Synthesis of Unsymmetric Phosphorotrithioates by Sequential Coupling of 1,1-Dichloro-N,N-diethylphosphanamine with Thiols and Sulfenyl chloride

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Supplementary Data

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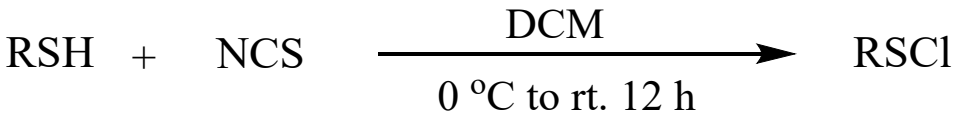
1. General information:

All chemicals were obtained from Sigma-Aldrich, Toyoko Chemical Industry, S. D. Fine and the $CHCl_3$ Solvent used in the reaction is from Qualigen having 0.05% water content, the progress of the reactions was monitored by thin-layer chromatography (TLC) on pre-coated silica-gel plates using Merck Silica Gel 60 F_{254}, Cat. No. 1.05554.0007 and visualized by short-wave ultraviolet light as well as by treatment with $KMnO_4$, Draggendroff reagent. Column chromatography was performed by hand using silica-gel (100–200 mesh, Silicycle).^{1}H, ^{13}C, ^{31}P NMR spectra were recorded on Brucker-Advance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$: 7.26 ppm and CD_4O 4.78, 3.30 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR solvent $CDCl_3$:77.0 ppm and CD_4O 49 ppm) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) down field from tetramethylsilane and are referenced to the carbon resonance of the solvent. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines respectively.

2. General procedure for synthesis of Starting Materials.

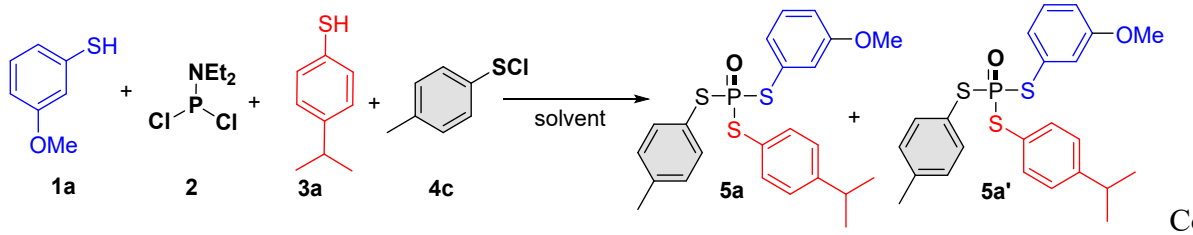
2.1 For the synthesis of Sulphenyl Chloride.



Sulfenyl Chlorides were prepared according to a reported literature[1-8]. N-chlorosuccinimide (2 mmol, 2 equiv.) was placed in oven dried 100 mL round bottom flask and dissolved in Dichloromethane (50 mL). Corresponding thiol (1 mmol, 1 equiv.) was added slowly at 0 °C and the reaction mixture was stirred at room temperature for 12 hours. After completion of the reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotatory evaporation, and purified by column chromatography on silica gel using Hexane and Ethyl acetate as eluent.

3. Screening of Solvents (Table 2).

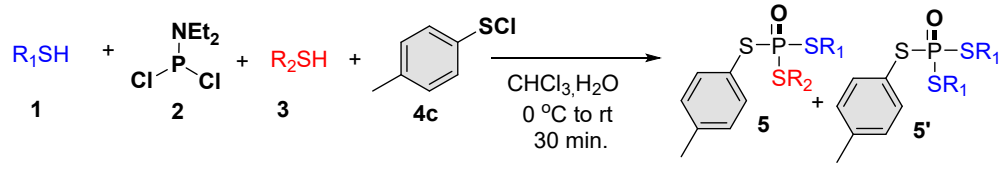
S.No.	reactant 1a (mmol)	reactant 2 (mmol)	reactant 3a (mmol)	reactant 4 (mmol)	solvent	yield[a] 5a:5a′
1.	1.5	2	1.5	1	DMSO	Traces
2.	1.5	2	1.5	1	DMF	Traces
3.	1.5	2	1.5	1	Ethyl acetate	ND
4.	1.5	2	1.5	1	ACN: H_2O (1:1)	Traces
5.	1.5	2	1.5	1	H_2O	ND
6.	1.5	2	1.5	1	Acetone	Traces
7.	1.5	2	1.5	1	Dioxane	38:4
8.	1.5	2	1.5	1	Polyethylene glycol (PEG)	ND
9.	1.5	2	1.5	1	Toluene	49:10
10.	1.5	2	1.5	1	PBS	ND



Co ndition, Dissolve (348 µL, 2 mmol) of reagent **2** in 6 mL solvent. Add reagent **1a** (190 µL, 1.5 mmol) dropwise after 2 minutes then add reagent **3a** (253 µL, 1.5 mmol). At last, add reagent **4a** (158 mg,1 mmol) at 0°C, stir for 10 minutes, and continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane. [a]Isolated yield.

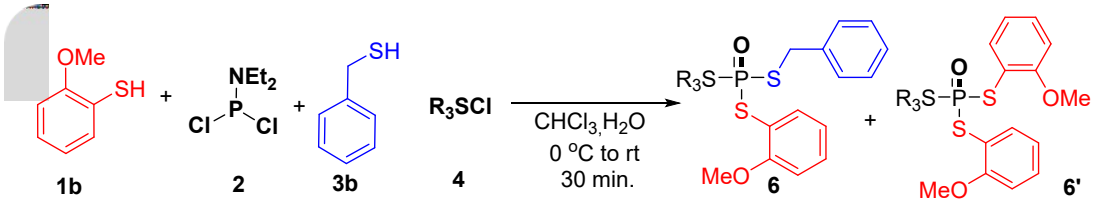
4. General procedure for synthesis of products Materials.

a) Synthesis of Product 5 (Scheme 1)



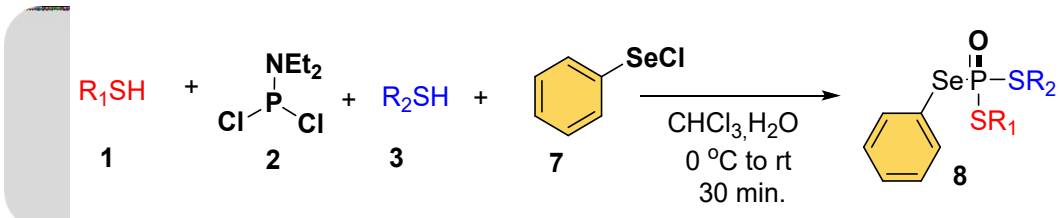
To a 25 mL of oven dried round bottom flask dissolve 2 mmol of reagent **2** in 6 mL $CHCl_3$. Add reagent **1** (1.5 mmol, 1 equiv.) dropwise, then after 2 minutes add reagent **3** (1.5 mmol, 1.5 equiv.) followed by the addition of **4c** (1 mmol, 1 equiv.) and add H_2O 3% v/v at 0°C in open air and stir for 10 minutes, and then continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane.

a) Synthesis of Product 6 (Scheme 2)



To a 25 mL oven dried round bottom flask dissolve 2 mmol of reagent **2** in 6 mL $CHCl_3$. Add reagent **1b** (1.5 mmol, 1.5 equiv.) dropwise, then after 2 minutes add reagent **3b** (1.5 mmol, 1.5 equiv.) followed by the addition of **4** (1 mmol, 1 equiv.) at 0°C in open air, stir for 10 minutes, and then continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane.

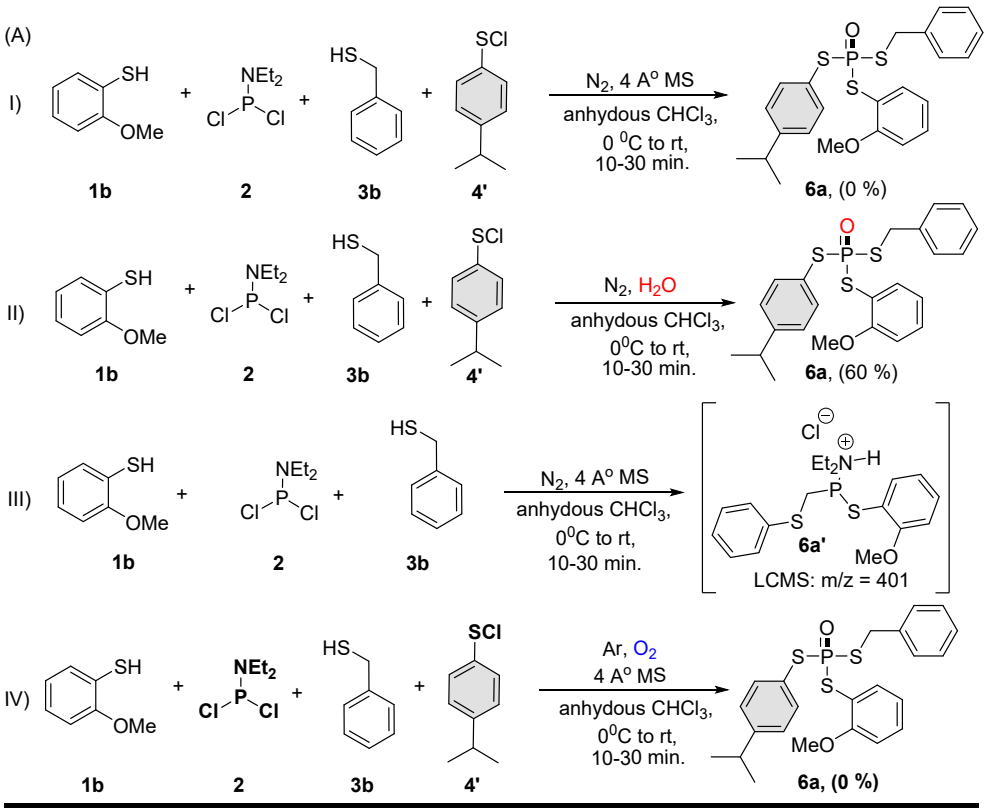
b) Synthesis of Product 8 (Scheme 3)



To a 25 mL oven dried round bottom flask dissolve 2 mmol of reagent **2** in 6 mL $CHCl_3$. Add reagent **1** (1.5 mmol, 1.5 equiv.) dropwise, then after 2 minutes reagent **3** (1.5 mmol, 1.5 equiv.) followed by the addition of **7** (1 mmol, 1 equiv.) at 0°C, stir for 10 minutes, and then continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4,

concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane.

5) Control Experiments

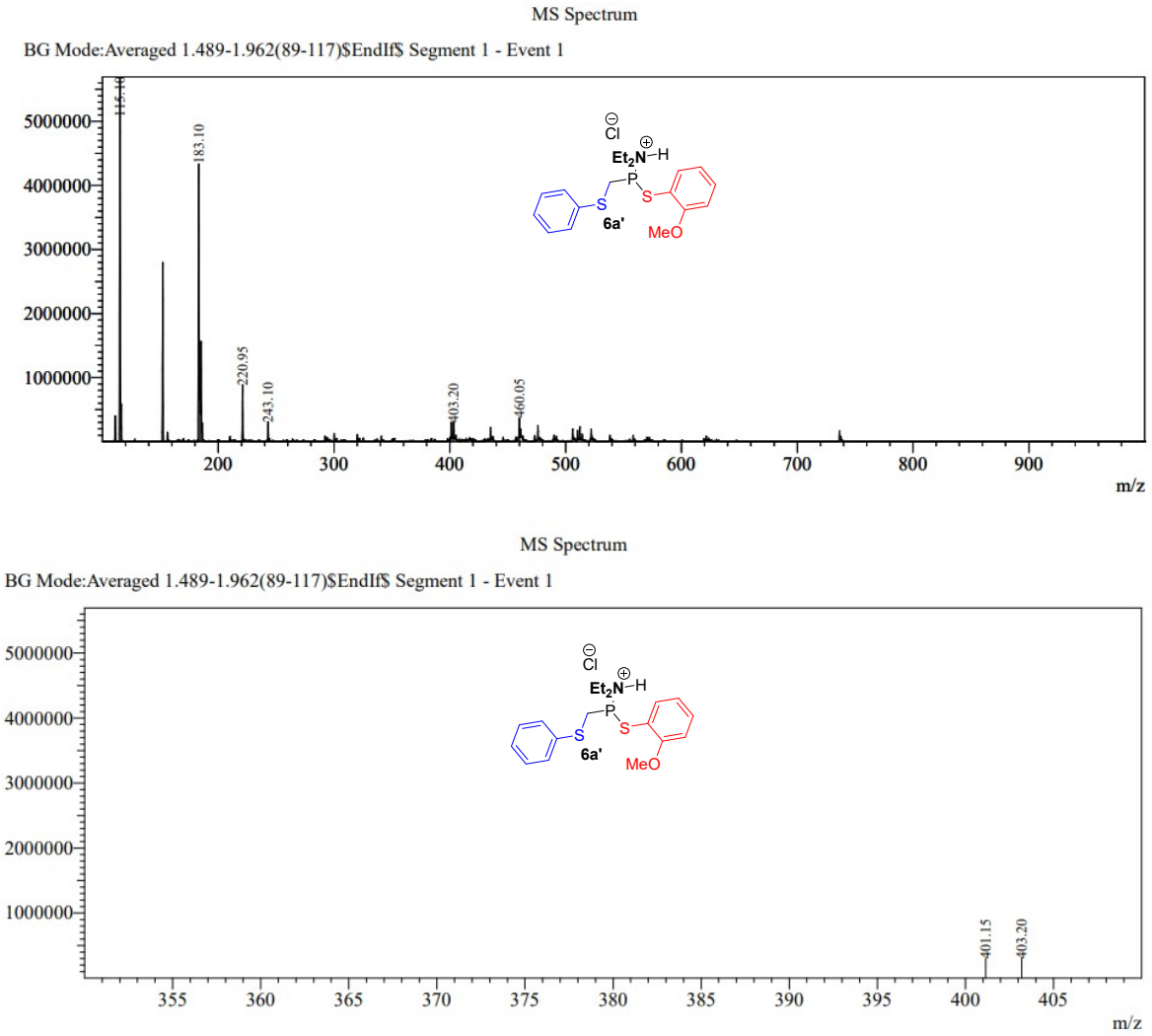


In experiment I) 2-methoxybenzenethiol **1b** (190 µL, 1.5 mmol, 1.5 equiv.) is loaded dropwise in dried round bottom flask having solution of reagent **2** (348 µL, 2 mmol, 2 equiv.) and anhydrous $CHCl_3$ under nitrogen atmosphere and the round bottom flask had activated 4º molecular sieves. Followed by addition of reagent **3b** (186 µL,1.5 mmol 2, 1.5 equiv.) dropwise and addition of reagent **4′** (186 mg,1 mmol, 1 equiv.) at 0 ºC and stirred for 30 minutes but no product is determined on TLC.

In experiment II) 2-methoxybenzenethiol **1b** (190 µL 1.5 mmol, 1.5 equiv.) is loaded dropwise in dried round bottom flask having solution of reagent **2** (348 µL, 2 mmol, 2 equiv.) and anhydrous $CHCl_3$ under nitrogen atmosphere. Followed by addition of reagent **3b** (186 µL ,1.5 mmol, 1.5 equiv.) drop-wisely and by addition of reagent **4′** (186 mg,1 mmol, 1 equiv.) at 0 ºC. Afterwards, 54 µL (3% v/v) of H_2O is added to the reaction mixture and stirred the reaction for 30 minutes. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary

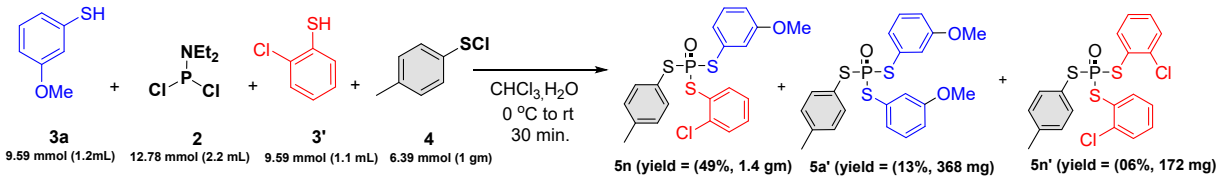
evaporation. Products were purified by column chromatography with the eluent EtOAc/ hexane.

In experiment III) 2-methoxybenzenethiol **1b** (190 µL,.5 mmol, 1.5 equiv.) is loaded dropwise in dried round bottom flask having solution of reagent **2** (348 µL, 2 mmol, 2 equiv.) and anhydrous $CHCl_3$ under nitrogen atmosphere and the round bottom flask had activated 4º molecular sieves. Followed by addition of reagent **3b** (186 µL, 1.5 mmol, 1.5 equiv.) dropwisely at 0 ºC and stirred for 30 minutes and the compound **6a′** was determined by LCMS.

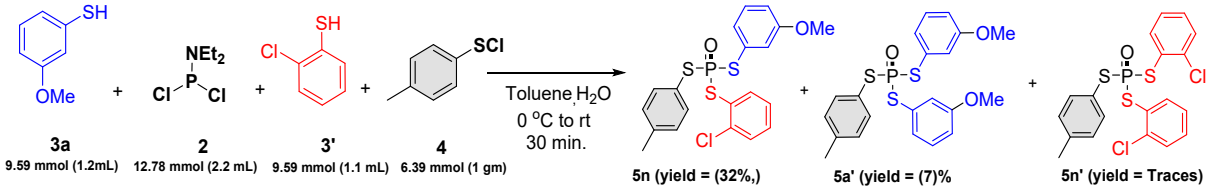


In Experiment IV, a solution of 2-methoxybenzenethiol **1b** (190 µL, 1.5 mmol, 1.5 equiv.) was slowly added to a dried round-bottom flask containing reagent **2** (348 µL, 2 mmol, 2 equiv.) and anhydrous $CHCl_3$ under an Argon atmosphere with an O_2 balloon. The round-bottom flask was equipped with activated 4Å molecular sieves. Subsequently, reagent **3b** (186 µL, 1.5 mmol, 1.5 equiv.) was added dropwise at 0°C and the mixture was stirred for 30 minutes. However, it is noteworthy that no product (**6a**) was detected on TLC analysis under these conditions.

5. Gram Scale Synthesis



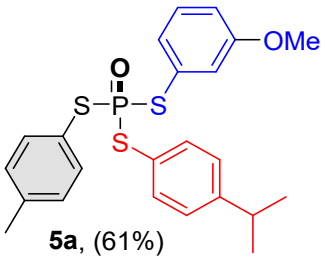
To a 100 mL of oven dried round bottom flask dissolve (2.2 mL, 12.78 mmol, 2 equiv.) of reagent **2** in 12 mL $CHCl_3$. Add reagent **3a** (1.2 mL, 9.59 mmol. 1.5 equiv.) dropwise, then reagent **3′** (1.1 mL, 9.59 mmol, 1.5 equiv.) followed by the addition of **4** (1 gm, 6.39 mmol, 1 equiv.) at 0°C and stir for 10 minutes, and then continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane.



To a 100 mL of oven dried round bottom flask dissolve (2.2mL, 2.78 mmol, 2 equiv.) of reagent **2** in 12 mL Toluene. Add reagent **3a** (1.2mL, 9.59 mmol. 1.5 equiv.) dropwise, then after 2 minutes add reagent **3′** (1.1 mL, 9.59 mmol. 1.5 equiv.) followed by the addition of **4** (1 gm, 6.39 mmol, 1 equiv.) at 0°C and stir for 10 minutes, and then continue stirring at room temperature (rt) for 20 min. After completion of reaction as monitored by TLC, the reaction mixture was extracted with ethyl acetate (25 mL x 3) and washed with water (50 mL x 2). The organic layer was dried over anhydrous Na_2SO_4, concentrated via rotary evaporation. All compound were purified by column chromatography with the eluent EtOAc/ hexane.

6. Characterization data of synthesized compounds

S-(4-isopropylphenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5a)

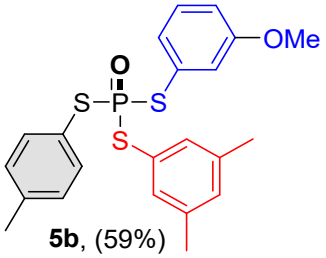


5a, (61%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (280mg, 61%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 m, 4H), 7.22 – 7.00 (m, 7H), 6.94 – 6.79 (m, 1H), 3.71 (s, 3H), 2.91 – 2.75 (m, 1H), 2.28 (d, J = 2.4 Hz, 3H),

1.17 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (s), 150.8 (d, J = 3.7 Hz), 140.1 (d, J = 3.7 Hz), 135.8 (d, J = 4.8 Hz), 135.7 (d, J = 4.6 Hz), 130.2 (d, J = 2.7 Hz), 129.9(d, J = 2.6 Hz), 127.9 (d, J = 6.9 Hz), 127.7 (d, J = 5.1 Hz), 127.6 (d, J = 2.8 Hz), 123.2 (d, J = 7.1 Hz), 123.1 (d, J = 7.0 Hz), 120.2 (d, J = 4.6 Hz), 116.1 (d, J = 3.1 Hz), 55.4 (s), 33.9 (s), 23.8 (s), 21.3(s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.36 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{23}H_{25}O_2PS_3H$ 461.0833; found, 461.0830.

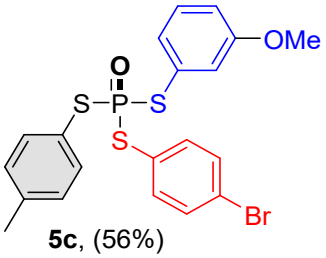
S-(3,5-dimethylphenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5b)



5b, (59%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (263mg, 59%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.47 (m, 1H), 7.40 – 7.26 (m, 4H), 7.07 (d, J = 8.4 Hz, 2H), 6.98 (s, 1H), 6.95 – 6.84 (m, 3H), 3.78 (s, 3H), 2.28 (d, J = 2.4 Hz, 3H), 2.23 (d, J = 2.6 Hz, 3H), 2.20 (d, J = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 143.0 (s), 140.2(s), 139.7 (s), 137.8 (d, J = 4.3 Hz), 137.1 (d, J = 4.1 Hz), 135.6 (d, J = 4.6 Hz), 131.8 (d, J = 3.0 Hz), 131.5 (s), 129.9 (d, J = 2.5 Hz), 127.5 (d, J = 3.0 Hz), 123.7 (s), 122.8 (s), 121.1 (s), 111.6 (s), 55.9 (s), 21.5 – 21.1 (m).^{31}P NMR (162 MHz, CDCl3) δ 54.95 (s). HRMS (ESI) m/z: calcd for [M + H]+ $C_{22}H_{23}O_2PS_3H$ 447.0676; found, 447.0675.

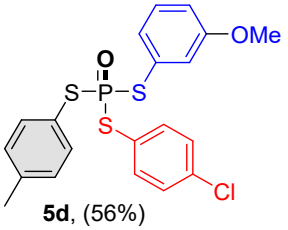
S-(4-bromophenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5c)



5c, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (277mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.40 – 7.26 (m, 6H), 7.22 – 7.14 (m, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.04 (dd, J = 5.3, 2.3 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.89 – 6.82 (m, 1H), 3.69 (d, J = 5.7 Hz, 3H), 2.27 (d, J = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 159.9 (d, J = 2.4 Hz), 140.4 (d, J = 3.7 Hz), 137.1 (d, J = 4.6 Hz), 135.8 (d, J = 4.8 Hz), 132.5 (d, J = 2.3 Hz), 130.2 (dd, J = 21.4, 2.8 Hz), 128.5 (s), 127.8 (t, J = 11.6 Hz), 127.4 (d, J = 7.0 Hz), 126.2 – 125.8 (m), 124.6 (d, J = 4.0 Hz), 122.6 (d, J = 7.2 Hz), 120.3 (d, J = 4.6 Hz), 116.2 (d, J = 3.2 Hz), 55.4 (s), 21.4 (s). ^{31}P NMR (162 MHz, CDCl3) δ 54.92 (s). HRMS (ESI) m/z: calcd for [M + H]+ $C_{20}H_{18}BrO_2PS_3H$ 496.9468; found, 496.9464.

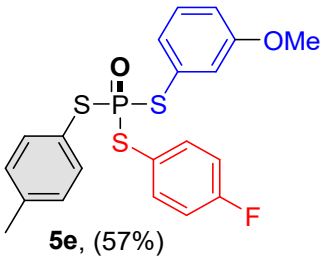
S-(4-chlorophenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5d)



5d, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (252mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.42 – 7.33 (m, 3H), 7.29 – 7.21 (m, 1H), 7.18 (dt, *J* = 4.1, 1.8 Hz, 2H), 7.09 (s, 4H), 6.90 – 6.84 (m, 1H), 3.72 (s, 3H), 2.29 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (s), 140.3 (s), 137.6 (d, *J* = 4.2 Hz), 135.8 (d, *J* = 4.9 Hz), 130.8 (d, *J* = 2.9 Hz), 130.3 (s), 130.2 – 129.9 (m), 127.8 (d, *J* = 5.2 Hz), 127.3 (s), 122.7 (s), 120.2 (d, *J* = 4.6 Hz), 116.3 (s), 55.4 (s), 21.3 (s). 31P NMR (162 MHz, CDCl3) δ 54.51 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}ClO_2PS_3H$ 452.9973; found, 452.9969.

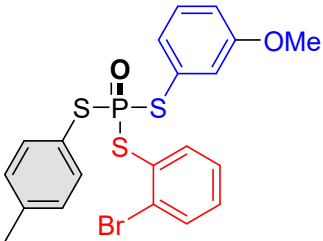
S-(4-fluorophenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5e)



5e, (57%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (248mg, 57%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.10 – 6.98 (m, 4H), 6.95 (dd, *J* = 11.9, 5.1 Hz, 2H), 6.87 – 6.82 (m, 1H), 3.68 (s, 3H), 2.26 (d, *J* = 2.5 Hz, 3H).^{13}C NMR (101 MHz, CDCl3) δ 159.8 (d, J = 2.4 Hz), 140.3 (d, J = 3.7 Hz), 137.8 (dd, J = 8.7, 4.4 Hz), 135.8 (d, J = 4.6 Hz), 130.2 (dd, J = 21.2, 2.7 Hz), 127.6 (dd, J = 19.9, 6.0 Hz), 122.7 (d, J = 7.3 Hz), 120.3 (d, J = 4.5 Hz), 116.6 (dd, J = 22.2, 2.5 Hz), 116.1 (d, J = 3.2 Hz), 55.4 (s), 21.3 (s). ^{19}F NMR (377 MHz, CDCl3) δ -110.18 – -110.35 (m). ^{31}P NMR (162 MHz, CDCl3) δ 55.50 (d, J = 6.1 Hz).). HRMS (ESI) m/z: calcd for [M + H]+ $C_{20}H_{18}FO_2PS_3H$ 437.0269; found, 437.0270.

S-(2-bromophenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5f)

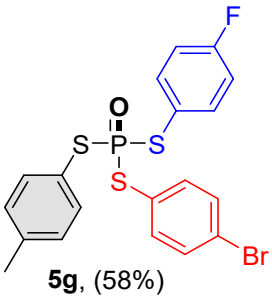


5f, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (277mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.8,

2.0 Hz, 1H), 7.67 – 7.61 (m, 1H), 7.43 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.24 (M, 3H), 7.18 – 7.08 (m, 4H), 6.97 – 6.90 (m, 1H), 3.80 – 3.77 (m, 3H), 2.35 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 2.6 Hz), 140.3 (d, *J* = 3.8 Hz), 137.7 (s), 137.3 (d, *J* = 4.0 Hz), 135.8 (d, *J* = 4.7 Hz), 133.7 (t, *J* = 5.1 Hz), 131.1 (s), 130.8 (d, *J* = 2.8 Hz), 130.1 (dd, *J* = 21.5, 2.7 Hz), 129.3 (d, *J* = 6.2 Hz), 129.0 (d, *J* = 6.5 Hz), 127.9 (dd, *J* = 16.7, 3.7 Hz), 127.5 (d, *J* = 7.3 Hz), 122.7 (d, *J* = 7.5 Hz), 120.3 (d, *J* = 4.6 Hz), 116.3 (d, *J* = 3.3 Hz), 55.4 (s), 21.3 (s). 31P NMR (162 MHz, CDCl3) δ 54.51 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}BrO_2PS_3H$ 496.9468; found, 496.9464.

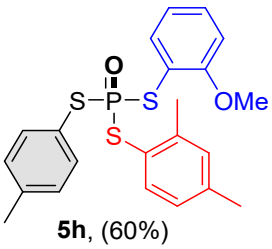
S-(4-bromophenyl) S-(4-fluorophenyl) S-(p-tolyl) phosphorotrithioate (5g)



5g, (58%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 04:96); (280mg, 58%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.24 (m, 7H), 7.12 – 7.07 (m, 2H), 6.98 (t, *J* = 8.5 Hz, 3H), 2.29 (d, *J* = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (d, *J* = 3.7 Hz), 140.4 (d, *J* = 3.8 Hz), 140.3 (d, *J* = 3.7 Hz), 137.8 (d, *J* = 4.5 Hz), 137.7 (d, *J* = 4.4 Hz), 137.0 (d, *J* = 4.6 Hz), 135.7 (d, *J* = 4.6 Hz), 132.4 (s), 130.3 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 2.8 Hz), 116.7 (d, *J* = 2.5 Hz), 116.5 (d, *J* = 2.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.16 – -110.33 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.22 (d, *J* = 6.1 Hz). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{15}BrFOPS_3H$ 484.9290; found, 484.9293.

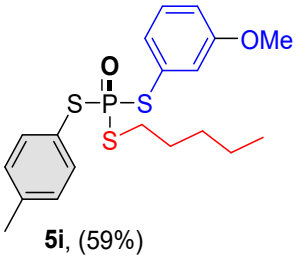
S-(2,4-dimethylphenyl) S-(2-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5h)



5h, (60%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (267mg, 60%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.41 – 7.32 (m, 3H), 7.32 – 7.24 (m, 1H), 7.04 (s, 2H), 6.96 (s, 1H), 6.89 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.87 – 6.79 (m, 2H), 3.75 (s, 3H), 2.26 (d, *J* = 2.4 Hz, 3H), 2.22 (d, *J* = 2.5 Hz, 3H), 2.19 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 143. (d, *J* = 4.6 Hz), 140.3 (d, *J* = 3.8 Hz), 139.8 (d, *J* = 3.6 Hz), 137.8 (d, *J* = 4.4 Hz), 137.1 (d, *J* = 4.2 Hz), 135.7 (d, *J* = 4.6 Hz), 131.8 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 3.1 Hz), 130.0 (d, *J* = 2.8 Hz), 127.5 (d, *J* = 2.9 Hz), 123.7(d, *J* = 6.9 Hz), 122.9 (d, *J* = 7.2 Hz), 121.1 (d, *J* = 2.7 Hz), 115.2 (d, *J* = 7.0 Hz), 111.6 (d, *J* = 2.7 Hz), 55.9 (s), 21.4 (s), 21.3 (s), 21.2 (s).^{31}P NMR (162 MHz, CDCl3) δ 54.95 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{23}O_2PS_3H$ 447.0676; found, 447.0681.

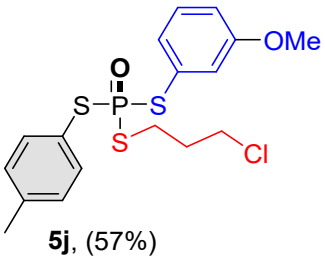
S-(3-methoxyphenyl) S-pentyl S-(p-tolyl) phosphorotrithioate (5i)



5i, (59%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (243mg, 59%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.12 – 7.06 (m, 4H), 6.86 (dd, *J* = 7.1, 1.2 Hz, 1H), 3.72 (s, 3H), 2.95 – 2.82 (m, 2H), 2.27 (d, *J* = 2.4 Hz, 3H), 1.70 – 1.55 (m, 2H), 1.27 – 1.21 (m, 4H), 0.81 (dd, *J* = 7.0, 4.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 2.5 Hz), 140.1 (d, *J* = 3.7 Hz), 135.7 (d, *J* = 4.7 Hz), 130.1 (dd, *J* = 21.1, 2.7 Hz), 128.0 (d, *J* = 7.0 Hz), 127.7 (d, *J* = 5.1 Hz), 123.3 (d, *J* = 7.1 Hz), 120.3 (d, *J* = 4.6 Hz), 116.0 (d, *J* = 3.3 Hz), 55.4 (s), 32.9 (dd, *J* = 7.0, 4.0 Hz), 30.7 (d, *J* = 9.3 Hz), 30.2 (t, *J* = 4.7 Hz), 29.7 (s), 22.1 (d, *J* = 3.0 Hz), 21.3 (d, *J* = 1.0 Hz), 13.9(d, *J* = 2.5 Hz). 31P NMR (162 MHz, CDCl3) δ 59.15 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{25}O_2PS_3H$ 413.0833; found, 413.0831.

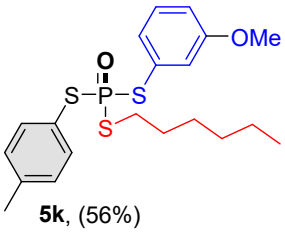
S-(3-chloropropyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5j)



5j, (57%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (238mg, 57%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.20 (dd, *J* = 12.5, 4.4 Hz, 1H), 7.15 – 7.05 (m, 4H), 6.88 (dd, *J* = 8.3, 0.9 Hz, 1H), 3.73 (s, 3H), 3.45 (t, *J* = 6.2 Hz, 2H), 3.01 (dt, *J* = 16.9, 6.9 Hz, 2H), 2.29 (d, *J* = 2.6 Hz, 3H), 2.02 (dd, *J* = 12.9, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 137.9 (d, *J* = 4.6 Hz), 136.3 (d, *J* = 6.5 Hz), 131.9 (d, *J* = 3.6 Hz), 129.2 (s), 128.7 (s), 127.7 (s), 121.3 (d, *J* = 2.9 Hz), 114.7 (d, *J* = 7.0 Hz), 111.7 (d, *J* = 2.7 Hz), 55.9 (s), 42.9 (d, *J* = 8.1 Hz), 36.9 (d, *J* = 3.5 Hz), 33.0 (d, *J* = 3.3 Hz), 30.0 (d, *J* = 3.9 Hz). ^{31}P NMR (162 MHz, CDCl3) δ 58.81 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{17}H_{20}ClO_2PS_3H$ 419.0128 found, 419.0130.

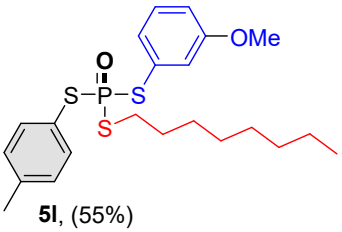
S-hexyl S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5k)



5k, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 6:94); (238mg, 56%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 1H), 7.09 (dd, *J* = 11.3, 4.8 Hz, 4H), 6.95 – 6.83 (m, 1H), 3.75 – 3.70 (m, 3H), 2.95 – 2.83 (m, 2H), 2.29 (d, *J* = 2.5 Hz, 3H), 1.58 (s, 2H), 1.22 – 1.17 (m, 6H), 0.82 – 0.78 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (s), 150.1 – 149.9 (m), 140.1(s), 135.7 (d, *J* = 4.7 Hz), 130.1 (dd, *J* = 21.1, 2.8 Hz), 128.0 (d, *J* = 6.8 Hz), 127.7 (d, *J* = 5.0 Hz), 123.2 (d, *J* = 7.3 Hz), 120.2 (d, *J* = 4.5 Hz), 116.0 (d, *J* = 3.4 Hz), 55.4 (s), 33.0 (d, *J* = 4.1 Hz), 31.1 (s), 30.5 (d, *J* = 4.9 Hz), 29.7 (s), 28.2 (s), 22.4 (s), 21.3 (s), 14.1 (d, *J* = 14.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.66 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{27}O_2PS_3H$ 427.0989 found, 427.0987.

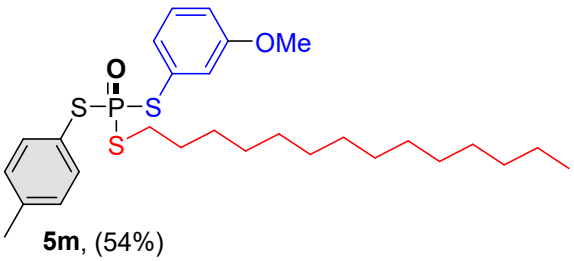
S-(3-methoxyphenyl) S-octyl S-(p-tolyl) phosphorotrithioate (5l)



5l, (55%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (249mg, 55%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.19 (dd, *J* = 10.3, 5.6 Hz, 1H), 7.12 – 7.05 (m, 4H), 6.86 (m, 1H), 3.72 (s, 3H), 2.99 – 2.78 (m, 2H), 2.28 (d, *J* = 2.5 Hz, 3H), 1.62 – 1.52 (m, 2H), 1.23 – 1.14 (m, 10H), 0.81 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 2.5 Hz), 140.1 (d, *J* = 3.7 Hz), 135.7 (d, *J* = 4.6 Hz), 130.1 (dd, *J* = 21.5, 2.7 Hz), 128.8 (s), 128.0 (d, *J* = 6.9 Hz), 127.7 (d, *J* = 5.0 Hz), 123.3 (d, *J* = 7.2 Hz), 120.2 (d, *J* = 4.6 Hz), 116.0 (d, *J* = 3.3 Hz), 55.4 (s), 33.0 (d, *J* = 4.0 Hz), 31.8 (d, *J* = 17.3 Hz), 30.4 (t, *J* = 9.5 Hz), 29.0 (d, *J* = 13.8 Hz), 28.5 (s), 23.0 (s), 22.6 (s), 21.3 (s), 14.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.69 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{31}O_2PS_3H$ 455.1302 found, 455.1303.

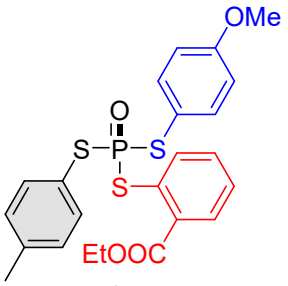
S-(3-methoxyphenyl) S-tetradecyl S-(p-tolyl) phosphorotrithioate (5m)



5m, (54%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (290mg, 54%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.2, 2.3 Hz, 2H), 7.19 (dd, *J* = 10.6, 5.3 Hz, 1H), 7.13 – 7.06 (m, 4H), 6.86 (dd, *J* = 8.3, 0.9 Hz, 1H), 3.72 (s, 3H), 2.87 (dt, *J* = 14.6, 7.4 Hz, 2H), 2.28 (d, *J* = 2.5 Hz, 3H), 1.64 – 1.53 (m, 2H), 1.27 – 1.12 (m, 22H), 0.80 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 2.4 Hz), 140.1 (d, *J* = 3.7 Hz), 135.7 (d, *J* = 4.8 Hz), 130.2 (d, *J* = 2.6 Hz), 130.1 (dd, *J* = 21.4, 2.6 Hz), 130.0 (d, *J* = 2.5 Hz), 128.0 (d, *J* = 7.1 Hz), 127.7 (d, *J* = 5.0 Hz), 123.2 (d, *J* = 7.0 Hz), 120.2 (d, *J* = 4.6 Hz), 116.0 (d, *J* = 3.3 Hz), 55.4 (s), 33.0 (d, *J* = 3.9 Hz), 31.9 (s), 30.5 (d, *J* = 4.9 Hz), 29.8 – 29.6 (m), 29.6 (s), 29.4 (s), 29.4 (s), 29.0 (s), 28.6 (s), 22.7 (s), 21.3 (s), 14.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.61 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{28}H_{43}O_2PS_3H$ 539.2246 found, 539.2241.

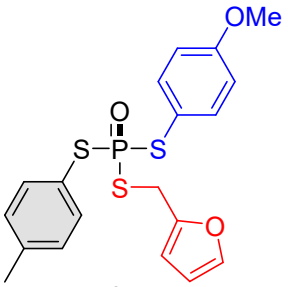
ethyl 2-((((4-methoxyphenyl)thio)(p-tolylthio)phosphoryl)thio)benzoate (5o)



5o (49%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (240mg, 49%) as a colorless oil;^{1}H NMR (400 MHz, CDCl3) δ 7.94 – 7.73 (m, 2H), 7.43 – 7.25 (m, 6H), 7.08 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 3.74 (s, 3H), 2.28 (d, J = 2.5 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 165.3 (s), 160.0 (s), 139.1 (d, J = 3.7 Hz), 136.5 (d, J = 4.5 Hz), 134.8 (d, J = 5.5 Hz), 134.7 (d, J = 4.5 Hz), 133.5 (d, J = 4.2 Hz), 129.7 (d, J = 1.2 Hz), 129.1 (d, J = 2.8 Hz), 127.6 (d, J = 1.9 Hz), 113.9 (d, J = 2.8 Hz), 60.5 (s), 54.3 (s), 28.6 (s), 13.2 (s).^{31}P NMR (162 MHz, CDCl3) δ 57.51 (s).

S-(furan-2-ylmethyl) S-(4-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5p)

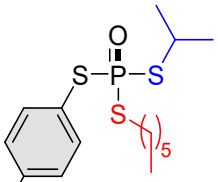


5p (53%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (223mg, 53%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.43 – 7.33 (m, 4H), 7.30 (dd, J = 1.8, 0.8 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 6.87 – 6.72 (m, 2H), 6.21 (d, J = 0.5 Hz, 2H), 4.09 (d, J = 12.6 Hz, 2H), 3.74 (s, 3H), 2.29 (d, J = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 161.1 (s), 149.3 (s), 142.7 (s), 140.2 (d, J = 3.7 Hz), 137.5 (d, J = 4.3 Hz), 135.7 (d, J = 4.6 Hz), 130.2 (d, J = 2.6 Hz), 123.0 (d, J = 7.0 Hz), 116.8 (d, J = 7.0 Hz), 115.0

(d, J = 2.8 Hz), 110.8 (s), 109.3 (s), 55.4 (s), 28.9 (d, J = 3.6 Hz), 21.3 (s). ^{31}P NMR (162 MHz, CDCl3) δ 59.90 (s).

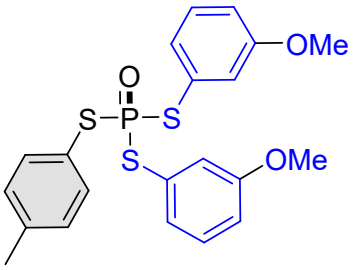
S-hexyl S-isopropyl S-(p-tolyl) phosphorotrithioate (5q)



5q (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (201mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.59 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.89 (m, 2H), 2.29 (d, *J* = 2.3 Hz, 3H), 1.62 (m, 2H), 1.37 (dd, *J* = 12.2, 6.9 Hz, 6H), 1.33 – 1.27 (m, 2H), 1.20 (dd, *J* = 6.7, 2.8 Hz, 4H), 0.81 (t, *J* = 4.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (s), 135.4 (s), 130.0 (s), 123.8 (s), 40.3 (s), 33.0 (d, J = 3.9 Hz), 31.2 (s), 30.4 (d, J = 5.2 Hz), 28.3 (s), 25.5 (d, J = 3.1 Hz), 25.4 (d, J = 2.9 Hz), 22.4 (s), 21.4 (s), 13.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.20 (s).

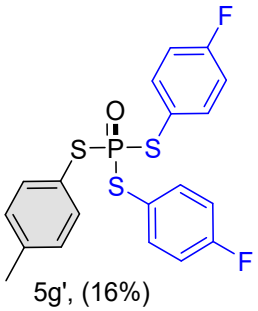
S,S-bis(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5a′)



5a', (19%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (85 mg, 19%) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.35 (dd, J = 8.2, 2.2 Hz, 2H), 7.19 (dd, J = 9.4, 6.6 Hz, 2H), 7.16 – 7.04 (m, 4H), 7.02 (dd, J = 4.1, 2.0 Hz, 2H), 6.94 – 6.81 (m, 2H), 3.71 (s, 6H), 2.29 (d, J = 2.5 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 159.8 (d, J = 2.7 Hz), 150.9 (d, J = 3.5 Hz), 135.8 (d, J = 4.6 Hz), 130.0 (d, J = 2.6 Hz), 127.7 (d, J = 5.6 Hz), 127.6 (d, J = 2.8 Hz), 123.1 (d, J = 7.0 Hz), 120.3 (d, J = 4.6 Hz), 116.1 (d, J = 3.2 Hz), 55.4 (s), 33.9 (s), 23.8 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 56.04 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{21}O_3PS_3H$ 449.0469; found, 449.0455.

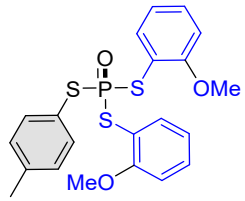
S,S-bis(4-fluorophenyl) S-(p-tolyl) phosphorotrithioate (5g)



5g', (16%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 03:97); (67mg, 16%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.35 – 7.31 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.01 – 6.94 (m, 4H), 2.28 (d, *J* = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1 (d, *J* = 3.7 Hz), 162.6 (d, *J* = 3.4 Hz), 140.4 (d, *J* = 3.8 Hz), 137.9 (d, *J* = 4.5 Hz), 137.8 (d, *J* = 4.4 Hz), 135.7 (d, *J* = 4.7 Hz), 130.3 (d, *J* = 2.8 Hz), 122.6 (d, *J* = 7.3 Hz), 121.8 (d, *J* = 3.3 Hz), 121.7 (d, *J* = 3.4 Hz), 116.7 (d, *J* = 2.5 Hz), 116.5 (d, *J* = 2.7 Hz), 21.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.16 (t, *J* = 6.5 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -99.04 – -126.58 (m). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{15}F_2OPS_3H$ 425.0013; found, 425.0008.

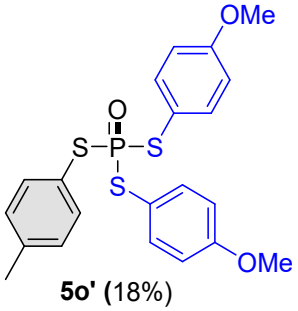
S,S-bis(2-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5h′)



5h', (19%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 13:87); (85 mg, 19 %) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dt, *J* = 7.7, 1.9 Hz, 2H), 7.36 (dd, *J* = 8.2, 2.2 Hz, 2H), 7.32 – 7.23 (m, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.84 (dd, *J* = 12.5, 5.0 Hz, 4H), 3.74 (s, 6H), 2.26 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, *J* = 4.5 Hz), 139.7 (d, *J* = 3.5 Hz), 137.6 (d, *J* = 4.3 Hz), 135.6 (d, *J* = 4.7 Hz), 131.4 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 2.6 Hz), 123.8 (d, *J* = 7.2 Hz), 121.1 (d, *J* = 2.4 Hz), 115.4 (d, *J* = 7.0 Hz), 111.6 (d, *J* = 2.2 Hz), 55.9 (s), 21.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.78 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{21}O_3PS_3H$ 449.0469; found, 449.0455.

S,S-bis(4-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5o′)

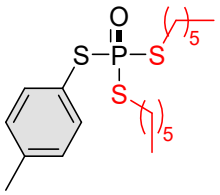


5o' (18%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (80 mg, 18 %) as a creamy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 6H), 7.08

(d, J = 8.0 Hz, 2H), 6.82 – 6.77 (m, 4H), 3.72 (s, 6H), 2.27 (d, J = 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, J = 3.2 Hz), 140.0 (d, J = 3.6 Hz), 137.5 (s), 135.6 (d, J = 4.5 Hz), 130.2 (d, J = 2.7 Hz), 123.2 (d, J = 6.8 Hz), 117.0 (d, J = 6.9 Hz), 114.9 (d, J = 2.4 Hz), 55.4 (s), 21.3 (s). ^{31}P NMR (162 MHz, CDCl3) δ 57.57 (s).

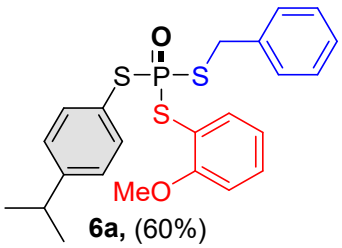
S,S-dihexyl S-(p-tolyl) phosphorotrithioate (5p′)



5q' (14%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (56 mg, 14 %) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 2.2 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 2.93 – 2.86 (m, 4H), 2.29 (d, J = 2.4 Hz, 3H), 1.67 – 1.60 (m, 4H), 1.31 (dd, J = 10.4, 4.4 Hz, 4H), 1.22 (td, J = 7.2, 3.9 Hz, 8H), 0.85 – 0.80 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6 (d, J = 4.6 Hz), 130.1 (d, J = 2.9 Hz), 40.2 (s), 33.0 (d, J = 3.9 Hz), 32.9 (d, J = 3.9 Hz), 31.2 (s), 28.3 (d, J = 2.5 Hz), 25.4 (d, J = 5.7 Hz), 22.5 (s), 21.3 (s), 14.0 (s). ^{31}P NMR (162 MHz, CDCl3) δ 62.50 (s).

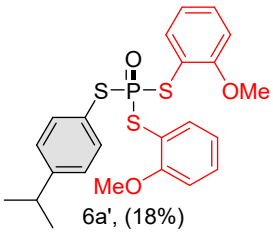
S-benzyl S-(4-isopropylphenyl) S-(2-methoxyphenyl) phosphorotrithioate (6a)



6a, (60%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (276mg, 60%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.55 (m, 1H), 7.49 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.43 – 7.32 (m, 1H), 7.33 – 7.18 (m, 7H), 6.95 (d, *J* = 5.7 Hz, 2H), 4.16 (dd, *J* = 11.7, 1.6 Hz, 2H), 3.85 (s, 3H), 2.97 – 2.83 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 150.8 (d, *J* = 3.5 Hz), 137.9 (d, *J* = 4.5 Hz), 136.4 (d, *J* = 6.4 Hz), 135.8 (d, *J* = 4.6 Hz), 131.8 (d, *J* = 3.4 Hz), 129.3 (s), 128.6 (s), 127.6 (s), 127.5 (d, *J* = 2.7 Hz), 123.6 (d, *J* = 6.9 Hz), 121.3 (d, *J* = 2.8 Hz), 114.9 (d, *J* = 6.9 Hz), 111.7 (d, *J* = 2.8 Hz), 55.9 (s), 36.8 (d, *J* = 3.5 Hz), 33.9 (s), 23.8 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.95 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{23}H_{25}O_2PS_3H$ 461.0833 found, 461.0830.

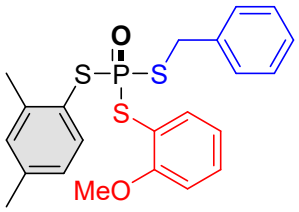
S-(4-isopropylphenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6a′)



6a', (18%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (85mg, 18%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.43 (m, 2H), 7.42 – 7.33 (m, 2H), 7.27 (t, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.87 – 6.75 (m, 4H), 3.72 (s, 6H), 2.90 – 2.71 (m, 1H), 1.15 (s, 3H), 1.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 150.5 (d, *J* = 3.6 Hz), 137.6 (d, *J* = 4.5 Hz), 135.7 (d, *J* = 4.6 Hz), 131.5 (d, *J* = 3.3 Hz), 127.4 (d, *J* = 2.7 Hz), 124.0 (d, *J* = 7.1 Hz), 121.1 (d, *J* = 2.5 Hz), 115.4 (d, *J* = 7.0 Hz), 111.7 (d, *J* = 2.5 Hz), 55.9 (s), 33.9 (s), 23.8 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.59 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{23}H_{25}O_3PS_3H$ 477.0731; found, 477.0726.

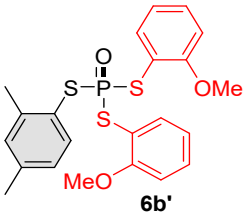
S-benzyl S-(2,4-dimethylphenyl) S-(2-methoxyphenyl) phosphorotrithioate (6b)



6b, (61%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (272mg, 61%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 1H), 7.42 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.31 (m, 1H), 7.23 – 7.14 (m, 5H), 7.00 (s, 1H), 6.88 (m, 3H), 4.07 (dd, *J* = 11.7, 3.9 Hz, 2H), 3.77 (s, 3H), 2.32 (d, *J* = 1.1 Hz, 3H), 2.23 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 142.9 (d, *J* = 4.6 Hz), 140.4 (d, *J* = 3.8 Hz), 137.9 (d, *J* = 4.3 Hz), 137.3 (d, *J* = 4.4 Hz), 136.5 (d, *J* = 6.6 Hz), 131.8 (dd, *J* = 18.0, 3.2 Hz), 129.3 (s), 128.7 (d, *J* = 13.0 Hz), 127.7 – 127.4 (m), 122.8 (d, *J* = 7.5 Hz), 121.2 (d, *J* = 2.4 Hz), 115.1 (d, *J* = 6.9 Hz), 111.7 (d, *J* = 2.8 Hz), 55.9 (s), 36.8 (d, *J* = 3.5 Hz), 21.6 (s), 21.2 (s). ^{31}P NMR (162 MHz, CDCl3) δ 58.65 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{23}O_2PS_3H$ 447.0676 found 447.0675.

S-(2,4-dimethylphenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6b′)

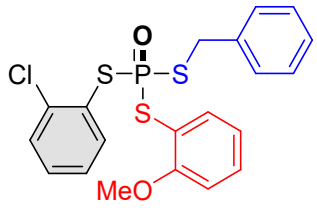


6b'

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (87mg, 19%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 7.9, 2.0 Hz, 2H), 7.39 (d, *J* = 2.4 Hz, 1H), 7.33 – 7.21 (m, 2H), 6.95 (s, 1H), 6.92 – 6.76 (m, 5H), 3.74 (s, 6H), 2.21 (d, *J* = 2.5 Hz, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.4 Hz), 143.0 (d, *J* = 4.6 Hz), 140.1 (d, *J* = 3.8 Hz), 137.7 (d, *J* = 4.3 Hz), 137.1 (d, *J* = 4.2

Hz), 131.7 (d, J = 3.0 Hz), 131.4 (d, J = 3.1 Hz), 127.4 (d, J = 2.9 Hz), 123.1 (d, J = 7.4 Hz), 121.1 (d, J = 2.6 Hz), 115.5 (d, J = 7.0 Hz), 111.6 (d, J = 2.4 Hz), 55.9 (s), 21.3 (d, J = 12.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.40 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{23}O_3PS_3H$ 463.0625; found, 463.0627.

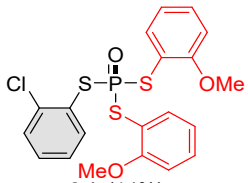
S-benzyl S-(2-chlorophenyl) S-(2-methoxyphenyl) phosphorotrithioate (6c)



6c, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (252mg, 56%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dt, J = 7.7, 1.9 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.49 – 7.19 (m, 9H), 7.04 – 6.88 (m, 2H), 4.22 (dd, J = 12.0, 3.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, J = 4.5 Hz), 138.6 (d, J = 5.7 Hz), 138.0 (d, J = 4.6 Hz), 137.6 (d, J = 4.4 Hz), 136.2 (d, J = 6.9 Hz), 132.0 (d, J = 3.6 Hz), 130.8 (d, J = 2.9 Hz), 130.3 (d, J = 2.5 Hz), 129.3 (s), 128.7 (s), 127.7 (s), 127.3 (d, J = 2.2 Hz), 127.0 (d, J = 6.9 Hz), 121.3 (d, J = 2.8 Hz), 114.5 (d, J = 7.4 Hz), 111.7 (d, J = 2.8 Hz), 55.9 (s), 37.1 (d, J = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.09 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}ClO_2PS_3H$ 452.9973 found 452.9969.

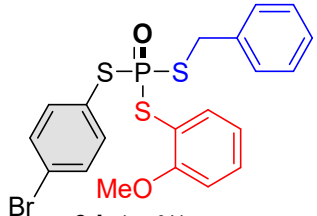
S-(2-chlorophenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6c′)



6c', (14%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (65mg, 14%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dt, J = 7.7, 1.9 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.32 – 7.20 (m, 3H), 7.11 (m, 2H), 6.79 (m, 4H), 3.68 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, J = 4.5 Hz), 138.4 (d, J = 5.9 Hz), 137.8 (d, J = 4.5 Hz), 137.2 (d, J = 4.2 Hz), 131.8 (d, J = 3.3 Hz), 130.6 (d, J = 2.4 Hz), 130.2 (d, J = 2.2 Hz), 127.5 (d, J = 6.7 Hz), 127.2 (d, J = 1.9 Hz), 121.1 (d, J = 2.5 Hz), 114.8 (d, J = 7.2 Hz), 111.7 (d, J = 2.8 Hz), 55.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.58 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}ClO_3PS_3H$ 468.9833 found 468.9829.

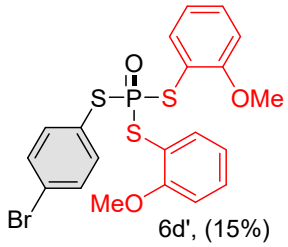
S-benzyl S-(4-bromophenyl) S-(2-methoxyphenyl) phosphorotrithioate (6d)



6d, (57%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (282mg, 57%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.40 – 7.35 (m, 2H), 7.36 – 7.28 (m, 3H), 7.24 – 7.17 (m, 5H), 6.87 (t, *J* = 8.0 Hz, 2H), 4.09 (d, *J* = 12.6 Hz, 2H), 3.87 – 3.71 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0 (d, *J* = 4.5 Hz), 137.1 (d, *J* = 4.7 Hz), 136.3 (d, *J* = 6.1 Hz), 132.4 (d, *J* = 2.5 Hz), 132.0 (d, *J* = 3.4 Hz), 129.3 (s), 128.7 (s), 127.8 (s), 126.3 (d, *J* = 7.1 Hz), 124.6 (d, *J* = 4.0 Hz), 121.3 (d, *J* = 2.6 Hz), 111.7 (d, *J* = 2.7 Hz), 55.9 (s), 36.9 (d, *J* = 3.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.14 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}BrO_2PS_3H$ 496.9468 found 496.9464.

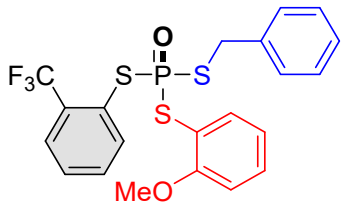
S-(4-bromophenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6d′)



6d', (15%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 13:87); (76 mg, 15%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.39 – 7.29 (m, 6H), 6.89 – 6.83 (m, 4H), 3.76 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 137.8 (d, *J* = 4.5 Hz), 136.9 (d, *J* = 4.7 Hz), 132.2 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 3.5 Hz), 126.7 (d, *J* = 6.9 Hz), 124.2 (d, *J* = 4.1 Hz), 121.2 (d, *J* = 2.5 Hz), 114.8 (d, *J* = 7.0 Hz), 111.7 (d, *J* = 2.6 Hz), 55.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.83 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}BrO_3PS_3H$ 512.9417; found, 512.9414.

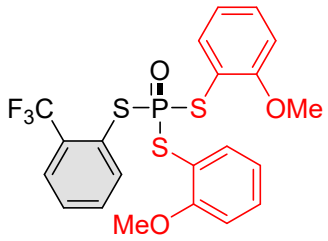
S-benzyl S-(2-methoxyphenyl) S-(2-(trifluoromethyl)phenyl) phosphorotrithioate (6e)



6e, (51%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (247mg, 51%) as a colorless oil;^{1}H ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 1H), 7.64 (d, *J* = 6.8 Hz, 1H), 7.50 – 7.31 (m, 4H), 7.26 – 7.17 (m, 5H), 6.87 (dd, *J* = 5.7, 4.5 Hz, 2H), 4.12 (dd, *J* = 12.2, 5.3 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 (d, *J* = 4.5 Hz), 138.6(s), 138.1 (d, *J* = 4.5 Hz), 138.0 (dd, *J* = 13.9, 4.6 Hz), 138.0 (d, *J* = 4.6 Hz), 136.1 (d, *J* = 6.8 Hz), 132.1 (d, *J* = 3.9 Hz), 129.9 (s), 129.3 (d, *J* = 3.8 Hz), 129.0 – 128.9 (m), 128.6 (d, *J* = 22.1 Hz), 128.5 (s), 127.7 (s), 127.2 (s), 121.3 (d, *J* = 2.9 Hz), 114.3 (s), 111.7 (d, *J* = 3.0 Hz), 55.8 (s), 37.0 (d, *J* = 3.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.25 (d, *J* = 34.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 55.27 (d, *J* = 23.5 Hz).). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{18}F_3O_2PS_3H$ 487.0237 found 487.0237.

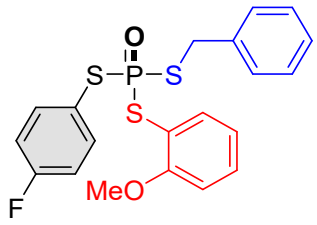
S,S-bis(2-methoxyphenyl) S-(2-(trifluoromethyl)phenyl) phosphorotrithioate (6e')



6e', (11%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 20:80); (55 mg, 11%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.47 (m, 2H), 7.40 (dd, *J* = 33.4, 12.3 Hz, 2H), 7.30 – 7.23 (m, 2H), 6.83 (t, *J* = 7.3 Hz, 4H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (d, *J* = 4.7 Hz), 138.2 (d, *J* = 4.6 Hz), 132.9 (d, *J* = 4.7 Hz), 132.3 (d, *J* = 3.7 Hz), 132.1 (s), 129.5 (d, *J* = 2.7 Hz), 127.2 (d, *J* = 1.9 Hz), 127.2 (d, *J* = 1.8 Hz), 126.1(d, *J* = 6.8 Hz), 121.2 (d, *J* = 3.0 Hz), 113.7 (d, *J* = 7.6 Hz), 111.8 (d, *J* = 3.0 Hz), 55.8 (s).^{19}F NMR (377 MHz, $CDCl_3$) δ -59.41 (d, *J* = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.80 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{18}F_3O_3PS_3H$ 503.0179 found 503.0187.

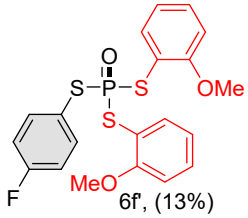
S-benzyl S-(4-fluorophenyl) S-(2-methoxyphenyl) phosphorotrithioate (6f)



6f, (53%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (231mg, 53%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 1H), 7.45 (m, 2H), 7.39 – 7.28 (m, 1H), 7.24 – 7.17 (m, 5H), 7.05 – 6.81 (m, 4H), 4.09 (d, *J* = 12.4 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 138.0 – 137.8 (m), 137.8 – 137.7 (m), 136.3 (d, *J* = 6.1 Hz), 131.9 (d, *J* = 3.3 Hz), 129.2 (s), 128.7 (s), 127.7 (s), 122.3 (dd, *J* = 7.1, 3.4 Hz), 121.3 (d, *J* = 2.8 Hz), 116.6 (d, *J* = 2.8 Hz), 116.4 (d, *J* = 2.8 Hz), 114.6 (s), 111.7 (d, *J* = 2.9 Hz), 55.9 (s), 36.8 (d, *J* = 3.7 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.46 – -110.65 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 58.67 (d, *J* = 6.4 Hz). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}FO_2PS_3H$ 437.0269 found 437.0264.

S-(4-fluorophenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6f')

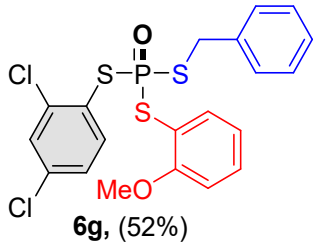


6f', (13%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 11:89); (58mg, 13%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 5H), 7.32 (m, 1H), 6.96 (t, *J* = 7.6 Hz, 4H), 6.85 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (d, *J* = 3.7 Hz), 162.5 (d, *J* = 3.7 Hz), 160.0 (d, *J* = 4.6 Hz), 137.8 (d, *J*

= 4.7 Hz), 137.7 (d, *J* = 4.5 Hz), 132.0 (d, *J* = 3.3 Hz), 122.1 (d, *J* = 3.2 Hz), 122.0 (d, *J* = 3.2 Hz), 121.3 (d, *J* = 2.6 Hz), 116.6 (d, *J* = 2.5 Hz), 116.4 (d, *J* = 2.4 Hz), 111.8 (d, *J* = 2.8 Hz), 55.9 (s).^{31}P NMR (162 MHz, $CDCl_3$) δ 55.27 (d, *J* = 5.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -104.72 – -116.85 (m). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}FO_3PS_3H$ 453.0126 found 453.0129.

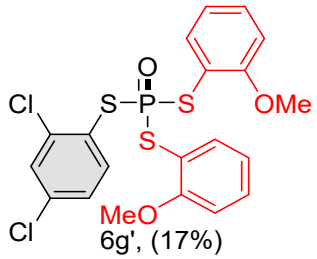
S-benzyl S-(2,4-dichlorophenyl) S-(2-methoxyphenyl) phosphorotrithioate (6g)



6g, (52%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (252mg, 52%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 1H), 7.47 – 7.39 (m, 1H), 7.35 – 7.26 (m, 8H), 7.05 – 6.92 (m, 2H), 4.21 – 4.17 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 138.0 (d, *J* = 4.6 Hz), 136.3 (d, *J* = 6.5 Hz), 131.9 (d, *J* = 3.5 Hz), 129.3 (d, *J* = 13.7 Hz), 128.7 (s), 128.5 (s), 127.7 (s), 121.3 (d, *J* = 2.9 Hz), 114.7 (s), 111.7 (d, *J* = 2.6 Hz), 55.9 (s), 36.8 (d, *J* = 3.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.74 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{17}Cl_2O_2PS_3H$ 486.9584 found 486.9589.

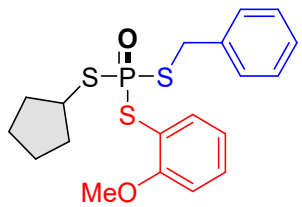
S-(2,4-dichlorophenyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6g′)



6g', (17%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 12:88); (85 mg, 17%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 2.2, 0.6 Hz, 1H), 7.31 (s, 2H), 7.16 – 7.09 (m, 1H), 6.86 (t, *J* = 7.8 Hz, 4H), 3.76 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.23 (s). 13C NMR (101 MHz, CDCl3) δ 160.1 (d, J = 4.6 Hz), 139.3 (d, J = 5.7 Hz), 137.9 (d, J = 4.5 Hz), 137.8 (d, J = 4.0 Hz), 136.0 (d, J = 3.3 Hz), 131.8(d, J = 3.4 Hz), 129.9(d, J = 2.3 Hz), 127.5 (d, J = 2.2 Hz), 126.2 (d, J = 6.5 Hz), 121.2 (d, J = 2.9 Hz), 114.6 (d, J = 7.1 Hz), 111.7 (d, J = 2.7 Hz), 55.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.23 (s). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}Cl_2O_3PS_3H$ 502.9533; found, 502.9533.

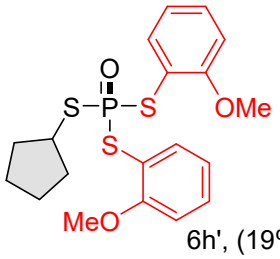
S-benzyl S-cyclopentyl S-(2-methoxyphenyl) phosphorotrithioate (6h)



6h, (54%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (221mg, 54%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.51 (m, 1H), 7.38 – 7.14 (m, 6H), 6.89 (d, *J* = 9.2 Hz, 2H), 4.13 (dd, *J* = 12.0, 9.3 Hz, 2H), 3.80 (s, 3H), 3.71 – 3.53 (m, 1H), 2.19 – 2.02 (m, 2H), 1.75 – 1.50 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 137.8 (d, *J* = 4.5 Hz), 136.4 (s), 131.7 (d, *J* = 3.3 Hz), 129.2 (s), 128.7 (d, *J* = 3.7 Hz), 127.6 (d, *J* = 8.1 Hz), 121.3 (s), 115.2 (s), 111.7 (d, *J* = 2.6 Hz), 55.9 (s), 47.0 (d, *J* = 4.0 Hz), 36.9 (d, *J* = 4.4 Hz), 35.2 (s), 24.3 (d, *J* = 2.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.41 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{23}O_2PS_3H$ 411.0676 found 411.0661.

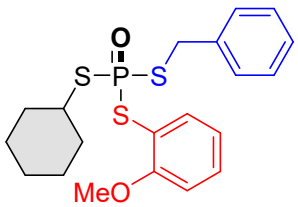
S-cyclopentyl S,S-bis(2-methoxyphenyl) phosphorotrithioate (6h′)



6h', (19%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (80 mg, 19%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.50 (m, 2H), 7.34 – 7.23 (m, 2H), 6.97 – 6.76 (m, 4H), 3.78 (s, 6H), 3.71 – 3.55 (m, 1H), 2.20 – 1.99 (m, 2H), 1.70 – 1.42 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 159.8 (d, J = 4.4 Hz), 137.5 (d, J = 4.3 Hz), 131.3 (d, J = 3.1 Hz), 121.1 (d, J = 2.6 Hz), 115.8 (d, J = 6.9 Hz), 111.6 (d, J = 2.5 Hz), 55.9 (s), 47.00 (d, J = 3.9 Hz), 35.1 (d, J = 5.5 Hz), 24.3 (s). 31P NMR (162 MHz, CDCl3) δ 57.88 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{23}O_3PS_3H$ 427.0563 found 427.0561.

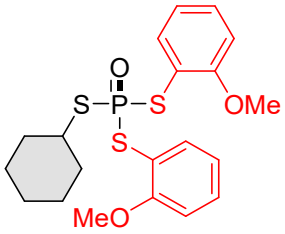
S-benzyl S-cyclohexyl S-(2-methoxyphenyl) phosphorotrithioate (6i)



6i, (53%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (224mg, 53%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.57 (m, 1H), 7.43 – 7.21 (m, 6H), 6.94 (dd, *J* = 6.4, 4.5 Hz, 2H), 4.27 – 4.13 (m, 2H), 3.87 (s, 3H), 3.62 – 3.44 (m, 1H), 2.09 (dd, *J* = 9.2, 3.7 Hz, 2H), 1.84 – 1.65 (m, 2H), 1.61 – 1.47 (m, 3H), 1.44 – 1.27 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (s), 137.7 (d, *J* = 4.5 Hz), 136.4 (d, *J* = 6.8 Hz), 131.6 (d, *J* = 3.6 Hz), 129.2 (s), 128.6 (s), 127.6 (s), 121.2 (d, *J* = 2.8 Hz), 115.4 (s), 111.7 (d, *J* = 2.6 Hz), 55.9 (s), 47.8 (d, *J* = 3.7 Hz), 37.0 (d, *J* = 3.4 Hz), 35.2 (d, *J* = 4.7 Hz), 25.9 (s), 25.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.46 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{25}O_2PS_3H$ 425.0833 found 425.0834.

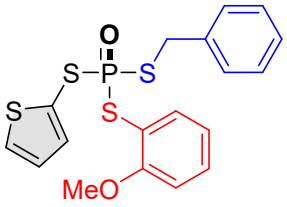
S-cyclohexyl S,S-bis(2-methoxyphenyl) phosphorotrithioate (6I')



6i', (18%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (79 mg, 18%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.30 (dd, *J* = 2.6, 1.2 Hz, 2H), 6.96 – 6.80 (m, 4H), 3.81 (s, 6H), 3.44 – 3.41 (m, 1H), 2.25 – 1.89 (m, 2H), 1.65 (m, 2H), 1.57 – 1.44 (m, 2H), 1.44 – 1.28 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7 (d, *J* = 4.4 Hz), 137.4 (d, *J* = 4.5 Hz), 131.3 (d, *J* = 3.2 Hz), 121.1 (d, *J* = 2.7 Hz), 116.2 (d, *J* = 7.1 Hz), 111.6 (d, *J* = 2.4 Hz), 55.9 (s), 47.8 (s), 47.7 (s), 35.2 (d, *J* = 4.8 Hz), 35.1 (d, *J* = 4.7 Hz), 25.9 (s), 25.3 (s).^{31}P NMR (162 MHz, $CDCl_3$) δ 59.86 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{25}O_3PS_3H$ 441.0719 found 441.0721.

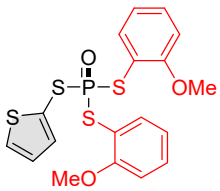
S-benzyl S-(2-methoxyphenyl) S-(thiophen-2-yl) phosphorotrithioate (6j)



6j, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (236mg, 56%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 1H), 7.42 (m, 1H), 7.34 (s, 1H), 7.26 – 7.17 (m, 6H), 7.01 – 6.97 (m, 1H), 6.88 (s, 2H), 4.18 – 4.06 (m, 2H), 3.82 – 3.78 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (s), 138.1 (d, *J* = 4.5 Hz), 137.7 (d, *J* = 6.4 Hz), 136.2 (d, *J* = 6.3 Hz), 132.3 (d, *J* = 5.1 Hz), 132.0 (d, *J* = 3.4 Hz), 129.3 (s), 128.7 (s), 128.3 – 127.9 (m), 127.8 (s), 123.6 (s), 121.4 (d, *J* = 2.8 Hz), 114.2 (s), 111.8 (d, *J* = 2.9 Hz), 55.9 (s), 36.8 (d, *J* = 3.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.70 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{18}H_{17}O_2PS_4H$ 424.9927 found 424.9926.

S,S-bis(2-methoxyphenyl) S-(thiophen-2-yl) phosphorotrithioate (6j′)

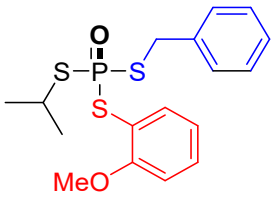


6j', (17%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (74 mg, 17%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 1H), 7.25 – 7.15 (m, 3H), 7.11 – 6.96 (m, 5H), 6.93 – 6.79 (m, 2H), 3.70 (d, *J* = 4.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (dd, *J* = 6.4, 2.5 Hz), 138.0 (d, *J* = 6.3 Hz), 130.1 (d, *J* = 2.7 Hz), 130.1 (d, *J* = 2.5 Hz), 128.1 (d, *J* = 3.8 Hz), 127.9 (d, *J* = 4.9 Hz), 127.8 (d, *J* = 5.1 Hz), 127.5 (d, *J* = 7.0 Hz), 127.1 (d, *J* = 6.9 Hz), 120.5 (d, *J* = 4.6 Hz), 120.4 (d, *J* = 4.7 Hz), 116.3 (d, *J* = 18.3 Hz), 116.3(d, *J* = 18.3 Hz), 55.4 (d, *J* = 3.4 Hz). ^{31}P NMR (162 MHz,

$CDCl_3$) δ 55.67. HRMS (ESI) m/z: [M + H]+ calcd for $C_{18}H_{17}O_3PS_4H$ 440.9816 found 440.9819.

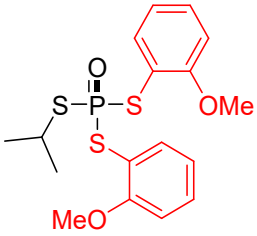
S-benzyl S-isopropyl S-(2-methoxyphenyl) phosphorotrithioate (6k)



6k, (58%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (222mg, 58%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 – 7.18 (m, 5H), 6.92 – 6.85 (m, 2H), 4.15 – 4.09 (m, 2H), 3.79 (s, 3H), 3.68 – 3.54 (m, 1H), 1.44 – 1.25 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1 – 159.8 (m), 137.8 (d, *J* = 4.5 Hz), 136.3 (dd, *J* = 10.8, 6.8 Hz), 131.7 (d, *J* = 3.4 Hz), 129.2 (s), 128.7 (d, *J* = 3.1 Hz), 127.7 (d, *J* = 7.1 Hz), 121.2 (d, *J* = 2.6 Hz), 115.3 (d, *J* = 7.0 Hz), 114.8 (s), 111.7 (d, *J* = 2.9 Hz), 55.9 (s), 40.4 (d, *J* = 3.8 Hz), 36.9 (dd, *J* = 12.7, 3.6 Hz), 25.4 (dd, *J* = 5.5, 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.32 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{17}H_{21}O_2PS_3H$ 385.0520 found 385.0507.

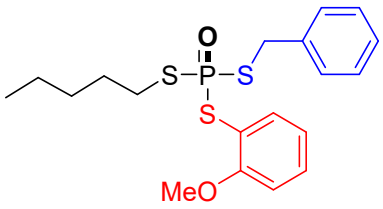
S-isopropyl S,S-bis(2-methoxyphenyl) phosphorotrithioate (6k′)



6k', (18%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (72 mg, 18%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 2H), 7.34 – 7.21 (m, 2H), 6.94 – 6.74 (m, 4H), 3.75 (s, 6H), 3.65 – 3.51 (m, 1H), 1.29 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 4.5 Hz), 137.5 (d, *J* = 4.5 Hz), 131.4 (d, *J* = 3.2 Hz), 121.1 (d, *J* = 2.4 Hz), 115.7 (d, *J* = 6.9 Hz), 111.6 (d, *J* = 2.7 Hz), 55.9(s), 40.4 (d, *J* = 3.8 Hz), 25.3 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.93 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{17}H_{21}O_3PS_3H$ 401.0410 found 401.0416.

