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A selective chromo-fluorogenic detection of DFP (a Sarin and Soman mimic) and DCNP (a Tabun mimic) with a unique probe based on a boron dipyrromethene (BODIPY) dye

Andrea Barba-Bon, Ana M.Costero, Salvador Gil, Ramón Martínez-Máñez and Félix Sancenón

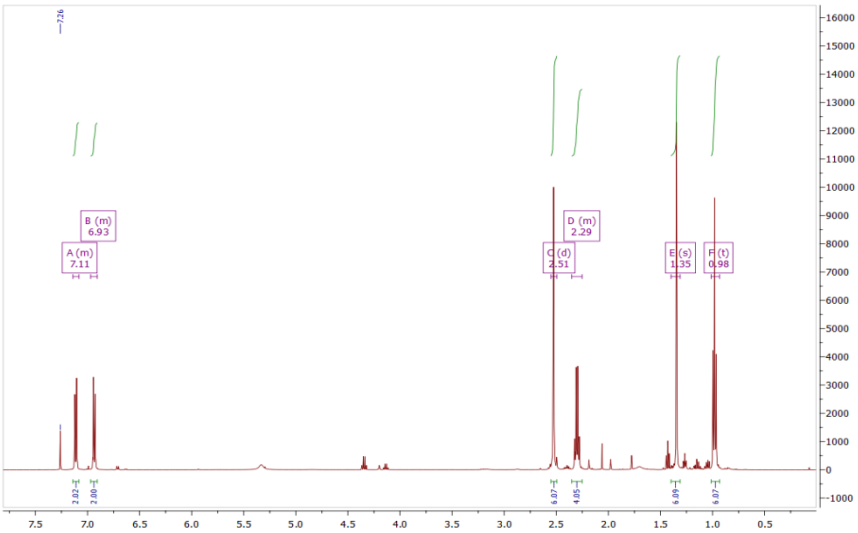

Figure 1. ^{1}H NMR spectrum of **P1** ($CDCl_3$).

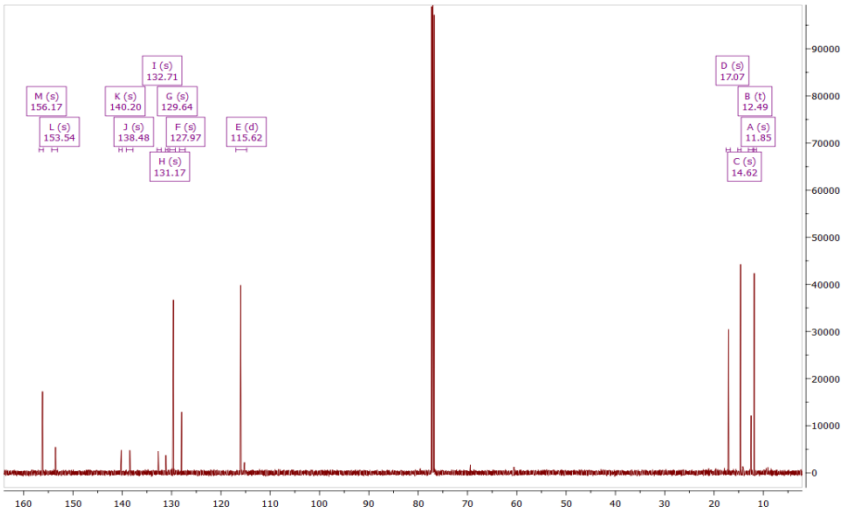

Figure 2. ^{13}C NMR spectrum of **P1** ($CDCl_3$).

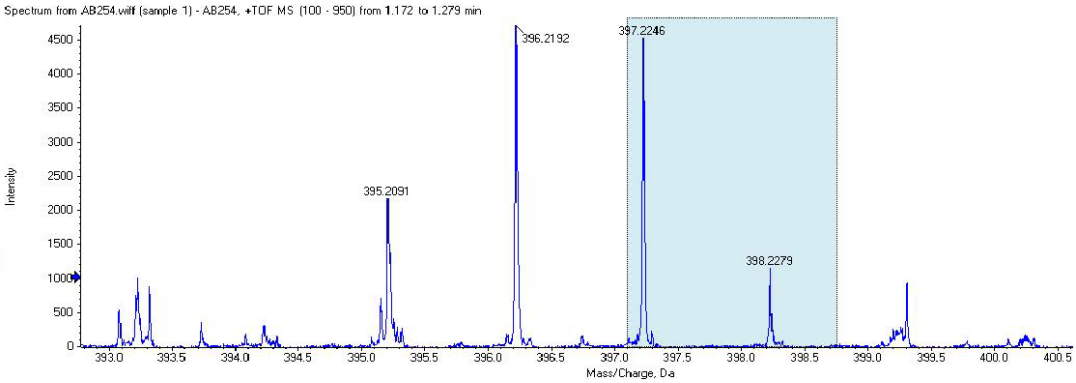

Figure 3. MS of **P1**.

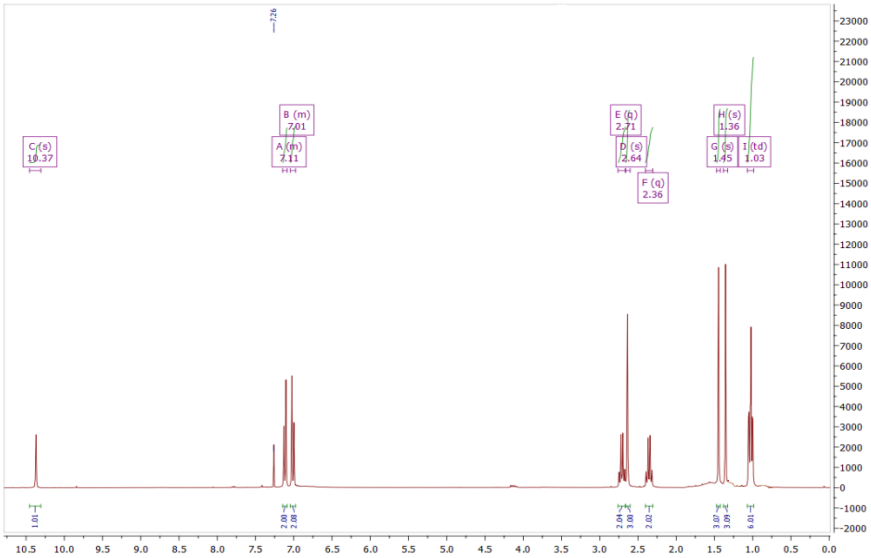

Figure 4. ^{1}H NMR spectrum of **P2** ($CDCl_3$).

