Supplementary materials

Rational design of cost-effective 4-styrylcoumarin fluorescent derivatives for biomolecules labeling

Eustáquio R[a], Ramalho JPP [b,c], Caldeira AT [a,b,d], Pereira A[a,b*]

[a] HERCULES Laboratory & IN2PAST—Associate Laboratory for Research and Innovation in Heritage, Arts, Sustainability and Territory, University of Évora, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal.

[b] Department of Chemistry and Biochemistry, School of Sciences and Technology, University of Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal.

[c] Laqv-Requimte, University of Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal.

[d] City U Macau Chair in Sustainable Heritage & Sino-Portugal Joint Laboratory of Cultural Heritage Conservation Science, University of Évora, Largo Marquês de Marialva 8, 7000-809 Évora, Portugal

* Corresponding author.

E-mail address: amlp@uevora.pt

1. NMR spectra

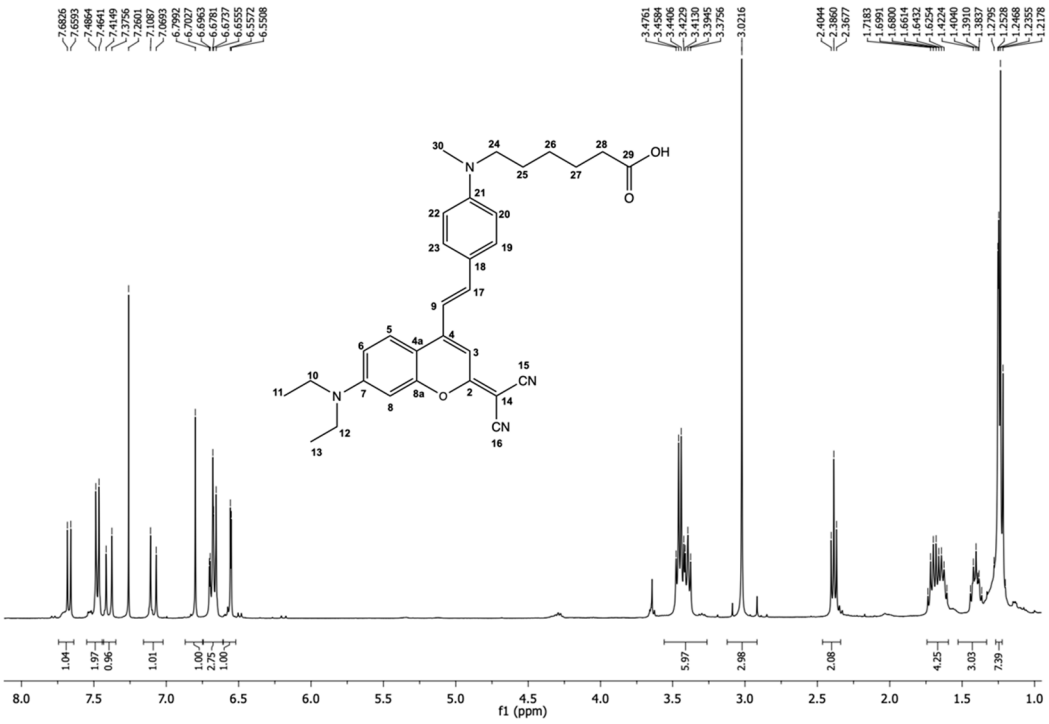

Figure S1 ^{1}H-NMR spectrum of **7** ($CDCl_3$, 400 MHz).

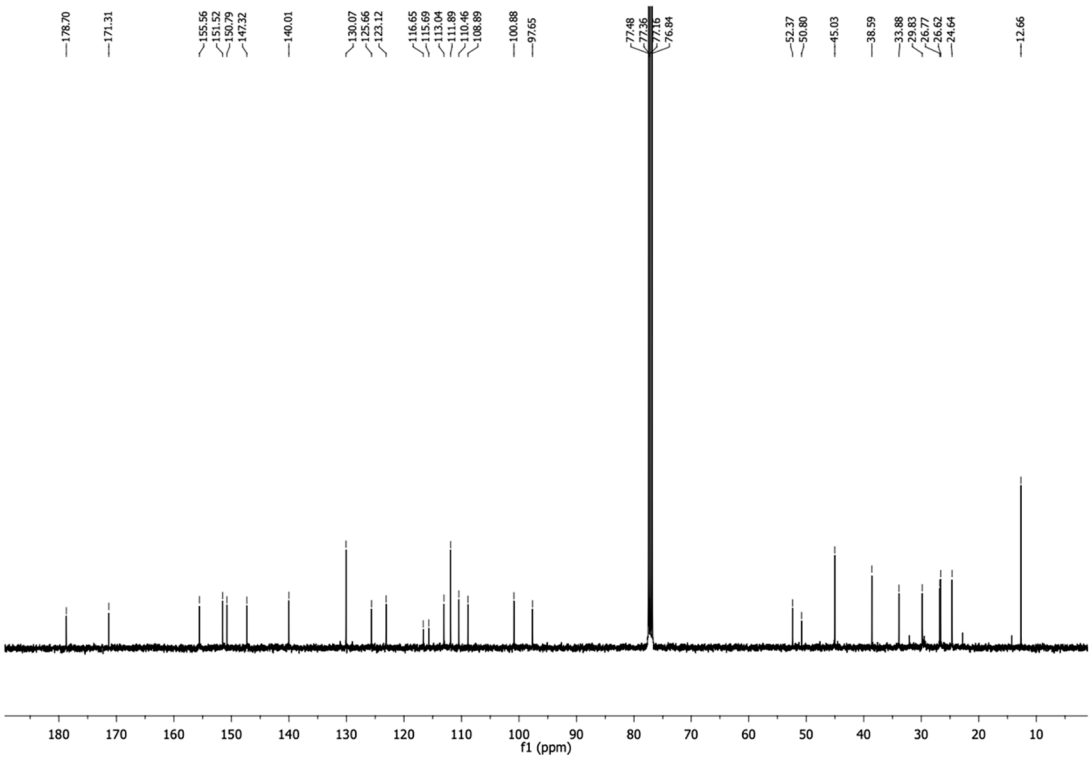

Figure S2 ^{13}C-NMR spectrum of **7** ($CDCl_3$, 100 MHz).

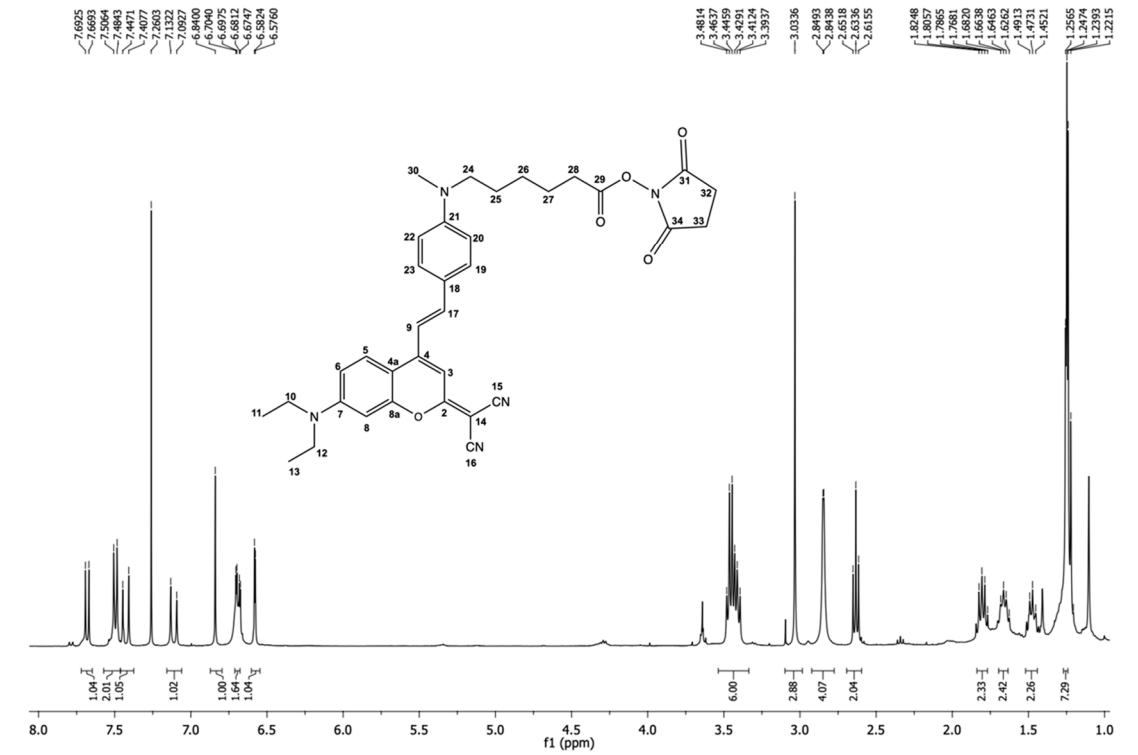

Figure S3 ^{1}H-NMR spectrum of **9** ($CDCl_3$, 400 MHz).