S-benzyl S-(2-methoxyphenyl) S-pentyl phosphorotrithioate (6l)

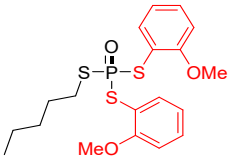


6l, (59%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (243mg, 59%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 1H), 7.37 – 7.21 (m, 6H), 6.90 (dd, *J* = 16.6, 8.3 Hz, 2H), 4.14 (dd, *J* = 11.9, 7.9 Hz, 2H), 3.81 (s, 3H), 2.95 – 2.87 (m, 2H), 1.62 (d, *J* = 7.6 Hz, 2H), 1.30 – 1.23 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0(s), 137.9 (d, *J* = 4.5 Hz), 136.5(s), 131.7 (d, *J* = 3.5

Hz), 129.2 (s), 128.7 (s), 127.6(s), 121.3 (d, J = 2.7 Hz), 115.1 (s), 111.7 (s), 55.9 (s), 36.8 (d, J = 3.4 Hz), 33.0 (d, J = 3.9 Hz), 30.7 (s), 30.1 (d, J = 5.3 Hz), 22.1 (s), 13.9 (s).^{31}P NMR (162 MHz, $CDCl_3$) δ 62.21 (s). HRMS (ESI) m/z: [M+H]+ calcd for $C_{19}H_{25}O_2PS_3H$ 413.0833 found 413.0831.

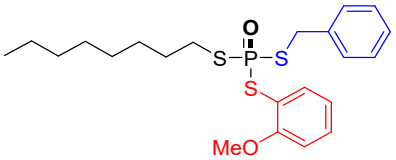
S,S-bis(2-methoxyphenyl) S-pentyl phosphorotrithioate (6l′)



6l', (17%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (72 mg, 17%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.34 – 7.27 (m, 2H), 6.87 (dd, J = 13.5, 7.9 Hz, 4H), 3.79 (s, 6H), 3.02 – 2.84 (m, 2H), 1.58 (s, 2H), 1.24 (dd, J = 7.2, 3.7 Hz, 4H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 4.5 Hz), 137.7 (d, J = 4.5 Hz), 131.4 (d, J = 3.2 Hz), 121.1 (d, J = 2.4 Hz), 115.5 (d, J = 7.0 Hz), 111.6 (d, J = 2.5 Hz), 55.9 (s), 33.0 (d, J = 3.9 Hz), 30.8 (s), 30.1 (d, J = 5.4 Hz), 22.1 (s), 13.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.82 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.35 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{19}H_{25}O_3PS_3H$ 429.0764; found, 429.0766.

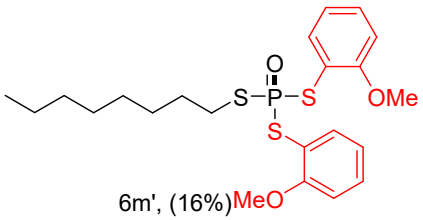
S-benzyl S-(2-methoxyphenyl) S-octyl phosphorotrithioate (6m)



6m, (56%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (254mg, 56%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 1H), 7.24 (m, 6H), 6.94 – 6.83 (m, 2H), 4.26 – 4.05 (m, 2H), 3.80 (s, 3H), 2.90 (m, 2H), 1.62 (s, 2H), 1.23 – 1.17 (m, 10H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, J = 4.5 Hz), 137.9 (d, J = 4.4 Hz), 136.4 (d, J = 6.5 Hz), 131.7 (d, J = 3.3 Hz), 129.2 (s), 128.7 (s), 127.6 (s), 121.3 (d, J = 2.7 Hz), 115.0 (s), 111.7 (d, J = 2.6 Hz), 55.9 (s), 36.8 (d, J = 3.5 Hz), 33.0 (d, J = 3.9 Hz), 31.7 (s), 30.4 (d, J = 5.3 Hz), 29.7 (s), 29.0 (d, J = 13.7 Hz), 28.6 (s), 22.6 (s), 14.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 62.25 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{31}O_2PS_3H$ 455.1303 found 455.1302.

S,S-bis(2-methoxyphenyl) S-octyl phosphorotrithioate (6m′)

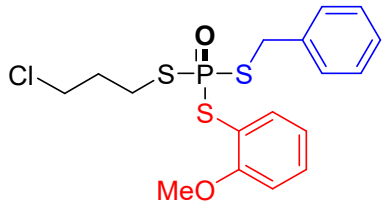


6m', (16%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (75 mg, 16%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.35 – 7.25 (m, 2H), 6.97 – 6.79 (m, 4H), 3.79 (s, 6H), 2.97 – 2.87 (m, 2H), 1.56 (dd, J = 15.0, 7.7 Hz, 2H), 1.22 – 1.17 (m, 10H), 0.79 (d, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 159.9 (d, *J* = 4.4 Hz), 137.7 (d, *J* = 4.5 Hz), 131.4 (d, *J* = 3.1 Hz), 121.1 (d, *J* = 2.5 Hz), 115.5 (d, *J* = 7.0 Hz), 111.6 (d, *J* = 2.8 Hz), 55.9 (s), 33.1 (d, *J* = 3.9 Hz), 31.7 (s), 30.4 (d, *J* = 5.5 Hz), 29.1 (s), 29.0 (s), 28.7 (s), 22.6 (s), 14.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.78 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{22}H_{31}O_3PS_3H$ 471.1233; found, 471.1229.

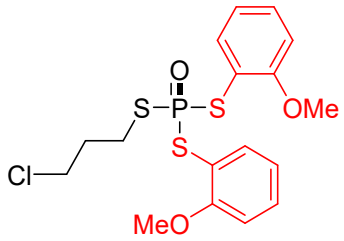
S-benzyl S-(3-chloropropyl) S-(2-methoxyphenyl) phosphorotrithioate (6n)



6n, (58%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (242mg, 58%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.50 (m, 1H), 7.39 – 7.12 (m, 6H), 7.00 – 6.78 (m, 2H), 4.16 (dd, *J* = 16.8, 8.2 Hz, 2H), 3.80 (s, 3H), 3.58 – 3.49 (m, 2H), 3.13 – 2.99 (m, 2H), 2.11 (dt, *J* = 13.0, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.5 Hz), 137.9 (d, *J* = 4.6 Hz), 136.3 (d, *J* = 6.5 Hz), 131.9 (d, *J* = 3.6 Hz), 129.2 (s), 128.7 (s), 127.7 (s), 121.3 (d, *J* = 2.9 Hz), 114.7 (d, *J* = 7.0 Hz), 111.7 (d, *J* = 2.7 Hz), 55.9 (s), 42.9 (d, *J* = 8.1 Hz), 36.9 (d, *J* = 3.5 Hz), 33.0 (d, *J* = 3.3 Hz), 30.0 (d, *J* = 3.9 Hz), 29.7(s). ^{31}P NMR (162 MHz, CDCl3) δ 62.46 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{17}H_{20}ClO_2PS_3H$ 419.0130 found 419.0130.

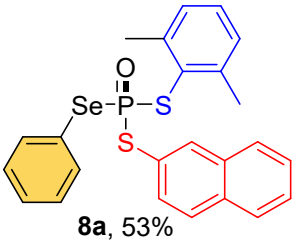
S-(3-chloropropyl) S,S-bis(2-methoxyphenyl) phosphorotrithioate (6n′)



6n', (18%)

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 8:92); (78mg, 18%) as a colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.0 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.03 – 6.86 (m, 2H), 3.81 (s, 6H), 3.54 (t, *J* = 6.2 Hz, 2H), 3.18 – 3.05 (m, 2H), 2.11 (dd, *J* = 13.1, 6.5 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 159.9 (d, J = 2.8 Hz), 130.1 (d, J = 2.8 Hz), 127.8 (d, J = 5.2 Hz), 127.5 (d, J = 7.3 Hz), 120.4 (d, J = 4.6 Hz), 116.2 (d, J = 3.2 Hz), 55.4 (s), 42.8 (s), 33.1 (d, J = 3.2 Hz), 30.0 (d, J = 3.9 Hz). ^{31}P NMR (162 MHz, CDCl3) δ 58.87 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{17}H_{20}ClO_3PS_3$ H 435.0011 found 435.0016.

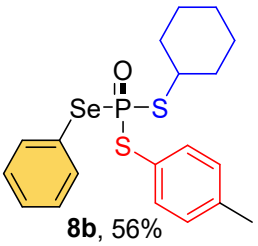
S-(2,6-dimethylphenyl) S-(naphthalen-2-yl) Se-phenyl phosphoroselenodithioate (8a)



8a, 53%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 3:97); (264mg, 53%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.71 (m, 4H), 7.56 – 7.48 (m, 2H), 7.46 – 7.37 (m, 4H), 7.32 – 7.26 (m, 2H), 6.97 (s, 1H), 6.93 – 6.83 (m, 1H), 2.22 (d, *J* = 2.6 Hz, 3H), 2.19 (d, *J* = 1.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0 (d, *J* = 4.5 Hz), 140.6 (s), 137.2 (d, *J* = 4.3 Hz), 136.5 (d, *J* = 4.1 Hz), 135.8 (dd, *J* = 6.4, 3.7 Hz), 133.4(d, *J* = 15.5 Hz), 132.0 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 2.7 Hz), 129.4 (d, *J* = 2.6 Hz), 128.8 (s), 128.0 (d, *J* = 3.4 Hz), 127.7 (d, *J* = 1.7 Hz), 127.6 (d, *J* = 3.0 Hz), 127.3 (s), 126.6 (s), 125.5 (d, *J* = 7.5 Hz), 124.8 (d, *J* = 7.3 Hz), 124.2 (d, *J* = 7.4 Hz), 122.9 (d, *J* = 7.1 Hz), 122.3 (d, *J* = 7.2 Hz), 21.3 (d, *J* = 19.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.45 (s), 48.04 (s), 46.63 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{24}H_{21}OPS_2Se$ H 500.0015 found 500.0008.

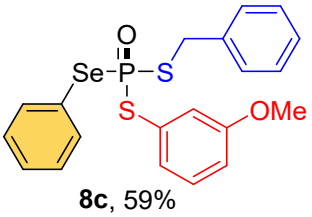
S-cyclohexyl Se-phenyl S-(p-tolyl) phosphoroselenodithioate (8b)



8b, 56%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 3:97); (264mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.20 (m, 3H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.39 (d, *J* = 13.9 Hz, 1H), 2.27 (d, *J* = 2.5 Hz, 3H), 2.02 – 1.87 (m, 2H), 1.67 – 1.51 (m, 2H), 1.42 (m, 3H), 1.35 – 1.18 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1 (d, *J* = 3.7 Hz), 136.4 (d, *J* = 4.2 Hz), 135.6 (d, *J* = 4.6 Hz), 130.1 (d, *J* = 2.6 Hz), 129.4(d, *J* = 2.4 Hz), 129.3 (d, *J* = 2.9 Hz), 126.1 (d, *J* = 7.6 Hz), 124.1 (d, *J* = 7.2 Hz), 48.2(d, *J* = 3.7 Hz), 35.2 (d, *J* = 4.1 Hz), 35.2 (dd, *J* = 8.1, 4.4 Hz), 35.2 (d, *J* = 4.6 Hz), 29.7 (s), 29.7 (s), 25.9 (s), 25.2 (s), 21.4 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.17 (s), 46.75 (s), 45.34 (s). HRMS (ESI) m/z: [M+H]+ calcd for $C_{19}H_{23}OPS_2Se$ H 443.0171 found 443.0157.

S-benzyl S-(3-methoxyphenyl) Se-phenyl phosphoroselenodithioate (8c)

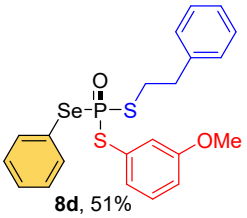


8c, 59%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (274mg, 56%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.42 – 7.14 (m, 10H), 7.13 – 7.02 (m, 2H), 6.89 (dd, *J* = 6.5, 2.2 Hz, 1H), 4.11 (dd, *J* = 12.4, 2.0 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (s), 136.6 (d, *J* = 4.2

Hz), 136.1 (d, J = 3.0 Hz), 130.1(d, J = 2.4 Hz), 129.6 (s), 129.5 (d, J = 2.2 Hz), 129.3 (d, J = 6.0 Hz), 128.7 (d, J = 3.4 Hz), 128.1 (d, J = 7.3 Hz), 127.8 (d, J = 5.4 Hz), 127.8 (d, J = 2.3 Hz), 120.4 (d, J = 4.7 Hz), 120.3 (d, J = 4.6 Hz), 116.3 (s), 55.4 (s), 36.8 (d, J = 3.6 Hz). ^{31}P NMR (162 MHz, CDCl3) δ 44.57 (s), 44.09 (s), 43.41 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{19}O2PS_2SeH$ 466.9808 found 466.9799.

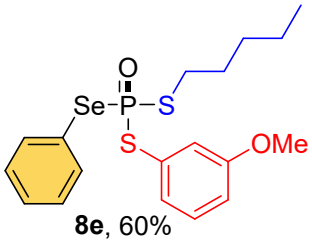
S-(3-methoxyphenyl) S-phenethyl Se-phenyl phosphoroselenodithioate (8d)



8d, 51%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (240mg, 51%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 2H), 7.37 – 7.04 (m, 10H), 6.93 – 6.83 (m, 2H), 3.77 (s, 3H), 3.17 – 3.07 (m, 2H), 2.96 – 2.85 (m, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.51 (s), 50.11 (s), 48.71 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 4.3 Hz), 139.5 (s), 137.9(d, J = 4.5 Hz), 136.4 (d, J = 3.9 Hz), 131.9 (d, J = 3.3 Hz), 129.4 (d, J = 2.5 Hz), 129.3 (d, J = 3.0 Hz), 128.7 (s), 128.6 (d, J = 19.7 Hz), 126.6 (d, J = 4.1 Hz), 125.8(d, J = 7.7 Hz), 121.3 (d, J = 2.9 Hz), 115.4 (d, J = 7.1 Hz), 111.6 (s), 55.8 (s), 36.8 (d, J = 4.4 Hz), 29.7 (s). ^{31}P NMR (162 MHz, CDCl3) δ 51.74 (s), 50.36 (s), 48.97 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{21}O_2PS_2SeH$ 480.9955 found 480.9964.

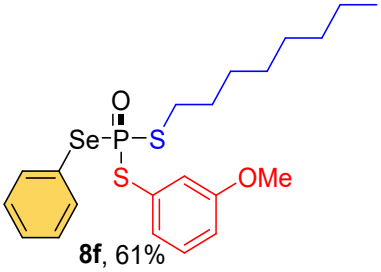
S-(3-methoxyphenyl) S-pentyl Se-phenyl phosphoroselenodithioate (8e)



8e, 60%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (267mg, 60%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.50 (m, 3H), 7.28 (dd, J = 14.7, 8.4 Hz, 4H), 6.97 – 6.83 (m, 2H), 3.80 (s, 3H), 2.92 – 2.81 (m, 2H), 1.59 (s, 2H), 1.29 – 1.20 (m, 4H), 0.80 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, J = 4.4 Hz), 137.90(d, J = 4.5 Hz), 136.4 (d, J = 4.1 Hz), 131.8 (d, J = 3.4 Hz), 129.4 (d, J = 2.5 Hz), 129.3 (d, J = 2.8 Hz), 126.0(d, J = 7.6 Hz), 121.3 (s), 115.5 (d, J = 6.9 Hz), 111.7 (s), 55.9 (s), 33.3 (d, J = 4.1 Hz), 30.8 (s), 30.1 (d, J = 4.8 Hz), 22.1 (s), 13.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.25 (s), 47.81 (s), 46.38 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{18}H_{23}O_2PS_2SeH$ 447.0121 found 447.0104.

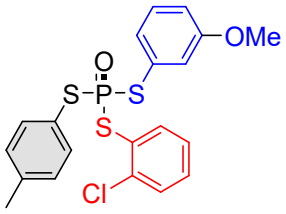
S-(3-methoxyphenyl) S-octyl Se-phenyl phosphoroselenodithioate (8f)



8f, 61%

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (273mg, 61%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.45 (m, 3H), 7.27 (d, *J* = 7.7 Hz, 4H), 6.97 – 6.82 (m, 2H), 3.81 (s, 3H), 2.97 – 2.85 (m, 2H), 1.64 – 1.55 (m, 2H), 1.18 (s, 10H), 0.81 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9 (d, *J* = 4.2 Hz), 137.9 (d, *J* = 4.5 Hz), 136.4 (d, *J* = 4.1 Hz), 131.8 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 2.3 Hz), 129.3 (d, *J* = 2.8 Hz), 126.0 (d, *J* = 7.6 Hz), 121.3 (d, *J* = 2.4 Hz), 115.5 (d, *J* = 7.0 Hz), 111.7 (d, *J* = 2.6 Hz), 55.8 (s), 33.4 (d, *J* = 3.9 Hz), 31.7 (s), 30.4 (d, *J* = 5.0 Hz), 29.1 (s), 28.9 (s), 28.6 (s), 22.6 (s), 14.1 (s).^{31}P NMR (162 MHz, $CDCl_3$) δ 49.29 (s), 47.87 (s), 46.43 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{21}H_{29}O_2PS_2SeH$ 489.1392 found 489.1386.

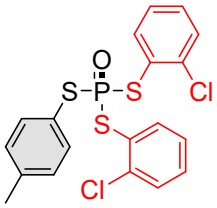
S-(2-chlorophenyl) S-(3-methoxyphenyl) S-(p-tolyl) phosphorotrithioate (5n)



5n

The title compound was purified by column chromatography with the eluent (EtOAc/hexane = 08:92); (1.4g, 49%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.35 (dd, *J* = 8.3, 2.2 Hz, 3H), 7.18 (d, *J* = 1.0 Hz, 3H), 7.06 (dd, *J* = 22.0, 5.2 Hz, 4H), 6.91 – 6.84 (m, 1H), 3.70 (s, 3H), 2.27 (d, *J* = 2.6 Hz, 3H). ^{13}C NMR (101 MHz,) δ 155.1 (d, *J* = 2.8 Hz), 135.6 (d, *J* = 3.8 Hz), 133.9 (d, *J* = 5.8 Hz), 132.9 (d, *J* = 4.0 Hz), 131.1 (d, *J* = 4.6 Hz), 126.1 (d, *J* = 2.9 Hz), 125.6 (d, *J* = 2.4 Hz), 125.5 (d, *J* = 2.9 Hz), 125.2 (d, *J* = 2.8 Hz), 123.1 (d, *J* = 5.3 Hz), 122.7 (d, *J* = 7.3 Hz), 122.6 (d, *J* = 2.2 Hz), 121.9 (d, *J* = 6.8 Hz), 118.0 (d, *J* = 7.4 Hz), 115.5 (d, *J* = 4.6 Hz), 111.5 (d, *J* = 3.5 Hz), 50.7 (s), 16.6 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.37 (s). HRMS (ESI) m/z: [M + H]+ calcd for $C_{20}H_{18}ClO_2PS_3H$ 452.9731 found 452.9733.

S,S-bis(2-chlorophenyl) S-(p-tolyl) phosphorotrithioate (5n′)

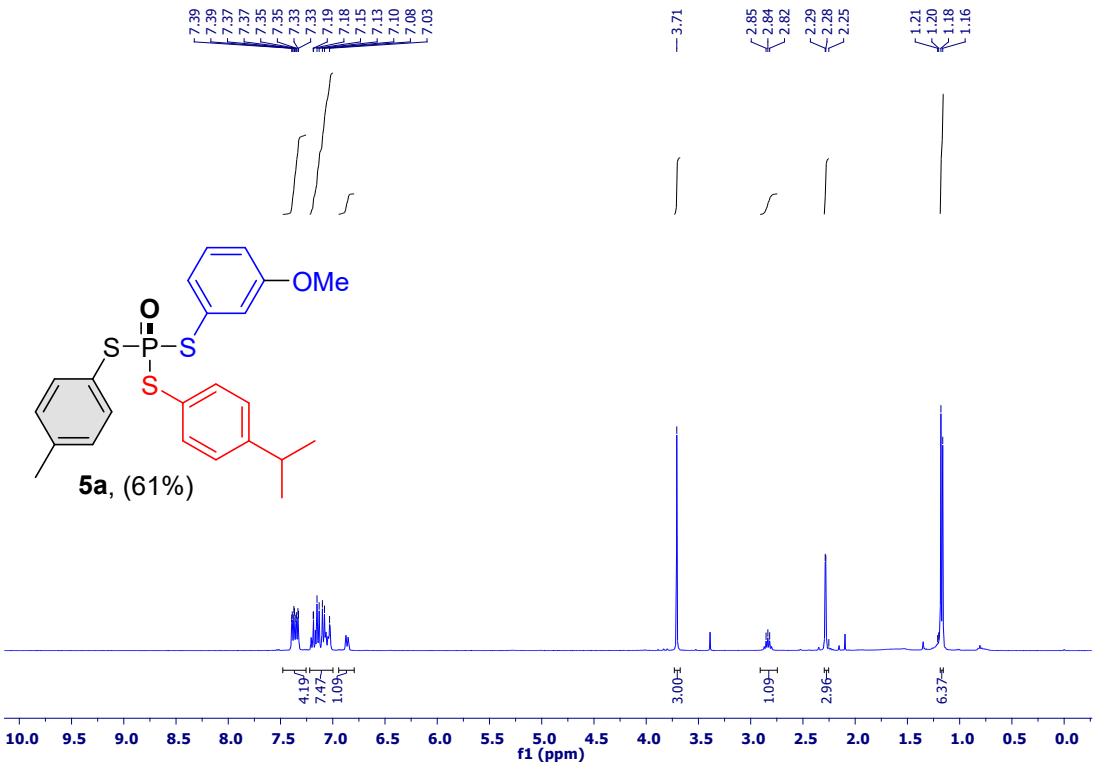


5n'

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 2H), 7.45 – 7.35 (m, 3H), 7.31 – 7.22 (m, 2H), 7.17 (dd, *J* = 12.4, 4.6 Hz, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 2.28 (d, *J* = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 135.6 (d, *J* = 3.7 Hz), 134.1 (d, *J* = 5.8 Hz), 133.0 (d, *J* = 4.4 Hz), 131.1 (d, *J* = 4.7 Hz), 126.2 (d, *J* = 3.0 Hz), 125.6 (d, *J* = 2.4 Hz), 125.5 (d, *J* = 3.0 Hz), 122.6 (d, *J* = 2.5 Hz), 121.7 (d, *J* = 6.9 Hz), 117.8 (d, *J* = 4.2 Hz), 16.6(s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.54 (s). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}Cl_2OPS_3H^+$ 456.9462 found 456.9463.

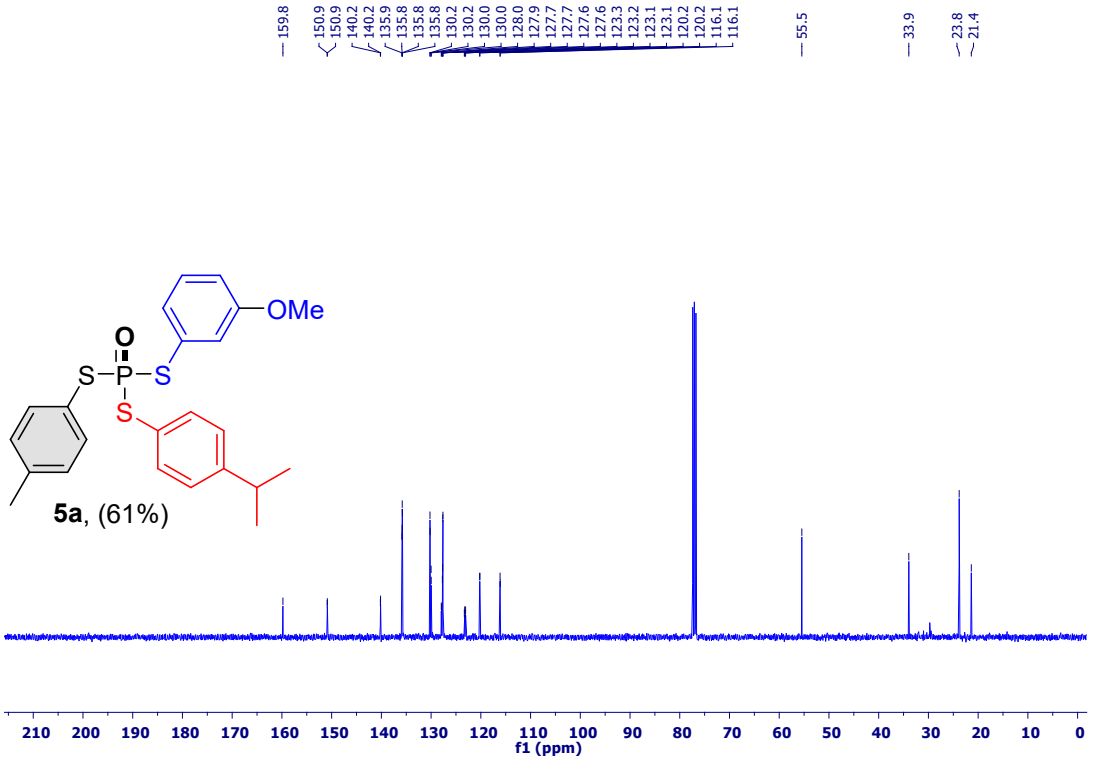
7. NMR Data

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



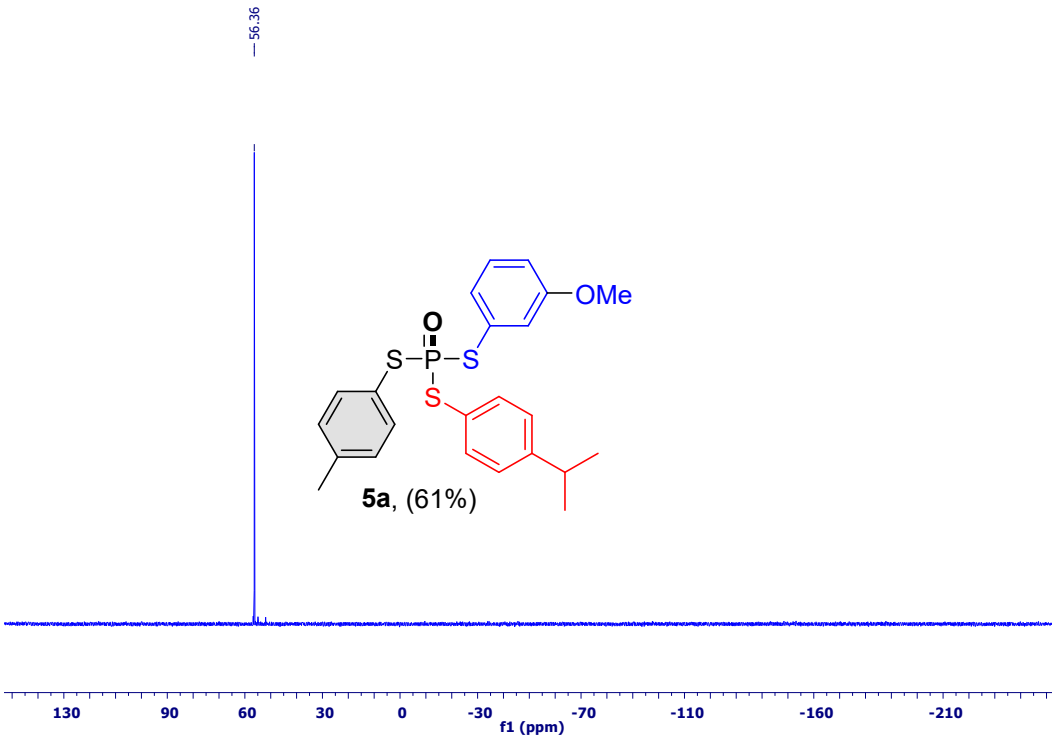
5a, (61%)

^{13}C NMR (101 MHz, $CDCl_3$)

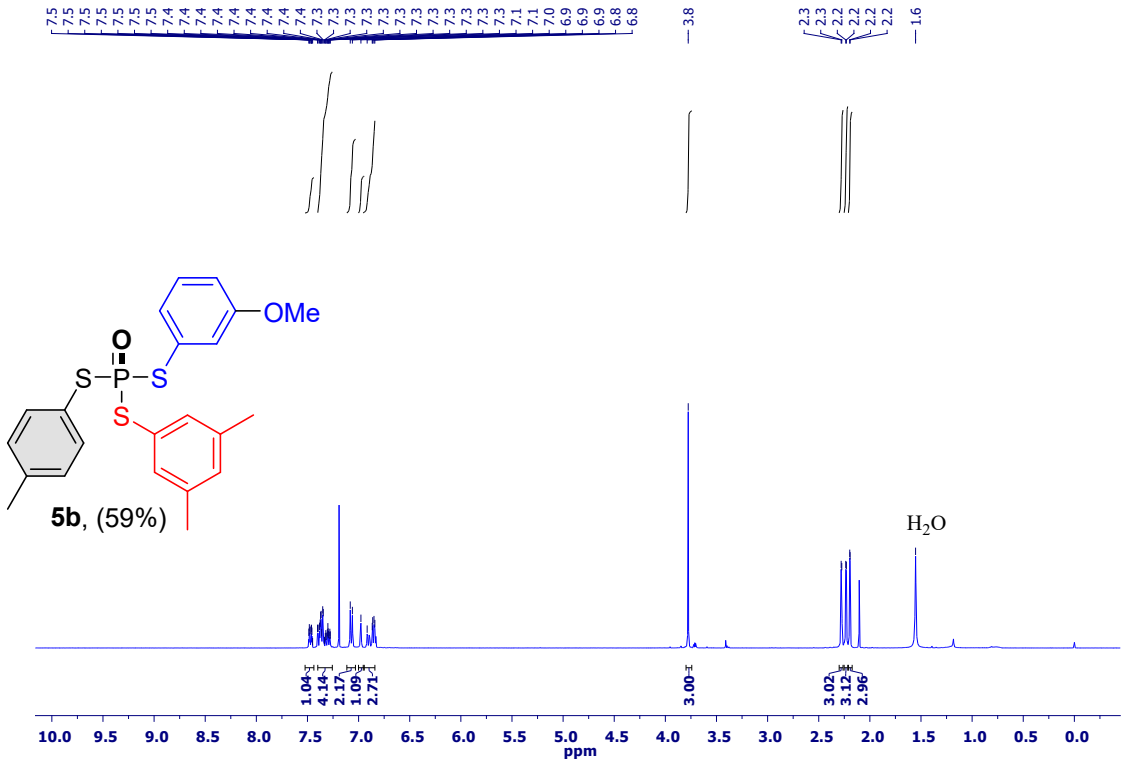


5a, (61%)

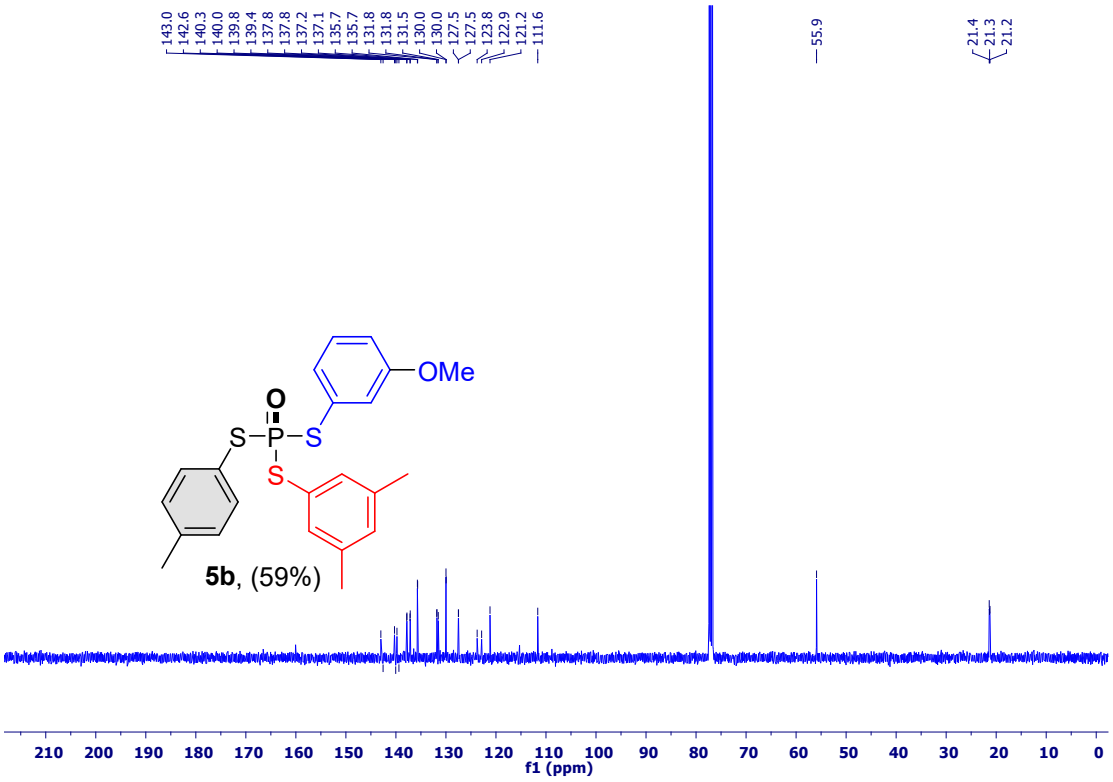
^{31}P NMR (162 MHz, $CDCl_3$)



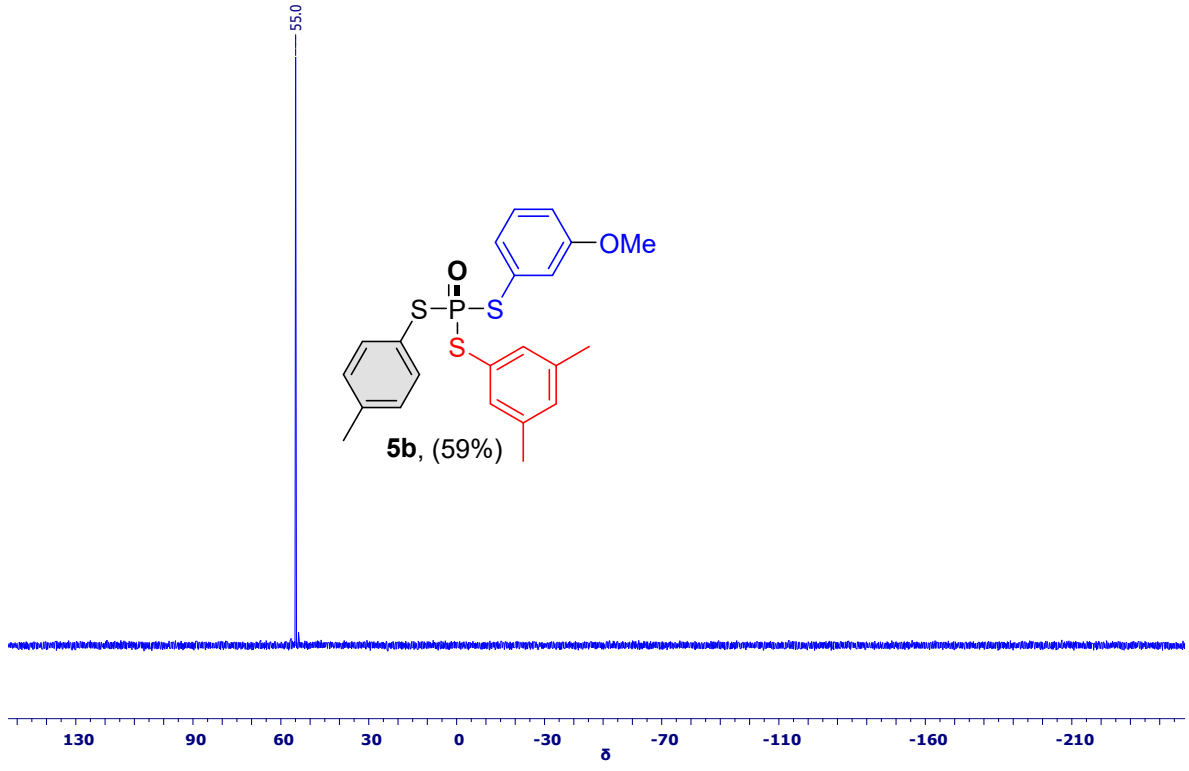
^{1}H NMR (400 MHz, $CDCl_3$)



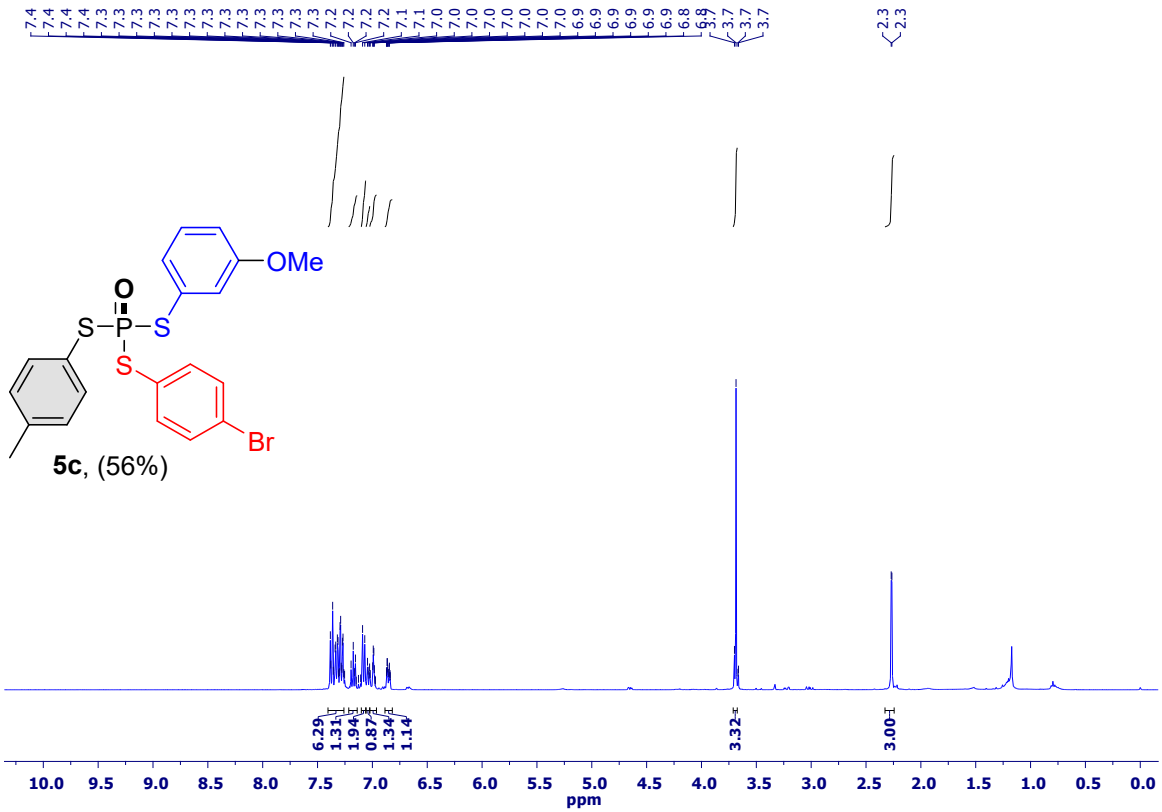
^{13}C NMR (101 MHz, $CDCl_3$)



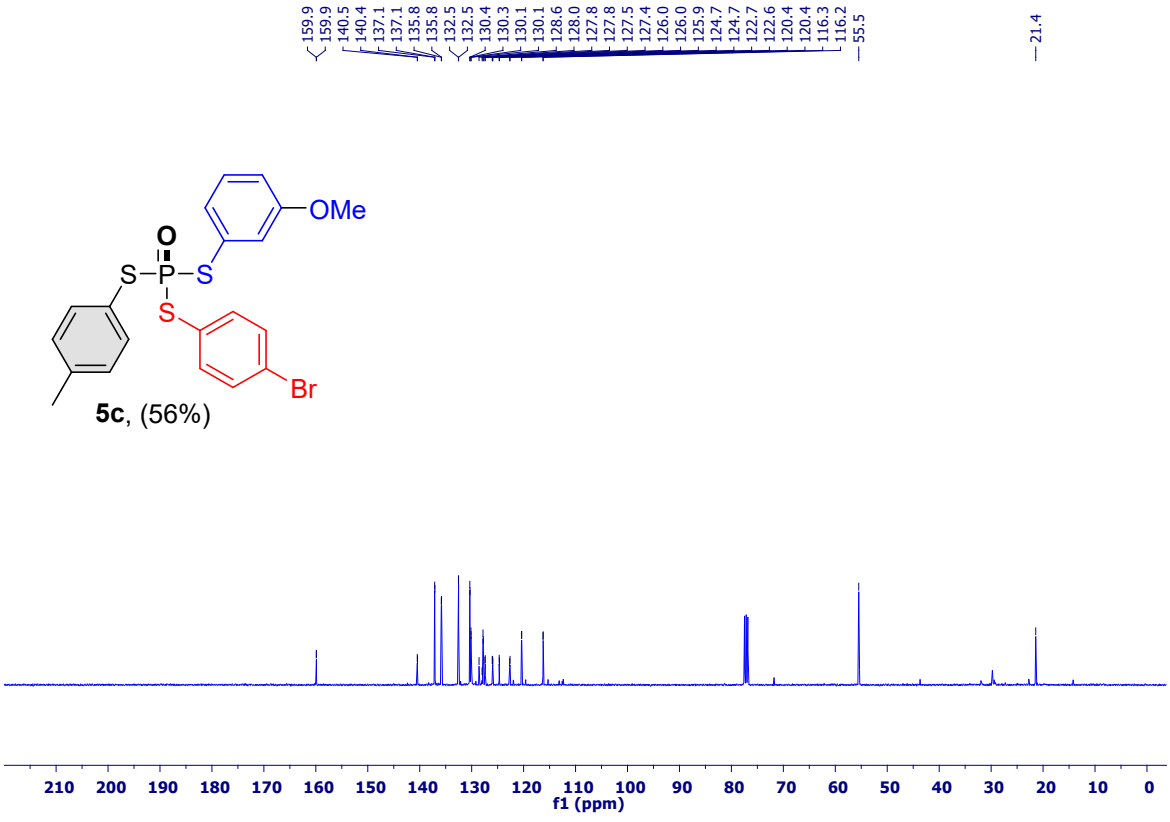
^{31}P NMR (162 MHz, $CDCl_3$)



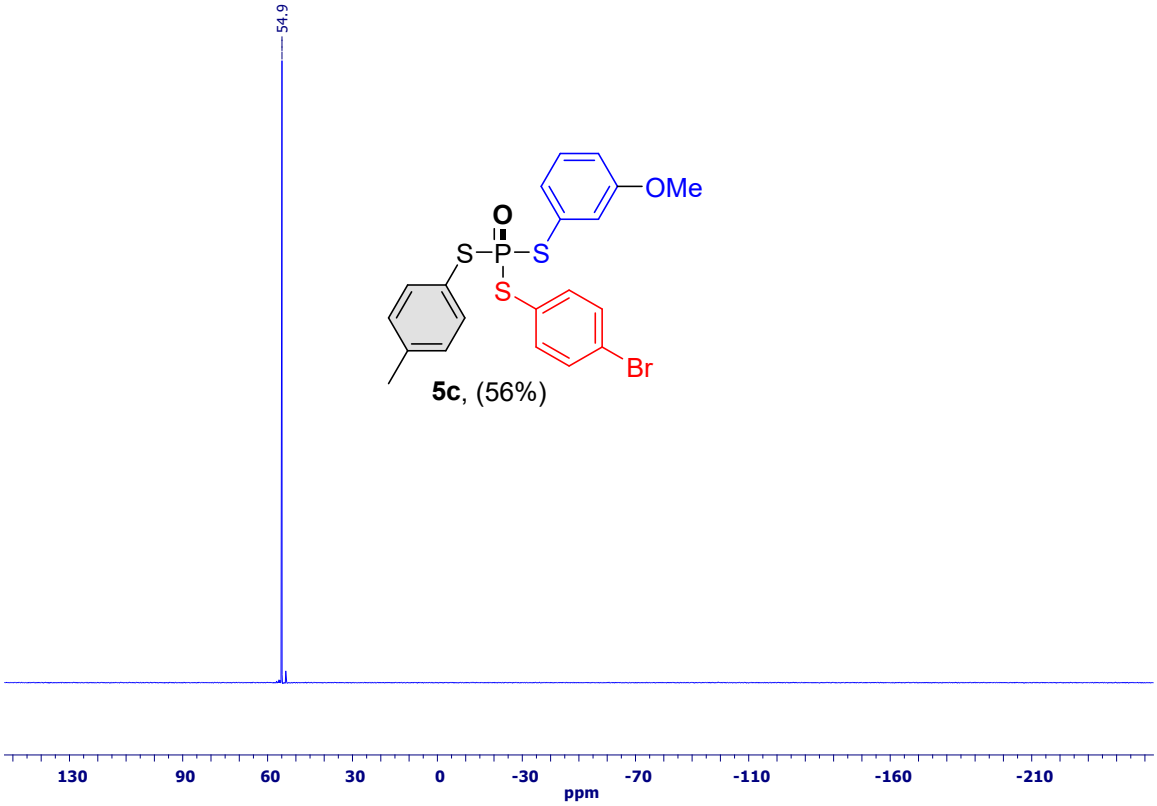
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

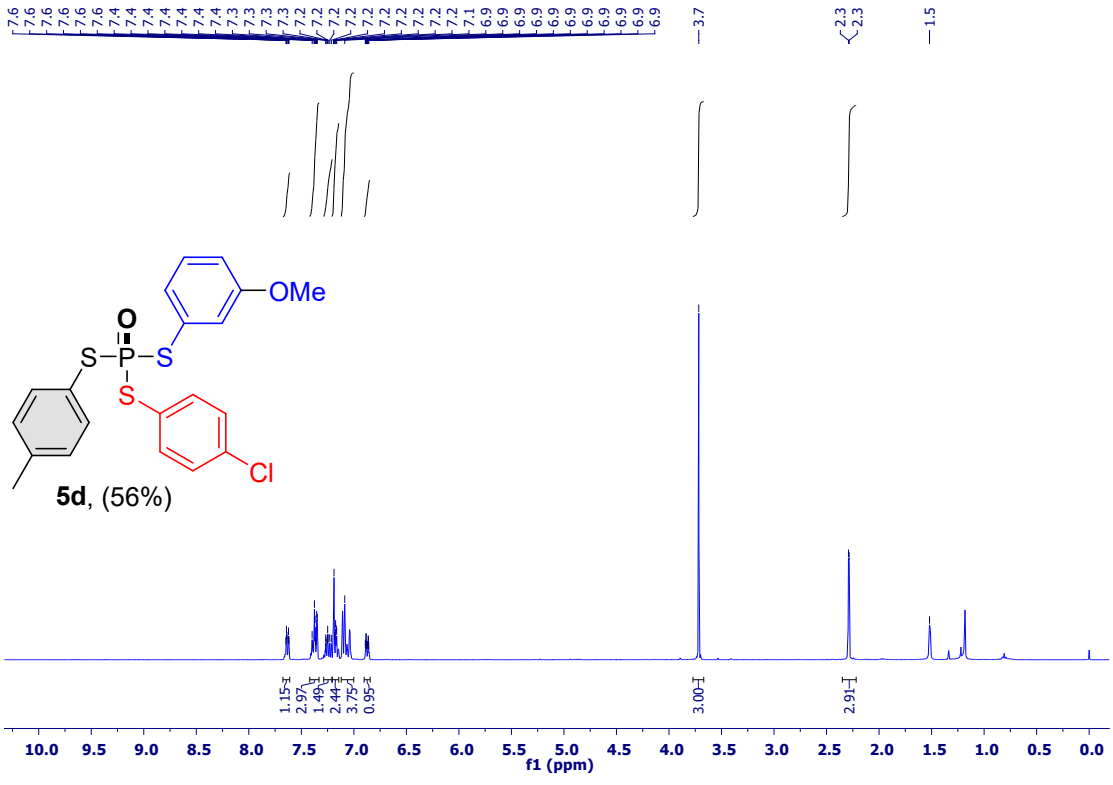


^{31}P NMR (162 MHz, $CDCl_3$)



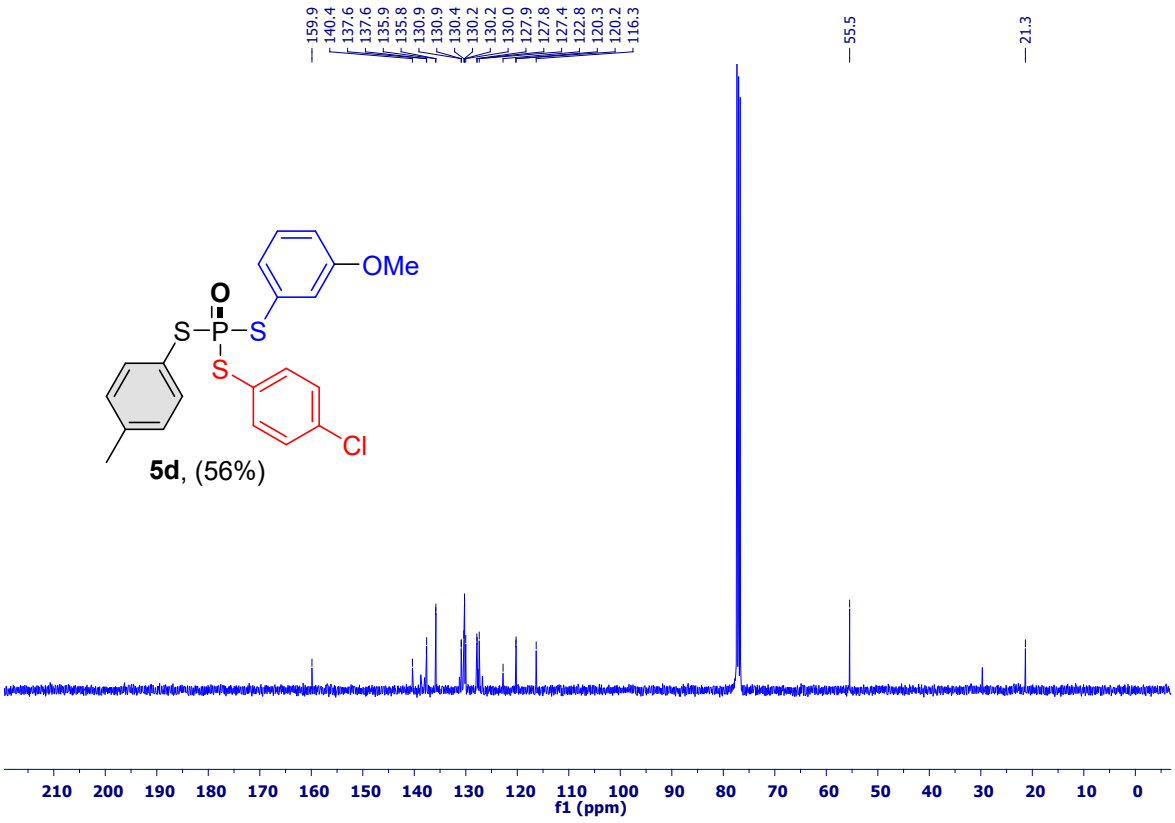
5c, (56%)

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

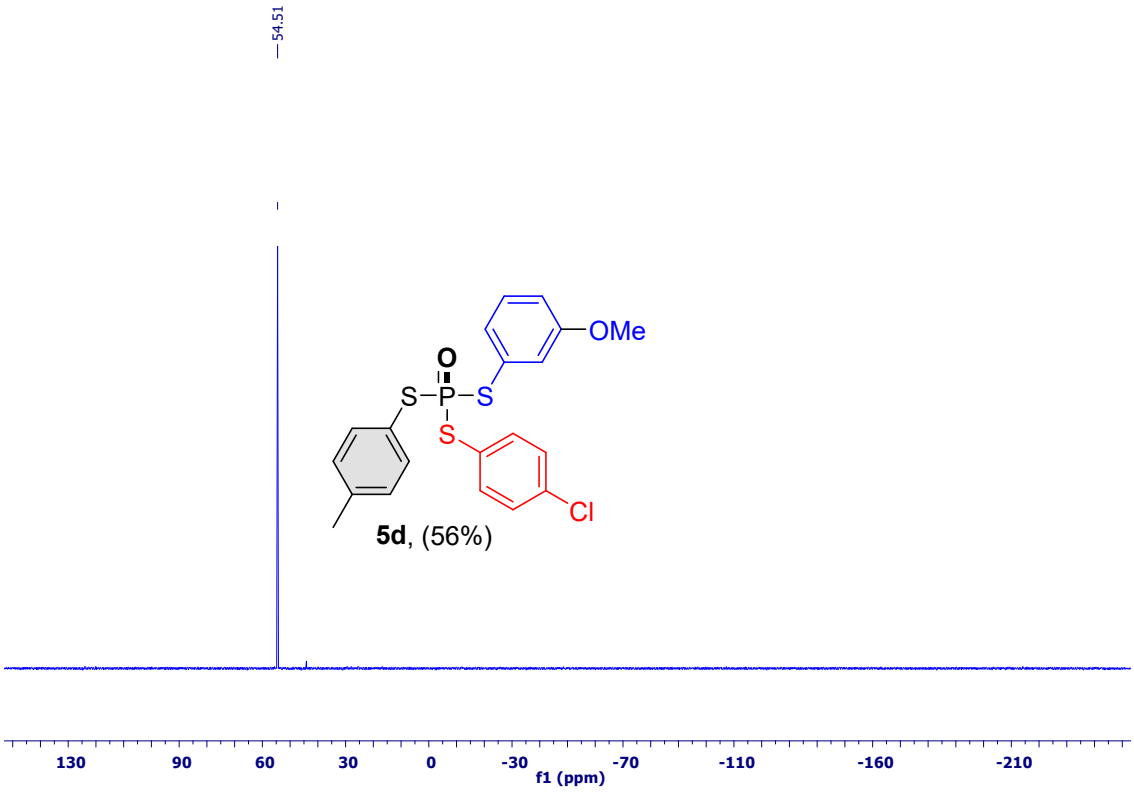


5d, (56%)

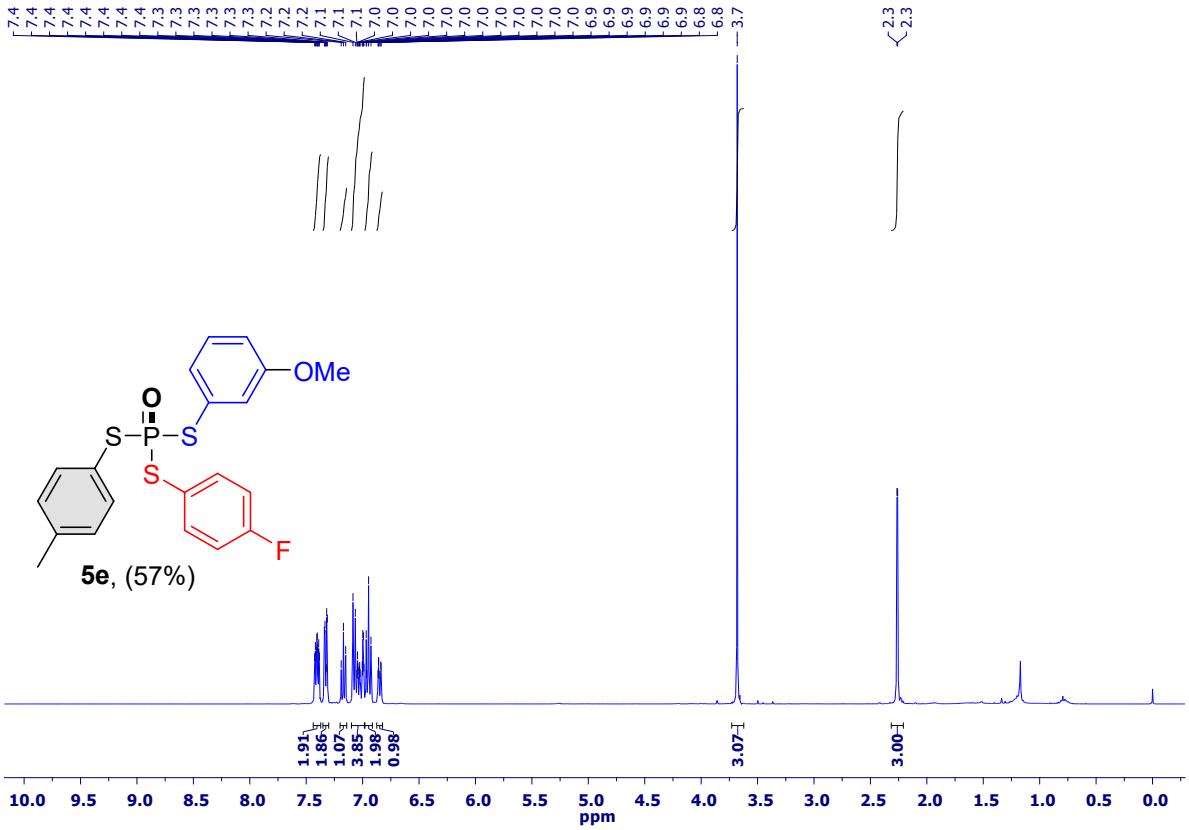
^{13}C NMR (101 MHz, $CDCl_3$)



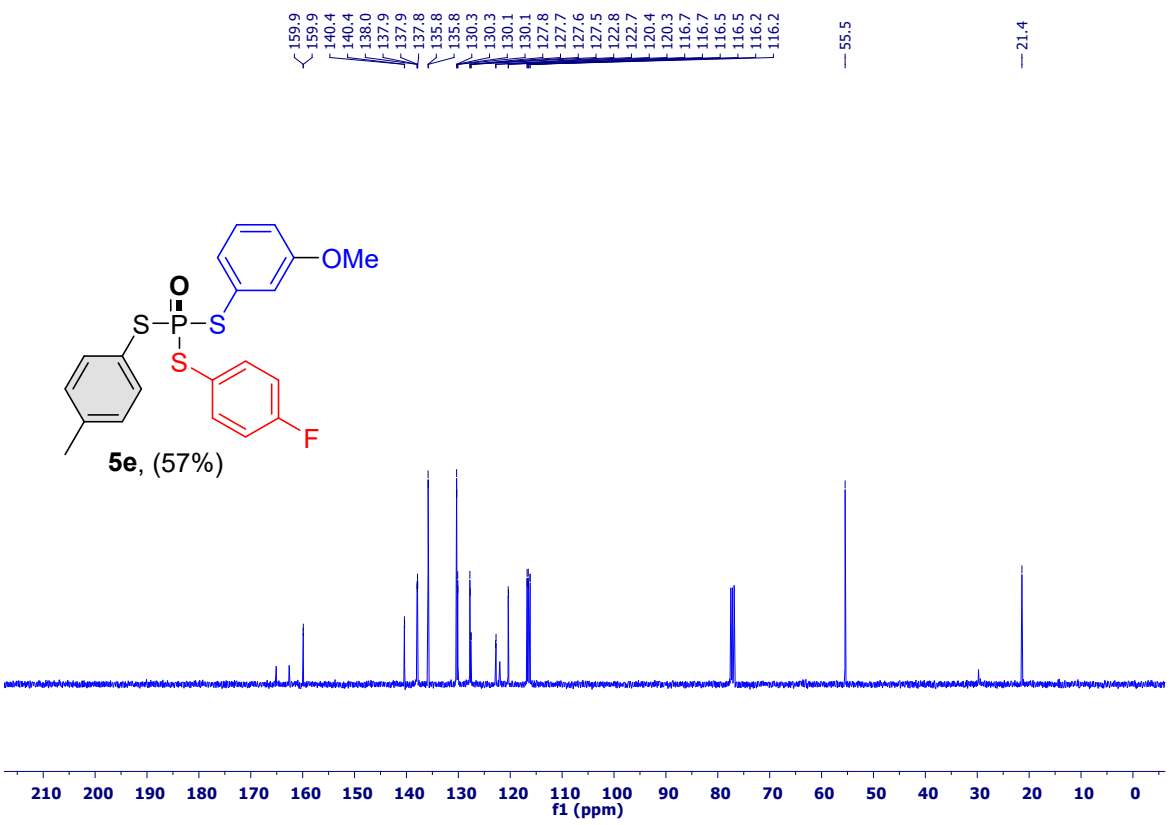
^{31}P NMR (162 MHz, $CDCl_3$)



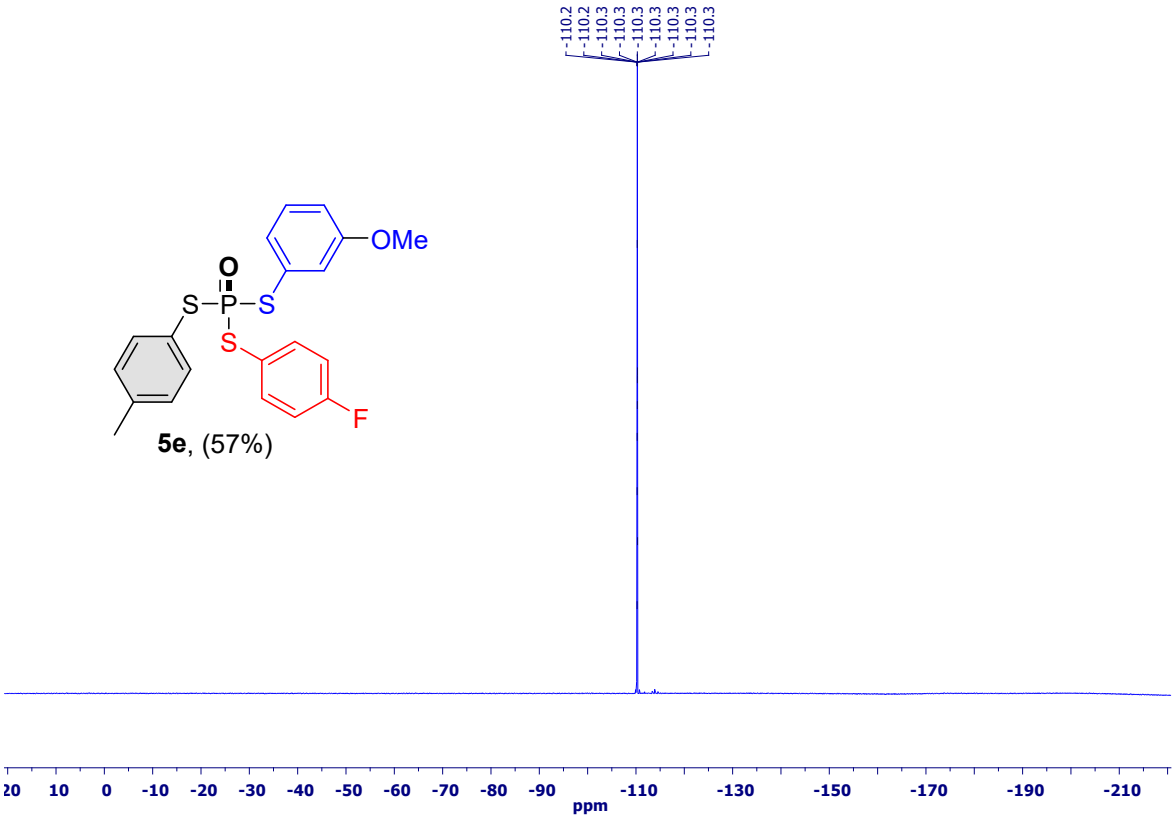
^{1}H NMR (400 MHz, $CDCl_3$)



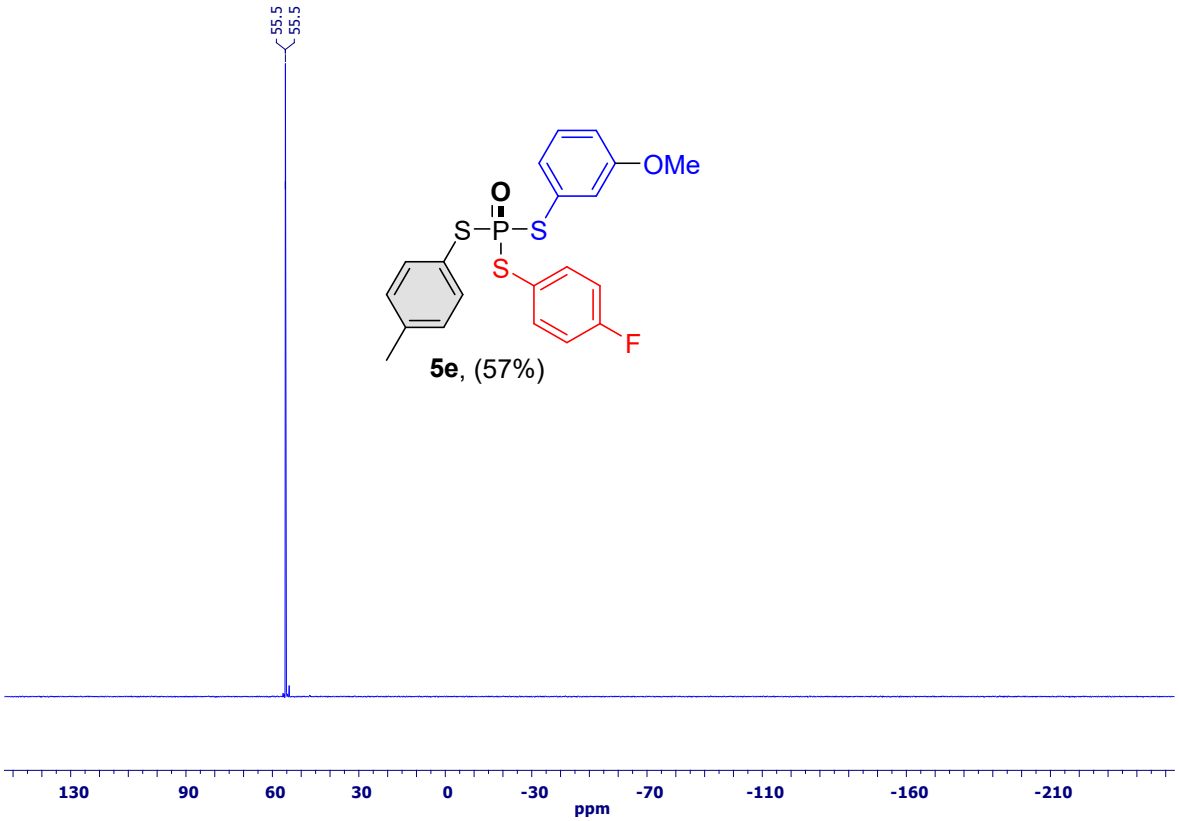
^{13}C NMR (101 MHz, $CDCl_3$)



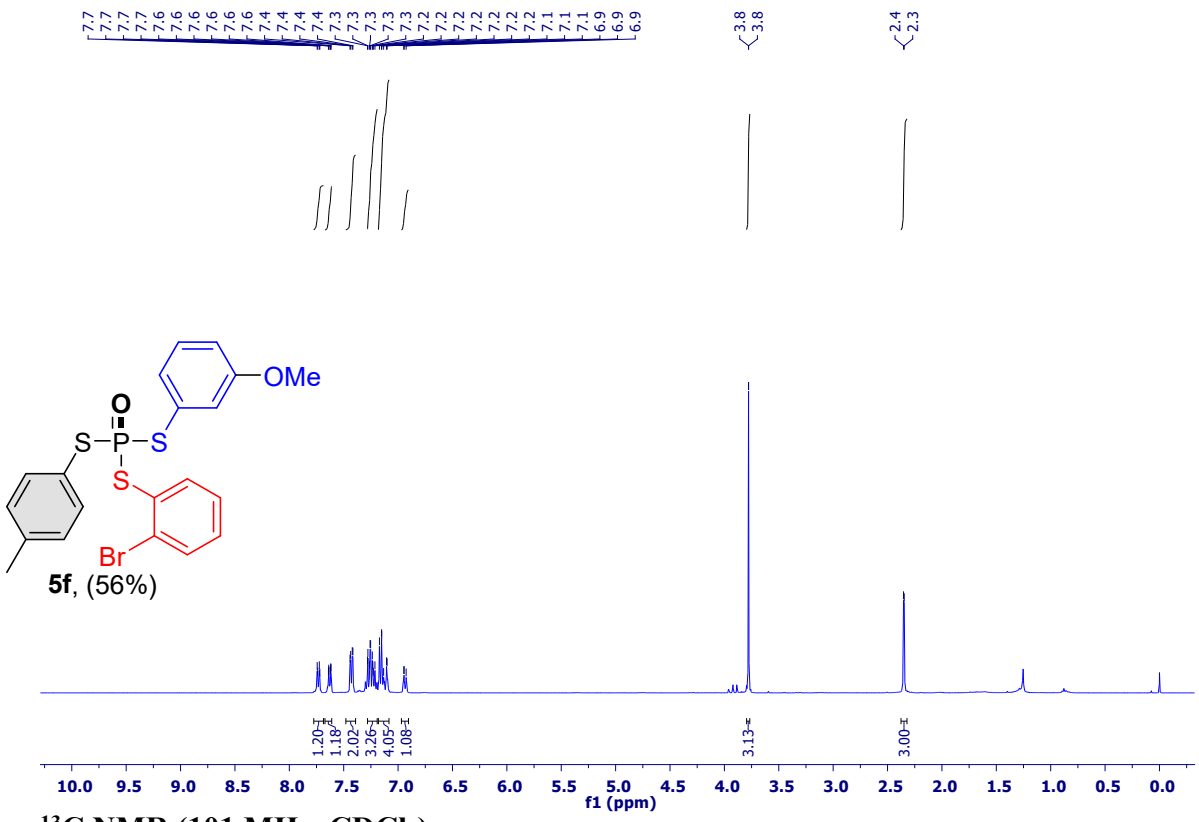
^{19}F NMR (377 MHz, $CDCl_3$



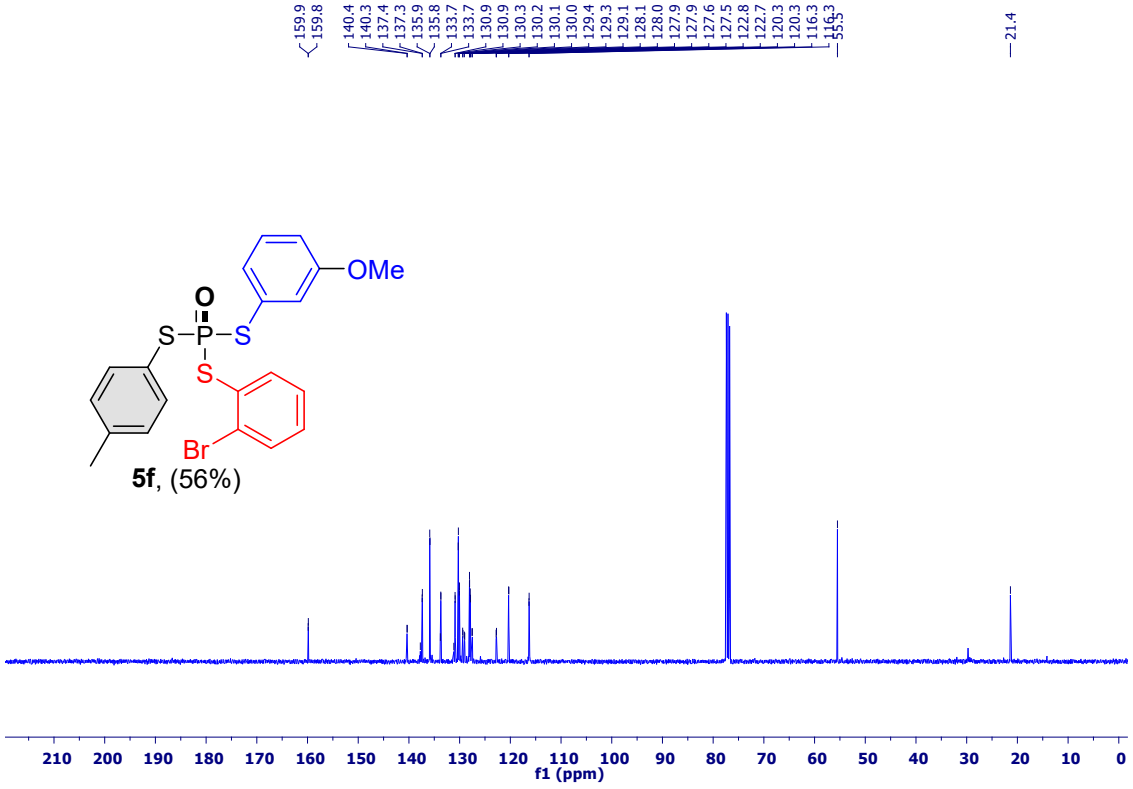
^{31}P NMR (162 MHz, $CDCl_3$)



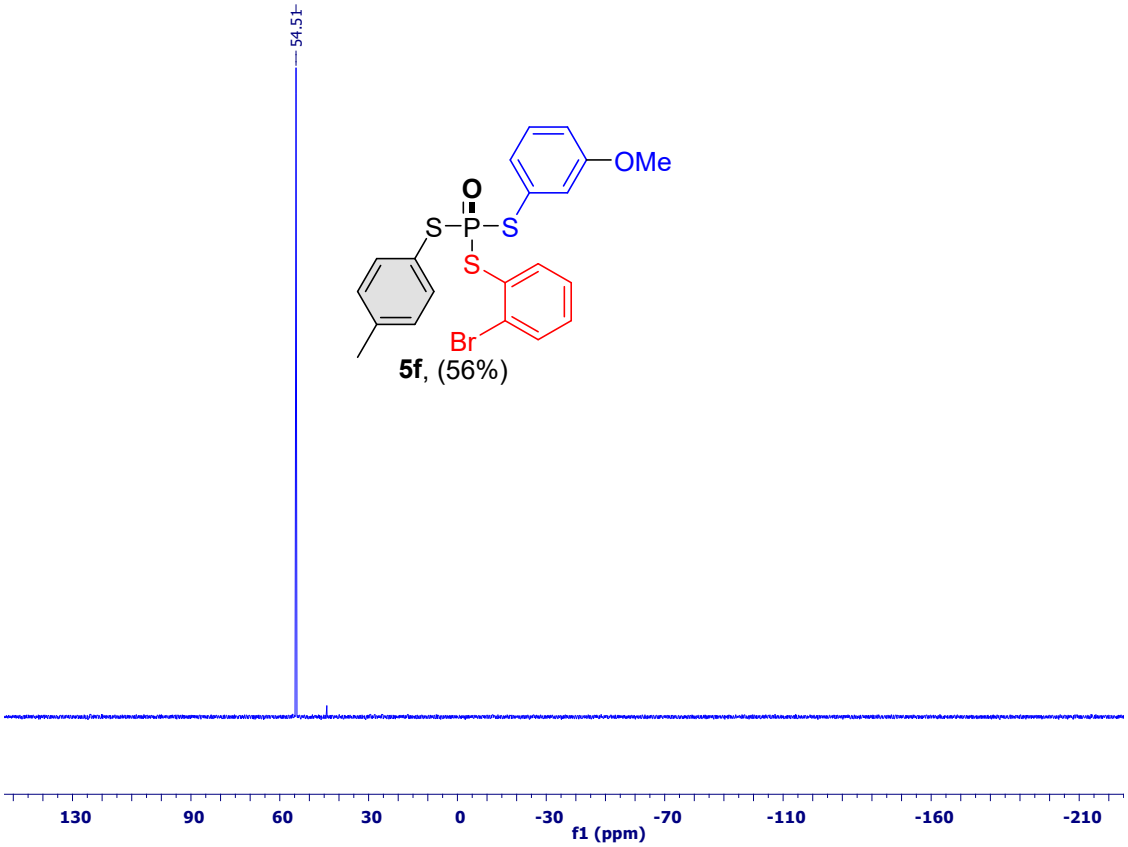
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

