Electronic Supplementary Information

for

Synthesis of mixed phosphorotrithioates from white phosphorus

Xinlei Huangfu, Yue Zhang, Peiyun Chen, Guozhang Lu, Yinwei Cao, Guo Tang,* and Yufen Zhao

Department of Chemistry, College of Chemistry and Chemical Engineering, and the Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen, Fujian 361005, China
E-mail: t12g21@xmu.edu.cn

General Information:

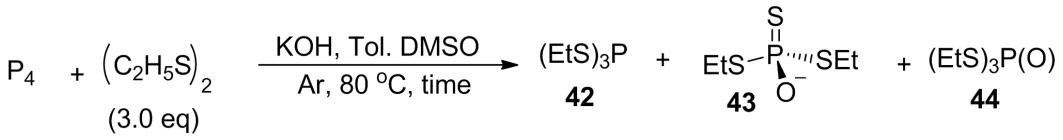
Spectroscopy data of the known compounds matches with the data reported in the corresponding references. ^{1}H, ^{13}C,^{31}P and ^{19}F NMR spectra were recorded on a Bruker Av400 spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as the internal standard for ^{1}H, and ^{13}C NMR (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.23 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, quint = quintet, m = multiplet), coupling constants in Hertz (Hz), integration. The products were purified by Column chromatography on silica gel 300 ─ 400 mesh. All products were further characterized by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

Experimental Section

Safety note for P_4: White phosphorus is spontaneously flammable; it should be stored in water or glove box. On the other hand, white phosphorus is soluble in toluene.

Preparation of P_4-toluene solution: A piece of white phosphorus was taken out of water and then put in ethanol under argon. One minute later, white phosphorus was taken out and the surface ethanol was blowed off with argon. Then, the dry white phosphorus was put in a round bottomed flask containing toluene. White phosphorus-toluene solution prepared with 0.1 mol/L (12.4 g/L) should be sealed in argon and stored away from light.

Formation of salt 43 monitored by ^{31}P NMR spectroscopy and HRMS



	42	43	44
5 min	90%	4%	5%
15 min	16%	72%	6%
45 min	0	98%	0

Fig. 1 The starting P_4 showed signal in the ^{31}P NMR spectrum at δ = -519 ppm.

Fig. 2 $(C_2H_5S)_2$ (3.0 equiv) and KOH were added to the solution of P_4, the reaction was conducted under standard conditions; the expected phosphorotrithioites [P(III), **42**] was produced (δ = 118 ppm) in 5 minutes and P_4 disappeared completely. In the meantime, there are two obvious peaks (δ = 75 and 63 ppm) that appeared. The signals at δ = 75 and δ = 63 ppm belong to salt **43** and phosphorotrithioate [P(V), **44**], respectively. Furthermore, two new weak peaks at 173 ppm and 180 ppm emerged. The signals at δ = 173 and 180 ppm may belong to $(C_2H_5S)_4P^+SC_2H_5^-$ and $(C_2H_5S)_4P^+OH^-$ species.

Fig. 3, **Fig. 4**, and **Fig. 5** As time progressed, the ^{31}P NMR signals of **42** and **44** disappeared gradually and the signal of salt **43** (δ = 75 ppm) increased. The reaction was almost complete after 45 min according to the ^{31}P NMR spectra.

Fig. 6, **Fig. 7**, and **Fig. 8** The reaction was conducted under standard conditions for 10 min. The reaction mixture was monitored by HRMS (FT-ICR-MS) and an electrospray ionization source in positive-ion mode.

P_4-Toluene:

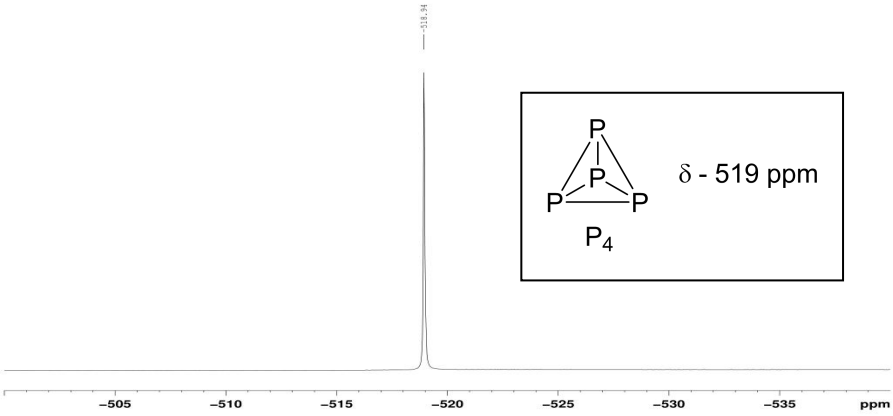


Fig. 1

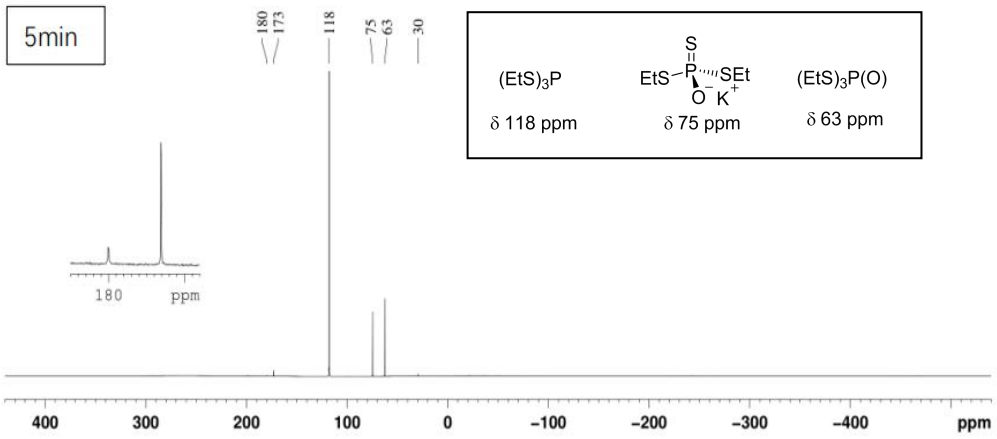


Fig. 2

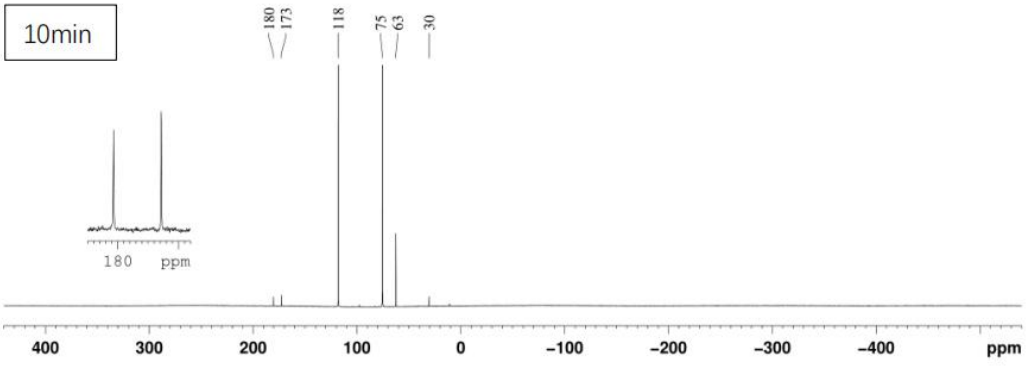


Fig. 3

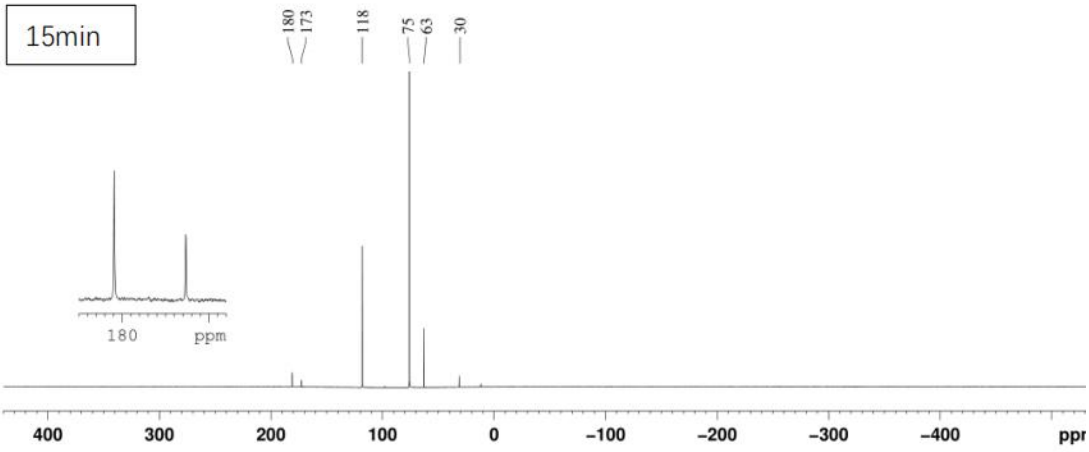

15min
180
173
118
75
63
30
180 ppm
400 300 200 100 0 −100 −200 −300 −400 ppm

Fig. 4

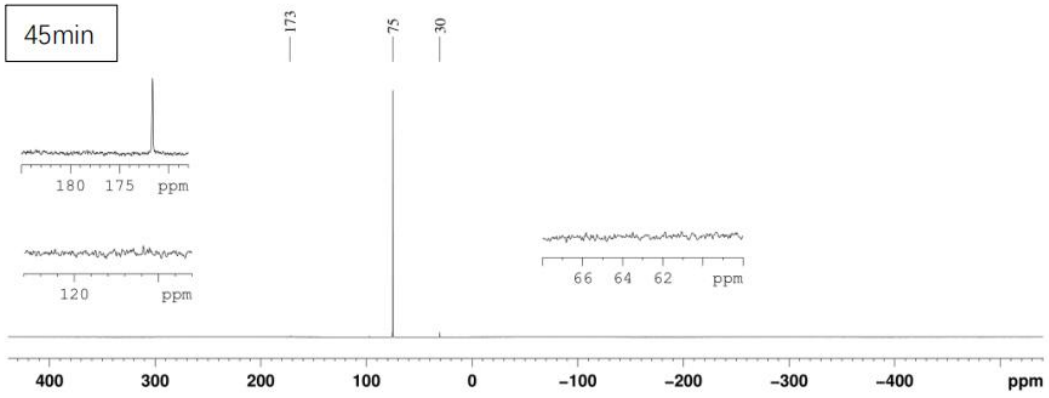
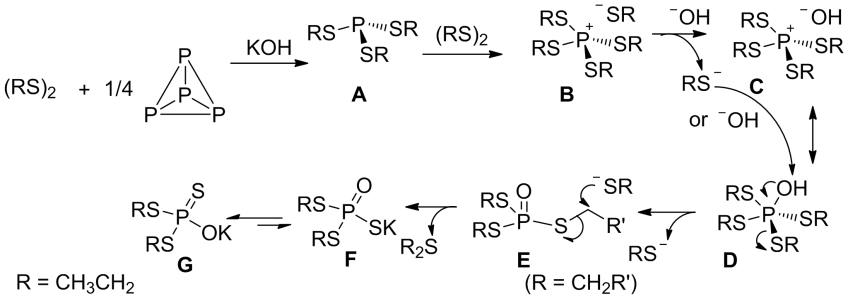

45min
173
75
30
180 175 ppm
120 ppm
66 64 62 ppm
400 300 200 100 0 −100 −200 −300 −400 ppm

Fig. 5

Reaction mechanism



Intermediate A (Compound 42) in reaction mechanism

HRMS calcd for $C_6H_{16}PS_3[M+H]^+$ 215.0146, found 215.0146.

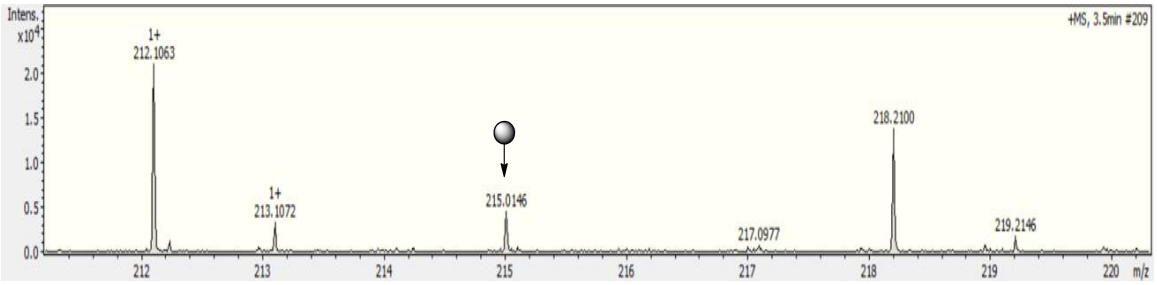


Fig. 6

Intermediate B or C in reaction mechanism

HRMS calcd for $C_8H_{20}PS_4^+$ $[M]^+$ 275.0180, found 275.0180.

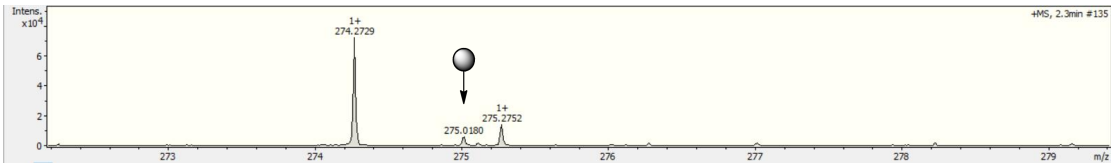


Fig. 7

Intermediate E (Compound 44) in reaction mechanism

HRMS calcd for $C_6H_{16}POS_3[M+H]^+$ 231.0095, found 231.0091, $C_6H_{15}POS_3Na[M+Na]^+$ 252.9915, found 252.9908.

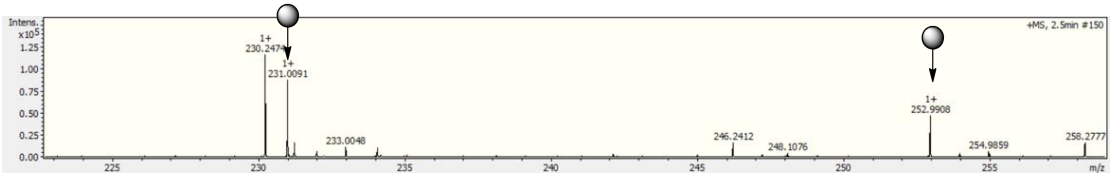
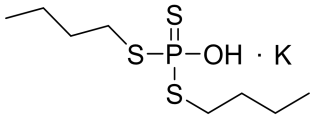


Fig. 8

Intermediate F or G (Compound 3) in reaction mechanism

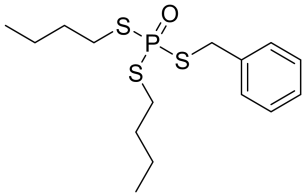
Phosphorotrithioic acid, *S*,*S*-dibutyl ester, potassium salt (**3, *CAS*** no. 1217597-47-1)



^{1}H NMR (400 MHz, $CDCl_3$): δ 2.89 (m, 4H), 1.67 (quint, *J* = 7.6 Hz, 4H), 1.42 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 35.6 (d, *J* = 3.2 Hz), 32.1 (d, *J* = 5.8 Hz), 22.3, 13.9. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 85.39. **ESI-MS** calcd for $C_9H_{23}OPS_3[M-H]^-$ 257.02, found 257.00.

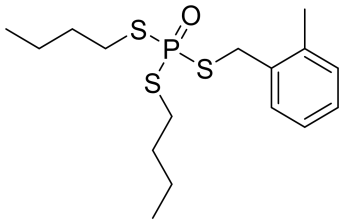
Spectral data

S-benzyl *S*,*S*-dibutyl phosphorotrithioate(**4**, ***CAS*** no.31173-07-6)



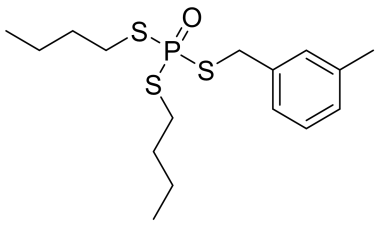
Colorless oil. Yield: 95% (From RCl); Yield: 95% (From RBr). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 4.19 (d, *J* = 12.4 Hz, 2H), 2.97 (quint, *J* = 7.2 Hz, 4H), 1.72 (quint, *J* = 7.4 Hz, 4H), 1.43 (dt, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.6 (d, *J* = 6.6 Hz), 129.4, 128.9, 127.9, 37.0 (d, *J* = 3.2 Hz), 32.8 (d, *J* = 4.4 Hz), 32.7 (d, *J* = 5.4 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.73. **HRMS** calcd for $C_{15}H_{25}OPS_3Na$ $[M+Na]^+$ 371.0697, found 371.0703.

S,S-dibutyl *S*-(2-methylbenzyl) phosphorotrithioate (**5**, New Compound.)



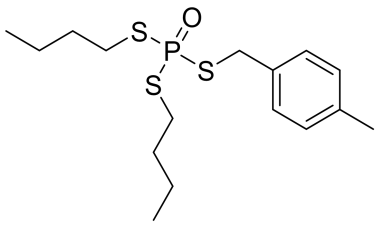
Colorless oil. Yield: 93%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32 (d, *J* = 7.4 Hz, 1H), 7.20-7.14 (m, 3H), 4.22 (d, *J* = 10.1 Hz, 2H), 2.99 (quint, *J* = 7.5 Hz, 4H), 2.41 (s, 3H), 1.73 (quint, *J* = 7.4 Hz, 4H), 1.43 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.2, 134.2 (d, *J* = 7.5 Hz), 130.8, 130.5, 128.3, 126.5, 35.3 (d, *J* = 4.2 Hz), 32.8 (d, *J* = 4.3 Hz), 32.7 (d, *J* = 4.4 Hz), 21.9, 19.4, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.53. **HRMS** calcd for $C_{16}H_{28}OPS_3$ $[M+H]^+$ 363.1034, found 363.1033.

S,S-dibutyl *S*-(3-methylbenzyl) phosphorotrithioate (**6**, New Compound.)



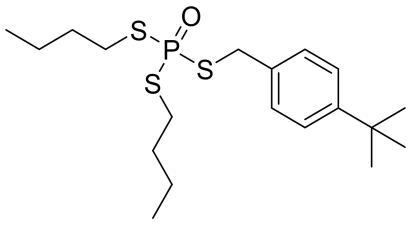
Colorless oil. Yield: 93%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22-7.16 (m, 3H), 7.08 (d, *J* = 7.5 Hz, 1H), 4.16 (d, *J* = 11.9 Hz, 2H), 2.98 (quint, *J* = 7.4 Hz, 4H), 2.34 (s, 3H), 1.72 (quint, *J* = 7.6 Hz, 4H), 1.43 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.6, 136.3 (d, *J* = 6.6 Hz), 130.1, 128.8, 128.6, 126.4, 36.9 (d, *J* = 4.2 Hz), 32.8 (d, *J* = 4.5 Hz), 32.6 (d, *J* = 4.8 Hz), 21.9, 21.5, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.06. **HRMS** calcd for $C_{16}H_{27}OPS_3Na$ $[M+Na]^+$ 385.0854, found 385.0854.

S,S-dibutyl *S*-(4-methylbenzyl) phosphorotrithioate (**7**, New Compound.)



Yellow oil. Yield: 92%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.16 (d, *J* = 12.1 Hz, 2H), 2.97 (quint, *J* = 7.3 Hz, 4H), 2.33 (s, 3H), 1.72 (quint, *J* = 7.8 Hz, 4H), 1.42 (dt, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.7, 133.4 (d, *J* = 6.5 Hz), 129.6, 129.3, 36.8 (d, *J* = 3.9 Hz), 32.8 (d, *J* = 5.6 Hz), 32.6 (d, *J* = 4.8 Hz), 21.9, 21.3, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.88. **HRMS** calcd for $C_{16}H_{27}OPS_3Na$ $[M+Na]^+$ 385.0854, found 385.0864.

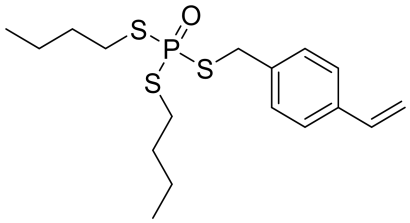
S,S-dibutyl *S*-(4-(tert-butyl)benzyl) phosphorotrithioate (**8**, New Compound.)



Colorless oil. Yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.18 (d, *J* = 12.1 Hz, 2H), 2.98 (quint, *J* = 7.5 Hz, 4H), 1.72 (quint, *J* = 7.5 Hz, 4H), 1.43 (dt, *J* = 7.4 Hz, 4H), 1.30 (s, 9H), 0.93 (t, *J* = 7.8 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.9, 133.3 (d, *J* = 6.5 Hz), 129.1, 125.8, 36.7 (d, *J* = 3.9 Hz), 34.7, 32.8 (d, *J* = 5.5 Hz), 32.6 (d, *J* = 4.8 Hz), 31.5, 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.93. **HRMS** calcd for $C_{19}H_{33}OPS_3Na$ $[M+Na]^+$ 427.1323, found 427.1323.

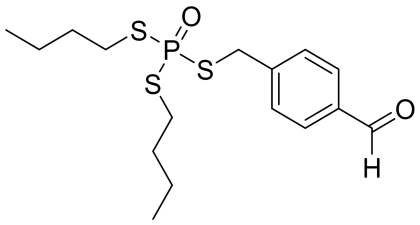
S,S-dibutyl *S*-(4-vinylbenzyl) phosphorotrithioate (**9**, New Compound.)



Colorless oil. Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.69 (dd, *J* = 17.6 Hz, *J* = 10.9 Hz, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 4.18 (d, *J* = 12.6 Hz, 2H), 2.97 (quint, *J* = 7.3 Hz, 4H), 1.71 (quint, *J* = 7.8 Hz, 4H), 1.42 (dt, *J* = 7.3 Hz, 4H), 0.92 (t, *J* = 7.8 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.2, 136.4, 136.0 (d, *J* = 5.5 Hz), 129.6, 126.7, 114.3, 36.8 (d, *J* = 4.0 Hz), 32.8 (d, *J* = 3.4 Hz), 32.6 (d, *J* = 5.4 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.79. **HRMS** calcd for $C_{17}H_{27}OPS_3Na$ $[M+Na]^+$ 397.0854, found 397.0855.

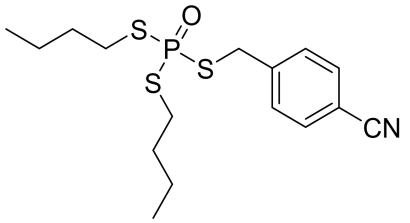
S,S-dibutyl *S*-(4-formylbenzyl) phosphorotrithioate (**10**, New Compound.)



Colorless oil. Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.24 (d, *J* = 13.9 Hz, 2H), 2.97 (quint, *J* = 7.5 Hz, 4H), 1.71 (quint, *J* = 7.4 Hz, 4H), 1.42 (dt, *J* = 7.6 Hz, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.8, 143.9 (d, *J* = 5.5 Hz), 135.83, 130.2, 130.1, 36.5 (d, *J* = 3.9 Hz), 32.9 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 4.4 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.40. **HRMS** calcd for $C_{16}H_{26}O_2PS_3$ $[M+H]^+$ 377.0827, found 377.0826.

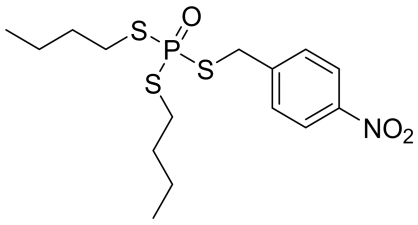
S,S-dibutyl *S*-(4-cyanobenzyl) phosphorotrithioate(**11**, New Compound.)



Light yellow oil. Yield: 86%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 4.21 (d, *J* = 14.3 Hz, 2H), 2.96 (quint, *J* = 7.7 Hz, 4H), 1.71 (quint, *J* = 7.5 Hz, 4H), 1.42 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 142.6 (d, *J* = 4.5 Hz), 132.6, 130.2, 118.7, 111.7, 36.3 (d, *J* = 3.3 Hz), 32.9 (d, *J* = 4.2 Hz), 32.6 (d, *J* = 5.2 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.19. **HRMS** calcd for $C_{16}H_{24}NOPS_3Na$ $[M+Na]^+$ 396.0650, found 396.0644.

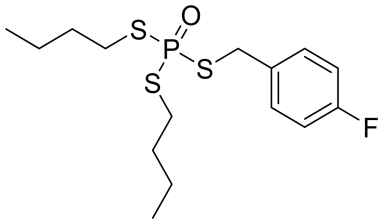
S,S-dibutyl *S*-(4-nitrobenzyl) phosphorotrithioate(**12**, New Compound.)



Yellow oil. Yield: 94%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 4.25 (d, *J* = 14.5 Hz, 2H), 2.97 (quint, *J* = 7.6 Hz, 4H), 1.71 (quint, *J* = 7.4 Hz, 4H), 1.42 (dt, *J* = 7.3 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.5, 144.7 (d, *J* = 4.4 Hz), 130.3, 124.0, 35.9 (d, *J* = 3.3 Hz), 33.0 (d, *J* = 4.2 Hz), 32.6 (d, *J* = 5.2 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.14. **HRMS** calcd for $C_{15}H_{24}NO_3PS_3Na$ $[M+Na]^+$ 416.0548, found 416.0556.

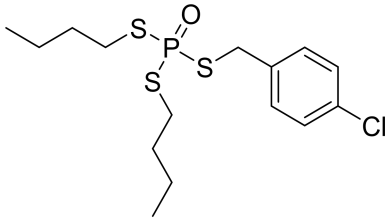
S,S-dibutyl *S*-(4-fluorobenzyl) phosphorotrithioate(**13**, New Compound.)



Light yellow oil. Yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.3 Hz, *J* = 5.4 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 4.17 (d, *J* = 13.3 Hz, 2H), 2.97 (quint, *J* = 7.5 Hz, 4H), 1.71 (quint, *J* = 7.6 Hz, 4H), 1.42 (dt, *J* = 7.2 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.4 (d, *J* = 247.1 Hz), 132.5 (dd, *J* = 6.6 Hz, *J* = 3.3 Hz), 131.1(d, *J* = 8.1 Hz), 115.8(d, *J* = 21.2 Hz), 36.2 (d, *J* = 3.4 Hz), 32.9 (d, *J* = 4.4 Hz), 32.7 (d, *J* = 5.6 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.37. **^{19}F NMR (377 MHz, CDCl3):** δ (ppm) -114.28. **HRMS** calcd for $C_{15}H_{25}FOPS_3$ $[M+H]^+$ 367.0784, found 367.0784.

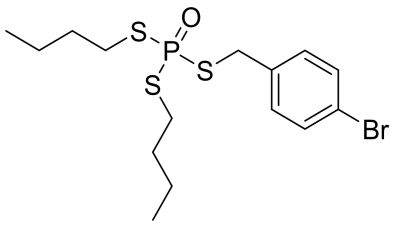
S,S-dibutyl *S*-(4-chlorobenzyl) phosphorotrithioate(**14**, ***CAS*** no.33574-46-8)



Light yellow oil. Yield: 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 4H), 4.15 (d, *J* = 13.2 Hz, 2H), 2.97 (quint, *J* = 7.5 Hz, 4H), 1.71 (quint, *J* = 7.2 Hz, 4H), 1.42 (dt, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.3 (d, *J* = 6.2 Hz), 133.8, 130.8, 129.0, 36.2 (d, *J* = 3.3 Hz), 32.9 (d, *J* = 3.4 Hz), 32.6 (d, *J* = 5.5 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.52. **HRMS** calcd for $C_{15}H_{25}ClOPS_3$ $[M+H]^+$ 383.0488, found 383.0488.

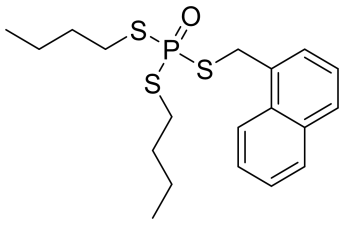
S-(4-bromobenzyl) *S,S*-dibutyl phosphorotrithioate(**15**, New Compound.)



Light yellow oil. Yield: 89%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.27-7.25 (m, 2H), 4.13 (d, *J* = 13.5 Hz, 2H), 2.96 (quint, *J* = 7.4 Hz, 4H), 1.74-1.68 (m, 4H), 1.42 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.9 (d, *J* = 5.6 Hz), 132.0, 131.1, 121.9, 36.3 (d, *J* = 3.2 Hz), 32.9 (d, *J* = 3.3 Hz), 32.6 (d, *J* = 5.6 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.49. **HRMS** calcd for $C_{15}H_{25}BrOPS_3$ $[M+H]^+$ 426.9983, found 426.9988.

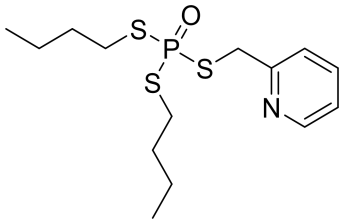
S,S-dibutyl *S*-(naphthalen-2-ylmethyl) phosphorotrithioate (**16,** New Compound.)



Light yellow oil. Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.57-7.53 (m, 2H), 7.51-7.48 (m, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 4.66 (d, *J* = 10.3 Hz, 2H), 2.98 (quint, *J* = 7.5 Hz, 4H), 1.71 (quint, *J* = 7.6 Hz, 4H), 1.40 (dt, *J* = 7.6 Hz, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 134.0, 131.9 (d, *J* = 6.9 Hz), 131.4, 129.1, 129.0, 128.3, 126.7, 126.1, 125.5, 123.8, 34.9 (d, *J* = 3.3 Hz), 32.8 (d, *J* = 3.5 Hz), 32.6 (d, *J* = 5.6 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.76. **HRMS** calcd for $C_{19}H_{27}OPS_3Na$ $[M+Na]^+$ 421.0854, found 421.0853.

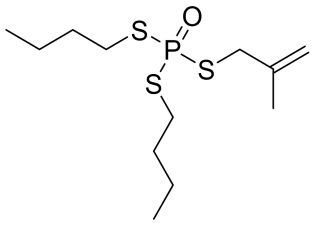
S,S-dibutyl *S*-(pyridin-2-ylmethyl) phosphorotrithioate(**17**, New Compound.)



Light yellow oil. Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 5.0 Hz, 1H), 7.68-7.65 (td, *J* = 7.7 Hz, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.21-7.19 (ddd, *J* = 7.8 Hz, *J* = 5.1 Hz, *J* = 1.1 Hz, 1H), 4.31 (d, *J* = 13.9 Hz, 2H), 2.98 (quint*d, *J* = 7.3 Hz, *J* = 1.2 Hz, 4H), 1.71 (quint, *J* = 7.5 Hz, 4H), 1.42 (dt, *J* = 7.5 Hz, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.5 (d, *J* = 5.5 Hz), 149.7, 136.9, 123.8, 122.6, 38.4 (d, *J* = 3.3 Hz), 32.8 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 5.5 Hz), 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.51. **HRMS** calcd for $C_{14}H_{25}NOPS_3$ $[M+H]^+$ 350.0830, found 350.0839.

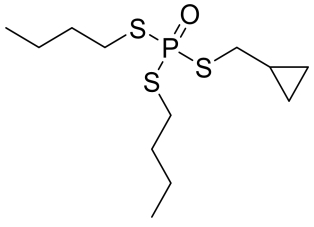
S,S-dibutyl *S*-(2-methylallyl) phosphorotrithioate(**18**, New Compound.)



Colorless oil. Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.05 (s, 1H), 4.92 (s, 1H), 3.61 (d, *J* = 12.8 Hz, 2H), 2.99 (quint, *J* = 7.3 Hz, 4H), 1.86 (s, 3H), 1.74 (quint, *J* = 7.5 Hz, 4H), 1.44 (dt, *J* = 7.4 Hz, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 140.1 (d, *J* = 5.5 Hz), 115.6, 39.9 (d, *J* = 3.6 Hz), 32.8 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 4.4 Hz), 21.9, 21.3, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.34. **HRMS** calcd for $C_{13}H_{25}OPS_3Na$ $[M+Na]^+$ 335.0697, found 335.0694.

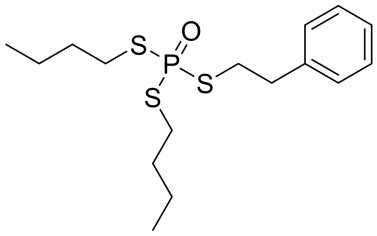
S,S-dibutyl *S*-(cyclopropylmethyl) phosphorotrithioate(**19**, New Compound.)



Light yellow oil. Yield: 90%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.99 (quint, *J* = 7.3 Hz, 4H), 2.93 (dd, *J* = 13.5 Hz, *J* = 7.4 Hz, 2H), 1.74 (quint, *J* = 7.5 Hz, 4H), 1.44 (dt, *J* = 7.5 Hz, 4H), 1.19-1.12 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 6H), 0.66-0.63 (m, 2H), 0.33 (dd, *J* = 12.1 Hz, *J* = 4.8 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 139.5, 128.8, 128.7, 126.9, 37.0 (d, *J* = 4.4 Hz), 34.1 (d, *J* = 3.5 Hz), 32.9 (d, *J* = 4.3 Hz), 32.6 (d, *J* = 5.5 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.31. **HRMS** calcd for $C_{12}H_{25}OPS_3Na$ $[M+Na]^+$ 335.0697, found 335.0697.

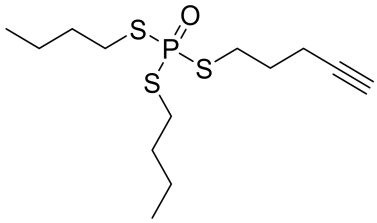
S,S-dibutyl *S*-phenethyl phosphorotrithioate(**20**, New Compound.)



Light yellow oil. Yield: 95%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.31 (*J* = 8.2 Hz, 1H), 7.30 (*J* = 7.1 Hz, 1H), 7.24-7.22 (m, 3H), 3.22 (quint, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H), 2.97 (quint, *J* = 7.3 Hz, 4H), 1.72 (quint, *J* = 7.4 Hz, 4H), 1.43 (dt, *J* = 7.5 Hz, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 139.5, 128.8, 128.7, 126.9, 37.0 (d, *J* = 4.4 Hz), 34.1 (d, *J* = 3.5 Hz), 32.9 (d, *J* = 4.3 Hz), 32.6 (d, *J* = 5.5 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, CDCl$_3$):** δ 64.81. **HRMS** calcd for $C_{16}H_{27}OPS_3Na$ $[M+Na]^+$ 385.0854, found 385.0855.

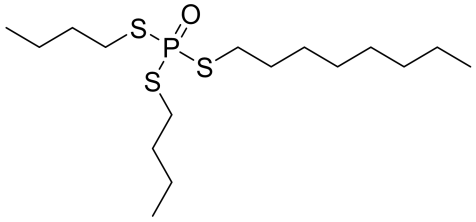
S,S-dibutyl *S*-(pent-4-yn-1-yl) phosphorotrithioate (**21,** New Compound.)



Light yellow oil. Yield: 93%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 3.13-3.08 (m, 2H), 2.99 (quint, *J* = 7.3 Hz, 4H), 2.37-2.34 (m, 2H), 2.02-1.97 (m, 3H), 1.74 (quint, *J* = 7.3 Hz, 4H), 1.44 (dt, *J* = 7.5 Hz, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 82.7, 69.6, 32.8 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 5.0 Hz), 31.8 (d, *J* = 3.3 Hz), 29.3 (d, *J* = 3.4 Hz), 21.9, 17.5, 13.6. **^{31}P NMR (162 MHz, CDCl$_3$):** δ 64.38. **HRMS** calcd for $C_{13}H_{25}OPS_3Na$ $[M+Na]^+$ 347.0697, found 347.0704.

S,S-dibutyl *S*-octyl phosphorotrithioate (**22,** New Compound.)

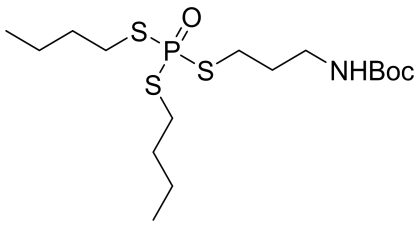


Colorless oil. Yield: 95%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 3.01-2.95 (m, 6H), 1.77-1.71 (m, 6H), 1.47-1.38 (m, 6H), 1.30-1.27 (m, 8H), 0.94 (t, *J* = 7.3 Hz, 6H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 33.1 (d, *J* = 3.4 Hz), 32.8 (d, *J* = 3.3 Hz), 32.6 (d, *J* = 4.5 Hz), 31.9, 30.6 (d, *J* = 4.8 Hz), 29.2, 29.1, 28.8, 22.8, 21.9, 14.2, 13.6. **^{31}P NMR (162 MHz, CDCl$_3$):** δ 64.81.

HRMS calcd for $C_{16}H_{35}OPS_3Na$ $[M+Na]^+$ 393.1480, found 393.1480.

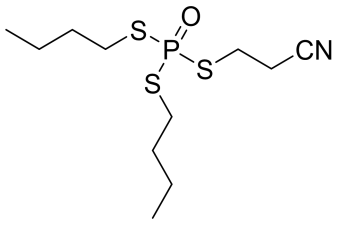
tert-butyl (3-((bis(butylthio)phosphoryl)thio)propyl)carbamate (**23,** New Compound.)



Colorless oil. Yield: 90%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 5.04 (s, NH), 3.27 (d, *J* = 6.0 Hz, 2H), 3.05-2.96 (m, 6H), 1.93 (quint, *J* = 6.7 Hz, 2H), 1.73 (quint, *J* = 7.5 Hz, 4H), 1.48-1.41 (m, 13H), 0.94 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 156.1, 38.7, 32.9 (d, *J* = 3.8 Hz), 32.6 (d, *J* = 5.4 Hz), 30.9, 30.1 (d, *J* = 3.3 Hz), 28.5, 21.9, 13.6. **^{31}P NMR (162 MHz, CDCl$_3$):** δ 65.20. **HRMS** calcd for $C_{16}H_{34}NO_3PS_3Na$ $[M+Na]^+$ 438.1331, found 438.1326.

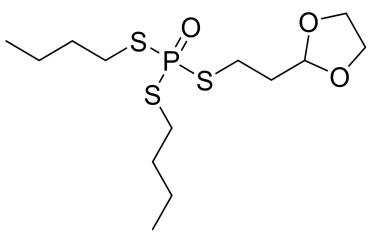
S,S-dibutyl *S*-(2-cyanoethyl) phosphorotrithioate(**24,** New Compound.)



Yellow oil. Yield: 76%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23-3.17 (m, 2H), 3.00 (quint, *J* = 7.5 Hz, 4H), 2.92 (t, *J* = 7.3 Hz, 2H), 1.74 (quint, *J* = 7.6 Hz, 4H), 1.45 (dt, *J* = 7.4 Hz, 4H), 0.95 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 117.7, 33.1 (d, *J* = 4.3 Hz), 32.6 (d, *J* = 5.5 Hz), 28.2 (d, *J* = 3.4 Hz), 21.9, 20.0 (d, *J* = 2.1 Hz), 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.64. **HRMS** calcd for $C_{11}H_{22}NOPS_3Na$ $[M+Na]^+$ 334.0502, found 334.0493.

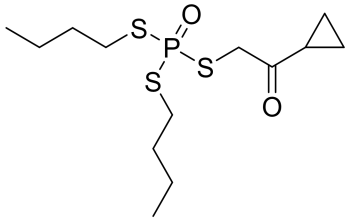
S-(2-(1,3-dioxolan-2-yl)ethyl) *S,S*-dibutyl phosphorotrithioate(**25,** New Compound.)



Colorless oil. Yield: 83%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.98 (t, *J* = 4.4 Hz, 1H), 3.98 (t, *J* = 7.2 Hz, 2H), 3.87 (t, *J* = 7.2 Hz, 2H), 3.08 (quint, *J* = 7.6 Hz, 2H), 2.99 (quint, *J* = 7.5 Hz, 4H), 2.15-2.12 (m, 2H), 1.73 (quint, *J* = 7.5Hz, 4H) , 1.44 (dt, *J* = 7.4 Hz, 4H), 0.93 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 102.8, 65.2, 34.8 (d, *J* = 4.4 Hz), 32.8 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 4.9 Hz), 27.3 (d, *J* = 4.4 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.42. **HRMS** calcd for $C_{13}H_{27}O_3PS_3Na$ $[M+Na]^+$ 381.0752, found 381.0751.

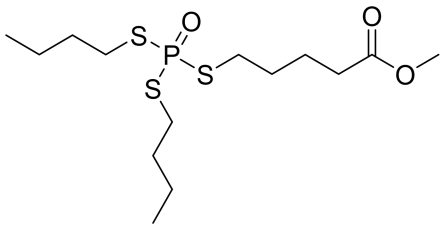
S,S-dibutyl *S*-(2-cyclopropyl-2-oxoethyl) phosphorotrithioate (**26,** New Compound.)