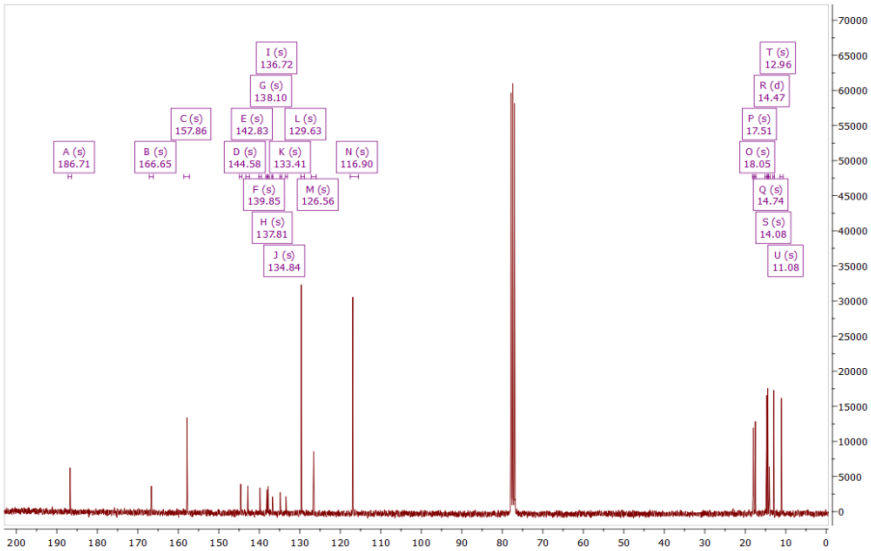

Figure 5. ^{13}C NMR spectrum of **P2** ($CDCl_3$).

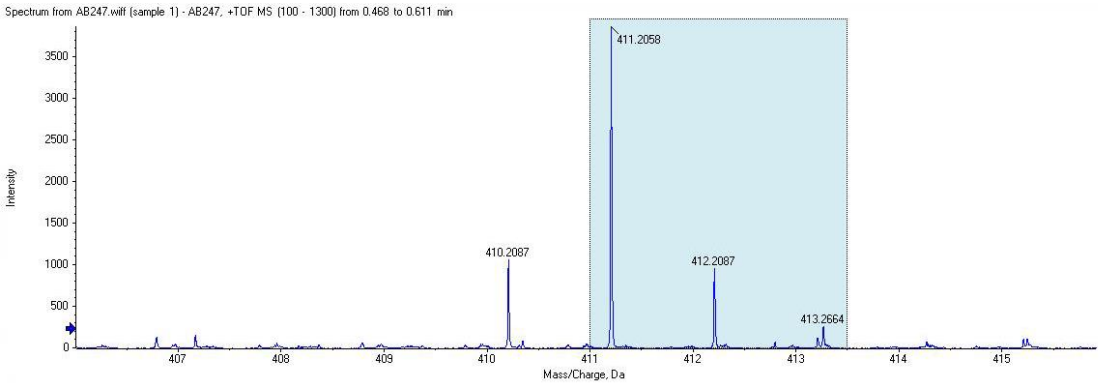

Figure 6. MS of **P2**.

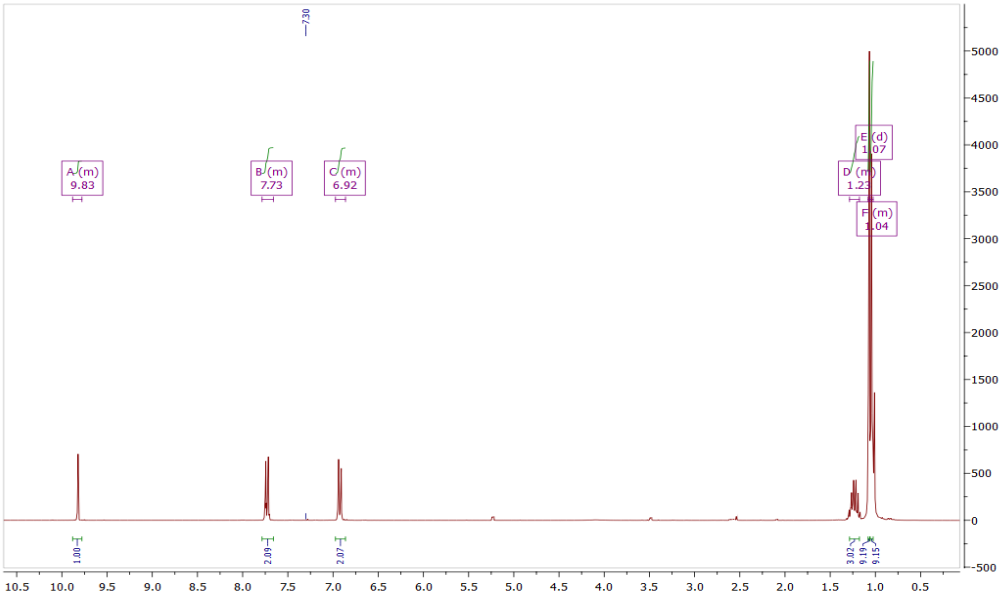

Figure 7. ^{1}H NMR spectrum of aldehyde **4** ($CDCl_3$).

Figure 8. ^{13}C NMR spectrum of aldehyde **4** ($CDCl_3$).

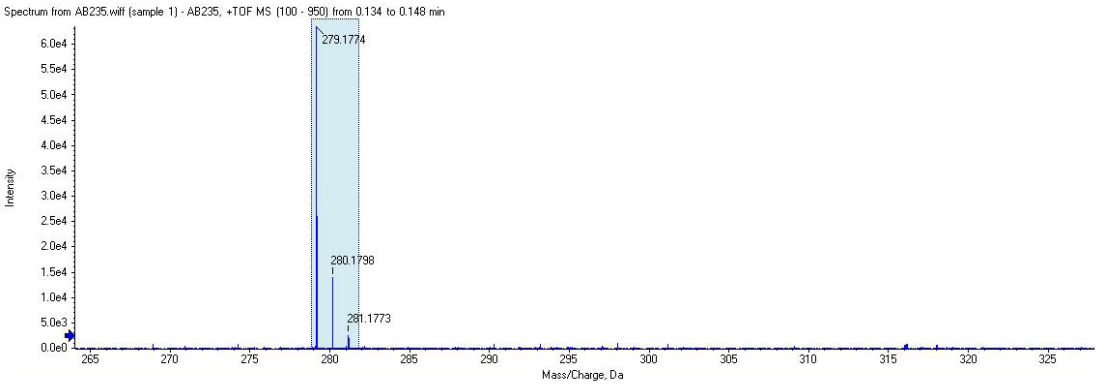

Figure 9. MS of aldehyde **4**.

