

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

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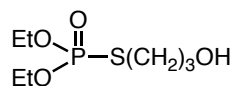
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Supplementary Materials. ^1H - and ^{13}C -NMR spectra were recorded on 400 MHz instrument and tetramethylsilane were used as standard. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, 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]

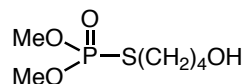
Typical procedure for synthesis of the *O,O*-diethyl *S*-4-hydroxybutyl phosphorothioic acid **3ba.** In a two-necked flask were placed $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (5.0 mg, 10 mol%), bis(4-hydroxybutyl) disulfide **1b** (0.25 mmol, 52.5 mg), and hypodiphosphoric acid tetraethyl esters **2a** (0.25 mmol, 68.0 mg) in water (H_2O , 0.25 mL) under an argon atmosphere, and the mixture was heated at 25 °C 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 $\text{AcOEt}:\text{MeOH} = 50:1$ to $\text{AcOEt}:\text{MeOH} = 33:1$), and silica gel (eluent: from $\text{AcOEt}:\text{toluene} = 10:1$ to AcOEt), giving *O,O*-diethyl *S*-4-hydroxybutyl phosphorothioic acid **3ba** (75.1 mg, 62%). **3ba**: Colorless oil. ^1H -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 $\text{C}_8\text{H}_{19}\text{O}_4\text{PS}$: 242.0741. Found: 242.0744.

O,O-Diethyl *S*-3-hydroxypropyl phosphorothioic acid (**3aa**).^[2] Yellow oil. ^1H -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, S2

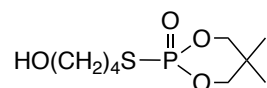
6.8 Hz), 3.80 (2H, t, $J = 5.6$ Hz), 4.10-4.24 (4H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 16.0 (d, $J = 7.5$ Hz), 27.1, 33.5, 59.1, 63.9 (d, $J = 5.9$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 29.5. IR (neat) ν 3418, 2982, 1238, 1016, 973 cm^{-1} . MS (EI) m/z 228 (M^+ , 7%), 170 ($\text{M}^+ - 58$, 100%). HRMS Calcd for $\text{C}_7\text{H}_{17}\text{O}_4\text{PS}$: 228.0585. Found: 228.0575.



O,O-Dimethyl *S*-4-hydroxybutyl phosphorothioic acid (**3bb**). Colorless oil. ^1H -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 ($\text{M}^+ - 72$, 100%). HRMS Calcd for $\text{C}_6\text{H}_{15}\text{O}_4\text{PS}$: 214.0429. Found: 214.0425.



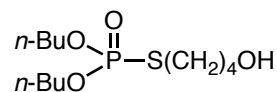
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxide (**3bc**) Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.91 (3H, s), 1.29 (3H, s), 1.66-1.71 (3H, m), 1.84 (2H, quintet, $J = 7.6$ Hz), 2.97 (2H, quintet, $J = 7.6$ Hz), 3.69 (2H, t, $J = 6.4$ Hz), 3.93 (2H, dd, $J = 23.6, 11.2$ Hz), 4.13 (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 ($\text{M}^+ - 72$, 100%). HRMS Calcd for $\text{C}_9\text{H}_{19}\text{O}_4\text{PS}$: 254.0742. Found: 254.0758.



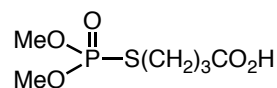
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (**3bd**). Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 0.94 (6H, t, $J = 7.2$ Hz), 1.42 (4H, sextet, $J = 7.6$ Hz), 1.64-1.72 (6H, m), 1.82 (2H, quintet, $J = 7.6$ Hz), 2.88 (2H, quintet, $J = 7.6$ Hz), 3.68 (2H, t, $J = 6.4$ Hz), 4.04-4.14 (4H, m). ^{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%).

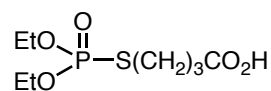
HRMS Calcd for $\text{C}_{12}\text{H}_{27}\text{O}_4\text{PS}$: 298.1368. Found: 298.1386.



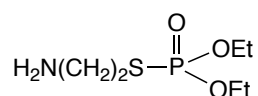
4-[[Bis(methoxy)phosphinothioyl]thio]butanoic acid (3cb) Colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 2.04 (2H, quintet, $J = 7.2$ Hz), 2.51 (2H, t, $J = 7.2$ Hz), 2.92 (2H, dt, $J = 15.6, 7.2$ Hz), 3.81 (6H, d, $J = 12.4$ Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 25.8 (d, $J = 5.2$ Hz), 29.9 (d, $J = 4.5$ Hz), 32.3, 53.9 (d, $J = 6.0$ Hz), 176.9. $^{31}\text{P-NMR}$ (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 $\text{C}_6\text{H}_{13}\text{O}_5\text{PS}$: 228.0232. Found: 228.0231.



4-[[Bis(ethoxy)phosphinothioyl]thio]butanoic acid (3ca) Colorless oil. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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. $^{31}\text{P-NMR}$ (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 $\text{C}_8\text{H}_{17}\text{O}_5\text{PS}$: 256.0534. Found: 256.0559.

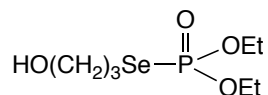


4-[[Bis(ethoxy)phosphinothioyl]thio]ethylamine (3da) Yellow oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.36 (6H, t, $J = 7.2$ Hz), 2.98-3.02 (4H, m), 4.20-4.28 (4H, m). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ 15.9 (d, $J = 6.8$ Hz), 32.3 (d, $J = 3.8$ Hz), 41.3 (d, $J = 4.6$ Hz), 66.1 (d, $J = 6.1$ Hz). $^{31}\text{P-NMR}$ (162 MHz, CDCl_3) δ 31.6. IR (neat) ν 3367, 2982, 1246, 1018, 971 cm^{-1} . MS (EI) m/z 214 ($M^+ + \text{H}$, 100%). HRMS Calcd for $\text{C}_6\text{H}_{17}\text{O}_3\text{NPS}$: 214.0661. Found: 214.0658.

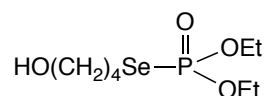


O,O-Diethyl Se-3-hydroxypropyl phosphoroselenoic acid (7aa). Colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.38 (6H, td, $J = 7.2, 0.8$ Hz), 1.96 (2H, dt, $J = 12.0, 6.4$ Hz), 3.09 (2H, dt, $J =$

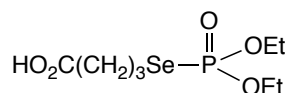
16.4, 6.8 Hz), 3.78 (2H, t, $J = 5.6$ Hz), 4.12-4.23 (4H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 16.0 (d, $J = 7.5$ Hz), 23.2 (d, $J = 4.4$ Hz), 33.7 (d, $J = 2.3$ Hz), 59.7, 63.7 (d, $J = 5.9$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 21.4. IR (neat) ν 3423, 2921, 1229, 1012 cm^{-1} . MS (EI) m/z 276 (M^+ , 6%), 218 ($\text{M}^+ - 58$, 100%). HRMS Calcd for $\text{C}_7\text{H}_{17}\text{O}_4\text{PSe}$: 276.0030. Found: 276.0036.



O,O-Diethyl Se-4-hydroxybutyl phosphoroselenoic acid (**7ba**). Colorless oil. ^1H -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 ($\text{M}^+ - 72$, 100%). HRMS Calcd for $\text{C}_8\text{H}_{19}\text{O}_4\text{PSe}$: 290.0186. Found: 290.0168.

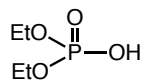


4-[Bis(ethoxy)phosphinoseleno]butanoic acid (**7ca**). Colorless oil. ^1H -NMR (400 MHz, CDCl_3) δ 1.30 (6H, t, $J = 7.2$ Hz), 2.06 (2H, quintet, $J = 7.2$ Hz), 2.85 (2H, t, $J = 7.2$ Hz), 2.87 (2H, quintet, $J = 7.2$ Hz), 4.05-4.16 (4H, m). ^{13}C -NMR (100 MHz, CDCl_3) δ 16.0 (d, $J = 7.6$ Hz), 25.3 (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 ($\text{M}^+ - 59$, 100%). HRMS Calcd for $\text{C}_8\text{H}_{17}\text{O}_5\text{PS}$: 256.0534. Found: 256.0559.

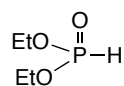


Diethyl phosphate (**4**). Yellow oil. ^1H -NMR (400 MHz, CDCl_3) δ 1.35 (7H, td, $J = 7.2, 1.2$ Hz), 4.11 (4H, quintet, $J = 7.2$ Hz). ^{13}C -NMR (100 MHz, CDCl_3) δ 17.0 (d, $J = 6.7$ Hz), 64.7 (d, $J = 6.0$ Hz). ^{31}P -NMR (162 MHz, CDCl_3) δ 0.7. IR (neat) ν 2986, 1226, 1166, 1034 cm^{-1} .

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.

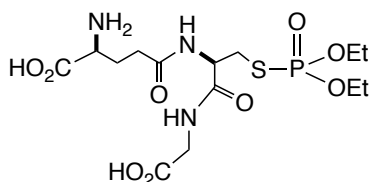


Diethyl phosphite (**5**). Colorless oil. 1H -NMR (400 MHz, $CDCl_3$) δ 1.38 (6H, td, $J = 7.2, 2.0$ Hz), 4.16 (4H, quintet, $J = 7.2, 1.2$ Hz), 6.82 (1H, dd, $J = 693.6, 1.6$ Hz). ^{13}C -NMR (100 MHz, $CDCl_3$) δ 16.3 (d, $J = 6.0$ Hz), 61.7 (d, $J = 6.1$ Hz). ^{31}P -NMR (162 MHz, $CDCl_3$) δ 7.30. 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.

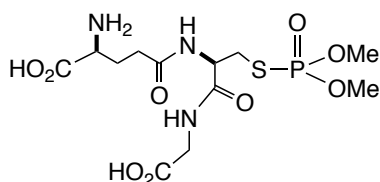


Typical procedure for synthesis of the

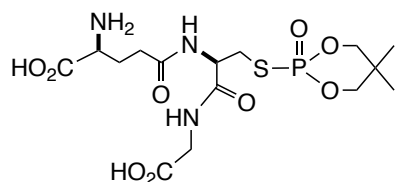
N-[*N*- L - γ -glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine **9a**. In a two-necked flask were placed $RhCl_3 \cdot 3H_2O$ (5.0 mg, 10 mol%), Glutathione (Oxidized Form) **8** (0.25 mmol, 153.0 mg), and hypodiphosphoric acid tetraethyl esters **2a** (0.25 mmol, 68.0 mg) in water (H_2O , 1.0 mL) under an argon atmosphere, and the mixture was heated at 40 $^{\circ}C$ 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 $^{\circ}C$ (H_2O /Acetone = 5:1). $[\alpha]_D^{28}$ -20.5 $^{\circ}$ (c 0.1, H_2O). 1H -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 (H₂O/Acetone = 5:1). $[\alpha]_D^{28}$ -27.9° (c 0.1, H₂O). ¹H-NMR (400 MHz, D₂O) 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). ¹³C-NMR (100 MHz, D₂O) 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. ³¹P-NMR (162 MHz, D₂O) δ 34.2. IR (KBr) ν 3447, 3020, 1656, 1223, 1027 cm⁻¹. HRMS Calcd for C₁₂H₂₃N₃O₉P: 416.0887. Found: 416.0878.



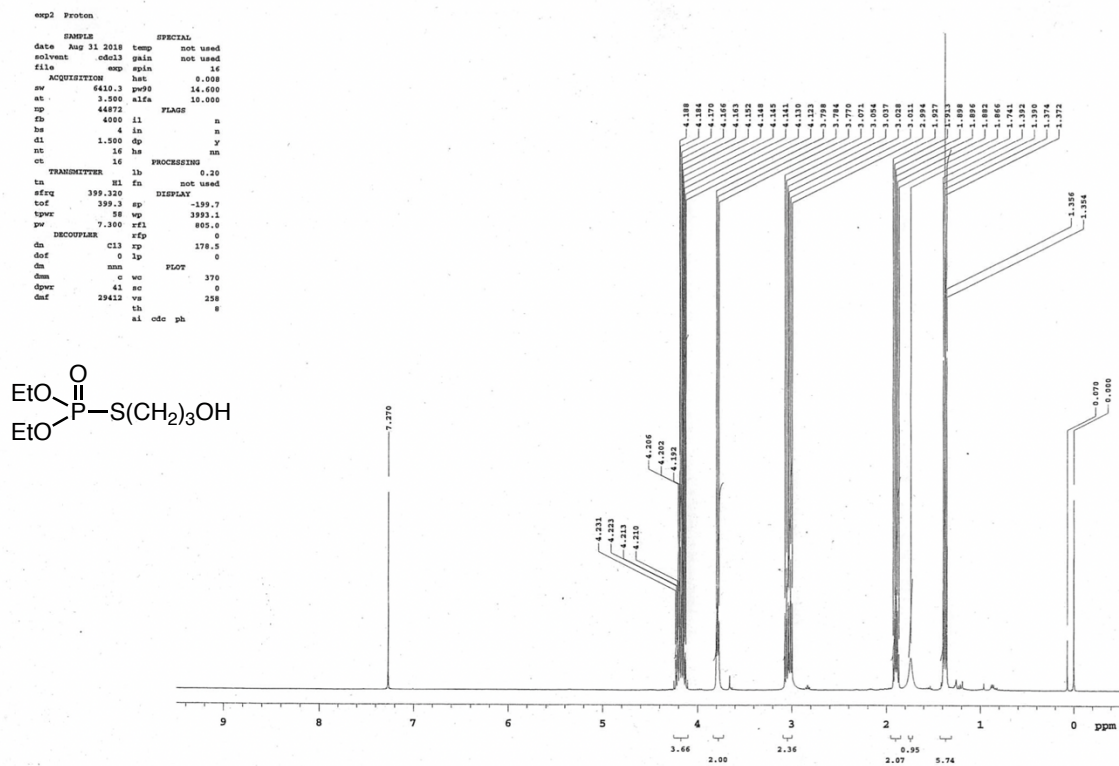
N-[*N*-*L*- γ -glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-*L*-cysteinyl]glycine (**9c**). Pale yellow oil. $[\alpha]_D^{28}$ -81.7° (c 0.1, H₂O). ¹H-NMR (400 MHz, D₂O) δ 0.97 (6H, s), 2.17 (2H, q, *J* = 7.6 Hz), 2.54 (2H, octet, *J* = 7.2 Hz), 2.95 (1H, dd, *J* = 14.4, 9.6 Hz), 3.25 (1H, dd, *J* = 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). ¹³C-NMR (100 MHz, D₂O) 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. ³¹P-NMR (162 MHz, D₂O) δ -2.7. IR (neat) ν 3275, 2964, 1732, 1655, 1541, 1058, 819 cm⁻¹. HRMS Calcd for C₁₅H₂₆N₃O₉PS: 455.1127. Calcd for M⁺+H (C₁₅H₂₇N₃O₉PS): 456.1206. Found: 456.1201.