Colorless oil. Yield: 86%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (d, *J* = 12.9 Hz, 2H), 3.03-2.98 (m, 4H), 2.16-2.12 (m, 1H), 1.74 (quint, *J* = 7.5 Hz, 4H), 1.44 (dt, *J* = 7.5 Hz, 4H), 1.14 (quint, *J* = 4.0 Hz, 2H), 1.02-0.99 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.5 (d, *J* = 5.5 Hz), 42.4 (d, *J* = 3.3 Hz), 32.9 (d, *J* = 4.4 Hz), 32.6 (d, *J* = 4.6 Hz), 21.9, 20.1, 13.6, 12.3. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.49. **HRMS** calcd for $C_{13}H_{26}O_2PS_3$ $[M+H]^+$ 341.0827, found 341.0826.

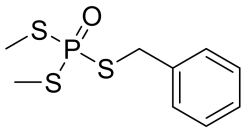
methyl 5-((bis(butylthio)phosphoryl)thio)pentanoate(**27,** New Compound.)



Colorless oil. Yield: 95%.

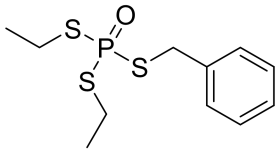
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 3H), 3.01-2.96 (m, 6H), 2.35 (t, *J* = 6.9 Hz, 2H), 1.82-1.71 (m, 8H), 1.44 (dt, *J* = 7.5 Hz, 4H), 0.94 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 173.6, 51.7, 33.4, 32.8 (d, *J* = 3.4 Hz), 32.6 (d, *J* = 5.4 Hz), 32.5 (d, *J* = 4.3 Hz), 30.0 (d, *J* = 4.4 Hz), 23.9, 21.9, 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.39. **HRMS** calcd for $C_{14}H_{29}O_3PS_3Na$ $[M+Na]^+$ 395.0909, found 395.0909.

S-benzyl *S,S*-dimethyl phosphorotrithioate(**28, *CAS*** no.32685-59-9)



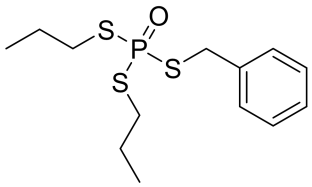
Colorless oil. Yield: 83% (From RCl); Yield: 85% (From RBr). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 1H), 4.19 (d, *J* = 12.6 Hz, 2H), 2.40 (d, *J* = 16.1 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.3 (d, *J* = 6.6 Hz), 129.2, 128.9, 127.9, 36.5 (d, *J* = 3.3 Hz), 14.4 (d, *J* = 4.4 Hz). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 66.94. **HRMS** calcd for $C_9H_{14}OPS_3$ $[M+H]^+$ 264.9939, found 264.9942.

S-benzyl *S,S*-diethyl phosphorotrithioate(**29, *CAS*** no.31234-03-4)



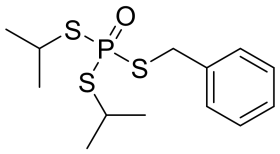
Light yellow oil. Yield: 90%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 4.20 (d, *J* = 12.4 Hz, 2H), 3.00 (dt, *J* = 7.9 Hz, 4H), 1.41 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.5 (d, *J* = 5.5 Hz), 129.4, 128.9, 127.9, 37.0 (d, *J* = 3.6 Hz), 27.7 (d, *J* = 4.3 Hz), 16.3 (d, *J* = 5.5 Hz). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.33. **HRMS** calcd for $C_{11}H_{17}OPS_3Na$ $[M+Na]^+$ 315.0071, found 315.0081.

S-benzyl *S,S*-dipropyl phosphorotrithioate(**30,** New Compound.)



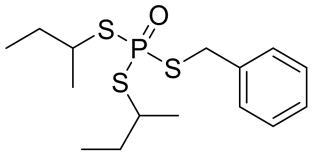
Colorless oil. Yield: 95%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 1H), 4.19 (d, *J* = 12.4 Hz, 2H), 2.95 (quint, *J* = 7.6 Hz, 4H), 1.77 (dt, *J* = 7.4 Hz, 4H), 1.01 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.5 (d, *J* = 5.7 Hz), 129.4, 128.9, 127.9, 37.0 (d, *J* = 3.5 Hz), 35.0 (d, *J* = 4.4 Hz), 24.1 (d, *J* = 5.4 Hz), 13.4. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 63.76. **HRMS** calcd for $C_{13}H_{21}OPS_3Na$ $[M+Na]^+$ 343.0384, found 343.0386.

S-benzyl *S,S*-diisopropyl phosphorotrithioate(**31, *CAS*** no.31173-04-3)



Light yellow oil. Yield: 95%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 2H), 3.68-3.59 (m, 2H), 1.46 (dd, *J* = 9.2 Hz, *J* = 7.3 Hz, 12H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.5 (d, *J* = 6.6 Hz), 129.4, 128.9, 127.9, 40.6 (d, *J* = 3.7 Hz), 37.3 (d, *J* = 4.4 Hz), 25.67, 25.64, 25.58, 25.54. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 60.16. **HRMS** calcd for $C_{13}H_{21}OPS_3Na$ $[M+Na]^+$ 343.0384, found 343.0391.

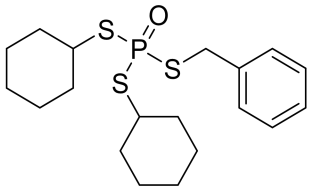
S-benzyl *S,S*-di-sec-butyl phosphorotrithioate(**32,** New Compound.)



Yellow oil. Yield: 95% (From RCl); Yield: 95% (From RBr). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 4.20 (dt, *J* = 11.9 Hz, *J* = 3.4 Hz, 2H), 3.51-3.45 (m, 2H), 1.79-1.69 (m, 4H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.45 (d, *J* = 6.9 Hz, 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.6 (d, *J* = 6.6 Hz), 129.4, 128.9, 127.8, 46.9-46.8 (m), 37.3 (d, *J* = 3.3 Hz), 31.5 (d, *J* = 6.4 Hz), 31.4 (d, *J* = 5.6 Hz), 23.2 (t, *J* = 3.4 Hz), 23.1 (t, *J* = 2.2 Hz), 11.43, 11.40. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 60.16. **HRMS** calcd for $C_{15}H_{25}OPS_3Na$ $[M+Na]^+$ 371.0697, found

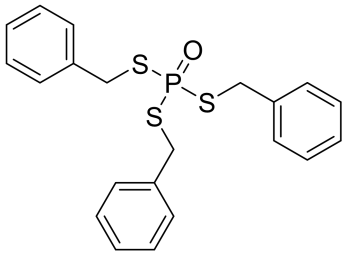
371.0704.

S-benzyl *S,S*-dicyclohexyl phosphorotrithioate(**33,** New Compound.)



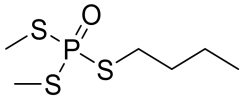
Light yellow oil. Yield: 87% (From RCl); Yield: 88% (From RBr). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 2H), 3.49-3.43 (m, 2H), 2.11-1.24 (m, 20H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.6 (d, *J* = 6.5 Hz), 129.4, 128.9, 127.8, 48.0 (d, *J* = 3.4 Hz), 37.4 (d, *J* = 3.3 Hz), 35.4 (dd, *J* = 12.6 Hz, *J* = 4.7 Hz), 26.0, 25.4. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 60.70. **HRMS** calcd for $C_{19}H_{29}OPS_3Na$ $[M+Na]^+$ 423.1010, found 423.1010.

S,S,S-tribenzyl phosphorotrithioate(**34, *CAS*** no.14974-76-6)



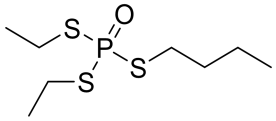
Colorless Wax. Yield: 88%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34-7.24 (m, 15H), 4.17 (d, *J* = 12.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.3 (d, *J* = 6.6 Hz), 129.4, 129.0, 128.0, 37.1 (d, *J* = 3.3 Hz). **^{31}P NMR (162 MHz, $CDCl_3$):** δ 61.83. **HRMS** calcd for $C_{21}H_{21}OPS_3Na$ $[M+Na]^+$ 439.0384, found 439.0384.

S-butyl *S,S*-dimethyl phosphorotrithioate(**35,** New Compound.)



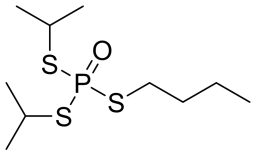
Yellow oil. Yield: 85%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.00 (quint, *J* = 7.4 Hz, 2H), 2.43 (d, *J* = 15.8 Hz, 6H), 1.74 (quint, *J* = 7.4 Hz, 2H), 1.45 (dt, *J* = 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ32.7 (d, *J* = 5.5 Hz), 32.5 (d, *J* = 4.4 Hz), 22.0, 14.4 (d, *J* = 4.3 Hz), 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 67.95. **HRMS** calcd for $C_6H_{16}OPS_3$ $[M+H]^+$ 231.0095, found 231.0105.

S-butyl *S,S*-diethyl phosphorotrithioate(**36,** New Compound.)



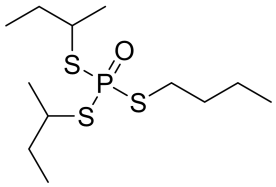
Light yellow oil. Yield: 95%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.00 (heptet, *J* = 7.5 Hz, 6H), 1.74 (quint, *J* = 7.5 Hz, 2H), 1.48-1.42 (m, 8H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ32.7 (d, *J* = 3.8 Hz), 32.6 (d, *J* = 4.6 Hz), 27.6 (d, *J* = 3.3 Hz), 21.9, 16.2 (d, *J* = 5.4 Hz), 13.6. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 64.24. **HRMS** calcd for $C_8H_{20}OPS_3$ $[M+H]^+$ 259.0408, found 259.0413.

S-butyl *S,S*-diisopropyl phosphorotrithioate(**37,** New Compound.)



Colorless oil. Yield: 92%. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.63 (heptet*d, *J* = 13.7 Hz, *J* = 7.0 Hz, 2H)), 2.98 (quint, *J* = 7.2 Hz, 2H), 1.73 (quint, *J* = 7.4 Hz, 2H), 1.48-1.43 (m, 14H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 40.4 (d, *J* = 3.4 Hz), 33.0 (d, *J* = 4.3 Hz), 32.6 (d, *J* = 5.5 Hz), 25.60 (d, *J* = 3.3 Hz), 25.56 (d, *J* = 3.5 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 61.25. **HRMS** calcd for $C_{10}H_{24}OPS_3$ $[M+H]^+$ 287.0721, found 287.0730.

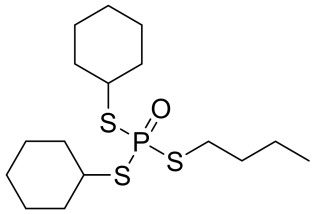
S,S-di-sec-butyl *S*-butyl phosphorotrithioate(**38,** New Compound.)



Colorless oil. Yield: 81%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51-3.43 (m, 2H), 3.01-2.95 (m, 2H), 1.79-1.70 (m, 6H), 1.48-1.43 (m, 8H), 1.02 (t, *J* = 7.3 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 46.73-46.65 (m), 33.0 (d, *J* = 4.3 Hz), 32.6 (d, *J* = 5.5 Hz), 31.45 (d, *J* = 6.2 Hz), 31.40 (d, *J* = 6.6 Hz), 23.1 (t, *J* = 3.8 Hz), 23.0 (t, *J* = 2.2 Hz), 21.9, 13.6, 11.39, 11.37. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 61.78. **HRMS** calcd for $C_{12}H_{27}OPS_3Na$ $[M+Na]^+$ 337.0854, found 337.0858.

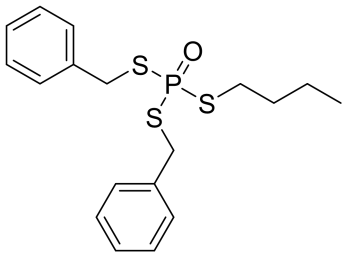
S-butyl *S,S*-dicyclohexyl phosphorotrithioate(**39,** New Compound.)



Colorless oil. Yield: 80%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.48-3.43 (m, 2H), 2.98 (quint, *J* = 7.0 Hz, 2H), 2.14-2.12 (m, 4H), 1.76-1.71 (m, 6H), 1.61-1.55 (m, 6H), 1.46-1.41 (m, 6H), 1.31-1.27 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 47.9 (d, *J* = 4.4 Hz), 35.4 (d, *J* = 3.4 Hz), 33.1 (d, *J* = 4.3 Hz), 32.5 (d, *J* = 5.5 Hz), 26.0, 25.4, 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 61.64. **HRMS** calcd for $C_{16}H_{31}OPS_3Na$ $[M+Na]^+$ 389.1167, found 389.1159.

S,S-dibenzyl *S*-butyl phosphorotrithioate(**40,** New Compound.)

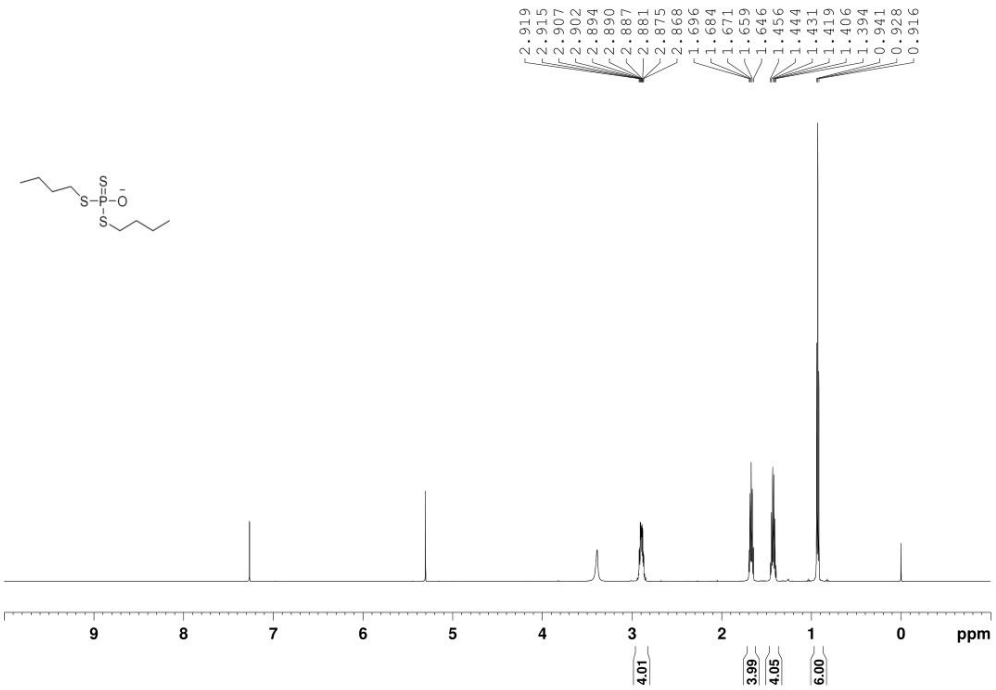


Colorless oil. Yield: 80%.

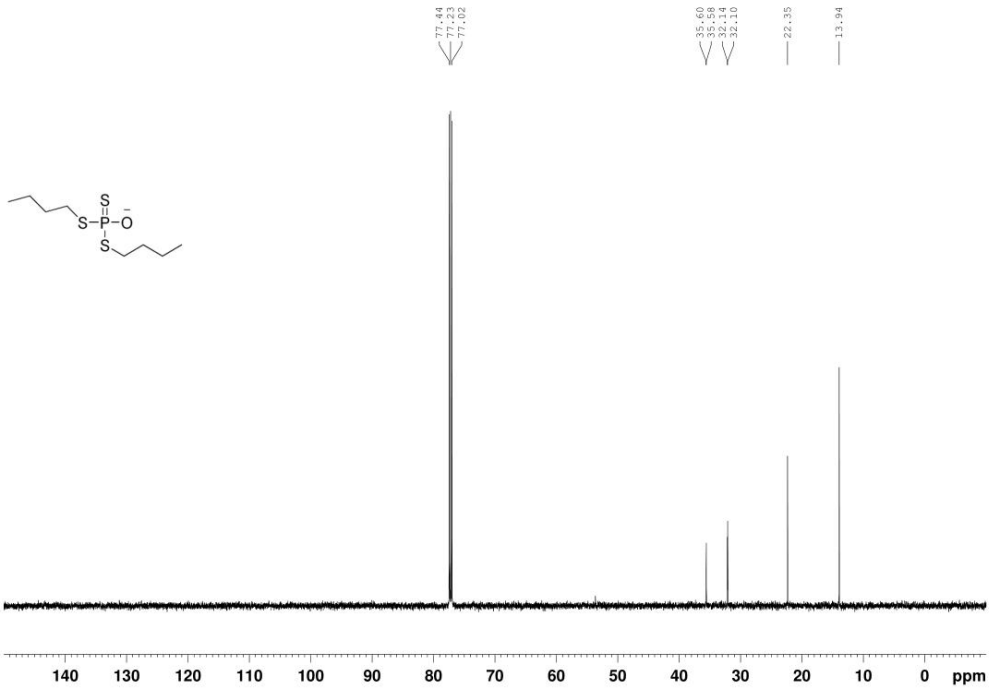
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H), 4.18 (d, *J* = 12.5 Hz, 4H), 2.97 (quint, *J* = 7.5 Hz, 2H), 1.70 (quint, *J* = 7.5 Hz, 2H), 1.41 (dt, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 136.4 (d, *J* = 6.6 Hz), 129.4, 128.9, 127.9, 37.0 (d, *J* = 3.3 Hz), 32.9 (d, *J* = 4.4 Hz), 32.7 (d, *J* = 5.5 Hz), 21.9, 13.7. **^{31}P NMR (162 MHz, $CDCl_3$):** δ 62.08. **HRMS** calcd for $C_{18}H_{24}OPS_3$ $[M+H]^+$ 383.0721, found 383.0720.

^{1}H、^{13}C、^{31}P and ^{19}F NMR spectra

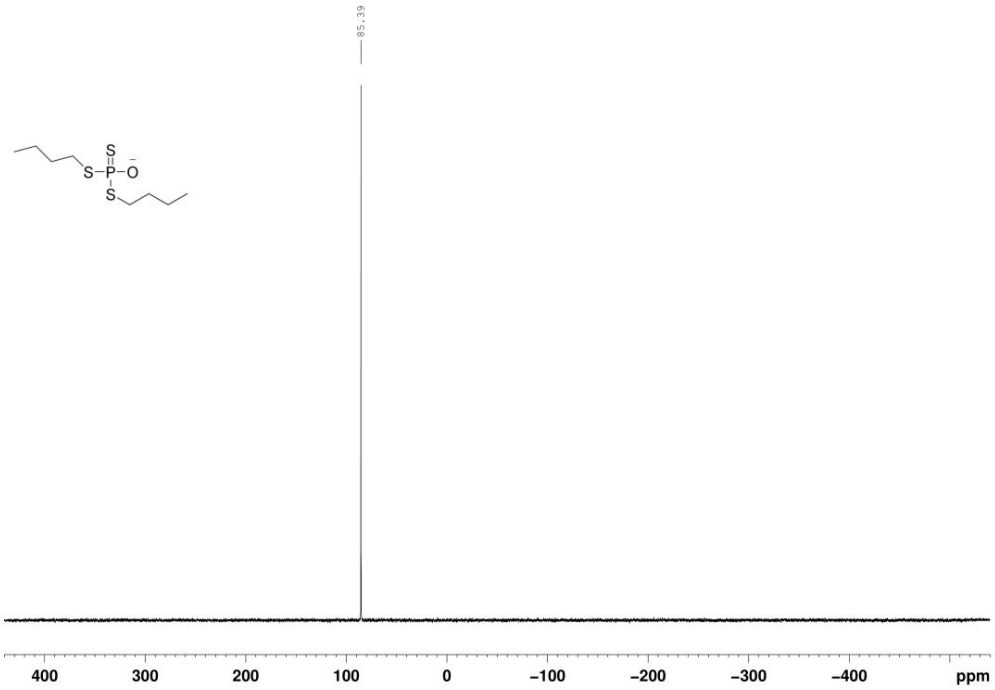
3



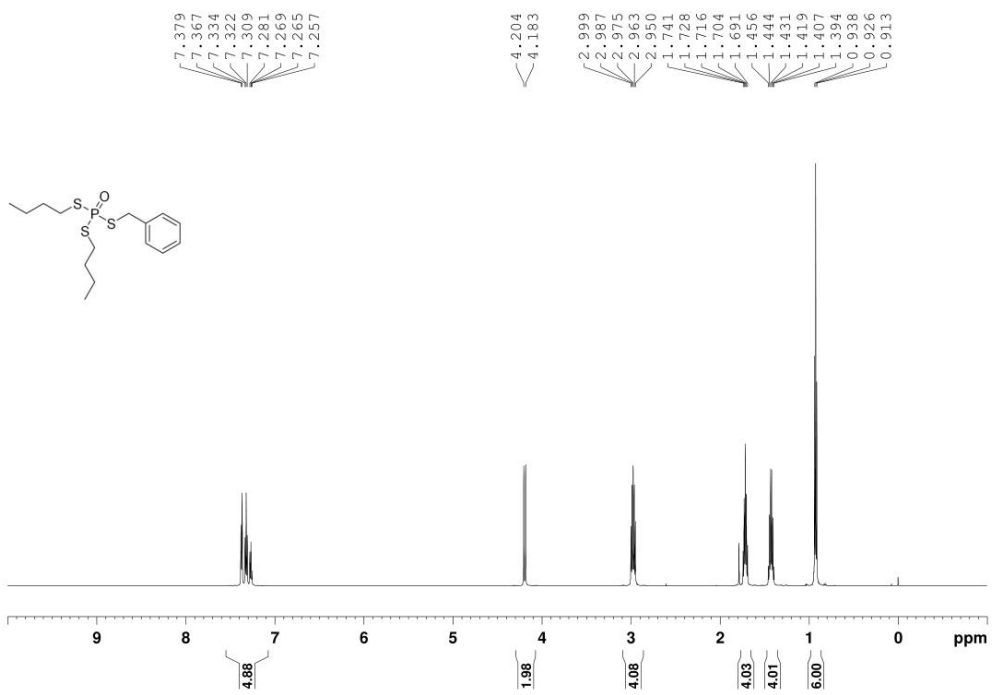
3



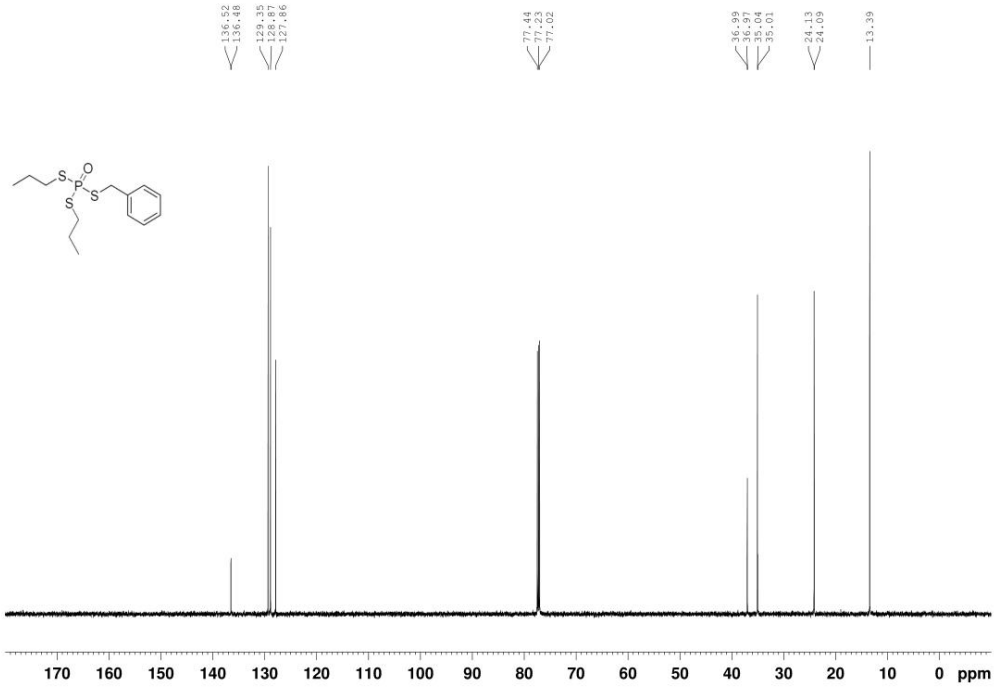
3


85.39
400
300
200
100
0
−100
−200
−300
−400
ppm

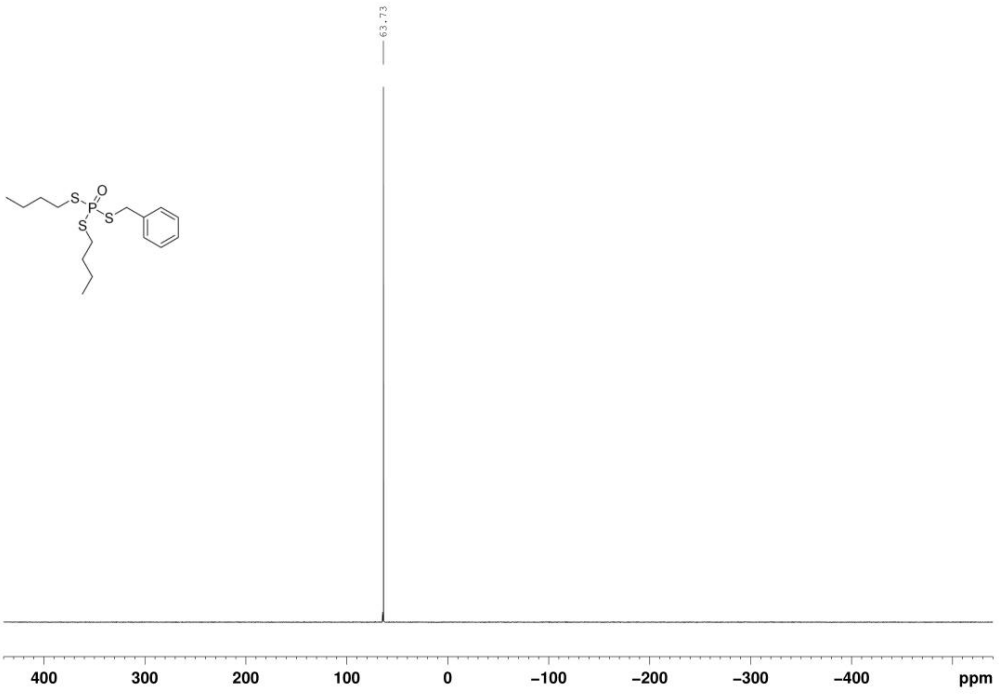
4


7.379
7.367
7.334
7.322
7.309
7.281
7.269
7.265
7.257
4.204
4.183
2.999
2.987
2.975
2.963
2.950
1.741
1.728
1.716
1.704
1.691
1.456
1.444
1.431
1.419
1.407
1.394
0.938
0.926
0.913
9
8
7
6
5
4
3
2
1
0
ppm
4.88
1.98
4.08
4.03
4.01
6.00

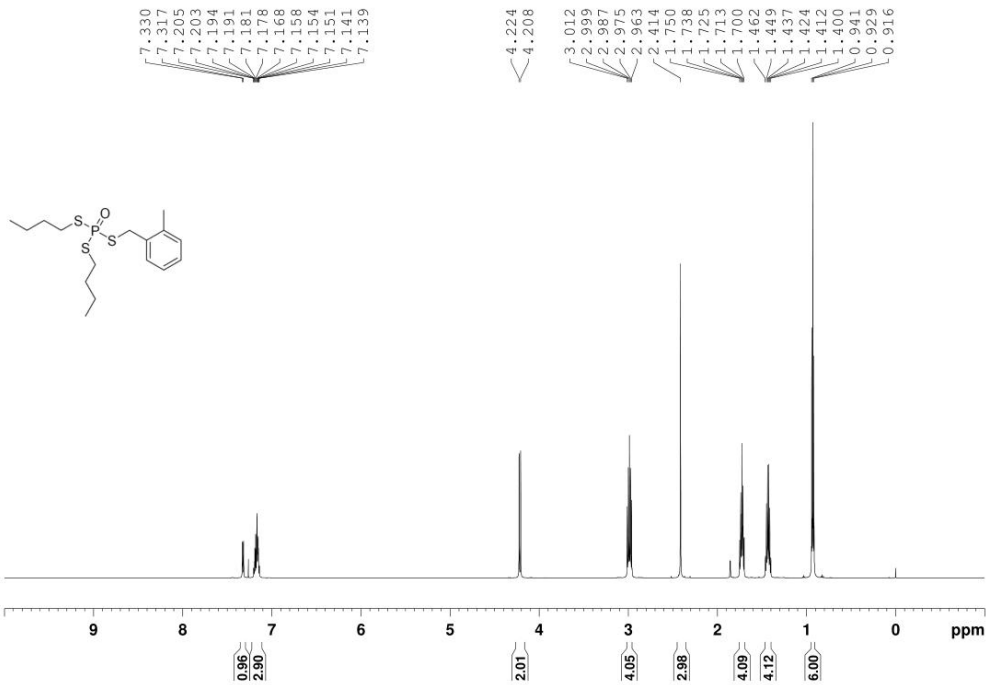
4


136.52
136.48
129.35
128.87
127.86
77.44
77.23
77.02
36.99
36.97
35.04
35.01
24.13
24.09
13.39
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

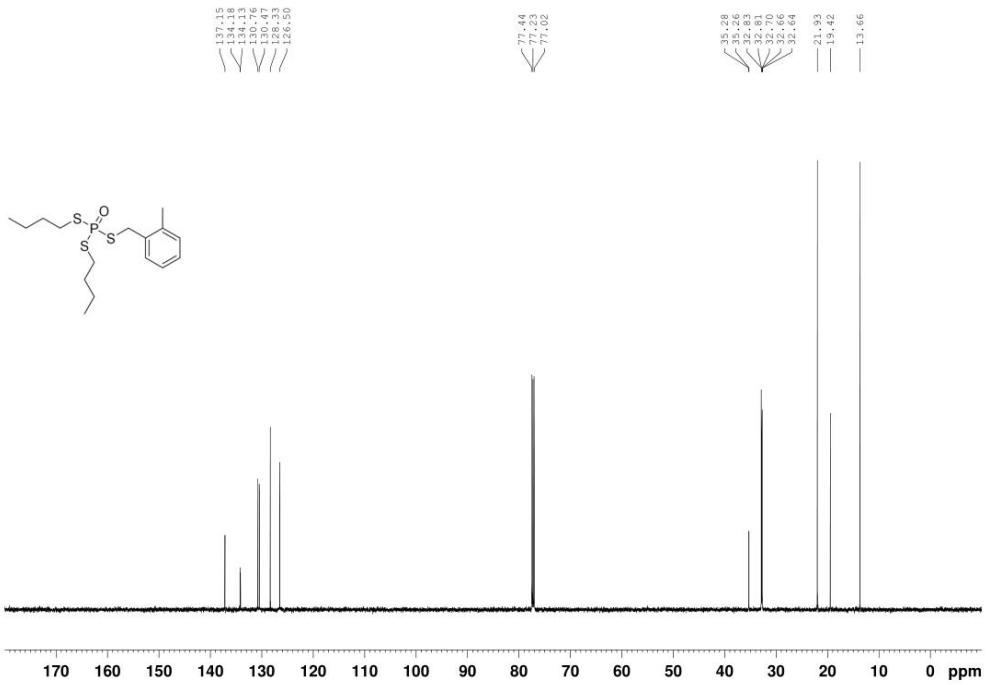
4


63.73
400 300 200 100 0 −100 −200 −300 −400 ppm

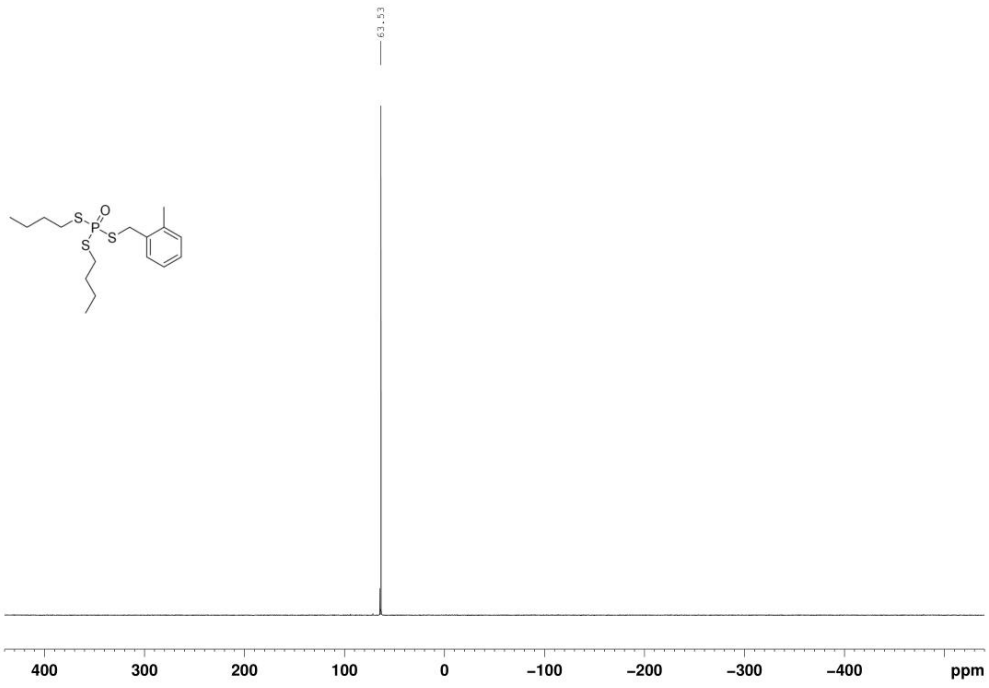
5


7.330
7.317
7.205
7.203
7.194
7.191
7.181
7.178
7.168
7.158
7.154
7.151
7.141
7.139
4.224
4.208
3.012
2.999
2.987
2.975
2.963
2.414
1.750
1.738
1.725
1.713
1.700
1.462
1.449
1.437
1.424
1.412
1.400
0.941
0.929
0.916
9
8
7
6
5
4
3
2
1
0
ppm
0.96
2.90
2.01
4.05
2.98
4.09
4.12
6.00

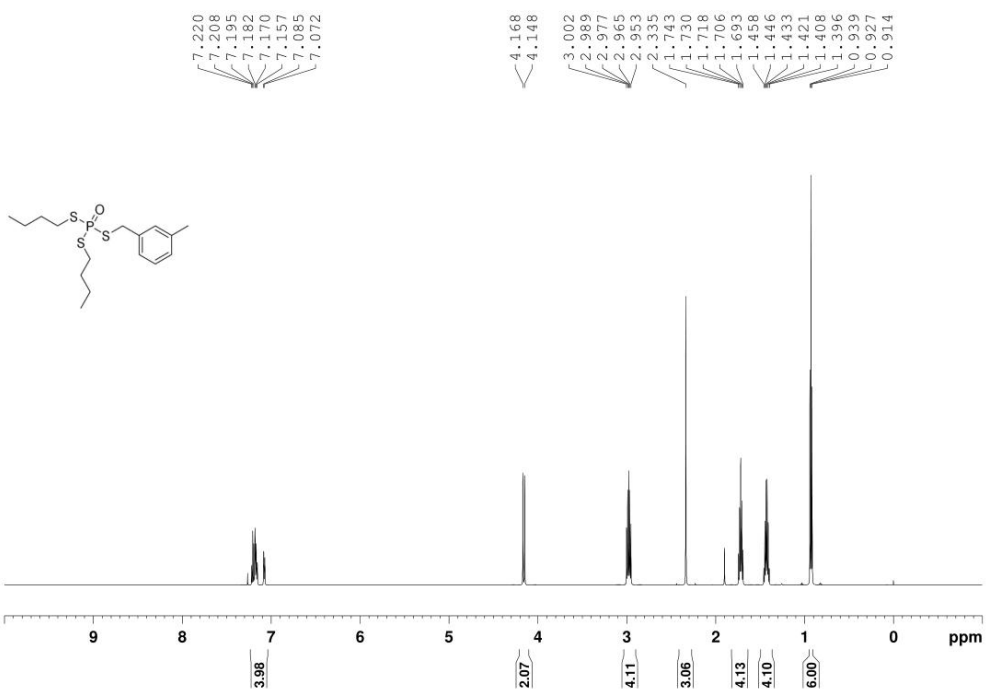
5


137.15
134.18
134.13
130.76
130.47
128.33
126.50
77.44
77.23
77.02
35.28
35.06
32.83
32.81
32.70
32.66
32.64
21.93
19.42
13.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

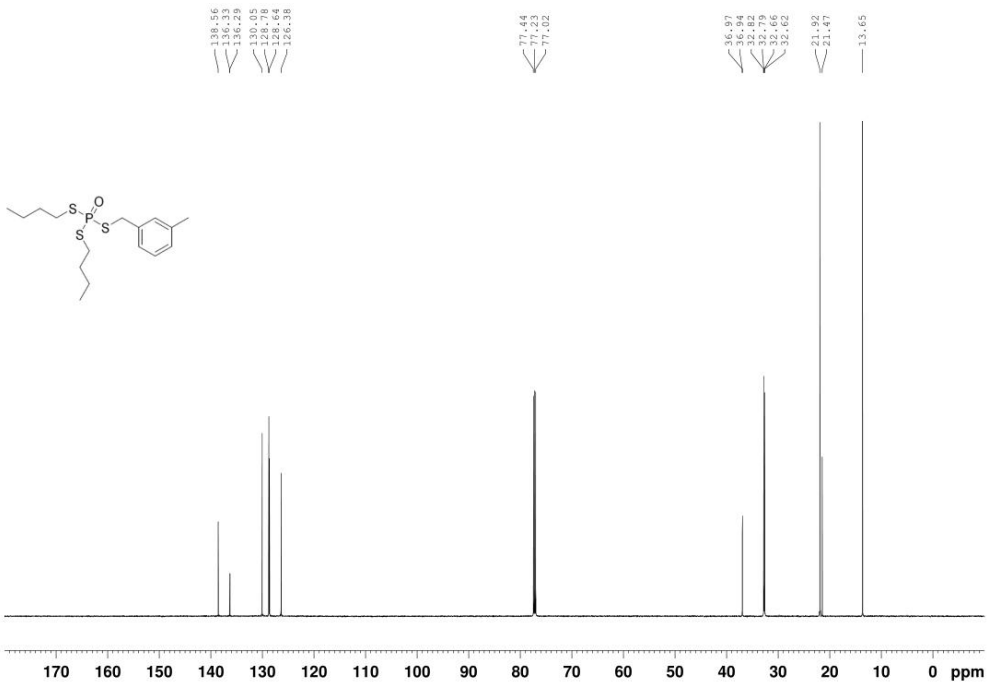
5


63.53
400
300
200
100
0
−100
−200
−300
−400
ppm

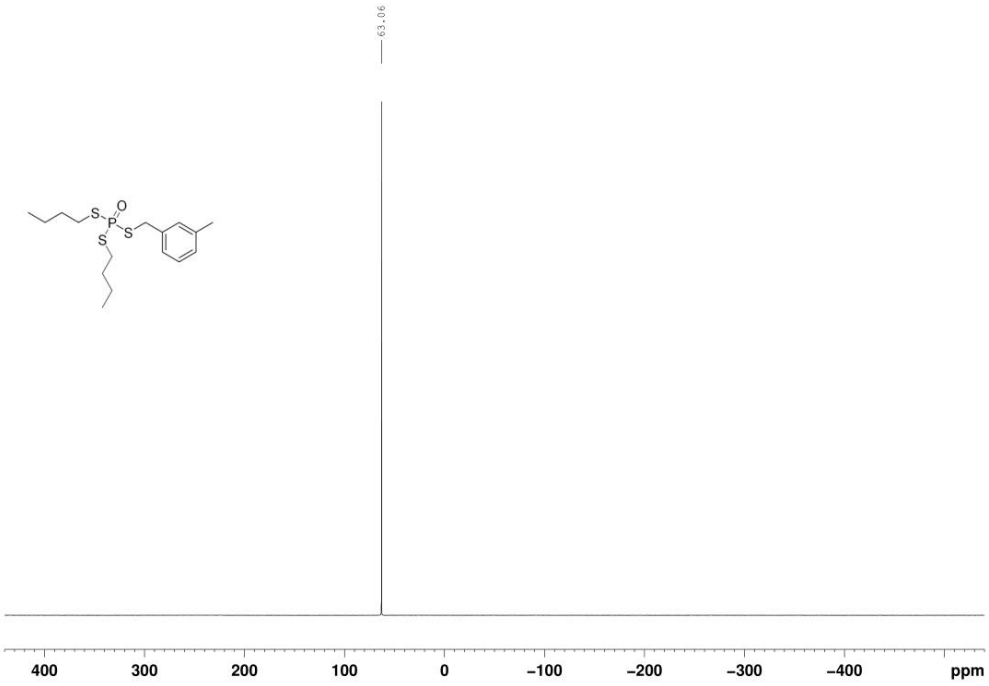
6


7.220
7.208
7.195
7.182
7.170
7.157
7.085
7.072
4.168
4.148
3.002
2.989
2.977
2.965
2.953
2.335
1.743
1.730
1.718
1.706
1.693
1.458
1.446
1.433
1.421
1.408
1.396
0.939
0.927
0.914
9
8
7
6
5
4
3
2
1
0
ppm
3.98
2.07
4.11
3.06
4.13
4.10
6.00