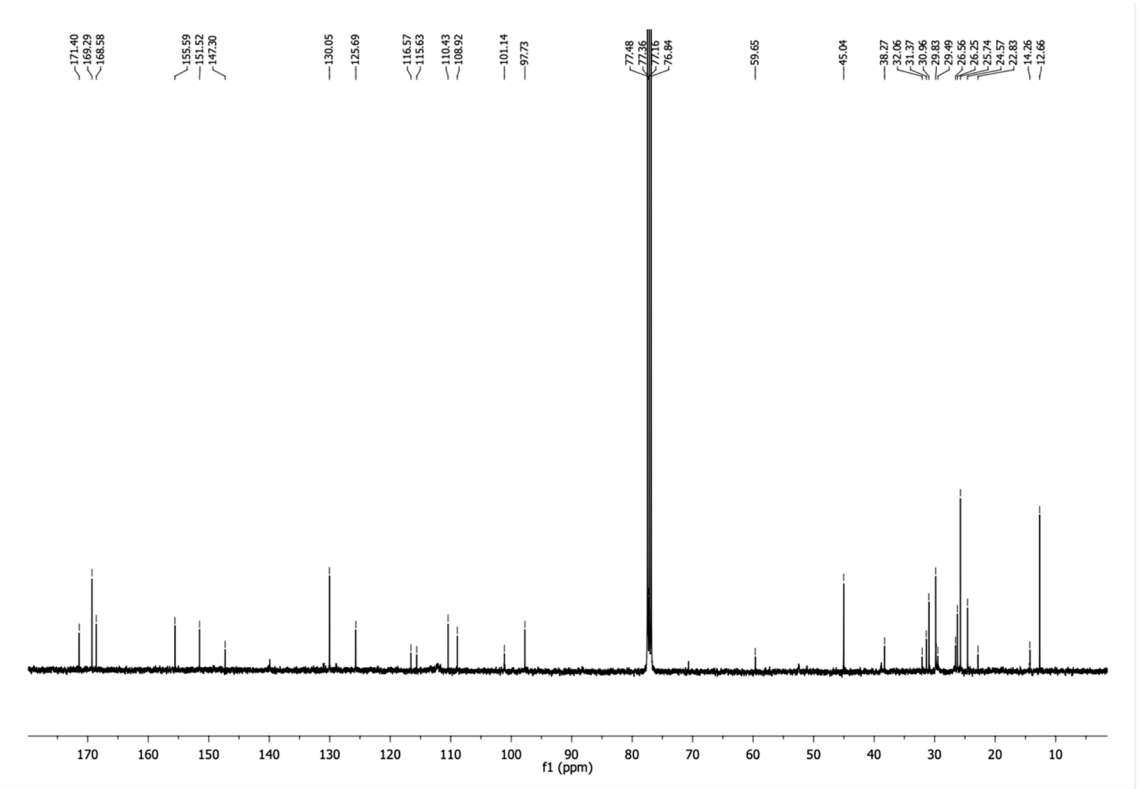

Figure S4 ^{13}C-NMR spectrum of **9** ($CDCl_3$, 100 MHz).

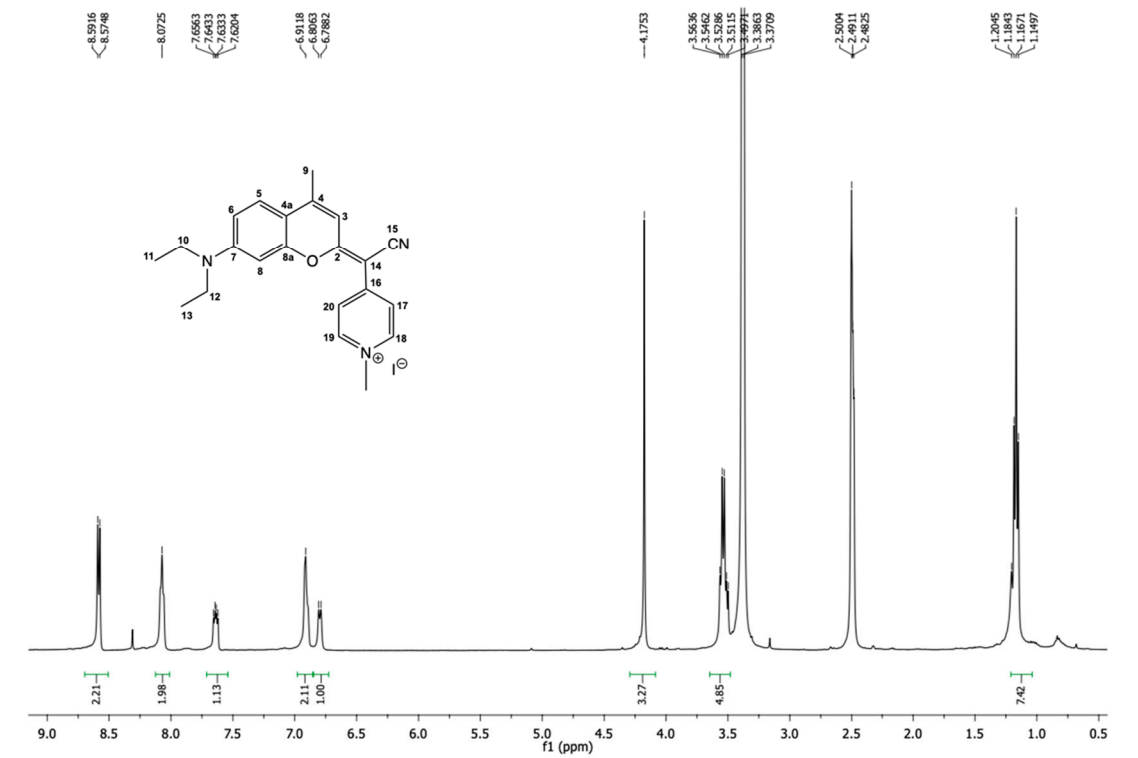

Figure S5 ^{1}H-NMR spectrum of **11** ($(CD_3)_2SO$, 400 MHz).

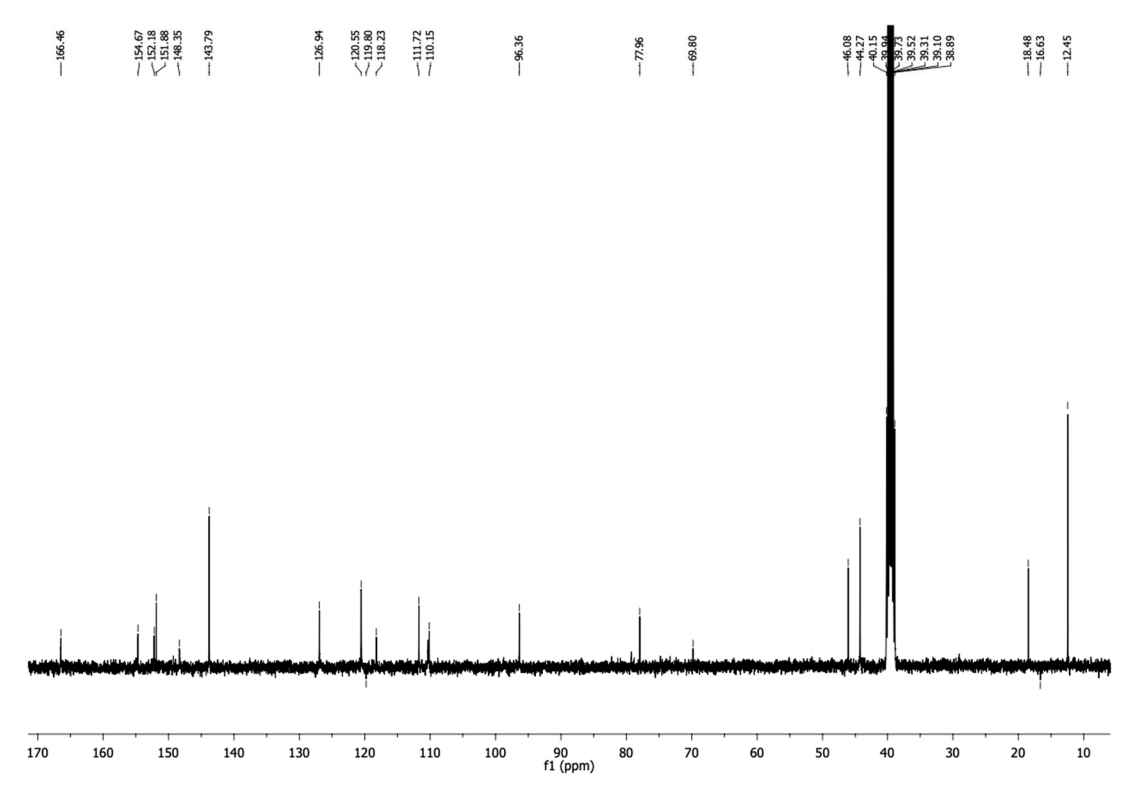

Figure S6 ^{13}C-NMR spectrum of **11** ($(CD_3)_2SO$, 100 MHz).

