Supplementary Electronic Information

Novel Crown-Ether- Methylenediphosphonotetrathioate Hybrids as Zn(II) Chelators

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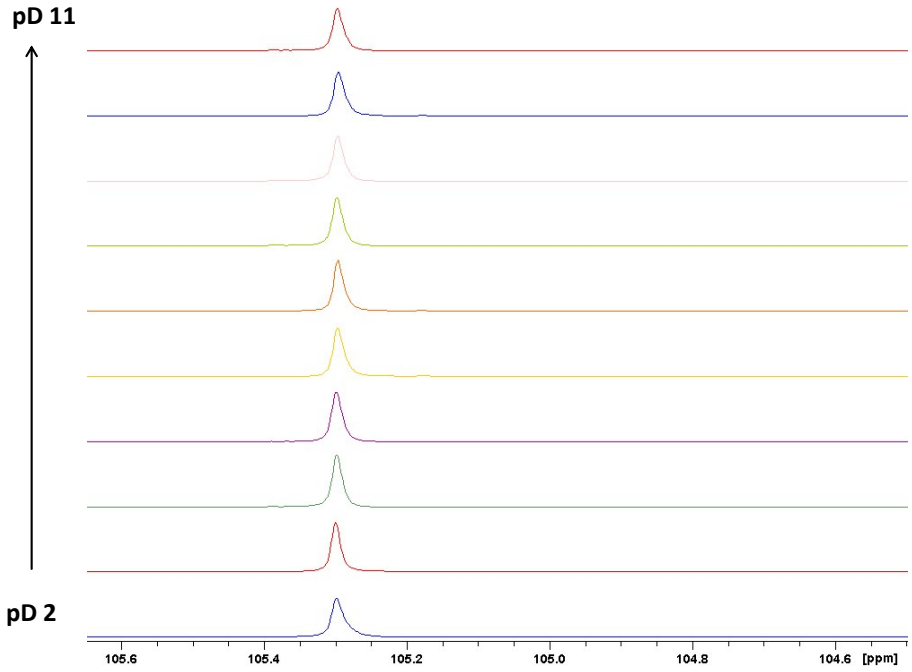
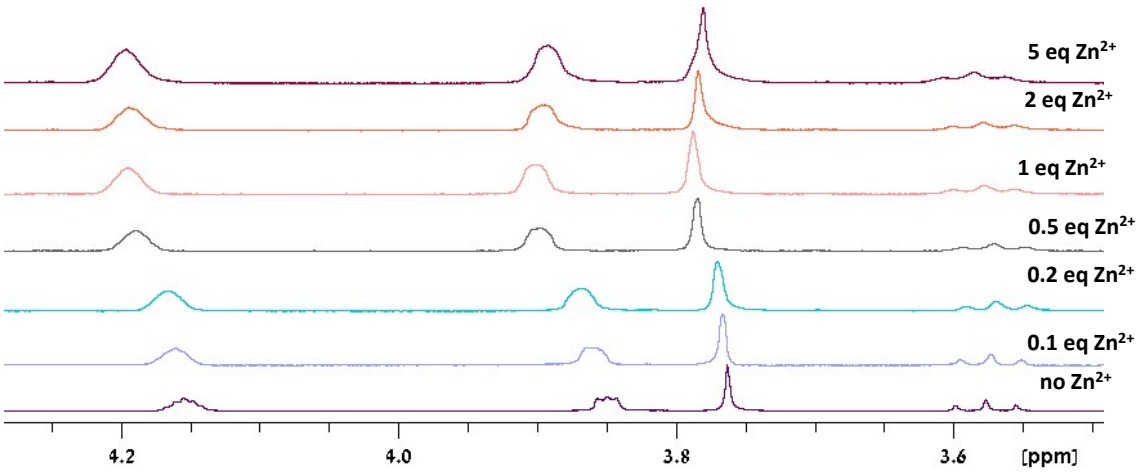
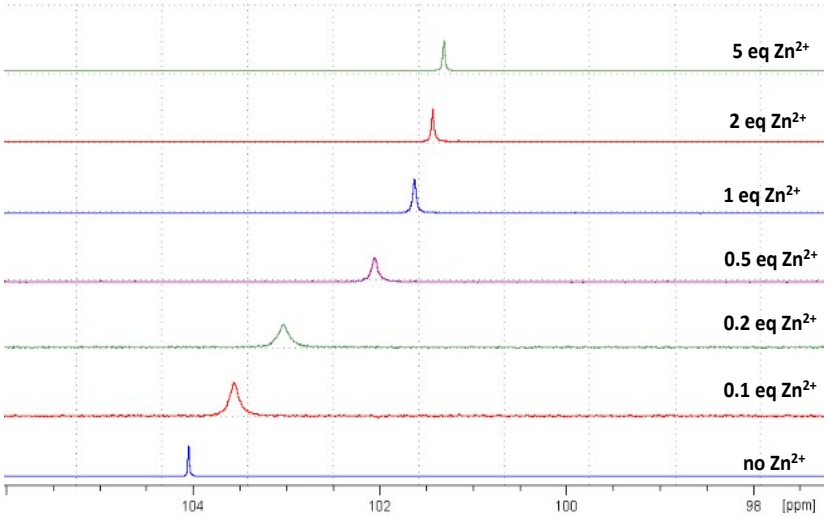


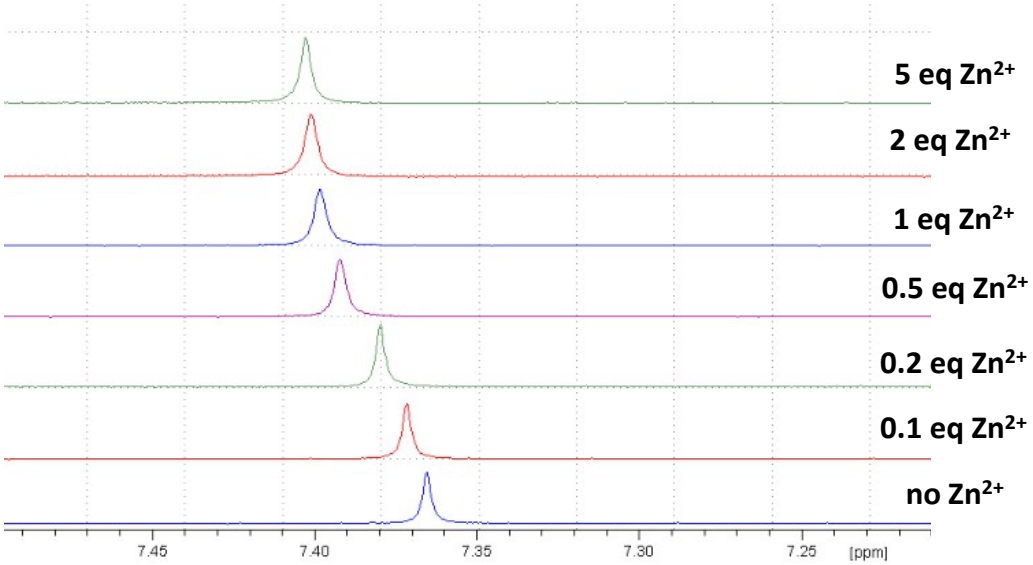
1.2. Fig. S2. Titration of 6 mM 11 in D_2O with $ZnCl_2$ monitored by ^{1}H-NMR at 600 MHz, 300 K.



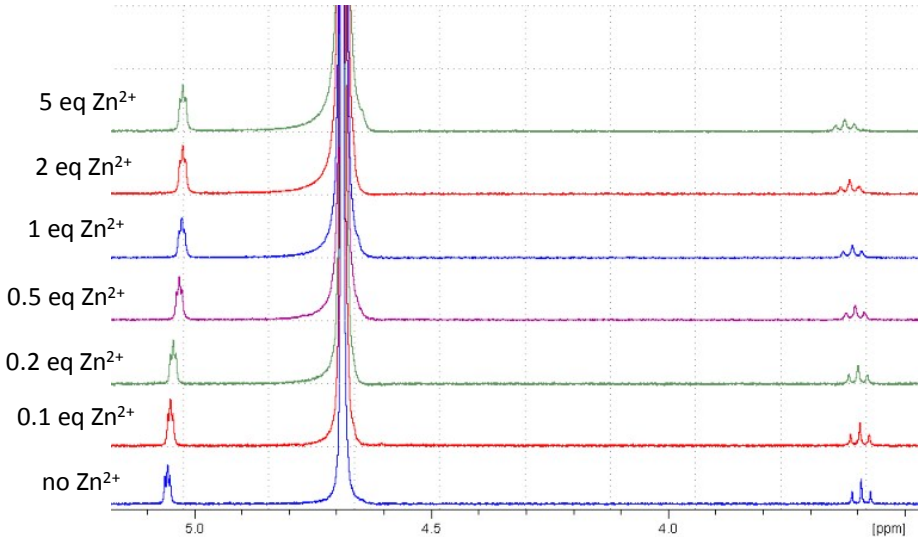
1.3. Fig. S3. Titration of 6 mM 9 in D_2O with $ZnCl_2$ solution. ^{31}P-NMR spectra were measured at 243 MHz, 300 K.



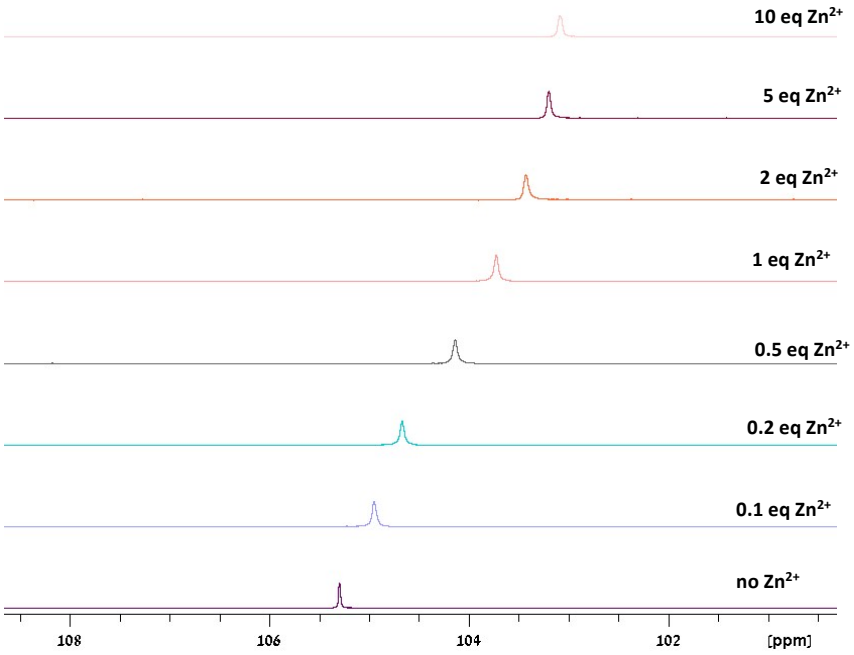
1.4. Fig. S4. Titration of 6 mM 9 in D_2O with $ZnCl_2$ as monitored by ^1H-NMR at 600 MHz, 300 K (aromatic region).



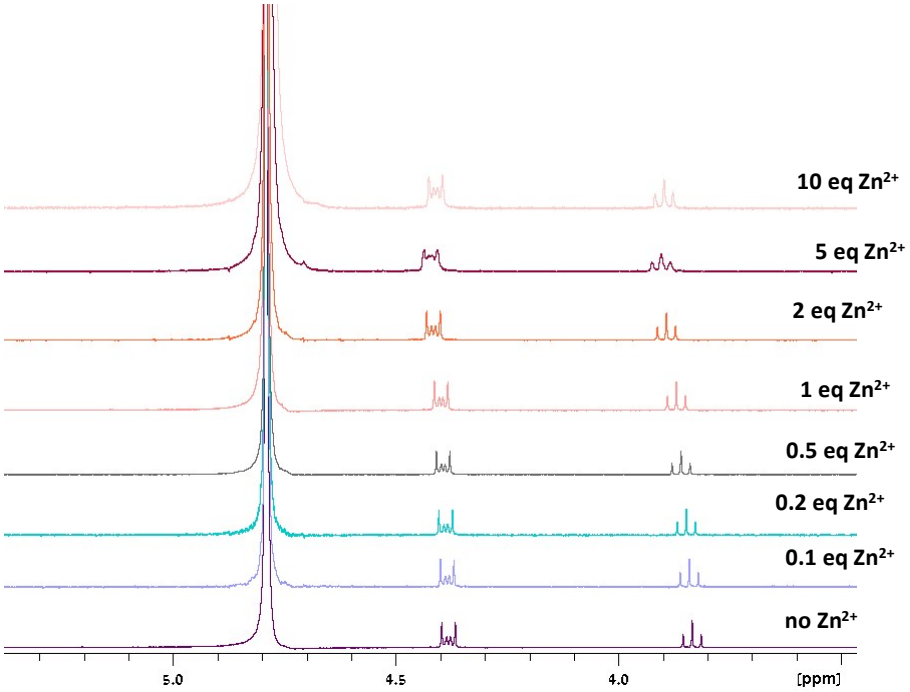
1.5. Fig. S5. Titration of 6 mM 9 in D_2O with $ZnCl_2$ as monitored by ^{1}H-NMR at 600 MHz, 300 K (aliphatic region).



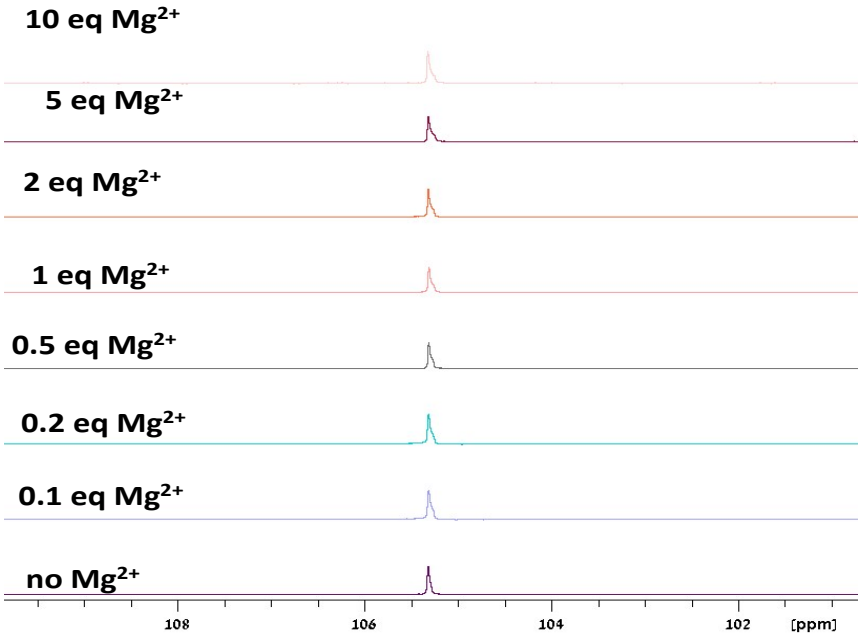
1.6. Fig. S6. Titration of 6 mM 7 in D_2O with $ZnCl_2$ as monitored by ^{31}P-NMR at 243 MHz, 300 K.



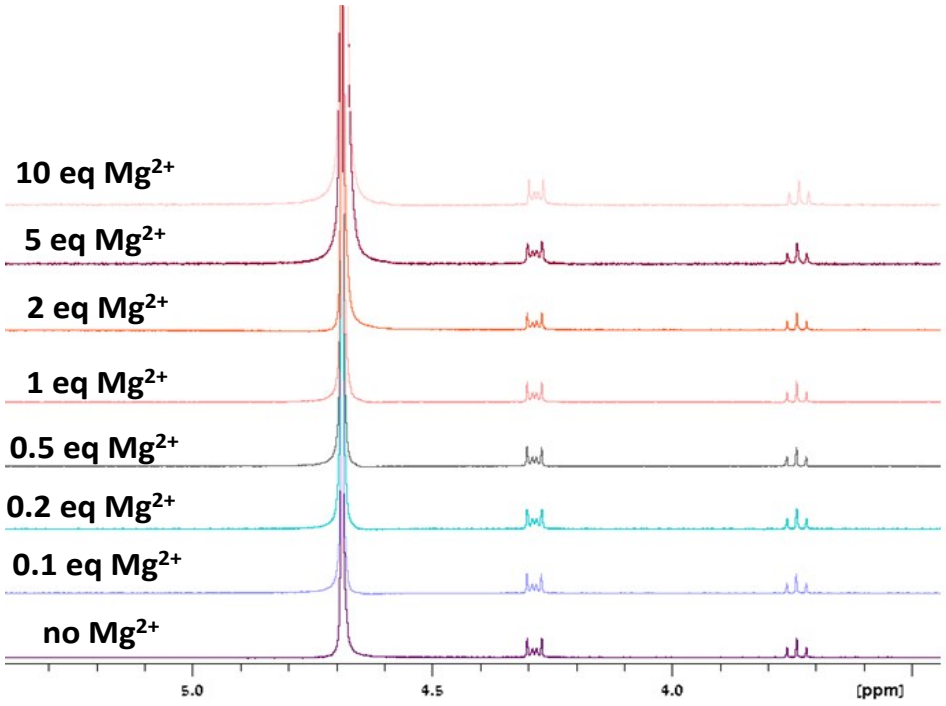
1.7. Fig. S7. Titration of 6 mM 7 in D_2O with $ZnCl_2$ as monitored by ^{1}H-NMR at 600 MHz, 300 K.



