Supporting information for

An Au(III)-Amino alcohol complex for degradation of organophosphorus pesticides

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Experimental section

General remarks. All the reactants and solvents and starting materials were purchased from commercial sources where available, and were used without purification.^{1}H NMR (500 MHz), ^{13}C NMR spectra were determined in a Bruker AV 500 spectrometer. Chemical shifts are reported in parts per million (ppm), calibrated to the solvent peak set.

Synthesis of 1. [Au(L)Cl_2]Cl·2H_2O: $NaAuCl_4$·2H_2O (218mg, 0.548mmol) was dissolved in 19.5 mL of absolute ethanol at room temperature. To this solution was added 500µL of a 1M ethanol solution of 2-(2-Aminoethylamino)ethanol (**L**). The product precipitated as an orange-brown solid, which was separated by filtration and recrystallized from EtOH to give **1** as yellow solid (175 mg; 79%). **^{1}H-NMR** (500.1 MHz, MeOD-d4), δ 3.85(t, 2H), δ 3.45-3.36(m, 4H), δ 3.25(t, 2H). **^{13}C-NMR** (125 MHz, MeOD-d4), δ 57.8, δ 51.8, δ 45.5, δ 36.8. **EM** (m/z) [Au(**L**)Cl_2]$^{+}$ = 371.

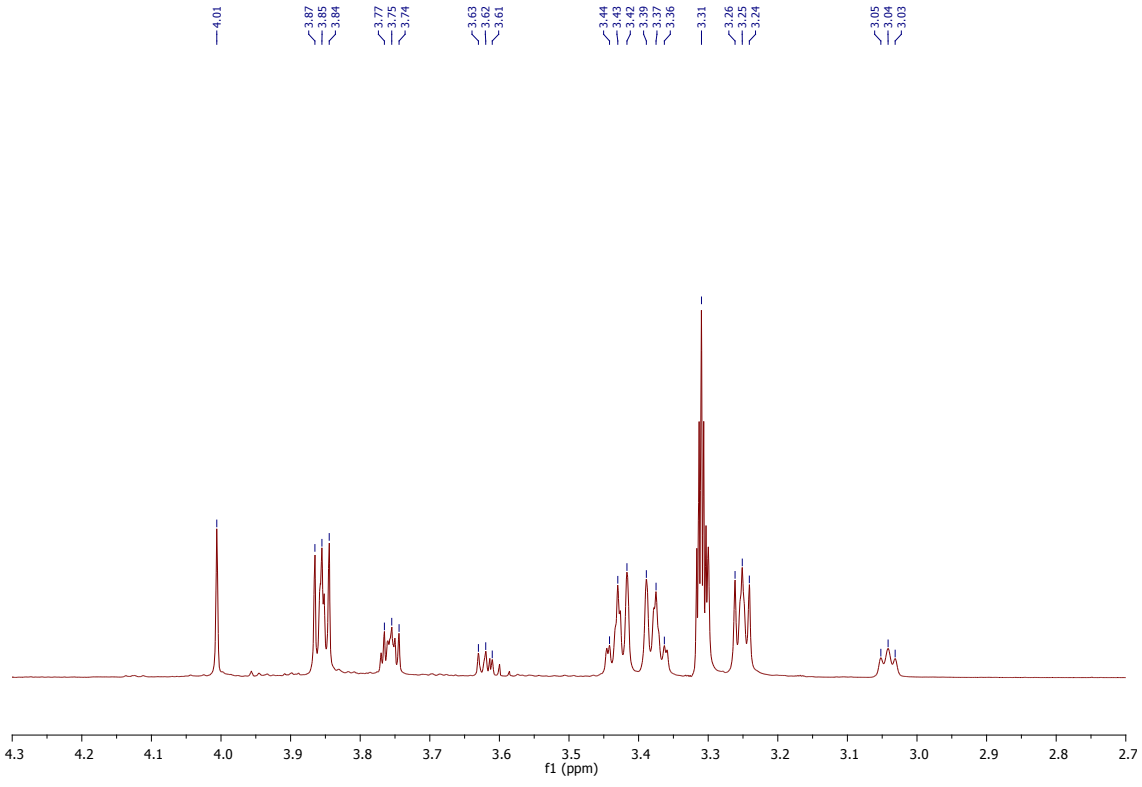

Figure S.1. ^{1}HNMR spectrum of **1** in MeOD-d_4.