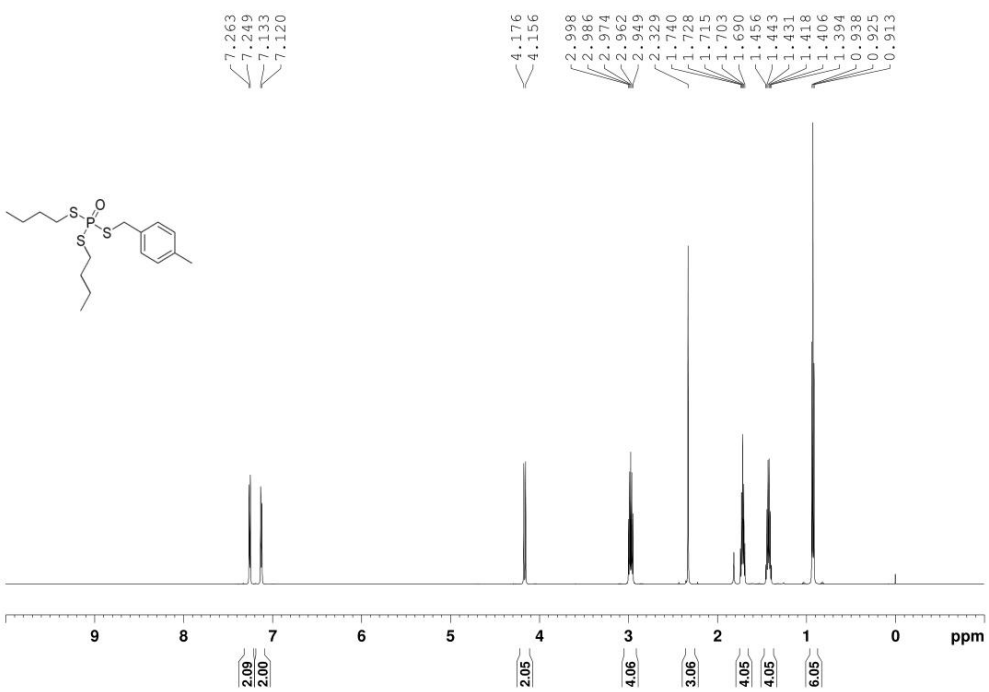
6


138.56
136.33
136.29
130.05
128.78
128.64
126.38
77.44
77.23
77.02
36.97
36.94
32.72
32.70
32.66
32.62
21.92
21.47
13.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

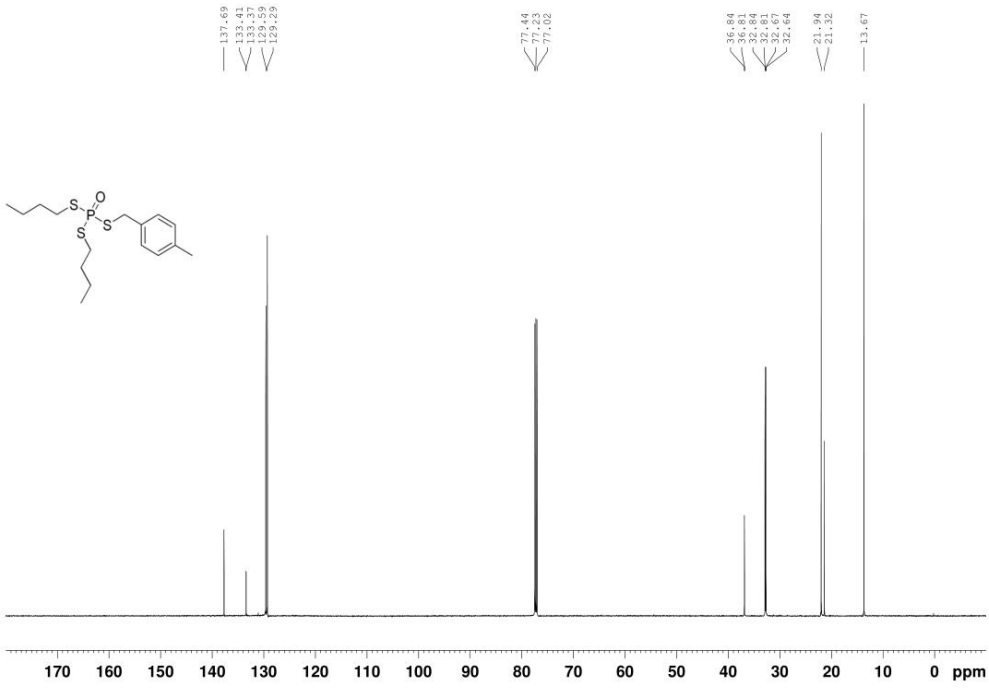
6


63.06
400 300 200 100 0 −100 −200 −300 −400 ppm

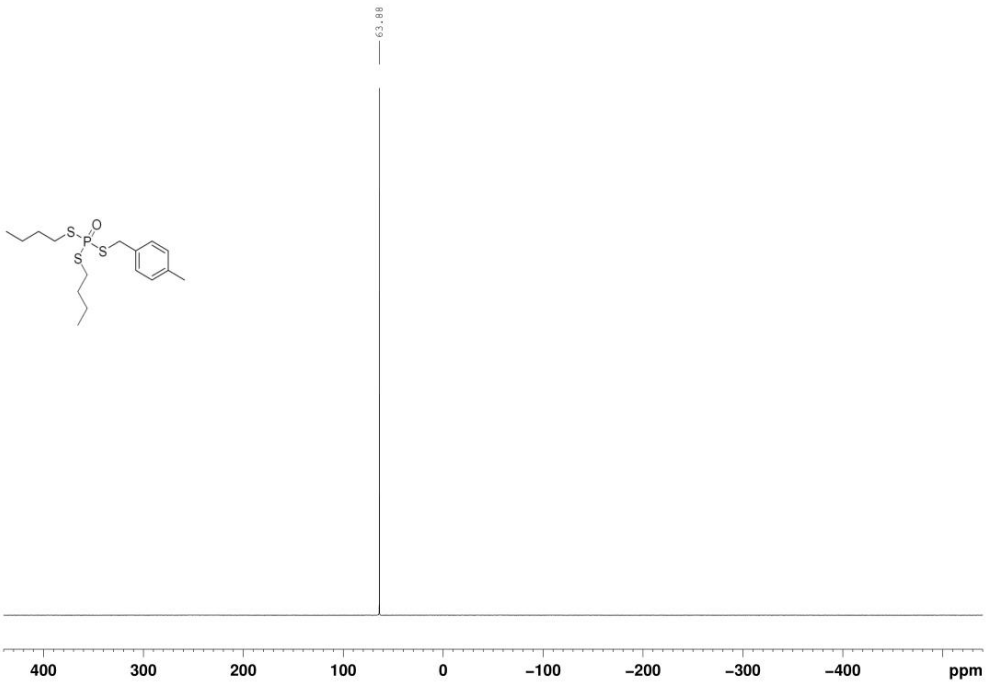
7


7.263
7.249
7.133
7.120
4.176
4.156
2.998
2.986
2.974
2.962
2.949
2.329
1.740
1.728
1.715
1.703
1.690
1.456
1.443
1.431
1.418
1.406
1.394
0.938
0.925
0.913
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.00
2.05
4.06
3.06
4.05
4.05
6.05

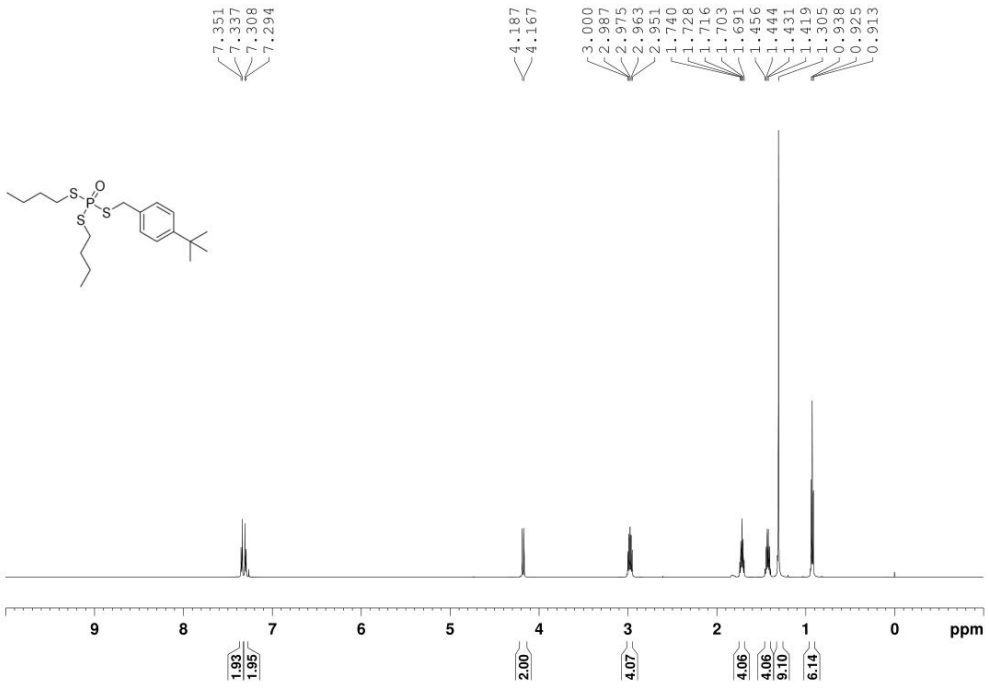
7


137.69
133.41
133.37
129.59
129.29
77.44
77.23
77.02
36.84
36.81
32.84
32.81
32.67
32.64
21.94
21.32
13.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

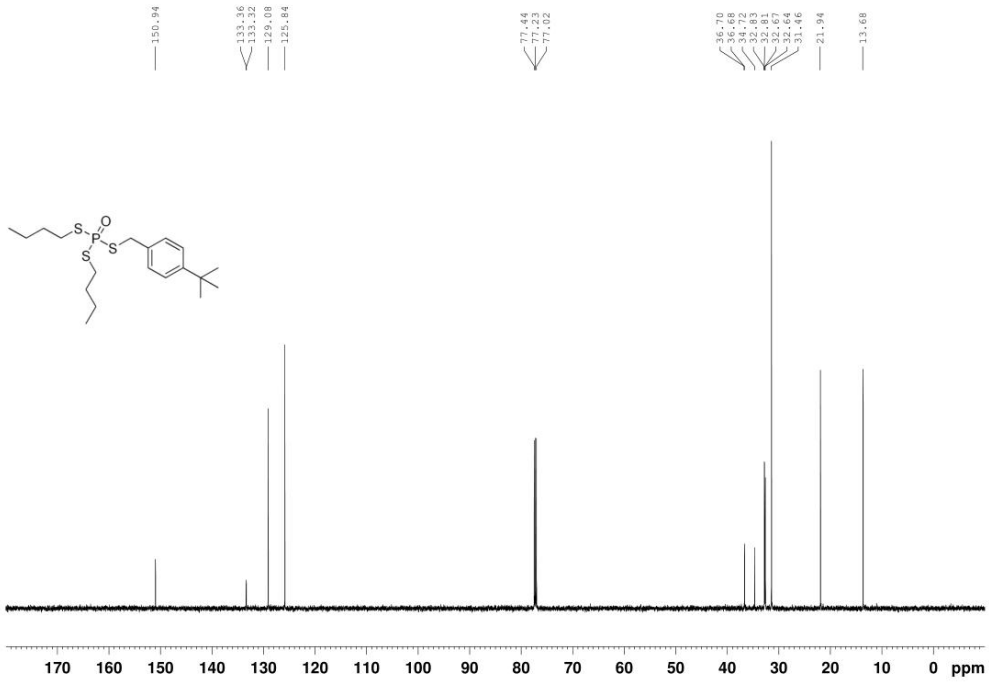
7


63.88
400
300
200
100
0
−100
−200
−300
−400
ppm

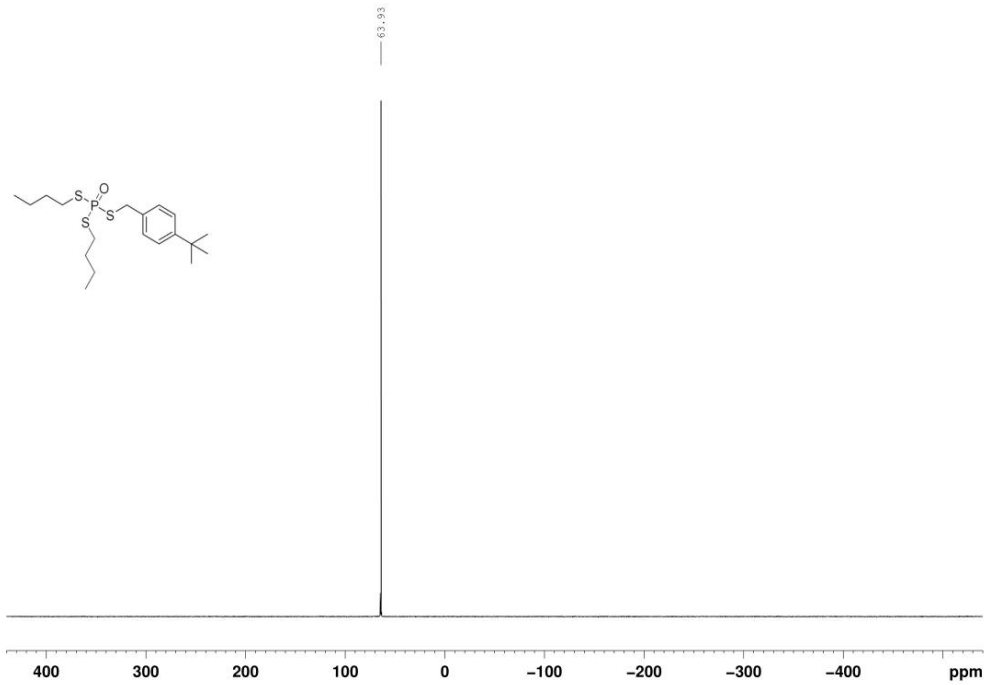
8


7.351
7.337
7.308
7.294
4.187
4.167
3.000
2.987
2.975
2.963
2.951
1.740
1.728
1.716
1.703
1.691
1.456
1.444
1.431
1.419
1.305
0.938
0.925
0.913
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.95
2.00
4.07
4.06
4.06
9.10
6.14

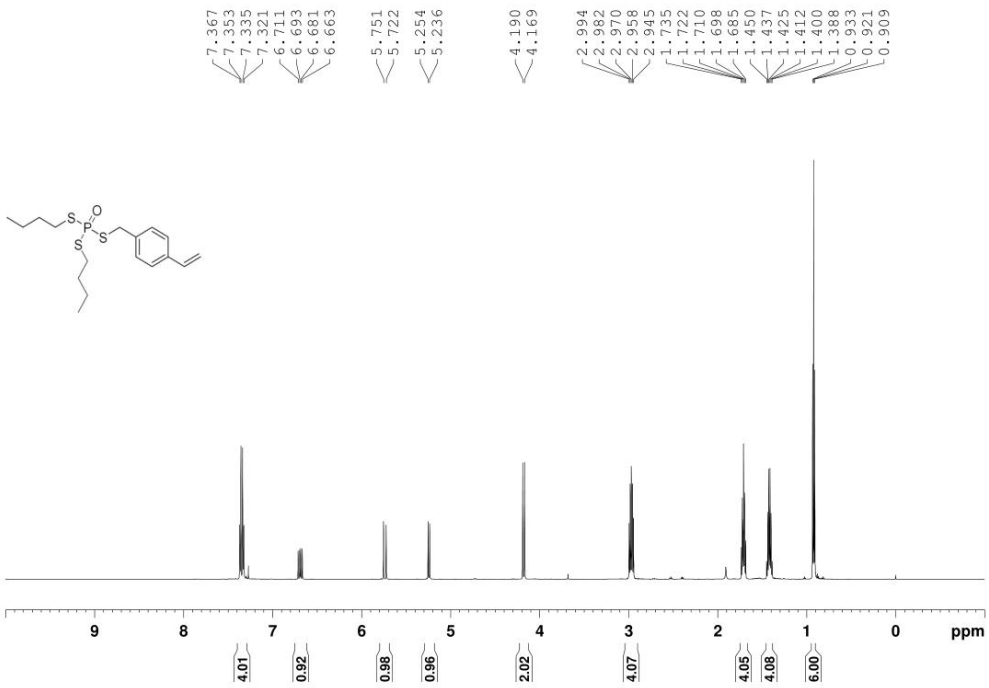
8


150.94
133.36
133.32
129.08
125.84
77.44
77.23
77.02
36.70
36.68
34.72
32.83
32.81
32.67
32.64
31.46
21.94
13.68
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

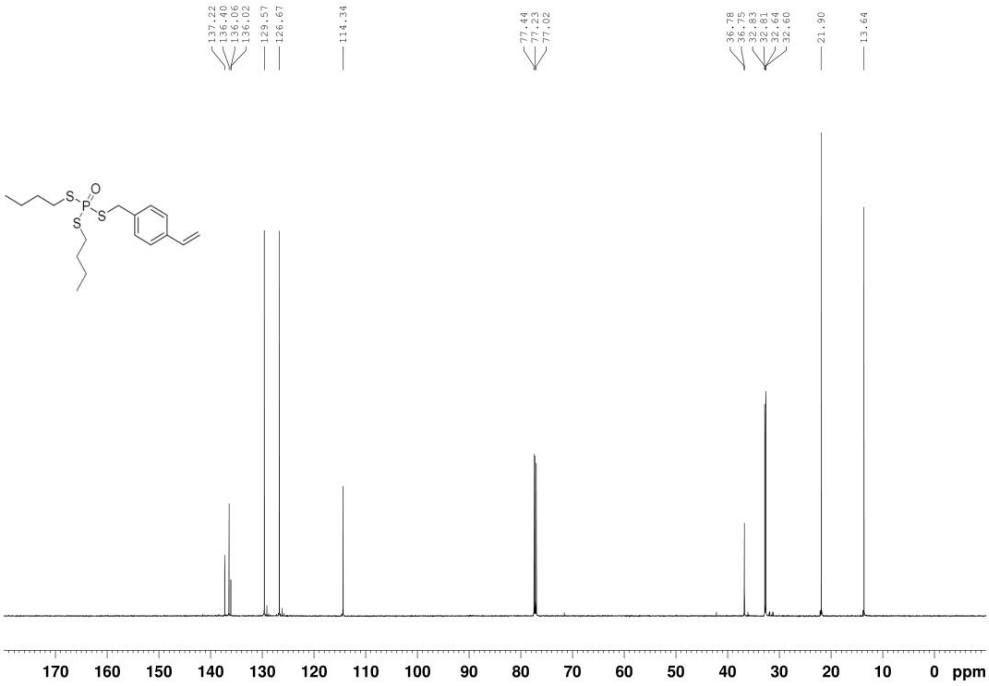
8


63.93
400 300 200 100 0 −100 −200 −300 −400 ppm

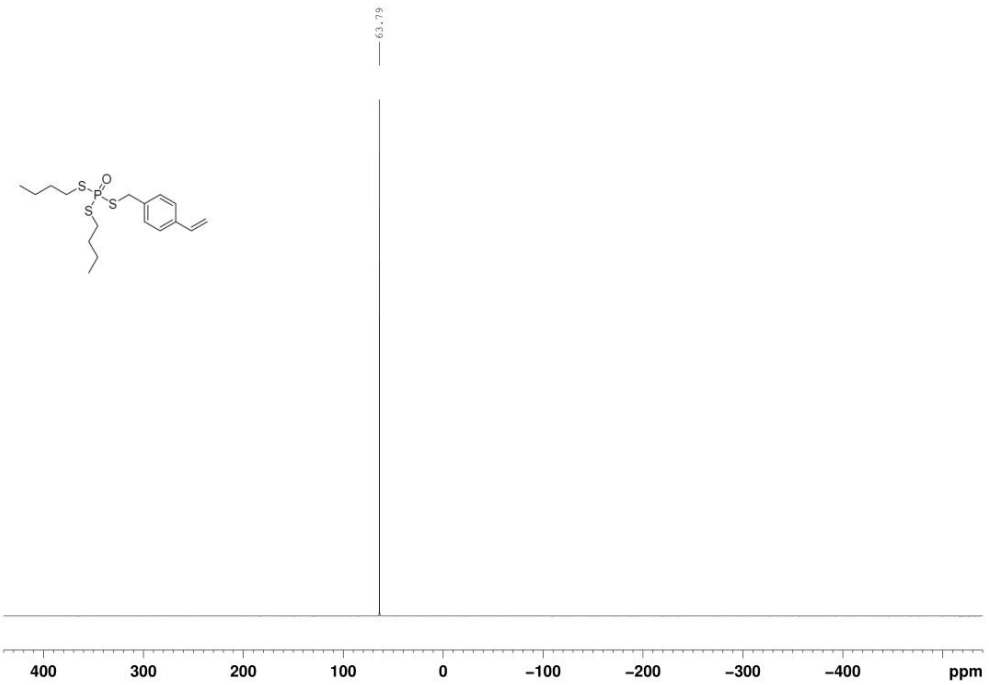
9


7.367
7.353
7.335
7.321
6.711
6.693
6.681
6.663
5.751
5.722
5.254
5.236
4.190
4.169
2.994
2.982
2.970
2.958
2.945
1.735
1.722
1.710
1.698
1.685
1.450
1.437
1.425
1.412
1.400
1.388
0.933
0.921
0.909
9 8 7 6 5 4 3 2 1 0 ppm
4.01
0.92
0.98
0.96
2.02
4.07
4.05
4.08
6.00

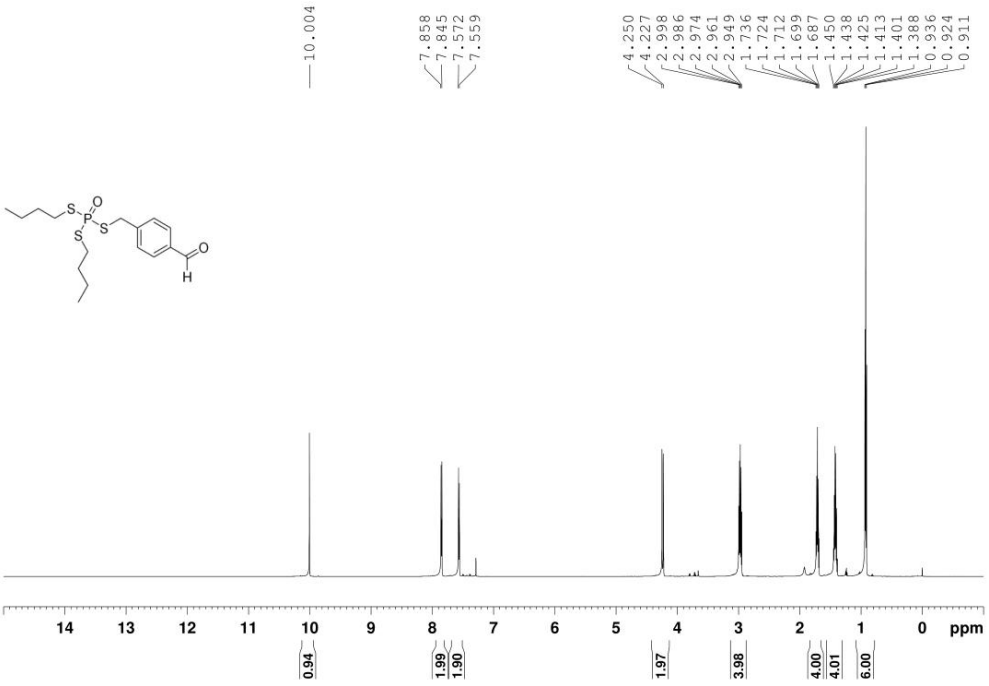
9


137.22
136.40
136.06
136.02
129.57
126.67
114.34
77.44
77.23
77.02
36.78
36.75
32.83
32.81
32.64
32.60
21.90
13.64
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

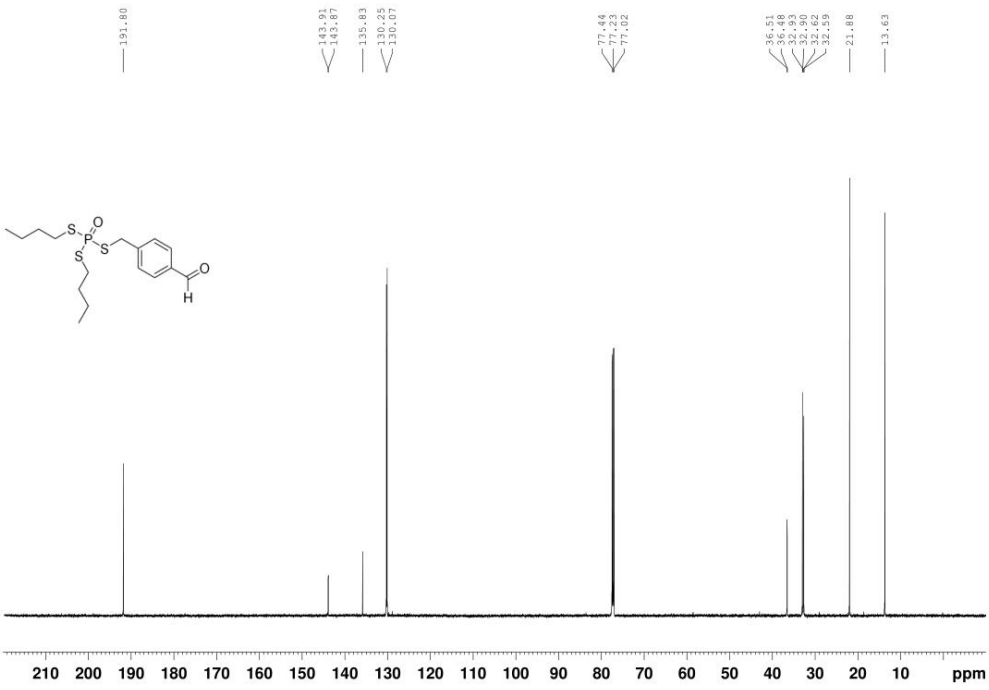
9


63.79
400
300
200
100
0
−100
−200
−300
−400
ppm

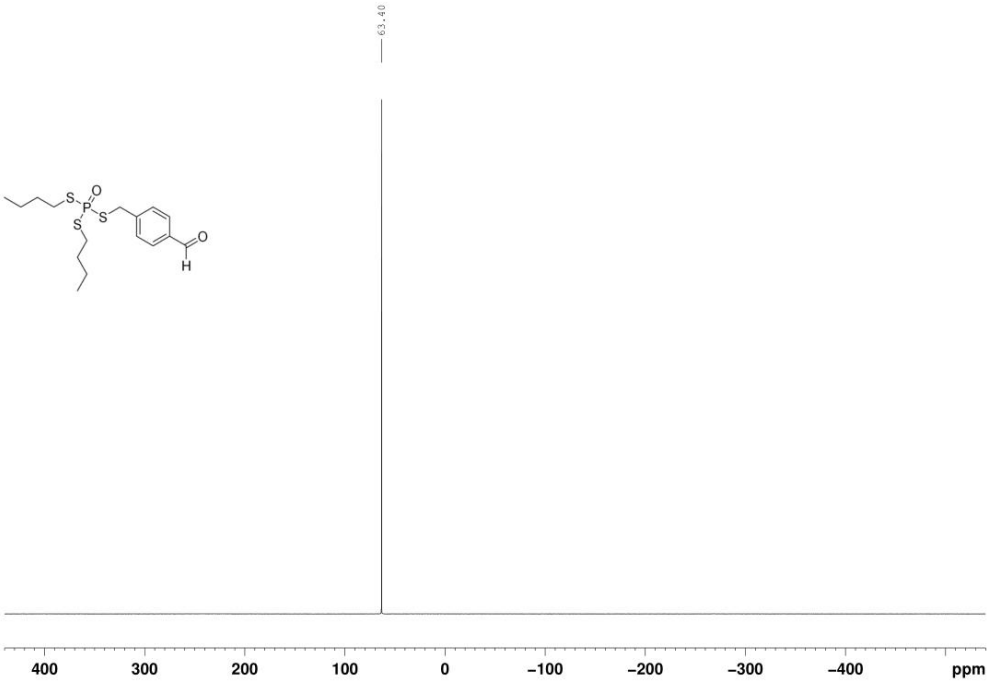
10


10.004
7.858
7.845
7.572
7.559
4.250
4.227
2.998
2.986
2.974
2.961
2.949
1.736
1.724
1.712
1.699
1.687
1.450
1.438
1.425
1.413
1.401
1.388
0.936
0.924
0.911
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
1.99
1.90
1.97
3.98
4.00
4.01
6.00

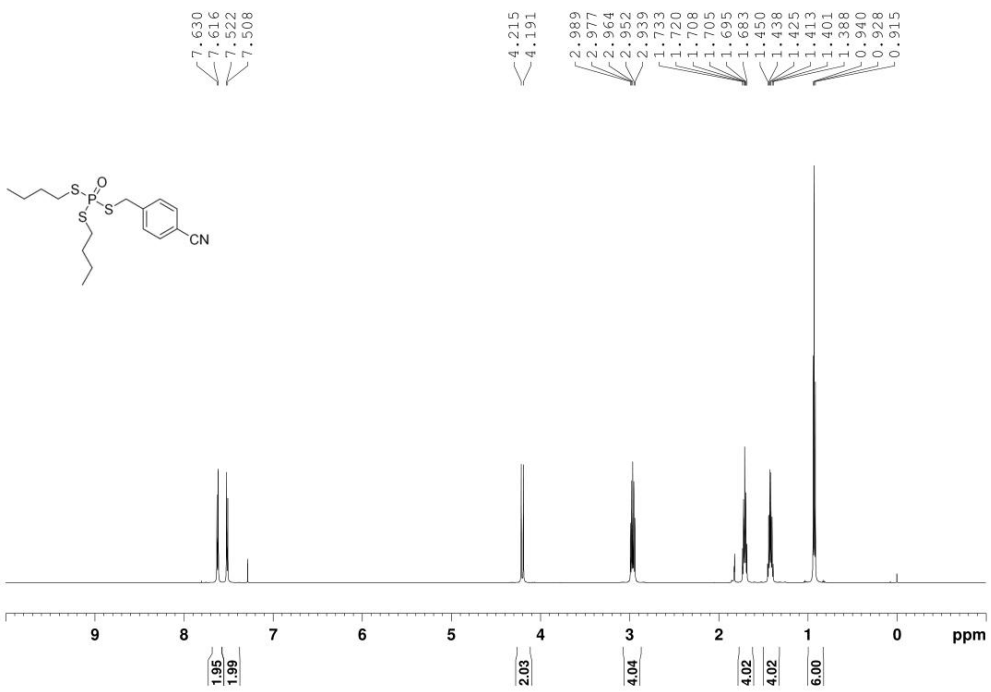
10


191.80
143.91
143.87
135.83
130.25
130.07
77.44
77.23
77.02
36.51
36.48
32.93
32.90
32.62
32.59
21.88
13.63
O
S
P
S
S
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

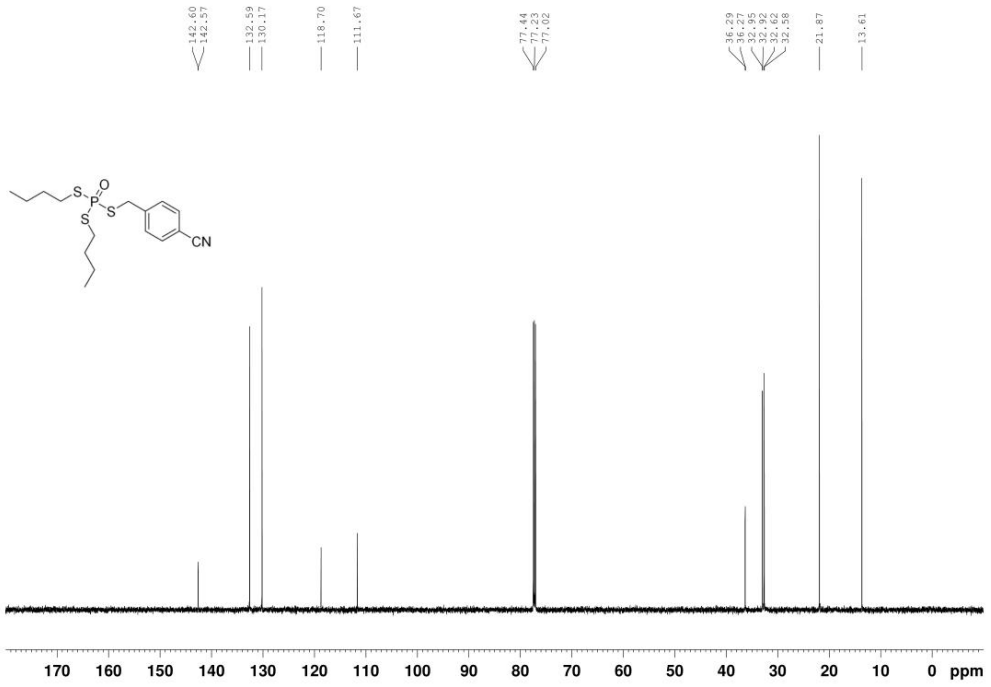
10


63.40
O
S
P
S
S
O
H
400 300 200 100 0 −100 −200 −300 −400 ppm

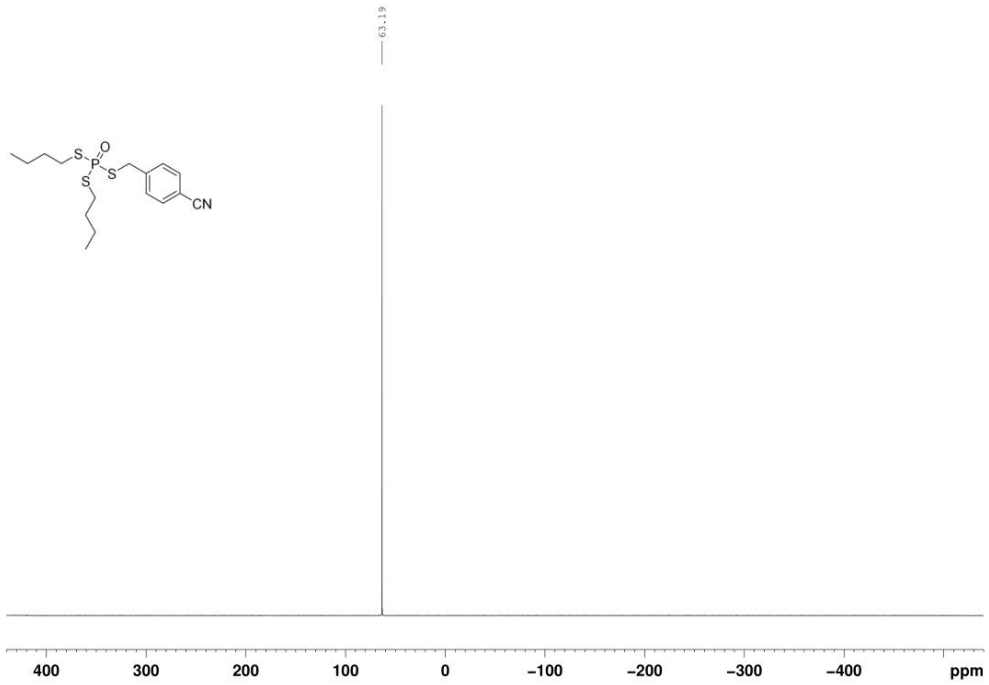
11


7.630
7.616
7.522
7.508
4.215
4.191
2.989
2.977
2.964
2.952
2.939
1.733
1.720
1.708
1.705
1.695
1.683
1.450
1.438
1.425
1.413
1.401
1.388
0.940
0.928
0.915
CN
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.99
2.03
4.04
4.02
4.02
6.00

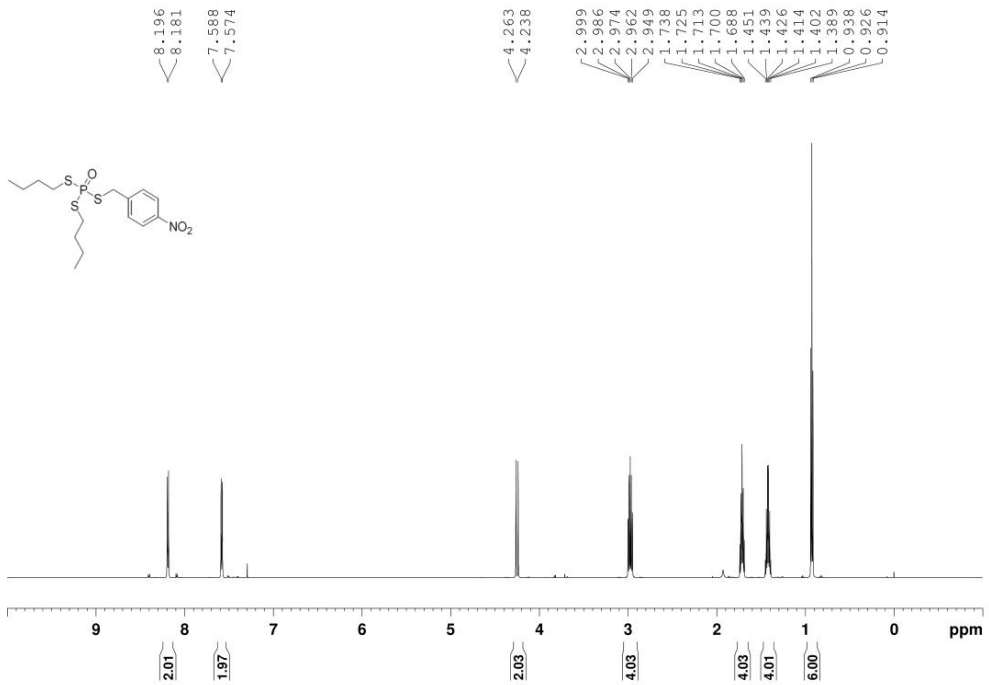
11


142.60
142.57
132.59
130.17
118.70
111.67
77.44
77.23
77.02
36.29
36.27
32.95
32.92
32.62
32.58
21.87
13.61
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

