Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of *S*-Alkyl Phosphorothioates/ Phosphorodithioates *via* Ring-Opening Reaction of Sulfonium Salts with S_8, *H*-phosphonates or P_4S_{10}, and Alcohols

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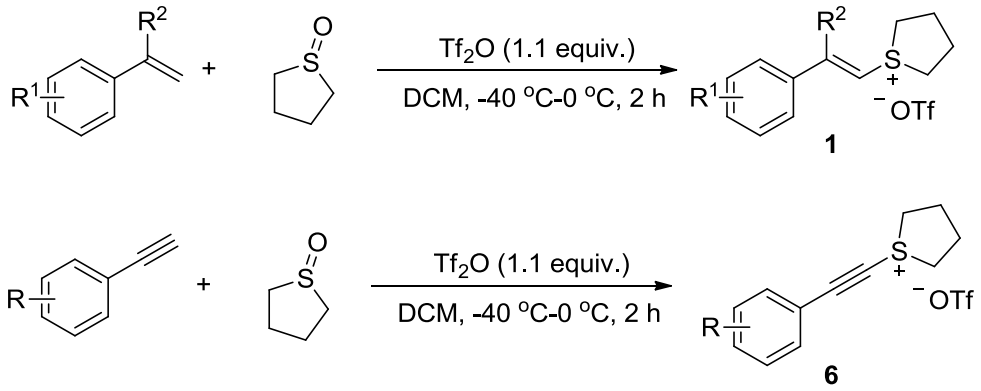
1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded at 400, 101, 162 and 376 MHz, respectively. Chemical shifts were quoted in ppm relative to $CDCl_3$ (δ_H = 7.26, δ_C = 77.0 ppm). Datas are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. The reactions were monitored by thin-layer chromatography (TLC) using GF_{254} silica gel-coated TLC plates. Mass spectra were performed on a spectrometer operating on ESI-TOF. Melting points were measured on a melting point apparatus and were uncorrected.

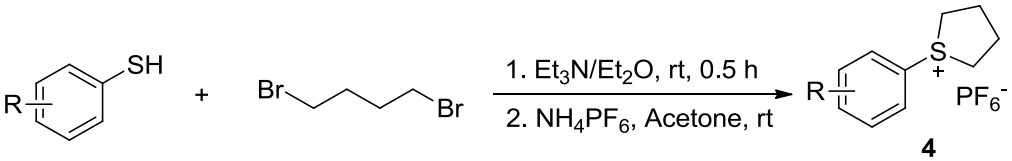
2. Experimental Section

General procedure for compounds 1 and 6



Compounds **1** and **6** were prepared according to Wen's work.[1] Under an argon atmosphere, tetramethylene sulfoxide (5.5 mmol, 1.1 equiv.) and anhydrous DCM (20 mL) were added to a 100 mL round bottom flask at -40 °C. The Tf_2O (1.1 equiv., 5.5 mmol) was added dropwise under argon, and then alkene or alkyne (5.0 mmol, 1.0 equiv.) was added gradually. The reaction mixture was stirred at -40 °C for 30 min before warming to 0 °C. Upon completion monitored by the TLC, the solvent was removed under reduced pressure. The resulted crude product was dissolved in a small amount of anhydrous DCM, which was slowly dropped into anhydrous ether (20 mL) to precipitate out the cyclic sulfonium salts solid. The solid was collected by filtration and washed three times with ether to afford the cyclic sulfonium salt **1** or **6**, or the crude product was purified by column chromatography on silica gel (DCM/MeOH, from 50:1 to 20:1) to afford the alkenyl/alkynyl sulfonium salt **1** or **6**.

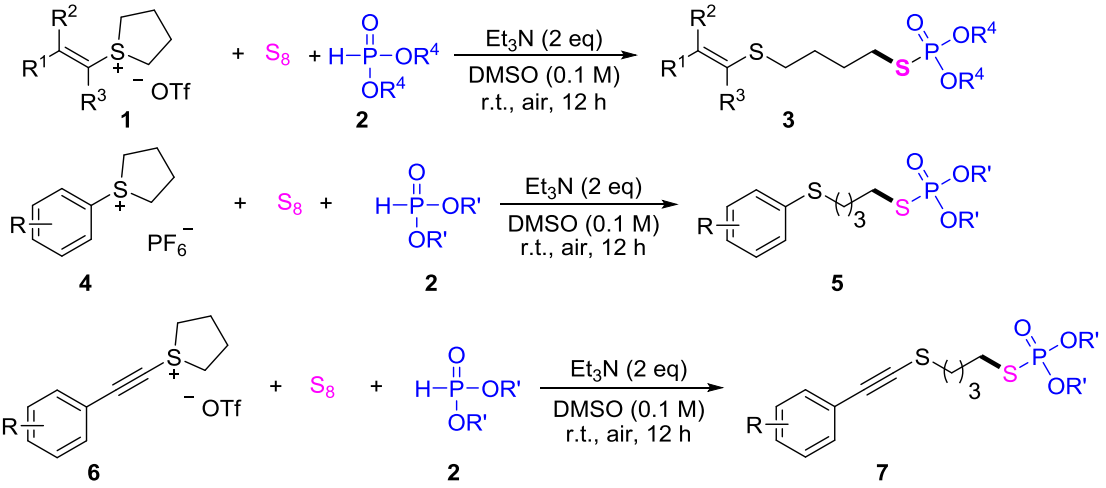
General procedure for compounds 4 [2, 3]



Triethylamine (15 mmol, 1.5 equiv.) was slowly added to a 100 mL round-bottom flask containing thiophenol (10 mmol, 1.0 equiv.), 1,4-dibromobutane (20 mmol, 2.0 equiv.) and Et_2O (20 mL). The reaction mixture was stirred for 30 min then diluted with Et_2O (20 mL) and washed with 1.2 N HCl (2 × 20 mL) and brine. The organic layer was dried over anhydrous sodium sulfate, concentrated under vacuum, and the crude material was dissolved in acetone (5 mL) and treated with NH_4PF_6 (10 mmol, 1.0 equiv.). After stirring overnight at room temperature, the reaction mixture was filtered through a medium porosity fritted-glass funnel, the filtrate was concentrated under reduced pressure, and Et_2O (10-20 mL) was added producing colorless crystals. The crystals were collected on a

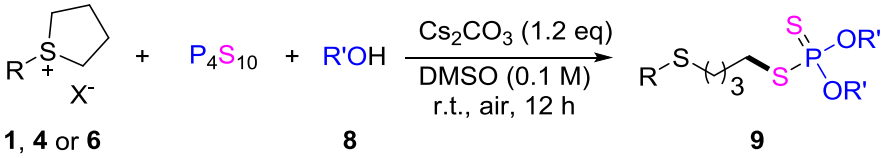
coarse fritted-glass funnel and washed with water (2 mL), ethanol (2 mL), and Et_2O (2 mL). The product was purified by recrystallization from acetone/Et_2O to give analytically pure product **4**.

General procedure for the synthesis of *S*-alkyl phosphorothioates 3, 5 and 7



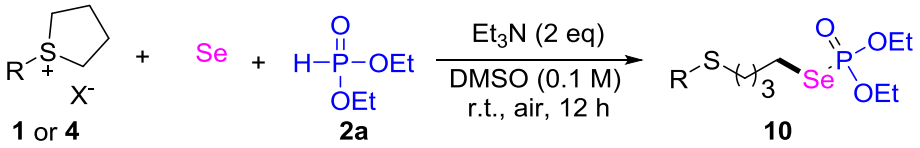
A 10 mL round-bottom flask equipped with a stirring bar was charged with cyclic sulfonium salt **1, 4** or **6** (0.3 mmol, 1 equiv.), S_8 (0.6 mmol, 2 equiv.), *H*-phosphonate **2** (0.6 mmol, 2 equiv.), Et_3N (0.6 mmol, 2 equiv.) and DMSO (3 mL). The reaction mixture was then stirred at room temperature for approximately 12 hours under air atmosphere, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 4:1-2:1) to afford the desired product **3**, **5** or **7**.

General procedure for the synthesis of *S*-alkyl phosphorodithioates 9



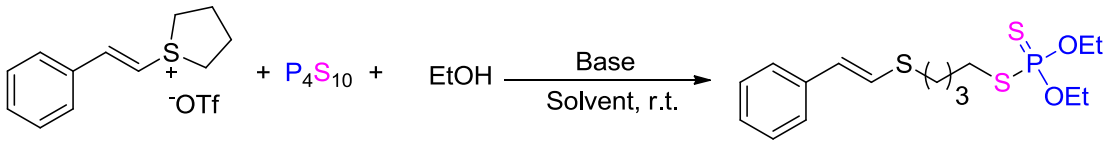
A 10 mL round-bottom flask equipped with a stirring bar was charged with cyclic sulfonium salt **1, 4** or **6** (0.3 mmol, 1 equiv.), P_4S_{10} (0.3 mmol, 1 equiv.), alcohol **8** (3 mmol, 10 equiv.), Cs_2CO_3 (0.36 mmol, 1.2 equiv.) and DMSO (3 mL). The reaction mixture was then stirred at room temperature for approximately 12 hours under air atmosphere, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 6:1-3:1) to afford the ring-opening product **9**.

General procedure for the synthesis of *S*-alkyl phosphoroselenenylates 10



A 10 mL round-bottom flask equipped with a stirring bar was charged with cyclic sulfonium salt **1**or **4** (0.3 mmol, 1 equiv.), Se powder (0.6 mmol, 2 equiv.), H-phosphonate **2a** (0.6 mmol, 2 equiv.), Et_3N (0.6 mmol, 2 equiv.) and DMSO (3 mL). The reaction mixture was then stirred at room temperature for approximately 12 hours under air atmosphere, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 4:1-2:1) to afford product **10**.

Reaction conditions optimization for *S*-alkyl phosphorodithioates [a]

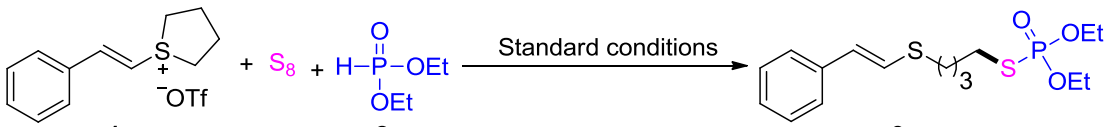


1a **9a**

Entry	Amount of P_4S_{10} (eq)	Solvent	Base	Yield of **3aa** % [b]
1	1.5	THF	Cs_2CO_3	78
2	1.5	DCM	Cs_2CO_3	76
3	1.5	CH_3CN	Cs_2CO_3	82
4	1.5	DMSO	Cs_2CO_3	84
5	1.5	Acetone	Cs_2CO_3	76
6	1.5	EtOAc	Cs_2CO_3	71
7	1.5	DMSO	K_2CO_3	64
8	1.5	DMSO	Na_2CO_3	58
9	1.5	DMSO	DBU	7
10	1.5	DMSO	Et_3N	65
11	1.2	DMSO	Cs_2CO_3	85
12	1.0	DMSO	Cs_2CO_3	85
13	0.9	DMSO	K_2CO_3	81
14 [c]	1.0	DMSO	Cs_2CO_3	84
15 [d]	**1.0**	**DMSO**	**Cs_2CO_3**	**85**
16 [e]	1.0	DMSO	Cs_2CO_3	79
17 [f]	1.0	DMSO	Cs_2CO_3	78
18 [g]	1.0	DMSO	Cs_2CO_3	85
19	1.0	DMSO	None	0

[a] unless others noted, conditions: **1a** (0.1 mmol, 1 equiv.), P_4S_{10}, EtOH (1 mmol, 10 equiv.), Solvent (1 mL), Base (0.2 mmol, 2 equiv.), r.t., 12 h, air atmosphere. [b] Estimated by ^{1}H NMR using diethyl phthalate as internal reference. [c] 1.5 equiv. of Cs_2CO_3 was used. [d] 1.2 equiv. of Cs_2CO_3 was used. [e] 1.0 equiv. of Cs_2CO_3 was used. [f] 8 equiv. of EtOH was used. [g] 15 equiv. of EtOH was used.

Gram-scale synthesis of 3aa



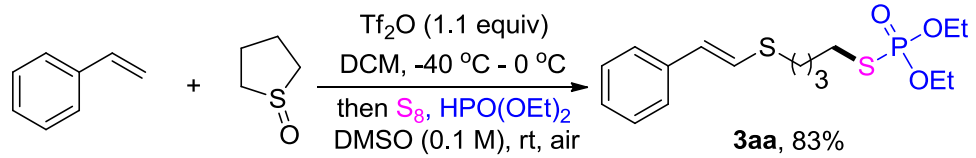
1a **2a** **3aa**

4 mmol, 1.3602 g 1.3108 g, 91% yield

A 10 mL round-bottom flask equipped with a stirring bar was charged with sulfonium salt **1a** (1.3602 g, 4 mmol),

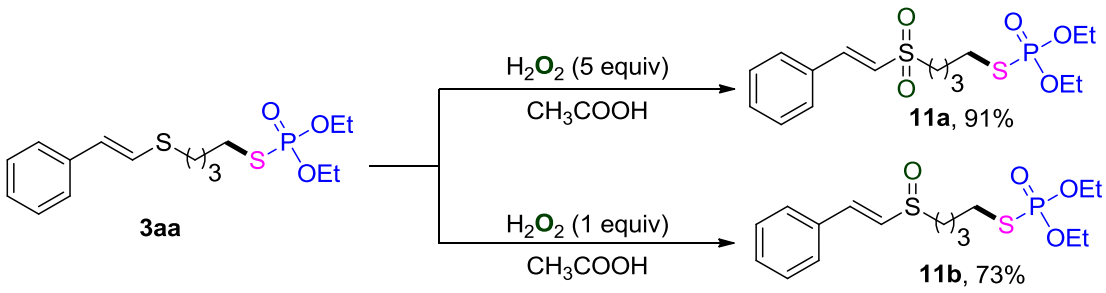
S_8 (0.2561 g, 8 mmol), *H*-phosphonate **2a** (1.1044 g, 8 mmol), Et_3N (0.8089 g, 8 mmol), in DMSO (40 mL). The reaction mixture was then stirred at room temperature for approximately 12 hours under air atmosphere, with progress monitored by TLC. Upon completion, 20 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (30 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified *via* flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 4:1-2:1) to afford 1.3108 g of **3aa**, yielding 91% based on **1a**.

One-pot synthesis of 3aa



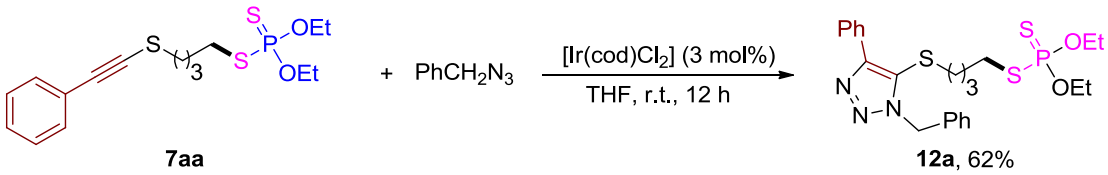
Under an argon atmosphere, sulfoxide (0.0573 g, 0.55 mmol, 1.1 equiv.) and anhydrous DCM (3.0 mL) were added to a 25.0 mL flask at -40 °C. The Tf_2O (0.1551 g, 0.55 mmol, 1.1 equiv.) was then added dropwise, followed by the gradual addition of styrene (0.0520 g, 0.5 mmol, 1.0 equiv.). The reaction mixture was stirred at -40 °C for 30 min before being warmed to 0 °C. After stirring for 2 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. Then, S_8 (0.0320 g, 1 mmol), $HPO(OEt)_2$ (0.1381 g, 1 mmol) and DMSO (5 mL) were added. The reaction mixture was stirred at room temperature for 12 h. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified via flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 4:1-2:1) to afford 0.1494 g of **3aa**, yielding 83% based on styrene.

Oxidation of product 3aa



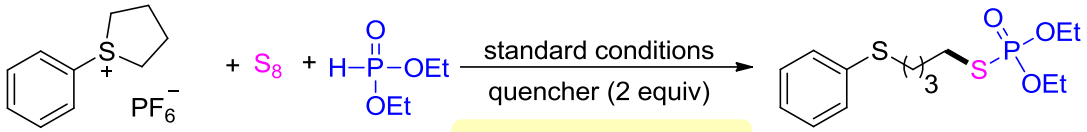
To a stirred solution of **3aa** (180.0 mg, 0.5 mmol, 1.0 equiv.) in 3 mL acetic acid was added hydrogen peroxide (35% aqueous solution, 1 equiv. or 5 equiv.), the reaction was heated to 100 °C using an oil bath and stirred for about 2 h. After completion, the reaction was allowed to cool to room temperature, then, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was then dried with anhydrous sodium sulfate, concentrated under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA 4:1-2:1) to obtain the corresponding oxidative products **11a** and **11b** in 91% and 73% yields, respectively.

Synthesis of 12a via [3+2] Cycloaddition Reaction of 7aa with $PhCH_2N_3$



Under an argon atmosphere, compound **7aa** (71.6 mg, 0.2 mmol), $PhCH_2N_3$ (39.9 mg, 0.3 mmol), $[Ir(cod)Cl_2]$(4.0 mg, 0.006 mmol) and THF (2 mL) were added to a 10 mL schlenk tube at room temperature for about 24 h. The resulting solution was concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA=2:1) to obtain 60.9 mg of **12a** as a light yellow oil in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.29 (m, 6H), 5.69 (s, 2H), 4.21 – 4.00 (m, 4H), 2.62 – 2.51 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.16 – 1.73 (m, 2H), 1.53 – 1.43 (m, 2H), 1.32 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 135.3, 130.6, 128.9, 128.6, 128.5, 128.3, 127.7, 126.9, 125.2, 63.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 52.1, 35.2, 32.7 (d, $J_{C\text{-}P}$ = 3.7 Hz), 29.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 27.9, 15.9 (d, $J_{C\text{-}P}$ = 8.2 Hz); ^{31}P NMR (162 MHz, Chloroform-*d*) δ 95.10. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{31}N_3O_3PS_2$: 492.1539; found: 492.1544.

Control experiments

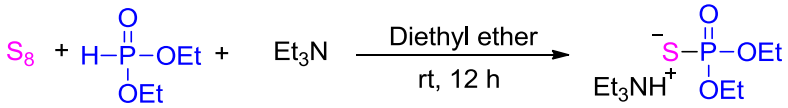


4a **2a** **5aa**

quencher	yield of 3aa
-----	93%
TEMPO	87%
BHT	89%

A 10 mL round-bottom flask equipped with a stirring bar was charged with sulfonium salt **4a** (0.0931 g, 0.3 mmol), S_8 (0.0192 g, 0.6 mmol), *H*-phosphonate **2a** (0.0828 g, 0.6 mmol), Et_3N (0.0607 g, 0.6 mmol), TEMPO (0.0937 g, 0.6 mmol) or BHT (0.1322 g, 0.6 mmol) in DMSO (3 mL). The reaction mixture was then stirred at room temperature for approximately 12 hours under air atmosphere, with progress monitored by TLC. Upon completion, 10 mL of H_2O was added to the mixture, followed by extraction with EtOAc three times (10 mL × 3). The organic phase was subsequently dried over anhydrous sodium sulfate, concentrated under vacuum, and the residue was purified *via* flash column chromatography using a petroleum ether/ethyl acetate eluent mixture (PE/EA 4:1-2:1) to afford 0.0872 g and 0.0892 g of **3aa** with the addition of TEMPO and BHT, yielding 87% and 89%, respectively.

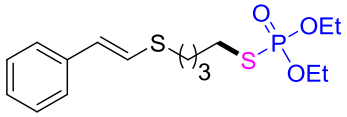
Synthesis of 2a'



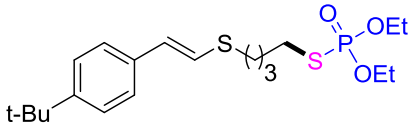
2a **2a'**

Compound **2a'** was synthesized according to the reference. [4] An oven dried round bottom flask was charged with diethyl *H*-phosphonate **2a** (324 mg, 2.30 mmol), and elemental sulfur (73.7 mg, 2.41 mmol). The flask was capped with a rubber septum and evacuated/back-filled with nitrogen. A 1:1 mixture of ethyl acetate:diethyl ether (8 mL/mmol substrate; limiting substrate conc. 0.125 M) was added via syringe and the reaction mixture was cooled down to 0 °C. Anhydrous triethylamine (0.96 mL, 6.90 mmol) was added dropwise, the reaction mixture was allowed to warm up to room temperature, and it was stirred for about 12 h. The solvents were evaporated under reduced pressure to obtain the product **2a'** directly used for the next step without further purification.

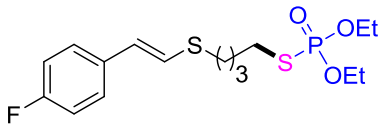
3. Characterization data of products



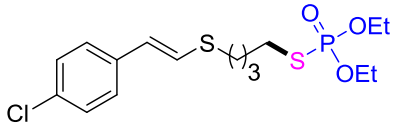
(E)-O,O-diethyl S-(4-(styrylthio)butyl) phosphorothioate (**3aa**): TLC (PE/EtOAc, 3:1), R_f = 0.49; Colorless liquid (100.6 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 3.5 Hz, 4H), 7.20 (d, *J* = 3.9 Hz, 1H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 4.24 - 4.10 (m, 4H), 2.91 - 2.77 (m, 4H), 1.94 - 1.84 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.8, 127.5, 127.1, 125.6, 124.8, 63.7 (d, J_{C-P} = 6.0 Hz), 32.1, 30.5 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 28.3, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}O_3PS_2$: 361.1055; found: 361.1057.



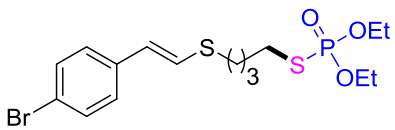
(E)-S-(4-((4-(tert-butyl)styryl)thio)butyl) O,O-diethyl phosphorothioate (**3ba**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (113.7 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.17 (m, 4H), 6.66-6.58 (m, 1H), 6.51 - 6.40 (m, 1H), 4.23 - 4.05 (m, 4H), 2.92 - 2.72 (m, 4H), 1.91-1.78 (m, 4H), 1.40 - 1.04 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 134.3, 127.8, 125.7, 125.4, 123.7, 63.7 (d, J_{C-P} = 5.9 Hz), 34.6, 32.2, 31.4, 30.5 (d, J_{C-P} = 3.7 Hz), 29.9 (d, J_{C-P} = 5.3 Hz), 28.3, 16.2 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{34}O_3PS_2$: 417.1681; found: 417.1685.



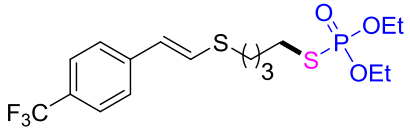
(E)-O,O-diethyl S-(4-((4-fluorostyryl)thio)butyl) phosphorothioate (**3ca**): TLC (PE/EtOAc, 3:1), R_f = 0.42; Colorless liquid (97.6 mg, 86%). δ 7.30 - 7.20 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 2H), 6.61 (d, *J* = 14.3 Hz, 1H), 6.45 (d, *J* = 14.9 Hz, 1H), 4.25 - 4.08 (m, 4H), 2.90 - 2.81 (m, 4H), 1.94 - 1.83 (m, 4H), 1.36 - 1.35(m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, J_{C-F} = 244.8 Hz), 133.3 (d, J_{C-F} = 3.2 Hz), 127.0 (d, J_{C-F} = 7.9 Hz), 126.4, 124.5 (d, J_{C-F} = 2.0 Hz), 115.6 (d, J_{C-F} = 21.5 Hz), 63.7 (d, J_{C-P} = 6.1 Hz), 32.1, 30.4 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.3 Hz), 28.3, 16.2 (d, J_{C-P} = 7.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.22; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}FO_3PS_2$: 379.0961; found: 379.0963



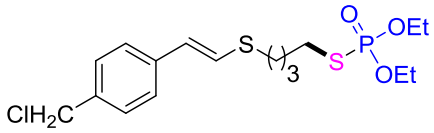
(E)-S-(4-((4-chlorostyryl)thio)butyl) O,O-diethyl phosphorothioate (**3da**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (98.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.17 (m, 4H), 6.69 (dd, *J* = 15.6, 3.6 Hz, 1H), 6.41 (dd, *J* = 15.6, 3.5 Hz, 1H), 4.24 - 4.08 (m, 4H), 2.90 - 2.82 (m, 4H), 1.93 - 1.84 (m, 4H), 1.38-1.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 132.5, 128.8, 126.7, 125.8, 125.7, 63.7 (d, J_{C-P} = 6.1 Hz), 32.0, 30.4 (d, J_{C-P} = 3.8 Hz), 29.9 (d, J_{C-P} = 5.3 Hz), 28.2, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}ClO_3PS_2$: 395.0666; found: 395.0669



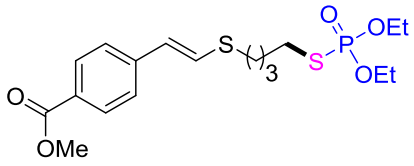
(E)-S-(4-((4-bromostyryl)thio)butyl) O,O-diethyl phosphorothioate (**3ea**): TLC (PE/EtOAc, 3:1), R_f = 0.43; Colorless liquid (110.7 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 4.22 - 4.07 (m, 4H), 2.91 - 2.79 (m, 4H), 1.85 - 1.81 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 131.8, 127.0, 126.0, 125.8, 120.6, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 32.0, 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.3, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}BrO_3PS_2$: 439.0161; found: 439.0164.



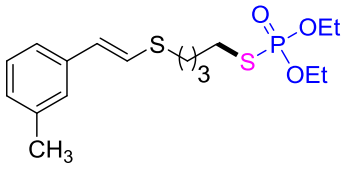
(E)-O,O-diethyl S-(4-((4-(trifluoromethyl)styryl)thio)butyl) phosphorothioate (**3fa**): TLC (PE/EtOAc, 3:1), R_f = 0.46; Colorless liquid (105.4 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 4.22 - 4.10 (m, 4H), 2.92 - 2.82 (m, 4H), 1.89 - 1.80 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 128.3 (q, $J_{C\text{-}F}$ = 32.4 Hz), 128.2, 125.5 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.4, 124.8, 124.2 (q, $J_{C\text{-}F}$ = 272.6 Hz), 63.5 (d, $J_{C\text{-}P}$ = 6.1 Hz), 31.7, 30.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.7 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.0, 16.0 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.37; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{25}F_3O_3PS_2$: 429.0929; found: 429.0925.



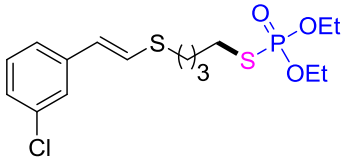
(E)-S-(4-((4-(chloromethyl)styryl)thio)butyl) O,O-diethyl phosphorothioate (**3ga**): TLC (PE/EtOAc, 3:1), R_f = 0.43; Colorless liquid (79.7 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.6 Hz, 4H), 6.71 (dd, *J* = 15.6, 2.6 Hz, 1H), 6.46 (d, *J* = 15.5 Hz, 1H), 4.21 - 3.95 (m, 6H), 3.59 (d, *J* = 4.4 Hz, 2H), 2.84 (s, 2H), 1.99 - 1.82 (m, 4H), 1.32 - 1.23 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 136.2, 129.4, 126.7, 125.8, 125.3, 63.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 44.5, 34.9 (d, $J_{C\text{-}P}$ = 3.9 Hz), 31.9, 31.4, 26.7, 16.1 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{27}ClO_3PS_2$: 409.0822; found: 409.0824.



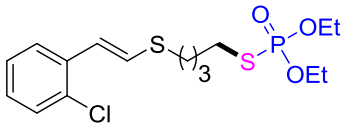
methyl (E)-4-(2-((4-((diethoxyphosphoryl)thio)butyl)thio)vinyl)benzoate (**3ha**): TLC (PE/EtOAc, 3:1), R_f = 0.38; Colorless liquid (106.7 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 - 7.88 (m, 2H), 7.33 (d, *J* = 6.6 Hz, 2H), 6.89 (dd, *J* = 15.6, 5.2 Hz, 1H), 6.46 (dd, *J* = 15.5, 4.9 Hz, 1H), 4.27 - 4.06 (m, 4H), 3.91 (d, *J* = 5.3 Hz, 3H), 2.96 - 2.77 (m, 4H), 1.94-1.85 (m, 4H), 1.43 - 1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 141.3, 130.1, 128.5, 128.1, 125.3, 125.18, 63.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 52.1, 31.8, 30.4 (d, $J_{C\text{-}P}$ = 3.8 Hz), 29.8 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.1, 16.1 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{28}O_5PS_2$: 419.1110; found: 419.1116.



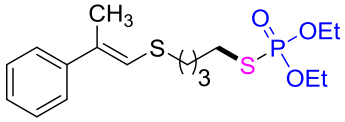
(E)-O,O-diethyl S-(4-((3-methylstyryl)thio)butyl) phosphorothioate (**3ia**): TLC (PE/EtOAc, 3:1), R_f = 0.57; Colorless liquid (91.0 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.01 (m, 4H), 6.75 - 6.59 (m, 1H), 6.52 - 6.38 (m, 1H), 4.22 - 4.11 (m, 4H), 2.93 - 2.72 (m, 4H), 2.40 - 2.24 (m, 3H), 1.84-1.83 (m, 4H), 1.44 - 1.28 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 136.9, 128.6, 127.8, 127.7, 126.3, 124.4, 122.8, 63.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 32.1, 30.5 (d, $J_{C\text{-}P}$ = 3.6 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.3, 21.5, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{28}O_3PS_2$: 375.1212; found: 375.1216.



(E)-S-(4-((3-chlorostyryl)thio)butyl) O,O-diethyl phosphorothioate (**3ja**): TLC (PE/EtOAc, 3:1), R_f = 0.55; Colorless liquid (99.5 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.26 (m, 1H), 7.24 - 7.18 (m, 1H), 7.15 - 7.09 (s, 2H), 6.73 (dd, *J* = 15.6, 2.7 Hz, 1H), 6.37 (dd, *J* = 15.6, 2.4 Hz, 1H), 4.22 - 4.07 (m, 4H), 2.90 - 2.82 (m, 4H), 1.91 - 1.73 (m, 4H), 1.38 - 1.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 134.6, 129.9, 126.9, 126.8, 125.3, 123.7, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 31.9, 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.8 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.2, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}ClO_3PS_2$: 395.0666; found: 395.0663.

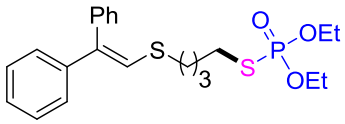


(E)-S-(4-((2-chlorostyryl)thio)butyl) O,O-diethyl phosphorothioate (**3ka**): TLC (PE/EtOAc, 3:1), R_f = 0.48; Colorless liquid (103.1 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.22 - 7.18 (m, 1H), 7.14 - 7.11 (m, 1H), 6.8 (d, *J* = 15.6 Hz, 1H), 6.7 (d, *J* = 15.6 Hz, 1H), 4.25 - 4.09 (m, 4H), 2.92 - 2.83 (m, 4H), 1.92 - 1.80 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 132.0, 129.8, 127.9, 127.0, 126.0, 122.4, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 31.8, 30.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 28.1, 16.1 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}ClO_3PS_2$: 395.0666; found: 395.0667.

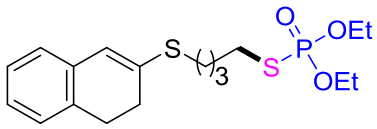


(E)-O,O-diethyl S-(4-((2-phenylprop-1-en-1-yl)thio)butyl) phosphorothioate (**3la**): TLC (PE/EtOAc, 3:1), R_f = 0.61; Colorless liquid (96.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.26 (m, 4H), 7.23 - 7.20 (m, 1H), 6.27 (s, 1H), 4.22 - 4.05 (m, 4H), 2.90 - 2.78 (m, 4H), 2.12 (s, 3H), 1.84 - 1.80 (m, 4H), 1.37 - 1.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 133.9, 128.4, 126.8, 125.1, 123.3, 63.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.5, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.7 (d, $J_{C\text{-}P}$ = 5.4 Hz), 29.2, 17.7, 16.1 (d, $J_{C\text{-}P}$ = 7.2

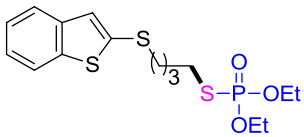
Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{28}O_3PS_2$: 375.1212; found: 375.1208.



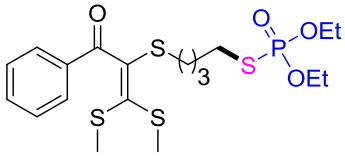
S-(4-((2,2-diphenylvinyl)thio)butyl) O,O-diethyl phosphorothioate (**3ma**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (115.3 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 10H), 6.55 (s, 1H), 4.23 - 4.07 (m, 4H), 2.89 - 2.74 (m, 4H), 1.88 - 1.81 (m, 4H), 1.34 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 139.5, 139.0, 129.7, 128.4, 128.3, 127.6, 127.1, 127.0, 125.7, 63.7 (d, J_{C-P} = 6.0 Hz), 34.2, 30.4 (d, J_{C-P} = 4.0 Hz), 29.7 (d, J_{C-P} = 5.4 Hz), 29.1, 16.1(d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{30}O_3PS_2$: 437.1368; found: 437.1366.



S-(4-((3,4-dihydronaphthalen-2-yl)thio)butyl) O,O-diethyl phosphorothioate (**3na**): TLC (PE/EtOAc, 3:1), R_f = 0.53; Colorless liquid (97.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.01 (m, 3H), 6.97 (d, *J* = 6.5 Hz, 1H), 6.21 (s, 1H), 4.24 - 4.06 (m, 4H), 2.95 - 2.79 (m, 6H), 2.39 (t, *J* = 7.0 Hz, 2H), 1.87 - 1.82 (m, 4H), 1.41 - 1.30 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.7, 134.4, 133.6, 127.3, 126.7, 126.1, 124.9, 119.7, 63.6 (d, J_{C-P} = 6.0 Hz), 30.4 (d, J_{C-P} = 3.9 Hz), 30.0(d, J_{C-P} = 5.5 Hz), 29.1, 28.4, 27.3, 16.1 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{28}O_3PS_2$: 387.1212; found: 387.1215.

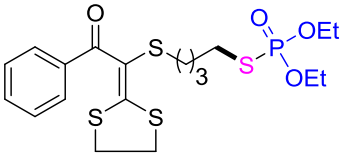


S-(4-(benzo[b]thiophen-2-ylthio)butyl) O,O-diethyl phosphorothioate (**3oa**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (107.8 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.45 - 7.36 (m, 3H), 4.20 - 4.07 (m, 4H), 2.90 - 2.77 (m, 4H), 1.87 - 1.79 (m, 2H), 1.74 - 1.67 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 139.1, 127.3, 126.6, 124.9, 124.5, 123.0, 122.6, 63.6 (d, J_{C-P} = 6.0 Hz), 34.2, 30.4 (d, J_{C-P} = 4.0 Hz), 29.7 (d, J_{C-P} = 5.4 Hz), 28.3, 16.1 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{24}O_3PS_3$: 391.0620; found: 391.0625.

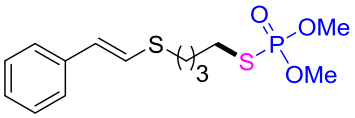


S-(4-((1,1-bis(methylthio)-3-oxo-3-phenylprop-1-en-2-yl)thio)butyl) O,O-diethyl phosphorothioate (**3pa**): TLC (PE/EtOAc, 3:1), R_f = 0.38; Colorless liquid (121.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.62 - 7.58 (m, 1H), 7.51 - 7.47 (m, 2H), 4.29 - 4.00 (m, 4H), 2.79 - 2.72 (m, 2H), 2.61 (t, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 2.08 (s, 3H), 1.77 - 1.62 (m, 4H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 139.0, 135.9, 133.8, 132.7, 129.5, 128.9, 63.6 (d, J_{C-P} = 5.9 Hz), 32.9, 30.4 (d, J_{C-P} = 4.0 Hz), 29.7 (d, J_{C-P} = 5.6 Hz), 28.4, 18.4, 16.3, 16.1 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR

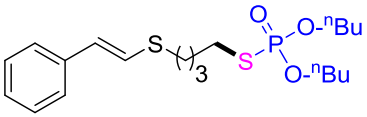
(162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{30}O_4PS_4$: 481.0759; found: 481.0766.



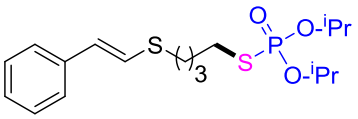
S-(4-((1-(1,3-dithiolan-2-ylidene)-2-oxo-2-phenylethyl)thio)butyl) O,O-diethyl phosphorothioate(**3qa**): TLC (PE/EtOAc, 3:1), R_f = 0.41; Colorless liquid (117.7 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.48 - 7.45 (m, 1H), 7.41 - 7.37 (m, 2H), 4.20 - 4.06 (m, 4H), 3.56 (t, *J* = 6.4 Hz, 2H), 3.40 (t, *J* = 6.4 Hz, 2H), 2.70 - 2.63 (m, 2H), 2.46 (t, *J* = 6.8 Hz, 2H), 1.62 - 1.55 (m, 2H), 1.51 - 1.44 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 176.8, 138.8, 131.2, 129.0, 127.7, 114.1, 63.6 (d, J_{C-P} = 6.0 Hz), 40.8, 35.6, 35.5, 30.4 (d, J_{C-P} = 3.9 Hz), 29.6 (d, J_{C-P} = 5.7 Hz), 27.9, 16.2 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{28}O_4PS_4$: 479.0603; found: 479.0608.



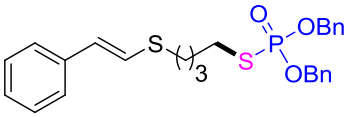
(E)-O,O-dimethyl S-(4-(styrylthio)butyl) phosphorothioate (**3ab**): TLC (PE/EtOAc, 3:1), R_f = 0.24; Colorless liquid (89.8 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.25 (m, 4H), 7.20 - 7.14 (m, 1H), 6.69 (dd, *J* = 15.6, 2.1 Hz, 1H), 6.48 (dd, *J* = 15.6, 2.0 Hz, 1H), 3.79 (dd, *J* = 12.6, 2.1 Hz, 6H), 2.91 - 2.79 (m, 4H), 1.83 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.5, 127.0, 125.6, 124.7, 53.9 (d, J_{C-P} = 6.0 Hz), 32.0, 30.4 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.2 Hz), 28.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{22}O_3PS_2$: 333.0742; found: 333.0744.



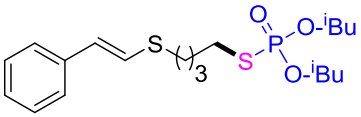
(E)-O,O-dibutyl S-(4-(styrylthio)butyl) phosphorothioate (**3ac**): TLC (PE/EtOAc, 3:1), R_f = 0.69; Colorless liquid (109.9 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.28 (m, 4H), 7.20 -7.18 (m, 1H), 6.70 (dd, *J* = 15.6, 3.6 Hz, 1H), 6.48 (dd, *J* = 15.5, 3.6 Hz, 1H), 4.13 - 3.98 (m, 4H), 2.91 - 2.77 (m, 4H), 1.83 - 1.82(m, 4H), 1.71 - 1.62 (m, 4H), 1.40 (m, 4H), 0.96 - 0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.4, 127.0, 125.5, 124.7, 67.3 (d, J_{C-P} = 6.5 Hz), 32.2(d, J_{C-P} = 7.3 Hz), 32.0, 30.4 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 28.3, 18.8, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{34}O_3PS_2$: 417.1681; found: 417.1685.



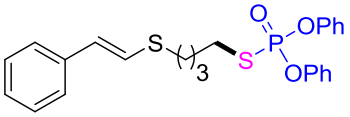
(E)-O,O-diisopropyl S-(4-(styrylthio)butyl) phosphorothioate (**3ad**): TLC (PE/EtOAc, 3:1), R_f = 0.57; Colorless liquid (100.2 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.28 (m, 4H), 7.19 - 7.13 (m, 1H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 4.77 - 4.71 (m, 2H), 2.91 - 2.76 (m, 4H), 1.86 - 1.83 (m, 4H), 1.36 (t, *J* = 6.7 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.4, 127.0, 125.6, 124.8, 72.7(d, J_{C-P} = 6.5 Hz), 32.0, 30.6 (d, J_{C-P} = 3.9 Hz), 29.8 (d, J_{C-P} = 6.0 Hz), 28.3, 24.0 (d, J_{C-P} = 4.1 Hz), 23.7 (d, J_{C-P} = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{30}O_3PS_2$: 389.1368; found: 389.1371.



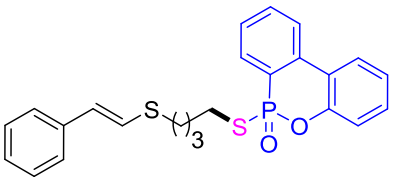
(E)-O,O-dibenzyl S-(4-(styrylthio)butyl) phosphorothioate (**3ae**): TLC (PE/EtOAc, 3:1), R_f = 0.52; Colorless liquid (123.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.26 (m, 15H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.16 - 5.09 (m, 4H), 2.84 - 2.75 (m, 2H), 2.70 (t, *J* = 6.6 Hz, 2H), 1.78 - 1.67 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 135.6, 135.5, 128.7, 128.7, 128.7, 128.2, 127.4, 127.0, 125.6, 124.7, 69.1, 69.0, 32.0, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.7 (d, $J_{C\text{-}P}$ = 5.7 Hz), 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{30}O_3PS_2$: 485.1368; found: 485.1374.



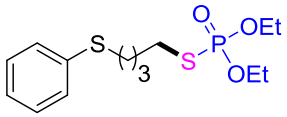
(E)-O,O-diisobutyl S-(4-(styrylthio)butyl) phosphorothioate (**3af**): TLC (PE/EtOAc, 3:1), R_f = 0.67; Colorless liquid (107.5 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.23 (m, 4H), 7.19 - 7.13 (m, 1H), 6.69 (dd, *J* = 15.6, 1.7 Hz, 1H), 6.47 (dd, *J* = 15.6, 1.5 Hz, 1H), 3.91 - 3.77 (m, 4H), 2.92 - 2.79 (m, 4H), 2.00 - 1.94 (m, 2H), 1.83 - 1.82 (m, 4H), 0.96 - 0.94 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.4, 127.0, 125.5, 124.7, 73.4 (d, $J_{C\text{-}P}$ = 6.9 Hz), 32.0, 30.3 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 29.0(d, $J_{C\text{-}P}$ = 7.5 Hz), 28.3, 18.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{34}O_3PS_2$: 417.1681; found: 417.1679.



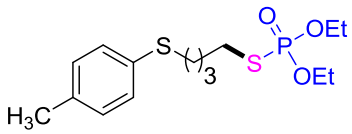
(E)-O,O-diphenyl S-(4-(styrylthio)butyl) phosphorothioate (**3ag**): TLC (PE/EtOAc, 3:1), R_f = 0.76; Colorless liquid (99.9 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.20 (m, 15H), 6.64 (d, *J* = 15.5 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 2.99 - 2.92 (m, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 1.72 - 1.62(m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (d, $J_{C\text{-}P}$ = 8.2 Hz), 150.2, 137.0, 130.0, 129.6, 128.8, 127.5, 127.1, 125.8, 125.6, 124.7, 120.8 (d, $J_{C\text{-}P}$ = 4.9 Hz), 120.3, 115.5, 31.9, 31.4 (d, $J_{C\text{-}P}$ = 4.2 Hz), 29.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 28.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{26}O_3PS_2$: 457.1055; found: 457.1058.



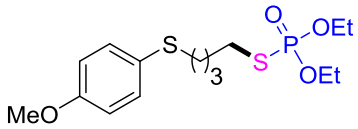
(E)-6-((4-(styrylthio)butyl)thio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**3ah**): TLC (PE/EtOAc, 3:1), R_f = 0.22; Colorless liquid (88.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 7.97 (m, 1H), 7.94 - 7.89 (m, 2H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.53 - 7.49(m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 - 7.15 (m, 7H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 3.01 - 2.81 (m, 2H), 2.74 (t, *J* = 6.9 Hz, 2H), 1.84 - 1.71 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, $J_{C\text{-}P}$ = 9.4 Hz), 137.0, 136.1 (d, $J_{C\text{-}P}$ = 7.4 Hz), 133.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.9, 130.5 (d, $J_{C\text{-}P}$ = 10.9 Hz), 128.8, 128.7, 127.4, 127.0, 125.9 (d, $J_{C\text{-}P}$ = 135.6 Hz), 125.6, 125.3, 125.1, 124.7, 124.0 (d, $J_{C\text{-}P}$ = 11.2 Hz), 122.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 120.5 (d, $J_{C\text{-}P}$ = 6.7 Hz), 31.9, 29.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 29.6 (d, $J_{C\text{-}P}$ = 3.2 Hz), 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{24}O_2PS_2$: 439.0950; found: 439.0944.



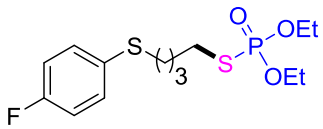
O,O-diethyl S-(4-(phenylthio)butyl) phosphorothioate (**5aa**): TLC (PE/EtOAc, 3:1), R_f = 0.56; Colorless liquid (93.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.23 (m, 4H), 7.19 - 7.16 (m, 1H), 4.23 - 4.06 (m, 4H), 2.95 - 2.91 (m, 2H), 2.88 - 2.77 (m, 2H), 1.88 - 1.71 (m, 4H), 1.40 - 1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 129.3, 129.0, 126.1, 63.6 (d, J_{C-P} = 6.0 Hz), 33.1, 30.5 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 28.0, 16.1 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{24}O_3PS_2$: 335.0899; found: 335.0897.



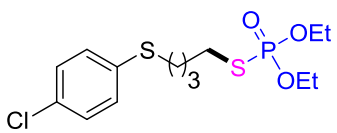
O,O-diethyl S-(4-(p-tolylthio)butyl) phosphorothioate(**5ba**): TLC (PE/EtOAc, 3:1), R_f = 0.56; Colorless liquid (96.2 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.23 - 4.06 (m, 4H), 2.92 - 2.79 (m, 4H), 2.32 (s, 3H), 1.86 -1.79 (m, 2H), 1.75 -1.68 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 132.4, 130.3, 129.8, 63.6 (d, J_{C-P} = 6.0 Hz), 33.9, 30.5 (d, J_{C-P} = 4.0 Hz), 29.8 (d, J_{C-P} = 5.5 Hz), 28.1, 21.1, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_3PS_2$: 349.1055; found: 349.1058.



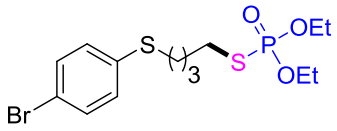
O,O-diethyl S-(4-((4-methoxyphenyl)thio)butyl) phosphorothioate (**5ca**): TLC (PE/EtOAc, 3:1), R_f = 0.48; Colorless liquid (95.1 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 4.21 - 4.09 (m, 4H), 3.80 (s, 3H), 2.86 - 2.78 (m, 4H), 1.85 - 1.77 (m, 2H), 1.71 - 1.64 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 133.4, 126.2, 114.6, 63.6 (d, J_{C-P}= 6.0 Hz), 55.4, 35.3, 30.5 (d, J_{C-P} = 4.0 Hz), 29.7 (d, J_{C-P} = 5.6 Hz), 28.2, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_4PS_2$: 365.1055; found: 365.1057.



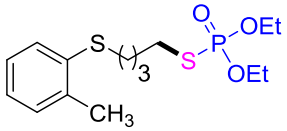
O,O-diethyl S-(4-((4-fluorophenyl)thio)butyl) phosphorothioate (**5da**): TLC (PE/EtOAc, 3:1), R_f = 0.63; Colorless liquid (94.1 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.27 (m, 2H), 7.01 - 6.99 (m, 2H), 4.22 - 4.05 (m, 4H), 2.91 - 2.79 (m, 4H), 1.87 - 1.77 (m, 2H), 1.74 - 1.65 (m, 2H), 1.39 - 1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J_{C-F} = 244.8 Hz), 132.5 (d, J_{C-F} = 7.9 Hz), 131.0 (d, J_{C-F} = 3.2 Hz), 116.1 (d, J_{C-F} = 21.7 Hz), 63.6 (d, J_{C-P} = 6.0 Hz), 34.5, 30.4 (d, J_{C-F} = 3.9 Hz), 29.7 (d, J_{C-F} = 5.4 Hz), 28.0, 16.1 (d, J_{C-P} = 7.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.52; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.87. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}FO_3PS_2$: 353.0805; found: 353.0801.



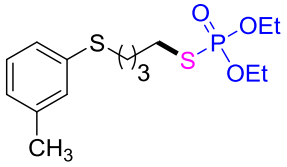
S-(4-((4-chlorophenyl)thio)butyl) O,O-diethyl phosphorothioate (**5ea**): TLC (PE/EtOAc, 3:1), R_f = 0.52; Colorless liquid (89.6 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.25 (m, 4H), 4.25 - 4.10 (m, 4H), 2.94 - 2.81 (m, 4H), 1.89 - 1.74 (m, 4H), 1.38 - 1.34(m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 132.1, 130.7, 129.1, 63.7 (d, J_{C-P} = 6.0 Hz), 33.5, 30.4 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 27.9, 16.2(d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}ClO_3PS_2$: 369.0509; found: 369.0513.



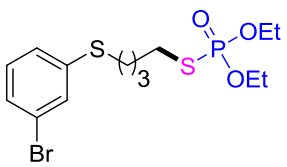
S-(4-((4-bromophenyl)thio)butyl) O,O-diethyl phosphorothioate(**5fa**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (105.4 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.32 (m, 2H), 7.28 - 7.14 (m, 2H), 4.23 - 4.04 (m, 4H), 2.93 - 2.73 (m, 4H), 1.81 - 1.74 (m, 4H), 1.37 - 1.33 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 132.1, 130.9, 119.9, 63.7(d, J_{C-P} = 6.1 Hz), 33.3, 30.4 (d, J_{C-P} = 4.0 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 27.9, 16.2(d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}BrO_3PS_2$: 413.0004; found: 413.0007.



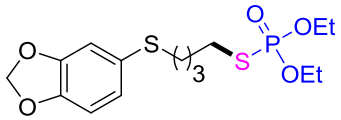
O,O-diethyl S-(4-(o-tolylthio)butyl) phosphorothioate(**5ga**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (85.7 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.6 Hz, 1H), 7.17 - 7.14 (m, 2H), 7.12 - 7.06 (m, 1H), 4.22 - 4.09 (m, 4H), 2.94 - 2.81 (m, 4H), 2.36 (s, 3H), 1.90 - 1.78 (m, 4H), 1.36 (t, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.7, 130.2, 127.9, 126.5, 125.7, 63.7 (d, J_{C-P} = 6.0 Hz), 32.3, 30.5 (d, J_{C-P} = 4.0 Hz), 30.0 (d, J_{C-P} = 5.5 Hz), 27.9, 20.5, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_3PS_2$: 349.1055; found: 349.1053.



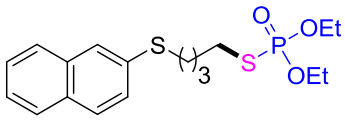
O,O-diethyl S-(4-(m-tolylthio)butyl) phosphorothioate (**5ha**): TLC (PE/EtOAc, 3:1), R_f = 0.59; Colorless liquid (86.8 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.10 (m, 3H), 6.99 (d, J = 6.7 Hz, 1H), 4.23 - 4.08 (m, 4H), 2.95 - 2.88 (m, 2H), 2.84 - 2.81(m, 2H), 2.32 (s, 3H), 1.84 - 1.74 (m, 4H), 1.40 - 1.32 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 136.1, 130.1, 128.9, 127.1, 126.4, 63.7 (d, J_{C-P} = 6.0 Hz), 33.2, 30.5 (d, J_{C-P} = 4.0 Hz), 29.9 (d, J_{C-P} = 5.5 Hz), 28.1, 21.5, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_3PS_2$: 349.1055; found: 349.1059.



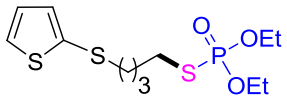
S-(4-((3-bromophenyl)thio)butyl) O,O-diethyl phosphorothioate (**5ia**): TLC (PE/EtOAc, 3:1), R_f = 0.55; Colorless liquid (106.6 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30-7.21 (m, 2H), 7.17 - 7.11 (m, 1H), 4.26 - 4.03 (m, 4H), 2.98 - 2.89 (m, 2H), 2.90 - 2.73 (m, 2H), 1.89 - 1.76 (m, 4H), 1.44 - 1.29 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 131.2, 130.3, 129.0, 127.4, 122.9, 63.7 (d, J_{C-P} = 6.1 Hz), 32.9, 30.4 (d, J_{C-P} = 3.9 Hz), 29.9 (d, J_{C-P} = 5.4 Hz), 27.8, 16.2(d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.83. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}BrO_3PS_2$: 413.0004; found: 413.0006.



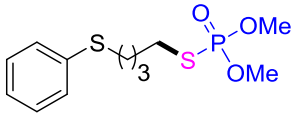
S-(4-(benzo[d][1,3]dioxol-5-ylthio)butyl) O,O-diethyl phosphorothioate (**5ja**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (96.5 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 - 6.89 (s, 2H), 6.75 - 6.72 (m, 1H), 5.96 (d, *J* = 2.3 Hz, 2H), 4.21 - 4.07 (m, 4H), 2.86 - 2.80(m, 4H), 1.85 - 1.76 (m, 2H), 1.73 - 1.64 (m, 2H), 1.39 - 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.1, 127.8, 125.5, 112.1, 108.8, 101.4, 63.6 (d, J_{C-P} = 6.0 Hz), 35.3, 30.5 (d, J_{C-P} = 3.9 Hz), 29.7 (d, J_{C-P} = 5.5 Hz), 28.1, 16.1(d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{24}O_5PS_2$: 379.0797; found: 379.0792.



O,O-diethyl S-(4-(naphthalen-2-ylthio)butyl) phosphorothioate (**5ka**): TLC (PE/EtOAc, 3:1), R_f = 0.55; Colorless liquid (108.4 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.73 (m, 4H), 7.49 - 7.38 (m, 3H), 4.21 - 4.06 (m, 4H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.90 - 2.81(m, 2H), 1.90 - 1.78 (m, 4H), 1.34 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 131.8, 128.5, 127.8, 127.5, 127.1, 127.1, 126.7, 125.8, 63.7 (d, J_{C-P} = 6.0 Hz), 33.1, 30.5 (d, J_{C-P} = 4.0 Hz), 29.9 (d, J_{C-P} = 5.5 Hz), 28.0, 16.2 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{26}O_3PS_2$: 385.1055; found: 385.1058.

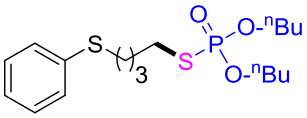


O,O-diethyl S-(4-(thiophen-2-ylthio)butyl) phosphorothioate (**5la**): TLC (PE/EtOAc, 3:1), R_f = 0.28; Colorless liquid (79.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 5.1 Hz, 1H), 7.12 (s, 1H), 6.98 (s, 1H), 4.23 - 4.09 (m, 4H), 2.87 - 2.78 (m, 4H), 1.86 - 1.81 (m, 2H), 1.76 - 1.68 (m, 2H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 133.9, 129.5, 127.7, 63.7 (d, J_{C-P} = 6.0 Hz), 38.3, 30.5 (d, J_{C-P} = 3.9 Hz), 29.6 (d, J_{C-P} = 5.5 Hz), 28.2, 16.2(d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{22}O_3PS_3$: 341.0463; found: 341.0461.

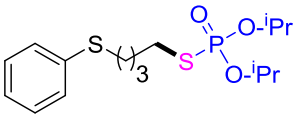


O,O-dimethyl S-(4-(phenylthio)butyl) phosphorothioate (**5ab**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (83.6 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.25 (m, 4H), 7.20 - 7.14 (m, 1H), 3.84 - 3.78 (m, 3H), 3.78 - 3.74 (m, 3H), 2.95 - 2.92 (m, 2H), 2.89 - 2.79 (m, 2H), 1.94 - 1.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 129.4, 129.0, 126.1, 53.9 (d, *J* = 6.0 Hz), 33.1, 30.4 (d, J_{C-P}

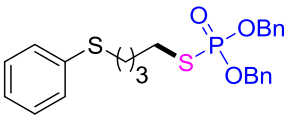
= 4.0 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{20}O_3PS_2$: 307.0586; found: 307.0582.



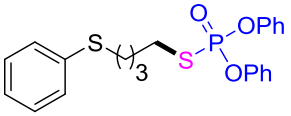
O,O-dibutyl S-(4-(phenylthio)butyl) phosphorothioate (**5ac**): TLC (PE/EtOAc, 3:1), R_f = 0.77; Colorless liquid (109.0 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.24 (m, 4H), 7.19 - 7.16 (m, 1H), 4.14 - 4.01 (m, 4H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.87 - 2.80 (m, 2H), 1.86 - 1.80 (m, 2H), 1.78 - 1.73 (m, 2H), 1.71 - 1.62 (m, 4H), 1.47 - 1.35 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 129.3, 129.0, 126.0, 67.3(d, $J_{C\text{-}P}$ = 6.4 Hz), 33.1, 32.2(d, *J* = 7.3 Hz), 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 28.0, 18.8, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{32}O_3PS_2$: 391.1525; found: 391.1526.



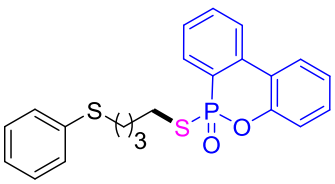
O,O-diisopropyl S-(4-(phenylthio)butyl) phosphorothioate (**5ad**): TLC (PE/EtOAc, 3:1), R_f = 0.77; Colorless liquid (97.9 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.26 (m, 4H), 7.19-7.16 (m, 1H), 4.78 - 4.67 (m, 2H), 2.93 (t, *J* = 7.0 Hz, 2H), 2.88 - 2.81 (m, 2H), 1.88 - 1.81 (m, 2H), 1.78 - 1.71 (m, 2H), 1.37 - 1.33 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 129.3, 129.0, 126.1, 72.7 (d, $J_{C\text{-}P}$ = 6.5 Hz), 33.2, 30.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 28.1, 24.0(dd, $J_{C\text{-}P}$ = 4.2 Hz), 23.9(dd, *J* = 5.5 Hz), 23.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{28}O_3PS_2$: 363.1212; found: 363.1217.



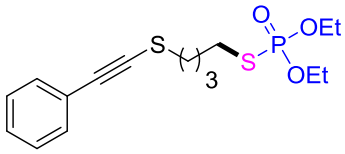
O,O-dibenzyl S-(4-(phenylthio)butyl) phosphorothioate (**5ae**): TLC (PE/EtOAc, 3:1), R_f = 0.78; Colorless liquid (119.7 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.23 (m, 14H), 7.18 - 7.15 (m, 1H), 5.18 - 5.06 (m, 4H), 2.84 - 2.71 (m, 4H), 1.79 - 1.58 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 135.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 129.3, 129.0, 128.7, 128.2, 126.1, 69.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 33.0, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 27.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{28}O_3PS_2$: 459.1212; found: 459.1218.



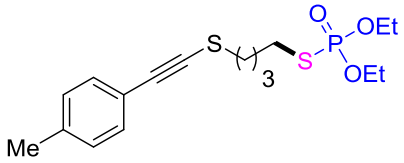
O,O-diphenyl S-(4-(phenylthio)butyl) phosphorothioate (**5af**): TLC (PE/EtOAc, 3:1), R_f = 0.78; Colorless liquid (87.8 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.15 (m, 15H), 2.98 - 2.88 (m, 2H), 2.82 (t, *J* = 7.0 Hz, 2H), 1.79 - 1.70 (m, 2H), 1.67 - 1.60 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3 (d, $J_{C\text{-}P}$ = 8.1 Hz), 136.3, 130.0, 129.4, 129.0, 126.2, 125.8, 120.8 (d, $J_{C\text{-}P}$ = 4.9 Hz), 33.1, 31.4 (d, $J_{C\text{-}P}$ = 4.2 Hz), 29.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 27.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{24}O_3PS_2$: 431.0899; found: 431.0903.



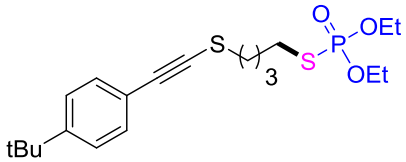
6-((4-(phenylthio)butyl)thio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5ag**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (91.6 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 - 7.90 (m, 3H), 7.73 - 7.69 (m, 1H), 7.55 - 7.51 (m, 1H), 7.41 - 7.37 (m, 1H), 7.32 - 7.15 (m, 7H), 2.98 - 2.79 (m, 4H), 1.86 - 1.76 (m, 2H), 1.71 - 1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, J_{C-P} = 9.4 Hz), 136.4, 136.2 (d, J_{C-P} = 7.5 Hz), 133.9 (d, J_{C-P} = 2.5 Hz), 130.9, 130.6 (d, J_{C-P} = 10.8 Hz), 129.3, 129.0, 128.8 (d, J_{C-P} = 14.9 Hz), 126.6, 126.1, 125.9 (d, J_{C-P} = 135.4 Hz), 125.2 (d, J_{C-P} = 16.3 Hz), 124.0 (d, J_{C-P} = 11.3 Hz), 122.5 (d, J_{C-P} = 12.2 Hz), 120.6 (d, J_{C-P} = 6.7 Hz), 33.1, 30.0 (d, J_{C-P} = 4.7 Hz), 29.7 (d, J_{C-P} = 3.3 Hz), 27.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}O_2PS_2$: 413.0793; found: 413.0787.



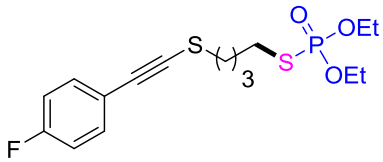
O,O-diethyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7aa**): TLC (PE/EtOAc, 3:1), R_f = 0.70; Colorless liquid (89.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.27 (m, 5H), 4.26 - 4.06 (m, 4H), 2.96 - 2.77 (m, 4H), 1.92 - 1.91 (m, 4H), 1.37 - 1.35 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.4, 128.2, 123.4, 93.4, 79.0, 63.7 (d, J_{C-P} = 5.9 Hz), 35.1, 30.5 (d, J_{C-P} = 4.0 Hz), 29.4 (d, J_{C-P} = 5.4 Hz), 28.17, 16.2 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{24}O_3PS_2$: 359.0899; found: 359.0902.



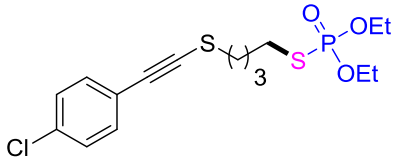
O,O-diethyl S-(4-((p-tolylethynyl)thio)butyl) phosphorothioate (**7ba**): TLC (PE/EtOAc, 3:1), R_f = 0.73; Colorless liquid (88.3 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 4.23 - 4.11 (m, 4H), 2.93 - 2.85 (m, 2H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.34 (s, 3H), 1.95 - 1.85 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.6, 129.2, 120.4, 93.5, 78.0, 63.7 (d, J_{C-P} = 6.0 Hz), 35.1, 30.5 (d, J_{C-P} = 4.0 Hz), 29.4 (d, J_{C-P} = 5.4 Hz), 28.2, 21.6, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{26}O_3PS_2$: 373.1055; found: 373.1059.



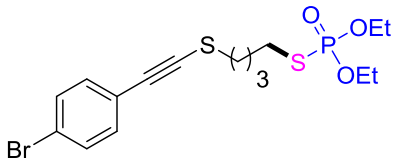
S-(4-(((4-(tert-butyl)phenyl)ethynyl)thio)butyl) O,O-diethyl phosphorothioate (**7ca**): TLC (PE/EtOAc, 3:1), R_f = 0.59; Colorless liquid (101.9 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.26 (m, 4H), 4.23 - 4.07 (m, 4H), 2.92 - 2.84 (m, 2H), 2.80 - 2.79 (m, 2H), 1.90 - 1.83 (m, 4H), 1.38 - 1.32 (m, 6H), 1.30-1.29 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 131.5, 125.4, 120.4, 93.4, 78.0, 63.7 (d, J_{C-P} = 6.0 Hz), 35.1, 34.9, 31.3, 30.5 (d, J_{C-P} = 4.0 Hz), 29.4 (d, J_{C-P} = 5.4 Hz), 28.1, 16.2 (d, J_{C-P} = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{32}O_3PS_2$: 415.1525; found: 415.1527.



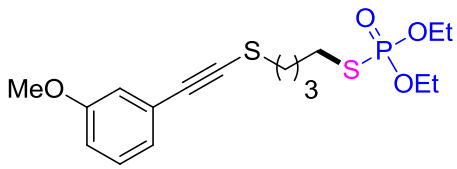
O,O-diethyl S-(4-(((4-fluorophenyl)ethynyl)thio)butyl) phosphorothioate (**7da**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (86.9 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.39 (m, 2H), 7.02 - 6.98 (m, 2H), 4.23 - 4.09 (m, 4H), 2.93 - 2.88 (m, 2H), 2.82 -2.77 (m, 2H), 1.91 (d, *J* = 2.2 Hz, 4H), 1.38 - 1.34(m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 248.1 Hz), 133.6 (d, $J_{C\text{-}F}$ = 8.3 Hz), 119.4 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 92.1, 78.6, 63.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 35.0, 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.1, 16.1 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.78; -110.79; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}FO_3PS_2$: 377.0805; found: 377.0802.



S-(4-(((4-chlorophenyl)ethynyl)thio)butyl) O,O-diethyl phosphorothioate (**7ea**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (91.9 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 2H), 4.27 - 4.04 (m, 4H), 2.94 - 2.85 (m, 2H), 2.82 (t, *J* = 6.4 Hz, 2H), 1.99 - 1.84 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 132.8, 128.8, 122.0, 92.3, 80.4, 63.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 35.1, 30.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.2, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}ClO_3PS_2$: 393.0509; found: 393.0511.

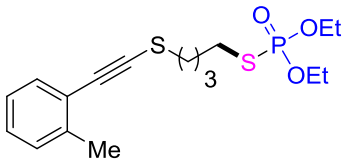


S-(4-(((4-bromophenyl)ethynyl)thio)butyl) O,O-diethyl phosphorothioate (**7fa**): TLC (PE/EtOAc, 3:1), R_f = 0.33; Colorless liquid (94.5 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.39 (m, 2H), 7.30 - 7.24 (m, 2H), 4.29 - 4.07 (m, 4H), 2.98 - 2.76 (m, 4H), 2.01 - 1.83 (m, 4H), 1.39 - 1.34 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 131.7, 122.4, 122.4, 92.4, 80.6, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 35.1, 30.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.2, 16.2 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}BrO_3PS_2$: 437.0004; found: 437.0009.

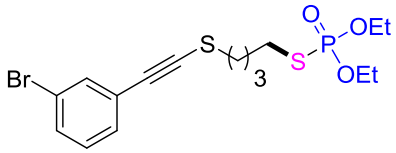


O,O-diethyl S-(4-(((3-methoxyphenyl)ethynyl)thio)butyl) phosphorothioate (**7ga**): TLC (PE/EtOAc, 3:1), R_f = 0.46; Colorless liquid (74.6 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 - 7.18 (m, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.85 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.22 - 4.11 (m, 4H), 3.80 (s, 3H), 2.93 - 2.86 (m, 2H), 2.82 (t, *J* = 6.6 Hz, 2H), 1.97 - 1.87 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 129.5, 124.4, 124.1, 116.3, 114.9, 93.3, 79.0, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 55.4,

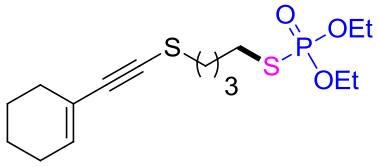
35.1, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.4 Hz), 28.2, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{26}O_4PS_2$: 389.1005; found: 389.1001.



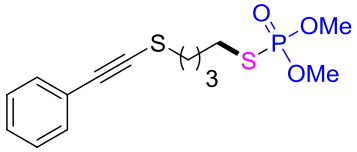
O,O-diethyl S-(4-((o-tolylethynyl)thio)butyl) phosphorothioate (**7ha**): TLC (PE/EtOAc, 3:1), R_f = 0.55; Colorless liquid (79.3 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 0.8 Hz, 2H), 7.13 - 7.12 (m, 1H), 4.23 - 4.09 (m, 4H), 2.93 - 2.86 (m, 2H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.42 (s, 3H), 1.98 - 1.87 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 131.8, 129.5, 128.2, 125.7, 123.3, 92.4, 82.6, 63.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 35.3, 30.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 28.2, 20.9, 16.2 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{26}O_3PS_2$: 373.1055; found: 373.1057.



S-(4-(((3-bromophenyl)ethynyl)thio)butyl) O,O-diethyl phosphorothioate (**7ia**): TLC (PE/EtOAc, 3:1), R_f = 0.58; Colorless liquid (95.8 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.19 - 7.15 (m, 1H), 4.22 - 4.07 (m, 4H), 2.94 - 2.85 (m, 2H), 2.82 (t, *J* = 6.5 Hz, 2H), 1.93 - 1.85 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 134.1, 131.3, 130.0, 129.9, 125.5, 122.2, 91.9, 81.1, 63.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 35.1, 30.5 (d, $J_{C\text{-}P}$ = 4.1 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 28.2, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}BrO_3PS_2$: 437.0004; found: 437.0007.

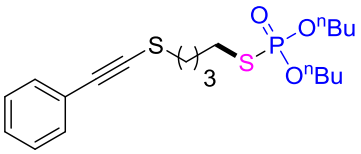


S-(4-((cyclohex-1-en-1-ylethynyl)thio)butyl) O,O-diethyl phosphorothioate (**7ja**): TLC (PE/EtOAc, 3:1), R_f = 0.72; Colorless liquid (40.2 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 4.23 – 4.09 (m, 4H), 2.92 – 2.79 (m, 2H), 2.71 (t, *J* = 5.9 Hz, 2H), 2.18 – 1.99 (m, 4H), 1.91 – 1.78 (m, 4H), 1.63 – 1.51 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 120.8, 95.2, 75.4, 63.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 35.0, 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 5.4 Hz), 29.2, 27.9, 25.6, 22.3, 21.4, 16.1 (d, $J_{C\text{-}P}$ = 7.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.91. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{28}O_3PS_2$: 363.1212; found: 363.1214.

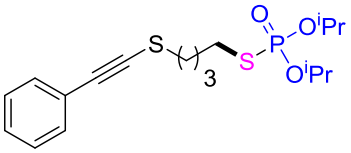


O,O-dimethyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7ab**): TLC (PE/EtOAc, 3:1), R_f = 0.29; Colorless liquid (81.2 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 3.0 Hz, 2H), 7.33 - 7.26 (m, 3H), 3.85 - 3.79 (m, 3H), 3.79 - 3.74 (m, 3H), 2.94 - 2.85 (m, 2H), 2.83 - 2.80 (m, 2H), 1.99 - 1.86 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.4, 128.2, 123.4, 93.4, 79.0, 54.0 (d, $J_{C\text{-}P}$ = 6.0

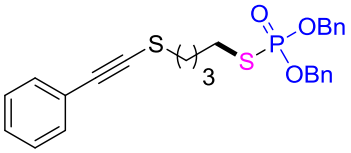
Hz), 53.9, 35.1, 30.5 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{20}O_3PS_2$: 331.0586; found: 331.0588.



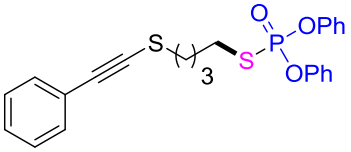
O,O-dibutyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7ac**): TLC (PE/EtOAc, 3:1), R_f = 0.38; Colorless liquid (98.3 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.0 Hz, 2H), 7.30 - 7.27 (m, 3H), 4.15 - 4.02 (m, 4H), 2.94 - 2.84 (m, 2H), 2.81 (t, *J* = 6.5 Hz, 2H), 1.97 - 1.85 (m, 4H), 1.72 - 1.63 (m, 4H), 1.47 - 1.34 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.4, 128.2, 123.5, 93.4, 79.0, 67.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 35.1, 32.3 (d, $J_{C\text{-}P}$ = 7.3 Hz), 30.4 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 28.2, 18.9, 13.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.01. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{32}O_3PS_2$: 415.1525; found: 415.1528.



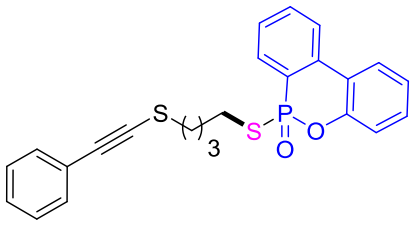
O,O-diisopropyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7ad**): TLC (PE/EtOAc, 3:1), R_f = 0.47; Colorless liquid (88.1 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.40 (m, 2H), 7.30 - 7.27 (m, 3H), 4.80 - 4.60 (m, 2H), 2.93 - 2.86 (m, 2H), 2.82 (t, *J* = 6.5 Hz, 2H), 1.98 - 1.84 (m, 4H), 1.37 - 1.34 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.4, 128.2, 123.5, 93.4, 79.1, 72.8 (d, $J_{C\text{-}P}$ = 6.5 Hz), 35.1, 30.6 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 28.3, 24.0 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.8 (d, $J_{C\text{-}P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.3. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{28}O_3PS_2$: 387.1212; found: 387.1217.



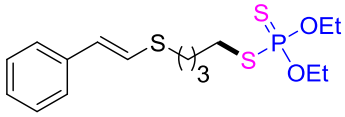
O,O-dibenzyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7ae**): TLC (PE/EtOAc, 3:1), R_f = 0.36; Colorless liquid (111.5 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.26 (m, 15H), 5.18 - 5.04 (m, 4H), 2.86 - 2.74 (m, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 1.87 - 1.76 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.6, 129.0, 128.7, 128.7, 128.4, 128.2, 123.4, 93.4, 79.0, 69.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 35.0, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 28.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}O_3PS_2$: 483.1212; found: 483.1209.



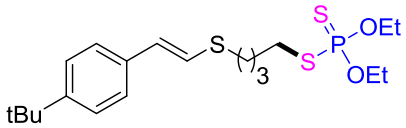
O,O-diphenyl S-(4-((phenylethynyl)thio)butyl) phosphorothioate (**7af**): TLC (PE/EtOAc, 3:1), R_f = 0.67; Colorless liquid (87.3 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.18 (m, 15H), 3.01 - 2.96 (m, 2H), 2.69 (t, *J* = 5.2 Hz, 2H), 1.80 - 1.79 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2 (d, $J_{C\text{-}P}$ = 8.1 Hz), 131.6, 130.0, 129.7, 128.4, 128.2, 125.8, 123.4, 120.9 (d, $J_{C\text{-}P}$ = 4.9 Hz), 120.4, 120.3 (d, $J_{C\text{-}P}$ = 5.0 Hz), 115.5, 93.4, 79.0, 34.9, 31.4 (d, $J_{C\text{-}P}$ = 4.2 Hz), 29.2 (d, $J_{C\text{-}P}$ = 5.6 Hz), 27.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{24}O_3PS_2$: 455.0899; found: 455.0905.



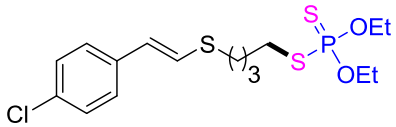
6-((4-((phenylethynyl)thio)butyl)thio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**7ag**): TLC (PE/EtOAc, 3:1), R_f = 0.35; Colorless liquid (79.9 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 7.90 (m, 3H), 7.73 - 7.69 (m, 1H), 7.55 - 7.51 (m, 1H), 7.41 - 7.37 (m, 3H), 7.32 - 7.24 (m, 5H), 3.03 - 2.82 (m, 2H), 2.77 - 2.74 (m, 2H), 1.91 - 1.86 (m, 2H), 1.71 - 1.66 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6 (d, J_{C-P} = 9.4 Hz), 136.2 (d, J_{C-P} = 7.5 Hz), 134.0 (d, J_{C-P} = 2.5 Hz), 131.6, 130.9, 130.6 (d, J_{C-P} = 10.9 Hz), 128.8 (d, J_{C-P} = 14.9 Hz), 128.4, 128.2, 126.6, 125.9 (d, J_{C-P} = 135.6 Hz), 125.2 (d, J_{C-P} = 16.9 Hz), 124.0 (d, J_{C-P} = 11.2 Hz), 123.4, 122.4 (d, J_{C-P} = 12.1 Hz), 120.6 (d, J_{C-P} = 6.7 Hz), 93.4, 79.0, 35.0, 29.6 (d, J_{C-P} = 3.3 Hz), 29.5 (d, J_{C-P} = 4.5 Hz), 28.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{22}O_2PS_2$: 437.0793; found: 437.0796.



(E)-O,O-diethyl S-(4-(styrylthio)butyl) phosphorodithioate (**9a**): TLC (PE/EtOAc, 20:1), R_f = 0.60; Colorless liquid (96.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 4.2 Hz, 4H), 7.15 - 7.10 (m, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 4.19 - 3.99 (m, 4H), 2.88 - 2.78 (m, 2H), 2.74 (t, *J* = 6.4 Hz, 2H), 1.75 - 1.74 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.5, 127.0, 125.6, 124.7, 64.0 (d, J_{C-P} = 6.0 Hz), 33.2 (d, J_{C-P} = 3.9 Hz), 32.07, 29.4 (d, J_{C-P} = 5.3 Hz), 28.3, 16.0 (d, J_{C-P} = 8.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}O_2PS_3$: 377.0827; found: 377.0829.

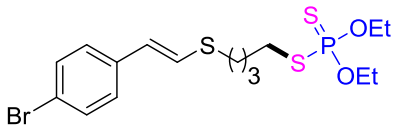


(E)-S-(4-((4-(tert-butyl)styryl)thio)butyl) O,O-diethyl phosphorodithioate (**9b**): TLC (PE/EtOAc, 20:1), R_f = 0.55; Colorless liquid (101.2 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 - 7.22 (m, 2H), 6.64 (d, *J* = 15.5 Hz, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 4.26 - 4.06 (m, 4H), 2.95 - 2.85 (m, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 1.89 - 1.81 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 134.3, 127.8, 125.7, 125.4, 123.7, 64.1 (d, J_{C-P} = 6.0 Hz), 34.6, 33.2 (d, J_{C-P} = 3.9 Hz), 32.2, 31.4, 29.5 (d, J_{C-P} = 5.3 Hz), 28.4, 16.0 (d, J_{C-P} = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{34}O_2PS_3$: 433.1453; found: 433.1457.

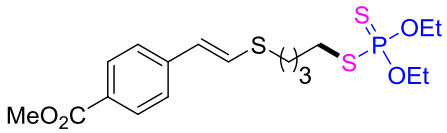


(E)-S-(4-((4-chlorostyryl)thio)butyl) O,O-diethyl phosphorodithioate (**9c**): TLC (PE/EtOAc, 20:1), R_f = 0.50; Colorless liquid (93.7 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.16 (m, 4H), 6.68 (dd, *J* = 15.6, 3.0 Hz, 1H), 6.40 (dd, *J* = 15.6, 2.9 Hz, 1H), 4.25 - 4.04 (m, 4H), 2.95 - 2.85 (m, 2H), 2.81 - 2.80 (m, 2H), 1.89 - 1.81 (m, 4H), 1.40 - 1.27 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.5, 132.4, 128.8,

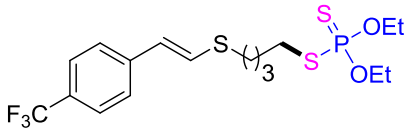
126.7, 125.8, 125.8, 64.0 (d, $J_{C\text{-}P}$ = 6.1 Hz), 33.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 32.0, 29.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.3, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}ClO_2PS_3$: 411.0437; found: 411.0438.



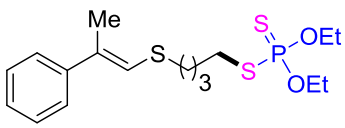
(E)-S-(4-((4-bromostyryl)thio)butyl) O,O-diethyl phosphorodithioate (**9d**): TLC (PE/EtOAc, 20:1), R_f = 0.50; Colorless liquid (112.0 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.17 - 7.09 (m, 2H), 6.70 (dd, *J* = 15.6, 2.2 Hz, 1H), 6.38 (dd, *J* = 16.0 Hz, *J* = 4.0 Hz, 1H), 4.23 - 4.08 (m, 4H), 2.92 - 2.87 (m, 2H), 2.81 - 2.73 (m, 2H), 1.89 - 1.81 (m, 4H), 1.39 - 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 131.7, 127.0, 125.9, 125.7, 120.5, 64.0 (d, $J_{C\text{-}P}$ = 6.1 Hz), 33.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 32.0, 29.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.2, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}BrO_2PS_3$: 454.9932; found: 454.9934.



methyl (E)-4-(2-((4-((diethoxyphosphorothioyl)thio)butyl)thio)vinyl)benzoate (**9e**): TLC (PE/EtOAc, 20:1), R_f = 0.23; Colorless liquid (92.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 4.25 - 4.04 (m, 4H), 3.90 (s, 3H), 3.01 - 2.77 (m, 4H), 1.92 - 1.77 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 141.4, 130.1, 128.6, 128.2, 125.4, 125.3, 64.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 52.1, 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 31.93, 29.5 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.2, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{28}O_4PS_3$: 435.0882; found: 435.0880.

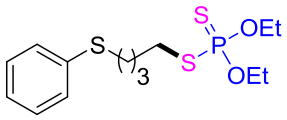


(E)-O,O-diethyl S-(4-((4-(trifluoromethyl)styryl)thio)butyl) phosphorodithioate (**9f**): TLC (PE/EtOAc, 20:1), R_f = 0.40; Colorless liquid (90.7 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 4.26 - 4.07 (m, 4H), 2.96 - 2.84 (m, 4H), 1.84 - 1.76 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.4, 128.3 (q, $J_{C\text{-}F}$ = 32.3 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.6, 125.1, 121.7 (q, $J_{C\text{-}F}$ = 272.6 Hz), 64.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 33.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 32.0, 29.5 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.2, 16.0 (d, $J_{C\text{-}P}$ = 8.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.13. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{25}F_3O_2PS_3$: 445.0701; found: 445.0706.

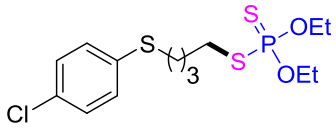


(E)-O,O-diethyl S-(4-((2-phenylprop-1-en-1-yl)thio)butyl) phosphorodithioate (**9g**): TLC (PE/EtOAc, 20:1), R_f = 0.59; Colorless liquid (97.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.28 (m, 4H), 7.22 (dd, *J* = 15.2, 8.2 Hz, 1H), 6.27 (s, 1H), 4.28 - 4.04 (m, 4H), 2.94 - 2.85 (m, 2H), 2.79 (t, *J* = 6.6

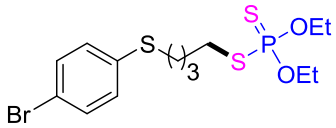
Hz, 2H), 2.12 (s, 3H), 1.84 - 1.80 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 134.0, 128.4, 126.8, 125.2, 123.3, 64.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.6, 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 1.8 Hz), 29.2, 17.7, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{28}O_2PS_3$: 391.0984; found: 391.0987.



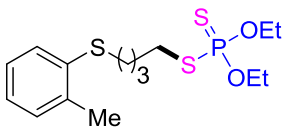
O,O-diethyl S-(4-(phenylthio)butyl) phosphorodithioate (**9h**): TLC (PE/EtOAc, 20:1), R_f = 0.55; Colorless liquid (87.3 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.18 (m, 4H), 7.13 - 7.09 (m, 1H), 4.29 - 3.97 (m, 4H), 2.90 - 2.76 (m, 4H), 1.80 - 1.63 (m, 4H), 1.35 - 1.26 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 129.4, 129.0, 126.1, 64.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.3(d, $J_{C\text{-}P}$ = 4.8 Hz), 29.5 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.1, 16.0 (d, $J_{C\text{-}P}$ = 8.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{24}O_2PS_3$: 351.0671; found: 351.0673.



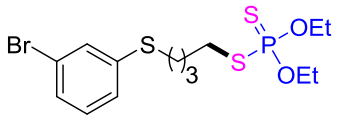
S-(4-((4-chlorophenyl)thio)butyl) O,O-diethyl phosphorodithioate(**9i**): TLC (PE/EtOAc, 20:1), R_f = 0.50; Colorless liquid (85.5 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.25 (m, 4H), 4.29 - 4.05 (m, 4H), 2.99 - 2.77 (m, 4H), 1.83 - 1.73 (m, 4H), 1.43 - 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 132.1, 130.8, 129.2, 64.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.5, 33.2 (d, $J_{C\text{-}P}$ = 3.2 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.0, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}ClO_2PS_3$: 385.0281; found: 385.0285.



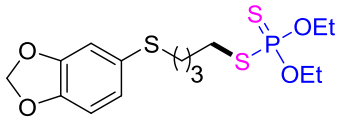
(4-((4-bromophenyl)thio)butyl) O,O-diethyl phosphorodithioate(**9j**): TLC (PE/EtOAc, 20:1), R_f = 0.56; Colorless liquid (99.2 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 4.28 - 4.07 (m, 4H), 2.93 - 2.84 (m, 4H), 1.86 - 1.69 (m, 4H), 1.37 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 132.1, 130.9, 119.9, 64.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 33.3, 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 27.9, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}BrO_2PS_3$: 428.9776; found: 428.9774.



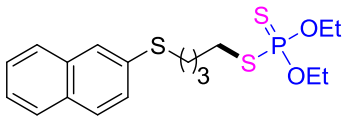
O,O-diethyl S-(4-(o-tolylthio)butyl) phosphorodithioate(**9k**): TLC (PE/EtOAc, 20:1), R_f = 0.50; Colorless liquid (75.5 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.3 Hz, 1H), 7.17 - 7.14 (m, 2H), 7.11 - 7.06 (m, 1H), 4.27 - 4.03 (m, 4H), 2.97 - 2.82 (m, 4H), 2.36 (s, 3H), 1.92 - 1.73 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 135.8, 130.2, 127.9, 126.5, 125.8, 64.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 32.4, 29.6 (d, $J_{C\text{-}P}$ = 5.3 Hz), 27.9, 20.5, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_2PS_3$: 365.0827; found: 365.0833.



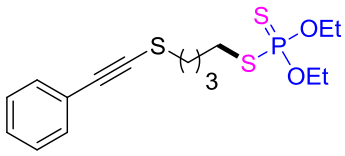
S-(4-((3-bromophenyl)thio)butyl) O,O-diethyl phosphorodithioate (**9l**): TLC (PE/EtOAc, 20:1), R_f = 0.60; Colorless liquid (95.3 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.33 - 7.19 (m, 2H), 7.16 - 7.12 (m, 1H), 4.32 - 3.95 (m, 4H), 3.00 - 2.80 (m, 4H), 1.90 - 1.69 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 131.3, 130.3, 129.0, 127.4, 122.9, 64.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 33.0, 29.5 (d, $J_{C\text{-}P}$ = 5.3 Hz), 27.8, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}BrO_2PS_3$: 428.9776; found: 428.9779.



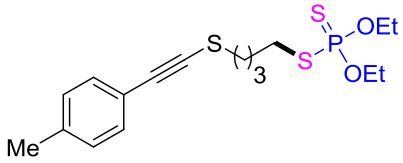
S-(4-(benzo[d][1,3]dioxol-5-ylthio)butyl) O,O-diethyl phosphorodithioate (**9m**): TLC (PE/EtOAc, 20:1), R_f = 0.25; Colorless liquid (99.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 6.3 Hz, 2H), 6.76 - 6.70 (m, 1H), 5.95 (s, 2H), 4.23 - 4.07 (m, 4H), 2.90 - 2.78 (m, 4H), 1.83 - 1.75 (m, 2H), 1.71 - 1.64(m, 2H), 1.35 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.1, 127.8, 125.4, 112.0, 108.7, 101.3, 63.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 35.25, 33.1 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.1, 15.9 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{24}O_4PS_3$: 395.0569; found: 395.0565.



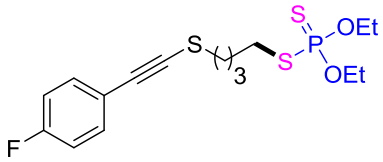
O,O-diethyl S-(4-(naphthalen-2-ylthio)butyl) phosphorodithioate (**9n**): TLC (PE/EtOAc, 20:1), R_f = 0.55; Colorless liquid (93.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.73 (m, 4H), 7.50 - 7.36 (m, 3H), 4.23 - 4.05 (m, 4H), 3.02 (t, *J* = 6.6 Hz, 2H), 2.93 - 2.79 (m, 2H), 1.88 - 1.75 (m, 4H), 1.33 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 133.8, 131.8, 128.5, 127.8, 127.4, 127.1, 127.0, 126.6, 125.7, 64.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 33.0, 29.5 (d, $J_{C\text{-}P}$ = 5.3 Hz), 28.0, 16.0 (d, $J_{C\text{-}P}$ = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{26}O_2PS_3$: 401.0827; found: 401.0824.



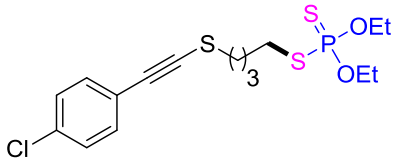
O,O-diethyl S-(4-((phenylethynyl)thio)butyl) phosphorodithioate (**9o**): TLC (PE/EtOAc, 20:1), R_f = 0.65; Colorless liquid (83.1 mg, 74%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 2H), 7.30 - 7.26 (m, 3H), 4.26 - 4.07 (m, 4H), 2.96 - 2.89 (m, 2H), 2.81 (t, *J* = 6.7 Hz, 2H), 1.98 - 1.83 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.4, 128.2, 123.4, 93.4, 79.0, 64.1 (d, $J_{C\text{-}P}$ = 6.0 Hz), 35.1, 33.2 (d, $J_{C\text{-}P}$ = 3.9 Hz), 29.0 (d, $J_{C\text{-}P}$ = 5.2 Hz), 28.2, 16.0 (d, $J_{C\text{-}P}$ = 8.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{24}O_2PS_3$: 375.0671; found: 375.0675.



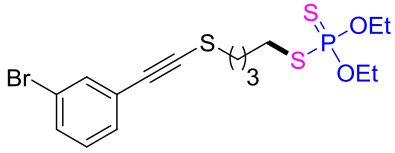
O,O-diethyl S-(4-((p-tolylethynyl)thio)butyl) phosphorodithioate (**9p**): TLC (PE/EtOAc, 20:1), R_f = 0.22; Colorless liquid (66.4 mg, 57%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 - 7.27(m, 2H), 7.11 - 7.09 (m, 2H), 4.23 - 4.05 (m, 4H), 2.94 - 2.89 (m, 2H), 2.84 - 2.76 (m, 2H), 2.34 (s, 3H), 1.92 - 1.86 (m, 4H), 1.39 - 1.30 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.6, 129.2, 120.4, 93.5, 78.0, 64.1 (d, J_{C-P} = 6.0 Hz), 35.2, 33.2 (d, J_{C-P} = 3.9 Hz), 29.0 (d, J_{C-P} = 5.2 Hz), 28.2, 21.6, 16.0 (d, J_{C-P} = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{26}O_2PS_3$: 389.0827; found: 389.0829.



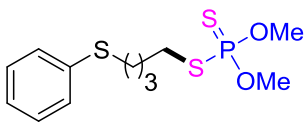
O,O-diethyl S-(4-(((4-fluorophenyl)ethynyl)thio)butyl) phosphorodithioate (**9q**): TLC (PE/EtOAc, 20:1), R_f = 0.52; Colorless liquid (71.8 mg, 61%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 3.6 Hz, 2H), 7.02 - 6.99 (m, 2H), 4.25 - 4.08 (m, 4H), 2.97 - 2.86 (m, 2H), 2.81 - 2.78 (m, 2H), 1.90 - 1.86 (m, 4H), 1.39 - 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F} = 250.5 Hz), 133.6 (d, J_{C-F} = 8.4 Hz), 119.5 (d, J_{C-F} = 3.5 Hz), 115.6 (d, J_{C-F} = 22.2 Hz), 92.2, 78.7, 64.0 (d, J_{C-P} = 6.1 Hz), 35.0, 33.1 (d, J_{C-P} = 3.8 Hz), 28.9 (d, J_{C-P} = 5.3 Hz), 28.2, 15.9 (d, J_{C-P} = 8.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}FO_2PS_3$: 393.0576; found: 393.0578.



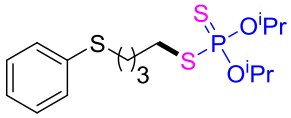
S-(4-(((4-chlorophenyl)ethynyl)thio)butyl) O,O-diethyl phosphorodithioate (**9r**): TLC (PE/EtOAc, 20:1), R_f = 0.63; Colorless liquid (77.3 mg, 63%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.29 - 7.25 (m, 2H), 4.26 - 4.07 (m, 4H), 2.96 - 2.89 (m, 2H), 2.82 (t, *J* = 6.6 Hz, 2H), 1.97 - 1.80 (m, 4H), 1.41 - 1.33 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 132.8, 128.8, 122.0, 92.3, 80.4, 64.1 (d, J_{C-P} = 6.1 Hz), 35.2, 35.2, 33.2 (d, J_{C-P} = 3.9 Hz), 29.0 (d, J_{C-P} = 5.2 Hz), 28.2, 16.0 (d, J_{C-P} = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}ClO_2PS_3$: 409.0281; found: 409.0278.



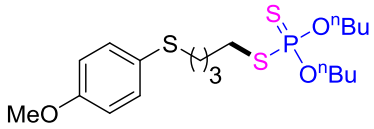
S-(4-(((3-bromophenyl)ethynyl)thio)butyl) O,O-diethyl phosphorodithioate (**9s**): TLC (PE/EtOAc, 20:1), R_f = 0.47; Colorless liquid (74.8 mg, 55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 4.23 - 4.10 (m, 4H), 2.97 - 2.89 (m, 2H), 2.82 - 2.80 (d, *J* = 6.6 Hz, 2H), 1.92 - 1.87 (m, 4H), 1.36 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 131.3, 130.0, 129.9, 125.5, 122.2, 92.0, 81.1, 64.1 (d, J_{C-P} = 6.2 Hz), 35.2, 33.2 (d, J_{C-P} = 5.3 Hz), 29.0 (d, J_{C-P} = 5.3 Hz), 28.3, 16.00 (d, J_{C-P} = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{23}BrO_2PS_3$: 452.9776; found: 452.9778.



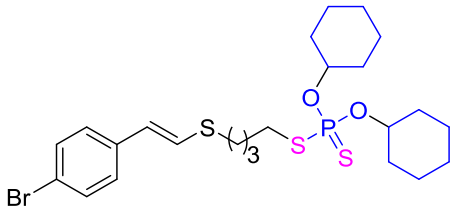
O,O-dimethyl S-(4-(phenylthio)butyl) phosphorodithioate (**9t**): TLC (PE/EtOAc, 20:1), R_f = 0.39 ; Colorless liquid (75.5 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.27 (m, 4H), 7.20 - 7.14 (m, 1H), 3.76 (dd, *J* = 15.0, 2.1 Hz, 6H), 2.97 - 2.80 (m, 4H), 1.87 - 1.68 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 129.4, 128.9, 126.1, 54.0 (d, J_{C-P} = 5.7 Hz), 33.2 (d, J_{C-P} = 3.9 Hz), 33.1, 29.4 (d, J_{C-P} = 5.1 Hz), 28.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 100.17; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{20}O_2PS_3$: 323.0358; found: 323.0361.



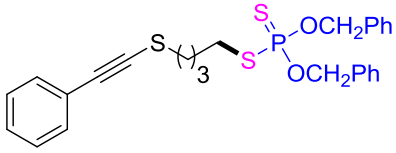
O,O-diisopropyl S-(4-(phenylthio)butyl) phosphorodithioate (**9u**): TLC (PE/EtOAc, 20:1), R_f = 0.74; Colorless liquid (82.9 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.26 (m, 4H), 7.19 - 7.16 (m, 1H), 4.87 - 4.75 (m, 2H), 2.95 - 2.85 (m, 4H), 1.87 - 1.71 (m, 4H), 1.34 (t, *J* = 5.5 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 129.4, 129.0, 126.1, 73.5 (d, J_{C-P} = 6.9 Hz), 33.3(d, J_{C-P} = 3.8 Hz), 33.3, 29.3 (d, J_{C-P} = 6.0 Hz), 28.1, 23.9 (d, J_{C-P} = 4.6 Hz), 23.6 (d, J_{C-P} = 5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 92.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{28}O_2PS_3$: 379.0984; found: 379.0981.



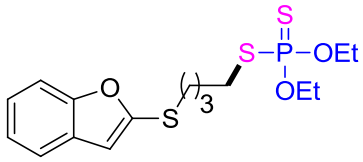
O,O-dibutyl S-(4-((4-methoxyphenyl)thio)butyl) phosphorodithioate (**9v**): TLC (PE/EtOAc, 20:1), R_f = 0.48; Colorless liquid (100.9 mg, 77%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.0 Hz, 2H), 6.85 (d, *J* = 7.2 Hz, 2H), 4.23 - 3.96 (m, 4H), 2.94 - 2.73 (m, 4H), 1.81 - 1.78 (m, 2H), 1.75 - 1.61 (m, 6H), 1.58 (s, 2H), 1.46 - 1.39 (m, 4H), 1.30 - 1.22 (m, 1H), 0.96 - 0.92 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 133.5, 126.3, 114.7, 67.8 (d, J_{C-P} = 6.7 Hz), 55.5, 35.5 (d, J_{C-P} = 6.5 Hz), 33.2 (d, J_{C-P} = 3.8 Hz), 32.1, 29.4 (d, J_{C-P} = 5.5 Hz), 28.3, 19.0, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{34}O_3PS_3$: 437.1402; found: 437.1408.



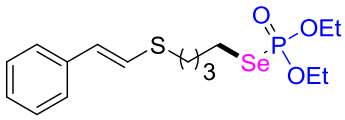
S-(4-((4-bromophenyl)thio)butyl) O,O-dicyclohexyl phosphorodithioate (**9w**): TLC (PE/EtOAc, 20:1), R_f = 0.53; Colorless liquid (94.4 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 4.64 - 4.51 (m, 2H), 2.93 (dt, *J* = 15.2, 6.6 Hz, 2H), 2.81 (t, *J* = 6.6 Hz, 2H), 2.05 - 1.68 (m, 14H), 1.55 - 1.47 (m, 3H), 1.41 - 1.20 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 131.8, 127.1, 126.1, 125.80 (s), 120.6, 78.3 (d, J_{C-P} = 7.6 Hz), 33.6 (d, J_{C-P} = 6.5 Hz), 33.3 (d, J_{C-P} = 6.5 Hz), 33.3, 32.1, 29.3 (d, J_{C-P} = 5.9 Hz), 28.4, 25.3, 23.8 (d, J_{C-P} = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 91.91. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{37}BrO_2PS_3$: 563.0871; found: 563.0875.



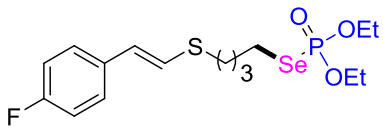
O,O-dibenzyl S-(4-((phenylethynyl)thio)butyl) phosphorodithioate (**9x**): TLC (PE/EtOAc, 3:1), R_f = 0.38; Colorless liquid (95.7 mg, 64%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.23 (m, 15H), 5.17 - 5.07 (m, 4H), 2.90 - 2.77 (m, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.87 - 1.69 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7 (d, J_{C-P} = 8.7 Hz), 131.6, 128.7, 128.7, 128.4, 128.4, 128.2, 123.5, 93.4, 79.1, 69.4 (d, J_{C-P} = 5.9 Hz), 35.0, 33.2 (d, J_{C-P} = 4.0 Hz), 28.8 (d, J_{C-P} = 5.6 Hz), 28.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 96.4. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}O_2PS_3$: 499.0984; found: 499.0992.



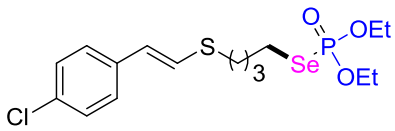
S-(4-(benzofuran-2-ylthio)butyl) O,O-diethyl phosphorodithioate (**9y**): TLC (PE/EtOAc, 10:1), R_f = 0.41; Colorless liquid (83.1 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 4.32 – 4.15 (m, 4H), 3.05 – 2.89 (m, 4H), 1.96 – 1.81 (m, 4H), 1.41 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 150.0, 128.5, 124.4, 122.8, 120.3, 111.2, 110.8, 63.8 (d, *J* = 6.1 Hz), 33.9, 32.9 (d, *J* = 3.8 Hz), 29.0 (d, *J* = 5.2 Hz), 28.5, 15.8 (d, *J* = 8.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.01. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{24}O_3PS_3$: 391.0620; found: 391.0625.



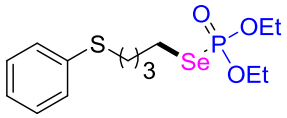
(E)-O,O-diethyl Se-(4-(styrylthio)butyl) phosphoroselenoate (**10a**): TLC (PE/EtOAc, 3:1), R_f = 0.37; Colorless liquid (105.1 mg, 86%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.15 (m, 5H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 4.31 - 4.05 (m, 4H), 2.94 - 2.80 (m, 4H), 1.95 - 1.84 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 128.7, 127.4, 127.0, 125.6, 124.8, 63.5 (d, J_{C-P} = 5.8 Hz), 32.0, 30.3 (d, J_{C-P} = 5.0 Hz), 29.3, 25.8 (d, J_{C-P} = 4.5 Hz), 16.1(d, J_{C-P} = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}O_3PSSe$: 409.0500; found: 409.0493.



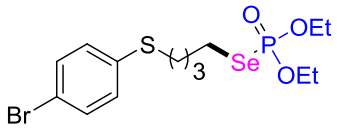
(E)-O,O-diethyl Se-(4-((4-fluorostyryl)thio)butyl) phosphoroselenoate (**10b**): TLC (PE/EtOAc, 3:1), R_f = 0.44; Colorless liquid (104.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.23 (m, 2H), 7.00 -6.96 (m, 2H), 6.61 (d, *J* = 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 4.25 - 4.06 (m, 4H), 2.94 - 2.87 (m, 2H), 2.81 (t, *J* = 7.1 Hz, 2H), 1.97 - 1.90 (m, 2H), 1.87 - 1.79 (m, 2H), 1.35 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (d, J_{C-F} = 247.3 Hz), 133.3 (d, J_{C-F} = 3.4 Hz), 127.0 (d, J_{C-F} = 7.9 Hz), 126.4, 124.5 (d, J_{C-F} = 2.2 Hz), 115.6 (d, J_{C-F} = 21.8 Hz), 63.5 (d, J_{C-P} = 5.9 Hz), 32.1, 30.3 (d, J_{C-P} = 4.2 Hz), 29.4, 25.8 (d, J_{C-P} = 4.7 Hz), 16.1 (d, J_{C-P} = 7.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.24; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}FO_3PSSe$: 427.0406; found: 427.0403.



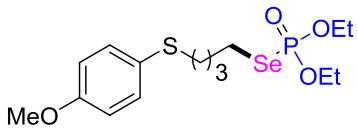
(E)-Se-(4-((4-chlorostyryl)thio)butyl) O,O-diethyl phosphoroselenoate (**10c**): TLC (PE/EtOAc, 3:1), R_f = 0.57; Colorless liquid (110.0 mg, 83%), 1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 4.23 - 4.10 (m, 4H), 2.91 - 2.87 (m, 2H), 2.82 (t, J = 7.1 Hz, 2H), 1.98 - 1.89 (m, 2H), 1.86 - 1.79 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 132.5, 128.9, 126.7, 125.9, 125.8, 63.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 32.0, 30.3 (d, $J_{C\text{-}P}$ = 4.2 Hz), 29.3, 25.8 (d, $J_{C\text{-}P}$ = 4.6 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{25}ClO_3PSSe$: 443.0110; found: 443.0111.



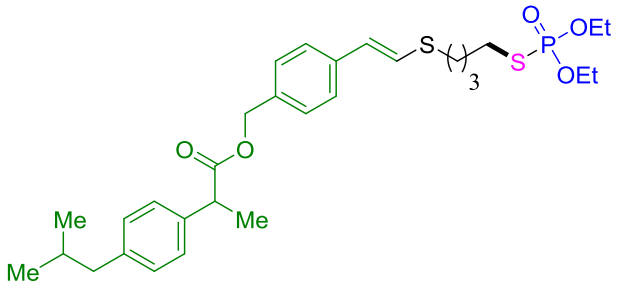
O,O-diethyl Se-(4-(phenylthio)butyl) phosphoroselenoate (**10d**): TLC (PE/EtOAc, 3:1), R_f = 0.36; Colorless liquid (96.1 mg, 84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.27 (m, 4H), 7.20 - 7.15 (m, 1H), 4.24 - 4.06 (m, 4H), 2.96 - 2.81 (m, 4H), 1.92 - 1.91 (m, 2H), 1.75- 1.72 (m, 2H), 1.39 - 1.35 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 129.4, 129.0, 126.1, 63.5(d, $J_{C\text{-}P}$ = 5.8 Hz), 33.2, 30.4 (d, $J_{C\text{-}P}$ = 4.3 Hz), 29.11, 25.9 (d, $J_{C\text{-}P}$ = 4.7 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{24}O_3PSSe$: 383.0344; found: 383.0347.



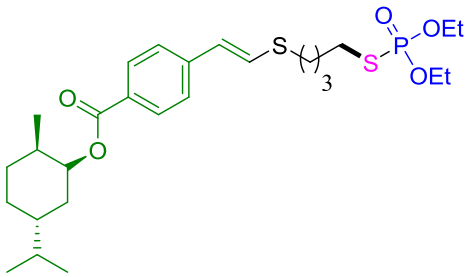
Se-(4-((4-bromophenyl)thio)butyl) O,O-diethyl phosphoroselenoate(**10e**): TLC (PE/EtOAc, 3:1), R_f = 0.50; Colorless liquid (107.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.23 - 4.09 (m, 4H), 2.97 - 2.82 (m, 4H), 1.93 (d, *J* = 7.3 Hz, 2H), 1.83 - 1.73 (m, 2H), 1.41 - 1.31 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 132.1, 130.9, 119.9, 63.5 (d, $J_{C\text{-}P}$ = 5.8 Hz), 33.3 (d, $J_{C\text{-}P}$ = 4.2 Hz), 28.9, 25.8 (d, $J_{C\text{-}P}$ = 4.4 Hz), 16.1(d, $J_{C\text{-}P}$ = 7.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{23}BrO_3PSSe$: 460.9449; found: 460.9447.



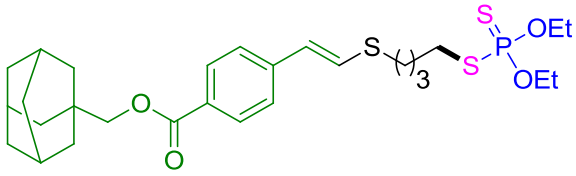
O,O-diethyl Se-(4-((4-methoxyphenyl)thio)butyl) phosphoroselenoate(**10f**): TLC (PE/EtOAc, 3:1), R_f = 0.57; Colorless liquid (90.1 mg, 73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.31 (m, 2H), 6.89 - 6.80 (m, 2H), 4.22 - 4.08 (m, 4H), 3.80 (d, *J* = 2.3 Hz, 3H), 2.90 - 2.79 (m, 4H), 1.93 - 1.85 (m, 2H), 1.70 - 1.66 (m, 2H), 1.39 - 1.35 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 133.5, 126.4, 114.7, 63.5 (d, $J_{C\text{-}P}$ = 5.8 Hz), 55.5, 35.4, 30.2 (d, $J_{C\text{-}P}$ = 4.3 Hz), 29.3, 25.9 (d, $J_{C\text{-}P}$ = 4.6 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{26}O_4PSSe$: 413.0449; found: 413.0454.



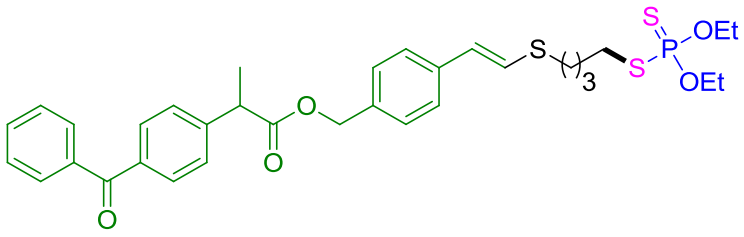
(E)-4-(2-((4-((diethoxyphosphoryl)thio)butyl)thio)vinyl)benzyl 2-(4-isobutylphenyl)propanoate (**3ra**): TLC (PE/EtOAc, 3:1), R_f = 0.68; Colorless liquid (116.3 mg, 67%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.14 (m, 6H), 7.09 (d, *J* = 6.4 Hz, 2H), 6.69 (d, *J* = 15.5 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.12 - 5.00 (m, 2H), 4.23 - 4.09 (m, 4H), 3.74 - 3.73 (m, 1H), 2.92 - 2.79 (m, 4H), 2.45 (d, *J* = 6.4 Hz, 2H), 1.83 (s, 4H), 1.50 (d, *J* = 6.8 Hz, 4H), 1.35 (d, *J* = 6.0 Hz, 6H), 0.92 - 0.88 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 140.7, 137.7, 136.9, 134.7, 129.4, 128.4, 127.3, 126.8, 125.6, 125.3, 66.2, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 45.2, 45.1, 32.1, 30.5 (d, $J_{C\text{-}P}$ = 3.9 Hz), 30.3, 29.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 28.3, 22.5, 18.5, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{44}O_5PS_2$: 579.2362; found: 579.2368.



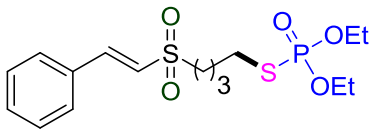
(1S,2R,5R)-5-isopropyl-2-methylcyclohexyl-4-((E)-2-((4-((diethoxyphosphoryl)thio)butyl)thio)vinyl)benzoate (**3sa**): TLC (PE/EtOAc, 3:1), R_f = 0.44; Colorless liquid (117.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 4.95 - 4.88 (m, 1H), 4.27 - 4.04 (m, 4H), 2.95 - 2.80 (m, 4H), 2.12 (d, *J* = 12.1 Hz, 1H), 1.98 - 1.90 (m, 1H), 1.91 - 1.79 (m, 5H), 1.73 (d, *J* = 11.5 Hz, 2H), 1.55 (t, *J* = 11.3 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 6H), 1.16 - 1.07 (m, 2H), 0.94 - 0.90 (m, 6H), 0.79 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 141.2, 130.1, 128.9, 128.3, 125.6, 125.2, 74.8, 63.7 (d, $J_{C\text{-}P}$ = 6.1 Hz), 47.4, 41.1, 34.4, 31.9, 31.5, 30.4 (d, $J_{C\text{-}P}$ = 4.0 Hz), 29.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 28.2, 26.6, 23.8, 22.2, 20.9, 16.7, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{44}O_5PS_2$: 543.2362; found: 543.2365.



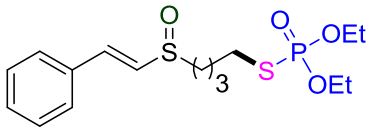
(E)-adamantan-1-ylmethyl 4-(2-((4-((diethoxyphosphoryl)thio)butyl)thio)vinyl)benzoate (**9ab**): TLC (PE/EtOAc, 10:1), R_f = 0.31; Colorless liquid (109.1 mg, 64%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 4.27 - 4.04 (m, 4H), 3.91 (s, 2H), 2.96 - 2.85 (m, 4H), 2.02 (s, 3H), 1.87 - 1.80 (m, 4H), 1.76 (d, *J* = 12.2 Hz, 3H), 1.69 (d, *J* = 12.8 Hz, 3H), 1.64 (s, 5H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 141.3, 130.1, 128.6, 128.4, 125.5, 125.2, 74.4, 64.1 (d, *J* = 6.1 Hz), 39.5, 37.1, 33.6, 33.2 (d, *J* = 3.9 Hz), 31.9, 29.4 (d, *J* = 5.2 Hz), 28.2, 28.1, 16.0 (d, *J* = 8.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 95.1. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{42}O_4PS_3$: 569.1977; found: 569.1984.



(E)-4-(2-((4-((diethoxyphosphorothioyl)thio)butyl)thio)vinyl)benzyl 2-(4-benzoylphenyl)propanoate (**9ac**): (PE/EtOAc, 4:1), R_f = 0.52; Colorless liquid (123.4 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.72 (m, 3H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.49 - 7.39 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 5.12 - 5.01 (m, 2H), 4.25 - 4.06 (m, 4H), 3.84 (q, *J* = 7.1 Hz, 1H), 2.99 - 2.85 (m, 2H), 2.81 (t, *J* = 6.3 Hz, 2H), 1.81 (s, 4H), 1.54 (d, *J* = 7.1 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5, 173.8, 140.7, 137.9, 137.5, 137.0, 134.3, 132.6, 131.6, 130.1, 129.3, 129.0, 128.6, 128.5, 128.4, 126.6, 125.6, 125.5, 66.4, 64.0 (d, *J* = 6.1 Hz), 45.4, 33.1 (d, *J* = 3.9 Hz), 32.0, 29.4 (d, *J* = 5.2 Hz), 28.3, 18.4, 15.6 (d, *J* = 8.3 Hz). HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{40}O_5PS_3$: 643.1770; found: 643.1174.