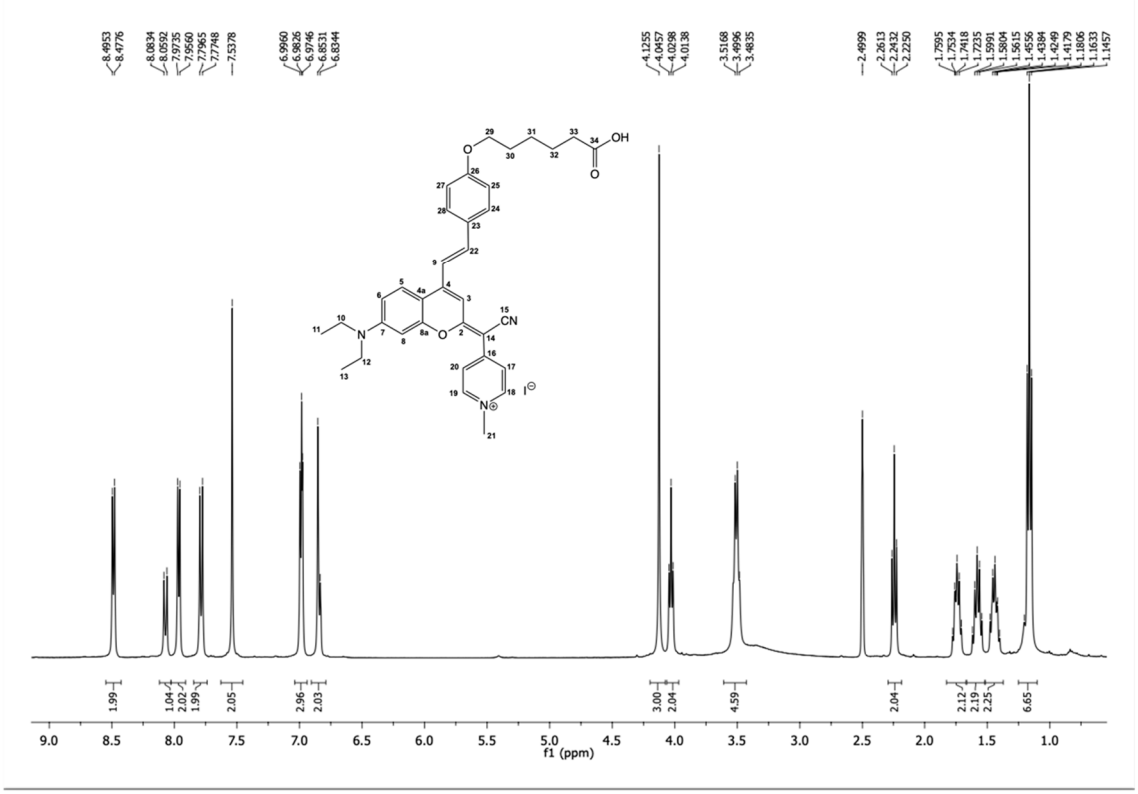

Figure S7 ^{1}H-NMR spectrum of **12** ($(CD_3)_2SO$, 400 MHz).

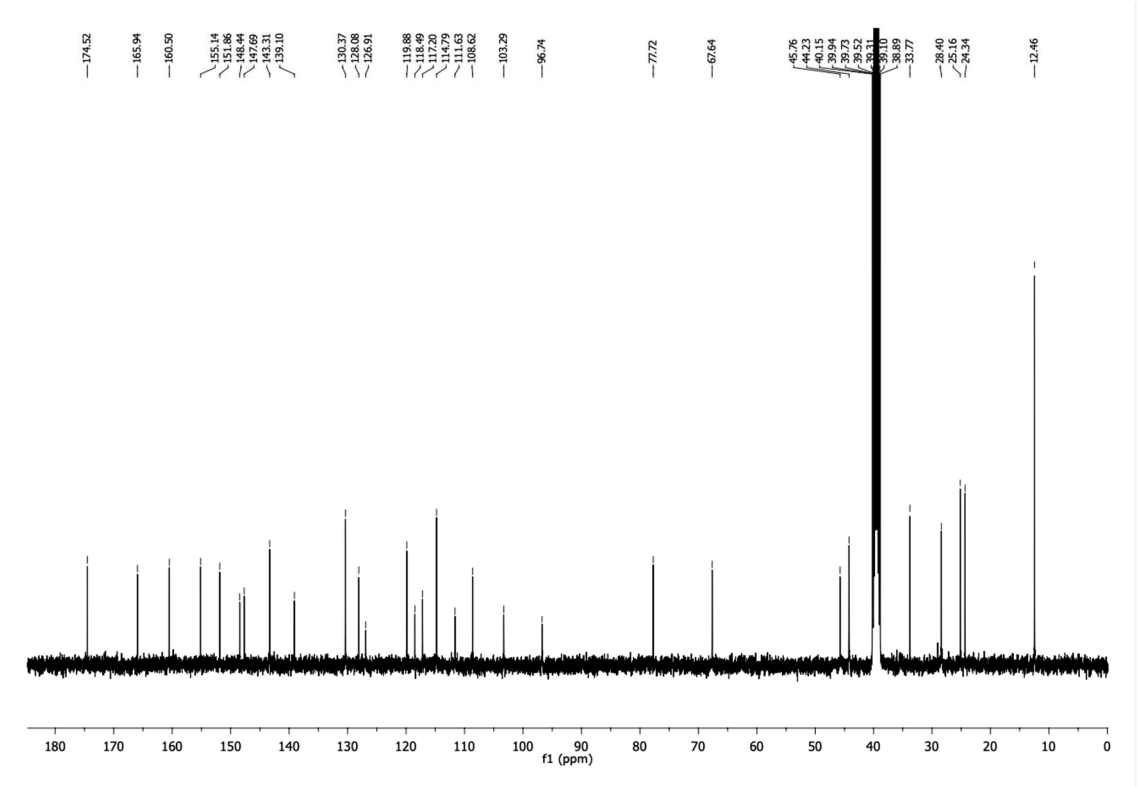

Figure S8 ^{13}C-NMR spectrum of **12** ($(CD_3)_2SO$, 100 MHz).

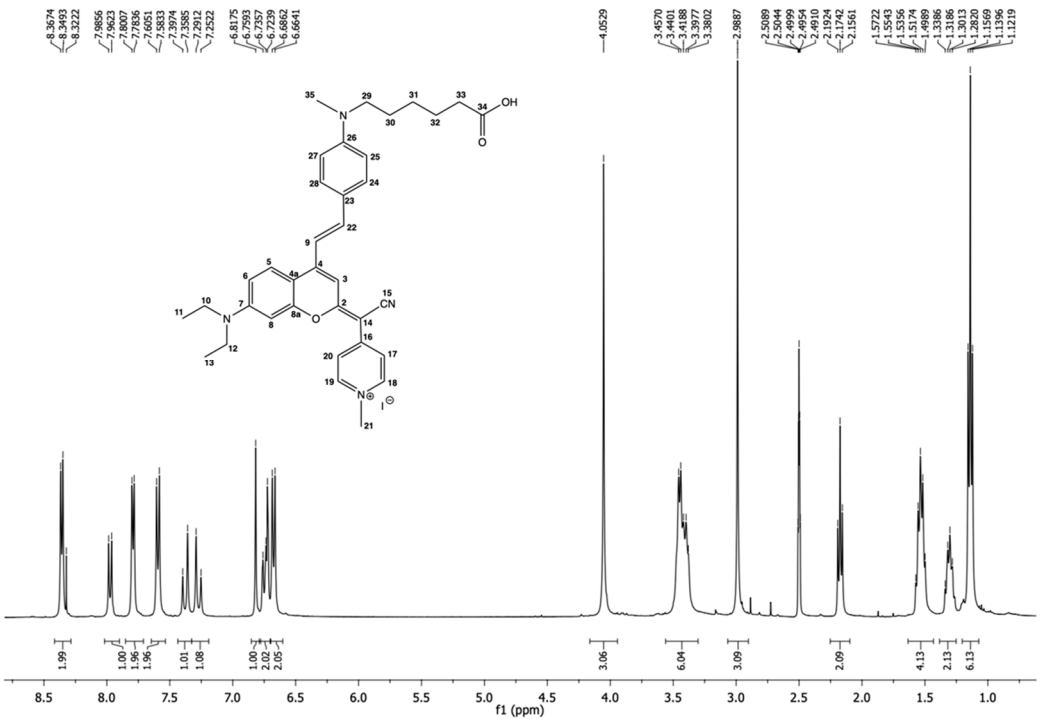

Figure S9 ^{1}H-NMR spectrum of **13** ($(CD_3)_2SO$, 400 MHz).

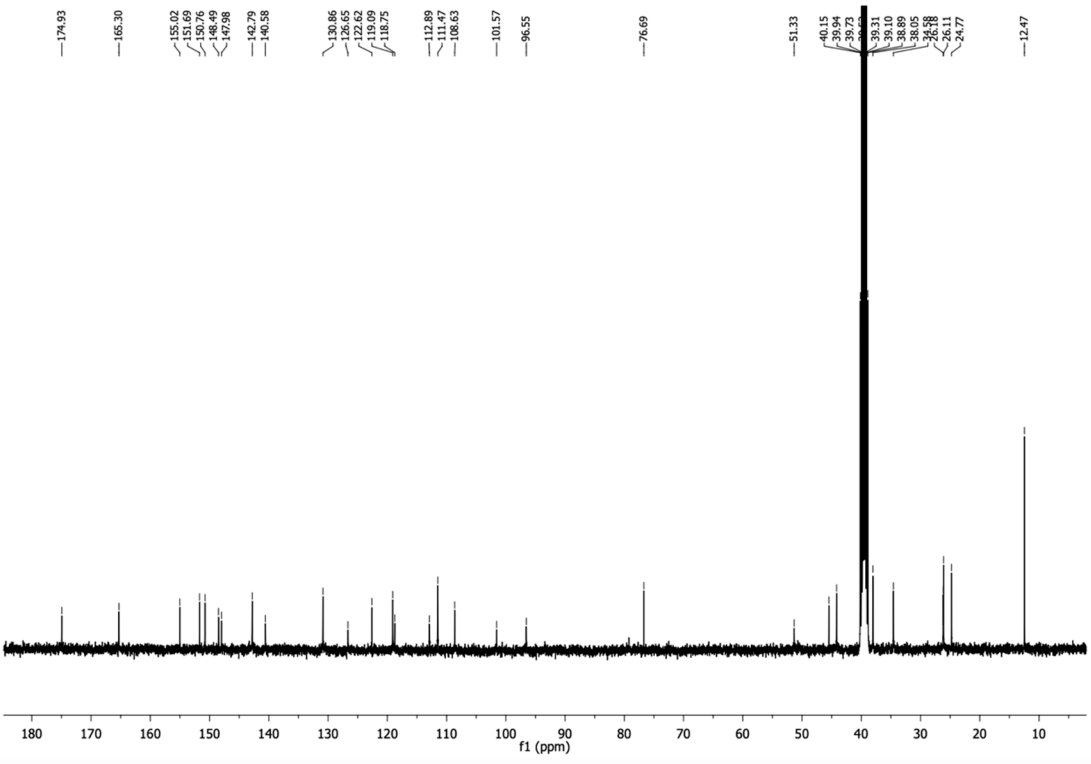

Figure S10 ^{13}C-NMR spectrum of **13** ($(CD_3)_2SO$, 100 MHz).

