Binding of Reactive Organophosphate by Oximes *via* Hydrogen Bond

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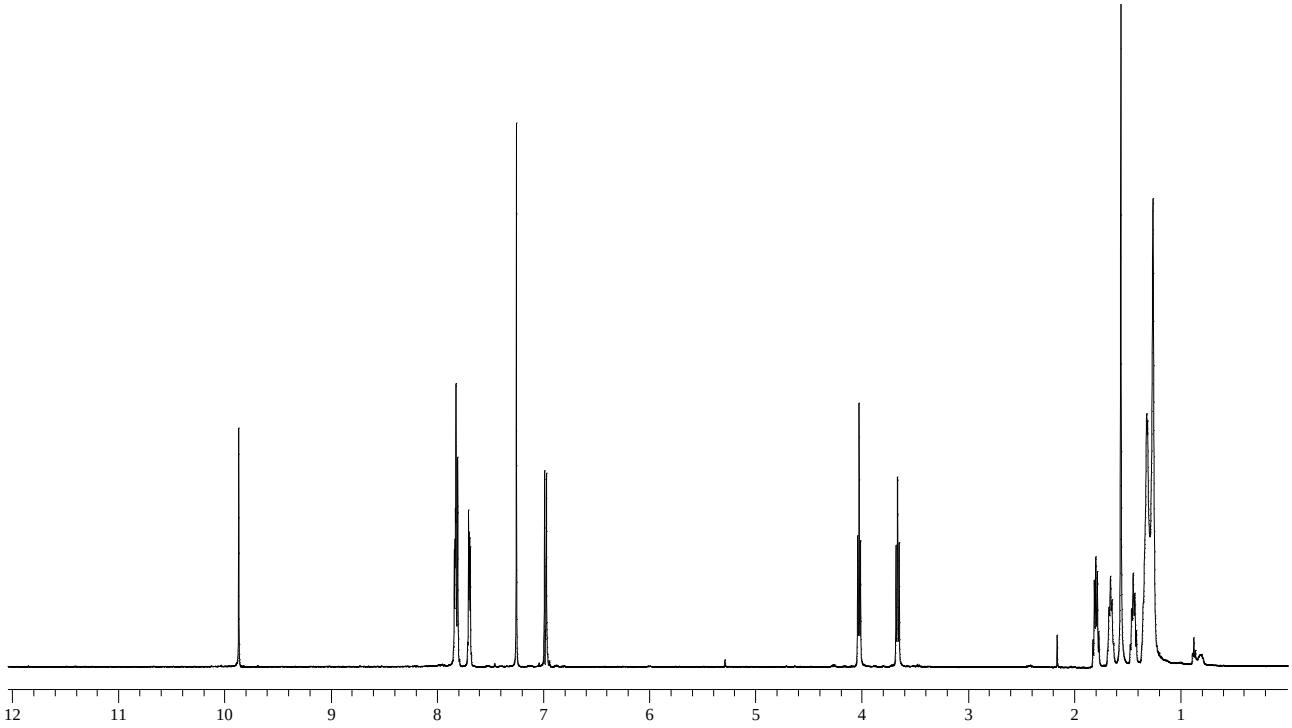
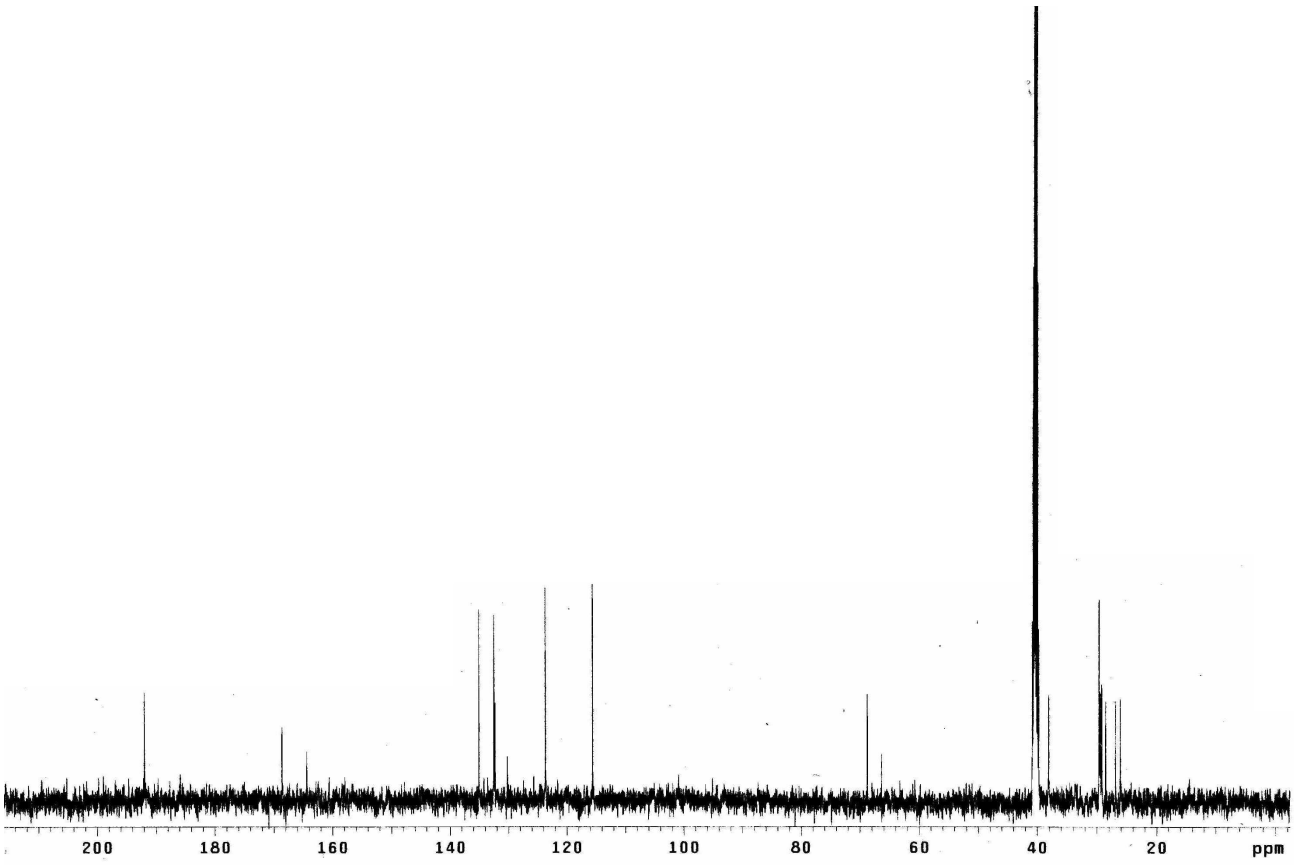
ELECTRONIC SUPPLEMENTARY MATERIAL