(E)-O,O-diethyl S-(4-(styrylsulfonyl)butyl) phosphorothioate (**11a**): TLC (PE/EtOAc, 1:3), R_f = 0.66; Colorless liquid (178.4 mg, 91%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 15.5 Hz, 1H), 7.47 - 7.45 (d, *J* = 6.9 Hz, 2H), 7.38 - 7.37 (m, 3H), 6.76 (d, *J* = 15.5 Hz, 1H), 4.23 - 3.94 (m, 4H), 3.03 (t, *J* = 7.1 Hz, 2H), 2.86 - 2.69 (m, 2H), 1.94 - 1.77 (m, 4H), 1.28 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 132.2, 131.6, 129.3, 128.8, 124.6, 63.9 (d, $J_{C\text{-}P}$ = 6.1 Hz), 54.5, 30.2 (d, $J_{C\text{-}P}$ = 3.8 Hz), 29.7 (d, $J_{C\text{-}P}$ = 4.9 Hz), 21.6, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.42. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}O_5PS_2$: 393.0954; found: 393.0958.



(E)-O,O-diethyl S-(4-(styrylsulfinyl)butyl) phosphorothioate (**11b**): TLC (PE/EtOAc, 1:3), Colorless liquid (137.3 mg, 73%), R_f = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.8 Hz, 2H), 7.34 - 7.30 (m, 3H), 7.18 (d, *J* = 16.9 Hz, 1H), 6.76 (d, *J* = 15.5 Hz, 1H), 4.15 - 4.00 (m, 4H), 2.85 - 2.69 (m, 4H), 1.94 - 1.78 (m, 4H), 1.31 - 1.26 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 133.9, 130.1, 129.9, 129.1, 127.8, 63.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 53.2, 30.3 (d, $J_{C\text{-}P}$ = 4.0 Hz), 30.1 (d, $J_{C\text{-}P}$ = 5.1 Hz), 29.8, 21.1, 16.2 (d, $J_{C\text{-}P}$ = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.6. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{26}O_4PS_2$: 377.1005; found: 377.1008.

4. References

[1] Wang, C.; Liu, B.; Shao, Z.; Zhou, J.; Shao, A.; Zou, L.-H.; Wen, J., Synthesis of 1,2-Diamines from Vinyl Sulfonium Salts and Arylamines. *Org. Lett.* **2022**, *24*, 6455-6459.

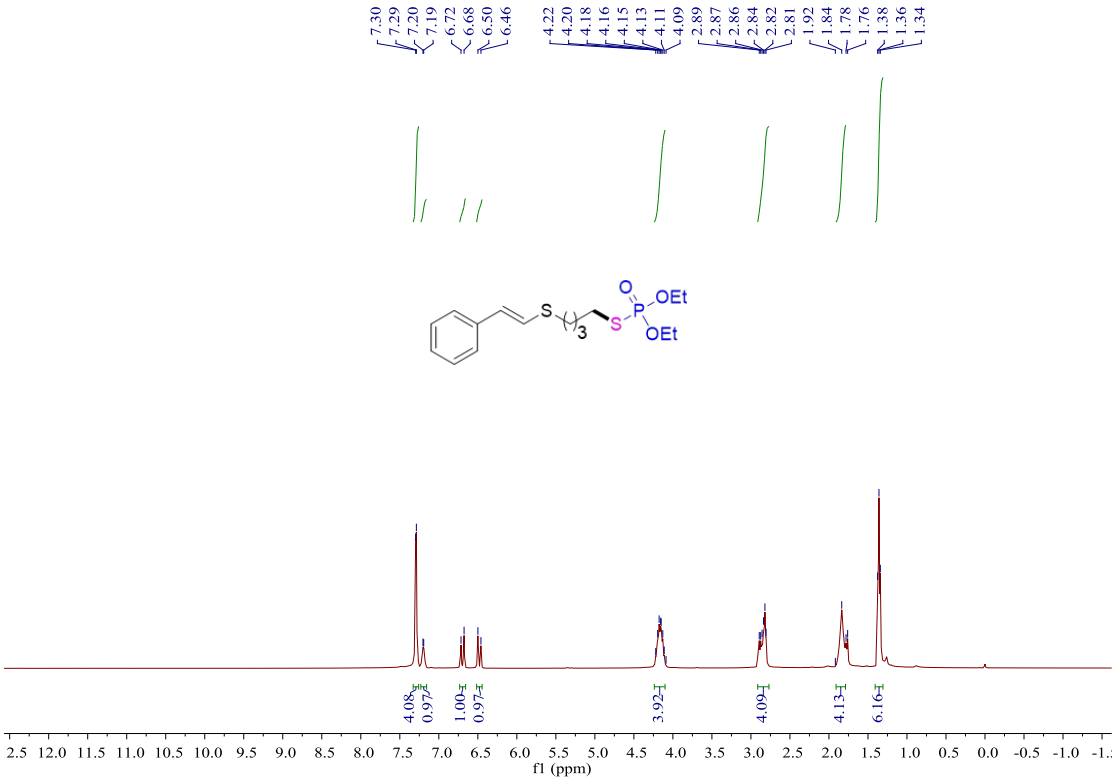
[2] Srogl, J.; Allred, G. D.; Liebeskind, L. S., Sulfonium Salts. Participants par Excellence in Metal-Catalyzed Carbon−Carbon Bond-Forming Reactions. *J. Am. Chem. Soc.* **1997**, *119*,

12376-12377.

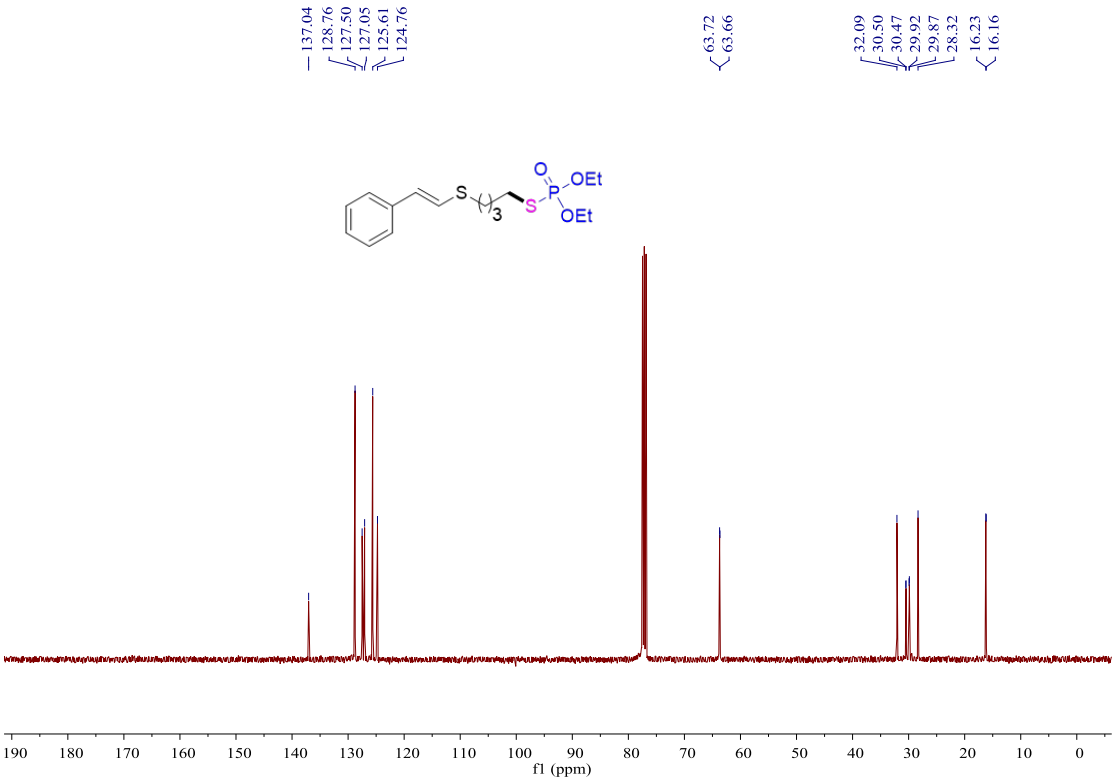
[3] Aukland, M. H.; Talbot, F. J. T.; Fernández-Salas, J. A.; Ball, M.; Pulis, A. P.; Procter, D. J., An Interrupted Pummerer/Nickel-Catalysed Cross-Coupling Sequence. *Angew. Chem. Int. Ed.* **2018**, *57*, 9785-9789.

[4] Sarkar, S.; Kalek, M., Metal-Free S-Arylation of Phosphorothioate Diesters and Related Compounds with Diaryliodonium Salts. *Org. Lett.* **2023,** *25*, 671-675.

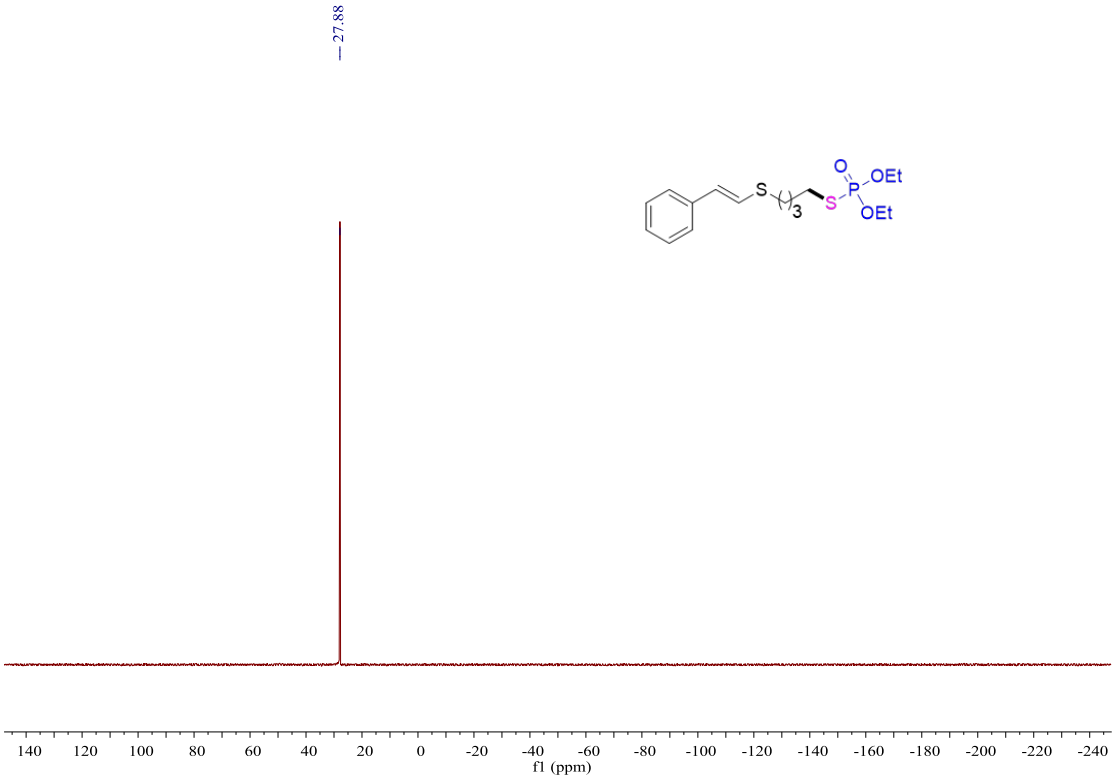
5. NMR spectra of products



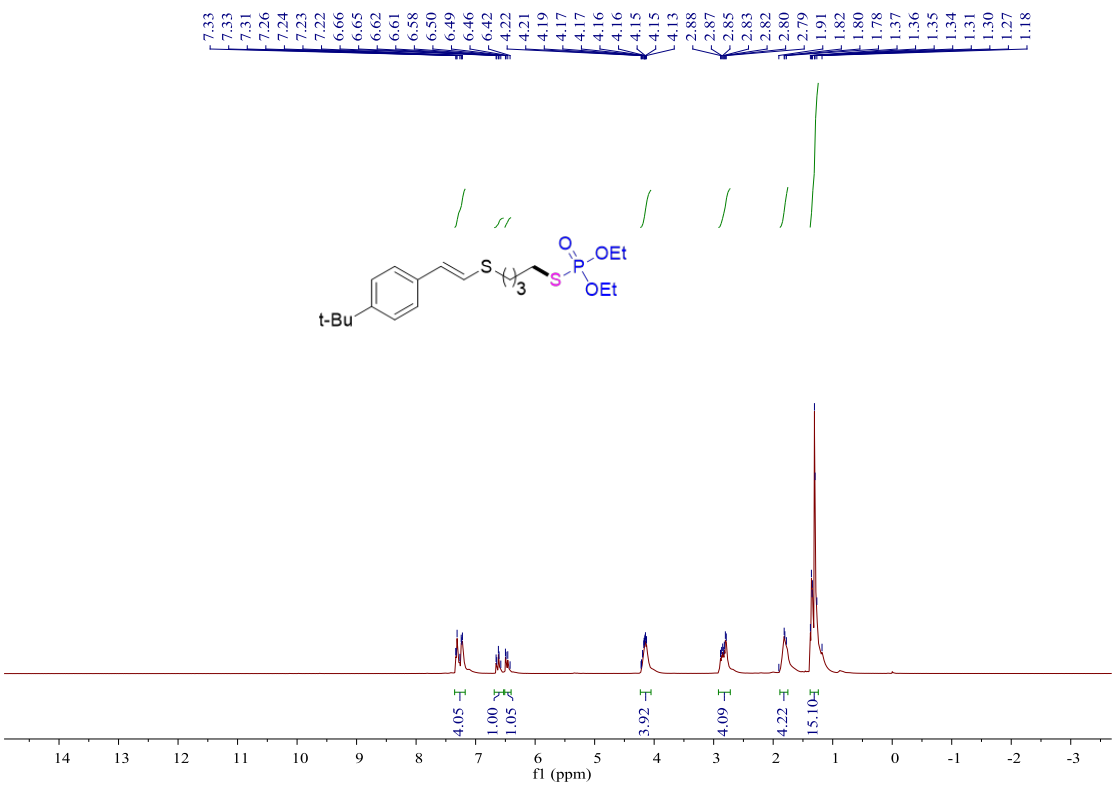
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3aa**



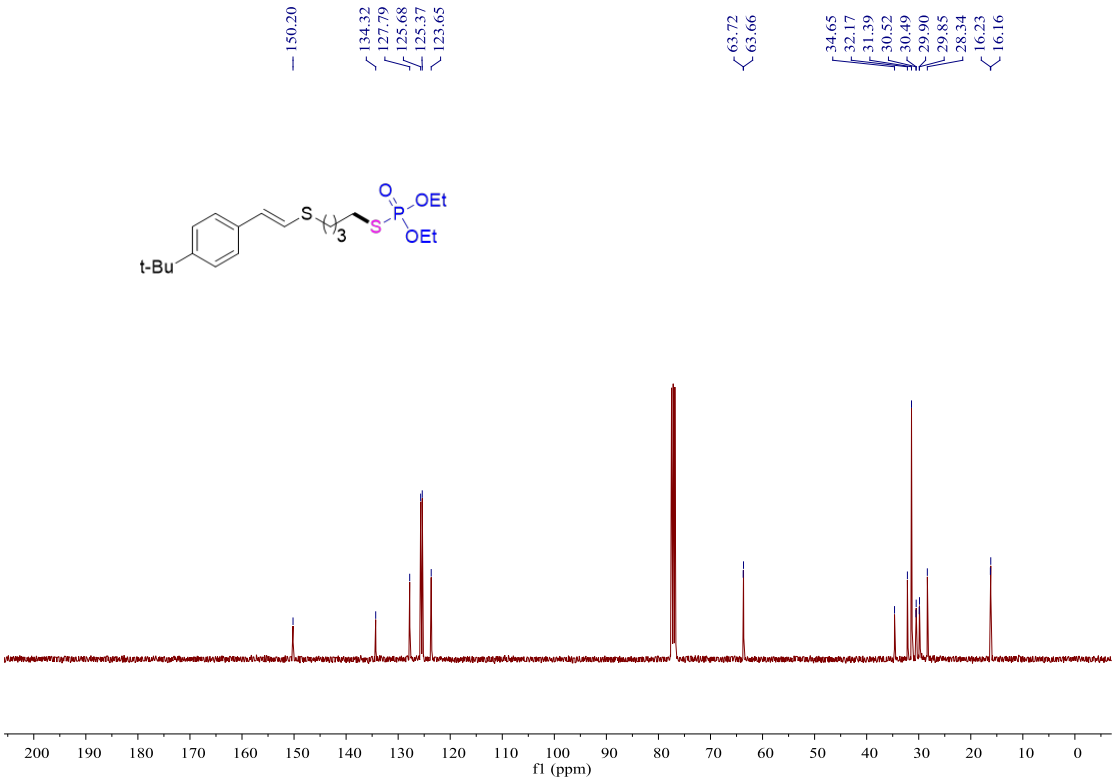
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3aa**



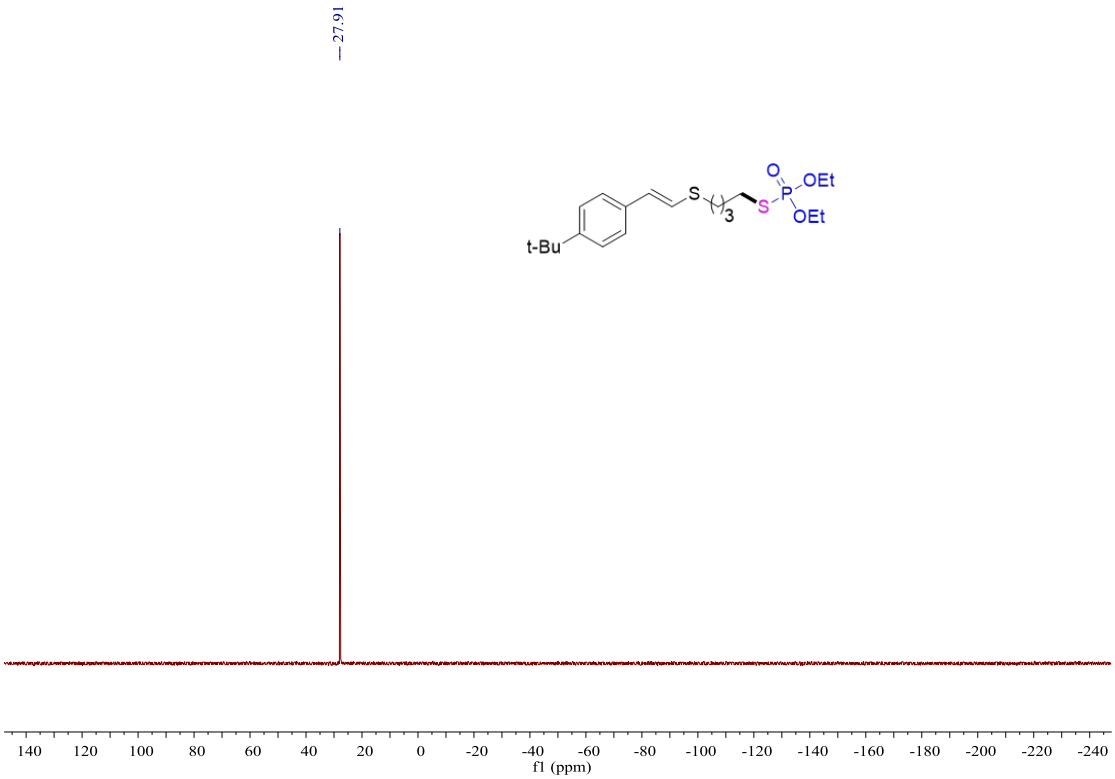
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3aa**



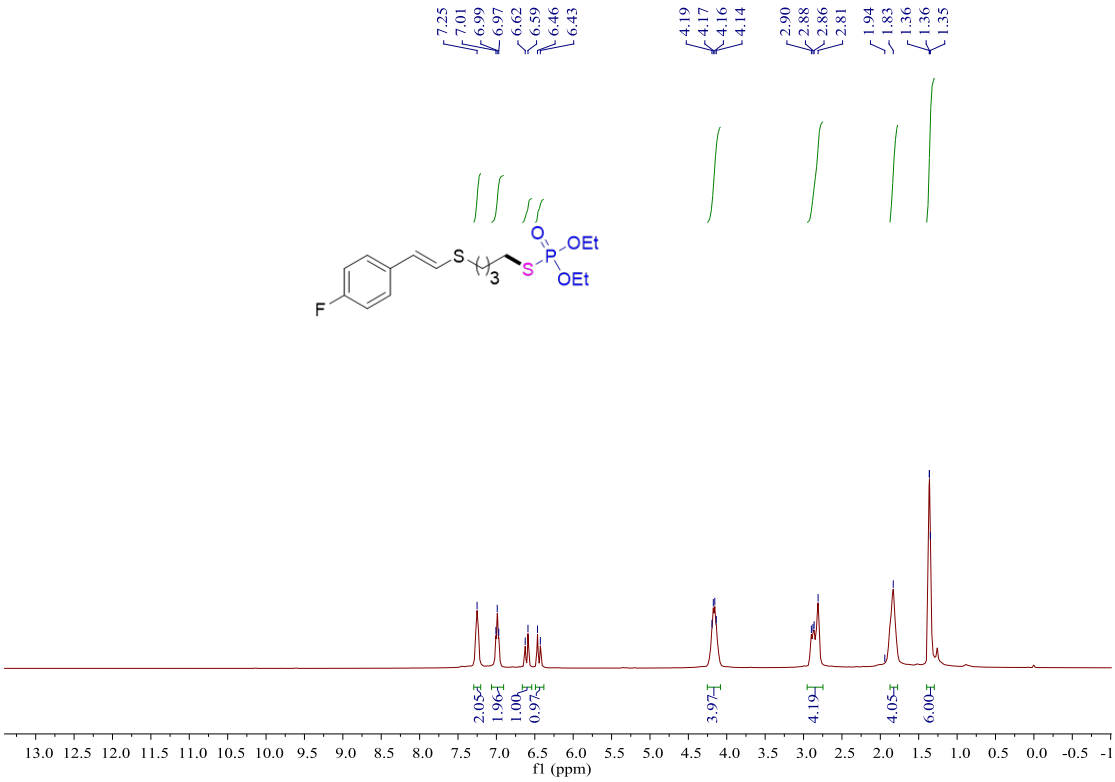
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ba**



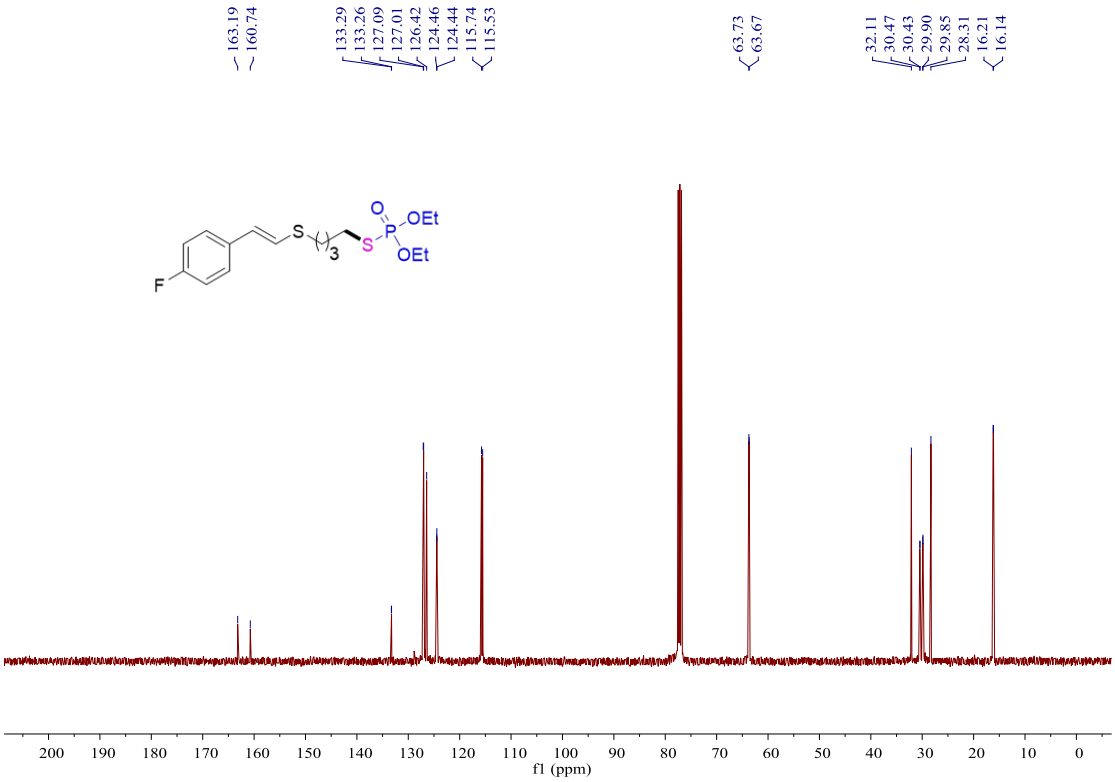
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ba**



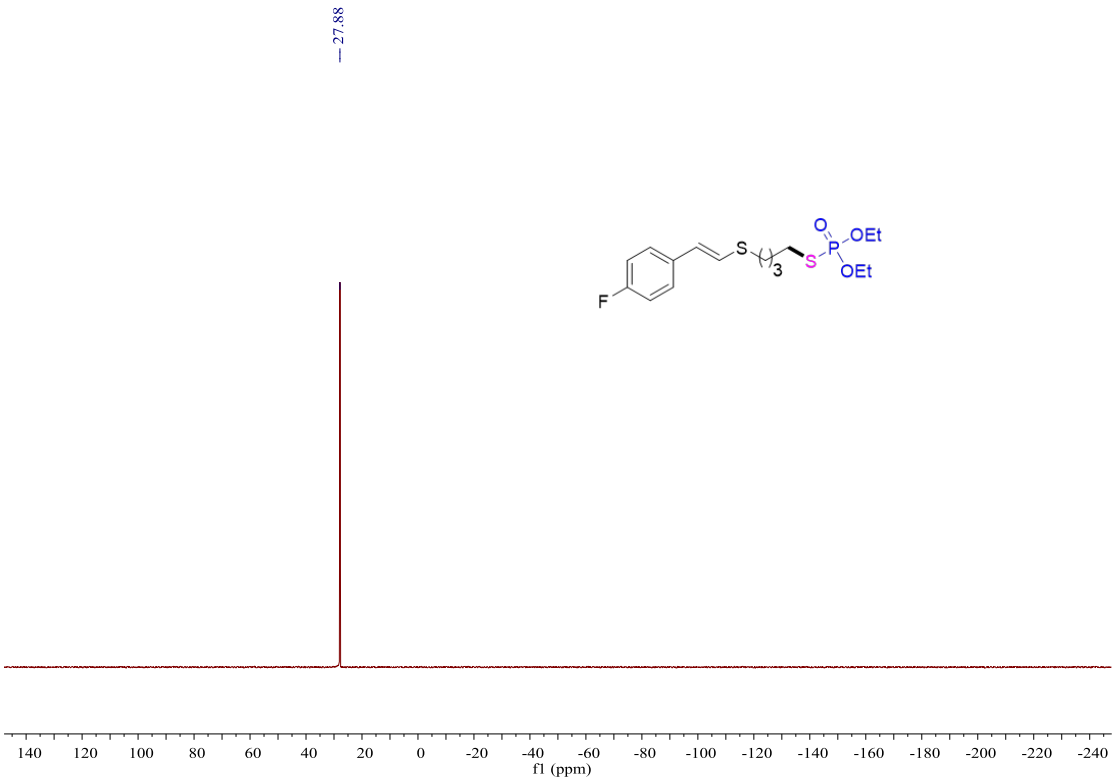
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ba**



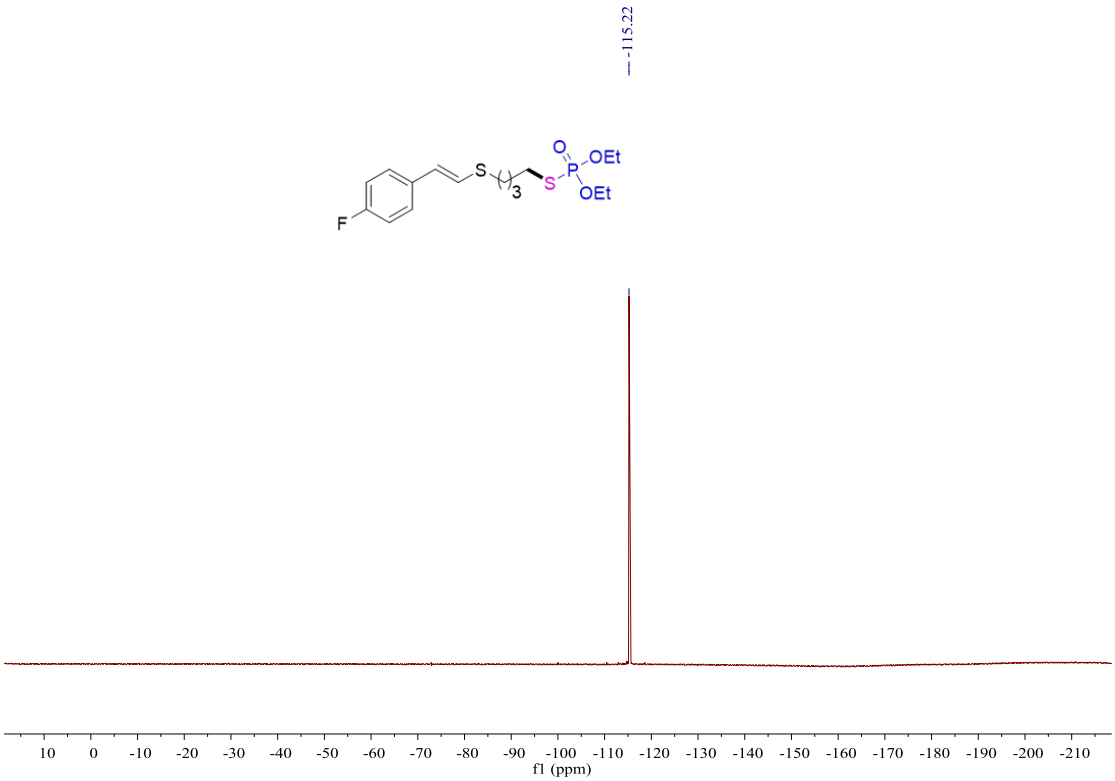
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ca**



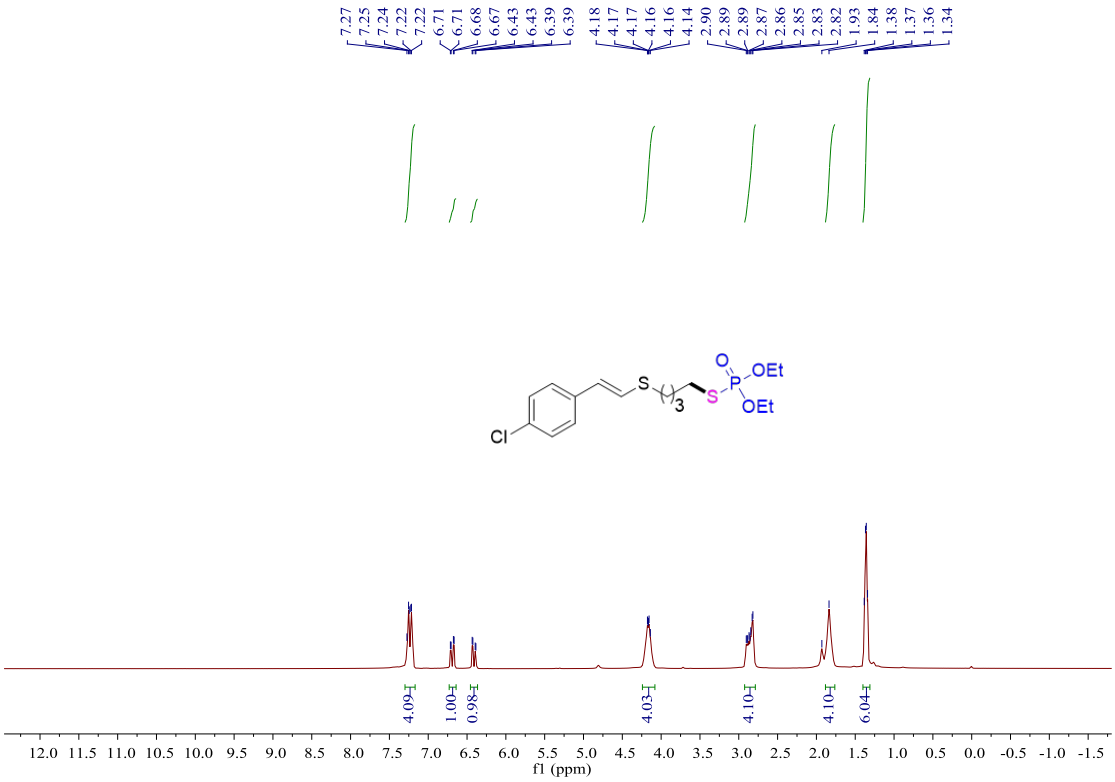
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ca**



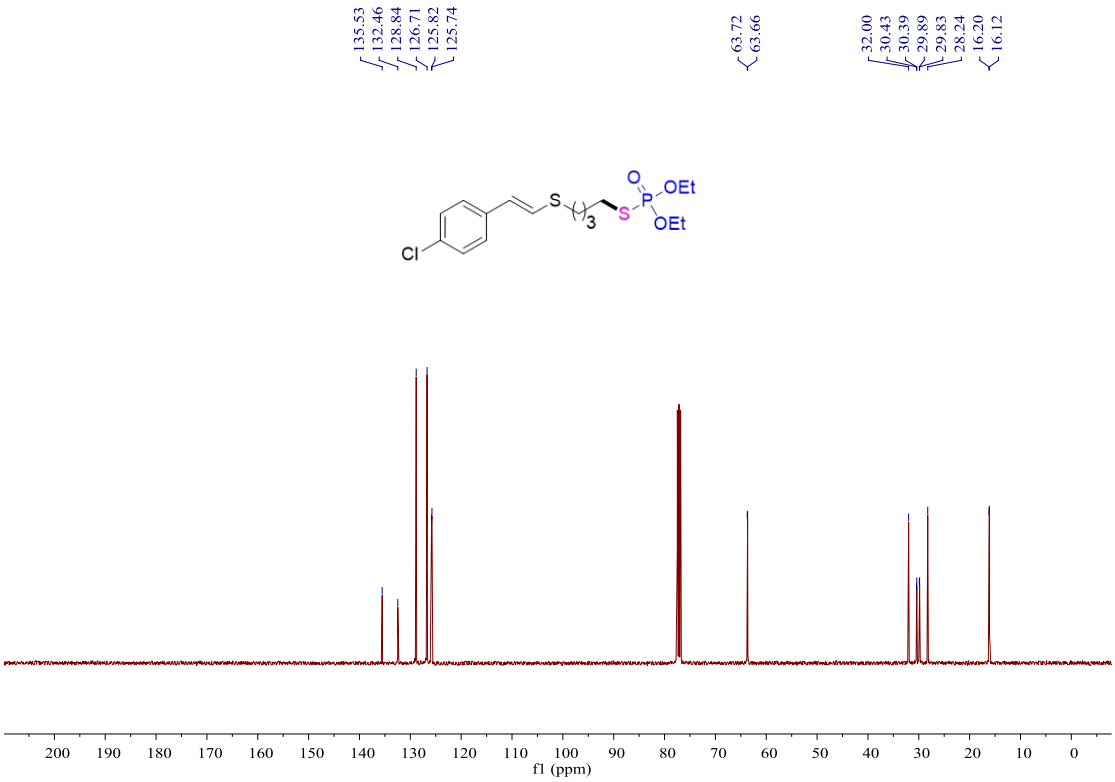
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ca**



^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3ca**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3da**



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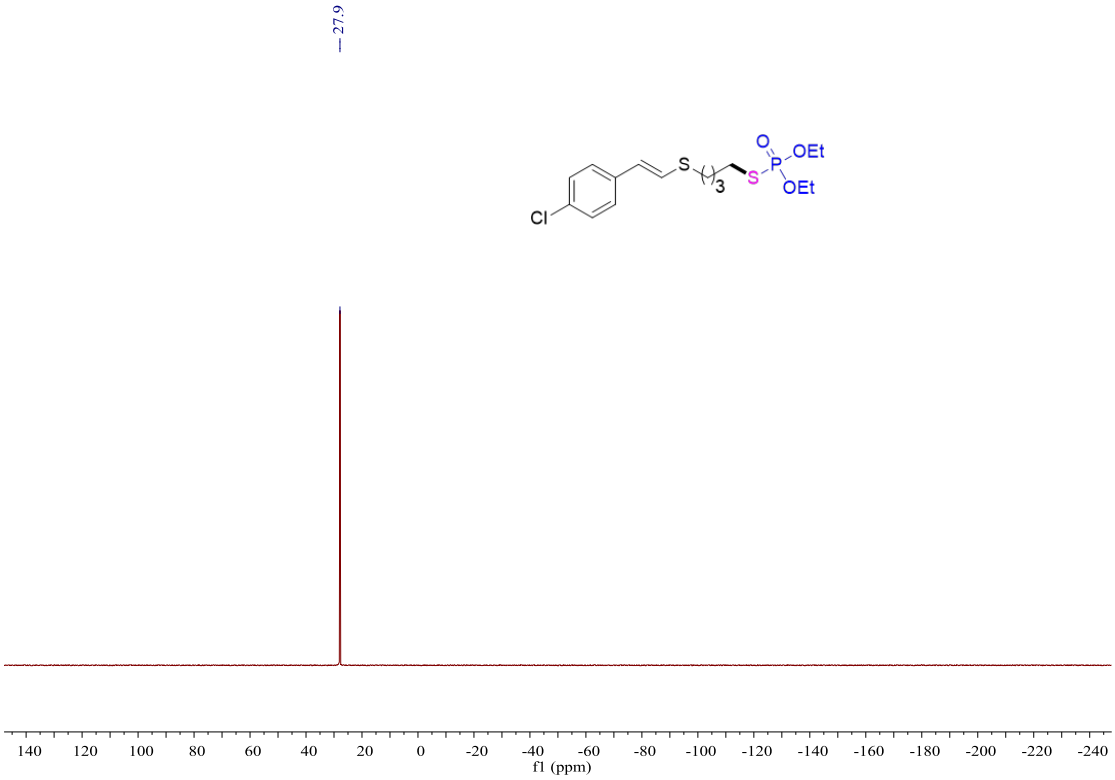
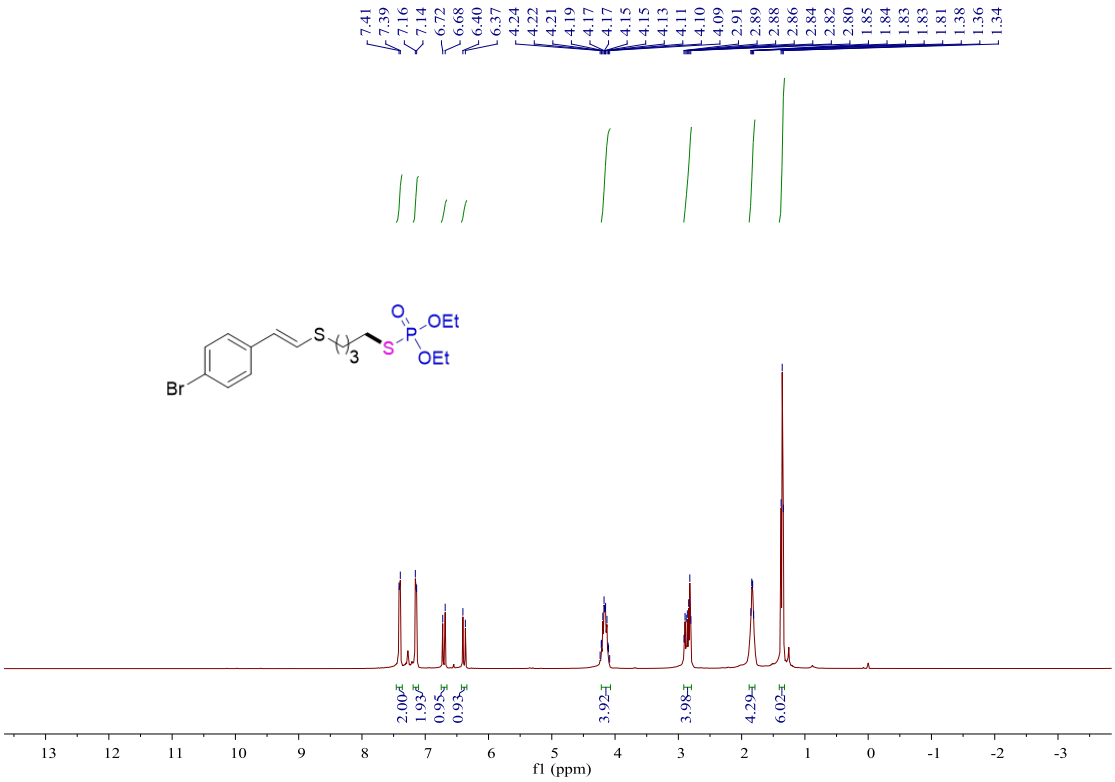
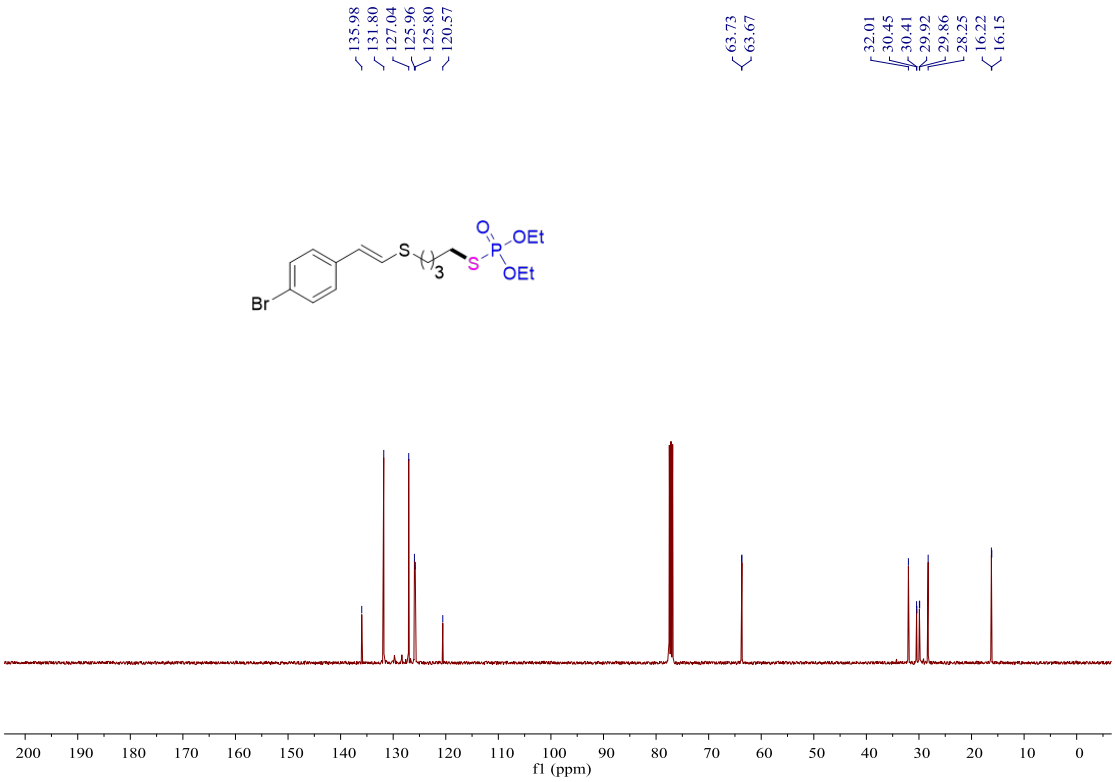


^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3da**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ea**



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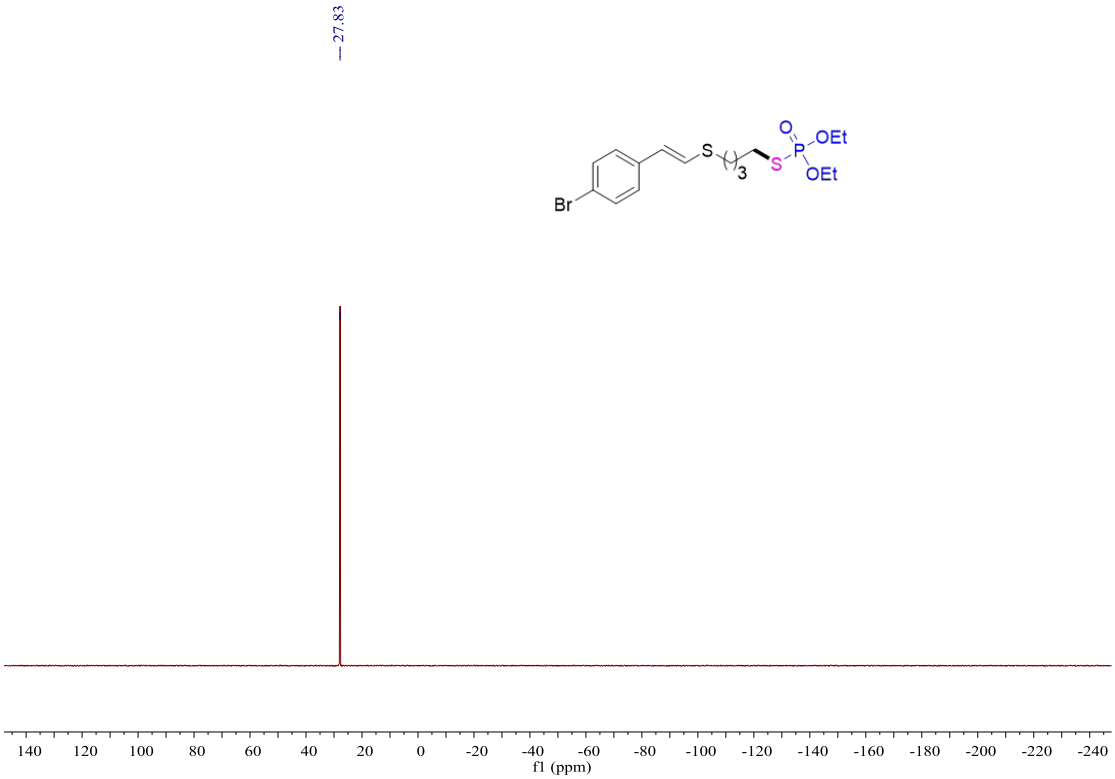

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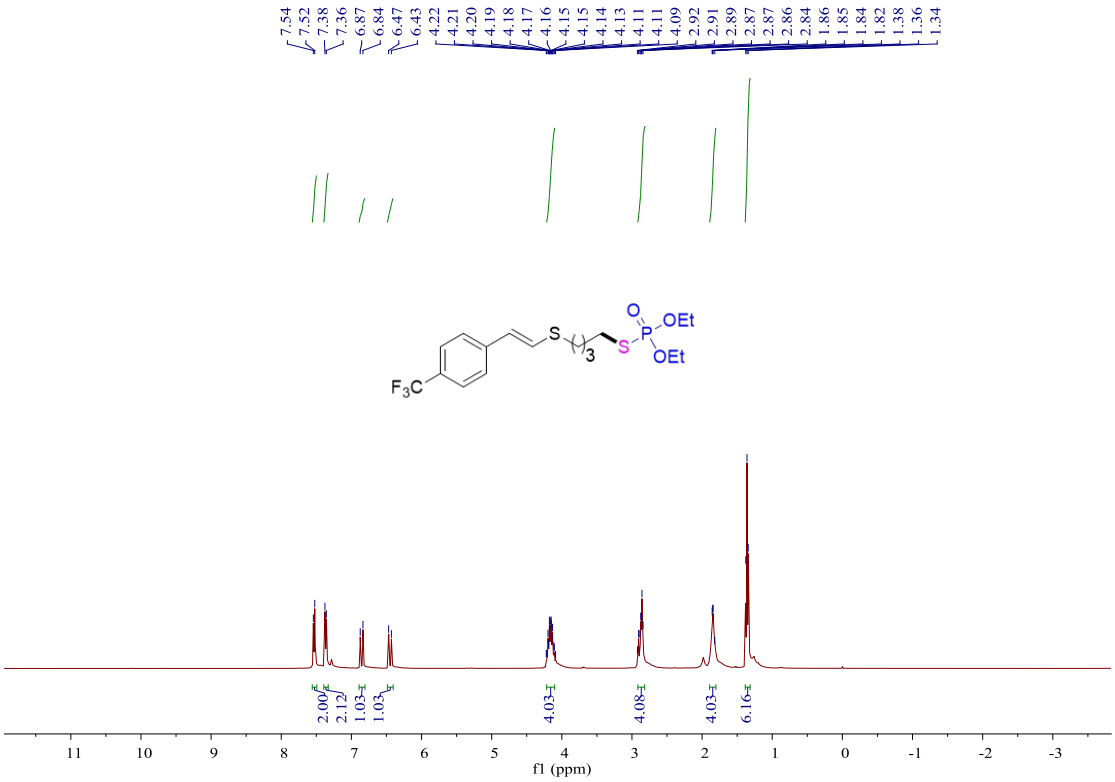
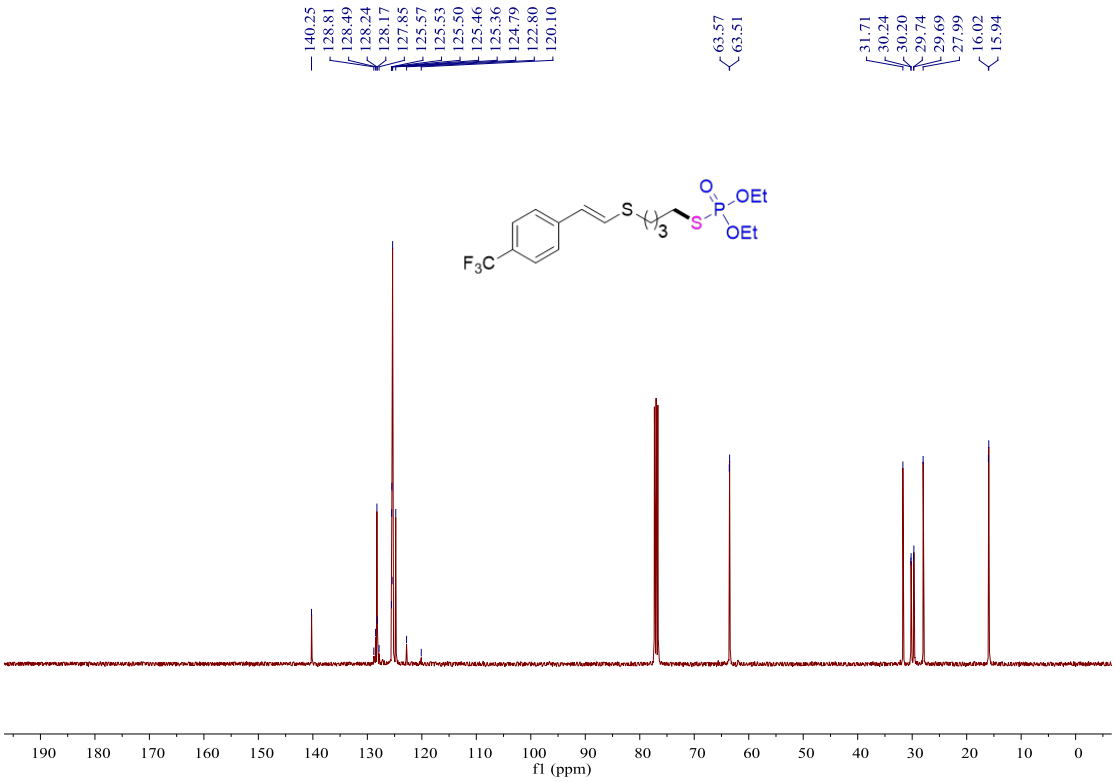
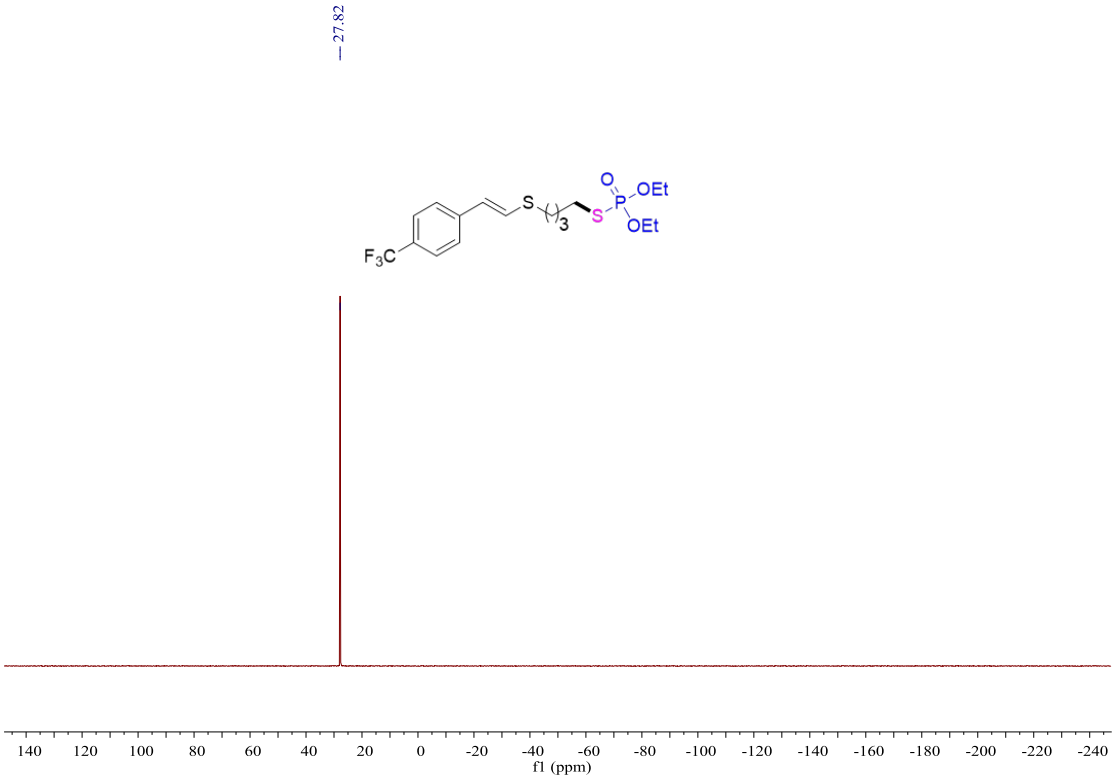


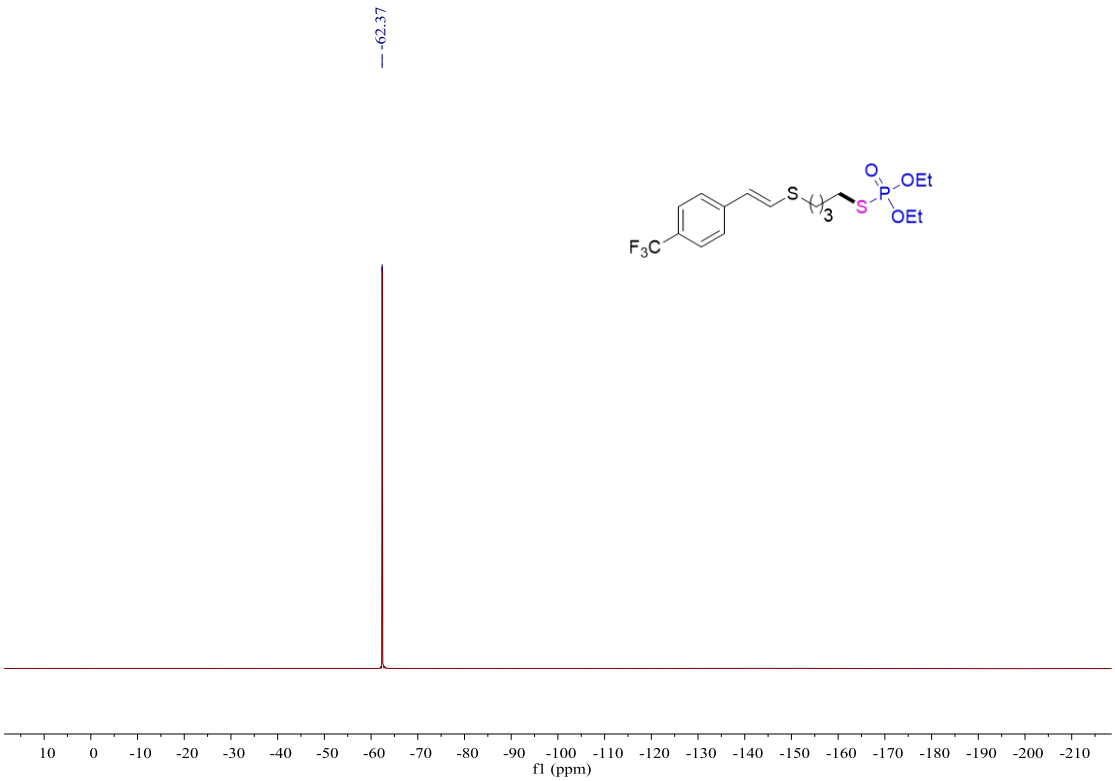
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3fa**



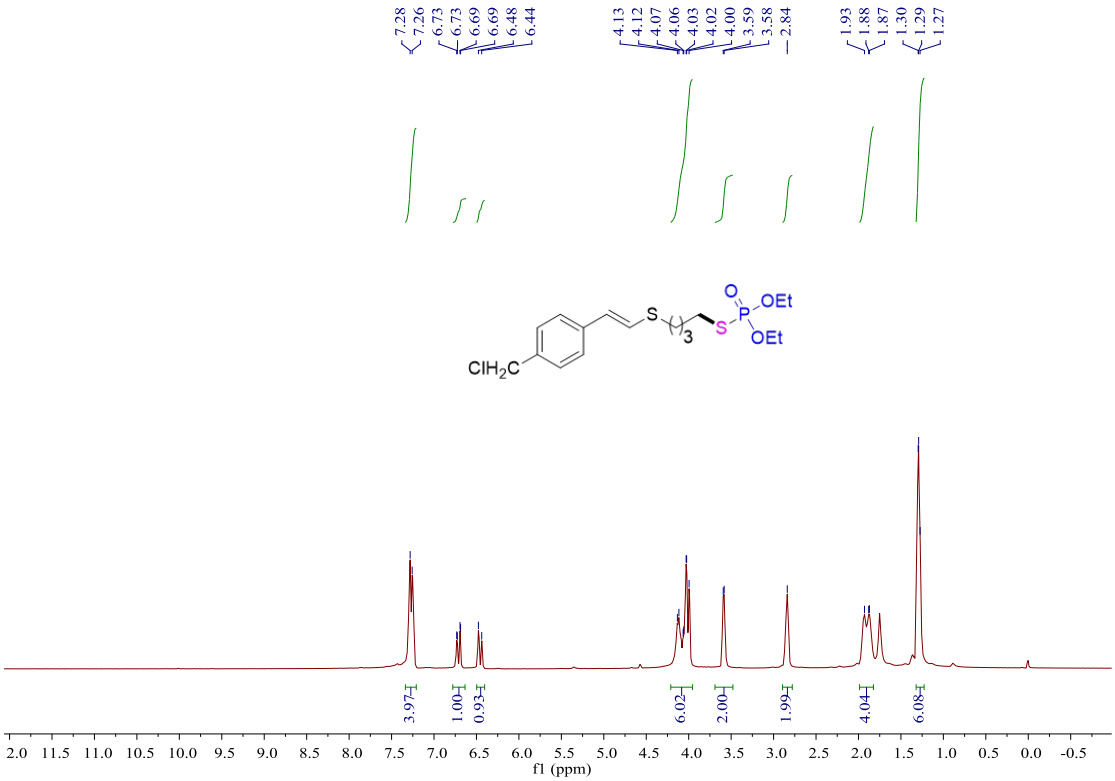
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3fa**



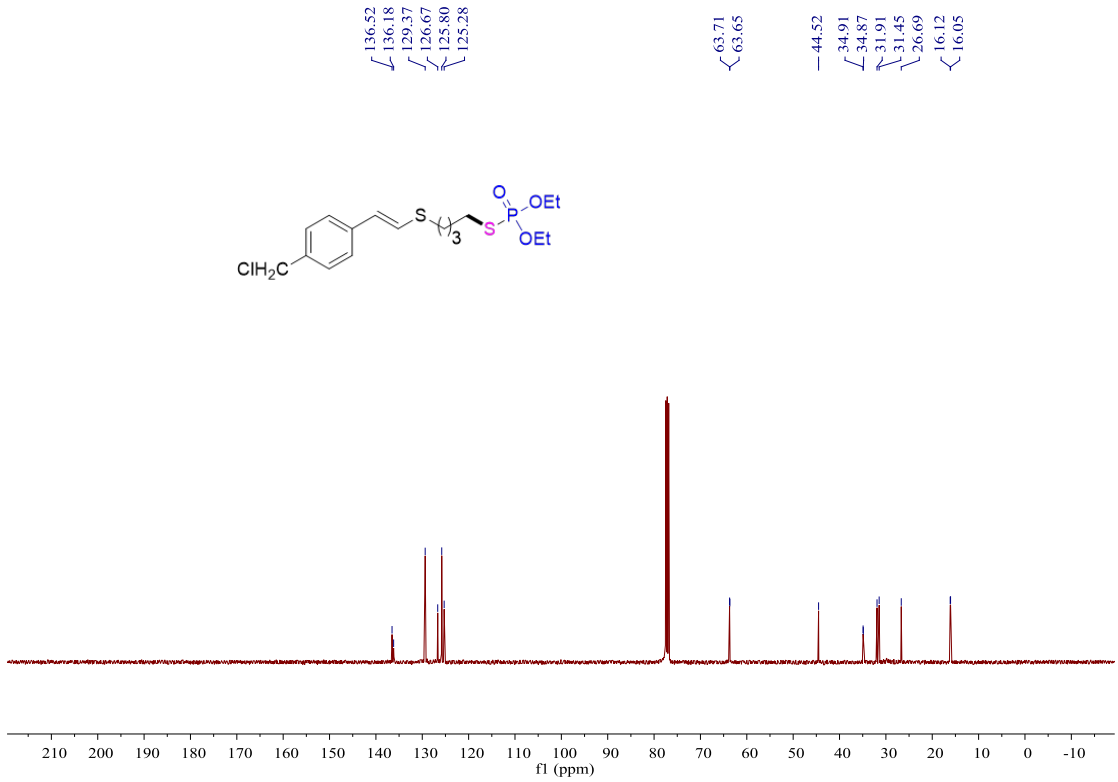
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3fa**



^{19}F NMR (376 MHz, $CDCl_3$) spectra of **3fa**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ga**



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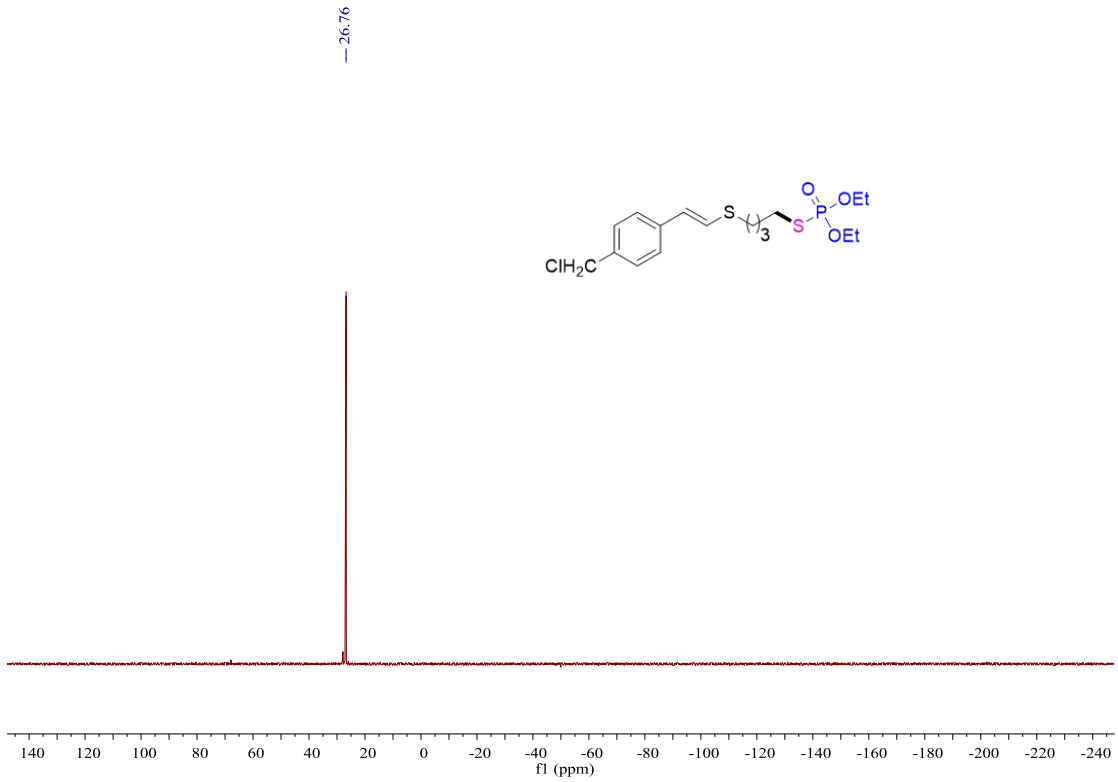

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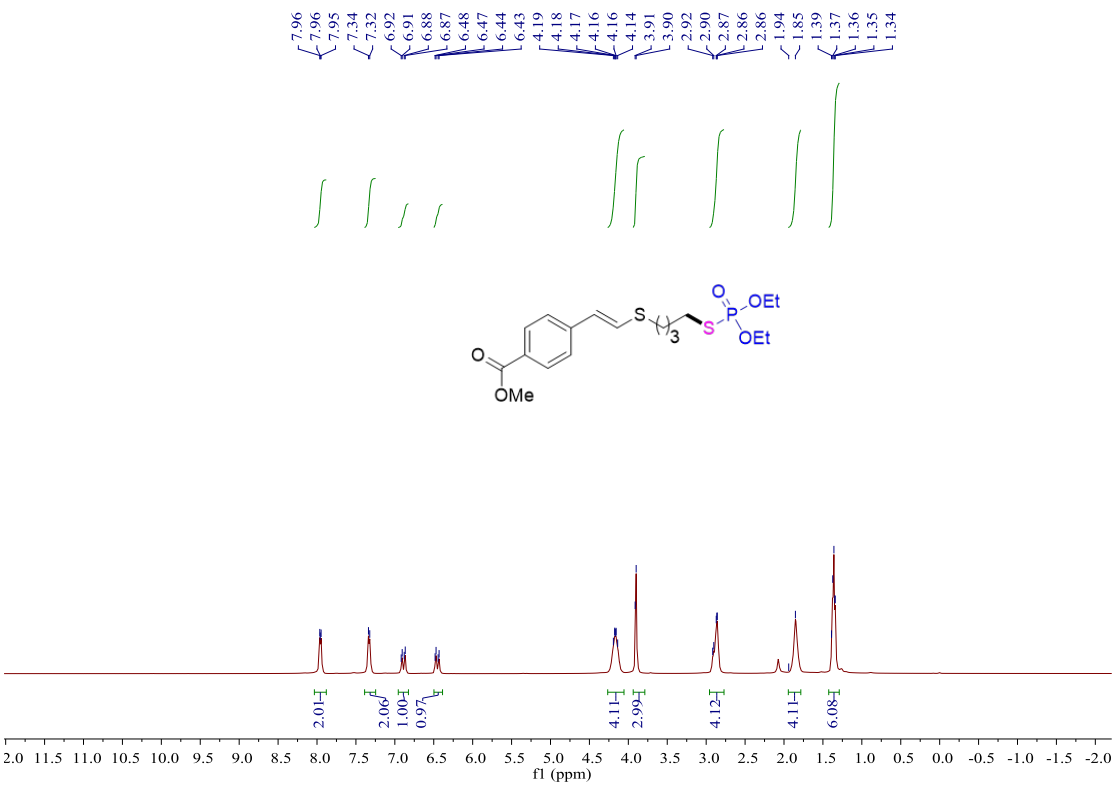
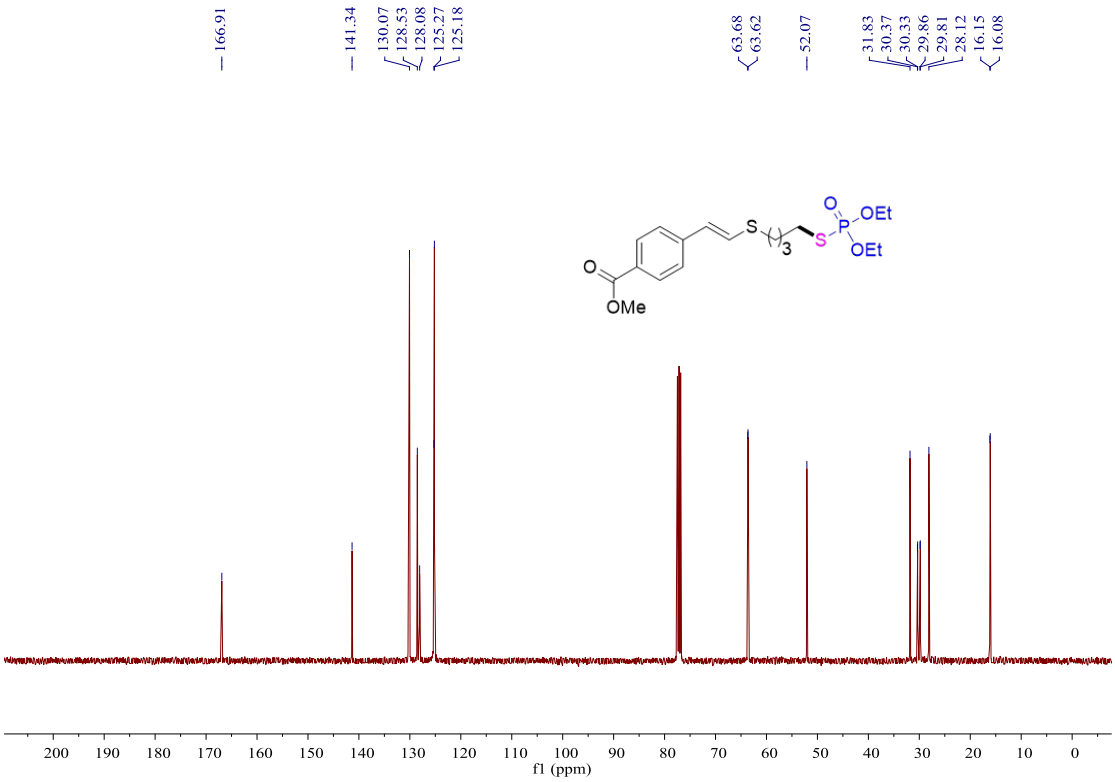
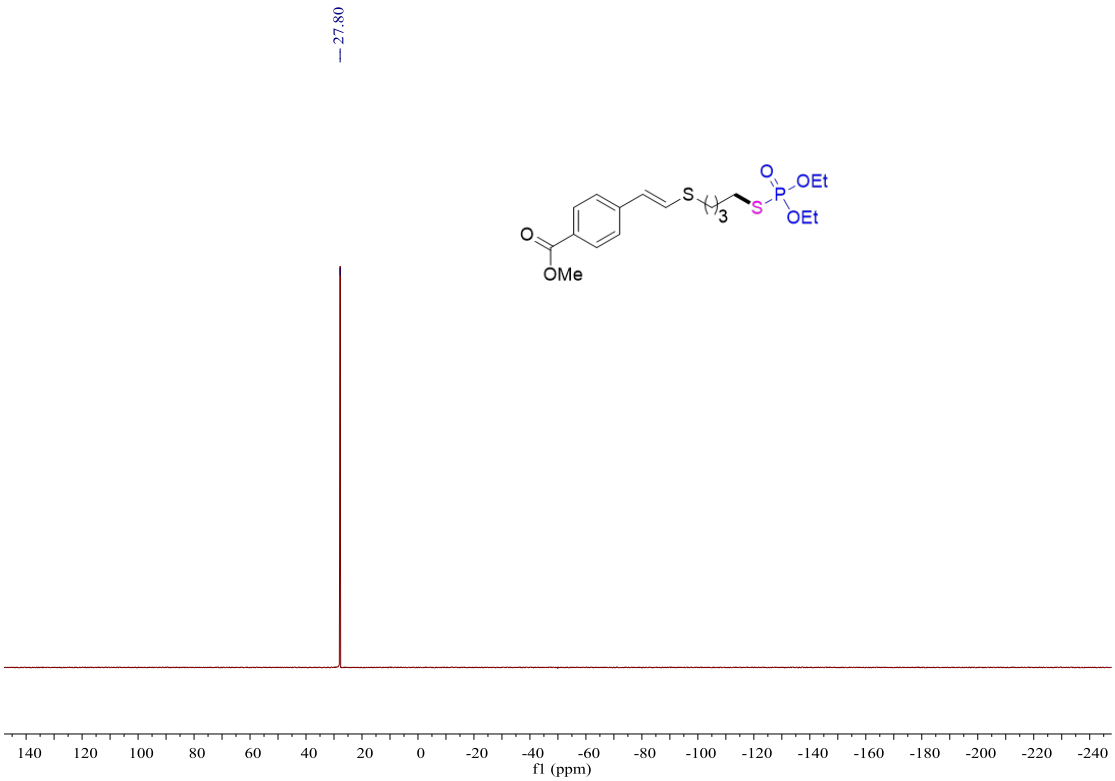


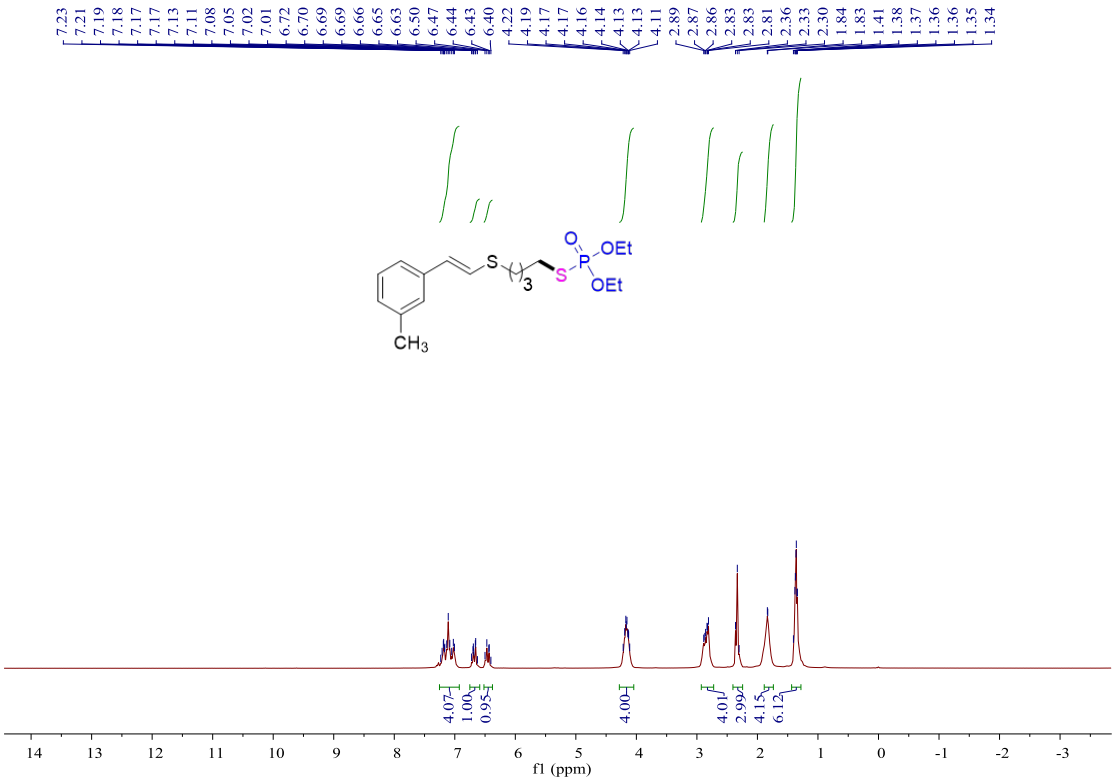
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ha**



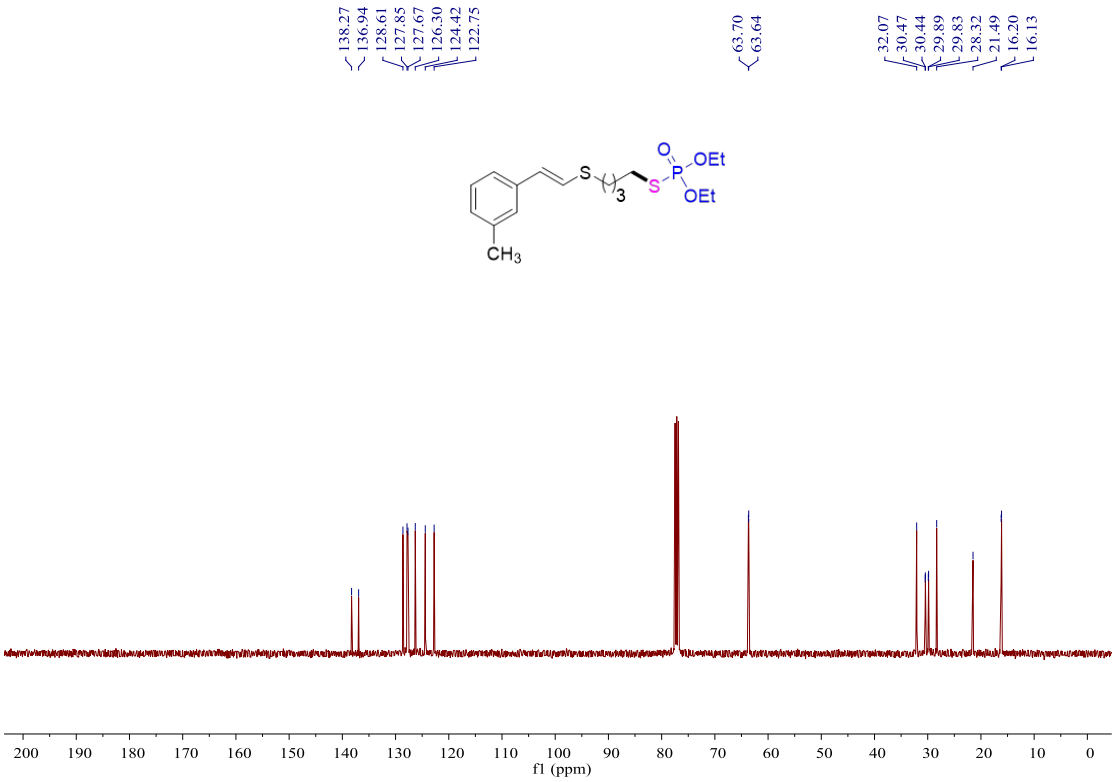
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ha**



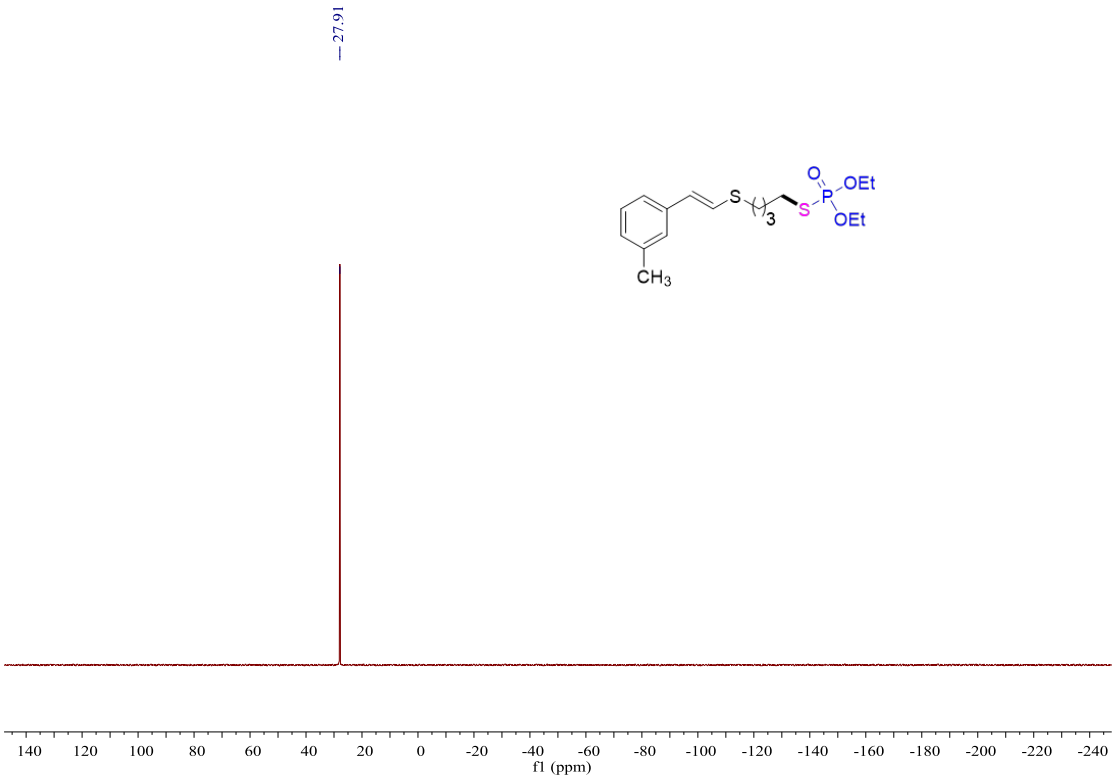
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ha**



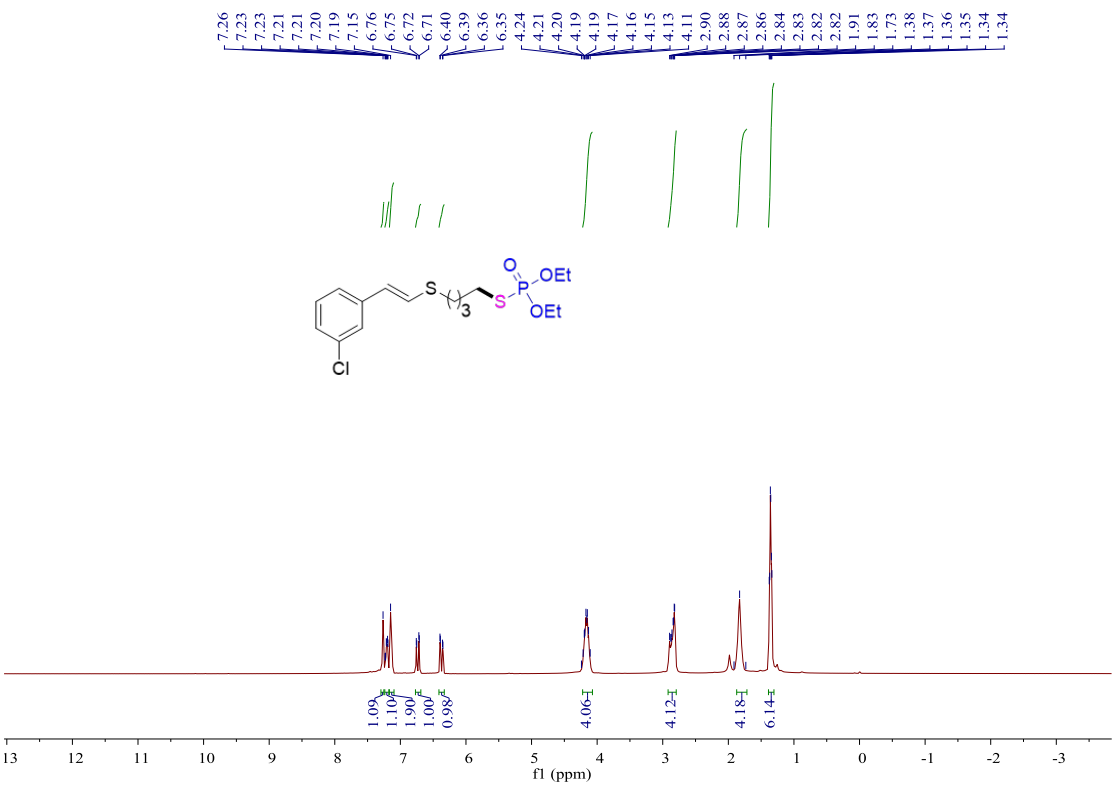
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ia**



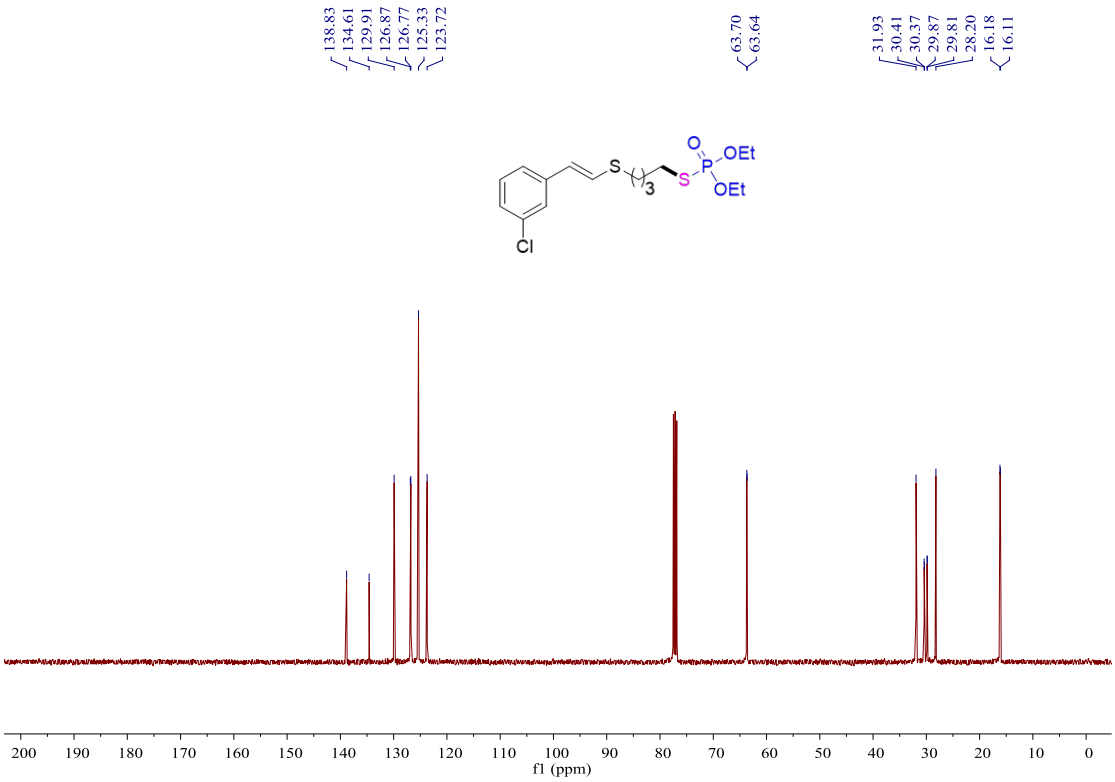
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ia**



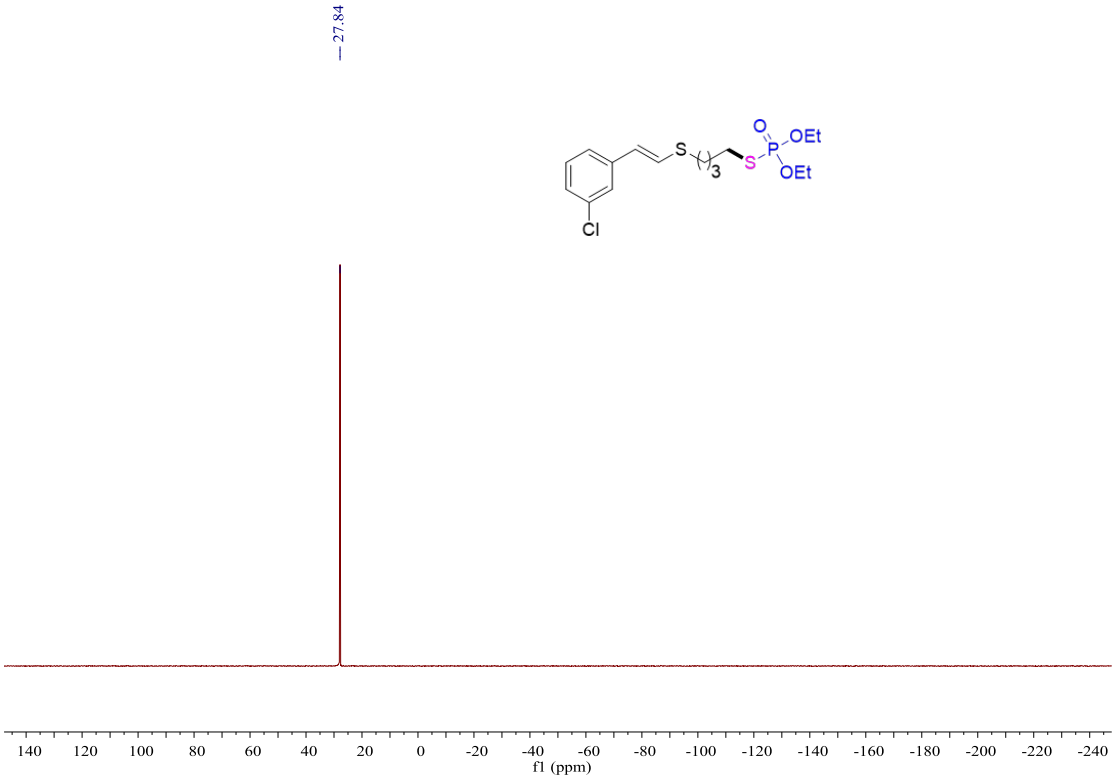
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ia**



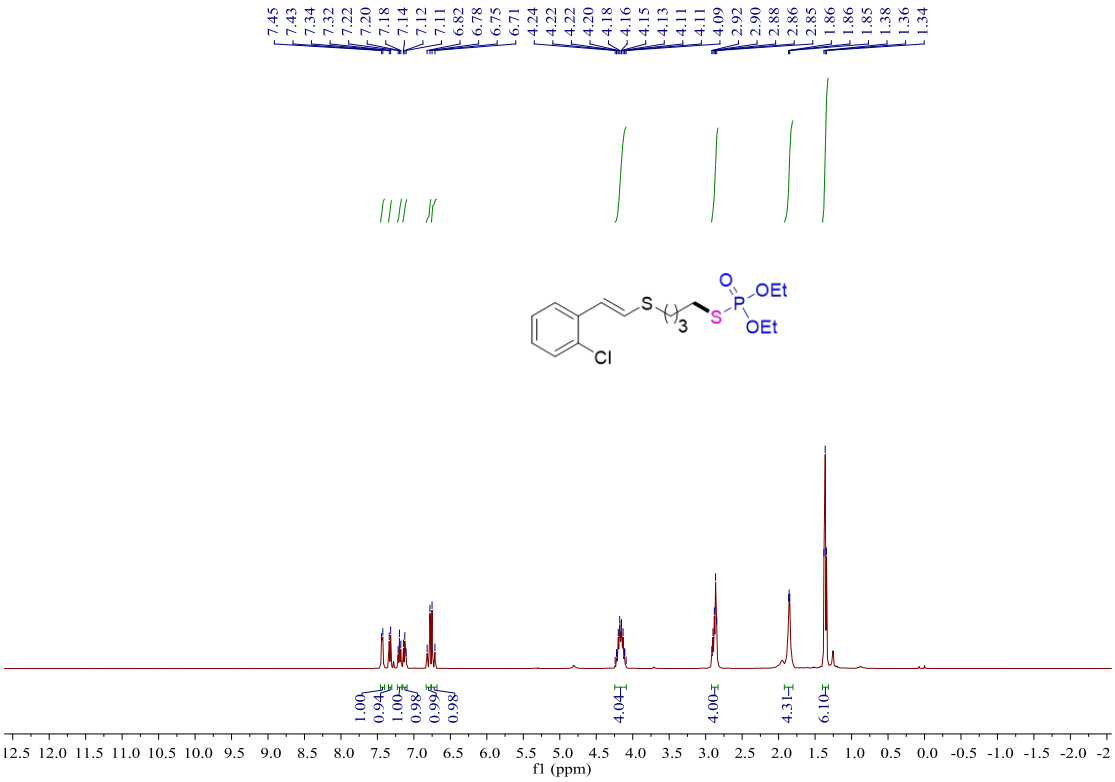
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ja**



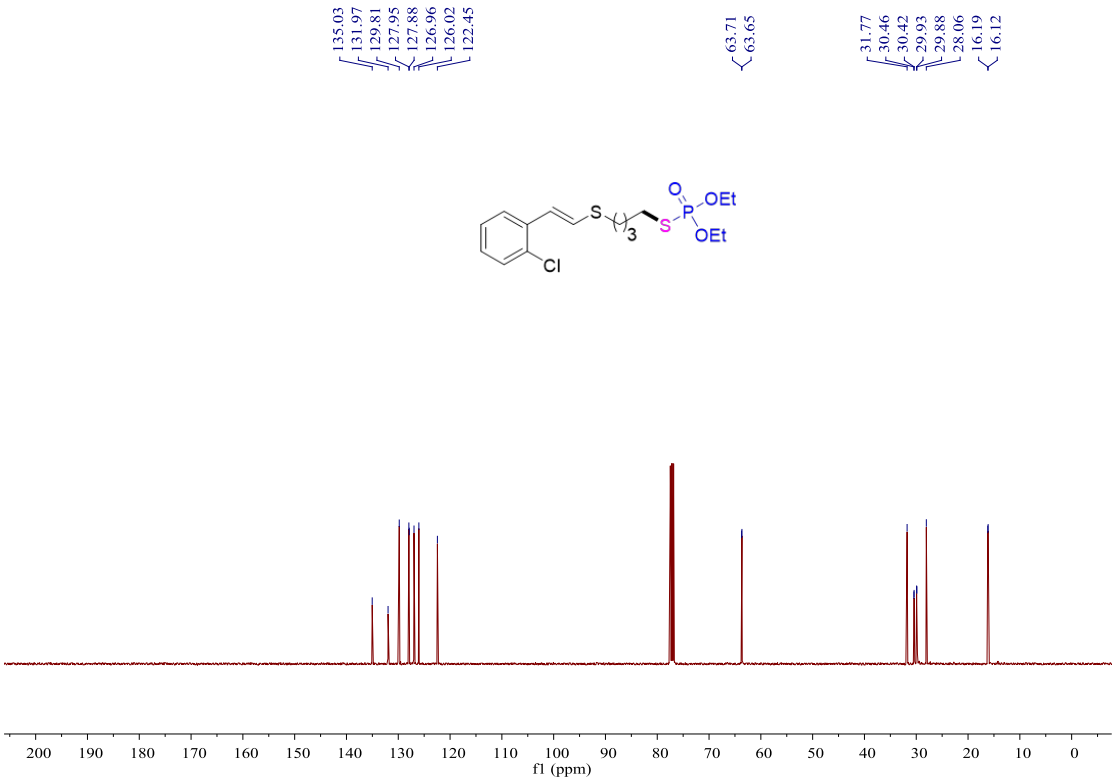
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ja**



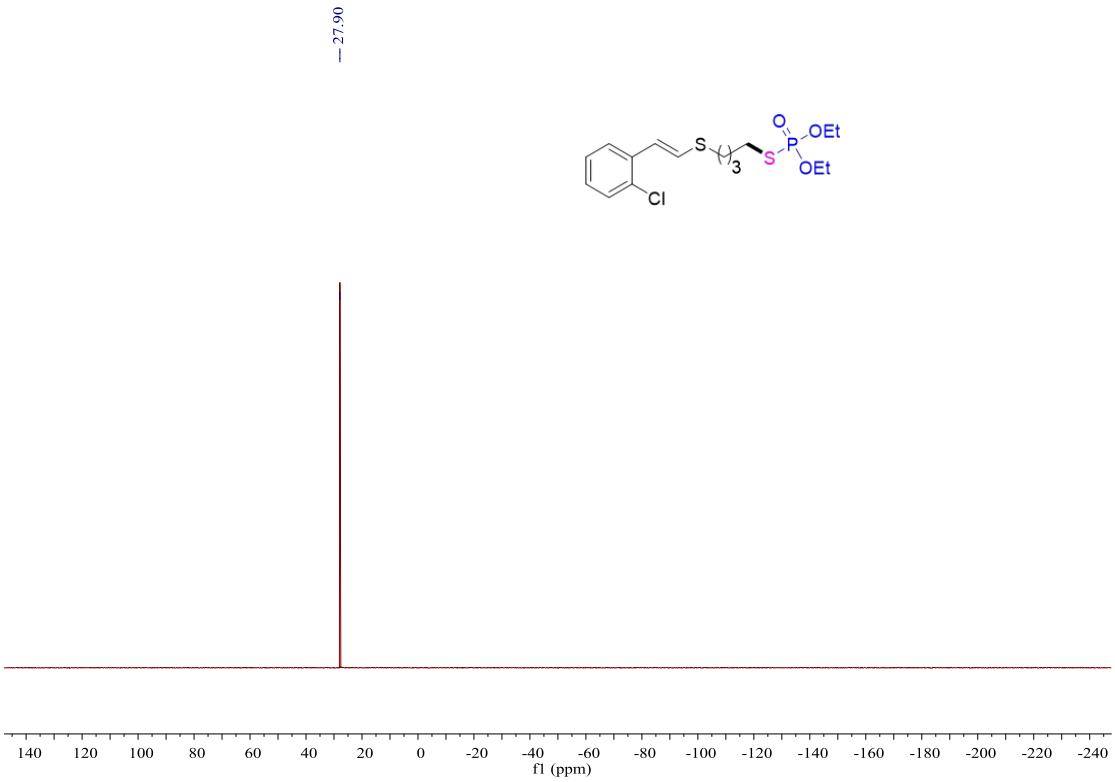
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ja**



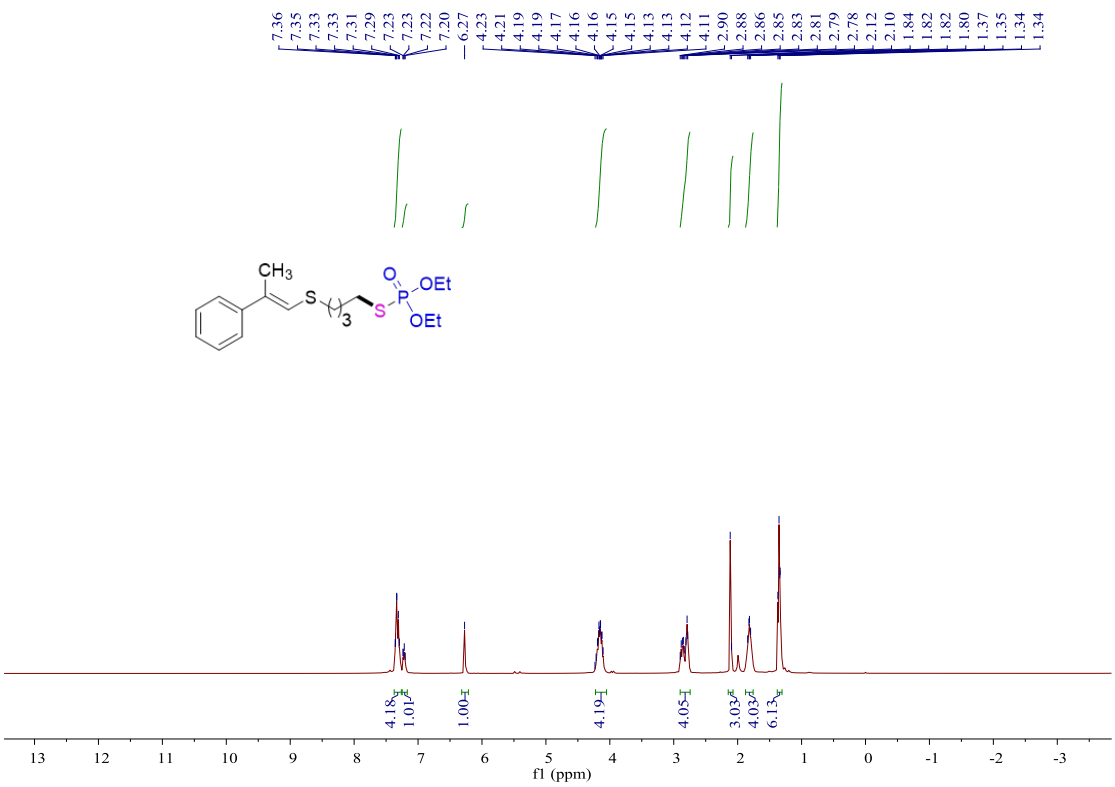
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ka**



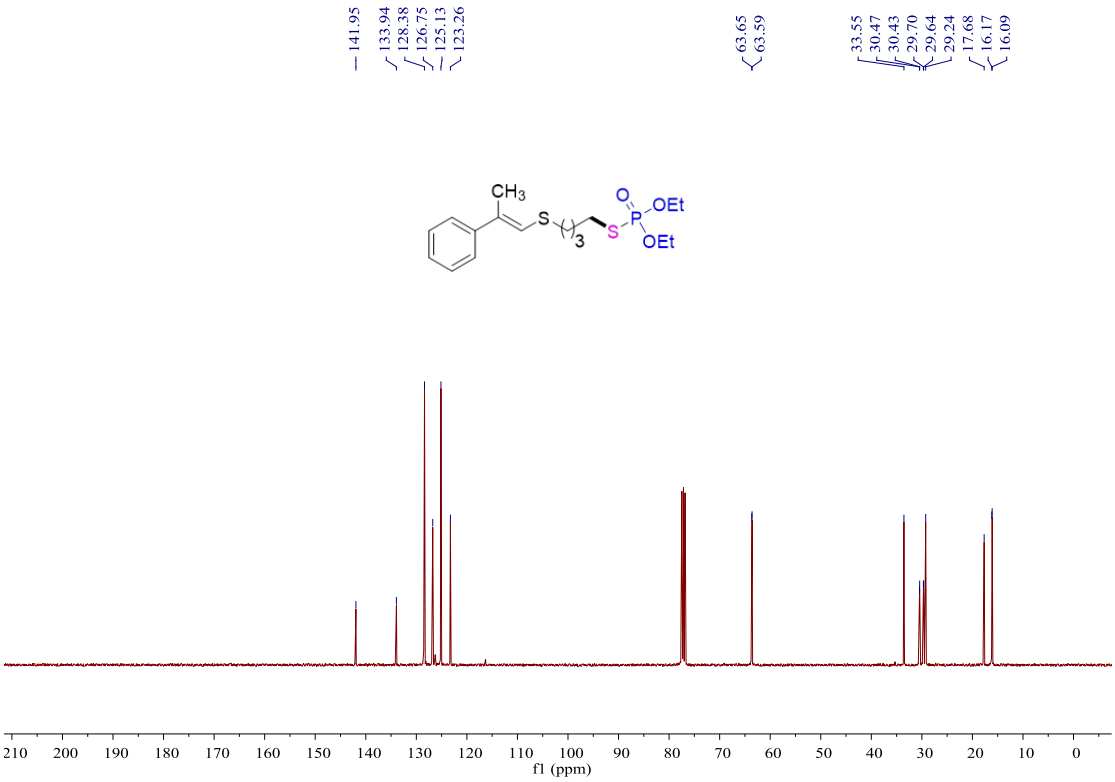
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ka**



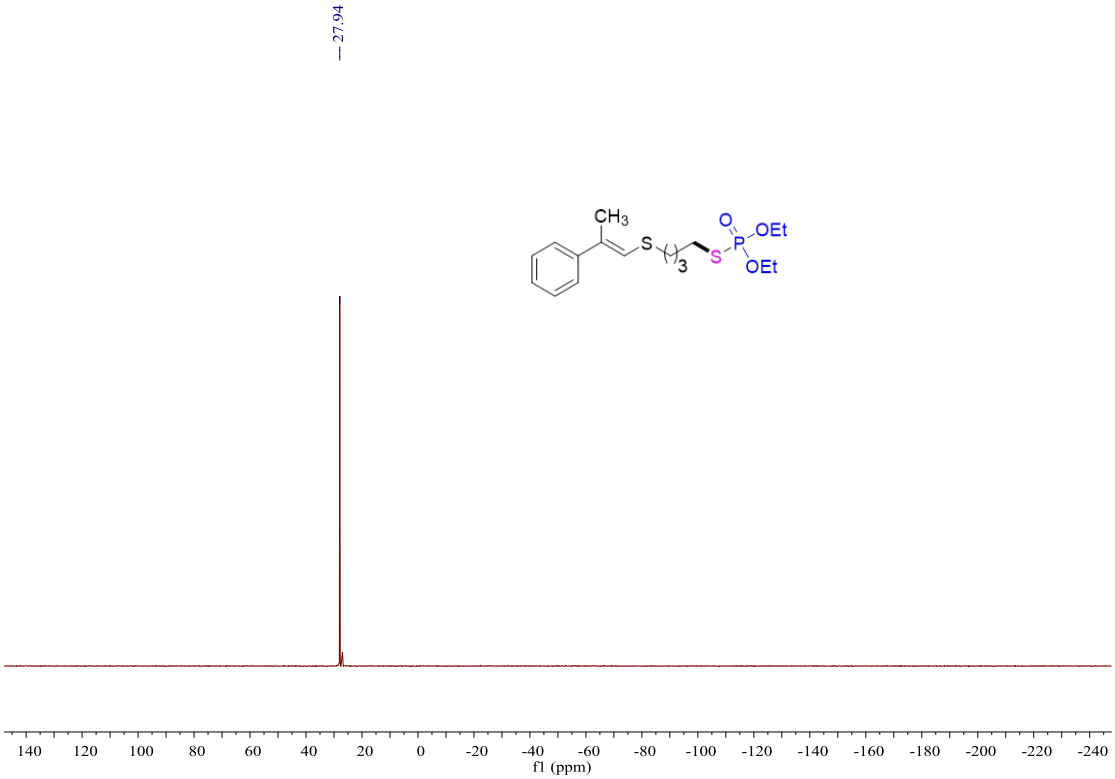
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ka**



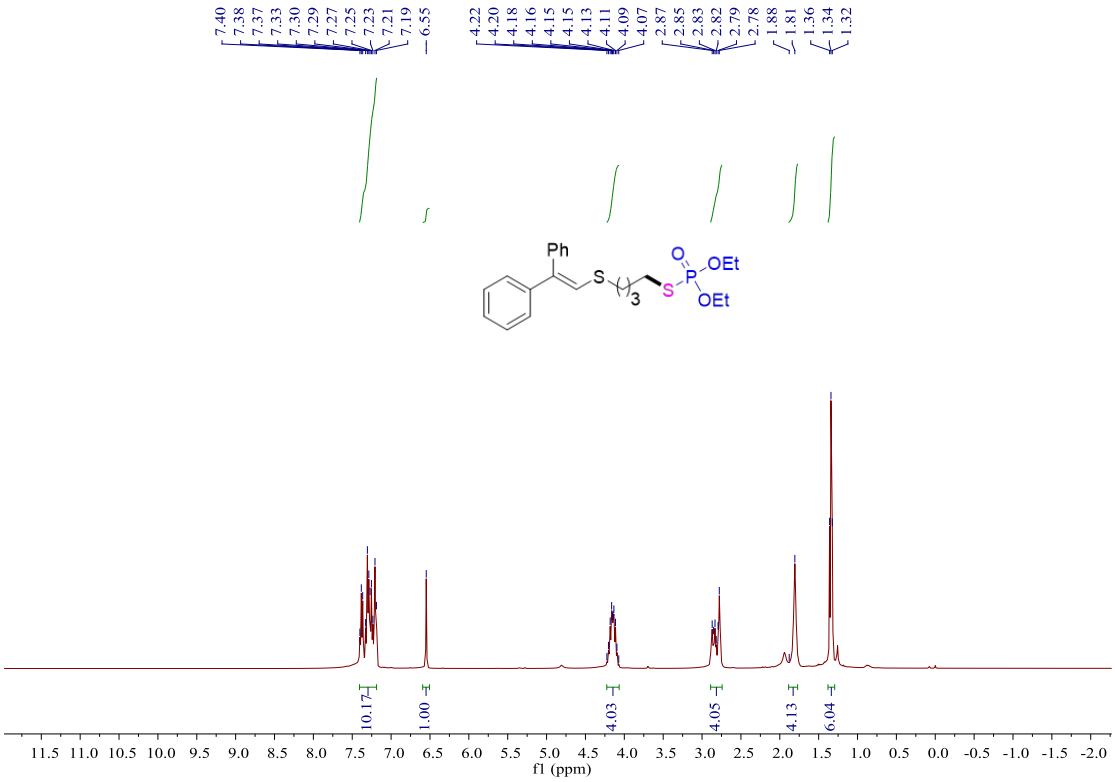
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3la**



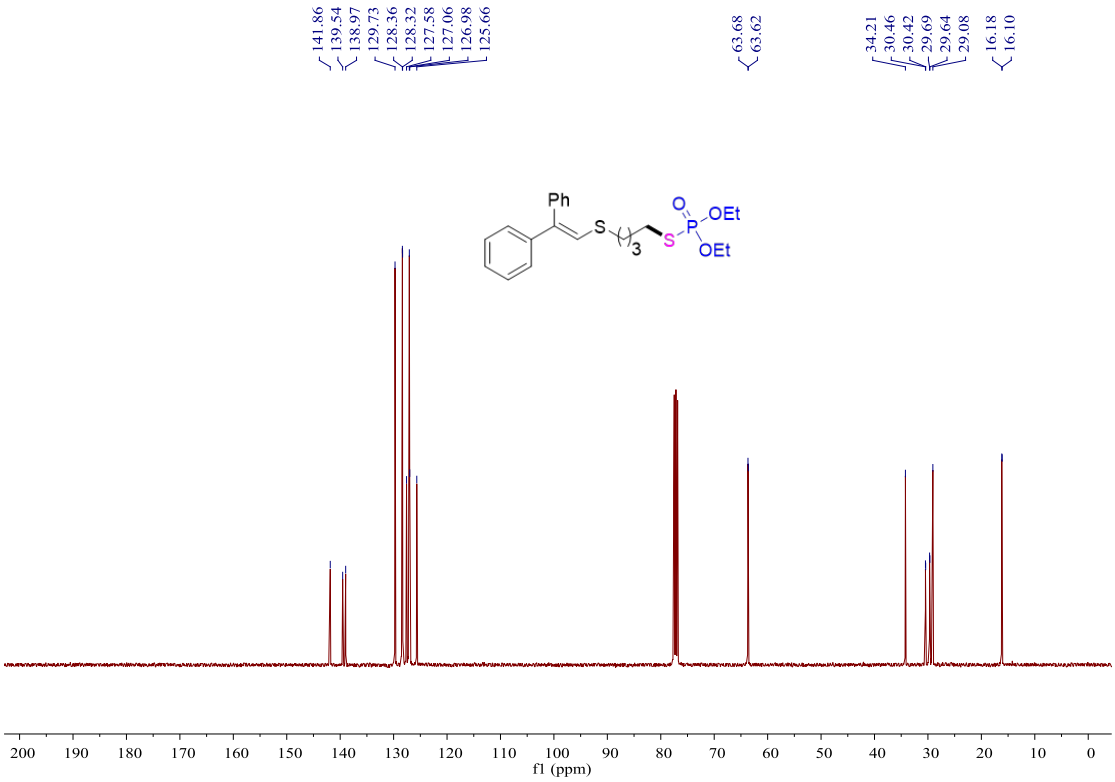
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3la**



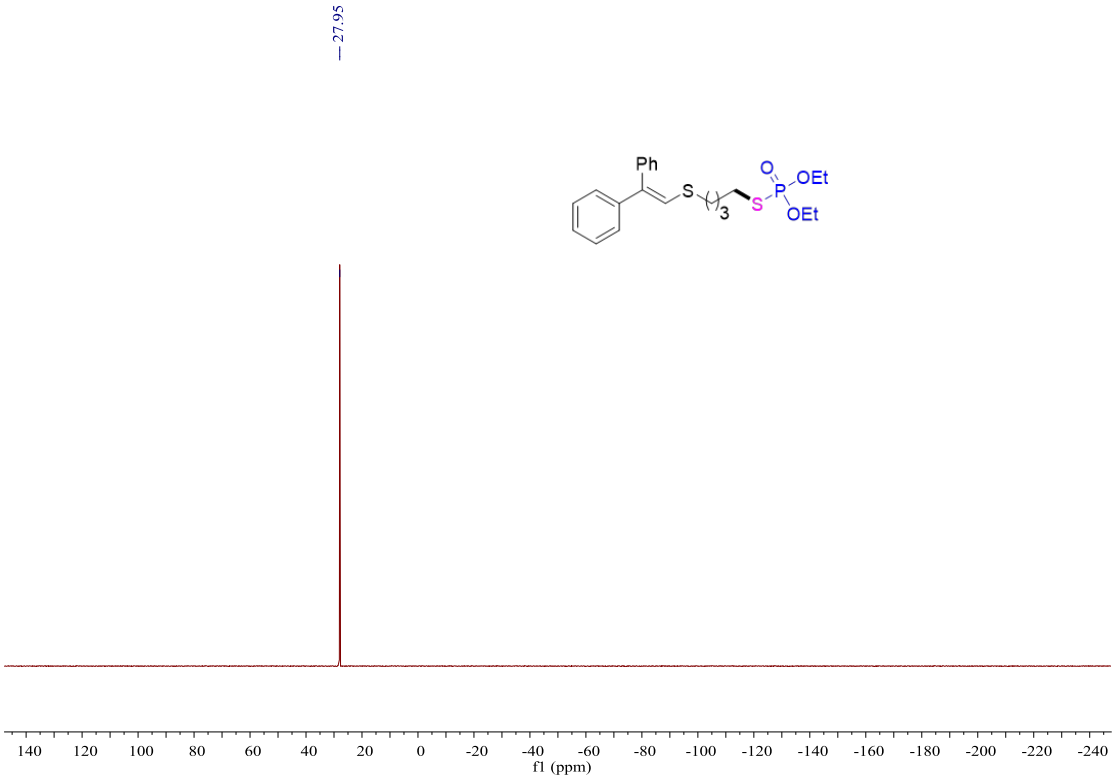
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3la**