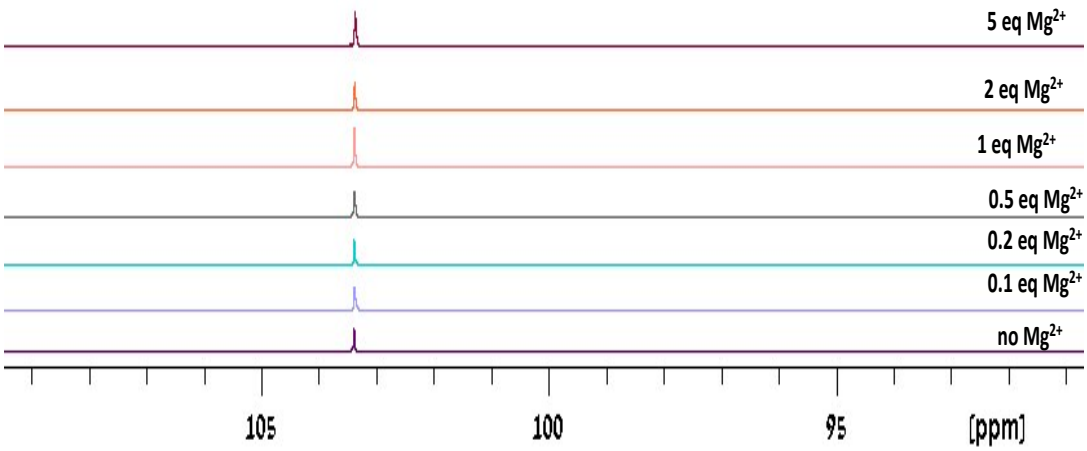
1.8. Fig. S8. Titration of 6 mM 7 in D_2O with $MgCl_2$ as monitored by ^{31}P-NMR at 243 MHz, 300 K.



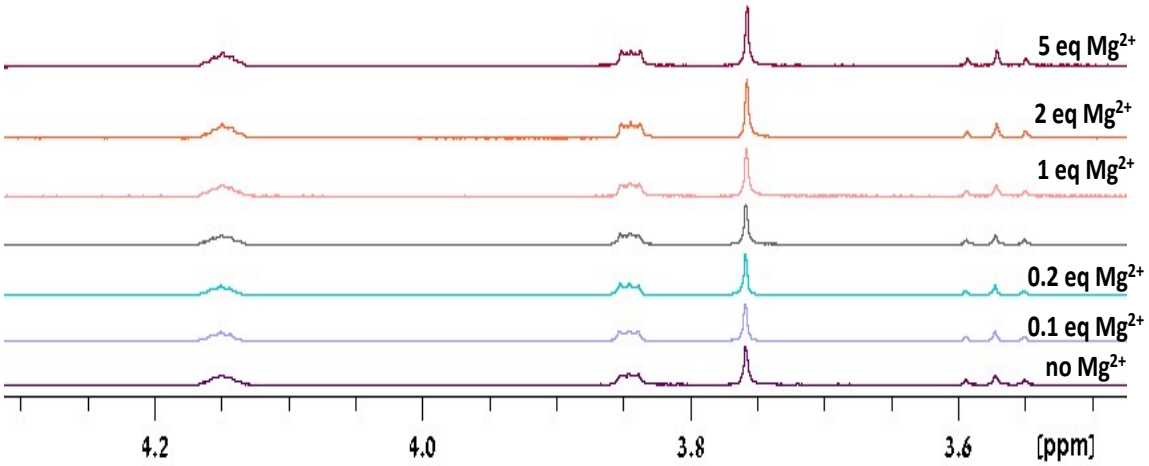
1.9. Fig. S9. Titration of 6 mM 7 in D_2O with $MgCl_2$ as monitored by ^{1}H-NMR at 600 MHz, 300 K.



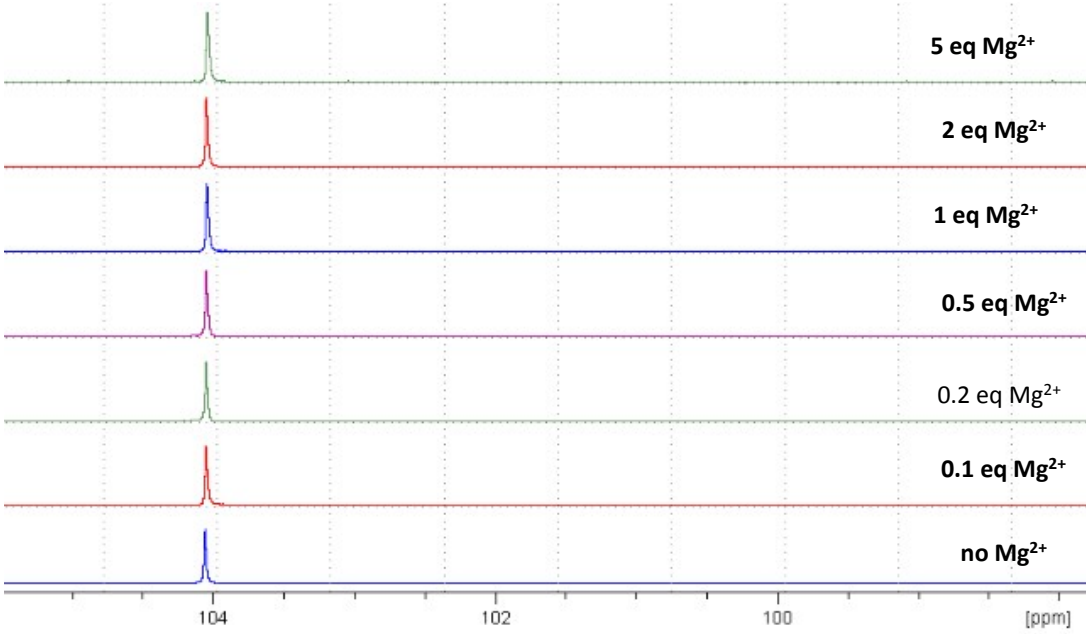
1.10. Fig. S10. Titration of 6 mM 11 in D_2O with $MgCl_2$ as monitored by ^{31}P-NMR at 243 MHz, 300 K.



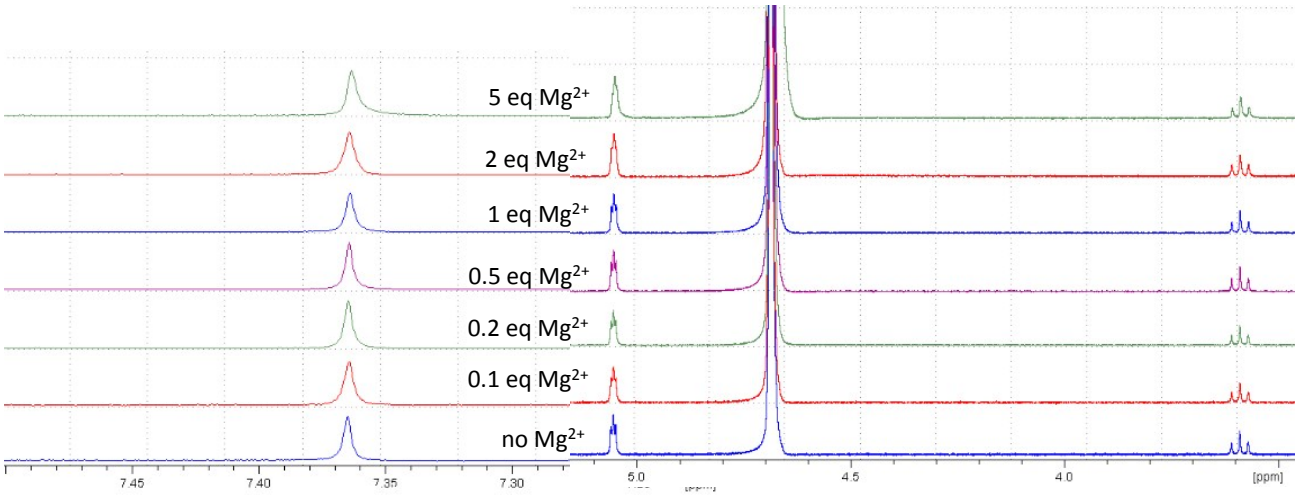
1.11. Fig. S11. Titration of 6 mM 11 in D_2O with $MgCl_2$ as monitored by ^1H-NMR at 600 MHz, 300 K.



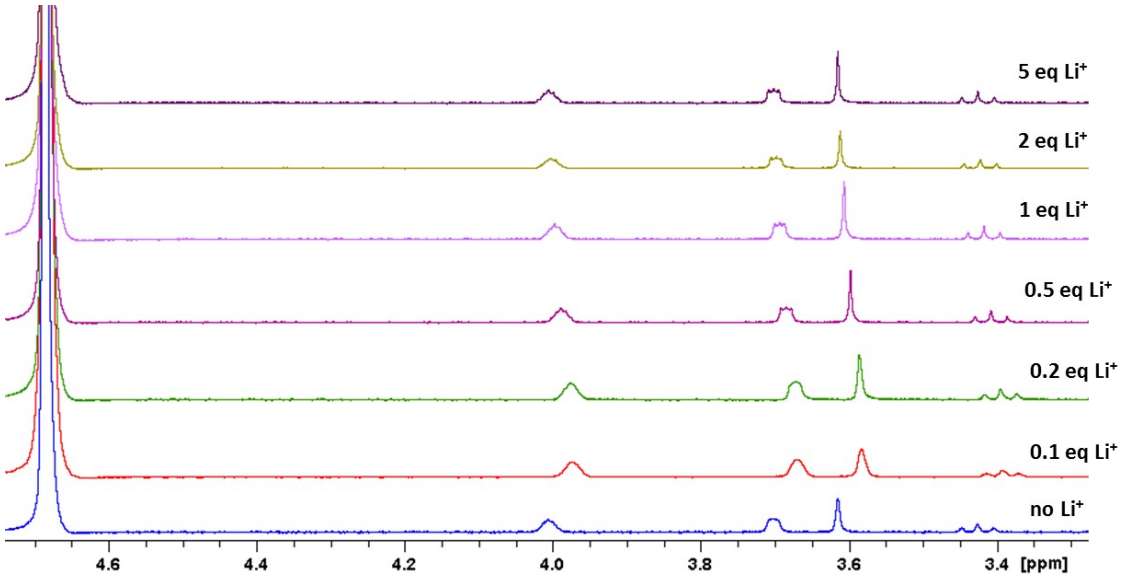
1.12. Fig. S12. Titration of 6 mM 9 in D_2O with $MgCl_2$ as monitored by ^{31}P-NMR at 243 MHz, 300 K.



1.13. Fig. S13. Titration of 6 mM 9 in D_2O with $MgCl_2$ as monitored by ^{1}H-NMR at 600 MHz, 300 K.



1.14. Fig. S14. Titration of 6 mM 11 in D_2O with LiCl as monitored by ^{1}H-NMR at 600 MHz, 300 K.



2. Fig. S15. Δδ of 7 as a function of the molar ratio of Zn(II) to ligand.

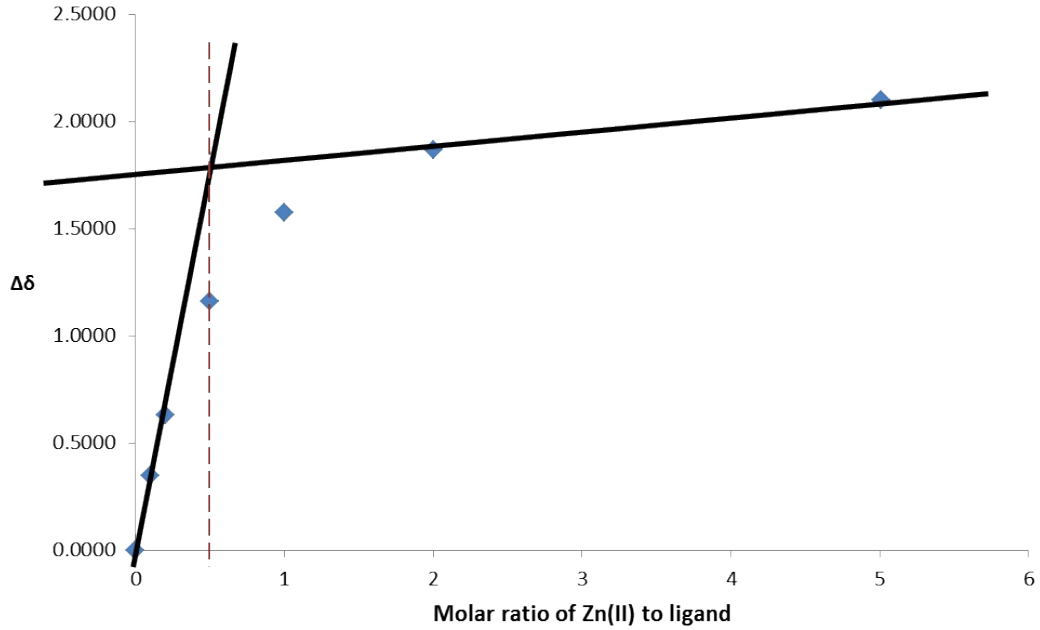
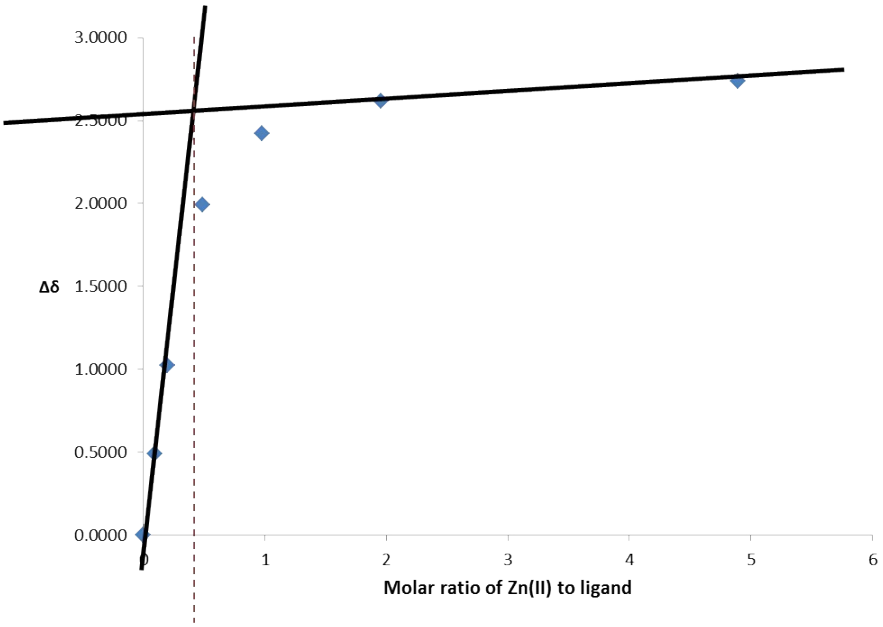
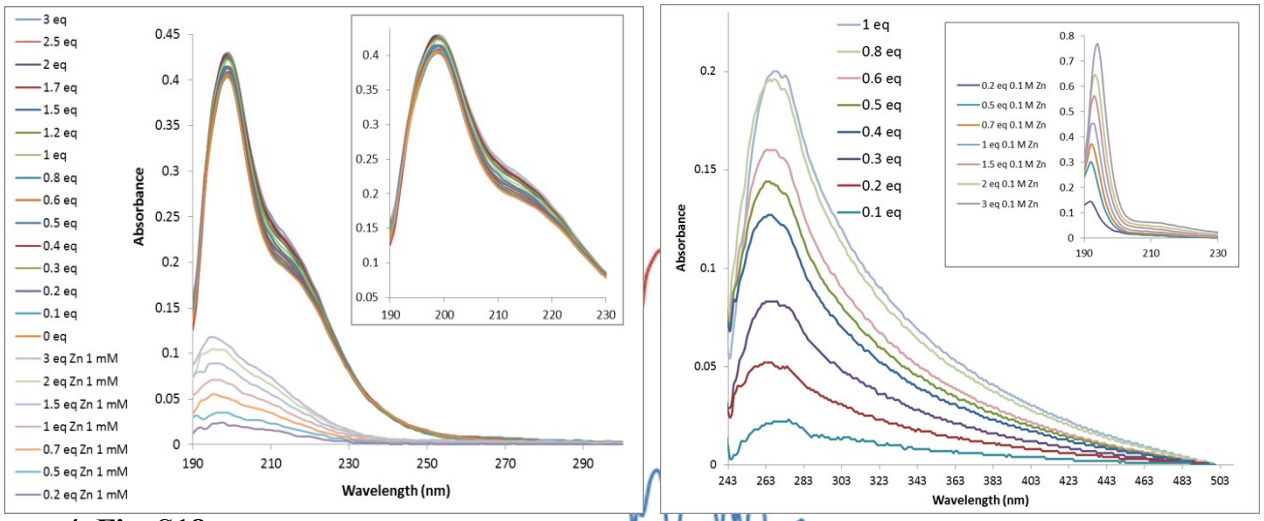


Fig. S16. Δδ of 9 as a function of the molar ratio of Zn(II) to ligand.

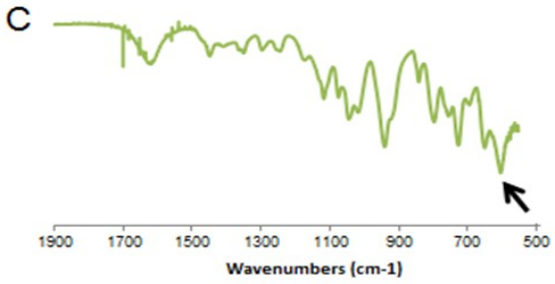


3. Fig. S17. UV monitored Zn(II)-titration of A) 0.01 mM 9 with 1 mM $ZnCl_2$ solution at pH 7.4 and B) 1 mM 9 with 0.1 M $ZnCl_2$ solution at pH 7.4, with 1 mM 9 as the blank. The insert graph indicates the addition of 0.1 M $ZnCl_2$ solution into TRIS buffer solution.