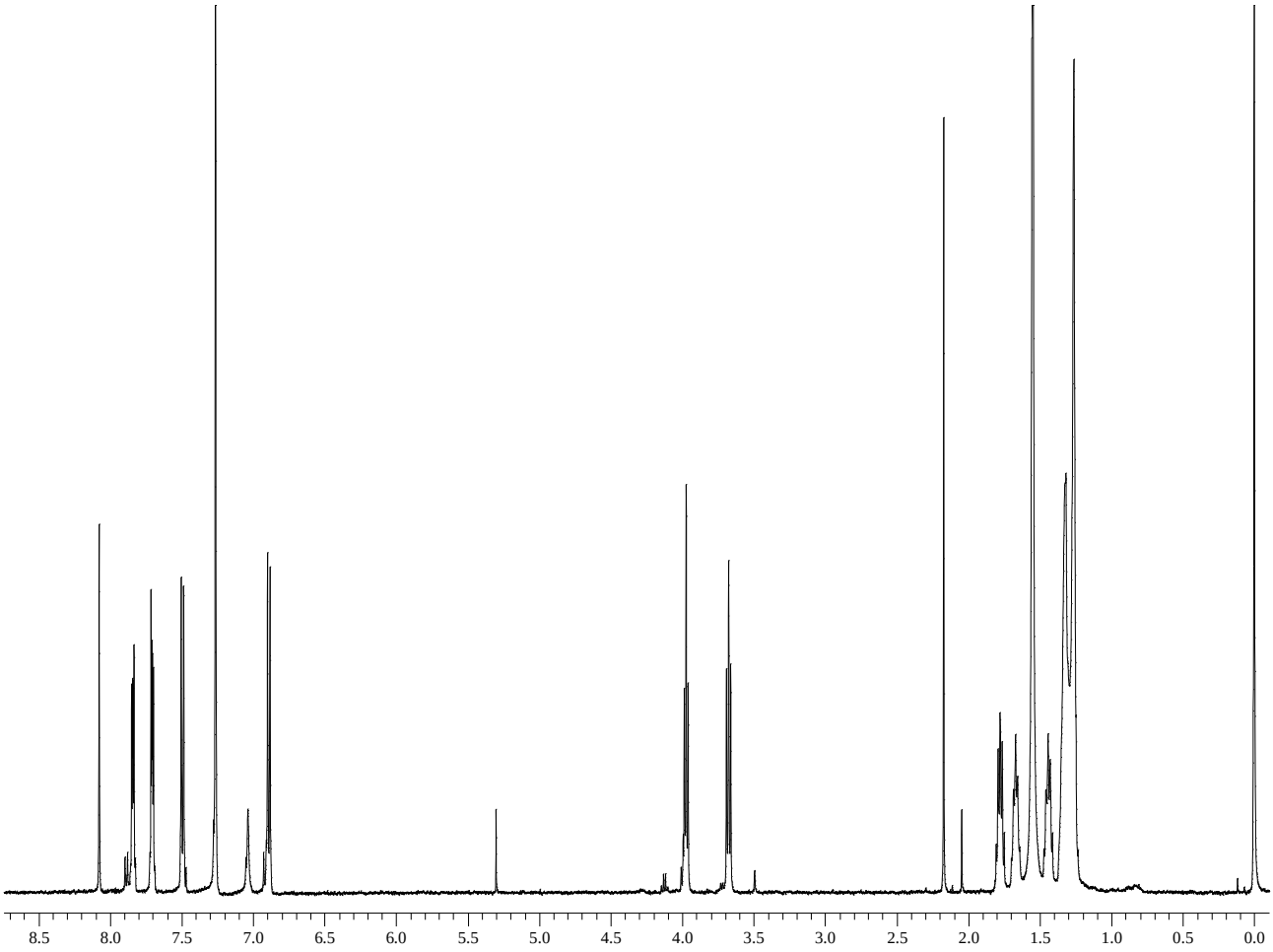
Table of Contents



^{1}H NMR spectrum of **6** in $CDCl_3$



^{13}C NMR spectrum of **6** in DMSO –d_6



^{1}H NMR spectrum of **3** in $CDCl_3$

General procedure for UV-VIS titration

Two equimolar (3.71 x 10^{-3} M) mother solutions of the selected oxime and **DMMP** were prepared in dry CH_3CN. . From these, different solutions with different ratio oxime/**DMMP** were prepared as reported below, and UV-VIS spectra were recorded. The absorption spectrum of each solution was recorded at 25°C and the stability constants of the complexes were determined using HYPERQUAD 2006 (version 3.1.60),[1] a software designed to extract equilibrium constants from potentiometric and/or spectrophotometric titration data. HYPERQUAD starts with an assumed complex formation scheme and uses a least-squares approach to derive the spectra of the complexes and the stability constants. There was also applied the $\chi 2$ test (chi-square), where the residuals should follow a normal distribution. So if the distribution is approximately normal, the value of the $\chi 2$ test should be around 12 or less. In all of the case, $\chi 2 \leq 10$. The final values are obtained by three independent measurements sets. Free Energy values were calculated by $\Delta G° = -RT\ln K$.

