Electronic Supplementary Information

for

Visible-light-mediated direct synthesis of phosphorotrithioates as potent anti-inflammatory agents from white phosphorus

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General Information:

Reagents were purchased from commercial sources and used without further purification. Spectroscopy data of the known compounds matches with the data reported in the corresponding references. ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker Av 400 spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as the internal standard for ^{1}H, and ^{13}C NMR (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm) and 85% H_3PO_4 as external standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in hertz (Hz), integration. ESI mass spectra was aquired on a Bruker Dalton Esquire 3000 Plus mass spectrometer. The unknown products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode. The products were purified by column chromatography on silica gel 300-400 mesh.

The impurity or residual solvents on the ^{1}H NMR and ^{13}C NMR spectra are trace of petroleum ether and AcOEt.

Experimental section:

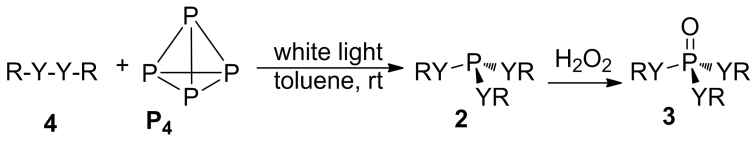
General procedure for the synthesis of 3: An oven-dried Schlenk tube containing Na_2eosinY (0.045 mmol, 0.05 equiv) was evacuated and purged with argon three times. Thiol (0.9 mmol, 1.0 equiv) and P_4 (9.3 mg, 0.3 mmol, 1/3 equiv) in toluene (2.0 mL) was added to the system at room temperature. Then DMSO (0.5 mL) was added. The reaction mixture was stirred and irradiated by white LEDs (3 W) at room temperature under Ar atmosphere for 12 h. After completion, H_2O_2 (0.5 mL) was added, and the mixture was extracted by EtOAc (3×10.0 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash chromatography using petroleum ether−AcOEt [from 50:1 to 10:1 (v/v)] as the eluent to give the corresponding product.

Reacting P4 with disulfides:

We first attempted the coupling of P_4 with diphenyl disulfide at 60 ^{o}C under an argon atmosphere, but no reaction was observed even after 20 hours (Table 1, entry 1). On irradiation

with white light (3 W LEDs, or 40 W CFL), the reaction afforded the corresponding triphenyl phosphorotrithioite **2** in 28% yield (Table 1, entry 1). In order to improve the conversion of P_4 to $P(SR)_3$, 5 equivalents of disulfide were used, giving 85% conversion and an isolated yield of 83% (entry 2). Di-4-chlorophenyl disulfide could also give the corresponding product in good yield (entries 3 and 4). Di-*p*-bromophenyl disulphide, di-*p*-methoxyphenyl disulphide, di-*p*-tolyl disulfide and diphenyl diselenide were also examined. Unfortunately, only trace amounts of desired products were detected (Table 1, entries 5-8).

Reacting P_4 with disulfides[a]



entry	Y	R	n[b]	**2**/ppm (yield)	**3**,yield (%)[c]
1	S	Ph	1.5	133.4 (28)	(0)[d], 28
2	S	Ph	3	133.4 (85)	83
3	S	4-ClC_6H_4	1.5	131.1 (32)	32
4	S	4-ClC_6H_4	3	131.1 (80)	80
5	S	4-$MeOC_6H_4$	5	-	0
7	S	4-BrC_6H_4	5	-	0
8	Se	Ph	5	complicated	decomposed

[a]Reaction conditions: (1) dichalcogenides, P (9.3 mg, 0.3 mmol), toluene (2.5 mL), irradiated with 3 W white LEDs at room temperature for 12 h under an argon atmosphere. (2) Oxidation with excess H_2O_2 (30%, 1 mL), 1 hour, the yield was calculated via ^{31}P NMR spectroscopy. ^{31}P NMR chemical shift for the $P(YR)_3$ product referenced to external 85% H_3PO_4. [b]Number of equivalents per phosphorus atom. [c]Isolated yield. [d]60 °C without light.

Anti-inflammatory Activity in *Vitro*

The in *vitro* anti-inflammatory activities of the synthesized compounds were evaluated by using a LPS-stimulated inflammation model. The RAW264.7 cells (Cell Bank of Chinese Academy of Sciences) were pretreated with different concentrations of compound **3f** for 2 h, followed by LPS (100 ng·mL^{-1}) stimulation for 3 hours at 37 ºC., then were harvested for mRNA analysis with quantitative polymerase chain reaction (qPCR) assay. The cells were homogenized in TRIZOL kit (Yesen, Shanghai, China) for the extraction of total RNA according to each manufacturer's protocol. The resulting RNA was used as a template for generating first-strand cDNA synthesis using cDNA synthesis SuperMix Kit (Yesen, Shanghai, China). Gene specific PCR primers were provided by Brogene Biotechnology (Xiamen, China). The sequences of gene-specific PCR primers are listed in Table S1. An equal amount of GAPDH messenger RNA (mRNA) was used as an internal standard. The SYBR green PCR Master Mix (Yesen, Shanghai, China) was used for real-time PCR analysis. The expression levels relative to the GAPDH control were calculated with the $2^{-\Delta\Delta Ct}$ method.

Table S1. List of qPCR primers

Gene	Forward Primer	Reverse Primer
GAPDH	CCTTCCGTGTTCCTACCC	CAACCTGGTCCTCAGTGTAG
TNF-α	GAACTGGCAGAAGAGGCACT	AGGGTCTGGGCCATAGAACT
IL-1β	AGAGCATCCAGCTTCAAAT	CATCTCGGAGCCTGTAGTG
IL-6	AGTTGCCTTCTTGGGACTGA	TCCACGATTTCCCAGAGAAC

MTT Assay for Cell Viability:

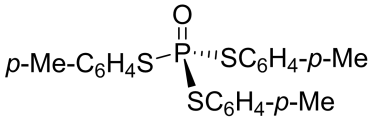
MTT was used to evaluate cell viability. RAW 264.7 cells were seeded at a density of 1×10^4 cells per well in a 96- well plate in RPMI 1640 medium and incubated at 37 °C overnight. The cells were treated in triplicate with vehicle alone or compound **3f** at different concentrations for 24 hours. MTT stock solution prepared in PBS was then added to each well to a final concentration of 0.5 mg/mL and incubated for 4 h at 37 °C. The supernatants were removed and resolved with DMSO (100 μL/well). The optical density of the samples was measured at 570 nm on a Microplate Reader (Thermo).

Statistical analyses

Student's t test was used to determine the differences between sets of data. Statistics were analyzed using GraphPad Prism 5(GraphPad, San Diego, CA, USA); $p<0.05$ was considered significant.

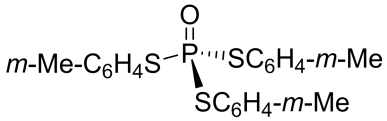
Spectral data

*S,S,S-Triphenyl Phosphorotrithioate (**3a**, CAS No. 13799-87-6)*



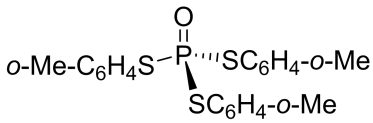
White solid. Yield: 65%. Mp: 130-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 - 7.40 (m, 6H), 7.14 (d, *J* = 8.47 Hz, 6H), 3.33(d, *J* = 2.5 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2 (d, *J* = 25.8 Hz), 135.8 (d, *J* = 4.5 Hz), 130.3 (d, *J* = 2.7 Hz), 123.4 (d, *J* = 7.3 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 56.7. HRMS calcd for $C_{21}H_{21}NaOPS_3^+$ $[M+Na]^+$ 439.0384, found 439.0384.

*S,S,S-Tri-m-tolyl Phosphorotrithioate (**3b**, New Compound)*



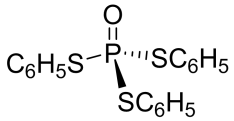
White solid. Yield: 50%. Mp: 50-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 - 7.32 (m, 6H), 7.26 - 7.19 (m, 6H), 2.33 (s, 9H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3 (d, *J* = 2.5 Hz), 136.3 (d, *J* = 4.8 Hz), 132.8 (d, *J* = 24.8 Hz), 130.7 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 2.2 Hz), 126.3 (d, *J* = 2.2 Hz), 21.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 55.7. HRMS calcd for $C_{21}H_{21}NaOPS_3^+$ $[M+Na]^+$ 439.0384, found 439.0380.

*S,S,S-Tri-o-tolyl Phosphorotrithioate (**3c**, CAS No. 35029-38-0)*



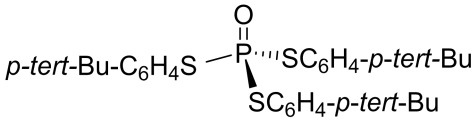
White solid. Yield: 40%. Mp: 55-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 - 7.46 (m, 3H), 7.21 - 7.18 (m, 3H), 7.15 - 7.14 (m, 3H), 7.07 (t, *J* = 7.8, 3H), 2.23 (d, *J* = 1.3 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5 (d, *J* = 4.8 Hz), 137.5 (d, *J* = 4.5 Hz), 131.1 (d, *J* = 2.7 Hz), 130.2 (d, *J* = 3.2 Hz), 126.7 (d, *J* = 2.8 Hz), 126.5 (d, *J* = 6.6 Hz), 21.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 52.5. HRMS calcd for $C_{21}H_{21}NaOPS_3^+$ $[M+Na]^+$ 439.0384, found 439.0385.

*S,S,S-Triphenyl Phosphorotrithioate (**3d**, **CAS** No. 597-82-1)*



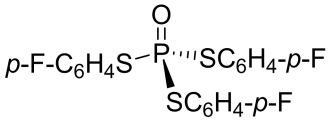
White solid. Yield: 60%. Mp: 110-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 - 7.51 (m, 6H), 7.40 - 7.37 (m, 3H), 7.35 - 7.32(m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9 (d, *J* = 5.3 Hz), 129.9 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 2.8 Hz), 126.8 (d, *J* = 6.4 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 55.5. HRMS calcd for $C_{21}H_{22}OPS_3^+$ $[M+H]^+$ 417.0565, found 417.0559.

*S,S,S-Tris(4-(tert-butyl)phenyl) Phosphorotrithioate (**3e**, New Compound)*



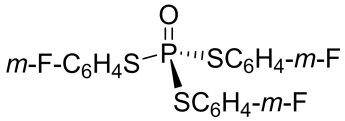
White solid. Yield: 55%. Mp: 100-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 - 7.43 (m, 6H), 7.36 - 7.35 (m, 6H), 1.31 (s, 27H) ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2 (d, *J* = 3.7 Hz), 135.6 (d, *J* = 4.6 Hz), 126.6 (d, *J* = 2.6 Hz), 123.6 (d, *J* = 6.7 Hz), 35.0, 31.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 56.4. HRMS calcd for $C_{30}H_{39}NaOPS_3^+$ $[M+Na]^+$ 565.1793, found 565.1786.

*S,S,S-Tris(4-fluorophenyl) Phosphorotrithioate (**3f**, New Compound)*



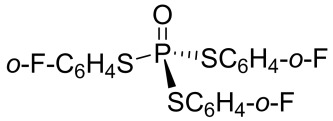
White solid. Yield: 80%. Mp: 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 - 7.47 (m, 6H), 7.06 (t, *J* = 8.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2 (dd, *J* = 252.1 Hz, *J* = 3.7 Hz), 138.0 (dd, *J* = 8.8 Hz, *J* = 4.5 Hz), 121.1 (dd, *J* = 6.0 Hz, *J* = 3.6 Hz), 116.8 (dd, *J* = 22.3 Hz, *J* = 2.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 57.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.2. HRMS calcd for $C_{18}H_{12}F_3NaOPS_3^+$ $[M+Na]^+$ 450.9632, found 450.9627.

*S,S,S-Tris(3-fluorophenyl) Phosphorotrithioate (**3g**, New Compound)*



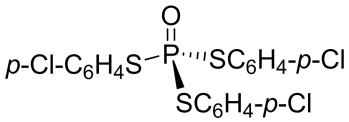
White solid. Yield: 60%. Mp: 116-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 - 7.32 (m, 6H), 7.28 - 7.25 (m, 3H), 7.15 - 7.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6 (dd, *J* = 251.6 Hz, *J* = 3.4 Hz), 131.6 (dd, *J* = 5.4 Hz, *J* = 3.7 Hz), 130.9 (dd, *J* = 8.2 Hz, *J* = 2.7 Hz), 128.1 (t, *J* = 8.4 Hz), 122.6 (dd, *J* = 23.0 Hz, *J* = 4.5 Hz), 117.5 (dd, *J* = 20.9 Hz, *J* = 3.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 53.6. ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.6. HRMS calcd for $C_{18}H_{12}F_3NaOPS_3^+$ $[M+Na]^+$ 450.9632, found 450.9625.

*S,S,S-Tris(2-fluorophenyl) Phosphorotrithioate (**3h**, New Compound)*



White solid. Yield: 45%. Mp: 75-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (t, *J* = 6.8, 3H), 7.42 - 7.40 (m, 3H), 7.14 (t, *J* = 7.9, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0 (dd, *J* = 250.8 Hz, *J* = 5.0 Hz), 138.2 (d, *J* = 4.3 Hz), 132.6 (dd, *J* = 7.9 Hz, *J* = 3.0 Hz), 125.0, 116.6 (dd, *J* = 22.8 Hz, *J* = 2.5 Hz), 113.9 (dd, *J* = 18.1 Hz, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 54.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.4. HRMS calcd for $C_{18}H_{12}F_3NaOPS_3^+$ $[M+Na]^+$ 450.9632, found 450.9630.

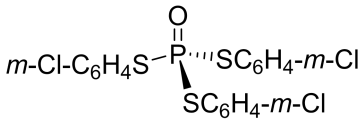
*S,S,S-Tris(4-chlorophenyl) Phosphorotrithioate(**3i**, CAS No. 35075-27-5)*



White solid. Yield: 65%. Mp: 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 6H), 7.33 (d, *J* = 8.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0 (d, *J* = 4.5 Hz), 136.9 (d, *J* = 4.3 Hz), 129.9 (d, *J* = 6.6 Hz), 124.8 (d, *J* = 7.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 52.8. HRMS

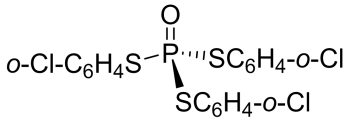
calcd for $C_{18}H_{12}Cl_3NaOPS_3^+$ $[M+Na]^+$ 498.8746, found 498.8739.

*S,S,S-Tris(3-chlorophenyl) Phosphorotrithioate(**3j**, New Compound)*



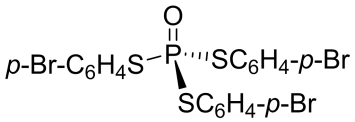
White solid. Yield: 47%. Mp: 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 3H) , 7.44 - 7.39 (m, 6H), 7.30 (t, J = 7.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (d, J = 4.7 Hz), 135.2 (d, J = 3.2 Hz), 133.9 (d, J = 5.1 Hz), 130.6 (d, J = 2.8 Hz), 130.5 (d, J = 2.6 Hz), 128.0 (d, J = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 52.8. HRMS calcd for $C_{18}H_{12}Cl_3NaOPS_3^+$ $[M+Na]^+$ 498.8746, found 498.8742.

*S,S,S-Tris(2-chlorophenyl) Phosphorotrithioate(**3k**, New Compound)*



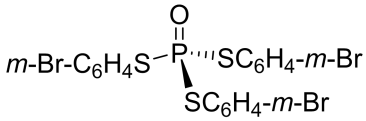
White solid. Yield: 45%. Mp: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.1 Hz, 3H), 7.45 (d, J = 8.2 Hz, 3H), 7.32 (t, J = 7.6, 3H), 7.32 (t, J = 7.7, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3 (d, J = 5.5 Hz), 138.1 (d, J = 4.1 Hz), 131.4 (d, J = 3.1 Hz), 130.6 (d, J = 2.8 Hz), 127.5 (d, J = 2.6 Hz), 126.3 (d, J = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 51.6. HRMS calcd for $C_{18}H_{13}Cl_3OPS_3^+$ $[M+H]^+$ 476.8926, found 476.8916.

*S,S,S-Tris(3-bromophenyl) Phosphorotrithioate(**3l**, New Compound)*



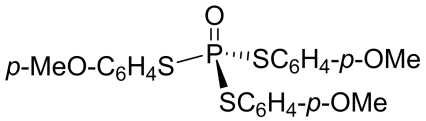
White solid. Yield: 50%. Mp: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.4 Hz, 6H), 7.36 (d, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2 (d, J = 5.1 Hz), 132.8 (d, J = 2.5 Hz), 125.4 (d, J = 7.2 Hz), 125.2 (d, J = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 53.6. HRMS calcd for $C_{18}H_{12}Br_3NaOPS_3^+$ $[M+Na]^+$ 630.7230, found 630.7224.

*S,S,S-Tris(3-bromophenyl) Phosphorotrithioate(**3m**, New Compound)*



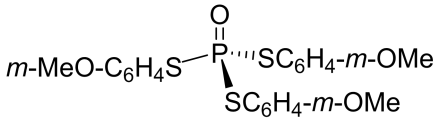
White solid. Yield: 45%. Mp: 78-80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.64 (m, 3H), 7.57 – 7.55 (m, 3H), 7.47 (d, J = 7.7, 3H), 7.26 – 7.23 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (d, J = 5.3 Hz), 134.3 (d, J = 4.4 Hz), 133.4 (d, J = 2.7 Hz), 130.8, 128.2 (d, J = 6.9 Hz), 123.1 (d, J = 3.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 54.2. HRMS calcd for $C_{18}H_{13}Br_3OPS_3^+$ $[M+H]^+$ 608.7411, found 608.7412.

*S,S,S-Tris(4-methoxyphenyl) Phosphorotrithioate(**3n**, New Compound)*



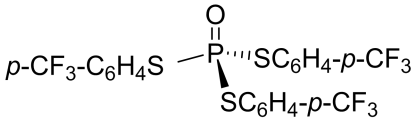
White solid. Yield: 60%. Mp: 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.8 Hz, 6H), 6.88 (d, *J* = 8.7 Hz, 6H), 3.81 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, *J* = 3.4 Hz), 137.6 (d, *J* = 4.1 Hz), 117.2 (d, *J* = 7.3 Hz), 115.1 (d, *J* = 2.3 Hz), 55.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 57.7. HRMS calcd for $C_{21}H_{22}O_4PS_3^+$ $[M+H]^+$ 465.0412, found 465.0403.

*S,S,S-Tris(3-methoxyphenyl) Phosphorotrithioate(**3o**, New Compound)*



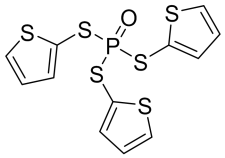
White solid. Yield: 55%. Mp: 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 - 7.24 (m, 3H), 7.14 - 7.12 (m, 3H), 7.10 - 7.09 (m, 3H), 6.95 - 6.92 (m, 3H), 3.81 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 2.7 Hz), 128.0 (d, *J* = 4.6 Hz), 127.9 (d, *J* = 7.3 Hz), 120.5 (d, *J* = 4.5 Hz), 116.4 (d, *J* = 3.2 Hz), 55.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 55.1. HRMS calcd for $C_{21}H_{22}O_4PS_3^+$ $[M+H]^+$ 465.0412, found 465.0403.

*S,S,S-Tris(4-(trifluoromethyl)phenyl) Phosphorotrithioate(**3p**, New Compound)*



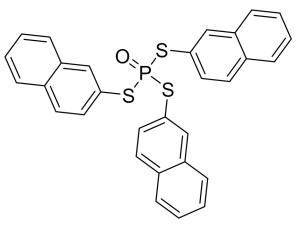
Wax. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 - 7.60 (m, 3H), 7.58- 7.54 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 135.9 (d, *J* = 5.4 Hz), 129.7 (q, *J* = 32.4 Hz), 126.8, 126.3 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 272.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 51.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.7. HRMS Calcd for $C_{21}H_{12}F_9NaOPS_3^+$ $[M+Na]^+$600.9635, found 600.9632.

*S,S,S-Tri(thiophen-2-yl) Phosphorotrithioate(**3r**, New Compound)*



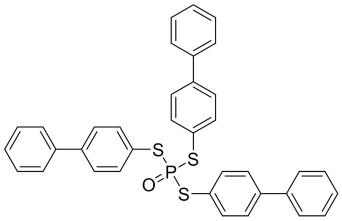
Wax. Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 - 7.54 (m, 3H), 7.36 - 7.34 (m, 3H), 7.11 – 7.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5 (d, *J* = 6.3 Hz), 133.1 (d, *J* = 5.3 Hz), 128.4 (d, *J* = 3.7 Hz), 121.1 (d, *J* = 7.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 59.1. HRMS calcd for $C_{12}H_{10}OPS_6^+$ $[M+H]^+$ 392.8788, found 392.8790.

*S,S,S-Tri(naphthalen-2-yl) Phosphorotrithioate(**3s**, CAS No. 14974-75-5)*



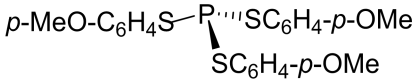
White solid. Yield: 45%. Mp: 193-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.0 (s, 3H), 7.86 - 7.81 (m, 9H), 7.62 – 7.50 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1 (d, *J* = 6.8 Hz), 133.7 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 2.1 Hz), 131.9 (d, *J* = 3.65 Hz), 129.1 (d, *J* = 1.5 Hz), 128.2, 127.9, 127.6, 126.9, 124.1 (d, *J* = 7.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 54.3. HRMS calcd for $C_{30}H_{22}OPS_3^+$ $[M+H]^+$ 525.0565, found 525.0556.

*S,S,S-Tri([1,1'-biphenyl]-4-yl) Phosphorotrithioate(**3t**, New Compound)*



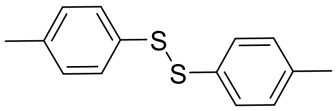
White solid. Yield: 50%. Mp: 145-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.5 Hz, 6H), 7.58 (d, *J* = 7.8 Hz, 12H), 7.44 (t, *J* = 7.5 Hz, 6H), 7.37 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9 (d, *J* = 3.8 Hz), 140.1, 136.2 (d, *J* = 4.7 Hz), 129.1, 128.2 (d, *J* = 2.6 Hz), 128.1, 127.4, 125.6 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 53.6. HRMS calcd for $C_{36}H_{28}OPS_3^+$ $[M+H]^+$ 603.1034, found 603.1030.

*Tris(4-methoxyphenyl) Phosphorotrithioite(**2n**, New Compound)*



White solid. Yield: 40%. Mp: 86-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 6H), 6.83 (d, *J* = 8.7 Hz, 6H), 3.79 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (d, *J* = 1.8 Hz), 136.3 (d, *J* = 3.6 Hz), 122.7 (d, *J* = 13.1 Hz), 114.9, 55.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 135.1. HRMS calcd for $C_{21}H_{21}NaO_3PS_3^+$ $[M+Na]^+$ 471.0283, found 471.0273.

