Electronic Supporting Information (ESI)

Development of new 2-piperidinium-4-styrylcoumarin derivatives with large Stokes shifts as potential fluorescent labels for biomolecules

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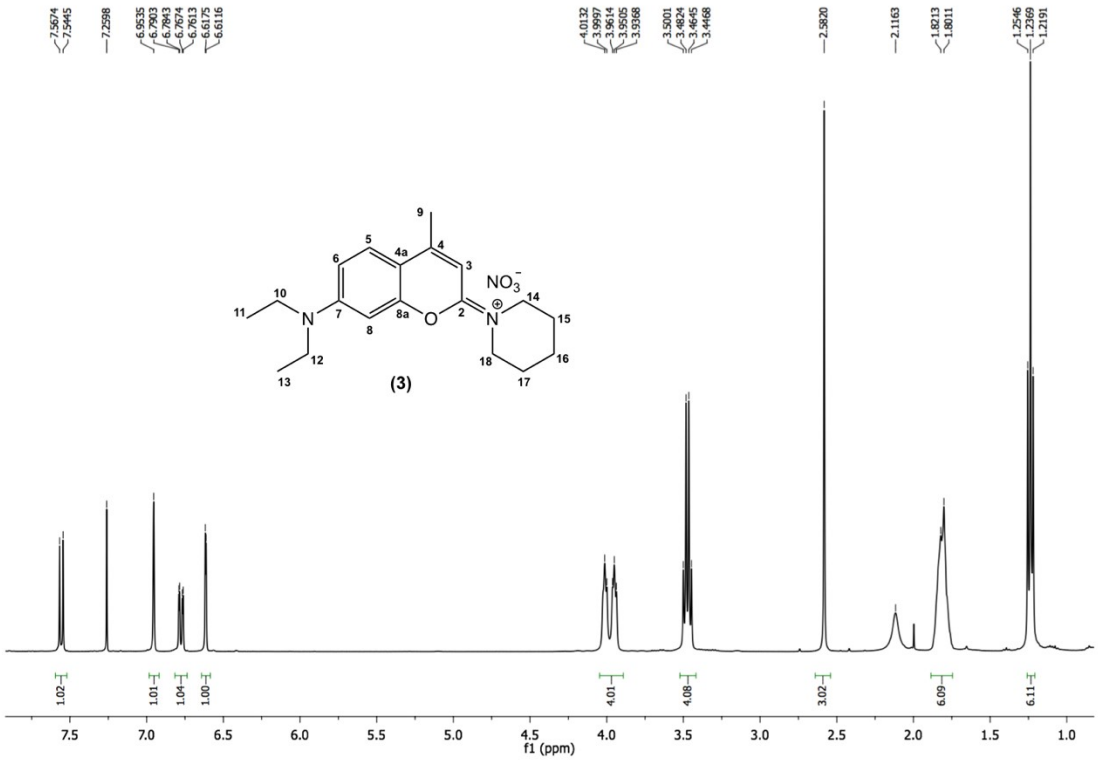
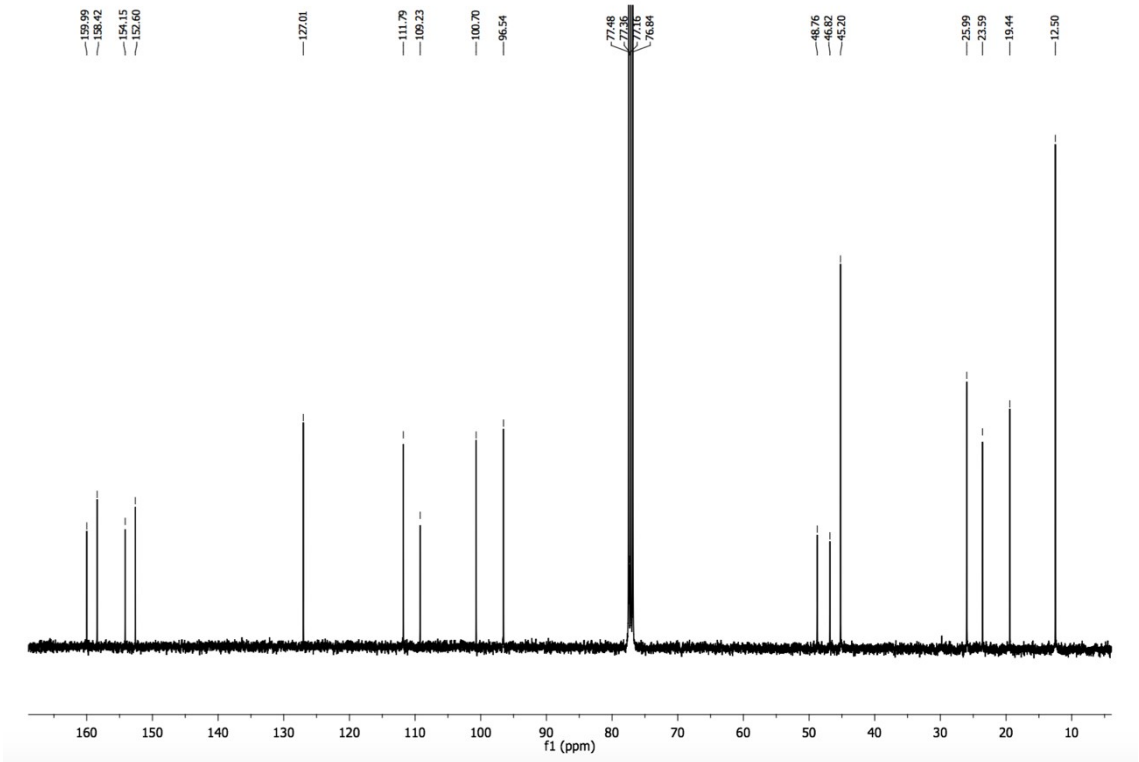
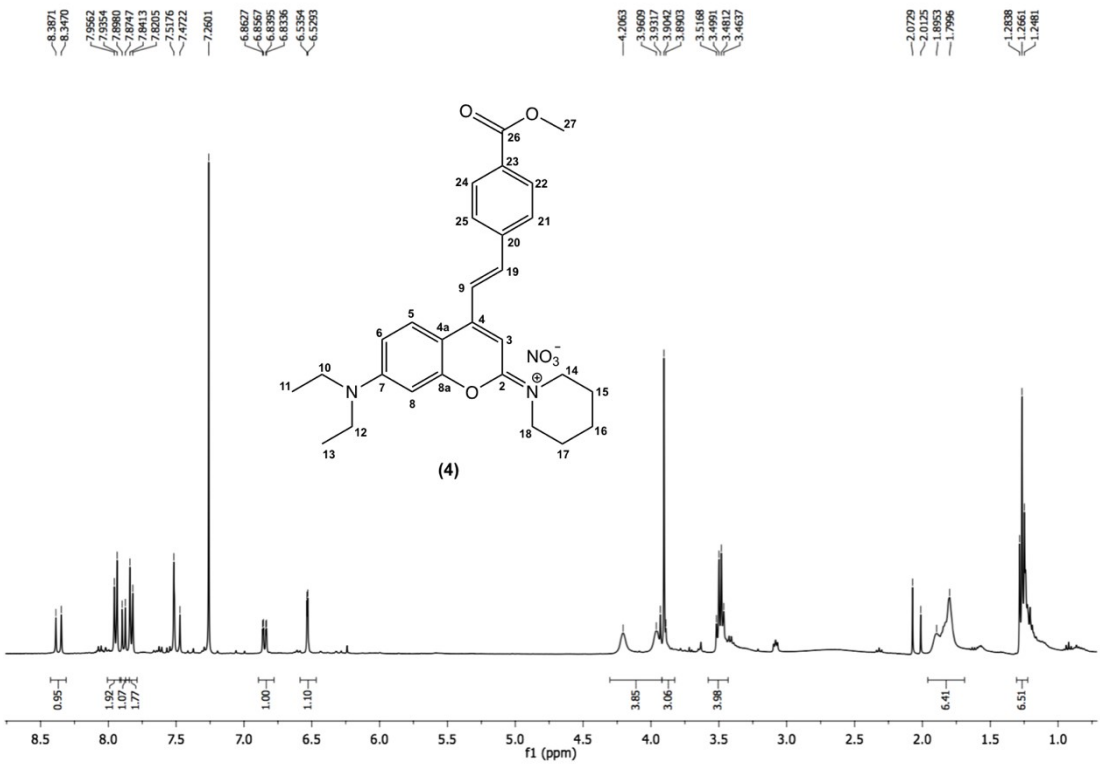
1 NMR spectra