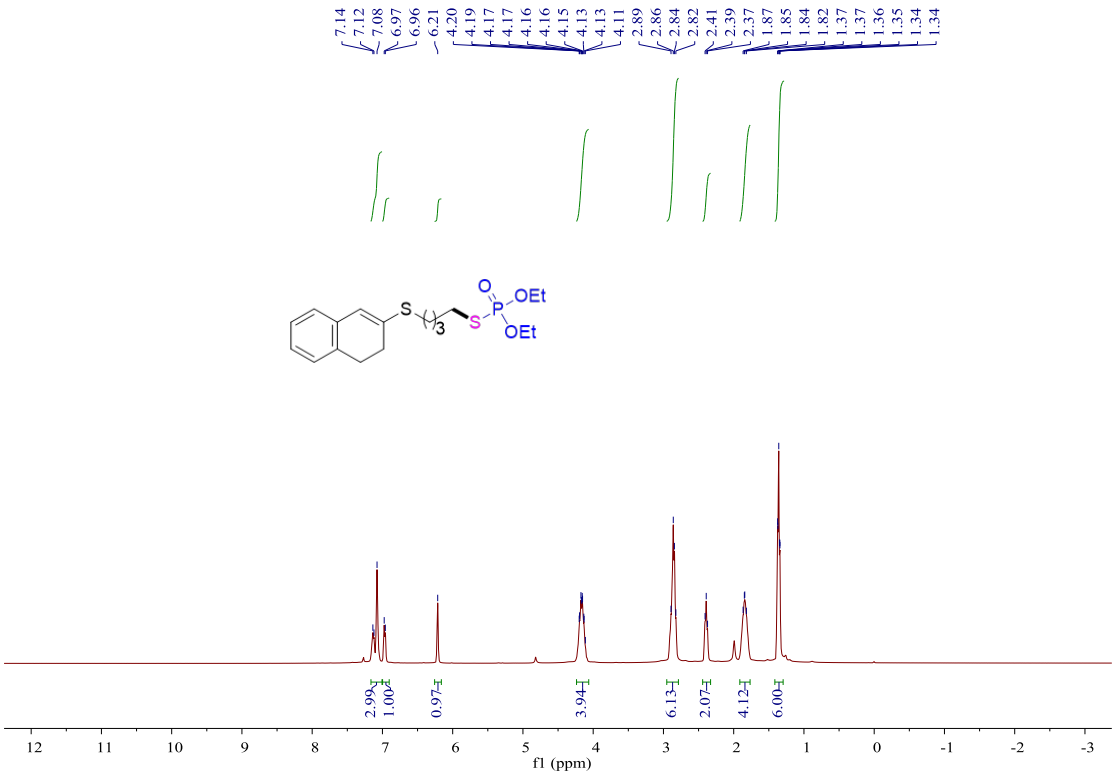
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ma**



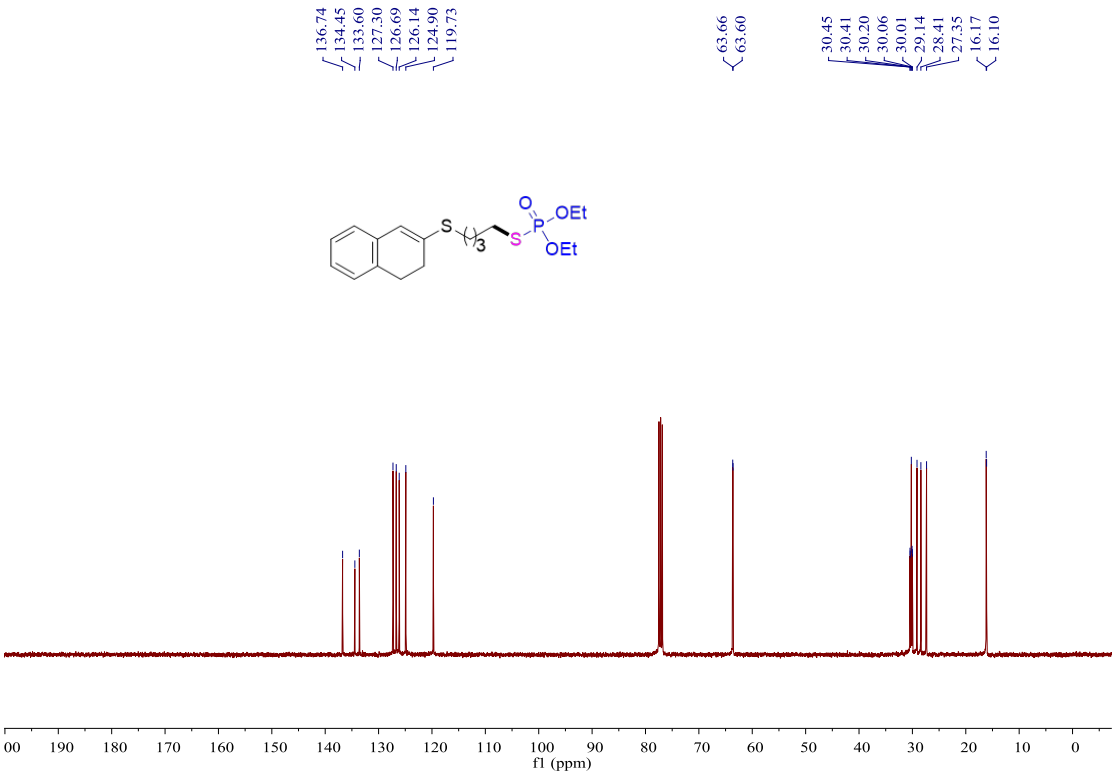
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ma**



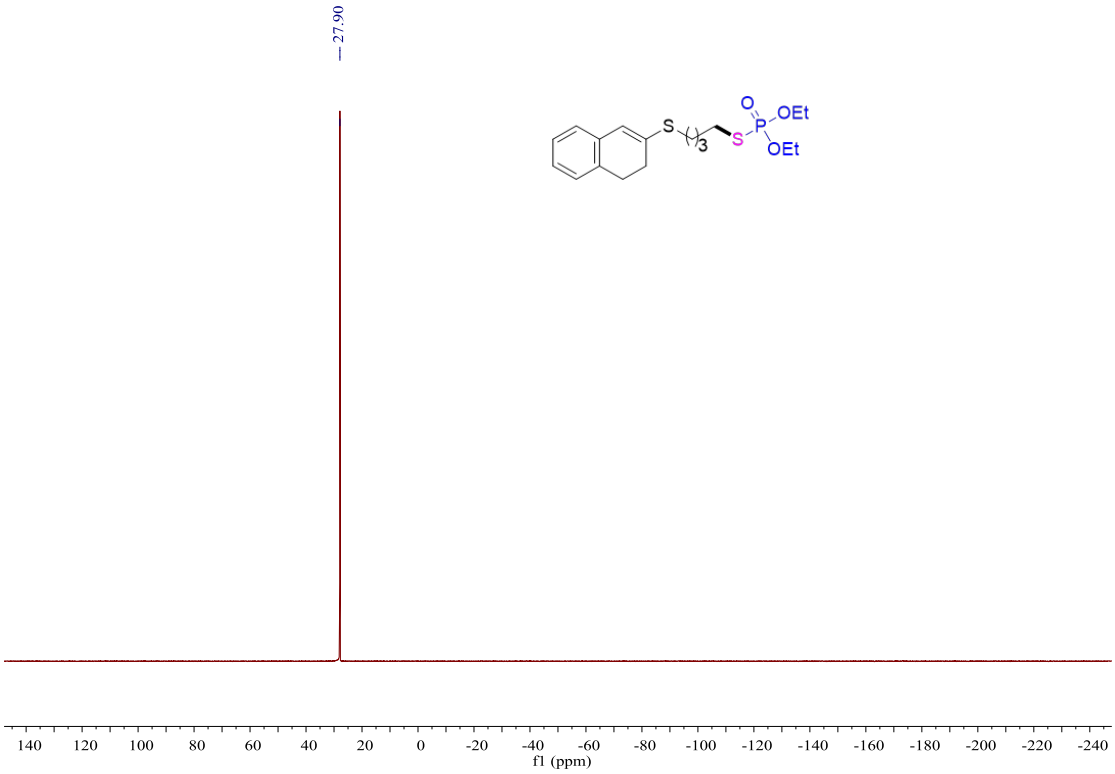
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ma**



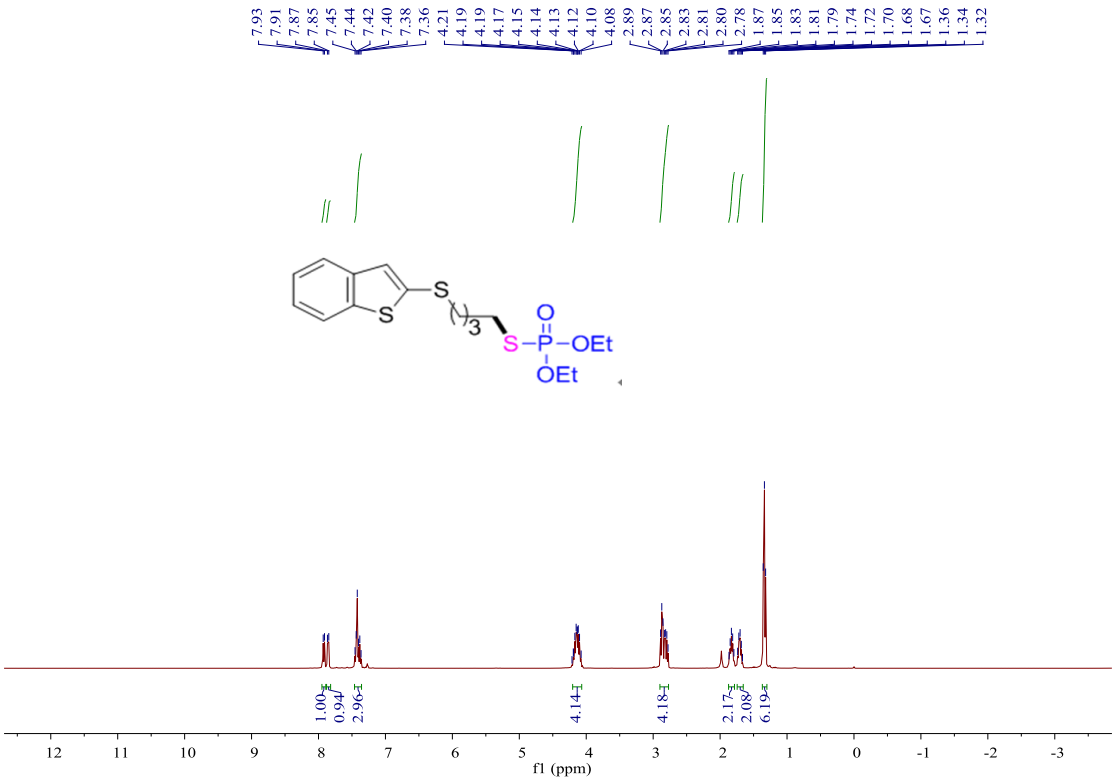
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3na**



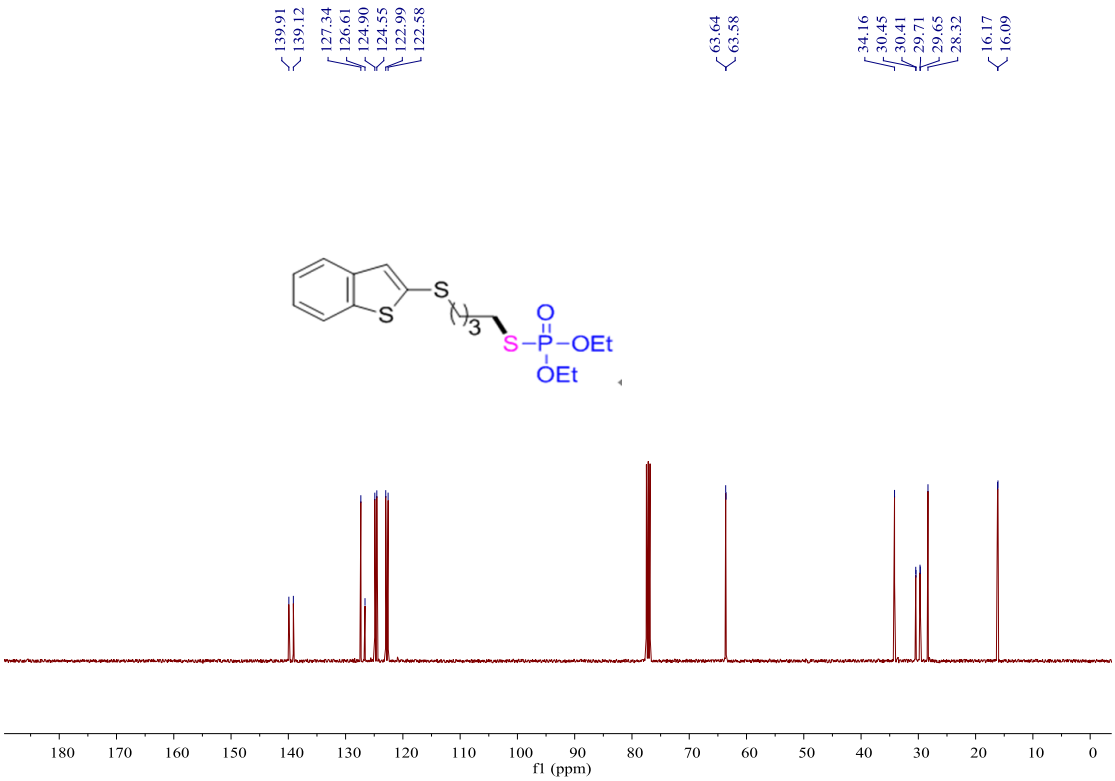
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3na**



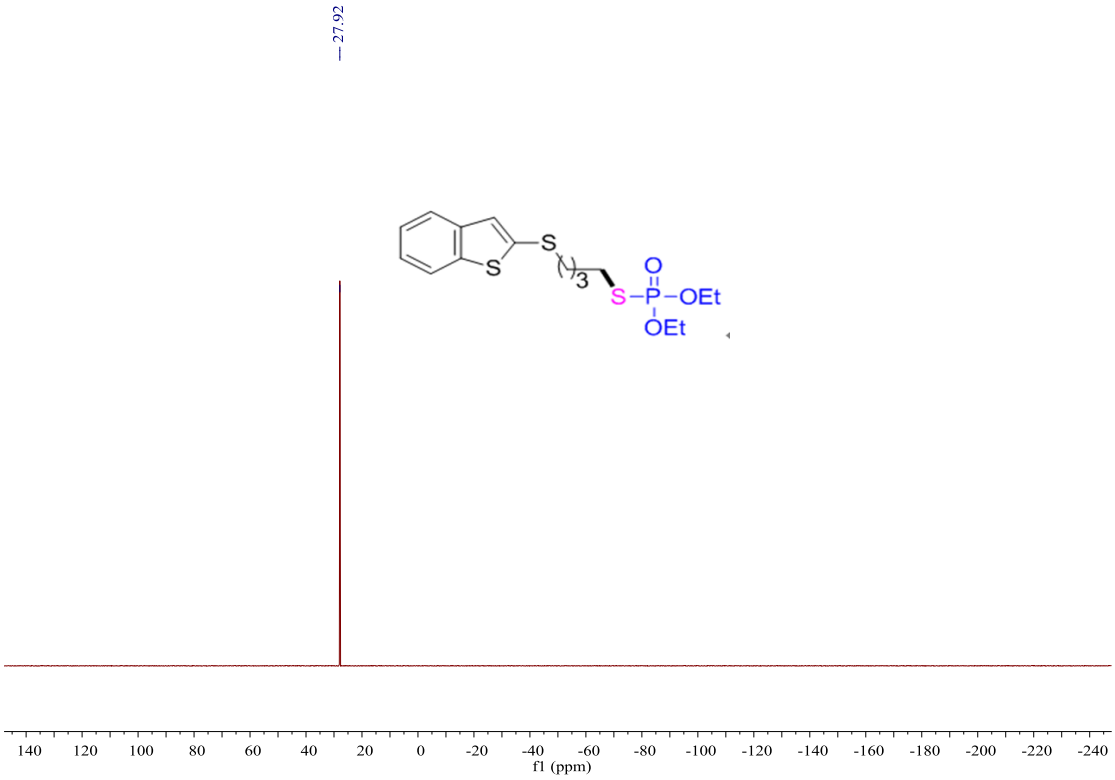
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3na**



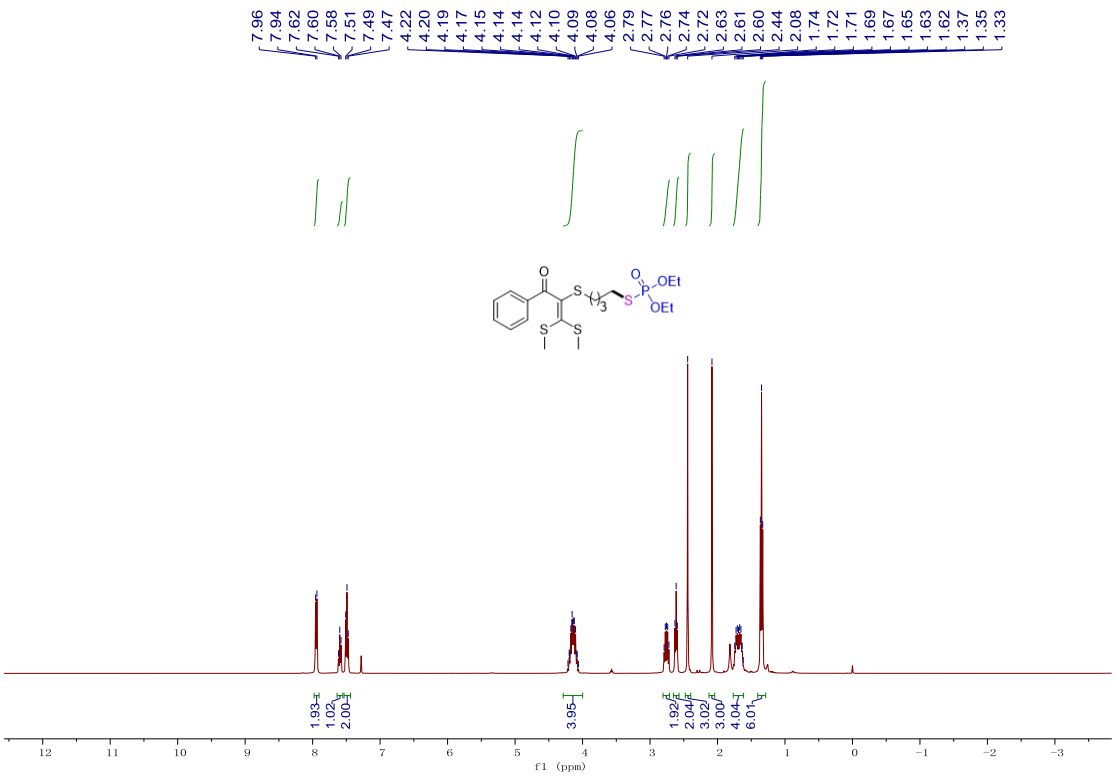
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3oa**



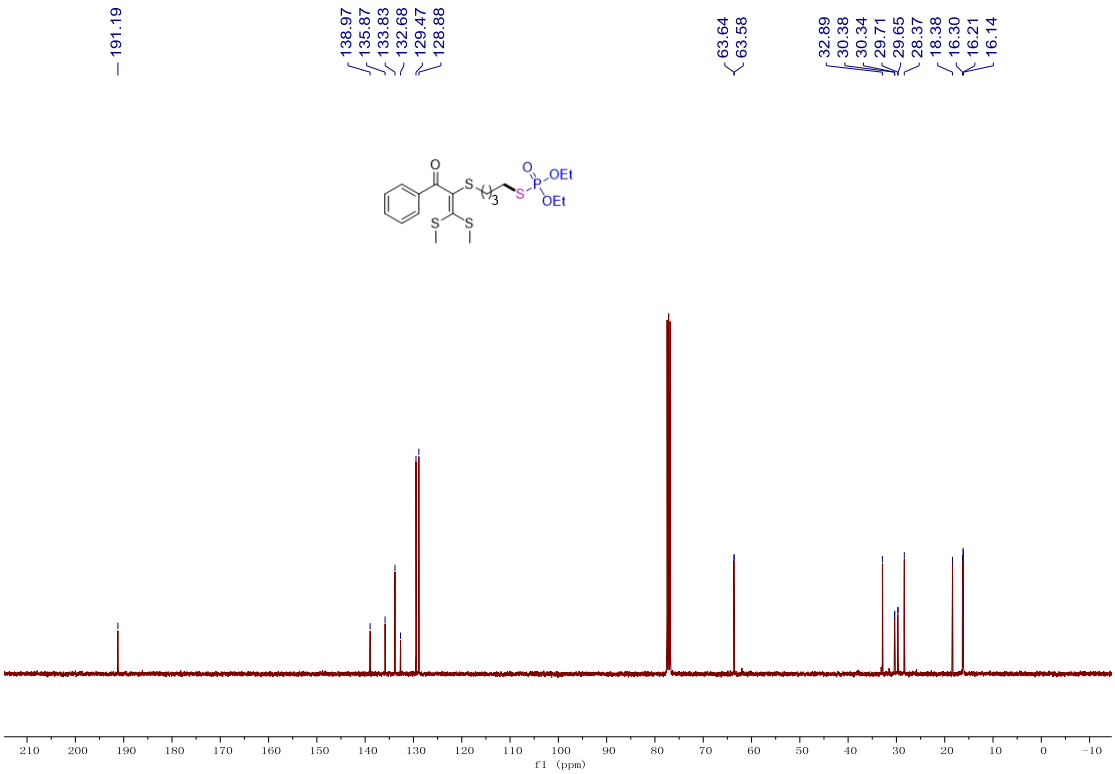
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3oa**



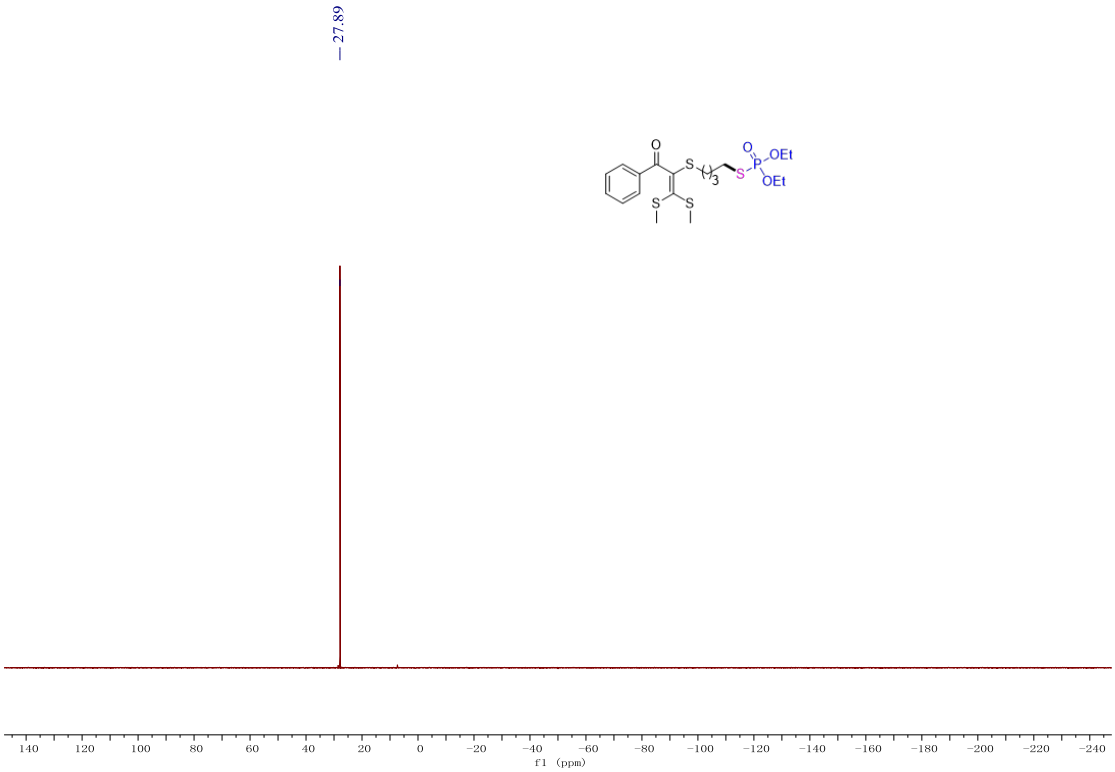
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3oa**



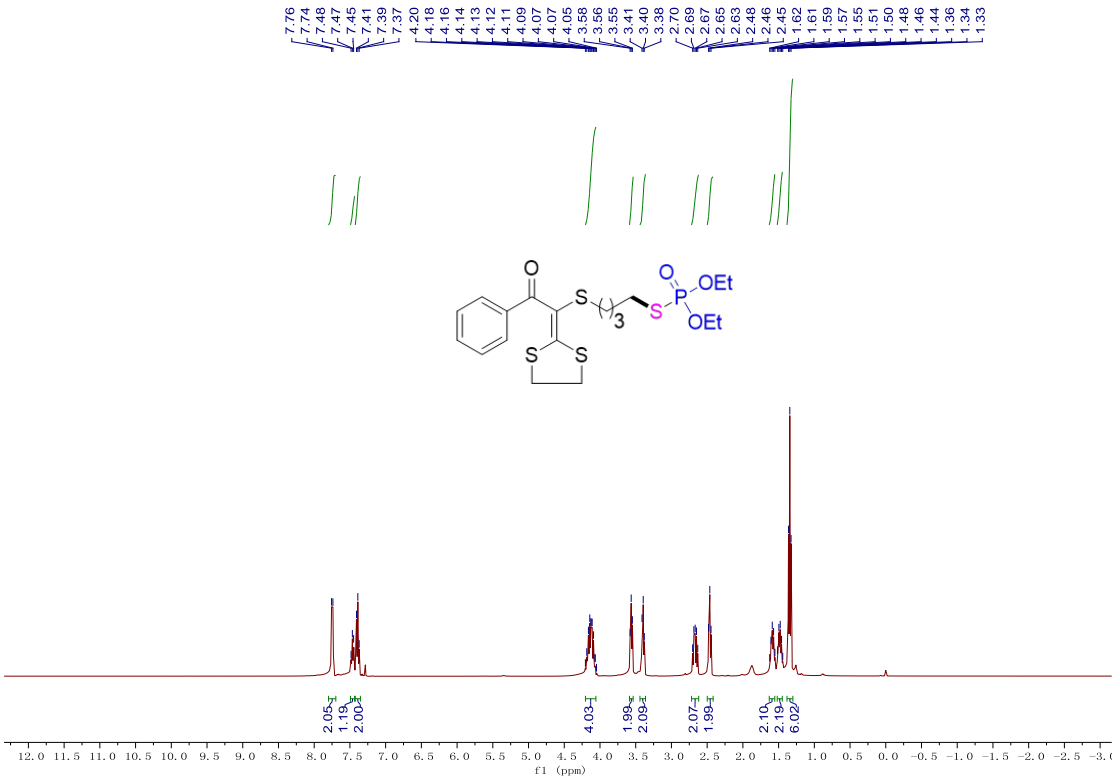
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3pa**



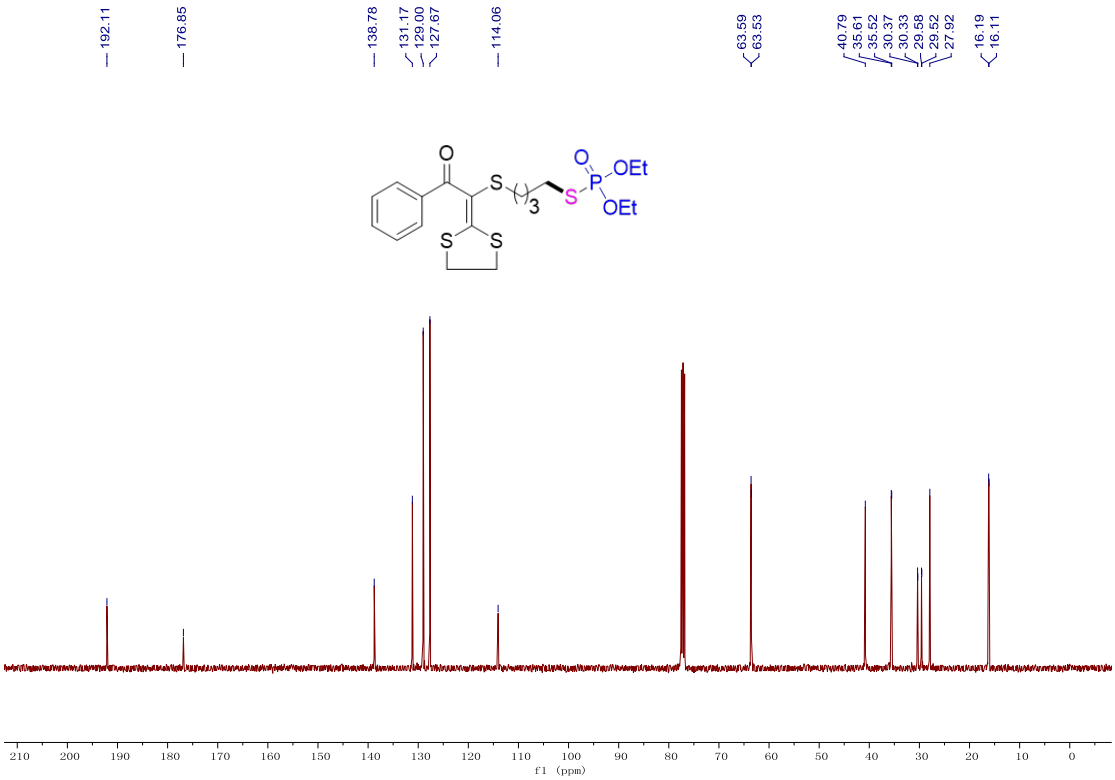
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3pa**



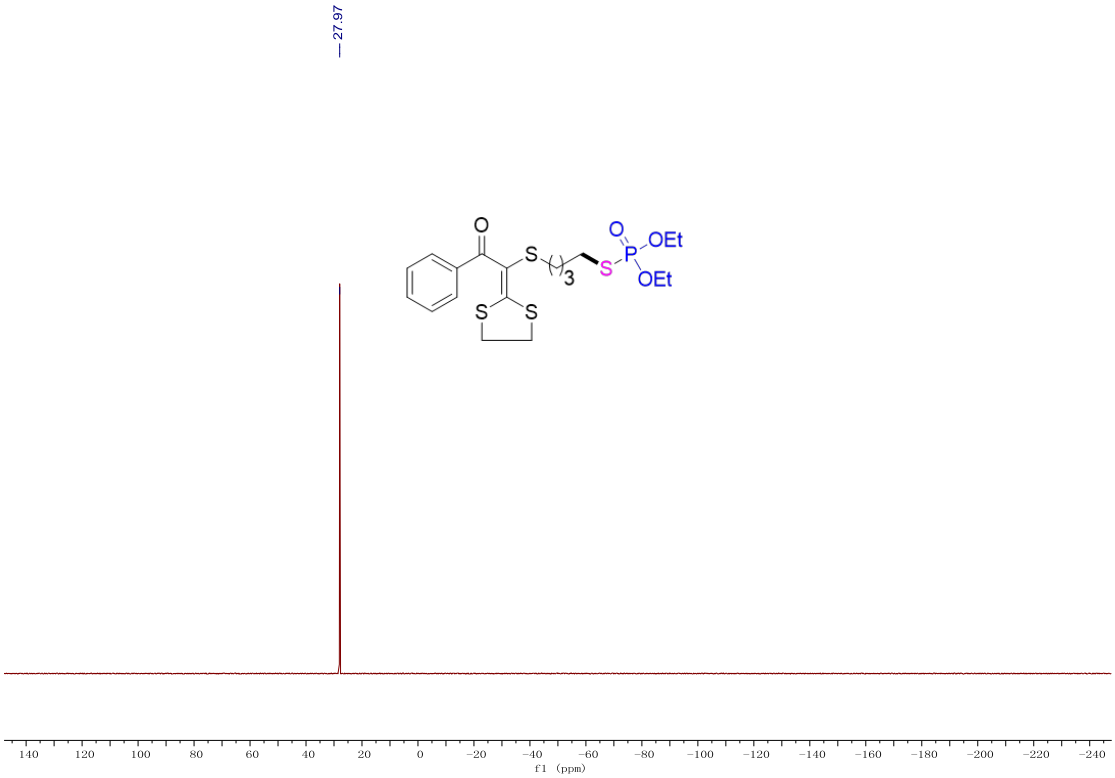
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3pa**



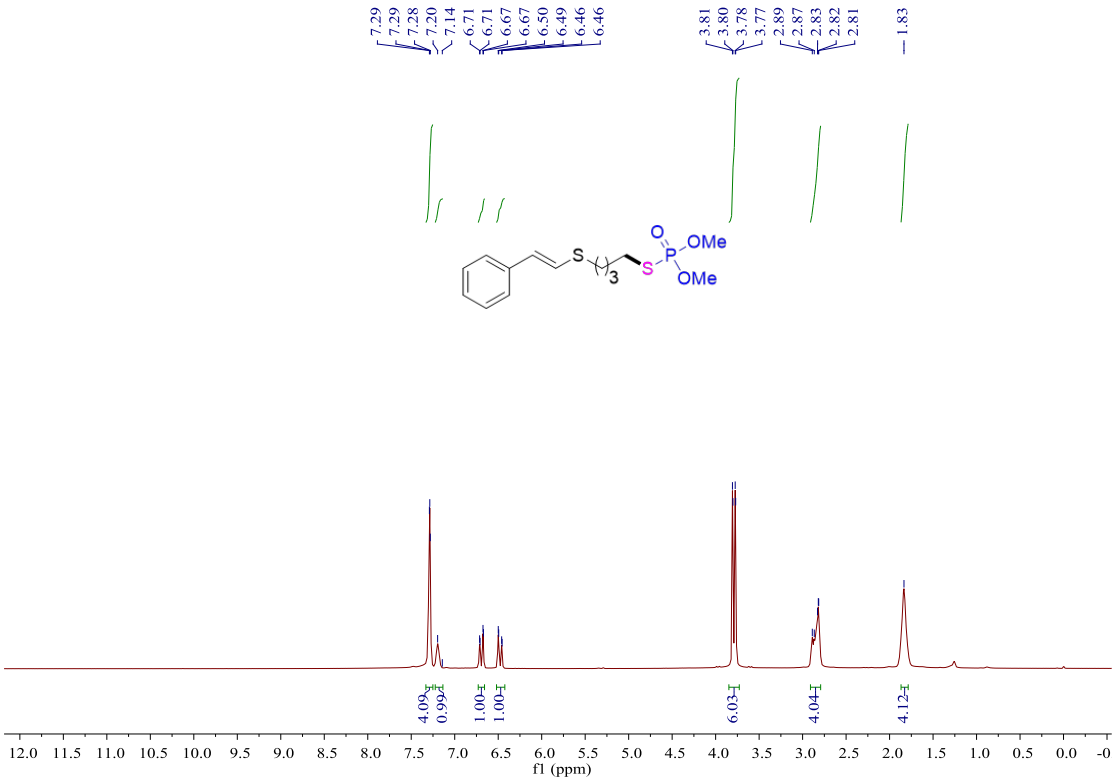
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3qa**



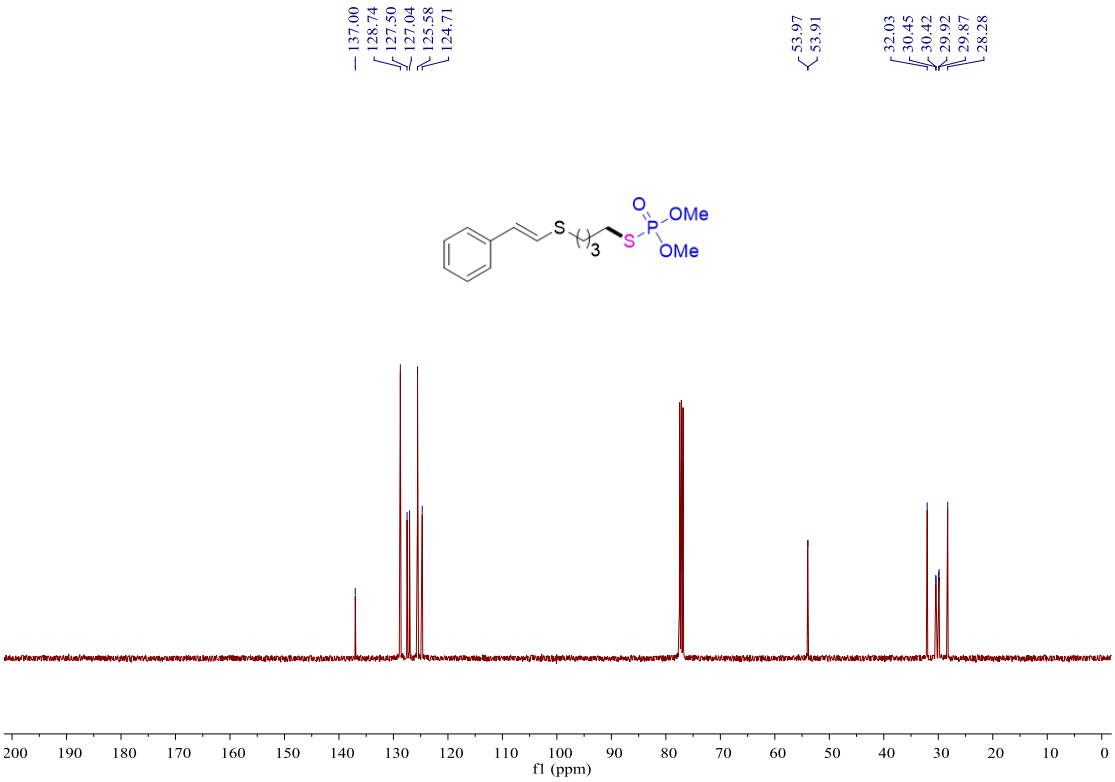
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3qa**



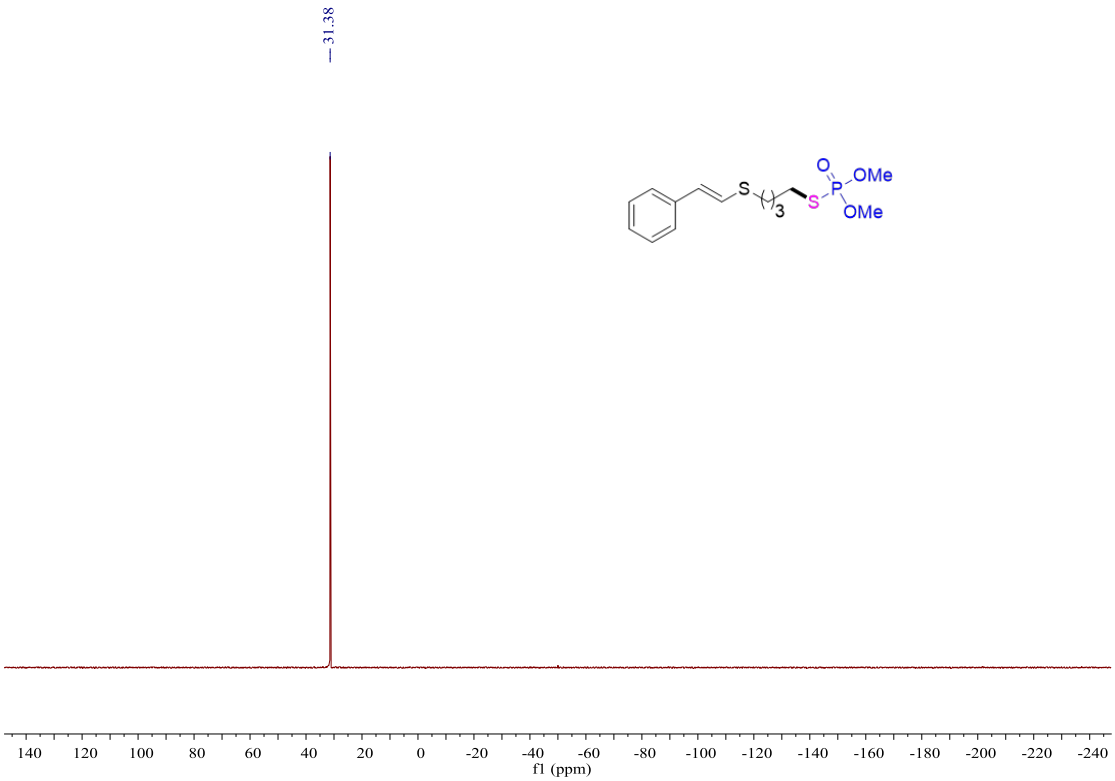
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3qa**



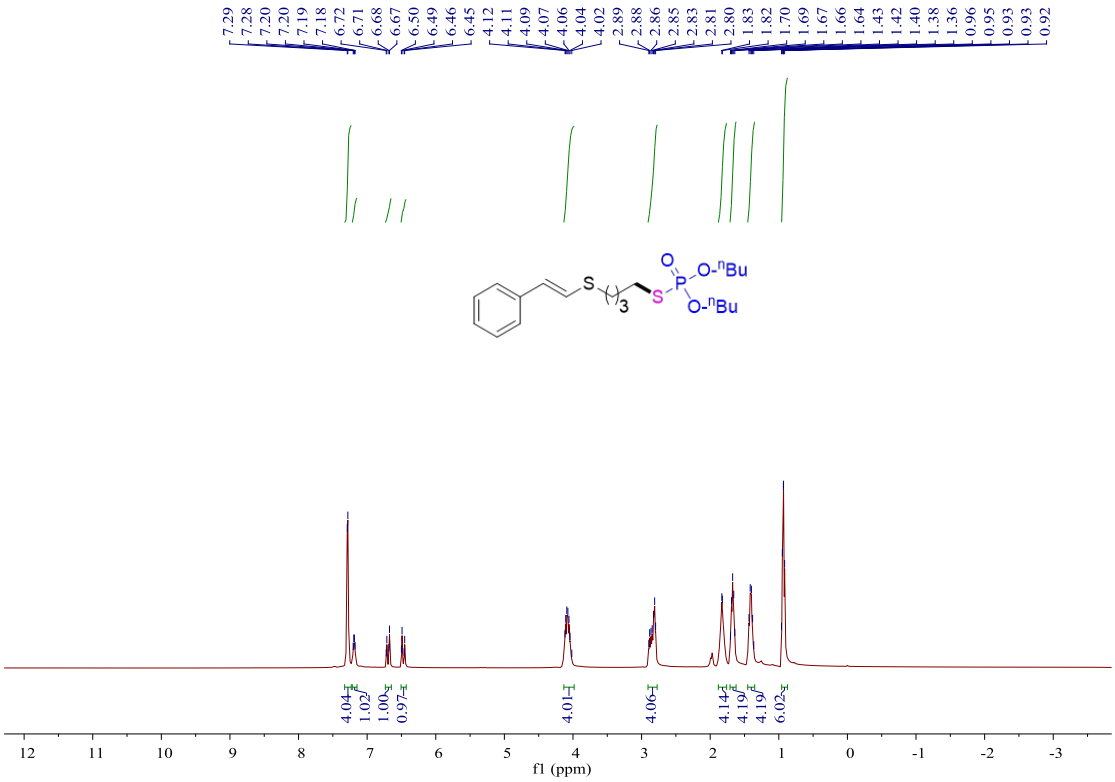
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ab**



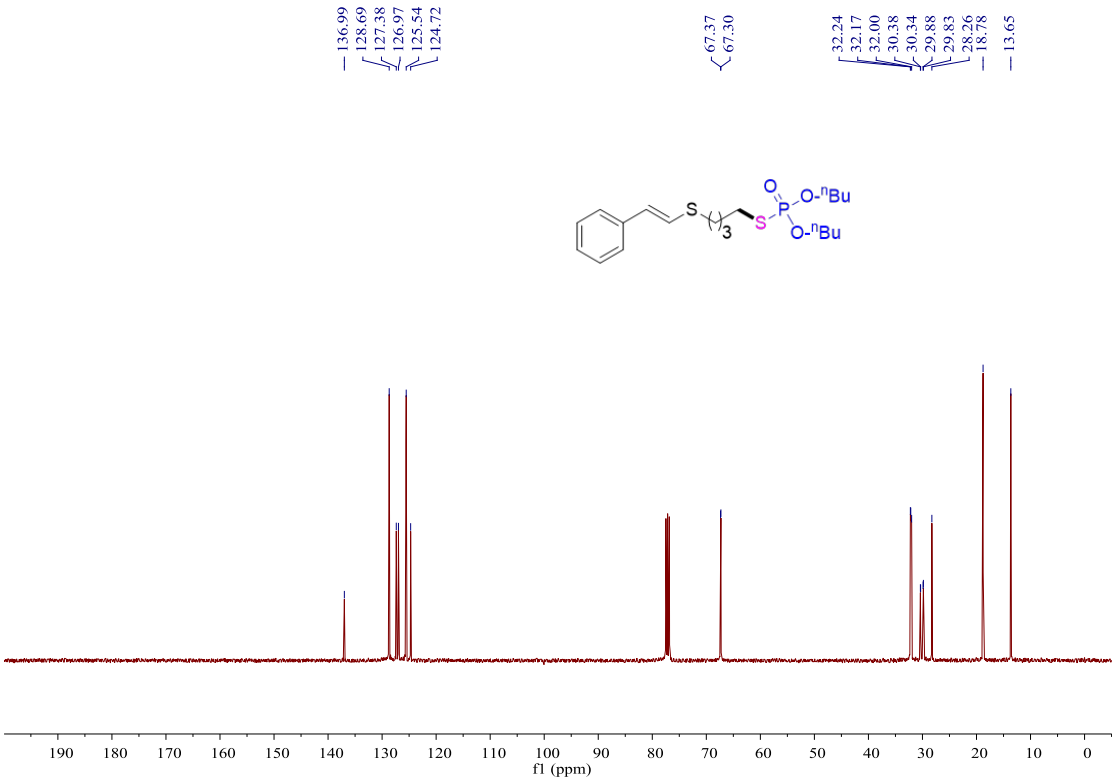
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ab**



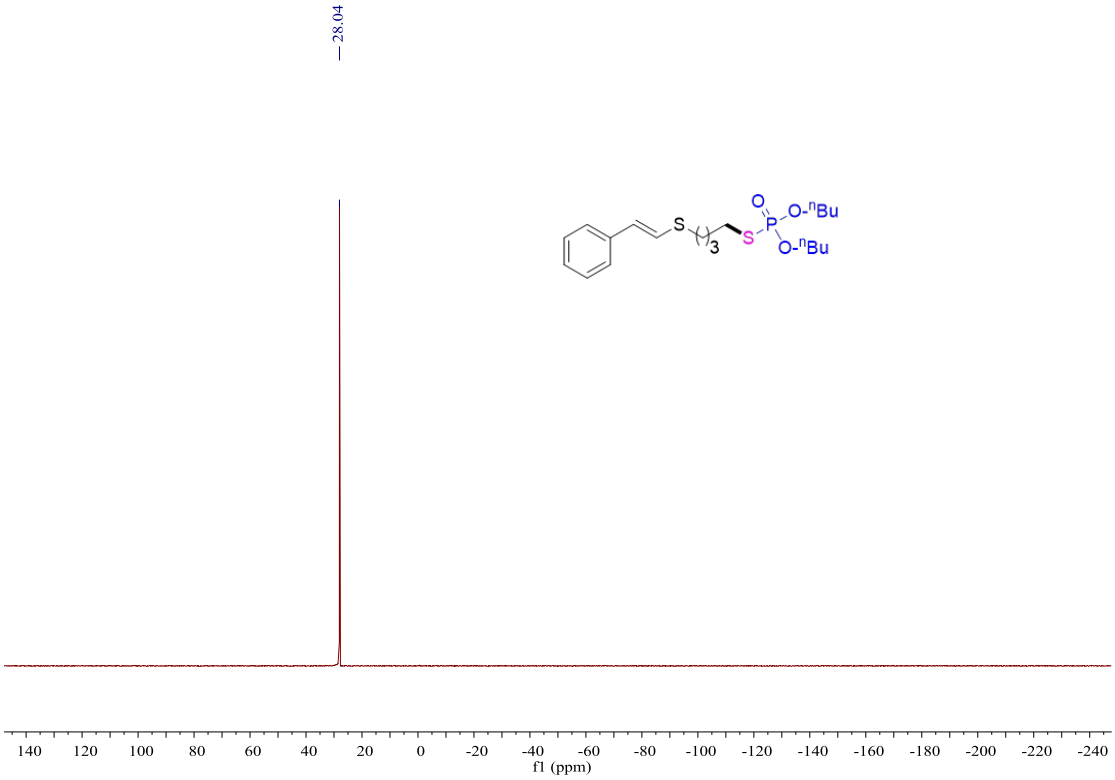
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ab**



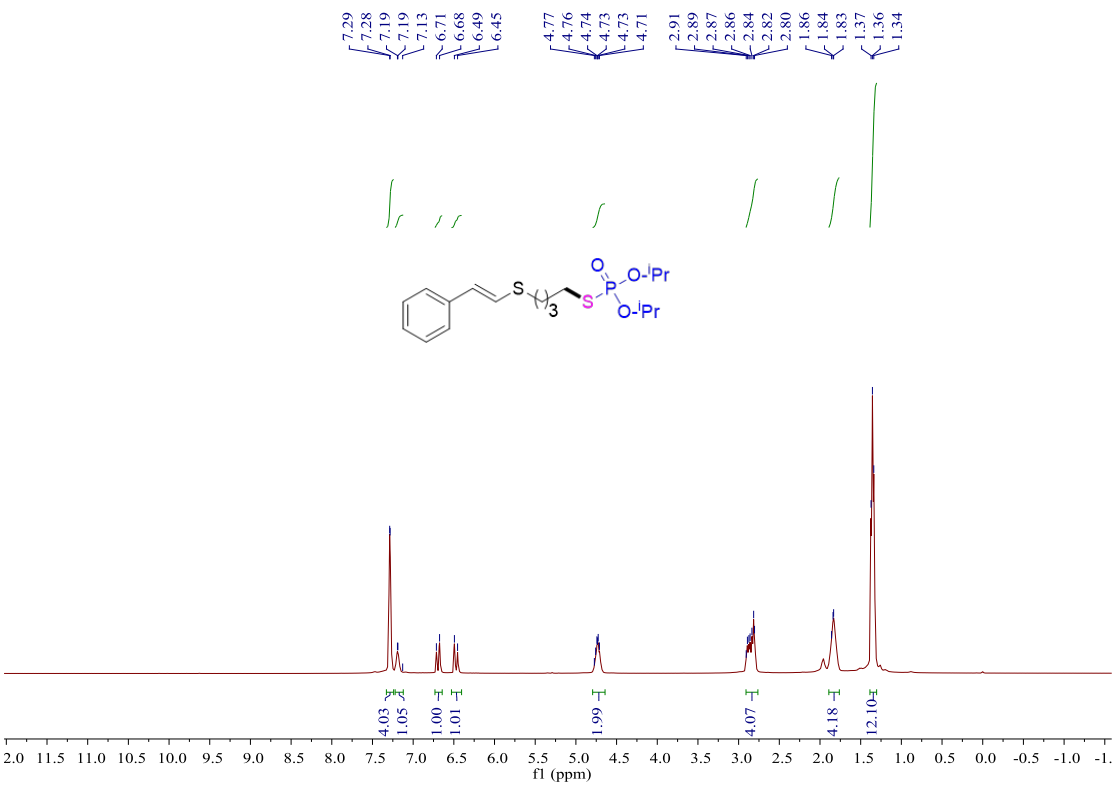
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ac**



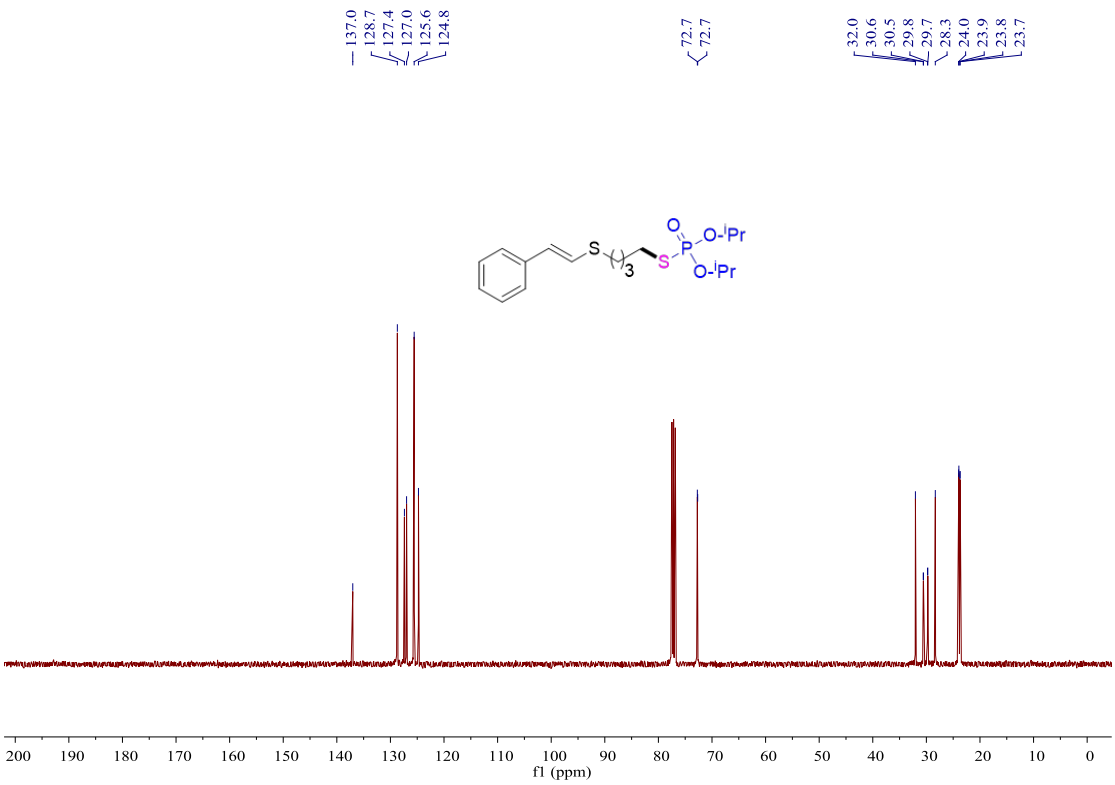
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ac**



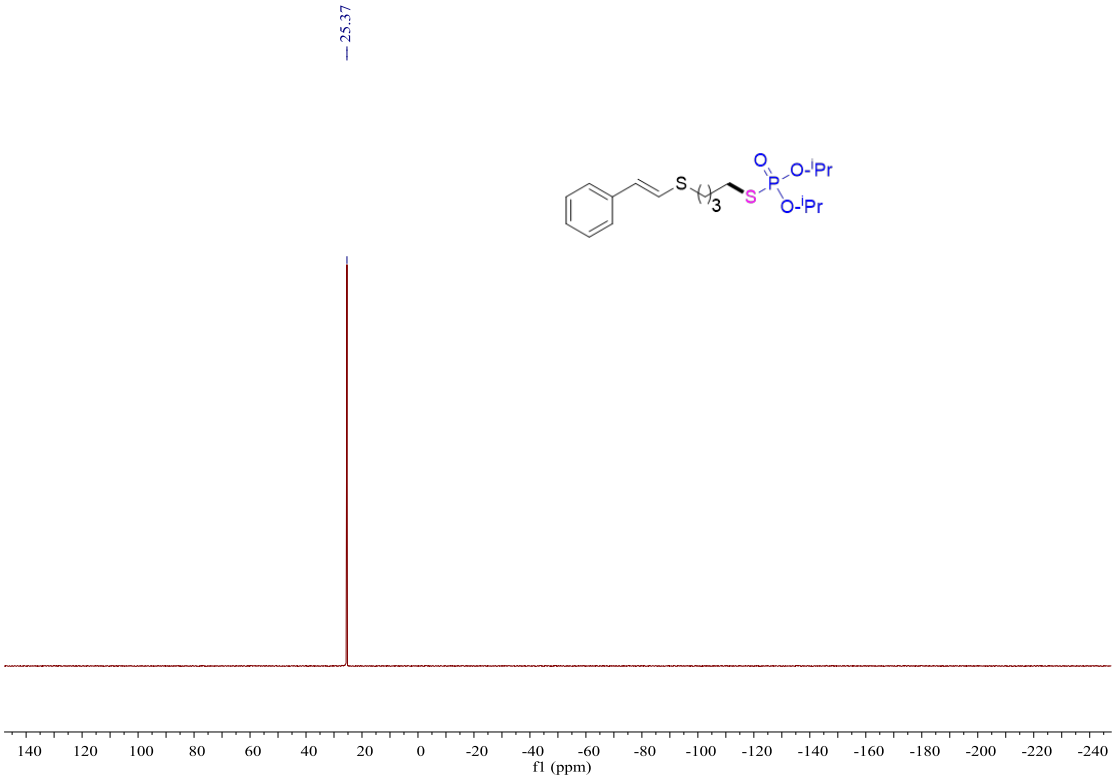
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ac**



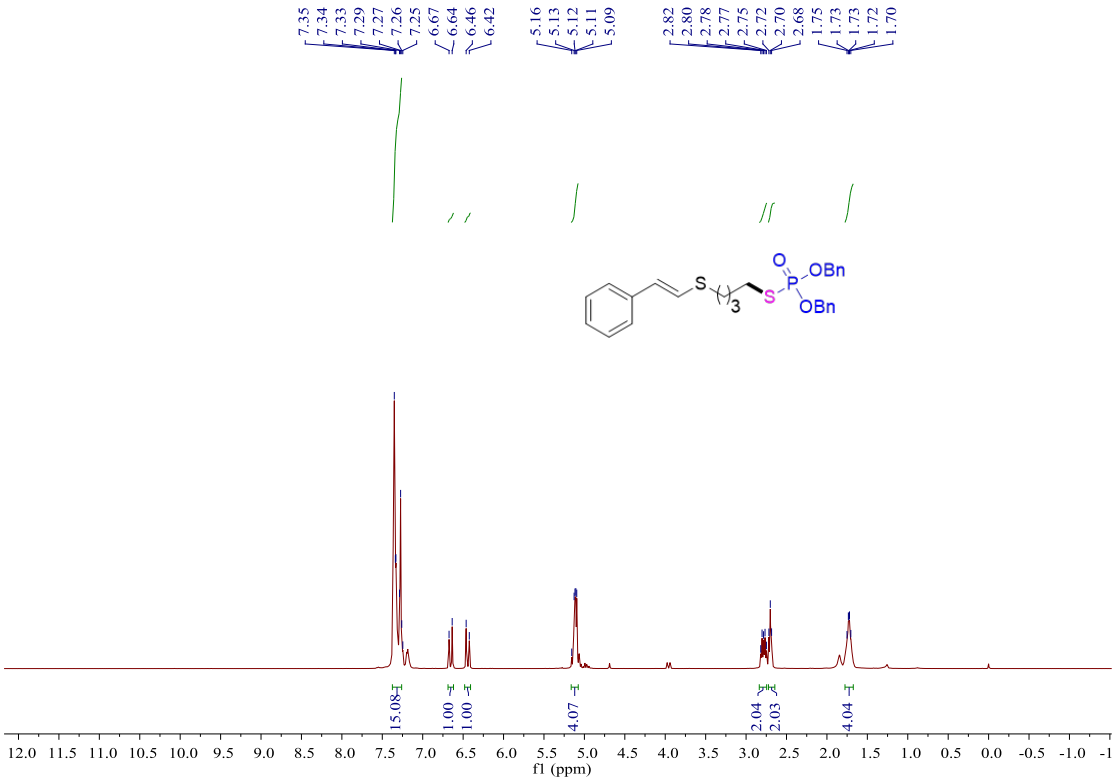
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ad**



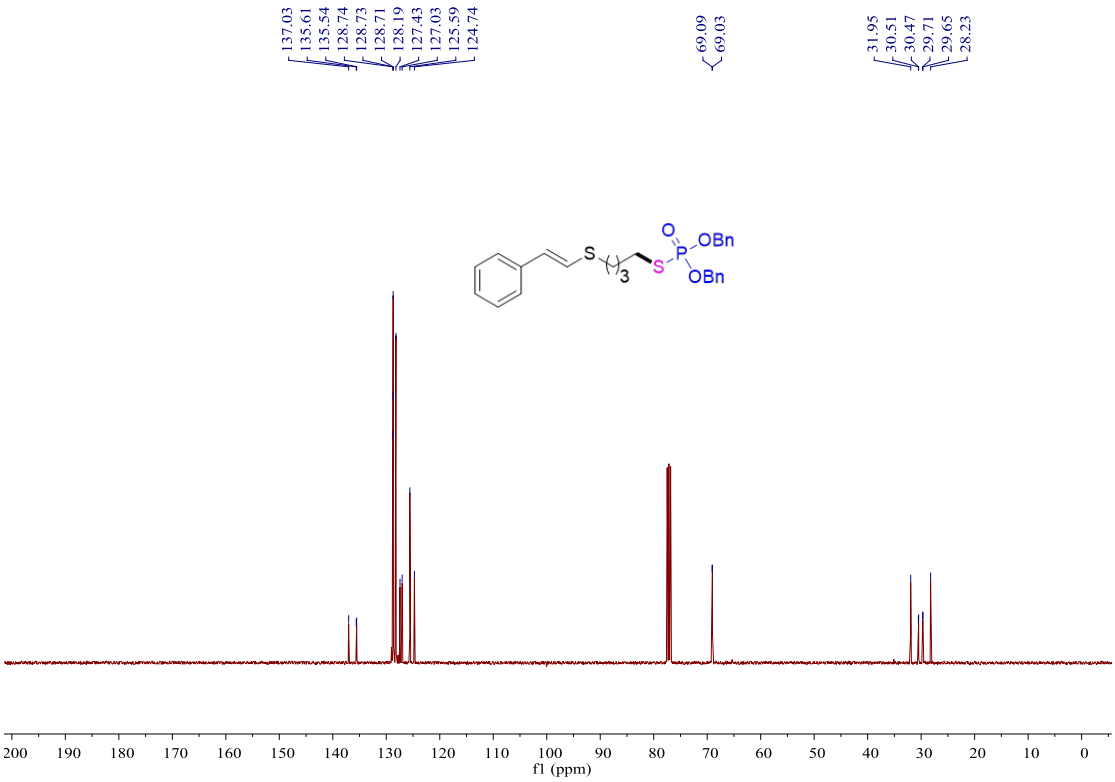
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ad**



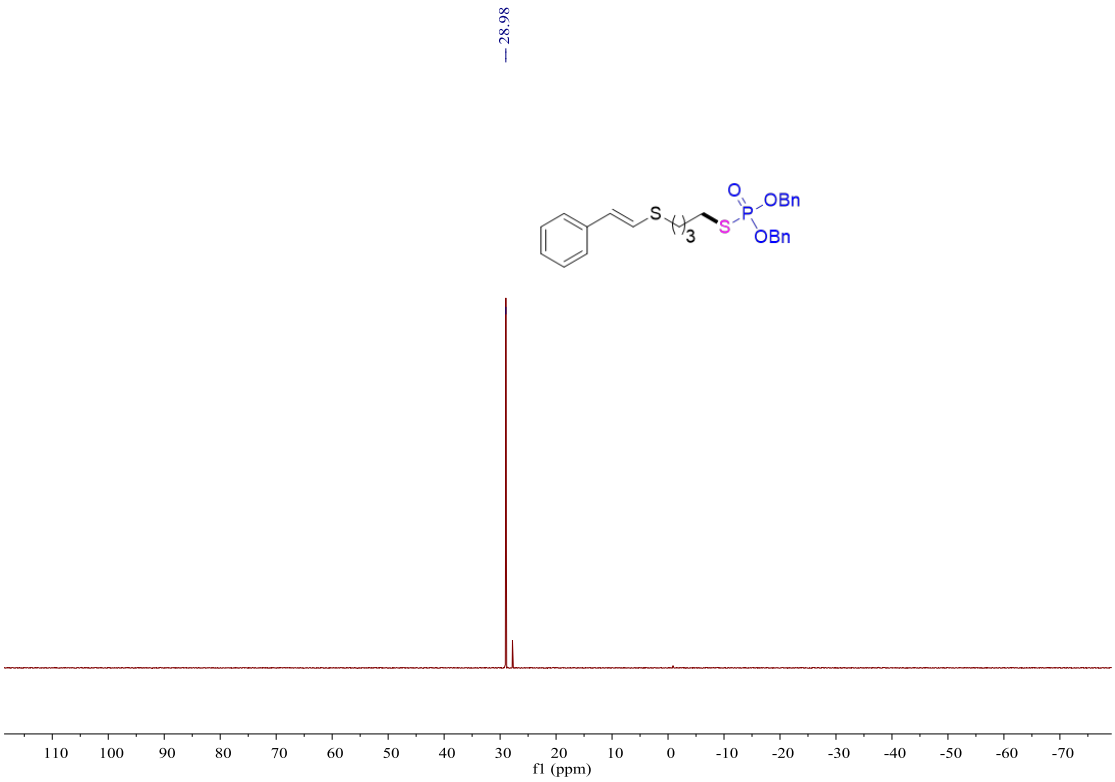
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ad**



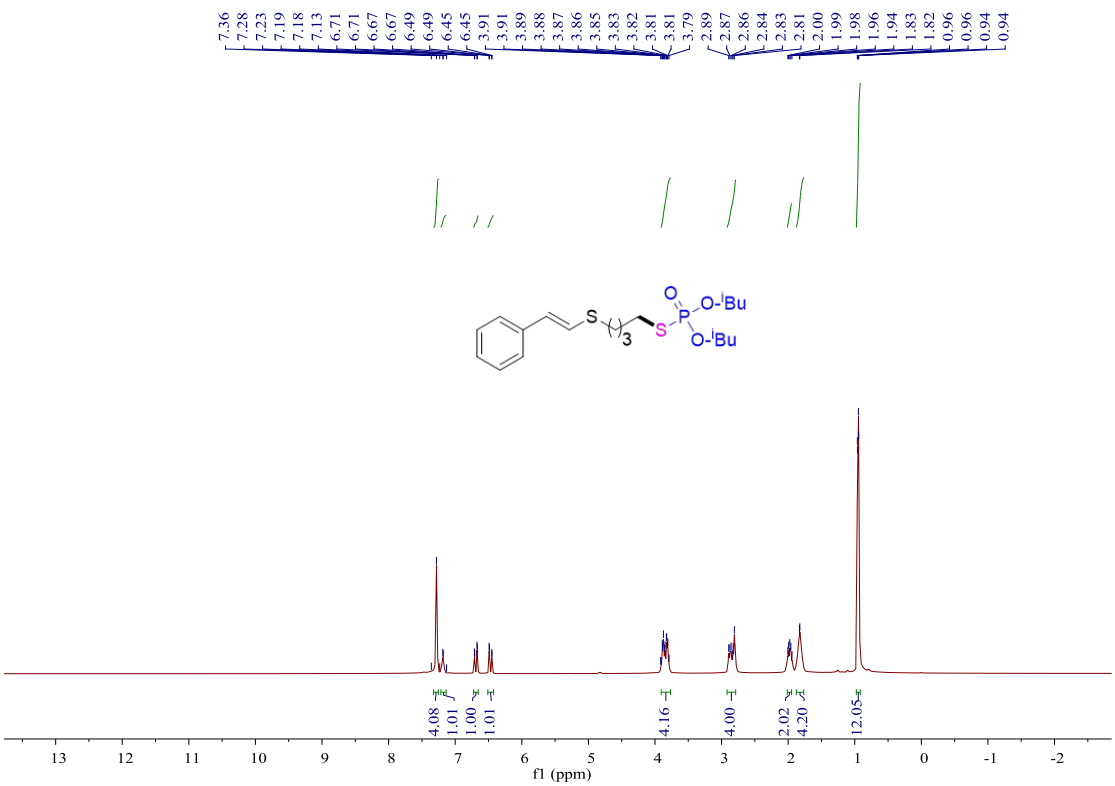
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ae**



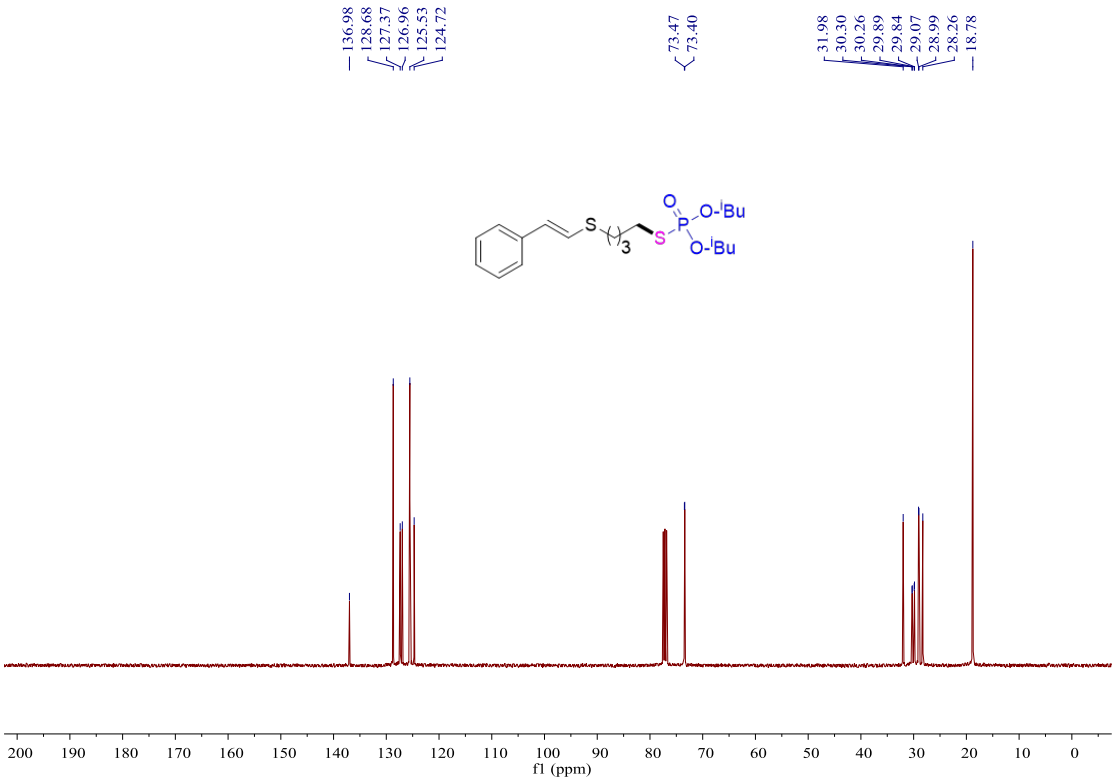
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ae**



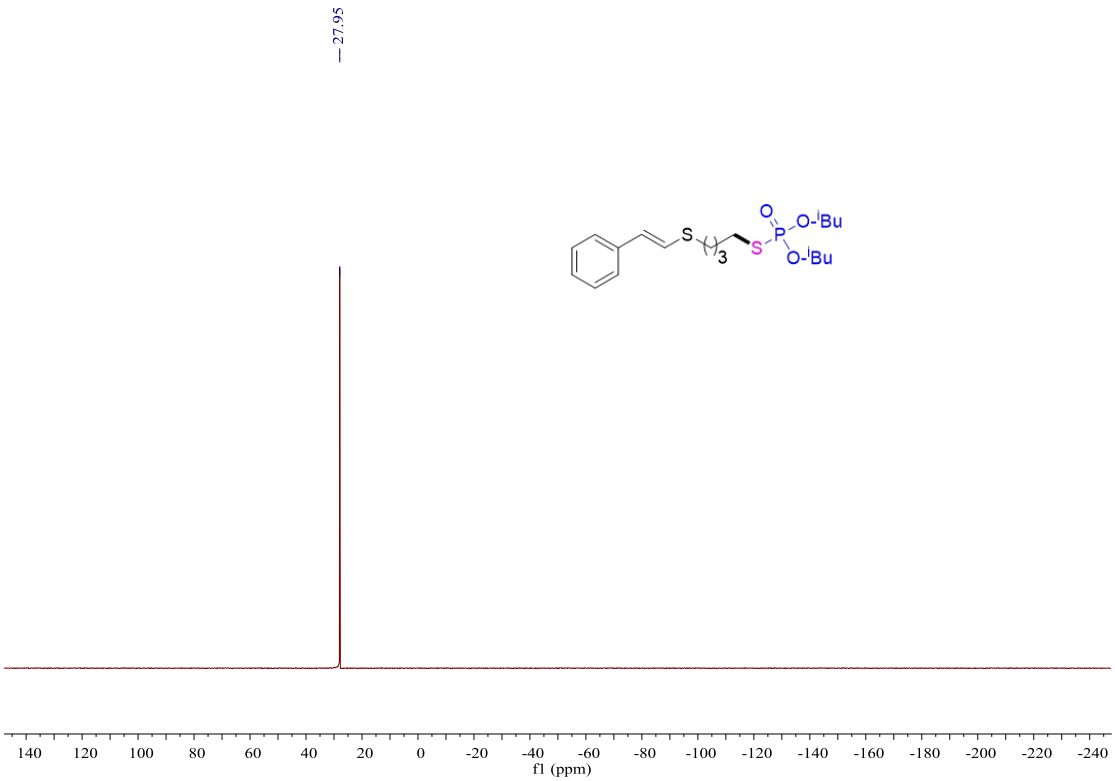
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ae**



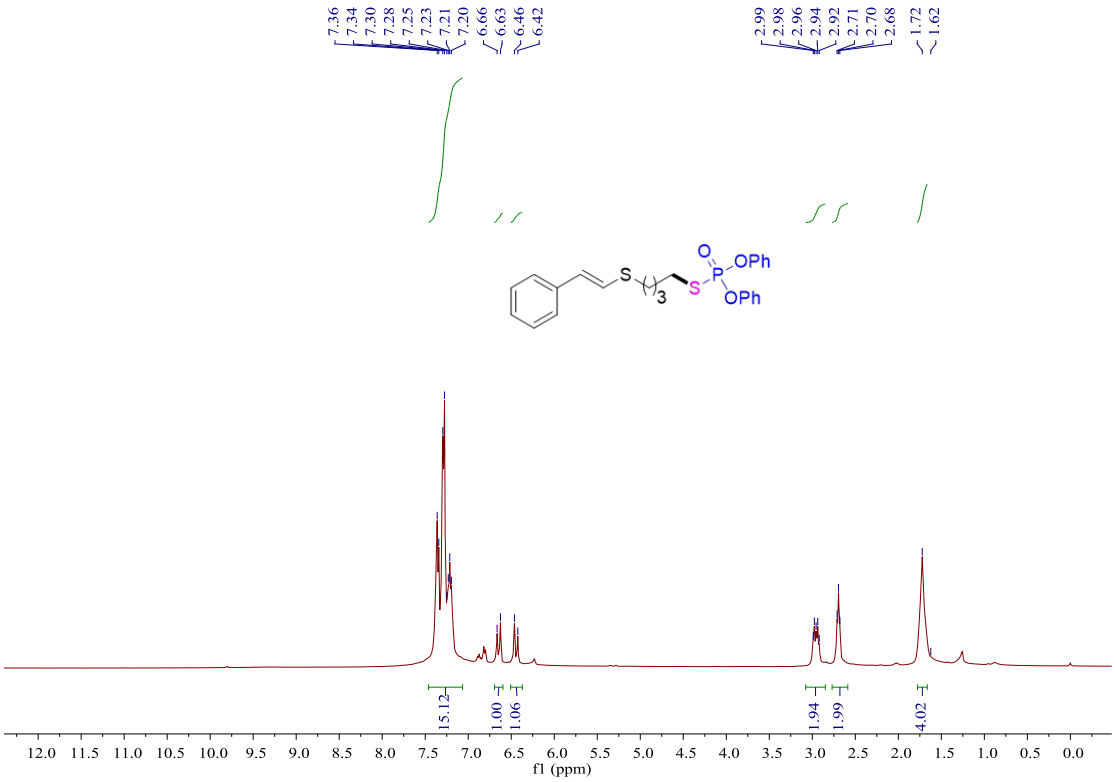
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3af**



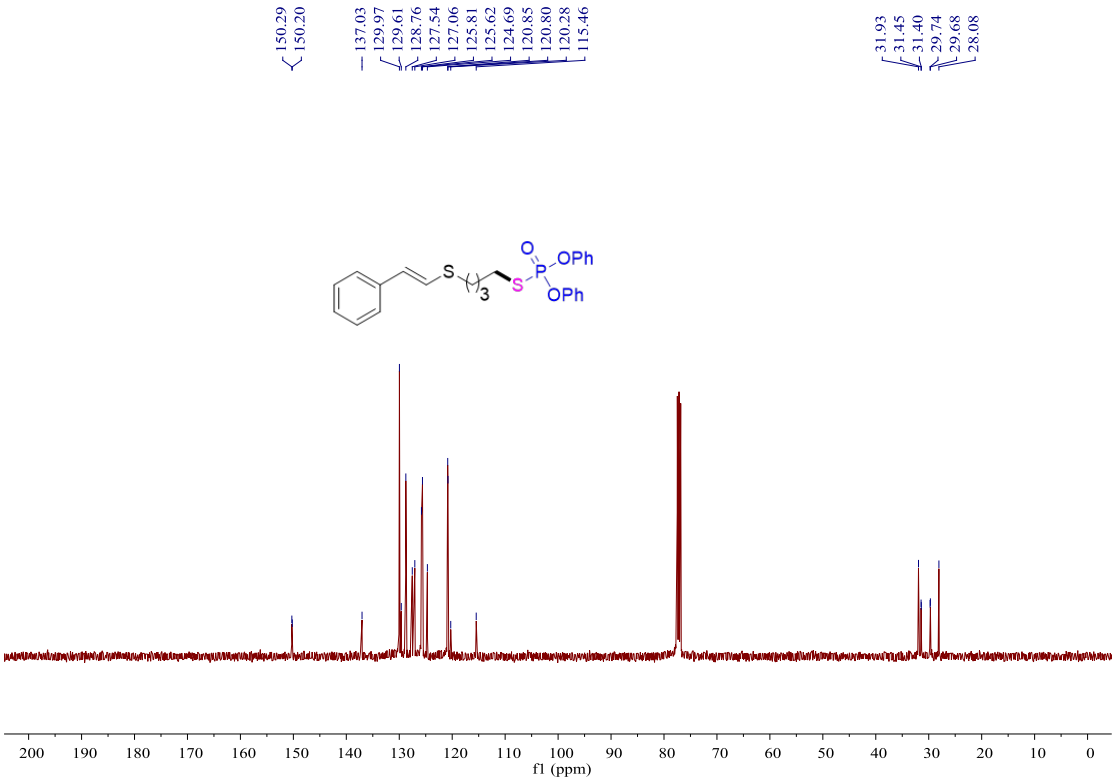
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3af**



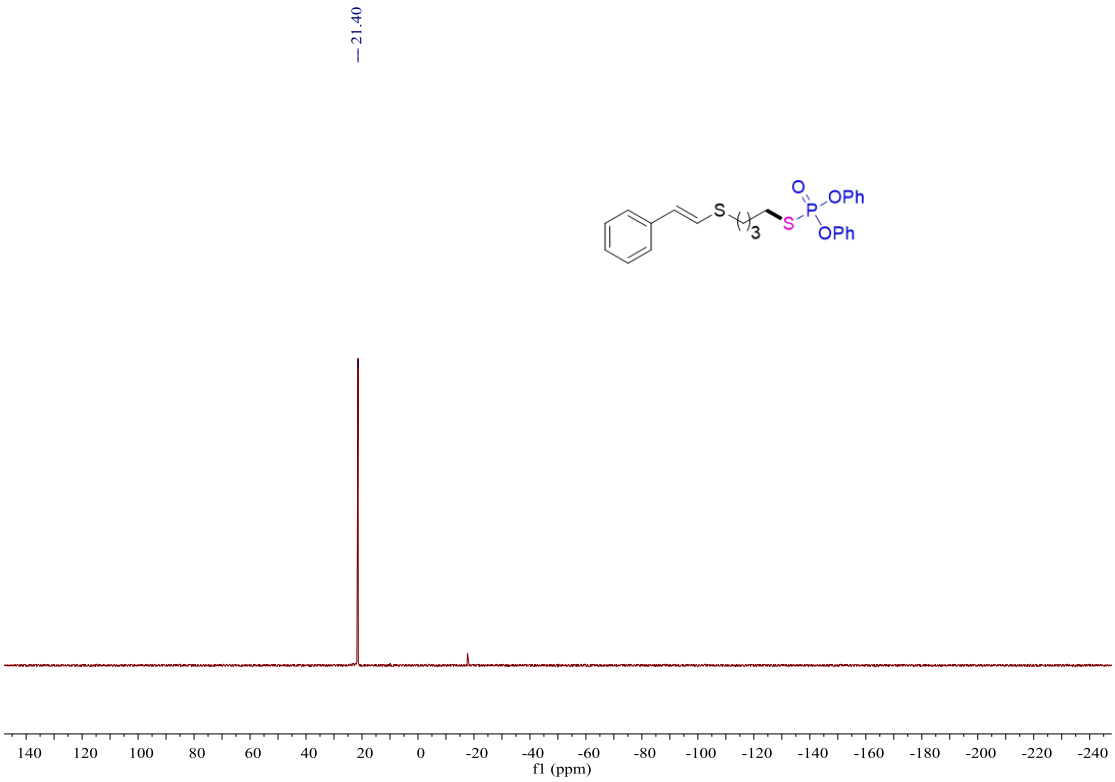
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3af**



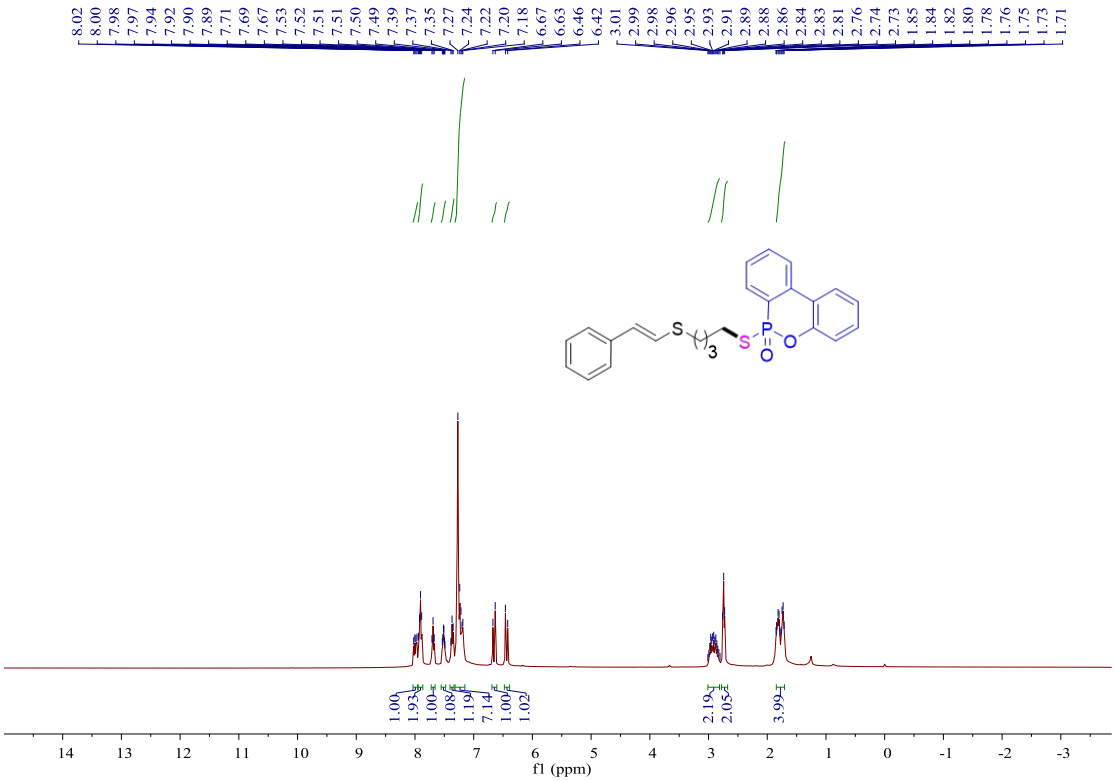
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ag**



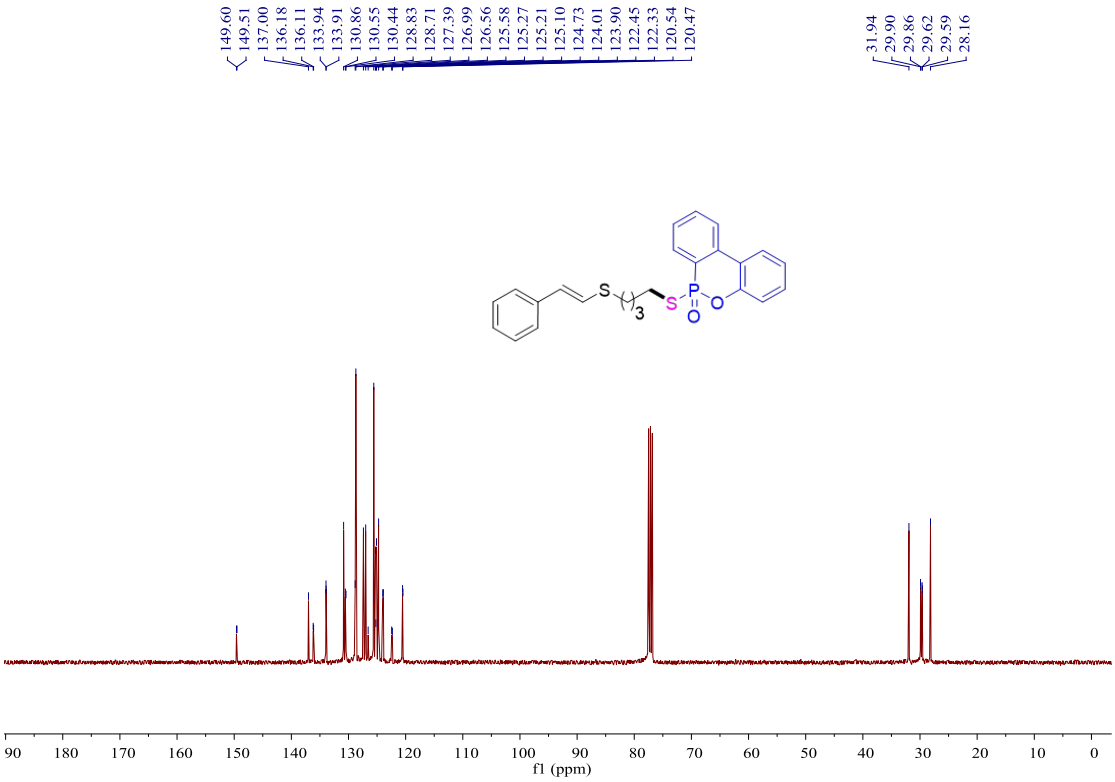
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ag**



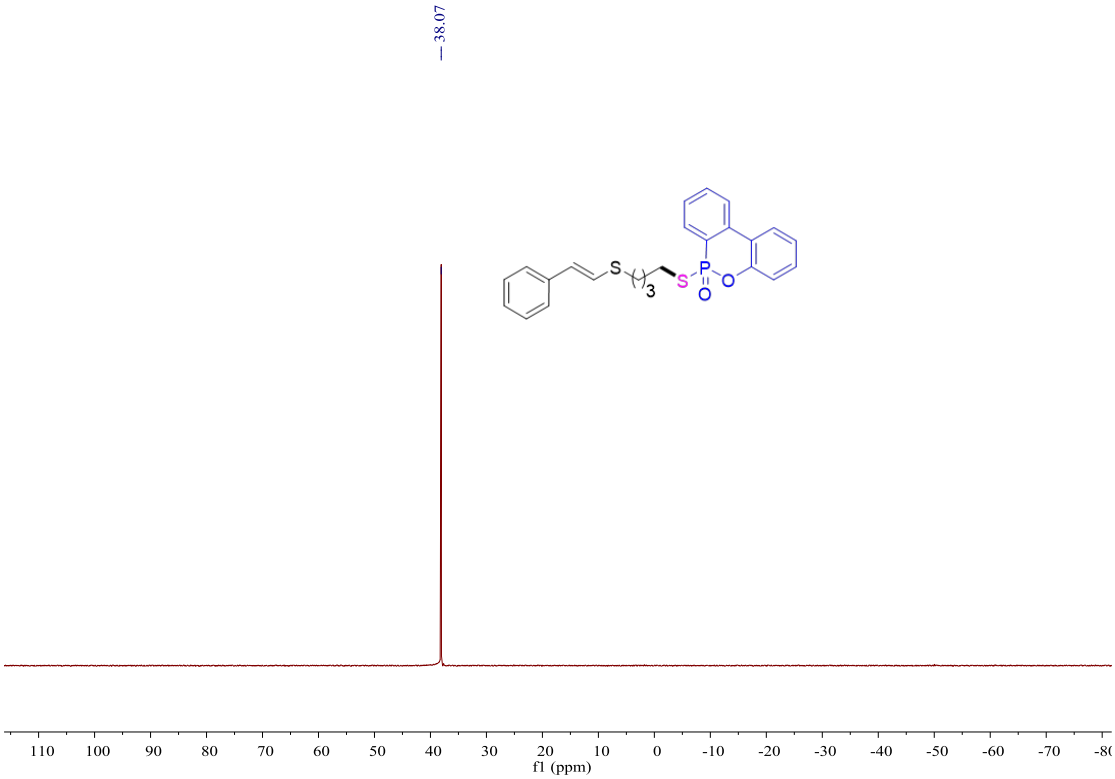
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ag**



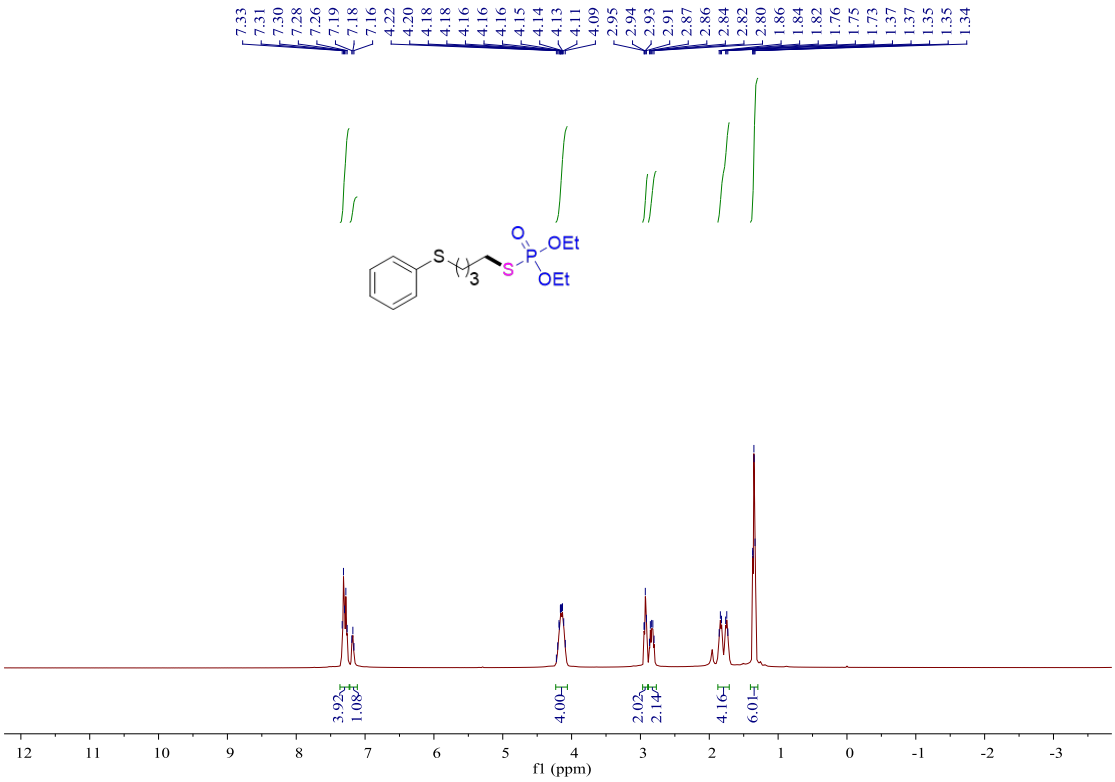
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ah**



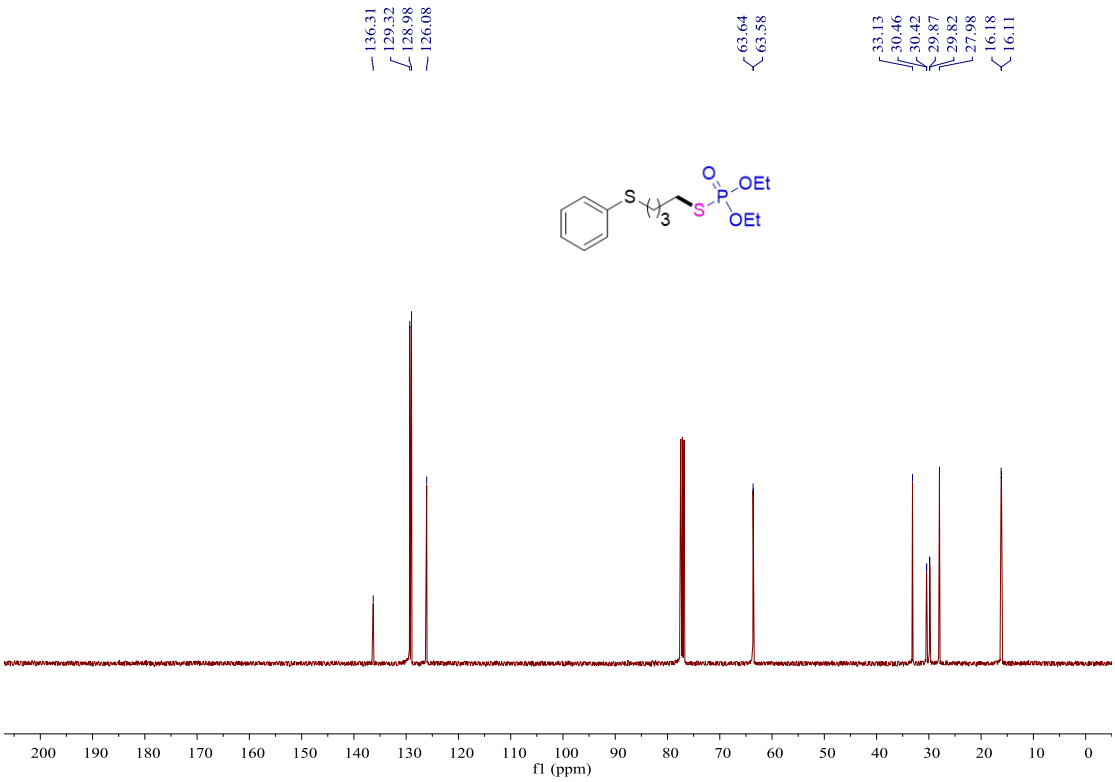
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ah**



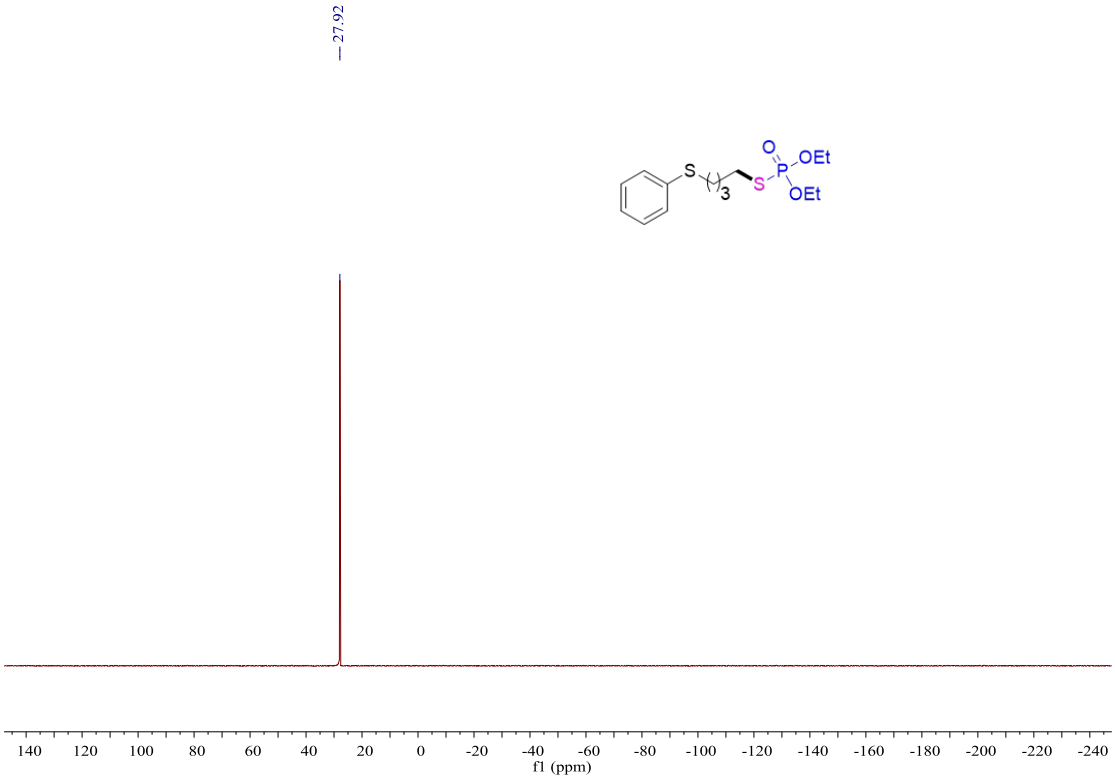
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ah**



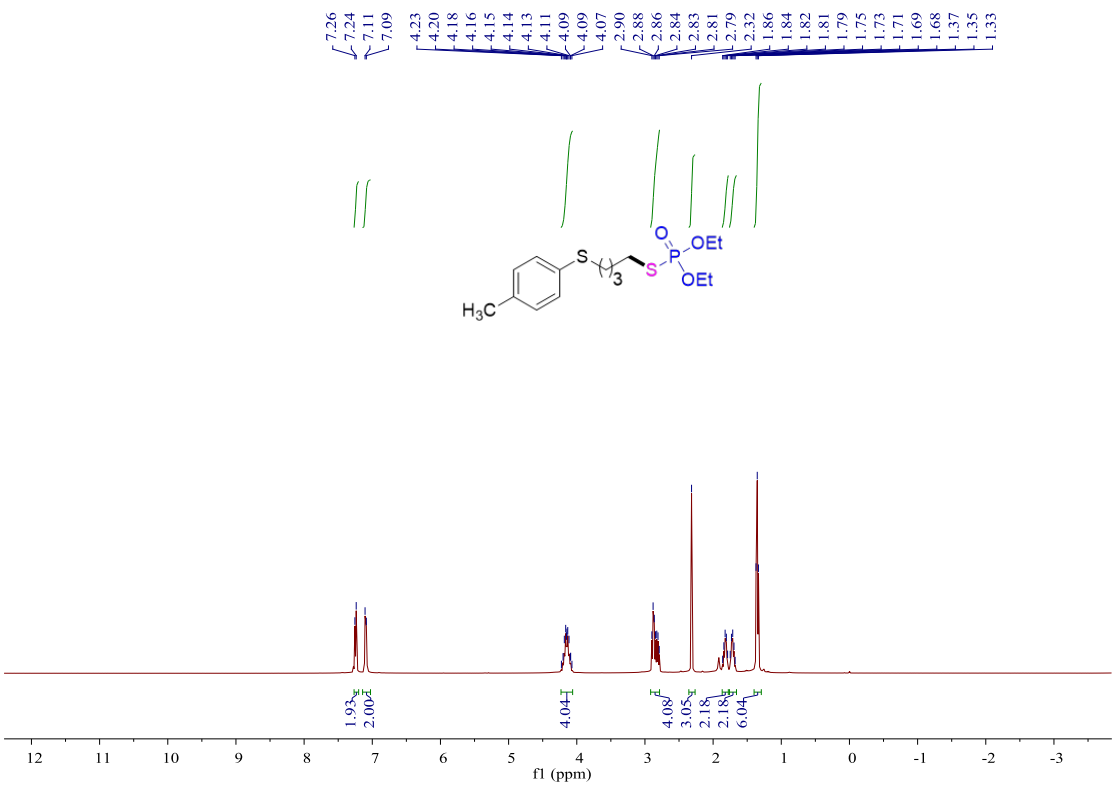
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5aa**



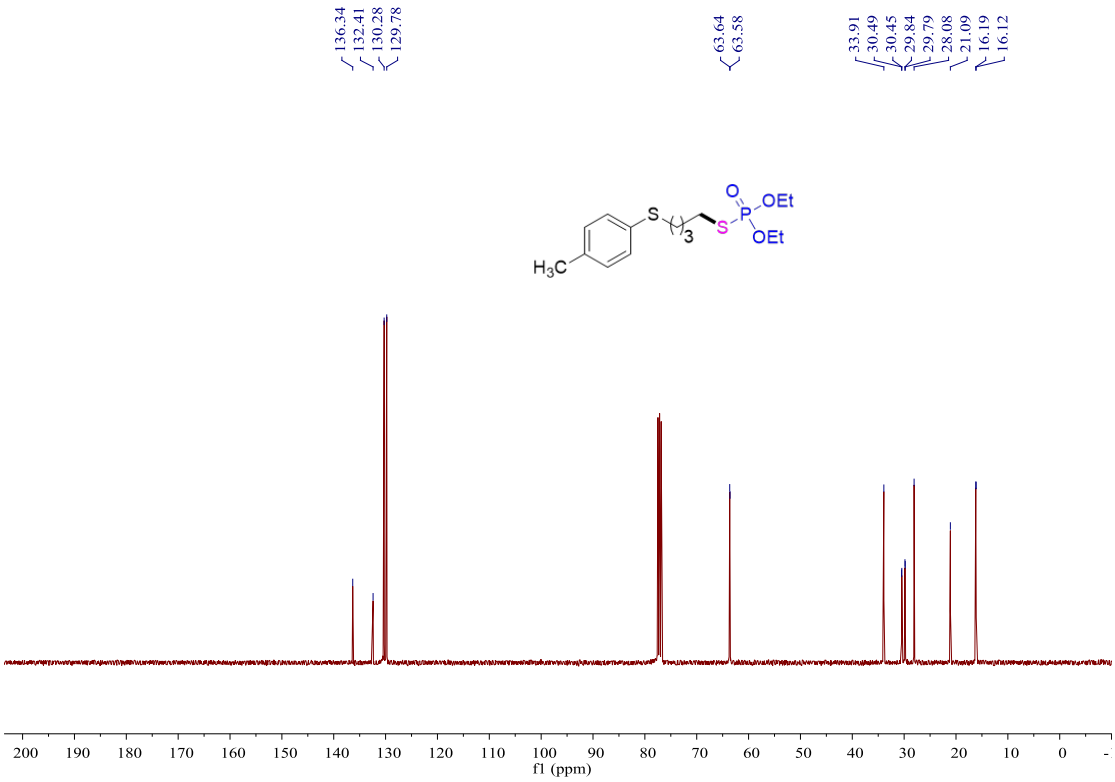
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5aa**



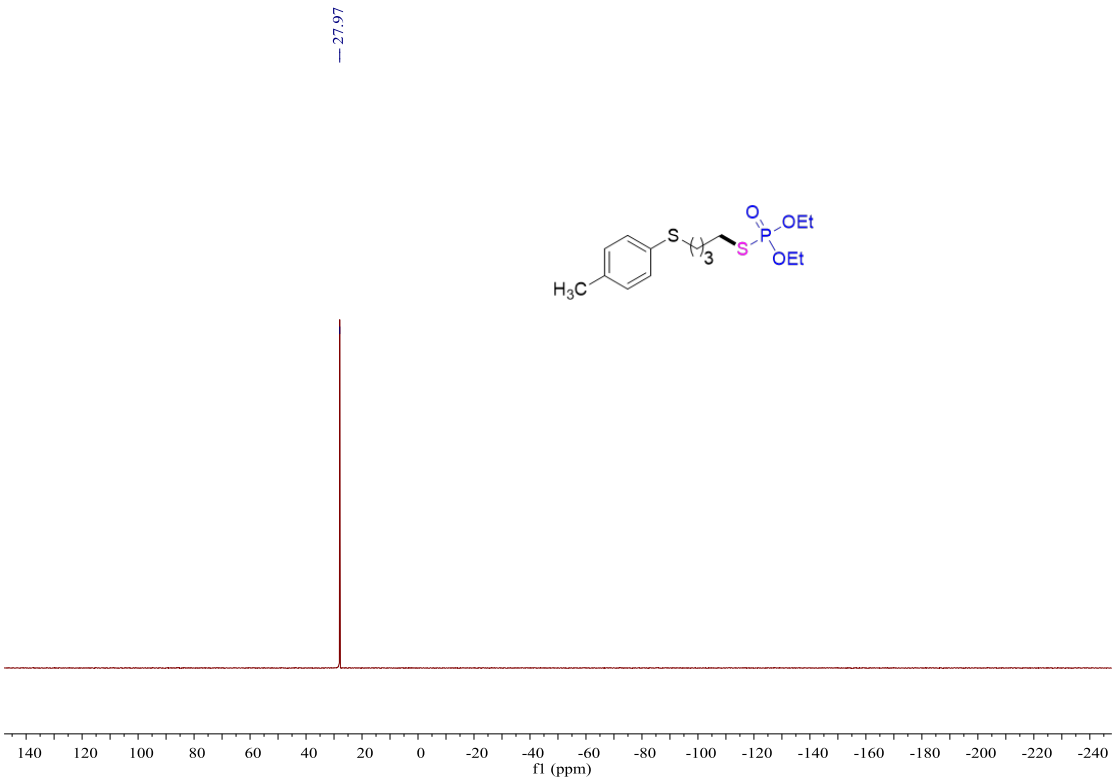
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5aa**



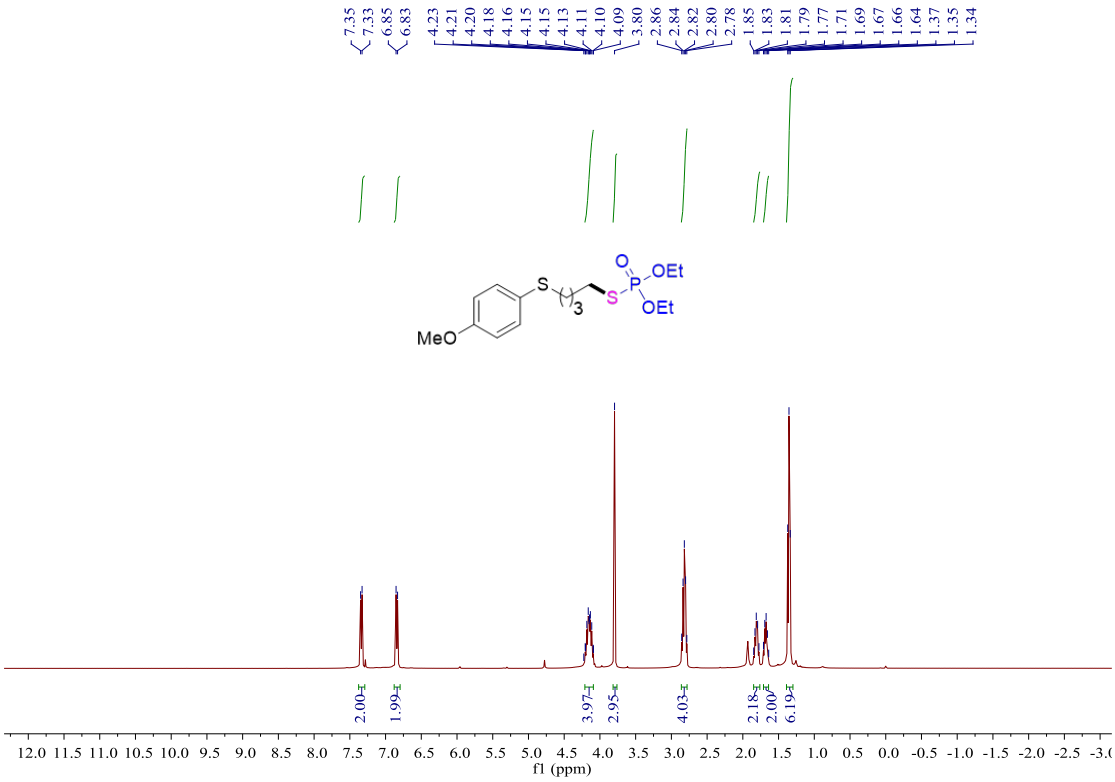
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ba**



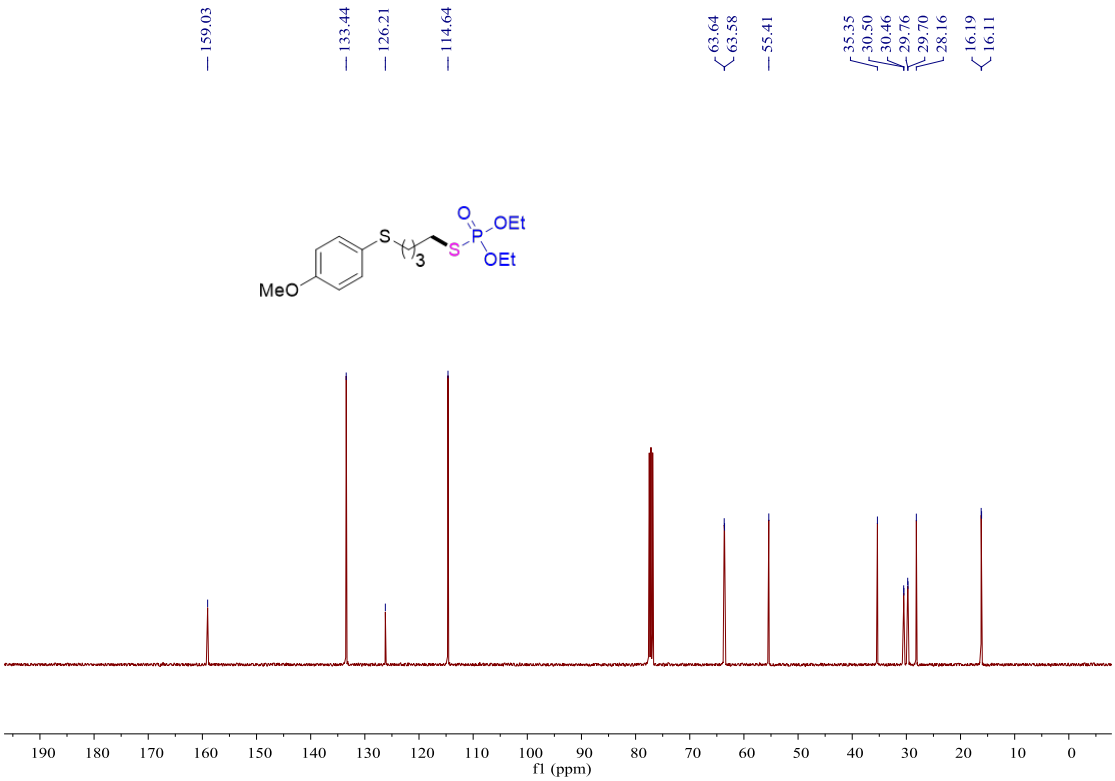
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ba**



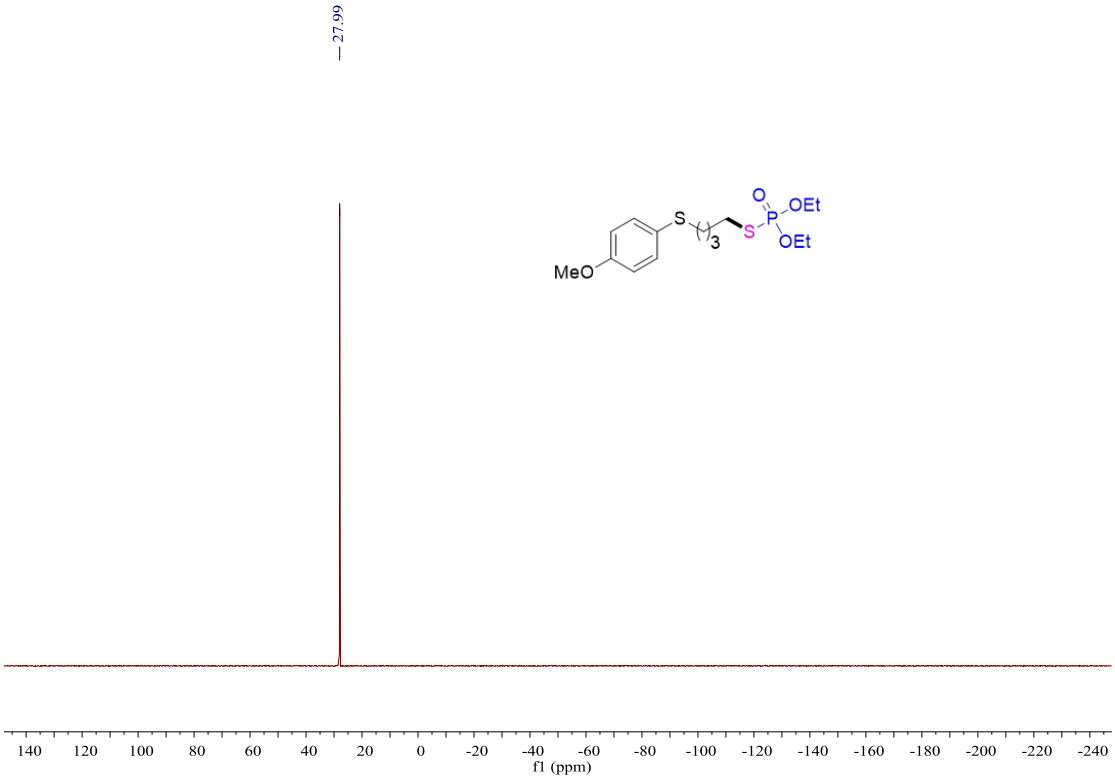
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ba**



