Evaluation of electron or charge transfer processes between chromenylium-based fluorophores and protonated-deprotonated aniline

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1. Figures

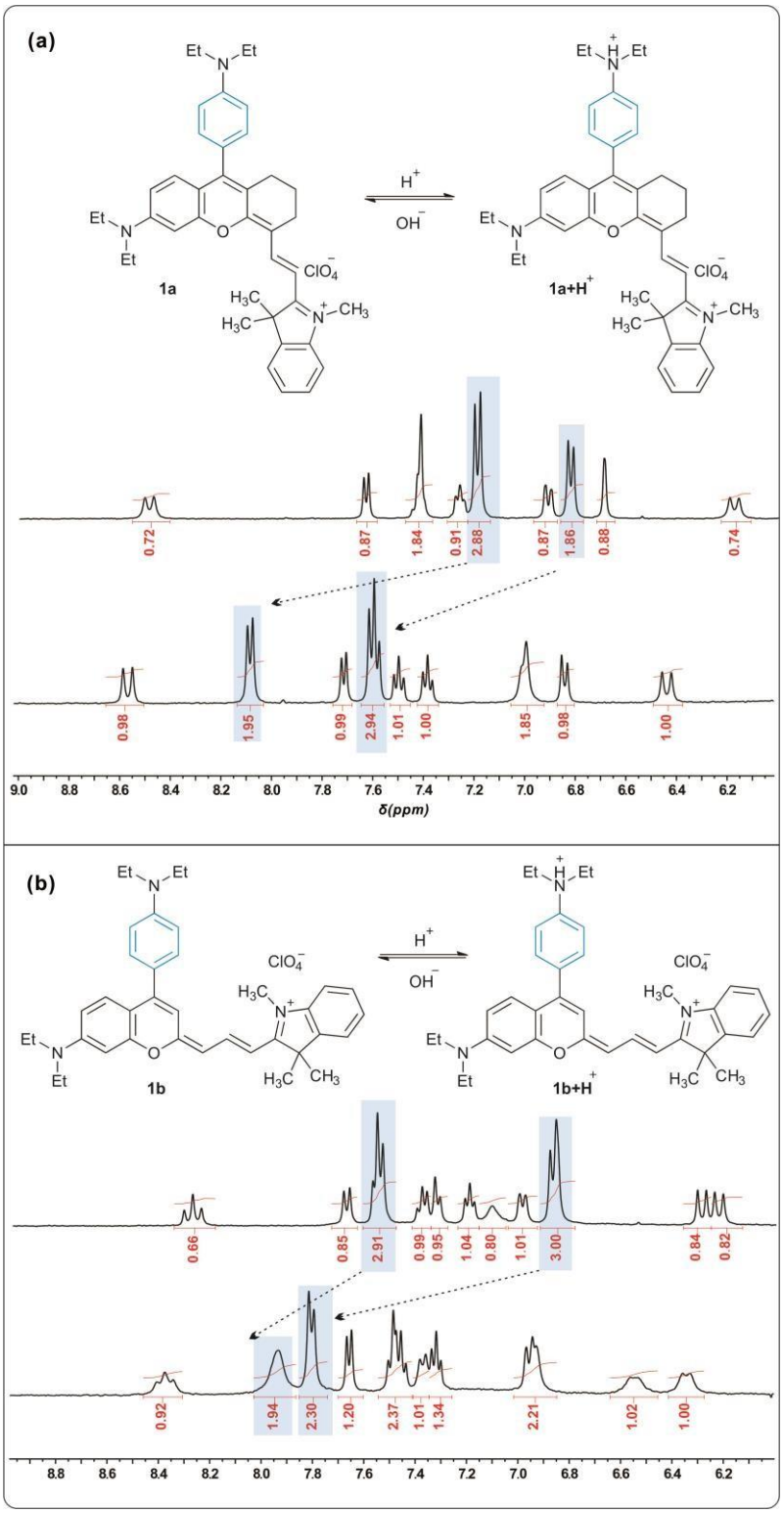


Fig. S1 ^{1}H NMR of dyes **1a-b** in DMSO-*d6* (top) and the acidic condition (bottom). (a) dye **1a**; (b) dye **1b**.

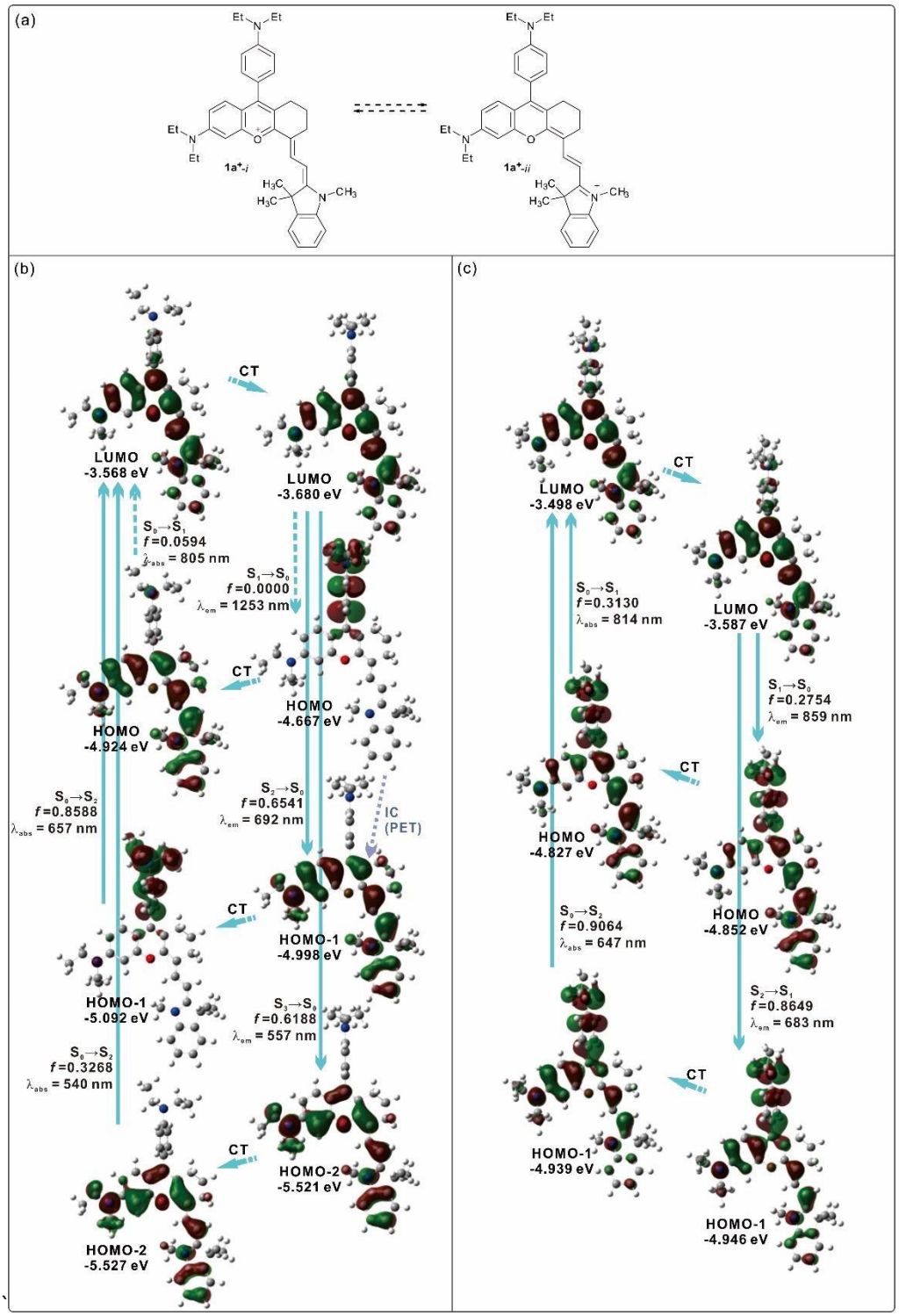


Fig. S2 The resonance equilibrium of **1a**$^{+}$ (a) and frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of dyes **1a**$^{+}$-*i* (b) and **1a**$^{+}$-*ii* (c). CT stands for conformation transformation. Excitation and radiative processes are represented by solid lines and the nonradiative processes by dotted lines. For details please refer to Tables S2 and S3.

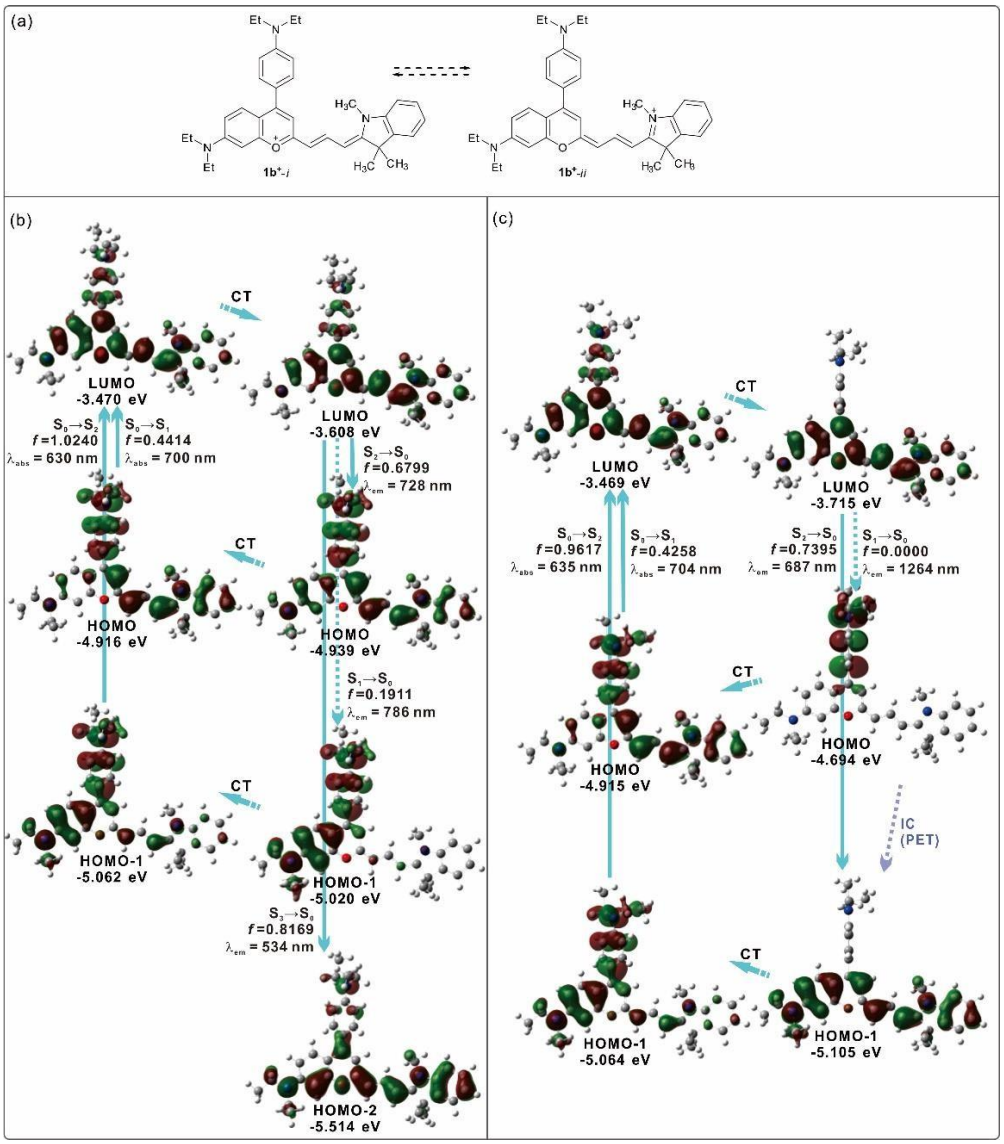


Fig. S3 The resonance equilibrium of **1b**$^{+}$ (a) and frontier molecular orbitals (FMOs) involved in the vertical excitation and emission of dyes **1b**$^{+}$-*i* (b) and **1b**$^{+}$-*ii* (c). CT stands for conformation transformation. Excitation and radiative processes are represented by solid lines and the nonradiative processes by dotted lines. For details please refer to Tables S2 and S3.

