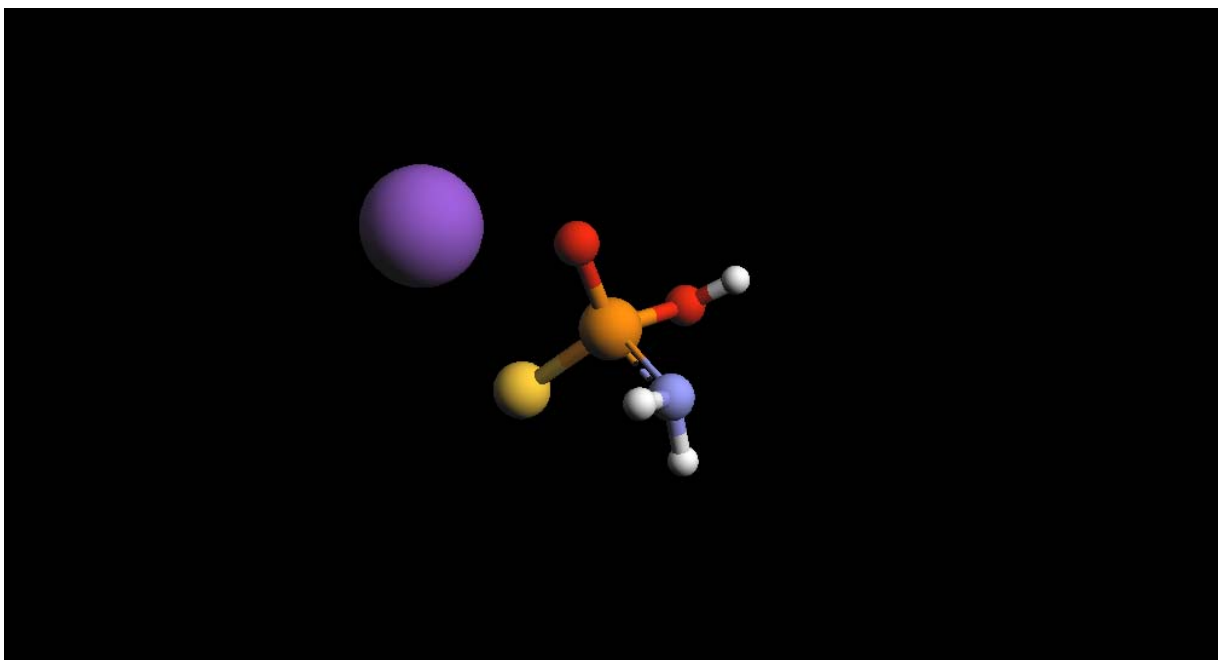


## SUPPLEMENTARY MATERIALS

## Structural Data for Picture 1A

```
HEADER
REMARK      From 1A.log
HETATM      1  O          1      -0.115  -1.369  -0.112
HETATM      2  P          1       0.830  -0.190   0.016
HETATM      3  S          1     -0.029   1.626  -0.062
HETATM      4  O          1       1.660  -0.229   1.420
HETATM      5  N          1       2.085  -0.441  -1.104
HETATM      6  H          1       2.181  -1.040   1.474
HETATM      7  H          1       1.737  -0.791  -1.986
HETATM      8  H          1       2.661   0.376  -1.259
HETATM      9  K          1     -2.395  -0.307  -0.011
CONNECT     1      2
CONNECT     2      1
CONNECT     3
CONNECT     4      6
CONNECT     5      7      8
CONNECT     6      4
CONNECT     7      5
CONNECT     8      5
CONNECT     9
END
```



