Supporting Information

for

Copper-Mediated Reaction of Oxazirconacyclopentenes with Dichlorophenylphosphine: A New Pathway for the Formation of 1,2-Oxaphosphole Derivatives

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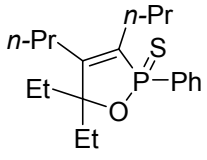
General Considerations

All reactions were carried out with standard Schlenk techniques under nitrogen atmosphere. THF, toluene was distilled and stored over sodium. All materials were commercially available and were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel or aluminium oxide purchased from commercial sources, and components were located by observation under UV light. ^{1}H NMR ^{13}C and ^{31}P NMR spectra were recorded on NMR spectrometer at ambient temperature with $CDCl_3$ as the solvent and TMS as internal standard. GC-MS spectra were recorded on Hewlett Packard GC-MS system. The reaction progress was monitored by GC.

Experimental Procedures

Typical procedure for the synthesis of 2,5-dihydro-1,2-oxaphosphole

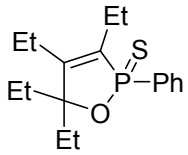
To a solution of Cp_2ZrCl_2 (176 mg, 0.6 mmol) in THF (3 mL) was added EtMgCl (2.0 M THF solution, 0.6 mL, 1.2 mmol) at -78 ^{o}C, and the mixture was stirred for 1 h at -78 ^{o}C. Then 4-octyne (77 μL，0.5 mmol) was added and the mixture was stirred for 1 h at 0 ^{o}C. 3-pentone (60 μL, 0.5 mmol) was added and the mixture was kept at 50 ^{o}C for 3 h. When the solution was cooled to 0 ^{o}C, CuCl (49 mg, 0.5 mmol) was added and the mixture was kept at 0 ^{o}C for 10 min. Dichlorophenylphosphine (82 μL, 0.6 mmol) was added and the mixture was kept at 50 ^{o}C overnight. HCl (1 M) (1 mL) was added to quench the reaction. Then sulfide powder (32 mg, 1 mmol) was added and mixture was stirred for 1 h. Finally, ethyl acetate was used to extract and evaporated in vacuo and the residue was purified by column chromatography on Al_2O_3 (PE : EA =50 : 1) to afford product **3a**.



5,5-Diethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-sulfide (3a)

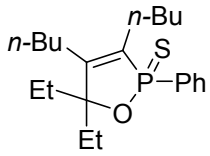
The crude product was purified by column chromatography on Al_2O_3 with petroleum: ethyl acetate = 50 : 1 to give the desired product as yellow oil 139.4 mg, isolated yield was 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 – 7.82 (m, 2H), 7.52 –

7.40 (m, 3H), 2.47 – 2.29 (m, 1H), 2.29 – 2.10 (m, 2H), 2.11 – 1.95 (m, 2H), 1.89 (td, *J* = 14.4, 7.3 Hz, 1H), 1.79 – 1.63 (m, 2H), 1.63 – 1.47 (m, 2H), 1.48 – 1.32 (m, 2H), 1.08 – 0.96 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 157.0 (d, *J* = 17.8 Hz), 135.2 (d, *J* = 102.1 Hz), 131.8, 131.4 (d, *J* = 12.5 Hz), 130.7 (d, *J* = 88.5 Hz), 128.2 (d, *J* = 13.4 Hz), 98.6, 32.1, 30.0 (d, *J* = 16.2 Hz), 29.7, 28.1 (d, *J* = 14.5 Hz), 22.4, 15.1, 14.5, 9.0, 8.4. ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 103.5; GC-MS (EI, m/z): 336; HRMS calcd for $C_{19}H_{30}OPS^+$ 337.1755, found 337.1753.



3,4,5,5-Tetraethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3b)

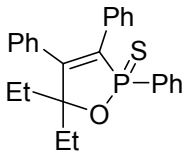
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 110.5 mg, isolated yield was 72%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 – 7.89 (m, 2H), 7.54 – 7.40 (m, 3H), 2.55 – 2.38 (m, 1H), 2.38 – 2.22 (m, 2H), 2.23 – 2.06 (m, 1H), 2.13 – 1.96 (m, 1H), 1.96 – 1.89 (m, 1H), 1.81 – 1.63 (m, 2H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.02 (t, *J* = 6.4 Hz, 3H), 1.00 (t, *J* = 6.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 157.9 (d, *J* = 17.1 Hz), 135.3 (d, *J* = 101.8 Hz), 131.9, 131.7 (d, *J* = 89.1 Hz), 131.5 (d, *J* = 12.5 Hz), 128.3 (d, *J* = 13.5 Hz), 98.7, 32.1, 29.8, 20.6 (d, *J* = 16.8 Hz), 18.9 (d, *J* = 14.7 Hz), 14.1, 13.5, 9.0, 8.5; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 100.8; GC-MS (EI, m/z): 308. HRMS calcd for $C_{17}H_{26}OPS^+$ 309.1442, found 309.1446.



3,4-Dibutyl-5,5-diethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3c)

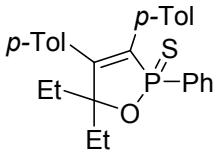
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 133.1 mg, isolated yield was 73%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 – 7.63 (m, 2H), 7.48 –

7.27 (m, 3H), 2.44 – 2.27 (m, 1H), 2.25 – 2.03 (m, 2H), 2.05 – 1.89 (m, 2H), 1.84 (td, J = 14.5, 7.3 Hz, 1H), 1.72 – 1.52 (m, 2H), 1.52 – 1.09 (m, 8H), 0.98 – 0.82 (m, 9H), 0.70 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 157.1 (d, J = 18.0 Hz), 135.2 (d, J = 102.1 Hz), 131.8, 131.5 (d, J = 12.5 Hz), 130.7 (d, J = 88.8 Hz), 128.2 (d, J = 13.4 Hz), 98.6, 32.2, 31.1, 29.7, 27.5 (d, J = 16.2 Hz), 25.6 (d, J = 14.5 Hz), 23.6, 23.0, 13.9, 13.7, 9.0, 8.4; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 101.5; GC-MS (EI, m/z): 364. HRMS calcd for $C_{21}H_{34}OPS^+$ 365.2068, found 365.2065.



5,5-Diethyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (3d)

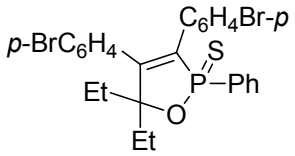
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 25 : 1 to give the desired product as yellow oil 109.0 mg, isolated yield was 54%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 – 7.78 (m, 2H), 7.47 – 7.30 (m, 3H), 7.28 – 7.17 (m, 5H), 7.15 – 7.08 (m, 2H), 7.06 – 6.94 (m, 3H), 2.01 – 1.86 (m, 3H), 1.75 – 1.63 (m, 1H), 1.16 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) 157.3 (d, J = 19.5 Hz), 135.1 (d, J = 91.9 Hz), 134.5 (d, J = 4.3 Hz), 133.5 (d, J = 88.4 Hz), 132.1, 131.8 (d, J = 16.8 Hz), 131.3 (d, J = 12.4 Hz), 129.4, 129.4, 128.8, 128.6 (d, J = 12.1 Hz), 128.4 (d, J = 13.7 Hz), 128.2, 127.9, 98.7, 31.9, 30.1, 9.3, 8.8; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 95.6; GC-MS (EI, m/z): 404. HRMS calcd for $C_{25}H_{26}POS^+$ 405.1442, found 405.1440.



5,5-Diethyl-2-phenyl-3,4-di-p-tolyl-5H-1,2-oxaphosphole 2-sulfide (3e)

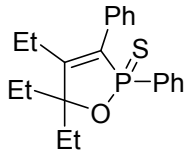
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 25 : 1 to give the desired product as yellow oil 103.7 mg, isolated yield was 48%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 – 7.88 (m, 2H), 7.51 – 7.38 (m, 3H), 7.16 (d, J = 7.7 Hz, 2H), 7.14 – 7.06 (m, 4H), 6.88 (d, J = 7.8 Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H), 2.04 – 1.94 (m, 2H), 1.89 – 1.62 (m, 2H), 1.22 (t, J = 7.3

Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.7 (d, J = 19.7 Hz), 138.4, 137.7, 135.2 (d, J = 104.1 Hz), 132.8 (d, J = 89.0 Hz), 131.9, 131.7 (d, J = 17.7 Hz), 131.3 (d, J = 12.2 Hz), 129.8 (d, J = 18.1 Hz), 129.5, 129.3, 129.2, 129.0, 128.8 (d, J = 6.5 Hz), 128.6, 128.4 (d, J = 13.6 Hz), 98.8, 77.5, 76.8, 31.9, 30.2, 21.4, 21.3, 9.3, 8.8; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 98.5; GC-MS (EI, m/z): 432. HRMS calcd for $C_{27}H_{30}OPS^+$ 433.1755, found 433.1756.



3,4-Bis(4-bromophenyl)-5,5-diethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3f)

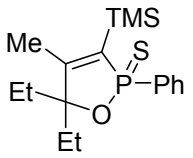
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 25 : 1 to give the desired product as white solid 126.5 mg, isolated yield was 45%. M.P. 71-73 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 – 7.85 (m, 2H), 7.52 – 7.39 (m, 5H), 7.22 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 7.9 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 2.09 – 1.88 (m, 3H), 1.72 (dq, J = 14.4, 7.2 Hz, 1H), 1.19 (t, J = 7.4 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4 (d, J = 19.5 Hz), 134.4 (d, J = 95.4 Hz), 133.4 (d, J = 83.7 Hz), 133.1 (d, J = 11.8 Hz), 132.4 (d, J = 2.6 Hz), 132.2, 131.7, 131.3 (d, J = 12.4 Hz), 130.9 (d, J = 5.2 Hz), 130.6 (d, J = 13.9 Hz), 130.3, 128.7, 128.5, 123.2, 122.7, 98.6, 31.8, 30.1, 9.3, 8.8; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 99.2; GC-MS (EI, m/z): 562. HRMS calcd for $C_{25}H_{24}Br_2OPS^+$ 560.9652, found 560.9658.



4,5,5-Triethyl-2,3-diphenyl-5H-1,2-oxaphosphole 2-sulfide (3g)

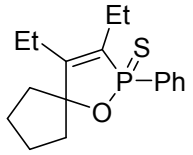
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 112.1 mg, isolated yield was 63%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 – 7.81 (m, 2H), 7.47 – 7.38 (m, 3H), 7.38 – 7.28 (m, 3H), 7.13 (d, J = 7.6 Hz, 2H), 2.27 – 2.11 (m, 1H), 2.02 – 1.91 (m, 2H), 1.79 – 1.72 (m, 2H), 1.61 (dt, J = 21.8, 7.2 Hz, 1H), 1.13 (t, J = 7.3

Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.4 (d, *J* = 20.0 Hz), 135.1 (d, *J* = 85.5 Hz), 135.0 (d, *J* = 103.1 Hz), 134.5 (d, *J* = 18.4 Hz), 132.08 (s), 131.7 (d, *J* = 12.6 Hz), 128.8, 128.5, 128.4 (d, *J* = 14.6 Hz), 128.0, 98.4, 31.9, 29.0, 19.5 (d, *J* = 14.2 Hz), 14.2, 9.5, 8.5; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 101.2; GC-MS (EI, m/z): 356. HRMS calcd for $C_{21}H_{26}OPS^+$ 357.1442, found 357.1443.



5,5-Diethyl-4-methyl-2-phenyl-3-(trimethylsilyl)-5H-1,2-oxaphosphole 2-sulfide (3h)

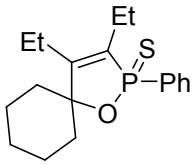
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 121.3 mg, isolated yield was 72%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 – 7.70 (m, 2H), 7.45 – 7.30 (m, 3H), 1.94 (d, *J* = 2.6 Hz, 3H), 1.92 – 1.83 (m, 1H), 1.77 (dt, *J* = 14.8, 7.3 Hz, 1H), 1.68 – 1.54 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.0 (d, *J* = 5.4 Hz), 135.8 (d, *J* = 101.5 Hz), 131.7, 131.4 (d, *J* = 12.6 Hz), 129.7 (d, *J* = 50.3 Hz), 128.1 (d, *J* = 13.3 Hz), 100.4, 31.4, 29.9, 16.4 (d, *J* = 23.5 Hz), 8.7, 8.5, -0.3; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 109.1; GC-MS (EI, m/z): 338. HRMS calcd for $C_{17}H_{28}OPSSi^+$ 339.1368, found 339.1365.



3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-sulfide (3j)

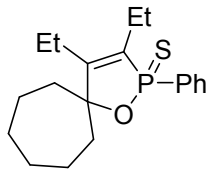
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 93.4 mg, isolated yield was 61%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 – 7.80 (m, 2H), 7.59 – 7.39 (m, 3H), 2.50 – 2.07 (m, 5H), 2.05 – 1.86 (m, 5H), 1.83 – 1.72 (m, 2H), 1.20 (t, *J* = 7.6 Hz, 3H), 0.85 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2 (d, *J* =

17.2 Hz), 134.7 (d, J = 102.3 Hz), 132.0 (d, J = 2.7 Hz), 132.0 (d, J = 88.7 Hz), 131.8 (d, J = 12.7 Hz), 128.3 (d, J = 13.5 Hz), 102.6, 39.1, 38.1, 38.0, 24.8, 24.4, 20.3 (d, J = 15.9 Hz), 18.9 (d, J = 14.8 Hz), 14.4, 13.7; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 98.5; GC-MS (EI, m/z): 306. HRMS calcd for $C_{17}H_{24}OPS^+$ 307.1285, found 307.1280.



3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.5]dec-3-ene 2-sulfide (3k)

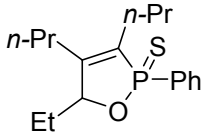
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 84.7 mg, isolated yield was 53%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 – 7.78 (m, 2H), 7.60 – 7.35 (m, 3H), 2.52 – 2.17 (m, 5H), 1.98 – 1.64 (m, 9H), 1.16 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.8 (d, J = 17.4 Hz), 134.9 (d, J = 102.7 Hz), 131.9, 131.8 (d, J = 12.7 Hz), 131.1 (d, J = 88.6 Hz), 128.3(d, J = 13.5 Hz), 94.4, 35.9, 35.2, 24.9, 21.9, 21.7, 20.5 (d, J = 15.9 Hz), 18.6 (d, J = 14.8 Hz), 14.2, 13.8; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 98.9; GC-MS (EI, m/z): 320. HRMS calcd for $C_{18}H_{26}OPS^+$ 321.1442, found 321.1447.



3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.6]undec-3-ene 2-sulfide (3l)

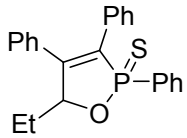
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 73.6 mg, isolated yield was 44%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 – 7.82 (m, 2H), 7.55 – 7.35 (m, 3H), 2.52 – 1.87 (m, 11H), 1.84 – 1.46 (m, 5H), 1.19 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0 (d, J = 17.8 Hz), 134.9 (d, J = 102.5 Hz), 132.0, 131.9 (d, J = 12.6 Hz), 129.7 (d, J = 88.8 Hz), 128.3 (d, J = 13.5 Hz), 97.5, 40.2, 39.2, 39.1, 28.7, 28.5, 23.2, 22.9, 20.6 (d, J = 16.0 Hz), 18.5 (d, J =

15.0 Hz), 14.2, 13.8; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 99.2; GC-MS (EI, m/z): 334. HRMS calcd for $C_{19}H_{28}OPS^+$ 335.1598, found 335.1591.



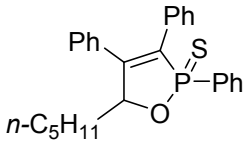
5-Ethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-sulfide (5a)

The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 129.6 mg, isolated yield was 84%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 – 7.84 (m, 2H), 7.54 – 7.38 (m, 3H), 4.19 – 4.08 (m, 1H), 2.97 – 2.87 (m, 1H), 2.41 (d, *J* = 15.4 Hz, 1H), 2.30 (td, *J* = 15.0, 7.7 Hz, 1H), 2.23 – 2.11 (m, 3H), 1.99 – 1.82 (m, 3H), 1.72 – 1.60 (m, 1H), 1.11 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.4 (d, *J* = 5.4 Hz), 134.4 (d, *J* = 106.9 Hz), 131.7, 131.4 (d, *J* = 10.8 Hz), 130.8 (d, *J* = 90.7 Hz), 128.1 (d, *J* = 12.9 Hz), 82.4 (d, *J* = 9.3 Hz), 33.5, 30.6 (d, *J* = 7.4 Hz), 29.5 (d, *J* = 15.3 Hz), 29.1 (d, *J* = 5.3 Hz), 23.4 (d, *J* = 17.6 Hz), 15.3, 12.6, 10.4; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 89.2; GC-MS (EI, m/z): 308. HRMS calcd for $C_{17}H_{26}OPS^+$ 309.1442, found 309.1448.



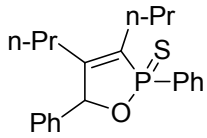
5-Ethyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (5b)

The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 120.1 mg, isolated yield was 64%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 – 8.01 (m, 0.3H), 7.87 – 7.79 (m, 2H), 7.46 – 7.33 (m, 5H), 7.32 – 7.26 (m, 3H), 7.22 – 7.05 (m, 5H), 5.81 – 5.76 (m, 1H), 5.59-5.60 (m, , 0.15H), 1.99 – 1.83 (m, 1.2H), 1.82 – 1.70 (m, 1H), 1.08 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0 (d, *J* = 20.5 Hz), 133.9 (d, *J* = 95.0 Hz), 133.0 (d, *J* = 28.0 Hz), 132.6 (d, *J* = 73.2 Hz), 132.2 (d, *J* = 2.5 Hz), 131.5 (d, *J* = 13.7 Hz), 131.3(d, *J* = 12.4 Hz), 129.2, 129.0 (d, *J* = 22.0 Hz), 128.5, 128.5, 128.4, 128.1, 89.5, 27.4, 9.1. ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 102.8, 102.1; GC-MS (EI, m/z): 376. HRMS calcd for $C_{23}H_{22}OPS^+$ 377.1129, found 377.1127.



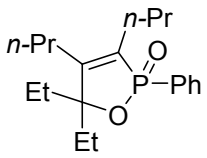
5-Pentyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (5c)

The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 117.3 mg, isolated yield was 56%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 – 7.98 (m, 1H), 7.93 – 7.73 (m, 2H), 7.63 – 7.50 (m, 2H), 7.44 – 7.33 (m, 5H), 7.32 – 7.26 (m, 4H), 7.22 – 7.06 (m, 8H), 6.89 (d, *J* = 7.4 Hz, 1H), 5.84 – 5.69 (m, 1H), 1.89 – 1.72 (m, 3H), 1.73 – 1.48 (m, 4H), 1.36 – 1.17 (m, 7H), 0.93 – 0.72 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.2 (d, *J* = 20.3 Hz), 152.5 (d, *J* = 20.5 Hz), 134.4 (d, *J* = 104.3 Hz), 133.8 (d, *J* = 118.6 Hz), 133.3 (d, *J* = 3.5 Hz), 132.7 (d, *J* = 11.6 Hz), 132.3, 132.2 (d, *J* = 7.7 Hz), 131.7 (d, *J* = 28.6 Hz), 131.6 (d, *J* = 13.7 Hz), 131.3 (d, *J* = 12.4 Hz), 129.4 (d, *J* = 5.3 Hz), 129.2 (d, *J* = 5.8 Hz), 129.2 (d, *J* = 7.1 Hz), 128.9, 128.7 (d, *J* = 13.5 Hz), 128.5, 128.4, 128.4, 128.2, 128.1, 88.8, 87.7, 34.9, 34.7, 31.4, 31.3, 25.7, 24.6, 22.5, 14.1, 14.0; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 102.9, 102,1; GC-MS (EI, m/z): 418. HRMS calcd for $C_{26}H_{28}OPS^+$ 419.1598, found 419.1563.



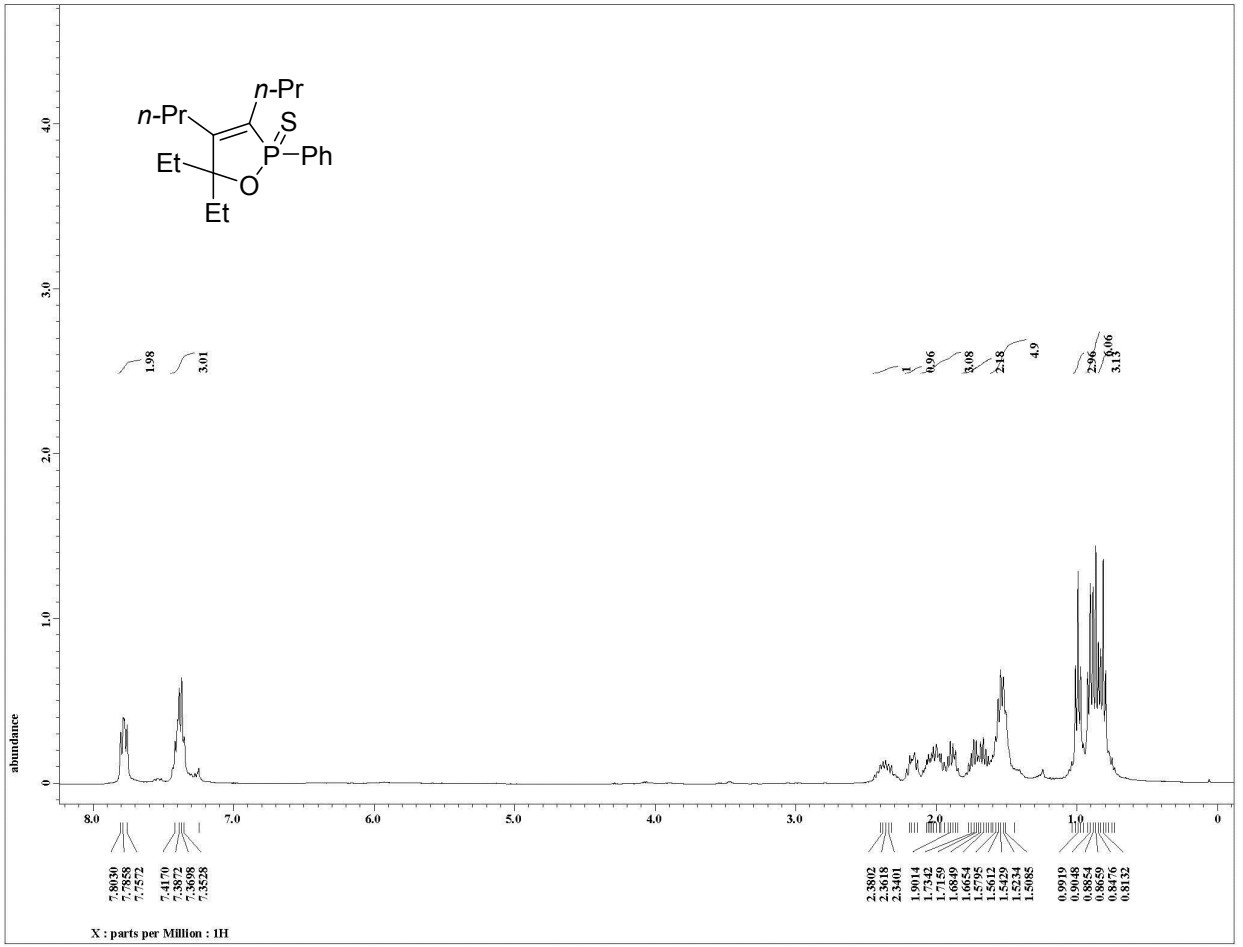
2,5-Diphenyl-3,4-dipropyl-2,5-dihydro-1,2-oxaphosphole 2-sulfide(5d)

The crude product was purified by column chromatography by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 53.4 mg, isolated yield was 15%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 – 7.87 (m, 2H), 7.54 – 7.34 (m, 8H), 6.01 – 5.99 (d, *J* = 7.8 Hz, 1H), 2.47 – 2.12 (m, 4H), 1.40 – 1.28 (m, 4H), 0.93 – 0.88 (m, 3H), 0.85 -0.78 (m, 3H); ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 106.7, 104,8; GC-MS (EI, m/z): 356.