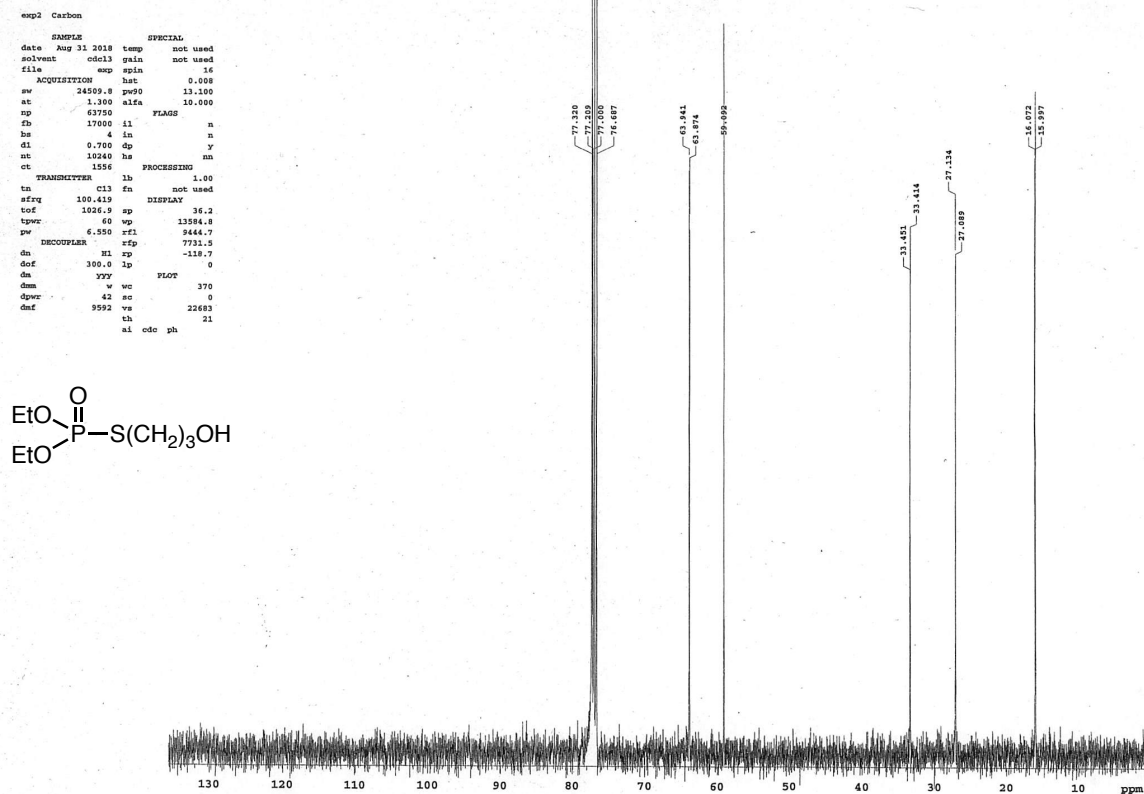
References

- [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) ¹H-NMR**



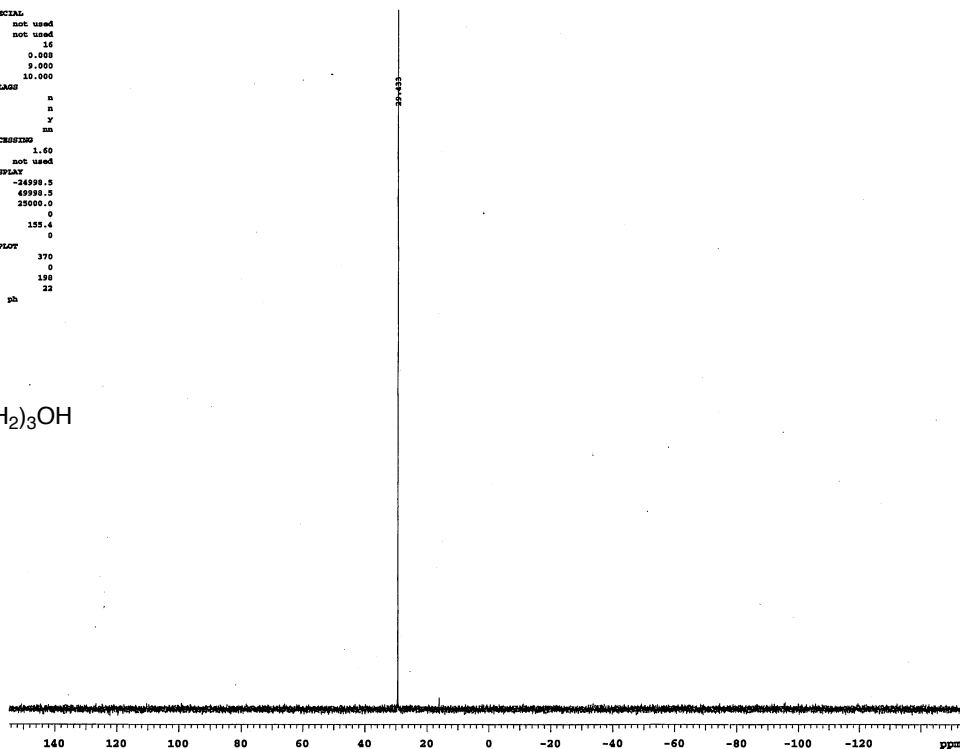
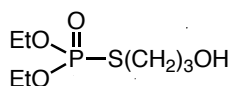
***O,O*-Diethyl *S*-3-hydroxypropyl phosphorothioic acid (3aa) ¹³C-NMR**



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

exp1 Phosphorus

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solvent	cdcl3	gain	not used
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sw	50000.0	pu90	9.000
nt	0.600	alfa	10.000
np	60000	FLAGS	
fb	15000	il	n
hs	4	in	n
dl	4.400	dp	y
nt	256	hs	nn
ct	4	PROCESSING	
TRANSMITTER	1b	1.60	
tn	931	fn	not used
sfreq	161.647	DISPLAY	
tof	4230.7	sp	-24990.5
tpwr	50	wp	49990.5
pw	4.100	rfl	25000.0
DECOUPLER		rfl	0
dn	hl	rp	159.4
dof	0	lp	0
da	any	PLOT	
dms	w	wo	370
dpr	42	se	0
dnt	9592	va	190
	th	22	
	nl	cdc	ph

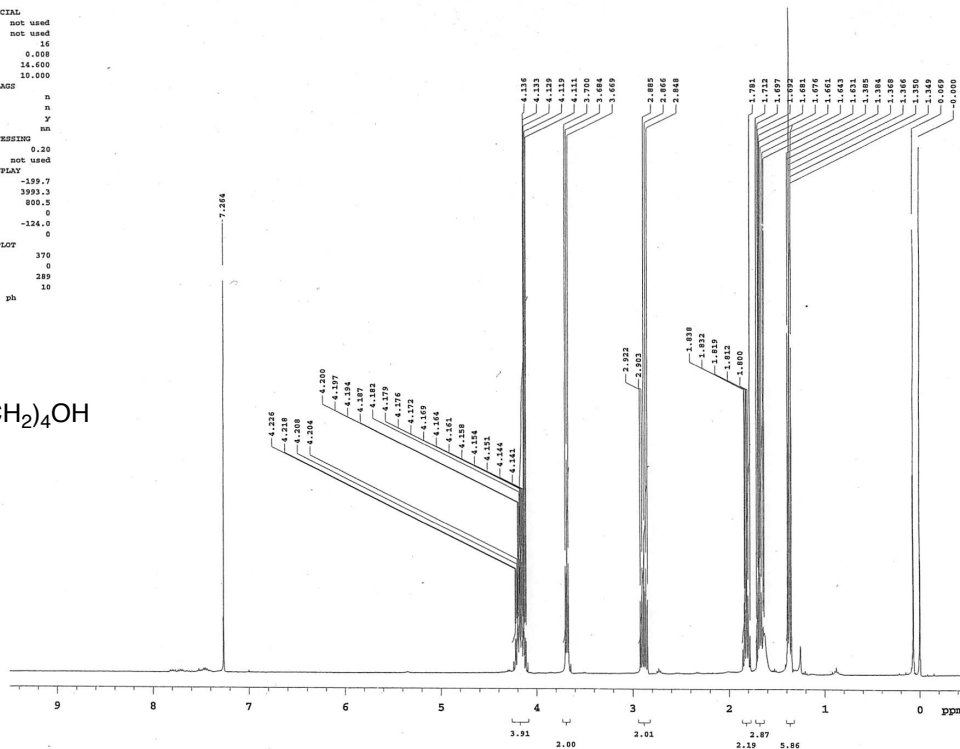
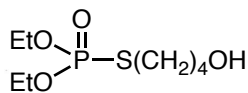


O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ¹H-NMR

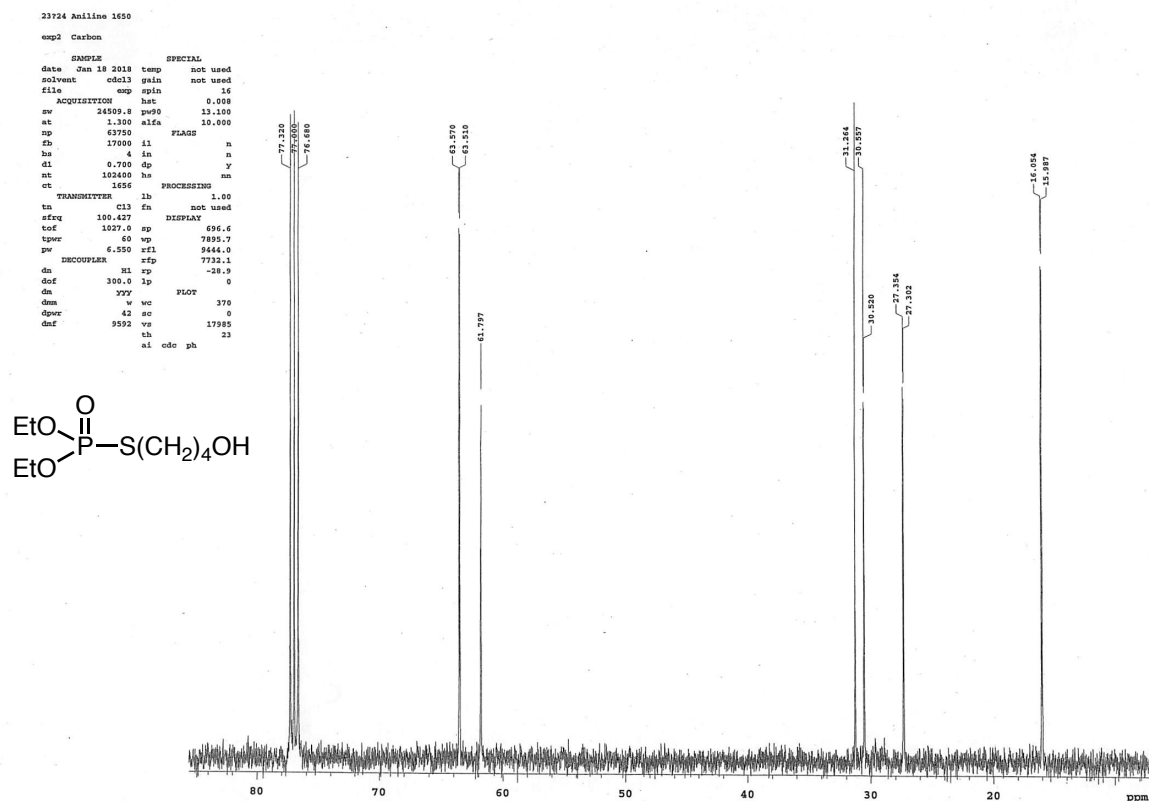
daturyon

exp10 Proton

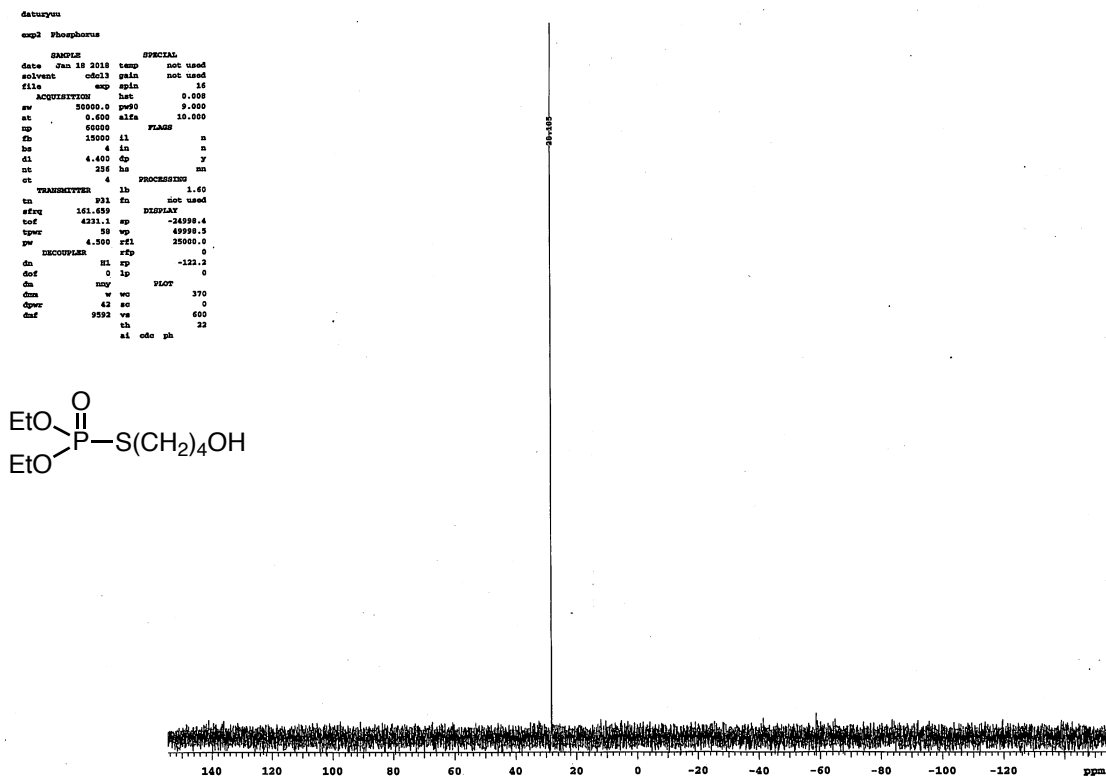
SAMPLE		SPECIAL	
date	Jan 18 2018	temp	not used
solvent	cdcl3	gain	not used
file	media/transo-	spin	16
end/ch-24-s-p-oo-	hst	0.008	
et-1h.fid	pu90	14.000	
ACQUISITION		alfa	10.000
sw	6410.3	FLAGS	
at	3.500	il	n
np	44872	in	n
fb	4000	dp	y
hs	4	hs	nn
dl	1.500	PROCESSING	
nt	16	1b	0.20
ct	16	fn	not used
TRANSMITTER	1b	DISPLAY	
tn	931	sp	-159.7
sfreq	399.131	wp	3993.3
tof	339.4	rfl	800.5
tpwr	58	rfl	0
pw	7.300	rp	-124.0
DECOUPLER		lp	0
dn	C13	PLOT	
dof	0	wo	370
da	nm	sc	0
dms	c	va	289
dpr	41	th	10
dnt	29412	nl	cdc
			ph



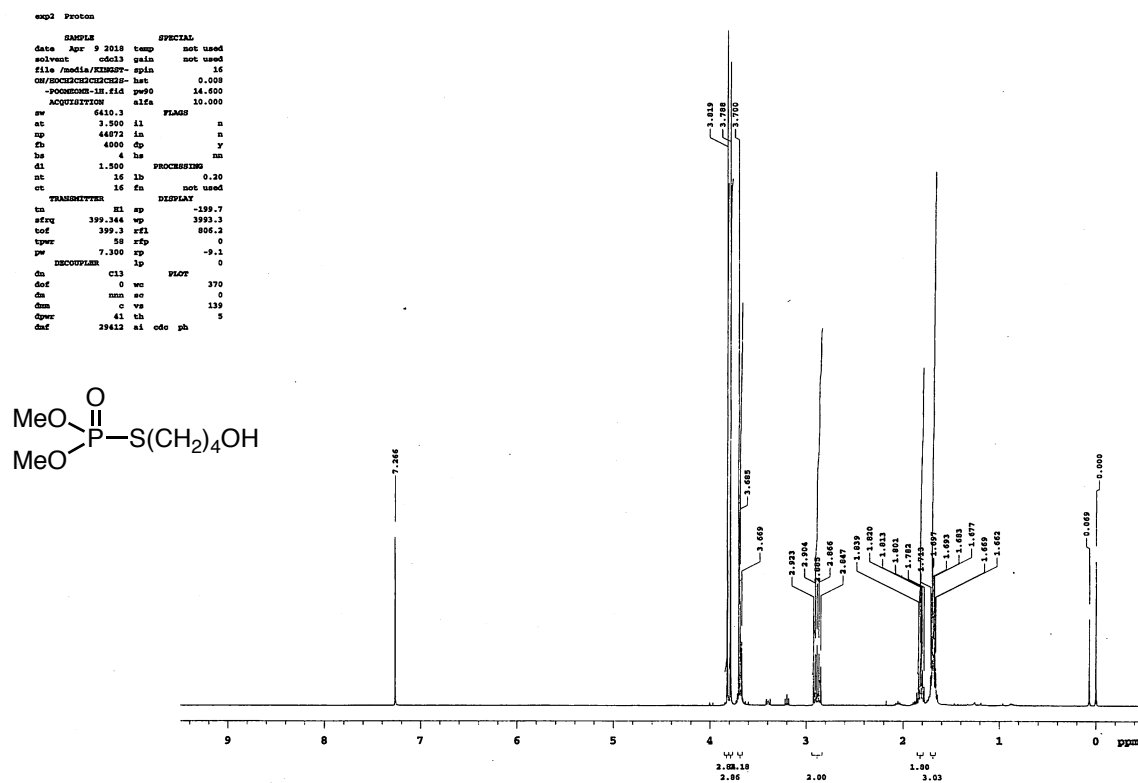
O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ¹³C-NMR



