Supporting Information

For

Rhodium-catalyzed Phosphorylation Reaction of Water-soluble Disulfides Using Hypodiphosphoric Acid Tetraalkyl Esters in Water

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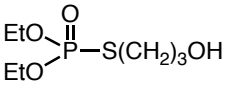
Supplementary Materials. ^{1}H- and ^{13}C-NMR spectra were recorded on 400 MHz instrument and tetramethylsilane were used as standard. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. IR spectra were measured on a FT/IR spectrometer. Melting points were determined with a micro melting point apparatus without correction. High-resolution mass spectra (HRMS) were measured on quadrupole or EI-TOF. Hypodiphosphoric acid tetraalkyl esters were synthesized by the literature methods.[1]

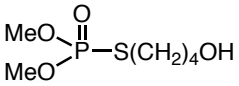
Typical procedure for synthesis of the *O,O*-diethyl *S*-4-hydroxybutyl phosphorothioic acid 3ba. In a two-necked flask were placed $RhCl_3 \cdot 3H_2O$ (5.0 mg, 10 mol%), bis(4-hydroxybutyl) disulfide **1b** (0.25 mmol, 52.5 mg), and hypodiphosphoric acid tetraethyl esters **2a** (0.25 mmol, 68.0 mg) in water (H_2O, 0.25 mL) under an argon atomosphere, and the mixture was heated at 25 ℃ for 36 h. The mixture was extracted three times with $CHCl_3$. Then, the $CHCl_3$ layer was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: from AcOEt:MeOH = 50:1 to AcOEt:MeOH = 33:1), and silica gel (eluent: from AcOEt:toluene = 10:1 to AcOEt), giving *O,O*-diethyl *S*-4-hydroxybutyl phosphorothioic acid **3ba** (75.1 mg, 62%). **3ba**: Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (6H, J = 7.2, 0.8 Hz), 1.68 (2H, bquintet, J = 6.0 Hz), 1.82 (2H, bquintet, J = 7.6 Hz), 2.89 (2H, dt, J = 14.8, 7.6 Hz), 3.68 (2H, t, J = 6.0 Hz), 4.11-4.23 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.0 (d, J = 6.7 Hz), 27.3 (d, J = 5.2 Hz), 30.5 (d, J = 3.7 Hz), 31.3, 61.8, 63.5 (d, J = 6.0 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 28.2. IR (neat) ν 3436, 2933, 1239, 1015, 972 cm^{-1}. MS (EI) m/z 242 (M^+, 6%), 170 (M^+-70, 100%). HRMS Calcd for $C_8H_{19}O_4PS$: 242.0741. Found: 242.0744.

O,O-Diethyl S-3-hydroxypropyl phosphorothioic acid (**3aa**).[2] Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (6H, t, J = 7.2 Hz), 1.90 (2H, quintet, J = 6.4 Hz), 3.04 (2H, dt, J = 17.2,

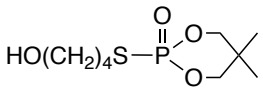
6.8 Hz), 3.80 (2H, t, J = 5.6 Hz), 4.10-4.24 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.0 (d, J = 7.5 Hz), 27.1, 33.5, 59.1, 63.9 (d, J = 5.9 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 29.5. IR (neat) ν 3418, 2982, 1238, 1016, 973 cm^{-1}. MS (EI) m/z 228 (M^+, 7%), 170 (M^+-58, 100%). HRMS Calcd for $C_7H_{17}O_4PS$: 228.0585. Found: 228.0575.



O,O-Dimethyl S-4-hydroxybutyl phosphorothioic acid (**3bb**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.66-1.71 (3H, m), 1.82 (2H, quintet, J = 7.6 Hz), 2.89 (2H, dt, J = 15.2, 7.6 Hz), 3.69 (2H, t, J = 6.4 Hz), 3.80 (6H, d, J = 12.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 27.4 (d, J = 5.2 Hz), 30.5 (d, J = 4.5 Hz), 31.2, 53.8 (d, J = 5.9 Hz), 61.9. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 31.2. IR (neat) ν 3420, 2950, 1241, 1020 cm^{-1}. MS (EI) m/z 214 (M^+, 2%), 142 (M^+-72, 100%). HRMS Calcd for $C_6H_{15}O_4PS$: 214.0429. Found: 214.0425.

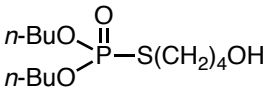


5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxide (**3bc**) Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.91 (3H, s), 1.29 (3H, s), 1.66-1.71 (3H, m), 1.84 (2H, quintet, J = 7.6 Hz), 2.97 (2H, quintet, J = 7.6 Hz), 3.69 (2H, t, J = 6.4 Hz), 3.93 (2H, dd, J = 23.6, 11.2 Hz), 4.13 (2H, dd, J = 10.8, 3.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.5, 22.0, 27.4 (d, J = 4.6 Hz), 29.6 (d, J = 3.0 Hz), 31.2, 32.5 (d, J = 6.8 Hz), 62.0. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 20.8. IR (neat) ν 3400, 2925, 1262, 1053 cm^{-1}. MS (EI) m/z 254 (M^+, 3%), 182 (M^+-72, 100%). HRMS Calcd for $C_9H_{19}O_4PS$: 254.0742. Found: 254.0758.

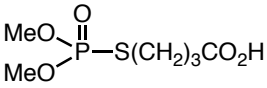


O,O-Dibutyl S-4-hydroxybutyl phosphorothioic acid (**3bd**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.94 (6H, t, J = 7.2 Hz), 1.42 (4H, sextet, J = 7.6 Hz), 1.64-1.72 (6H, m), 1.82 (2H, quintet, J = 7.6 Hz), 2.88 (2H, quintet, J = 7.6 Hz), 3.68 (2H, t, J = 6.4 Hz), 4.04-4.14 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 13.6, 18.7, 27.4 (d, J = 5.3 Hz), 30.5 (d, J = 3.7 Hz), 31.3, 32.1 (d, J = 7.5 Hz), 62.0, 67.3 (d, J = 6.0 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 27.8. IR (neat)

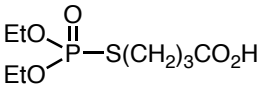
ν 3436, 2960, 1459, 1244, 1020 cm^{-1}. MS (EI) m/z 298 (M^+, 3%), 115 (M^+-183, 100%). HRMS Calcd for $C_{12}H_{27}O_4PS$: 298.1368. Found: 298.1386.



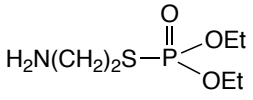
4-{[Bis(methoxy)phosphinothioyl]thio}butanoic acid (**3cb**) Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.04 (2H, quintet, J = 7.2 Hz), 2.51 (2H, t, J = 7.2 Hz), 2.92 (2H, dt, J = 15.6, 7.2 Hz), 3.81 (6H, d, J = 12.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.8 (d, J = 5.2 Hz), 29.9 (d, J = 4.5 Hz), 32.3, 53.9 (d, J = 6.0 Hz), 176.9. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 30.8. IR (neat) ν 2955, 1730, 1213, 1021 cm^{-1}. MS (EI) m/z 228 (M^+, 7%), 169 (M^+-59, 100%). HRMS Calcd for $C_6H_{13}O_5PS$: 228.0232. Found: 228.0231.



4-{[Bis(ethoxy)phosphinothioyl]thio}butanoic acid (**3ca**) Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (6H, td, J = 7.2, 0.8 Hz), 2.05 (2H, quintet, J = 7.2 Hz), 2.52 (2H, t, J = 7.2 Hz), 2.92 (2H, dt, J = 15.6, 7.2 Hz), 4.12-4.22 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.0 (d, J = 6.7 Hz), 25.9 (d, J = 4.5 Hz), 29.9 (d, J = 3.7 Hz), 32.3, 63.8 (d, J = 6.0 Hz), 176.9. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 27.2. IR (neat) ν 2933, 1731, 1015, 772 cm^{-1}. MS (EI) m/z 256 (M^+, 4%), 197 (M^+-59, 100%). HRMS Calcd for $C_8H_{17}O_5PS$: 256.0534. Found: 256.0559.

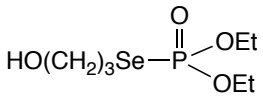


4-{[Bis(ethoxy)phosphinothioyl]thio}ethylamine (**3da**) Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.36 (6H, t, J = 7.2 Hz), 2.98-3.02 (4H, m), 4.20-4.28 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.9 (d, J = 6.8 Hz), 32.3 (d, J = 3.8 Hz), 41.3 (d, J = 4.6 Hz), 66.1 (d, J = 6.1 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 31.6. IR (neat) ν 3367, 2982, 1246, 1018, 971 cm^{-1}. MS (EI) m/z 214 (M^++H, 100%). HRMS Calcd for $C_6H_{17}O_3NPS$: 214.0661. Found: 214.0658.

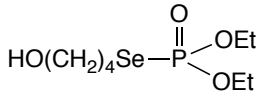


O,O-Diethyl Se-3-hydroxypropyl phosphoroselenoic acid (**7aa**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 (6H, td, J = 7.2, 0.8 Hz), 1.96 (2H, dt, J = 12.0, 6.4 Hz), 3.09 (2H, dt, J =

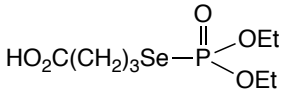
16.4, 6.8 Hz), 3.78 (2H, t, J = 5.6 Hz), 4.12-4.23 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.0 (d, J = 7.5 Hz), 23.2 (d, J = 4.4 Hz), 33.7 (d, J = 2.3 Hz), 59.7, 63.7 (d, J = 5.9 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 21.4. IR (neat) ν 3423, 2921, 1229, 1012 cm^{-1}. MS (EI) m/z 276 (M^+, 6%), 218 (M^+-58, 100%). HRMS Calcd for $C_7H_{17}O_4PSe$: 276.0030. Found: 276.0036.



O,O-Diethyl Se-4-hydroxybutyl phosphoroselenoic acid (**7ba**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.37 (6H, t, J = 7.2 Hz), 1.67 (2H, quintet, J = 6.4 Hz), 1.90 (2H, quintet, J = 7.6 Hz), 2.92 (2H, quintet, J = 7.2 Hz), 3.68 (2H, t, J = 6.4 Hz), 4.11-4.22 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.9 (d, J = 7.6 Hz), 26.0 (d, J = 4.6 Hz), 27.8 (d, J = 4.6 Hz), 32.3, 61.7, 63.4 (d, J = 6.1 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 20.9 (t, J = 245.7 Hz). IR (neat) ν 3434, 2933, 2869, 1241, 1013 cm^{-1}. MS (EI) m/z 290 (M^+, 6%), 218 (M^+-72, 100%). HRMS Calcd for $C_8H_{19}O_4PSe$: 290.0186. Found: 290.0168.

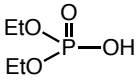


4-[Bis(ethoxy)phosphinoseleno]butanoic acid (**7ca**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.30 (6H, t, J = 7.2 Hz), 2.06 (2H, quintet, J = 7.2 Hz), 2.85 (2H, t, J = 7.2 Hz), 2.87 (2H, quintet, J = 7.2 Hz), 4.05-4.16 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.0 (d, J = 7.6 Hz), 25.3 (d, J = 4.6 Hz), 26.2 (d, J = 3.8 Hz), 33.4, 63.6 (d, J = 6.1 Hz), 177.2. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 20.5 (t, J = 244.1 Hz). IR (neat) ν 3520, 2984, 1730, 1225, 1011 cm^{-1}. MS (EI) m/z 256 (M^+, 4%), 197 (M^+-59, 100%). HRMS Calcd for $C_8H_{17}O_5PS$: 256.0534. Found: 256.0559.

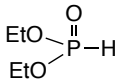


Diethyl phosphate (**4**). Yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.35 (7H, td, J = 7.2, 1.2 Hz), 4.11 (4H, quintet, J = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.0 (d, J = 6.7 Hz), 64.7 (d, J = 6.0 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 0.7. IR (neat) ν 2986, 1226, 1166, 1034 cm^{-1}.

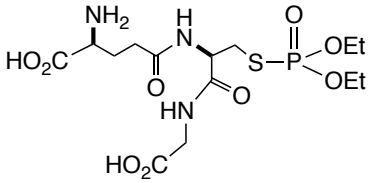
MS (EI) m/z 155 (M^++1, 14%), 154 (M^+, 2%), 127 (M^+-27, 100%). HRMS Calcd for $C_4H_{12}O_4P$ (M^++1): 155.0473. Found: 155.0472.



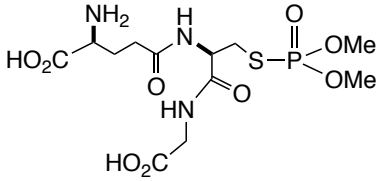
Diethyl phosphite (**5**). Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 (6H, td, J = 7.2, 2.0 Hz), 4.16 (4H, quintetd, J = 7.2, 1.2 Hz), 6.82 (1H, dd, J = 693.6, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 16.3 (d, J = 6.0 Hz), 61.7 (d, J = 6.1 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 7.30. IR (neat) ν 3548, 2985, 2910, 1258, 1045 cm^{-1}. MS (EI) m/z 139 (M^++1, 100%). HRMS Calcd for $C_7H_{12}O_3P$ (M^++1): 139.0524. Found: 139.0542.



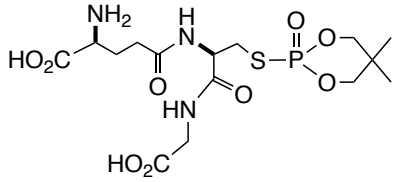
Typical procedure for synthesis of the *N-[N-L-γ-glutamyl-S-(diethoxyphosphinyl)-L-cysteinyl]glycine* 9a. In a two-necked flask were placed $RhCl_3 \cdot 3H_2O$ (5.0 mg, 10 mol%), Glutathione (Oxidized Form) **8** (0.25 mmol, 153.0 mg), and hypodiphosphoric acid tetraethyl esters **2a** (0.25 mmol, 68.0 mg) in water (H_2O, 1.0 mL) under an argon atmosphere, and the mixture was heated at 40 ℃ for 36 h. The mixture was extracted three times with $CHCl_3$. Then, the Water layer was concentrated under reduced pressure, and the residue was purified by reversed phase column chromatography (eluent: from H_2O/TFA = 100/0.01 to H_2O/MeCN/TFA = 95/5/0.01), giving *N*-[*N*-*L*-γ-glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine **9a** (171.0 mg, 77%). **9a**: Pale yellow solid. M.p. 160.0-161.0 °C (H_2O/Acetone = 5:1). $[\alpha]_D^{28}$ -20.5° (c 0.1, H_2O). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.34 (6H, t, J = 7.2 Hz), 2.17 (2H, quintet, J = 7.6 Hz), 2.54 (2H, octet, J = 7.6 Hz), 3.11-3.20 (1H, m), 3.34 (1H, td, J = 14.0, 4.8 Hz), 3.85 (1H, t, J = 6.4 Hz), 3.97 (2H, d, J = 3.6 Hz), 4.17-4.25 (4H, m), 4.68 (1H, dd, J = 8.4, 4.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.1 (d, J = 6.7 Hz), 25.5, 30.9, 31.0, 41.1, 52.6, 53.3 (d, J = 3.7 Hz), 65.6 (d, J = 6.8 Hz), 171.5, 172.1, 172.8, 174.3. ^{31}P-NMR (162 MHz, $CDCl_3$) δ 30.6. IR (KBr) ν 3285, 1668, 1539, 1204 cm^{-1}. HRMS Calcd for $C_{14}H_{26}N_3O_9PS$: 443.1127. Calcd for M^++H ($C_{14}H_{27}N_3O_9PS$): 444.1206. Found: 444.1200.



N-[N-L-γ-glutamyl-S-(dimethoxyphosphinyl)-L-cysteinyl]glycine (**9b**). Colorless solid. M.p. 165.3-166.7 °C (H_2O/Acetone = 5:1). $[\alpha]_D^{28}$ -27.9° (c 0.1, H_2O). ^{1}H-NMR (400 MHz, D_2O) δ 2.20 (2H, q, J = 7.2 Hz), 2.59 (2H, octet, J = 7.2 Hz), 3.16 (1H, ddd, J = 18.0, 13.6, 8.4 Hz), 3.34 (1H, td, J = 14.4, 5.2 Hz), 3.82 (6H, d, J = 13.2 Hz), 3.99 (3H, m), 4.69 (1H, dd, J = 8.4, 5.2 Hz). ^{13}C-NMR (100 MHz, D_2O) δ 25.5, 30.85 (d, J = 3.8 Hz), 30.92, 41.1, 52.8, 53.2 (d, J = 3.7 Hz), 54.8 (d, J = 6.7 Hz), 171.4, 172.4, 172.9, 174.4. ^{31}P-NMR (162 MHz, D_2O) δ 34.2. IR (KBr) ν 3447, 3020, 1656, 1223, 1027 cm^{-1}. HRMS Calcd for $C_{12}H_{23}N_3O_9N_3PS$: 416.0887. Found: 416.0878.



N-[N-L-γ-glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-L-cysteinyl]glycine (**9c**). Pale yellow oil. $[\alpha]_D^{28}$ -81.7° (c 0.1, H_2O). ^{1}H-NMR (400 MHz, D_2O) δ 0.97 (6H, s), 2.17 (2H, q, J = 7.6 Hz), 2.54 (2H, octet, J = 7.2 Hz), 2.95 (1H, dd, J = 14.4, 9.6 Hz), 3.25 (1H, dd, J = 14.0, 4.8 Hz), 3.88 (4H, d, J = 11.6 Hz), 3.92 (1H, t, J = 6.4 Hz), 3.99 (2H, s), 4.73 (1H, dd, J = 9.2, 4.8 Hz). ^{13}C-NMR (100 MHz, D_2O) δ 20.7, 26.4 (d, J = 35.6 Hz), 31.7, 32.3 (d, J = 4.5 Hz), 39.2, 41.9, 53.2, 53.5, 77.0 (d, J = 5.9 Hz), 173.1, 173.3, 173.7, 175.2. ^{31}P-NMR (162 MHz, D_2O) δ -2.7. IR (neat) ν 3275, 2964, 1732, 1655, 1541, 1058, 819 cm^{-1}. HRMS Calcd for $C_{15}H_{26}N_3O_9PS$: 455.1127. Calcd for M^++H ($C_{15}H_{27}N_3O_9PS$): 456.1206. Found: 456.1201.