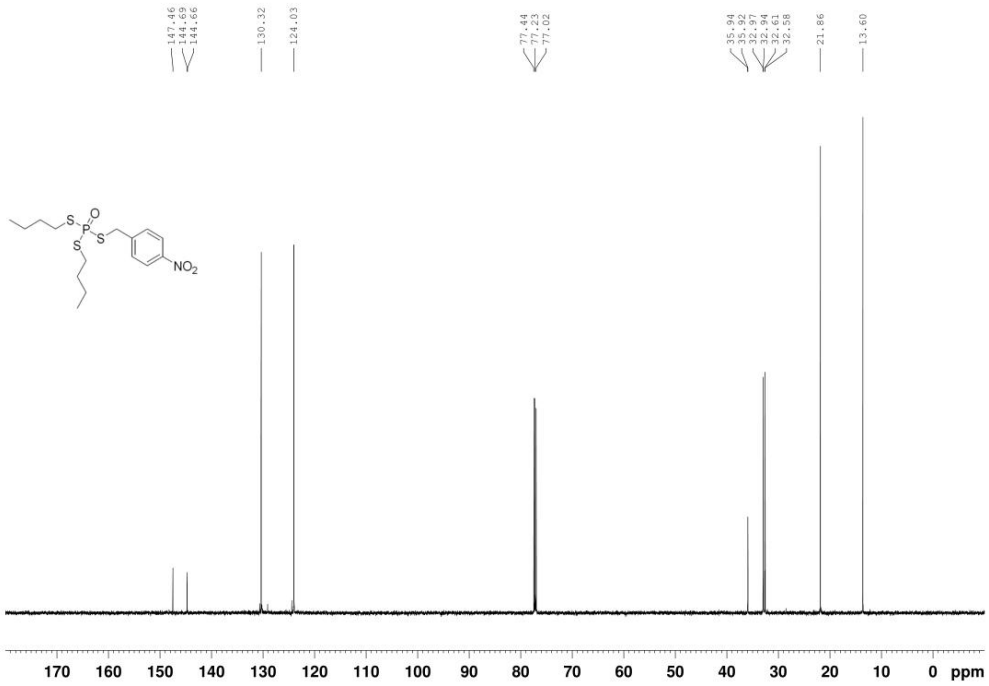
11


63.19
CN
400
300
200
100
0
−100
−200
−300
−400
ppm

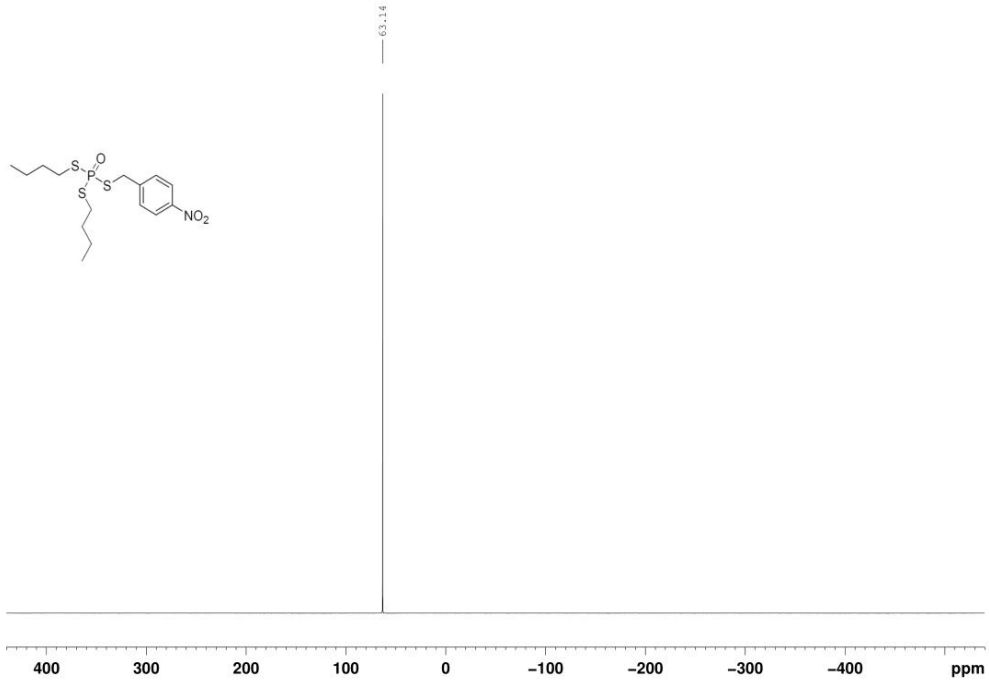
12


8.196
8.181
7.588
7.574
4.263
4.238
2.999
2.986
2.974
2.962
2.949
1.738
1.725
1.713
1.700
1.688
1.451
1.439
1.426
1.414
1.402
1.389
0.938
0.926
0.914
NO2
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.97
2.03
4.03
4.03
4.01
6.00

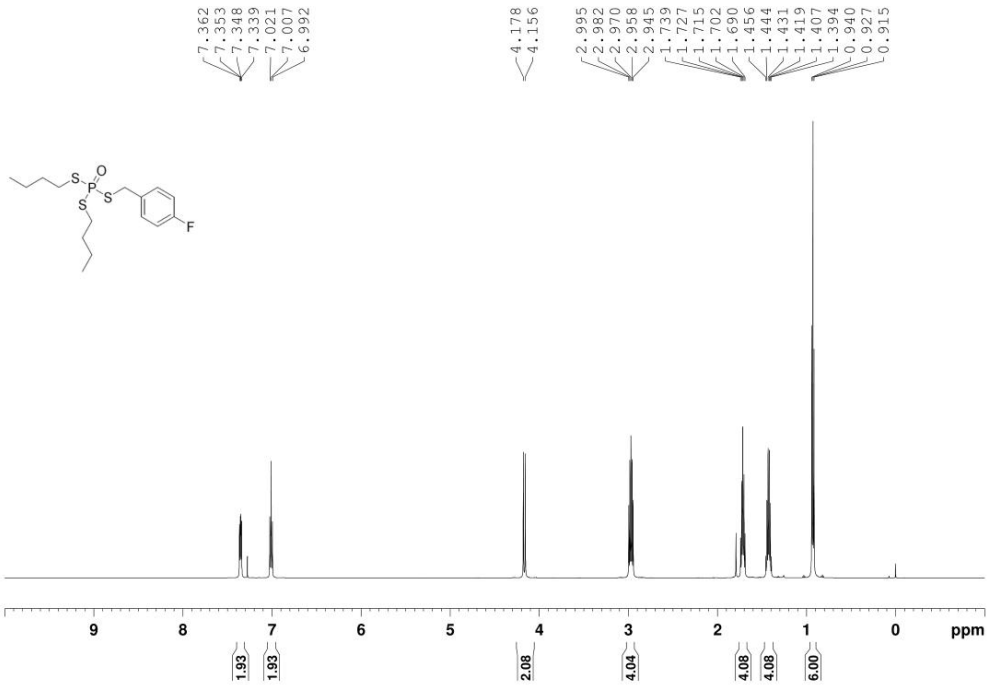
12


147.46
144.69
144.66
130.32
124.03
77.44
77.23
77.02
35.94
35.92
32.97
32.84
32.61
32.58
21.86
13.60
NO2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

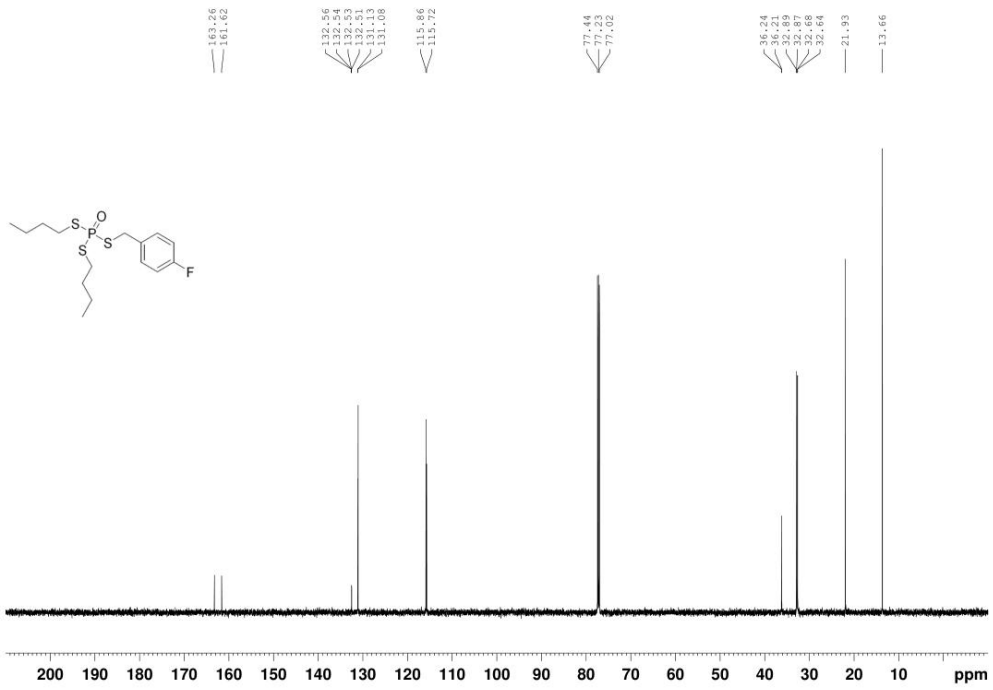
12


63.14
NO2
400 300 200 100 0 −100 −200 −300 −400 ppm

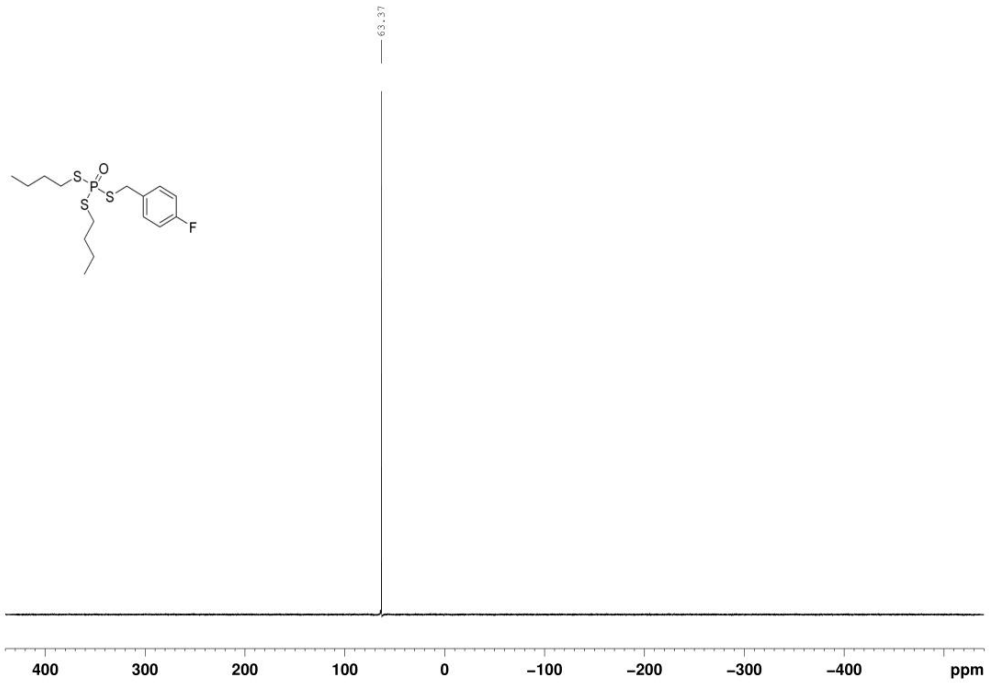
13


7.362
7.353
7.348
7.339
7.021
7.007
6.992
4.178
4.156
2.995
2.982
2.970
2.958
2.945
1.739
1.727
1.715
1.702
1.690
1.456
1.444
1.431
1.419
1.407
1.394
0.940
0.927
0.915
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.93
2.08
4.04
4.08
4.08
6.00

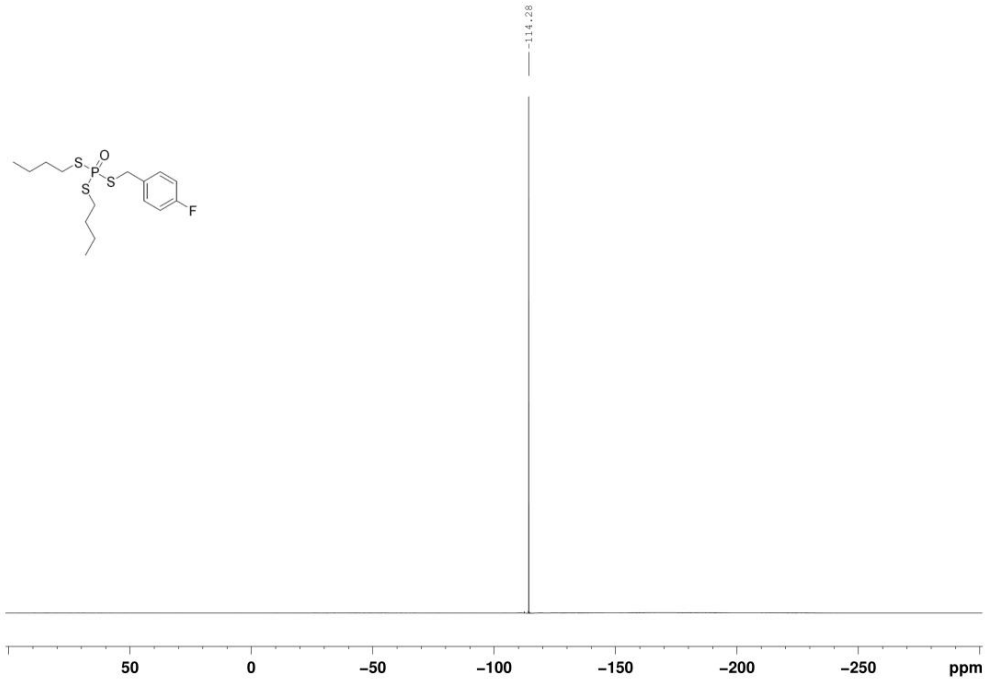
13


163.26
161.62
132.56
132.54
132.53
132.51
131.13
131.08
115.86
115.72
77.44
77.23
77.02
36.24
36.21
32.89
32.87
32.68
32.64
21.93
13.66
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

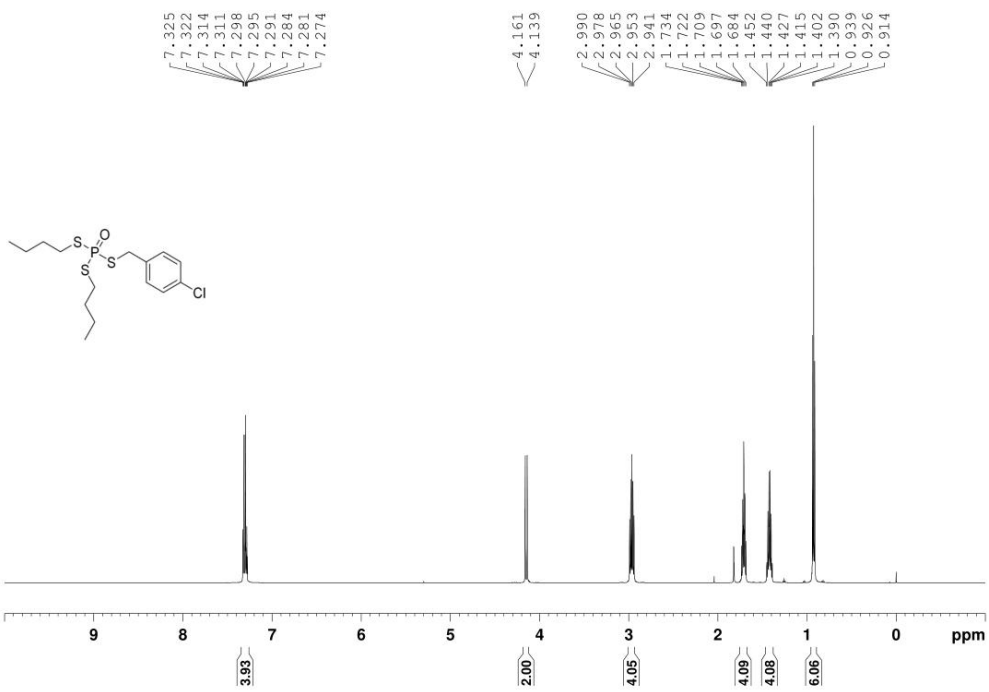
13


63.37
400
300
200
100
0
−100
−200
−300
−400
ppm

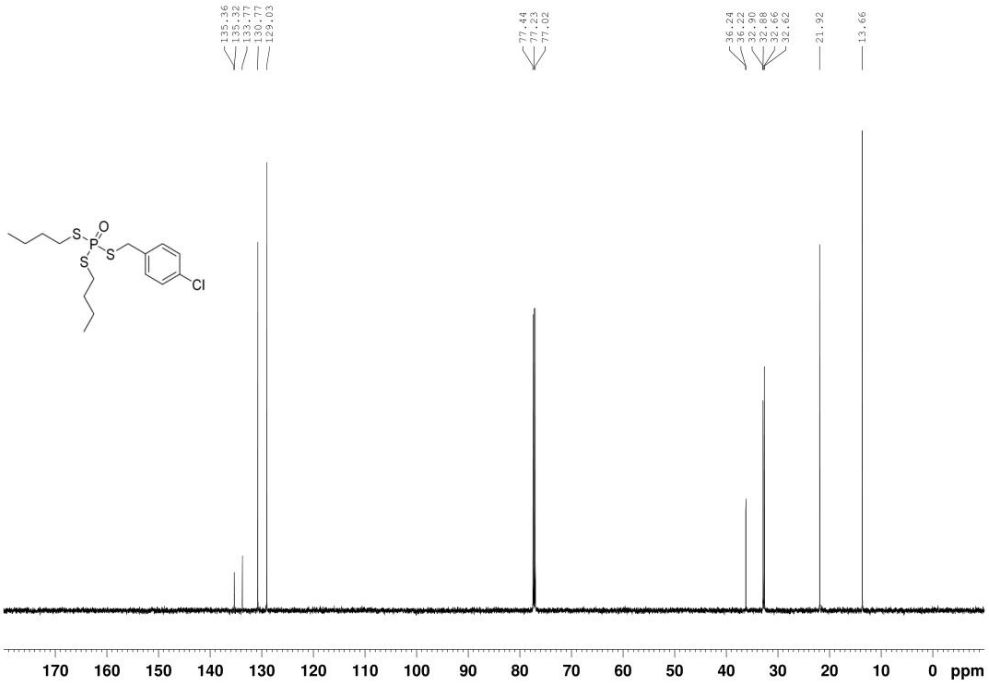
13


-114.28
50
0
−50
−100
−150
−200
−250
ppm

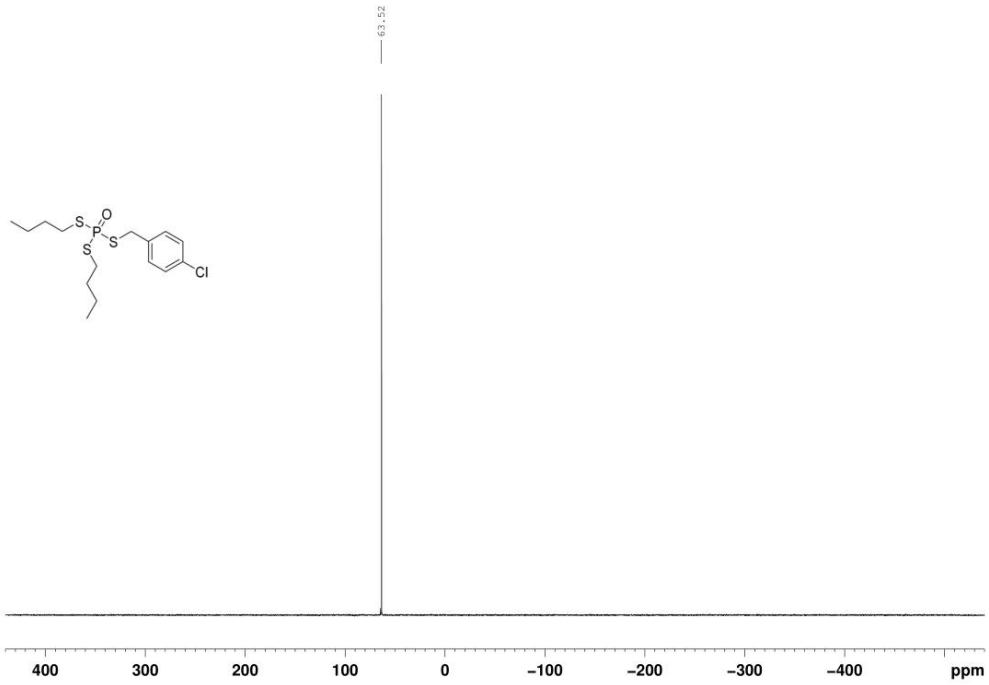
14


7.325
7.322
7.314
7.311
7.298
7.295
7.291
7.284
7.281
7.274
4.161
4.139
2.990
2.978
2.965
2.953
2.941
1.734
1.722
1.709
1.697
1.684
1.452
1.440
1.427
1.415
1.402
1.390
0.939
0.926
0.914
Cl
9
8
7
6
5
4
3
2
1
0
ppm
3.93
2.00
4.05
4.09
4.08
6.06

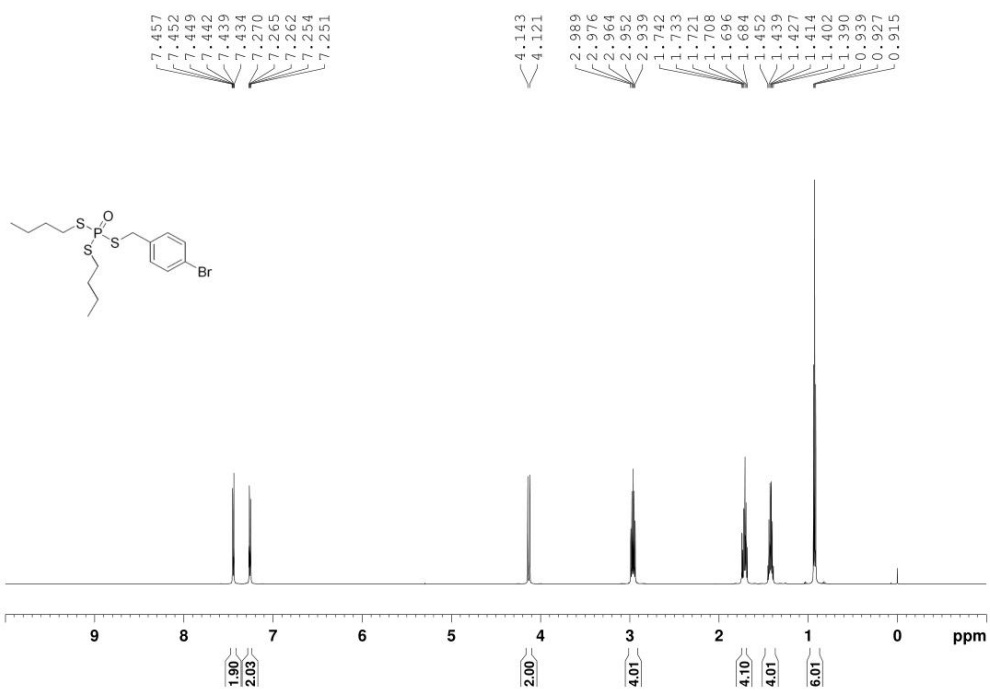
14


135.36
135.32
133.77
130.77
129.03
77.44
77.23
77.02
36.24
36.22
32.90
32.88
32.66
32.62
21.92
13.66
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

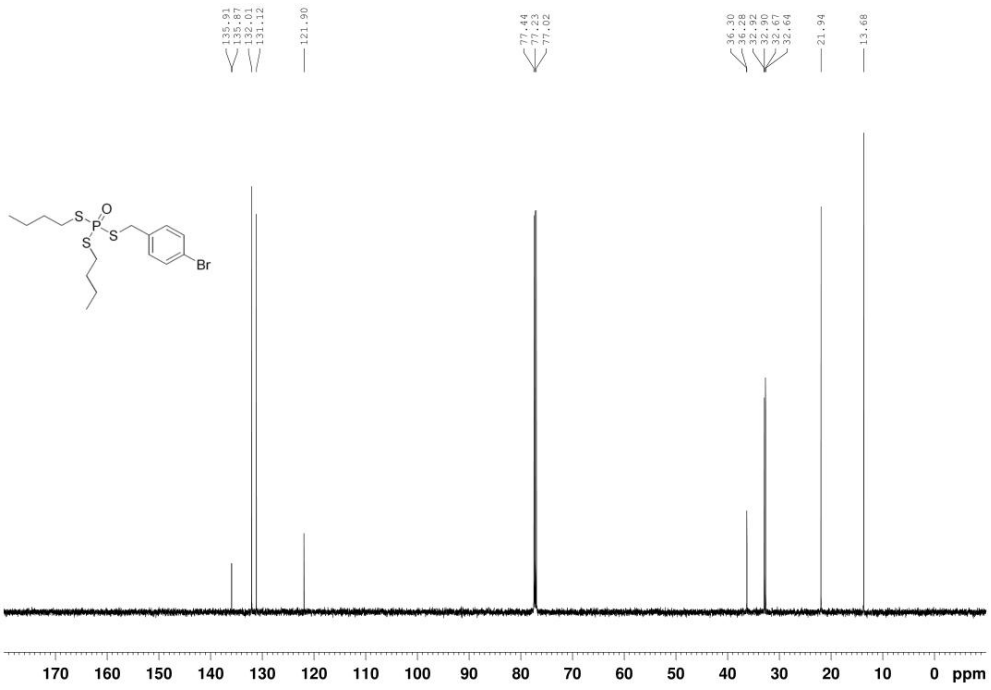
14


63.52
Cl
400
300
200
100
0
−100
−200
−300
−400
ppm

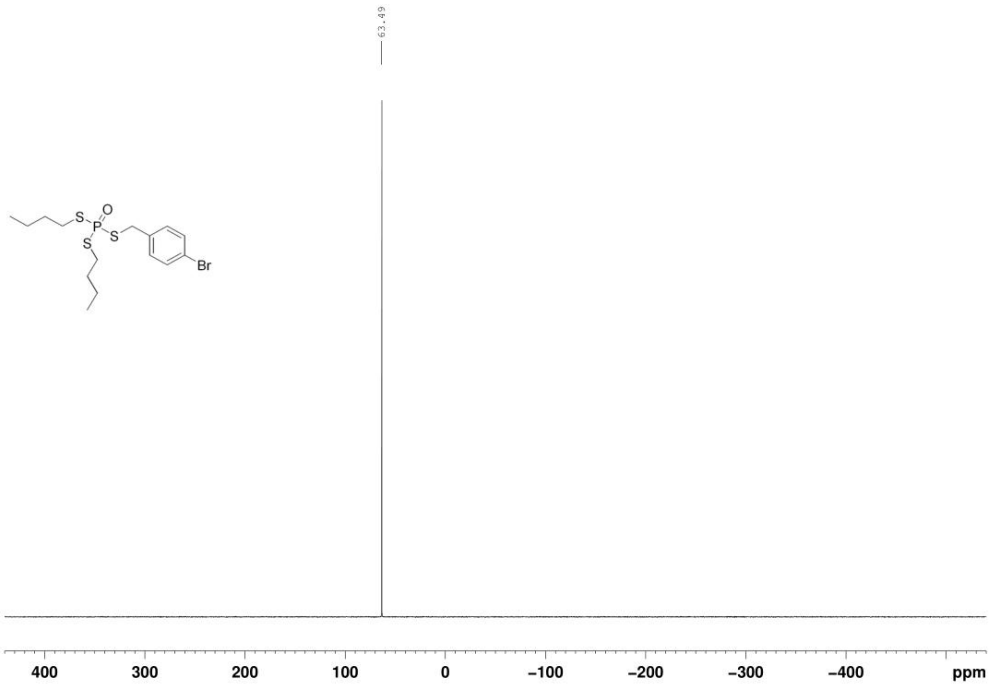
15


7.457
7.452
7.449
7.442
7.439
7.434
7.270
7.265
7.262
7.254
7.251
4.143
4.121
2.989
2.976
2.964
2.952
2.939
1.742
1.733
1.721
1.708
1.696
1.684
1.452
1.439
1.427
1.414
1.402
1.390
0.939
0.927
0.915
Br
9
8
7
6
5
4
3
2
1
0
ppm
1.90
2.03
2.00
4.01
4.10
4.01
6.01

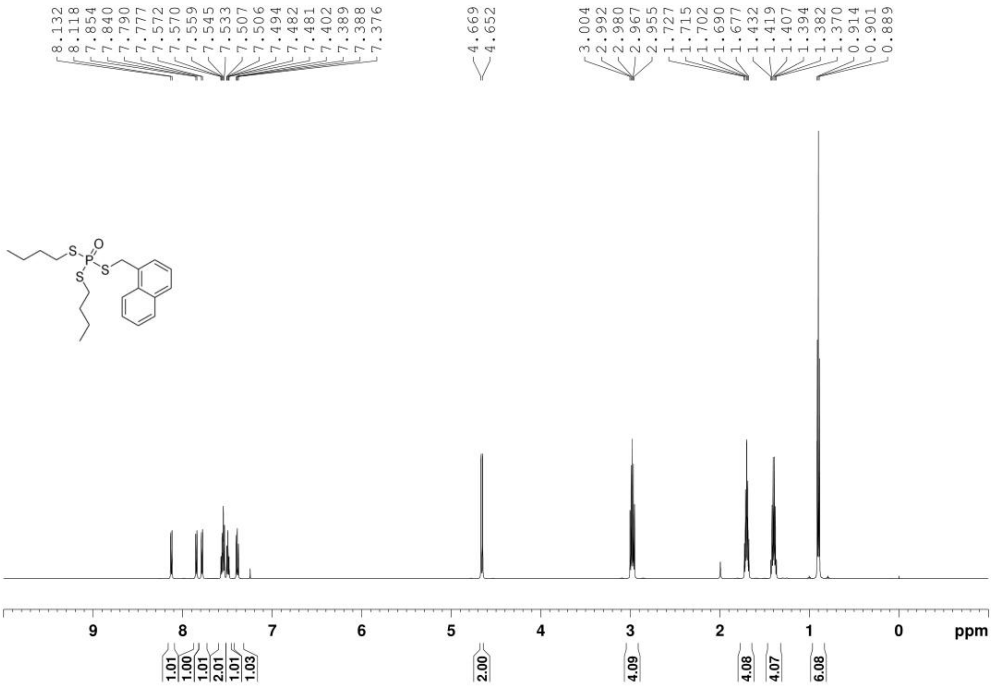
15


135.91
135.87
132.01
131.12
121.90
77.44
77.23
77.02
36.30
36.28
32.92
32.90
32.67
32.64
21.94
13.68
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

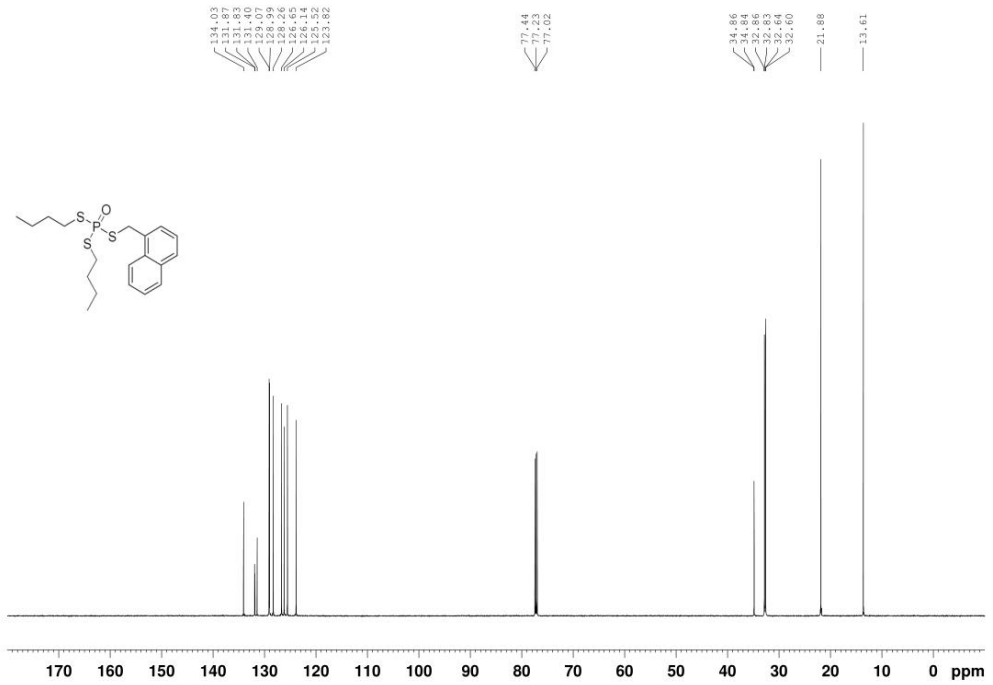
15


63.49
Br
400 300 200 100 0 −100 −200 −300 −400 ppm

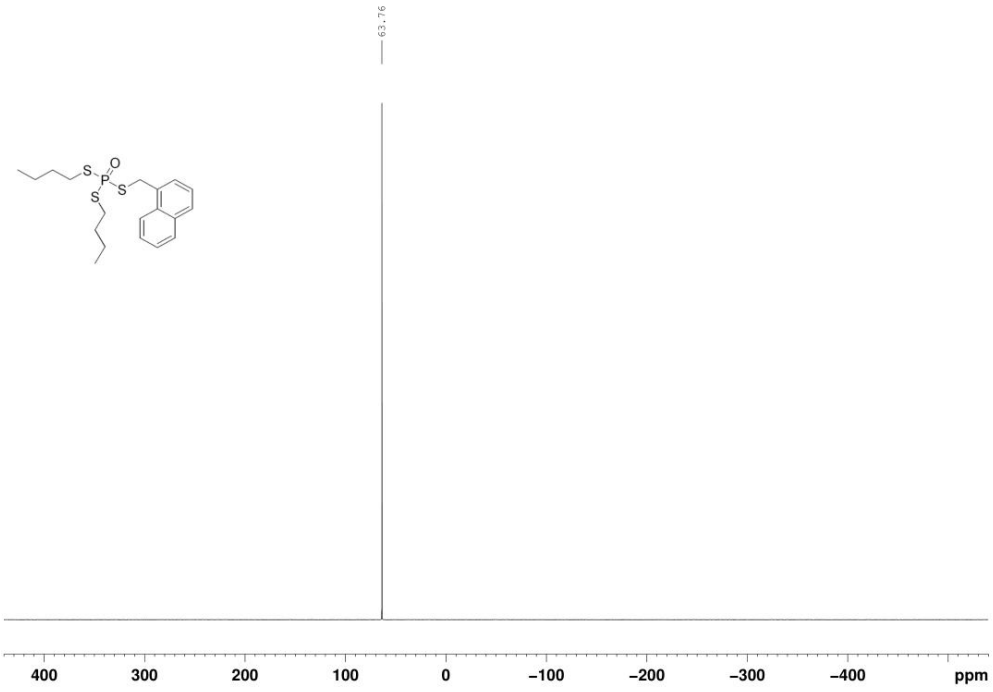
16


8.132
8.118
7.854
7.840
7.790
7.777
7.572
7.570
7.559
7.545
7.533
7.507
7.506
7.494
7.482
7.481
7.402
7.389
7.388
7.376
4.669
4.652
3.004
2.992
2.980
2.967
2.955
1.727
1.715
1.702
1.690
1.677
1.432
1.419
1.407
1.394
1.382
1.370
0.914
0.901
0.889
ppm
1.01
1.00
1.01
2.01
1.01
1.03
2.00
4.09
4.08
4.07
6.08

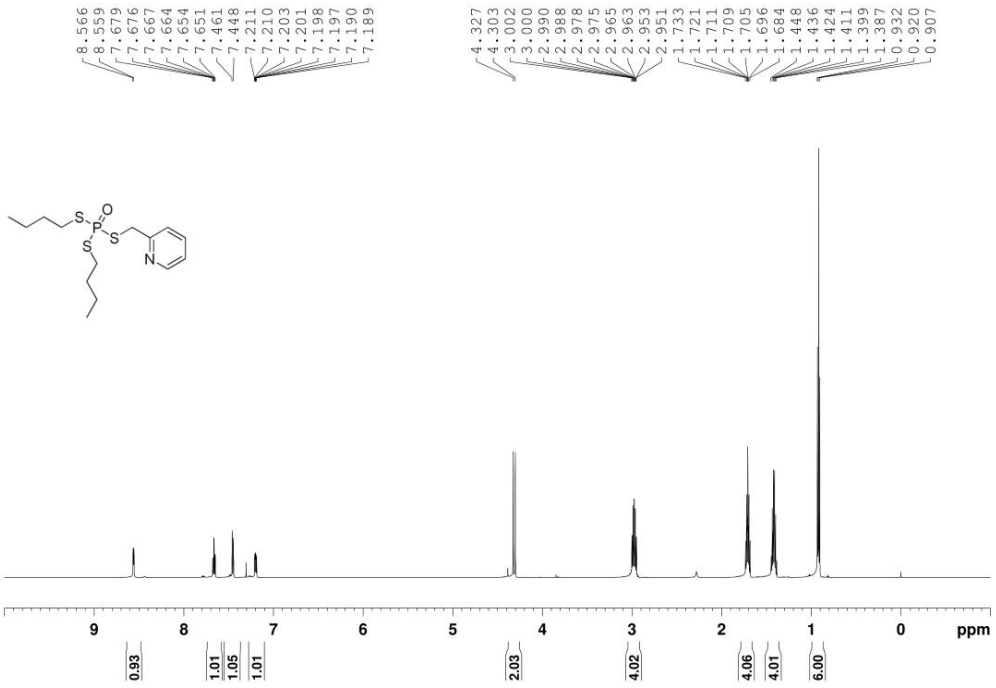
16


134.03
131.87
131.83
131.40
129.07
128.99
128.26
126.65
126.14
125.52
123.82
77.44
77.23
77.02
34.86
34.84
32.86
32.83
32.64
32.60
21.88
13.61
ppm

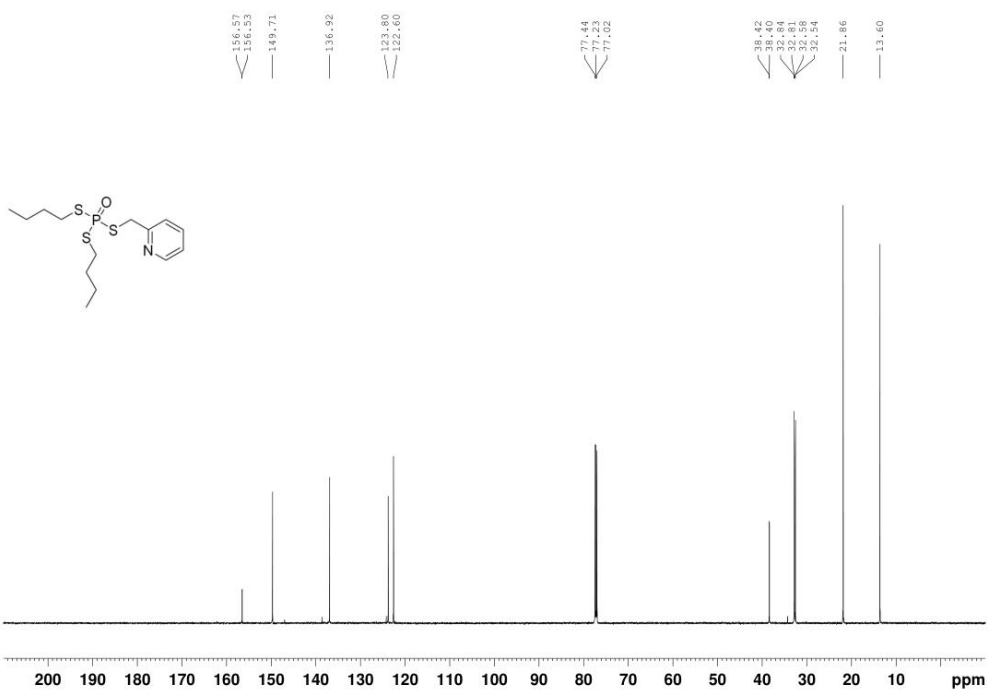
16


63.76
400
300
200
100
0
−100
−200
−300
−400
ppm

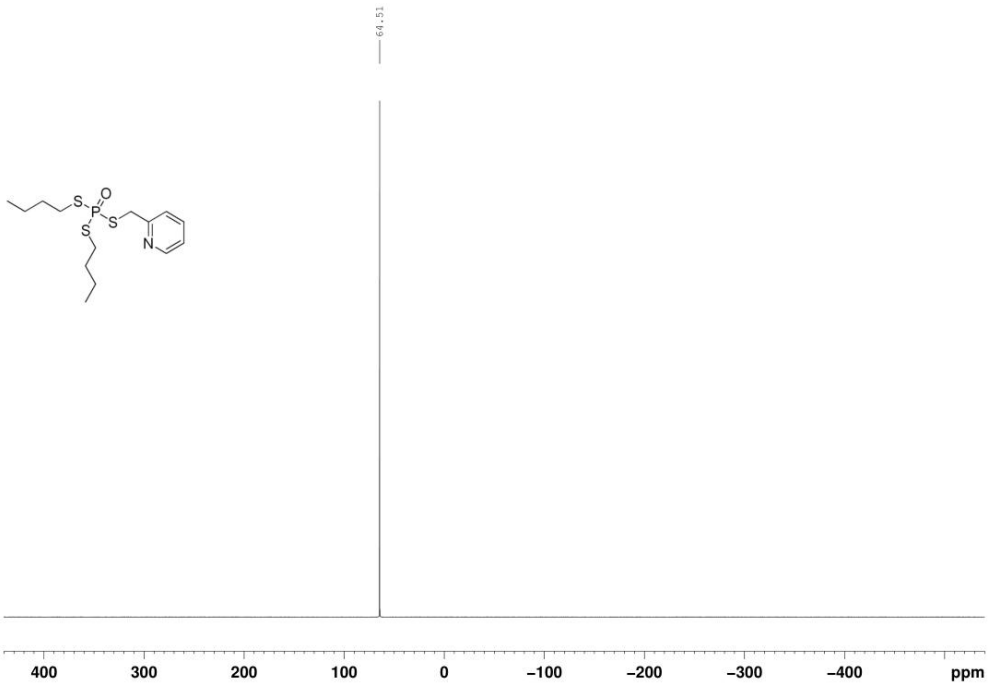
17


8.566
8.559
7.679
7.676
7.667
7.664
7.654
7.651
7.461
7.448
7.211
7.210
7.203
7.201
7.198
7.197
7.190
7.189
4.327
4.303
3.002
3.000
2.990
2.988
2.978
2.975
2.965
2.963
2.953
2.951
1.733
1.721
1.711
1.709
1.705
1.696
1.684
1.448
1.436
1.424
1.411
1.399
1.387
0.932
0.920
0.907
9
8
7
6
5
4
3
2
1
0
ppm
0.93
1.01
1.05
1.01
2.03
4.02
4.06
4.01
6.00