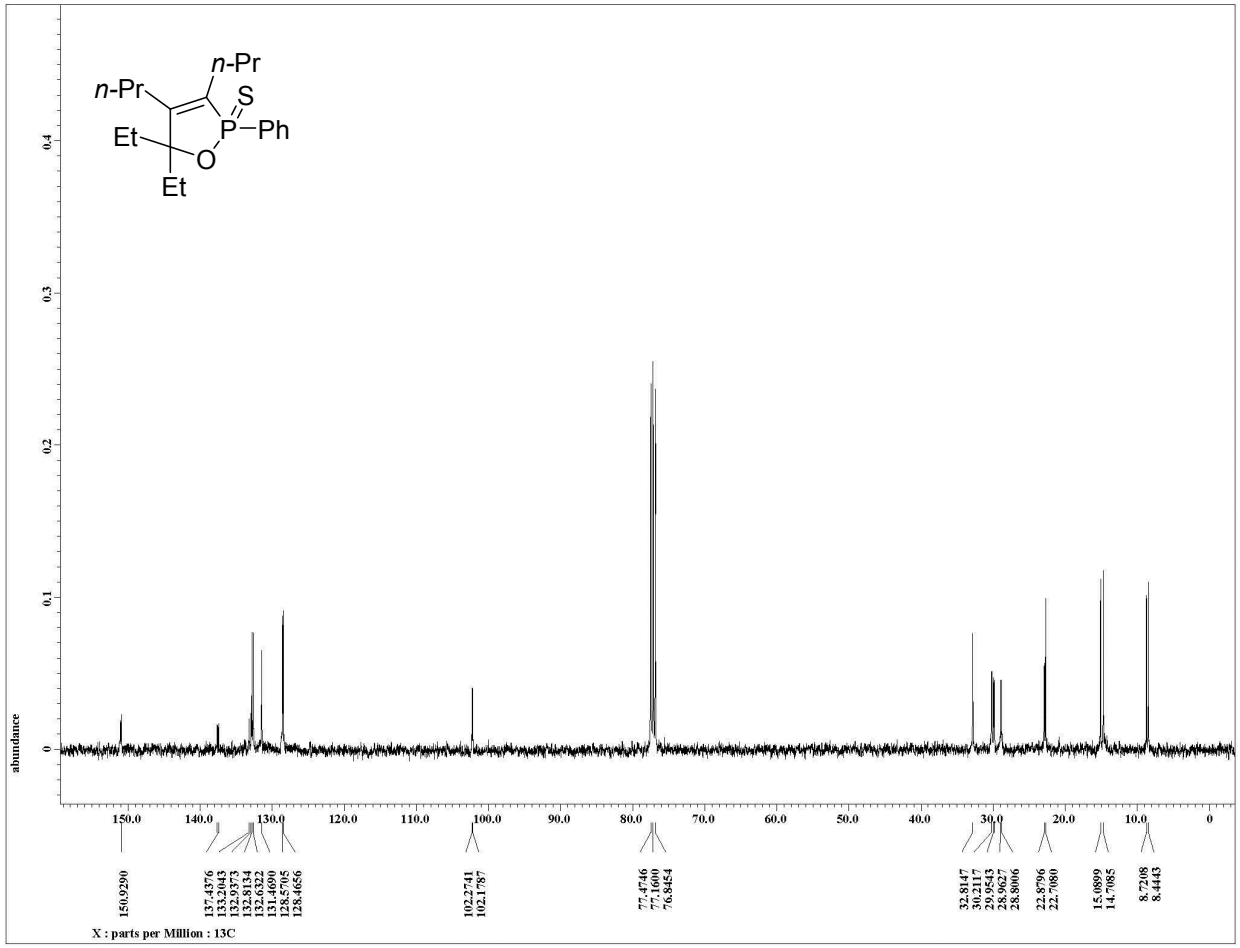


5,5-Diethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-oxide (4a)

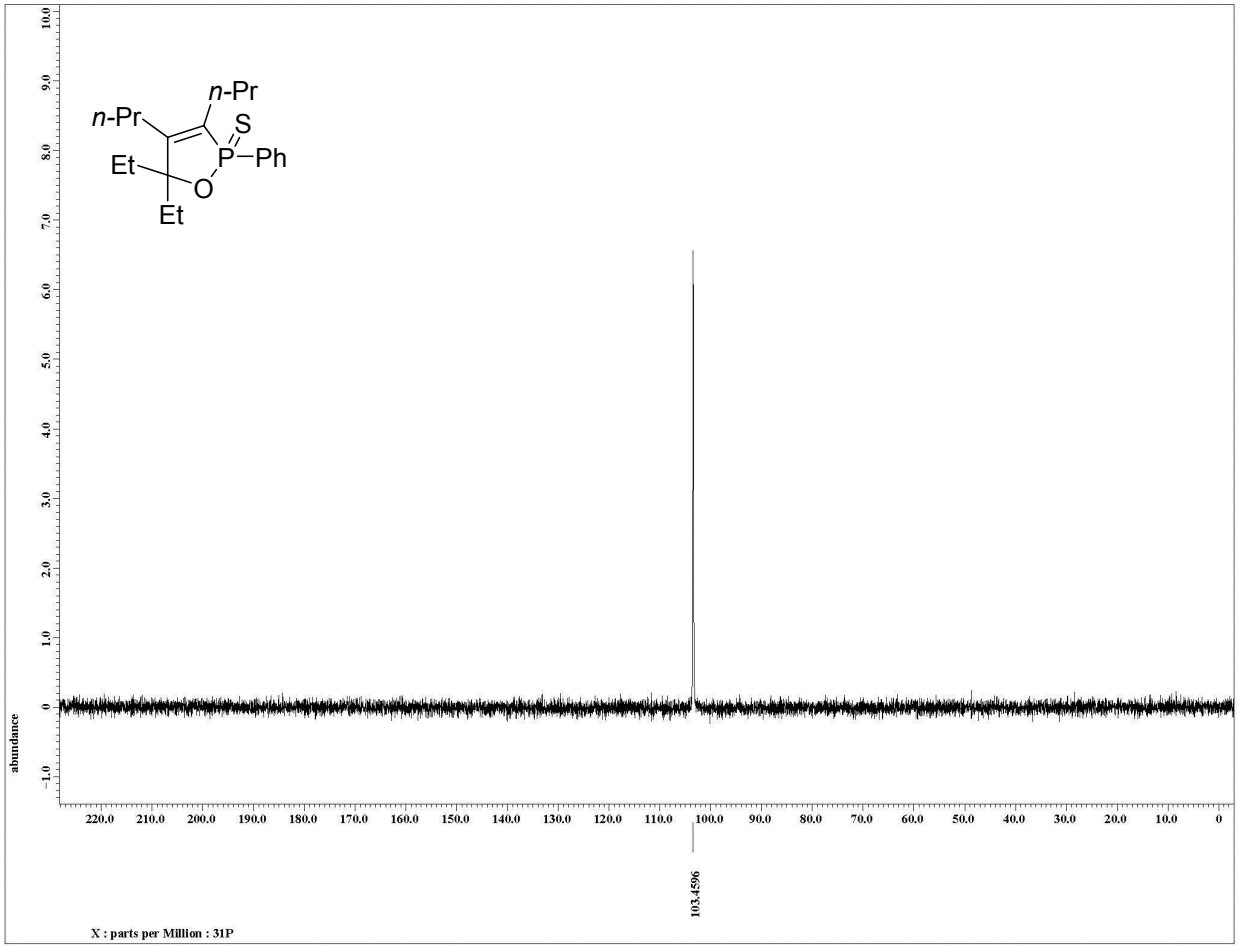
The crude product was purified by column chromatography on Al_2O_3 with petroleum : ethyl acetate = 10 : 1 to give the desired product as yellow oil 86.5 mg, isolated yield was 54%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 – 7.72 (m, 2H), 7.46 – 7.30 (m, 3H), 2.49 – 2.25 (m, 1H), 2.17 (dt, *J* = 13.3, 8.4 Hz, 1H), 2.11 – 1.83 (m, 2H), 1.79 – 1.65 (m, 2H), 1.60 – 1.46 (m, 5H), 0.99 (t, *J* = 7.3 Hz, 3H), 0.94 – 0.84 (m, 6H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.0 (d, *J* = 11.6 Hz), 137.5 (d, *J* = 17.6 Hz), 133.1 (d, *J* = 26.7 Hz), 132.7 (d, *J* = 18.8 Hz), 131.5, 128.5 (d, *J* = 10.0 Hz), 102.2 (d, *J* = 9.4 Hz), 32.8, 30.2 (d, *J* = 4.5 Hz), 29.9 (d, *J* = 10.2 Hz), 28.9 (d, *J* = 16.7 Hz), 22.9 (d, *J* = 4.0 Hz), 22.7, 15.1, 14.7, 8.7, 8.4; ^{31}P NMR (80 MHz, $CDCl_3$, 85% H_3PO_4) δ 116.4; GC-MS (EI, m/z): 320. HRMS calcd for $C_{19}H_{20}O_2P^+$ 321.1983, found 321.1986.