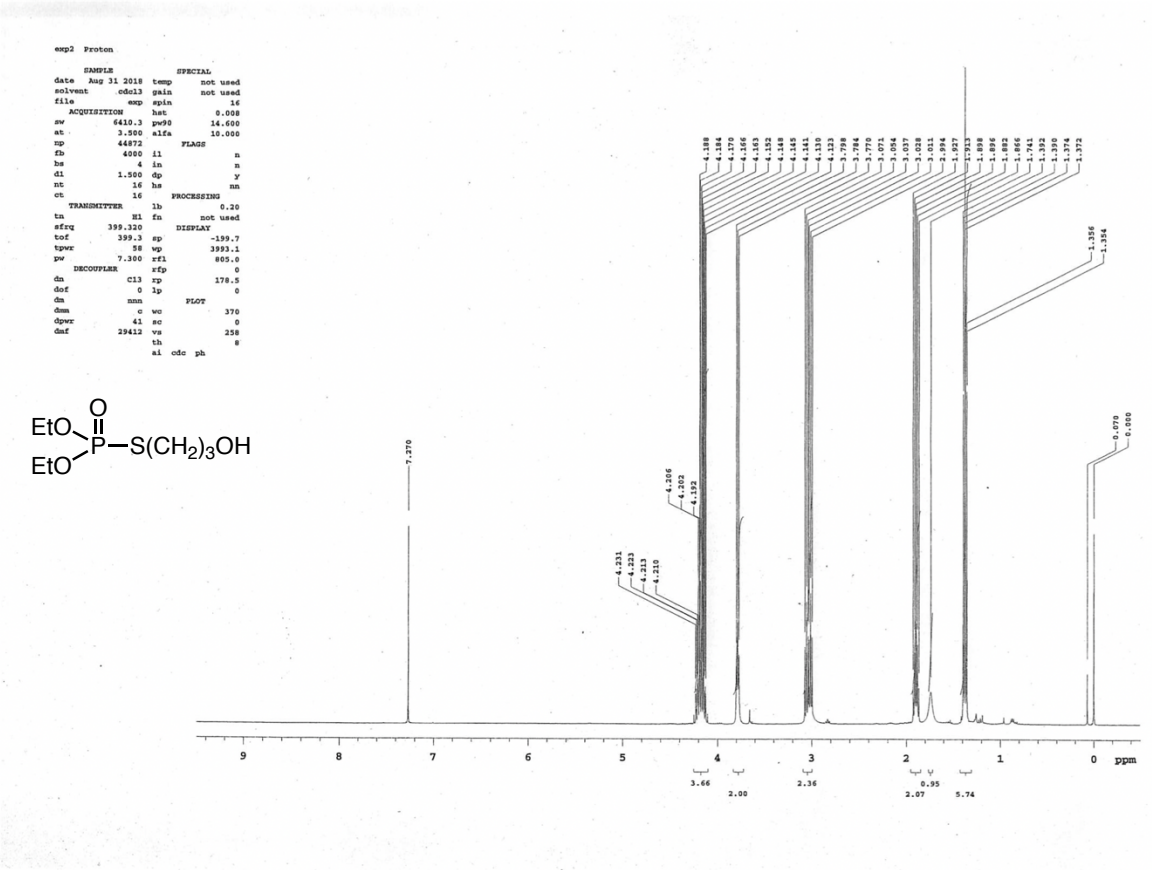


References

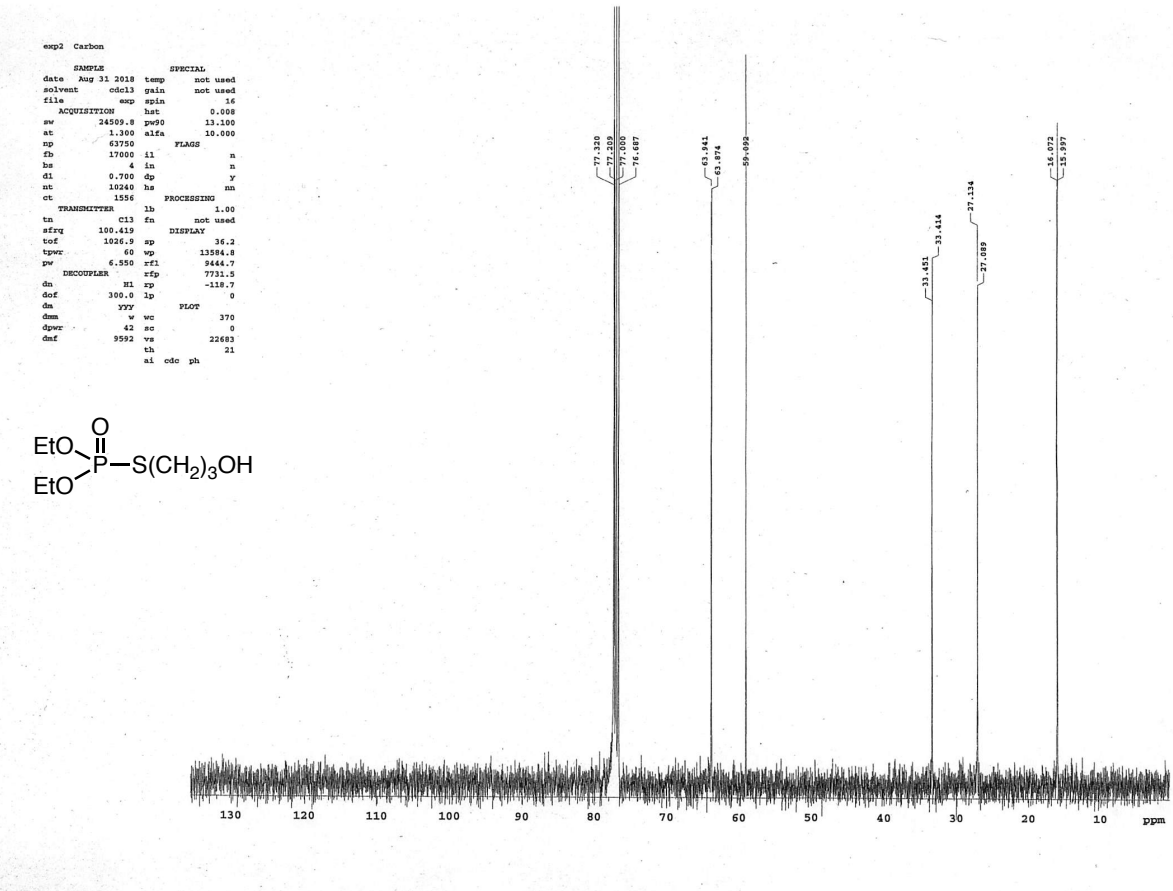
[1] Zhou, Y.; Yin, S.; Gao, Y.; Zhao, Y.; Goto, M.; Han, L.-B. *Angew. Chem. Int. Ed.* **2010**, *49*, 6852-6855.

[2] Renard, P.-Y.; Schwebel, H.; Vayron, P.; Josien, L.; Valleix, A.; Mioskowski, C. *Chem. Eur. J.* **2002**, *8*, 2910-2916.

O,O-Diethyl *S*-3-hydroxypropyl phosphorothioic acid (**3aa**) ^{1}H-NMR

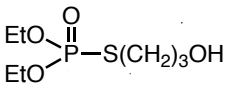


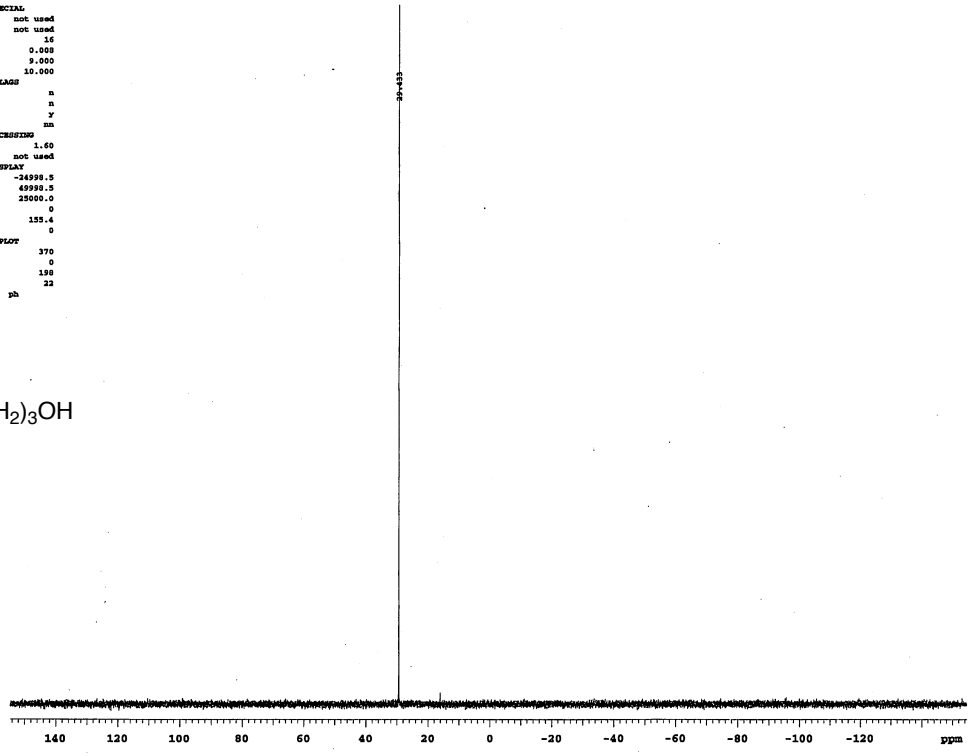
O,O-Diethyl *S*-3-hydroxypropyl phosphorothioic acid (**3aa**) ^{13}C-NMR



O,O-Diethyl *S*-3-hydroxypropyl phosphorothioic acid (3aa) ^{31}P-NMR

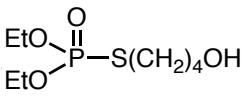
```
exp2  Phosphorus

      SAMPLE                    SPECIAL
date     Aug 31 2018  temp          not used
solvent       cdcl3   gain          not used
file            exp   spin                16
   ACQUISITION        hst                0.008
sw          50000.0   pw90               9.000
at            0.600   alfa              10.000
np            60000         FLAGS
fb            15000   il                     n
bs                4   in                     n
d1            4.400   dp                     y
nt              256   hs                    nn
ct                4
   TRANSMITTER        PROCESSING
                      lb                  1.60
tn              P31   fn              not used
sfrq        161.647         DISPLAY
tof          4230.7   sp              -24998.5
tpwr             58   wp               49998.5
pw            4.500   rfl              25000.0
   DECOUPLER          rfp                    0
dn               H1   rp                155.4
dof               0   lp                     0
dm              nny         PLOT
dmm               w   wc                   370
dpwr             42   sc                     0
dmf            9592   vs                   198
                      th                    22
                      ai  cdc  ph
```

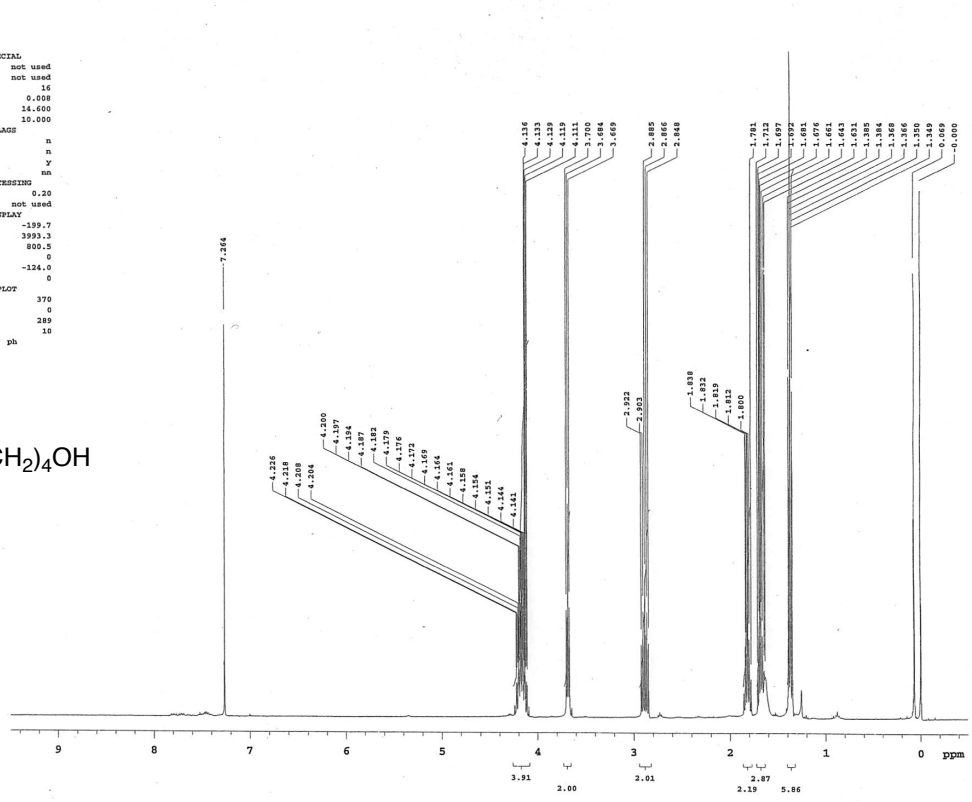




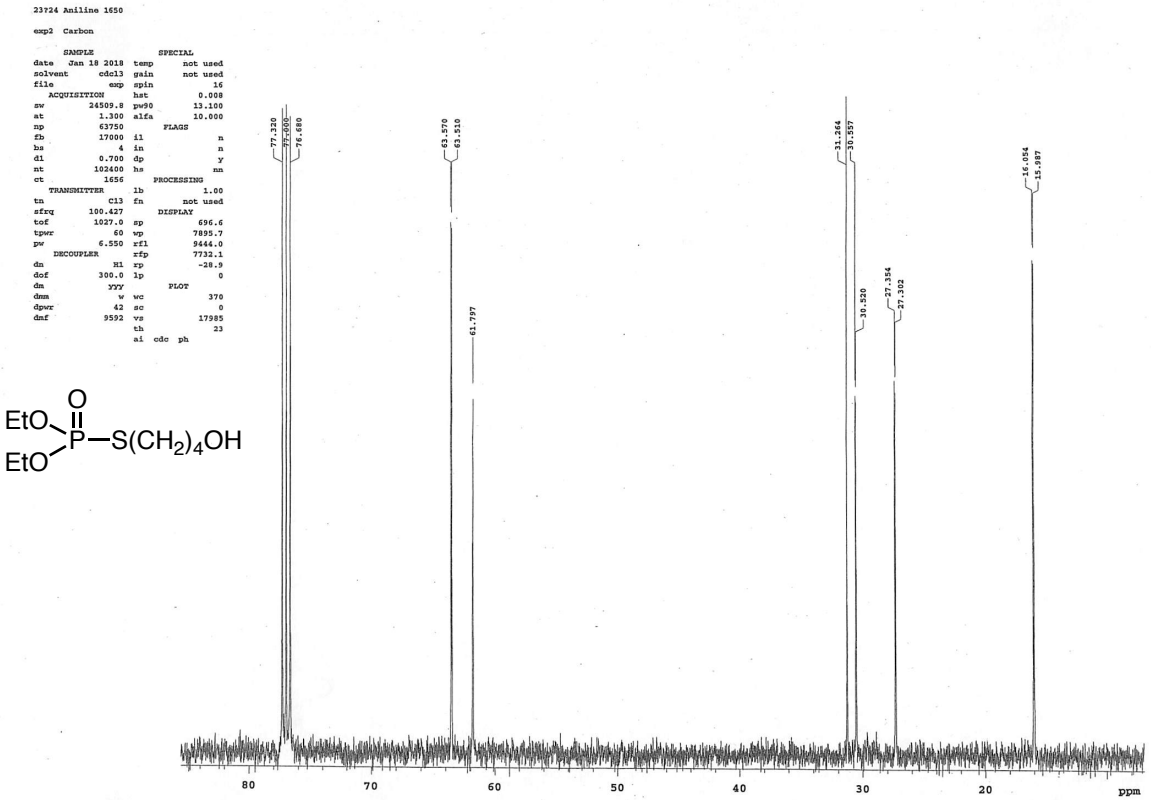
O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ^{1}H-NMR

```
daturyuu

exp10  Proton

      SAMPLE                    SPECIAL
date     Jan 18 2019  temp          not used
solvent       cdcl3   gain          not used
file /media/Transc-   spin                16
end/ch-ch24-s-p-oo-   hst                0.008
          et-1h.fid   pw90              14.600
   ACQUISITION        alfa              10.000
sw          6410.3         FLAGS
at            3.500   il                     n
np            44872   in                     n
fb             4000   dp                     y
bs                4   hs                    nn
d1            1.500         PROCESSING
nt               16   lb                  0.20
ct               16   fn              not used
   TRANSMITTER                DISPLAY
tn               H1   sp              -199.7
sfrq        399.351   wp              3993.3
tof           399.4   rfl              800.5
tpwr             58   rfp                    0
pw            7.300   rp              -124.0
   DECOUPLER          lp                     0
dn               C13
dof               0   wc                   370
dm              nnn   sc                     0
dmm               c   vs                   289
dpwr             41   th                    10
dmf           29412   ai  cdc  ph
```