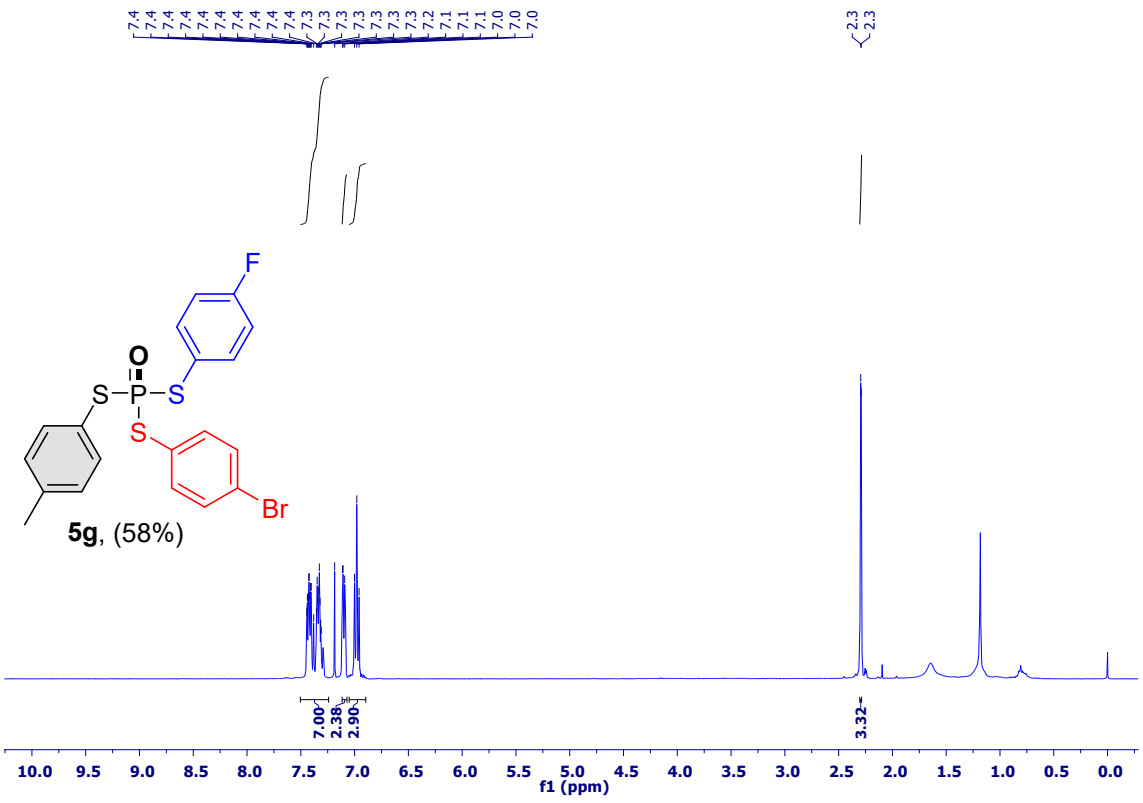


^{31}P NMR (162 MHz, $CDCl_3$)



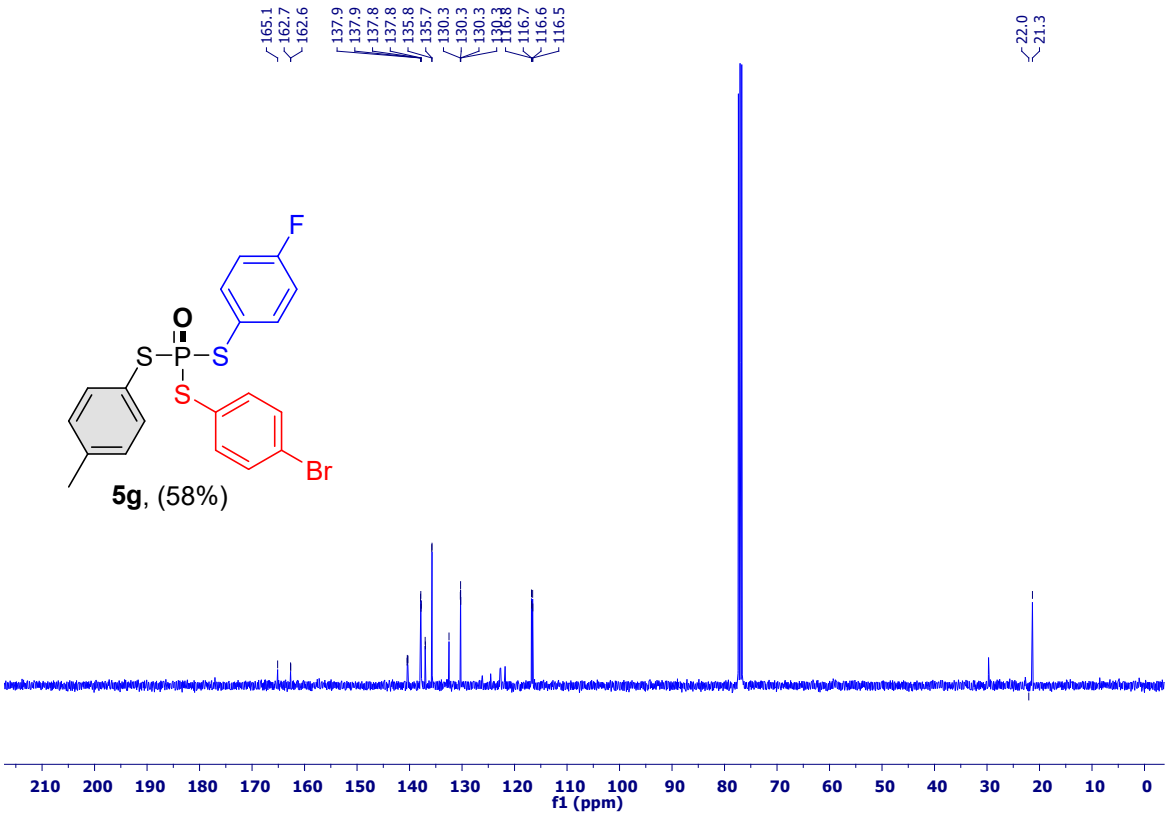
5f, (56%)

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

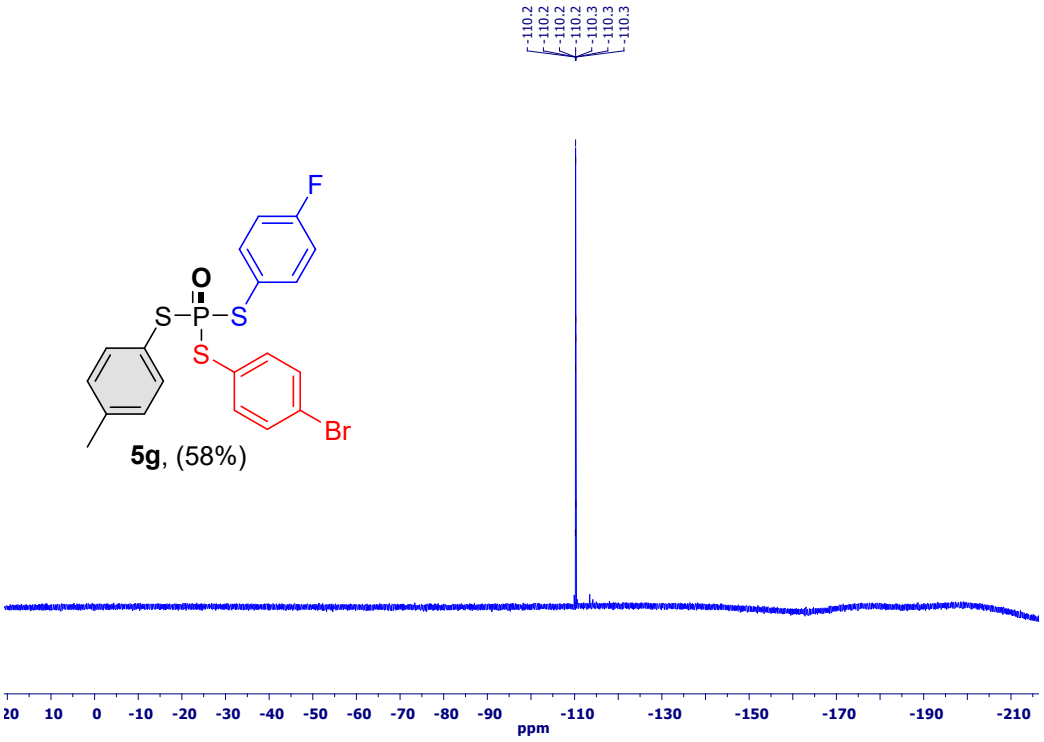


5g, (58%)

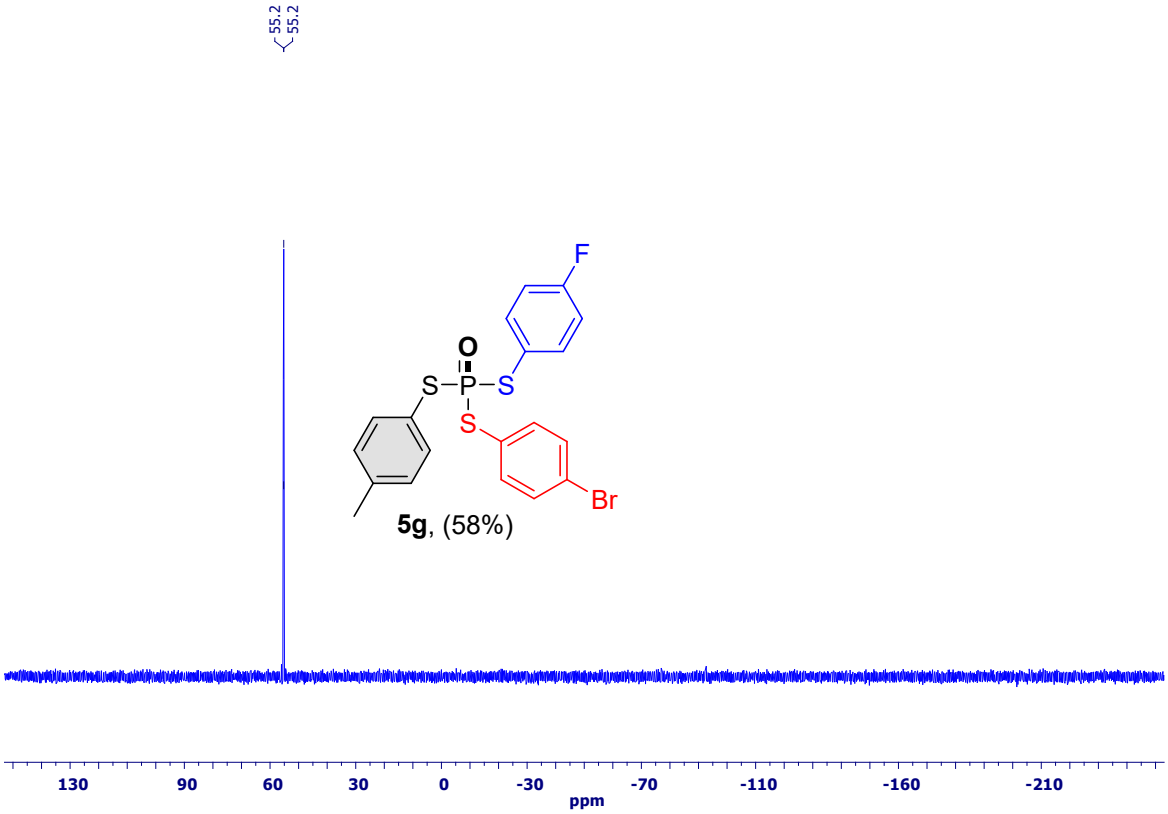
^{13}C NMR (101 MHz, $CDCl_3$)



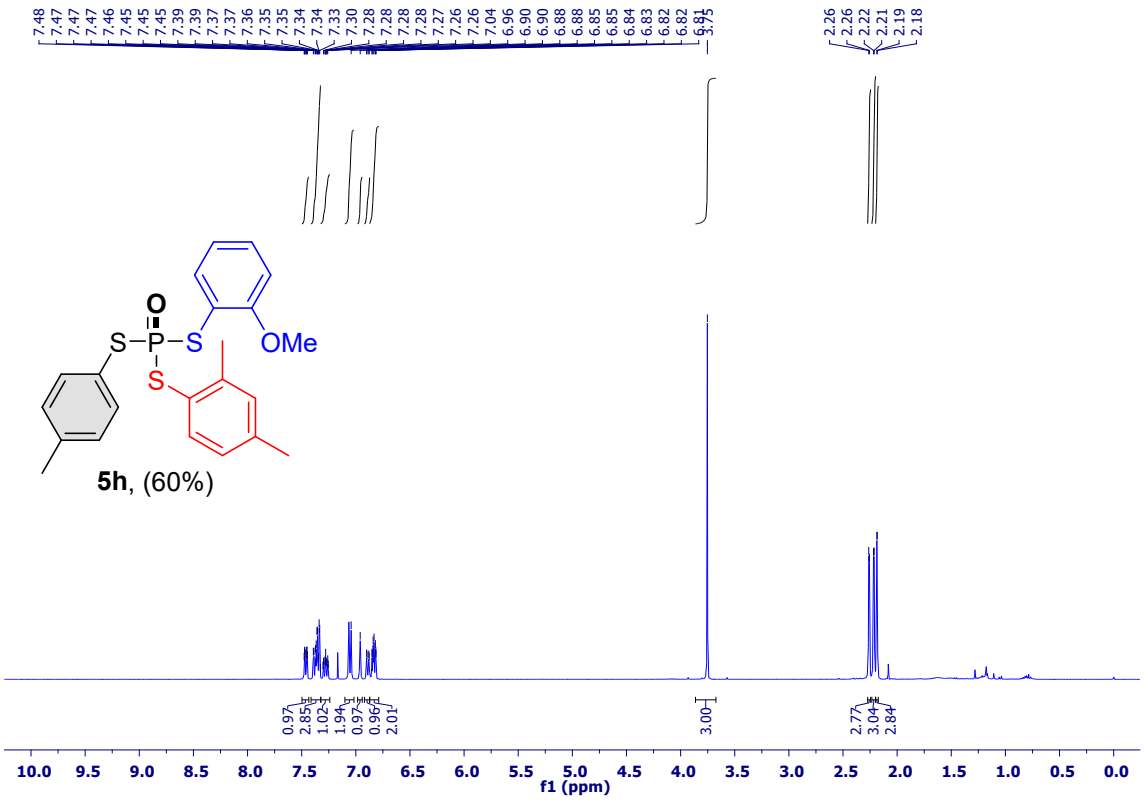
^{19}F NMR (377 MHz, $CDCl_3$



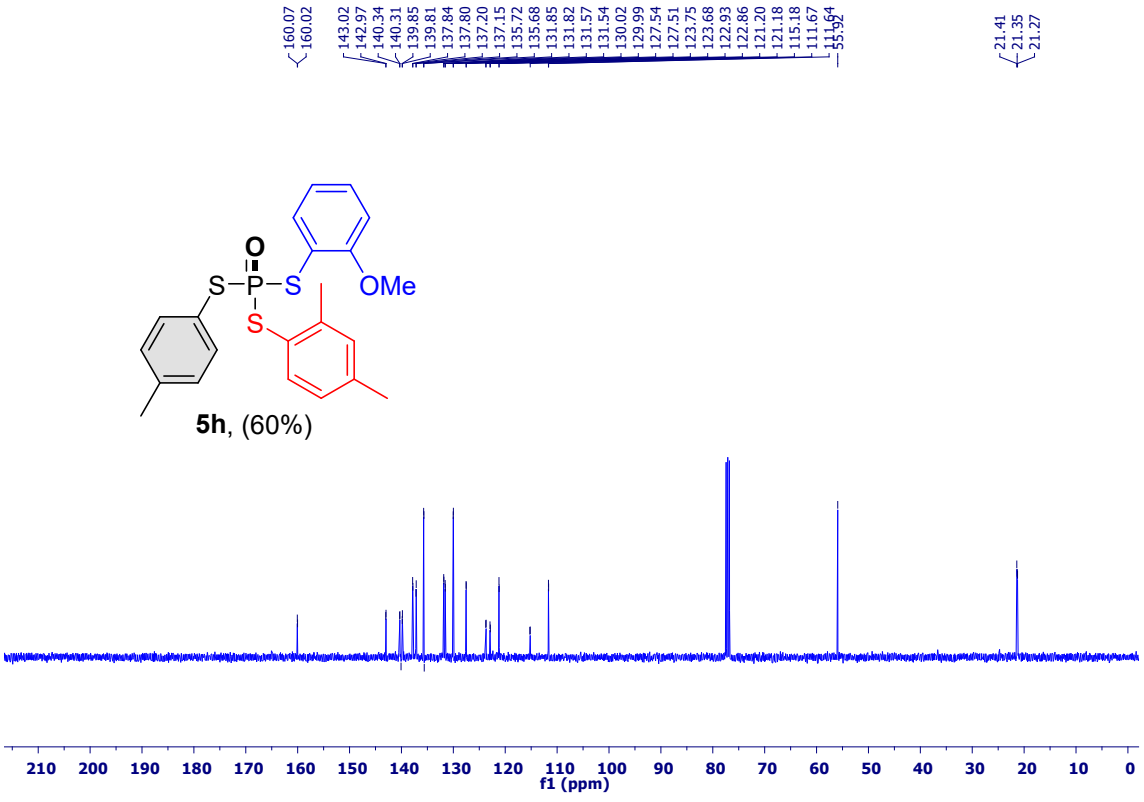
^{31}P NMR (162 MHz, $CDCl_3$)



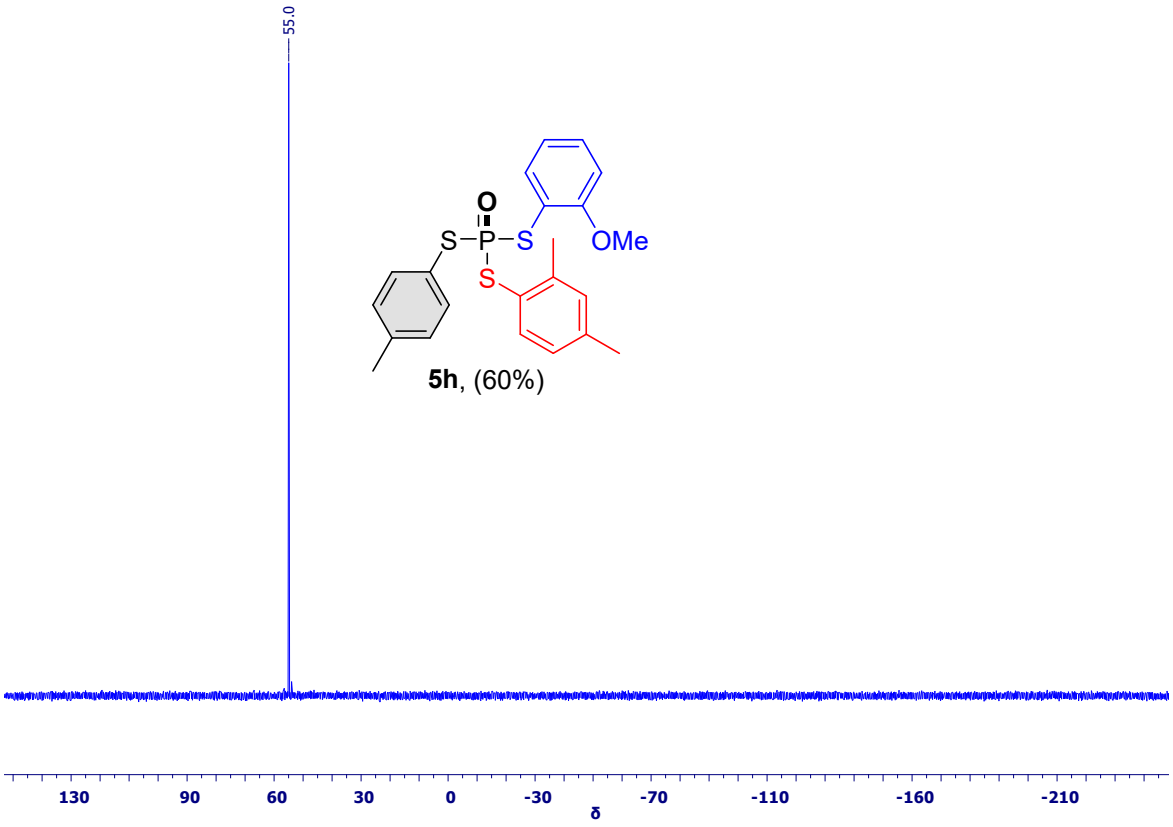
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

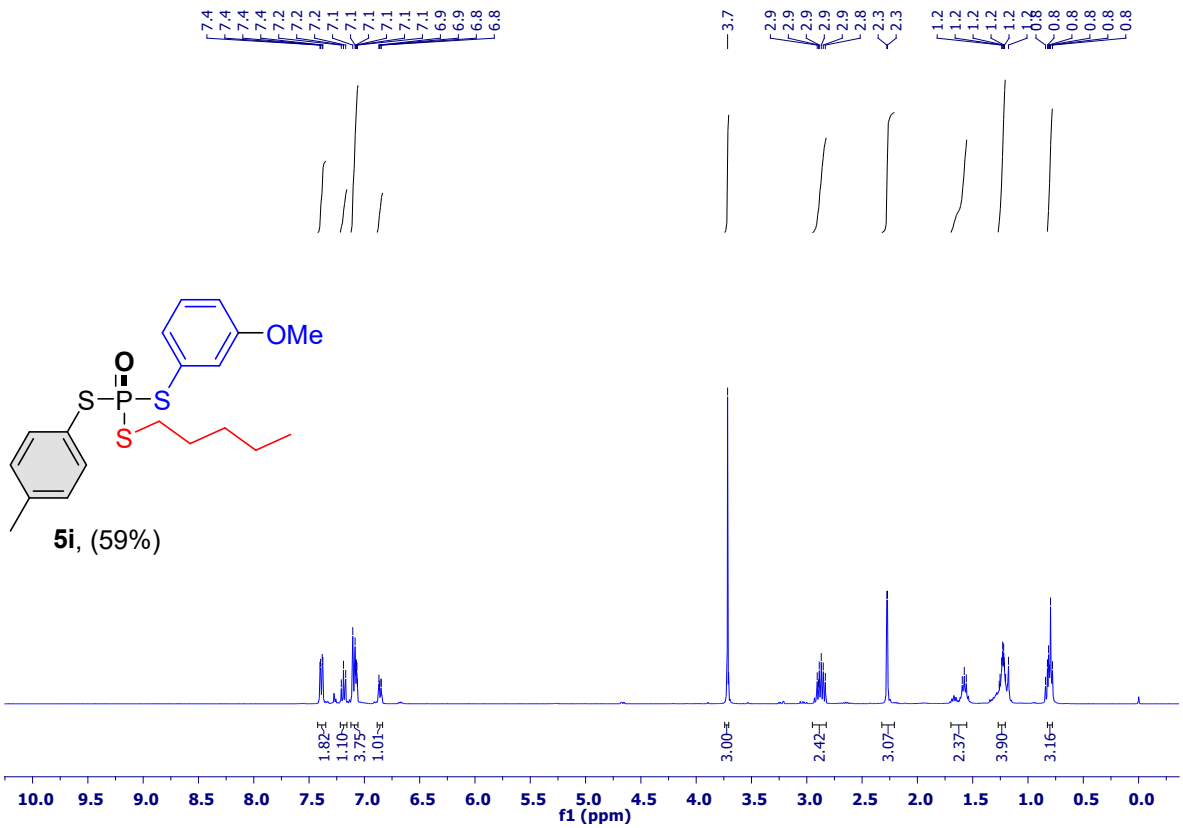


^{31}P NMR (162 MHz, $CDCl_3$)



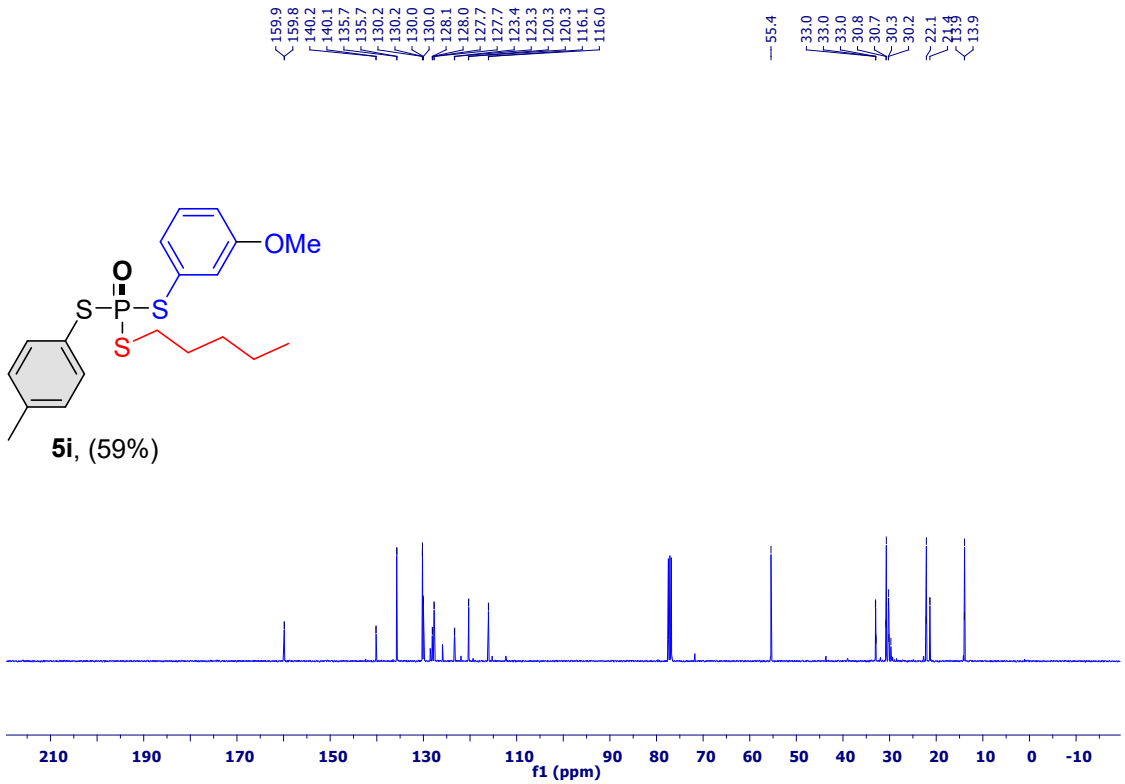
5h, (60%)

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

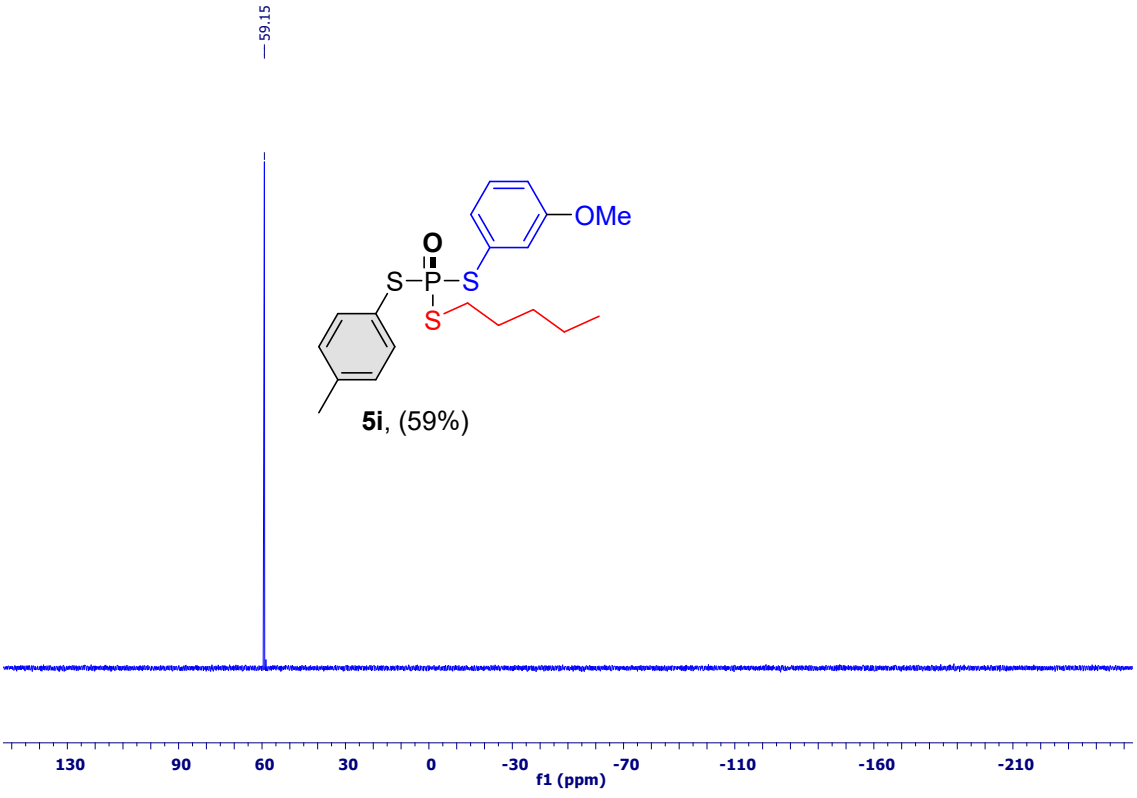


5i, (59%)

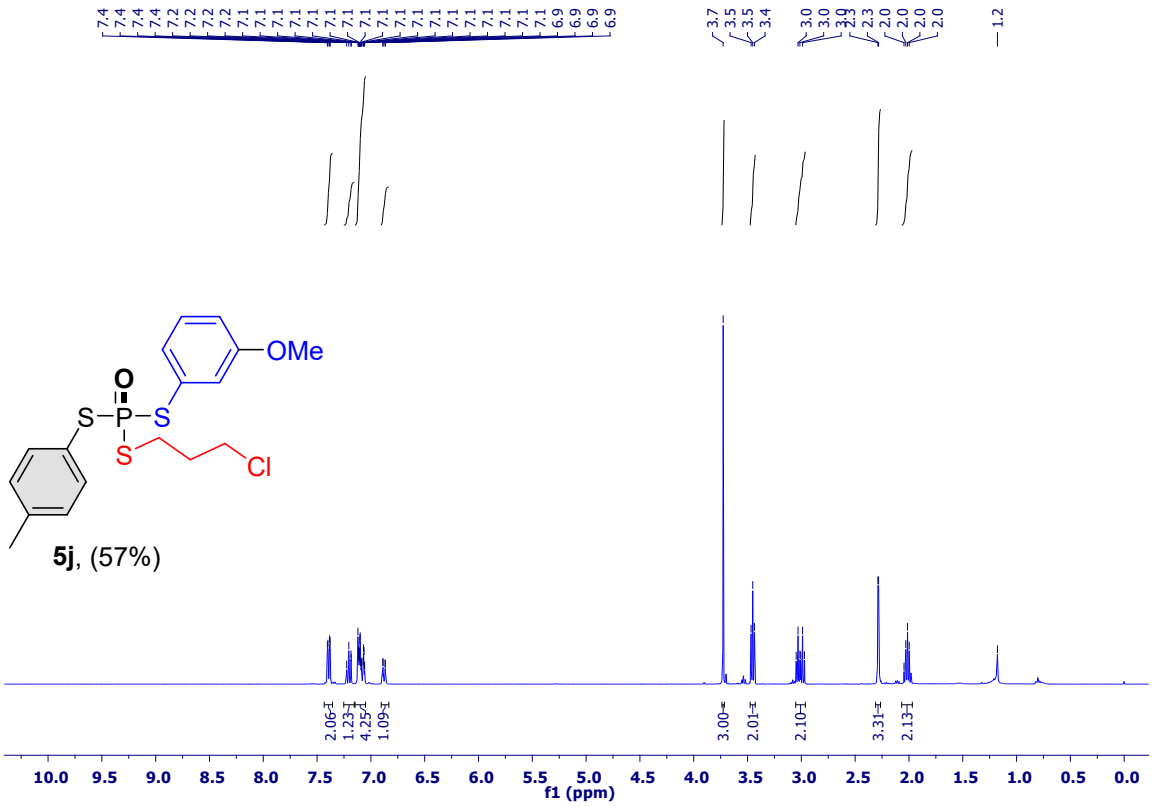
^{13}C NMR (101 MHz, $CDCl_3$)



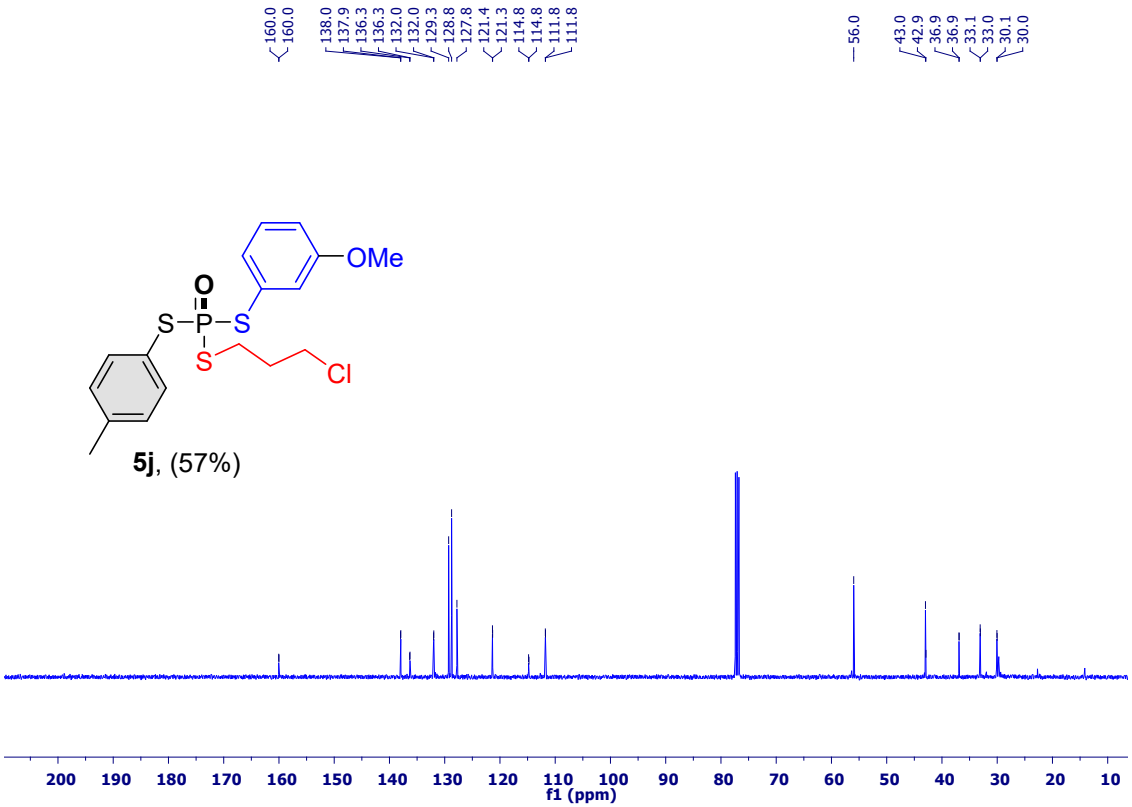
^{31}P NMR (162 MHz, $CDCl_3$)



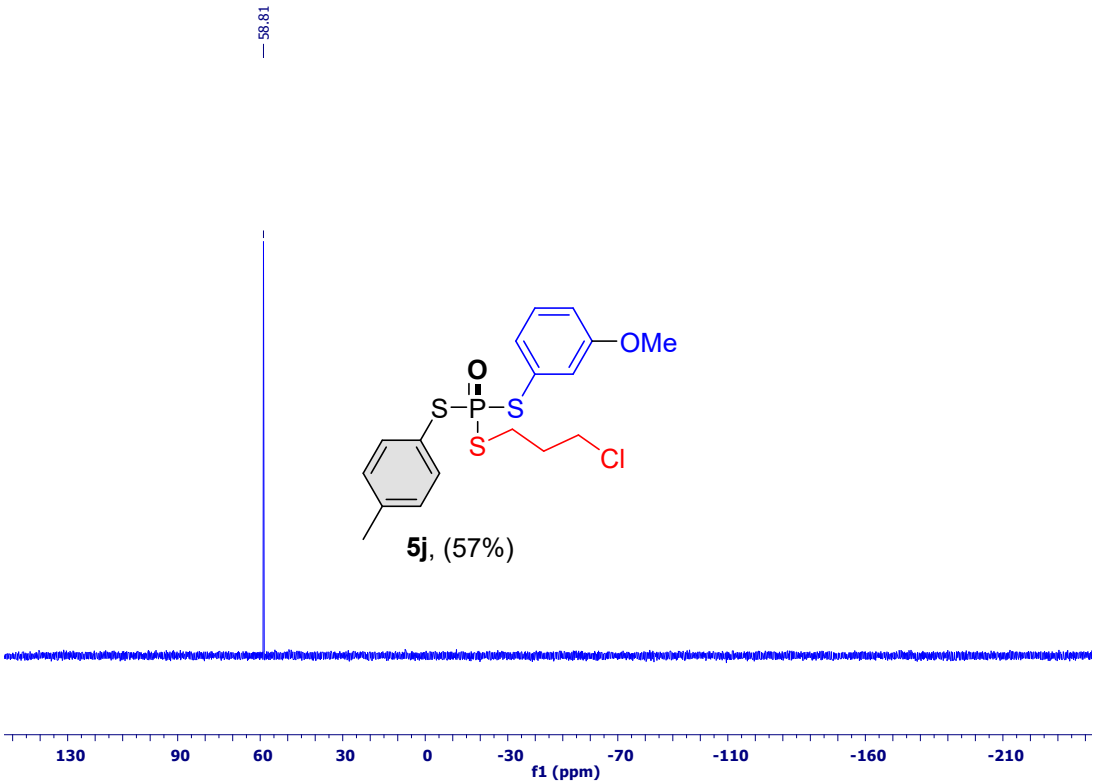
^{1}H NMR (400 MHz, $CDCl_3$)



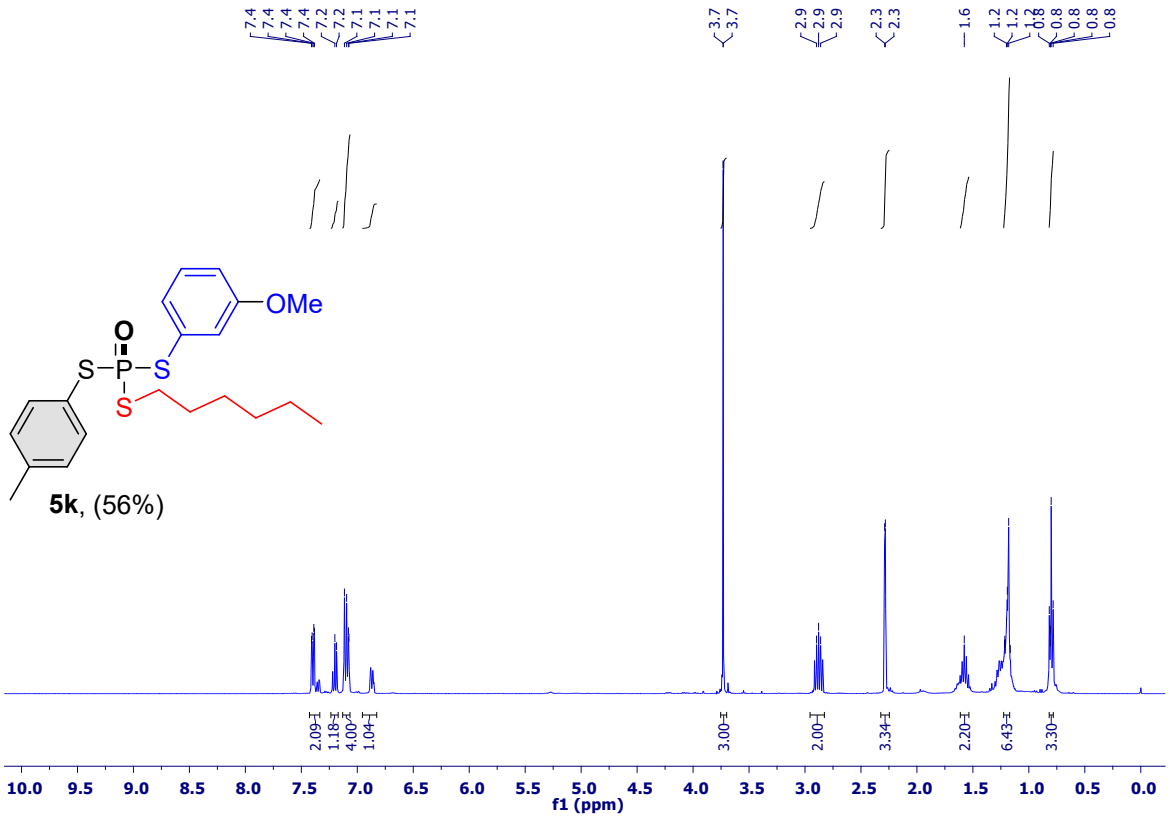
^{13}C NMR (101 MHz, $CDCl_3$)



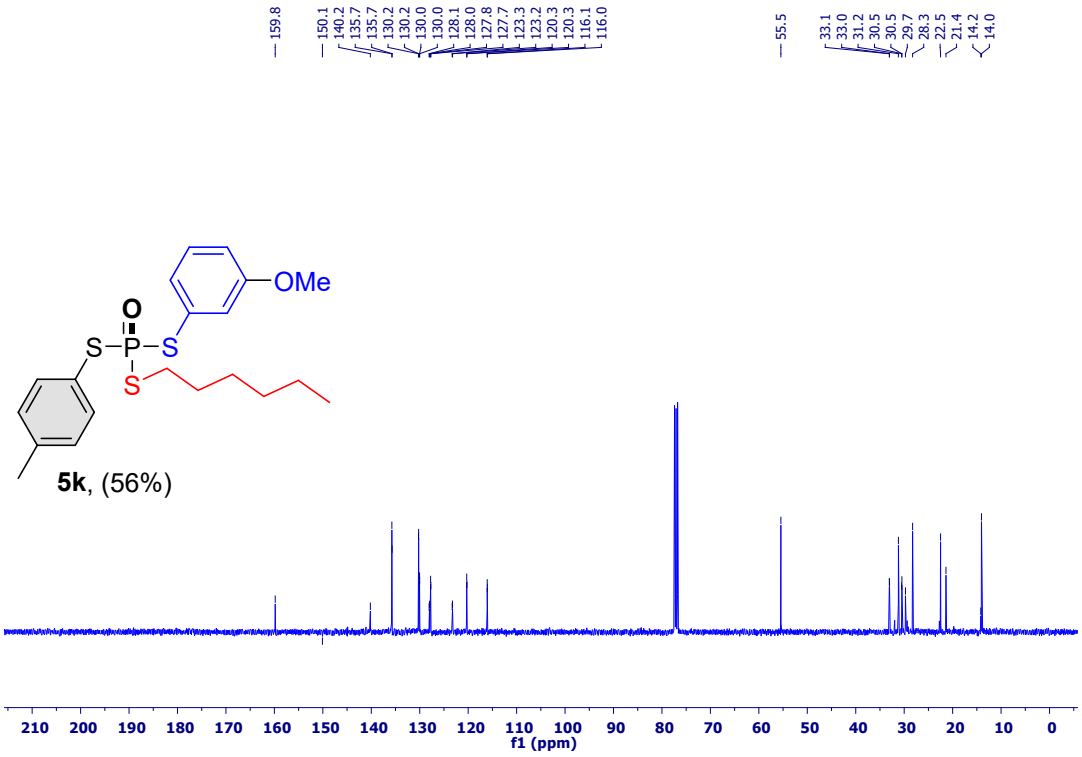
^{31}P NMR (162 MHz, $CDCl_3$)



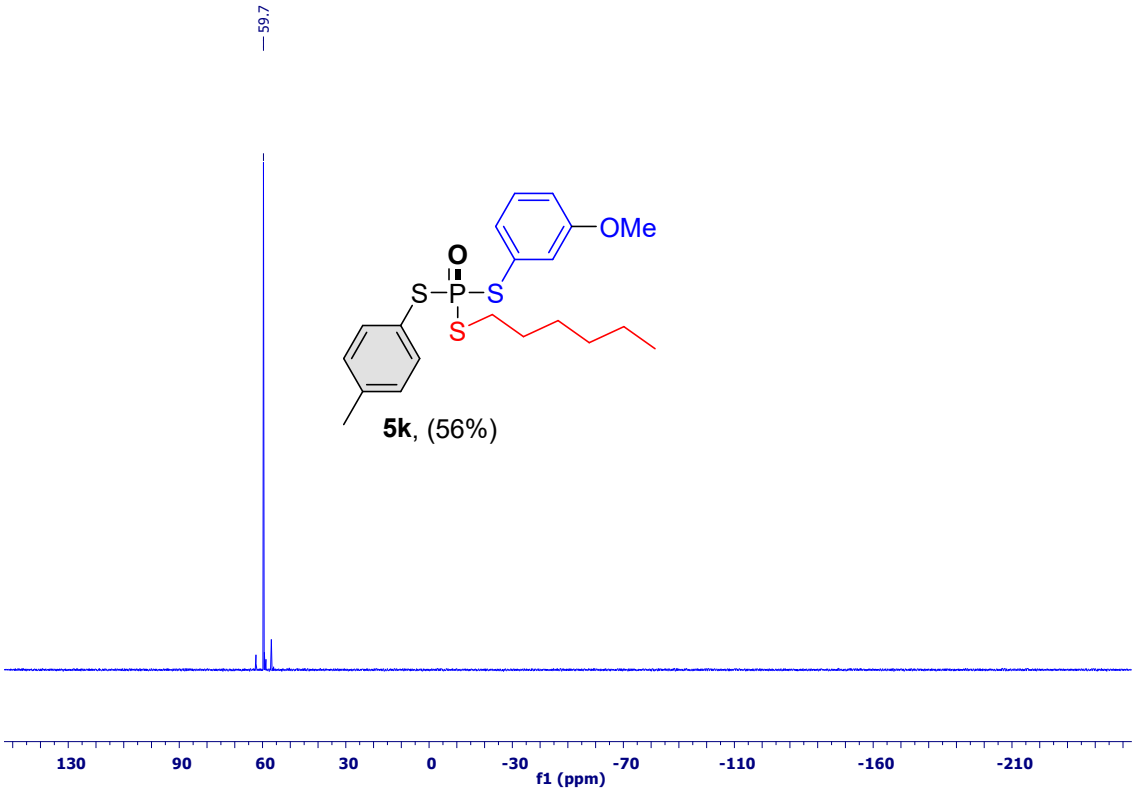
^{1}H NMR (400 MHz, $CDCl_3$)



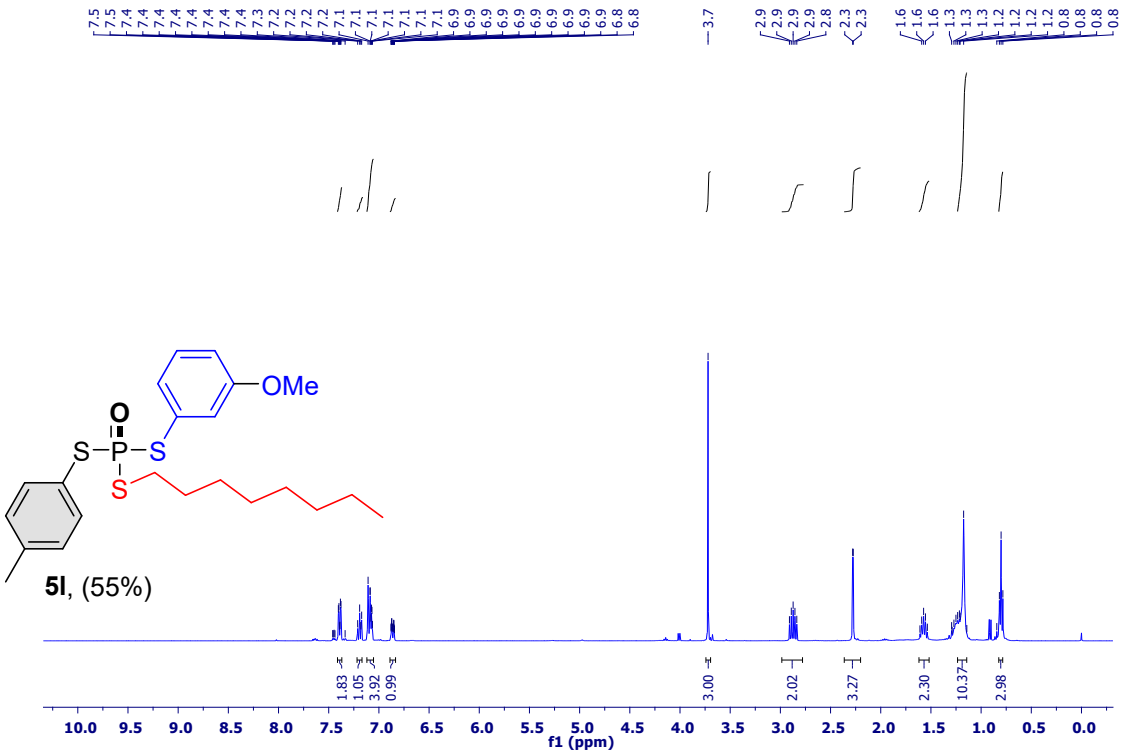
^{13}C NMR (101 MHz, $CDCl_3$)



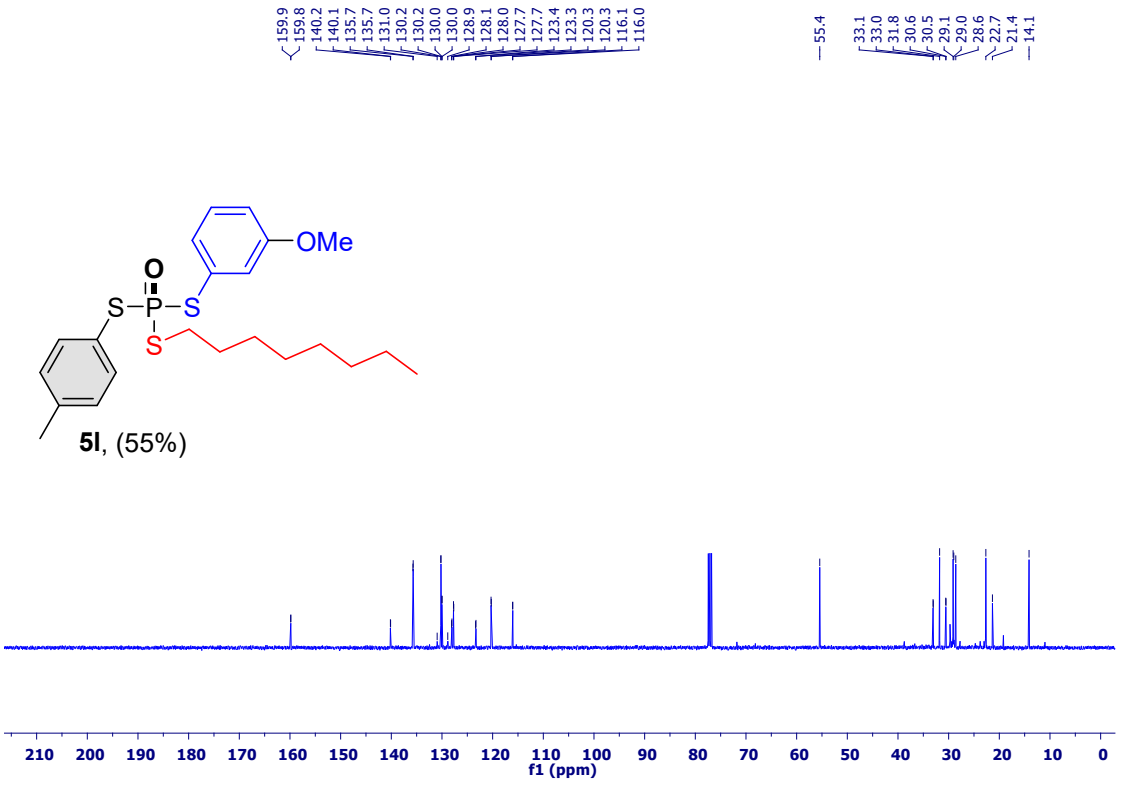
^{31}P NMR (162 MHz, $CDCl_3$



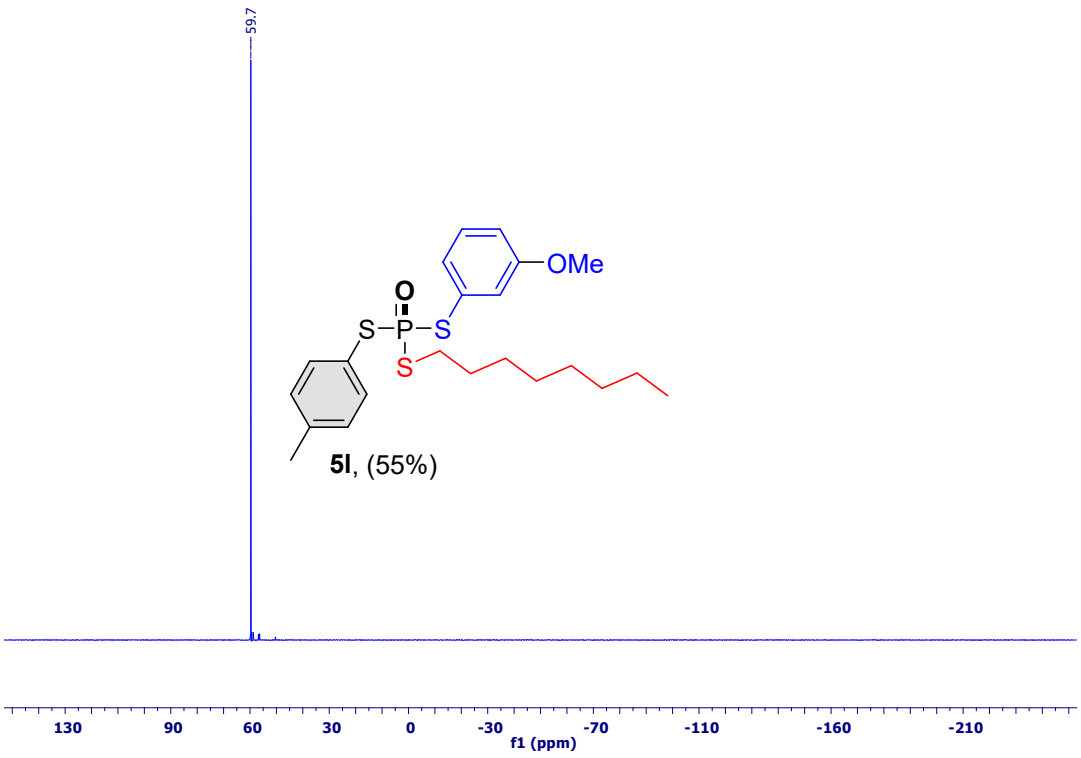
^{1}H NMR (400 MHz, $CDCl_3$



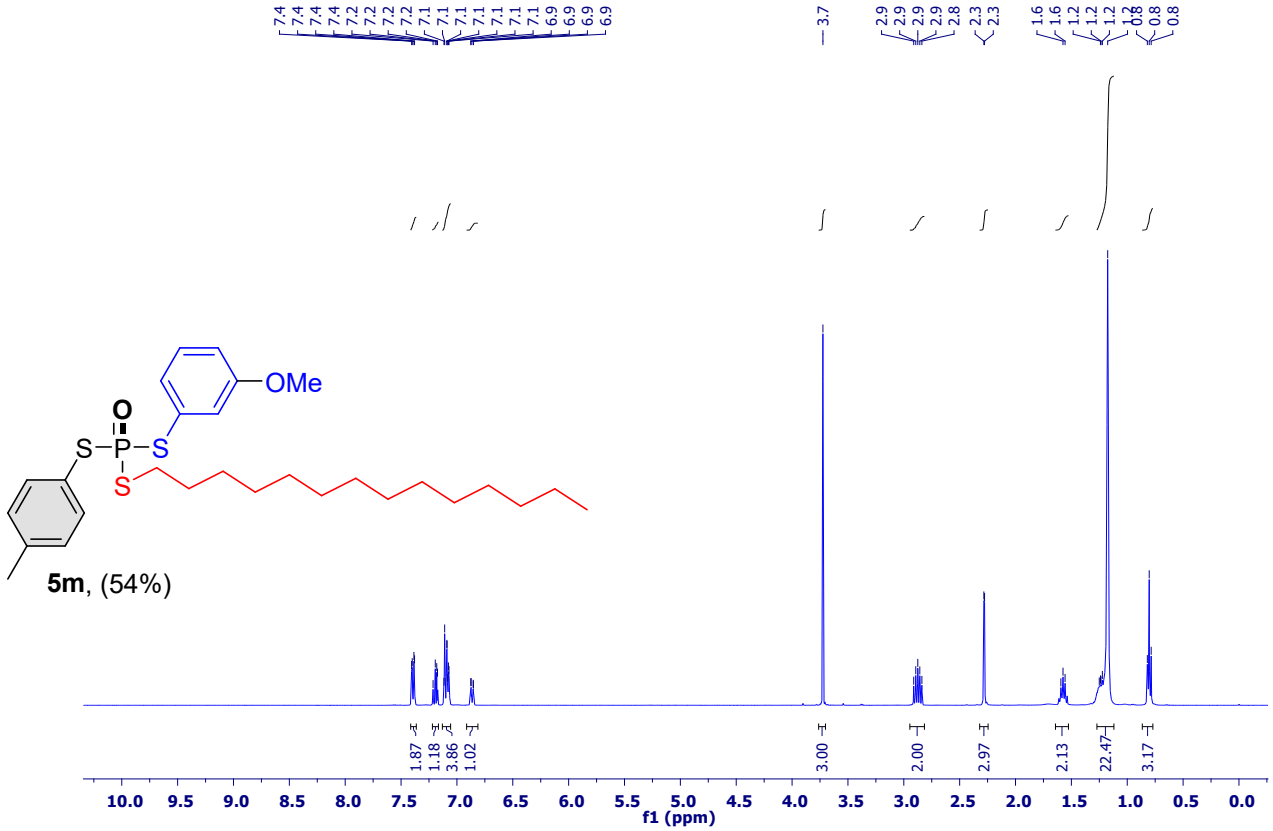
^{13}C NMR (101 MHz, $CDCl_3$)



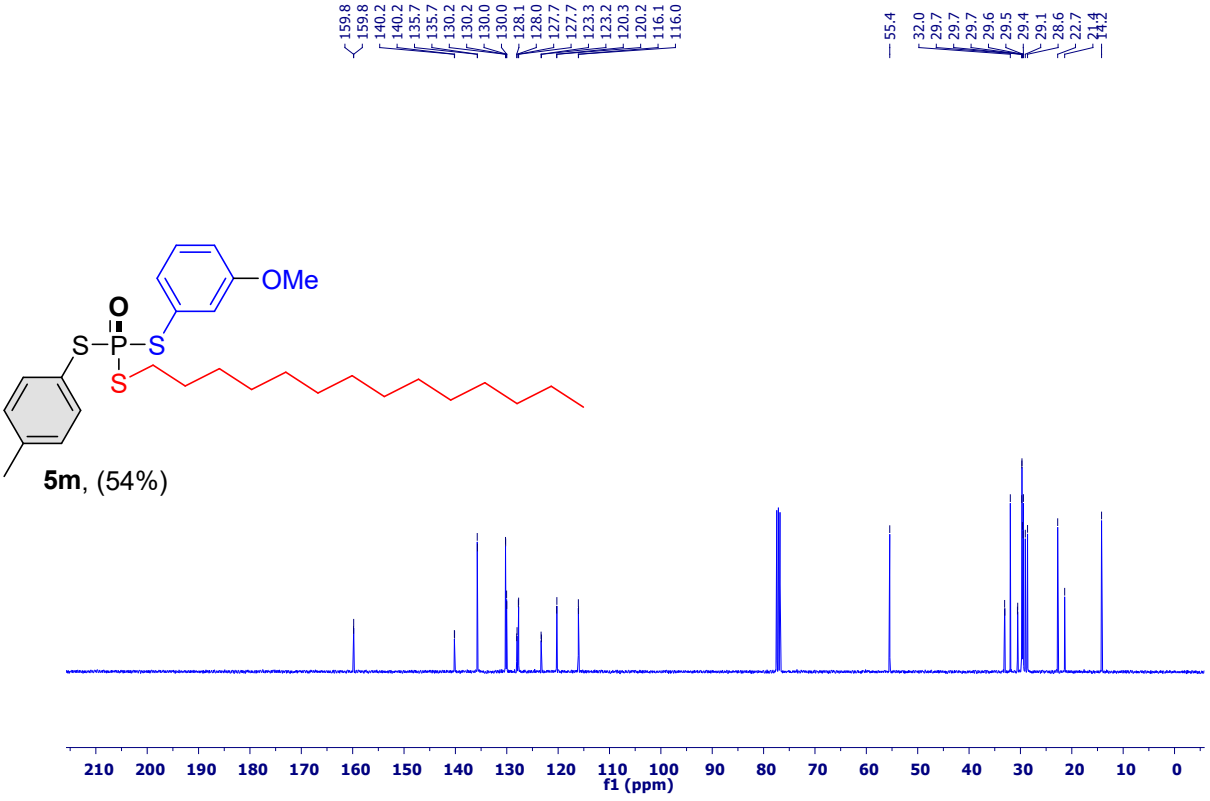
^{31}P NMR (162 MHz, $CDCl_3$



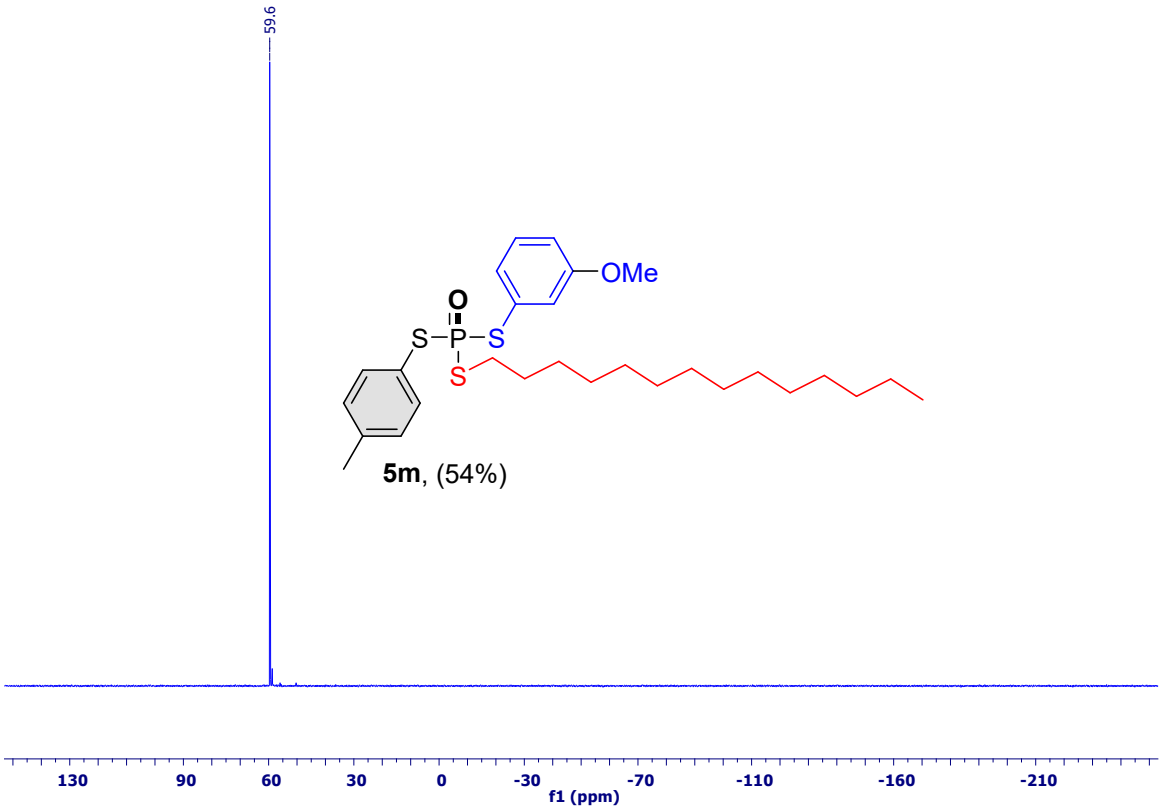
^{1}H NMR (400 MHz, $CDCl_3$)



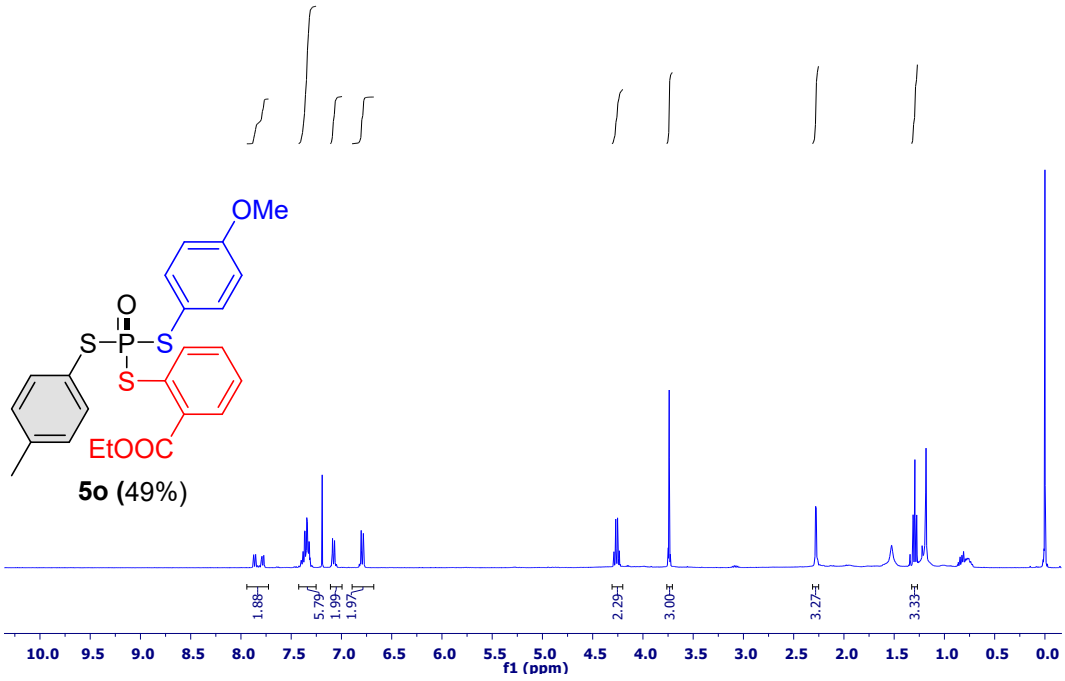
^{13}C NMR (101 MHz, $CDCl_3$)



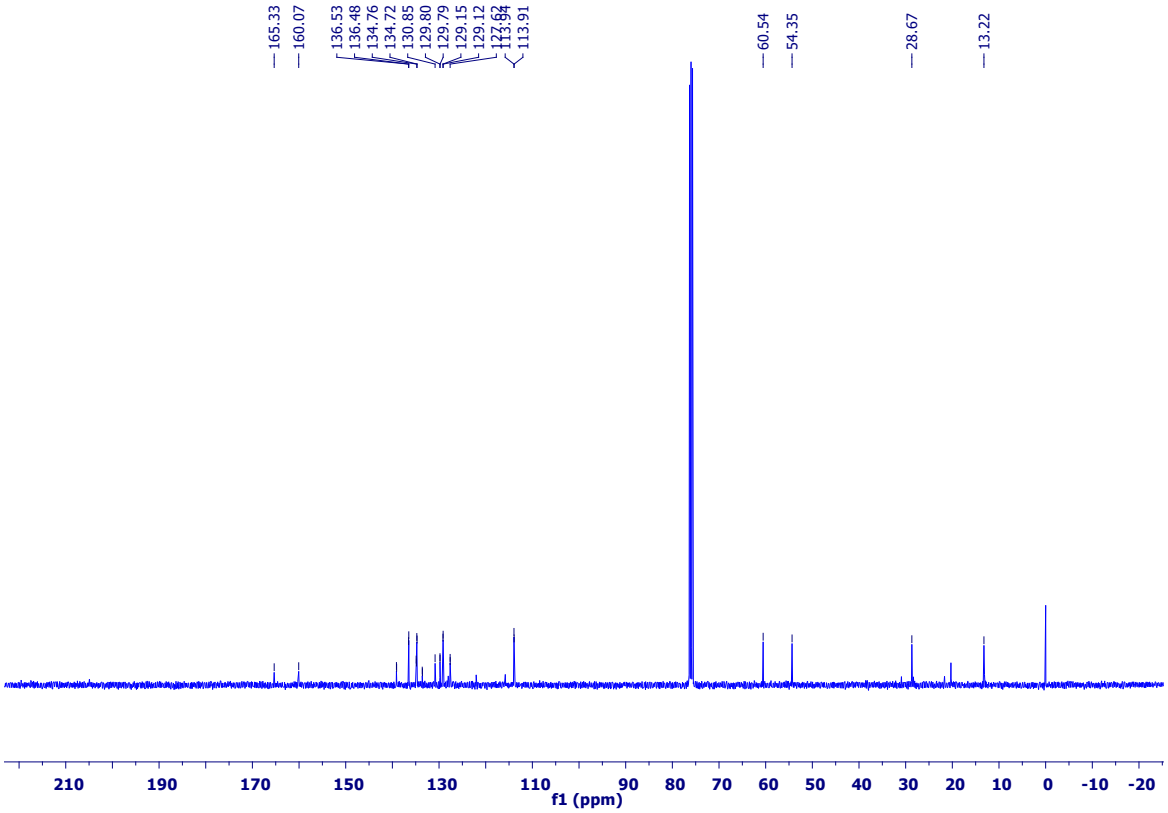
^{31}P NMR (162 MHz, $CDCl_3$



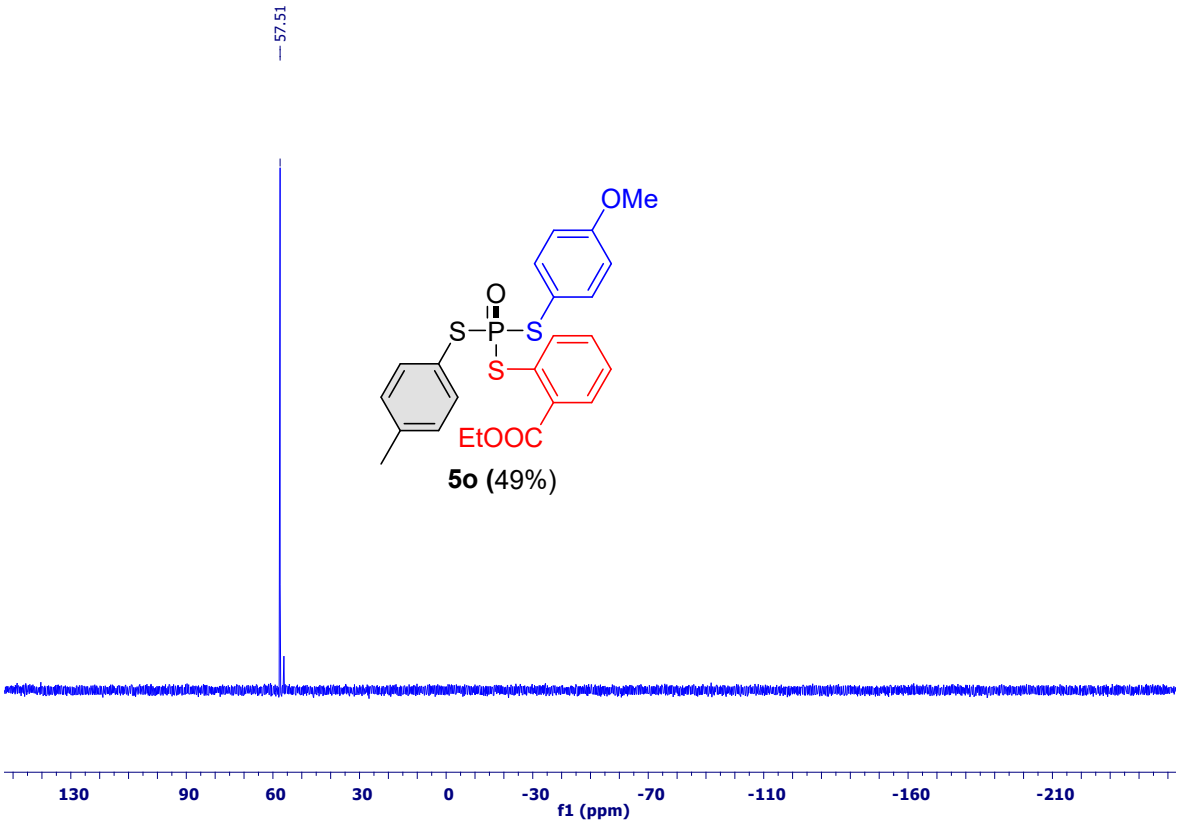
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

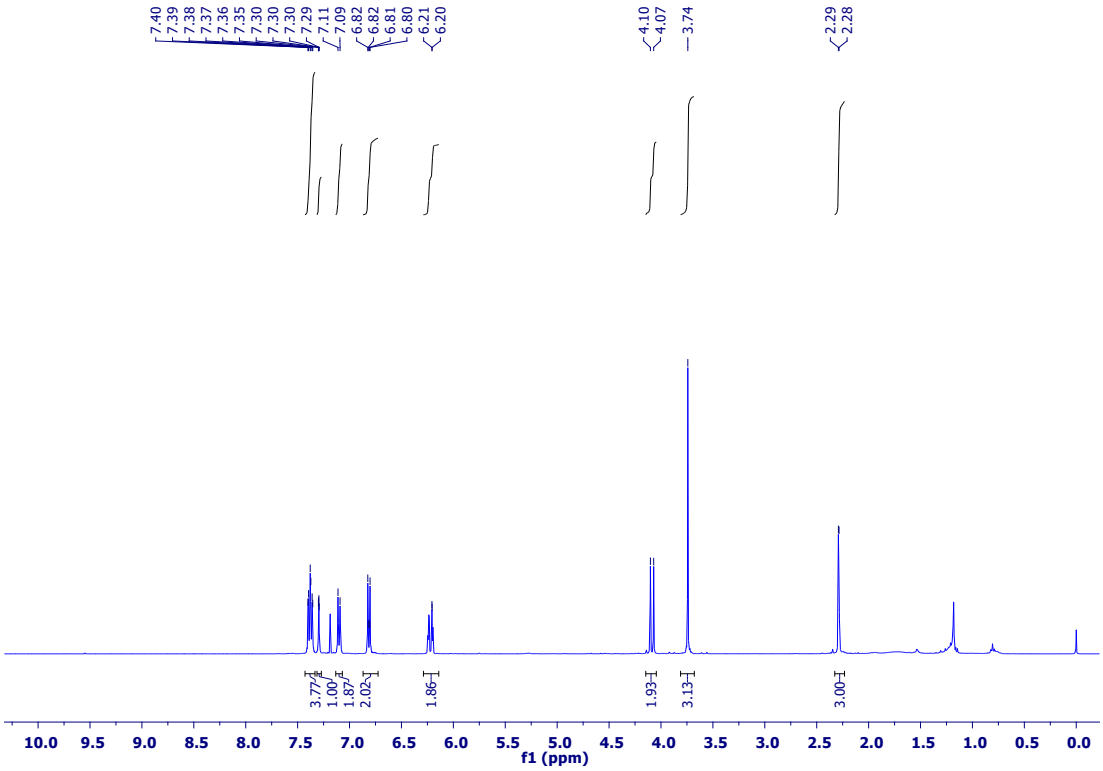


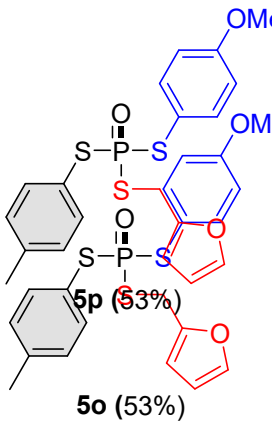
^{31}P NMR (162 MHz, $CDCl_3$)



5o (49%)

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

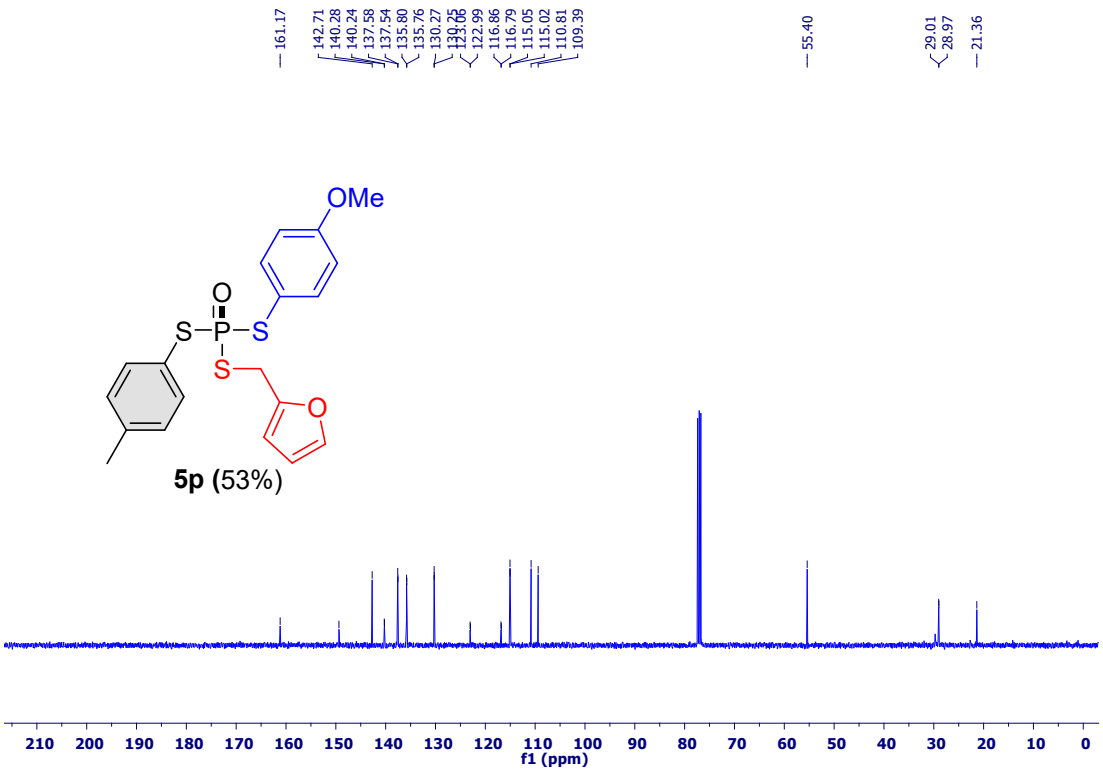




5p (53%)