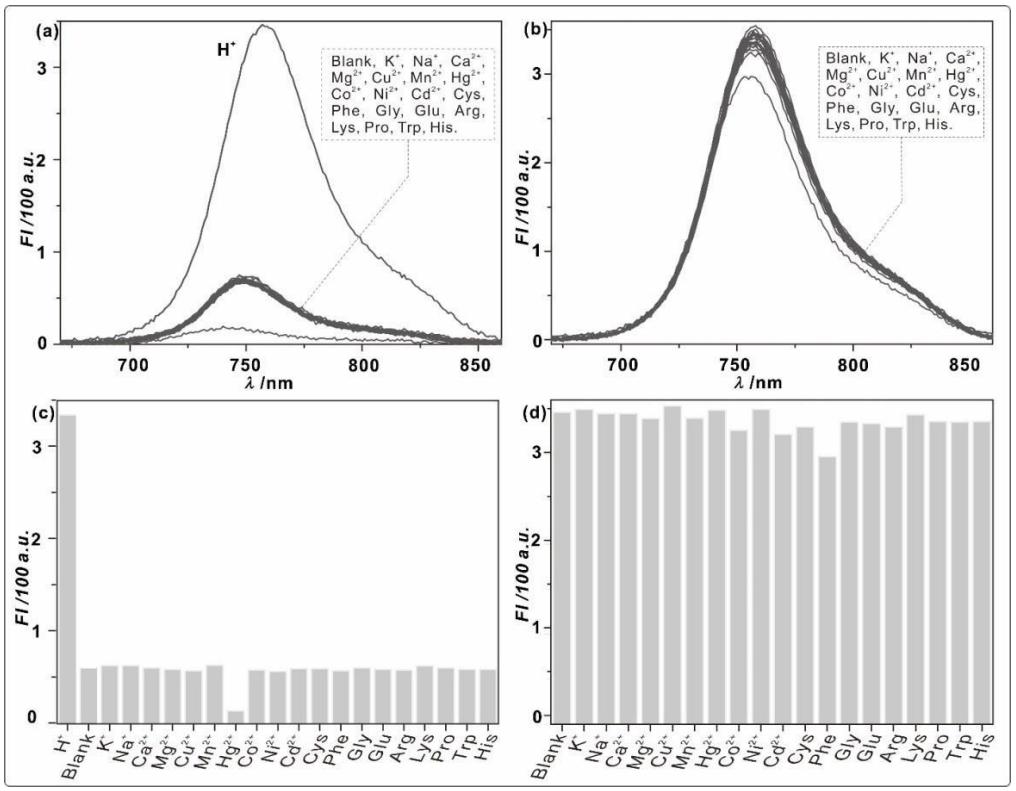


Fig. S4 Fluorescence responses of dye **1a** (10 μM) to different analytes, K^+ (100 mM), Na^+ (100 mM), Ca^{2+} (0.5 mM), Mg^{2+} (0.5 mM), Cd^{2+} (0.3 mM), Cu^{2+} (0.3 mM), Co^{2+} (0.3 mM), Hg^{2+} (0.3 mM), Mn^{2+} (0.3 mM), Ni^{2+} (0.3 mM), Cys (0.1 mM), Phe (0.1 mM), Gly (0.1 mM), Glu (0.1 mM), Arg (0.1 mM), Lys (0.1 mM), Pro (0.1 mM), Try (0.1 mM) and His (0.1 mM) were included: (a, c) tested in Britton-Robinson Buffer (pH = 7.0); (b, d) tested in Britton-Robinson Buffer (pH = 3.0).

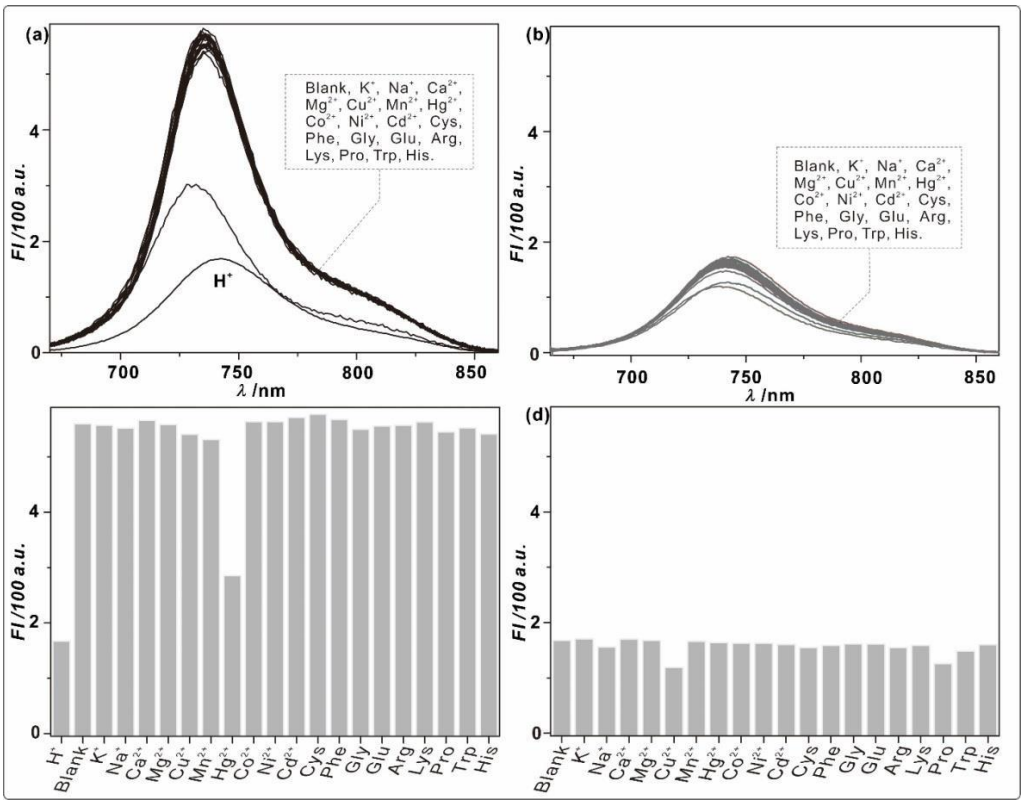


Fig. S5 Fluorescence responses of dye **1b** (10 μM) to different analytes, K^+ (100 mM), Na^+ (100 mM), Ca^{2+} (0.5 mM), Mg^{2+} (0.5 mM), Cd^{2+} (0.3 mM), Cu^{2+} (0.3 mM), Co^{2+} (0.3 mM), Hg^{2+} (0.3 mM), Mn^{2+} (0.3 mM), Ni^{2+} (0.3 mM), Cys (0.1 mM), Phe (0.1 mM), Gly (0.1 mM), Glu (0.1 mM), Arg (0.1 mM), Lys (0.1 mM), Pro (0.1 mM), Try (0.1 mM) and His (0.1 mM) were included: (a, c) tested in Britton-Robinson Buffer (pH = 7.0); (b, d) tested in Britton-Robinson Buffer (pH = 2.0).

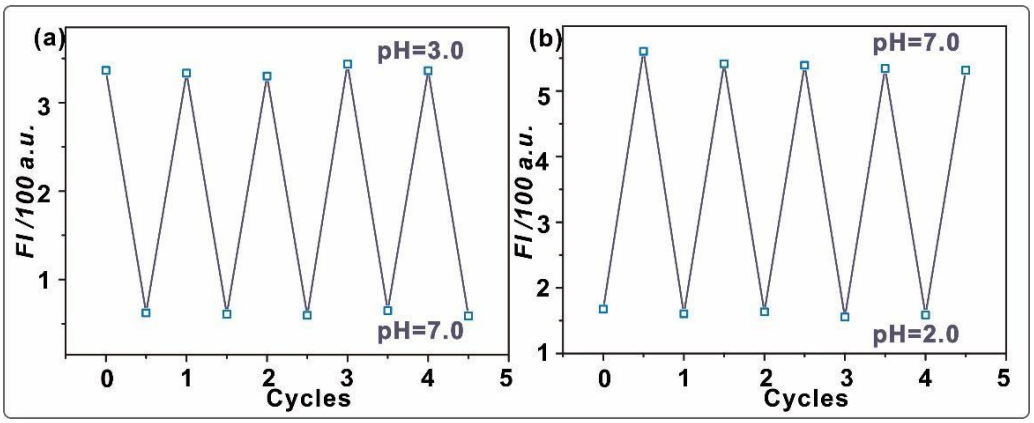


Fig. S6 The reversible optical responses of dyes **1a-b** at different pH conditions: (a) dye **1a**; (b) dye **1b**.

2. Tables

Table S1. Stability of different conjugated structures of dyes **1a**$^+$**-c**$^+$ and their protonated forms.

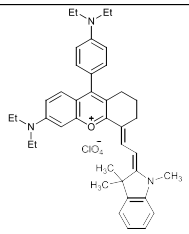
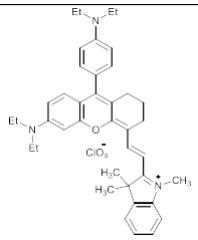
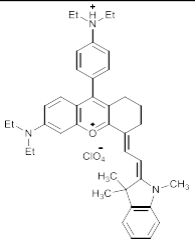
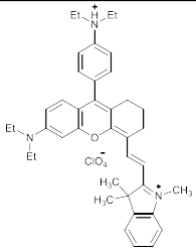
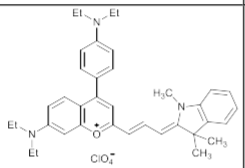
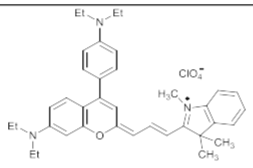
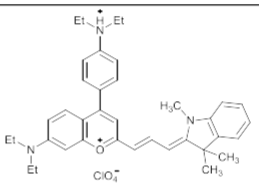
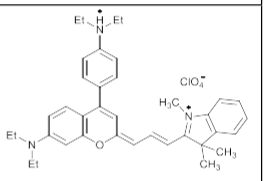
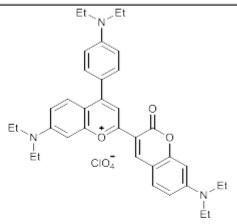
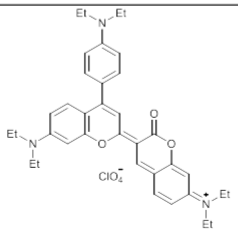
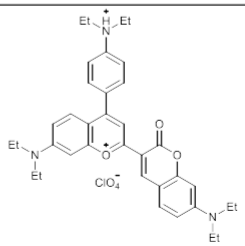
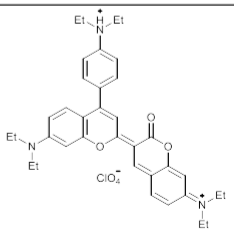
Structures				
Dye No.	**1a**$^+$-*i*	**1a**$^+$-*ii*	**1a**$^+$-*i* + **H**$^+$	**1a**$^+$-*ii* + **H**$^+$
HF(hartree)	-1793.0302226	-1793.0418659 **stable**	-1793.4811741 **stable**	-1793.4792696
Structures				
Dye No.	**1b**$^+$-*i*	**1b**$^+$-*ii*	**1b**$^+$-*i* + **H**$^+$	**1b**$^+$-*ii* + **H**$^+$
HF(hartree)	-1676.268848	-1676.2689758 **stable**	-1676.7042854 **stable**	-1676.7042852 **stable**
Structures				
Dye No.	**1c**$^+$-*i*	**1c**$^+$-*ii*	**1c**$^+$-*i* + H$^+$	**1c**$^+$-*ii* + H$^+$
HF(hartree)	-1787.4815541 **stable**	-1787.4815541 **stable**	-1787.9135717 **stable**	-1787.9135717 **stable**

Table S2 Selected parameters for the vertical excitation (UV-vis absorptions) of dyes **1a**$^+$**-c**$^+$ and **1c**$^+$+**H**$^+$ based on the optimized ground state geometries in water.

dyes	Electronic transitions	Excitation energy		$\lambda_{exp.}$/nm	f [a]	Composition[b]	CI[c]
		E/eV	λ/nm				
1a$^+$-*i*	$S_0 \rightarrow S_1$	1.54	805	719	0.0594	H-1→L	0.68998
						H→L	-0.15369
	$S_0 \rightarrow S_2$	1.89	657		0.8588	H-2→L	0.17744
						H-1→L	0.15168
						H→L	0.66923
	$S_0 \rightarrow S_3$	2.30	540		0.3268	H-2→L	0.64913
						H→L	-0.17332
						H→L+1	-0.21105
1a$^+$-*ii*	$S_0 \rightarrow S_1$	1.52	814	719	0.3130	H-1→L	0.47843
						H→L	0.52001
	$S_0 \rightarrow S_2$	1.92	647		0.9064	H-2→L	-0.13695
						H-1→L	0.51057
						H→L	-0.47092
	$S_0 \rightarrow S_3$	2.34	530		0.1881	H-2→L	0.65193
						H-1→L+1	0.10090
						H→L+1	-0.21809
1b$^+$-*i*	$S_0 \rightarrow S_1$	1.77	700	702	0.4414	H-1→L	-0.44875
						H→L	0.54037
	$S_0 \rightarrow S_2$	1.97	630		1.0240	H-2→L	0.15884
						H-1→L	0.51829
						H→L	0.44391
	$S_0 \rightarrow S_3$	2.35	527		0.1316	H-2→L	0.62009
						H→L+1	-0.30807
1b$^+$-*ii*	$S_0 \rightarrow S_1$	1.76	704	702	0.4258	H-1→L	0.44039
						H→L	0.54760
	$S_0 \rightarrow S_2$	1.95	635		0.9617	H-2→L	0.16250
						H-1→L	0.52590
						H→L	-0.43315
	$S_0 \rightarrow S_3$	2.34	529		0.1490	H-2→L	0.62225
						H→L+1	0.29875
1c$^+$-*i*, **1c**$^+$-*ii*	$S_0 \rightarrow S_1$	1.76	703		0.5880	H-1→L	-0.14753
						H→L	0.67363
						H→L+1	0.13549
	$S_0 \rightarrow S_2$	1.89	656	583	0.9505	H-1→L	0.67754
						H→L	0.16885
1c$^+$-*i* **+ H**$^+$ **1c**$^+$-*ii* **+ H**$^+$	$S_0 \rightarrow S_1$	1.84	674	668	0.9585	H-1→L	-0.10442
						H→L	0.69856
	$S_0 \rightarrow S_2$	2.11	588		0.1557	H-1→L	0.64355
						H→L	-0.27374

[a] Oscillator strength. [b] H stands for HOMO and L stands for LUMO. [c] Coefficient of the wave function for each excitations.