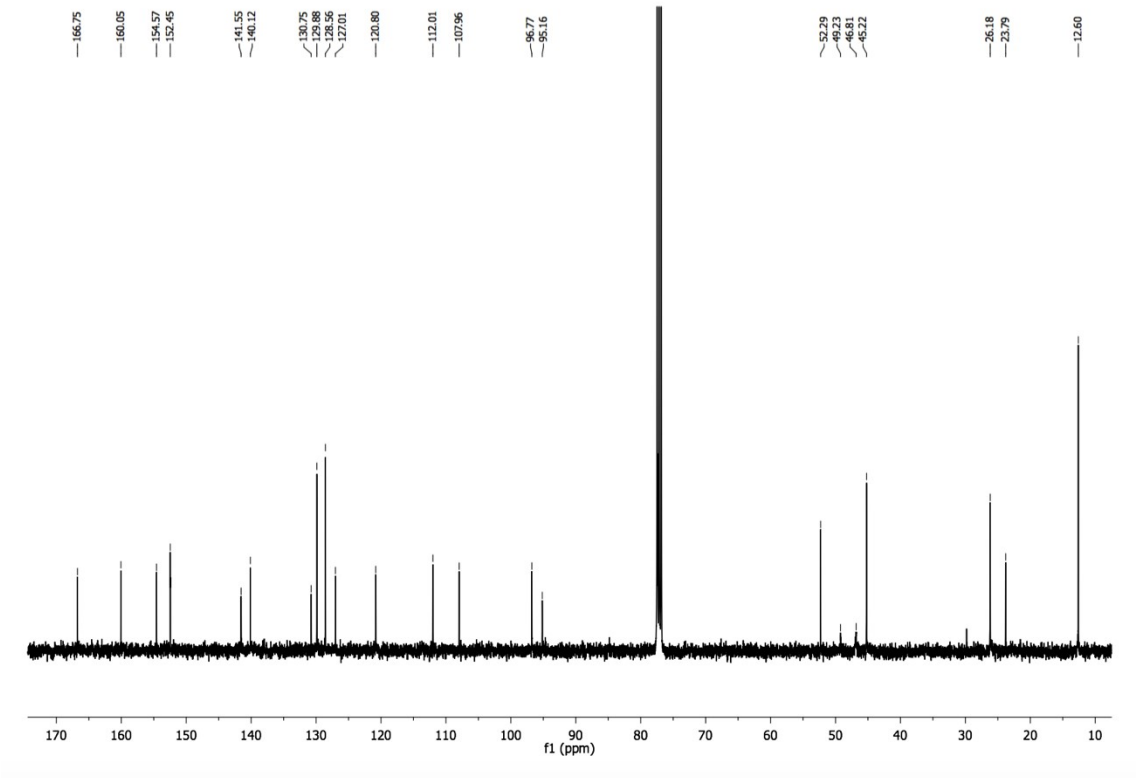
*^{1}H-NMR spectrum of **3** ($CDCl_3$, 400 MHz)*



*^{13}C-NMR spectrum of **3** ($CDCl_3$, 100 MHz)*



*^{1}H-NMR spectrum of **4** ($CDCl_3$, 400 MHz)*



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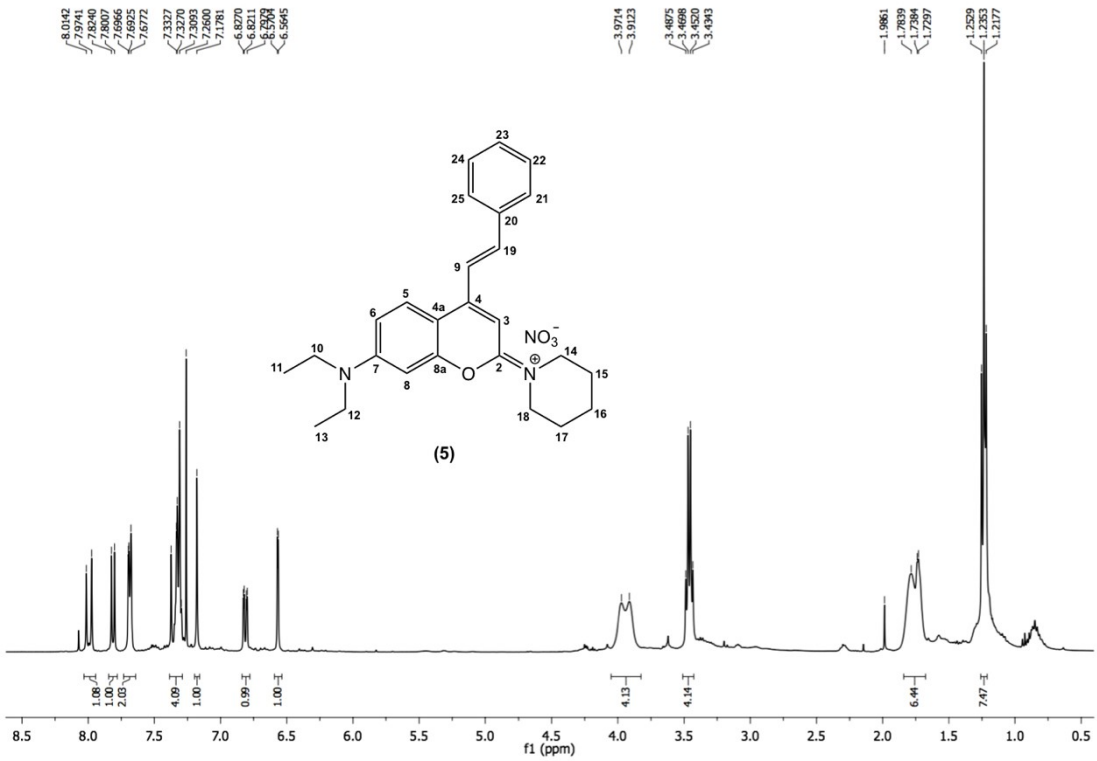
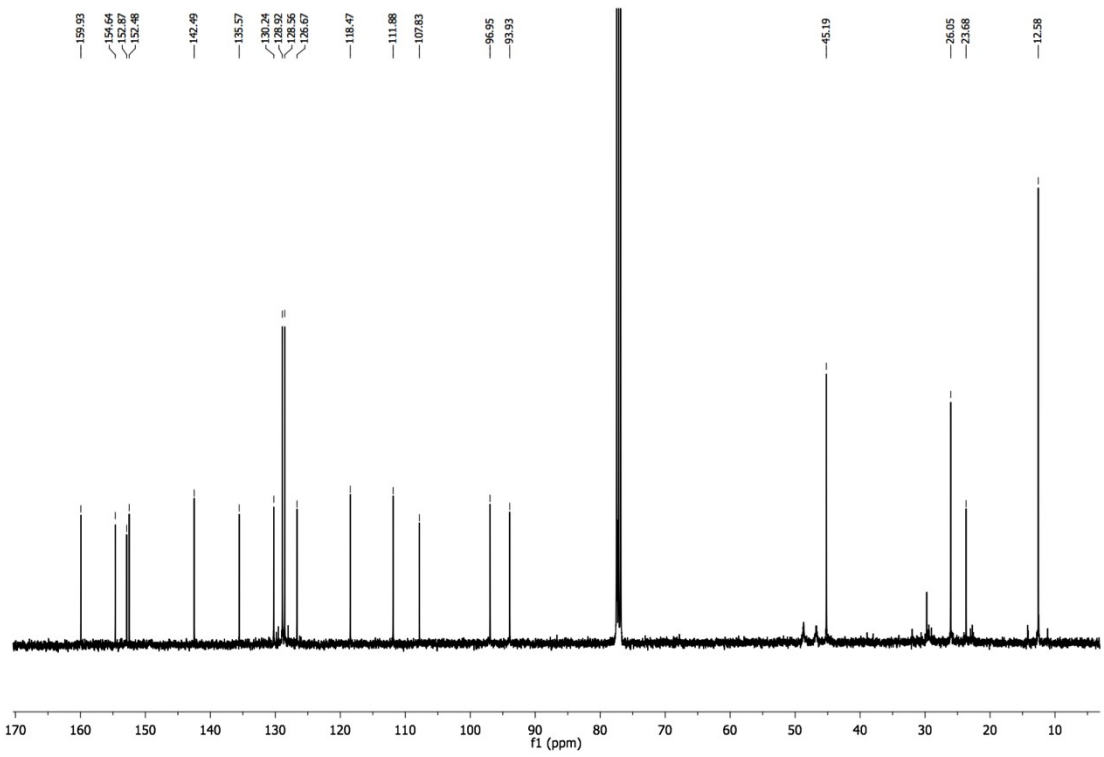