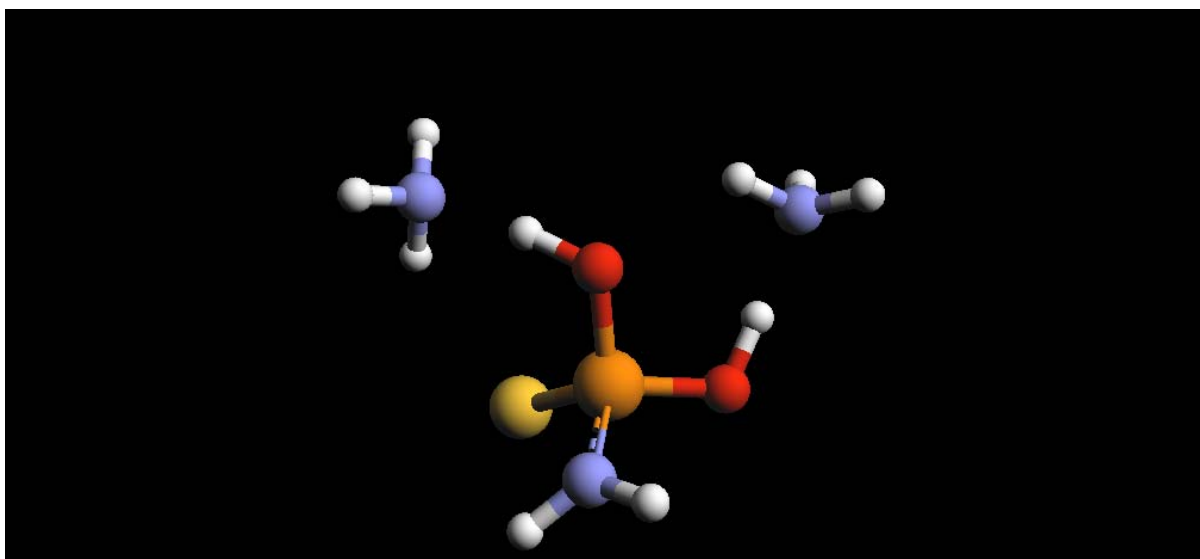
**Fig. (1A).** The **1'** complex in the thione form (the psalmk.pdb file). The  $K^{(+)}$  cation coloured in magenta.