Table S3 Selected parameters for emission related of dyes **1a**$^+$**-c**$^+$ and **1c**$^+$+**H**$^+$ based on the optimized lowest singlet excited state geometries in water.

dyes	Electronic transitions	Excitation energy		$\lambda_{exp.}$/nm	f [a]	Composition[b]	CI[c]
		E/eV	λ/nm				
1a$^+$-*i*	$S_0 \rightarrow S_1$	0.99	1253		0.0001	H→L	0.70704
	$S_0 \rightarrow S_2$	1.79	692	749	0.6541	H-2→L	0.24650
						H-1→L	0.66110
	$S_0 \rightarrow S_3$	2.22	557		0.6188	H-2→L	0.63765
						H-1→L	-0.25265
1a$^+$-*ii*	$S_0 \rightarrow S_1$	1.44	859		0.2754	H-1→L	0.48779
						H→L	0.51099
	$S_0 \rightarrow S_2$	1.82	683	749	0.8649	H-1→L	0.50836
						H→L	-0.48692
1b$^+$-*i*	$S_0 \rightarrow S_1$	1.58	786		0.1911	H-1→L	0.64202
						H→L	-0.28502
	$S_0 \rightarrow S_2$	1.70	728	736	0.6799	H-2→L	-0.21337
						H-1→L	0.26429
						H→L	0.61837
	$S_0 \rightarrow S_3$	2.32	534		0.8169	H-2→L	0.62598
						H→L	0.19000
						H→L+1	0.25150
1b$^+$-*ii*	$S_0 \rightarrow S_1$	0.98	1264		0.0000	H→L	0.70710
	$S_0 \rightarrow S_2$	1.80	687	736	0.7395	H-2→L	0.27270
						H-1→L	0.64718
1c$^+$-*i*, **1c**$^+$-*ii*	$S_0 \rightarrow S_1$	0.69	1804		0.0000	H→L	0.70710
	$S_0 \rightarrow S_2$	1.80	689	691	0.7900	H-2→L	0.19666
						H-1→L	0.67687
1c$^+$-*i* + **H**$^+$	$S_0 \rightarrow S_1$	0.76	1641		0.0000	H→L	0.70709
1c$^+$-*ii* + **H**$^+$							
	$S_0 \rightarrow S_2$	1.96	631	719	0.0078	H-2→L	0.69752
						H-1→L	0.11469
	$S_0 \rightarrow S_3$	2.02	615		0.3000	H-2→L	-0.11572
						H-1→L	0.68645
	$S_0 \rightarrow S_8$	2.85	435		0.4055	H→L+1	0.57753
						H→L+2	0.24345
						H→L+3	0.13786
						H→L+4	0.25217

[a] Oscillator strength. [b] H stands for HOMO and L stands for LUMO. [c] Coefficient of the wave function for each excitations.

4. Appendix

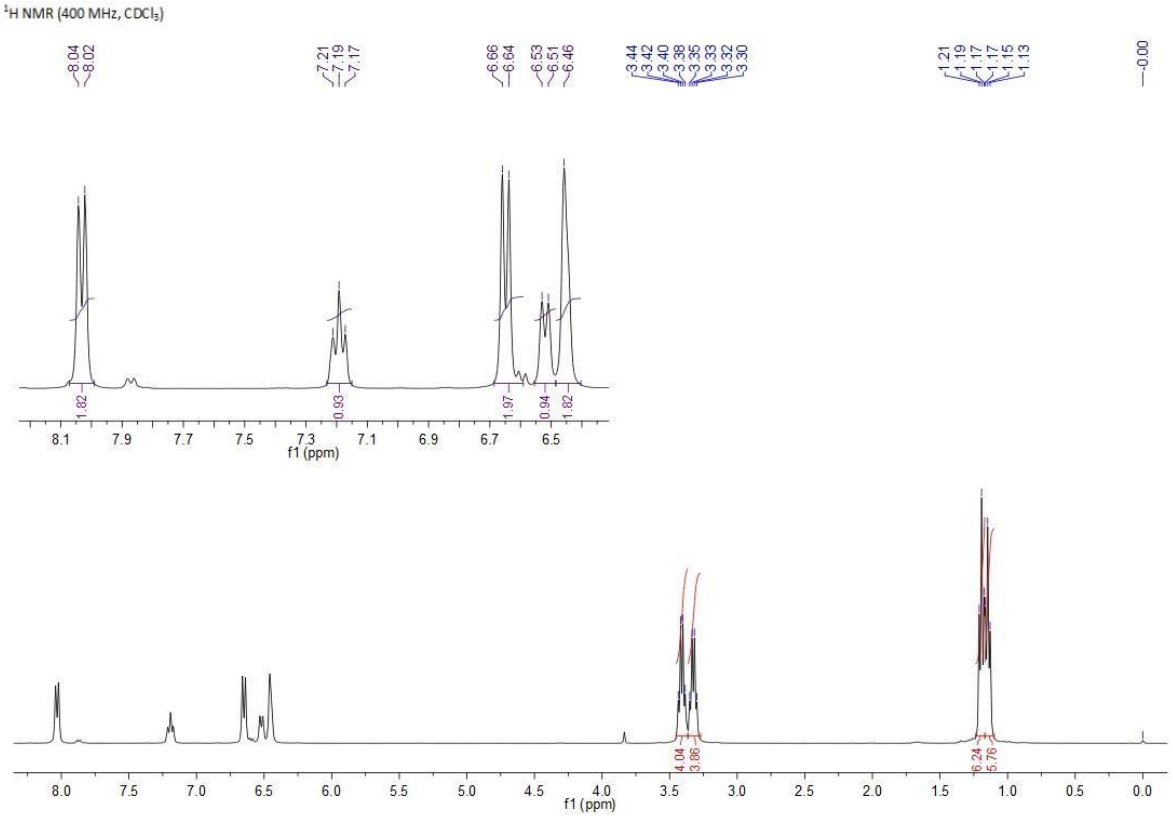


Fig. S7 ^{1}H NMR of **3.**

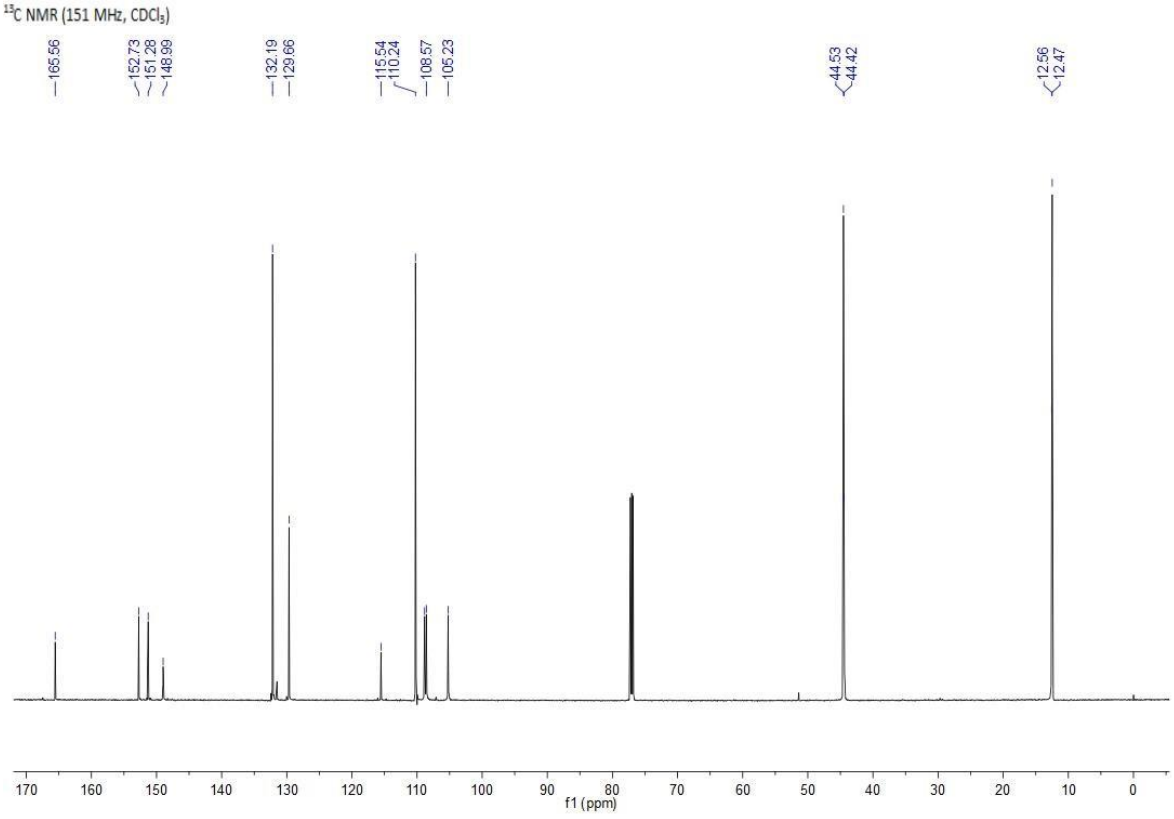


Fig. S8 ^{13}C NMR of **3.**

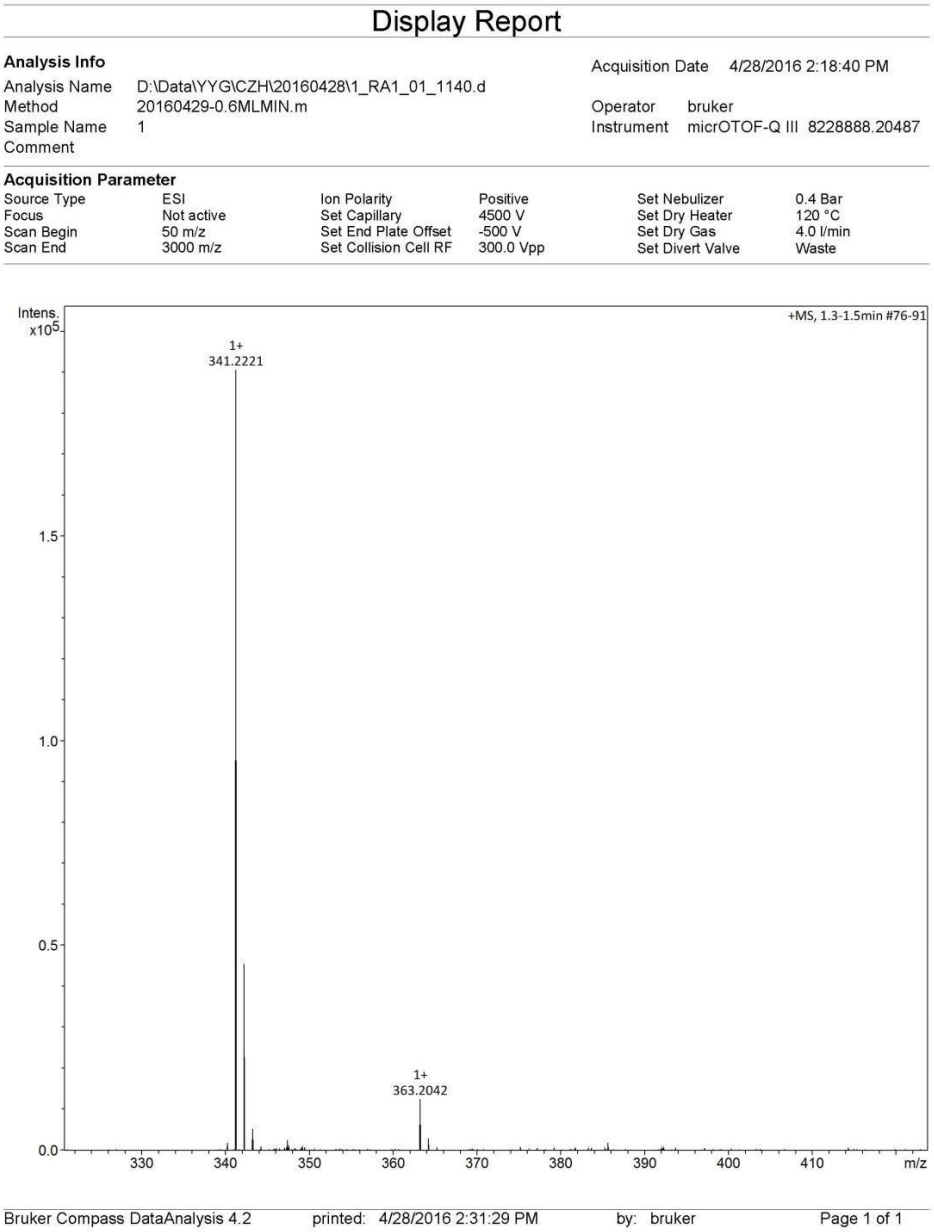


Fig. S9 HRMS(ESI$^+$) of **3**.

