Electronic Supplementary Material (ESI) for New Journal of Chemistry.

New flexible molecular probes bearing dansyl and TEMPO moieties for host-guest interactions in solution and gels

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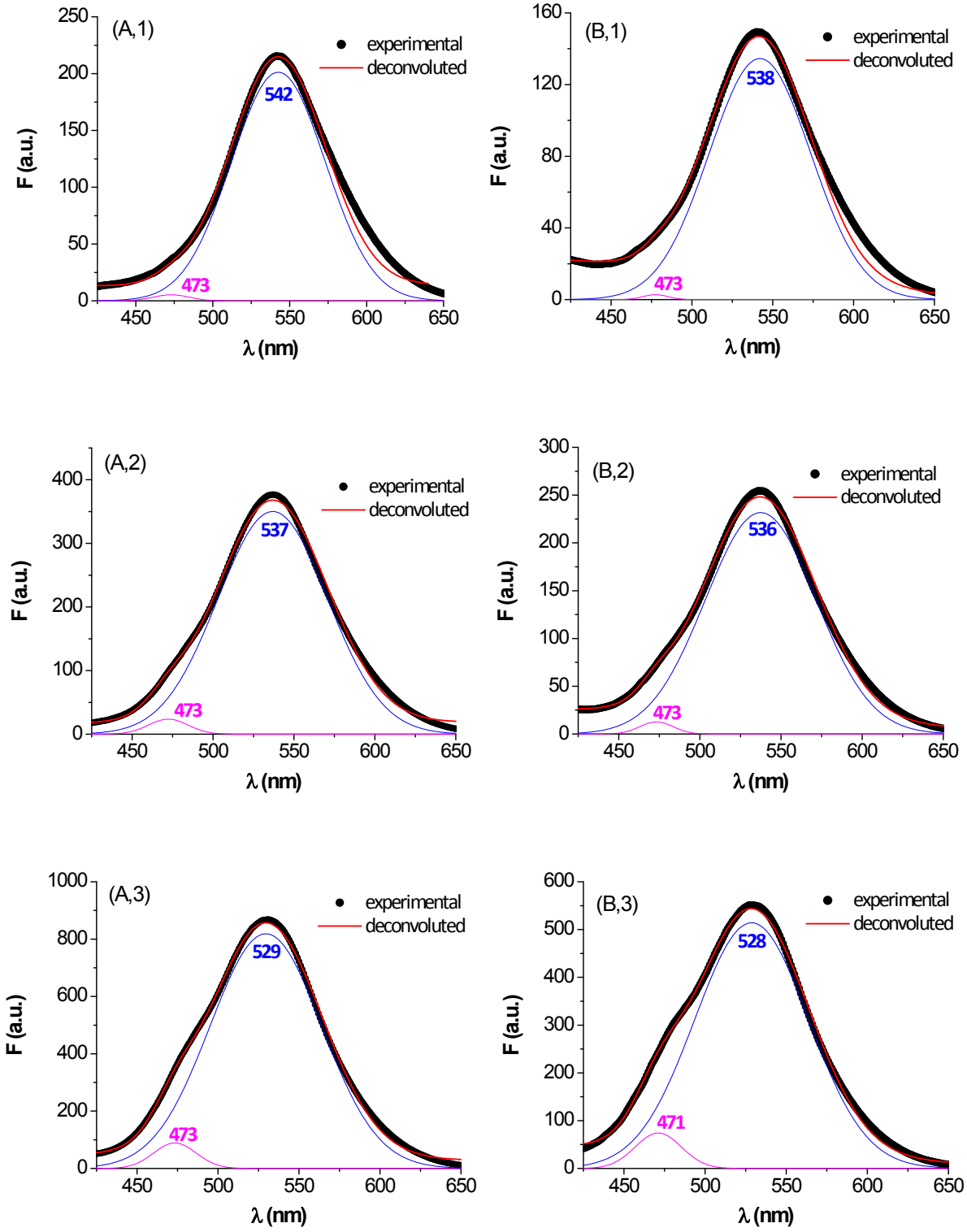


Fig. S1. Deconvolution of the fluorescence spectra of (A) $DA_{1.7}$ and (B) $DA_{1.7}T$ in water in the absence (1) and in the presence of β-CD at 10^{-3} M (2) and 10^{-2} M (3) concentrations.

Table S1. Position (λ, in nm) and relative area (A, in %) of the two fluorescence bands obtained by deconvolution of the emission spectra of $DA_{1.n}$ and $DA_{1.n}T$ in the absence and in the presence of β-CD

	$DA_{1.n}$				**$DA_{1.n}T$**			
[β-CD] (M)	**λ_1**	**A_1**	**λ_2**	**A_2**	**λ_1**	**A_1**	**λ_2**	**A_2**
0	473	0.9	542	99.1	473	0.3	538	99.7
10^{-3}	473	2.4	537	97.6	473	1.7	536	98.3
10^{-2}	473	4.2	529	95.8	471	5.6	528	94.4

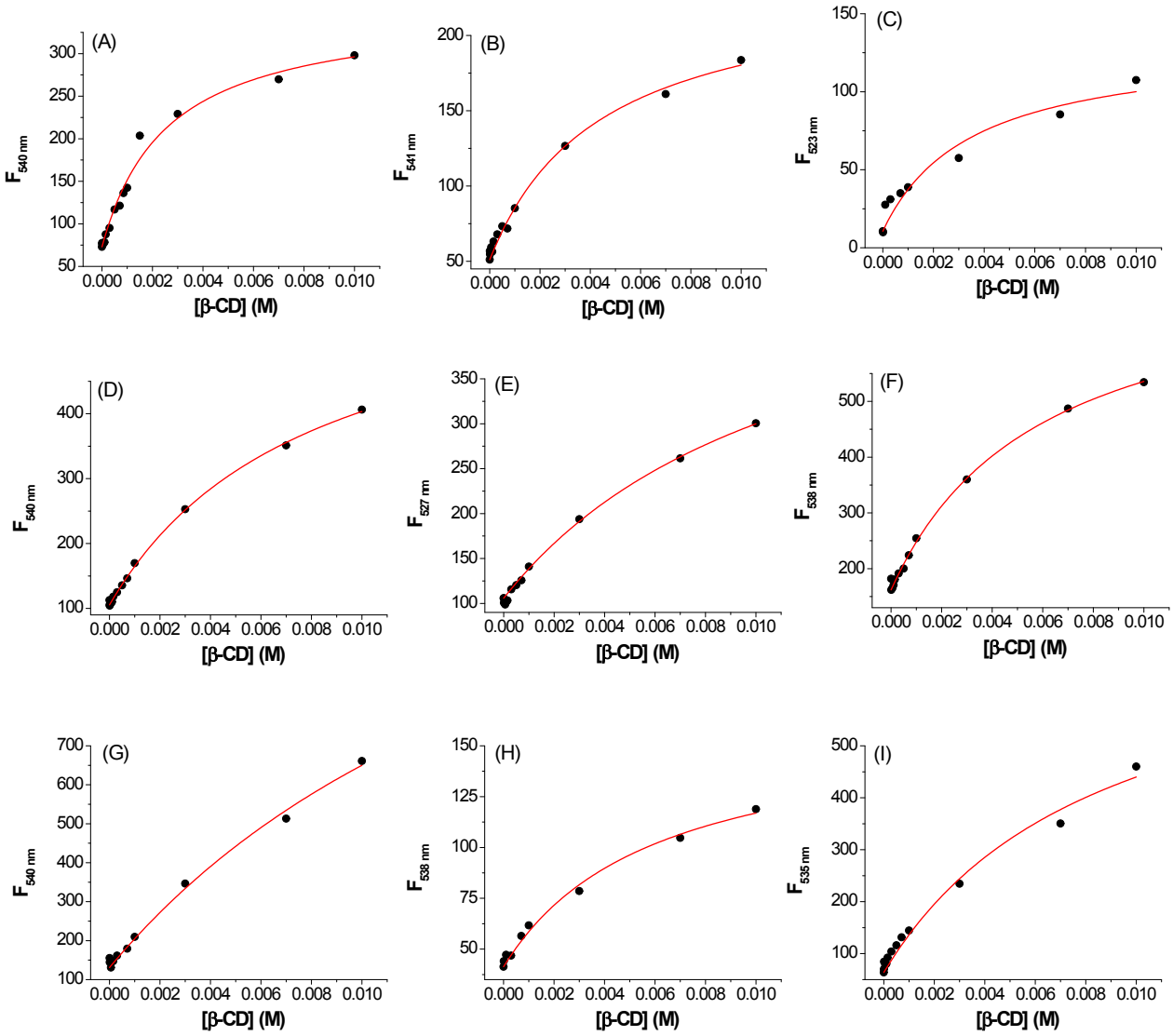
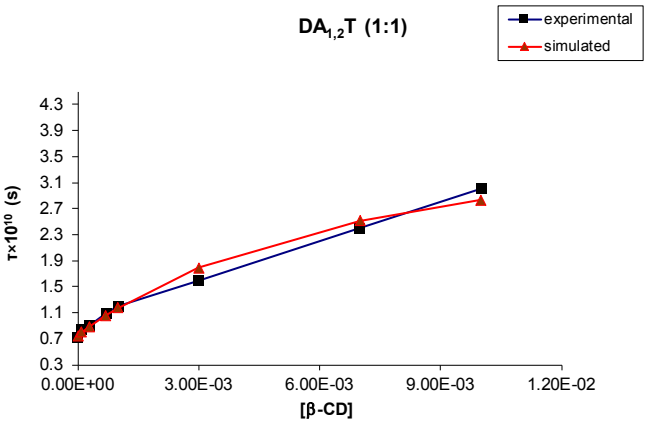
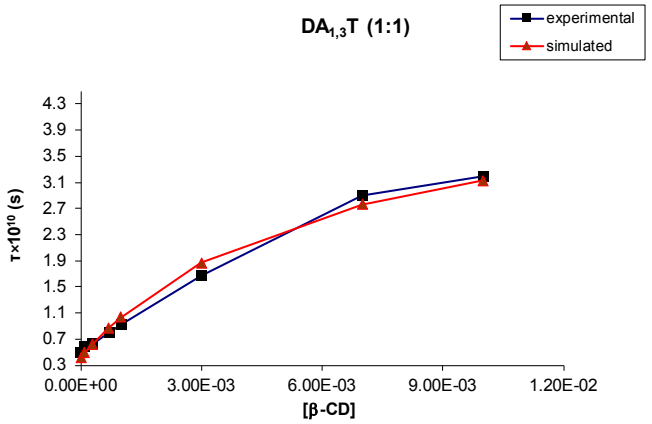
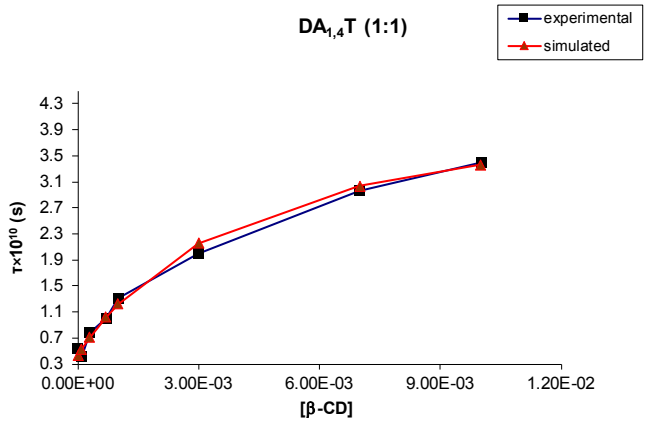
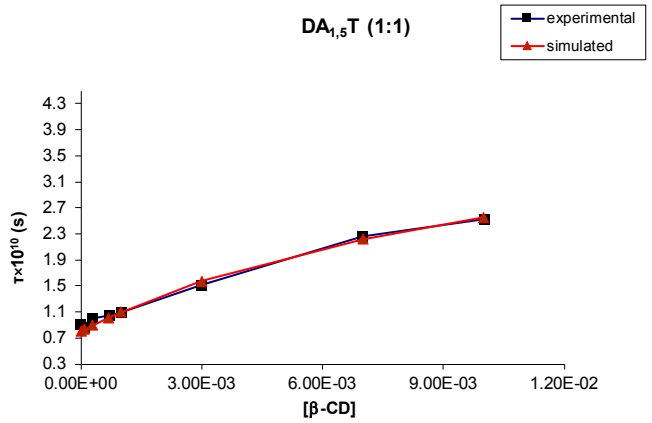


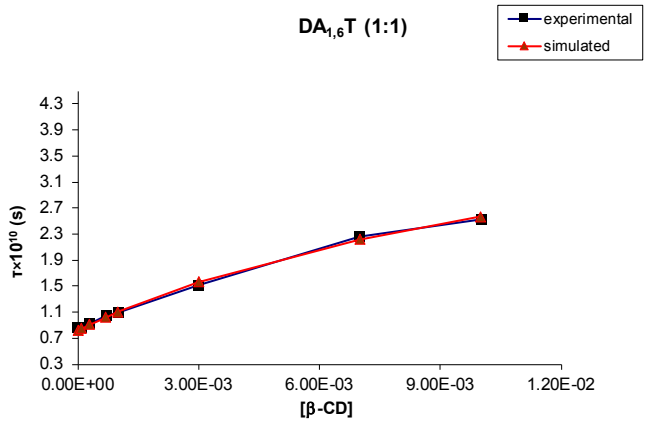
Fig. S2. Dependence of the normalized fluorescence emission of $DA_{1.n}T$ probes on the cyclodextrin concentration. The solid lines represent the best fits according to eq. (3) for (A) $DA_{1.2}T$, (B) $DA_{1.3}T$, (C) $DA_{1.4}T$, (D) $DA_{1.5}T$, (E) $DA_{1.6}T$, (F) $DA_{1.7}T$, (G) $DA_{1.8}T$, (H) $DA_{1.10}T$, (I) $DA_{1.12}T$.


DA1,2T (1:1)
experimental
simulated
τ×10¹⁰ (s)
4.3
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]


DA1,3T (1:1)
experimental
simulated
τ×10¹⁰ (s)
4.3
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]


DA1,4T (1:1)
experimental
simulated
τ×10¹⁰ (s)
4.3
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]


DA1,5T (1:1)
experimental
simulated
τ×10¹⁰ (s)
4.3
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]


DA1,6T (1:1)
experimental
simulated
τ×10¹⁰ (s)
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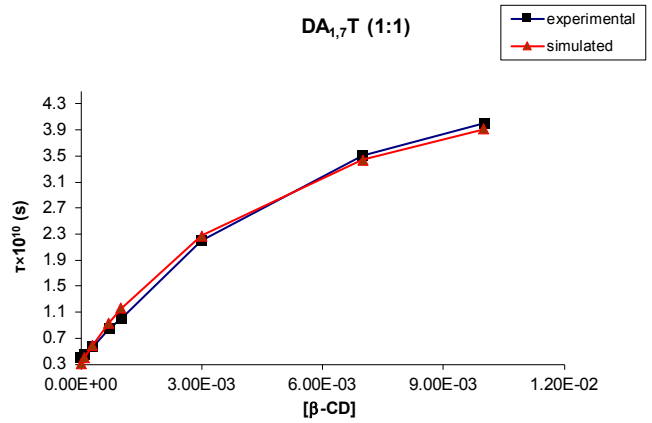
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]


DA1,7T (1:1)
experimental
simulated
τ×10¹⁰ (s)
4.3
3.9
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0.3
0.00E+00
3.00E-03
6.00E-03
9.00E-03
1.20E-02
[β-CD]

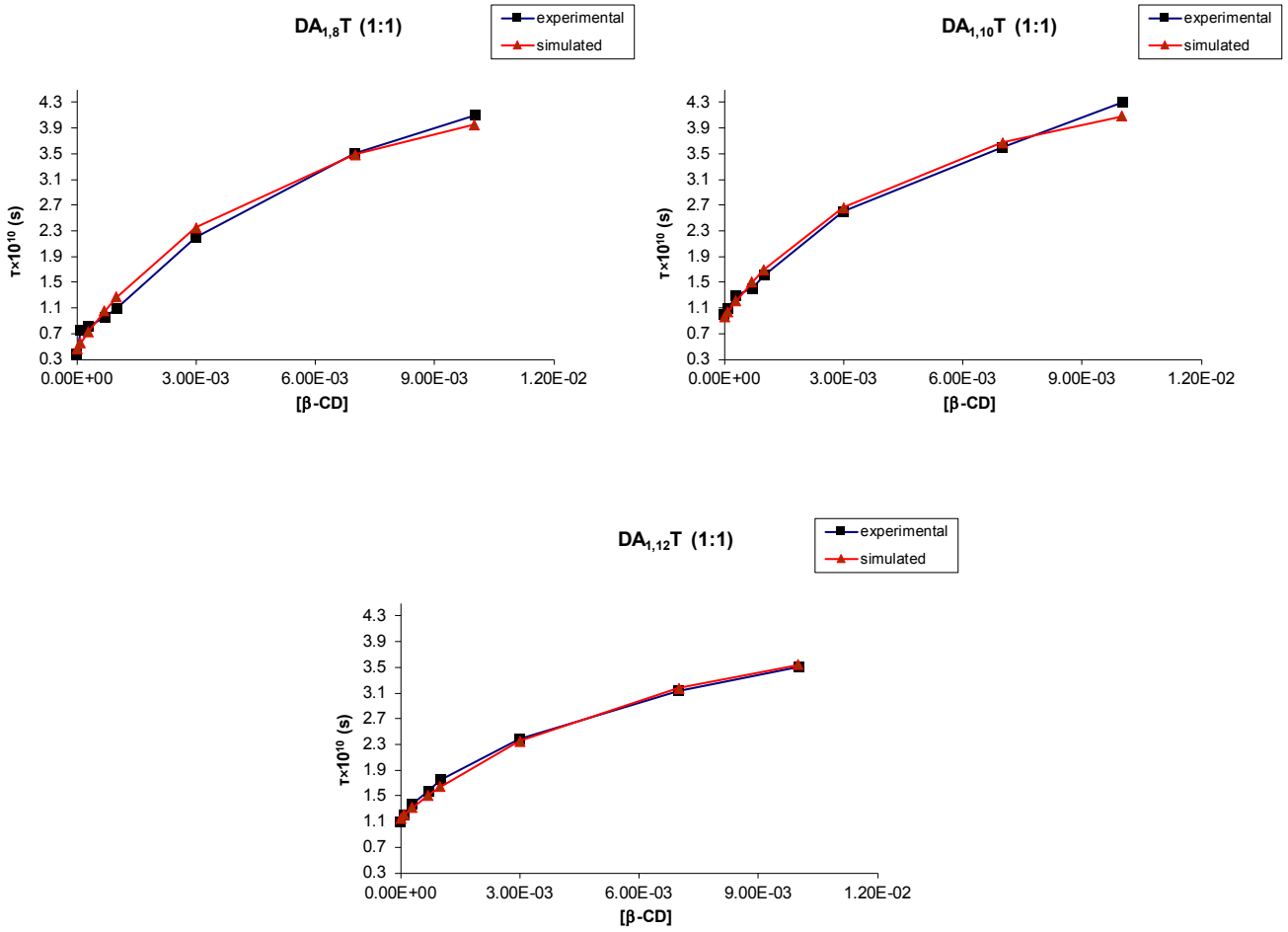


Fig. S3. Dependence of the rotational correlation time of $DA_{1.n}T$ probes on the cyclodextrin concentration.

NMR spectra of $DA_{1.3}$ and $DA_{1.3}T$ (reduced with hydrazine) in the absence and in the presence of β-cyclodextrin

The NMR spectra of $DA_{1.3}$ and $DA_{1.3}T$ (reduced with hydrazine) have been recorded in the absence and in the presence of β-CD in deuterated water and in DMSO. This allowed us to evidence the differences in chemical shifts of the proton signals assigned to the dansyl group. Unfortunately, the corresponding dual probe, $DA_{1.3}T$, is not soluble in deuterated water at concentrations that would allow us to record NMR spectra. While fluorescence and EPR measurements can be performed at concentrations of ~10^{-6}–10^{-4} M, NMR measurements require higher concentrations of the probes (~10^{-2} M). Moreover, while the complex of $DA_{1.3}$ with β-CD is soluble in deuterated water, the solid complex of $DA_{1.3}T$ separated from solution. Therefore, in this case both β-CD and $DA_{1.3}T$ were in too low concentration in solution to record the NMR spectra.

For this reason, we recorded the NMR spectra in another polar solvent that solubilizes both $DA_{1.3}T$ and the mixture $DA_{1.3}T$/β-CD. As can be noticed from Figs. S4, S5 and Tables S1, S2, chemical shifts in the NMR spectrum of the $DA_{1.3}T$/β-CD mixture are observed for protons of the dansyl group but not of the TEMPO moiety. This sustain our conclusion, based on fluorescence and EPR data, that the dansyl moiety is involved in the inclusion process.

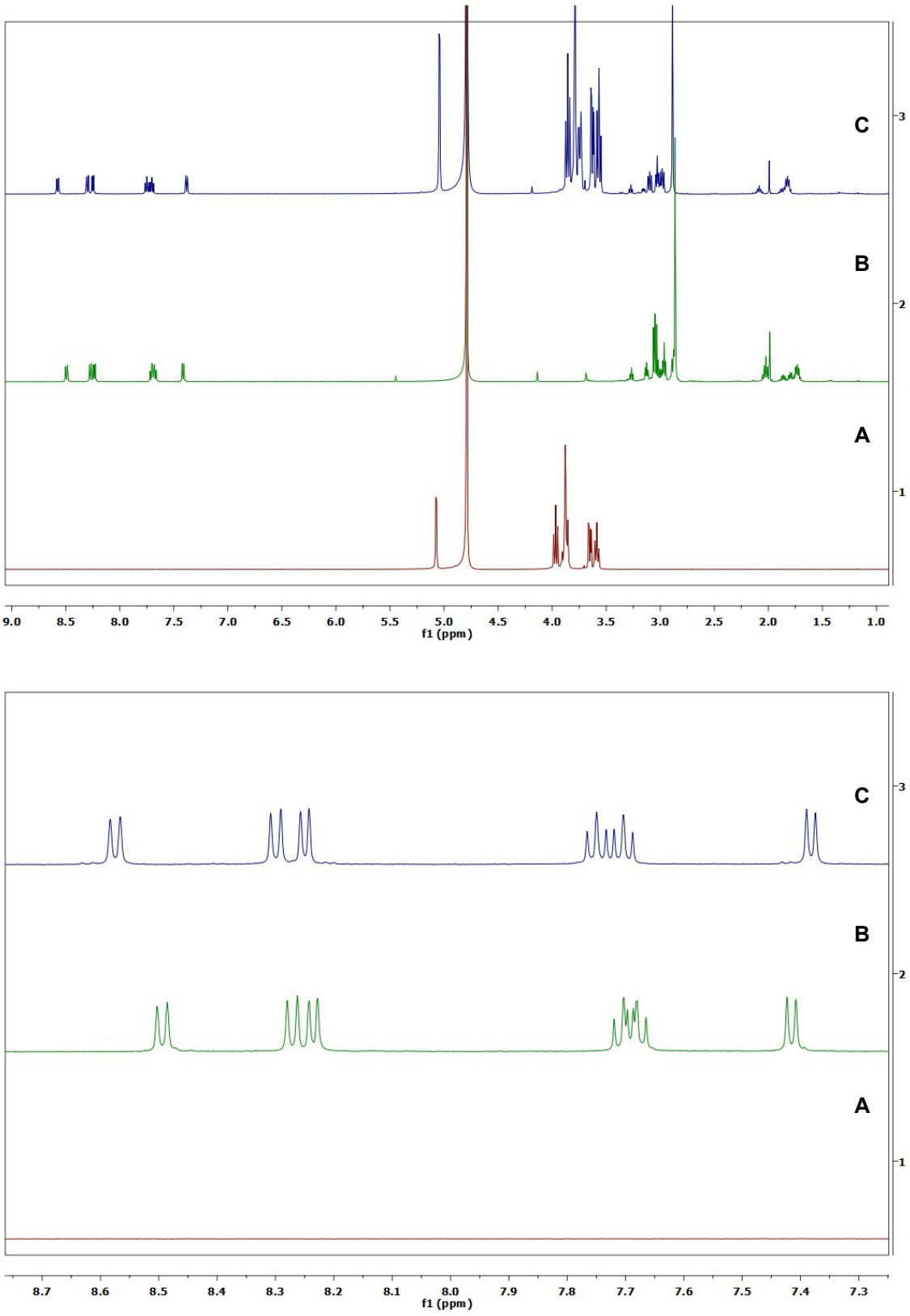
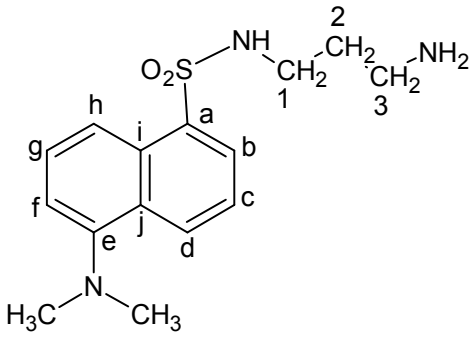
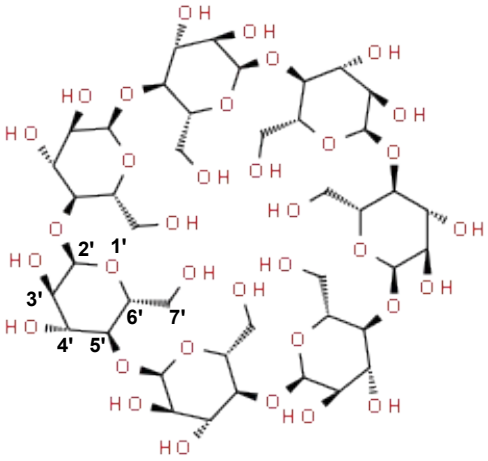


Fig. S4. ^{1}H-NMR spectra in D_2O of: **A** – β-cyclodextrin, **B** – $DA_{1,3}$; **C** - β-cyclodextrin + $DA_{1,3}$.