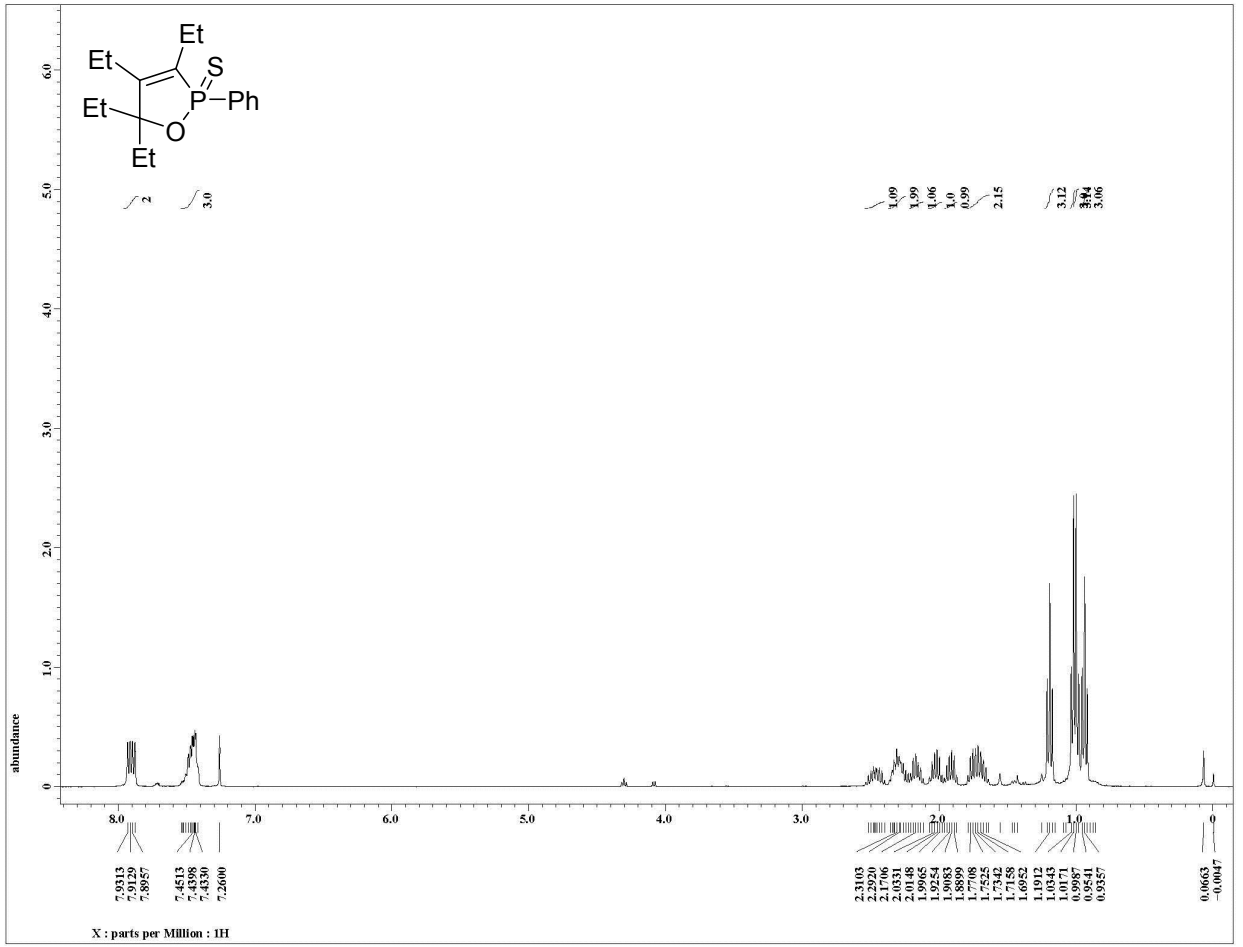
^{1}H NMR of Compound **3a**



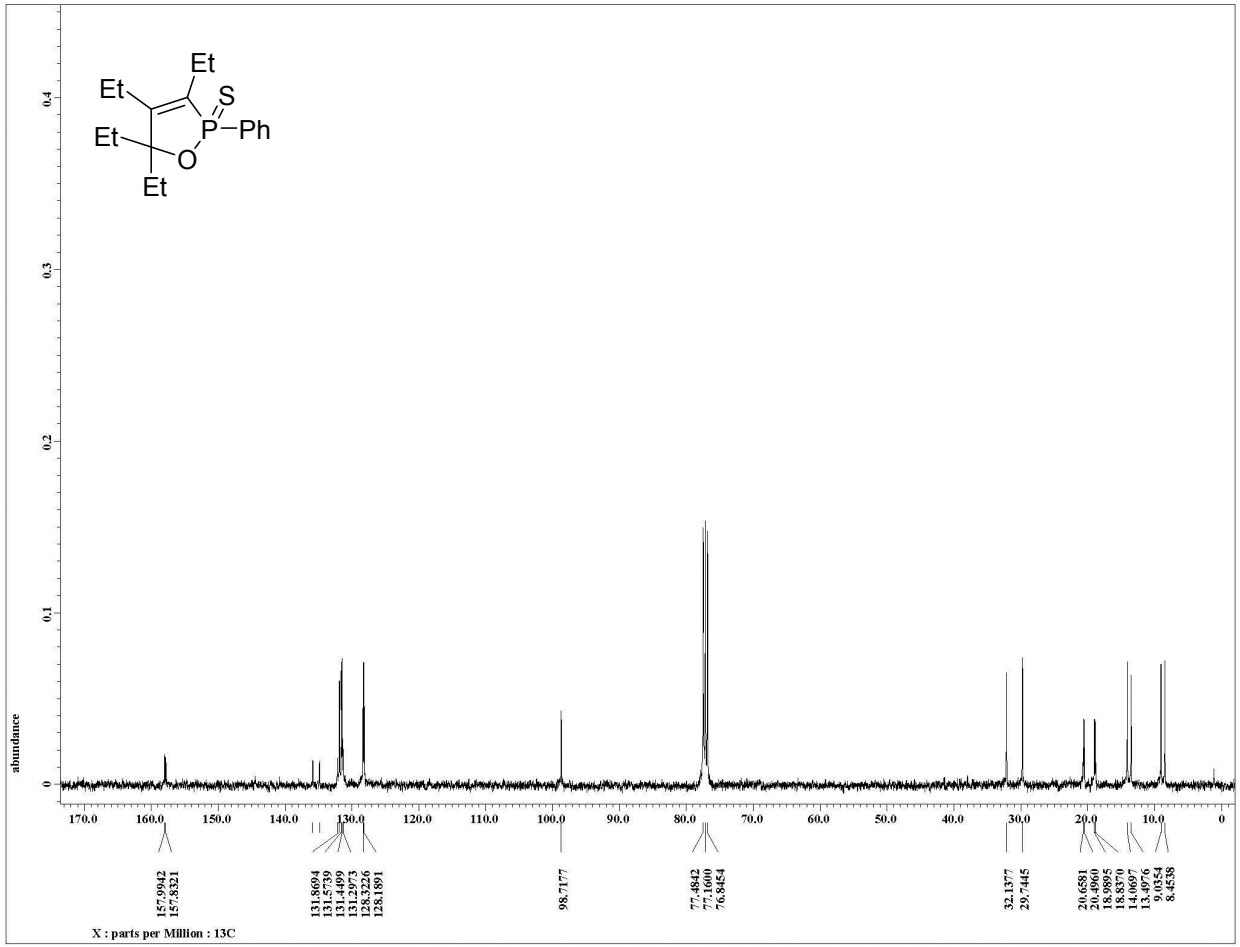
^{13}C NMR of Compound **3a**



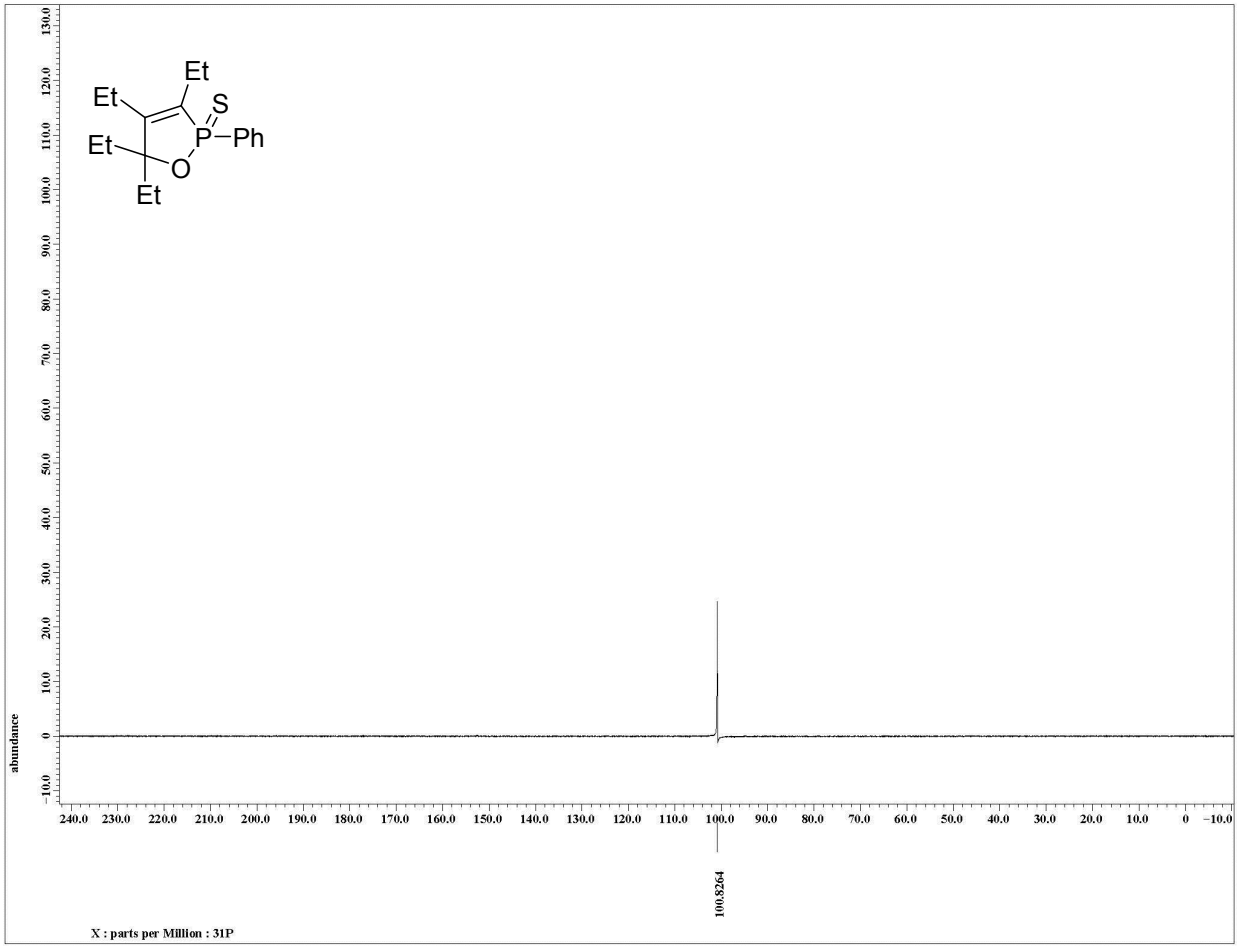
^{31}P NMR of Compound **3a**



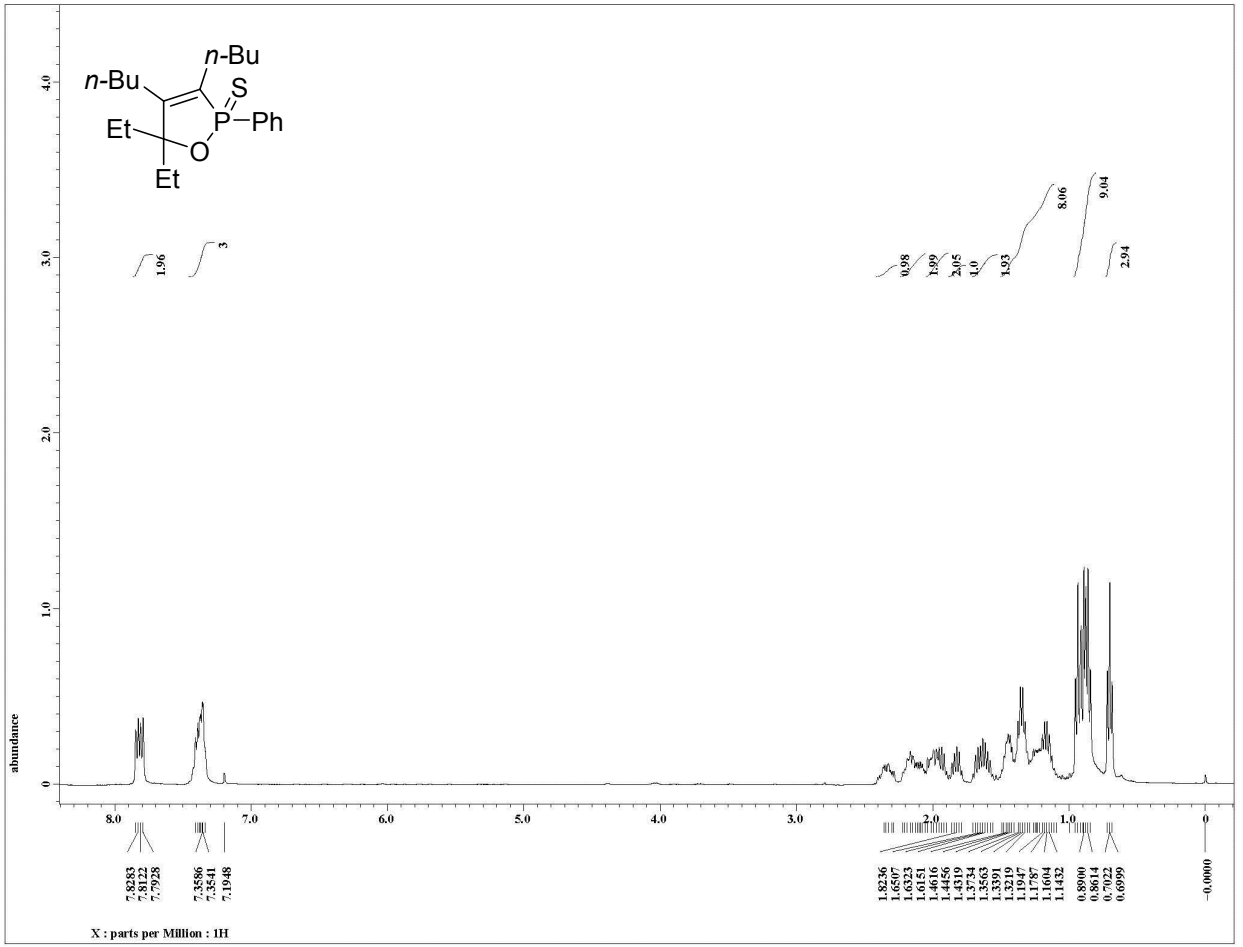
^{1}H NMR of Compound **3b**



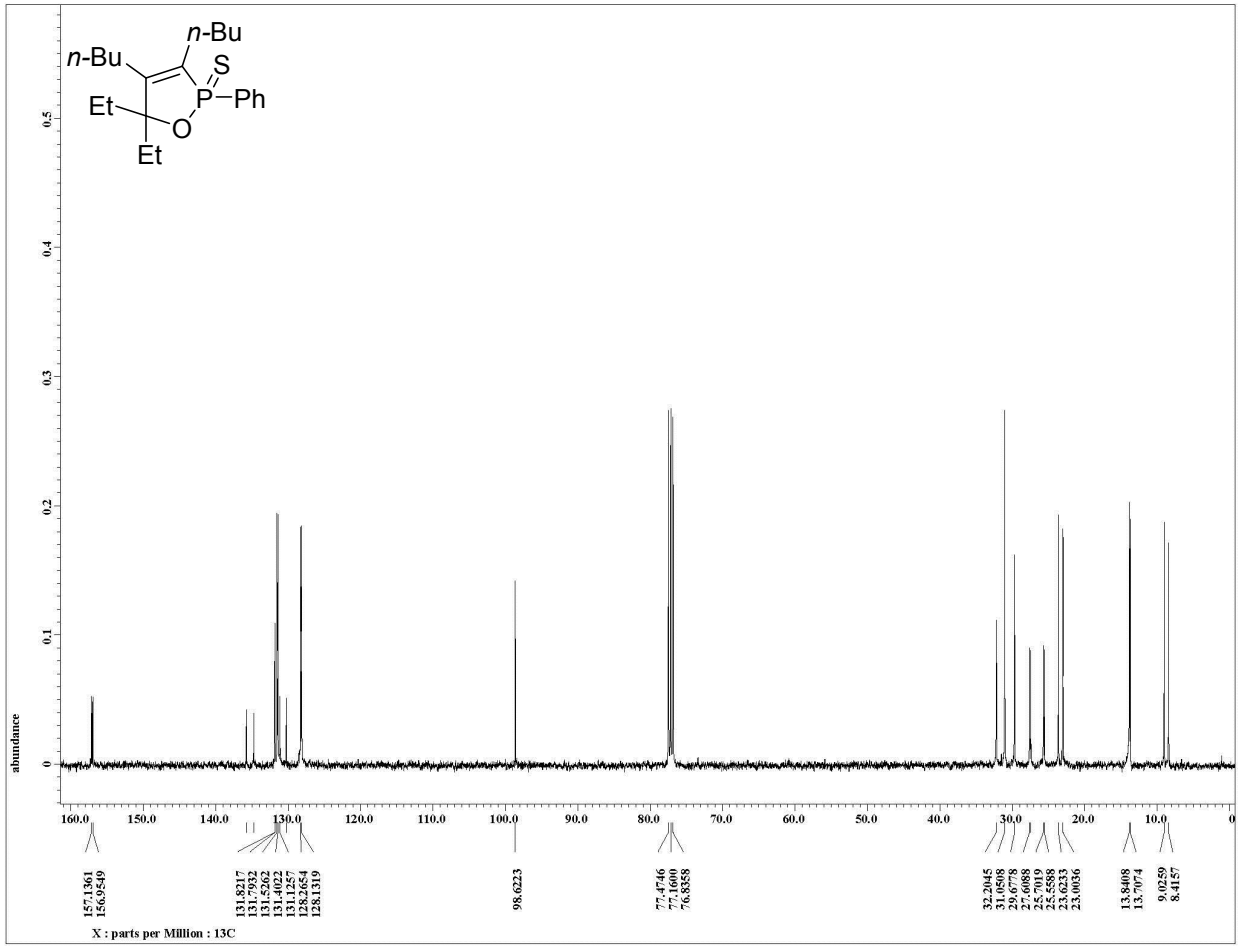
^{13}C NMR of Compound **3b**



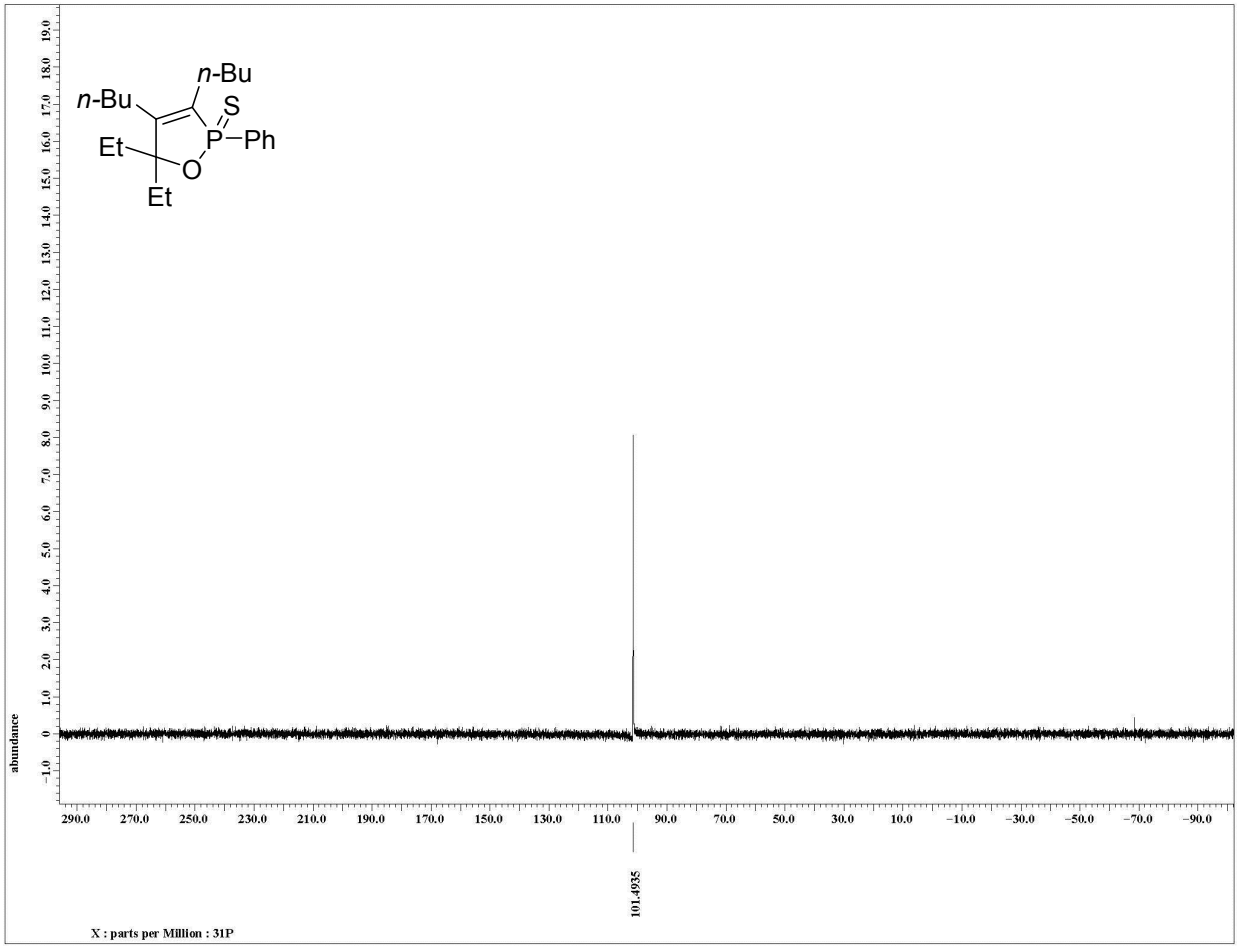
^{31}P NMR of Compound **3b**



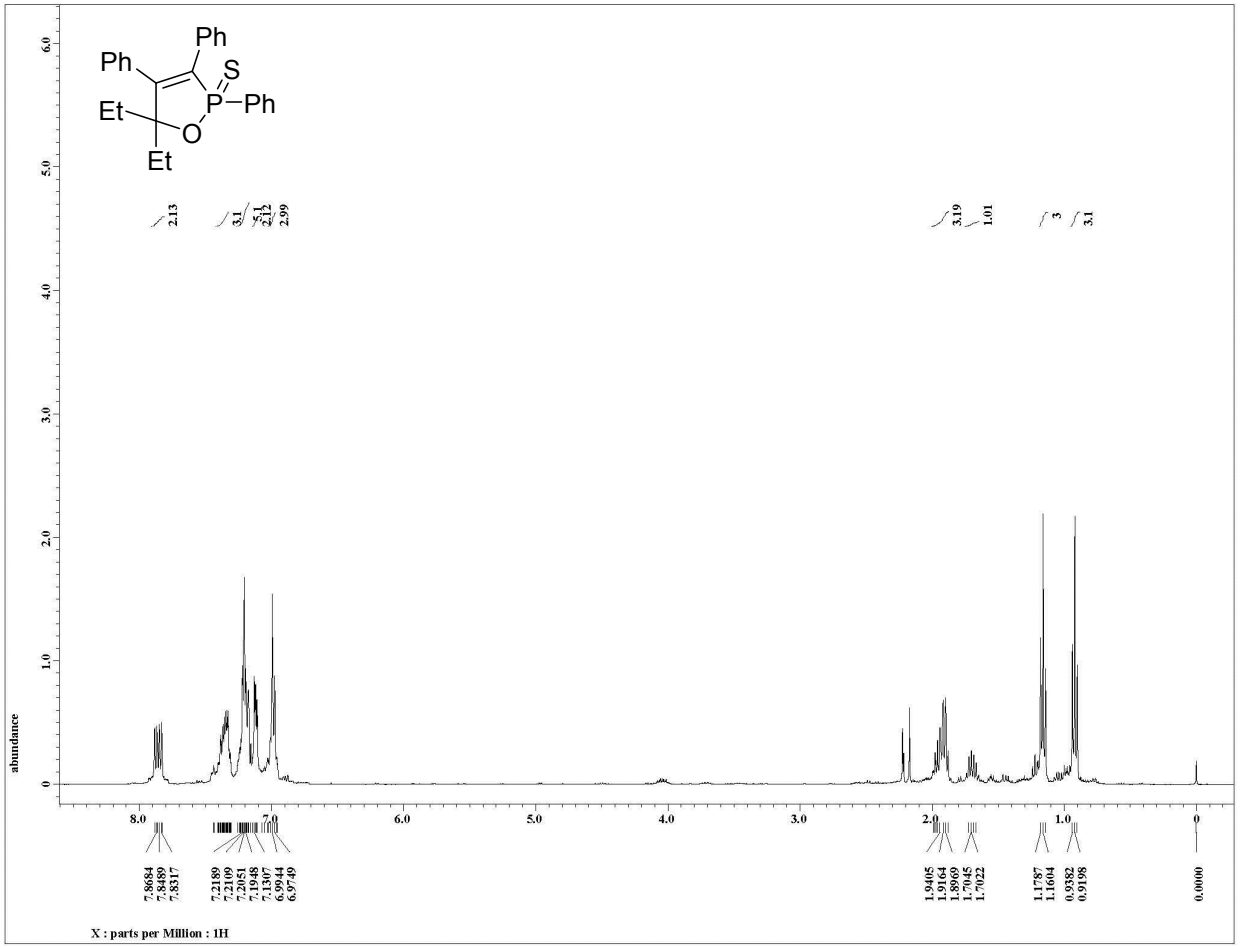
^{1}H NMR of Compound **3c**



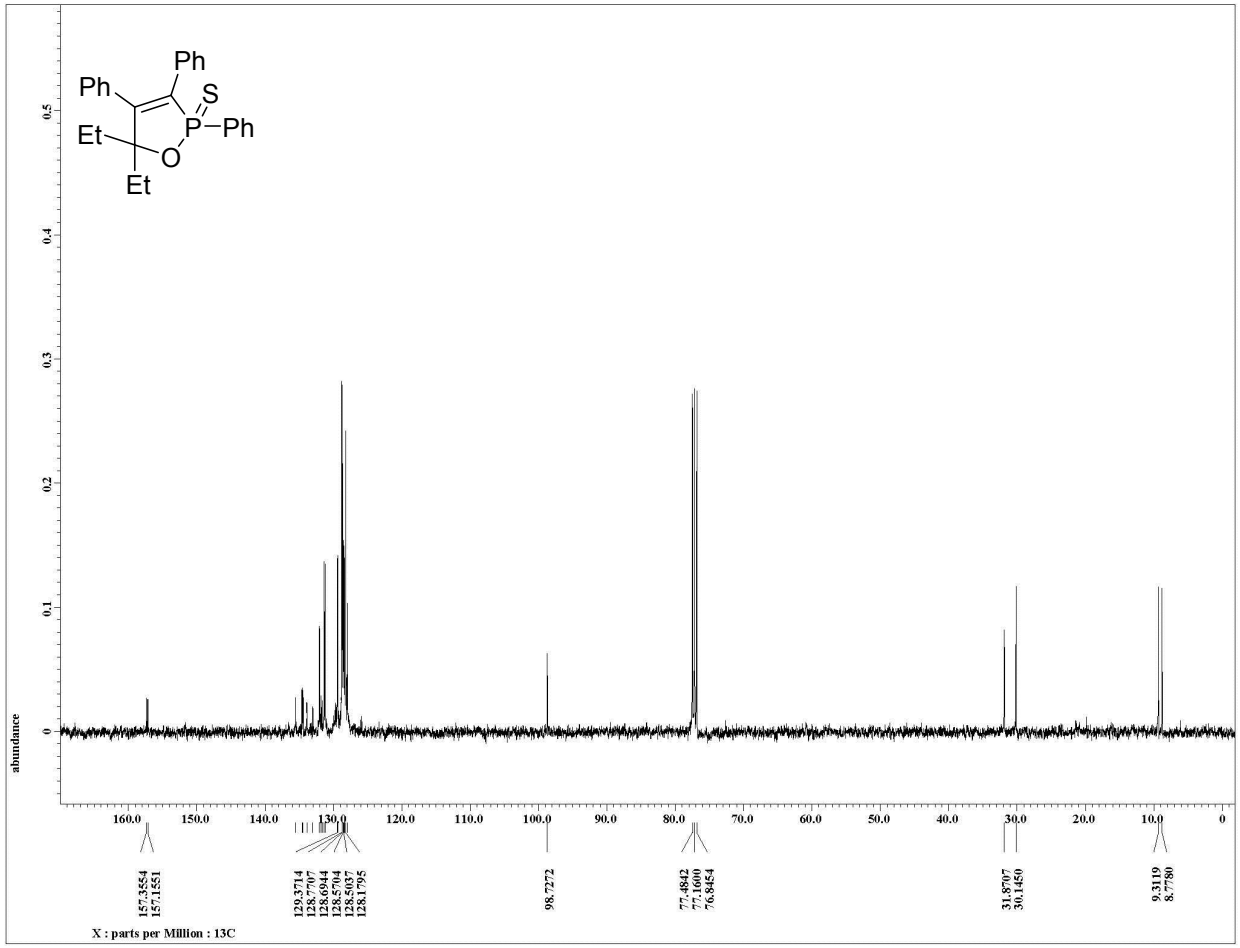