*UV-Vis titration between **1** and **DMMP***

Solution	[**1**]	[**DMMP**]	$A_{264\ nm}$
1	5,84E-05	0	0,85236
2	5,81E-05	1,48E-05	0,85348
3	5,79E-05	2,94E-05	0,85404
4	5,77E-05	4,40E-05	0,85323
5	5,74E-05	5,84E-05	0,85218
6	5,72E-05	7,27E-05	0,85033
7	5,70E-05	8,70E-05	0,84890
8	5,68E-05	1,01E-04	0,84738
9	5,66E-05	1,15E-04	0,84610
10	5,64E-05	1,29E-04	0,84671
11	5,61E-05	1,43E-04	0,84637
12	5,41E-05	2,75E-04	0,82206
13	5,21E-05	3,98E-04	0,79873
14	5,00E-05	5,12E-04	0,77603
15	4,86E-05	6,18E-04	0,75470
16	4,70E-05	7,18E-04	0,73543
17	4,56E-05	8,12E-04	0,71686
18	4,42E-05	1,06E-03	0,69688
19	4,29E-05	1,15E-03	0,67833
20	4,17E-05	1,24E-03	0,66102
21	4,00E-05	1,32E-03	0,64492
22	3,94E-05	1,39E-03	0,62677
23	3,84E-05	1,72E-03	0,60972

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                                       std devn     beta

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*UV-Vis titration between **2** and **DMMP***

Solution	[**2**]	[**DMMP**]	$A_{264\ nm}$
1	2,01E-05	0	0,42713
2	1,98E-05	6,08E-05	0,42139
3	1,95E-05	1,20E-04	0,39697
4	1,91E-05	1,77E-04	0,38982
5	1,88E-05	2,32E-04	0,39146
6	1,83E-05	3,37E-04	0,38149
7	1,72E-05	5,30E-04	0,36153
8	1,44E-05	1,06E-03	0,31849
9	1,09E-05	1,91E-03	0,24471
10	4,57E-06	3,60E-03	0,13557
11	1,43E-06	6,15E-03	0,05889

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*UV-Vis titration between **3** and **DMMP***

Solution	[**3**]	[**DMMP**]	$A_{217\ nm}$
1	1,77E-05	0	0,92820
2	1,77E-05	1,48E-05	0,92595
3	1,76E-05	2,94E-05	0,92385
4	1,75E-05	4,40E-05	0,92125
5	1,74E-05	7,27E-05	0,91705
6	1,73E-05	8,70E-05	0,91476
7	1,73E-05	1,01E-04	0,91258
8	1,72E-05	1,15E-04	0,91052
9	1,71E-05	1,43E-04	0,90639
10	1,64E-05	2,75E-04	0,88591
11	1,59E-05	3,98E-04	0,86624
12	1,53E-05	5,12E-04	0,84793
13	1,48E-05	6,18E-04	0,83037
14	6,67E-06	1,06E-03	0,80786
15	6,36E-06	1,18E-03	0,78584
16	6,09E-06	1,29E-03	0,76583
17	5,83E-06	1,39E-03	0,74814
18	5,60E-06	1,48E-03	0,71726
19	5,38E-06	1,57E-03	0,71430
20	5,19E-06	1,65E-03	0,70244
21	5,00E-06	1,72E-03	0,69061
22	4,52E-06	1,68E-03	0,67914
23	4,52E-06	1,80E-03	0,66792
24	4,52E-06	1,91E-03	0,65801
25	2,26E-06	3,71E-03	0,52520
26	1,61E-06	4,91E-03	0,47665
27	1,06E-06	6,10E-03	0,44110
28	7,10E-07	7,30E-03	0,40003