$DA_{1.3}$ structure



β-Cyclodextrin structure

Table S1. Chemical shifts of DA1.3 and β-CD protons in D_2O

Compounds protons	Chemical shifts of β-CD (ppm)	Chemical shifts of $DA_{1,3}$ (ppm)	Chemical shifts of β-CD + $DA_{1,3}$ (ppm)	$\Delta\delta = \left\lvert \delta_{BCD\ or\ DA_{1,3}} - \delta_{BCD+DA_{1,3}} \right\rvert$	
				ppm	Hz
H-b	-	8.23	8.25	0.02	11.1
H-c	-	7.68	7.70	0.02	11.2
H-d	-	8.49	8.57	0.08	40.3
H-f	-	7.41	7.38	0.03	17.2
H-g	-	7.70	7.74	0.05	22.8
H-h	-	8.27	8.30	0.03	14.1
H-1	-	2.96	3.02	0.06	32.0
H-2	-	1.73	1.82	0.09	45.70
H-3	-	2.88	2.98	0.11	52.3
$-N(CH_3)_2$	-	2.86	2.88	0.02	11.8
H-2	5.07	-	5.04	0.03	15.2
H-3	3.58	-	3.56	0.02	10.1
H-4	3.97	-	3.85	0.12	55.8
H-5	3.90-3.85	-	3.79-3.72	0.11-0.13	57.5-64.8
H-6	3.65	-	3.63	0.02	12.0
H-7	3.90-3.85	-	3.79-3.72	0.11-0.13	57.5-64.8

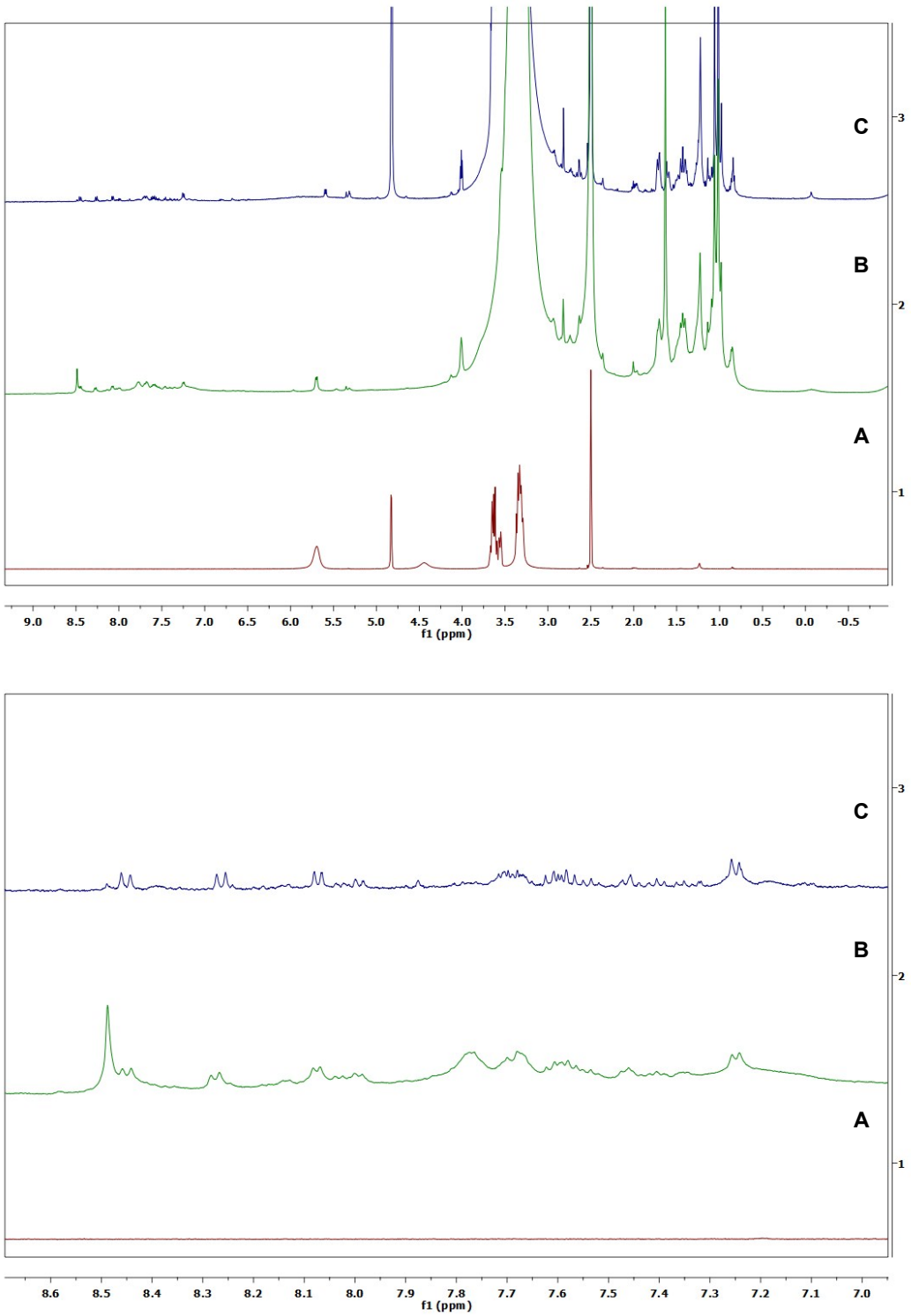
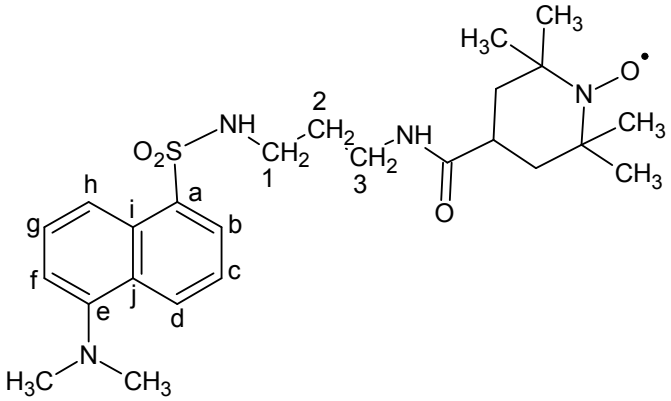
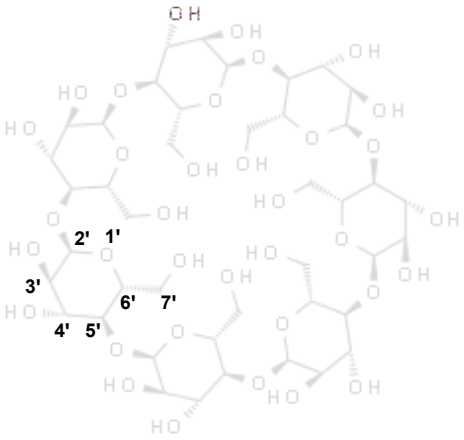


Fig. S5. ^{1}H-NMR spectra in DMSO of: **A** – β-cyclodextrin, **B** – $DA_{1,3}T$; **C** - β-cyclodextrin + $DA_{1,3}T$.



$DA_{1.3}T$ structure



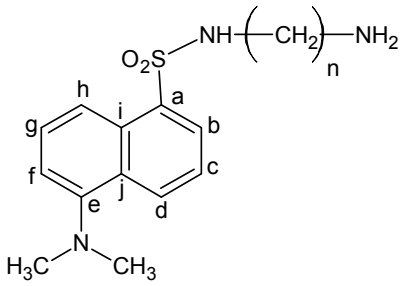
β-Cyclodextrin structure

Table S2. Chemical shifts of $DA_{1.3}T$ and β-CD protons in DMSO

Compounds protons	Chemical shifts of β-CD (ppm)	Chemical shifts of $DA_{1,3}T$ (ppm)	Chemical shifts of β-CD + $DA_{1,3}T$ (ppm)	$\Delta\delta = \left\lvert \delta_{BCD\ or\ DA_{1,3}T} - \delta_{BCD + DA_{1,3}T} \right\rvert$	
				ppm	Hz
H-b	-	8.08	8.06	0.02	9.6
H-c	-	7.62-7.53	7.64-7.55	0.02	9.4
H-d	-	8.45	8.43	0.02	8.98
H-f	-	7.25	7.23	0.02	9.7
H-g	-	7.62-7.53	7.64-7.55	0.02	9.4
H-h	-	8.28	8.26	0.02	10.8
H-1	-	2.93	2.92	0.01	6.7
H-2	-	1.43	1.40	0.03	15.3
H-3	-	2.74	2.72	0.02	9.6
$-N(CH_3)_2$	-	2.82	2.81	0.01	6.2
H-2′	4.83	-	4.82	0.01	4.5
H-3′	3.36-3.29	-	Overlapped with water signal from DMSO	-	-
H-4′	3.67-3.55	-	3.65-3.52	0.02-0.03	11.1-15.6
H-5′	3.67-3.55	-	3.65-3.52	0.02-0.03	11.1-15.6
H-6′	3.36-3.29	-	Overlapped with water signal from DMSO	-	-
H-7′	3.67-3.55	-	3.65-3.52	0.02-0.03	11.1-15.6
-CH (TEMPO)	-	2.63	2.63	0	0.0
$-CH_2$-(TEMPO)	-	1.74	1.74	0	0.0
$-CH_3$ (TEMPO)	-	1.06 and 1.02	1.055-1.015	0.005	1.6

Spectral characterization of $DA_{1,n}$

Notation of H atoms for assignment of NMR ^1H signals



n= 2,3,4,5,6,7,8,10,12

MAD-2, n=2, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-NH_2

MAD-3, n=3, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-NH_2

MAD-4, n=4, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-NH_2

MAD-5, n=5, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-NH_2

MAD-6, n=6, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-$\overset{6}{C}H_2$-NH_2

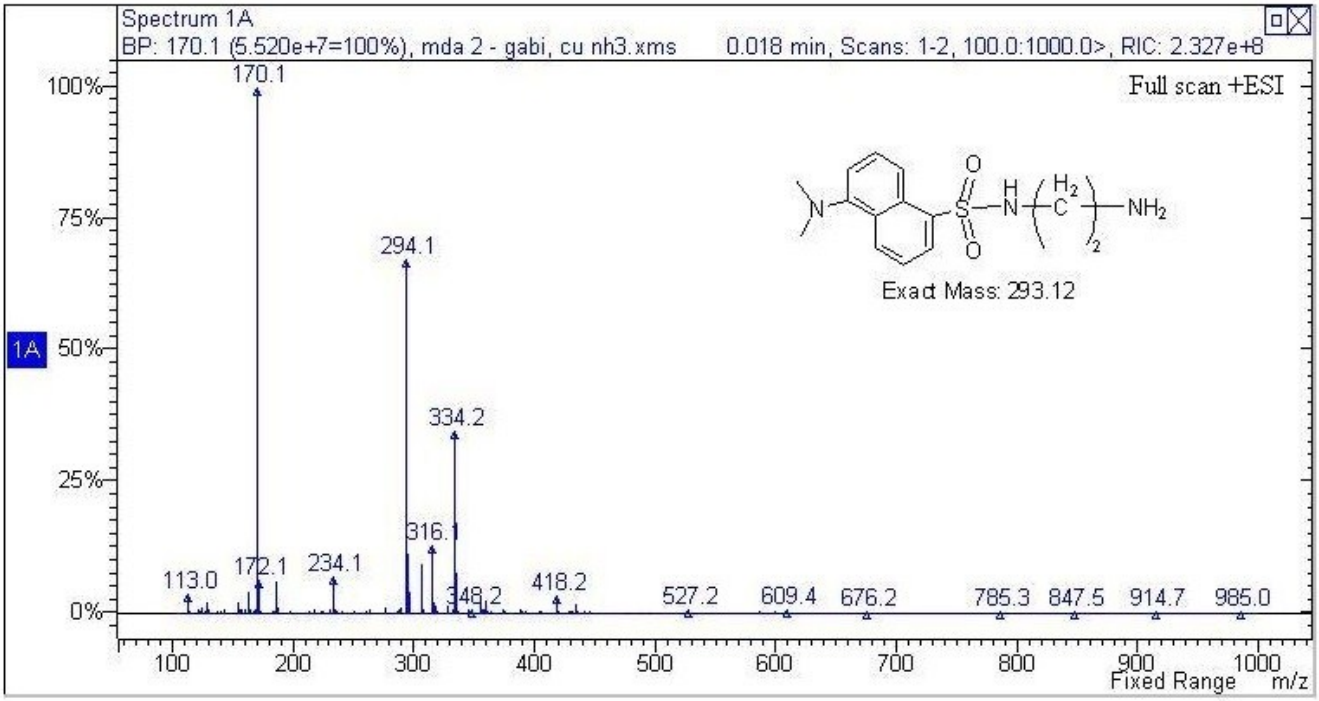
MAD-7, n=7, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-$\overset{6}{C}H_2$-$\overset{7}{C}H_2$-NH_2

MAD-8, n=8, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-$\overset{6}{C}H_2$-$\overset{7}{C}H_2$-$\overset{8}{C}H_2$-NH_2

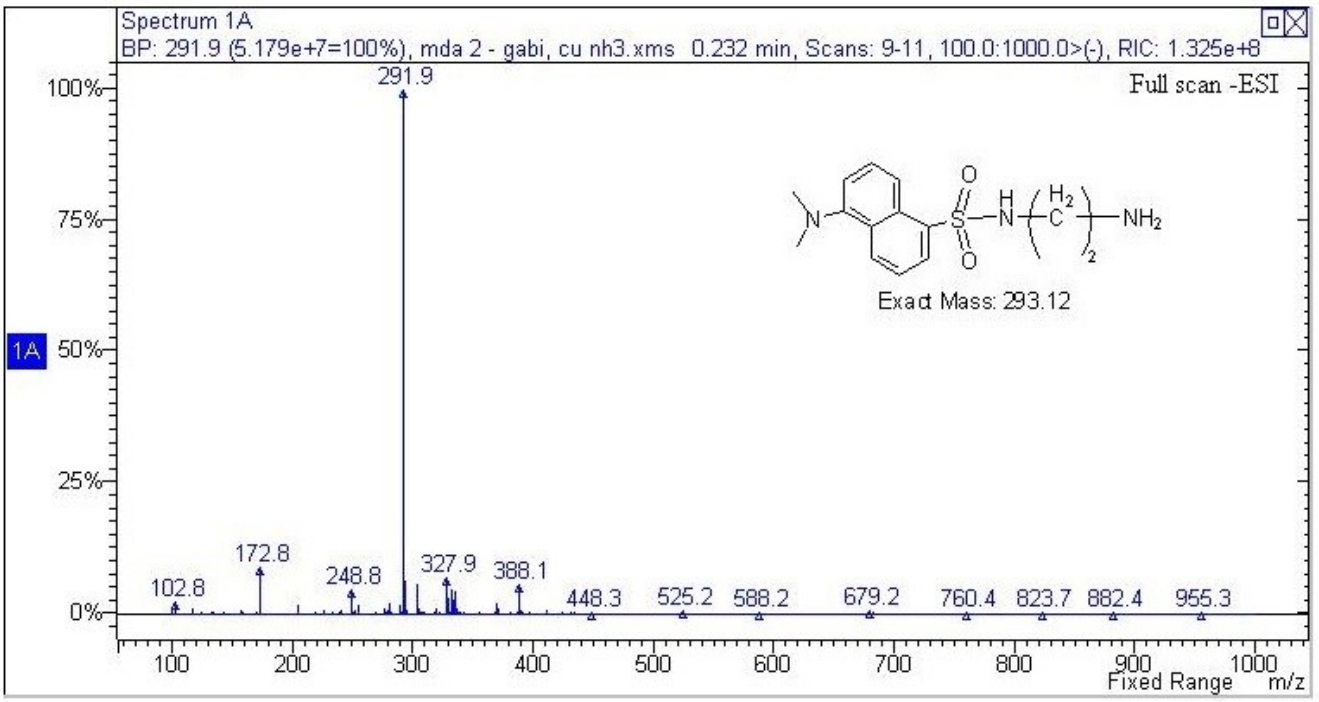
MAD-10, n=10, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-$\overset{6}{C}H_2$-$\overset{7}{C}H_2$-$\overset{8}{C}H_2$-$\overset{9}{C}H_2$-$\overset{10}{C}H_2$-NH_2

MAD-12, n=12, -NH-$\overset{1}{C}H_2$-$\overset{2}{C}H_2$-$\overset{3}{C}H_2$-$\overset{4}{C}H_2$-$\overset{5}{C}H_2$-$\overset{6}{C}H_2$-$\overset{7}{C}H_2$-$\overset{8}{C}H_2$-$\overset{9}{C}H_2$-$\overset{10}{C}H_2$-$\overset{11}{C}H_2$-$\overset{12}{C}H_2$-NH_2

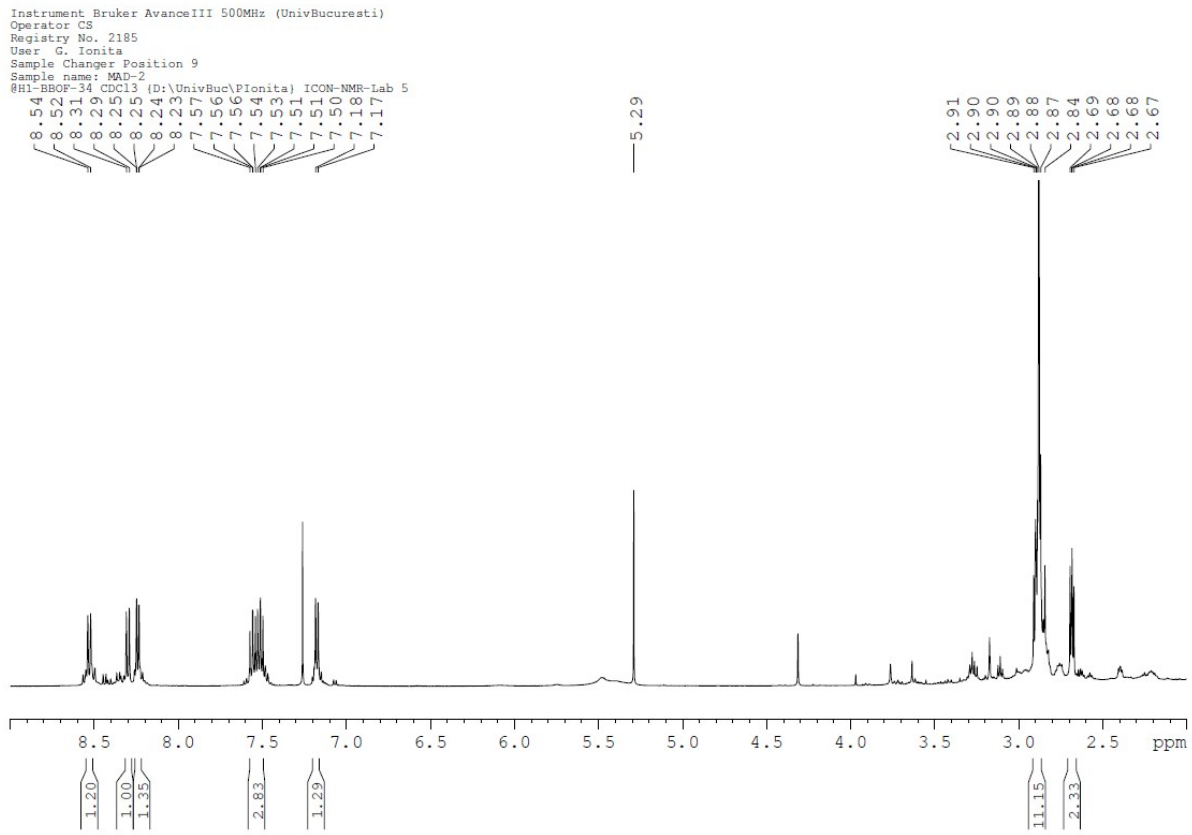
$DA_{1.2}$ (dansyl ethylenediamine)



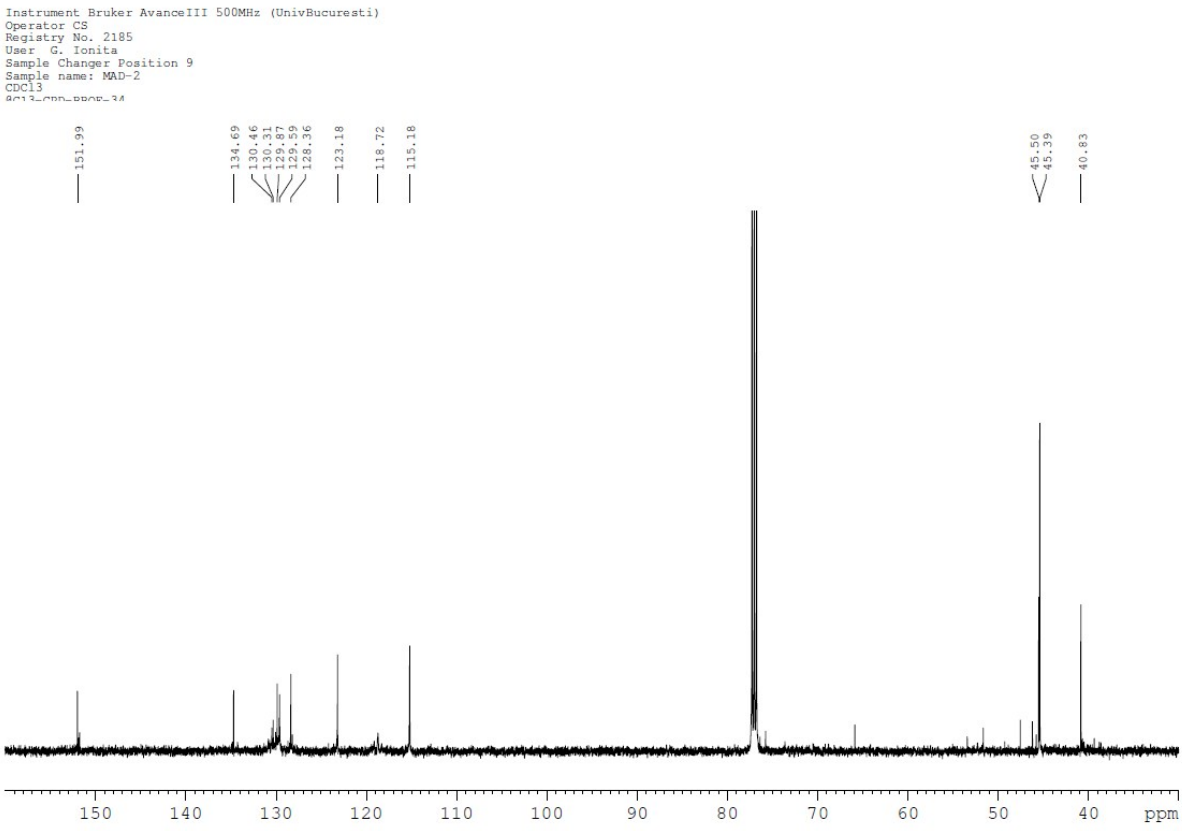
ESI-MS (*m/z*): 294 ($DA_{1.2}$ + H^+)



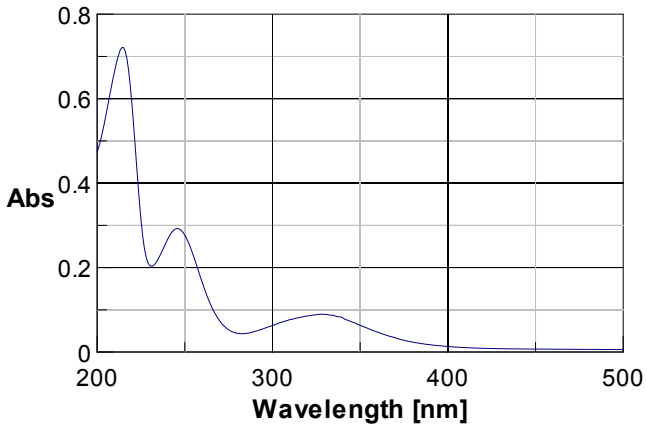
ESI-MS (*m/z*): 292 ($DA_{1.2}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.2}$