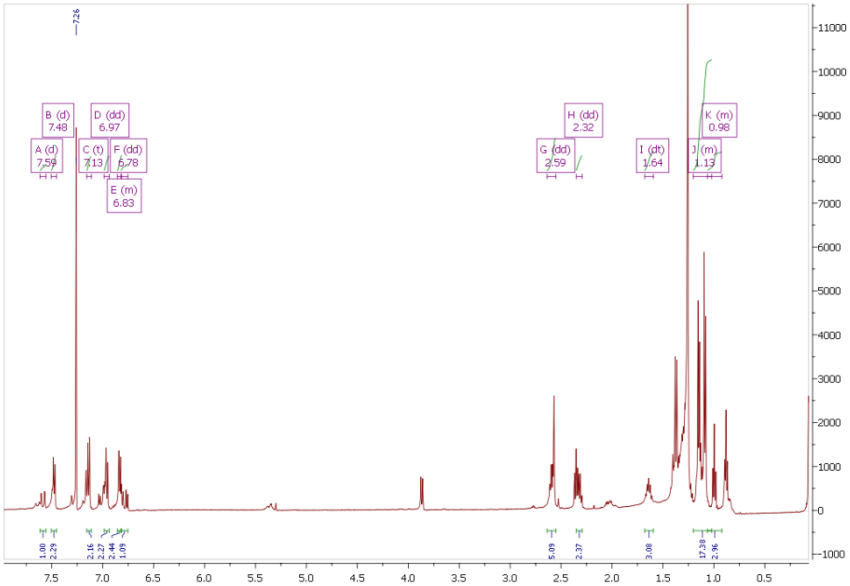

Figure 10. ^{1}H NMR spectrum of **P3** ($CDCl_3$).

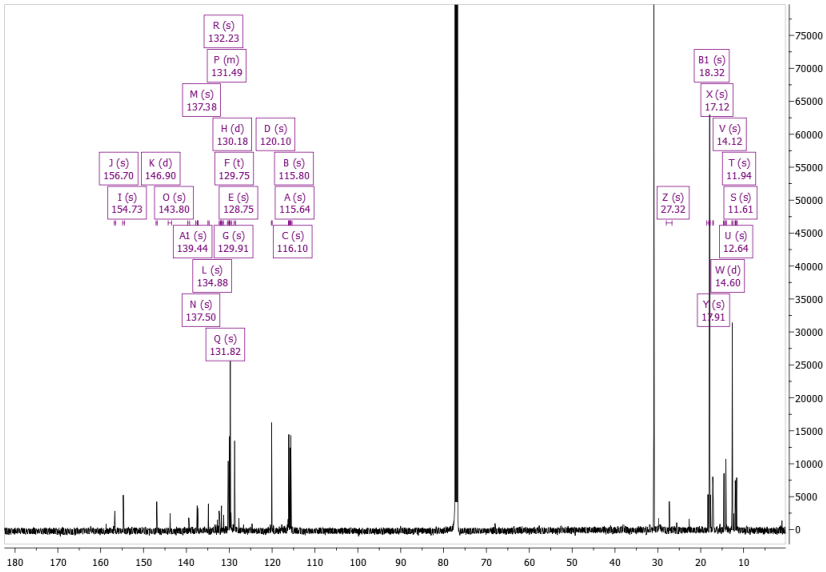

Figure 11. ^{13}C NMR spectrum of **P3** ($CDCl_3$).

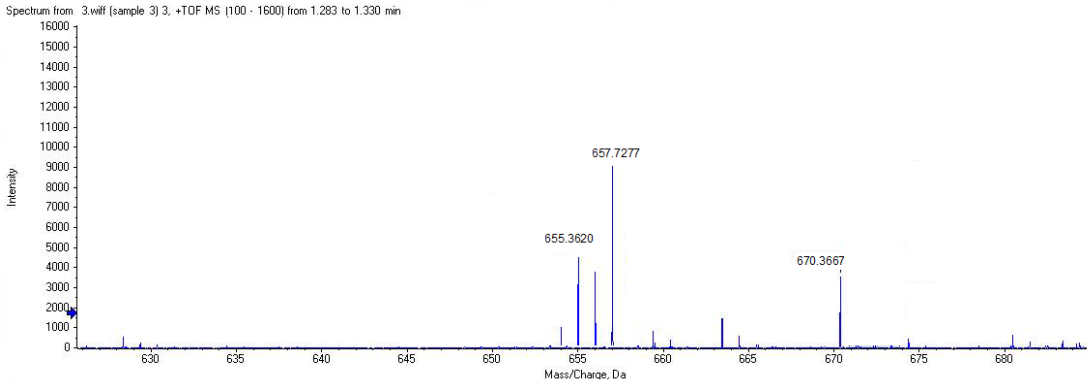

Figure 12. MS of **P3**.

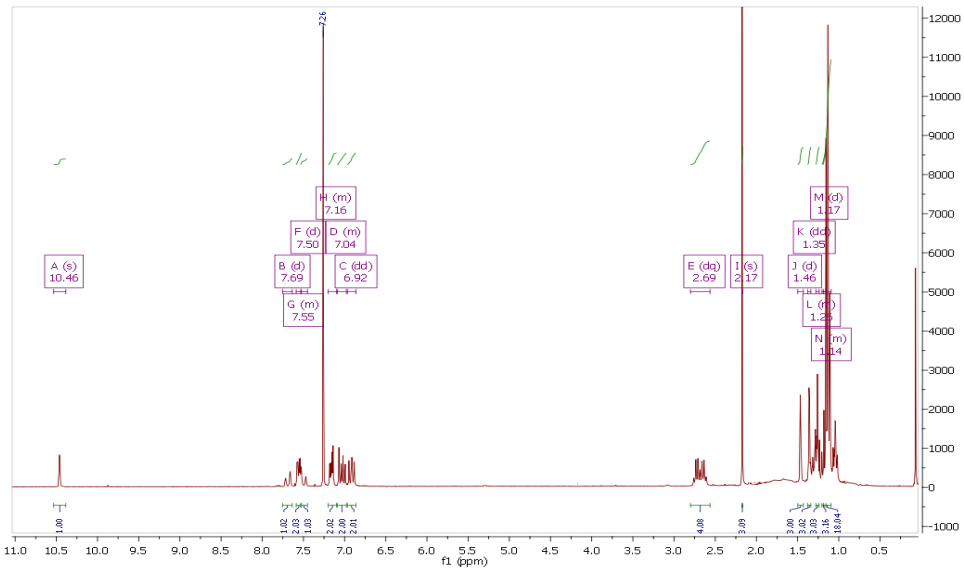

Figure 13. ^{1}H NMR spectrum of **P4** ($CDCl_3$).