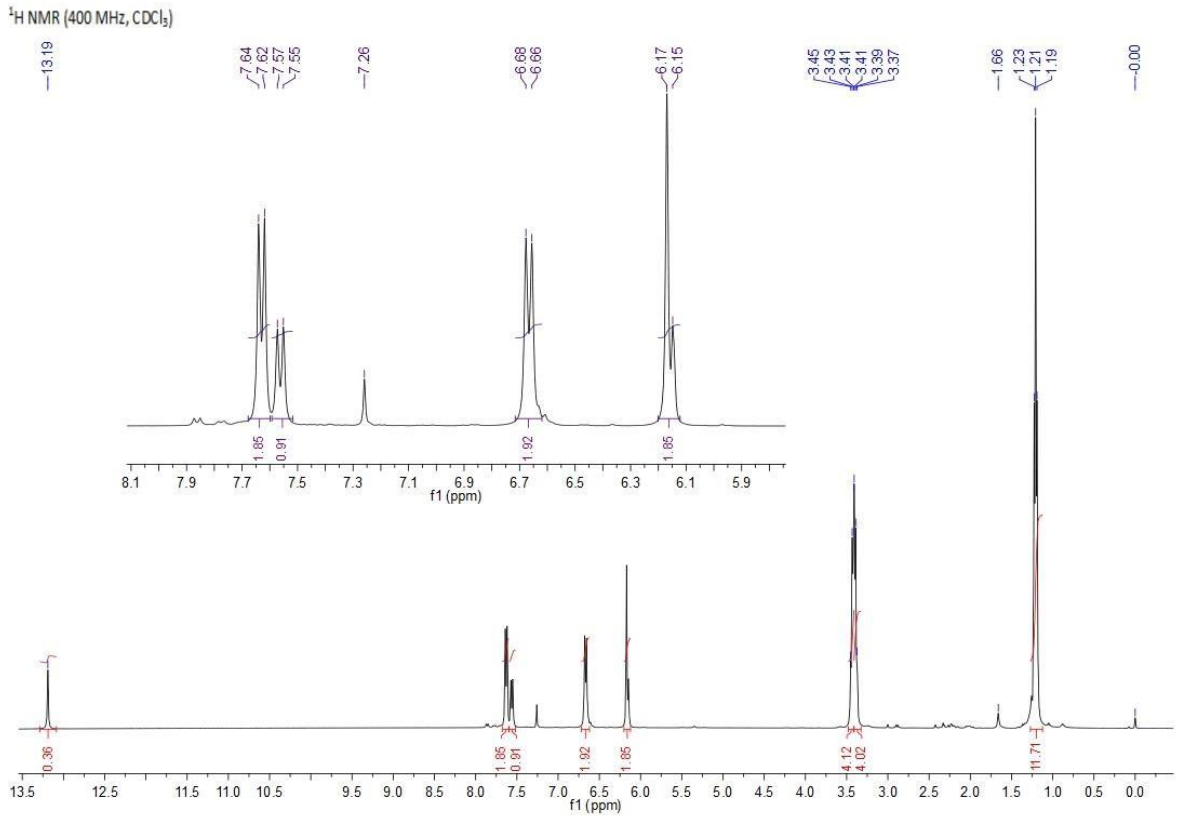


Fig. S10 ^{1}H NMR of **4.**

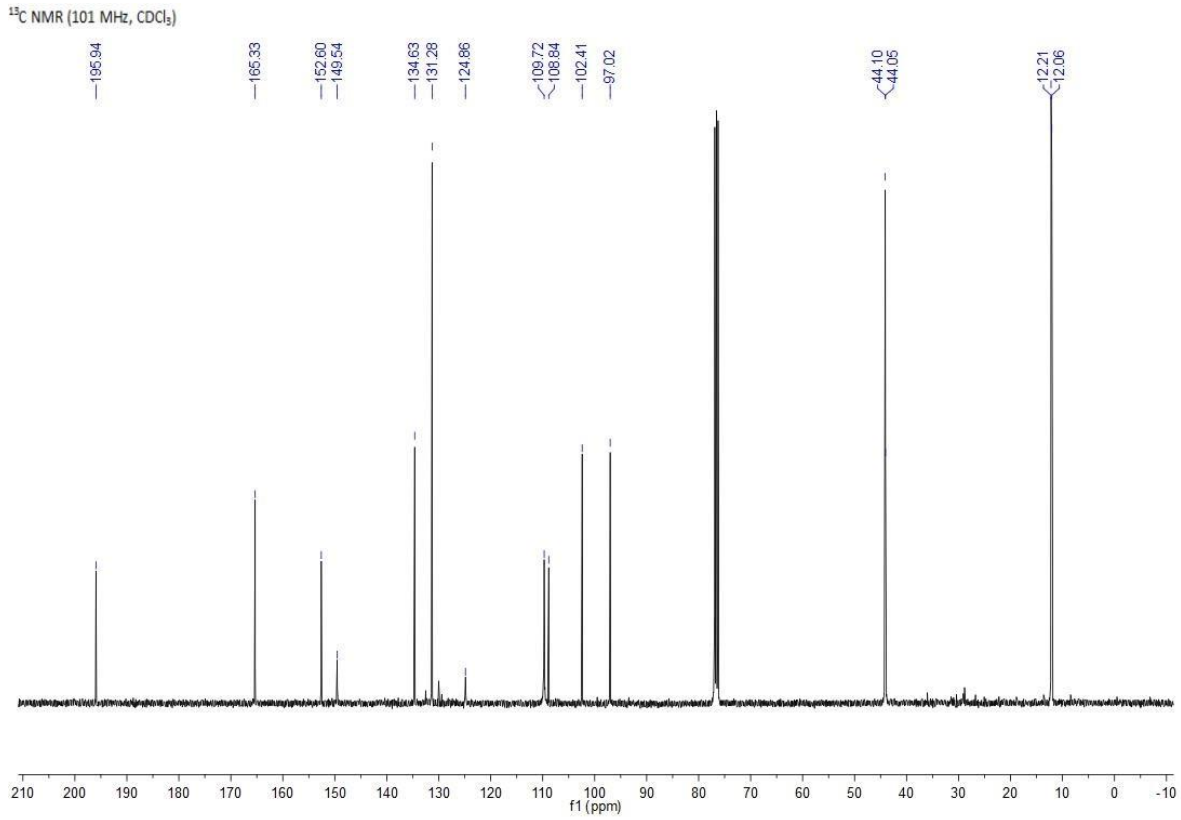


Fig. S11 ^{13}C NMR of **4.**

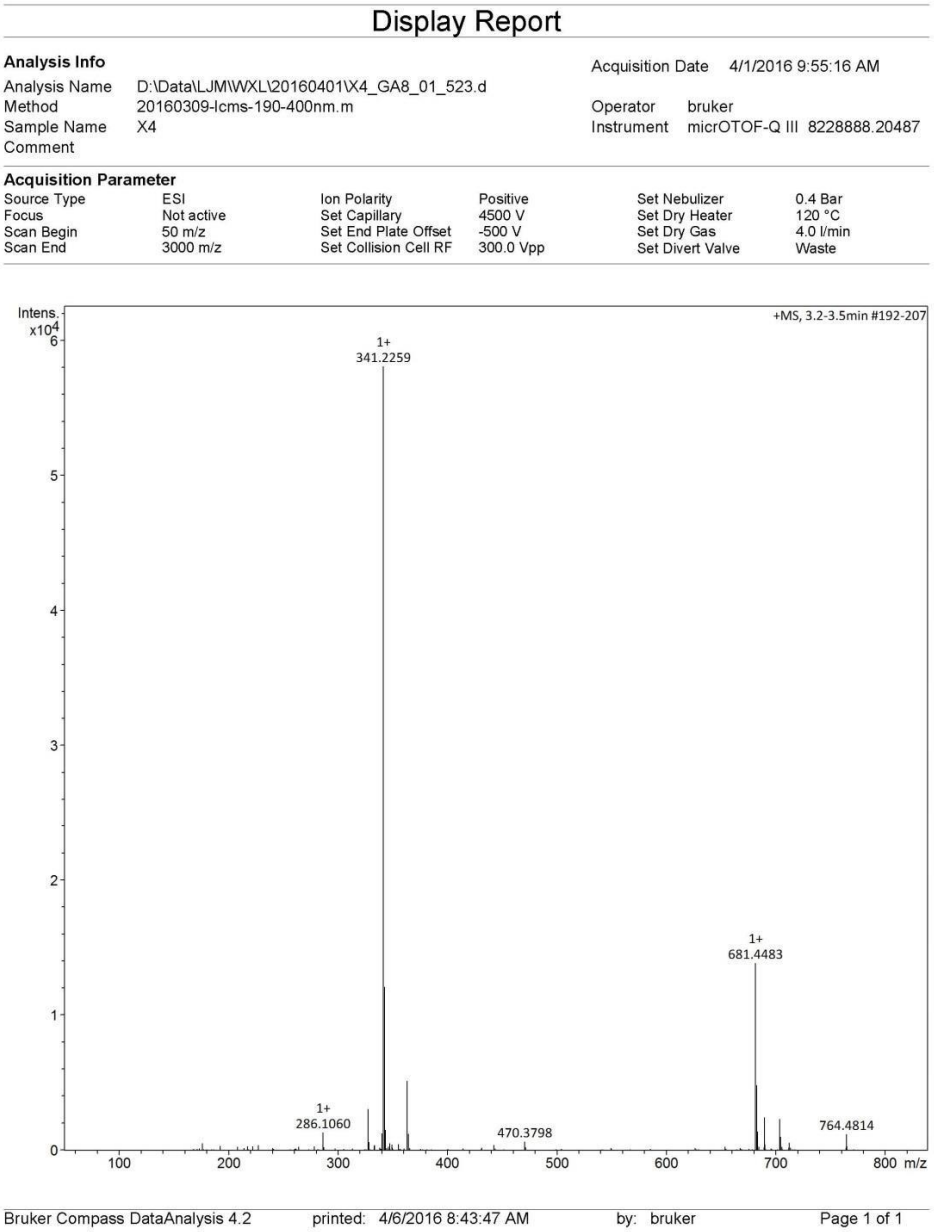


Fig. S12 HRMS(ESI$^+$) of **4**.

