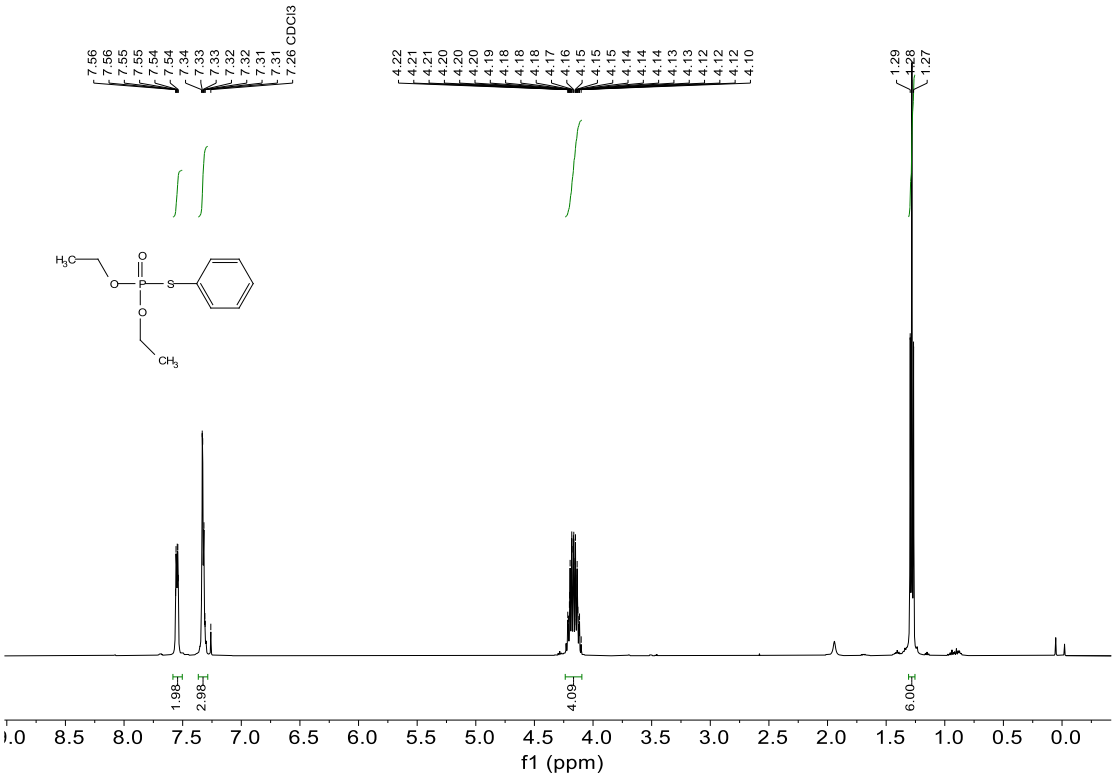


Colorless oil; **^{1}H NMR ($CDCl_3$, 500 MHz):** δ 7.55-7.53 (m, 4H), 7.34-7.29 (m, 6H), 4.20-4.14 (m, 2H), 1.28 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz):** δ 133.50, 133.45, 129.49, 128.15 (d, *J* = 1.8 Hz), 62.09 (d, *J* = 9.2 Hz), 16.51 (d, *J* = 2.6 Hz); **^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz):** δ 157.52; **HRMS:** $[M+Na]^+$ m/z calcd for $C_{14}H_{15}OPS_2Na^+$ 317.0194, found 317.0195.

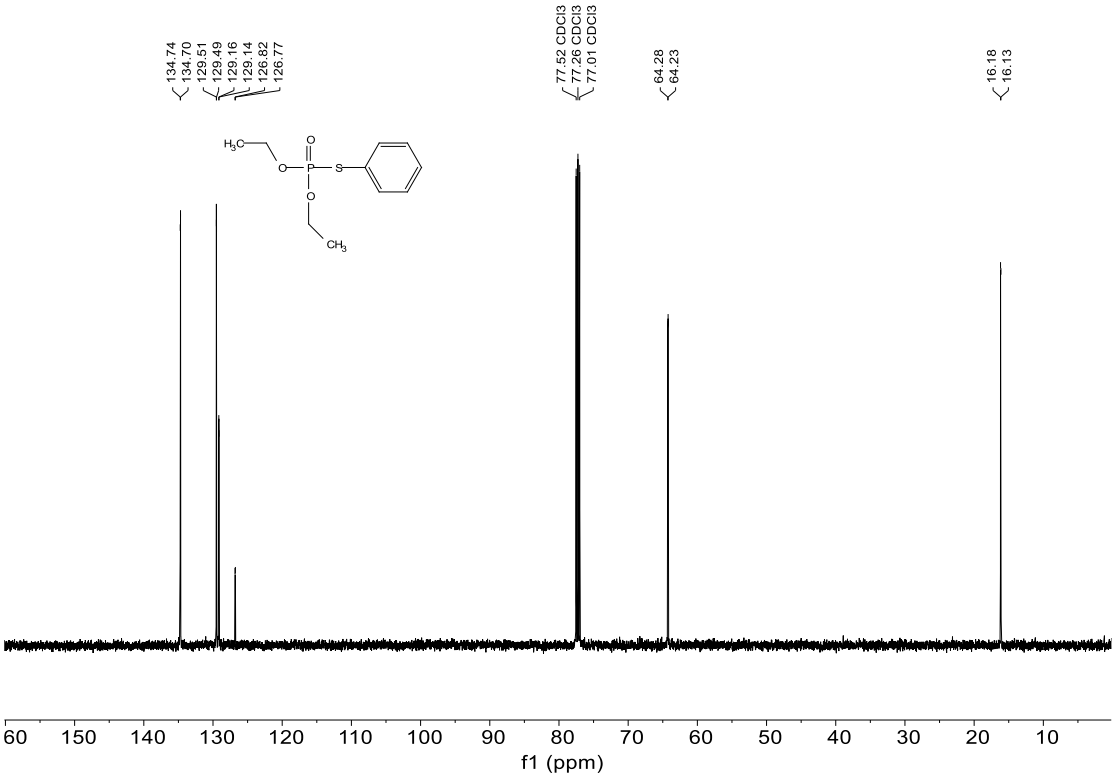
7. Supplementary Reference

1. Y. Liu, J. Kim, H. Seo, S. Park and J. Chae, *Adv. Synth. Catal.*, 2015, **357**, 2205-2212.
2. X. Qiu, X. Yang, Y. Zhang, S. Song and N. Jiao, *Org. Chem. Front.*, 2019, **6**, 2220-2225.

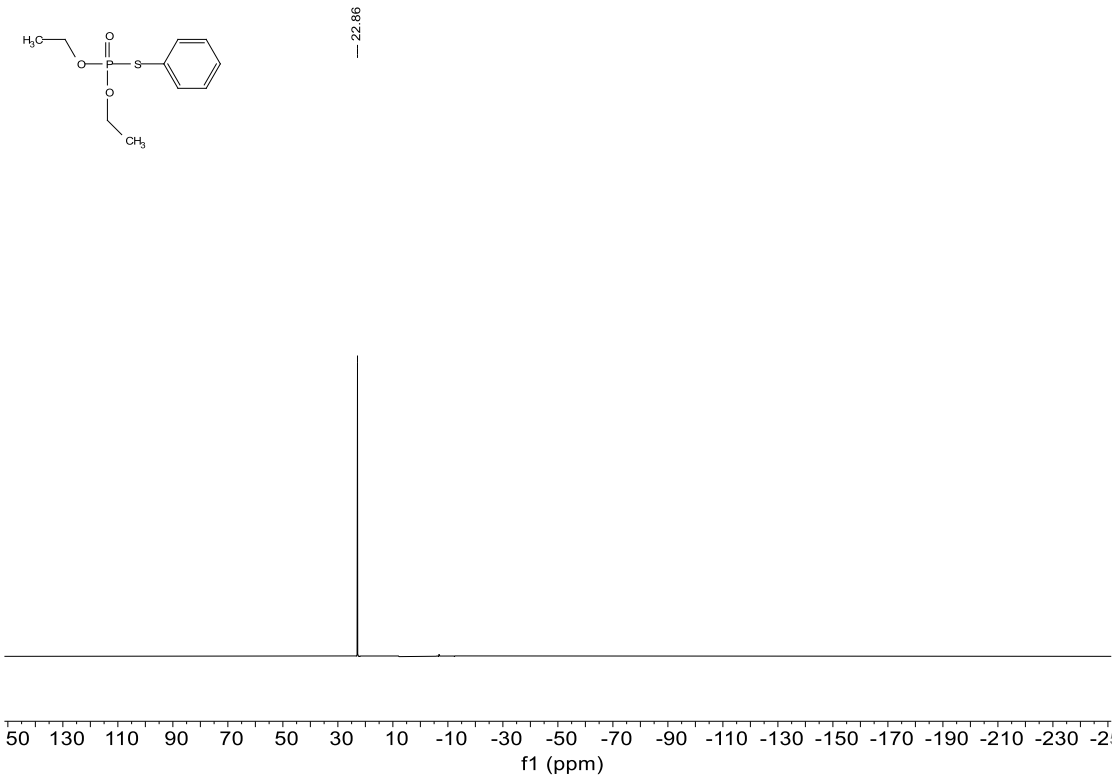
8. NMR spectrum of isolated products.



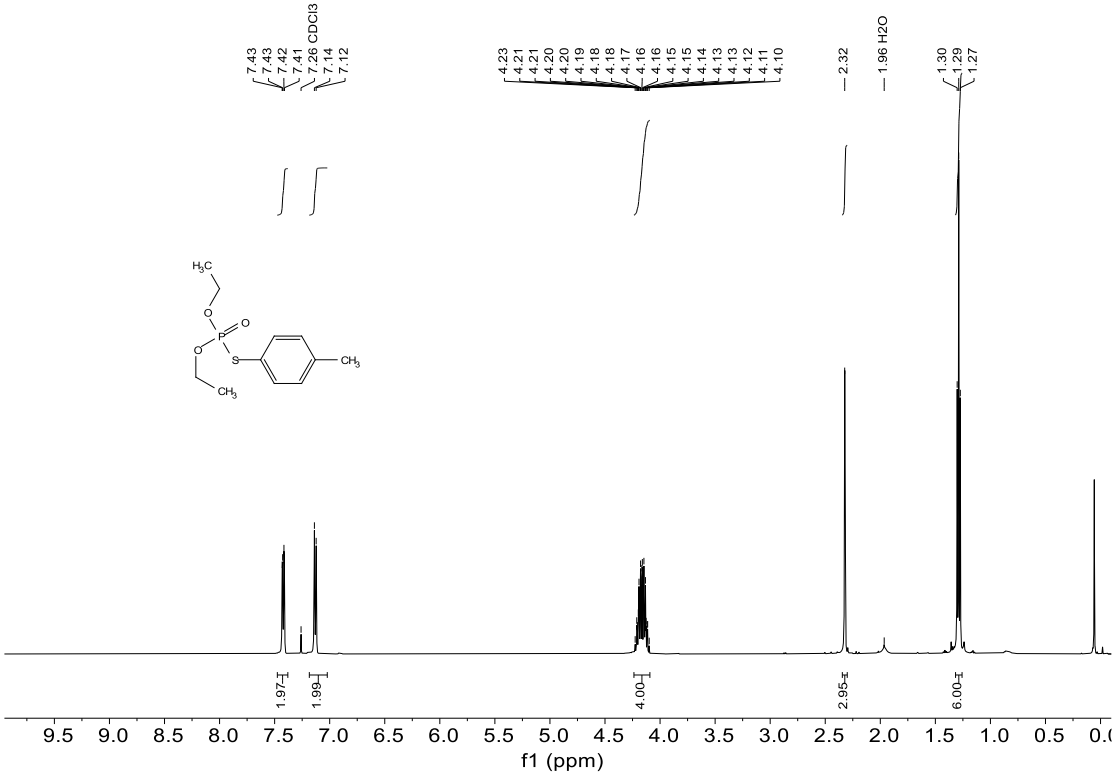
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4a**



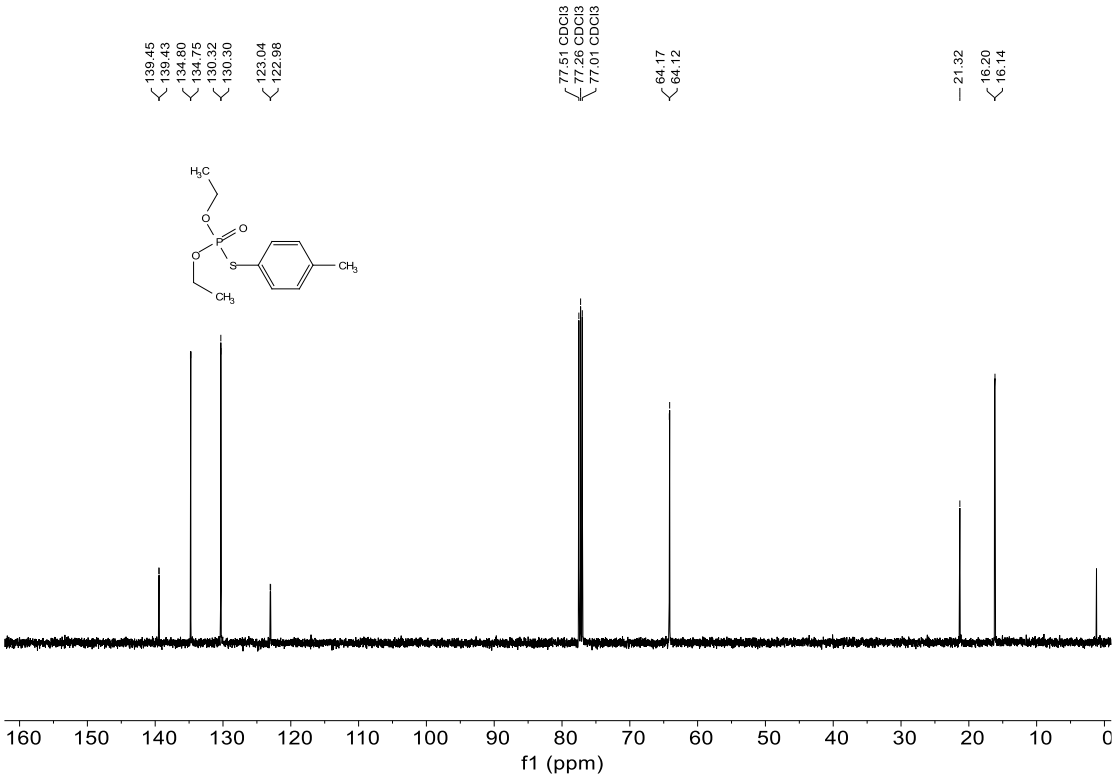
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4a**



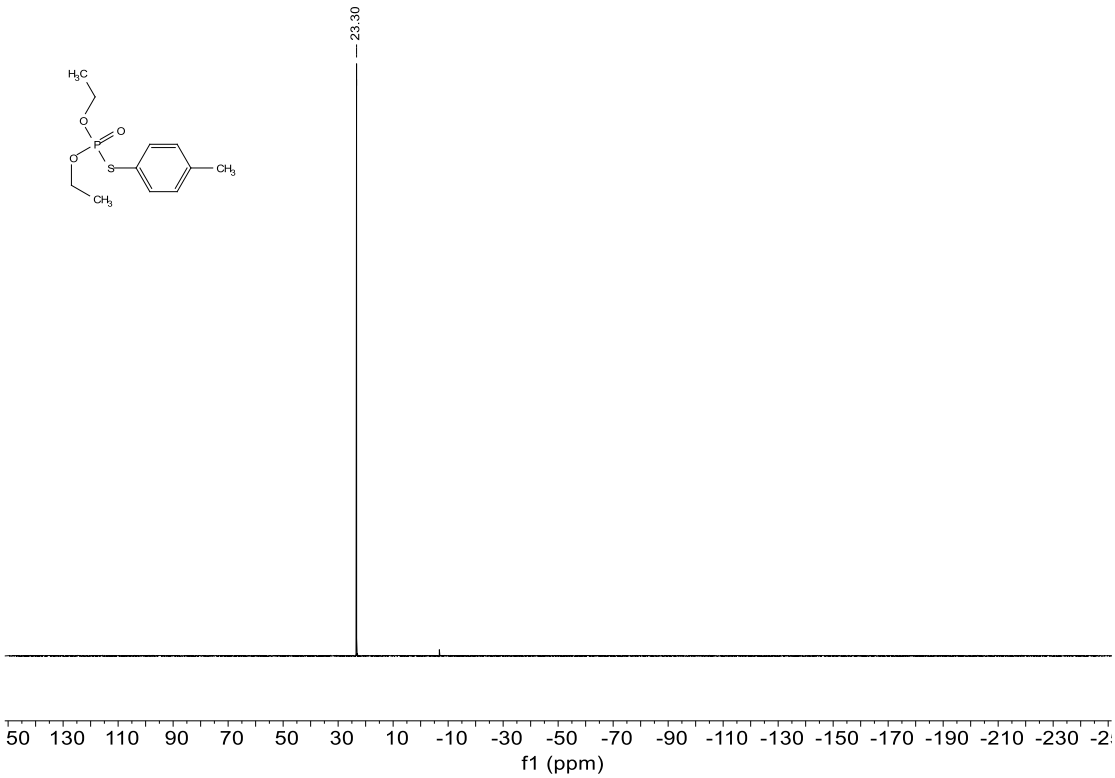
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4a**



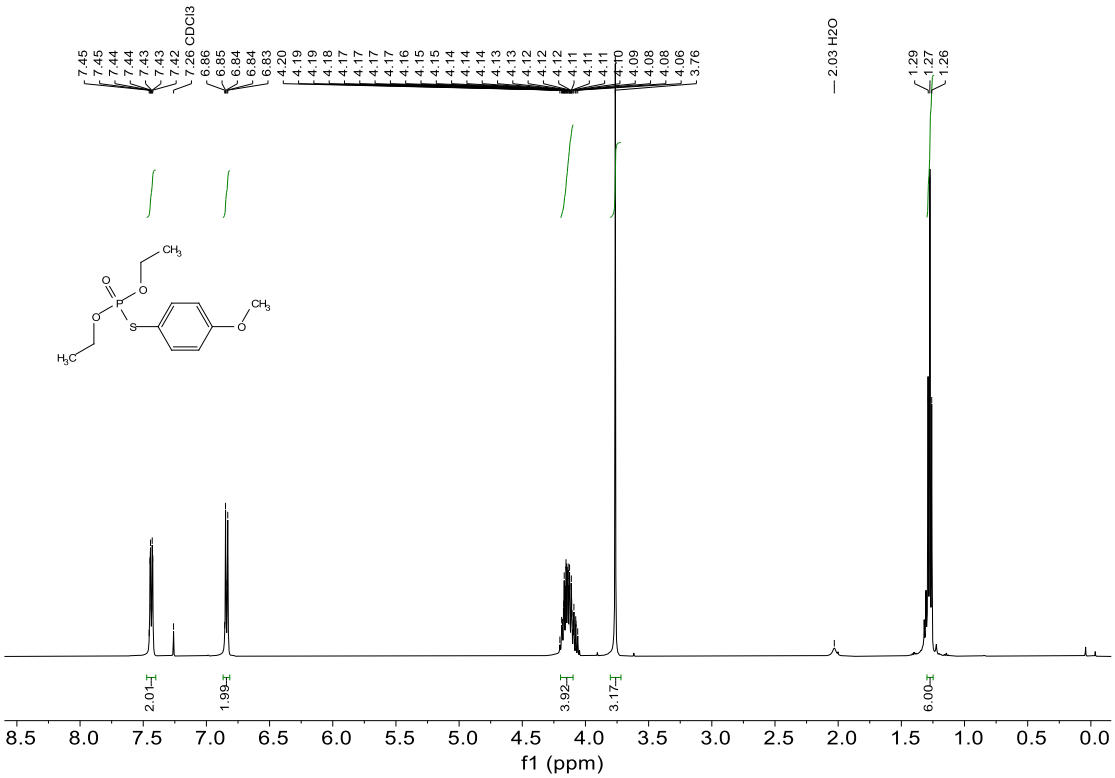
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4b**



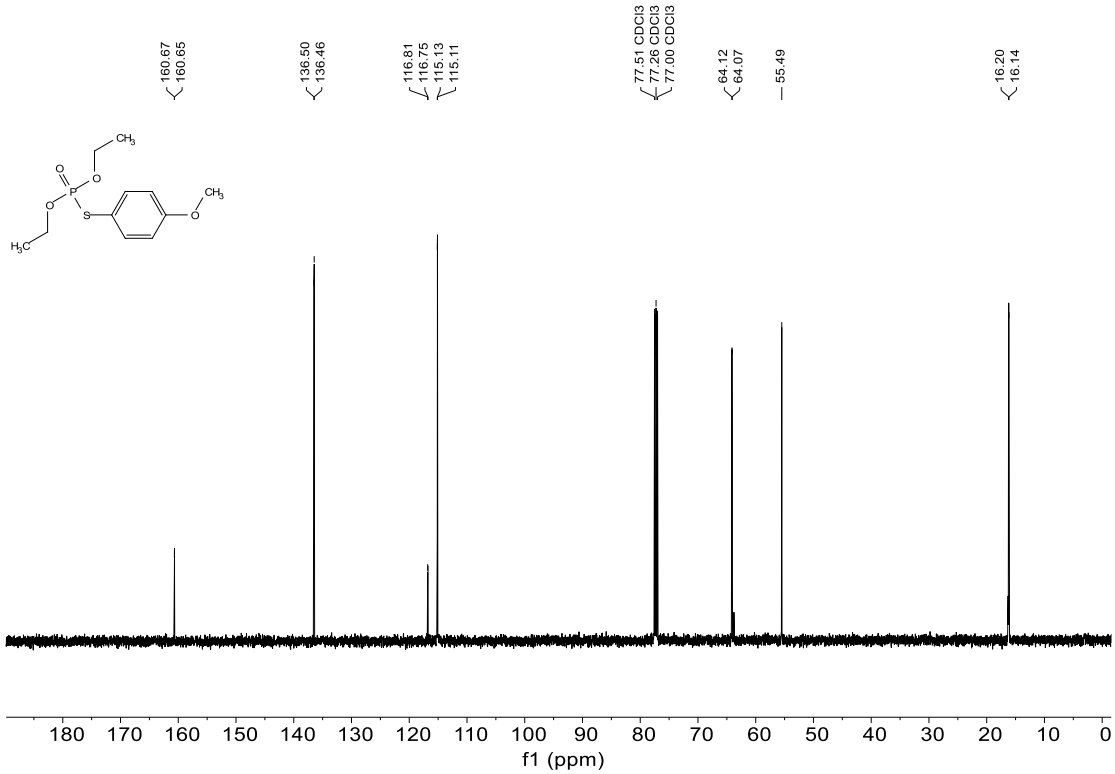
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4b**



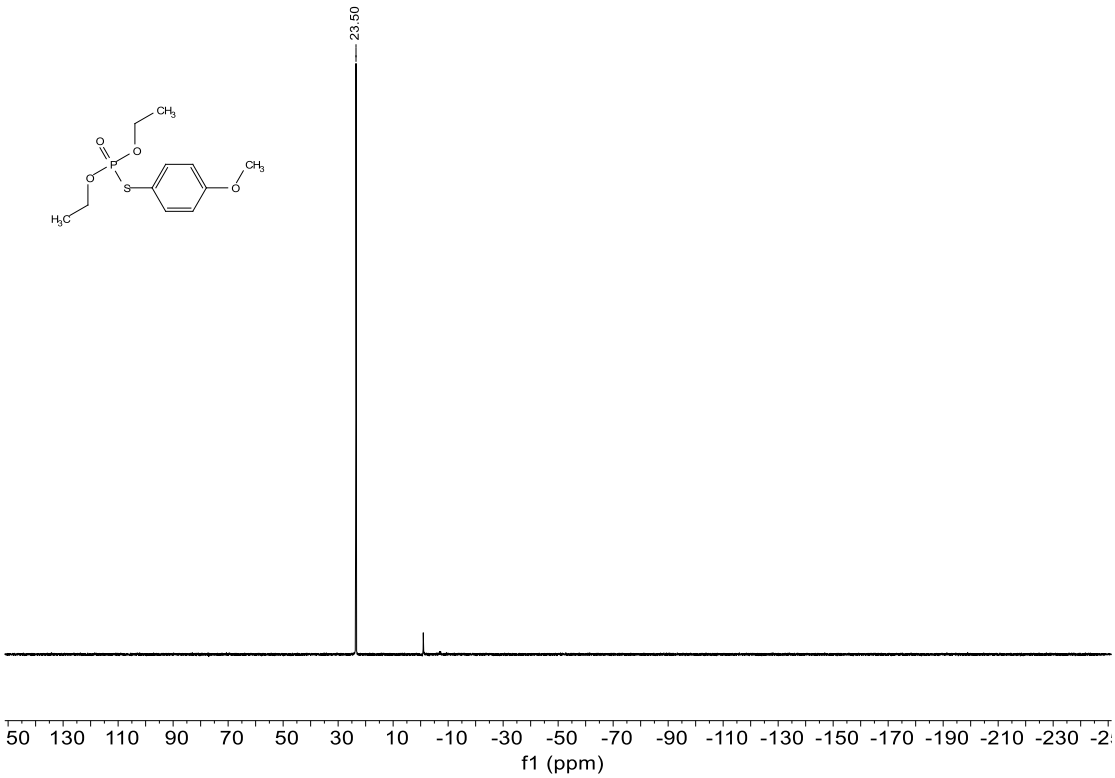
$^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of compound **4b**



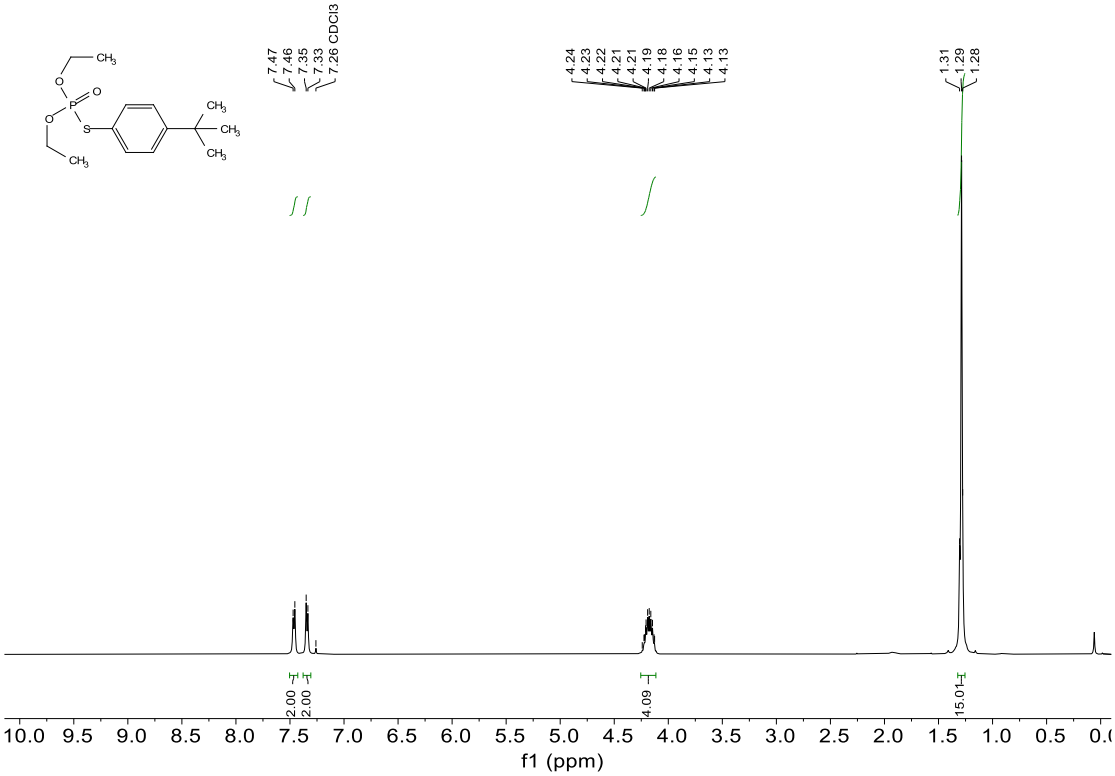
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4c**



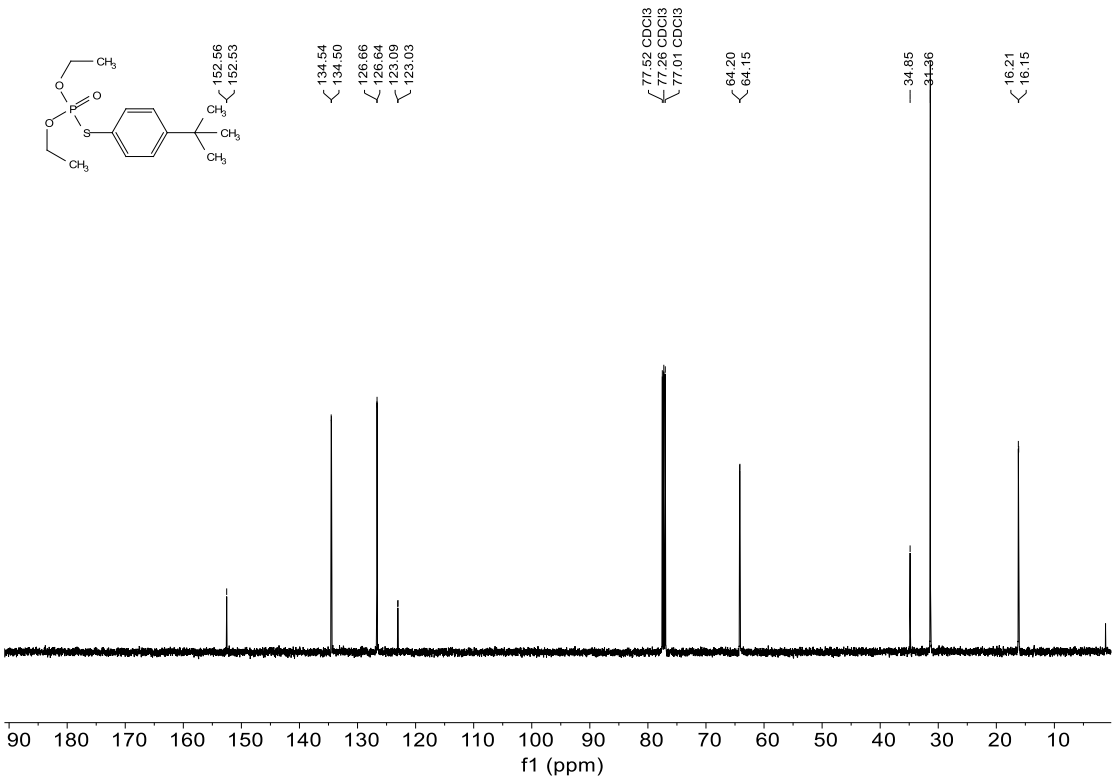
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4c**



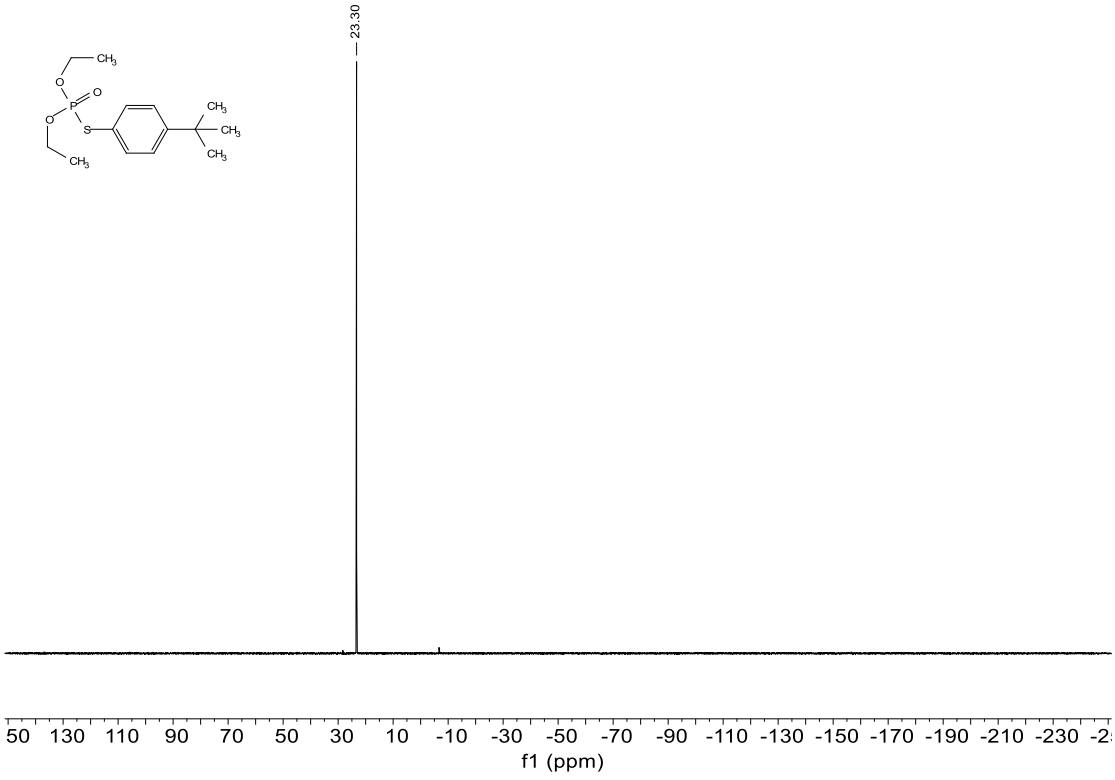
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4c**



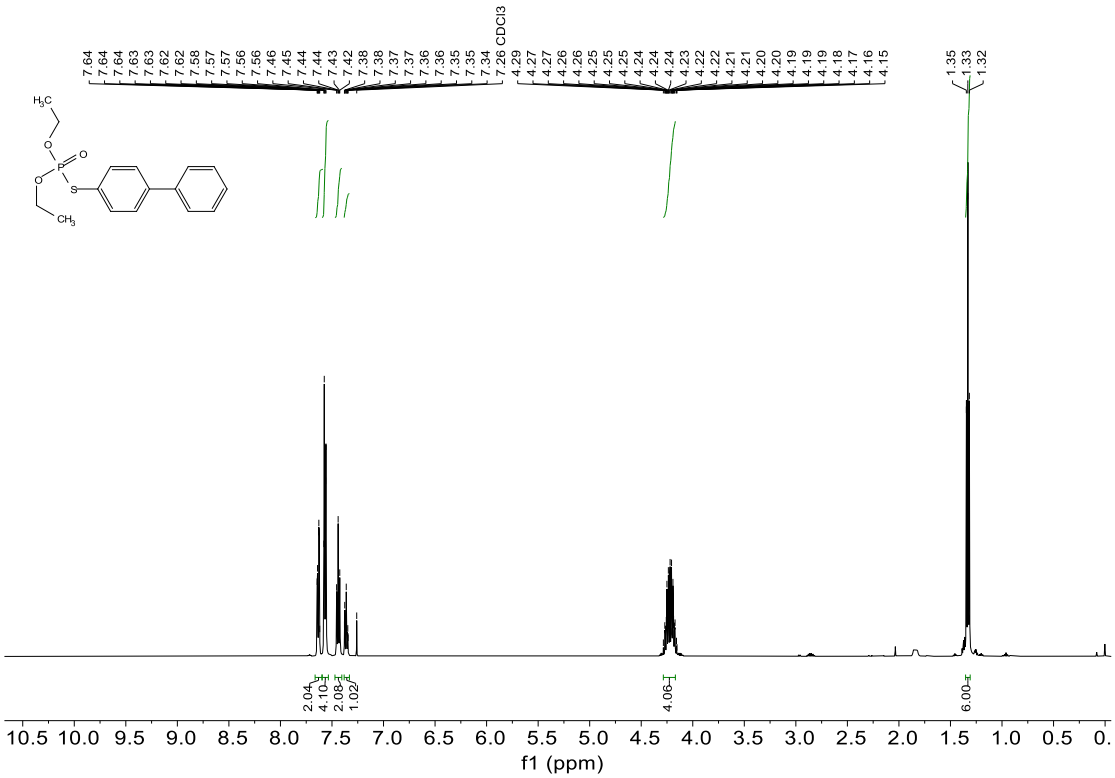
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4d**



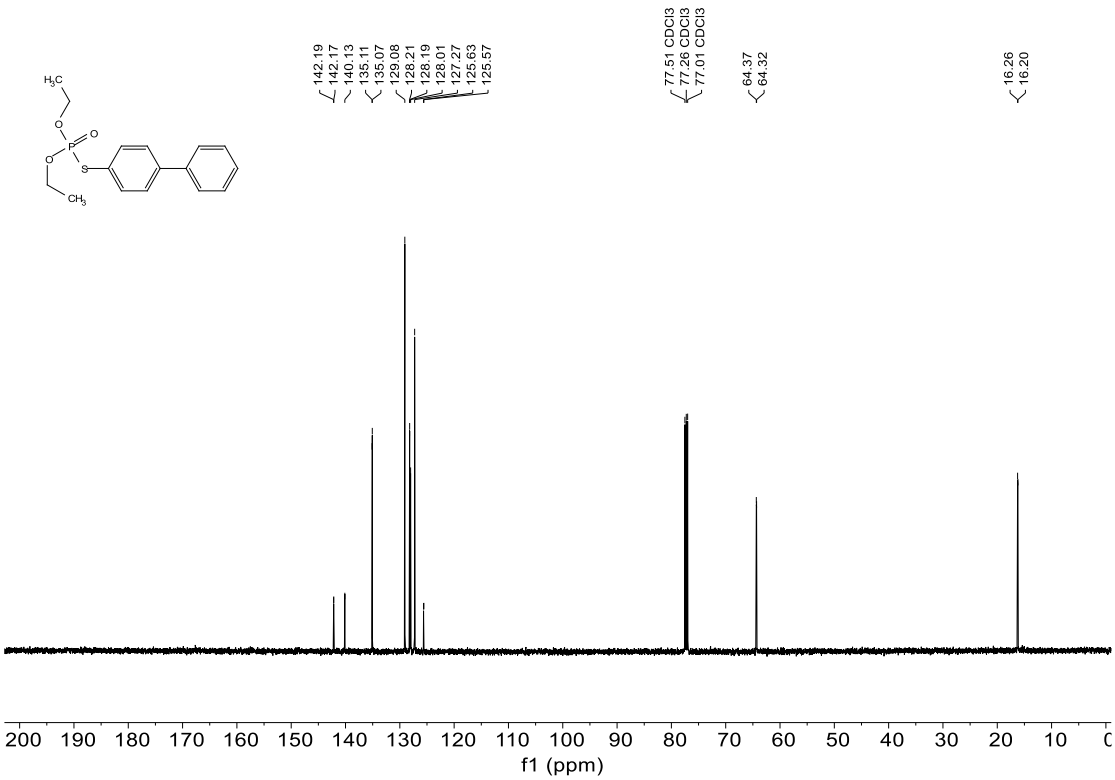
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4d**



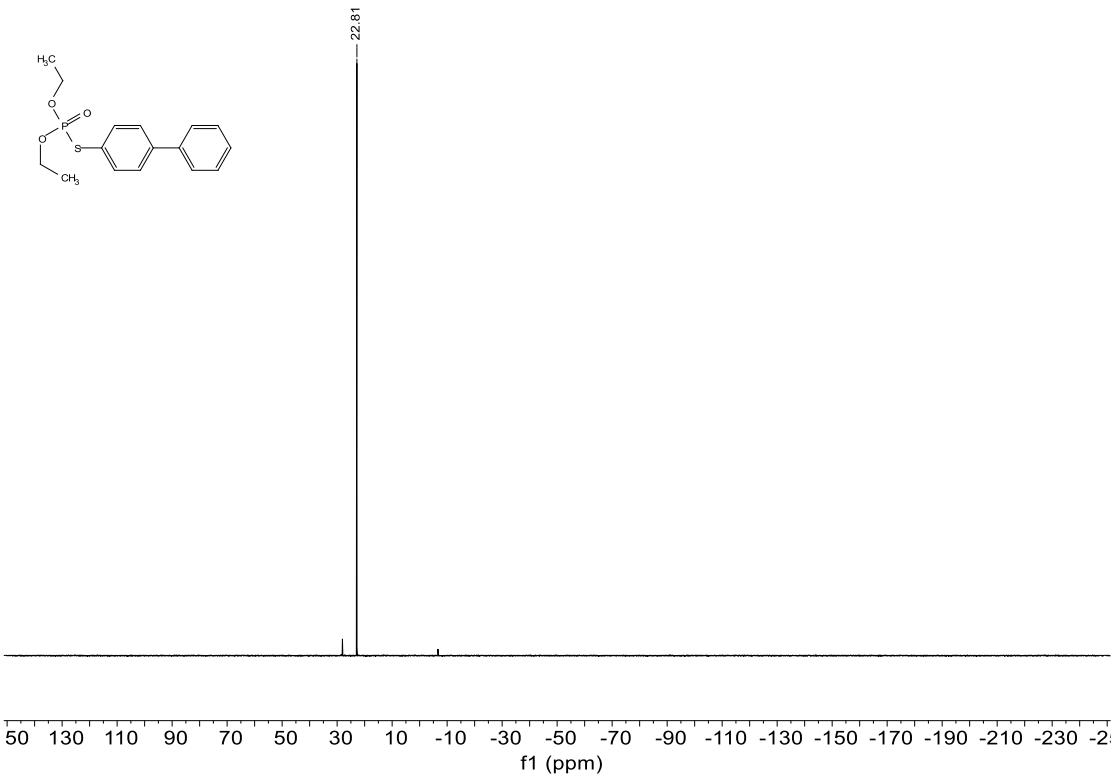
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4d**



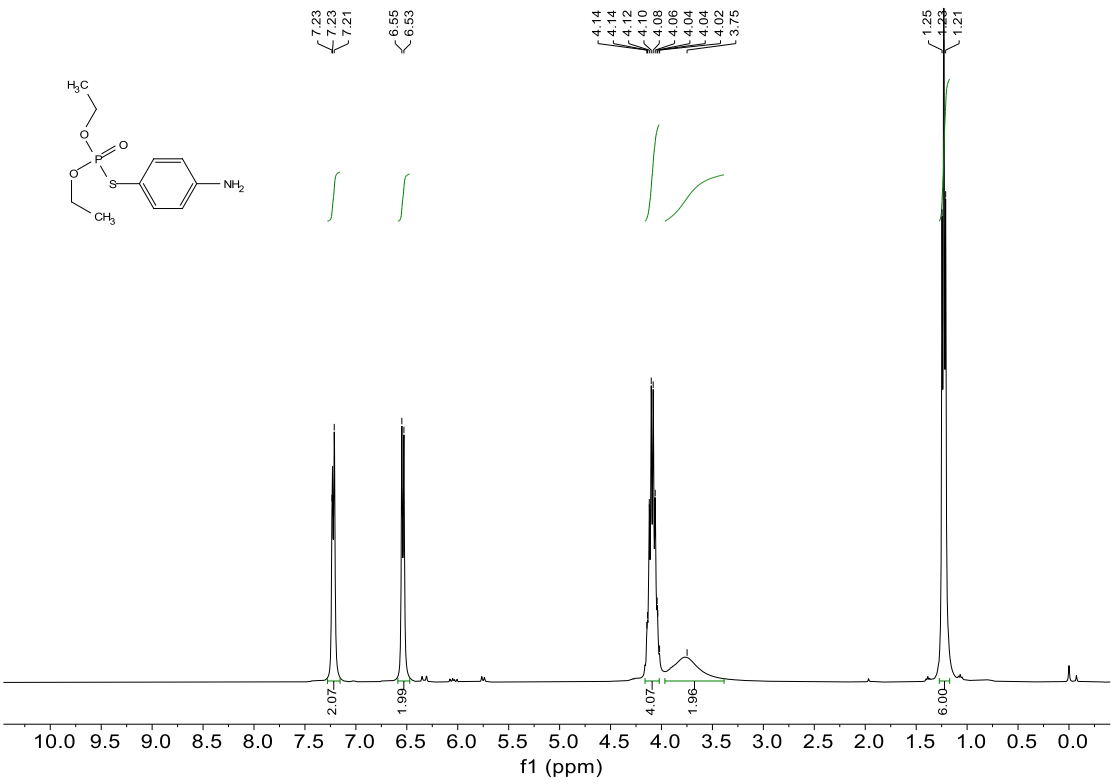
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4e**



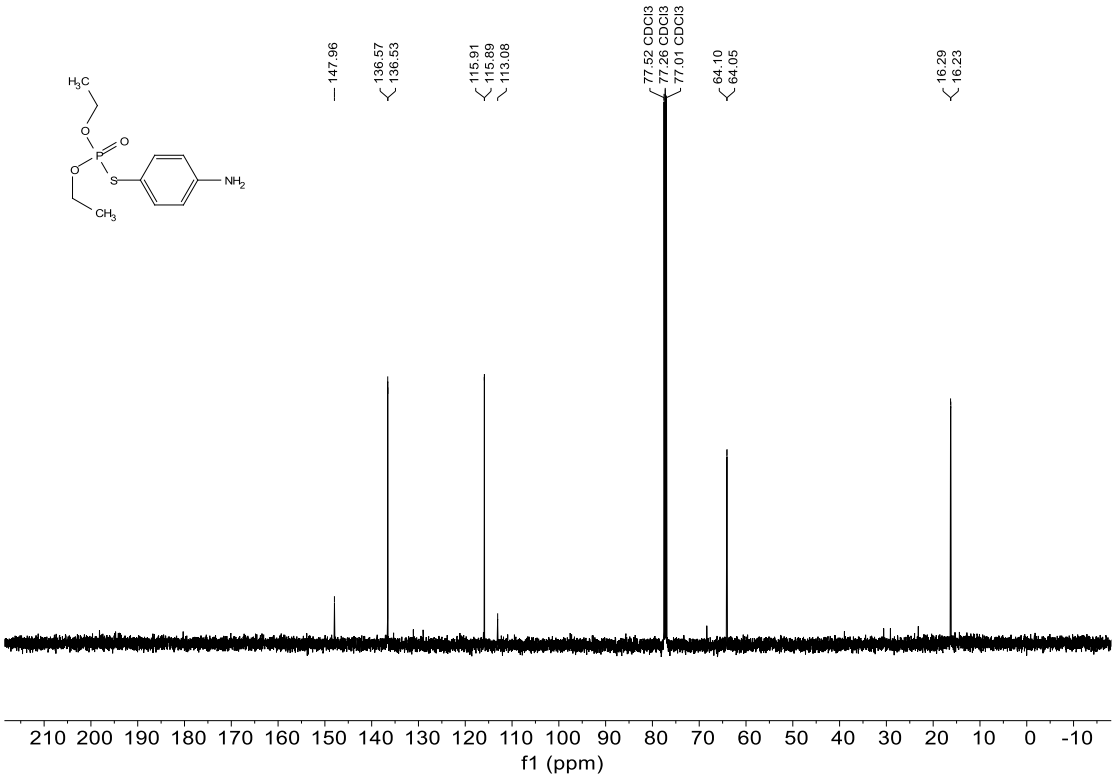
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4e**