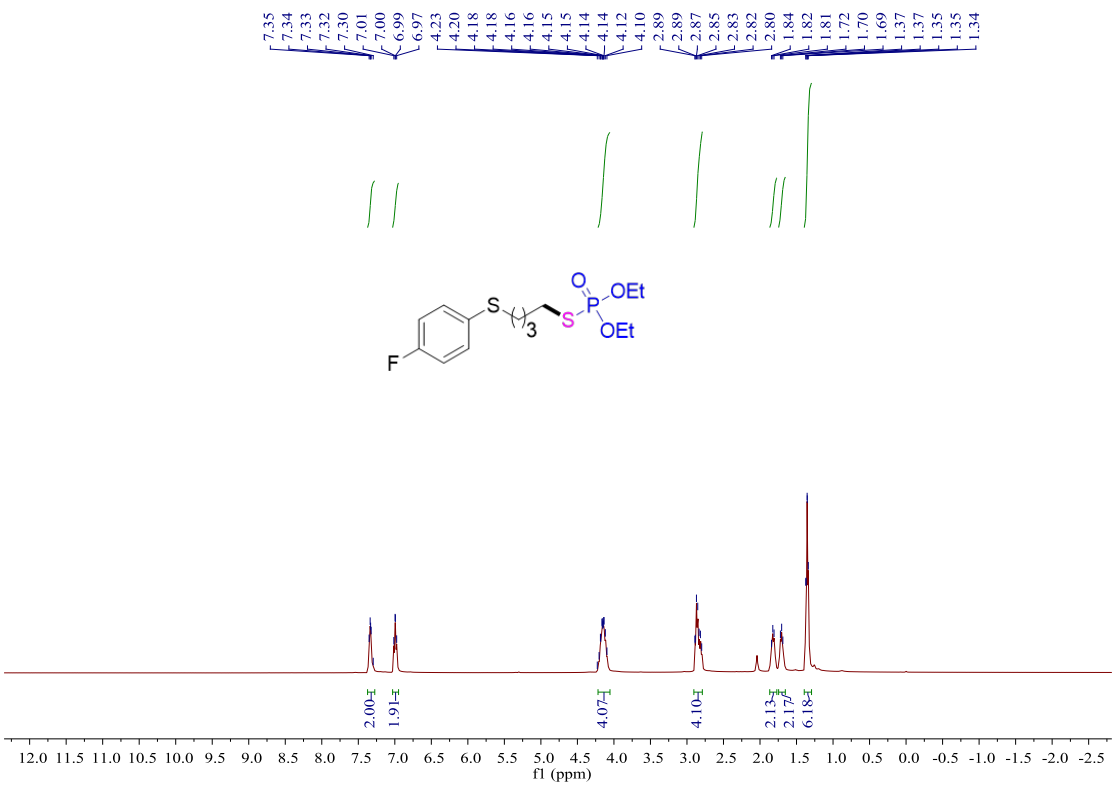
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ca**



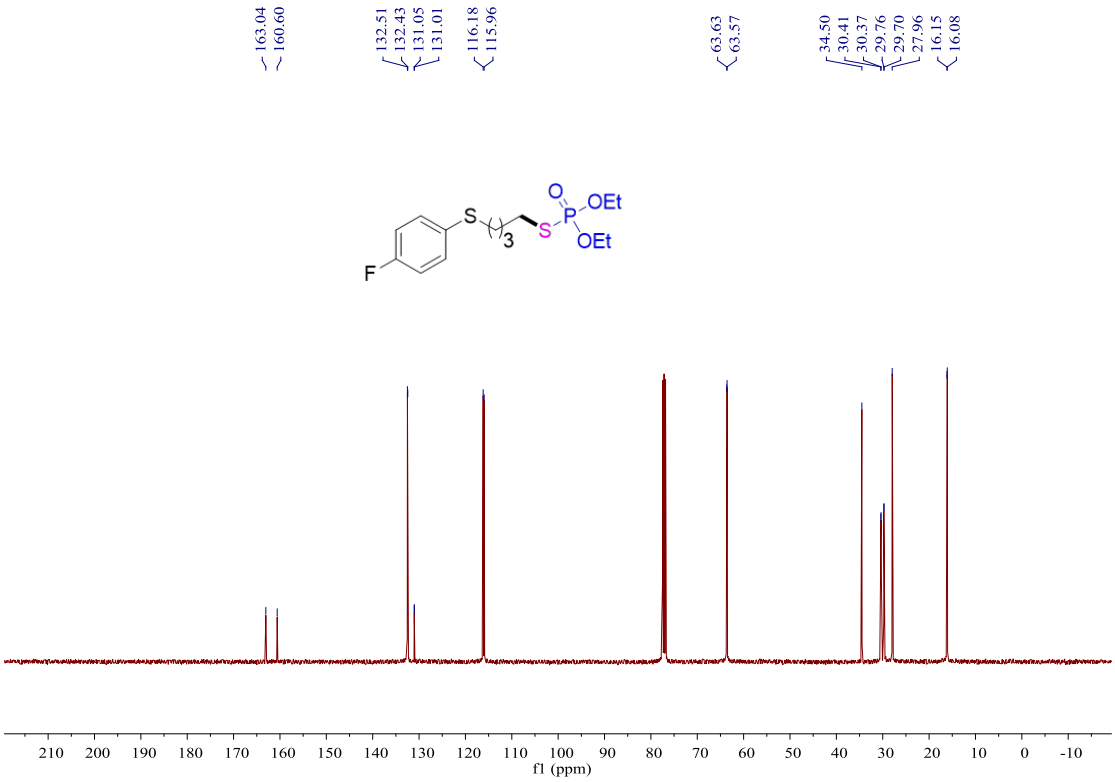
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ca**



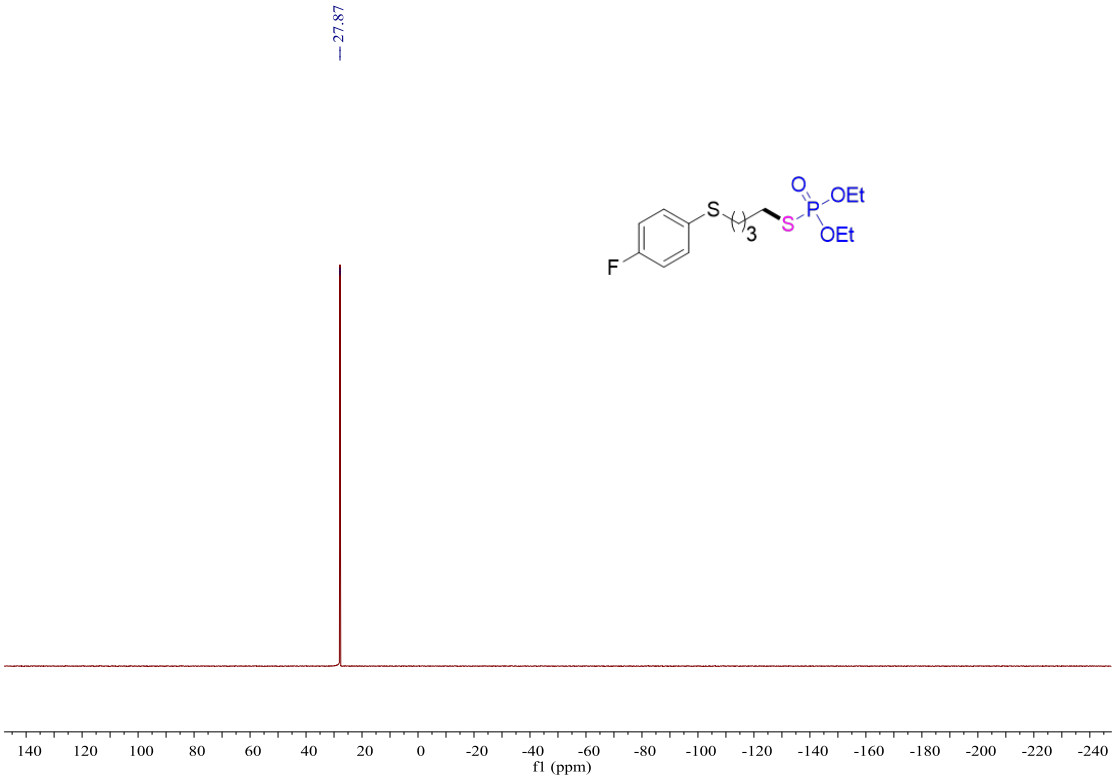
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ca**



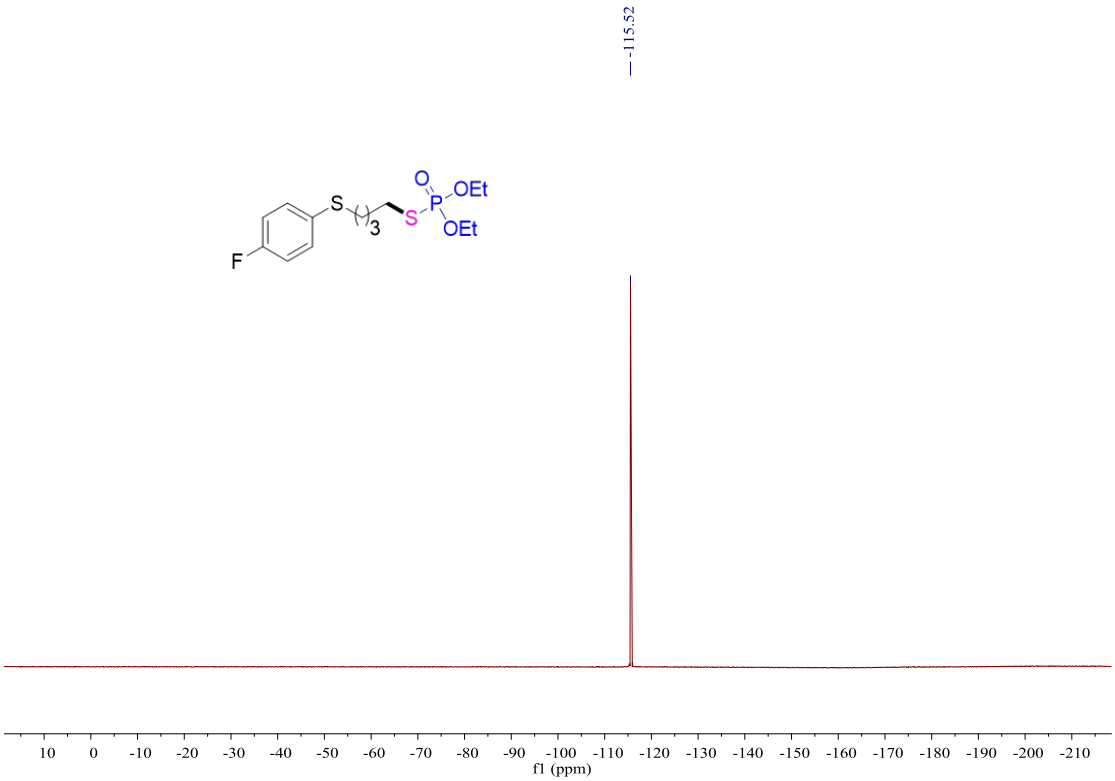
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5da**



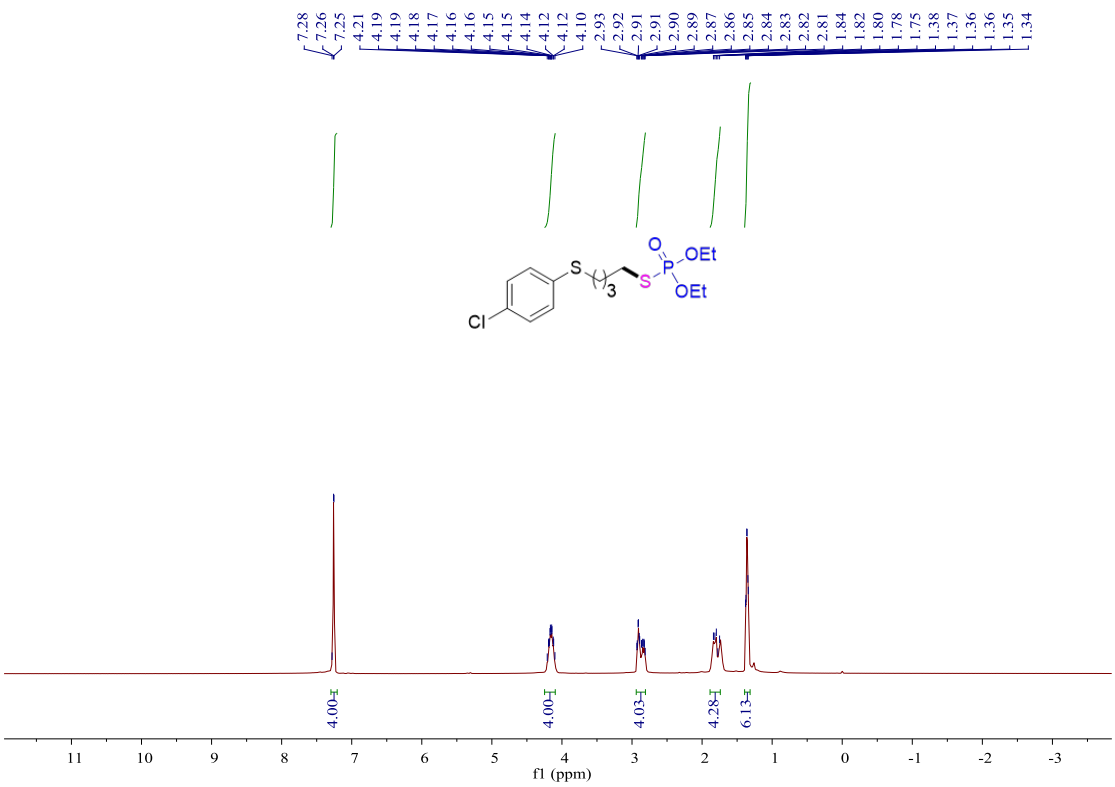
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5da**



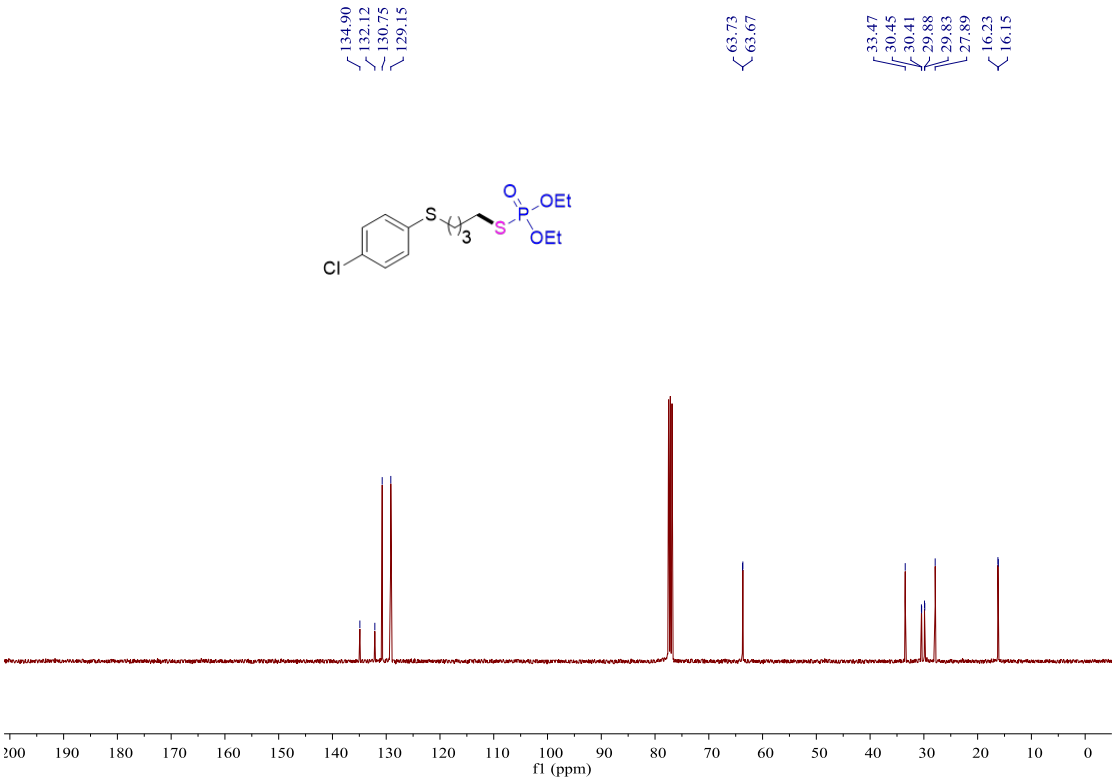
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5da**



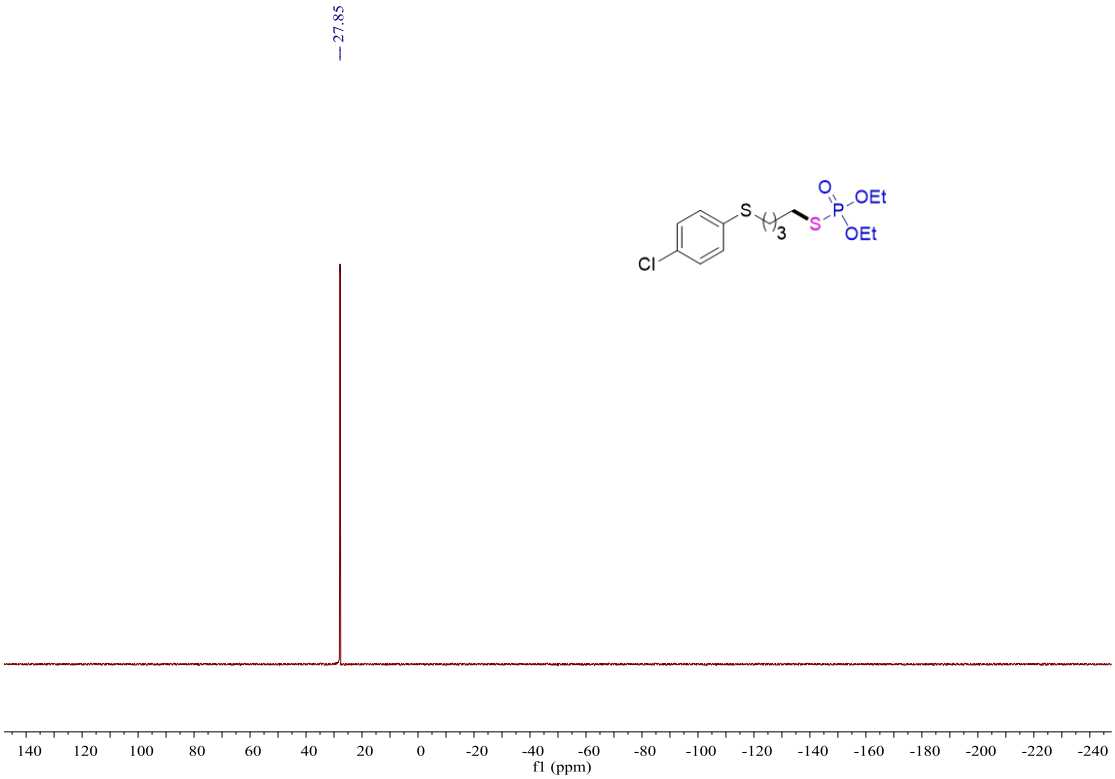
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **5da**



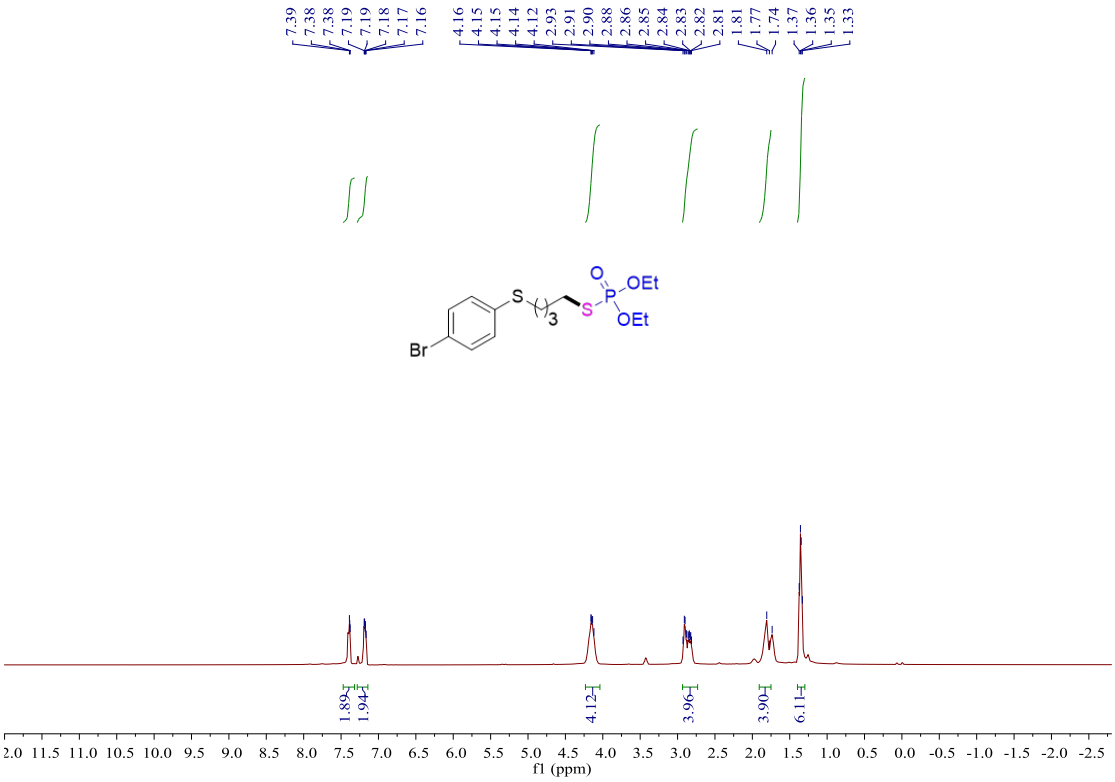
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ea**



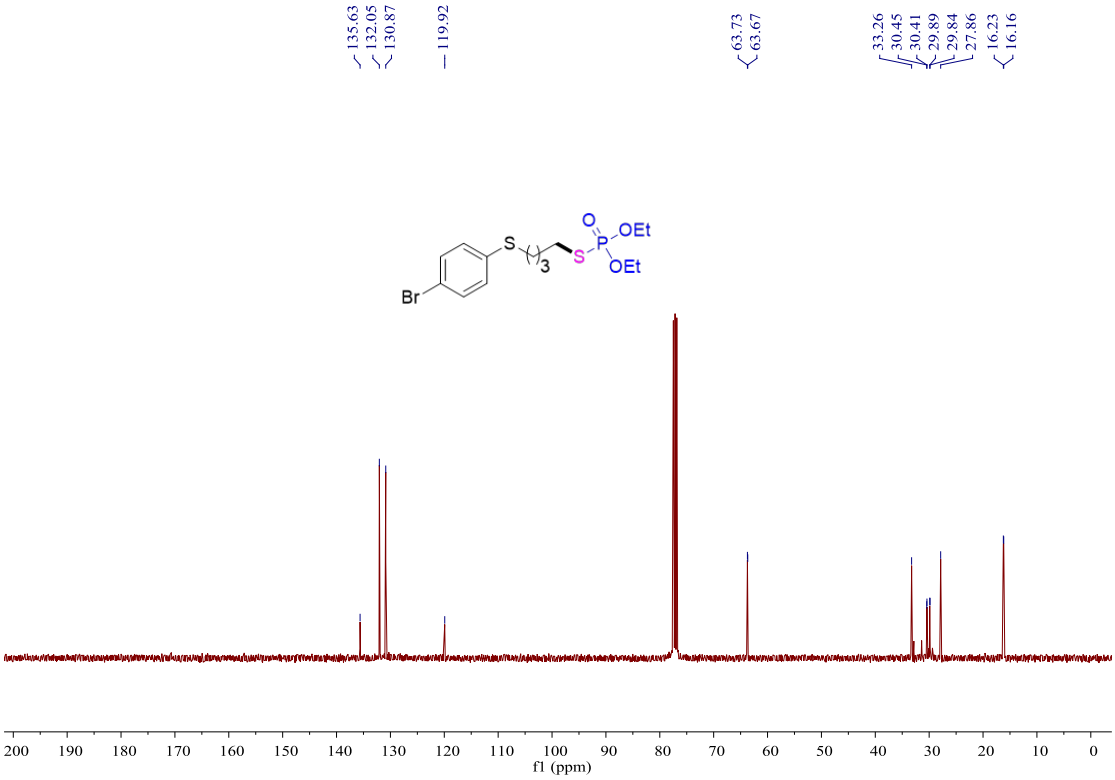
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ea**



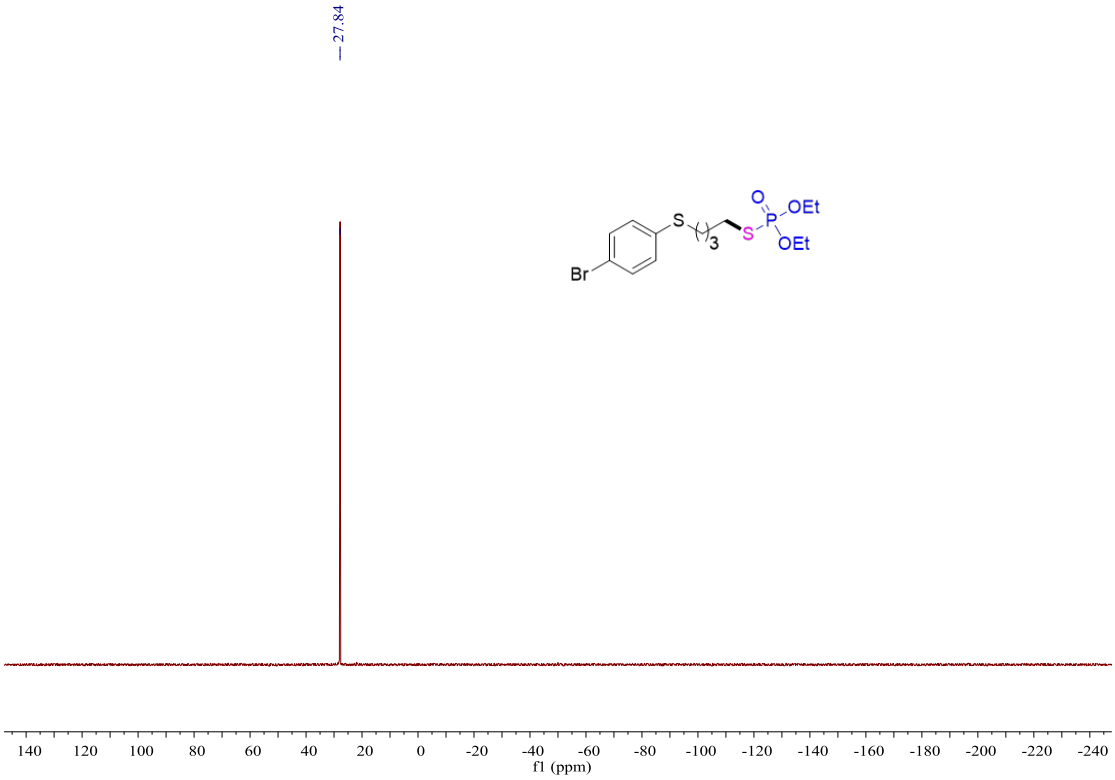
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ea**



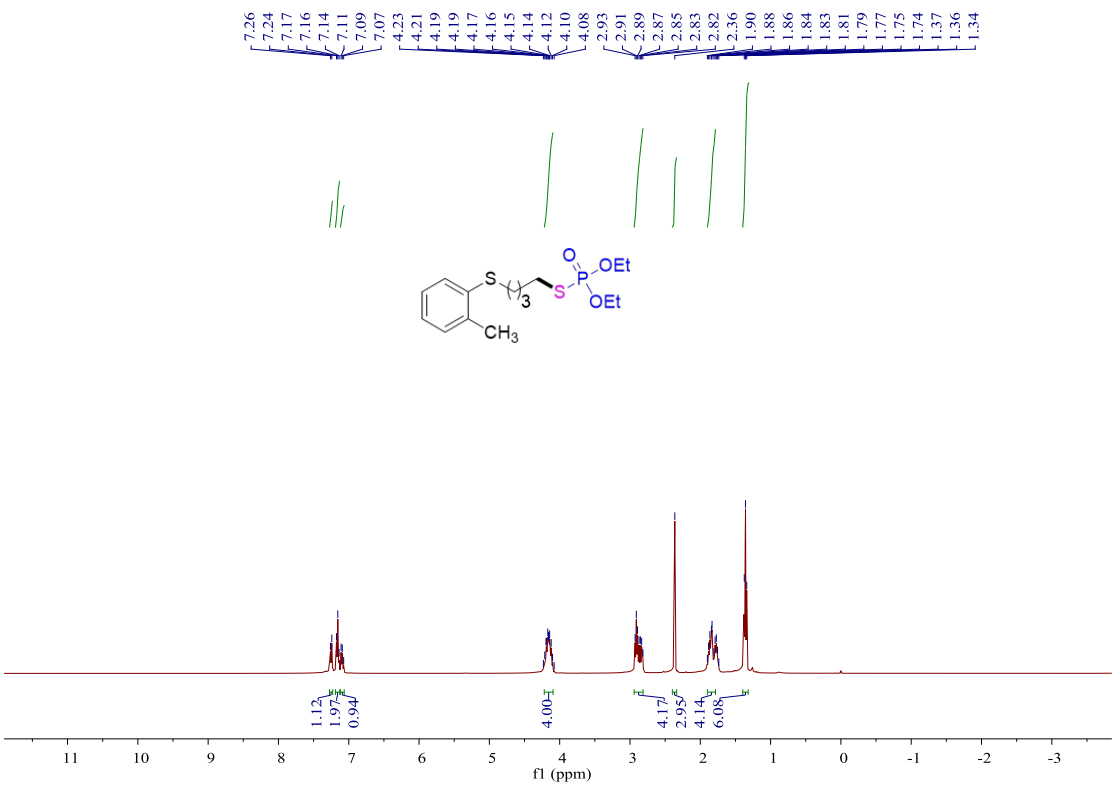
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5fa**



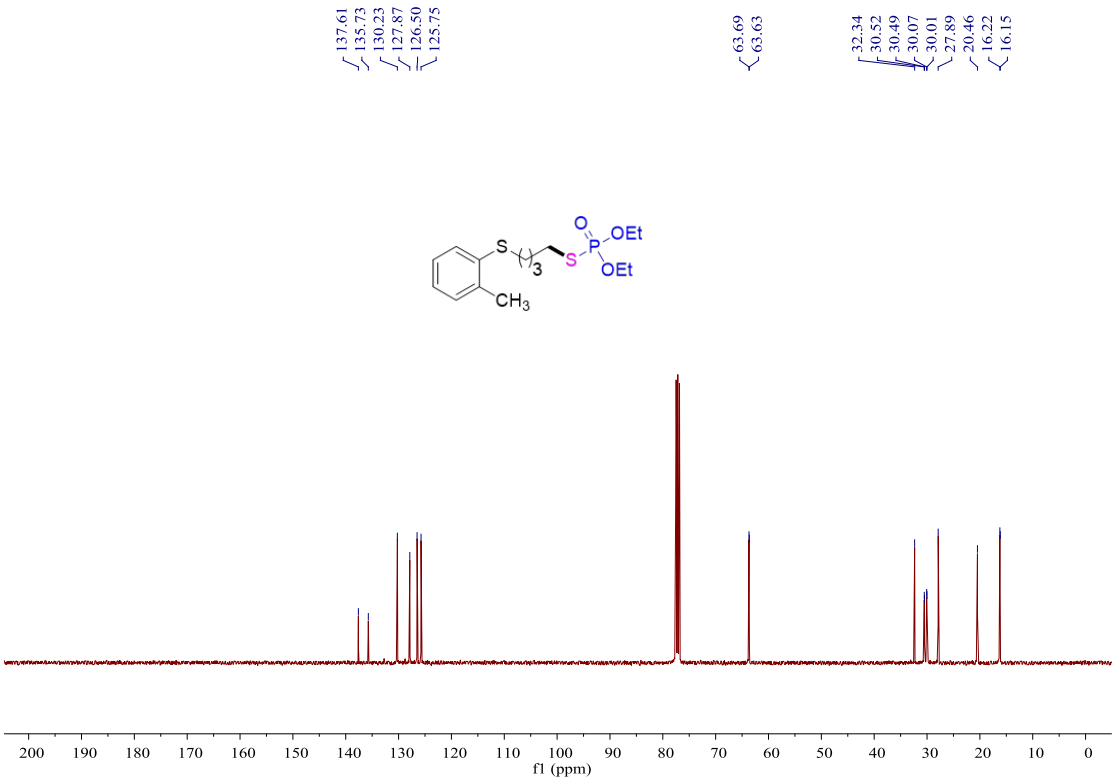
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5fa**



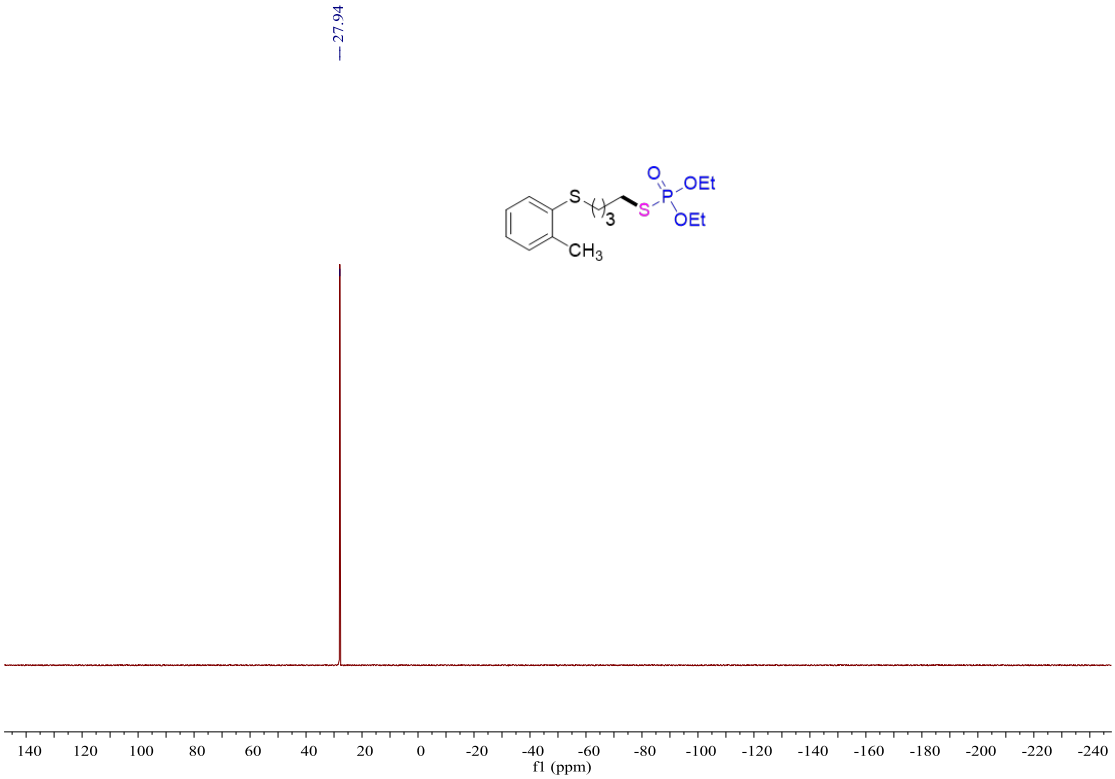
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5fa**



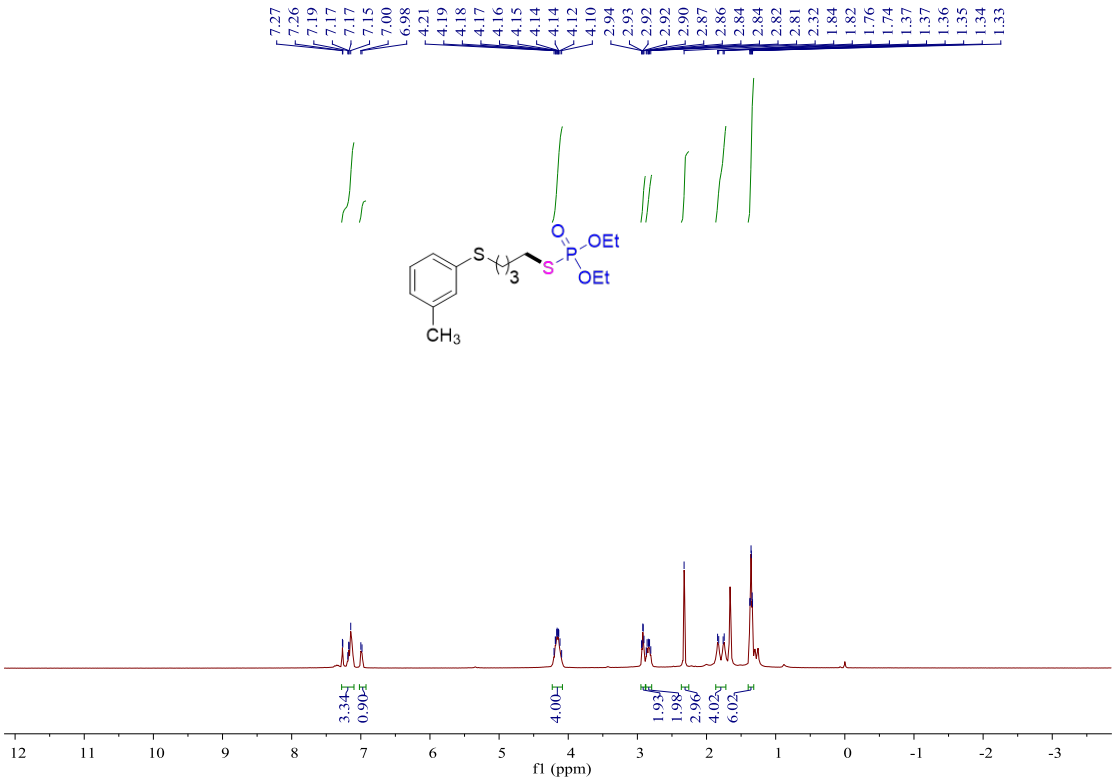
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ga**



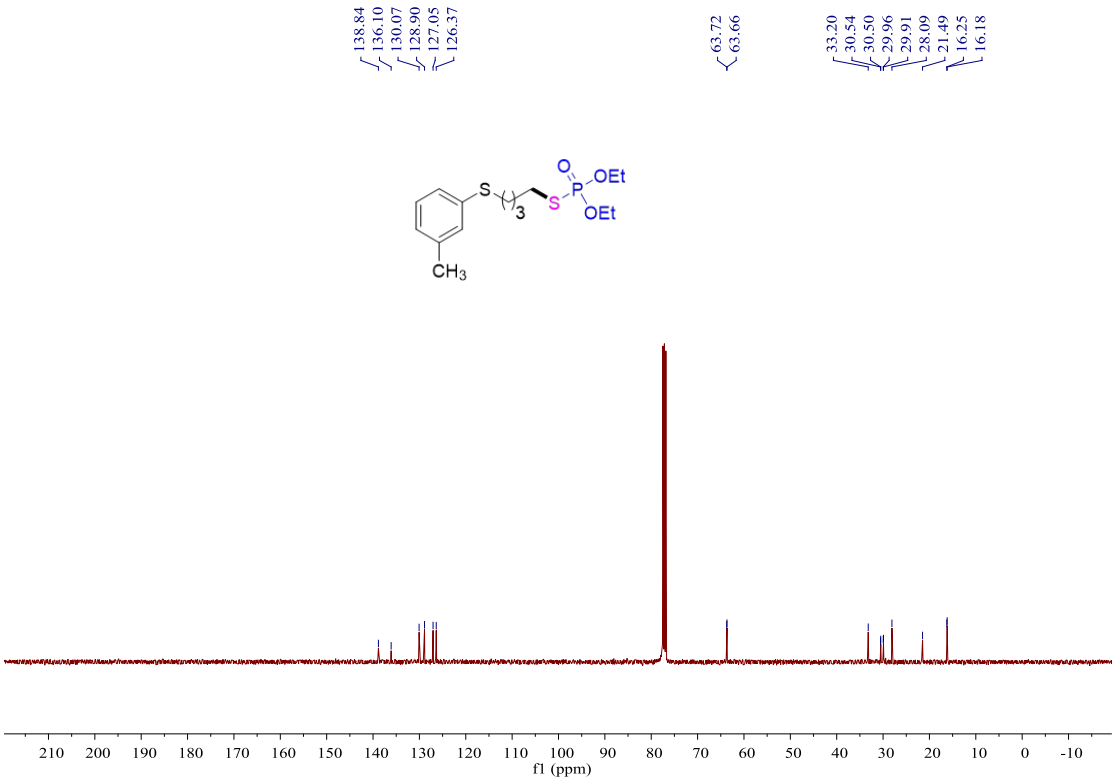
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ga**



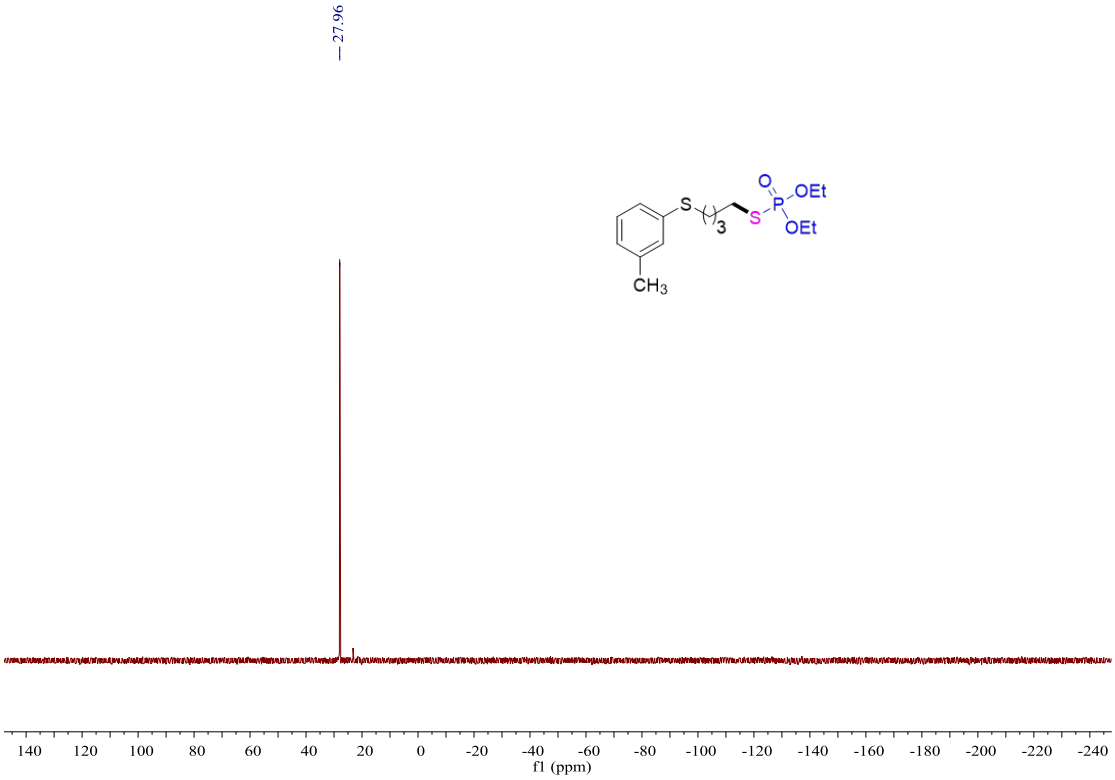
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ga**



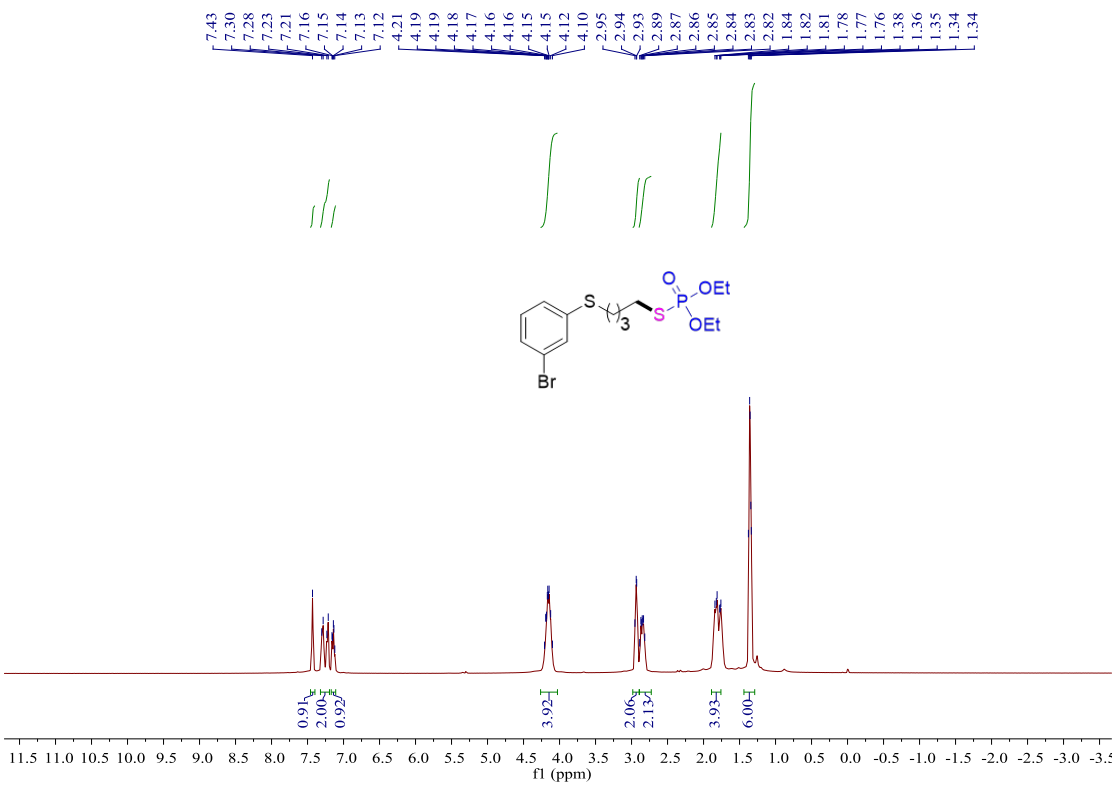
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ha**



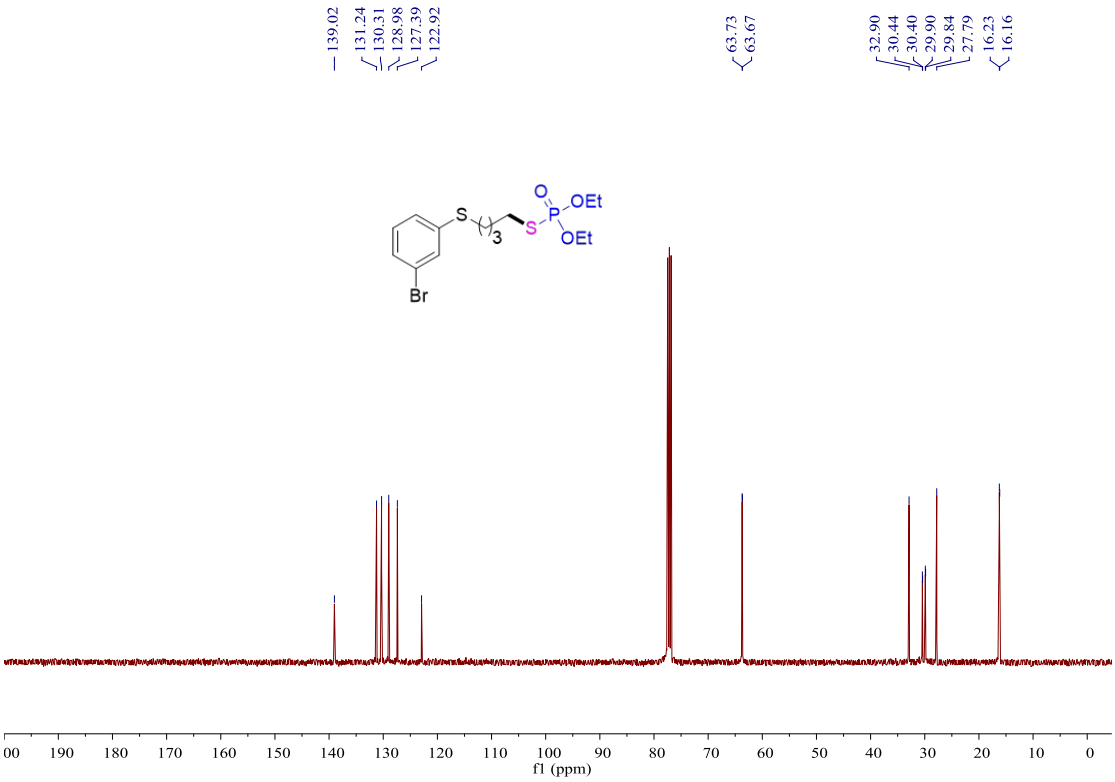
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ha**



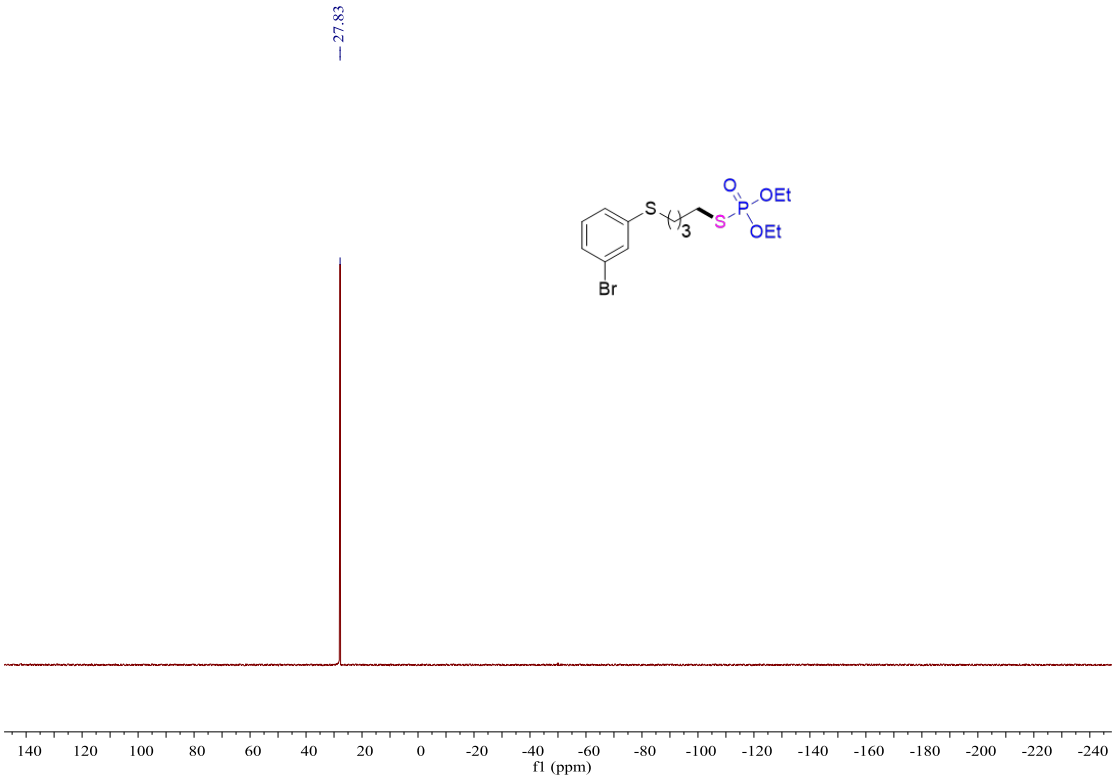
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ha**



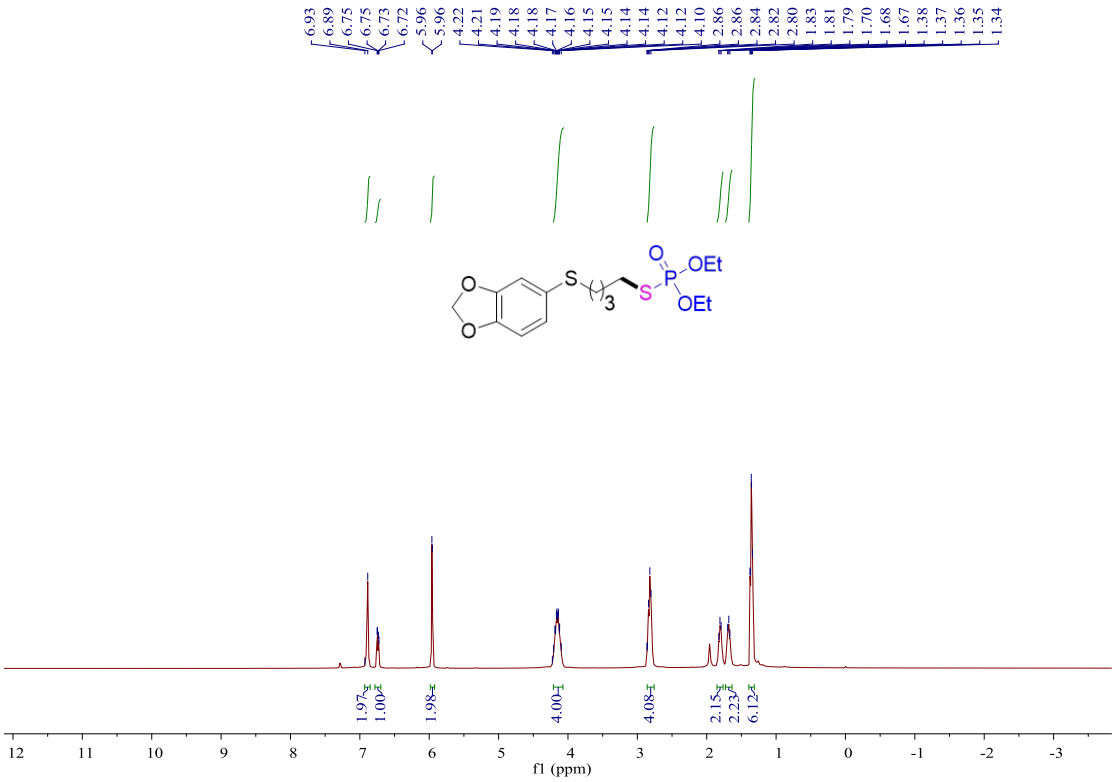
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ia**



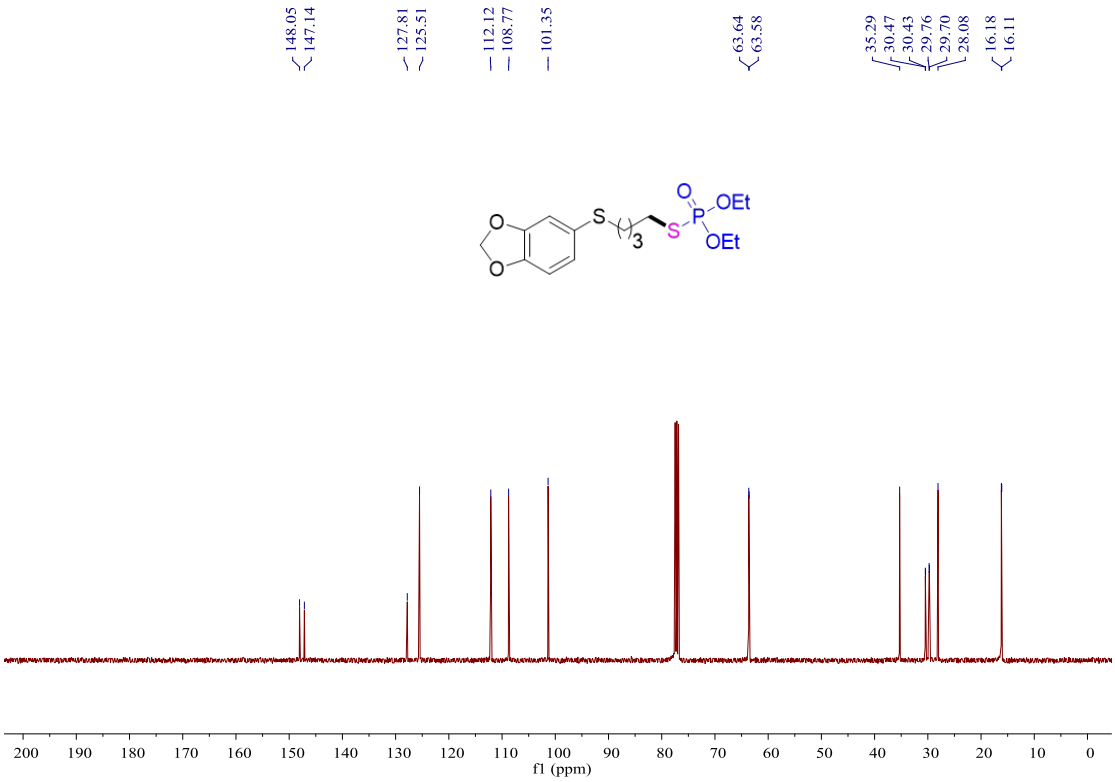
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ia**



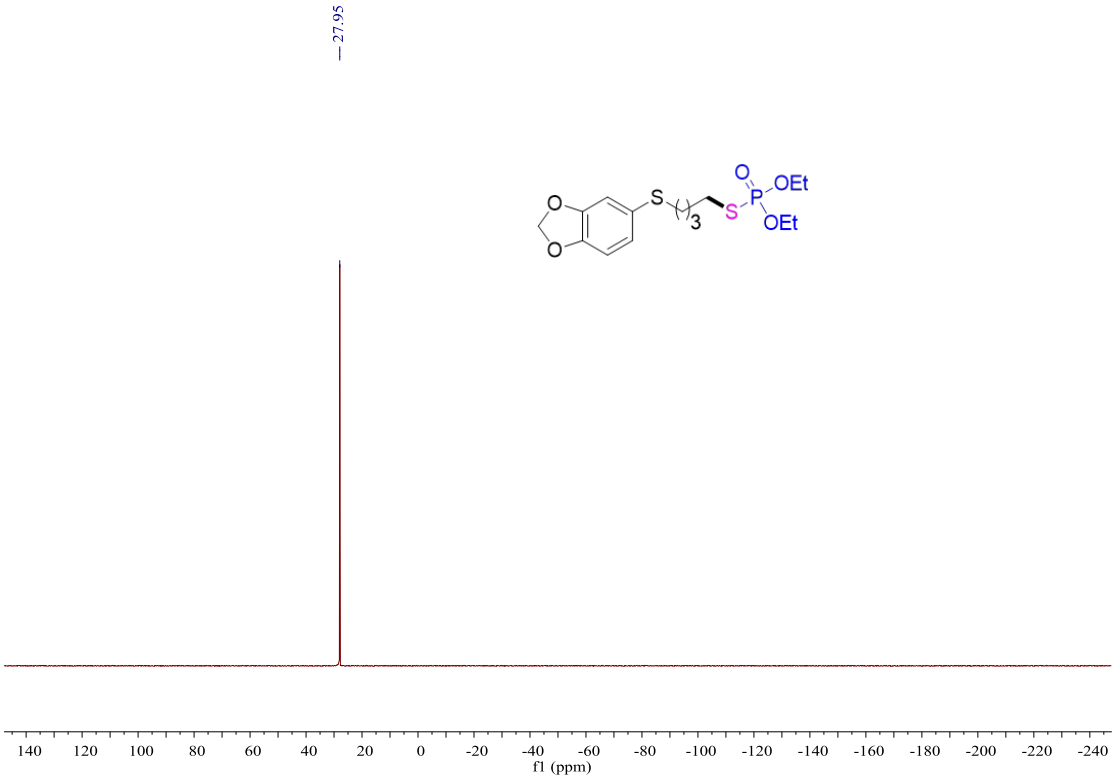
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ia**



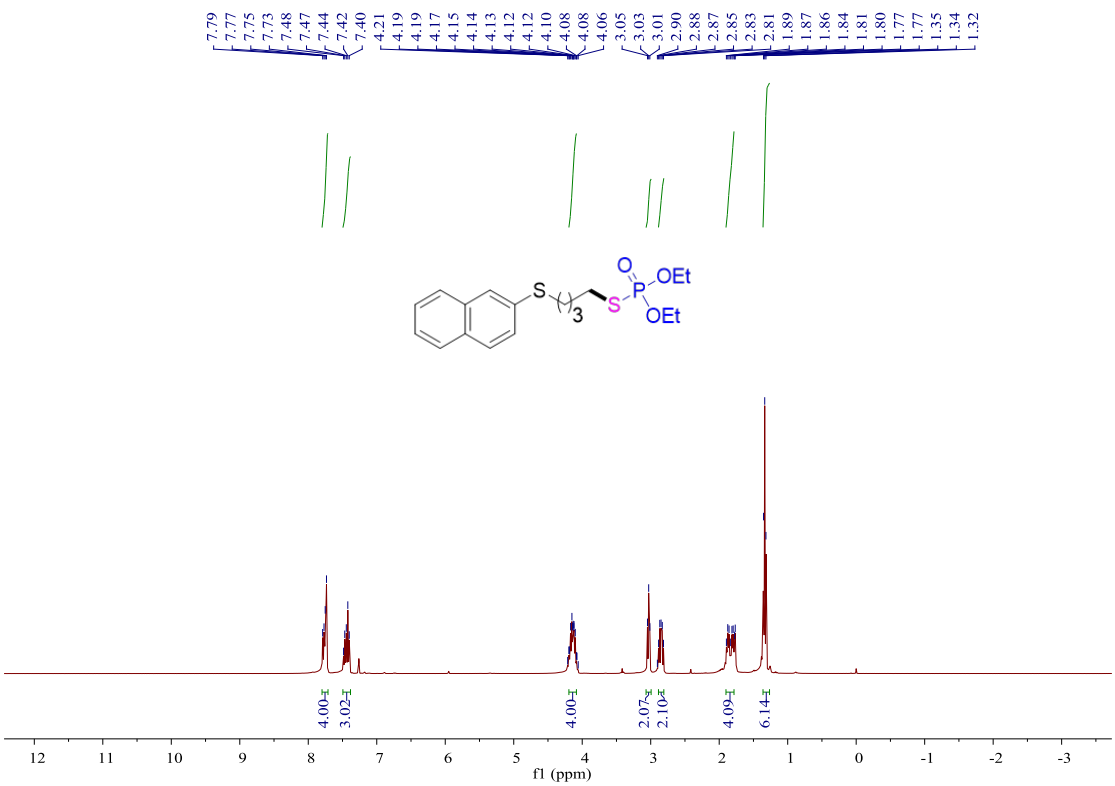
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ja**



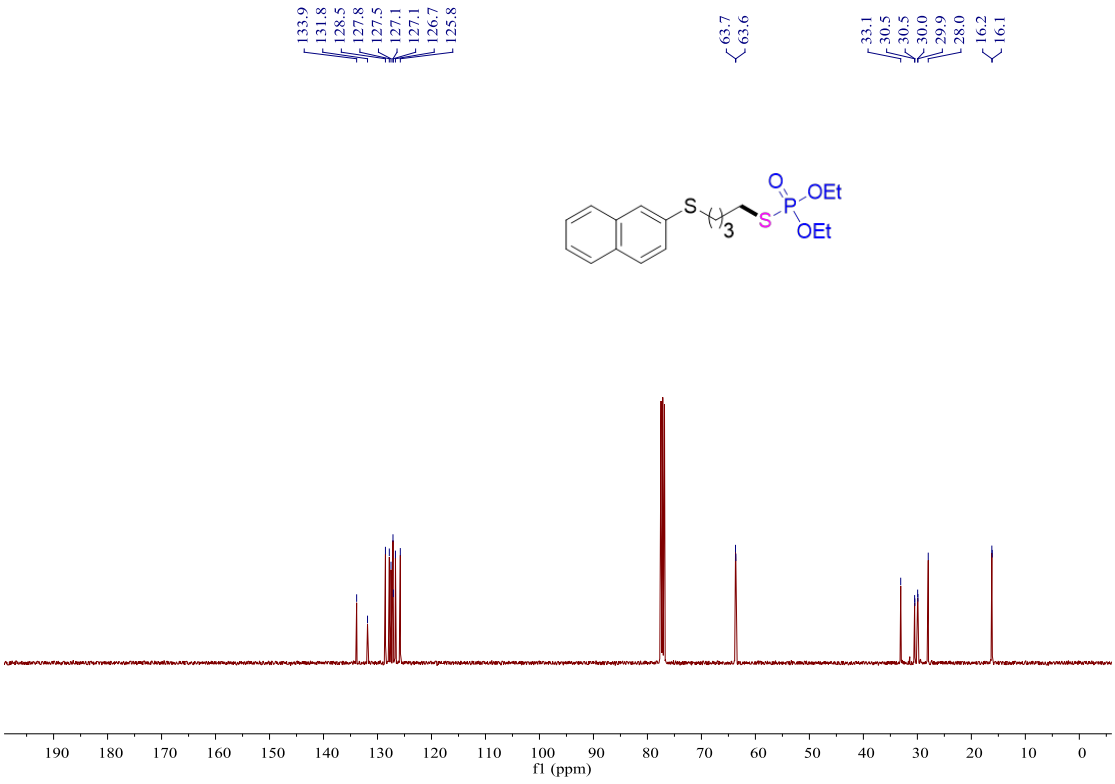
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ja**



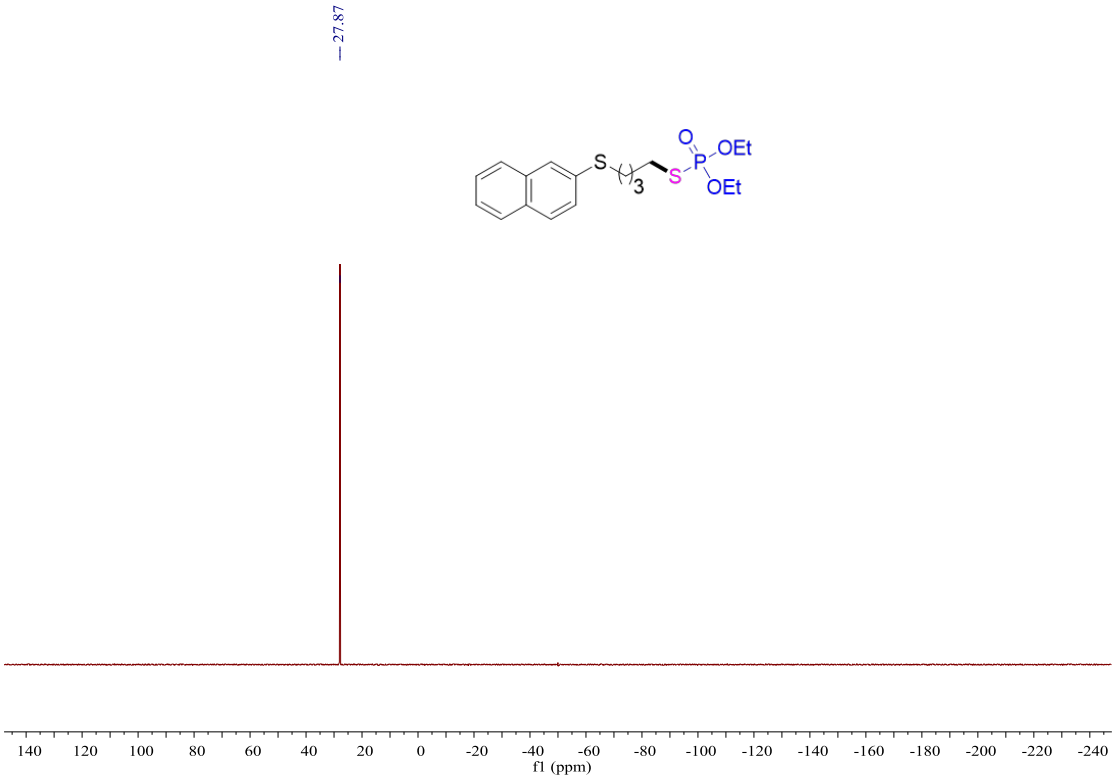
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ja**



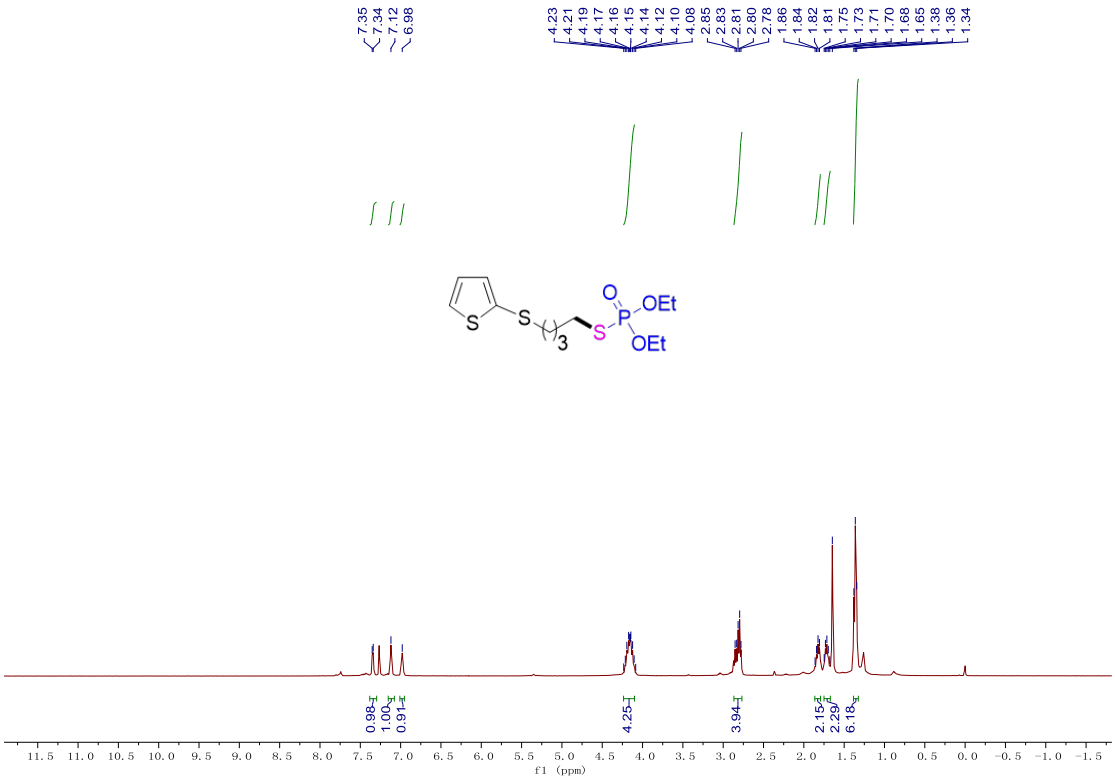
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ka**



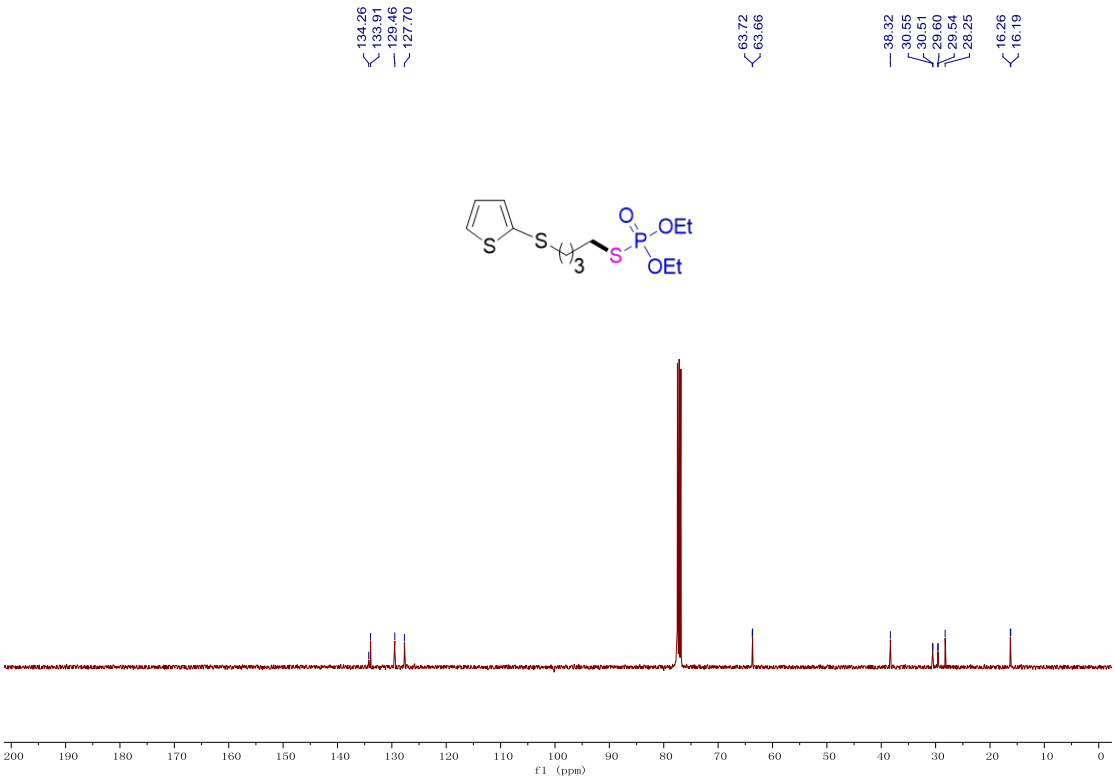
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ka**



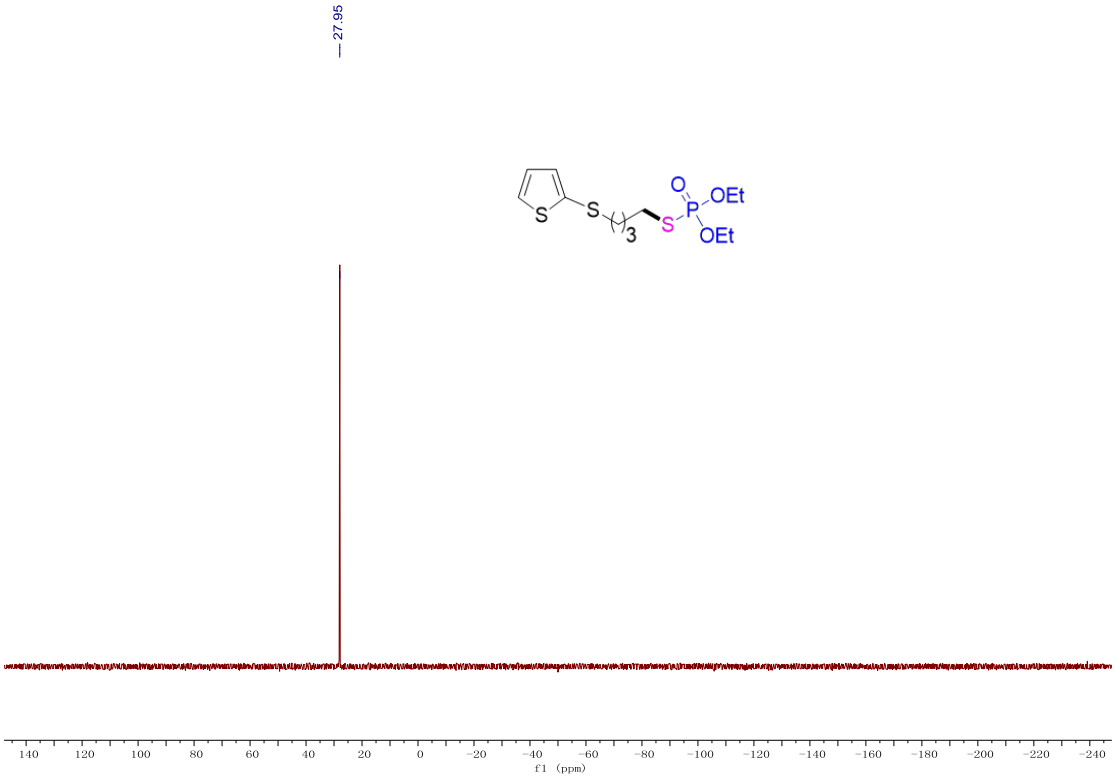
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ka**



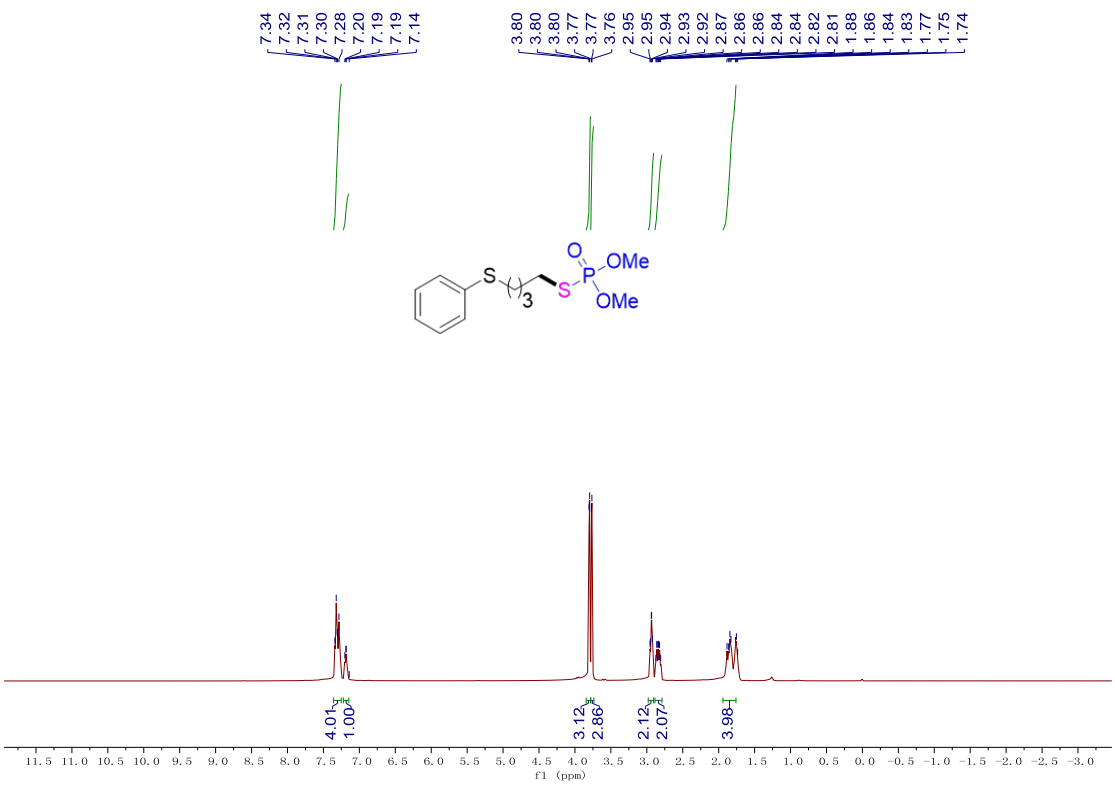
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5la**



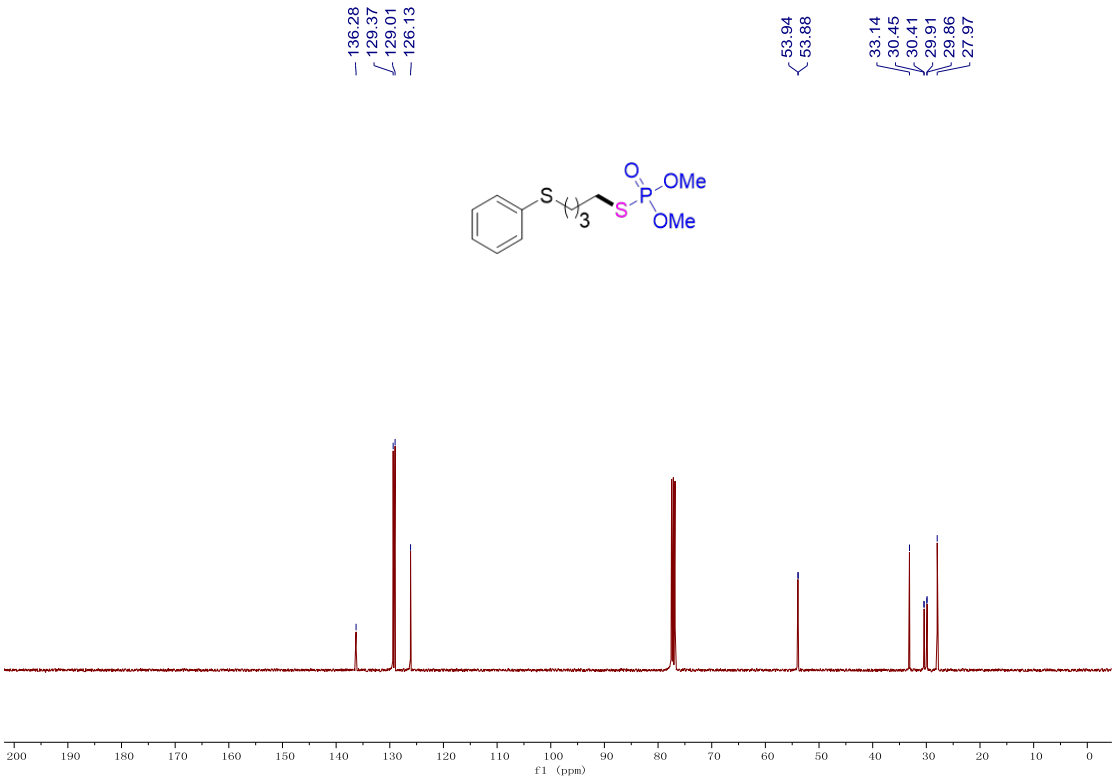
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5la**



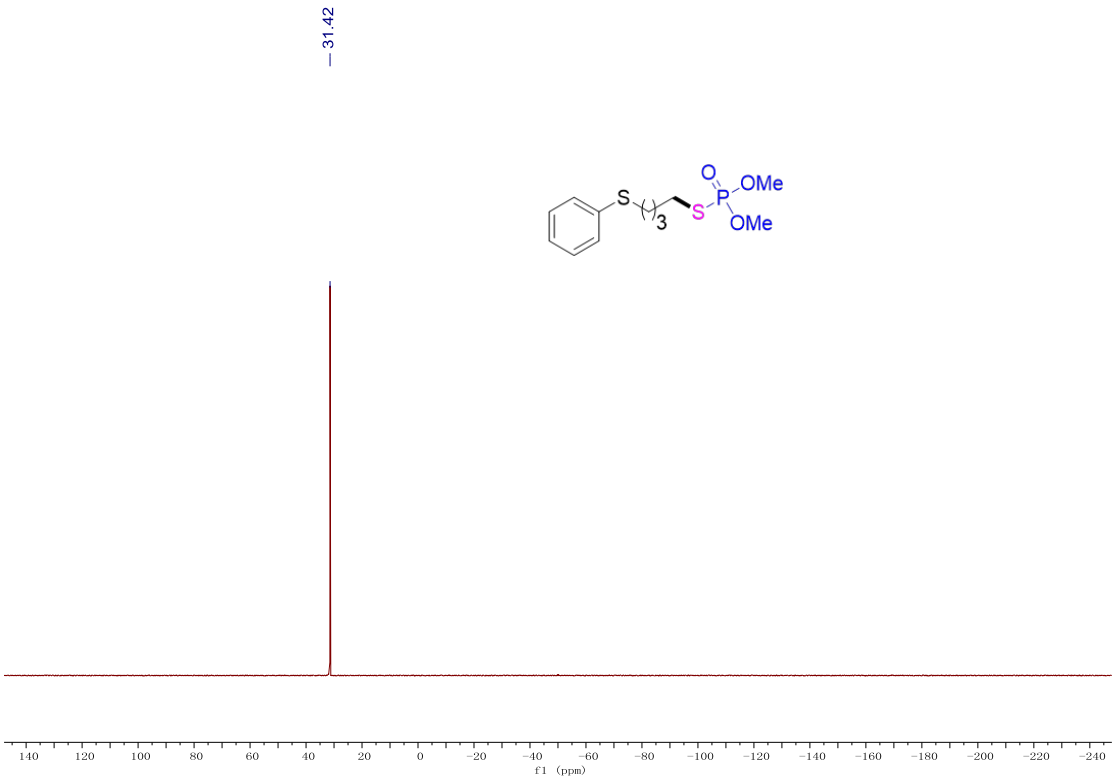
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5la**



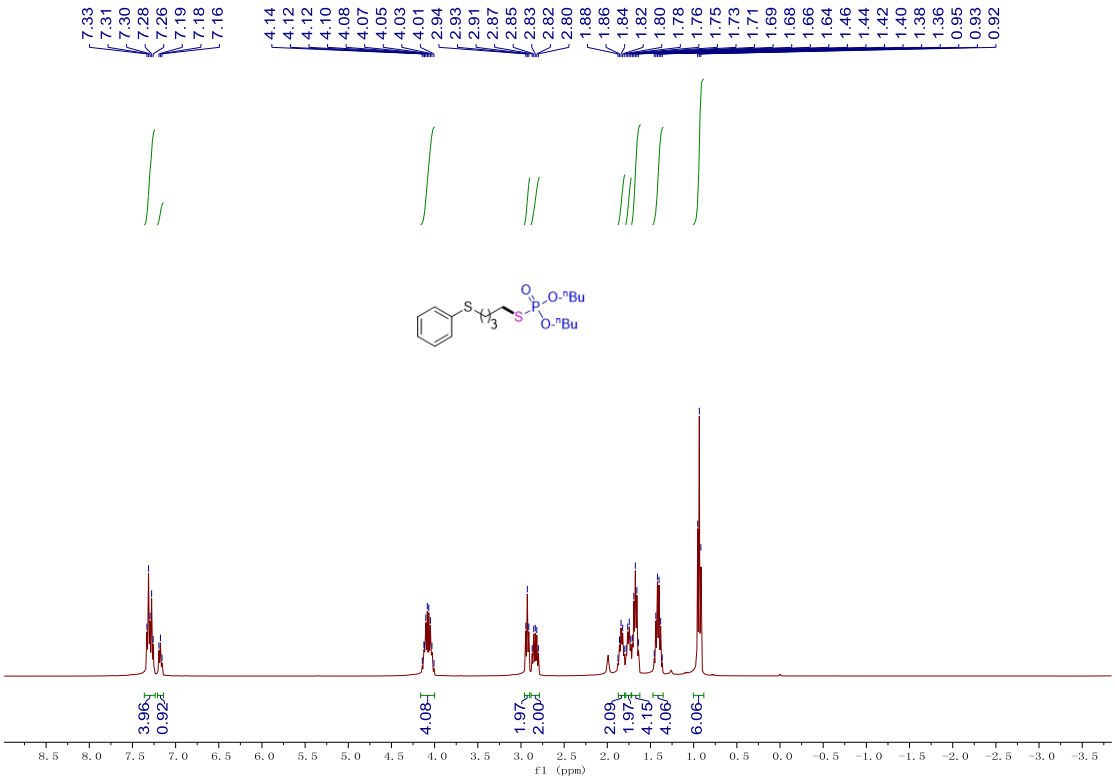
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ab**



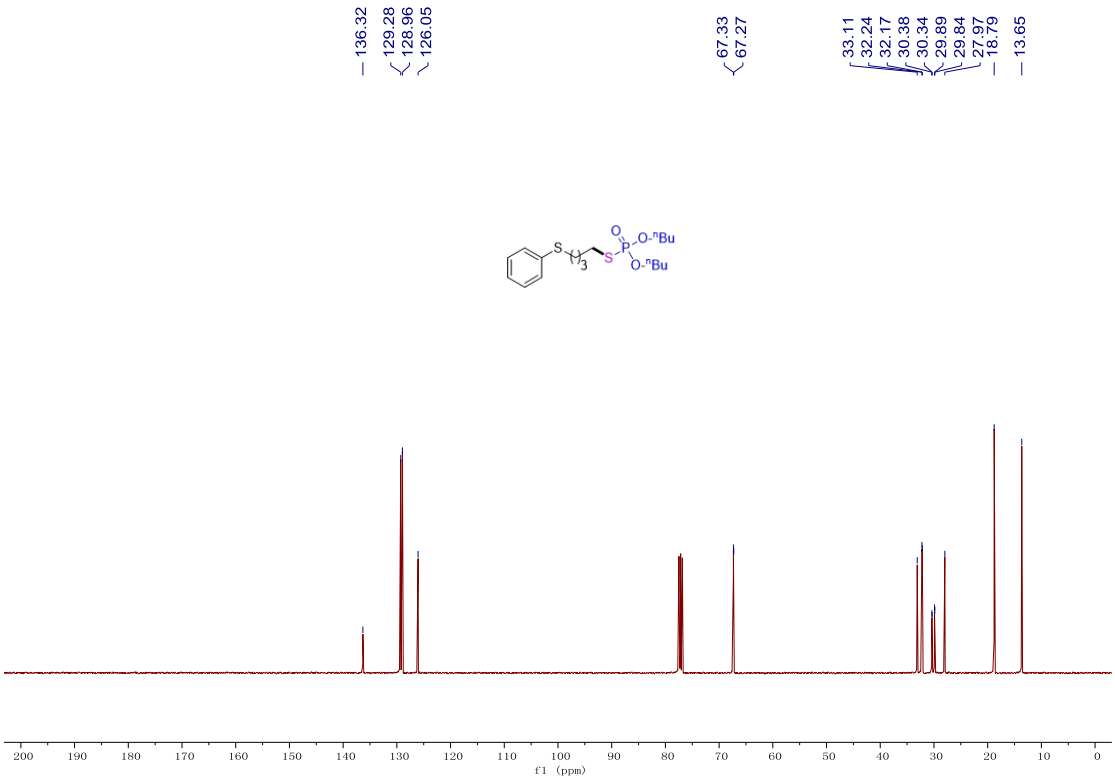
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ab**



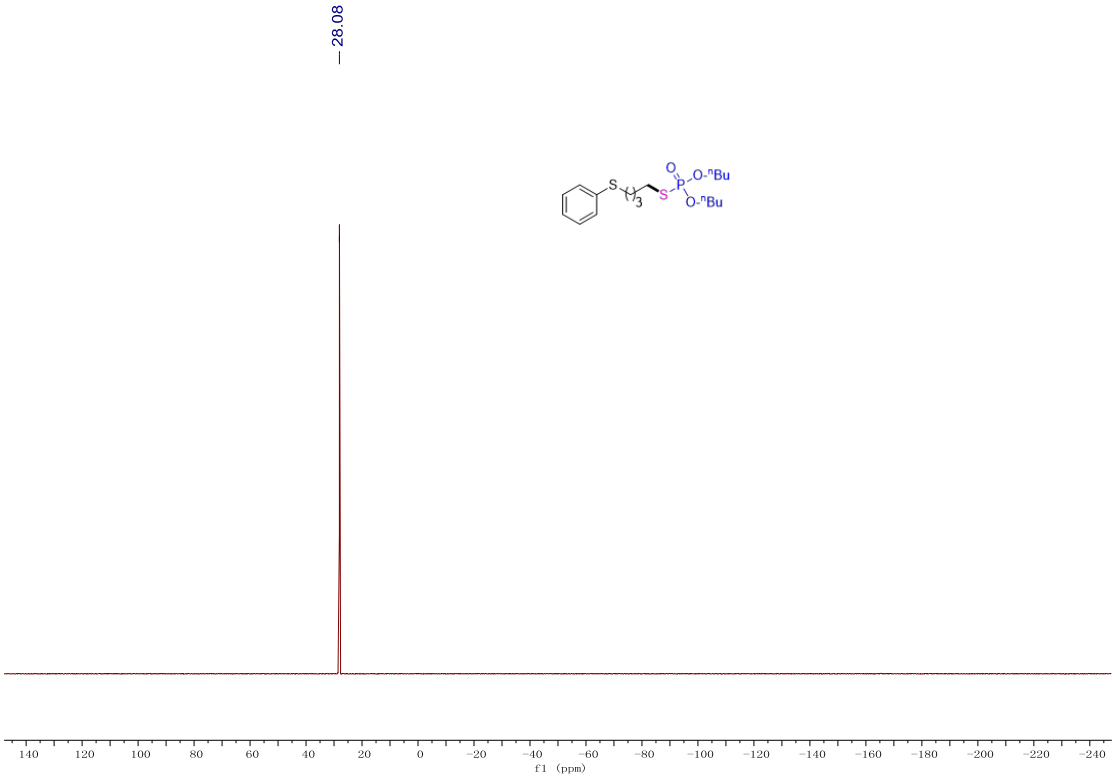
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ab**



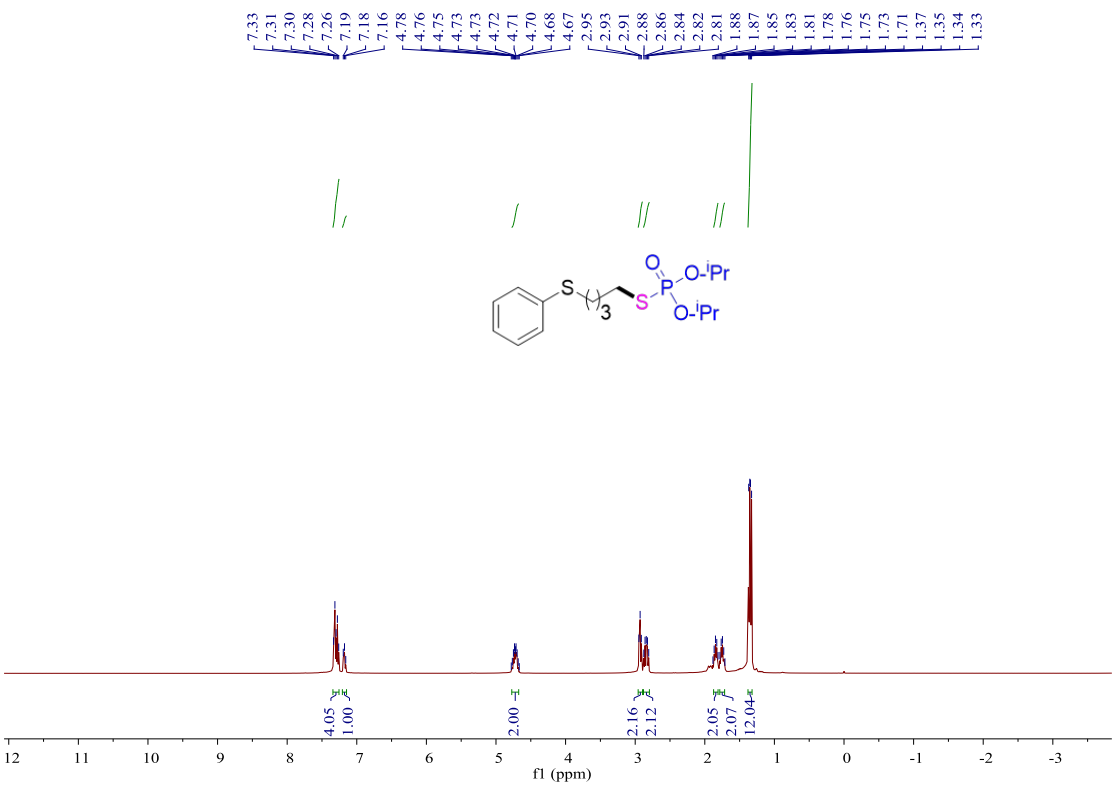
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ac**



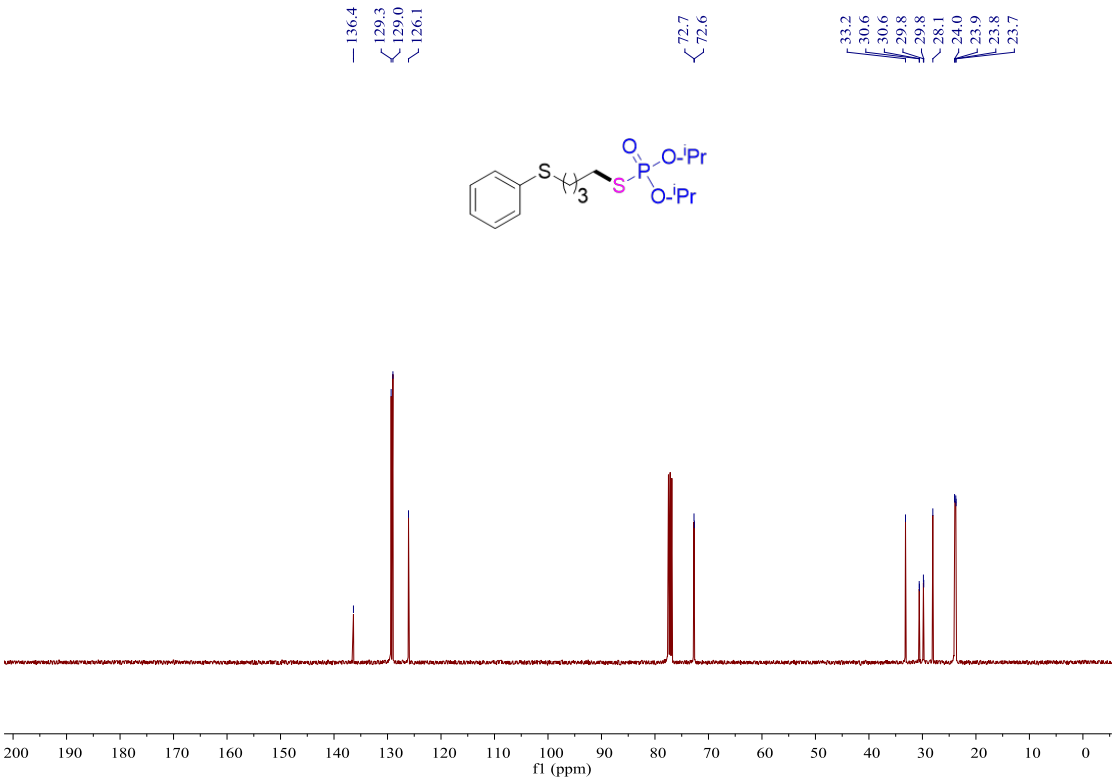
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ac**



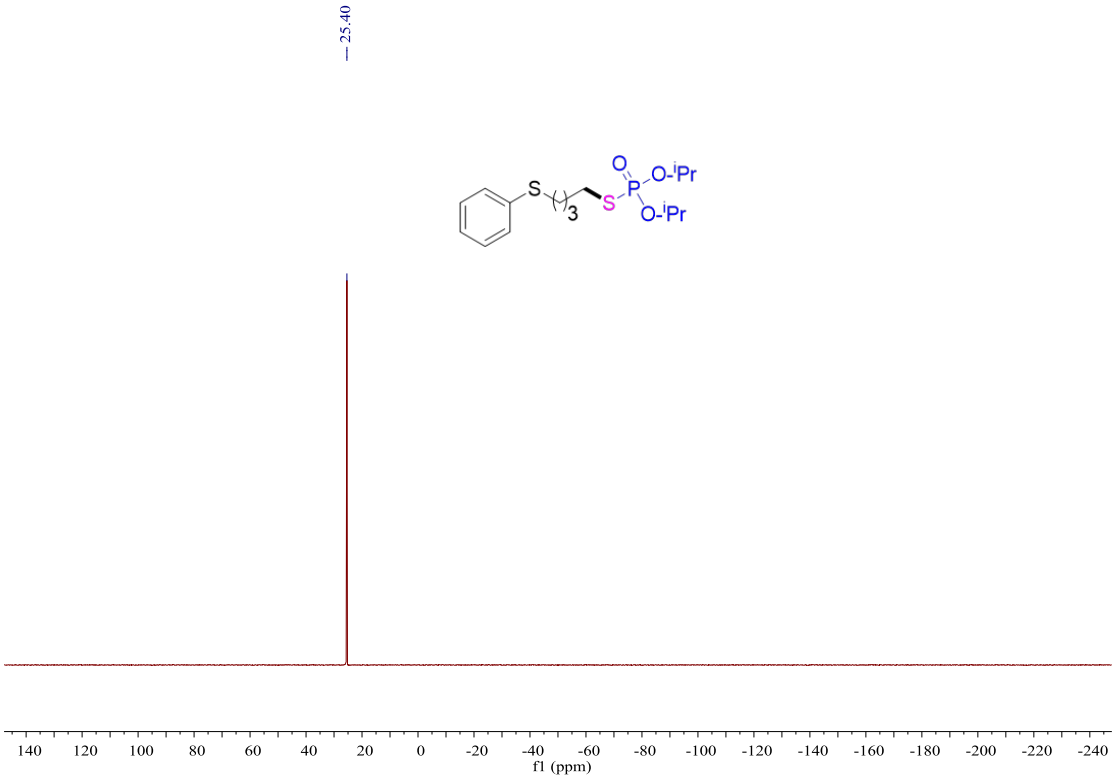
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ac**



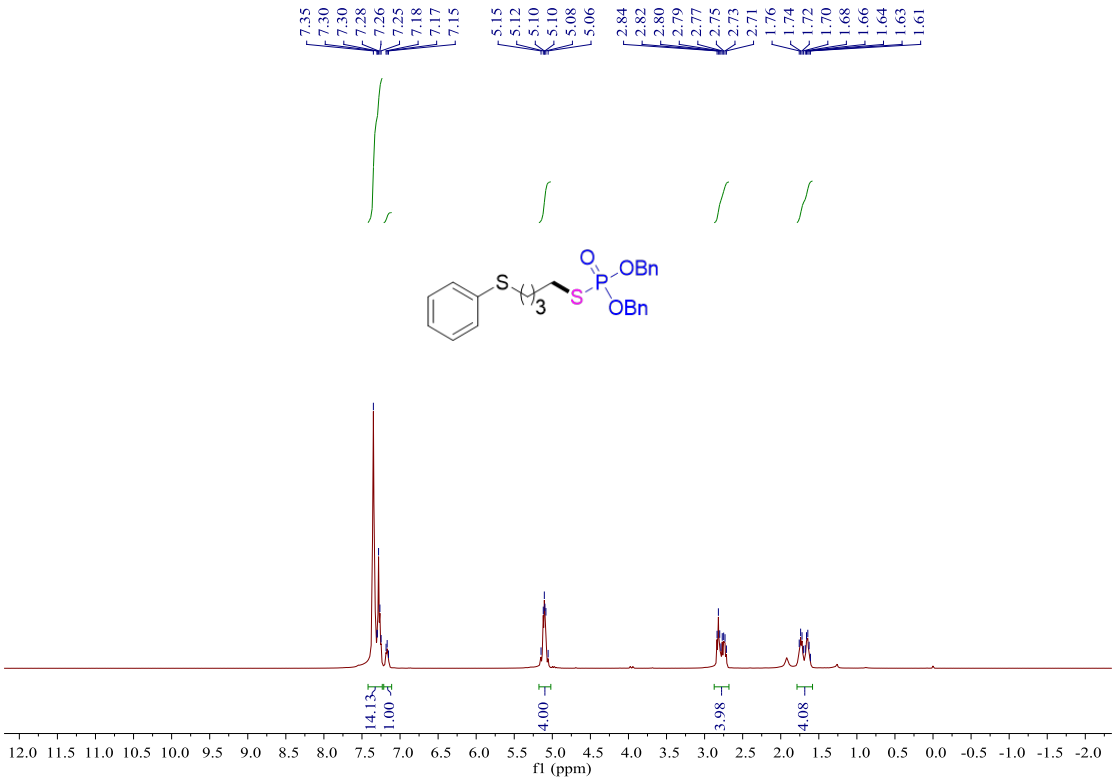
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ad**



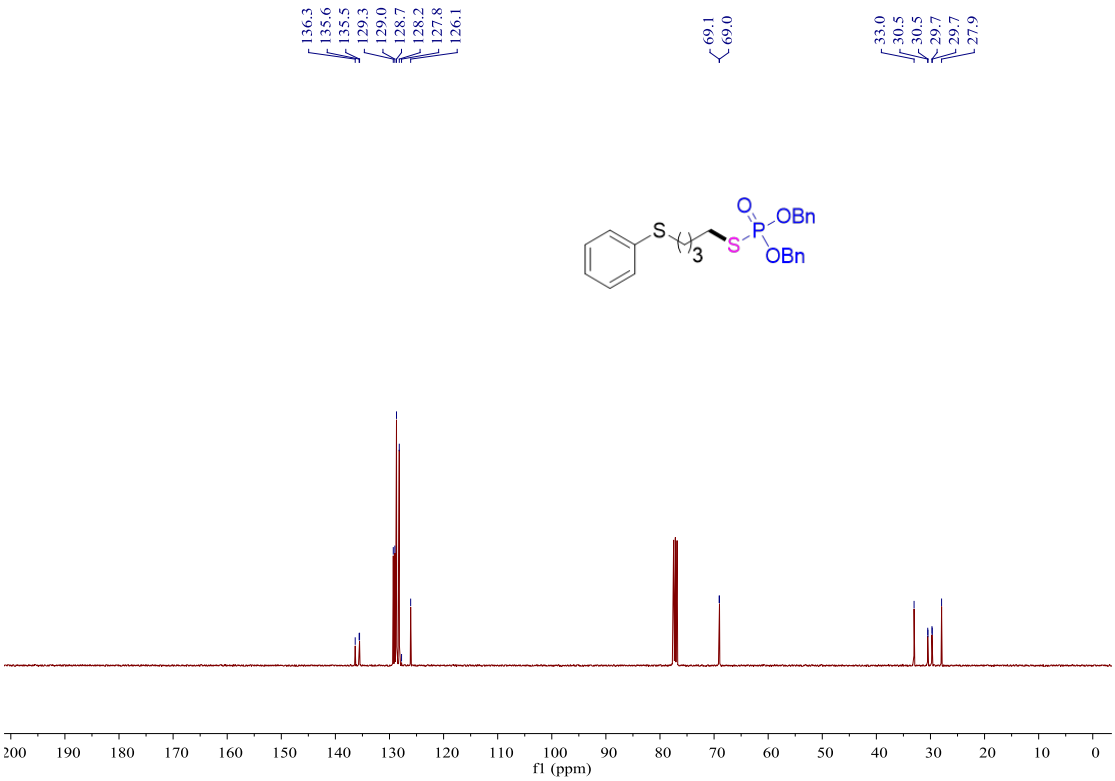
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ad**



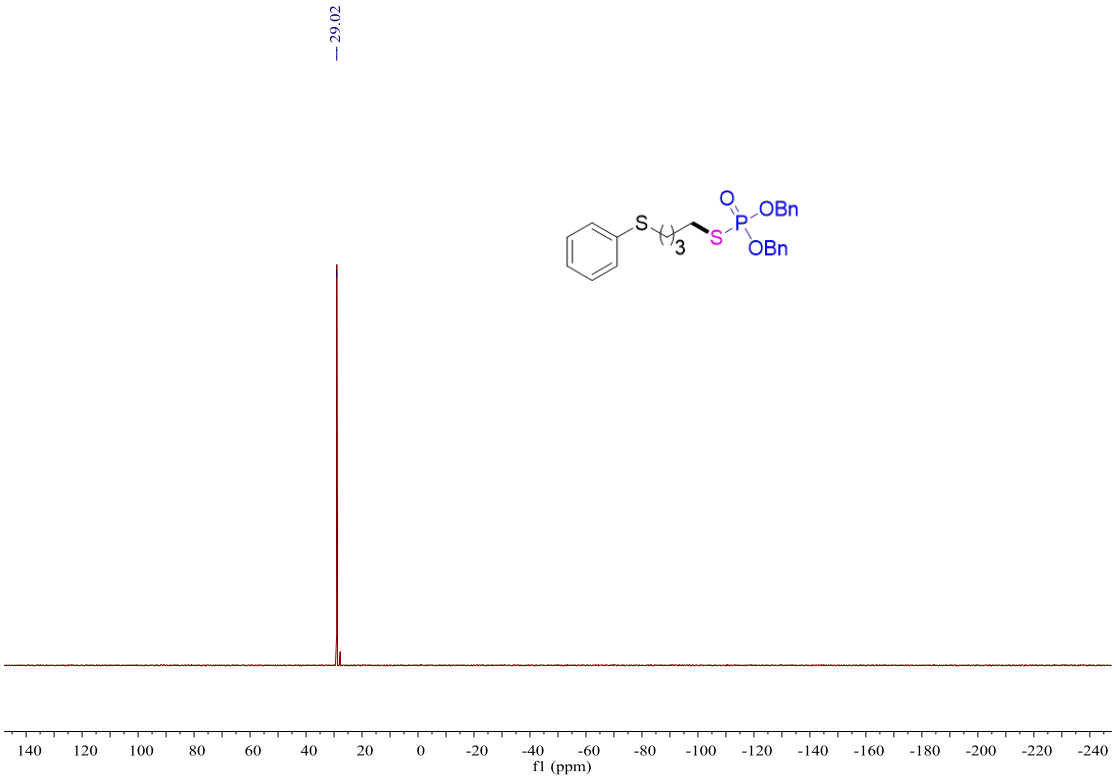
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ad**



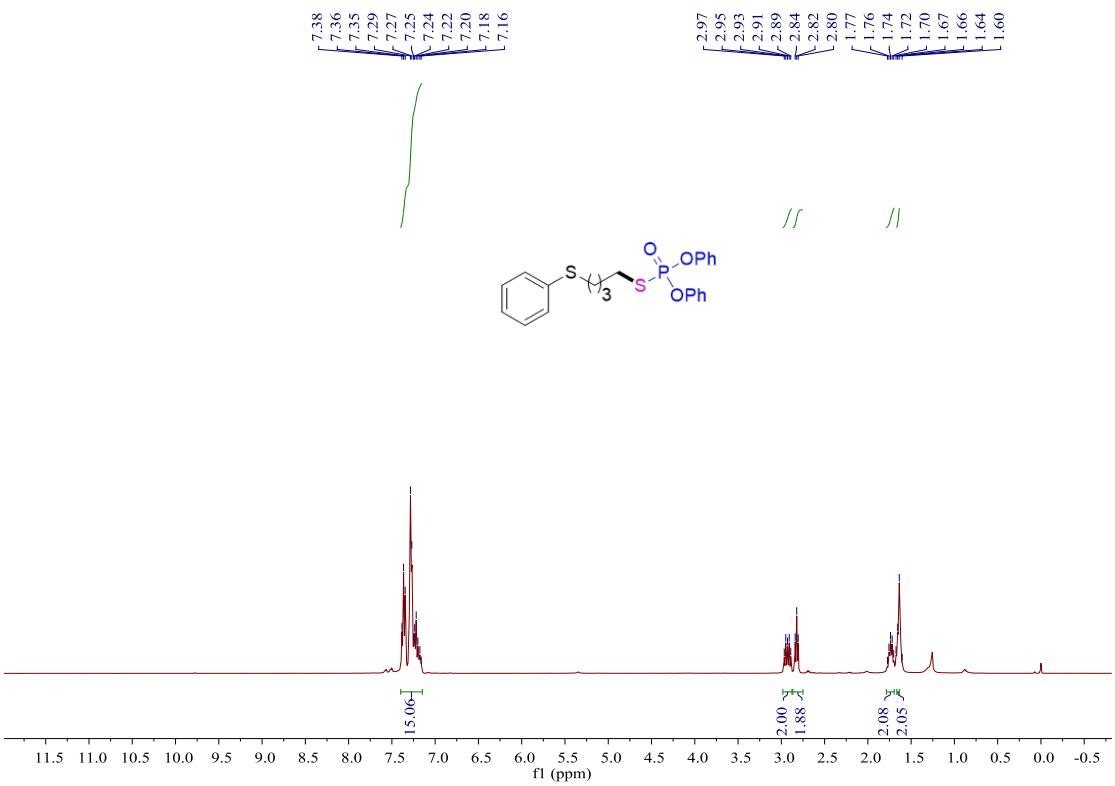
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ae**



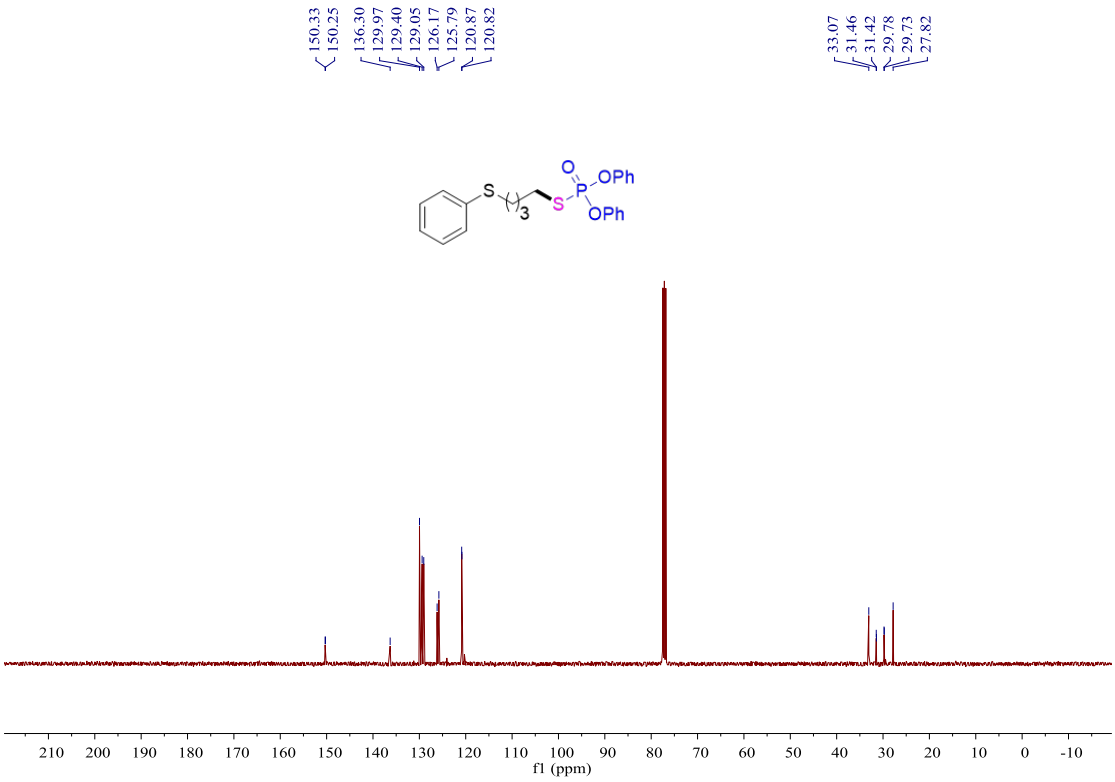
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ae**