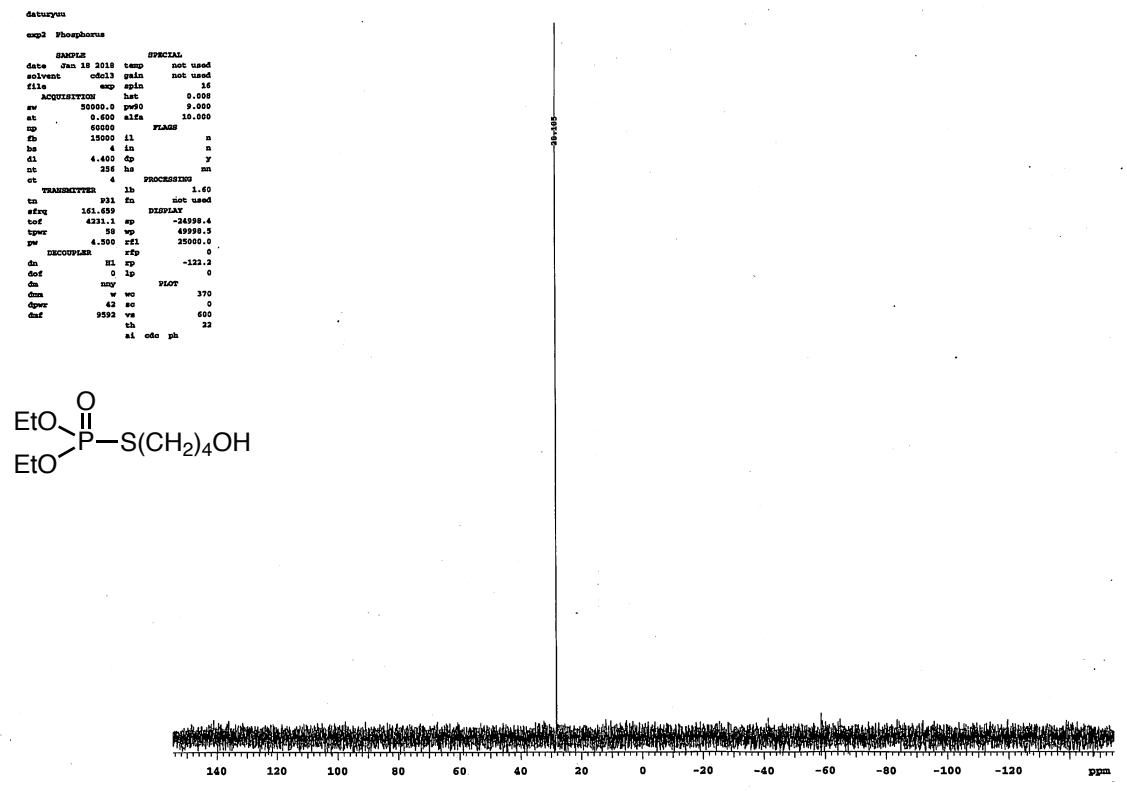




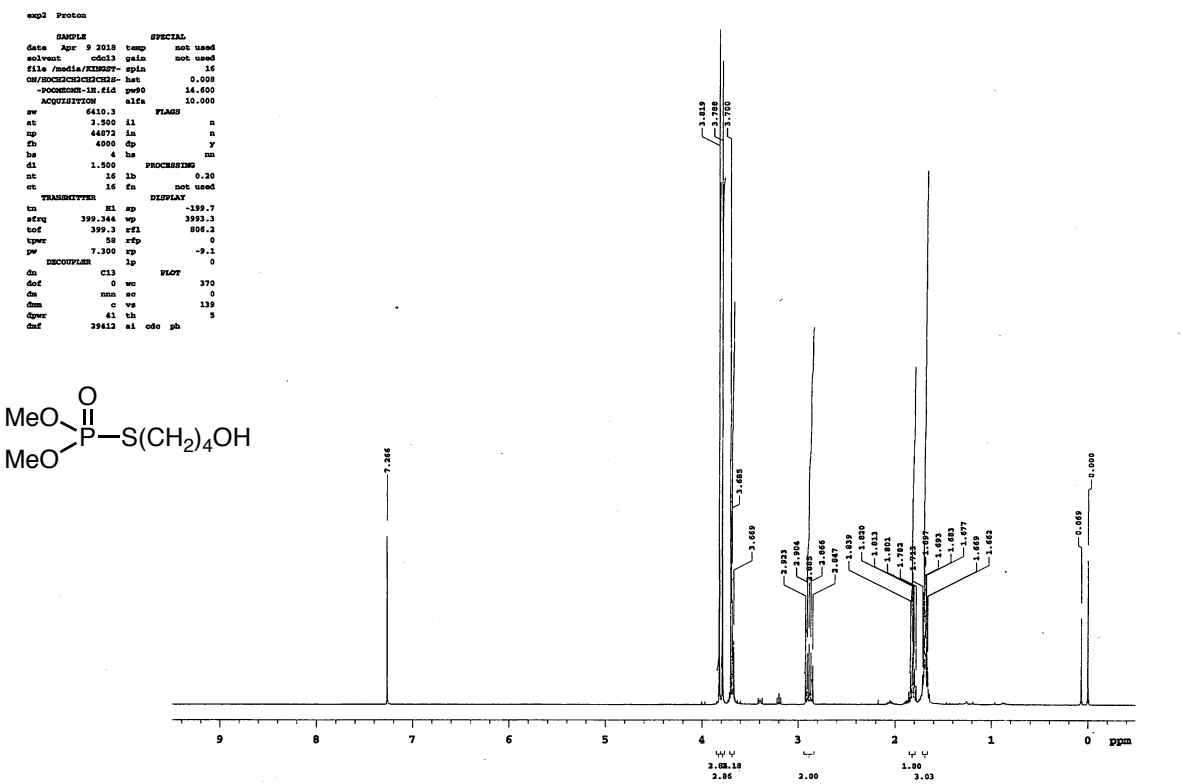
O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ^{13}C-NMR



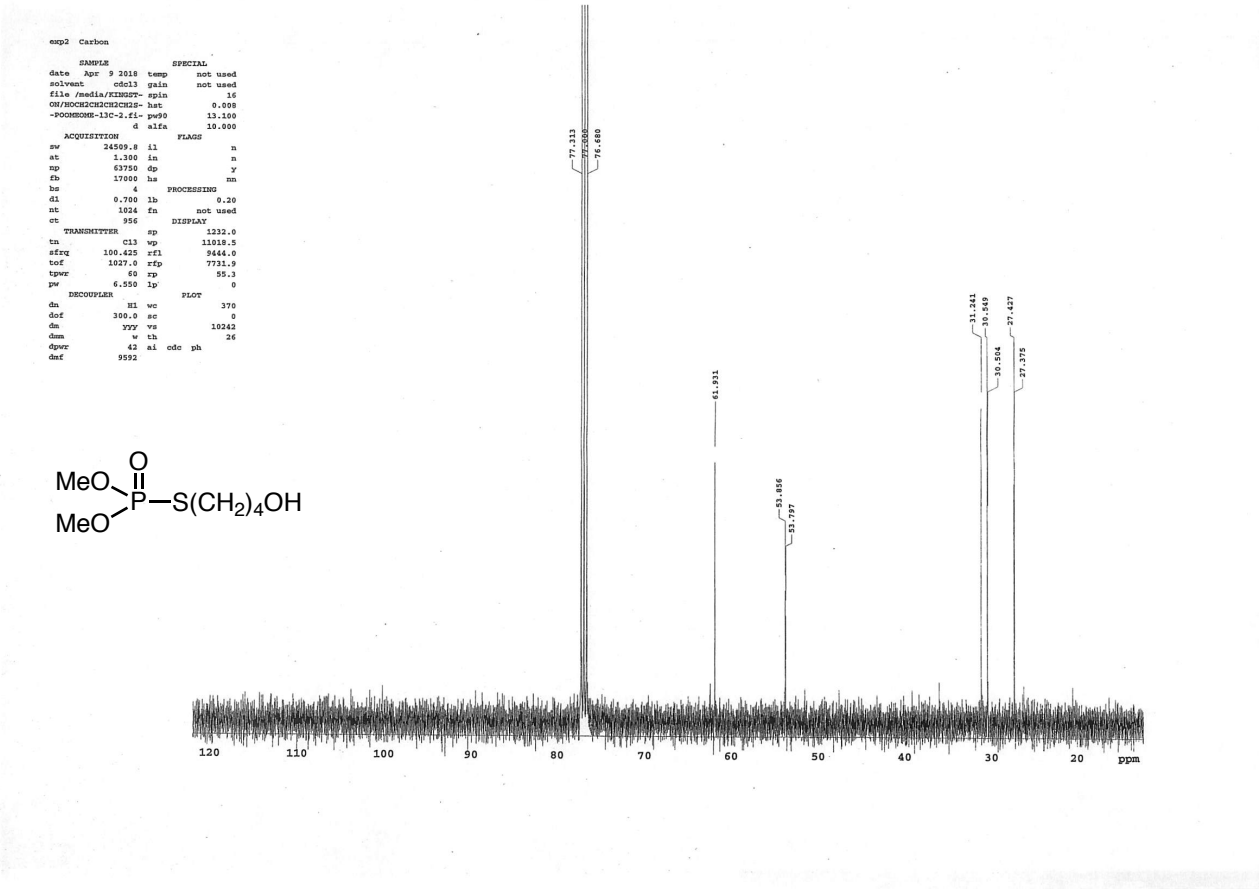
O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ^{31}P-NMR



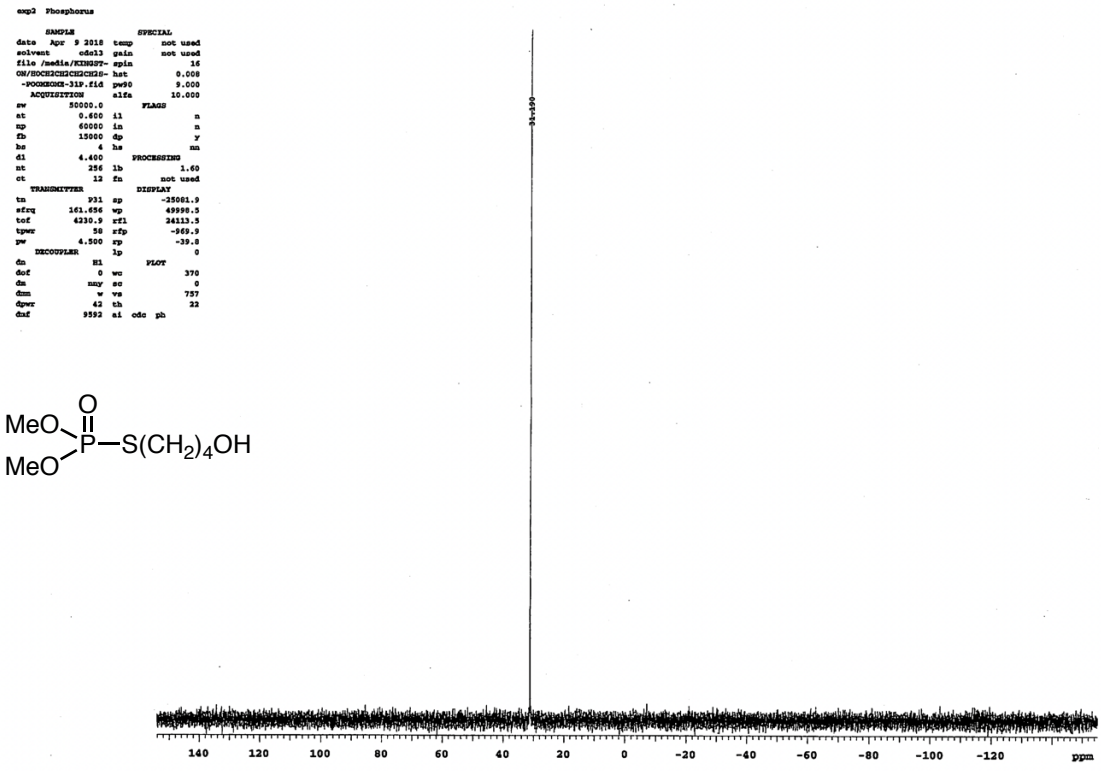
O,O-Dimethyl *S*-4-hydroxybutyl phosphorothioic acid (**3bb**) ^{1}H-NMR



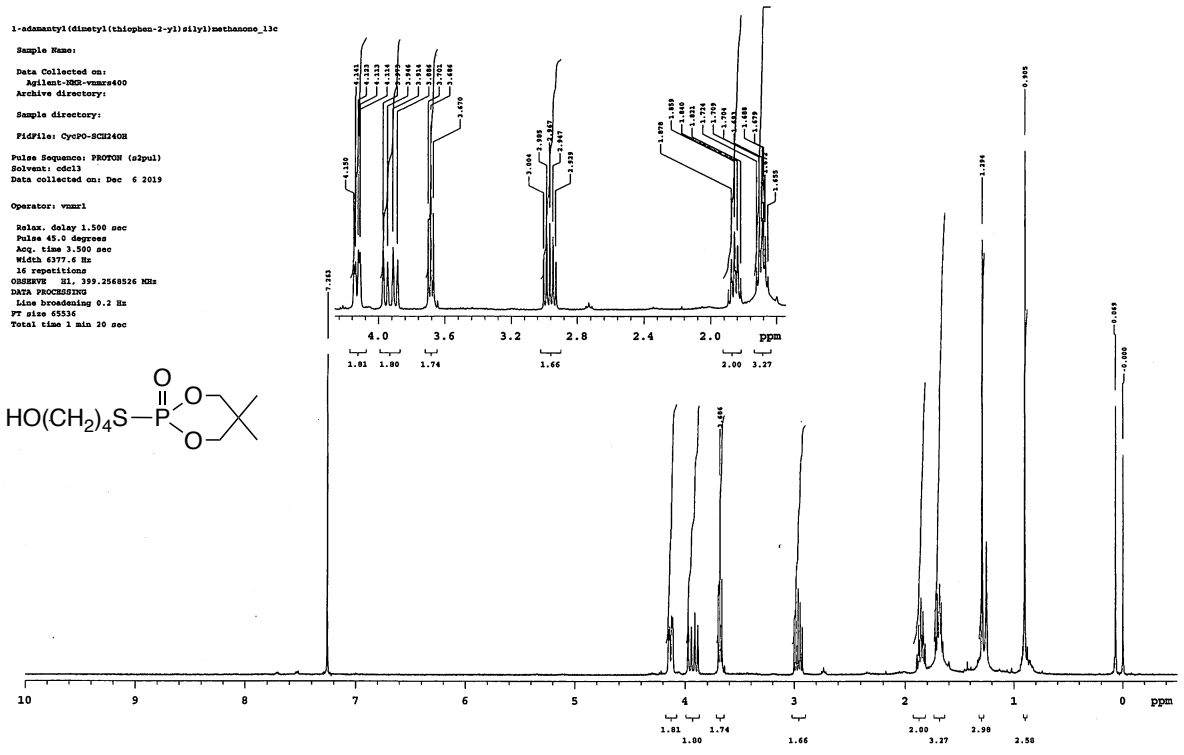
O,O-Dimethyl *S*-4-hydroxybutyl phosphorothioic acid (**3bb**) ^{13}C-NMR



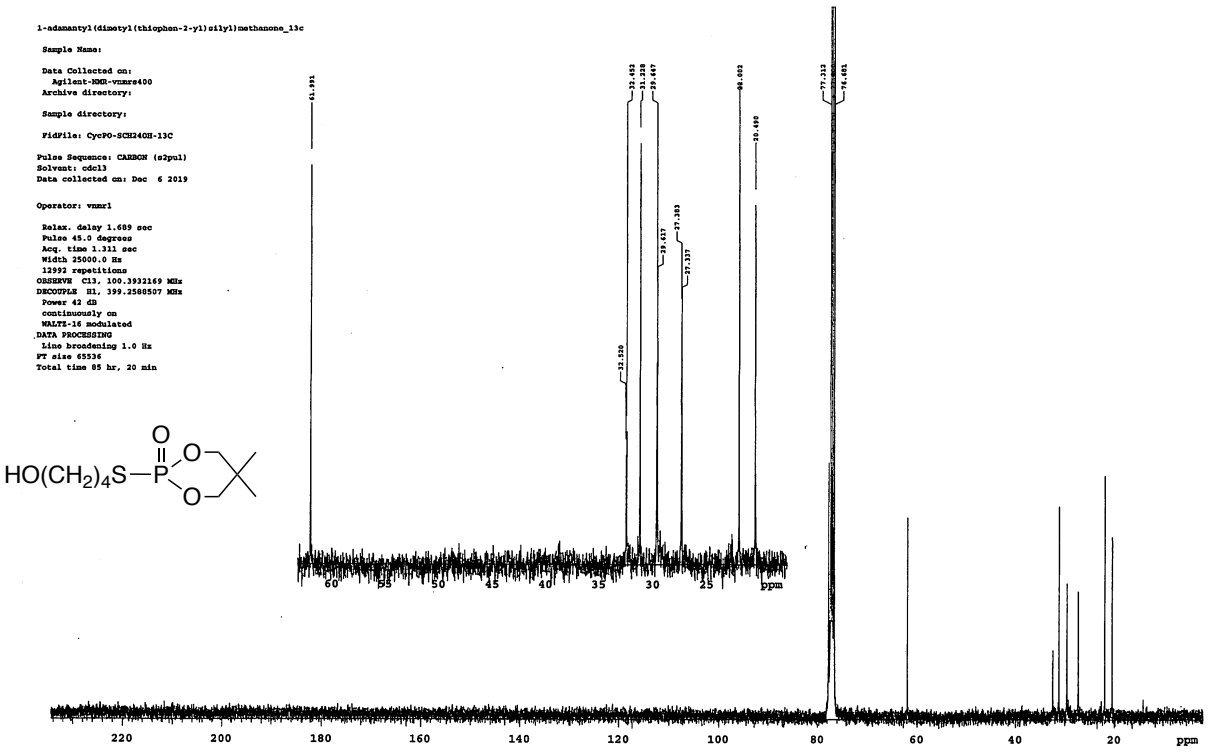
O,O-Dimethyl *S*-4-hydroxybutyl phosphorothioic acid (**3bb**) ^{31}P-NMR



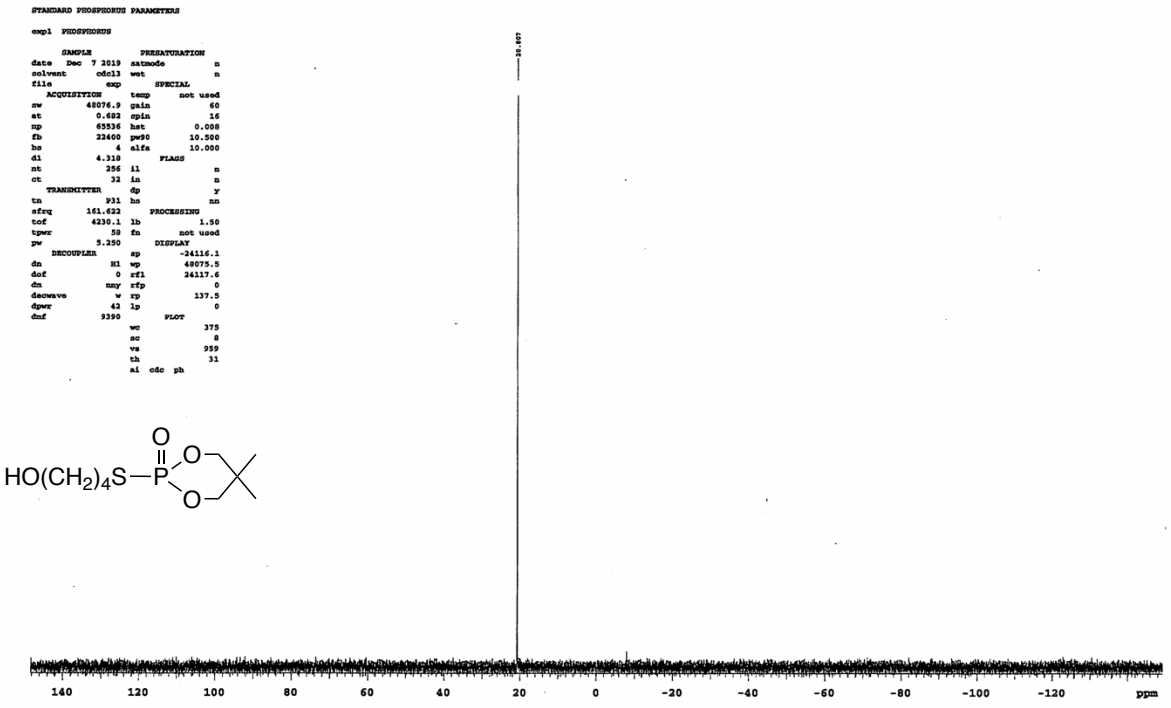
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxid*e* (**3bc**) ^{1}H-NMR