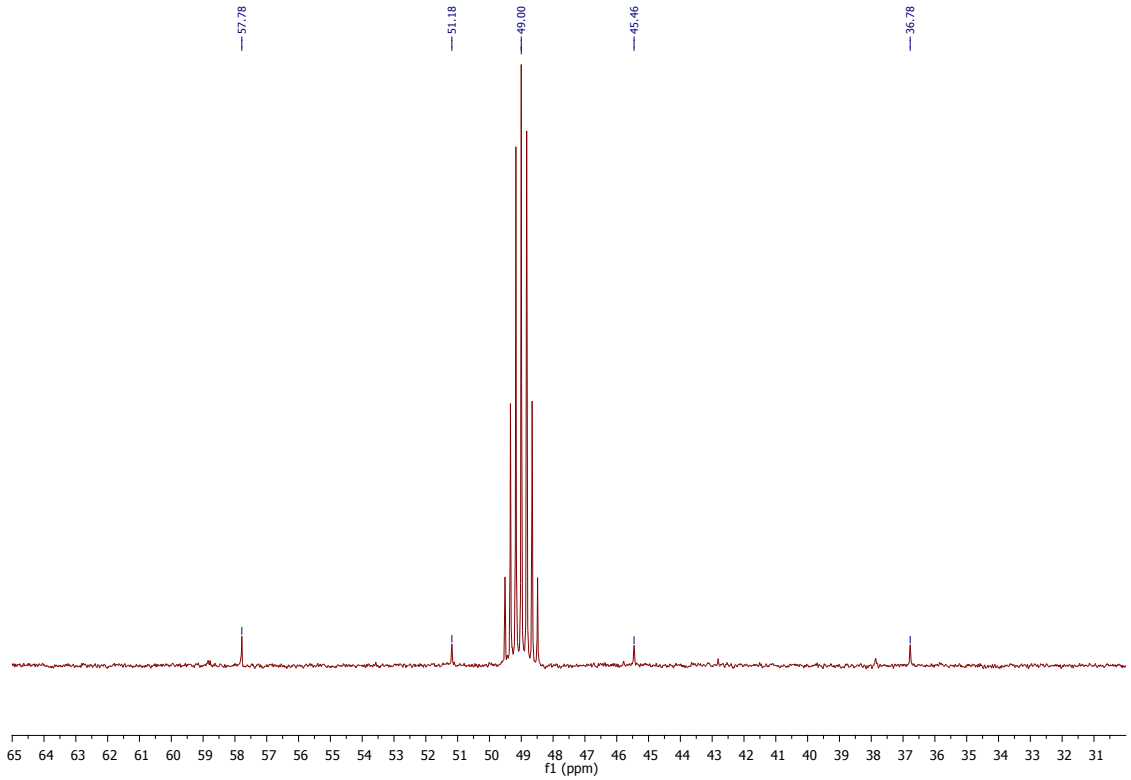

Figure S.2. ^{13}CNMR spectrum of **1** in MeOD-d4.