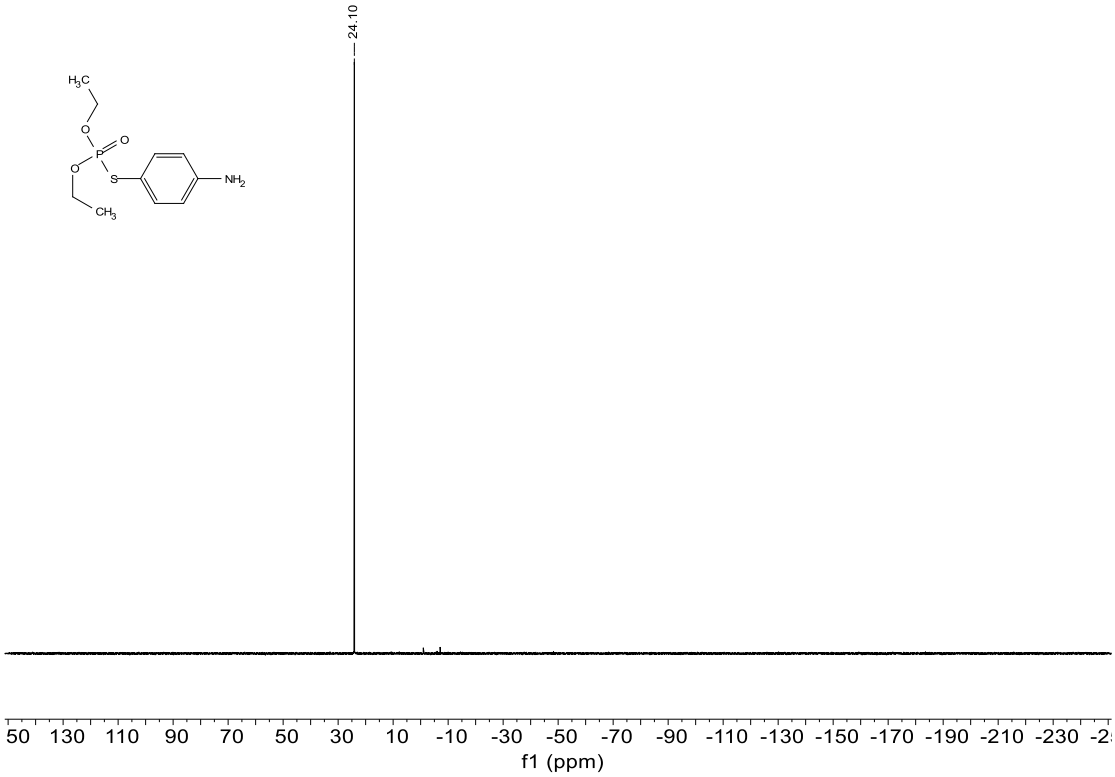
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4e**



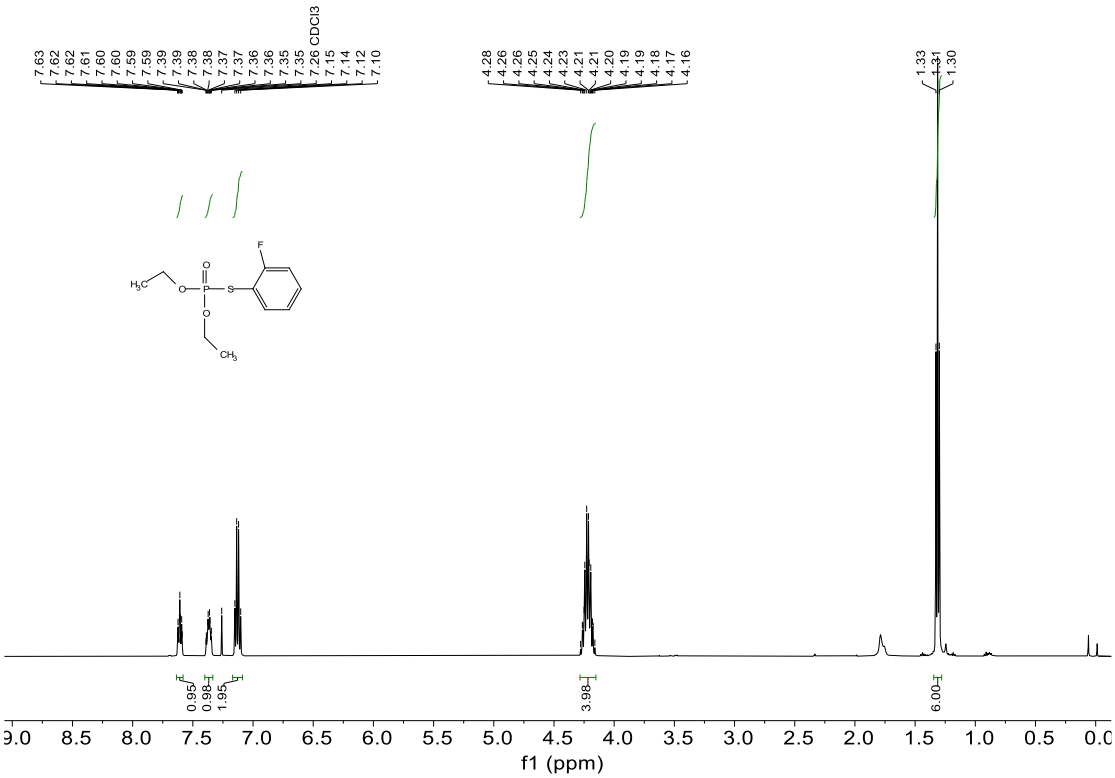
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4f**



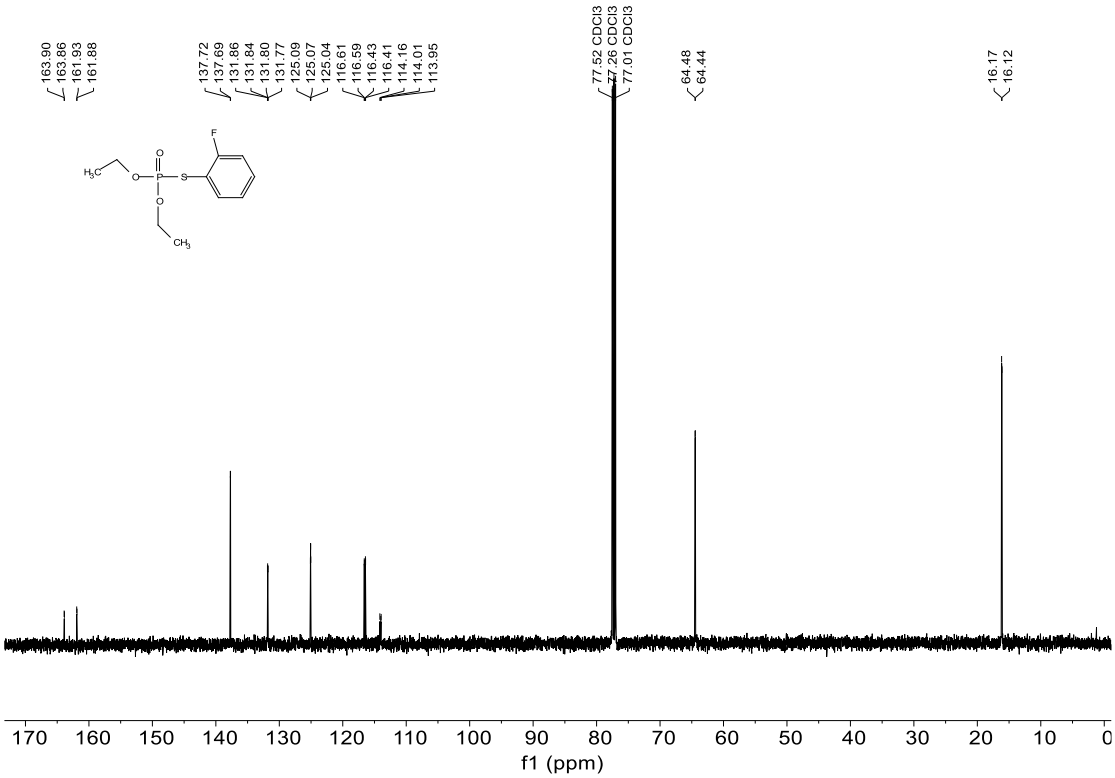
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **4f**



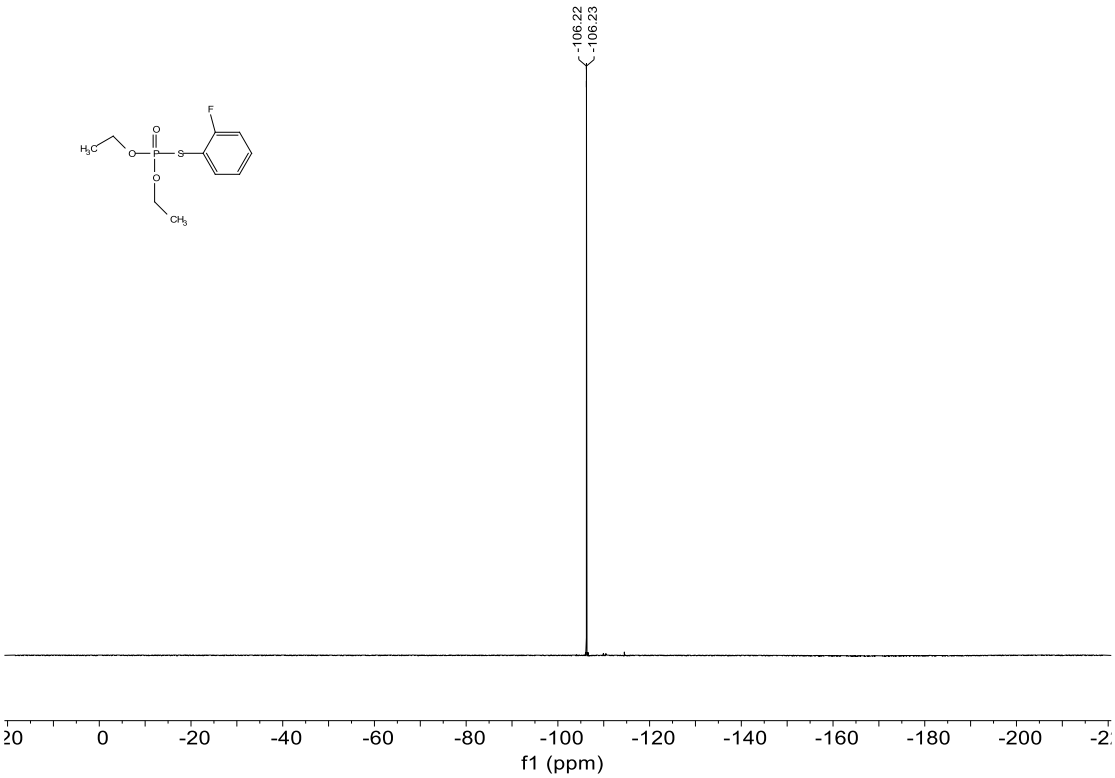
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4f**



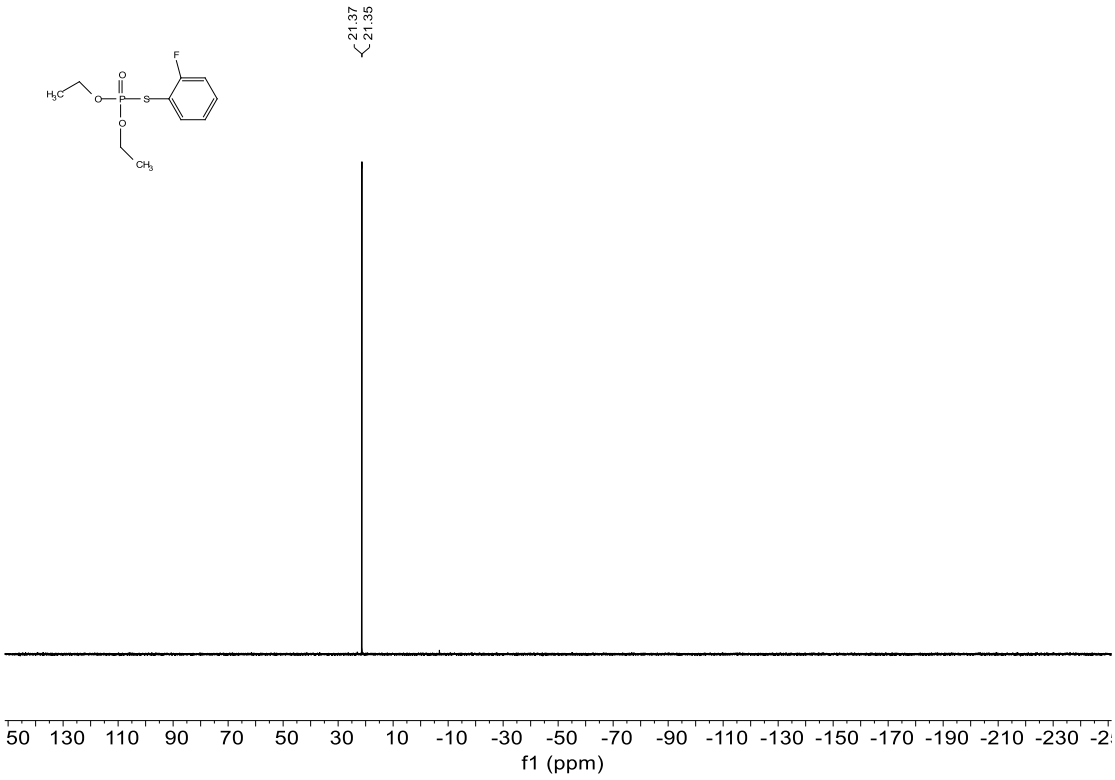
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **4g**



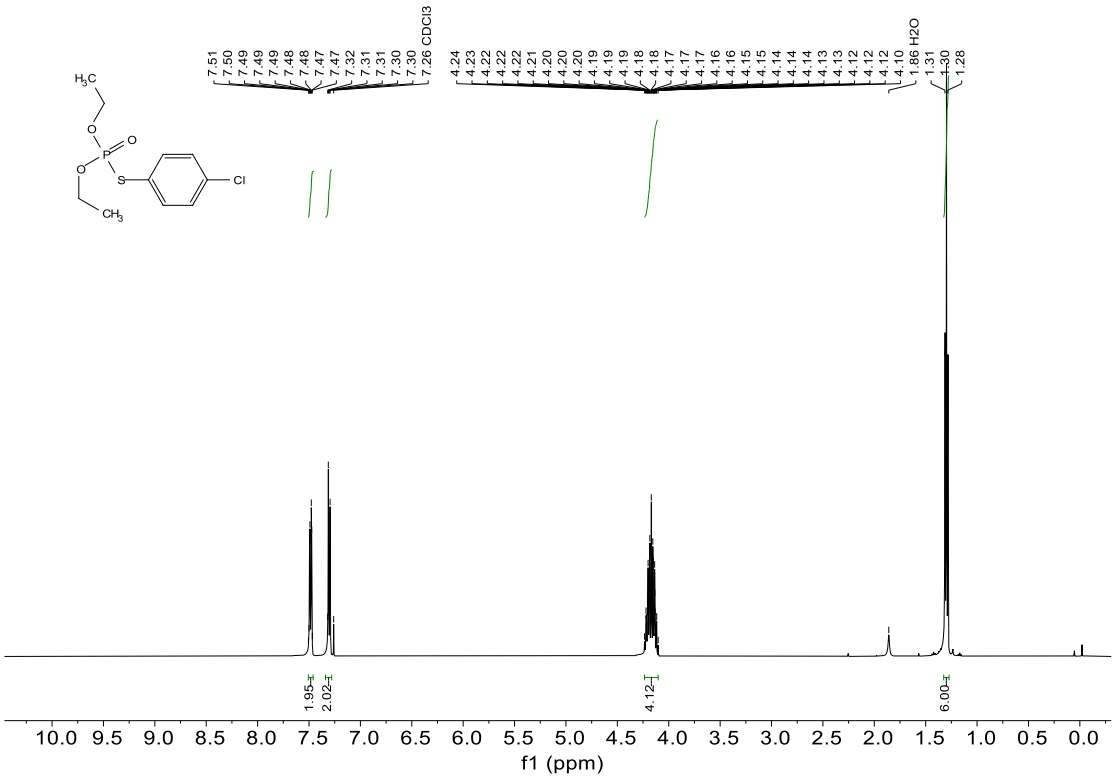
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4g**



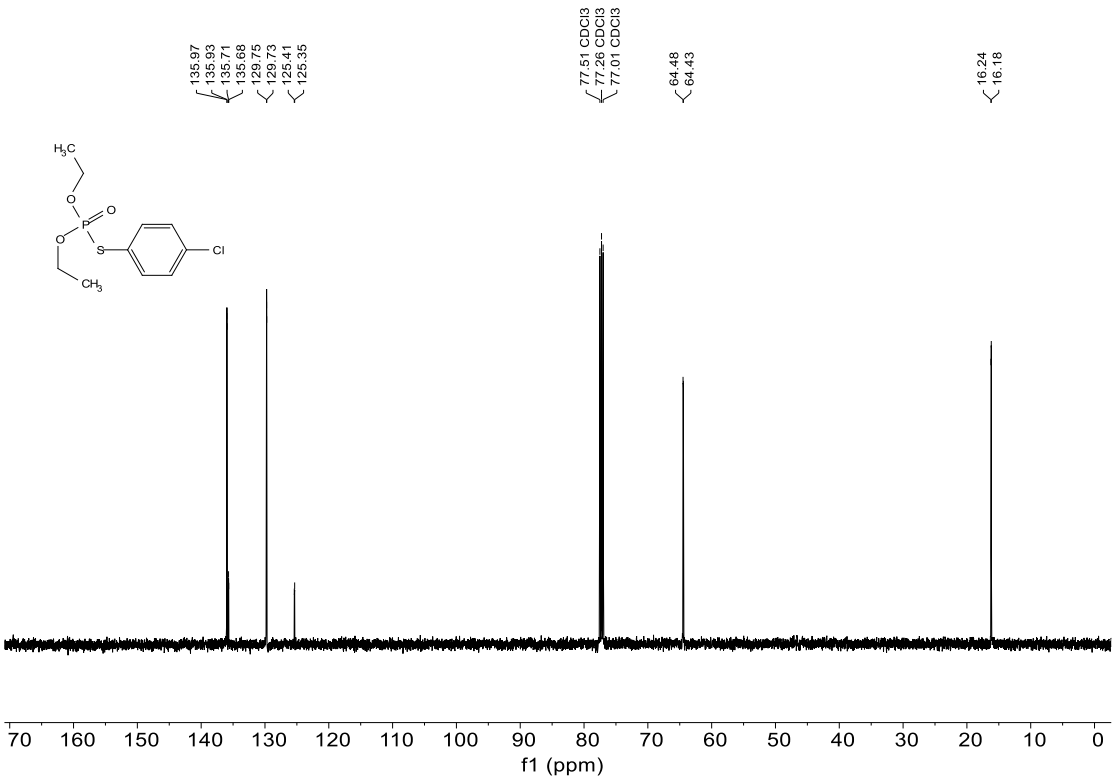
$^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) spectrum of compound **4g**



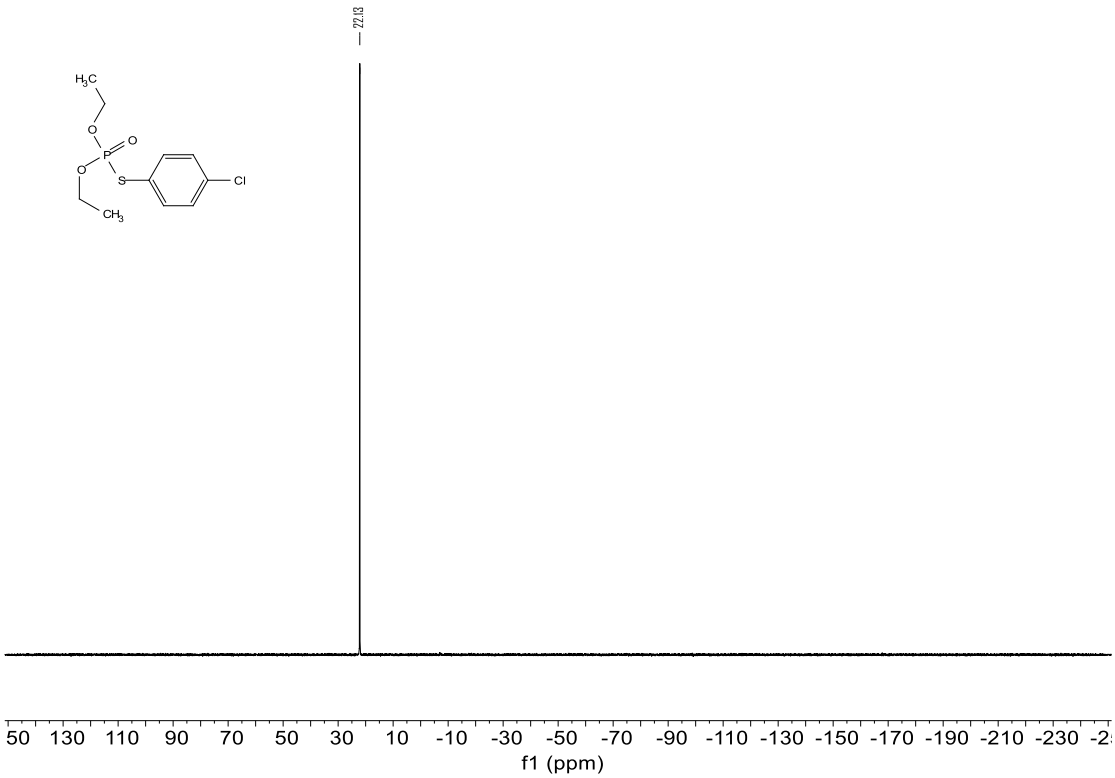
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4g**



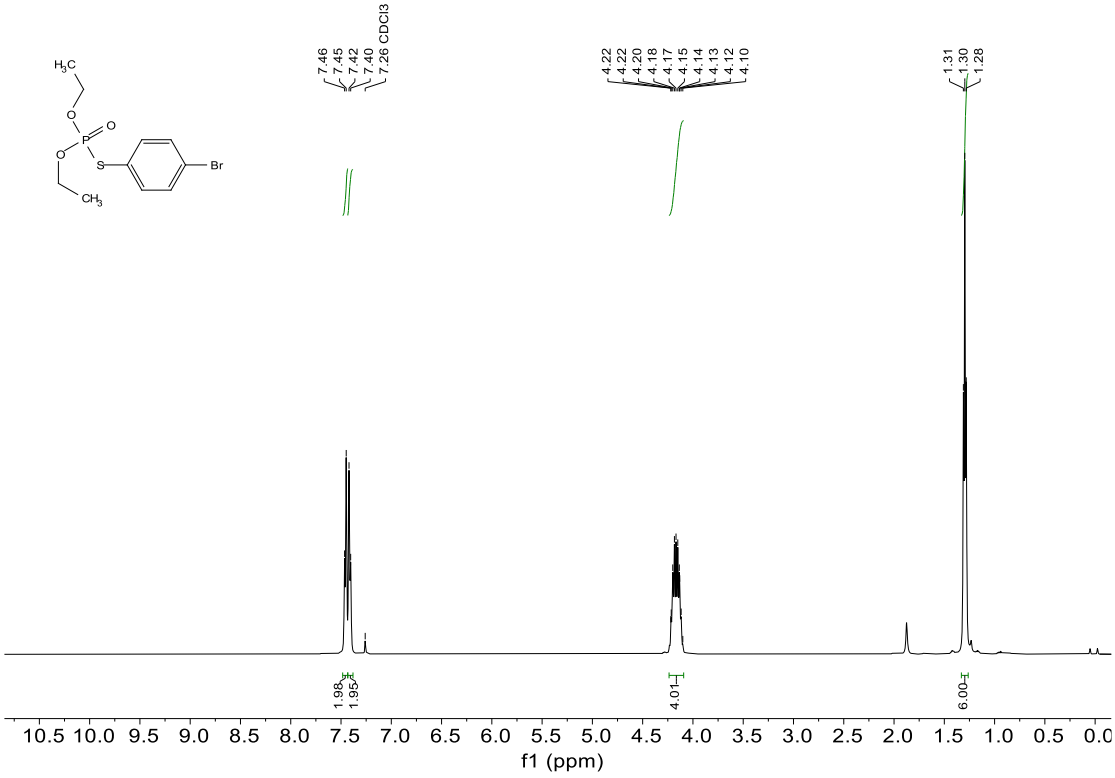
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4h**



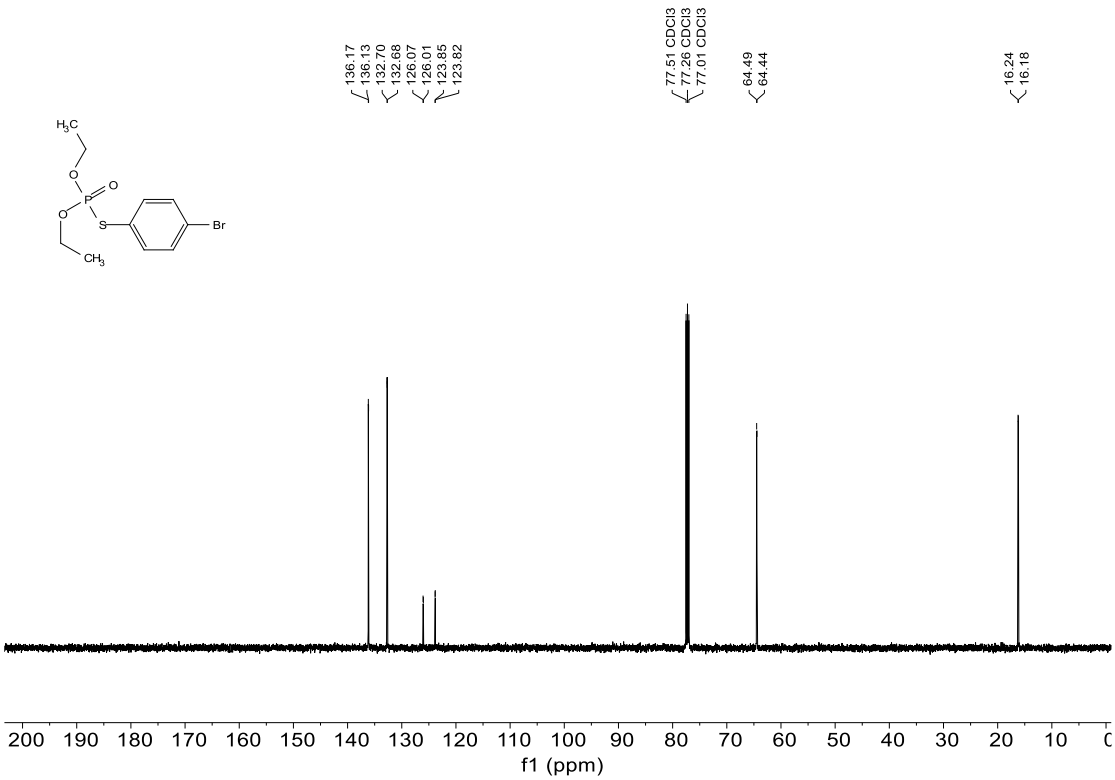
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4h**



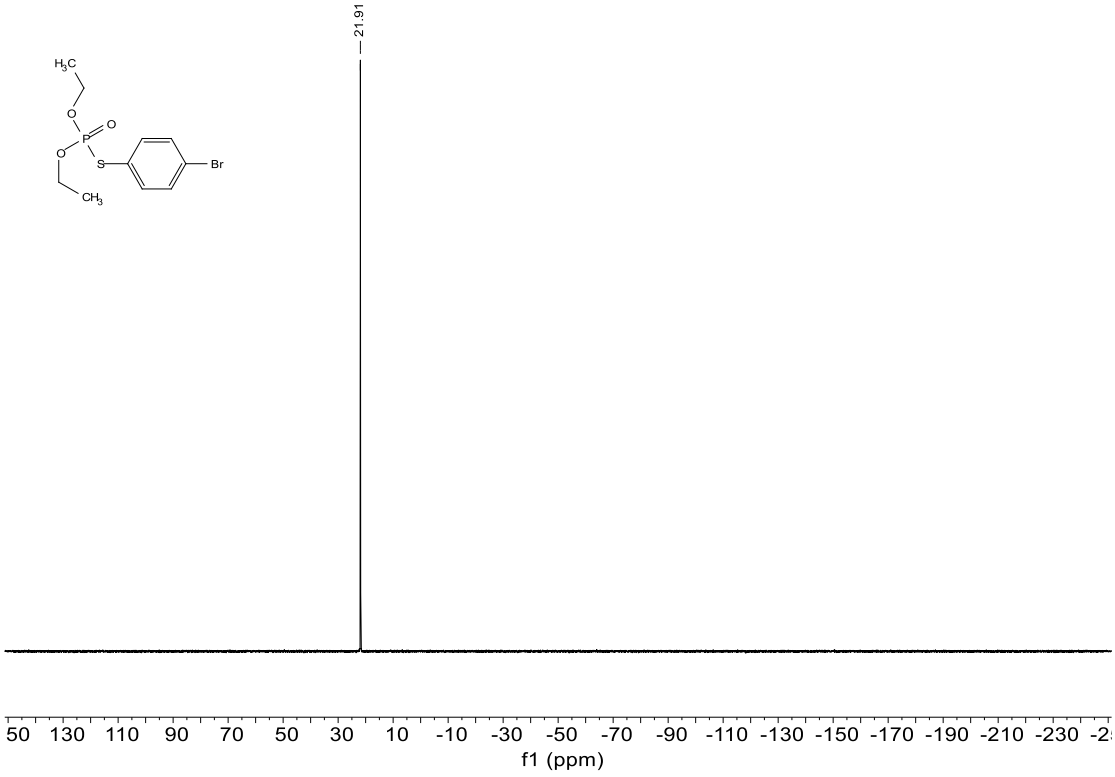
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4h**



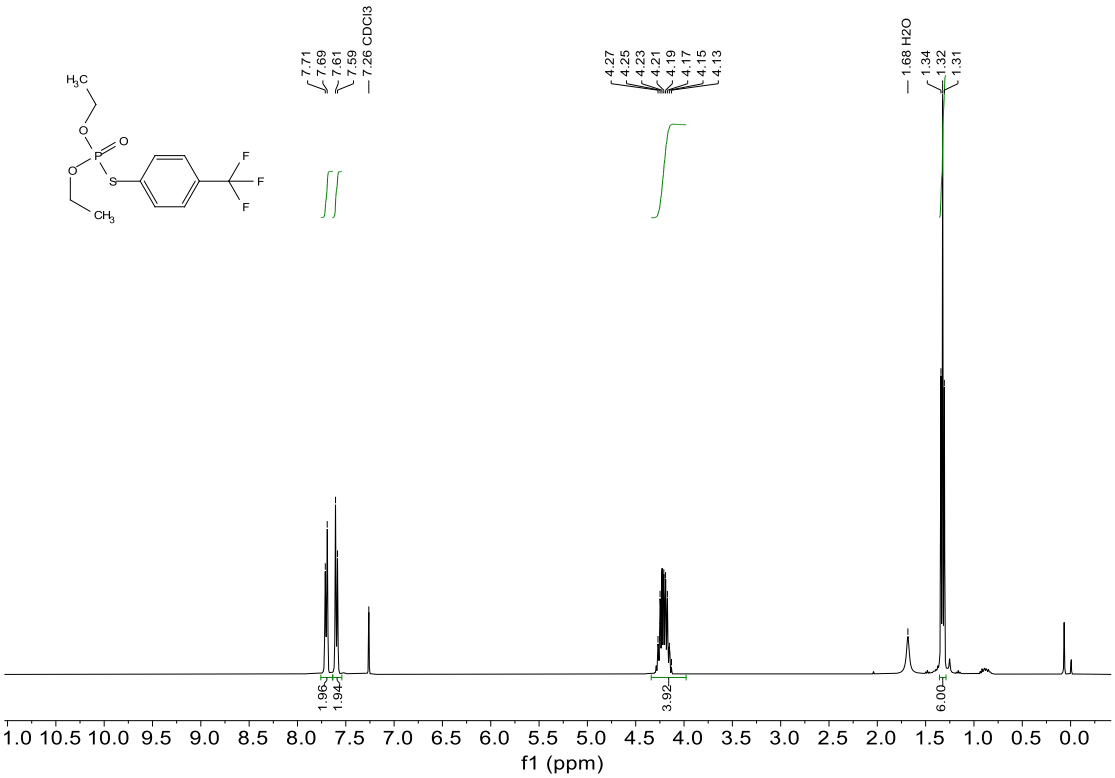
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4i**



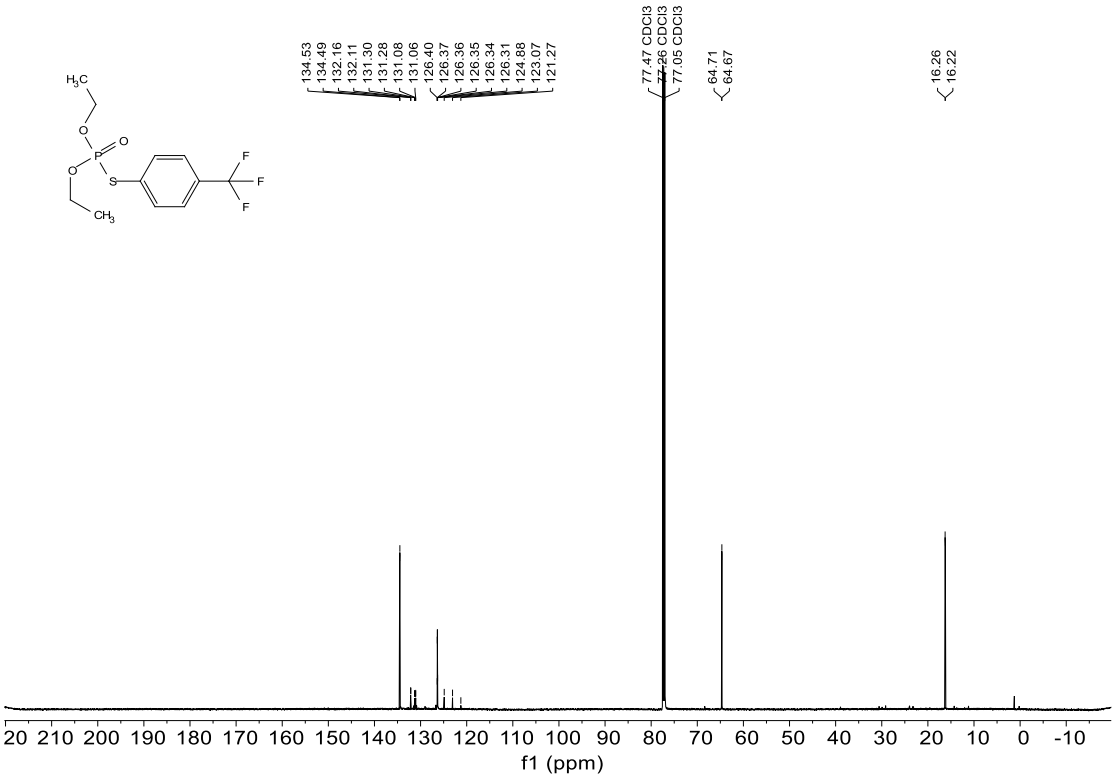
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4i**



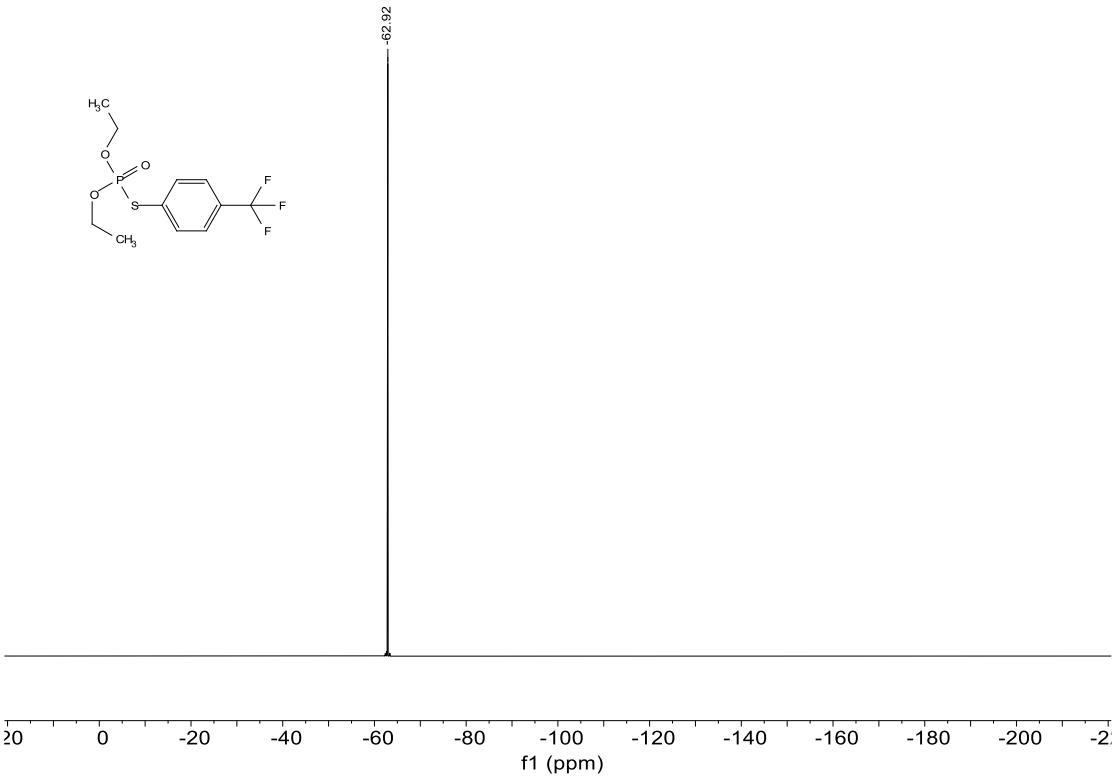
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4i**



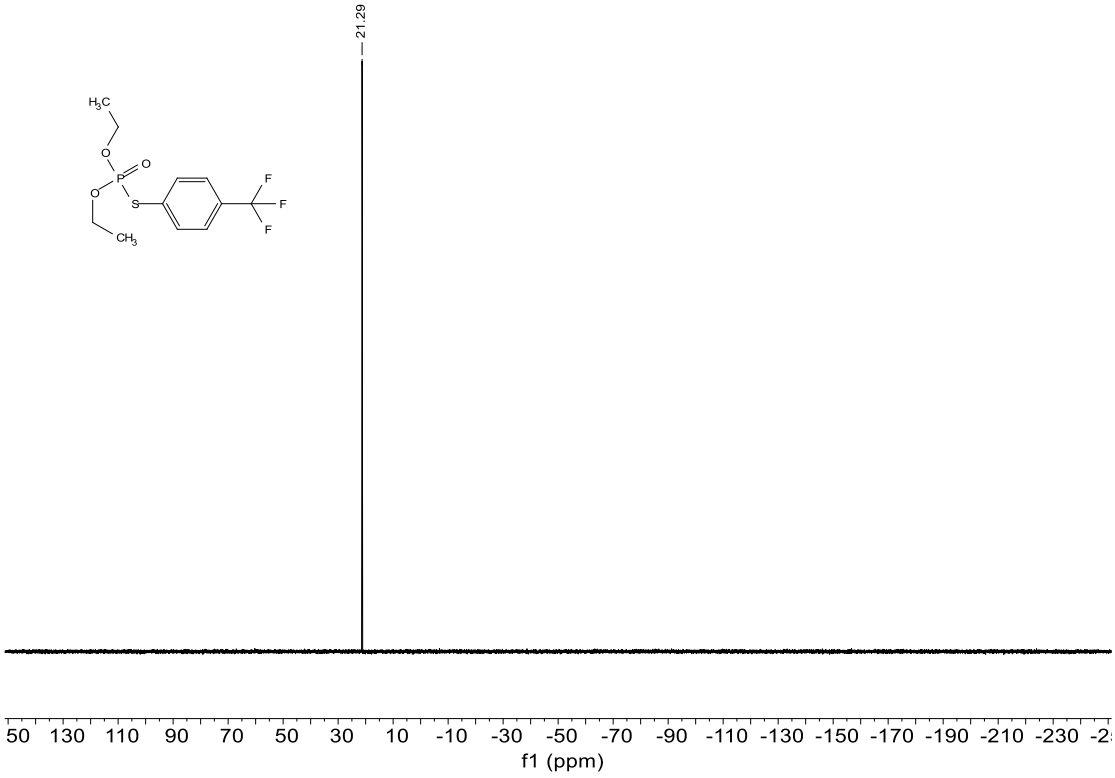
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4j**



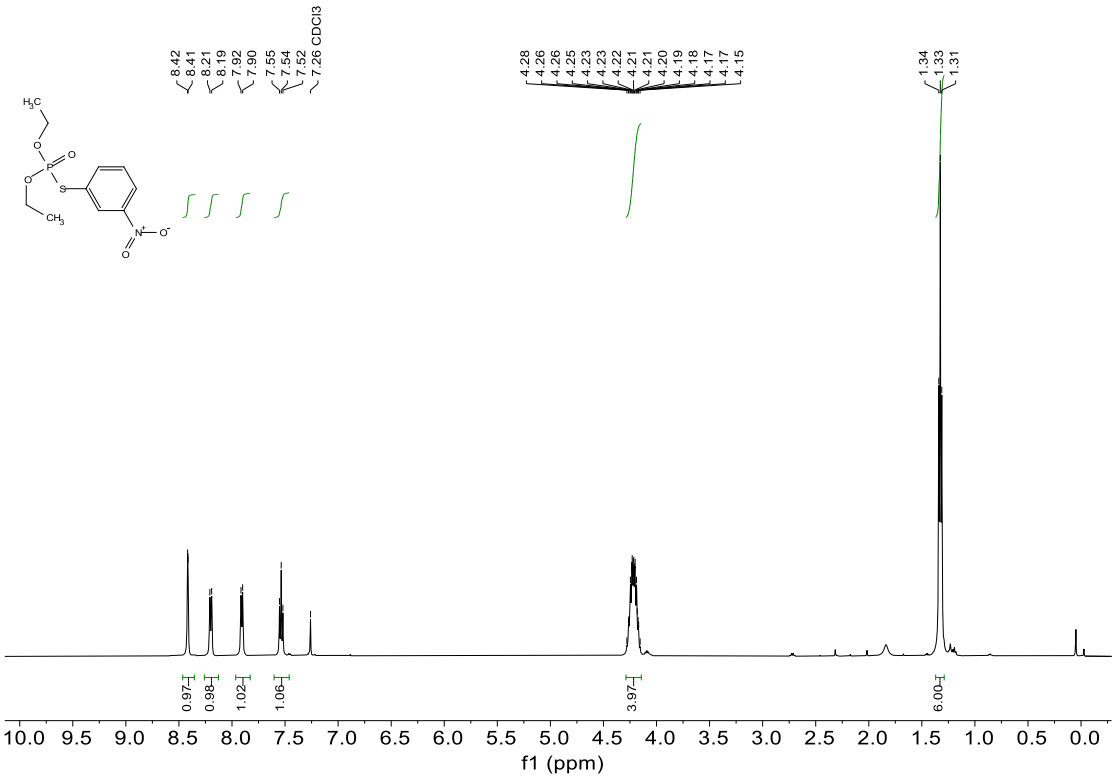
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) spectrum of compound **4j**



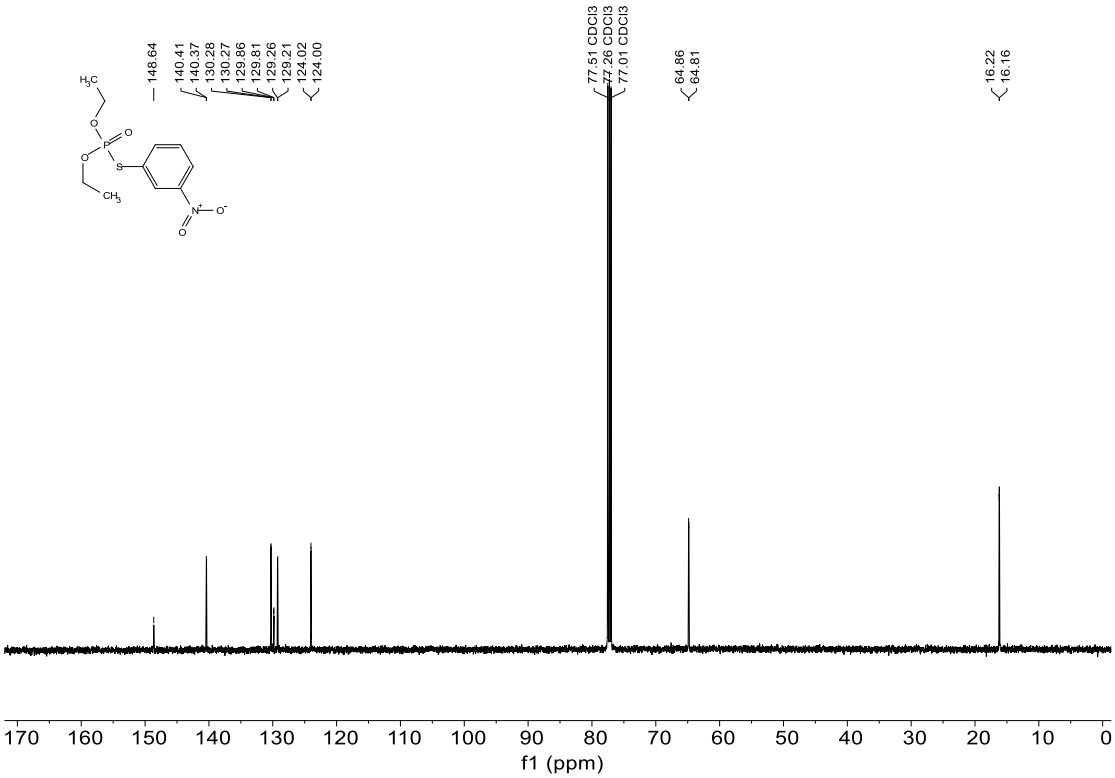
^{19}F NMR (471 MHz, $CDCl_3$) spectrum of compound **4j**