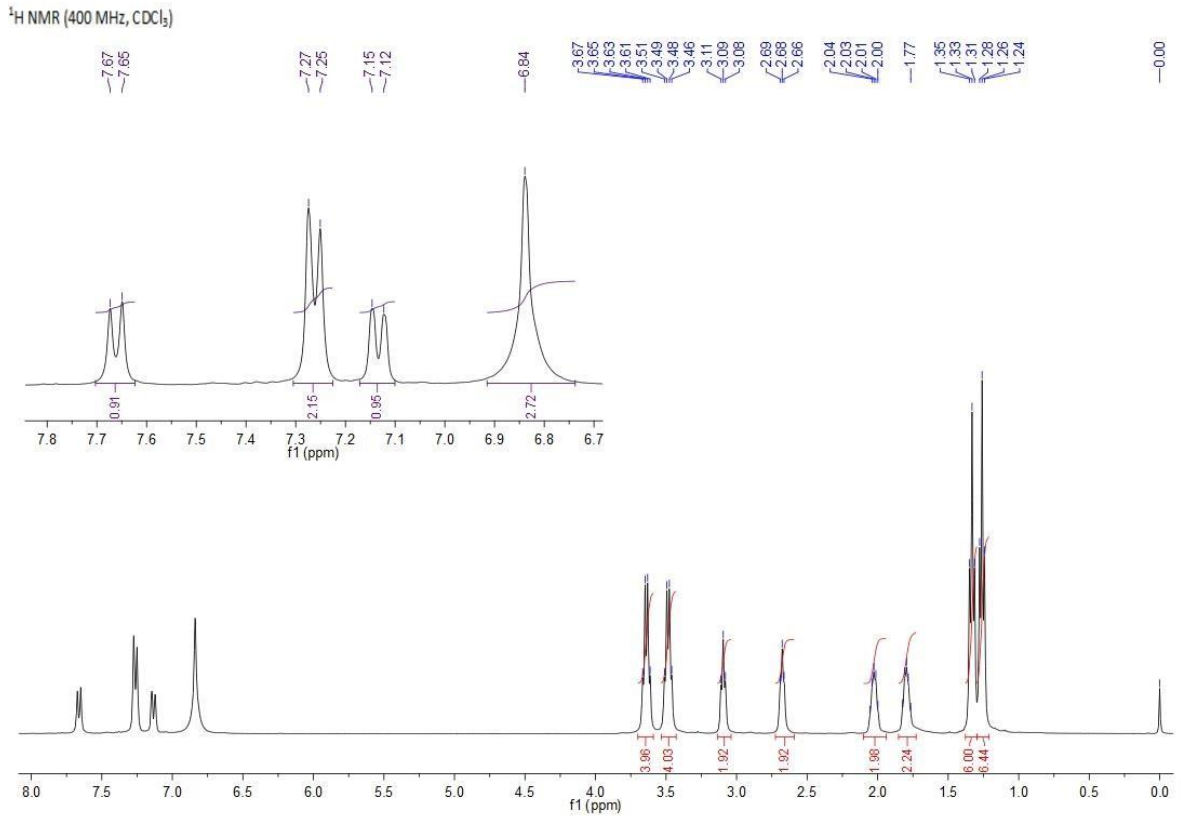


Fig. S13 ^{1}H NMR of **5.**

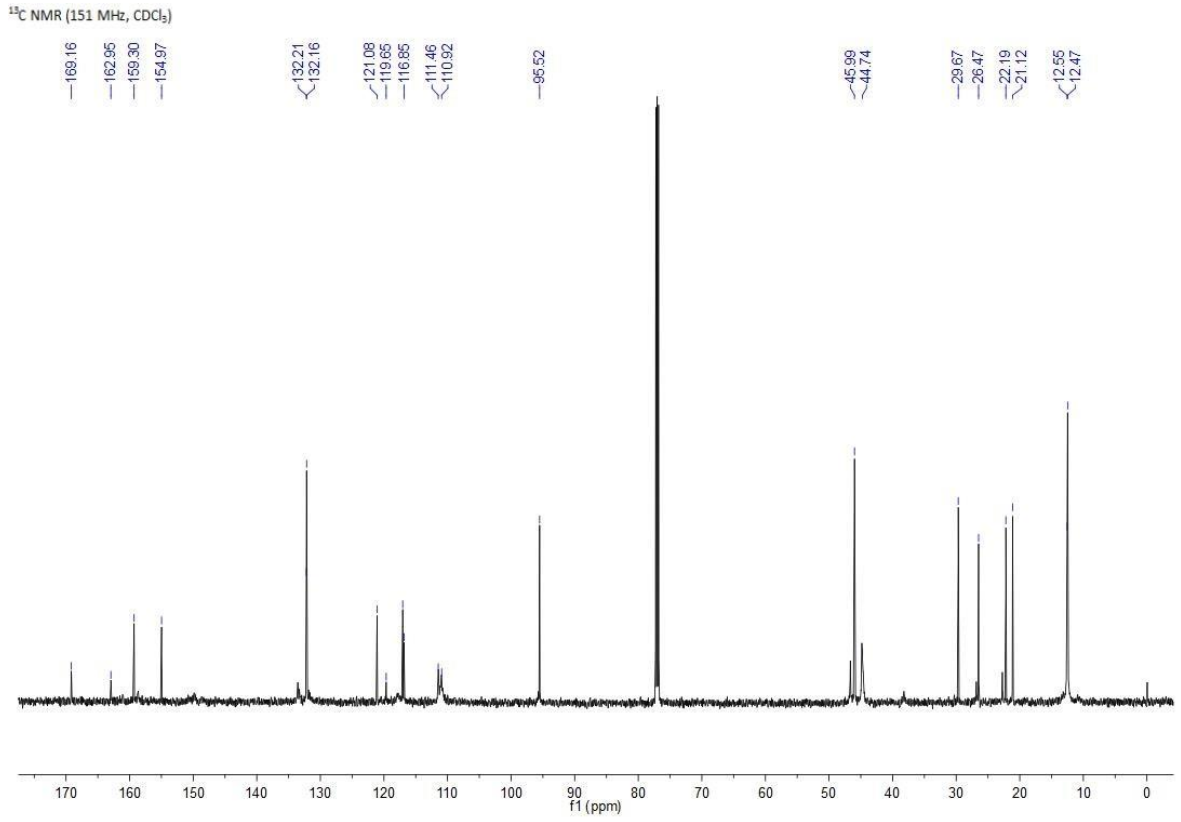


Fig. S14 ^{13}C NMR of **5.**

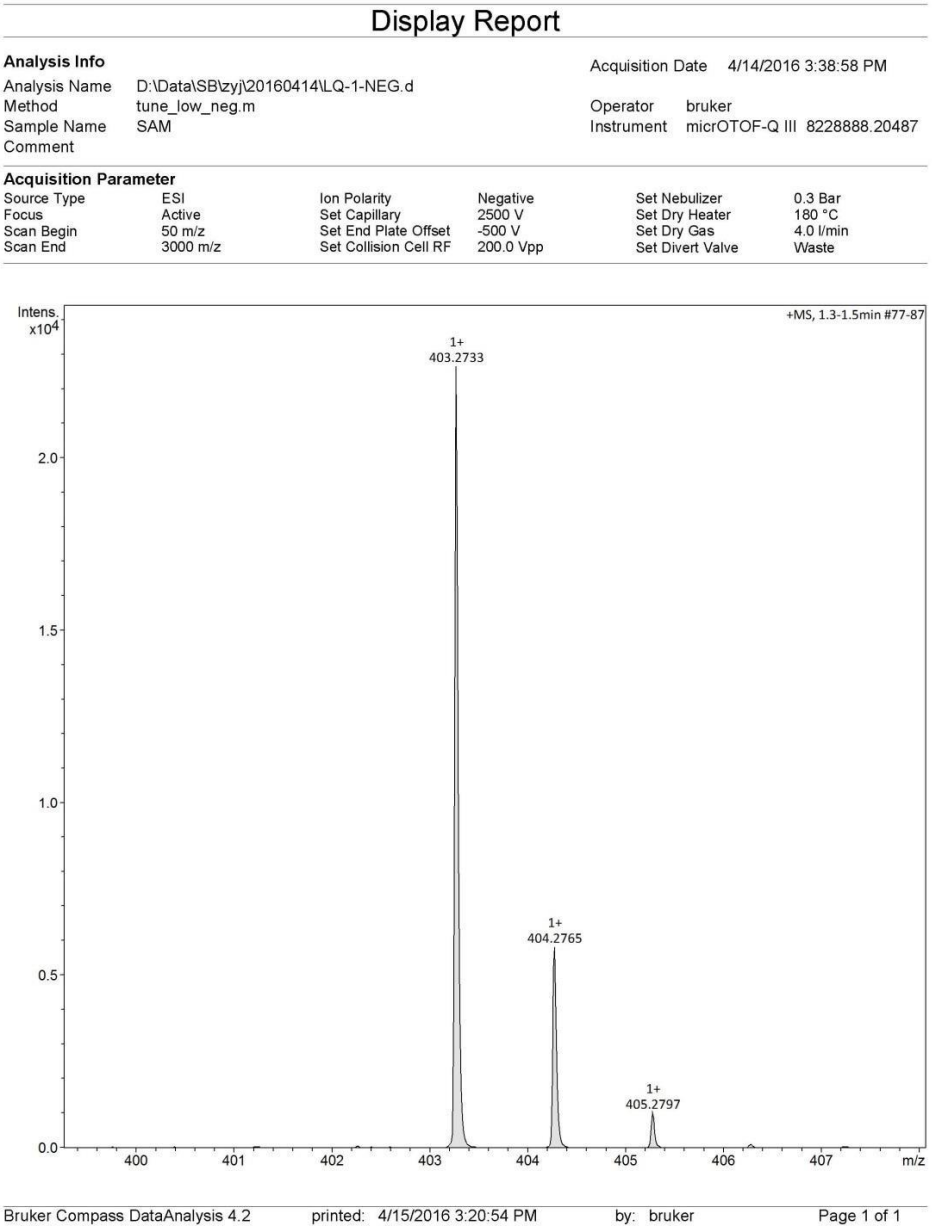


Fig. S15 HRMS(ESI+) of **5**.