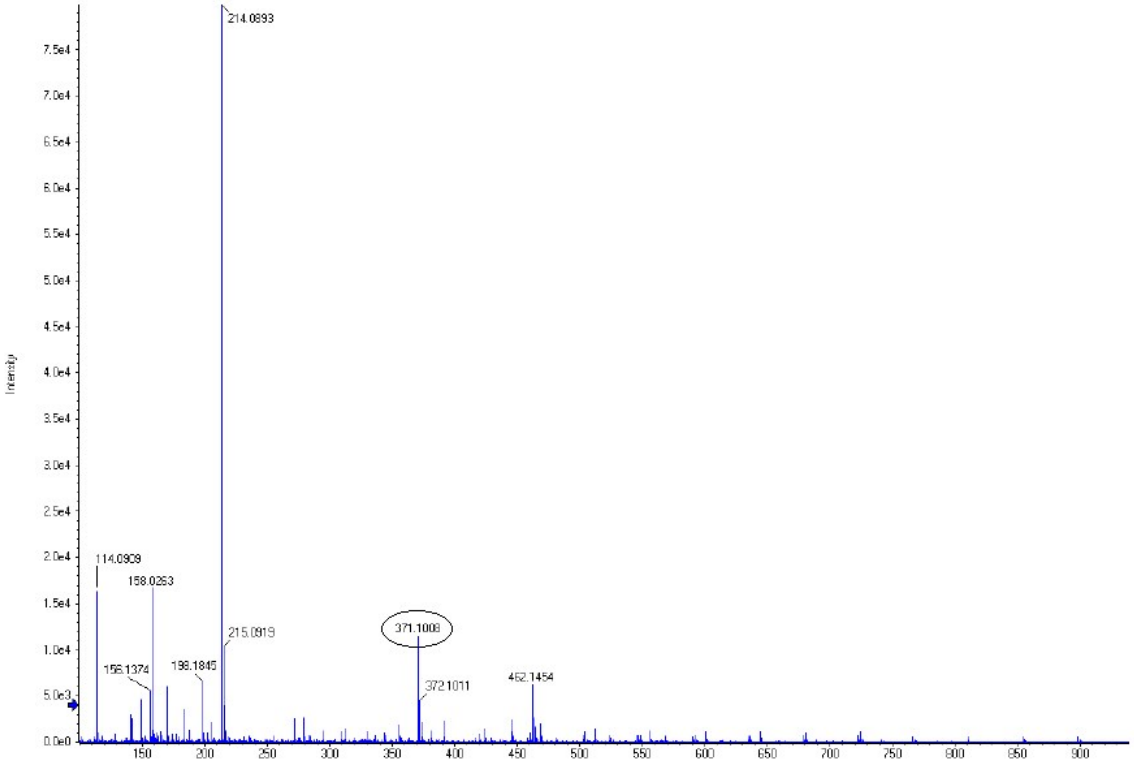

Figure S.3. MS spectrum of **1** (ESI+)

Synthesis of 5:

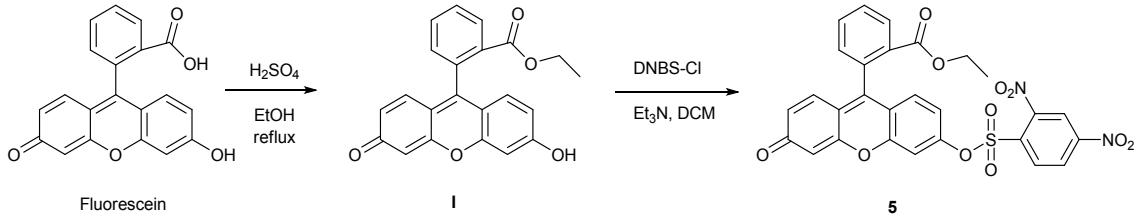

Figure SI-1. Synthetic route for indicator **5**.

*Fluorescein ethyl ester (**I**):* H_2SO_4 (1.5 ml) was added dropwise to the solution of fluorescein (1.0 g, 3.01mmol) in EtOH (20 mL) at room temperature. After stirring at reflux for 18 h, EtOH was evaporated under reduced pressure and the resulting mixture was diluted with CH_3Cl. Solid $NaHCO_3$ was added to the solution until gas evolution creased. The heterogeneous mixture was filtered, and the organic phase was evaporated. The resulting precipitated was recrystallized from EtOH to give **I** as orange-brown crystals with a green lustre (920 mg, 93%). **^{1}H-NMR** (500.1 MHz, MeOD-d4), δ 8.31 (dd, *J*=7.8, 1.3 Hz, 1H), 7.87 (td, *J*=7.5, 1.6 Hz, 1H), 7.80 (td, *J*=7.6, 1.5 Hz, 1H), 7.46 (dd, *J*=7.4, 1.3 Hz, 1H), 7.06 (s, 1H), 7.03 (s, 1H), 6.78 (d, *J*=2.1 Hz, 2H), 6.74 (d, *J*=2.2 Hz, 1H), 6.71 (d, *J*=2.2 Hz, 1H), 4.03 (q, *J*=7.1 Hz, 2H), 0.95 (t, *J*=7.1 Hz, 3H).