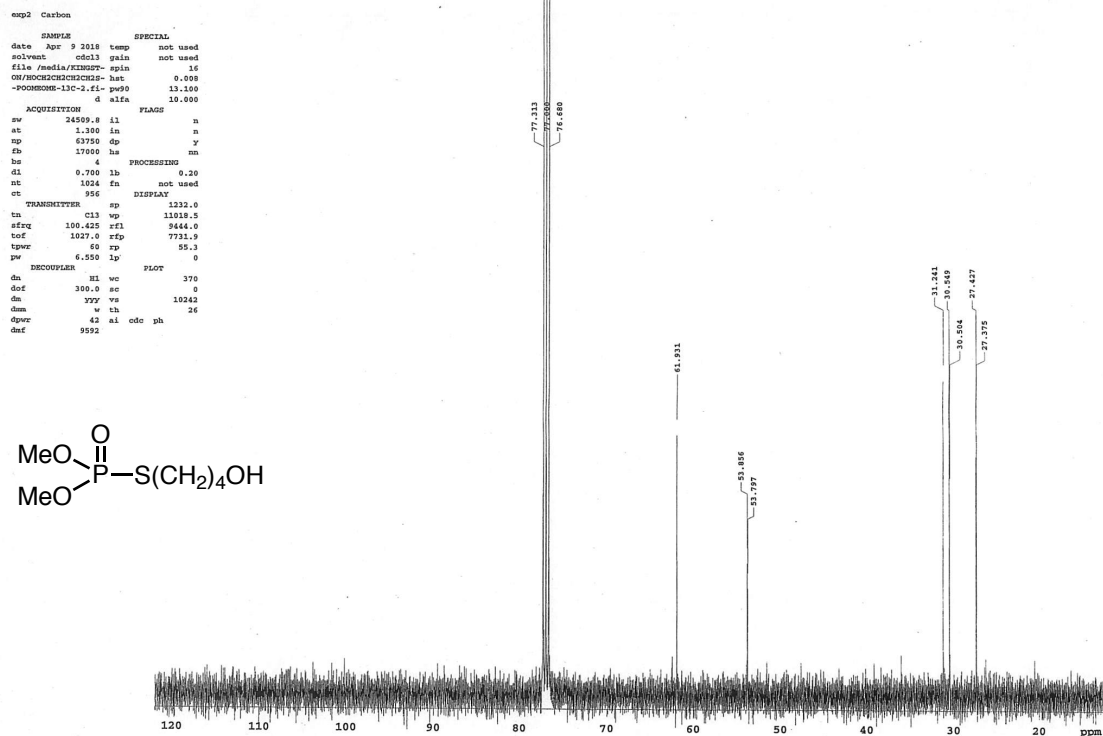
O,O-Diethyl *S*-4-hydroxybutyl phosphorothioic acid (3ba) ³¹P-NMR



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



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

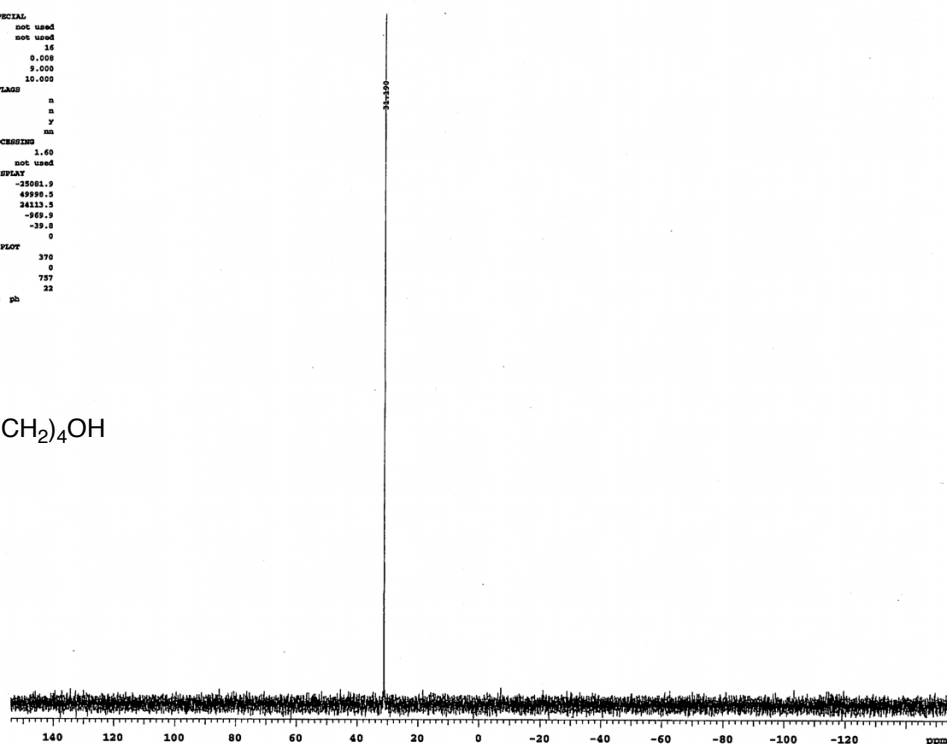
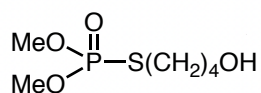


O,O-Dimethyl *S*-4-hydroxybutyl phosphorothioic acid (3bb) ³¹P-NMR

exp3 Phosphorus

```

SPECIAL
Date: 9/2018 temp: not used
solvent: cdcl3 gain: not used
file: /media/KIMMUP- spin: 16
CW/PROBHD/CHNCHNCHN- hat: 0.000
-POCKCHN-31P.fid pw90: 9.000
ACQUISITION: 10.000
pw: 8000.0
at: 0.600 il: n
tp: 60000 in: n
rb: 15000 dp: 7
hs: 4 ha: nn
dl: 4.400 PROCESSING: 1.60
nt: 256 lb: not used
ct: 12 fn: not used
TRANSMITTER: P31 sp: -25061.9
sfreq: 161.056 wp: 49998.5
tcf: 4230.9 rfl: 26113.3
tpwr: 50 rfp: -969.9
pw: 4.500 rp: -39.0
DECOUPLER: 1a
da: 0 wo: 370
dof: 0 wo: 0
dm: w vs: 757
dpr: 42 th: 22
dnd: 1992 si: odo ph:
  
```



5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxide (3bc) ¹H-NMR

1-adamantyl (dimethyl (thiophen-2-yl)silyl)methanone_13c

Sample Name:

Date Collected on:

Agilent-100-vnmr400

Archive directory:

Sample directory:

File: CycPO-3CH240H

Pulse Sequence: PROTON (zgpg3)

Solvent: cdcl3

Date collected on: Dec 6 2019

Operator: vnmr1

Relax. delay 3.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 6377.6 Hz

16 repetitions

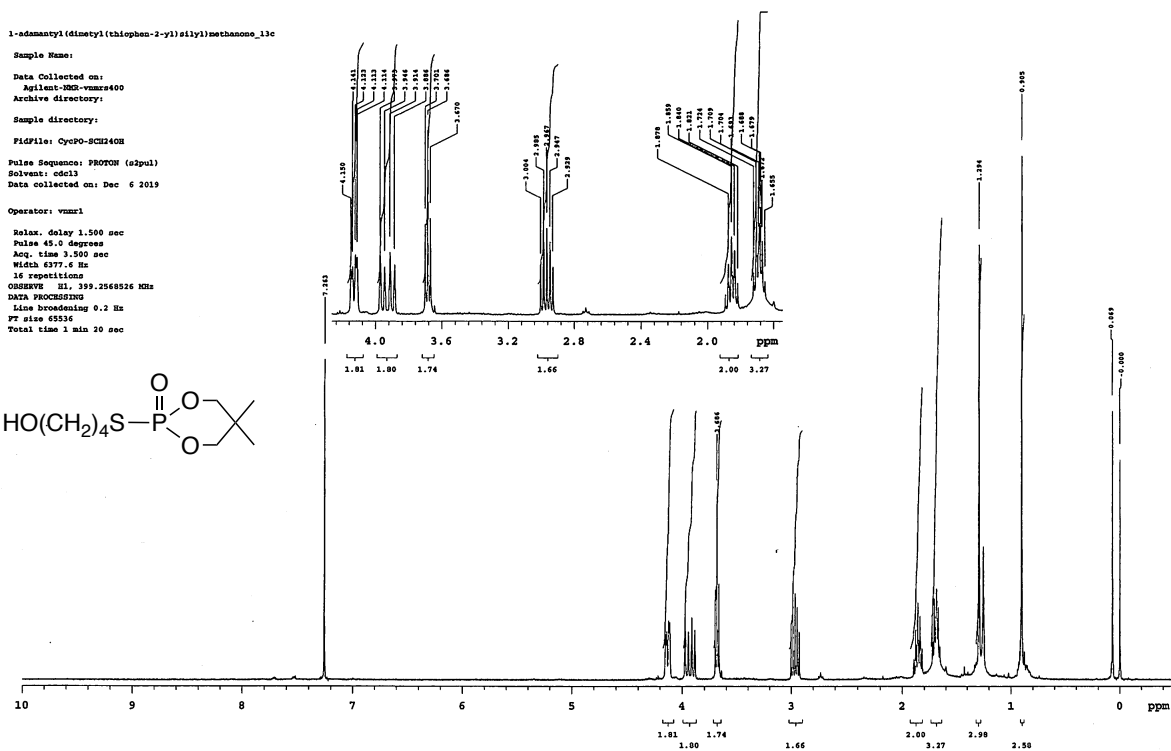
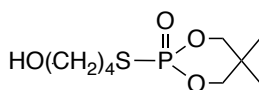
OBSERVE: H1, 399.256526 MHz