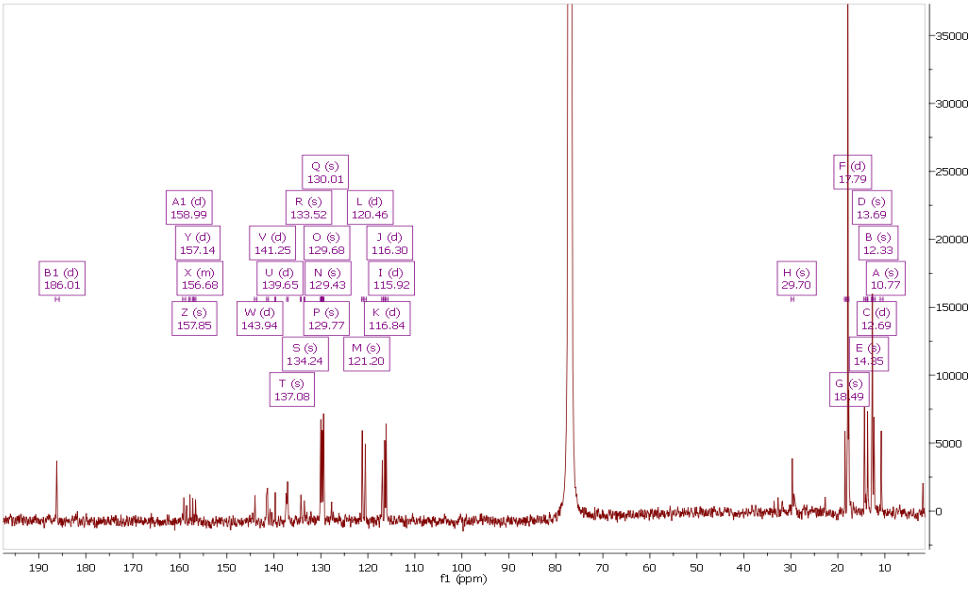

Figure 14. ^{13}C NMR spectrum of **P4** ($CDCl_3$).

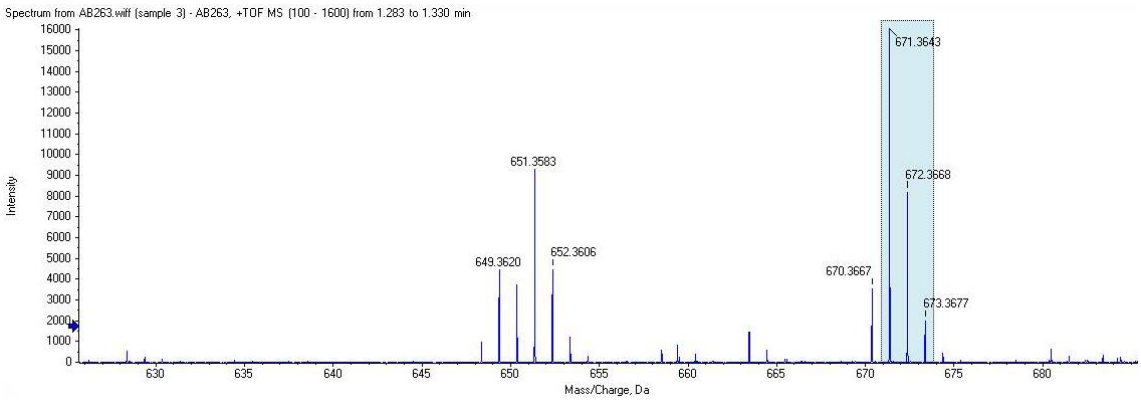

Figure 15. MS of **P4**.

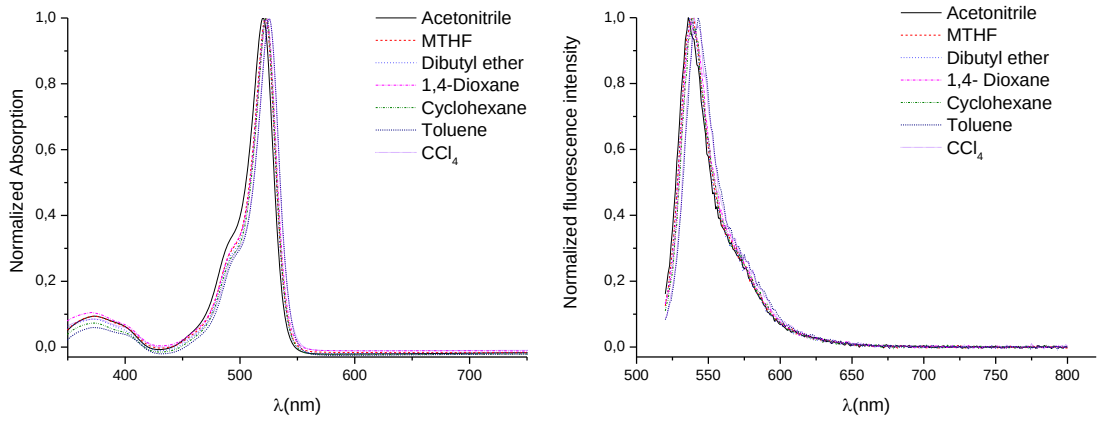

Figure 16. Absorption (left) and fluorescence emission (right) spectra of **P1** in different solvents. The intensities in this figure are normalized to the same value at the wavelength of maximum intensity.

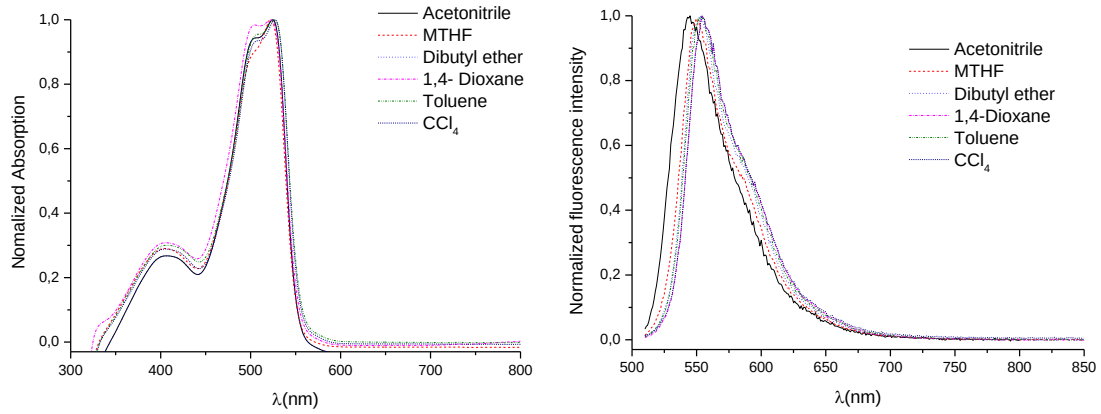

Figure 17. Absorption (left) and fluorescence emission (right) spectra of **P2** in different solvents. The intensities in this figure are normalized to the same value at the wavelength of maximum intensity.