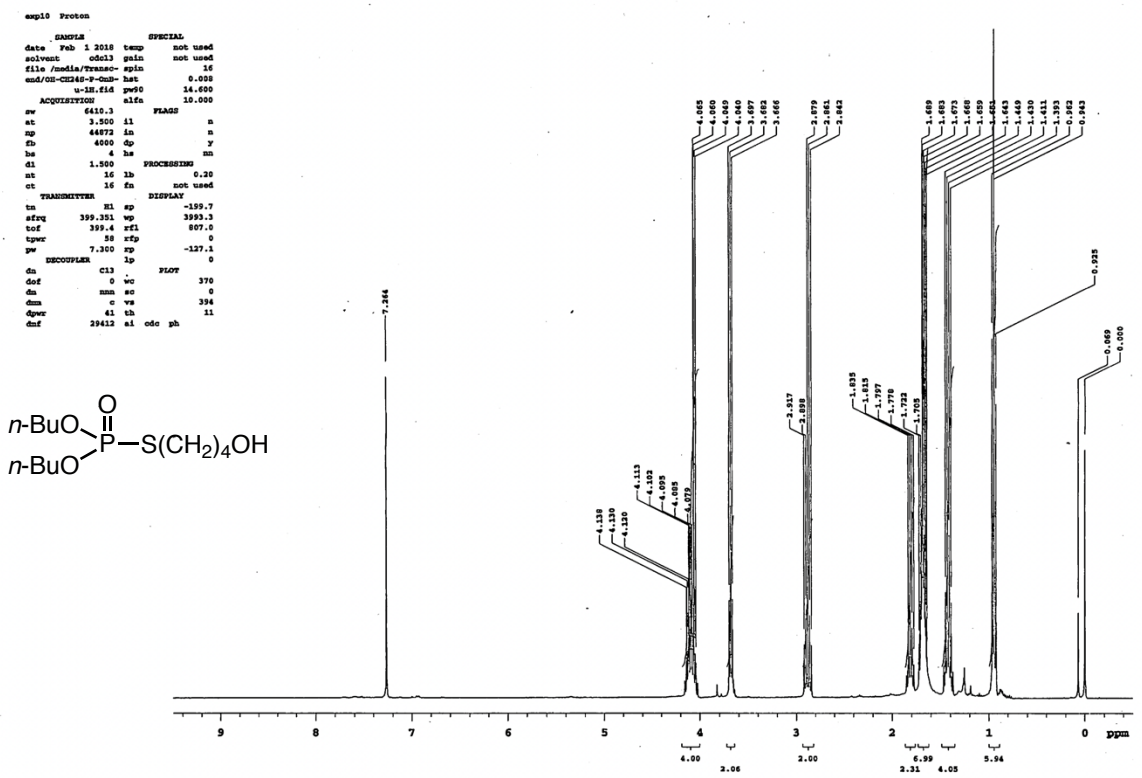
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxid*e* (3bc) ^{13}C-NMR



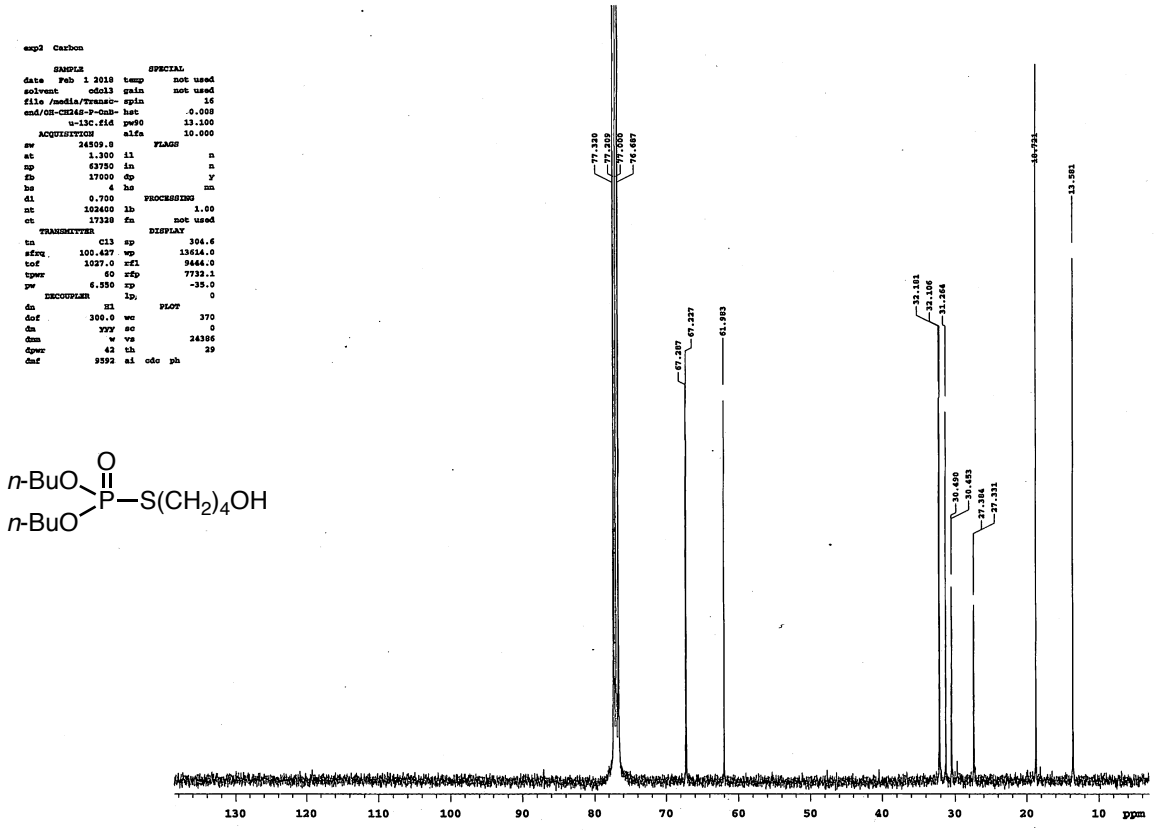
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxid*e* (3bc) ^{31}P-NMR



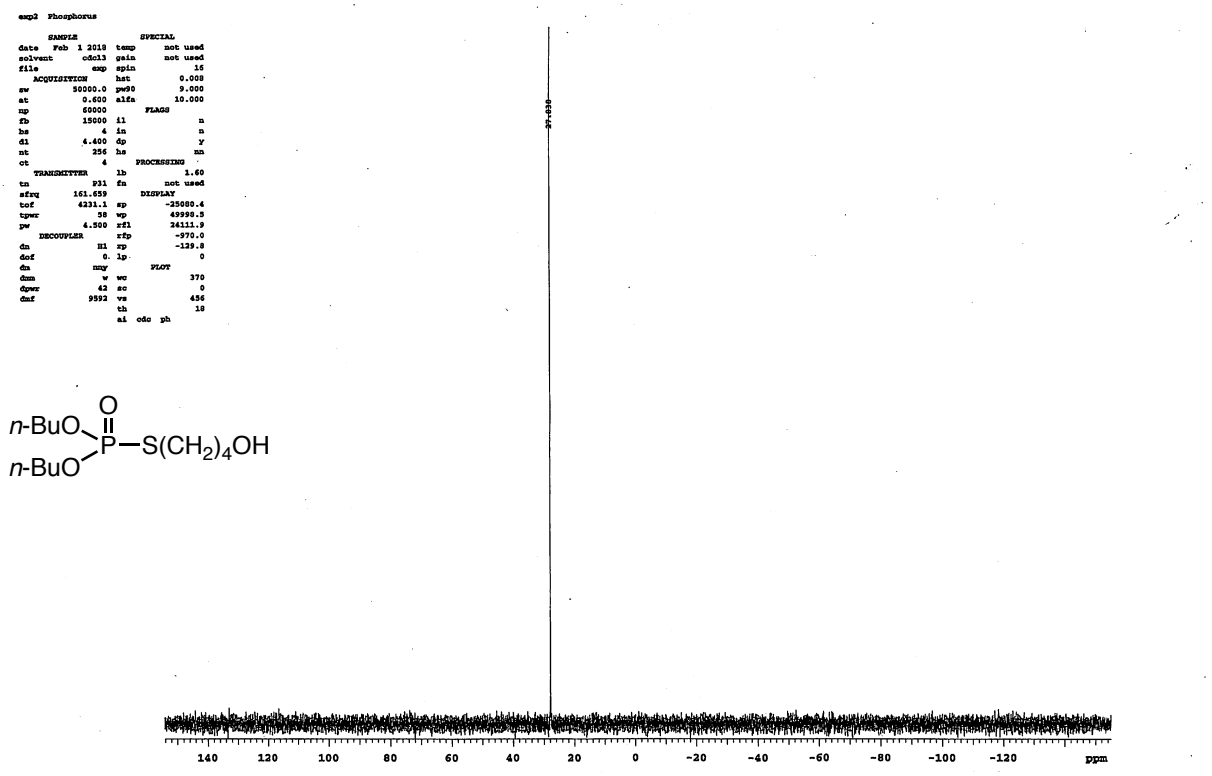
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (**3bd**) ^{1}H-NMR



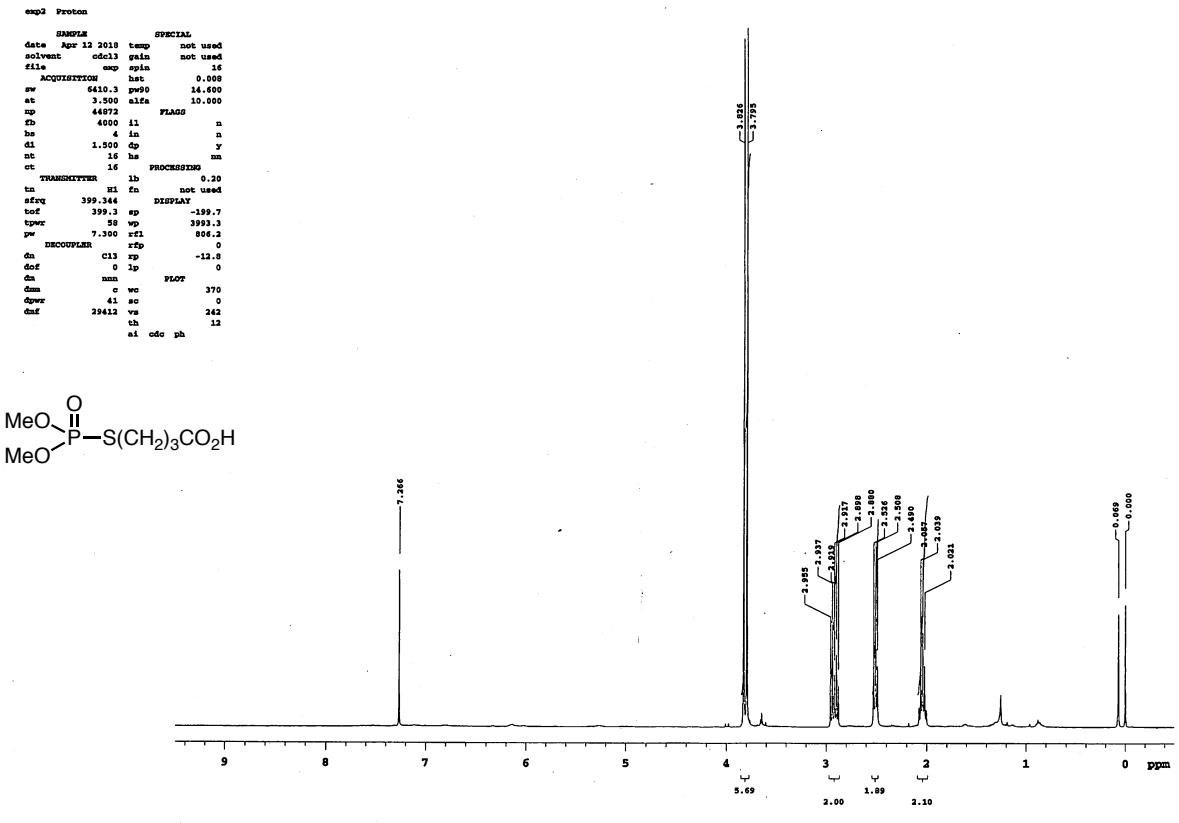
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (**3bd**) ^{13}C-NMR



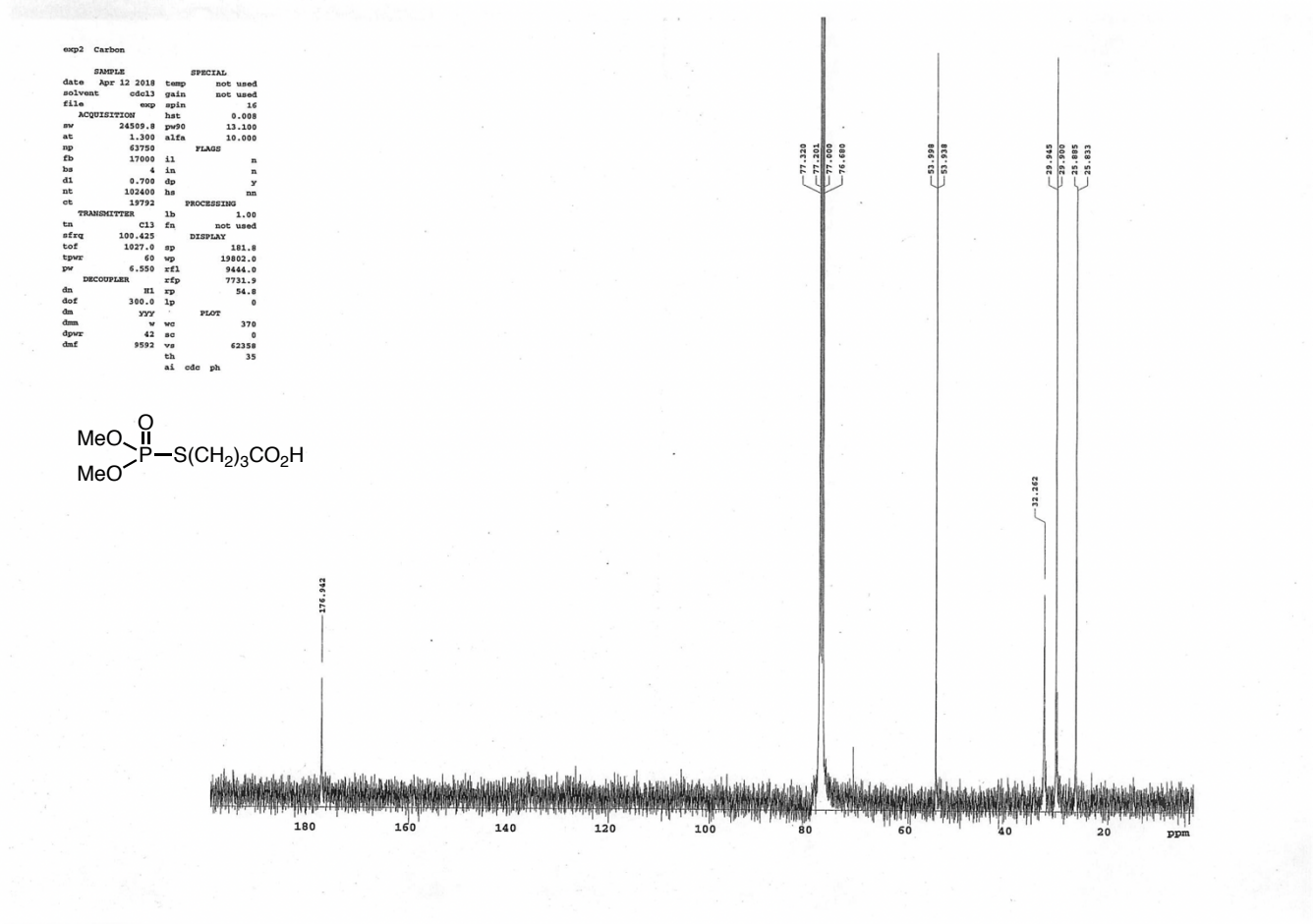
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (**3bd**) ^{31}P-NMR



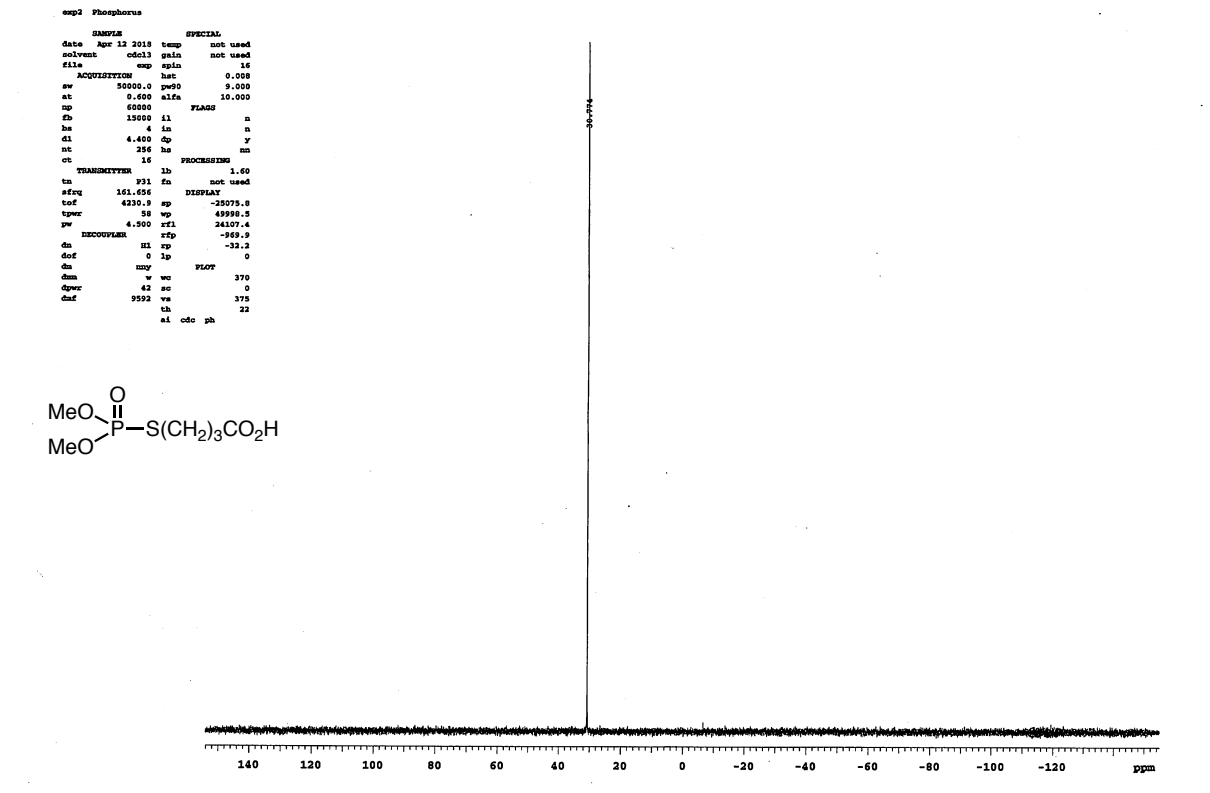
4-{[Bis(methoxy)phosphinothioyl]thio}butanoic acid (**3cb**) ^{1}H-NMR