DATA PROCESSING

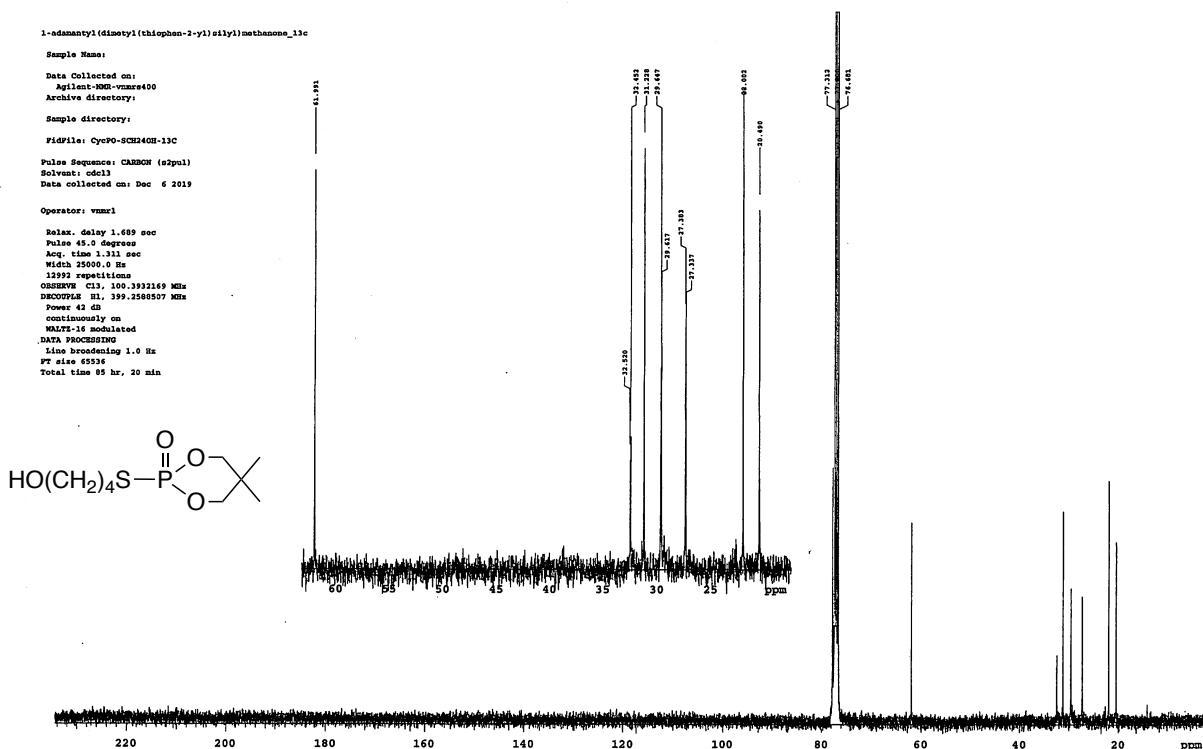
Line broadening 0.2 Hz

PT size 65536

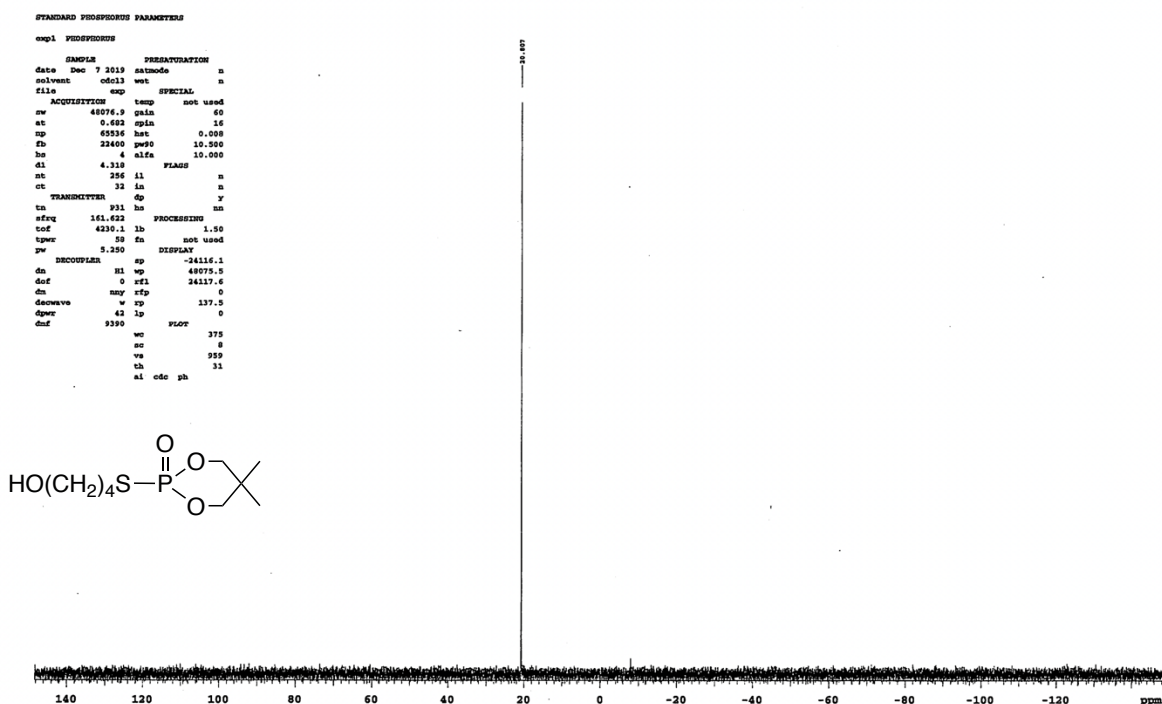
Total time 1 min 10 sec



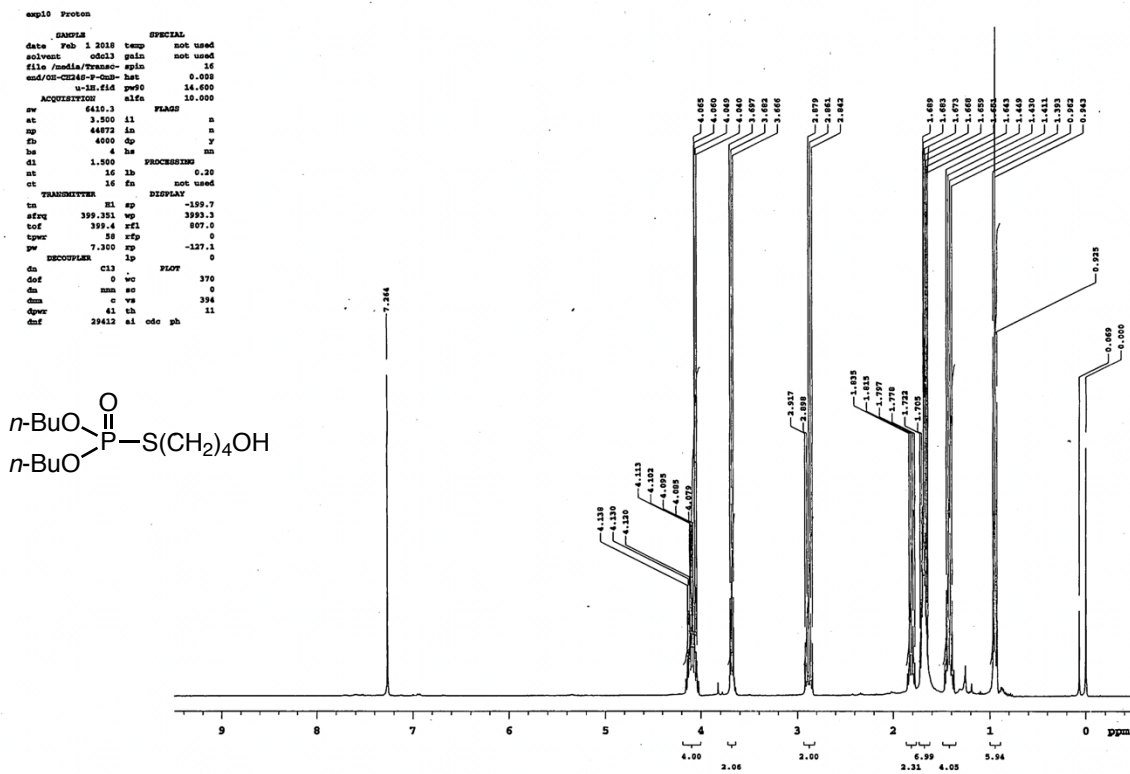
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxide (3bc) ¹³C-NMR



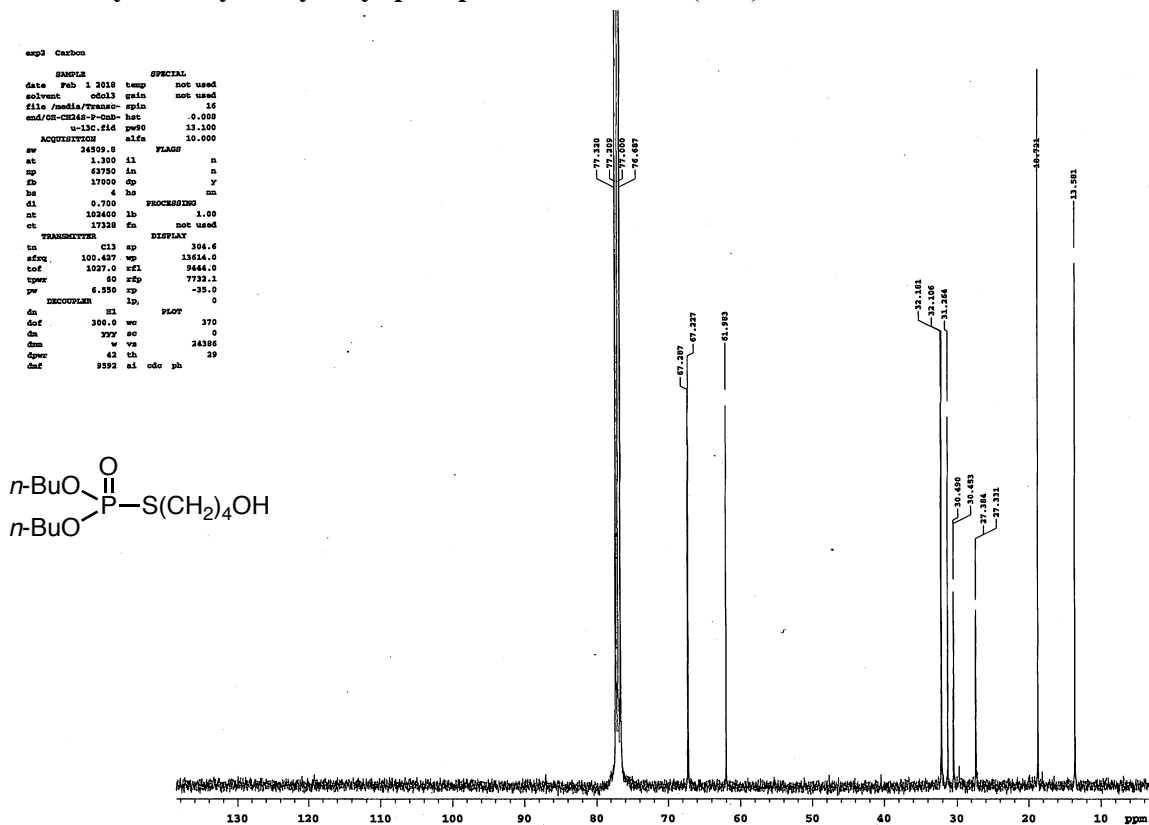
5,5-Dimethyl-2-(4-hydroxybutylthio)-1,3,2-dioxaphosphinate 2-oxide (3bc) ³¹P-NMR



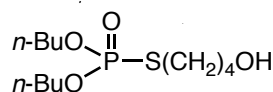
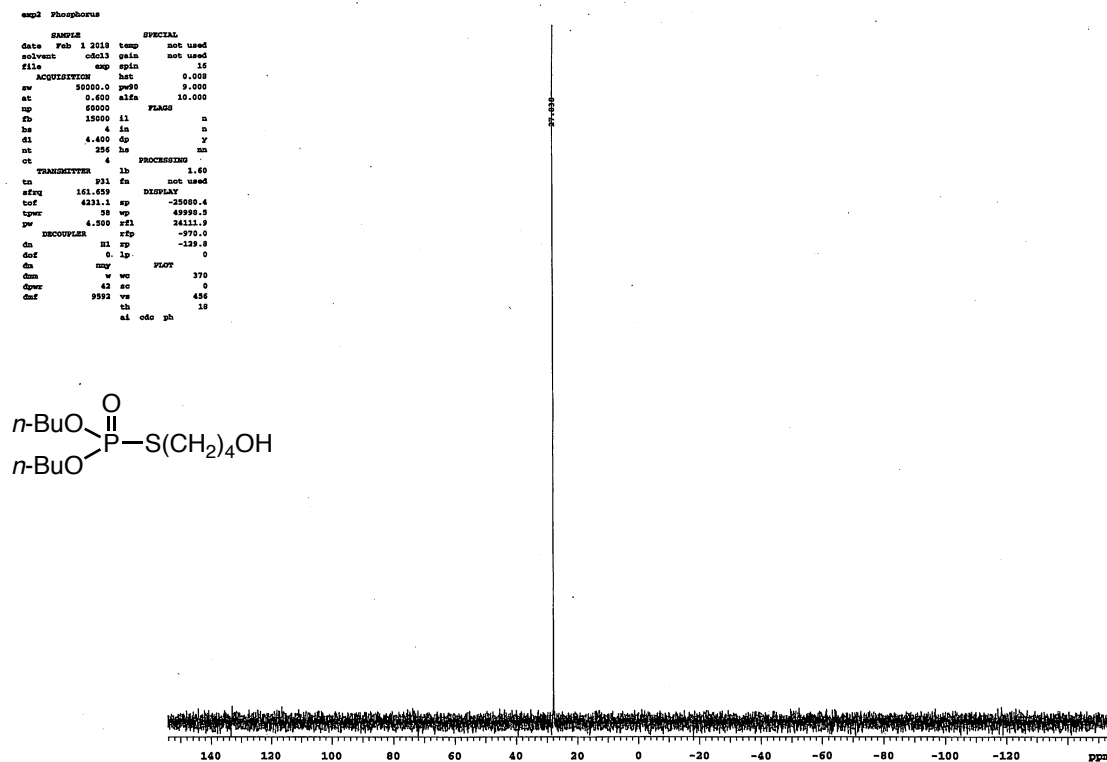
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (3bd) ¹H-NMR



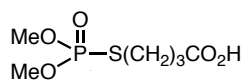
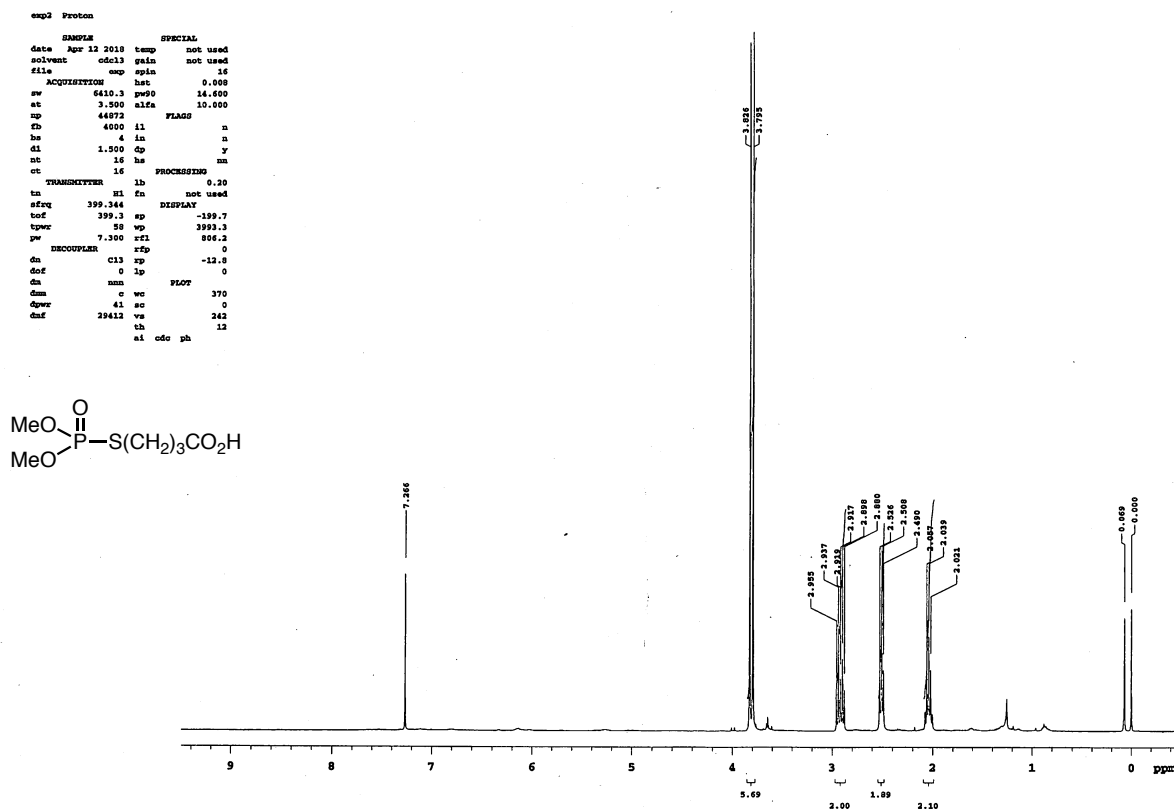
O,O-Dibutyl *S*-4-hydroxybutyl phosphorothioic acid (3bd) ¹³C-NMR



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



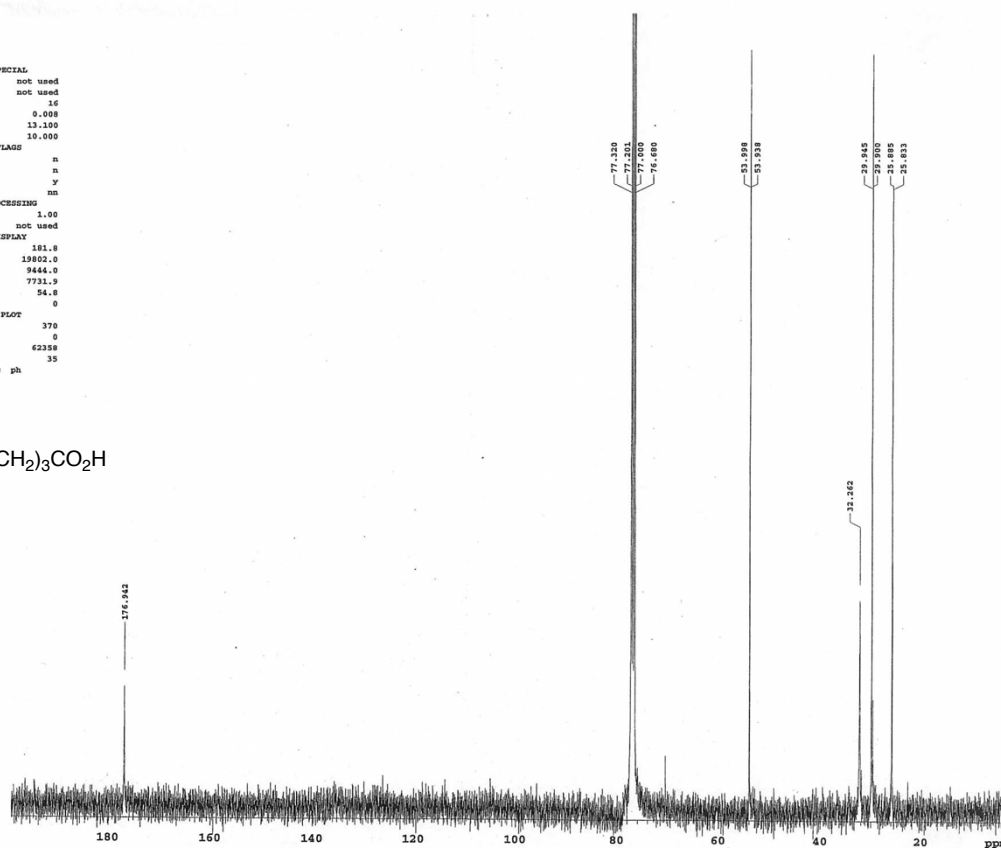
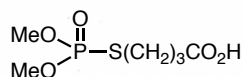
4-[[Bis(methoxy)phosphinothioyl]thio]butanoic acid (3cb) ¹H-NMR