A **B**



4. Fig. S18. FT-IR spectra at 1900-500 cm^{-1} region: A) compound 11, B) 11-Zn(II) (2:1) and C) 11-Zn(II) (1:1).



5. Fig. S19. ^{13}C-NMR of compound 11 (Et_3NH^+ salt) before and after Na(I)-addition, in D_2O, with MeOH as internal standard.

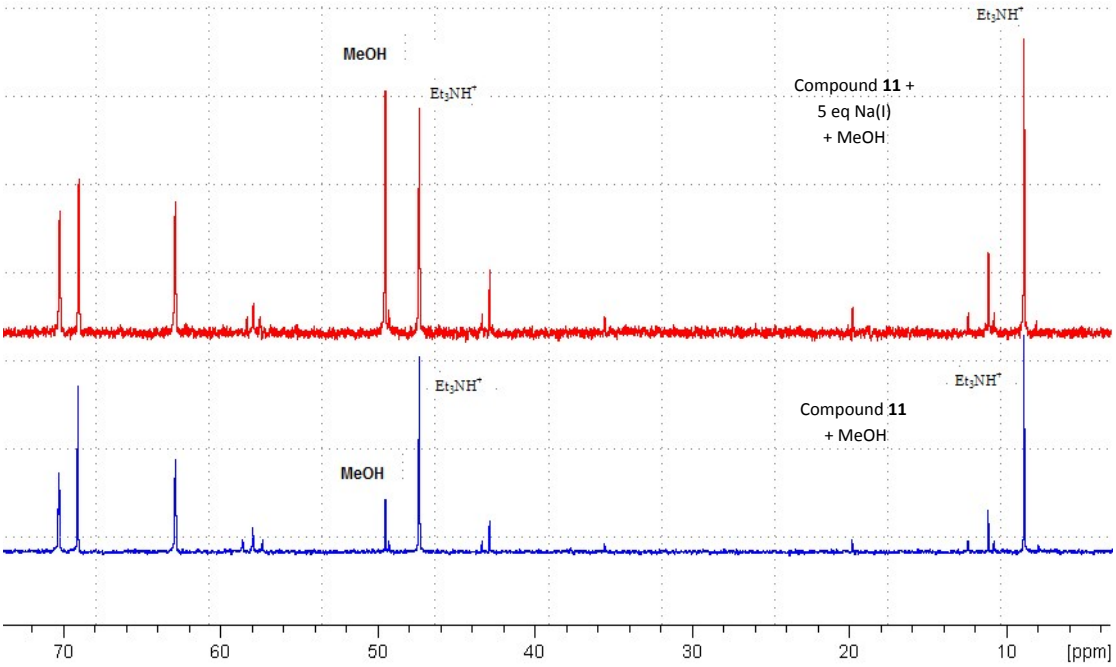
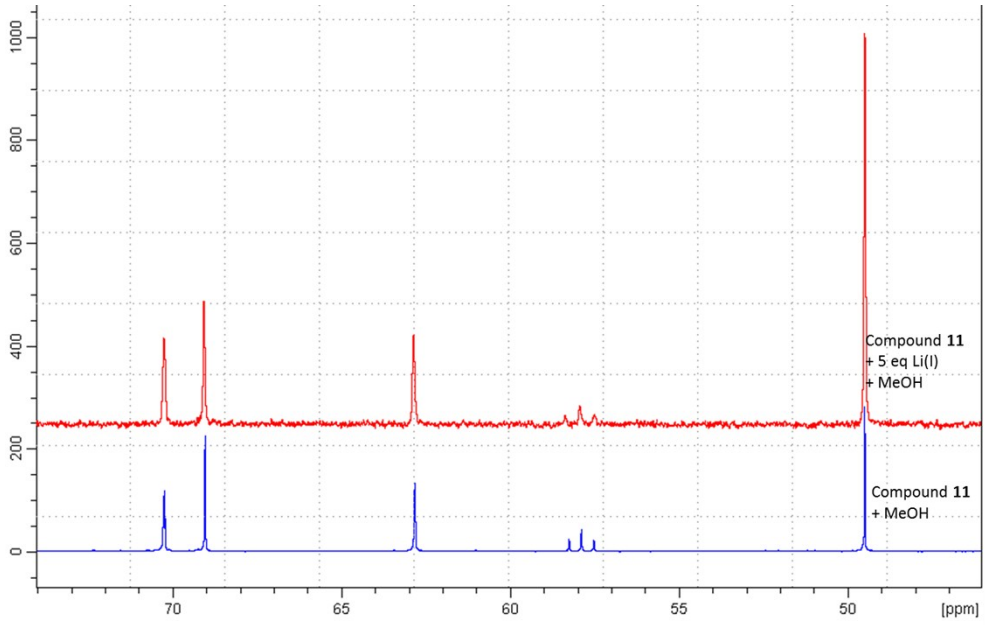
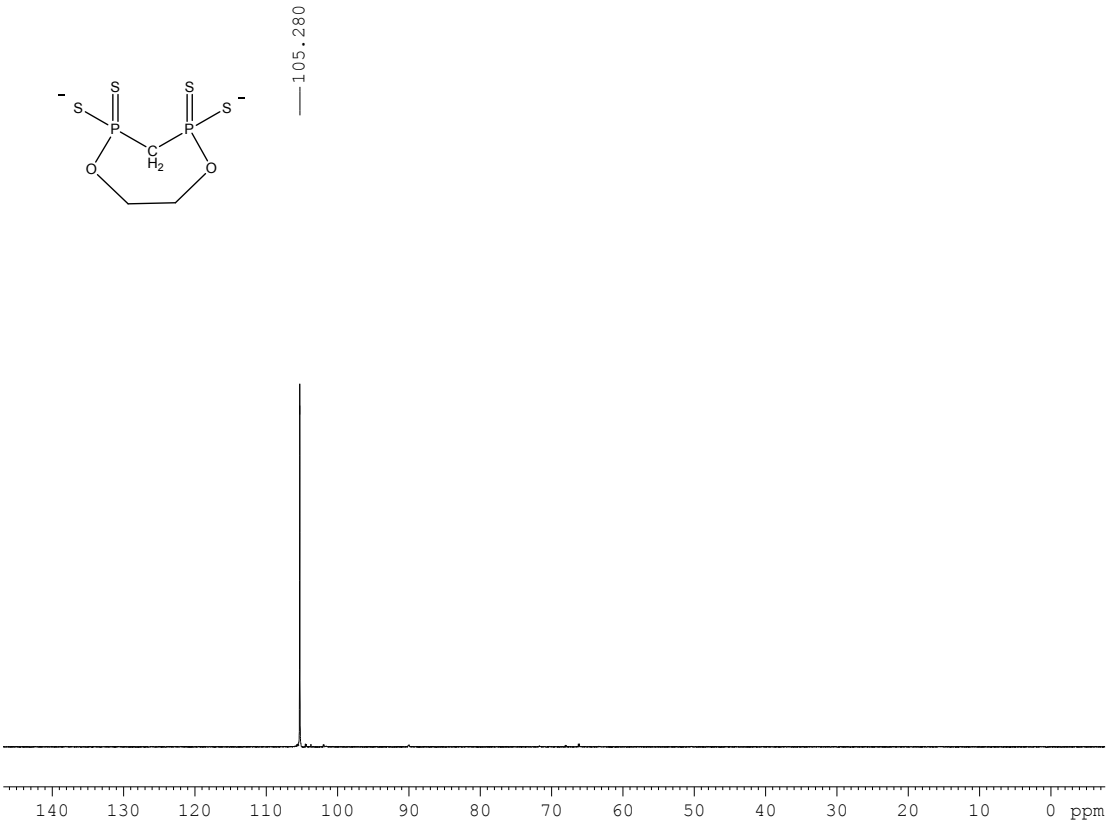


Fig. S20. ^{13}C-NMR of compound 11 before and after Li(I)-addition, in D_2O, with MeOH as internal standard.