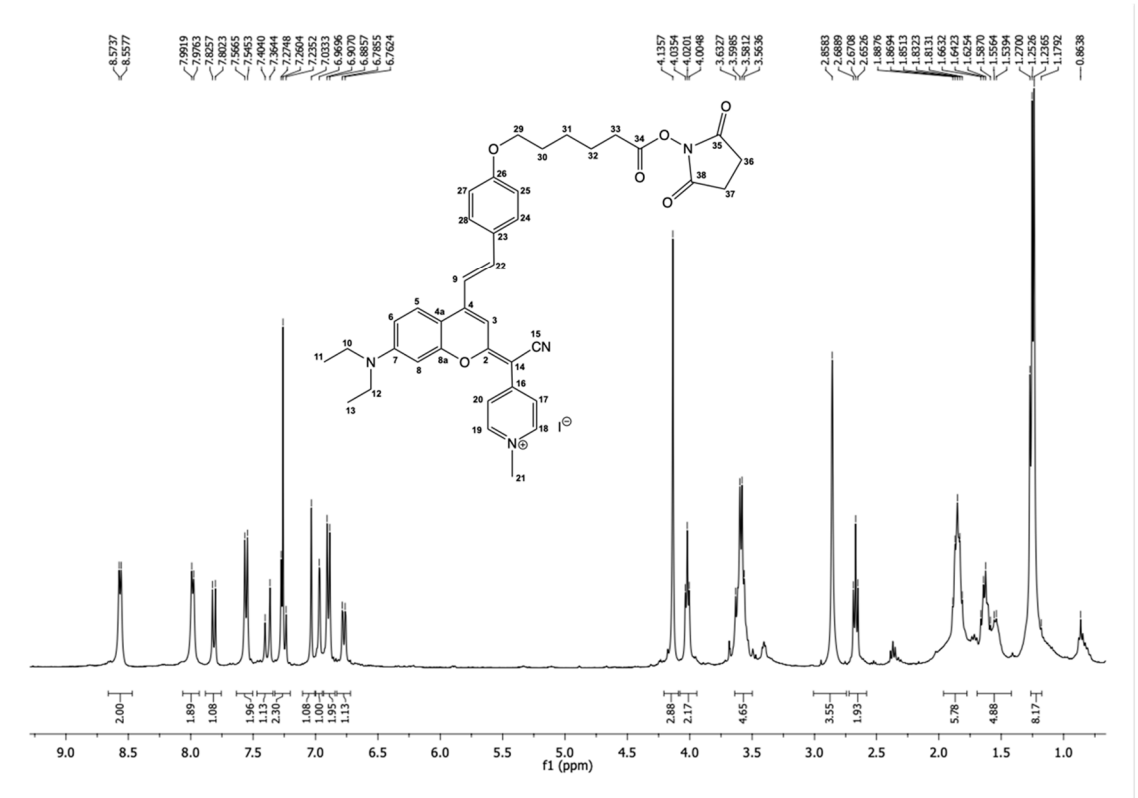

Figure S11 ^{1}H-NMR spectrum of **14** ($CDCl_3$, 400 MHz).

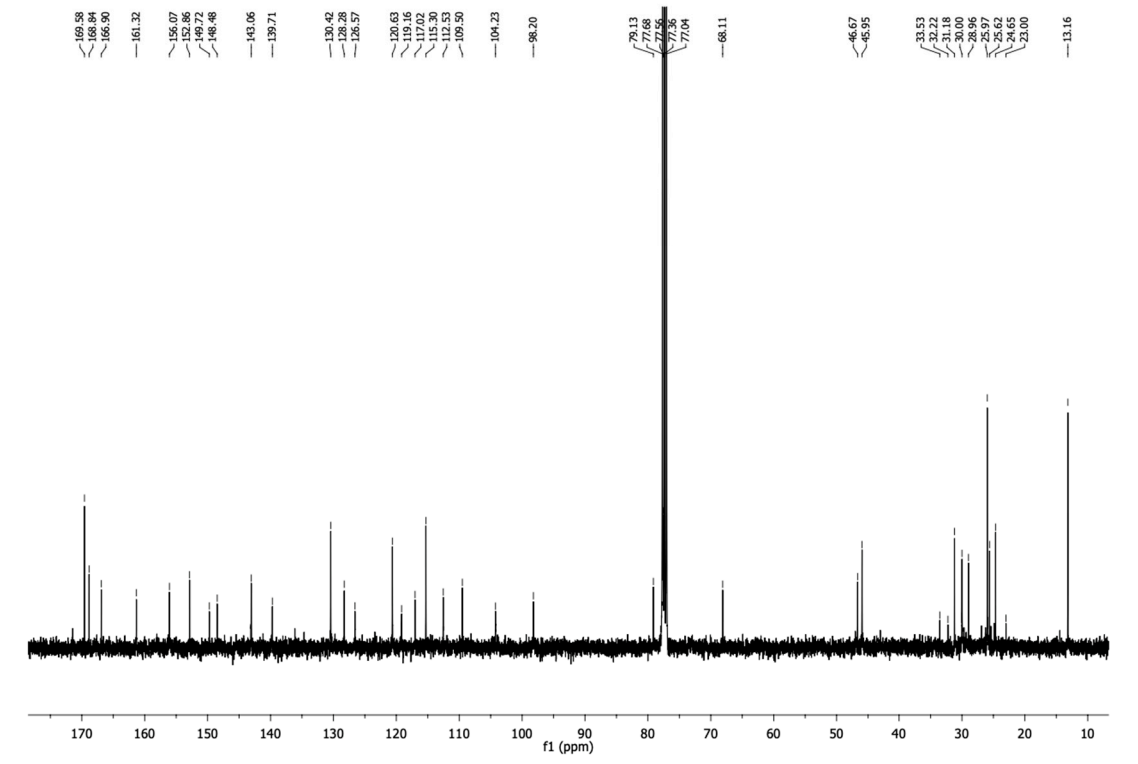

Figure S12 ^{13}C-NMR spectrum of **14** ($CDCl_3$, 100 MHz).

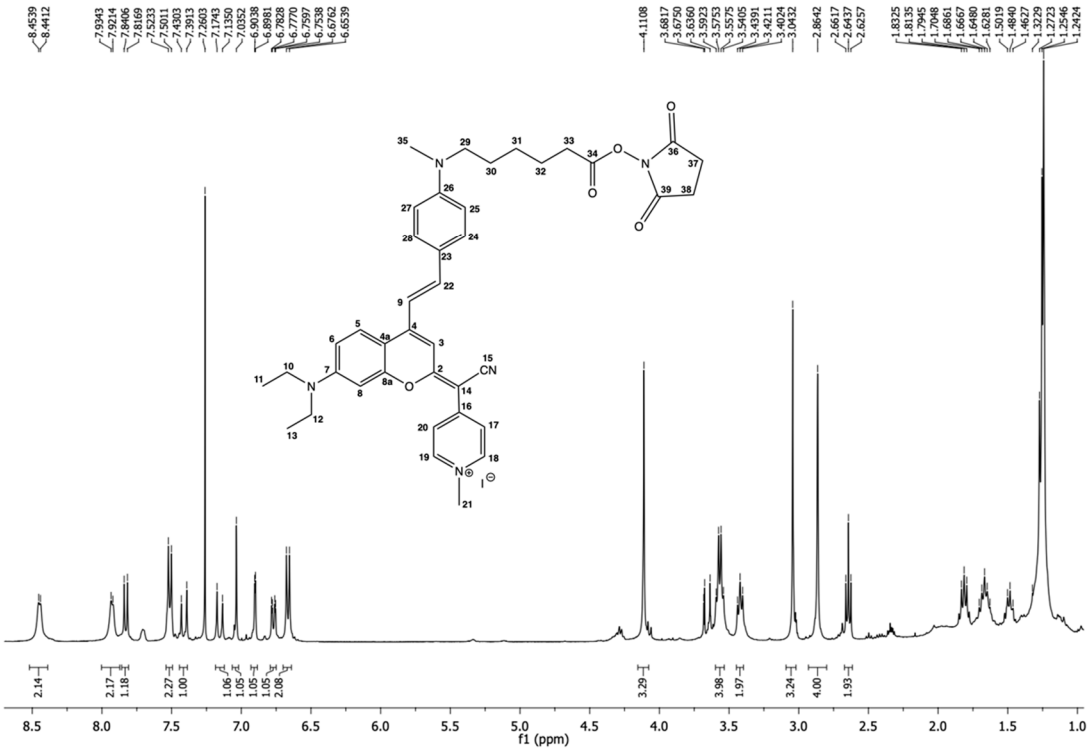

Figure S13 ^{1}H-NMR spectrum of **15** ($CDCl_3$, 400 MHz).