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

exp2 Carbon

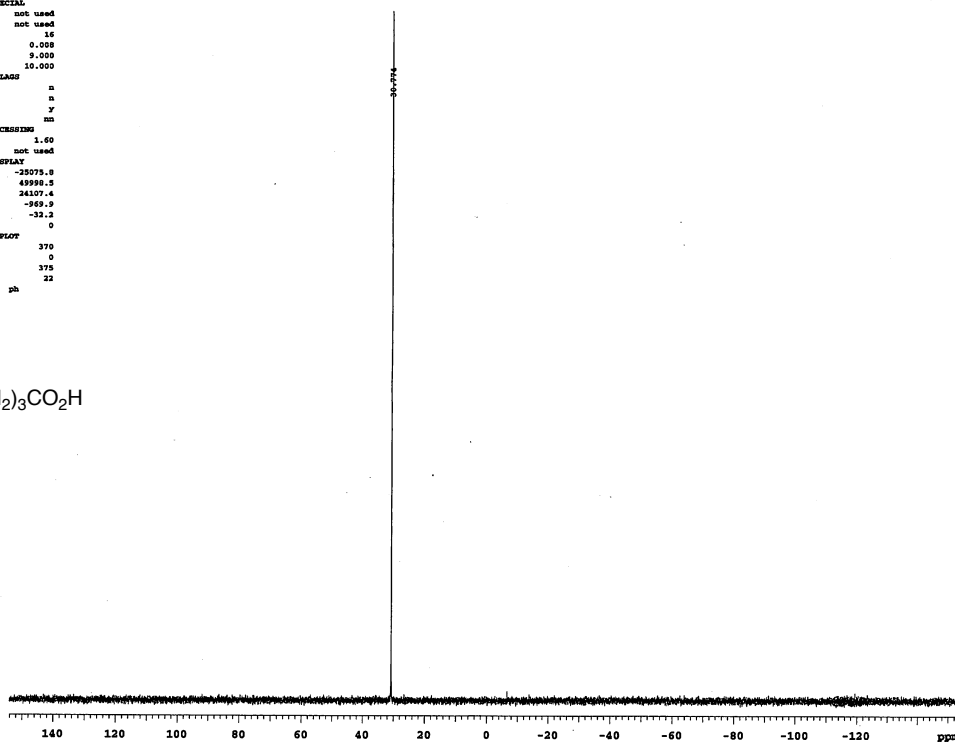
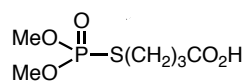
SAMPLE		SPECIAL	
date	Apr 12 2018	temp	not used
solvent	cdcl3	gain	not used
file		exp	16
ACQUISITION		has	0.008
sv	24509.8	pu90	13-130
at	1.300	alfa	10.000
np	63750	FLAGS	
fb	17000	il	n
hs	4	in	n
dl	0.700	dp	y
nt	102400	hs	nn
ct	19792	PROCESSING	
TRANSMITTER		lb	1.00
ta		fn	not used
sfreq	100.625	fn	DISPLAY
tof	1027.0	sp	181.8
tpwr	60	wp	19802.0
pw	6.550	rfl	9444.0
DECOUPLER		rfp	7731.9
dn	HI	rp	54.8
dof	300.0	lp	0
dm	yyy	plot	
dma	w	wo	370
dprc	42	ac	8
daf	9592	ve	62358
th			35
al	cdc	ph	



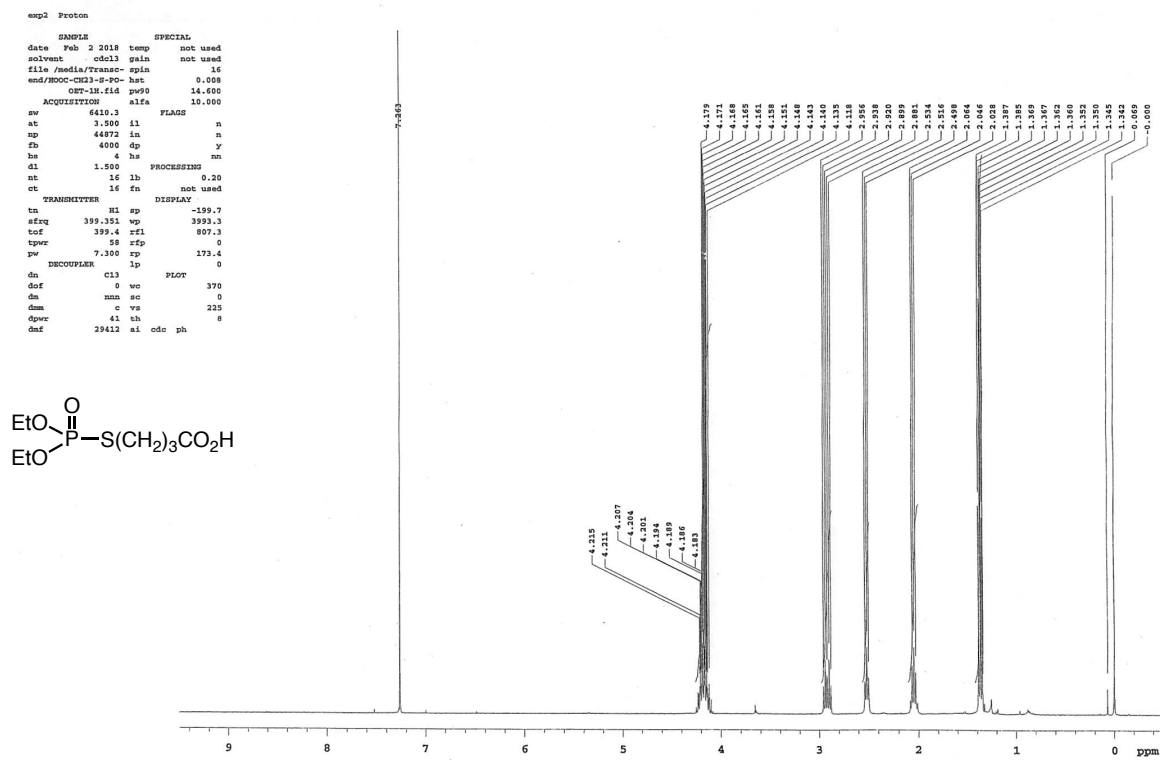
4-[[Bis(methoxy)phosphinothioyl]thio]butanoic acid (3cb) ³¹P-NMR

exp2 Phosphorus

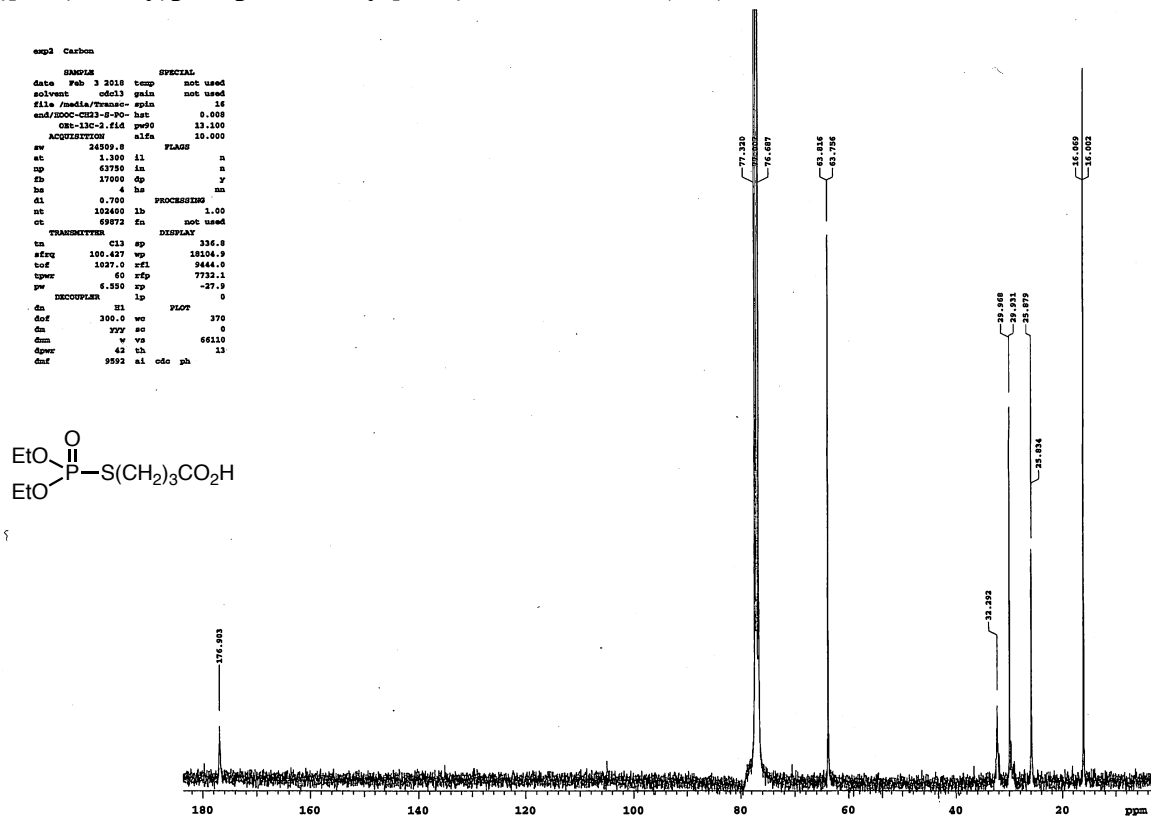
SAMPLE		SPECIAL	
date	Apr 12 2018	temp	not used
solvent	cdcl3	gain	not used
file		exp	16
ACQUISITION		has	0.008
sv	50000.0	pu90	9.000
at	0.600	alfa	10.000
np	60000	FLAGS	
fb	15000	il	n
hs	4	in	n
dl	4.400	dp	y
nt	256	hs	nn
ct	16	PROCESSING	
TRANSMITTER		lb	1.60
ta		fn	not used
sfreq	161.456	fn	DISPLAY
tof	4330.8	sp	-25075.8
tpwr	58	wp	49998.5
pw	4.500	rfl	24107.4
DECOUPLER		rfp	-369.9
dn	HI	rp	-32.2
dof	0	lp	0
dm	mmv	plot	
dma	w	wo	370
dprc	42	ac	0
daf	9592	ve	375
th			22
al	cdc	ph	



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



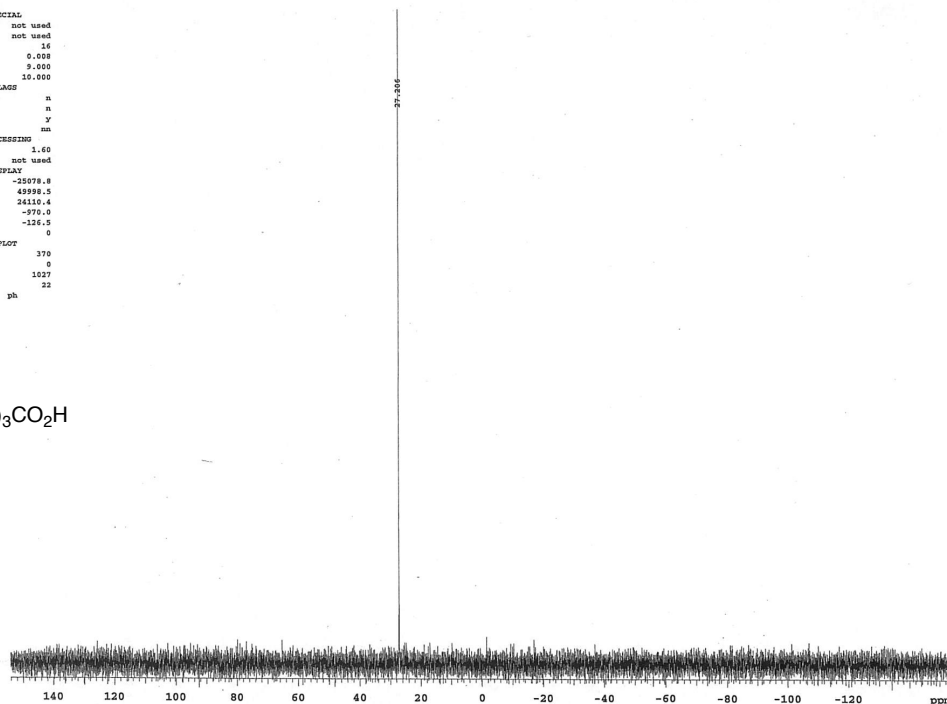
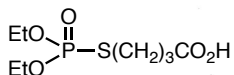
4-[[Bis(ethoxy)phosphinothioyl]thio]butanoic acid (3ca) ¹³C-NMR



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

exp3 Phosphorus

SAMPLE		SPECIAL	
date	Feb 2 2018	temp	not used
solvent	cdcl3	gain	not used
file /media/transfer	spia	16	
end/HOOC-CH2-S-PO-	hat	0.008	
QNT-11P-118	pu00	9.000	
ACQUISITION		ALFA	
sv	50000.0	FLAGS	
at	0.600	il	n
ap	60000	in	n
fb	15000	dp	y
ha	4	hs	mm
dl	4.400	PROCESSING	
nt	256	lb	1.60
et	8	fm	not used
TRANSMITTER		DISPLAY	
tn	731	sp	-25078.6
rftv	161.653	wp	48988.5
tof	4231.1	rfl	24110.4
tpwr	58	rft	-970.0
pw	4.500	tp	-135.5
DECOUPLER		PLOT	
dn	81	lp	0
dof	0	wc	370
dm	nmv	sc	0
dms	w	vs	1027
dpr	42	th	22
dnt	9592	ai	cdc ph



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

Sample Name:

Data Collected on:
Agilent-VNM-400
Archive directory:

Sample directory:

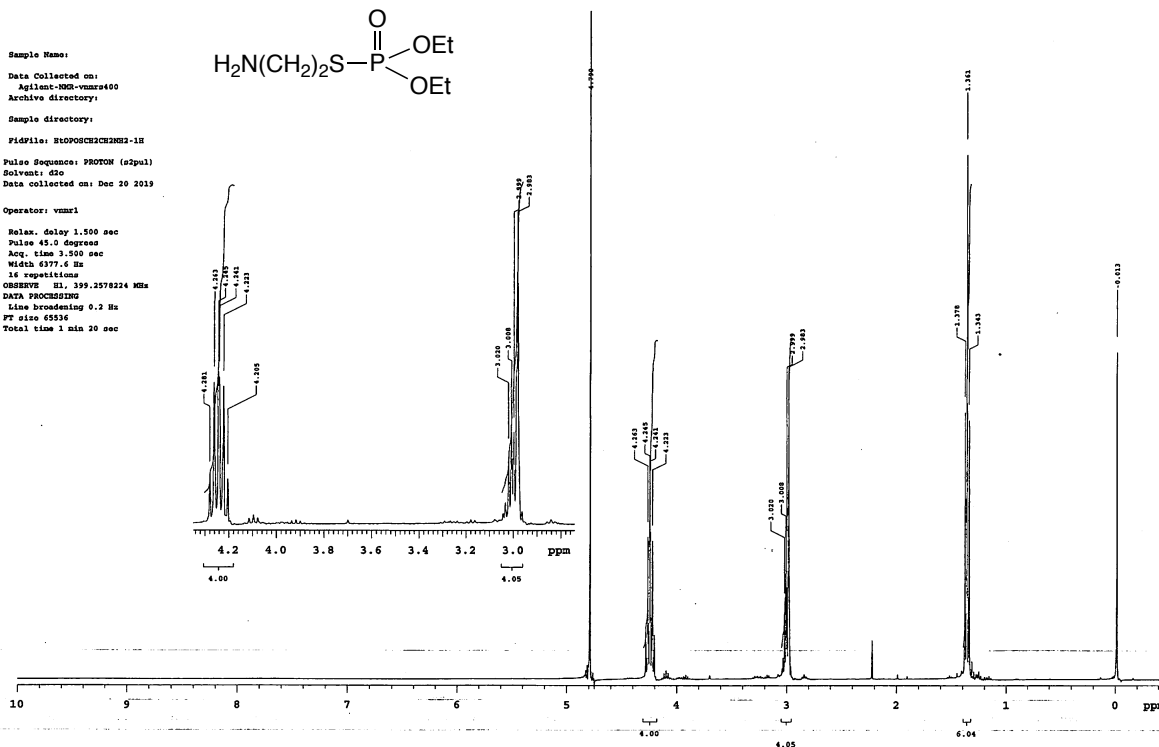
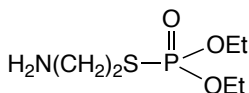
File: 400M000000000-1H

Pulse Sequence: PRQ1 (n2pul)
Solvent: d2o

Date collected on: Dec 20 2013

Operator: vnmr1

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6177.6 Hz
16 repetitions
OBSERVE 51.359.2578224 MHz
DATA PROCESSING
Line broadening 0.2 Hz
PT size 65536
Total time 1 min 20 sec