^{13}C NMR of Compound **3c**



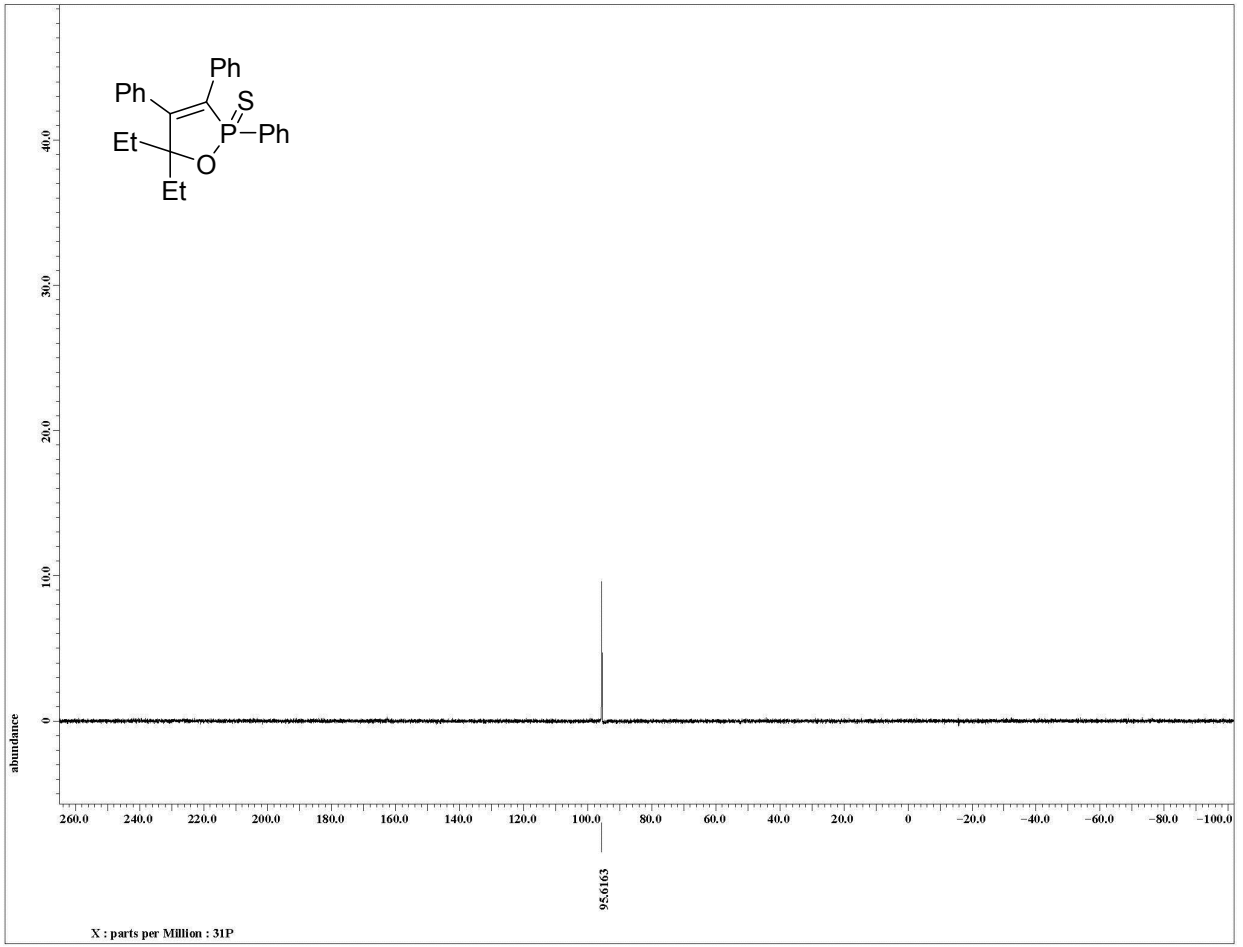
^{31}P NMR of Compound **3c**



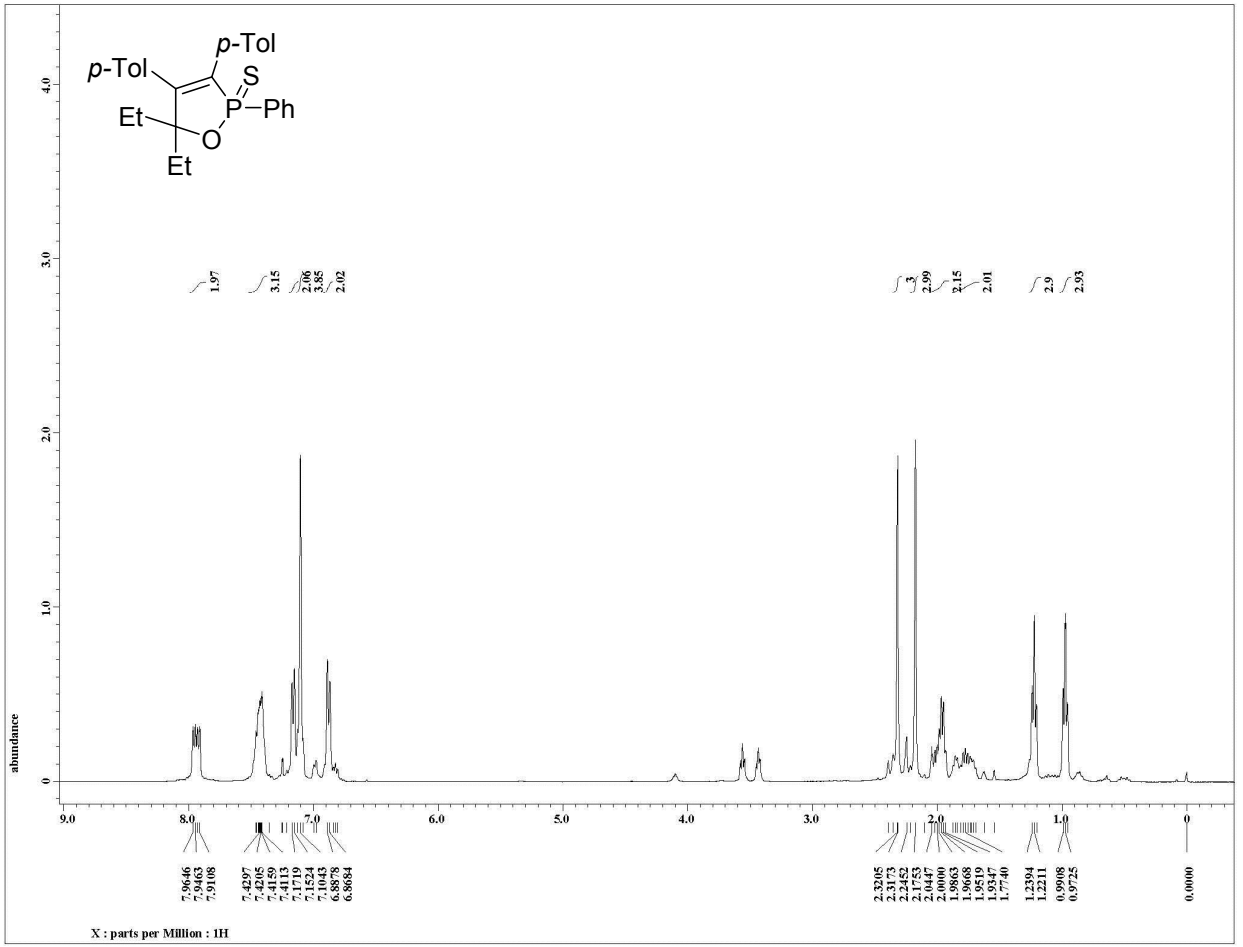
^{1}H NMR of Compound **3d**



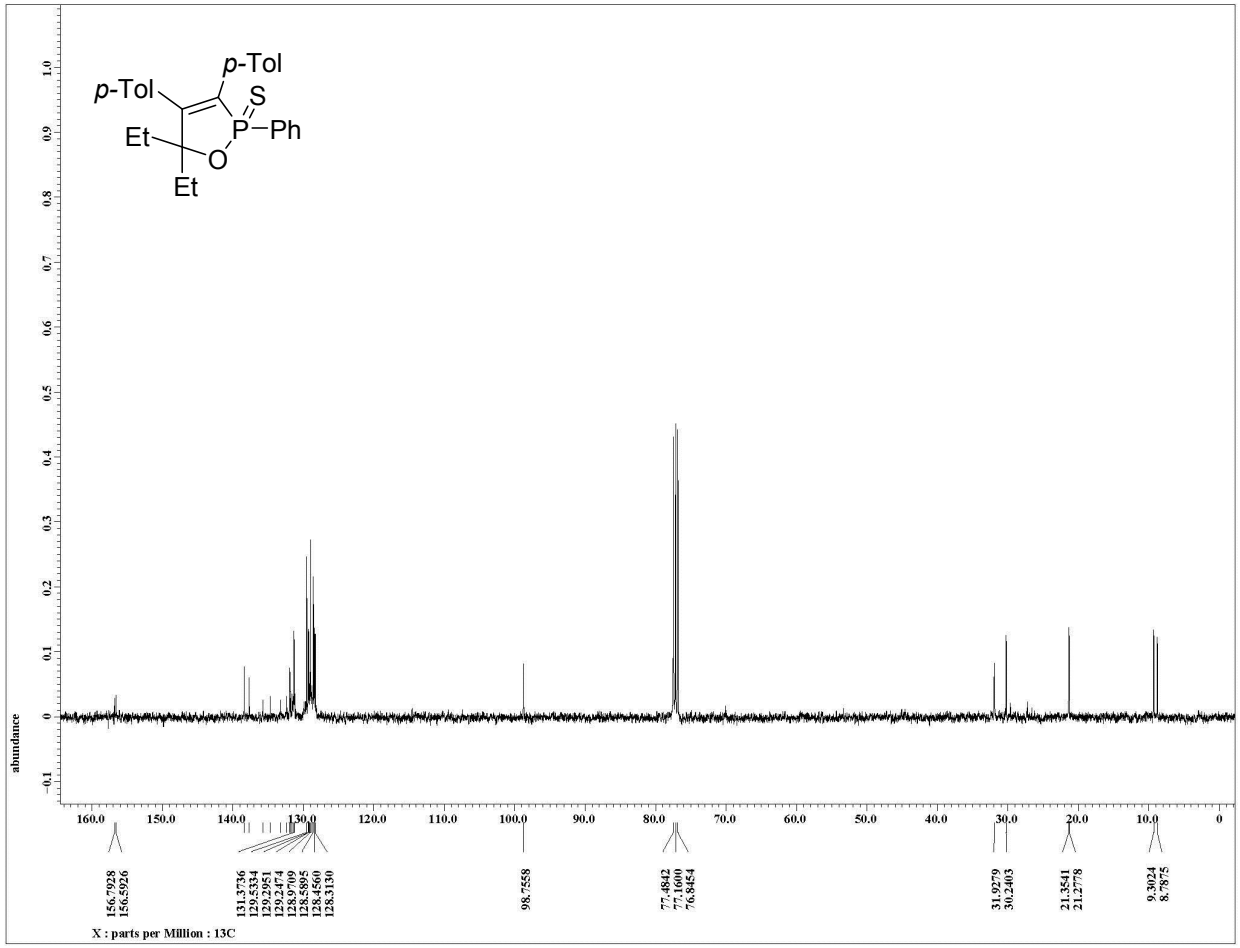
^{13}C NMR of Compound **3d**



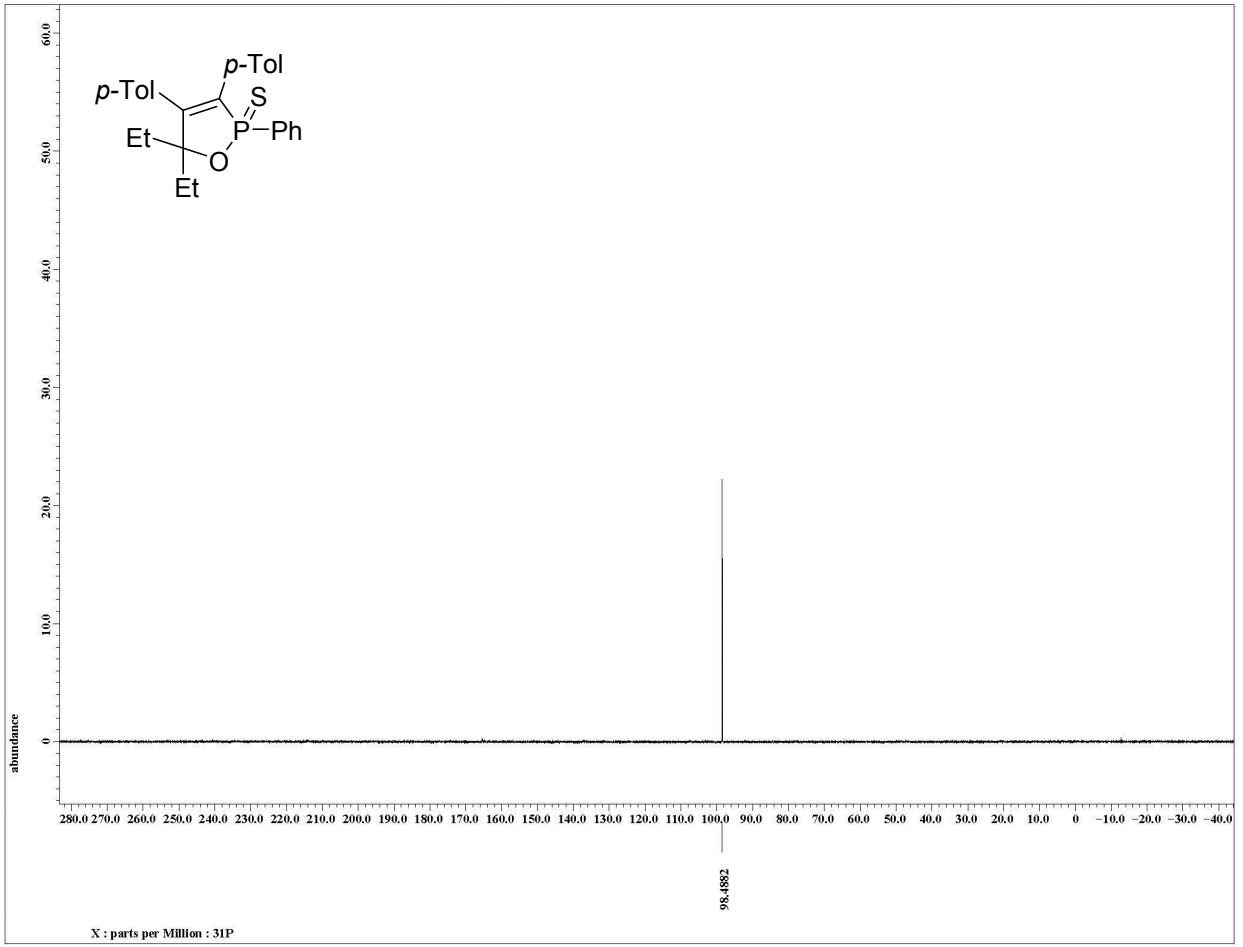
^{31}P NMR of Compound **3d**



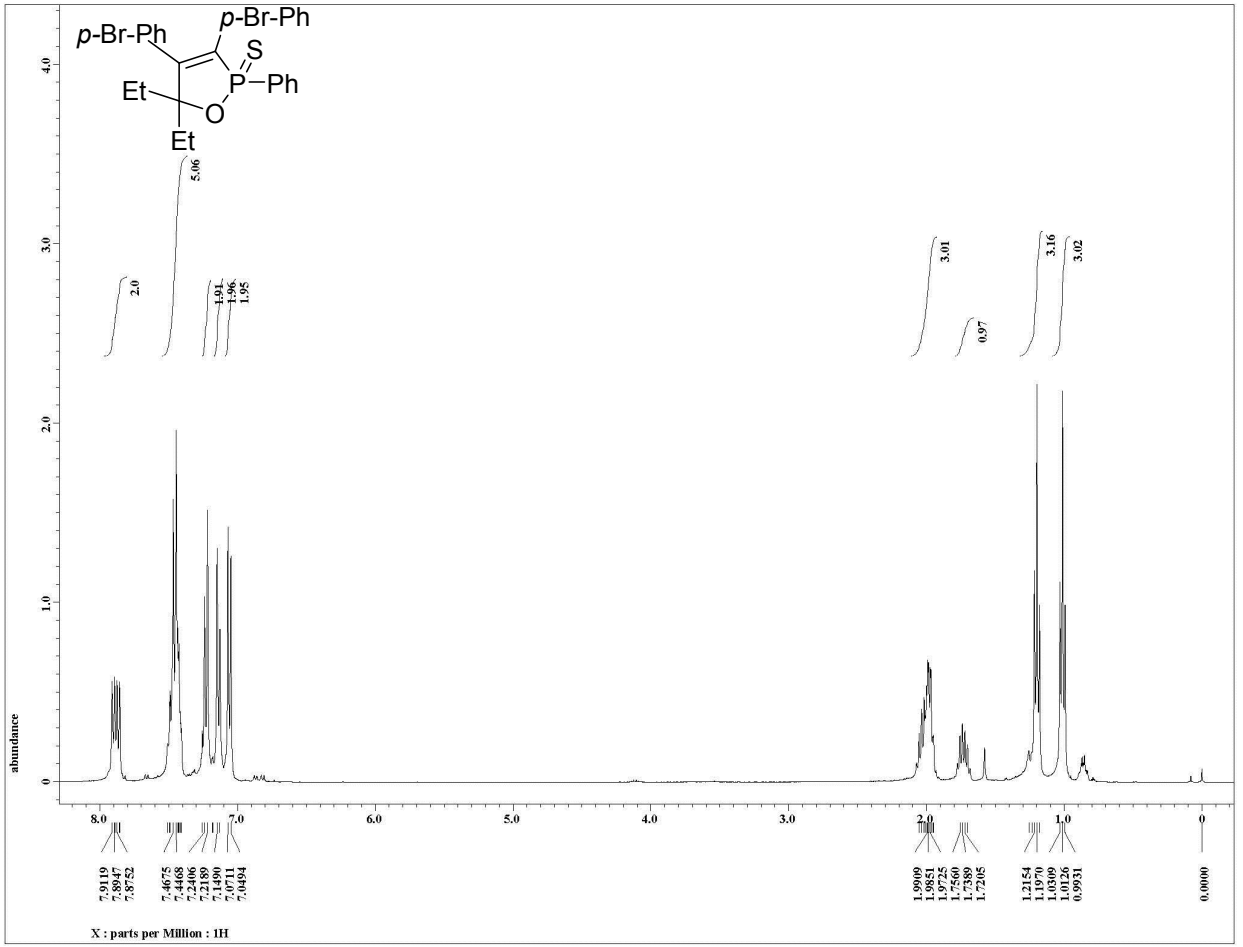
^{1}H NMR of Compound **3e**



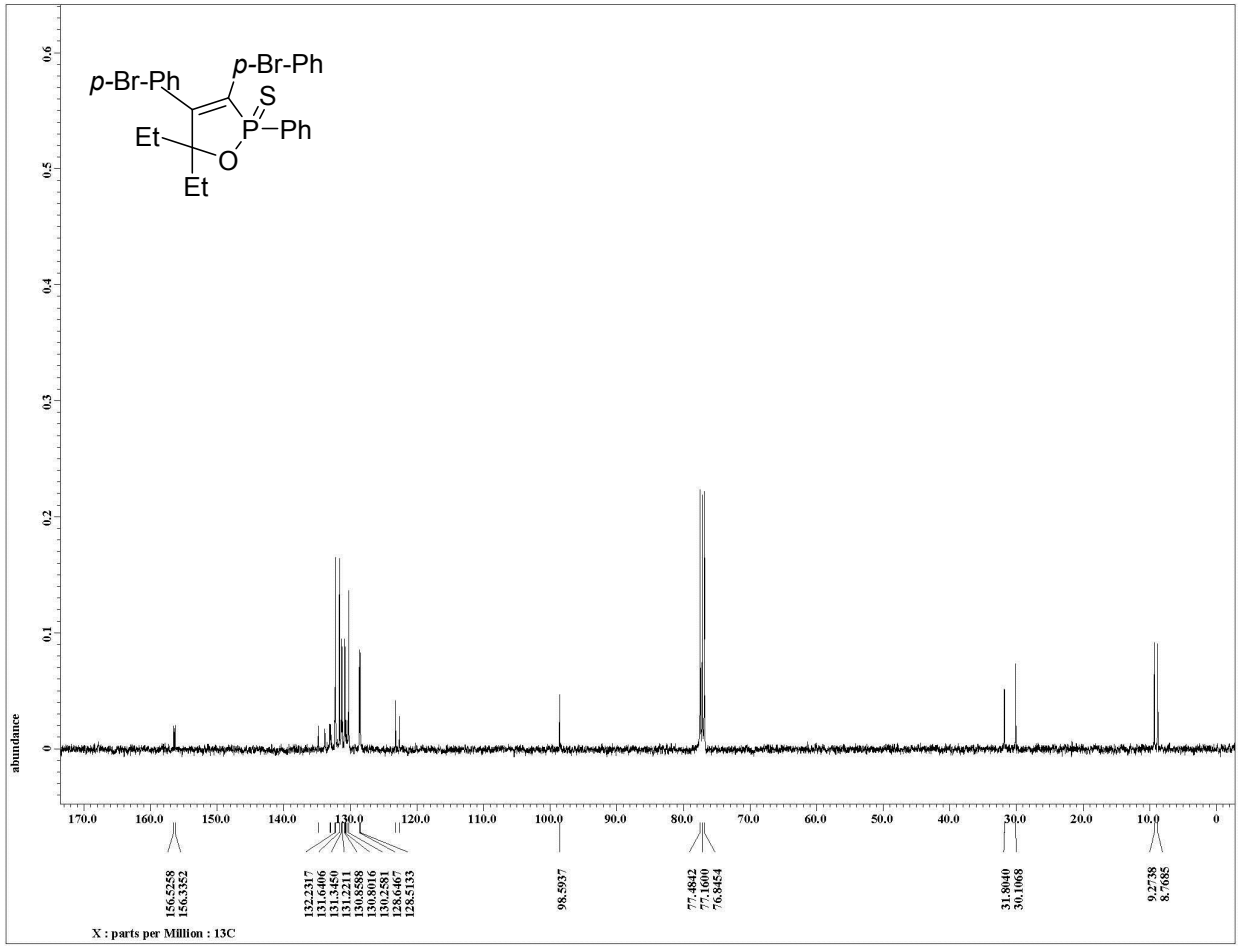
^{13}C NMR of Compound **3e**



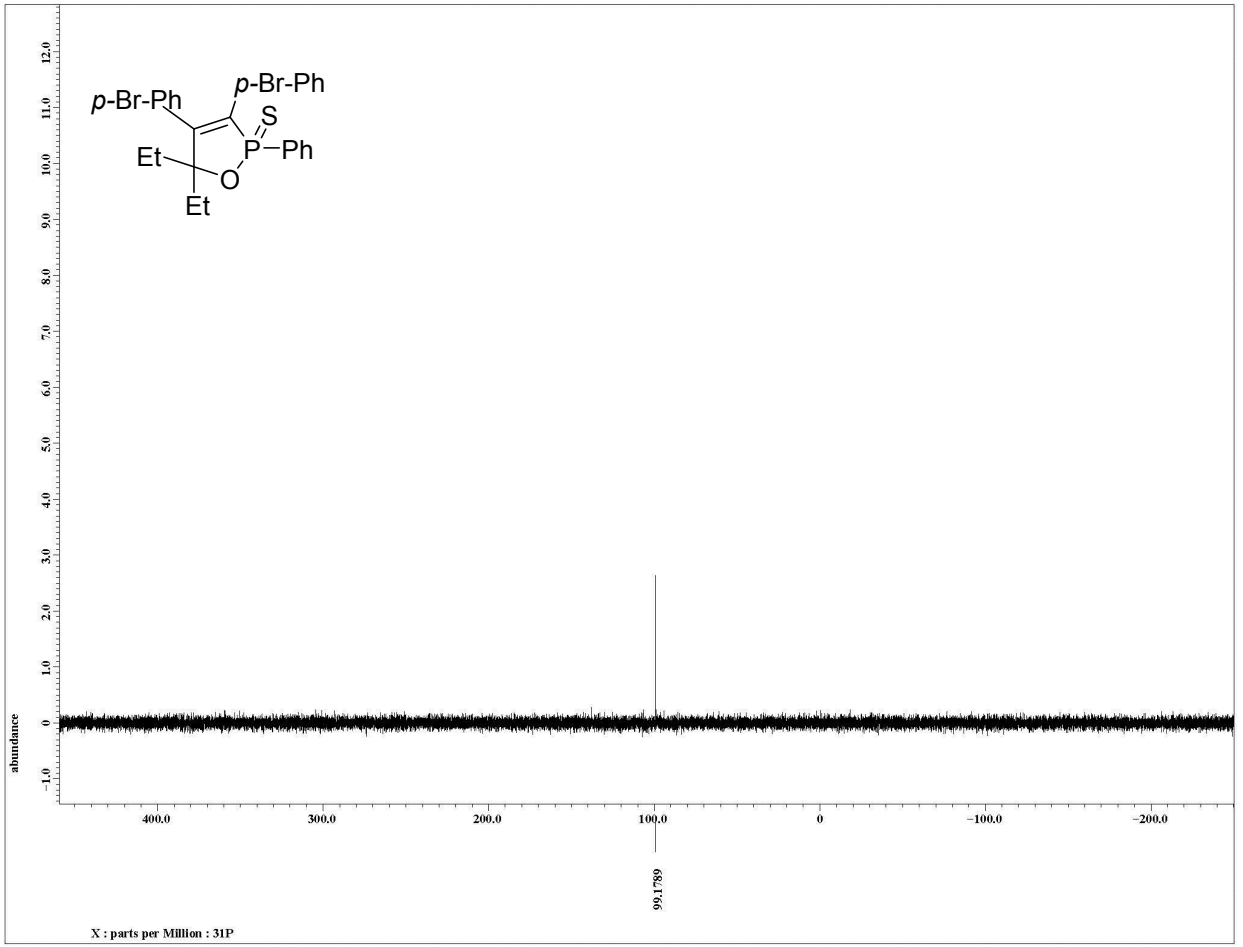
^{31}P NMR of Compound **3e**