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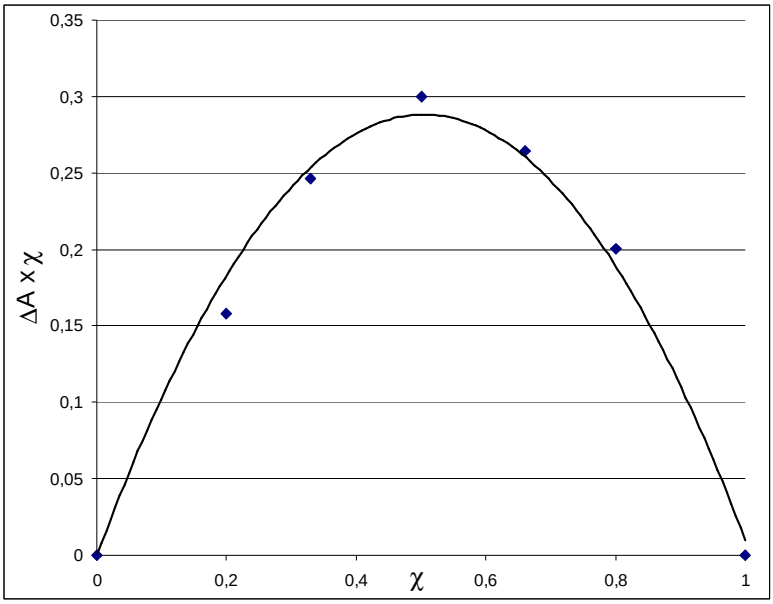
Determination of Stoichiometry

Stoichiometries of the complexes were investigated by the Job plot method using spectrophotometric measurements. The samples were prepared by mixing equimolecular stock solutions (3.7 x 10^{-3} M) in dry CH_3CN of the appropriate oxime and **DMMP** to cover the whole range of molar fractions keeping constant the total concentration. The UV absorbance was recorded at 264 nm for oxime **1** and **2**, and at 217 nm for oxime **3**, and the changes in absorbance, compared to the uncomplexed oxime species (ΔA) were calculated and reported versus the oxime mole fraction. These plots show invariably a maximum at 0.5 mol fraction of oxime indicating its 1:1 complex formation with the **DMMP**.

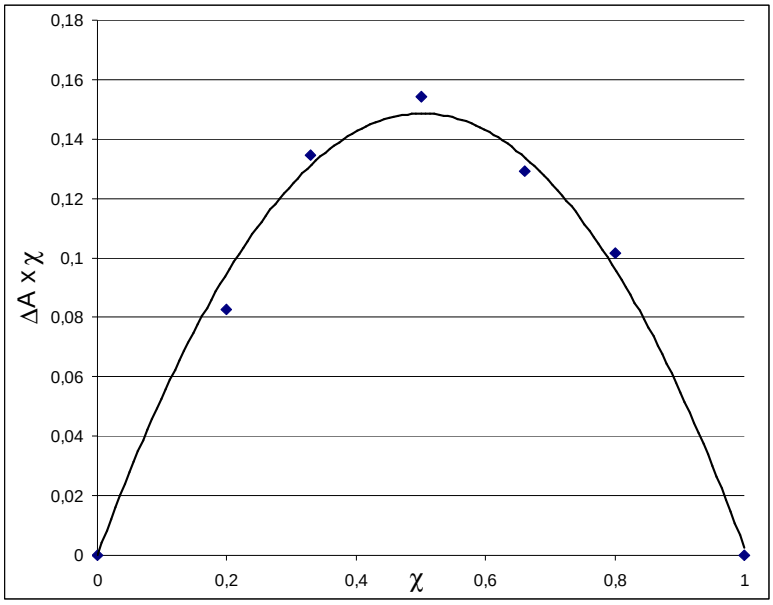
Job Plot between **1** and **DMMP**

X	V_{oxime} (µL)	V_{DMMP}(µL)	ΔA	ΔA x χ
1	200	0	0	0
0,8	175	25	0,250693	0,2005544
0,66	150	50	0,400633	0,26441778
0,5	100	100	0,600393	0,3001965
0,33	50	150	0,746633	0,24638889
0,2	25	175	0,789083	0,1578166
0	0	200	0,831639	0