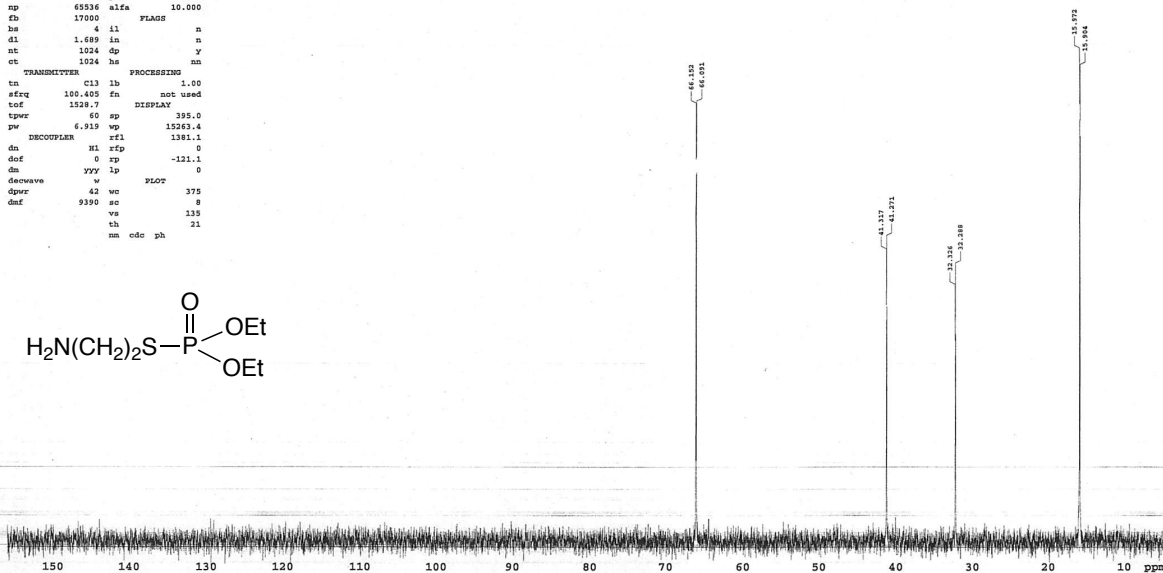
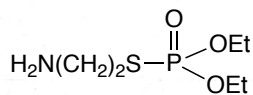


4-{{Bis(ethoxy)phosphinothioyl}thio}ethylamine (3da) ¹³C-NMR

STANDARD PHOSPHORUS PARAMETERS

exp1 CARBON

SAMPLE		PRESENTATION	
date	Dec 20 2019	satmode	n
solvent	d2o	wet	n
file	/media/KINGST-	SPECIAL	n
ON/ROPOSCHECHER- temp	not used		
ACQUISITION	spin	16	
av	25000.0	hsc	0.008
at	1.311	pw90	13.838
rp	65536	alfa	10.000
fb	17000	FLAGS	
ba	4	il	n
dl	1.689	in	n
nt	1024	dp	y
ct	1024	hs	nn
TRANSMITTER		PROCESSING	
ta	C13	lb	1.00
sfreq	100.625	fn	not used
tof	1528.7	DISPLAY	
tpwr	60	sp	395.0
pw	6.919	wp	15263.4
DECOUPLER	rl	rfl	1381.1
dn	hl	rfd	0
dof	0	rp	-121.1
dm	yyy	lp	0
decouave	w		
dprc	42	wo	375
dof	9390	sc	8
		vs	135
		th	21
		nm	cdc
		ph	

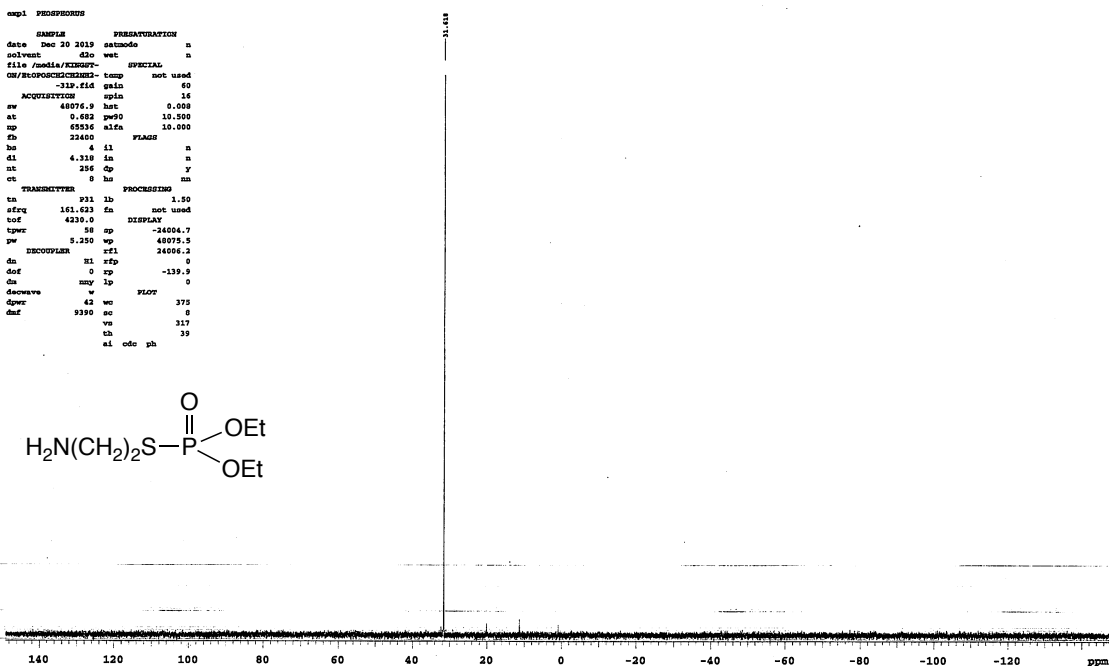
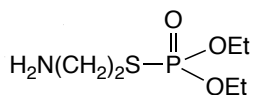


4-{{Bis(ethoxy)phosphinothioyl}thio}ethylamine (3da) ³¹P-NMR

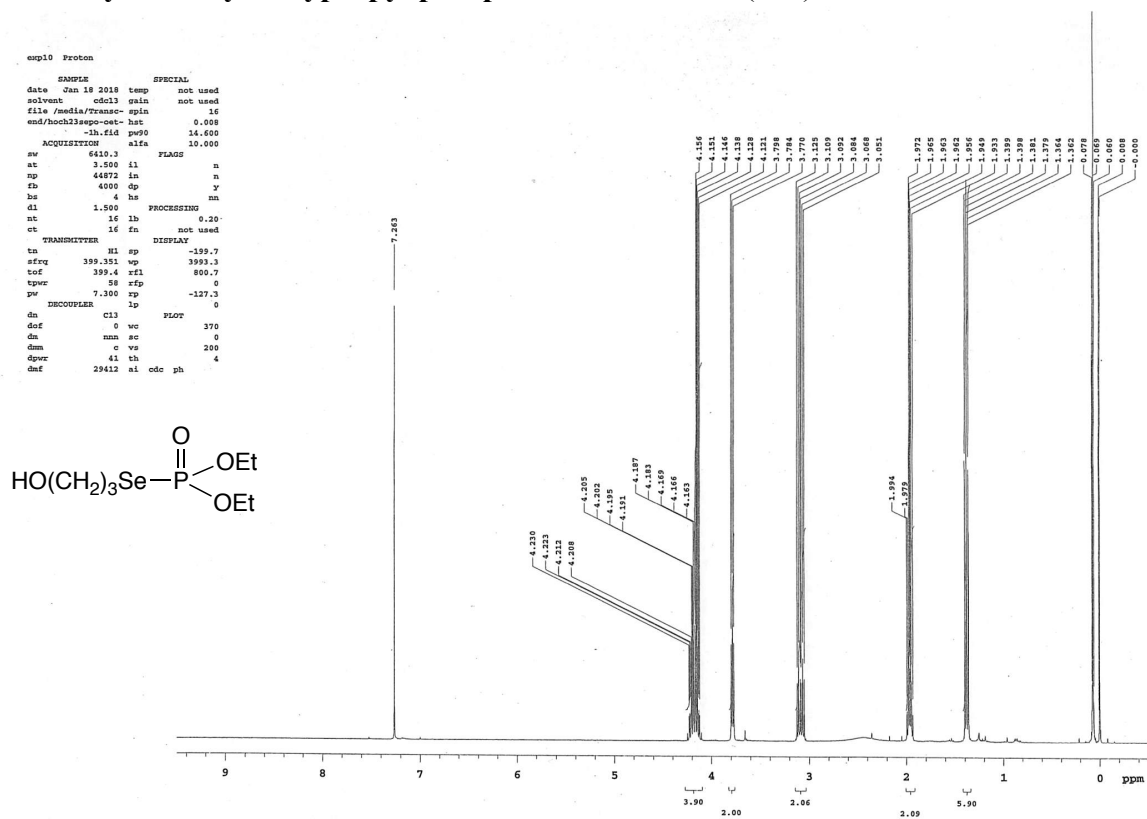
STANDARD PHOSPHORUS PARAMETERS

exp1 PHOSPHORUS

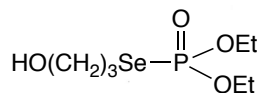
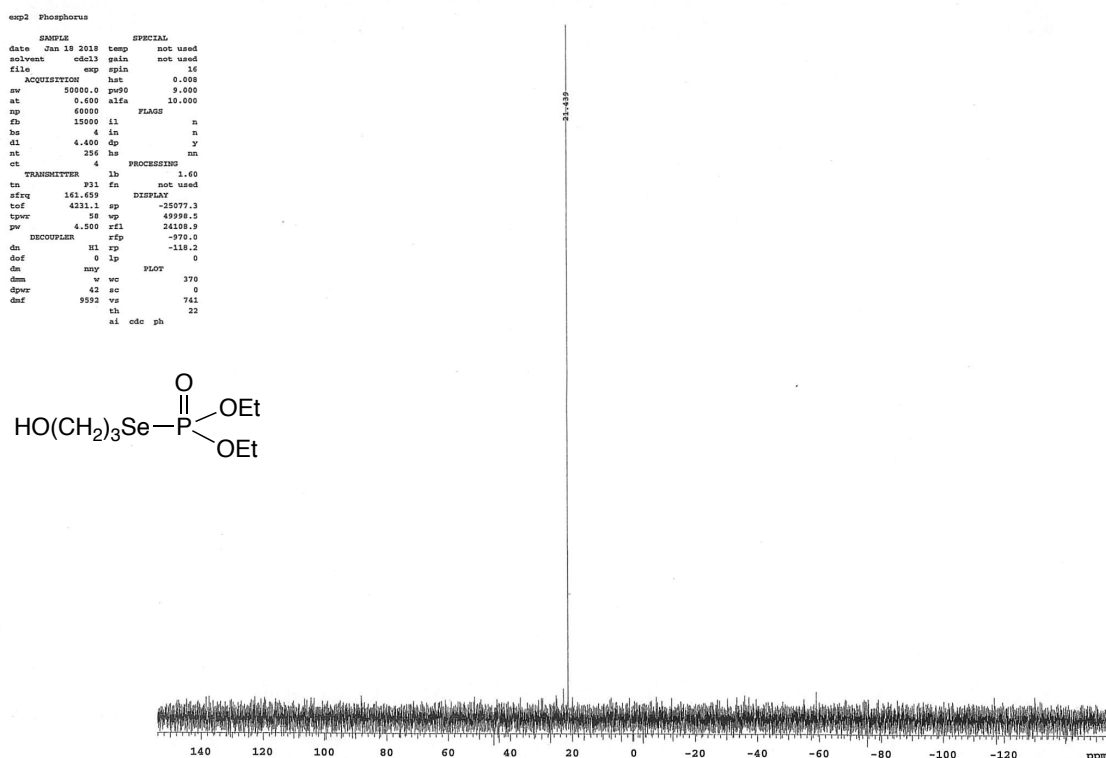
SAMPLE		PRESENTATION	
date	Dec 20 2019	satmode	n
solvent	d2o	wet	n
file	/media/KINGST-	SPECIAL	n
ON/ROPOSCHECHER- temp	not used		
ACQUISITION	spin	16	
av	48076.9	hsc	0.008
at	0.483	pw90	10.000
rp	65536	alfa	10.000
fb	23400	FLAGS	
ba	4	il	n
dl	4.319	in	n
nt	256	dp	y
ct	8	hs	nn
TRANSMITTER		PROCESSING	
ta	P31	lb	1.50
sfreq	161.623	fn	not used
tof	4230.0	DISPLAY	
tpwr	58	sp	-24004.7
pw	5.250	wp	48075.5
DECOUPLER	rl	rfl	24006.2
dn	hl	rfd	0
dof	0	rp	-139.9
dm	my	lp	0
decouave	w		
dprc	42	wo	375
dof	9390	sc	8
		vs	317
		th	39
		nm	cdc
		ph	



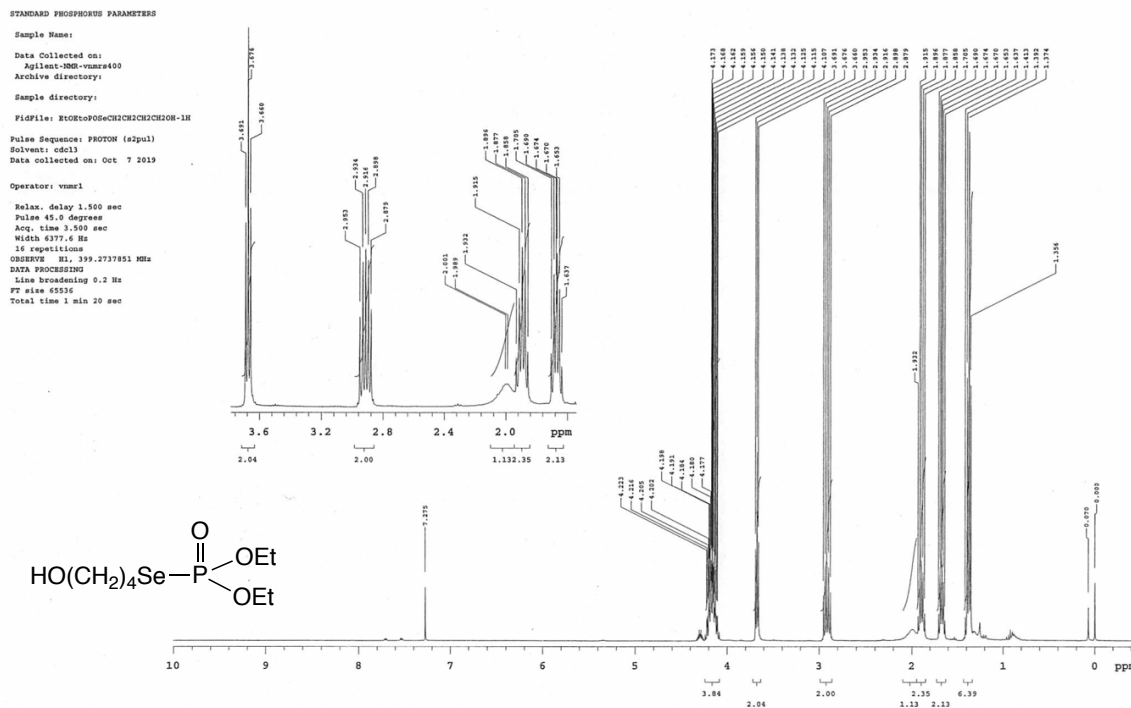
***O,O*-Diethyl *Se*-3-hydroxypropyl phosphoroselenoic acid (7aa) ¹H-NMR**



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



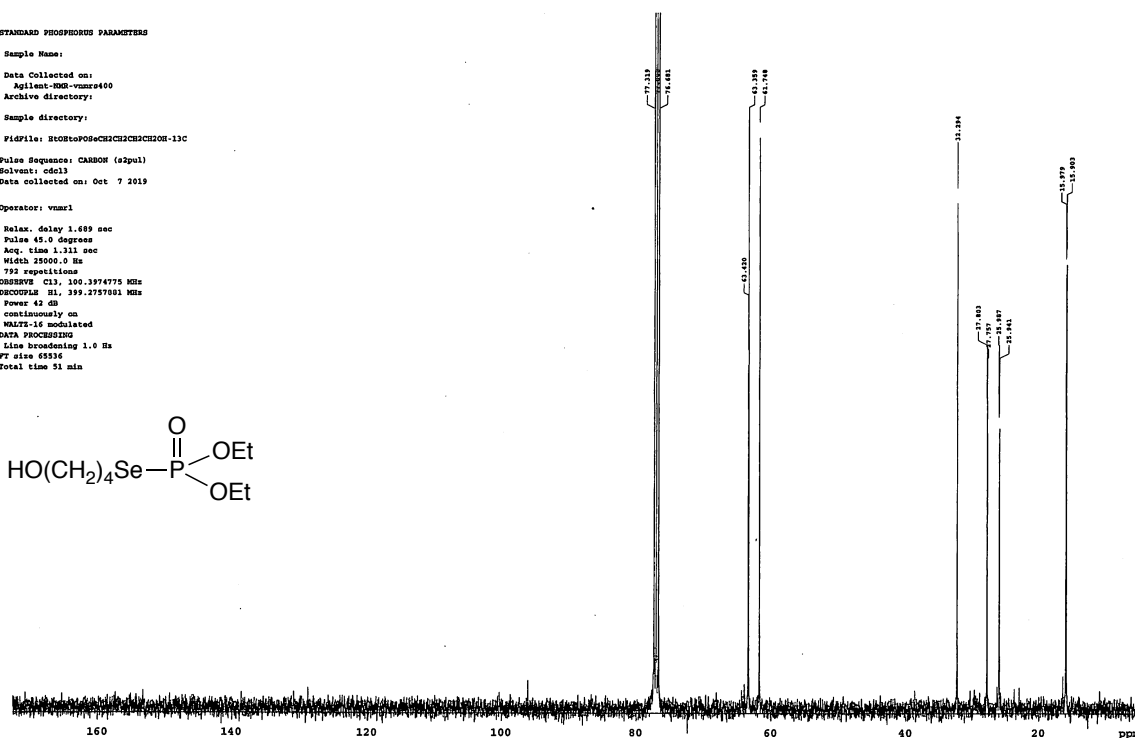
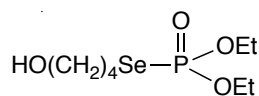
***O,O*-Diethyl *Se*-4-hydroxybutyl phosphoroselenoic acid (7ba) ¹H-NMR**