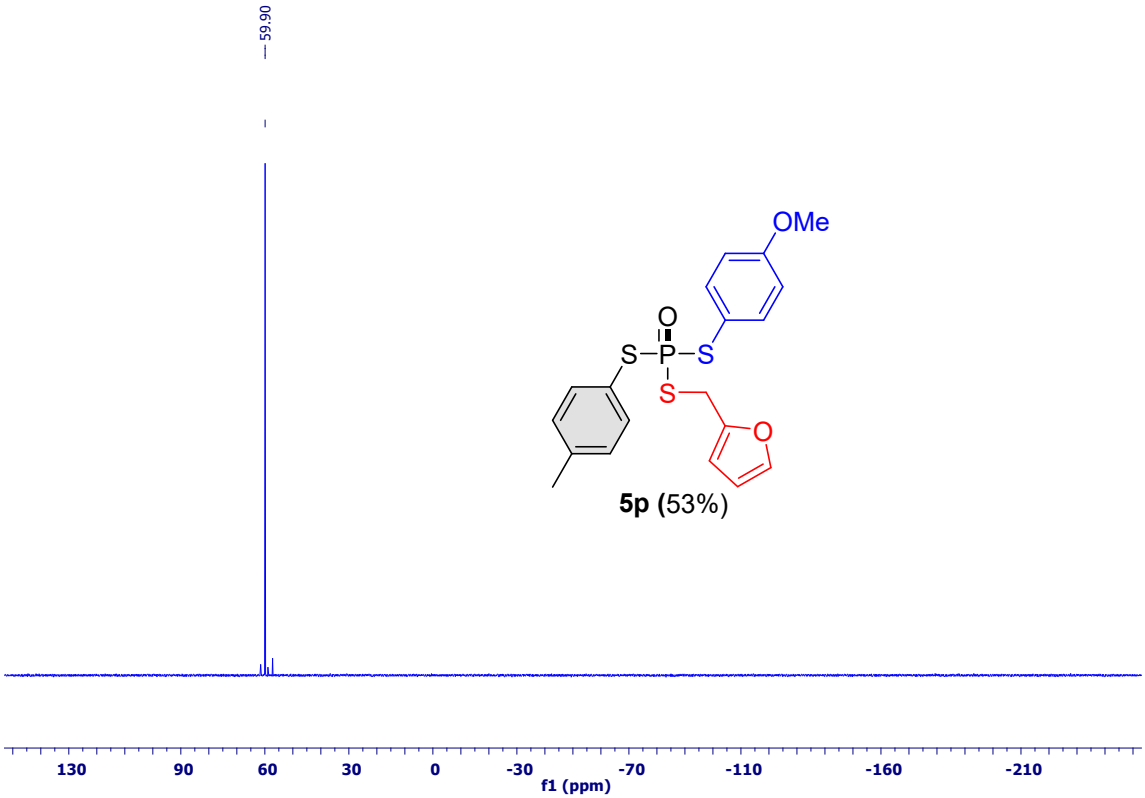
5o (53%)

^{13}C NMR (101 MHz, $CDCl_3$)

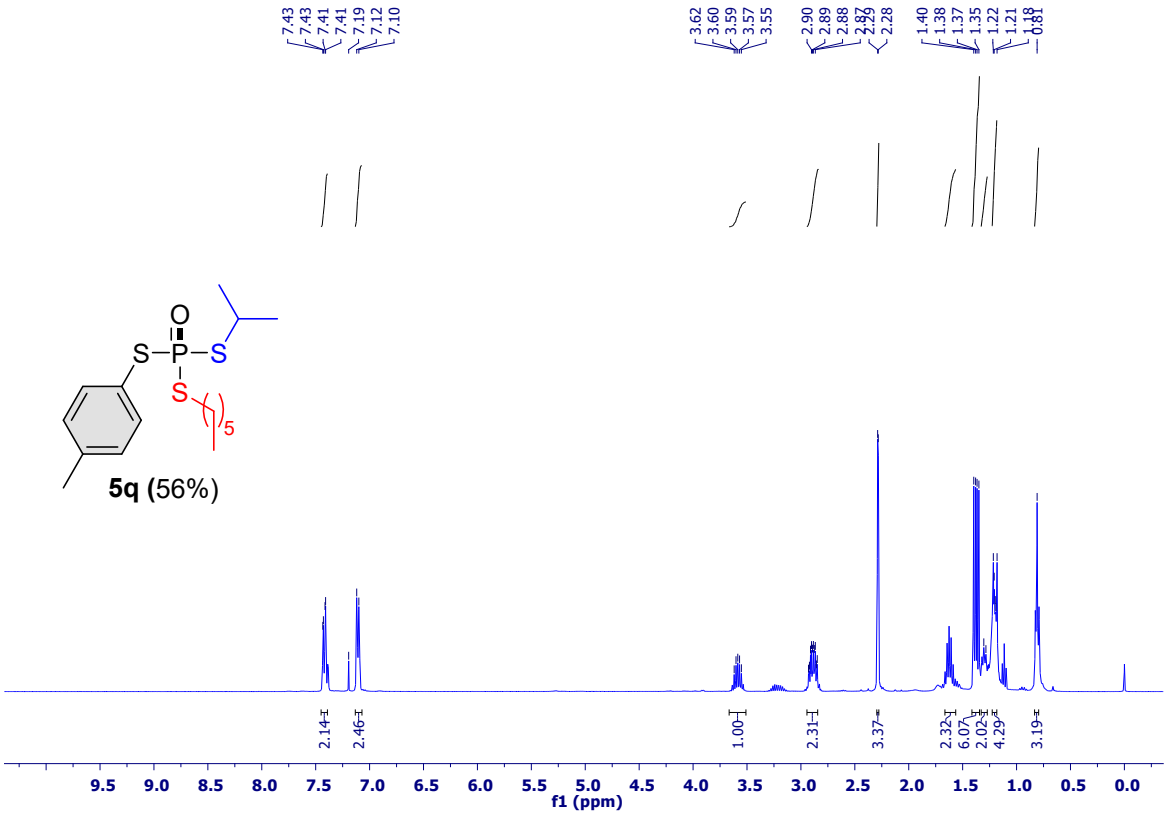


5p (53%)

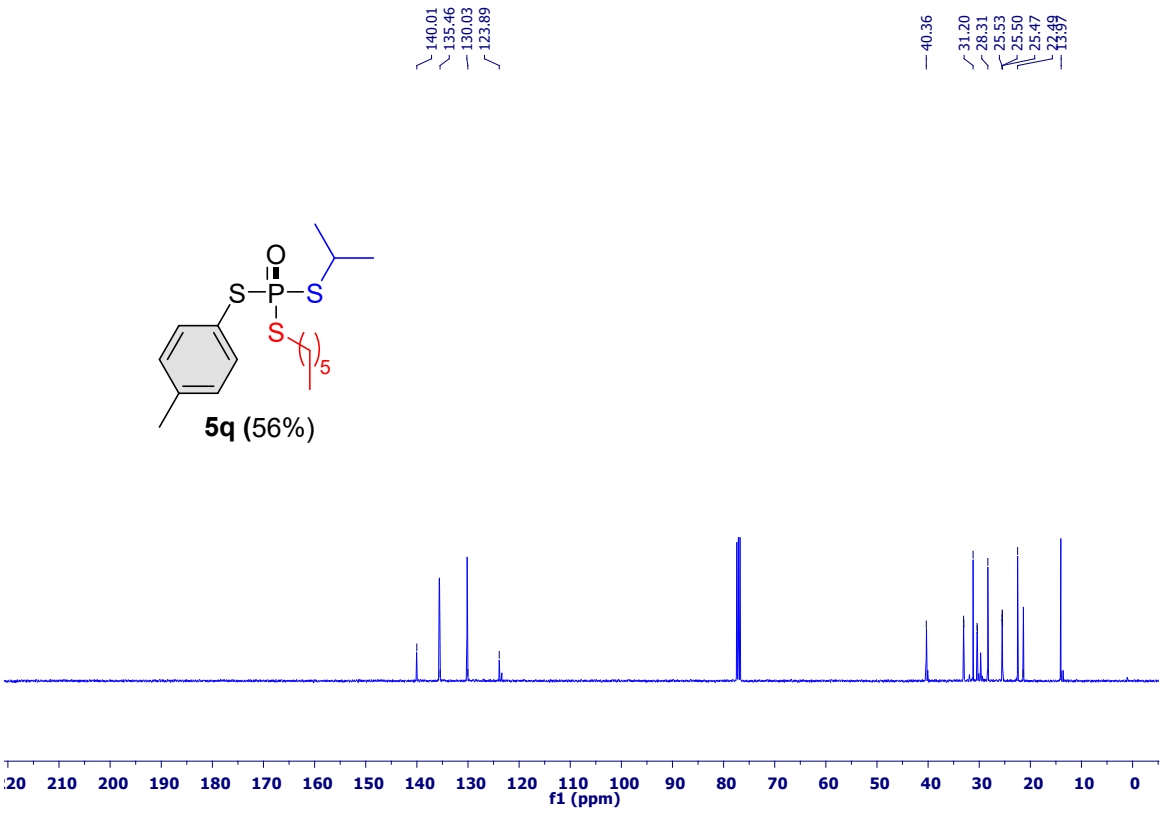
^{31}P NMR (162 MHz, $CDCl_3$)



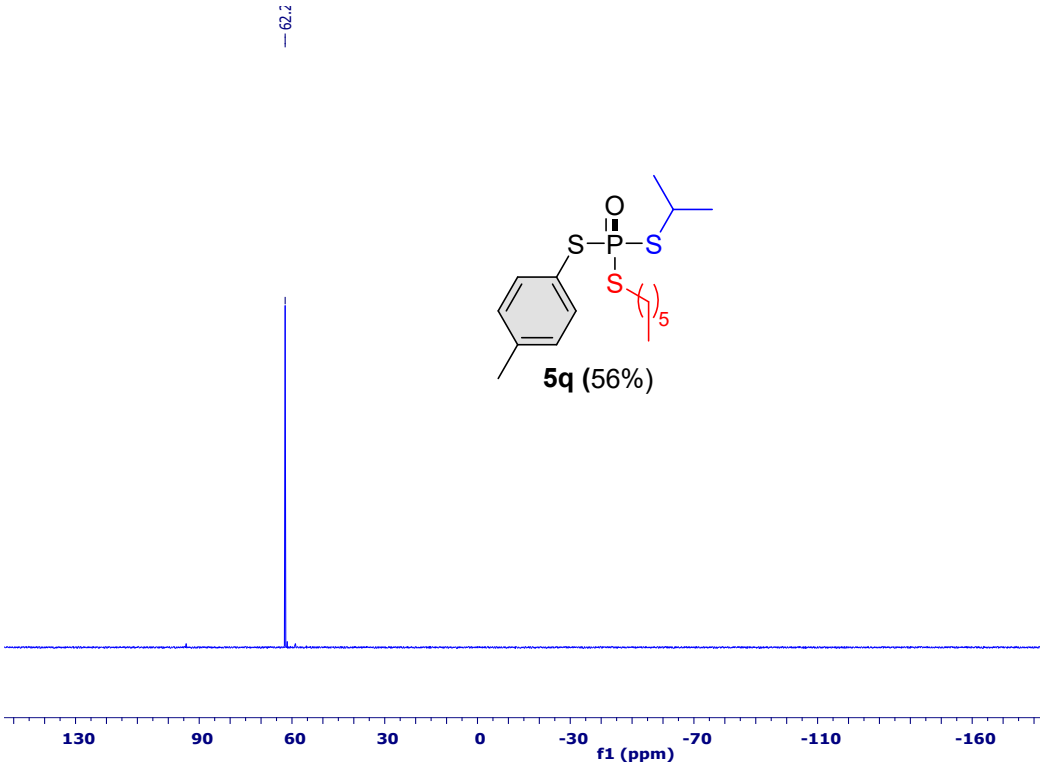
^{1}H NMR (400 MHz, $CDCl_3$)



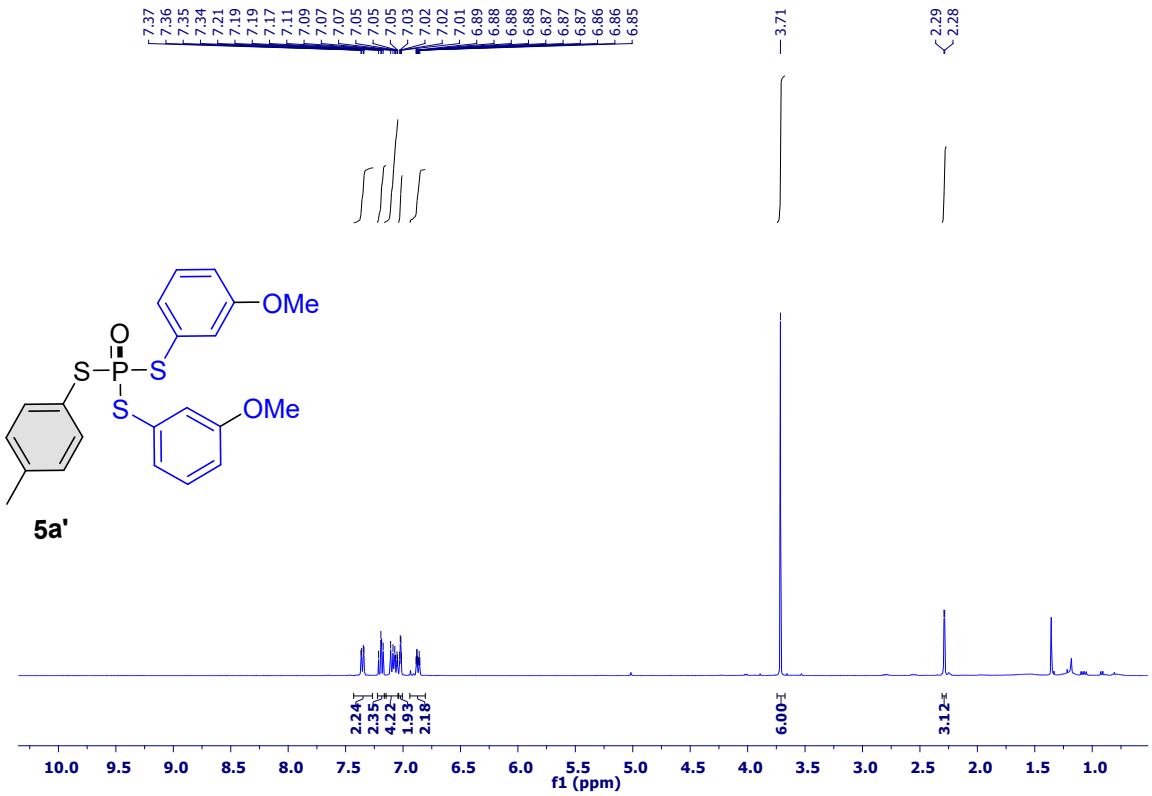
^{13}C NMR (101 MHz, $CDCl_3$)



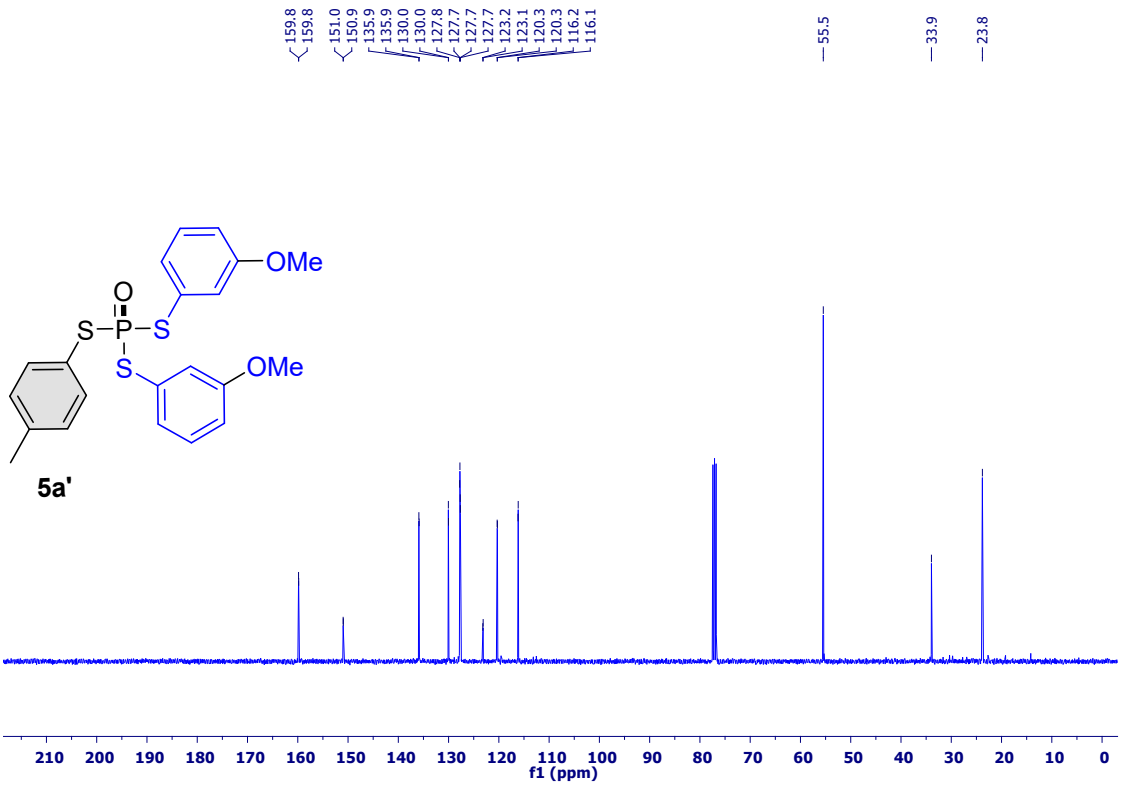
^{31}P NMR (162 MHz, $CDCl_3$)



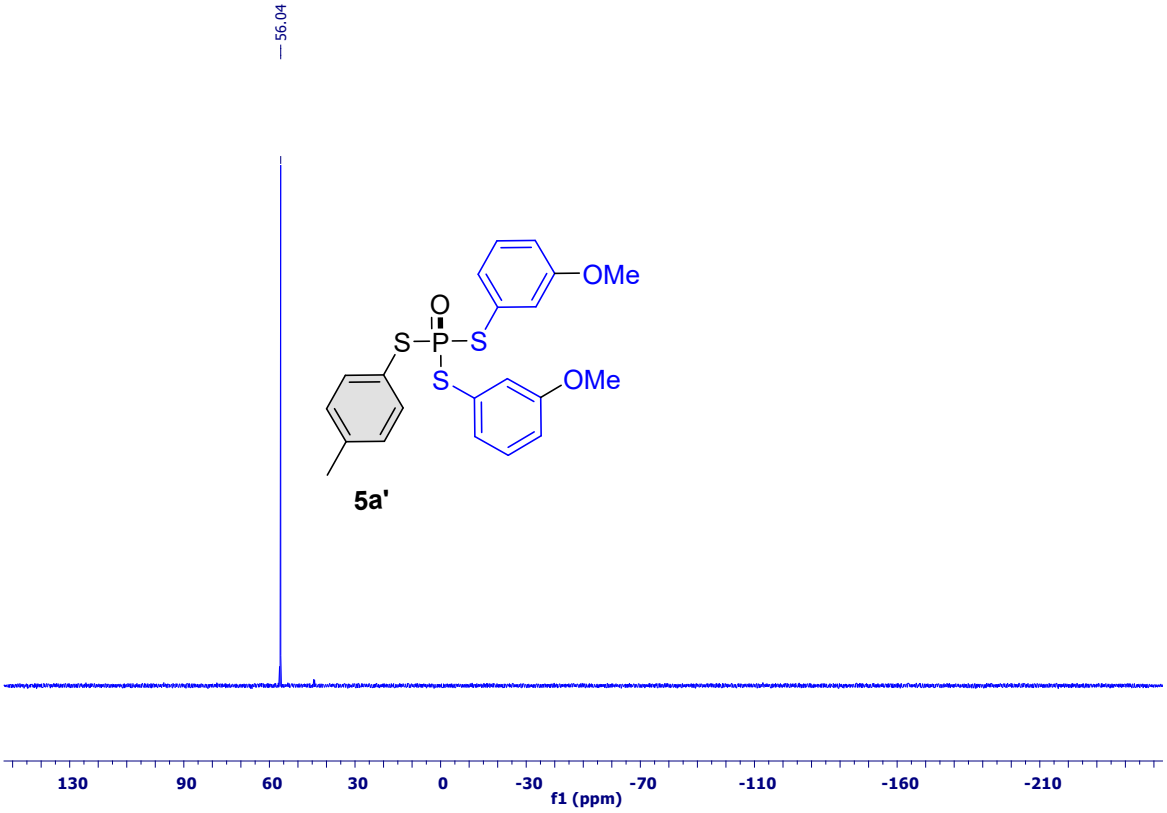
^{1}H NMR (400 MHz, $CDCl_3$)



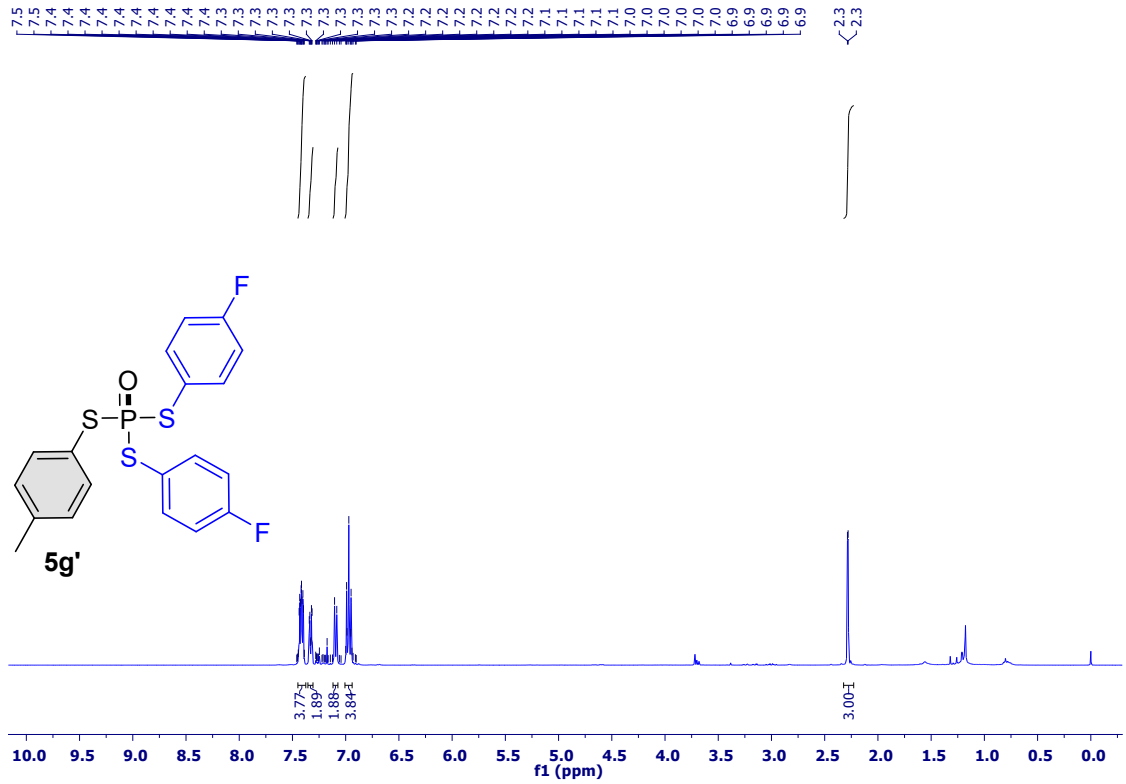
^{13}C NMR (101 MHz, CDCl3)



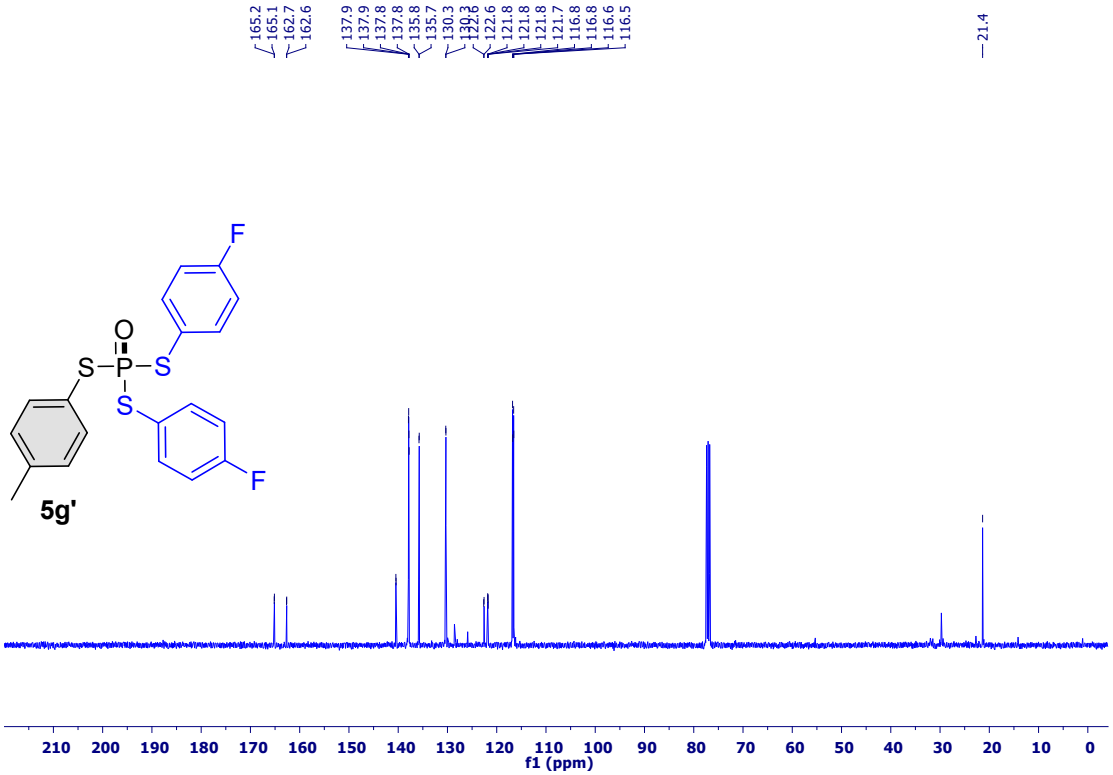
^{31}P NMR (162 MHz, $CDCl_3$)



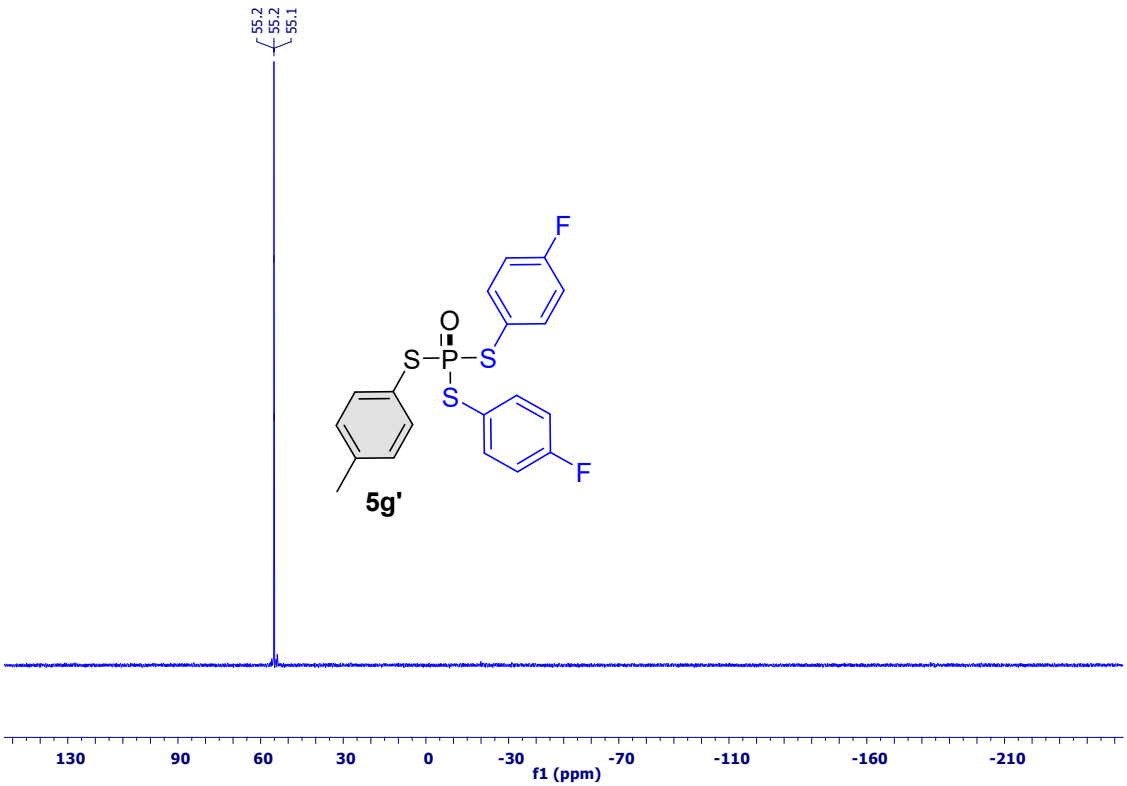
^{1}H NMR (400 MHz, $CDCl_3$)



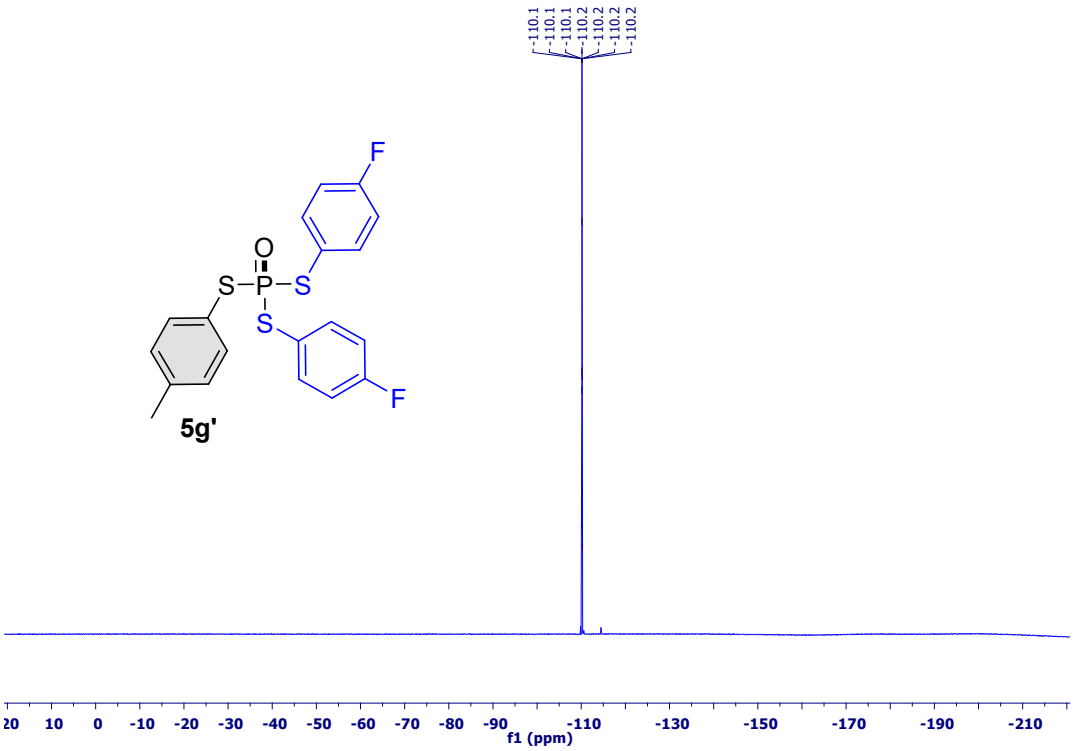
^{13}C NMR (101 MHz, $CDCl_3$)



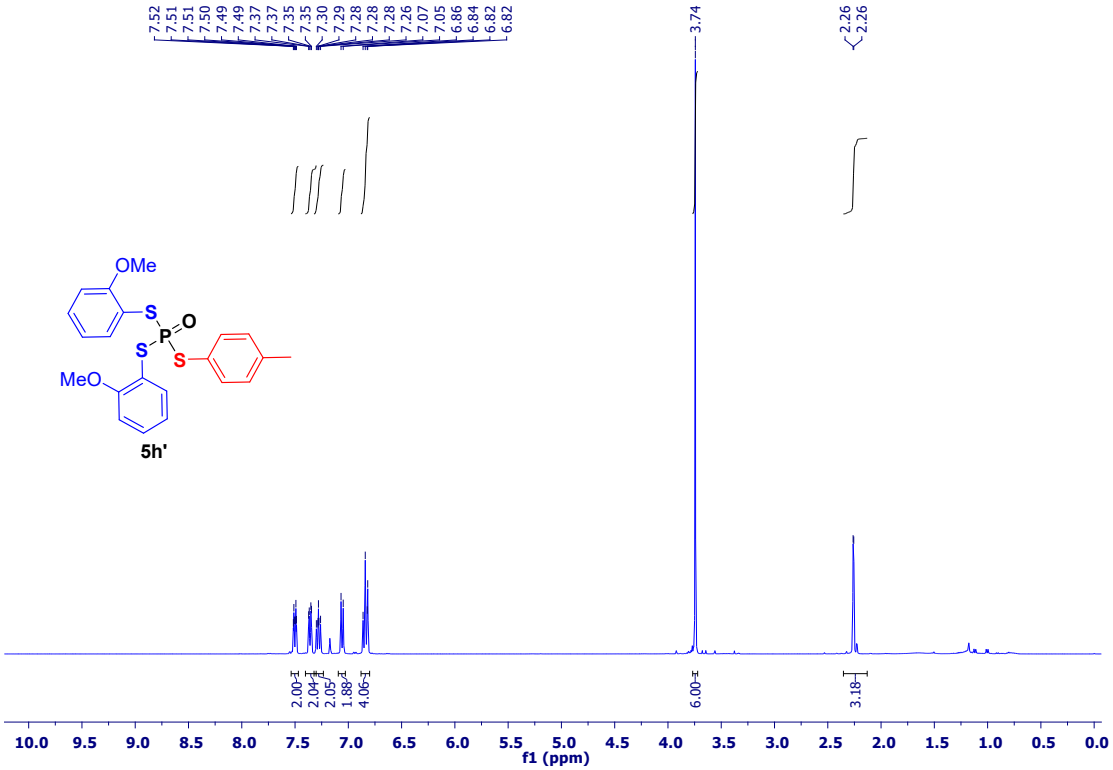
^{31}P NMR (162 MHz, $CDCl_3$)



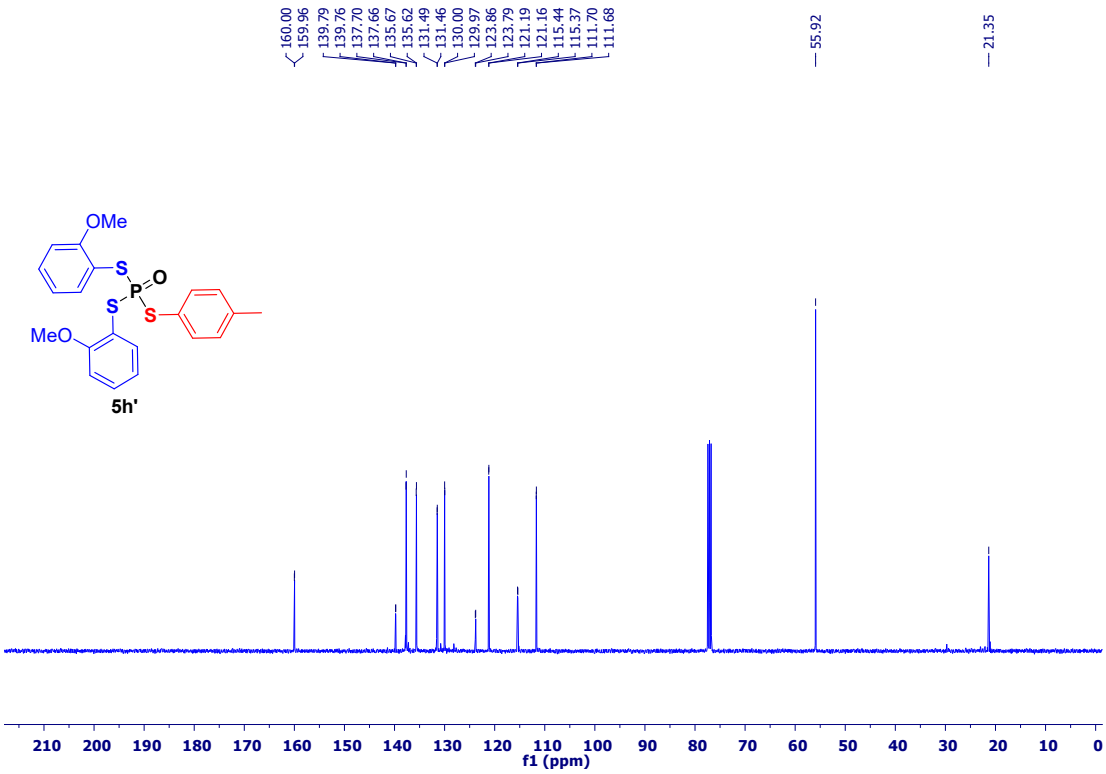
^{19}F NMR (377 MHz, $CDCl_3$)



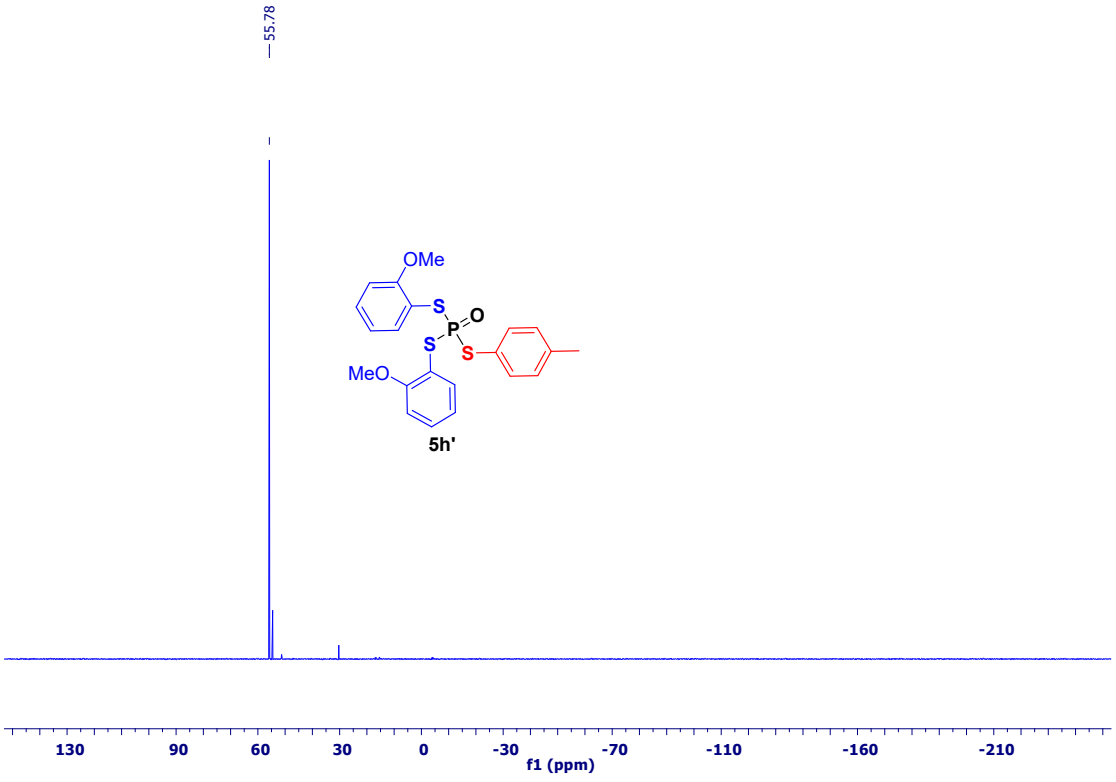
^{1}H NMR (400 MHz, $CDCl_3$)



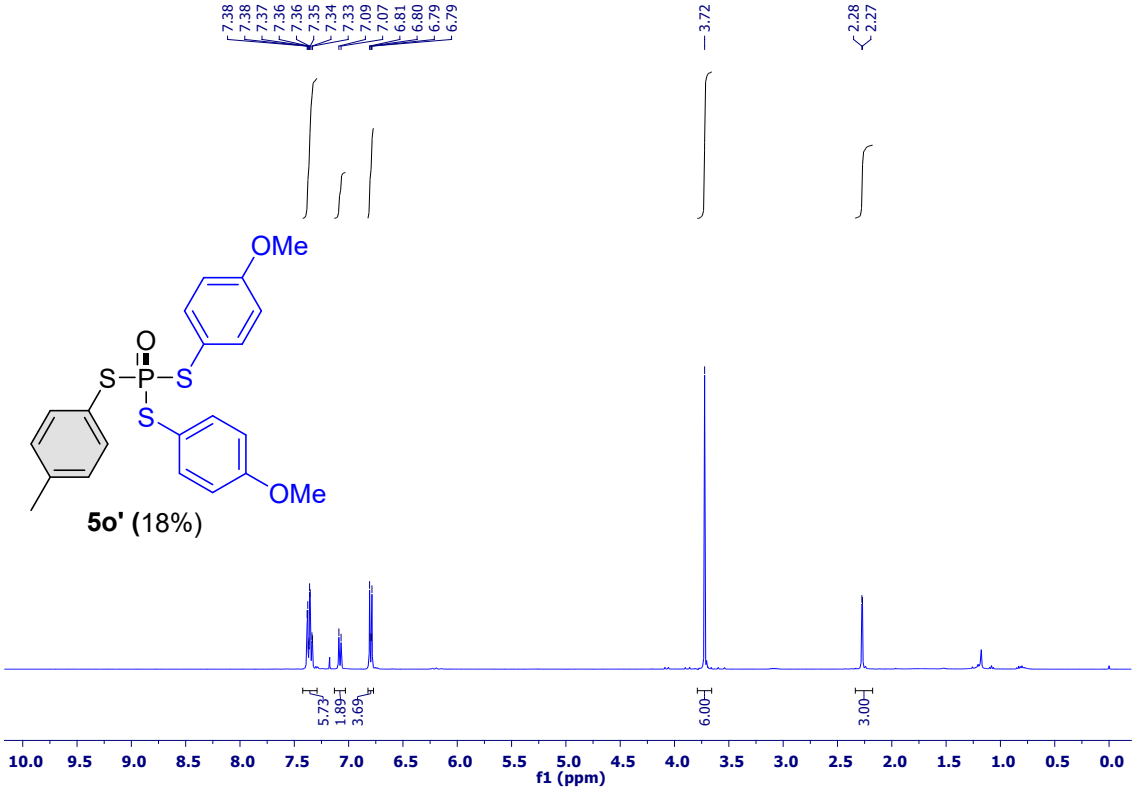
^{13}C NMR (101 MHz, $CDCl_3$)



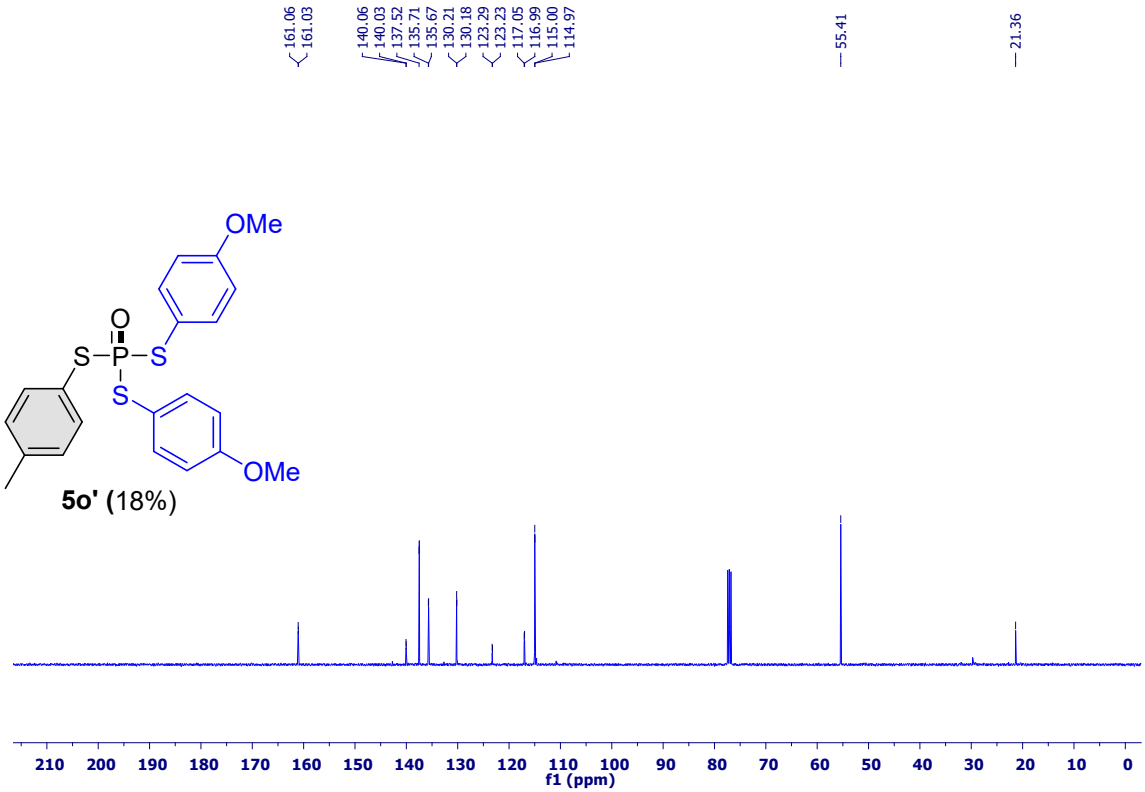
^{31}P NMR (162 MHz, $CDCl_3$)



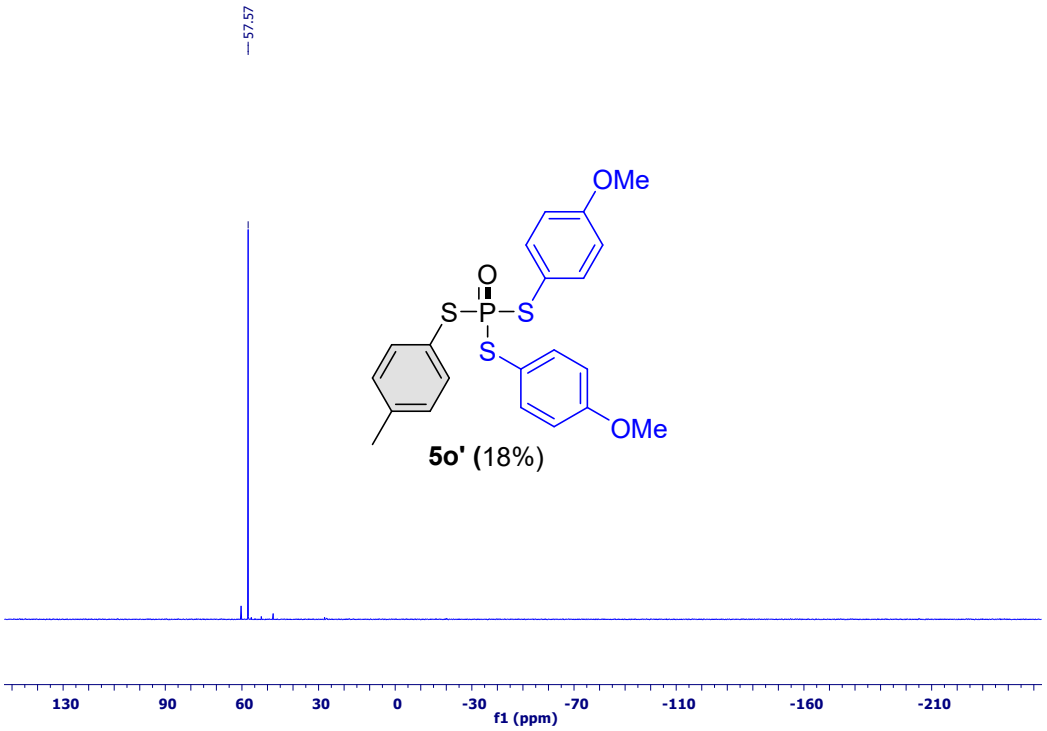
^{1}H NMR (400 MHz, $CDCl_3$)



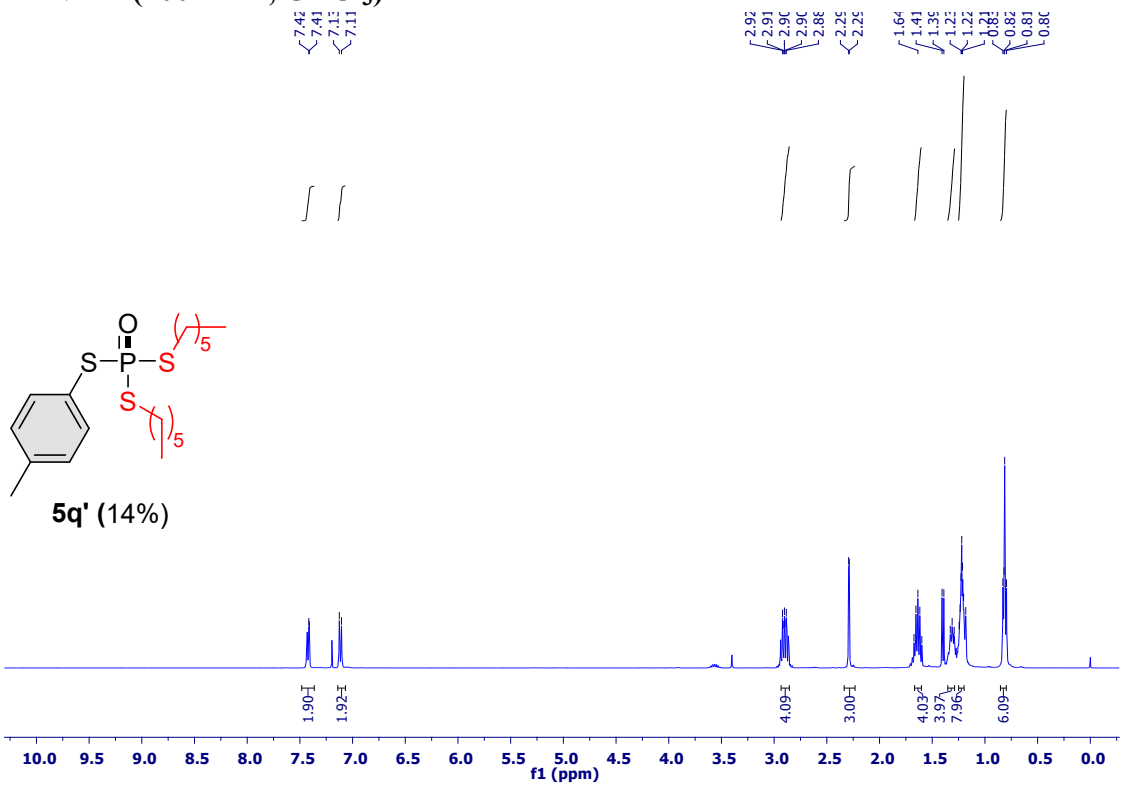
^{13}C NMR (101 MHz, $CDCl_3$)



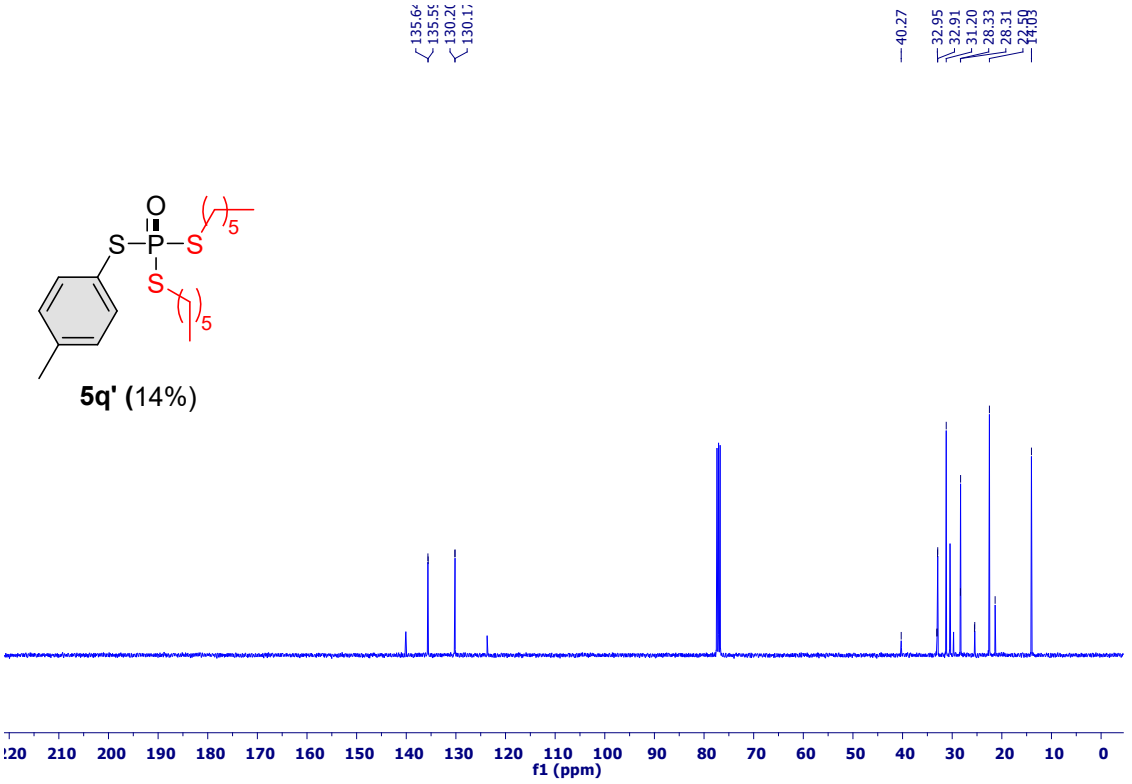
^{31}P NMR (162 MHz, $CDCl_3$)



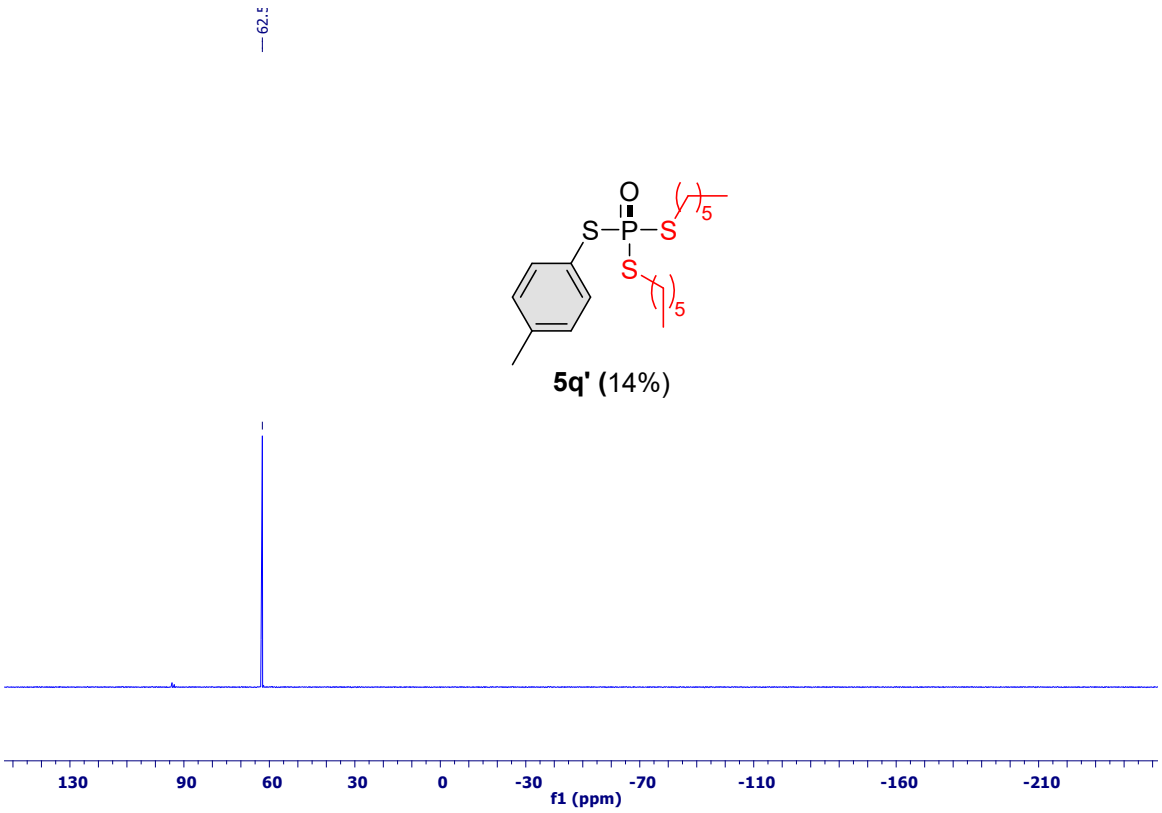
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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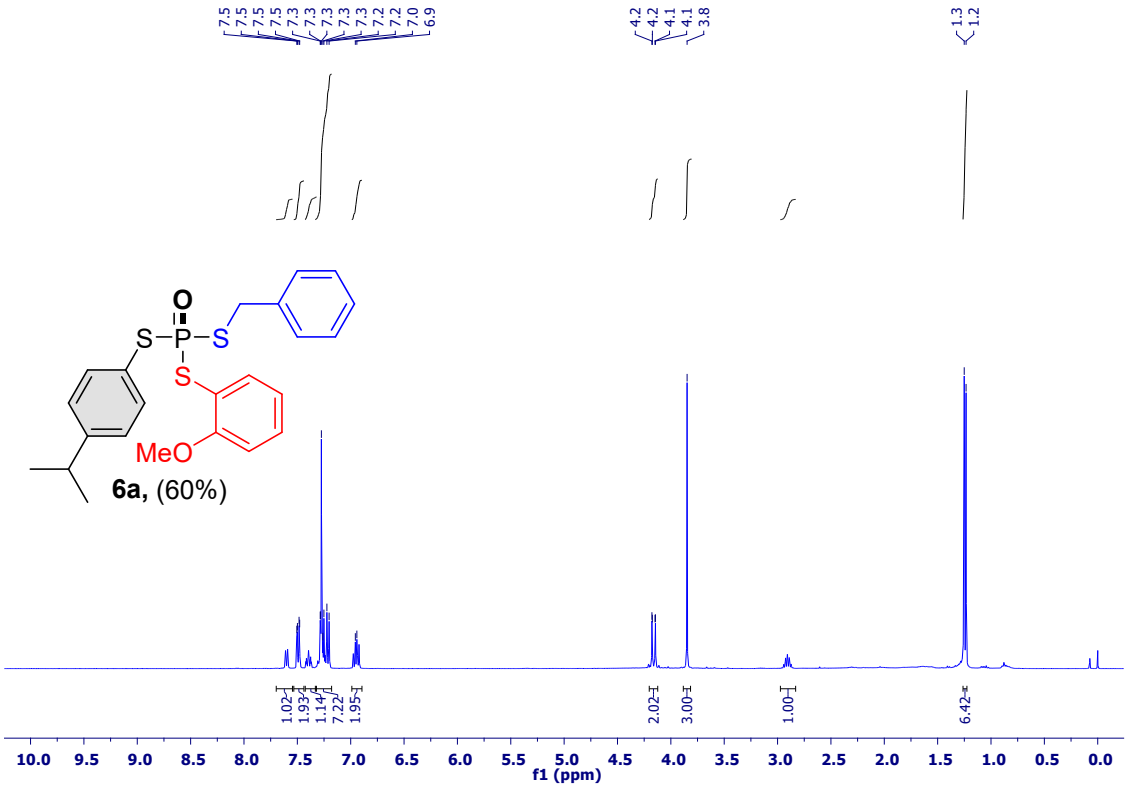

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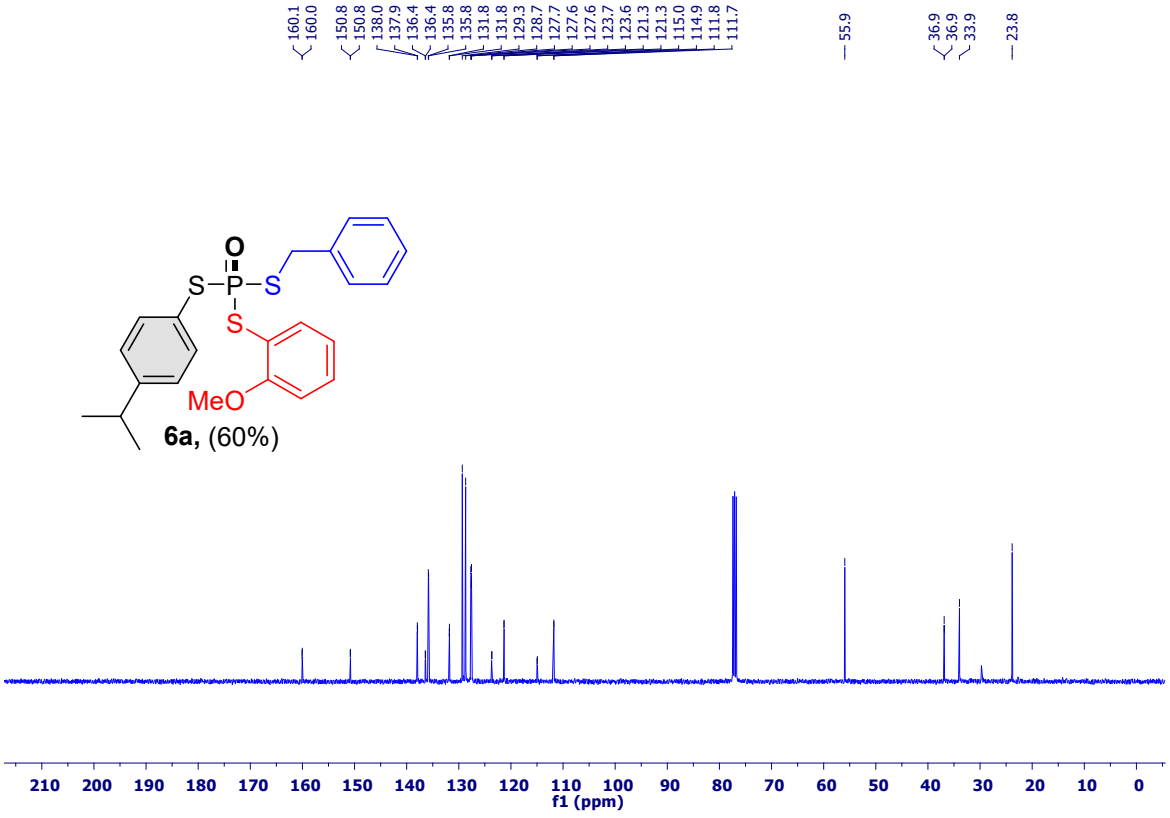
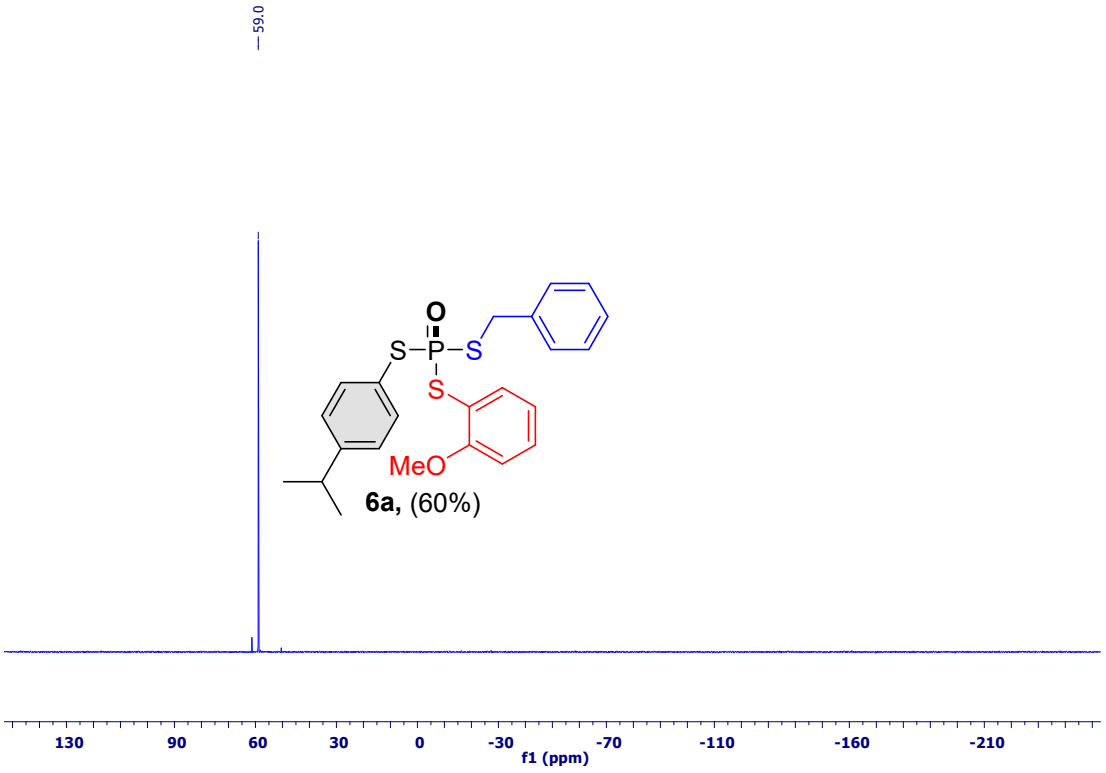


^{31}P NMR (162 MHz, $CDCl_3$



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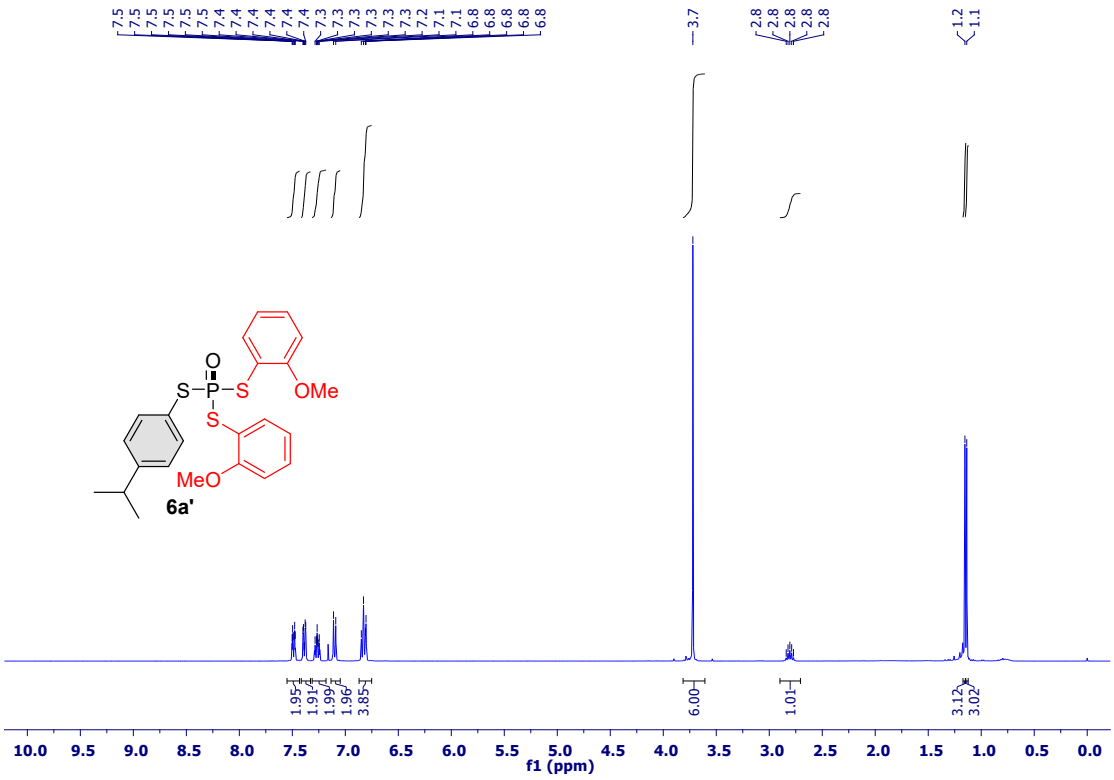
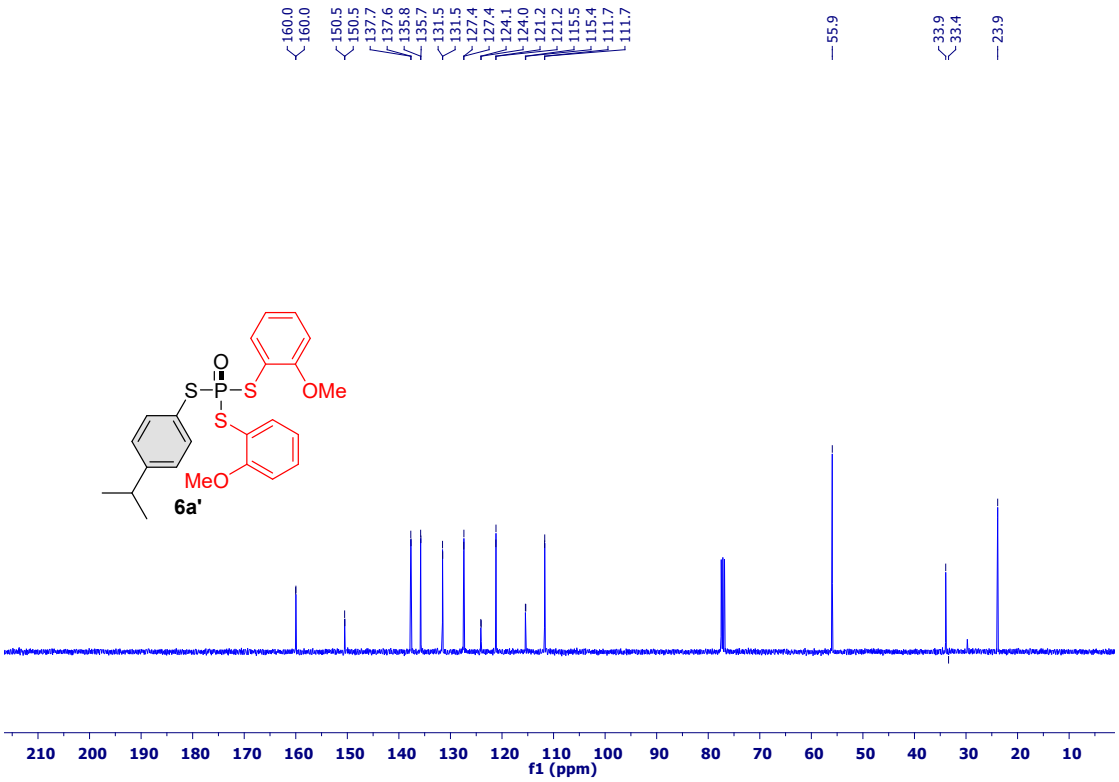
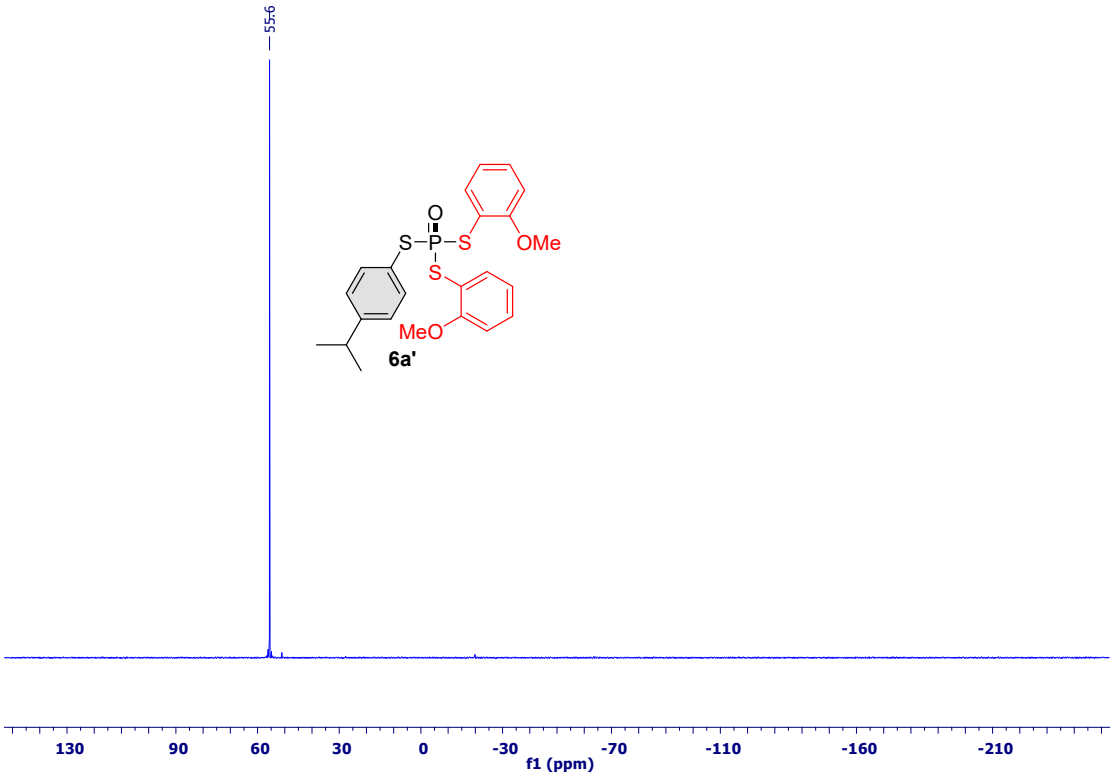


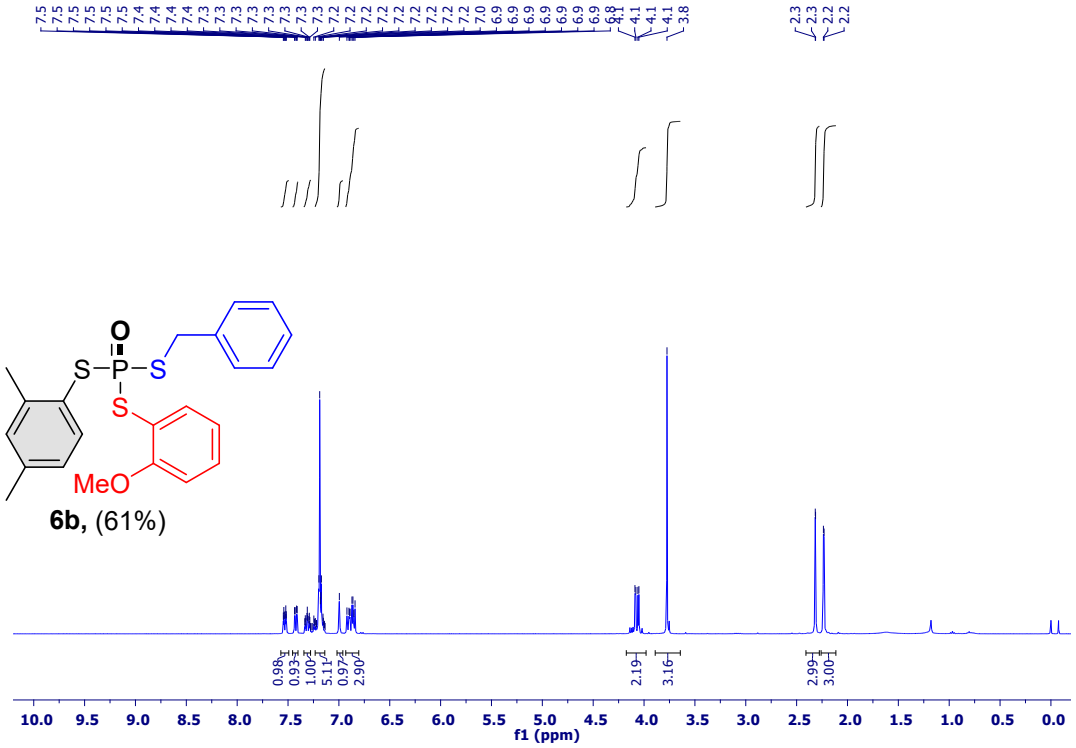
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