*Dinitrobenzenesulfonyl Fluorescein ethyl ester (**5**):* the above compound **I** (108 mg, 0.3 mmol) and 2,4-dinitrobenzenesulfonyl chloride (240 mg, 0.9 mmol) were dissolved in CH_2CL_2 (10 mL). Then 100 µL of Et_3N was added and the reaction solution was stirred overnight at room temperature. After the evaporation of the solvent, the crude product was purified by silica gel column chromatography with an eluent of 1:1 (v/v) hexane/ethyl acetate to give the compound **5** as orange crystals in 70% yield (125 mg). **^{1}H-NMR** (300.1 MHz, $CDCl_3$), δ 8.69 (d, *J* = 2.1 Hz, 1H), 8.56 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.34 – 8.26 (m, 2H), 7.78 – 7.67 (m, 2H), 7.35 – 7.27 (m, 2H), 7.07 – 6.97 (m, 2H), 6.87 (d, *J* = 9.0, 1H), 6.54 (dd, *J* = 9.6, 1.8 Hz, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 3.71 (q, *J* = 7.2, 2H), 1.05 (t, *J* = 6.9 Hz, 3H).

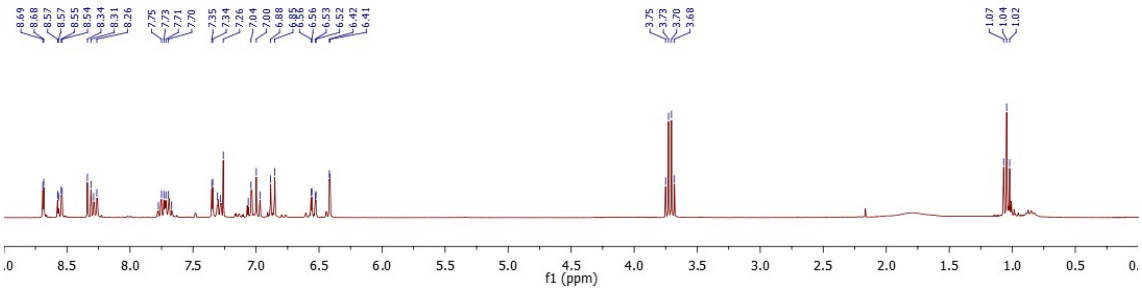

Figure S.4. ^{1}HNMR spectrum of **5** in $CDCl_3$.

Hydrolysis of methidation. 2.5 10^{-2} mmol (7.0 mg) of methidation were dissolved in 0.5 mL of MeOD:D_2O (9:1). 2.5 10^{-2} mmol (10.0 mg) of **1** were added to the solution. Immediately an amorphous solid appeared. The solid (7.7 mg) was separated by filtration and then, the solution was transferred to an NMR tube and the corresponding spectra were registered.