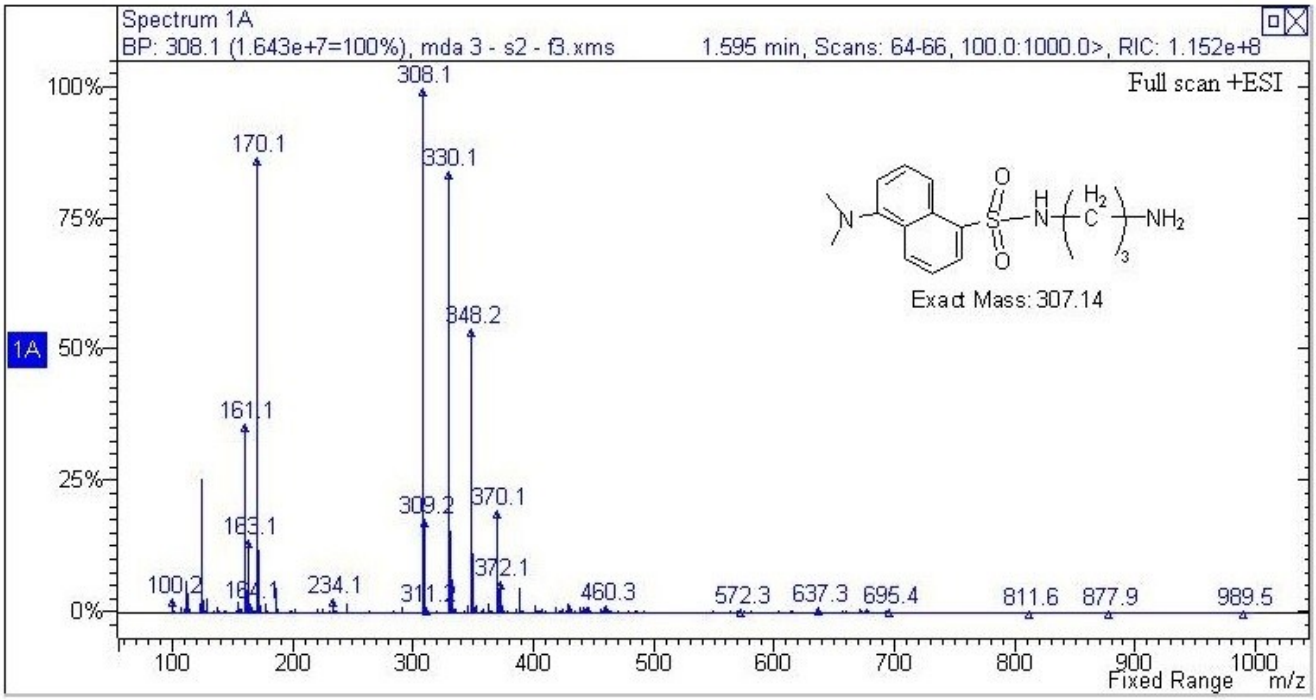


^{13}C NMR spectrum of compound $DA_{1.2}$

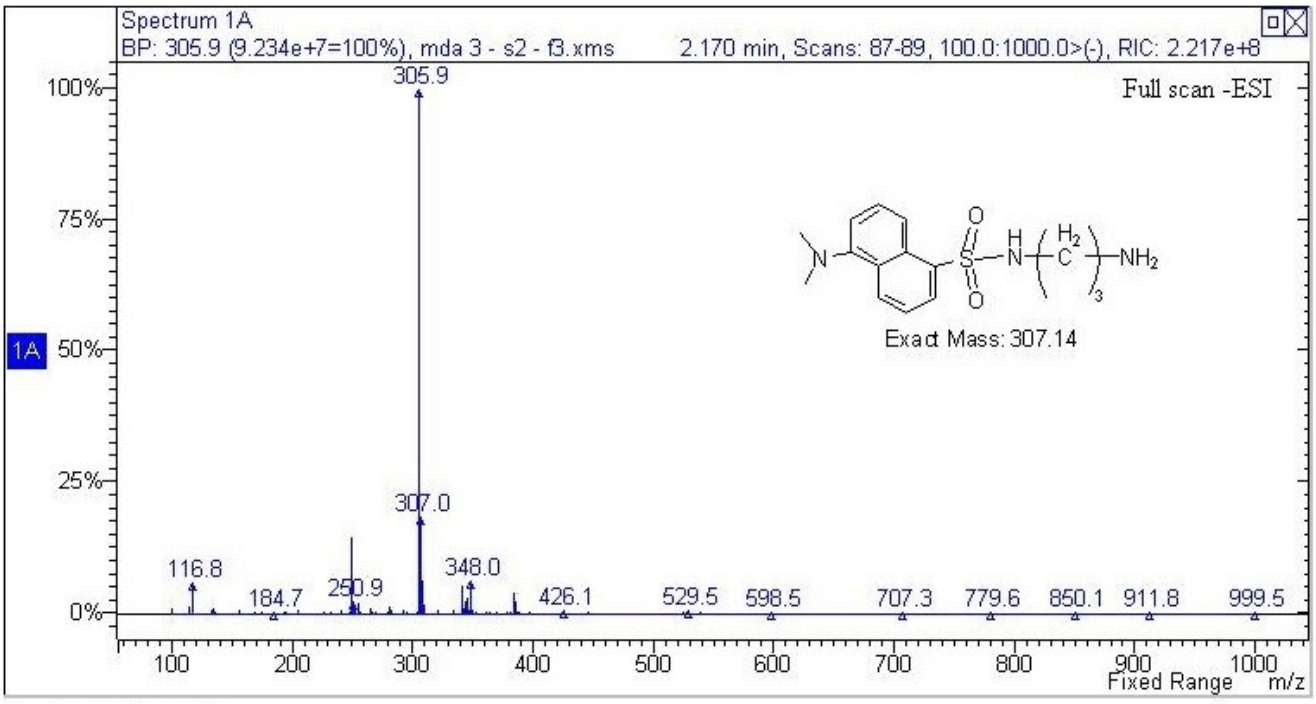


UV-Vis spectrum of compound $DA_{1.2}$

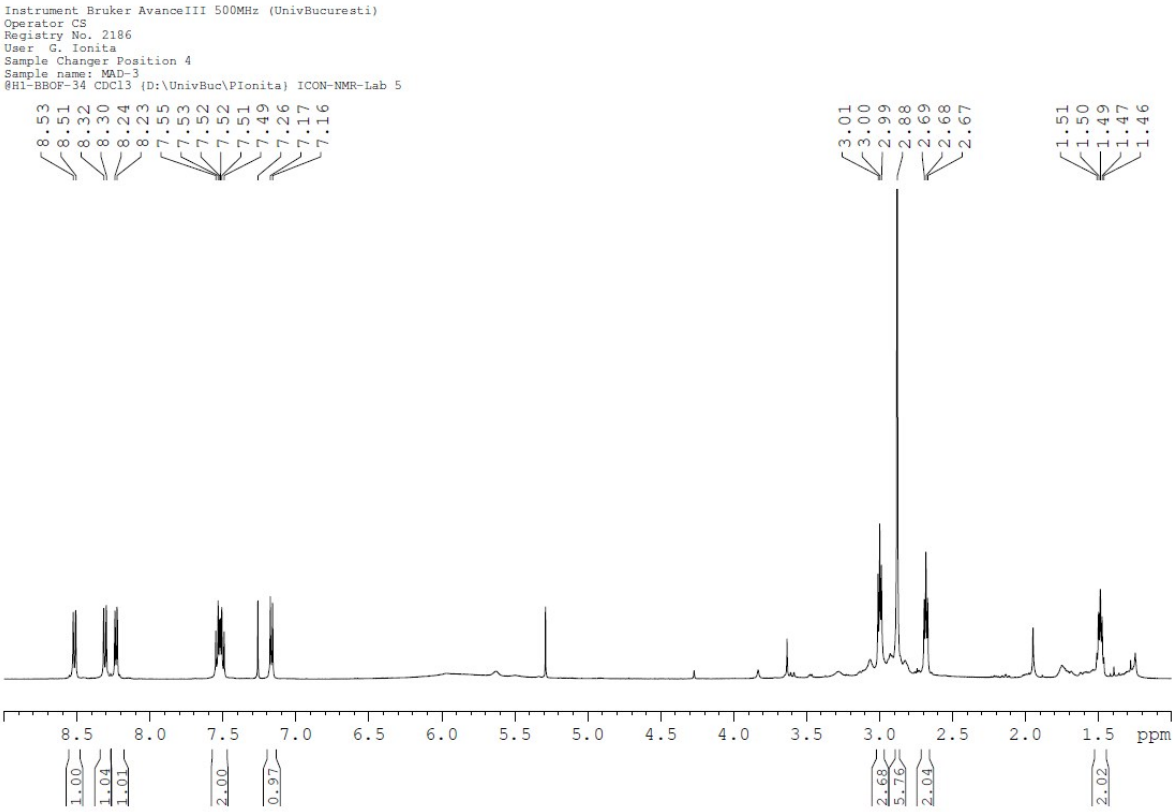
$DA_{1.3}$ (dansyl 1,3-diaminopropane)



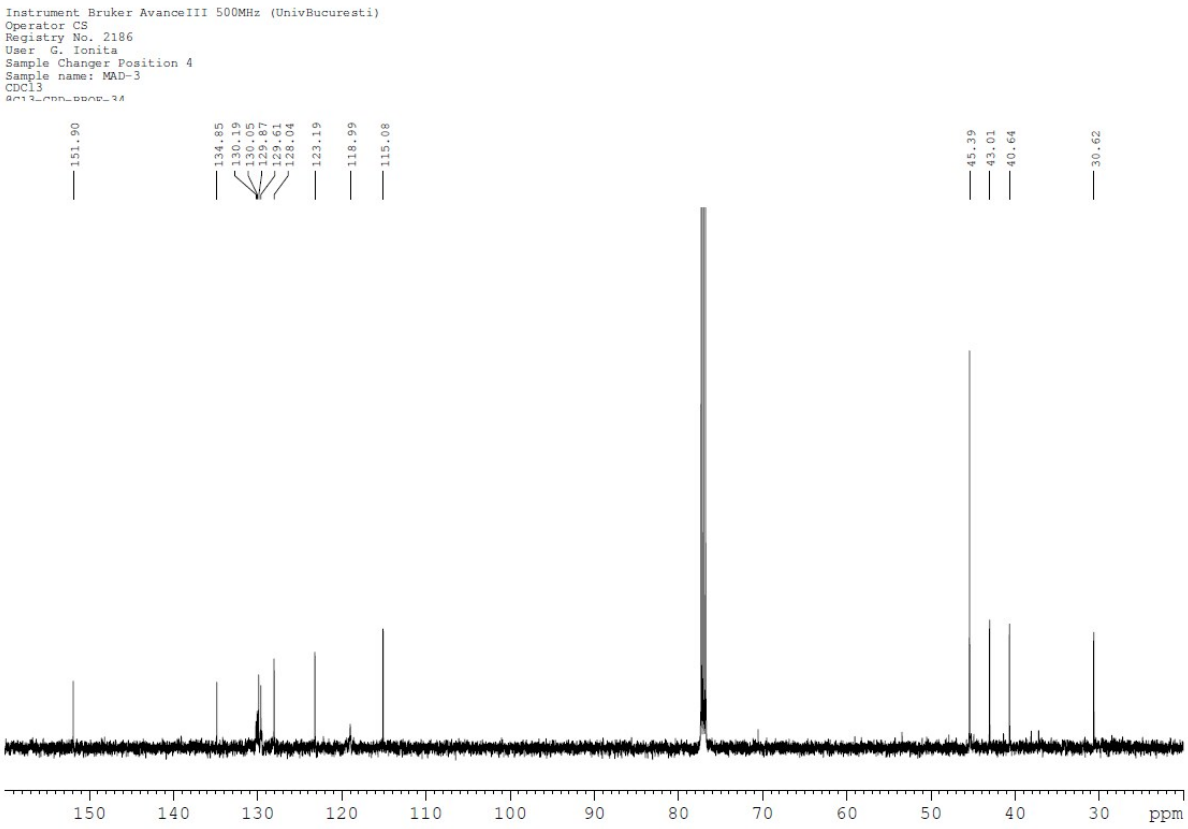
ESI-MS (*m/z*): 308 ($DA_{1.3}$ + H^+)



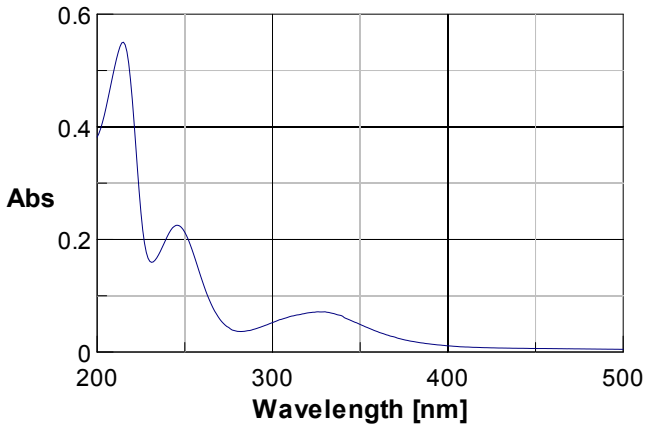
ESI-MS (*m/z*): 306 ($DA_{1.3}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.3}$

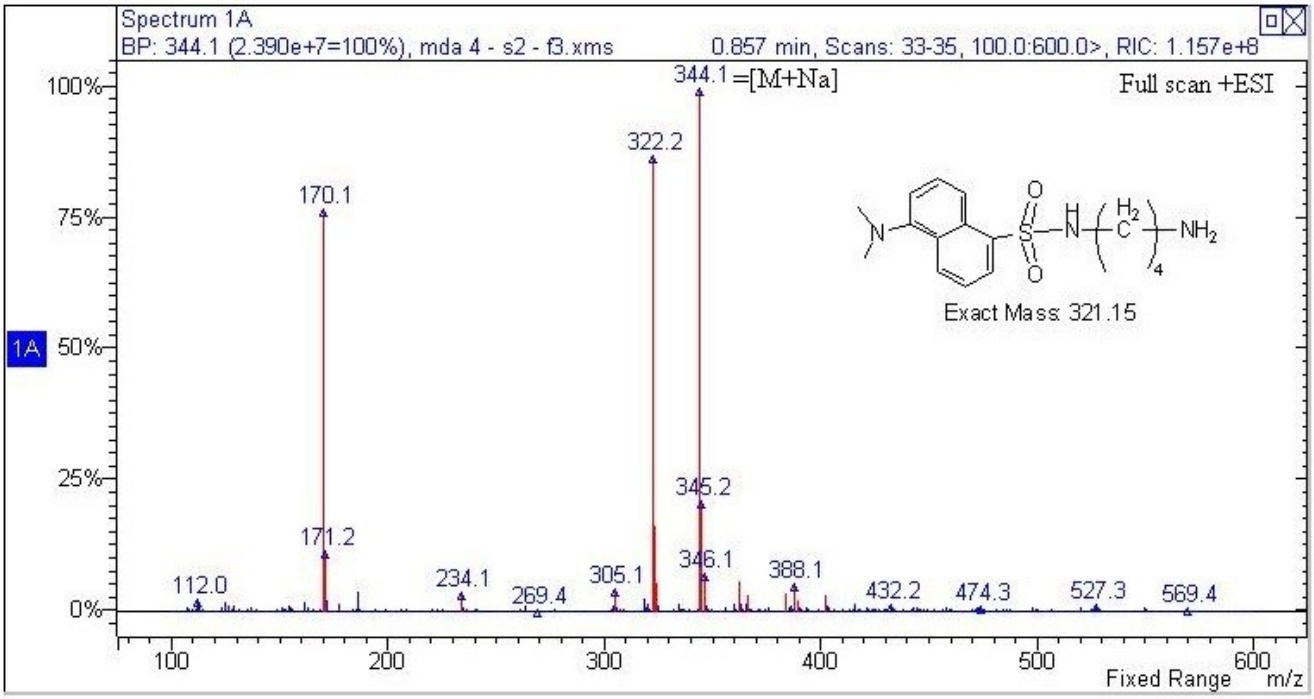


^{13}C NMR spectrum of compound $DA_{1.3}$

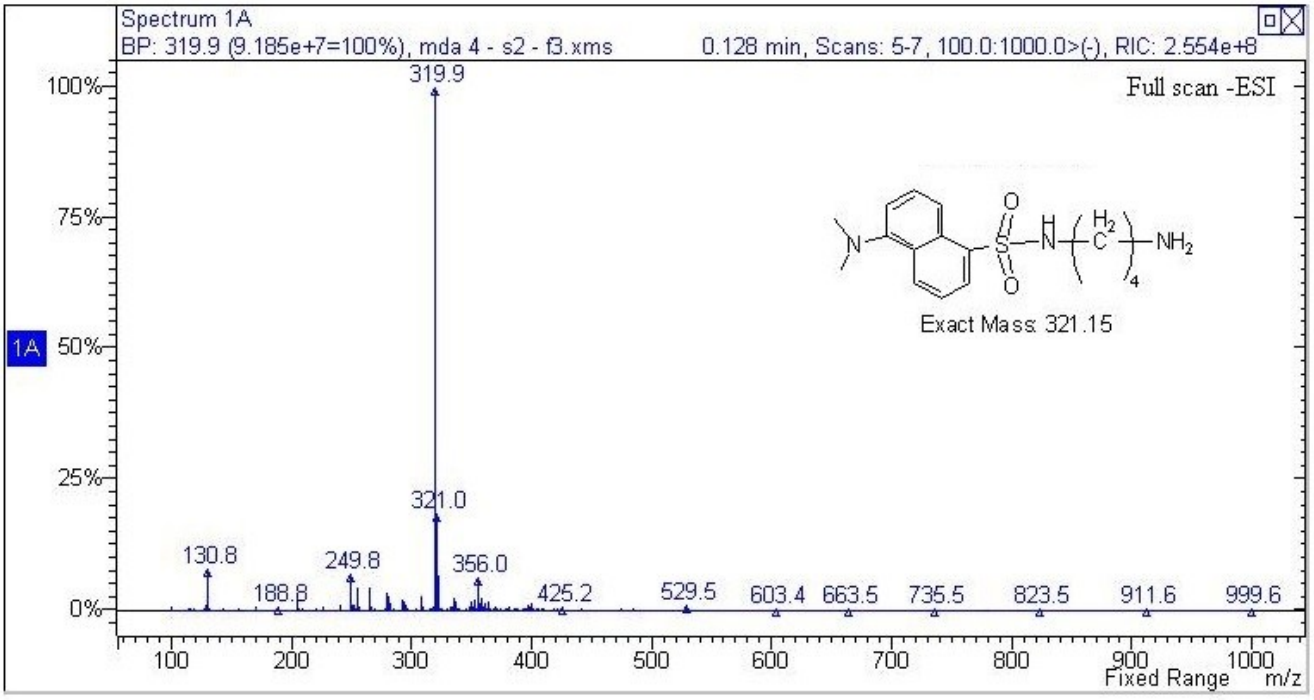


UV-Vis spectrum of compound $DA_{1.3}$

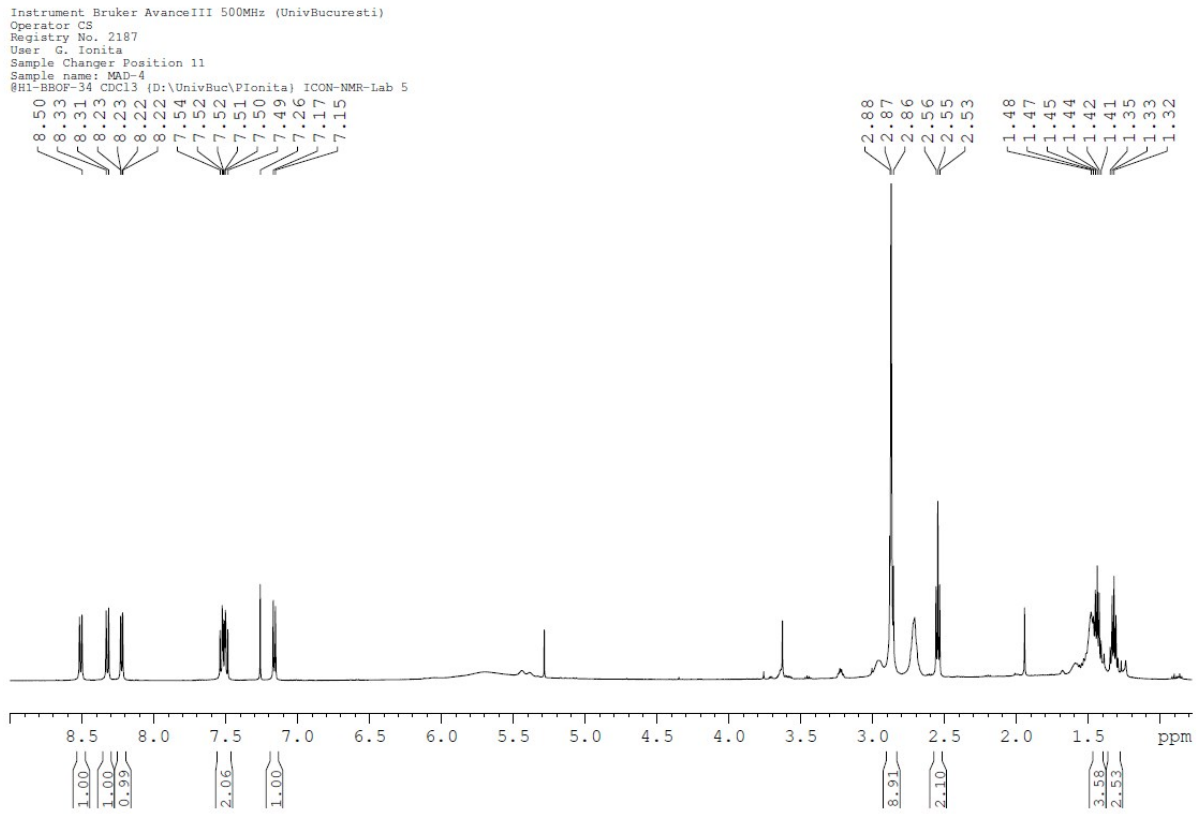
$DA_{1.4}$ (dansyl 1,4-diaminobutane)



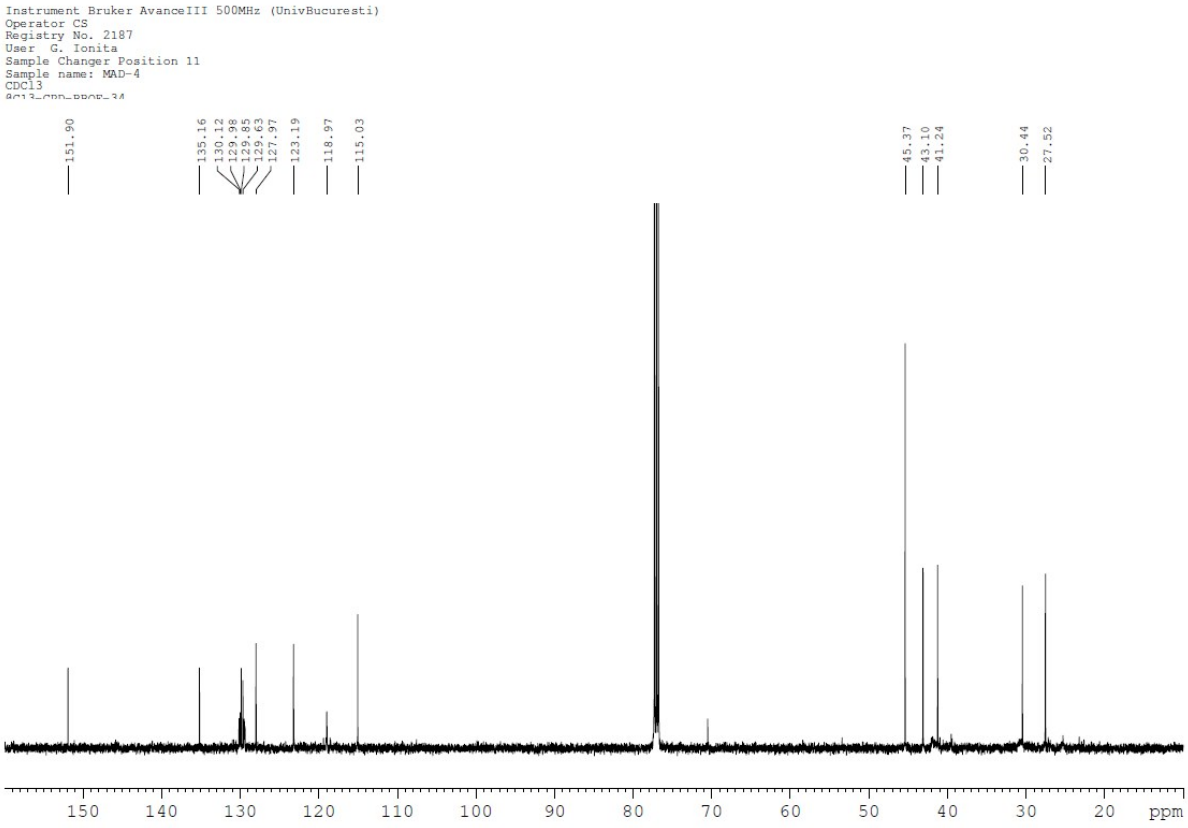
ESI-MS (*m/z*): 321 ($DA_{1.4}$ + H^+)



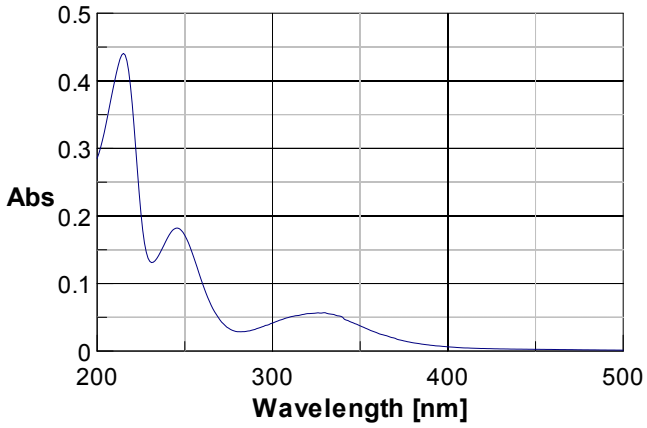
ESI-MS (*m/z*): 320 ($DA_{1.4}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.4}$