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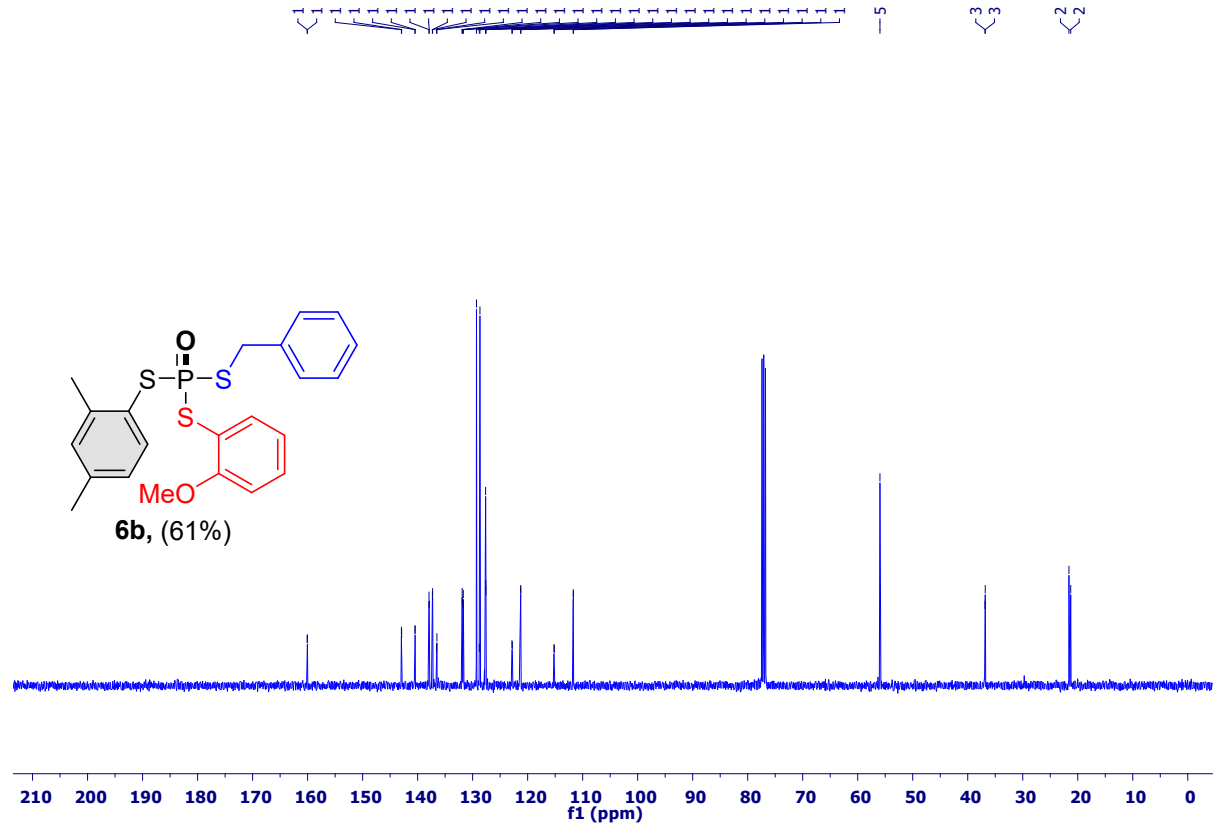
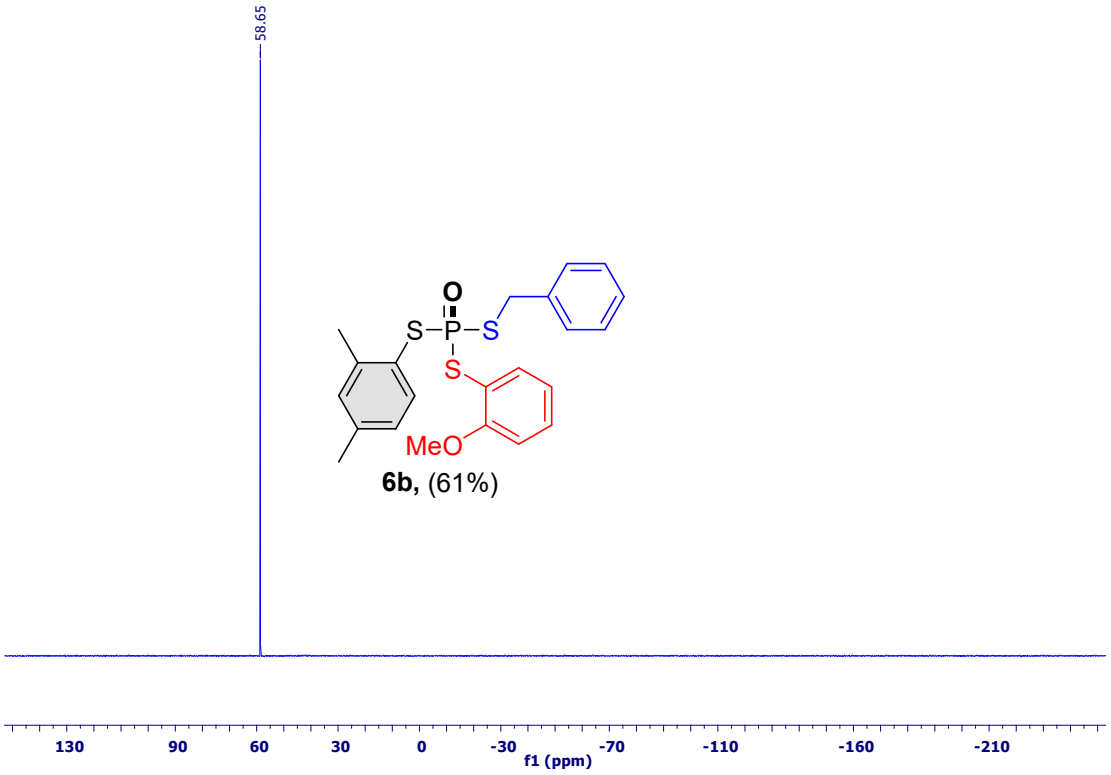


^{31}P NMR (162 MHz, $CDCl_3$



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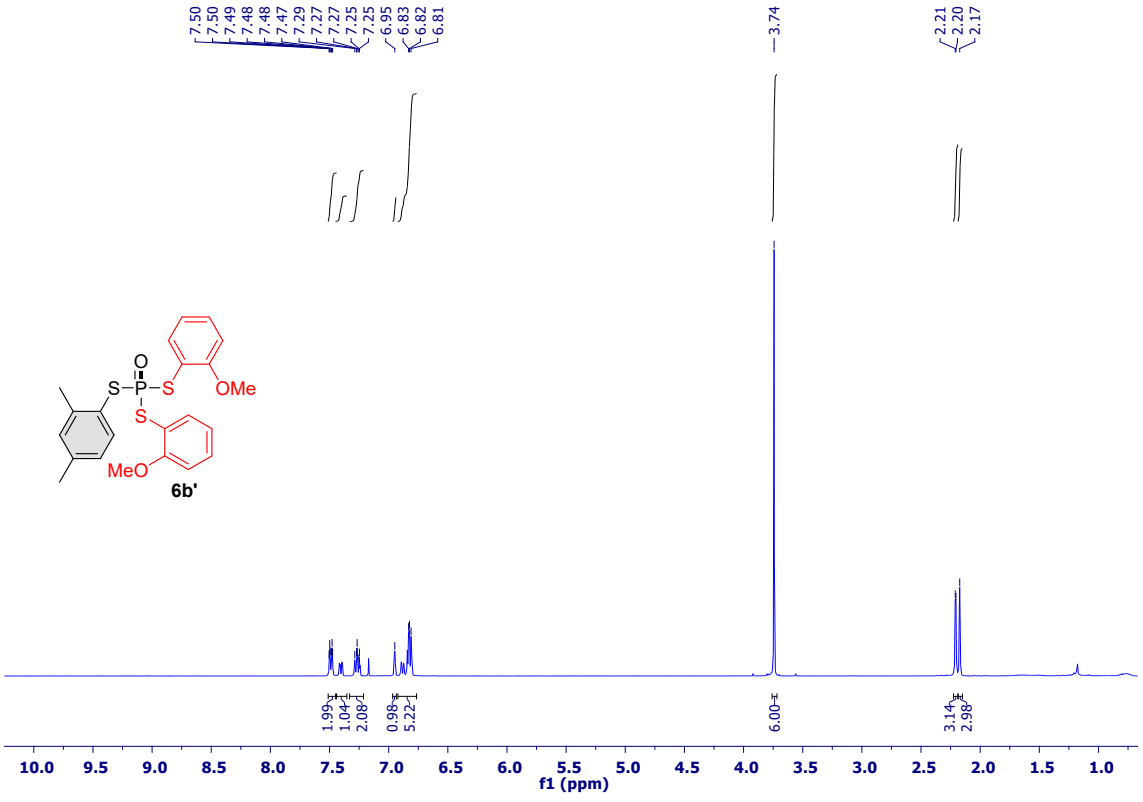
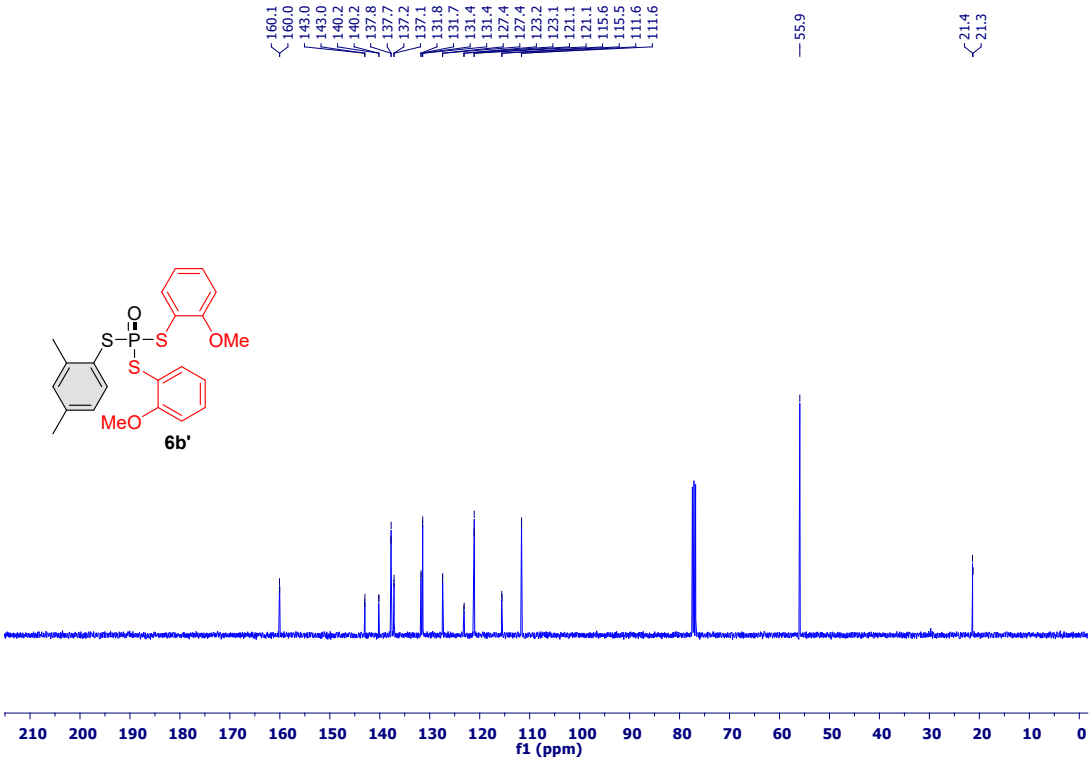


^{13}C NMR (101 MHz, $CDCl_3$)



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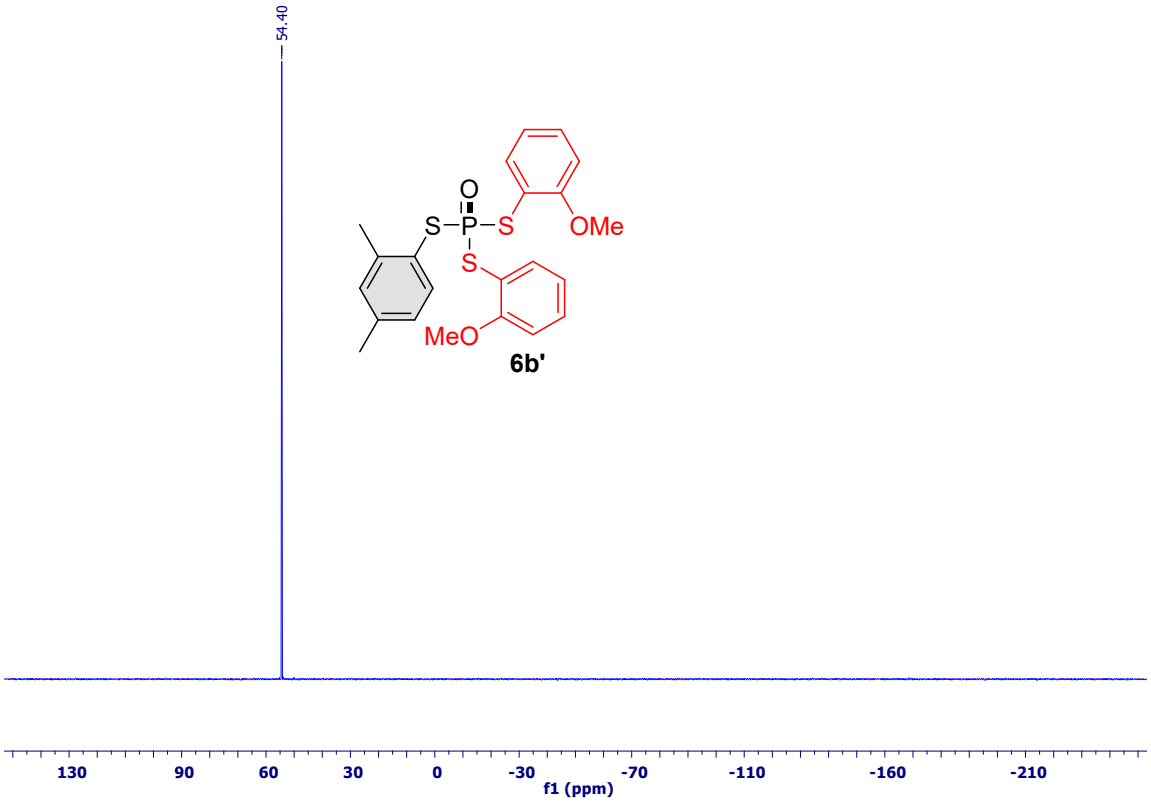

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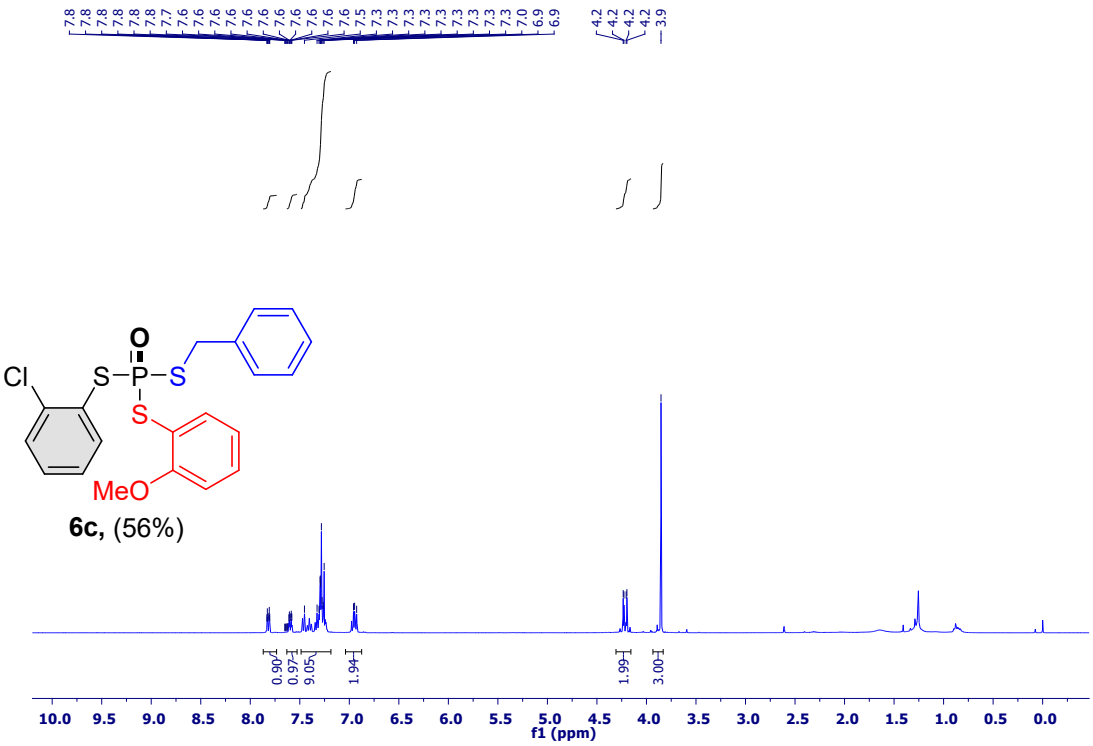
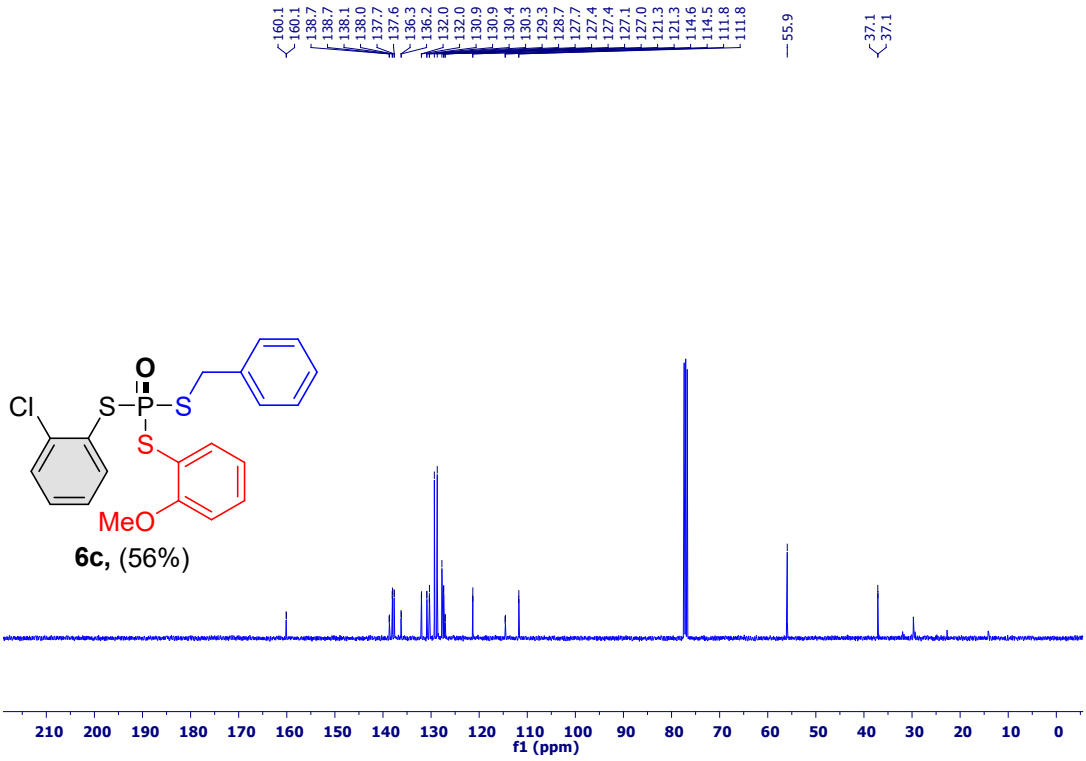
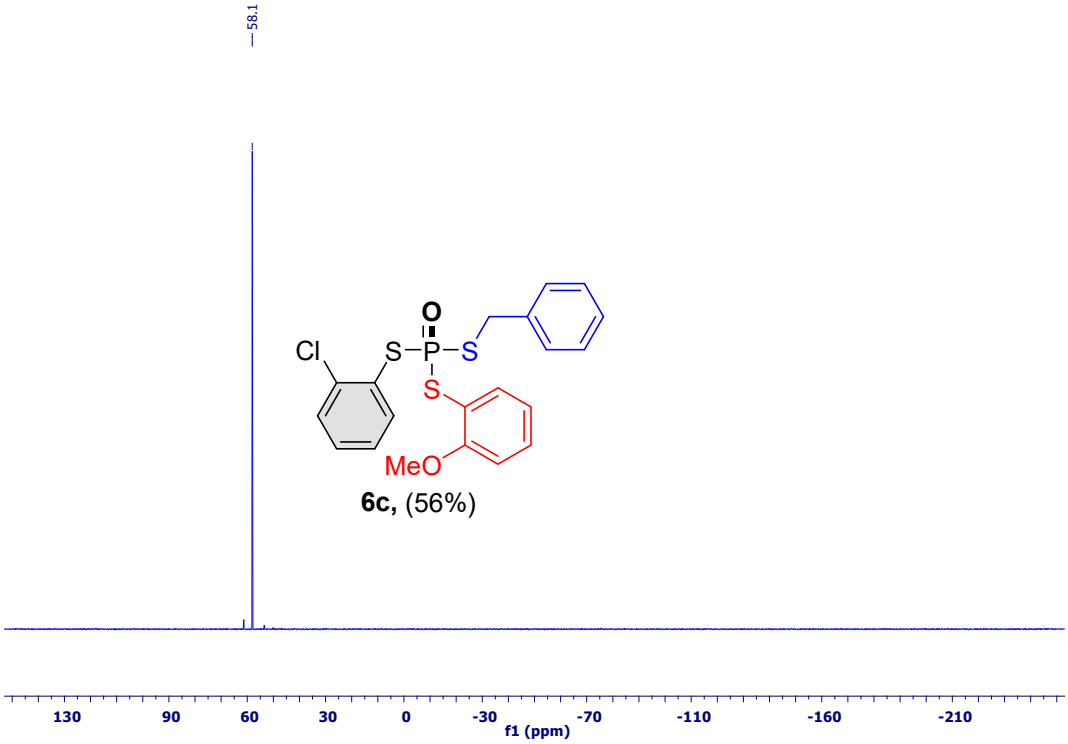


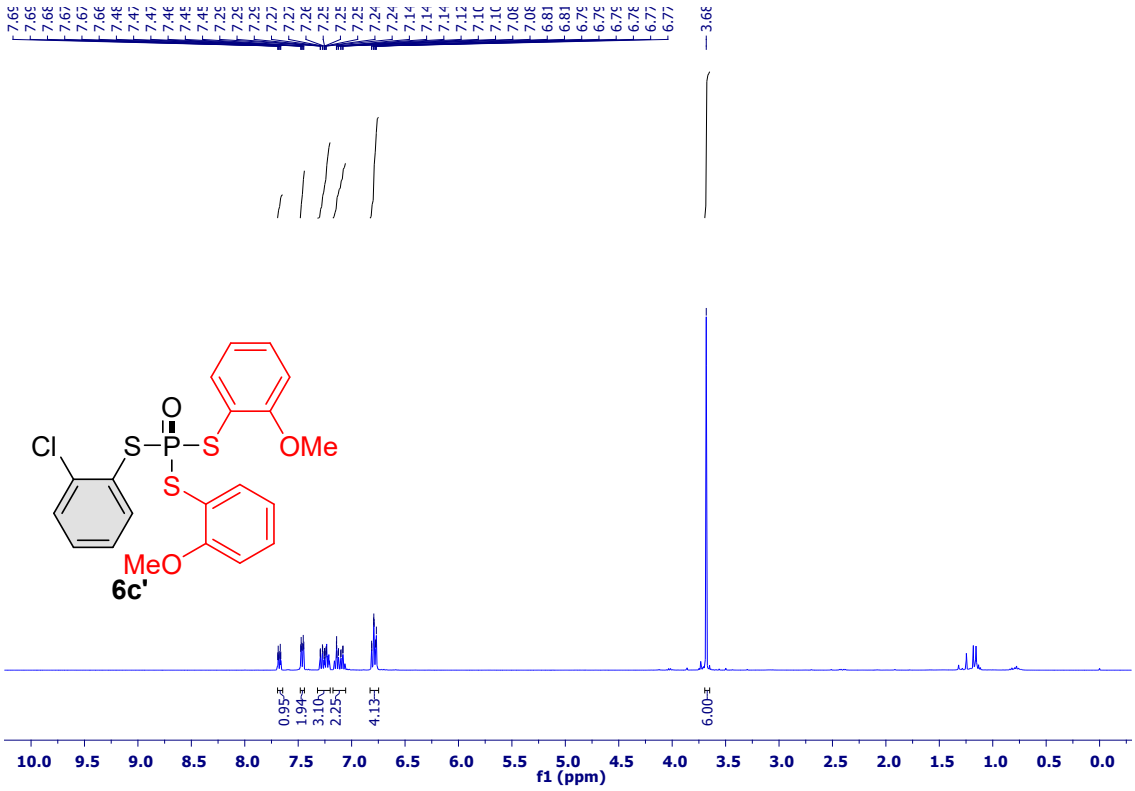
^{13}C NMR (101 MHz, $CDCl_3$)



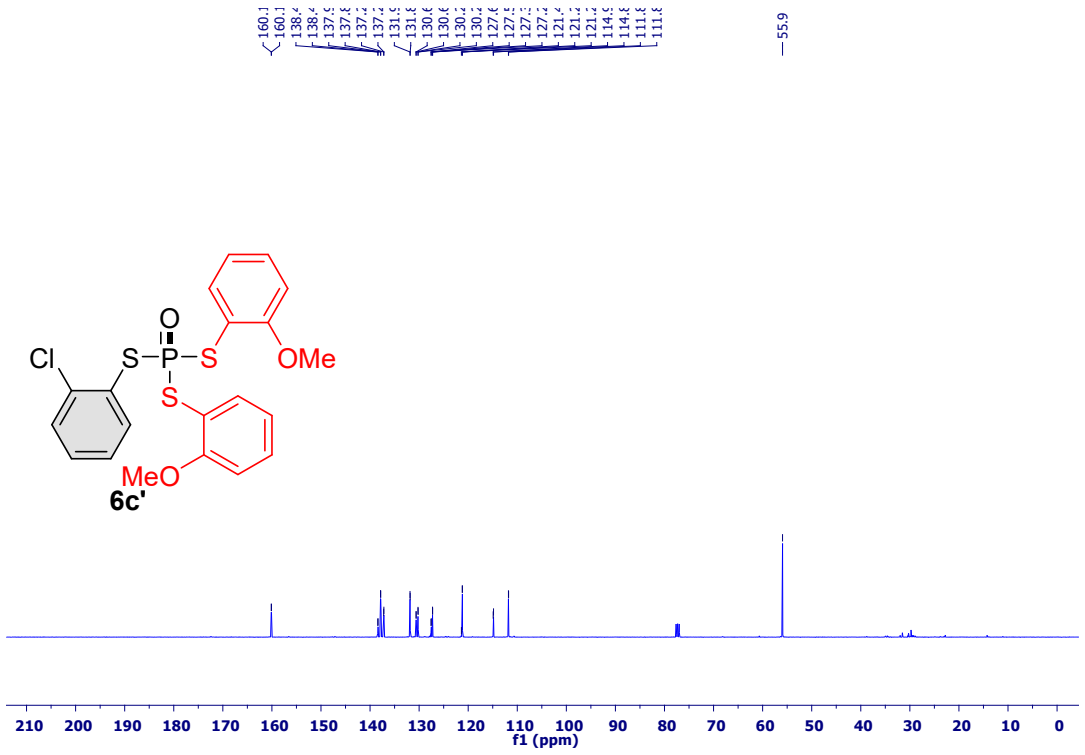
^{31}P NMR (162 MHz, $CDCl_3$



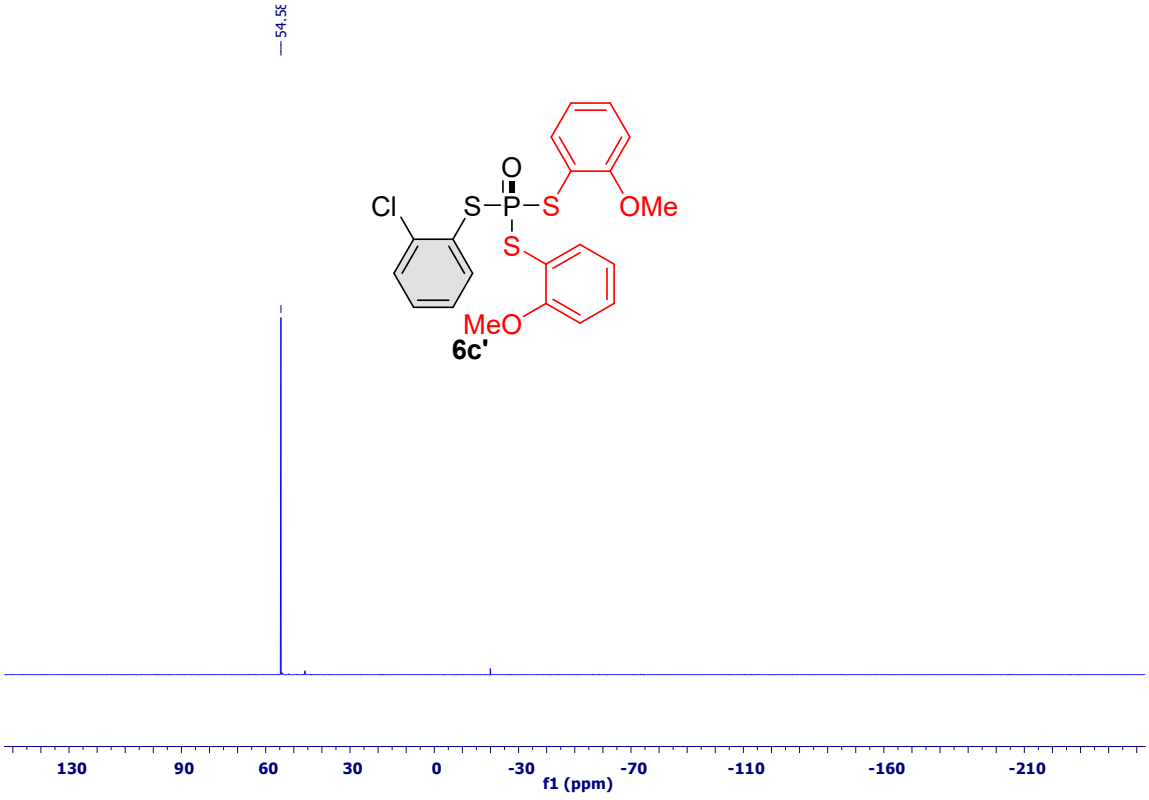
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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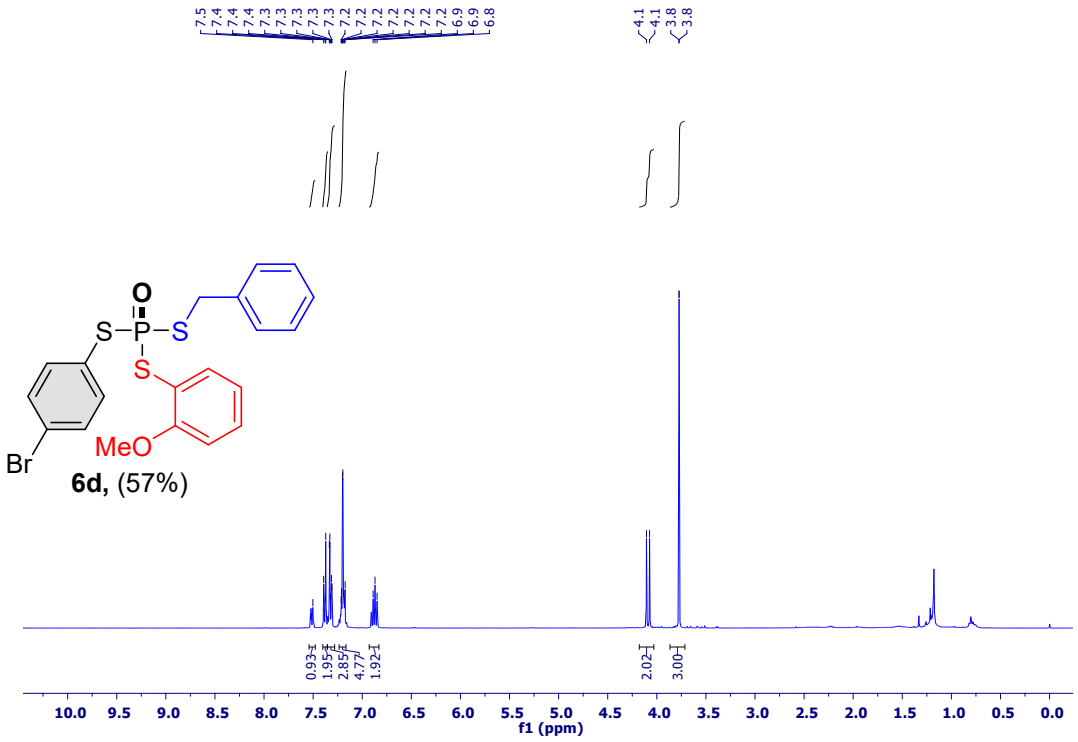

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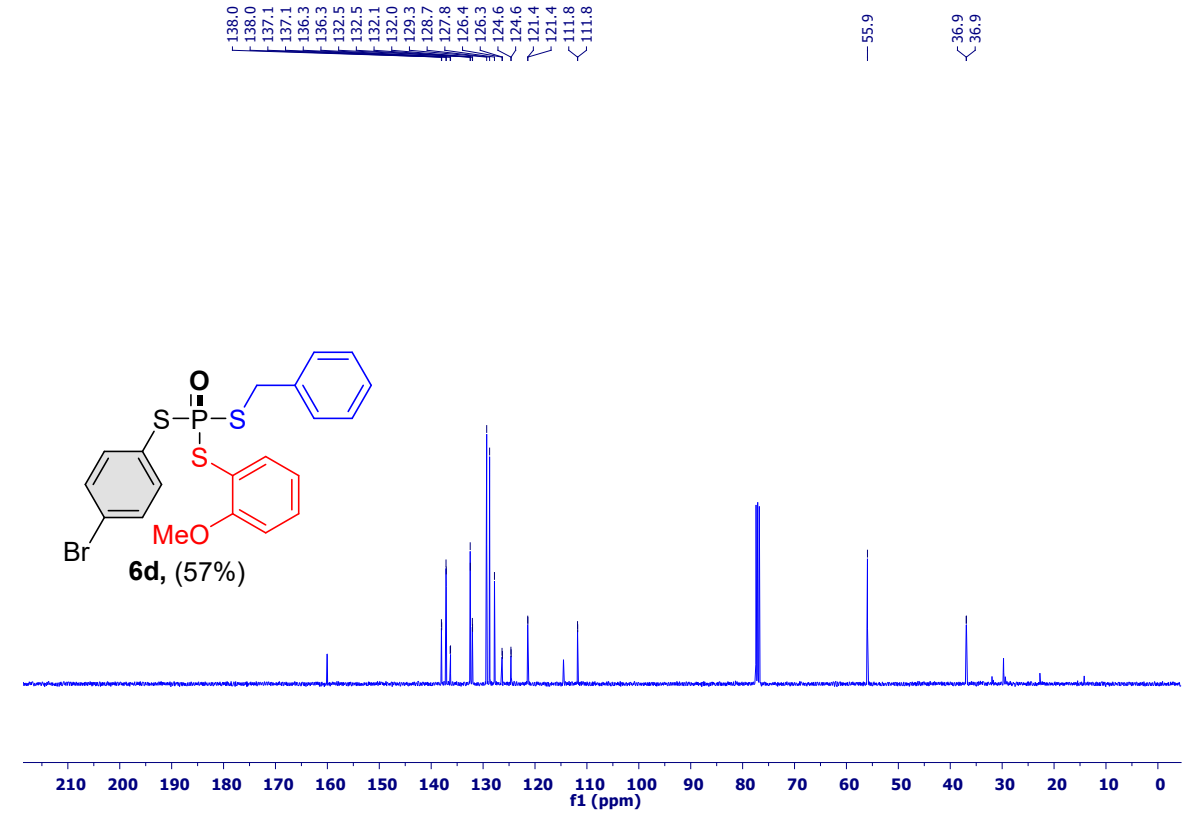
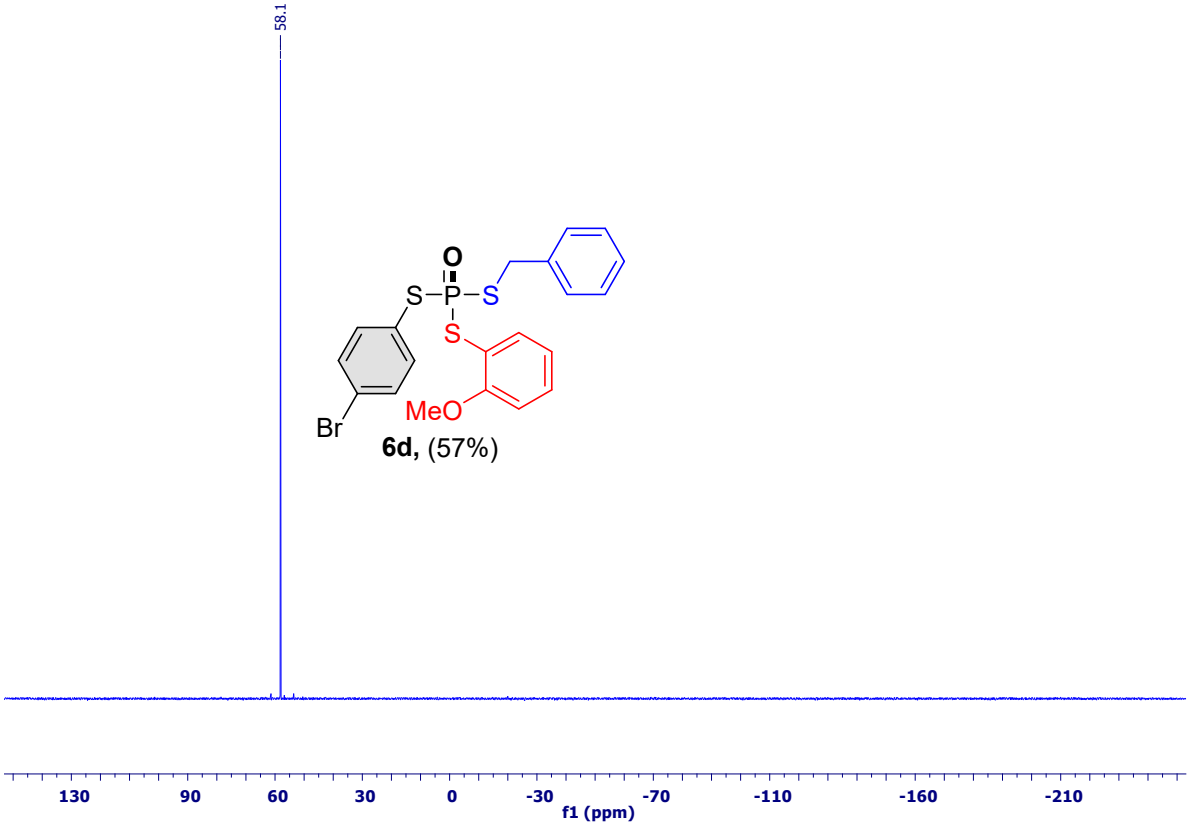


^{31}P NMR (162 MHz, $CDCl_3$



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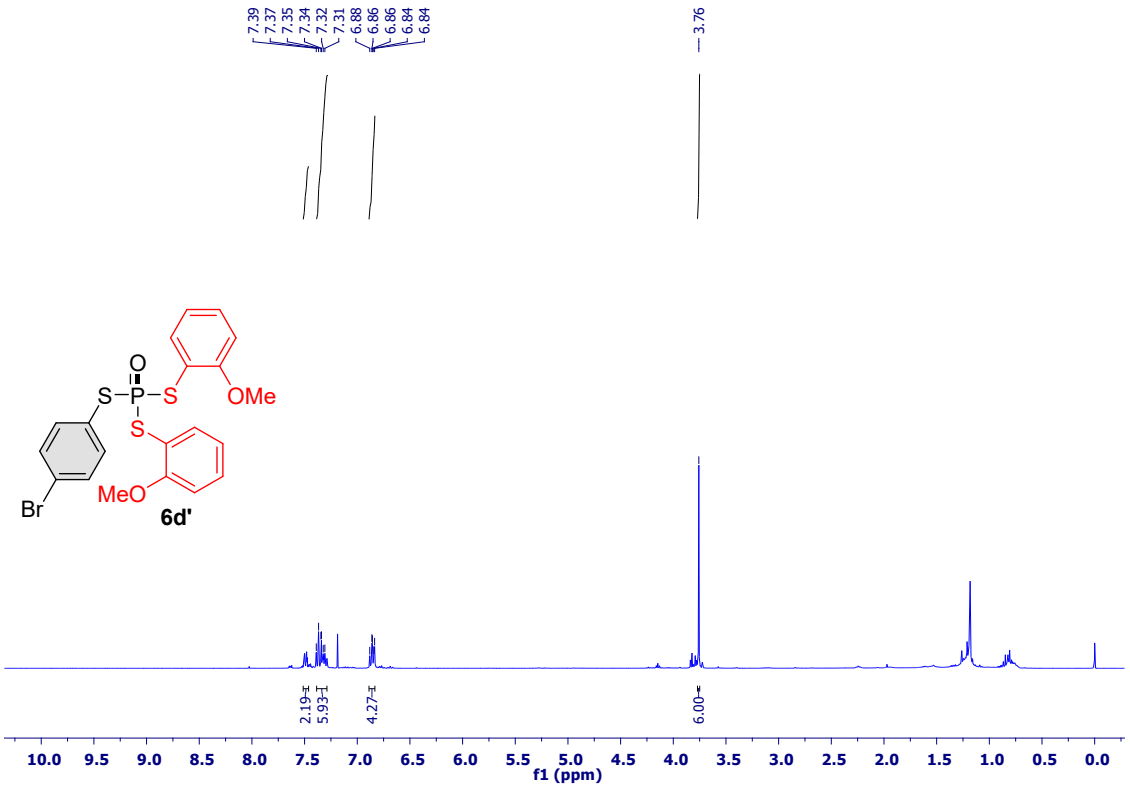
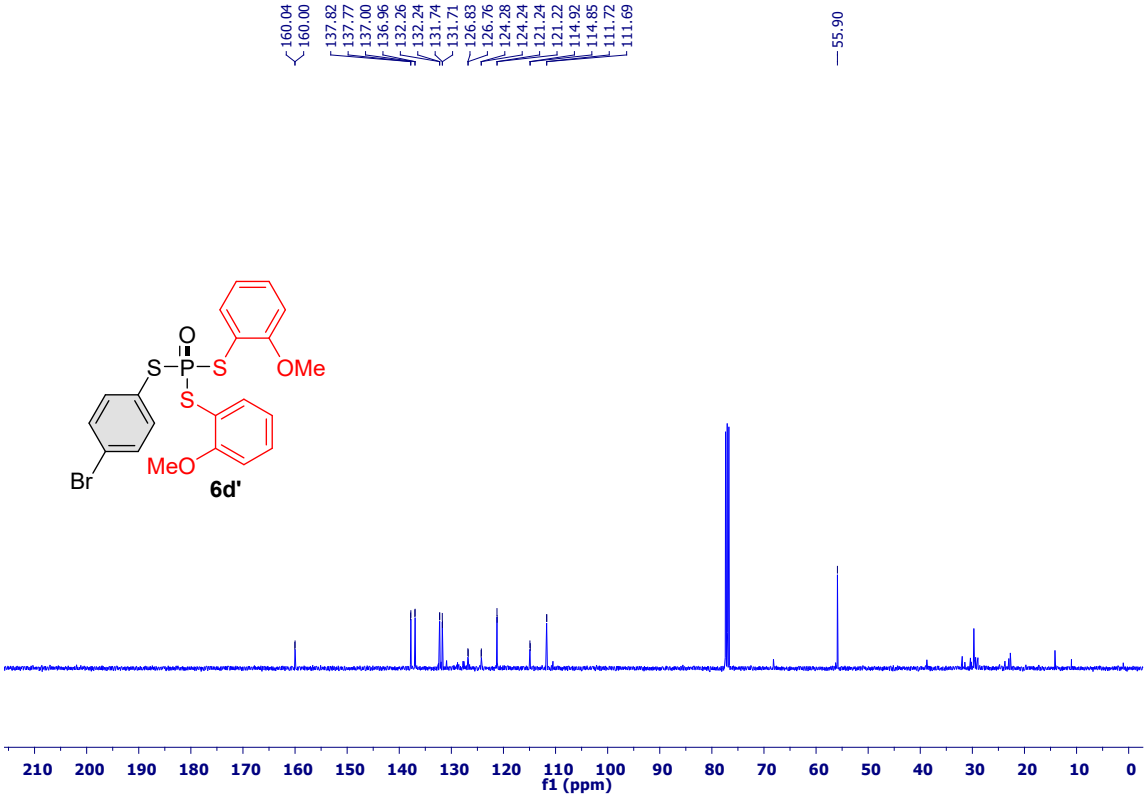
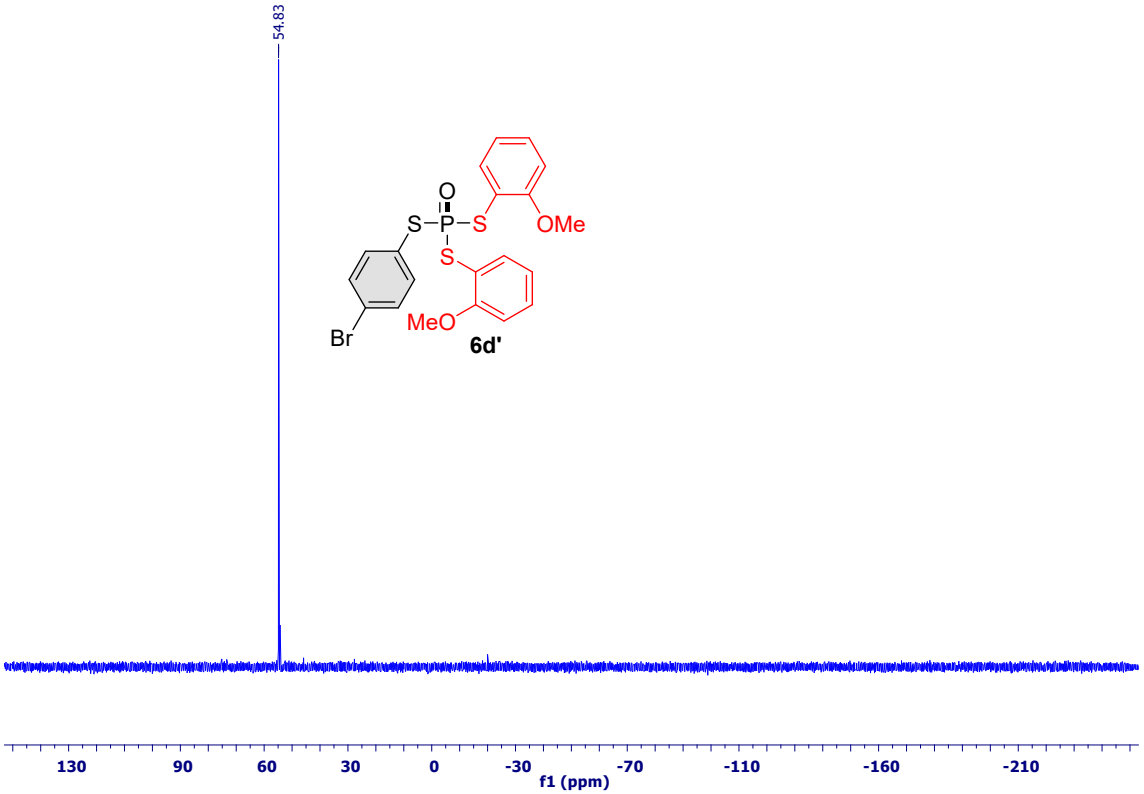


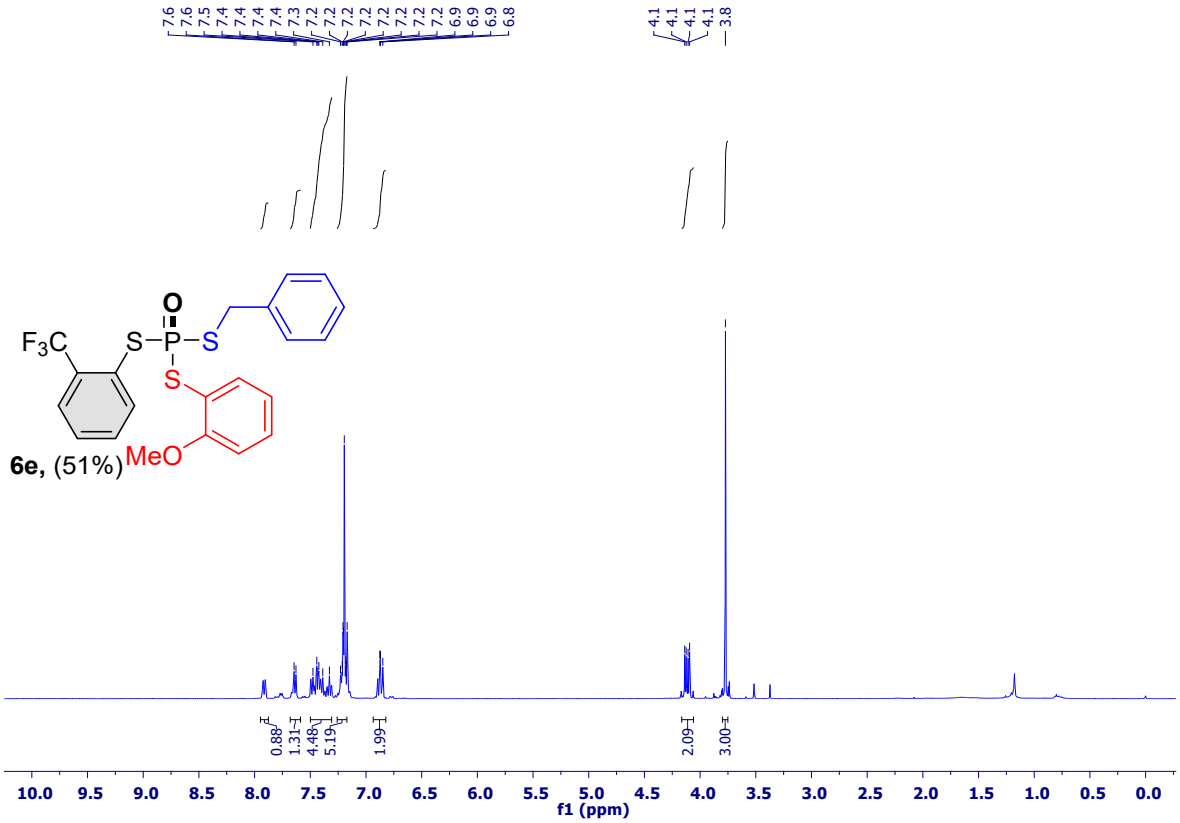
^{13}C NMR (101 MHz, $CDCl_3$)



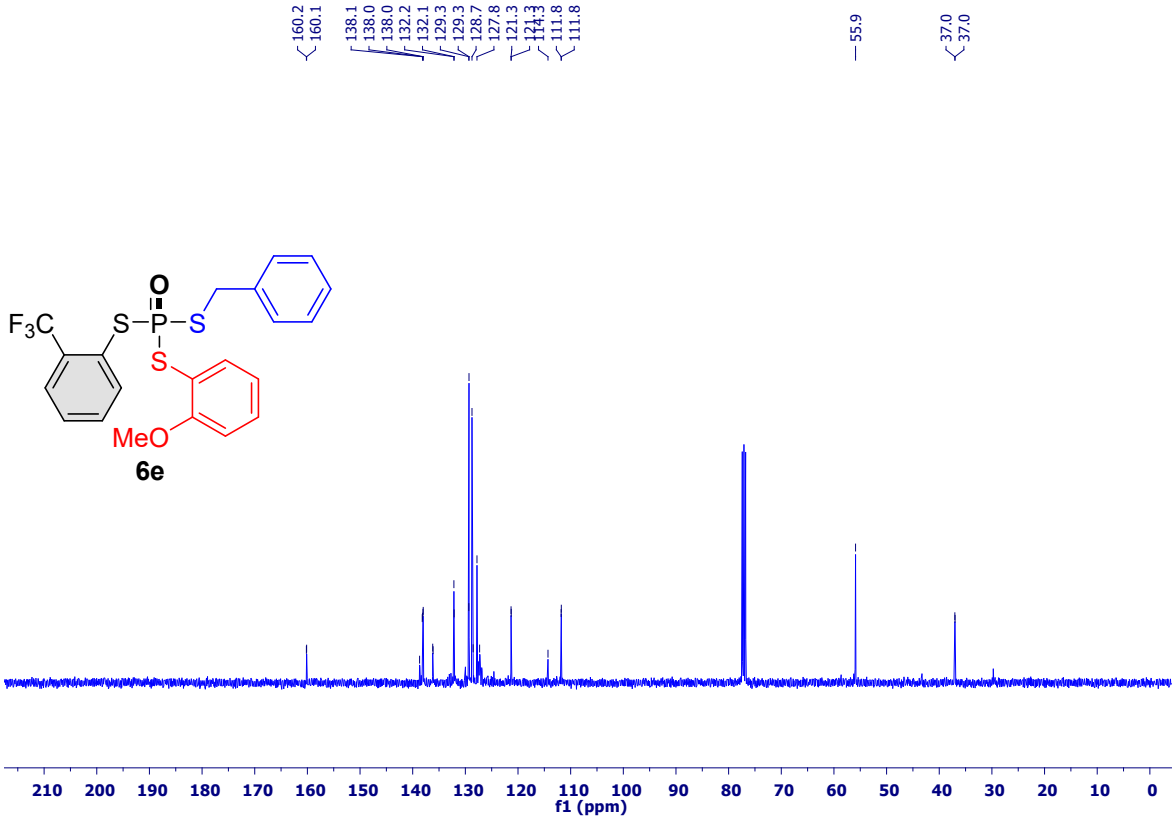
^{31}P NMR (162 MHz, $CDCl_3$



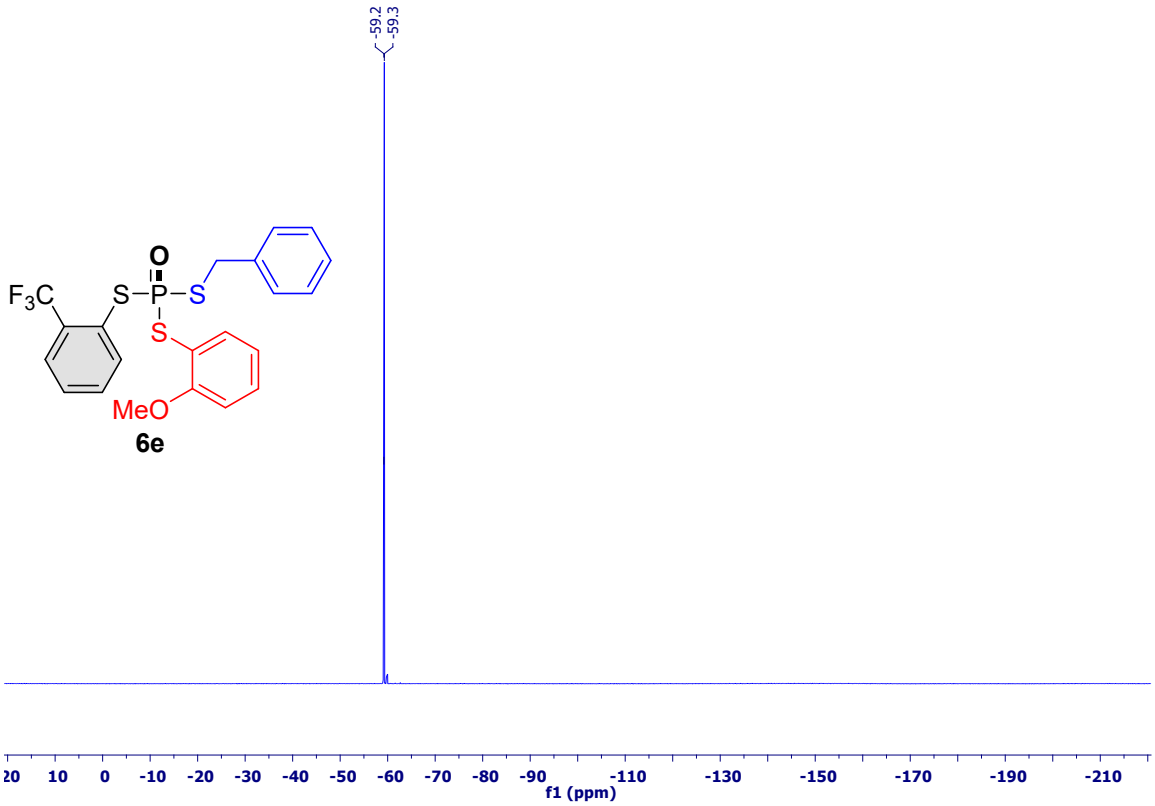
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{19}F NMR (377 MHz, $CDCl_3$



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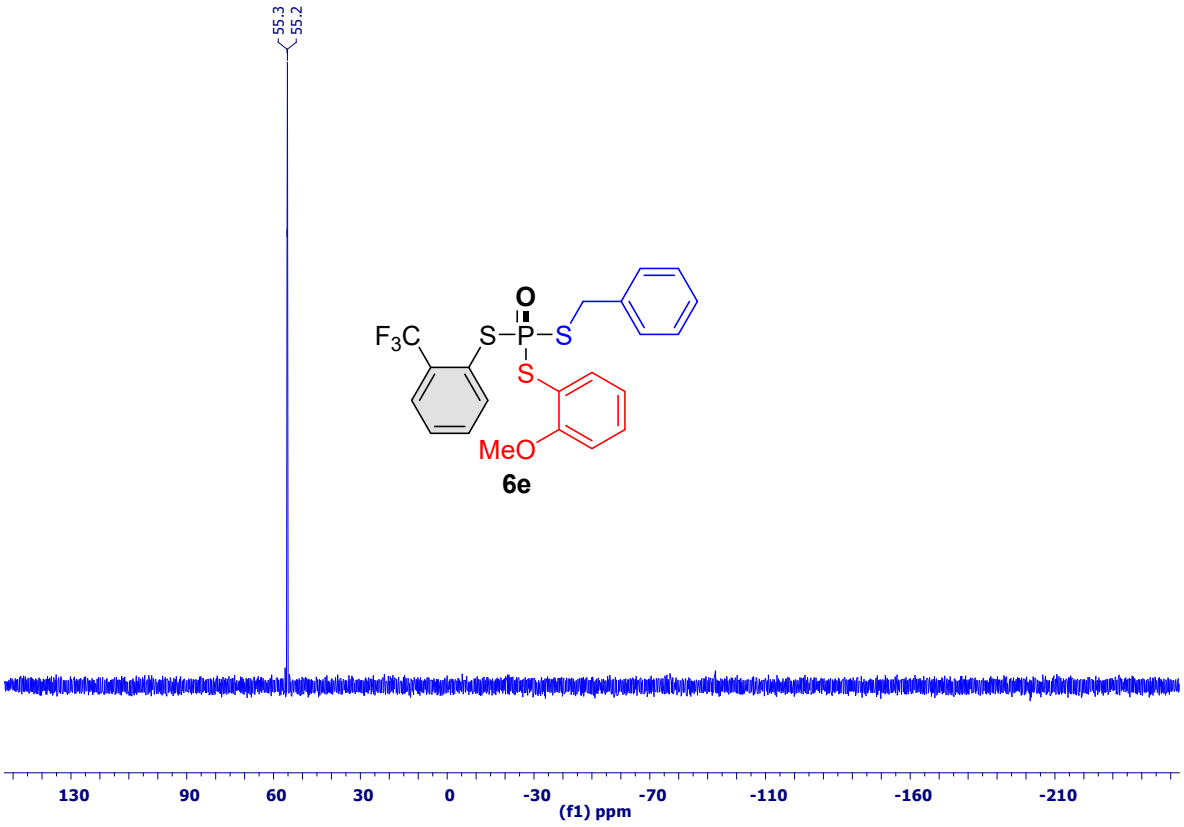
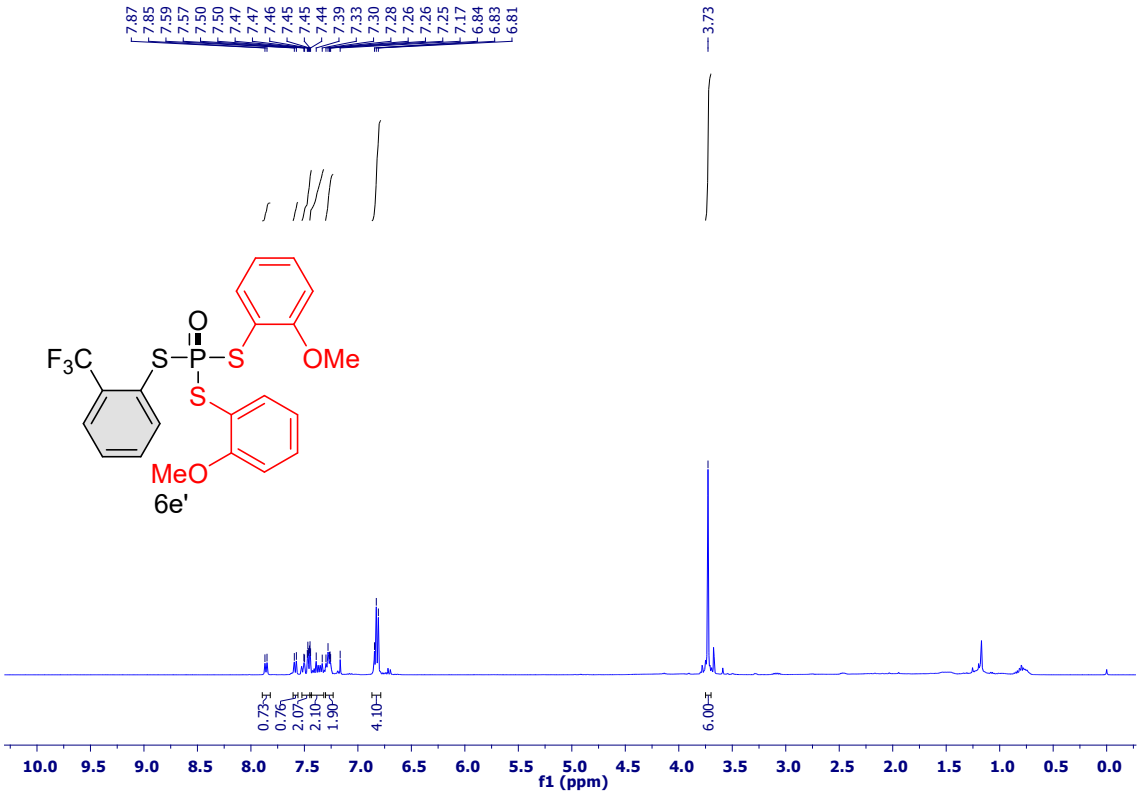
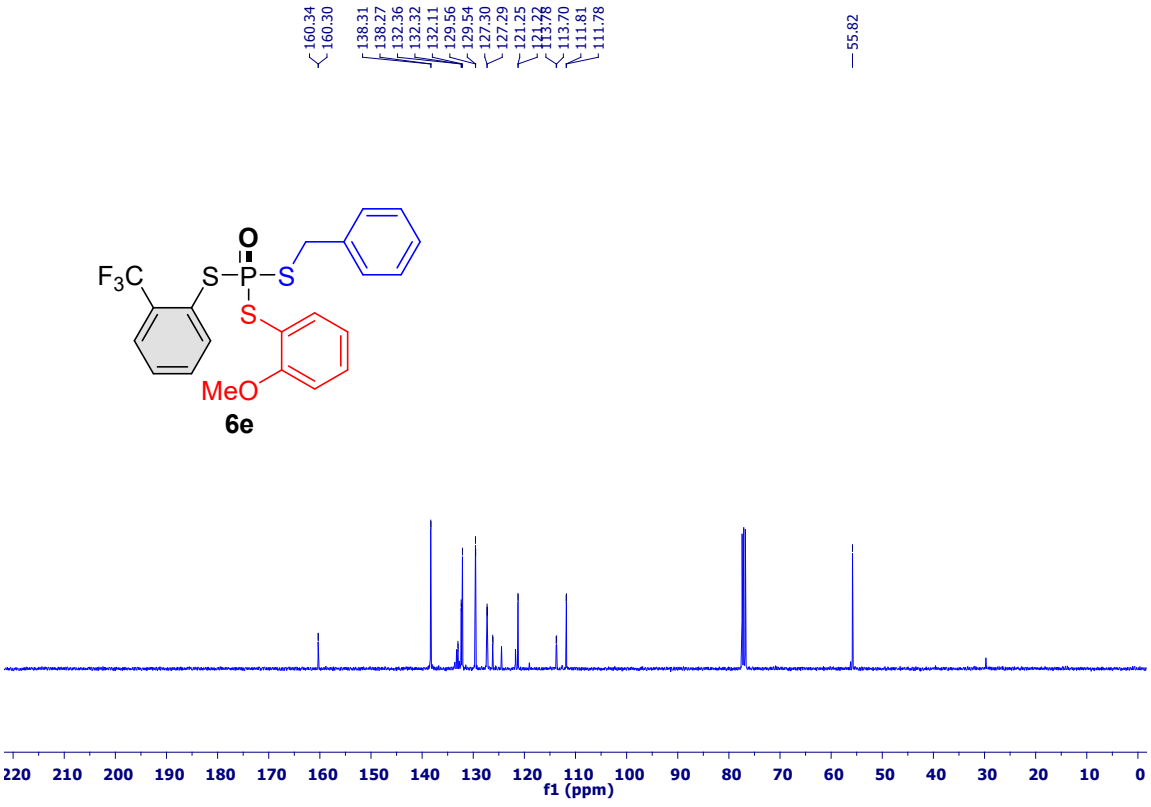


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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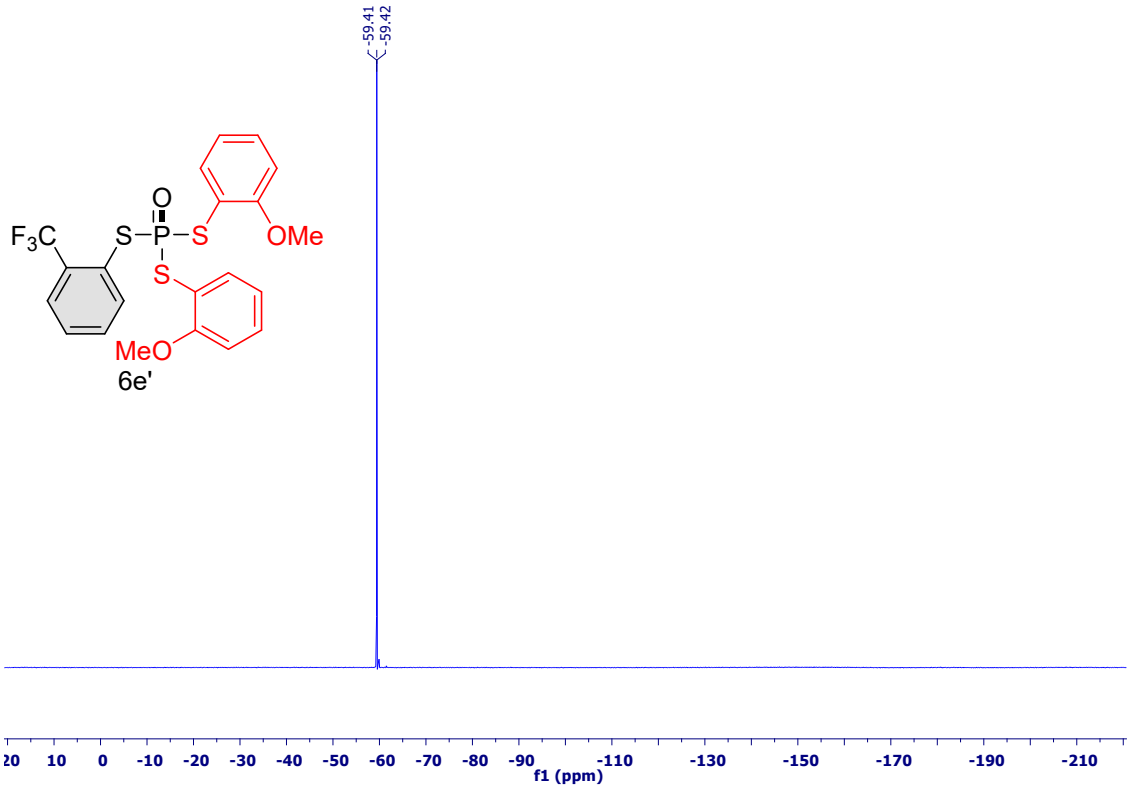
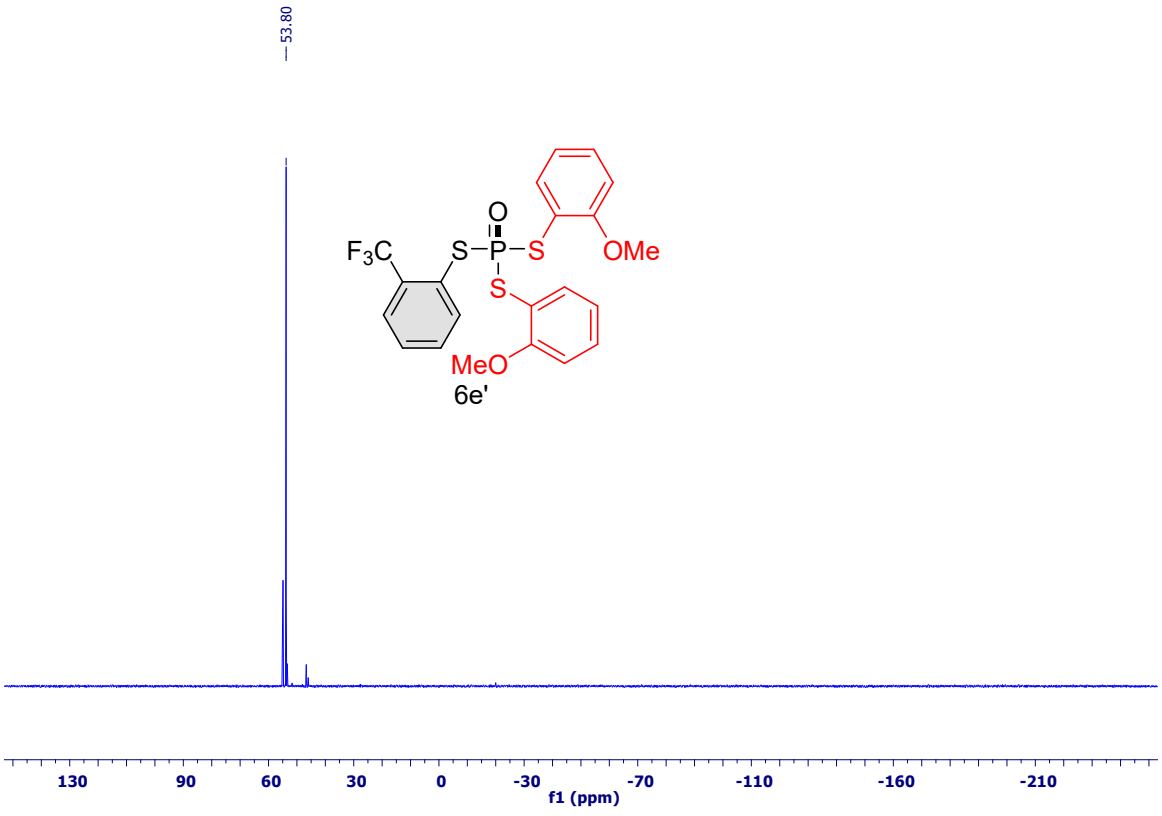


^{31}P NMR (162 MHz, $CDCl_3$)



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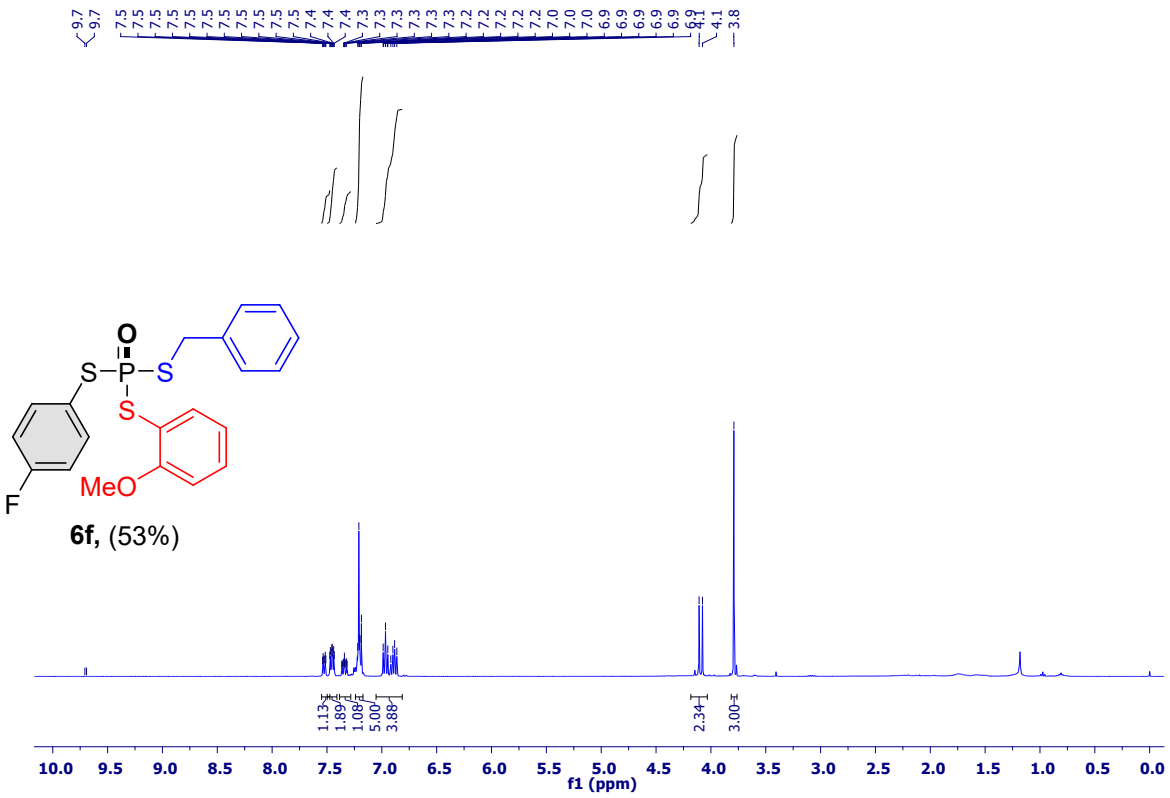