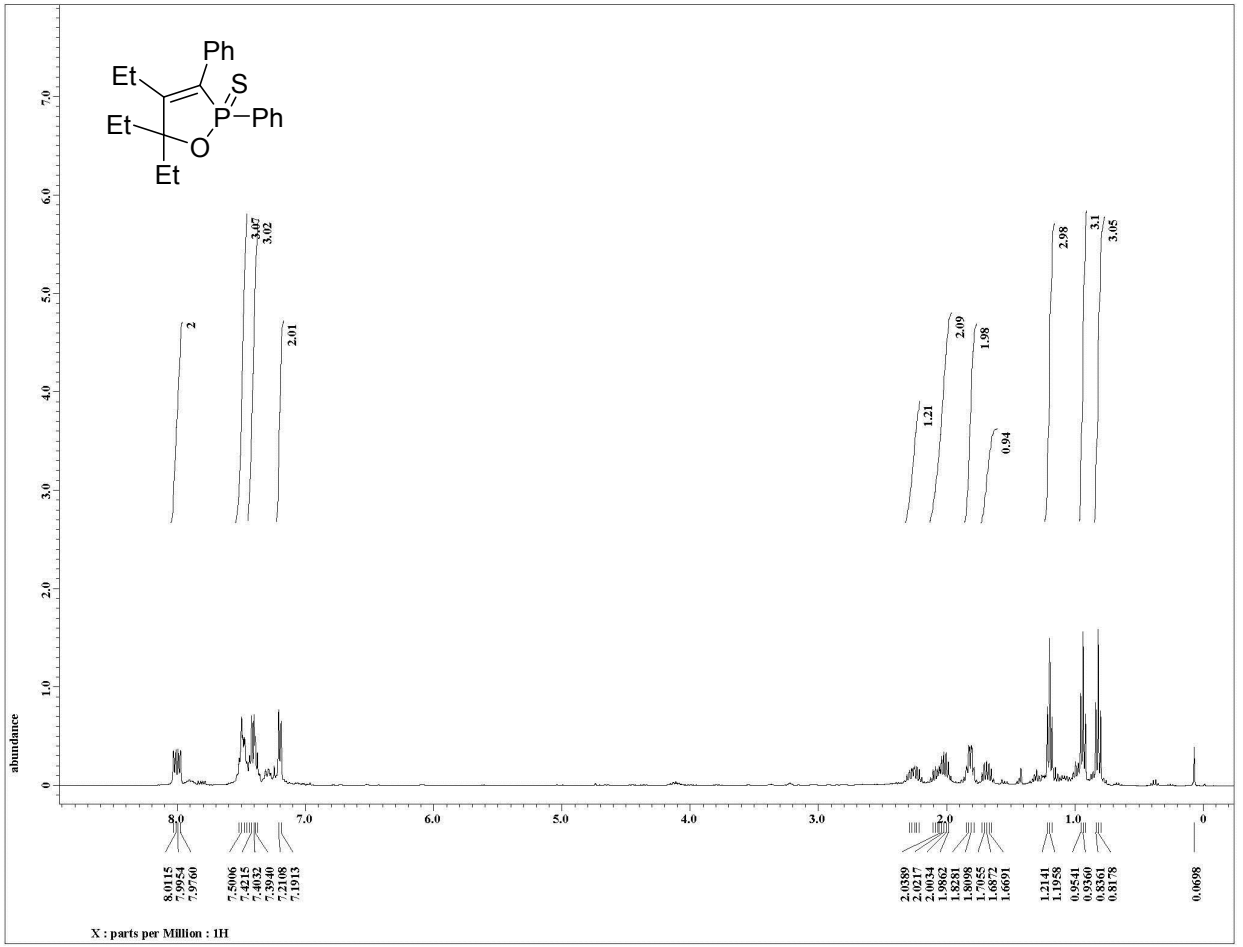
^{1}H NMR of Compound **3f**



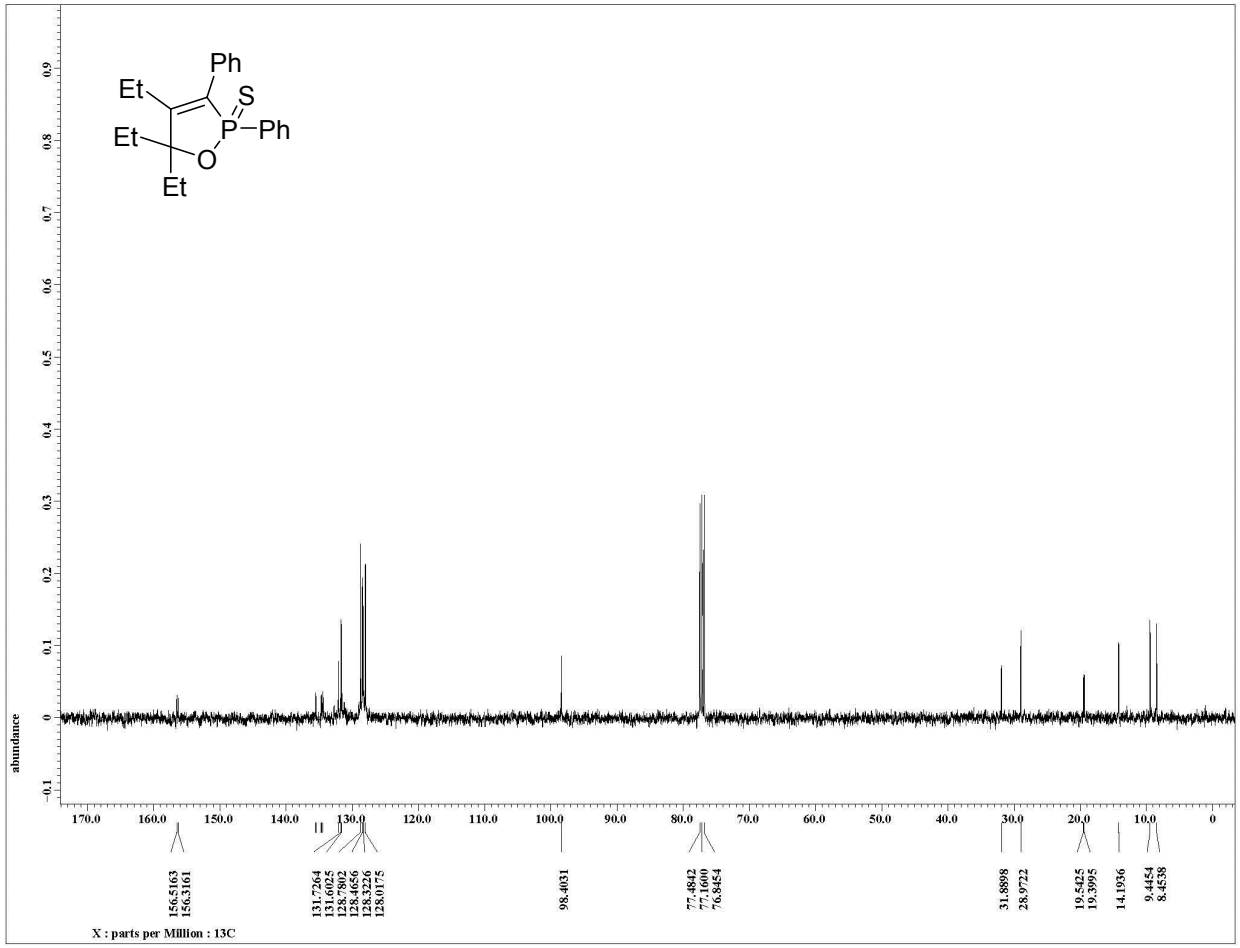
^{13}C NMR of Compound **3f**



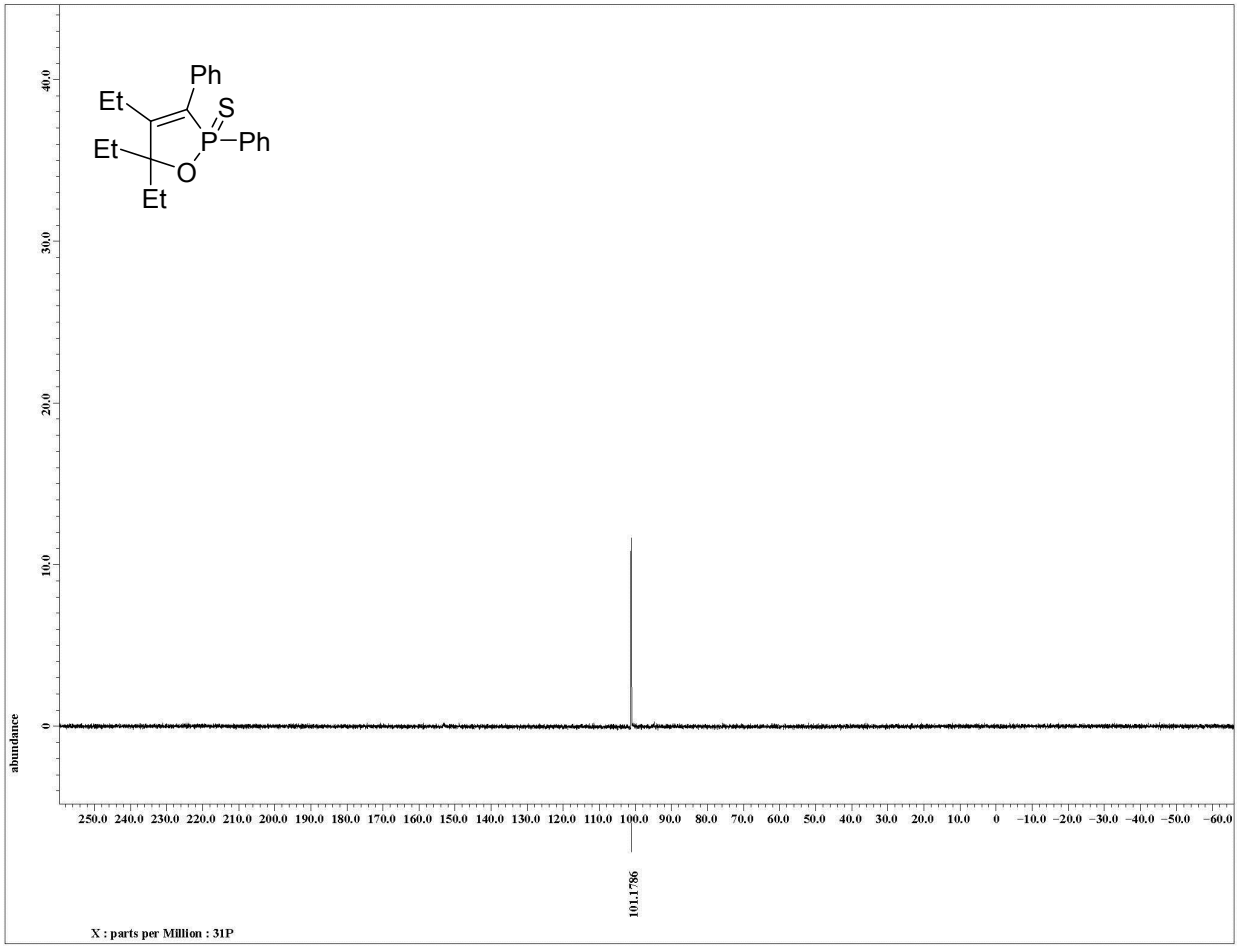
^{31}P NMR of Compound **3f**



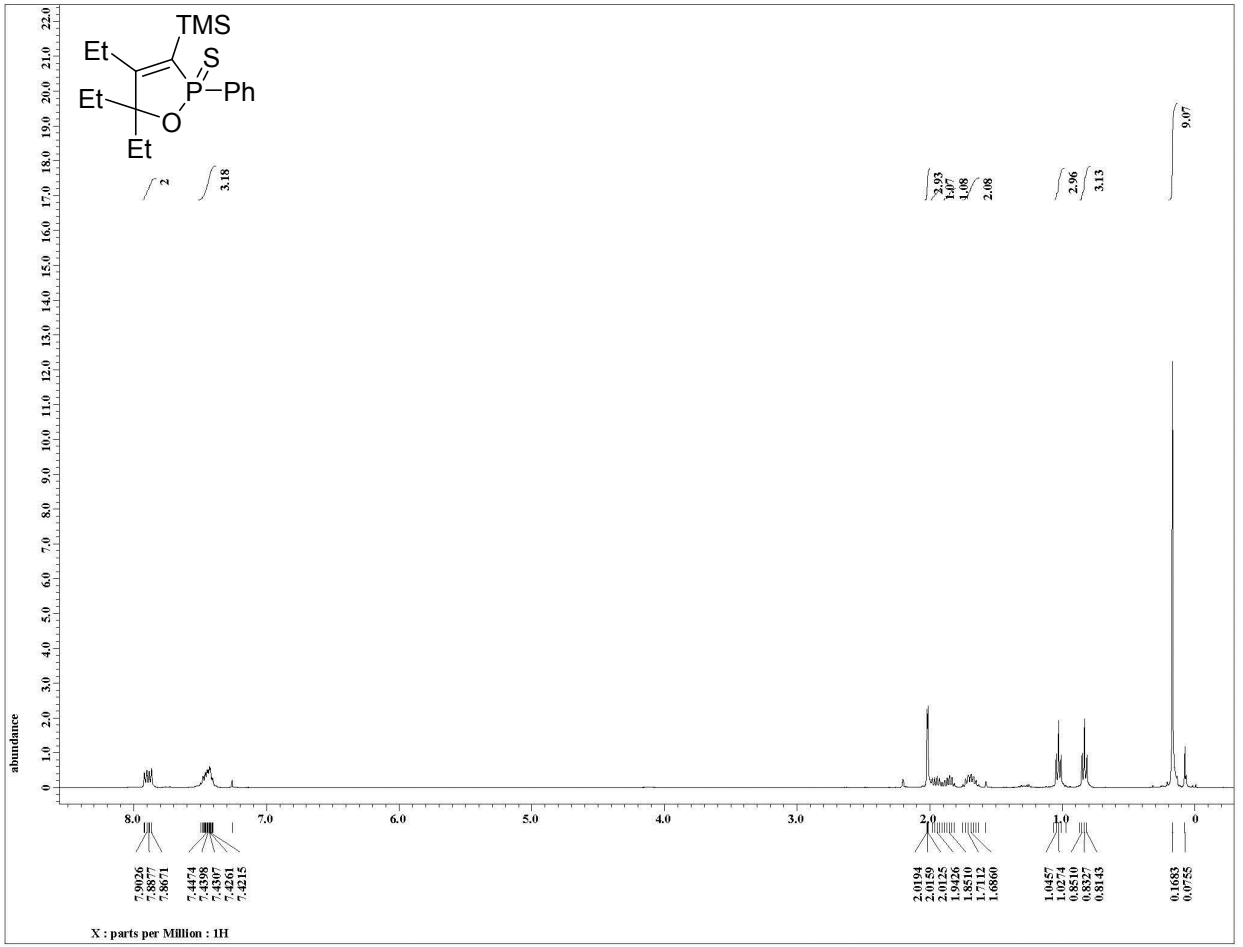
^{1}H NMR of Compound **3g**



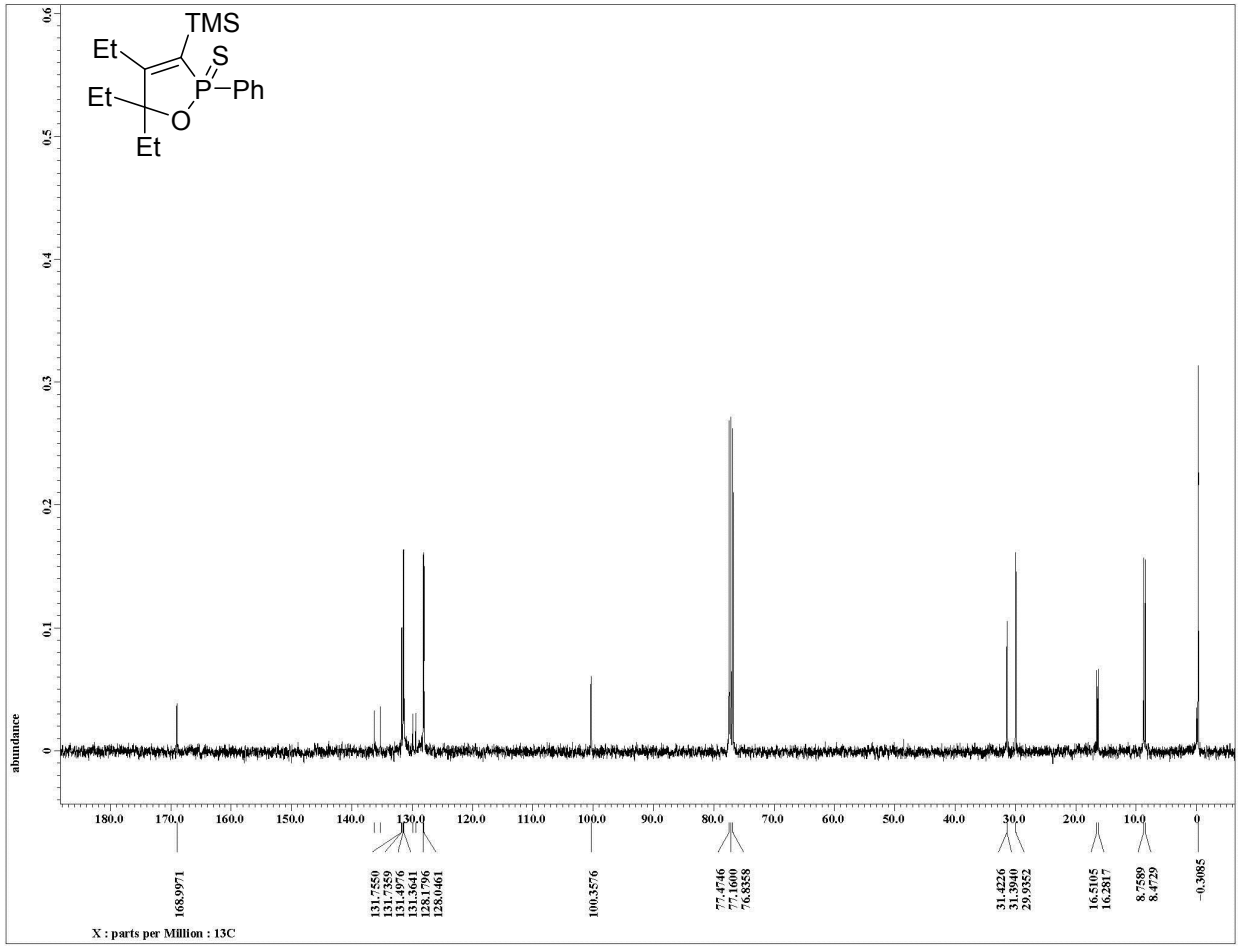
^{13}C NMR of Compound **3g**



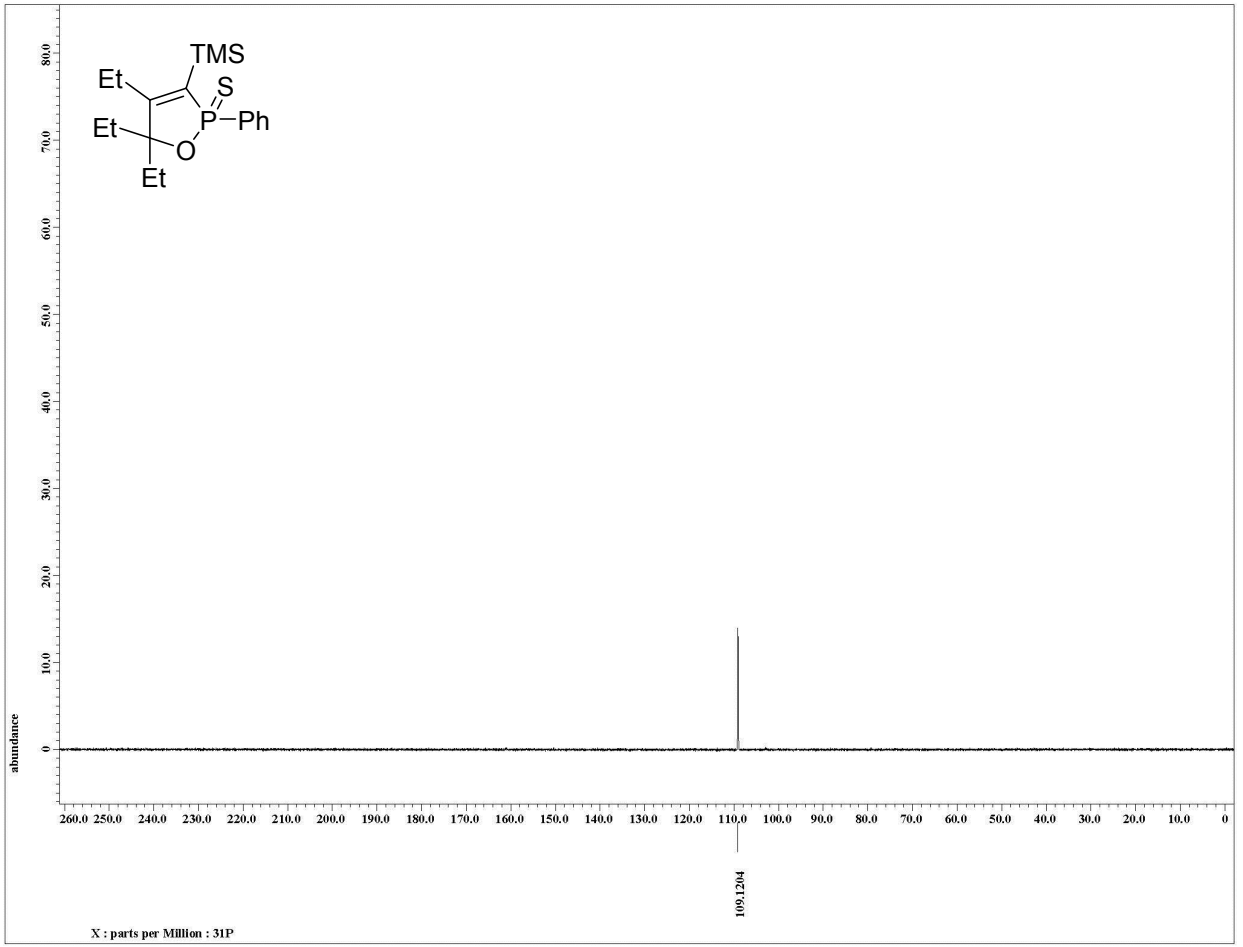
^{31}P NMR of Compound **3g**



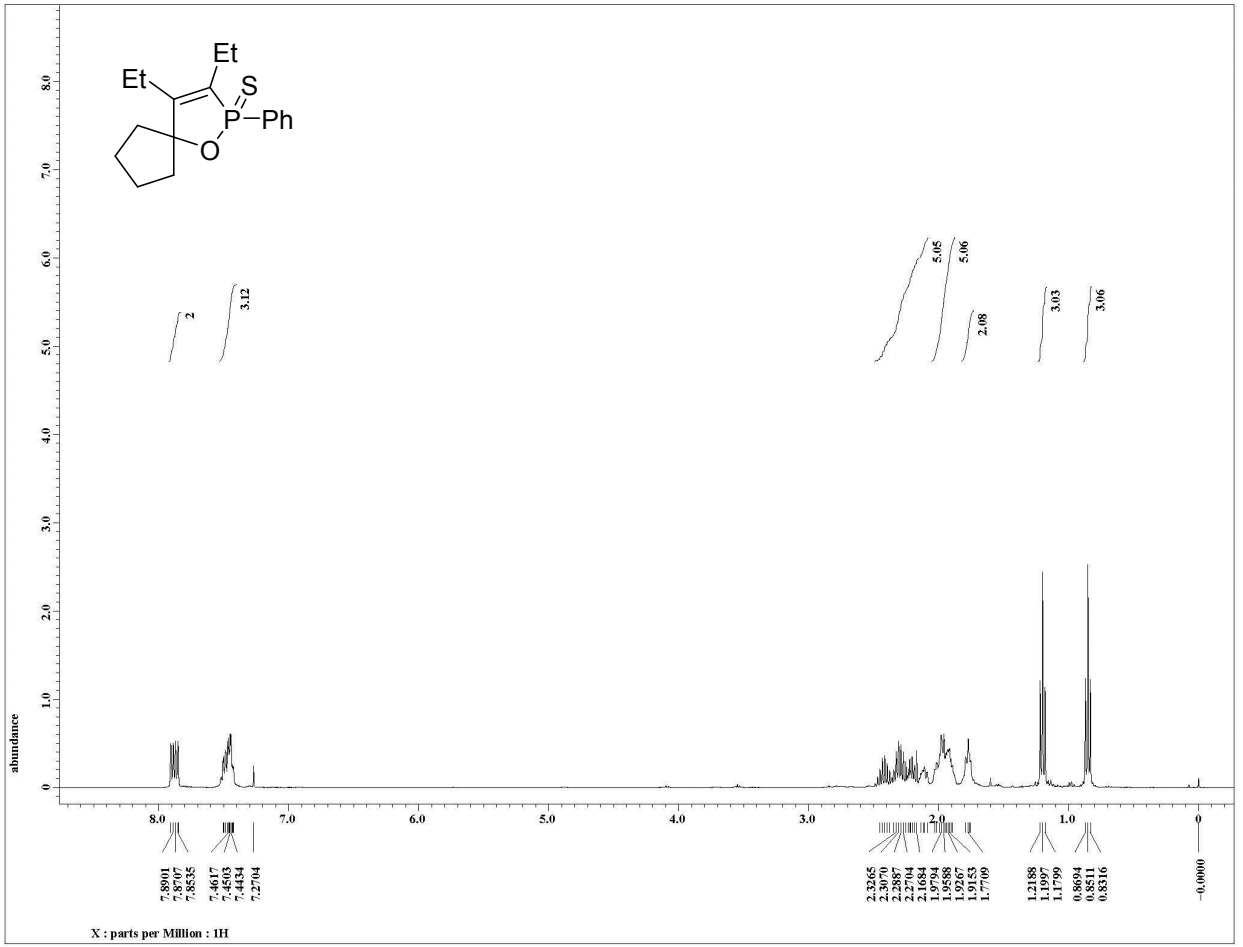
^{1}H NMR of Compound **3h**