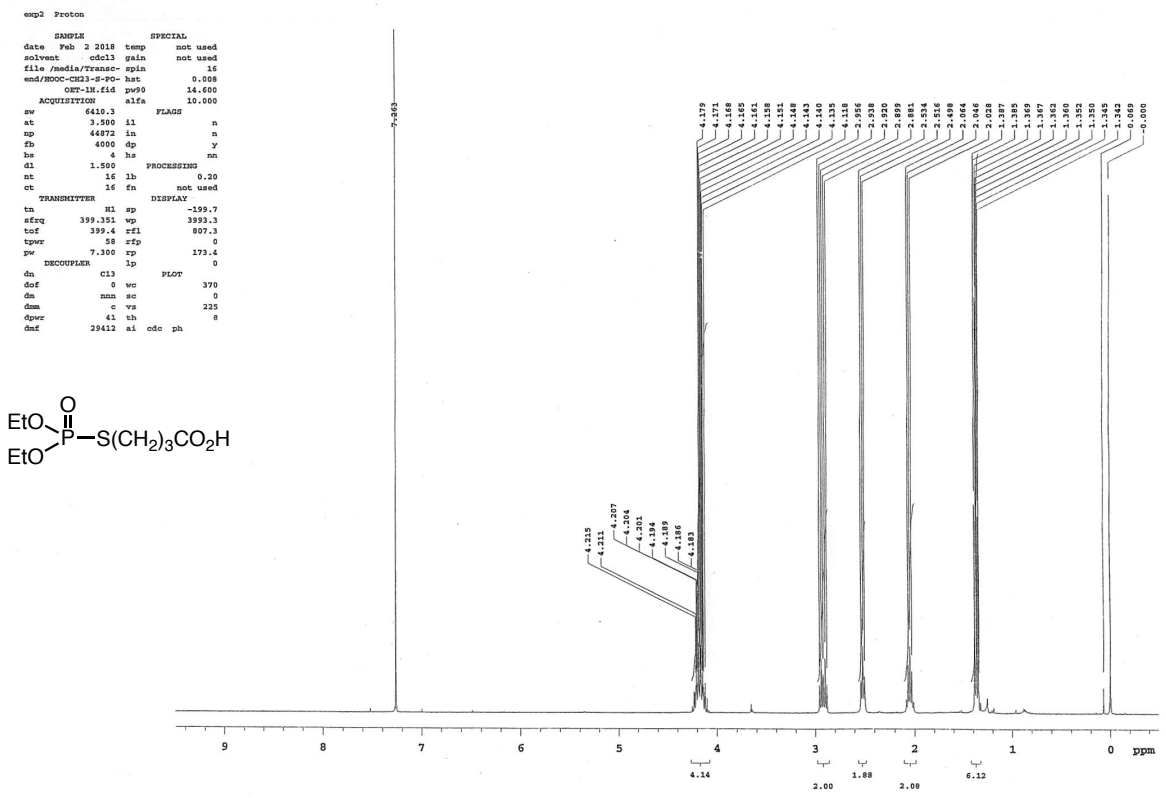
4-{[Bis(methoxy)phosphinothioyl]thio}butanoic acid (3cb) ^{13}C-NMR



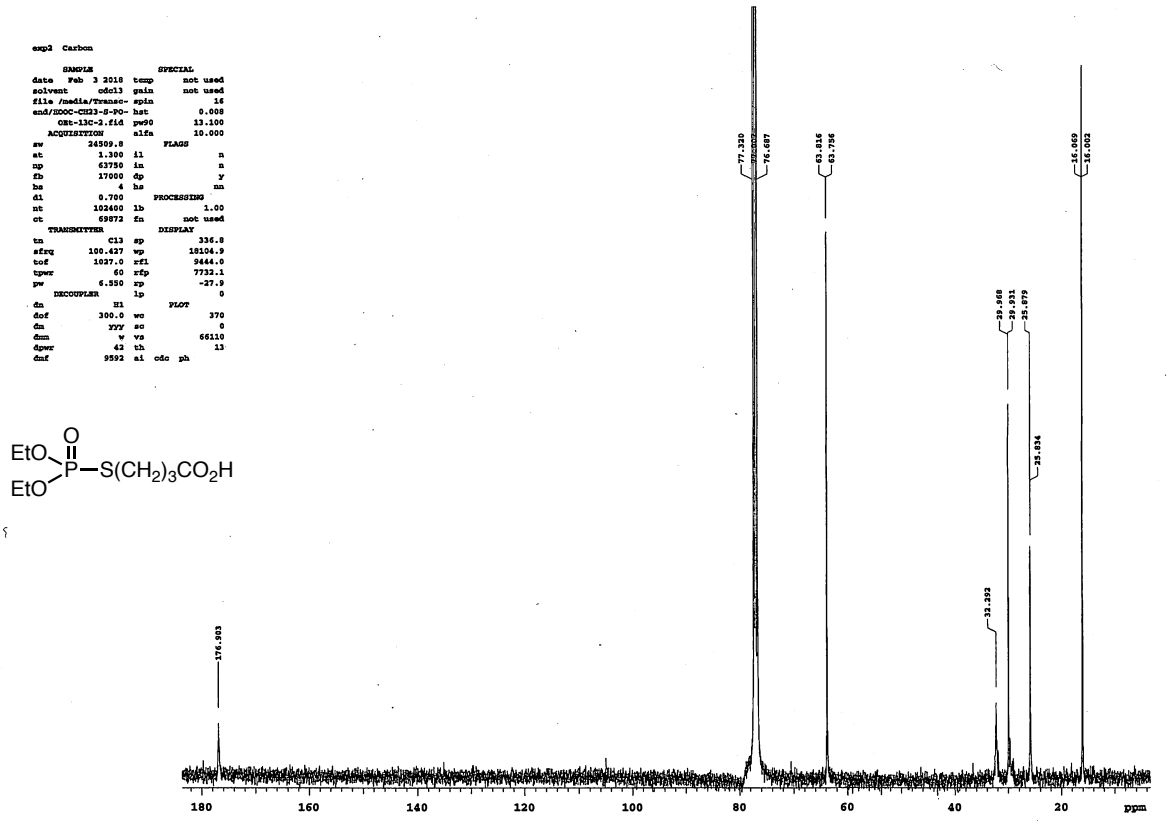
4-{[Bis(methoxy)phosphinothioyl]thio}butanoic acid (3cb) ^{31}P-NMR



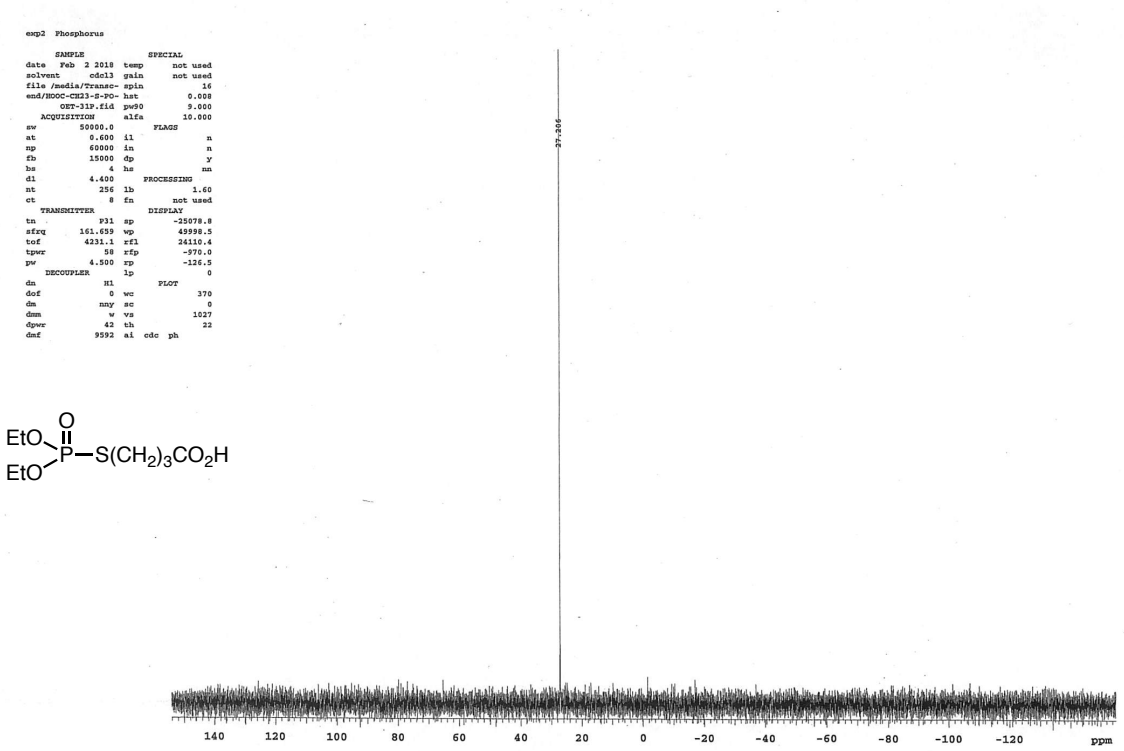
4-{[Bis(ethoxy)phosphinothioyl]thio}butanoic acid (3ca) ^{1}H-NMR



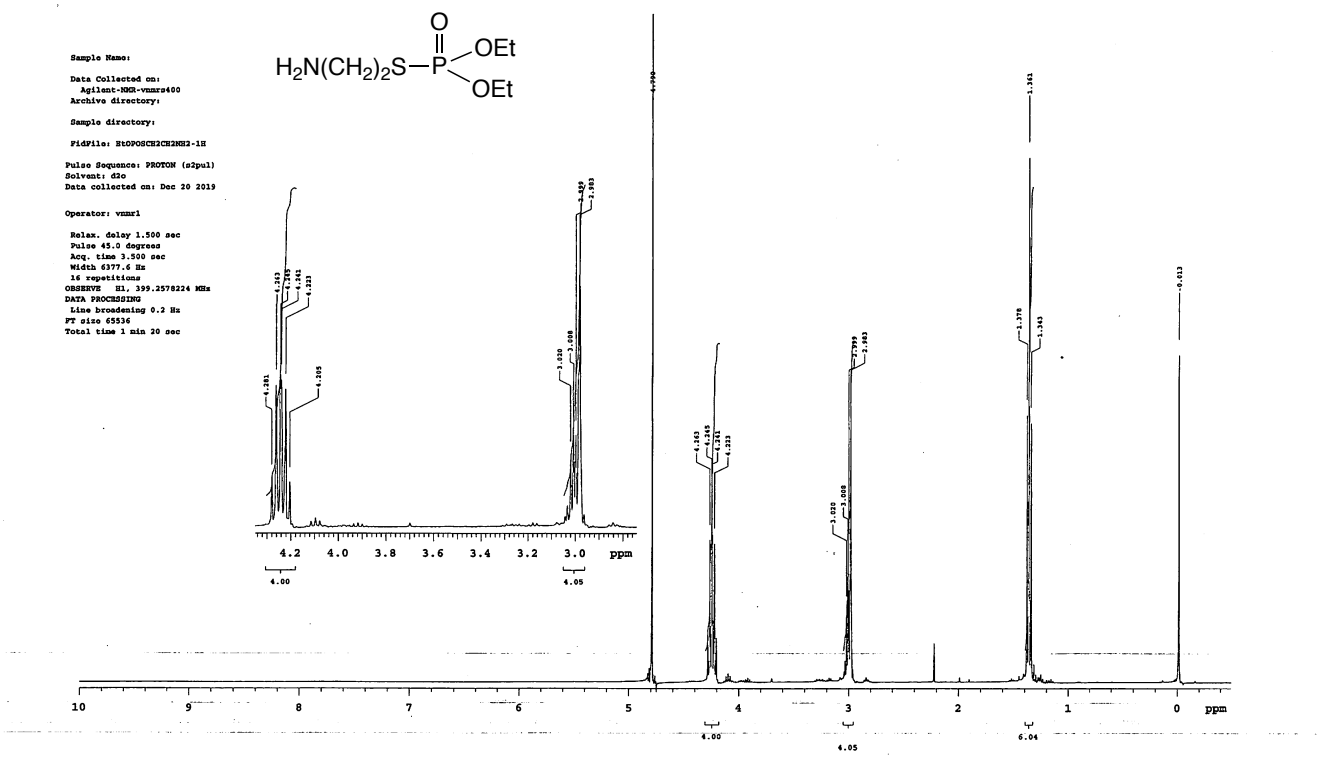
4-{[Bis(ethoxy)phosphinothioyl]thio}butanoic acid (3ca) ^{13}C-NMR



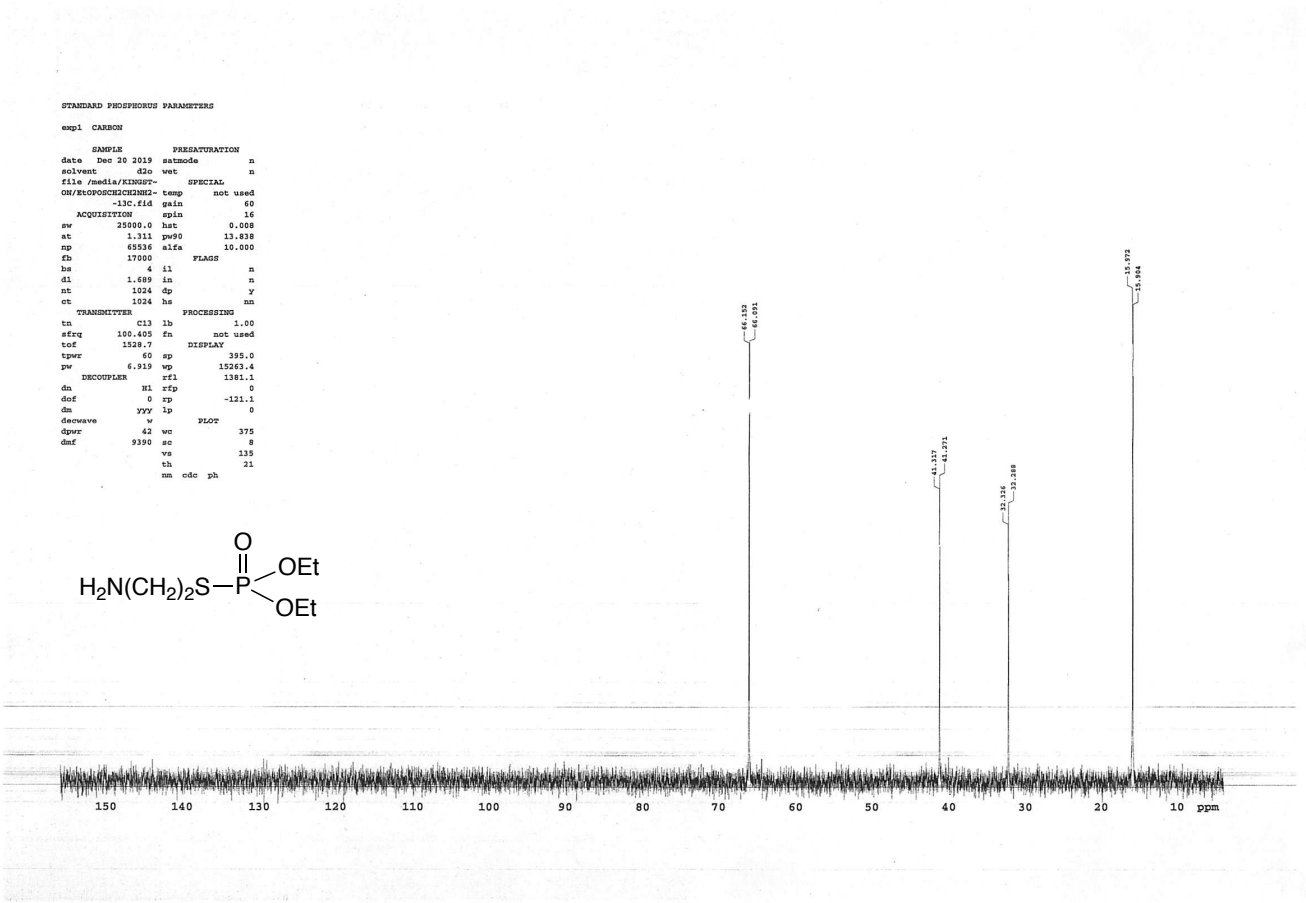
4-{[Bis(ethoxy)phosphinothioyl]thio}butanoic acid (3ca) ^{31}P-NMR