*^{1}H-NMR spectrum of **5** ($CDCl_3$, 400 MHz)*



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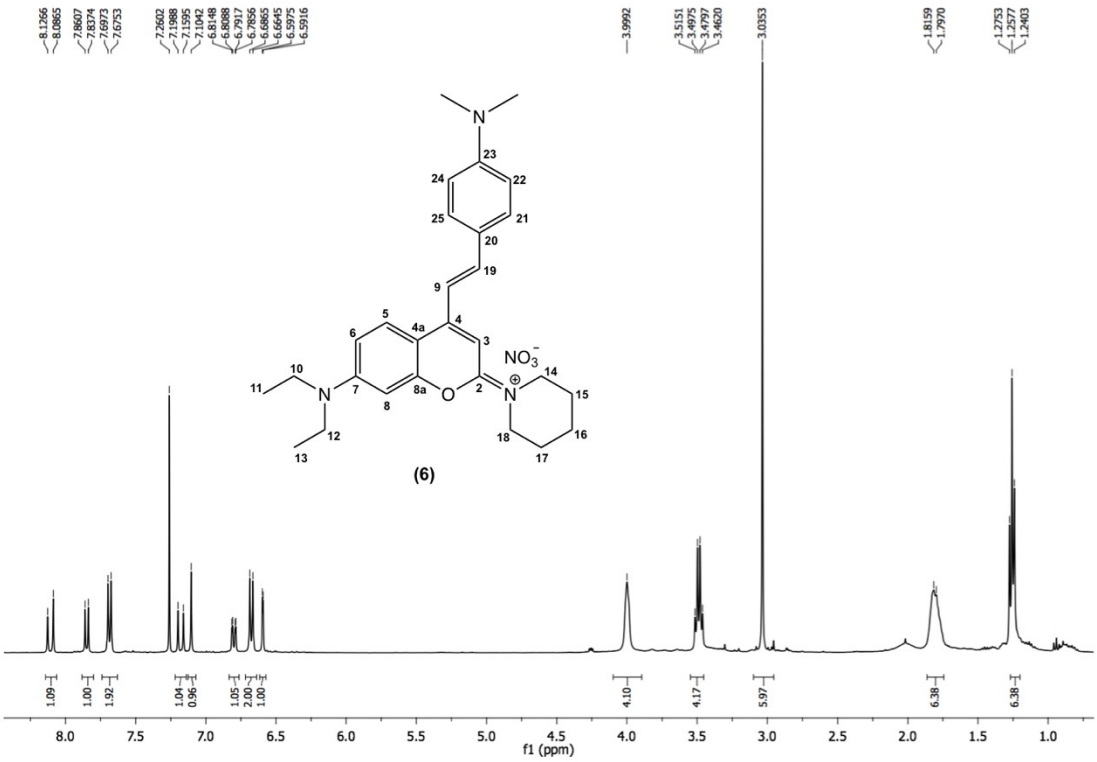

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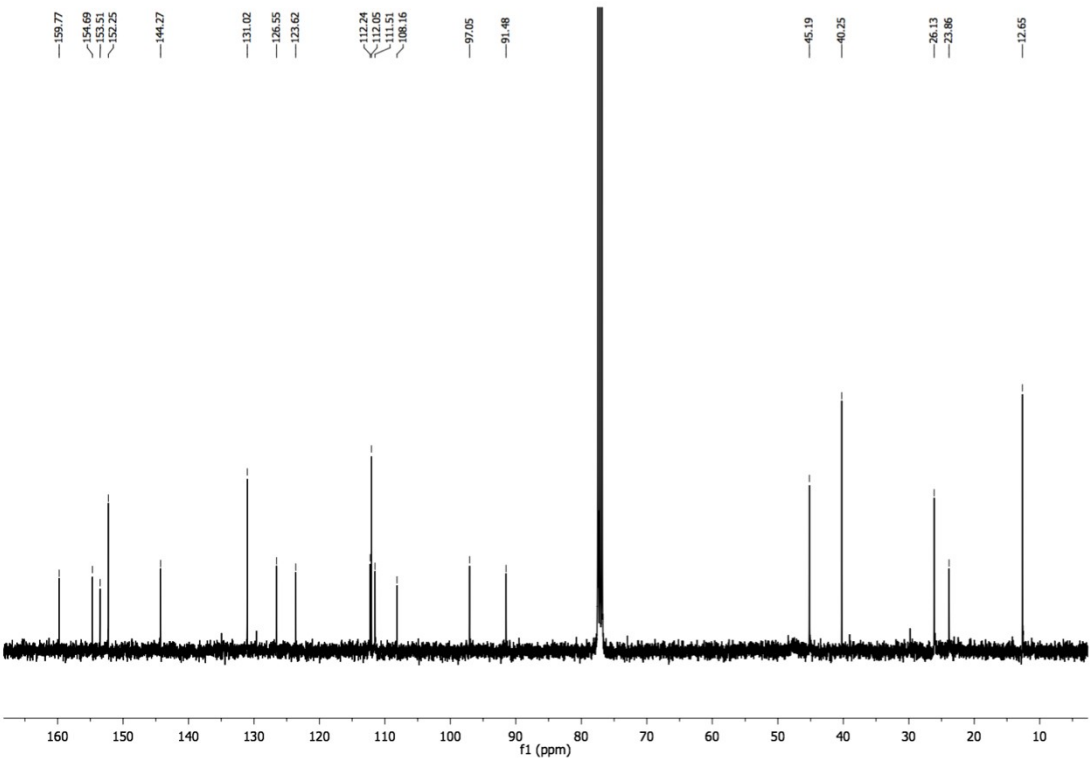

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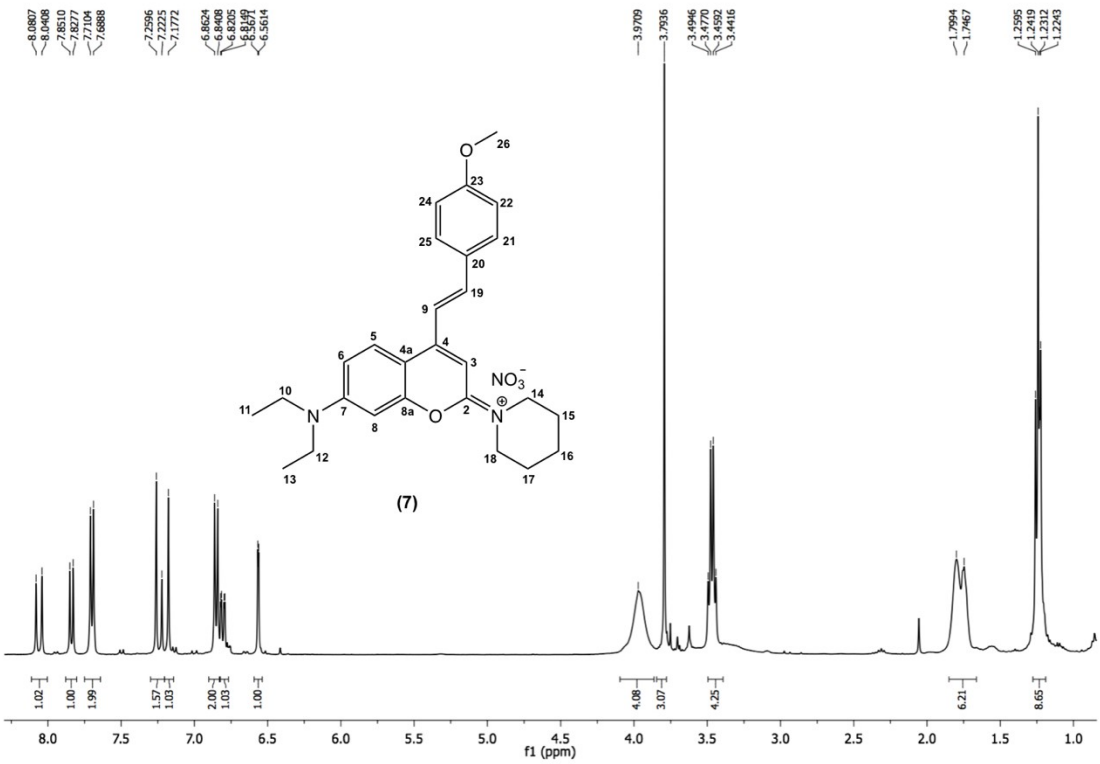