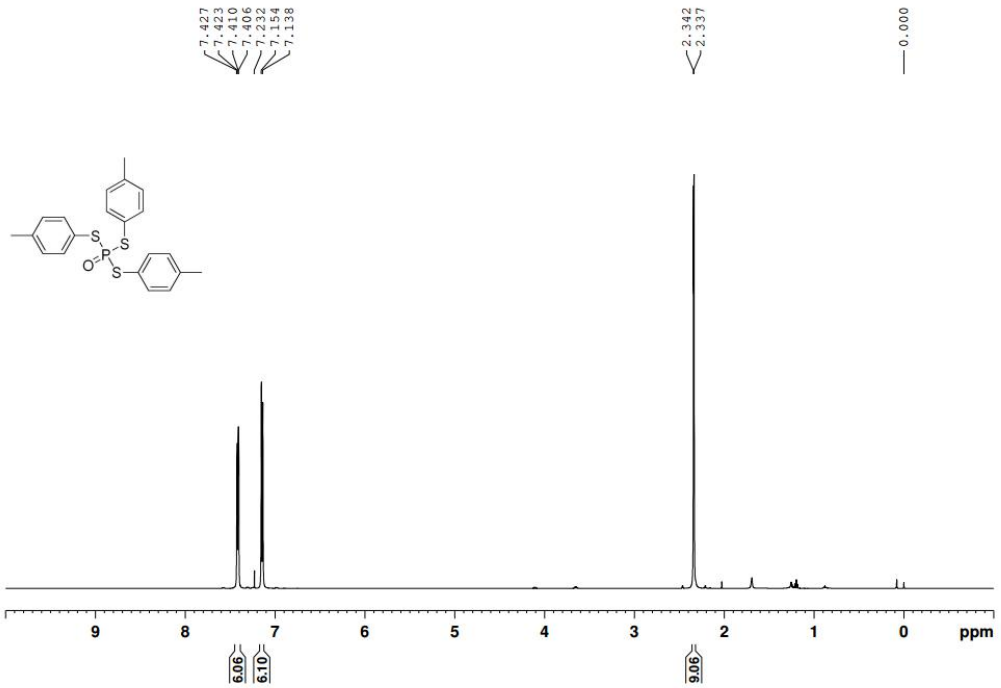
*1,2-Di-p-tolyldisulfane(**1a**, CAS No. 103-19-5)*



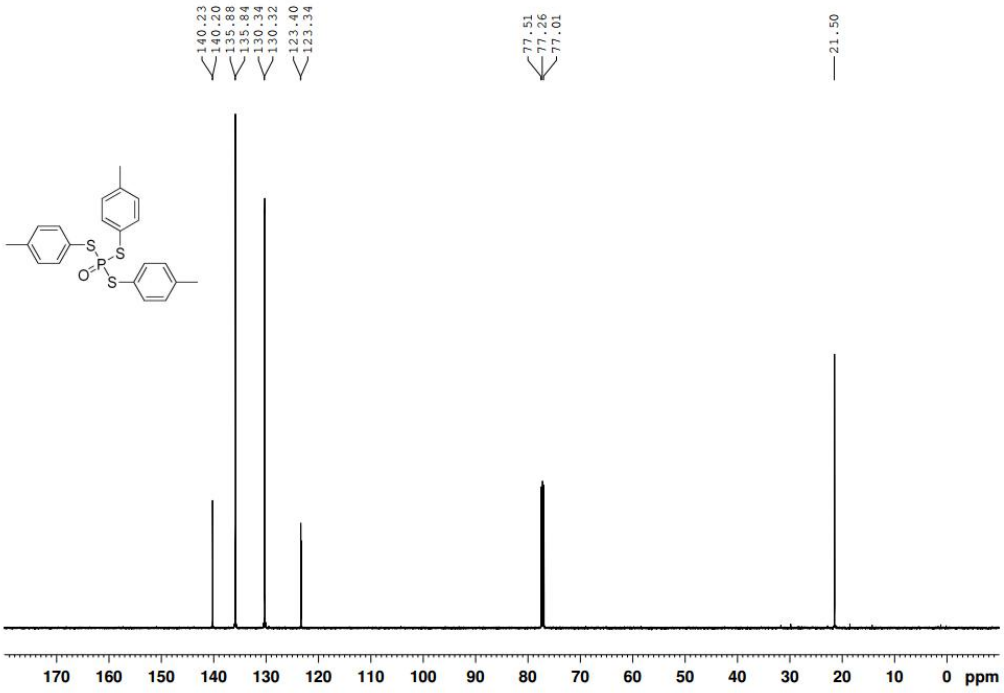
White solid. Yield: 35%. Mp: 42-44 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.7 Hz, 4H), 7.11 (d, *J* = 8.2 Hz , 4H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 134.1, 129.9, 128.7, 21.3.