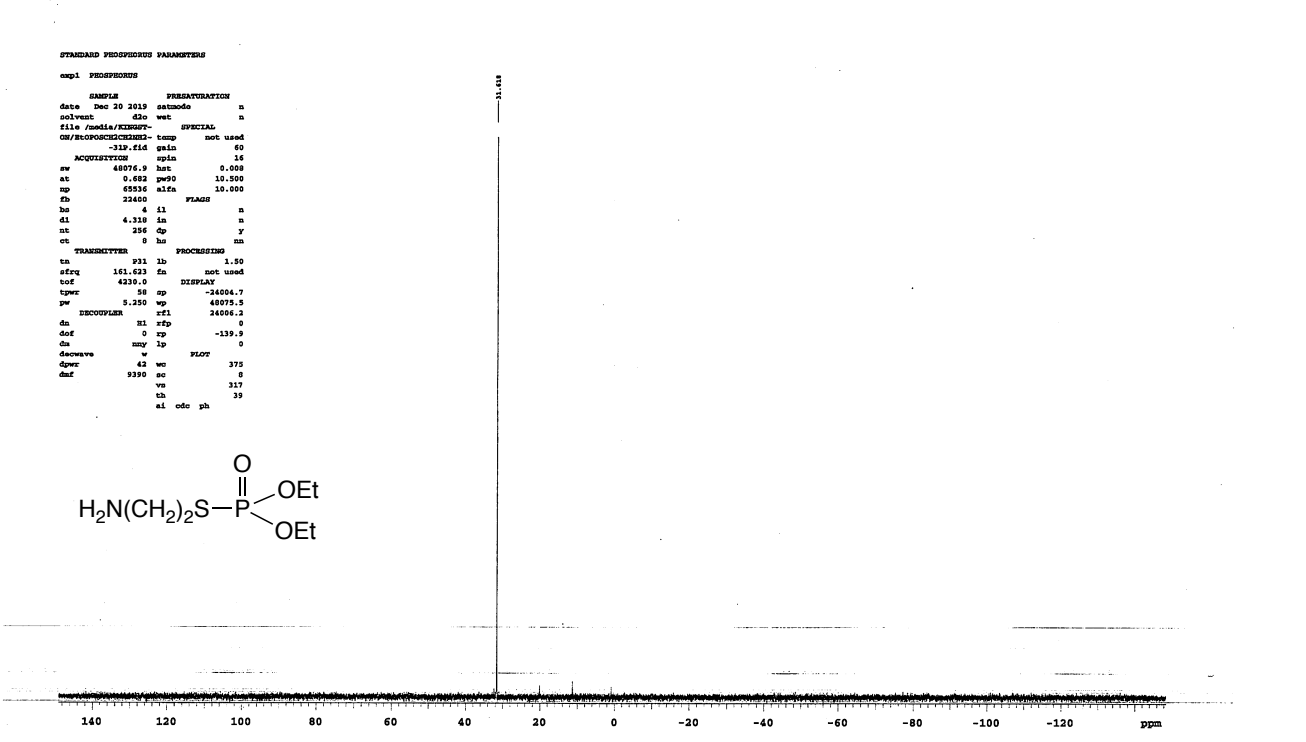
4-{[Bis(ethoxy)phosphinothioyl]thio}ethylamine (3da) ^{1}H-NMR



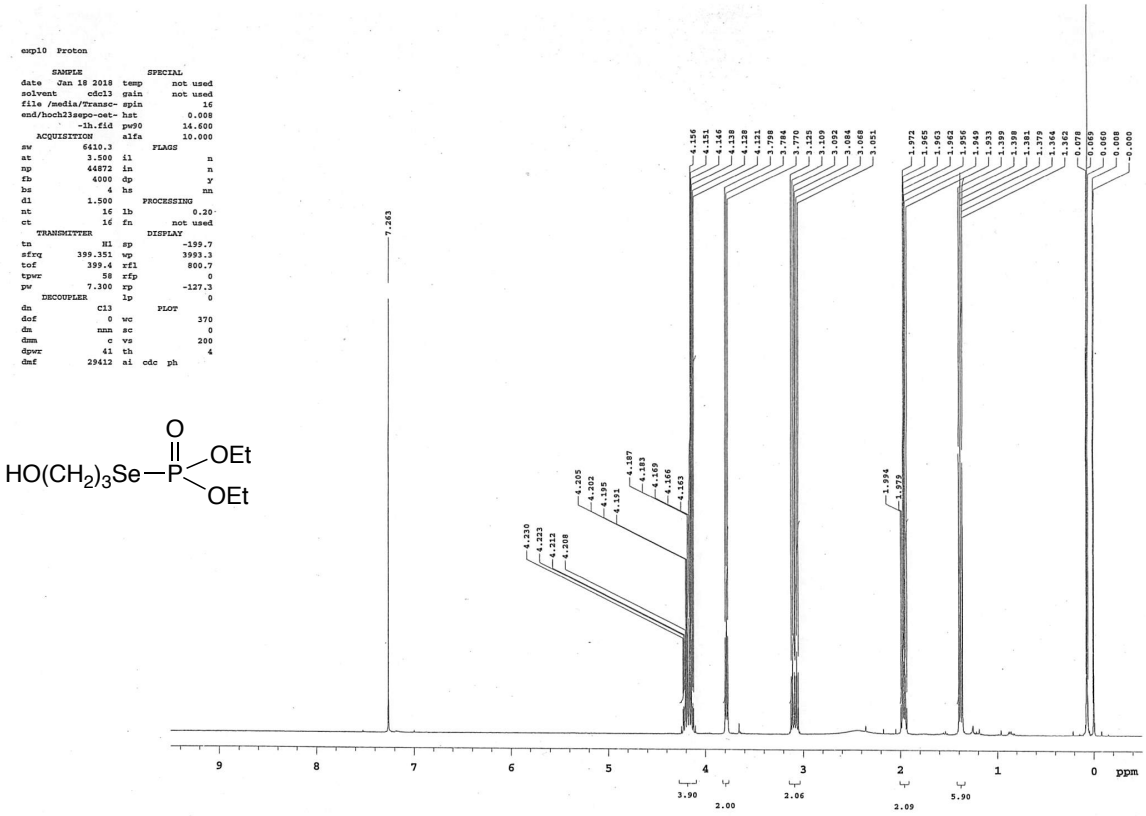
4-{[Bis(ethoxy)phosphinothioyl]thio}ethylamine (3da) ^{13}C-NMR



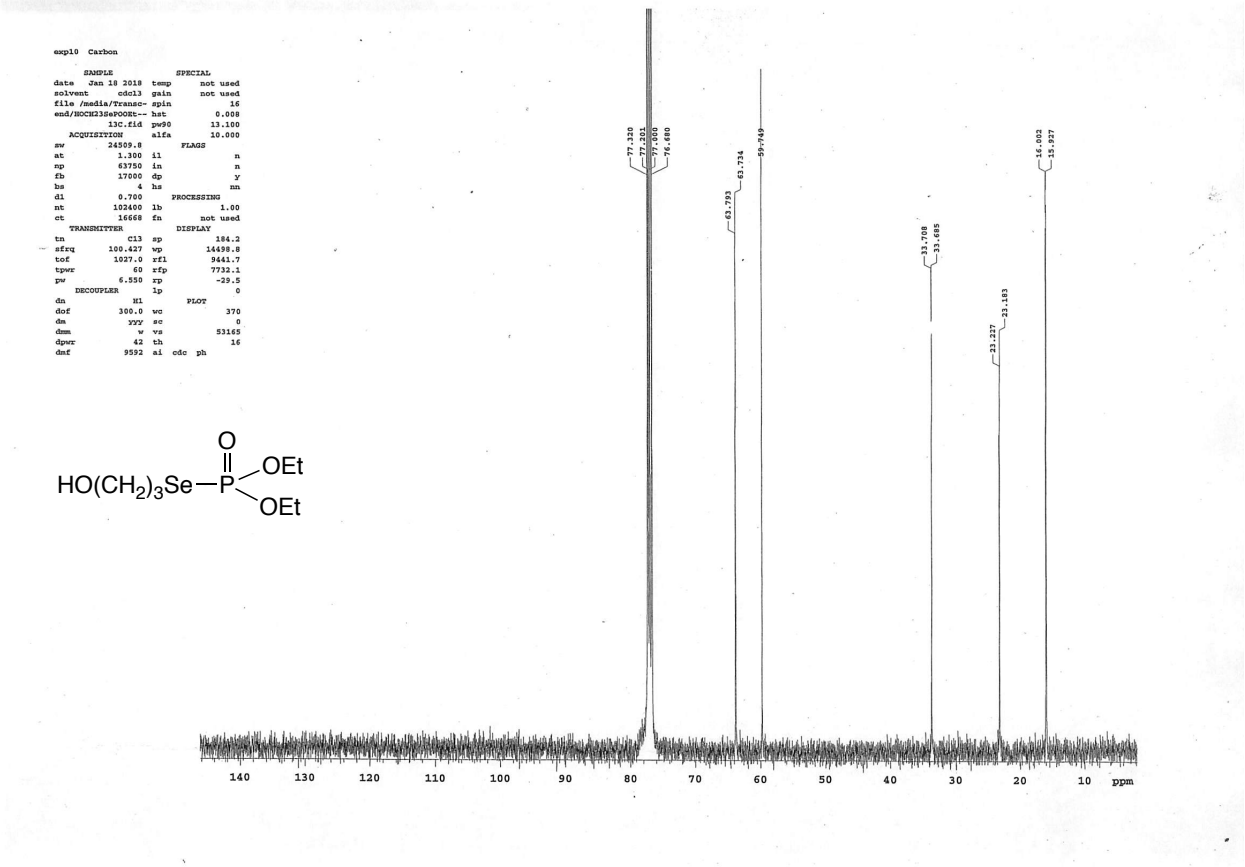
4-{[Bis(ethoxy)phosphinothioyl]thio}ethylamine (3da) ^{31}P-NMR



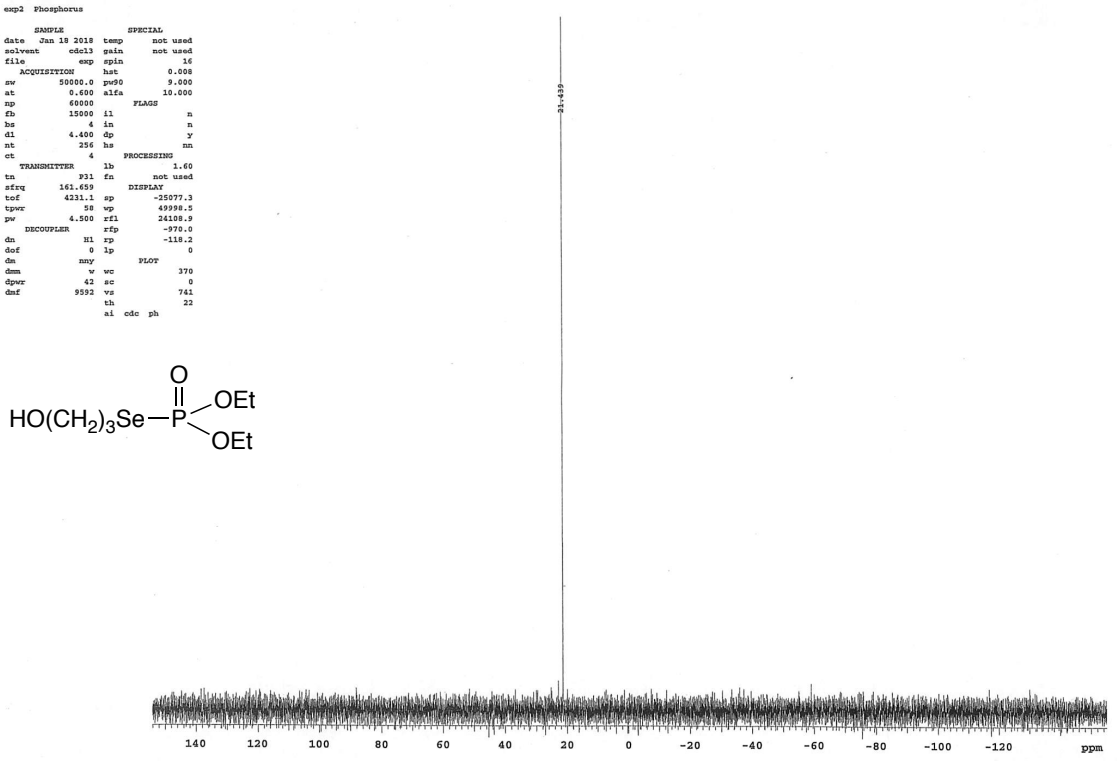
O,O-Diethyl *Se*-3-hydroxypropyl phosphoroselenoic acid (**7aa**) ^{1}H-NMR



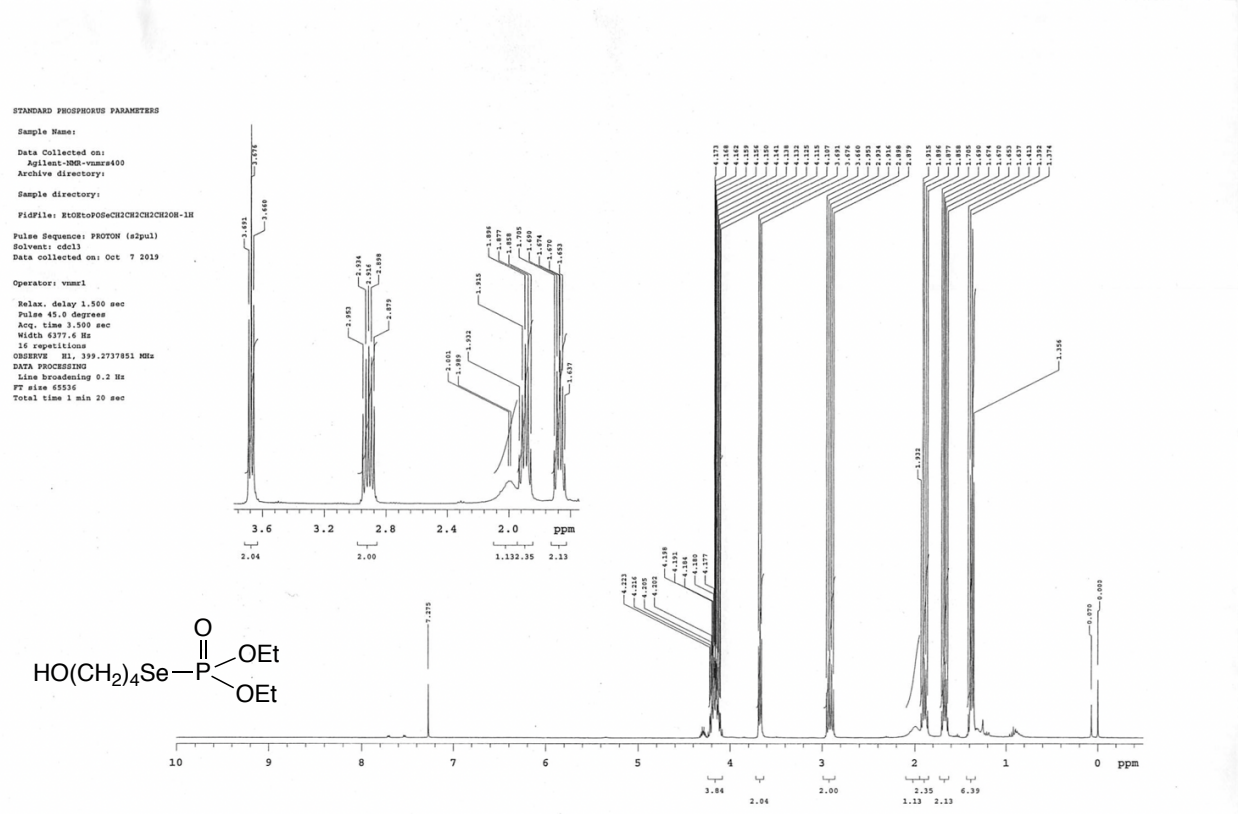
O,O-Diethyl *Se*-3-hydroxypropyl phosphoroselenoic acid (**7aa**) ^{13}C-NMR



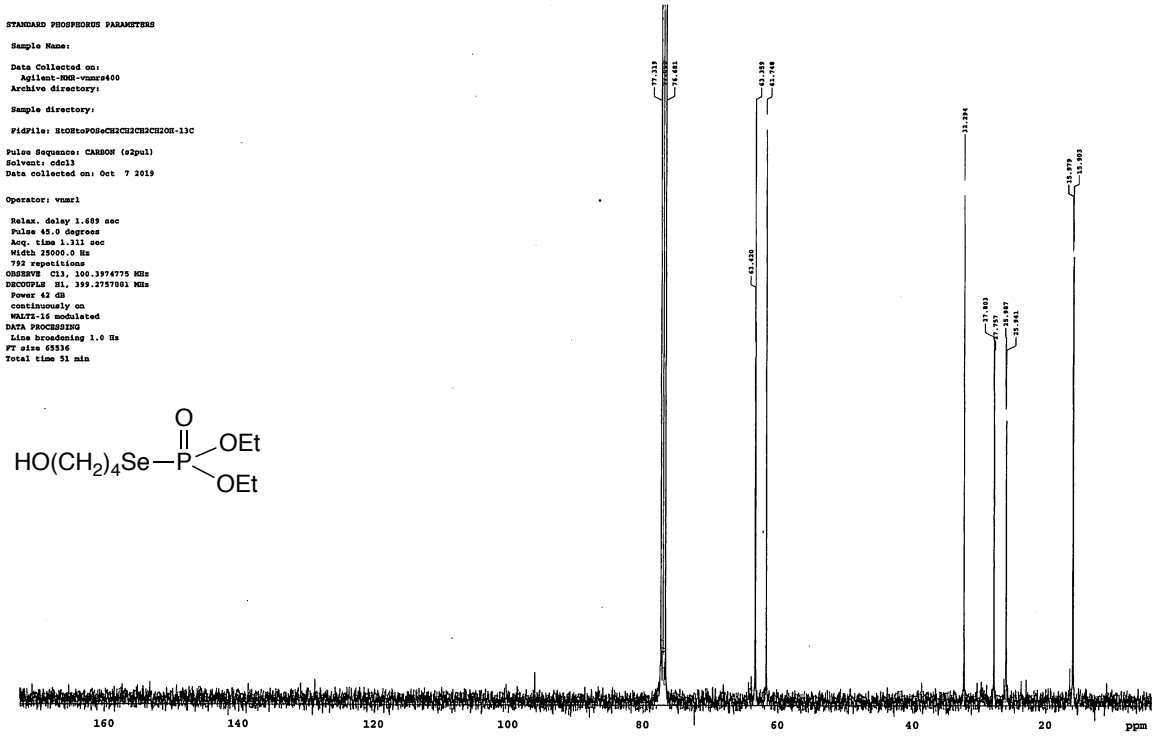
O,O-Diethyl *Se*-3-hydroxypropyl phosphoroselenoic acid (**7aa**) ^{31}P-NMR