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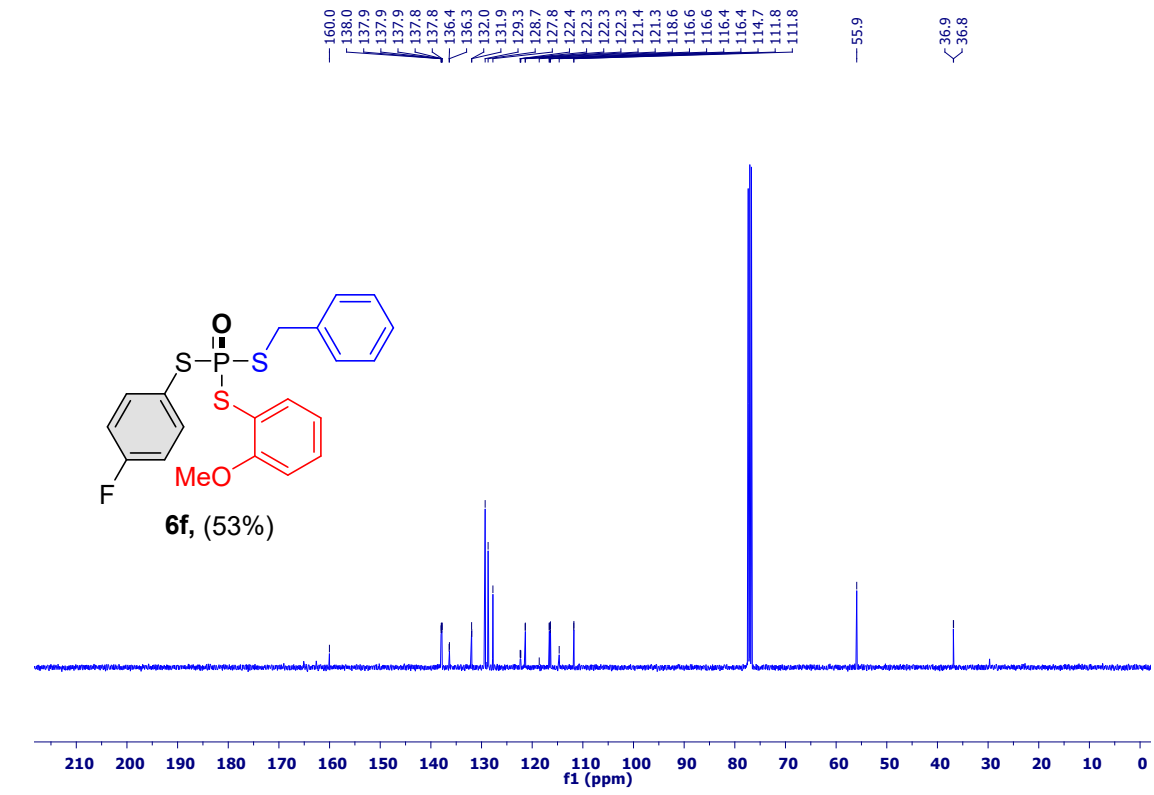
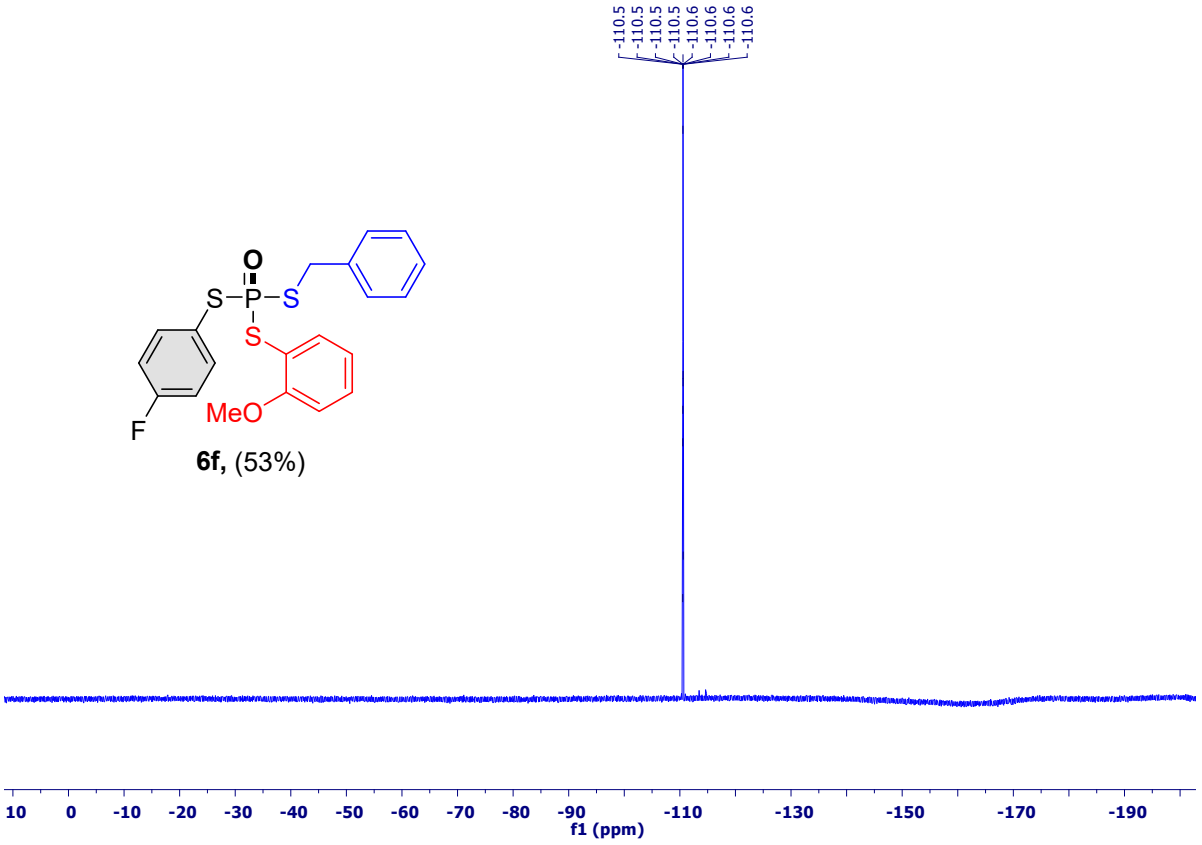
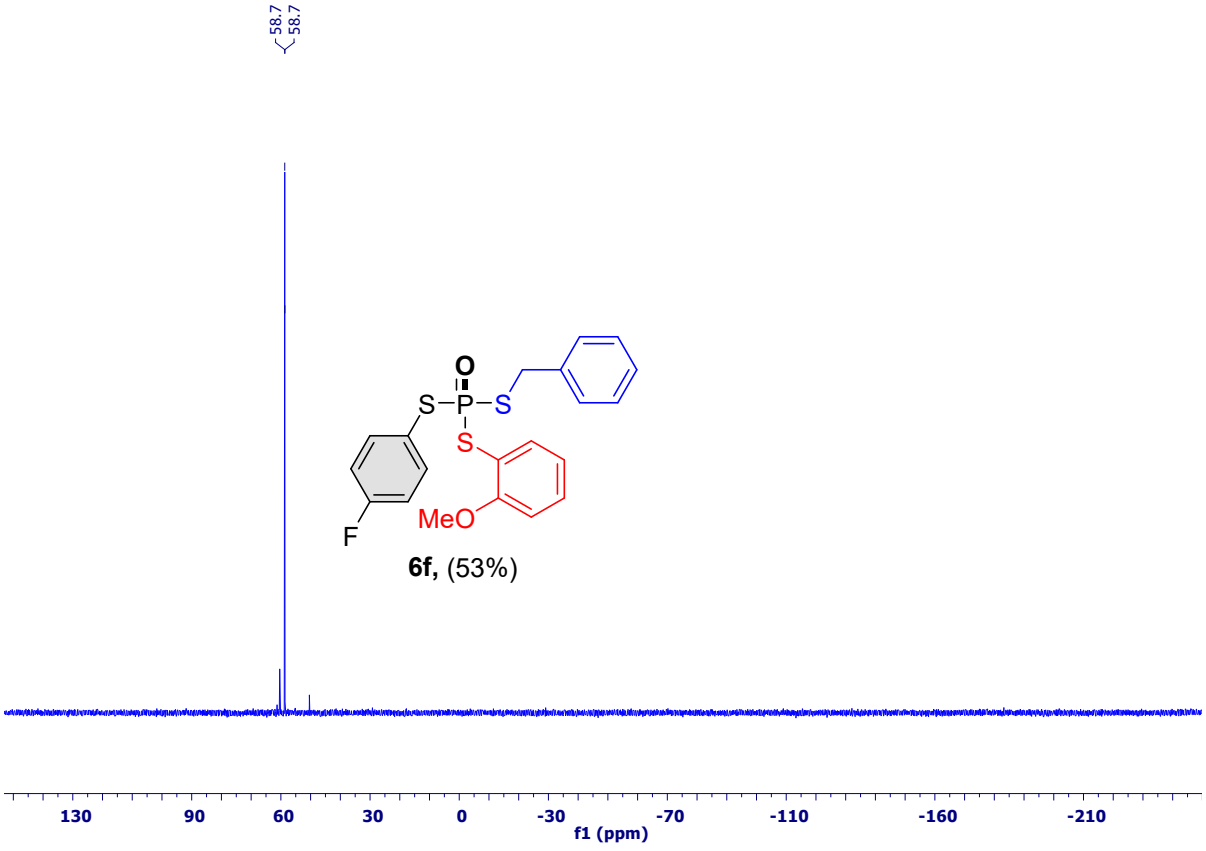


^{19}F NMR (377 MHz, $CDCl_3$



6f, (53%)

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



6f, (53%)

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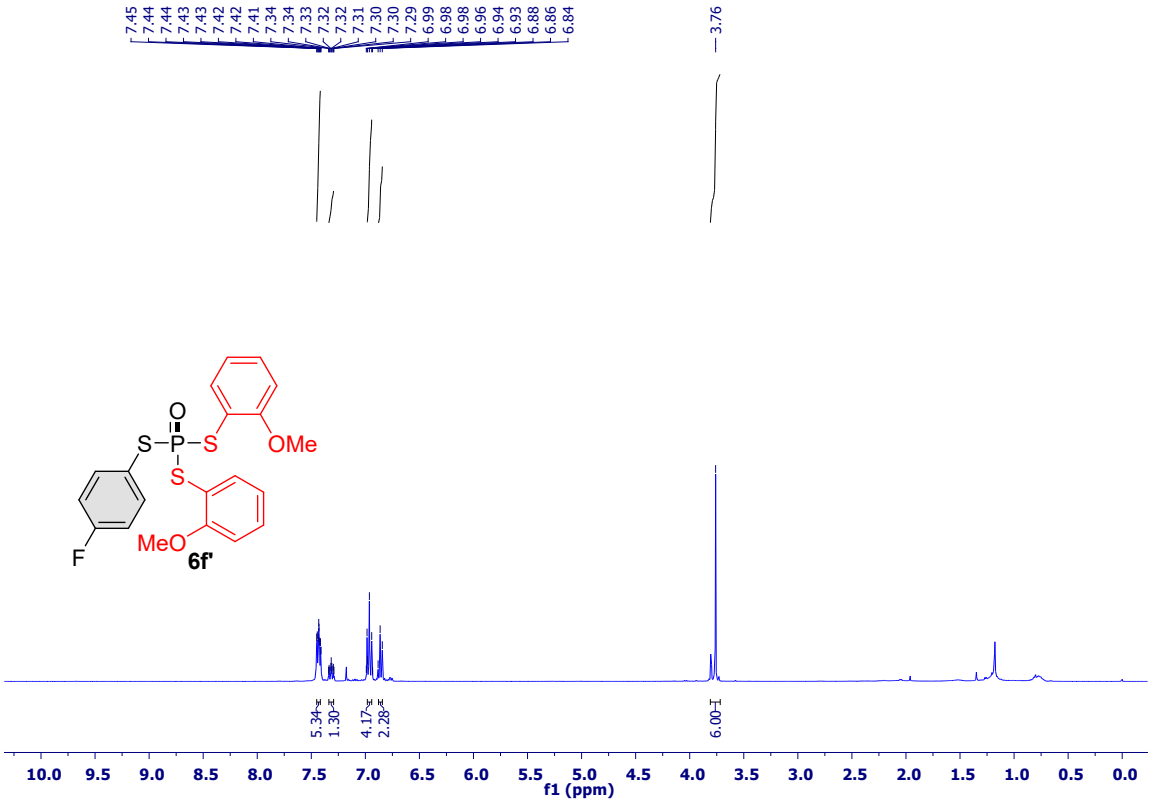

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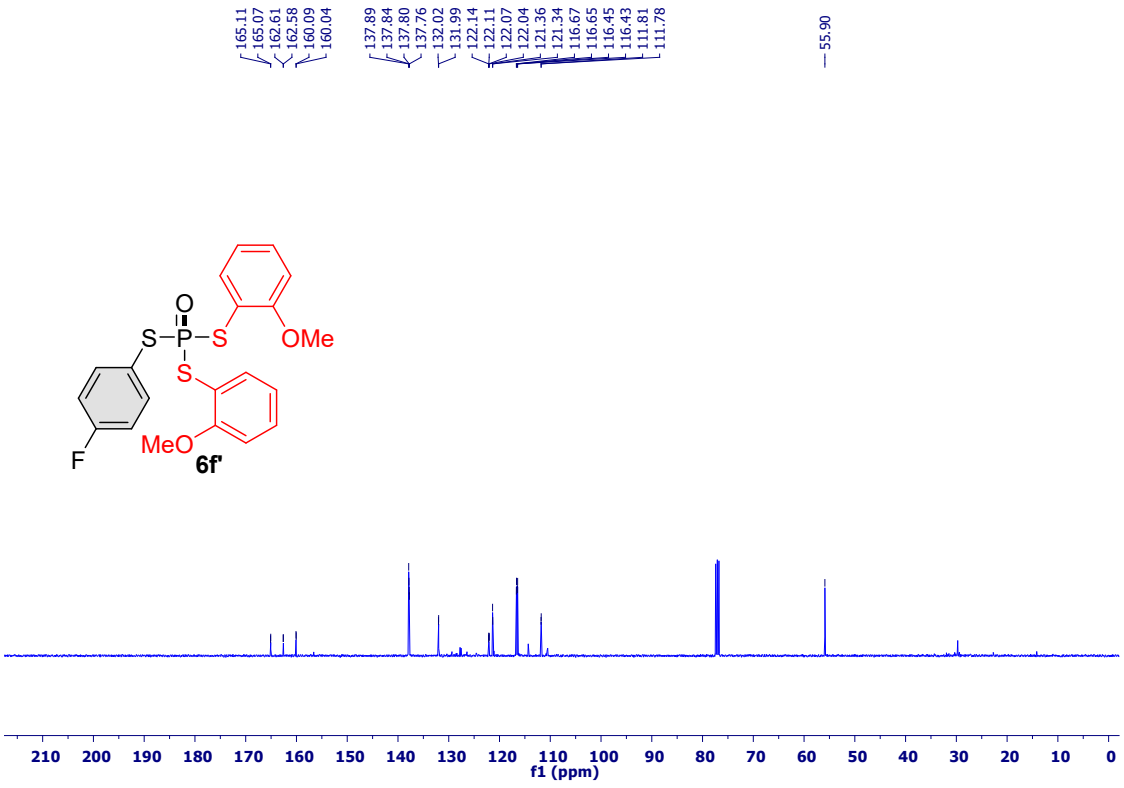

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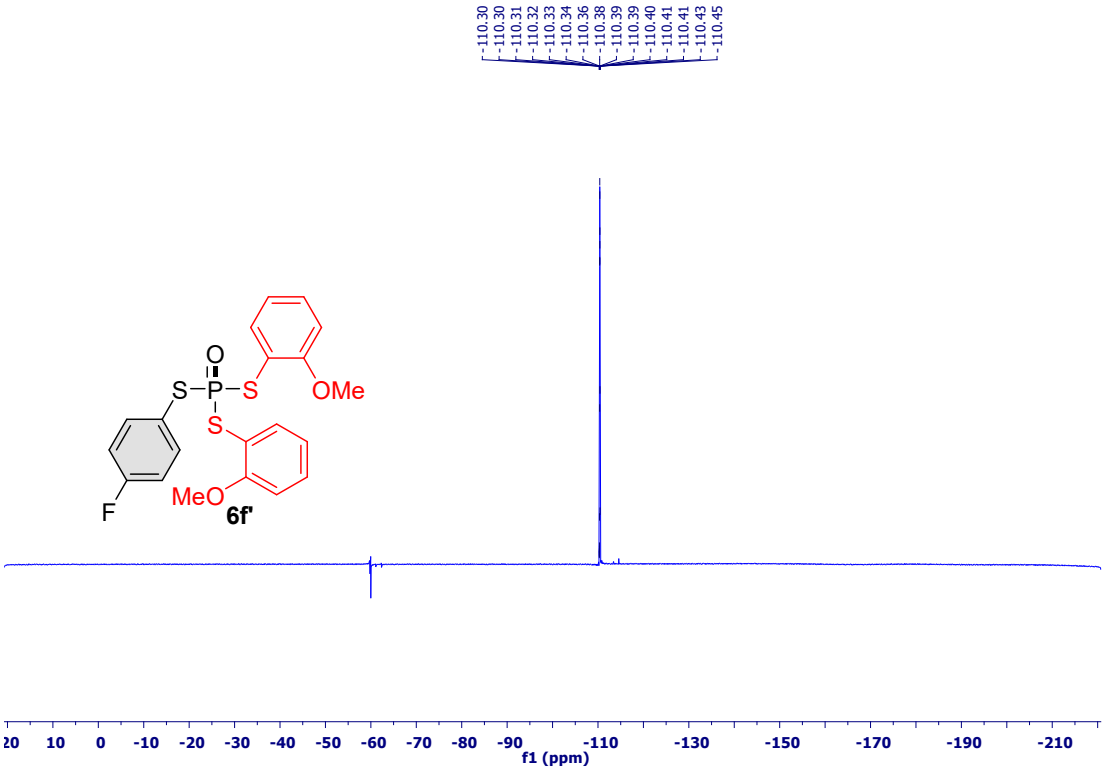

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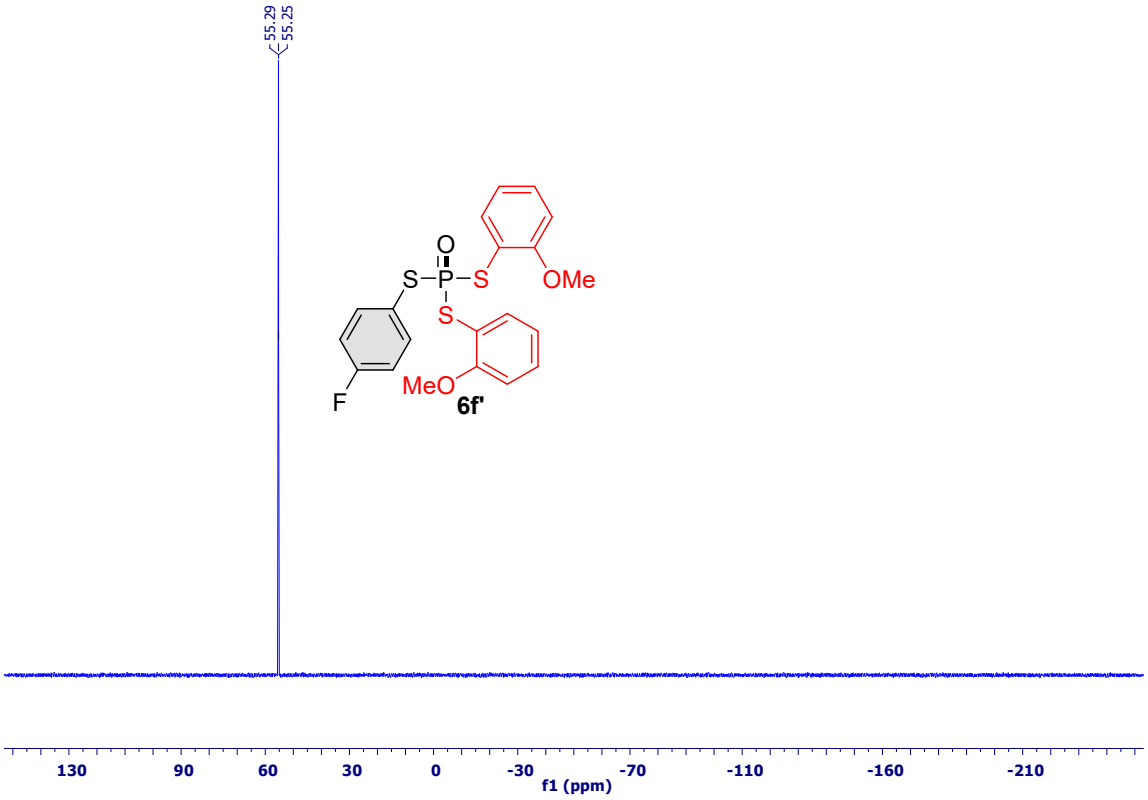
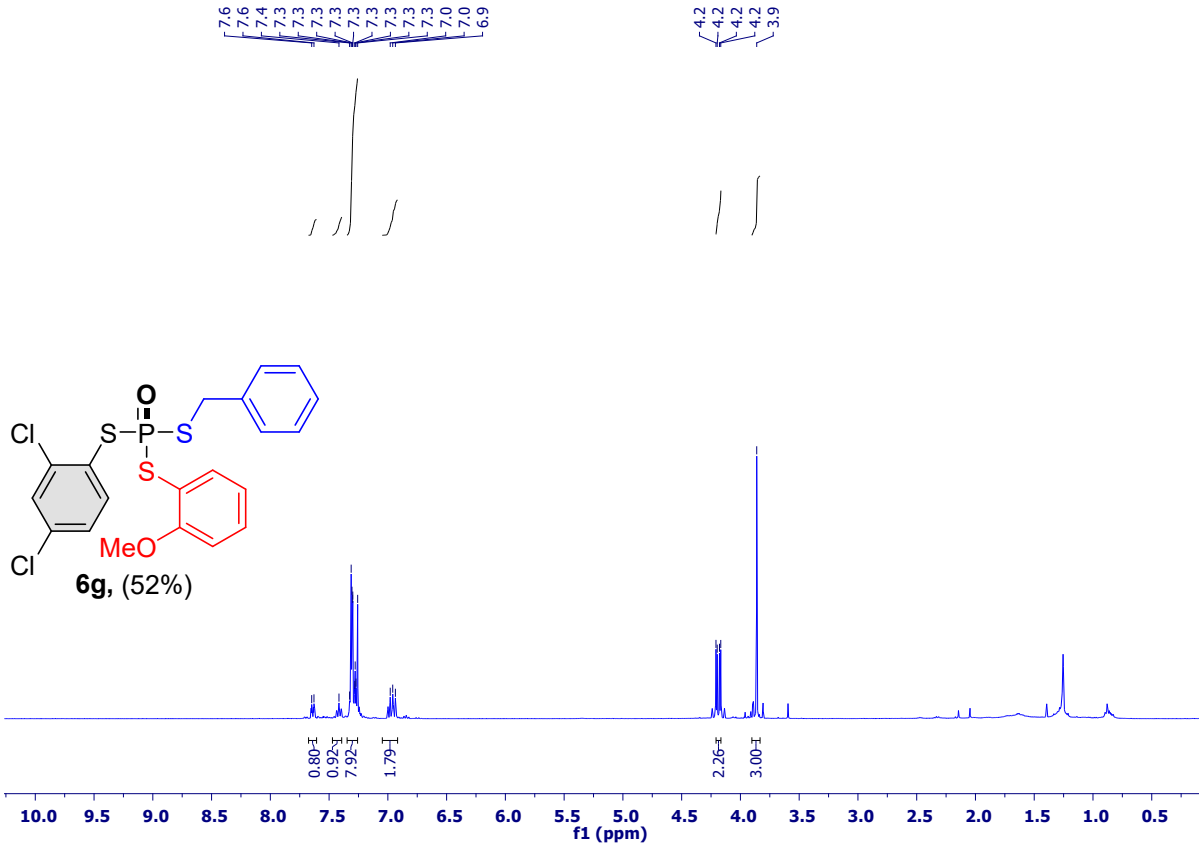


^{1}H NMR (400 MHz, $CDCl_3$)



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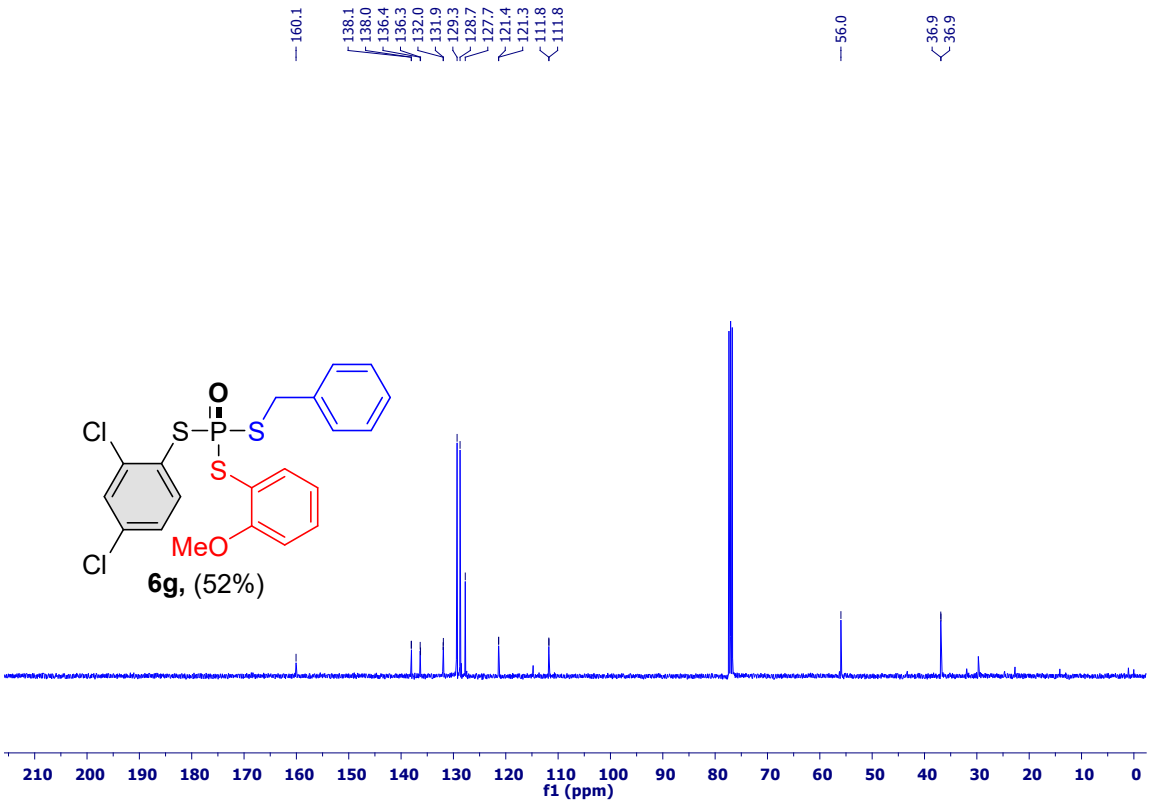
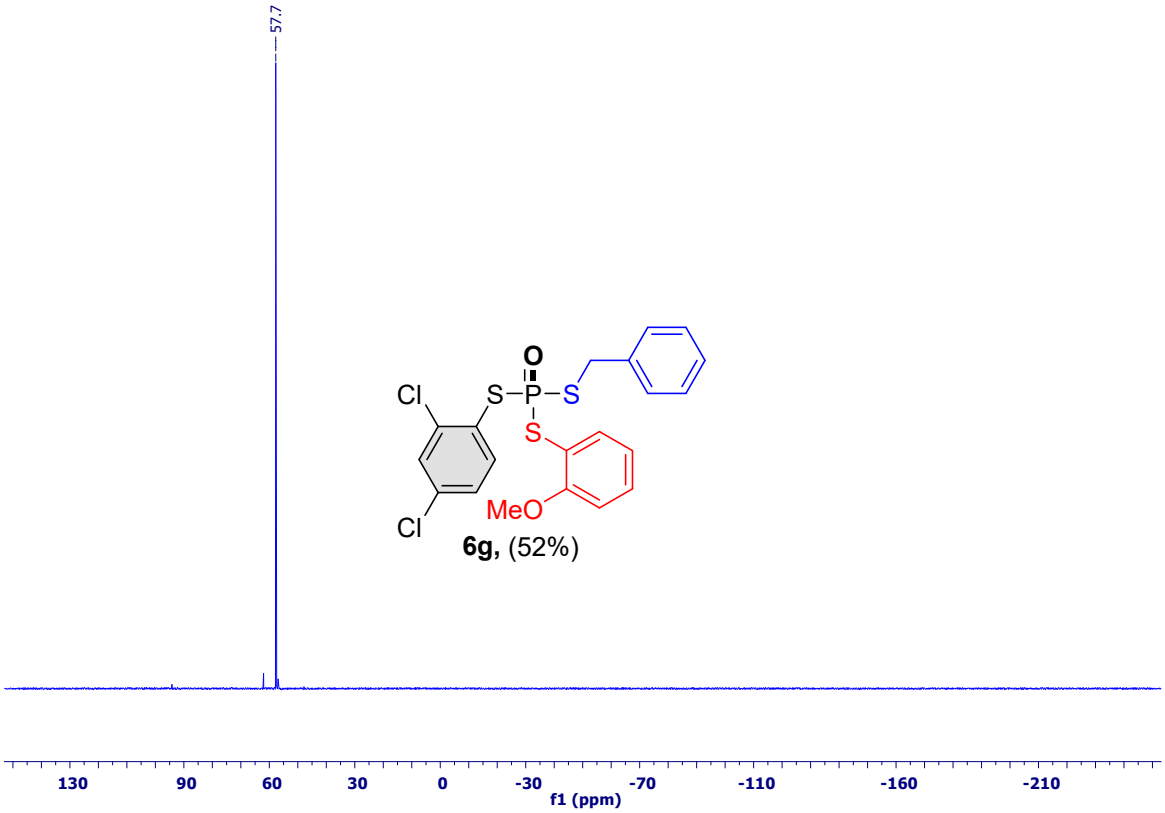


^{31}P NMR (162 MHz, $CDCl_3$)



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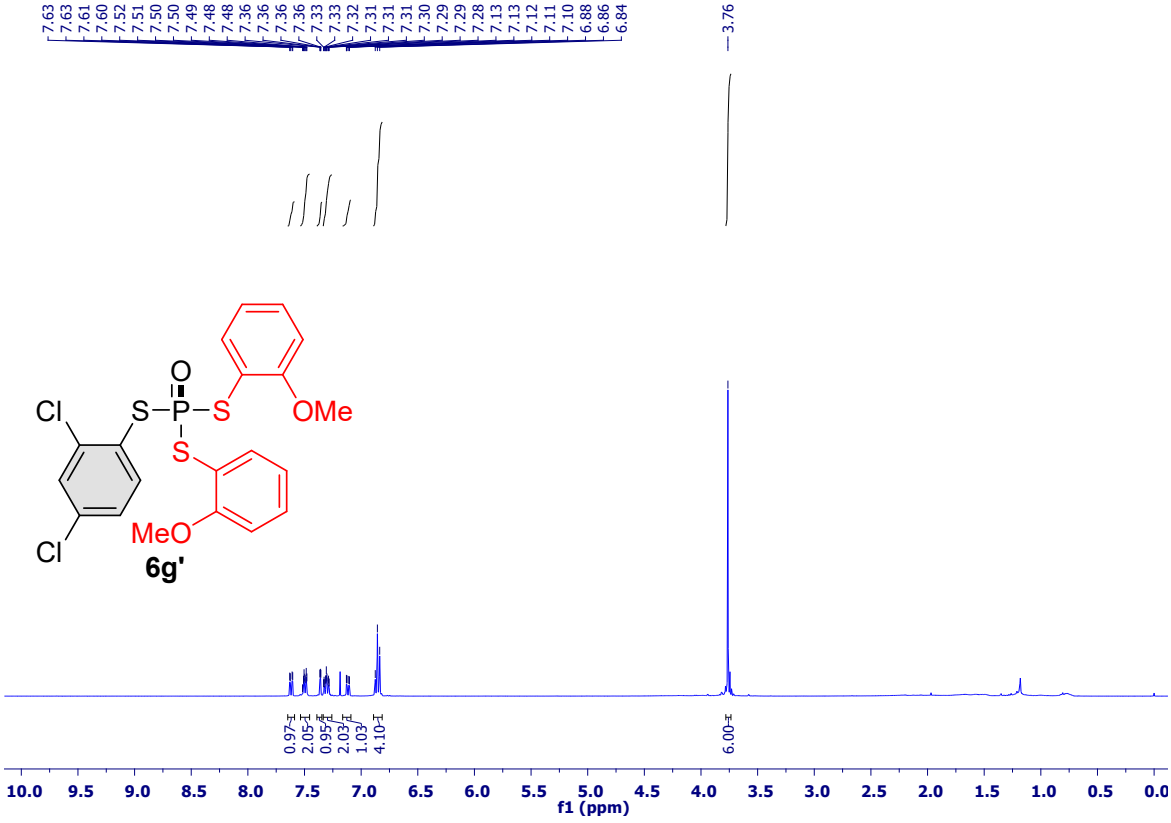
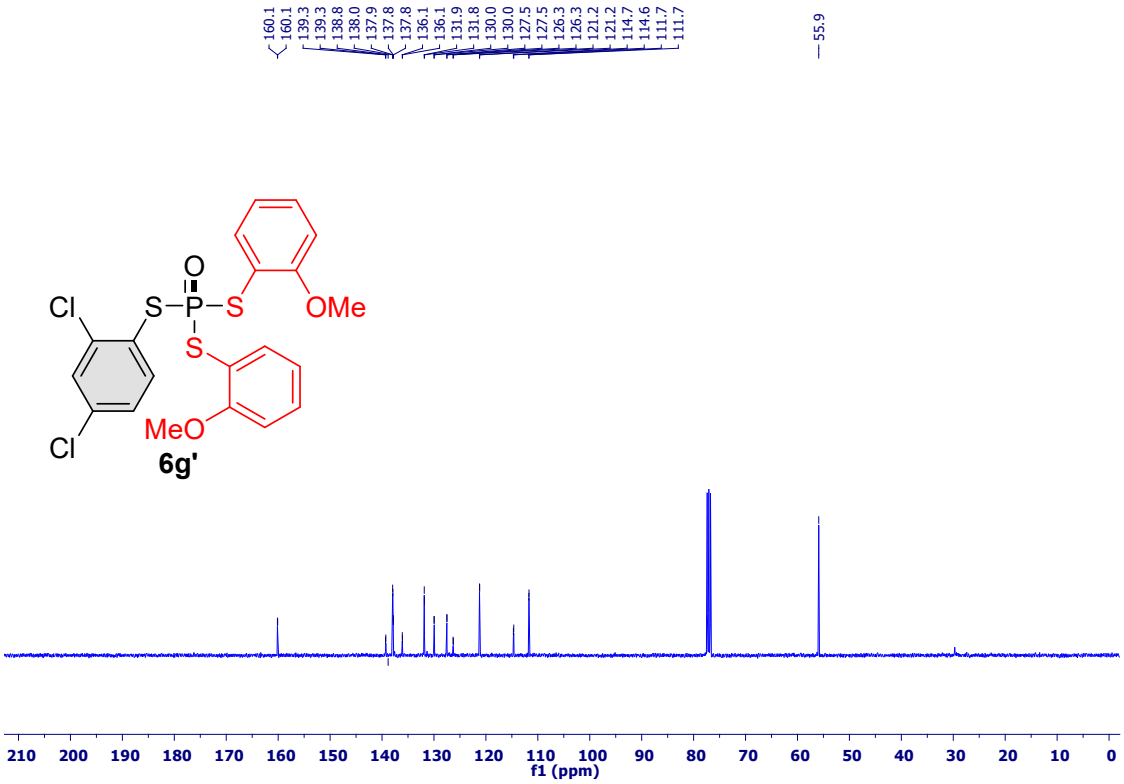
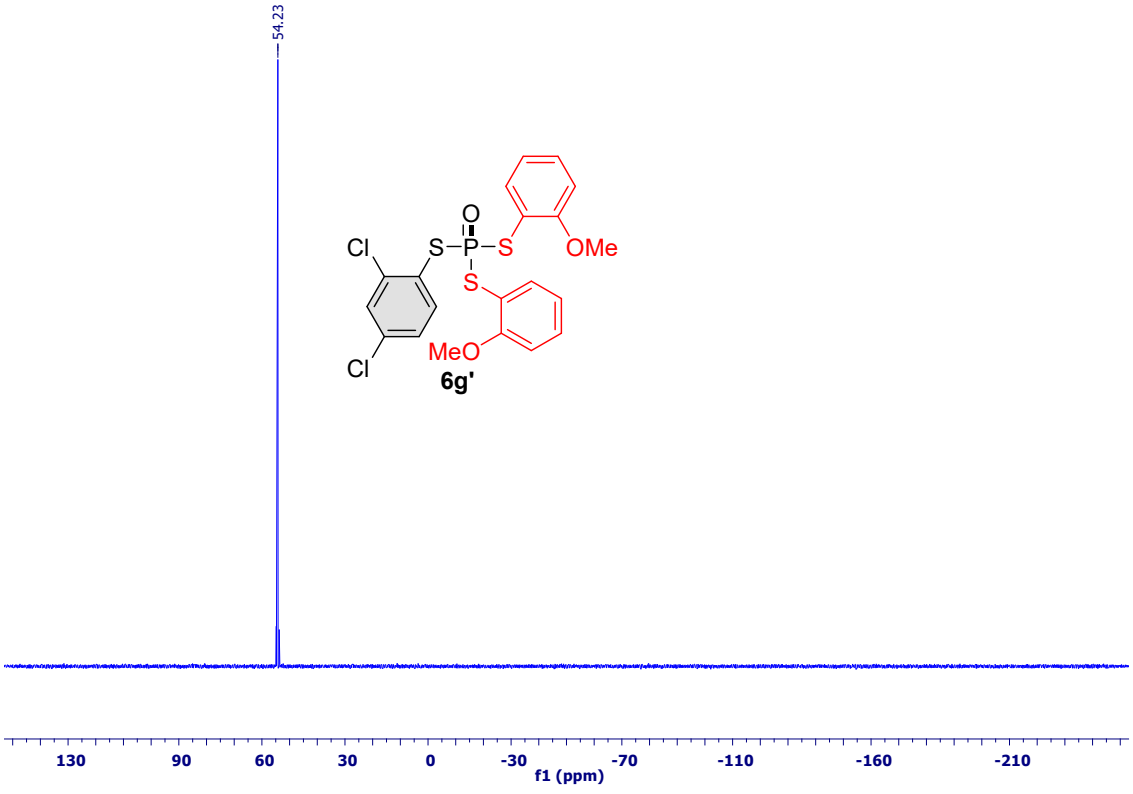


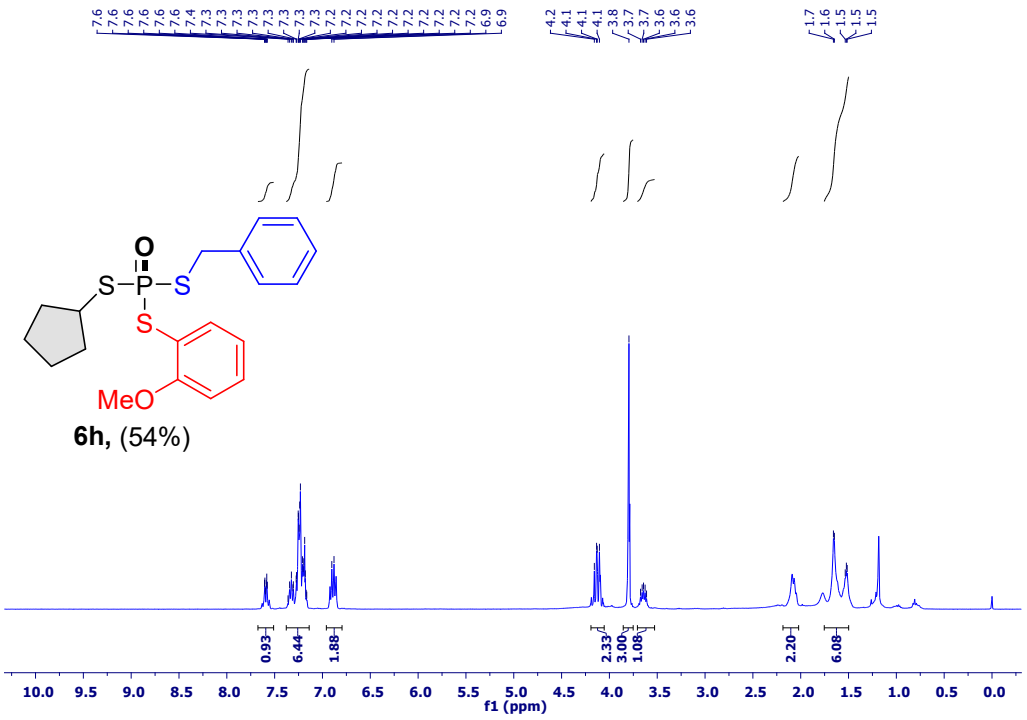
^{13}C NMR (101 MHz, $CDCl_3$)



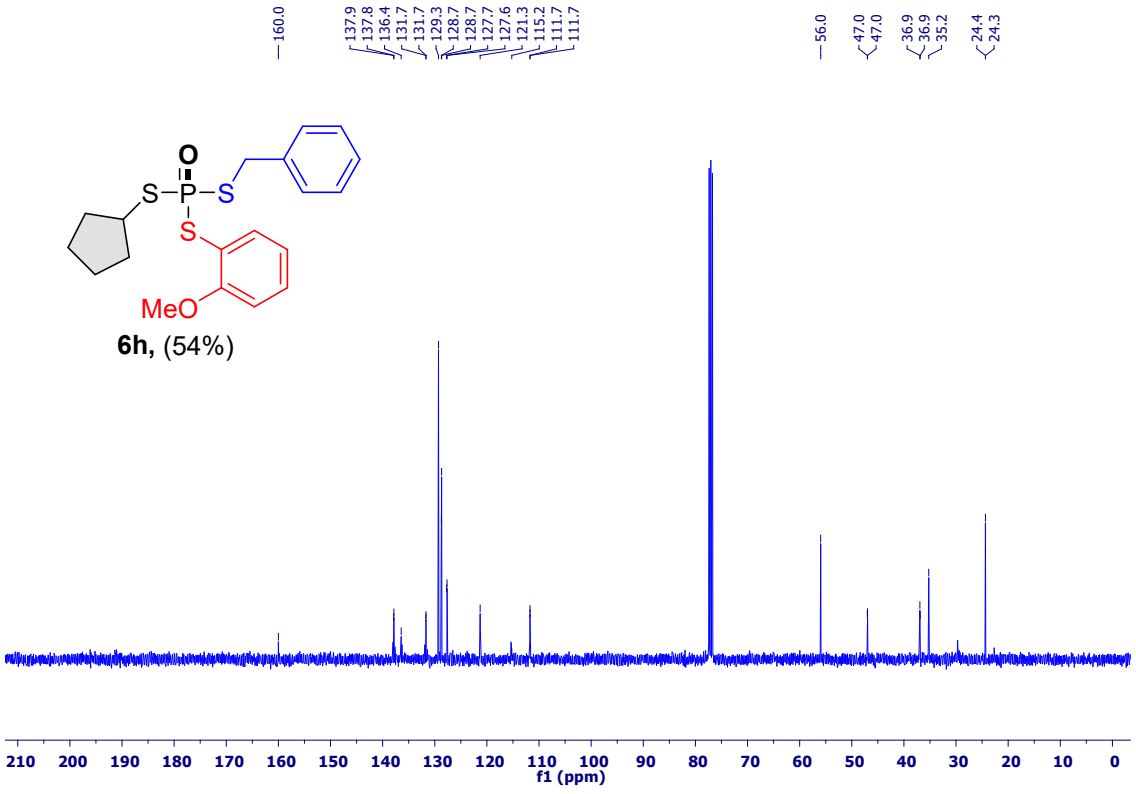
^{31}P NMR (162 MHz, $CDCl_3$)



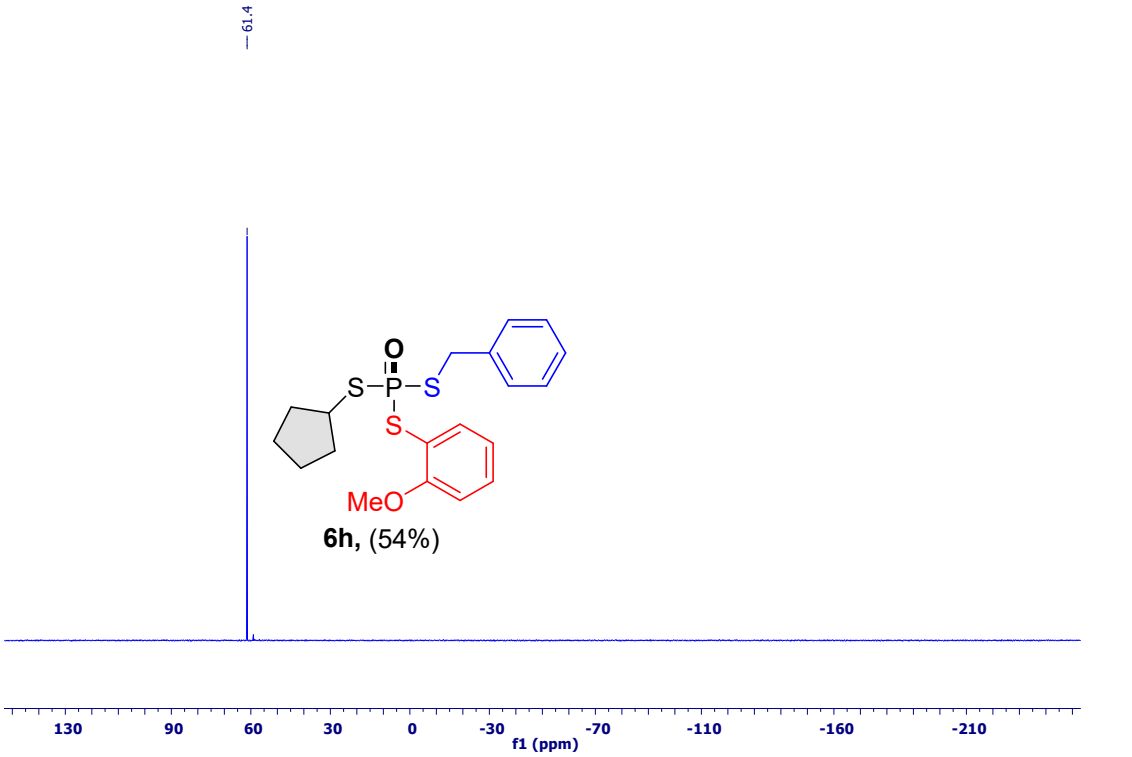
^{1}H NMR (400 MHz, $CDCl_3$)



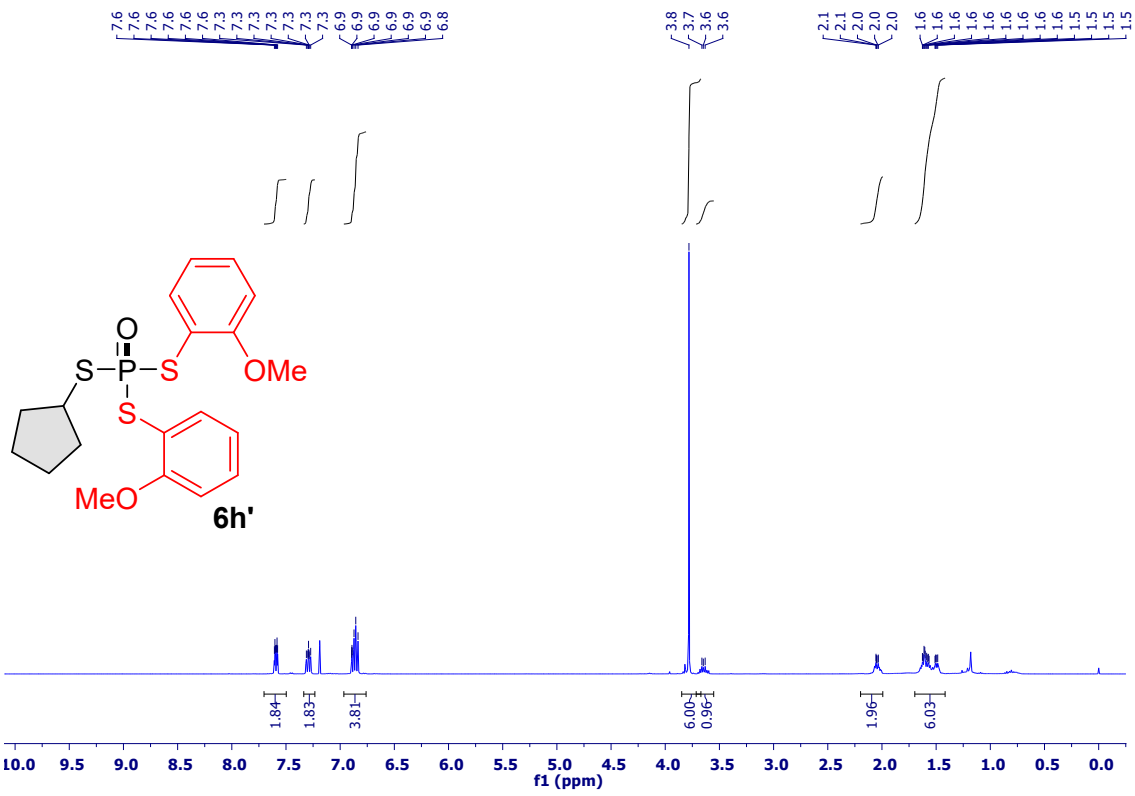
^{13}C NMR (101 MHz, $CDCl_3$)



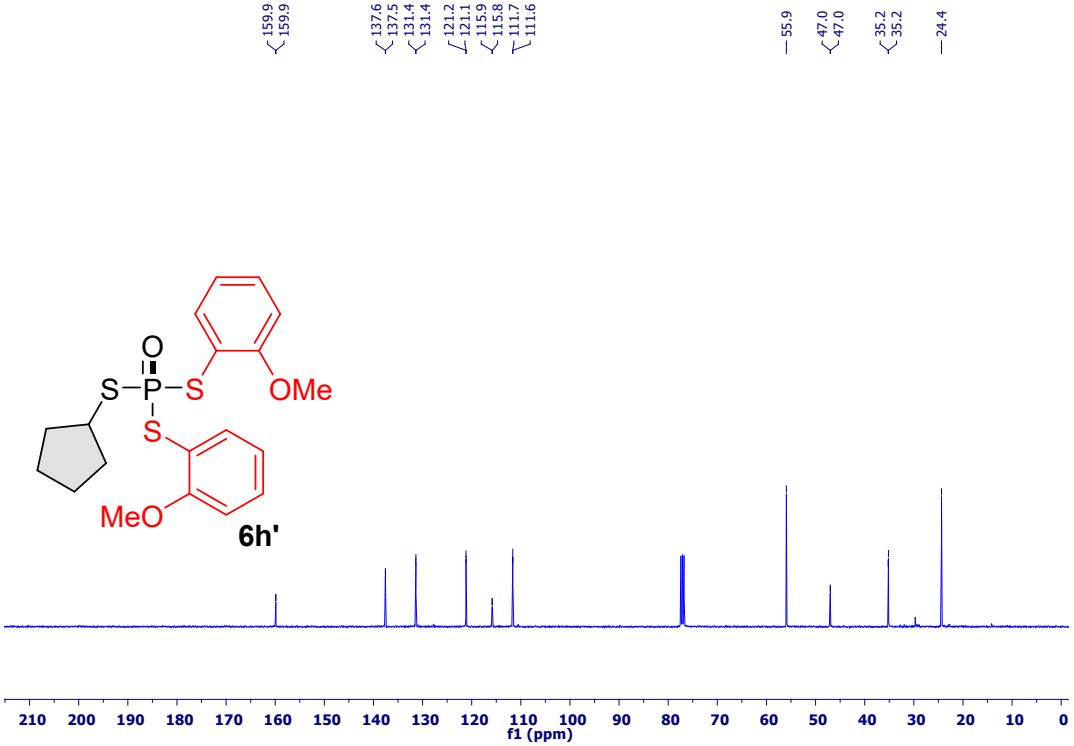
^{31}P NMR (162 MHz, $CDCl_3$)



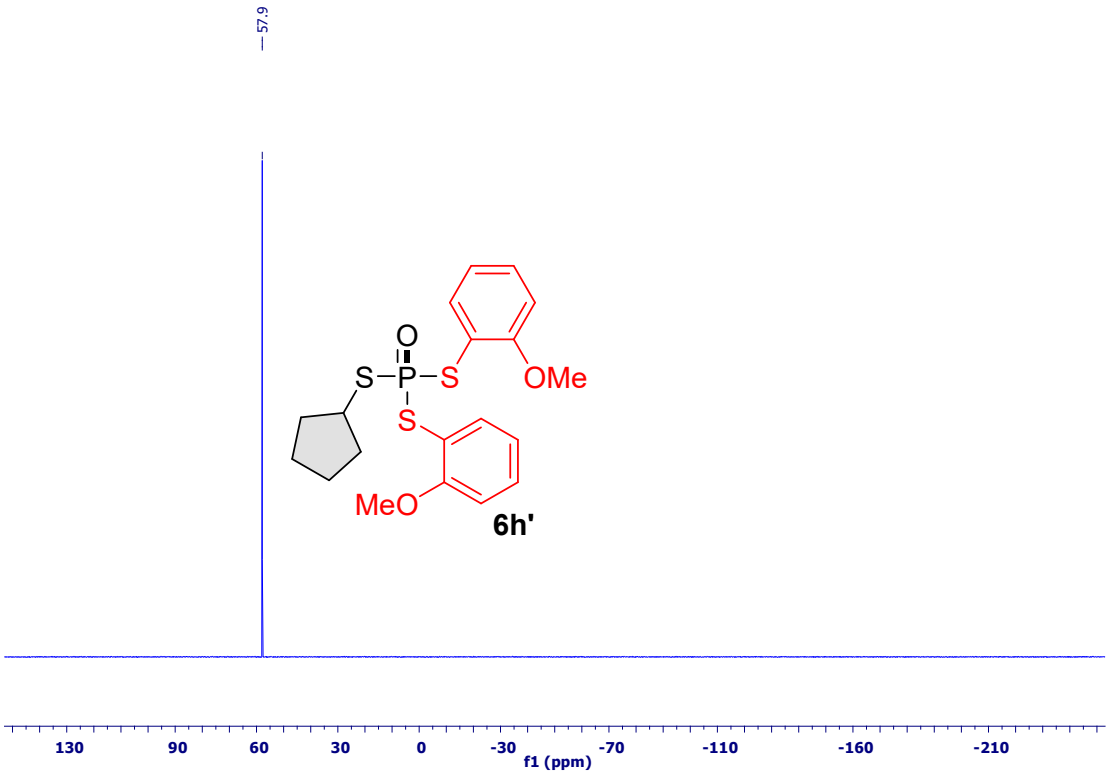
^{1}H NMR (400 MHz, $CDCl_3$)



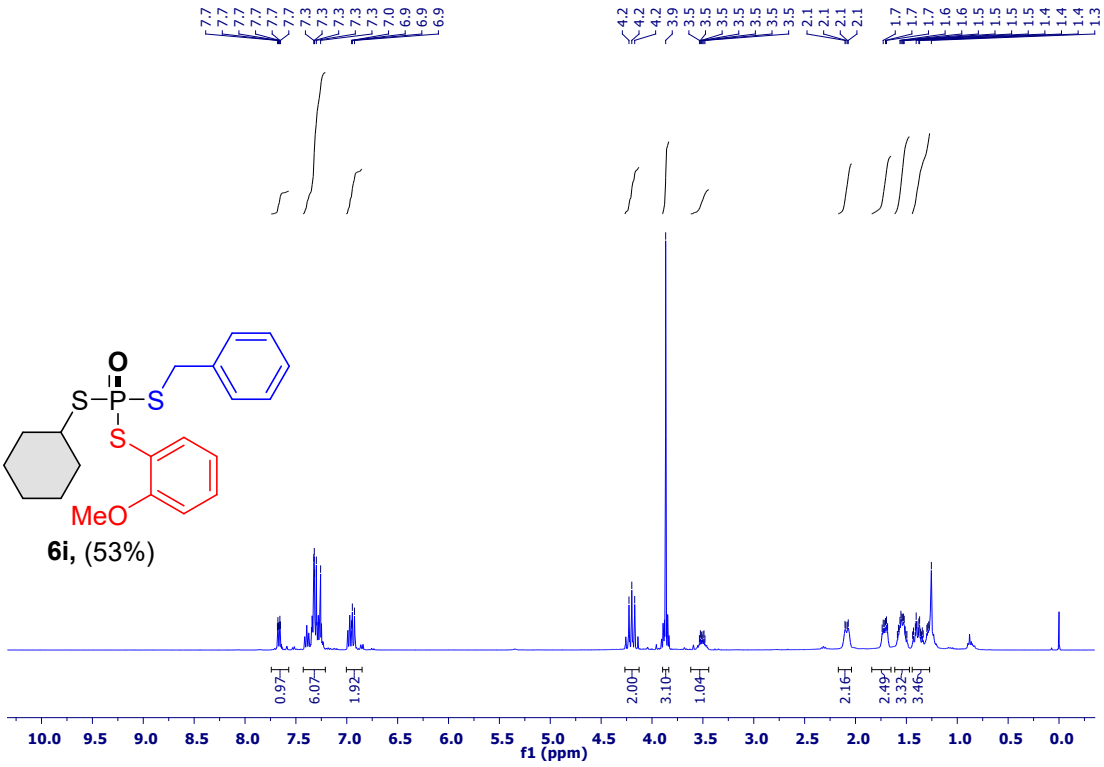
^{13}C NMR (101 MHz, $CDCl_3$)



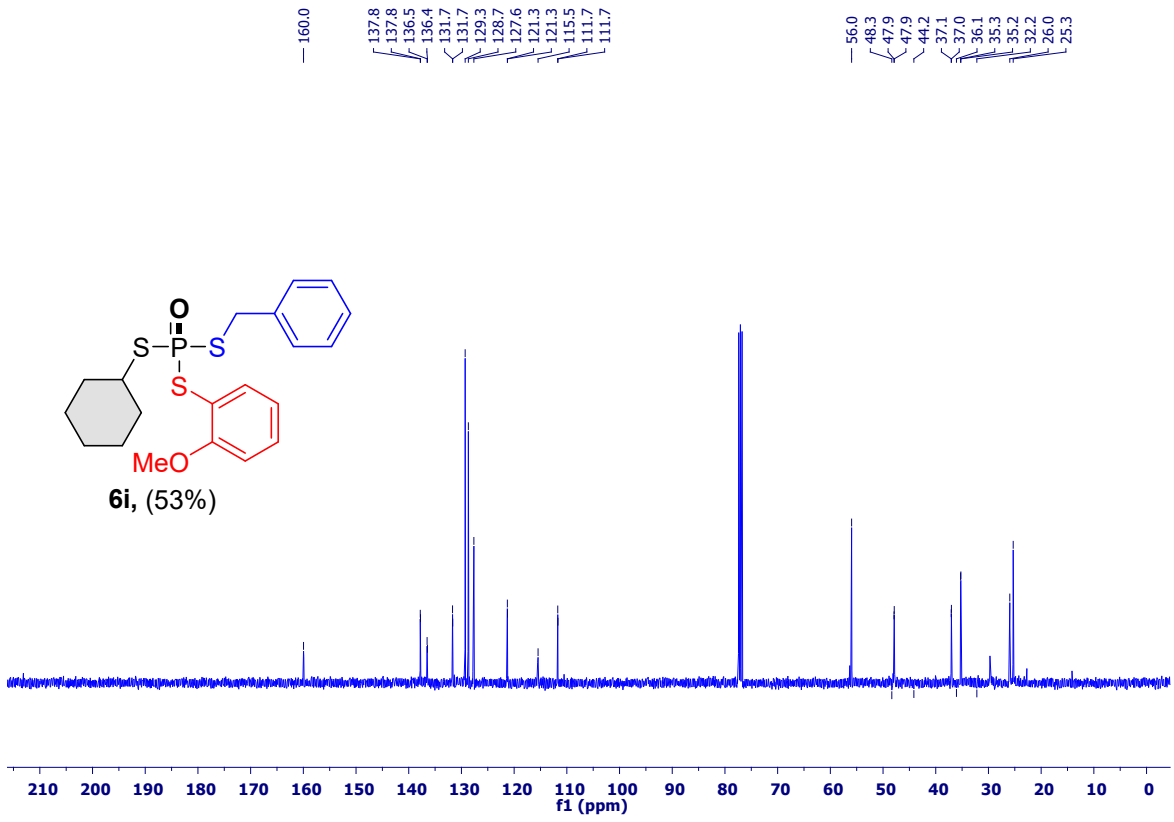
^{31}P NMR (162 MHz, $CDCl_3$)



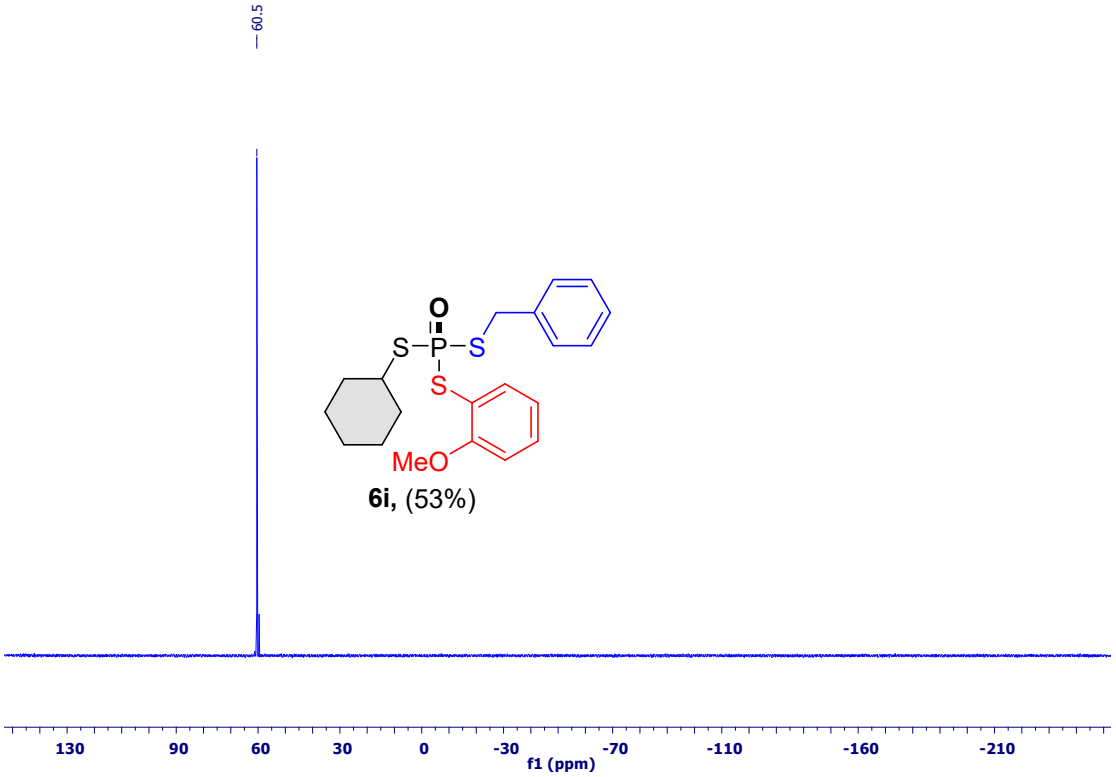
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

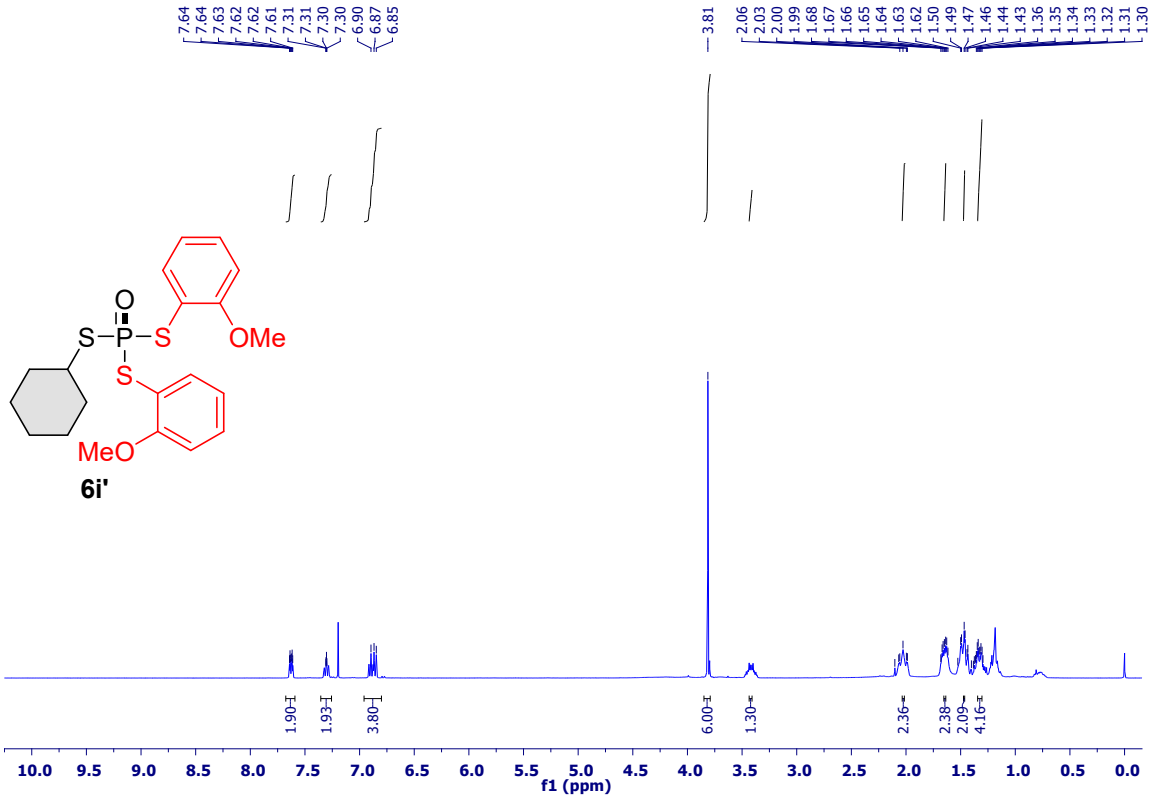


^{31}P NMR (162 MHz, $CDCl_3$)



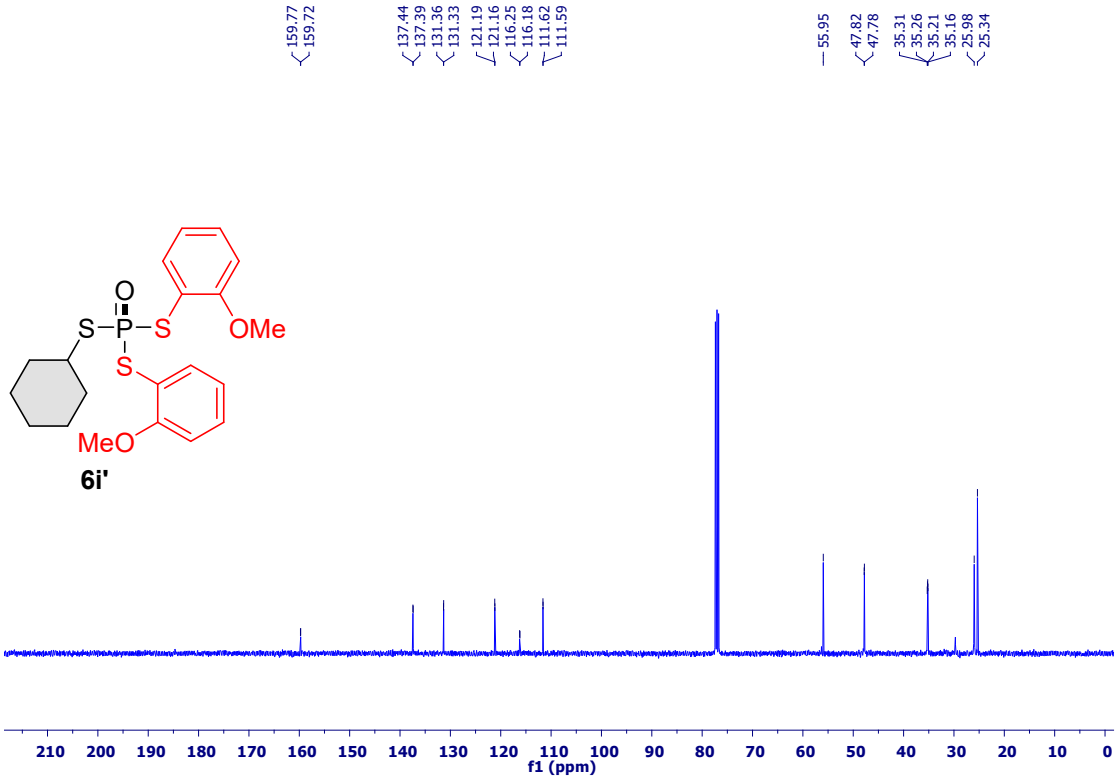
6i, (53%)

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

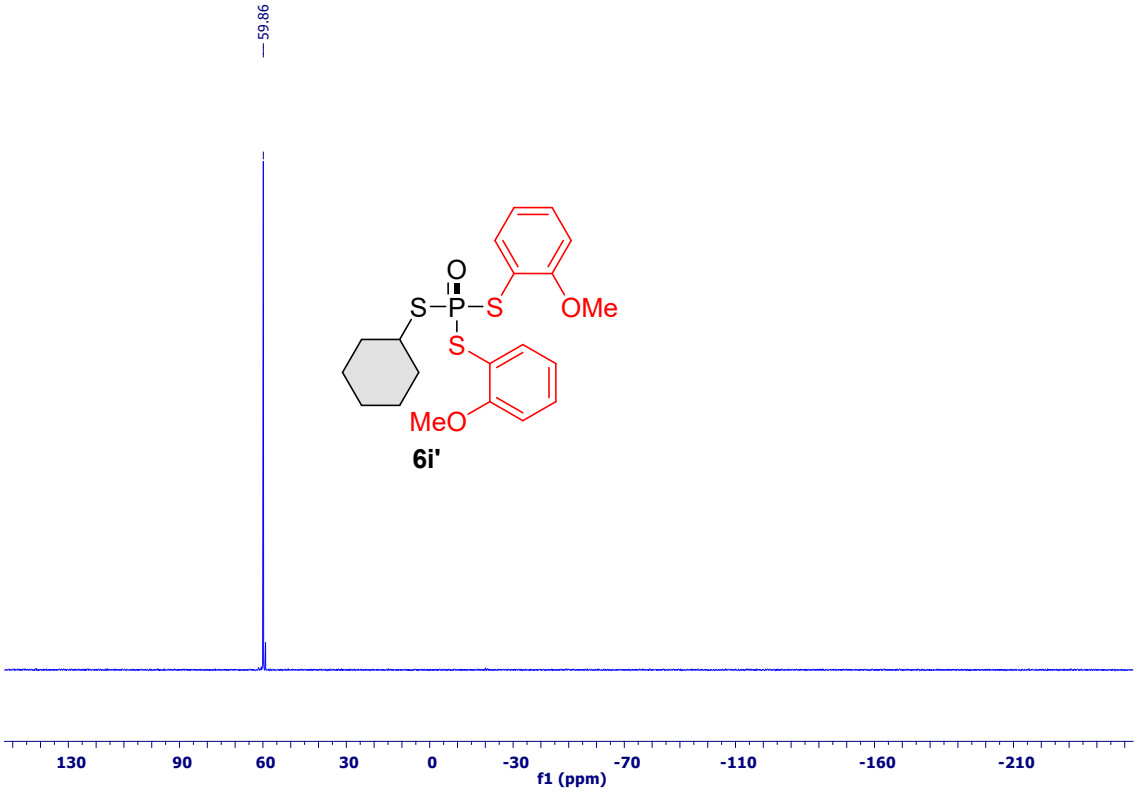


6i'

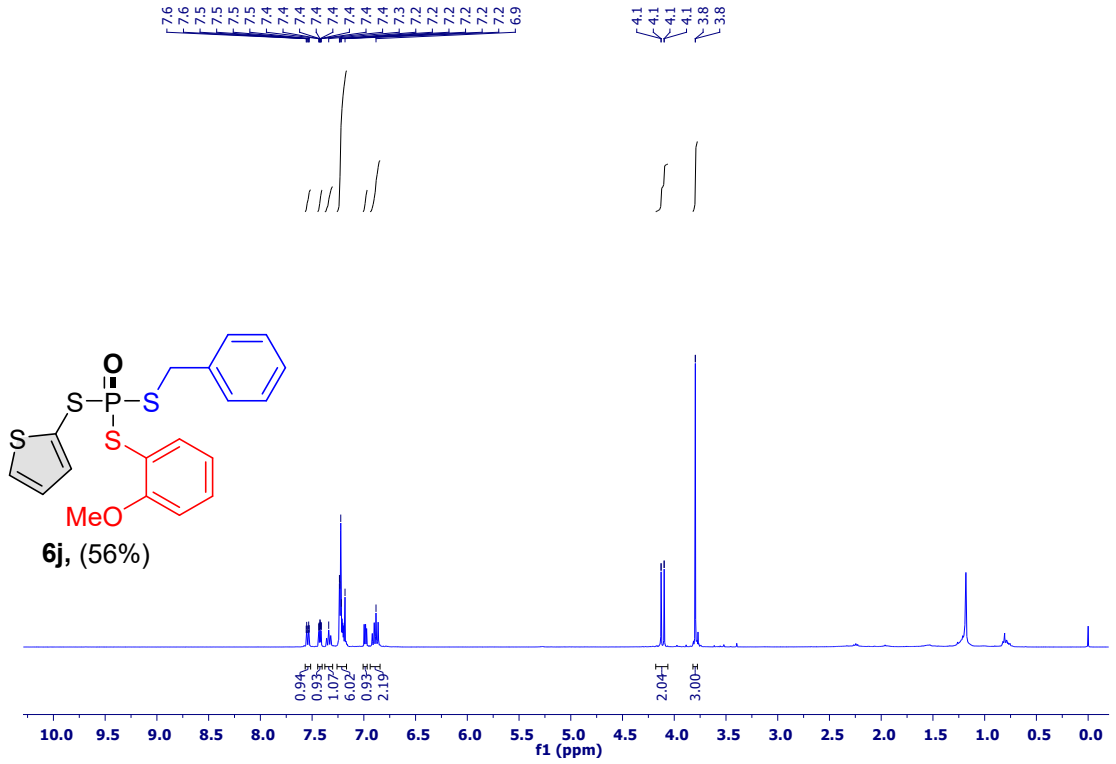
^{13}C NMR (101 MHz, $CDCl_3$)



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

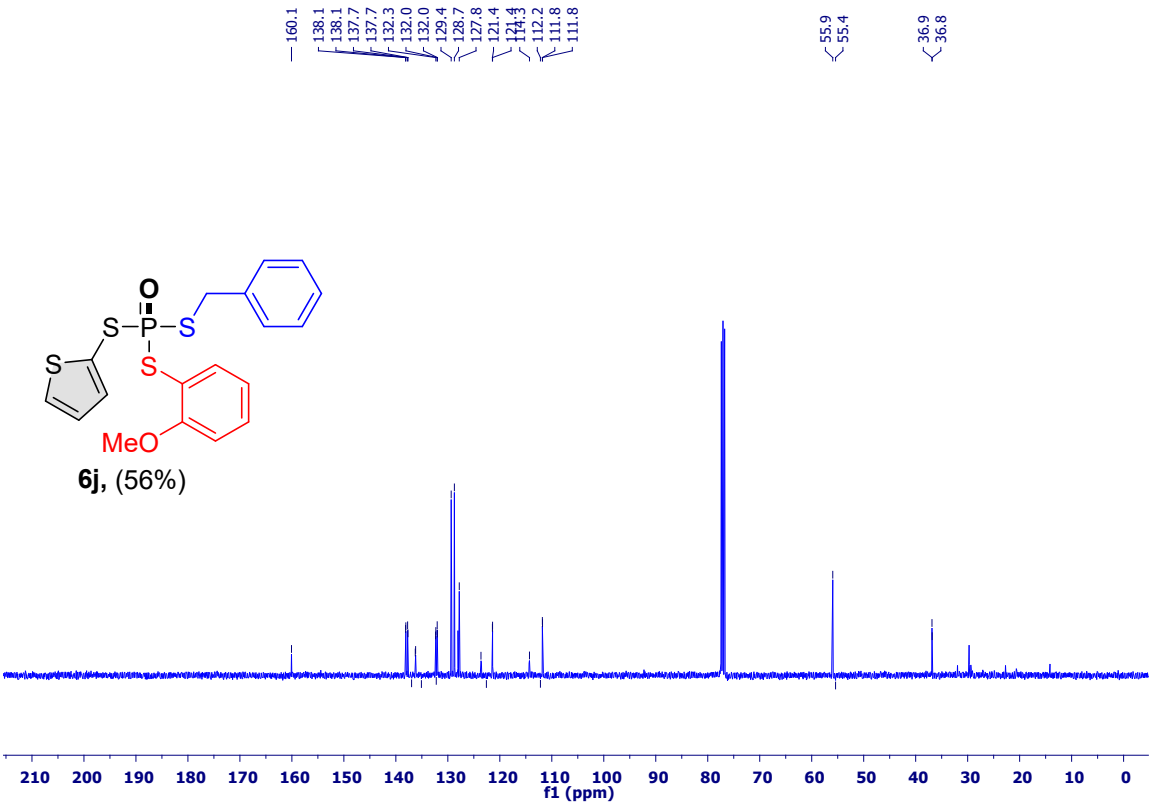


^{1}H NMR (400 MHz, $CDCl_3$)