NMR spectra

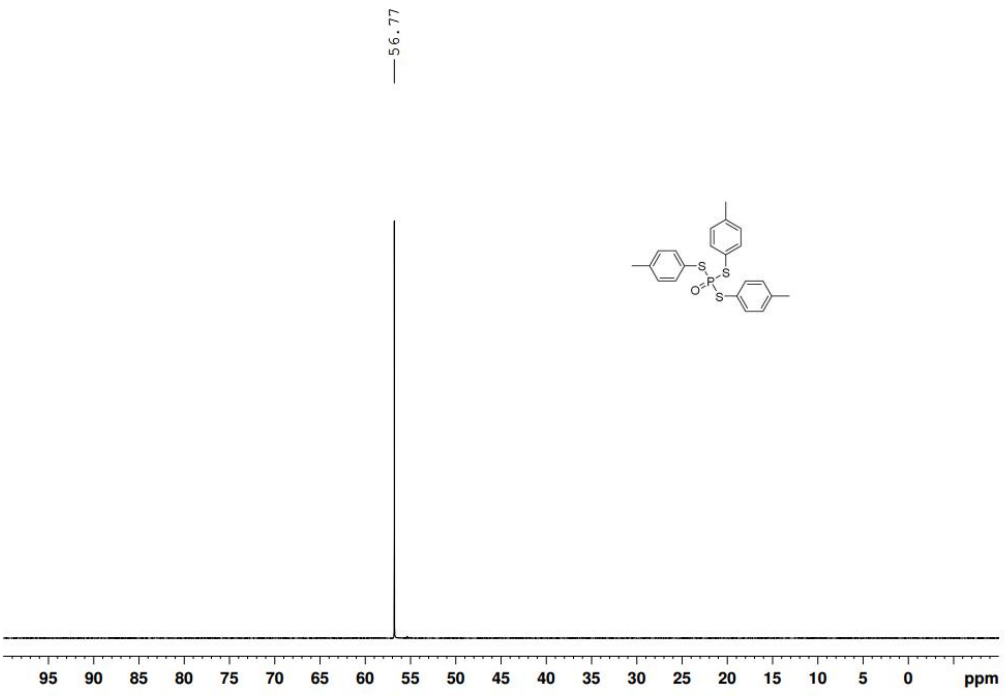
^{1}H NMR of 3a



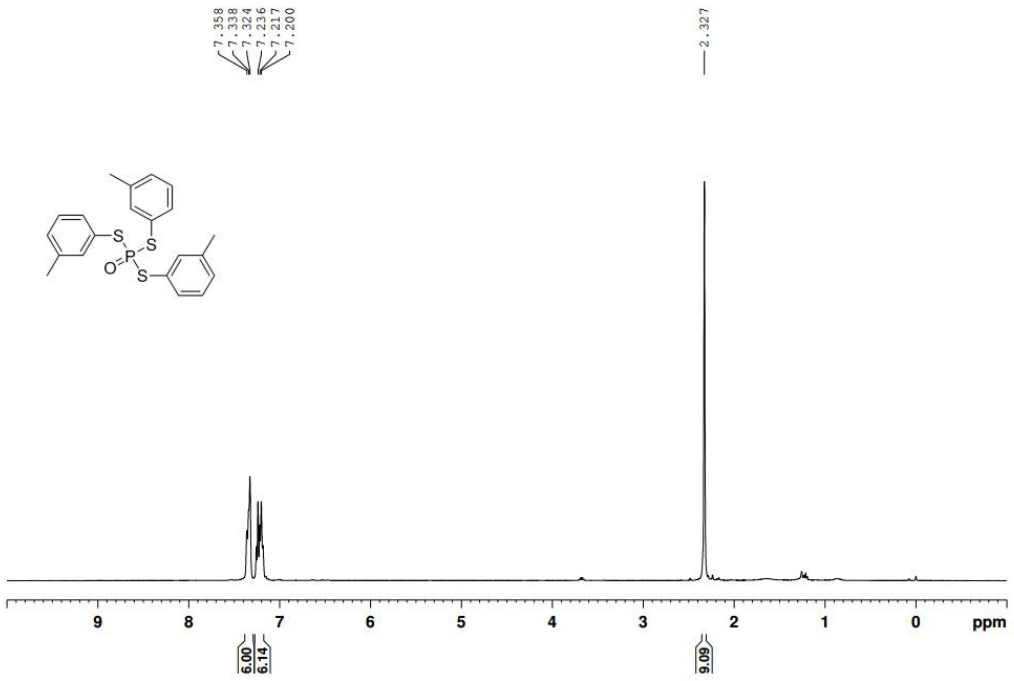
^{13}C NMR of 3a



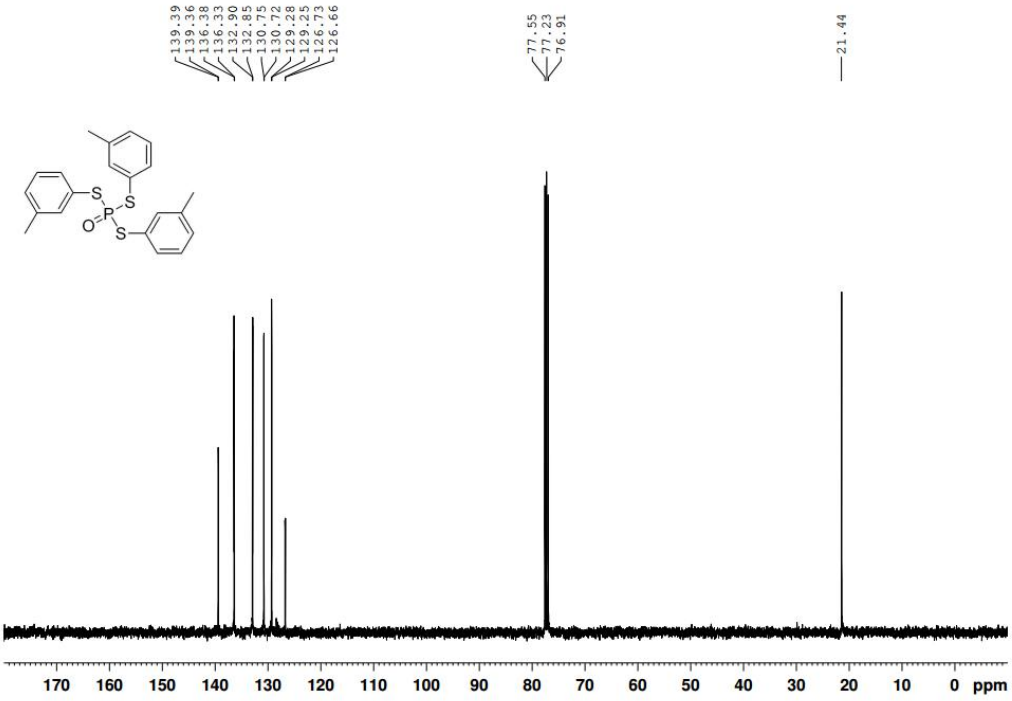
^{31}P NMR of 3a



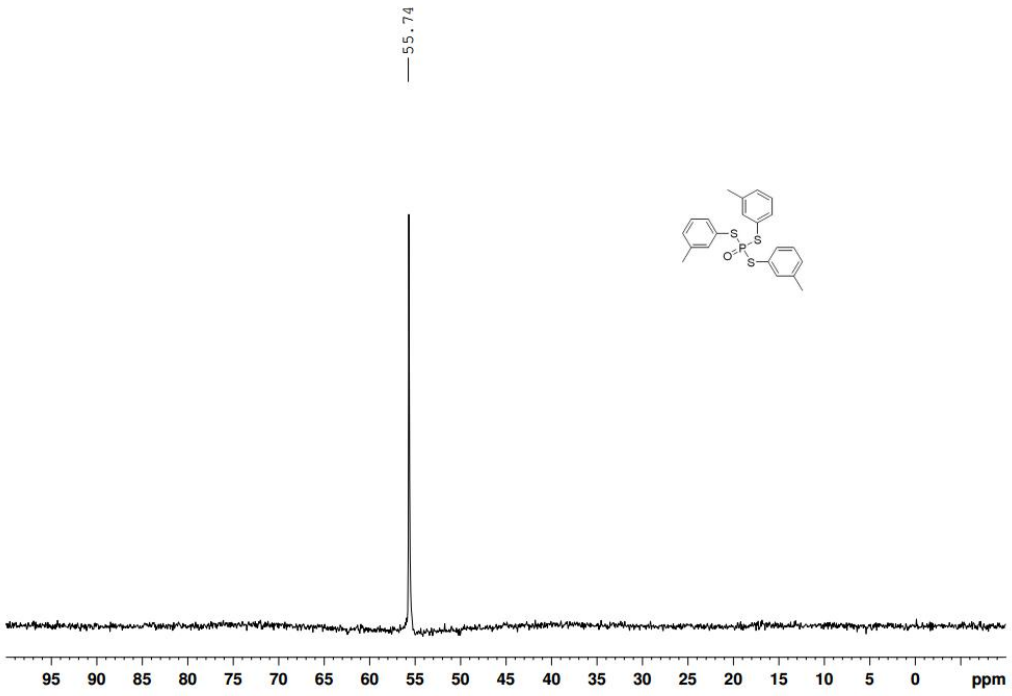
^{1}H NMR of 3b



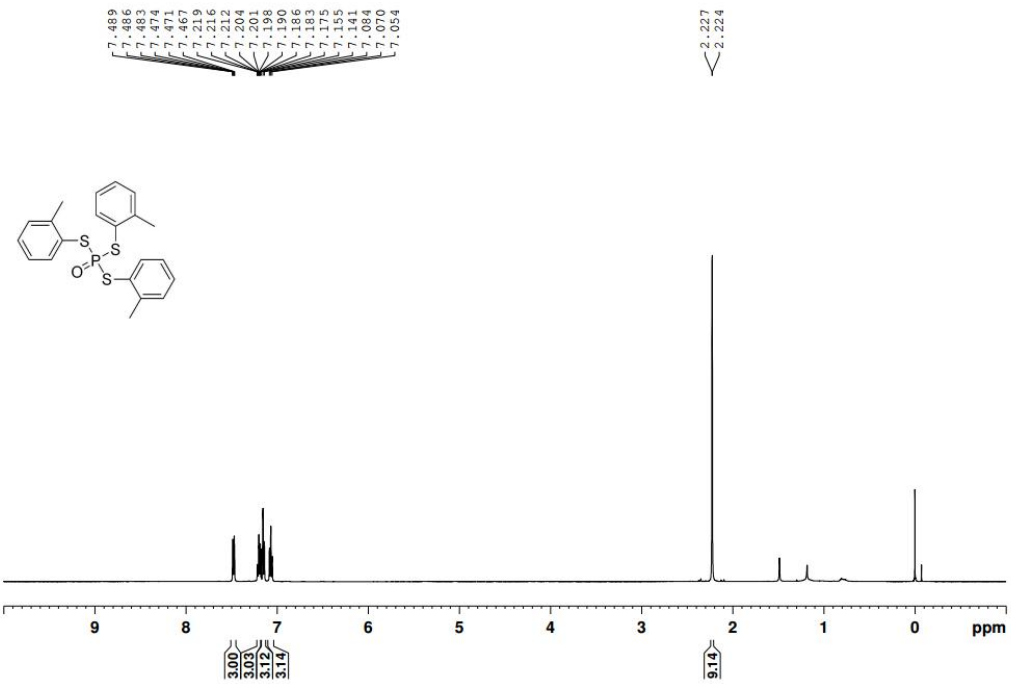
^{13}C NMR of 3b



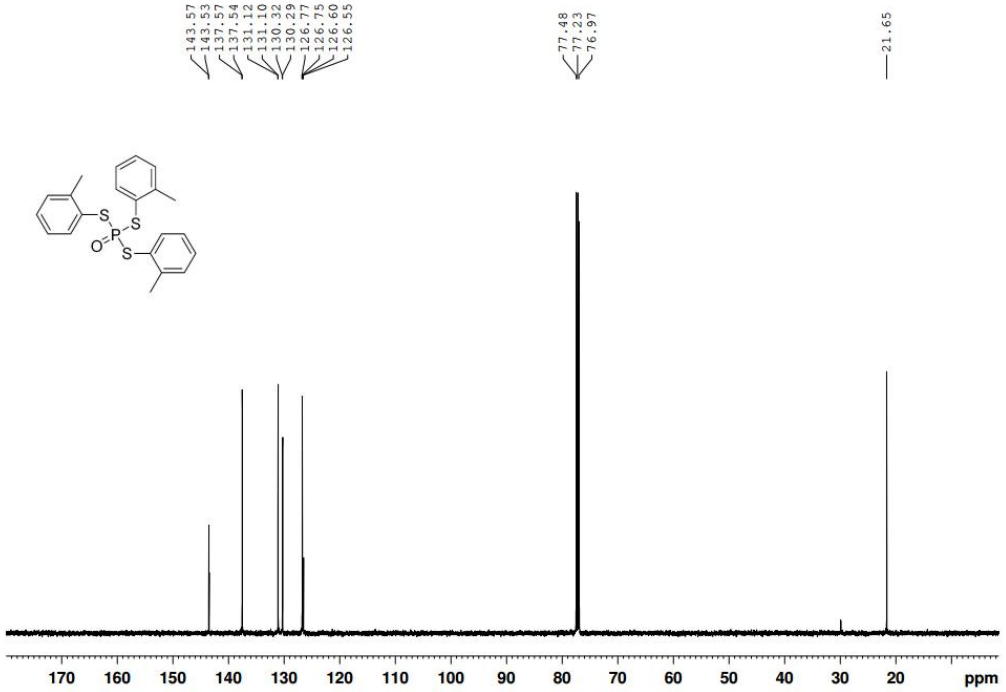
^{31}P NMR of 3b



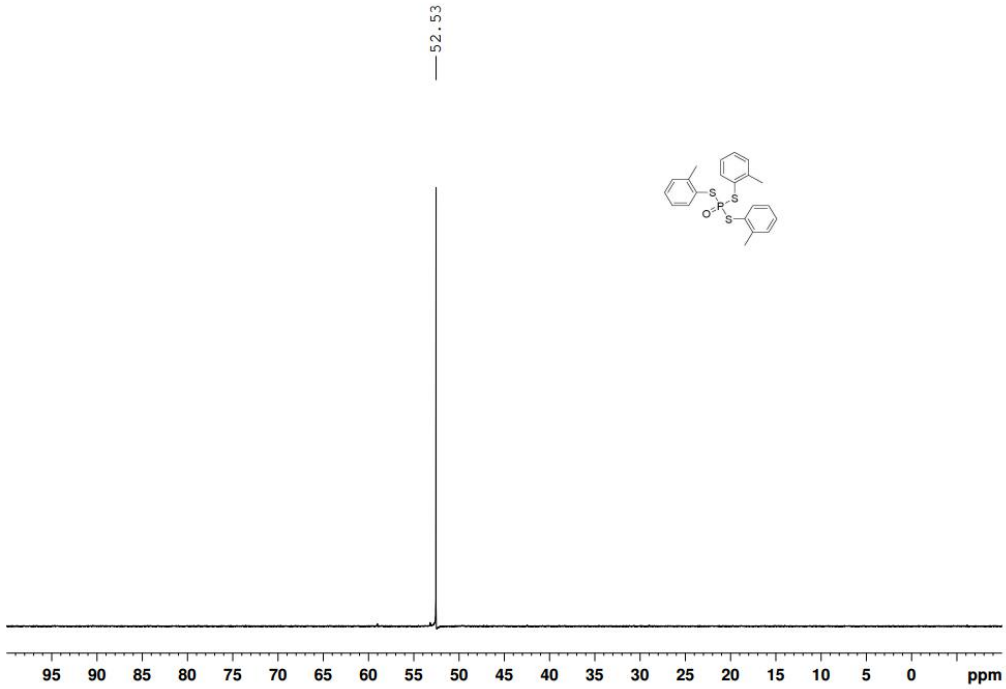
^{1}H NMR of 3c



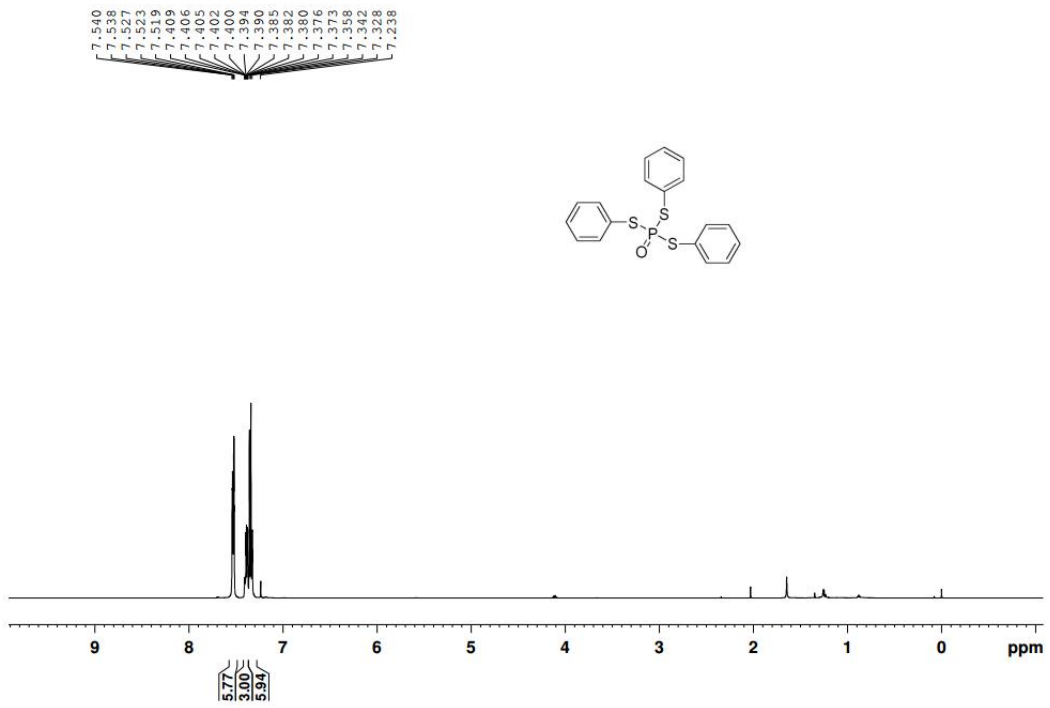
^{13}C NMR of 3c



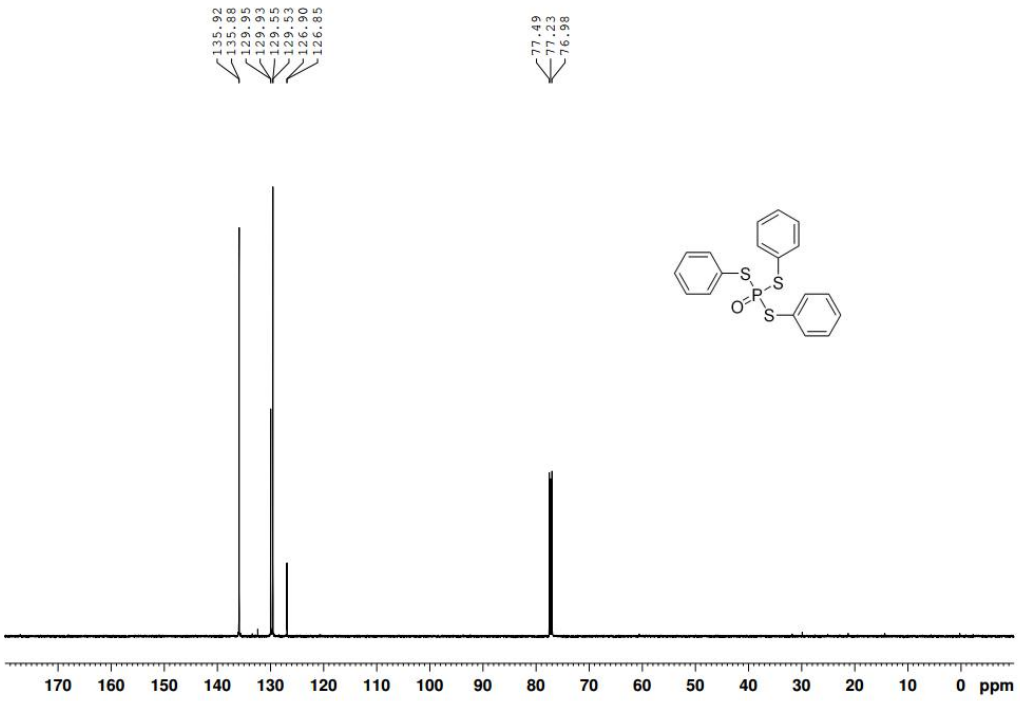
^{31}P NMR of 3c



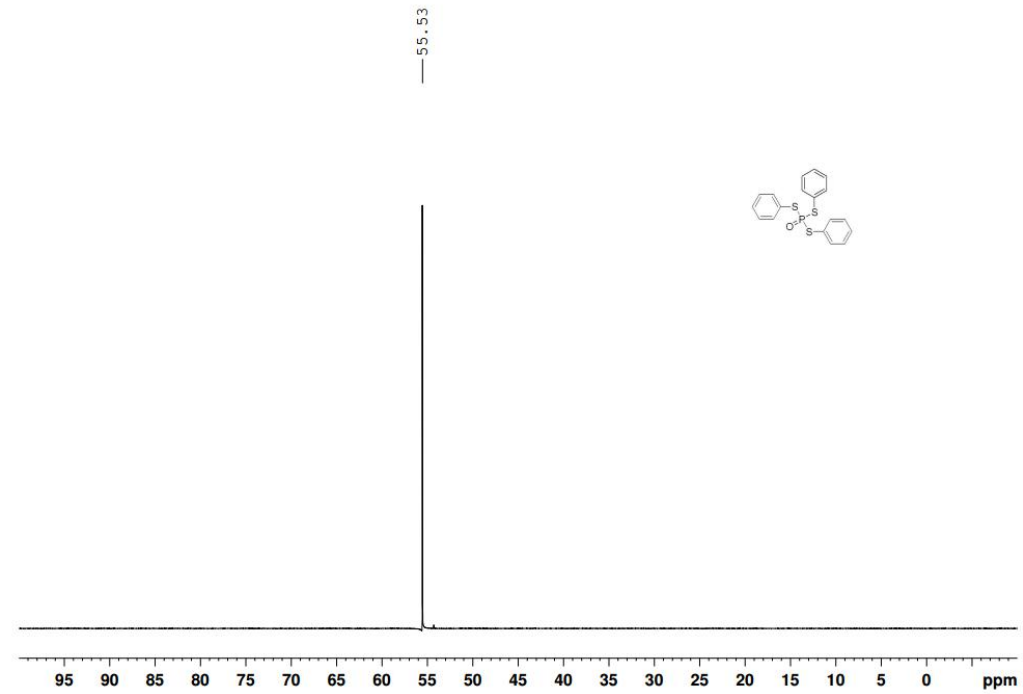
^{1}H NMR of 3d



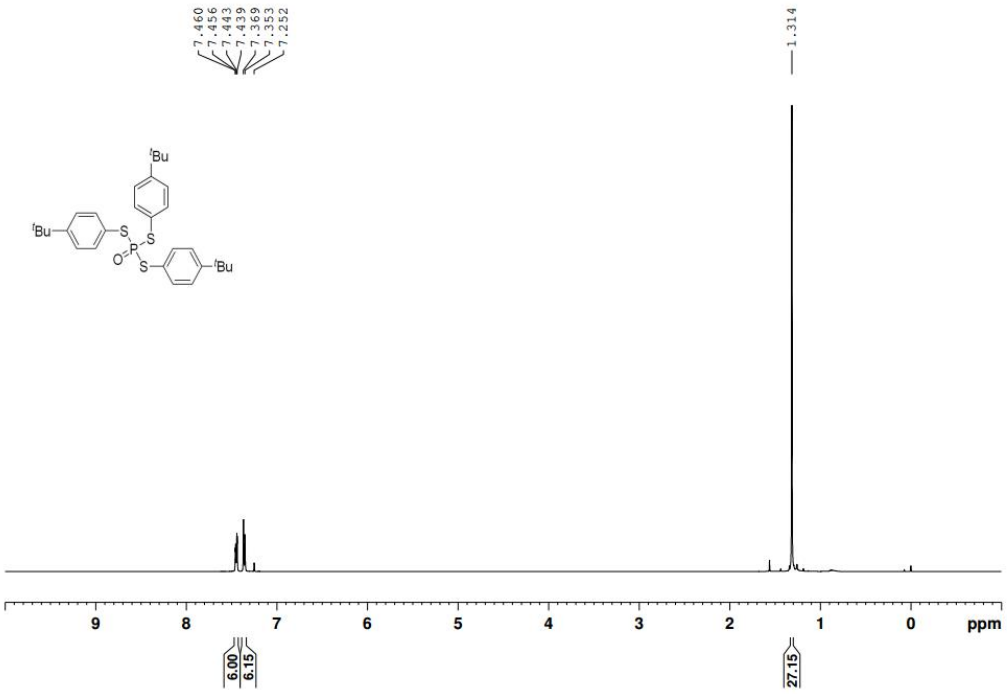
^{13}C NMR of 3d



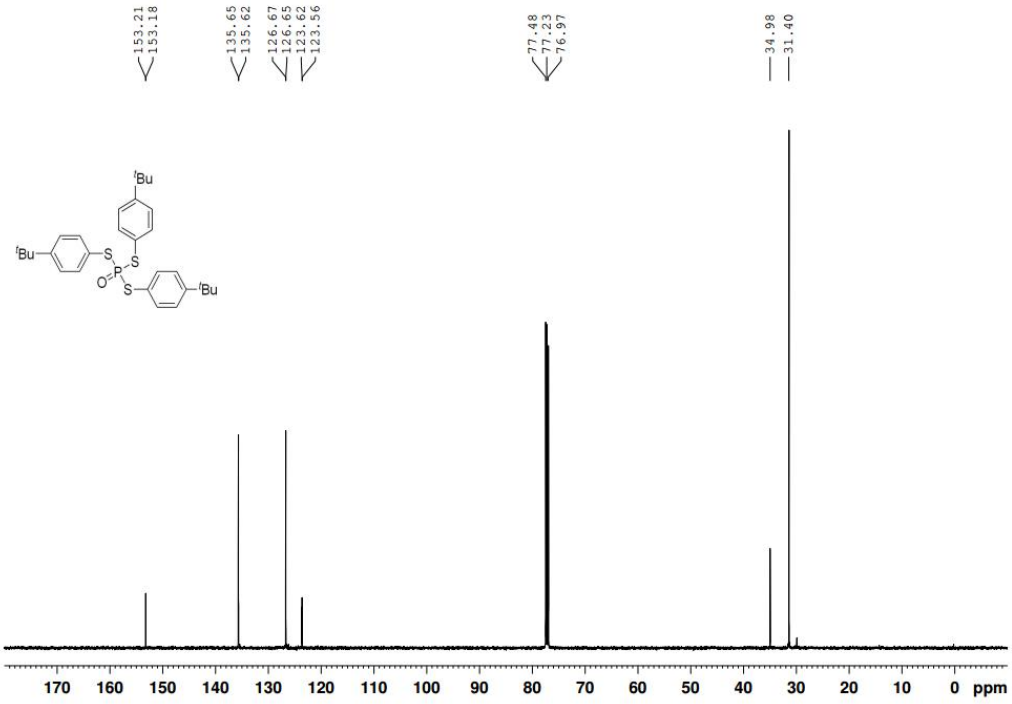
^{31}P NMR of 3d