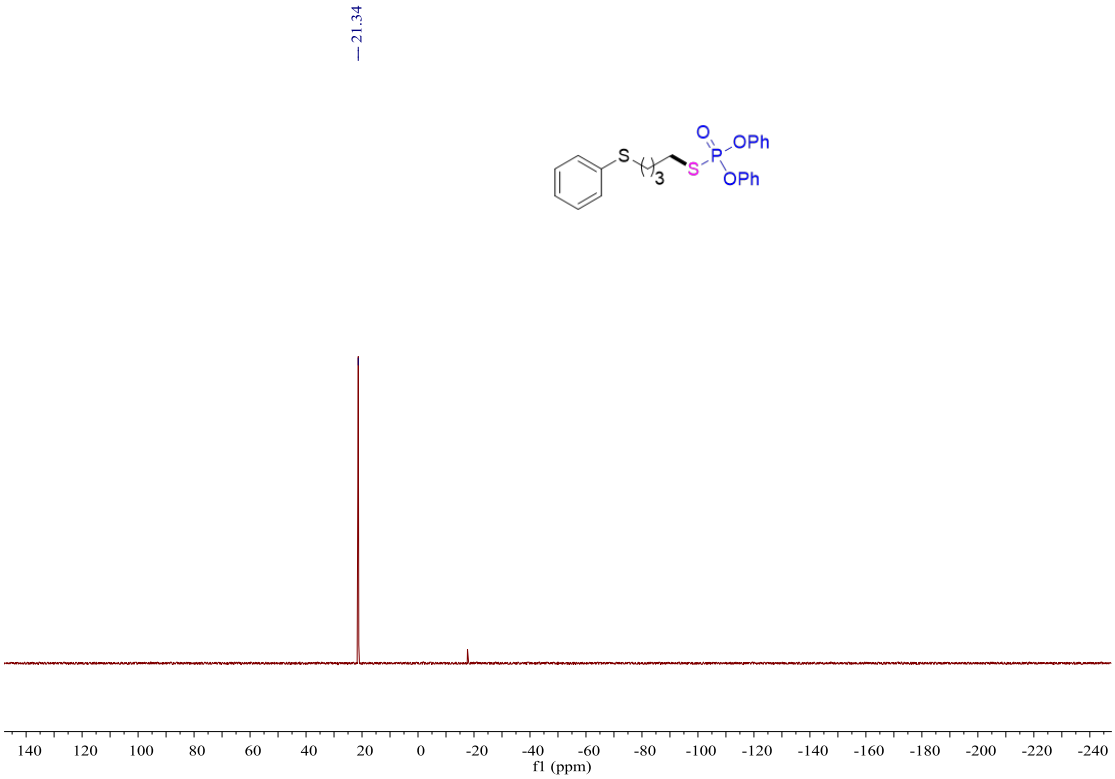
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ae**



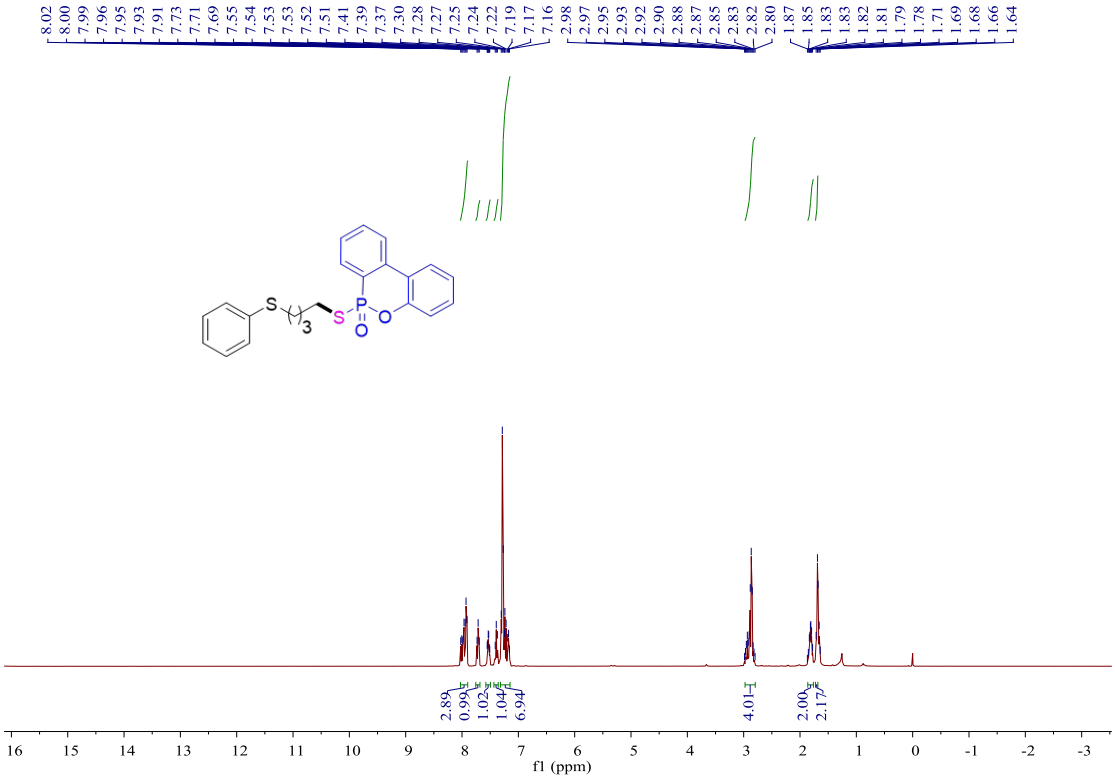
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5af**



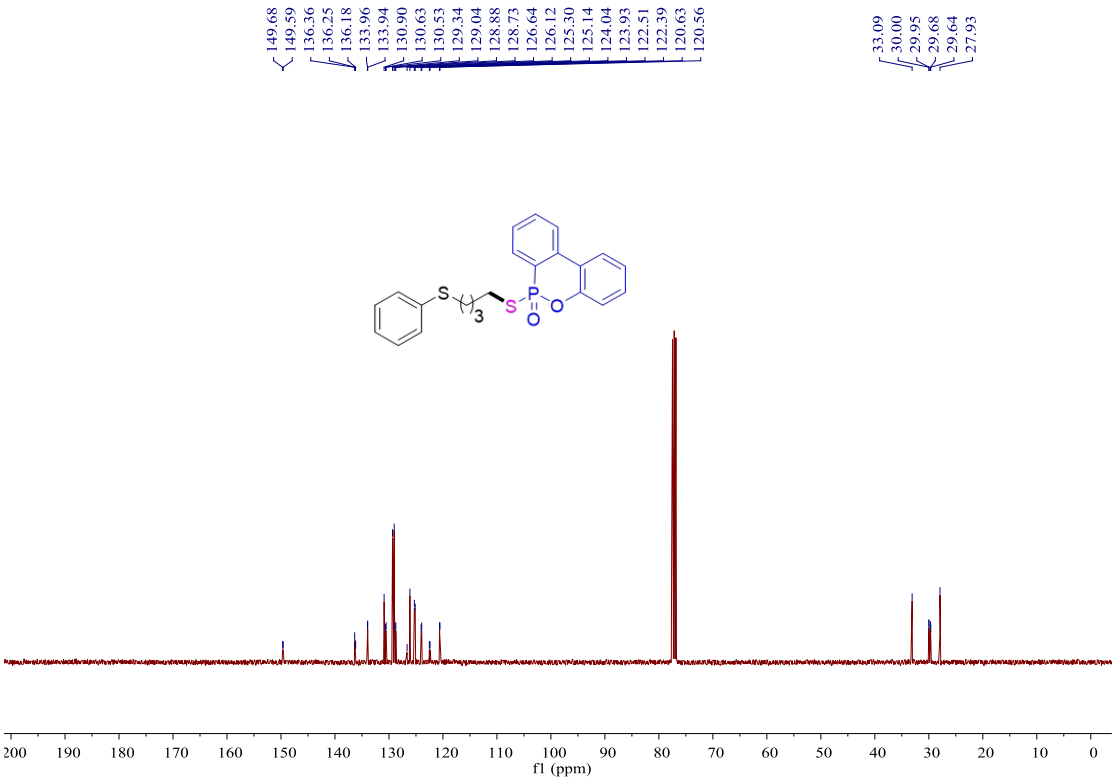
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5af**



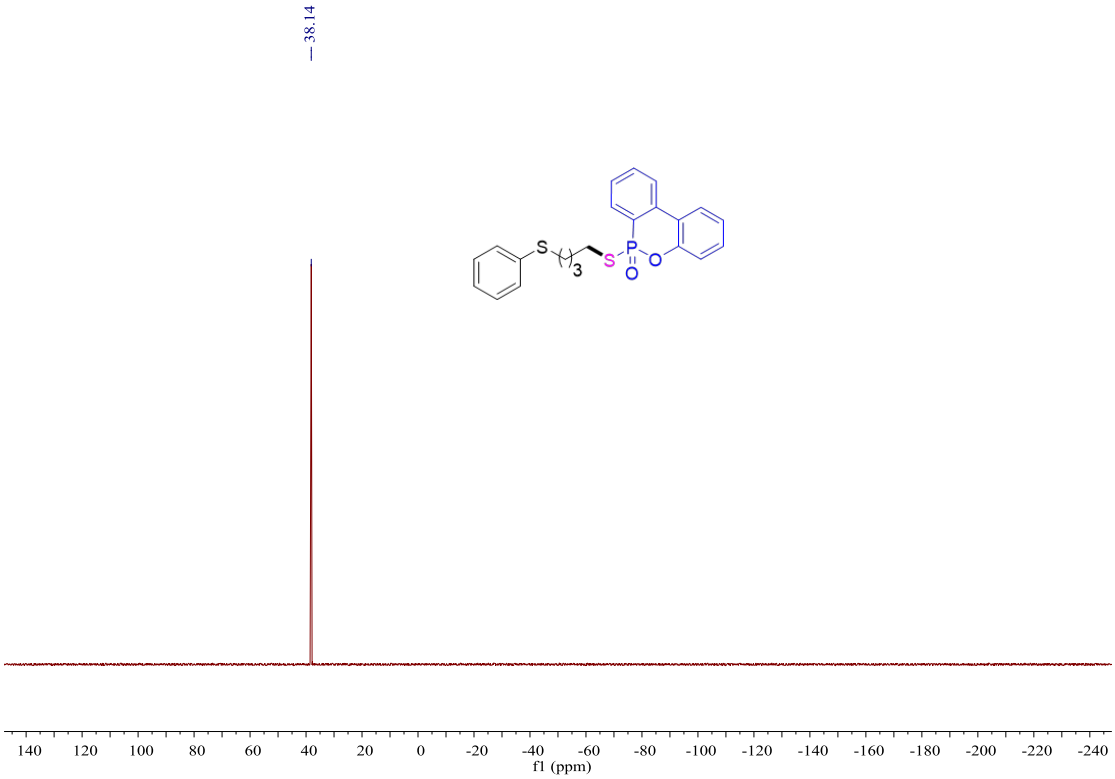
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5af**



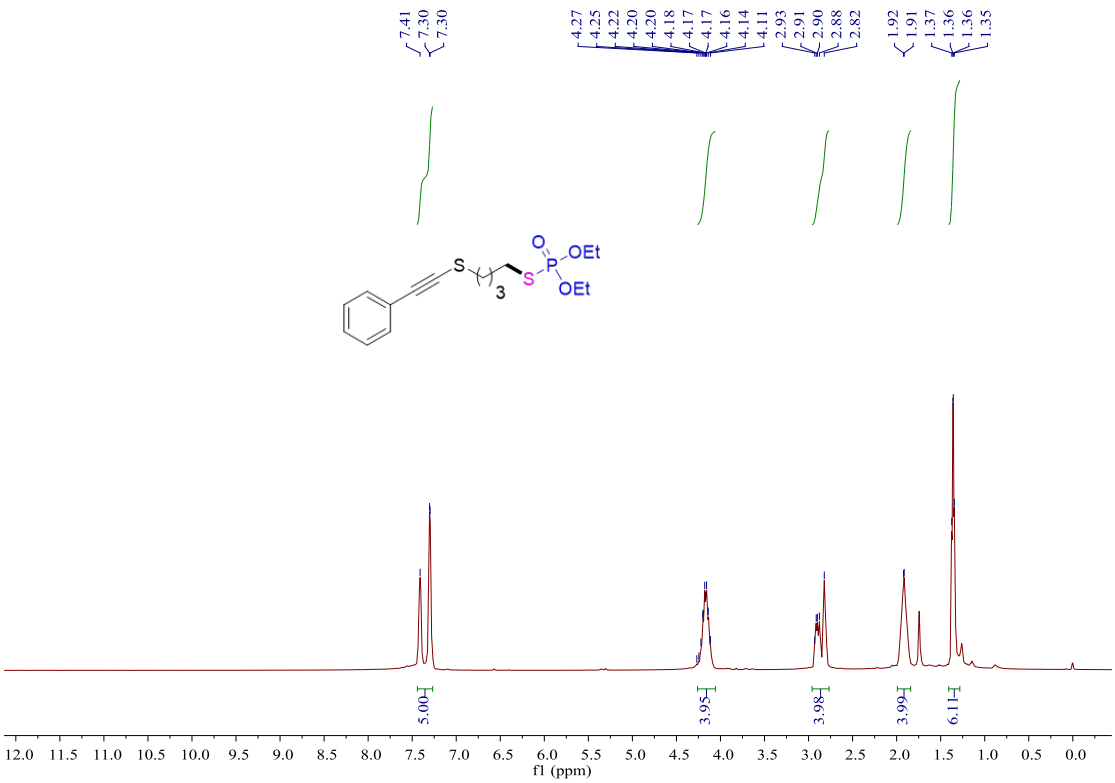
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **5ag**



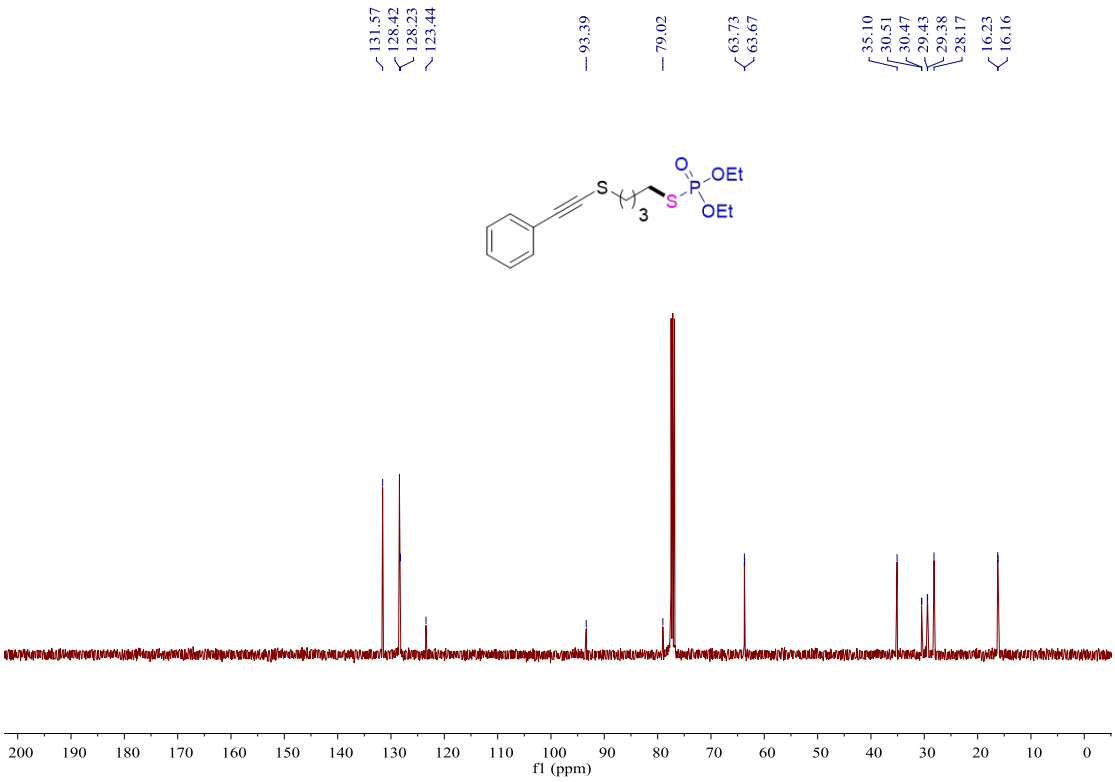
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **5ag**



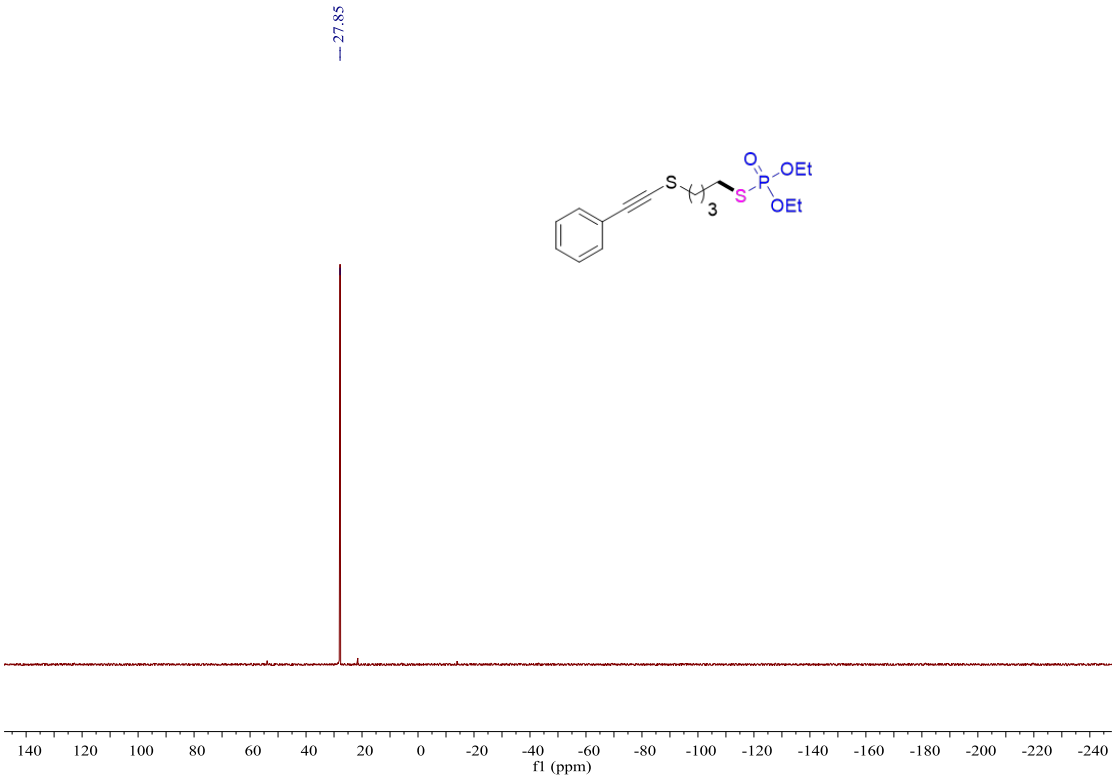
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **5ag**



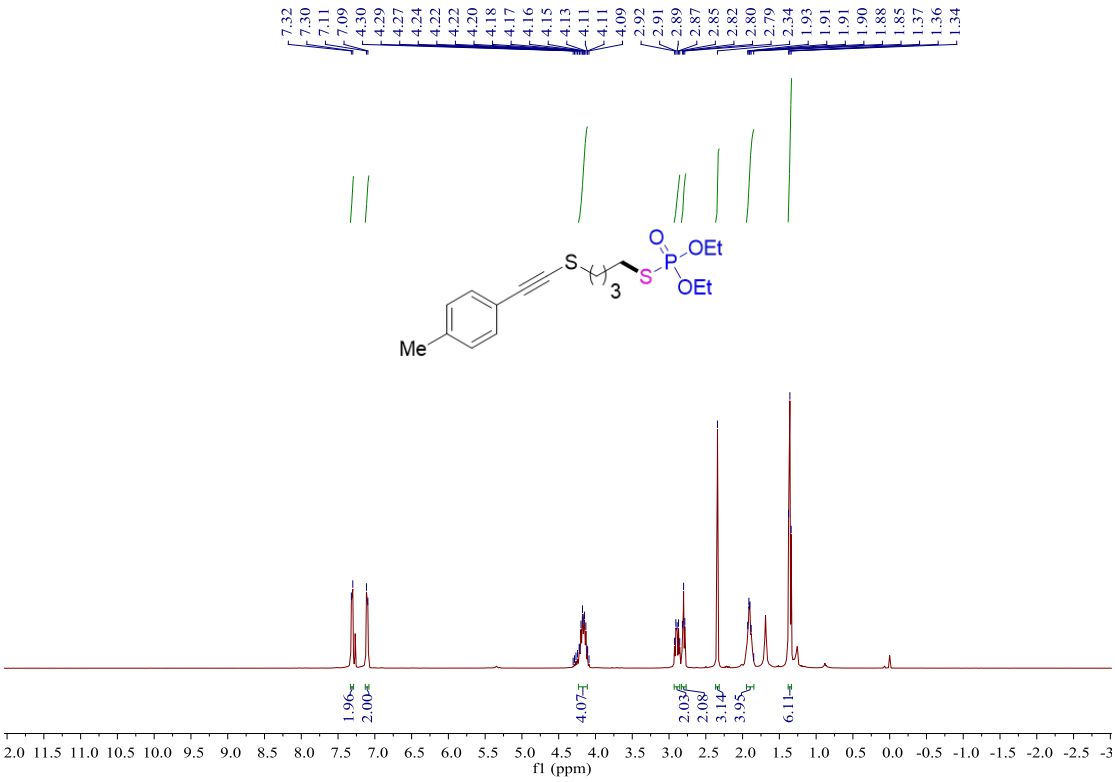
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7aa**



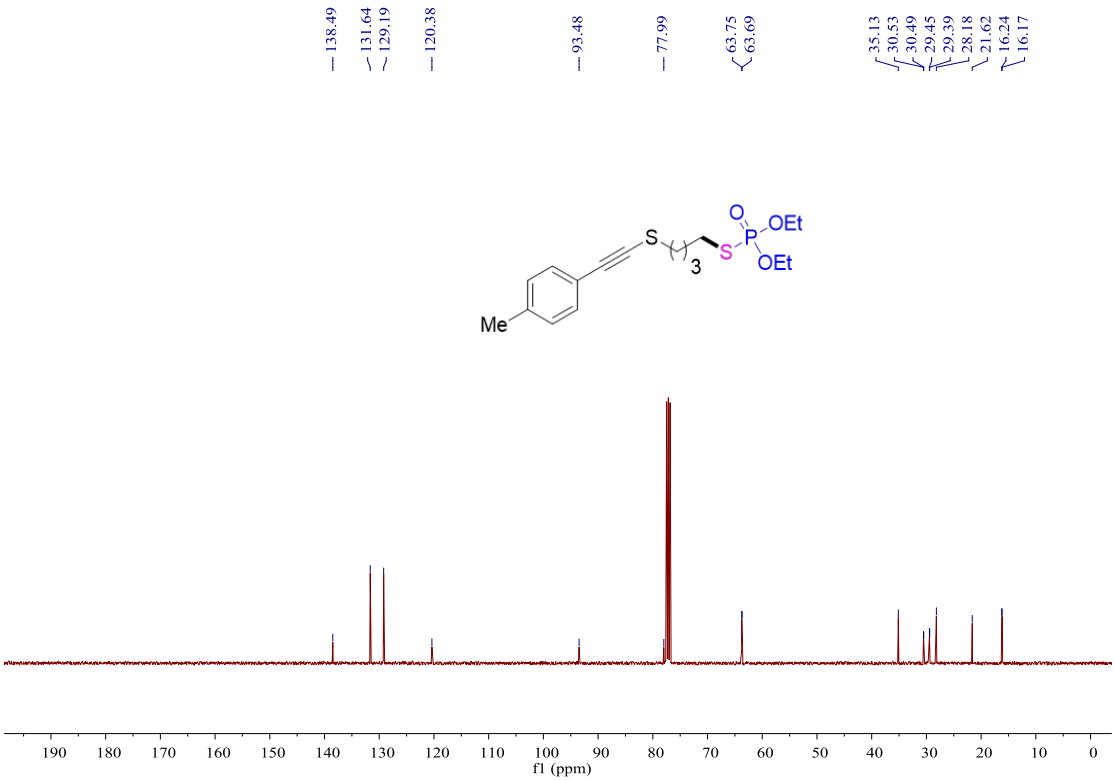
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7aa**



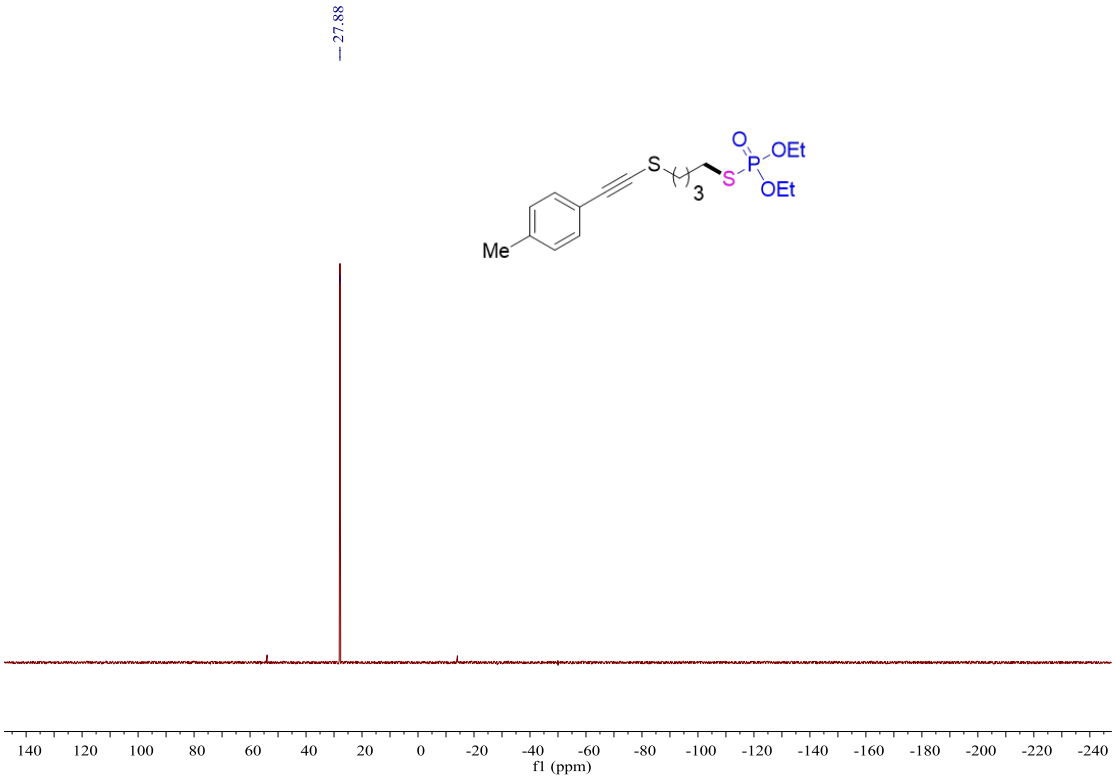
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7aa**



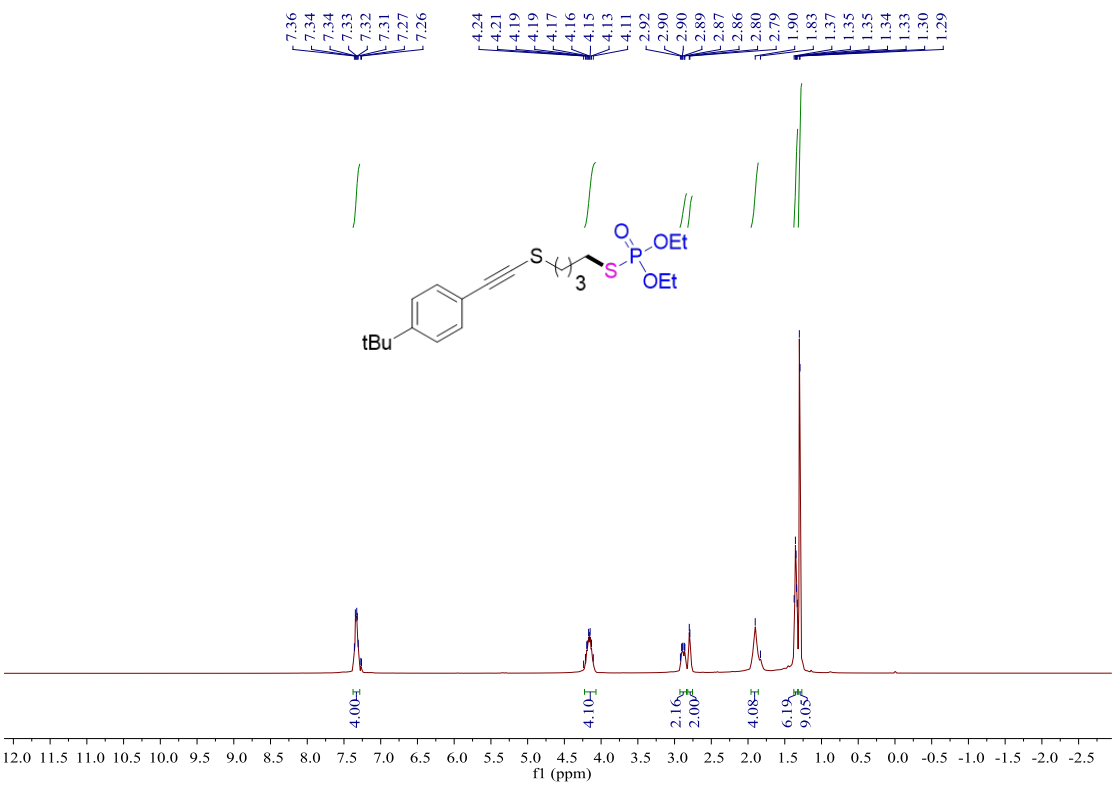
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ba**



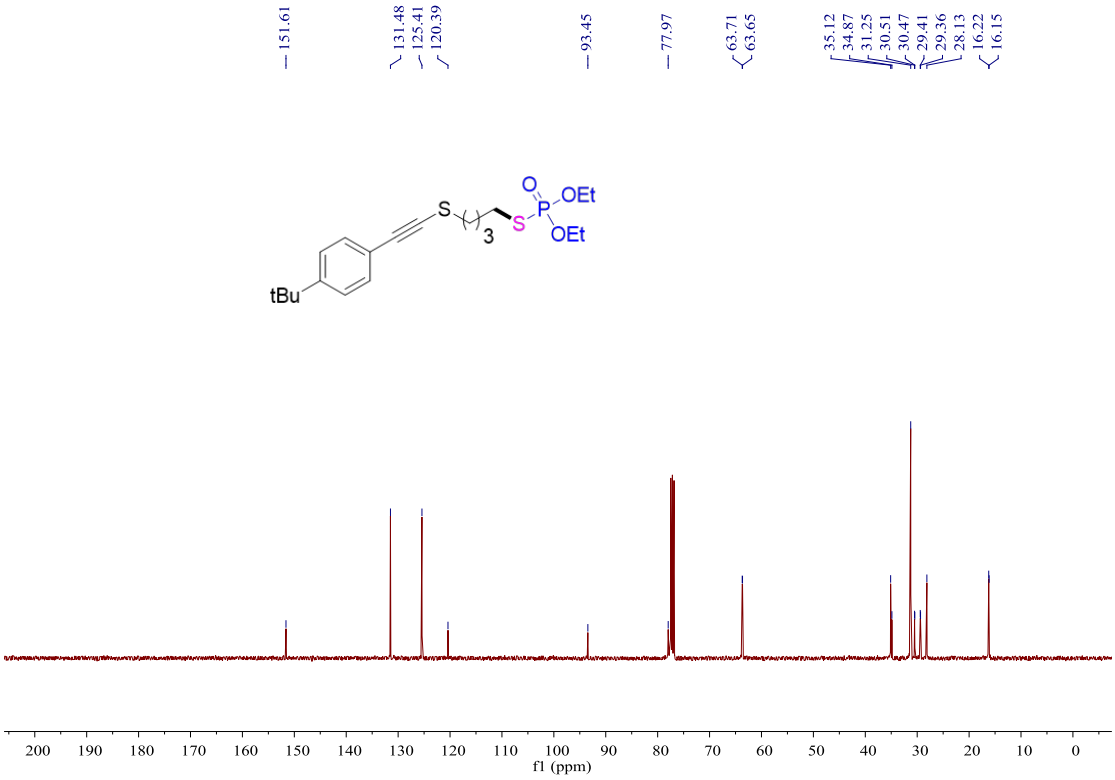
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ba**



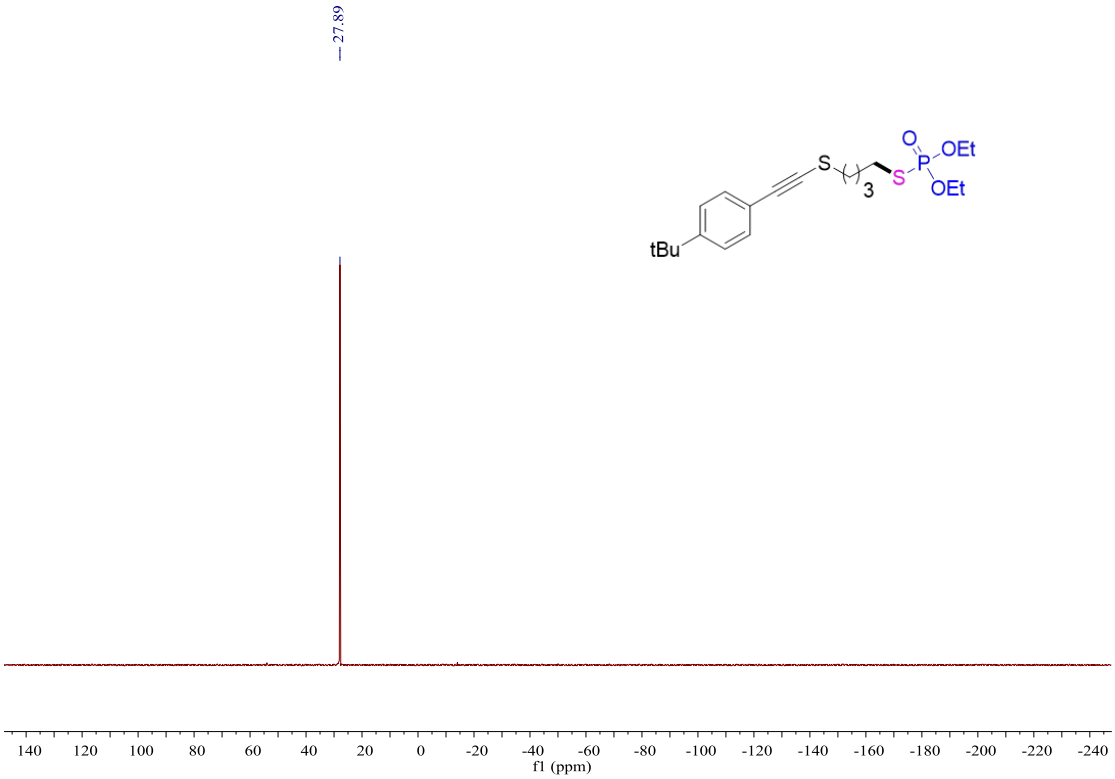
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ba**



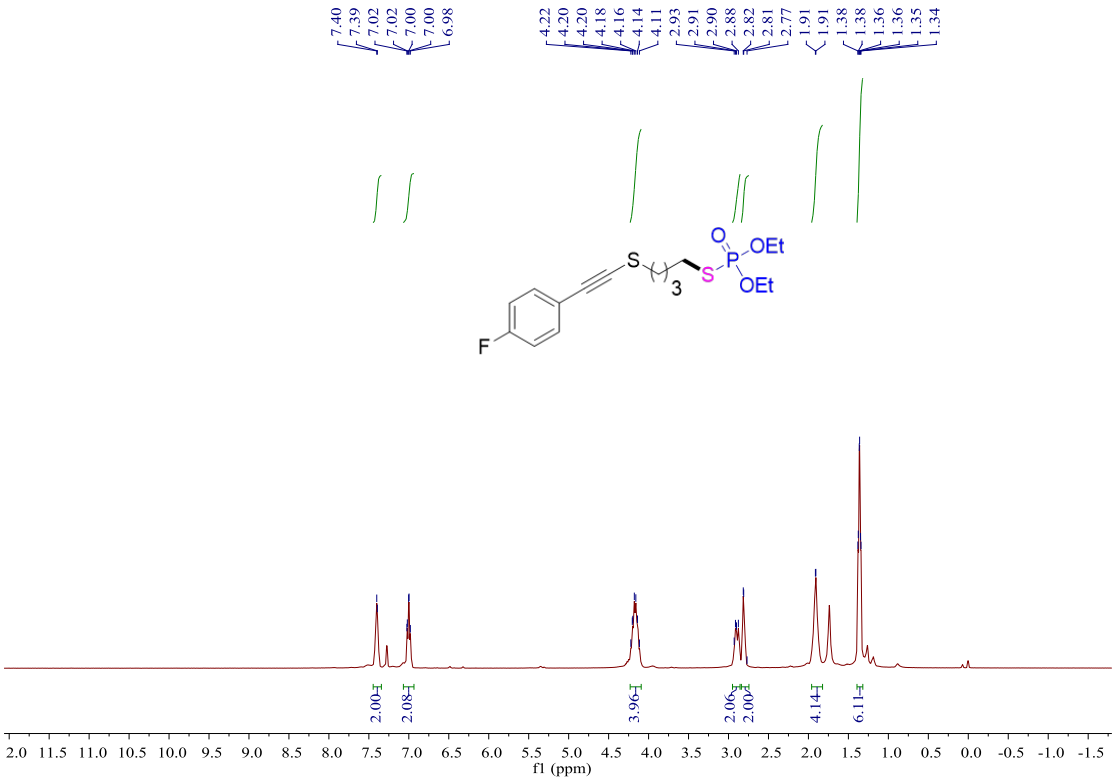
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ca**



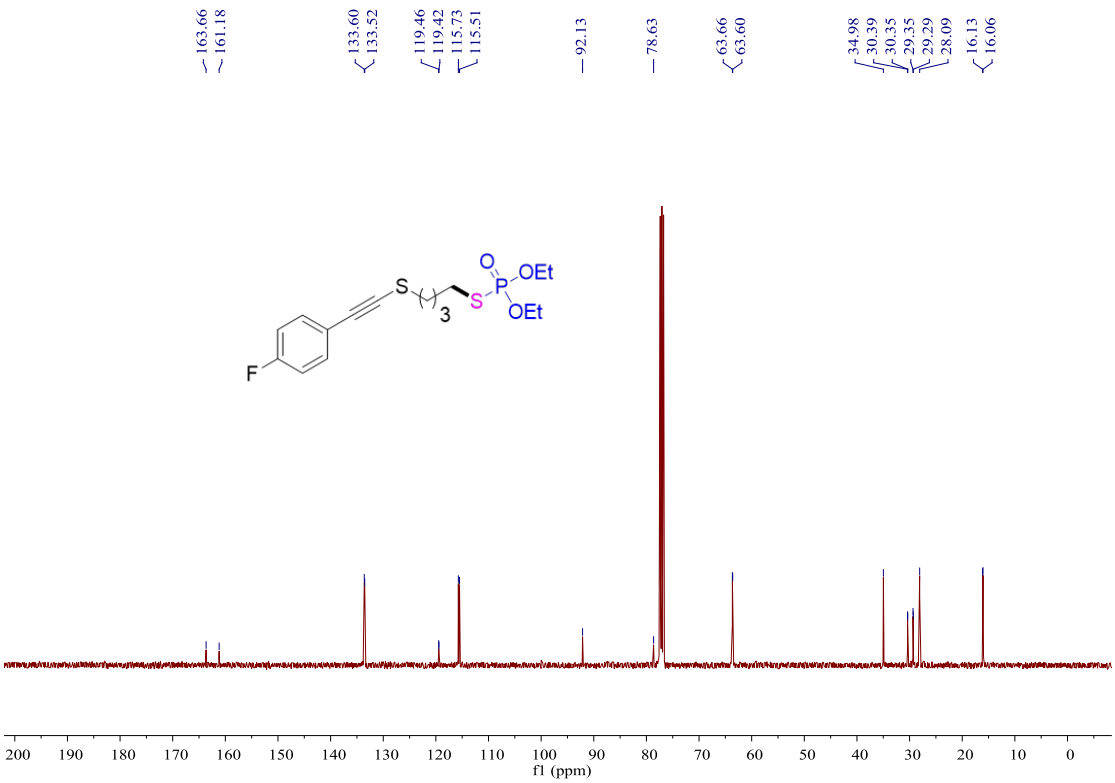
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ca**



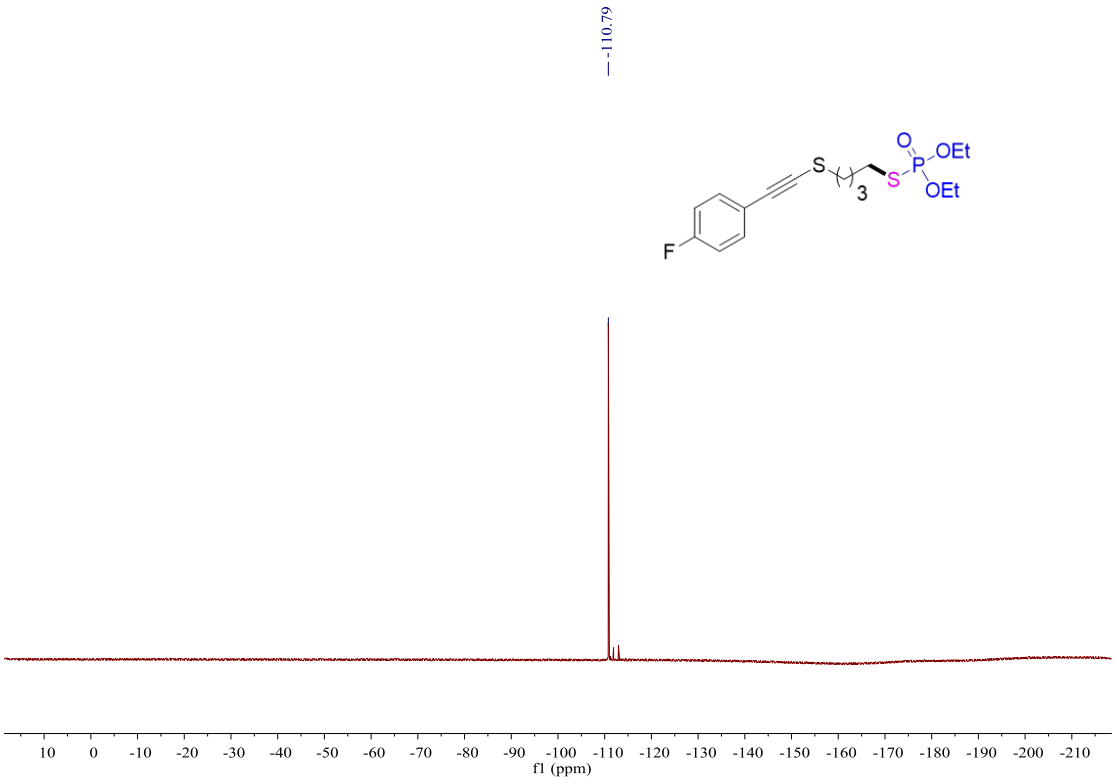
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ca**



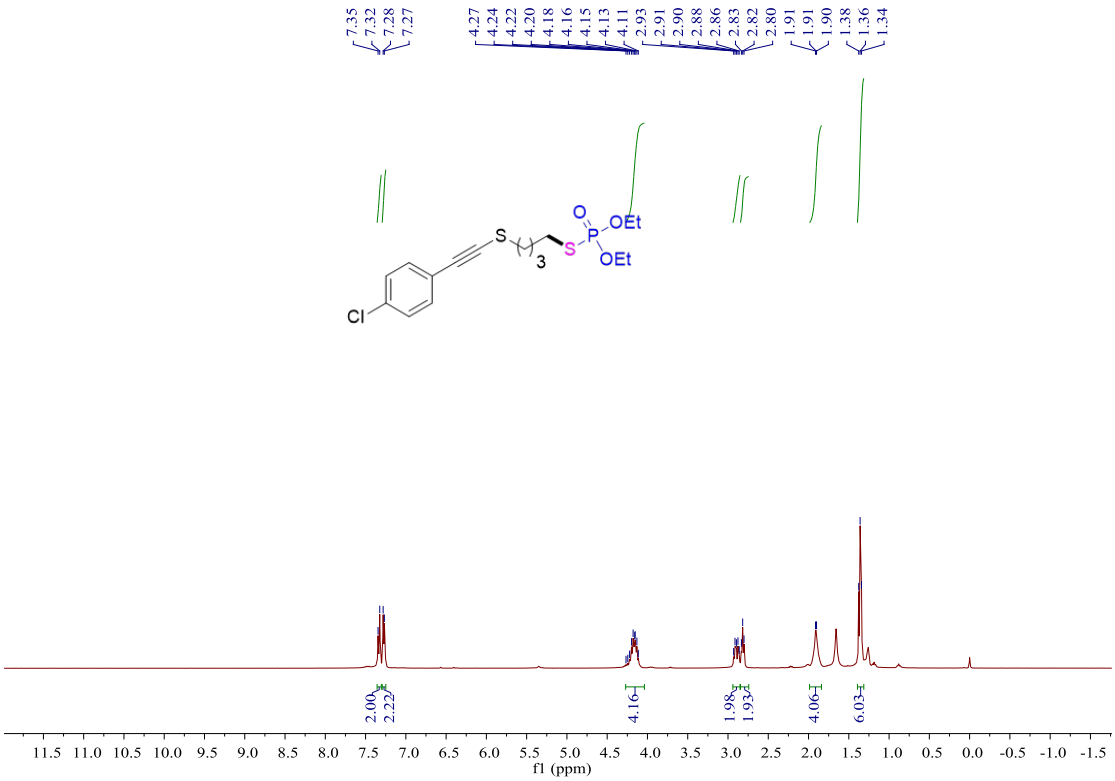
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7da**



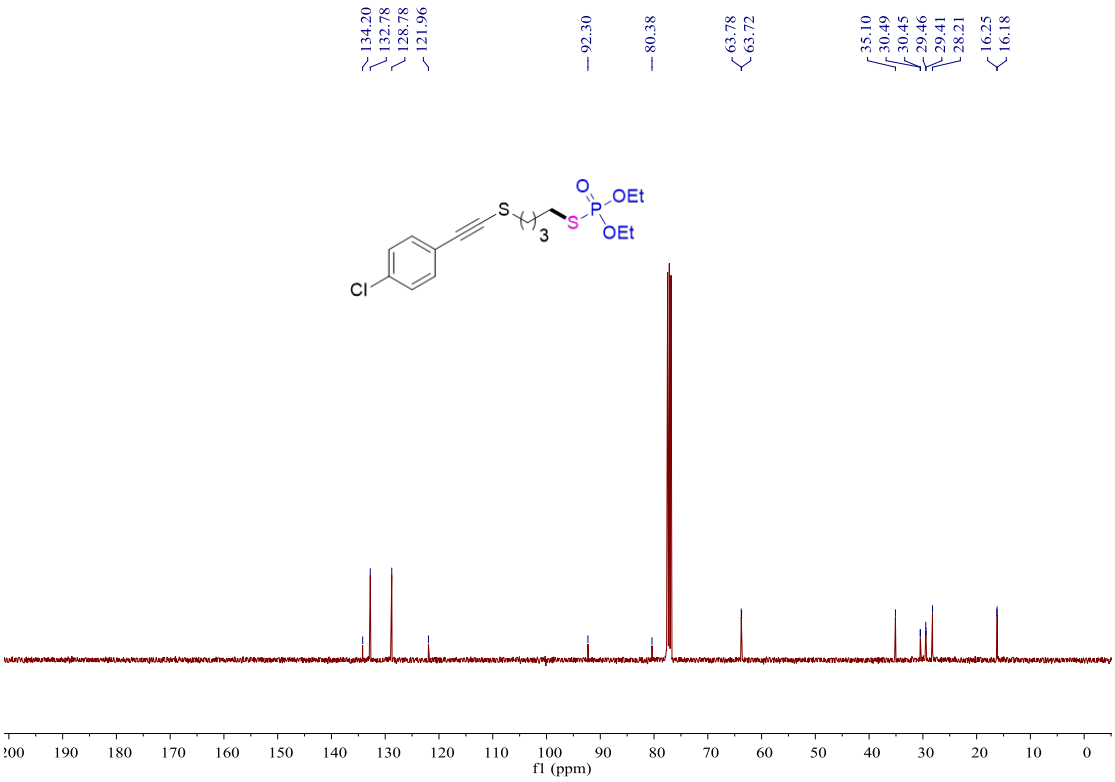
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7da**



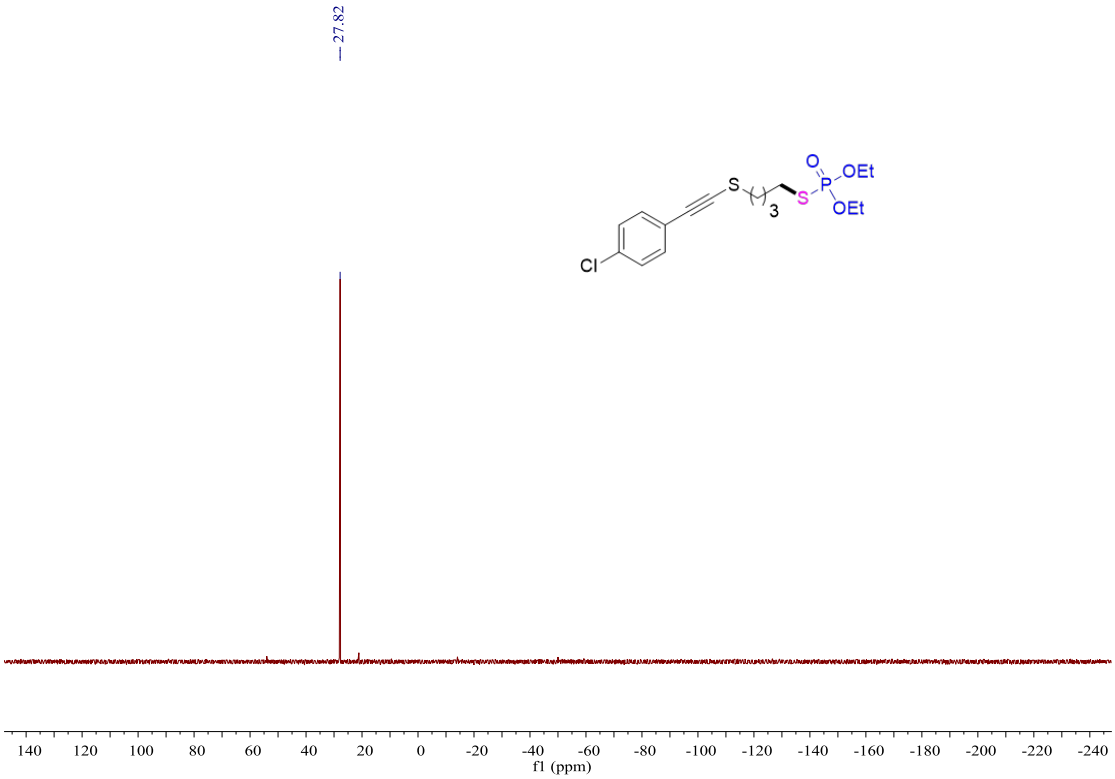
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7da**



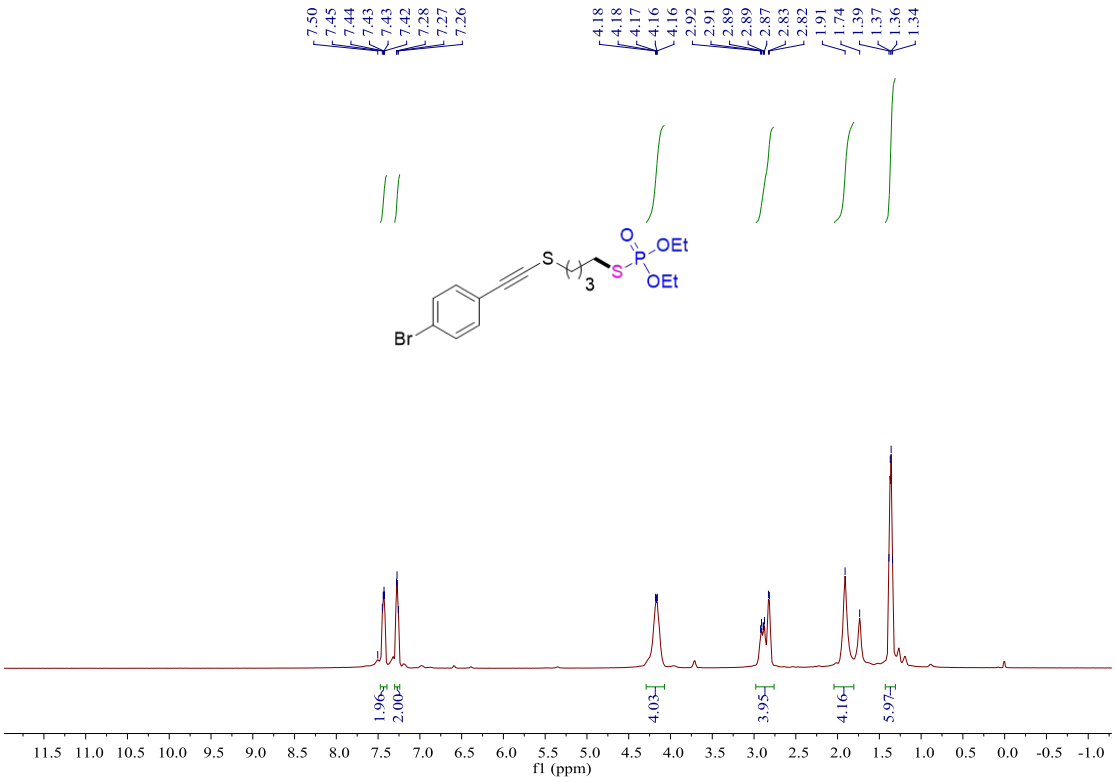
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ea**



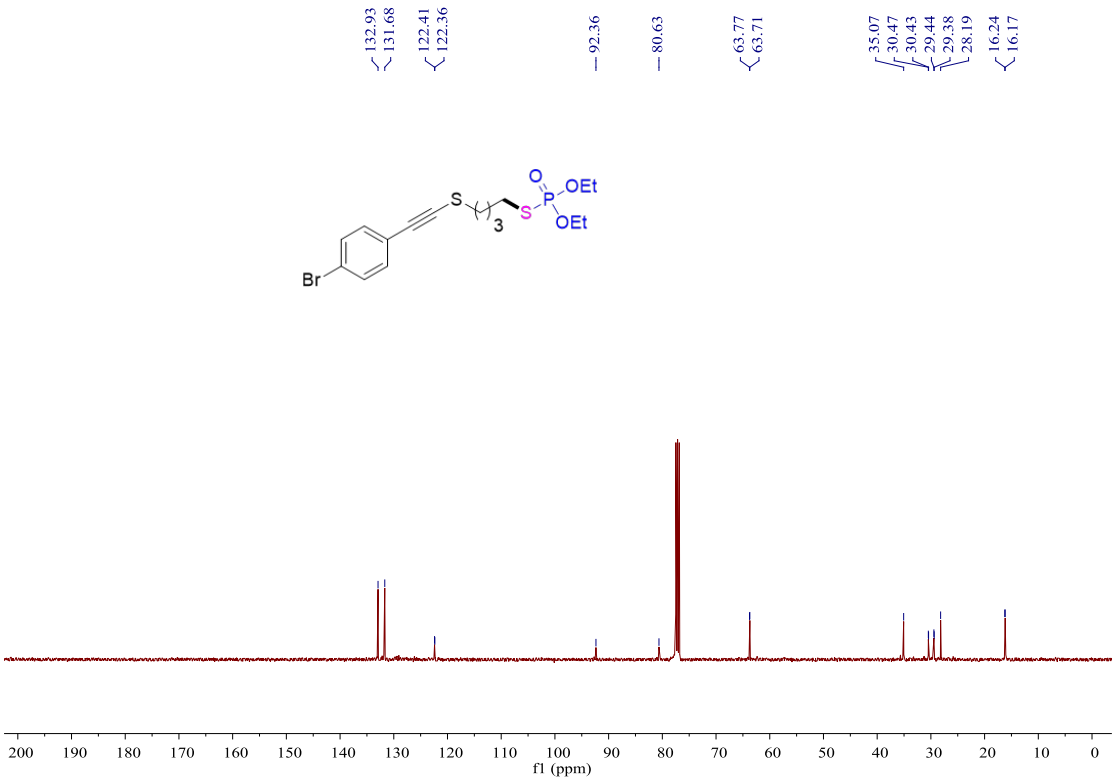
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ea**



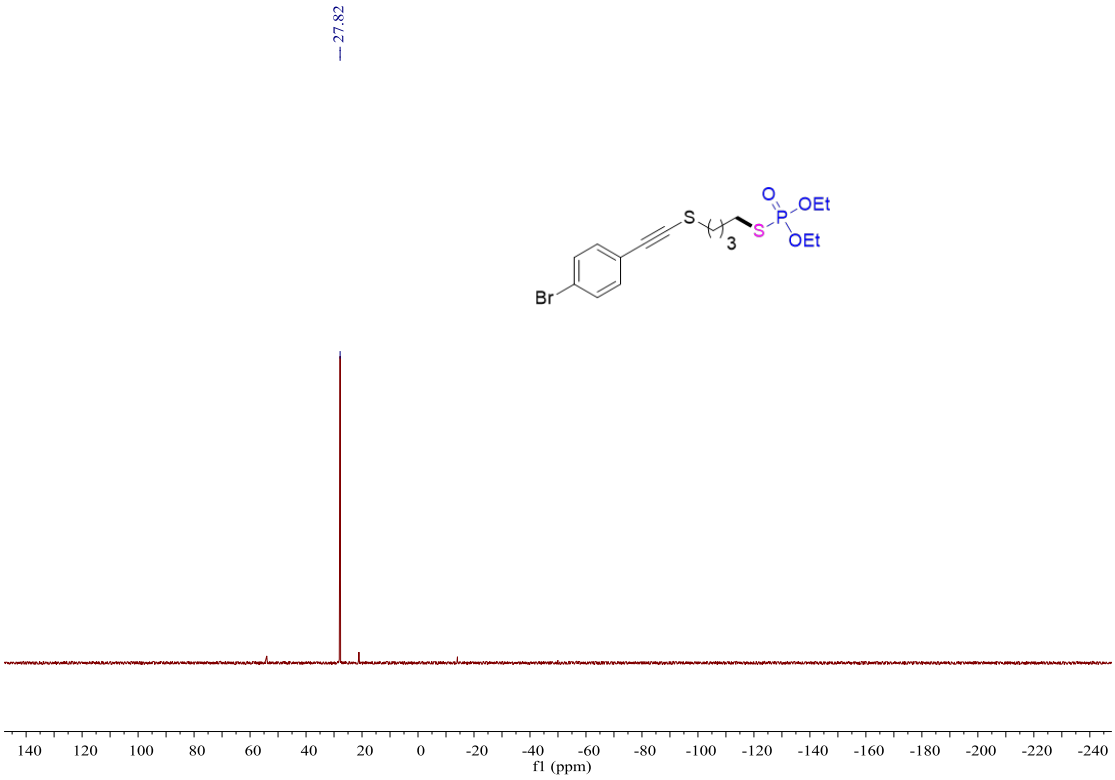
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ea**



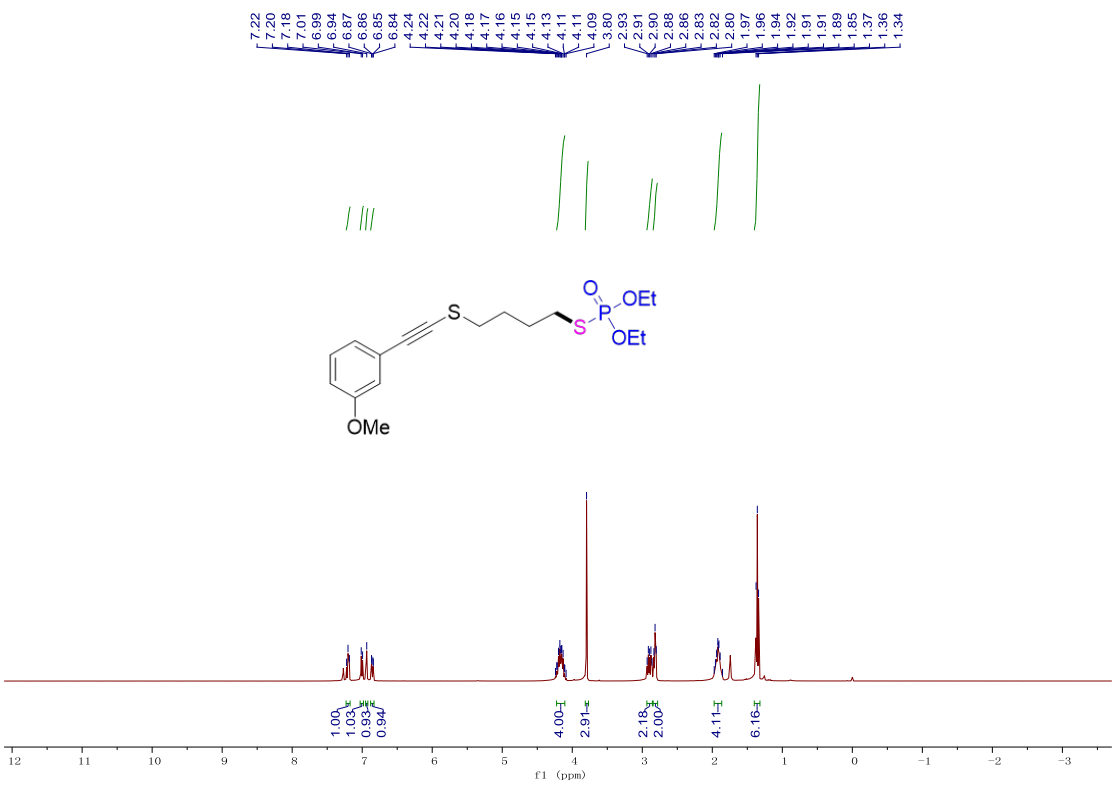
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7fa**



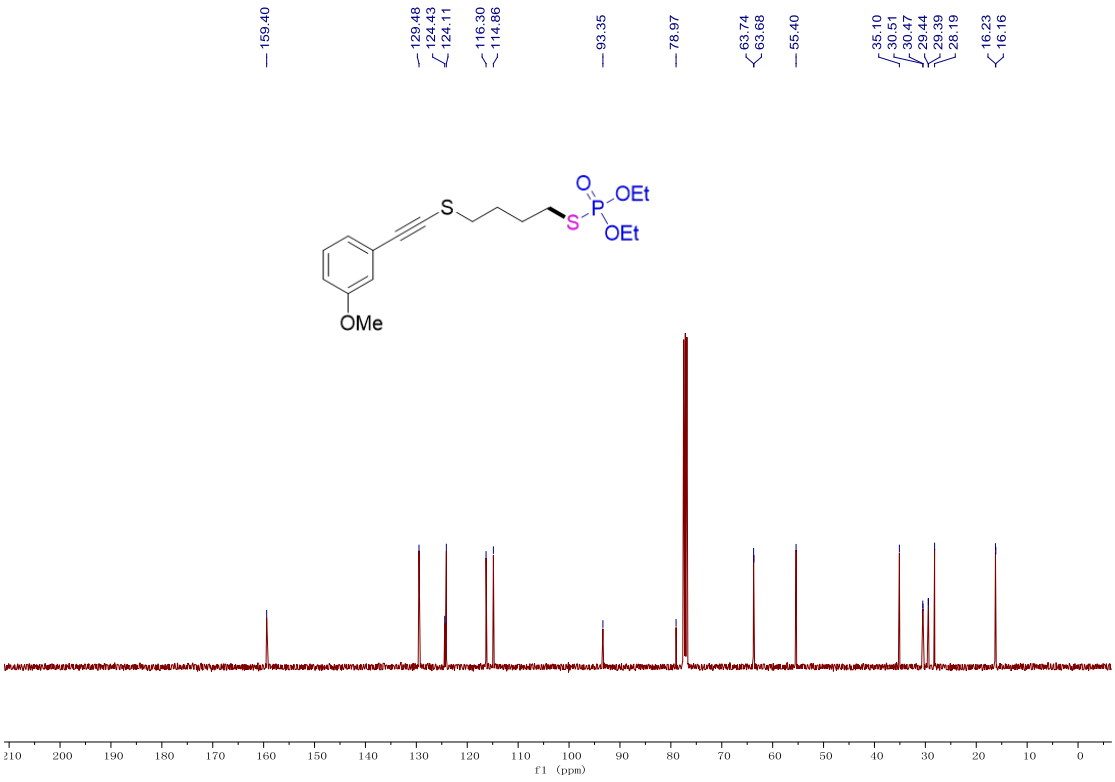
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7fa**



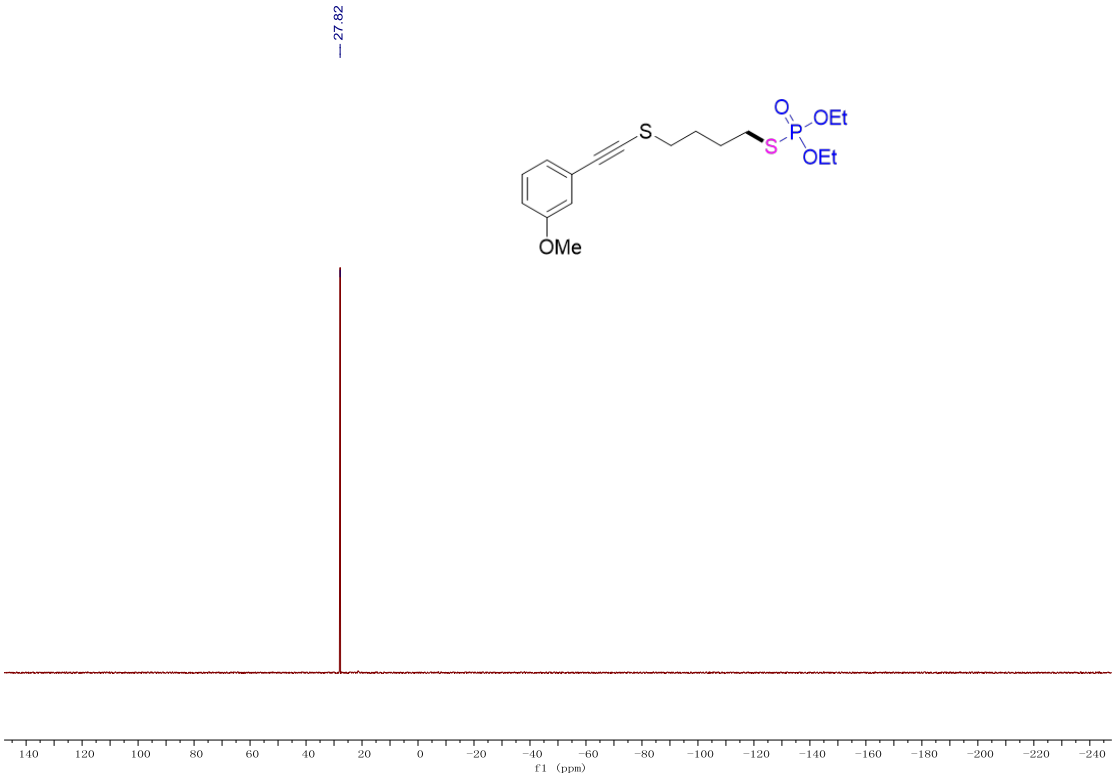
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7fa**



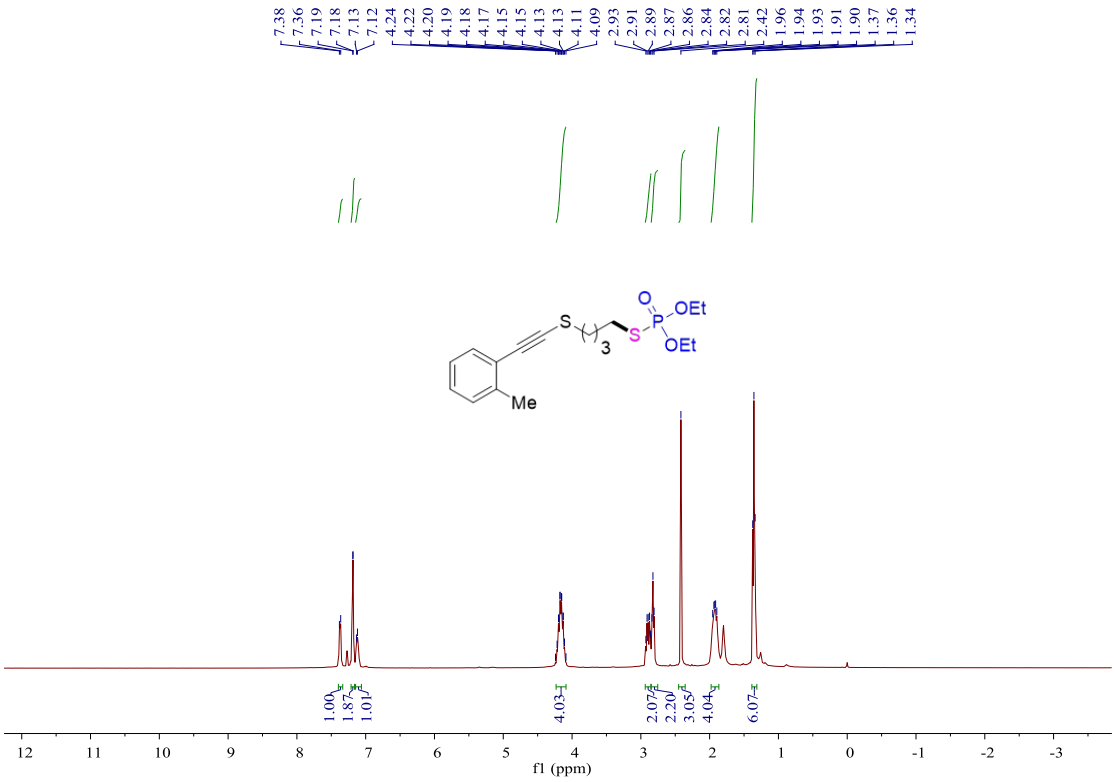
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ga**



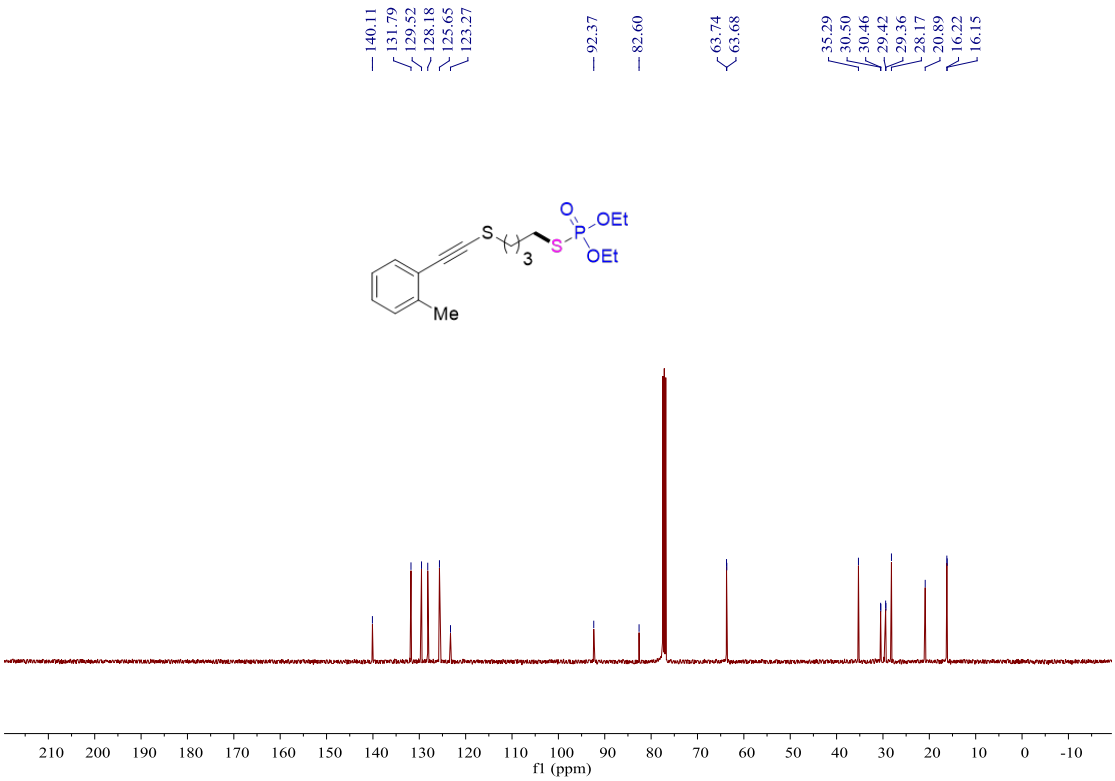
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ga**



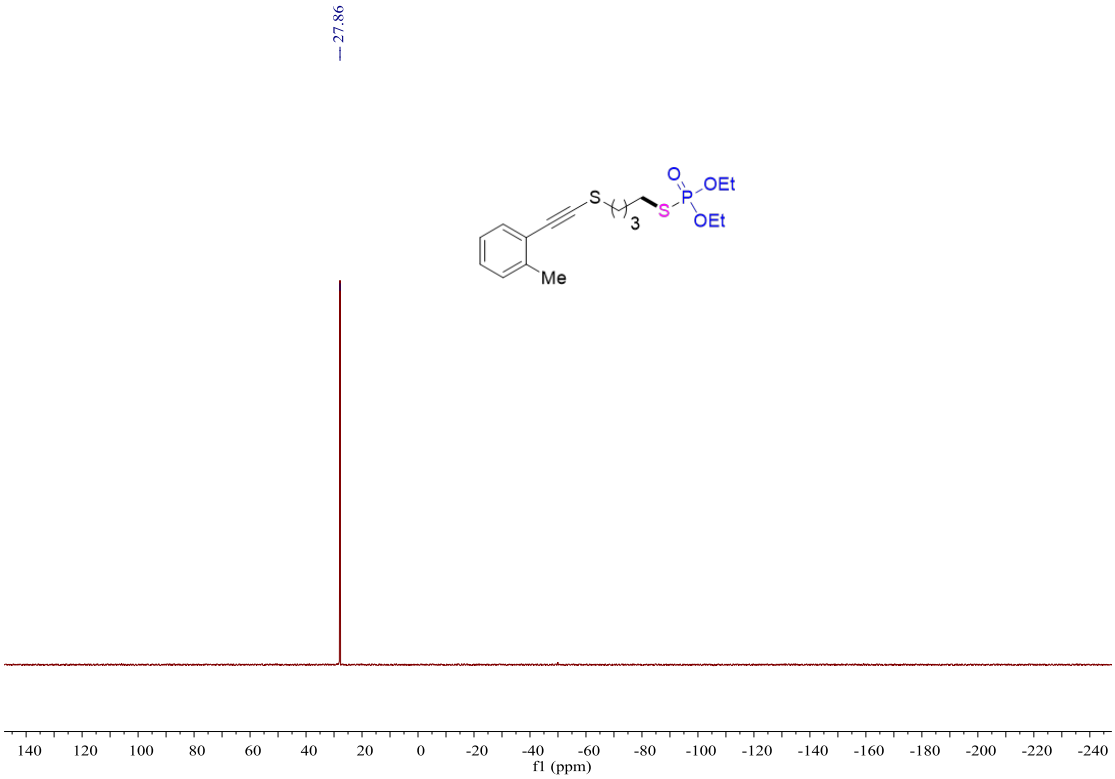
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ga**



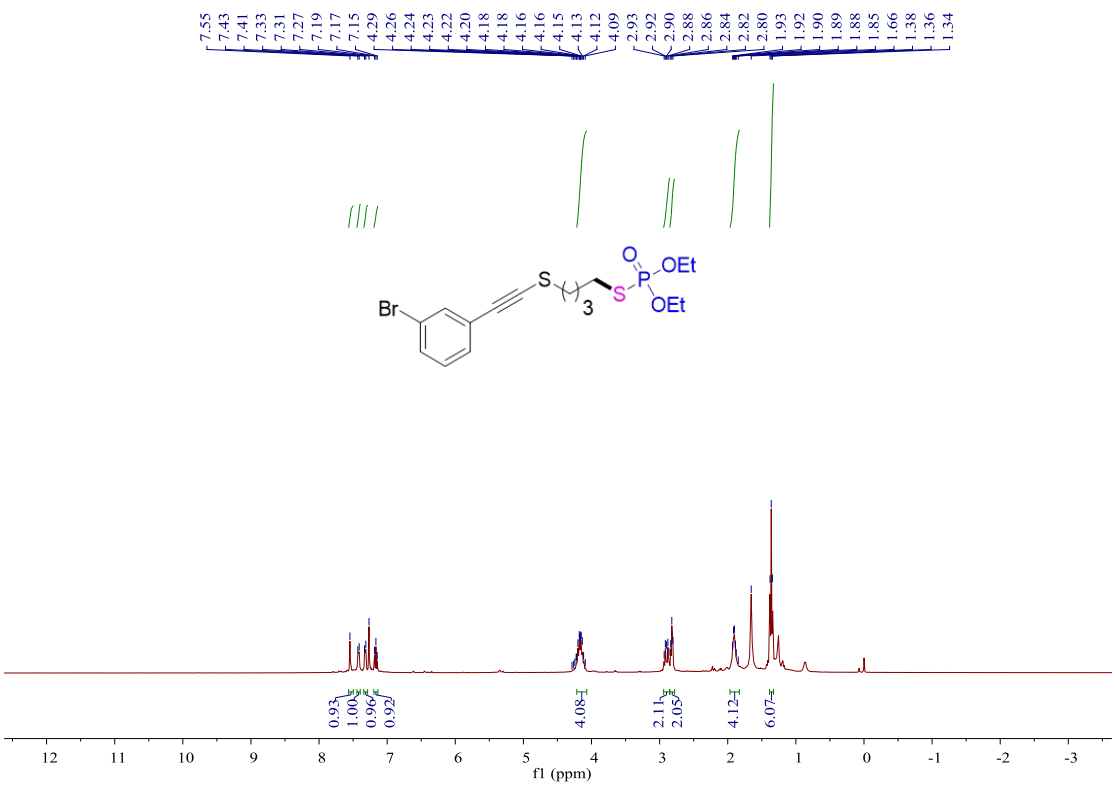
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ha**



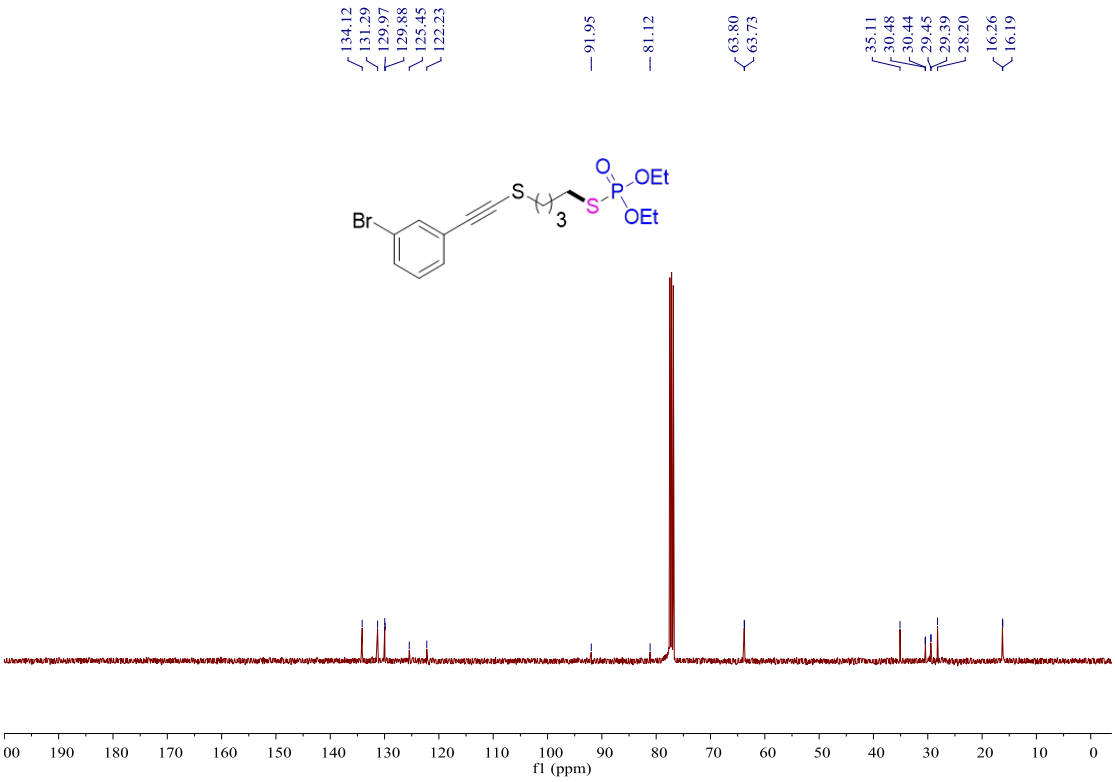
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ha**



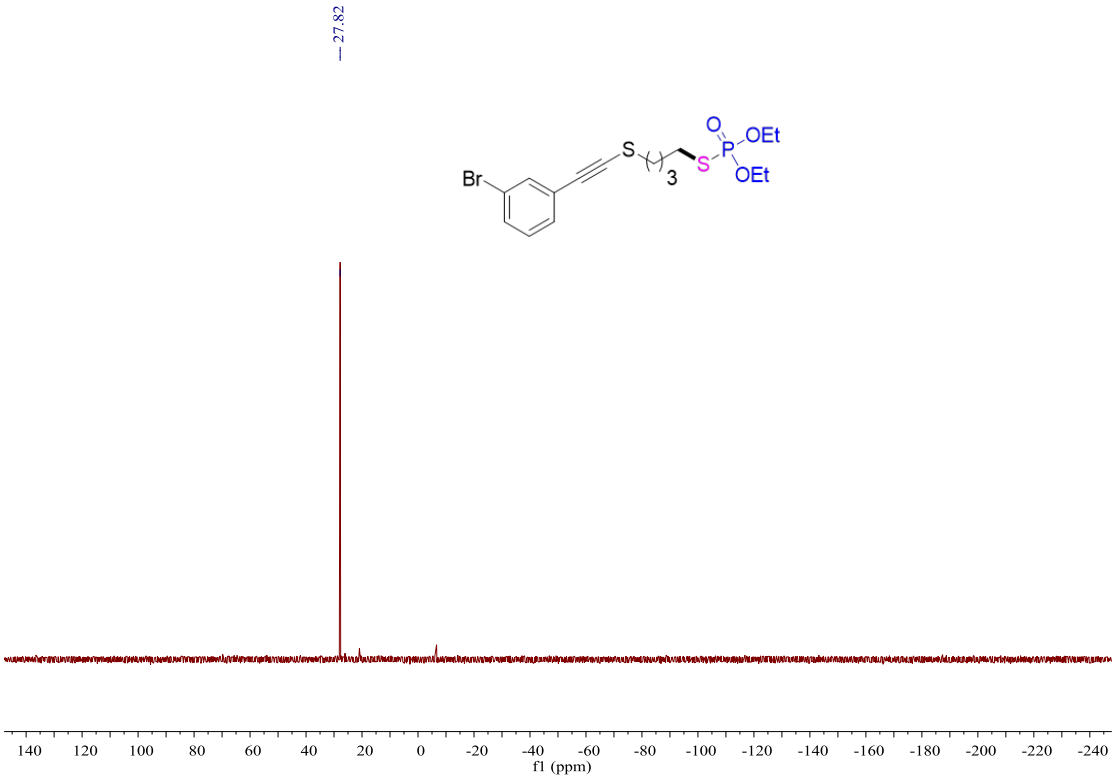
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ha**



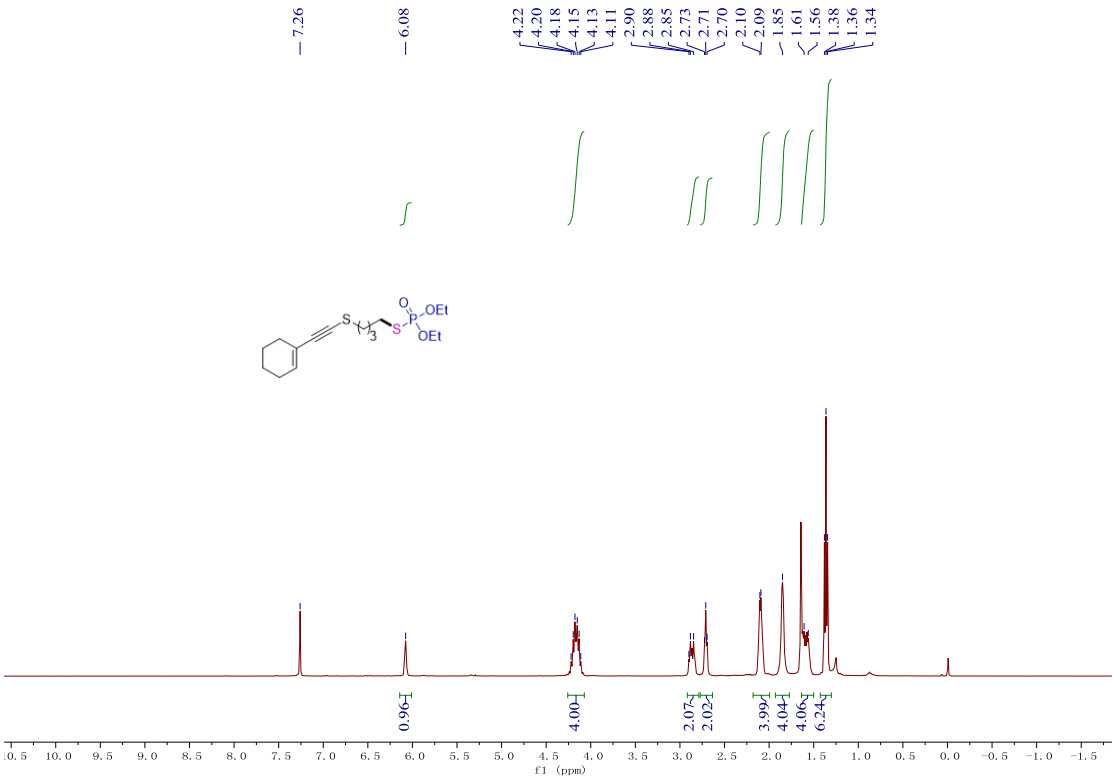
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ia**



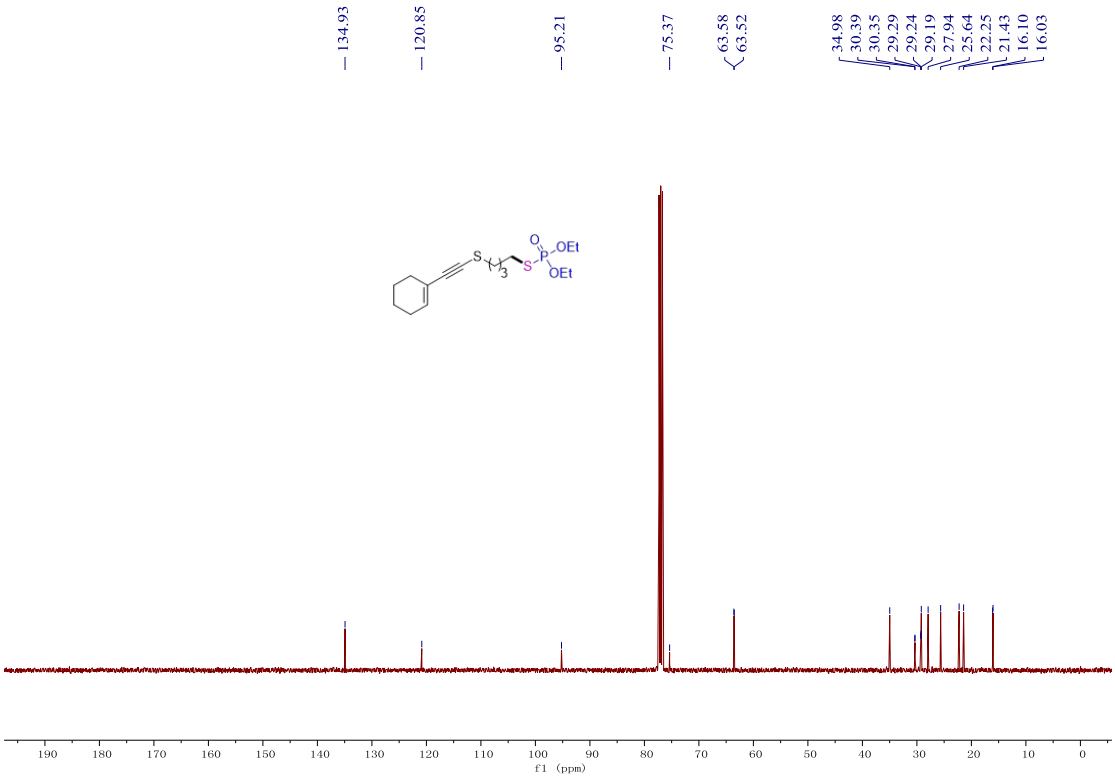
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ia**



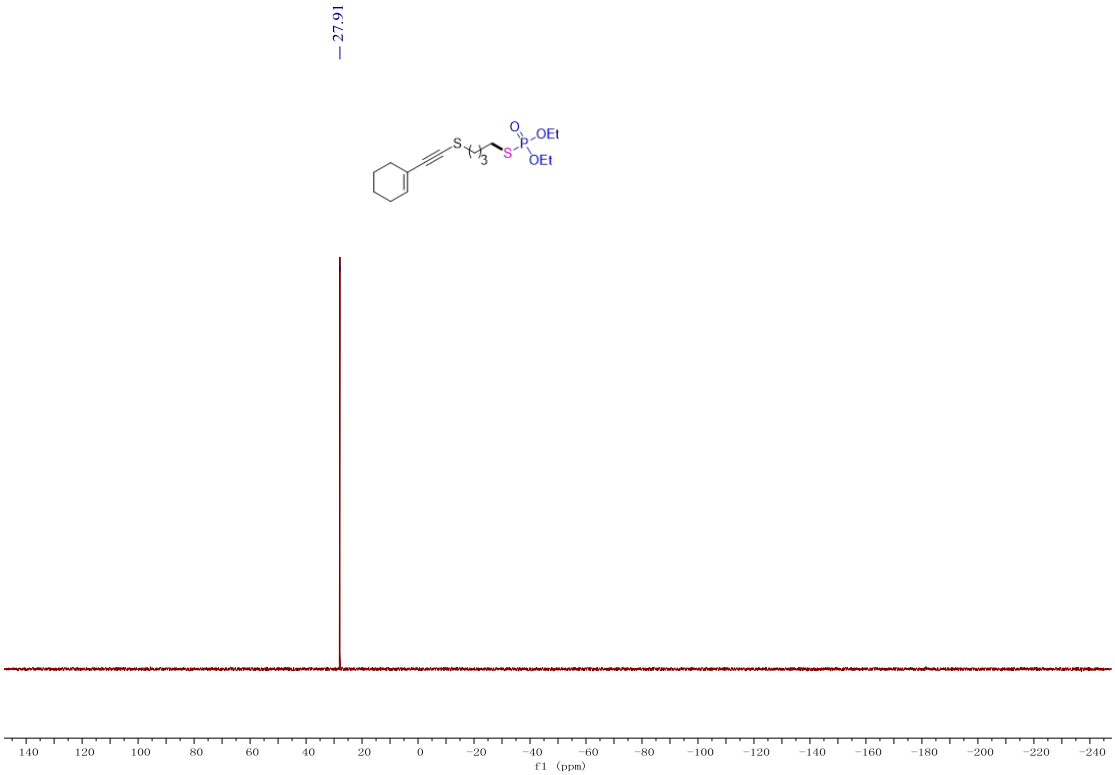
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ia**



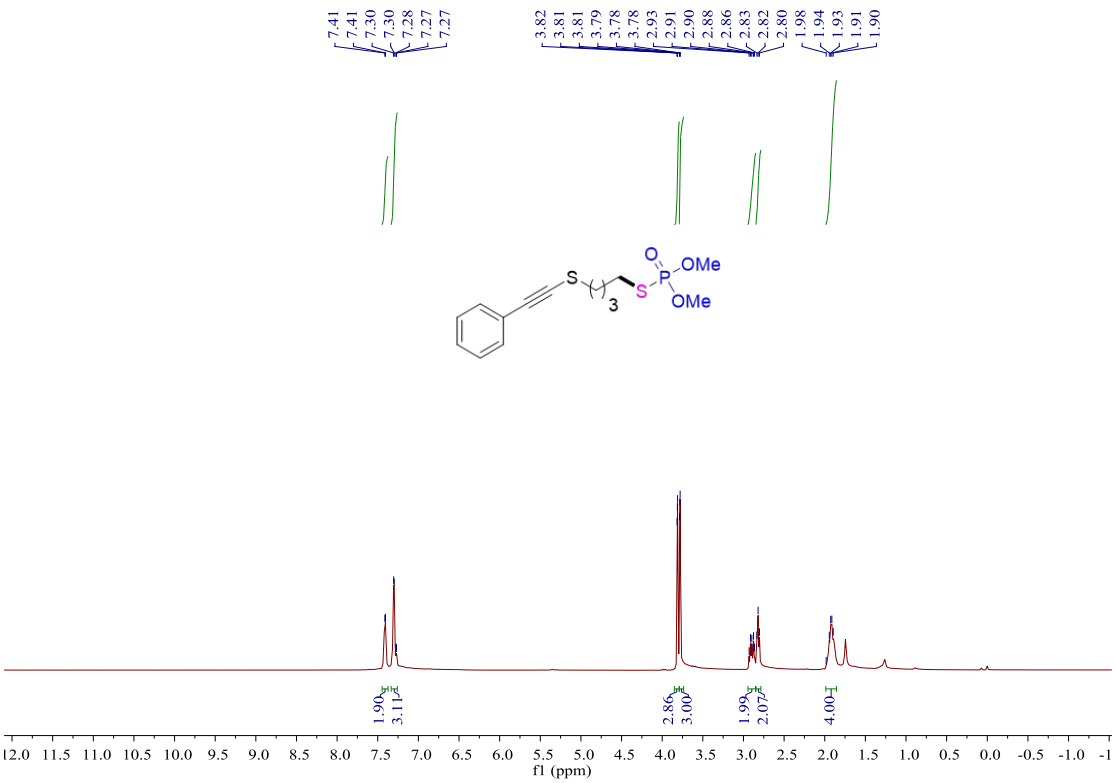
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ja**



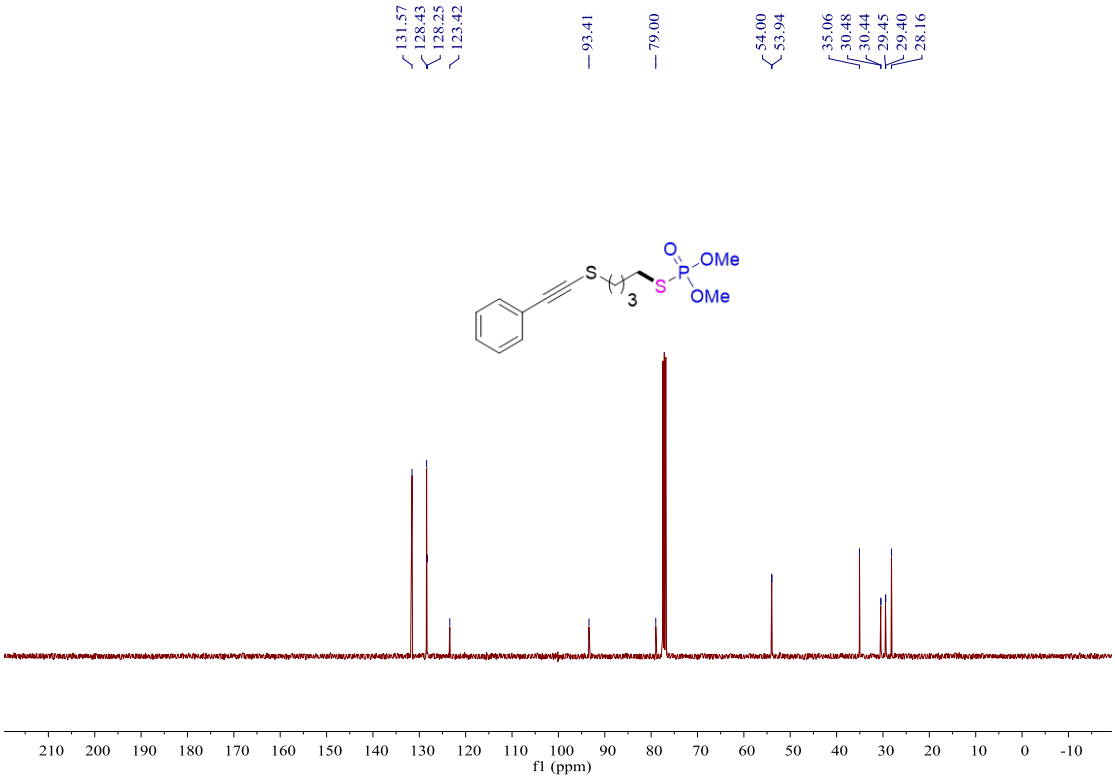
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ja**



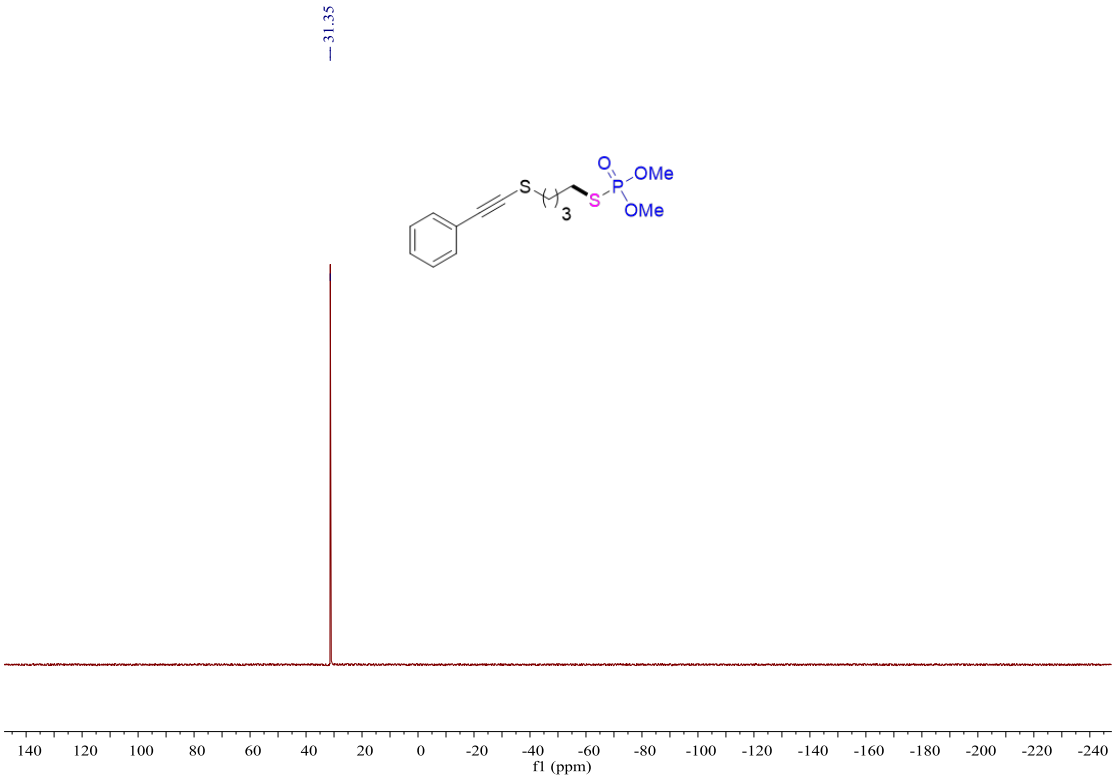
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ja**



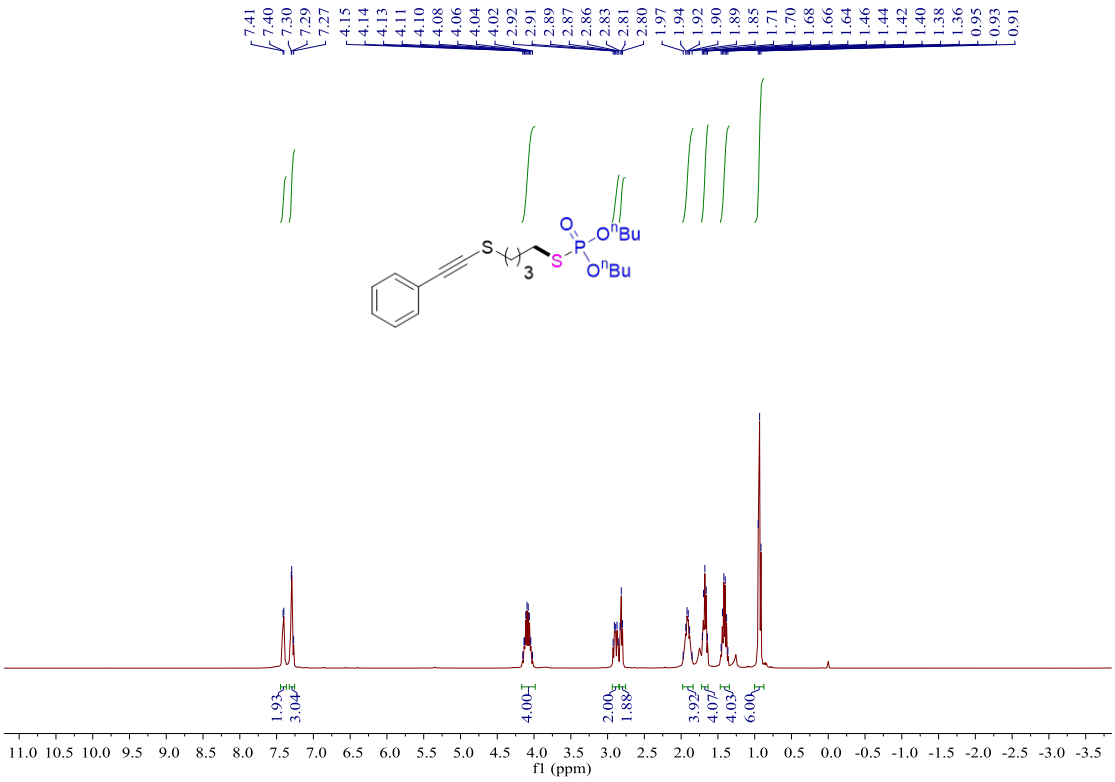
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ab**



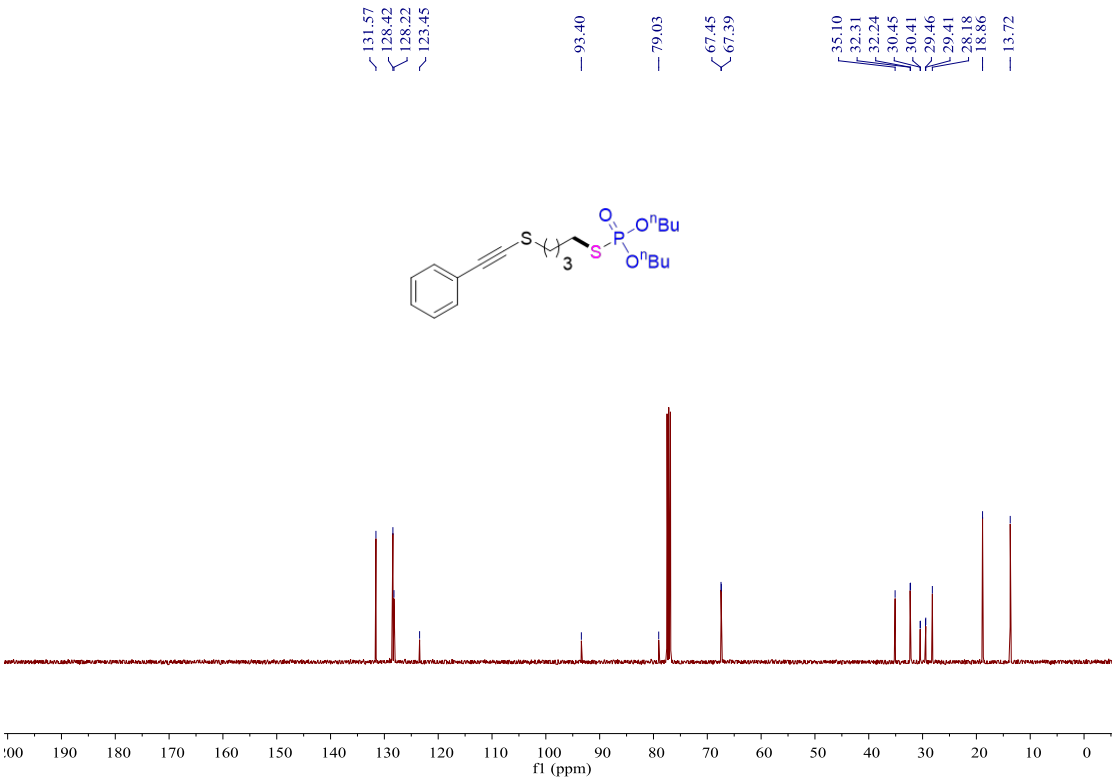
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ab**



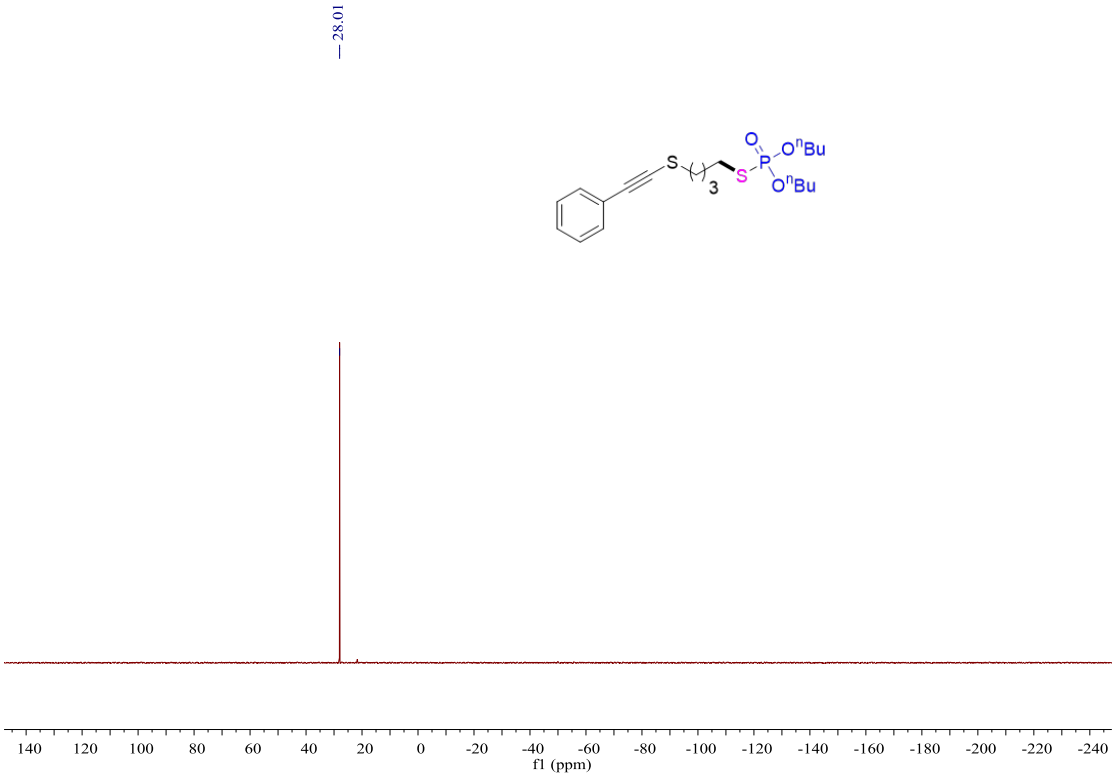
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ab**



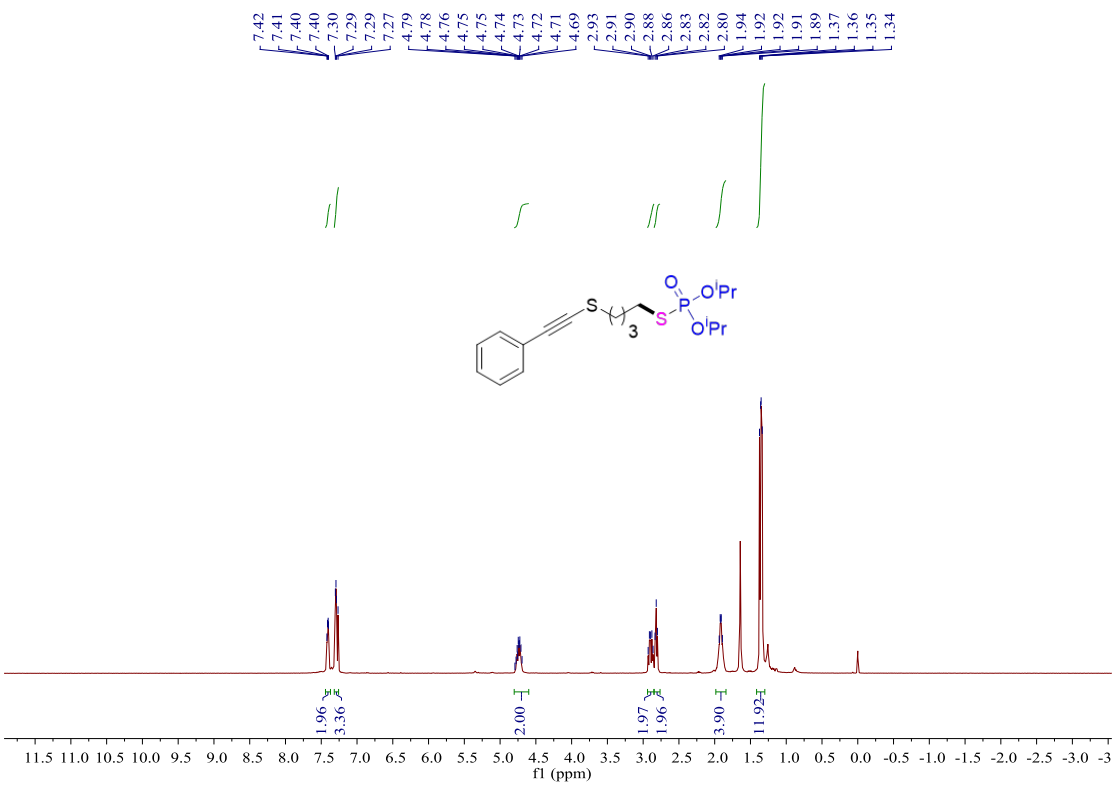
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ac**



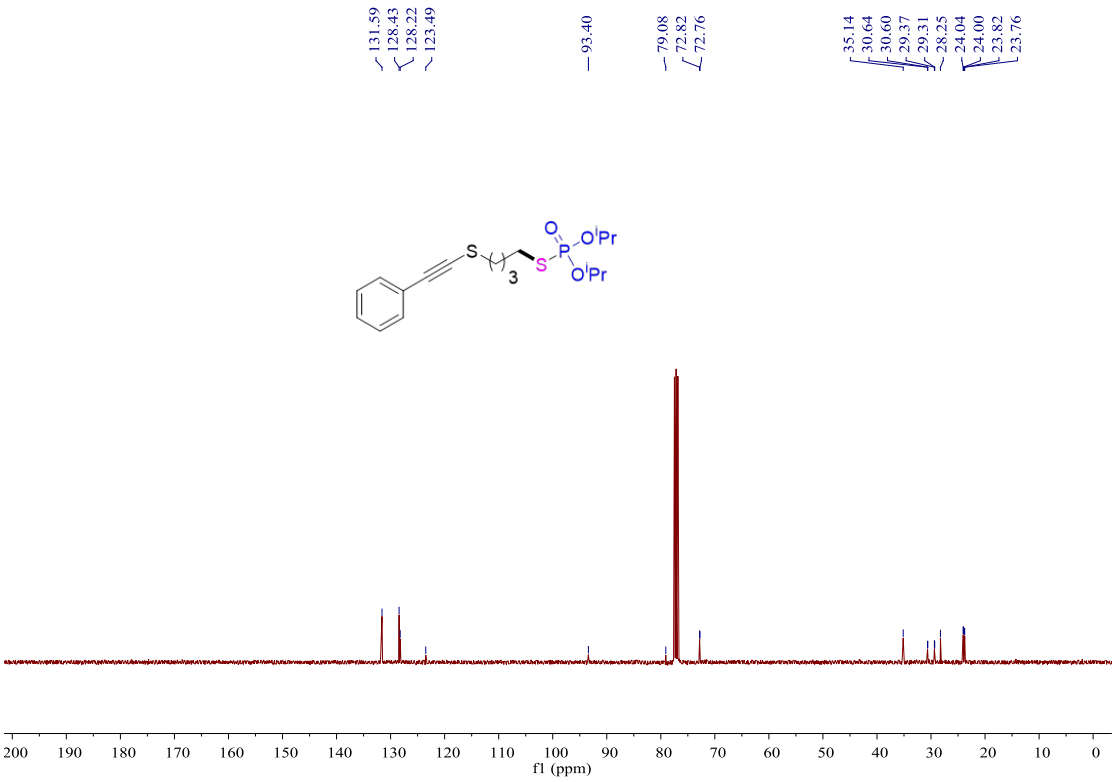
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ac**