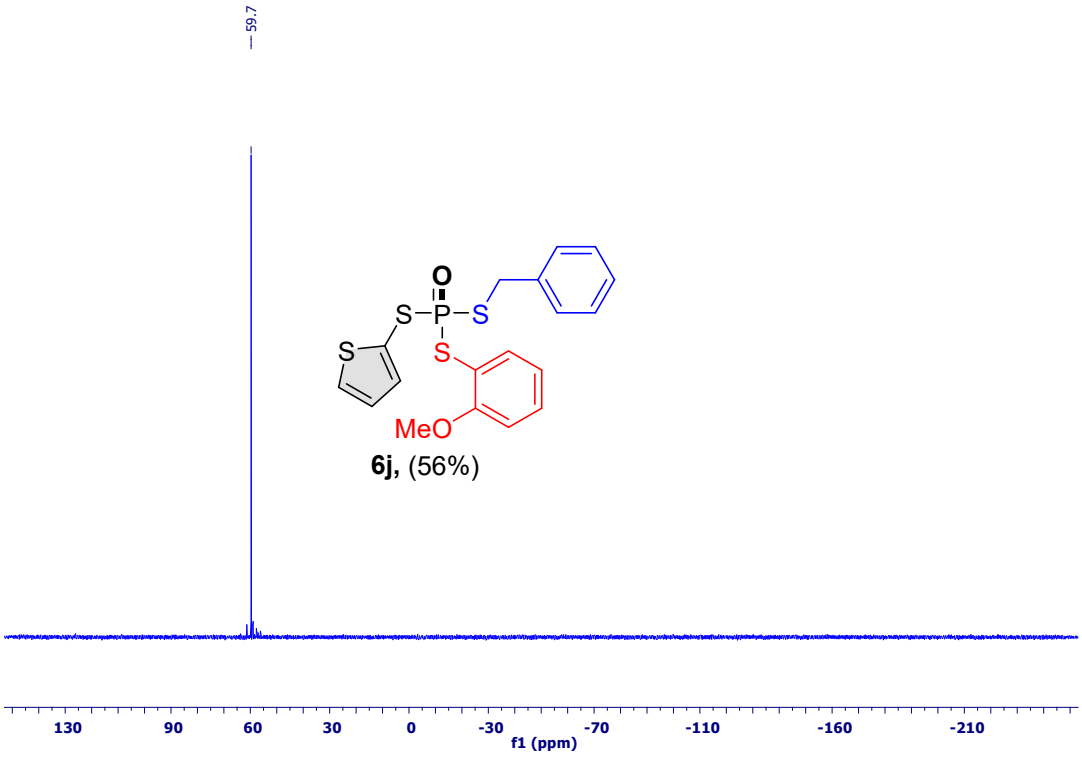
6j, (56%)

^{13}C NMR (101 MHz, $CDCl_3$)

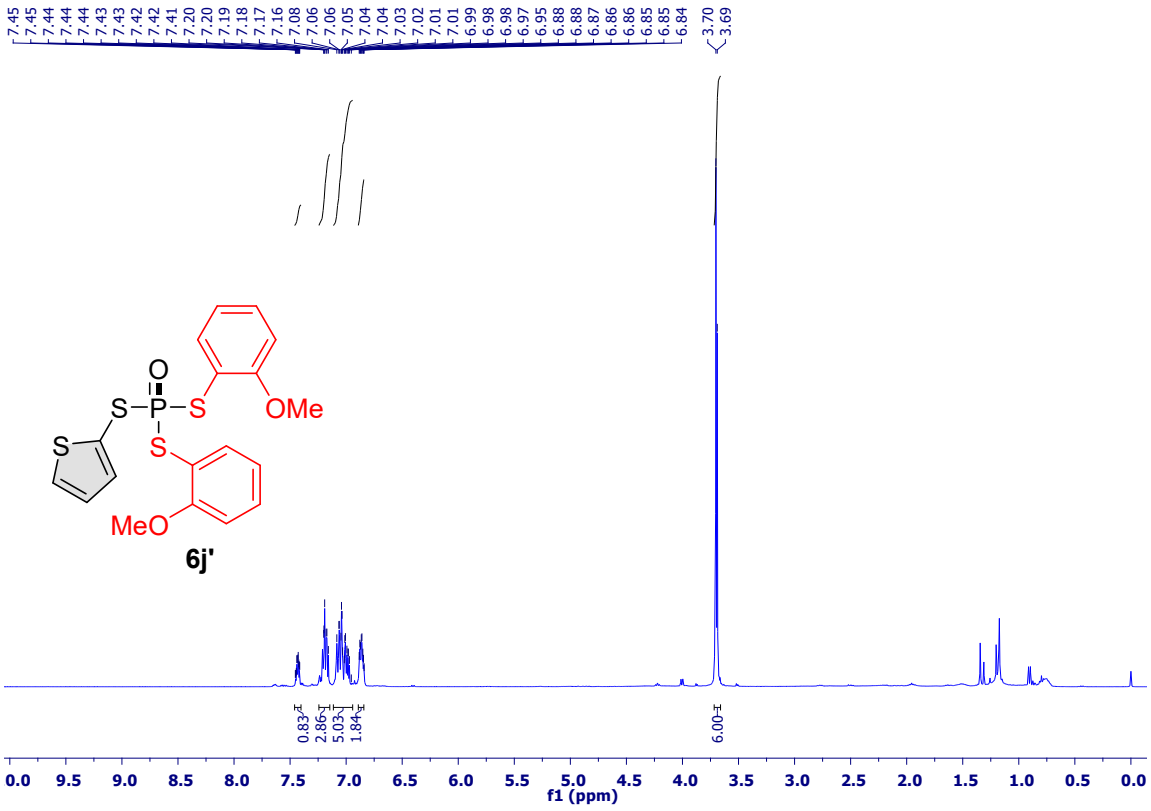


6j, (56%)

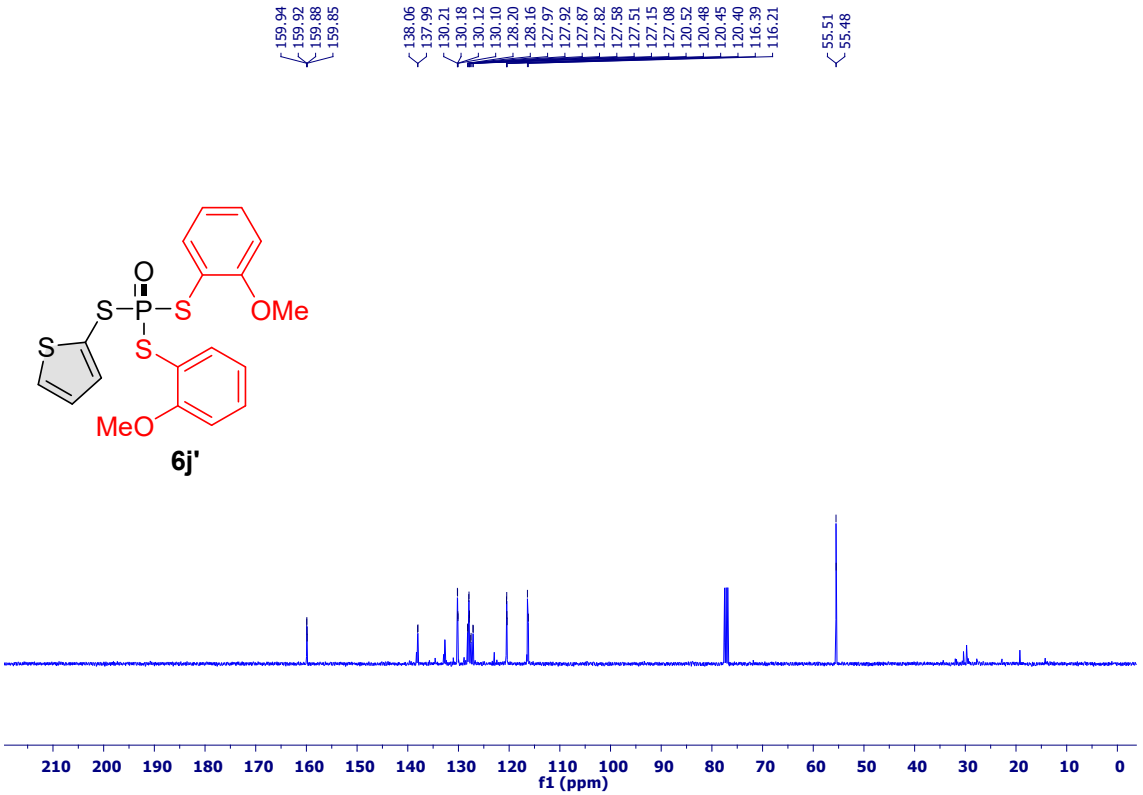
^{31}P NMR (162 MHz, $CDCl_3$)



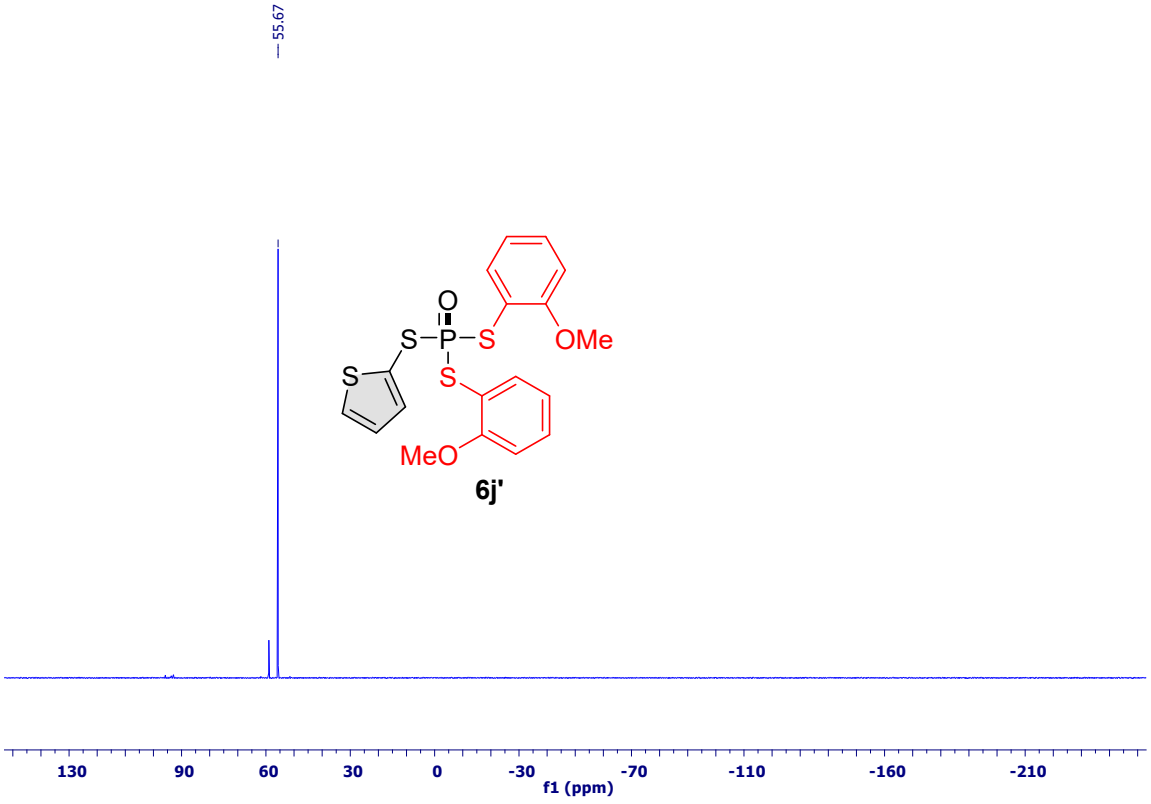
^{1}H NMR (400 MHz, $CDCl_3$)



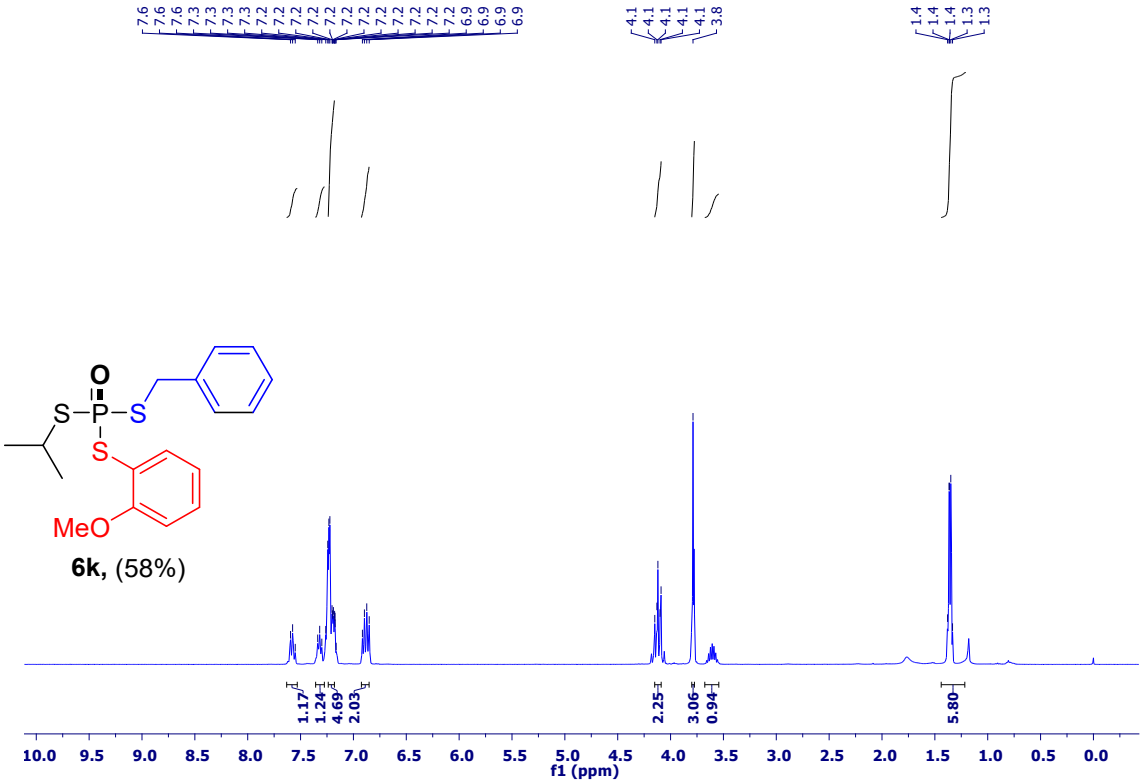
^{13}C NMR (101 MHz, $CDCl_3$)



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

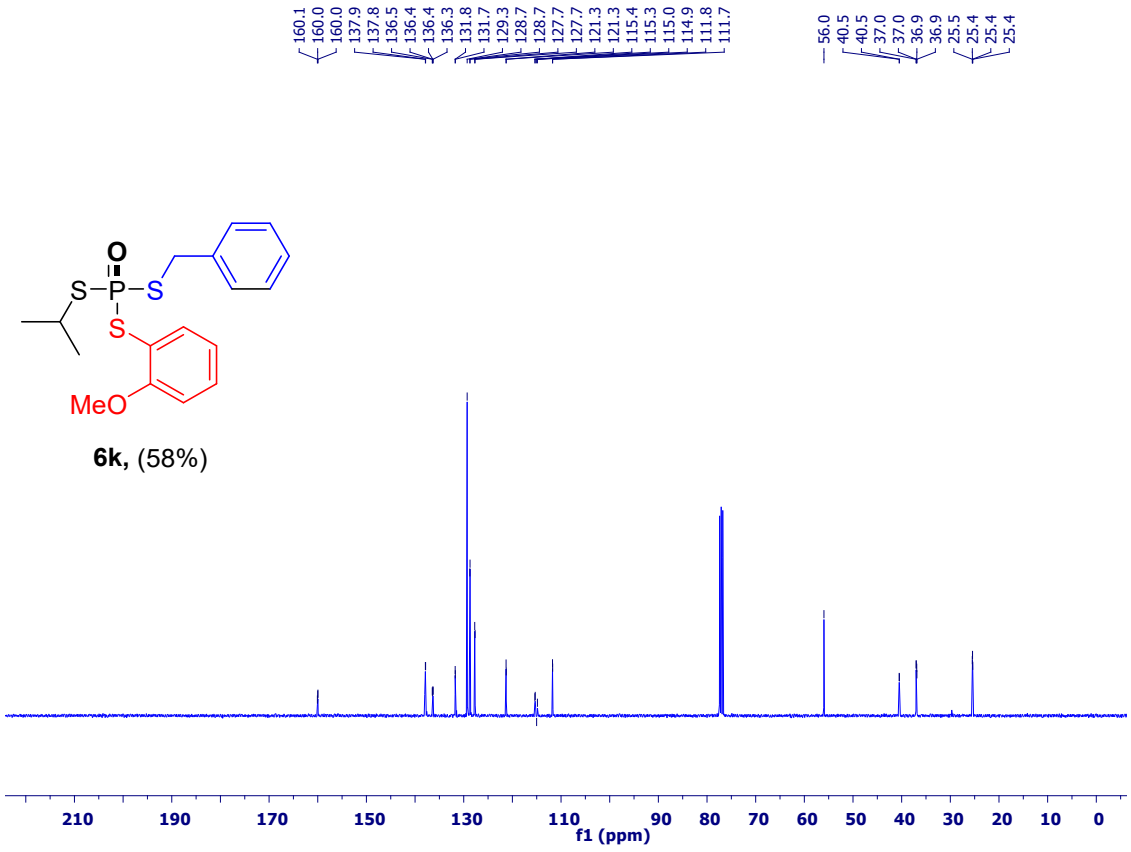


^{1}H NMR (400 MHz, $CDCl_3$)



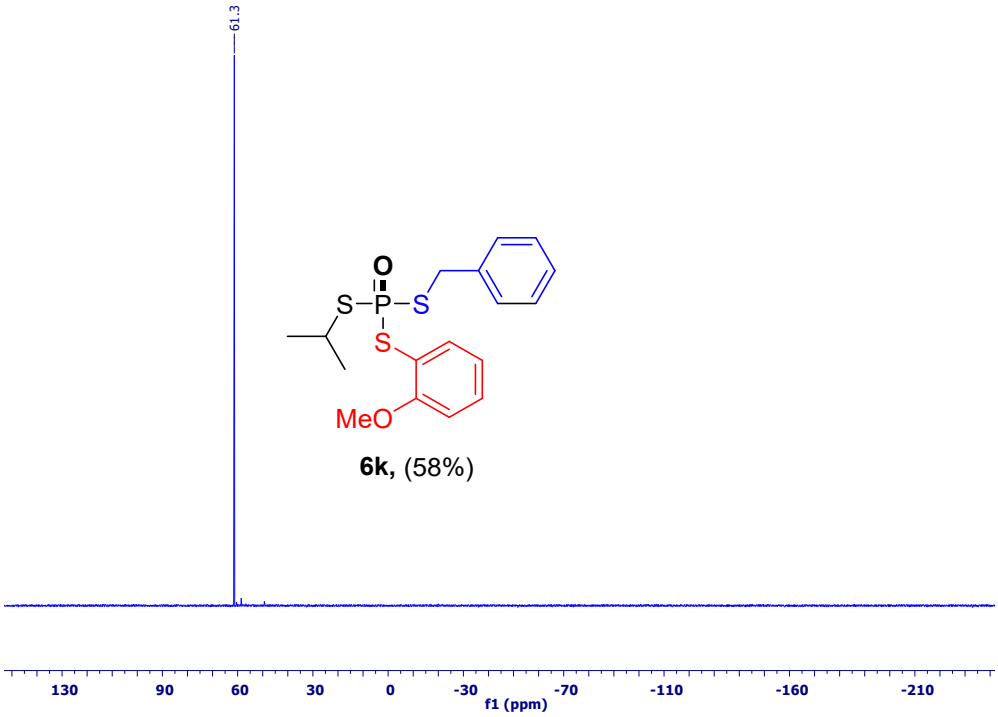
6k, (58%)

^{13}C NMR (101 MHz, $CDCl_3$)



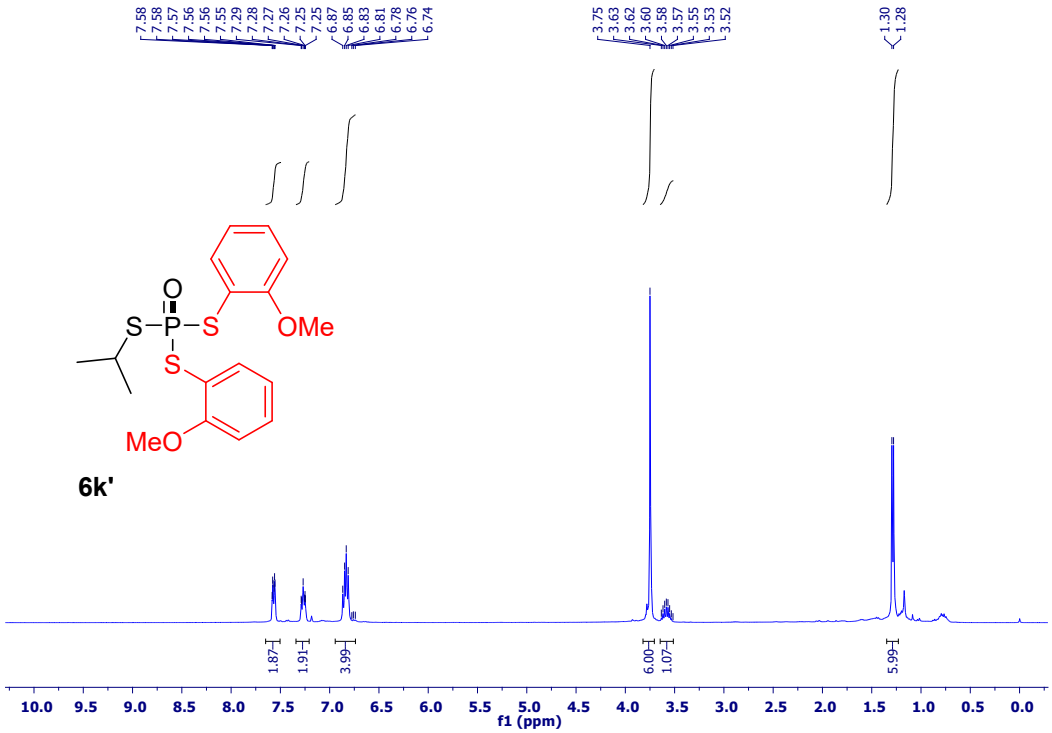
6k, (58%)

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



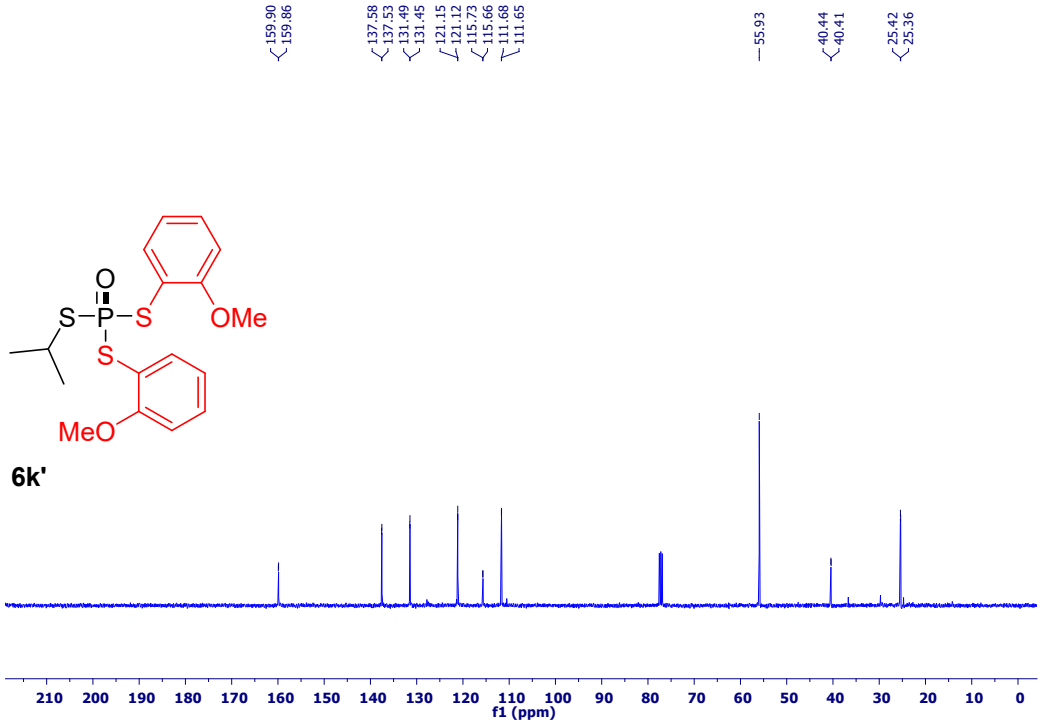
6k, (58%)

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

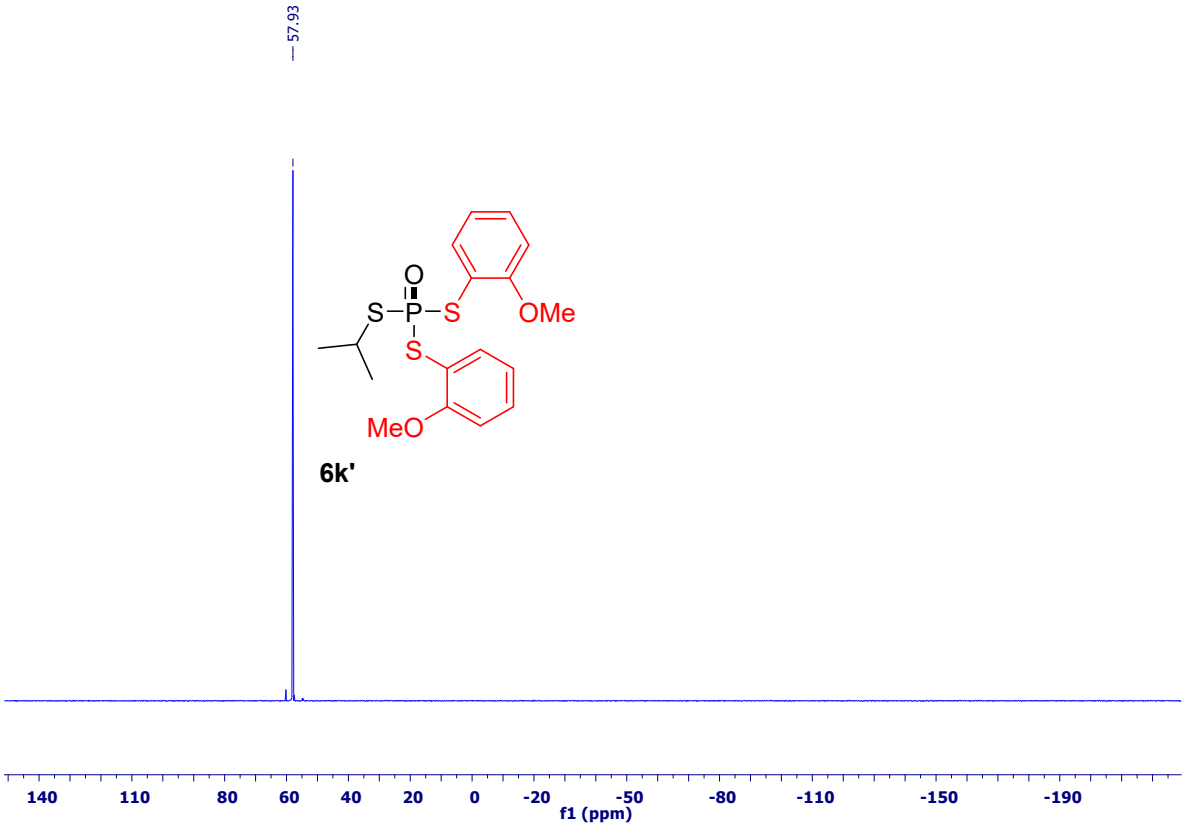


6k'

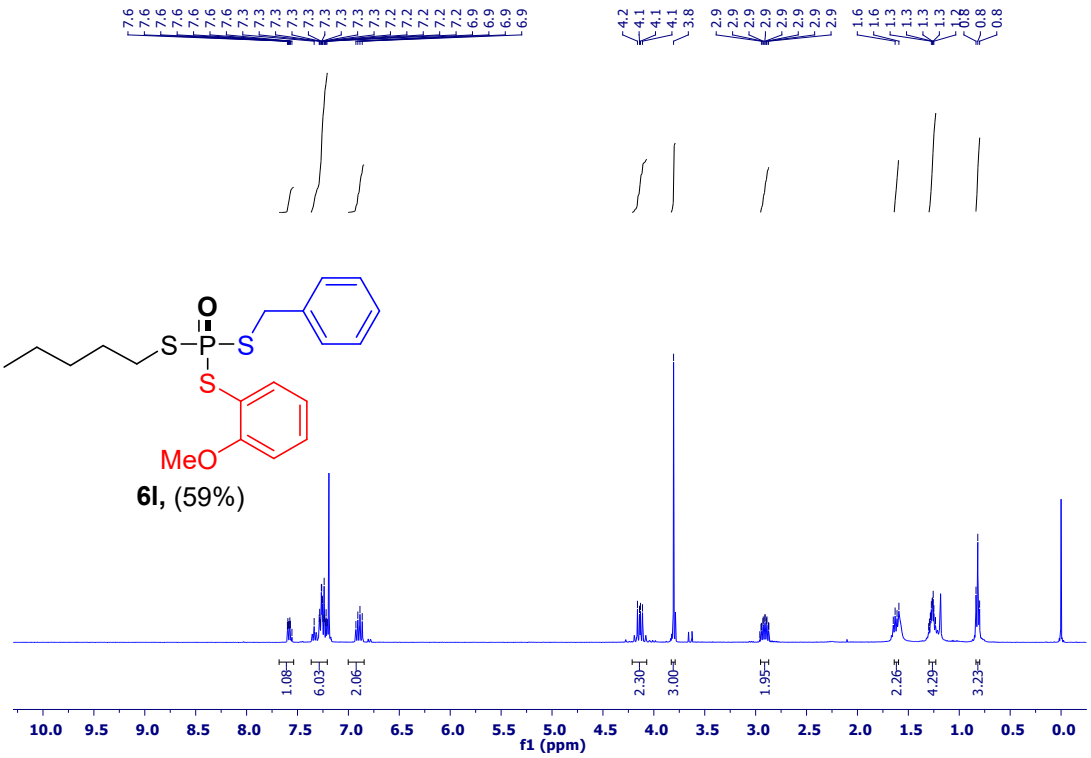
^{13}C NMR (101 MHz, $CDCl_3$)



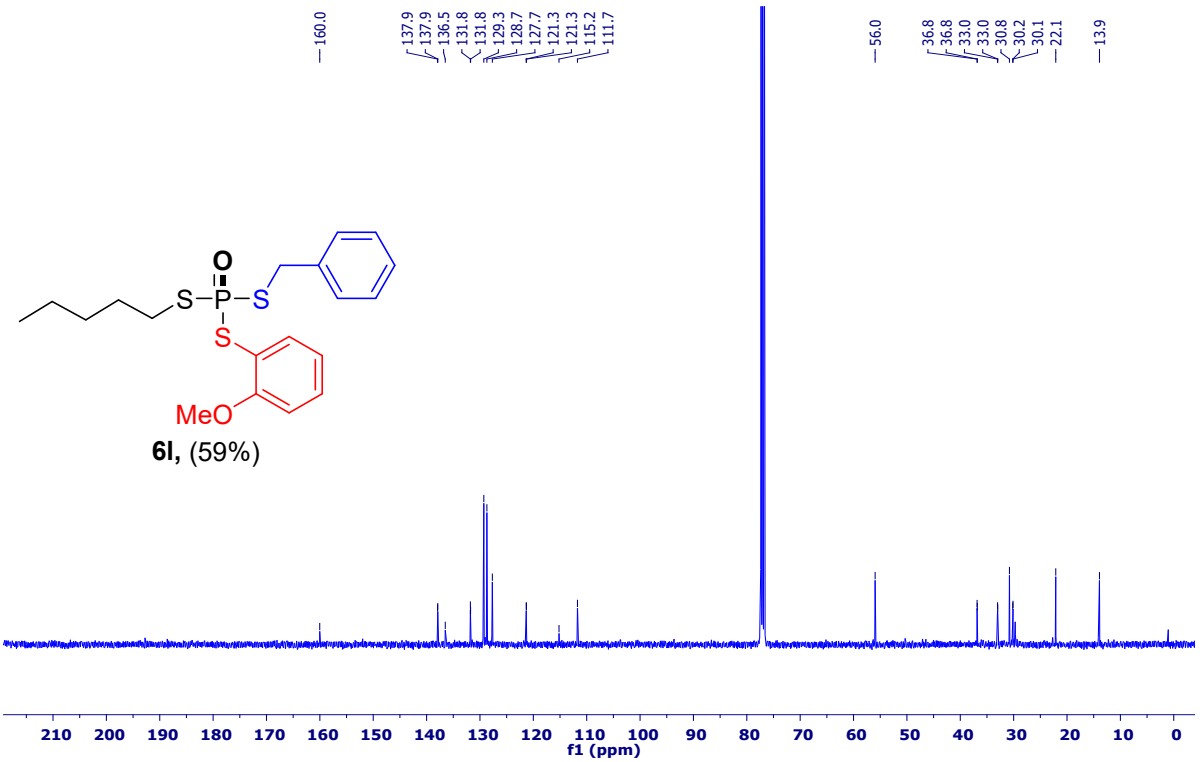
^{31}P NMR (162 MHz, $CDCl_3$)



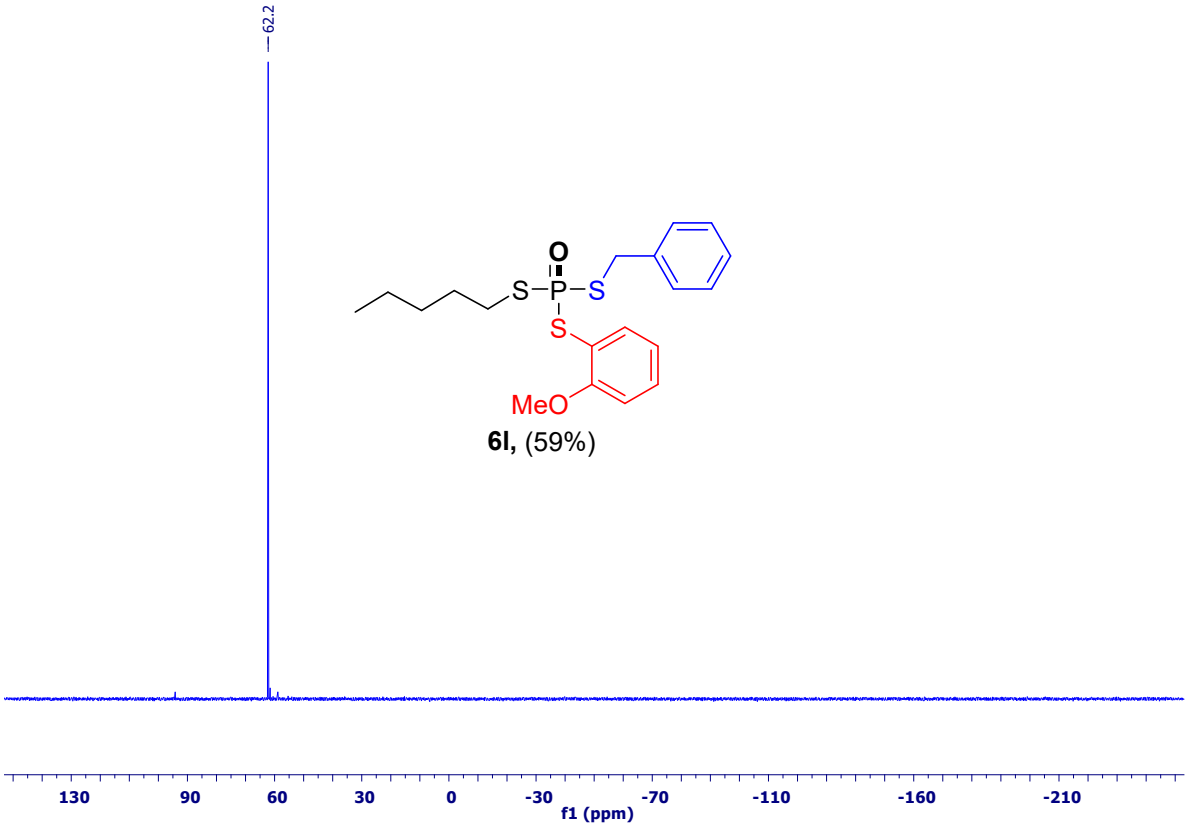
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

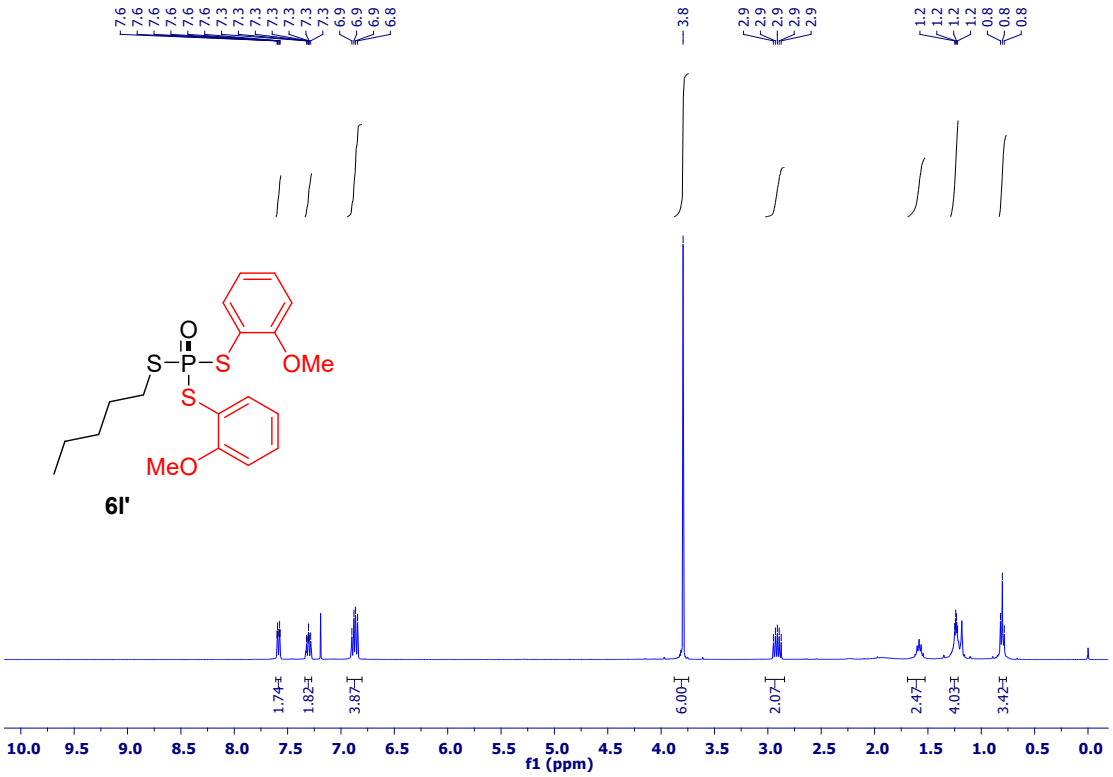


^{31}P NMR (162 MHz, $CDCl_3$)



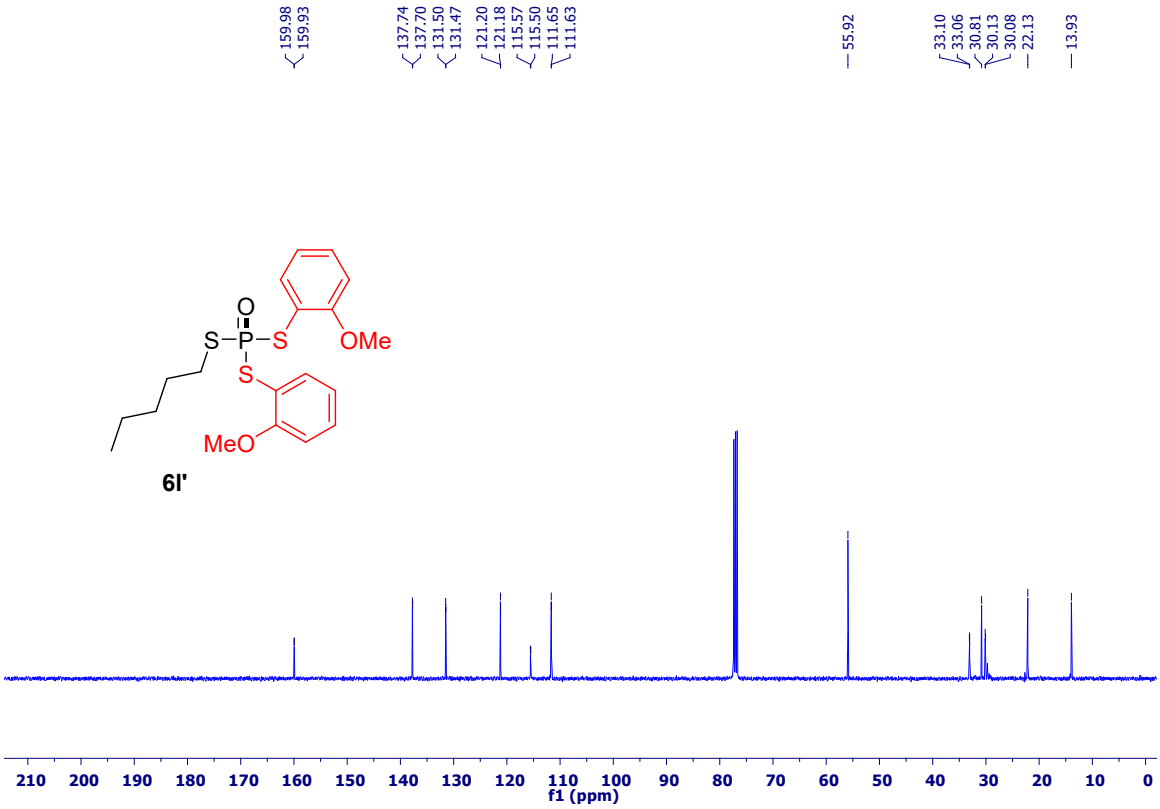
6l, (59%)

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

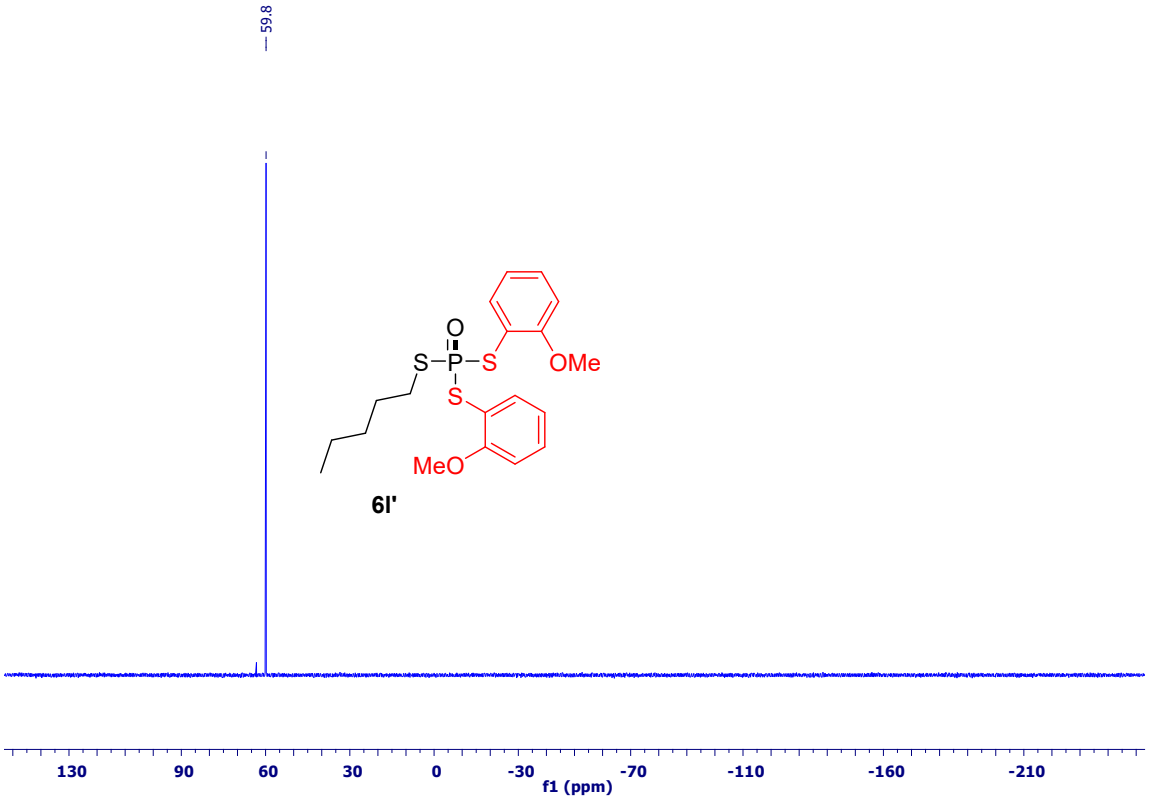


6l'

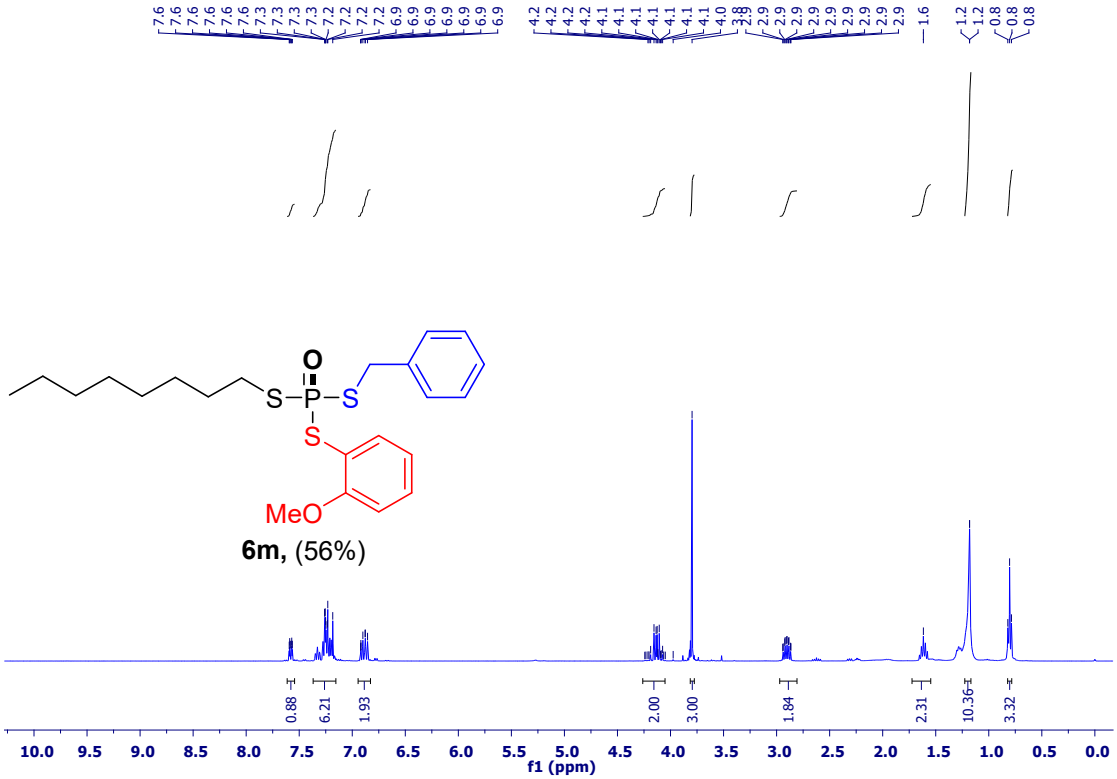
^{13}C NMR (101 MHz, $CDCl_3$)



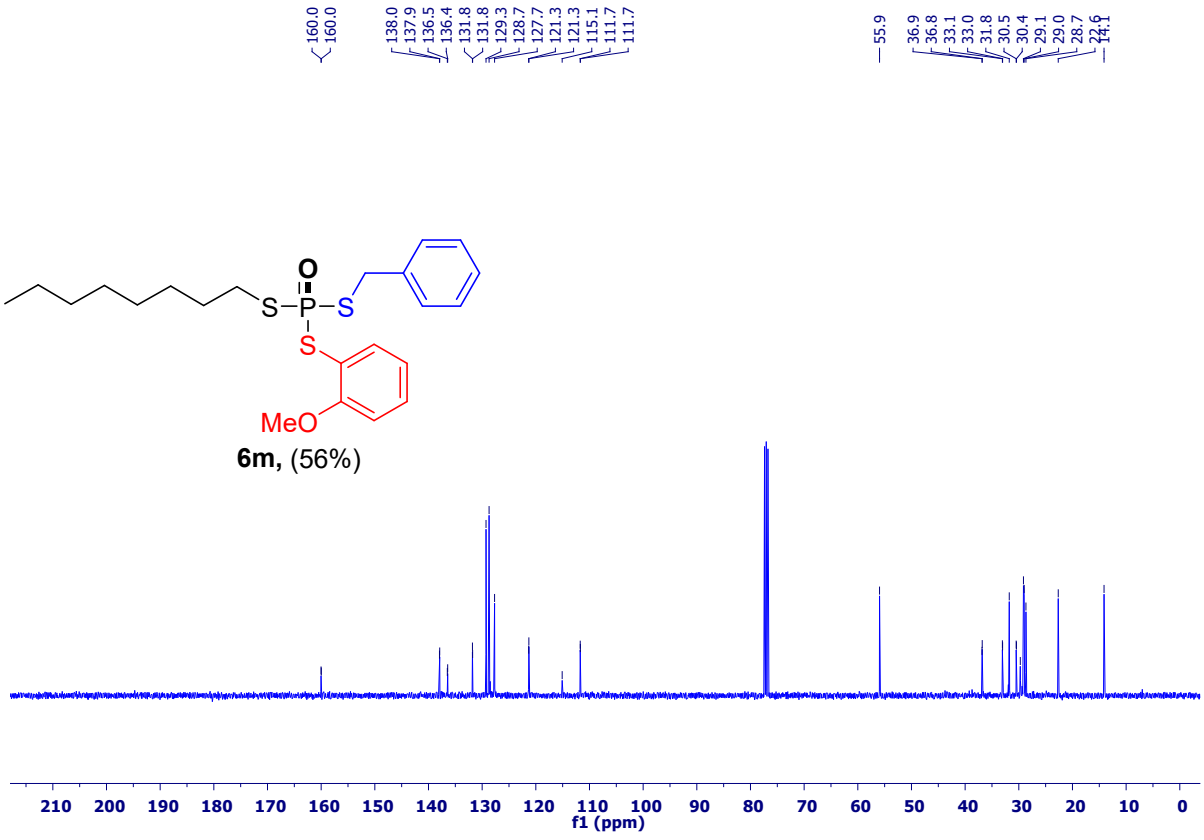
^{31}P NMR (162 MHz, $CDCl_3$)



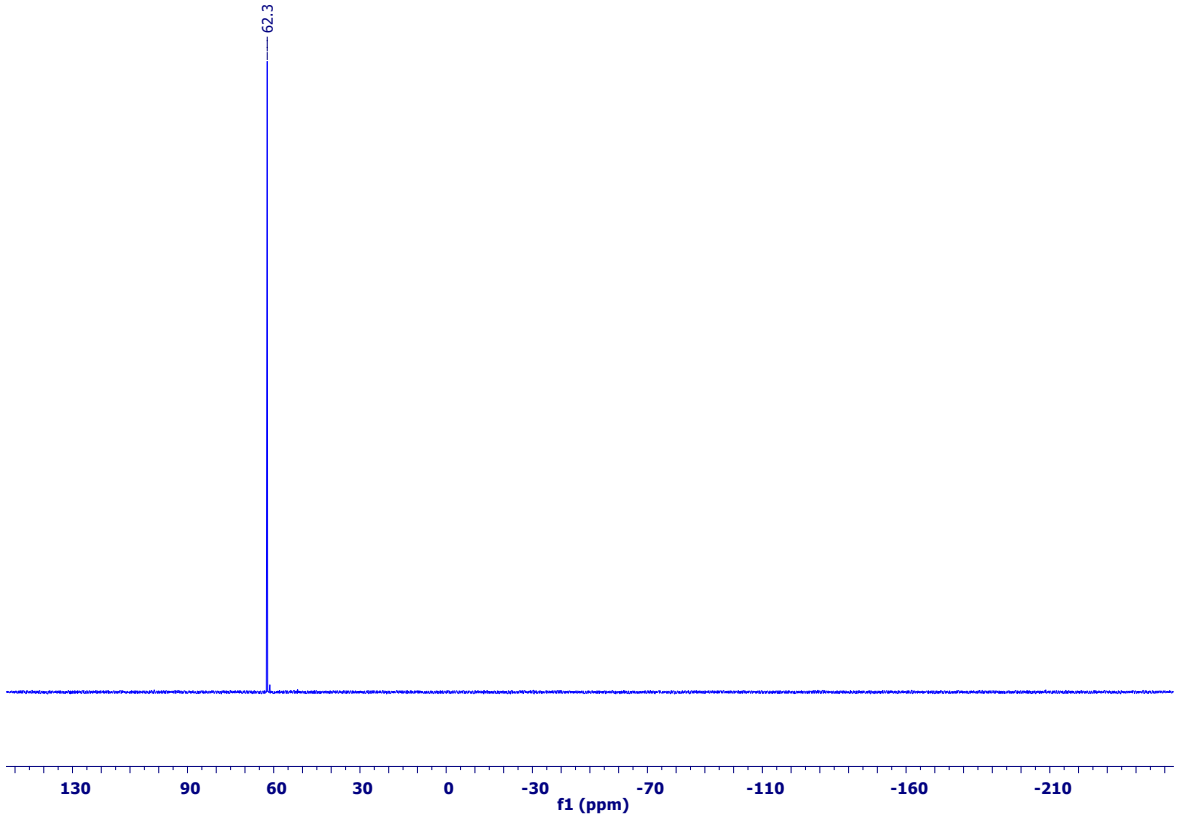
^{1}H NMR (400 MHz, $CDCl_3$)



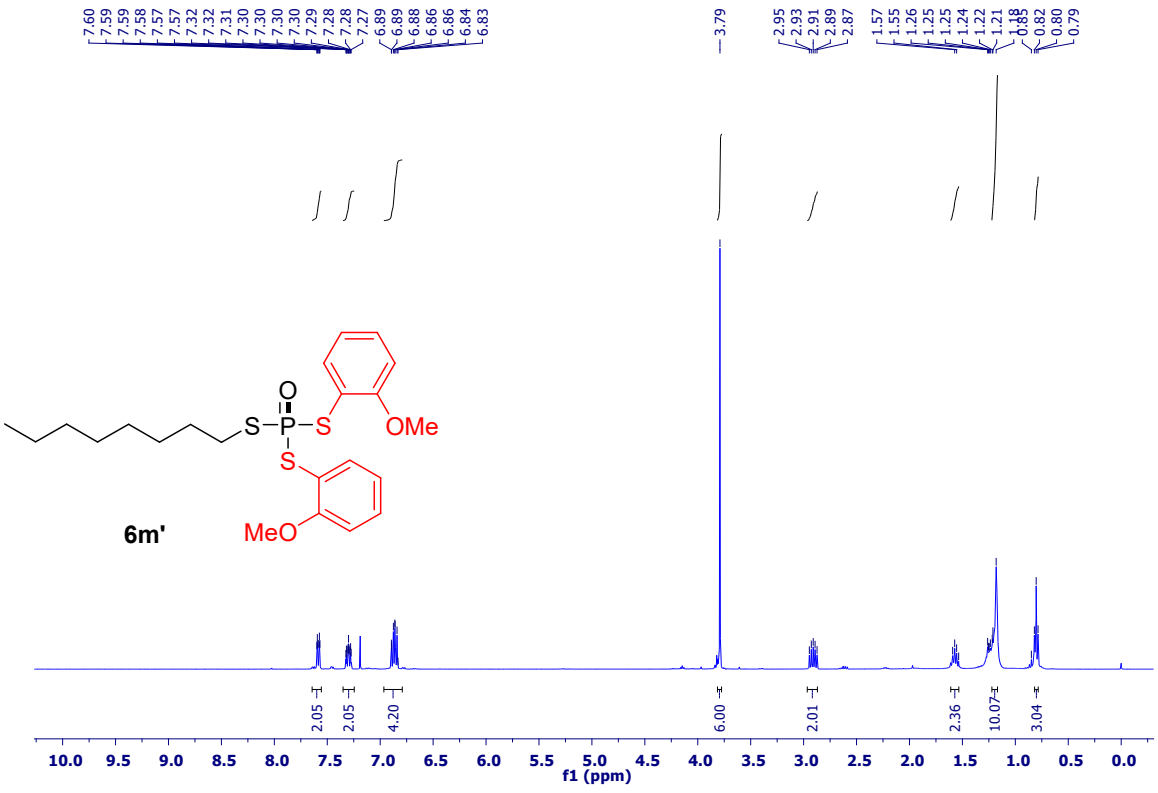
^{13}C NMR (101 MHz, $CDCl_3$)



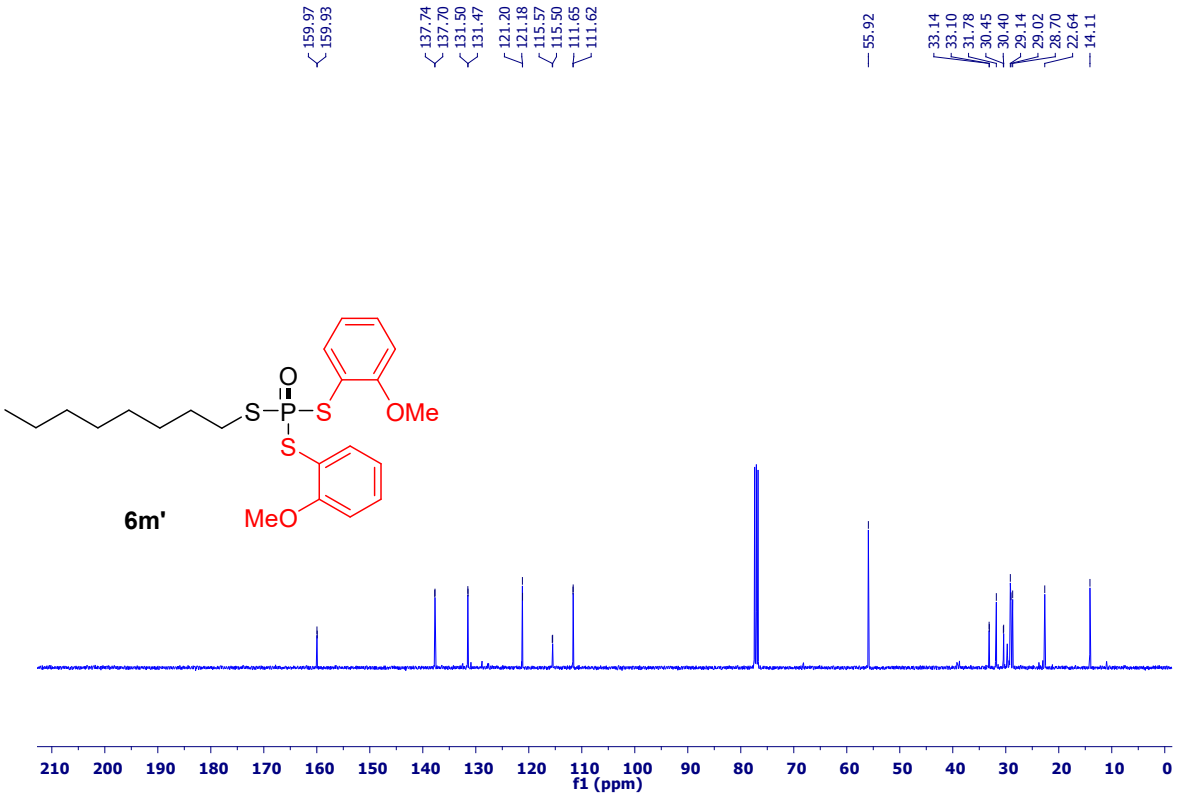
^{31}P NMR (162 MHz, $CDCl_3$)



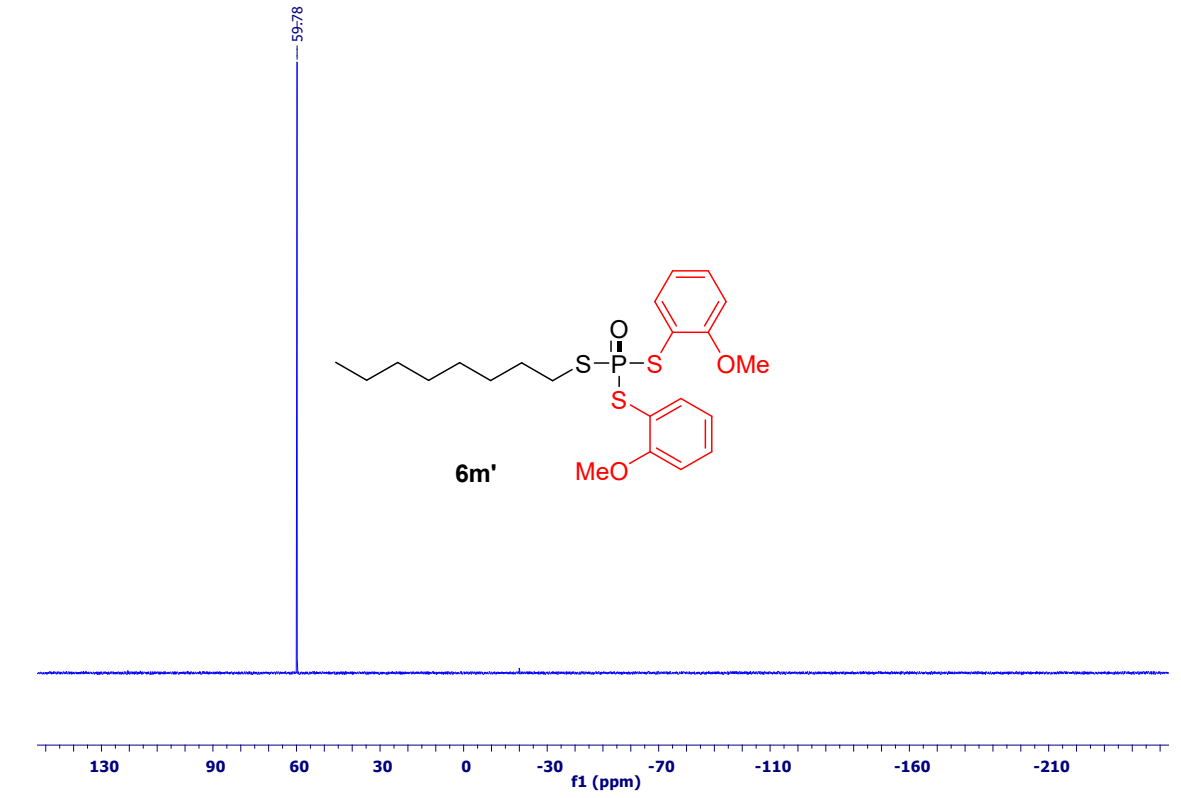
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

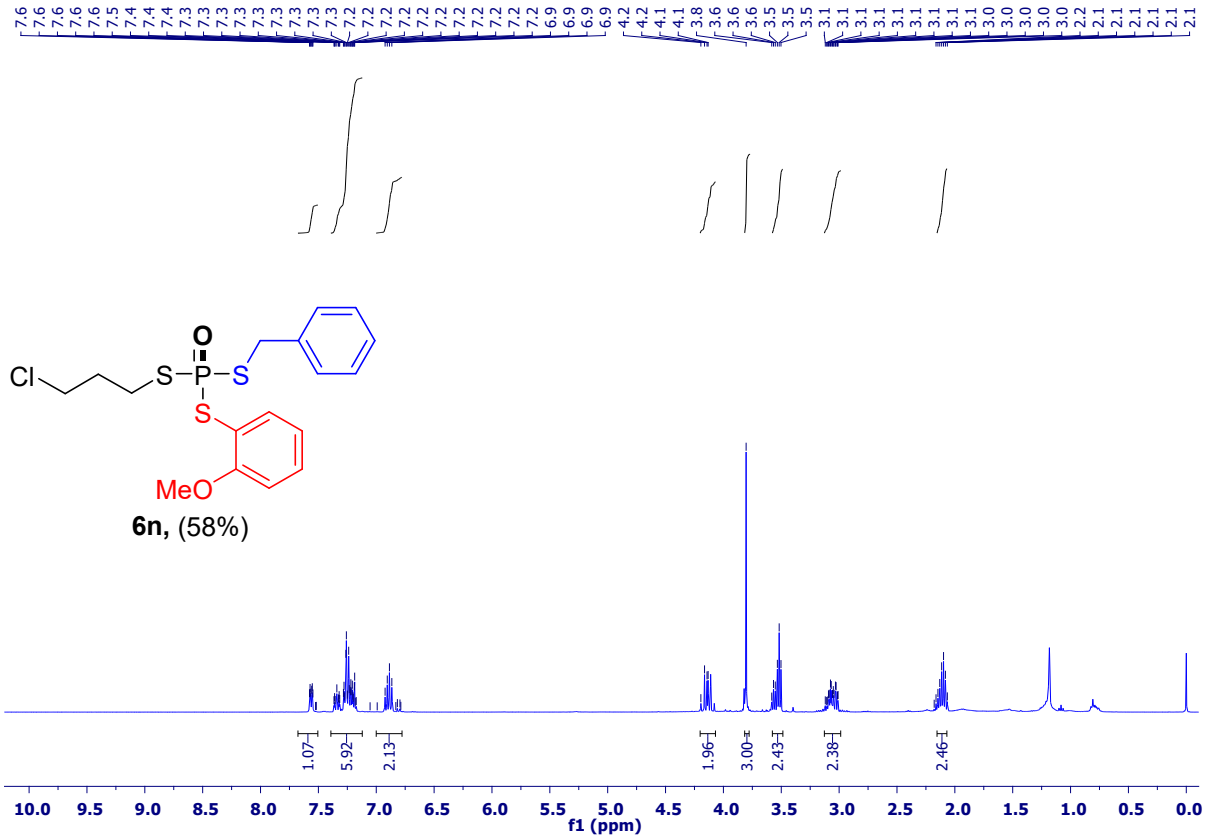


^{31}P NMR (162 MHz, $CDCl_3$)

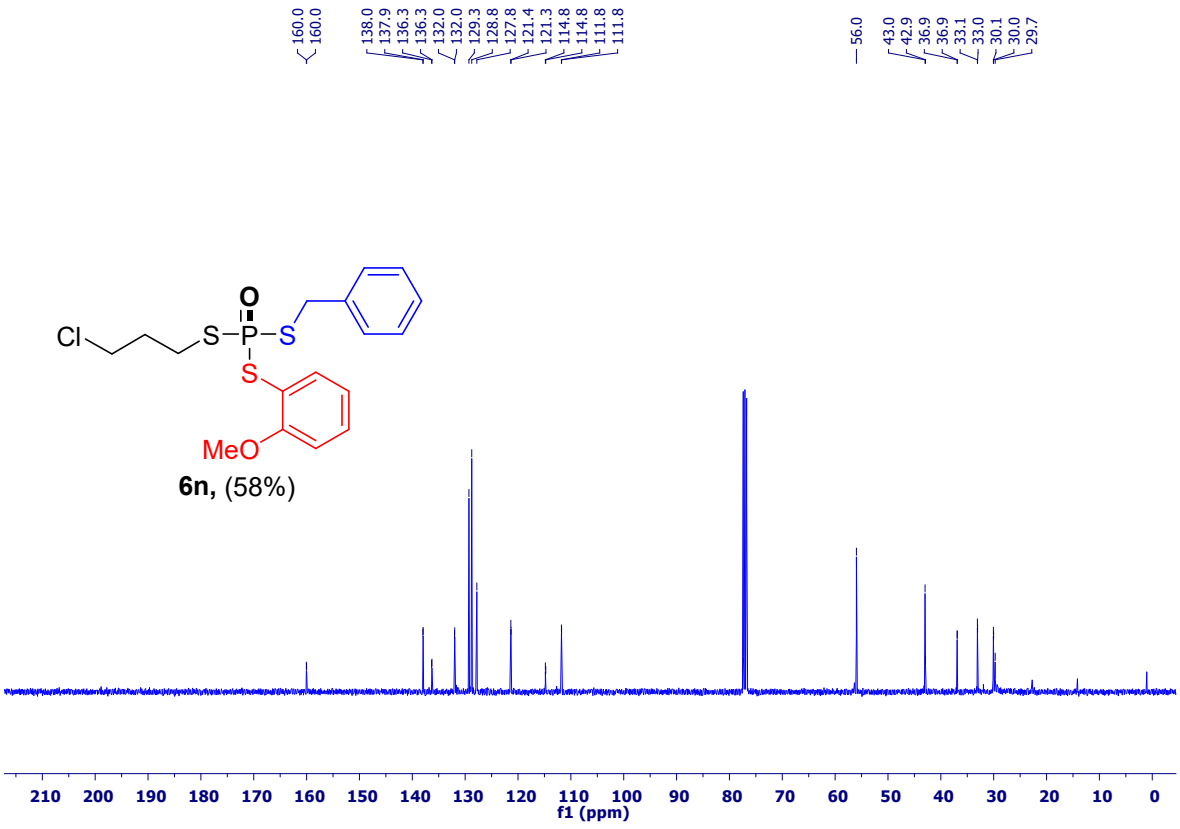


^{1}H

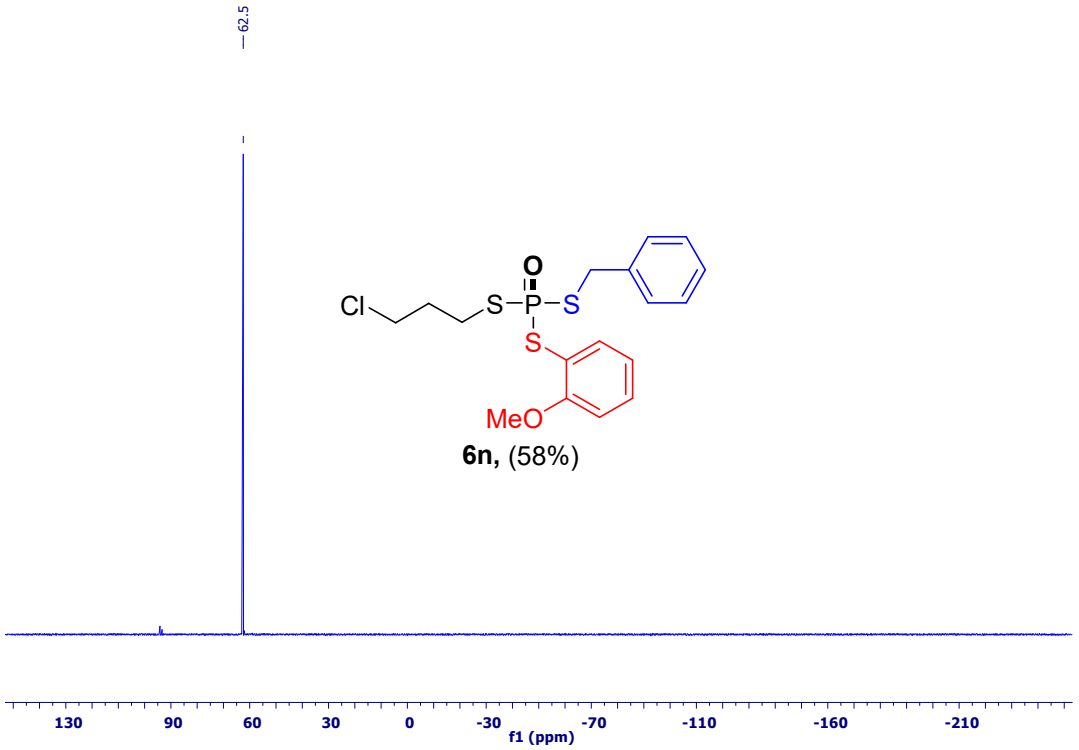
NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

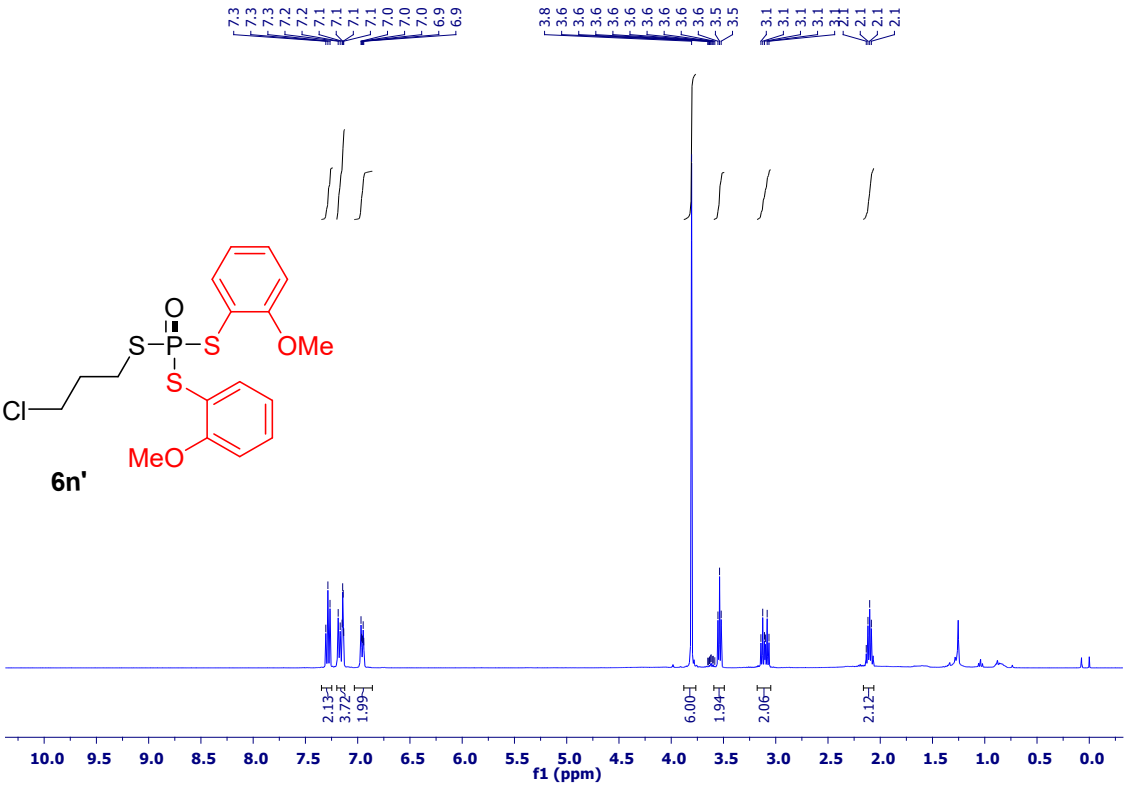


^{31}P NMR (162 MHz, $CDCl_3$)