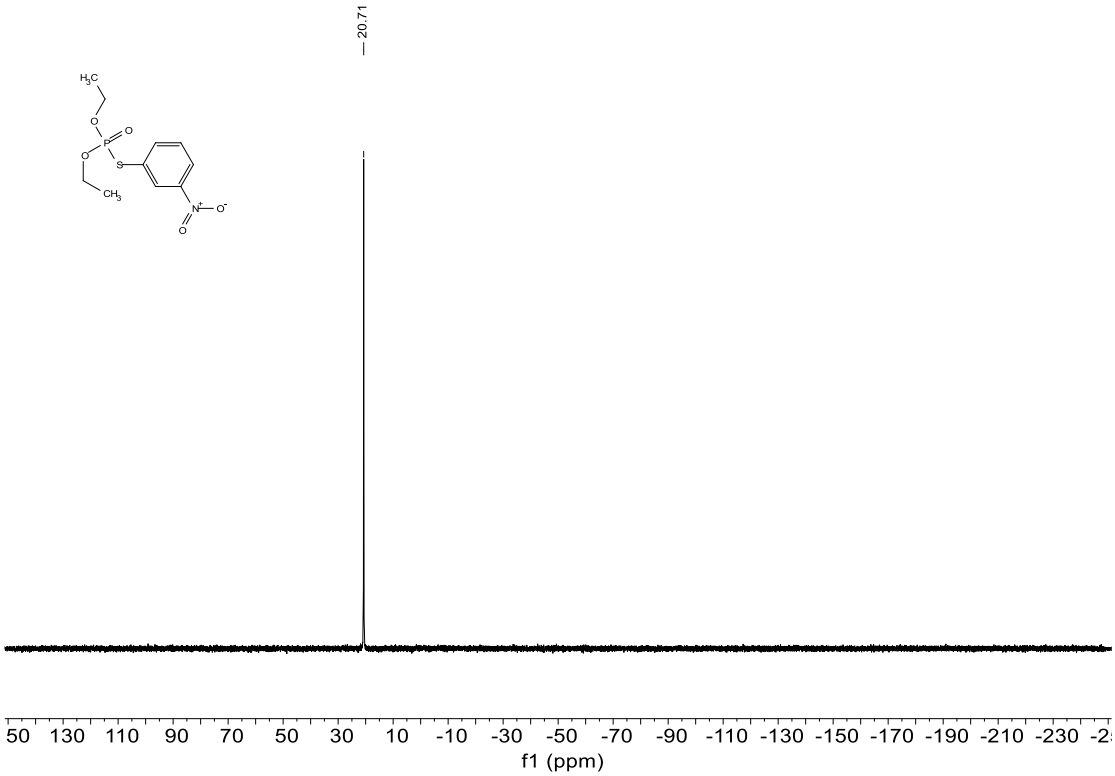
$^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) spectrum of compound **4j**



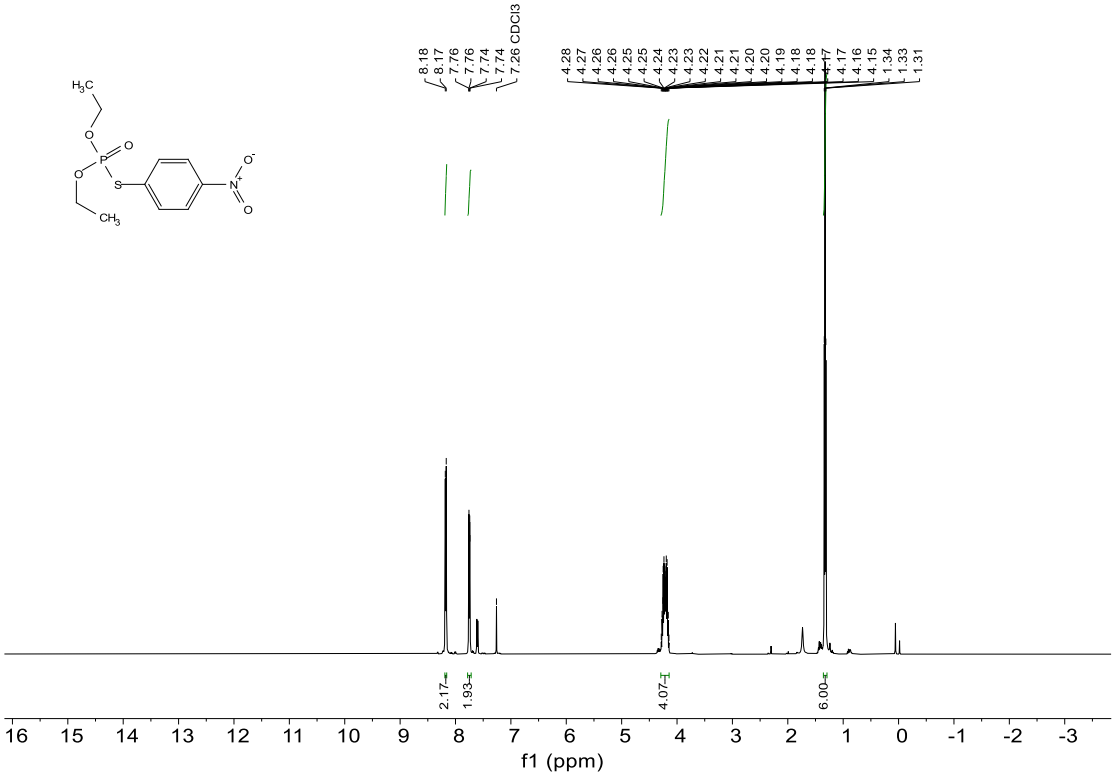
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4k**



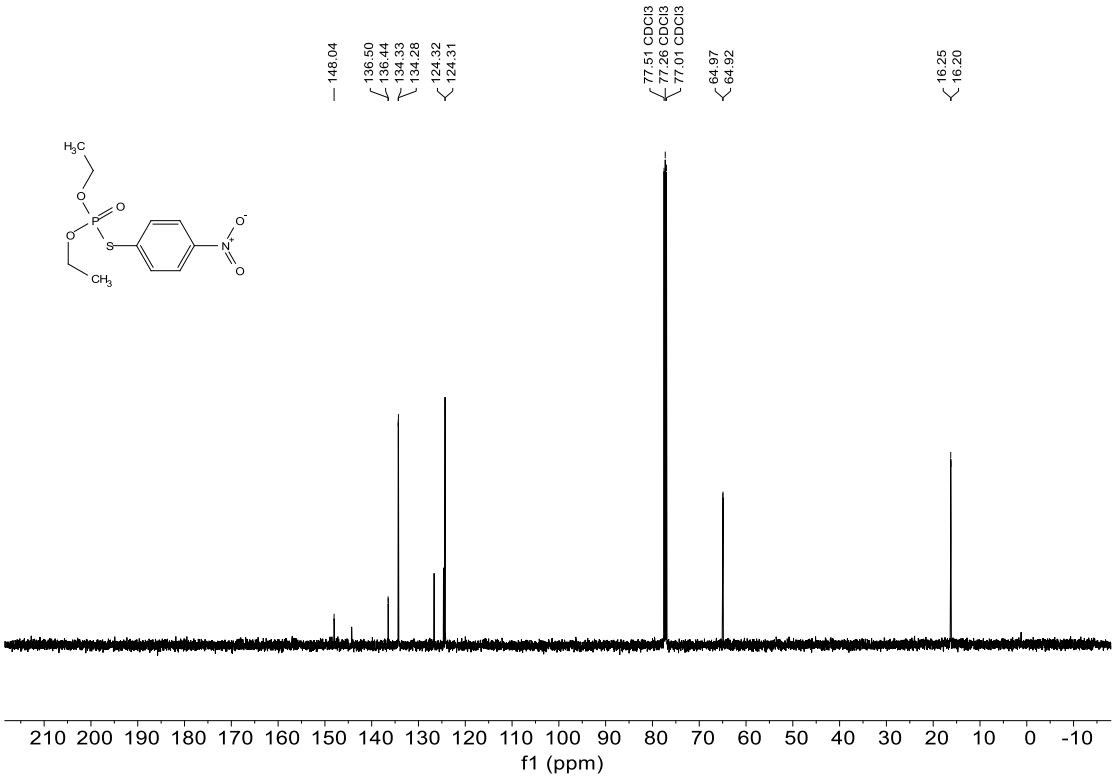
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4k**



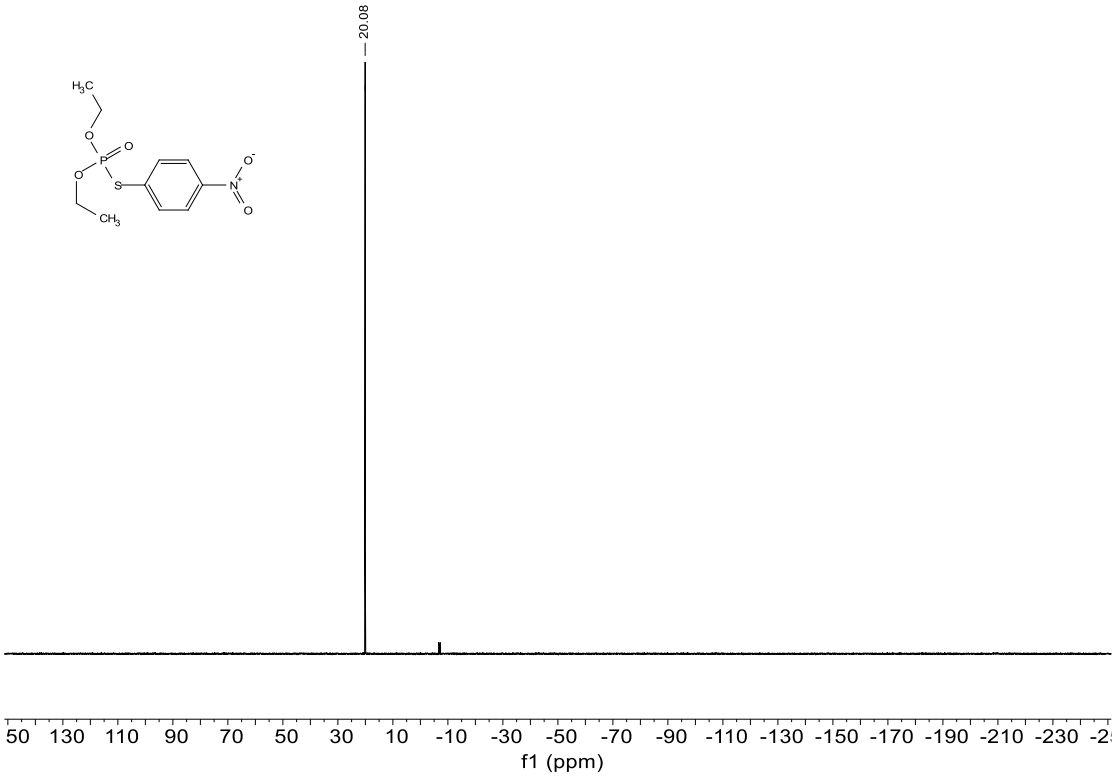
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4k**



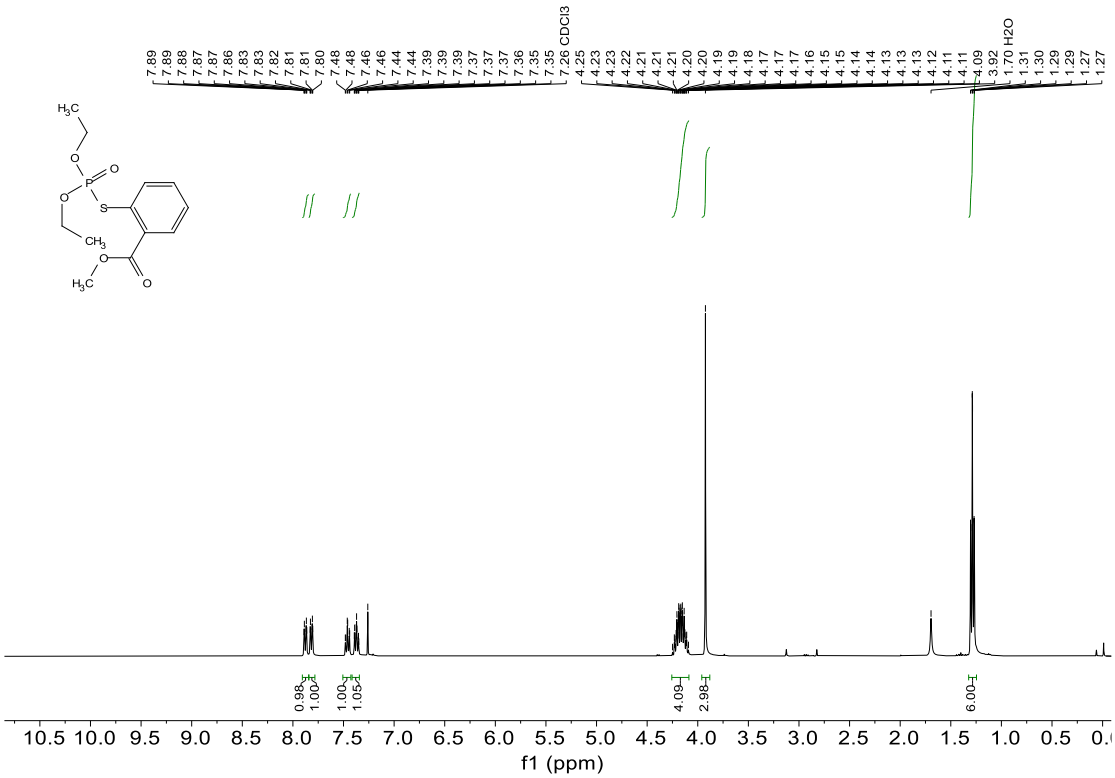
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4l**



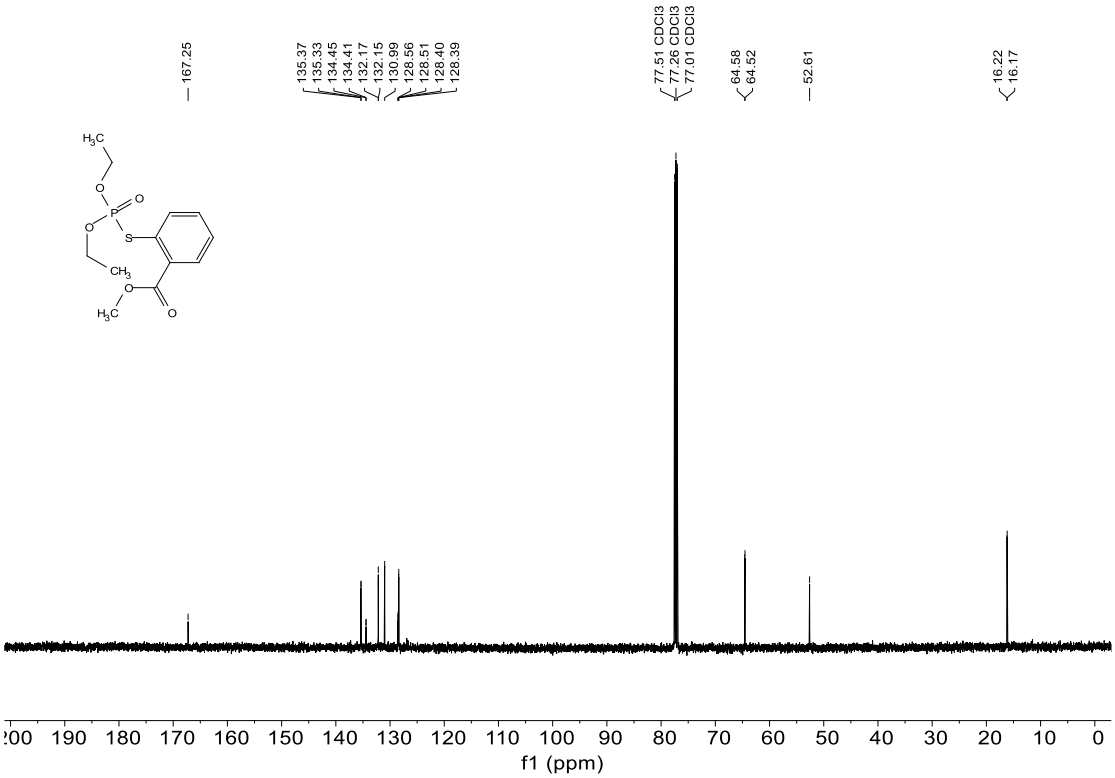
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4l**



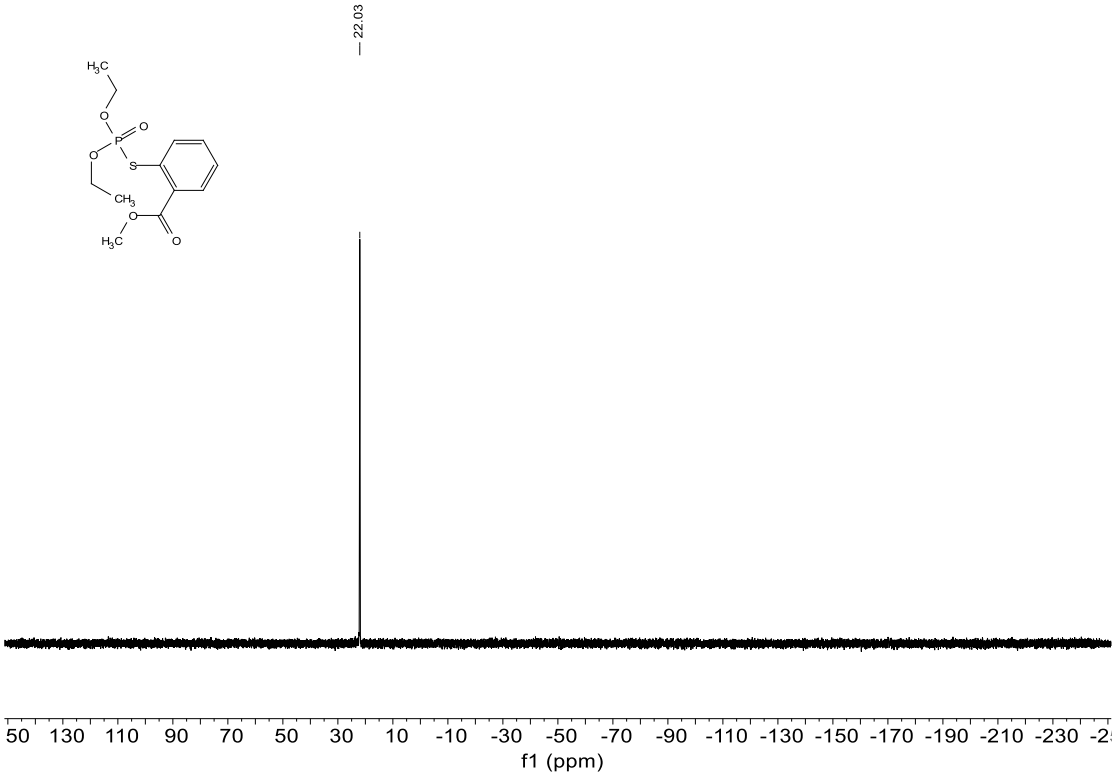
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4l**



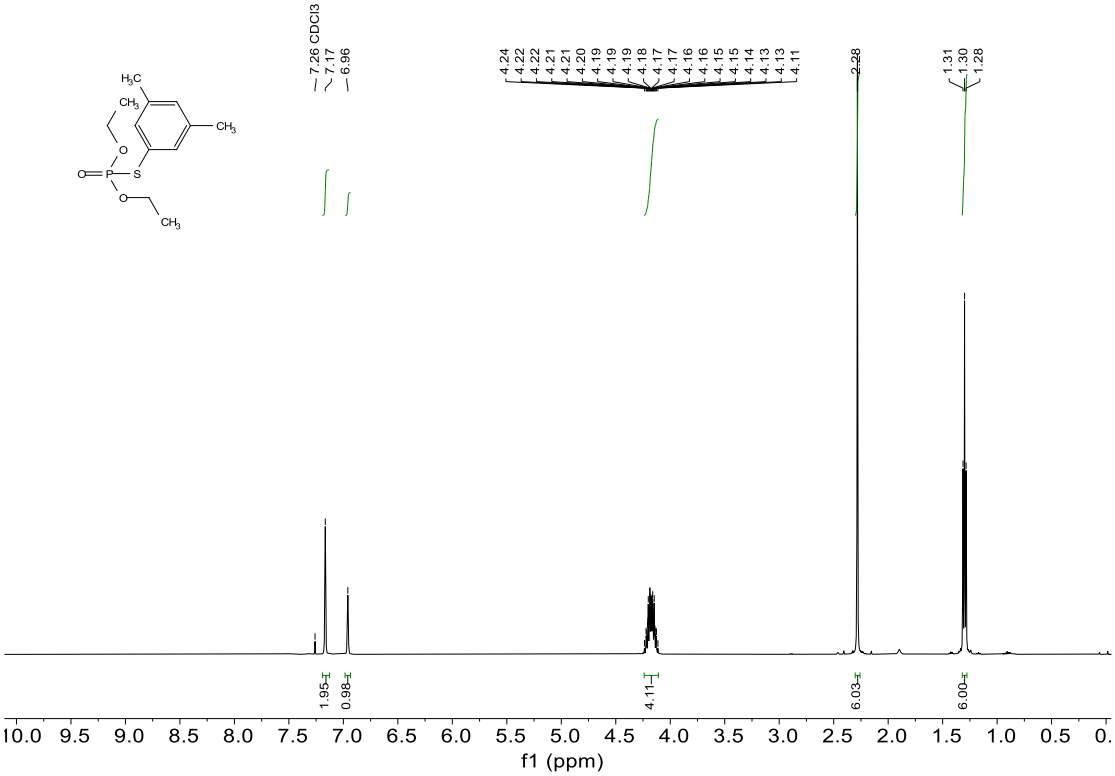
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4m**



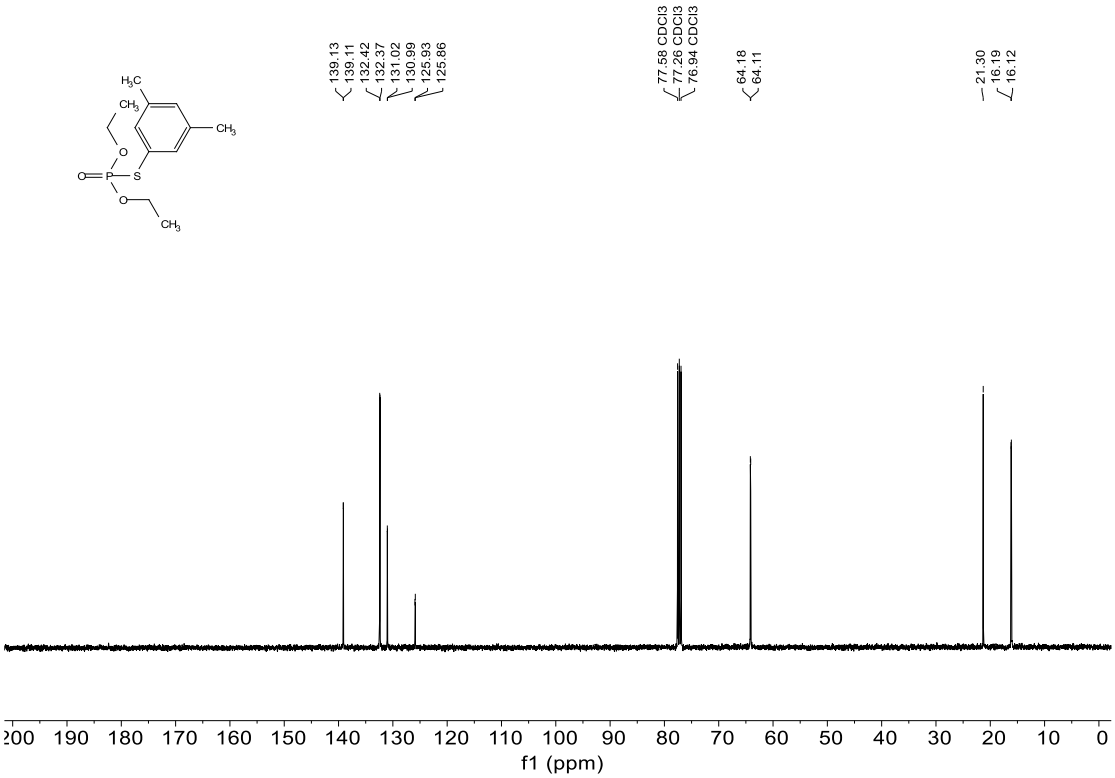
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4m**



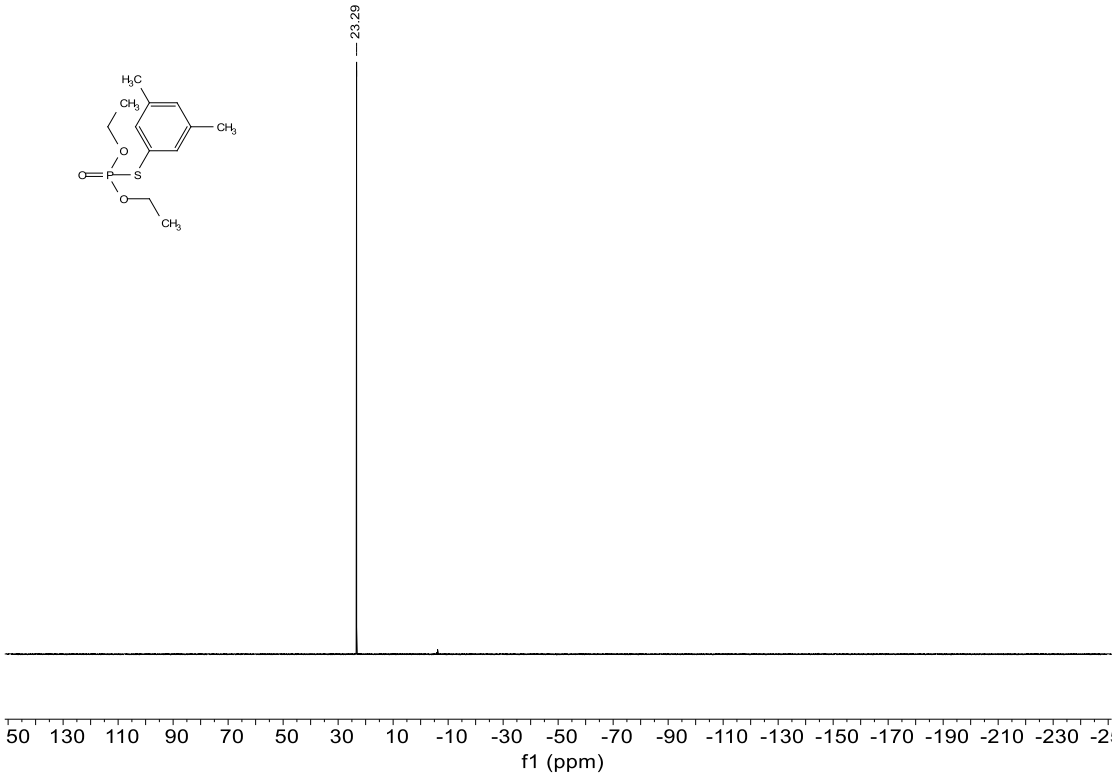
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4m**



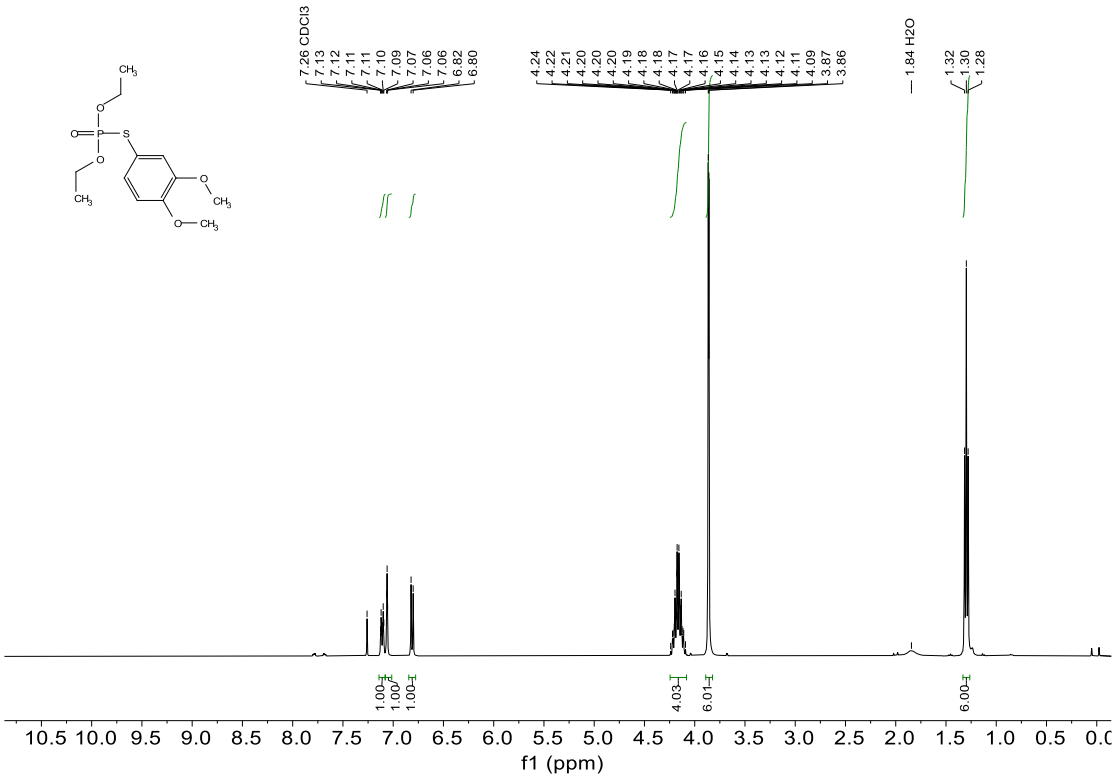
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4n**



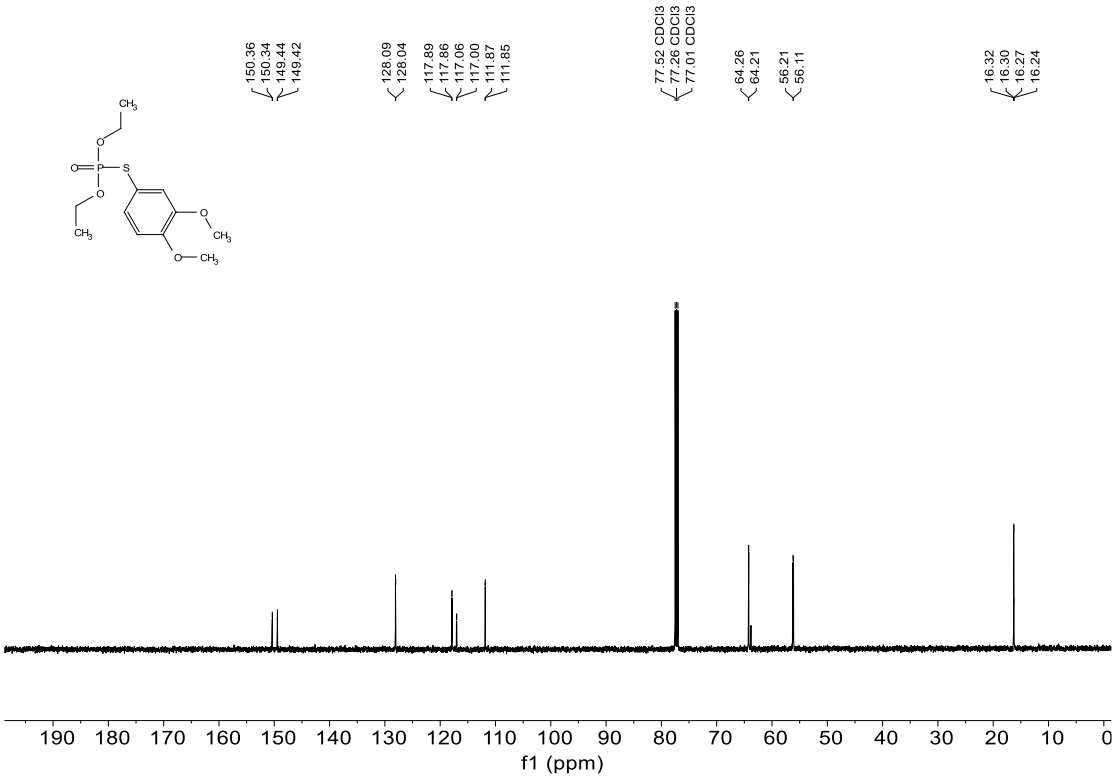
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4n**



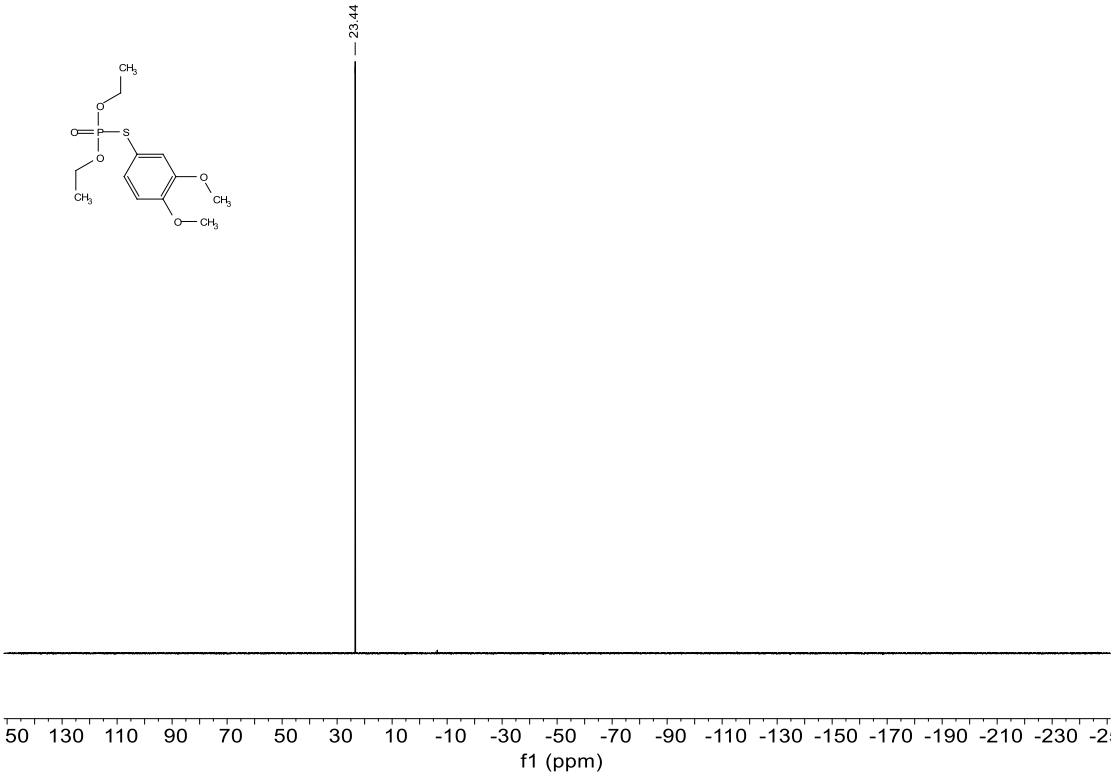
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4n**



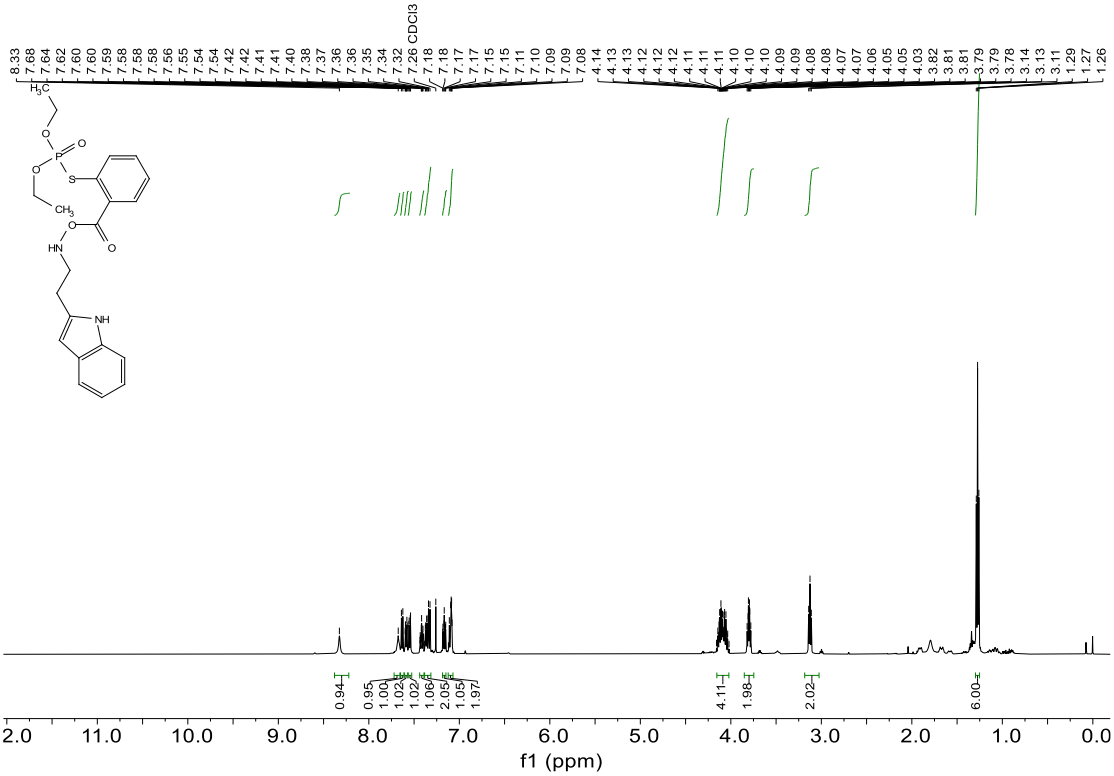
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4o**



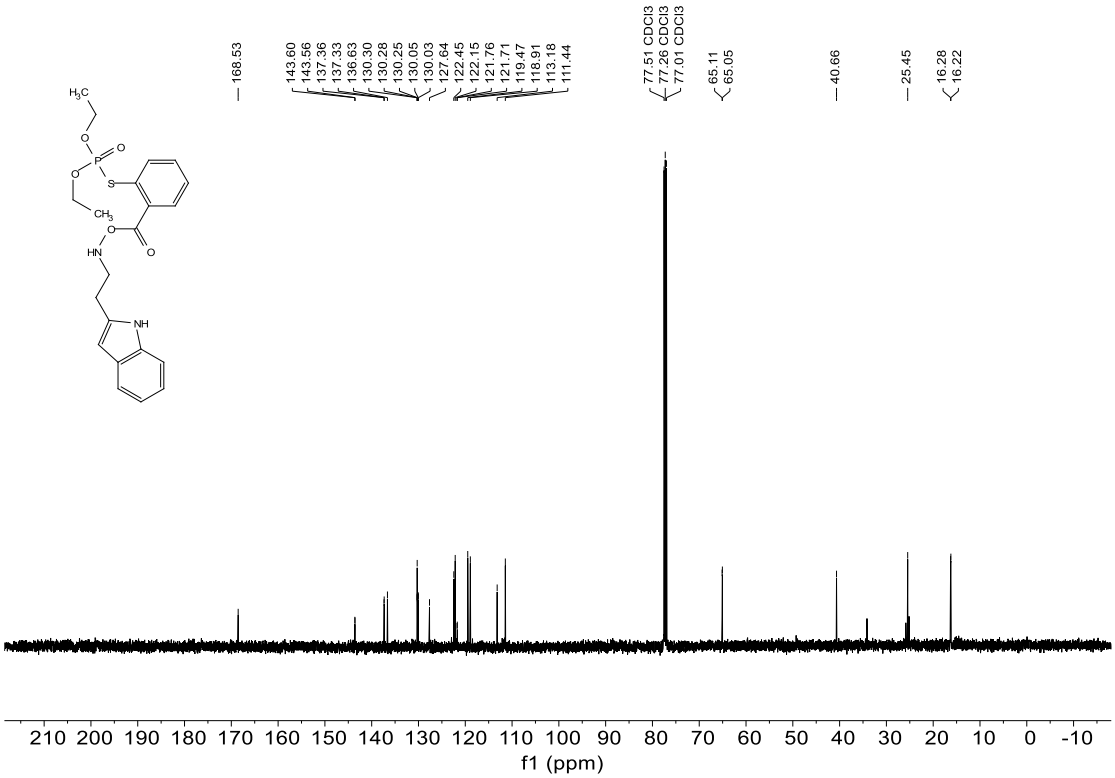
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4o**



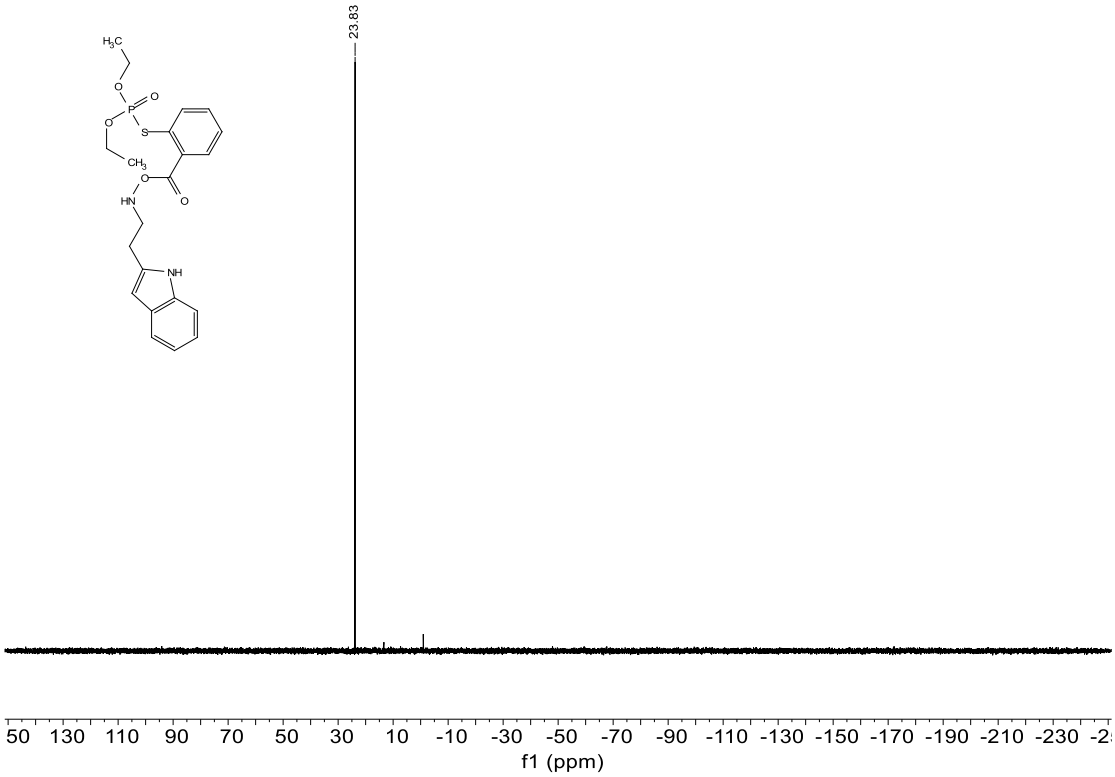
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4o**



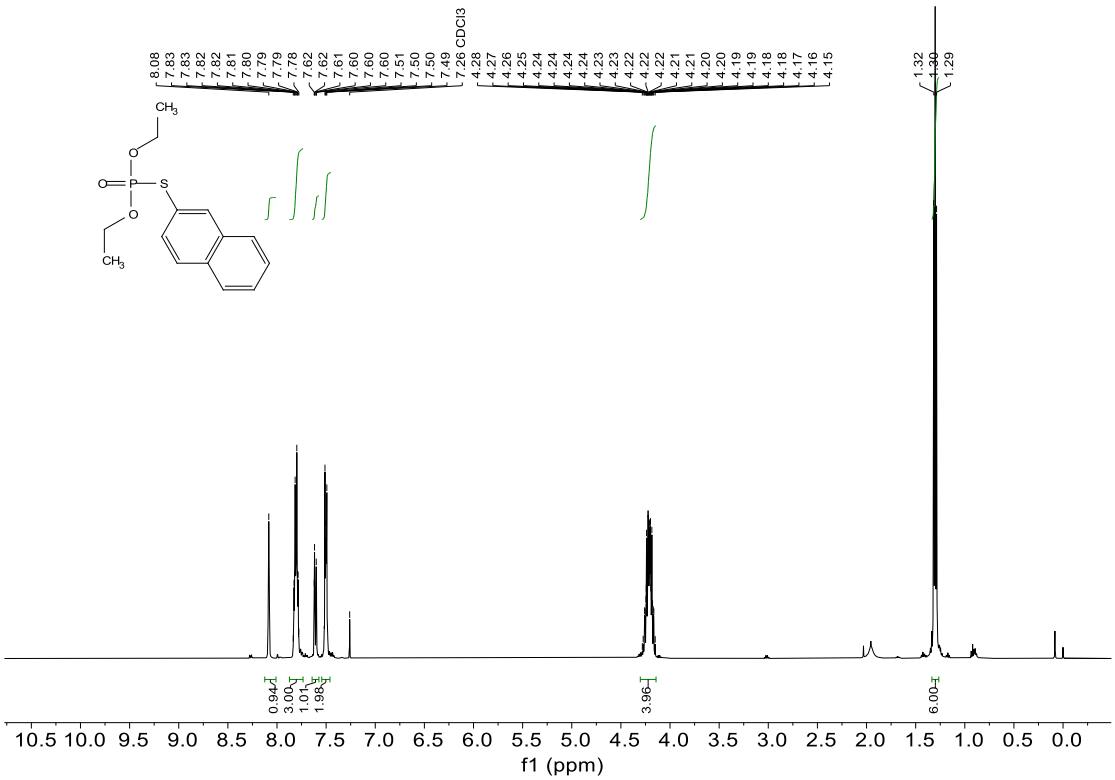
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4p**



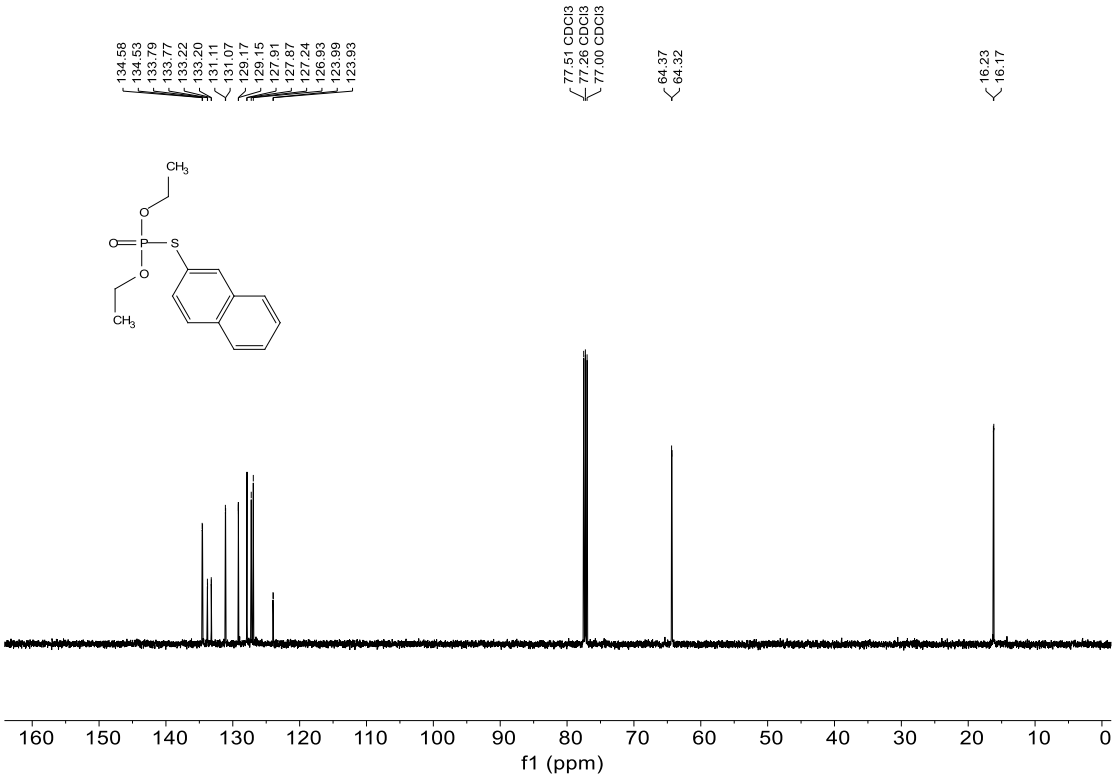
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$ spectrum of compound **4p**