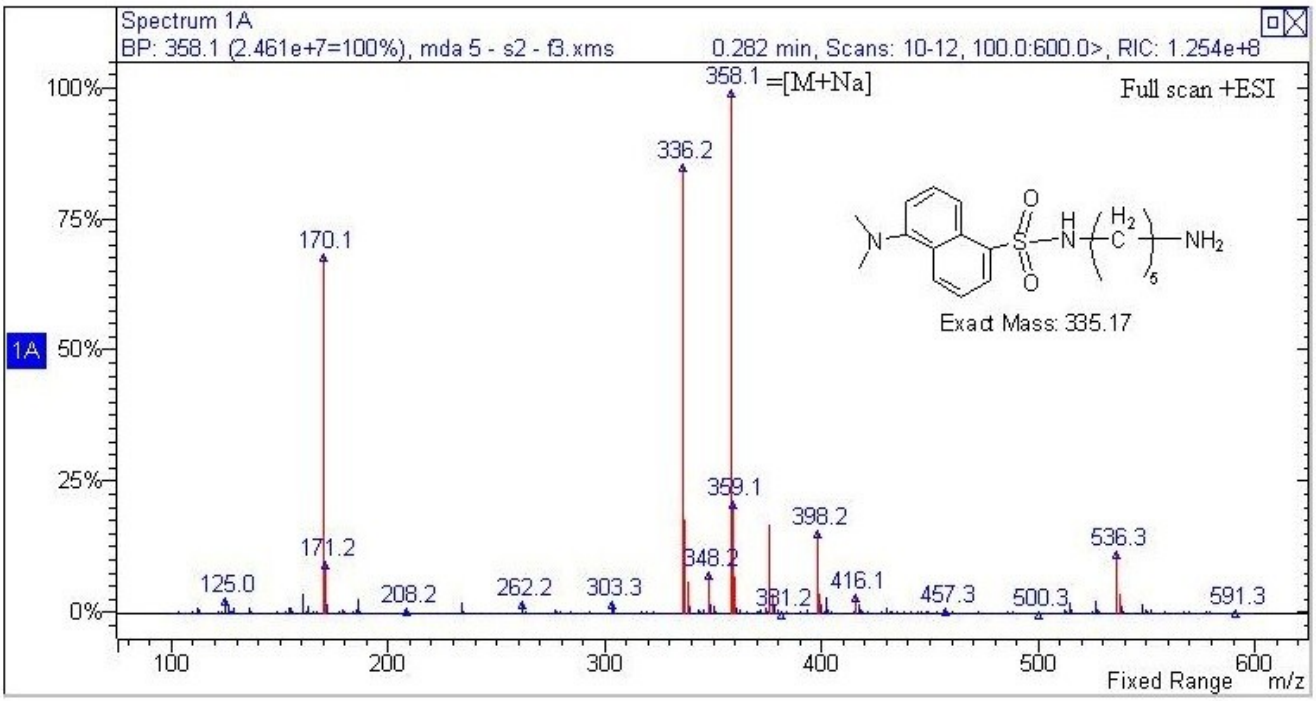


^{13}C NMR spectrum of compound $DA_{1.4}$

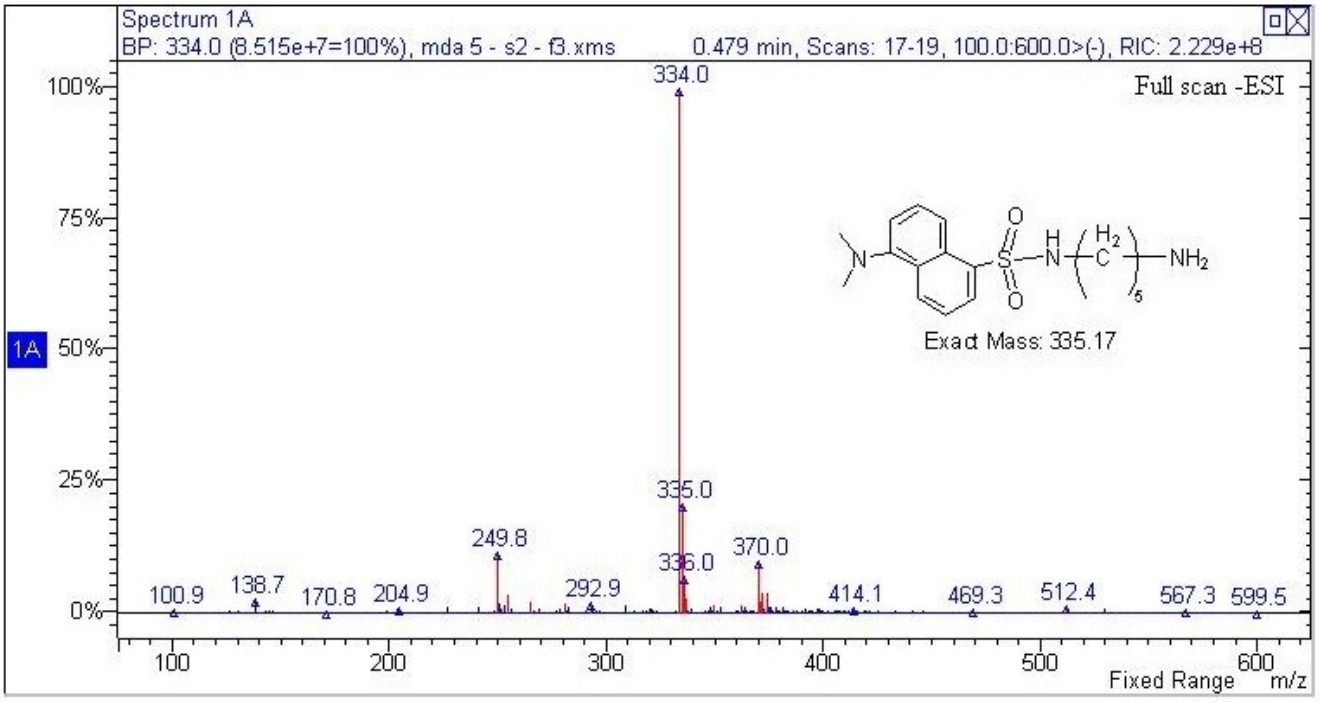


UV-Vis spectrum of compound $DA_{1.4}$

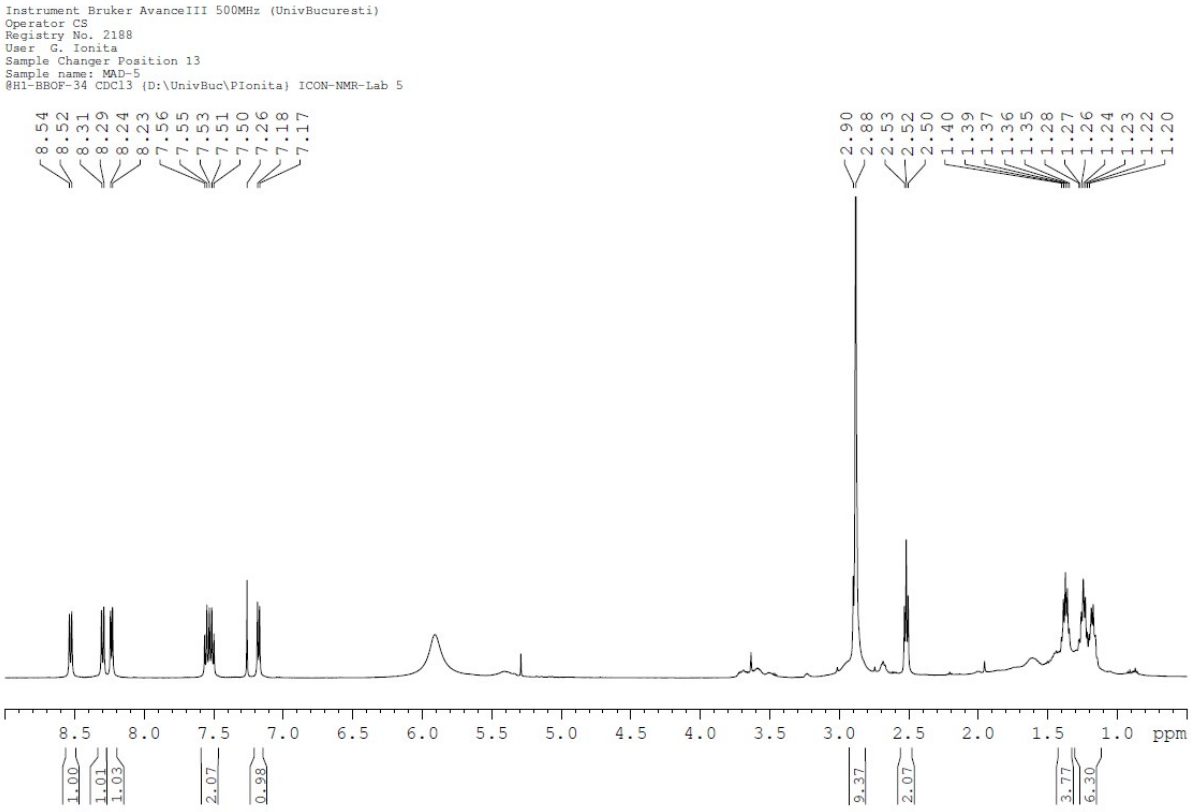
$DA_{1.5}$ (dansyl 1,5-diaminopentane)



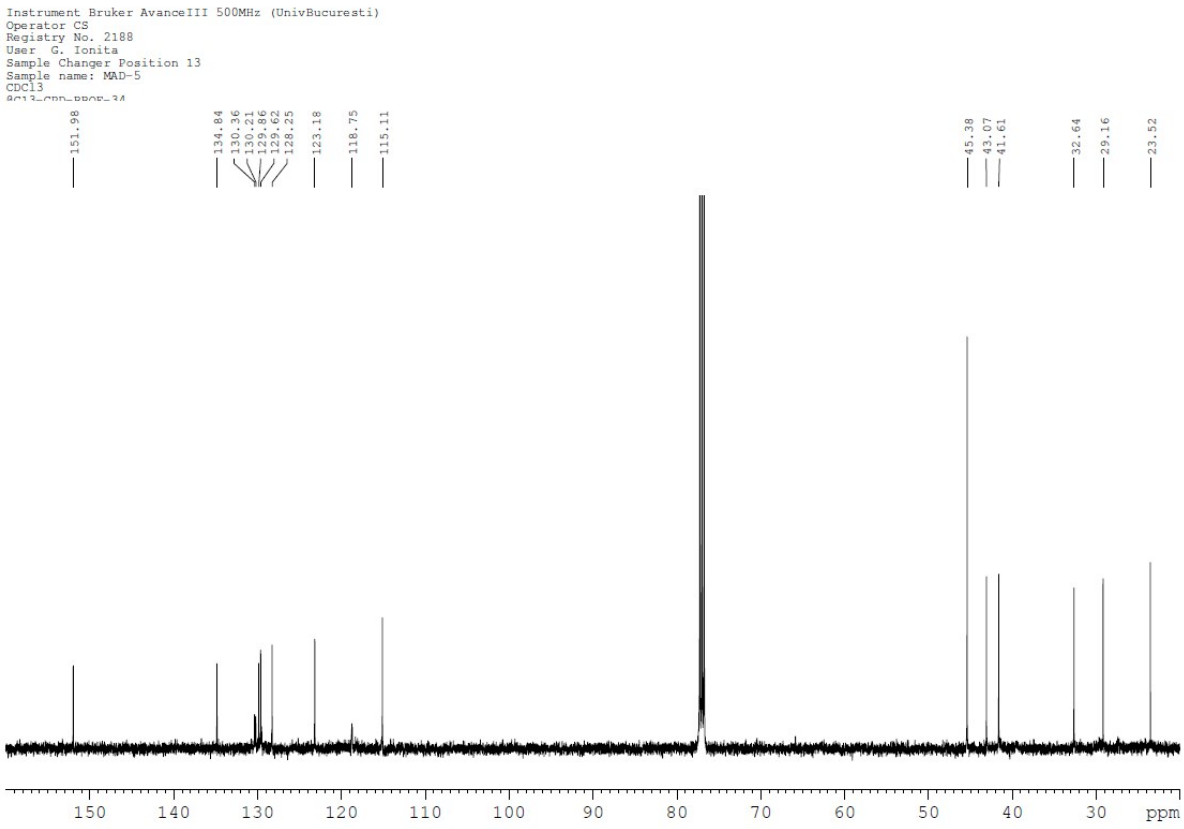
ESI-MS (*m/z*): 335 ($DA_{1.5}$ + H^+)



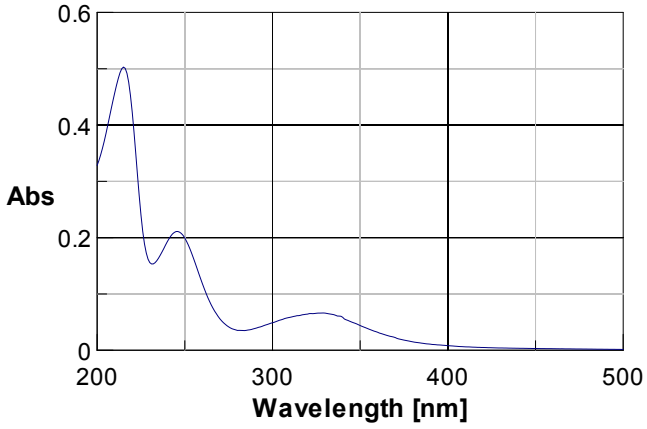
ESI-MS (*m/z*): 334 ($DA_{1.5}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.5}$

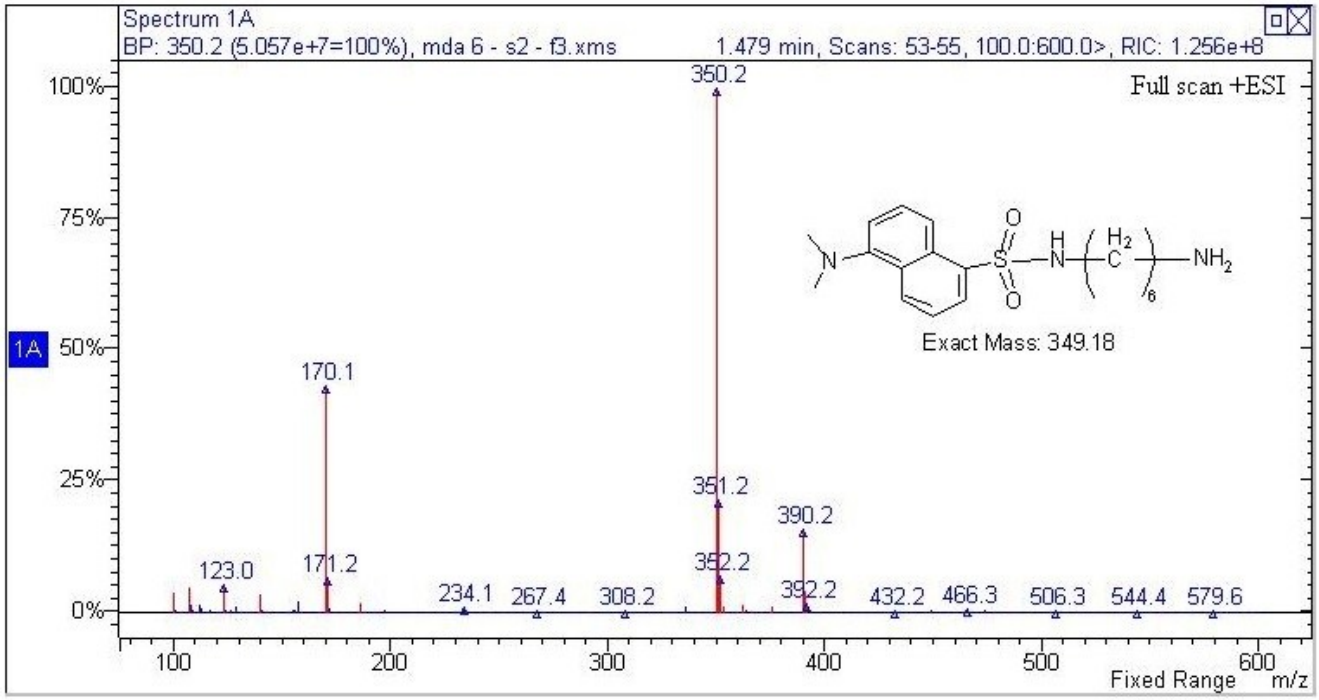


^{13}C NMR spectrum of compound $DA_{1.5}$

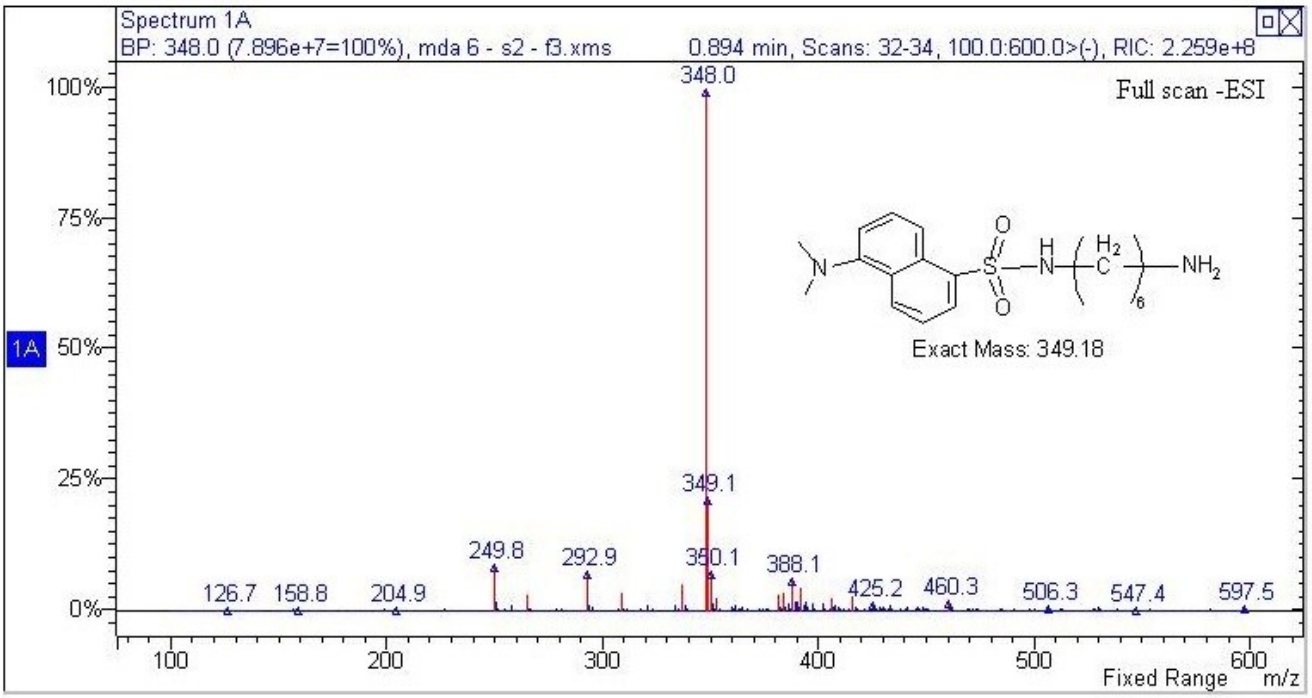


UV-Vis spectrum of compound $DA_{1.5}$

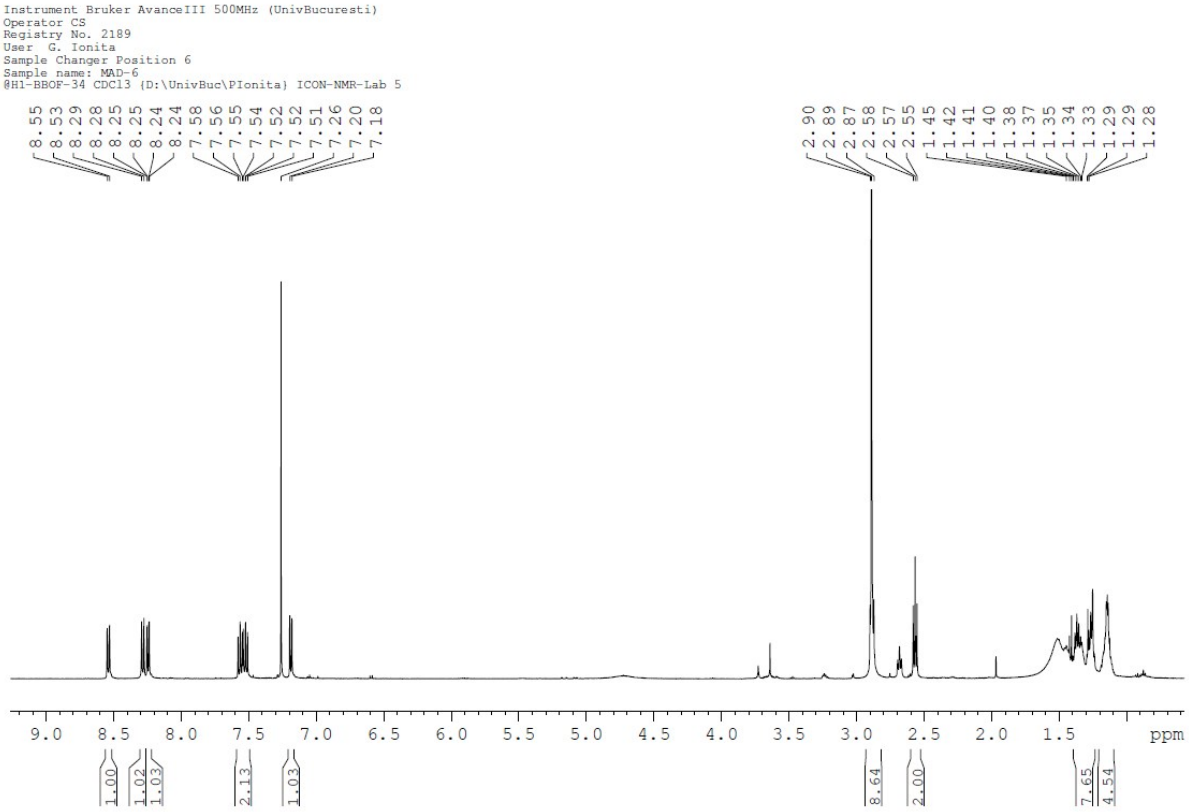
$DA_{1.6}$ (dansyl 1,6-diaminohexane)



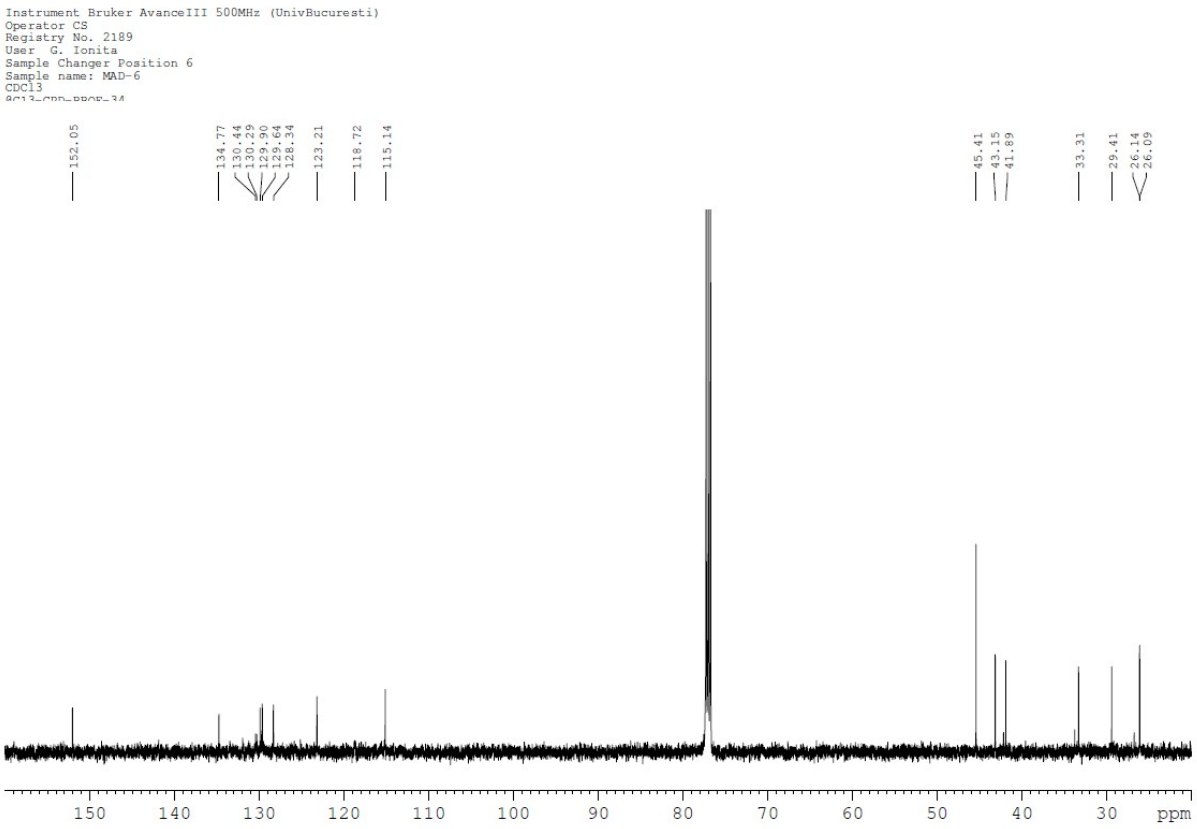
ESI-MS (*m/z*): 350 ($DA_{1.6}$ + H^+)



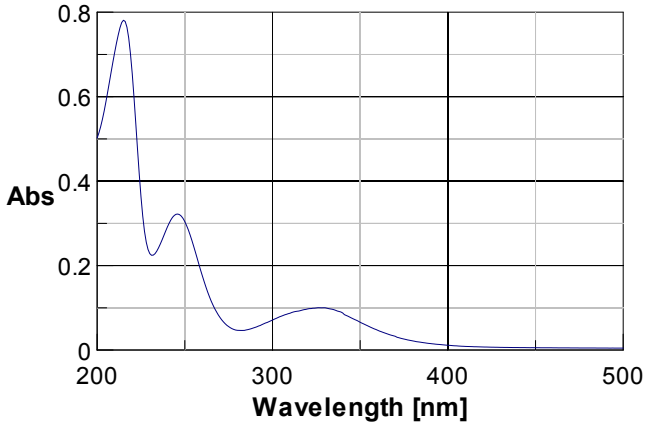
ESI-MS (*m/z*): 348 ($DA_{1.6}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.6}$