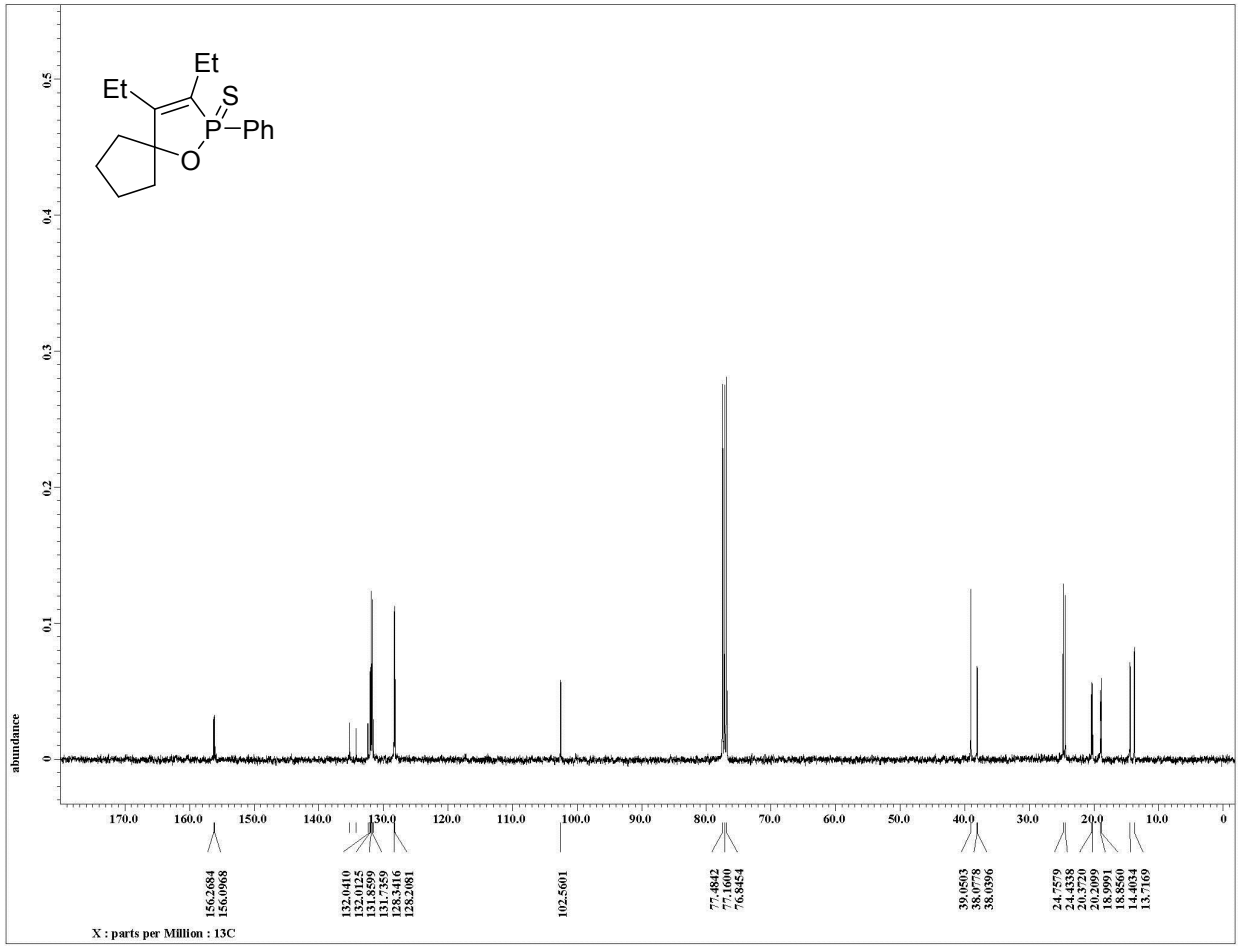
^{13}C NMR of Compound **3h**



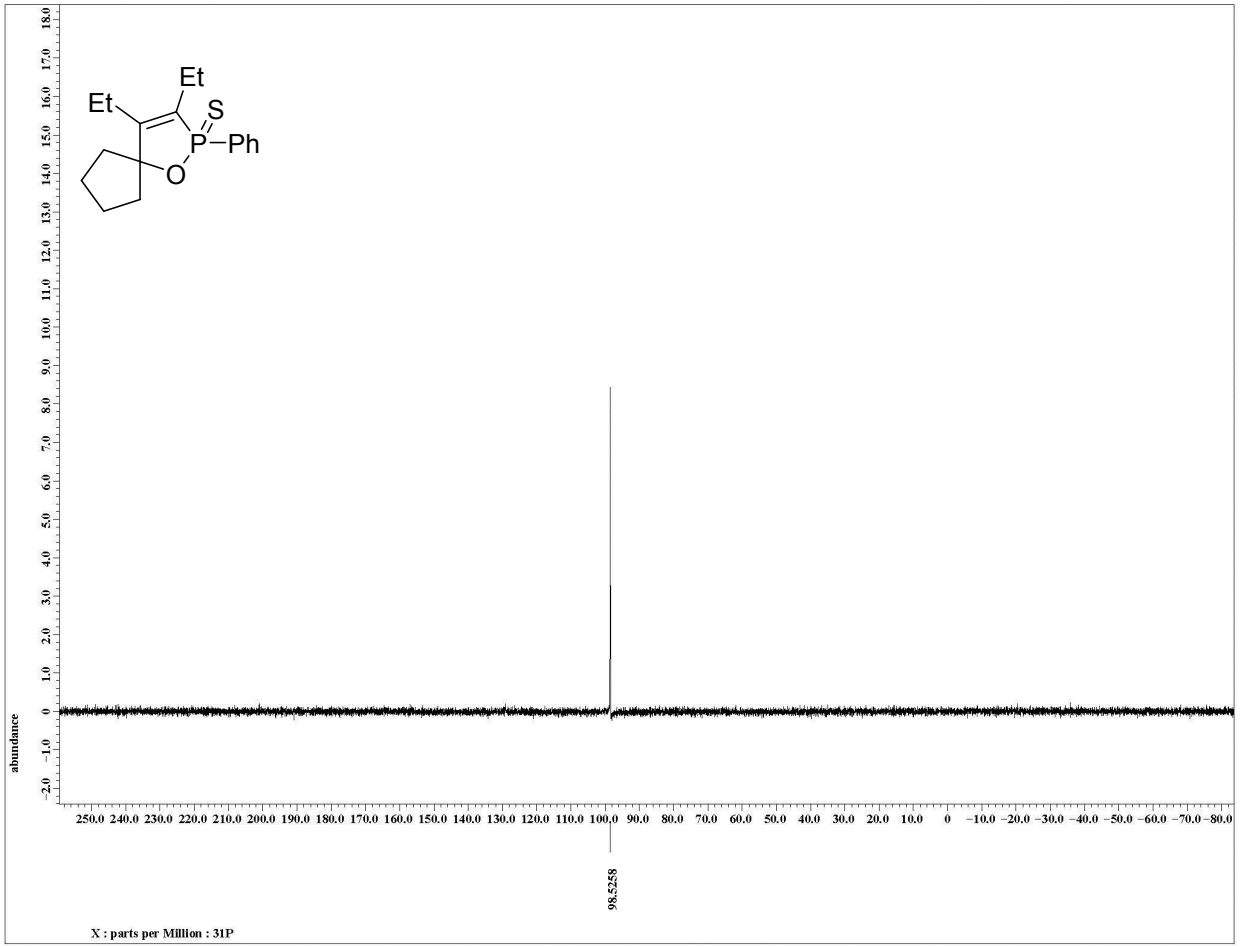
^{31}P NMR of Compound **3h**



^{1}H NMR of Compound **3j**



^{13}C NMR of Compound **3j**



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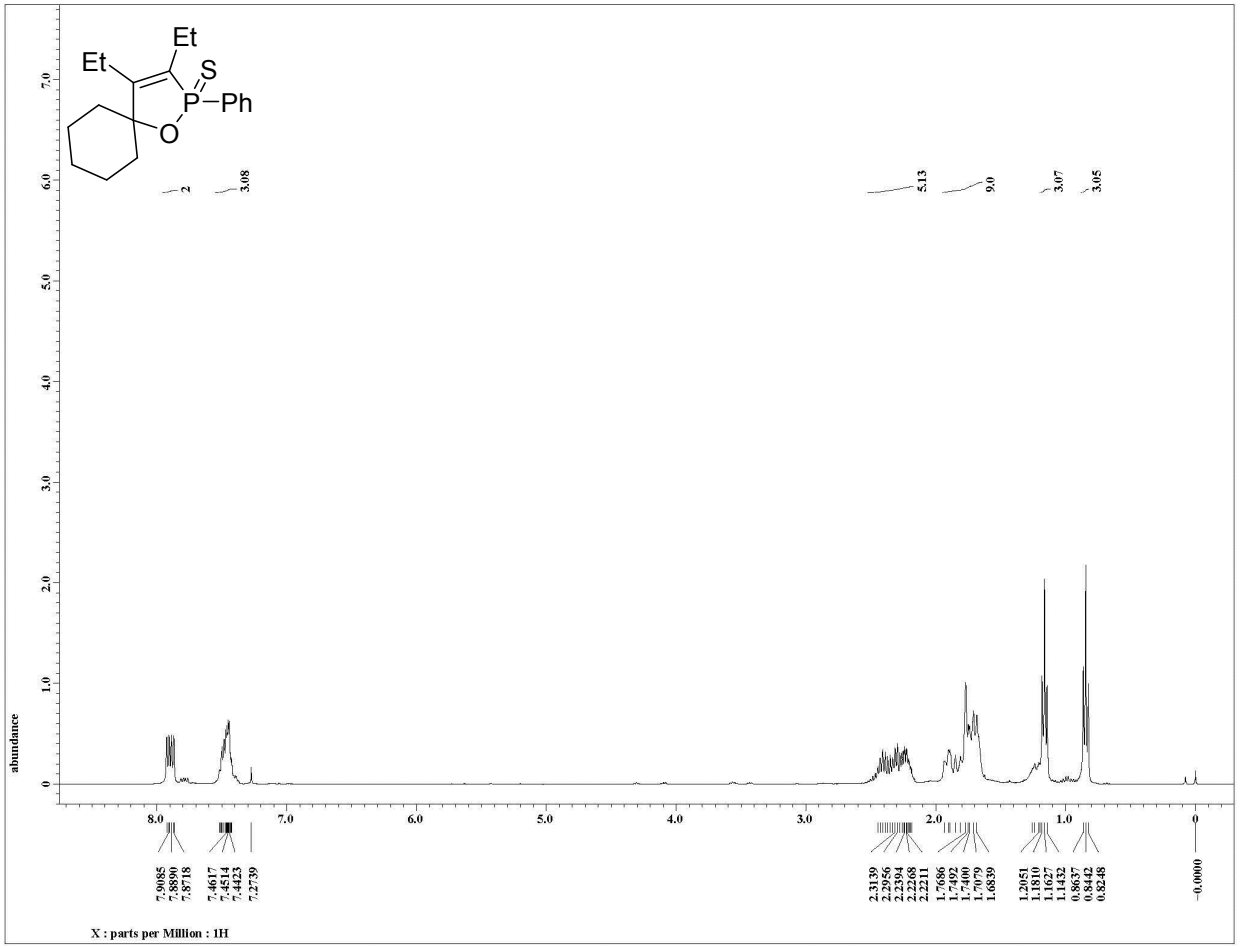
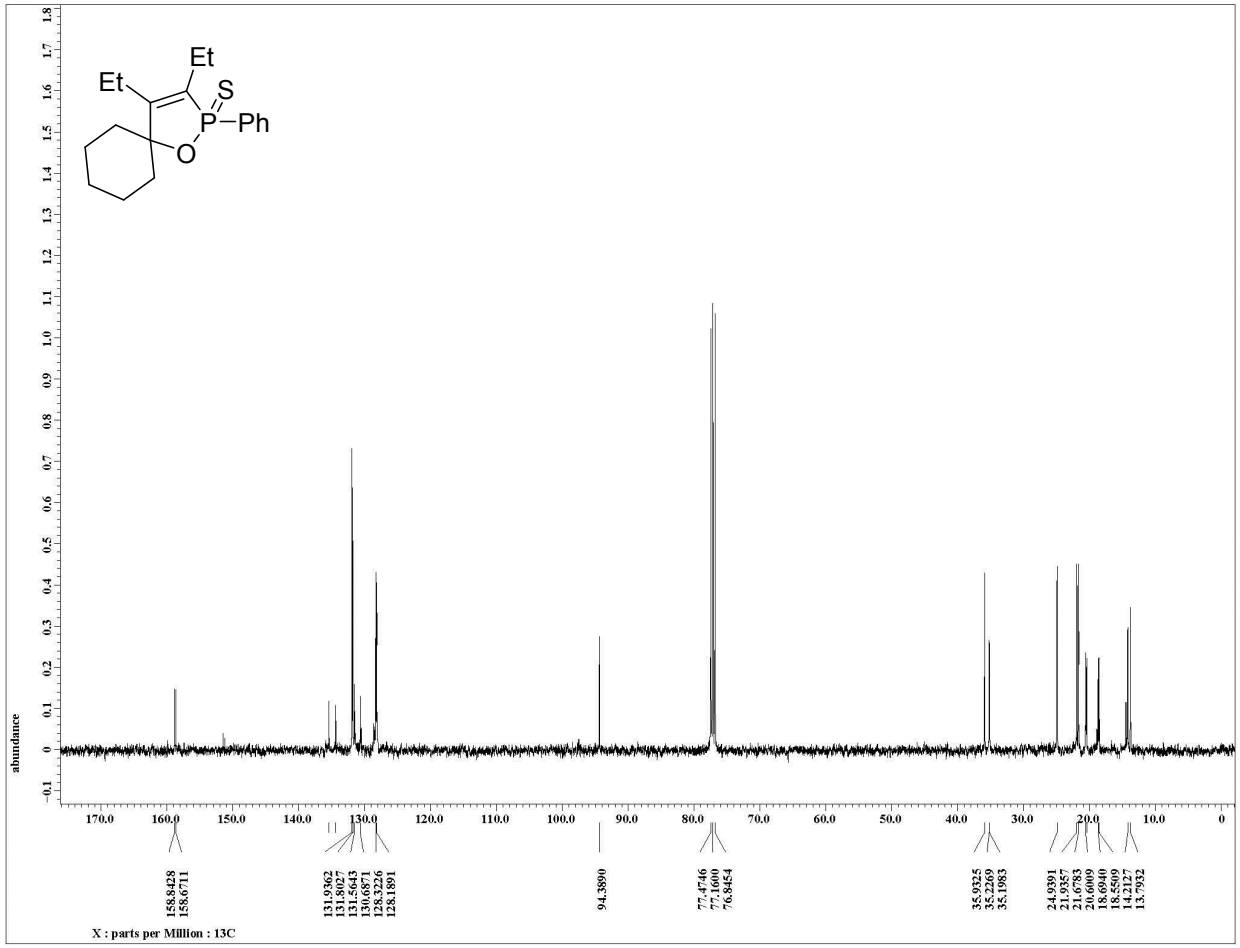


^{1}H NMR of Compound **3k**



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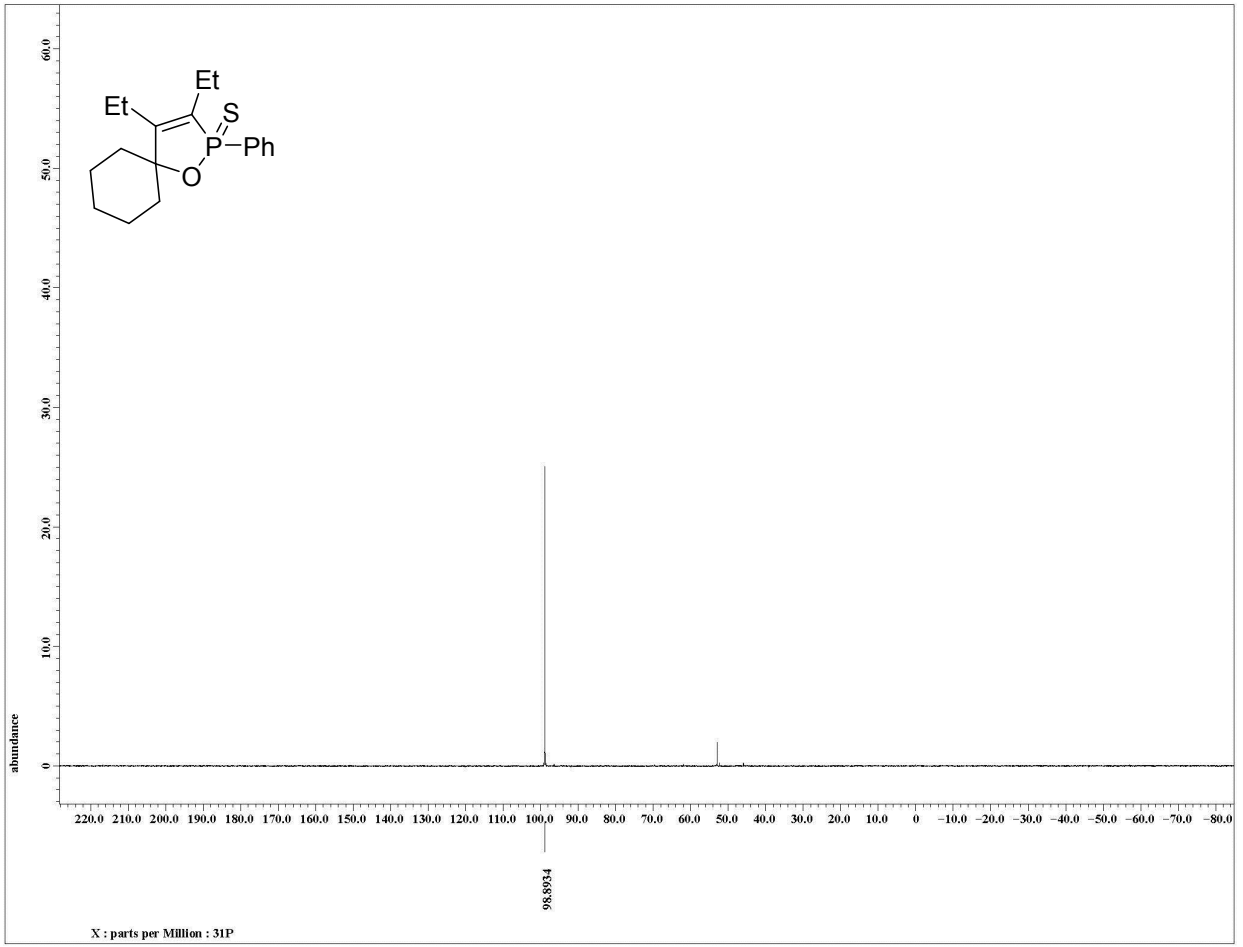
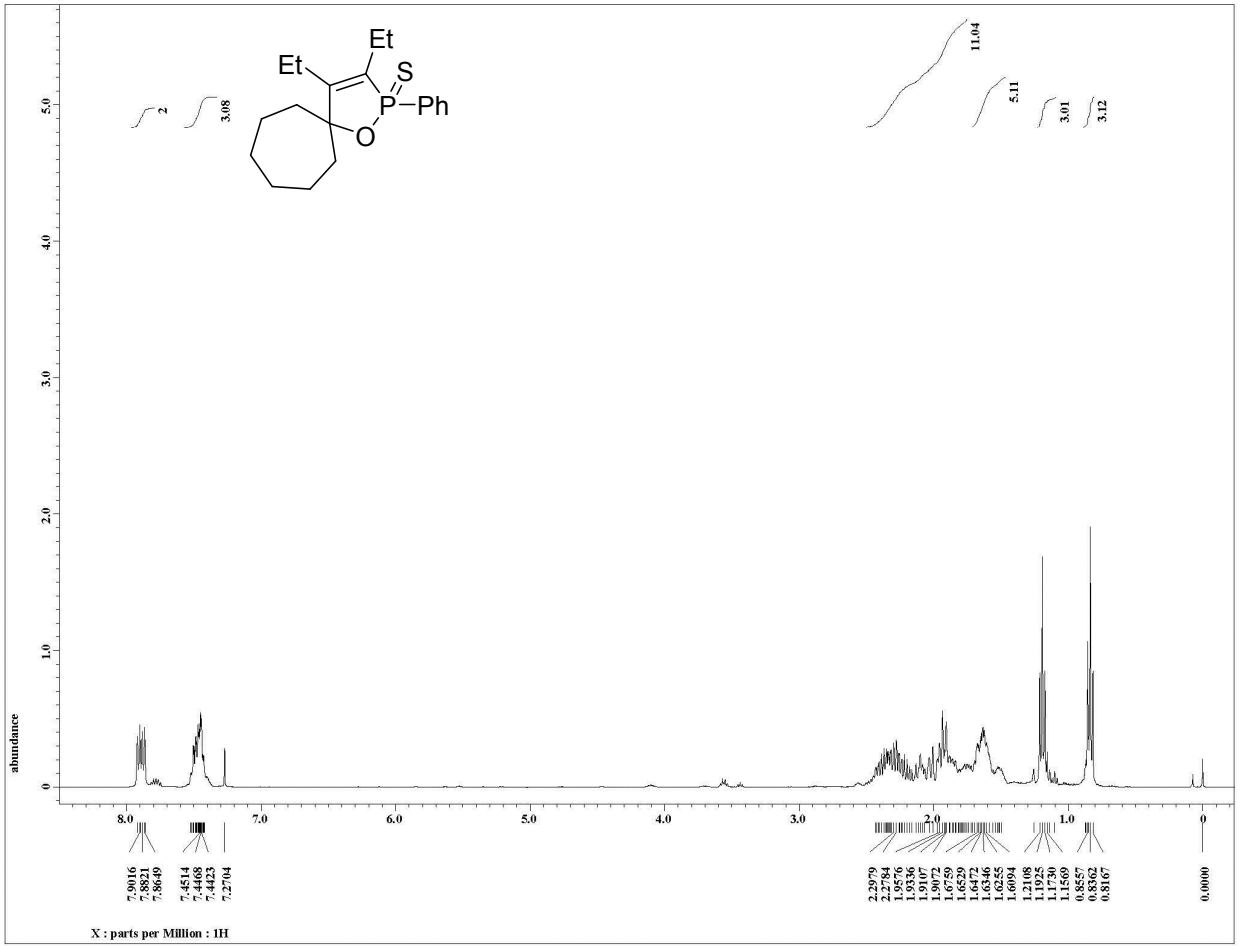
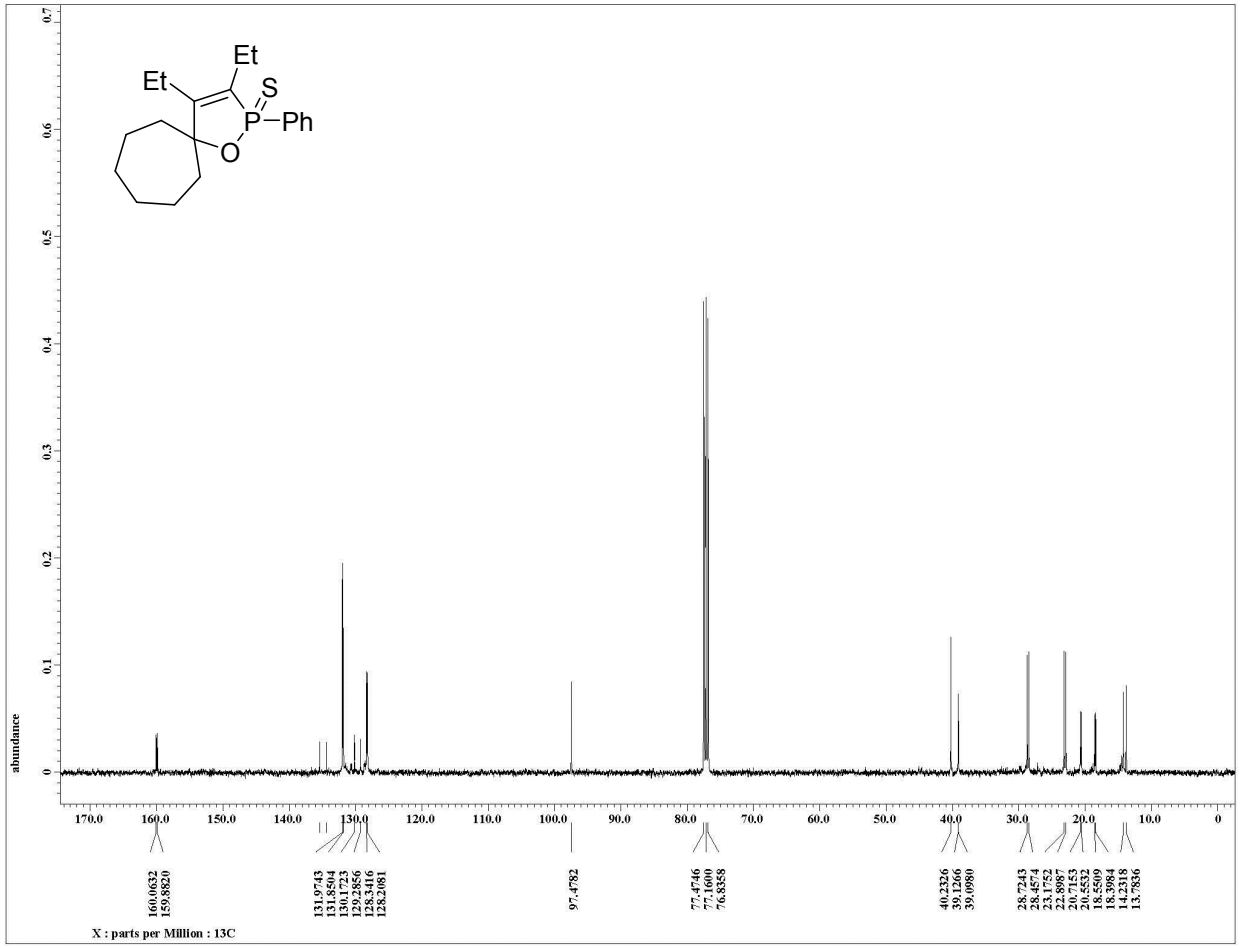