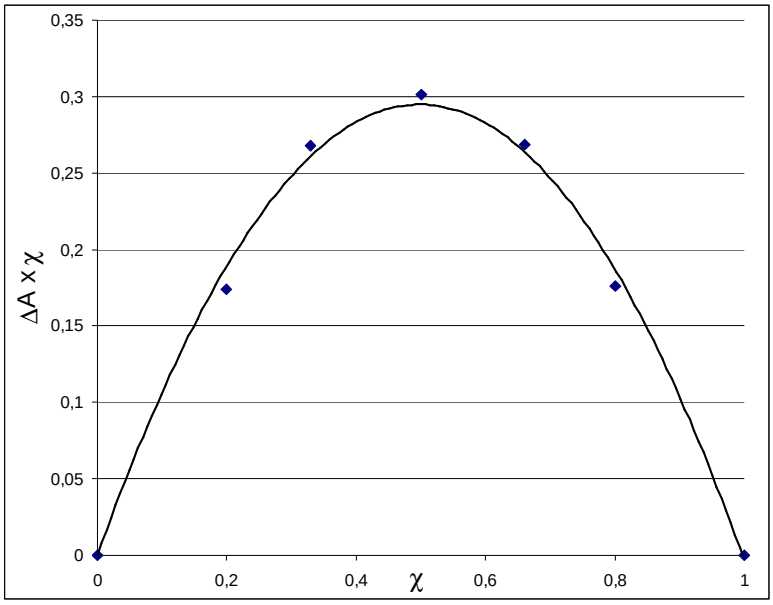
Job Plot between **2** and **DMMP**

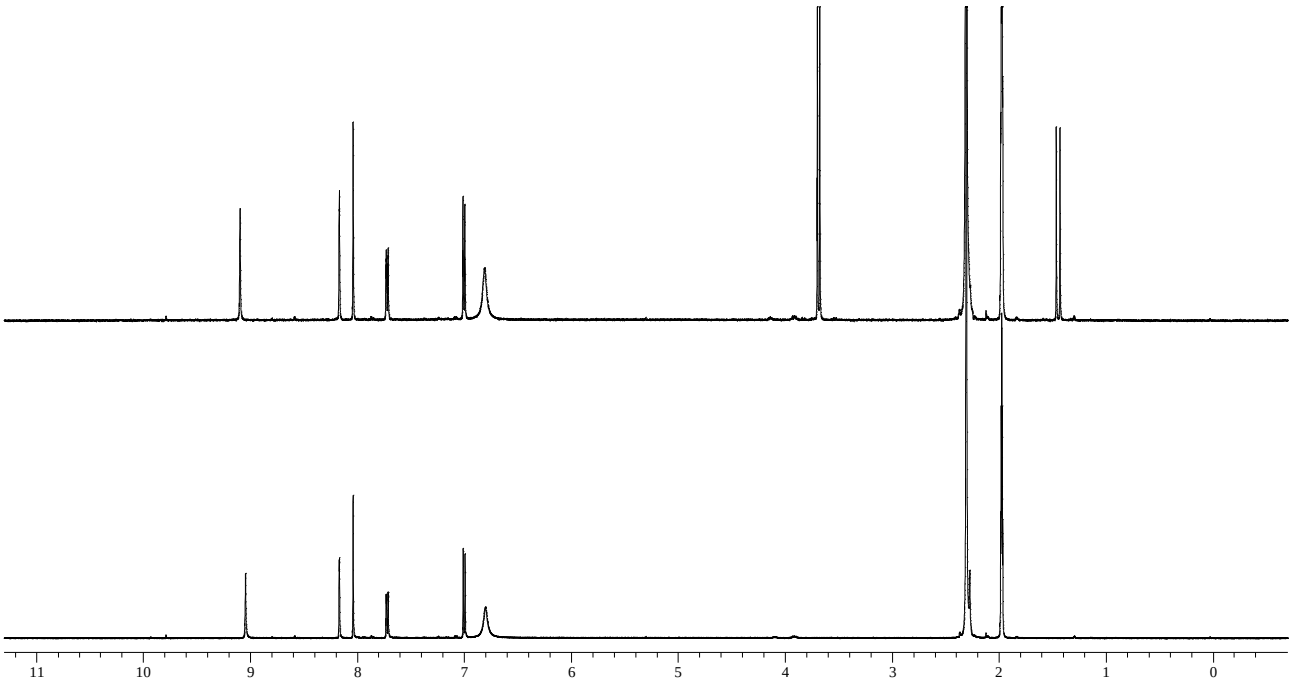
X	V_{oxime} (µL)	V_{DMMP}(µL)	ΔA	ΔA x χ
1	200	0	0	0
0,8	175	25	0,12719	0,101752
0,66	150	50	0,19579	0,1292214
0,5	100	100	0,30819	0,154095
0,33	50	150	0,40819	0,1347027
0,2	25	175	0,41248	0,082496
0	0	200	0,42423	0