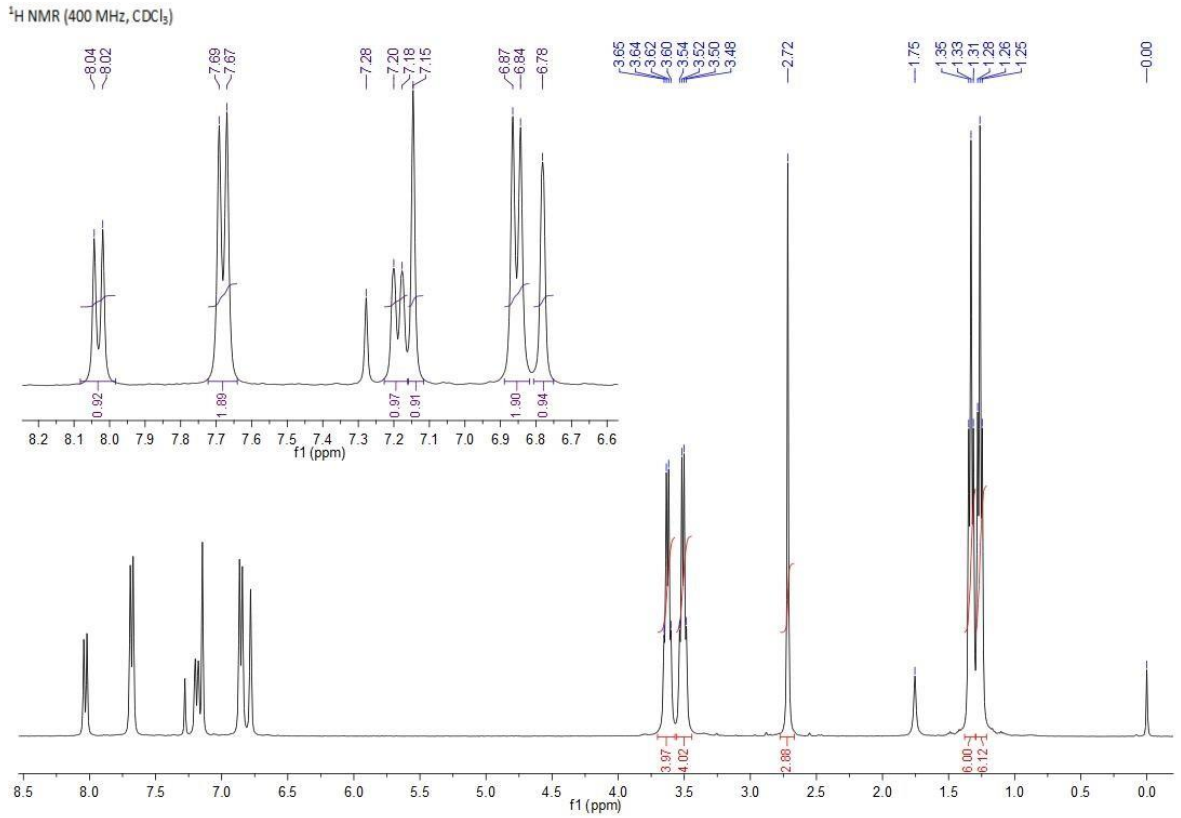


Fig. S16 ^{1}H NMR of **6.**

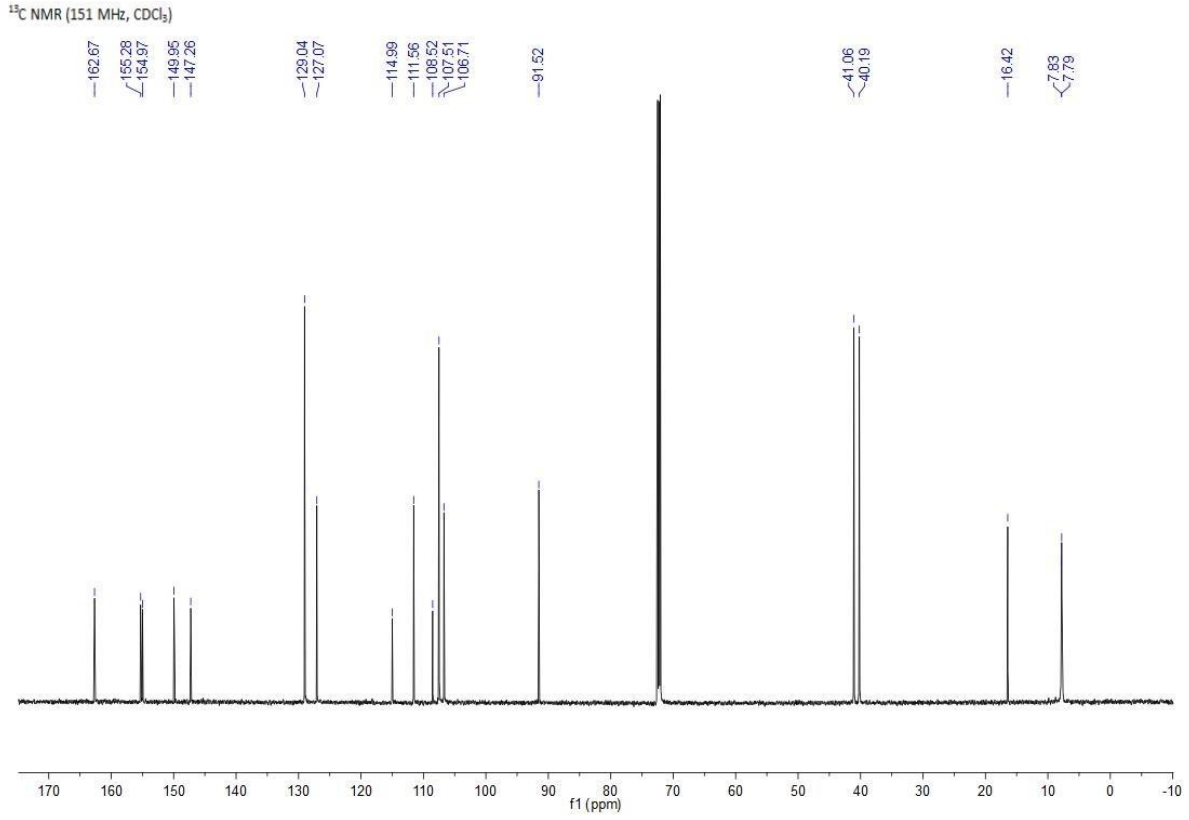


Fig. S17 ^{13}C NMR of **6.**

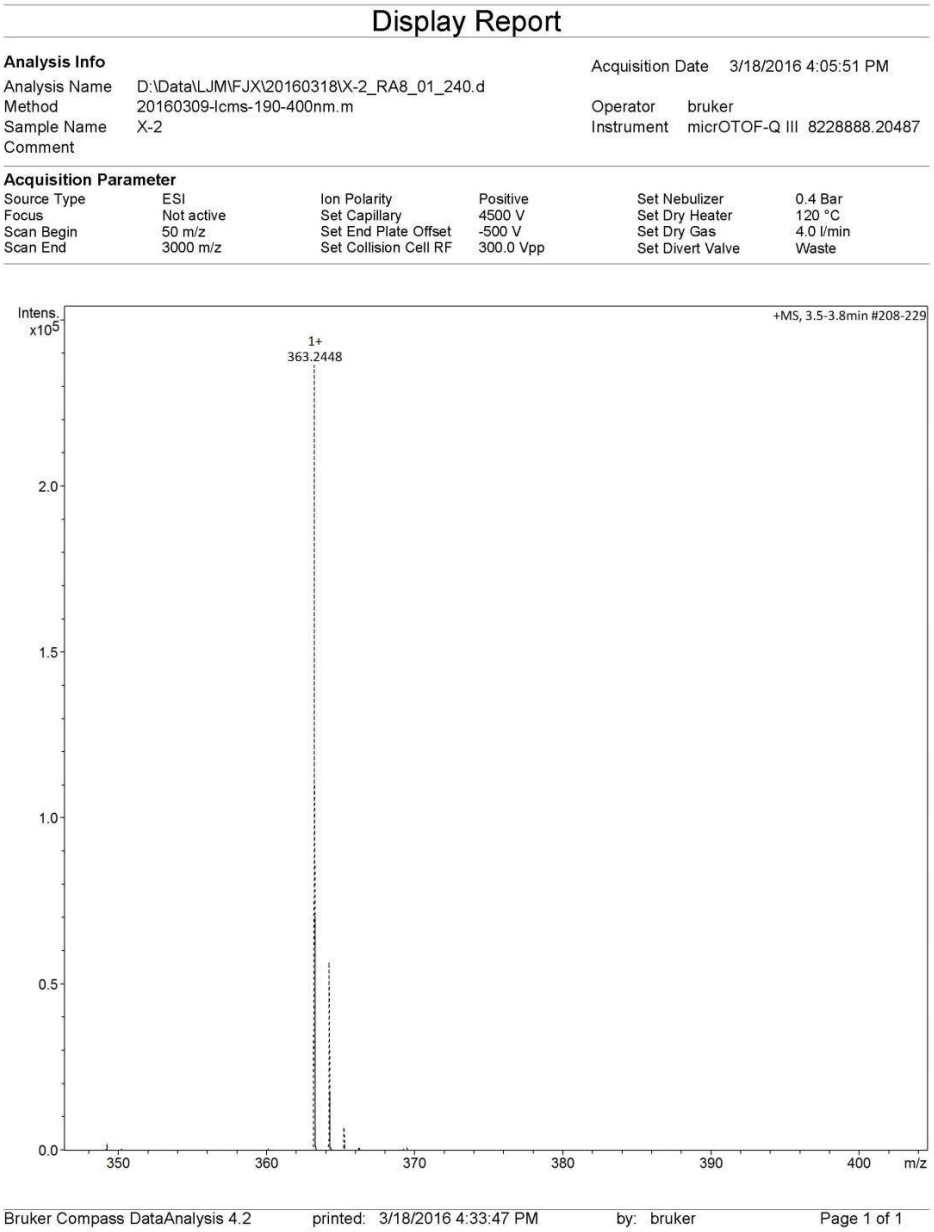


Fig. S18 HRMS(ESI$^+$) of **6**.