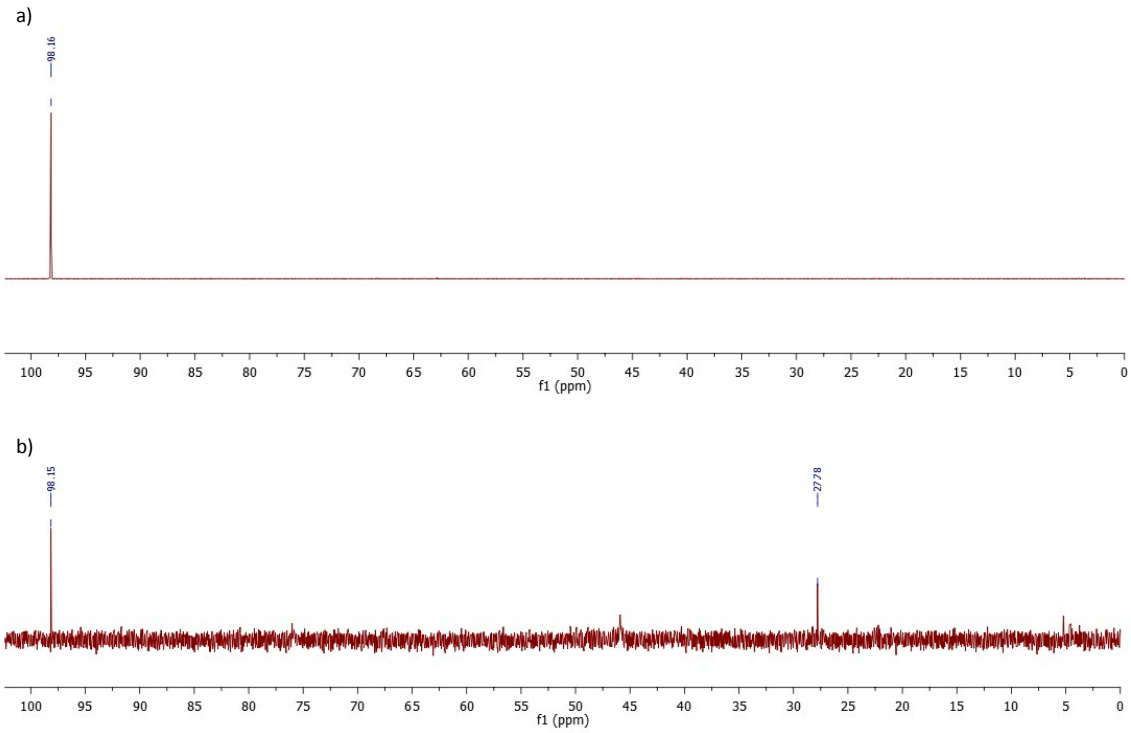

Figure S-5: ^{31}P NMR spectra of methidathion (a) and its hydrolytic products (b) after reaction with **1**.