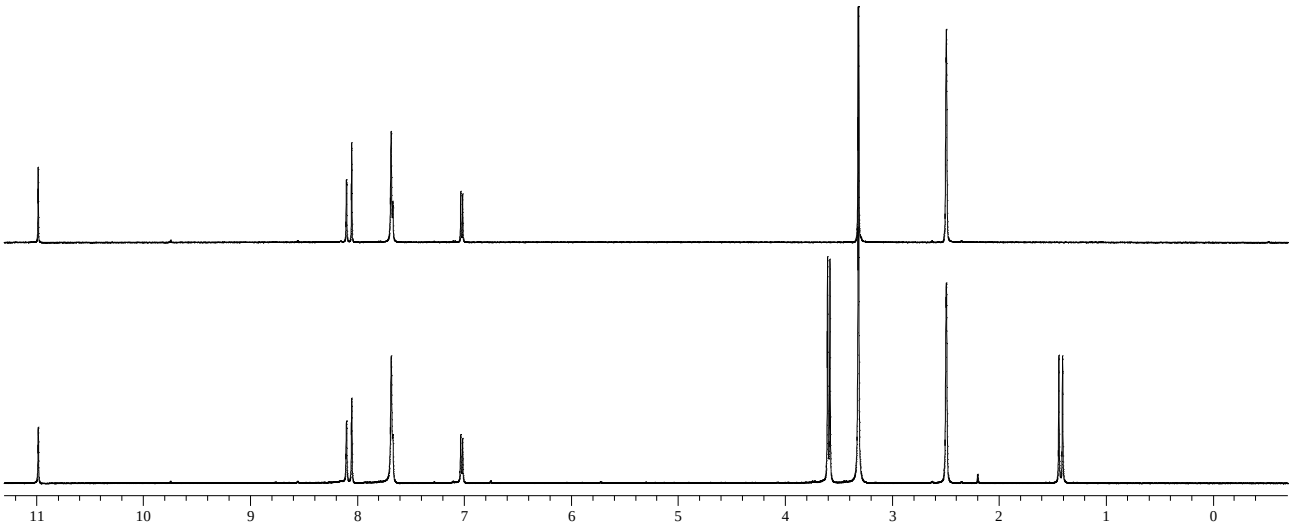
Job Plot between **3** and **DMMP**

X	V_{oxime} (µL)	V_{DMMP}(µL)	ΔA	ΔA x χ
1	200	0	0	0
0,8	175	25	0,22027	0,176216
0,66	150	50	0,4068	0,268488
0,5	100	100	0,60217	0,301085
0,33	50	150	0,81238	0,2680854
0,2	25	175	0,8702	0,17404
0	0	200	0,91742	0