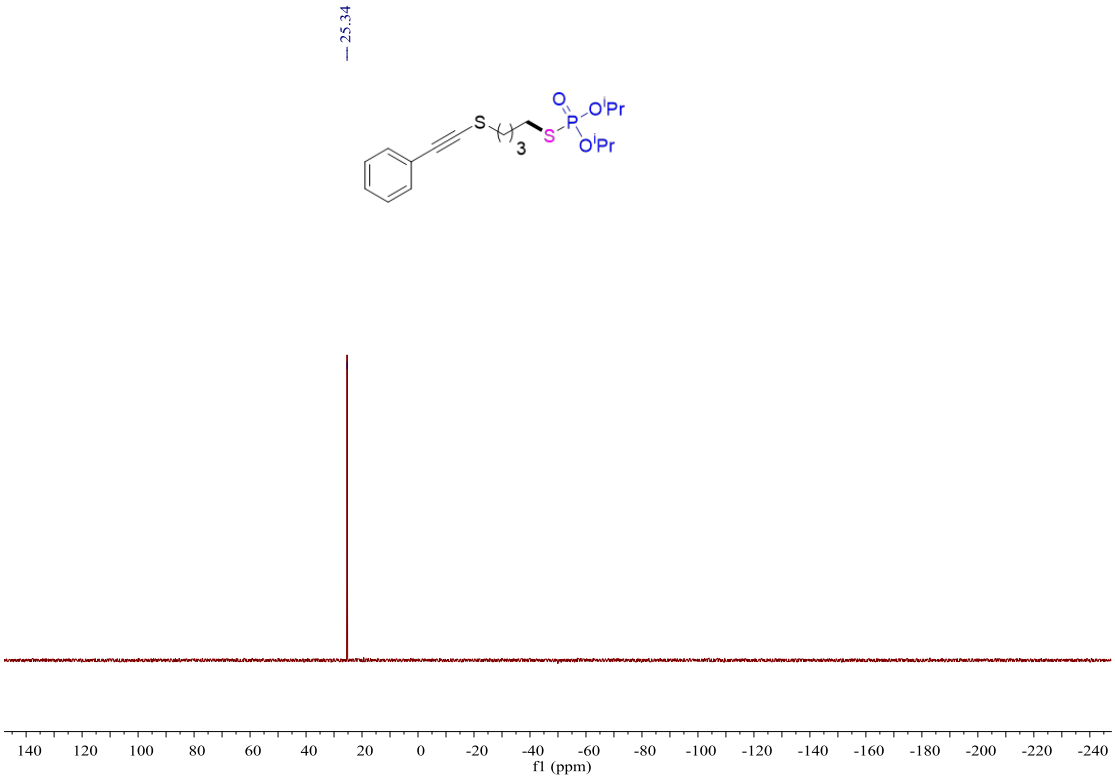
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ac**



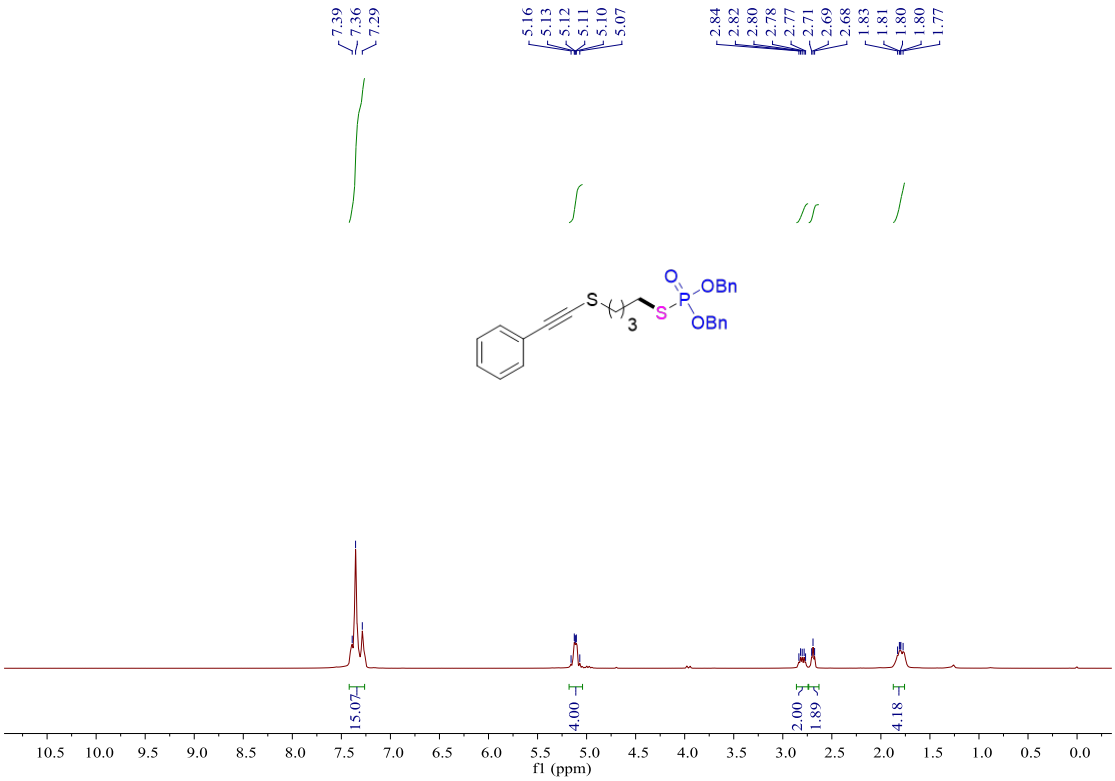
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ad**



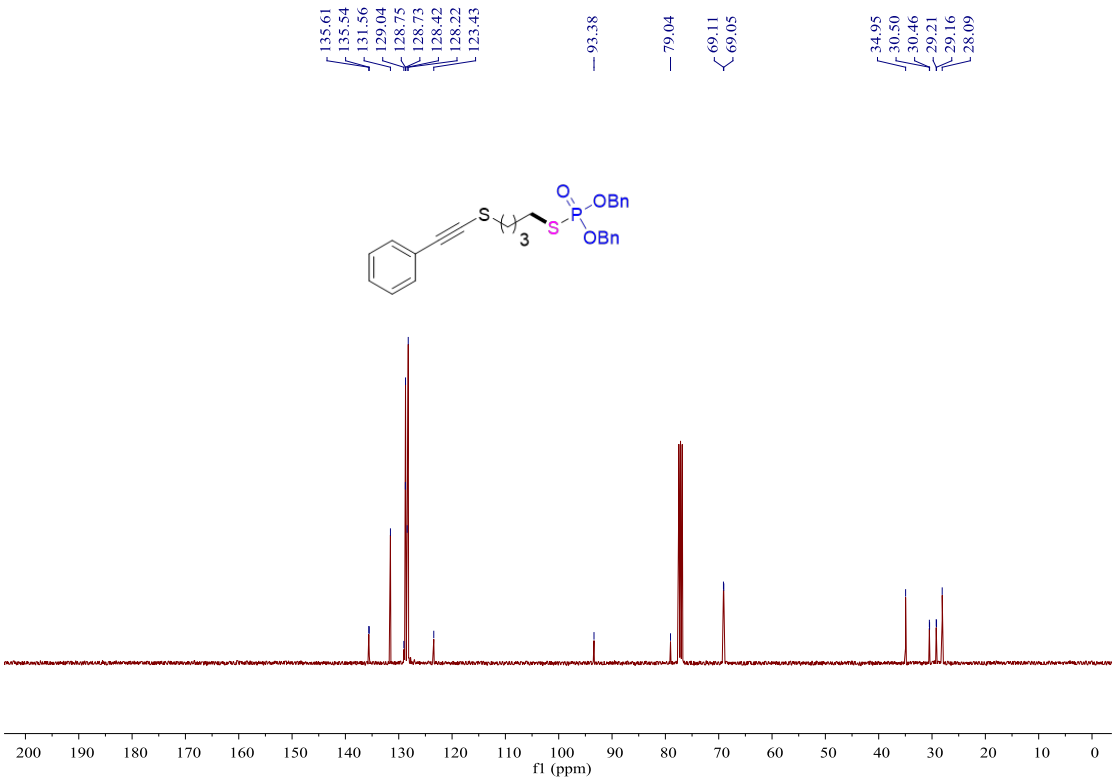
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ad**



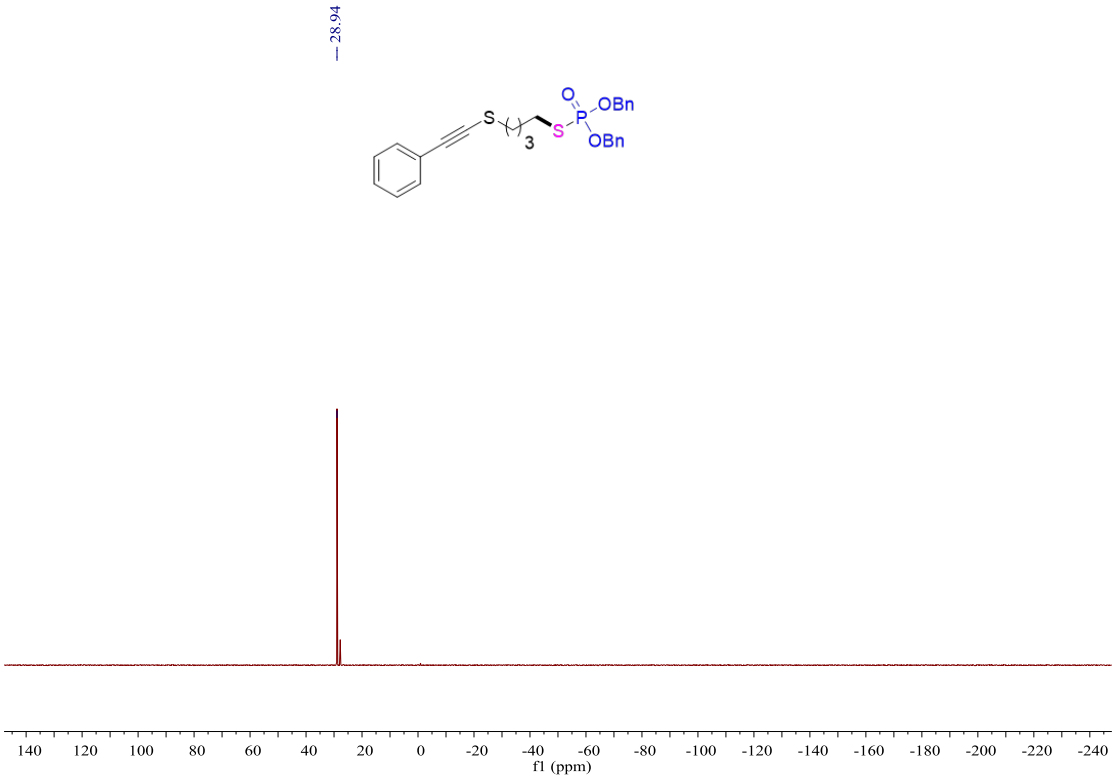
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ad**



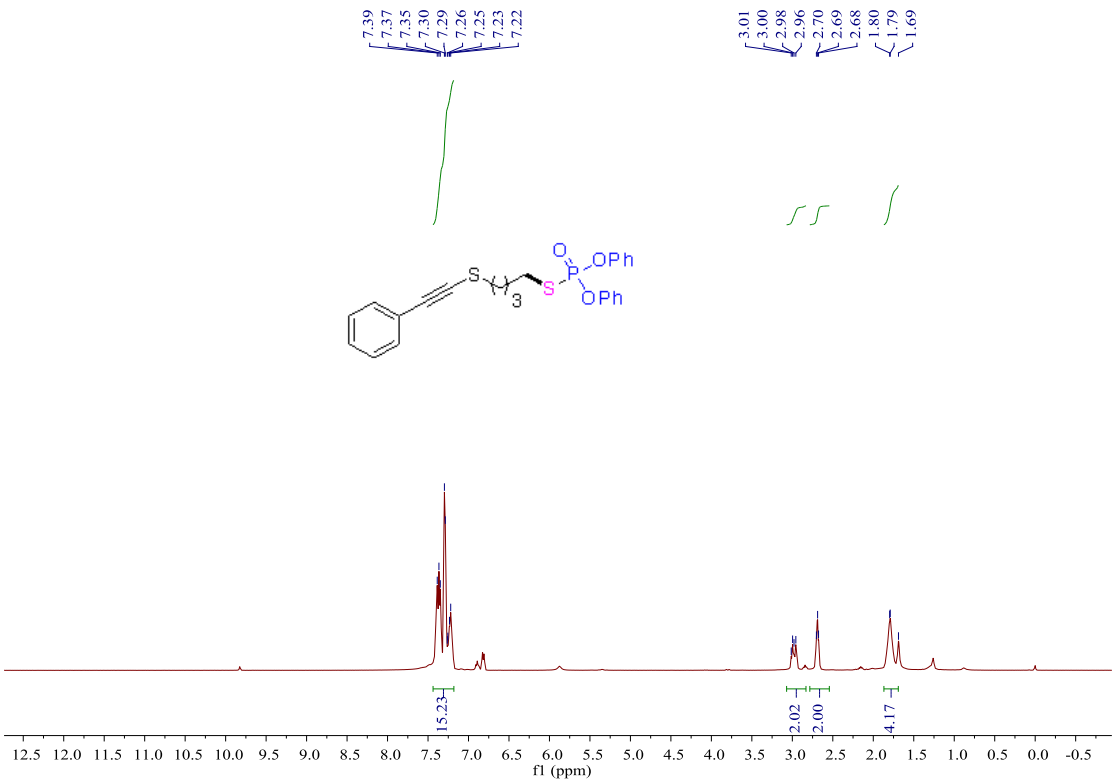
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ae**



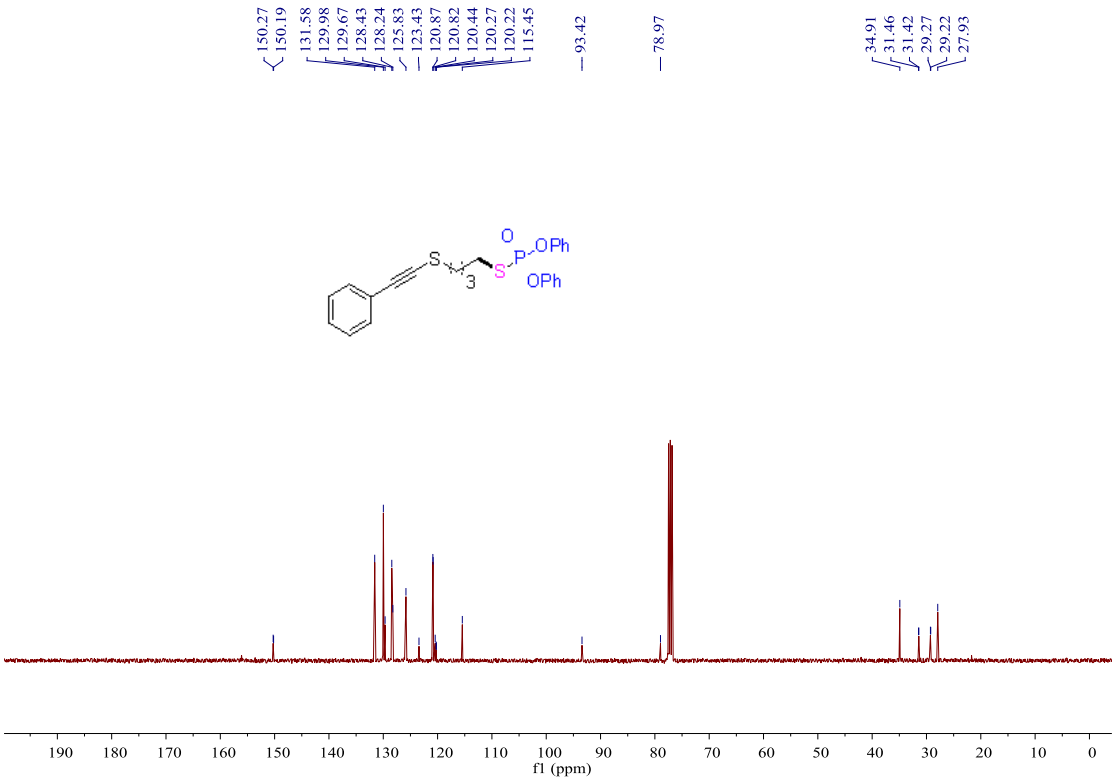
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ae**



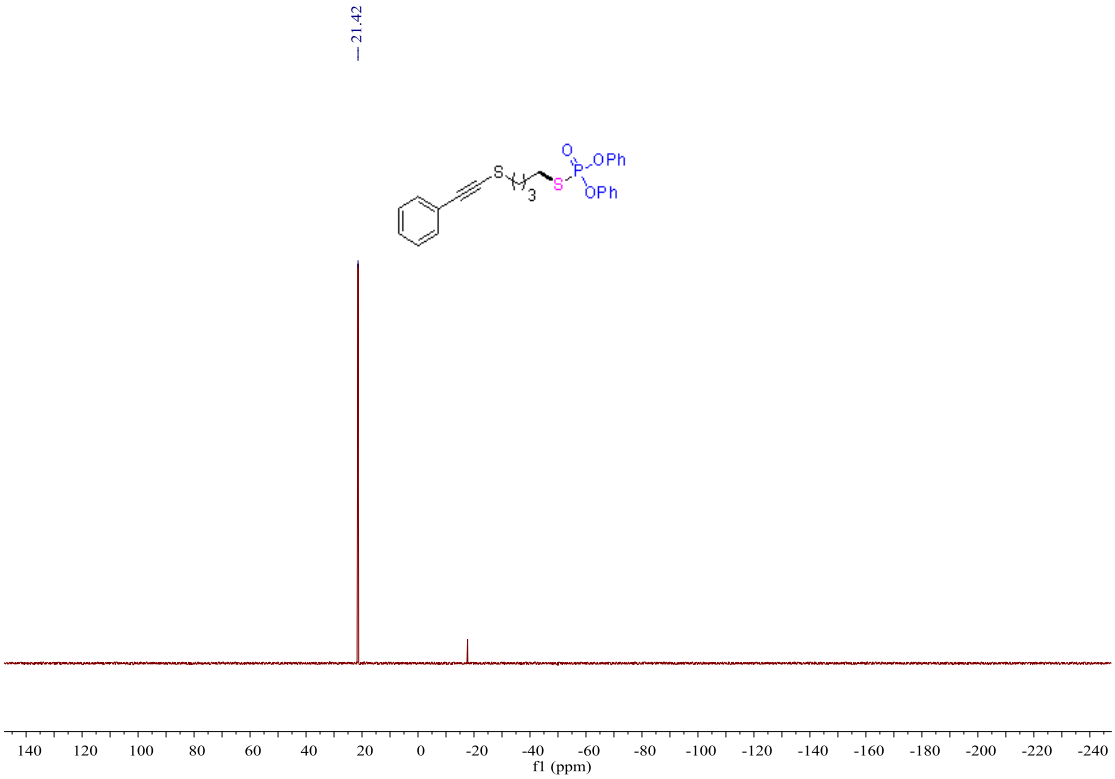
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ae**



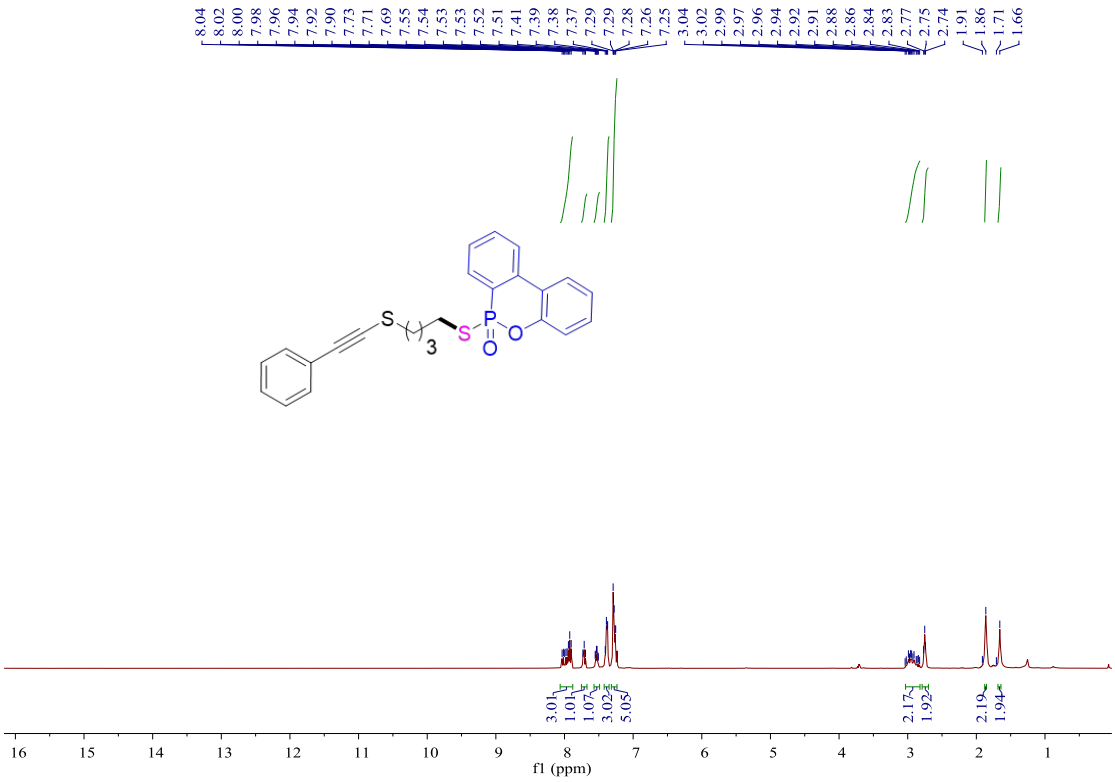
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7af**



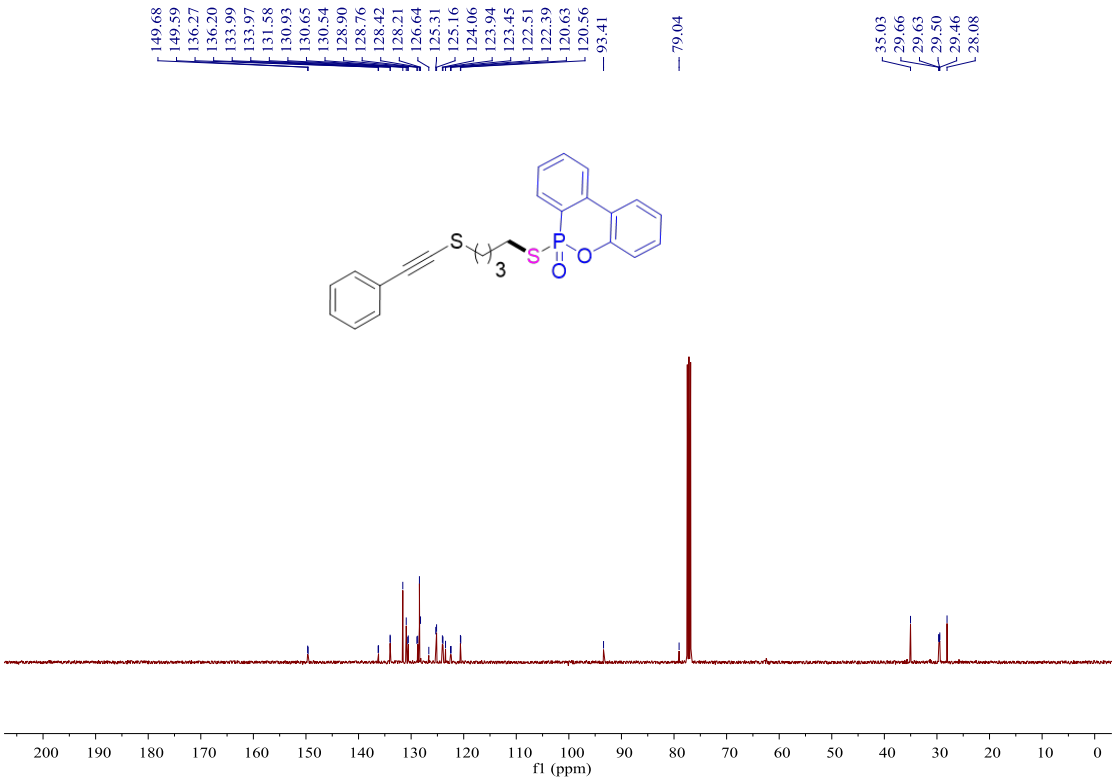
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7af**



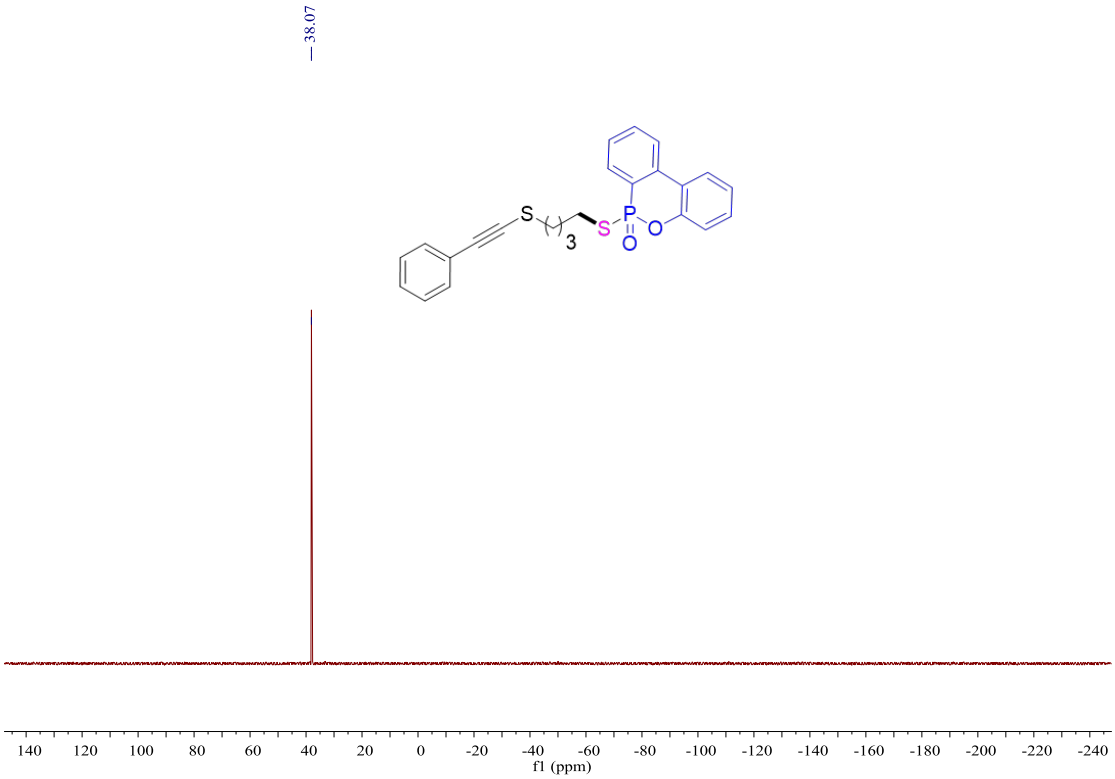
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7af**



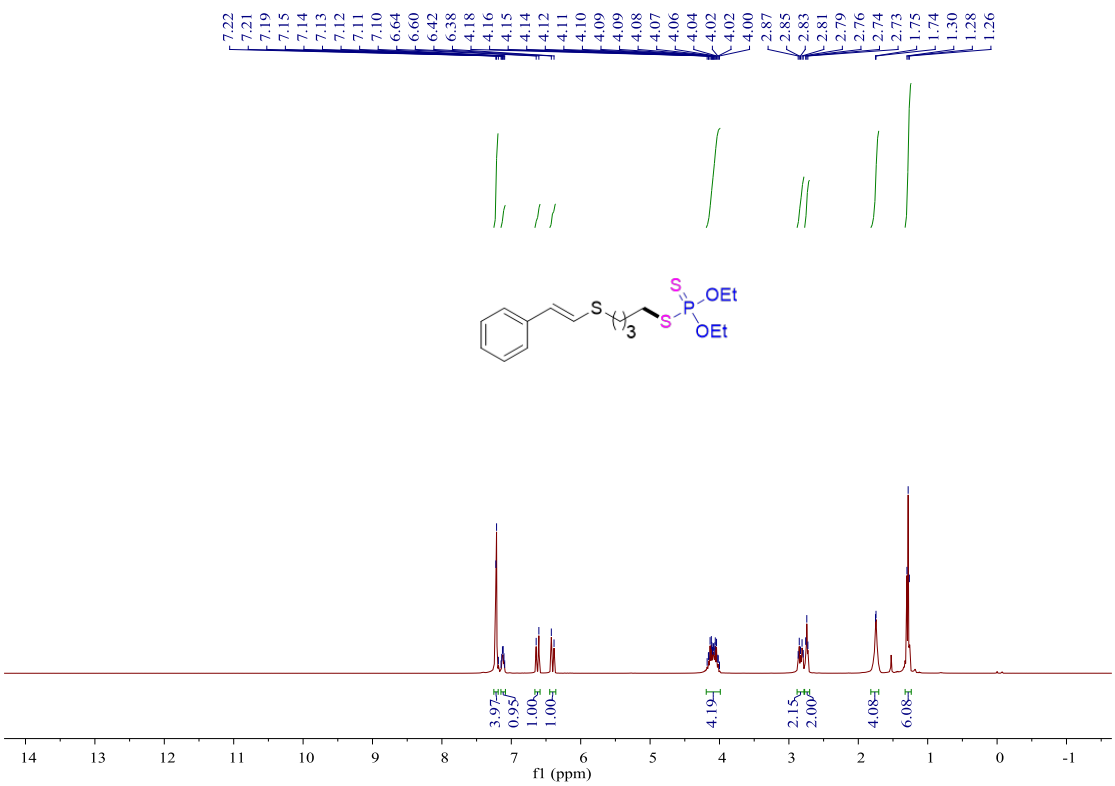
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **7ag**



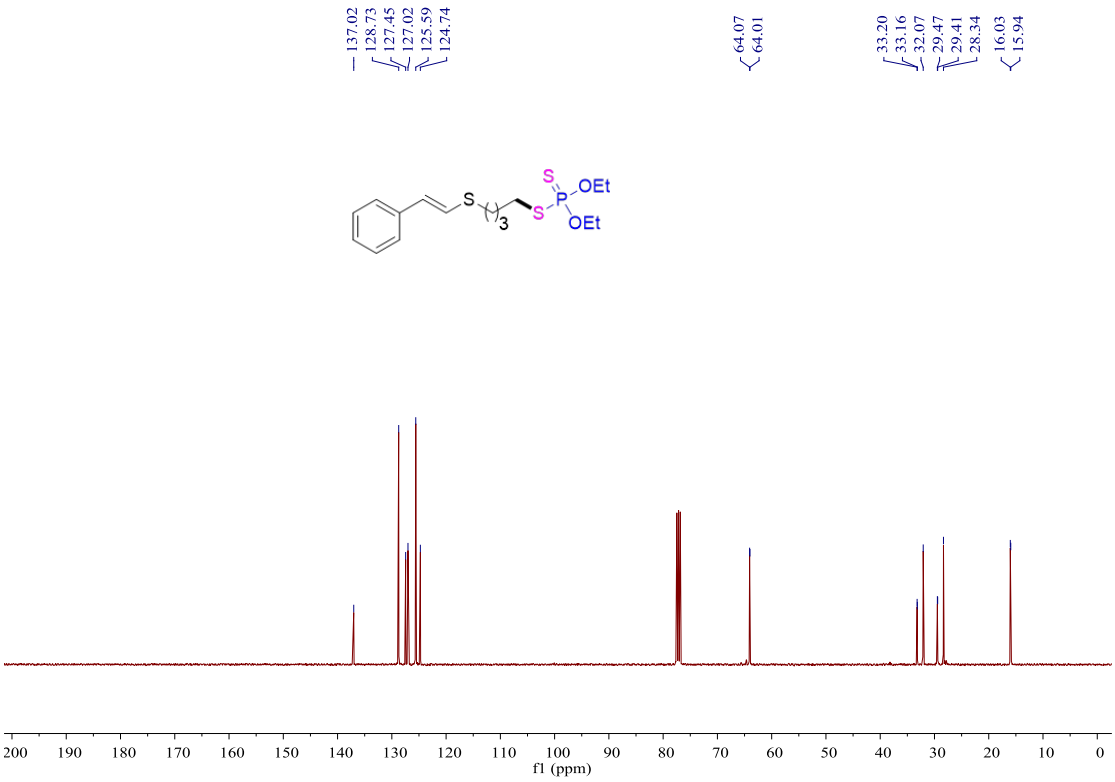
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **7ag**



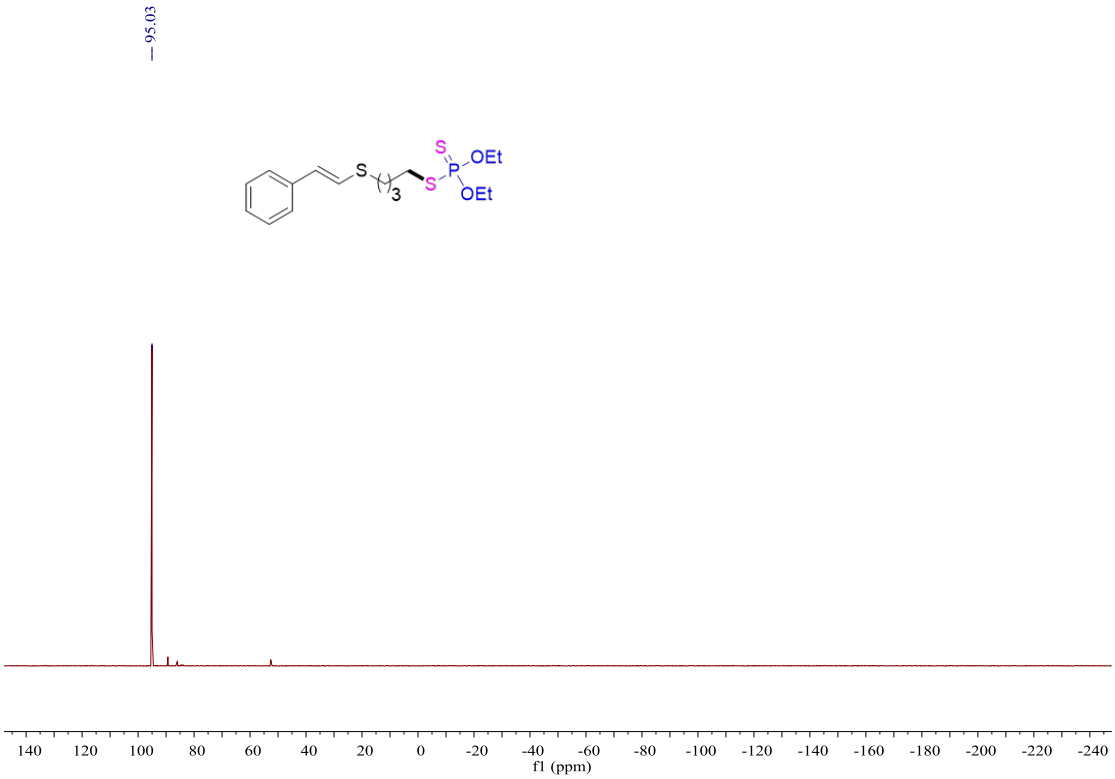
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **7ag**



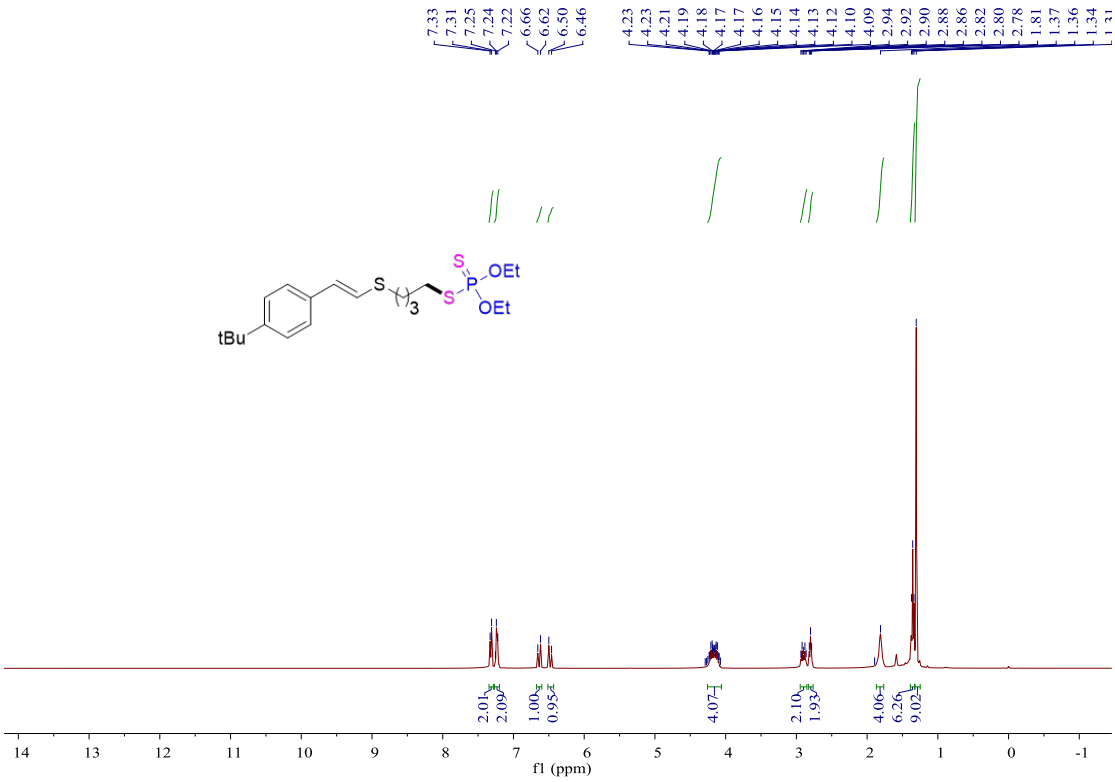
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9a**



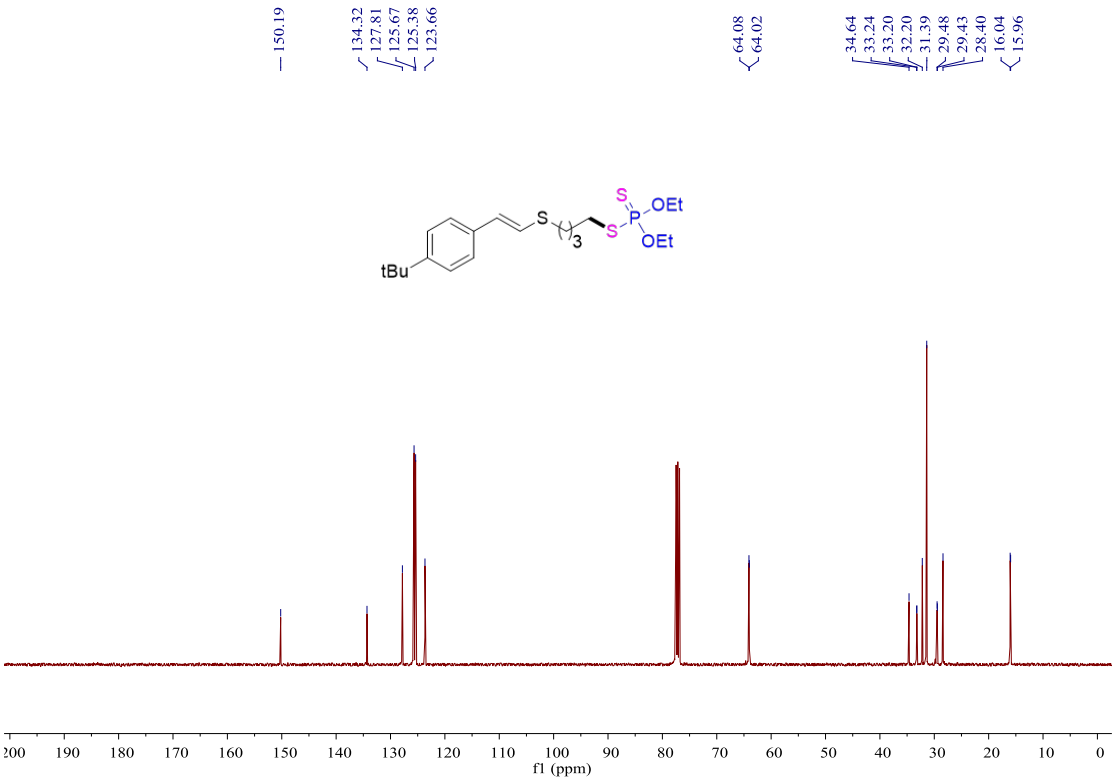
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9a**



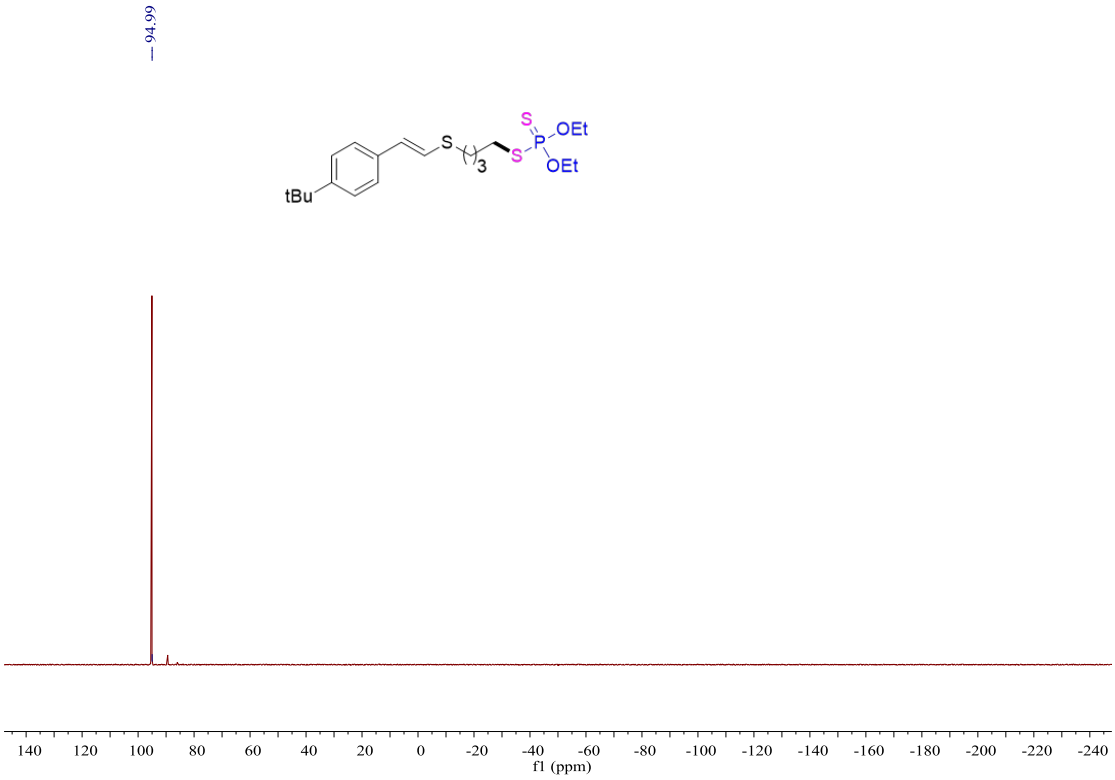
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9a**



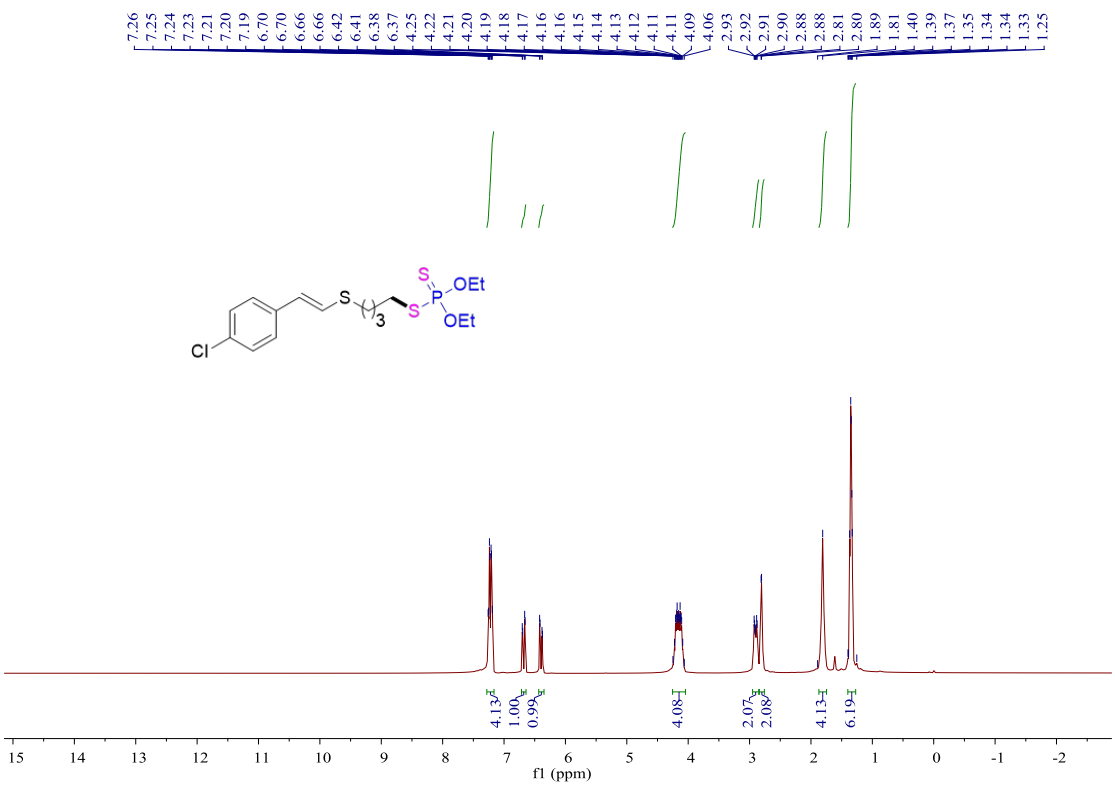
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9b**



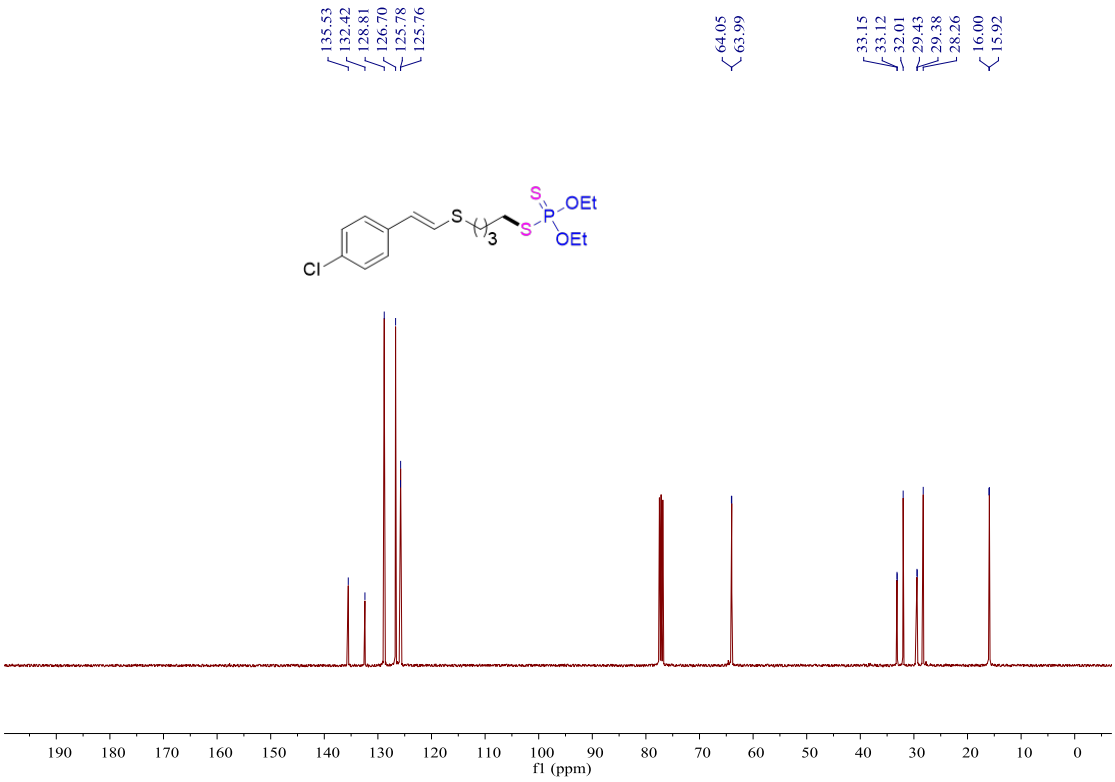
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9b**



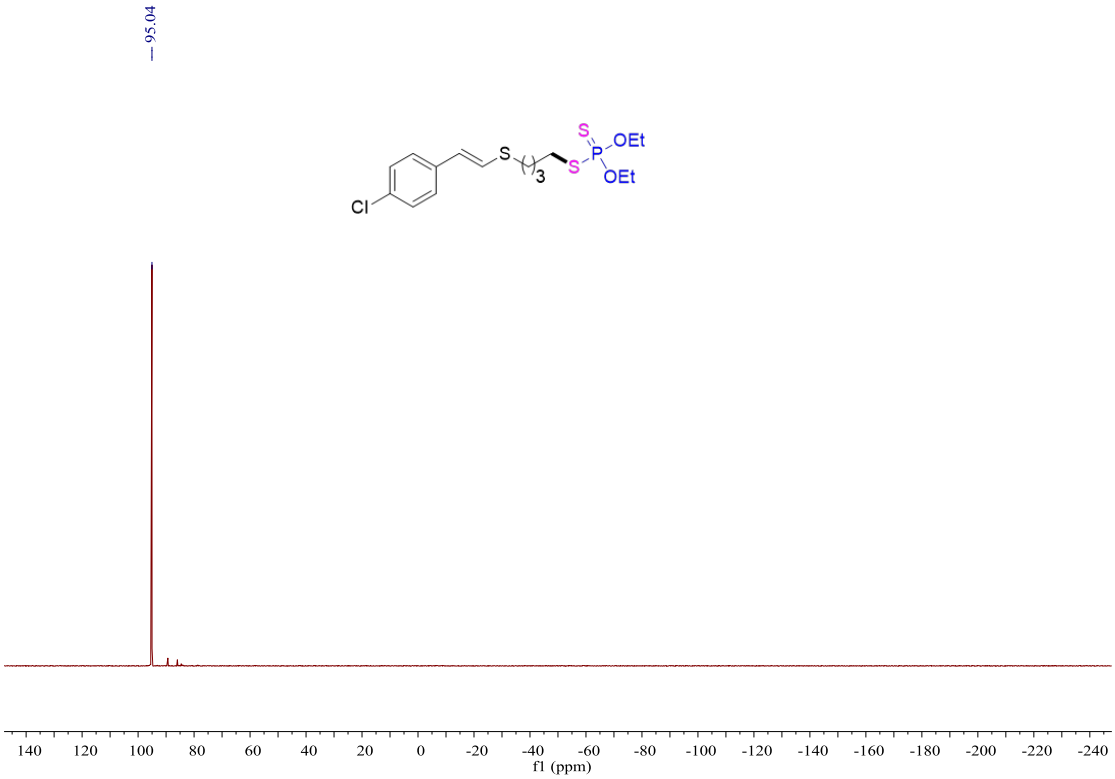
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9b**



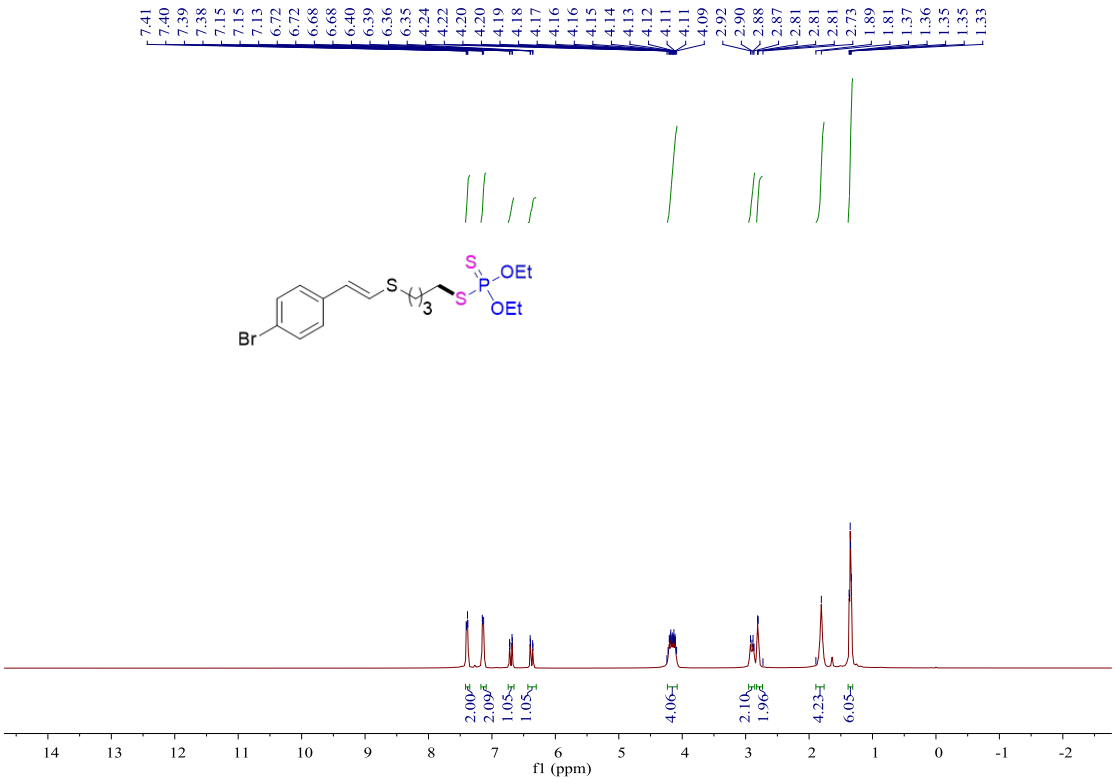
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9c**



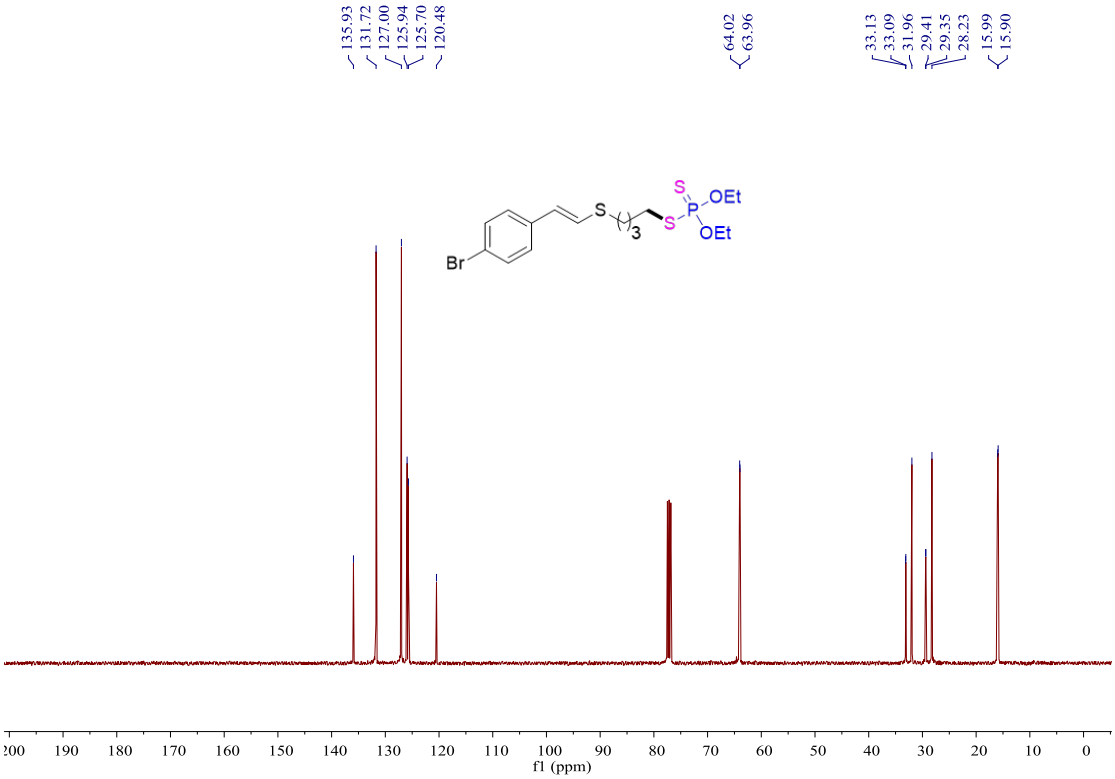
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9c**



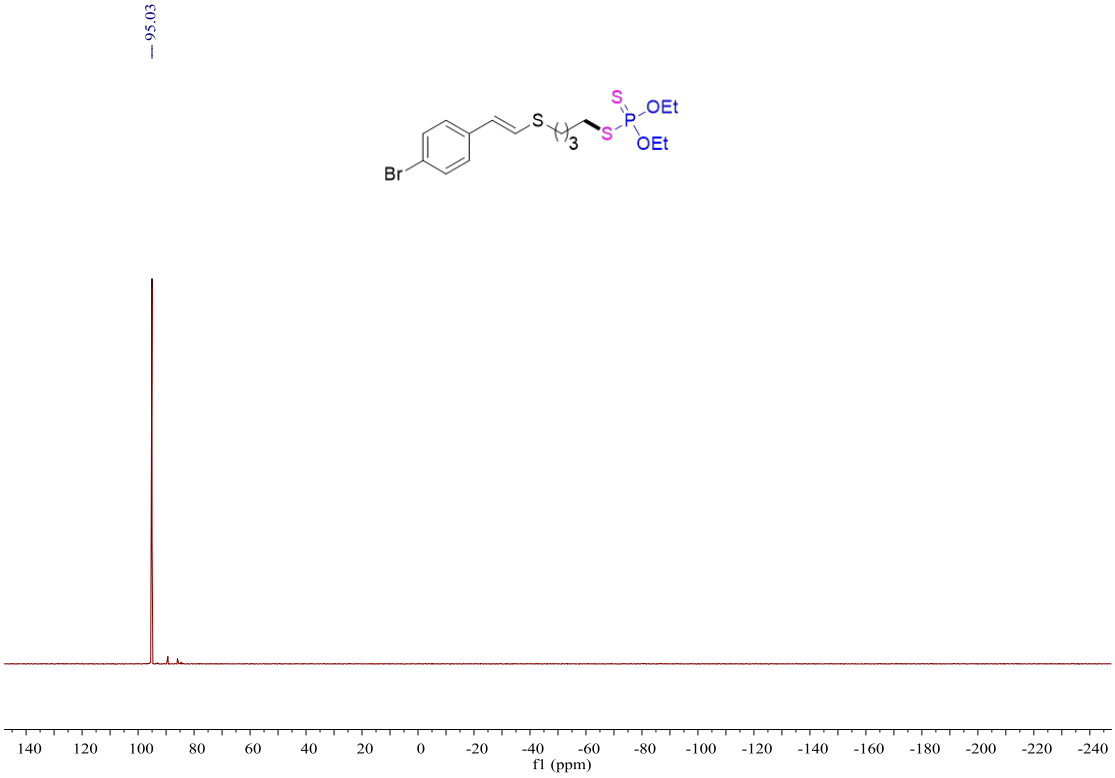
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9c**



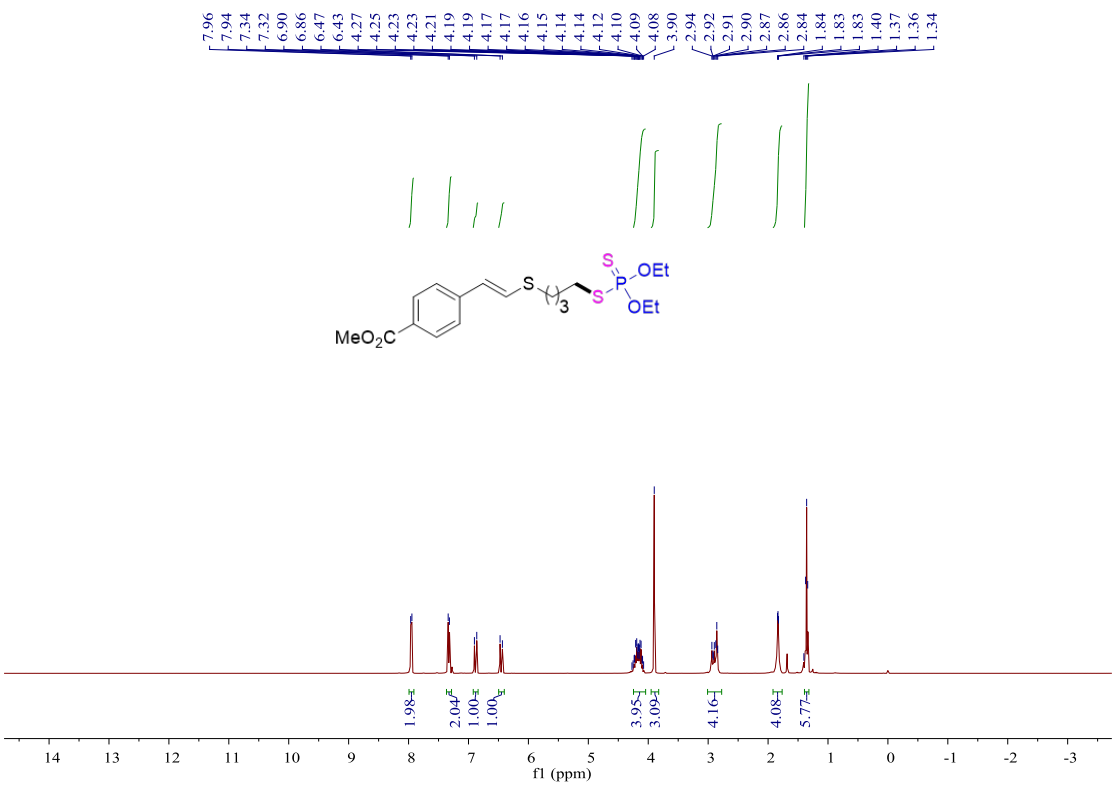
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9d**



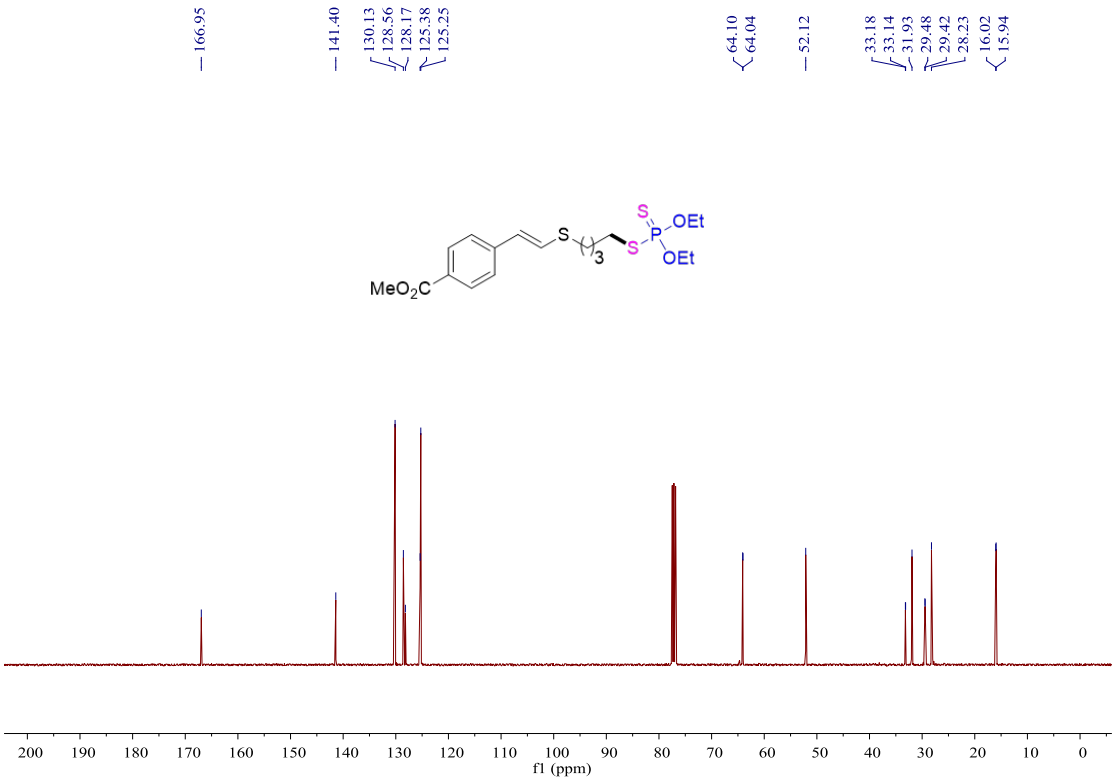
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9d**



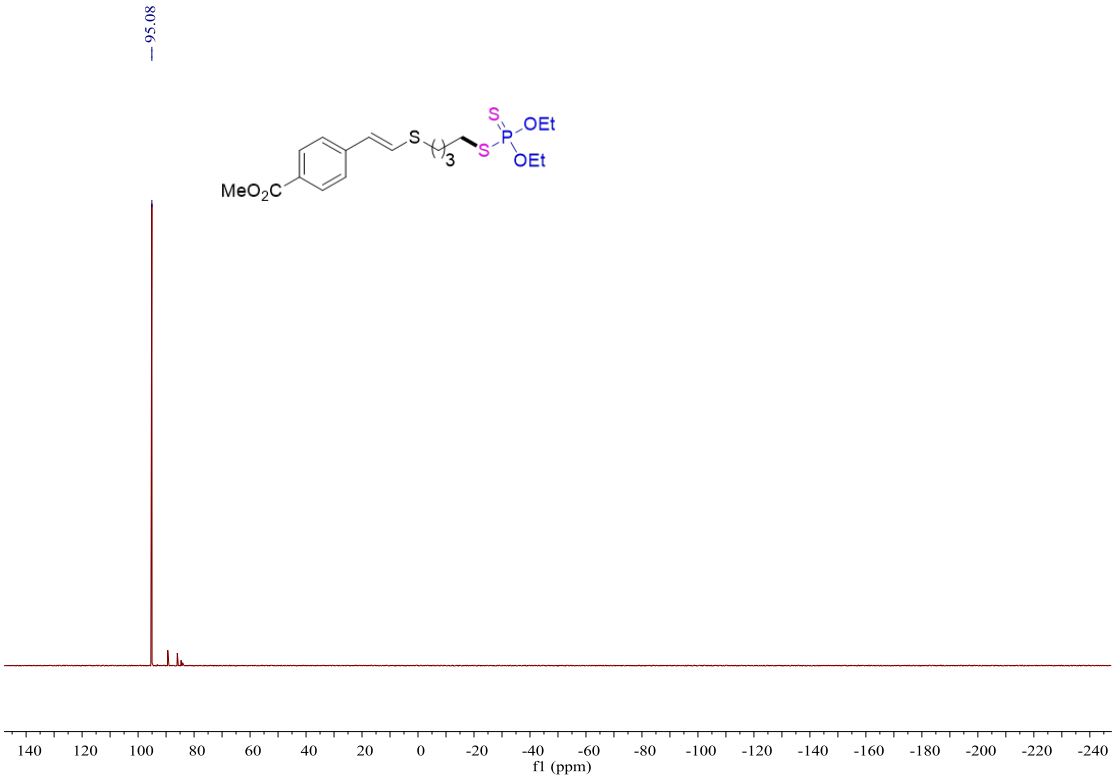
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9d**



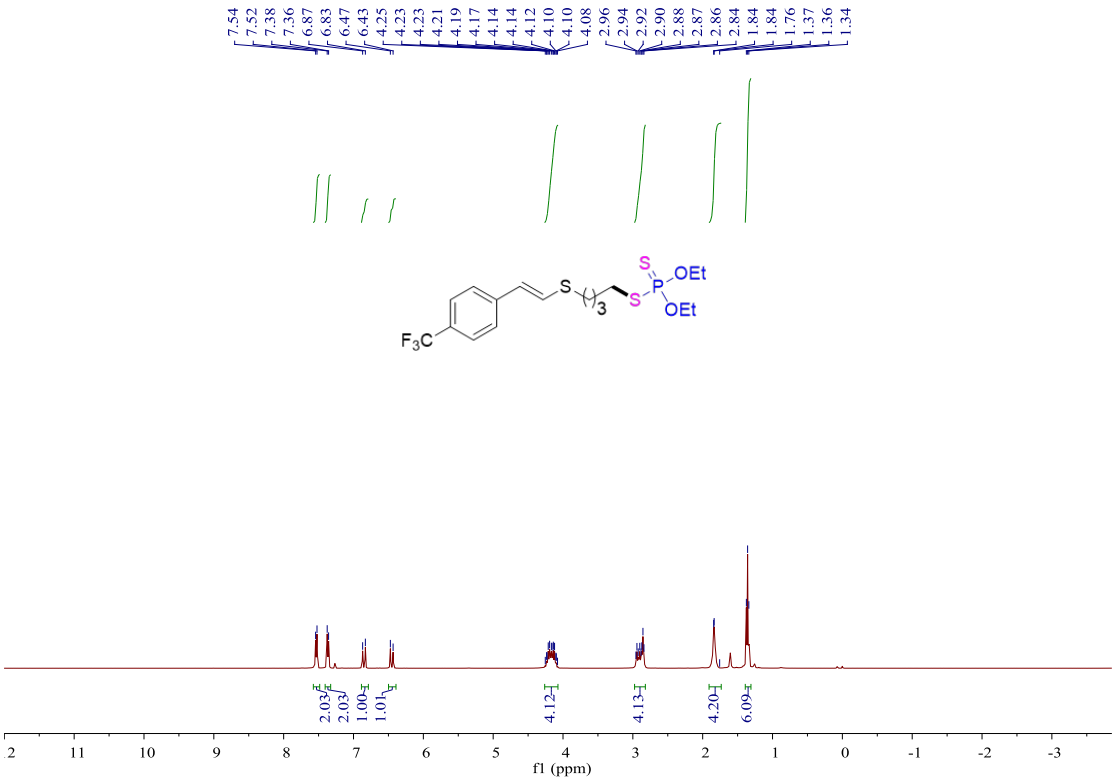
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9e**



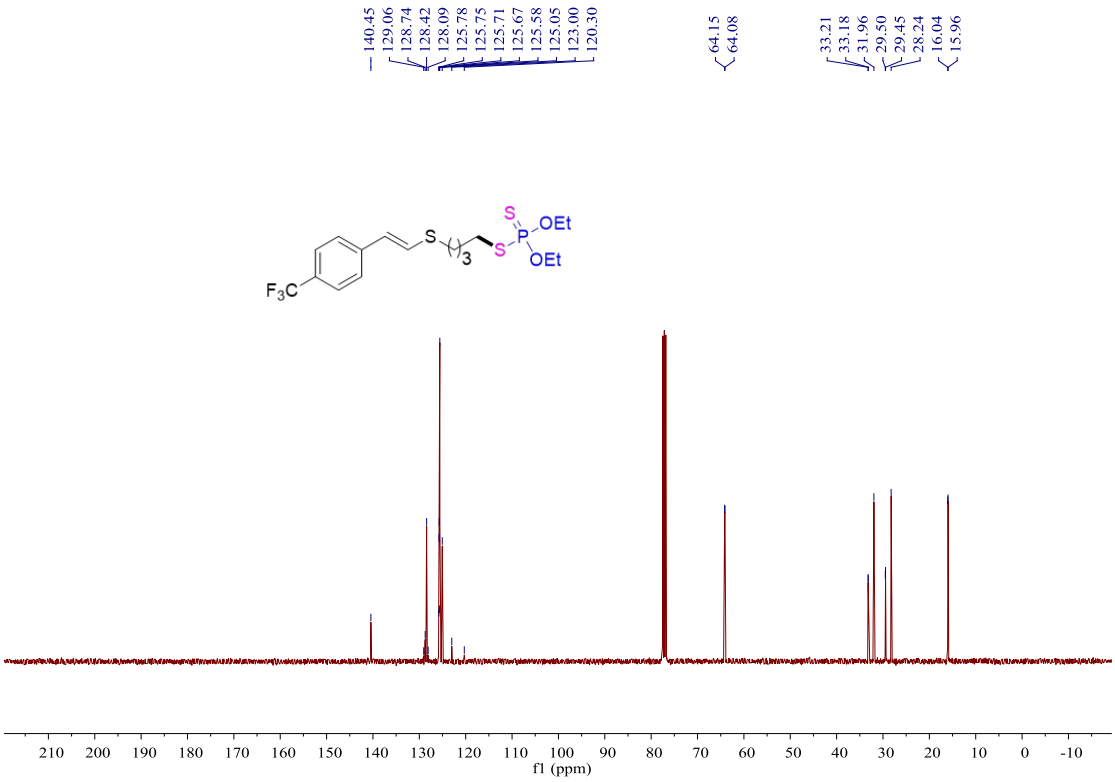
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9e**



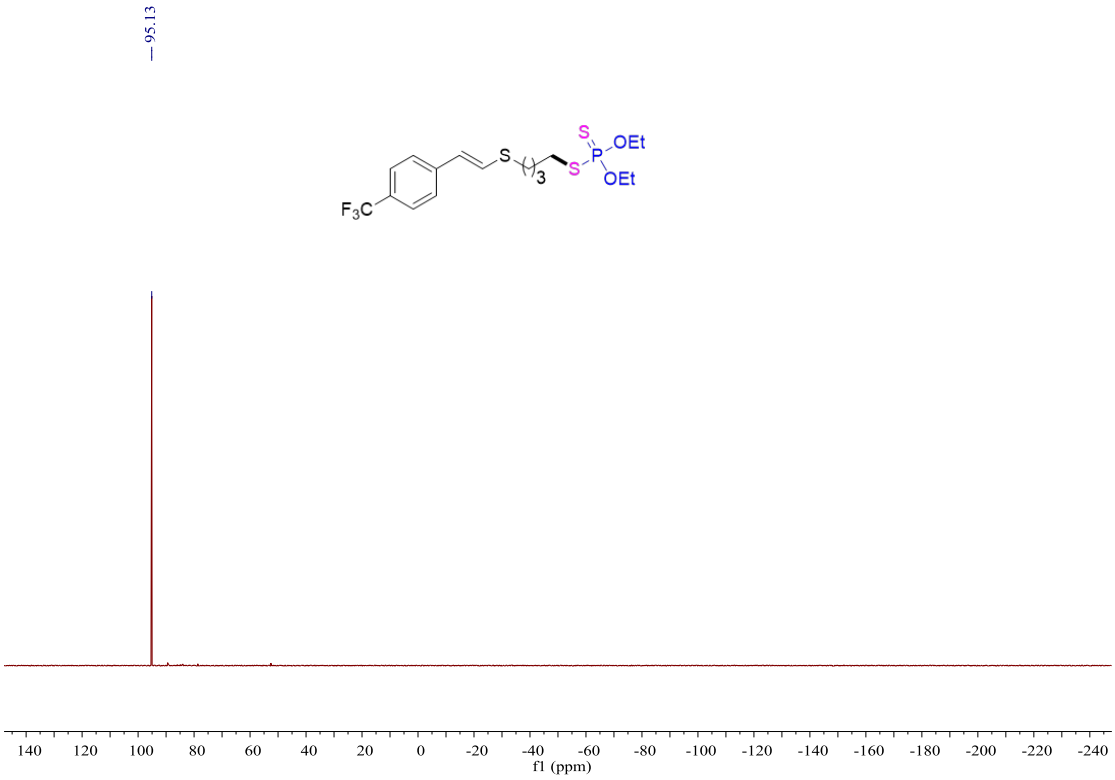
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9e**



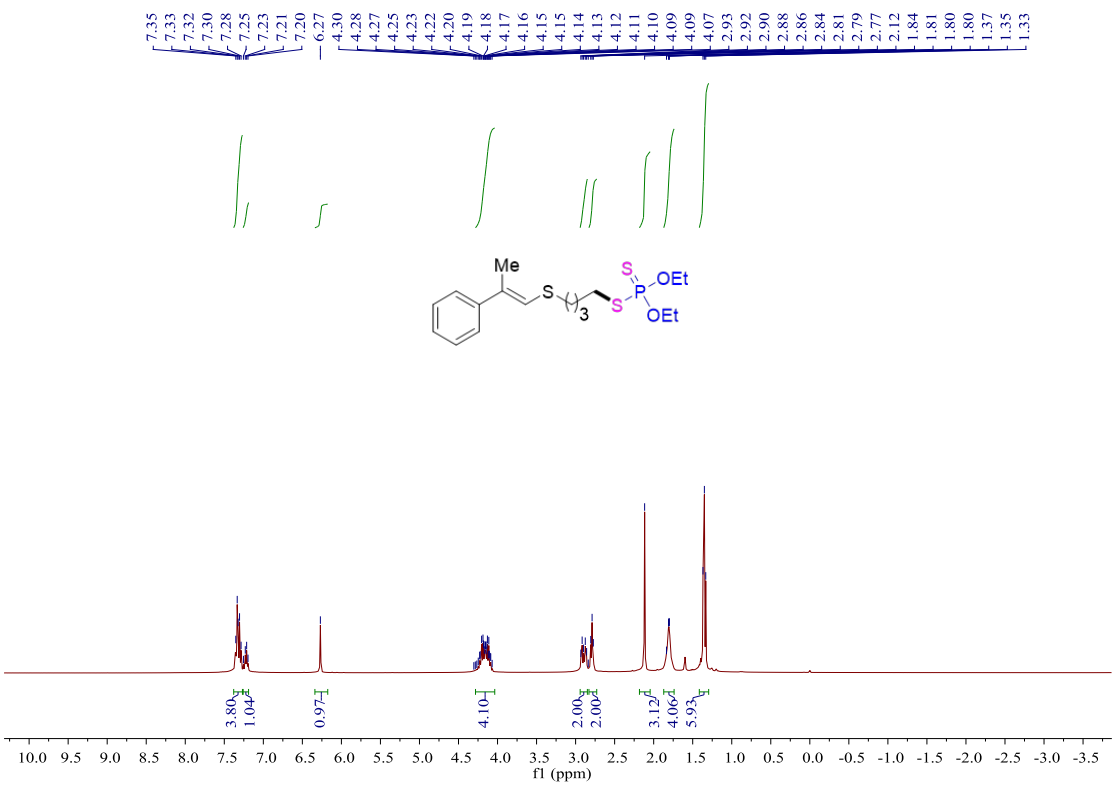
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9f**



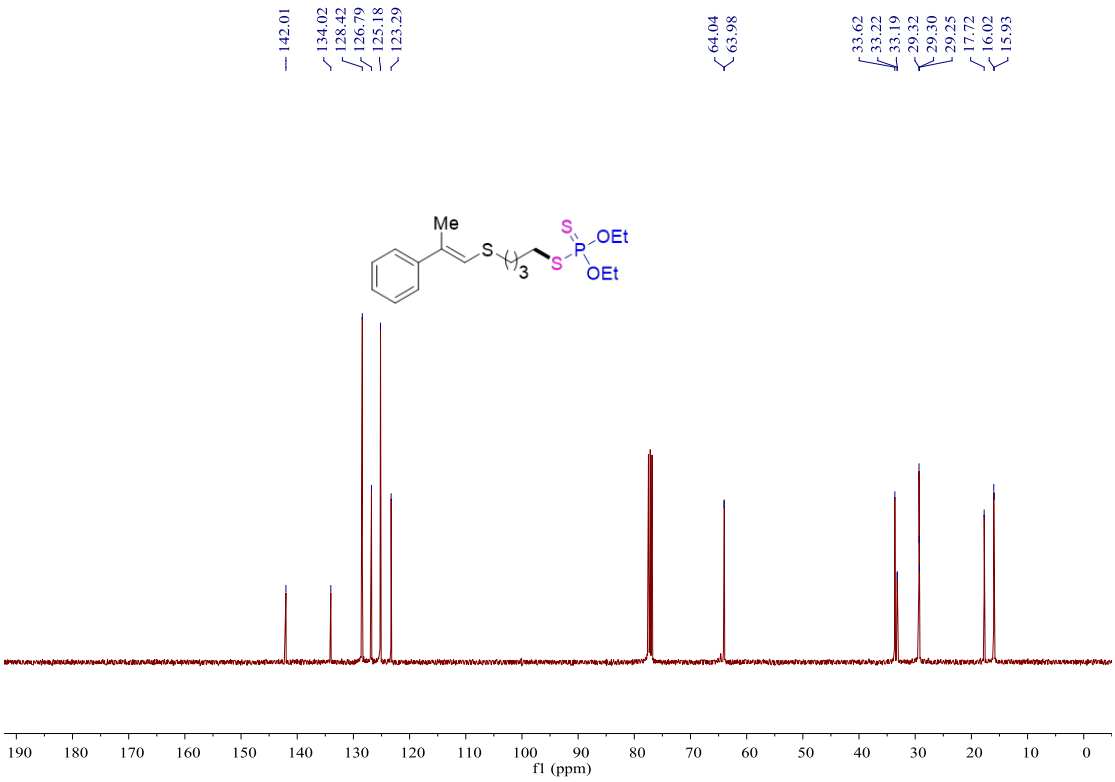
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9f**



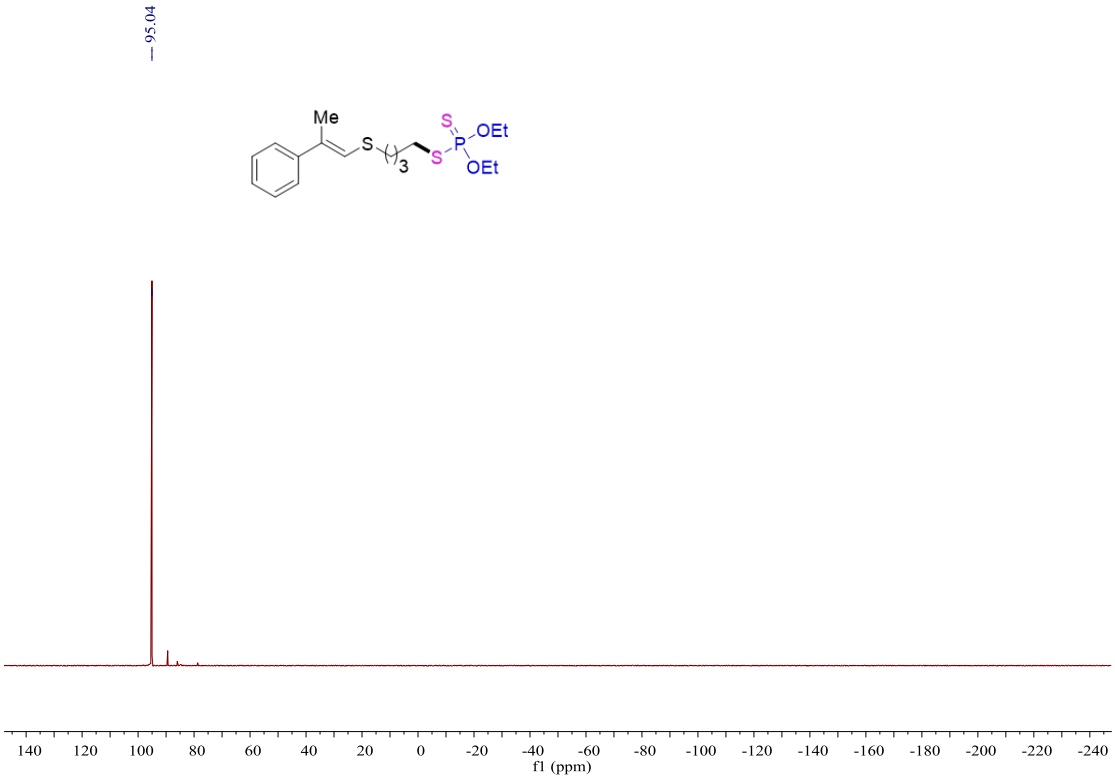
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9f**



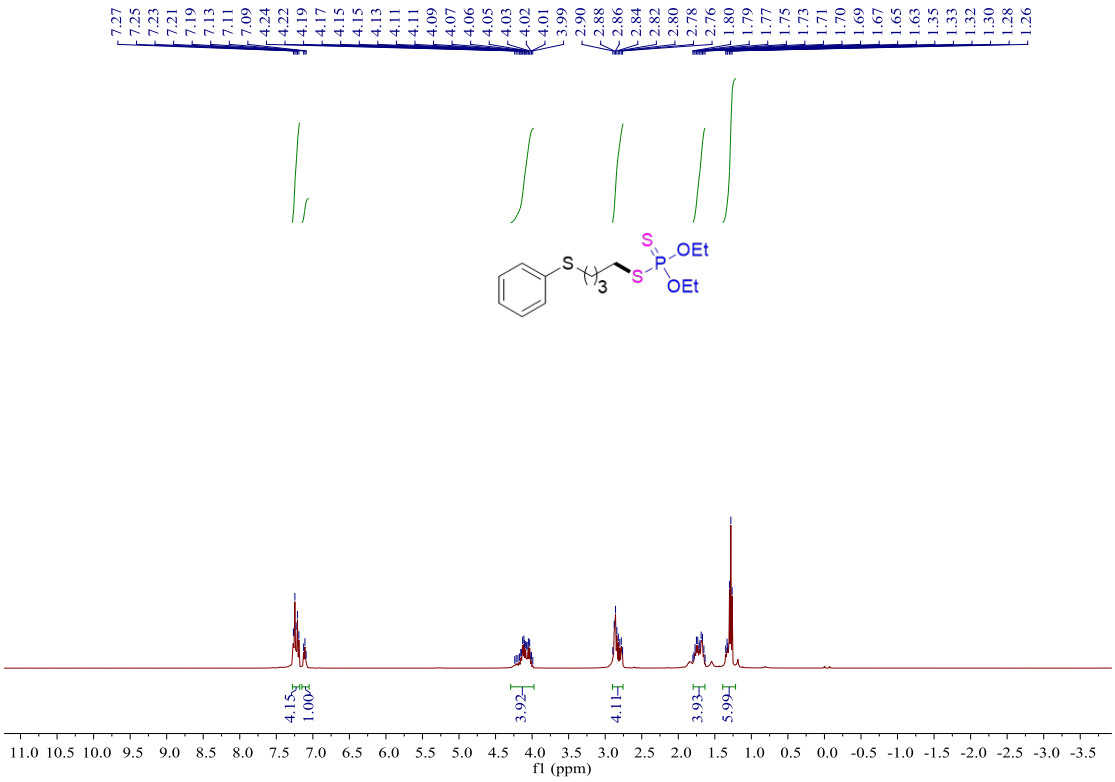
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9g**



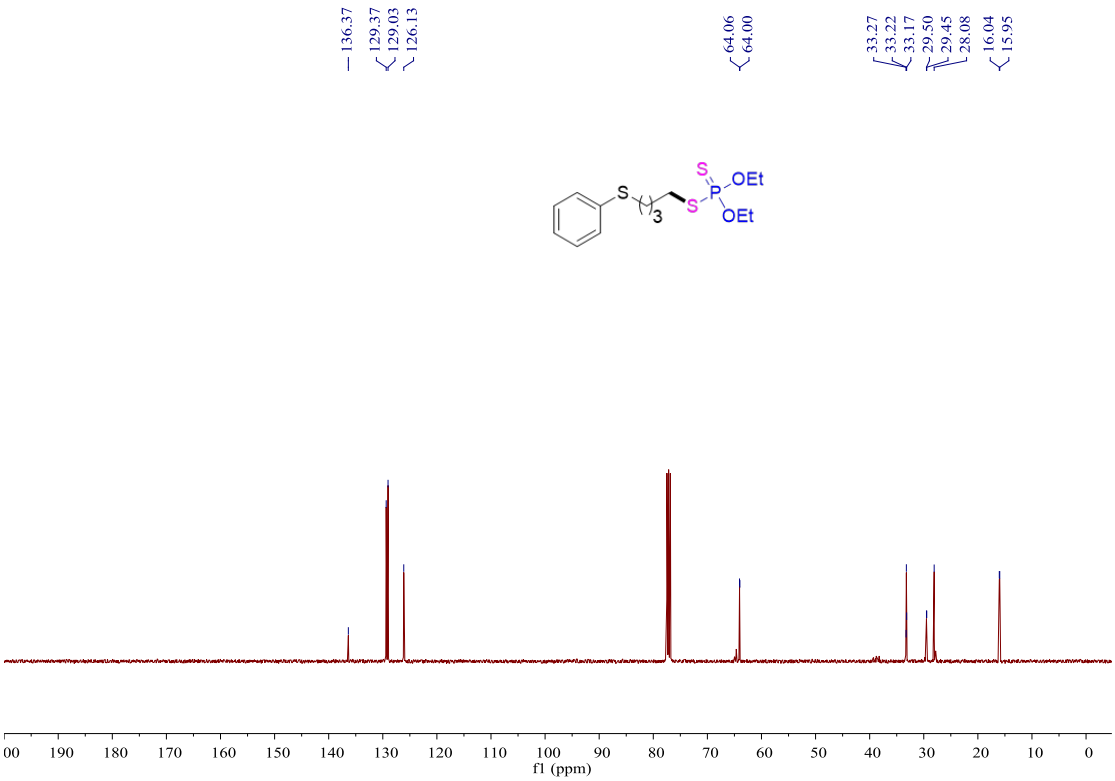
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9g**



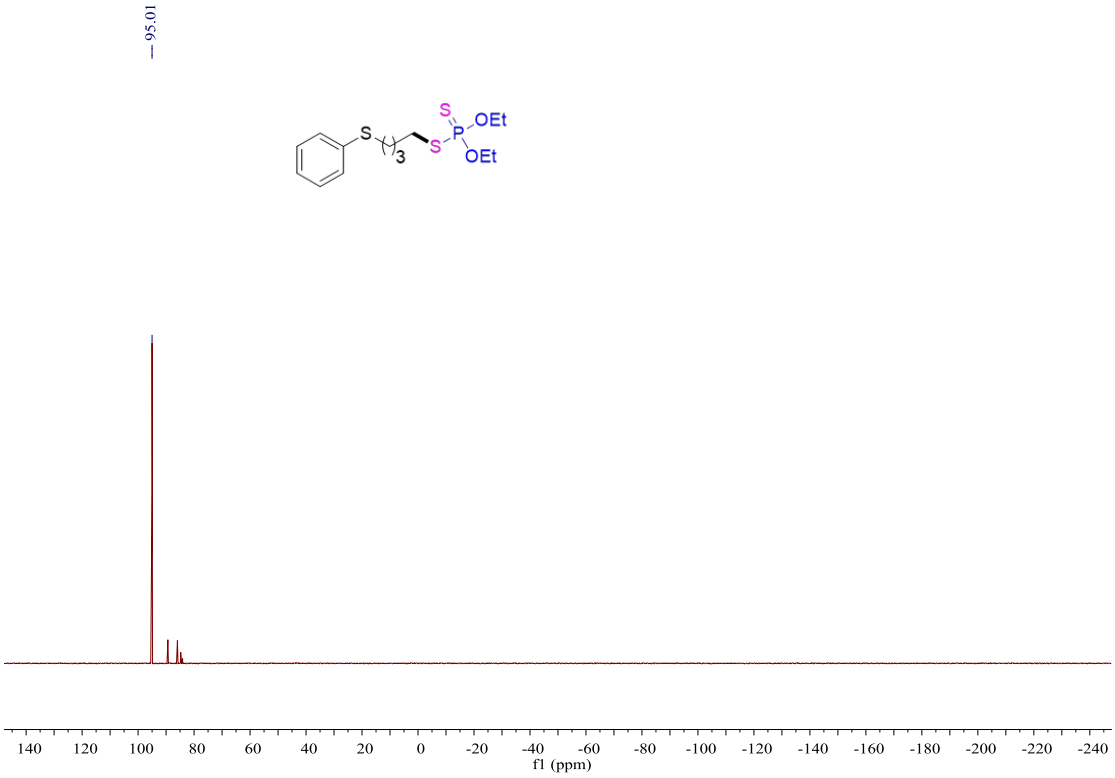
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9g**



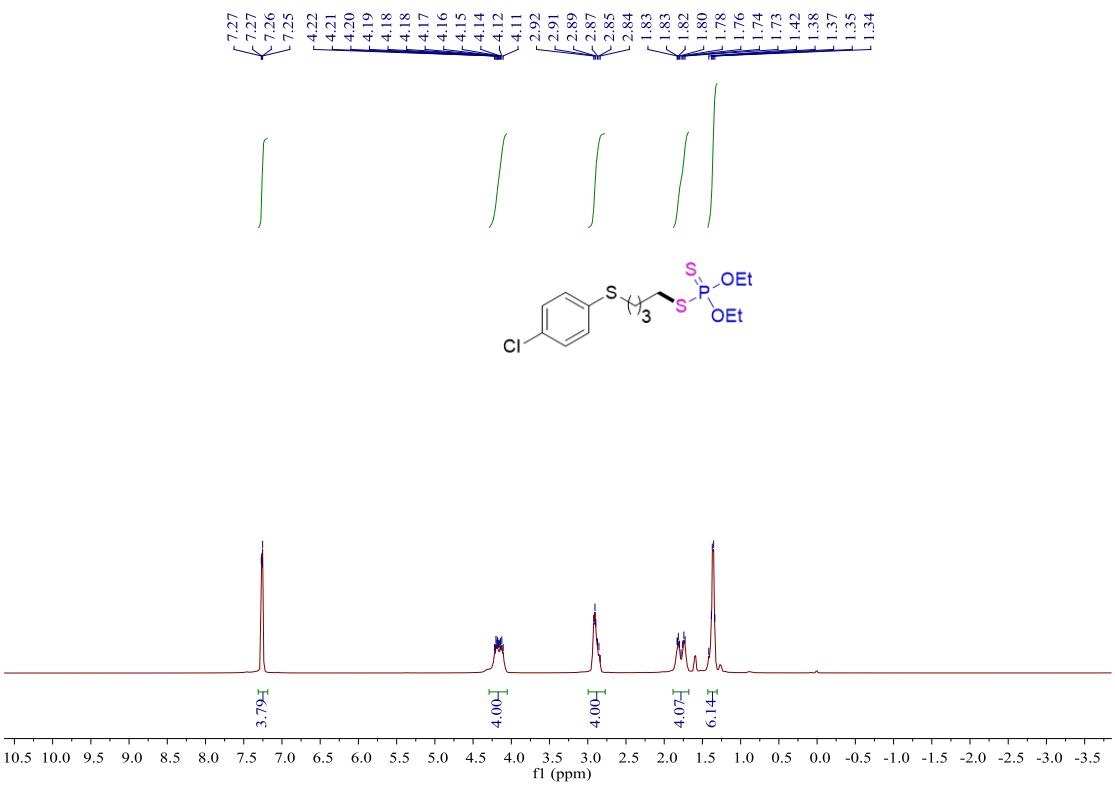
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9h**



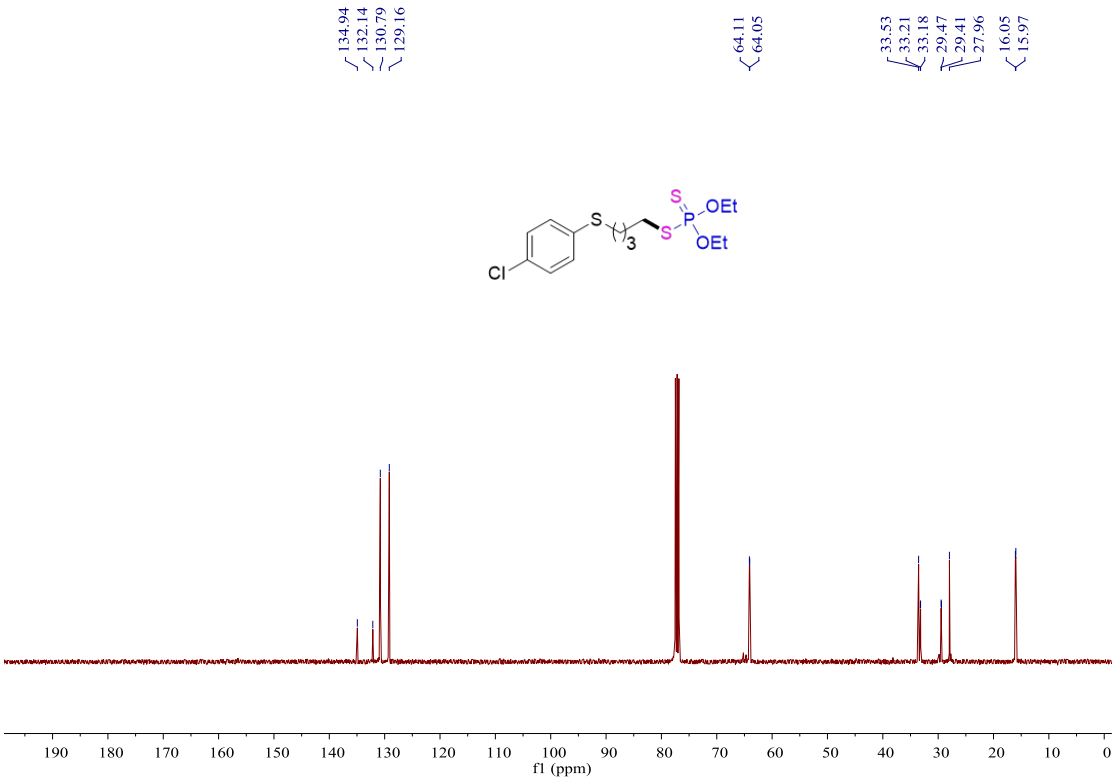
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9h**



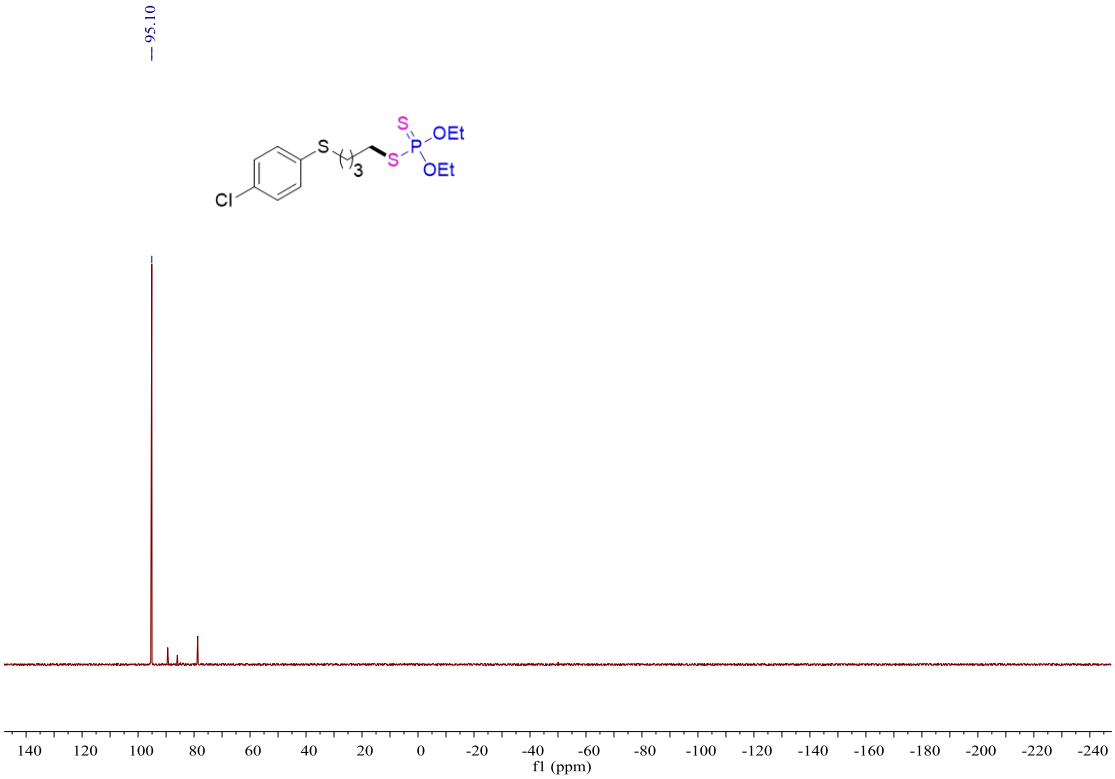
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9h**



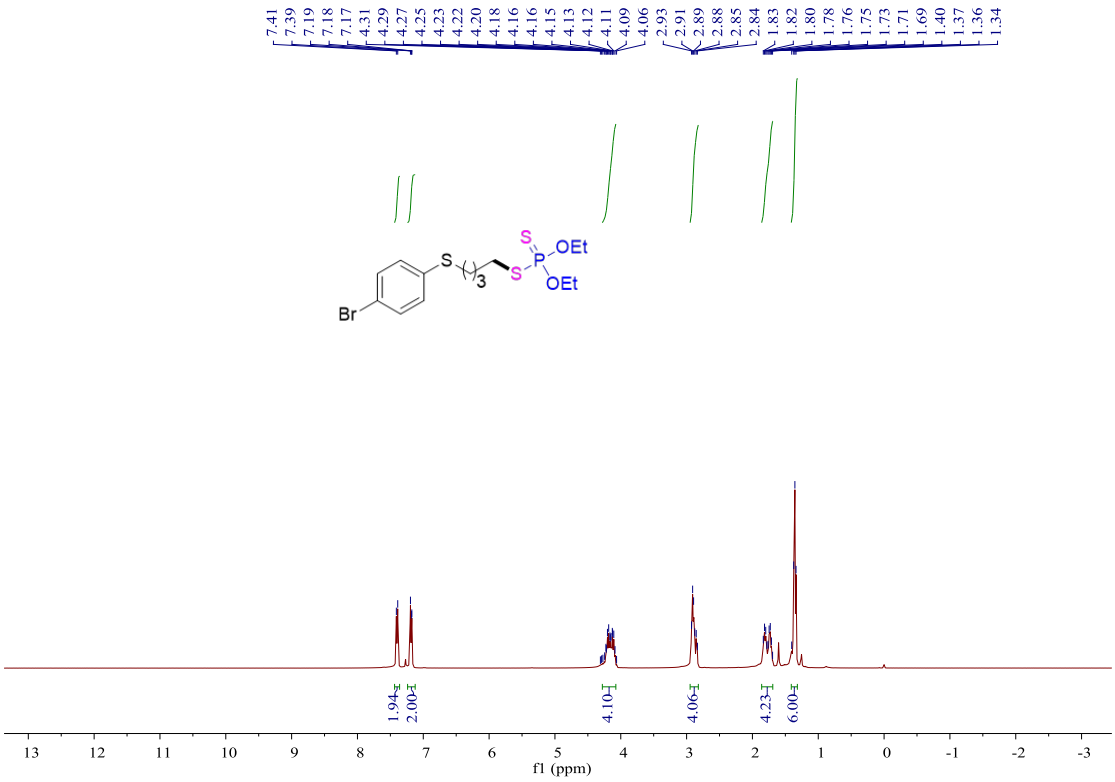
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9i**



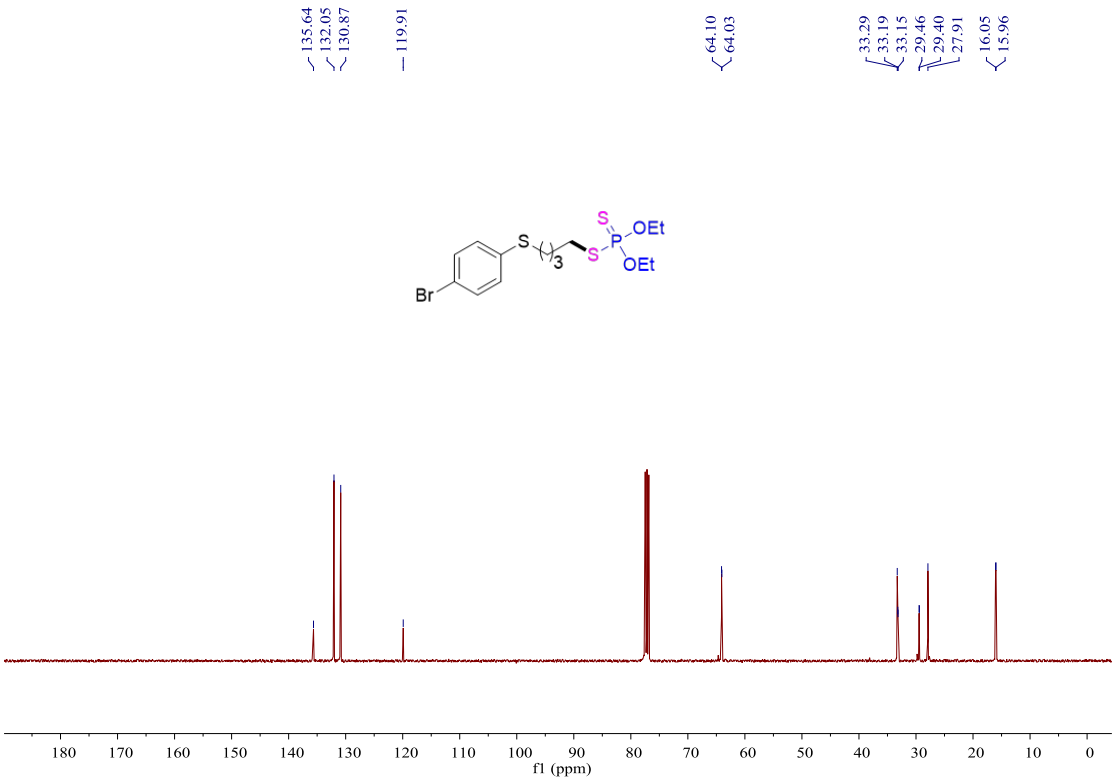
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9i**



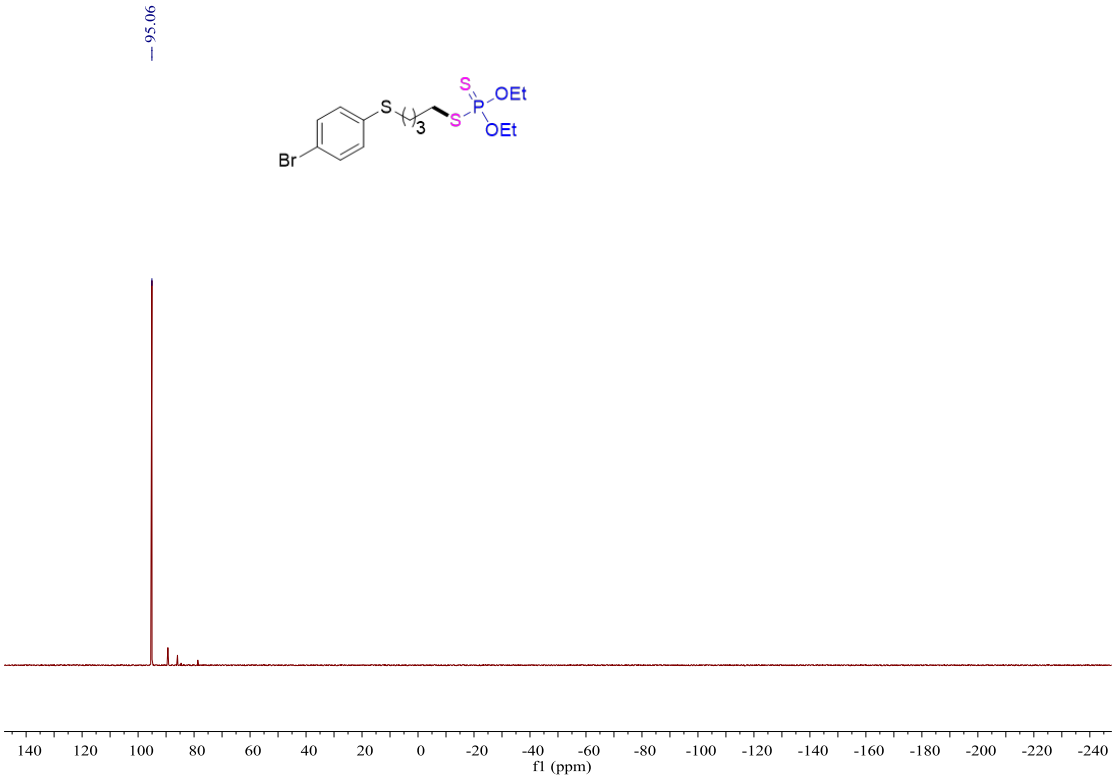
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9i**



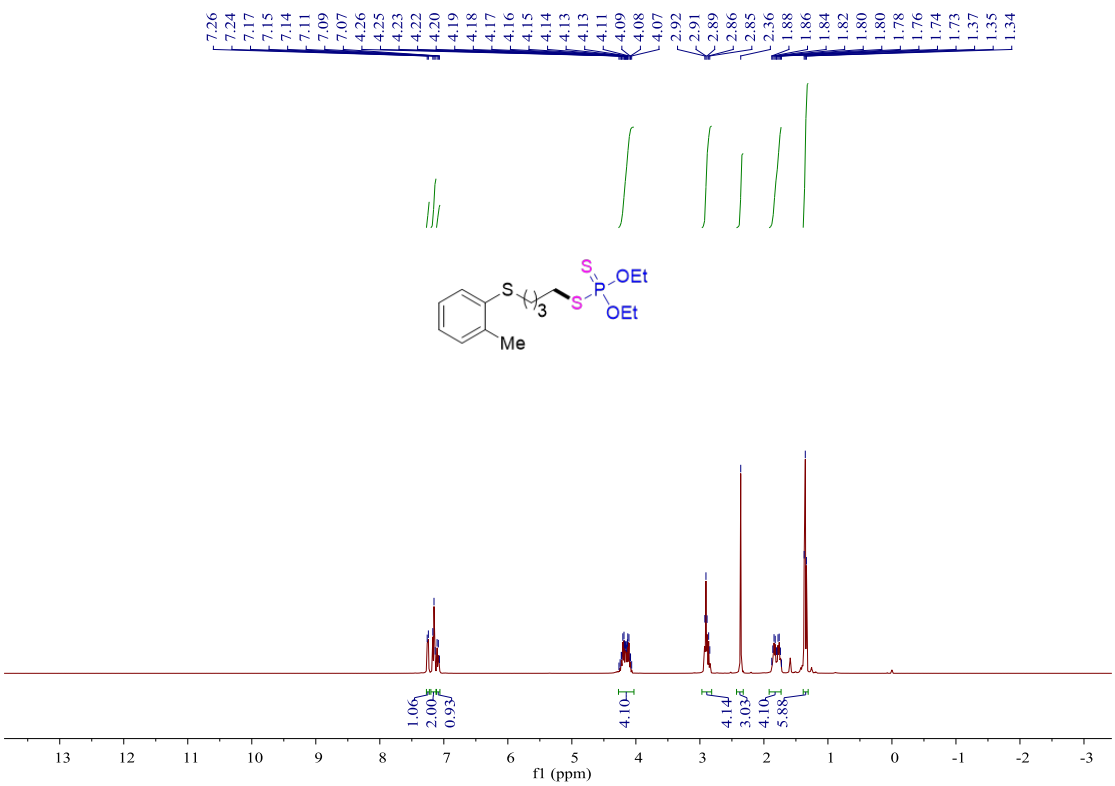
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9j**