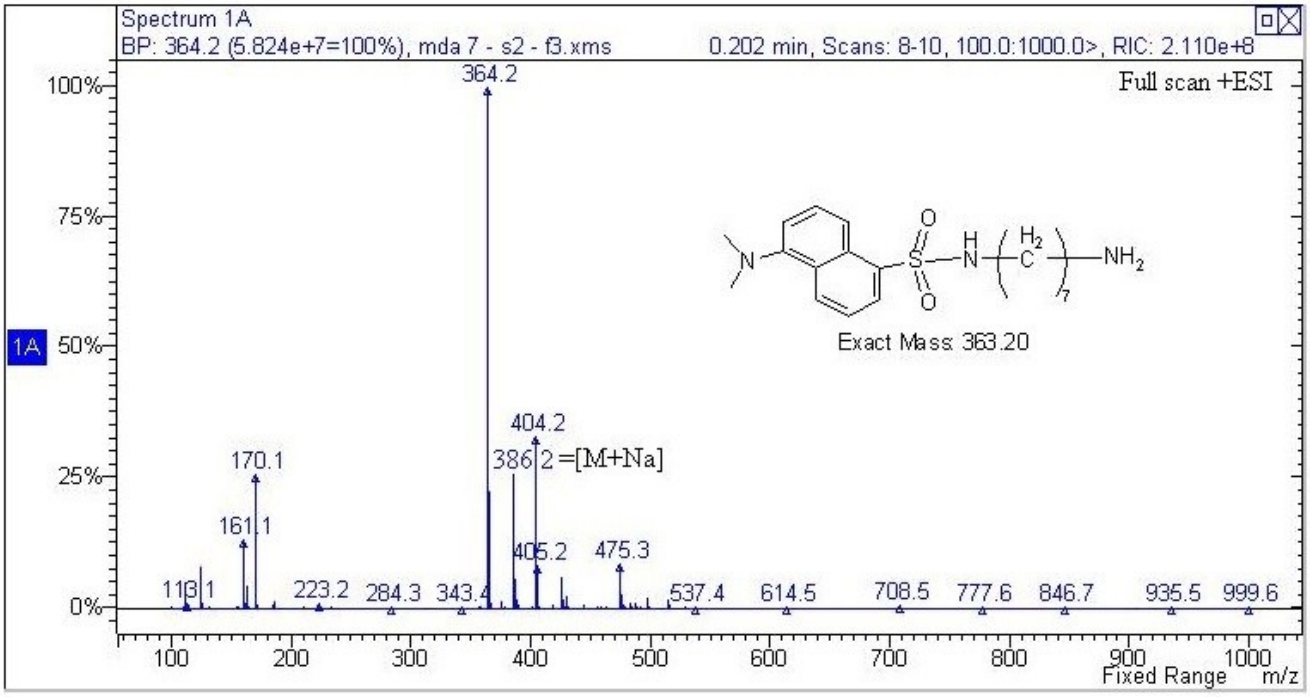


^{13}C NMR spectrum of compound $DA_{1.6}$

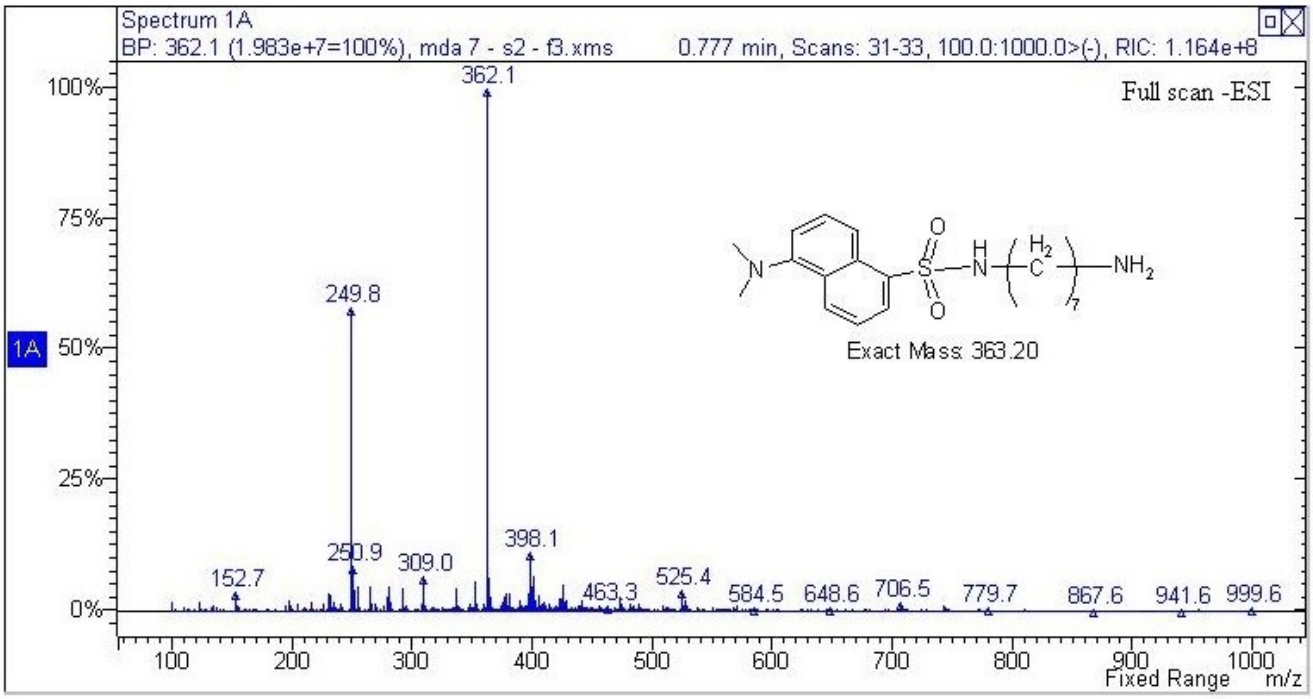


UV-Vis spectrum of compound $DA_{1.6}$

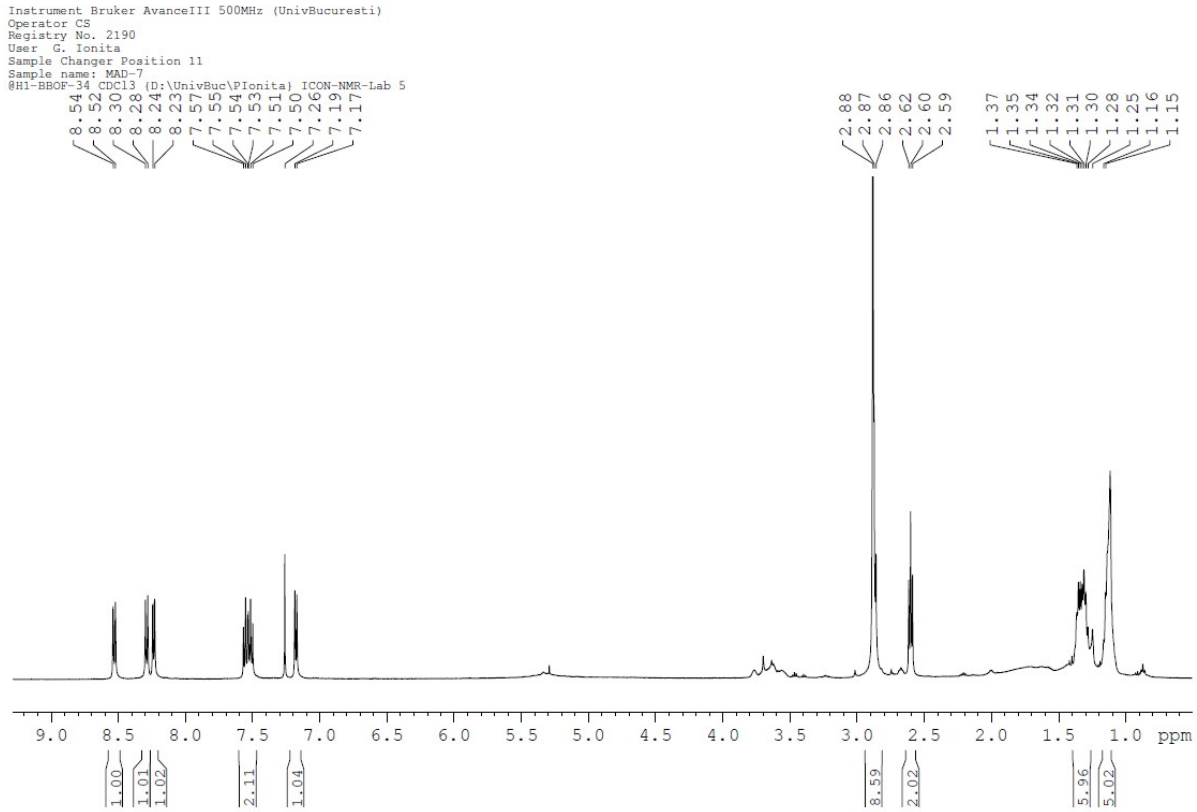
$DA_{1.7}$ (dansyl 1,7-diaminoheptane)



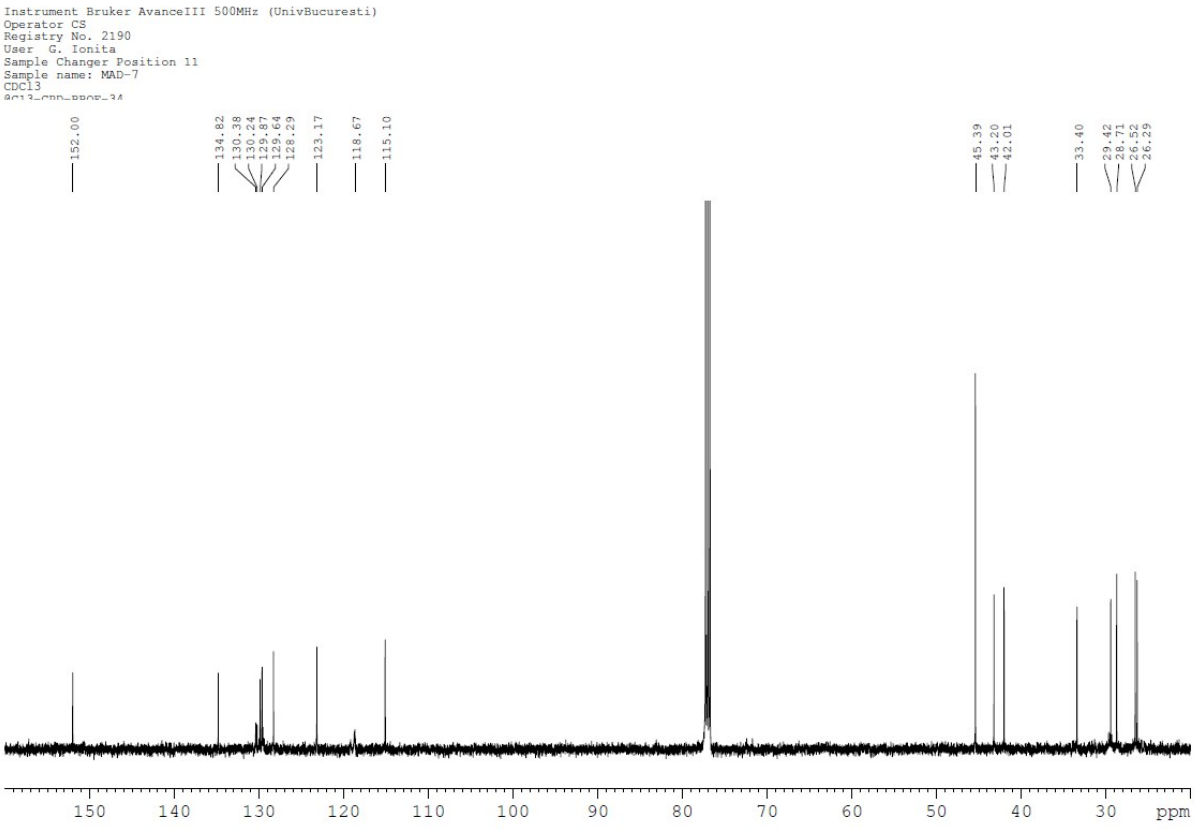
ESI-MS (*m/z*): 364 ($DA_{1.7}$ + H^+)



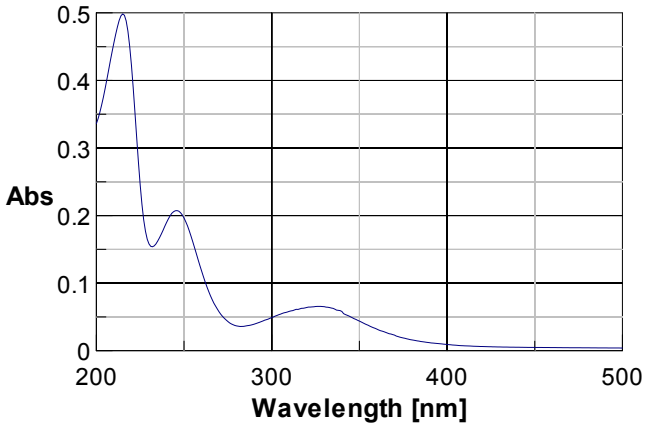
ESI-MS (*m/z*): 362 ($DA_{1.7}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.7}$

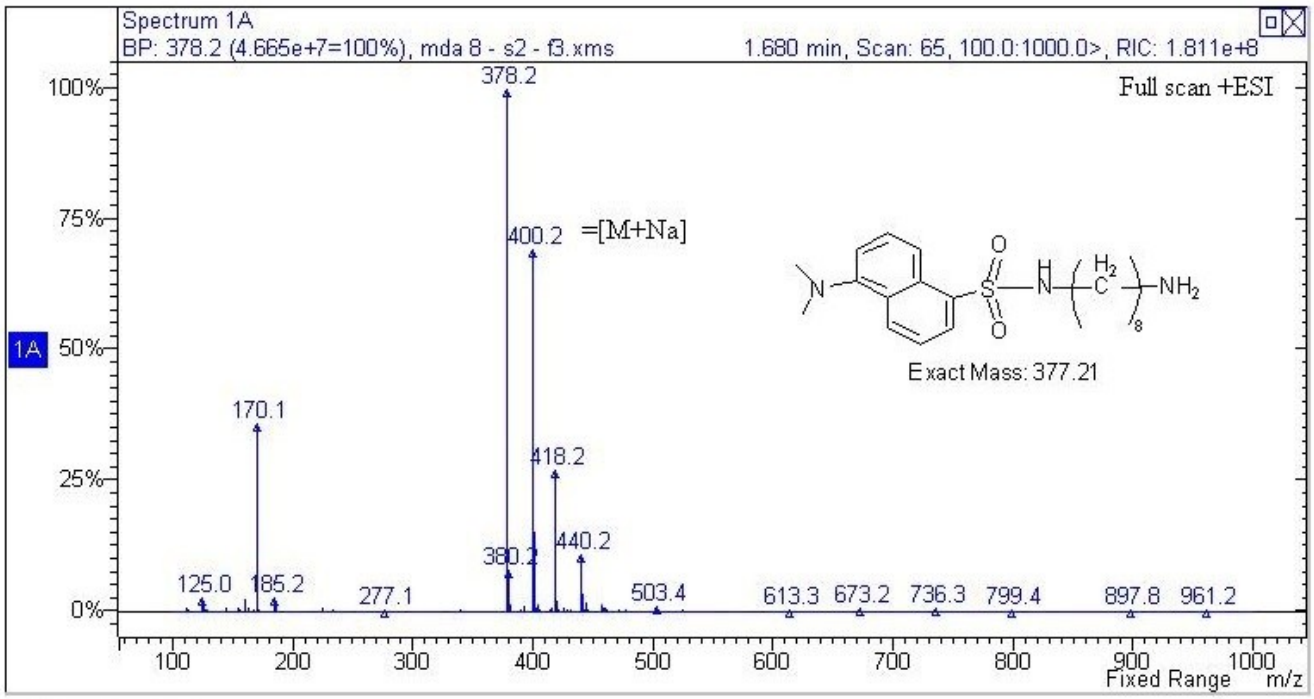


^{13}C NMR spectrum of compound $DA_{1.7}$

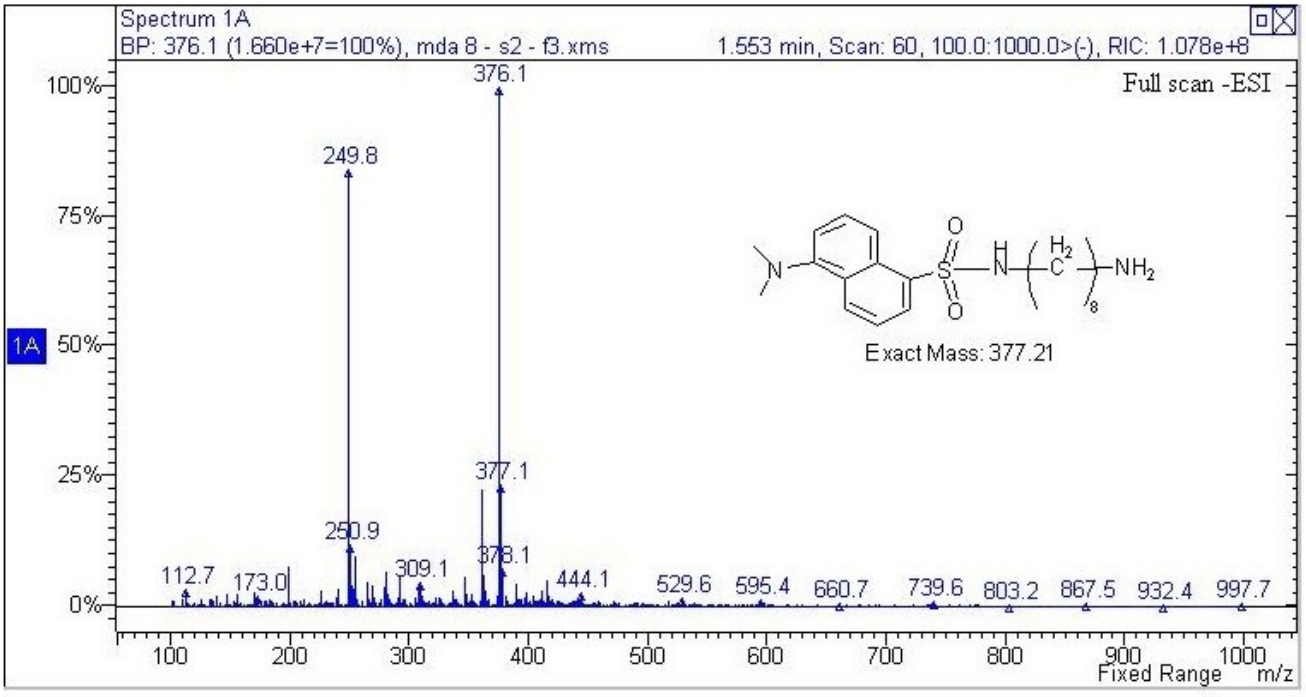


UV-Vis spectrum of compound $DA_{1.7}$

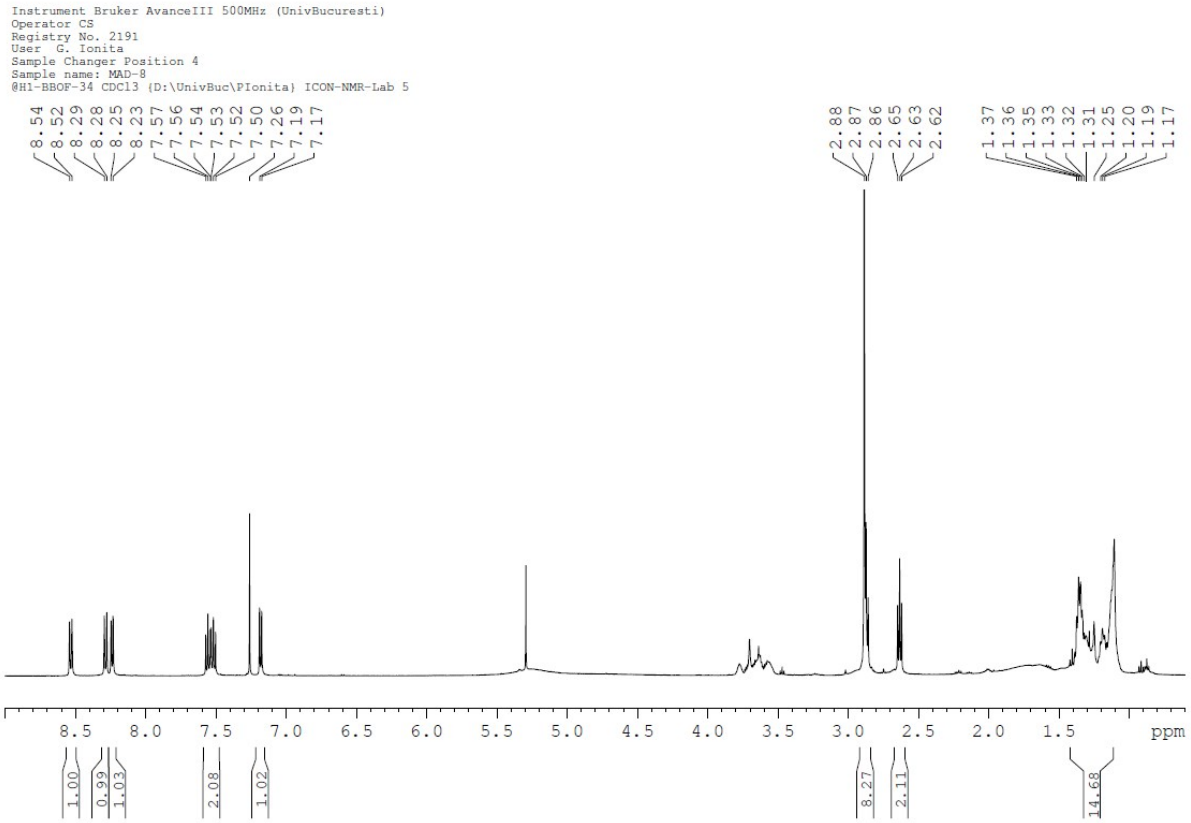
$DA_{1.8}$ (dansyl 1,8-diaminooctane)



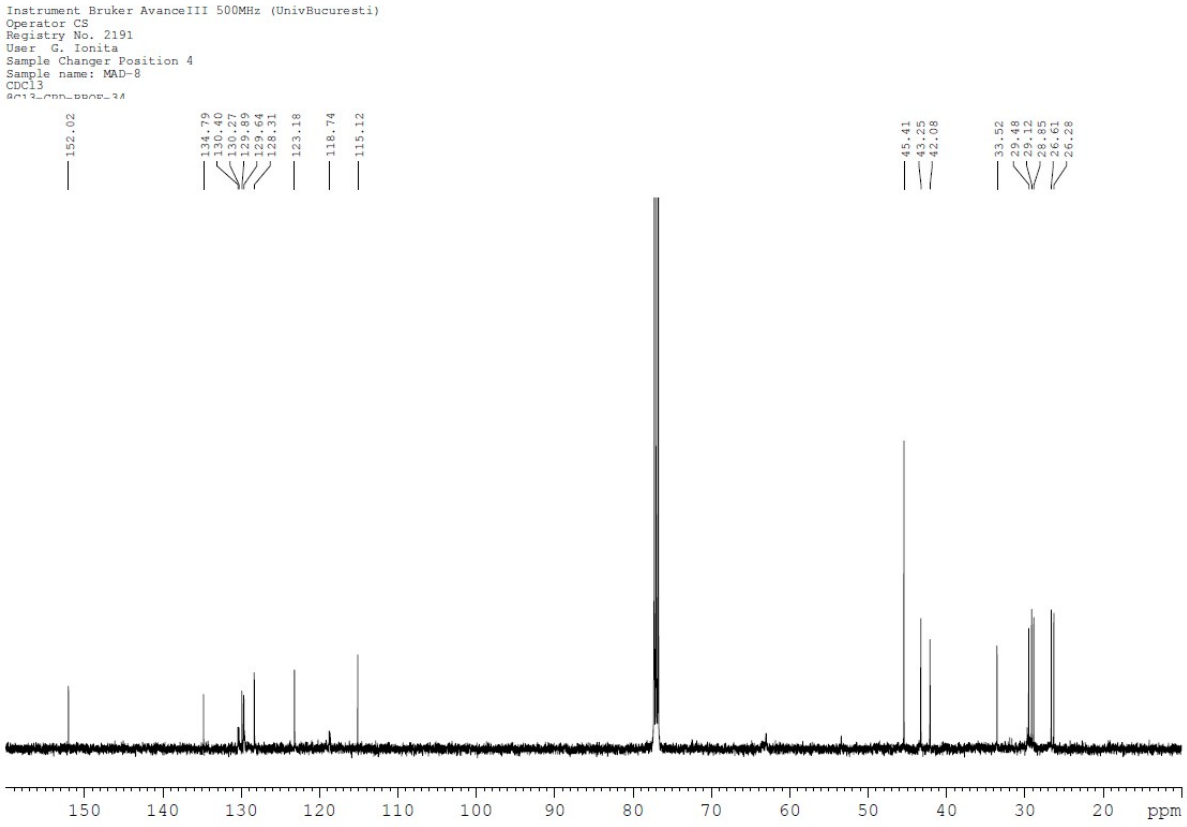
ESI-MS (*m/z*): 378 ($DA_{1.8}$ + H^+)



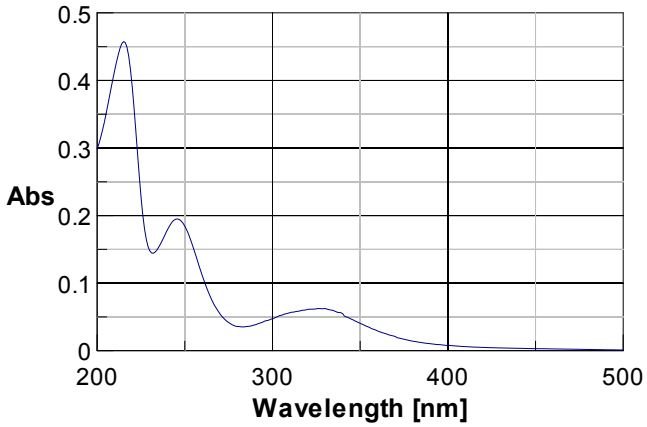
ESI-MS (*m/z*): 376 ($DA_{1.8}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.8}$