## Structural Data for Picture 2A

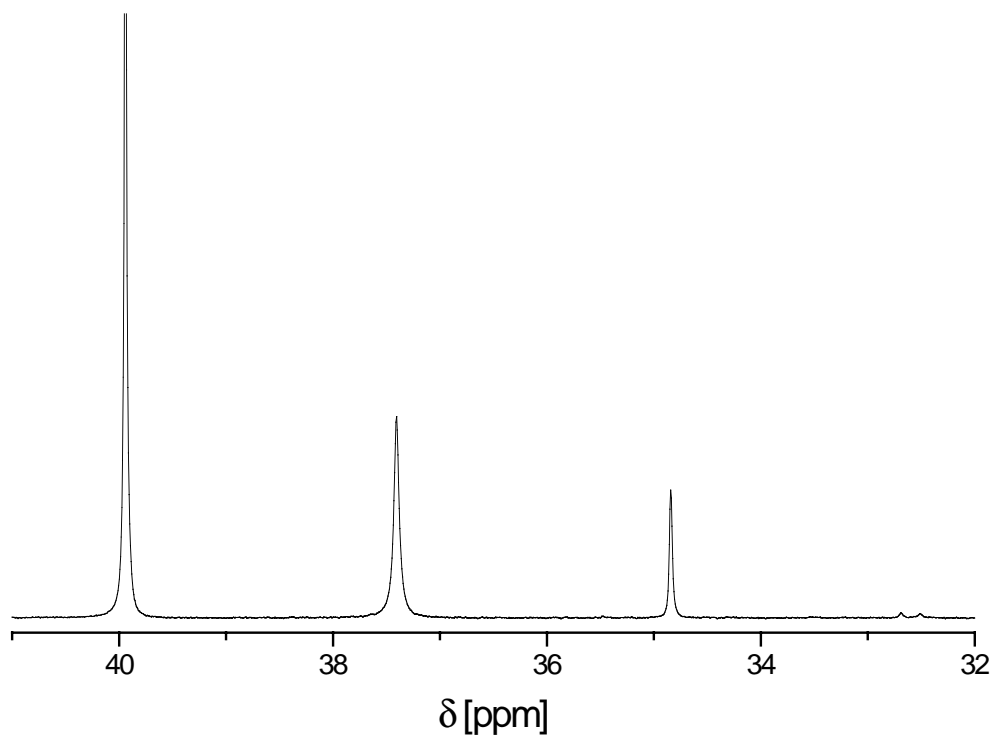
```

HEADER
REMARK      From 2A.log
HETATM      1  O          1          0.282   0.888   0.730
HETATM      2  P          1          0.026  -0.611   0.156
HETATM      3  N          1         -0.260  -1.630   1.419
HETATM      4  S          1         -1.478  -0.730  -1.160
HETATM      5  O          1          1.497  -0.998  -0.273
HETATM      6  H          1          2.103  -0.157  -0.422
HETATM      7  H          1         -1.152  -2.079   1.495
HETATM      8  H          1          0.490  -1.950   2.004
HETATM      9  H          1         -2.292   1.644  -0.259
HETATM     10  N          1         -1.892   2.324   0.387
HETATM     11  H          1         -0.552   1.533   0.631
HETATM     12  H          1         -1.789   3.215  -0.074
HETATM     13  H          1         -2.486   2.421   1.196
HETATM     14  N          1          2.945   1.136  -0.476
HETATM     15  H          1          2.251   1.659   0.045
HETATM     16  H          1          3.821   1.098   0.021
HETATM     17  H          1          3.074   1.525  -1.396
CONNECT      1    11
CONNECT      2     5
CONNECT      3     7     8
CONNECT      4
CONNECT      5     2     6
CONNECT      6     5    14
CONNECT      7     3
CONNECT      8     3
CONNECT      9    10
CONNECT     10     9    11    12    13
CONNECT     11     1    10
CONNECT     12    10
CONNECT     13    10
CONNECT     14     6    15    16    17
CONNECT     15    14
CONNECT     16    14
CONNECT     17    14
END

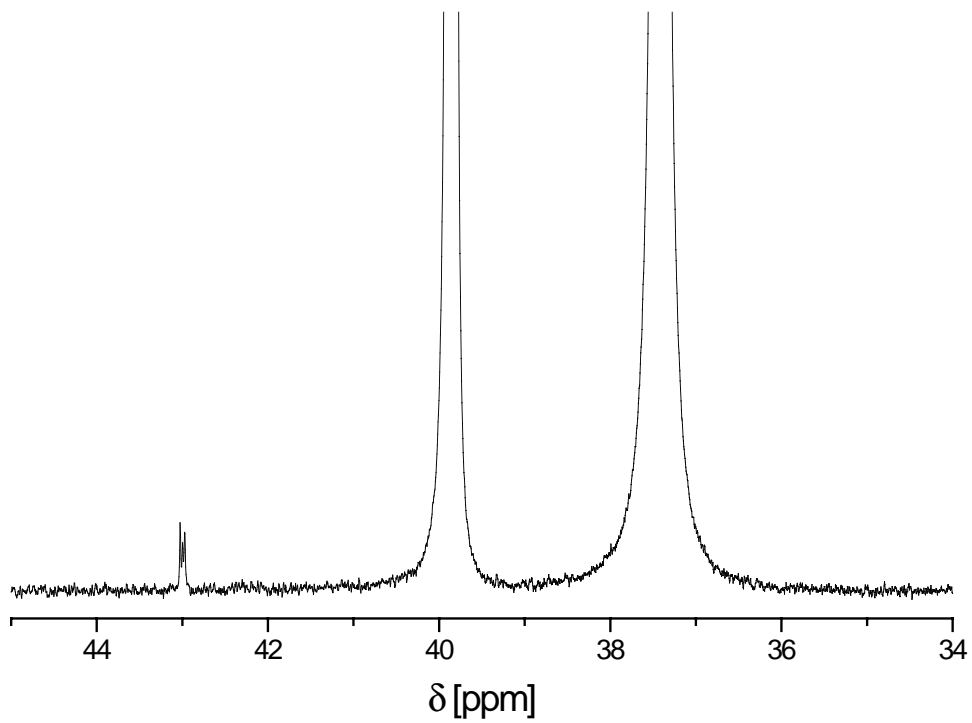
```