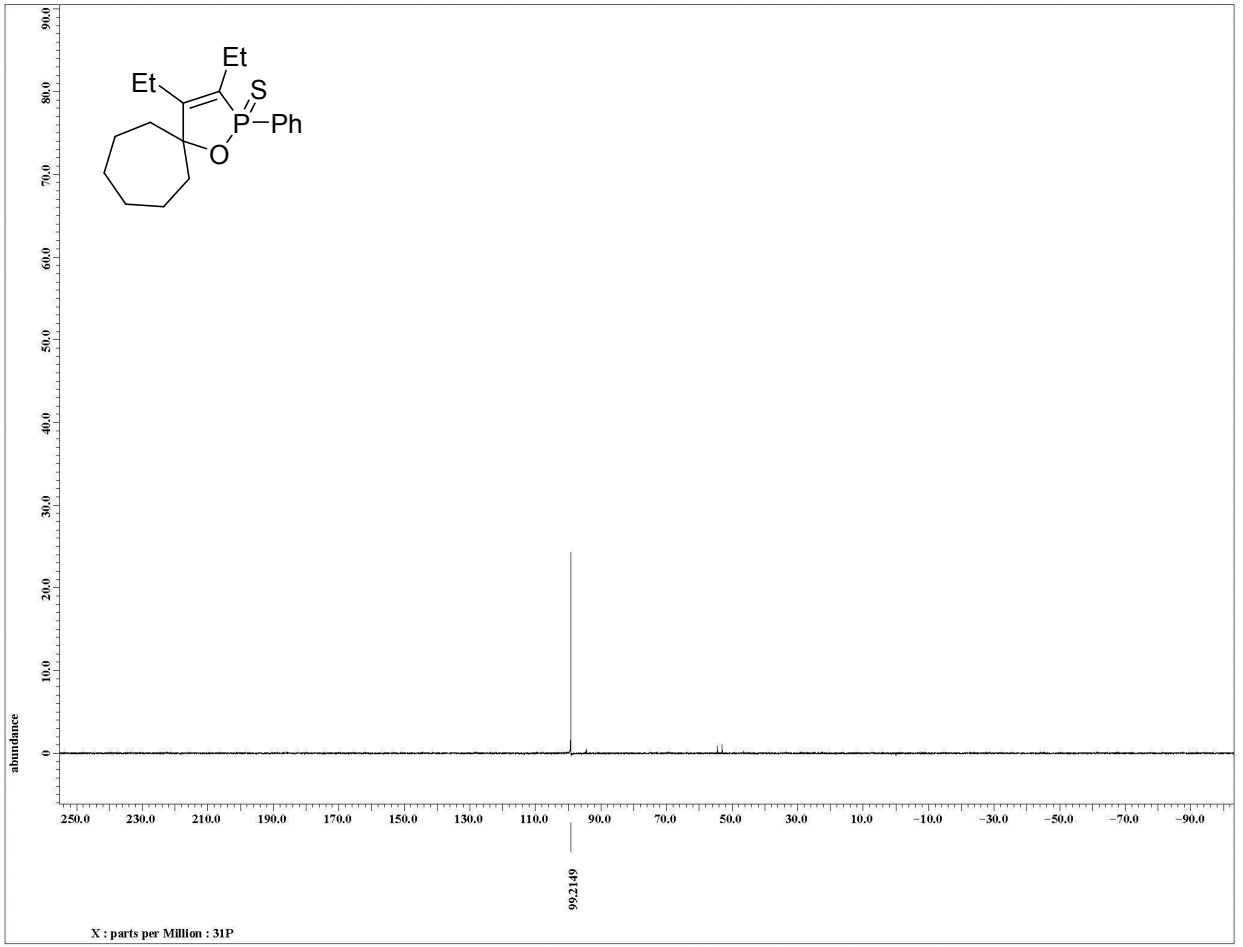
^{31}P NMR of Compound **3k**



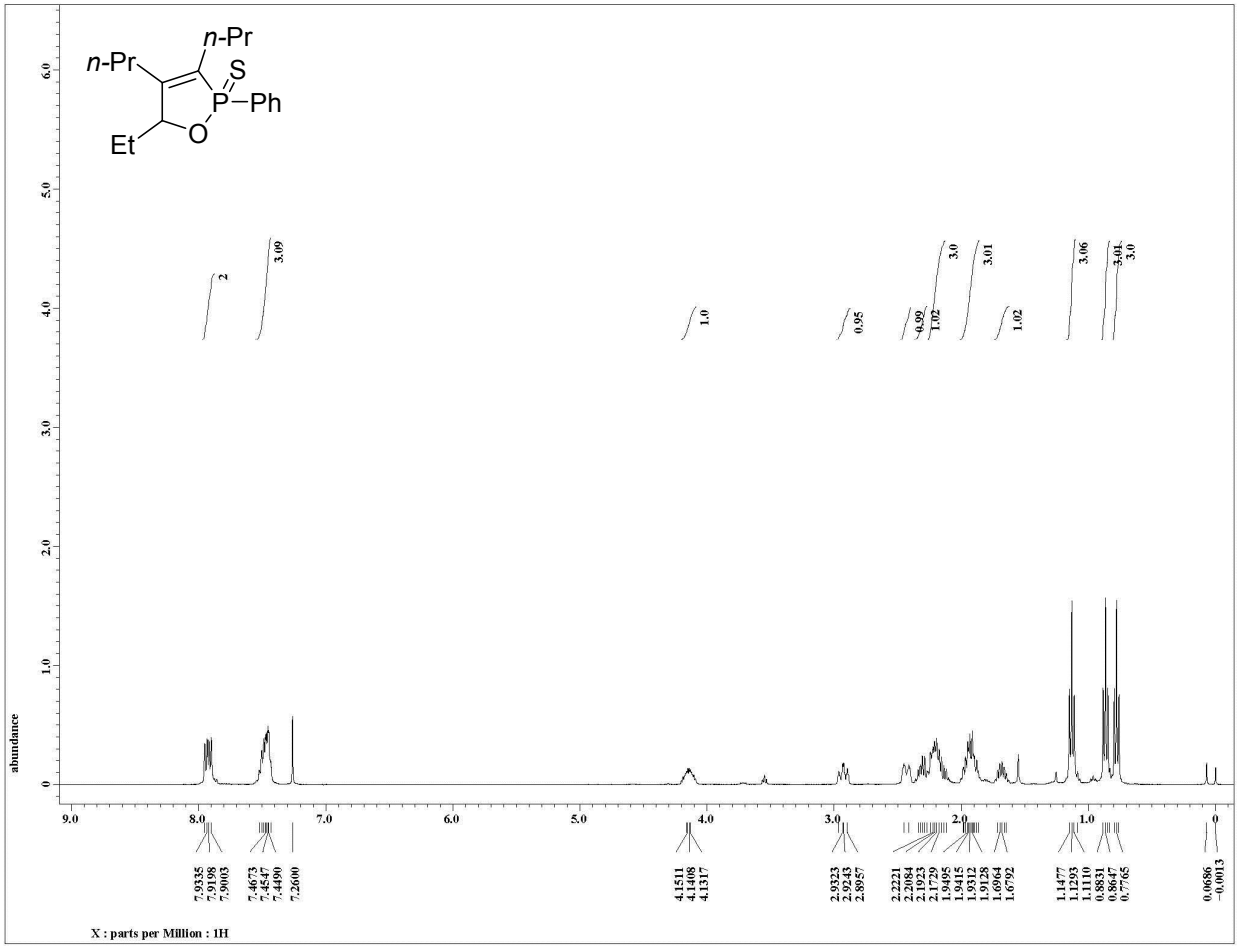
^{1}H NMR of Compound **3l**



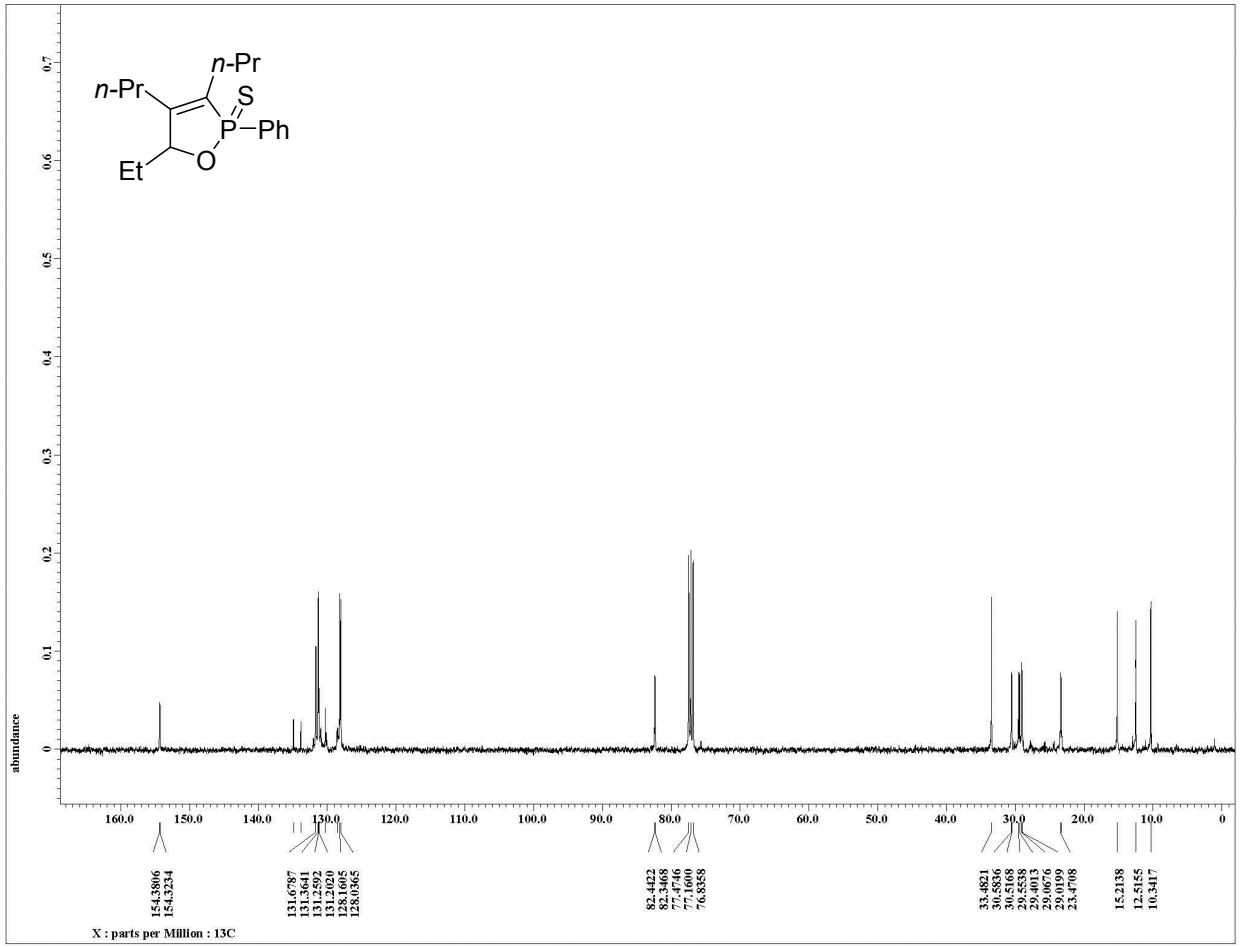
^{13}C NMR of Compound **3l**



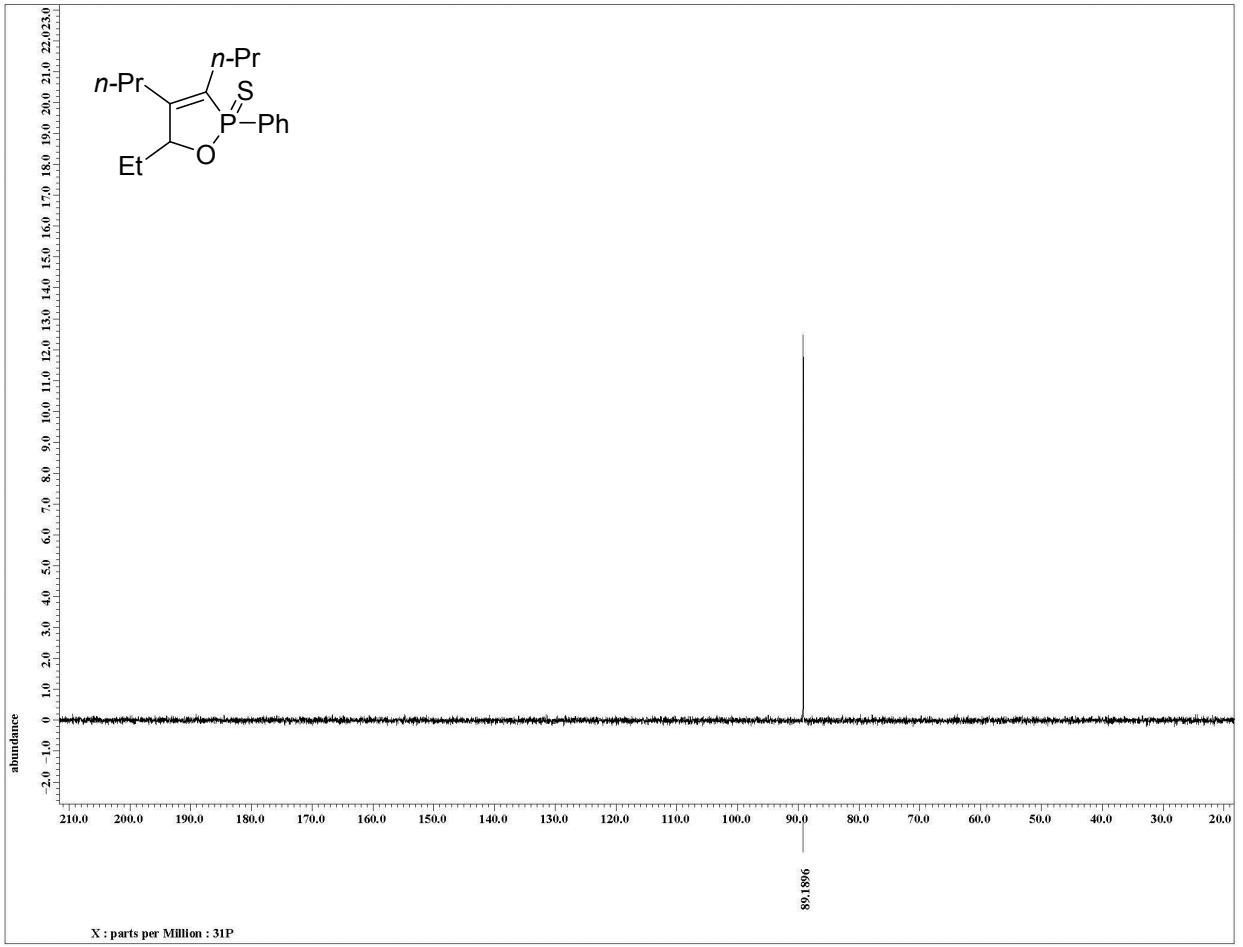
^{31}P NMR of Compound **3l**



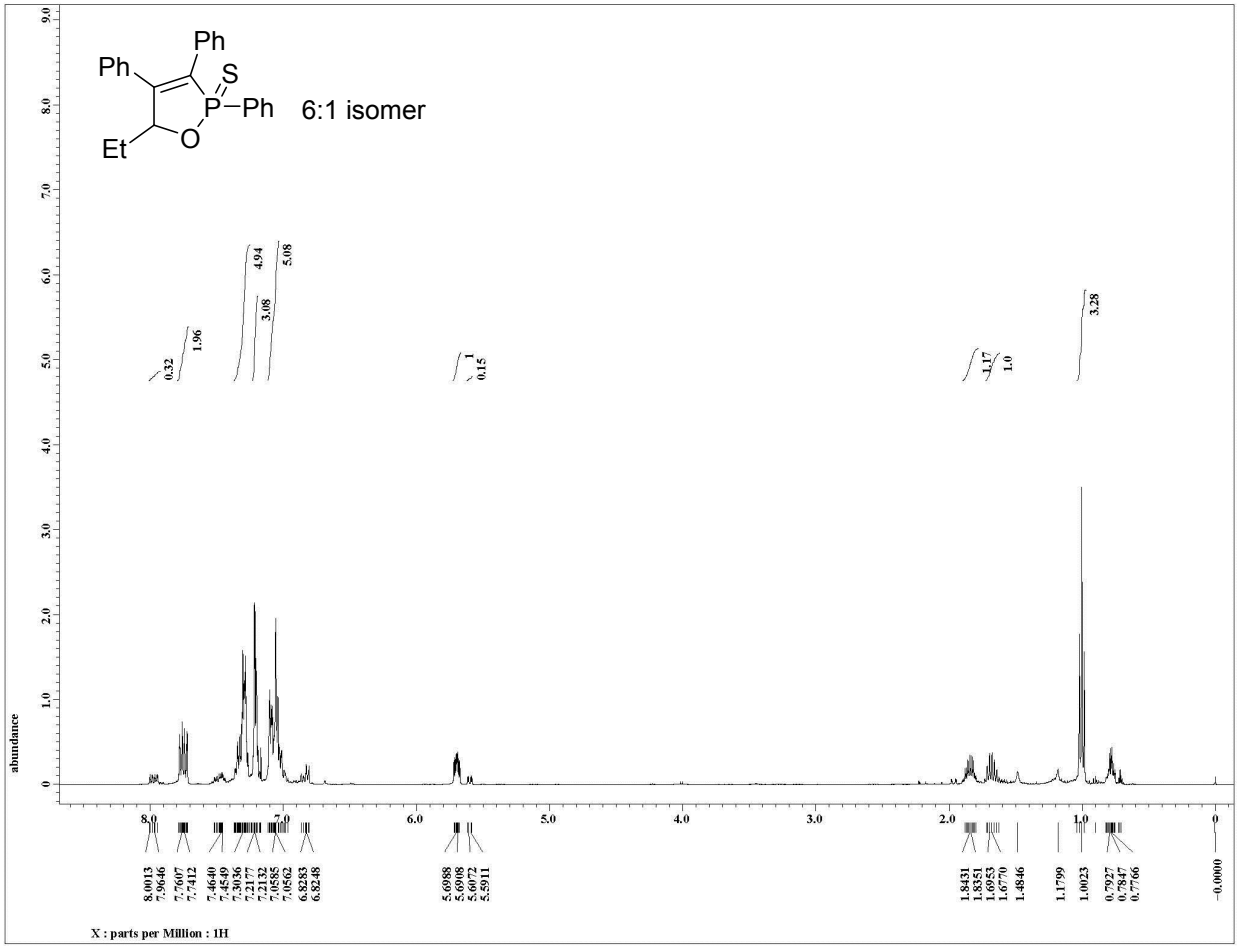
^{1}H NMR of Compound **5a**



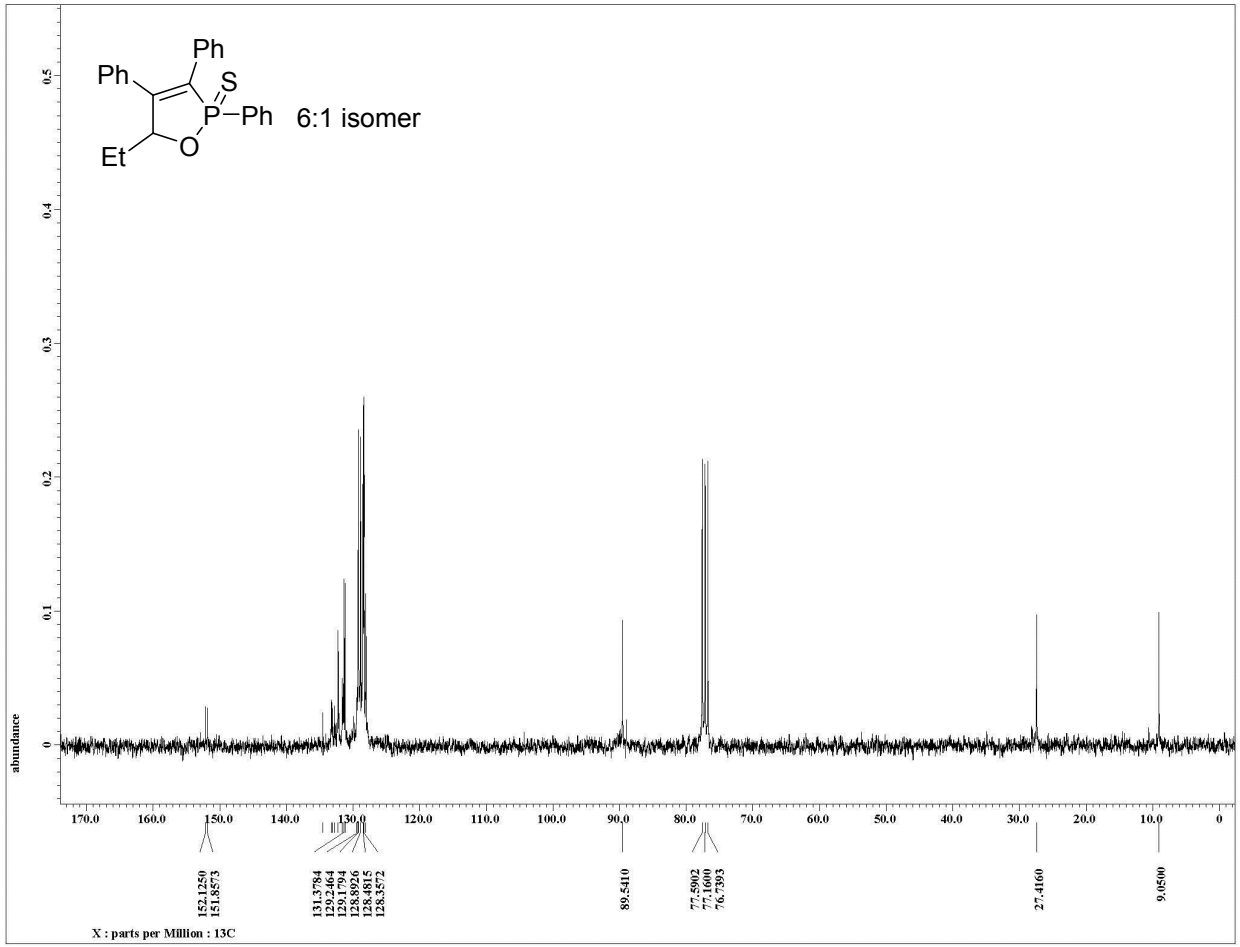
^{13}C NMR of Compound **5a**



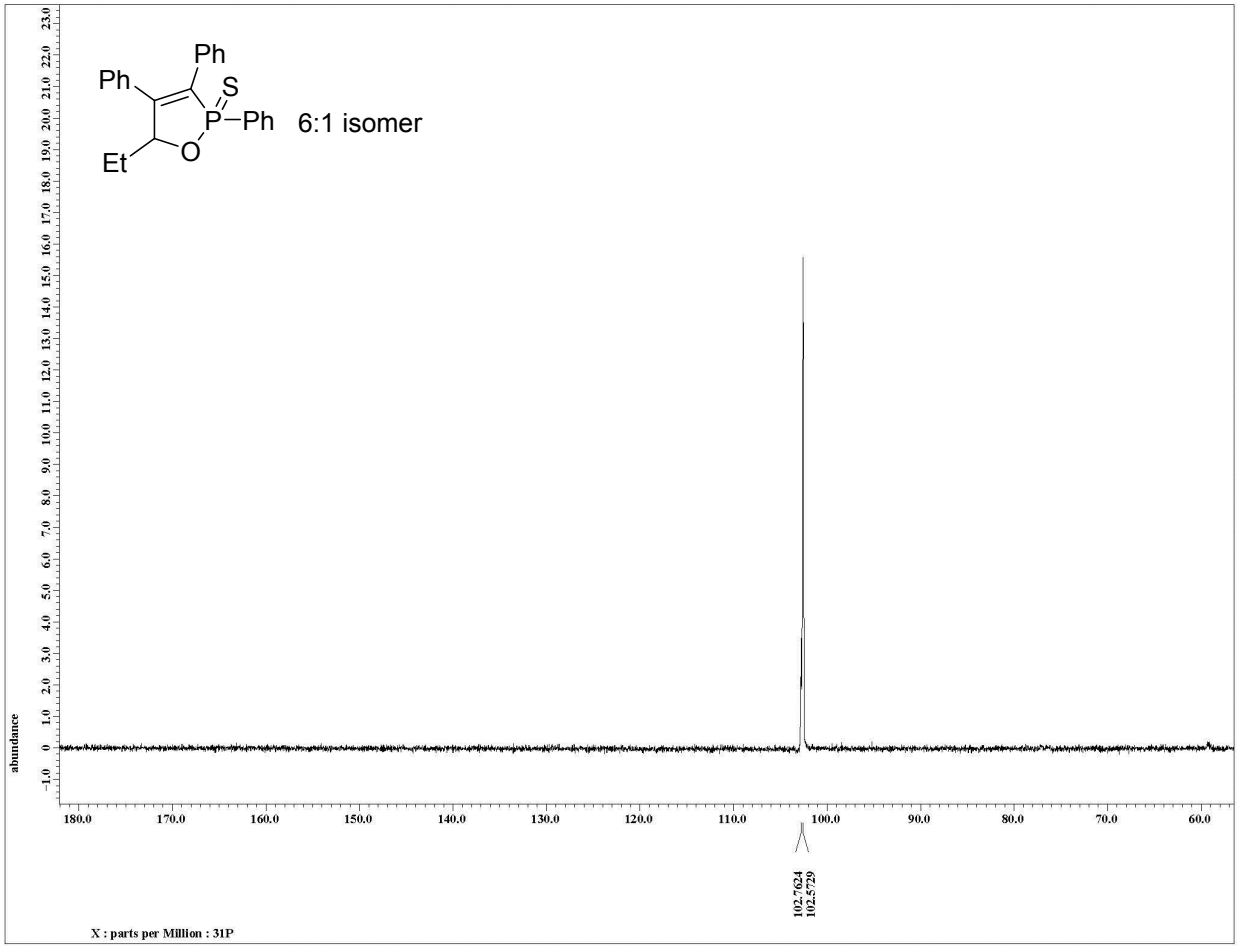
^{31}P NMR of Compound **5a**



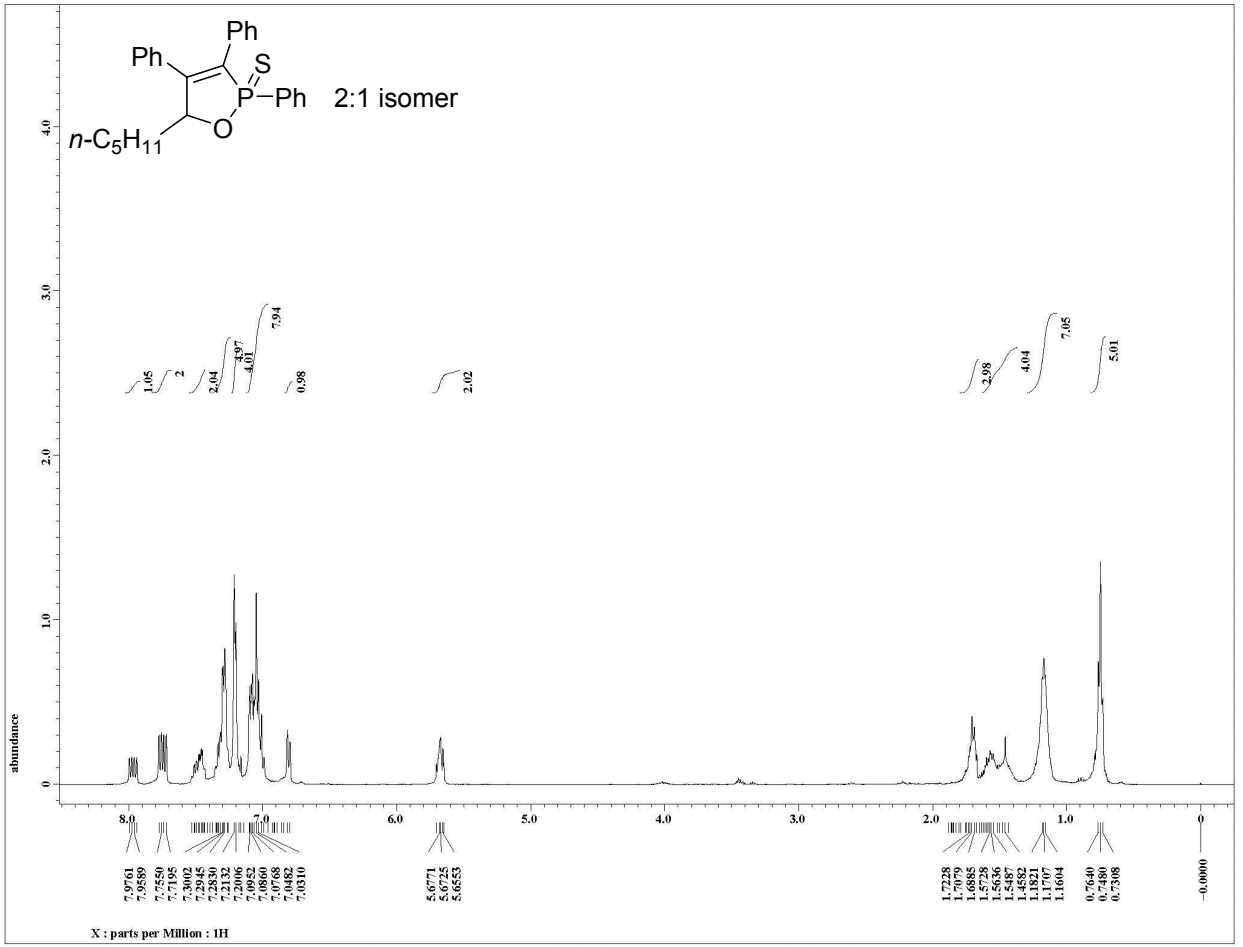
^{1}H NMR of Compound **5b**