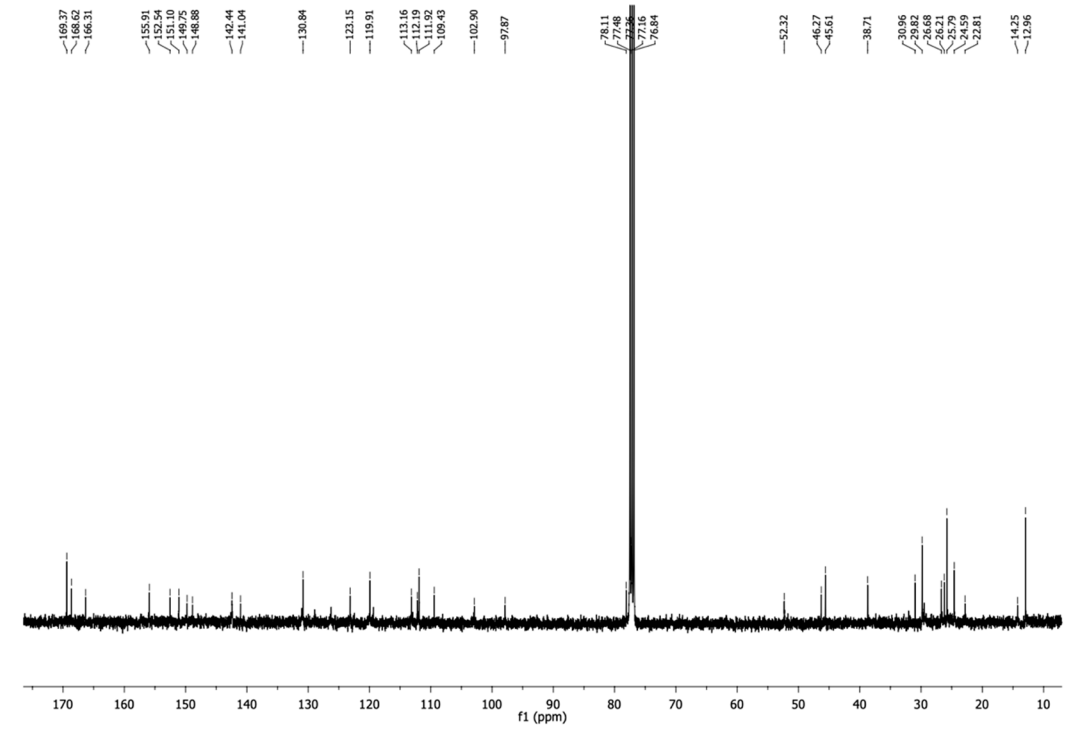

Figure S14 ^{13}C-NMR spectrum of **15** ($CDCl_3$, 100 MHz).

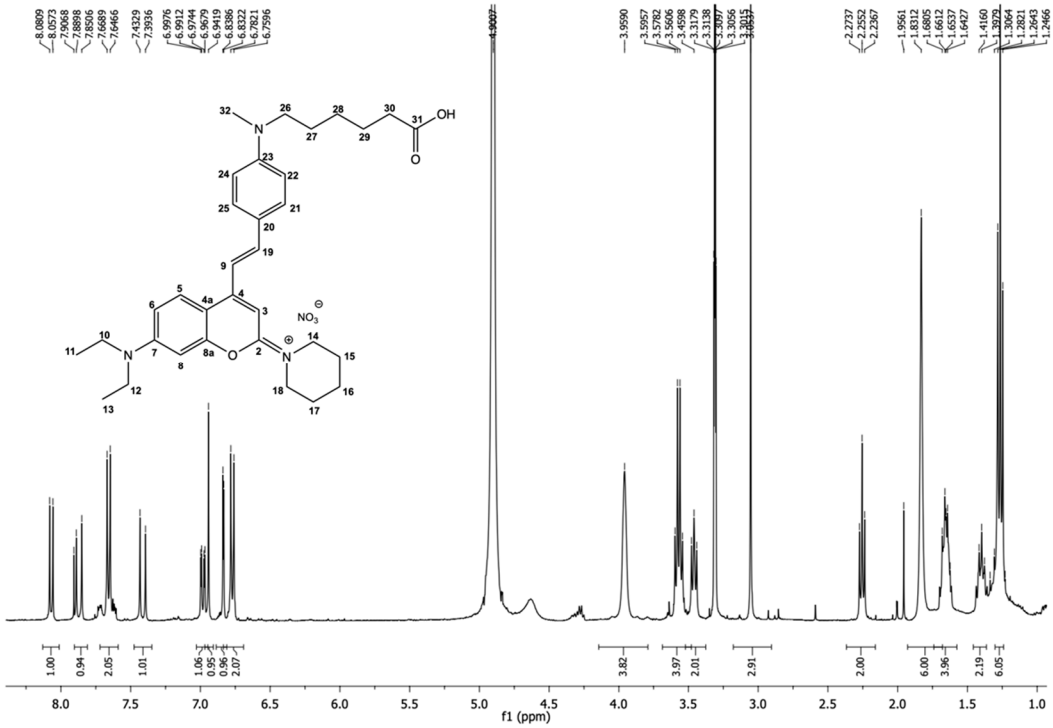

Figure S15 ^{1}H-NMR spectrum of **18** (CD_3OD, 400 MHz).

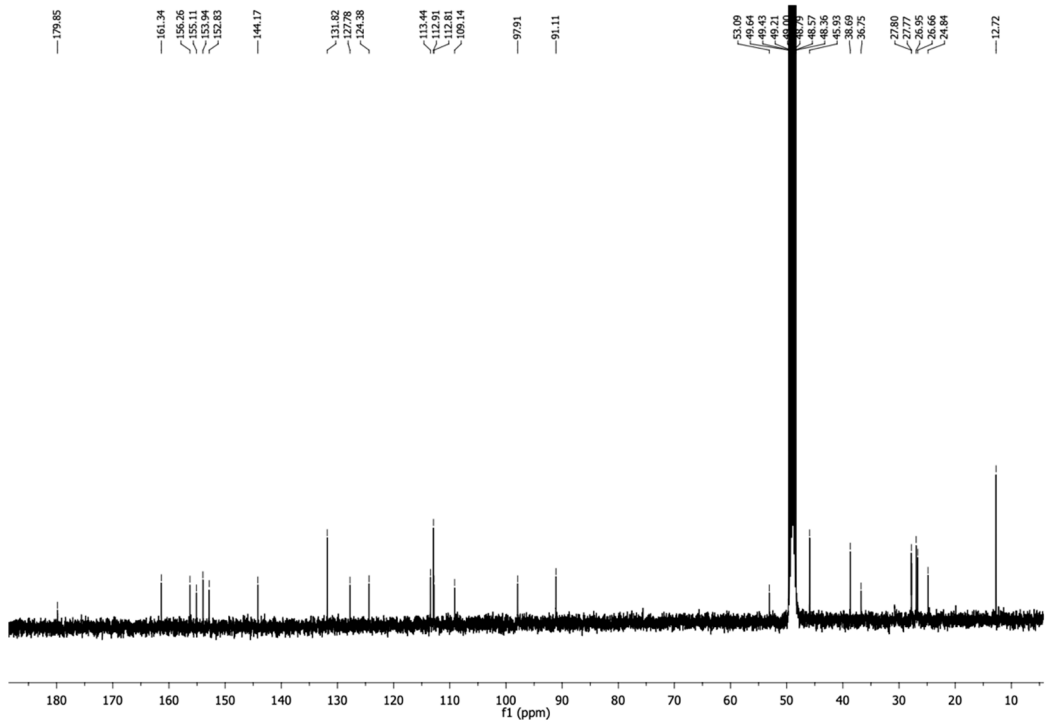

Figure S16 ^{13}C-NMR spectrum of **18** (CD_3OD, 100 MHz).

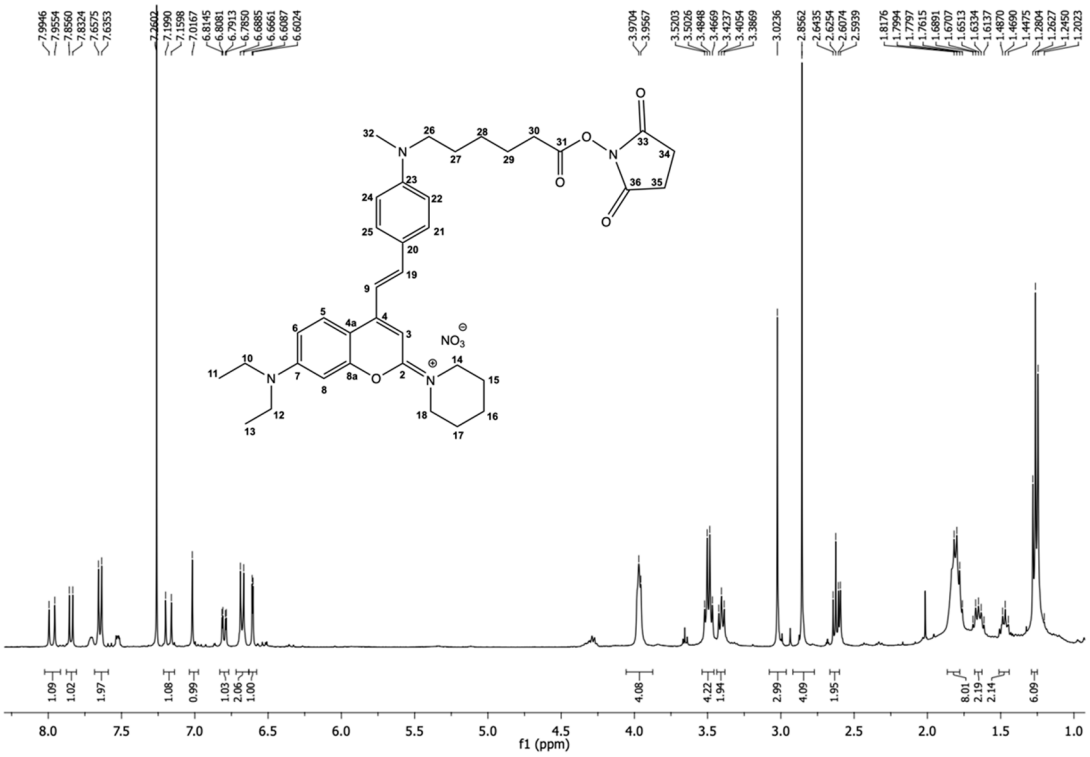

Figure S17 ^{1}H-NMR spectrum of **20** ($CDCl_3$, 400 MHz).