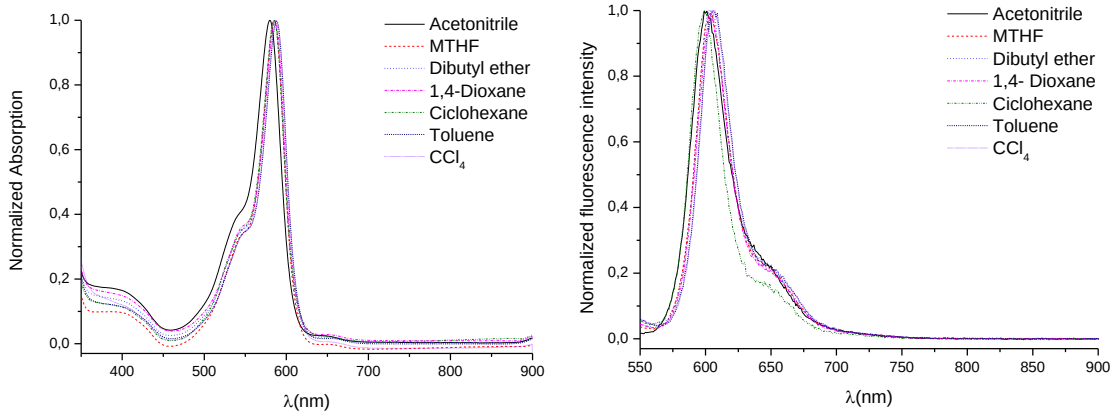

Figure 18. Absorption (left) and fluorescence emission (right) spectra of **P3** in different solvents. The intensities in this figure are normalized to the same value at the wavelength of maximum intensity.

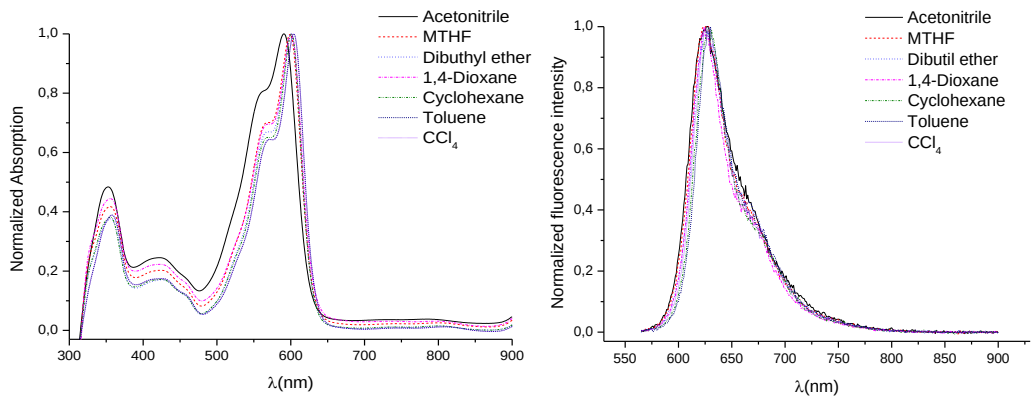

Figure 19. Absorption (left) and fluorescence emission (right) spectra of **P4** in different solvents. The intensities in this figure are normalized to the same value at the wavelength of maximum intensity.

Table 1. Photophysical parameters of compounds **P1**-**P4** in different solvents.

Probe	Solvent	λ_{abs}(max/nm)	λ_{em}(max/nm)	$\Delta\upsilon$ [a] (cm^{-1})	log ε	ϕ [b]
P1	Acetonitrile	520.0	535.9	570	5.00	0.62
	MTHF	522.0	540.0	638	4.98	0.61
	Dibutyl ether	522.0	537.0	535	5.03	0.63
	1,4-Dioxane	523.0	538.0	533	4.98	0.63
	Cyclohexane	523.5	538.9	545	5.06	0.55
	Toluene	525.5	542.9	609	5.01	0.60
	CCl4	525.5	540.1	514	5.04	0.57
P2	Acetonitrile	517.0	545.0	993	4.87	0.46
	MTHF	522.5	549.8	950	4.92	0.53
	Dibutyl ether	524.5	552.9	979	4.93	0.47
	1,4-Dioxane	522.5	552.9	1022	4.90	0.48
	Cyclohexane	-[c]	-	-	-	-
	Toluene	526.5	554.0	943	4.89	0.53
	CCl4	527.0	552.8	886	4.99	0.54
P3	Acetonitrile	580.0	600.2	580	4.87	0.60
	MTHF	585.0	603.8	490	4.85	0.62
	Dibutyl ether	585.0	603.3	519	4.92	0.62
	1,4-Dioxane	586.5	603.8	489	4.87	0.65
	Cyclohexane	585.0	598.9	518	4.43	0.56
	Toluene	588.0	605.8	499	4.83	0.62
	CCl4	588.5	604.8	460	4.87	0.59
P4	Acetonitrile	591.0	624.8	915	4.92	0.52
	MTHF	599.0	625.9	717	4.88	0.54
	Dibuthyl ether	600.5	627.3	711	5.00	0.54
	1,4-Dioxane	600.5	628.0	729	4.95	0.58
	Cyclohexane	601.0	624.8	634	4.98	0.57
	Toluene	604.0	627.9	633	4.91	0.58
	CCl_4	604.1	629.9	680	5.02	0.56

[a] Stokes shift
[b] Quantum yields were calculated using rhodamine B in ethanol (ϕ_{EtOH}= 0.49) for **P1** and **P2** and rhodamine 101 in ethanol + 0.01% HCl (ϕ_{EtOH}= 1.0) for **P3** and **P4** as standard.
[c] **P2** was not soluble in Cyclohexane.

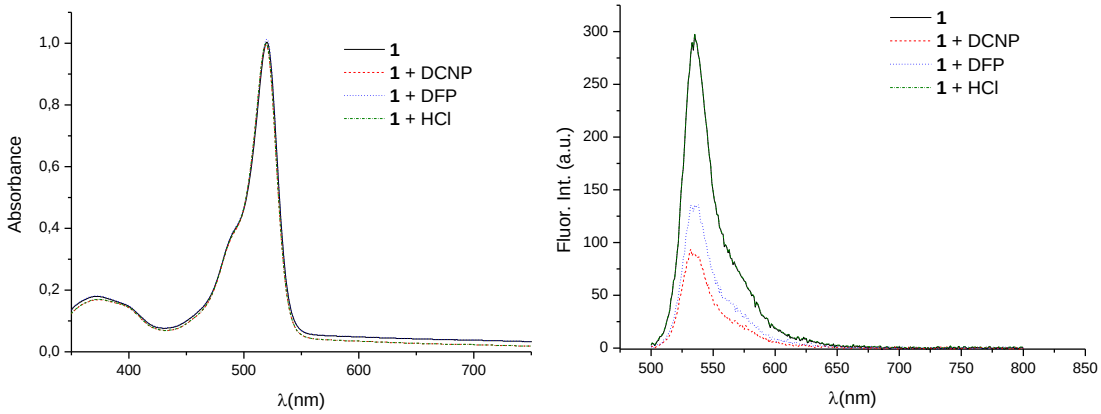

Figure 20. Absorption spectra (left) and fluorescence (right) spectra (λ_{ex}=490 nm) of **P1** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) alone and in the presence of DCNP, DFP and acid media.