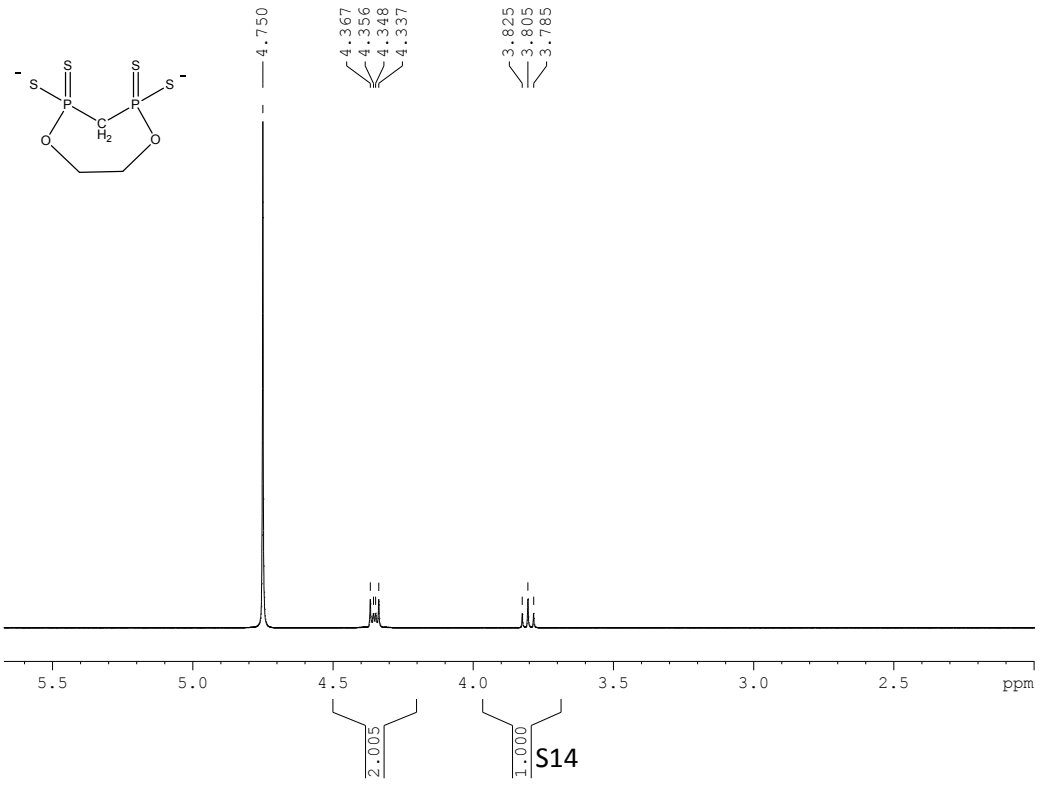


6. Spectral characterization of compounds 7-13.

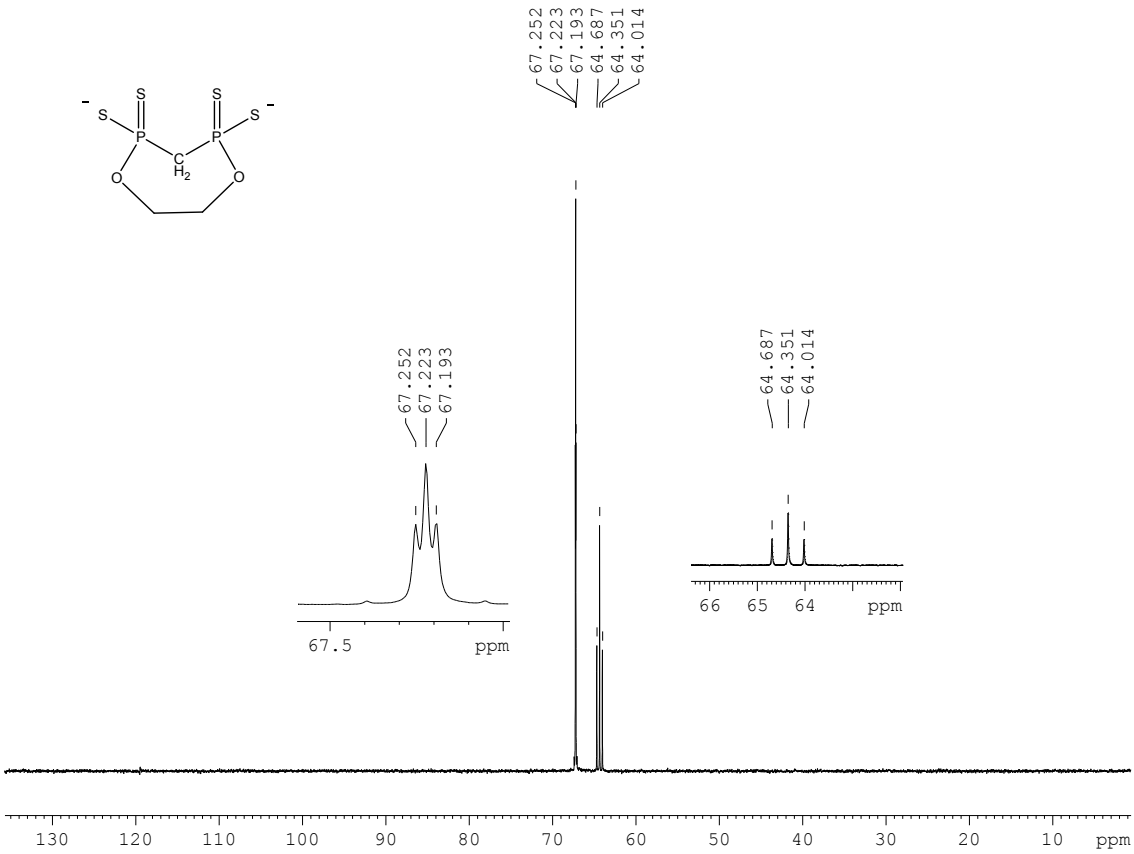
^{31}P-NMR of compound **7**



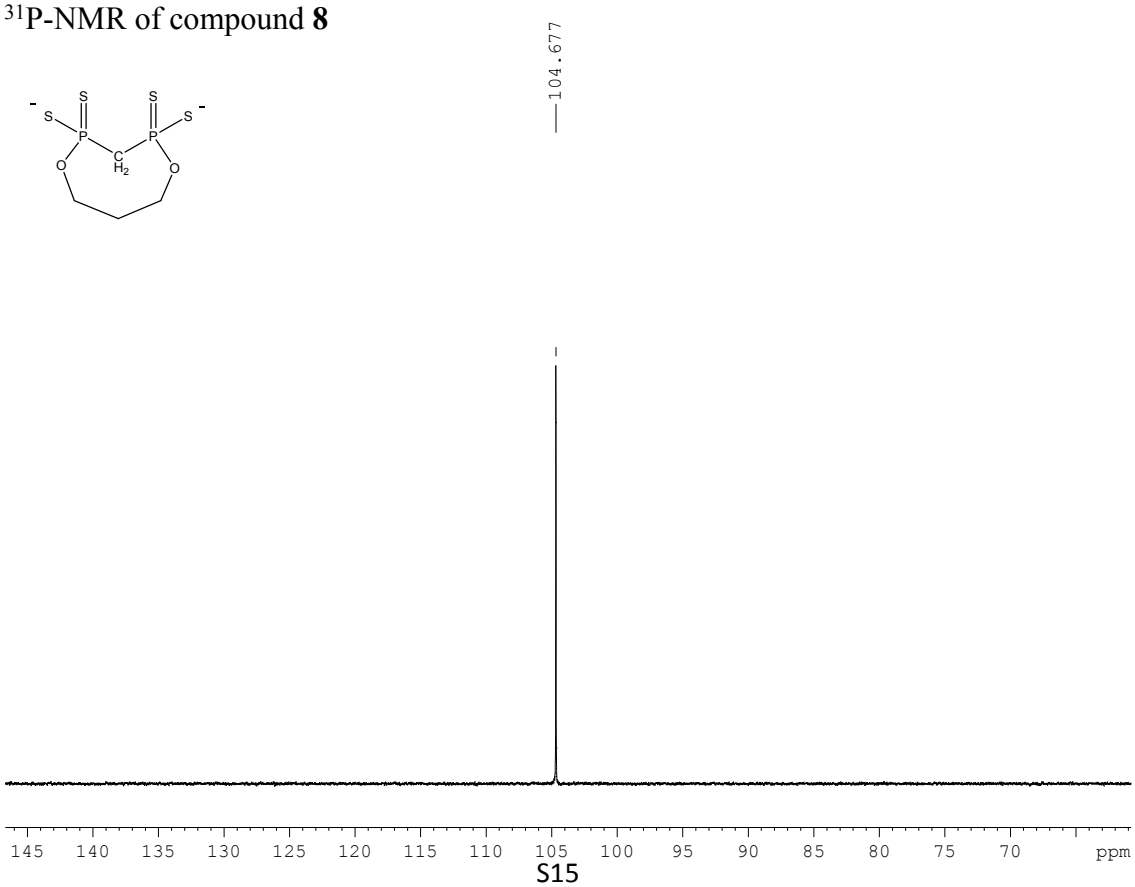
^{1}H-NMR of compound **7**



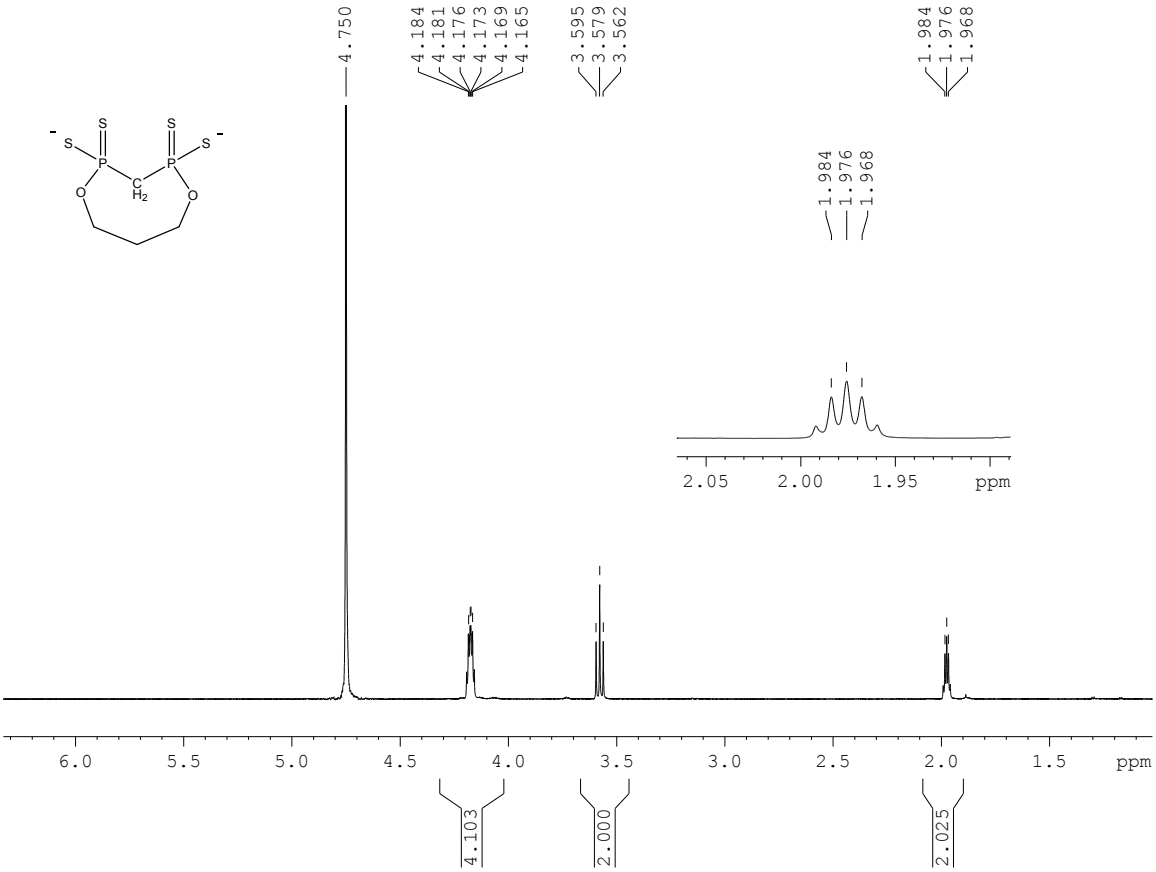
^{13}C-NMR of compound **7**



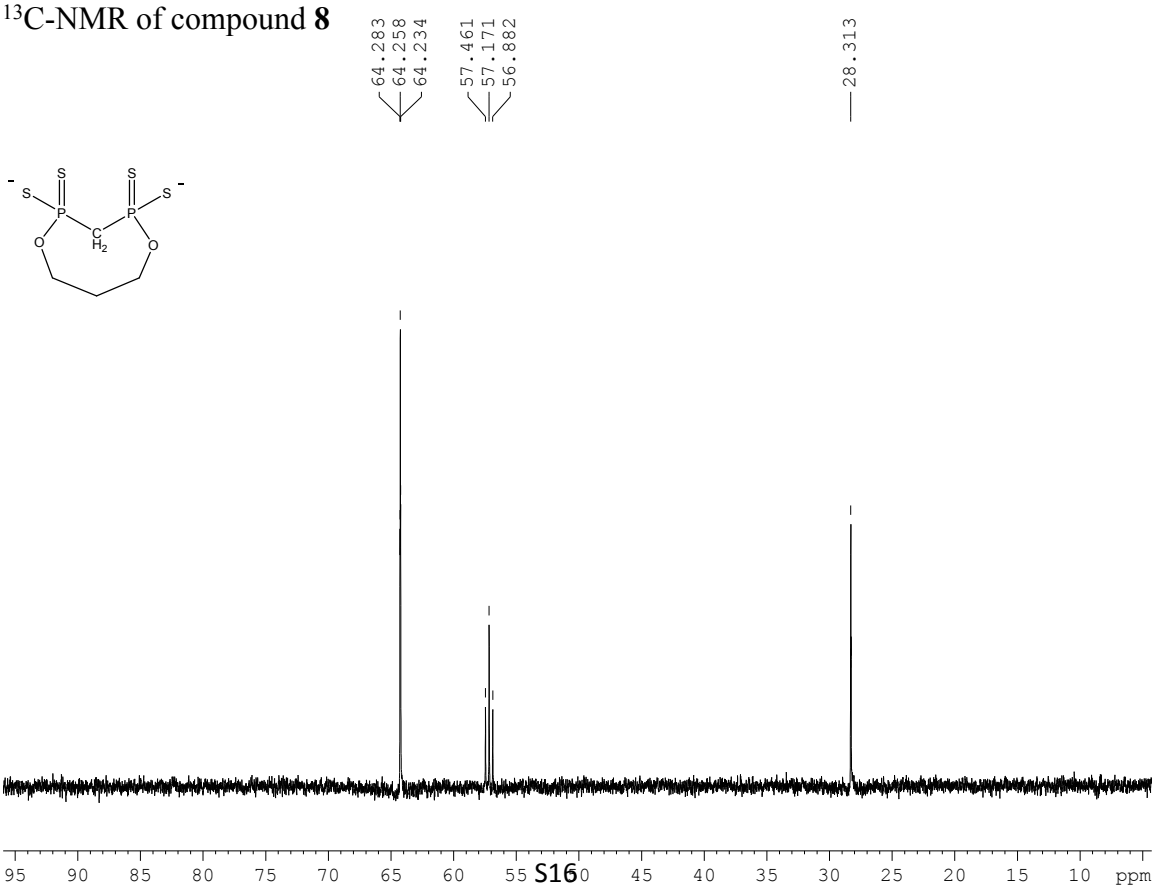
^{31}P-NMR of compound **8**



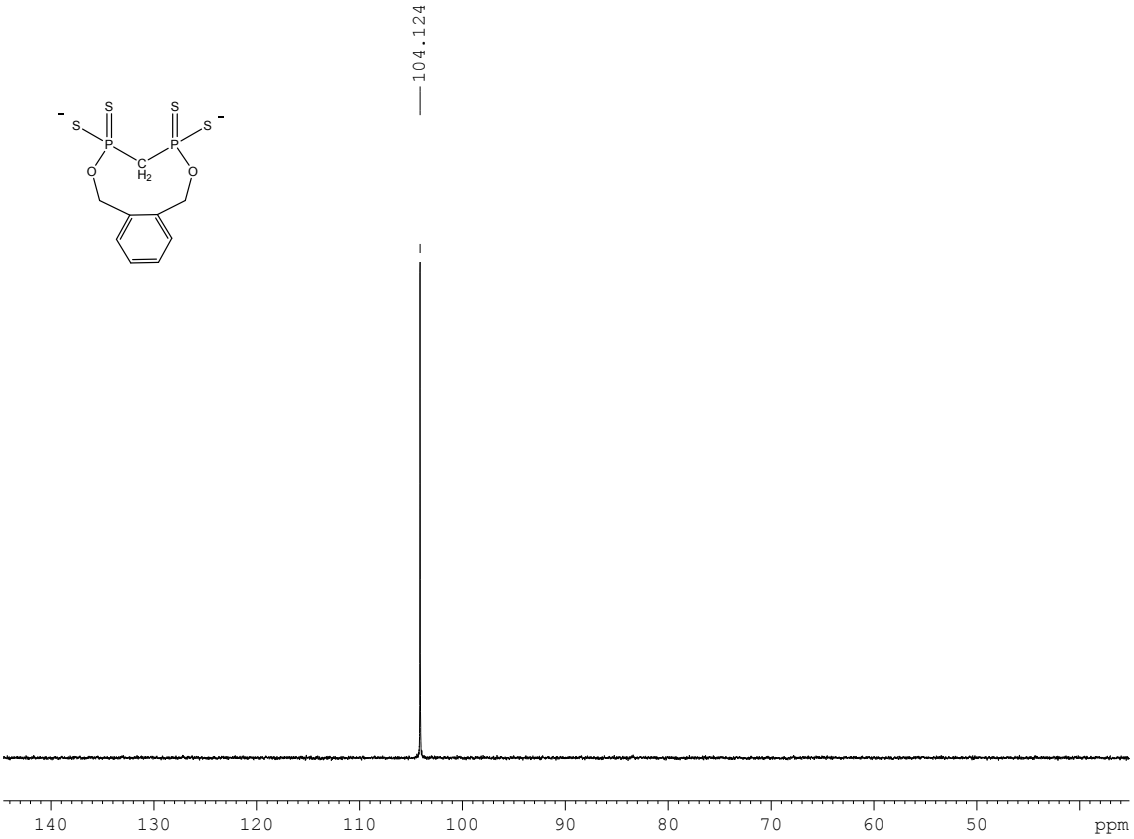
^{1}H-NMR of compound **8**



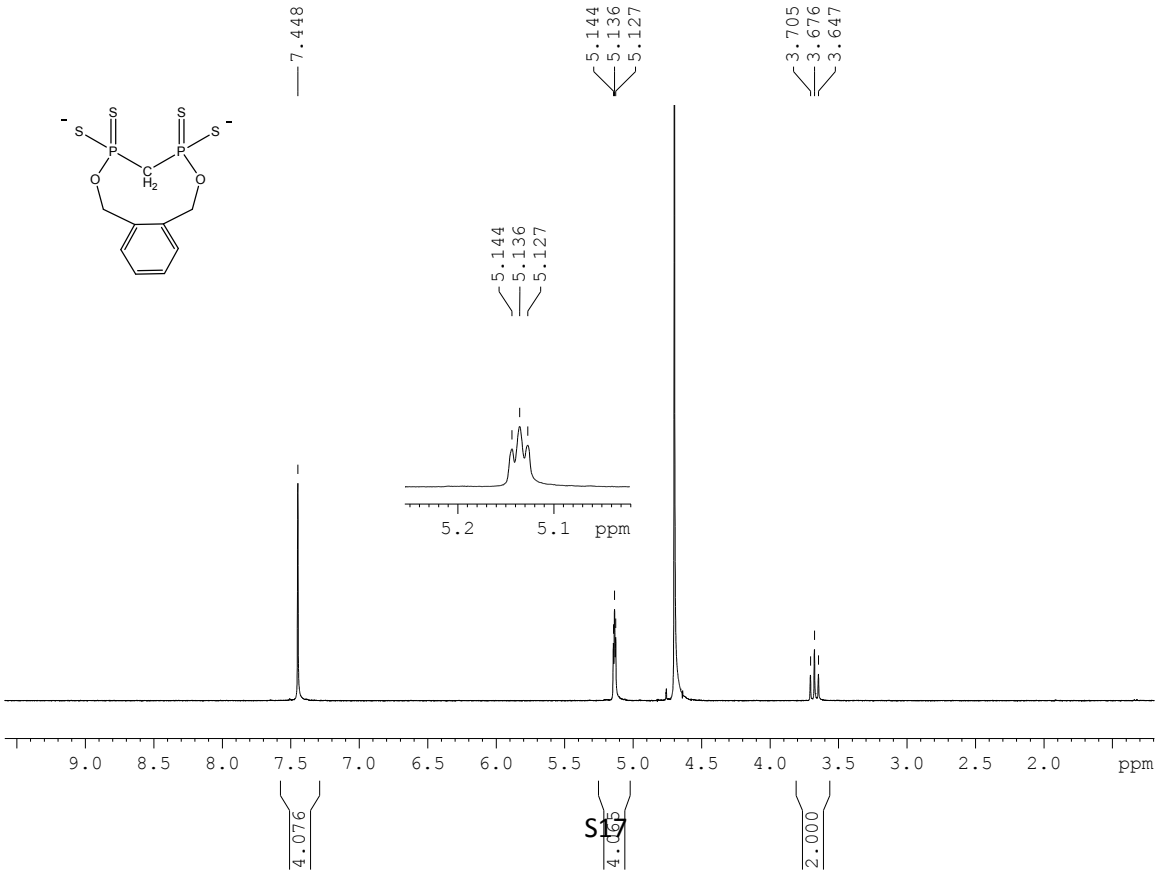
^{13}C-NMR of compound **8**



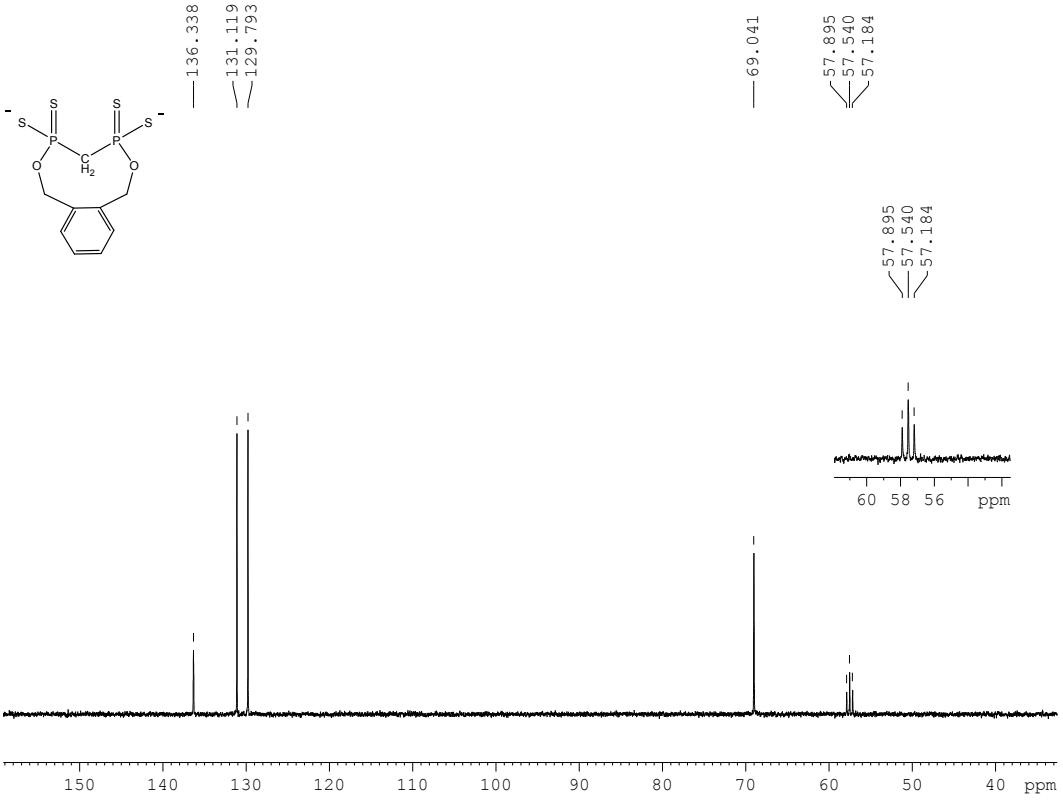
^{31}P-NMR of compound **9**



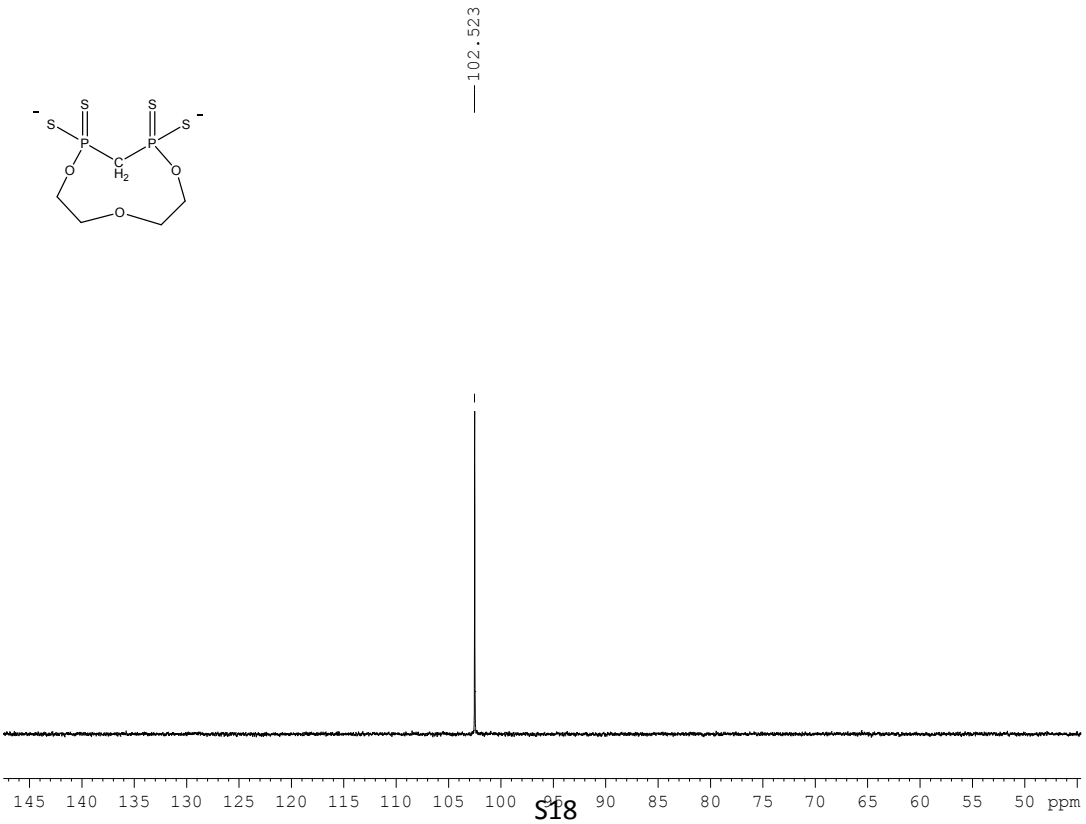