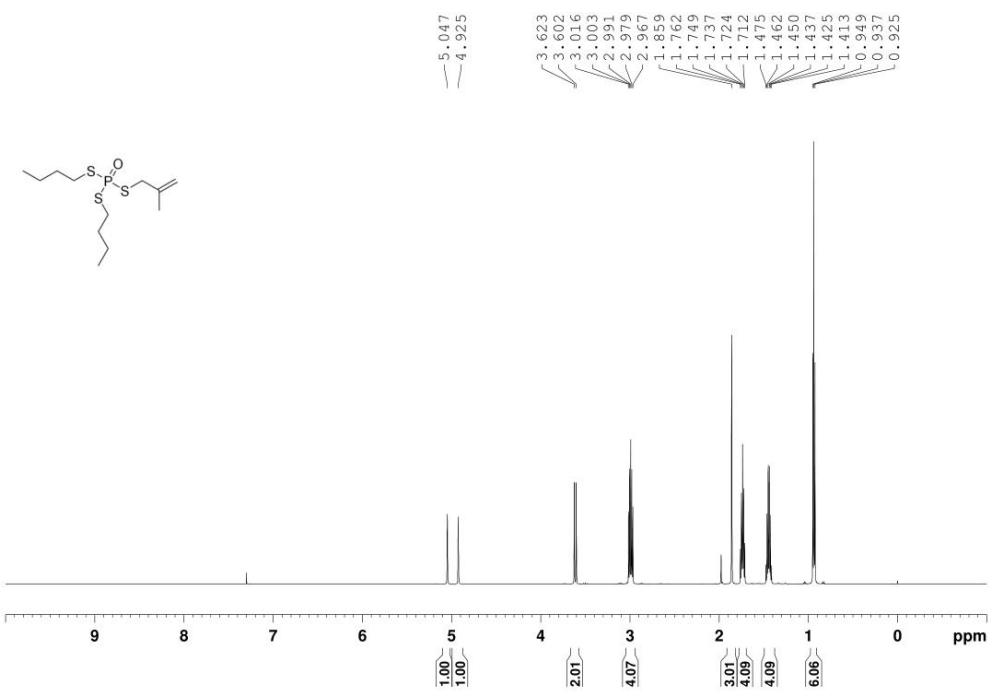
17


156.57
156.53
149.71
136.92
123.80
122.60
77.44
77.23
77.02
38.42
38.40
32.84
32.81
32.58
32.54
21.86
13.60
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

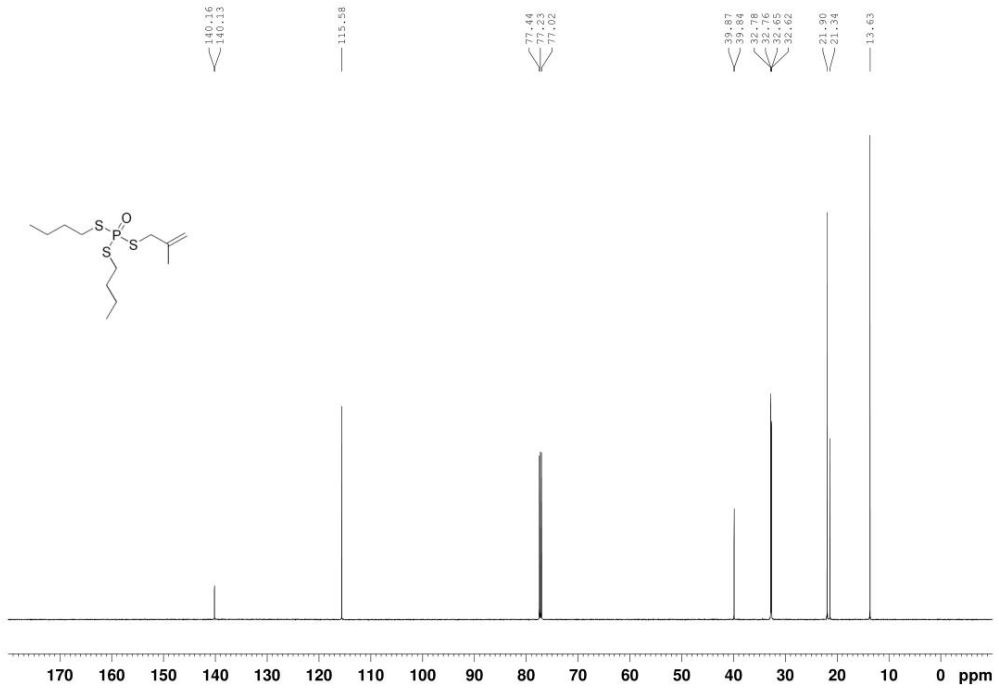
17


64.51
400 300 200 100 0 −100 −200 −300 −400 ppm

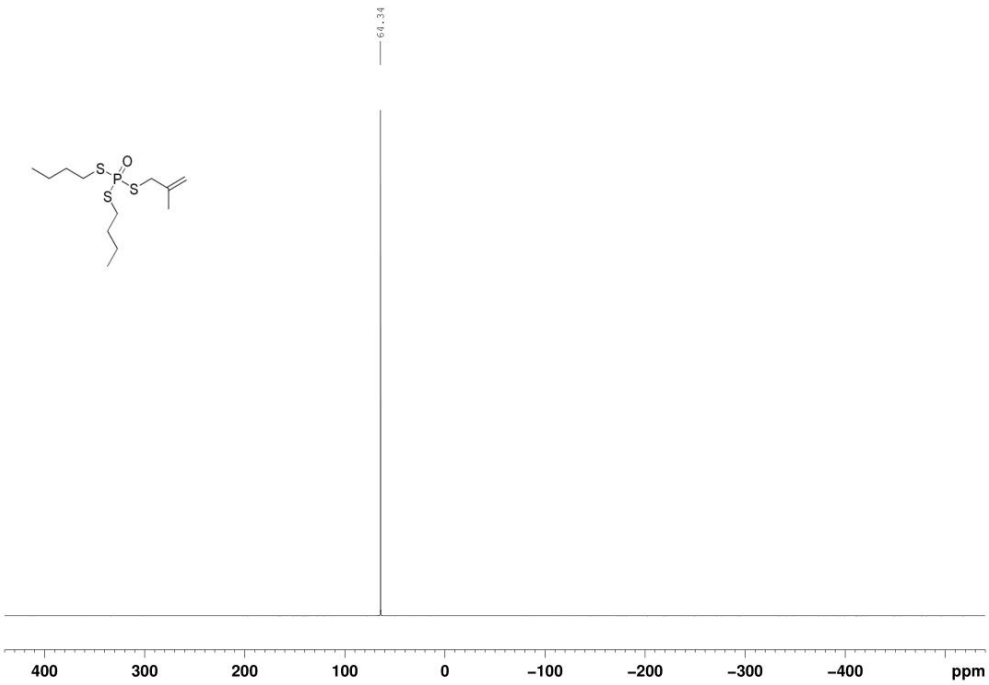
18


5.047
4.925
3.623
3.602
3.016
3.003
2.991
2.979
2.967
1.859
1.762
1.749
1.737
1.724
1.712
1.475
1.462
1.450
1.437
1.425
1.413
0.949
0.937
0.925
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
2.01
4.07
3.01
4.09
4.09
6.06

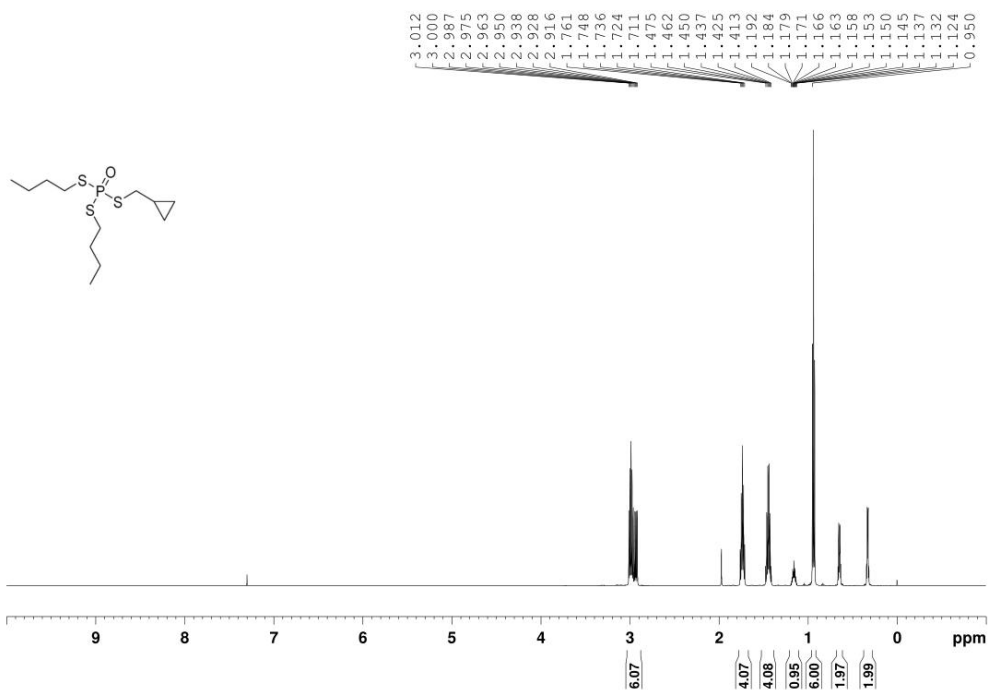
18


140.16
140.13
115.58
77.44
77.23
77.02
39.87
39.84
32.78
32.76
32.65
32.62
21.90
21.54
13.63
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

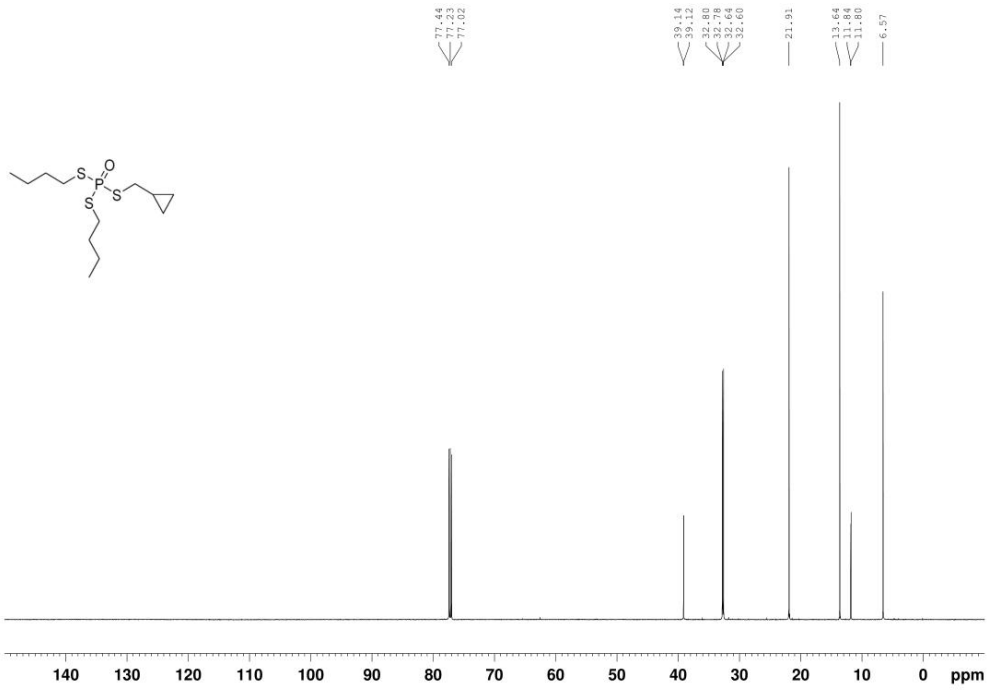
18


64.34
400
300
200
100
0
−100
−200
−300
−400
ppm

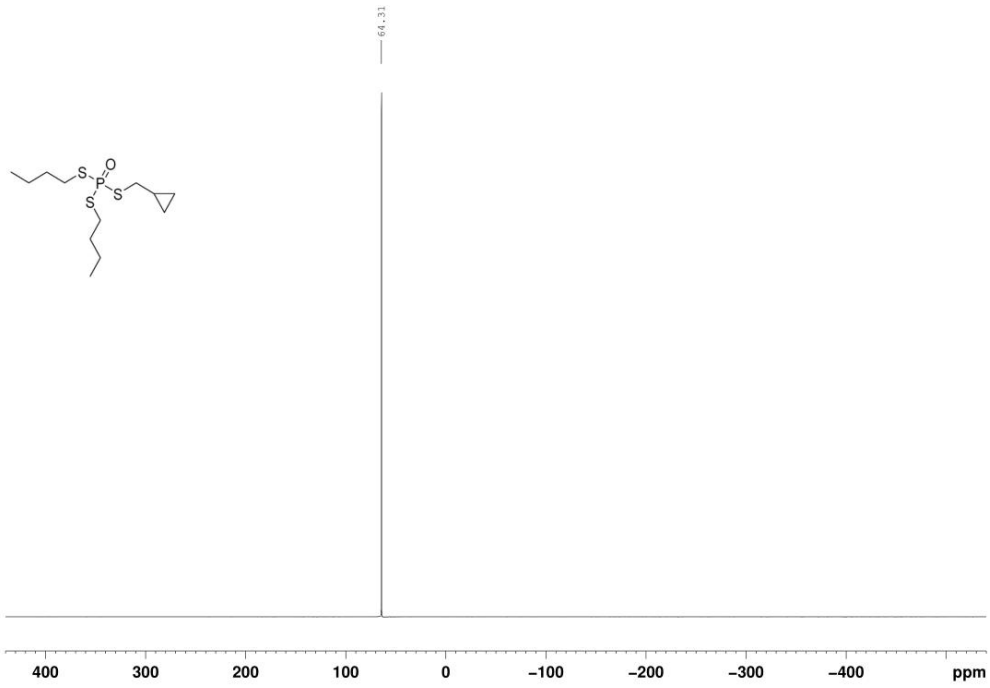
19


3.012
3.000
2.987
2.975
2.963
2.950
2.938
2.928
2.916
1.761
1.748
1.736
1.724
1.711
1.475
1.462
1.450
1.437
1.425
1.413
1.192
1.184
1.179
1.171
1.166
1.163
1.158
1.153
1.150
1.145
1.137
1.132
1.124
0.950
9
8
7
6
5
4
3
2
1
0
ppm
6.07
4.07
4.08
0.95
6.00
1.97
1.99

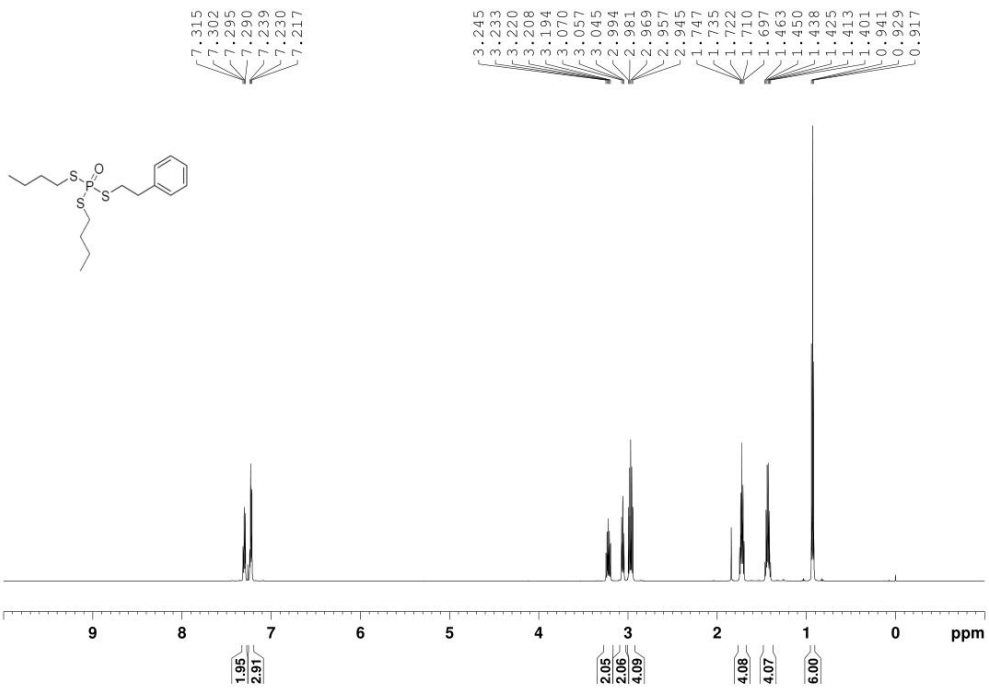
19


77.44
77.23
77.02
39.14
39.12
32.80
32.78
32.64
32.60
21.91
13.64
11.84
11.80
6.57
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

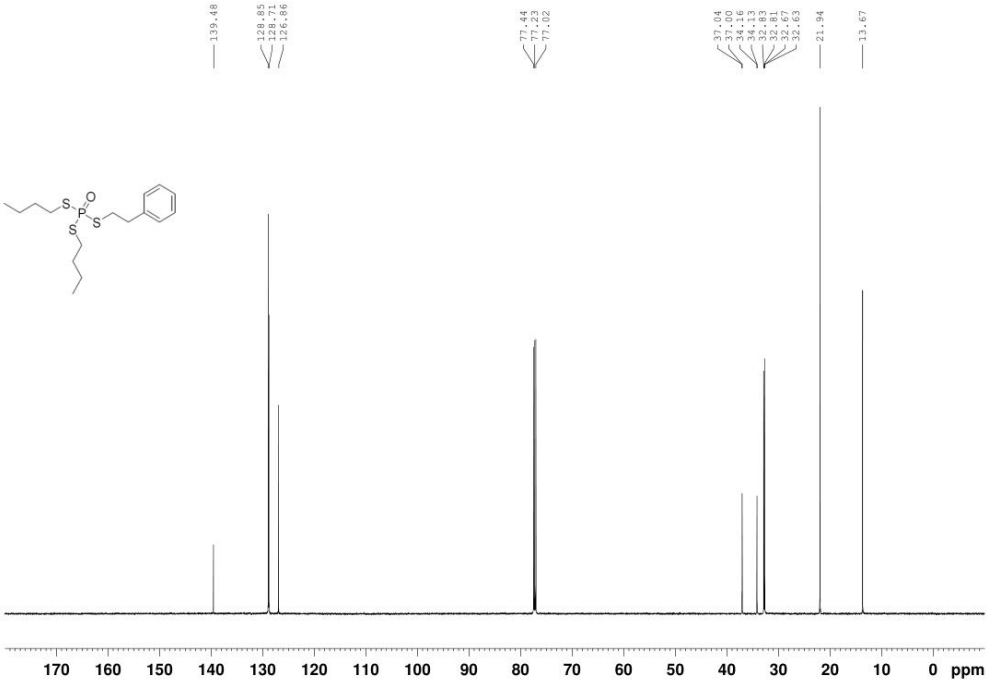
19


64.31
400
300
200
100
0
−100
−200
−300
−400
ppm

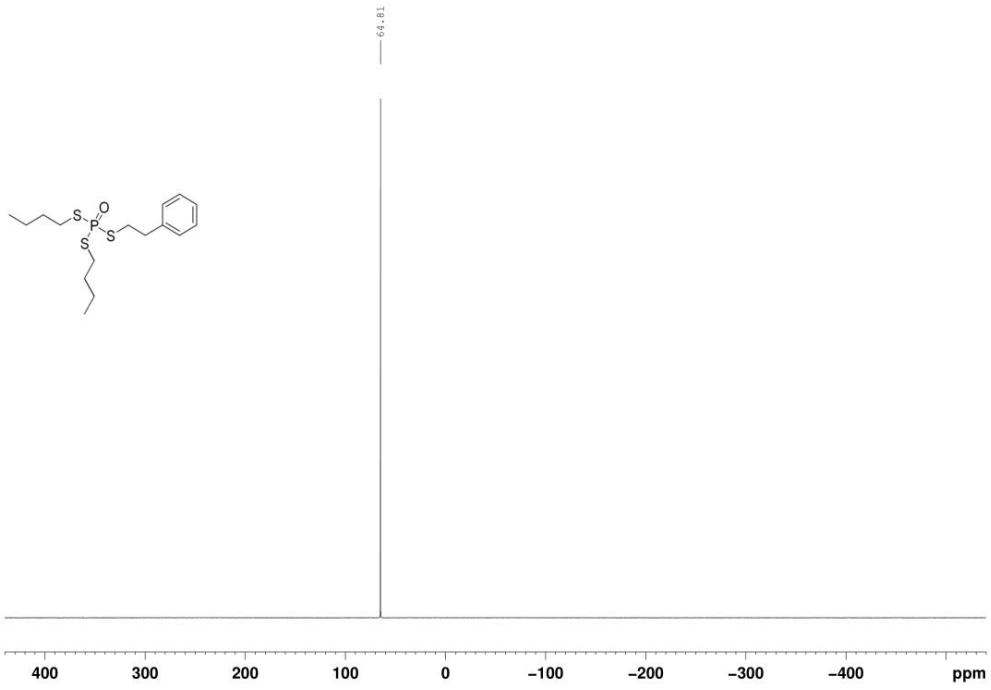
20


7.315
7.302
7.295
7.290
7.239
7.230
7.217
3.245
3.233
3.220
3.208
3.194
3.070
3.057
3.045
2.994
2.981
2.969
2.957
2.945
1.747
1.735
1.722
1.710
1.697
1.463
1.450
1.438
1.425
1.413
1.401
0.941
0.929
0.917
9
8
7
6
5
4
3
2
1
0
ppm
1.95
2.91
2.05
2.06
4.09
4.08
4.07
6.00

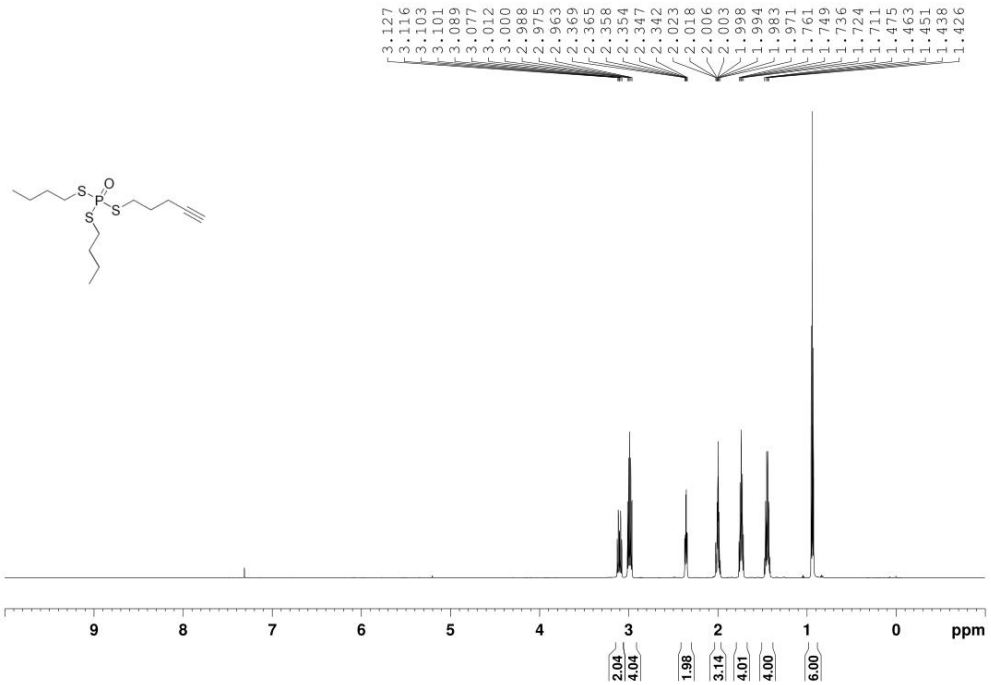
20


139.48
128.85
128.71
126.86
77.44
77.23
77.02
37.04
37.00
34.16
33.13
32.83
32.81
32.67
32.63
21.94
13.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

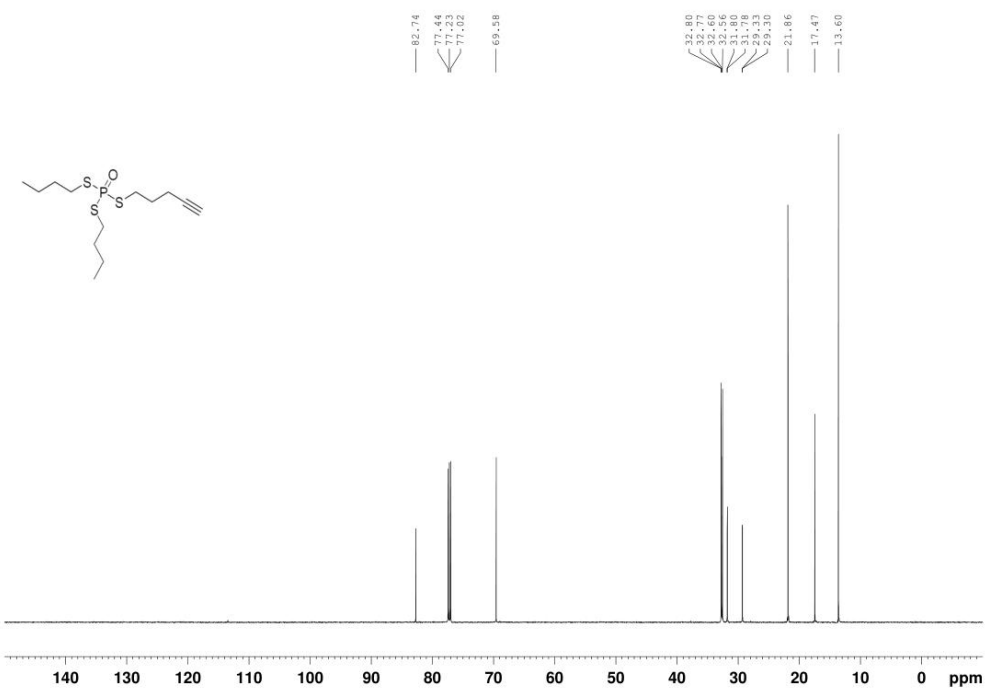
20


64.81
400
300
200
100
0
−100
−200
−300
−400
ppm

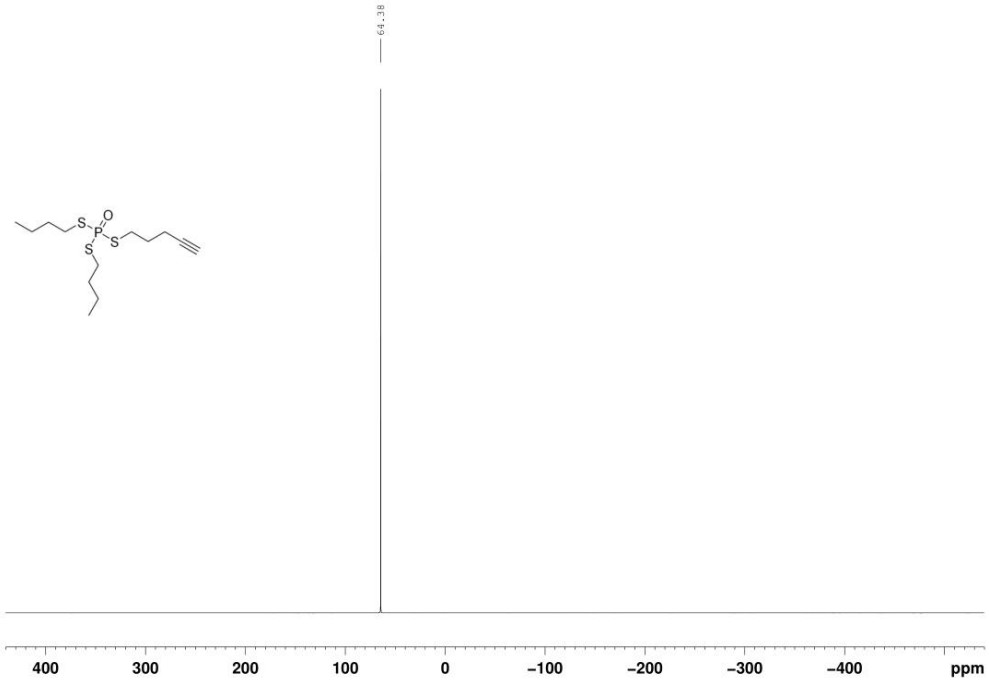
21


3.127
3.116
3.103
3.101
3.089
3.077
3.012
3.000
2.988
2.975
2.963
2.369
2.365
2.358
2.354
2.347
2.342
2.023
2.018
2.006
2.003
1.998
1.994
1.983
1.971
1.761
1.749
1.736
1.724
1.711
1.475
1.463
1.451
1.438
1.426
9
8
7
6
5
4
3
2
1
0
ppm
2.04
4.04
1.98
3.14
4.01
4.00
6.00

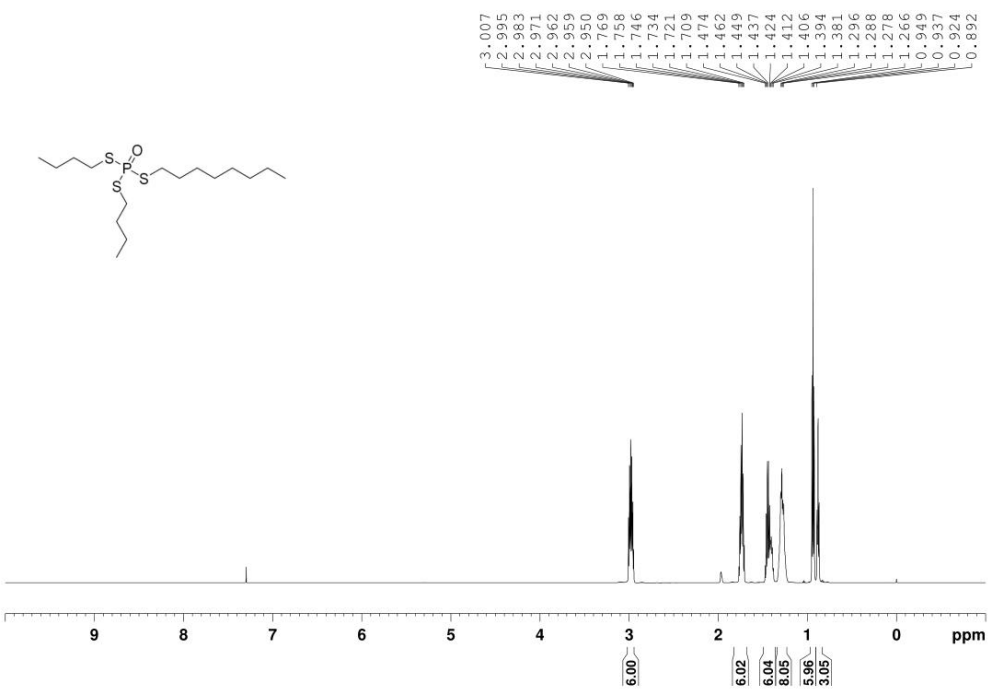
21


82.74
77.44
77.23
77.02
69.58
32.80
32.77
32.60
32.56
31.80
31.78
29.33
29.30
21.86
17.47
13.60
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

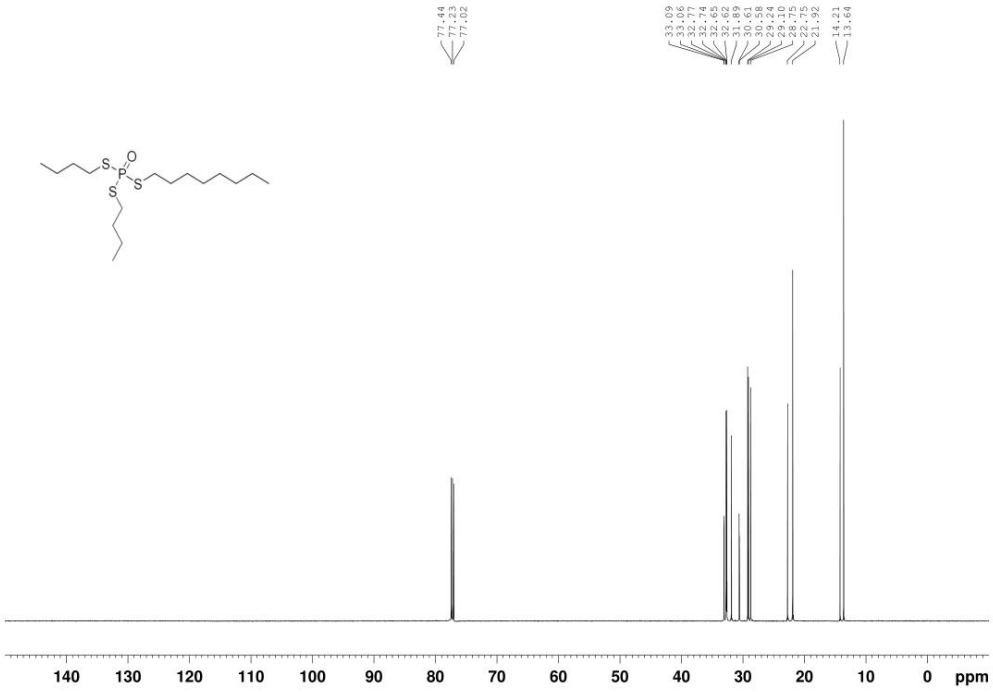
21


64.38
400
300
200
100
0
−100
−200
−300
−400
ppm

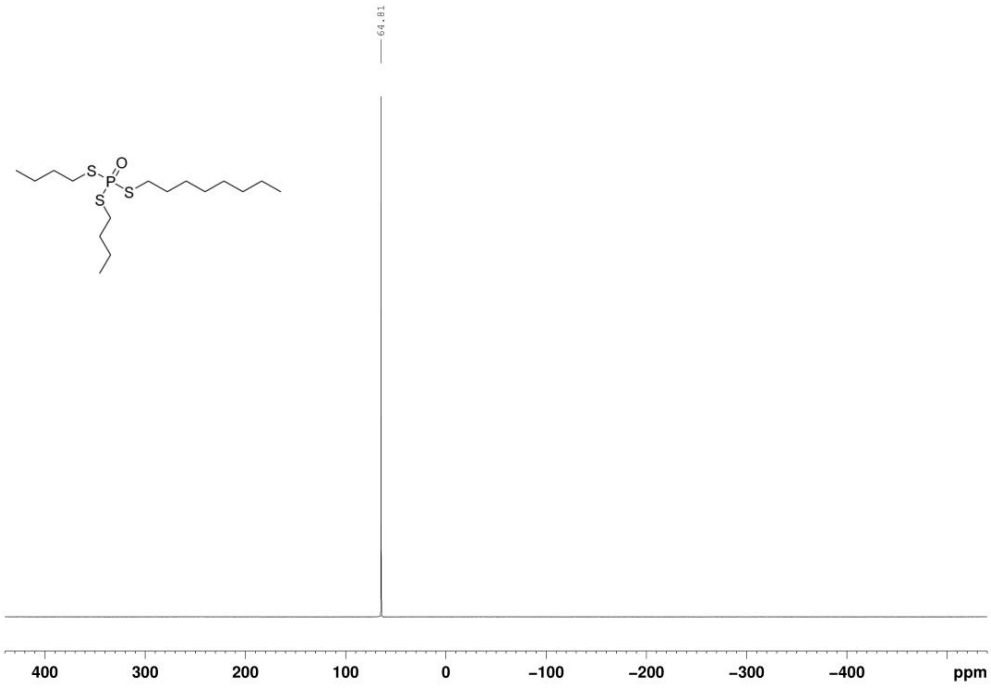
22


3.007
2.995
2.983
2.971
2.962
2.959
2.950
1.769
1.758
1.746
1.734
1.721
1.709
1.474
1.462
1.449
1.437
1.424
1.412
1.406
1.394
1.381
1.296
1.288
1.278
1.266
0.949
0.937
0.924
0.892
9
8
7
6
5
4
3
2
1
0
ppm
6.00
6.02
6.04
8.05
5.96
3.05

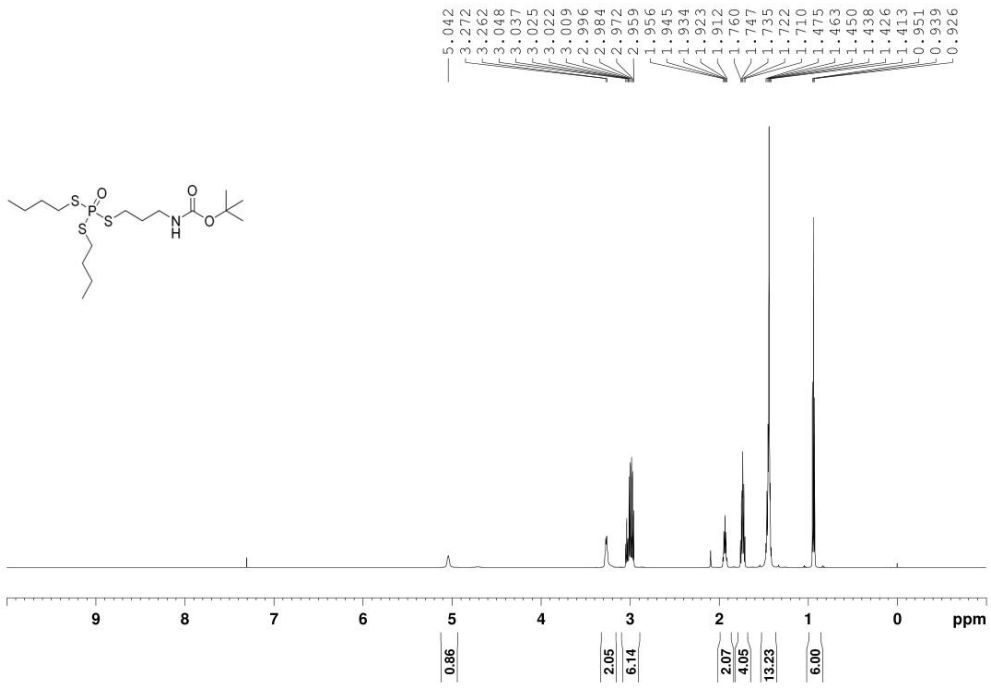
22


77.44
77.23
77.02
33.09
33.06
32.77
32.74
32.65
32.62
31.89
30.61
30.58
29.24
29.10
28.75
22.75
21.92
14.21
13.64
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