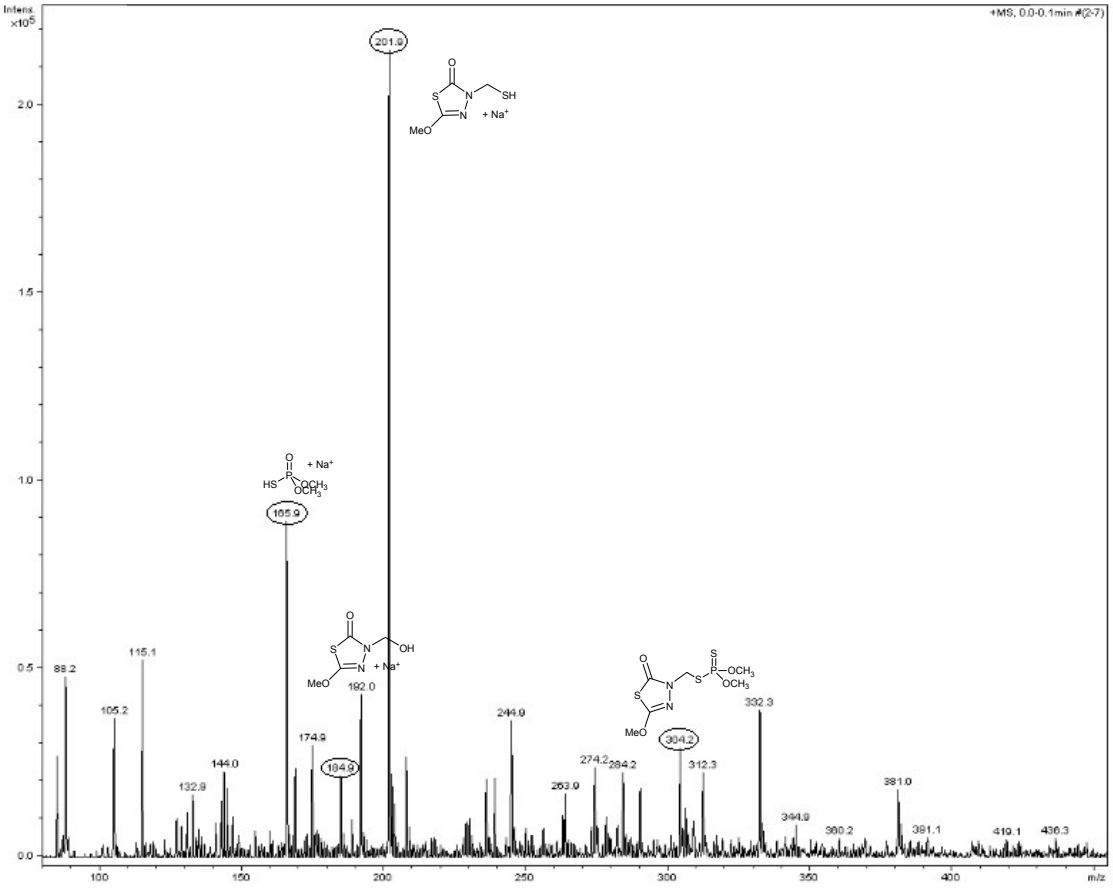

Figure S-6: MS spectrum of the liquid phase obtained in the hydrolysis of methidathion (ESI+).

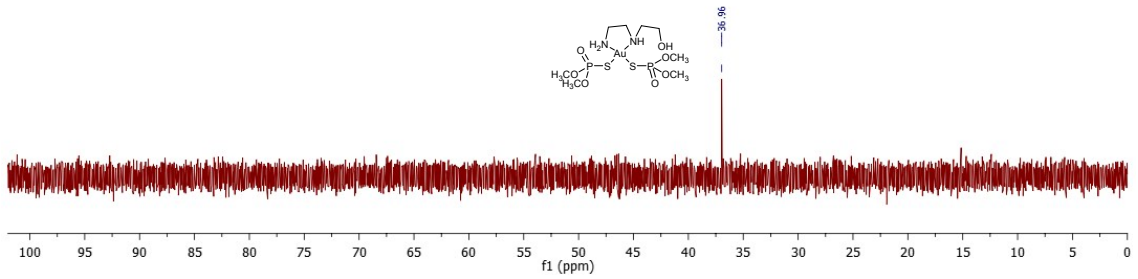

Figure S-7: ^{31}P NMR spectra of the precipitated obtained after treatment of methidathion with **1**.

Hydrolysis of azinphos-methyl. 2.5 10^{-2} mmol (7.9 mg) of azinphos-methyl were dissolved in 0.5 mL of MeOD:D_2O (9:1). 2.5 10^{-2} mmol (10.0 mg) of **1** were added to the solution. Immediately the solution became claudy and after 12 hours a solid precipitated. The solid was separated by filtration and then, DMSO-d_6 was added the obtained solution was transferred to an NMR tube and the corresponding spectra were registered and 7.3 mg of a remaining solid was isolated. The ^{1}H NMR spectrum showed azinphos-methyl (65%) and thiomethyl benzazimide (**7)** (35%). The ratio **7**/**1** was around 1.5.