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

STANDARD PHOSPHORUS PARAMETERS

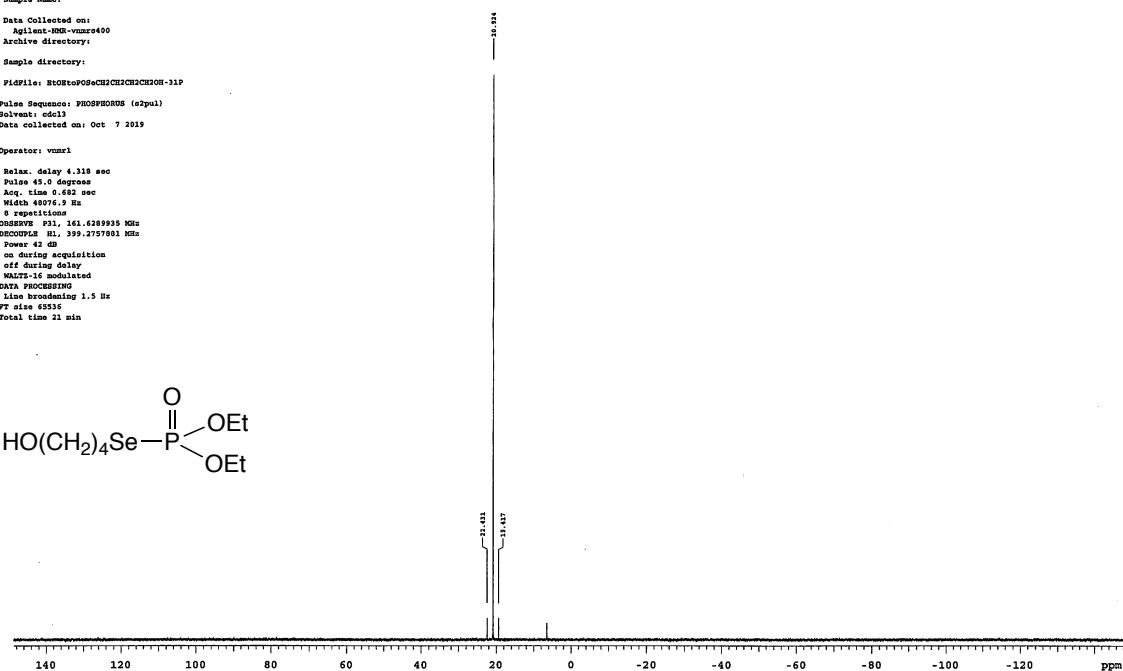
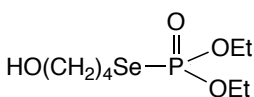
Sample Name:
Data Collected on:
Agilent-VNM-400
Archive directory:
Sample directory:
FidFile: StOStoPOSeCH2CH2CH2CH2OH-13C
Pulse Sequence: CARBON (zgpg3)
Solvent: cdcl3
Data collected on: Oct 7 2019
Operator: vnmr1
Relax. delay 1.659 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 19000.0 Hz
792 repetitions
OBSERVE C13, 100.6274775 MHz
DECOUPLE H1, 399.2757881 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 51 min



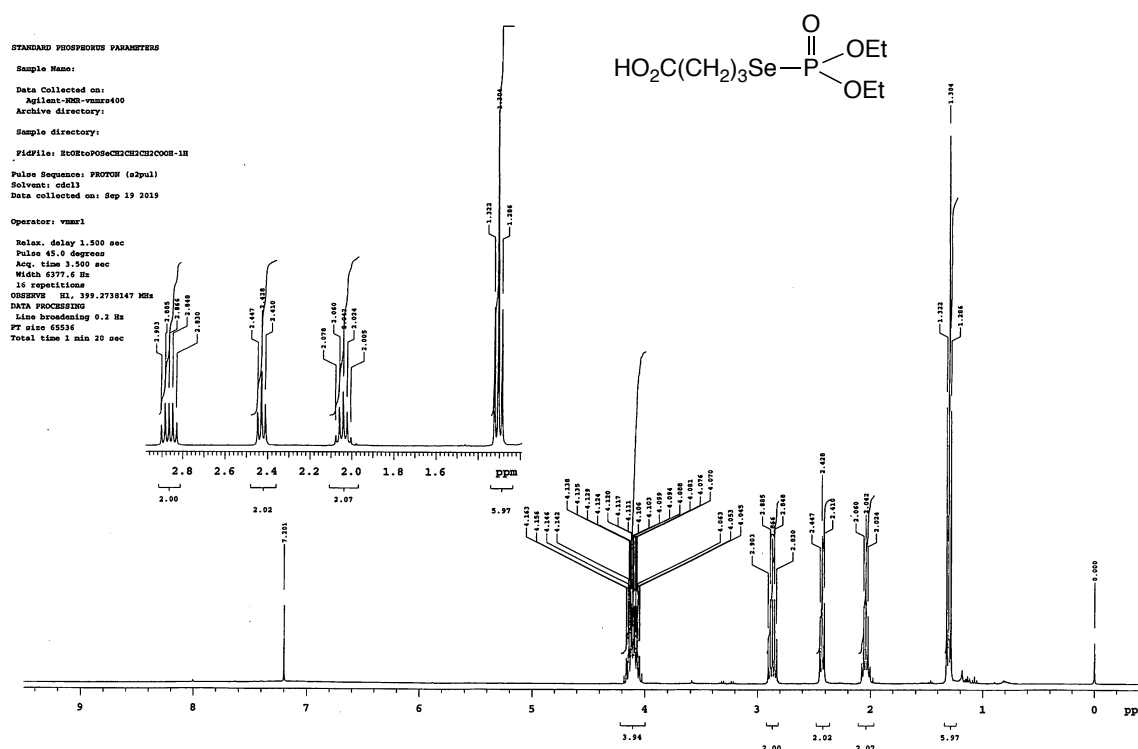
O,O-Diethyl *Se*-4-hydroxybutyl phosphoroselenoic acid (7ba) ³¹P-NMR

STANDARD PHOSPHORUS PARAMETERS

Sample Name:
Data Collected on:
Agilent-VNM-400
Archive directory:
Sample directory:
FidFile: StOStoPOSeCH2CH2CH2CH2OH-31P
Pulse Sequence: PHOSPHORUS (zgpg3)
Solvent: cdcl3
Data collected on: Oct 7 2019
Operator: vnmr1
Relax. delay 4.318 sec
Pulse 45.0 degrees
Acq. time 0.682 sec
Width 48976.0 Hz
8 repetitions
OBSERVE P31, 161.6389935 MHz
DECOUPLE H1, 399.2757881 MHz
Power 42 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536
Total time 21 min



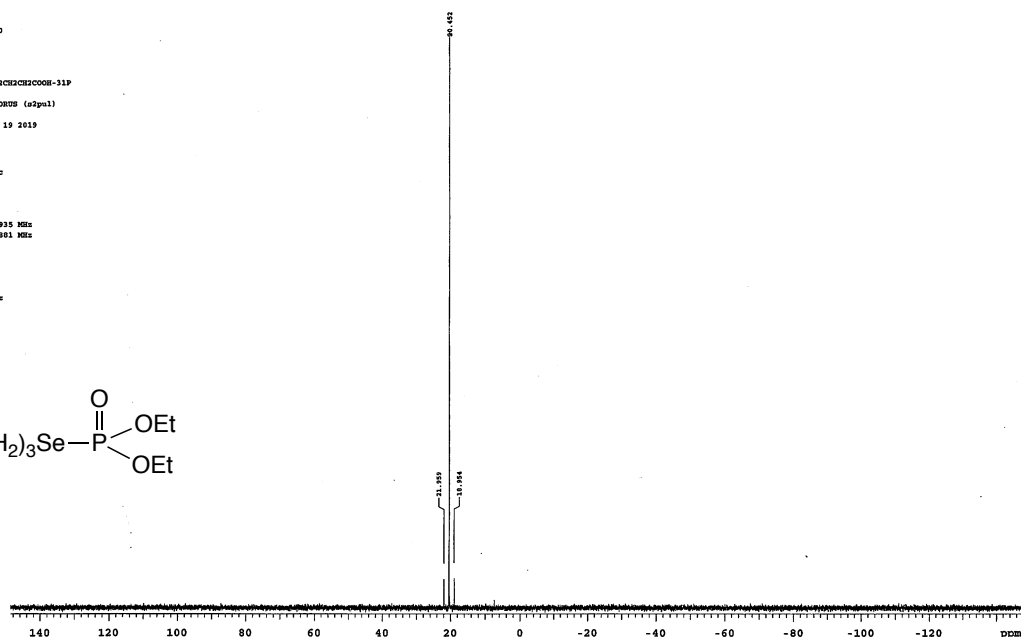
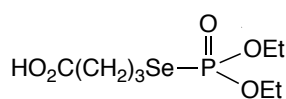
4-[Bis(ethoxy)phosphinoseleno]butanoic acid (7ca) ¹H-NMR



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

STANDARD PHOSPHORUS PARAMETERS

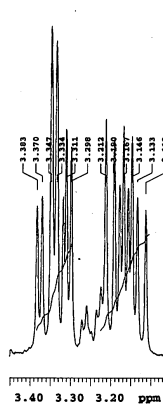
Sample Name:
Data Collected on:
Agilent-800-mmre400
Archive directory:
Sample directory:
FidFile: H08toP05eCH2CH2CH2COOH-31P
Pulse Sequence: PHOSPHORUS (zgpg1)
Solvent: cdcl3
Data collected on: Sep 19 2019
Operator: vmm1
Relax. delay 4.118 sec
Pulse 45.0 degrees
Acq. time 0.682 sec
Width 48076.5 Hz
4 repetitions
OBSERVE P31, 161.6289935 MHz
PROCPAR H1, 399.2707861 MHz
Power 42 dB
on during acquisition
off during delay
MAGTE-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536
Total time 21 min



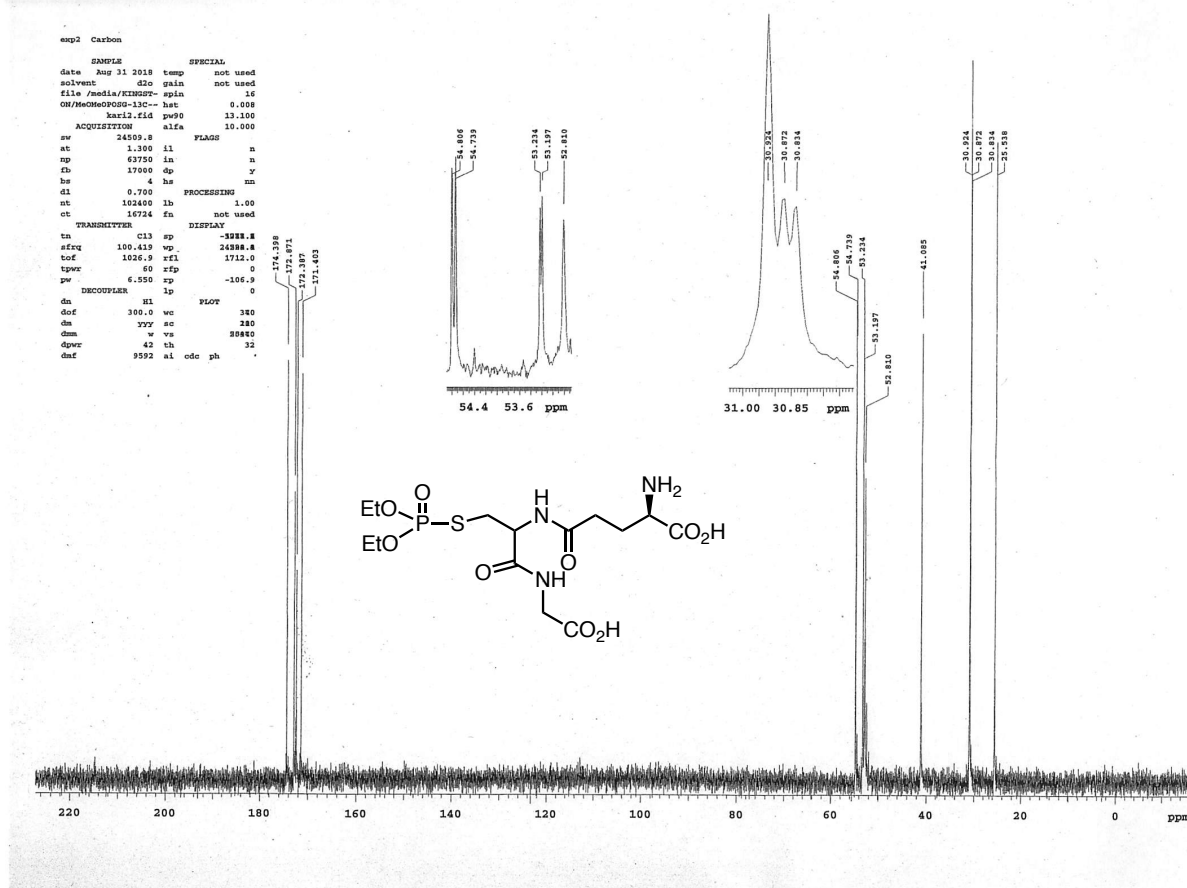
N-[N-L-γ-glutamyl-S-(diethoxyphosphinyl)-L-cysteinyl]glycine (9a) ¹H-NMR