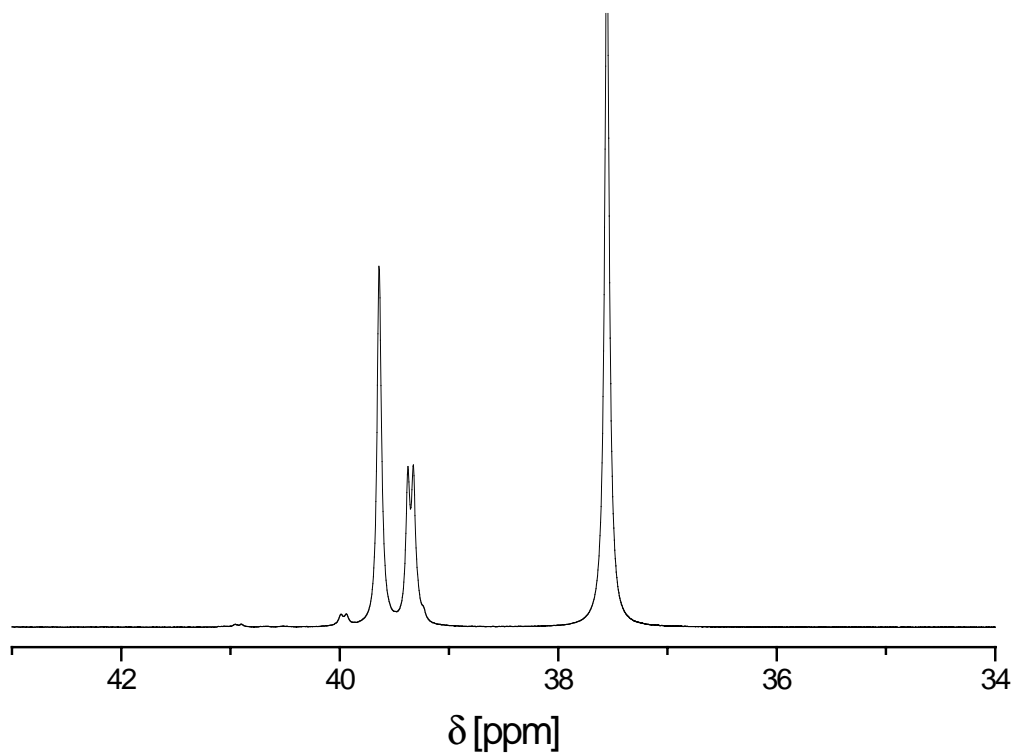
**Fig. (2A).** The **1** complex in the thione form (the tiosf.pdb file). Two  $\text{NH}_4^{(+)}$  cations released protons towards oxygen atoms.



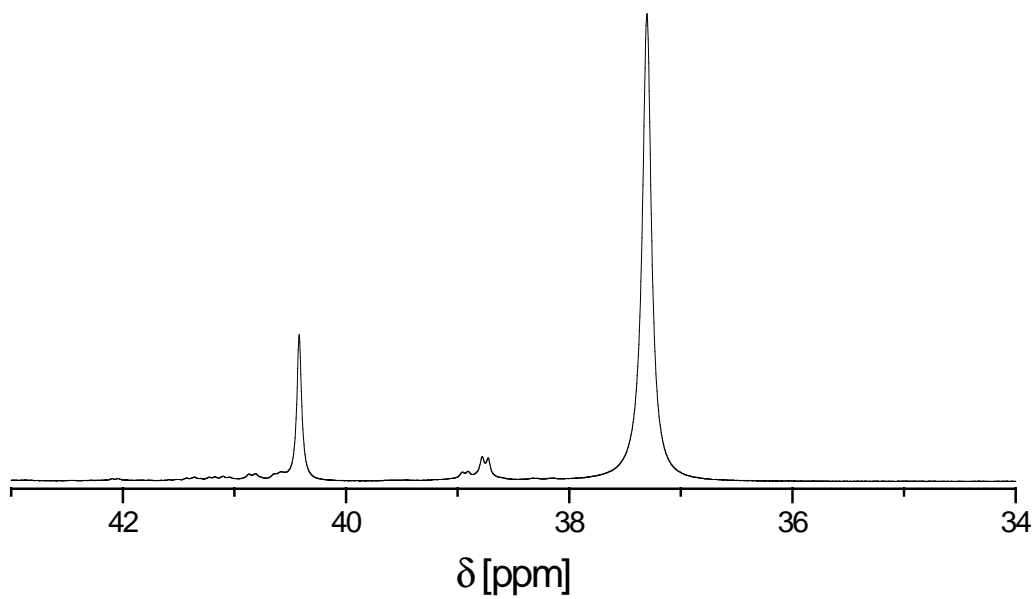
$^{31}\text{P}$  NMR spectrum of thiophosphorylated histidine post-reaction mixture.



$^{31}\text{P}$  NMR spectrum of thiophosphorylated thymidine post-reaction mixture.



<sup>31</sup>P NMR spectrum of thiophosphorylated glucose post-reaction mixture.



<sup>31</sup>P NMR spectrum of thiophosphorylated 2-deoxyribose post-reaction mixture.