^{1}H-NMR of compound **9**



^{13}C-NMR of compound **9**



^{31}P-NMR of compound **10**



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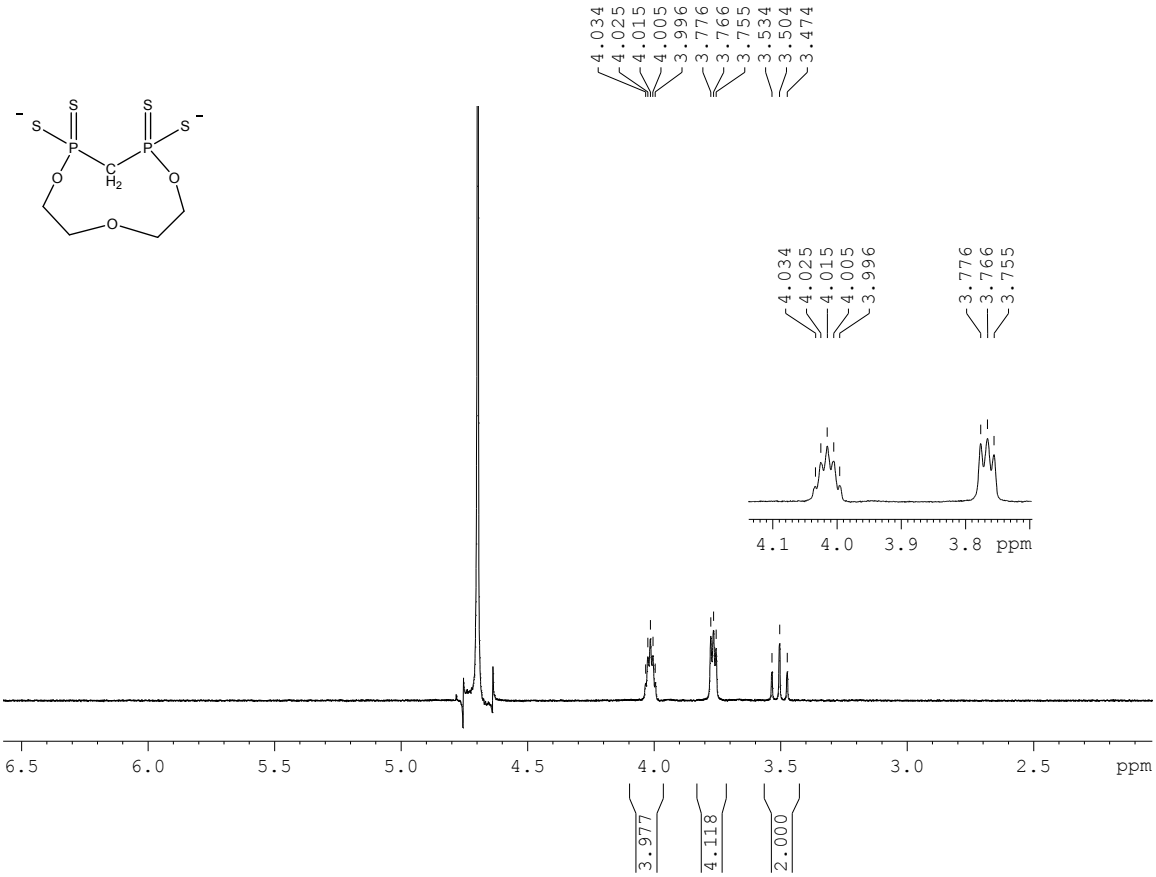

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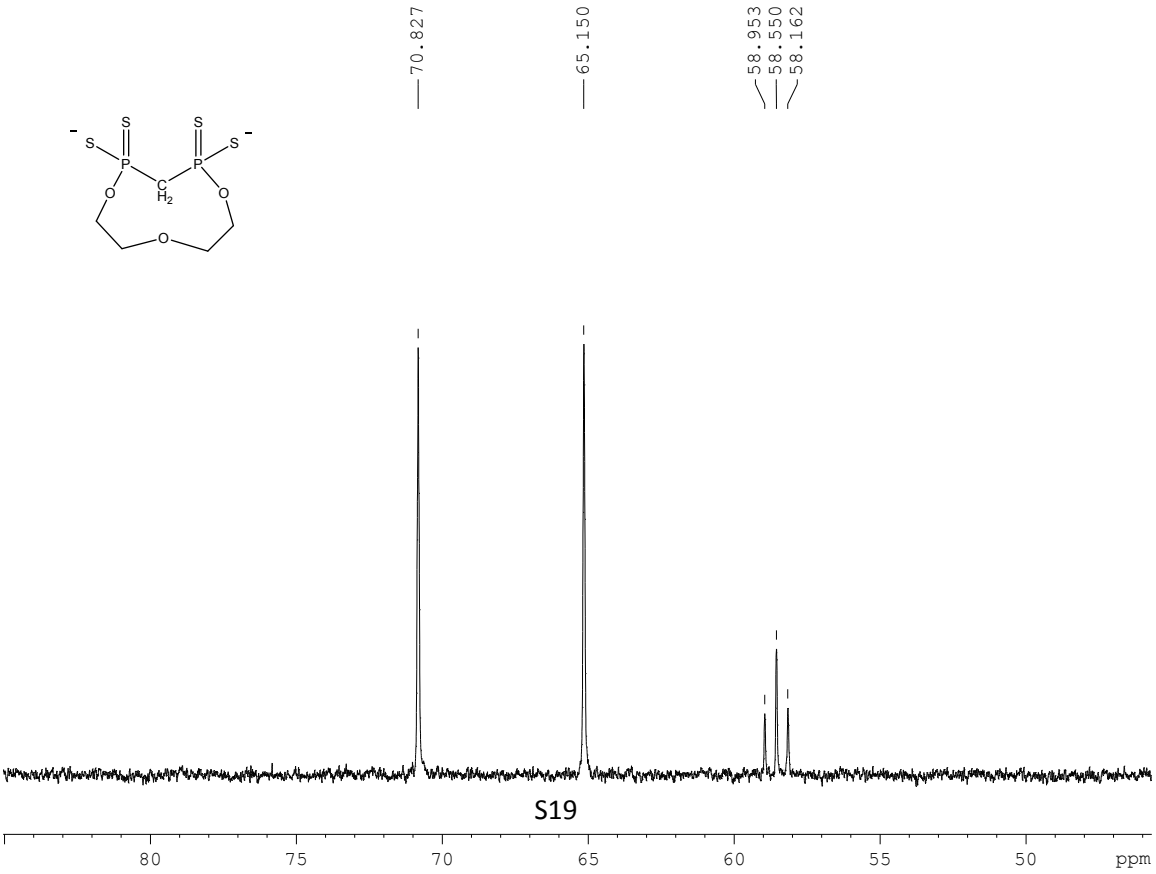
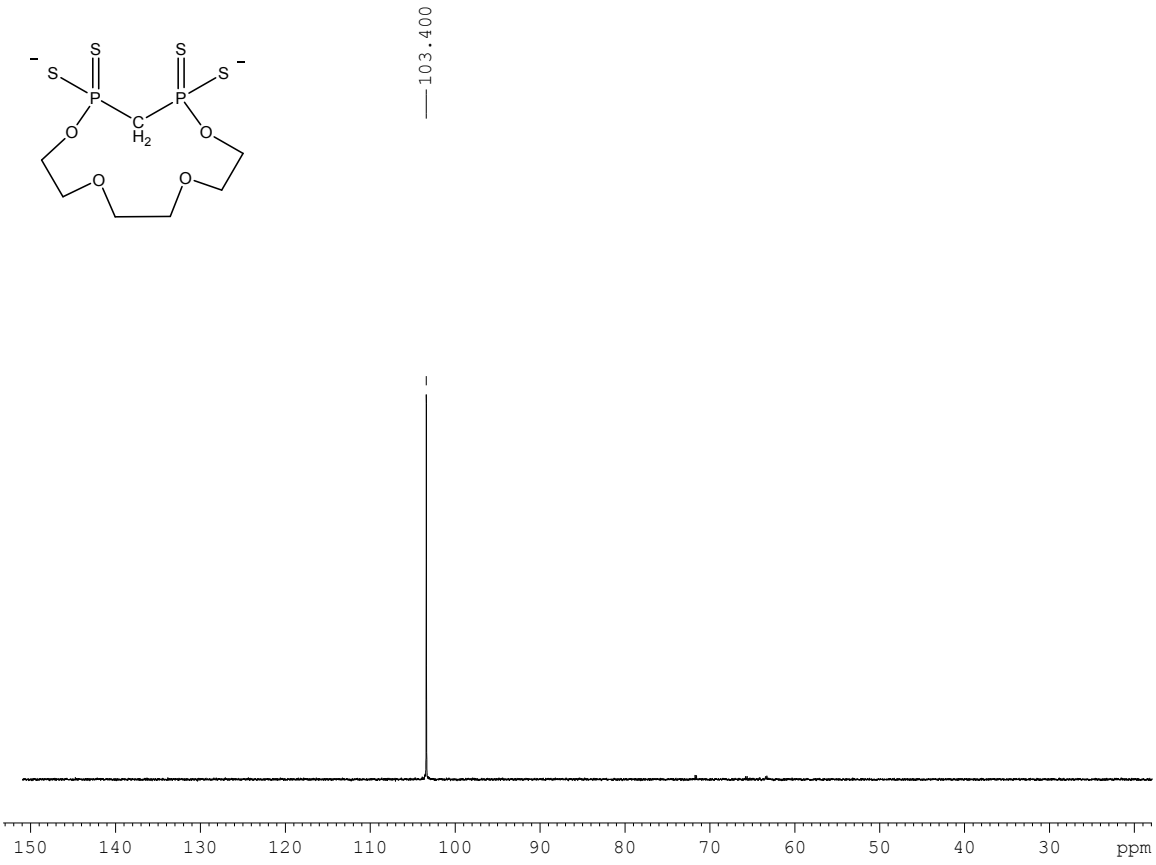


^{31}P-NMR of compound **11**



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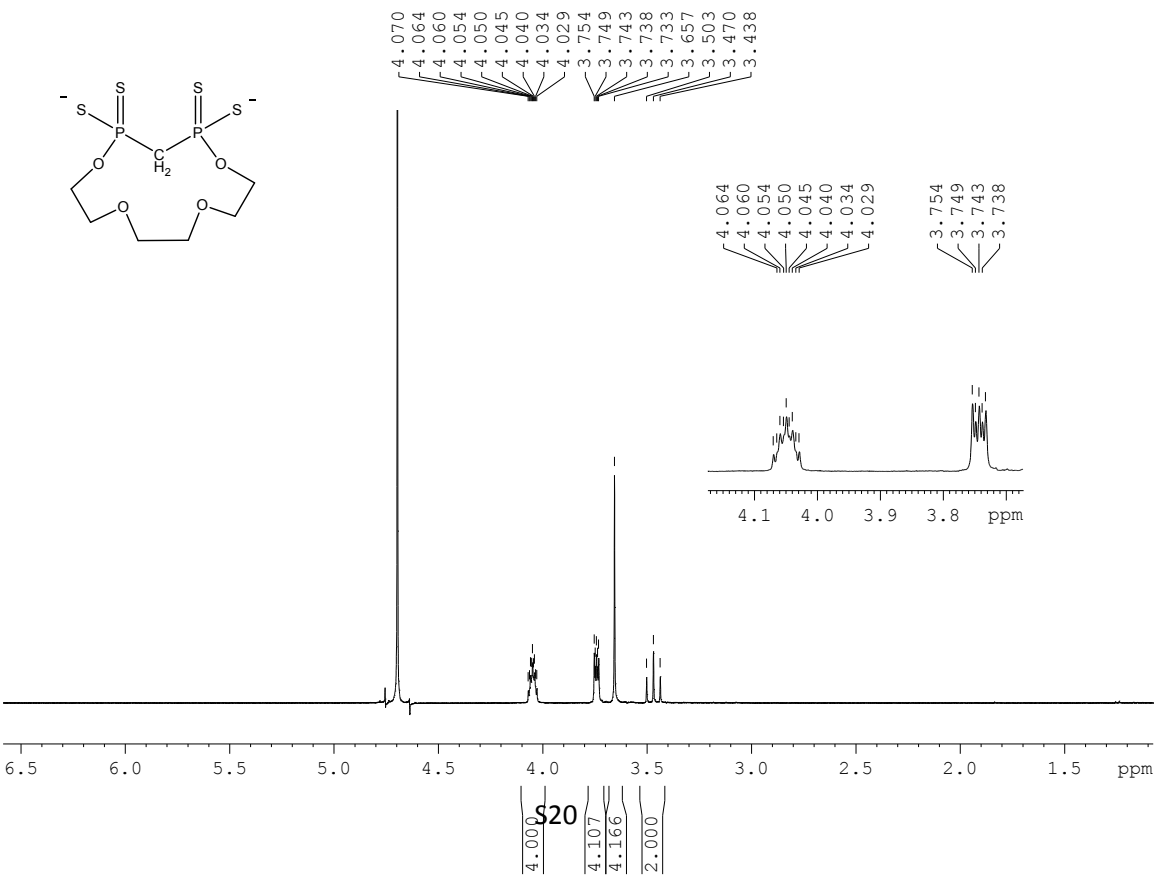

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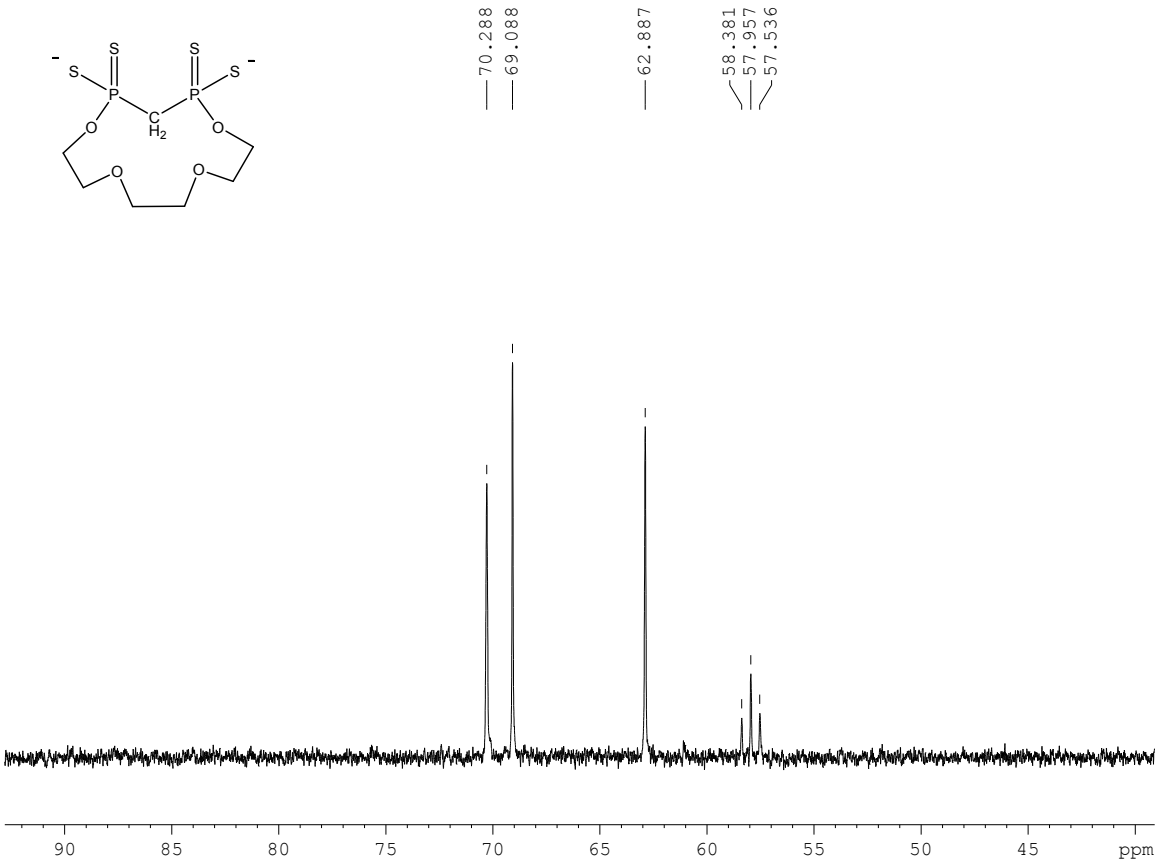
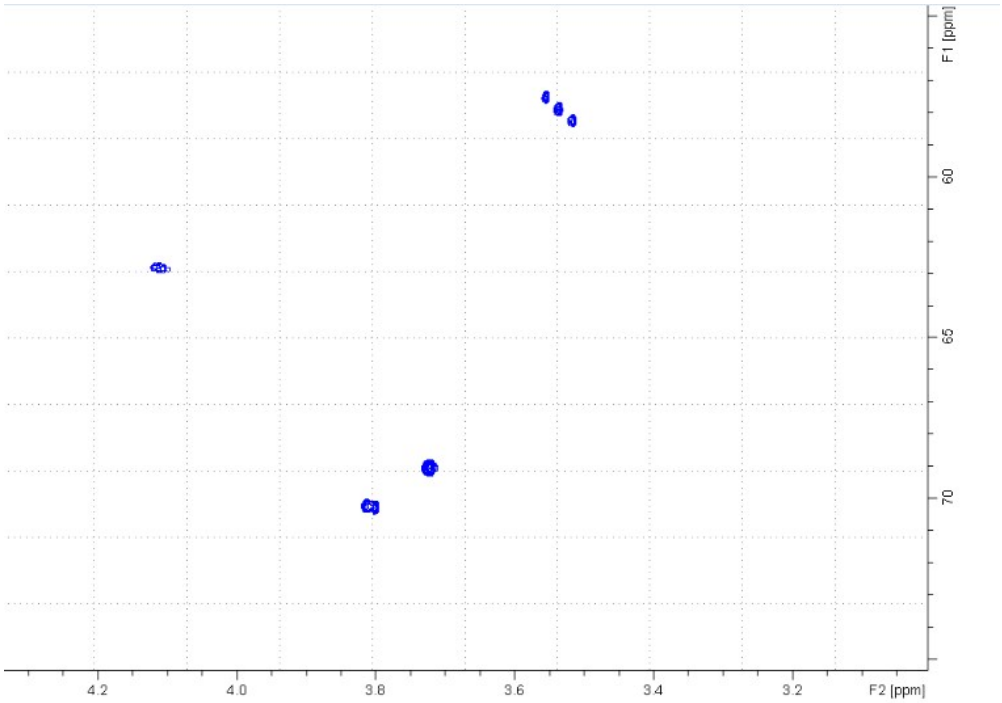
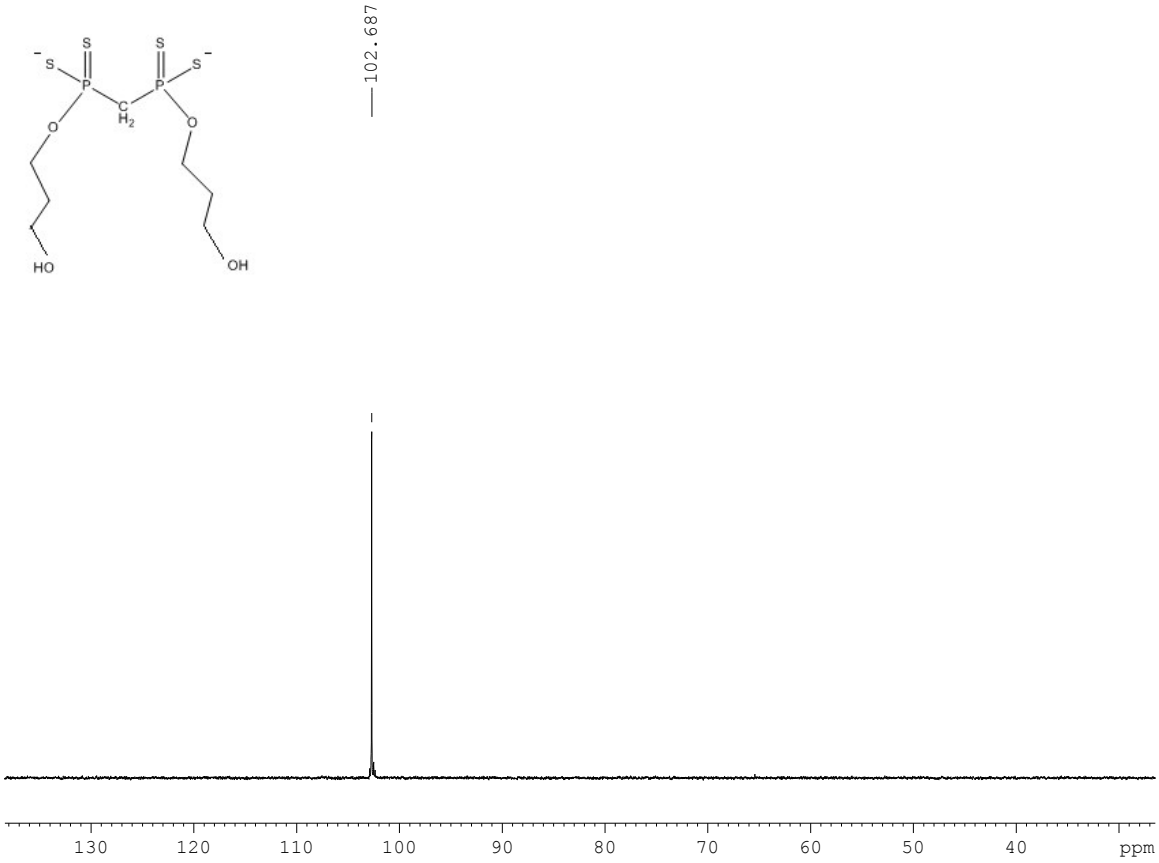