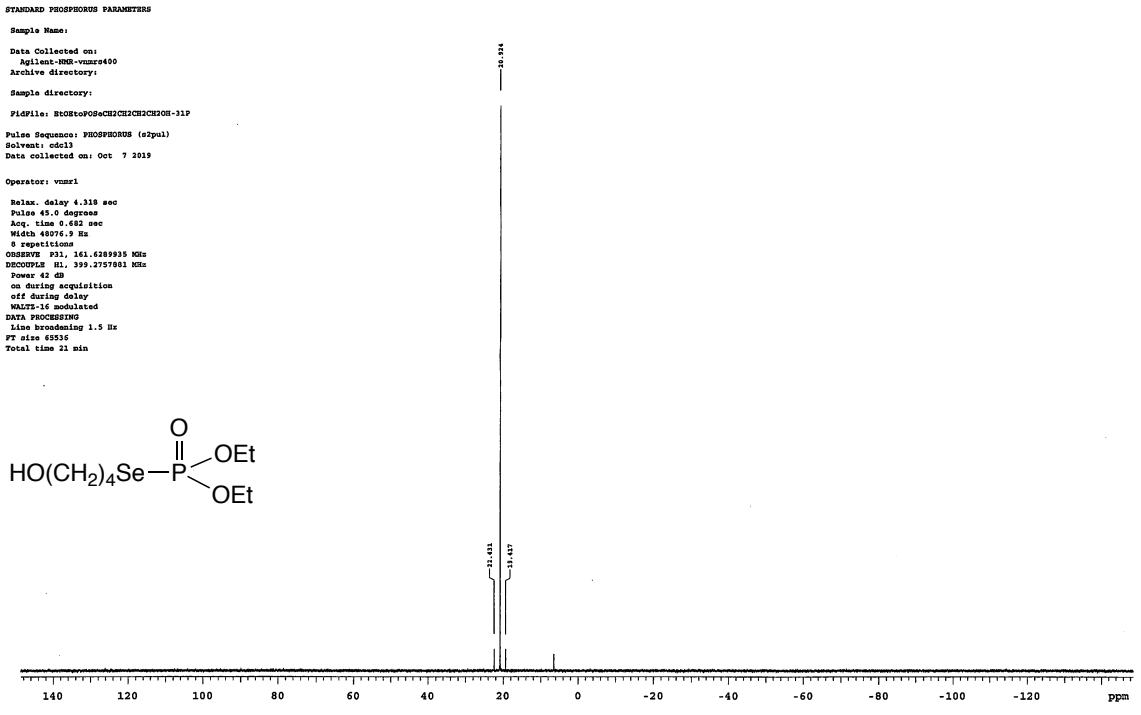
O,O-Diethyl *Se*-4-hydroxybutyl phosphoroselenoic acid (**7ba**) ^{1}H-NMR



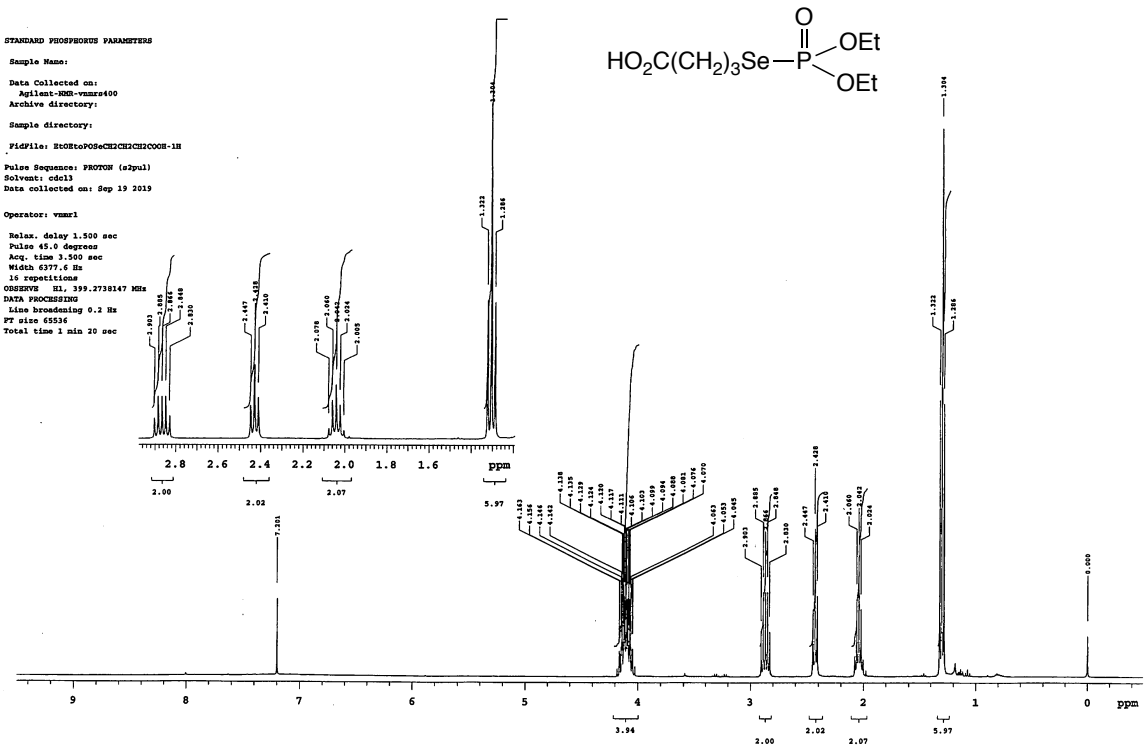
O,O-Diethyl *Se*-4-hydroxybutyl phosphoroselenoic acid (**7ba**) ^{13}C-NMR



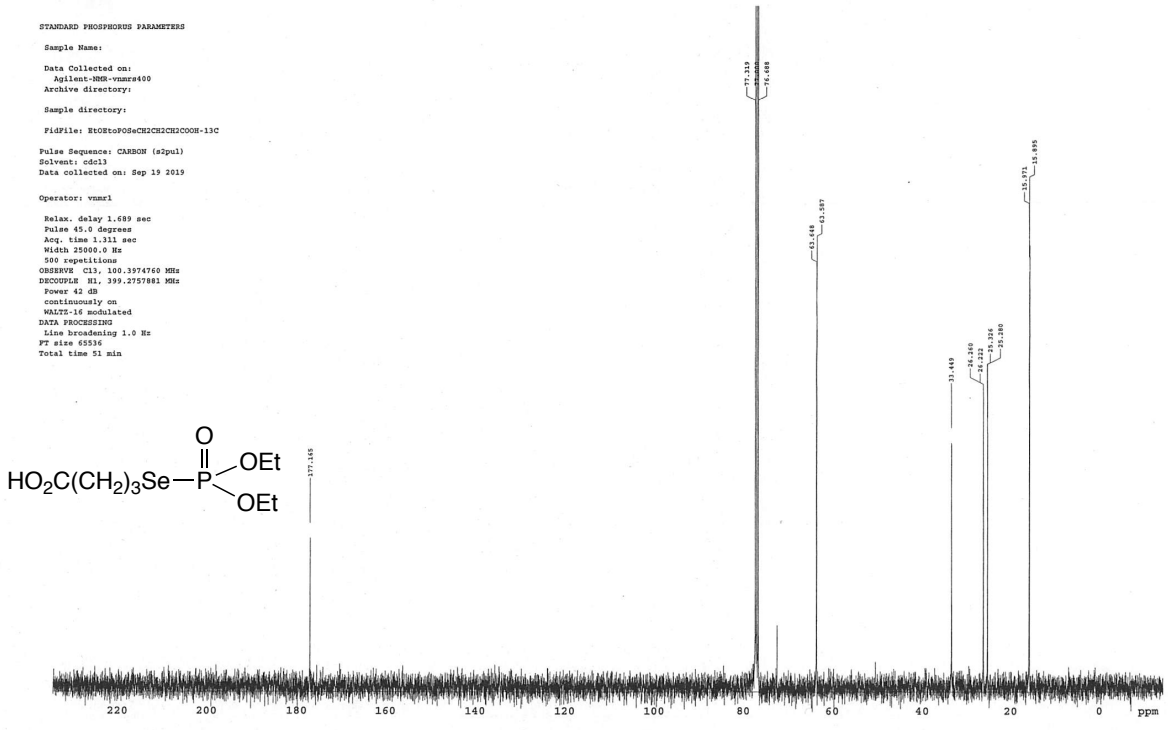
O,O-Diethyl *Se*-4-hydroxybutyl phosphoroselenoic acid (**7ba**) ^{31}P-NMR



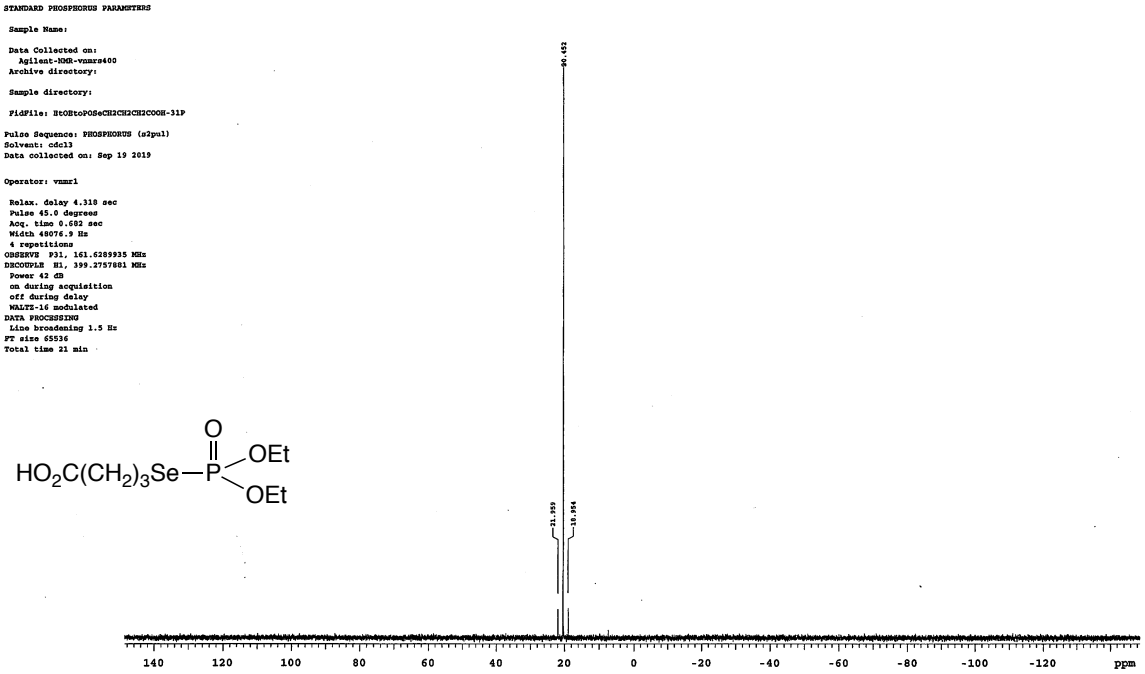
4-[Bis(ethoxy)phosphinoseleno]butanoic acid (7ca) ^{1}H-NMR



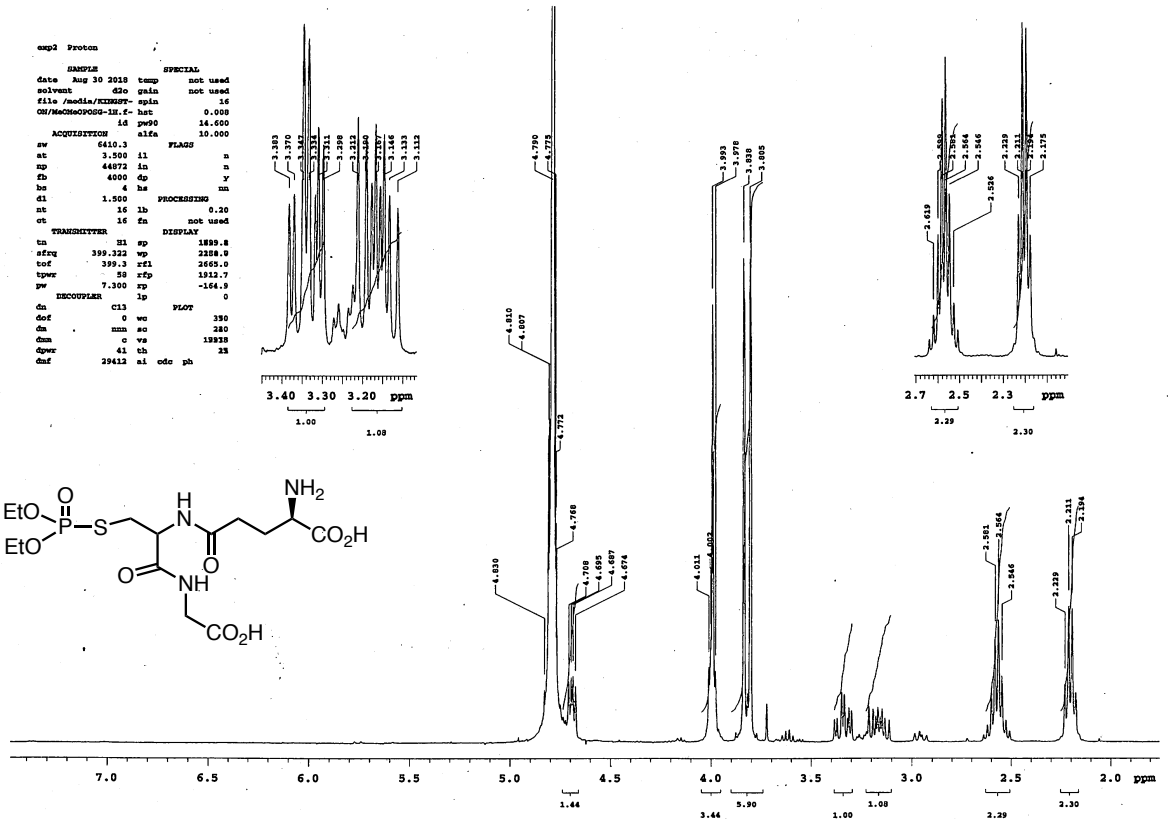
4-[Bis(ethoxy)phosphinoseleno]butanoic acid (7ca) ^{13}C-NMR



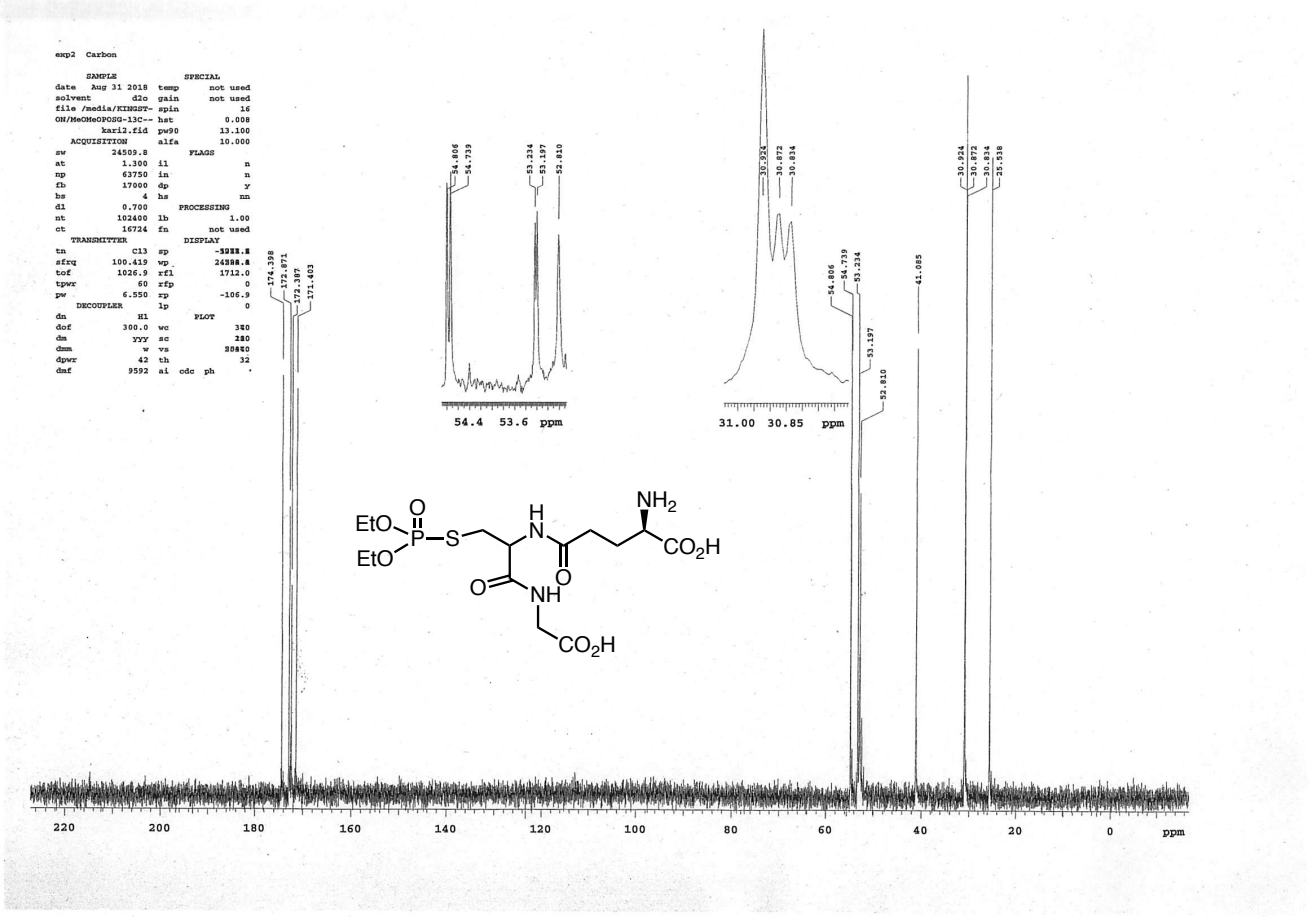
4-[Bis(ethoxy)phosphinoseleno]butanoic acid (7ca) ^{31}P-NMR