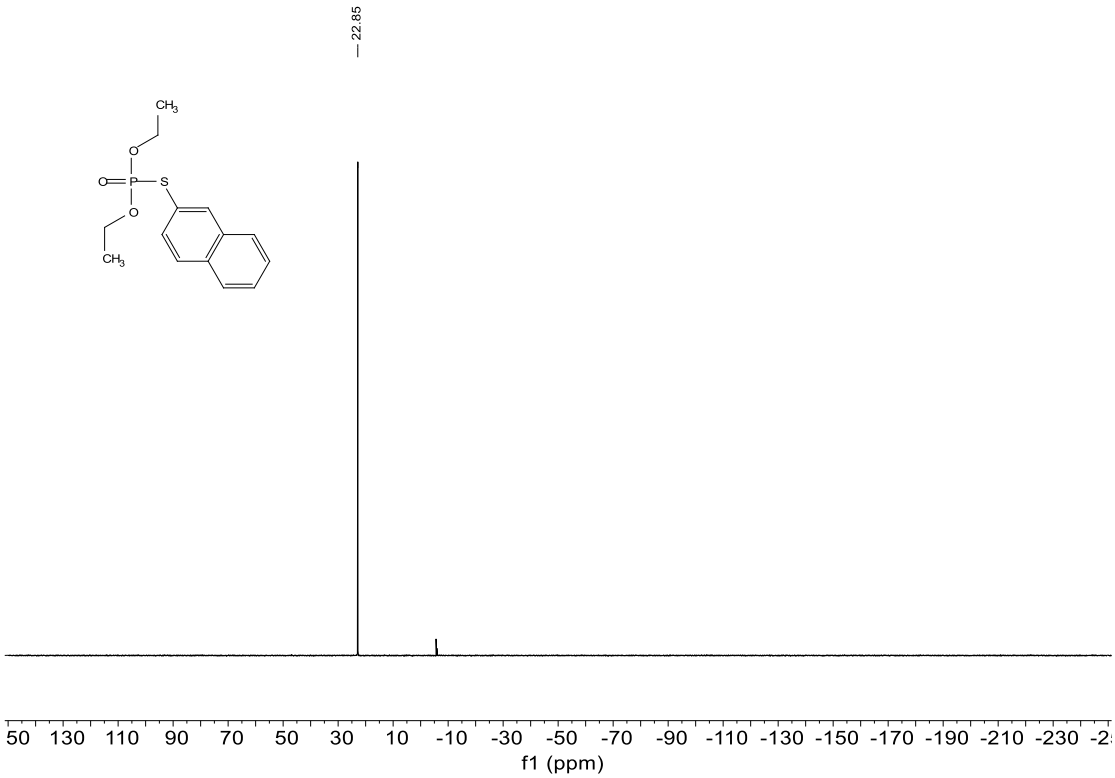
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4p**



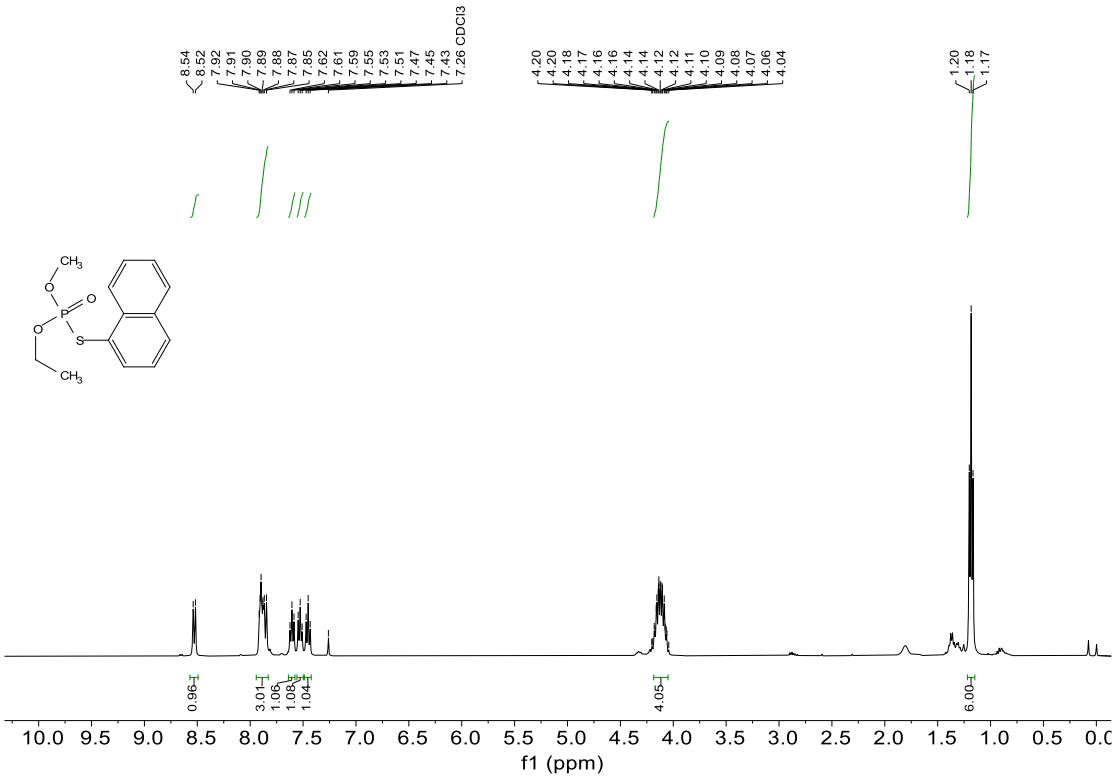
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4q**



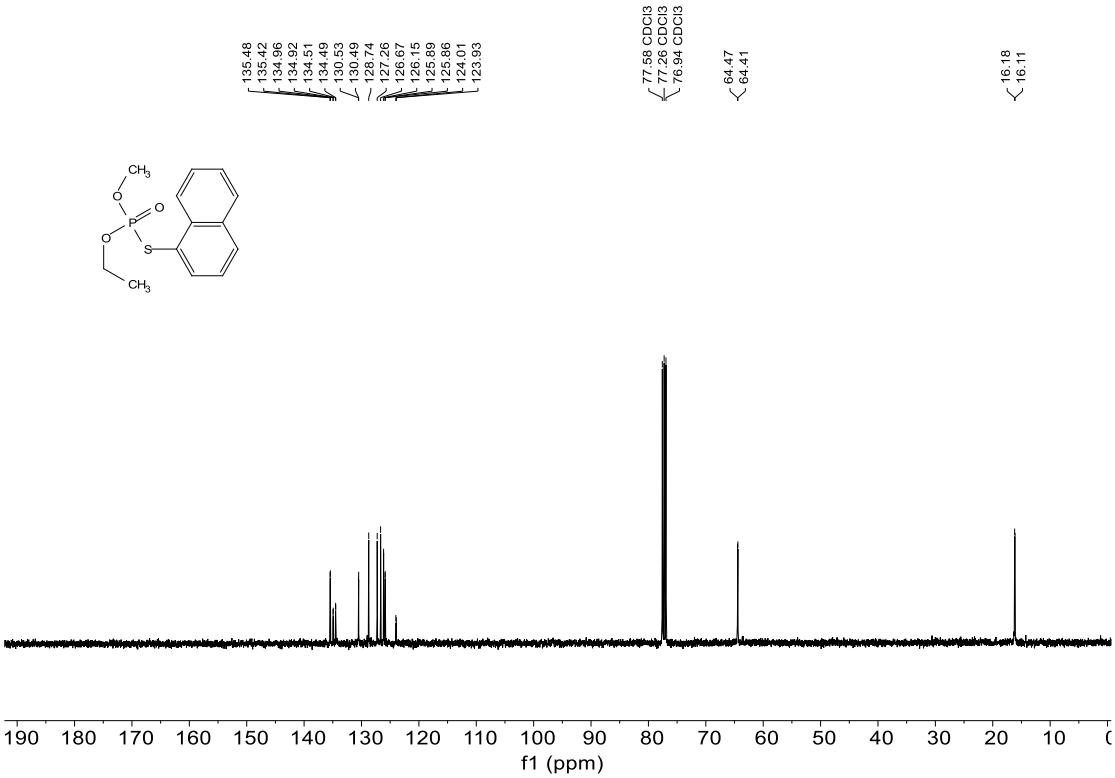
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4q**



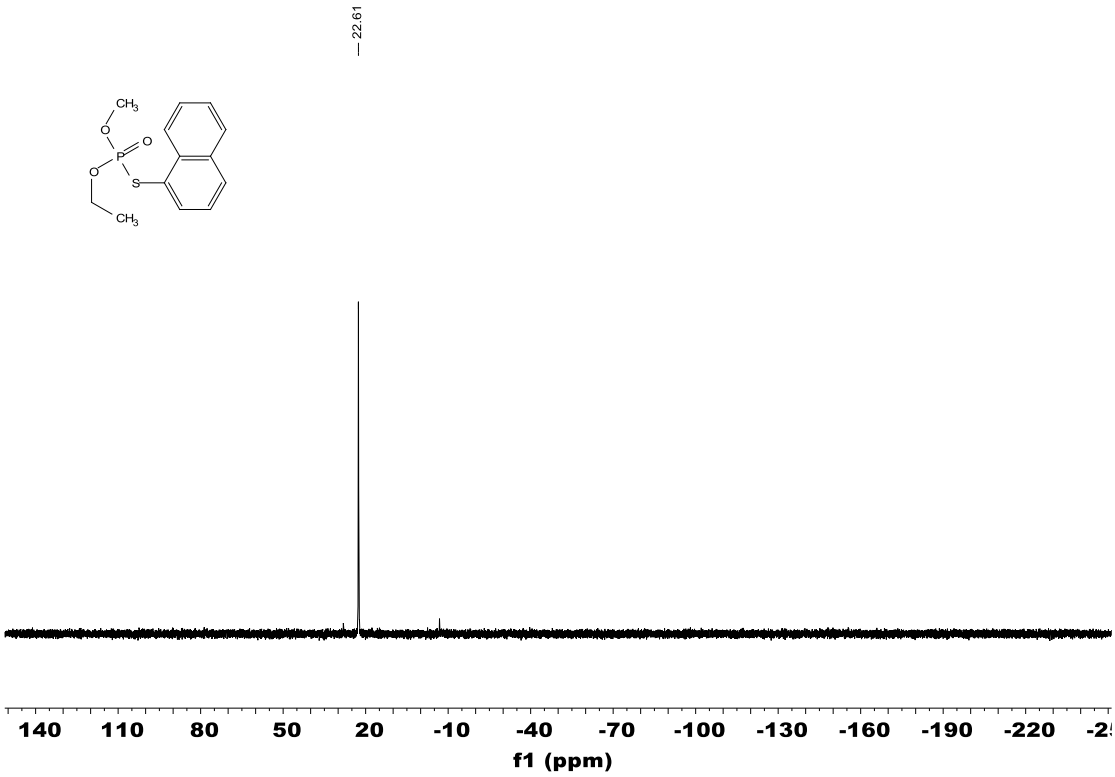
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4q**



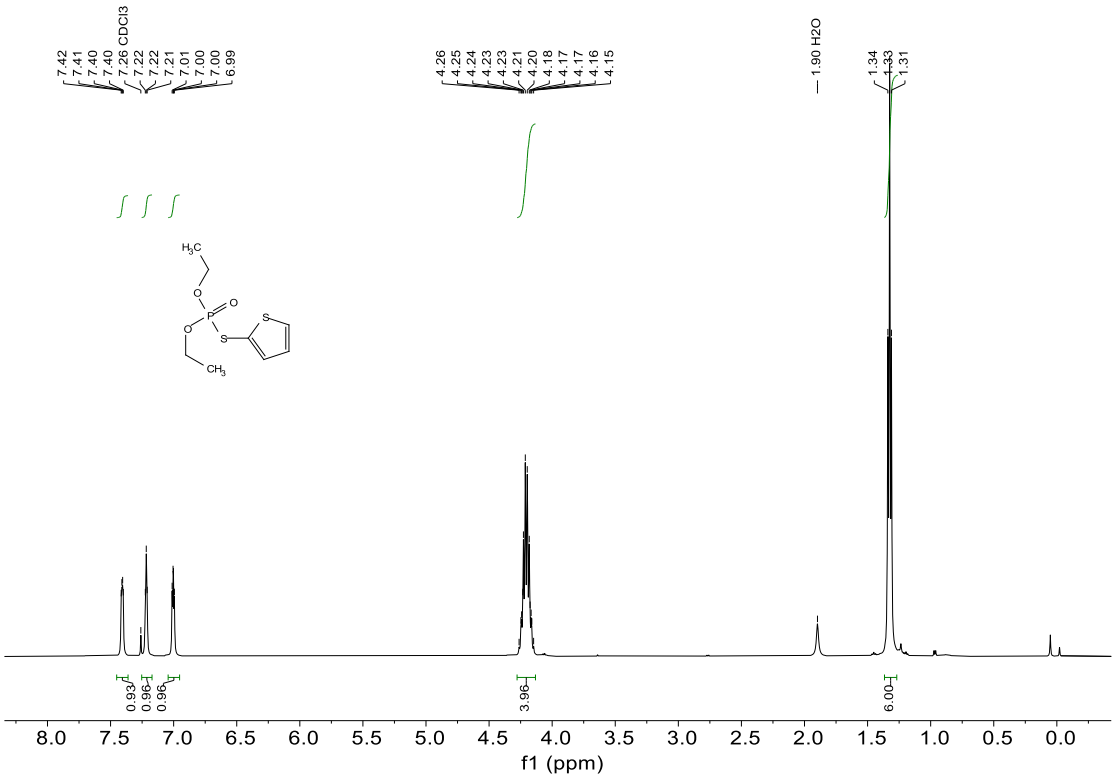
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4r**



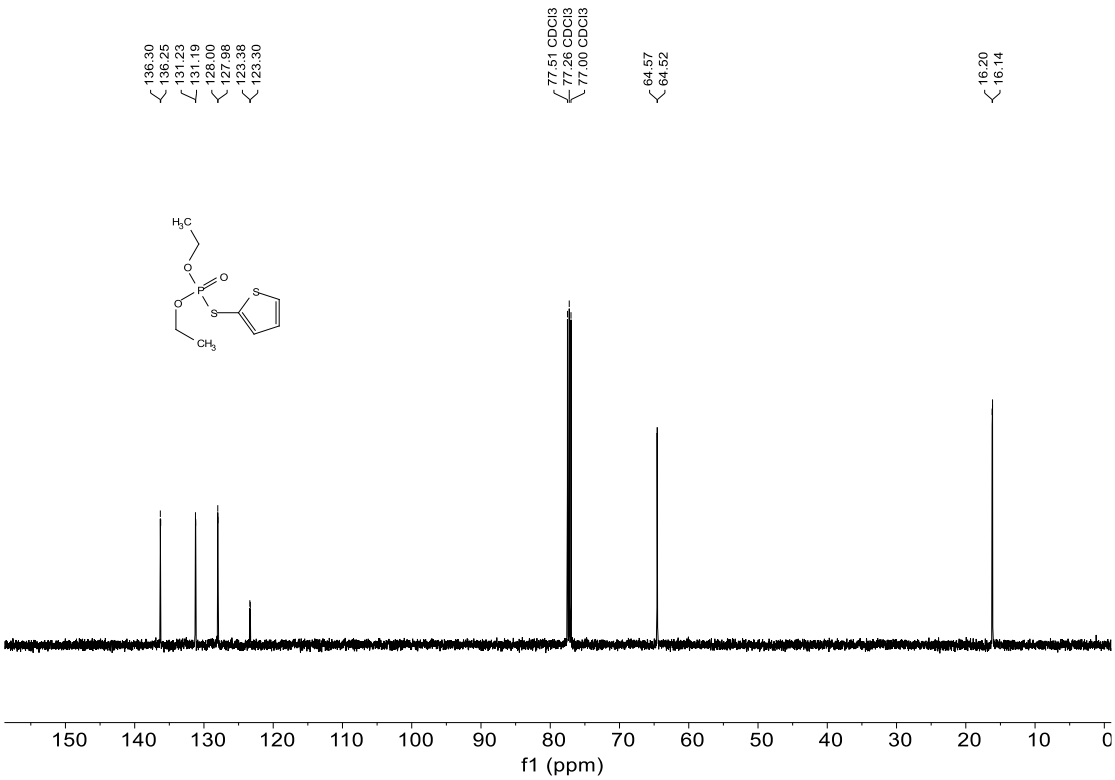
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4r**



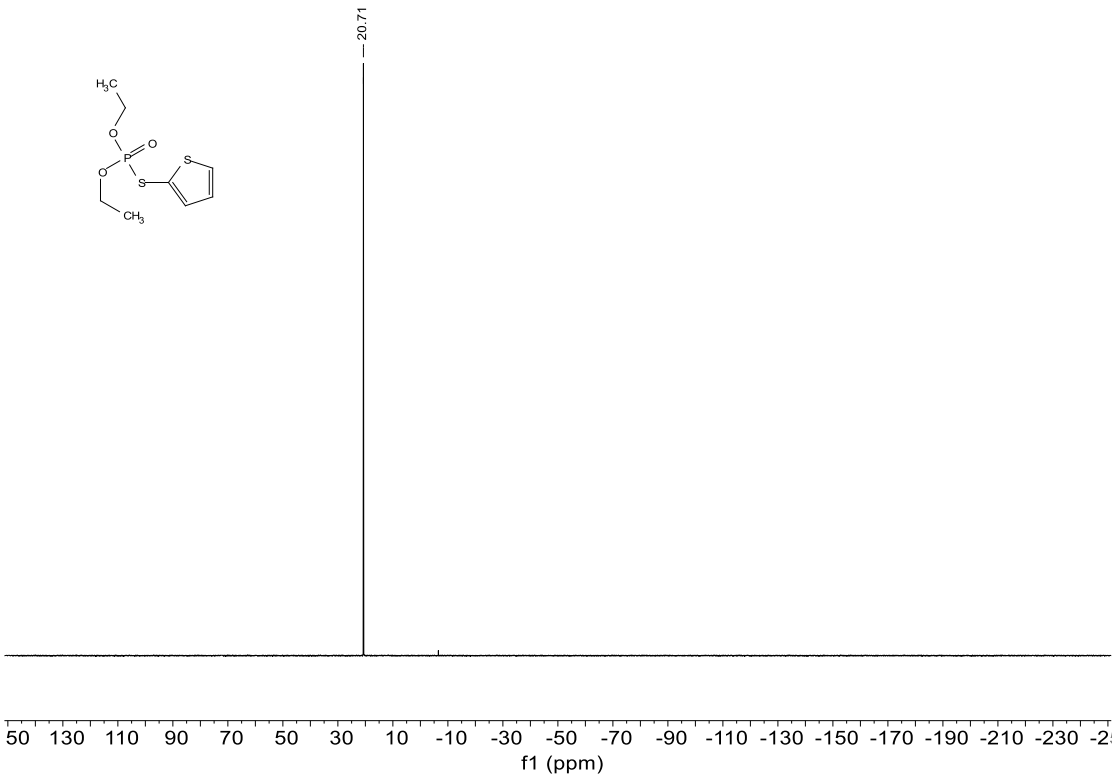
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4r**



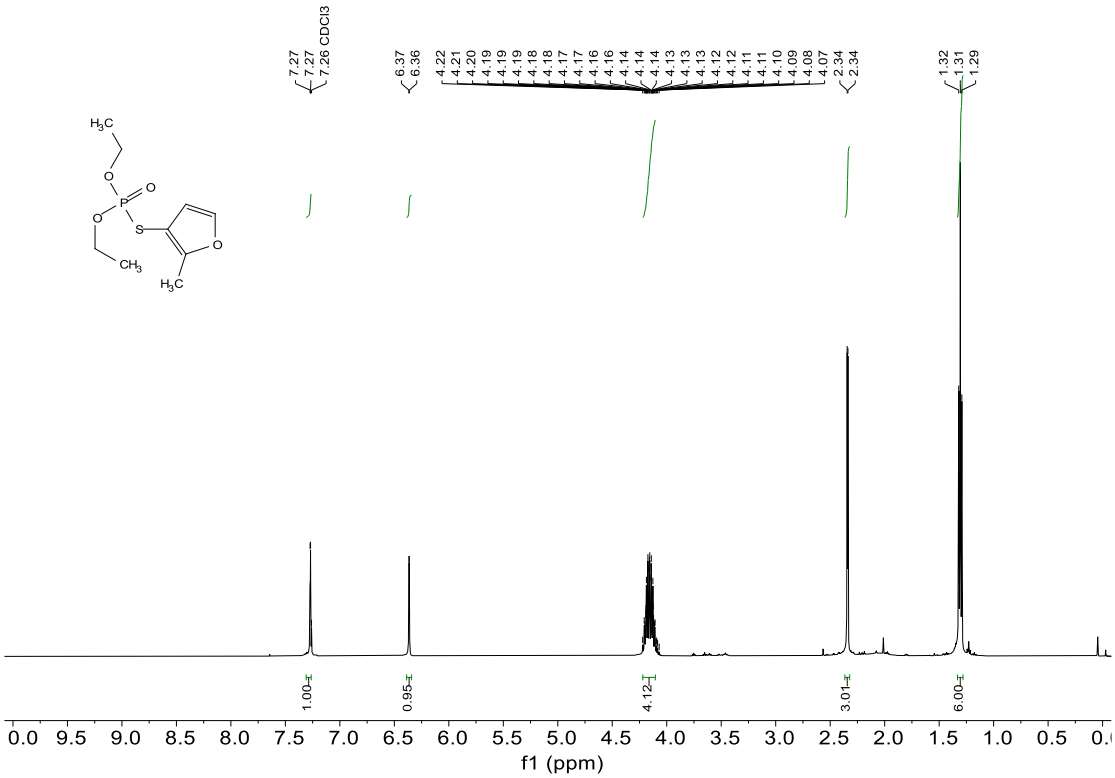
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4s**



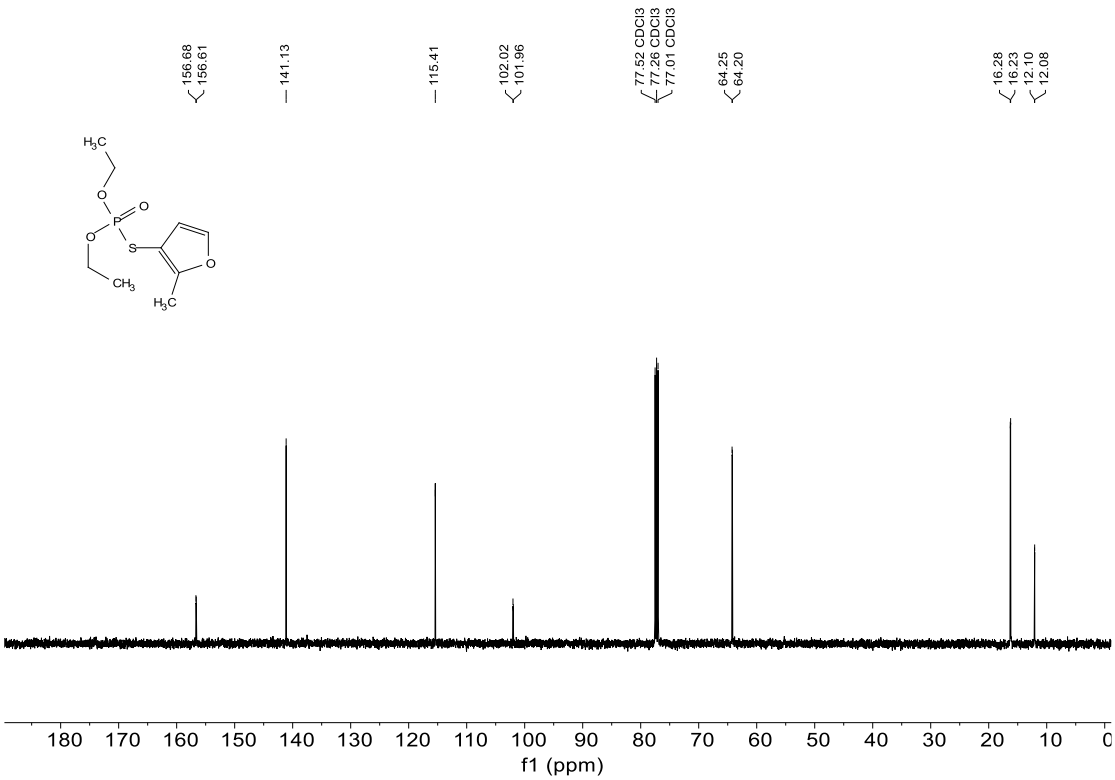
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **4s**



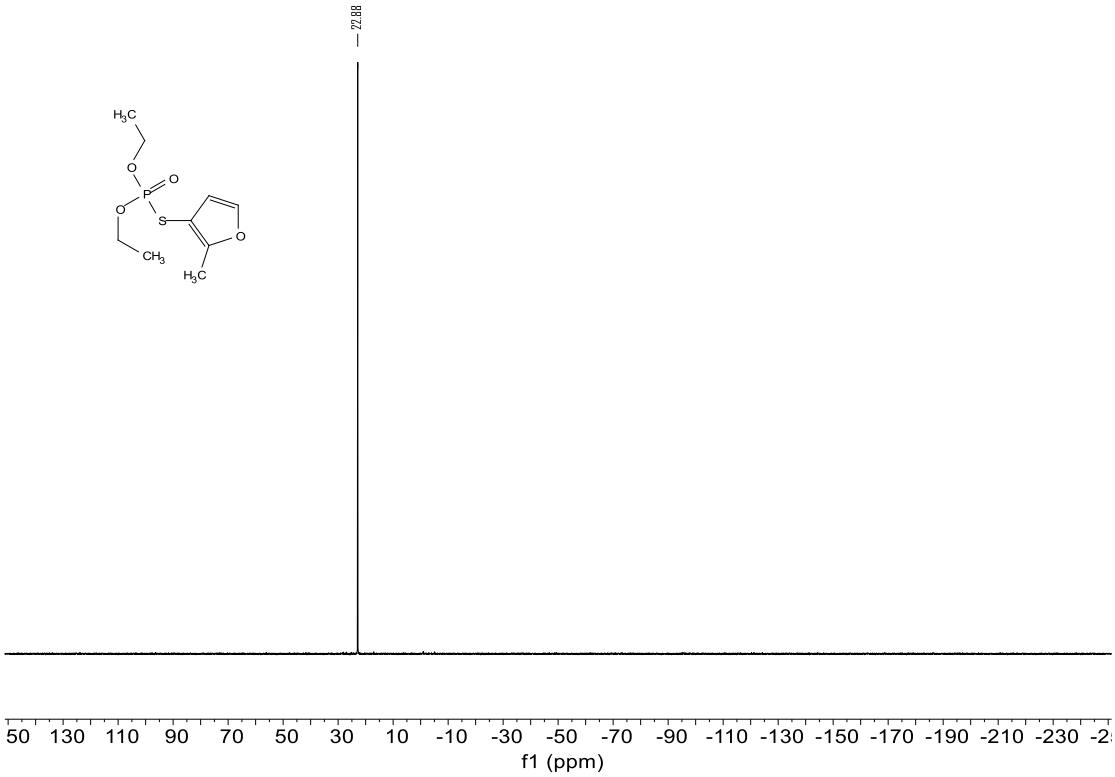
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4s**



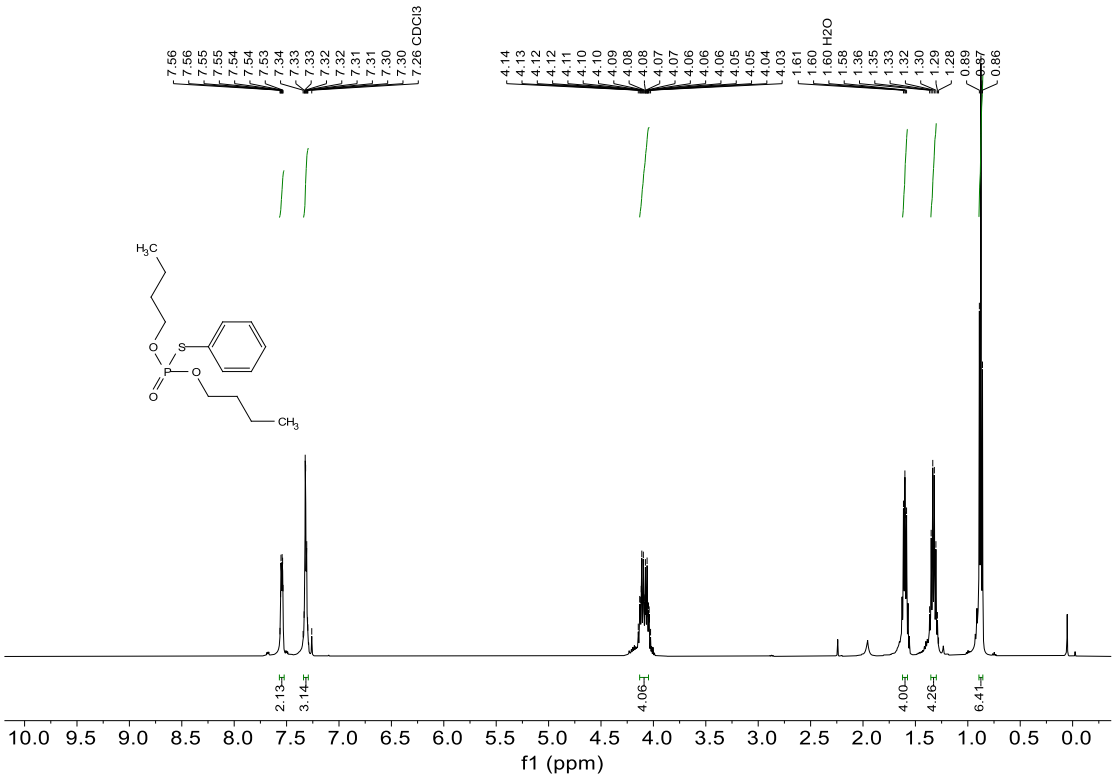
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4t**



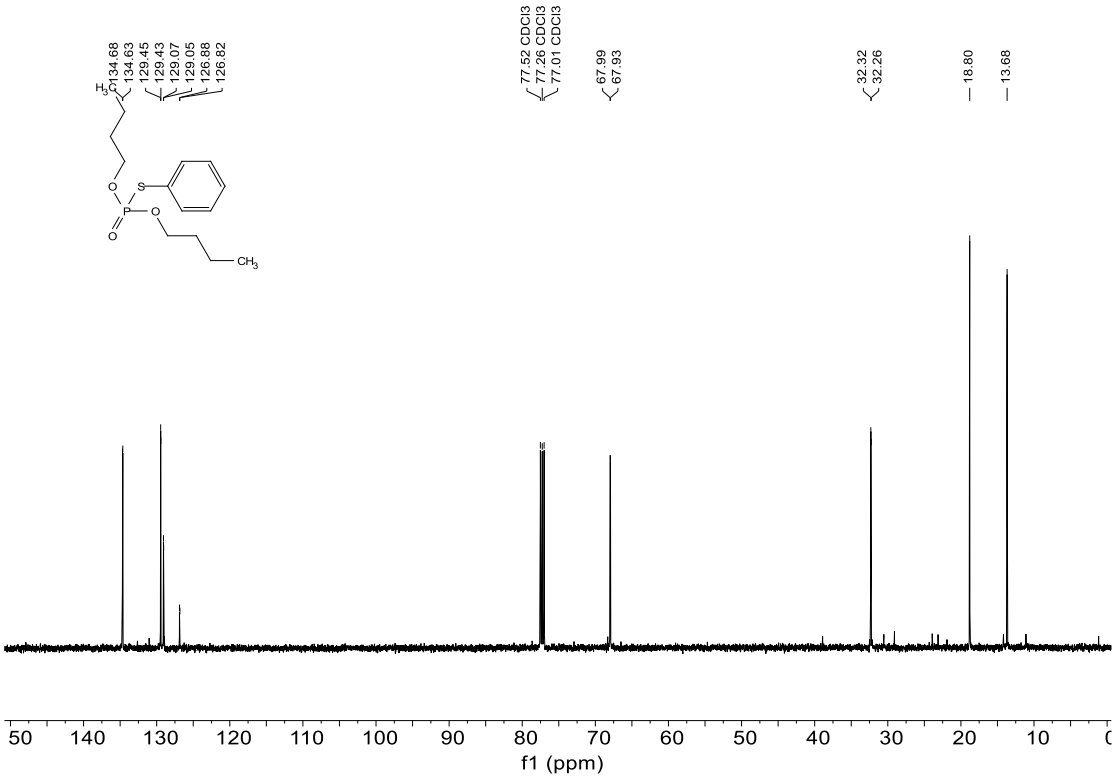
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **4t**



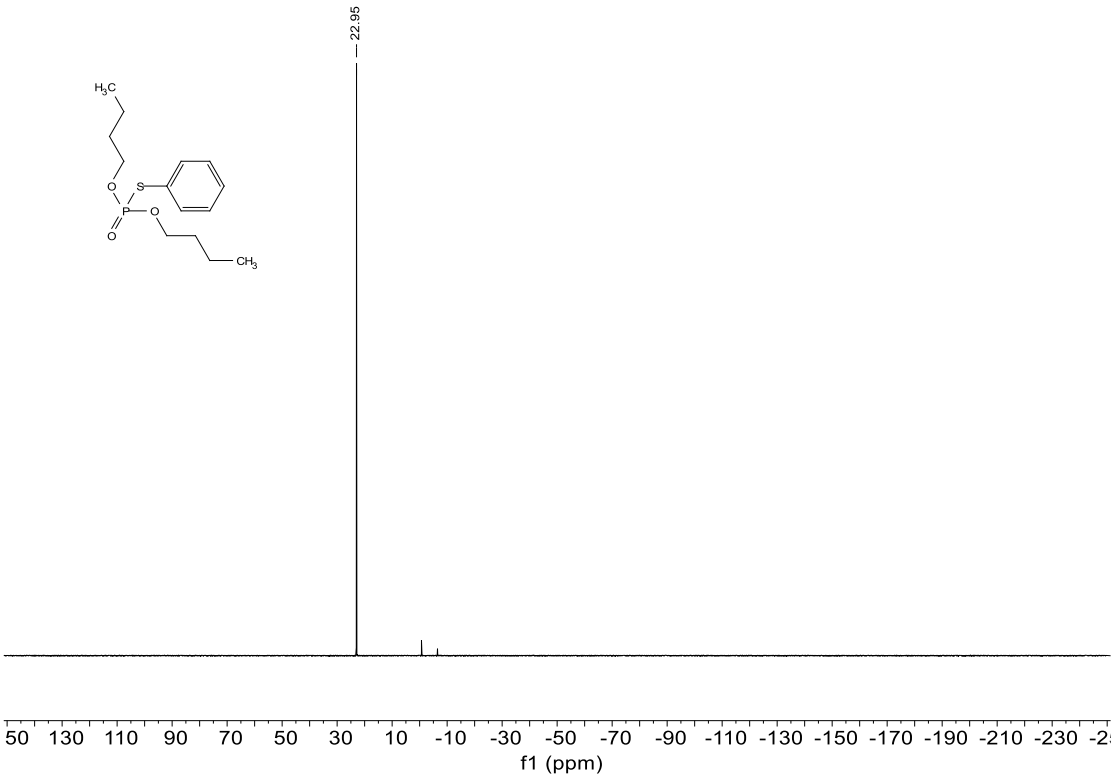
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **4t**



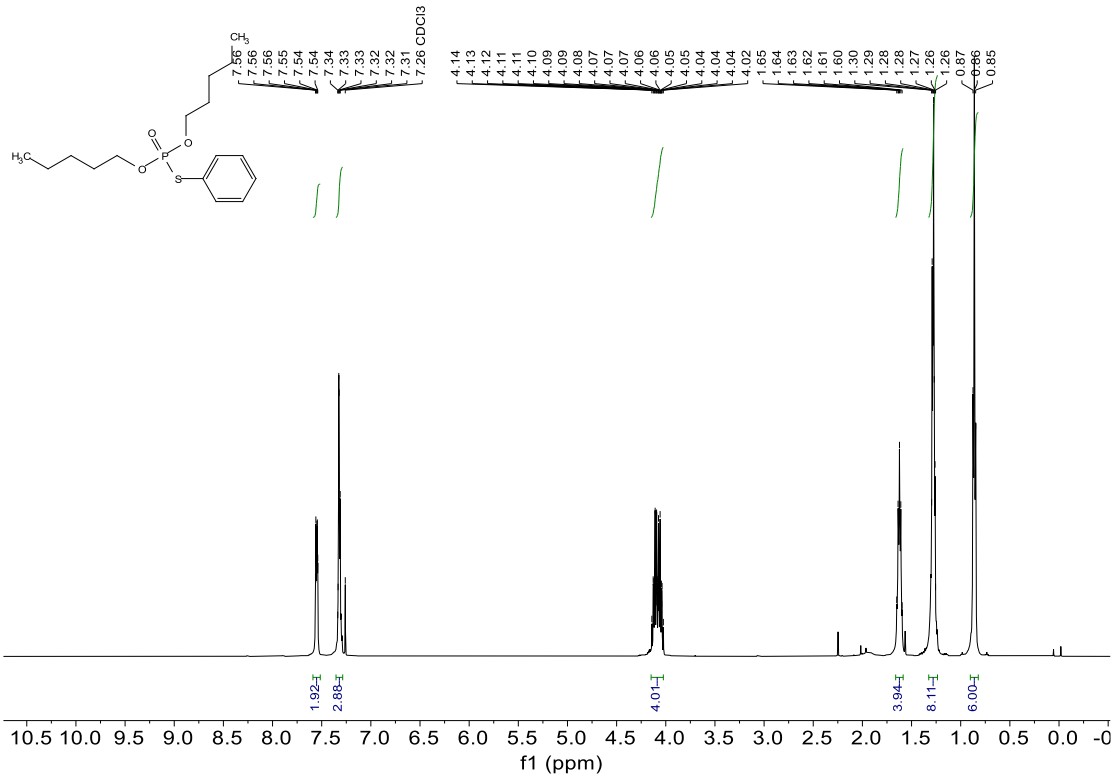
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5a**



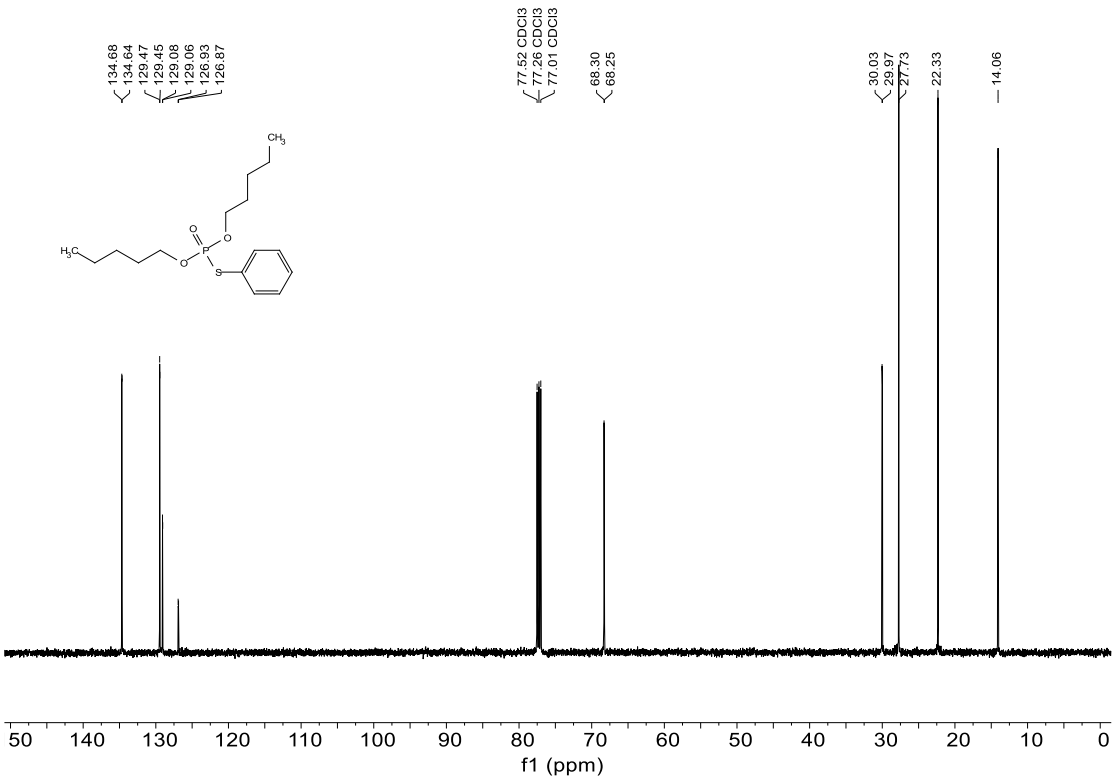
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **5a**



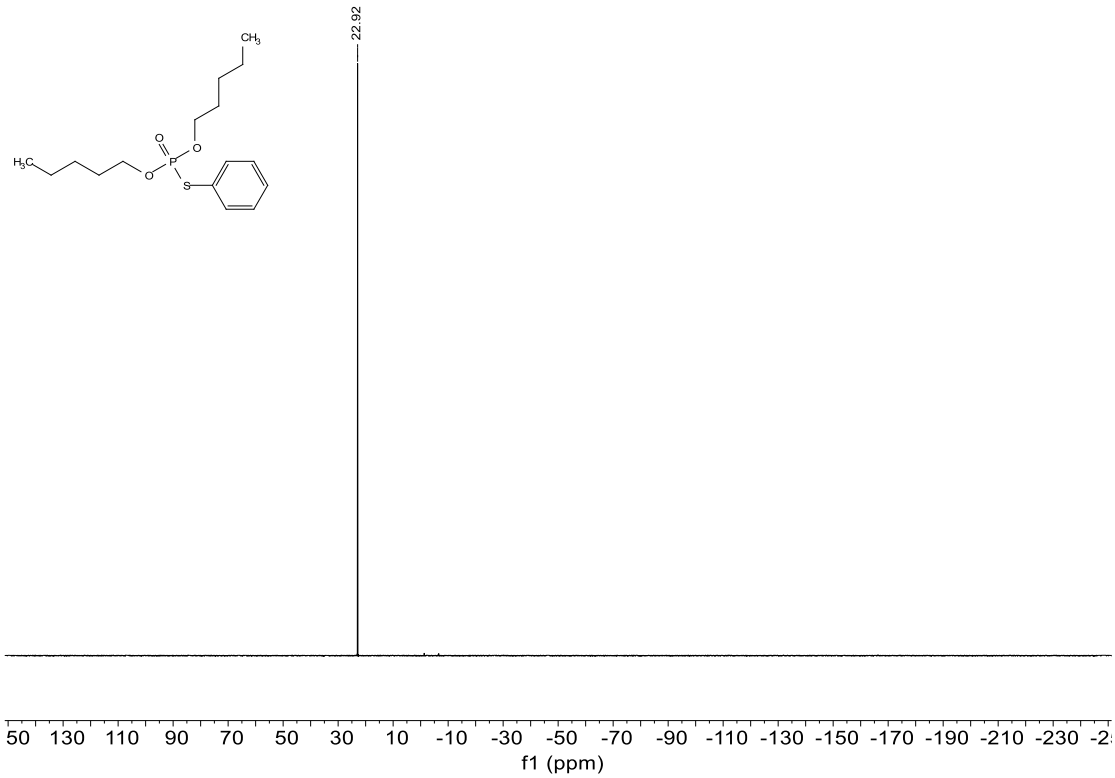
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5a**



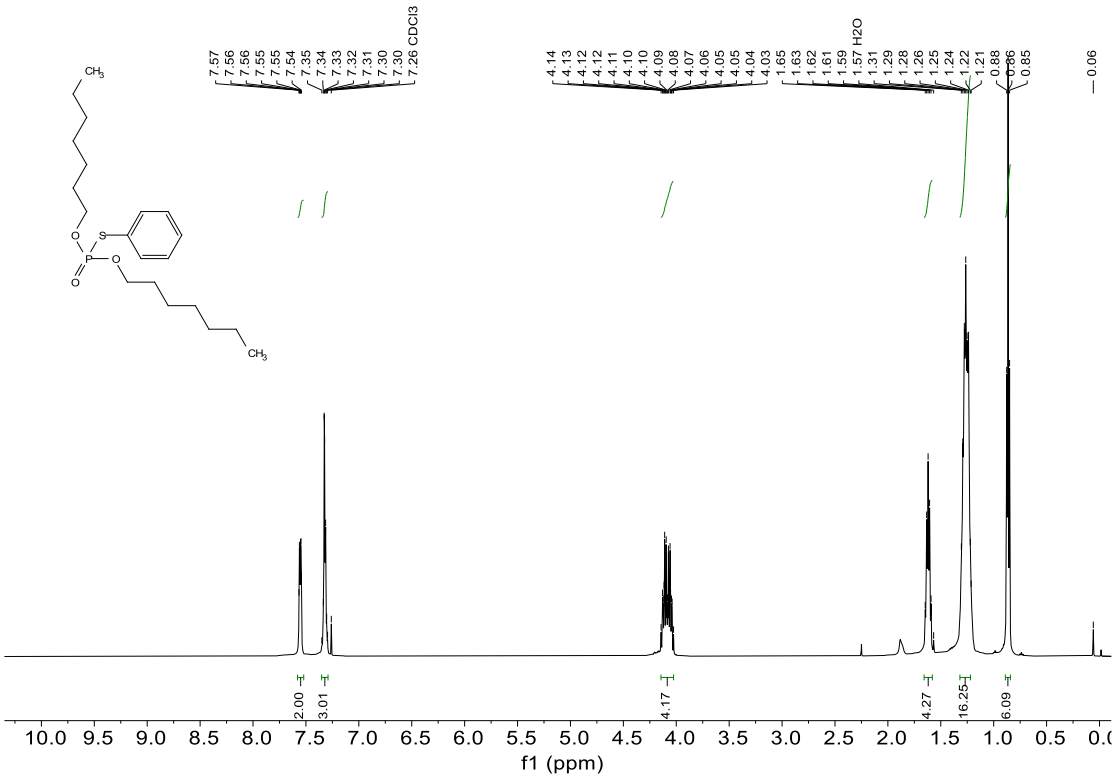
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5b**