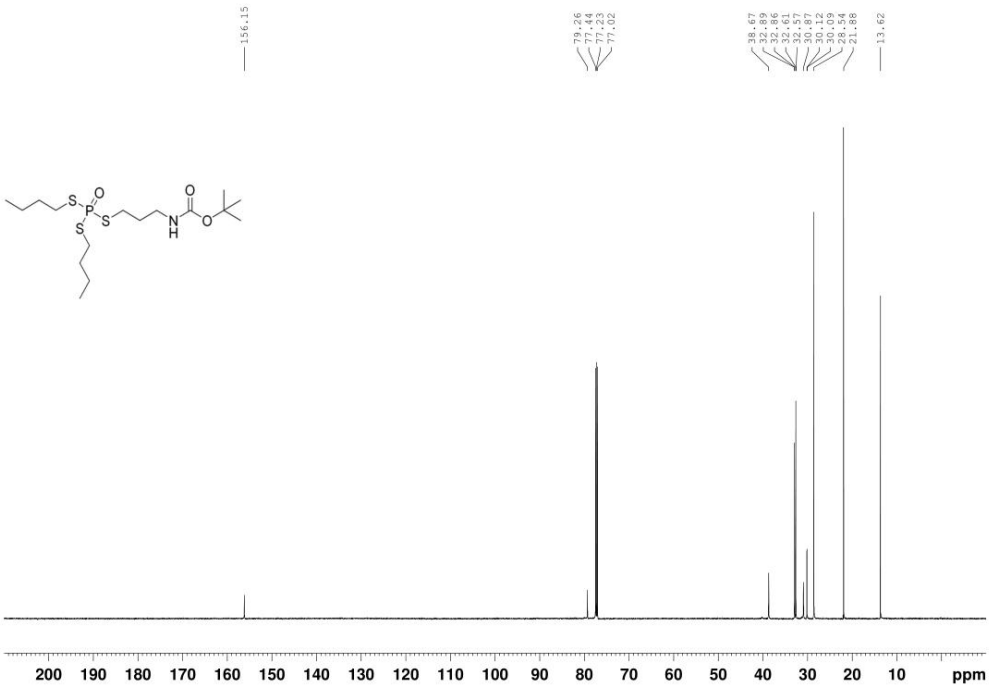
22


64.81
400
300
200
100
0
−100
−200
−300
−400
ppm

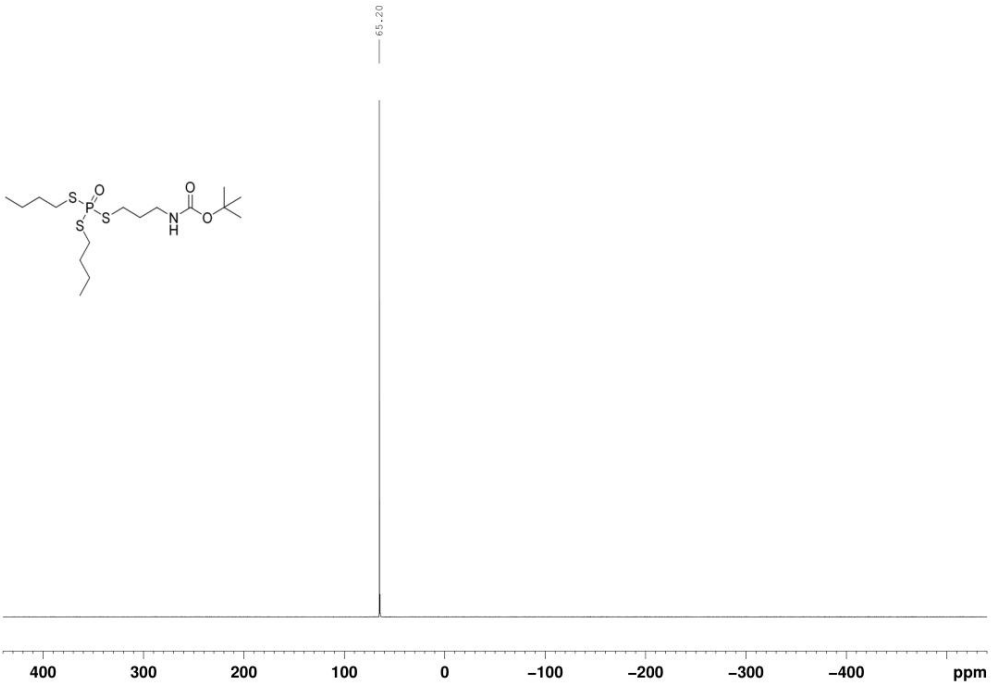
23


5.042
3.272
3.262
3.048
3.037
3.025
3.022
3.009
2.996
2.984
2.972
2.959
1.956
1.945
1.934
1.923
1.912
1.760
1.747
1.735
1.722
1.710
1.475
1.463
1.450
1.438
1.426
1.413
0.951
0.939
0.926
9
8
7
6
5
4
3
2
1
0
ppm
0.86
2.05
6.14
2.07
4.05
13.23
6.00

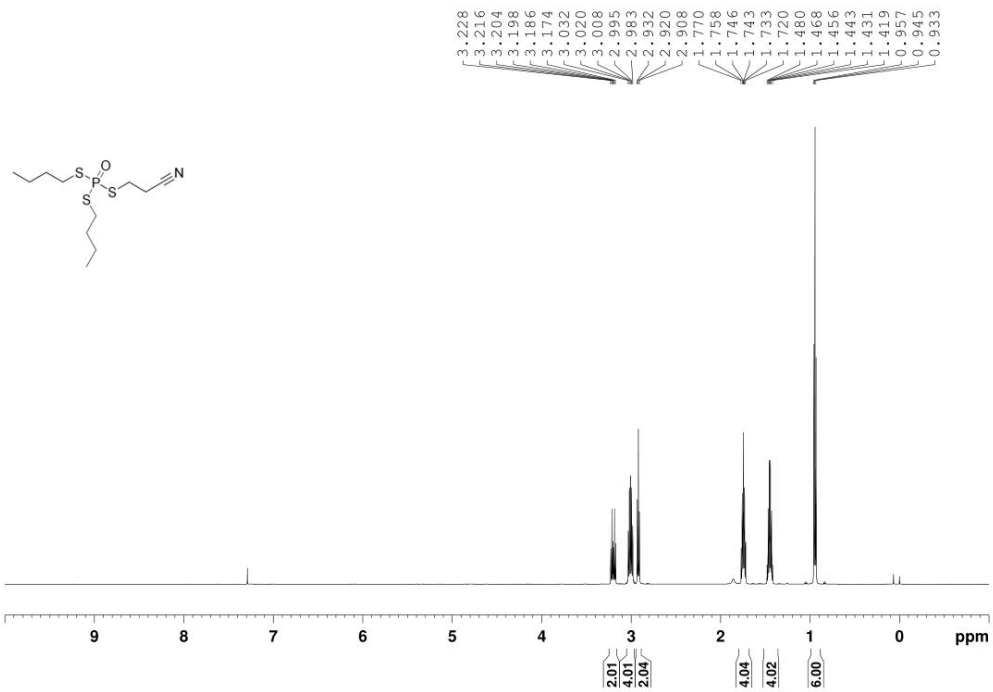
23


156.15
79.26
77.44
77.23
77.02
38.67
32.89
32.86
32.61
32.57
30.97
30.72
30.09
28.54
21.88
13.62
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

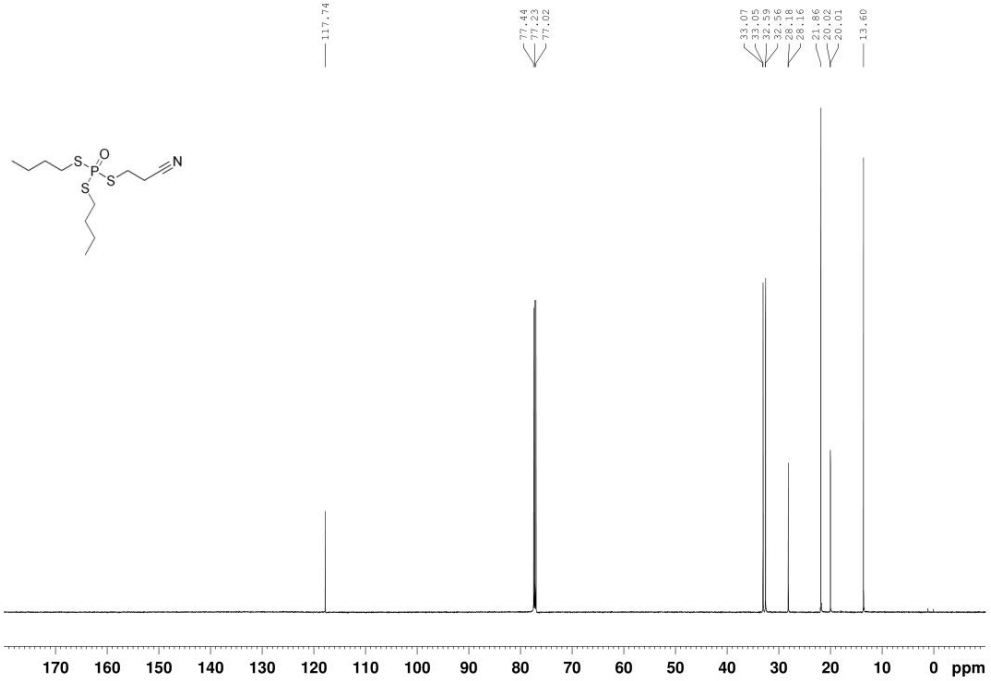
23


65.20
400 300 200 100 0 −100 −200 −300 −400 ppm

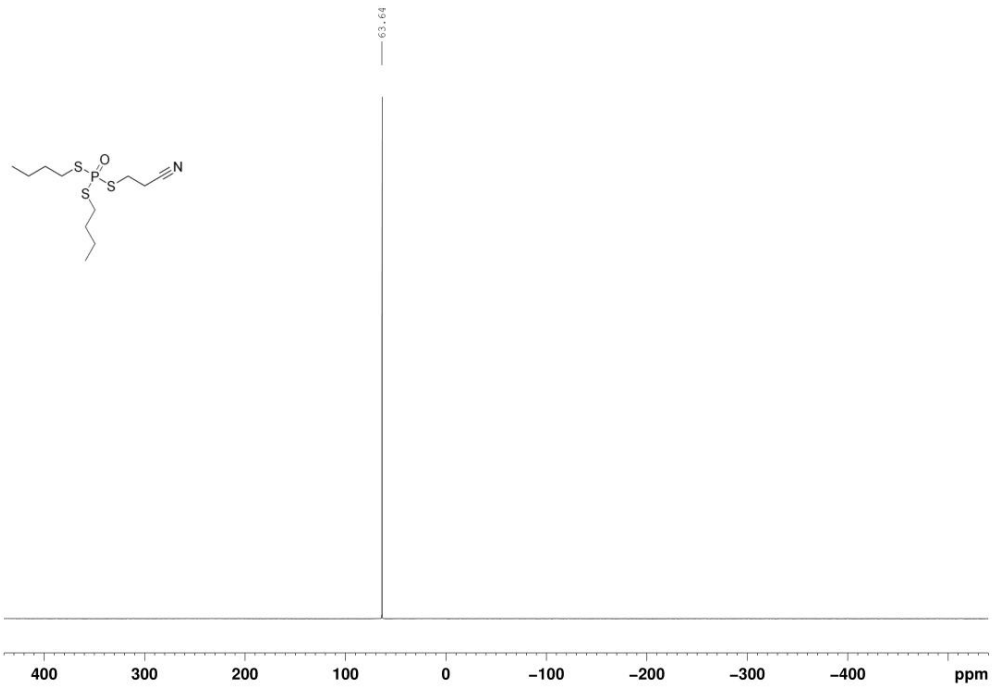
24


3.228
3.216
3.204
3.198
3.186
3.174
3.032
3.020
3.008
2.995
2.983
2.932
2.920
2.908
1.770
1.758
1.746
1.743
1.733
1.720
1.480
1.468
1.456
1.443
1.431
1.419
0.957
0.945
0.933
9
8
7
6
5
4
3
2
1
0
ppm
2.01
4.01
2.04
4.04
4.02
6.00

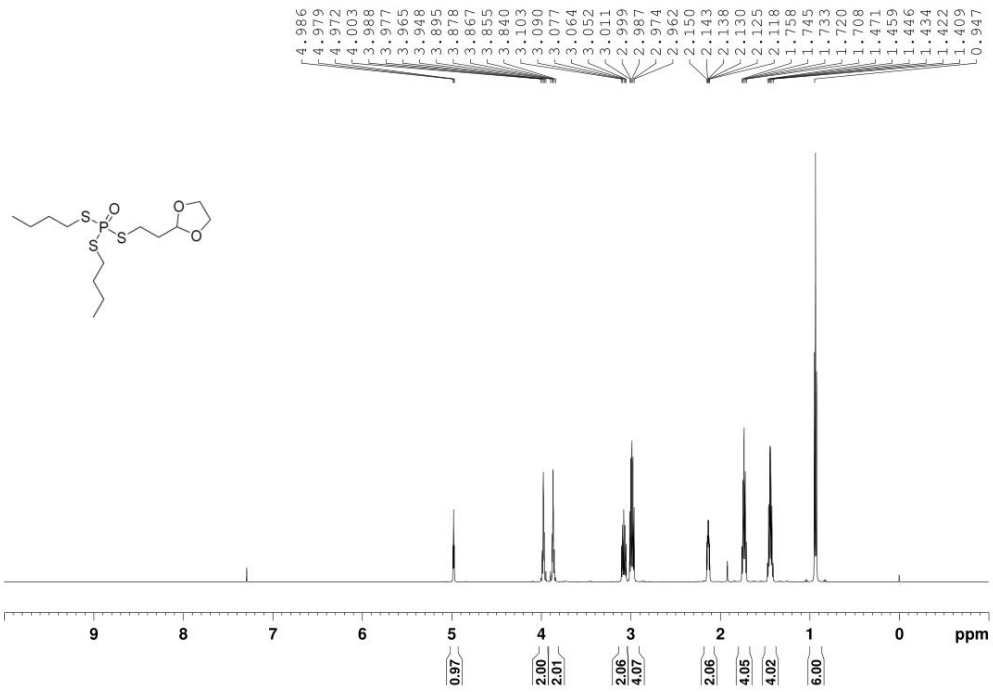
24


117.74
77.44
77.23
77.02
33.07
33.05
32.59
32.56
28.18
28.16
21.86
20.02
20.01
13.60
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

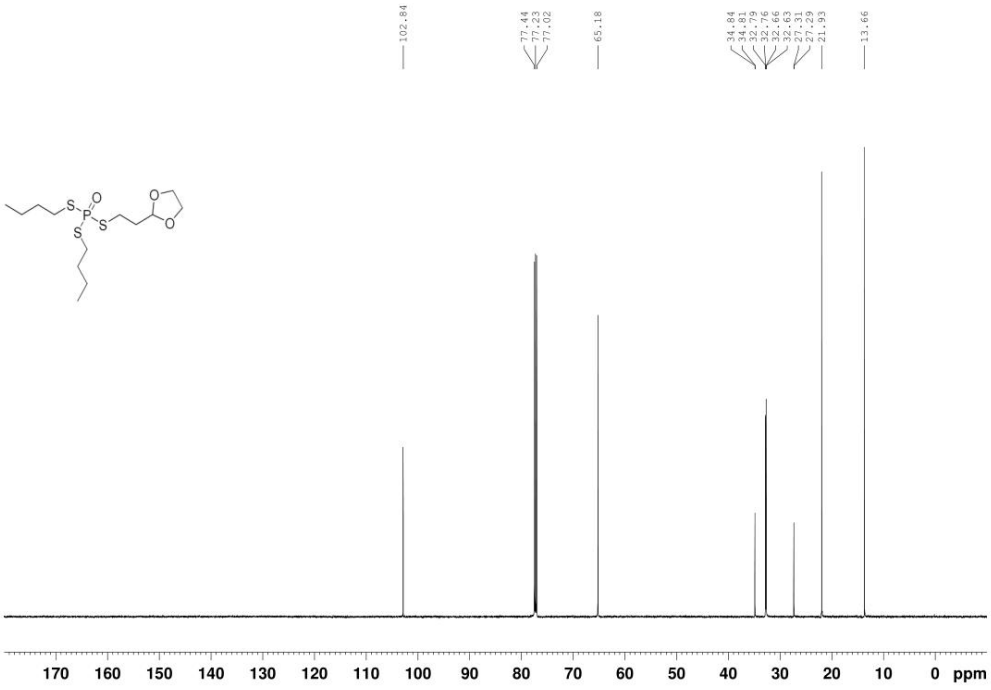
24


63.64
400
300
200
100
0
−100
−200
−300
−400
ppm

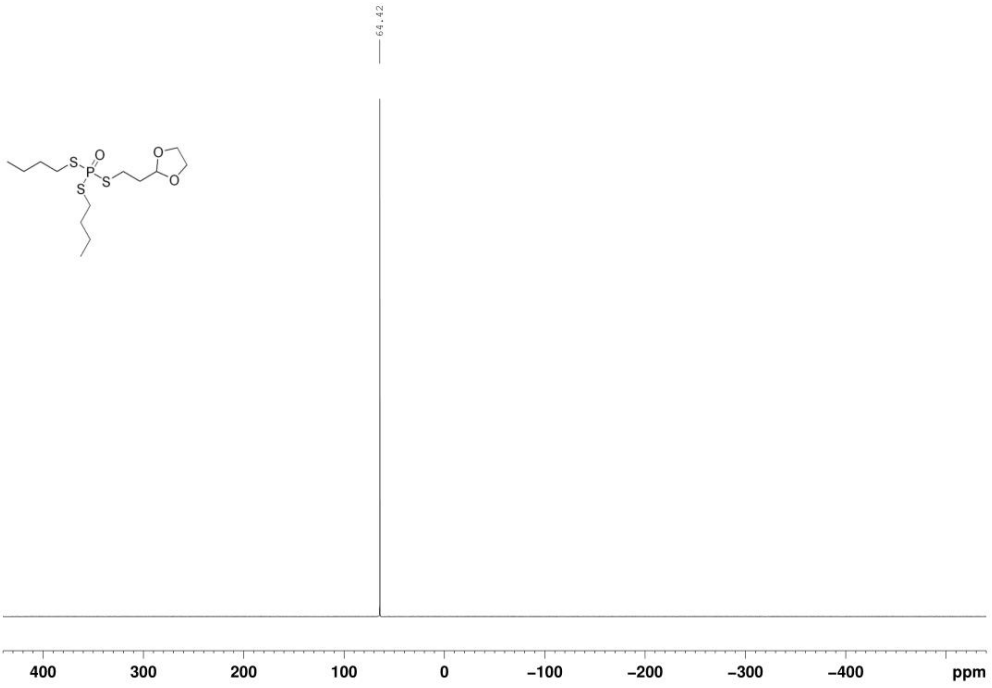
25


4.986
4.979
4.972
4.003
3.988
3.977
3.965
3.948
3.895
3.878
3.867
3.855
3.840
3.103
3.090
3.077
3.064
3.052
3.011
2.999
2.987
2.974
2.962
2.150
2.143
2.138
2.130
2.125
2.118
1.758
1.745
1.733
1.720
1.708
1.471
1.459
1.446
1.434
1.422
1.409
0.947
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.00
2.01
2.06
4.07
2.06
4.05
4.02
6.00

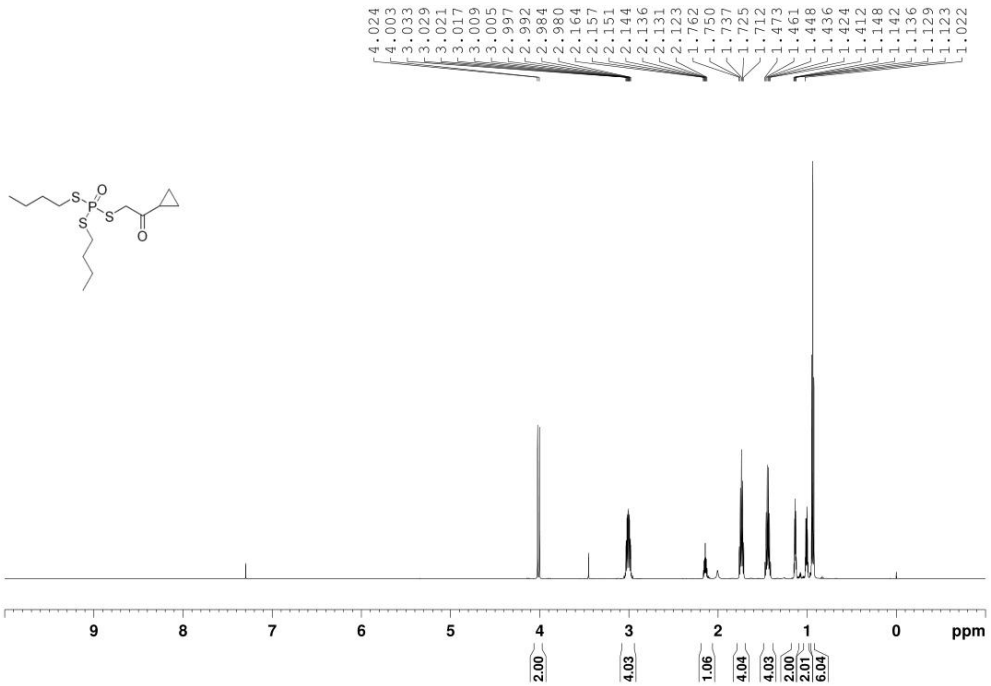
25


102.84
77.44
77.23
77.02
65.18
34.84
34.81
32.79
32.76
32.66
32.63
27.31
27.29
21.93
13.66
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

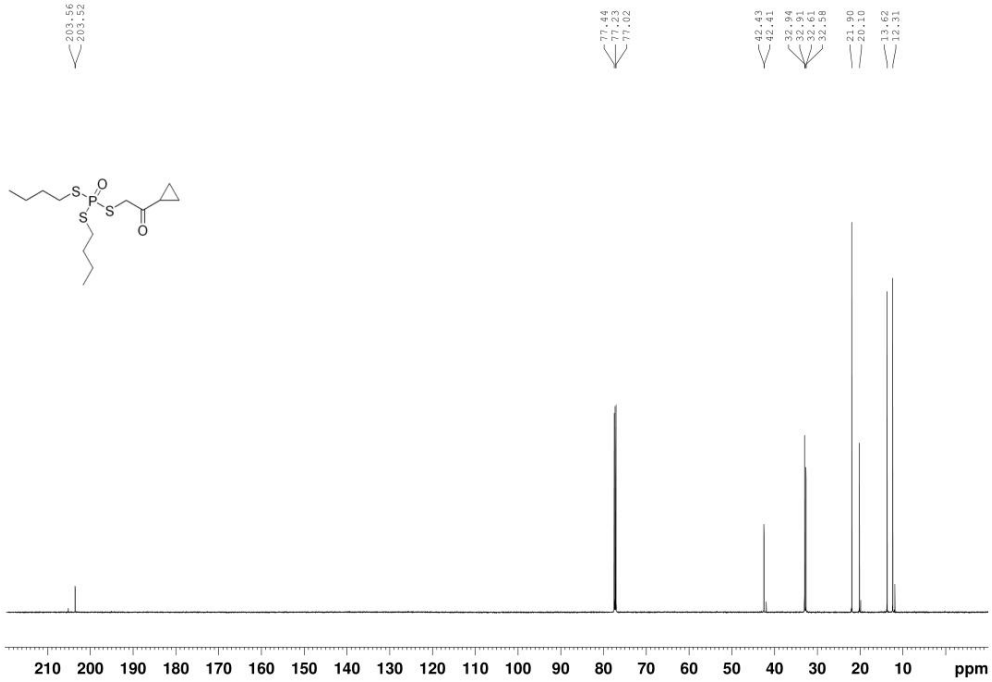
25


64.42
400 300 200 100 0 −100 −200 −300 −400 ppm

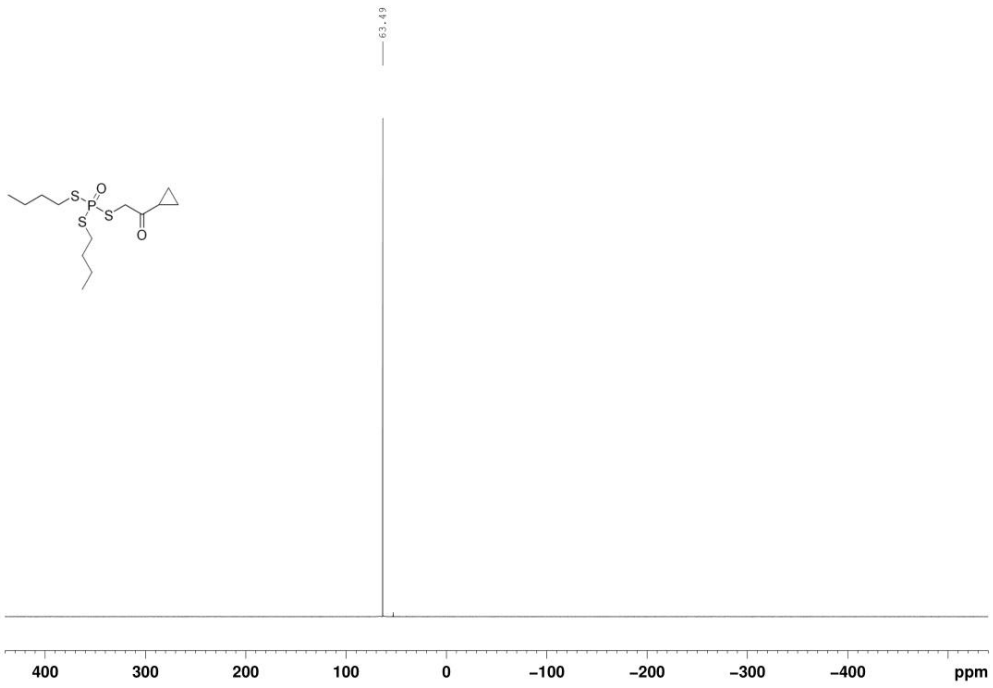
26


4.024
4.003
3.033
3.029
3.021
3.017
3.009
3.005
2.997
2.992
2.984
2.980
2.164
2.157
2.151
2.144
2.136
2.131
2.123
1.762
1.750
1.737
1.725
1.712
1.473
1.461
1.448
1.436
1.424
1.412
1.148
1.142
1.136
1.129
1.123
1.022
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.03
1.06
4.04
4.03
2.00
2.01
6.04

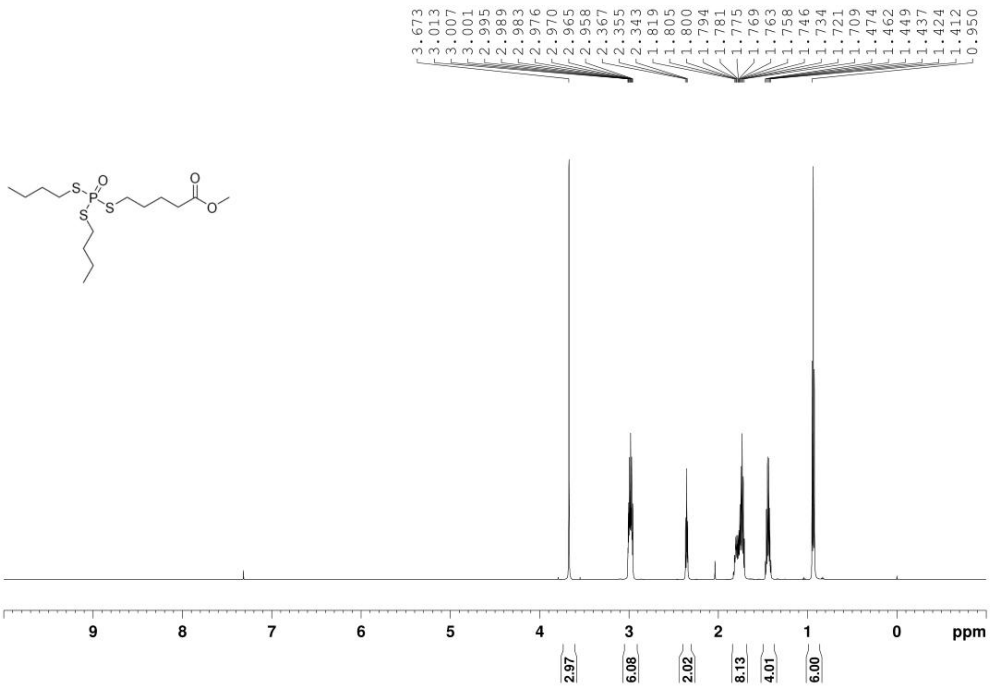
26


203.56
203.52
77.44
77.23
77.02
42.43
42.41
32.94
32.91
32.61
32.58
21.90
20.10
13.62
12.31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

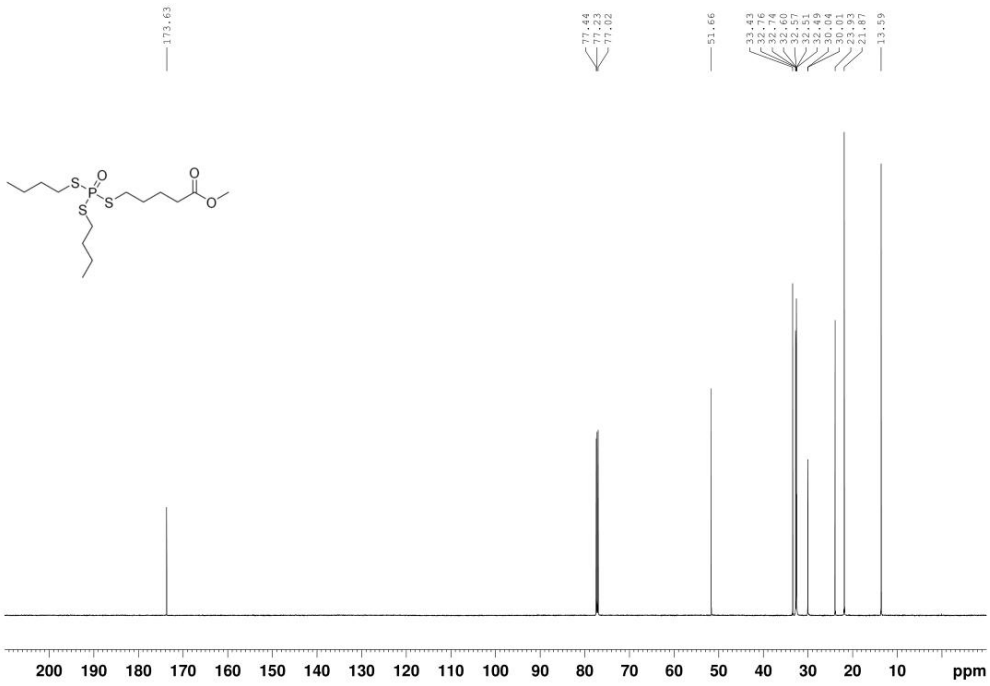
26


63.49
400
300
200
100
0
−100
−200
−300
−400
ppm

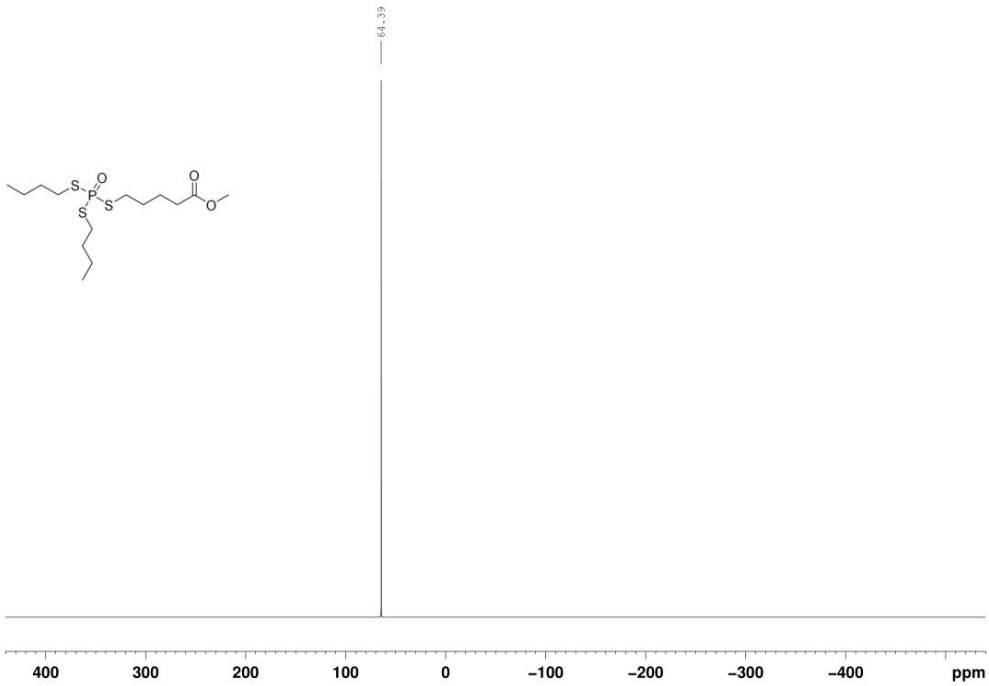
27


3.673
3.013
3.007
3.001
2.995
2.989
2.983
2.976
2.970
2.965
2.958
2.367
2.355
2.343
1.819
1.805
1.800
1.794
1.781
1.775
1.769
1.763
1.758
1.746
1.734
1.721
1.709
1.474
1.462
1.449
1.437
1.424
1.412
0.950
9
8
7
6
5
4
3
2
1
0
ppm
2.97
6.08
2.02
8.13
4.01
6.00

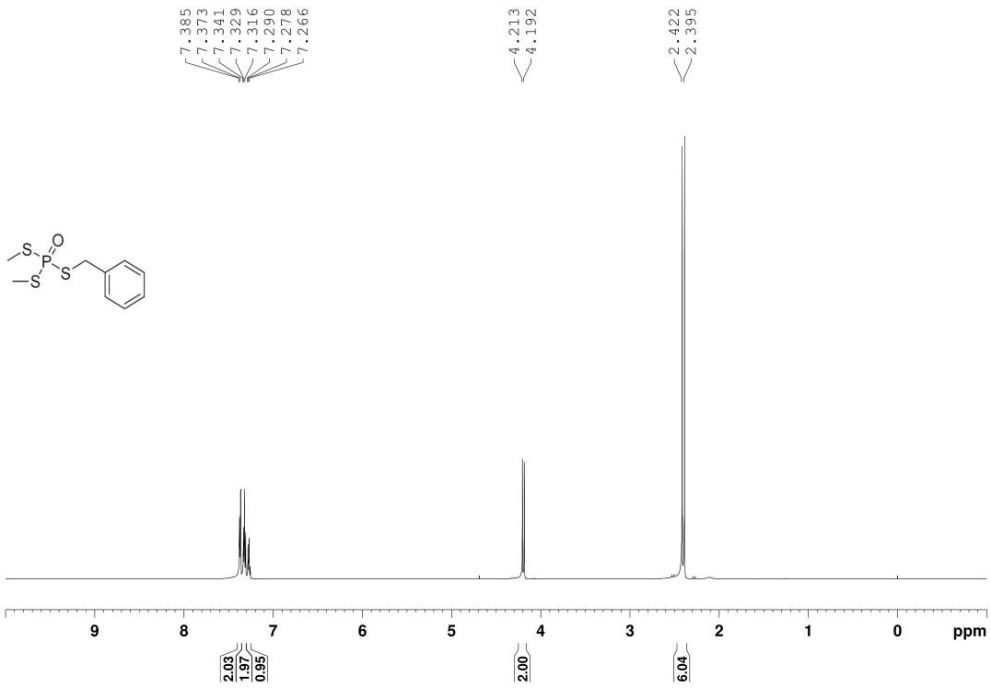
27


173.63
77.44
77.23
77.02
51.66
33.43
32.76
32.74
32.60
32.57
32.51
32.49
30.04
30.01
23.93
21.87
13.59
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

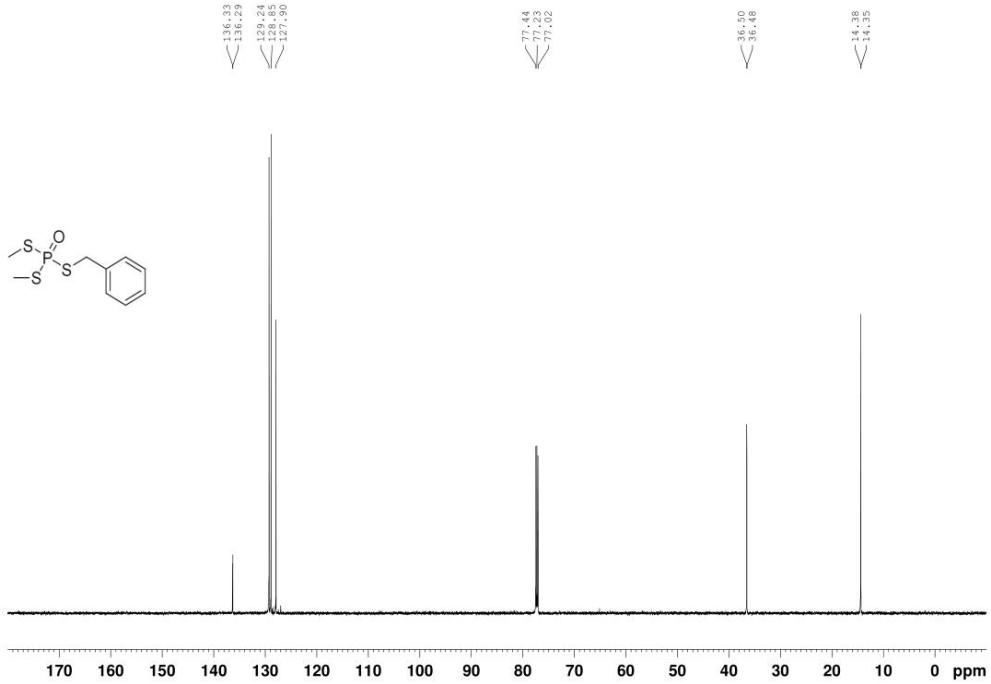
27


64.39
400 300 200 100 0 −100 −200 −300 −400 ppm

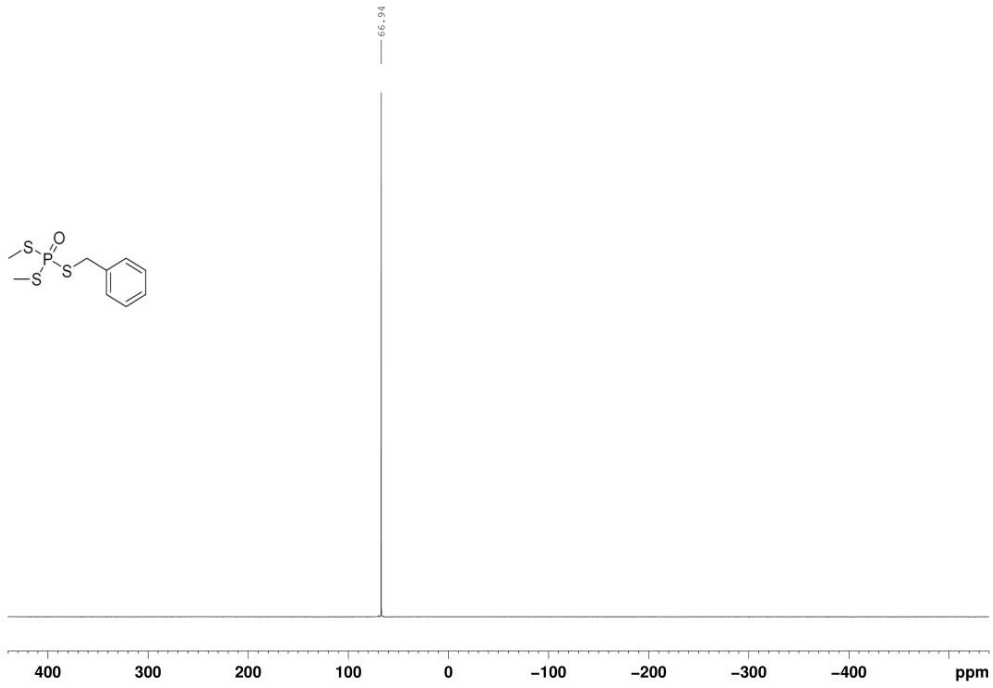
28


7.385
7.373
7.341
7.329
7.316
7.290
7.278
7.266
4.213
4.192
2.422
2.395
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.97
0.95
2.00
6.04

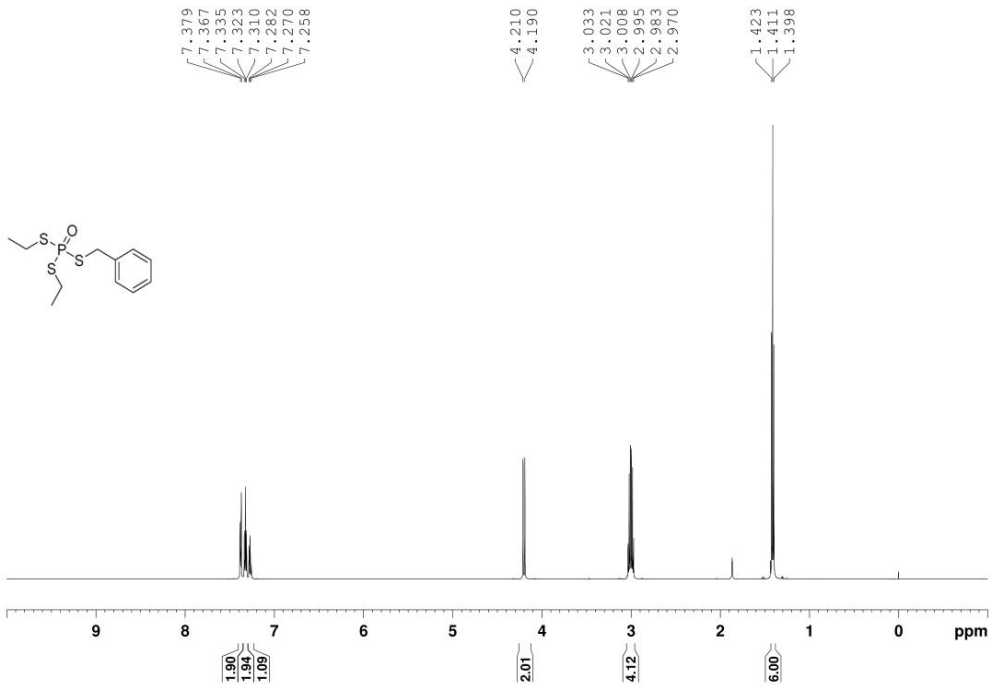
28


136.33
136.29
129.24
128.85
127.90
77.44
77.23
77.02
36.50
36.48
14.38
14.35
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