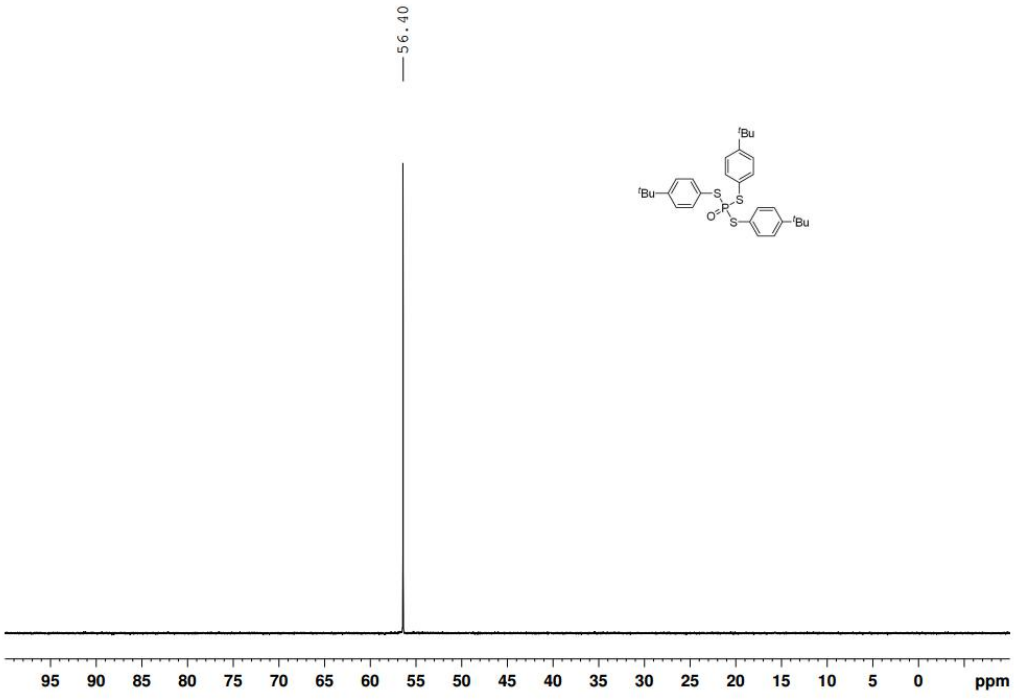
^{1}H NMR of 3e



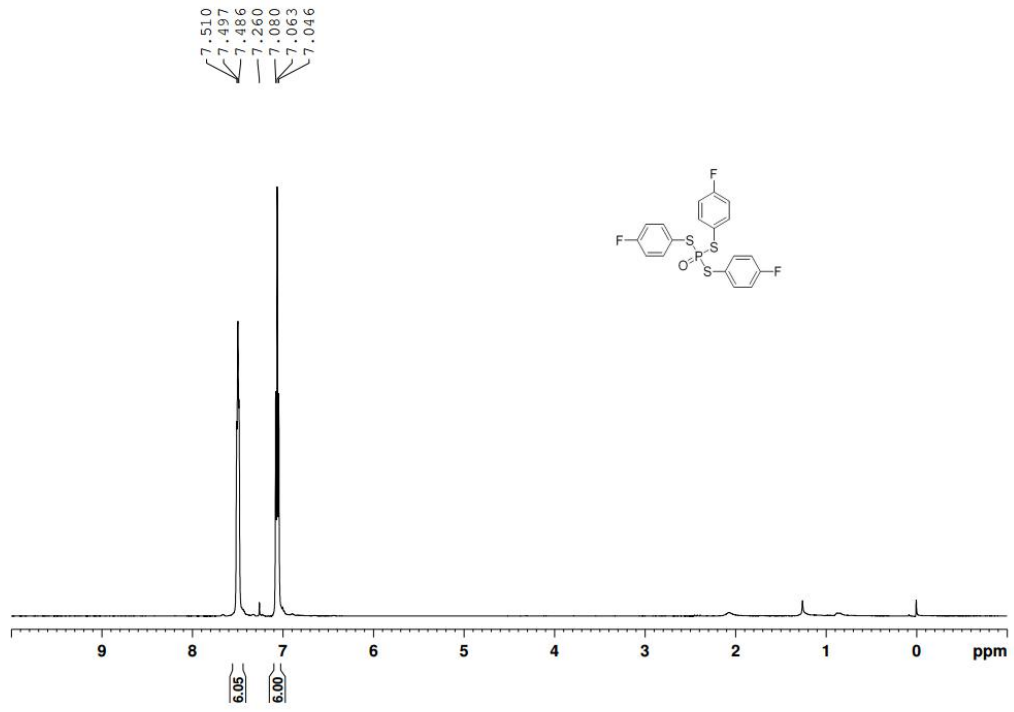
^{13}C NMR of 3e



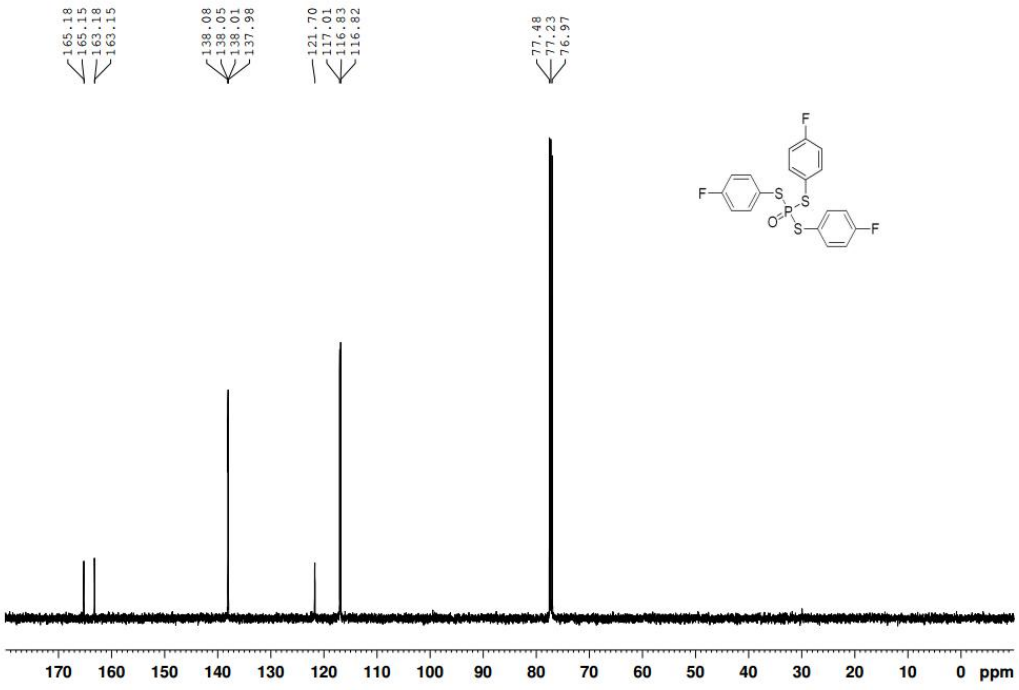
^{31}P NMR of 3e



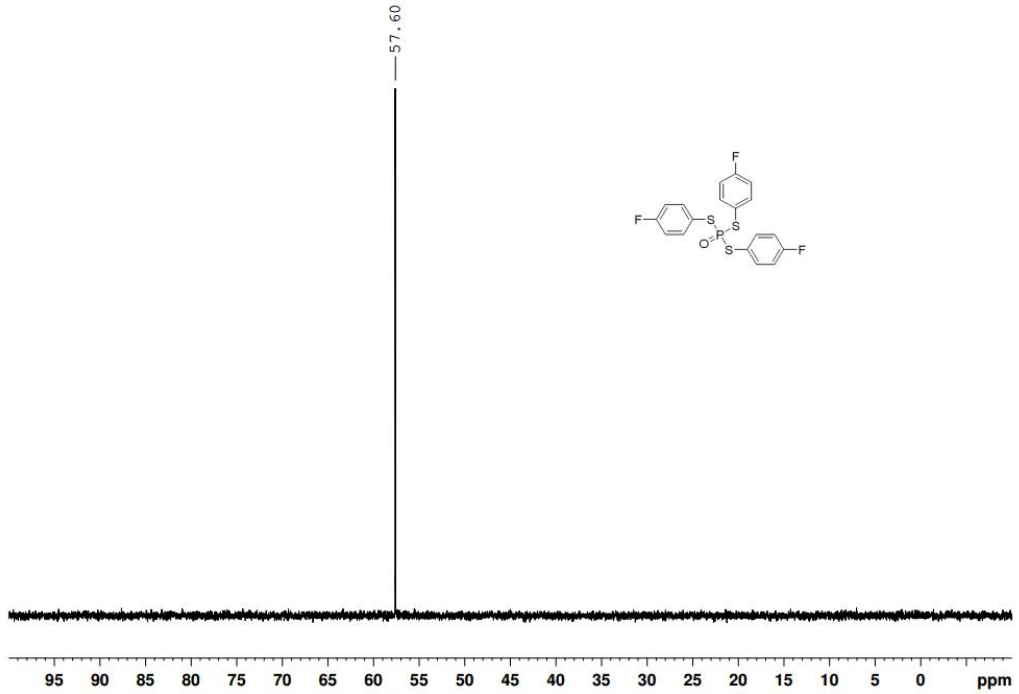
^{1}H NMR of 3f



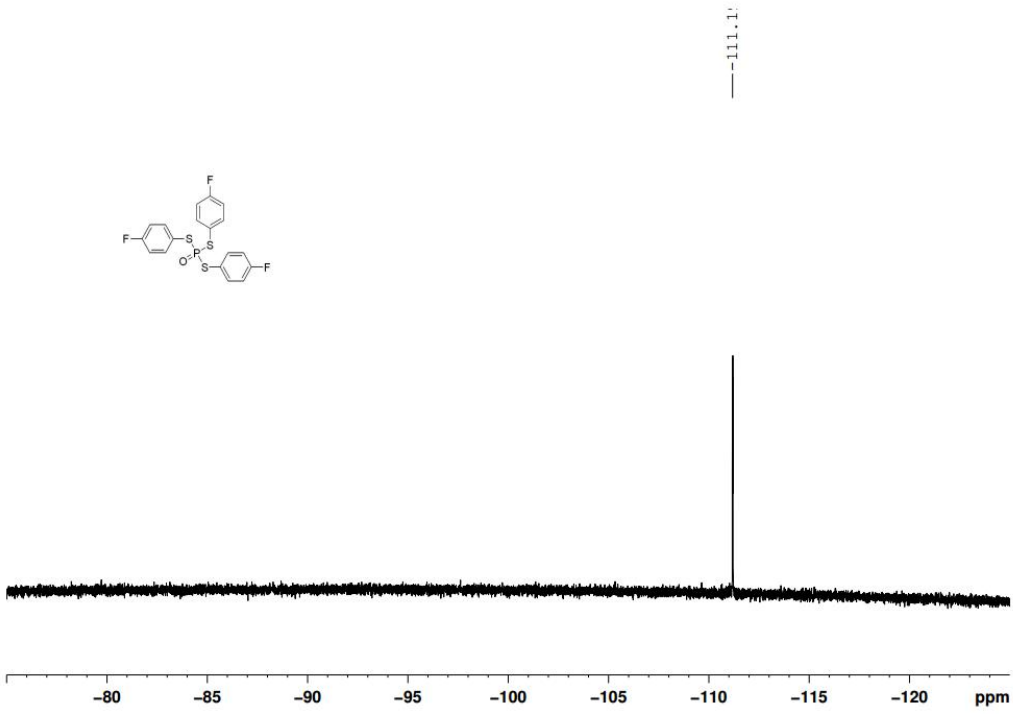
^{13}C NMR of 3f



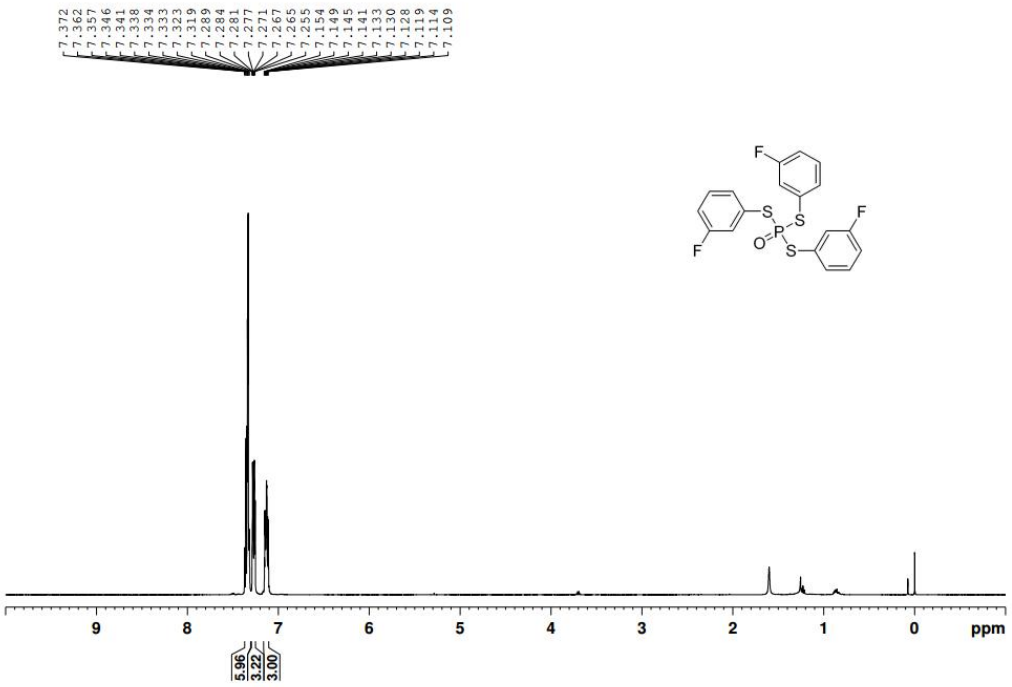
^{31}P NMR of 3f



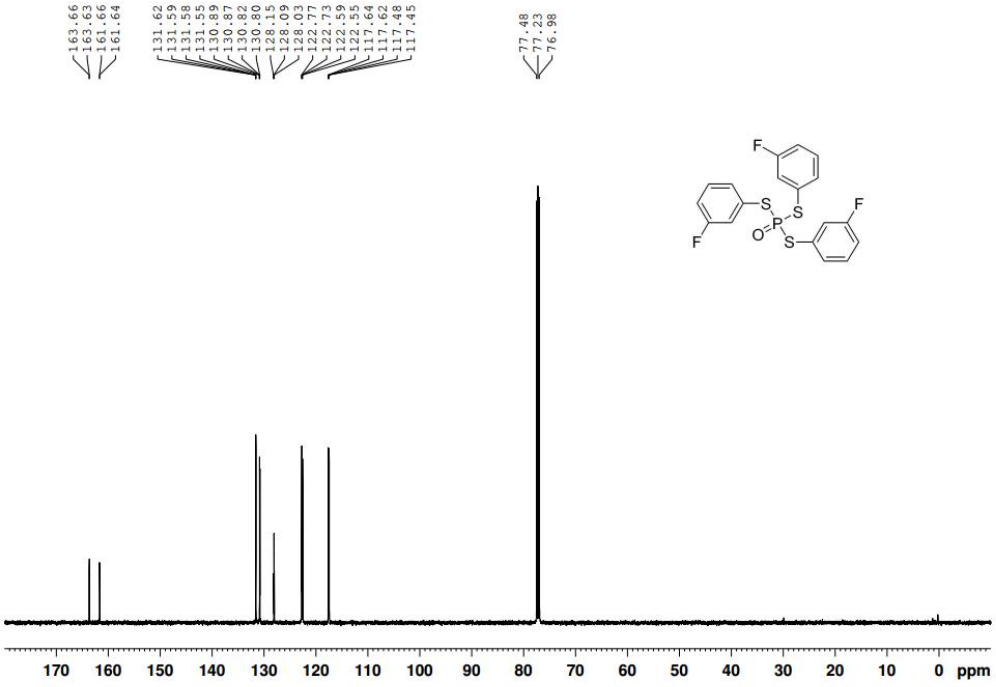
^{19}F NMR of 3f



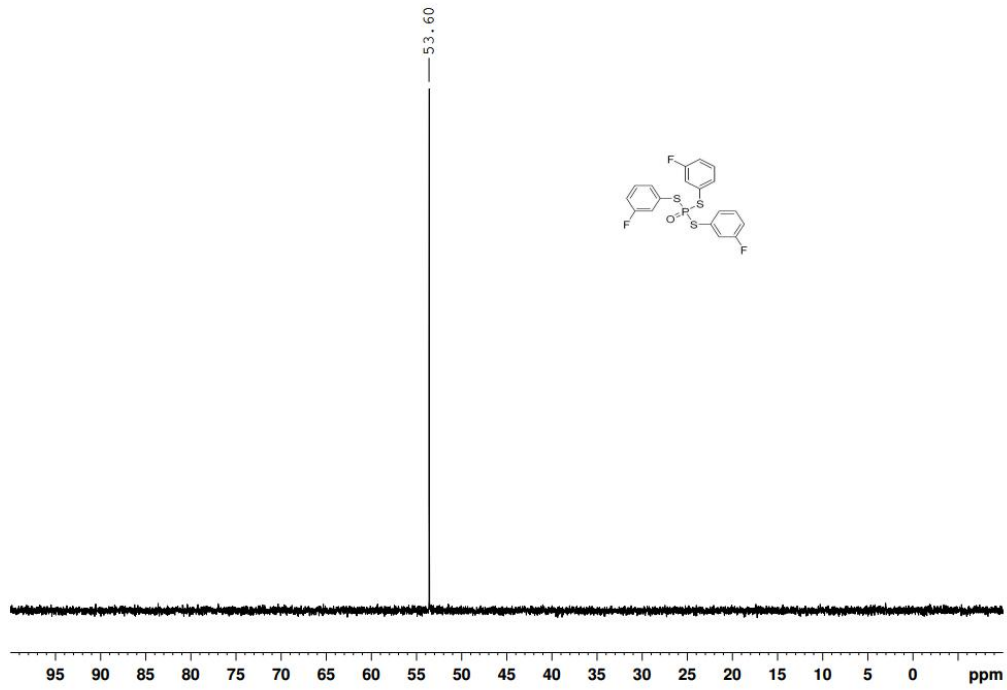
^{1}H NMR of 3g



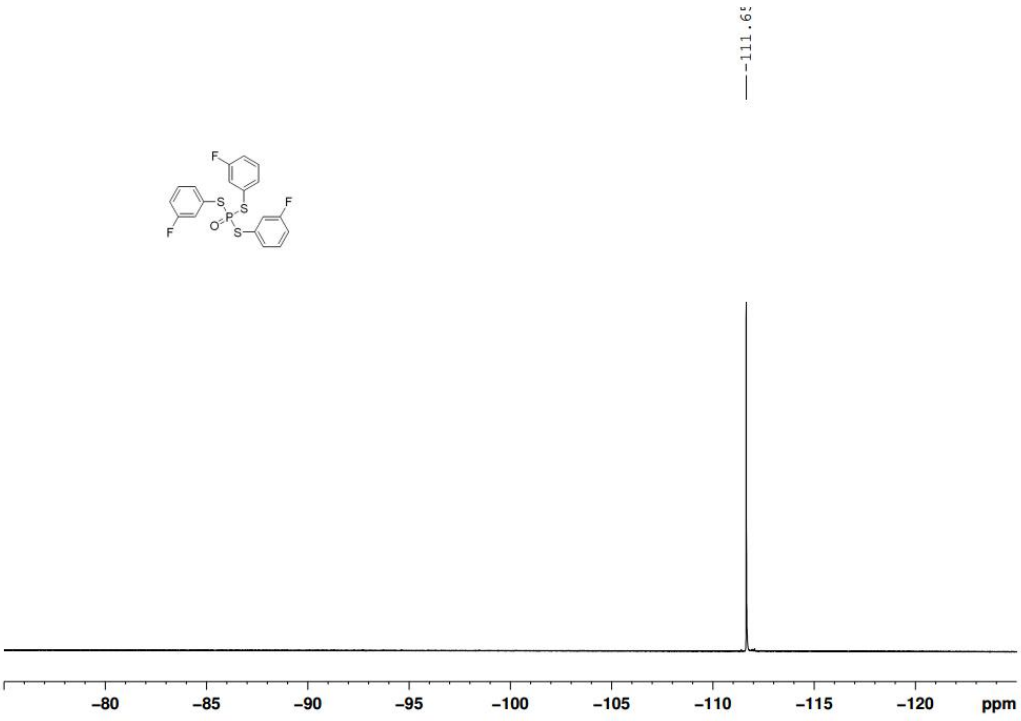
^{13}C NMR of 3g



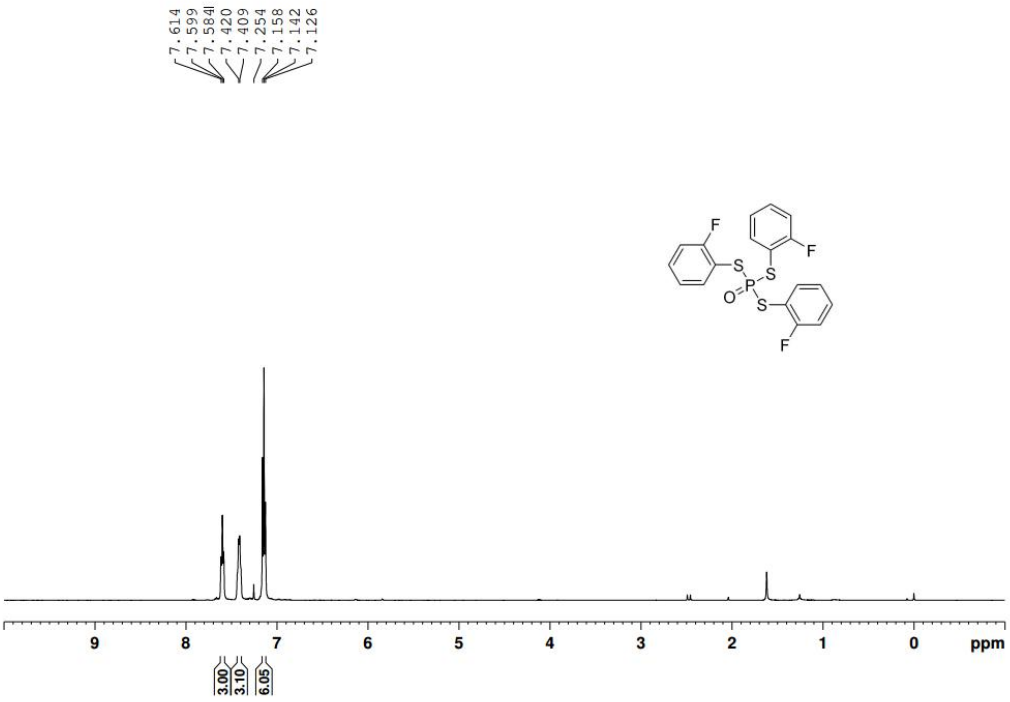
^{31}P NMR of 3g



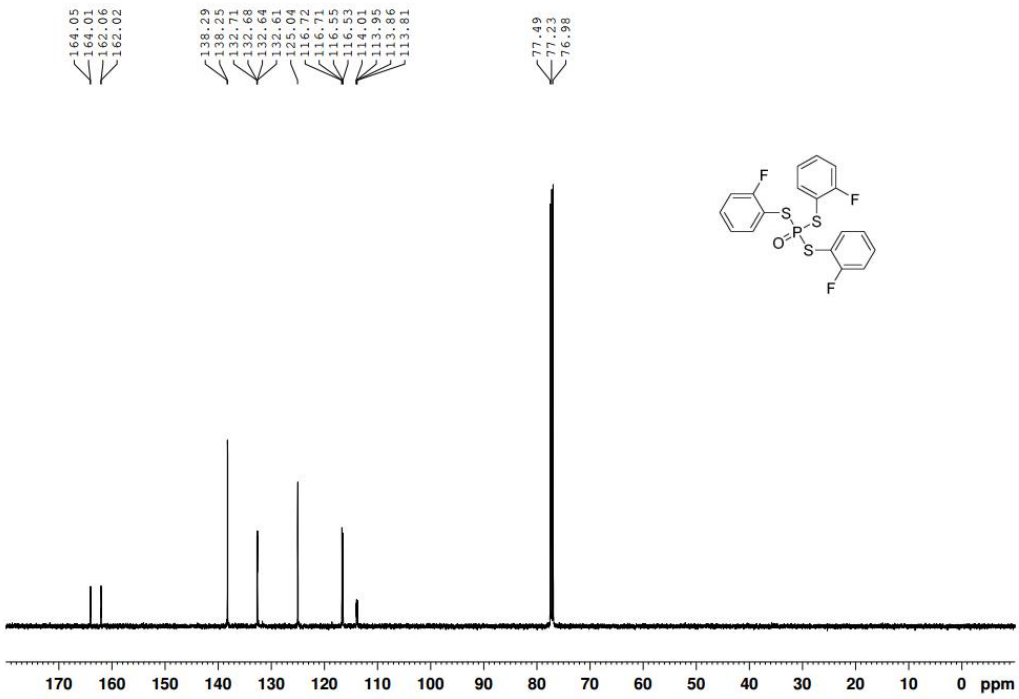
^{19}F NMR of 3g



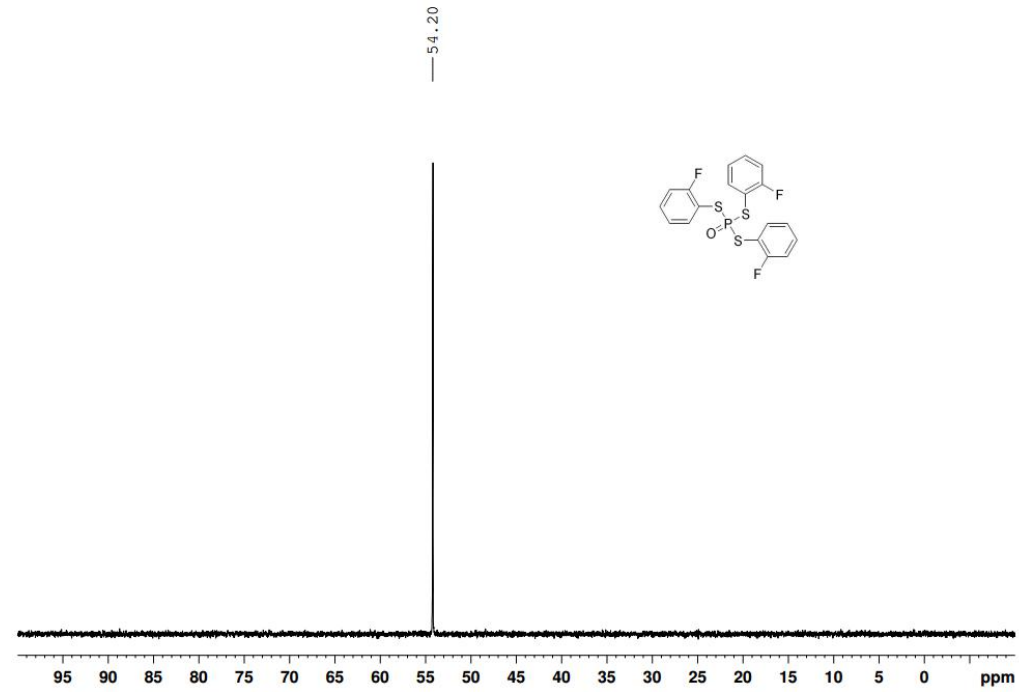
^{1}H NMR of 3h



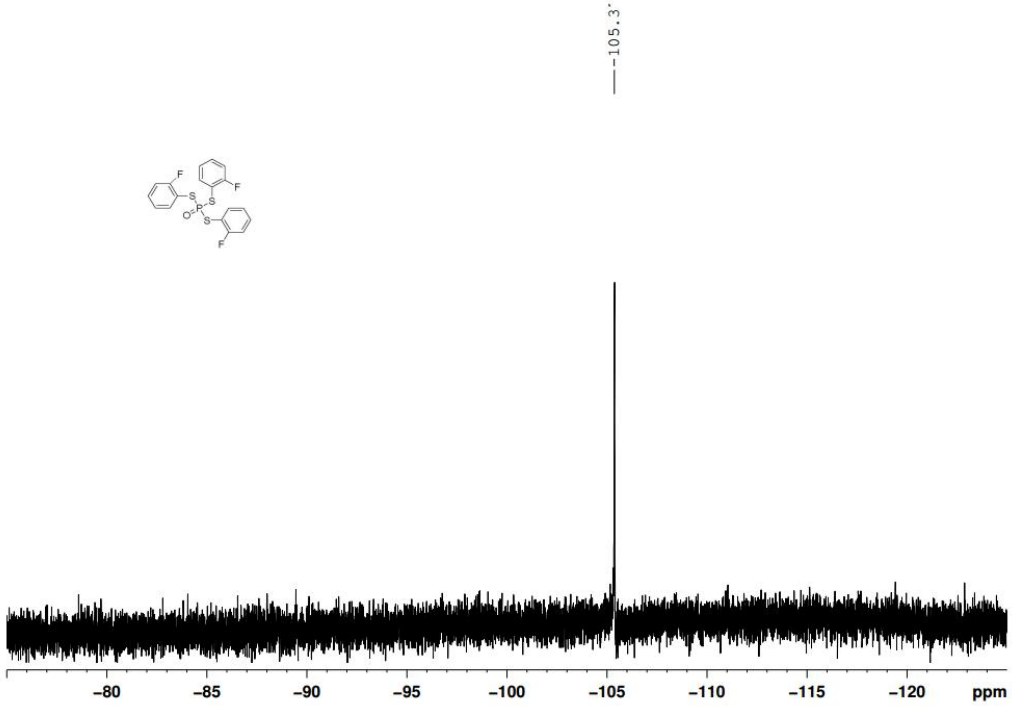