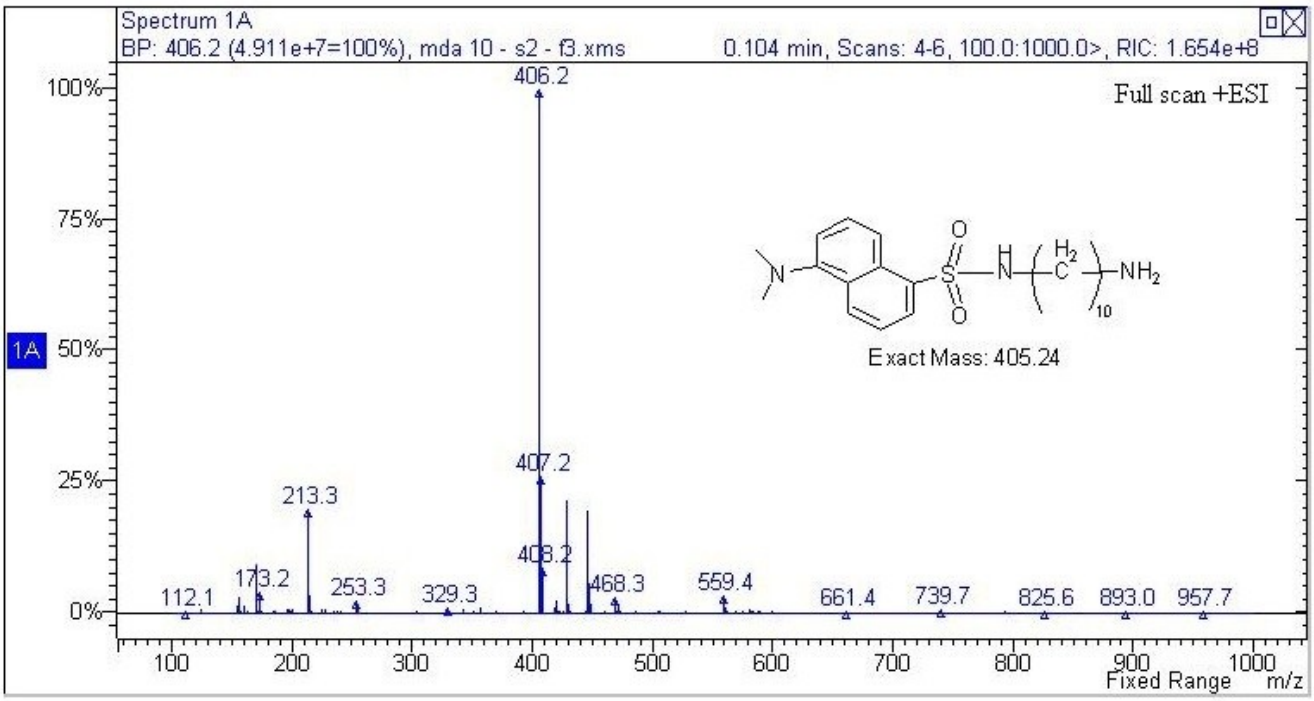


^{13}C NMR spectrum of compound $DA_{1.8}$

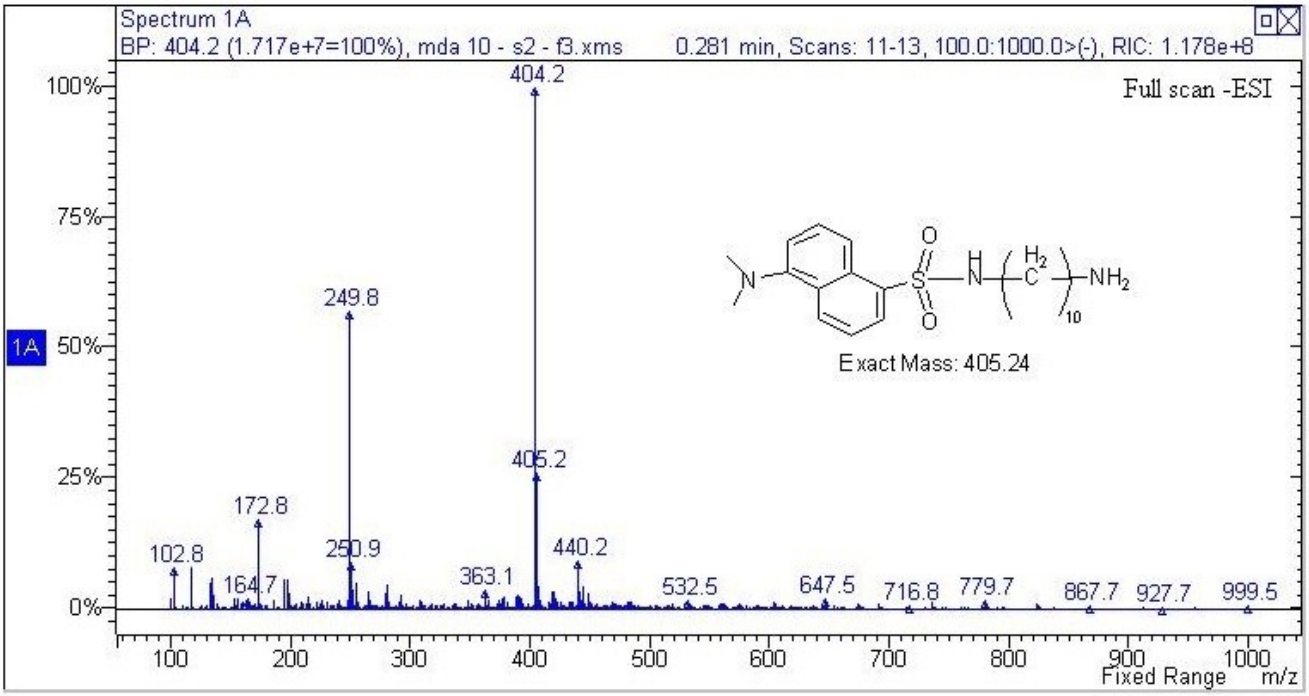


UV-Vis spectrum of compound $DA_{1.8}$

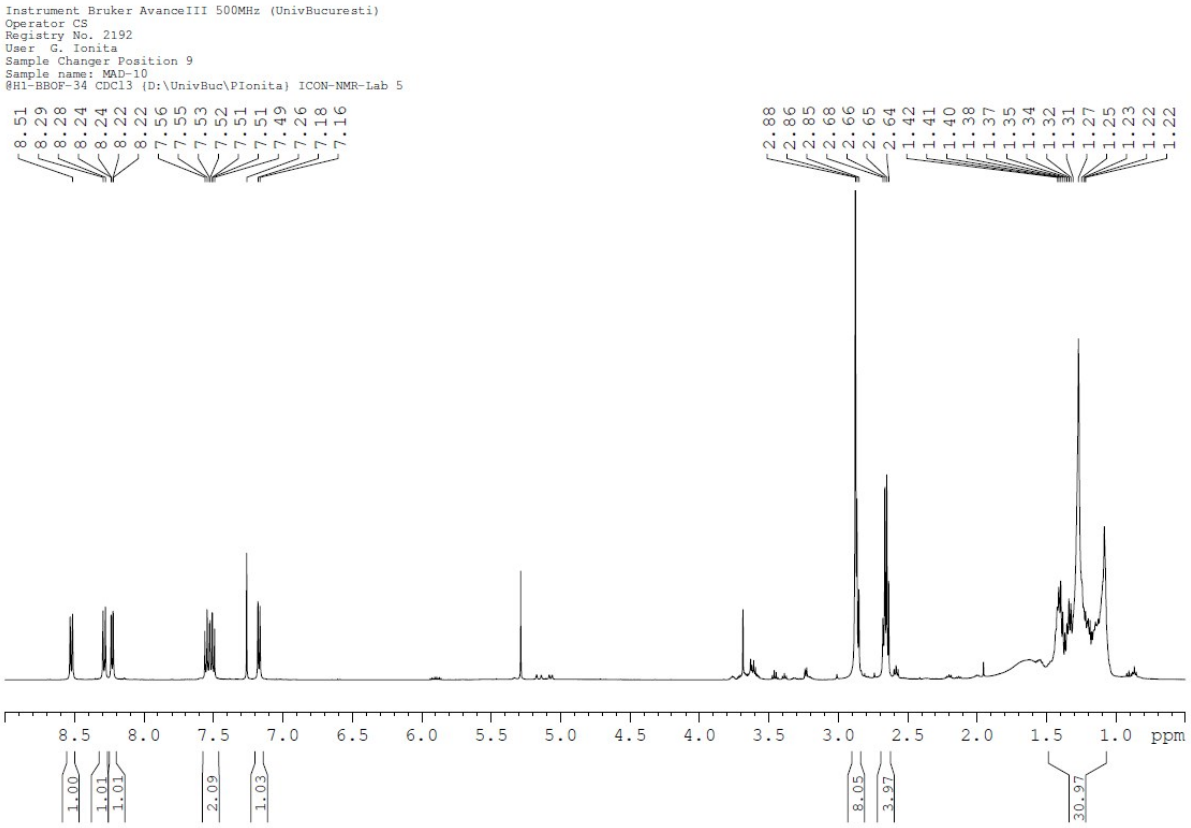
$DA_{1.10}$ (dansyl 1,10-diaminodecane)



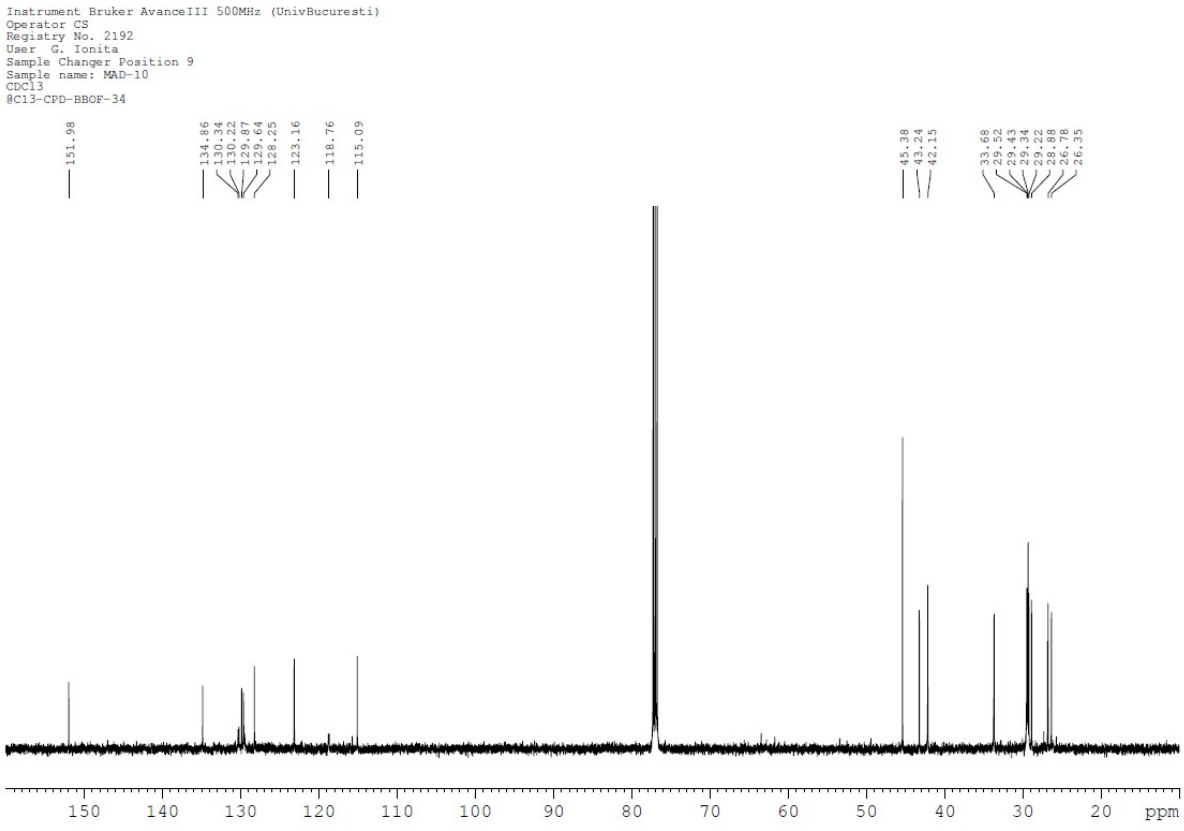
ESI-MS (*m/z*): 406 ($DA_{1.10}$ + H^+)



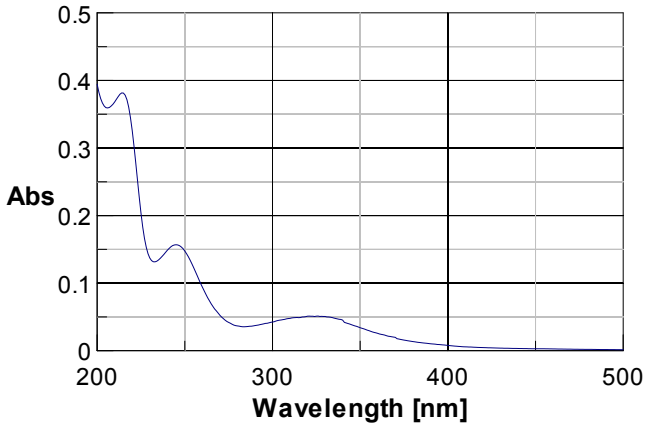
ESI-MS (*m/z*): 404 ($DA_{1.10}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.10}$

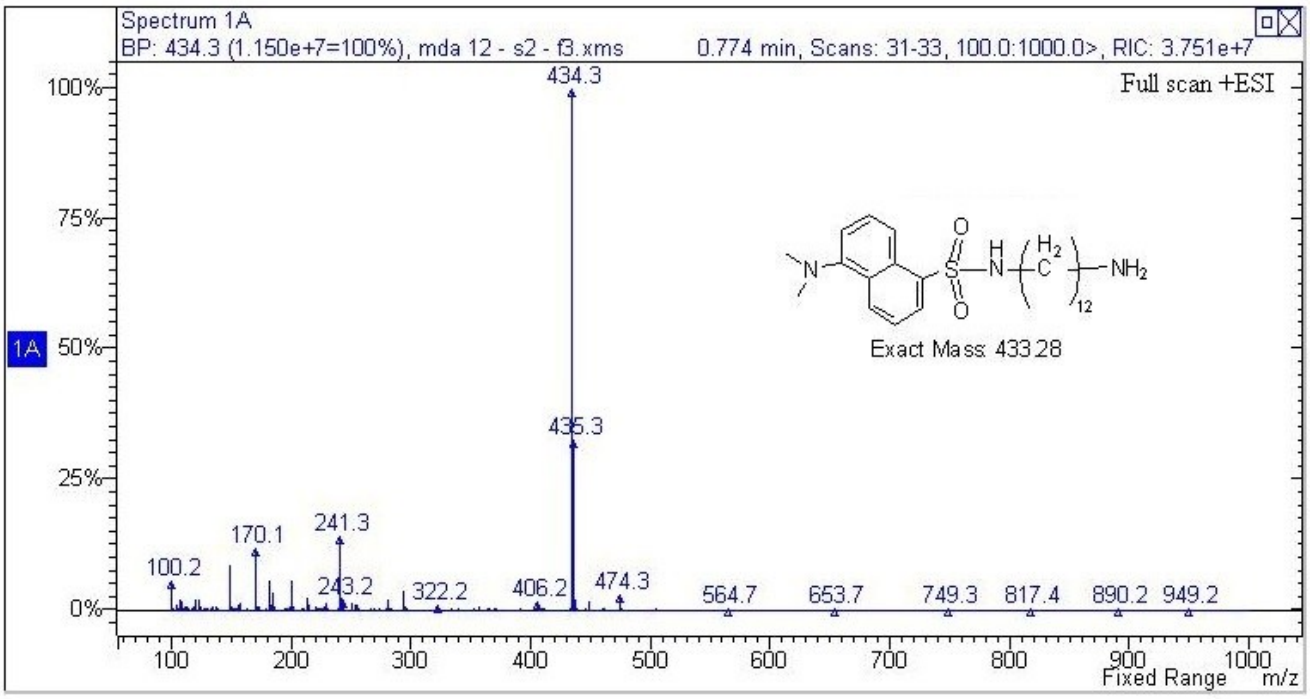


^{13}C NMR spectrum of compound $DA_{1.10}$

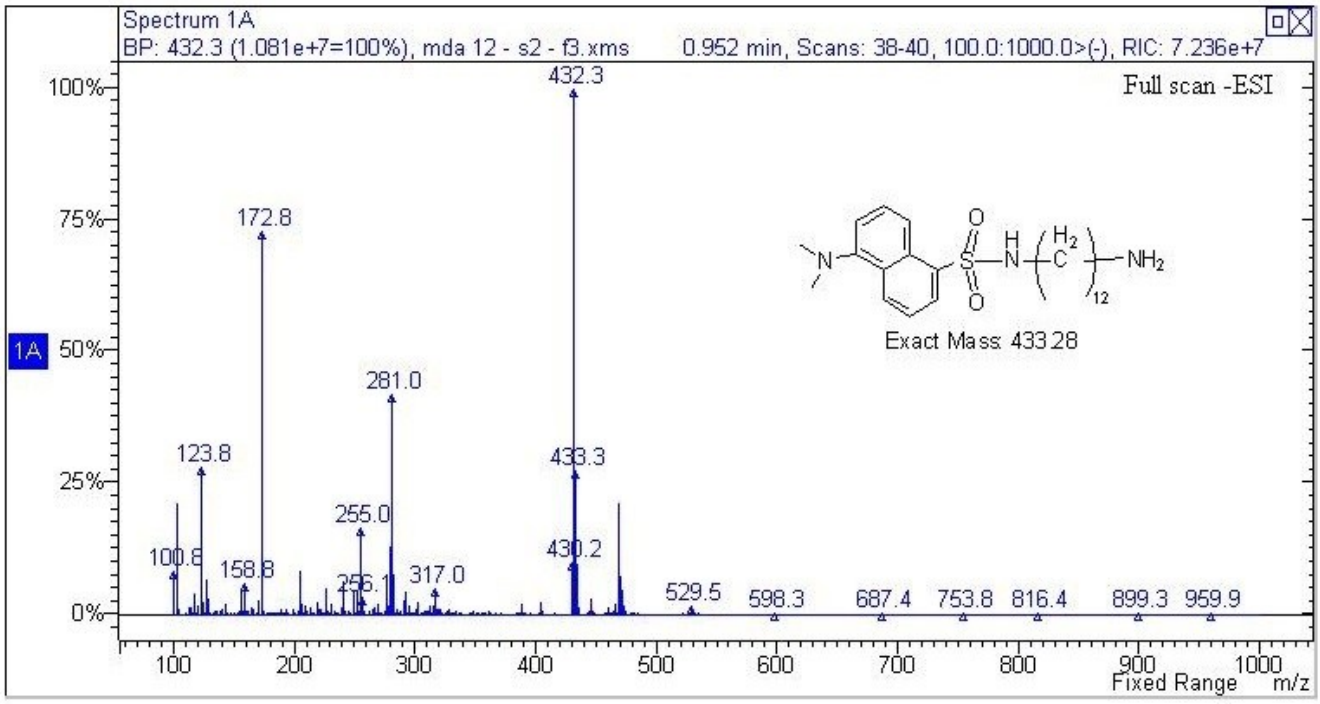


UV-Vis spectrum of compound $DA_{1.10}$

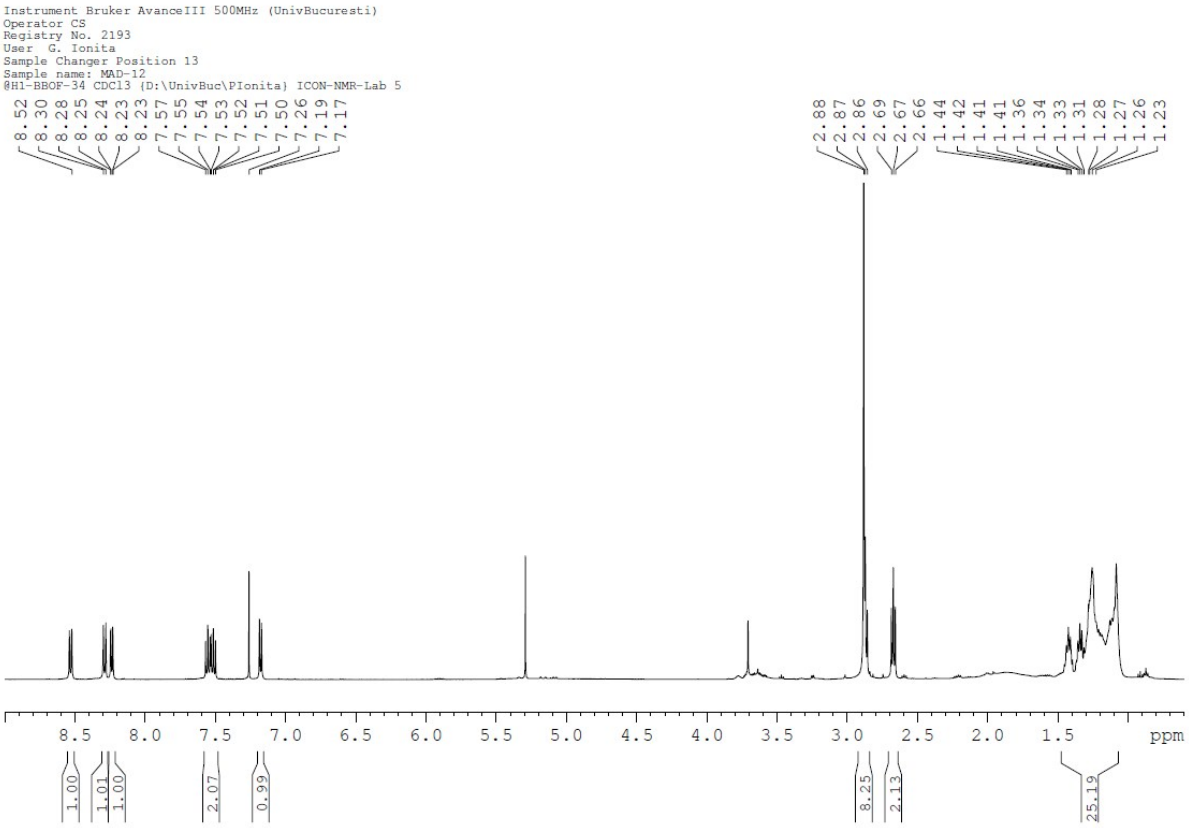
$DA_{1.12}$ (dansyl 1,12-diaminododecane)



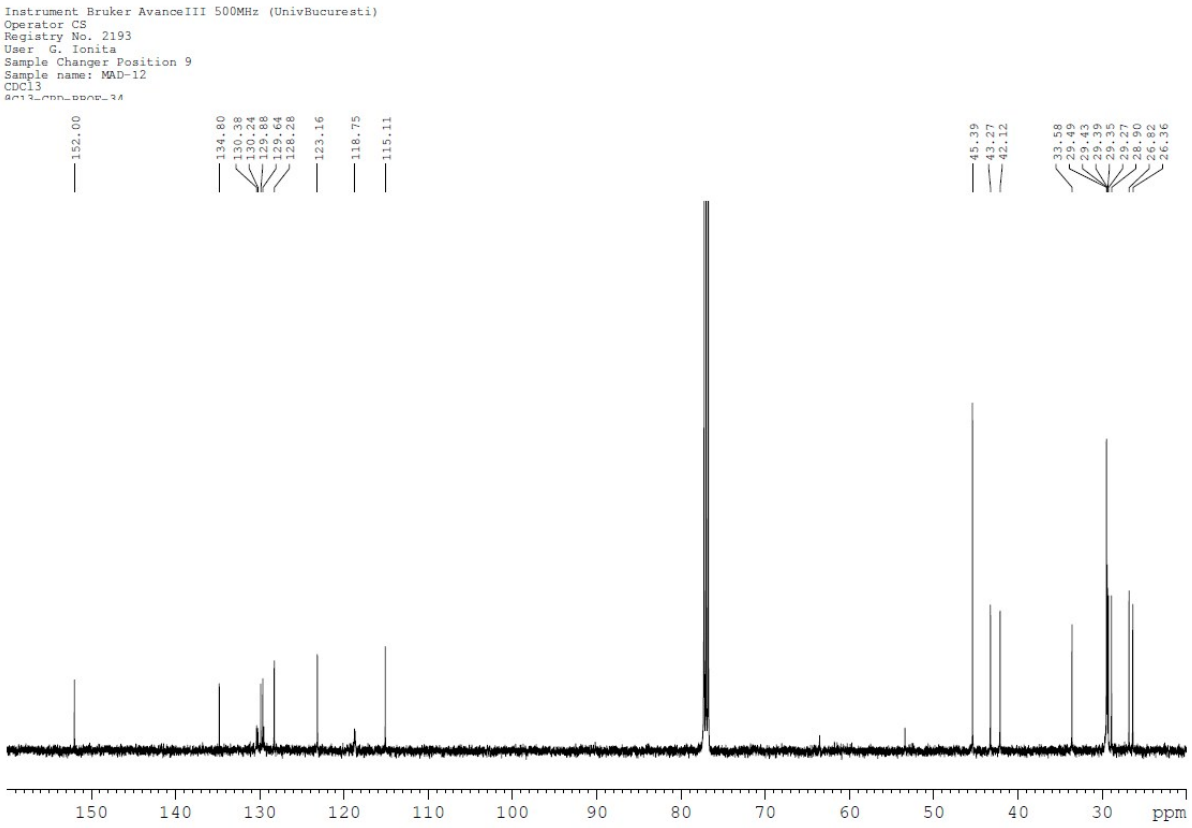
ESI-MS (*m/z*): 434 ($DA_{1.12}$ +H^+)



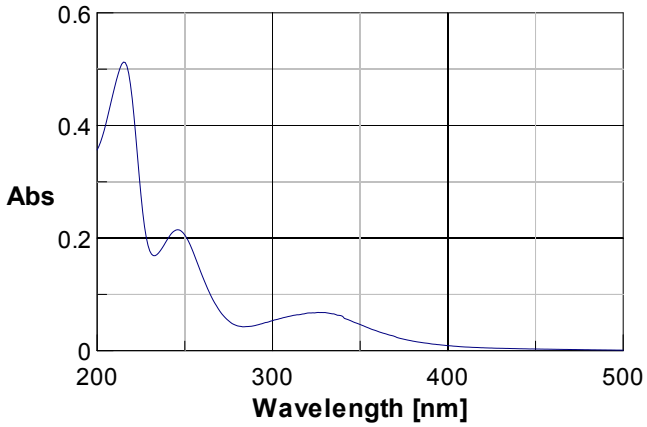
ESI-MS (*m/z*): 432 ($DA_{1.12}$ - H^+)



^{1}H NMR spectrum of compound $DA_{1.12}$



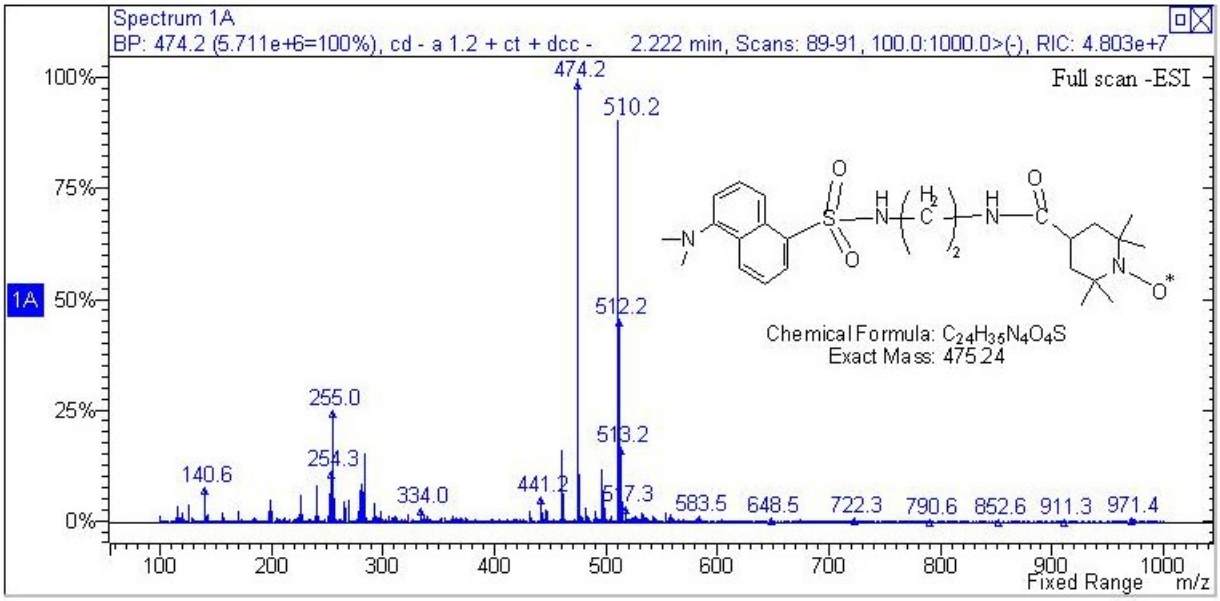
^{13}C NMR spectrum of compound $DA_{1.12}$