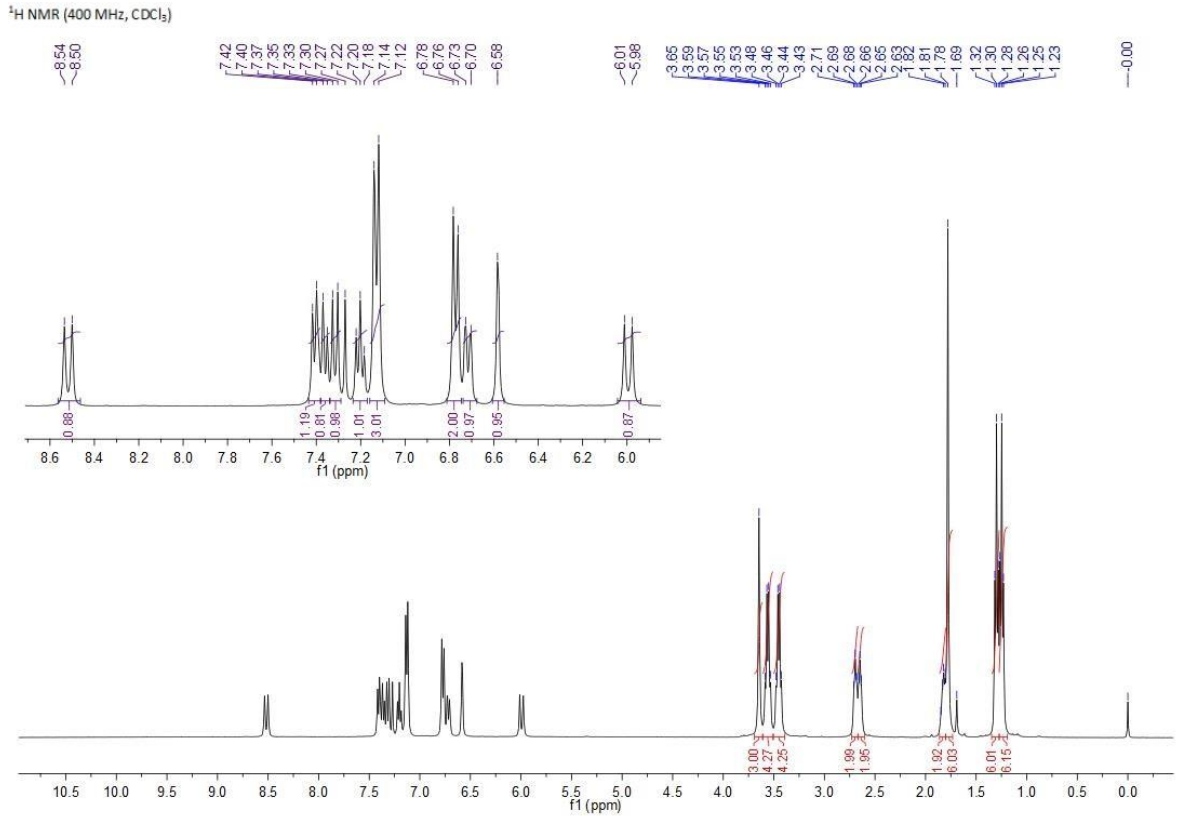


Fig. S19 ^{1}H NMR of dye **1a.**

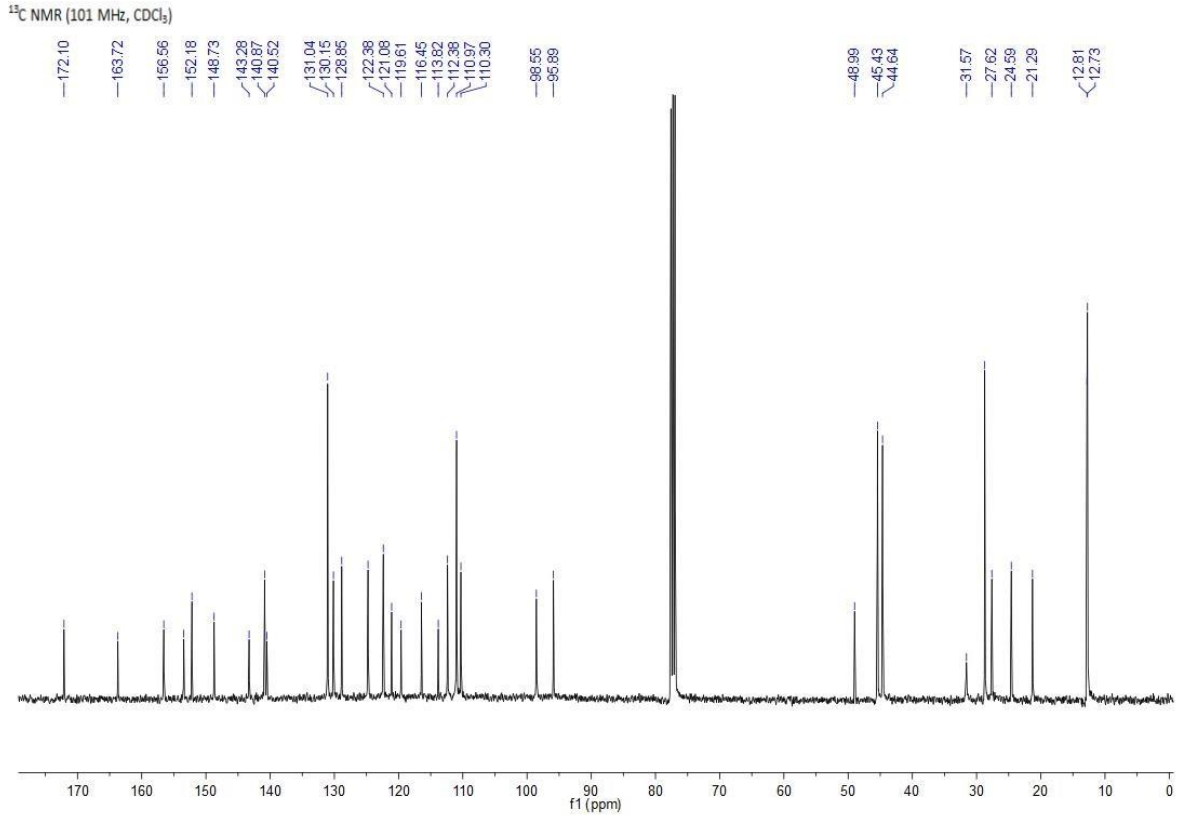


Fig. S20 ^{13}C NMR of dye **1a.**

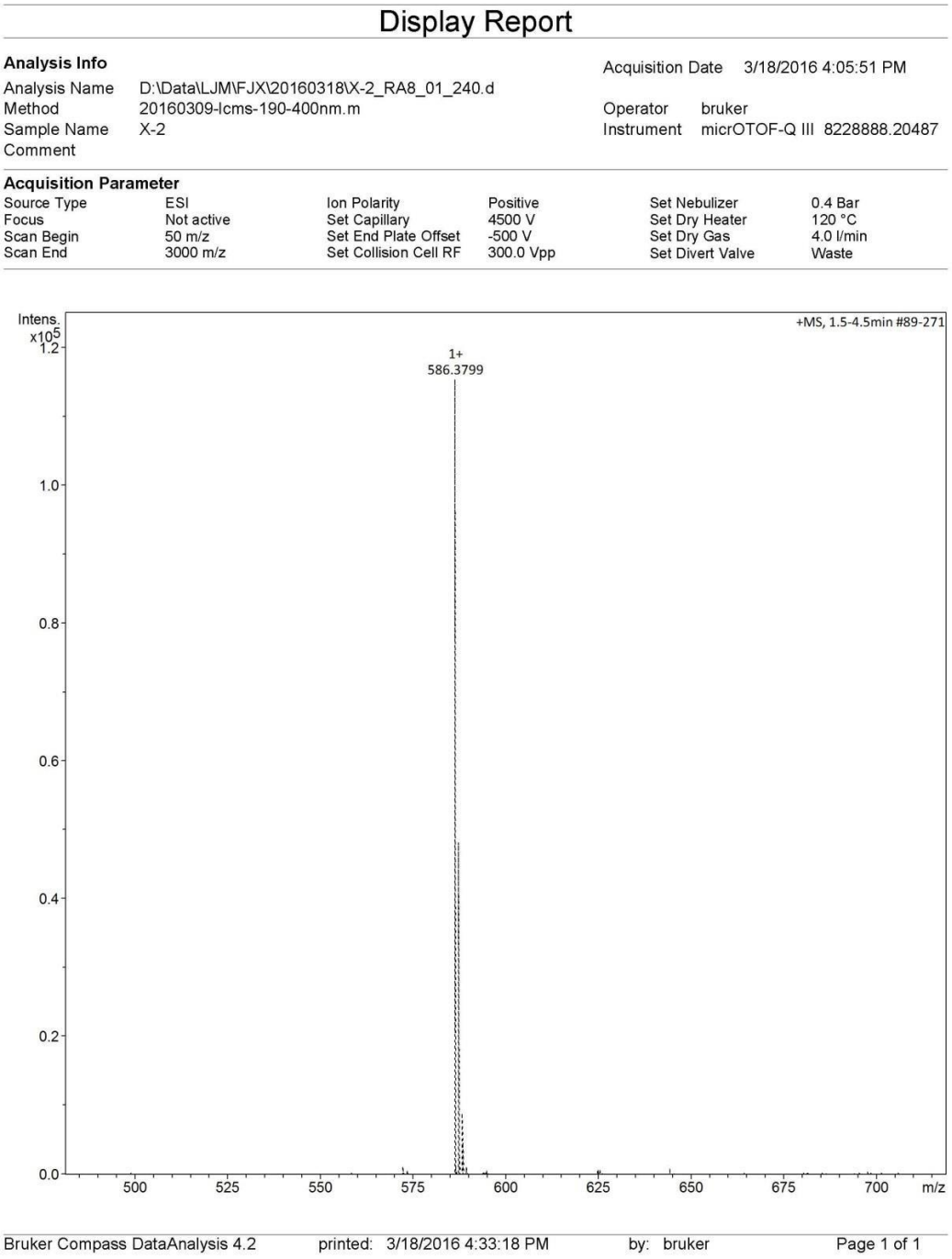


Fig. S21 HRMS(ESI$^+$) of dye **1a**.