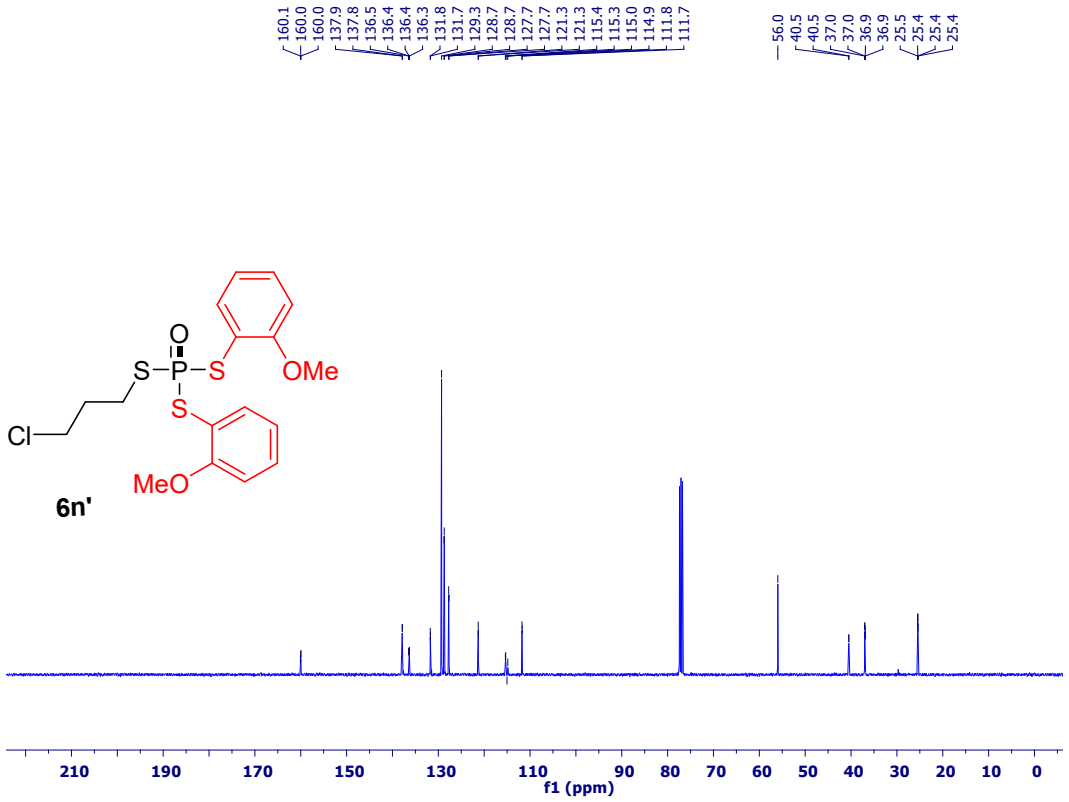
6n, (58%)

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

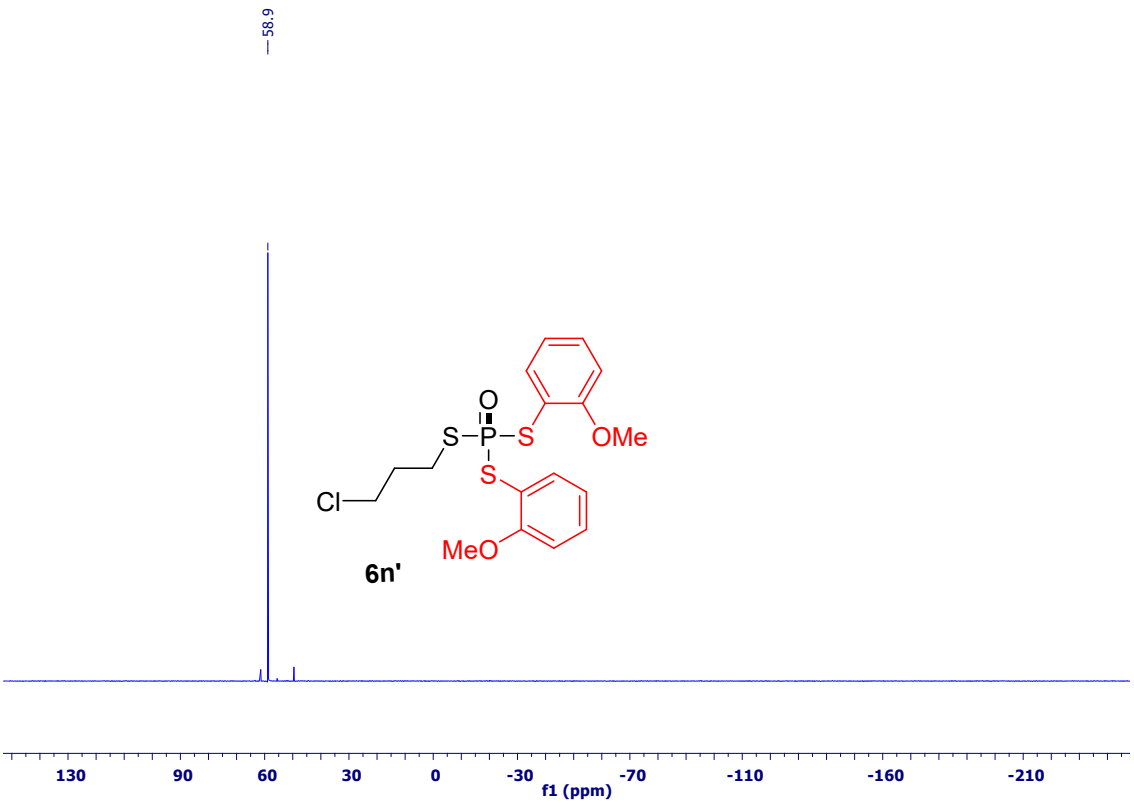


6n'

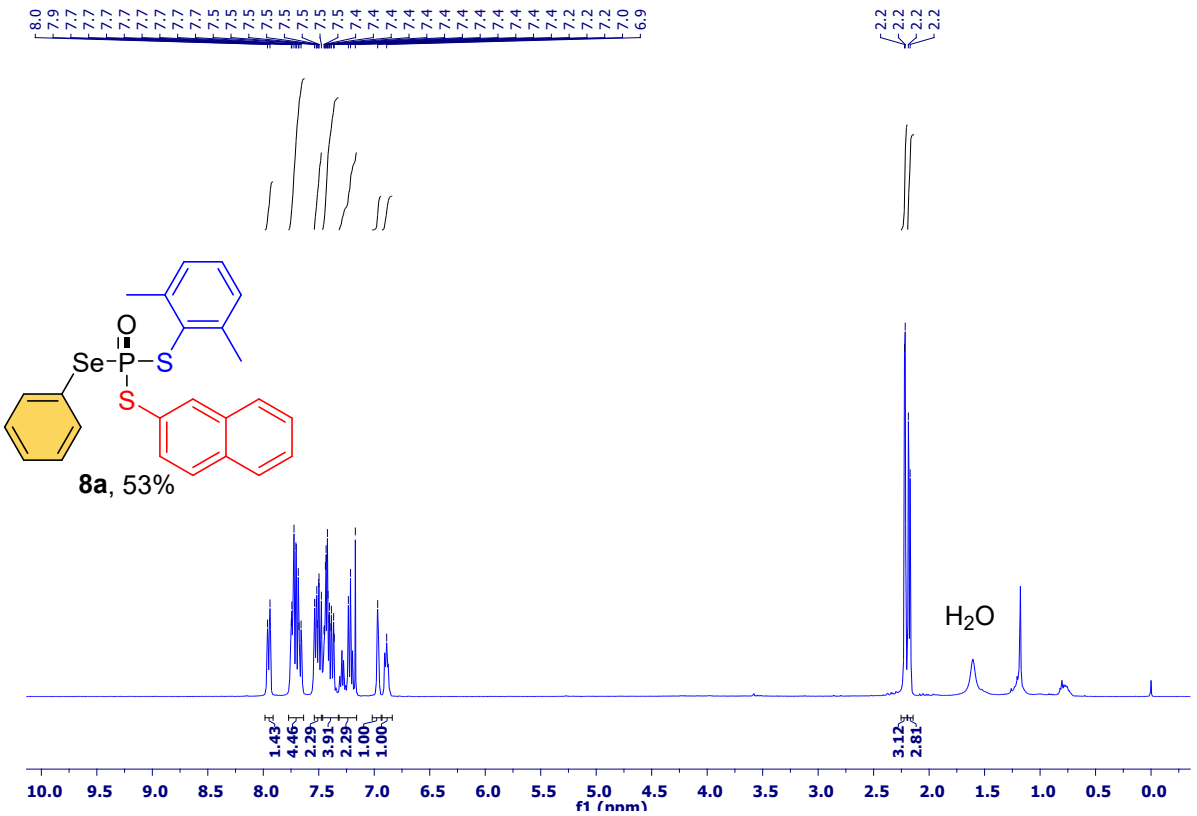
^{13}C NMR (101 MHz, $CDCl_3$)



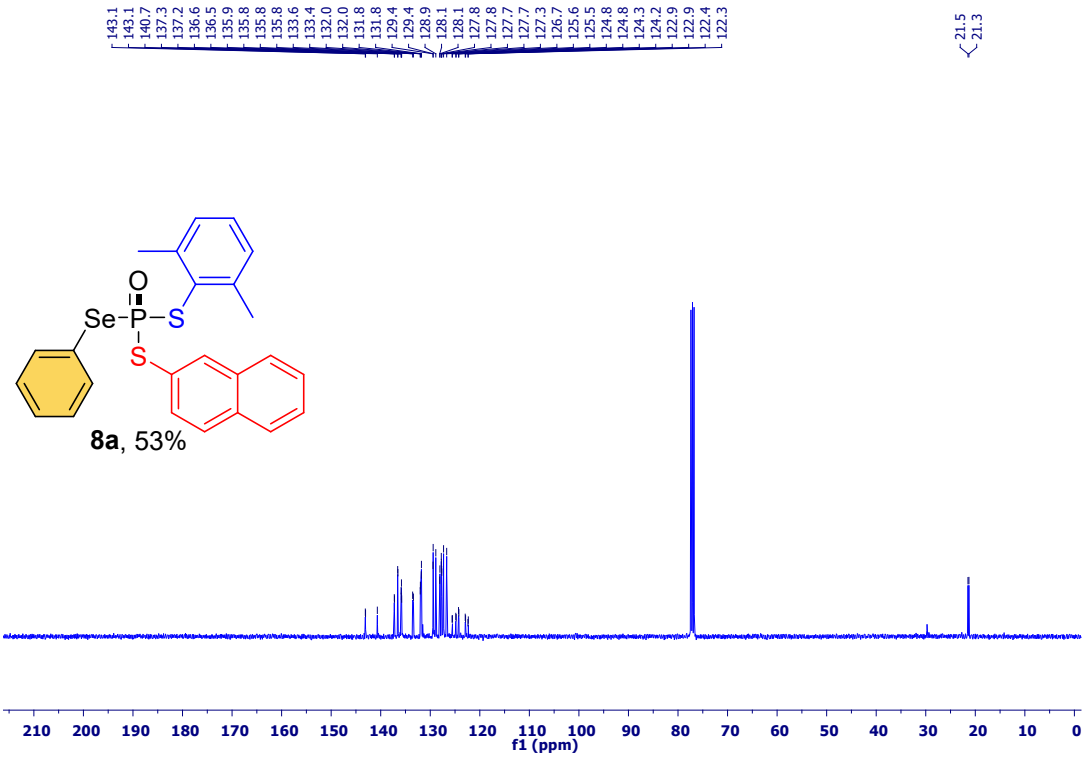
^{31}P NMR (162 MHz, $CDCl_3$)



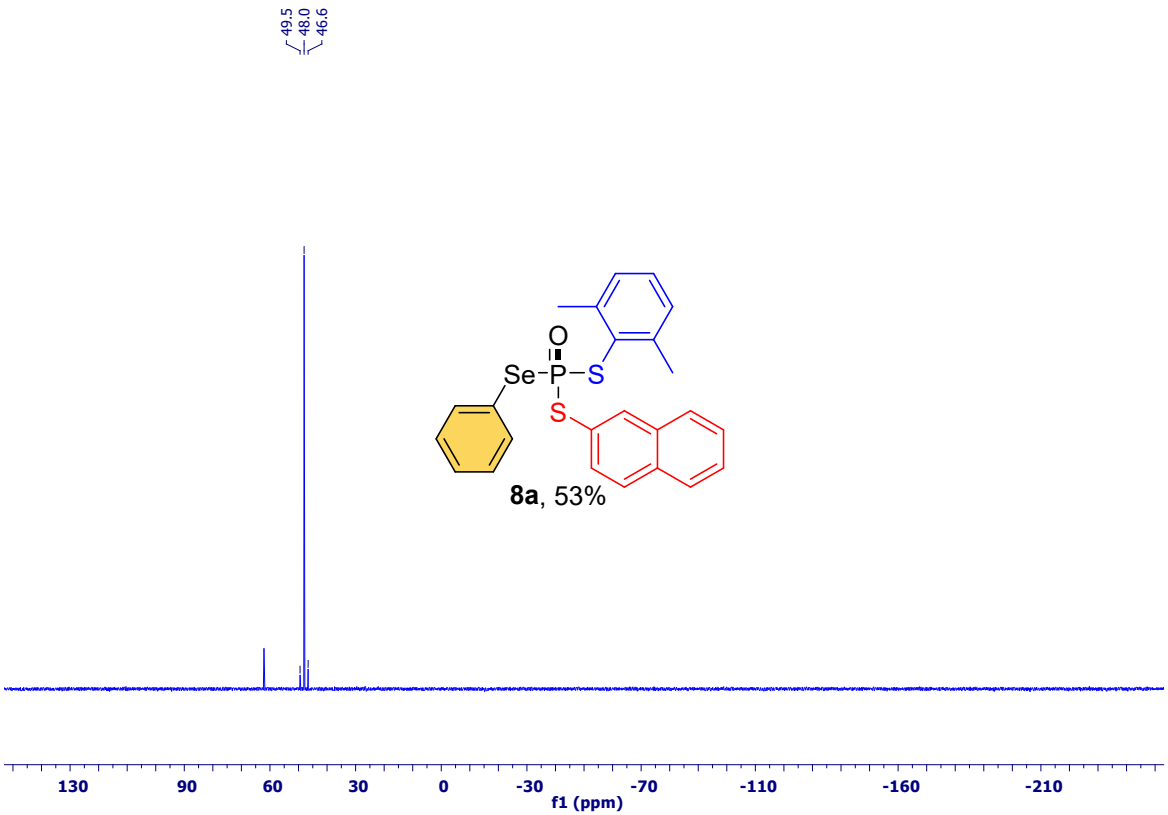
^{1}H NMR (400 MHz, $CDCl_3$)



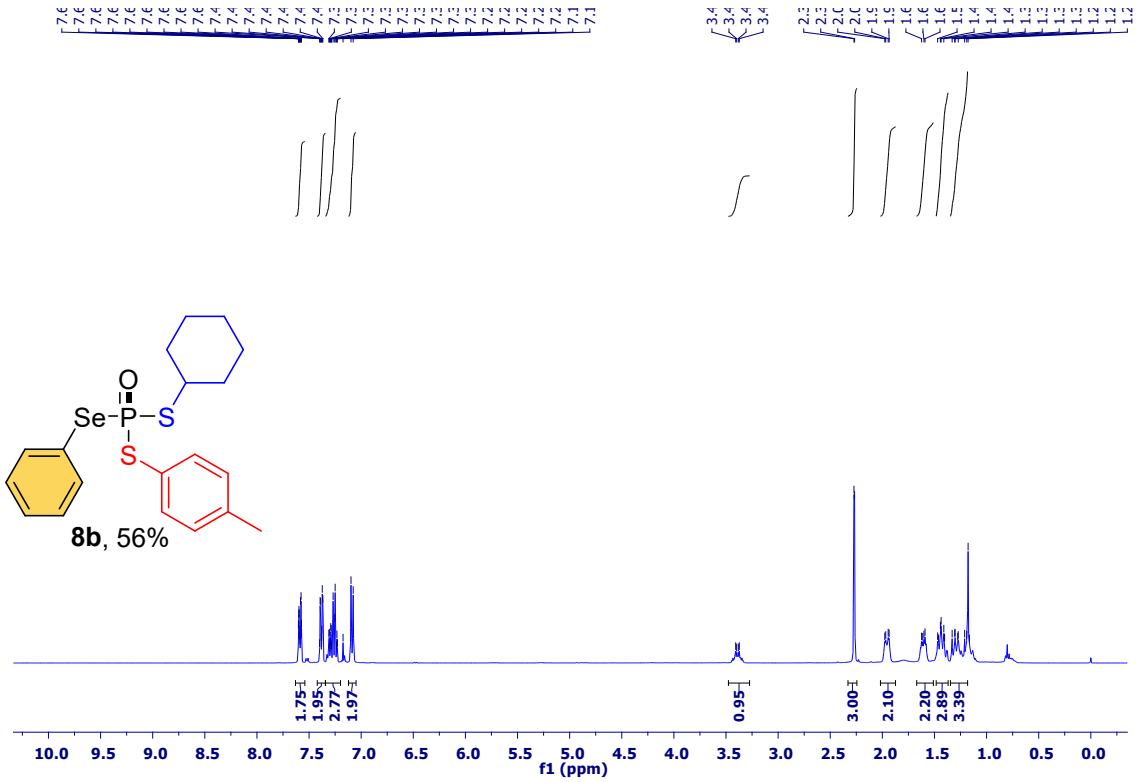
^{13}C NMR (101 MHz, $CDCl_3$)



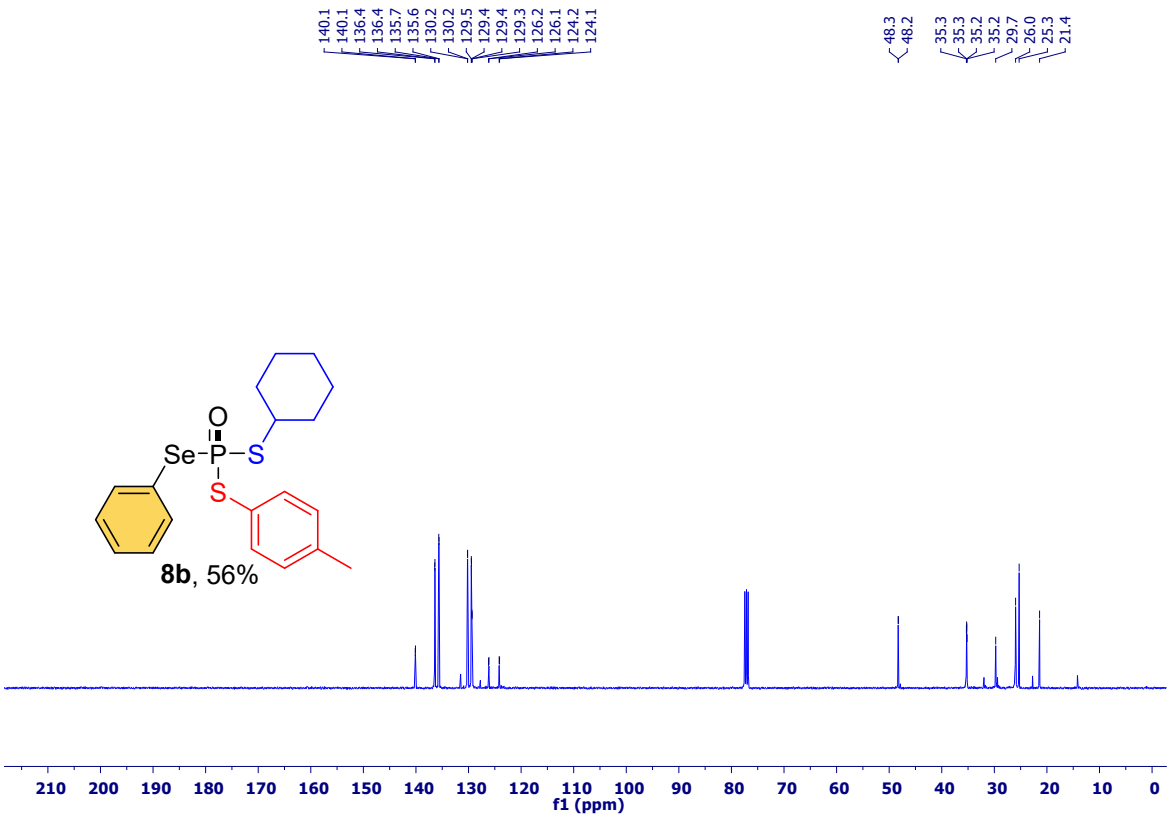
^{31}P NMR (162 MHz, $CDCl_3$)



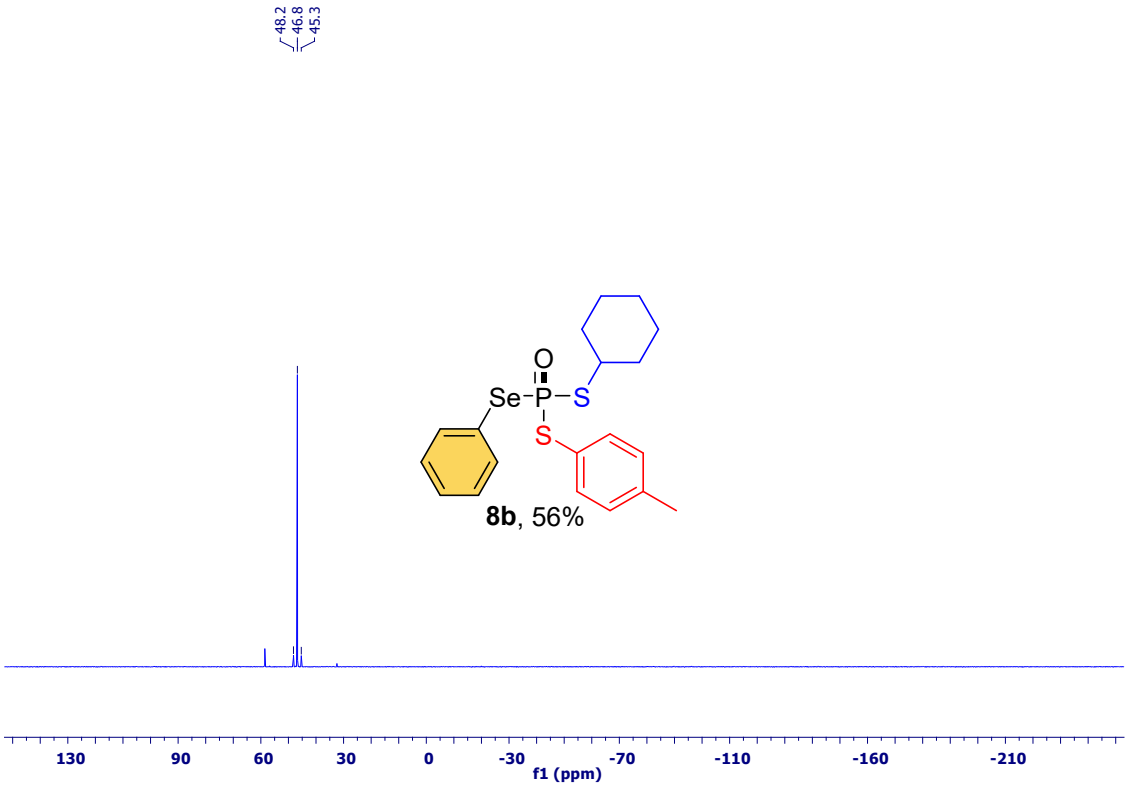
^{1}H NMR (400 MHz, $CDCl_3$)



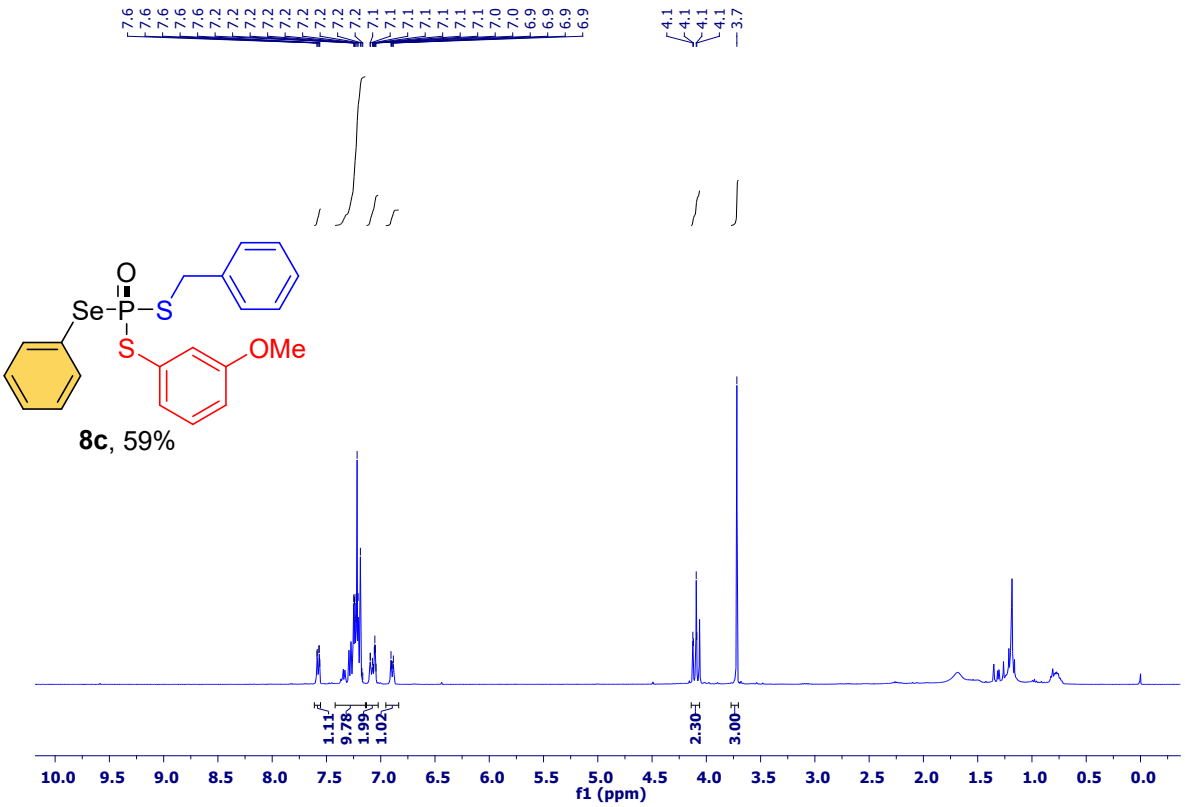
^{13}C NMR (101 MHz, $CDCl_3$)



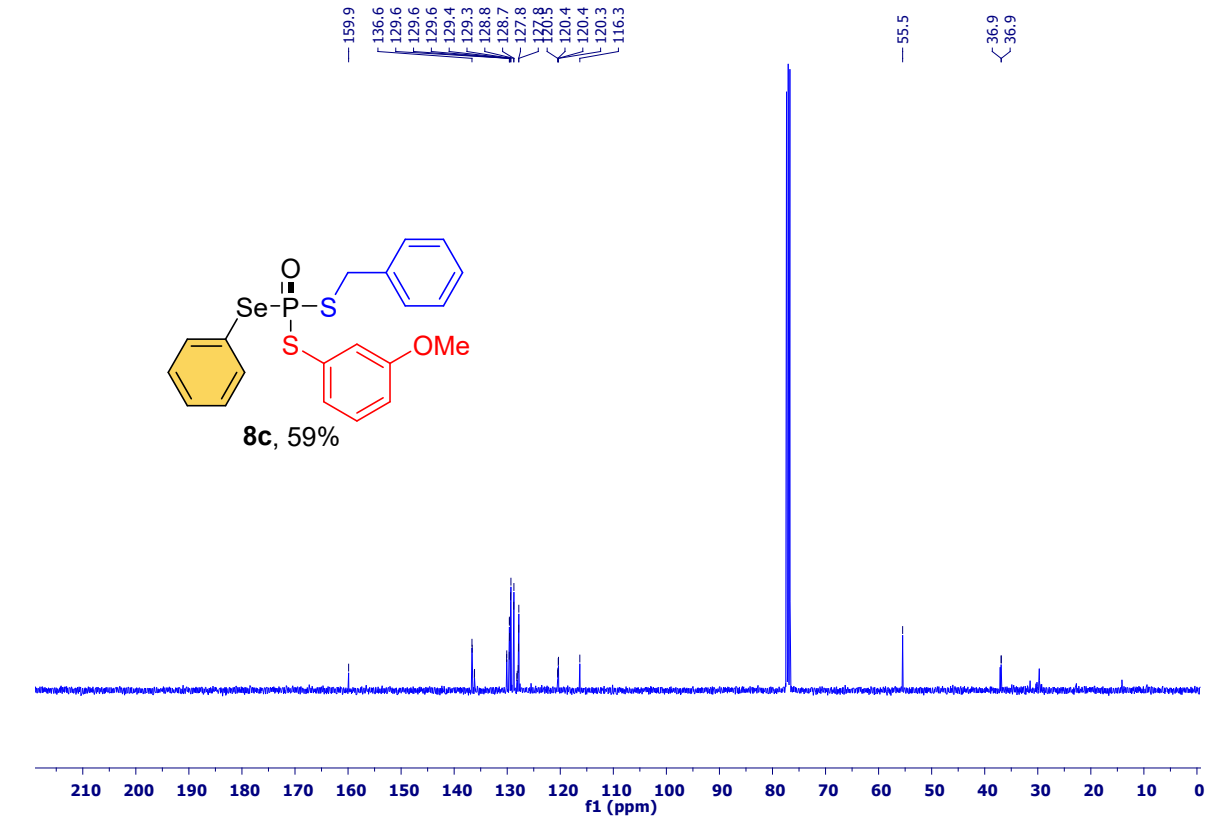
^{31}P NMR (162 MHz, $CDCl_3$)



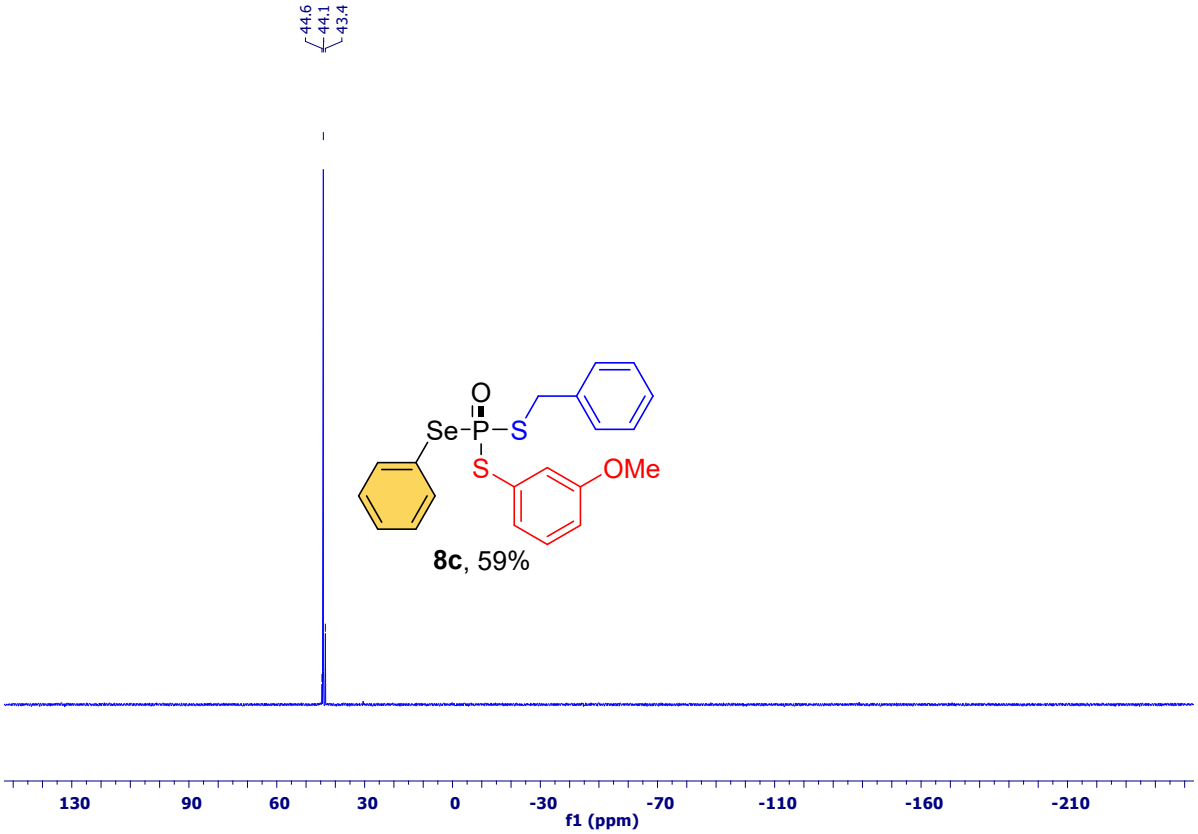
^{1}H NMR (400 MHz, $CDCl_3$)



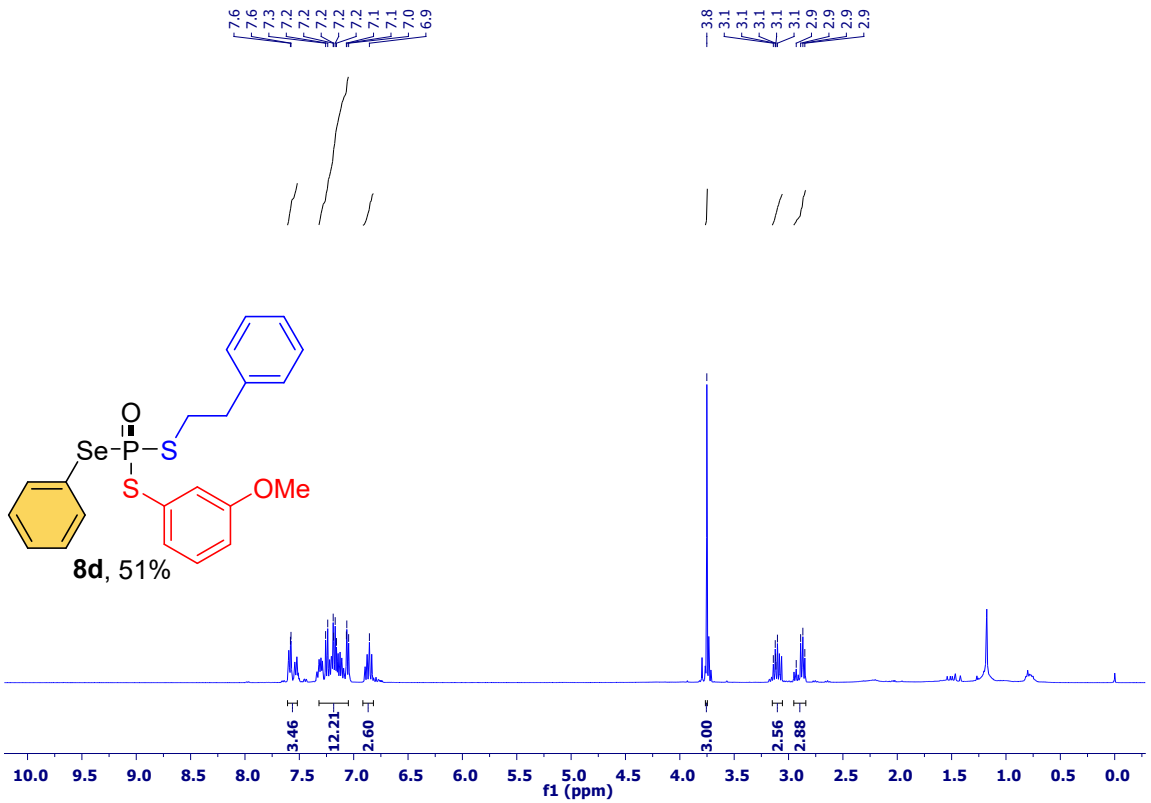
^{13}C NMR (101 MHz, $CDCl_3$)



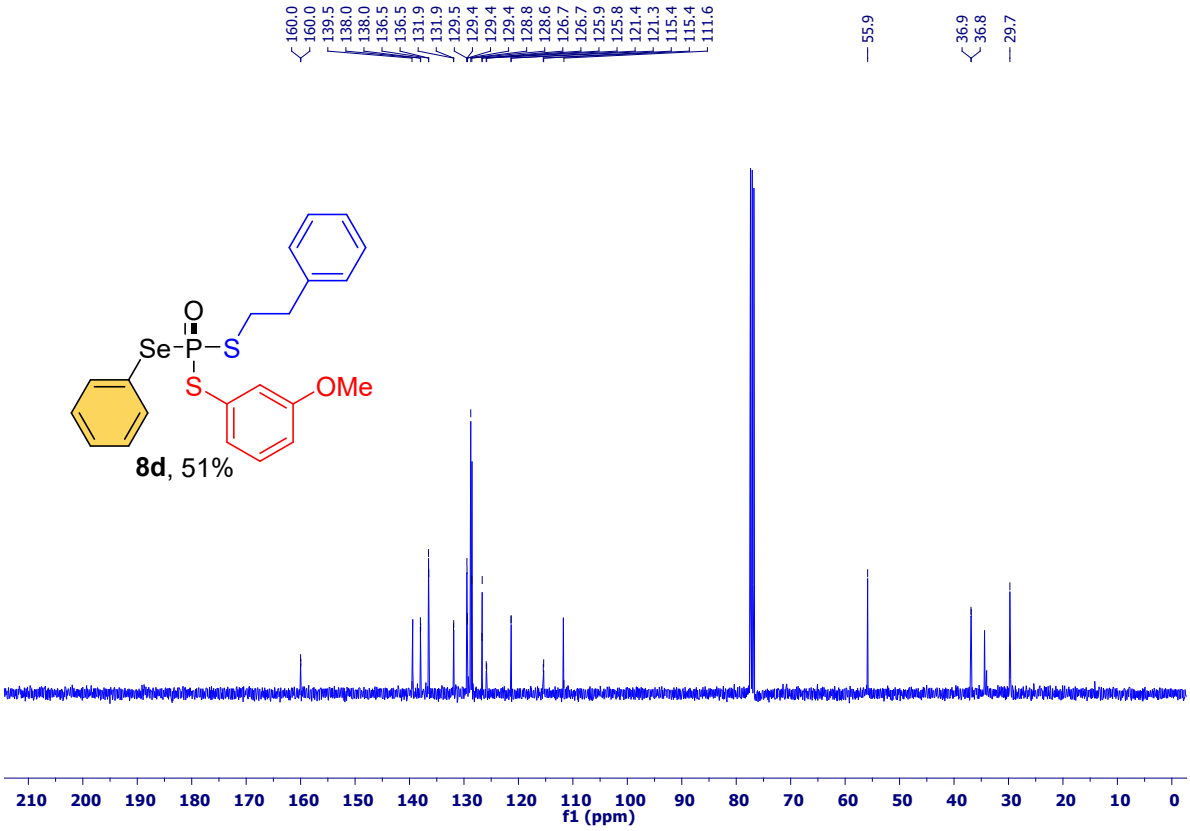
^{31}P NMR (162 MHz, $CDCl_3$)



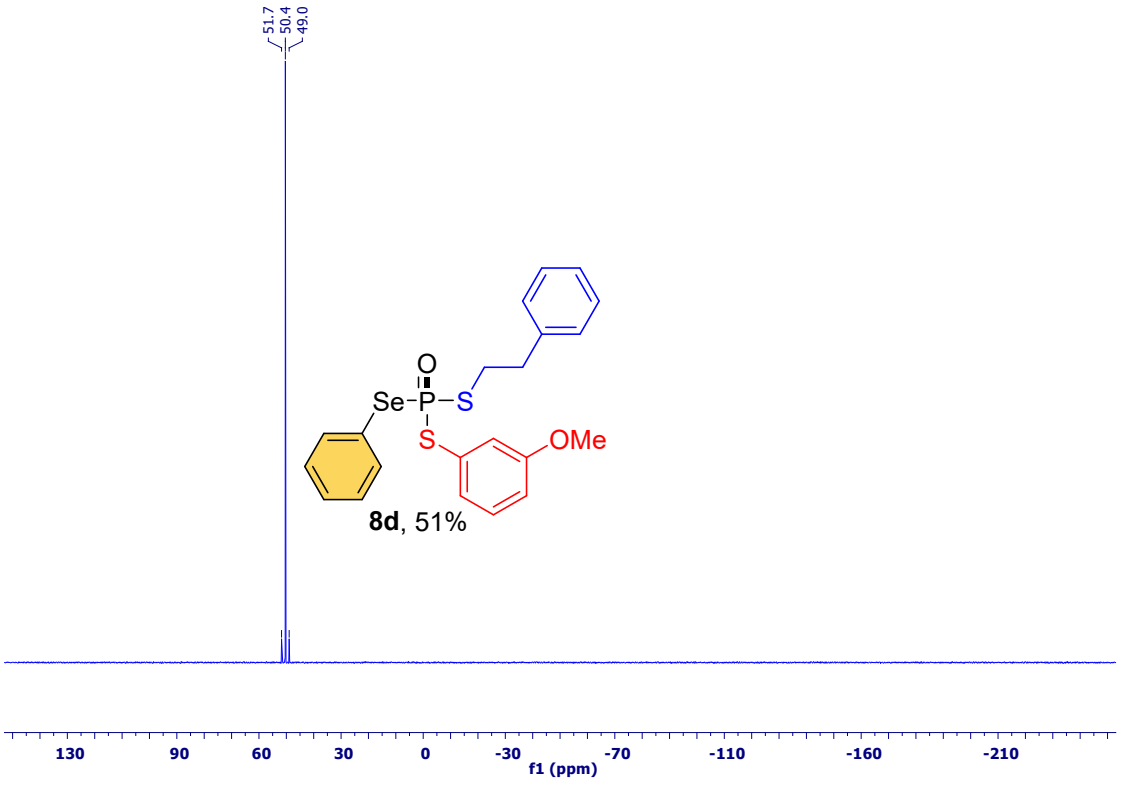
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

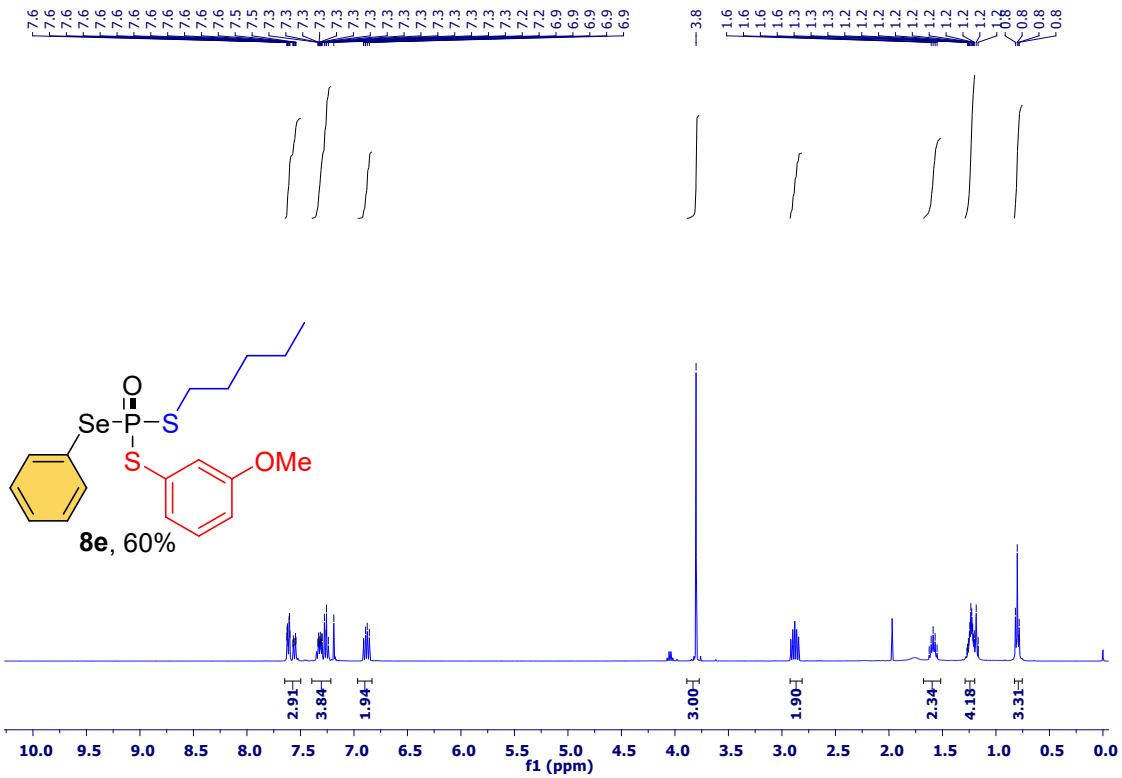


^{31}P NMR (162 MHz, $CDCl_3$)

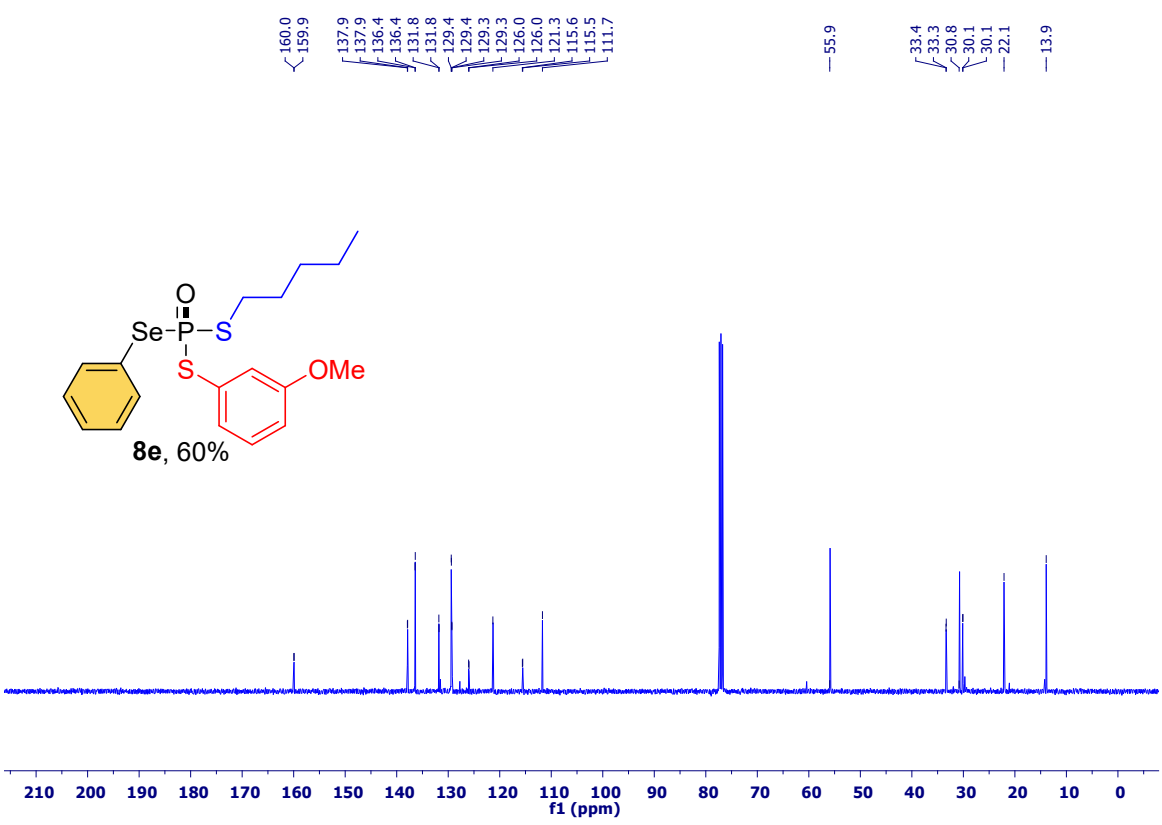


1

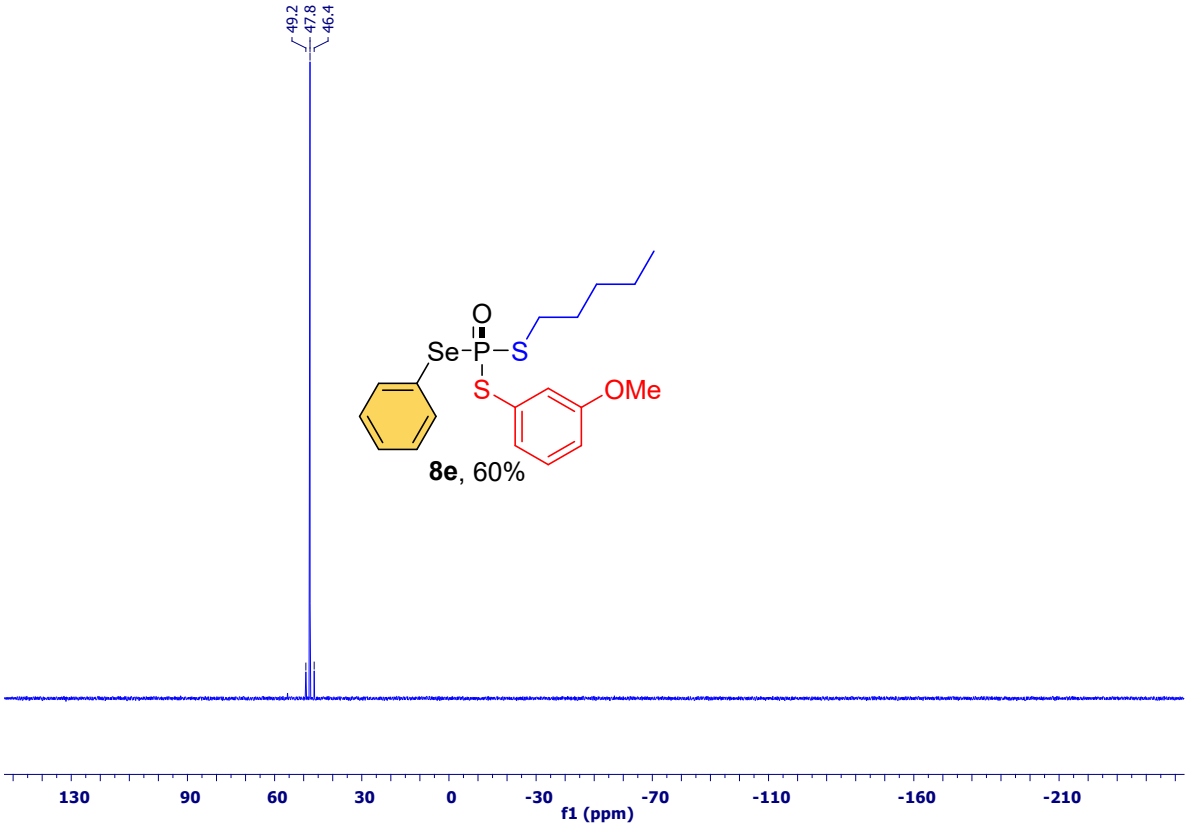
H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

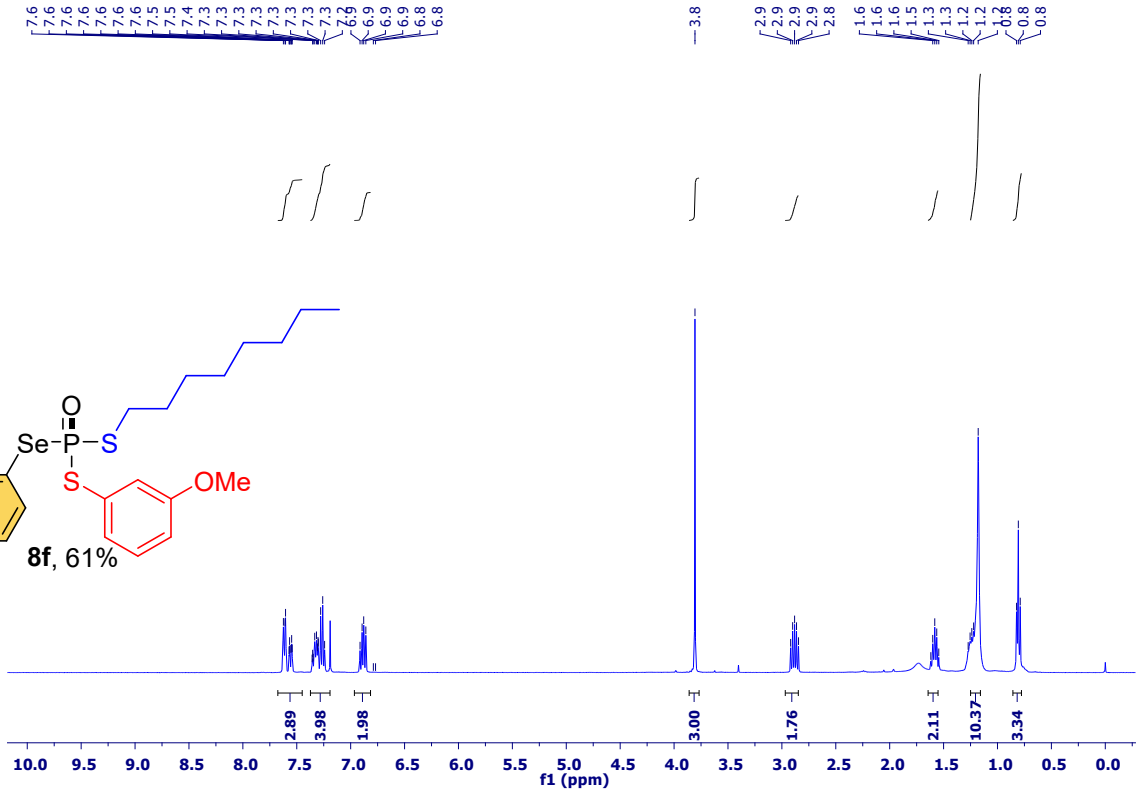


^{31}P NMR (162 MHz, $CDCl_3$)



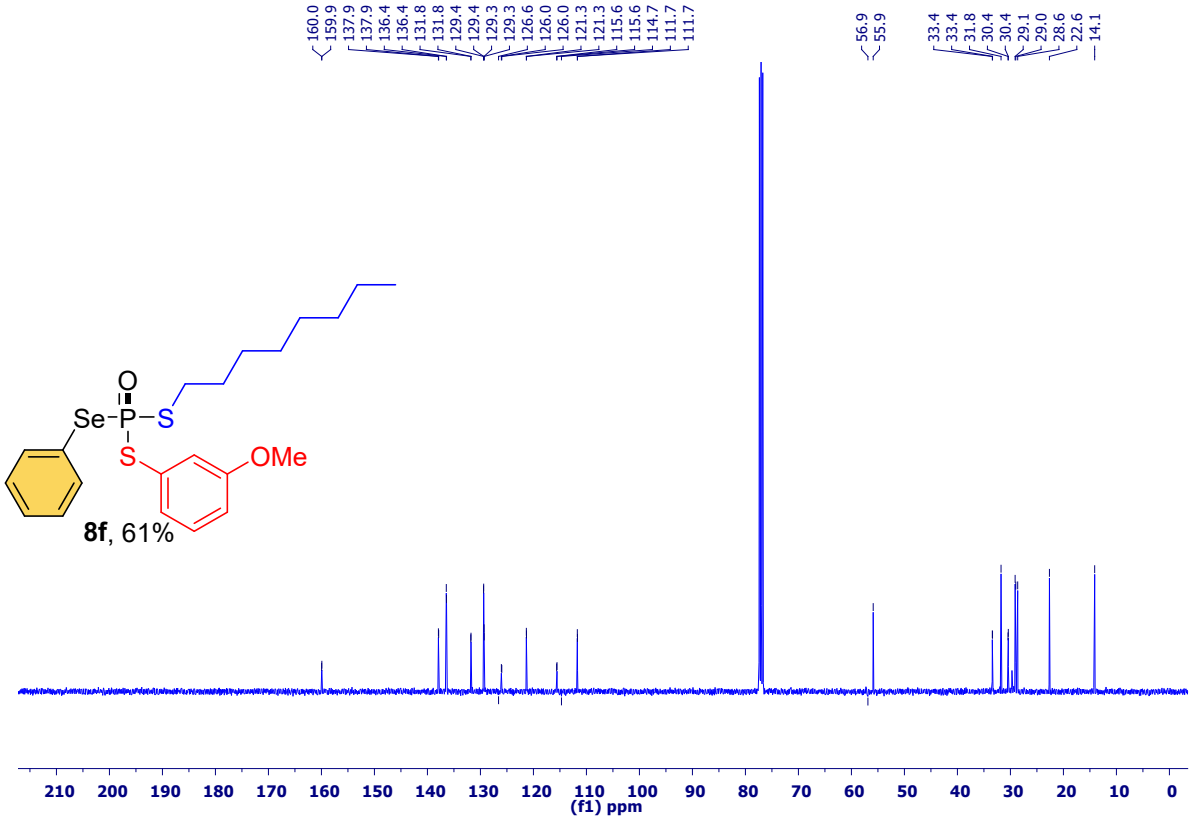
8e, 60%

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

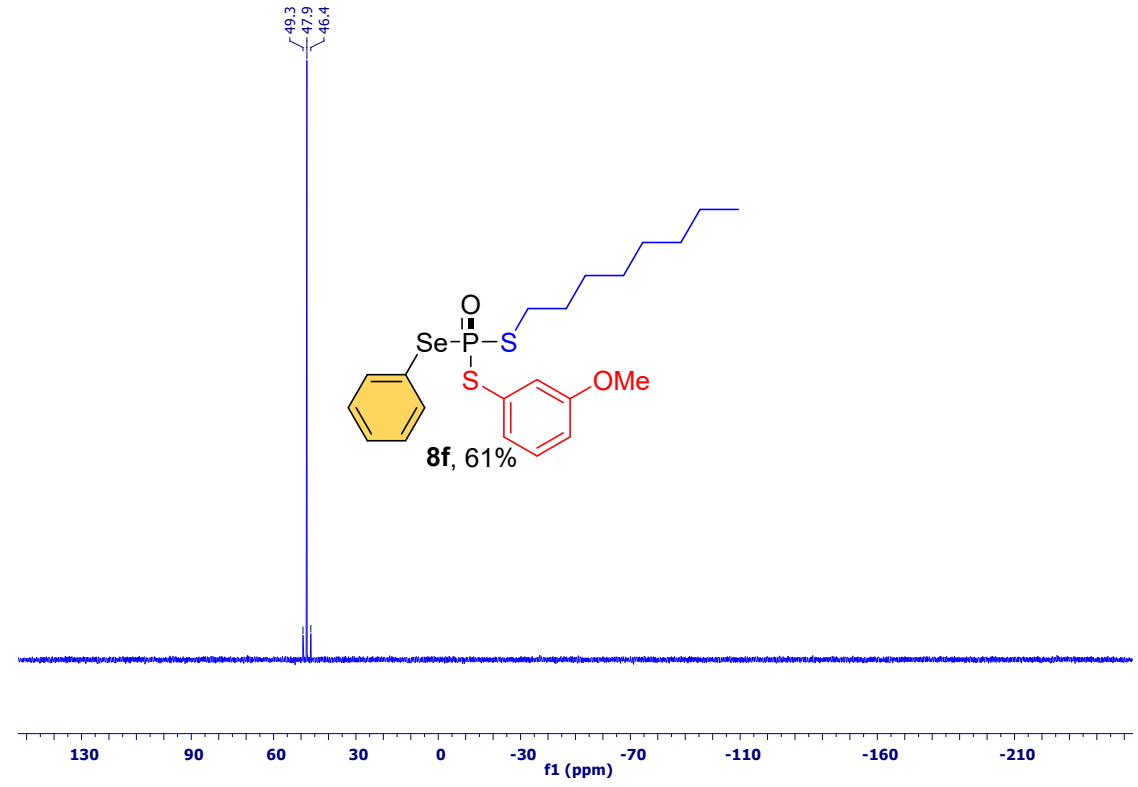


8f, 61%

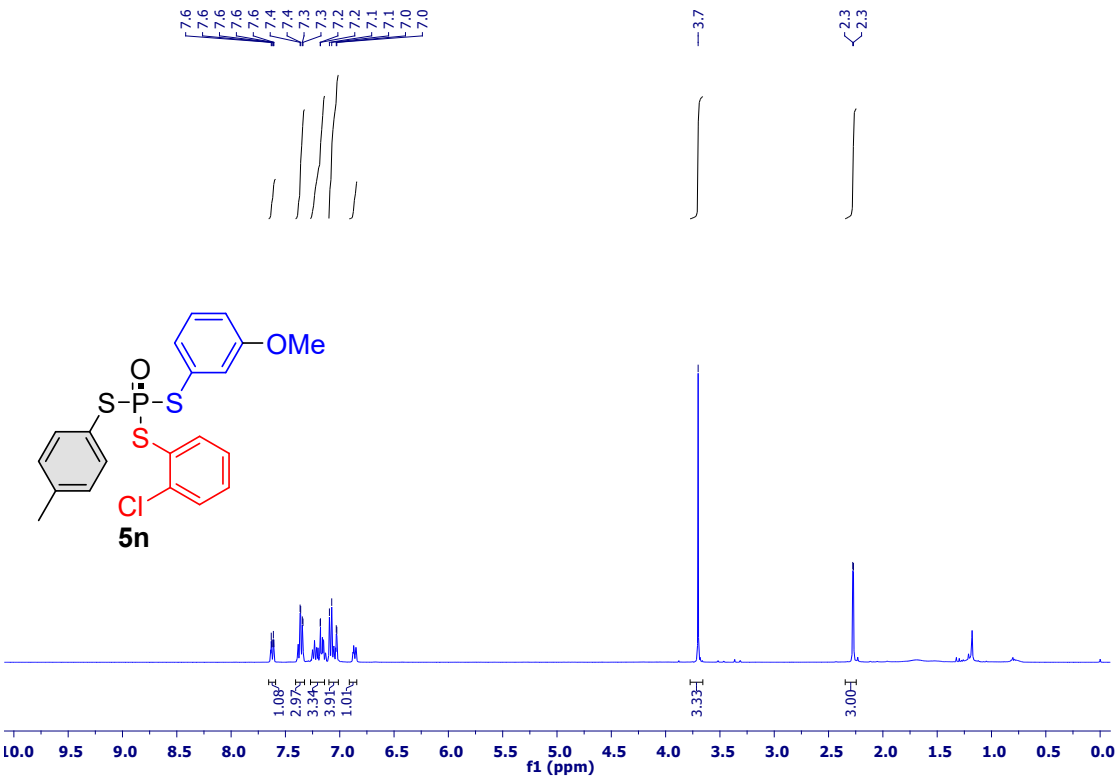
^{13}C NMR (101 MHz, $CDCl_3$)



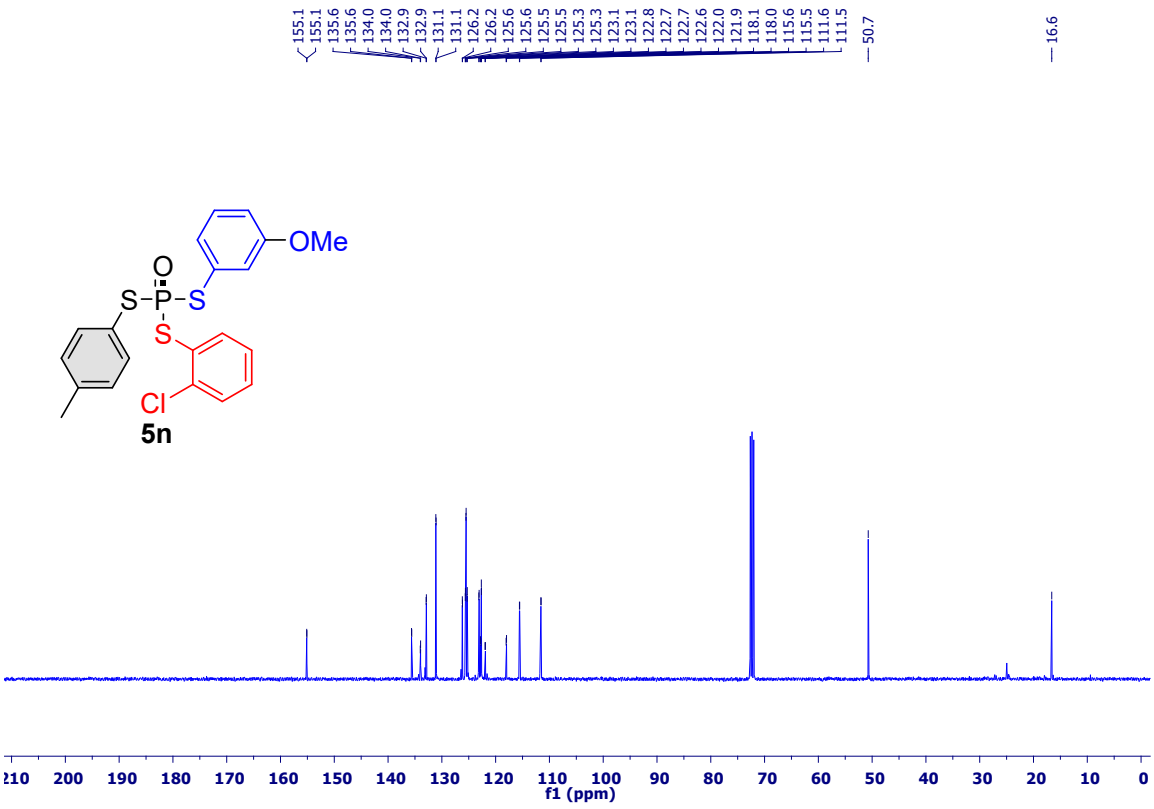
^{31}P NMR (162 MHz, $CDCl_3$)



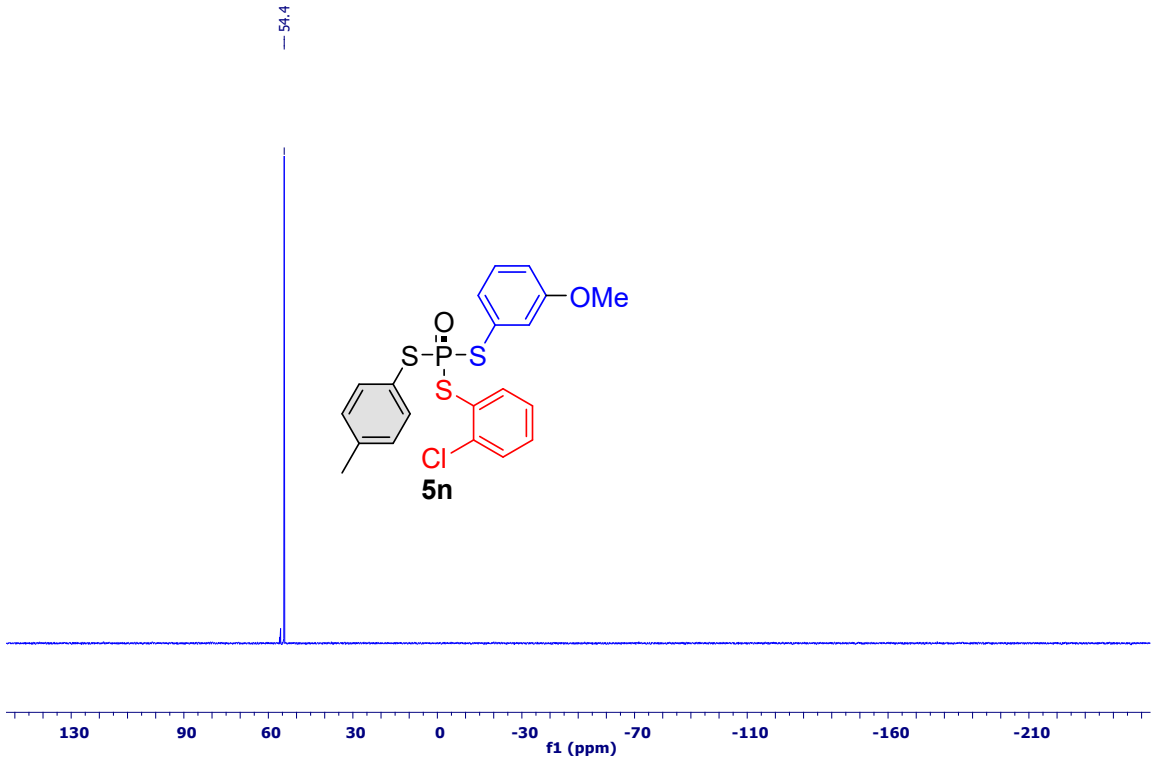
^{1}H NMR (400 MHz, $CDCl_3$)



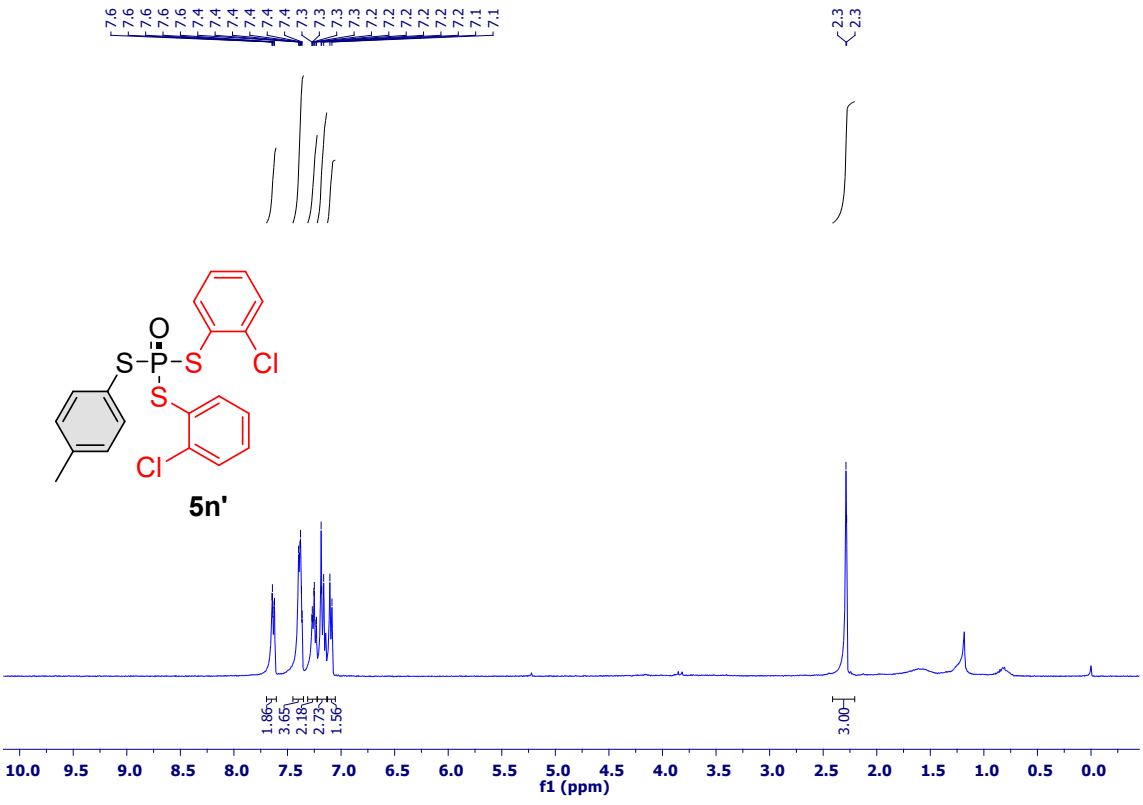
^{13}C NMR (101 MHz, $CDCl_3$)



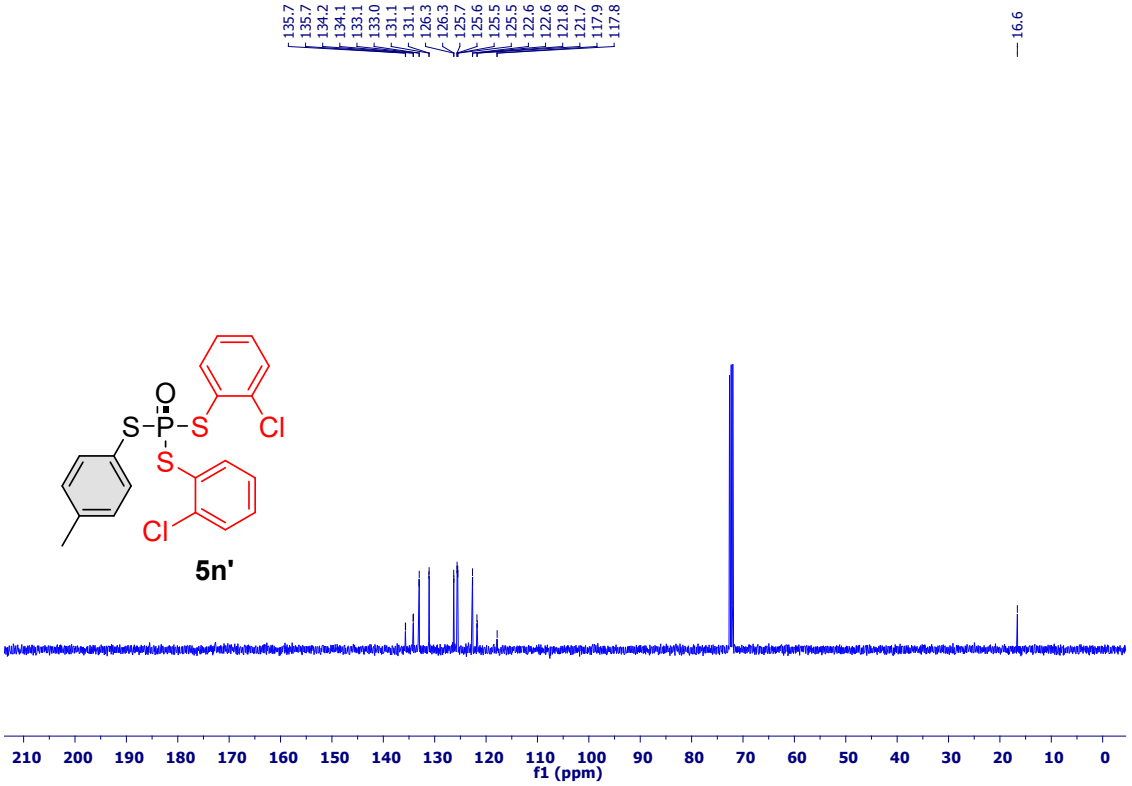
^{31}P NMR (162 MHz, $CDCl_3$)



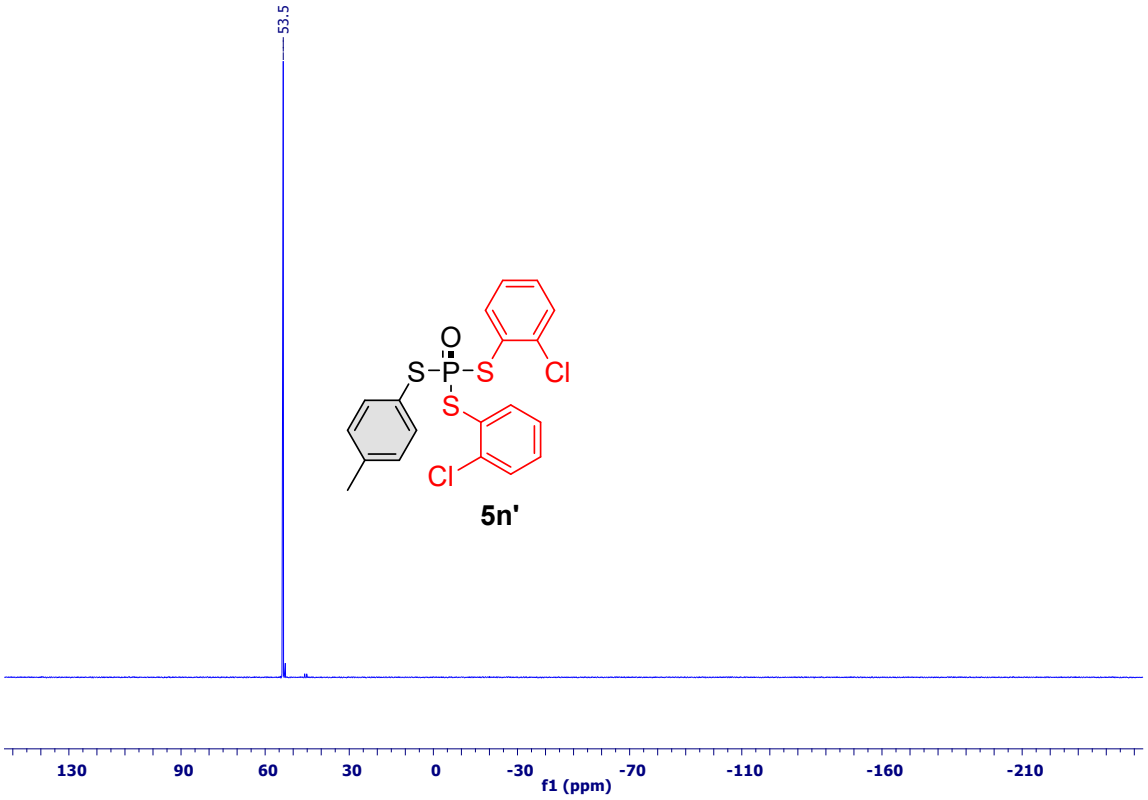
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



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



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