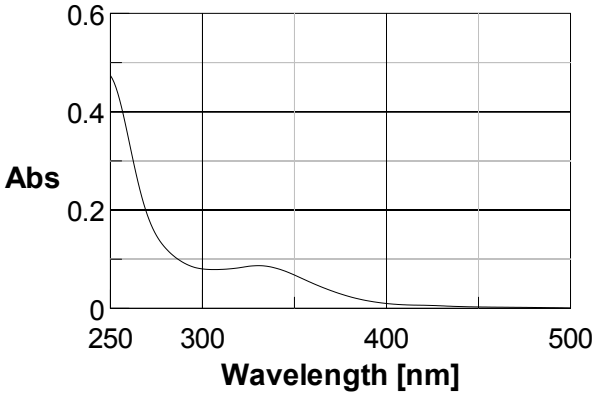
UV-Vis spectrum of compound $DA_{1.12}$

Spectral characterization of $DA_{1.n}T$

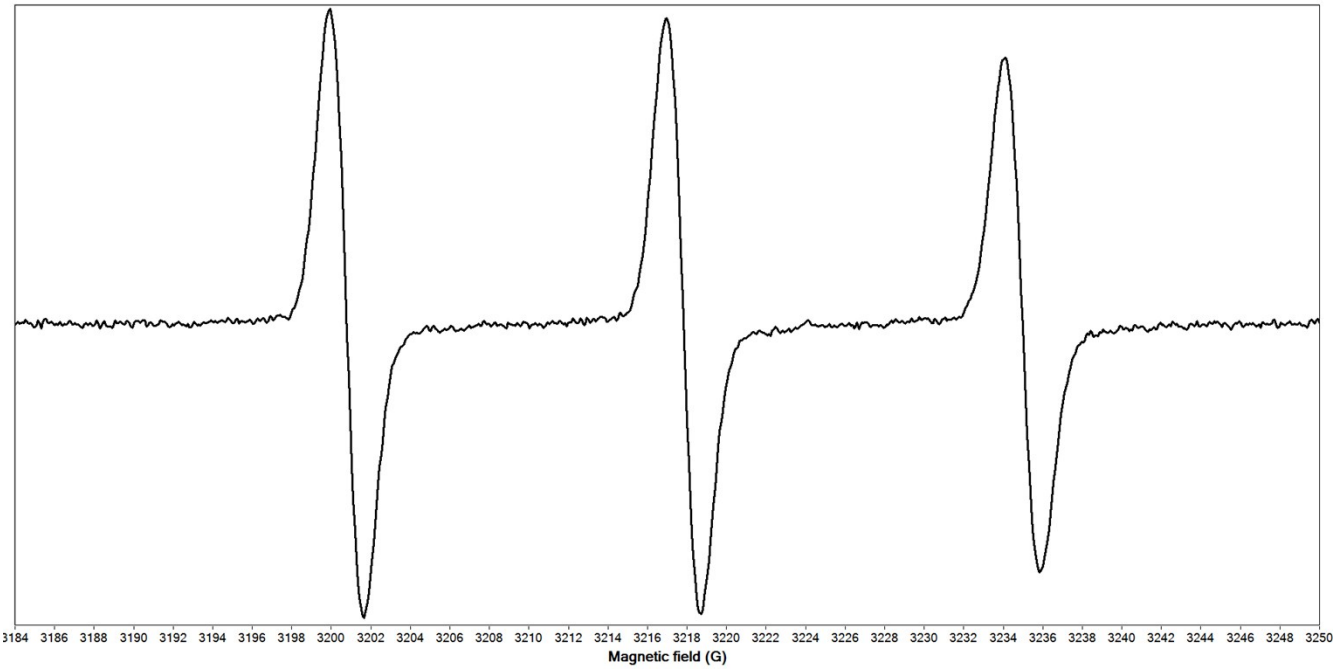
$DA_{1.2}T$



ESI-MS (*m/z*): 474 ($DA_{1.2}T$ - H^+)

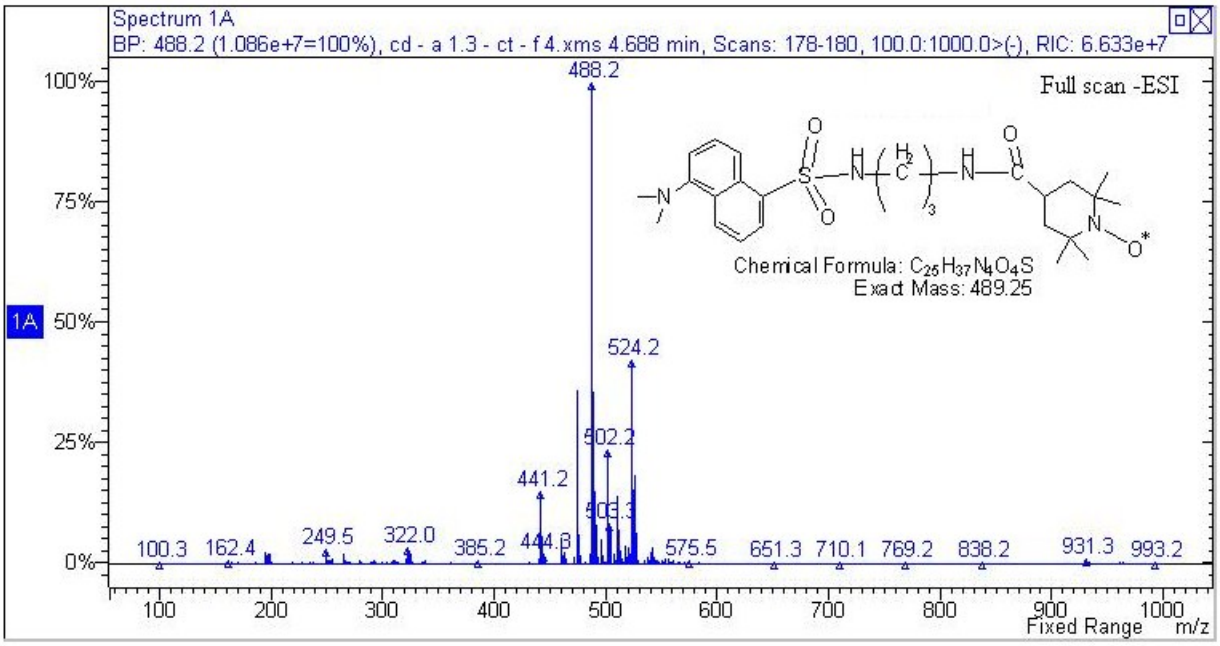


UV-Vis spectrum of compound $DA_{1.2}T$

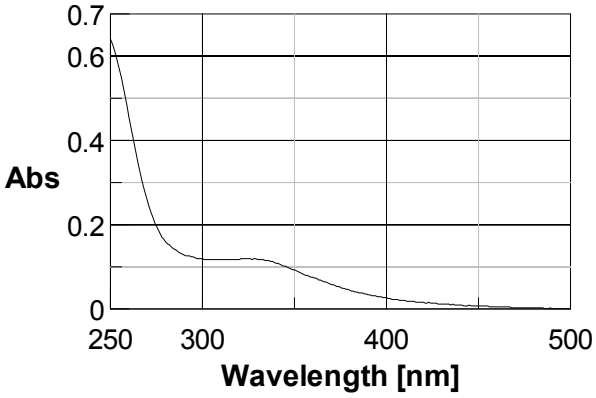


EPR spectrum of $DA_{1.2}T$

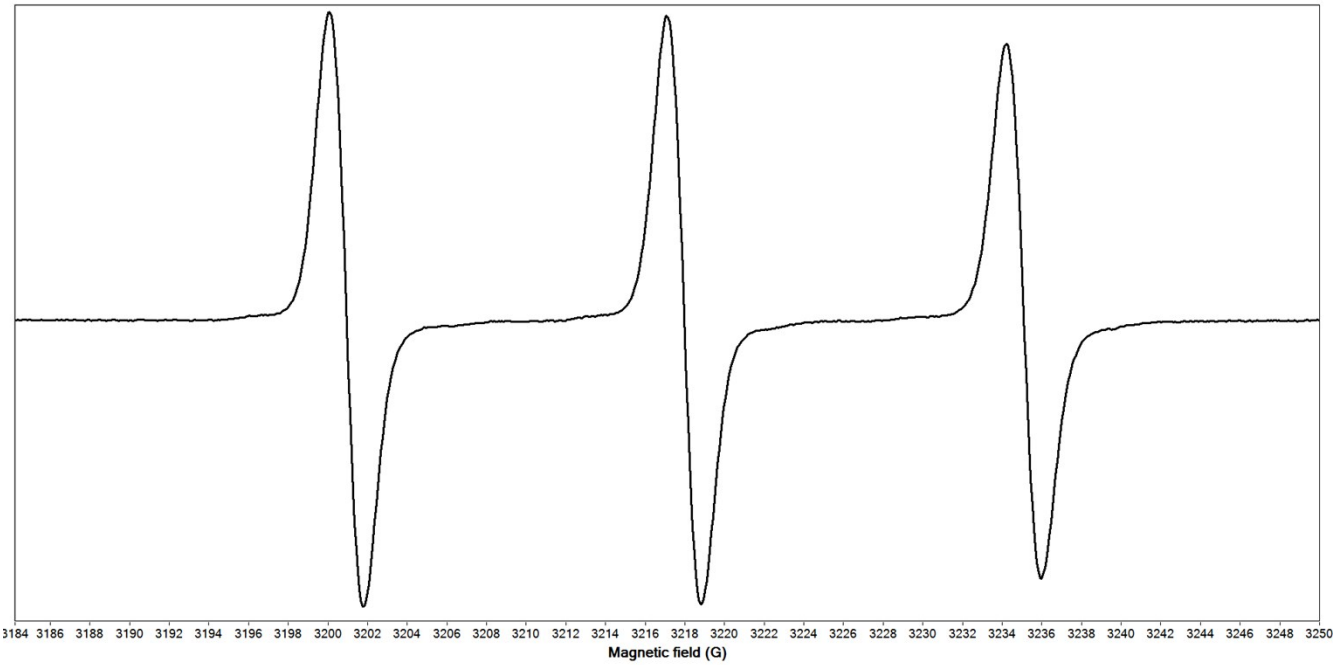
$DA_{1.3}T$



ESI-MS (*m/z*): 488 ($DA_{1.3}T$ - H^+)

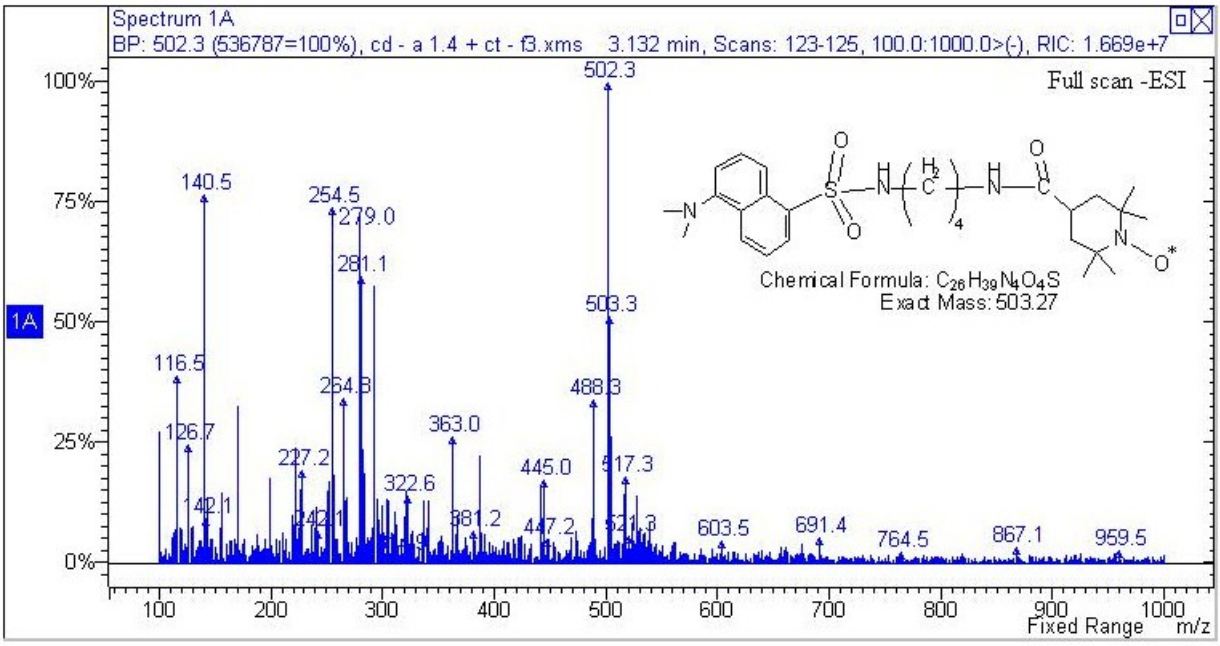


UV-Vis spectrum of compound $DA_{1.3}T$

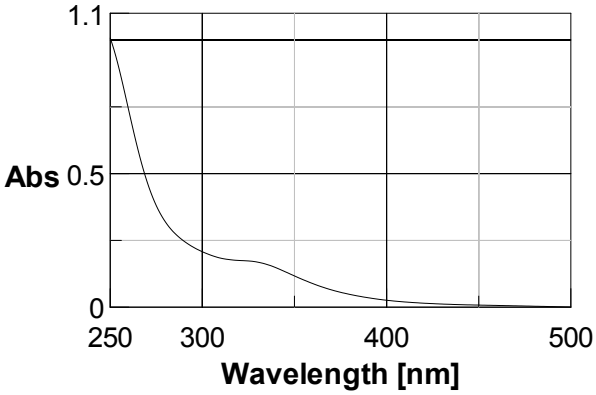


EPR spectrum of $DA_{1.3}T$

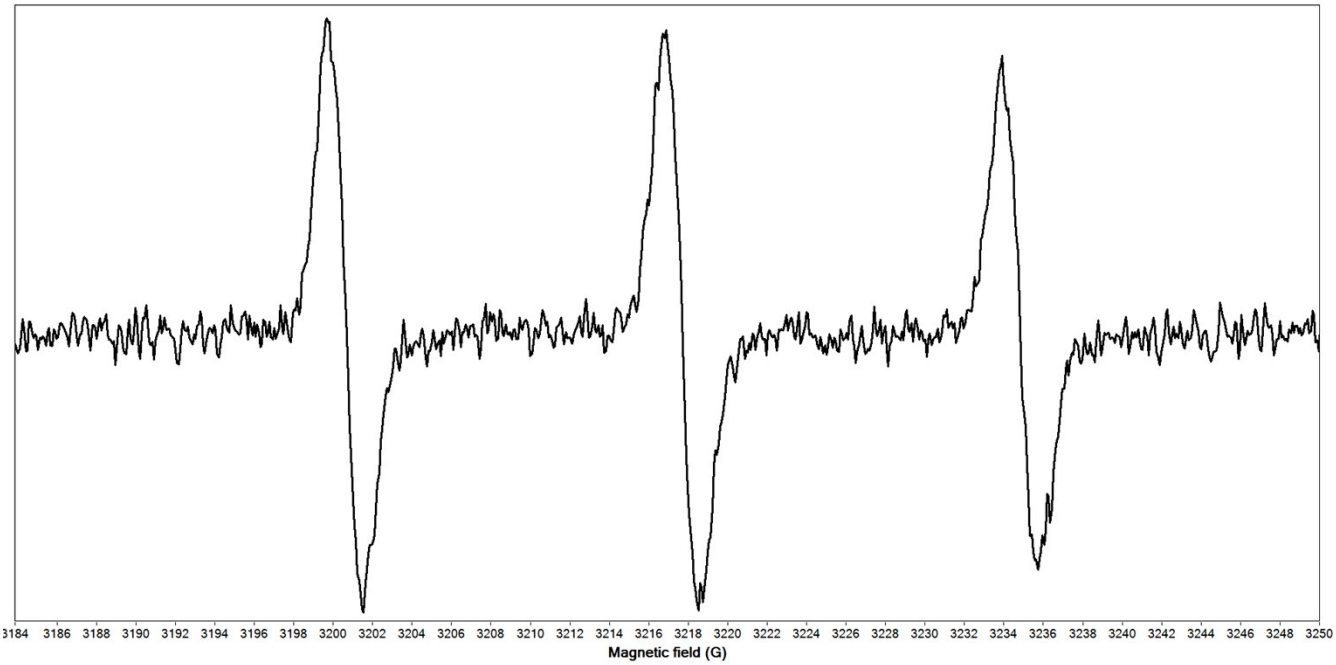
$DA_{1.4}T$



ESI-MS (*m/z*): 502 ($DA_{1.4}T$ - H^+)

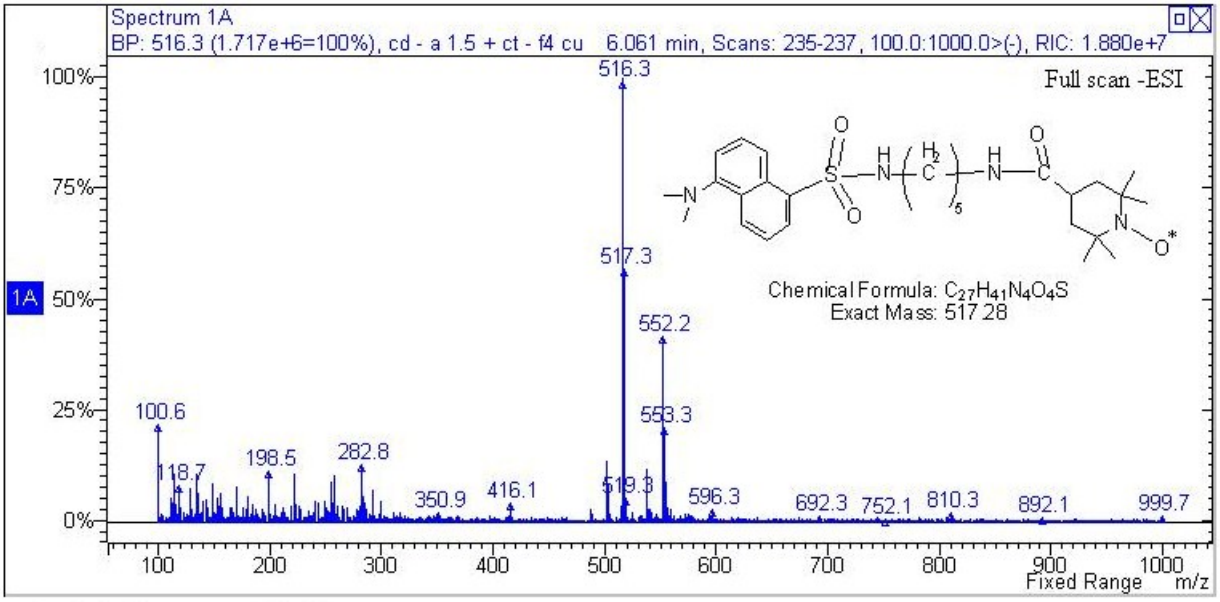


UV-Vis spectrum of compound $DA_{1.4}T$

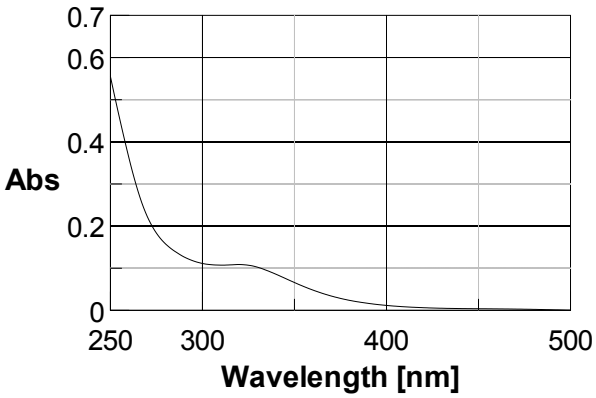


EPR spectrum of $DA_{1.4}T$

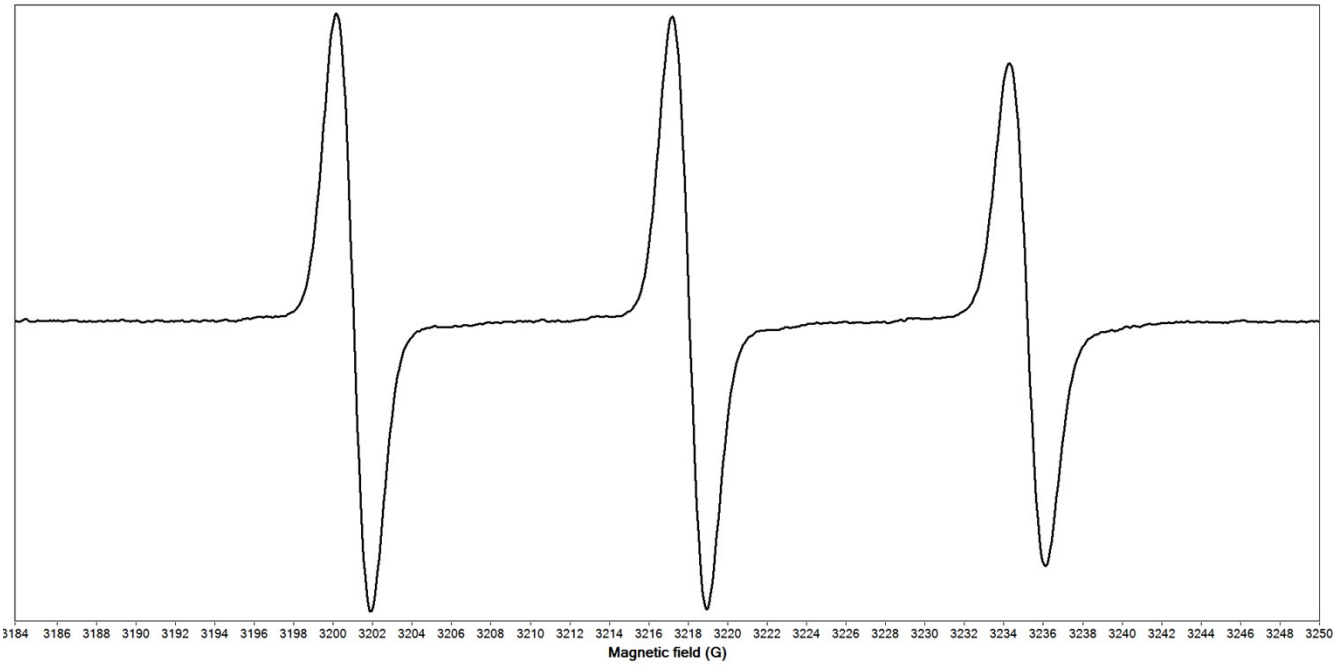
$DA_{1.5}T$



ESI-MS (*m/z*): 516 ($DA_{1.5}T$ - H^+)

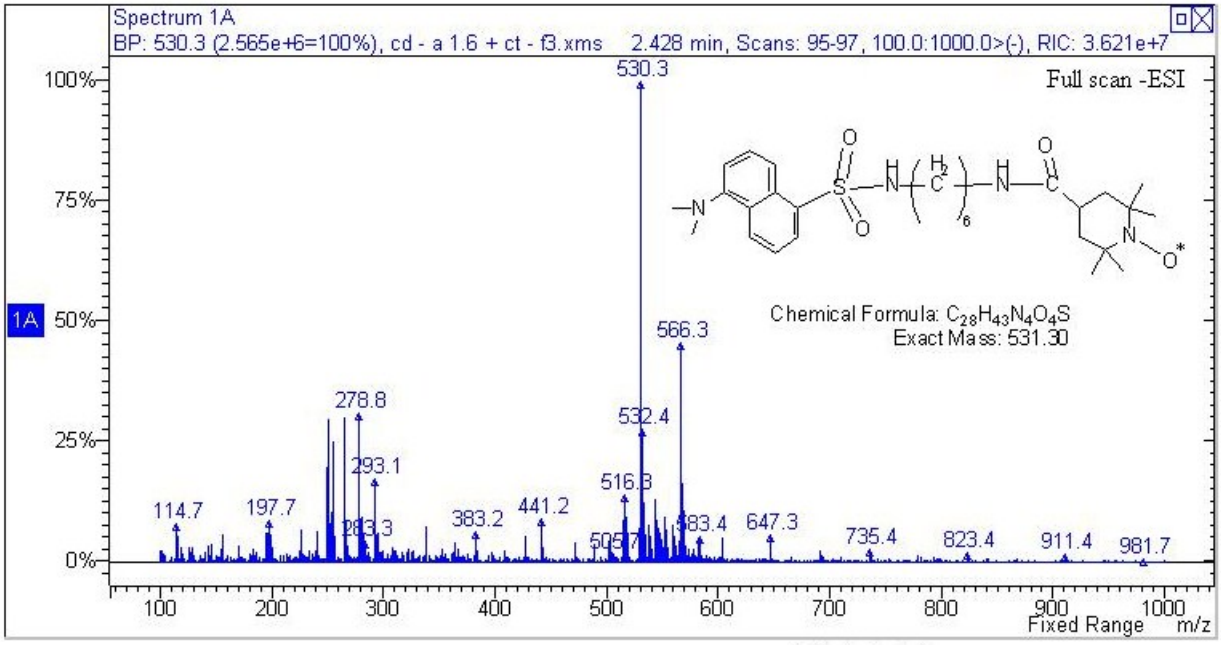


UV-Vis spectrum of compound $DA_{1.5}T$

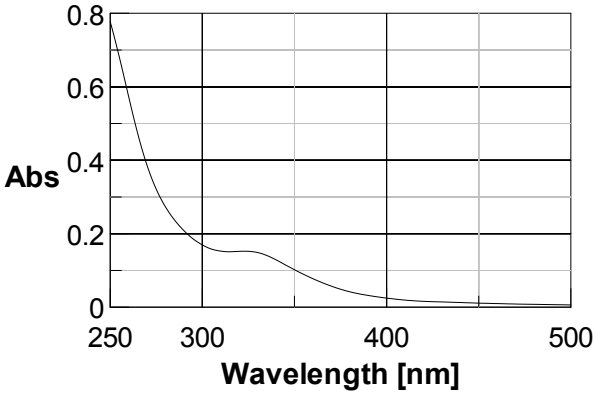


EPR spectrum of $DA_{1.5}T$

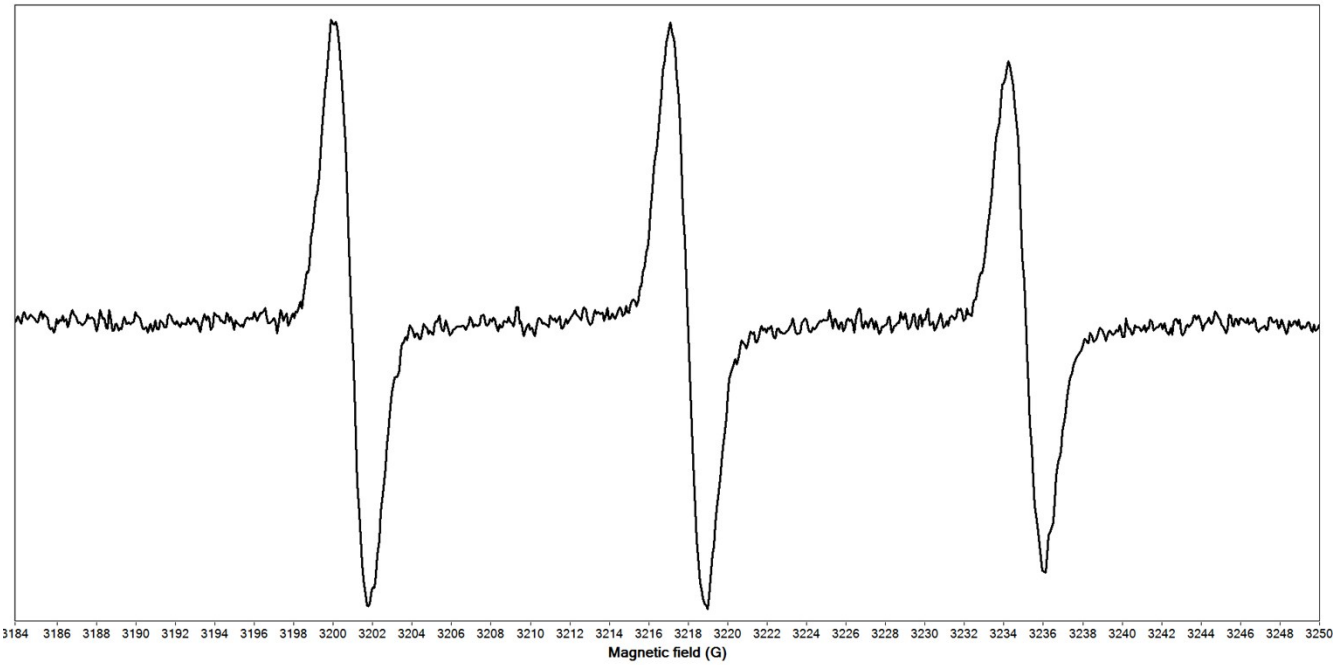
$DA_{1.6}T$



ESI-MS (*m/z*): 530 ($DA_{1.6}T$ - H^+)