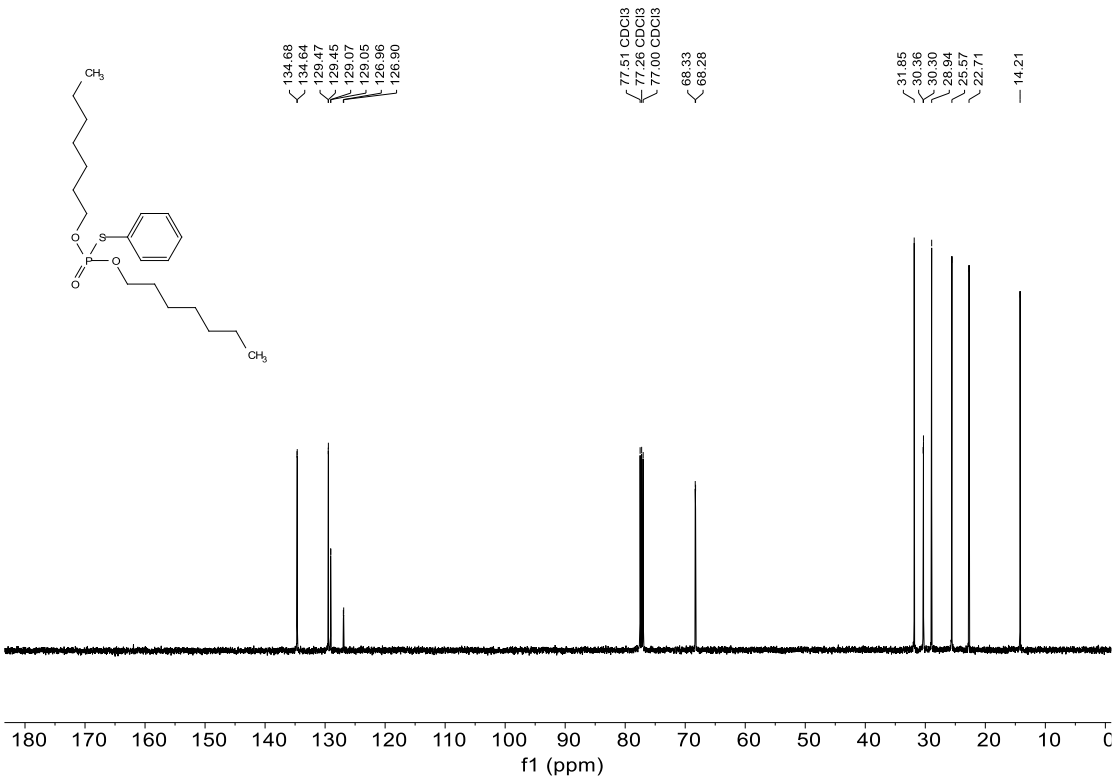
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5b**



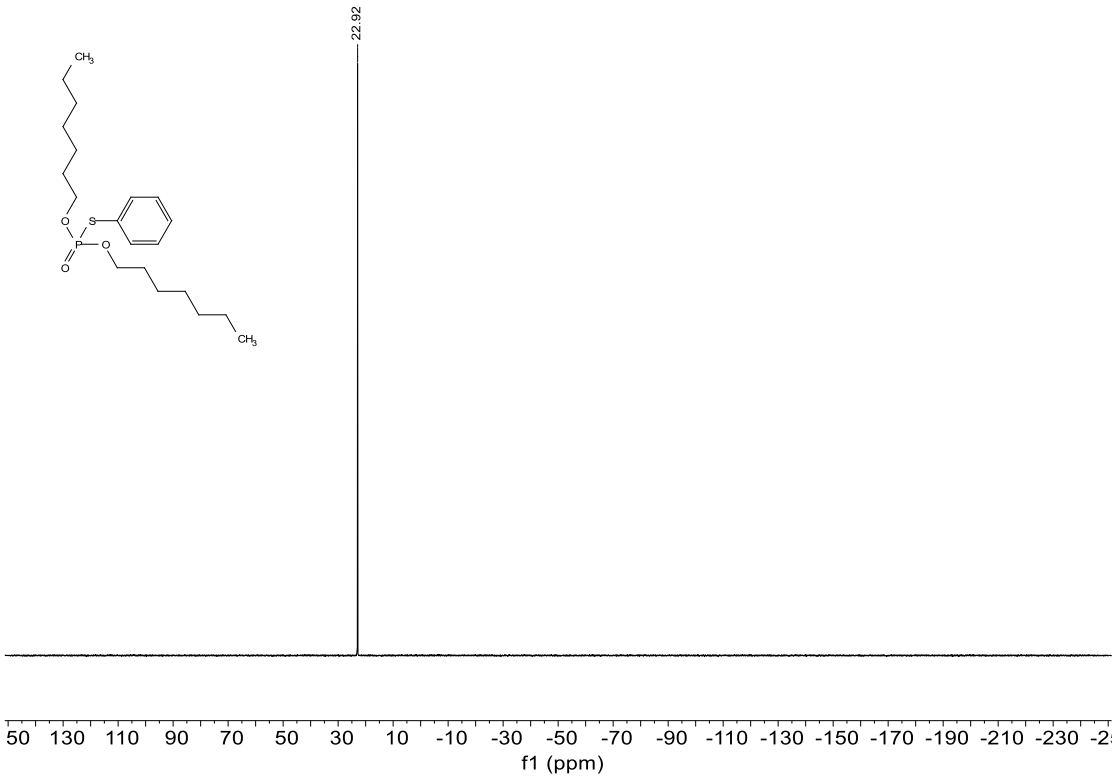
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5b**



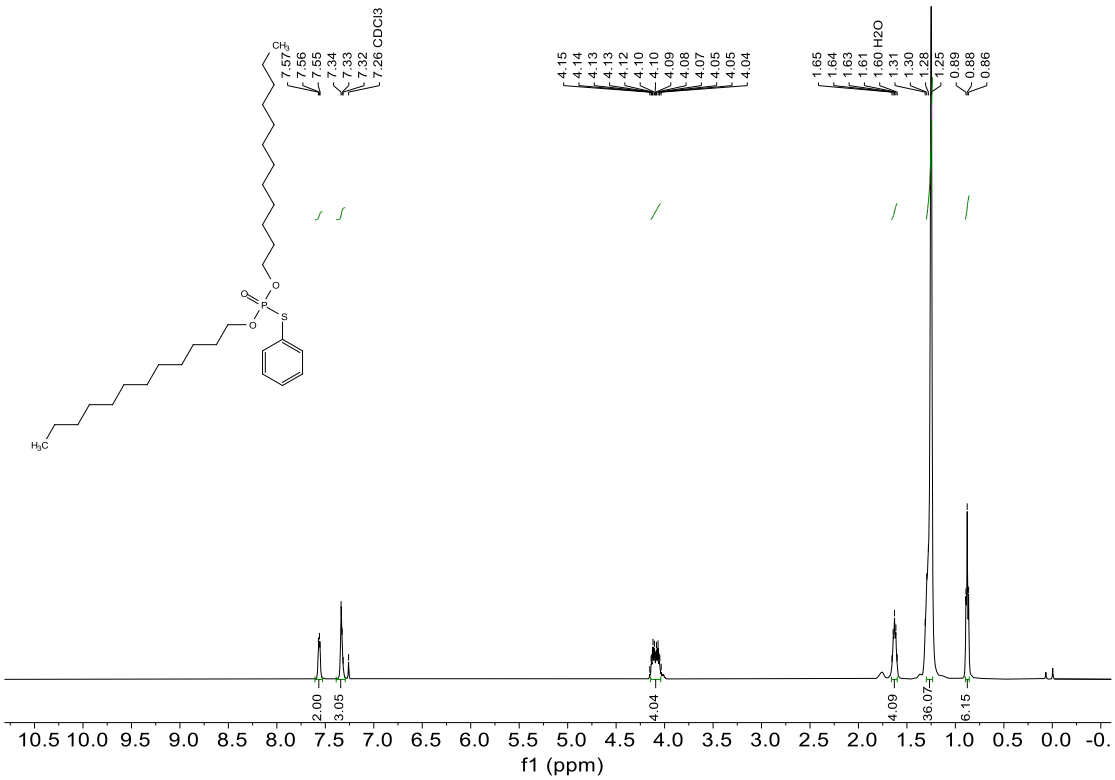
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5c**



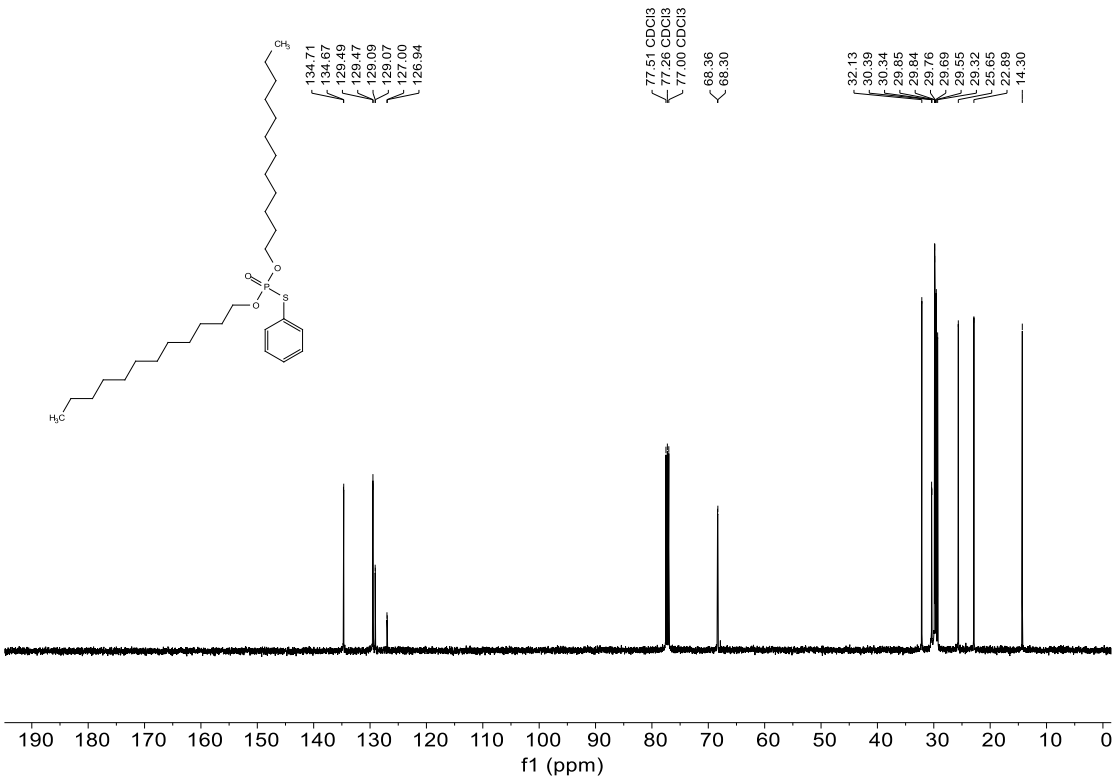
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **5c**



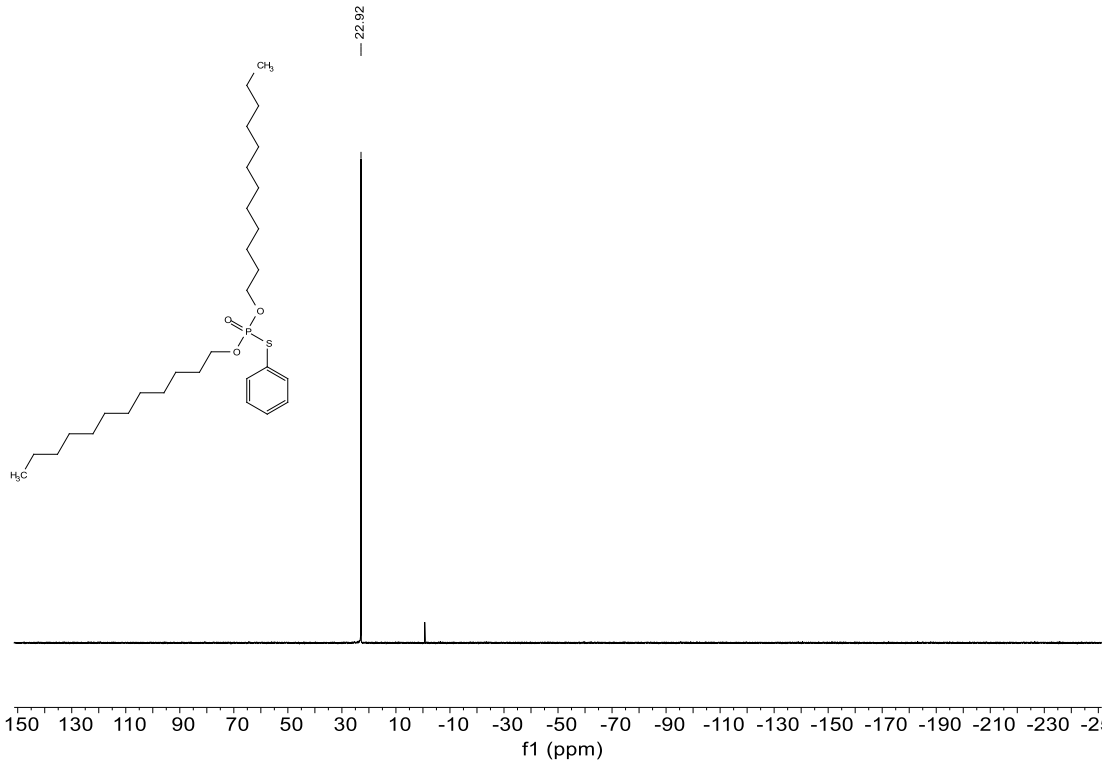
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5c**



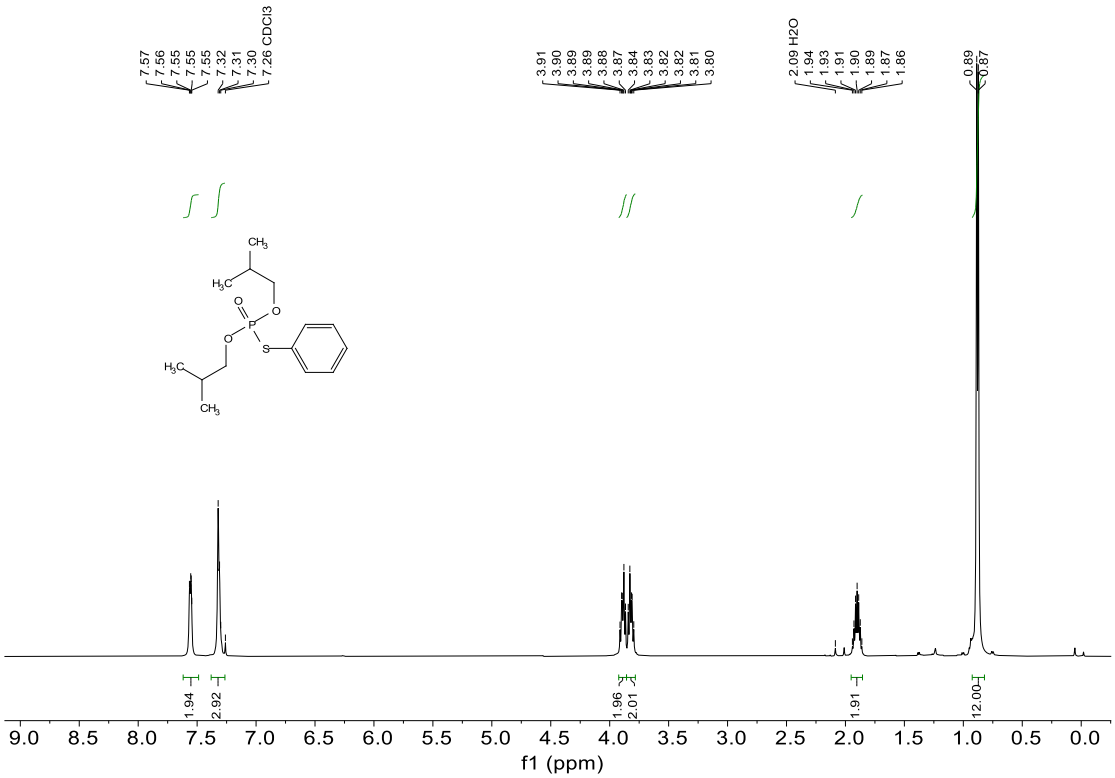
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5d**



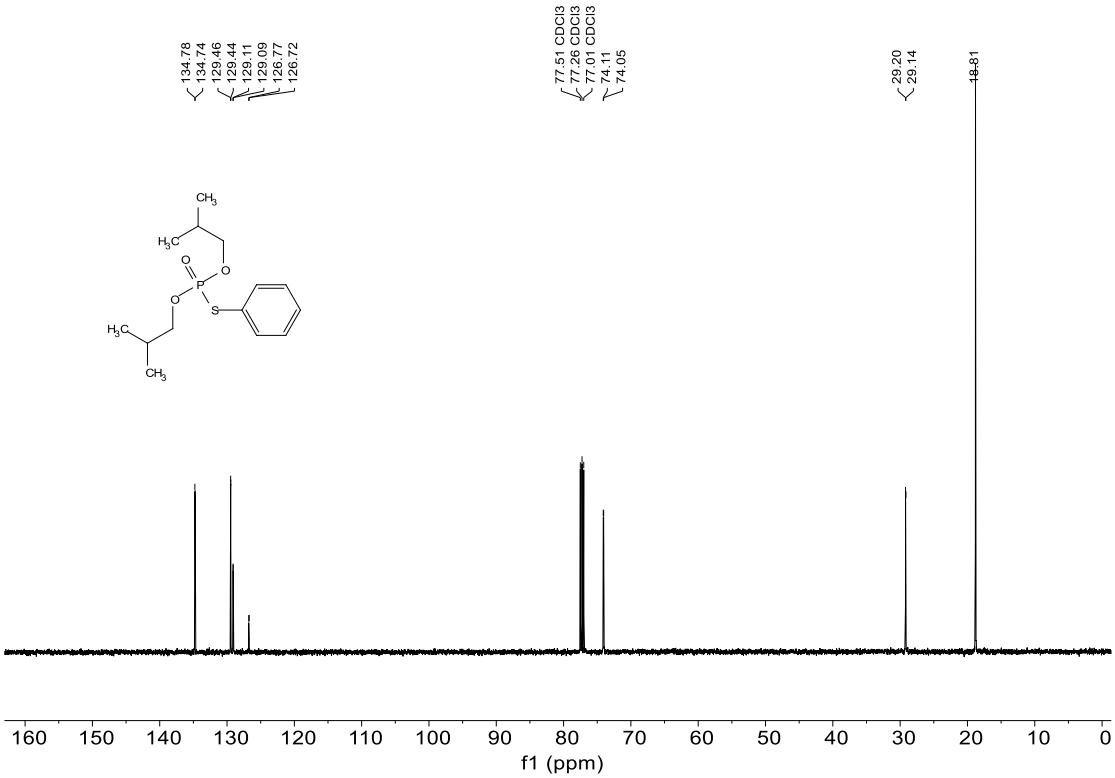
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5d**



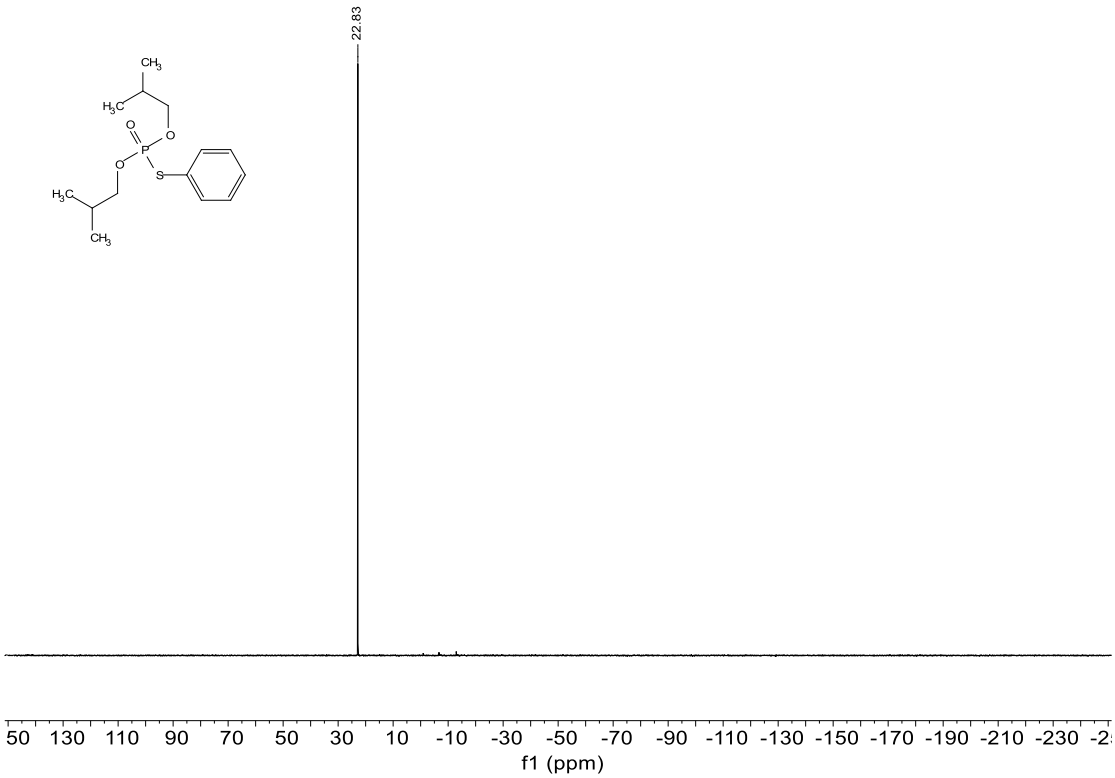
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5d**



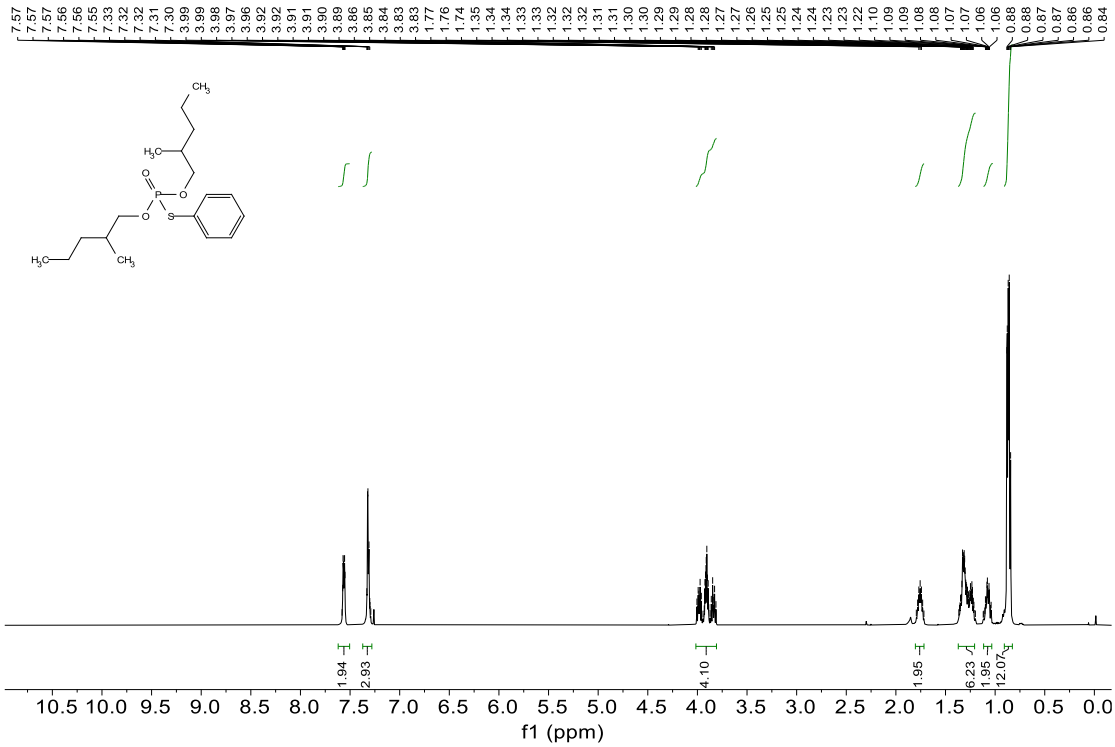
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5e**



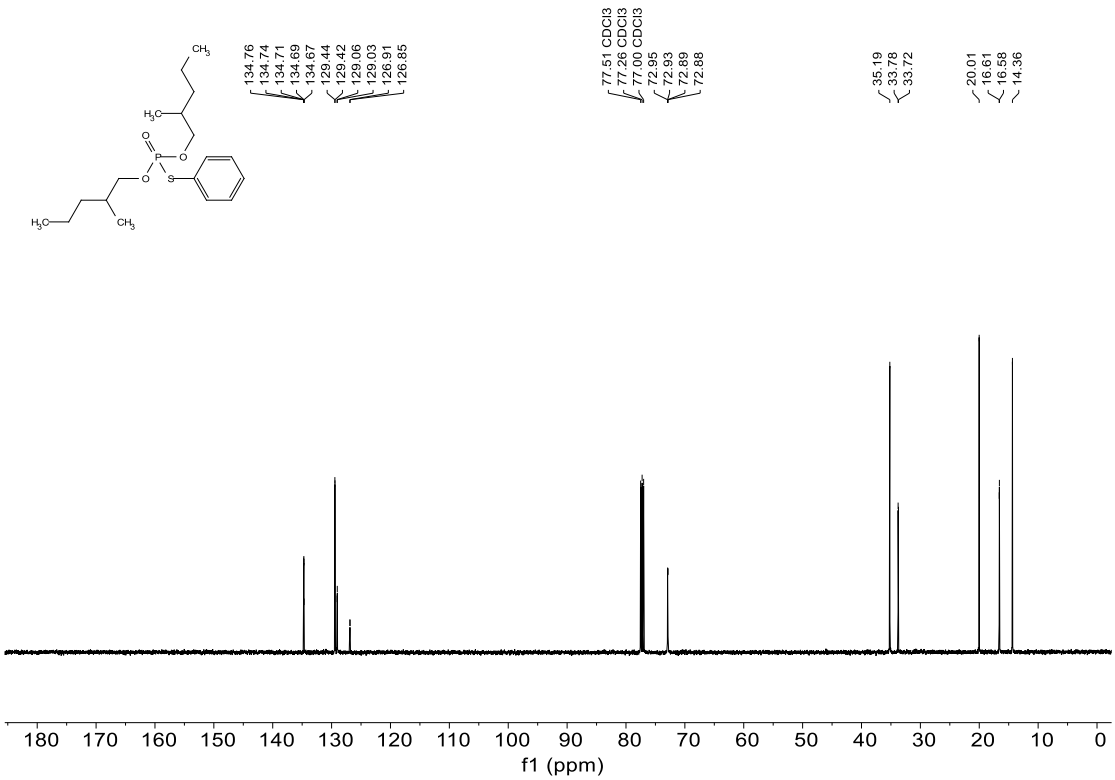
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **5e**



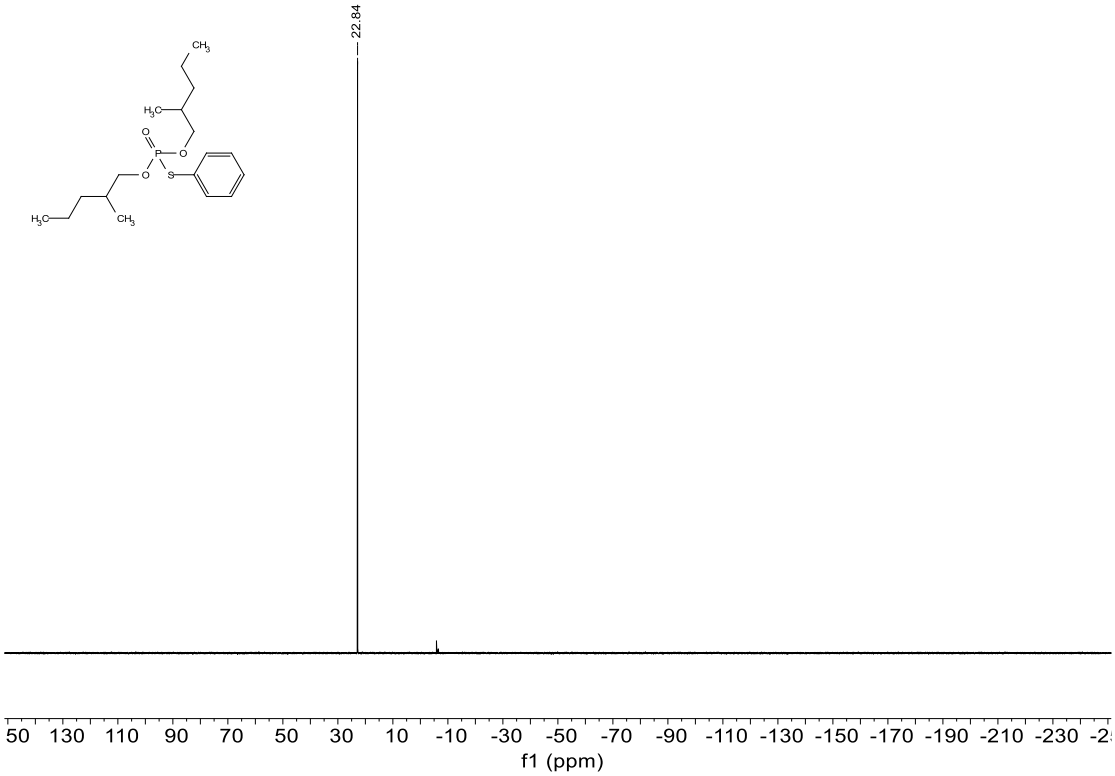
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5e**



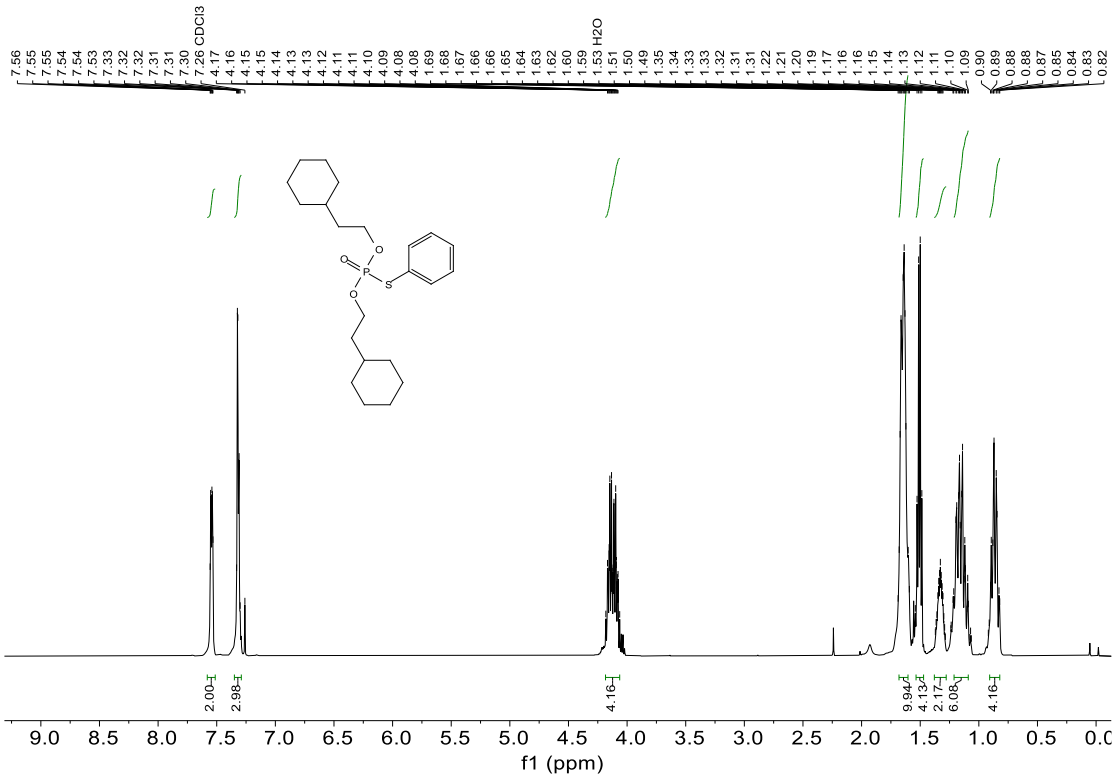
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5f**



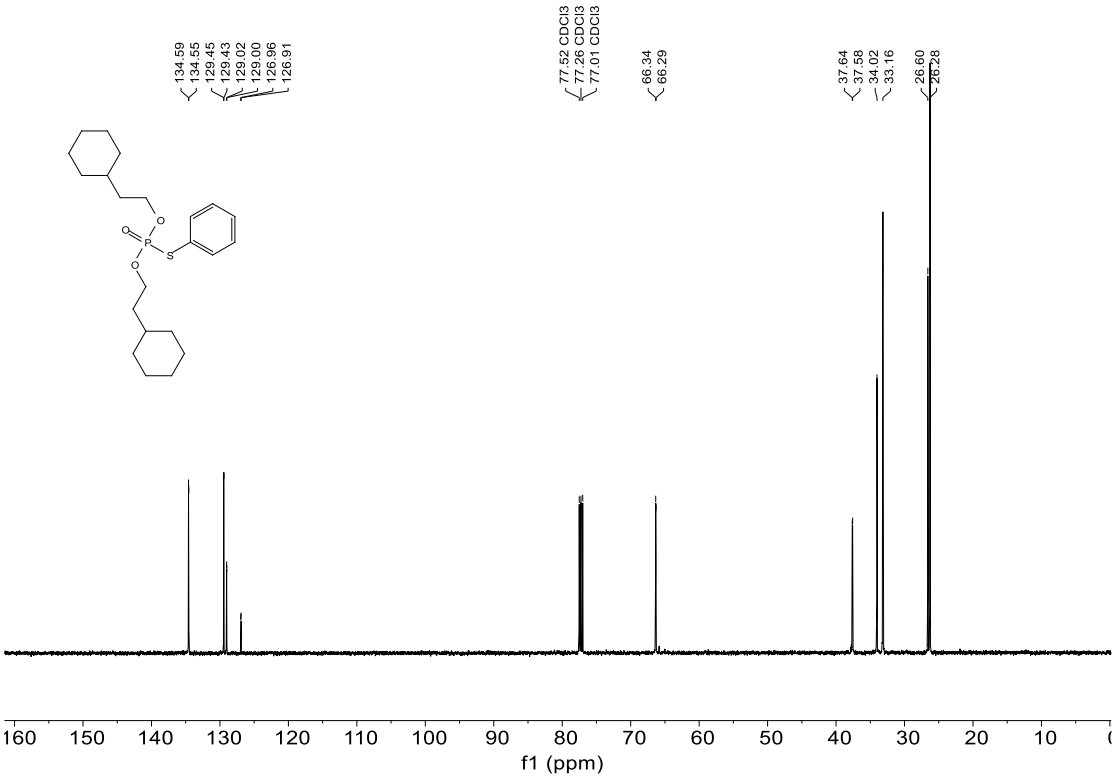
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5f**



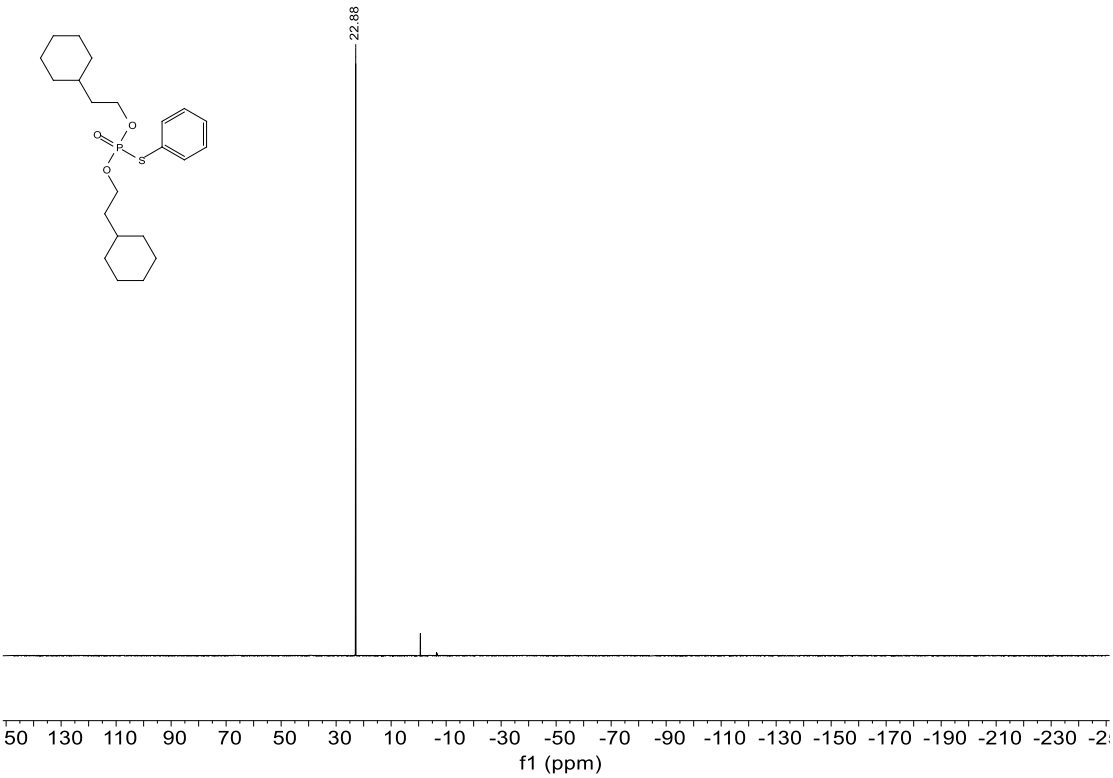
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5f**



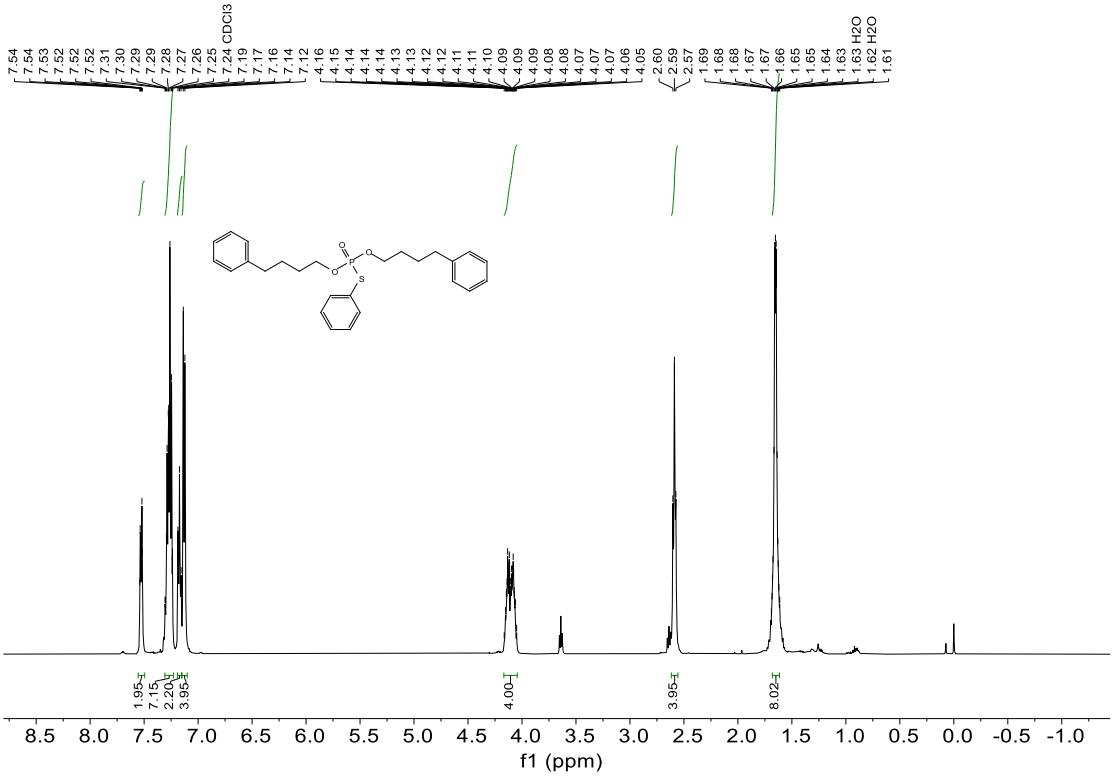
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5g**



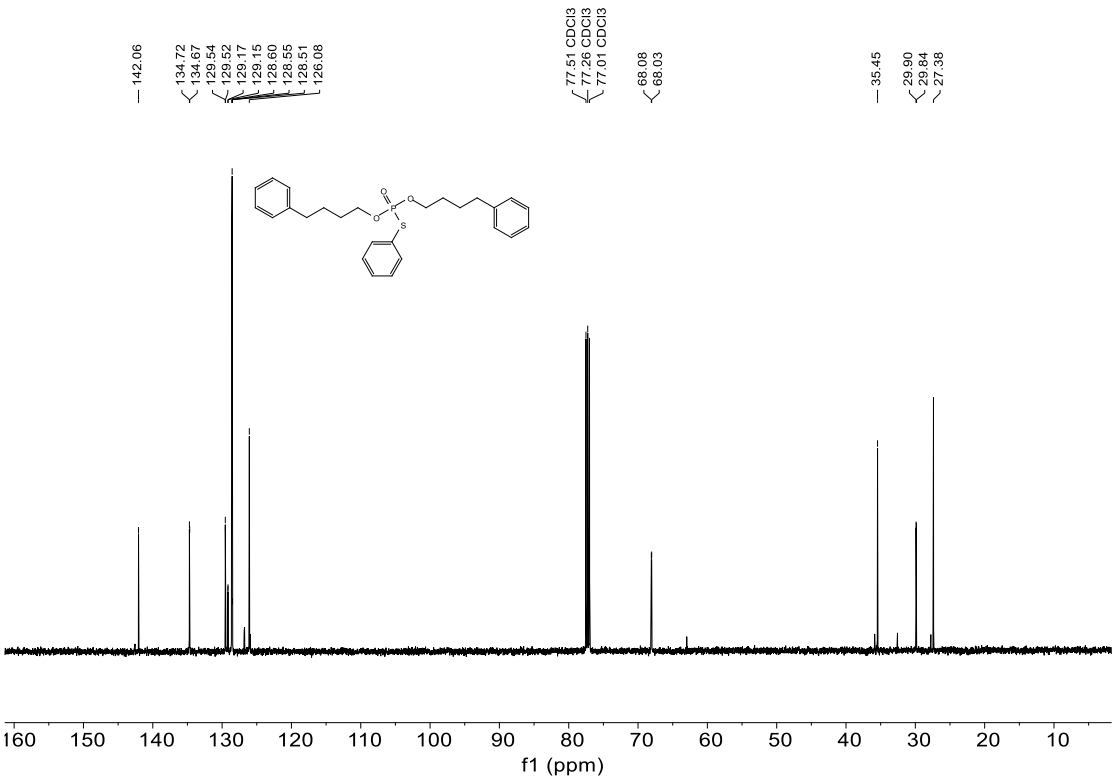
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **5g**



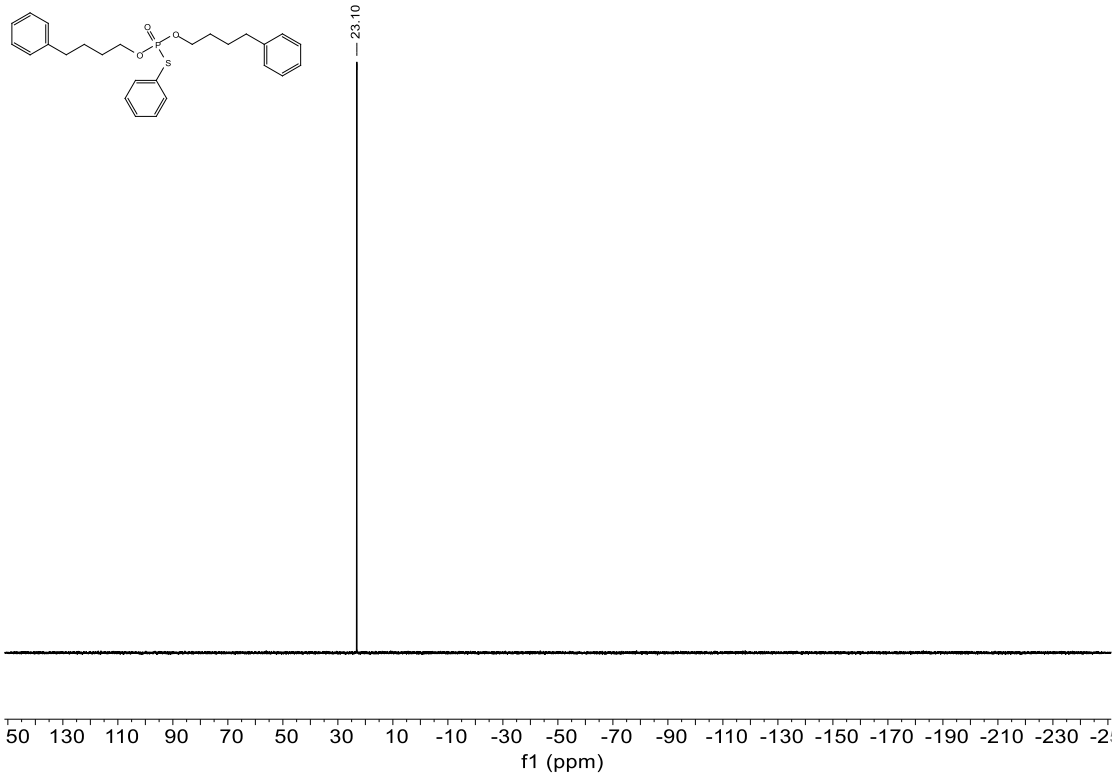
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5g**