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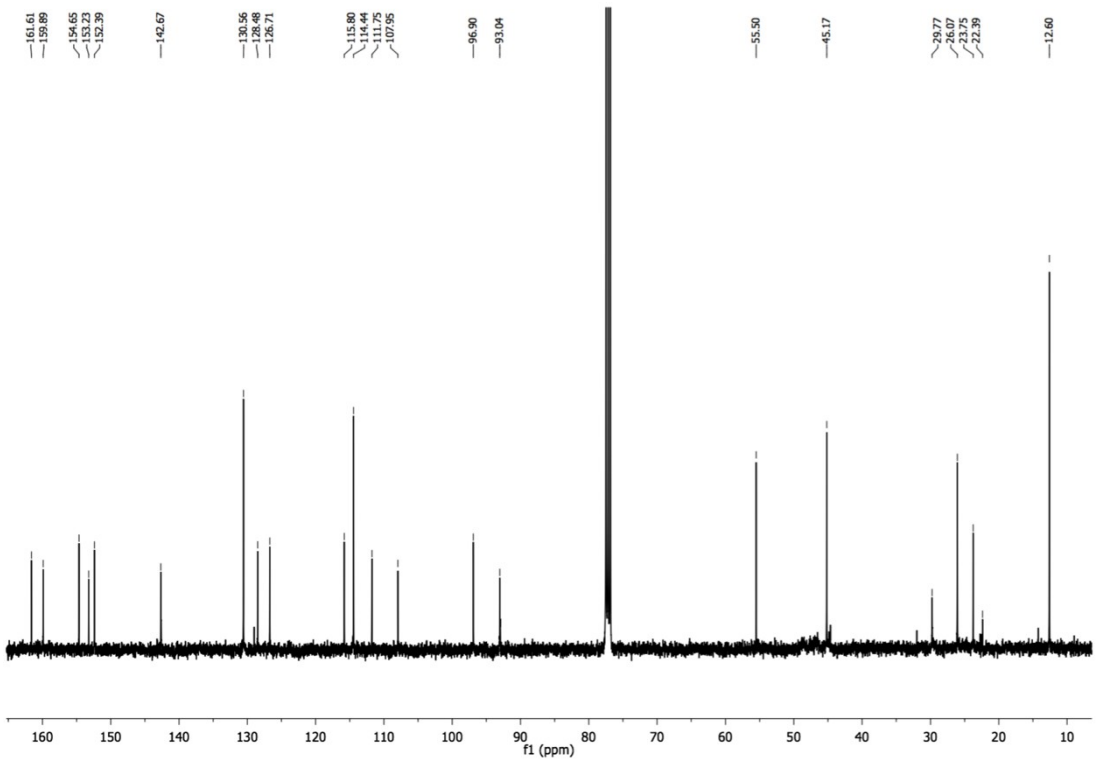

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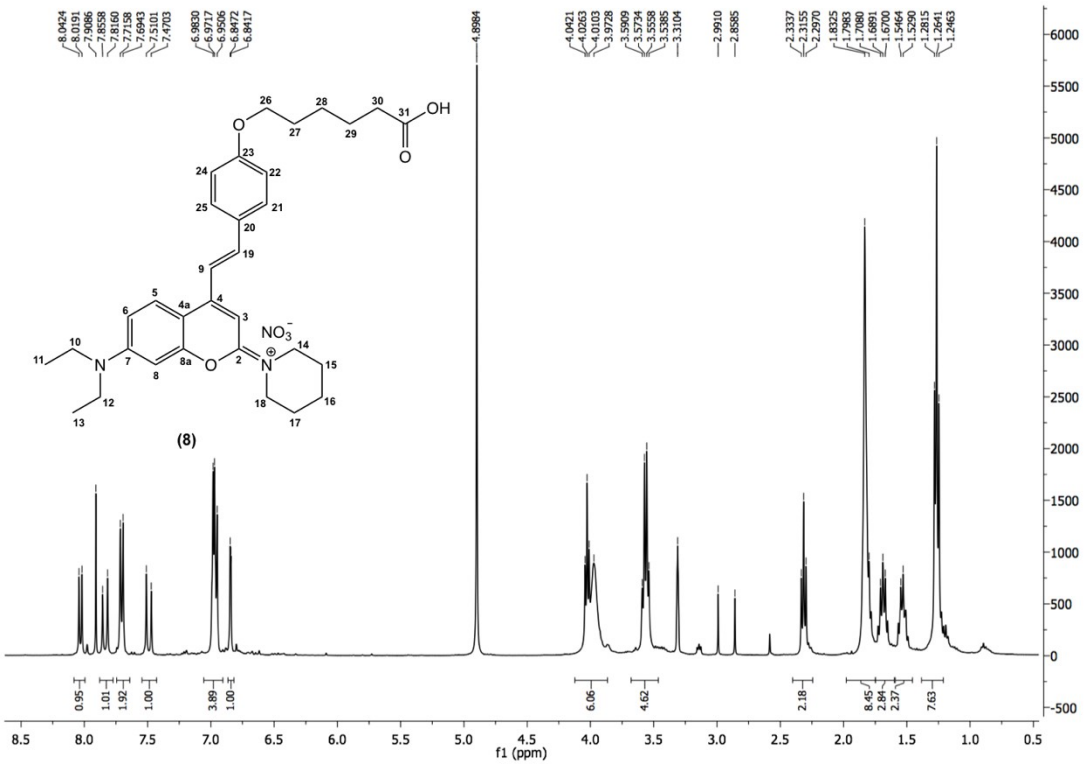

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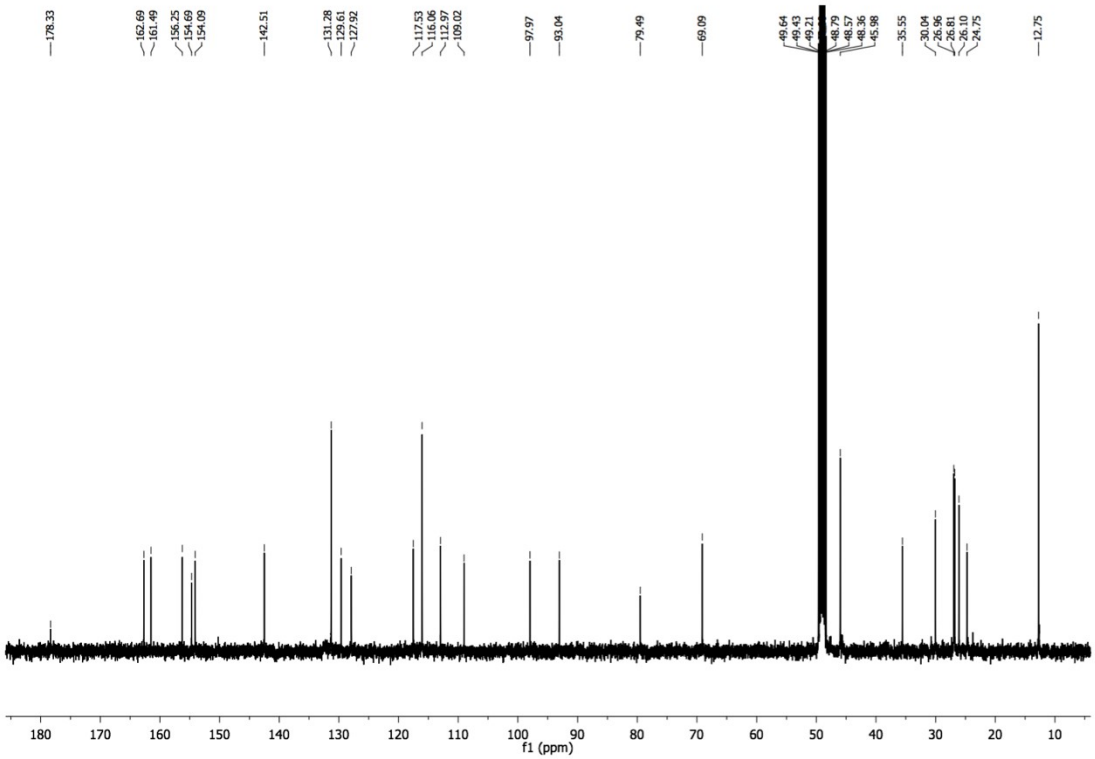