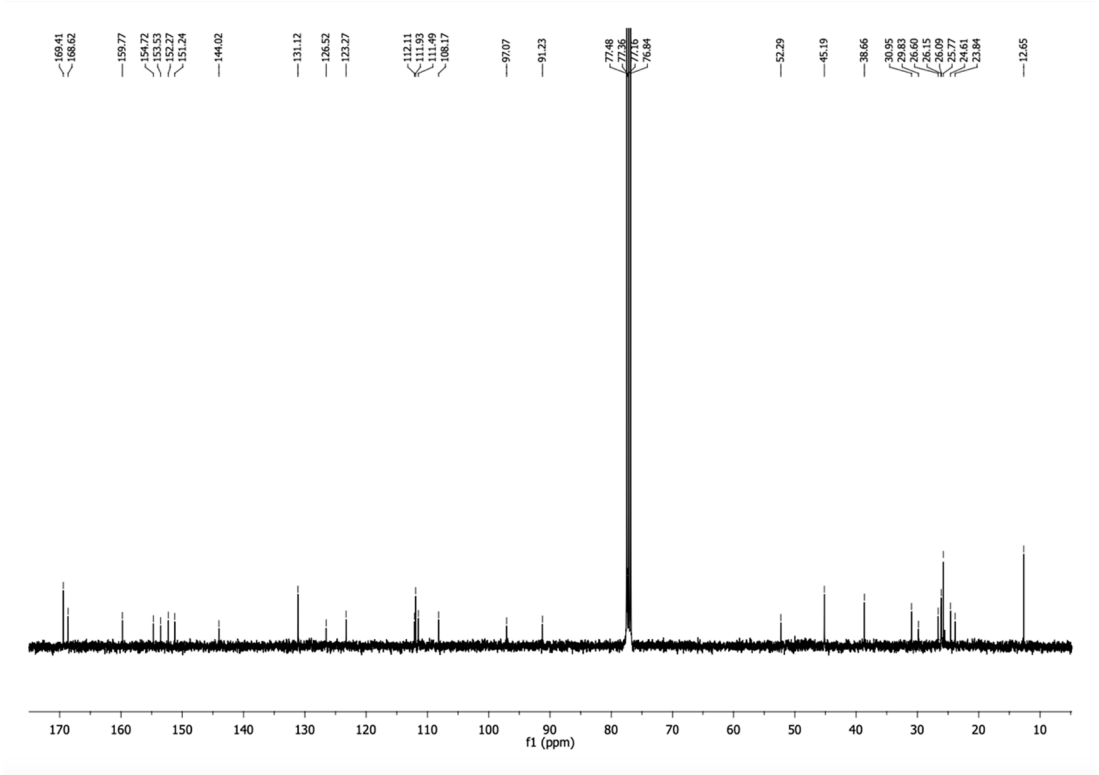

Figure S18 ^{13}C-NMR spectrum of **20** ($CDCl_3$, 100 MHz).

2. Mass spectra

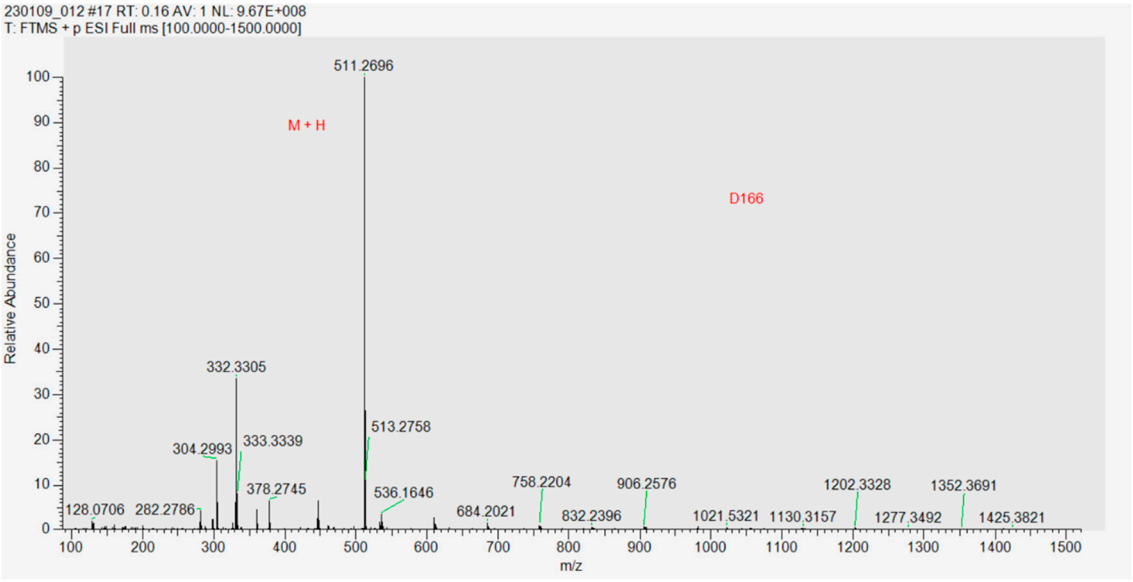

Figure S19 Mass spectrum of **7**.

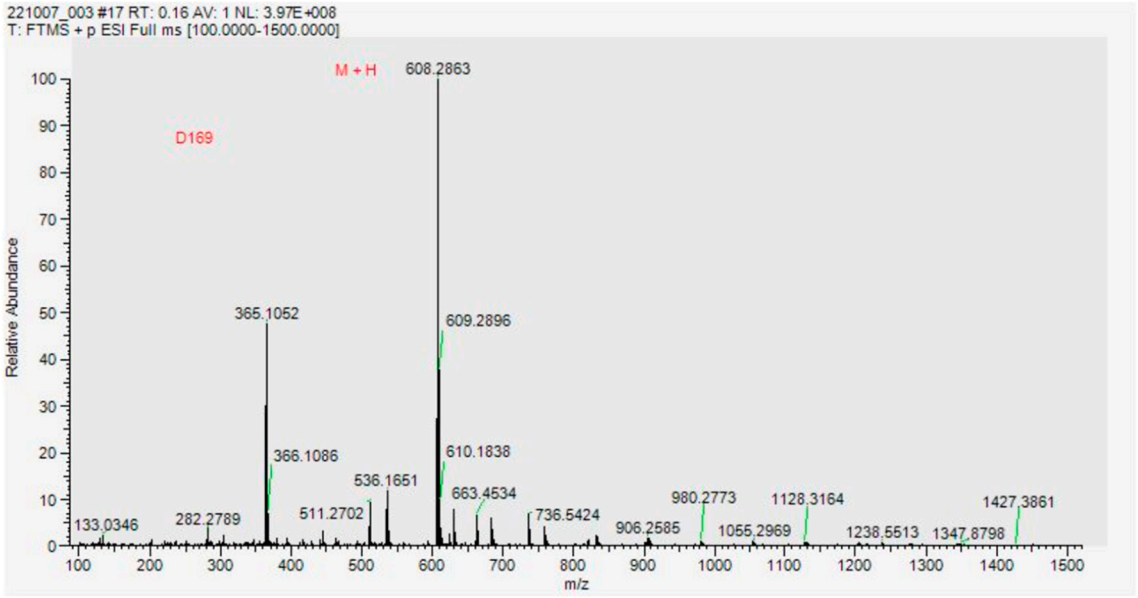

Figure S20 Mass spectrum of **9**.