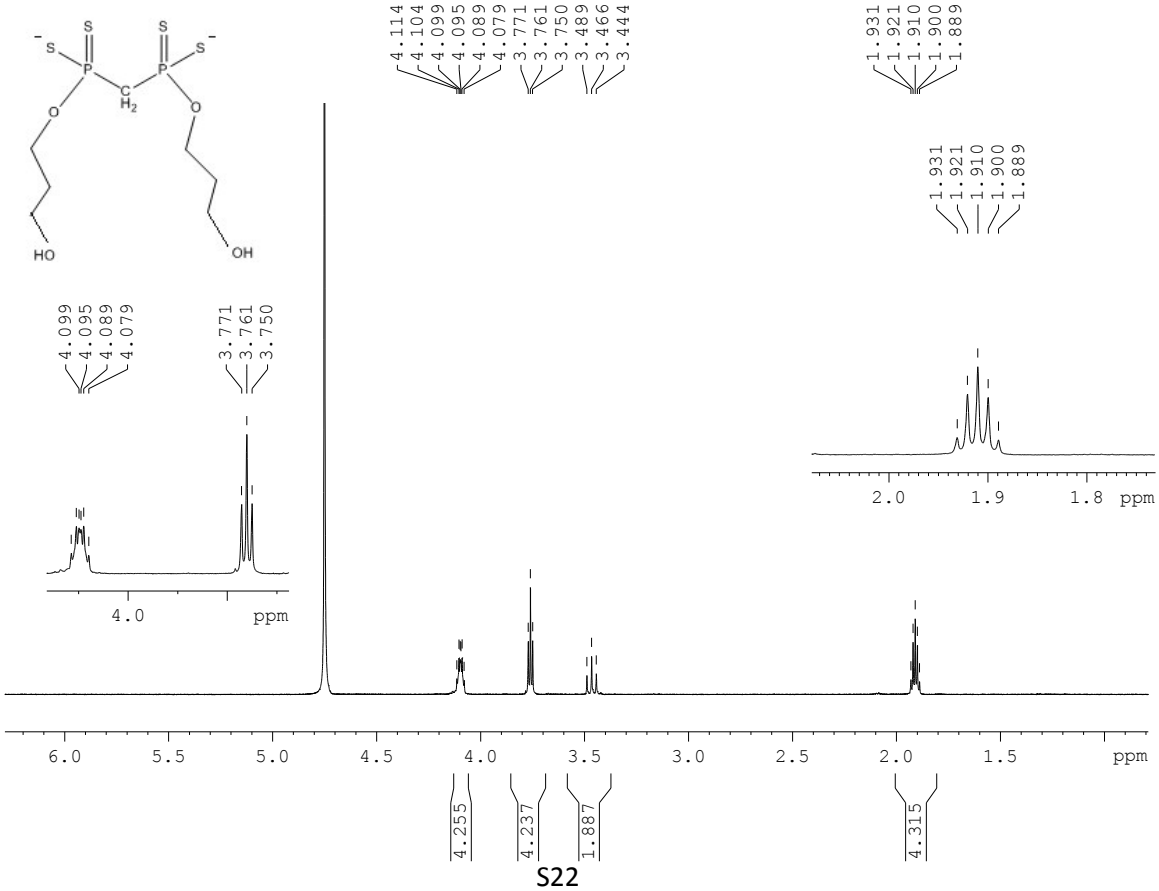
HMQC of compound **11**



^{31}P-NMR of compound **12**



^{1}H-NMR of compound **12**



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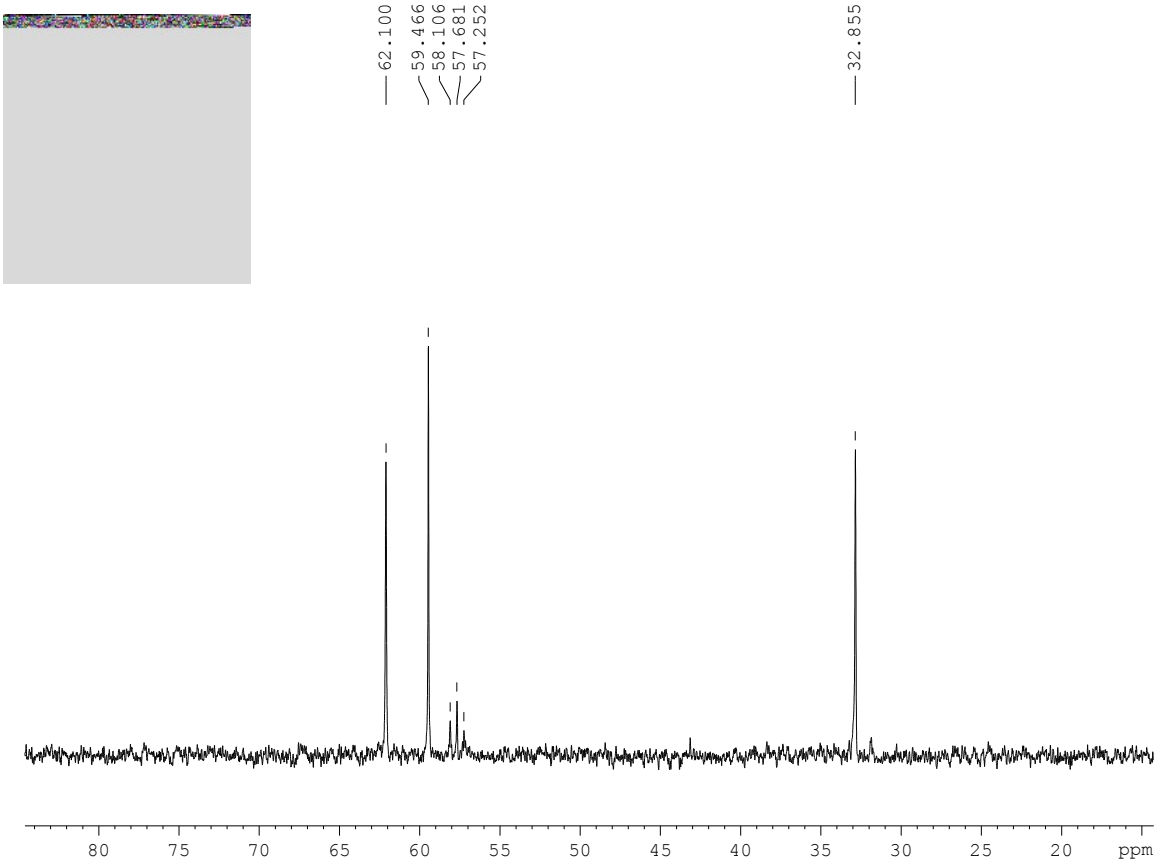
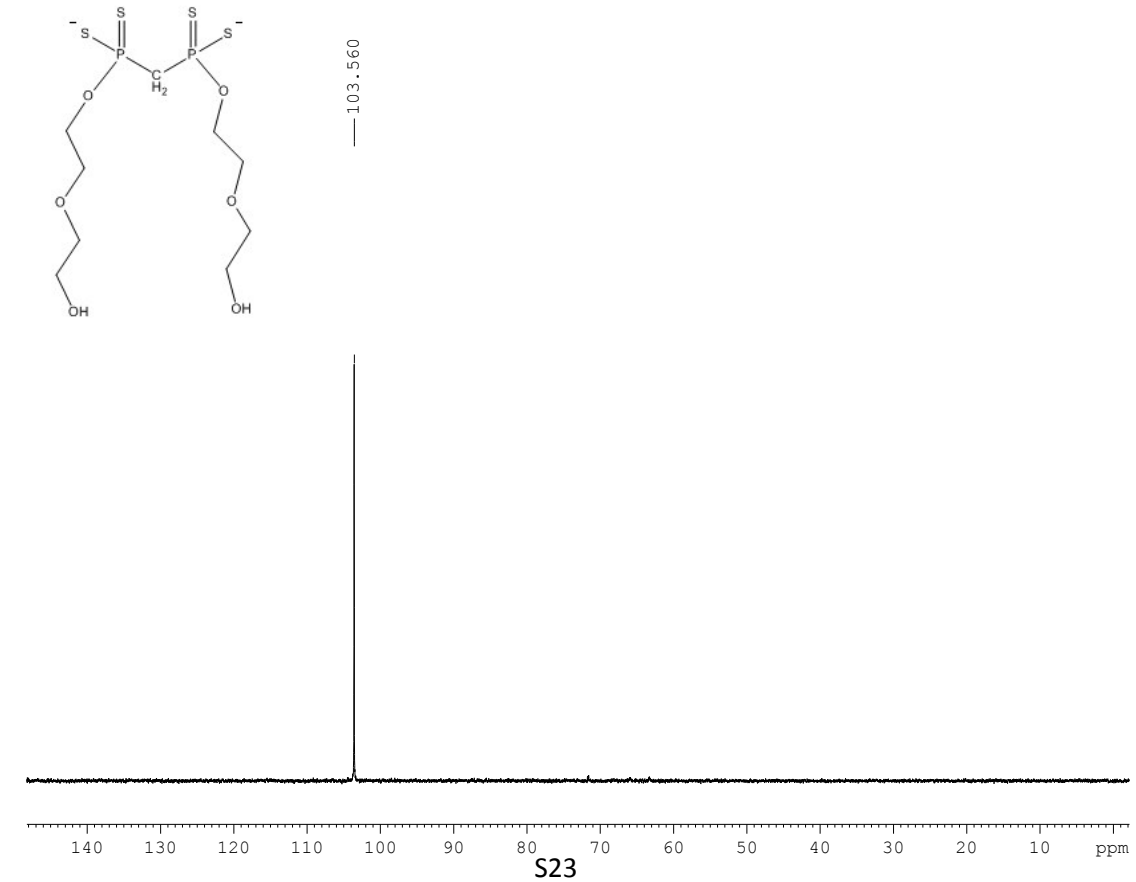


^{31}P-NMR of compound **13**



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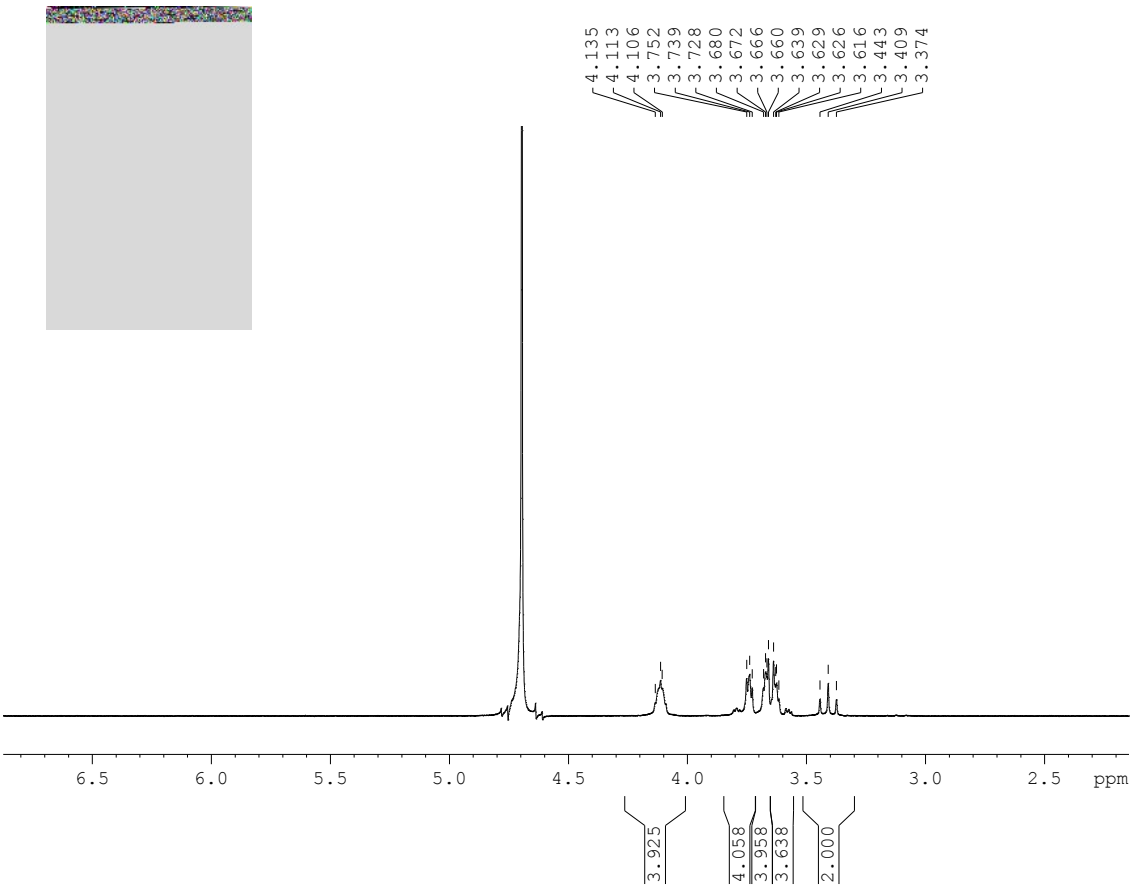
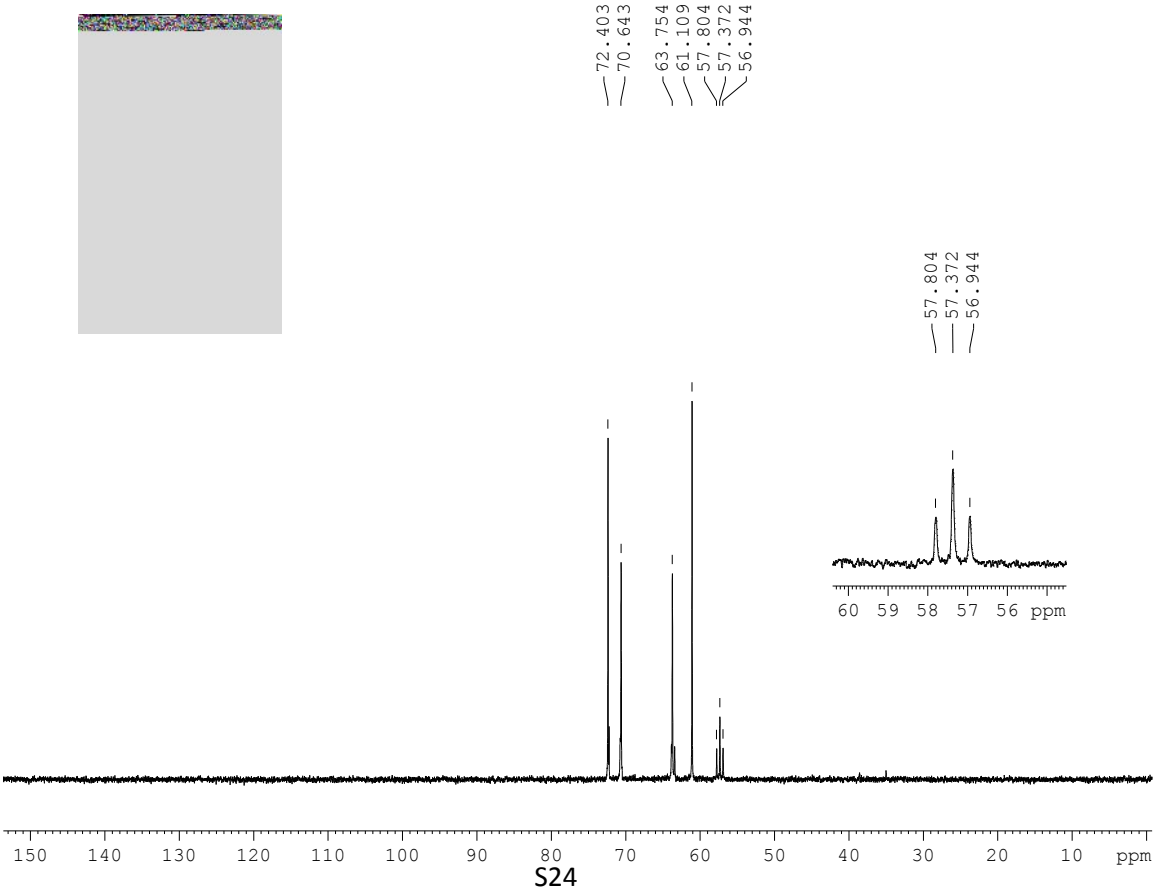


^{13}C-NMR of compound **13**



7. X-ray crystal structure of 11-Zn(II) complex

Table 1. Crystal data and structure refinement for 11-Zn(II) complex.