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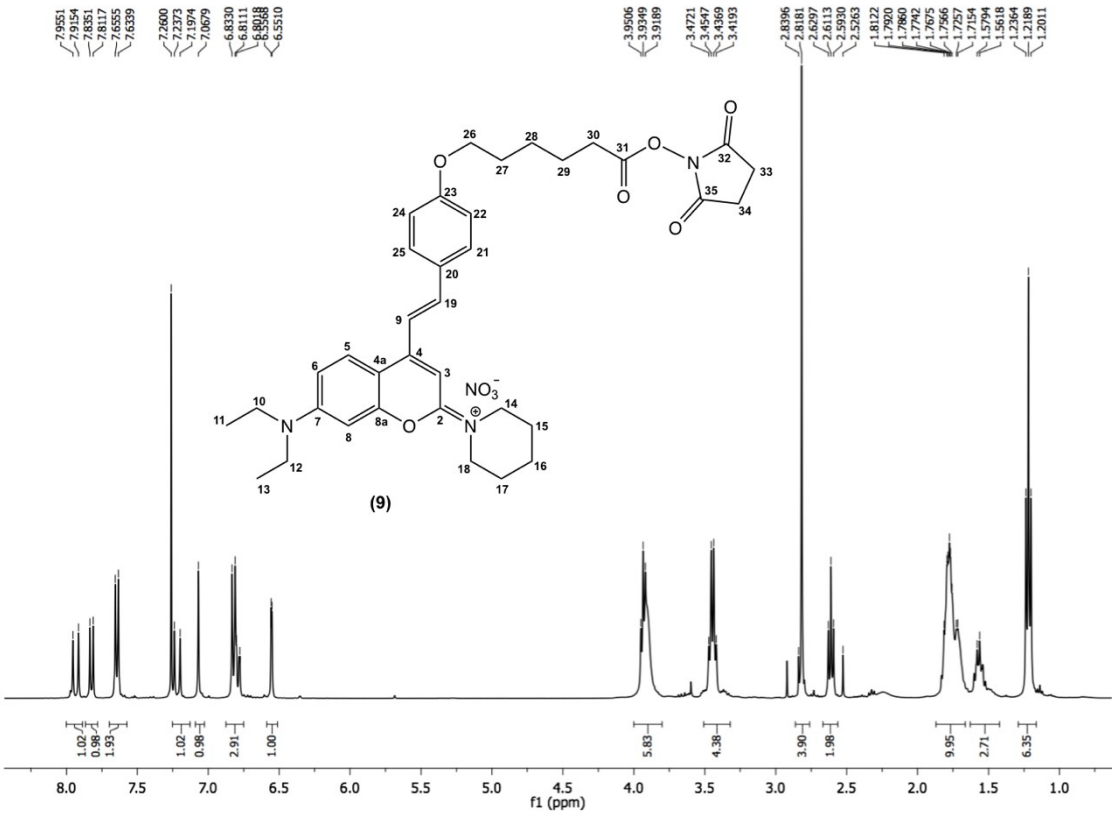
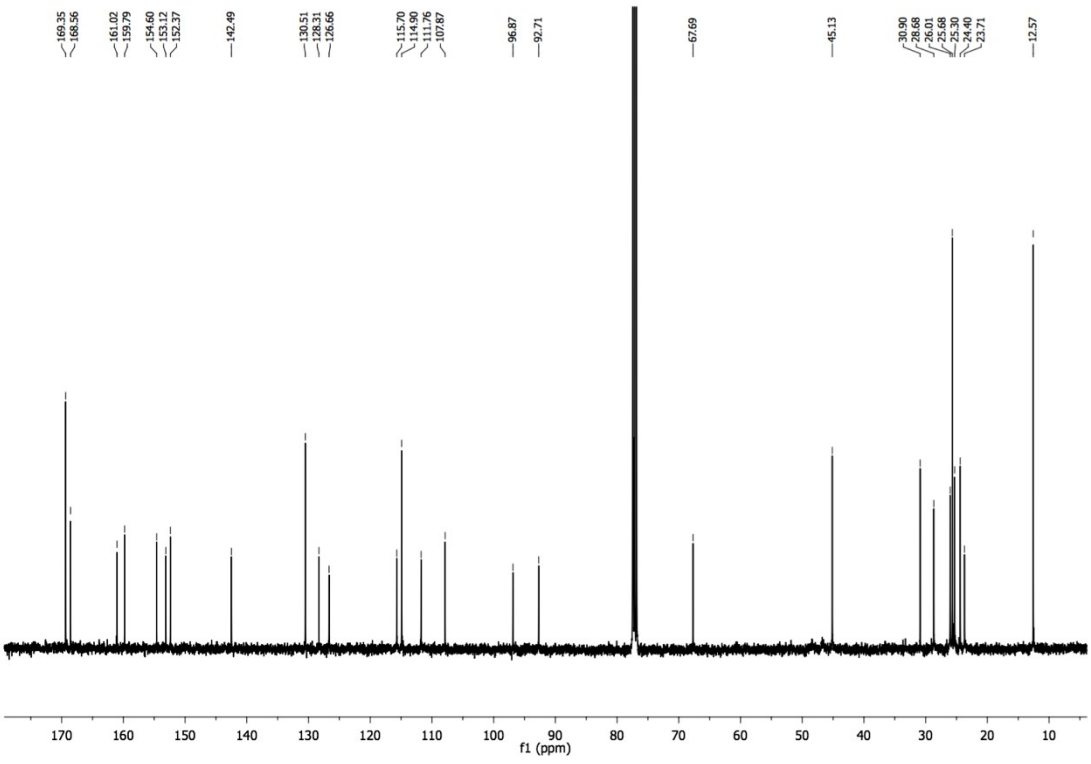
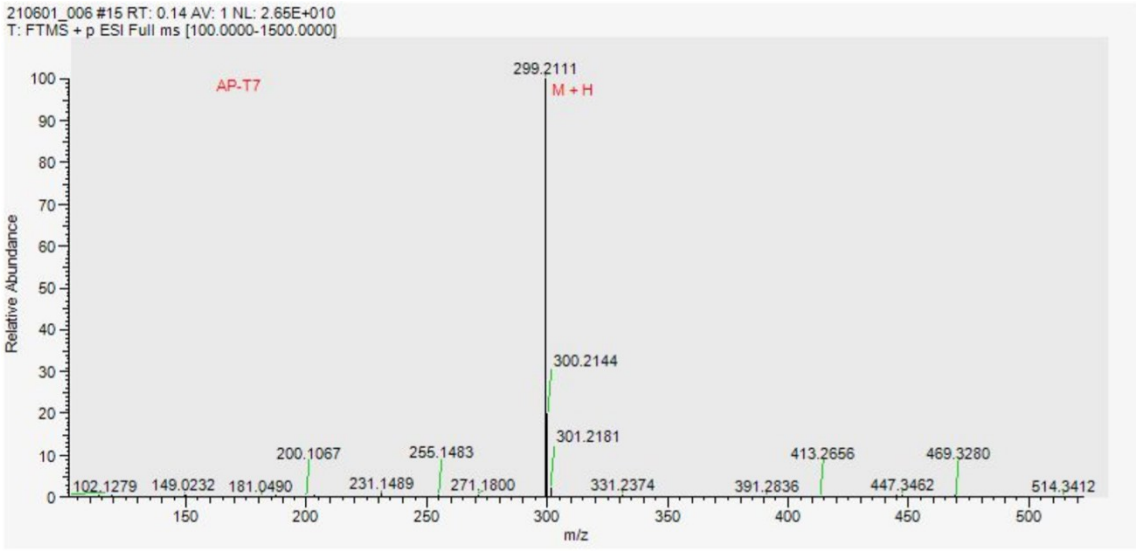