^{13}C NMR of 3h



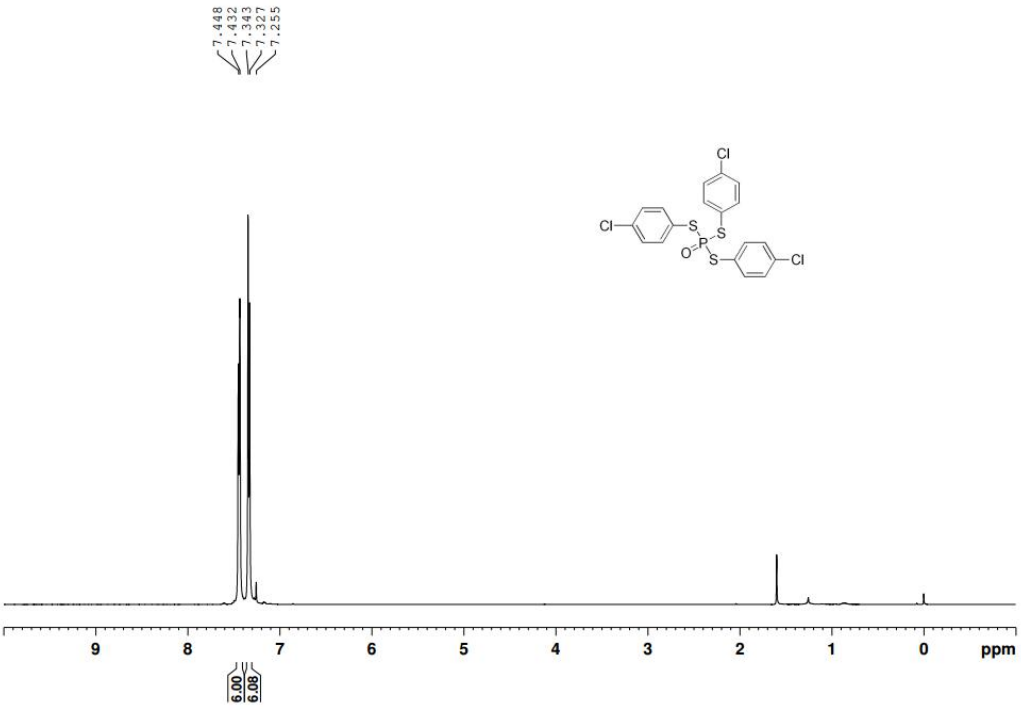
^{31}P NMR of 3h



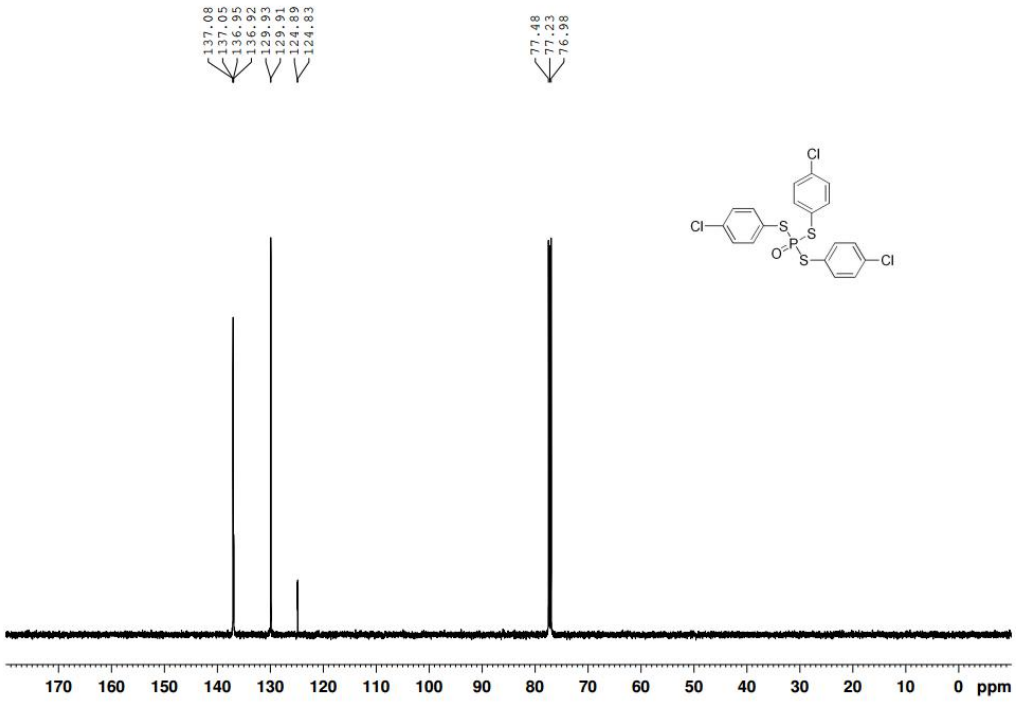
^{19}F NMR of 3h



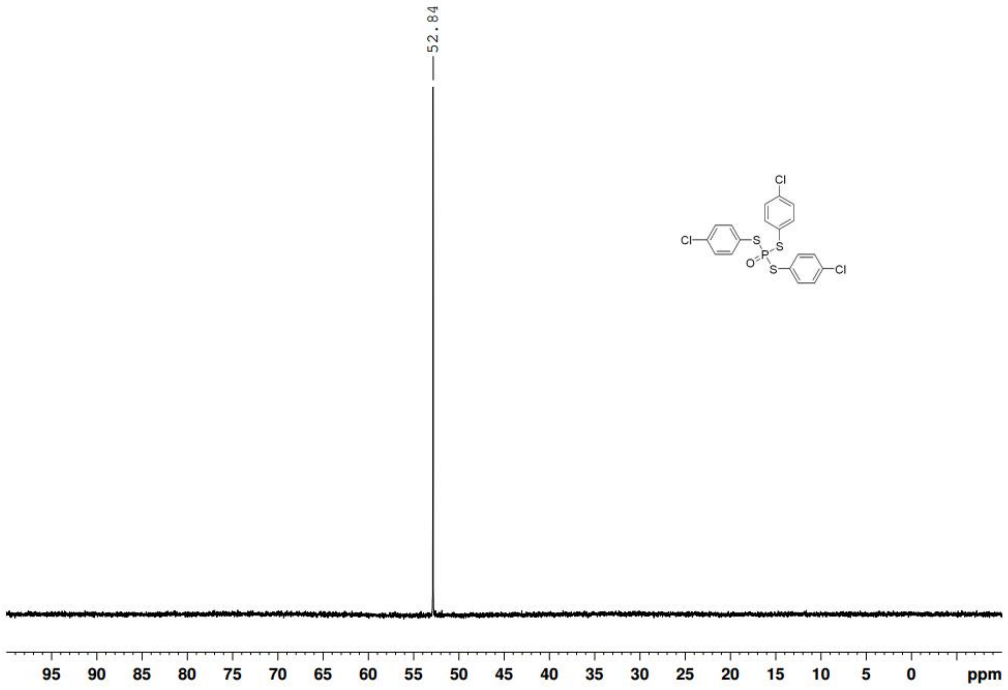
^{1}H NMR of 3i



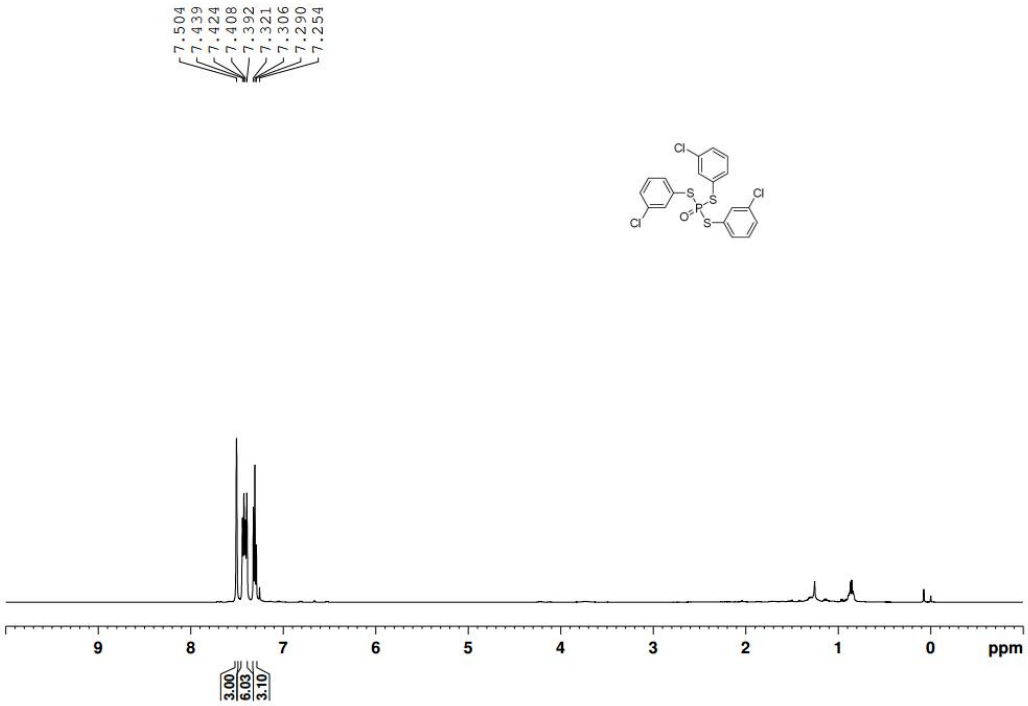
^{13}C NMR of 3i



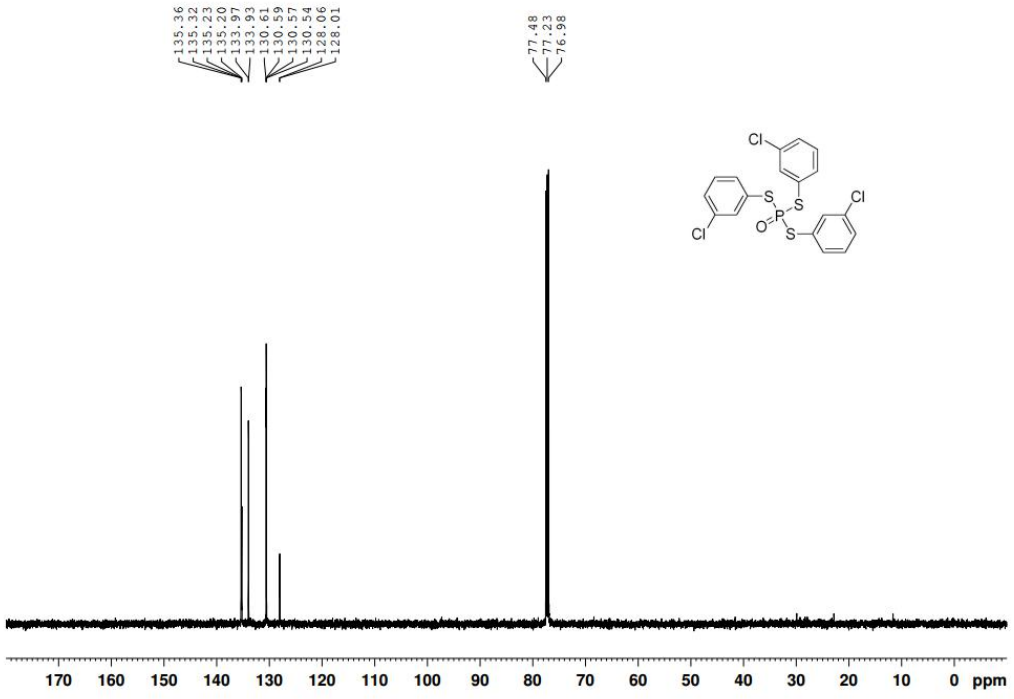
^{31}P NMR of 3i



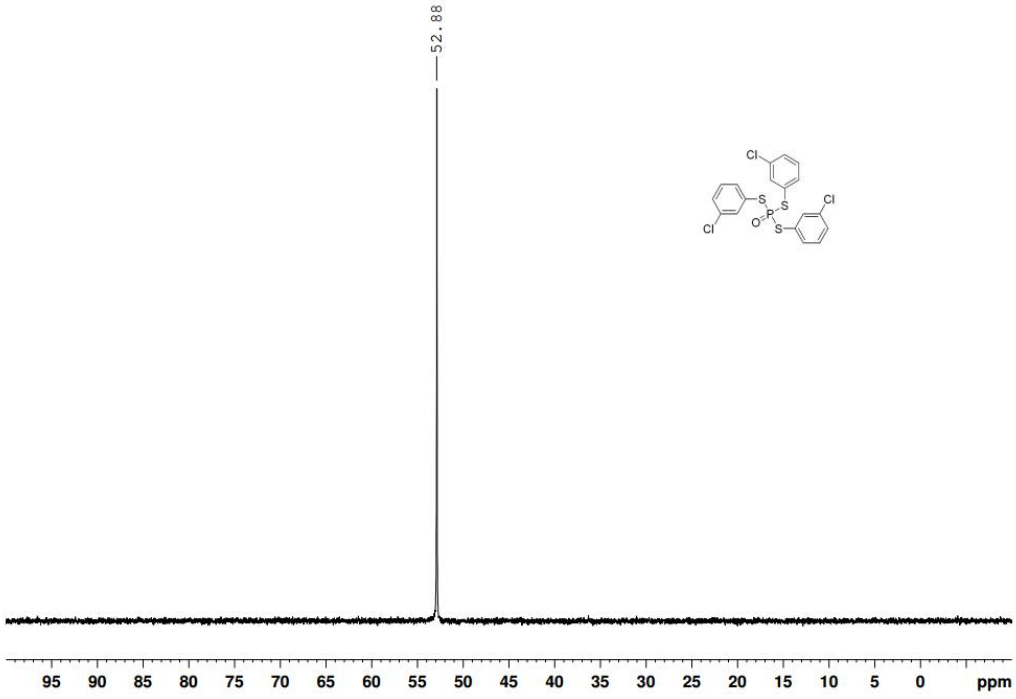
^{1}H NMR of 3j


7.504
7.439
7.424
7.408
7.392
7.321
7.306
7.290
7.254
Cl
S
P
O
S
S
Cl
Cl
9
8
7
6
5
4
3
2
1
0
ppm
3.00
6.03
3.10

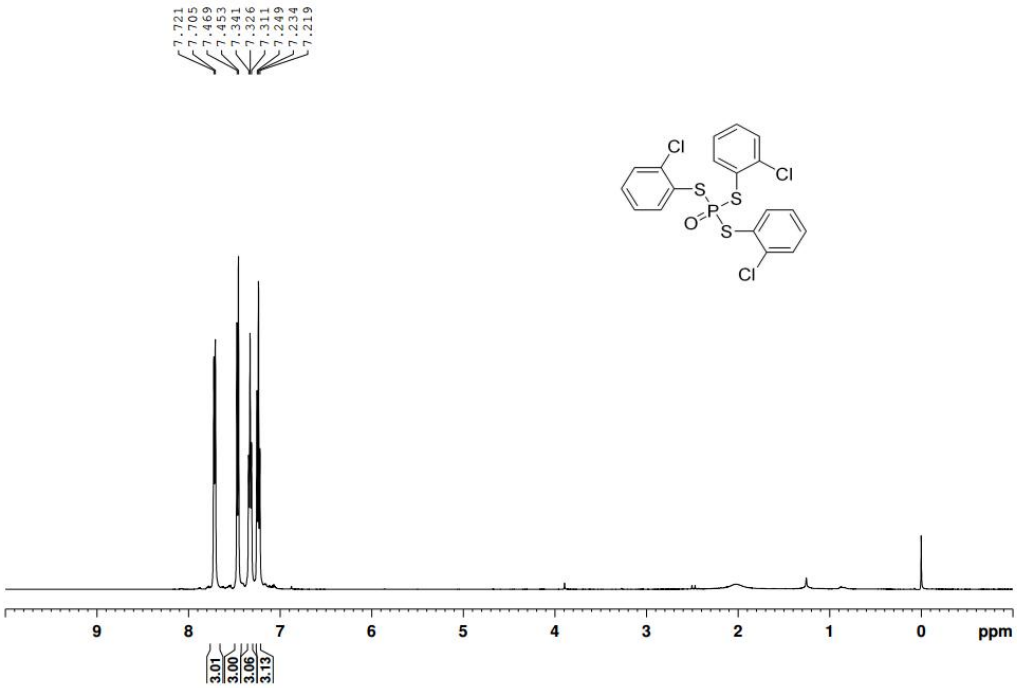
^{13}C NMR of 3j


135.36
135.32
135.23
135.20
133.97
133.93
130.61
130.59
130.57
130.54
128.06
128.01
77.48
77.23
76.98
Cl
S
P
O
S
S
Cl
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