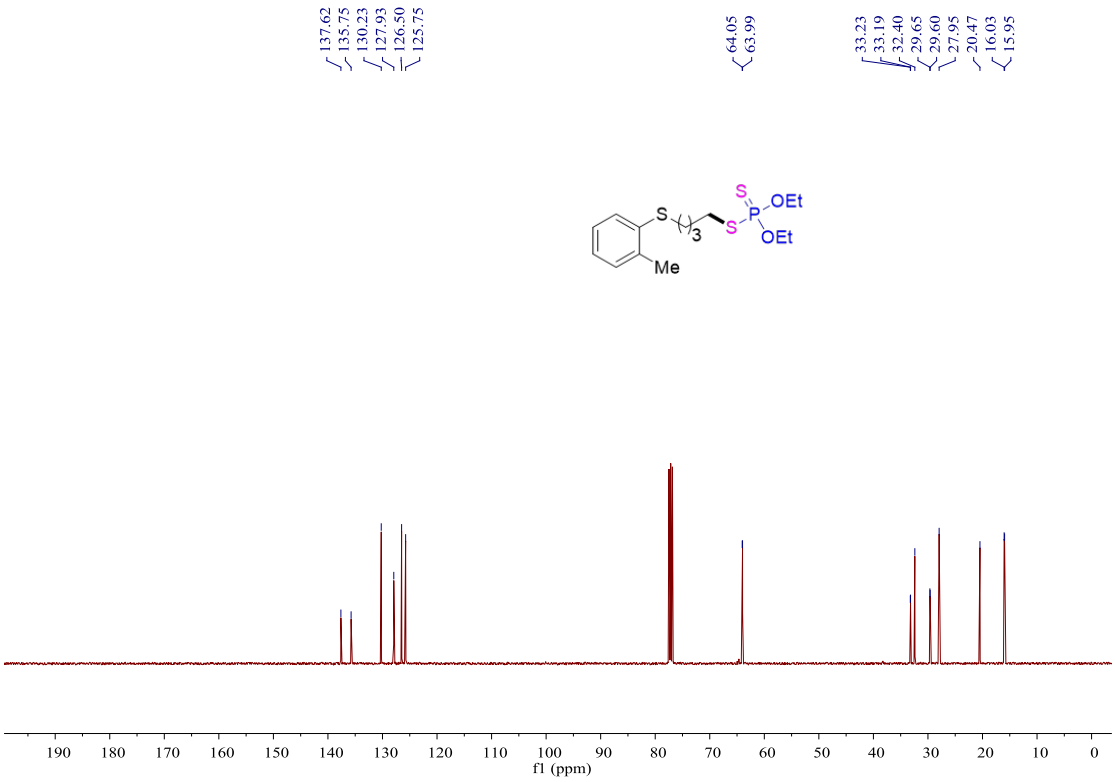
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9j**



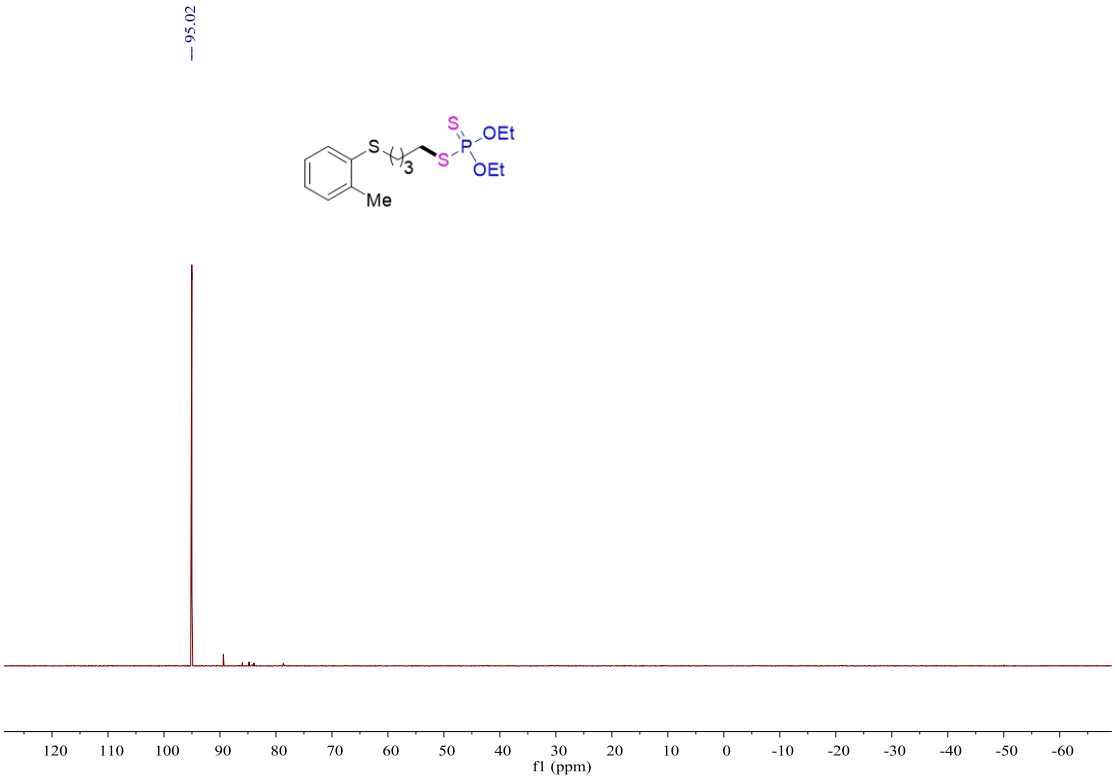
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9j**



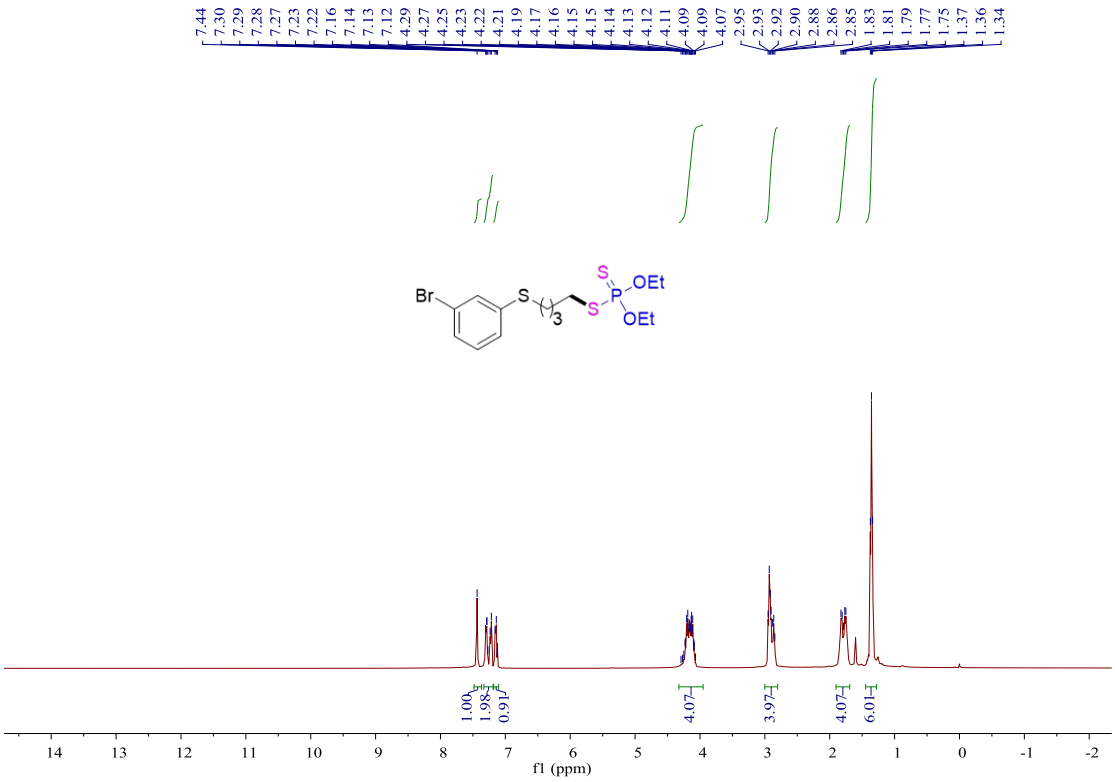
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9k**



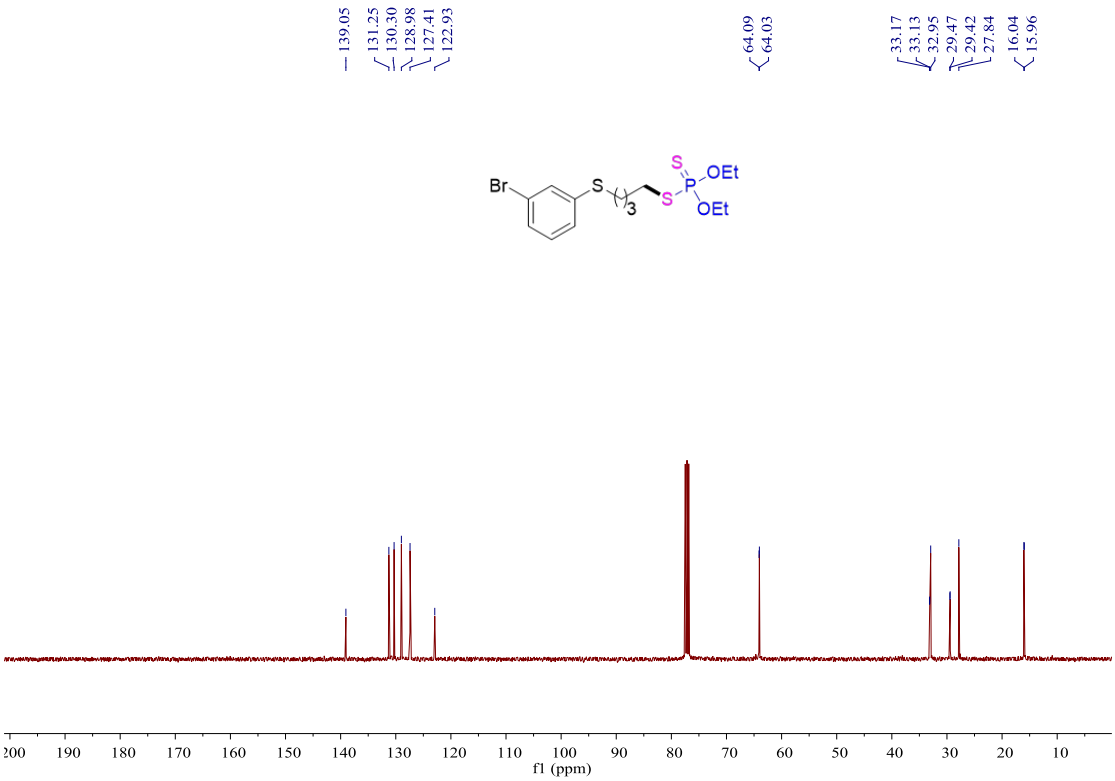
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9k**



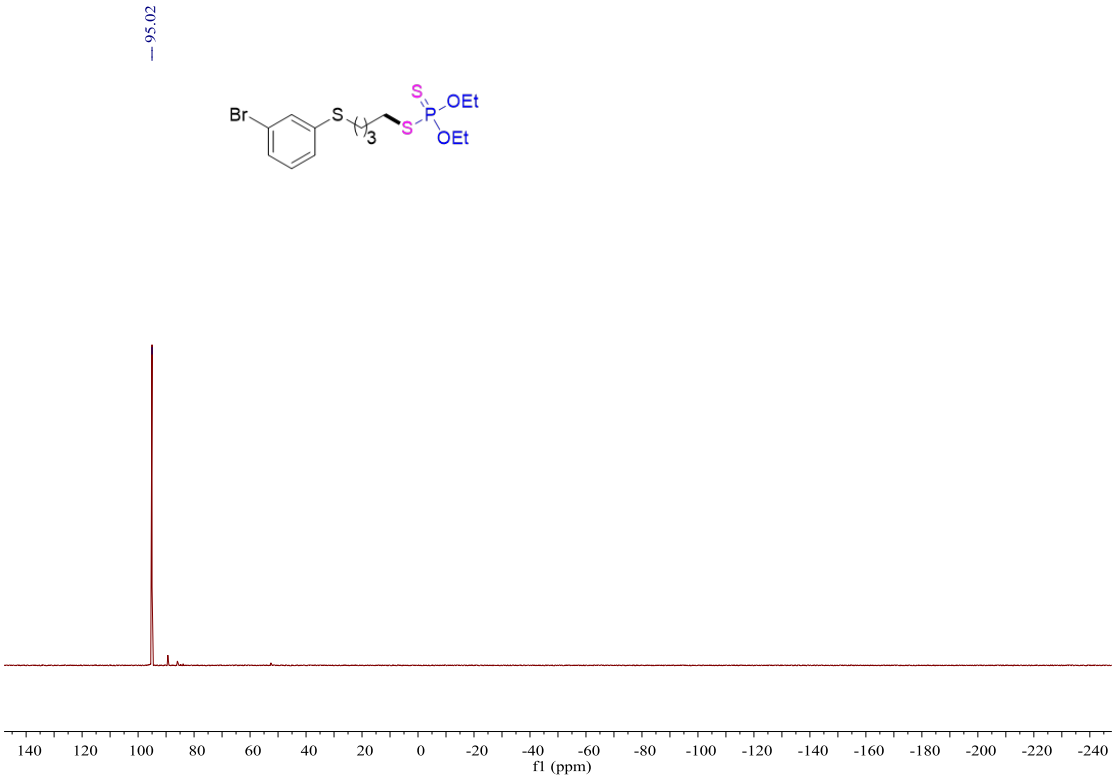
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9k**



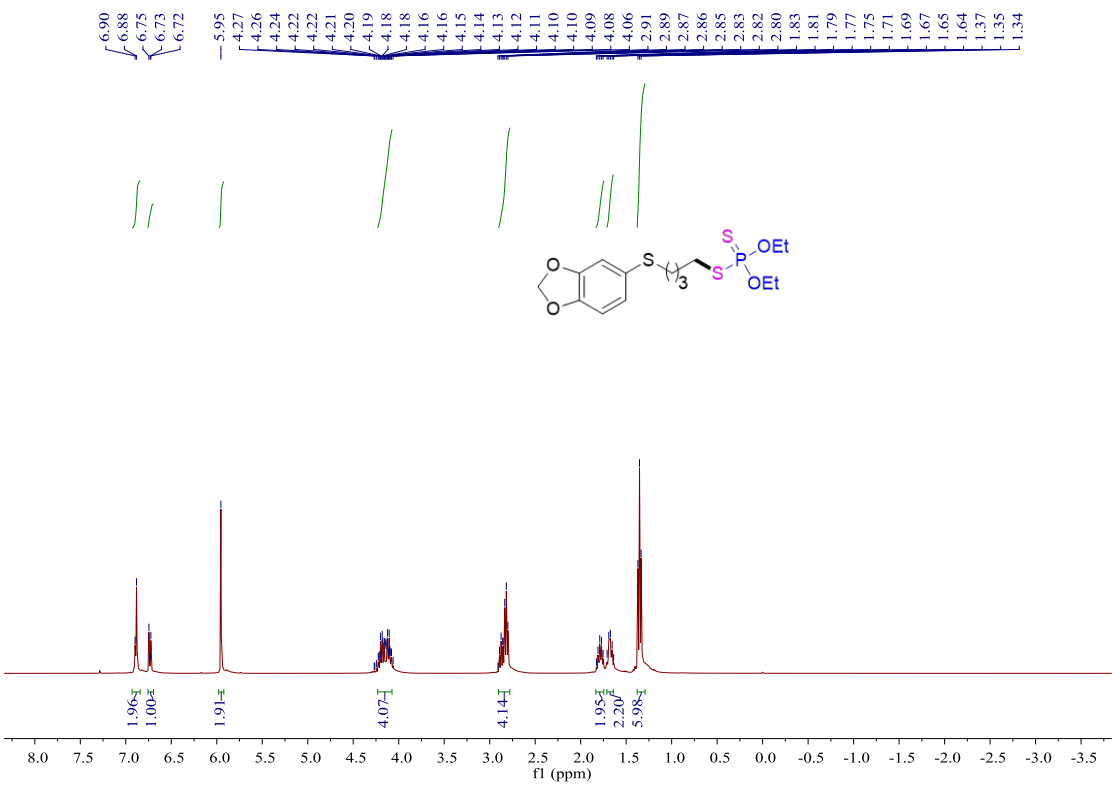
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9l**



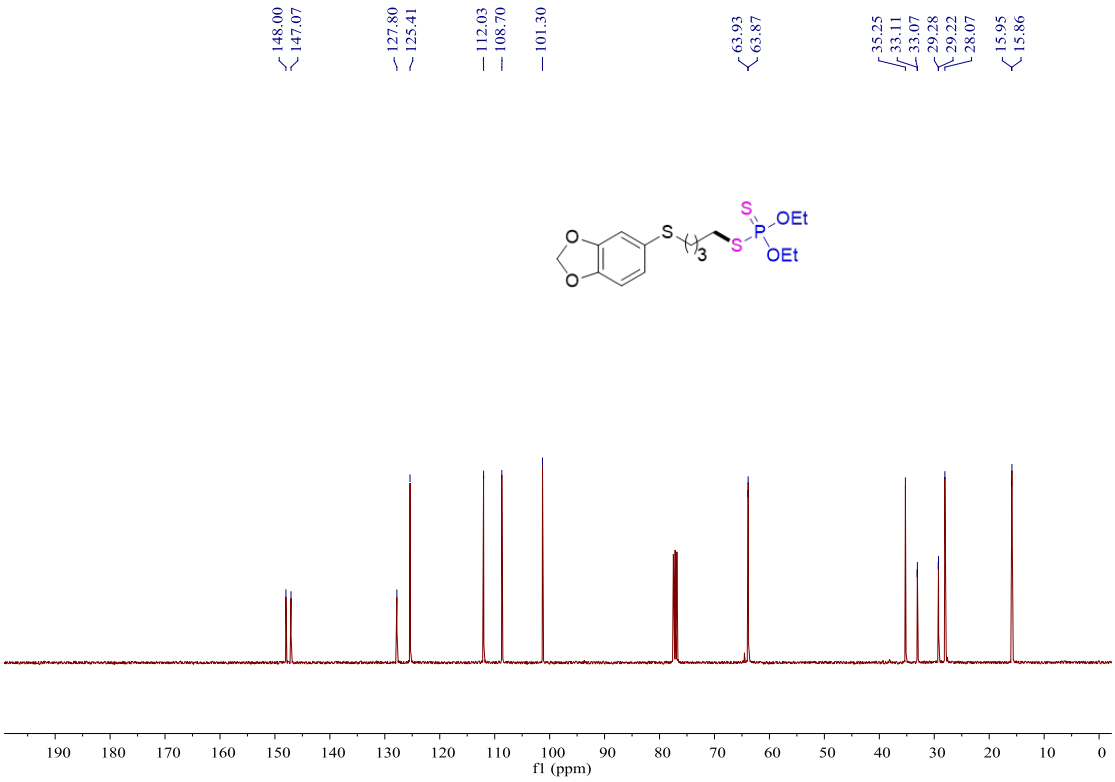
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9l**



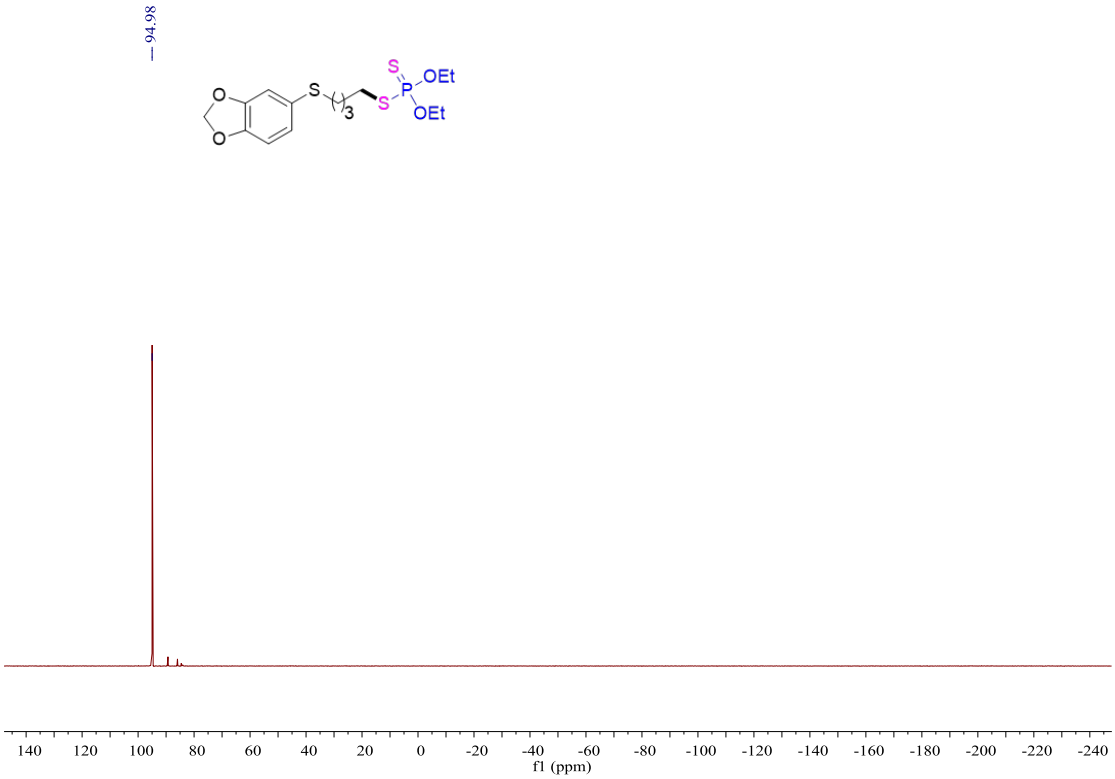
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9l**



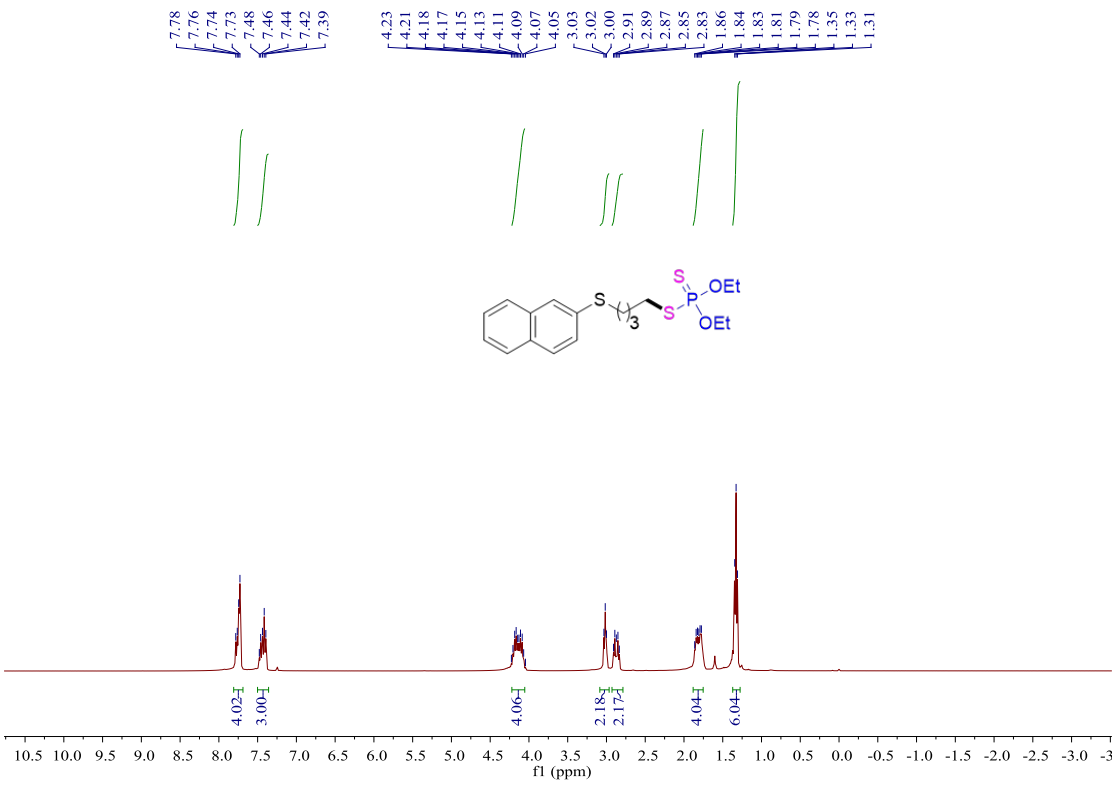
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9m**



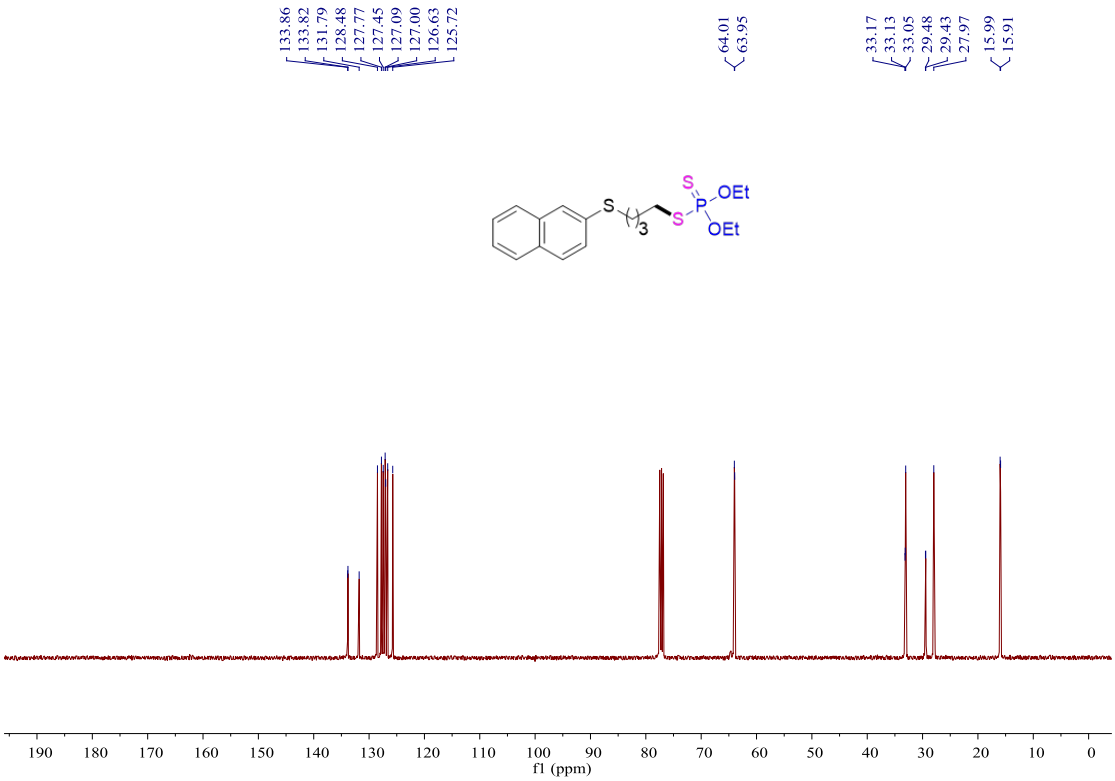
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9m**



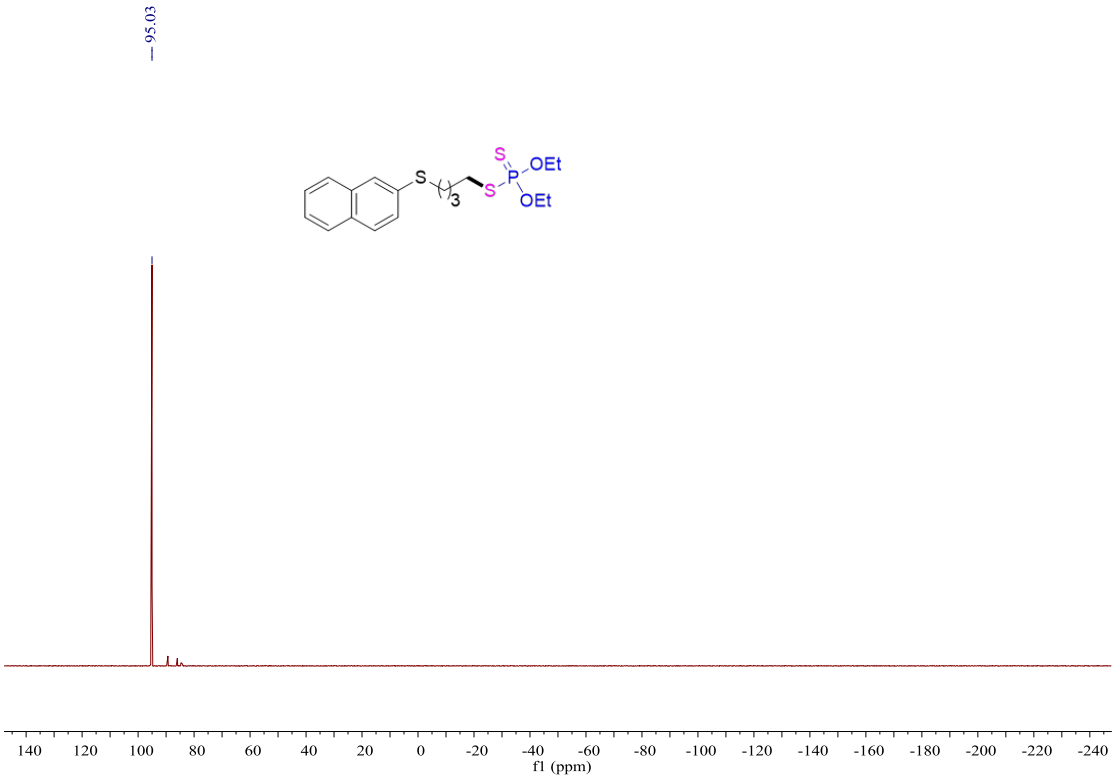
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9m**



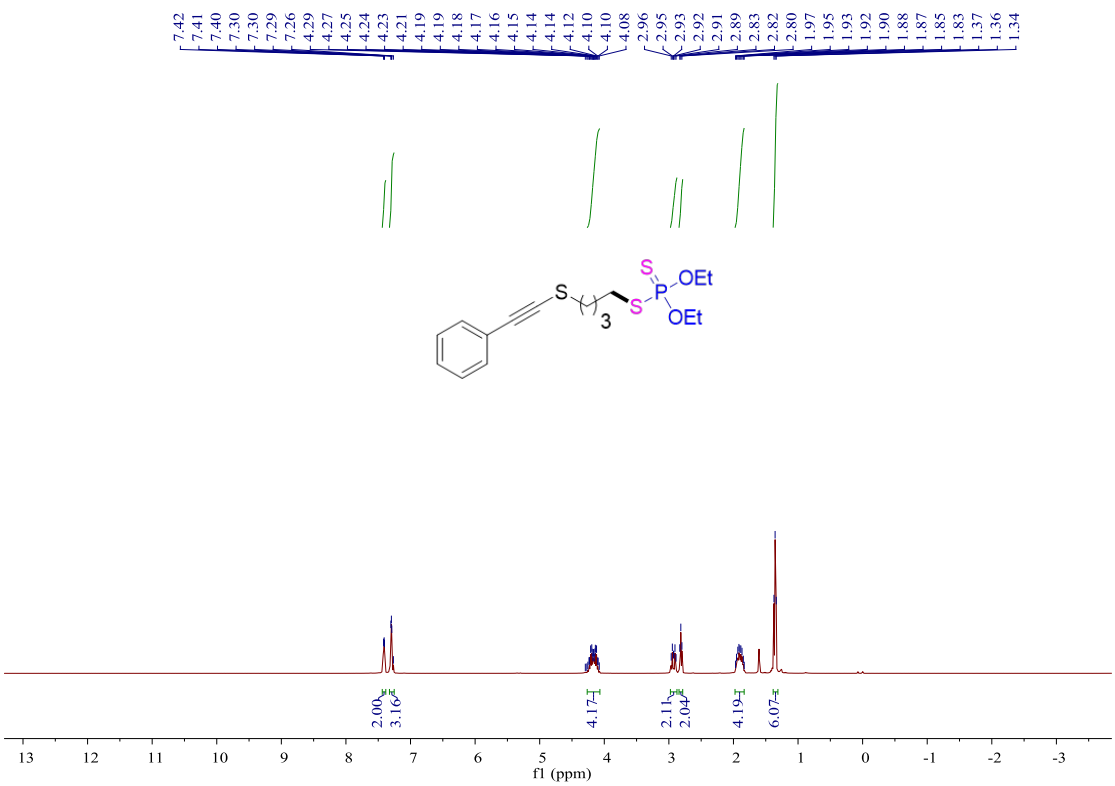
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9n**



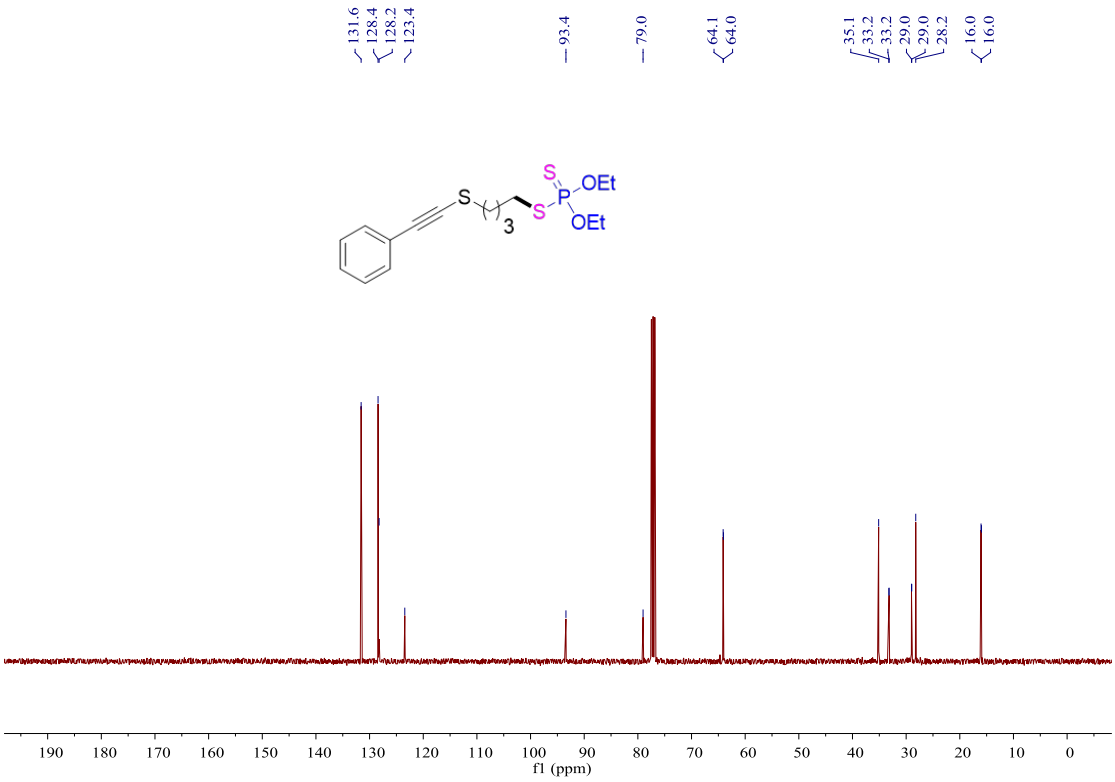
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9n**



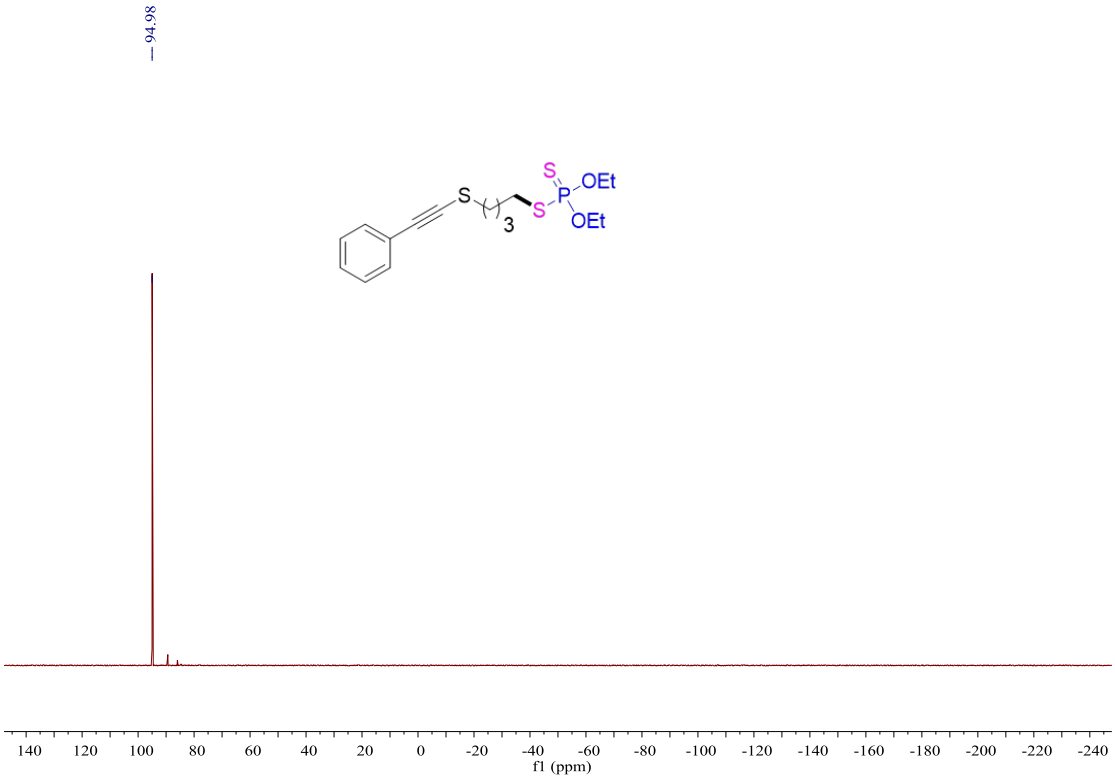
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9n**



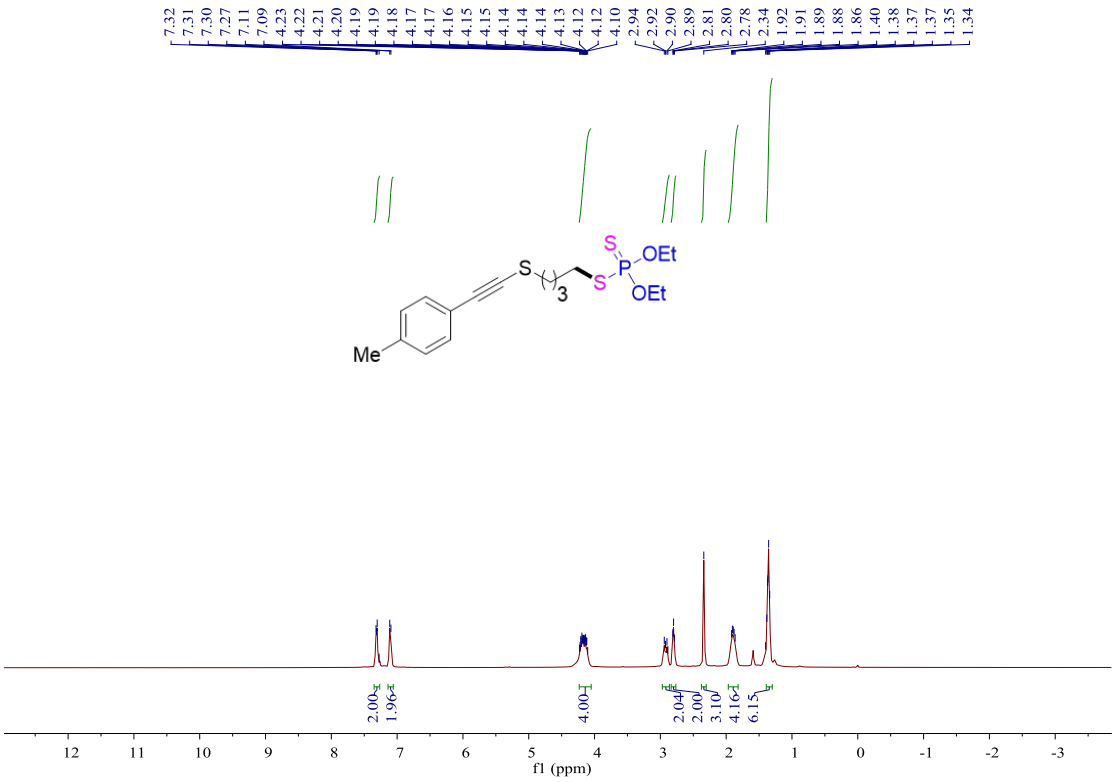
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9o**



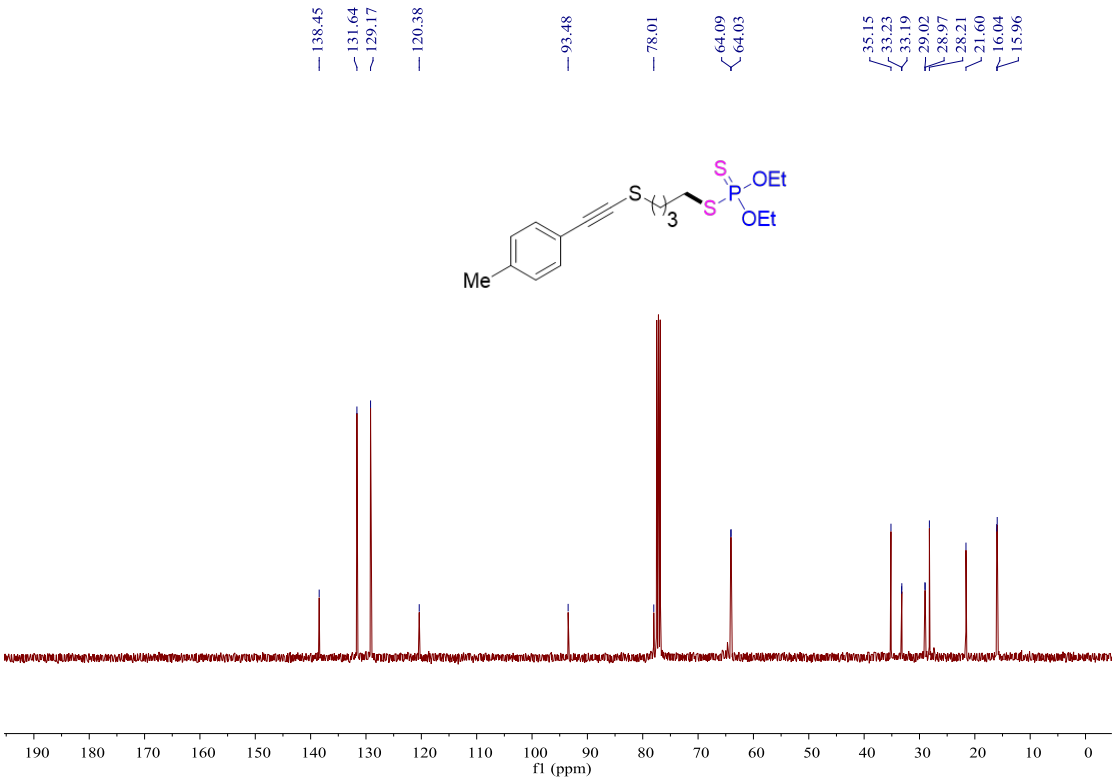
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9o**



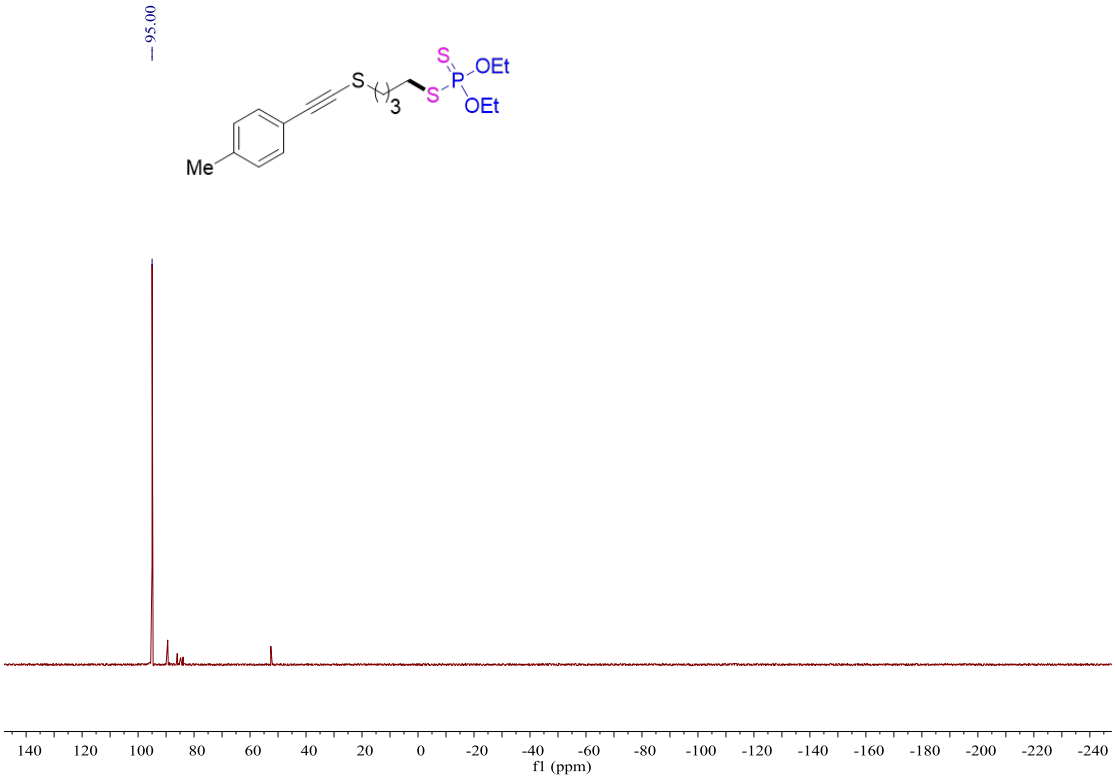
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9o**



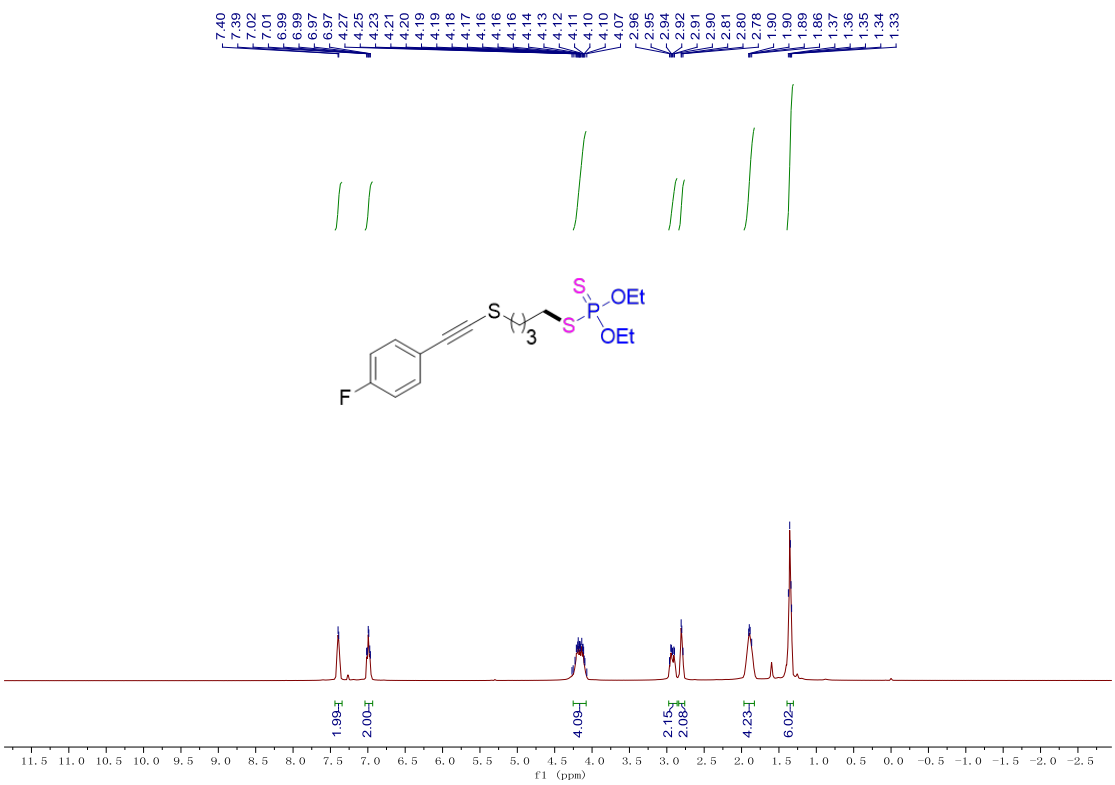
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9p**



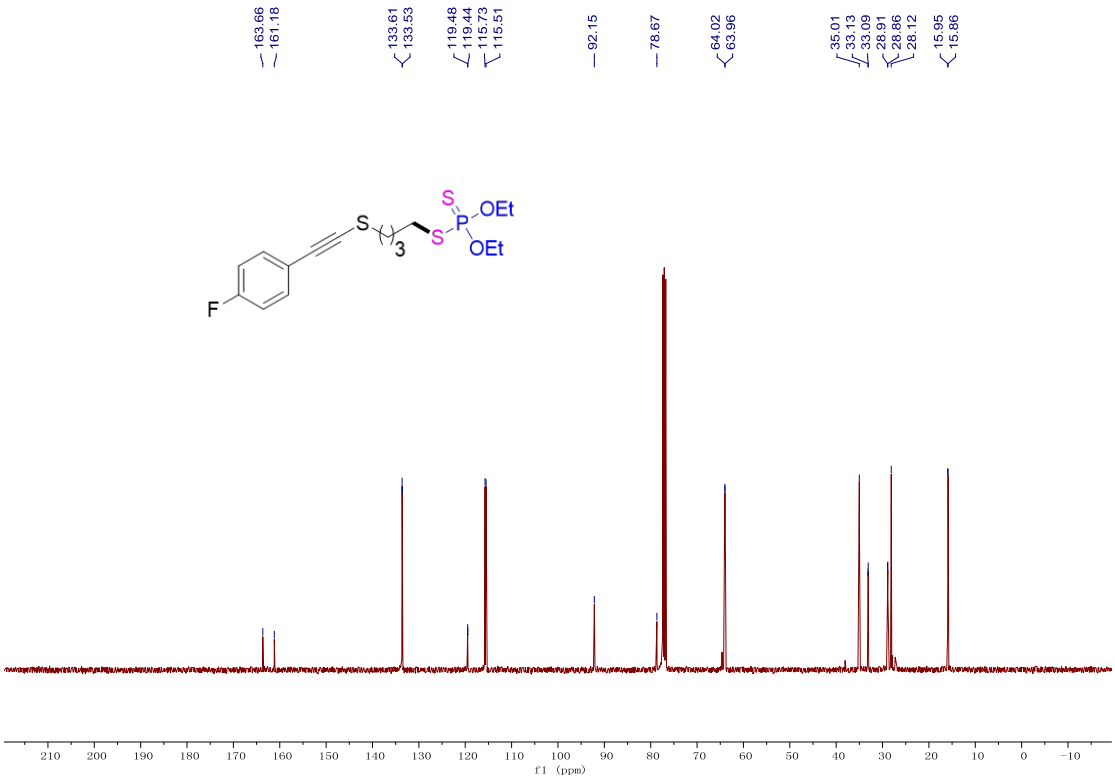
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9p**



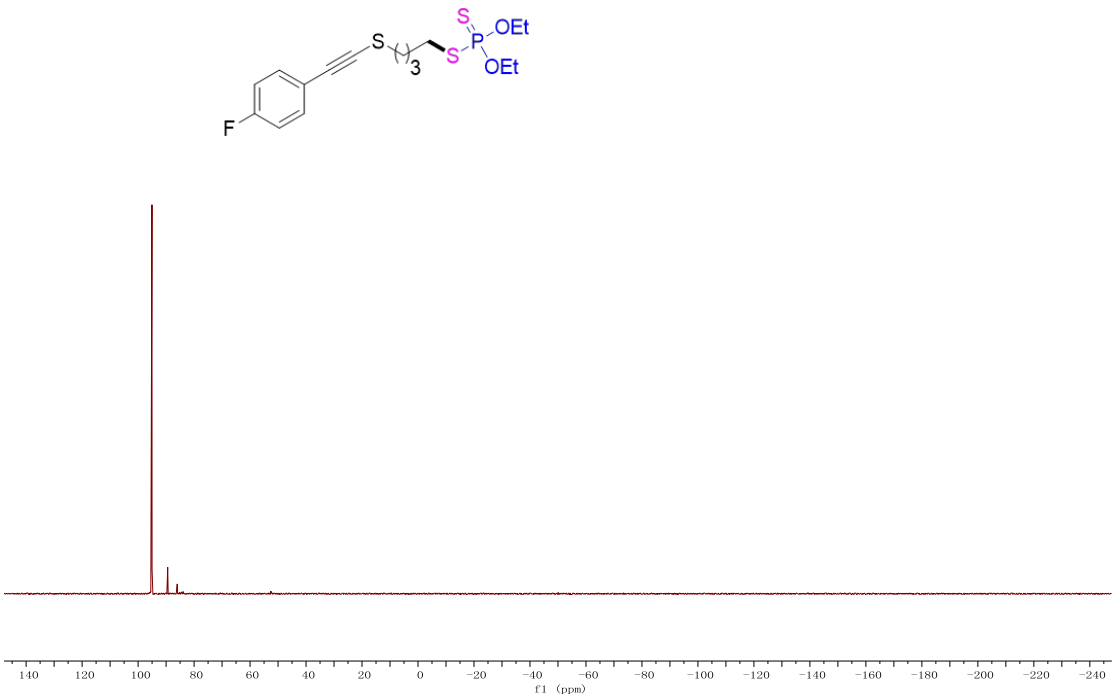
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9p**



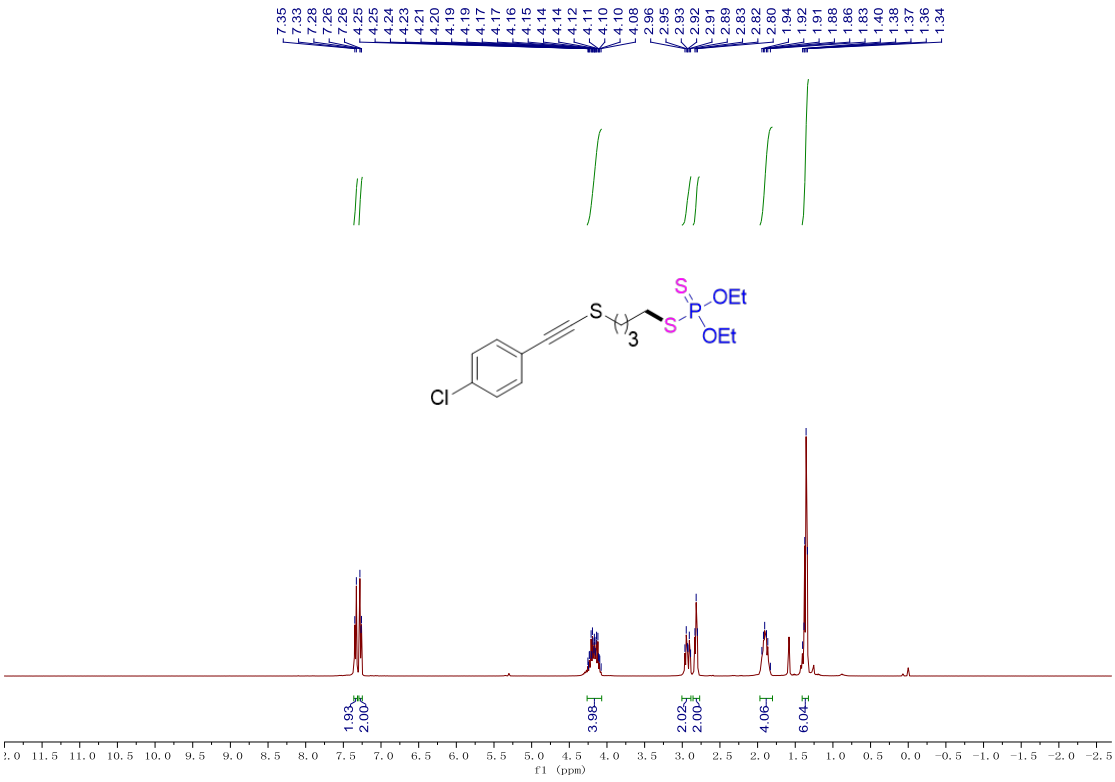
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9q**



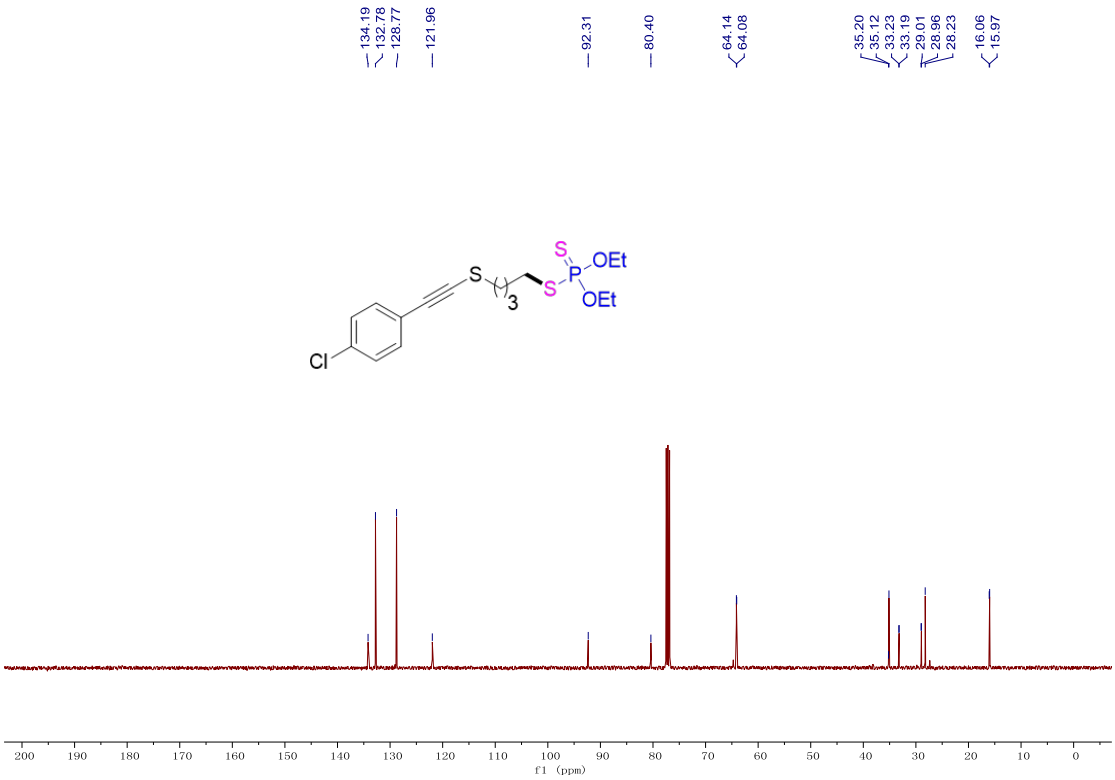
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9q**



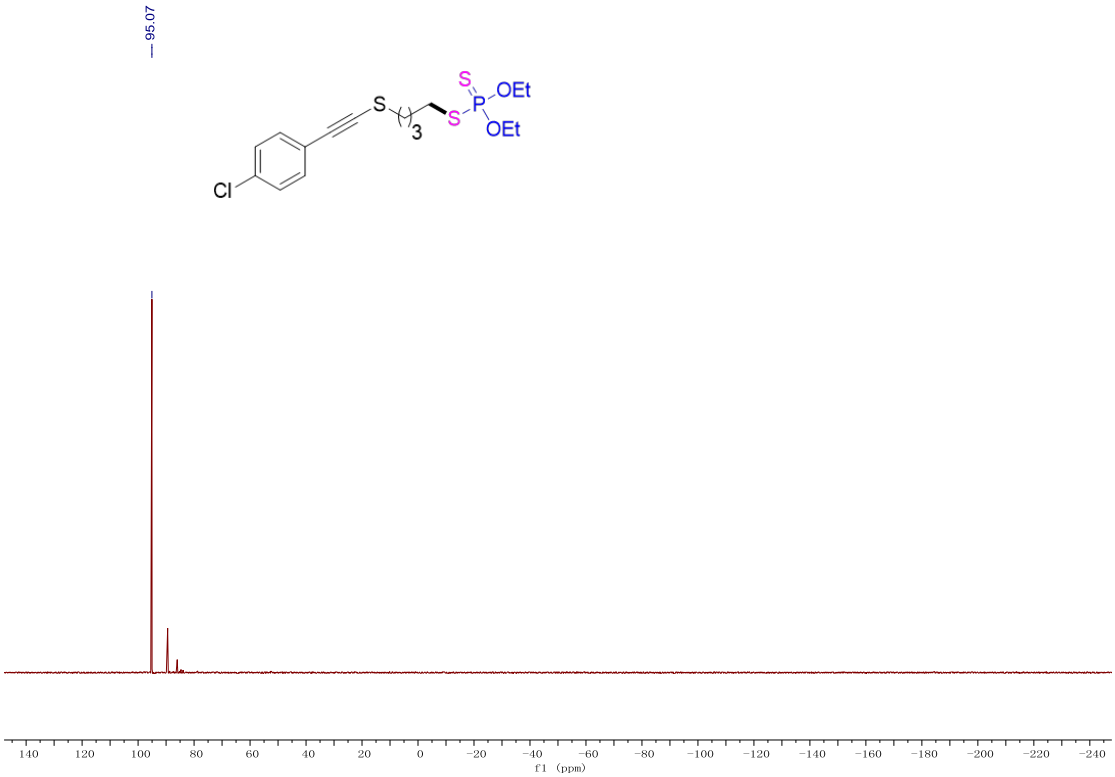
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9q**



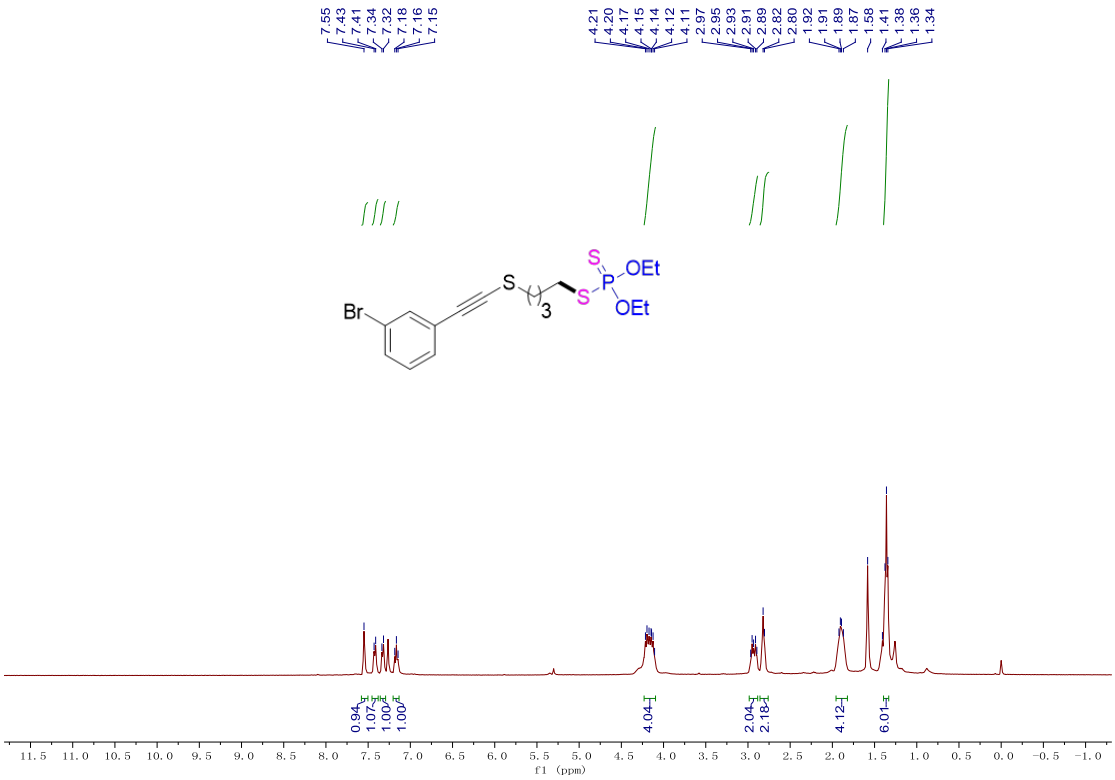
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9r**



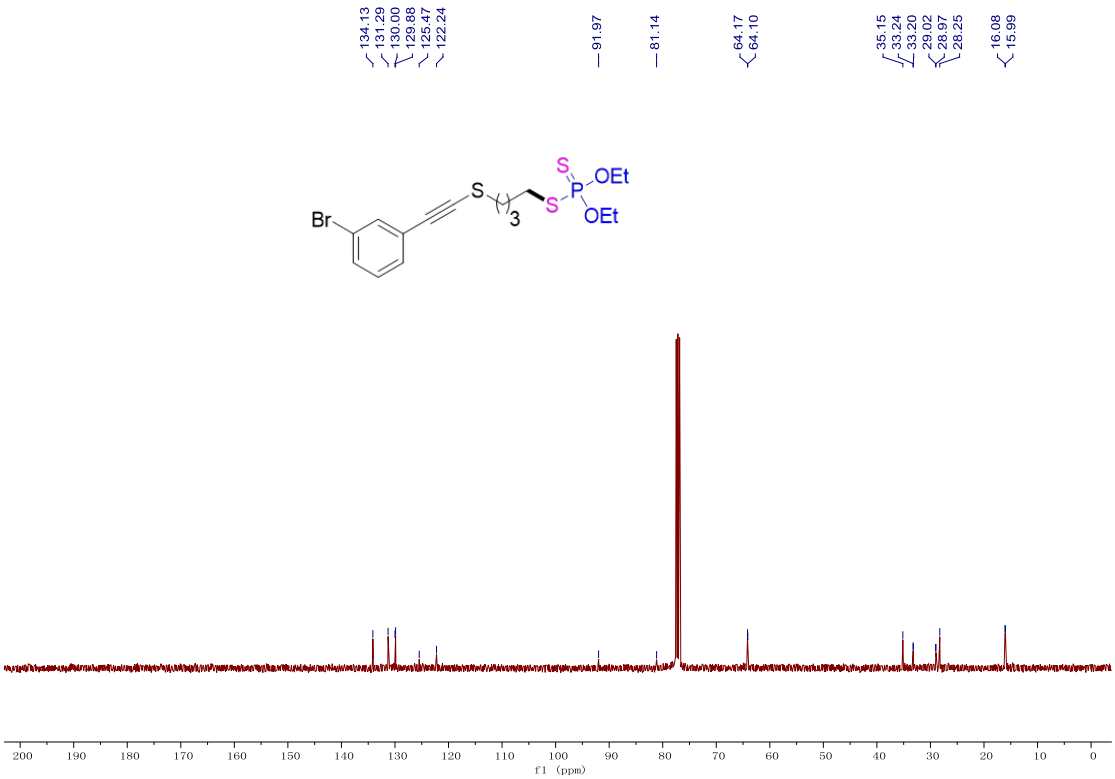
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9r**



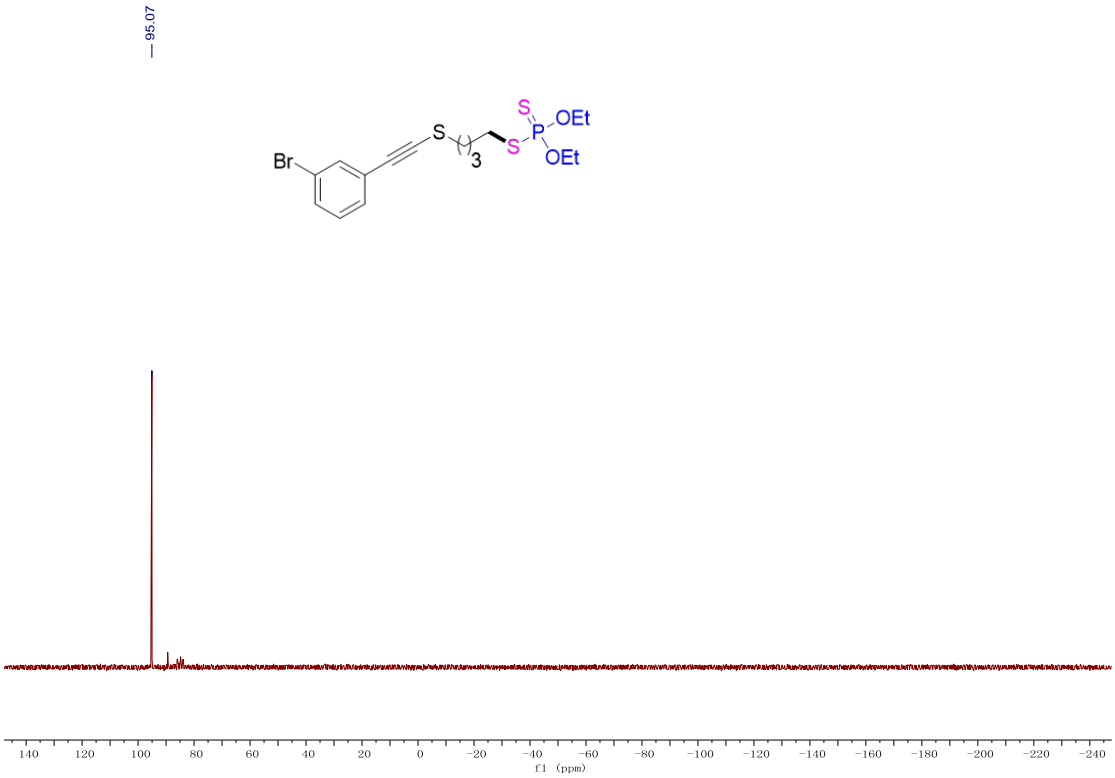
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9r**



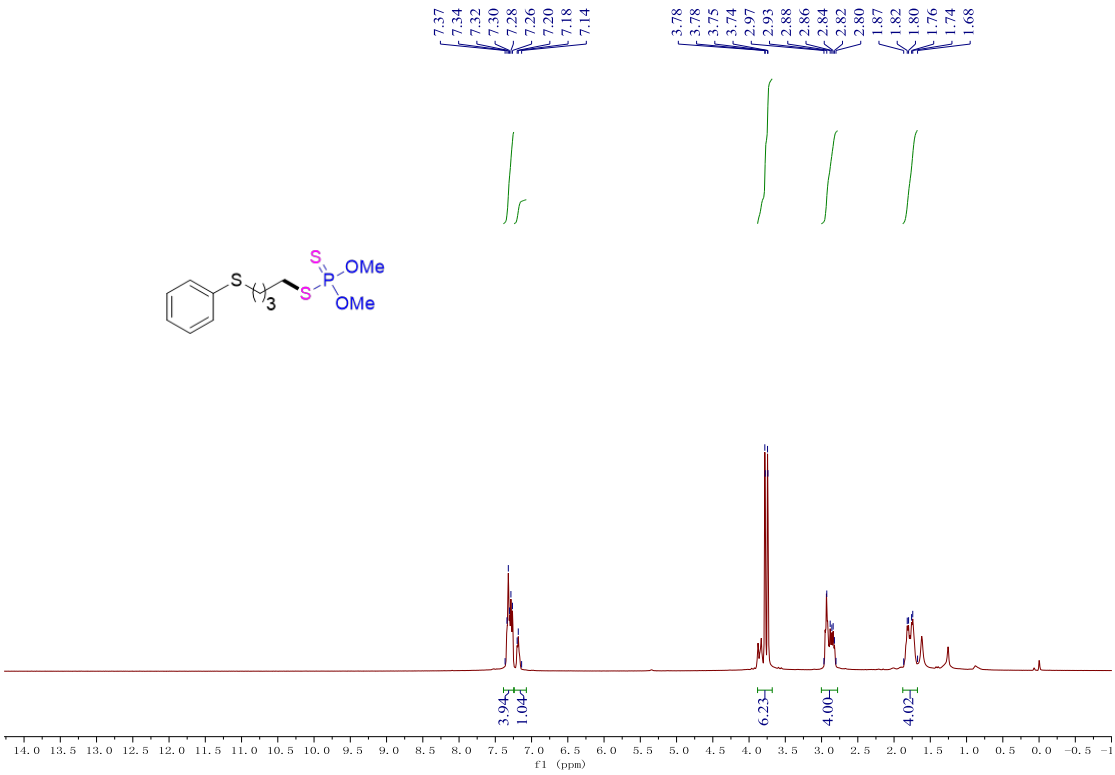
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9s**



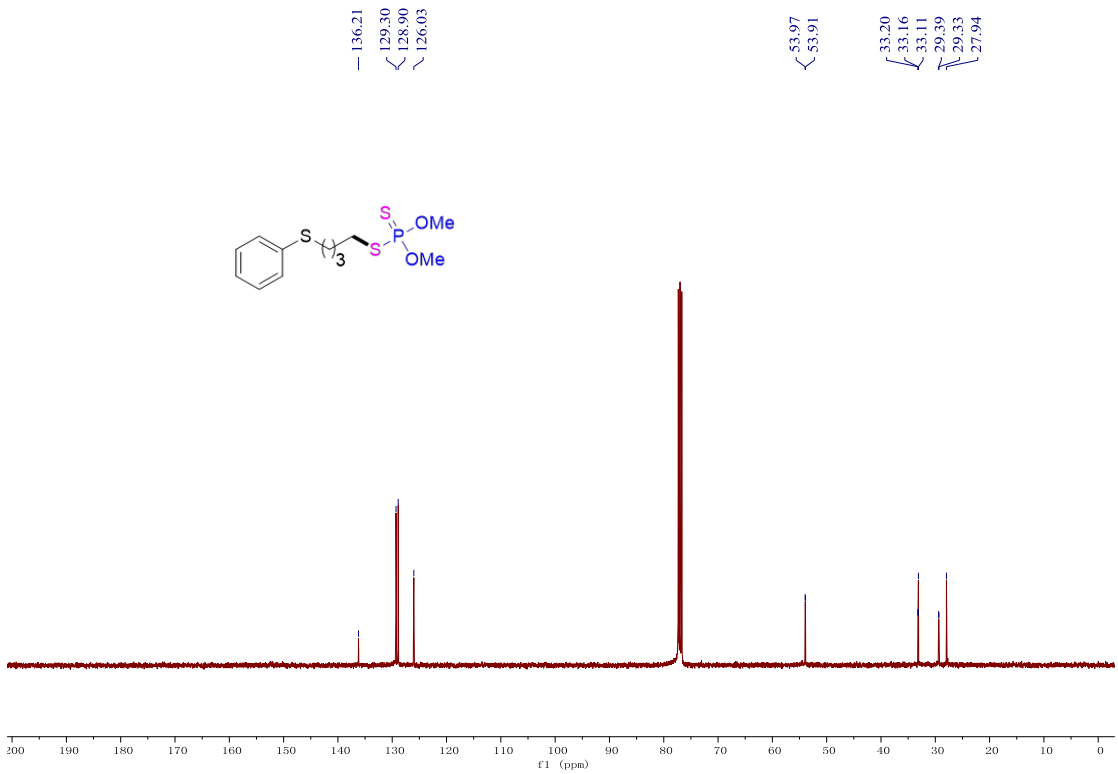
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9s**



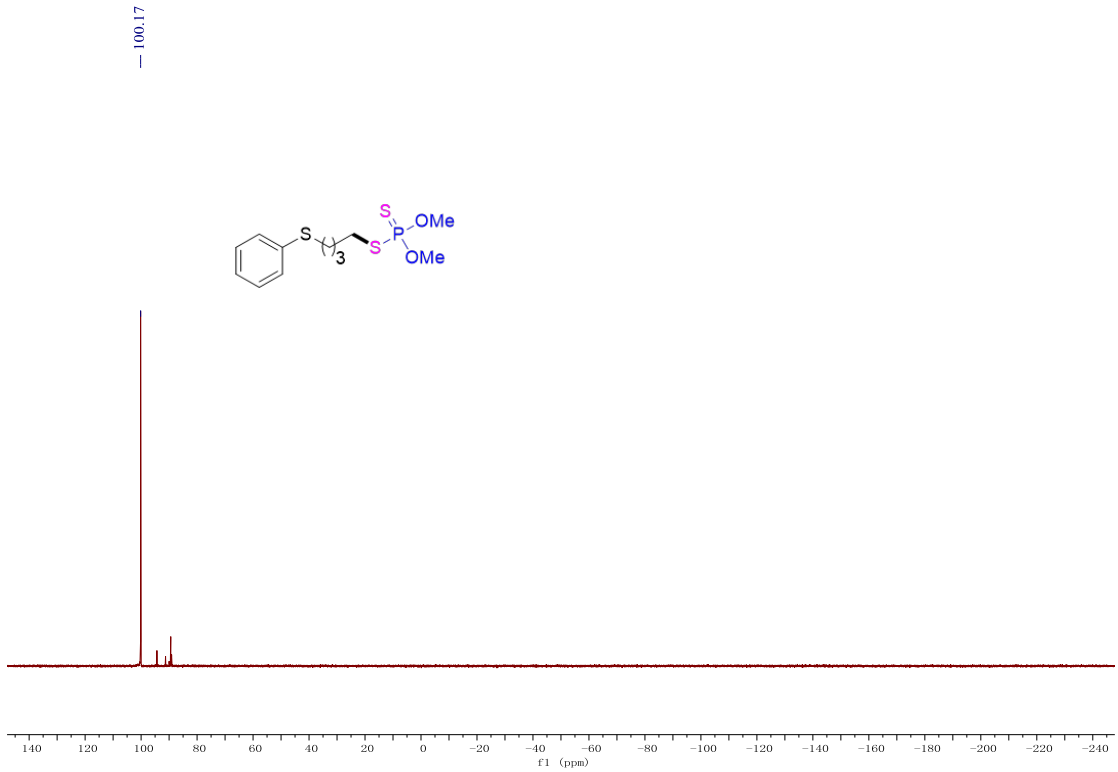
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9s**



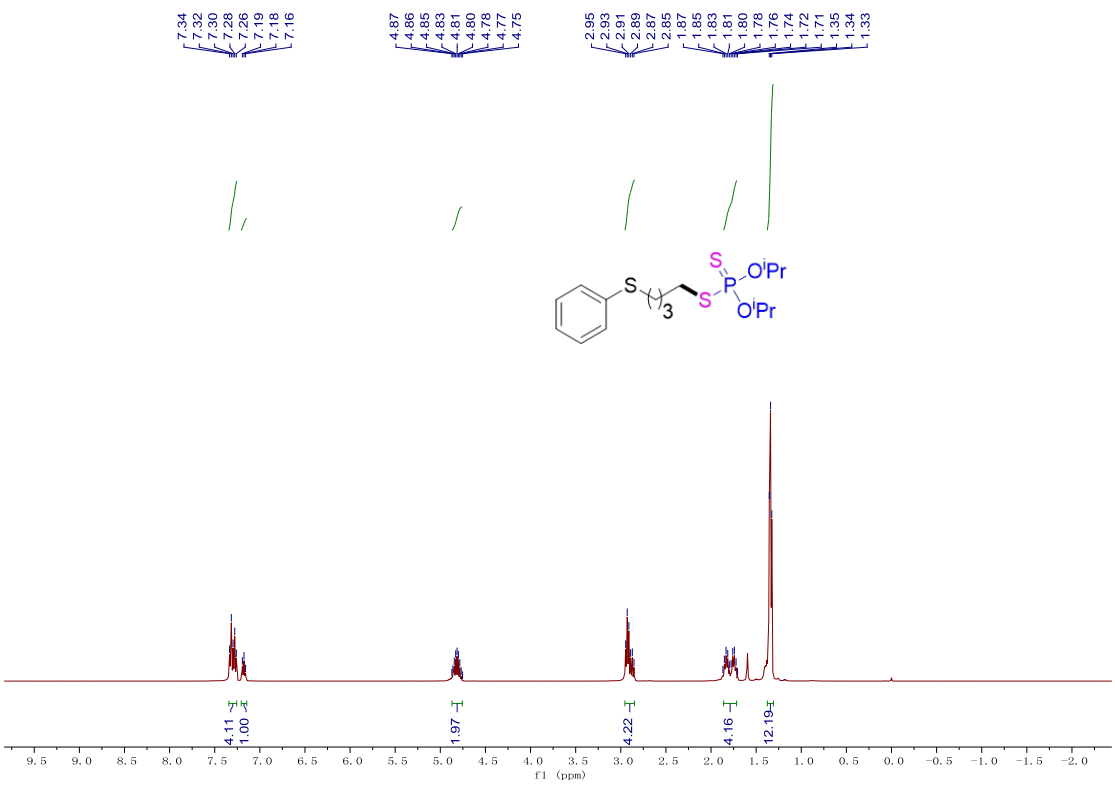
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9t**



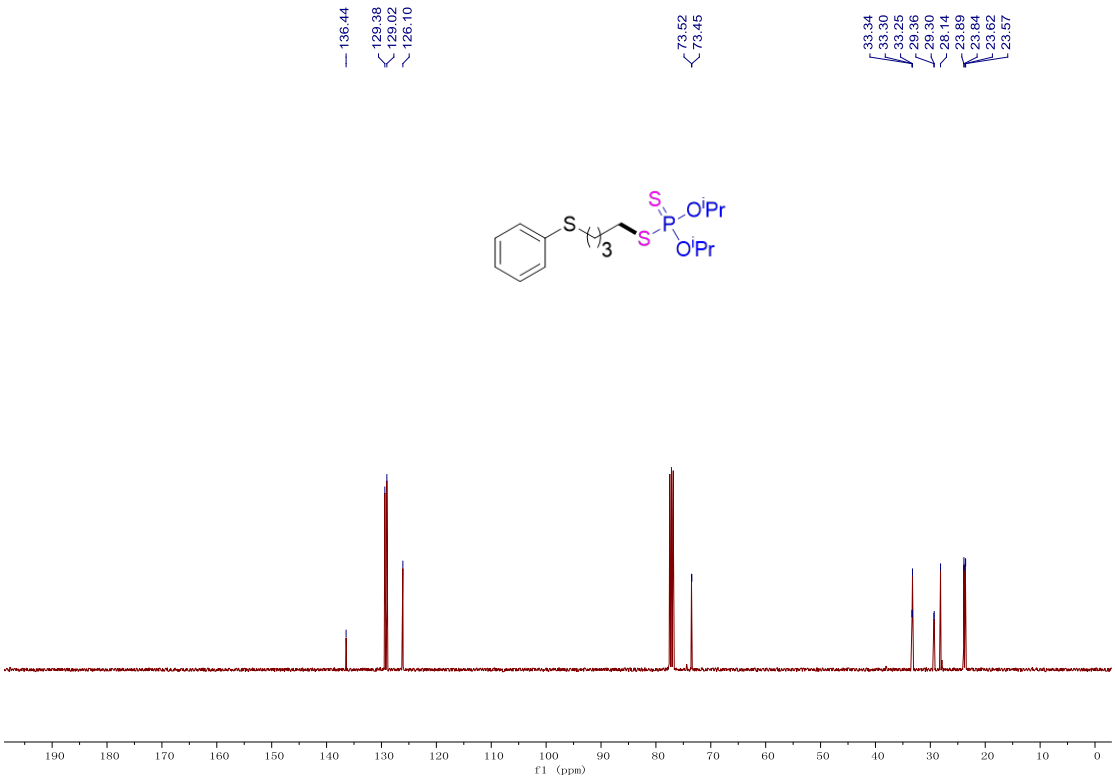
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9t**



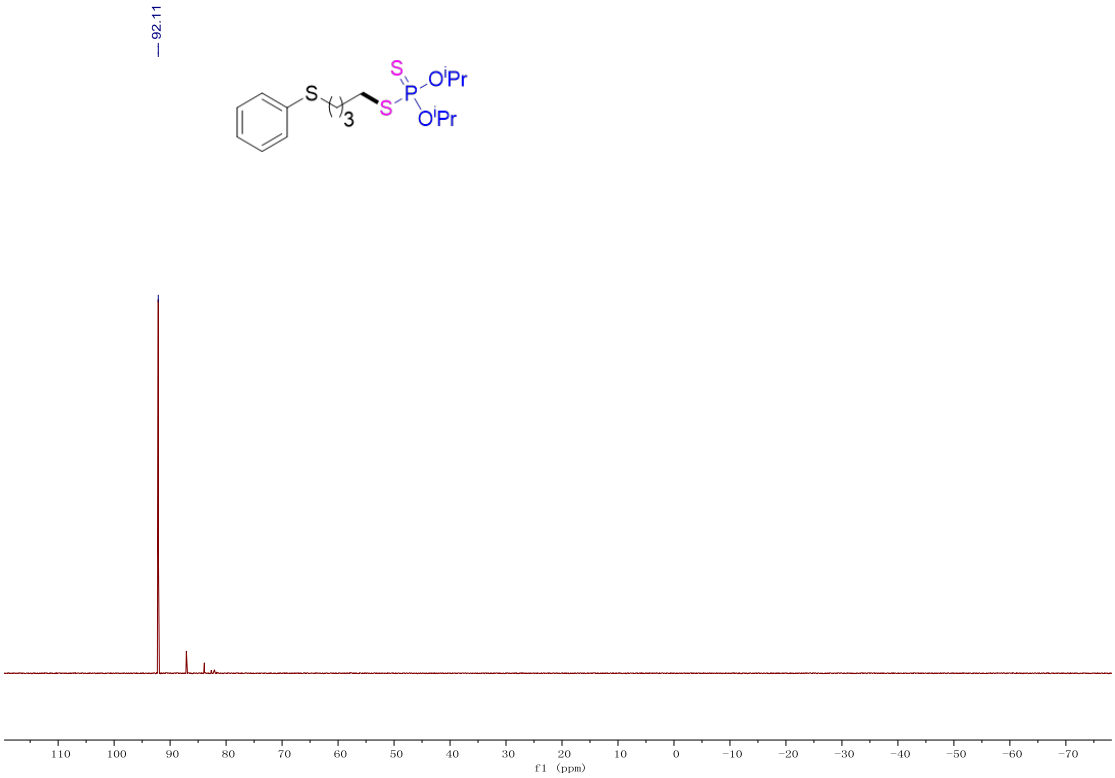
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9t**



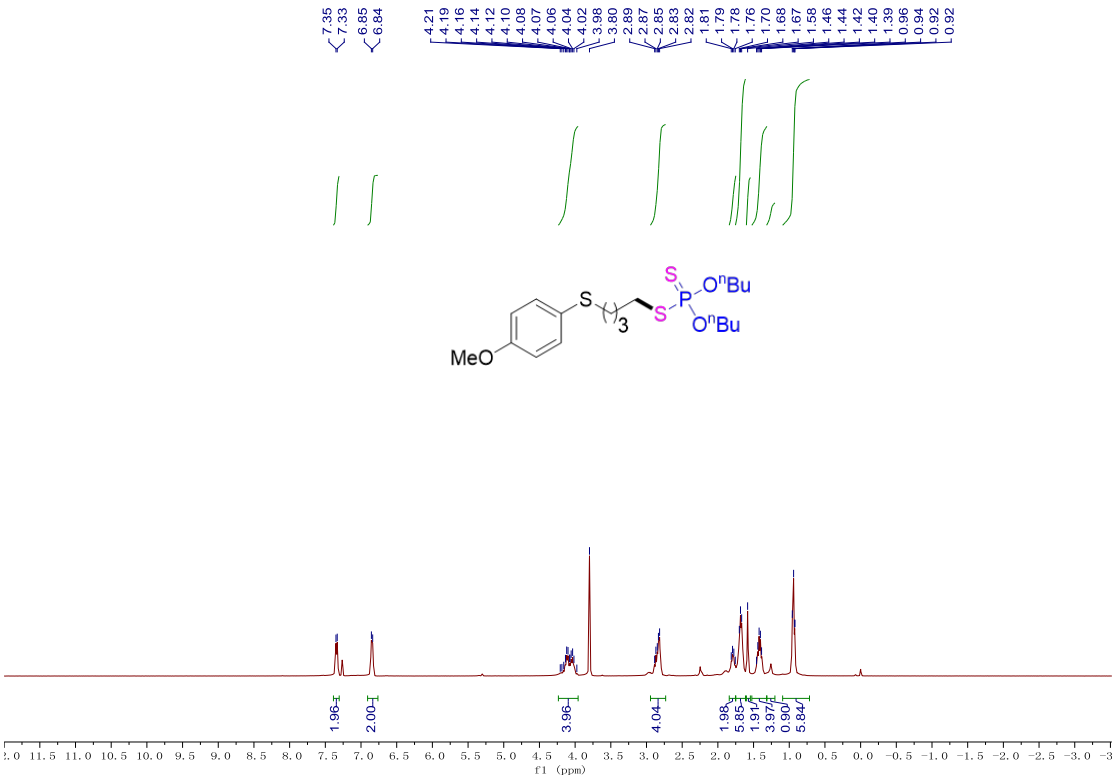
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9u**



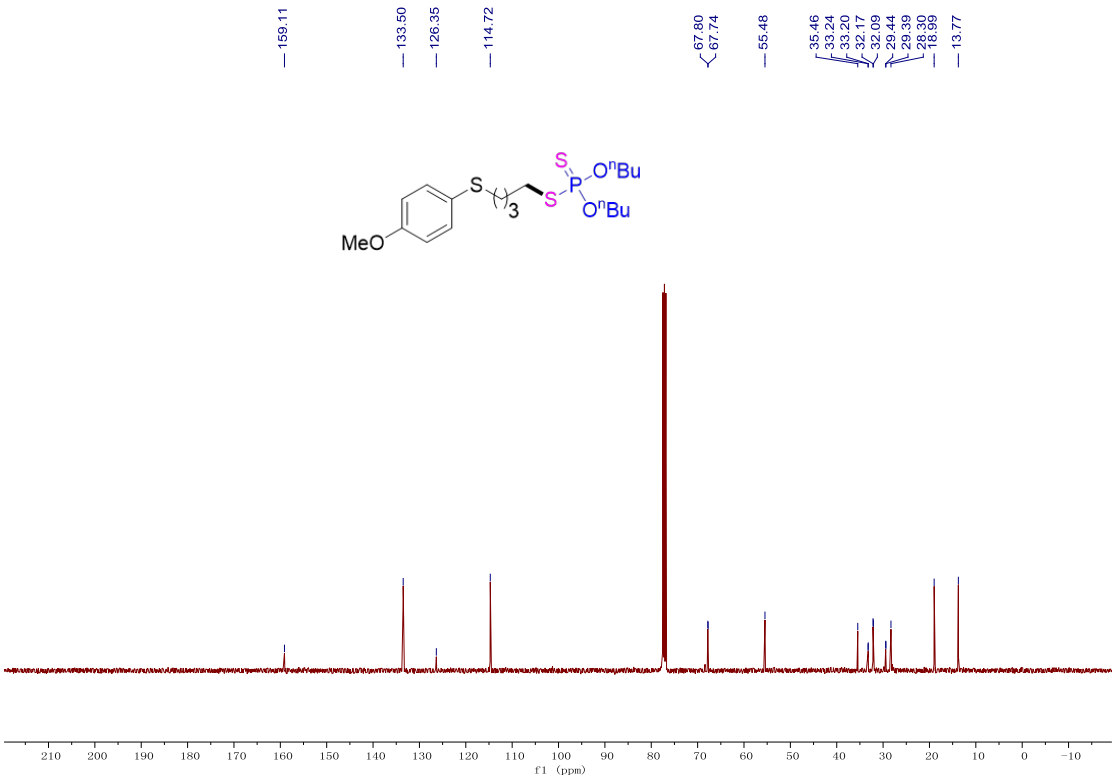
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9u**



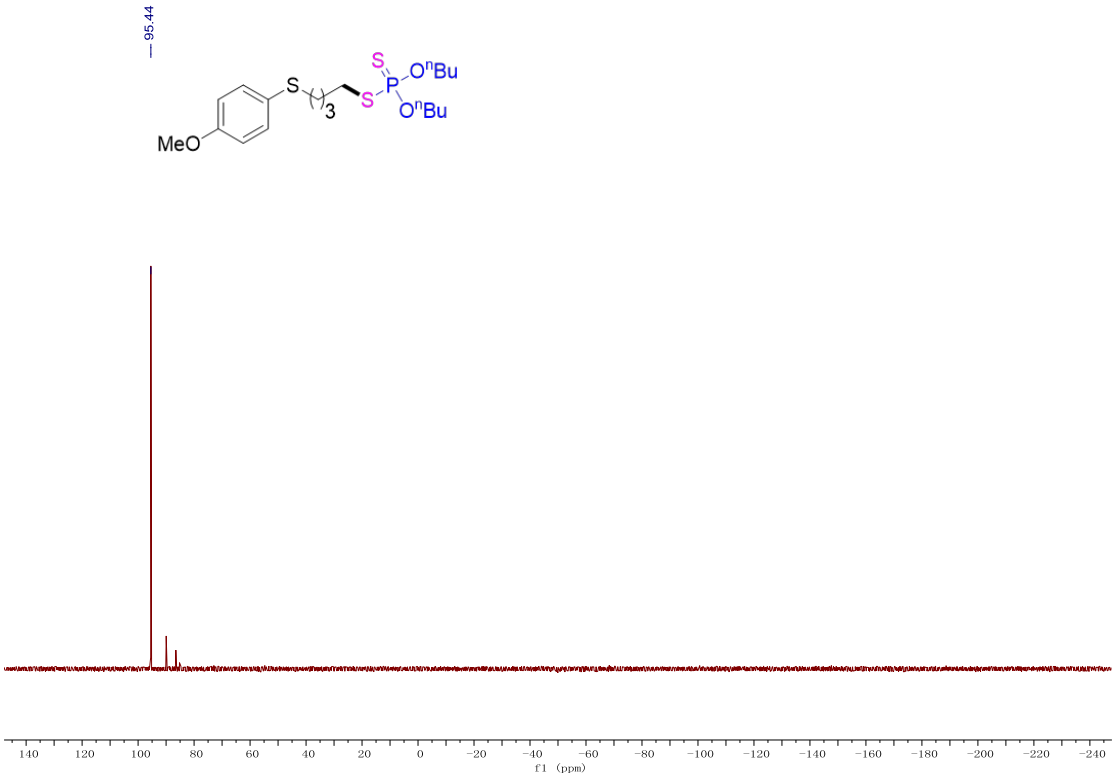
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9u**



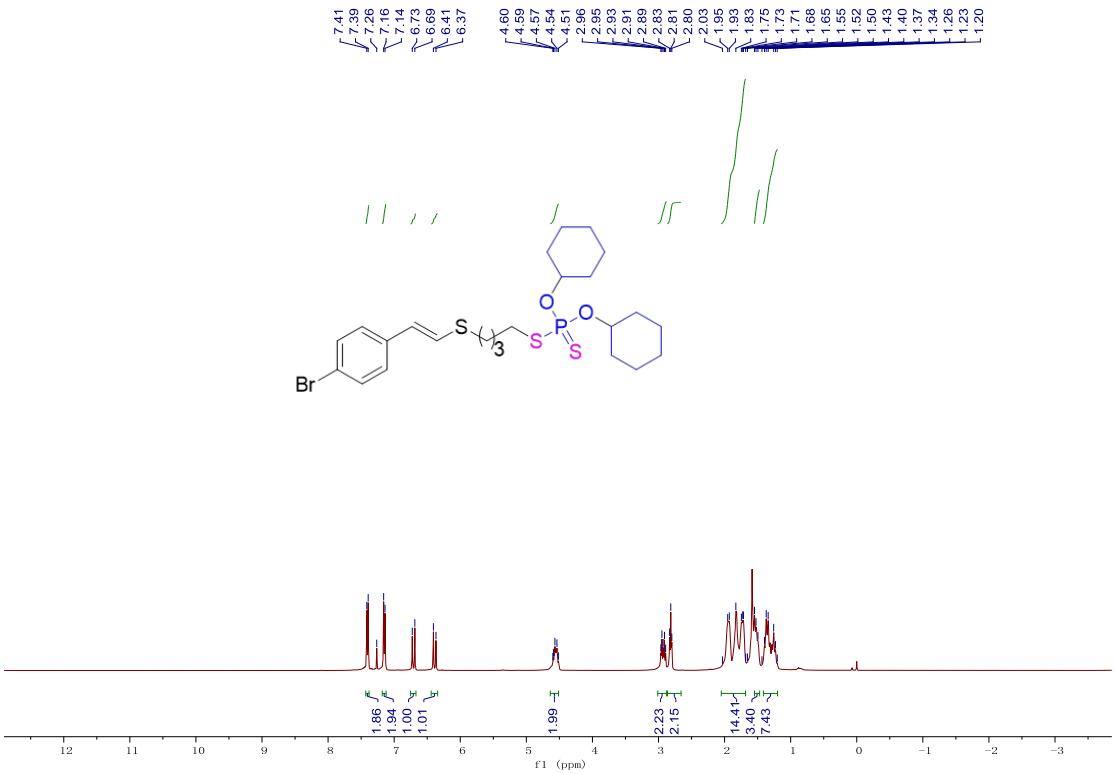
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9v**



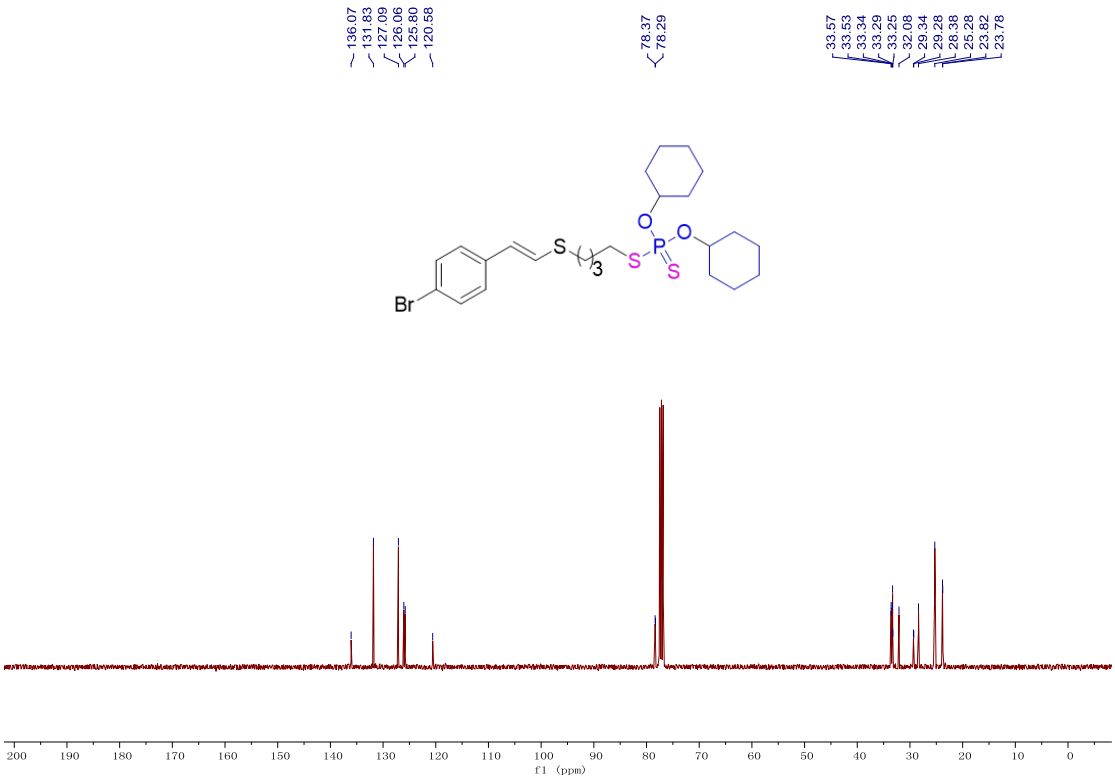
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9v**



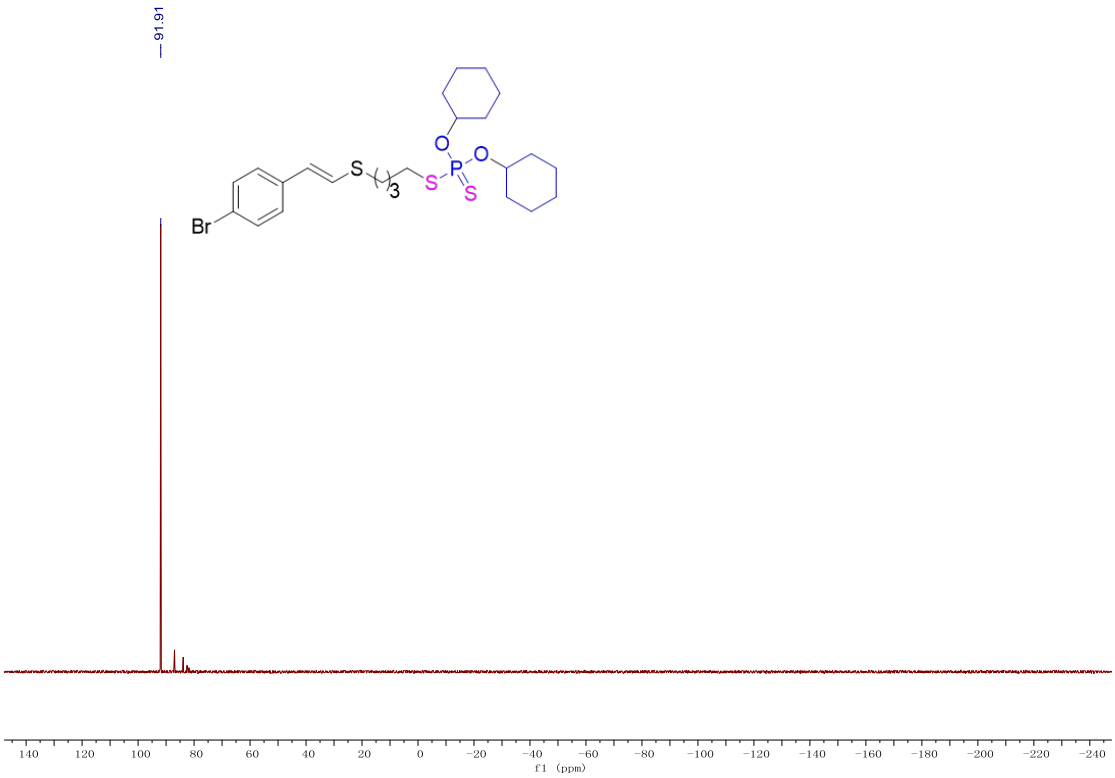
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9v**



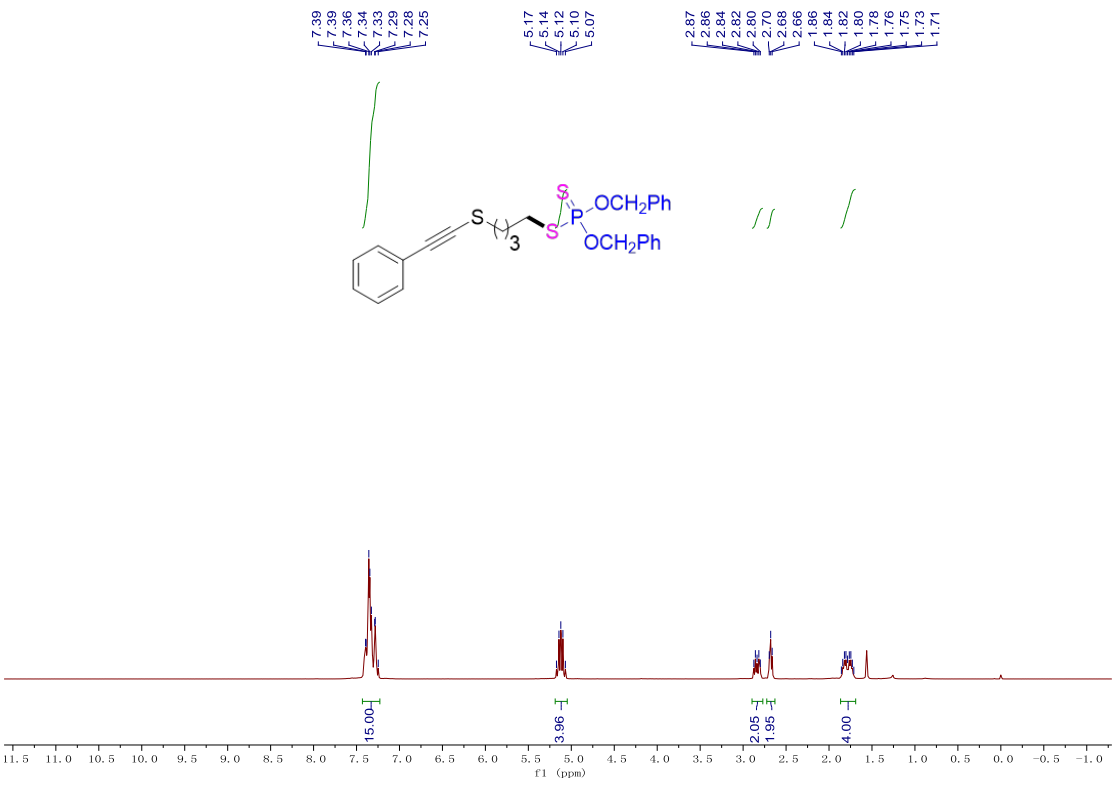
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9w**



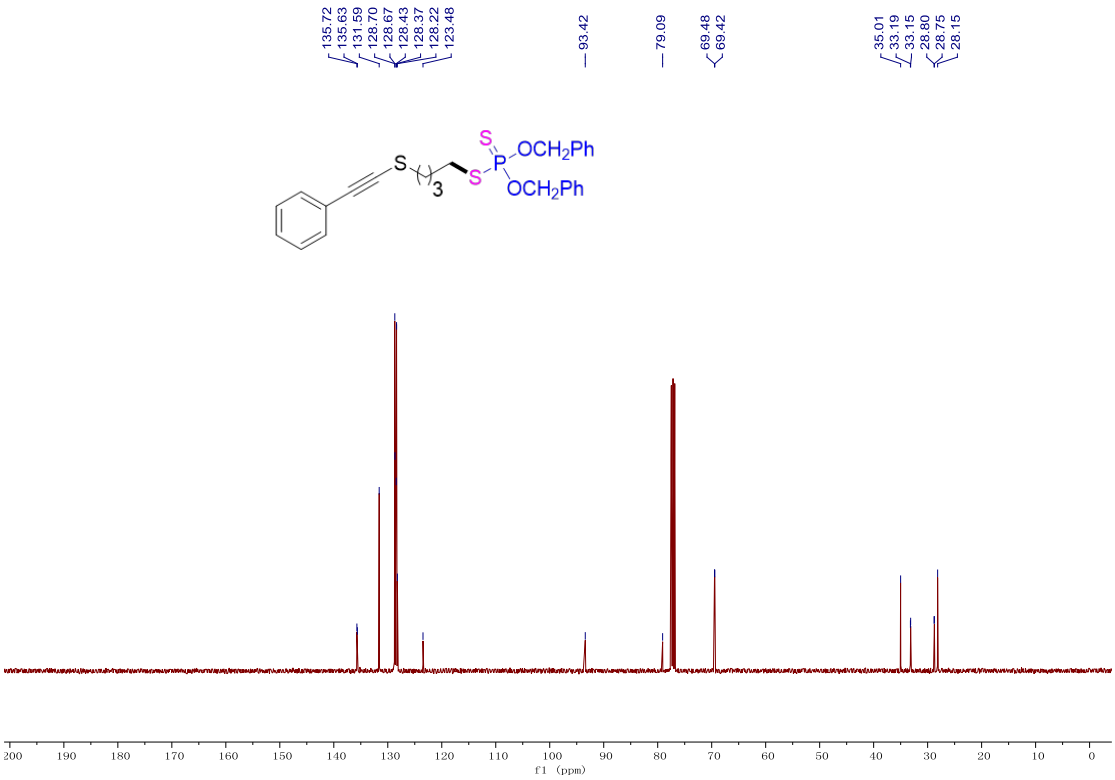
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9w**



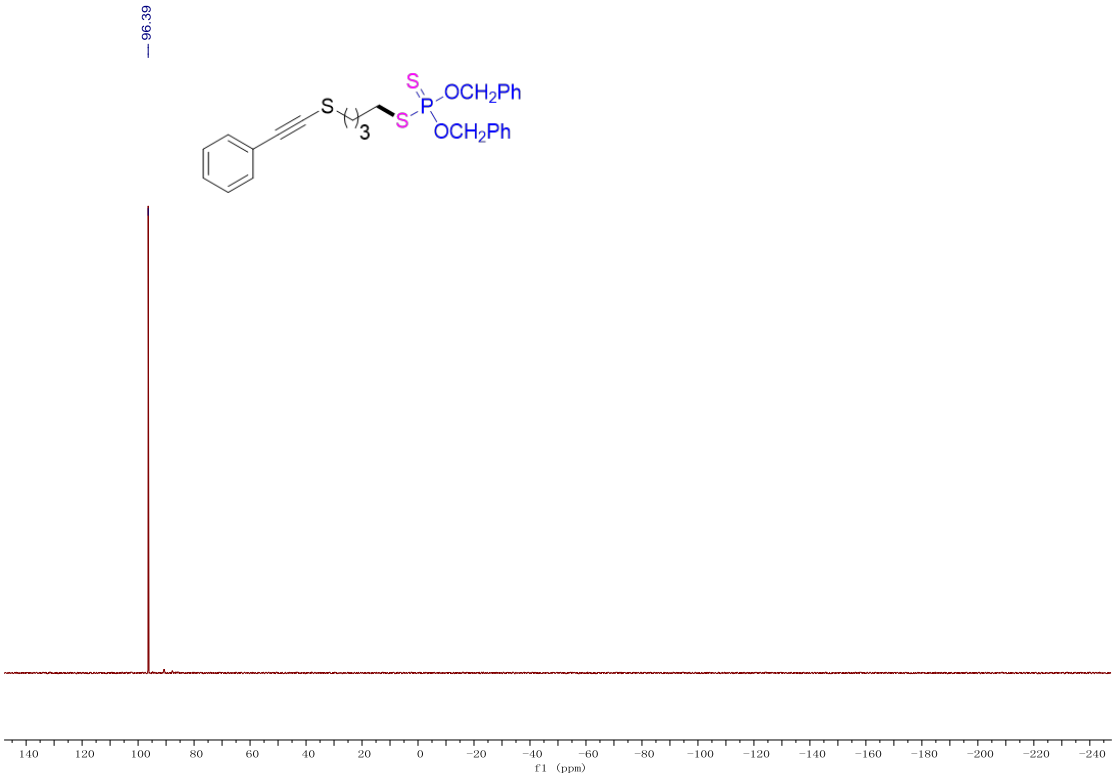
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9w**



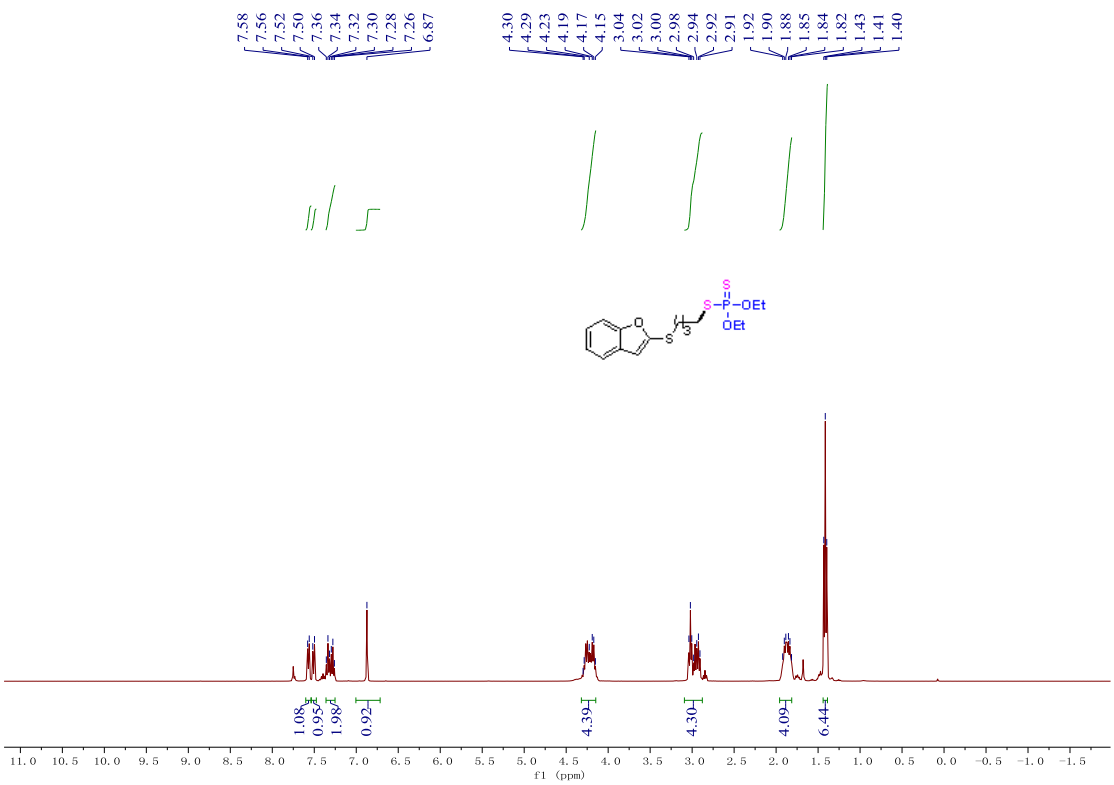
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9x**