Empirical formula	C20 H48 N Na O10 P4 S8 Zn
Formula weight	931.31
Temperature	100(2) K
Wavelength	1.54187 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.227(3) A alpha = 90 deg. b = 19.931(6) A beta = 91.939(12) deg. c = 19.854(7) A gamma = 90 deg.
Volume	4045(2) A^3
Z, Calculated density	4, 1.529 Mg/m^3
Absorption coefficient	6.701 mm^-1
F(000)	1936
Crystal size	0.150 x 0.100 x 0.050 mm
Theta range for data collection	3.143 to 68.246 deg.
Limiting indices	-12<=h<=12, -23<=k<=24, -23<=l<=18

Reflections collected / unique	43806 / 7316 [R(int) = 0.0575]
Completeness to theta = 67.687	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7305 and 0.4331
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7316 / 5 / 424
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.1454
R indices (all data)	R1 = 0.0639, wR2 = 0.1525
Extinction coefficient	n/a
Largest diff. peak and hole	1.559 and -0.733 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 11-Zn(II) complex.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zn(1)	9045(1)	1149(1)	8007(1)	27(1)

S(1)	8378(1)	554(1)	8932(1)	31(1)
S(2)	8879(1)	267(1)	7215(1)	35(1)
S(3)	7480(1)	1980(1)	7803(1)	28(1)
S(4)	11193(1)	1526(1)	8090(1)	34(1)
S(5)	13579(1)	1685(1)	9217(1)	34(1)
S(6)	8756(1)	603(1)	10578(1)	33(1)
S(7)	7350(1)	-145(1)	5793(1)	40(1)
S(8)	5875(1)	2700(1)	6544(1)	32(1)
P(1)	11669(1)	1718(1)	9065(1)	24(1)
P(2)	9120(1)	1057(1)	9734(1)	24(1)
P(3)	7302(1)	2081(1)	6794(1)	22(1)
P(4)	8159(1)	587(1)	6320(1)	26(1)
O(1)	11078(3)	2436(2)	9285(2)	33(1)
O(2)	9531(3)	3570(2)	9175(2)	32(1)
O(3)	7424(3)	3097(2)	9866(2)	26(1)
O(4)	8573(3)	1823(2)	9723(2)	27(1)
O(5)	9290(3)	946(2)	5902(2)	35(1)
O(6)	11712(3)	1513(2)	5709(2)	42(1)
O(7)	11066(3)	2802(2)	6024(2)	29(1)
O(8)	8685(3)	2295(1)	6494(2)	22(1)
Na(1)	9677(2)	2894(1)	10260(1)	23(1)
C(1)	10871(4)	1192(2)	9674(2)	24(1)
C(2)	11547(6)	3046(2)	8965(3)	42(1)
C(3)	10400(6)	3397(3)	8654(3)	41(1)
C(4)	8242(5)	3706(2)	8912(3)	37(1)
C(5)	7331(5)	3709(2)	9483(2)	34(1)
C(6)	6723(4)	2554(2)	9551(2)	29(1)
C(7)	7180(4)	1904(2)	9847(3)	29(1)

C(8)	7015(4)	1286(2)	6363(2)	25(1)
C(9)	10393(6)	558(3)	5680(3)	46(1)
C(10)	11608(5)	852(3)	5969(3)	48(1)
C(11)	12593(5)	1895(3)	6142(3)	46(1)
C(12)	12410(5)	2609(3)	5986(3)	40(1)
C(13)	10658(5)	2932(2)	6695(2)	32(1)
C(14)	9189(4)	2957(2)	6692(2)	26(1)
N(1)	5186(5)	4746(2)	6941(3)	51(1)
C(15)	6548(6)	4663(3)	6744(3)	55(2)
C(16)	7515(7)	4534(4)	7322(4)	62(2)
C(17)	4802(6)	5477(3)	7034(3)	52(2)
C(18)	5645(6)	5837(3)	7541(3)	54(2)
C(19)	4285(8)	4388(5)	6486(5)	97(3)
C(20)	4370(8)	4535(5)	5757(4)	97(3)
O(9)	4293(6)	2817(2)	7986(3)	74(2)
O(10)	4745(5)	4148(3)	8202(3)	72(1)

Table 3. Bond lengths [A] and angles [deg] for 11-Zn(II) complex.

Zn(1)-S(1)	2.3085(14)
Zn(1)-S(4)	2.3228(14)
Zn(1)-S(3)	2.3297(13)
Zn(1)-S(2)	2.3618(14)
S(1)-P(2)	2.0099(16)
S(2)-P(4)	2.0038(18)
S(3)-P(3)	2.0142(17)
S(4)-P(1)	2.0173(18)
S(5)-P(1)	1.9676(17)

S(6)-P(2)	1.9514(17)
S(7)-P(4)	1.9633(17)
S(8)-P(3)	1.9624(16)
P(1)-O(1)	1.619(3)
P(1)-C(1)	1.813(5)
P(2)-O(4)	1.626(3)
P(2)-C(1)	1.819(5)
P(3)-O(8)	1.611(3)
P(3)-C(8)	1.820(4)
P(4)-O(5)	1.615(4)
P(4)-C(8)	1.822(4)
O(1)-C(2)	1.460(6)
O(1)-Na(1)	2.612(4)
O(2)-C(4)	1.427(6)
O(2)-C(3)	1.429(6)
O(2)-Na(1)	2.541(4)
O(3)-C(6)	1.430(5)
O(3)-C(5)	1.438(5)
O(3)-Na(1)	2.442(3)
O(4)-C(7)	1.463(5)
O(4)-Na(1)	2.624(3)
O(5)-C(9)	1.448(6)
O(5)-Na(1)#1	2.674(4)
O(6)-C(10)	1.422(7)
O(6)-C(11)	1.442(7)
O(6)-Na(1)#1	2.529(4)
O(7)-C(12)	1.432(6)
O(7)-C(13)	1.433(6)

O(7)-Na(1)#1	2.468(3)
O(8)-C(14)	1.465(5)
O(8)-Na(1)#1	2.708(3)
Na(1)-O(7)#2	2.468(3)
Na(1)-O(6)#2	2.529(4)
Na(1)-O(5)#2	2.674(4)
Na(1)-O(8)#2	2.708(3)
C(1)-H(1A)	0.91(5)
C(1)-H(1B)	0.92(5)
C(2)-C(3)	1.483(8)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.491(7)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.492(7)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.471(9)
C(9)-H(9A)	0.9900

C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.466(8)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.503(6)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
N(1)-C(19)	1.455(9)
N(1)-C(15)	1.469(8)
N(1)-C(17)	1.522(8)
N(1)-H(1)	1.0000
C(15)-C(16)	1.511(9)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.486(8)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19)-C(20)	1.481(12)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
O(9)-H(9C)	0.8498
O(9)-H(9D)	0.8487
O(10)-H(10C)	0.834(5)
O(10)-H(10D)	0.833(5)

S(1)-Zn(1)-S(4)	114.43(5)
S(1)-Zn(1)-S(3)	106.54(5)
S(4)-Zn(1)-S(3)	115.14(5)
S(1)-Zn(1)-S(2)	97.52(5)
S(4)-Zn(1)-S(2)	109.53(5)
S(3)-Zn(1)-S(2)	112.36(5)
P(2)-S(1)-Zn(1)	105.11(6)
P(4)-S(2)-Zn(1)	111.62(6)
P(3)-S(3)-Zn(1)	106.37(6)
P(1)-S(4)-Zn(1)	109.04(6)
O(1)-P(1)-C(1)	98.66(19)
O(1)-P(1)-S(5)	111.45(14)
C(1)-P(1)-S(5)	110.24(16)
O(1)-P(1)-S(4)	110.22(14)
C(1)-P(1)-S(4)	115.53(16)
S(5)-P(1)-S(4)	110.27(7)

O(4)-P(2)-C(1)	101.49(18)
O(4)-P(2)-S(6)	111.85(13)
C(1)-P(2)-S(6)	110.04(16)
O(4)-P(2)-S(1)	109.70(13)
C(1)-P(2)-S(1)	111.55(16)
S(6)-P(2)-S(1)	111.79(7)
O(8)-P(3)-C(8)	100.76(18)
O(8)-P(3)-S(8)	113.21(12)
C(8)-P(3)-S(8)	108.79(15)
O(8)-P(3)-S(3)	110.08(12)
C(8)-P(3)-S(3)	112.88(16)
S(8)-P(3)-S(3)	110.80(7)
O(5)-P(4)-C(8)	99.08(19)
O(5)-P(4)-S(7)	110.56(14)
C(8)-P(4)-S(7)	109.51(16)
O(5)-P(4)-S(2)	110.43(15)
C(8)-P(4)-S(2)	114.82(16)
S(7)-P(4)-S(2)	111.76(8)
C(2)-O(1)-P(1)	119.2(3)
C(2)-O(1)-Na(1)	103.2(3)
P(1)-O(1)-Na(1)	136.69(18)
C(4)-O(2)-C(3)	111.7(4)
C(4)-O(2)-Na(1)	116.0(3)
C(3)-O(2)-Na(1)	117.8(3)
C(6)-O(3)-C(5)	112.7(3)
C(6)-O(3)-Na(1)	117.9(2)
C(5)-O(3)-Na(1)	110.8(3)
C(7)-O(4)-P(2)	115.9(3)

C(7)-O(4)-Na(1)	104.5(2)
P(2)-O(4)-Na(1)	127.93(17)
C(9)-O(5)-P(4)	119.9(3)
C(9)-O(5)-Na(1)#1	100.8(3)
P(4)-O(5)-Na(1)#1	138.42(18)
C(10)-O(6)-C(11)	109.1(4)
C(10)-O(6)-Na(1)#1	119.3(3)
C(11)-O(6)-Na(1)#1	117.0(3)
C(12)-O(7)-C(13)	114.0(4)
C(12)-O(7)-Na(1)#1	110.5(3)
C(13)-O(7)-Na(1)#1	119.5(3)
C(14)-O(8)-P(3)	116.4(3)
C(14)-O(8)-Na(1)#1	103.3(2)
P(3)-O(8)-Na(1)#1	131.13(16)
O(3)-Na(1)-O(7)#2	143.82(12)
O(3)-Na(1)-O(6)#2	142.35(13)
O(7)#2-Na(1)-O(6)#2	66.21(12)
O(3)-Na(1)-O(2)	67.21(12)
O(7)#2-Na(1)-O(2)	146.56(13)
O(6)#2-Na(1)-O(2)	94.30(13)
O(3)-Na(1)-O(1)	110.82(12)
O(7)#2-Na(1)-O(1)	86.55(12)
O(6)#2-Na(1)-O(1)	87.65(13)
O(2)-Na(1)-O(1)	64.83(11)
O(3)-Na(1)-O(4)	67.44(11)
O(7)#2-Na(1)-O(4)	91.33(12)
O(6)#2-Na(1)-O(4)	149.39(12)
O(2)-Na(1)-O(4)	94.26(12)

O(1)-Na(1)-O(4) 69.71(11)

O(3)-Na(1)-O(5)#2 81.72(11)

O(7)#2-Na(1)-O(5)#2 106.56(13)

O(6)#2-Na(1)-O(5)#2 64.02(12)

O(2)-Na(1)-O(5)#2 86.55(11)

O(1)-Na(1)-O(5)#2 138.47(12)

O(4)-Na(1)-O(5)#2 145.88(12)

O(3)-Na(1)-O(8)#2 86.26(11)

O(7)#2-Na(1)-O(8)#2 65.93(10)

O(6)#2-Na(1)-O(8)#2 94.33(12)

O(2)-Na(1)-O(8)#2 145.83(12)

O(1)-Na(1)-O(8)#2 148.55(11)

O(4)-Na(1)-O(8)#2 94.90(11)

O(5)#2-Na(1)-O(8)#2 67.92(10)

P(1)-C(1)-P(2) 126.6(3)

P(1)-C(1)-H(1A) 103(3)

P(2)-C(1)-H(1A) 105(3)

P(1)-C(1)-H(1B) 110(3)

P(2)-C(1)-H(1B) 101(3)

H(1A)-C(1)-H(1B) 110(4)

O(1)-C(2)-C(3) 107.9(4)

O(1)-C(2)-H(2A) 110.1

C(3)-C(2)-H(2A) 110.1

O(1)-C(2)-H(2B) 110.1

C(3)-C(2)-H(2B) 110.1

H(2A)-C(2)-H(2B) 108.4

O(2)-C(3)-C(2) 108.3(4)

O(2)-C(3)-H(3A) 110.0

C(2)-C(3)-H(3A)	110.0
O(2)-C(3)-H(3B)	110.0
C(2)-C(3)-H(3B)	110.0
H(3A)-C(3)-H(3B)	108.4
O(2)-C(4)-C(5)	108.4(4)
O(2)-C(4)-H(4A)	110.0
C(5)-C(4)-H(4A)	110.0
O(2)-C(4)-H(4B)	110.0
C(5)-C(4)-H(4B)	110.0
H(4A)-C(4)-H(4B)	108.4
O(3)-C(5)-C(4)	111.6(4)
O(3)-C(5)-H(5A)	109.3
C(4)-C(5)-H(5A)	109.3
O(3)-C(5)-H(5B)	109.3
C(4)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
O(3)-C(6)-C(7)	109.9(4)
O(3)-C(6)-H(6A)	109.7
C(7)-C(6)-H(6A)	109.7
O(3)-C(6)-H(6B)	109.7
C(7)-C(6)-H(6B)	109.7
H(6A)-C(6)-H(6B)	108.2
O(4)-C(7)-C(6)	108.8(4)
O(4)-C(7)-H(7A)	109.9
C(6)-C(7)-H(7A)	109.9
O(4)-C(7)-H(7B)	109.9
C(6)-C(7)-H(7B)	109.9
H(7A)-C(7)-H(7B)	108.3

P(3)-C(8)-P(4)	126.4(2)
P(3)-C(8)-H(8A)	105.7
P(4)-C(8)-H(8A)	105.7
P(3)-C(8)-H(8B)	105.7
P(4)-C(8)-H(8B)	105.7
H(8A)-C(8)-H(8B)	106.2
O(5)-C(9)-C(10)	109.0(5)
O(5)-C(9)-H(9A)	109.9
C(10)-C(9)-H(9A)	109.9
O(5)-C(9)-H(9B)	109.9
C(10)-C(9)-H(9B)	109.9
H(9A)-C(9)-H(9B)	108.3
O(6)-C(10)-C(9)	107.5(5)
O(6)-C(10)-H(10A)	110.2
C(9)-C(10)-H(10A)	110.2
O(6)-C(10)-H(10B)	110.2
C(9)-C(10)-H(10B)	110.2
H(10A)-C(10)-H(10B)	108.5
O(6)-C(11)-C(12)	108.2(4)
O(6)-C(11)-H(11A)	110.0
C(12)-C(11)-H(11A)	110.0
O(6)-C(11)-H(11B)	110.0
C(12)-C(11)-H(11B)	110.0
H(11A)-C(11)-H(11B)	108.4
O(7)-C(12)-C(11)	111.5(4)
O(7)-C(12)-H(12A)	109.3
C(11)-C(12)-H(12A)	109.3
O(7)-C(12)-H(12B)	109.3

C(11)-C(12)-H(12B) 109.3

H(12A)-C(12)-H(12B) 108.0

O(7)-C(13)-C(14) 109.0(4)

O(7)-C(13)-H(13A) 109.9

C(14)-C(13)-H(13A) 109.9

O(7)-C(13)-H(13B) 109.9

C(14)-C(13)-H(13B) 109.9

H(13A)-C(13)-H(13B) 108.3

O(8)-C(14)-C(13) 108.2(3)