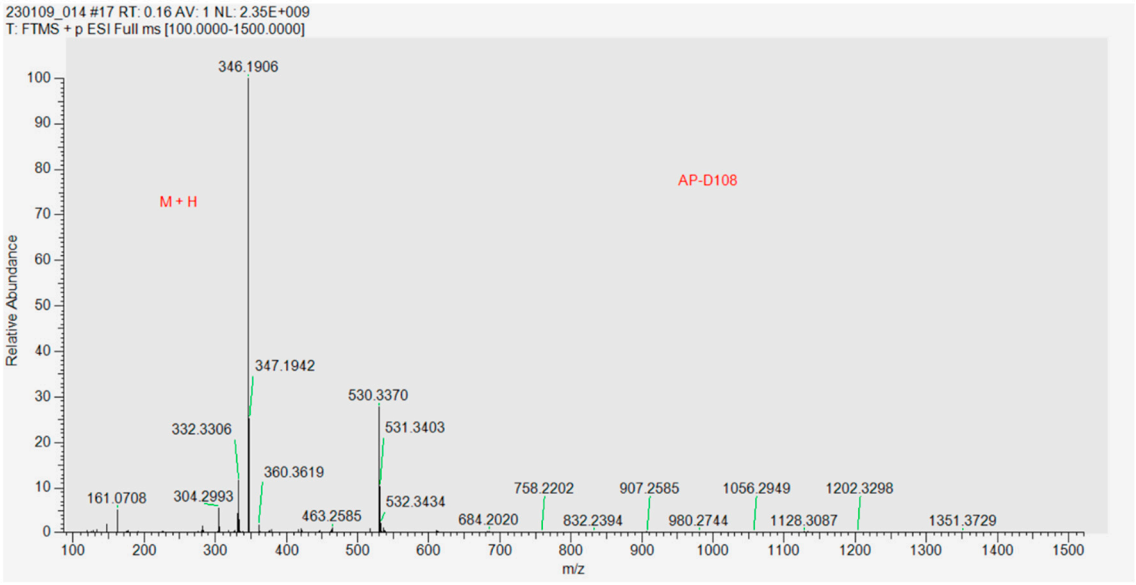

Figure S21 Mass spectrum of **11**.

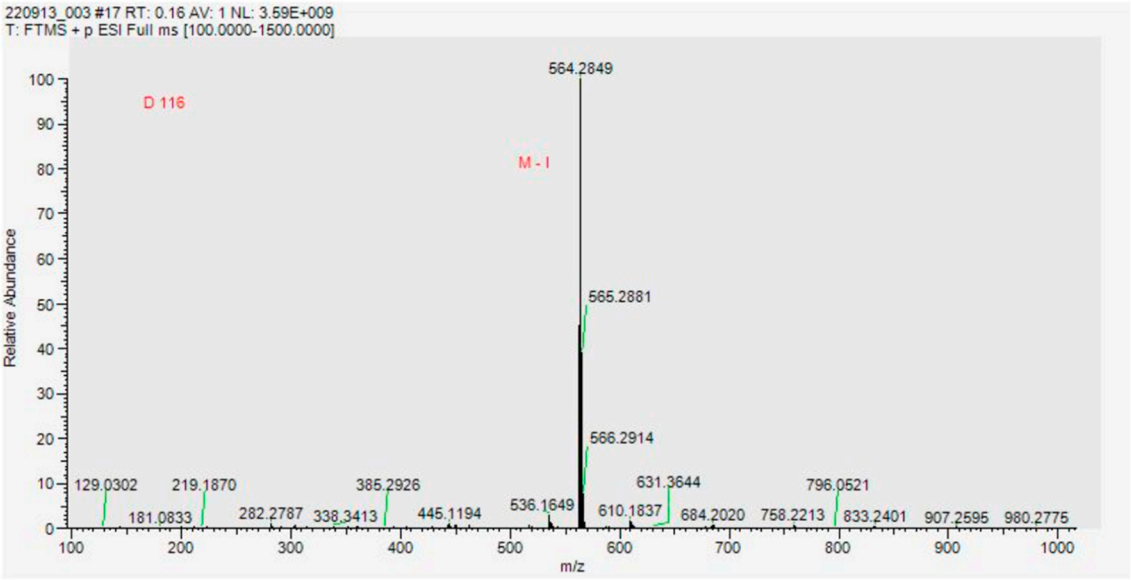

Figure S22 Mass spectrum of **12**.

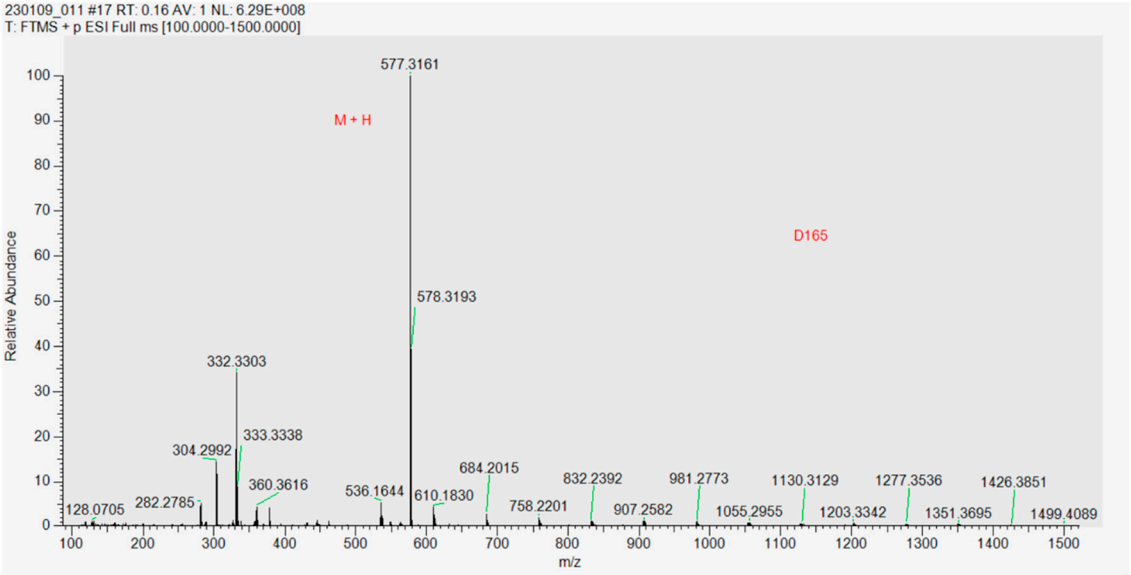

Figure S23 Mass spectrum of **13**.

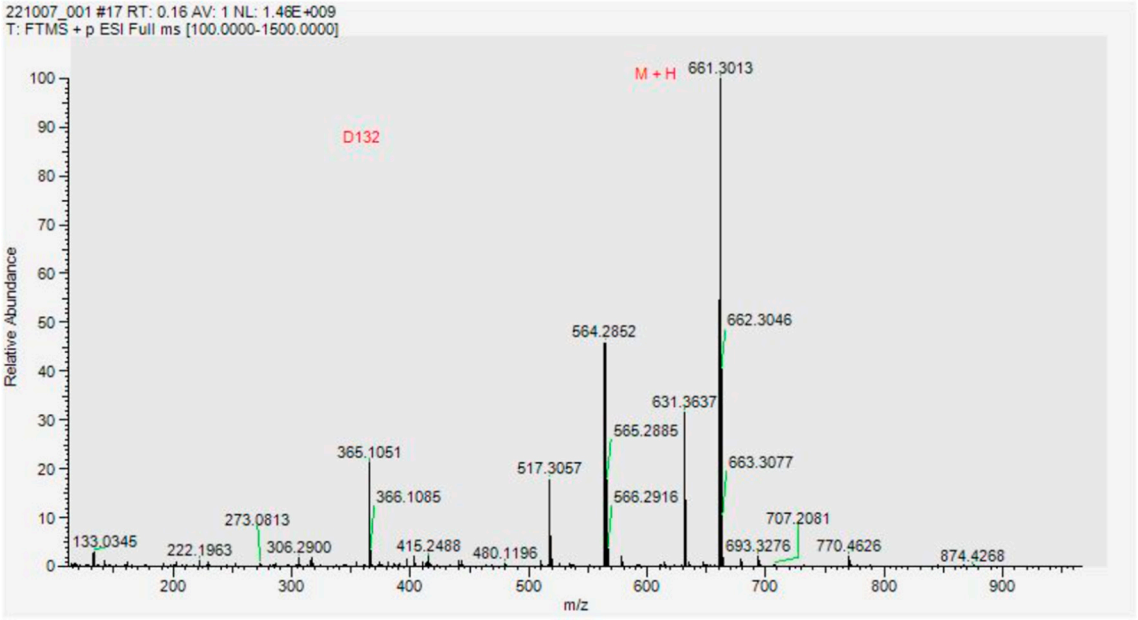

Figure S24 Mass spectrum of **14**.

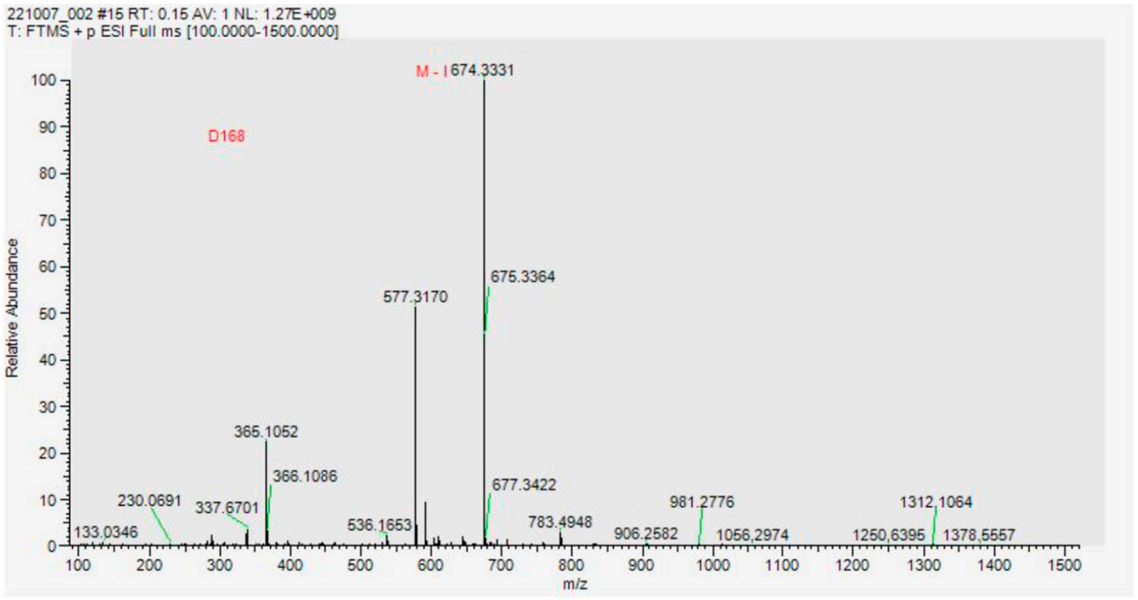

Figure S25 Mass spectrum of **15**.