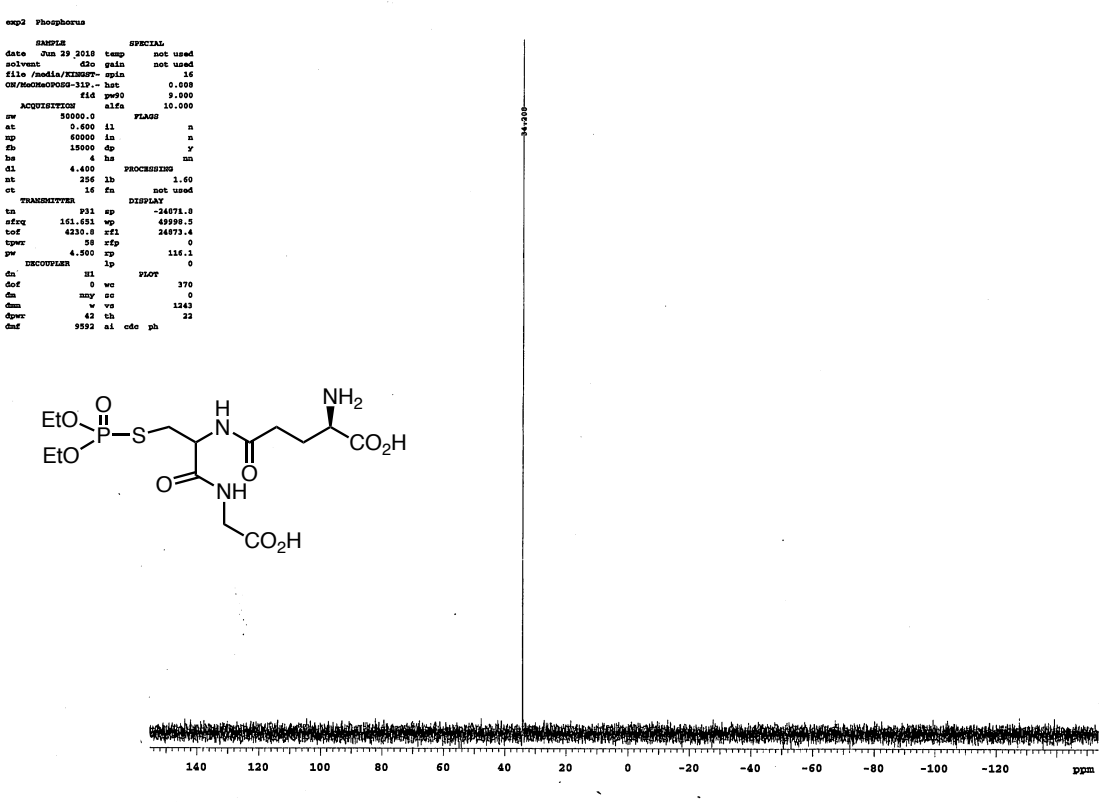
***N*-[*N*-*L*-γ-glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine (9a)** ^{1}H-NMR



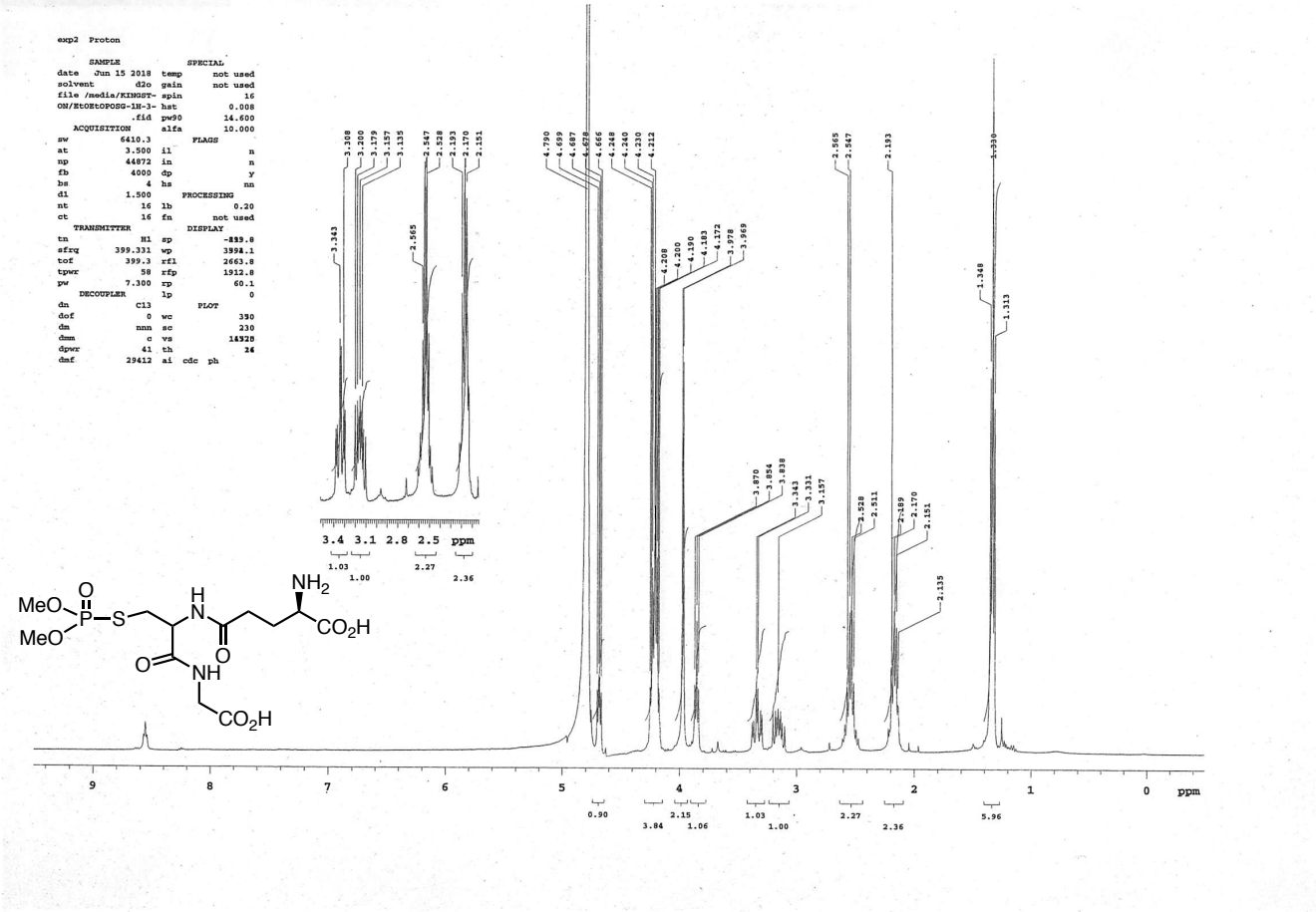
***N*-[*N*-*L*-γ-glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine (9a)** ^{13}C-NMR



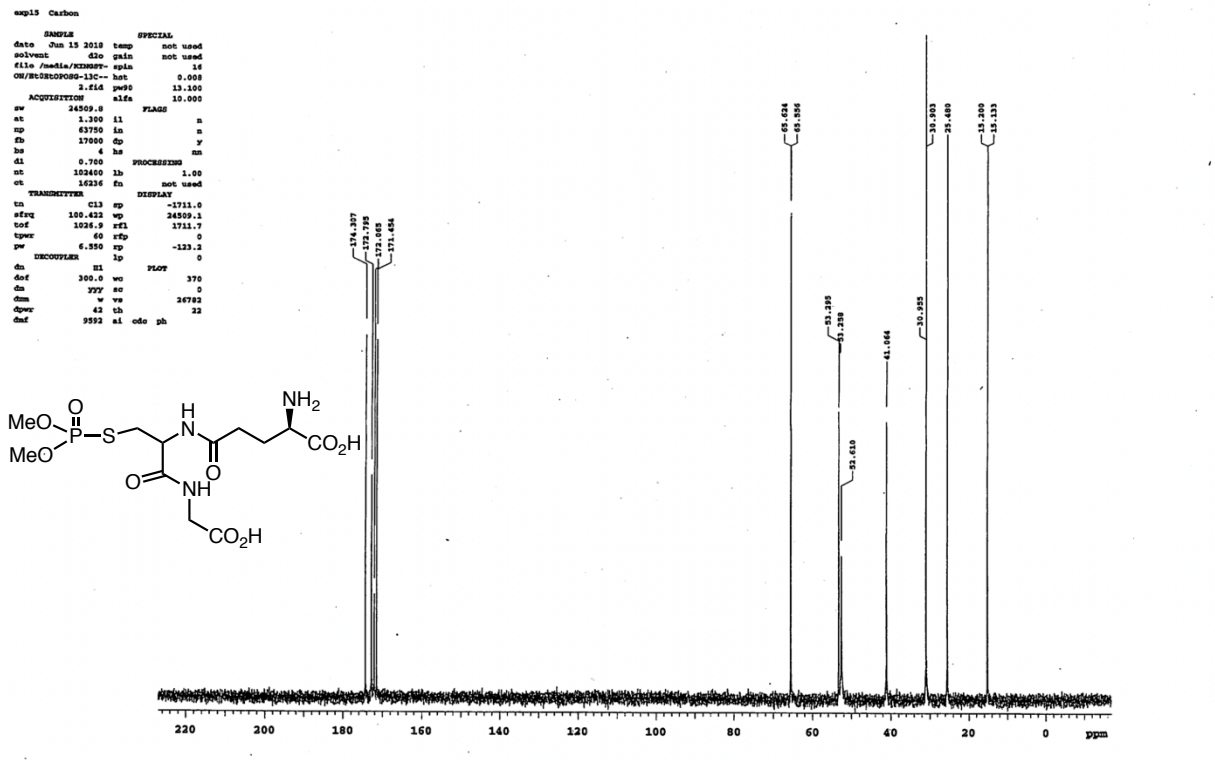
***N*-[*N*-*L*-γ-glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine (9a)** ^{31}P-NMR



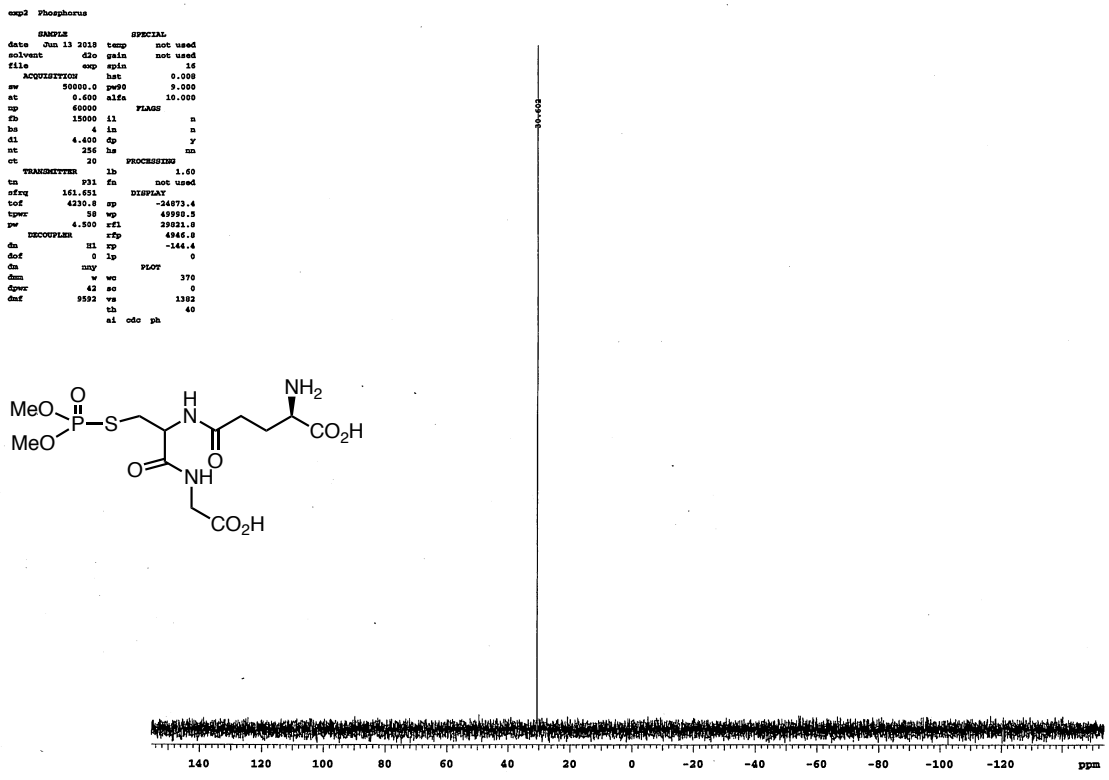
***N*-[*N*-*L*-γ-glutamyl-*S*-(dimethoxyphosphinyl)-*L*-cysteinyl]glycine (9b)** ^{1}H-NMR



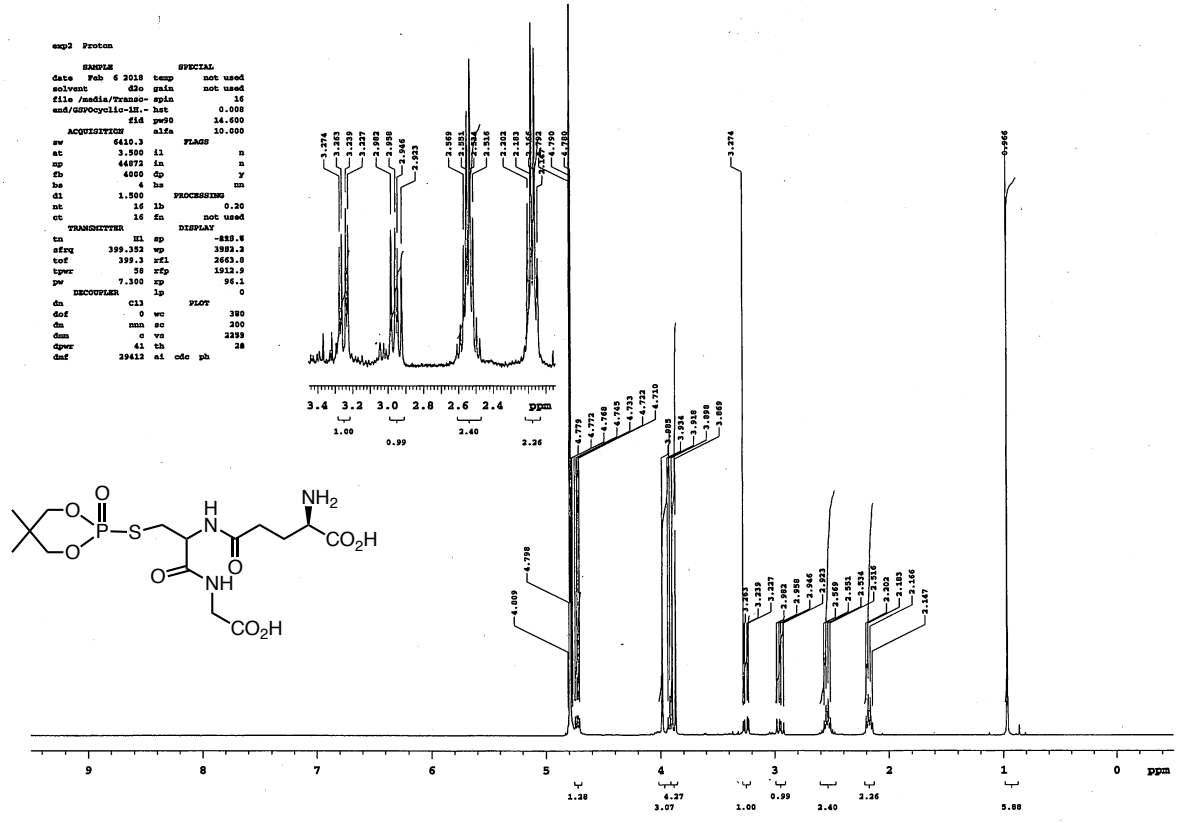
***N*-[*N*-*L*-γ-glutamyl-*S*-(dimethoxyphosphinyl)-*L*-cysteinyl]glycine (9b)** ^{13}C-NMR



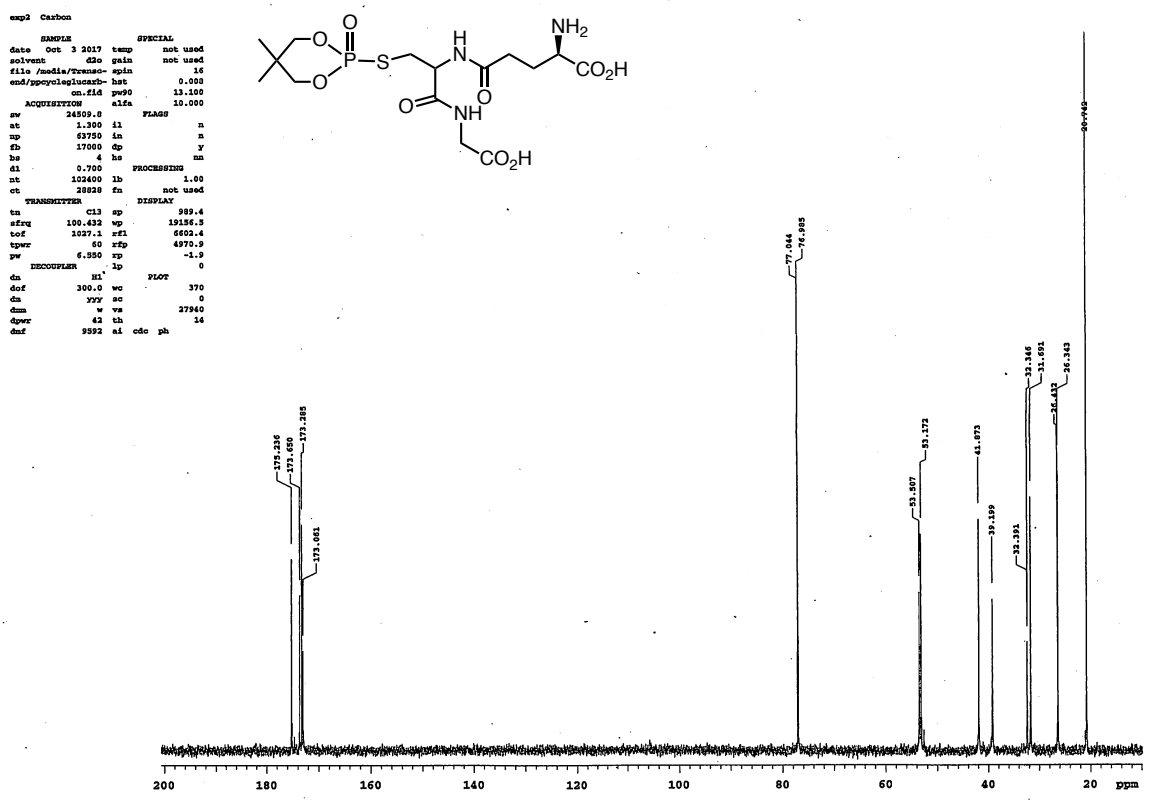
***N*-[*N*-*L*-γ-glutamyl-*S*-(dimethoxyphosphinyl)-*L*-cysteinyl]glycine (9b)** ^{31}P-NMR



***N*-[*N*-*L*-γ-glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-*L*-cysteinyl]glycine (9c)** ^{1}H-NMR



***N*-[*N*-*L*-*γ*-glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-*L*-cysteinyl]glycine (9c)** ^{13}C-NMR



***N*-[*N*-*L*-*γ*-glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-*L*-cysteinyl]glycine (9c)** ^{31}P-NMR