*^{1}H-NMR spectrum of **9** ($CDCl_3$, 400 MHz)*



*^{13}C-NMR spectrum of **9** ($CDCl_3$, 100 MHz)*

2 Mass spectra



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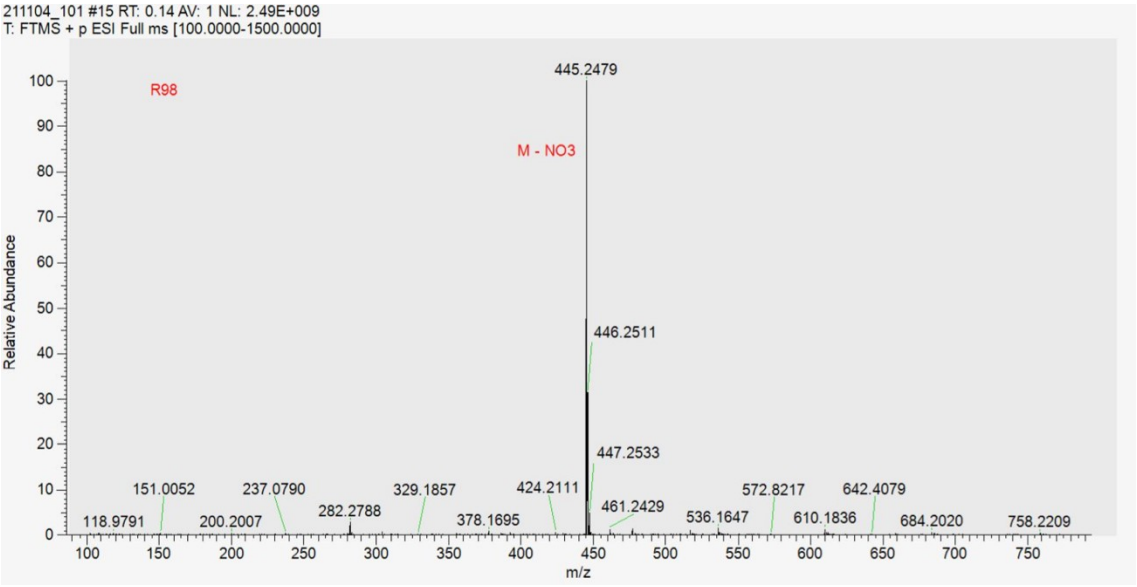

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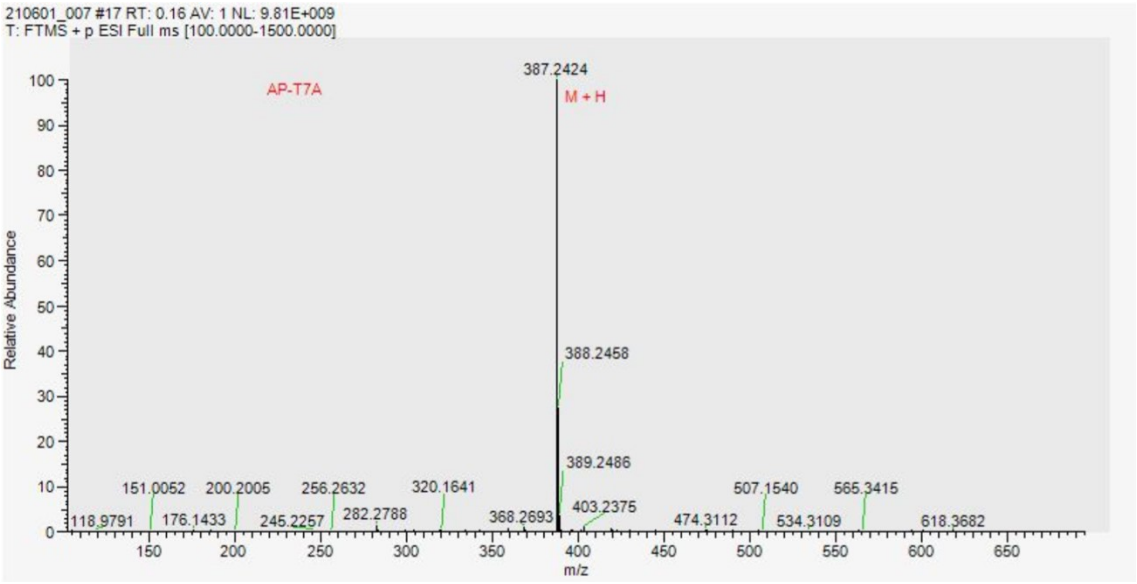

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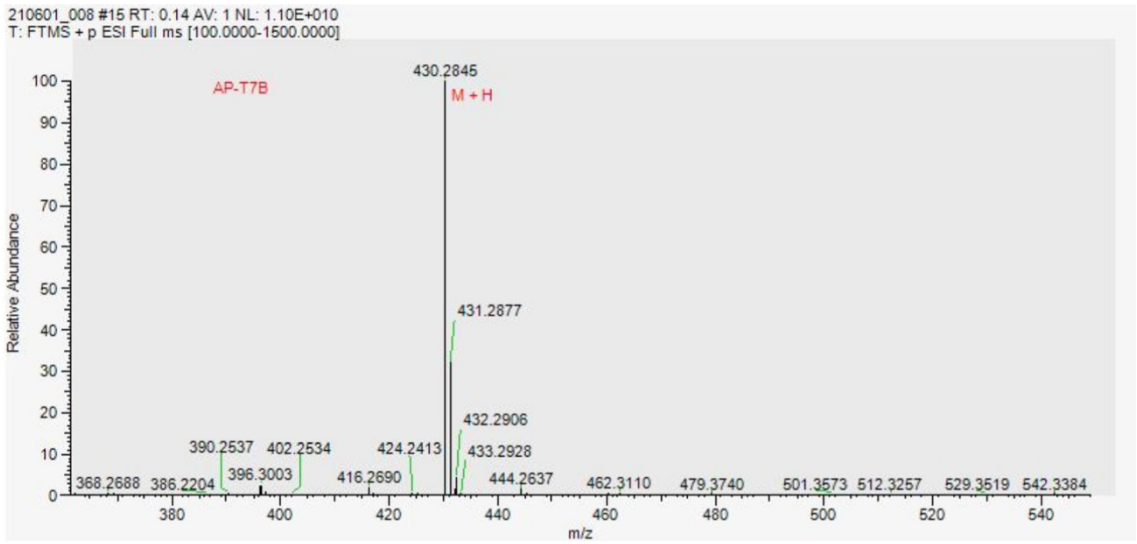
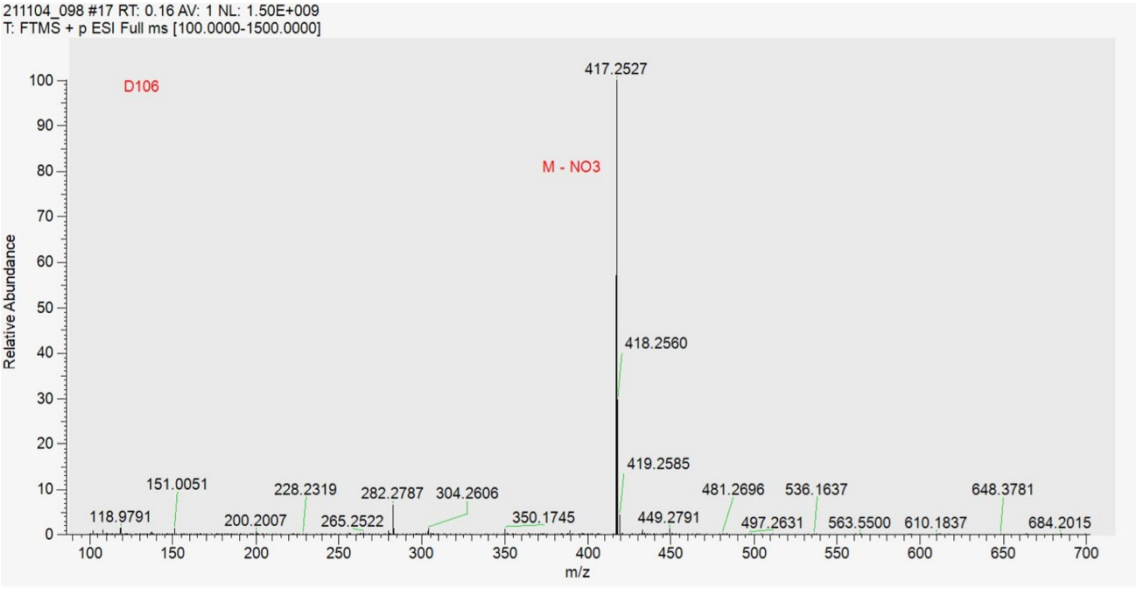
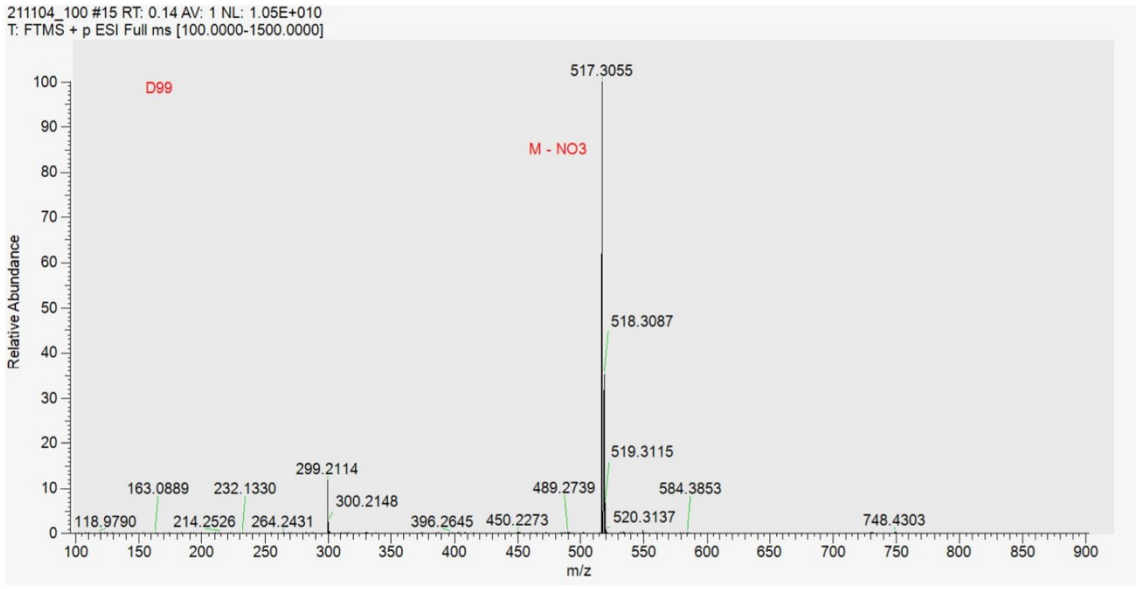