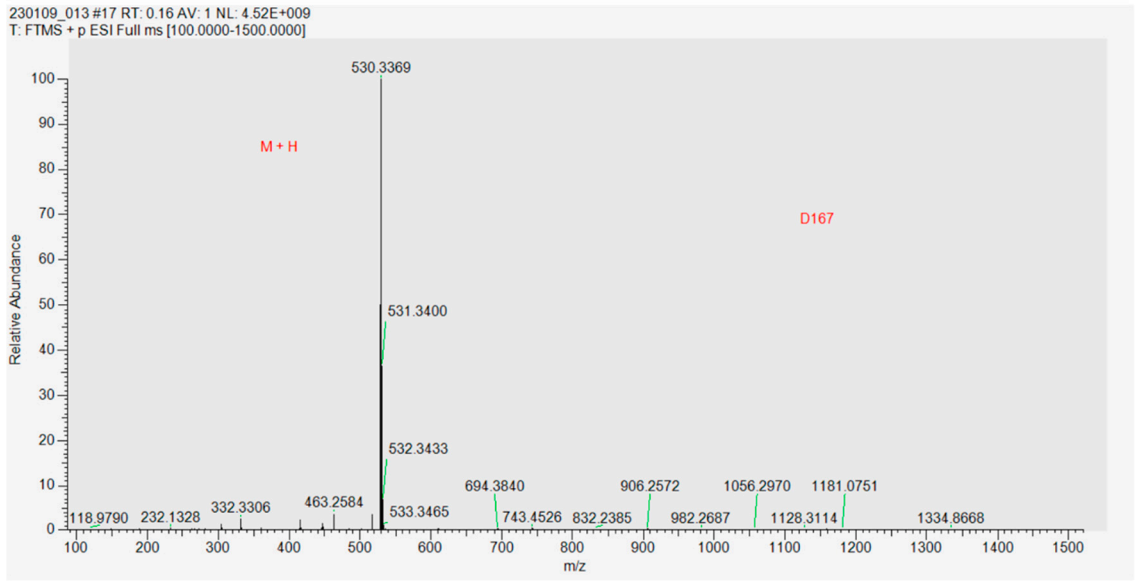

Figure S26 Mass spectrum of **18**.

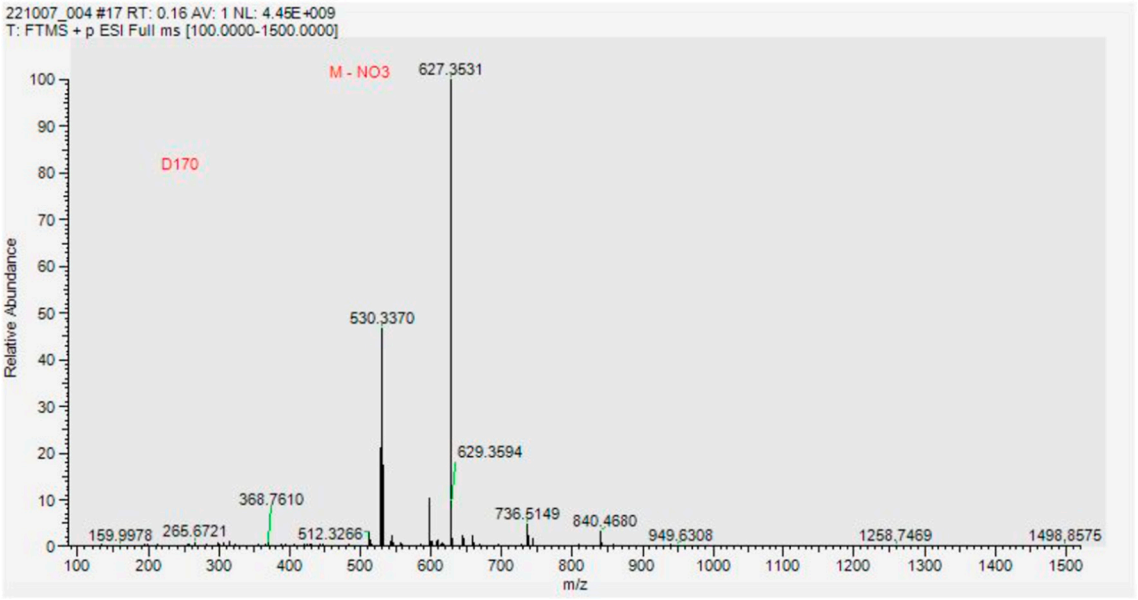

Figure S27 Mass spectrum of **20**.

3. Quantum chemical calculations

Table S1. Calculated absorption data of the lowest energy transition of selected derivatives.

Compound		Wavelength (nm)	f	Composition	Δ**r** (Å)
8	$S_0 \rightarrow S_1$	507.6	0.637	HOMO->LUMO (99%)	2.287
	$S_0 \rightarrow S_2$	455.9	1.352	H-1->LUMO (99%)	1.609
9	$S_0 \rightarrow S_1$	543.6	1.467	HOMO->LUMO (98%)	3.753
	$S_0 \rightarrow S_2$	495.2	0.709	H-1->LUMO (99%)	3.048
14	$S_0 \rightarrow S_1$	563.1	0.929	HOMO->LUMO (98%)	1.682
	$S_0 \rightarrow S_2$	485.5	1.372	H-1->LUMO (97%)	3.249
15	$S_0 \rightarrow S_1$	599.1	1.747	HOMO->LUMO (93%)	4.373
	$S_0 \rightarrow S_2$	535.6	0.689	H-1->LUMO (94%)	2.402
19	$S_0 \rightarrow S_1$	467.3	0.772	HOMO->LUMO (97%)	8.836
	$S_0 \rightarrow S_2$	434.8	1.166	H-1->LUMO (97%)	4.706
20	$S_0 \rightarrow S_1$	525.3	1.546	HOMO->LUMO (98%)	4.045
	$S_0 \rightarrow S_2$	456.8	0.518	H-1->LUMO (98%)	3.694

Table S2. Selected bond distances (Å), dihedral angle (°) and BLA (Å) of the compounds in the ground S_0 and excited S_1 states.

	r[10-18]		r[18-37]		r[37-39]		BLA		D[3-10-18-37]	
Compound	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
8	1.450	1.405	1.353	1.383	1.451	1.436	0.10	0.04	18.9	0.7
9	1.442	1.417	1.359	1.385	1.440	1.430	0.08	0.04	12.6	0.1
14	1.447	1.416	1.355	1.375	1.448	1.439	0.09	0.05	15.5	1.4
15	1.438	1.426	1.362	1.377	1.437	1.433	0.08	0.05	8.4	1.8
19	1.449	1.408	1.353	1.383	1.449	1.436	0.10	0.04	19.9	3.6
20	1.441	1.430	1.360	1.377	1.439	1.439	0.08	0.06	15.4	7.4

Table S3. Calculated emission data of the lowest energy transition of selected derivatives.

Compound		Wavelength (nm)	f	Composition	τ (ns)
8	$S_1 \rightarrow S_0$	576.2	0.546	HOMO->LUMO (99%)	9.11
9	$S_1 \rightarrow S_0$	583.2	1.543	HOMO->LUMO (99%)	3.30
14	$S_1 \rightarrow S_0$	602.8	0.877	HOMO->LUMO (98%)	6.21
15	$S_1 \rightarrow S_0$	623.0	1.850	HOMO->LUMO (95%)	3.14
19	$S_1 \rightarrow S_0$	522.7	0.702	HOMO->LUMO (98%)	5.83
20	$S_1 \rightarrow S_0$	560.2	1.678	HOMO->LUMO (99%)	2.80

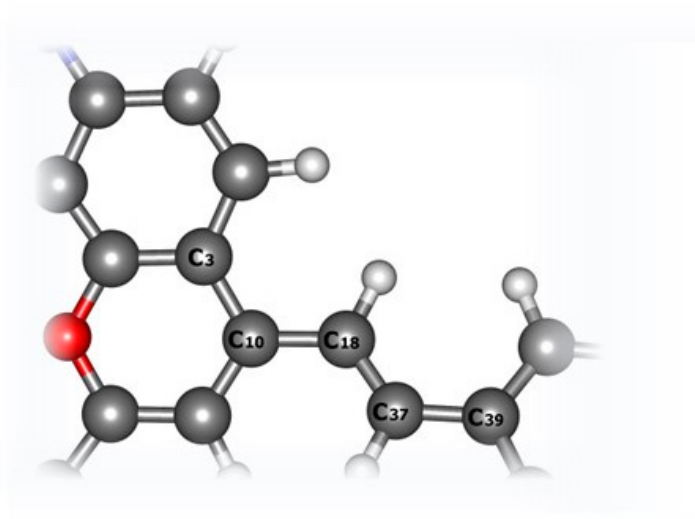

Figure S28 Numbering scheme adopted to all fluorescent dyes.