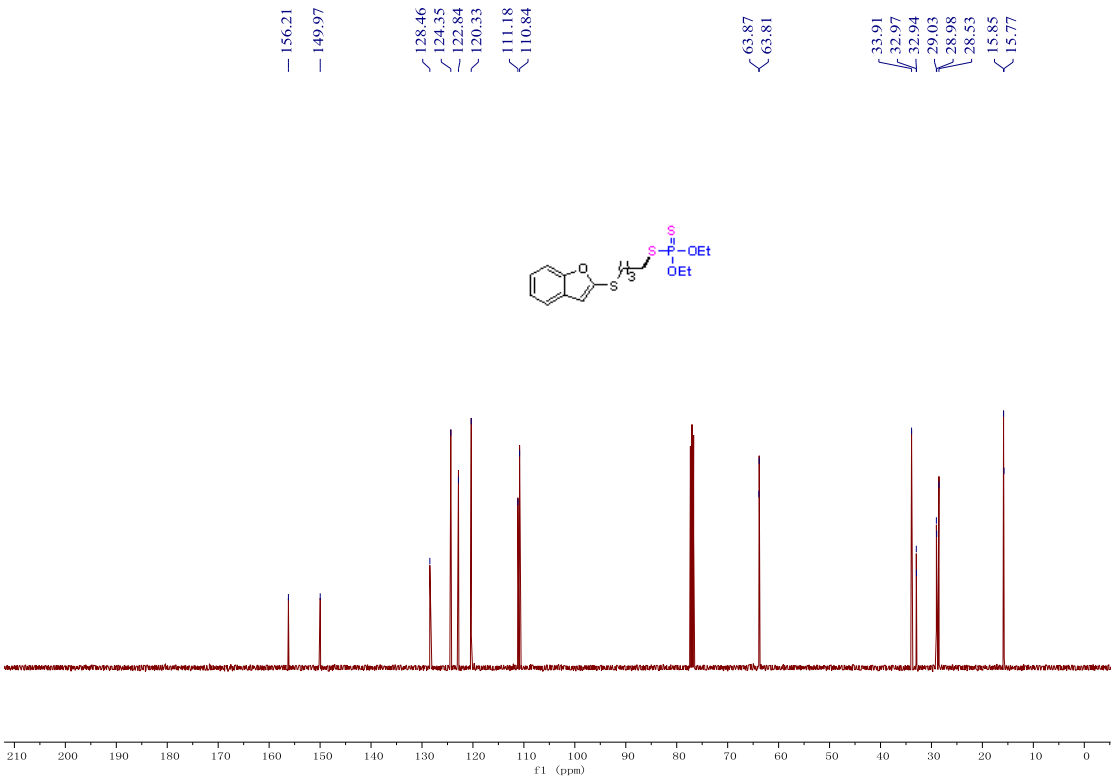
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9x**



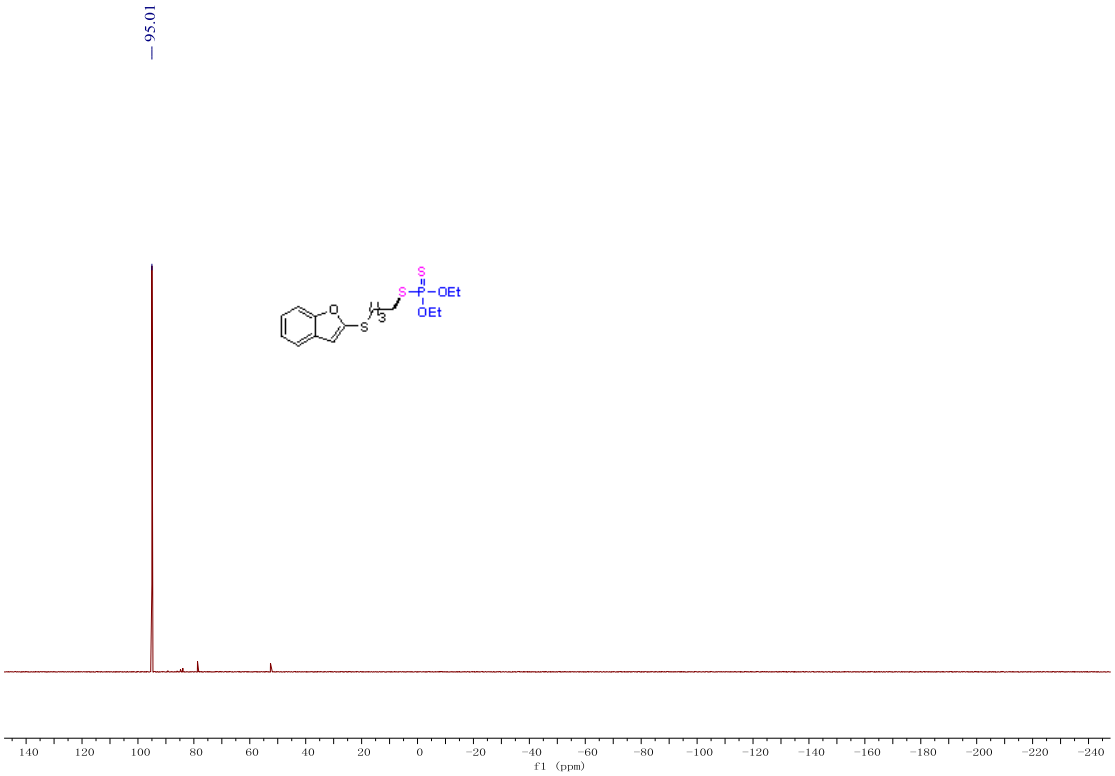
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9x**



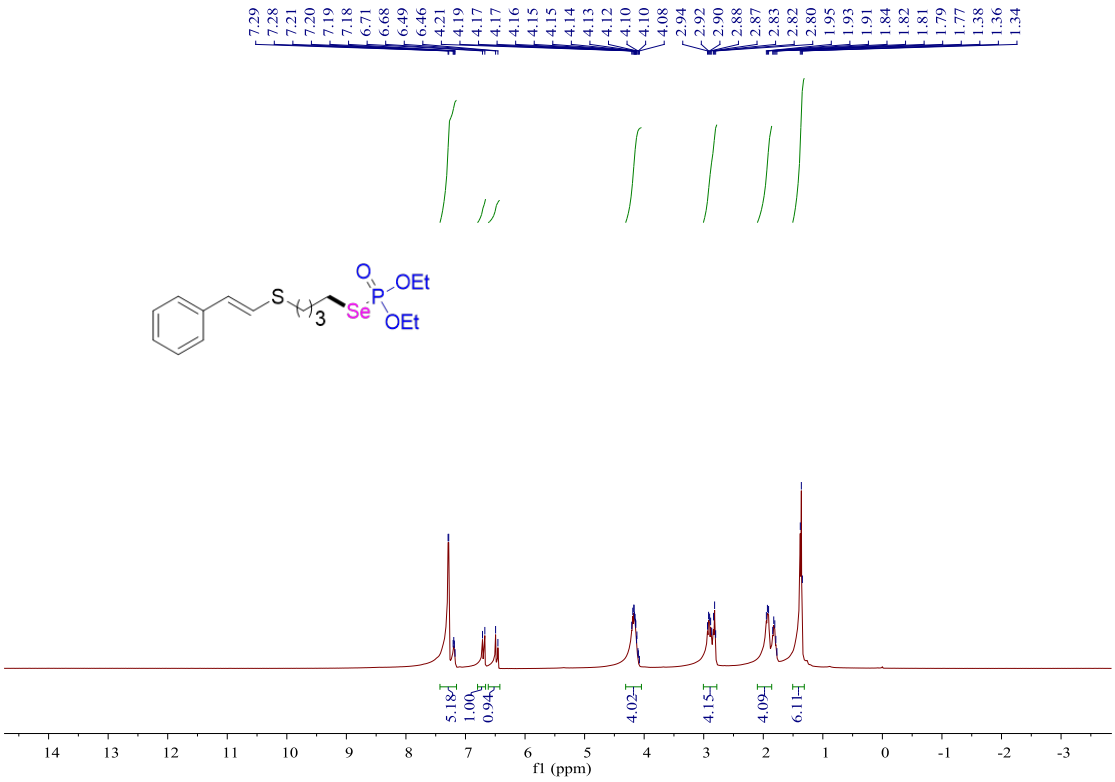
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9y**



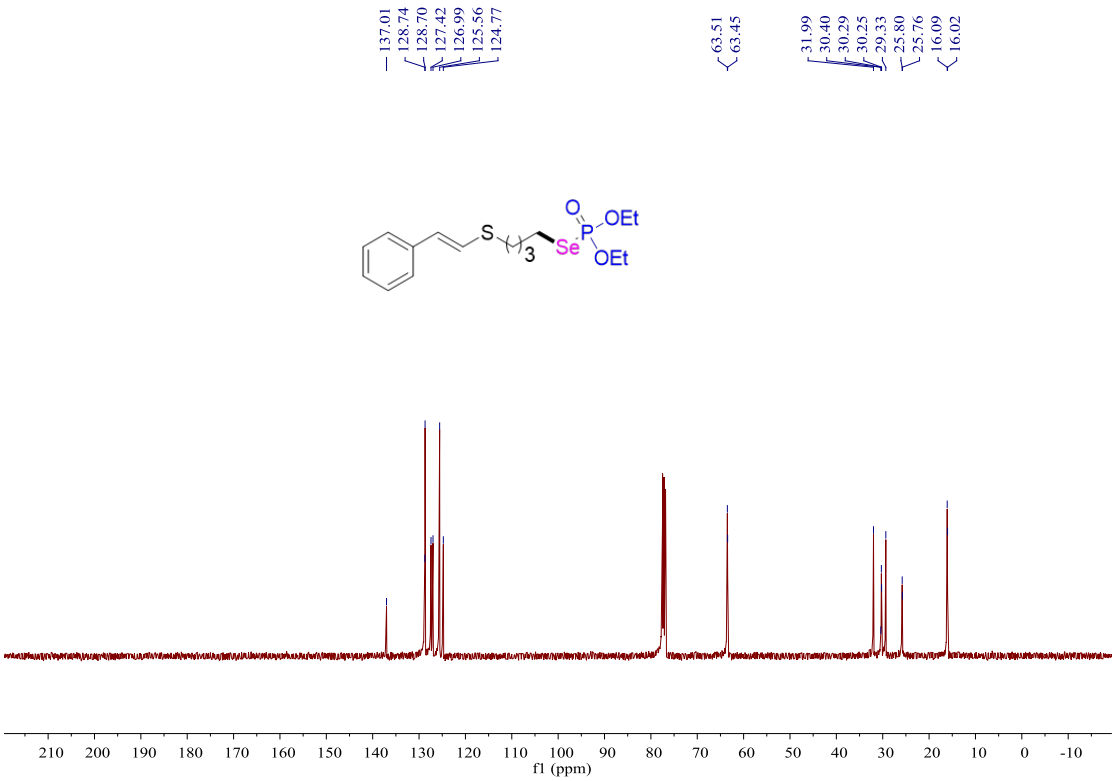
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9y**



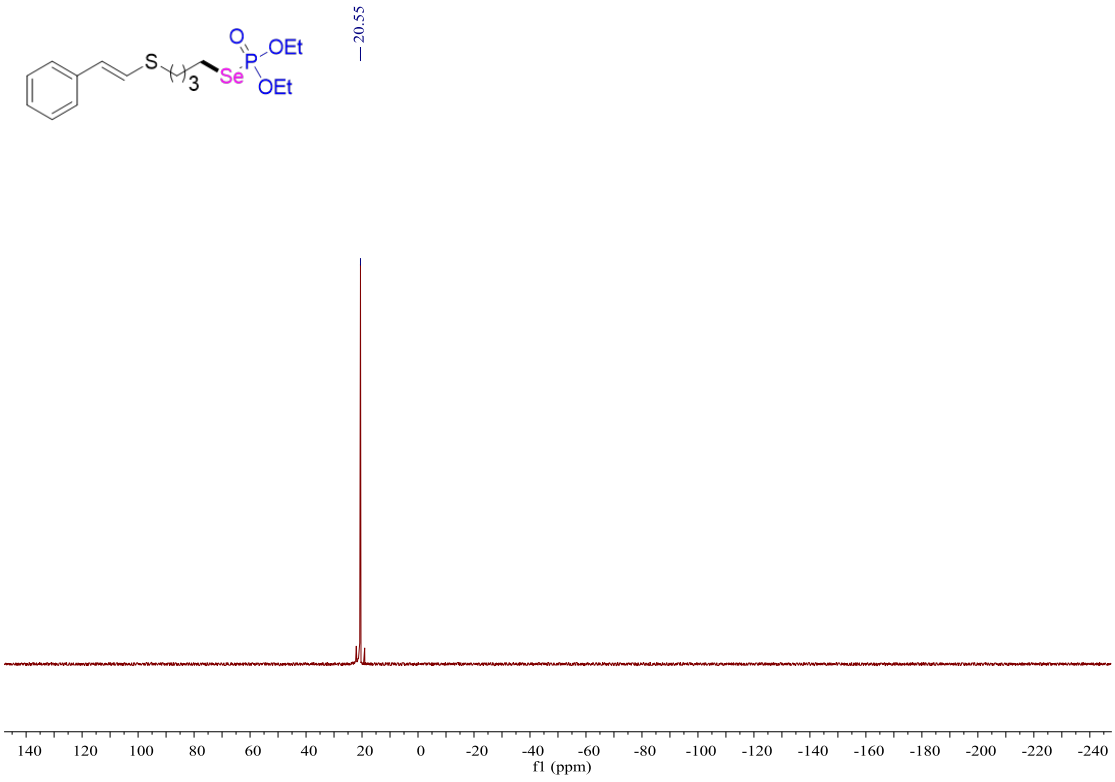
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9y**



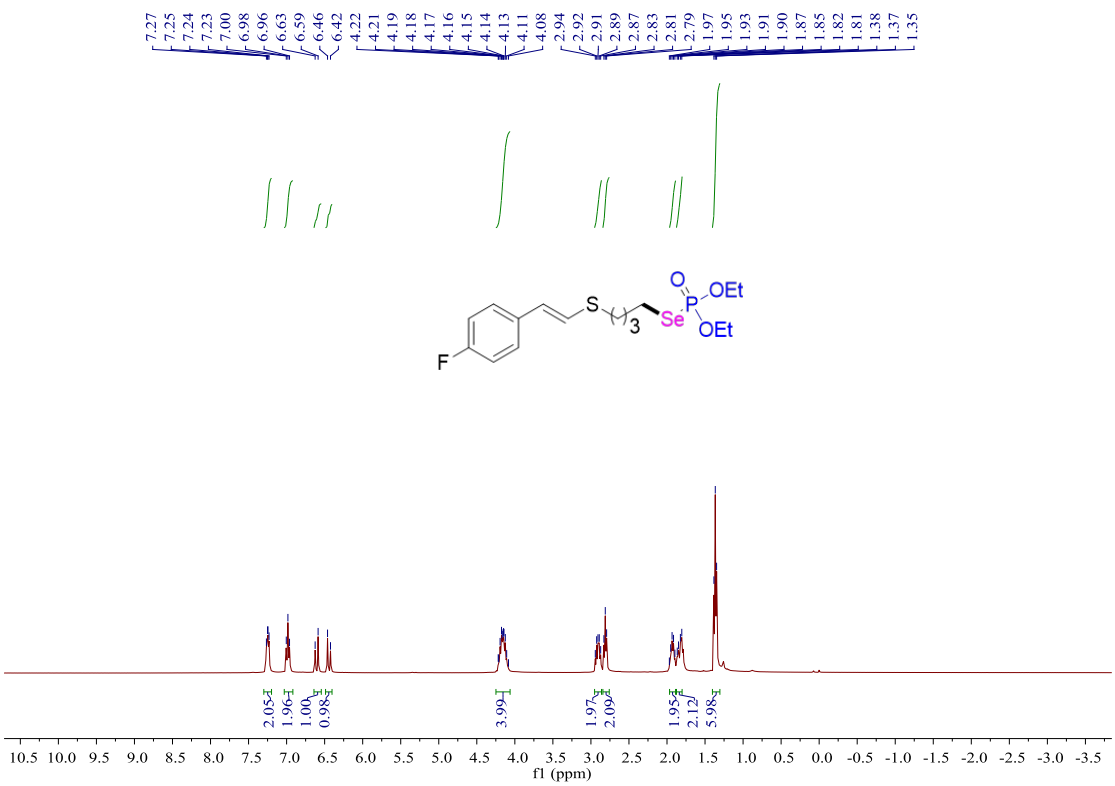
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10a**



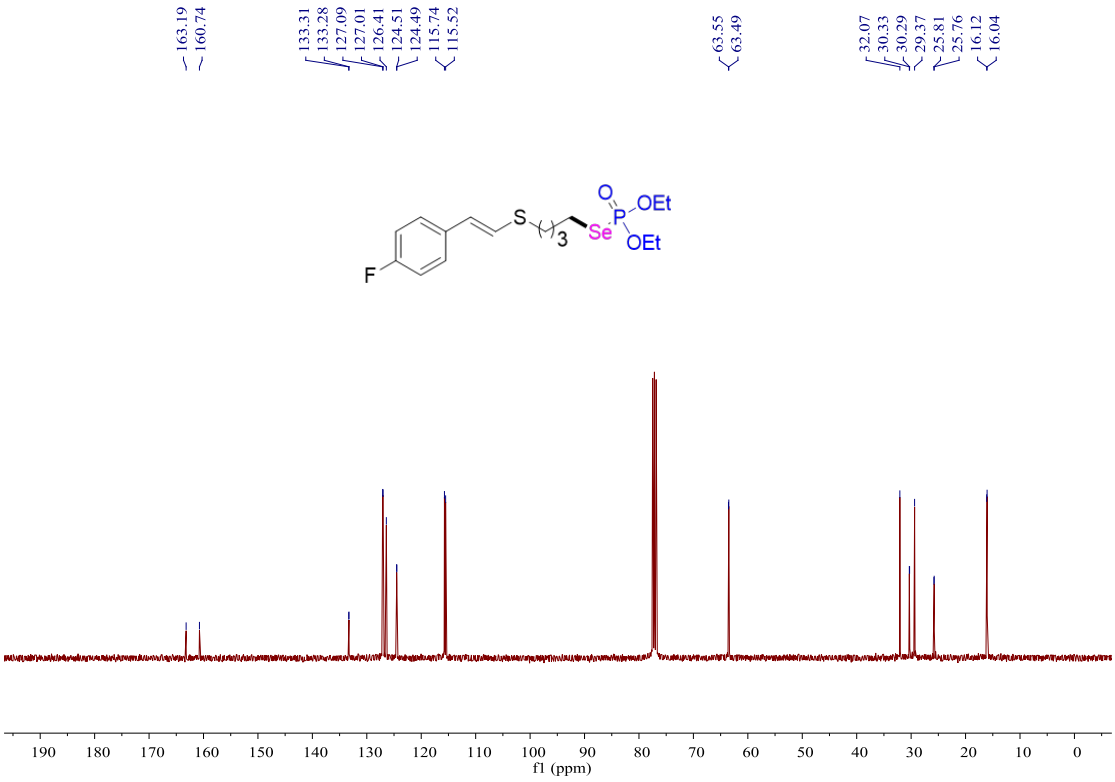
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10a**



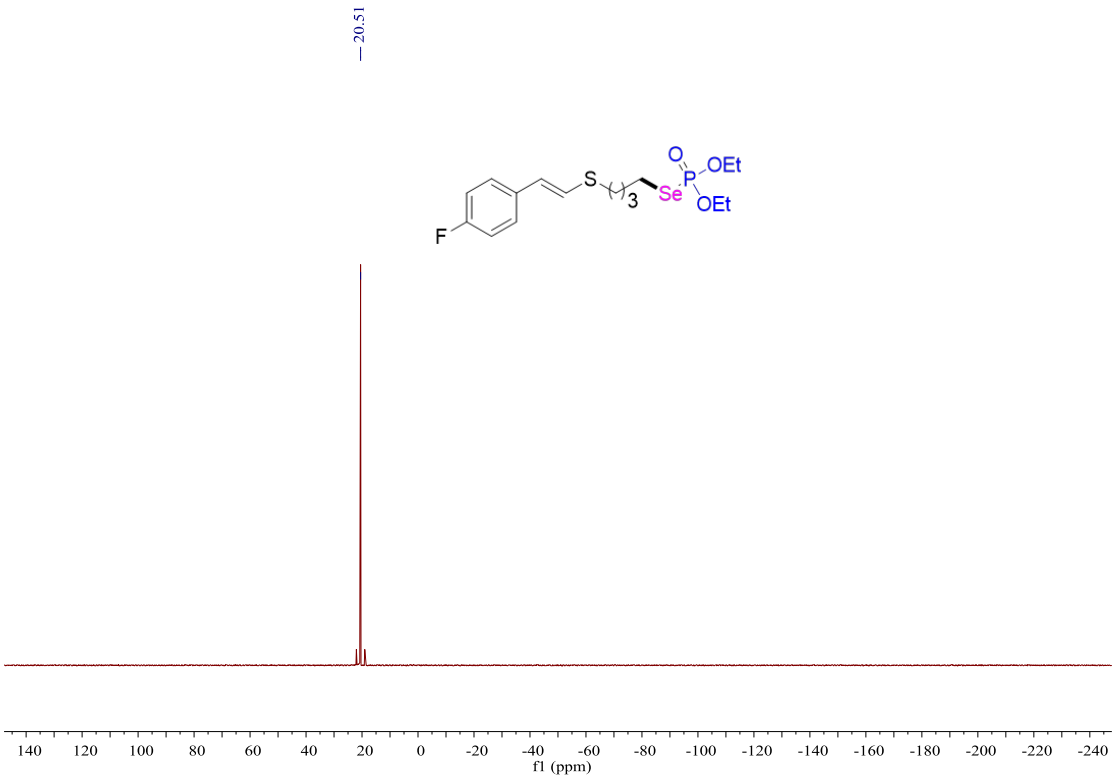
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10a**



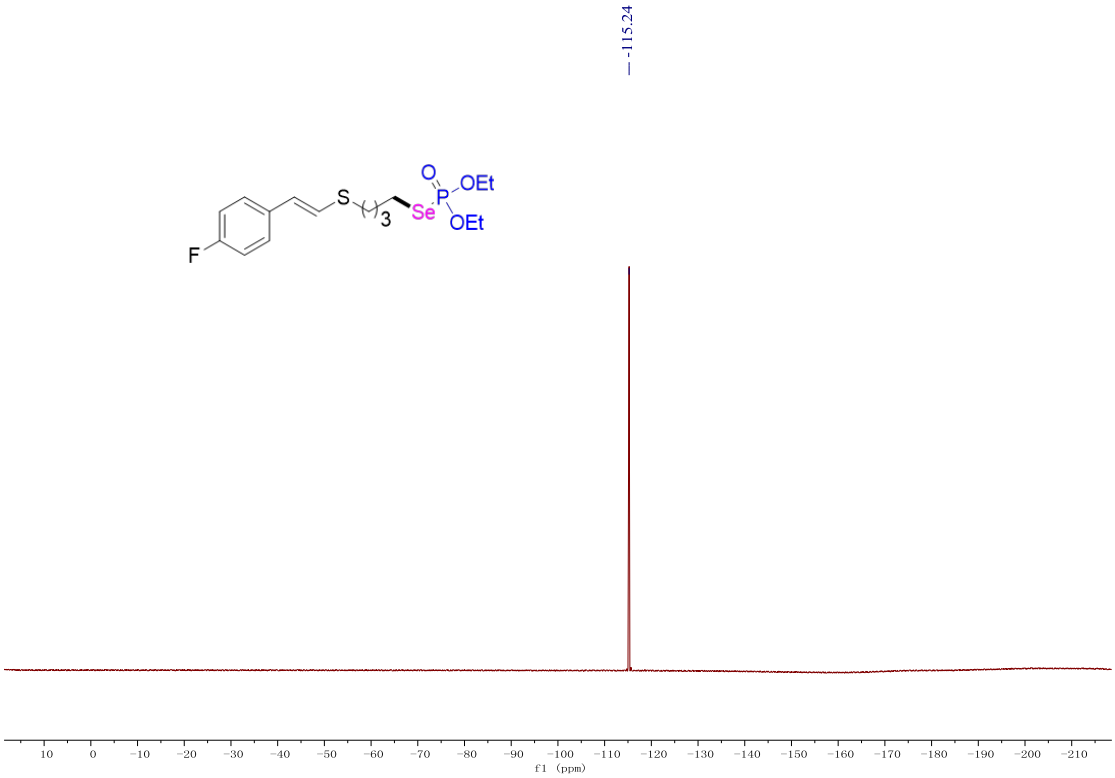
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10b**



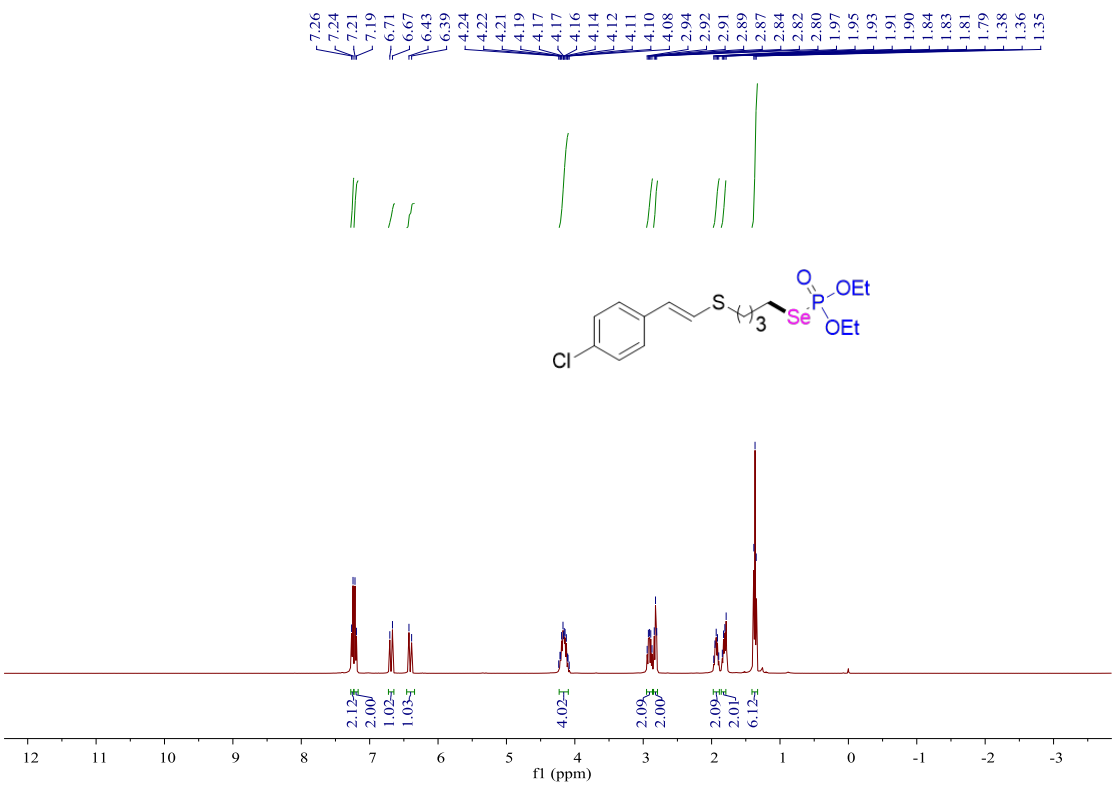
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10b**



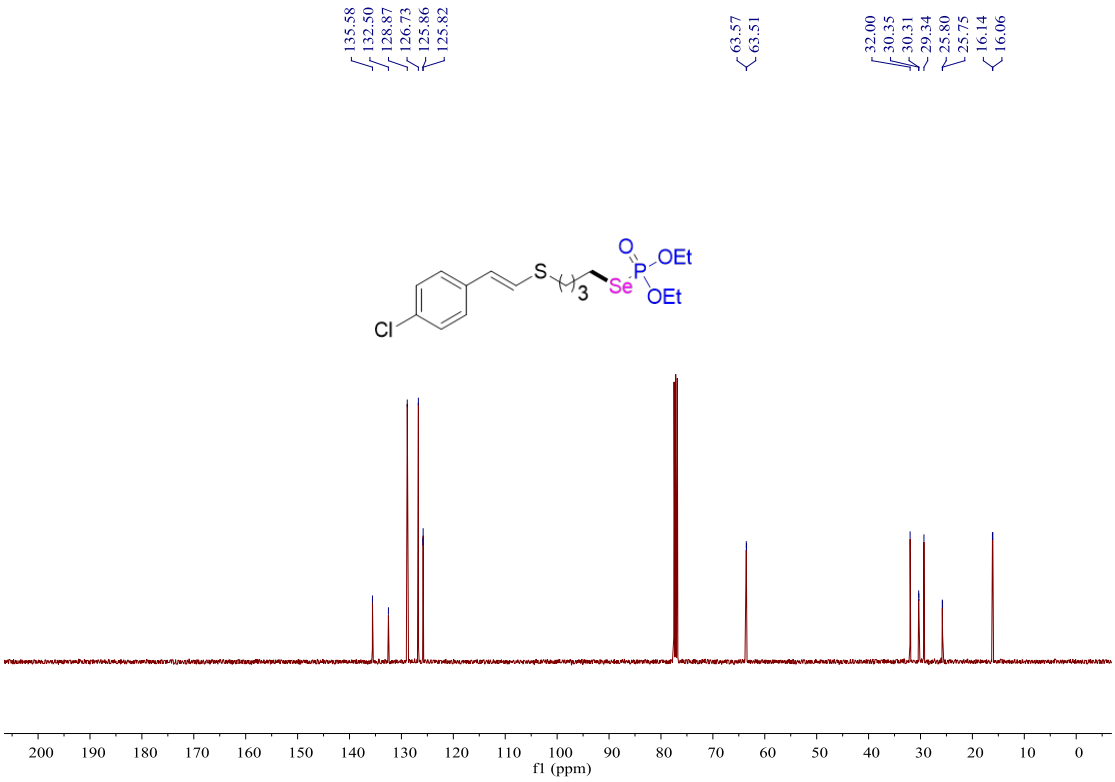
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10b**



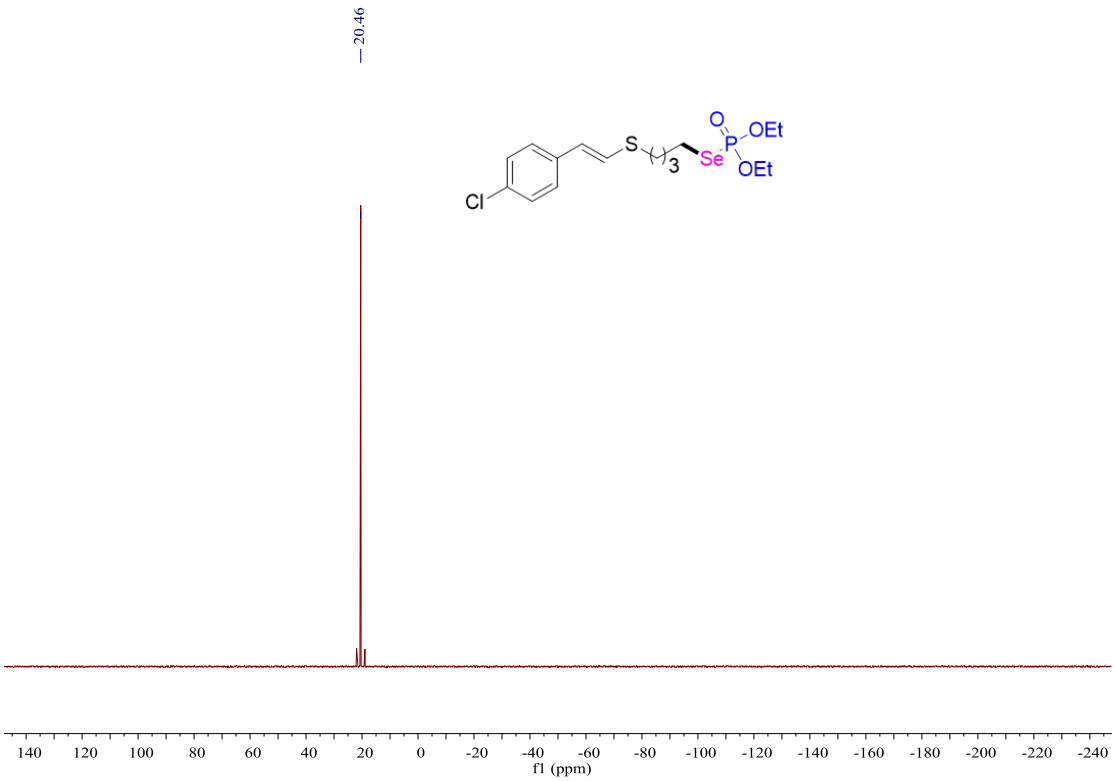
^{19}F NMR (376 MHz, $CDCl_3$) spectra of **10b**



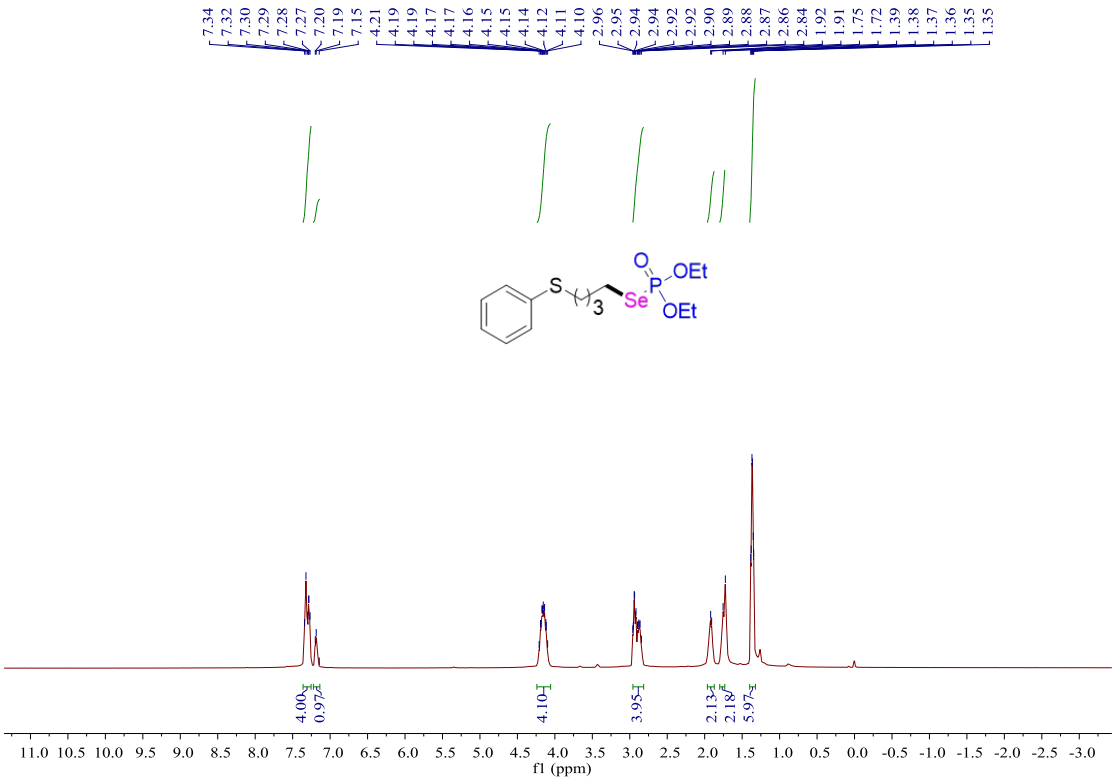
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10c**



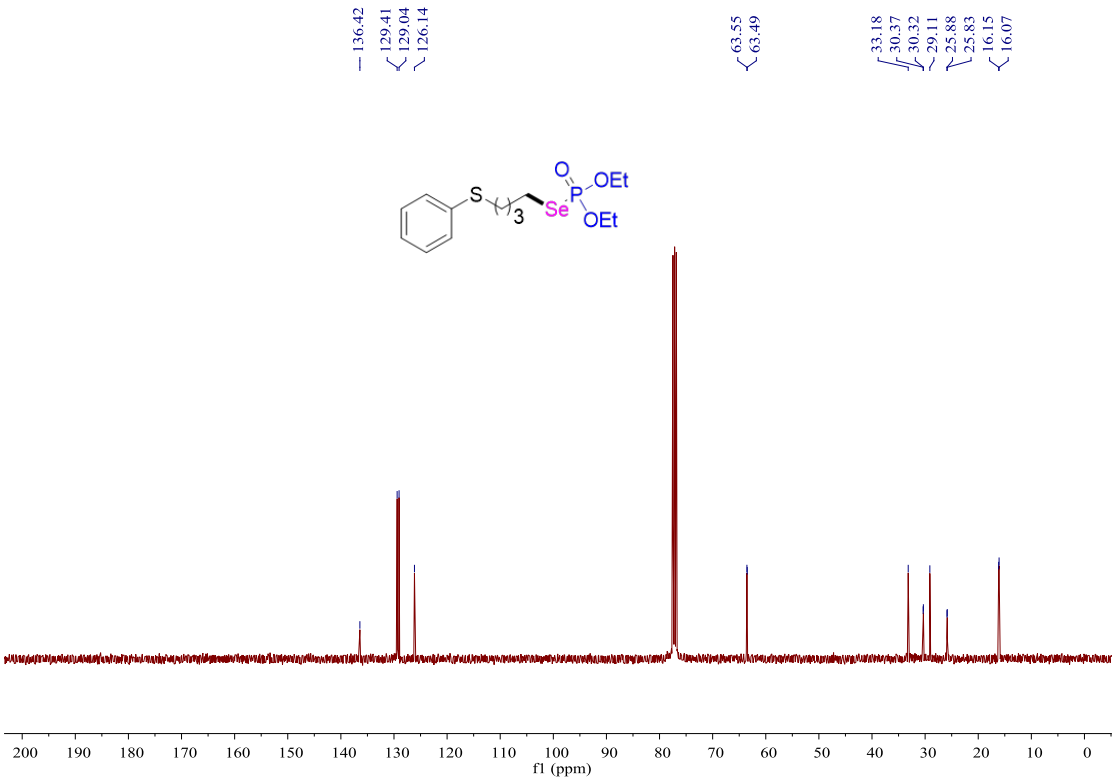
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10c**



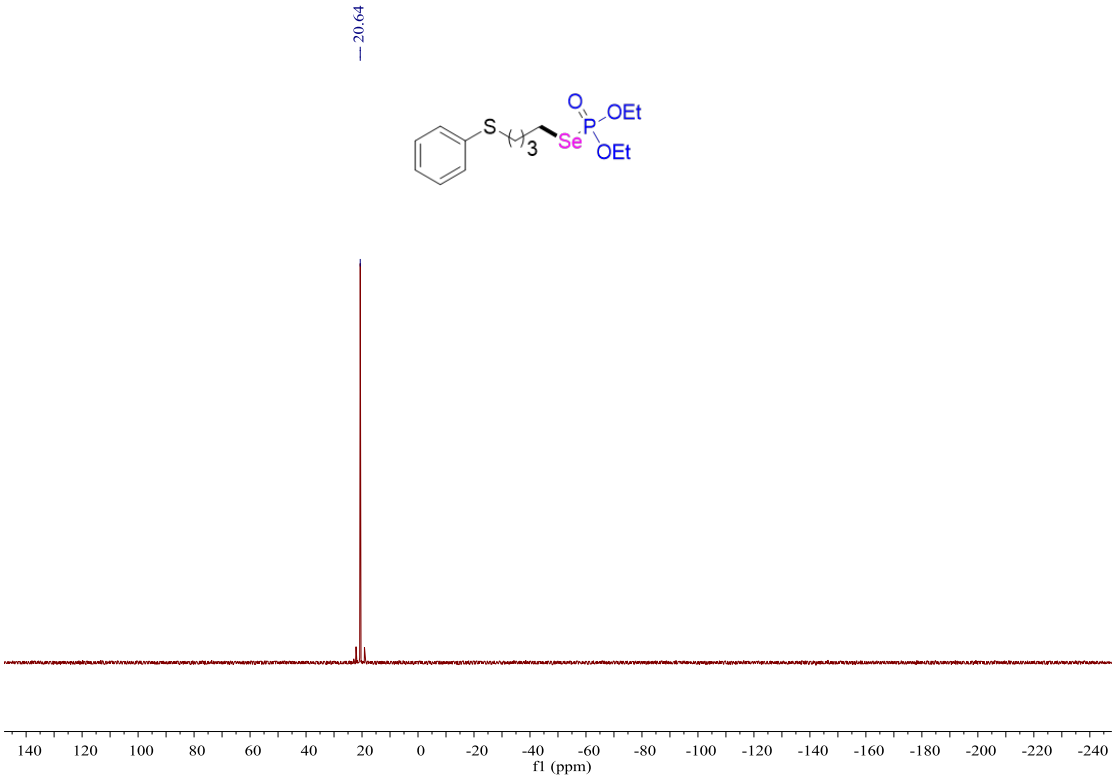
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10c**



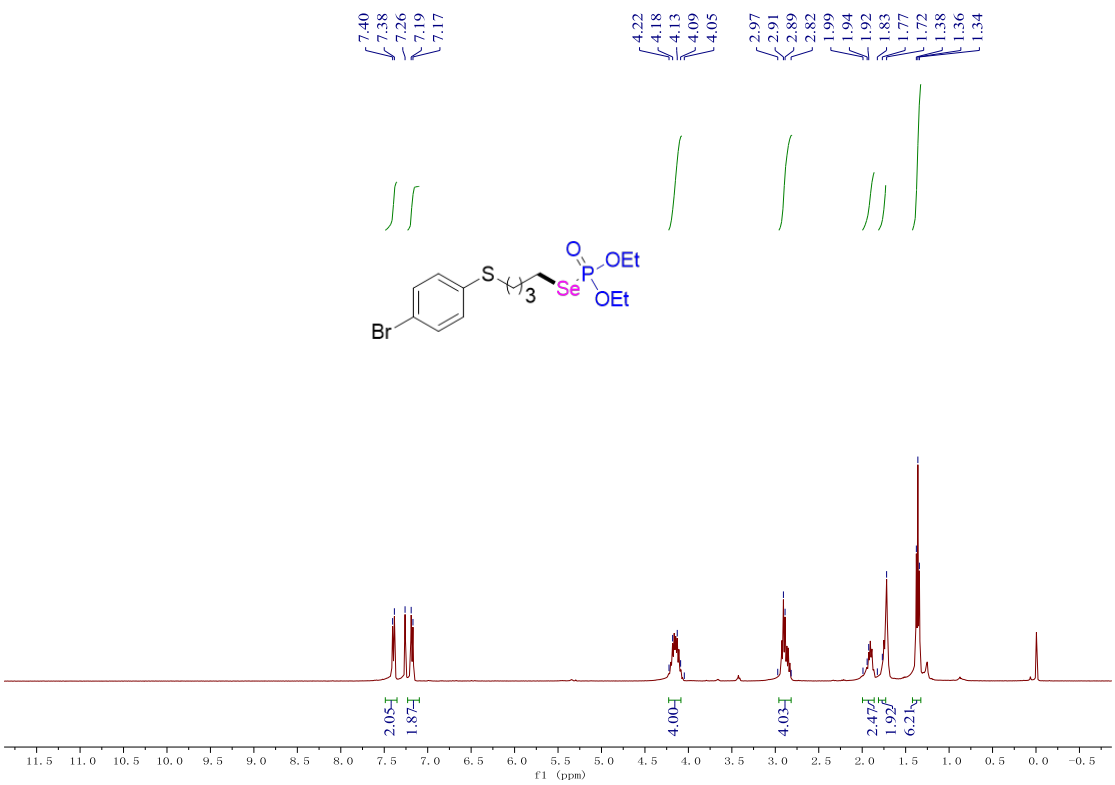
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10d**



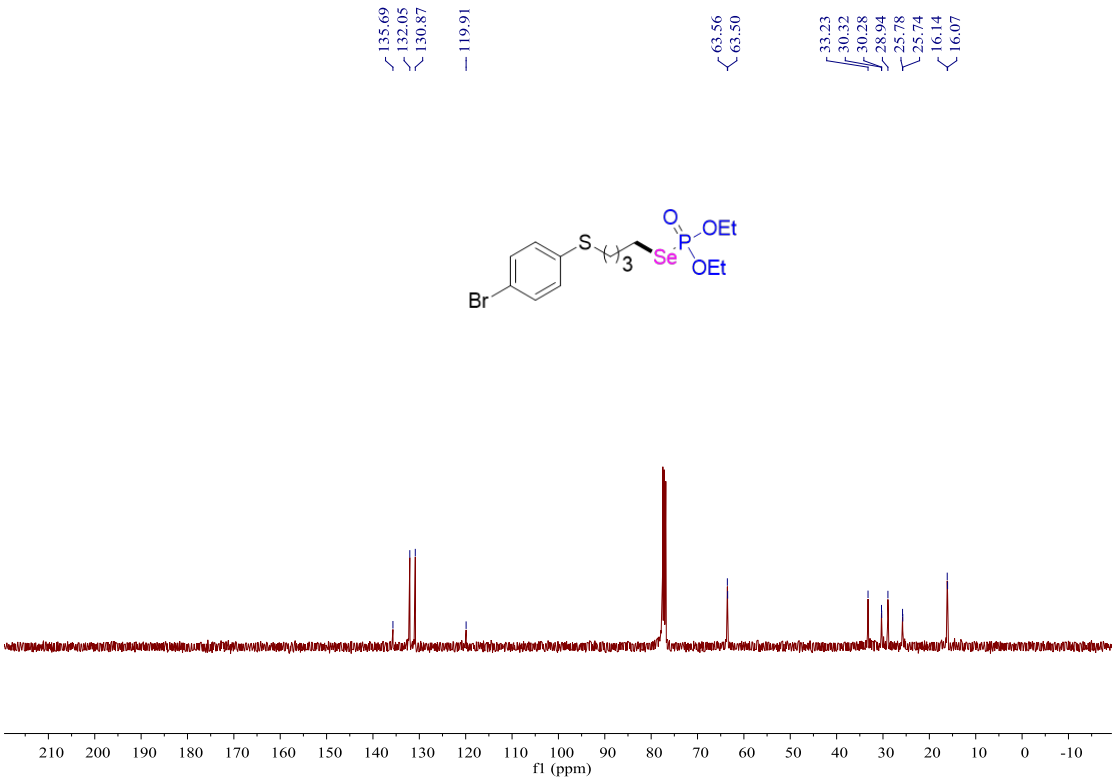
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10d**



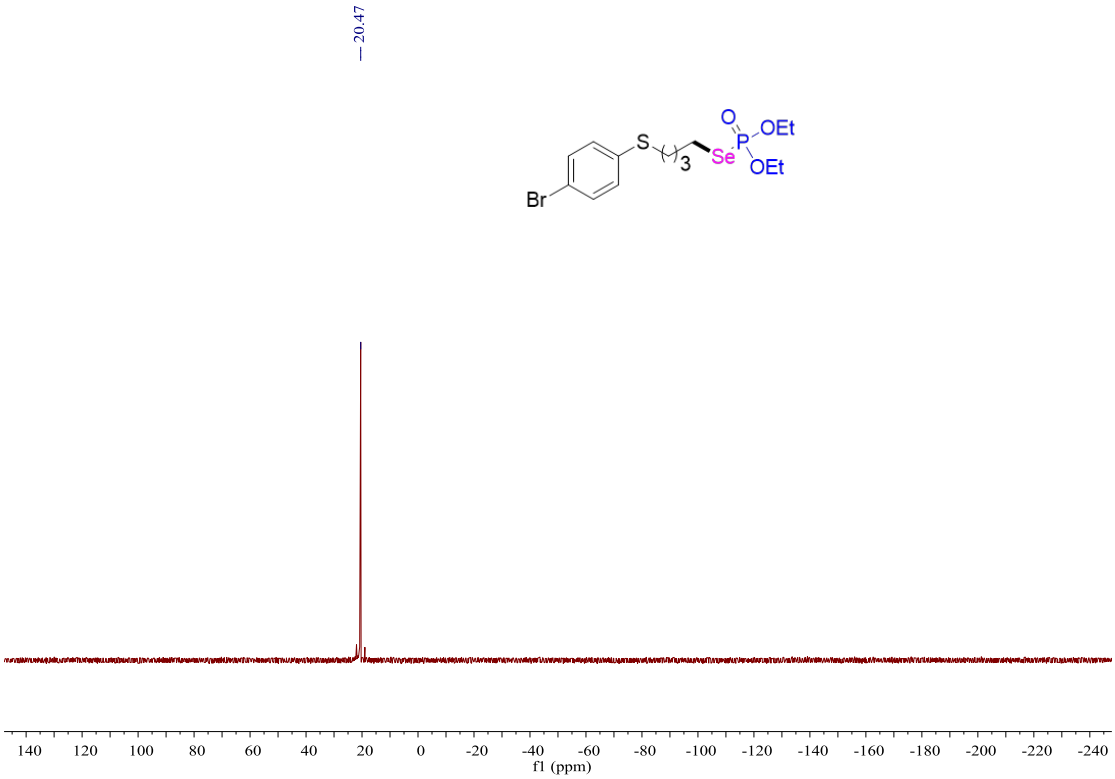
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10d**



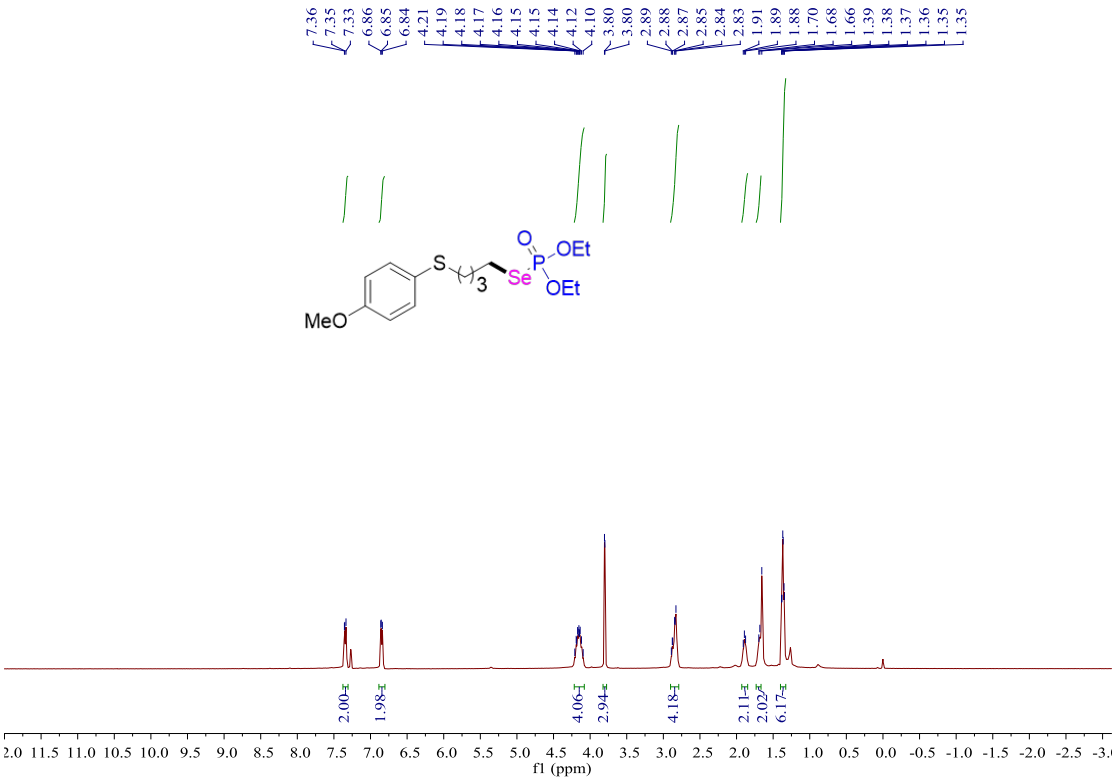
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10e**



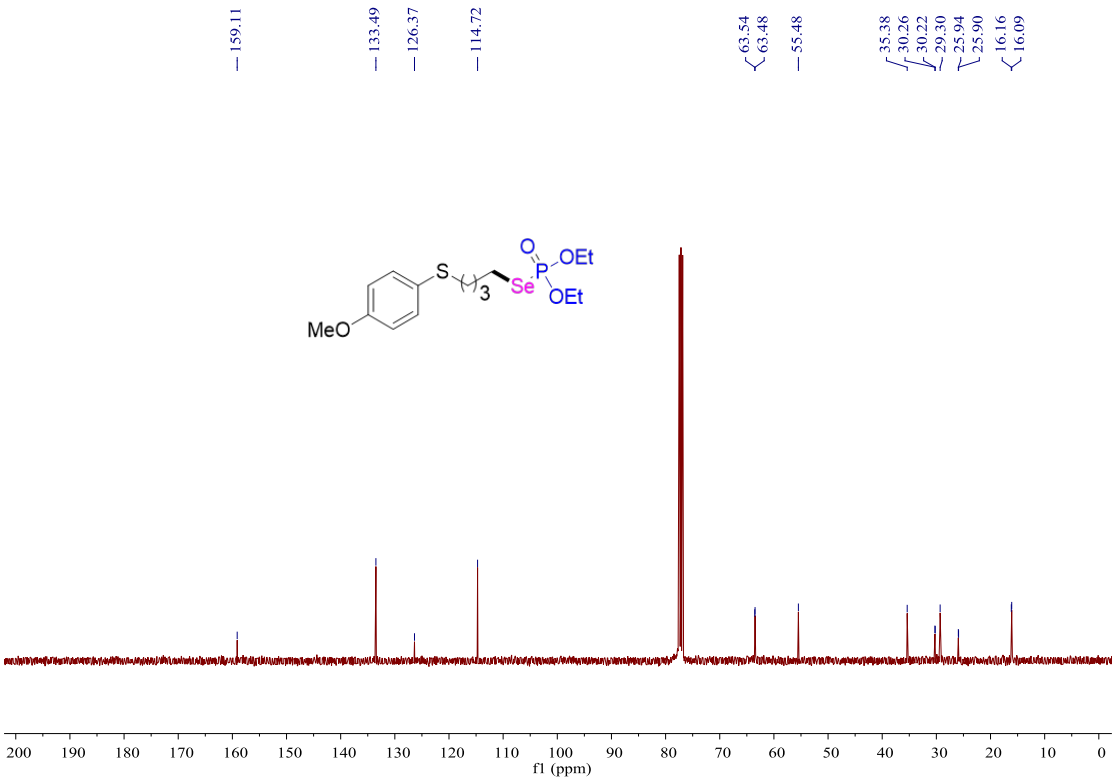
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10e**



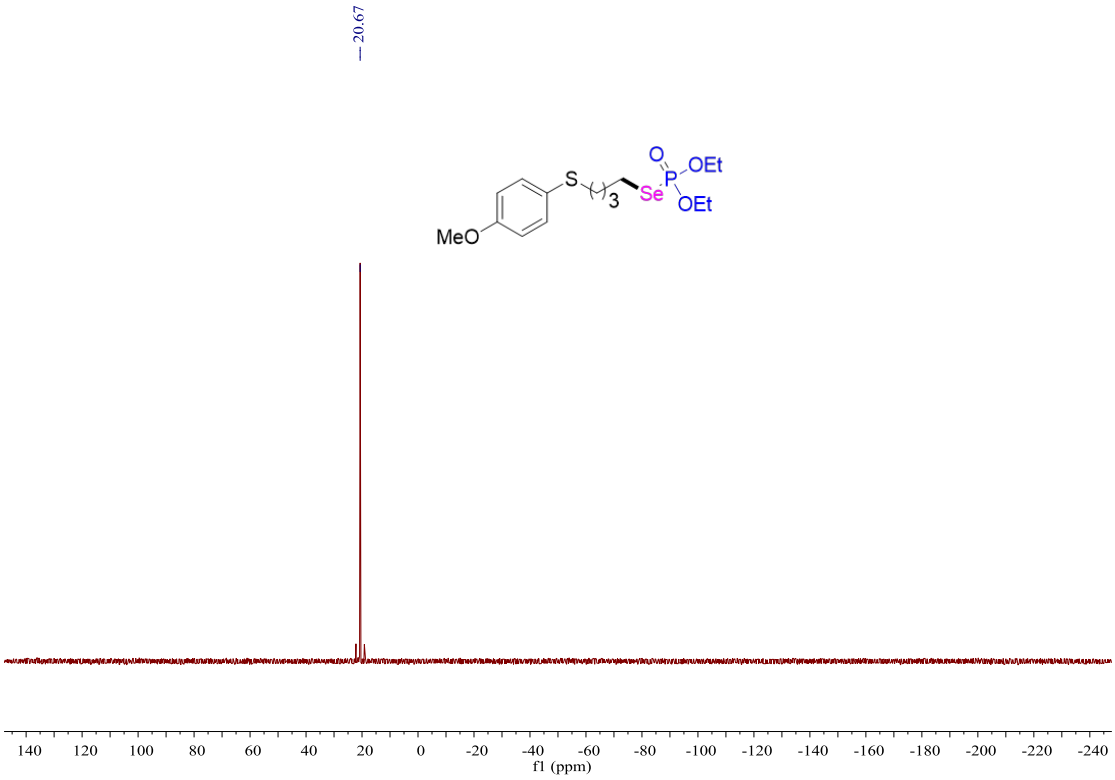
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10e**



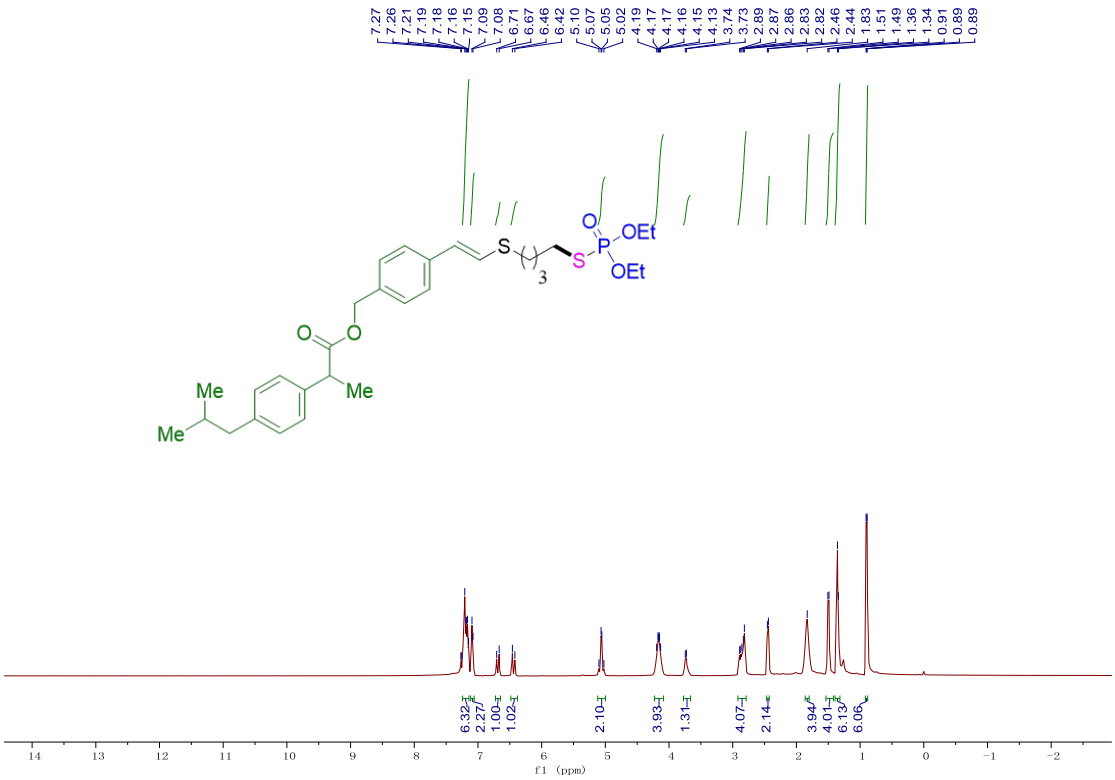
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **10f**



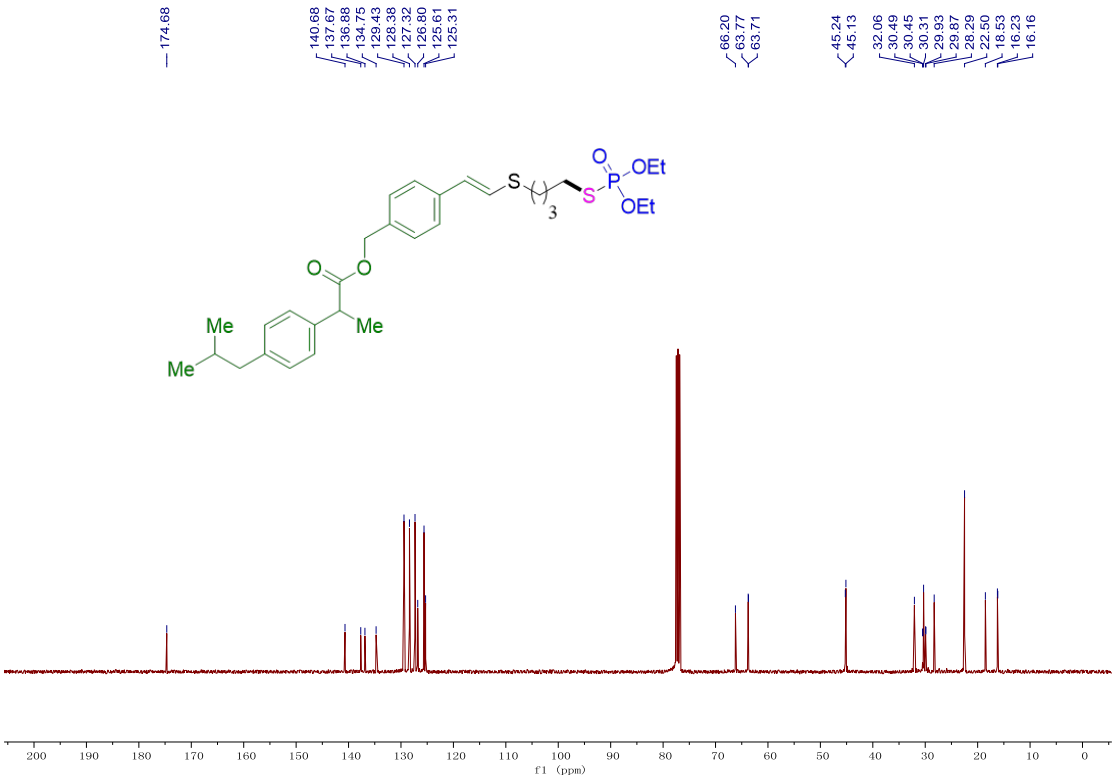
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **10f**



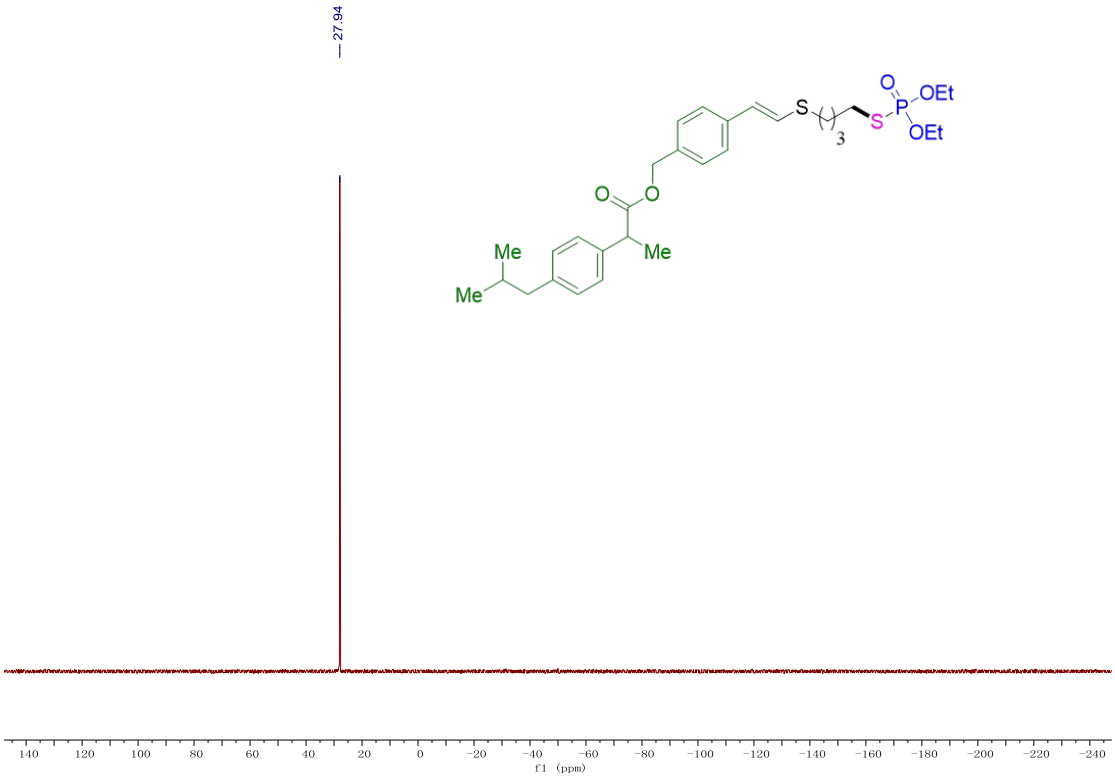
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **10f**



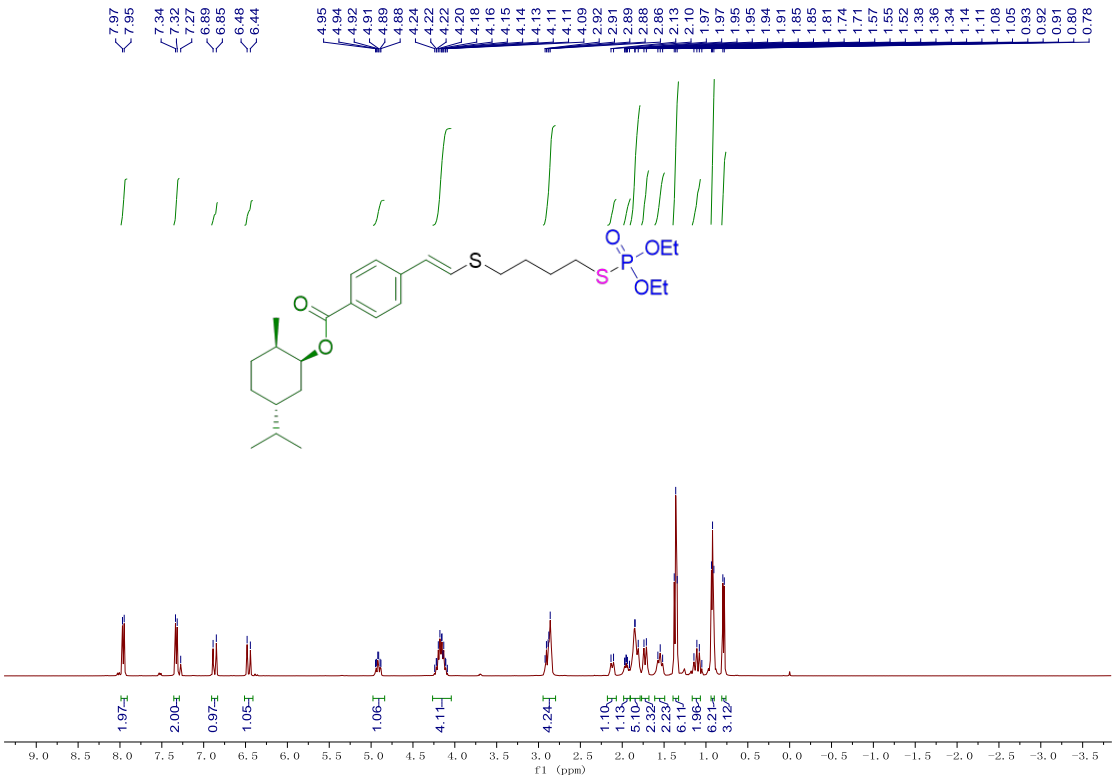
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3ra**



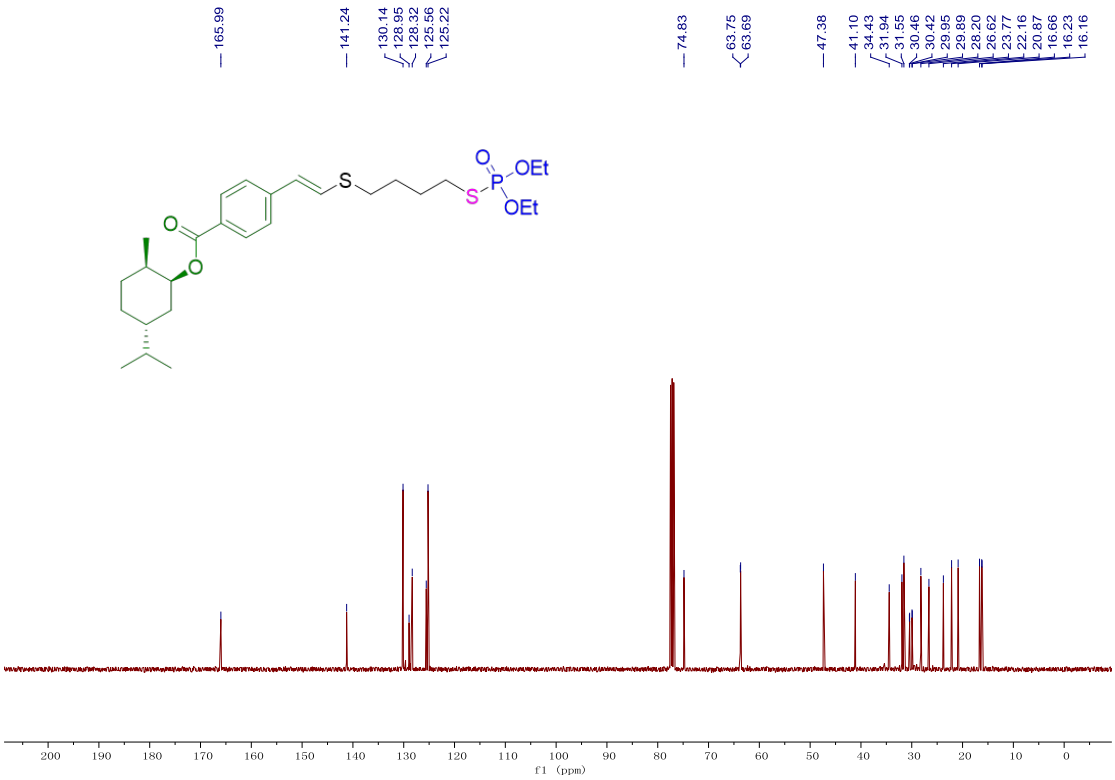
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3ra**



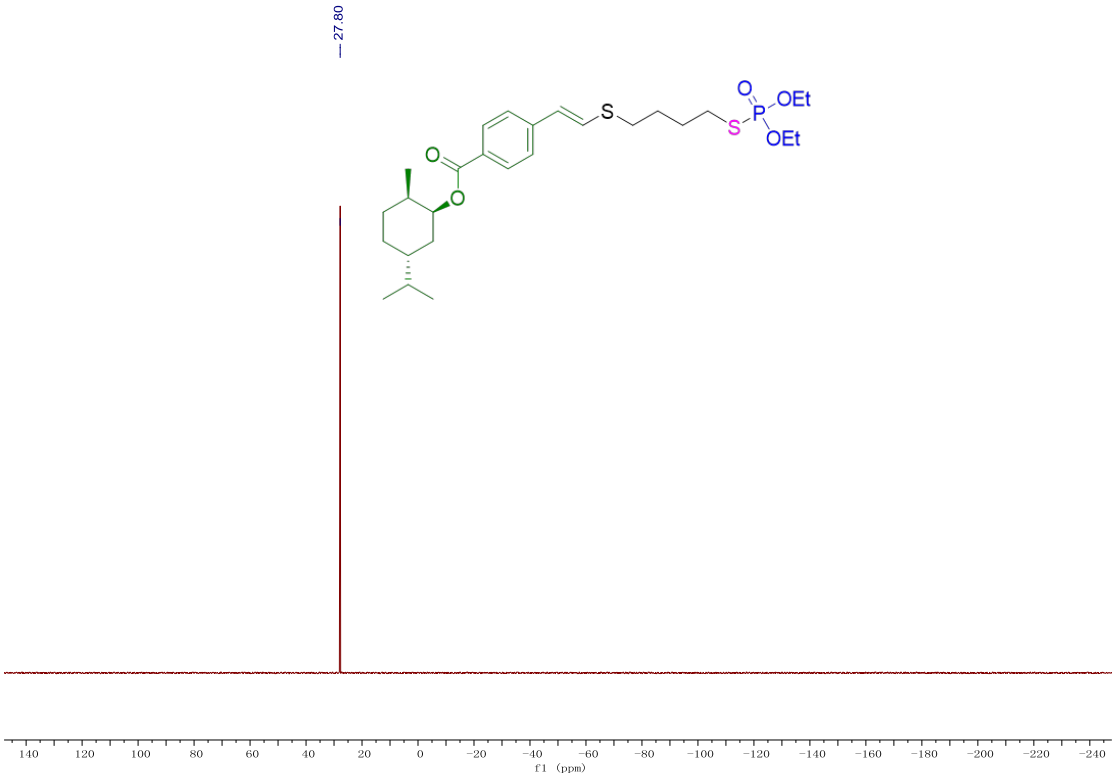
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3ra**



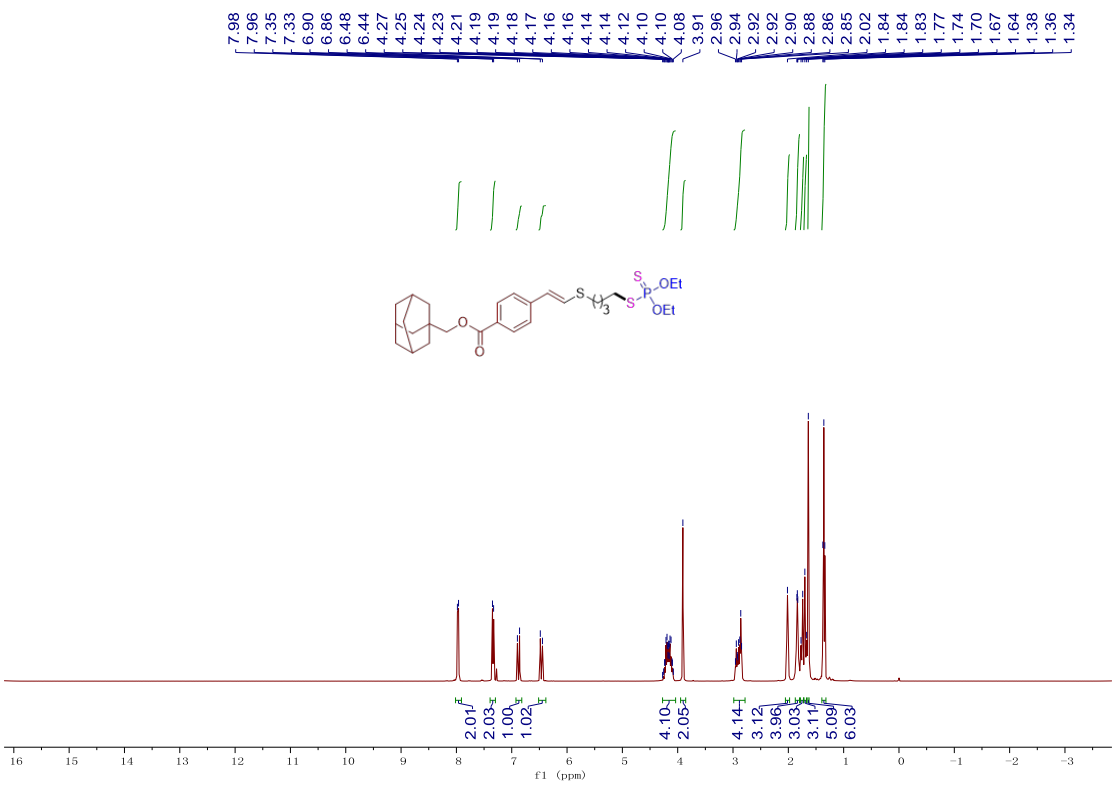
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3sa**



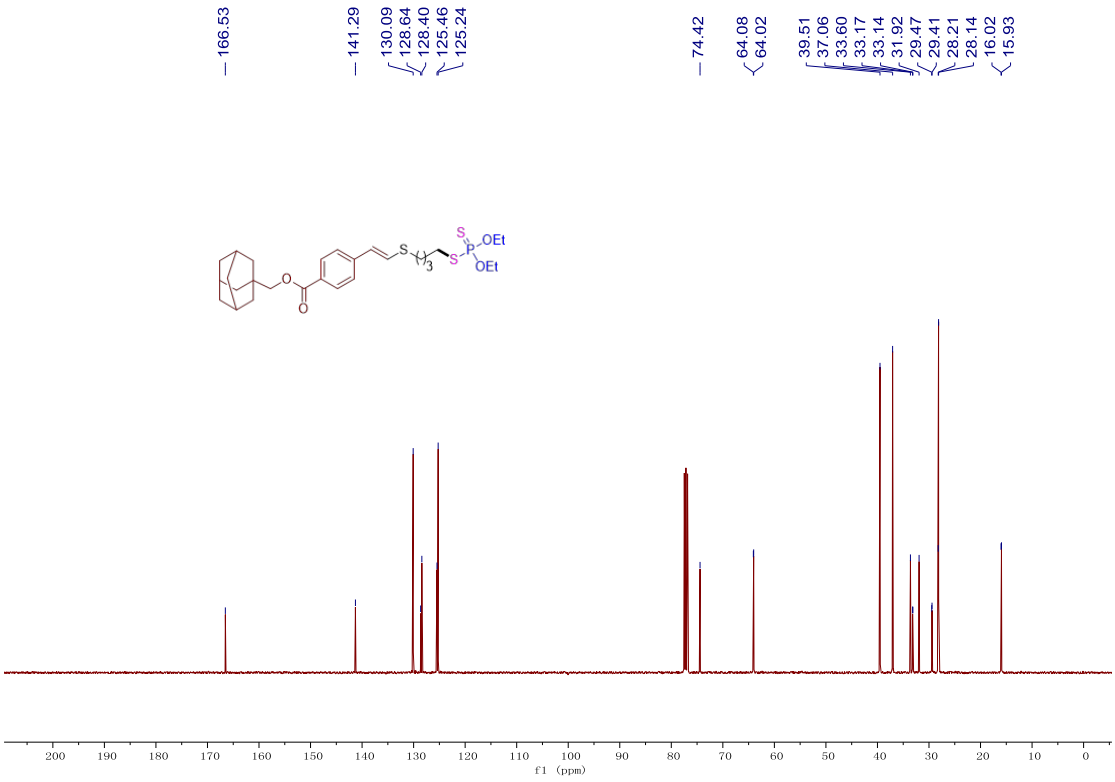
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **3sa**



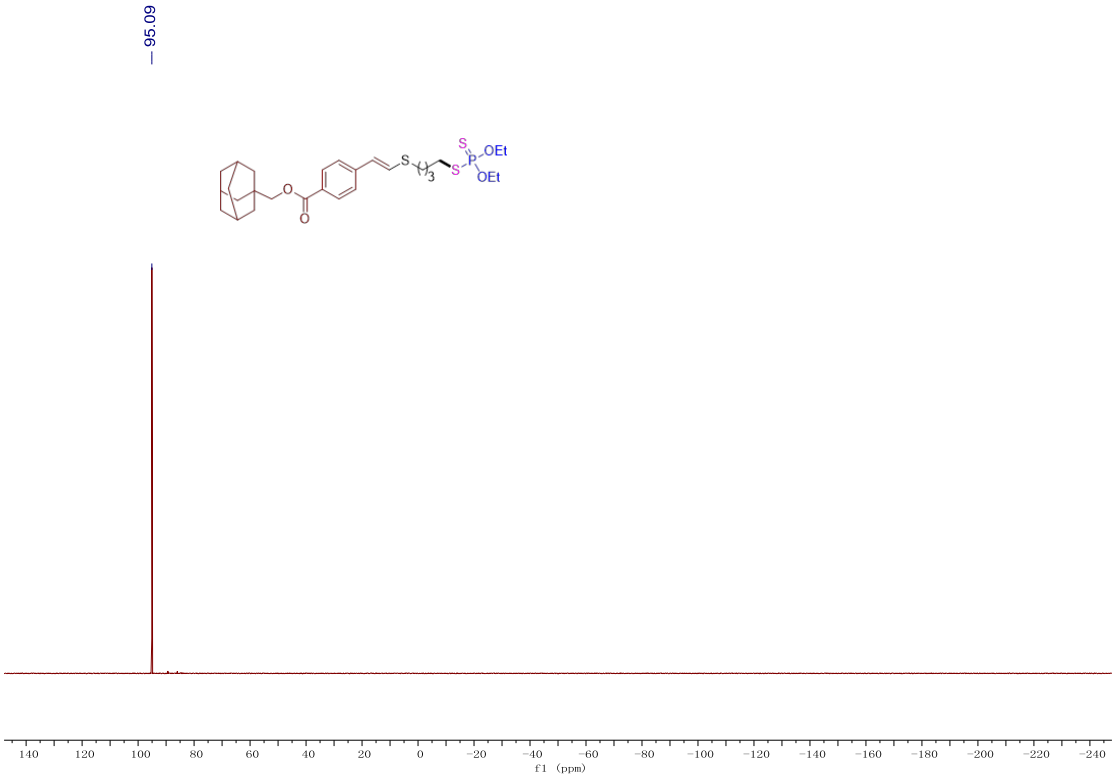
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **3sa**



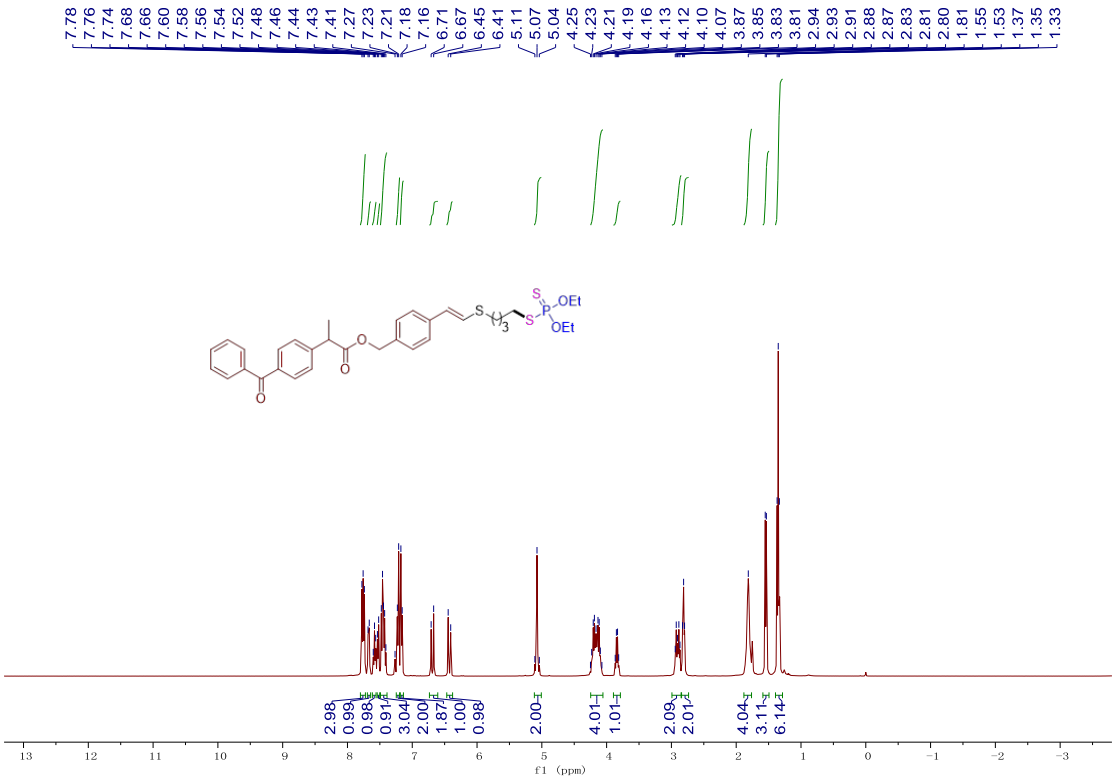
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9ab**



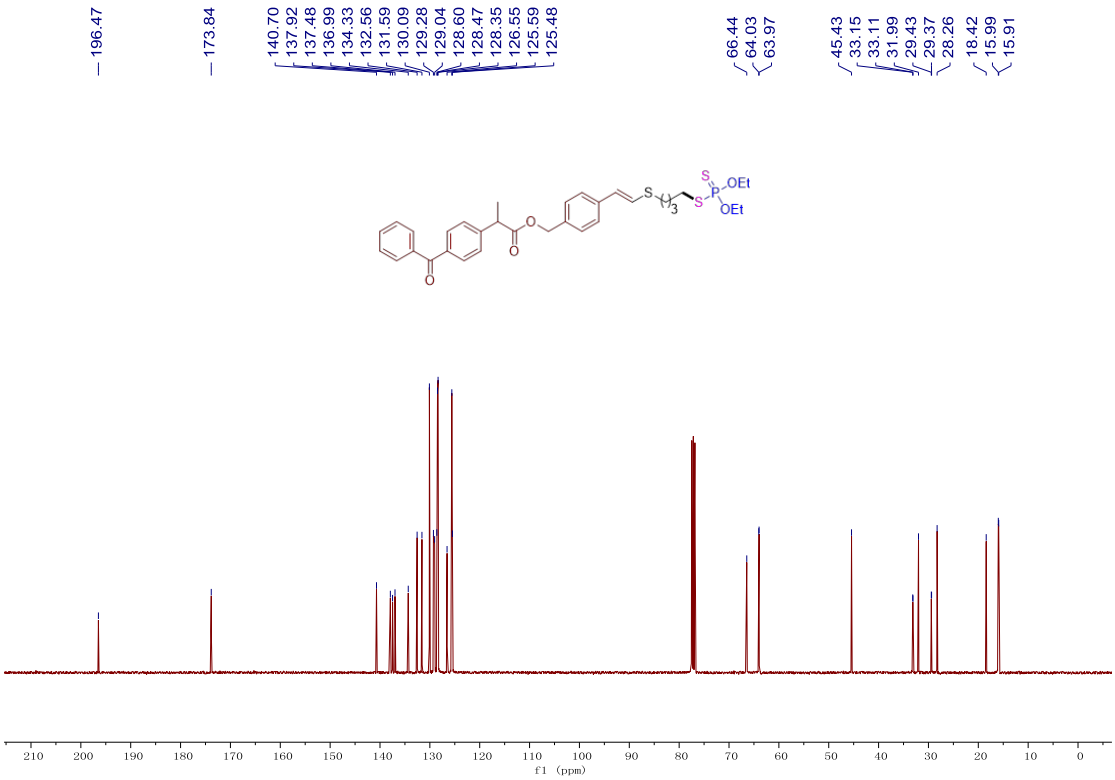
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9ab**



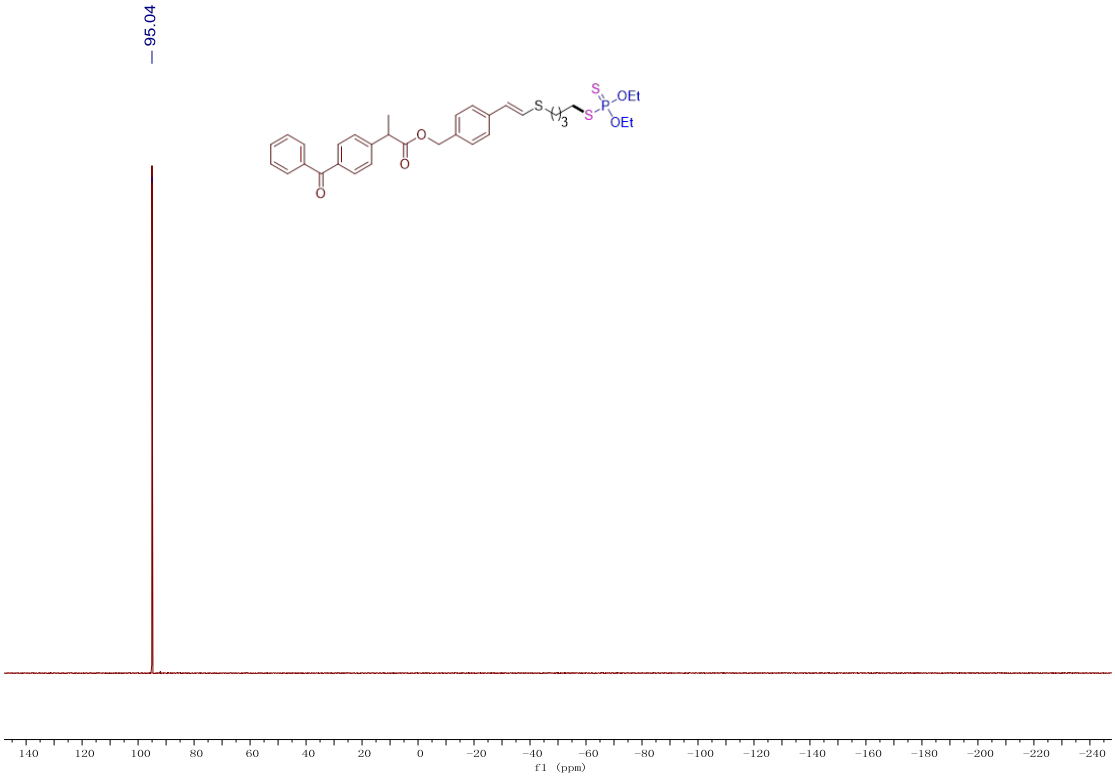
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9ab**



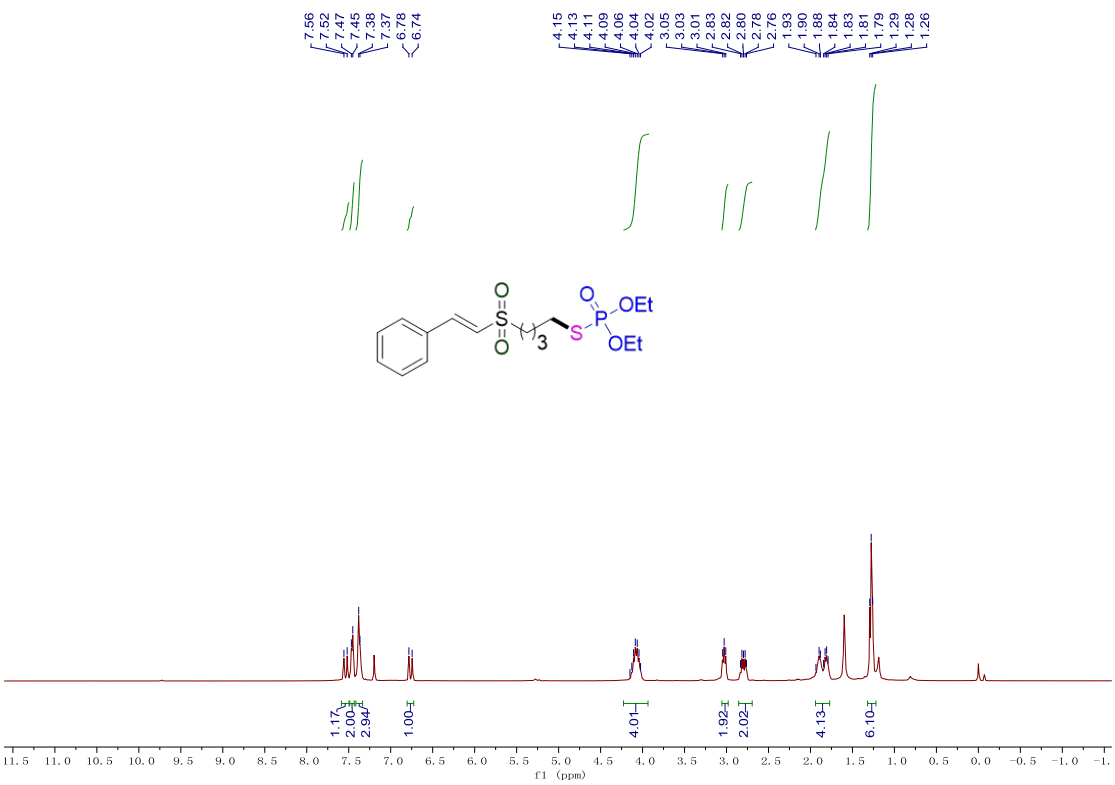
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **9ac**



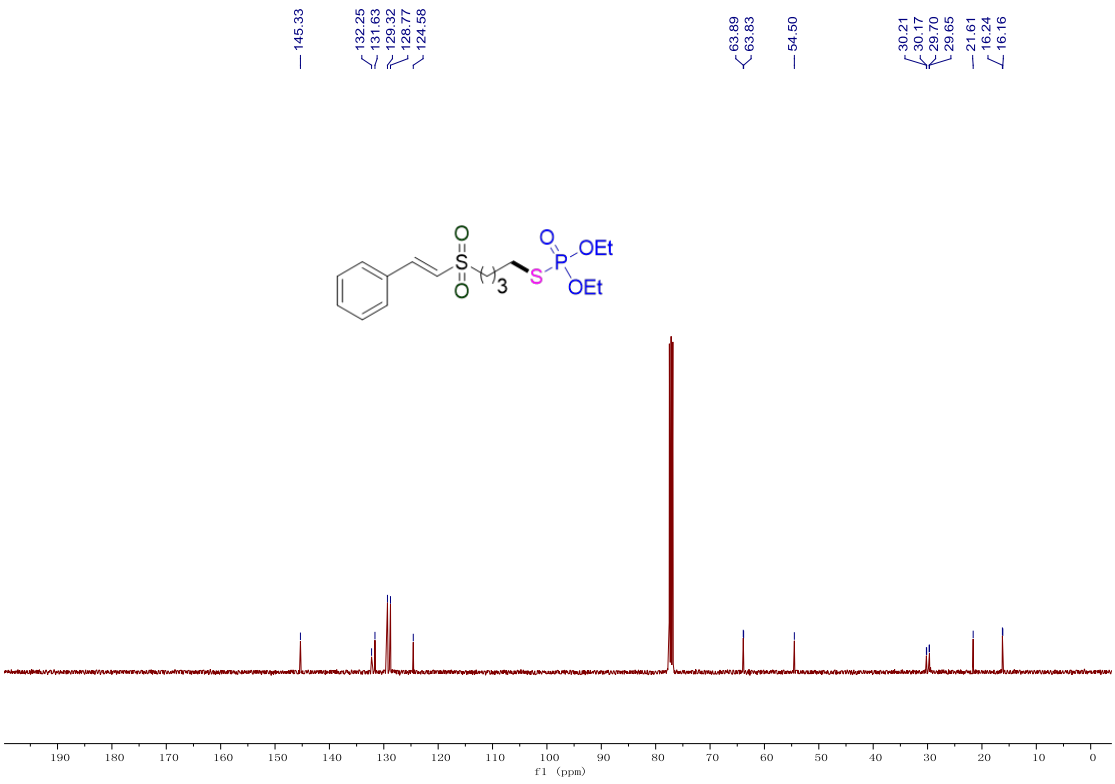
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **9ac**



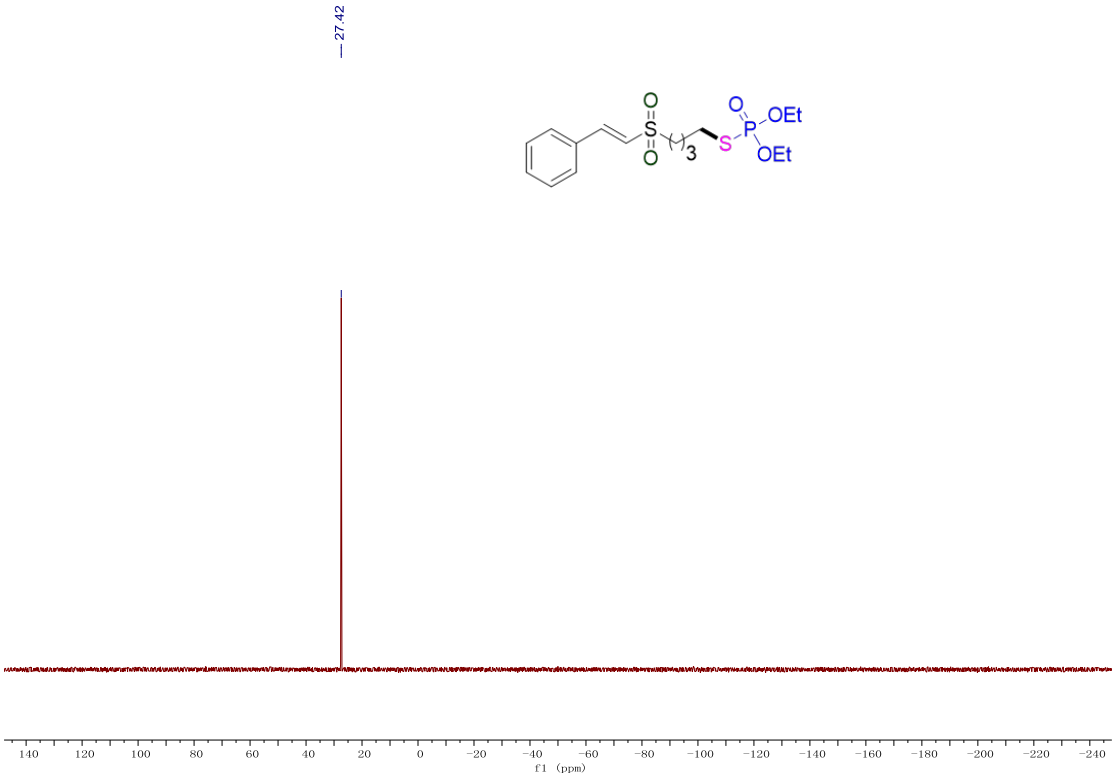
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **9ac**



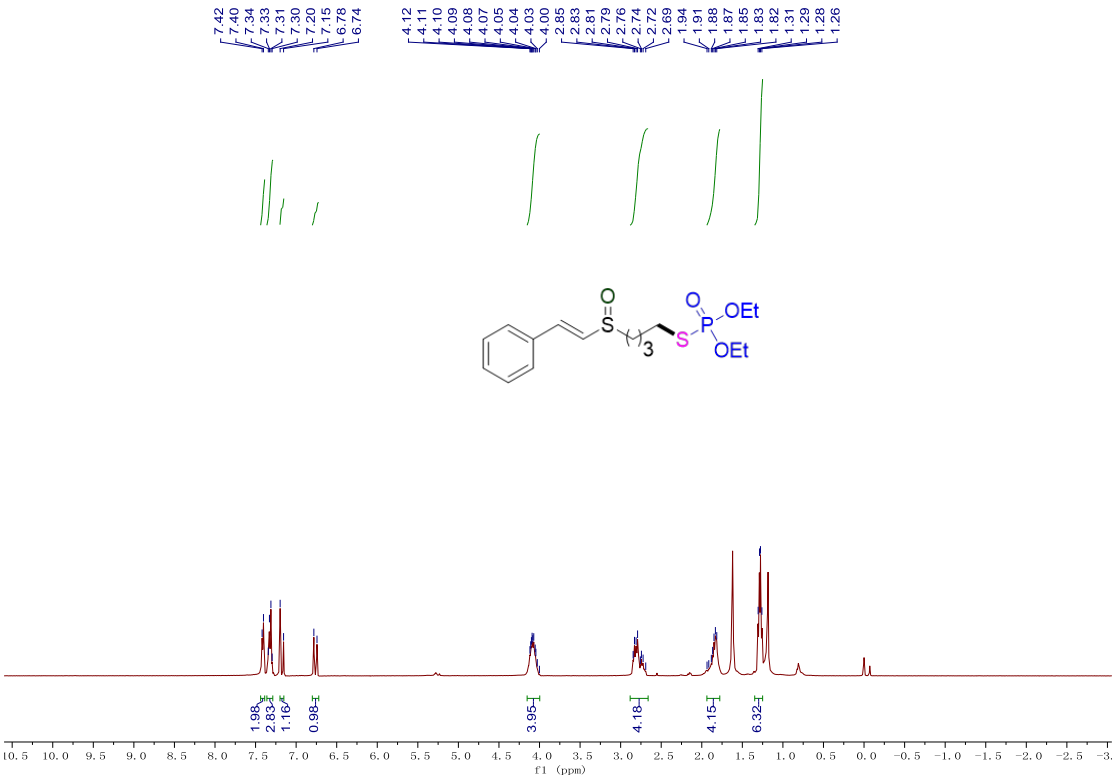
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **11a**



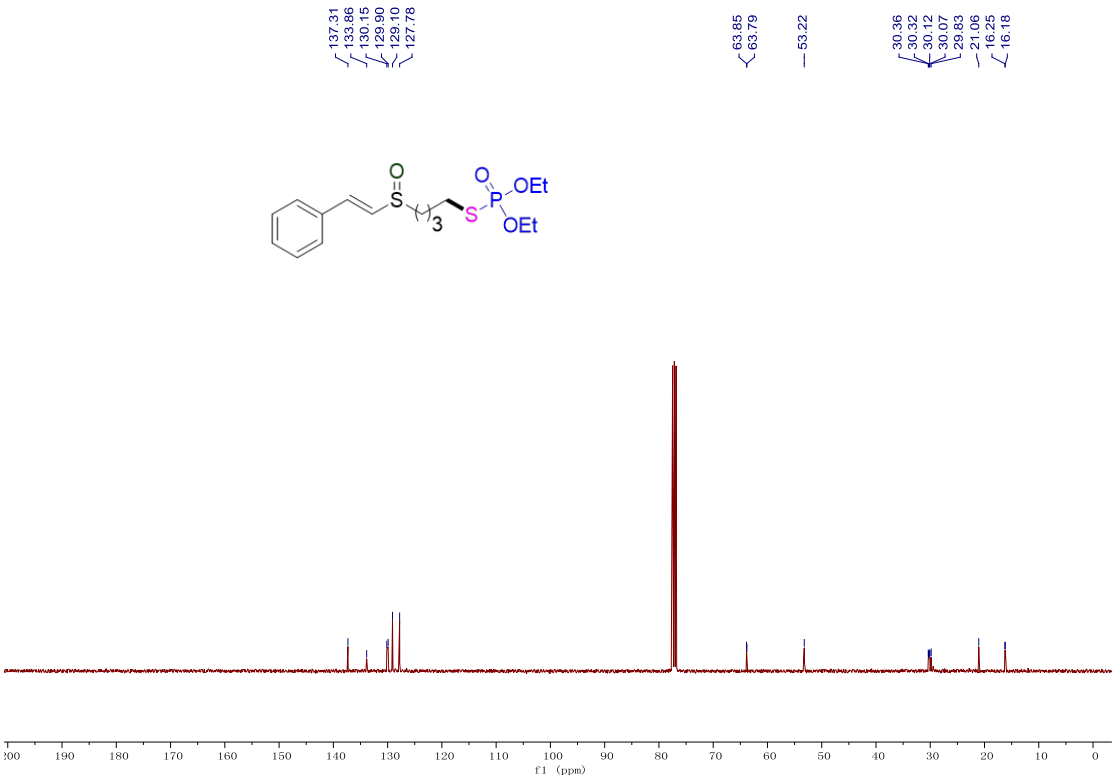
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **11a**



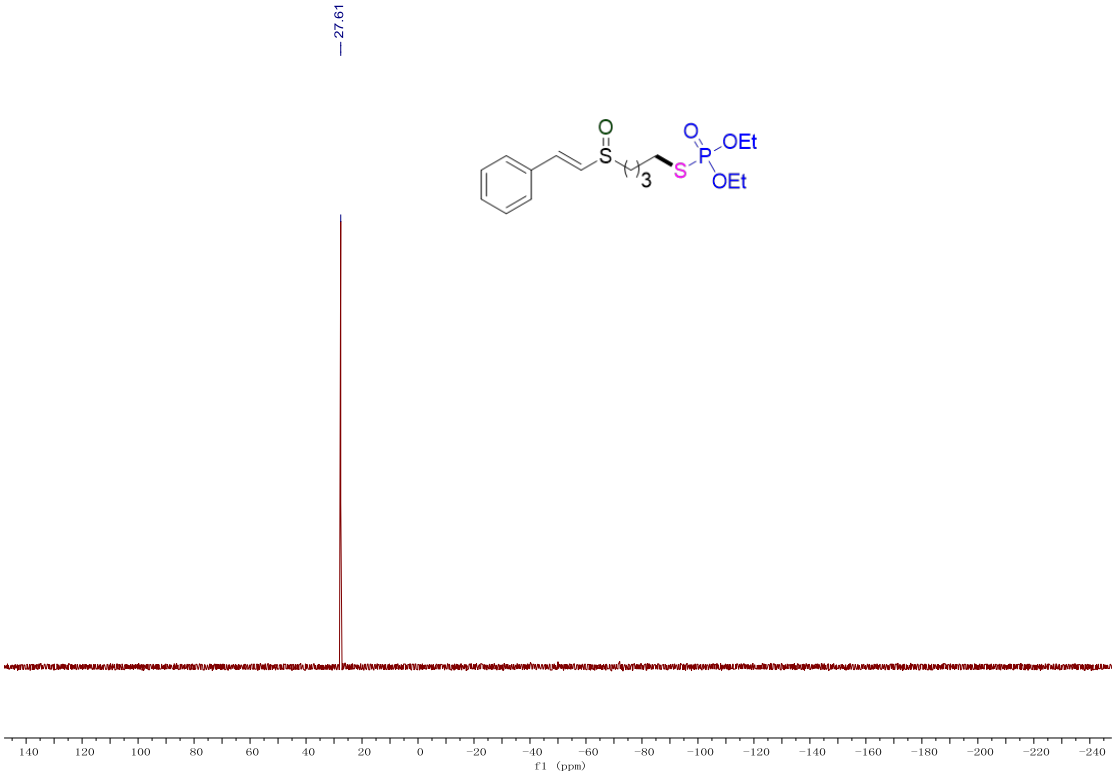
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **11a**



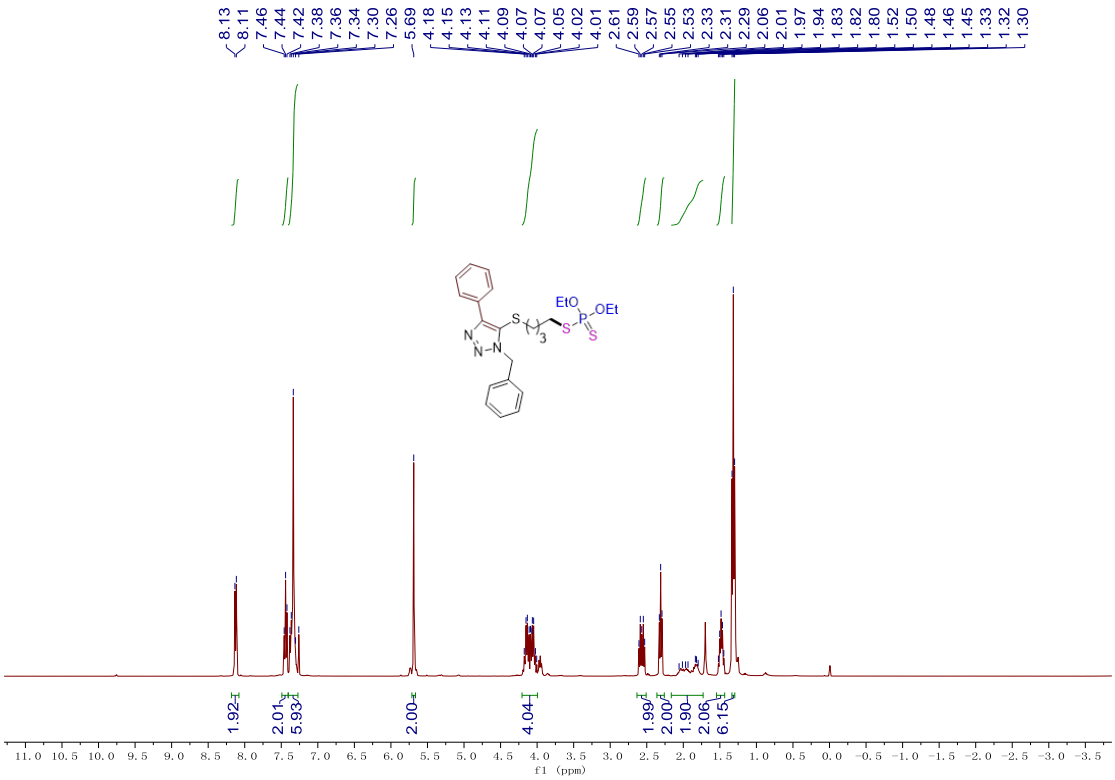
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **11b**



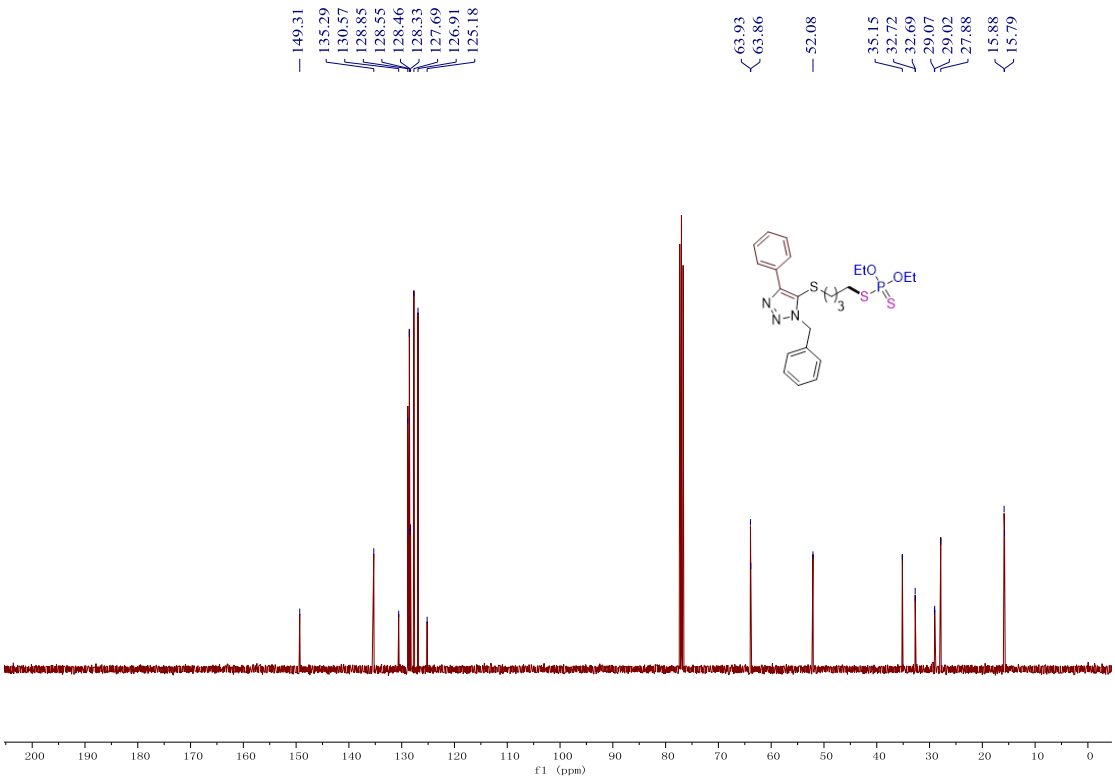
^{13}C NMR (101 MHz, $CDCl_3$) spectra of **11b**



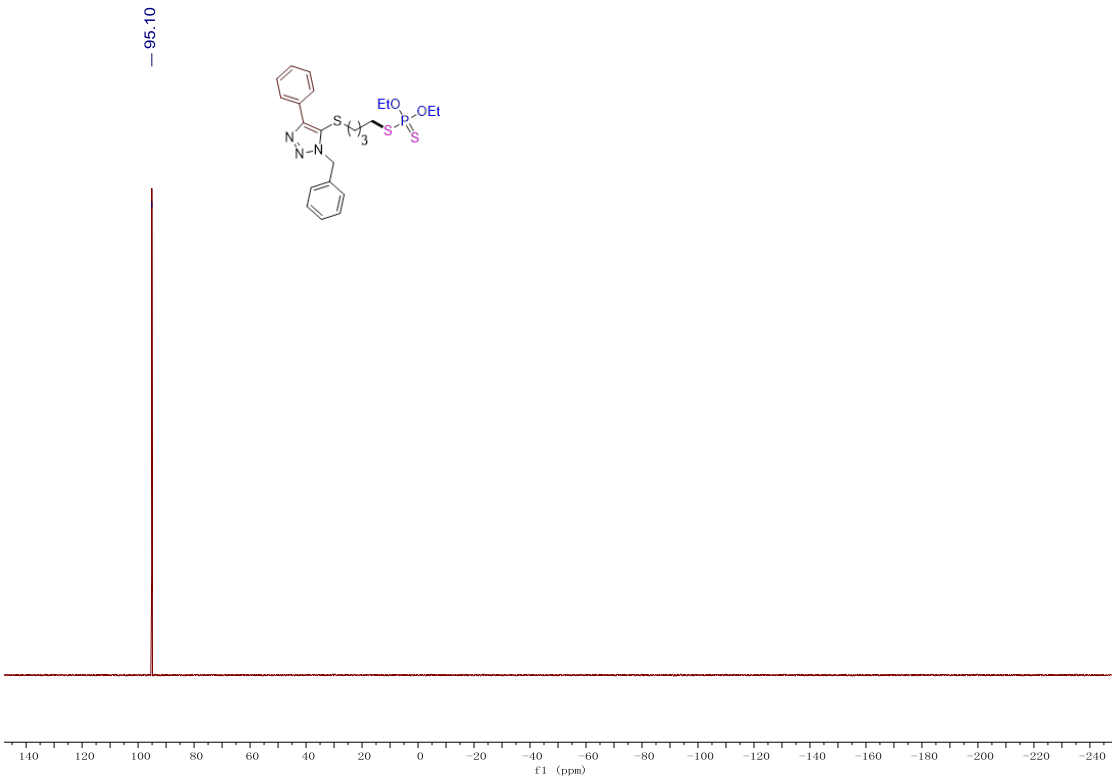
^{31}P NMR (162 MHz, $CDCl_3$) spectra of **11b**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **12a**



^{13}C NMR (101 MHz, $CDCl_3$) spectra of **12a**



^{31}P NMR (162 MHz, $CDCl_3$) spectra of **12a**