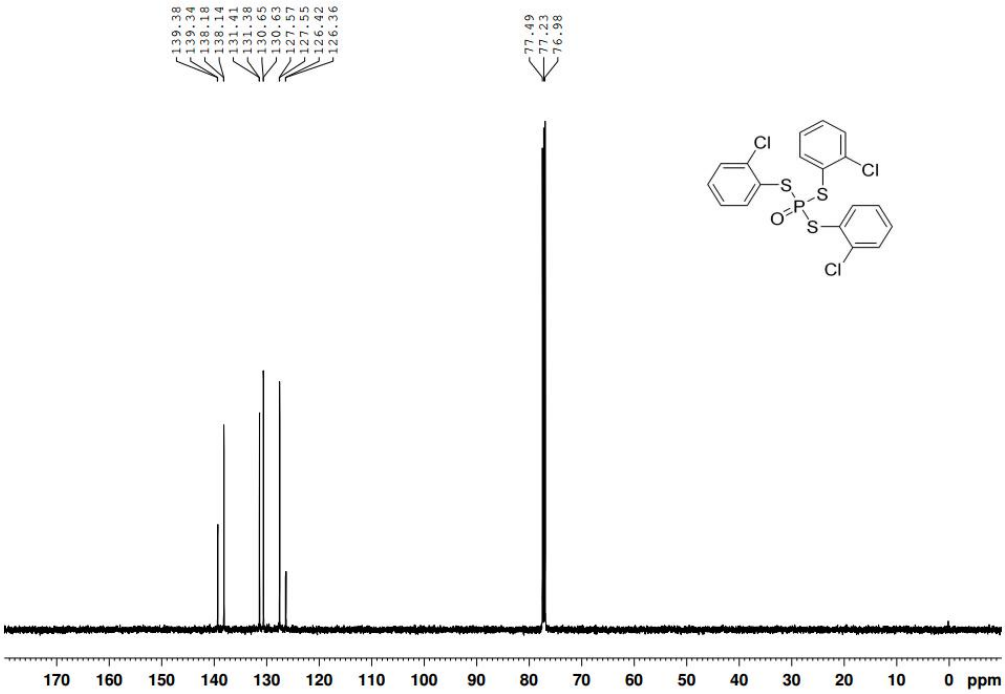
^{31}P NMR of 3j



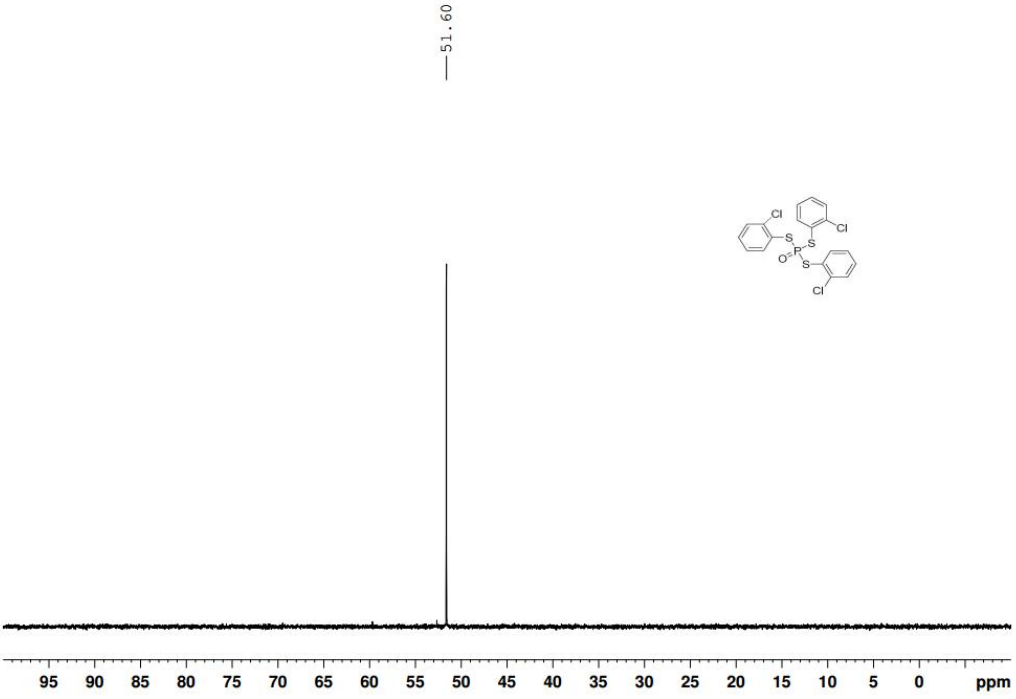
^{1}H NMR of 3k



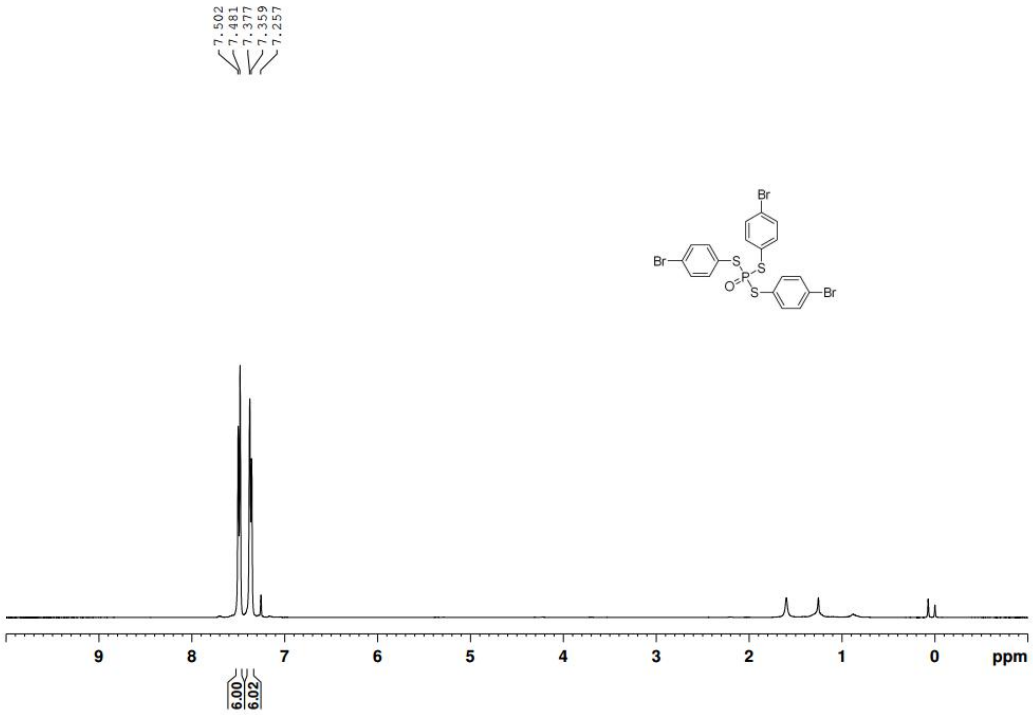
^{13}C NMR of 3k



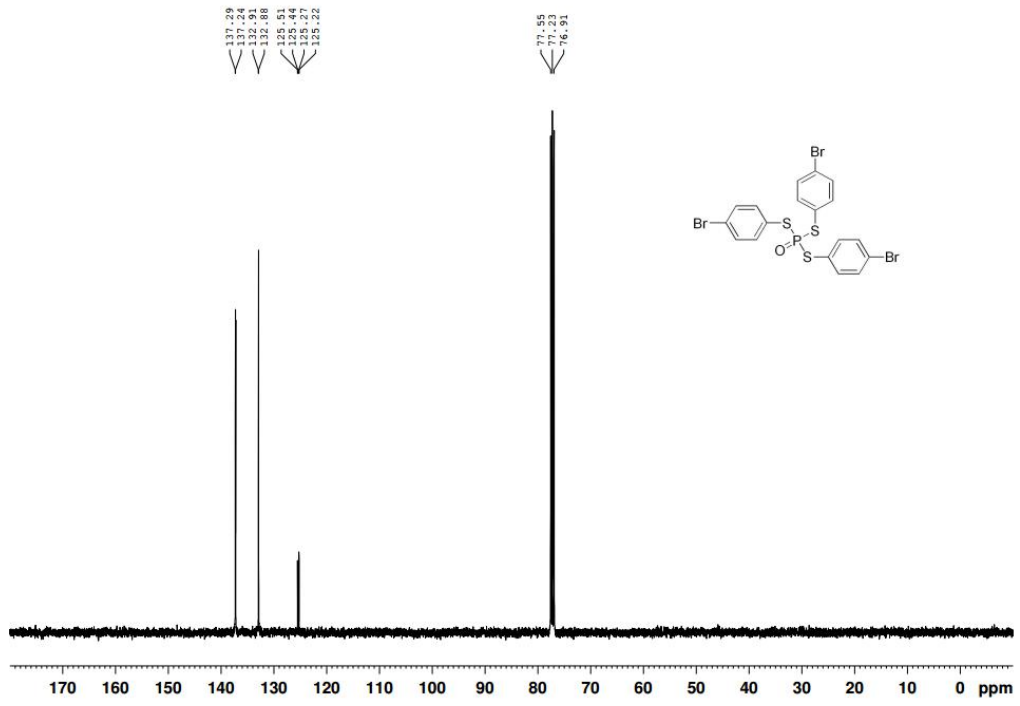
^{31}P NMR of 3k



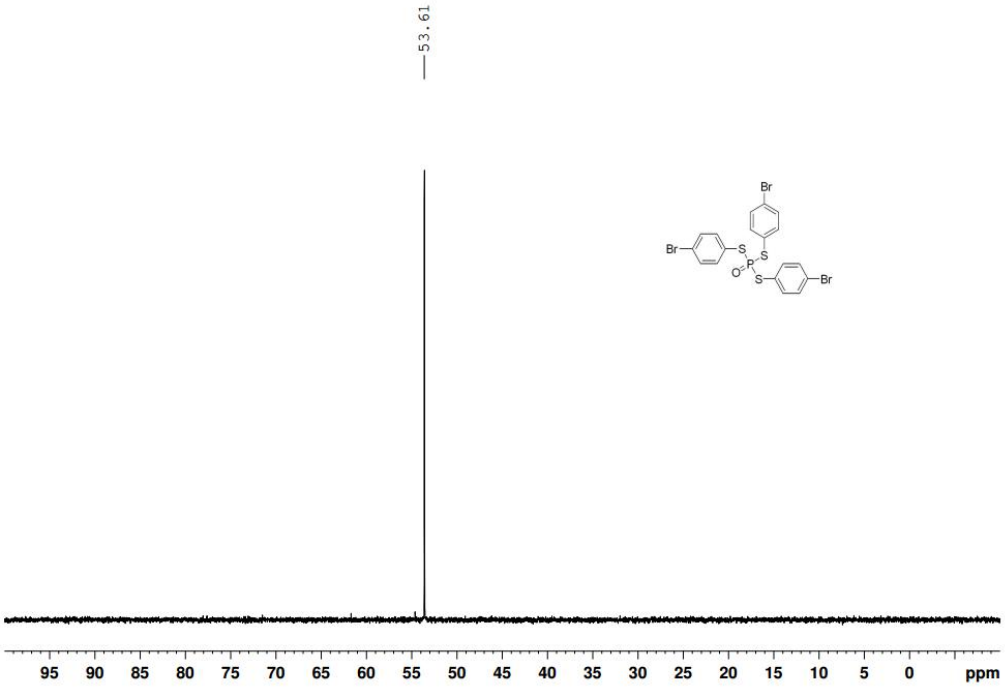
^{1}H NMR of 3l



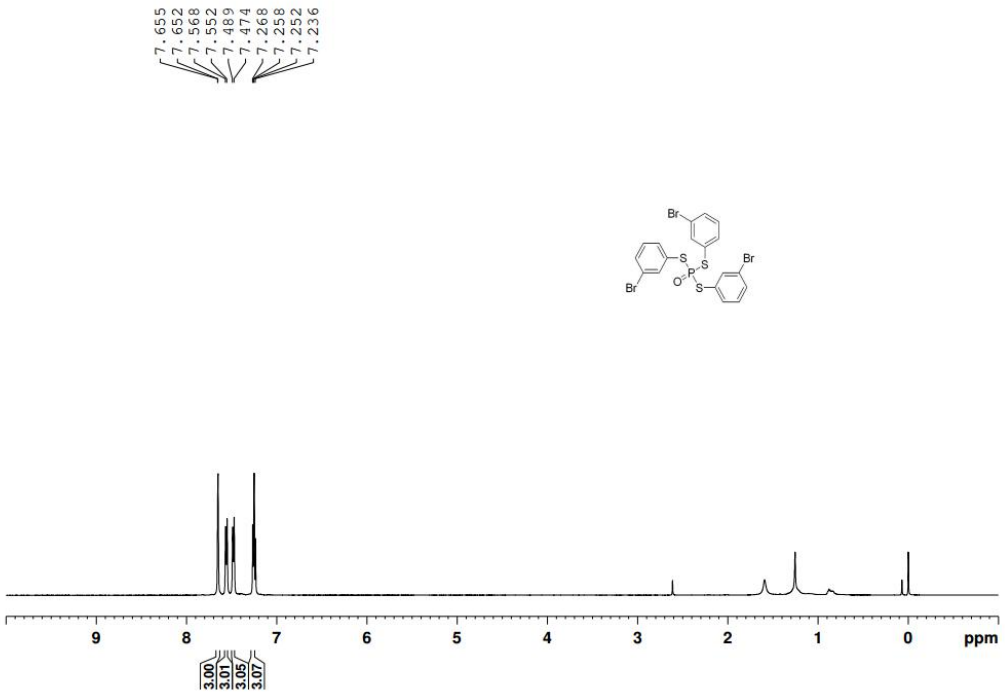
^{13}C NMR of 3l



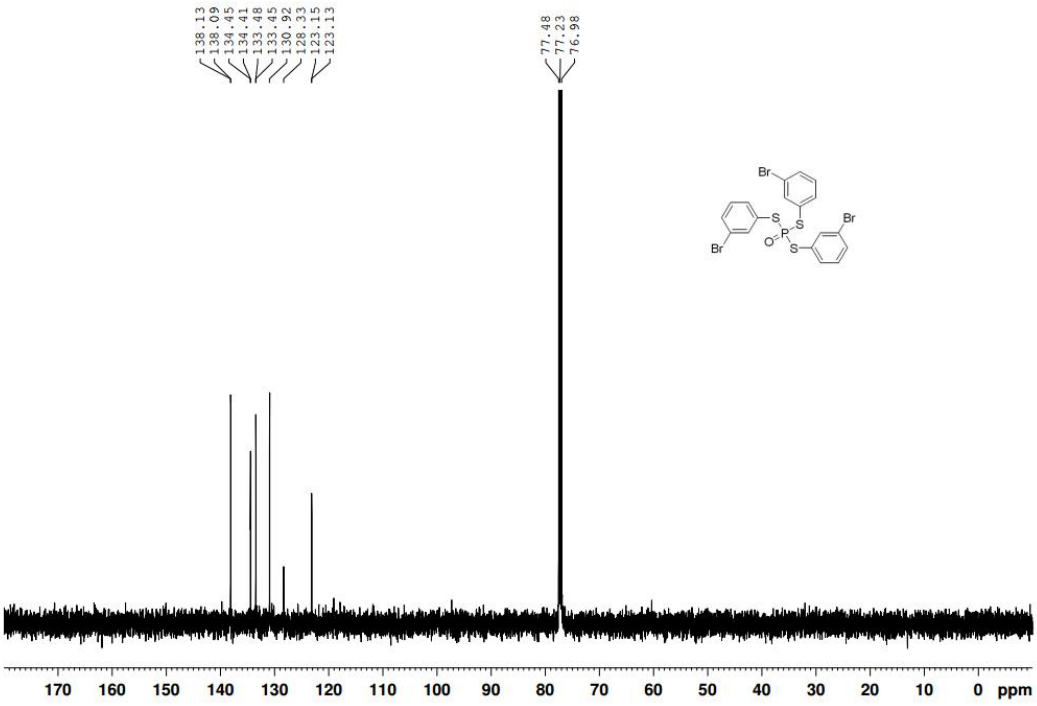
^{31}P NMR of 3l


53.61
Br
Br
S
P
O
S
S
Br
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 ppm

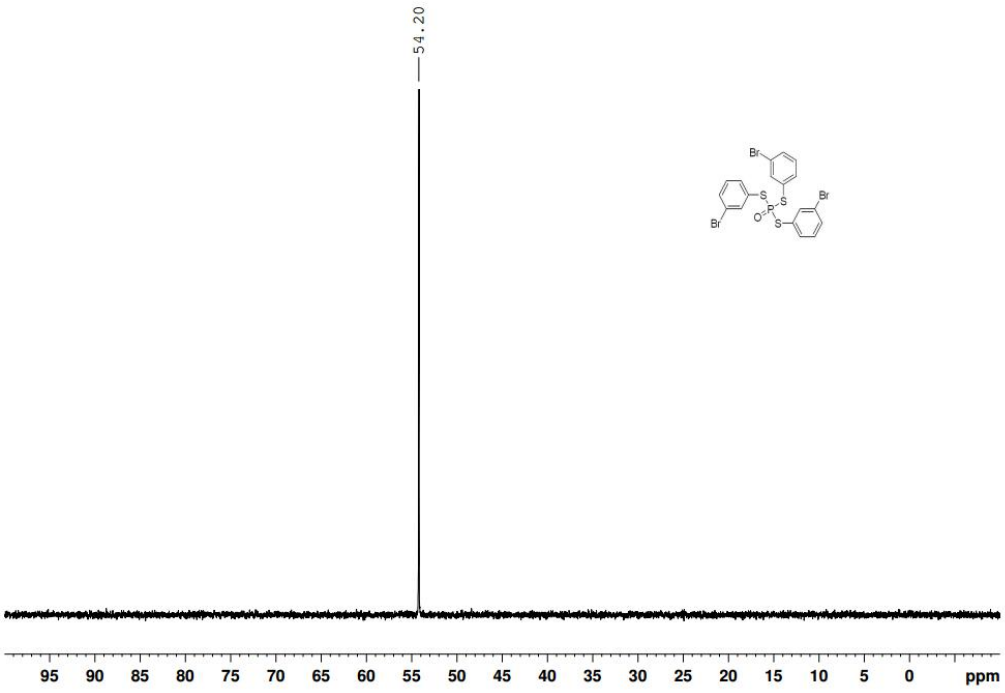
^{1}H NMR of 3m


7.655
7.652
7.568
7.552
7.489
7.474
7.268
7.258
7.252
7.236
Br
Br
S
P
O
S
S
Br
9 8 7 6 5 4 3 2 1 0 ppm
3.00
3.01
3.05
3.07