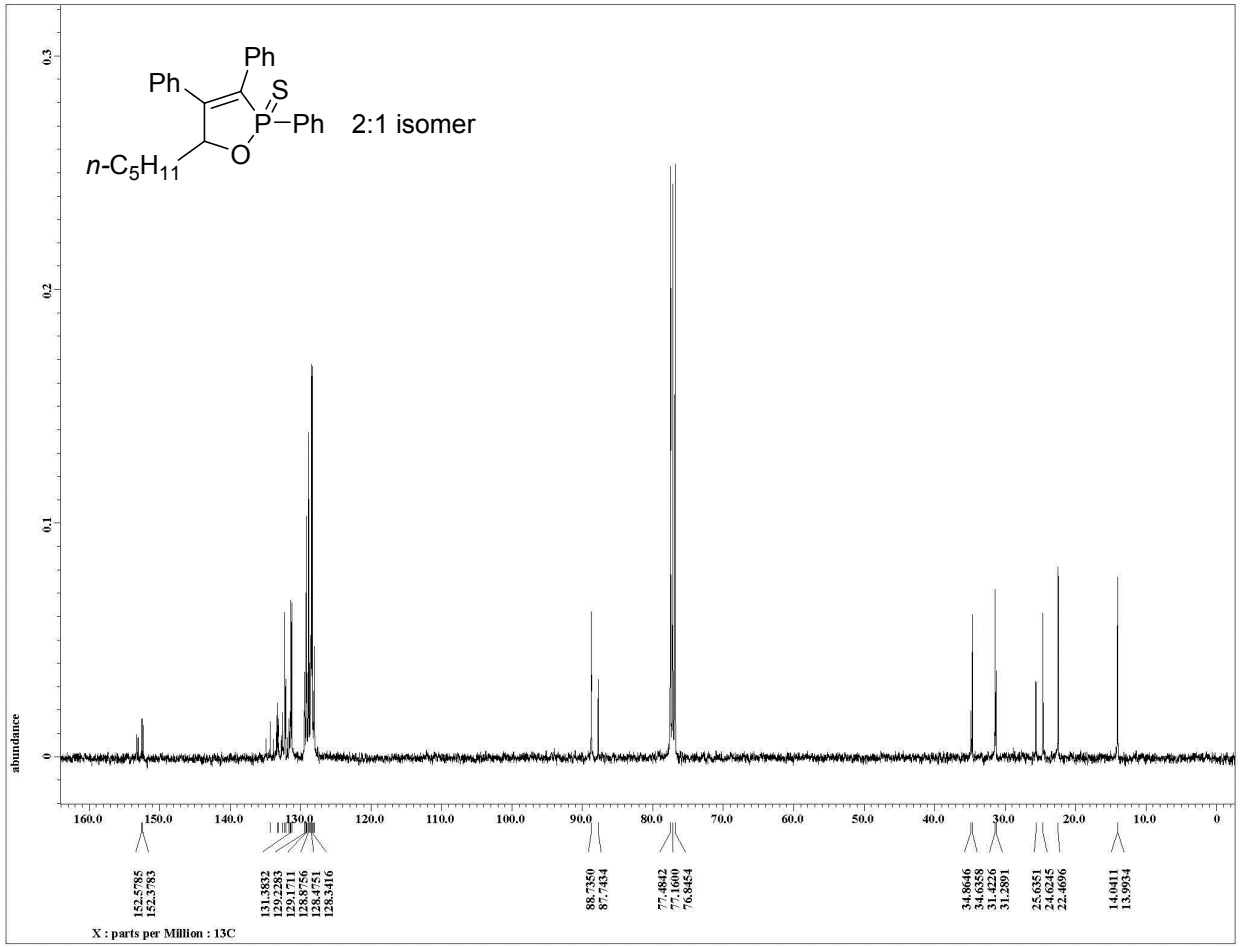
^{13}C NMR of Compound **5b**



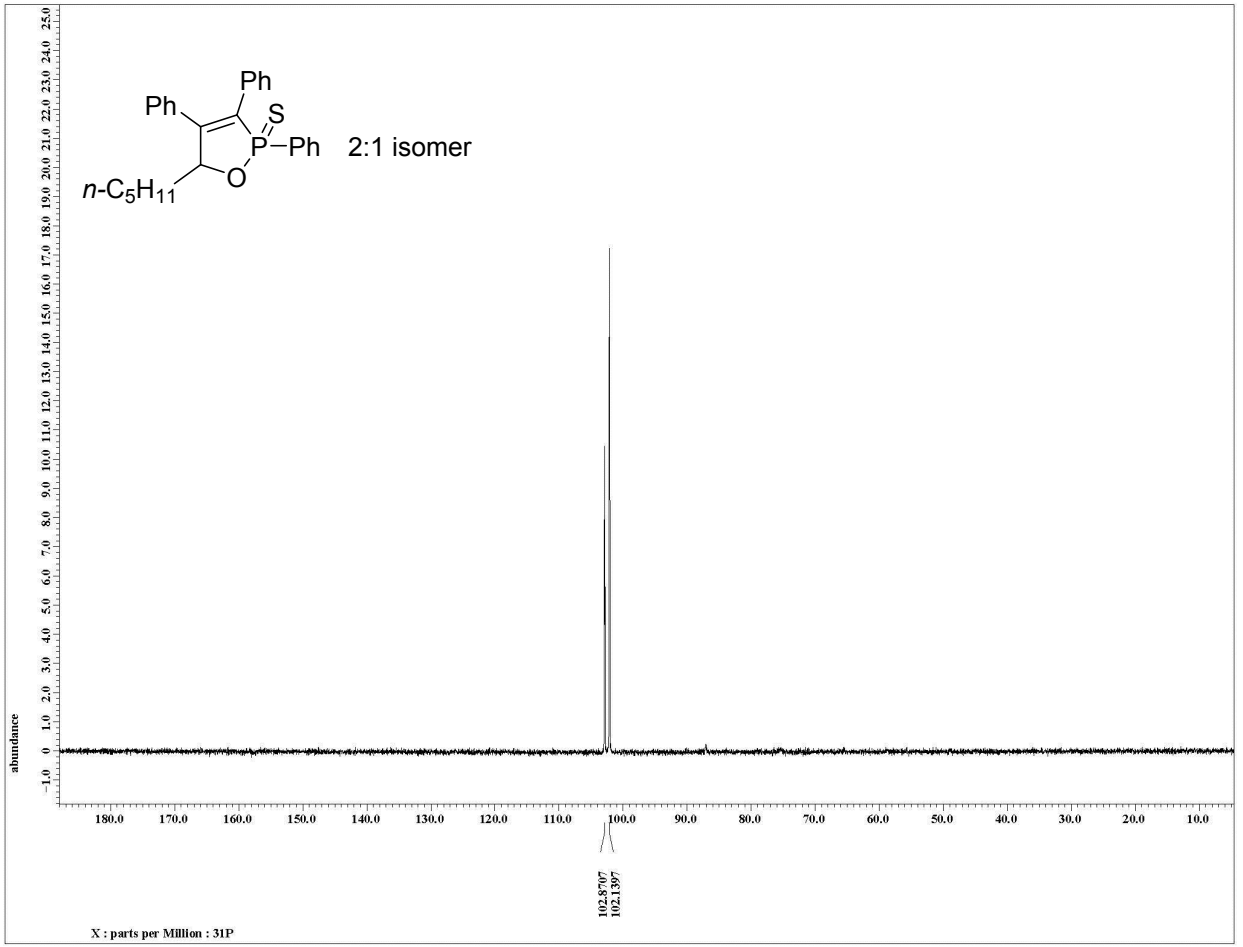
^{31}P NMR of Compound **5b**



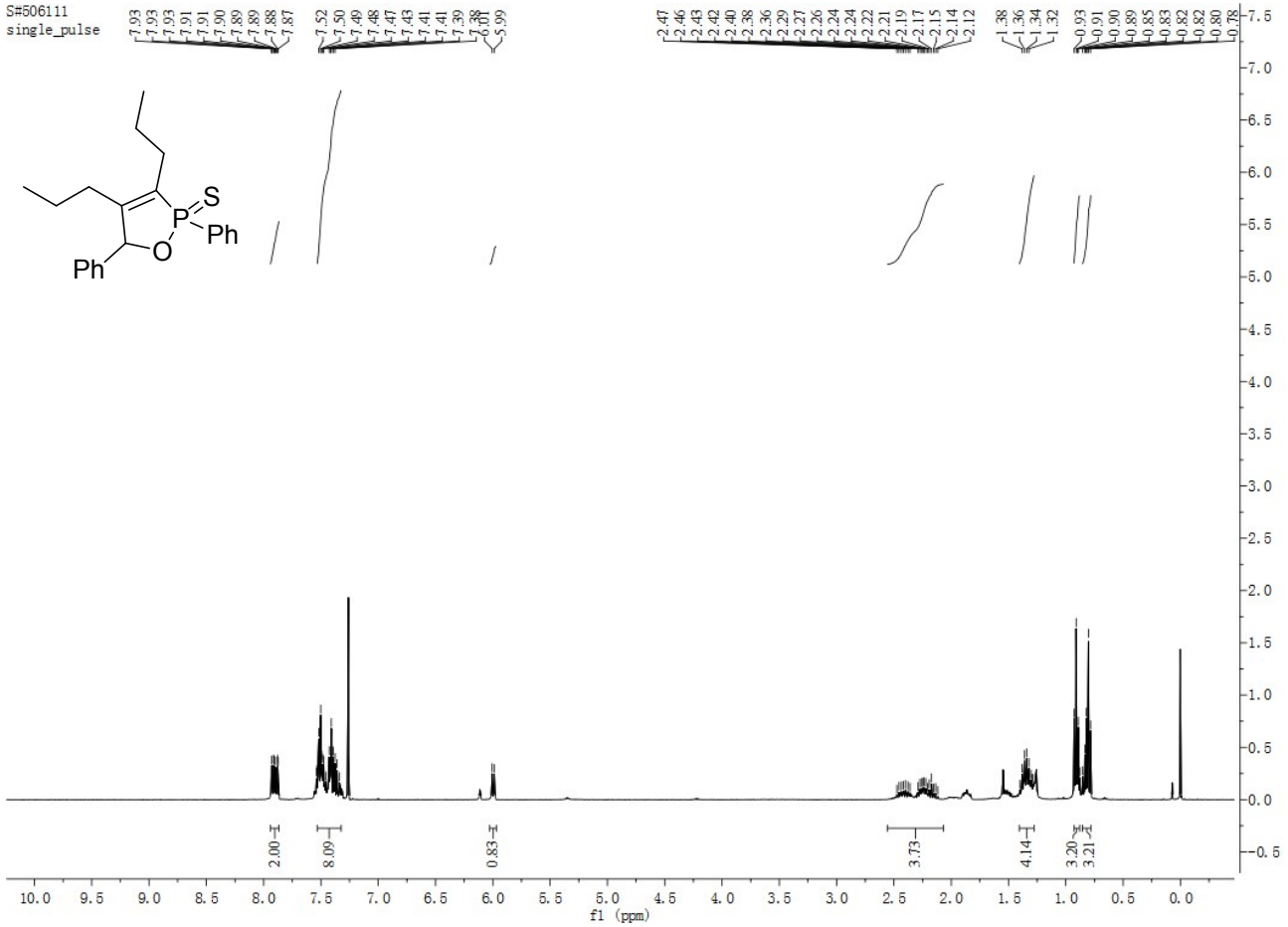
^{1}H NMR of Compound **5c**



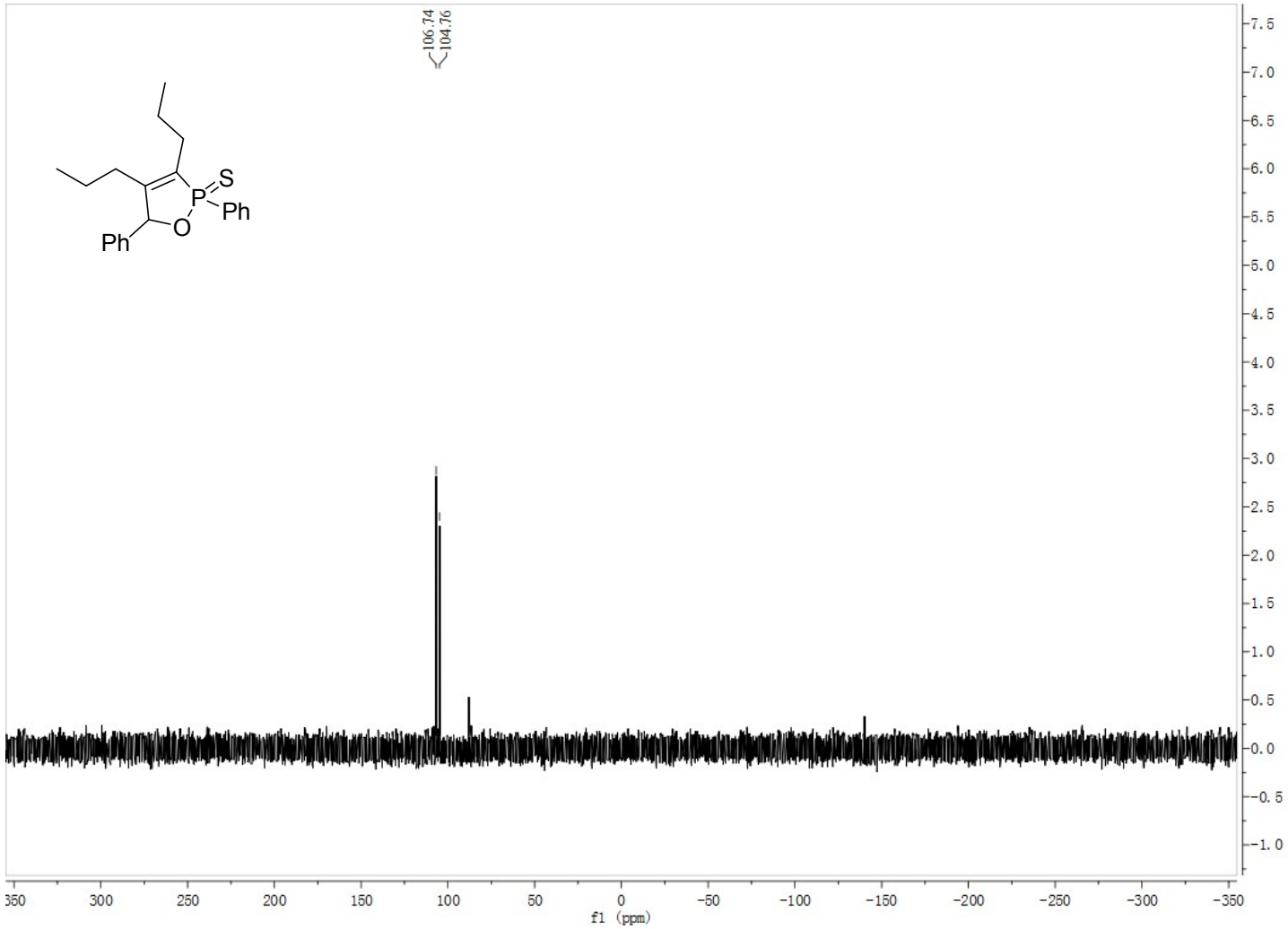
^{13}C NMR of Compound **5c**



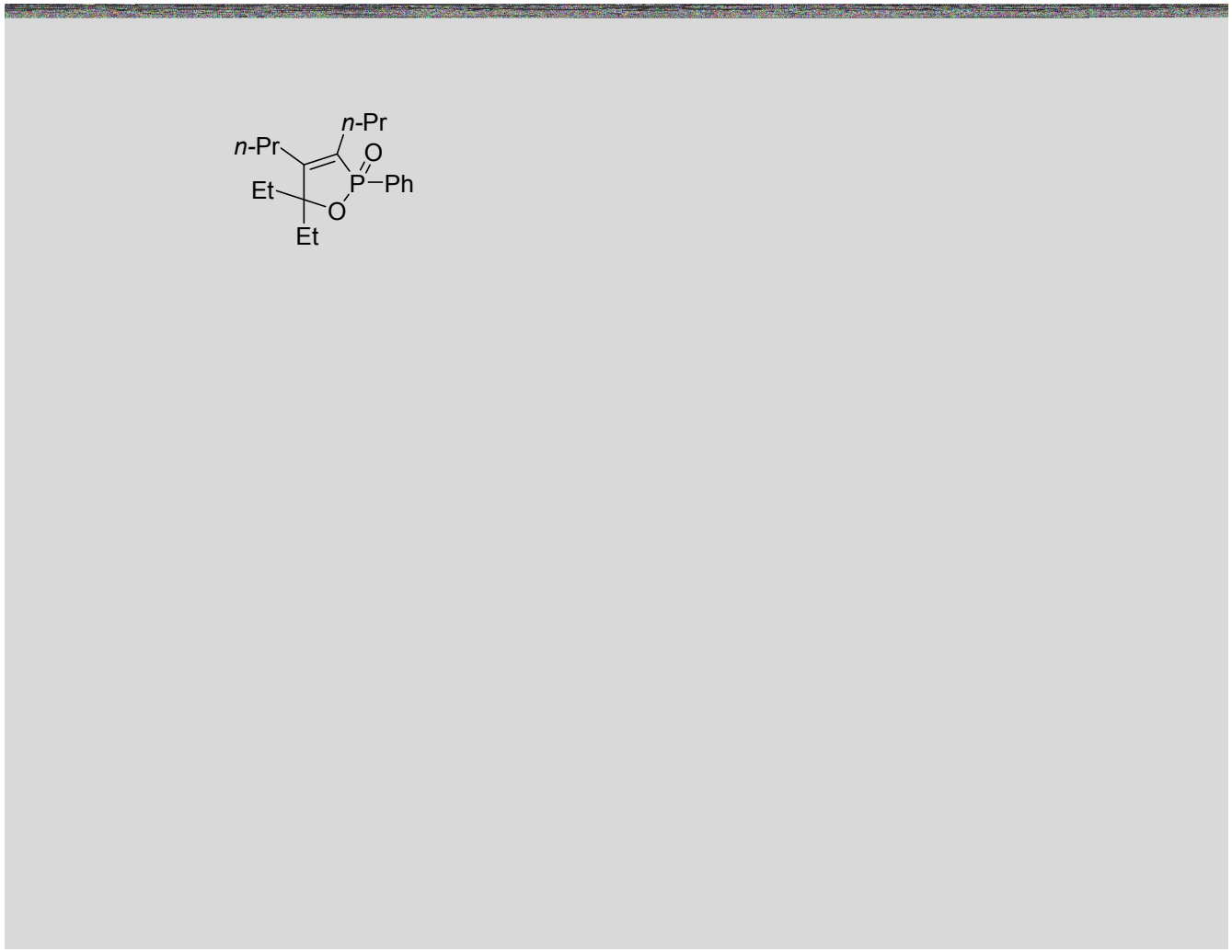
^{31}P NMR of Compound **5c**



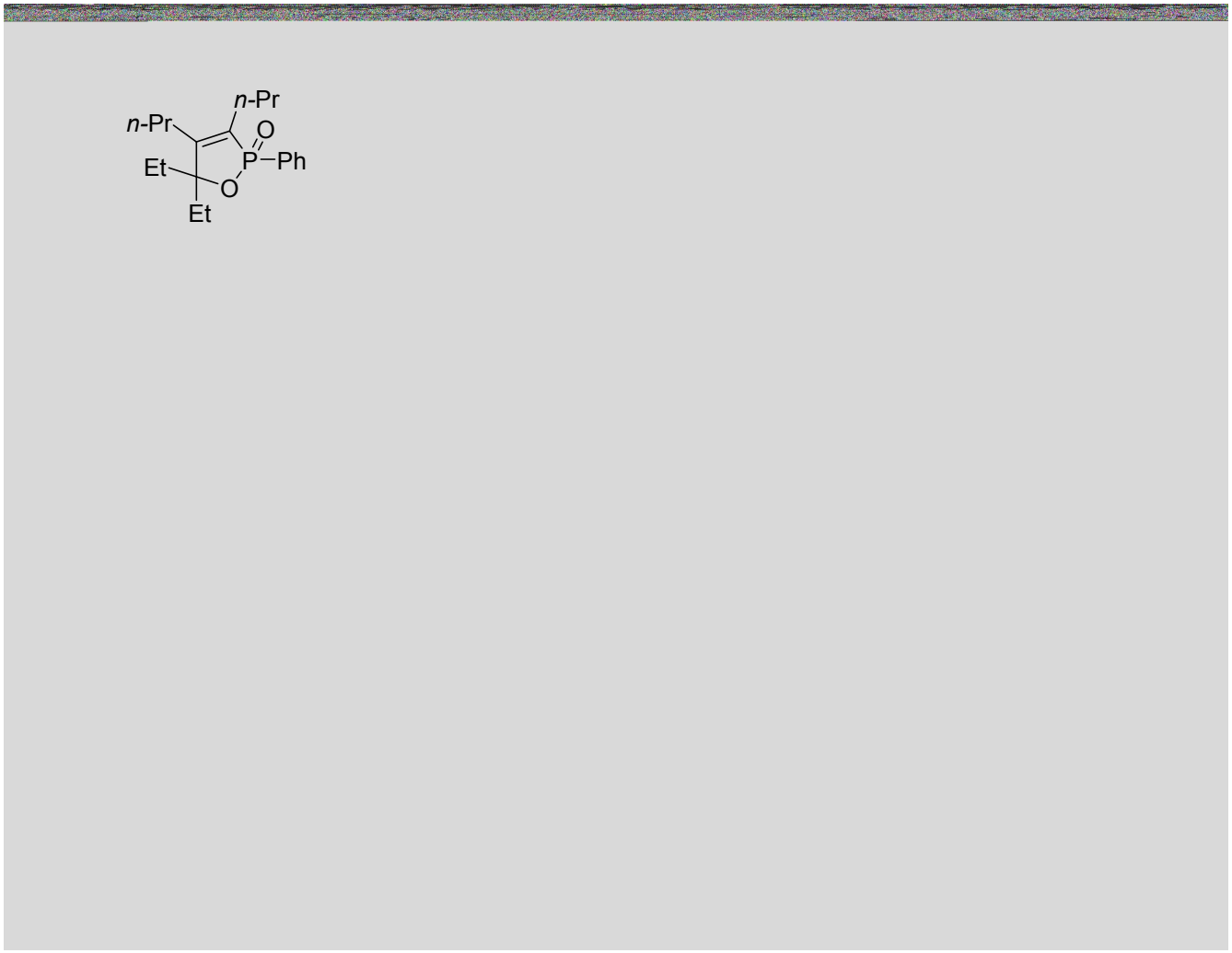
^{1}H NMR of Compound **5d**



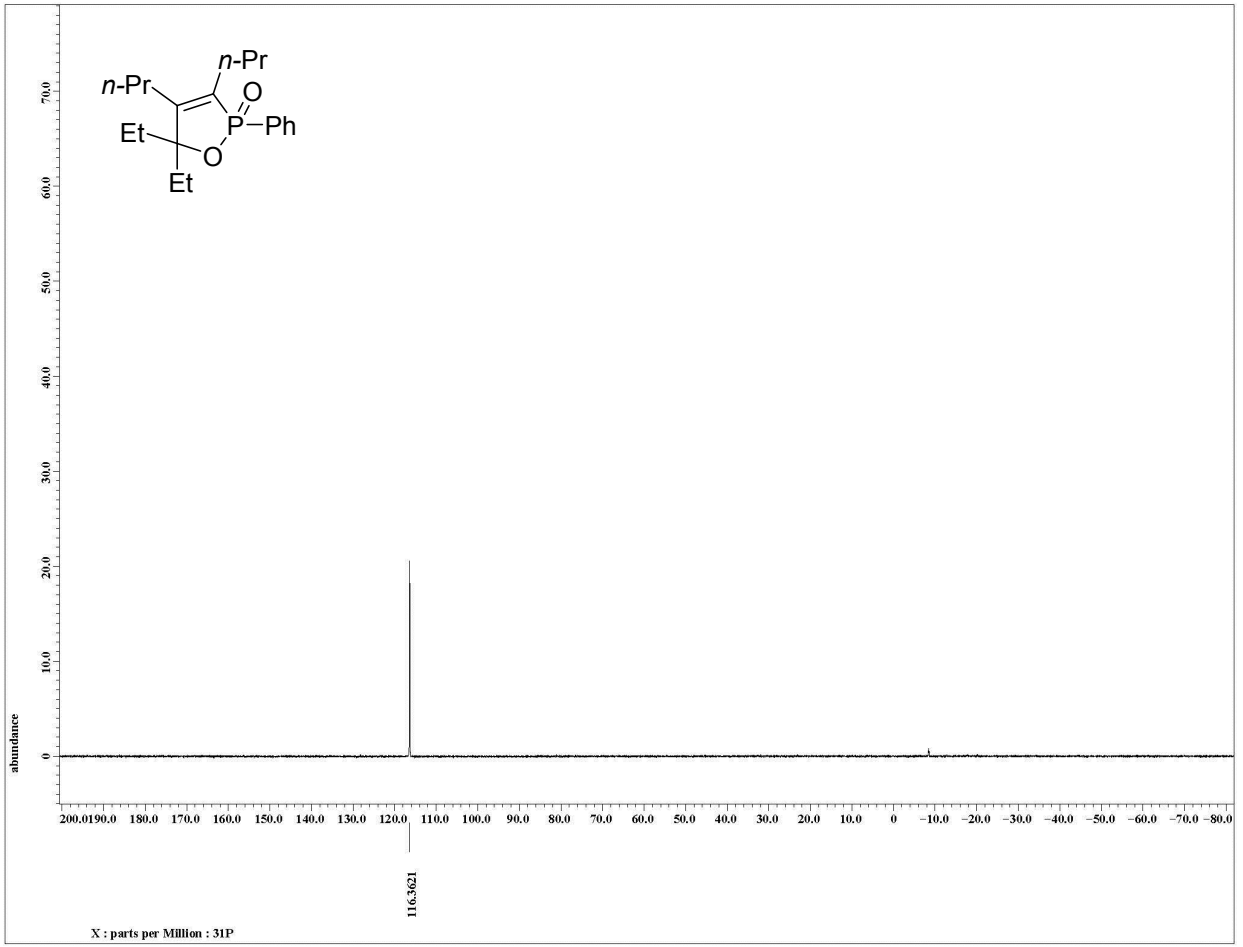
^{31}P NMR of Compound **5d**



^{1}H NMR of Compound **4a**



^{13}C NMR of Compound **4a**



^{31}P NMR of Compound **4a**