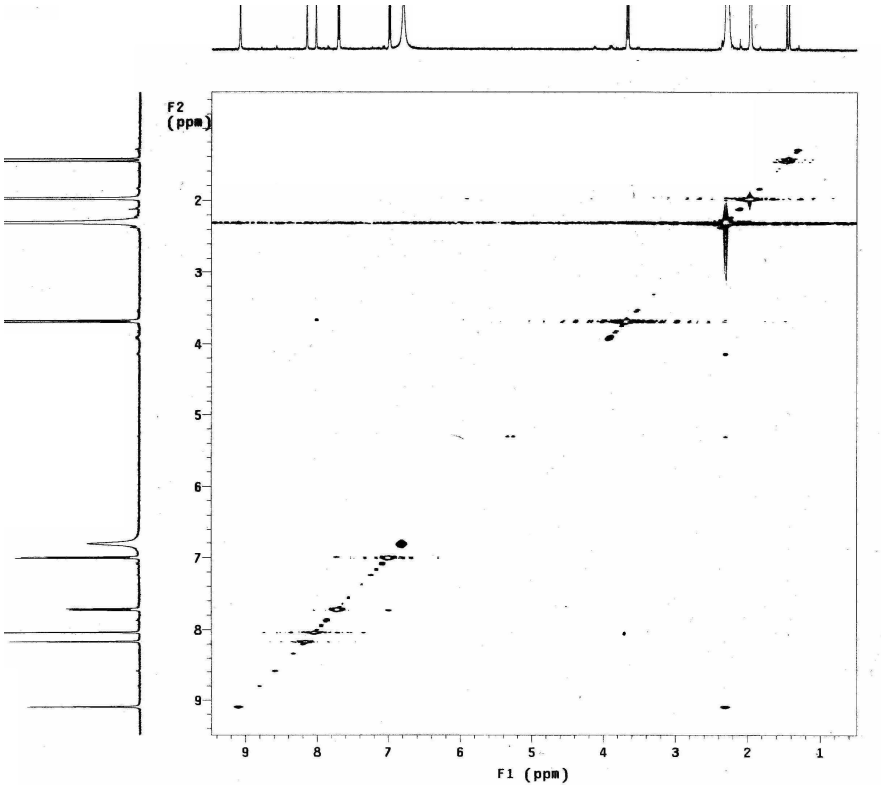


^{1}H NMR spectra of **2** (down) and **2** + 1 eq. of **DMMP** (up) in CD_3CN (1×10^{-3} M)



^{1}H NMR spectra of **2** (down) and **2** + 1 eq. of **DMMP** (up) in DMSO-d_6 (1×10^{-3} M)

T-ROESY of 2 + DMMP



TROESY of **2** + 1 eq. of **DMMP** in CD_3CN (1×10^{-3} M)

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1. (a) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739. (b) Alfimov, M. V.; Gromov, S. P.; Fedorov, Yu. V.; Fedorova, O. A.; Vedernikov, A. I.; Churakov, A. V.; Kuz'mina, L. G.; Howard, J. A. K.; Bossmann, S.; Braun, A.; Woerner, M.; Sears, D. F., Jr.; Saltiel, J. *J. Am. Chem. Soc.* **1999**, *121*, 4992-5000. (c) Fedorova, O. A.; Fedorov, Yu. V.; Vedernikov, A. I.; Gromov, S. P.; Yescheulova, O. V.; Alfimov, M. V.; Woerner, M.; Bossmann, S.; Braun, A.; Saltiel, J. *J. Phys. Chem. A* **2002**, *106*, 6213-6222