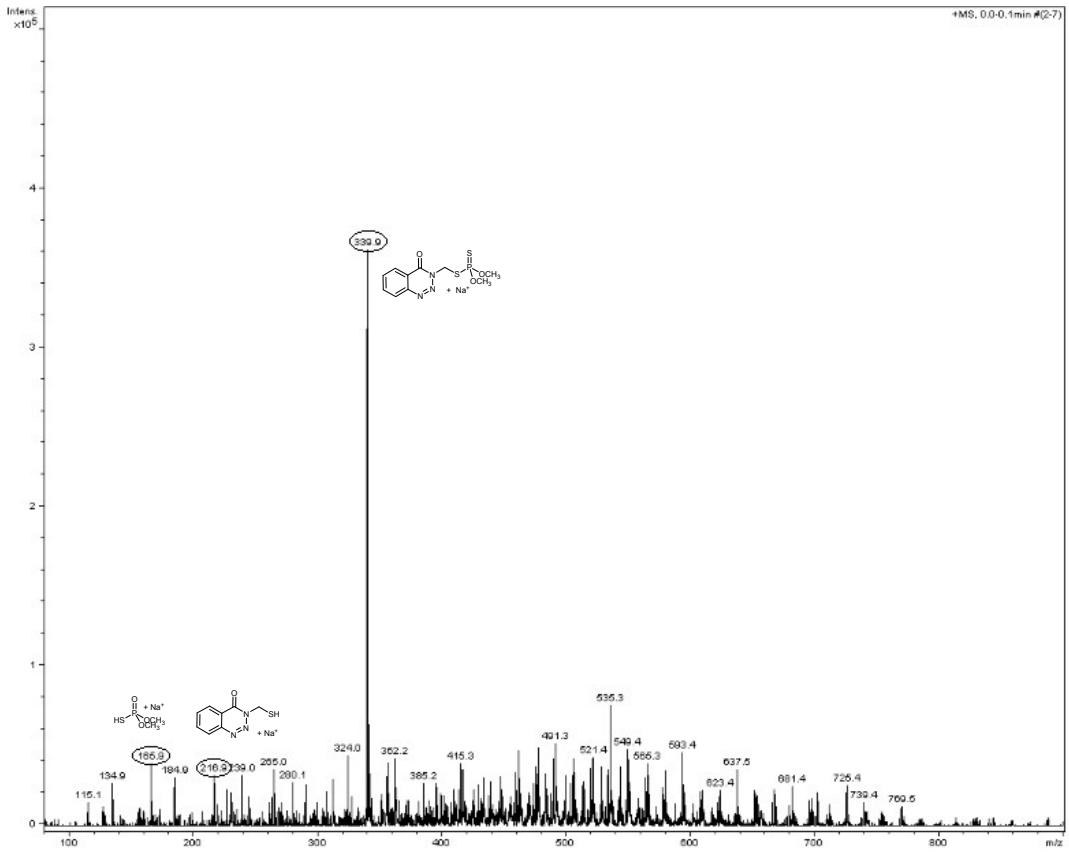

Figure S-8: MS spectrum of the liquid phase obtained in the hydrolysis of azinphos-methyl (ESI+)

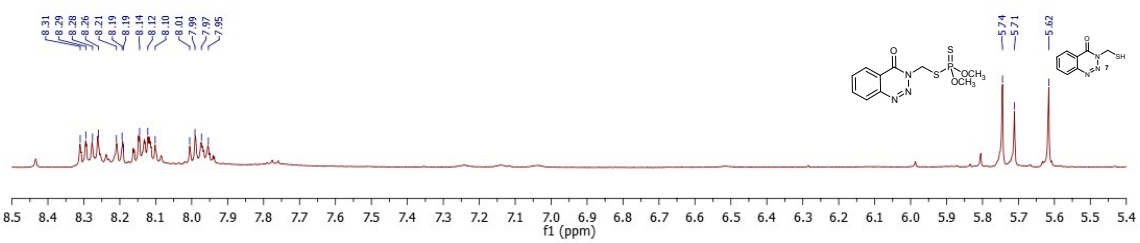

Figure S-9: ^{1}H NMR spectra of the DMSO soluble part of the precipitated obtained after treatment of azinphos-methyl with **1**