*Mass spectrum of **6***



*Mass spectrum of **7***



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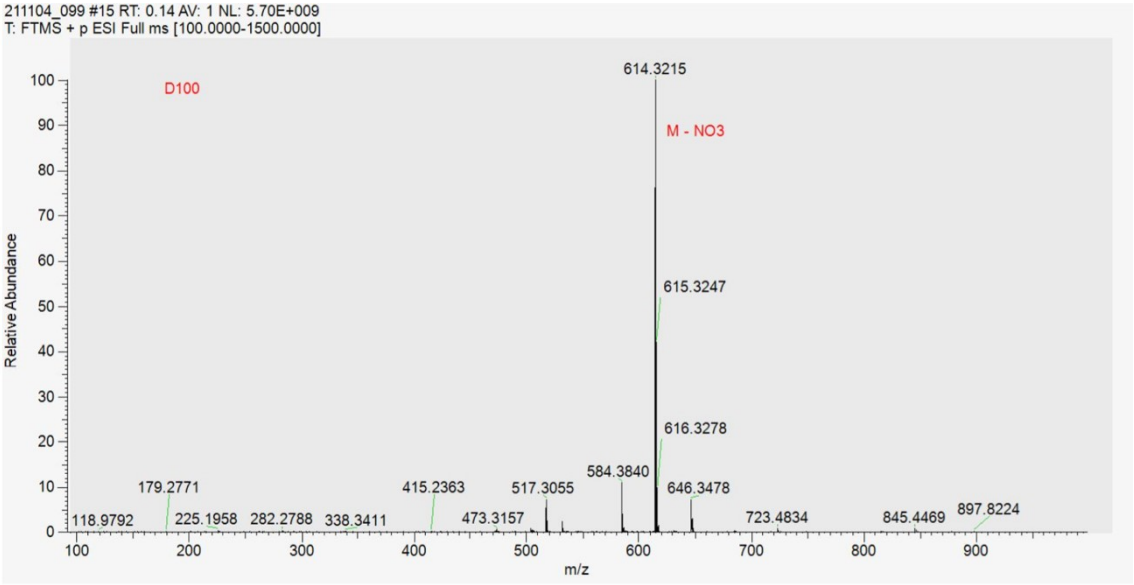
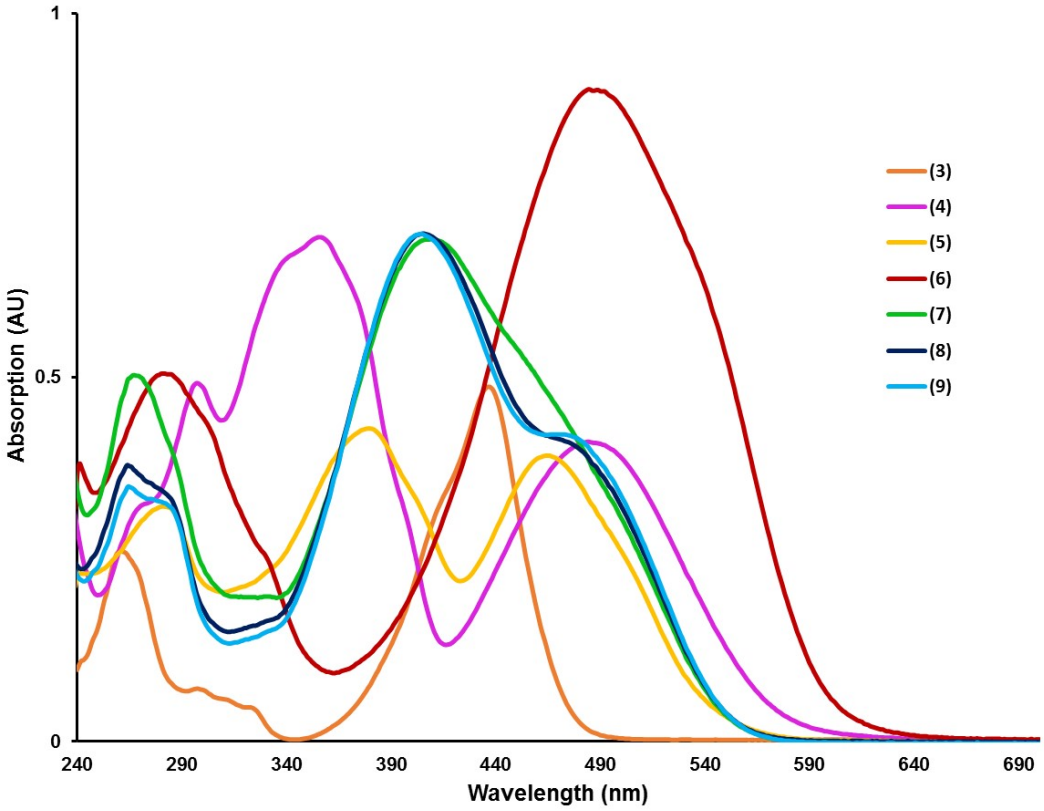


*Mass spectrum of **9***

3 UV/Vis spectra



*UV/Vis spectra of **3** to **9***

4 Quantum chemical calculations

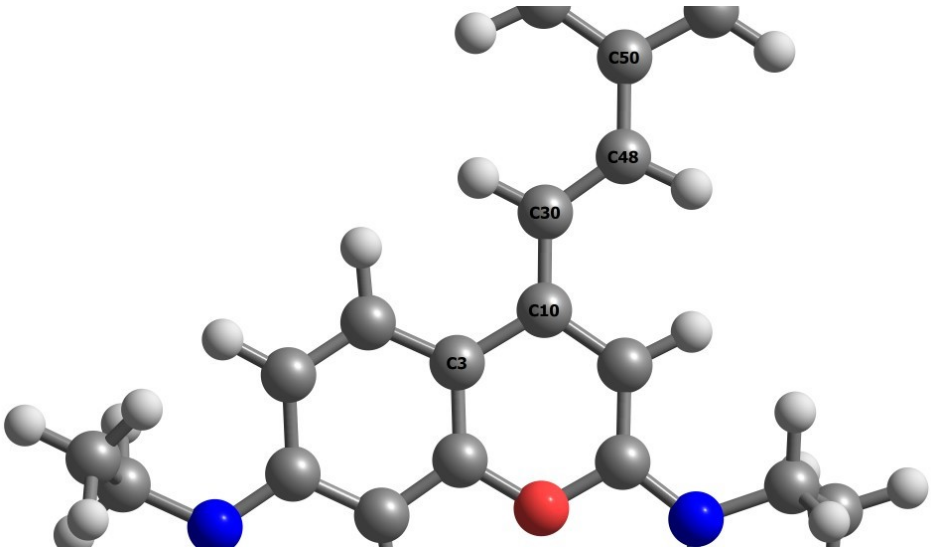


Figure S1. Numbering scheme adopted common to all compounds.