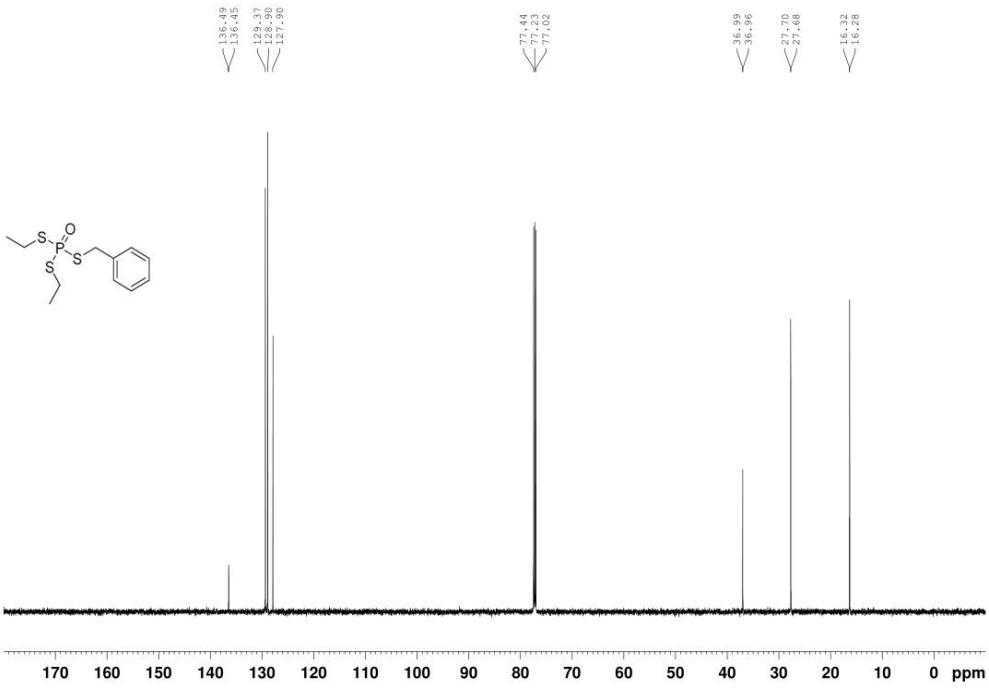
28


66.94
400
300
200
100
0
−100
−200
−300
−400
ppm

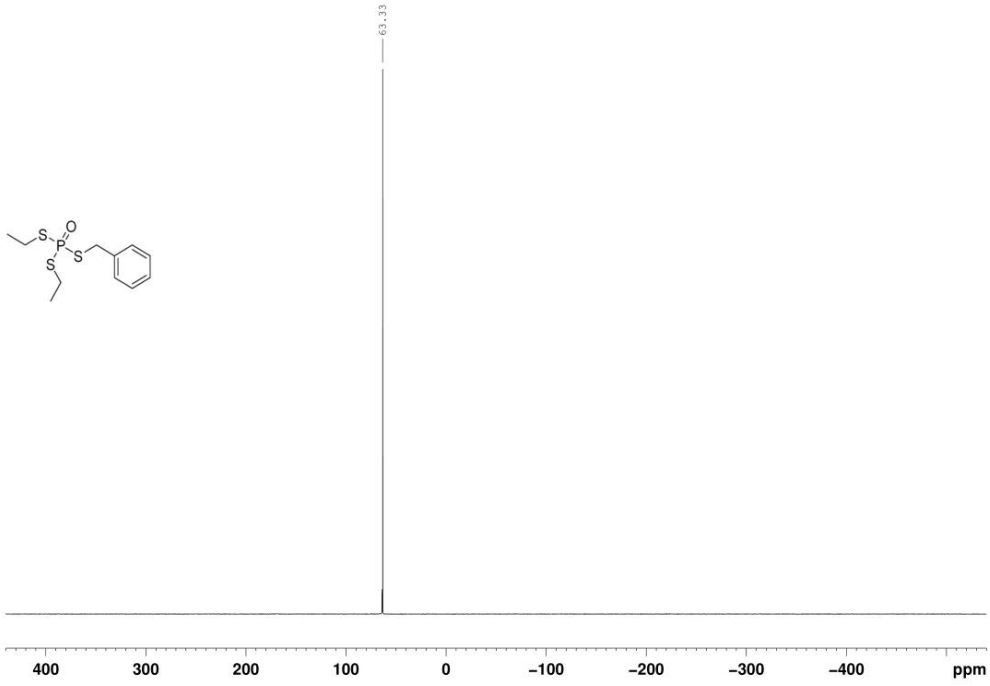
29


7.379
7.367
7.335
7.323
7.310
7.282
7.270
7.258
4.210
4.190
3.033
3.021
3.008
2.995
2.983
2.970
1.423
1.411
1.398
9
8
7
6
5
4
3
2
1
0
ppm
1.90
1.94
1.09
2.01
4.12
6.00

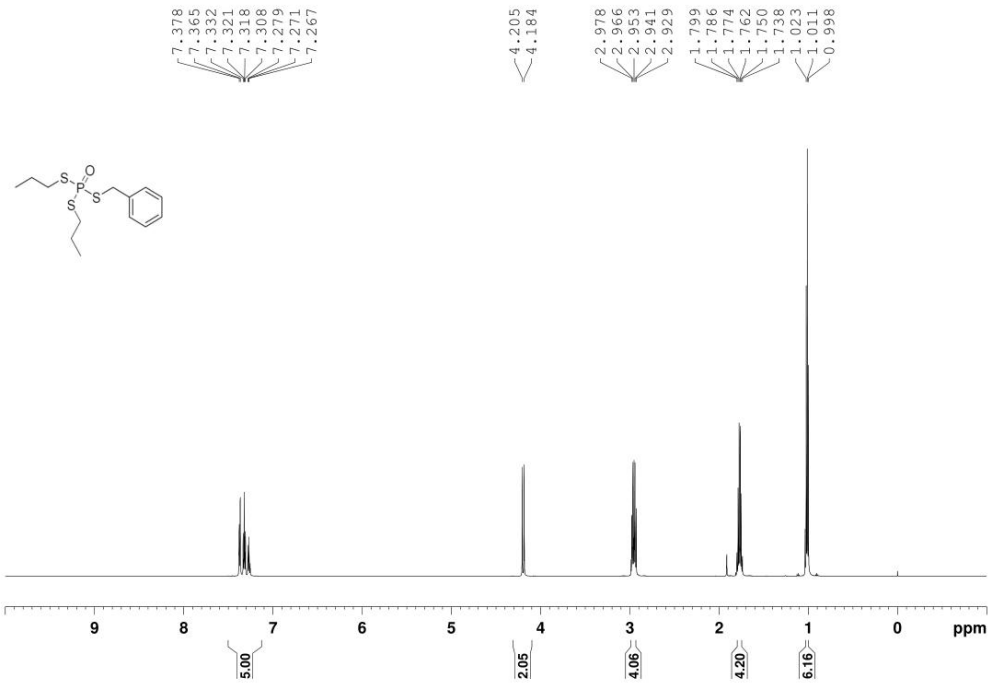
29


136.49
136.45
129.37
128.90
127.90
77.44
77.23
77.02
36.99
36.96
27.70
27.68
16.32
16.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

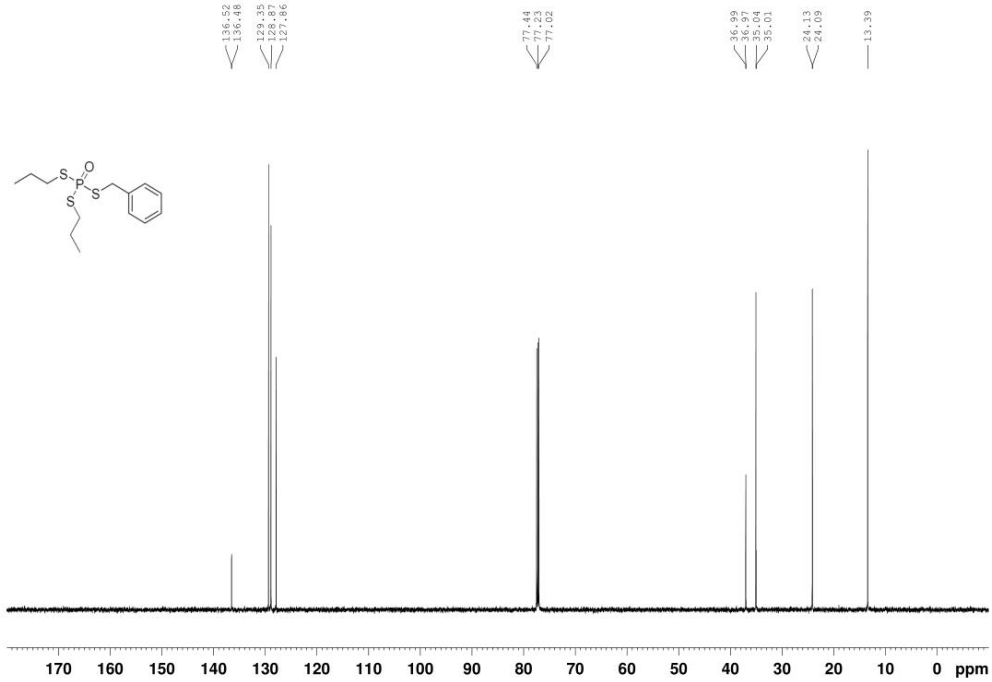
29


63.33
400 300 200 100 0 −100 −200 −300 −400 ppm

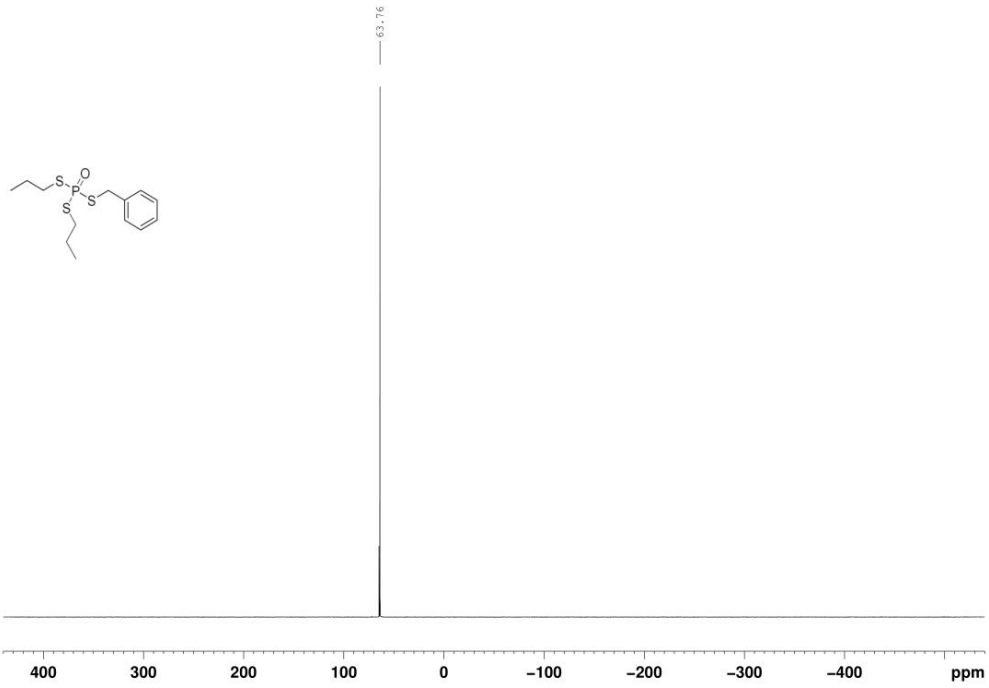
30


7.378
7.365
7.332
7.321
7.318
7.308
7.279
7.271
7.267
4.205
4.184
2.978
2.966
2.953
2.941
2.929
1.799
1.786
1.774
1.762
1.750
1.738
1.023
1.011
0.998
9
8
7
6
5
4
3
2
1
0
ppm
5.00
2.05
4.06
4.20
6.16

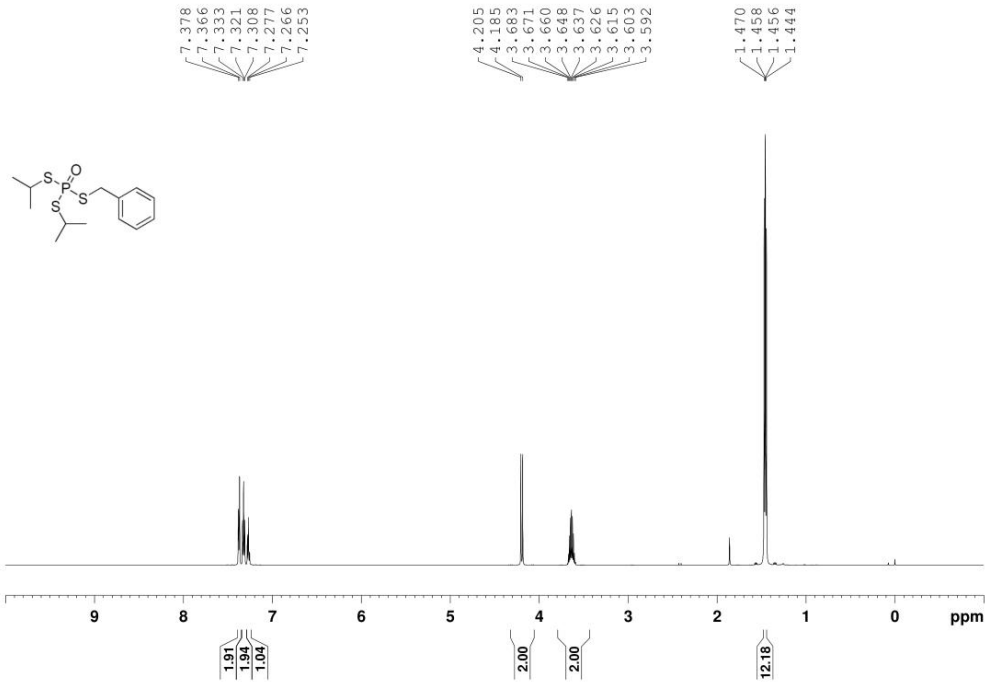
30


136.52
136.48
129.35
128.87
127.86
77.44
77.23
77.02
36.99
36.97
35.04
35.01
24.13
24.09
13.39
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

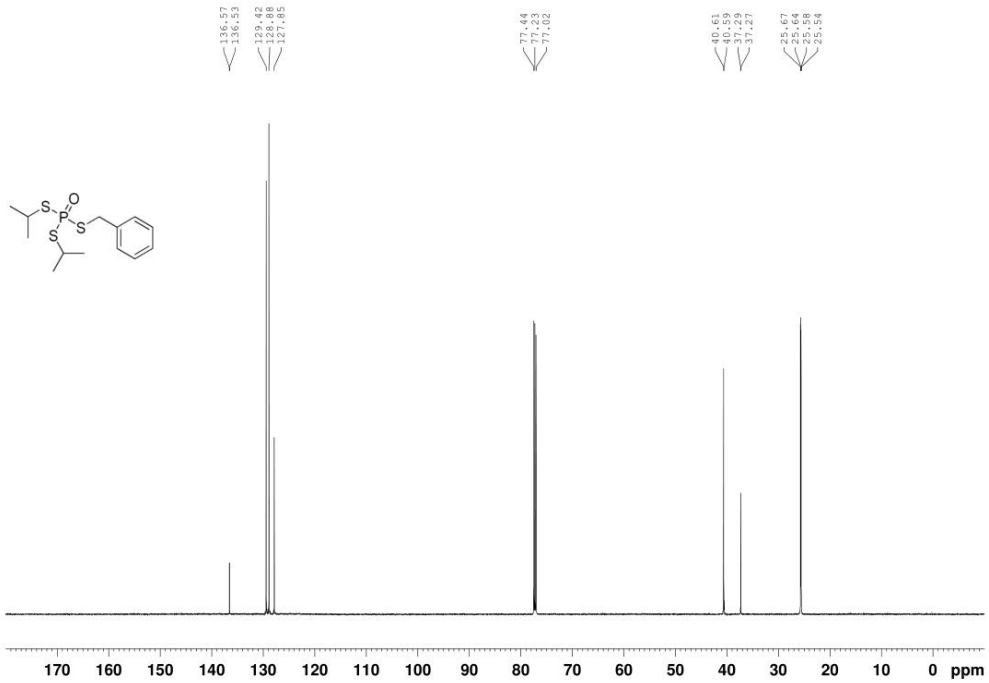
30


63.76
400
300
200
100
0
−100
−200
−300
−400
ppm

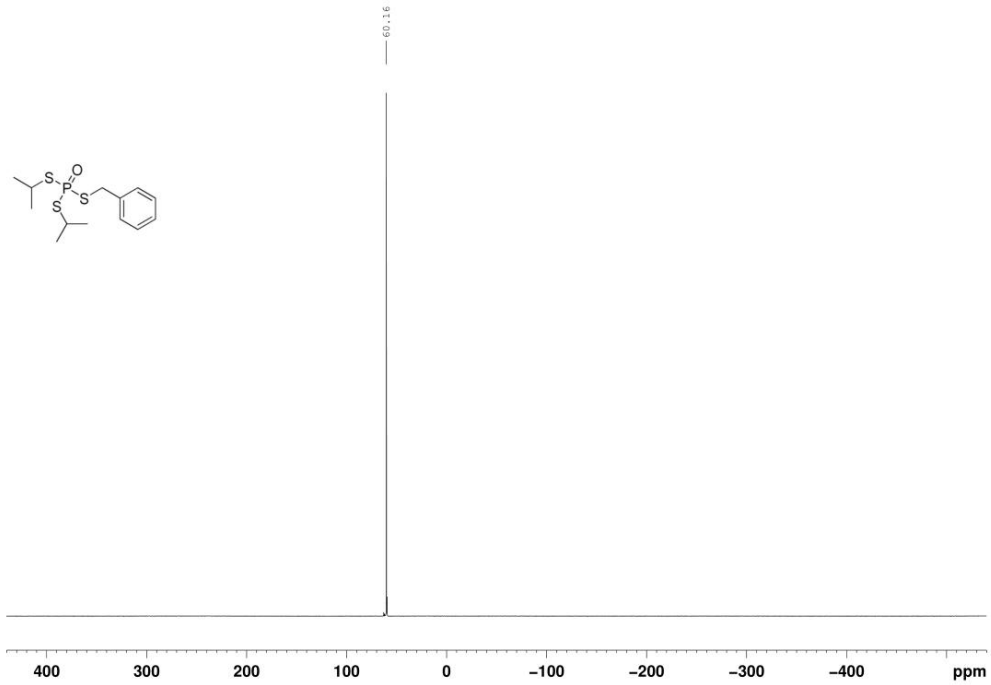
31


7.378
7.366
7.333
7.321
7.308
7.277
7.266
7.253
4.205
4.185
3.683
3.671
3.660
3.648
3.637
3.626
3.615
3.603
3.592
1.470
1.458
1.456
1.444
9
8
7
6
5
4
3
2
1
0
ppm
1.91
1.94
1.04
2.00
2.00
12.18

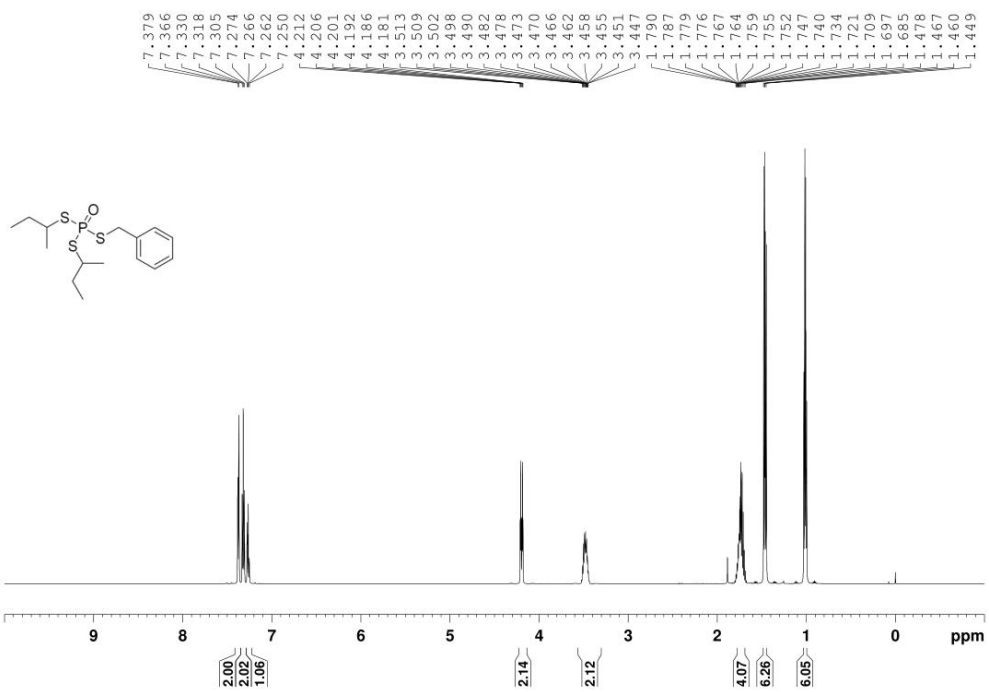
31


136.57
136.53
129.42
128.88
127.85
77.44
77.23
77.02
40.61
40.59
37.29
37.27
25.67
25.64
25.58
25.54
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

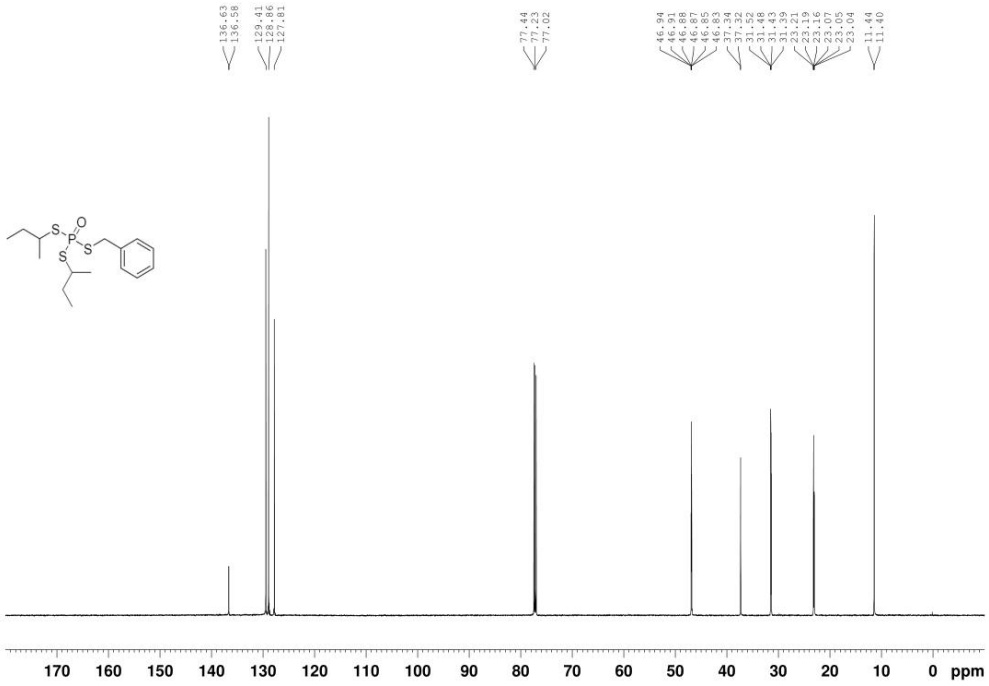
31


60.16
400 300 200 100 0 −100 −200 −300 −400 ppm

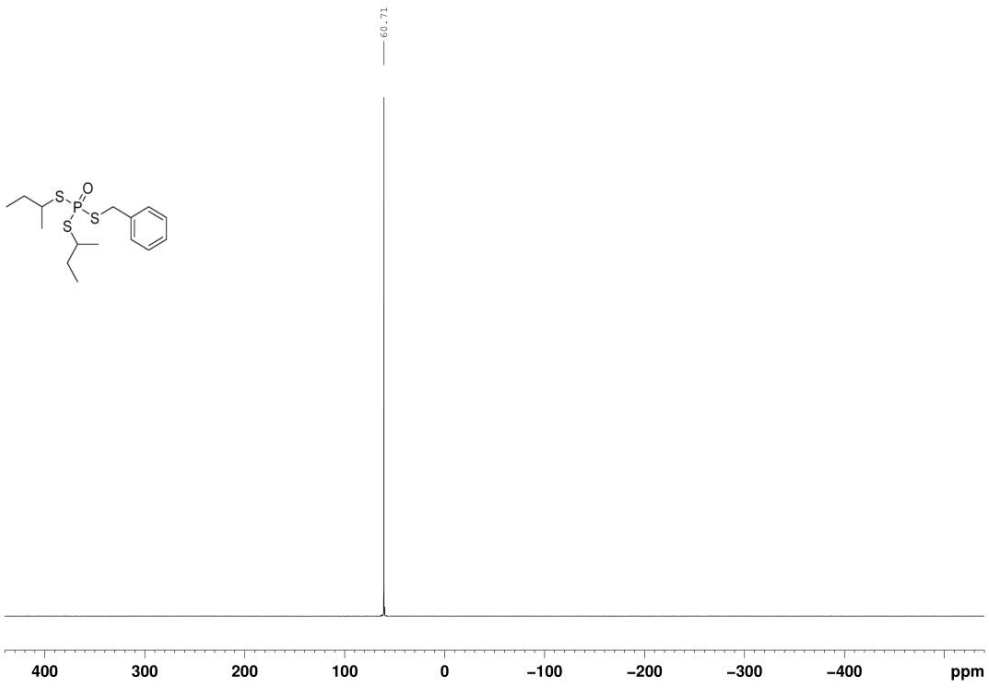
32


7.379
7.366
7.330
7.318
7.305
7.274
7.266
7.262
7.250
4.212
4.206
4.201
4.192
4.186
4.181
3.513
3.509
3.502
3.498
3.490
3.482
3.478
3.473
3.470
3.466
3.462
3.458
3.455
3.451
3.447
1.790
1.787
1.779
1.776
1.767
1.764
1.759
1.755
1.752
1.747
1.740
1.734
1.721
1.709
1.697
1.685
1.478
1.467
1.460
1.449
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
1.06
2.14
2.12
4.07
6.26
6.05

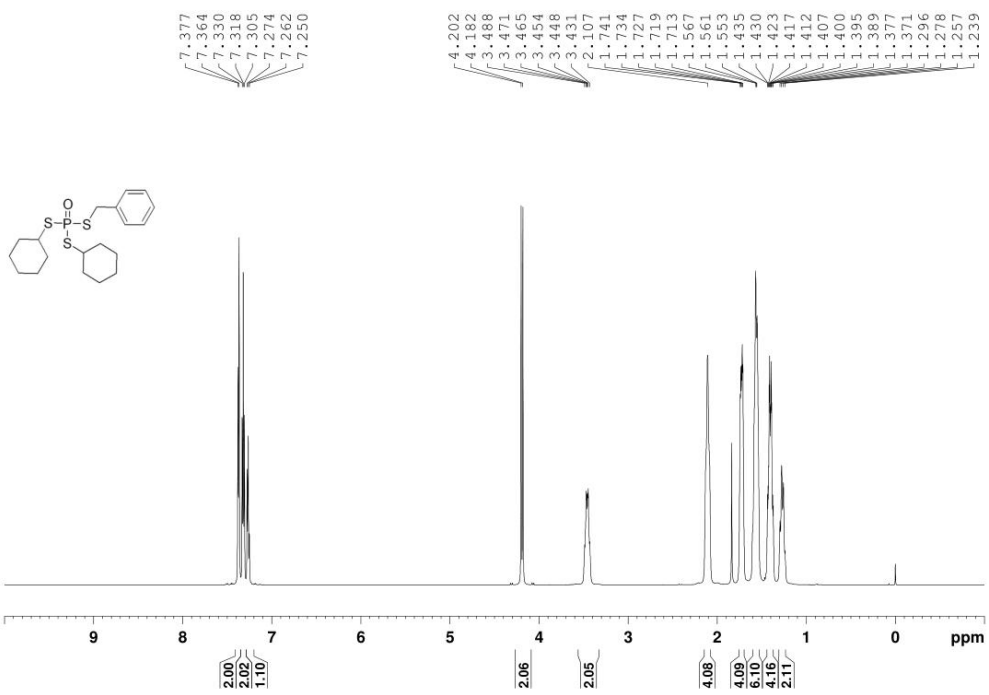
32


136.63
136.58
129.41
128.86
127.81
77.44
77.23
77.02
46.94
46.91
46.88
46.87
46.85
46.83
37.34
37.32
31.52
31.48
31.43
31.39
23.21
23.19
23.16
23.07
23.05
23.04
11.44
11.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

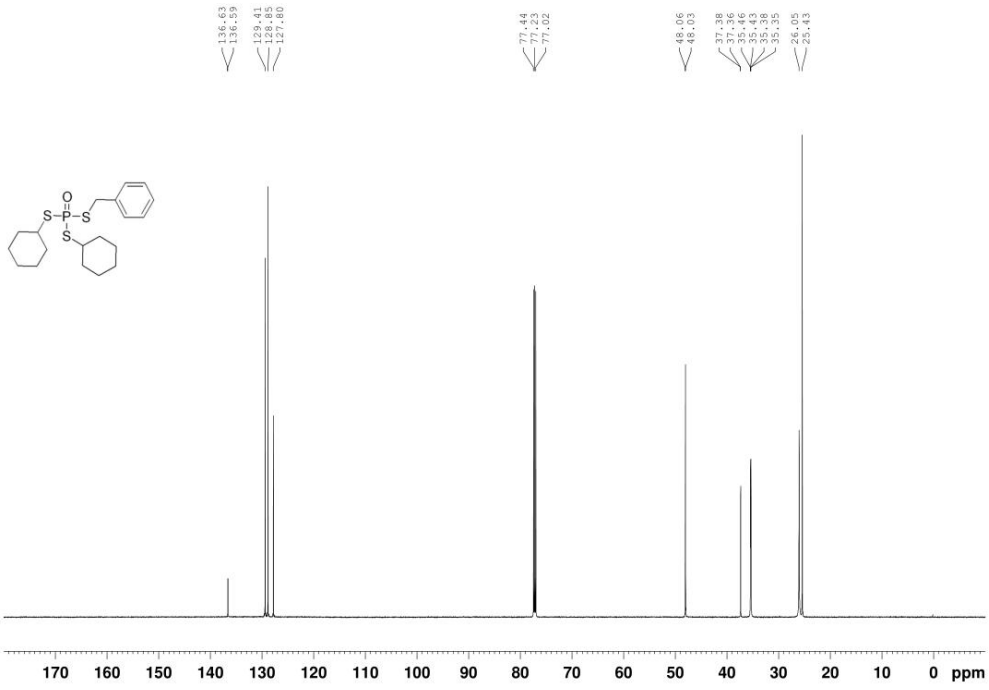
32


60.71
400
300
200
100
0
−100
−200
−300
−400
ppm

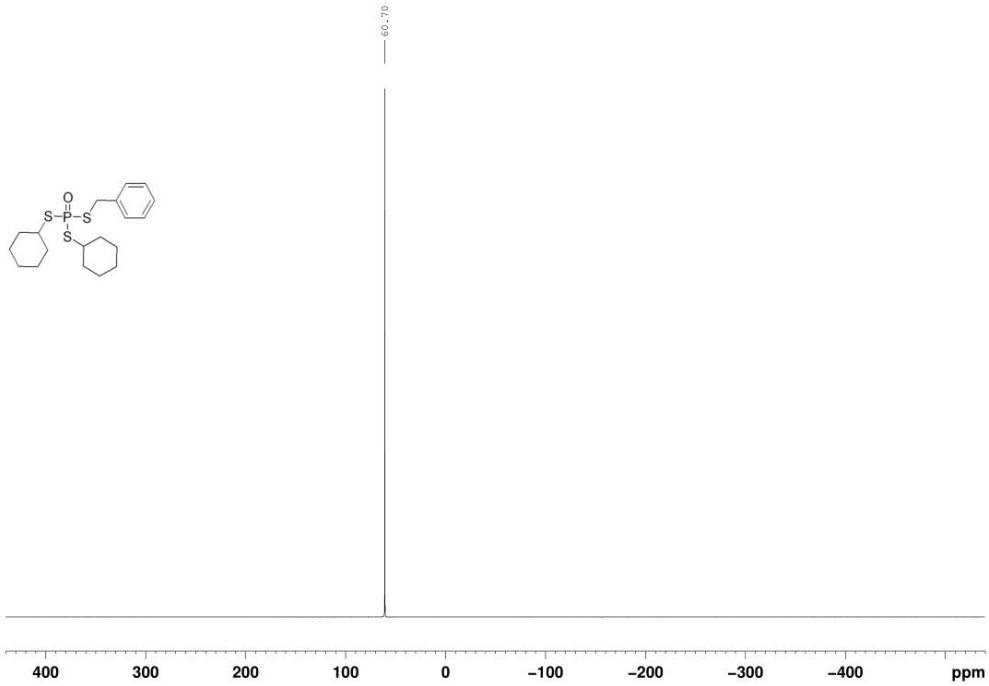
33


7.377
7.364
7.330
7.318
7.305
7.274
7.262
7.250
4.202
4.182
3.488
3.471
3.465
3.454
3.448
3.431
2.107
1.741
1.734
1.727
1.719
1.713
1.567
1.561
1.553
1.435
1.430
1.423
1.417
1.412
1.407
1.400
1.395
1.389
1.377
1.371
1.296
1.278
1.257
1.239
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
1.10
2.06
2.05
4.08
4.09
6.10
4.16
2.11

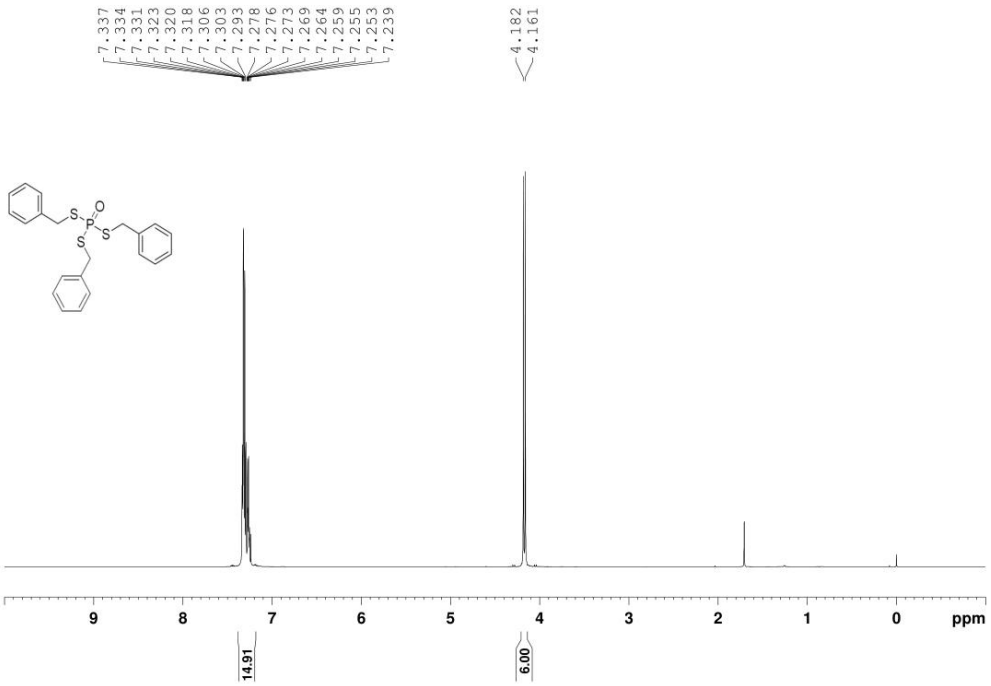
33


136.63
136.59
129.41
128.85
127.80
77.44
77.23
77.02
48.06
48.03
37.38
37.36
35.46
35.43
35.38
35.35
26.05
25.43
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

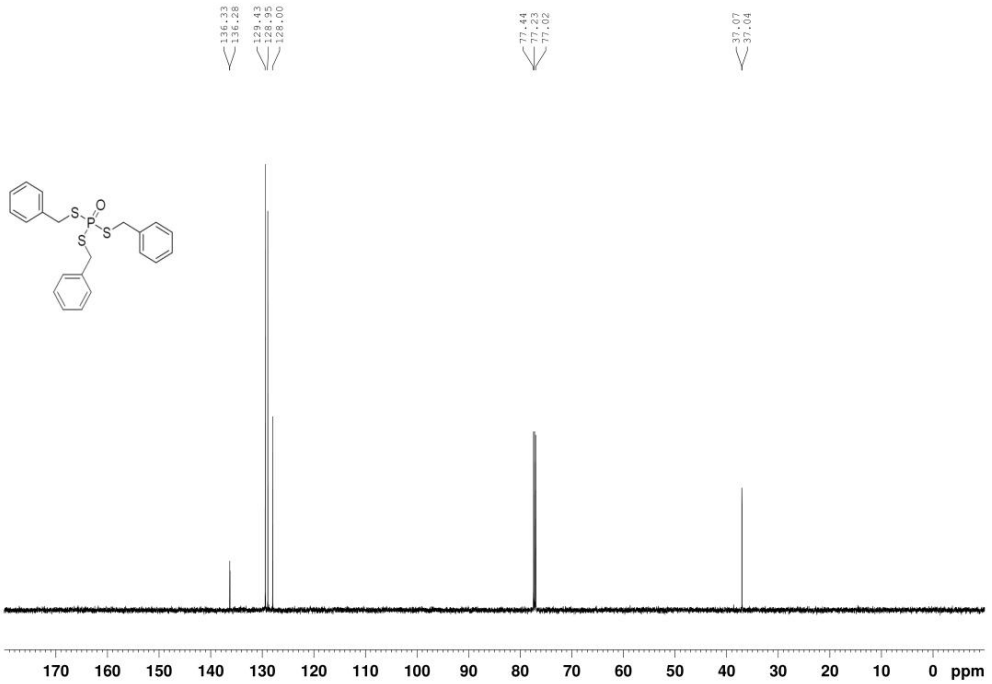
33


60.70
400 300 200 100 0 −100 −200 −300 −400 ppm

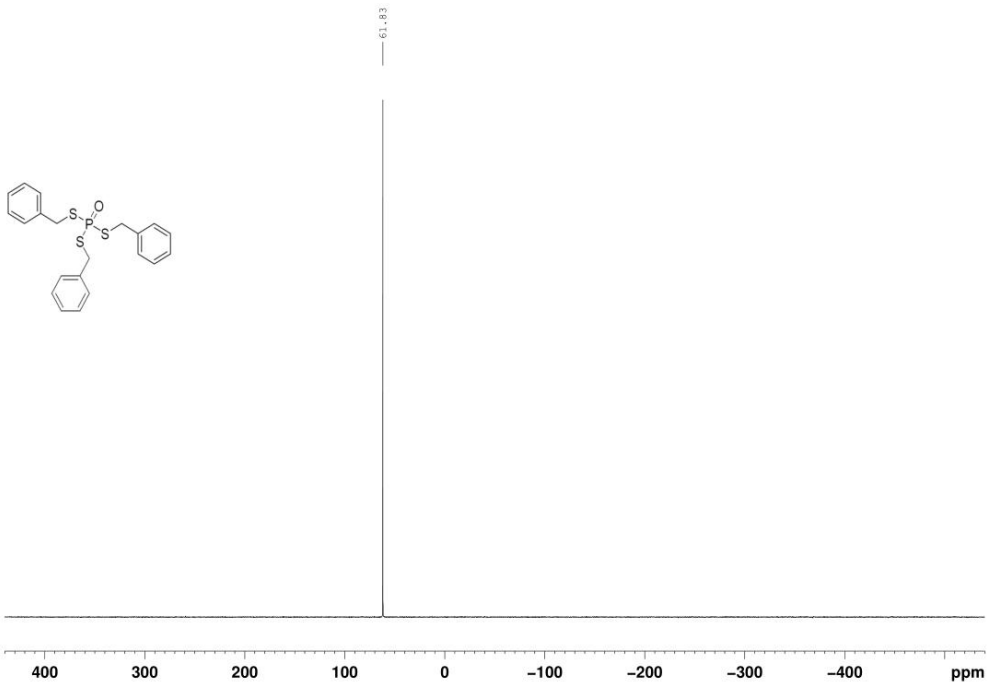
34


7.337
7.334
7.331
7.323
7.320
7.318
7.306
7.303
7.293
7.278
7.276
7.273
7.269
7.264
7.259
7.255
7.253
7.239
4.182
4.161
9
8
7
6
5
4
3
2
1
0
ppm
14.91
6.00