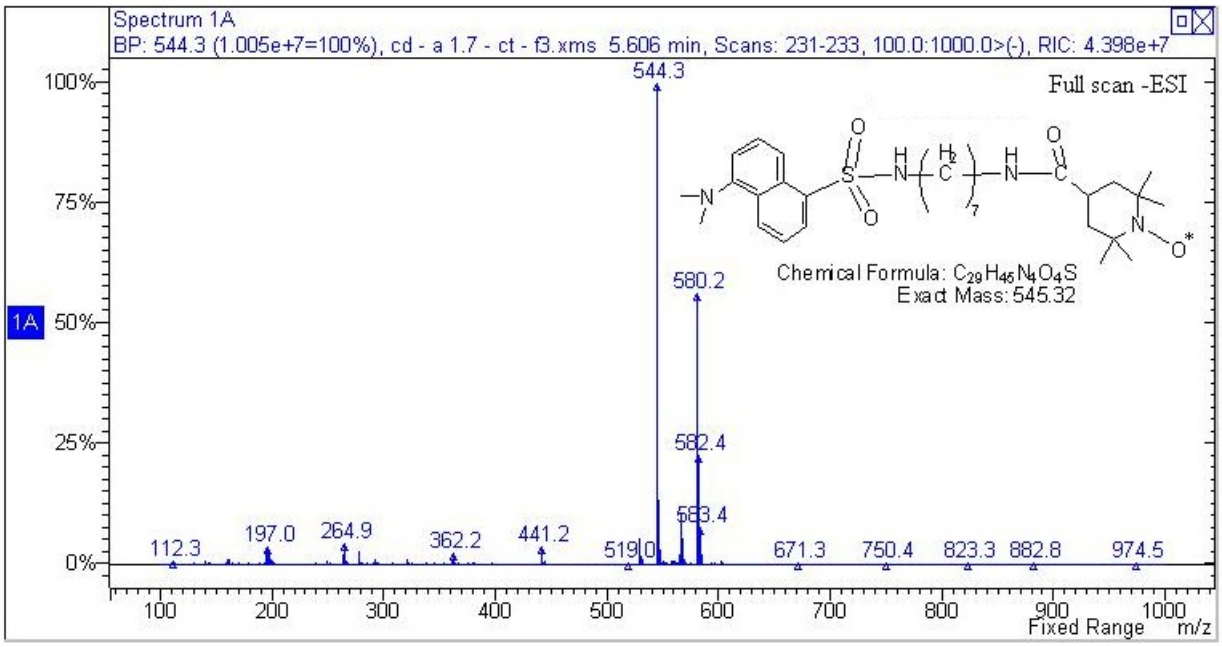


UV-Vis spectrum of compound $DA_{1.6}T$

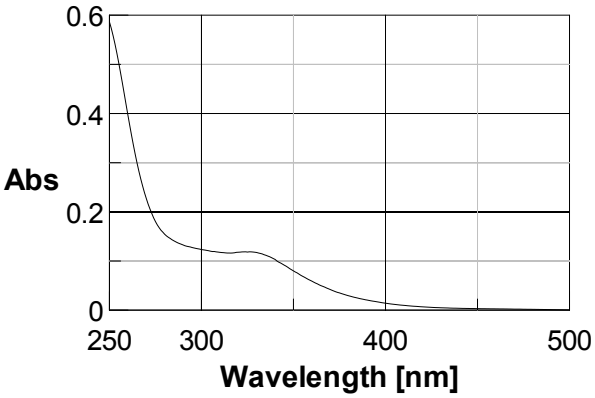


EPR spectrum of $DA_{1.6}T$

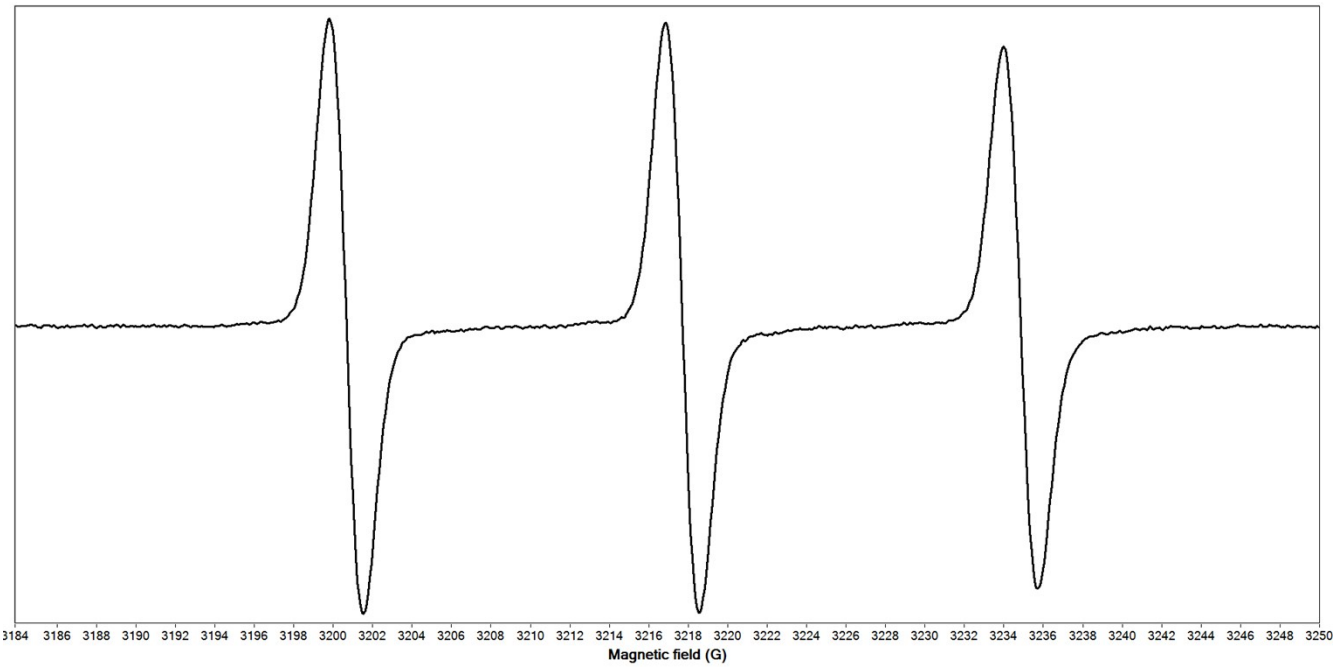
$DA_{1.7}T$



ESI-MS (*m/z*): 544 ($DA_{1.7}T$ - H^+)

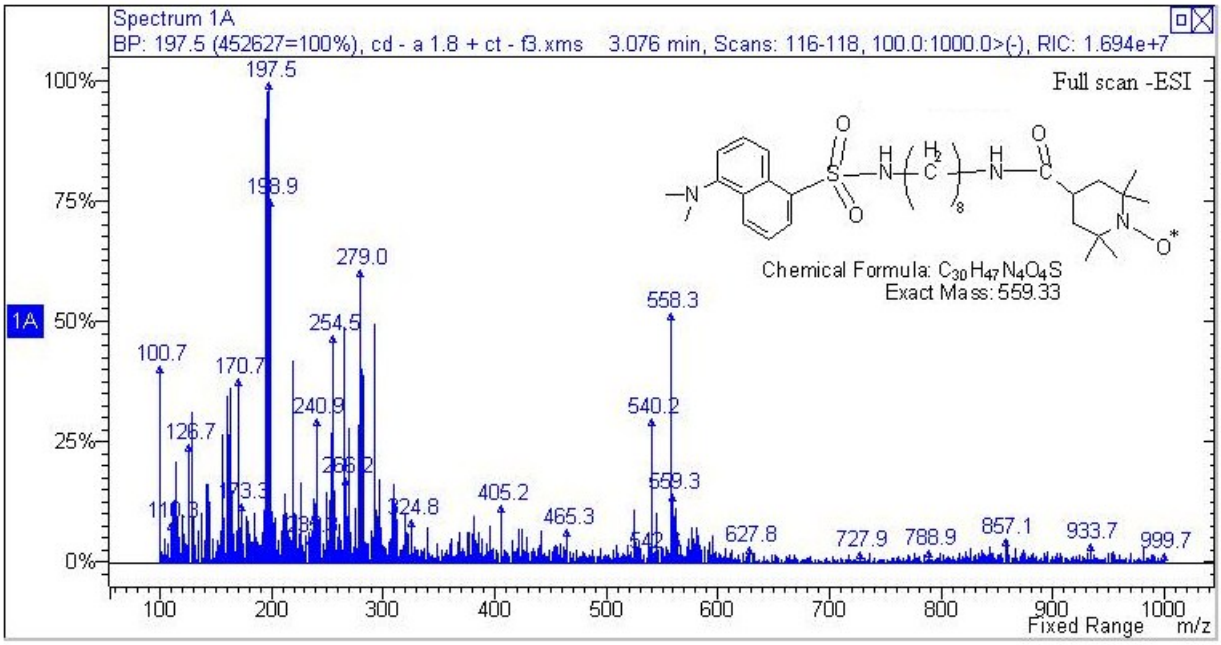


UV-Vis spectrum of compound $DA_{1.7}T$

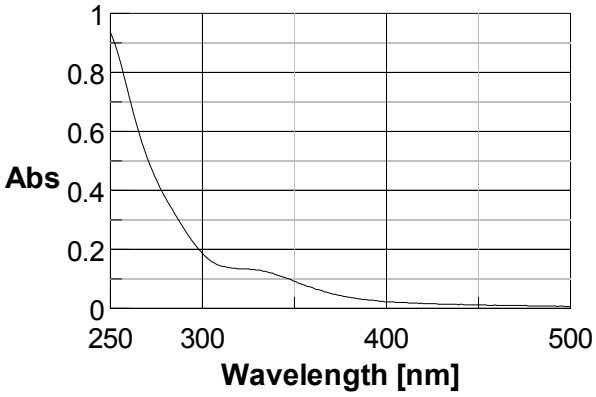


EPR spectrum of $DA_{1.7}T$

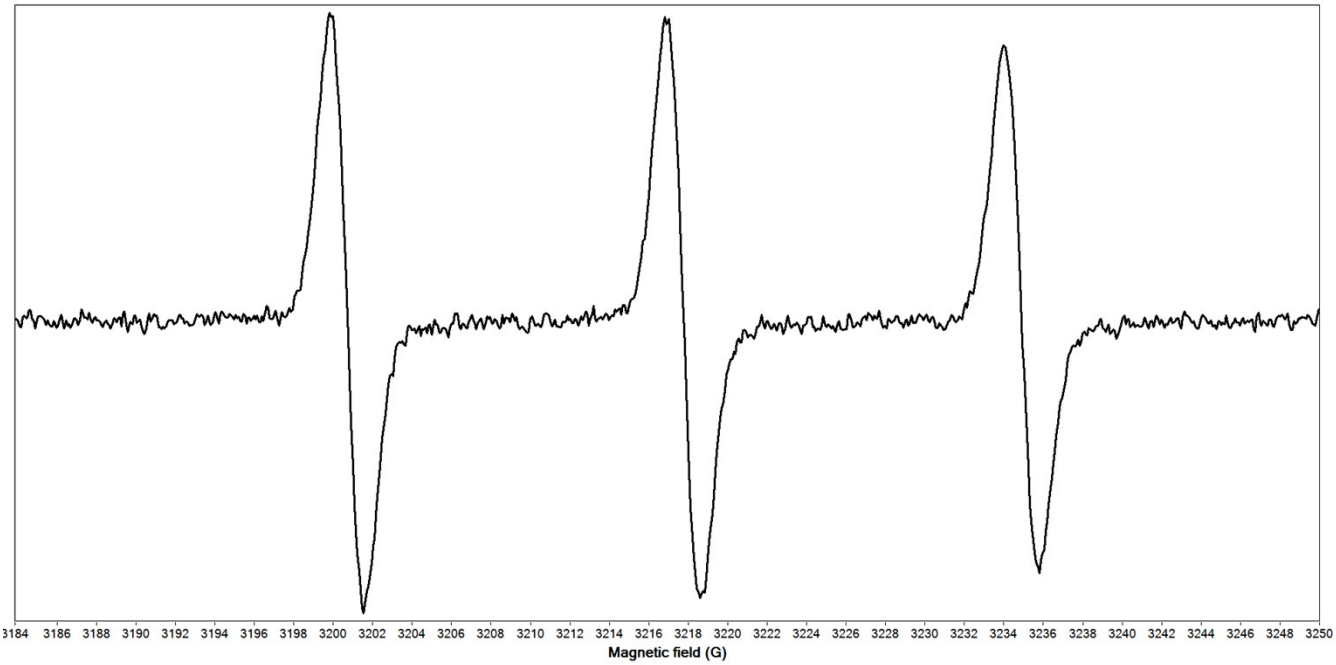
$DA_{1.8}T$



ESI-MS (*m/z*): 558 ($DA_{1.8}T$ - H^+)

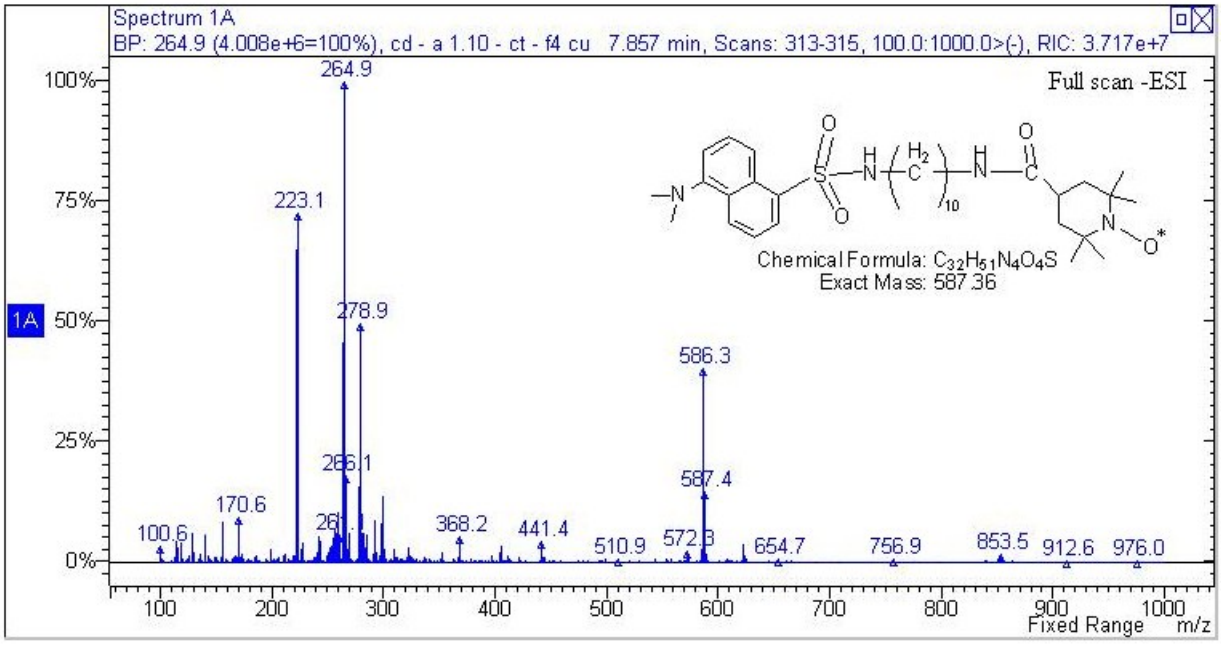


UV-Vis spectrum of compound $DA_{1.8}T$

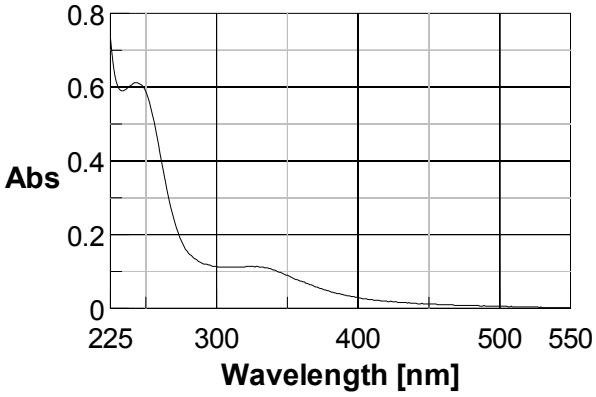


EPR spectrum of $DA_{1.8}T$

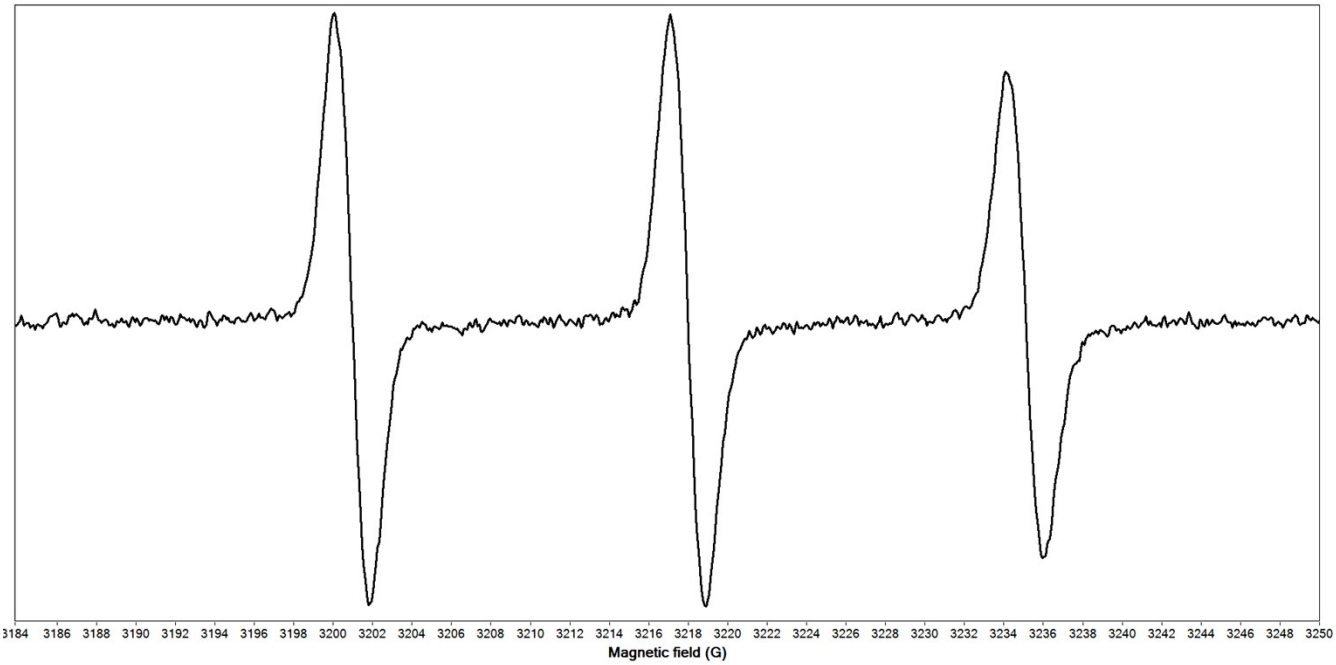
$DA_{1.10}T$



ESI-MS (*m/z*): 586 ($DA_{1.10}T$ - H^+)

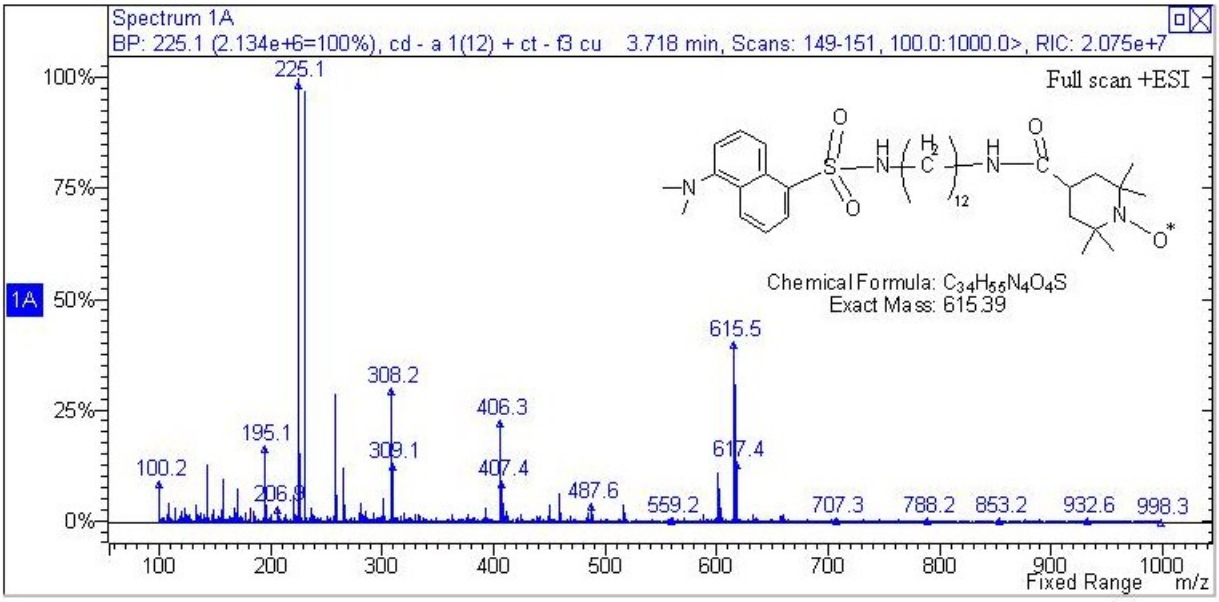


UV-Vis spectrum of compound $DA_{1.10}T$

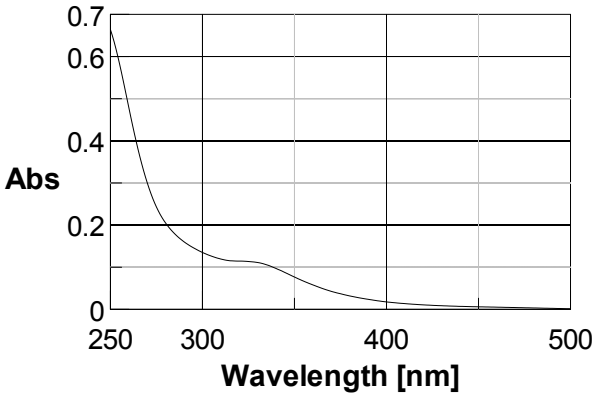


EPR spectrum of $DA_{1.10}T$

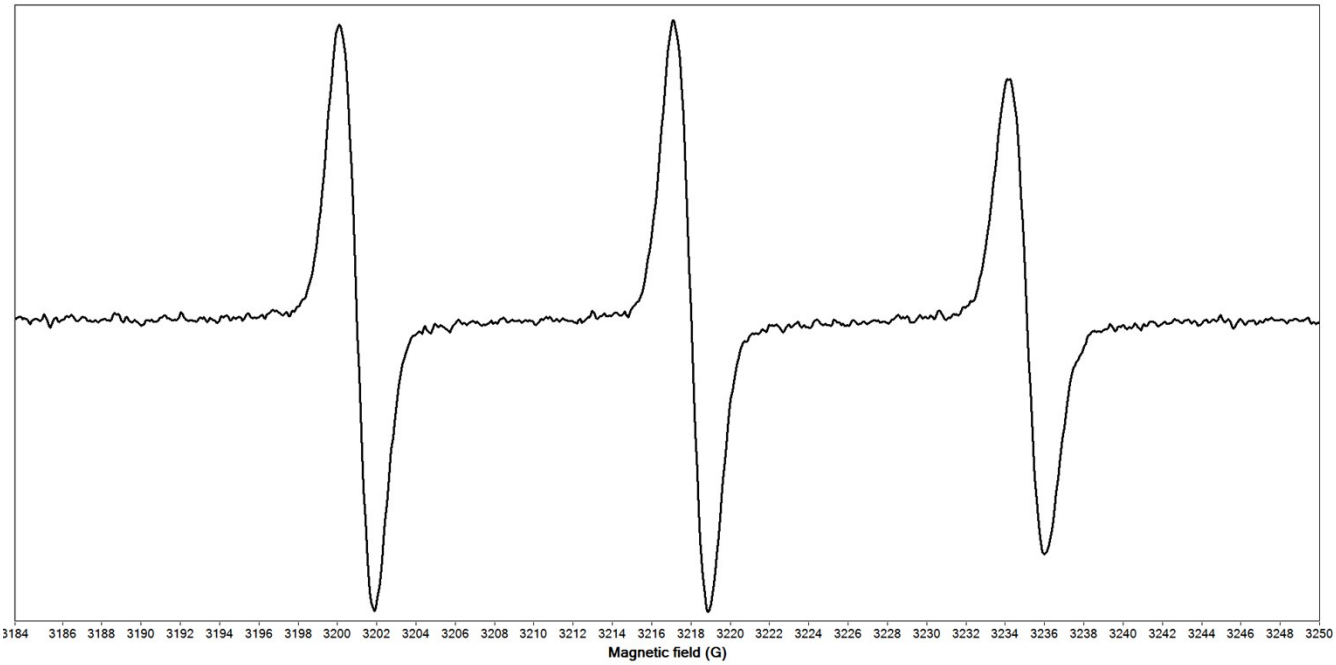
$DA_{1.12}T$



ESI-MS (*m/z*): 615 ($DA_{1.12}T$)



UV-Vis spectrum of compound $DA_{1.12}T$



EPR spectrum of $DA_{1.12}T$