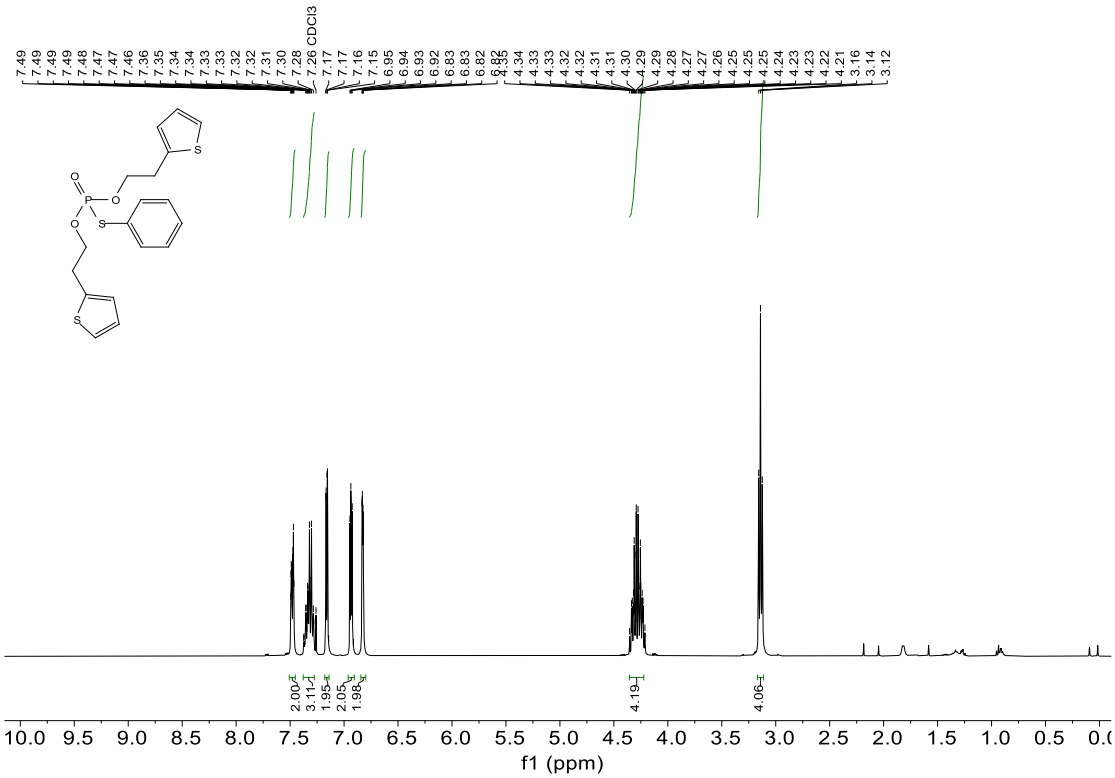
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5h**



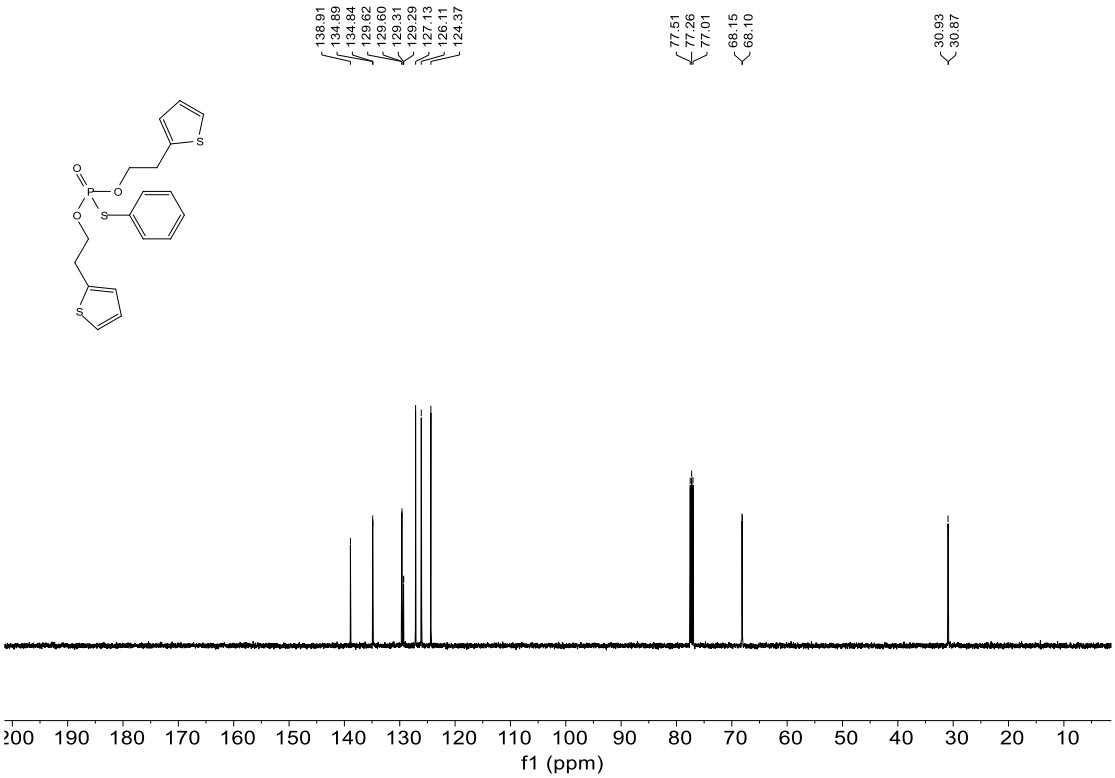
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5h**



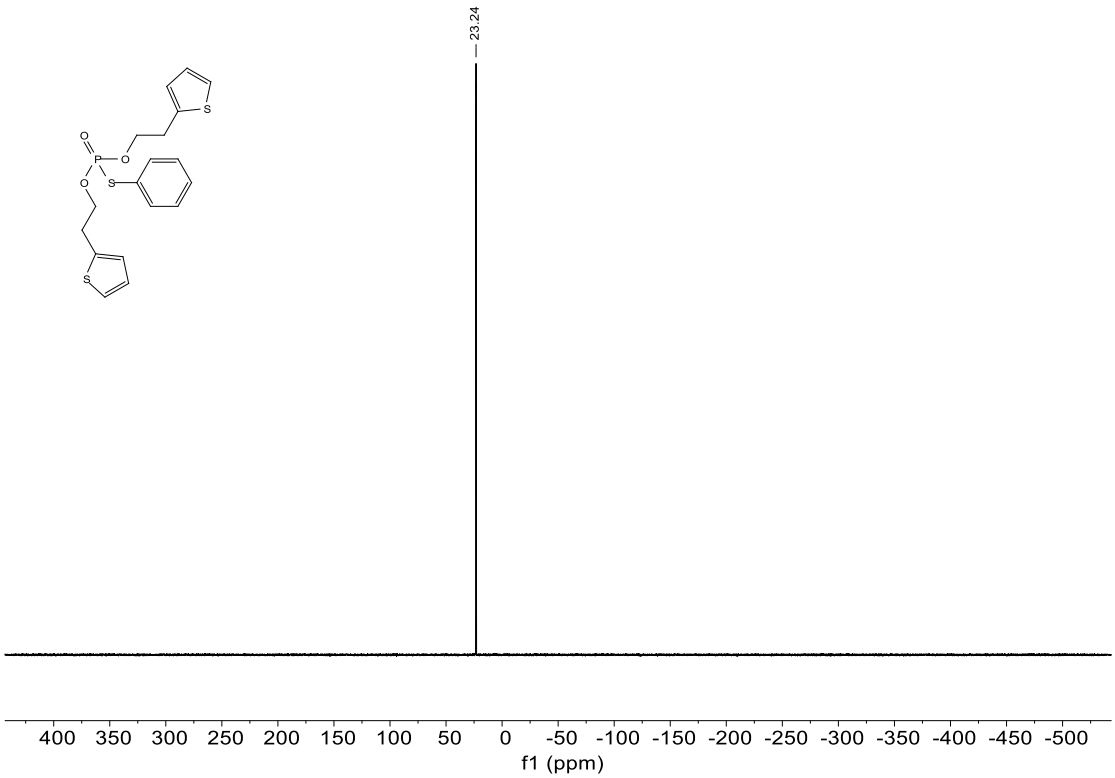
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5h**



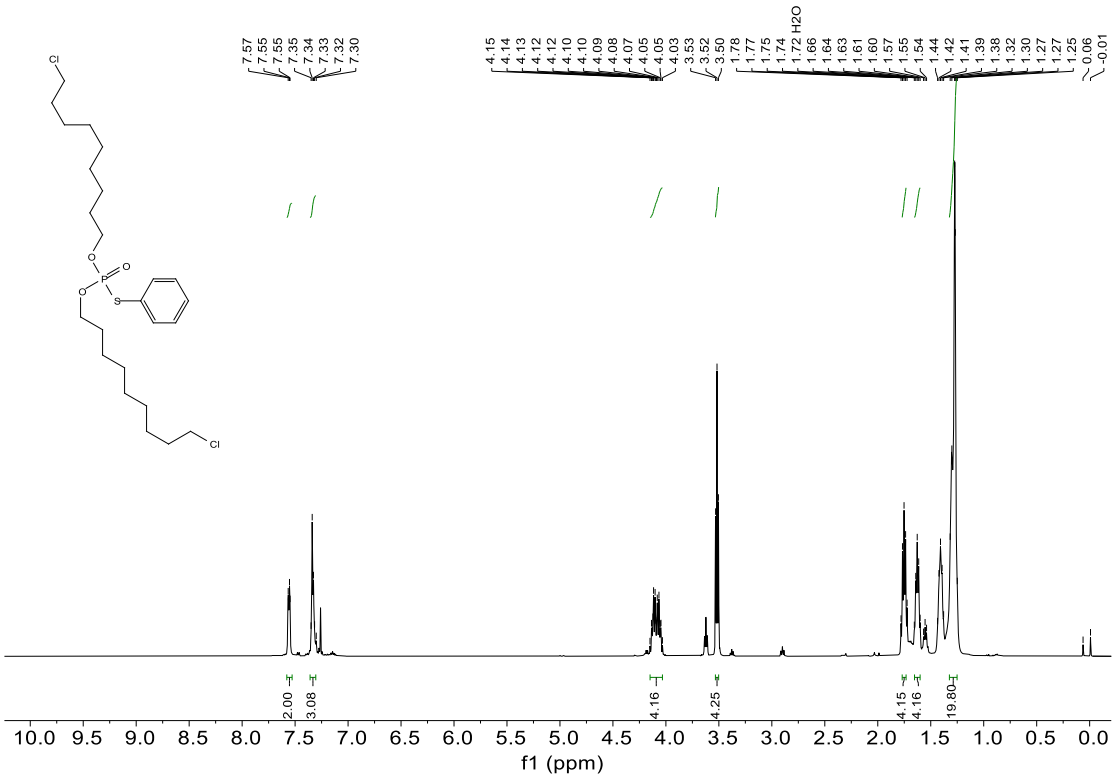
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**



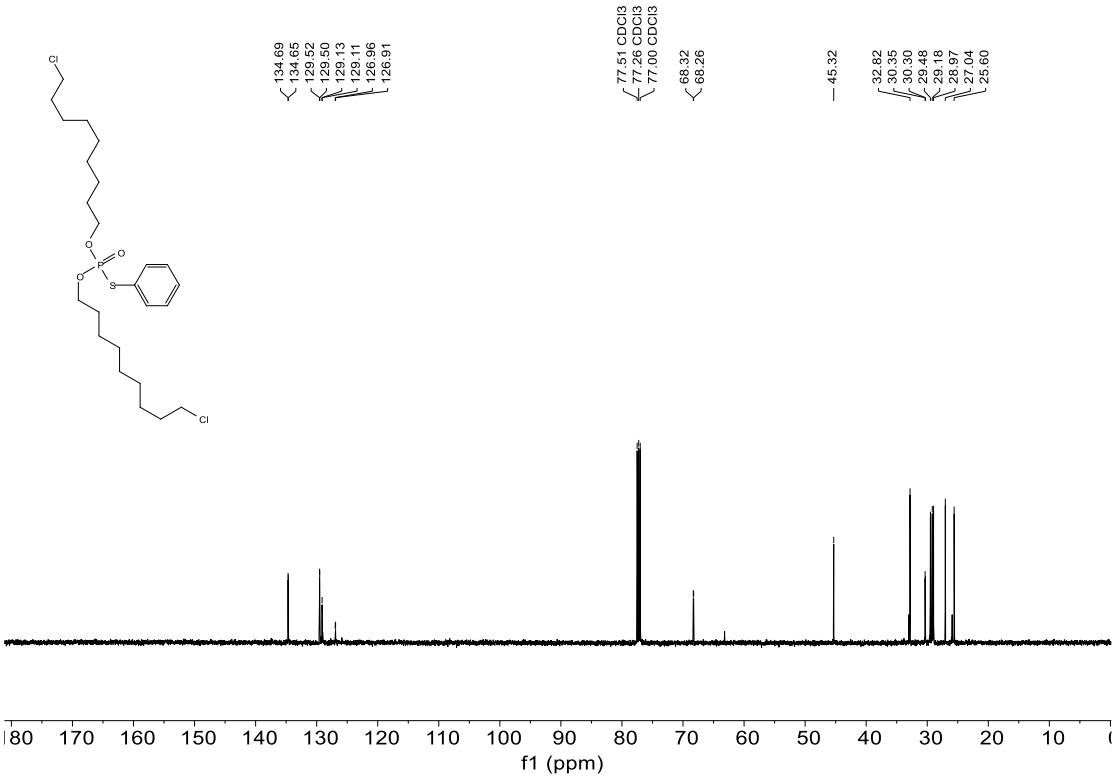
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of compound **5i**



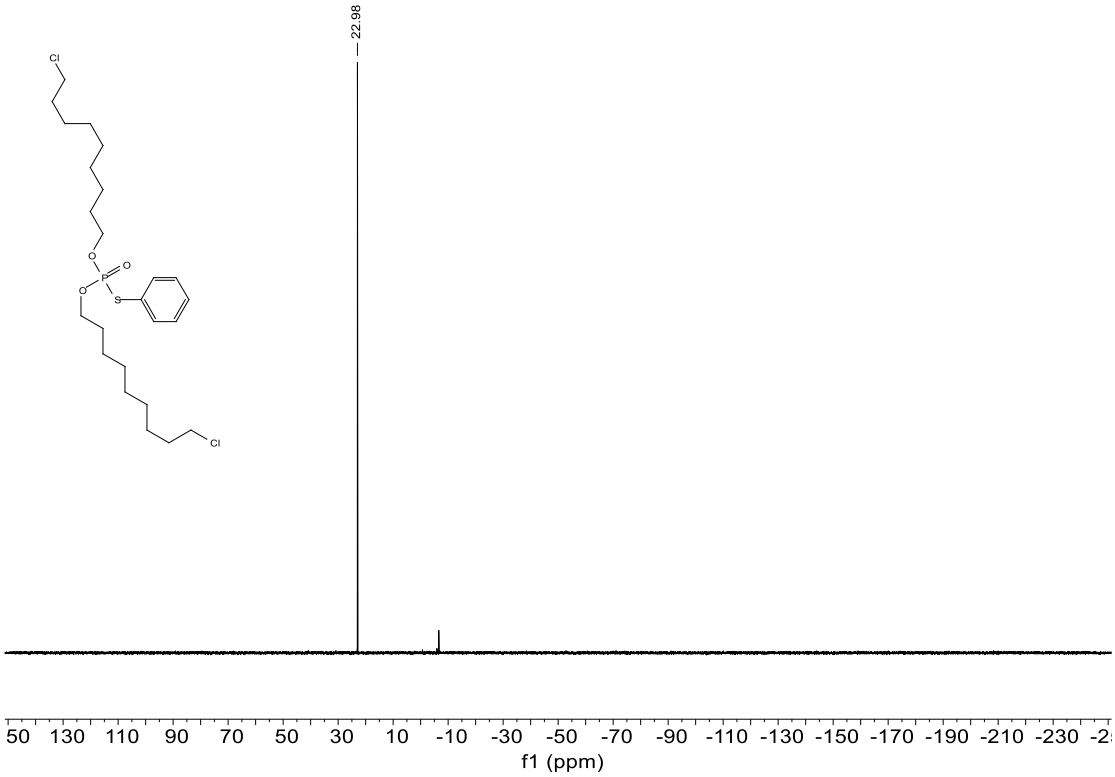
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5i**



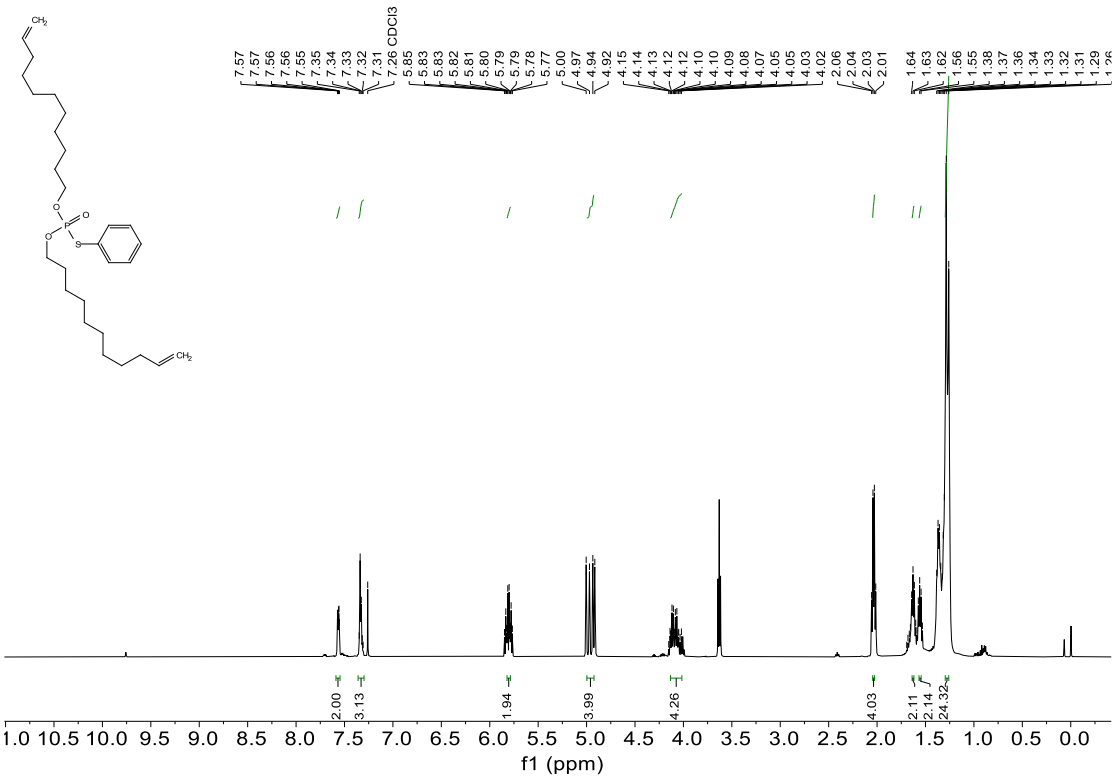
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5j**



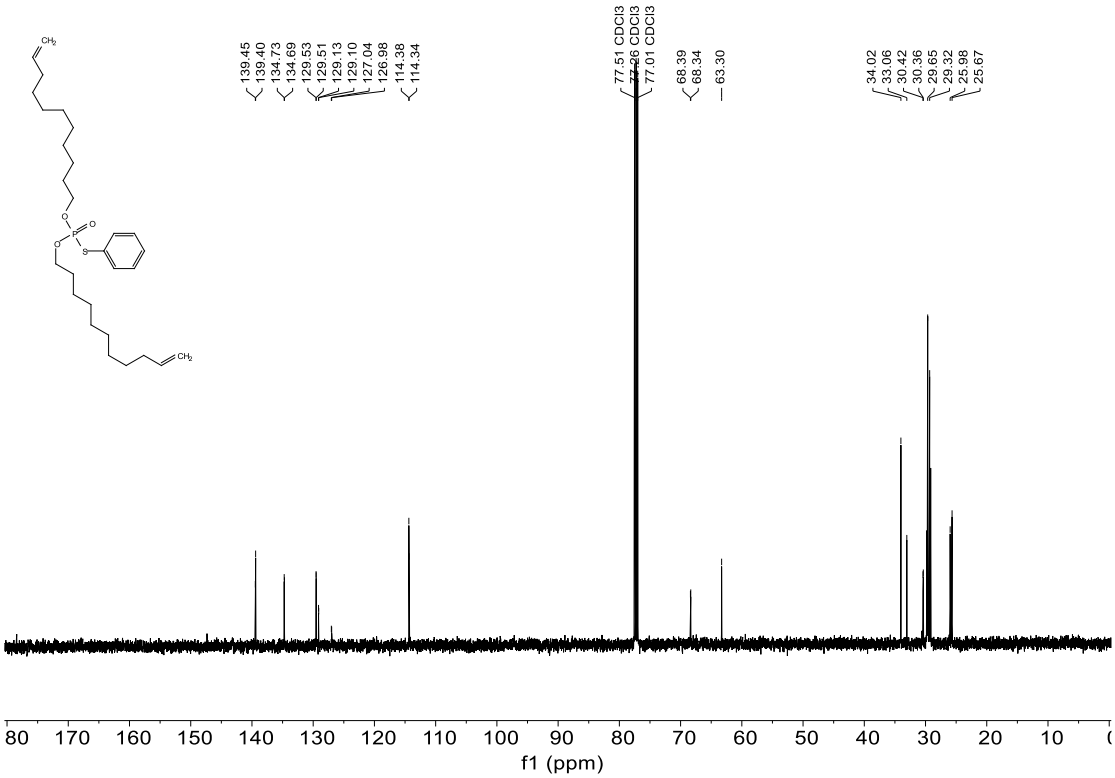
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5j**



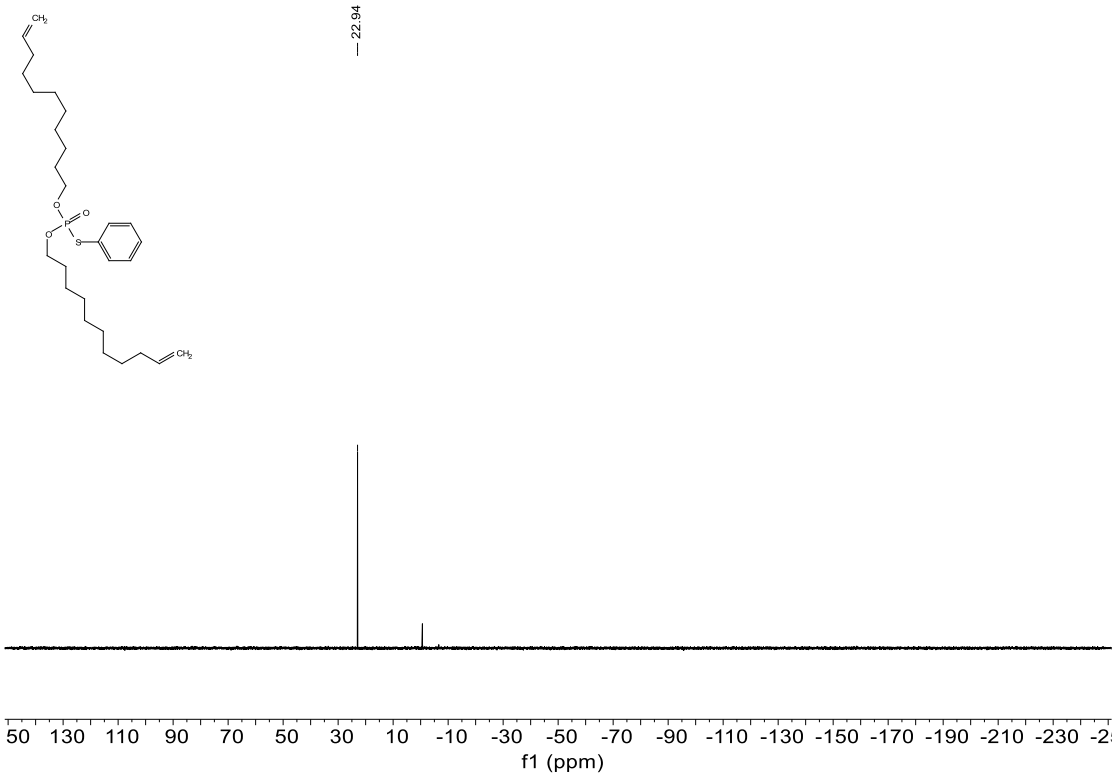
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5j**



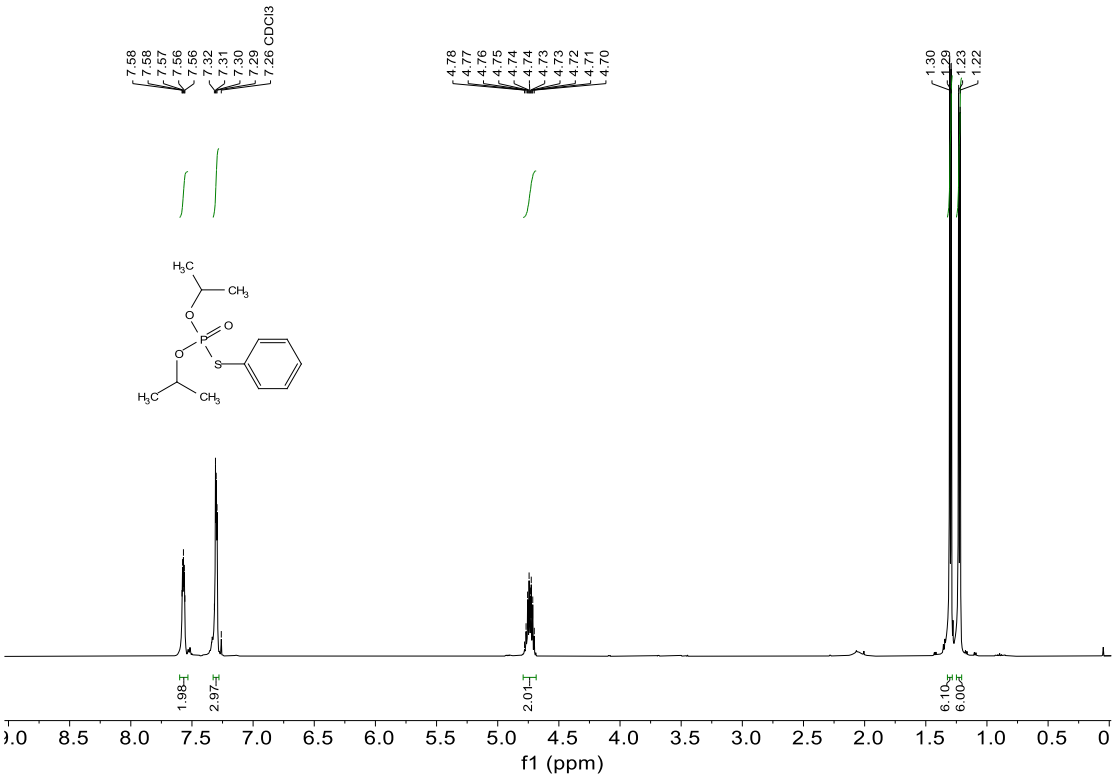
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5k**



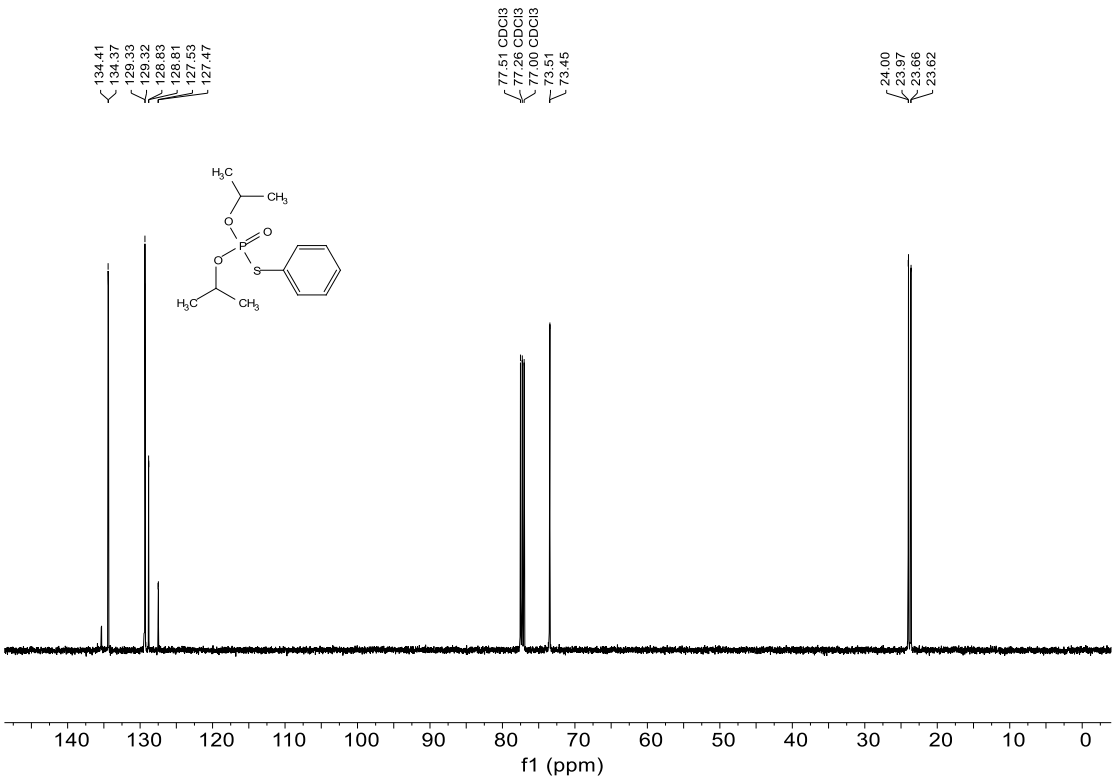
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **5k**



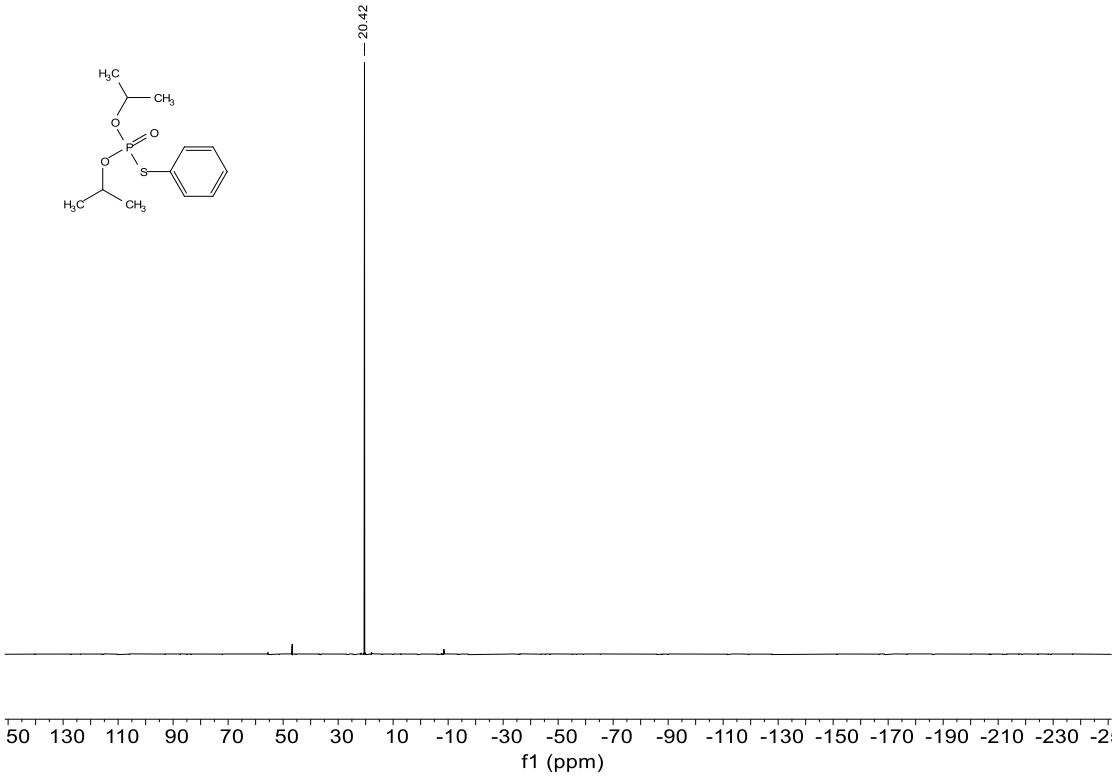
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5k**



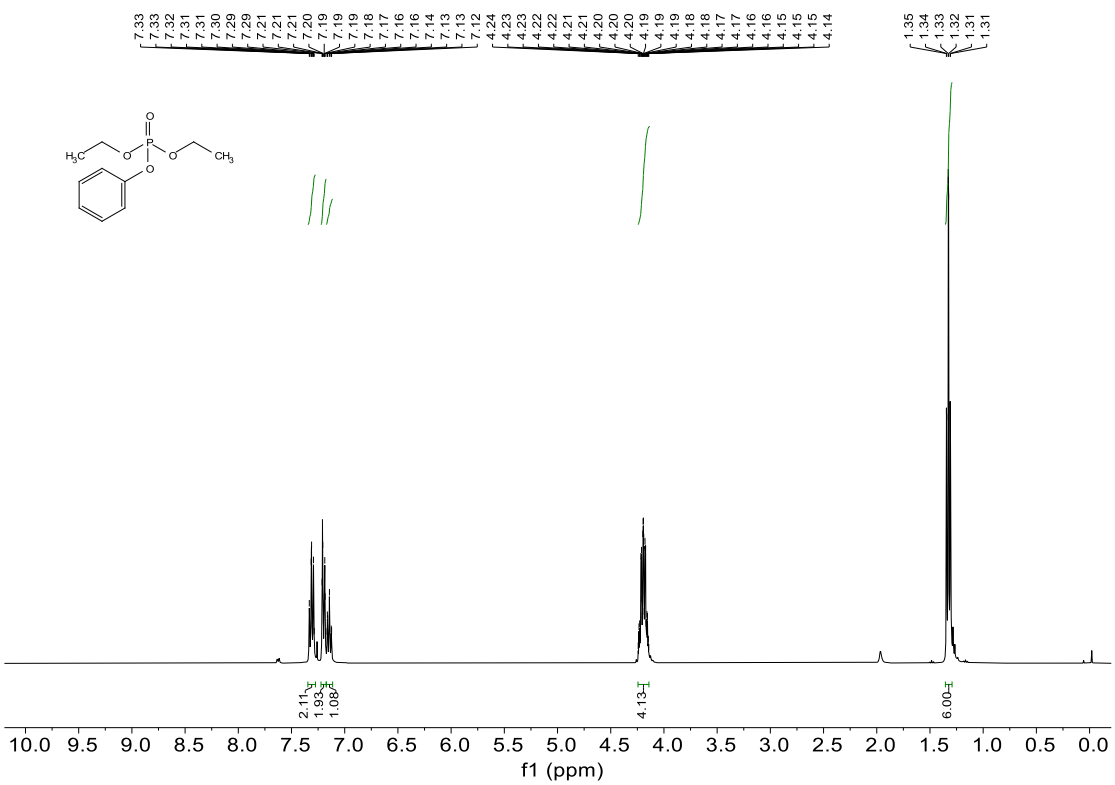
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5l**



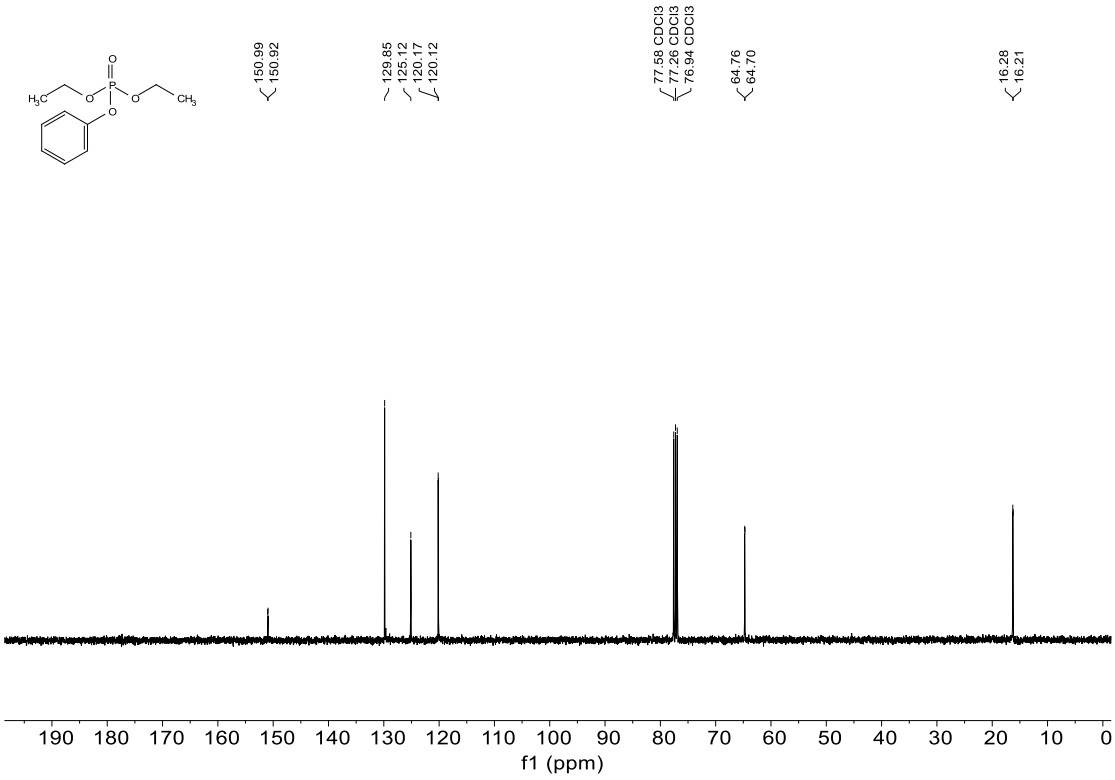
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **5l**



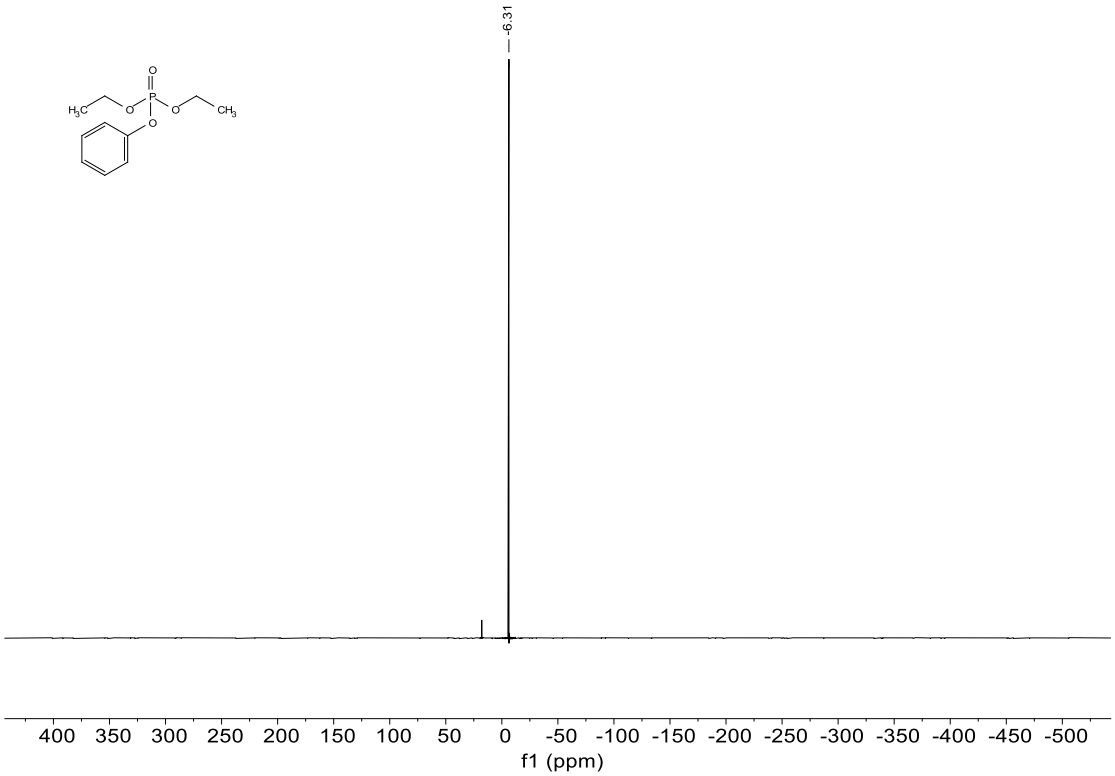
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **5l**



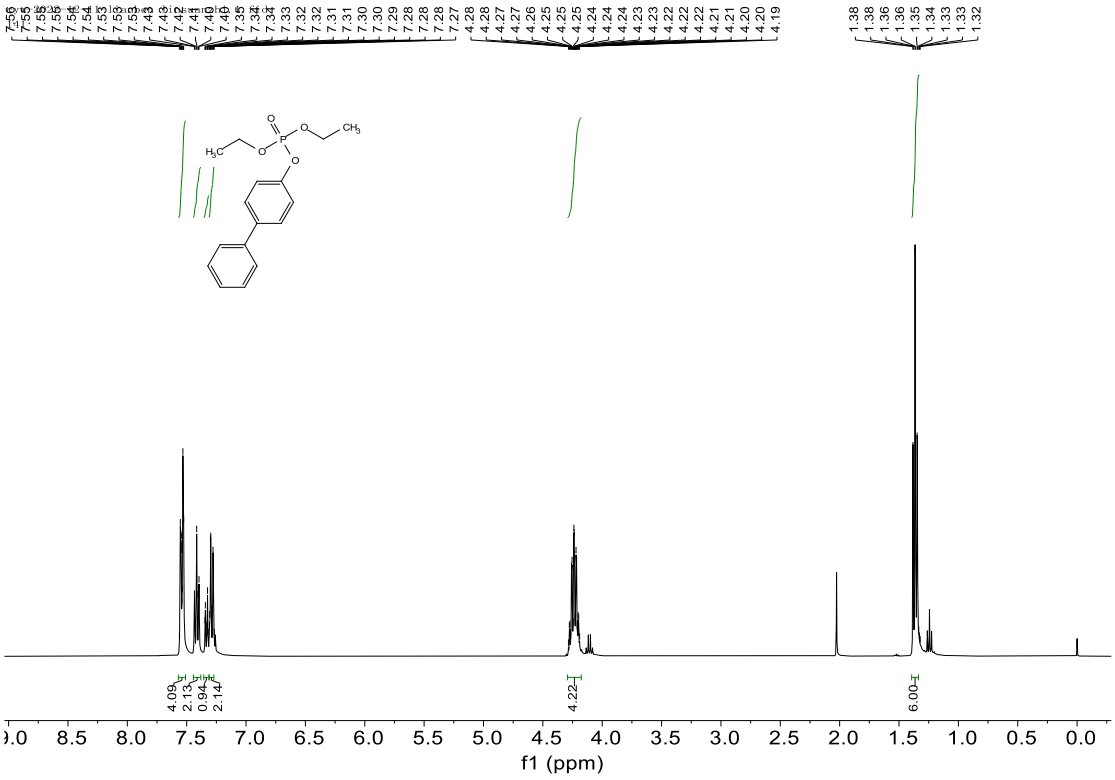
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **7a**



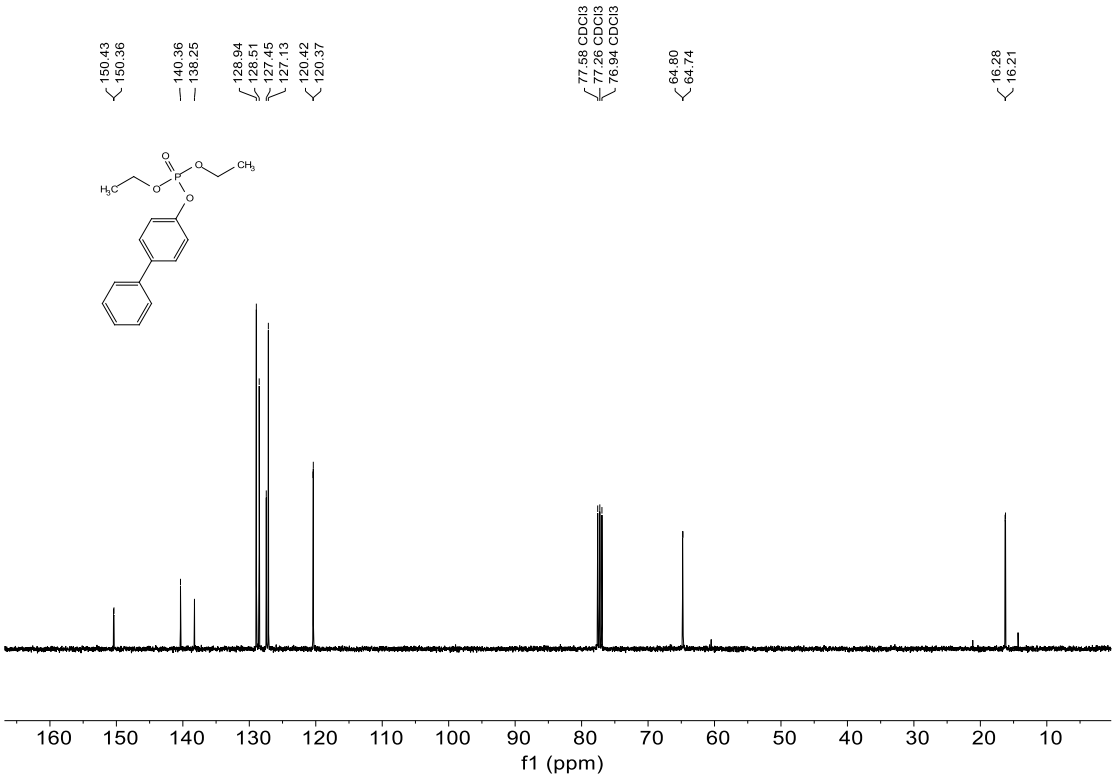
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) spectrum of compound **7a**