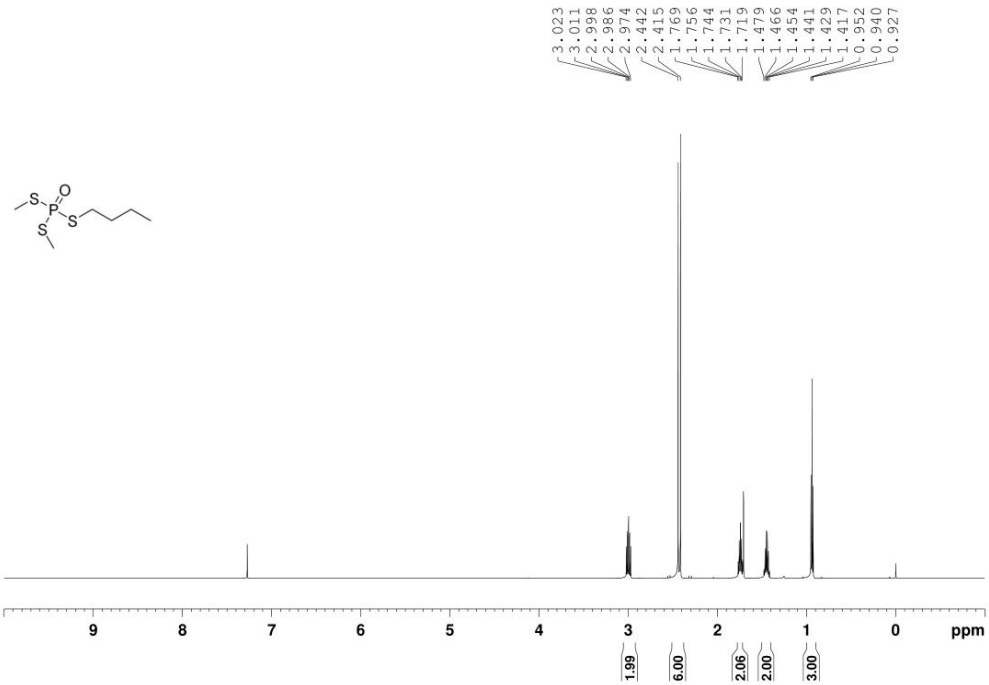
34


136.33
136.28
129.43
128.95
128.00
77.44
77.23
77.02
37.07
37.04
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

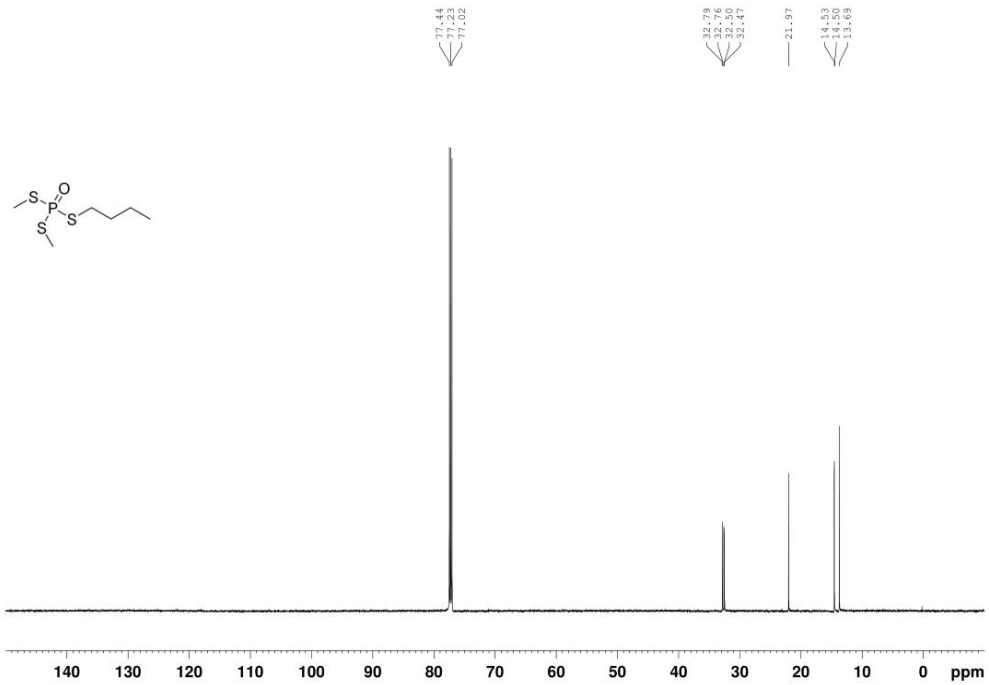
34


61.83
400
300
200
100
0
−100
−200
−300
−400
ppm

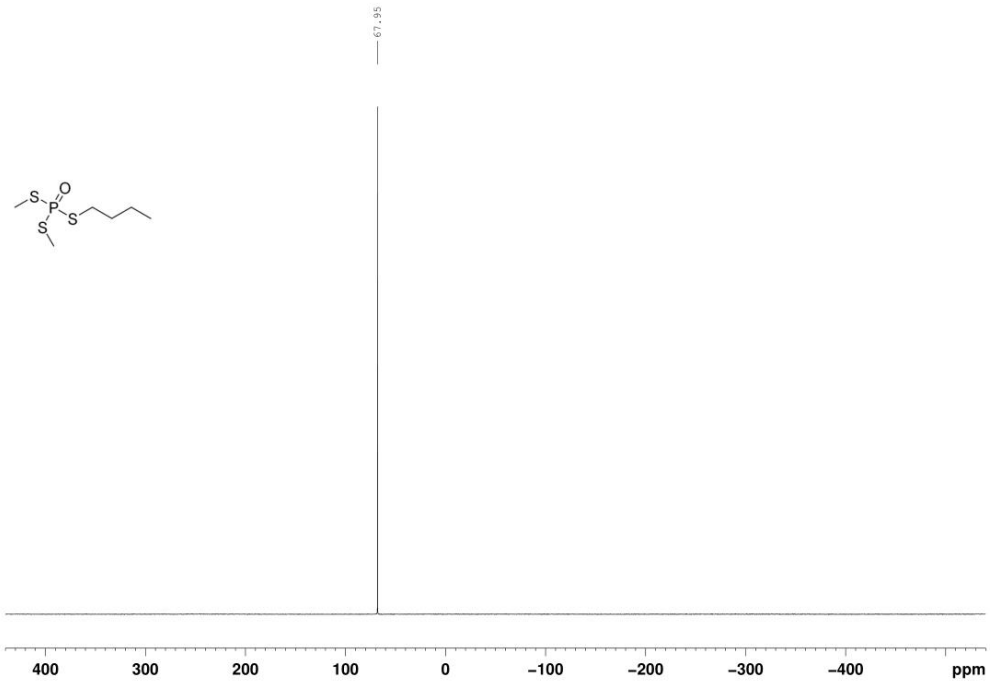
35


3.023
3.011
2.998
2.986
2.974
2.442
2.415
1.769
1.756
1.744
1.731
1.719
1.479
1.466
1.454
1.441
1.429
1.417
0.952
0.940
0.927
9
8
7
6
5
4
3
2
1
0
ppm
1.99
6.00
2.06
2.00
3.00

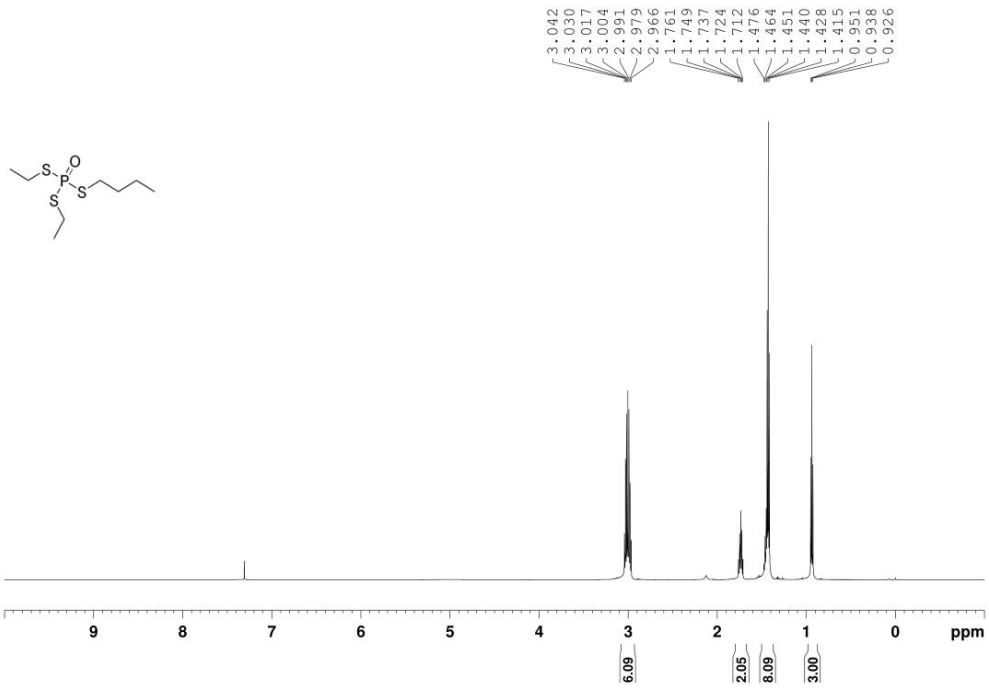
35


77.44
77.23
77.02
32.79
32.76
32.50
32.47
21.97
14.53
14.50
13.69
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

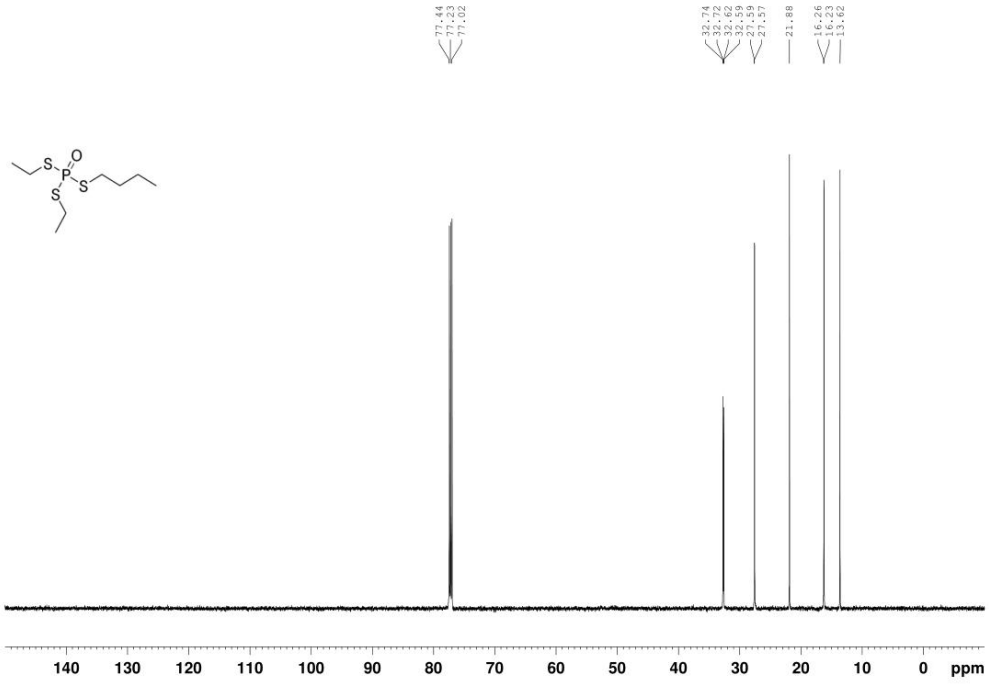
35


67.95
400
300
200
100
0
−100
−200
−300
−400
ppm

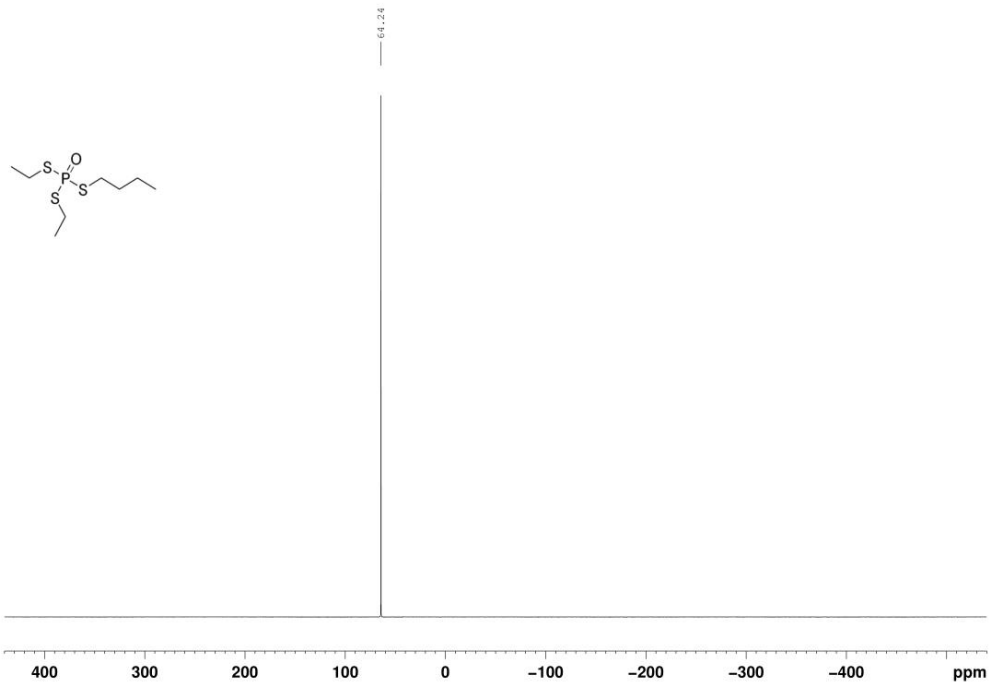
36


3.042
3.030
3.017
3.004
2.991
2.979
2.966
1.761
1.749
1.737
1.724
1.712
1.476
1.464
1.451
1.440
1.428
1.415
0.951
0.938
0.926
9
8
7
6
5
4
3
2
1
0
ppm
6.09
2.05
8.09
3.00

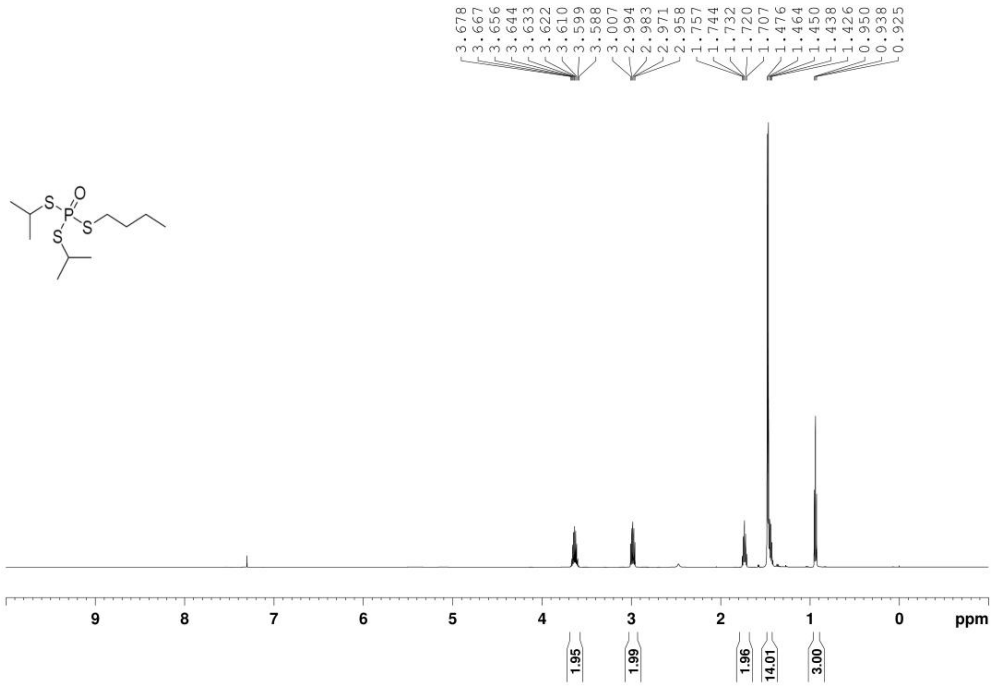
36


77.44
77.23
77.02
32.74
32.72
32.62
32.59
27.59
27.37
21.88
16.26
16.23
13.62
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

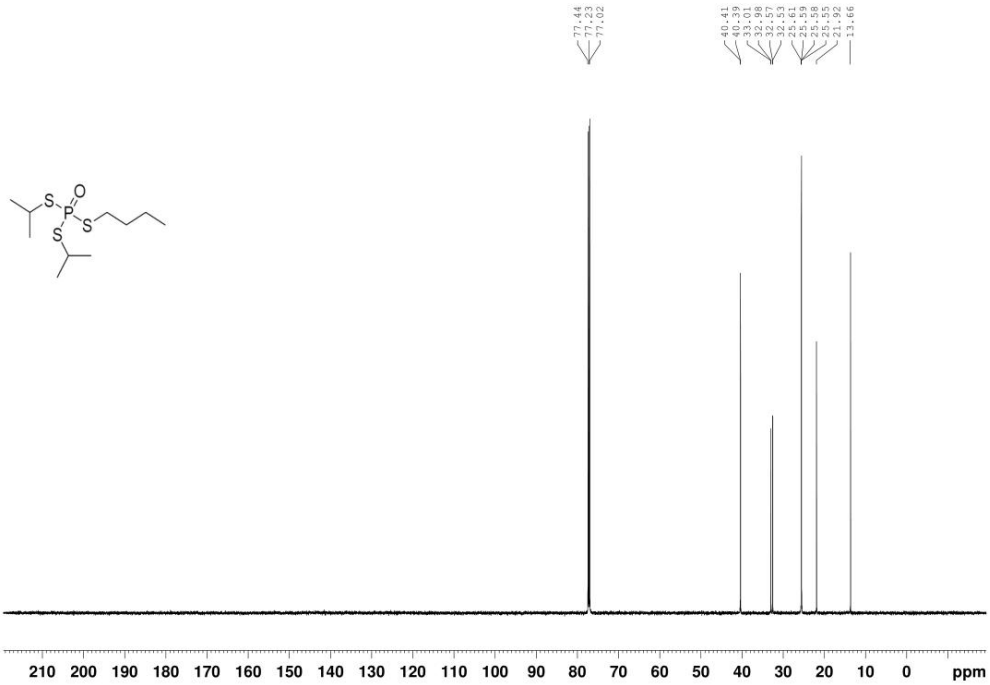
36


64.24
400
300
200
100
0
−100
−200
−300
−400
ppm

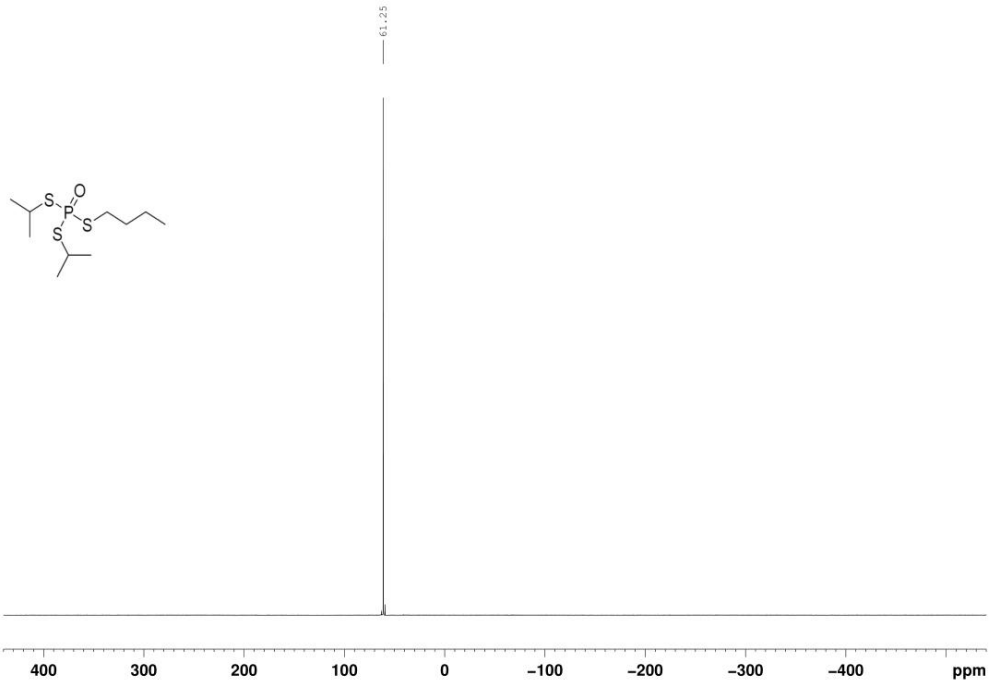
37


3.678
3.667
3.656
3.644
3.633
3.622
3.610
3.599
3.588
3.007
2.994
2.983
2.971
2.958
1.757
1.744
1.732
1.720
1.707
1.476
1.464
1.450
1.438
1.426
0.950
0.938
0.925
9
8
7
6
5
4
3
2
1
0
ppm
1.95
1.99
1.96
14.01
3.00

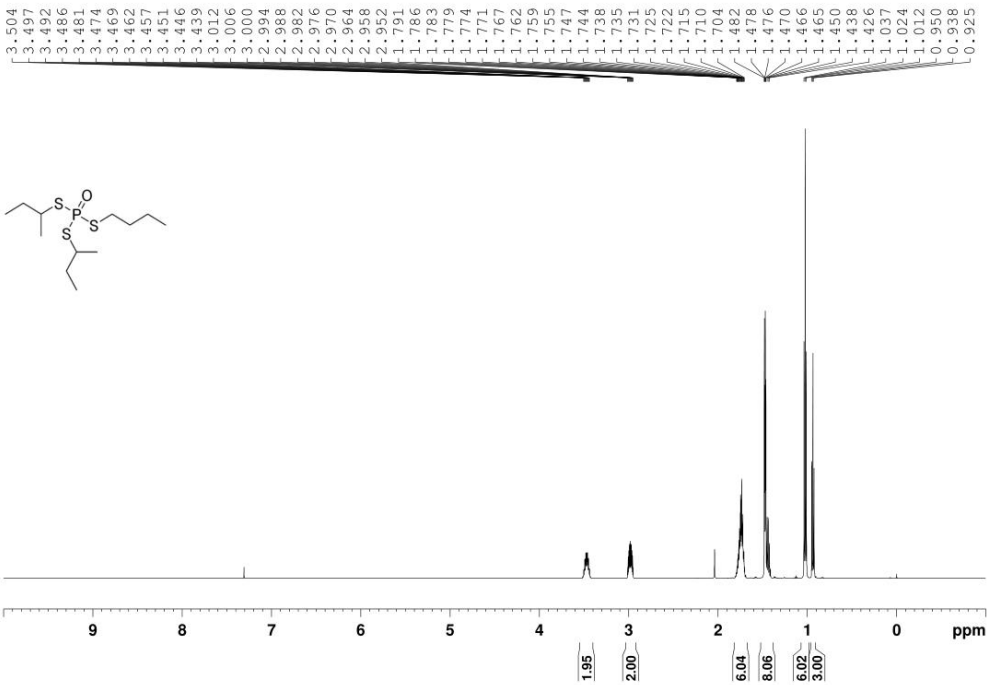
37


77.44
77.23
77.02
40.41
40.19
33.01
32.98
32.57
32.53
25.61
25.59
25.58
25.55
21.92
13.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

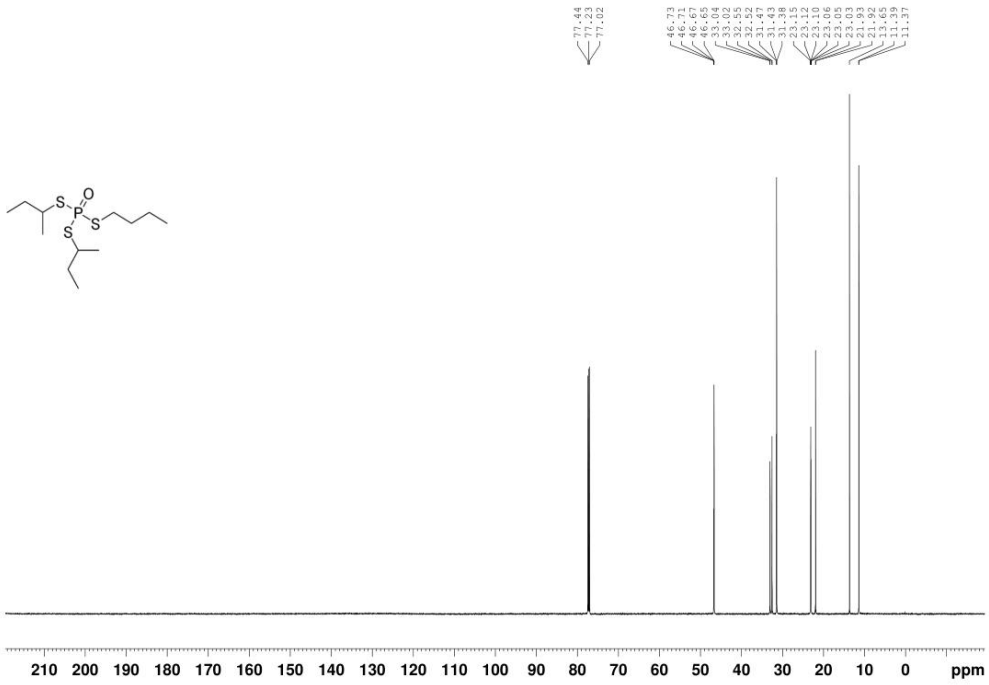
37


61.25
400 300 200 100 0 −100 −200 −300 −400 ppm

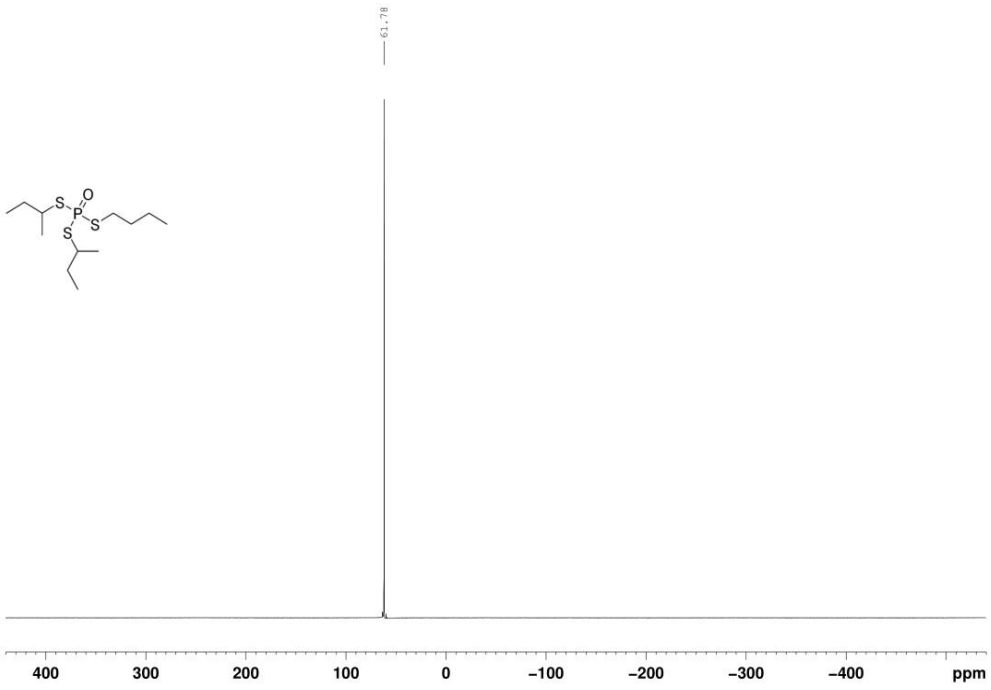
38


3.504
3.497
3.492
3.486
3.481
3.474
3.469
3.462
3.457
3.451
3.446
3.439
3.012
3.006
3.000
2.994
2.988
2.982
2.976
2.970
2.964
2.958
2.952
1.791
1.786
1.783
1.779
1.774
1.771
1.767
1.762
1.759
1.755
1.747
1.744
1.738
1.735
1.731
1.725
1.722
1.715
1.710
1.704
1.482
1.478
1.476
1.470
1.466
1.465
1.450
1.438
1.426
1.037
1.024
1.012
0.950
0.938
0.925
S
O
P
S
S
9
8
7
6
5
4
3
2
1
0
ppm
1.95
2.00
6.04
8.06
6.02
3.00

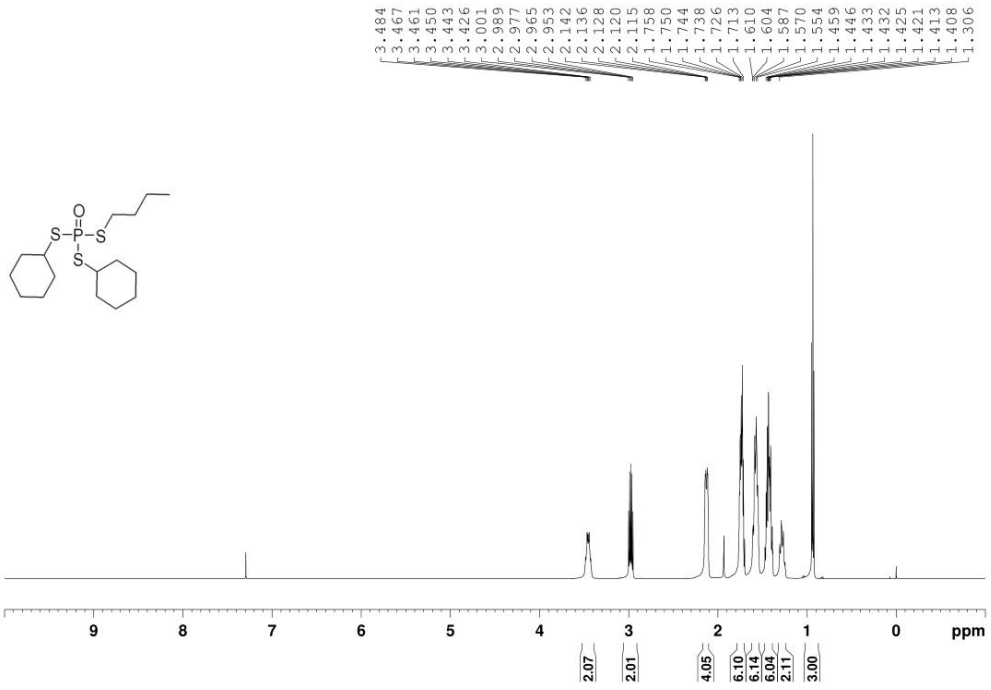
38


77.44
77.23
77.02
46.73
46.71
46.67
46.65
33.04
33.02
32.55
32.50
31.47
31.43
31.38
23.15
23.12
23.10
23.06
23.05
23.03
23.01
21.92
13.65
11.39
11.37
S
O
P
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

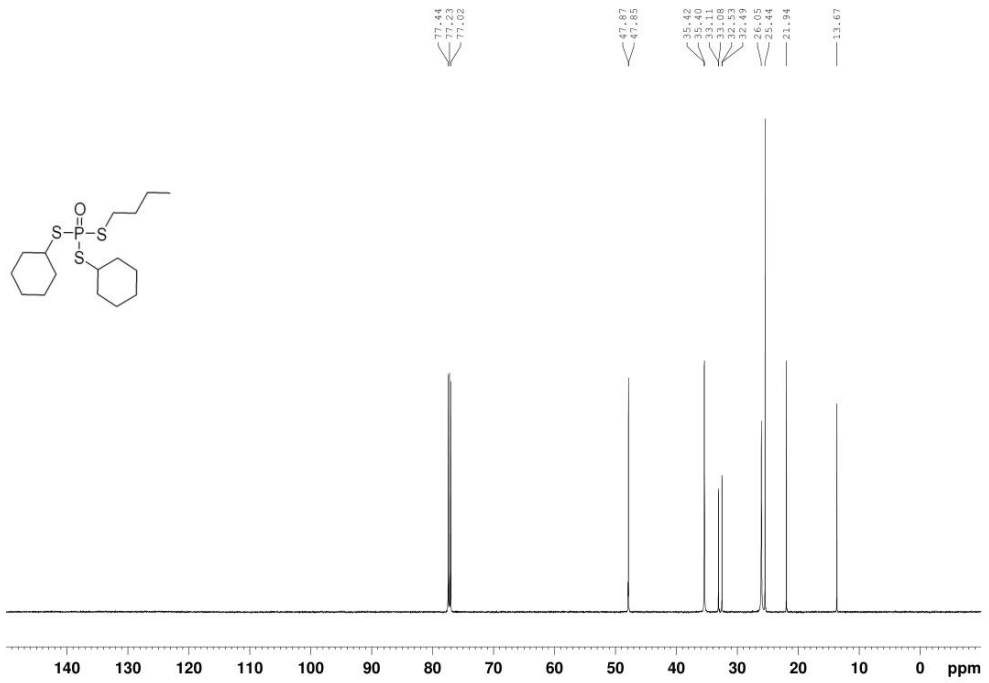
38


61.78
400
300
200
100
0
−100
−200
−300
−400
ppm

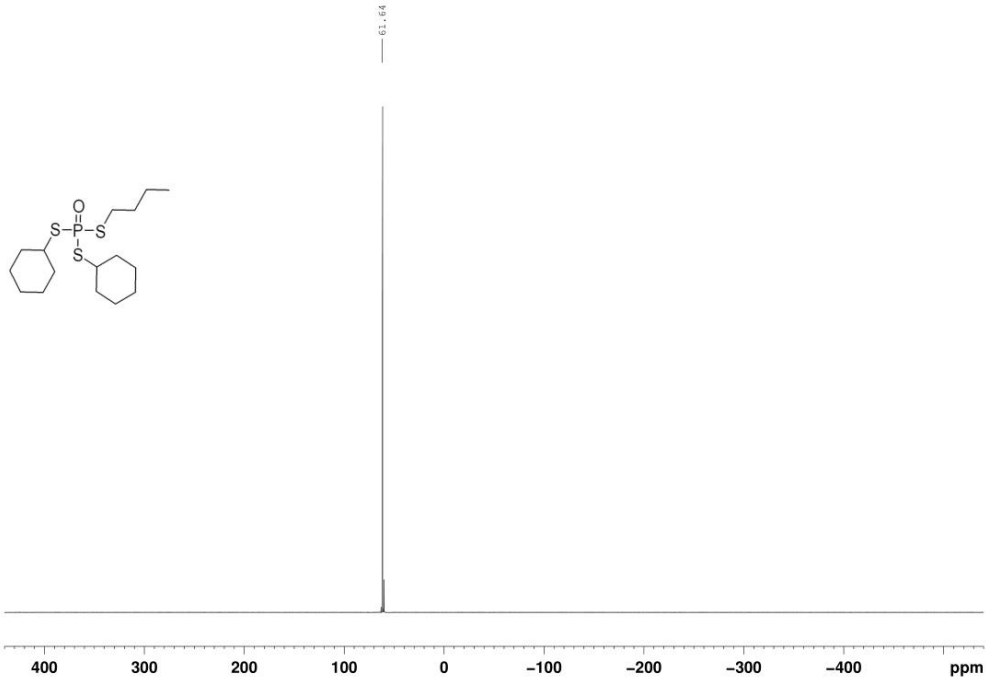
39


3.484
3.467
3.461
3.450
3.443
3.426
3.001
2.989
2.977
2.965
2.953
2.142
2.136
2.128
2.120
2.115
1.758
1.750
1.744
1.738
1.726
1.713
1.610
1.604
1.587
1.570
1.554
1.459
1.446
1.433
1.432
1.425
1.421
1.413
1.408
1.306
9
8
7
6
5
4
3
2
1
0
ppm
2.07
2.01
4.05
6.10
6.14
6.04
2.11
3.00

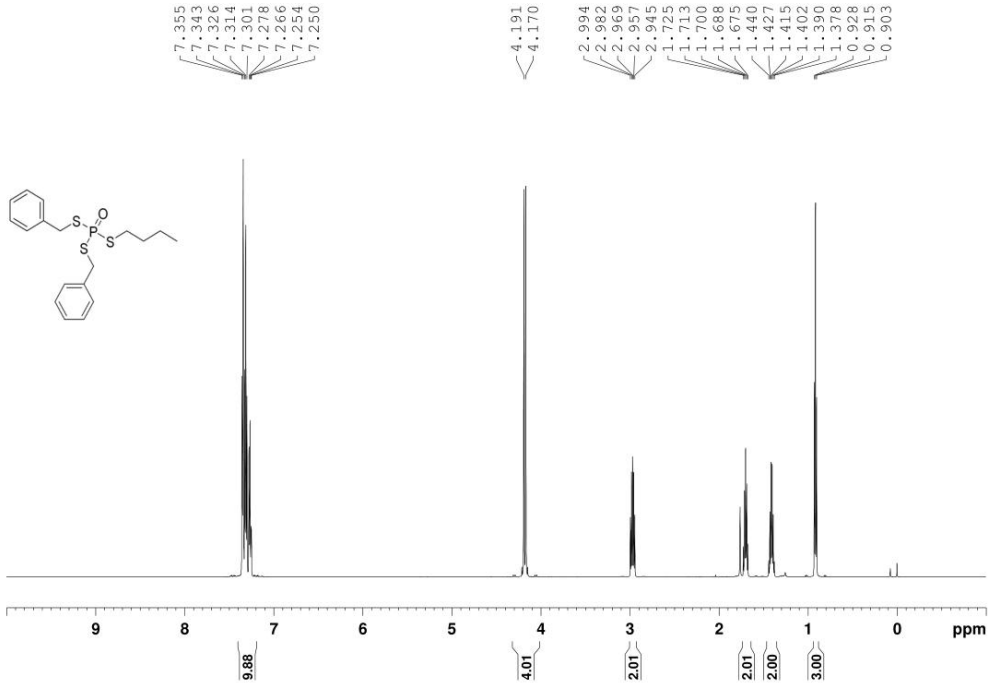
39


77.44
77.23
77.02
47.87
47.85
35.42
35.40
33.11
33.08
32.53
32.49
26.05
25.44
21.94
13.67
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

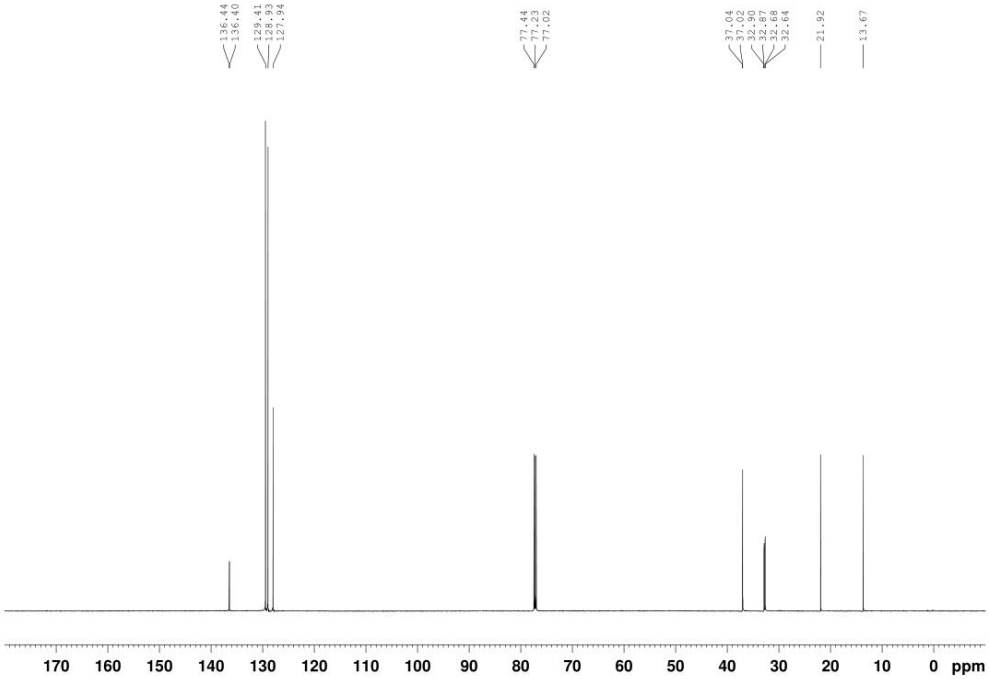
39


61.64
400
300
200
100
0
−100
−200
−300
−400
ppm

40


7.355
7.343
7.326
7.314
7.301
7.278
7.266
7.254
7.250
4.191
4.170
2.994
2.982
2.969
2.957
2.945
1.725
1.713
1.700
1.688
1.675
1.440
1.427
1.415
1.402
1.390
1.378
0.928
0.915
0.903
9
8
7
6
5
4
3
2
1
0
ppm
9.88
4.01
2.01
2.01
2.00
3.00

40


136.44
136.40
129.41
128.93
127.94
77.44
77.23
77.02
37.04
37.02
32.90
32.87
32.68
32.64
21.92
13.67
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

40