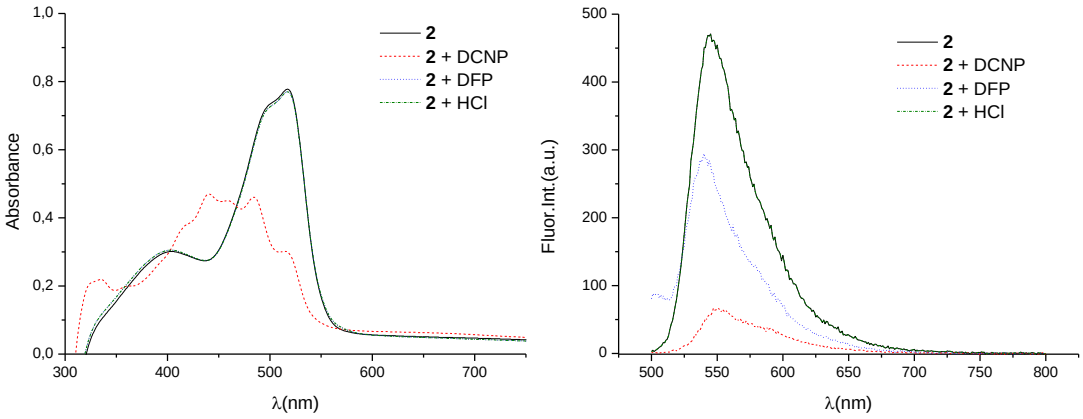

Figure 21. Absorption spectra (left) and fluorescence (right) spectra (λ_{ex}=490 nm) of **P2** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) alone and in the presence of DCNP, DFP and acid media.

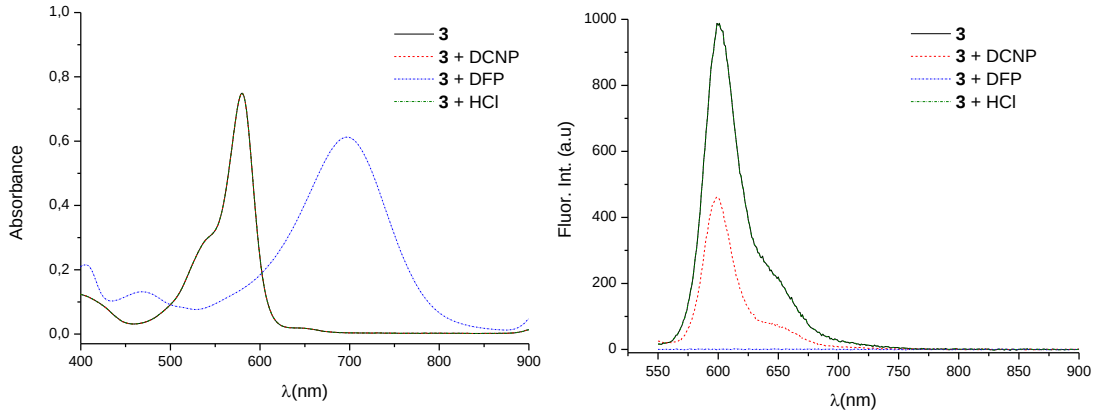

Figure 22. Absorption spectra (left) and fluorescence (right) spectra (λ_{ex}=540 nm) of **P3** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) alone and in the presence of DCNP, DFP and acid media.

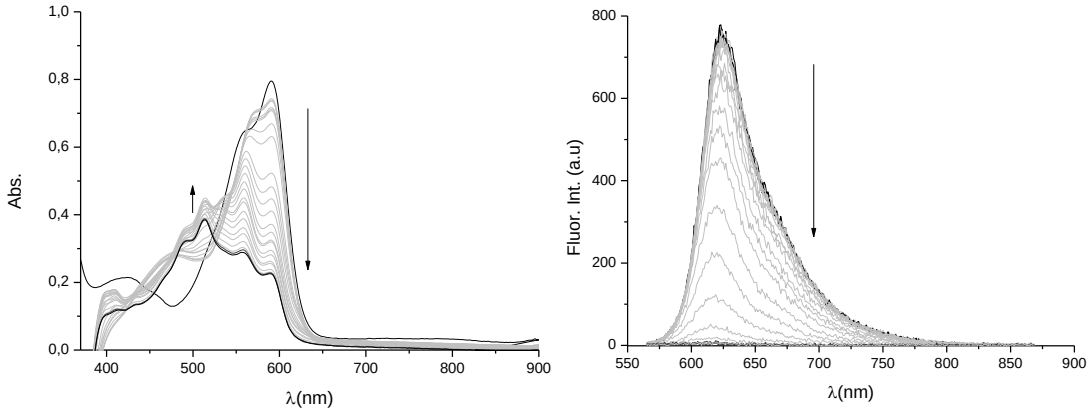

Figure 23. Absorption (left) and fluorescence (right) response (λ_{ex}=555 nm) of **P4** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) to incremental amounts of DCNP.

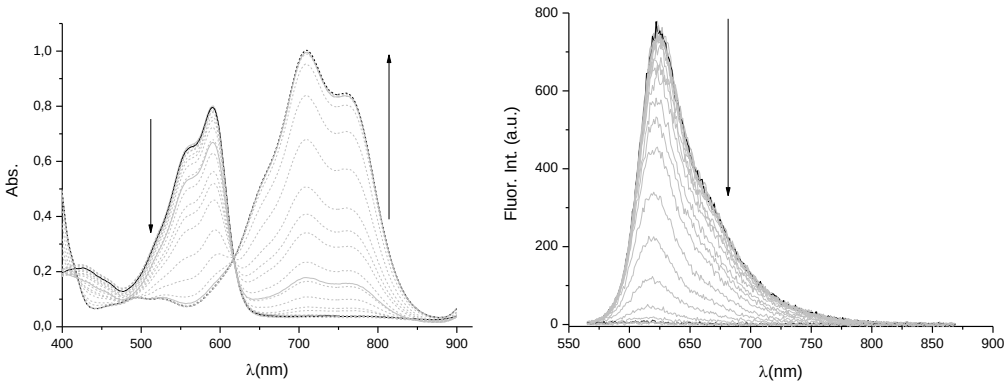

Figure 24. Absorption (left) and fluorescence (right) response (λ_{ex}=555 nm) of **P4** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) to incremental amounts of DFP.

Table 2. Photophysical parameters of **P4** in different solvents alone and in presence of DCNP and DFP.