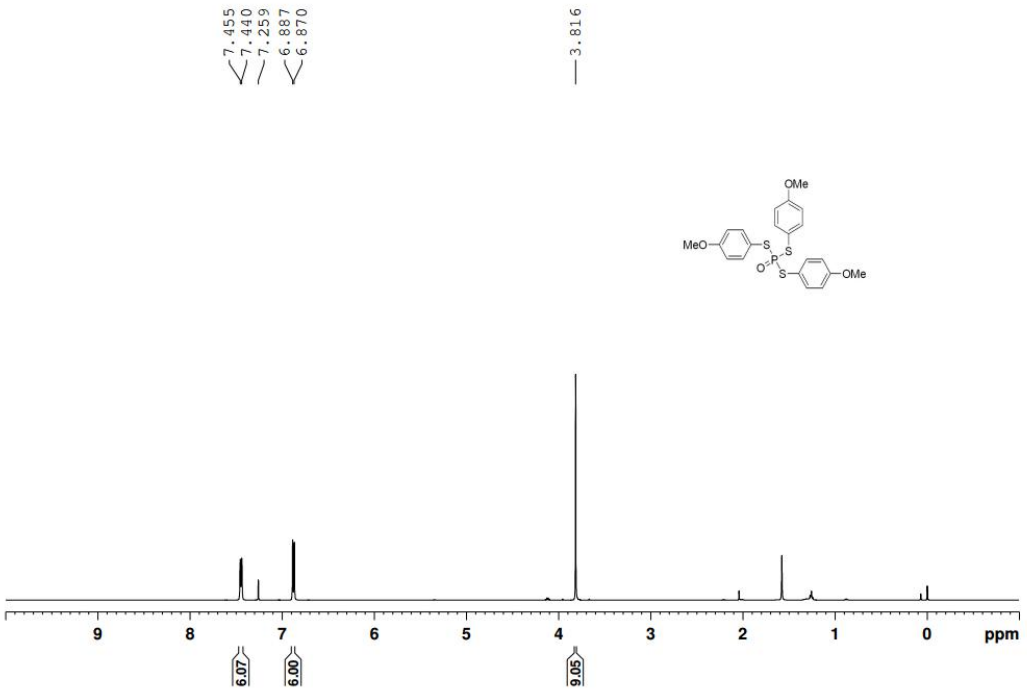
^{13}C NMR of 3m



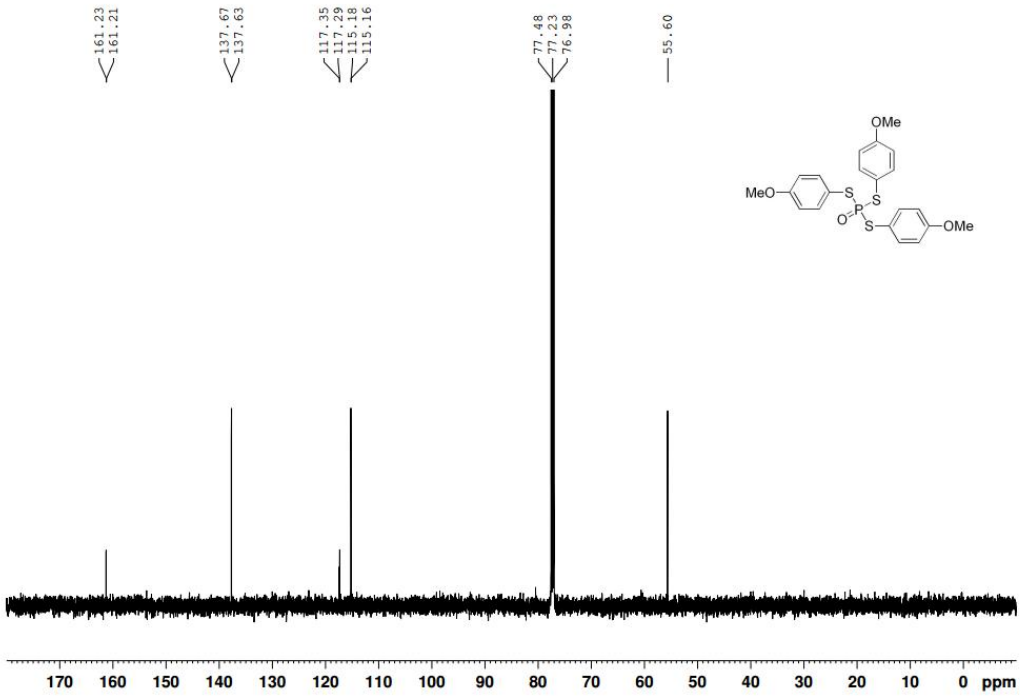
^{31}P NMR of 3m



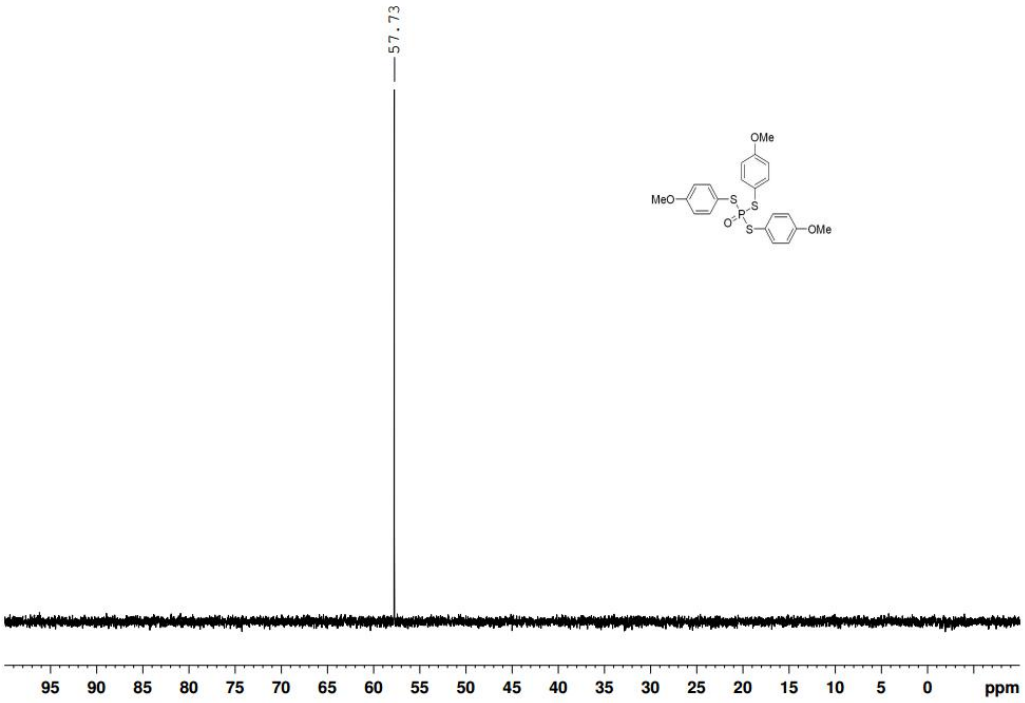
^{1}H NMR of 3n



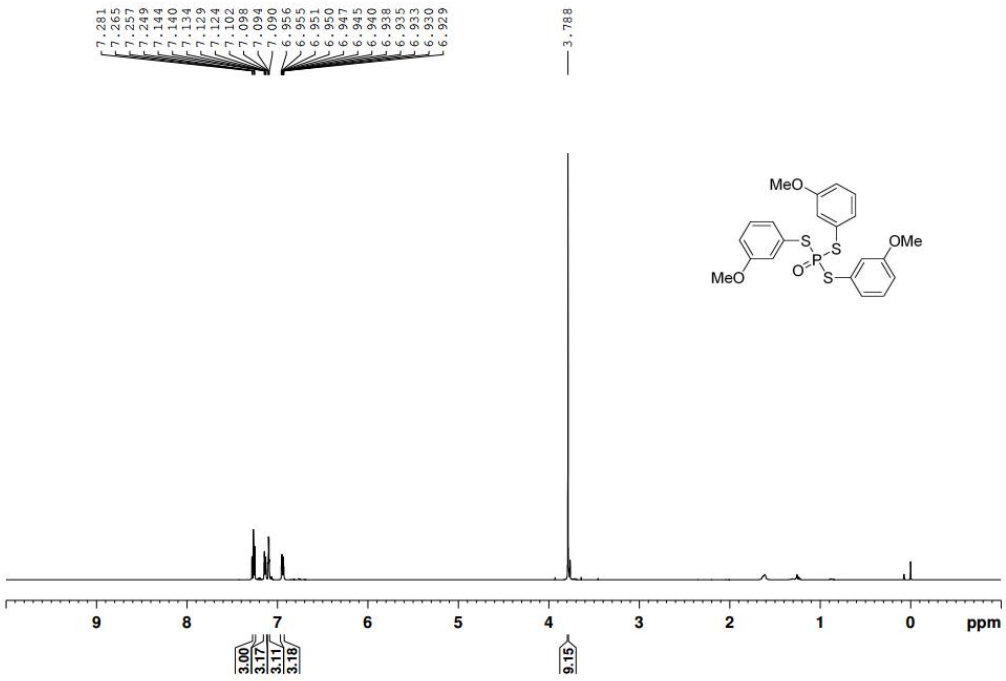
^{13}C NMR of 3n



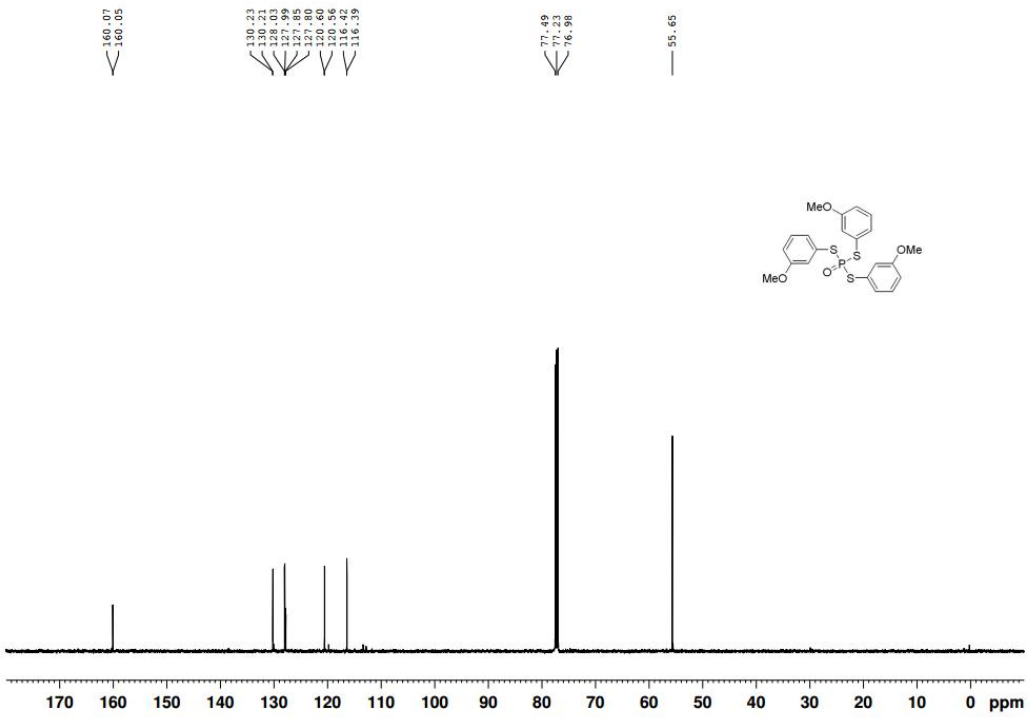
^{31}P NMR of 3n



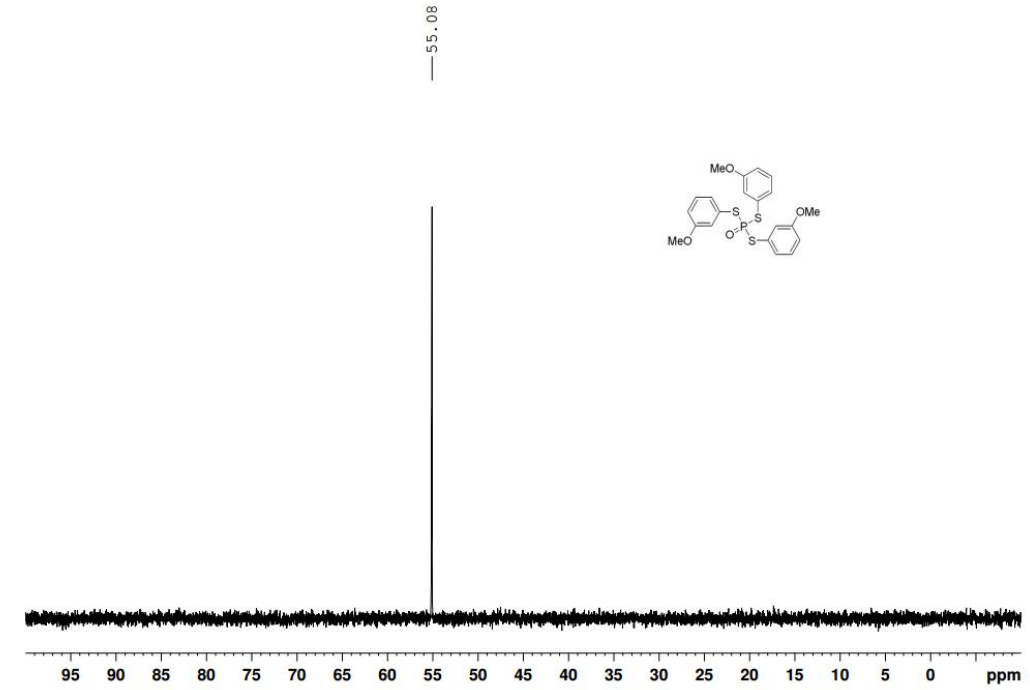
^{1}H NMR of 3o



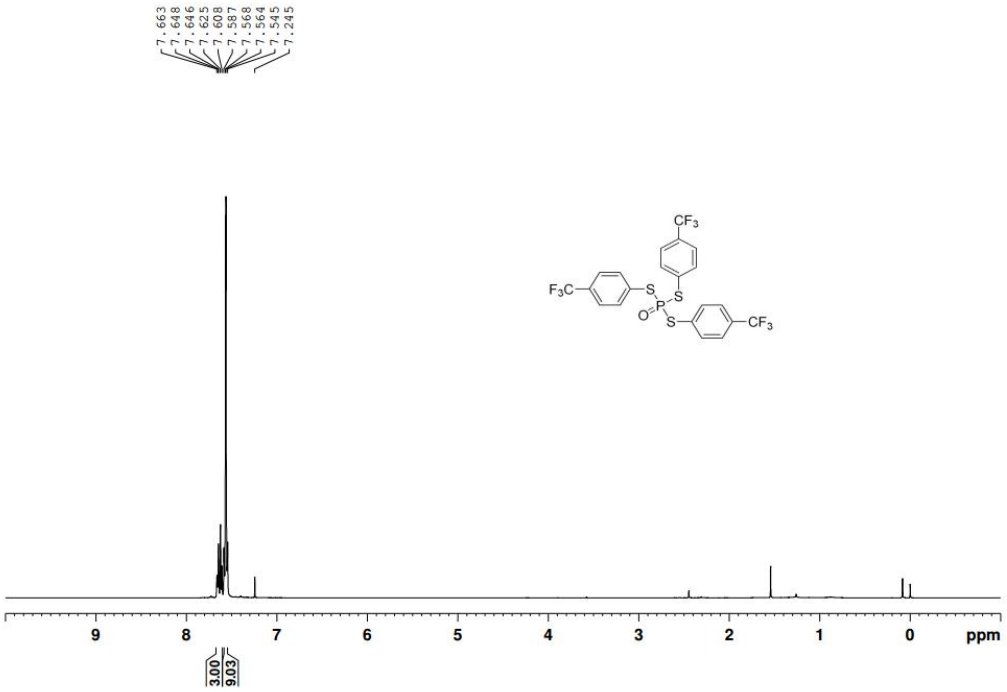
^{13}C NMR of 3o



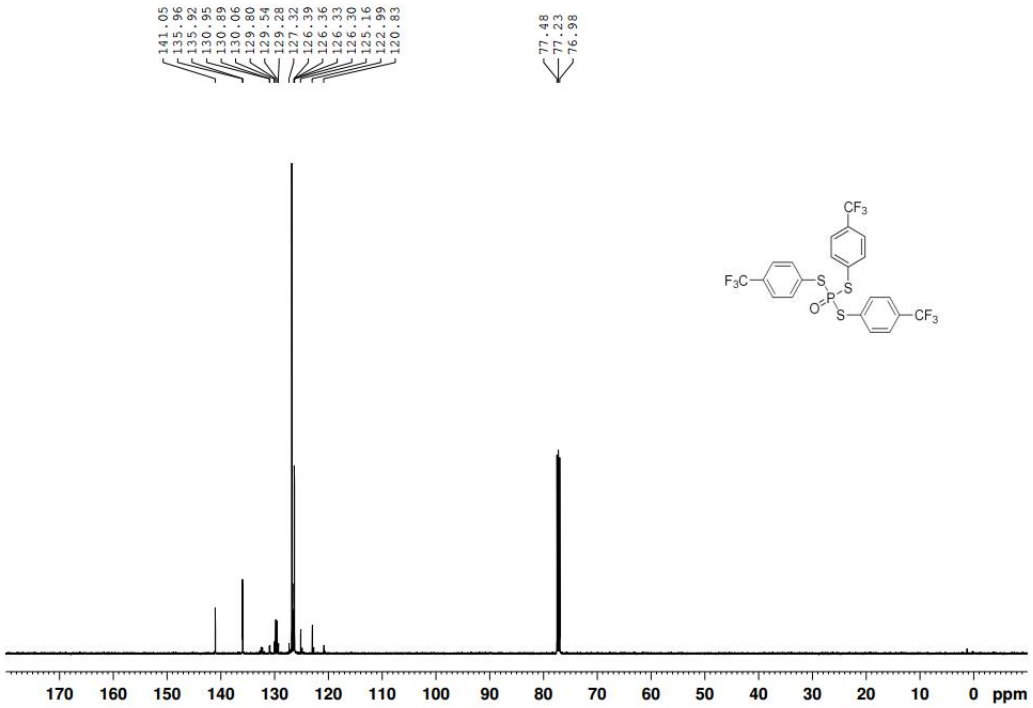
^{31}P NMR of 3o



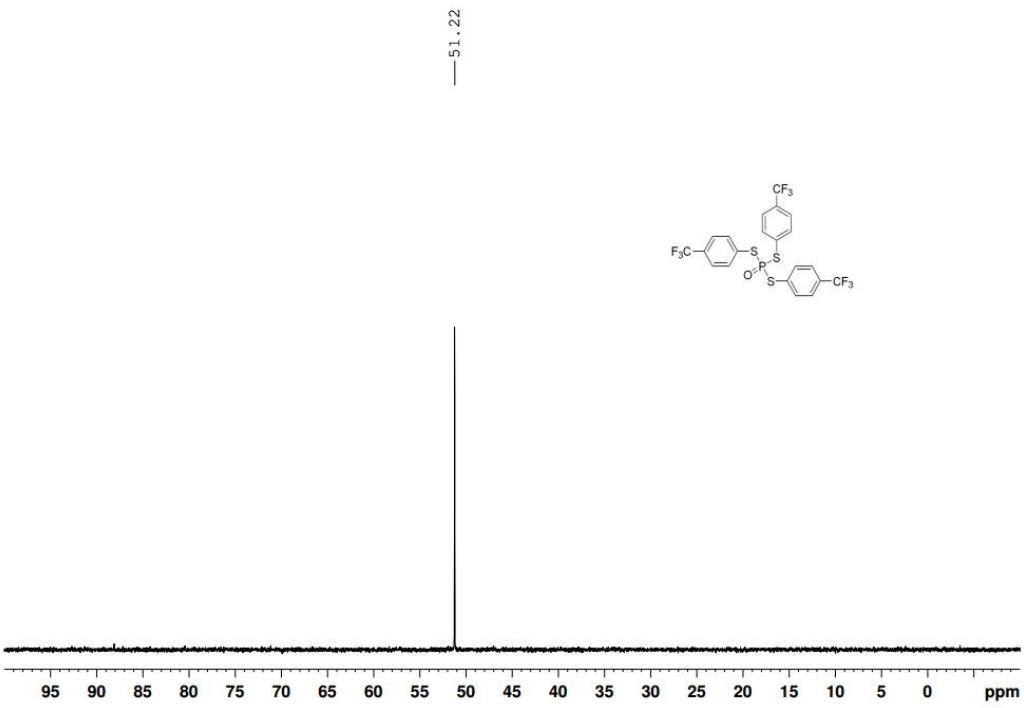
^{1}H NMR of 3p



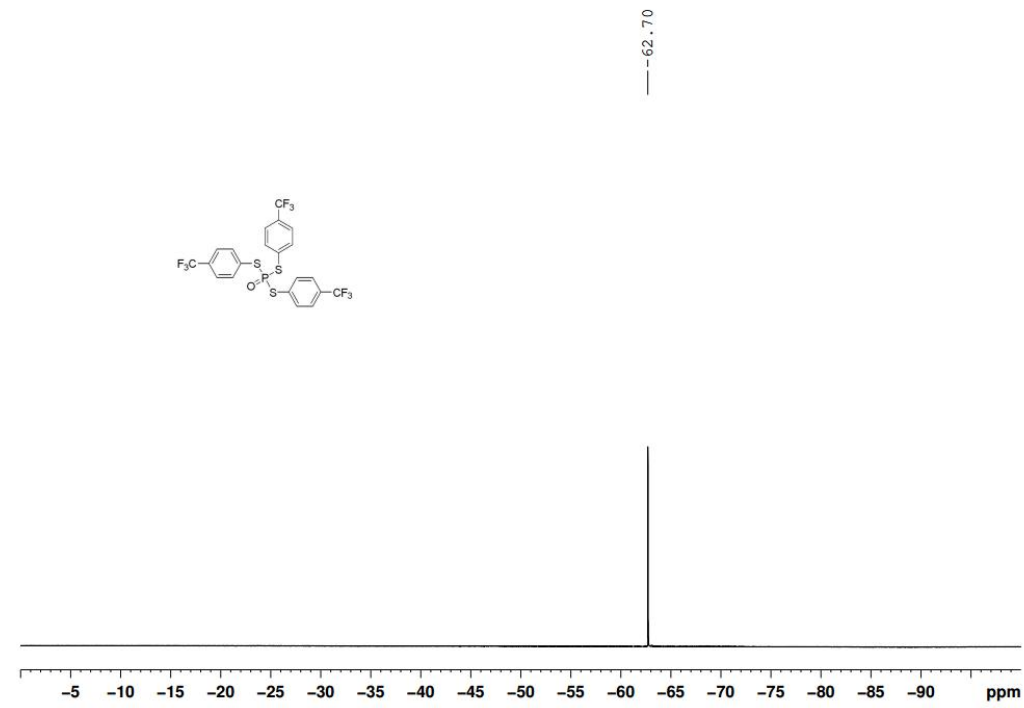
^{13}C NMR of 3p



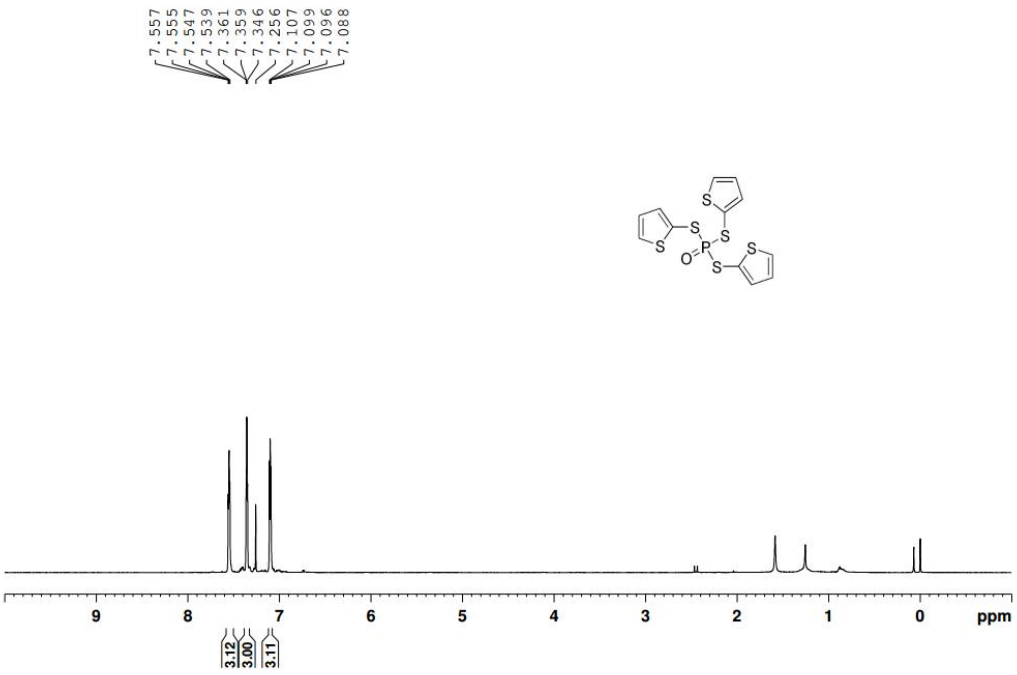
^{31}P NMR of 3p



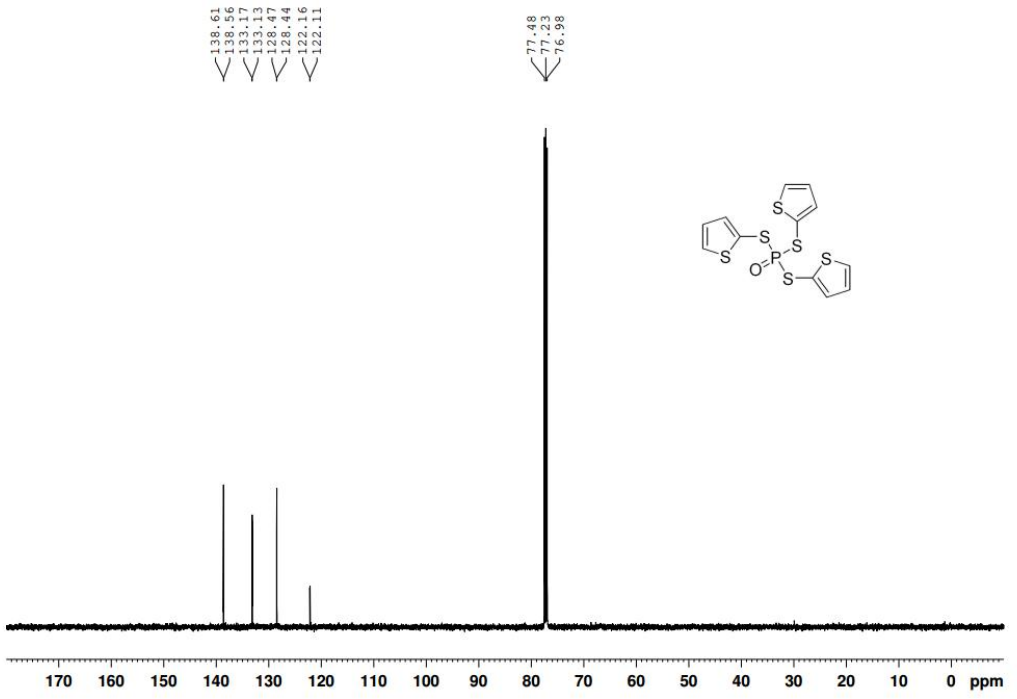
^{19}F NMR of 3p



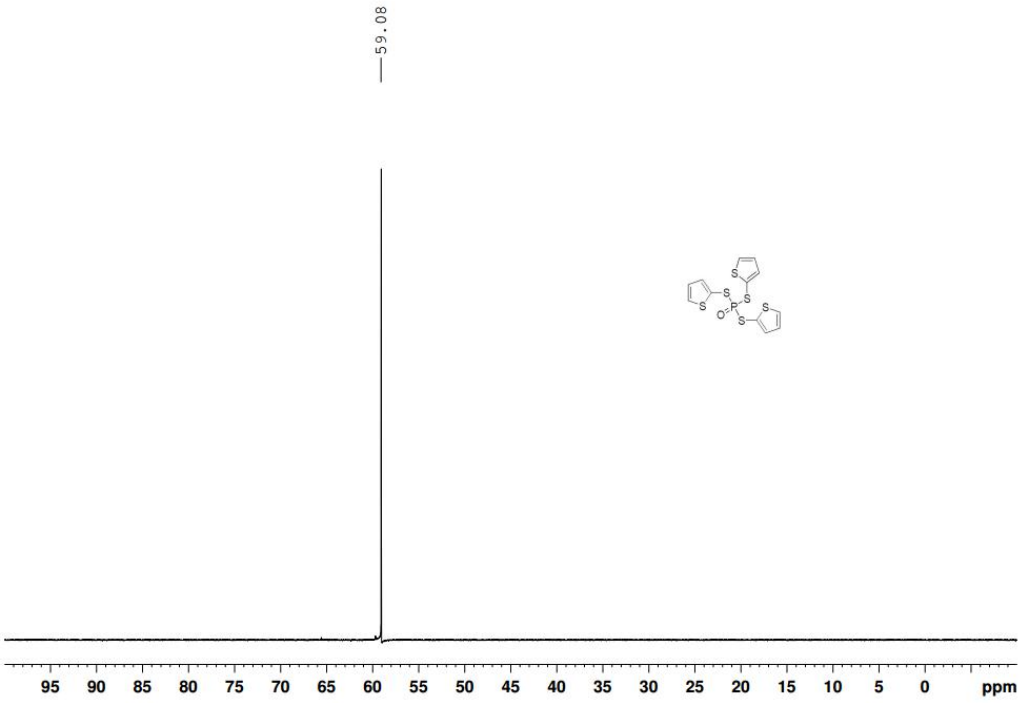
^{1}H NMR of 3r



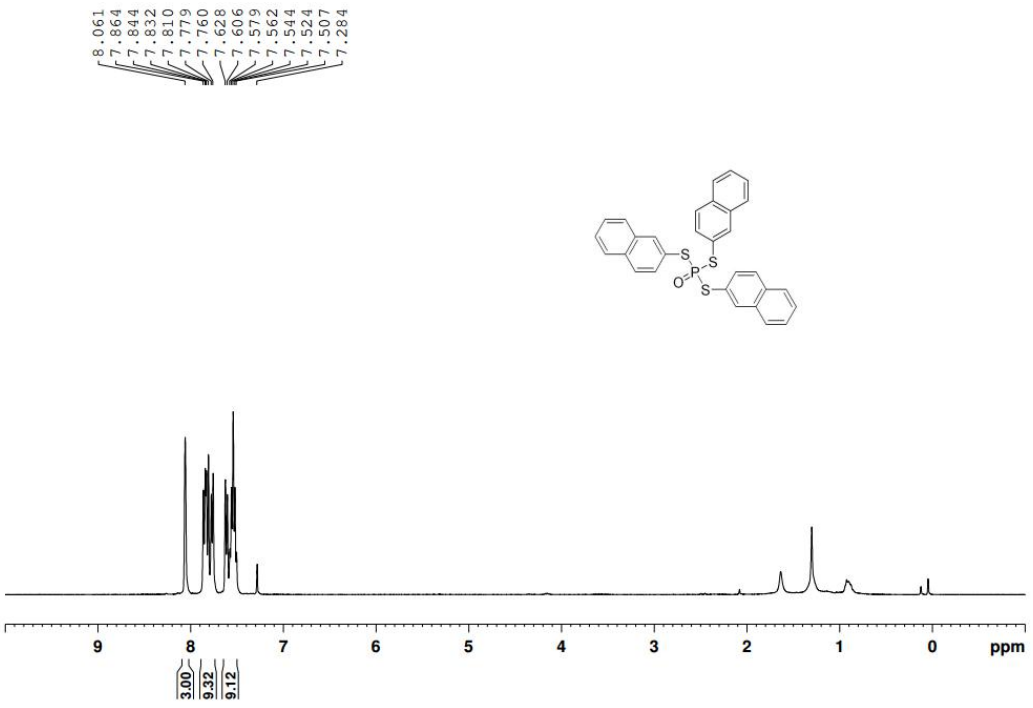
^{13}C NMR of 3r



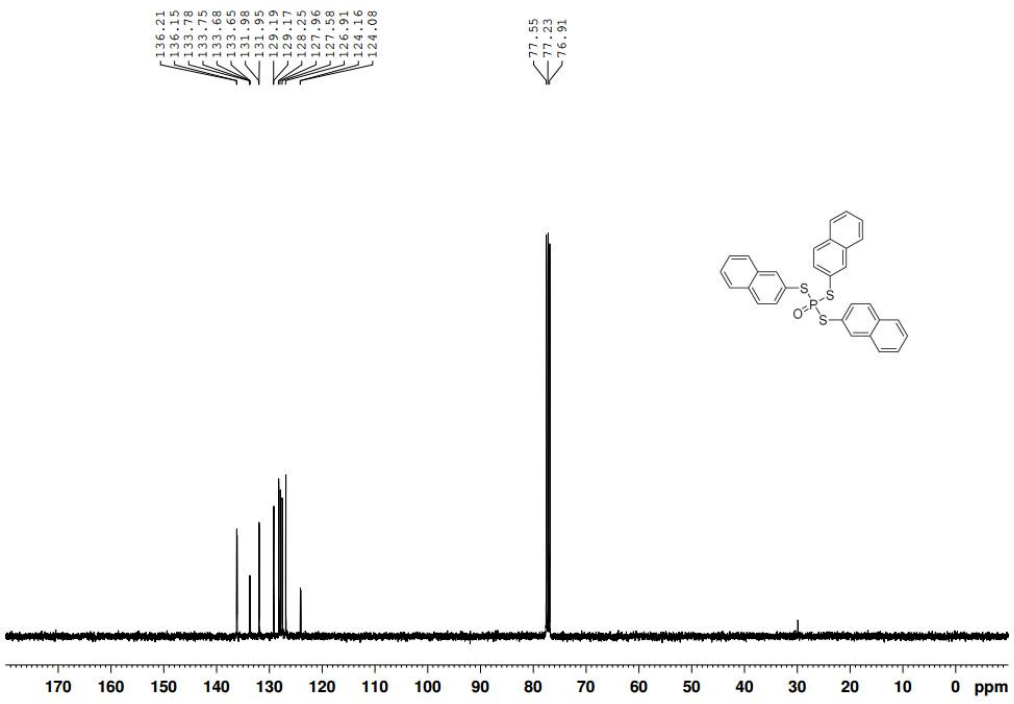
^{31}P NMR of 3r



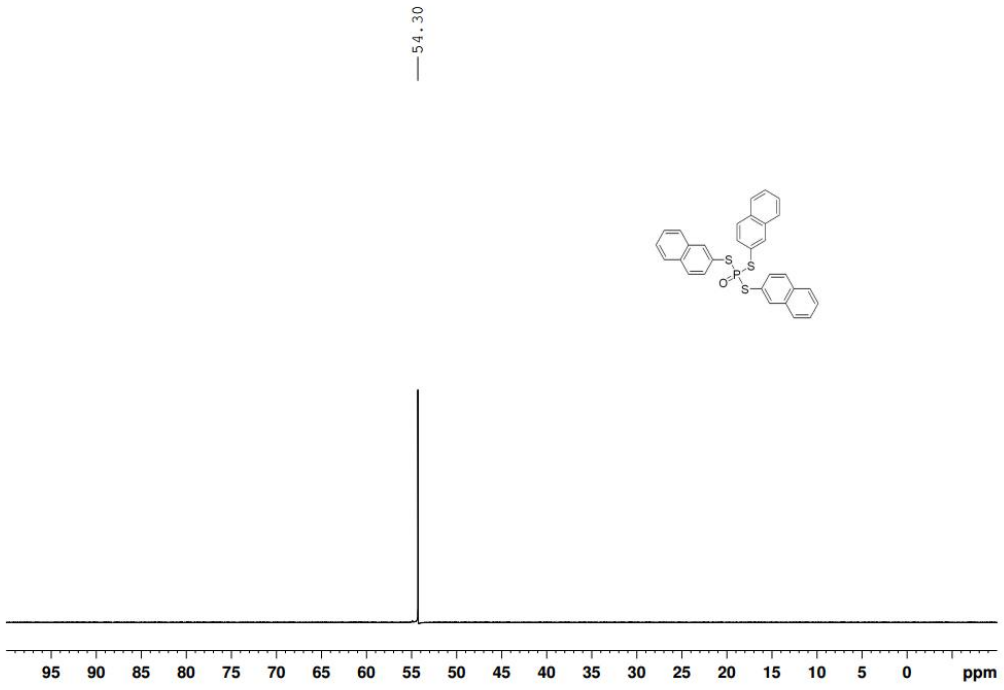
^{1}H NMR of 3s



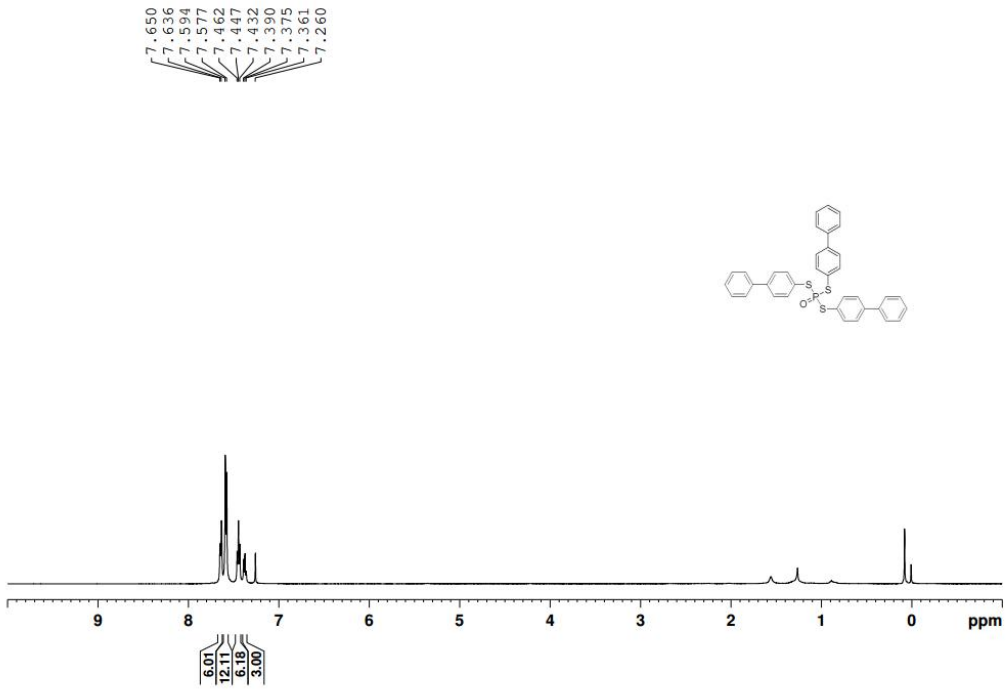
^{13}C NMR of 3s



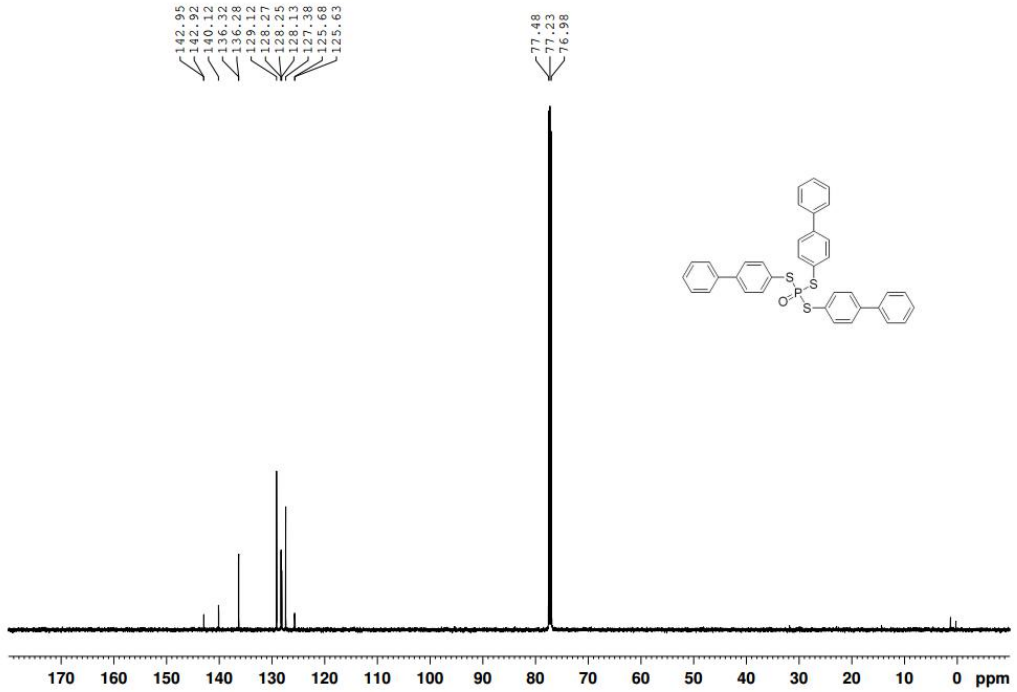
^{31}P NMR of 3s



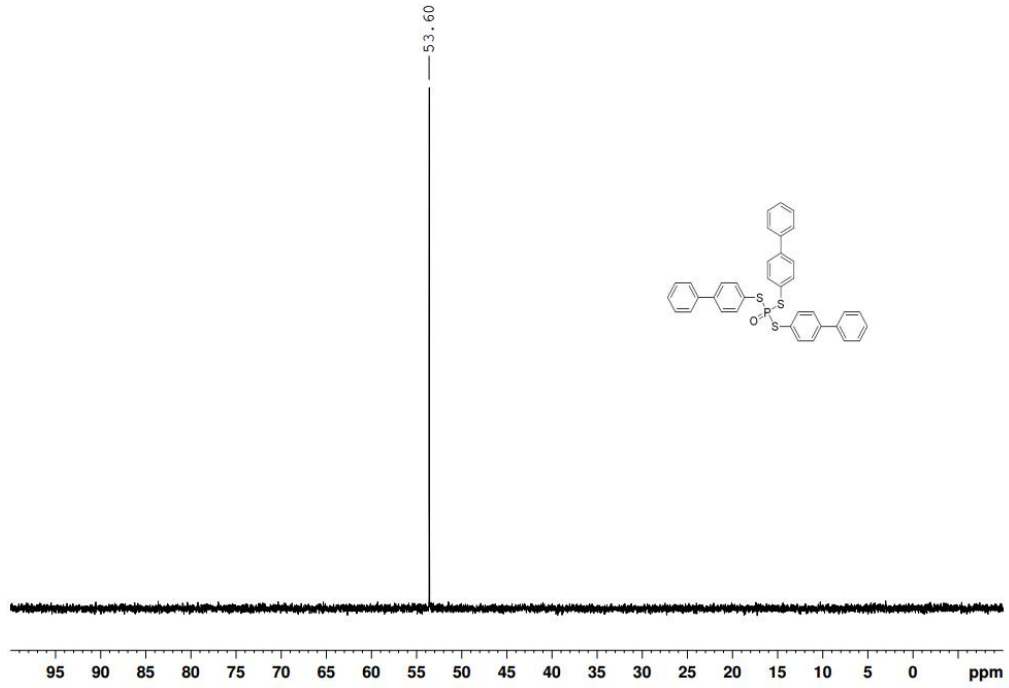
^{1}H NMR of 3t



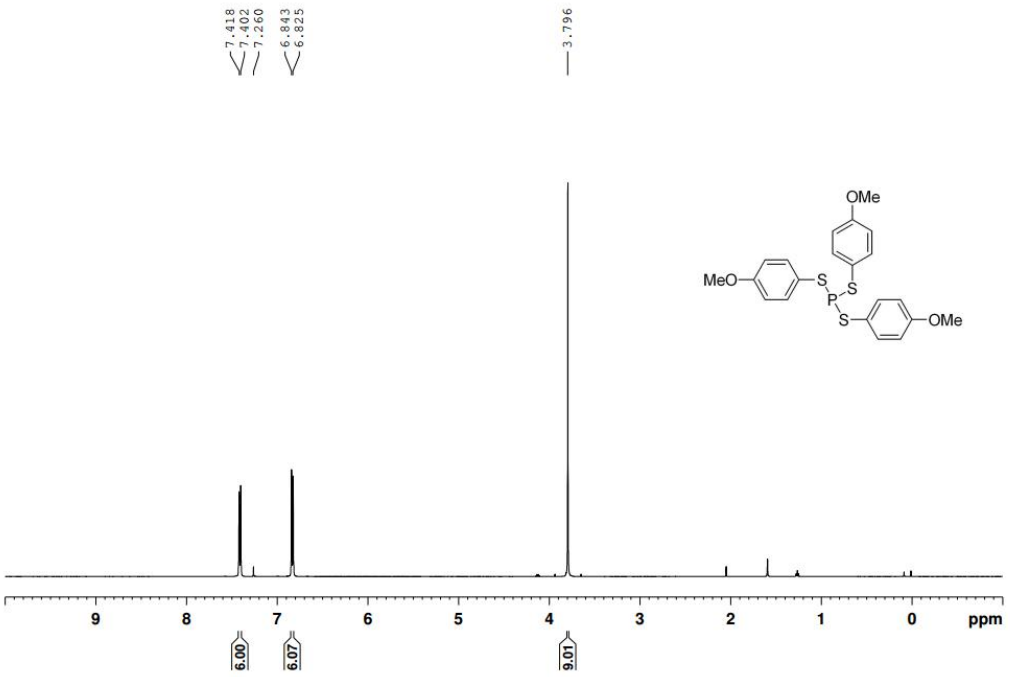
^{13}C NMR of 3t



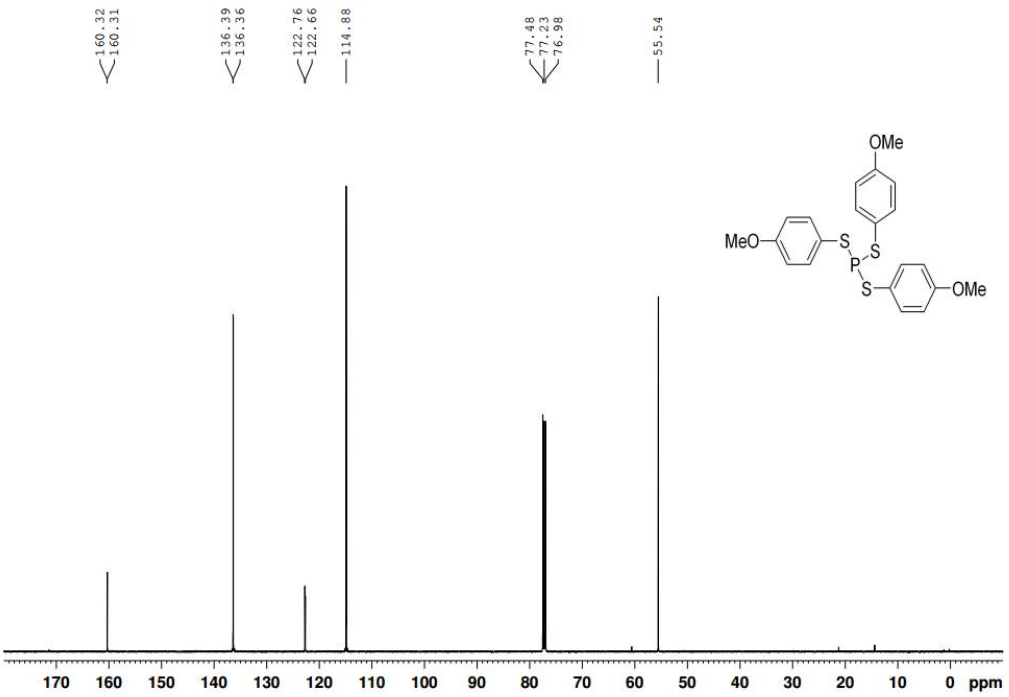
^{31}P NMR of 3t



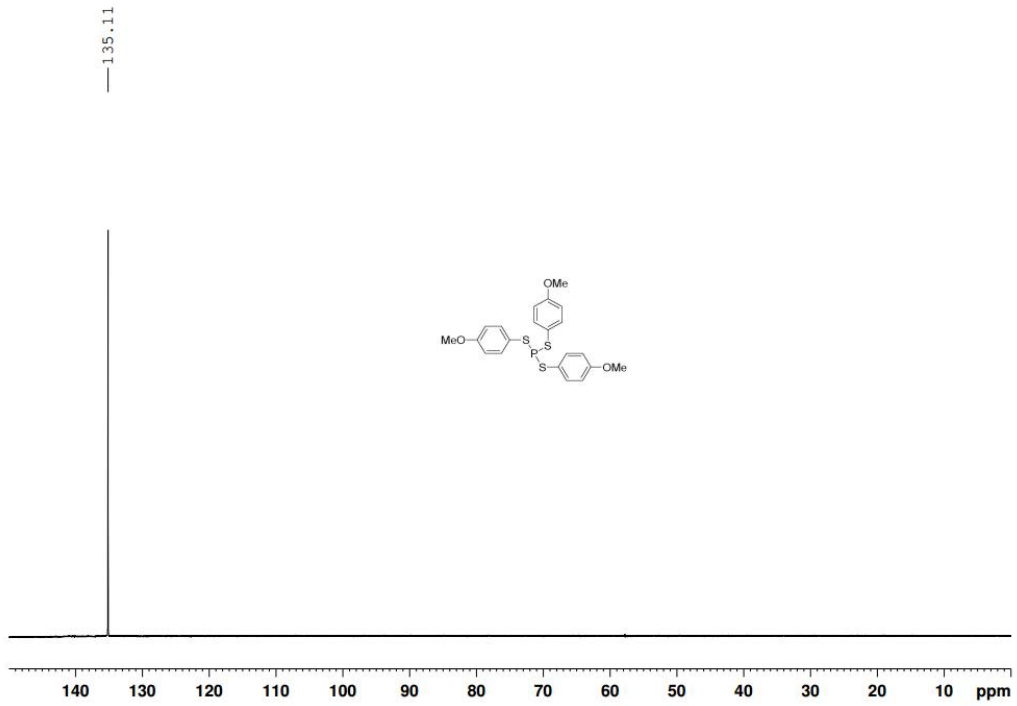
^{1}H NMR of 2n



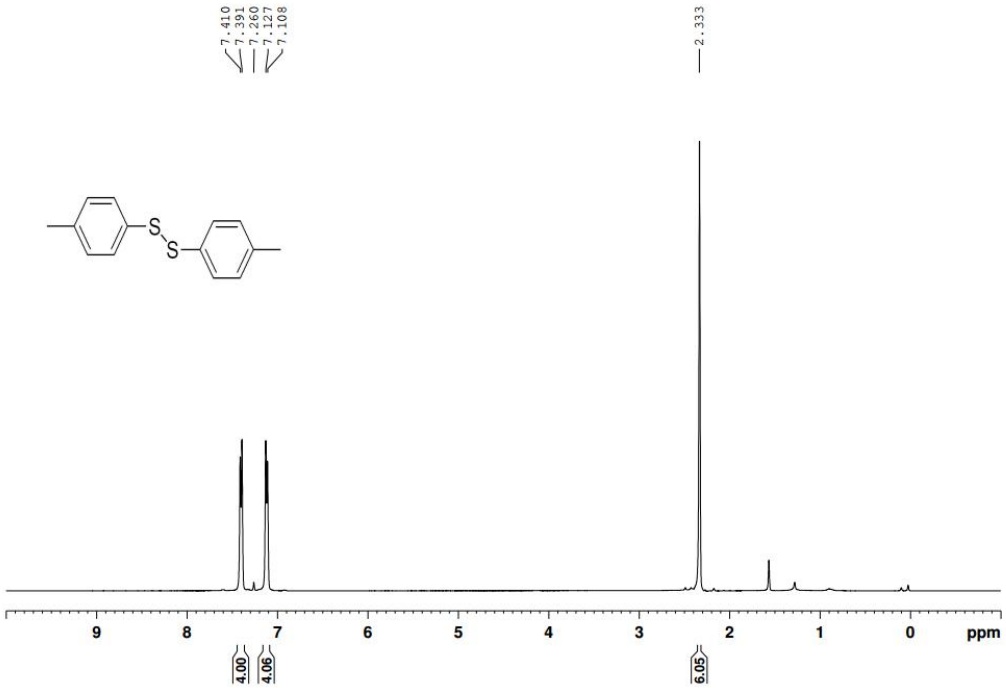
^{13}C NMR of 2n



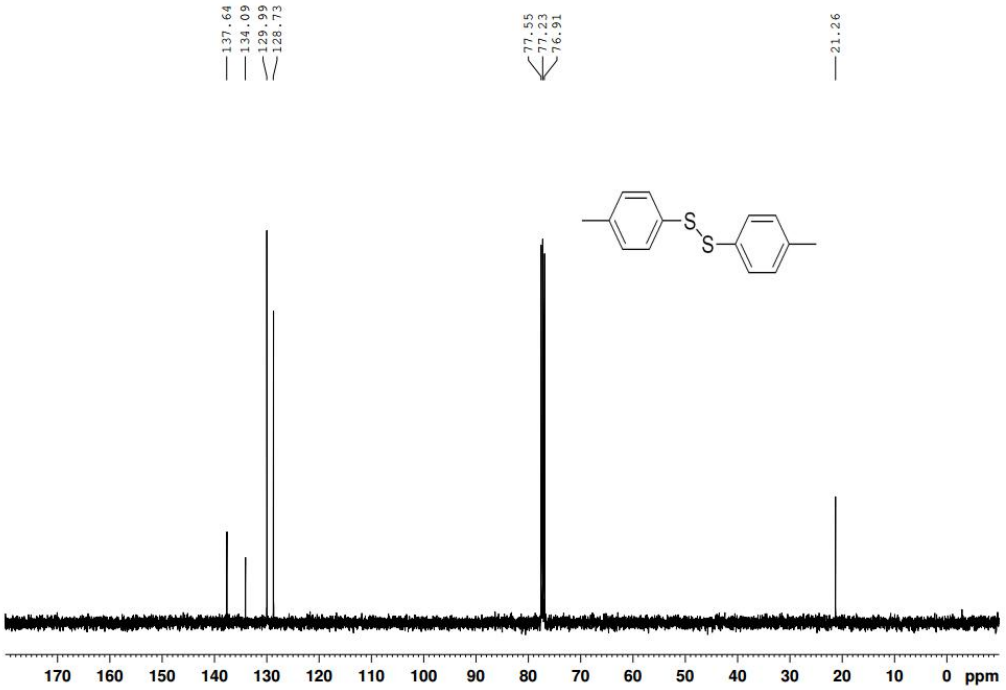
^{31}P NMR of 2n



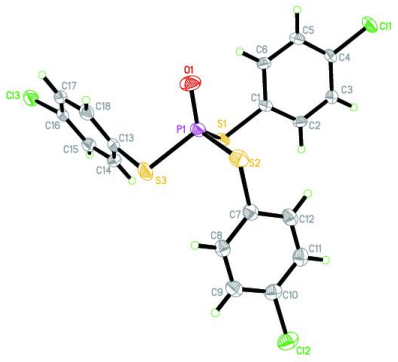
^{1}H NMR of 1a



^{13}C NMR of 1a



Crystallographic spectrum for 3i:



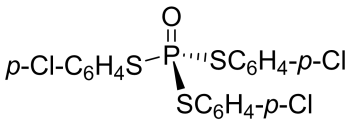


Table 1 Crystal data and structure refinement for 3i.

Identification code	y
Empirical formula	$C_{18}H_{12}Cl_3OPS_3$
Formula weight	477.78
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	12.268(2)
b/Å	8.6753(17)
c/Å	37.965(7)
α/°	90.00
β/°	92.878(3)
γ/°	90.00
Volume/Å^3	4035.5(13)
Z	8
ρ_{calc}g/cm^3	1.573
μ/mm^{-1}	0.850
F(000)	1936.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.14 to 50
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -45 ≤ l ≤ 45
Reflections collected	13996
Independent reflections	3545 [R_{int} = 0.1323, R_{sigma} = 0.0805]
Data/restraints/parameters	3545/0/235
Goodness-of-fit on F^2	1.148
Final R indexes [I>=2σ (I)]	R_1 = 0.0534, wR_2 = 0.1351
Final R indexes [all data]	R_1 = 0.0596, wR_2 = 0.1390
Largest diff. peak/hole / e Å^{-3}	0.52/-0.33

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3i. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S2	3287.9(6)	5267.9(9)	3774.7(2)	37.0(2)
Cl2	6107.3(7)	9765.9(10)	2910.0(2)	50.9(3)
P1	4309.5(7)	3801.6(10)	4068.0(2)	39.3(2)
S1	4971.6(7)	2116.8(10)	3750.5(3)	49.0(3)
Cl3	1185.4(10)	7028.9(11)	5423.7(3)	62.8(3)
S3	3187.4(10)	2547.4(10)	4340.7(3)	56.7(3)
Cl1	1241.2(9)	-553.0(13)	2743.1(3)	65.2(3)
O1	5204(2)	4557(3)	4270.9(7)	59.6(8)
C7	4204(2)	6410(3)	3533.8(8)	30.1(6)
C10	5389(2)	8422(3)	3150.9(8)	33.5(7)
C8	3936(3)	6636(3)	3180.3(8)	35.1(7)
C12	5094(3)	7172(3)	3693.7(8)	36.1(7)
C9	4517(3)	7666(4)	2988.7(8)	37.4(7)
C11	5693(3)	8165(4)	3496.9(9)	38.5(7)
C1	3839(3)	1446(4)	3479.9(9)	39.4(8)
C16	1778(3)	5880(4)	5109.1(9)	42.7(8)
C13	2676(3)	3970(4)	4631.1(8)	42.0(8)
C2	3167(3)	285(4)	3594.1(9)	41.1(8)
C3	2351(3)	-300(4)	3371.6(10)	44.8(9)
C4	2228(3)	251(4)	3032.7(10)	43.3(8)
C18	3249(3)	4311(4)	4943.3(9)	44.8(8)