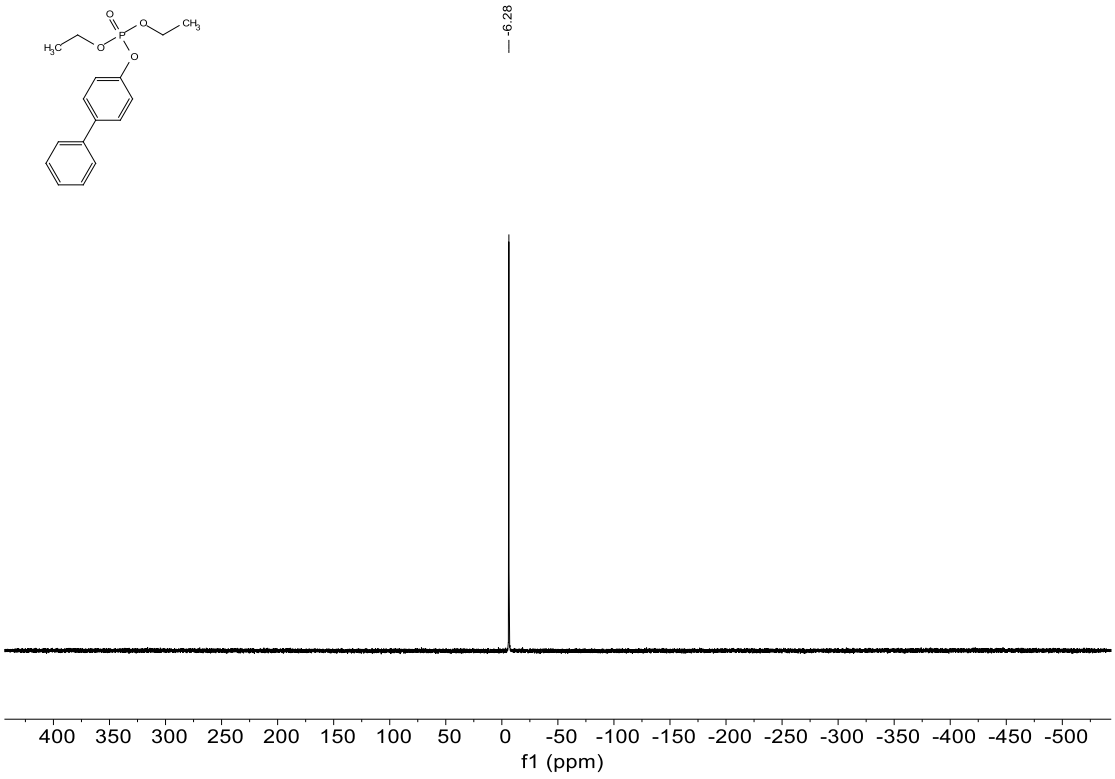
$^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of compound **7a**



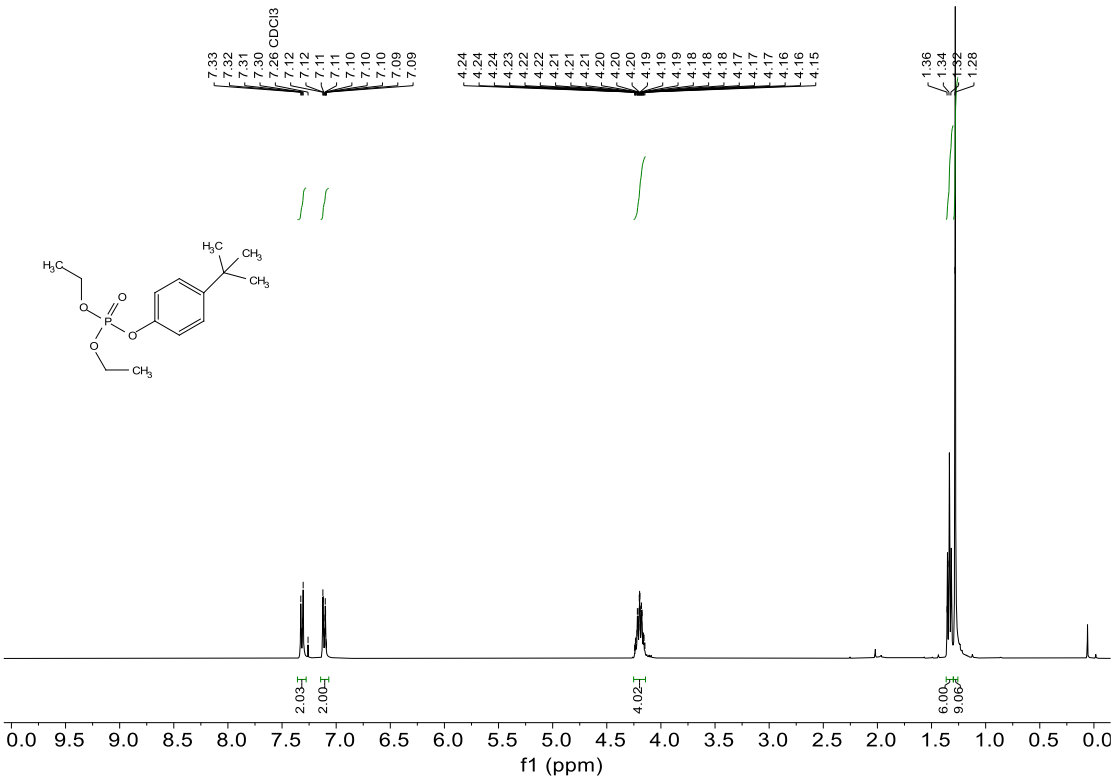
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7b**



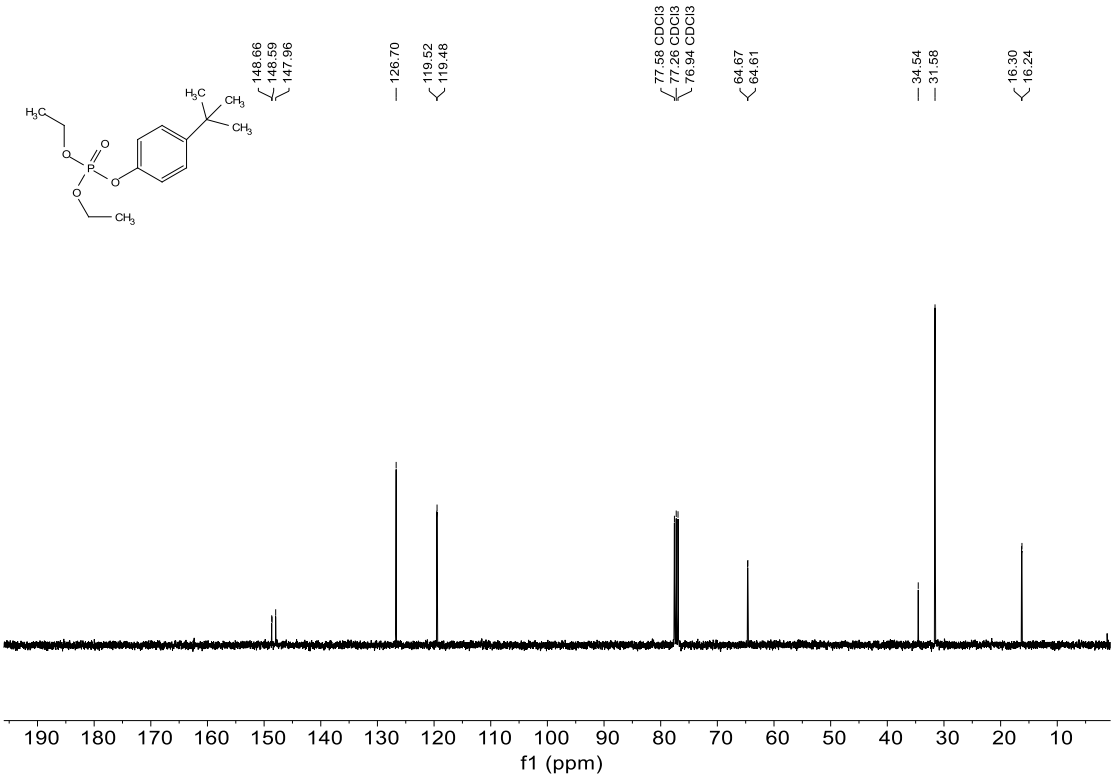
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **7b**



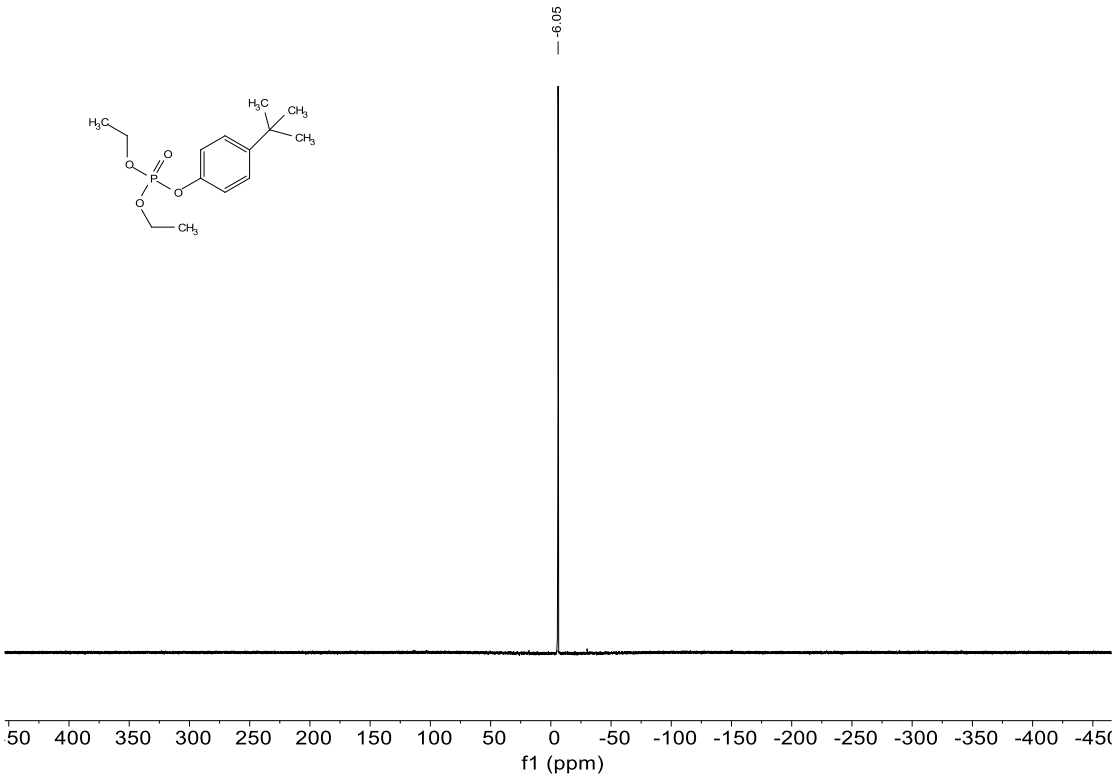
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7b**



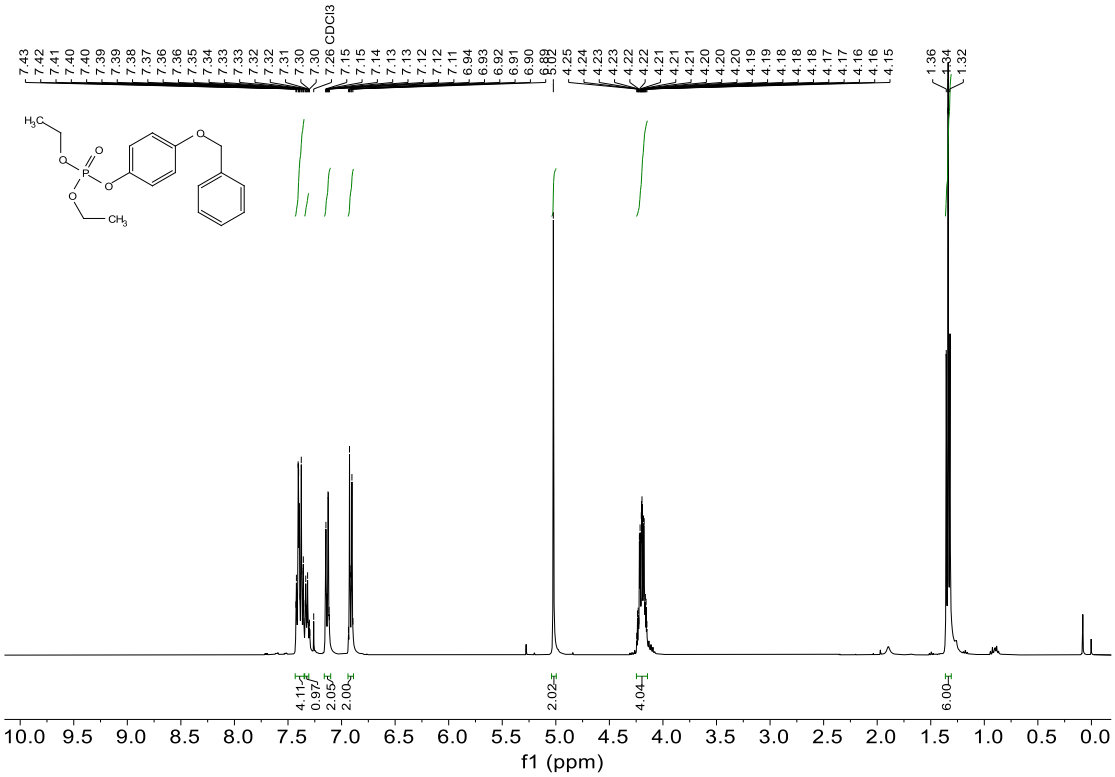
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7c**



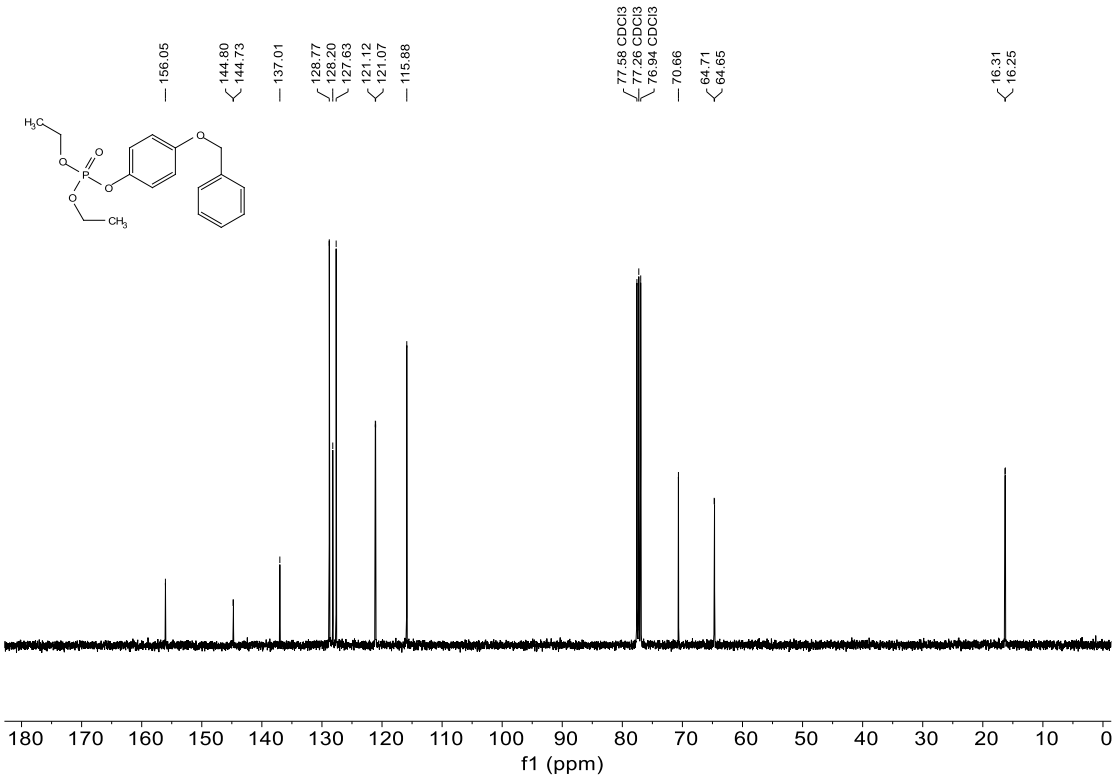
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **7c**



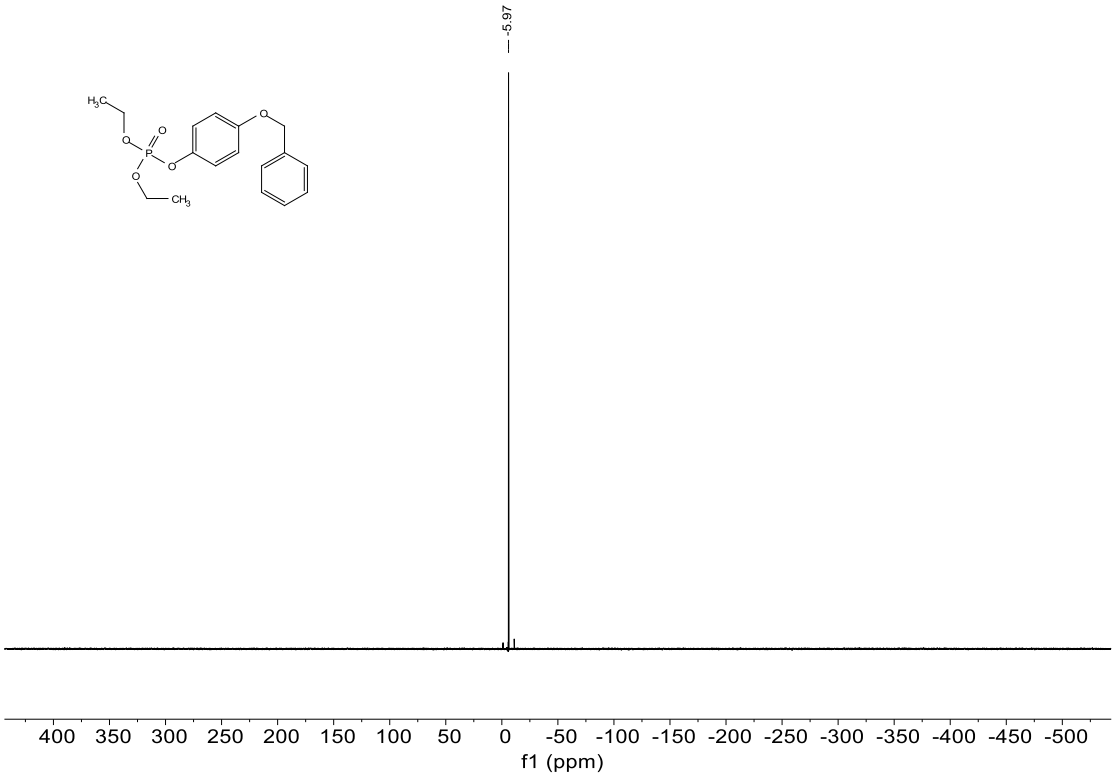
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7c**



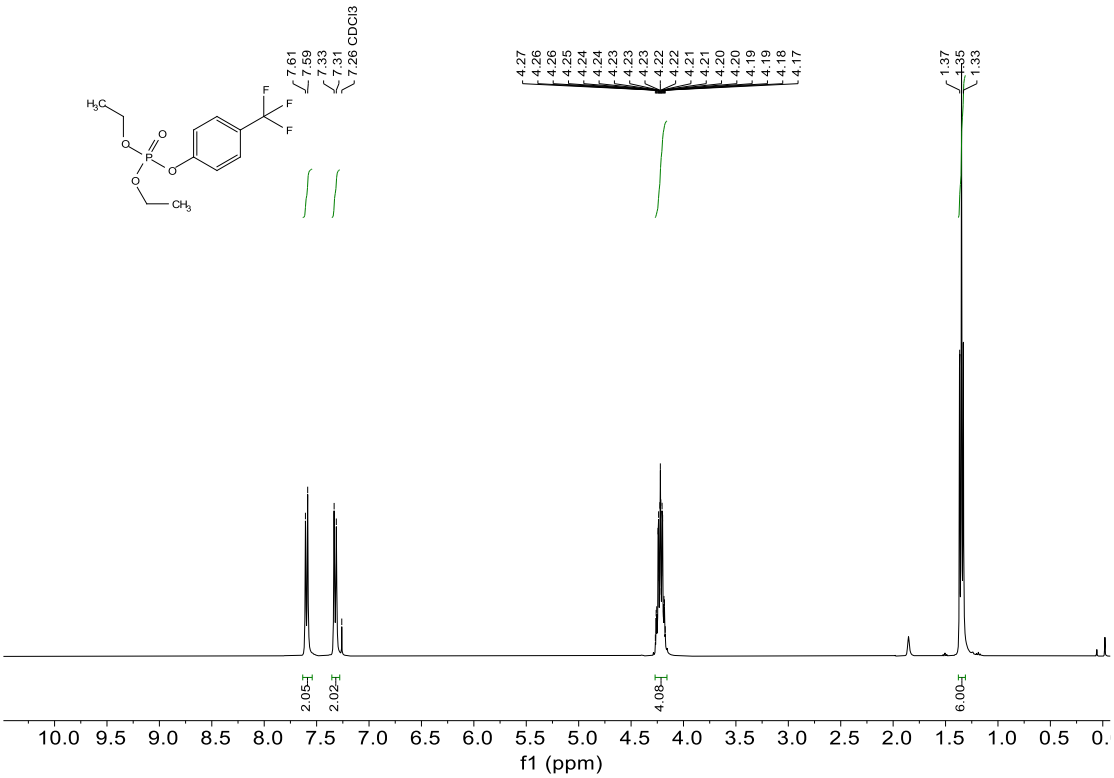
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7d**



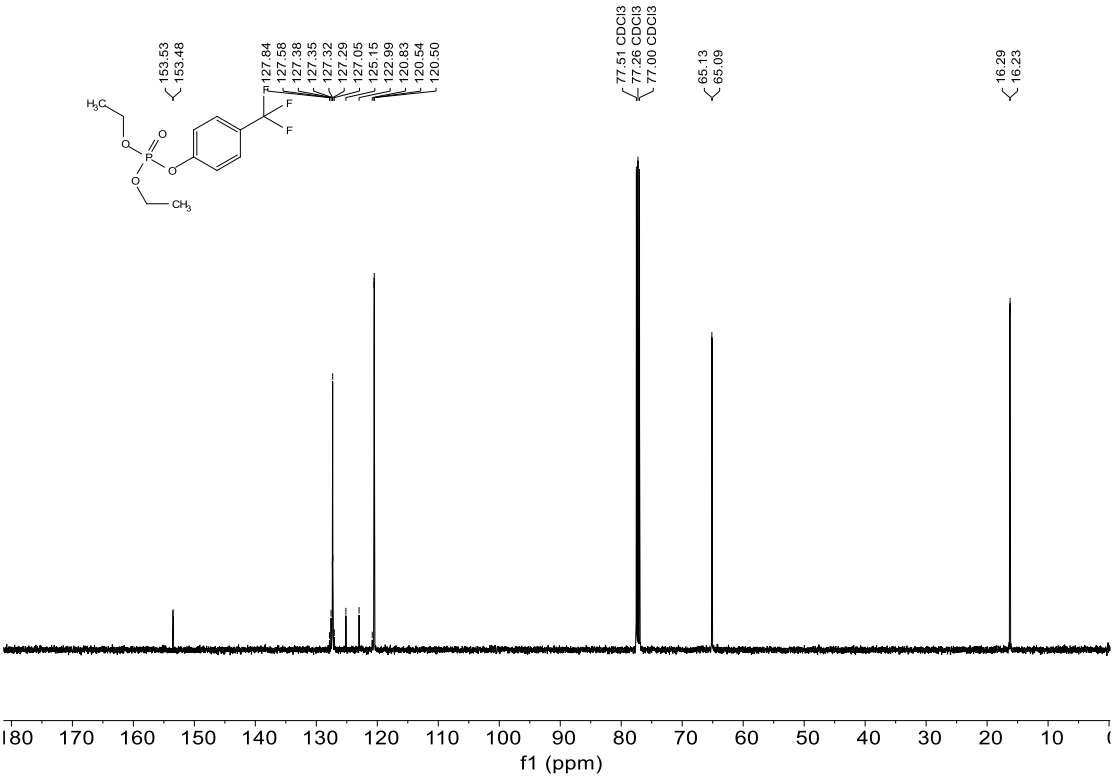
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **7d**



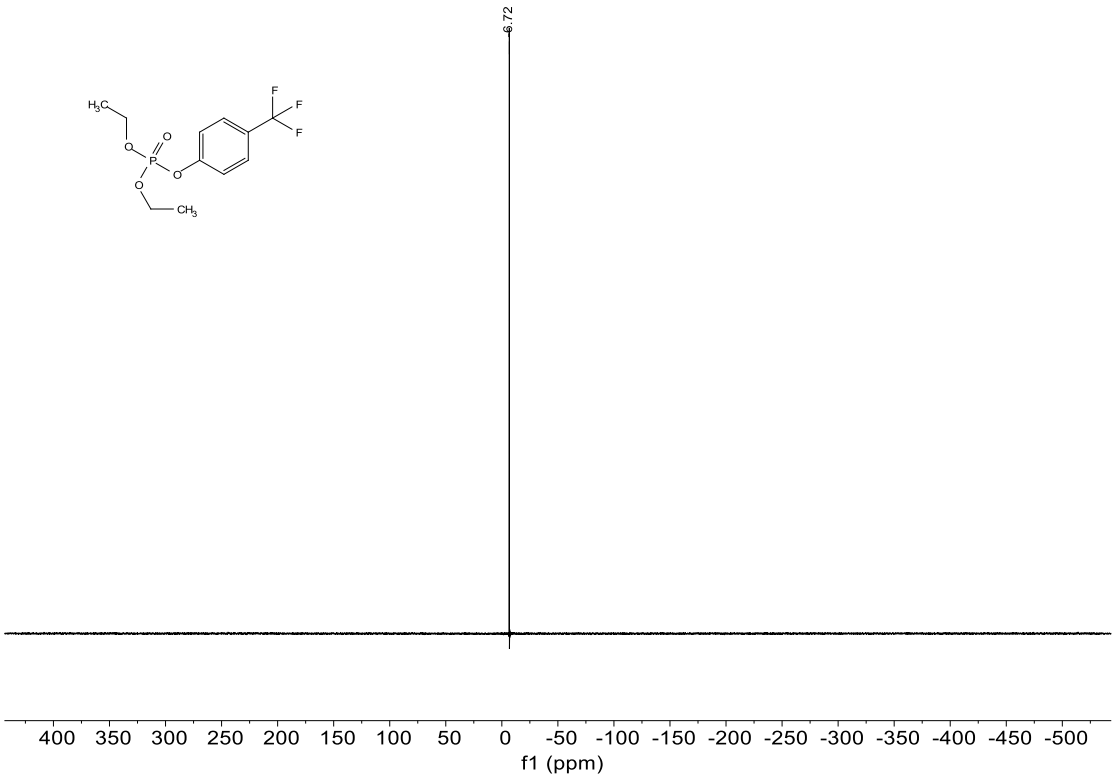
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7d**



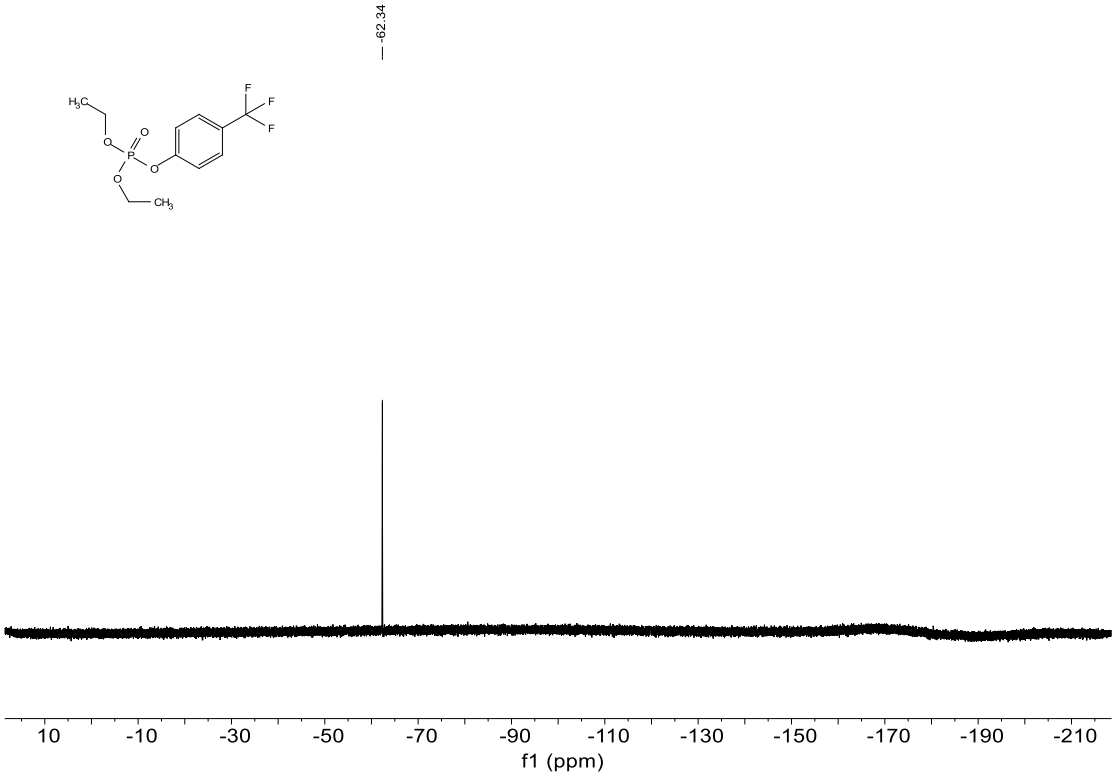
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **7e**



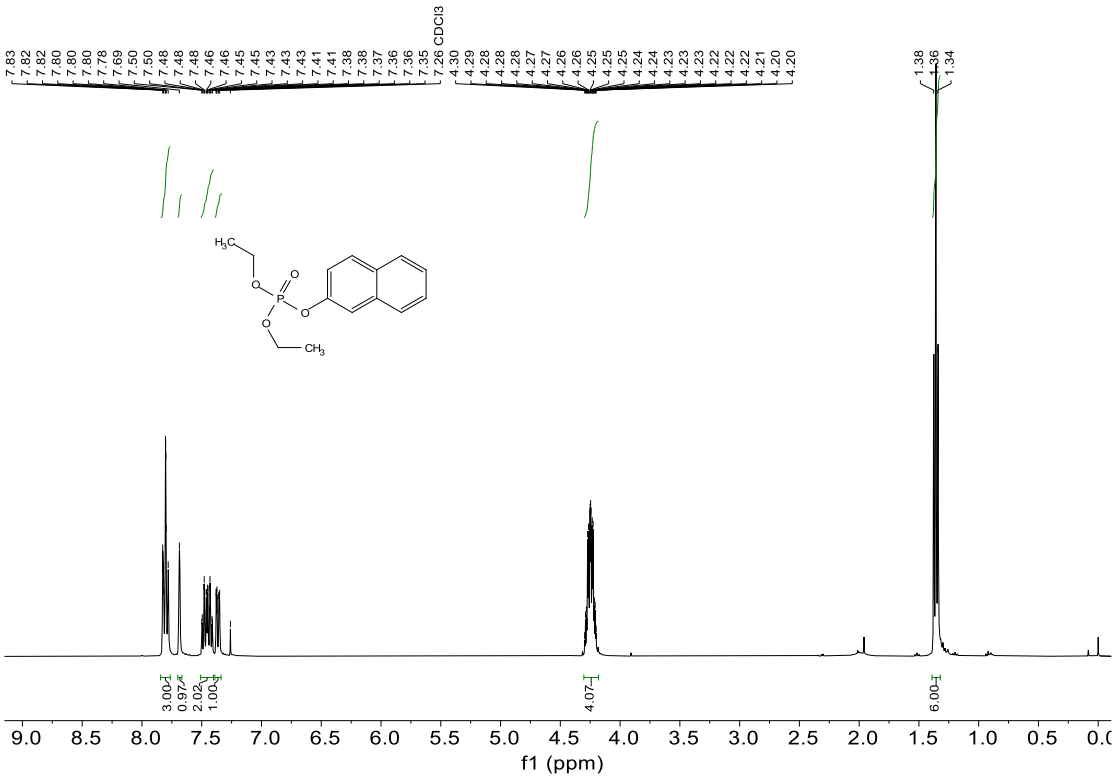
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **7e**



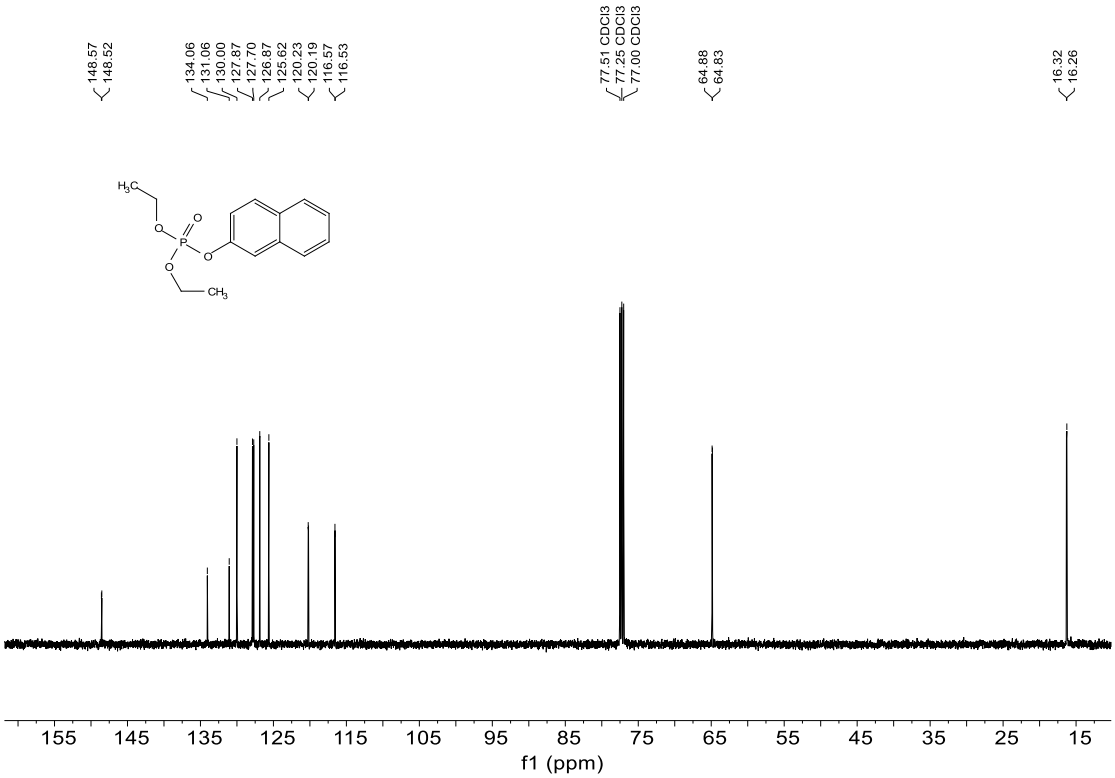
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7e**



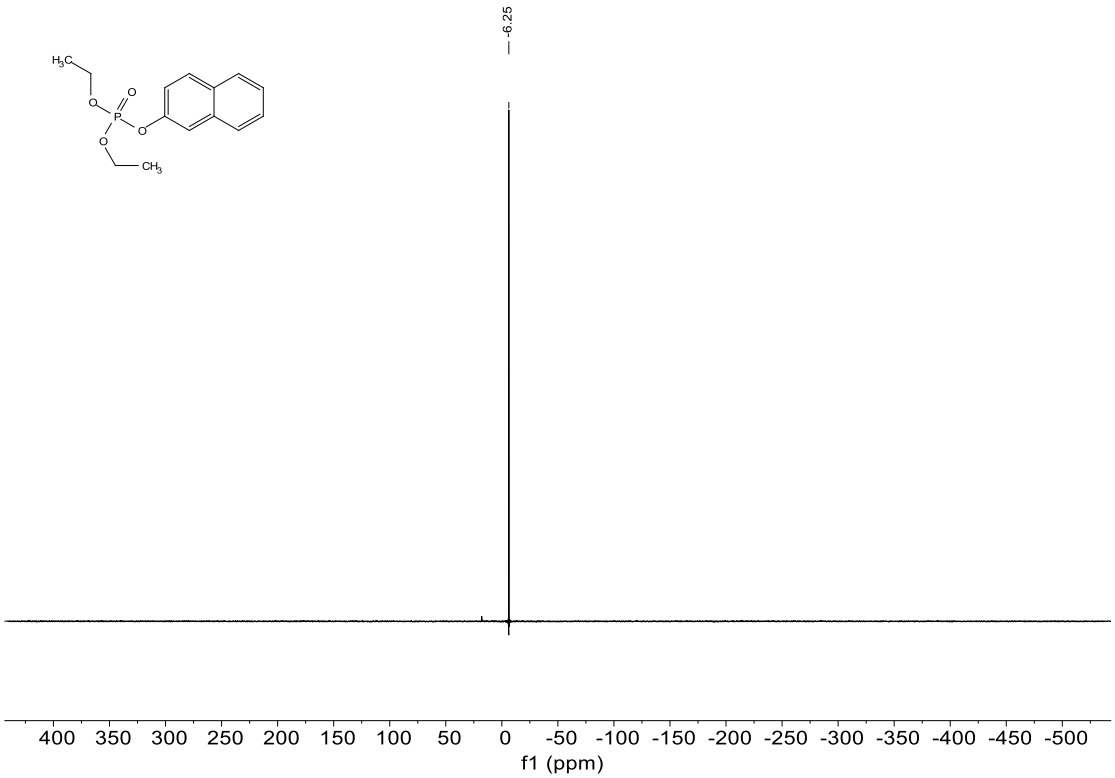
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$) spectrum of compound **7e**



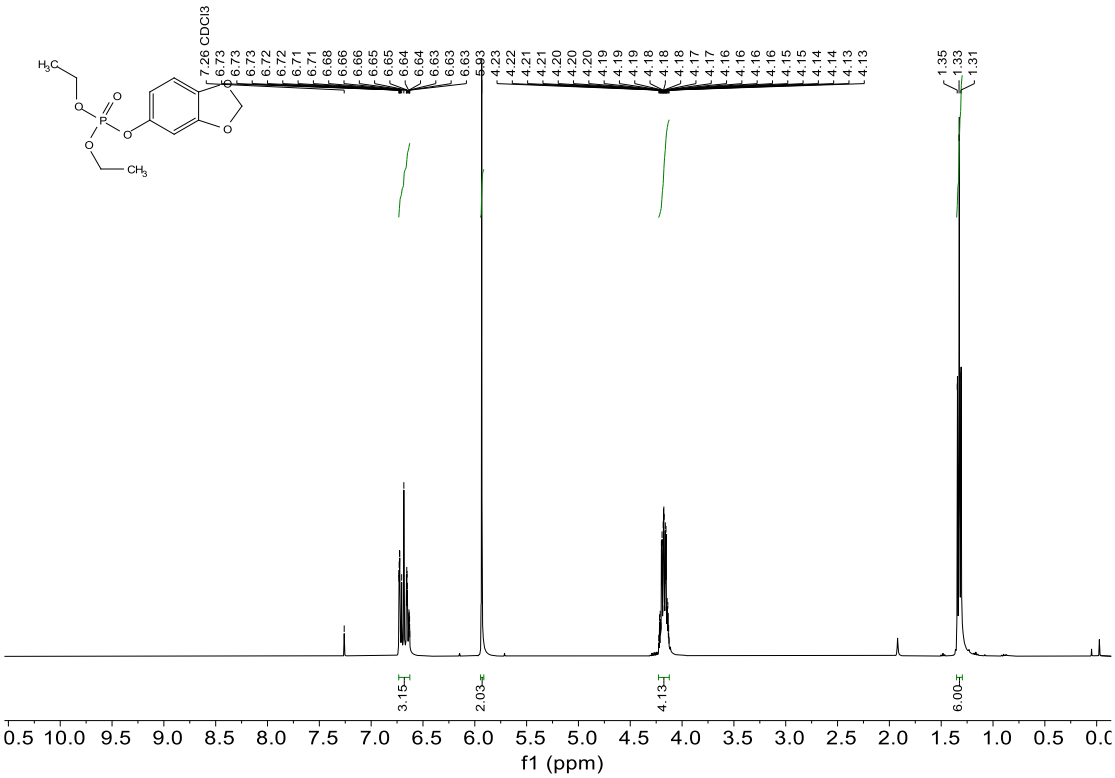
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7f**



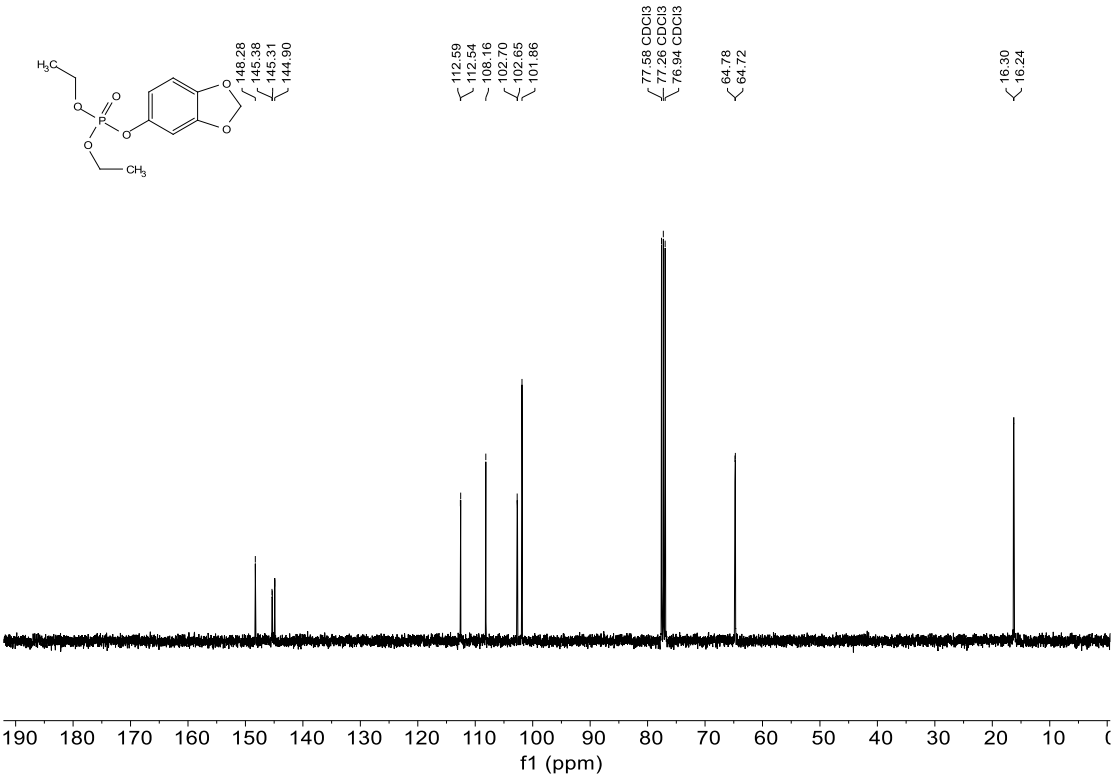
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) spectrum of compound **7f**



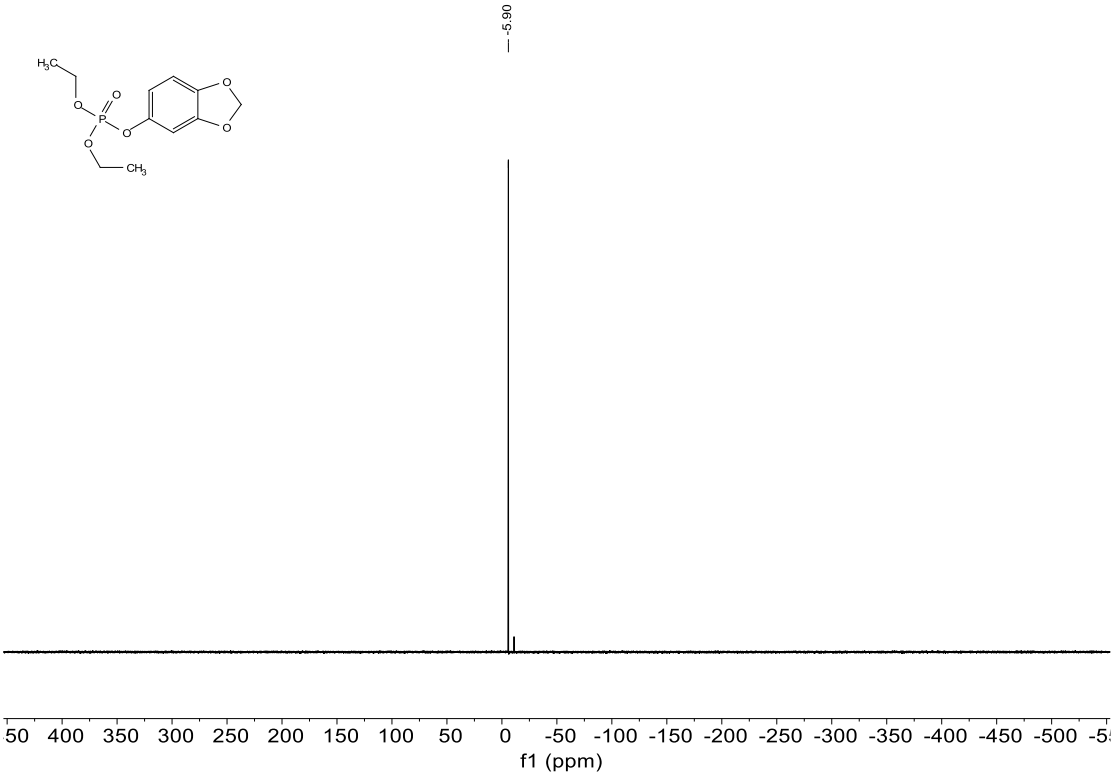
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7f**



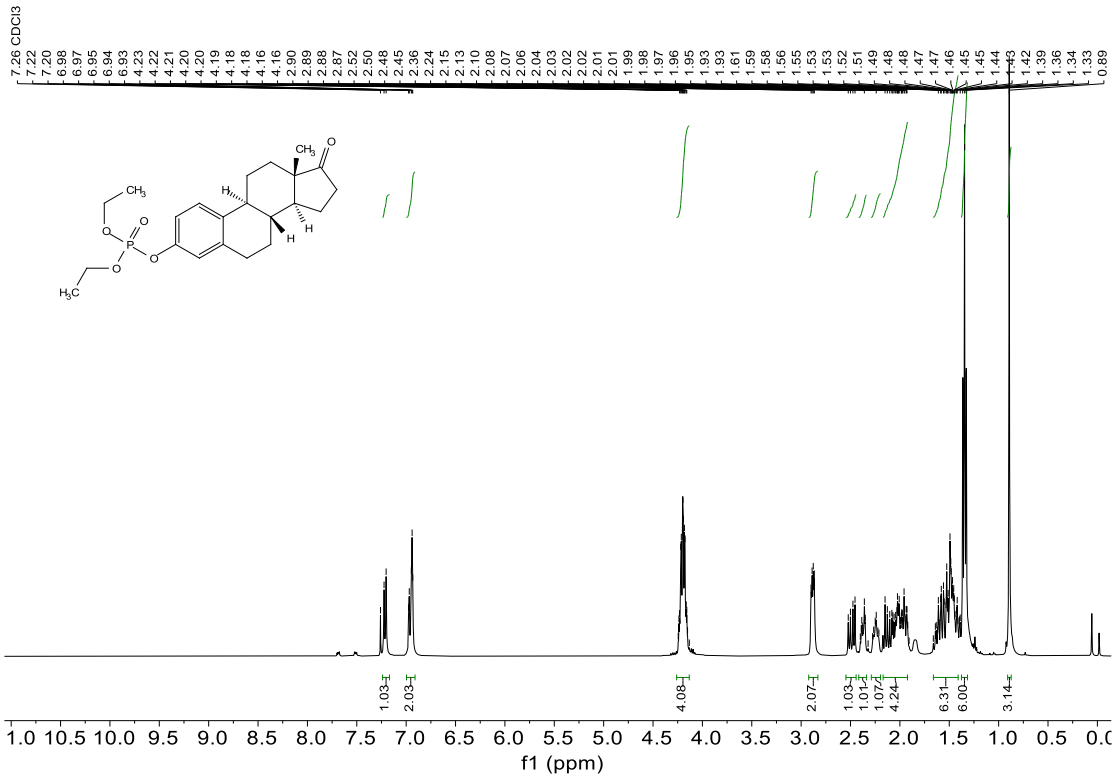
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7g**