Table S1. Selected bond distances (Å) and dihedral angle (°) of the compounds in the ground S_0 and excited S_1 states.

	r[C10-C30]		r[C30-C48]		r[C48-C50]		D_h[C3-C10-C30-C48]	
Compound	**S_0**	**S_1**	**S_0**	**S_1**	**S_0**	**S_1**	**S_0**	**S_1**
4	1.456	1.408	1.349	1.384	1.459	1.431	25.5	2.1
5	1.454	1.408	1.350	1.381	1.457	1.439	23.9	3.1
6	1.440	1.430	1.360	1.378	1.438	1.438	14.5	6.8
7	1.449	1.407	1.353	1.383	1.450	1.436	20.9	5.1
9	1.449	1.408	1.353	1.383	1.449	1.436	19.9	3.6

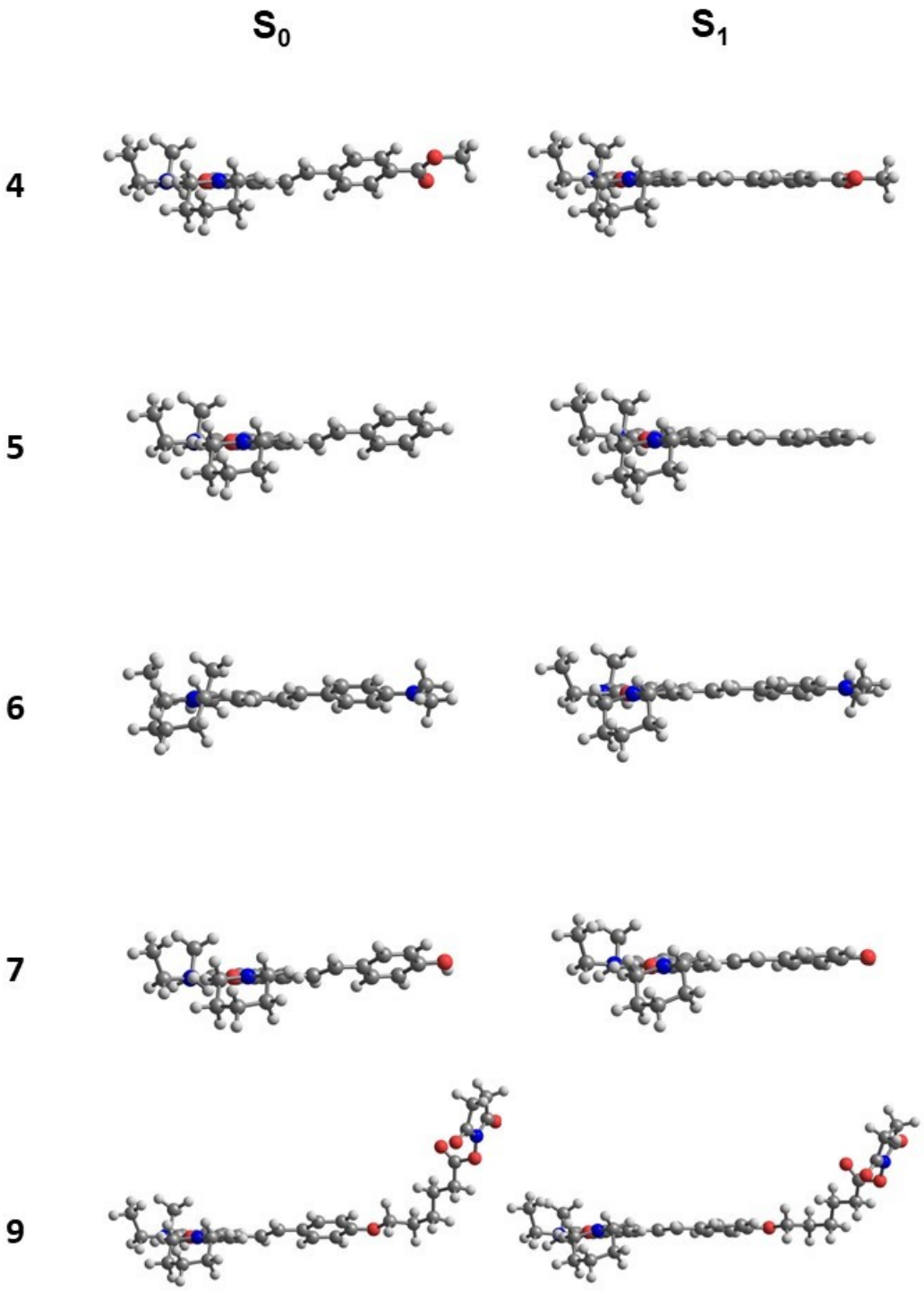


Figure S2. Optimized structures of the compounds in the ground S_0 and excited S_1 states.

Table S2. Calculated absorption data for the compounds and the main orbitals involved in the transitions.

Compound 4

State	λ (nm)	f	Major MO → MO transitions
S_1	494	0.534	HOMO->LUMO (99%)
S_2	389	1.377	H-1->LUMO (99%)
S_3	333	0.087	H-2->LUMO (94%)
S_4	324	0.271	HOMO->L+1 (94%)
S_5	304	0.041	H-3->LUMO (93%)

Compound 5

State	λ (nm)	f	Major MO → MO transitions
S_1	473	0.618	HOMO->LUMO (99%)
S_2	391	1.163	H-1->LUMO (99%)
S_3	324	0.057	H-2->LUMO (95%)
S_4	304	0.026	H-3->LUMO (95%)
S_5	300	0.196	HOMO->L+1 (89%)

Compound 6

State	λ (nm)	f	Major MO → MO transitions
S_1	526	1.535	HOMO->LUMO (98%)
S_2	457	0.518	H-1->LUMO (98%)
S_3	324	0.072	H-3->LUMO (11%), H-2->LUMO (82%)
S_4	309	0.113	H-3->LUMO (29%), HOMO->L+1 (56%)
S5	305	0.036	H-3->LUMO (48%), H-2->LUMO (15%), H->L+1 (17%)

Compound 7

State	λ (nm)	f	Major MO → MO transitions
S_1	468	0.714	HOMO->LUMO (98%)
S_2	429	1.141	H-1->LUMO (98%)
S_3	322	0.047	H-2->LUMO (93%)
S_4	296	0.150	HOMO->L+1 (83%), HOMO->L+2 (10%)
S_5	292	0.012	H-3->LUMO (85%)

Compound 9

State	λ (nm)	f	Major MO → MO transitions
S_1	467	0.772	HOMO->LUMO (97%)
S_2	435	1.166	H-1->LUMO (97%)
S_3	322	0.049	H-2->LUMO (92%)
S_4	296	0.093	H-3->LUMO (16%), HOMO->L+1 (68%)
S_5	294	0.051	H-3->LUMO (66%), HOMO->L+1 (14%)

Table S3. Calculated emission data for the studied compounds and the main orbitals involved in the $S_1 \rightarrow S_0$ transitions.

Compoud	λ (nm)	*f*	Major MO → MO transitions
4	578	0.450	HOMO->LUMO (99%)
5	539	0.530	HOMO->LUMO (99%)
6	558	1.655	HOMO->LUMO (99%)
7	525	0.647	HOMO->LUMO (99%)
9	523	0.702	HOMO->LUMO (99%)