C6	3686(3)	2018(4)	3138.3(9)	44.7(8)
C5	2887(3)	1419(4)	2913.8(10)	46.3(9)
C15	1212(3)	5579(4)	4795.5(9)	46.7(8)
C14	1665(3)	4619(4)	4555.8(9)	46.7(9)
C17	2802(3)	5274(4)	5185.2(9)	45.5(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3i. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	27.4(4)	40.0(4)	43.3(5)	5.4(3)	0.4(3)	-8.9(3)
Cl2	43.9(6)	53.2(5)	56.7(6)	13.6(4)	11.6(4)	-12.8(4)
P1	39.3(5)	38.8(5)	39.2(5)	7.3(3)	-3.0(4)	-8.2(4)
S1	33.7(5)	51.7(5)	61.7(6)	0.6(4)	4.0(4)	0.9(4)
Cl3	78.2(8)	57.3(6)	55.2(6)	-10.3(4)	24.3(5)	-20.7(5)
S3	80.9(8)	37.8(5)	53.6(6)	4.5(4)	25.6(5)	-13.5(5)
Cl1	51.1(6)	73.7(7)	70.0(7)	-22.9(5)	-3.5(5)	1.0(5)
O1	60.9(19)	57.8(16)	57.3(17)	8.5(12)	-25.5(14)	-12.4(13)
C7	25.9(16)	26.9(14)	37.5(17)	-1.3(12)	1.5(12)	-1.9(11)
C10	27.4(16)	33.8(15)	40.2(18)	3.3(13)	9.5(13)	-1.9(12)
C8	29.4(17)	38.2(17)	37.2(17)	-7.2(13)	-2.9(13)	-5.8(13)
C12	36.0(18)	39.0(17)	32.6(17)	0.1(13)	-3.9(13)	-7.0(13)
C9	36.6(19)	44.3(17)	31.5(17)	0.5(13)	3.4(13)	-3.7(14)
C11	29.3(18)	38.0(16)	48(2)	-0.3(14)	-0.9(14)	-9.0(13)
C1	35.3(18)	36.0(17)	47.5(19)	-3.0(14)	7.4(14)	4.4(14)
C16	54(2)	39.5(17)	35.3(18)	5.1(14)	7.0(15)	-18.4(16)
C13	55(2)	37.6(17)	34.1(18)	5.7(13)	8.2(15)	-16.3(16)
C2	42(2)	37.6(17)	44(2)	4.3(14)	7.9(15)	4.6(15)
C3	41(2)	34.3(17)	60(2)	-2.4(15)	15.4(17)	-0.5(14)
C4	36.7(19)	39.7(17)	53(2)	-11.5(15)	3.7(16)	7.4(14)
C18	44(2)	47.8(19)	42(2)	17.4(16)	-3.6(15)	-7.3(16)
C6	46(2)	37.7(17)	51(2)	4.9(15)	12.8(17)	-0.7(15)
C5	53(2)	43.0(19)	44(2)	1.8(15)	8.2(17)	9.4(16)
C15	39(2)	57(2)	44(2)	3.8(16)	3.1(15)	-11.5(16)
C14	46(2)	59(2)	35.0(19)	2.2(15)	-4.8(15)	-18.7(17)
C17	53(2)	49(2)	33.5(18)	8.7(15)	-4.8(16)	-20.0(17)

Table 4 Bond Lengths for 3i.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2	P1	2.0711(12)	C8	C9	1.374(4)
S2	C7	1.785(3)	C12	C11	1.377(4)
Cl2	C10	1.747(3)	C1	C2	1.386(5)
P1	S1	2.0850(13)	C1	C6	1.392(5)
P1	S3	2.0721(12)	C16	C15	1.373(5)
P1	O1	1.464(3)	C16	C17	1.379(5)
S1	C1	1.783(4)	C13	C18	1.380(5)
Cl3	C16	1.742(4)	C13	C14	1.380(5)
S3	C13	1.789(4)	C2	C3	1.374(5)
Cl1	C4	1.740(4)	C3	C4	1.374(5)
C7	C8	1.380(4)	C4	C5	1.386(5)
C7	C12	1.389(4)	C18	C17	1.376(5)
C10	C9	1.375(5)	C6	C5	1.369(5)
C10	C11	1.366(5)	C15	C14	1.371(5)

Table 5 Bond Angles for 3i.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	S2	P1	103.69(11)	C2	C1	C6	119.7(3)
S2	P1	S1	111.25(5)	C6	C1	S1	119.0(3)
S2	P1	S3	101.06(6)	C15	C16	Cl3	119.6(3)
S3	P1	S1	102.04(5)	C15	C16	C17	121.7(3)
O1	P1	S2	115.18(11)	C17	C16	Cl3	118.8(3)
O1	P1	S1	108.34(13)	C18	C13	S3	119.9(3)
O1	P1	S3	118.14(12)	C18	C13	C14	120.3(3)
C1	S1	P1	104.30(11)	C14	C13	S3	119.6(3)
C13	S3	P1	102.00(11)	C3	C2	C1	120.2(3)
C8	C7	S2	116.8(2)	C2	C3	C4	119.3(3)
C8	C7	C12	120.1(3)	C3	C4	Cl1	119.5(3)
C12	C7	S2	122.8(2)	C3	C4	C5	121.4(3)
C9	C10	Cl2	119.1(2)	C5	C4	Cl1	119.1(3)
C11	C10	Cl2	119.5(2)	C17	C18	C13	120.0(3)
C11	C10	C9	121.5(3)	C5	C6	C1	120.2(3)
C9	C8	C7	120.2(3)	C6	C5	C4	119.1(3)
C11	C12	C7	119.3(3)	C14	C15	C16	119.2(4)
C8	C9	C10	119.1(3)	C15	C14	C13	120.0(3)
C10	C11	C12	119.8(3)	C18	C17	C16	118.8(3)
C2	C1	S1	121.1(3)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3i.

Atom	*x*	*y*	*z*	U(eq)
H8	3361	6089	3071	42
H12	5283	7012	3931	43
H9	4322	7849	2752	45
H11	6302	8660	3599	46
H2	3268	-100	3822	49
H3	1887	-1061	3450	54
H18	3938	3889	4990	54
H6	4128	2810	3062	54
H5	2787	1791	2685	56
H15	530	6020	4746	56
H14	1290	4406	4342	56
H17	3183	5513	5396	55