O(8)-C(14)-H(14A) 110.0

C(13)-C(14)-H(14A) 110.0

O(8)-C(14)-H(14B) 110.0

C(13)-C(14)-H(14B) 110.0

H(14A)-C(14)-H(14B) 108.4

C(19)-N(1)-C(15) 111.4(5)

C(19)-N(1)-C(17) 112.6(5)

C(15)-N(1)-C(17) 113.0(5)

C(19)-N(1)-H(1) 106.4

C(15)-N(1)-H(1) 106.4

C(17)-N(1)-H(1) 106.4

N(1)-C(15)-C(16) 114.8(6)

N(1)-C(15)-H(15A) 108.6

C(16)-C(15)-H(15A) 108.6

N(1)-C(15)-H(15B) 108.6

C(16)-C(15)-H(15B) 108.6

H(15A)-C(15)-H(15B) 107.5

C(15)-C(16)-H(16A) 109.5

C(15)-C(16)-H(16B) 109.5

H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-N(1)	113.4(5)
C(18)-C(17)-H(17A)	108.9
N(1)-C(17)-H(17A)	108.9
C(18)-C(17)-H(17B)	108.9
N(1)-C(17)-H(17B)	108.9
H(17A)-C(17)-H(17B)	107.7
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(1)-C(19)-C(20)	116.9(9)
N(1)-C(19)-H(19A)	108.1
C(20)-C(19)-H(19A)	108.1
N(1)-C(19)-H(19B)	108.1
C(20)-C(19)-H(19B)	108.1
H(19A)-C(19)-H(19B)	107.3
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

H(9C)-O(9)-H(9D) 109.5

H(10C)-O(10)-H(10D) 104.2(13)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2 #2 x,-y+1/2,z+1/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 11-Zn(II) complex.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zn(1)	30(1)	26(1)	24(1)	-2(1)	-2(1)	-1(1)
S(1)	38(1)	25(1)	29(1)	1(1)	-6(1)	-9(1)
S(2)	50(1)	26(1)	30(1)	-5(1)	-7(1)	8(1)
S(3)	34(1)	27(1)	22(1)	-2(1)	3(1)	4(1)
S(4)	29(1)	48(1)	25(1)	-2(1)	2(1)	-5(1)
S(5)	24(1)	40(1)	38(1)	-2(1)	-1(1)	-1(1)
S(6)	50(1)	20(1)	28(1)	0(1)	7(1)	-4(1)
S(7)	60(1)	23(1)	36(1)	-6(1)	-5(1)	-8(1)
S(8)	27(1)	34(1)	35(1)	-1(1)	-1(1)	11(1)
P(1)	23(1)	23(1)	27(1)	-2(1)	1(1)	0(1)
P(2)	29(1)	16(1)	27(1)	-1(1)	0(1)	-3(1)
P(3)	22(1)	21(1)	22(1)	-1(1)	1(1)	2(1)
P(4)	34(1)	19(1)	26(1)	-4(1)	2(1)	-2(1)
O(1)	38(2)	21(2)	41(2)	3(1)	12(2)	-1(1)
O(2)	46(2)	24(2)	28(2)	3(1)	9(1)	2(1)

O(3)	31(2)	21(2)	26(2)	0(1)	-4(1)	1(1)
O(4)	24(2)	21(2)	37(2)	0(1)	3(1)	-2(1)
O(5)	41(2)	19(2)	45(2)	-4(1)	13(2)	2(1)
O(6)	35(2)	24(2)	65(3)	1(2)	4(2)	4(1)
O(7)	23(2)	33(2)	32(2)	-5(1)	0(1)	-1(1)
O(8)	24(2)	20(1)	24(2)	-4(1)	2(1)	0(1)
Na(1)	23(1)	21(1)	24(1)	2(1)	-2(1)	-2(1)
C(1)	30(2)	16(2)	25(2)	0(2)	-2(2)	-3(2)
C(2)	51(3)	24(2)	51(3)	0(2)	23(3)	-6(2)
C(3)	63(4)	27(2)	33(3)	2(2)	20(2)	-1(2)
C(4)	57(3)	25(2)	28(3)	3(2)	-5(2)	2(2)
C(5)	42(3)	26(2)	32(3)	5(2)	-7(2)	7(2)
C(6)	24(2)	31(2)	31(2)	-6(2)	-4(2)	-2(2)
C(7)	24(2)	26(2)	37(3)	-3(2)	6(2)	-6(2)
C(8)	28(2)	22(2)	26(2)	-1(2)	0(2)	-2(2)
C(9)	53(3)	28(3)	59(4)	0(2)	19(3)	9(2)
C(10)	40(3)	38(3)	65(4)	3(3)	7(3)	12(2)
C(11)	32(3)	53(3)	52(4)	6(3)	-2(2)	5(2)
C(12)	24(2)	49(3)	48(3)	-7(2)	-1(2)	-1(2)
C(13)	31(2)	32(2)	32(3)	-3(2)	-2(2)	-6(2)
C(14)	33(2)	18(2)	28(2)	-6(2)	5(2)	-1(2)
N(1)	55(3)	42(3)	57(3)	-1(2)	9(2)	10(2)
C(15)	57(4)	56(4)	52(4)	-8(3)	4(3)	16(3)
C(16)	53(4)	74(5)	59(4)	-7(3)	-7(3)	12(3)
C(17)	53(4)	53(4)	52(4)	0(3)	7(3)	5(3)
C(18)	48(3)	49(4)	68(4)	-6(3)	14(3)	1(3)
C(19)	70(3)	112(5)	106(5)	-58(4)	-35(4)	52(3)
C(20)	70(3)	112(5)	106(5)	-58(4)	-35(4)	52(3)

O(9)	90(4)	48(3)	89(4)	20(2)	65(3)	24(2)
O(10)	75(3)	61(3)	79(4)	14(3)	19(3)	7(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 11-Zn(II) complex.

	x	y	z	U(eq)
H(1A)	11140(50)	1370(20)	10080(30)	20(12)
H(1B)	11170(40)	760(20)	9650(20)	17(11)
H(2A)	12179	2931	8616	50
H(2B)	11992	3338	9305	50
H(3A)	10688	3808	8420	49
H(3B)	9949	3102	8319	49
H(4A)	7974	3358	8580	44
H(4B)	8221	4147	8683	44
H(5A)	7539	4094	9782	40
H(5B)	6422	3765	9303	40
H(6A)	6868	2557	9061	35
H(6B)	5775	2609	9618	35
H(7A)	7039	1900	10338	35
H(7B)	6678	1529	9639	35
H(8A)	6782	1403	5890	48(17)
H(8B)	6213	1098	6555	32(14)
H(9A)	10413	563	5182	56
H(9B)	10310	87	5830	56
H(10A)	11580	863	6467	57

H(10B)	12371	580	5841	57
H(11A)	13509	1762	6067	55
H(11B)	12404	1810	6620	55
H(12A)	12947	2881	6308	49
H(12B)	12715	2700	5527	49
H(13A)	11025	3365	6857	38
H(13B)	10982	2573	7002	38
H(14A)	8891	3075	7146	31
H(14B)	8860	3302	6370	31
H(1)	5119	4528	7392	61
H(15A)	6819	5072	6504	66
H(15B)	6588	4283	6423	66
H(16A)	8399	4500	7149	94
H(16B)	7291	4113	7546	94
H(16C)	7482	4904	7645	94
H(17A)	4850	5711	6595	63
H(17B)	3884	5498	7174	63
H(18A)	6534	5874	7376	82
H(18B)	5665	5587	7966	82
H(18C)	5291	6287	7614	82
H(19A)	3382	4488	6621	116
H(19B)	4429	3901	6552	116
H(20A)	4254	5018	5682	145
H(20B)	3683	4289	5506	145
H(20C)	5229	4397	5602	145
H(9C)	4151	2478	8233	111
H(9D)	4711	2696	7645	111
H(10C)	4025(16)	4170(40)	7992(18)	107

H(10D)	4840(70)	3741(10)	8290(50)	107

Table 6. Torsion angles [deg] for 11-Zn(II) complex.

C(1)-P(1)-O(1)-C(2)	174.4(4)
S(5)-P(1)-O(1)-C(2)	58.6(4)
S(4)-P(1)-O(1)-C(2)	-64.2(4)
C(1)-P(1)-O(1)-Na(1)	7.7(3)
S(5)-P(1)-O(1)-Na(1)	-108.1(2)
S(4)-P(1)-O(1)-Na(1)	129.1(2)
C(1)-P(2)-O(4)-C(7)	-172.8(3)
S(6)-P(2)-O(4)-C(7)	-55.5(3)
S(1)-P(2)-O(4)-C(7)	69.1(3)
C(1)-P(2)-O(4)-Na(1)	-35.8(3)
S(6)-P(2)-O(4)-Na(1)	81.5(2)
S(1)-P(2)-O(4)-Na(1)	-153.91(15)
C(8)-P(4)-O(5)-C(9)	-174.1(4)
S(7)-P(4)-O(5)-C(9)	-59.2(4)
S(2)-P(4)-O(5)-C(9)	65.0(4)
C(8)-P(4)-O(5)-Na(1)#1	-6.8(3)
S(7)-P(4)-O(5)-Na(1)#1	108.1(3)
S(2)-P(4)-O(5)-Na(1)#1	-127.7(2)
C(8)-P(3)-O(8)-C(14)	175.1(3)
S(8)-P(3)-O(8)-C(14)	59.2(3)
S(3)-P(3)-O(8)-C(14)	-65.5(3)
C(8)-P(3)-O(8)-Na(1)#1	34.5(2)
S(8)-P(3)-O(8)-Na(1)#1	-81.5(2)
S(3)-P(3)-O(8)-Na(1)#1	153.89(15)

O(1)-P(1)-C(1)-P(2)	63.5(3)
S(5)-P(1)-C(1)-P(2)	-179.7(2)
S(4)-P(1)-C(1)-P(2)	-53.9(3)
O(4)-P(2)-C(1)-P(1)	-49.8(3)
S(6)-P(2)-C(1)-P(1)	-168.4(2)
S(1)-P(2)-C(1)-P(1)	66.9(3)
P(1)-O(1)-C(2)-C(3)	123.0(4)
Na(1)-O(1)-C(2)-C(3)	-66.3(4)
C(4)-O(2)-C(3)-C(2)	-160.9(4)
Na(1)-O(2)-C(3)-C(2)	-22.9(5)
O(1)-C(2)-C(3)-O(2)	61.3(5)
C(3)-O(2)-C(4)-C(5)	165.7(4)
Na(1)-O(2)-C(4)-C(5)	26.9(5)
C(6)-O(3)-C(5)-C(4)	-79.2(5)
Na(1)-O(3)-C(5)-C(4)	55.3(4)
O(2)-C(4)-C(5)-O(3)	-54.3(5)
C(5)-O(3)-C(6)-C(7)	162.6(4)
Na(1)-O(3)-C(6)-C(7)	31.5(5)
P(2)-O(4)-C(7)-C(6)	-157.0(3)
Na(1)-O(4)-C(7)-C(6)	56.8(4)
O(3)-C(6)-C(7)-O(4)	-61.2(5)
O(8)-P(3)-C(8)-P(4)	50.9(3)
S(8)-P(3)-C(8)-P(4)	170.2(2)
S(3)-P(3)-C(8)-P(4)	-66.4(3)
O(5)-P(4)-C(8)-P(3)	-64.3(3)
S(7)-P(4)-C(8)-P(3)	180.0(2)
S(2)-P(4)-C(8)-P(3)	53.3(3)
P(4)-O(5)-C(9)-C(10)	-121.1(4)

Na(1)#1-O(5)-C(9)-C(10)	67.5(5)
C(11)-O(6)-C(10)-C(9)	159.8(5)
Na(1)#1-O(6)-C(10)-C(9)	21.7(6)
O(5)-C(9)-C(10)-O(6)	-62.6(6)
C(10)-O(6)-C(11)-C(12)	-164.2(5)
Na(1)#1-O(6)-C(11)-C(12)	-25.0(6)
C(13)-O(7)-C(12)-C(11)	81.1(5)
Na(1)#1-O(7)-C(12)-C(11)	-56.8(5)
O(6)-C(11)-C(12)-O(7)	53.7(6)
C(12)-O(7)-C(13)-C(14)	-165.8(4)
Na(1)#1-O(7)-C(13)-C(14)	-32.0(5)
P(3)-O(8)-C(14)-C(13)	150.5(3)
Na(1)#1-O(8)-C(14)-C(13)	-58.9(4)
O(7)-C(13)-C(14)-O(8)	63.3(5)
C(19)-N(1)-C(15)-C(16)	-137.1(7)
C(17)-N(1)-C(15)-C(16)	94.9(7)
C(19)-N(1)-C(17)-C(18)	175.2(6)
C(15)-N(1)-C(17)-C(18)	-57.5(7)
C(15)-N(1)-C(19)-C(20)	-53.8(8)
C(17)-N(1)-C(19)-C(20)	74.4(8)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2 #2 x,-y+1/2,z+1/2

8. Calculation of association constants of compounds 7, 9 and 11 with Zn(II)

^{31}P-NMR measurements were performed at 243 MHz, 300 K, 6 mM ligand in D_2O and 0.2 M $ZnCl_2$ solution.

Fig. S21. Calculated and experimental Δδ of compound **7** titrated by Zn(II) and monitored by ^{31}P-NMR vs. number of equivalents of Zn(II).

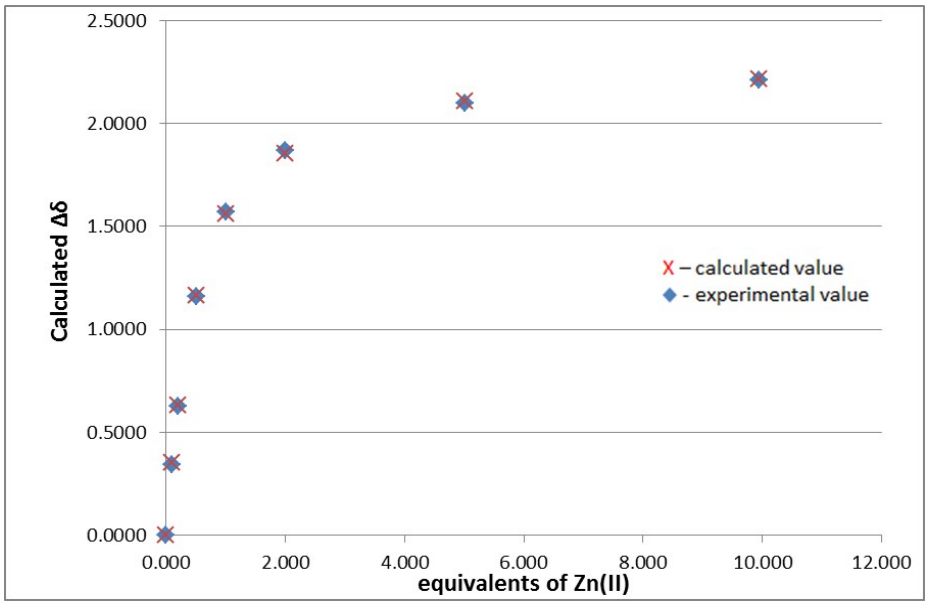


Fig. S22. Calculated and experimental Δδ of compound **9** titrated by Zn(II) and monitored by ^{31}P-NMR vs. number of equivalents of Zn(II).

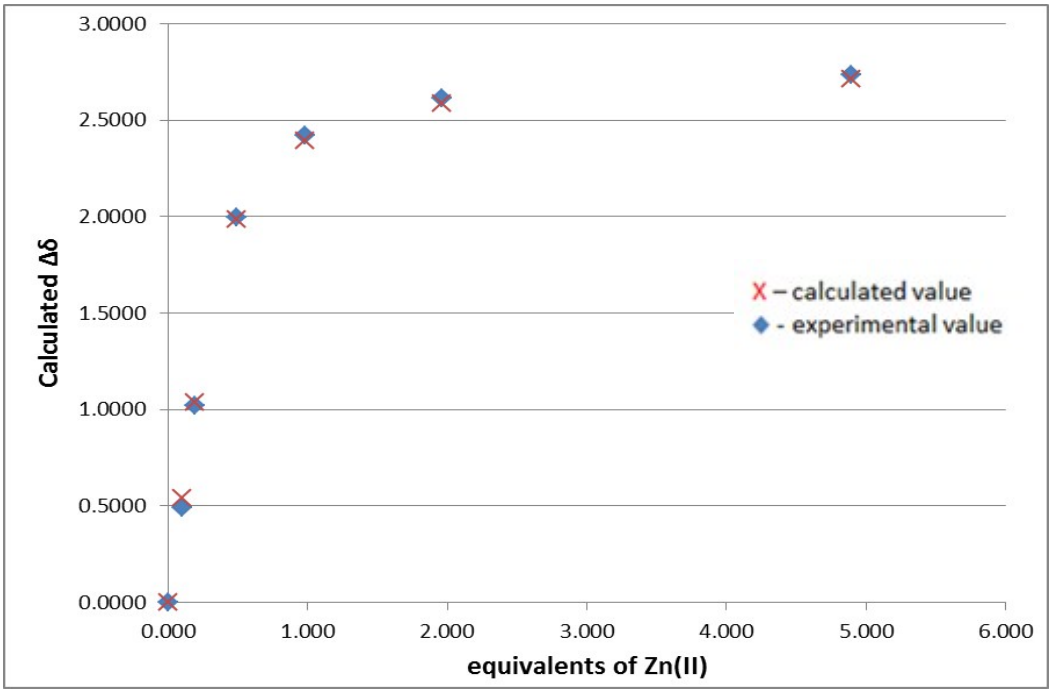


Fig. S23. Calculated and experimental Δδ of compound **11** titrated by Zn(II) and monitored by ^{31}P-NMR vs. number of equivalents of Zn(II).