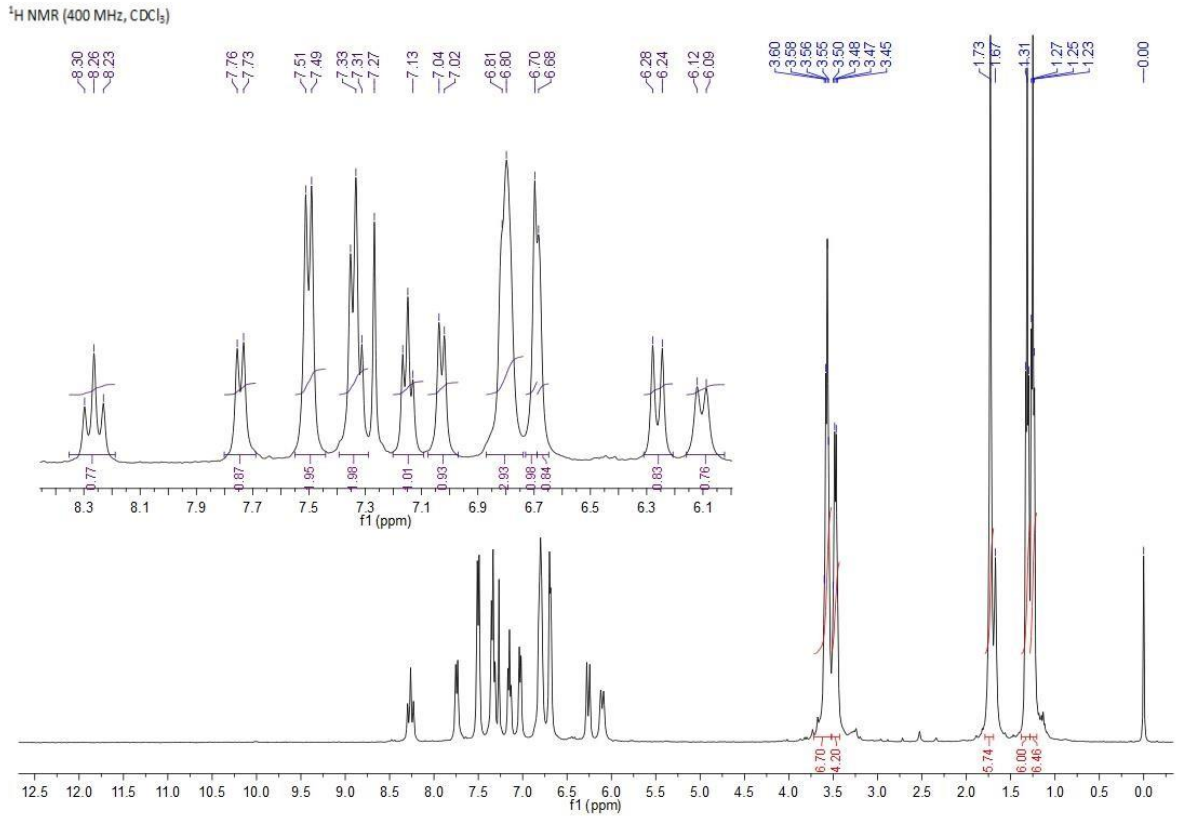


Fig. S22 ^{1}H NMR of dye **1b.**

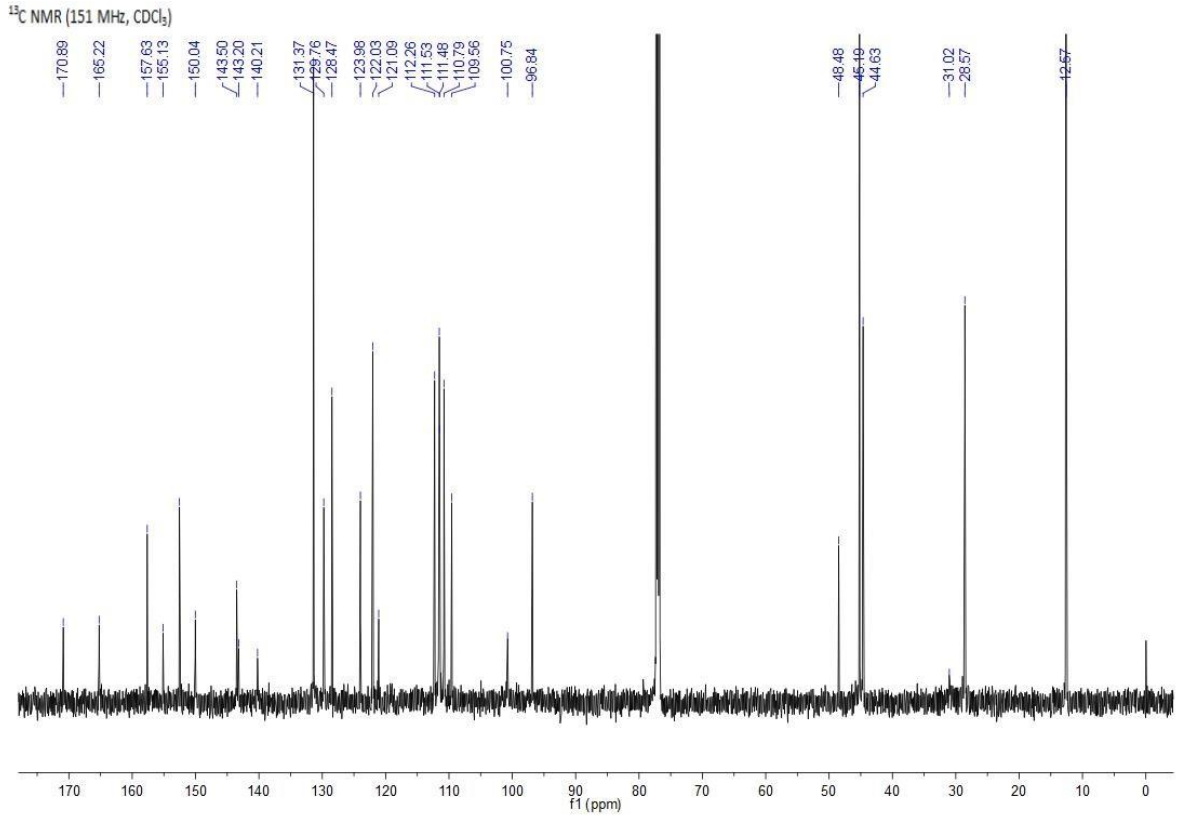


Fig. S23 ^{13}C NMR of dye **1b.**

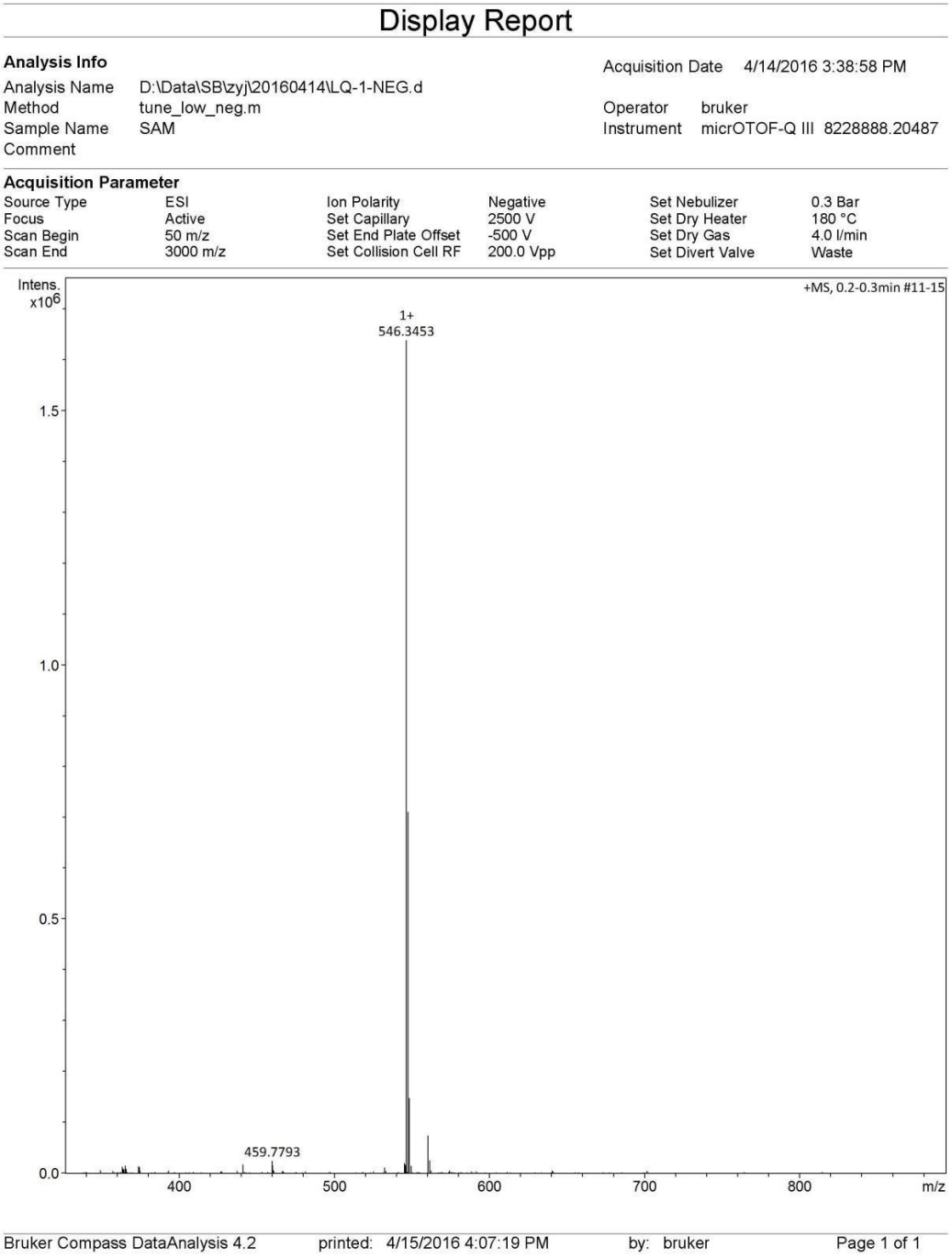


Fig. S24 HRMS(ESI$^+$) of dye **1b**.

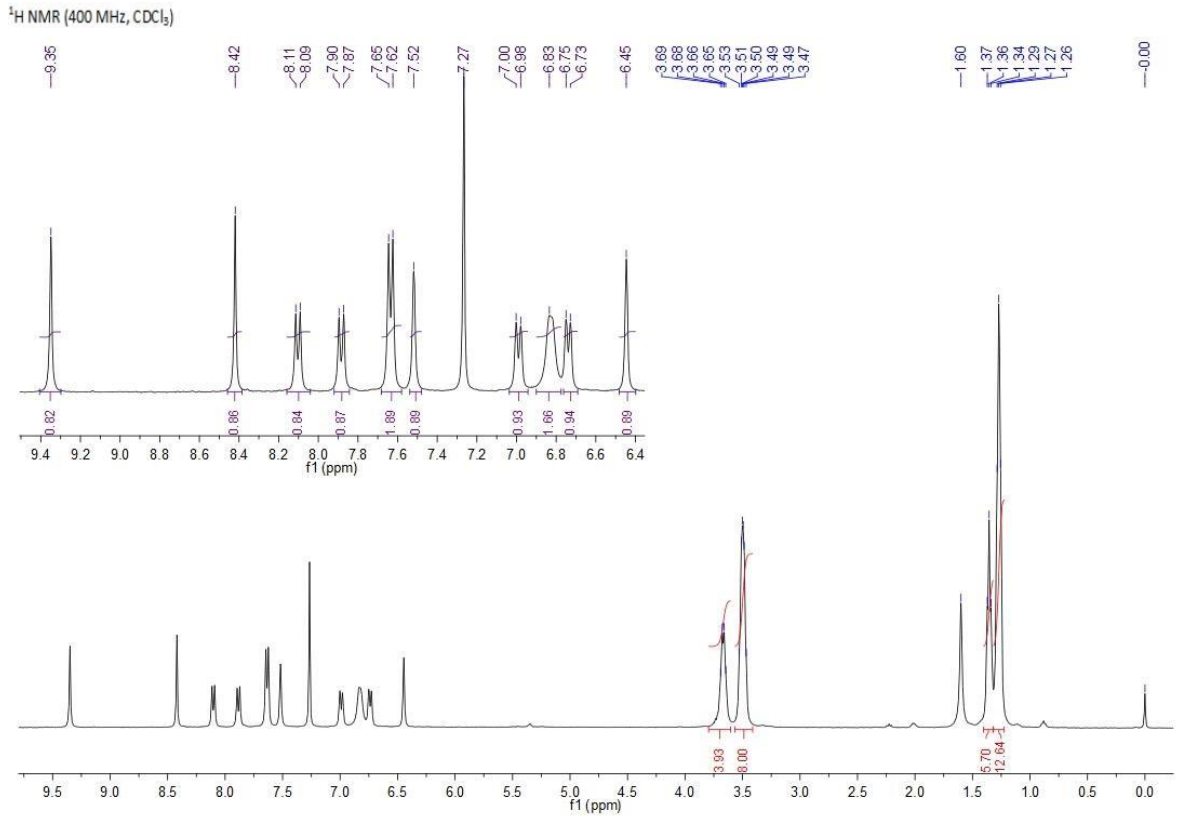


Fig. S25 ^{1}H NMR of dye **1c.**

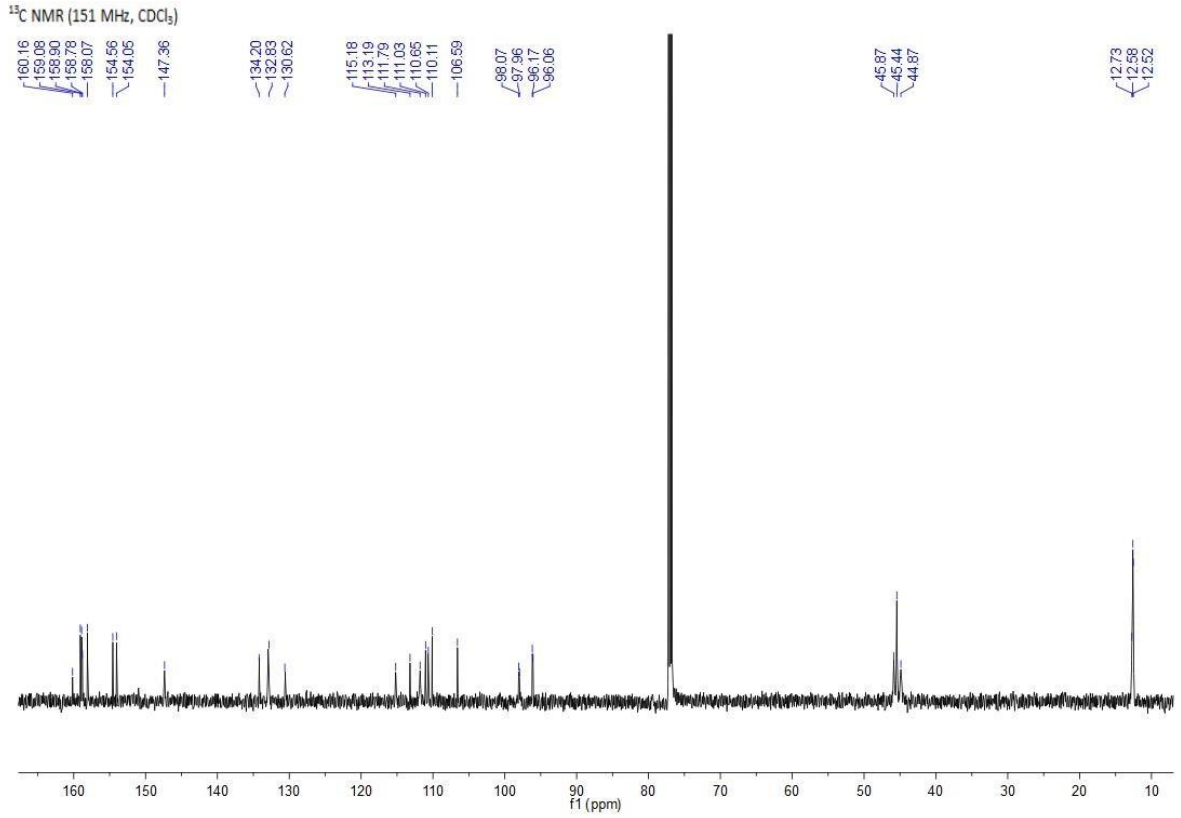


Fig. S26 ^{13}C NMR of dye **1c.**

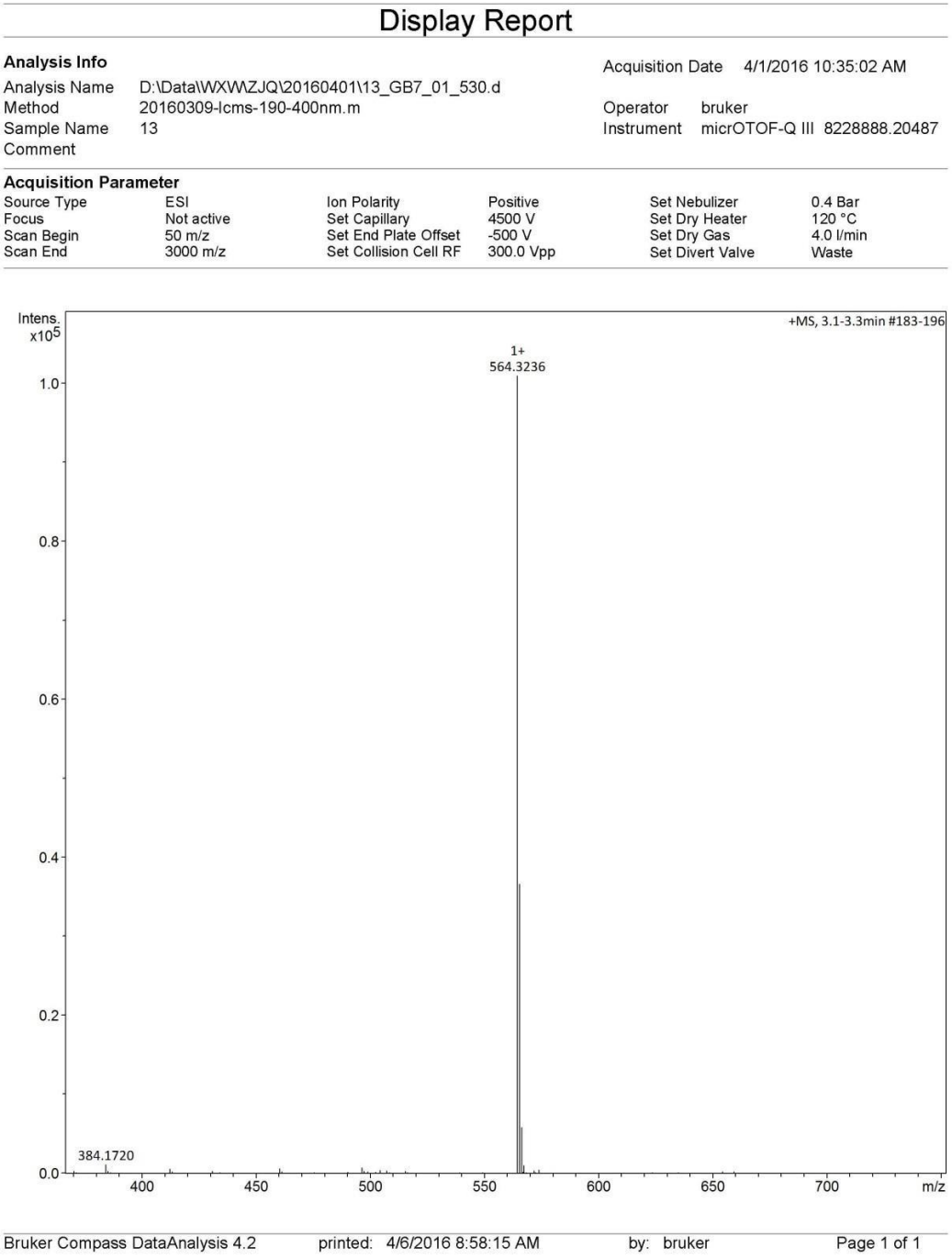


Fig. S27 HRMS(ESI$^+$) of dye **1c**.