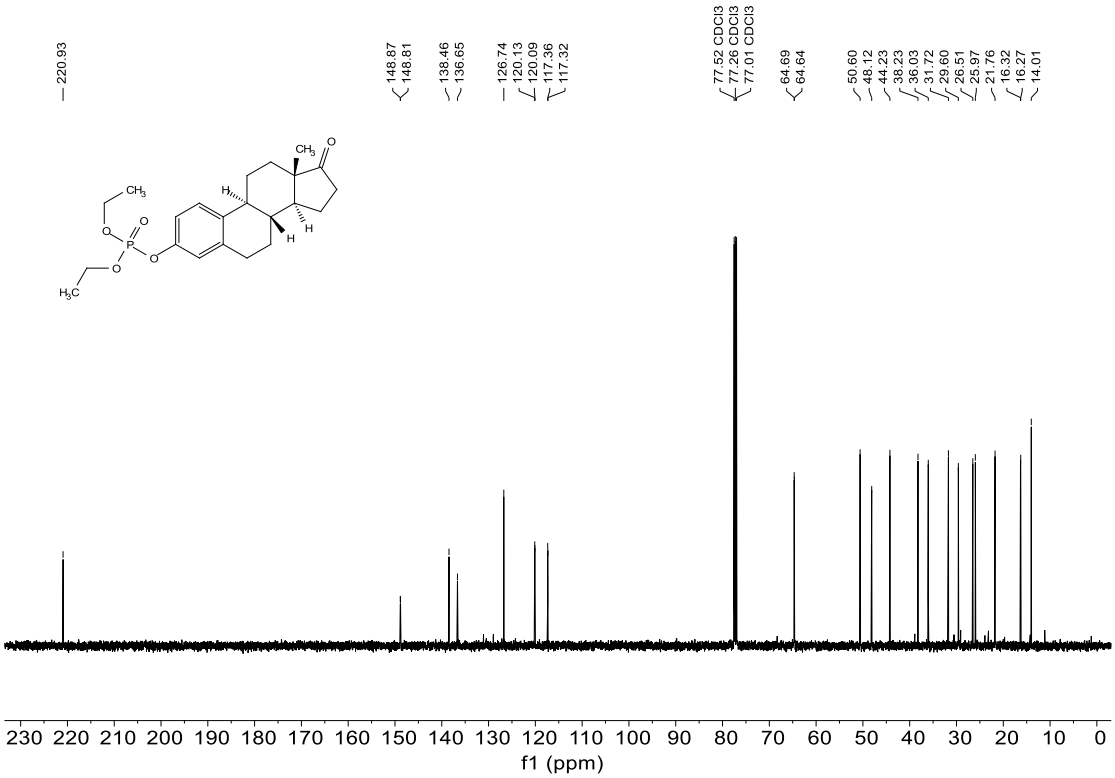
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **7g**



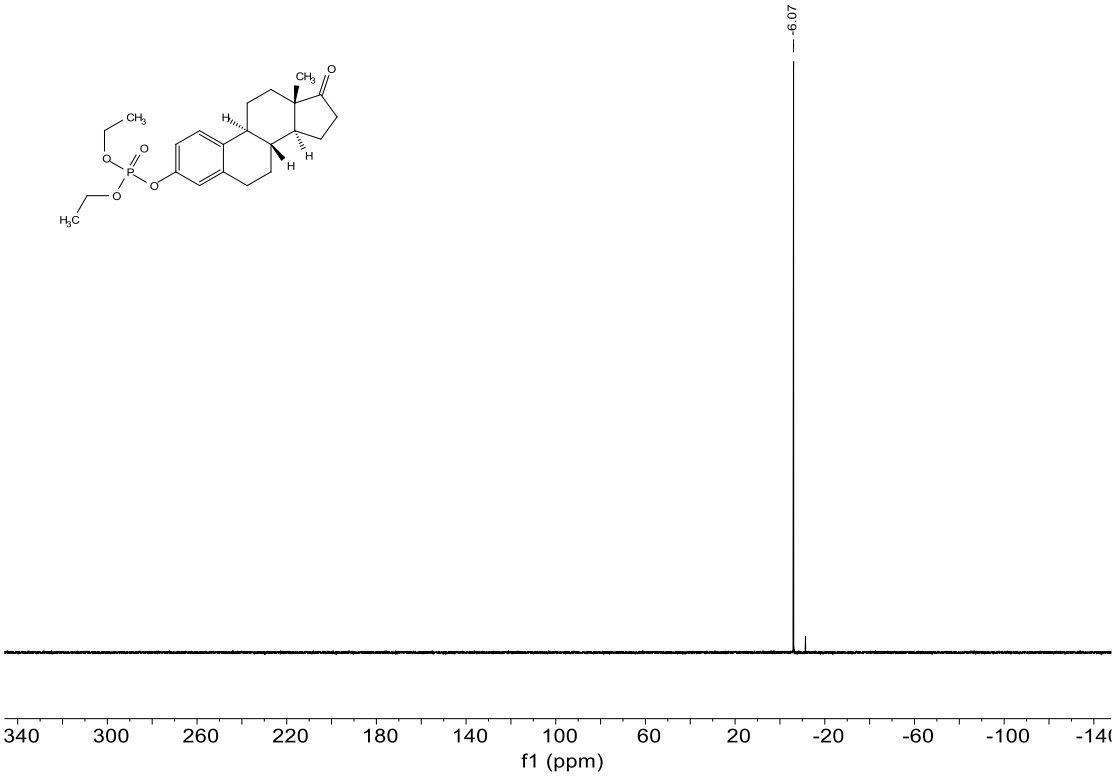
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7g**



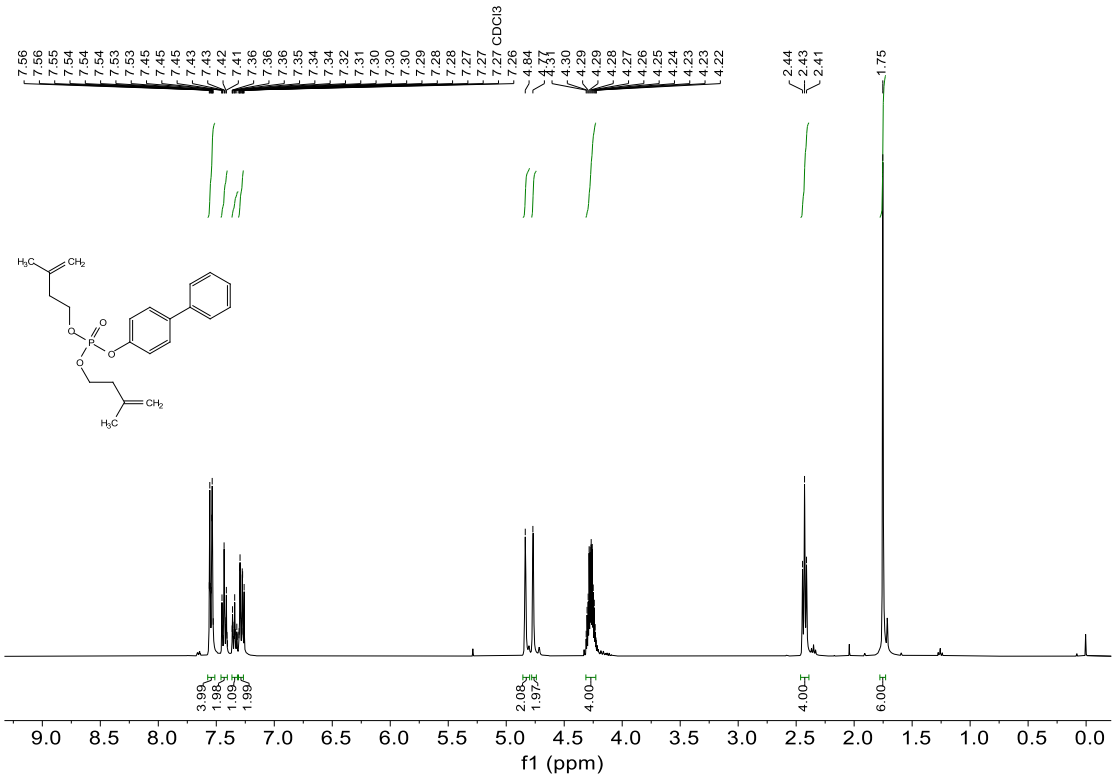
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7h**



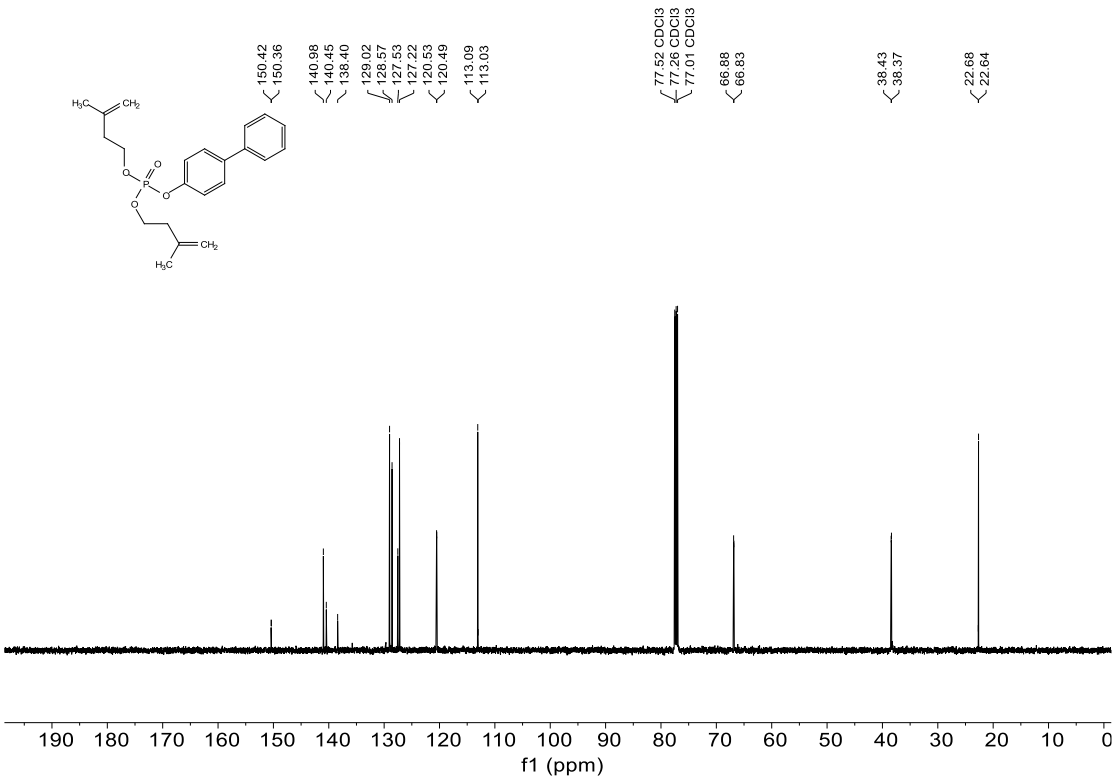
^{13}C{^{1}H} NMR (101MHz, $CDCl_3$) spectrum of compound **7h**



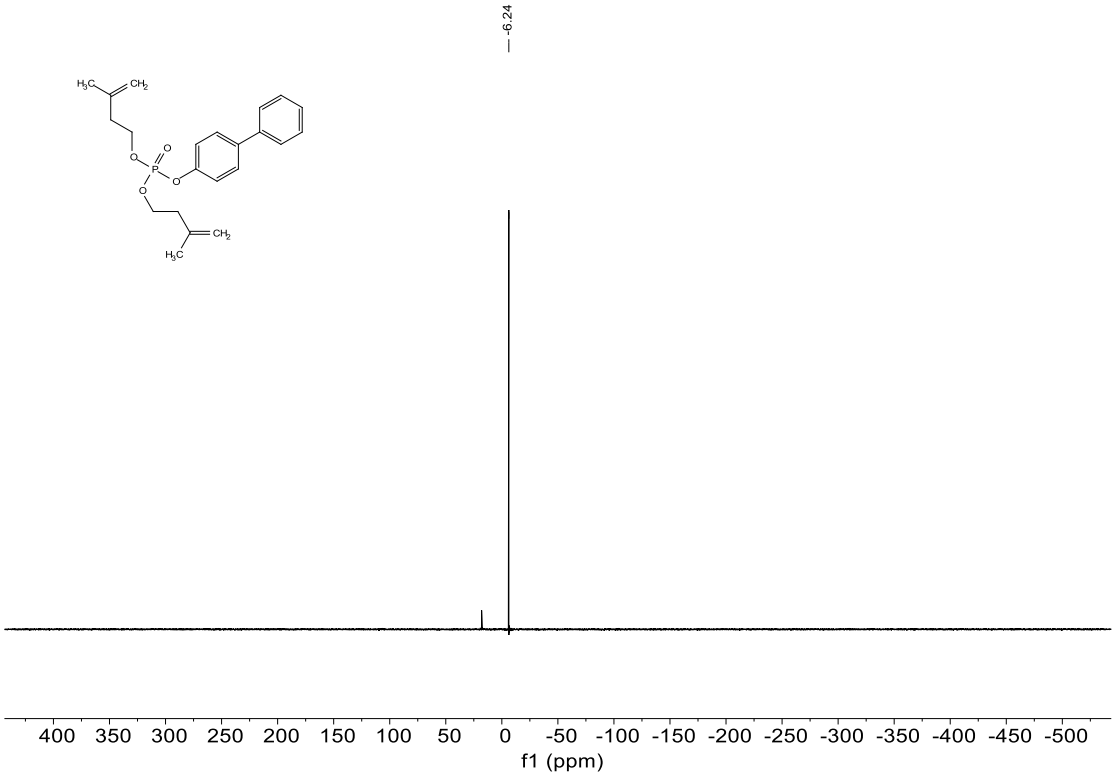
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7h**



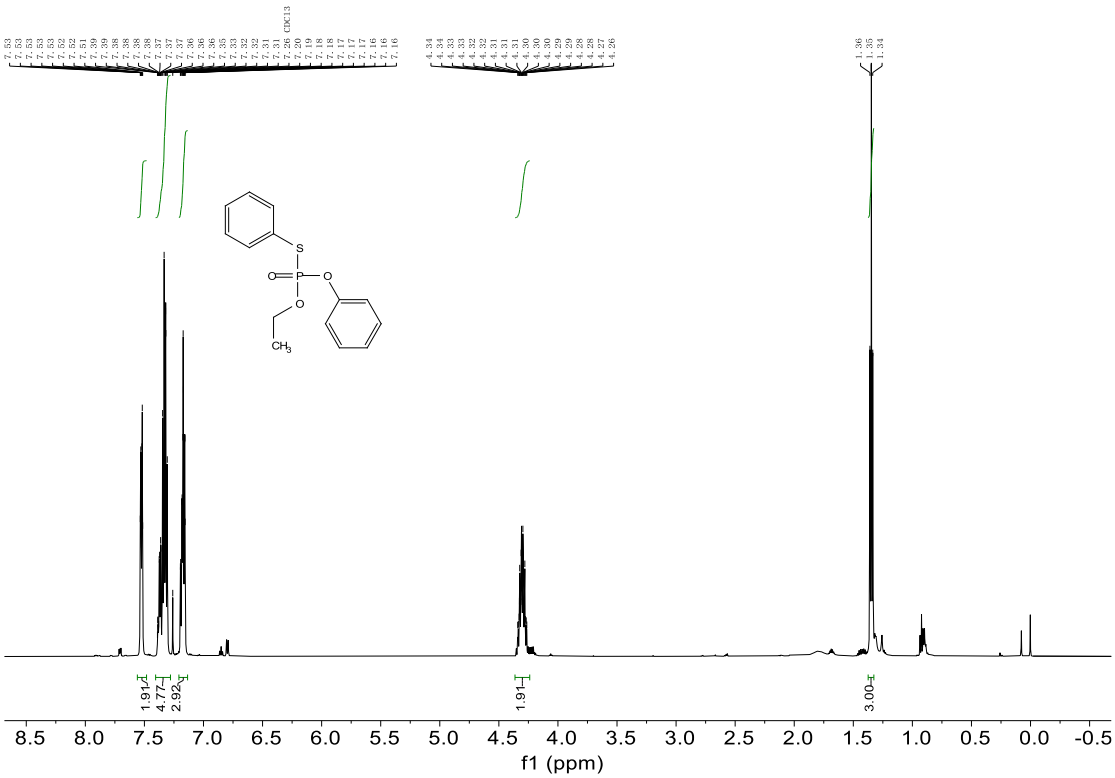
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7i**



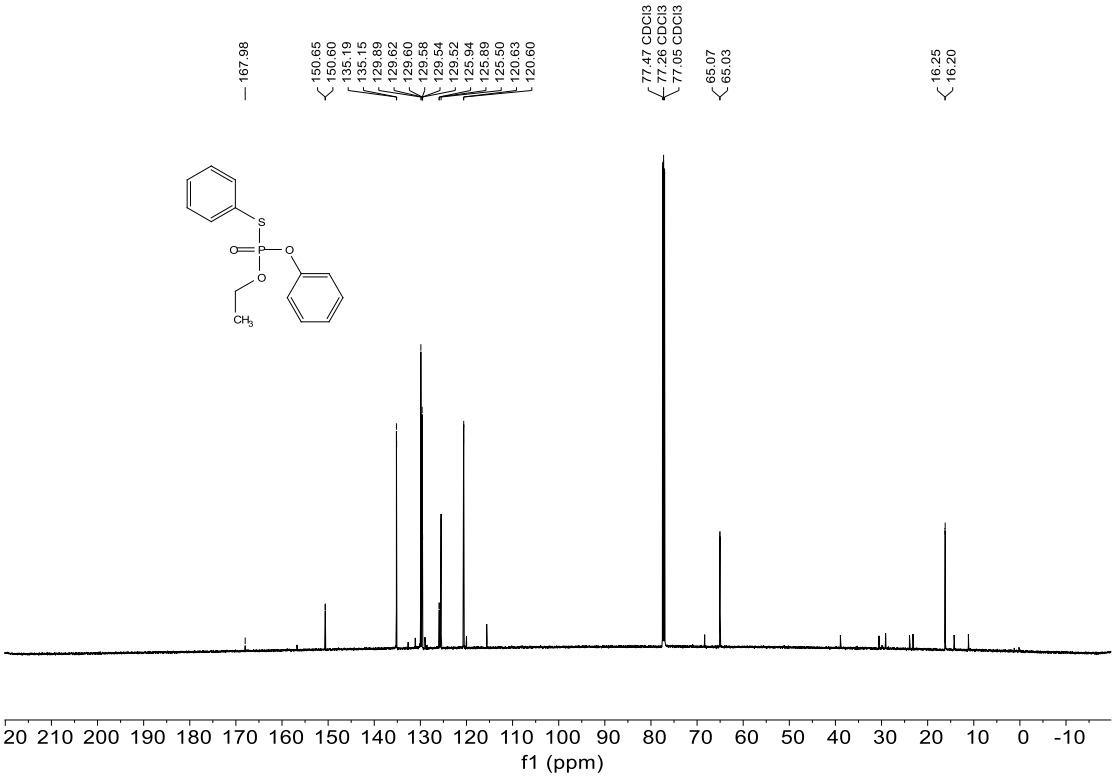
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **7i**



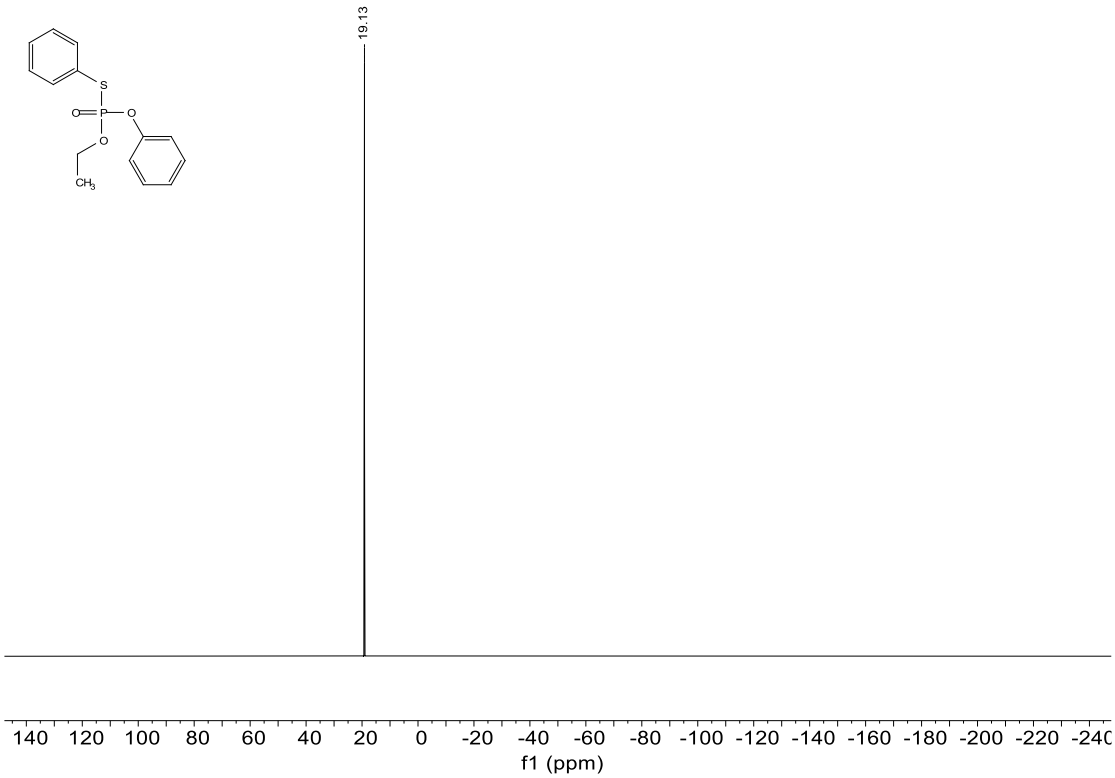
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **7i**



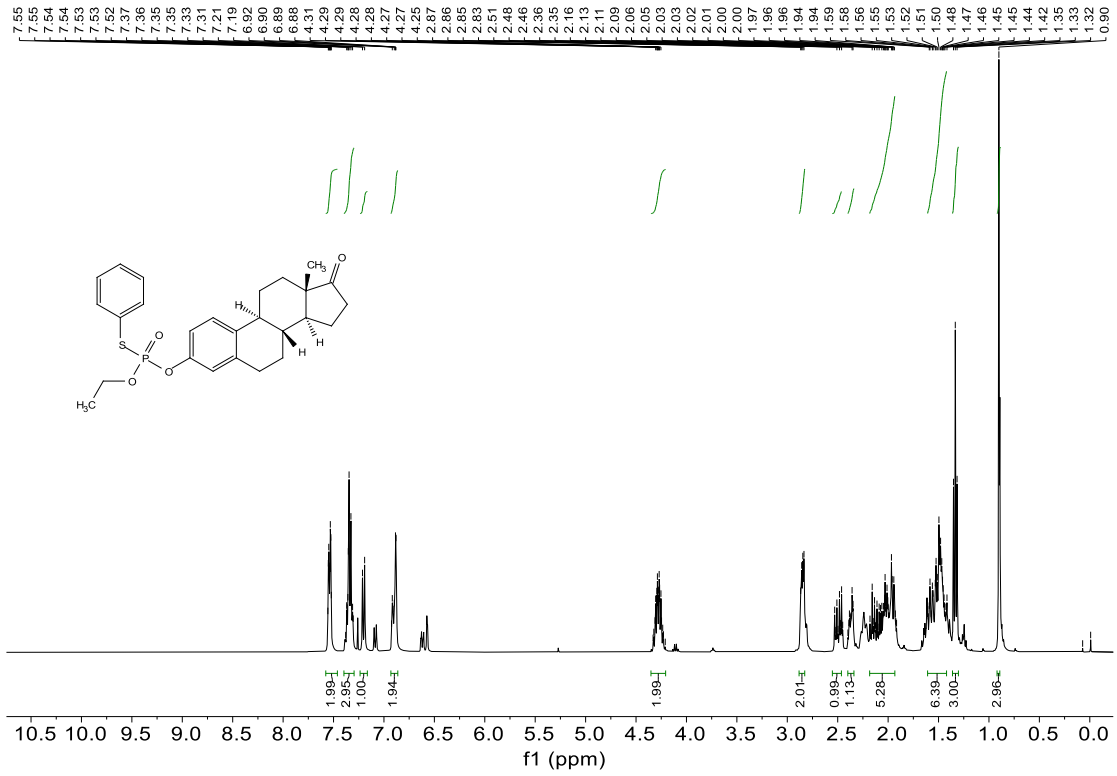
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **8a**



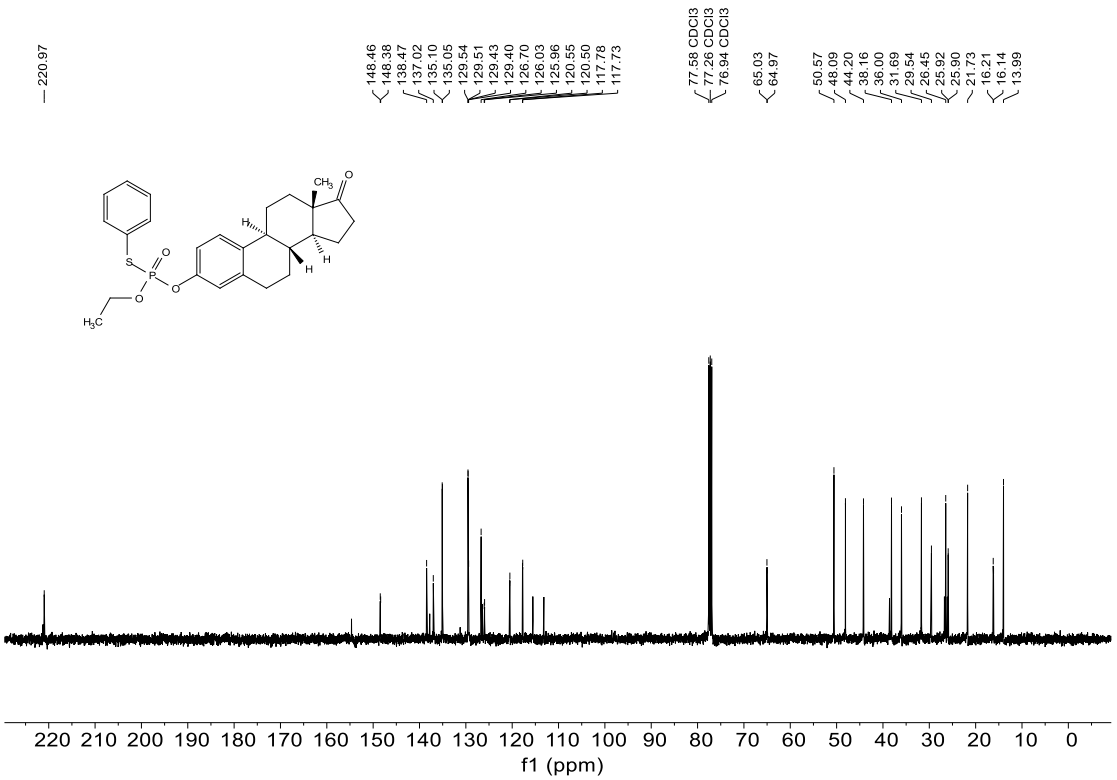
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) spectrum of compound **8a**



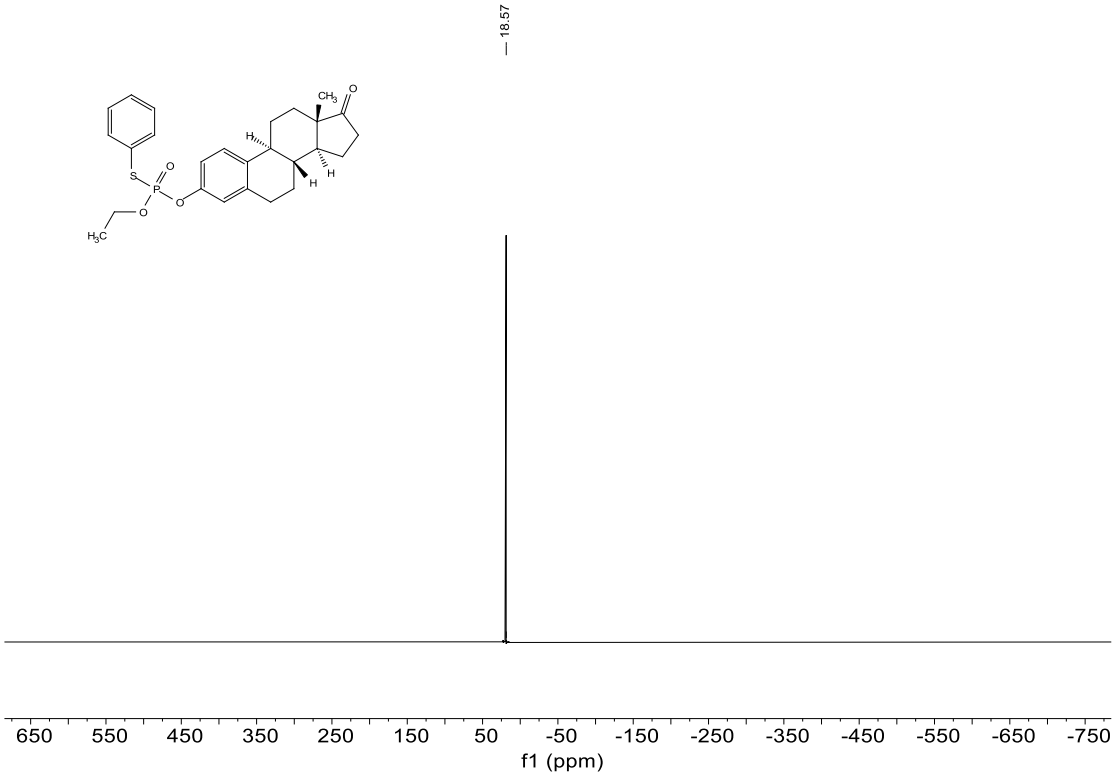
$^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of compound **8a**



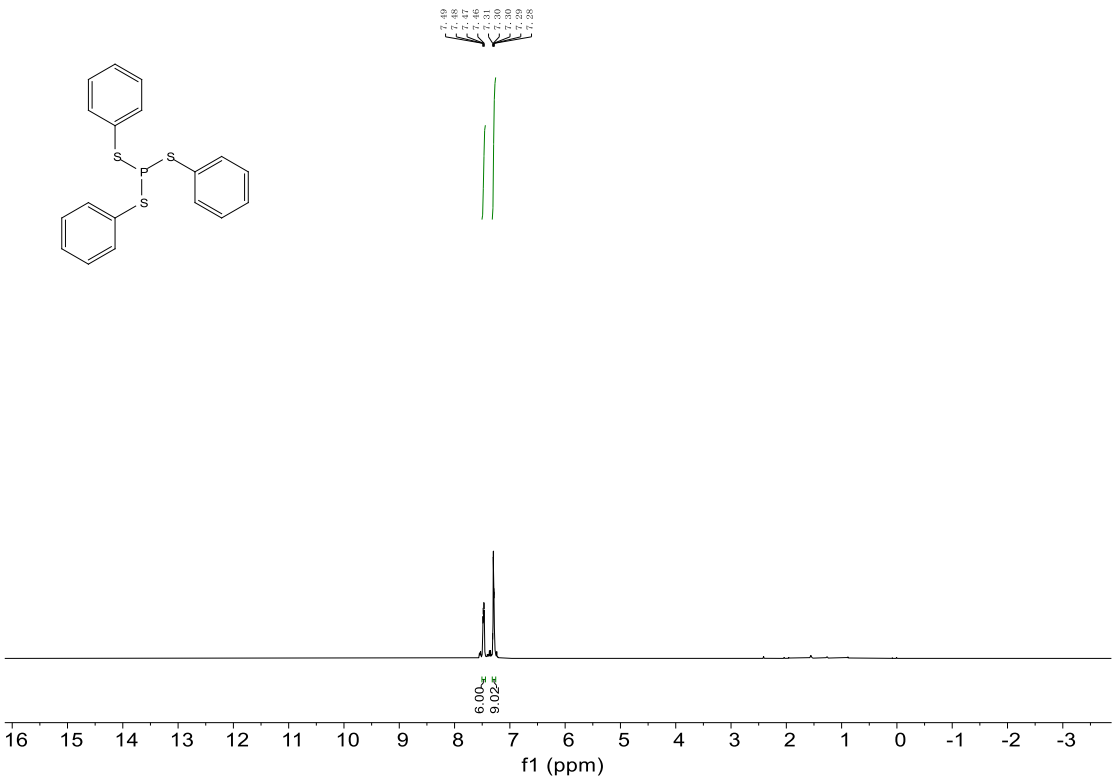
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8b**



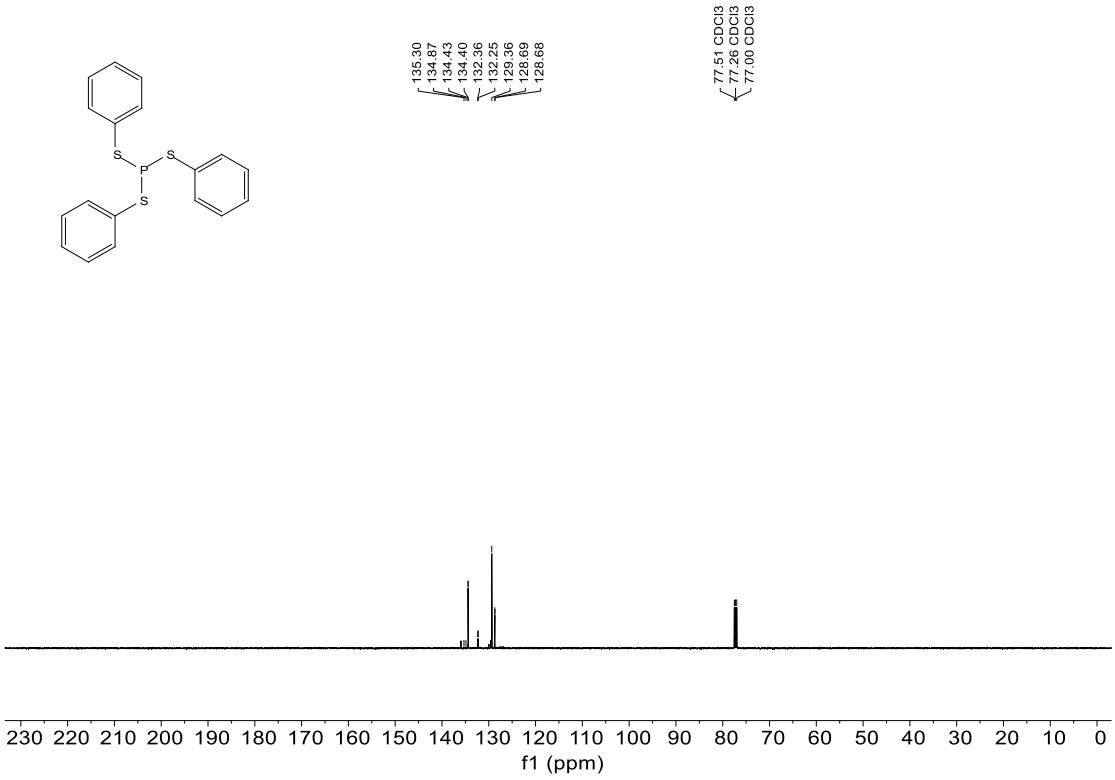
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of compound **8b**



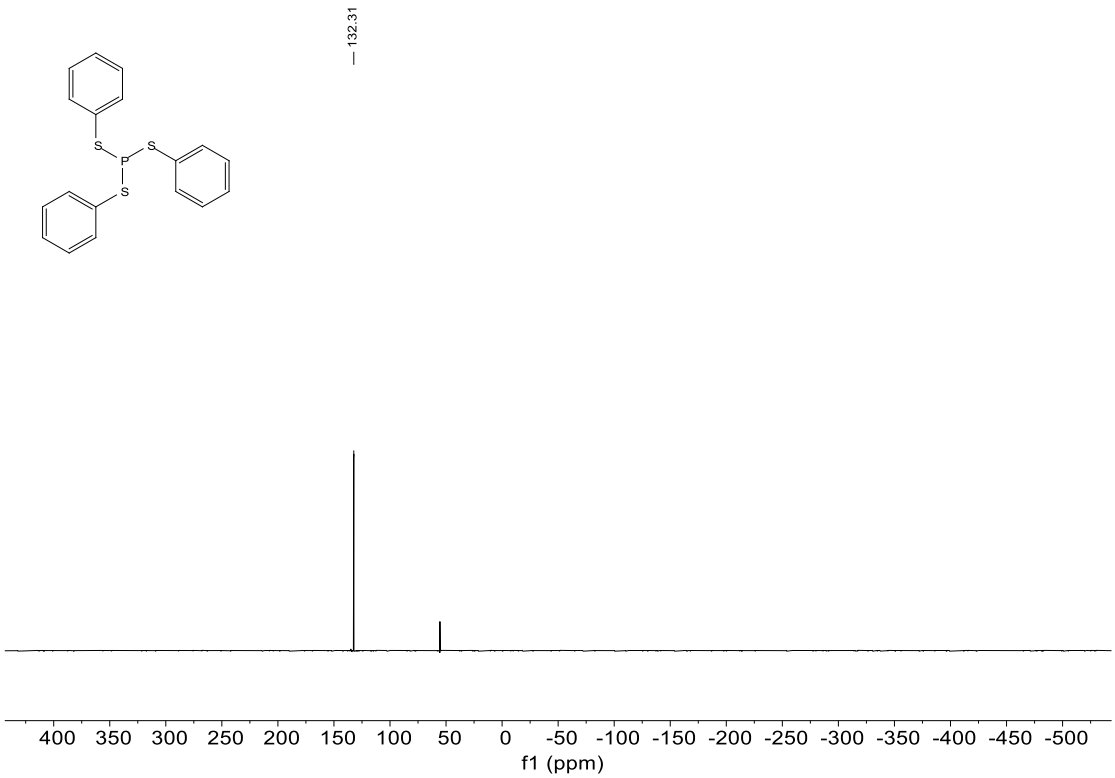
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **8b**



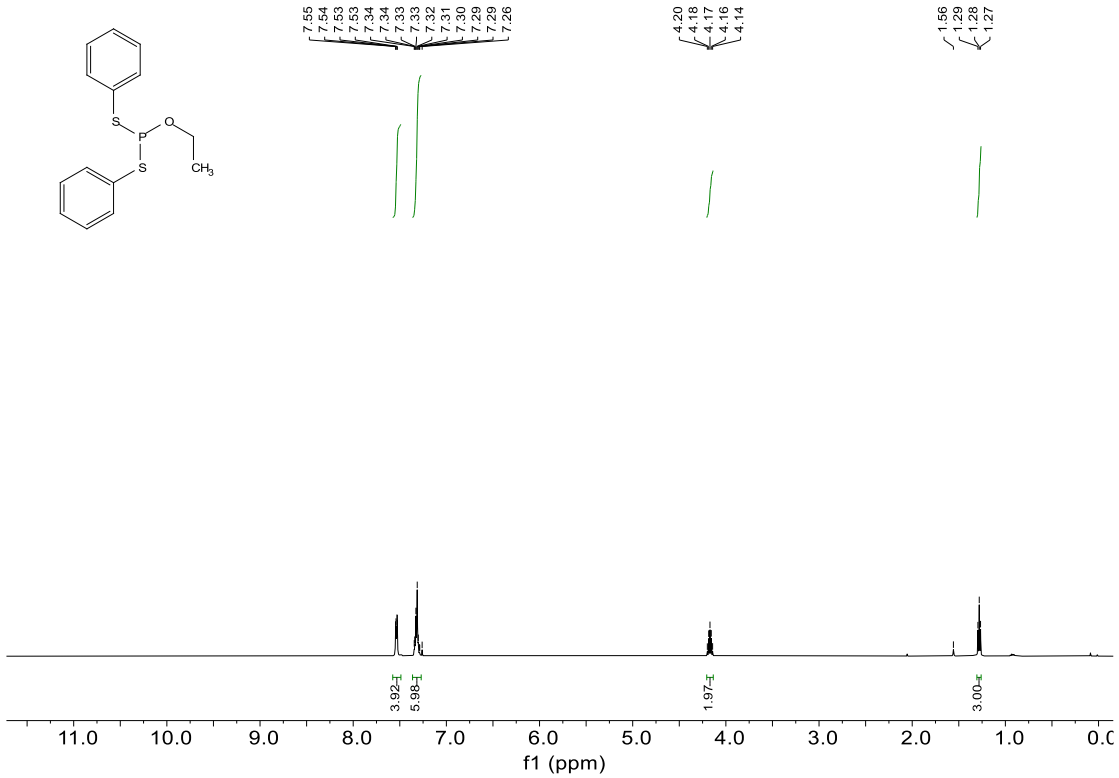
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **9**



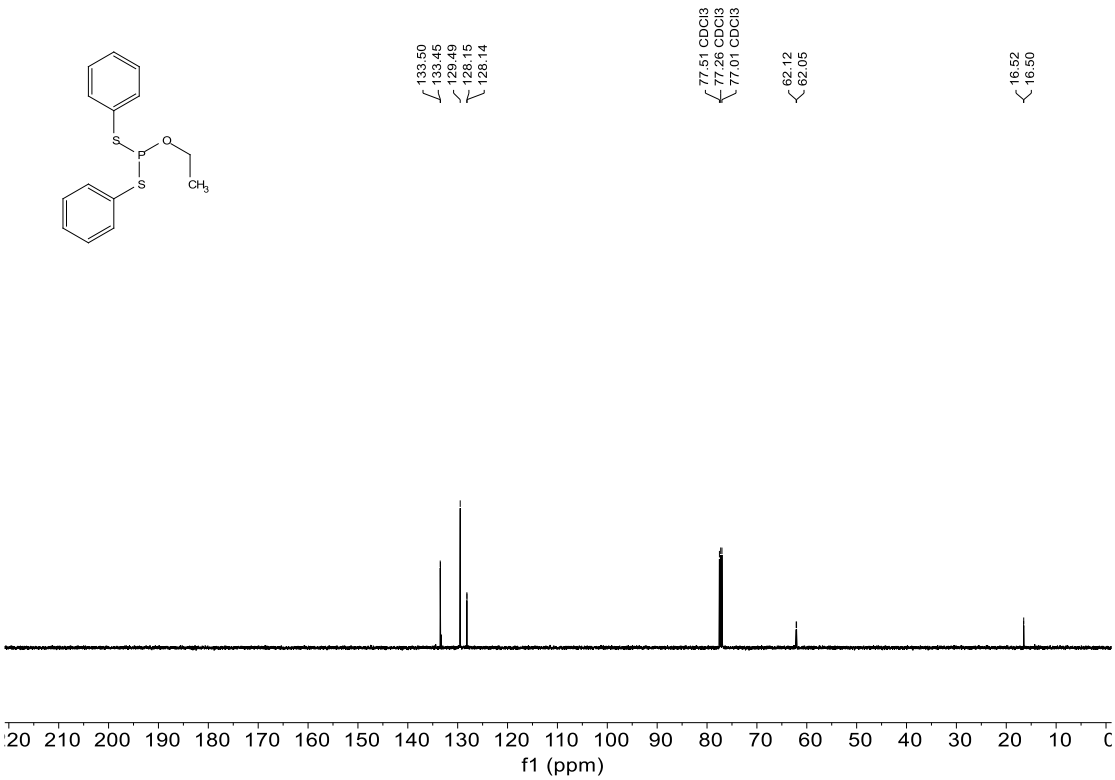
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **9**



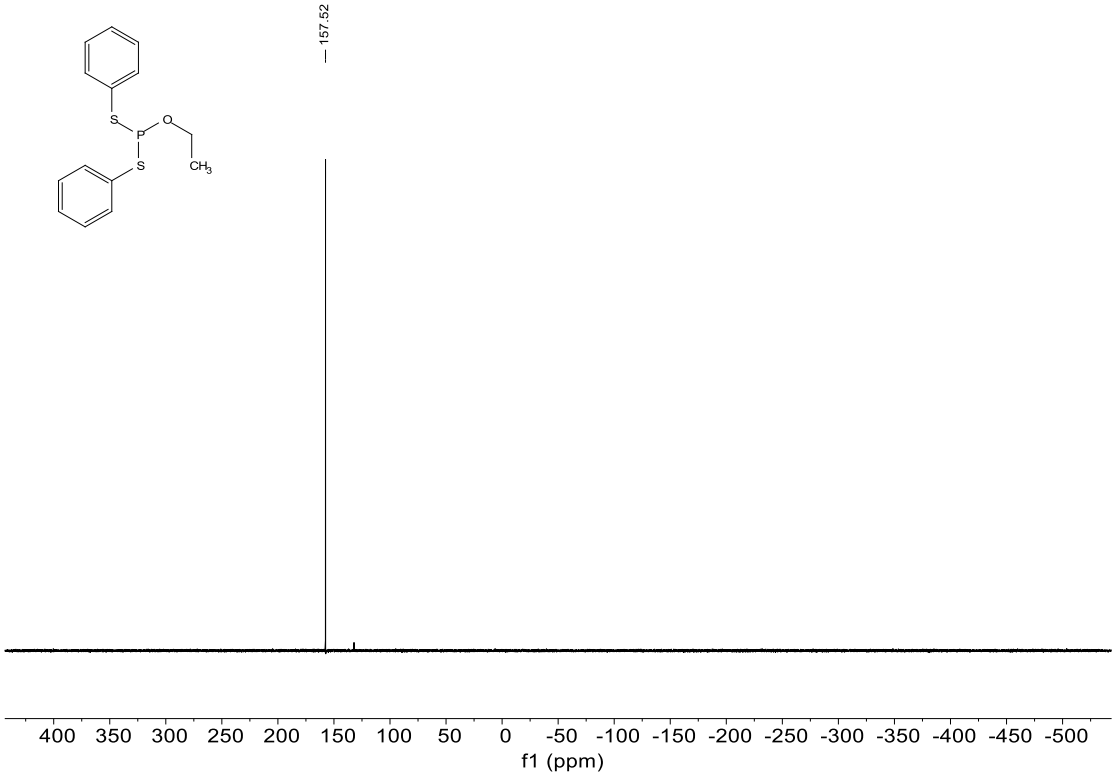
$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **9**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **10**



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) spectrum of compound **10**



$^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectrum of compound **10**