exp3 Proton

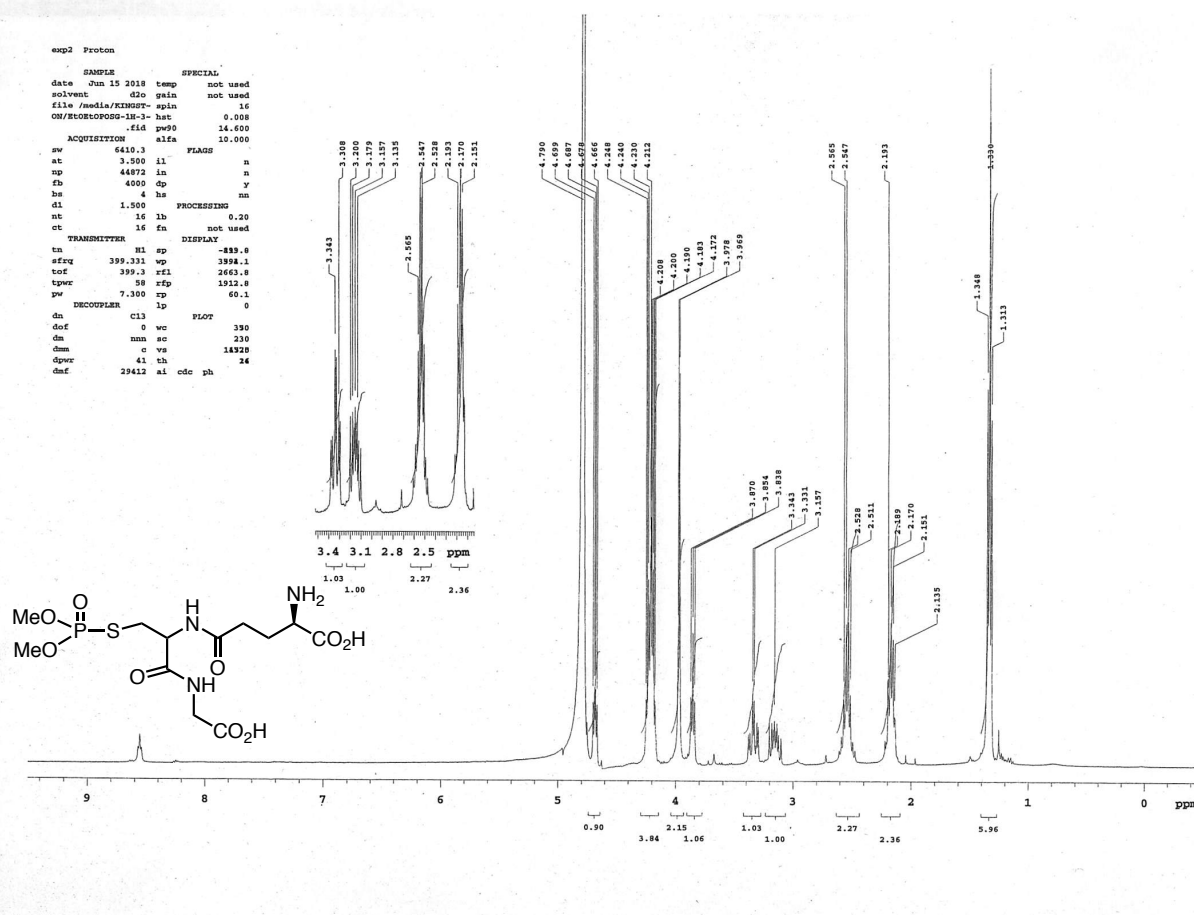
date Aug 30 2018 temp not used
solvent d2o gain not used
file /media/KIMMUT- spin 16
CH/MeCHOPPOG-IN-F- hat 0.000
id pw90 14.600
alpha 10.000
ACQUISITION
nu 6410.3
at 3.500 il n
sp 44872 in n
fb 4000 dp y
bo 4 ha na
dl 1.500 PROCESSING
nt 16 lb 0.20
ot 16 fa not used
TRANSMITTER DISPLAY
tx H1 sp 1889.8
rfq 399.312 wp 2358.9
tof 399.3 rfl 2665.0
tpr 50 rfp 1912.7
pw 7.100 zp -164.9
DECOUPLER
on C13
def 0 wo PLOT
dm mm so 280
dm c va 19928
dpr 41 th
daf 29413 si cdc ph 23



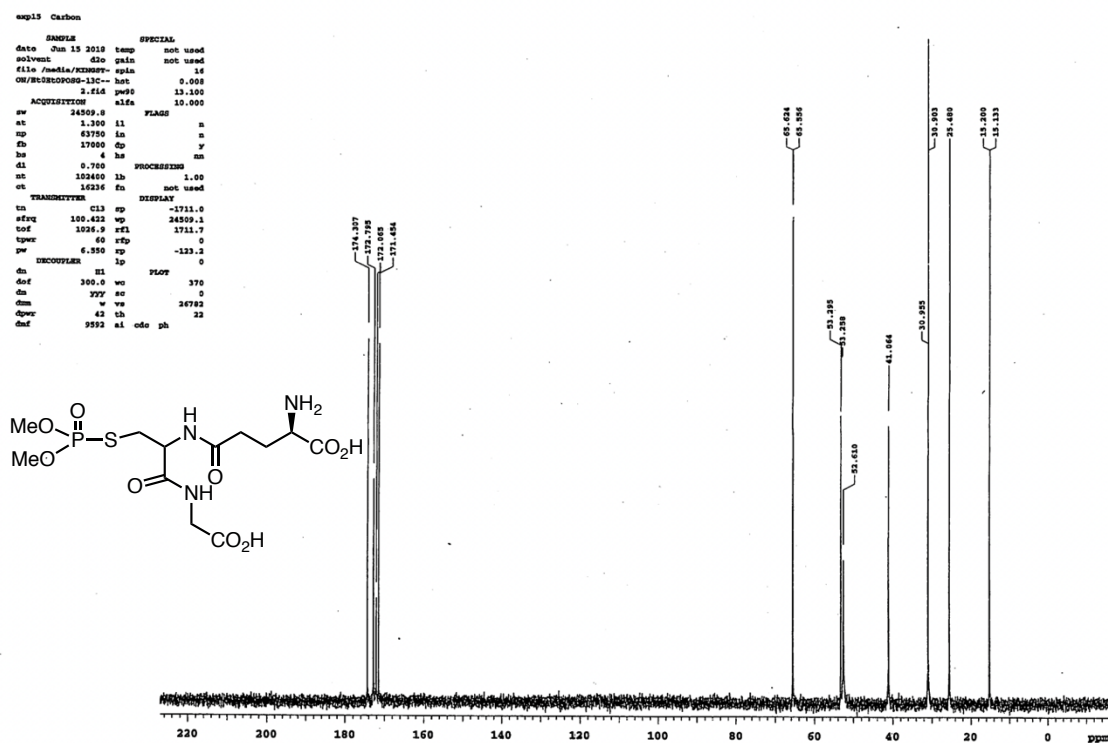
N-[*N*-*L*- γ -glutamyl-*S*-(diethoxyphosphinyl)-*L*-cysteinyl]glycine (9a) ^{13}C -NMR



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



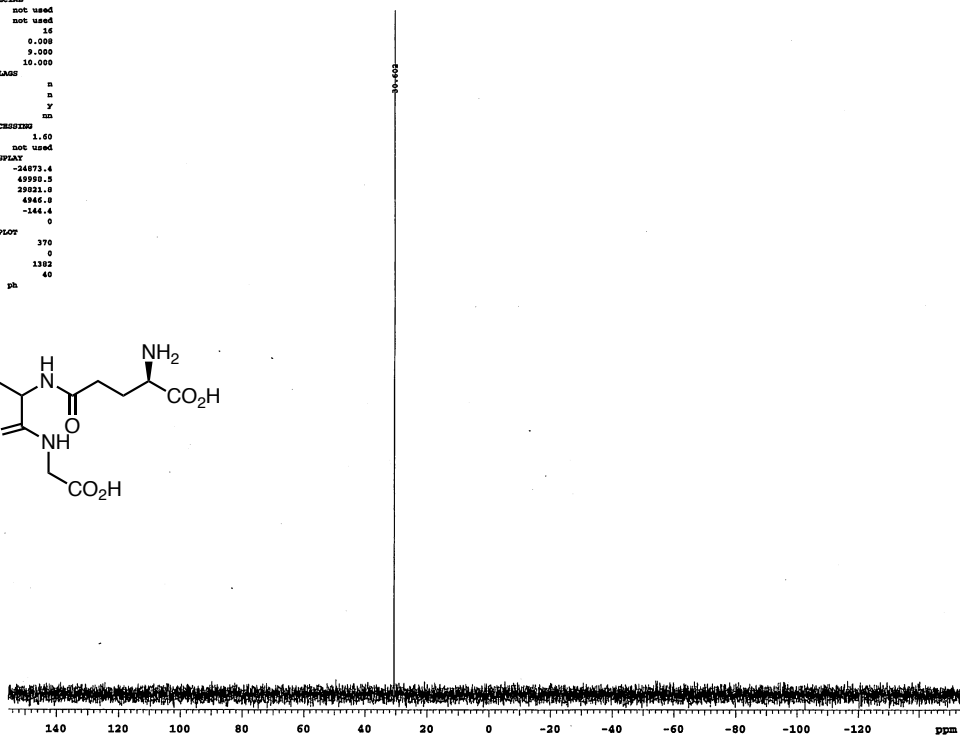
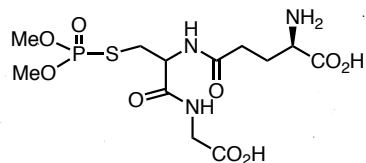
N-[*N*-*L*- γ -glutamyl-*S*-(dimethoxyphosphinyl)-*L*-cysteinyl]glycine (9b) ¹³C-NMR



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

exp2 Phosphorus

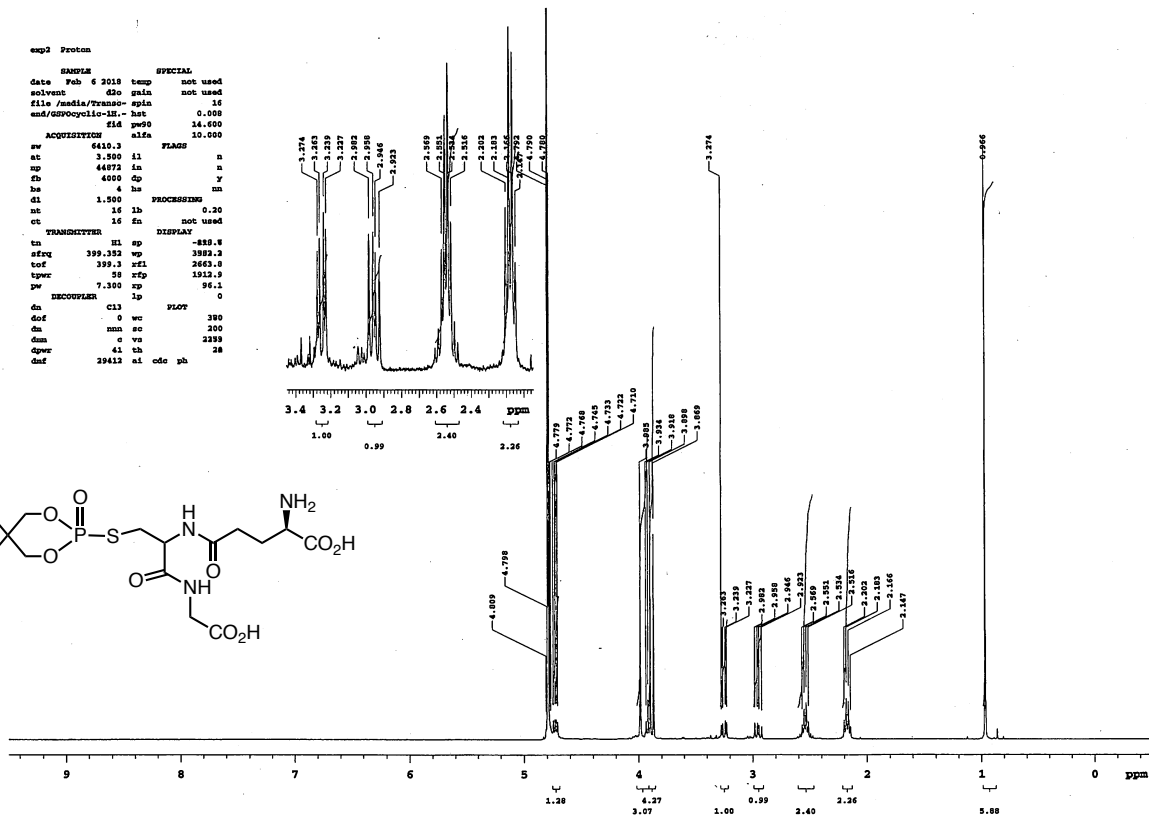
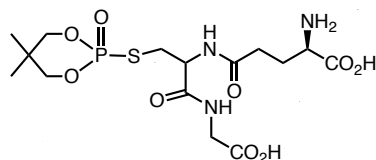
SAMPLE		SPECIAL	
date	Jun 13 2018	temp	not used
solvent	d2o	gain	not used
file	exp	spin	16
ACQUISITION	exp	has	0.000
sv	50000.0	pw90	9.000
at	0.000	alpha	10.000
mp	80000	flags	n
fn	15000	l1	n
hs	4	in	n
dl	4.400	dp	y
nt	256	ha	m
ct	20	PROCESSING	1.00
TRANSMITTER	P31	fn	not used
sfreq	161.851	sp	DISPLAY
tof	4230.8	wp	-24873.4
tpwr	50	rfp	49950.5
pw	4.500	rfl	29821.0
DECOUPLER	H1	rp	4946.0
dn	0	lp	-144.4
dof	0	plot	0
dun	my	w	370
dpwr	42	so	0
dnt	9592	th	1302
	si	odo	ph



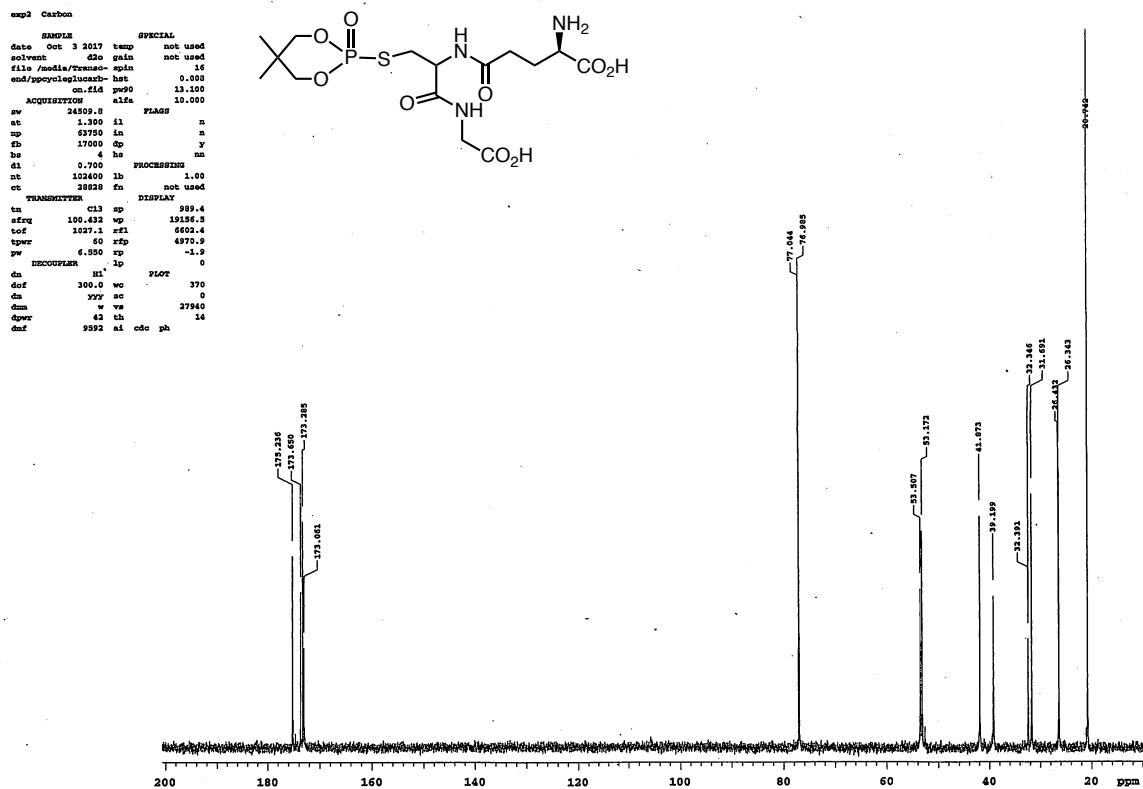
N-[*N*-*L*- γ -glutamyl-2-(1,3,2-dioxaphosphorinane-2-oxide)-*L*-cysteinyl]glycine (9c) ^1H -NMR

exp2 Proton

SAMPLE		SPECIAL	
date	Feb 6 2018	temp	not used
solvent	d2o	gain	not used
file	media/Transo-	spin	16
end/ODD/ODD-15-	has	0.000	
ACQUISITION	exp	pw90	14.600
sv	4010.3	alpha	10.000
at	3.500	l1	n
mp	44872	in	n
fn	4000	dp	y
hs	4	ha	m
dl	1.500	PROCESSING	0.20
nt	16	lb	not used
ct	16	fn	not used
TRANSMITTER	H1	sp	DISPLAY
sfreq	399.352	wp	-850.8
tof	399.3	rfl	3982.2
tpwr	50	rfp	2863.0
pw	7.300	rp	1312.9
DECOUPLER	C13	lp	96.1
dn	0	plot	0
dof	0	wc	380
dun	0	so	200
dpwr	41	th	2339
dnt	29412	si	cdc



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



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