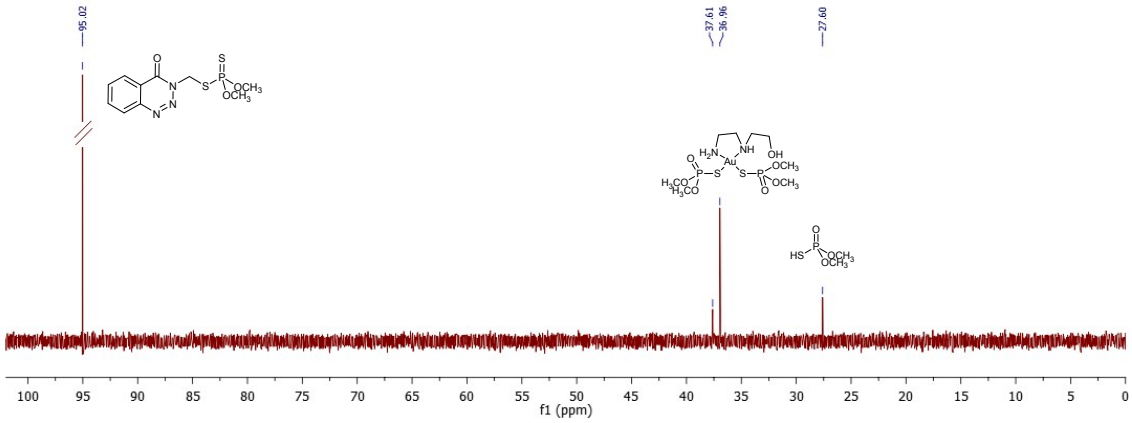

Figure S-10: ^{31}P NMR spectra of the DMSO soluble part of the precipitated obtained after treatment of azinphos-methyl with **1**.

Spectroscopic studies: CH_3CN was purchased at spectroscopic grade from Aldrich Chemicals Co., used as received, and was found to be free of fluorescent impurities. Fluorescence spectra were recorded using a Varian Cary Eclipse spectrofluorimeter. Fluorescence quantum yields were measured at room temperature in the N_2-purgued solution in relation to Fluorescein in 0.1 M NaOH (Φ_F = 0.85)[1] as standard. The fluorescence quantum yields were calculated from Eq. (1).[2] Here, F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium.

$$\Phi_{exp} = \Phi_{ref}\frac{F\{1-exp(-A_{ref}ln10)\}n^2}{F_{ref}\{1-exp(-A\,ln10)\}n_{ref}^2} \qquad (1)$$

Fluorescence control experiments: Numerous control experiments were performed in order to ensure that the fluorescence signal was because the reaction of the released thiol group (after the P-S bond cleavage) with **5** and not by the other possible species in solution. For that purpose the fluorescence of **5** was monitored in presence of: OP pesticides (methidathion and azinphos-methyl), compound **1** and thioacetic acid. As shown in figure SI-5, only the presence of free thiols produce an enhancement of the fluorescence emission, whereas the probe **5** remains in silent in the presence of the other analytes.

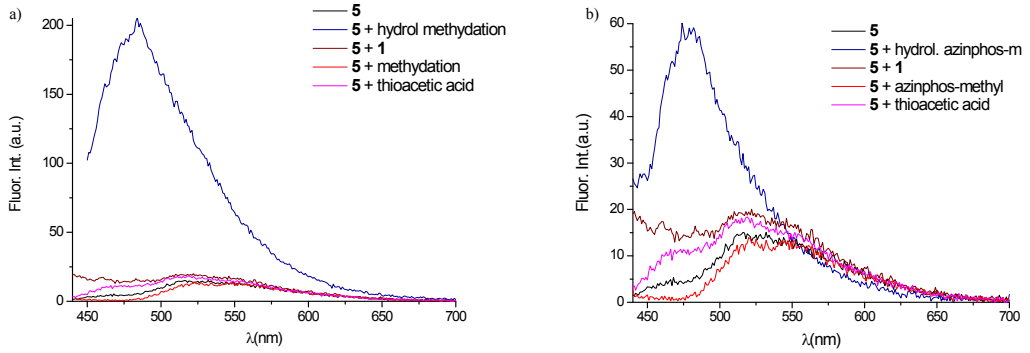

Figure S-11: Fluorescence emission spectra (λ_{ex}= 430 nm) for methidathion (a) and azinphos-methyl (b) of **5** (10^{-5} M in CH_3CN) alone (black trace) and in the presence of the hydrolyzed OP pesticide (blue trace), complex **1**(burgundy trace), pesticide (red trace) and thioacetic acid (pink trace).

References

1. K. G. Casey and E. L. Quitevis, *J. Phys. Chem.*, **1988**, *92*, 6590-6594.
2. P. Didier, G. Ulrich, Y. Mely and R. Ziessel, *Org. Biomol. Chem.*, **2009**, *7*, 3639-3642