						DCNP				**DFP**			
Dye	Solvent	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$
P4	Acetonitrile	591.0	4.92	624.8	0.52	515.0	4.56	625.0	$5\cdot10^{-4}$	715.5	5.00	625.0	$5\cdot10^{-4}$
	MTHF	599.0	4.88	625.9	0.54	522.0	4.45	625.9	$6\cdot10^{-4}$	725.8	4.92	625.9	$6\cdot10^{-4}$
	Dibutyl ether	600.5	5.00	627.3	0.54	523.0	4.81	624.7	$2\cdot10^{-4}$	720.1	5.12	624.7	$2\cdot10^{-4}$
	1,4-Dioxane	600.5	4.95	628.0	0.58	522.5	4.70	627.5	$1\cdot10^{-4}$	718.9	5.01	627.5	$1\cdot10^{-4}$
	Cyclohexane	601.0	4.98	624.8	0.57	521.5	4.37	625.3	$3\cdot10^{-4}$	720.3	5.08	625.3	$3\cdot10^{-4}$
	Toluene	604.0	4.91	627.9	0.58	525.5	4.69	626.7	$7\cdot10^{-4}$	722.5	5.10	626.7	$7\cdot10^{-4}$
	CCl_4	604.1	5.02	629.9	0.56	525.5	4.84	626.5	$2\cdot10^{-4}$	722.9	5.09	626.5	$2\cdot10^{-4}$

[a] quantum yields were calculated using rhodamine 101 in ethanol + 0.01% HCl (ϕ_{EtOH}= 1.0) as standard.

Table 3. Photophysical parameters of compounds **P1-P3** in different solvents, alone and in the presence of nerve agent mimics.

						DCNP				DFP			
Dye	Solvent	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$	λ_{abs} (nm)	log ε	λ_{em} (nm)	$\phi^{[a]}$
P1	Acetonitrile	520.0	5.00	535.9	0.62	520.0	5.00	535.9	0.23	520.0	5.00	535.9	0.24
	MTHF	522.0	4.98	540.0	0.61	522.0	4.99	540.1	0.24	522.0	4.99	540.0	0.25
	Dibutyl ether	522.0	5.03	537.0	0.63	522.0	5.03	537.1	0.24	522.0	5.03	538.0	0.26
	1,4-Dioxane	523.0	4.98	538.0	0.63	523.0	4.99	538.0	0.27	523.0	4.99	538.0	0.29
	Cyclohexane	523.5	5.06	538.9	0.55	523.5	5.06	538.9	0.20	523.5	5.06	538.9	0.24
	Toluene	525.5	5.01	542.9	0.60	525.5	5.00	542.9	0.30	525.5	5.01	543.0	0.31
	CCl_4	525.5	5.04	540.1	0.57	525.5	5.04	540.1	0.24	525.5	5.04	540.1	0.25
P2	Acetonitrile	517.0	4.87	545.0	0.46	489.7	4.66	549.6	0.14	517.0	4.87	545.0	0.20
	MTHF	522.5	4.92	549.8	0.53	487.5	4.75	547.6	0.09	522.5	4.92	549.8	0.25
	Dibutyl ether	524.5	4.93	552.9	0.47	490.5	4.81	553.9	0.07	524.5	4.93	552.98	0.22
	1,4-Dioxane	522.5	4.90	552.9	0.48	493.0	4.70	550.7	0.06	522.5	4.90	551.9	0.21
	Cyclohexane	-[b]	-	-	-	-	-	-	-	-	-	-	-
	Toluene	526.5	4.89	554.0	0.53	488.5	4.72	539.1	0.15	526.5	4.89	554.0	0.27
	CCl_4	527.0	4.99	552.8	0.54	472.0	4.69	556.0	0.04	527.0	4.99	552.64	0.29
P3	Acetonitrile	580.0	4.87	600.2	0.60	580.0	4.87	600.2	0.33	697.0	4.77	-	-
	MTHF	585.0	4.85	603.8	0.62	585.0	4.85	603.8	0.31	686.0	4.63	-	-
	Dibutyl ether	585.0	4.92	603.3	0.62	585.0	4.92	603.3	0.36	585.0	4.92	-	-
	1,4-Dioxane	586.5	4.87	603.8	0.65	586.5	4.87	603.8	0.34	691.0	4.56	-	-
	Cyclohexane	585.0	4.43	598.9	0.56	585.0	4.43	598.9	0.18	690.0	4.29	-	-
	Toluene	588.0	4.83	605.8	0.62	588.0	4.83	605.8	0.37	679.0	4.68	-	-
	CCl_4	588.5	4.87	604.8	0.59	588.5	4.87	604.8	0.32	694.5	4.69	-	-

[a] Quantum yields were calculated using rhodamine B in ethanol (ϕ_{EtOH}= 0.49) for **P1** and **P2** and rhodamine 101 in ethanol + 0.01% HCl (ϕ_{EtOH}= 1.0) for **P3** as standard.
[b] **P2** was not soluble in Cyclohexane.

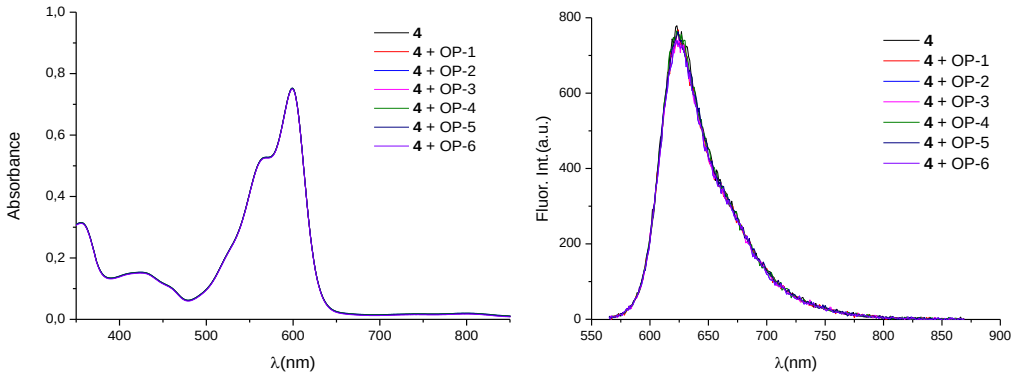

Figure 25. Absorbance (left) and fluorescence (λ_{ex}=555 nm) (right) spectra of **P4** (1.0 x 10^{-5} mol dm^{-3} in CH_3CN) alone and in presence of organo-phosphorous derivatives (OP1-OP6).

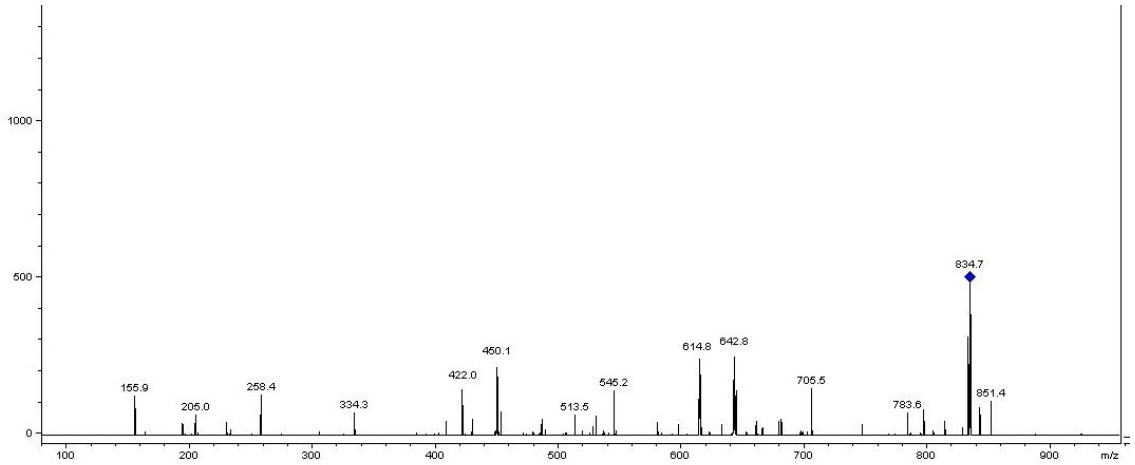

Figure 26. Mass Spectra of **P4** +DCNP; [M^++1] = 834.7

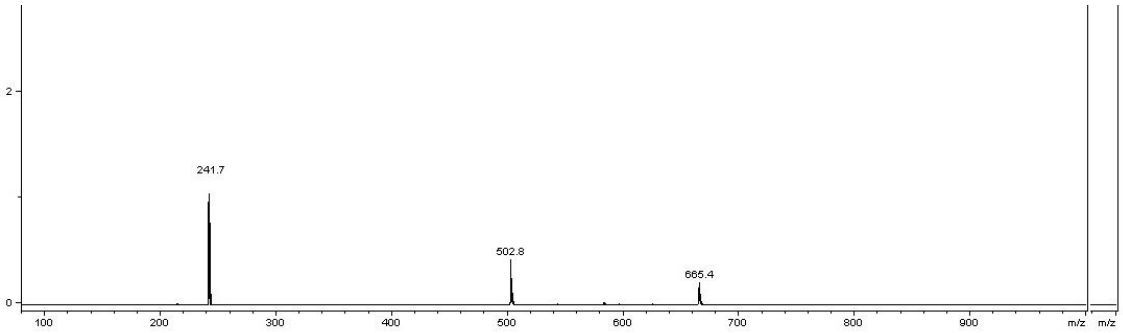

Figure 27.Mass Spectra of **P4** + DFP; [M^+-HCO+OH] = 655.4

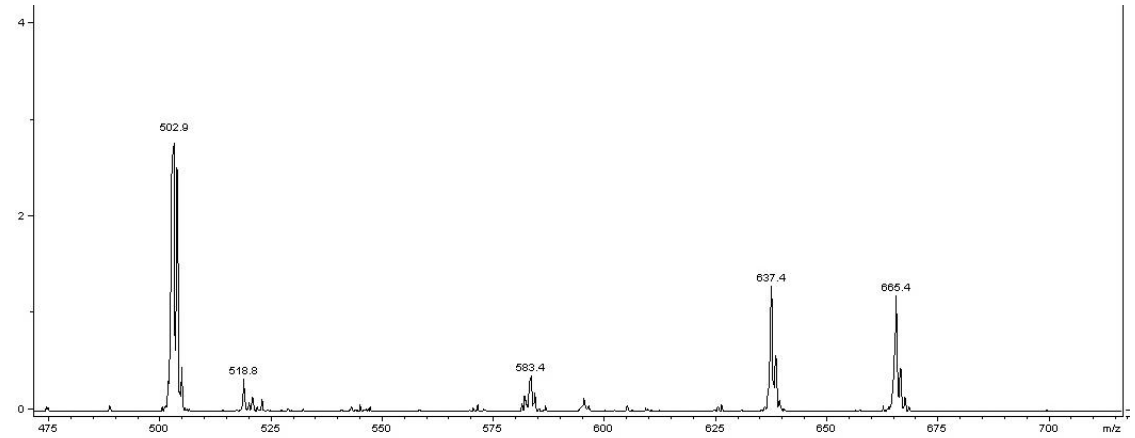

Figure 28.Mass Spectra of **P3** + DFP; [M^++2] = 655.4; [M^+-CO] = 637.4

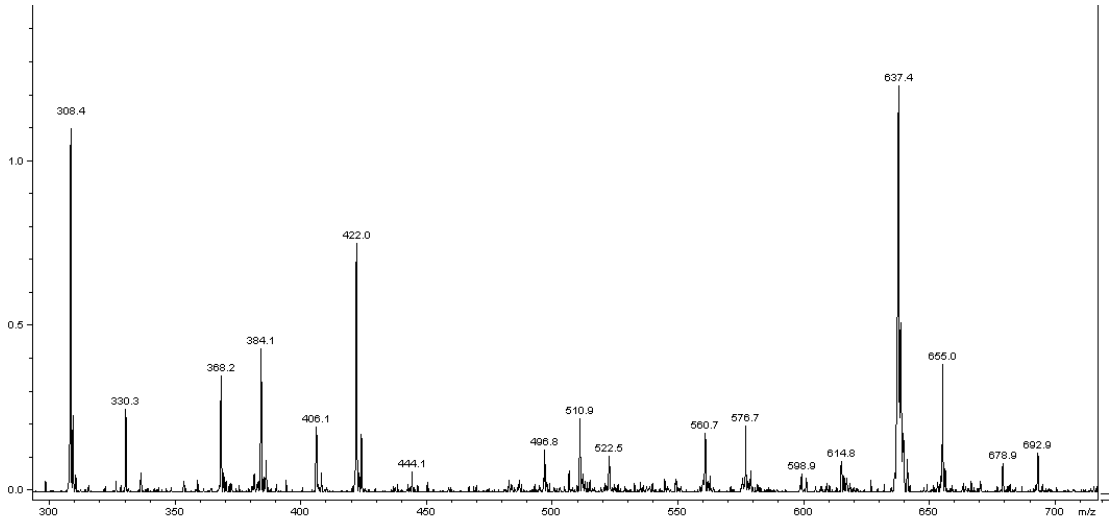

Figure 29.Mass Spectra of **P2** + DCNP; $[M^{+}+2\ MeOH] = 637.4$

Mass Spectra were determined in a Bruker ESQUIRE 3000 PLUS Ion-trap Mass Spectrometer.
Characteristics:
- Mass Spectrometer ion-trap is coupled to a high performance liquid chromatograph AGILENT 1100 (HPLC-MS).
- The equipment has an electrospray (ESI) source.
-Direct infusion of the sample.
Nebulizer: 10psi
Dry gas: 6 l / min
Dry temperature: 3250ºC
Target: 30000
Scan: 80-1000 m / z