

*Supporting Information for:*

# Switching of Emissive and NLO Properties in Push-Pull Chromophores with Crescent PPV-like Structures

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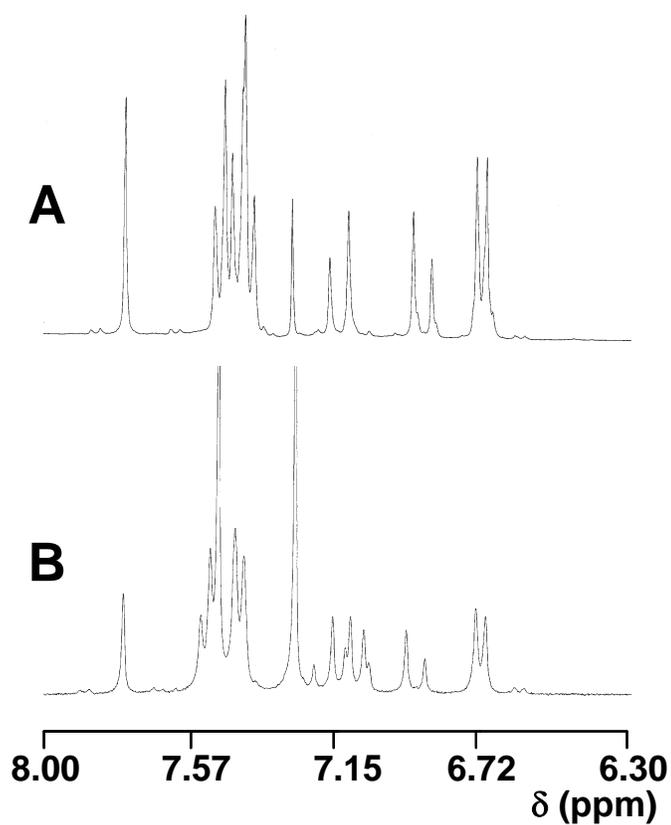
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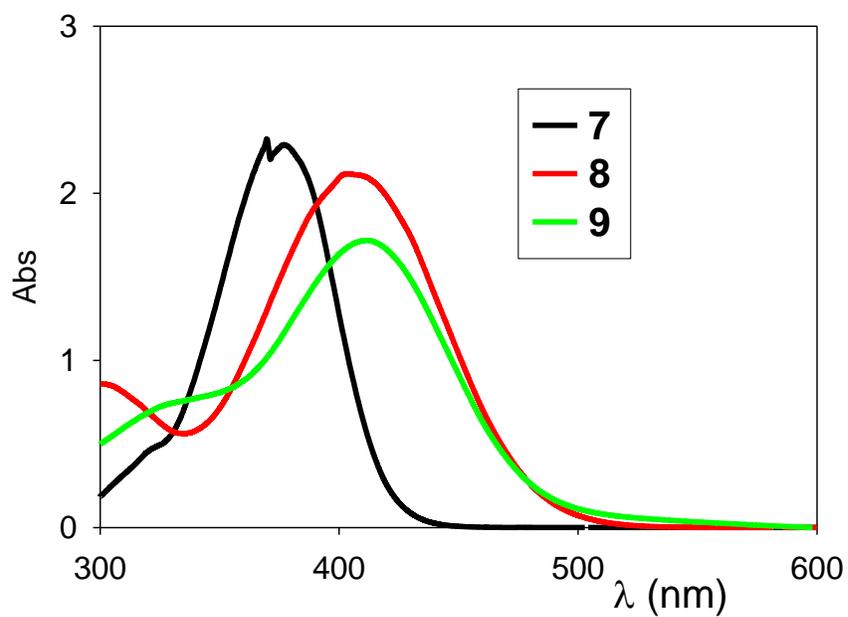
c) Istituto per lo Studio delle Macromolecole (ISMAL), CNR, Via Bassini 15, 20133 Milano, Italy.

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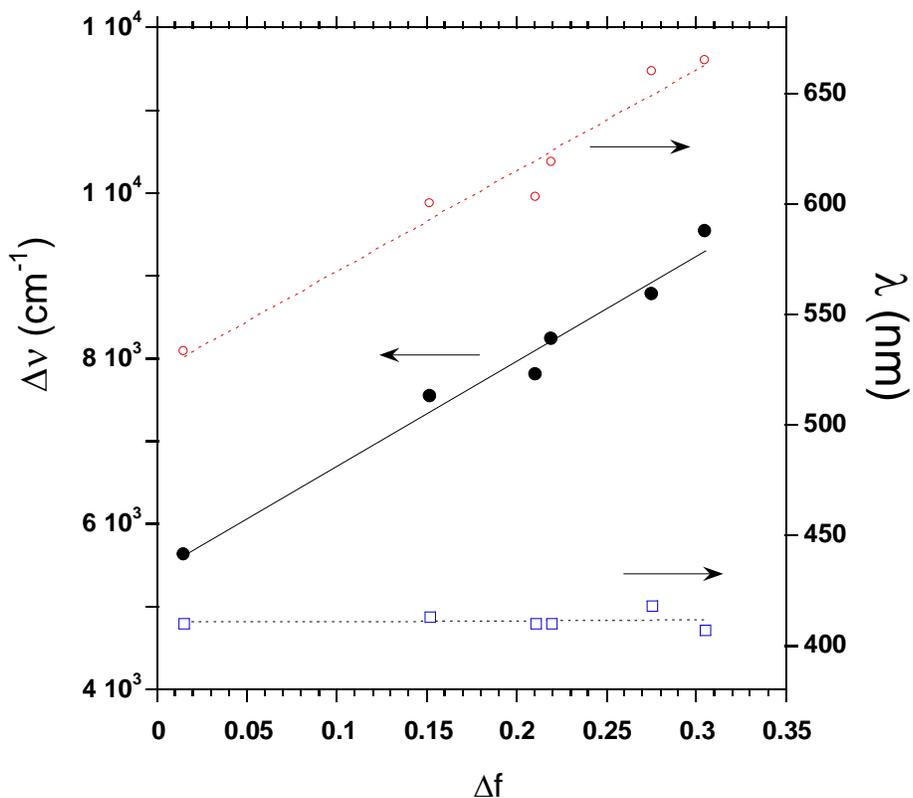
e) INSTM Research Unit, University of Pavia.



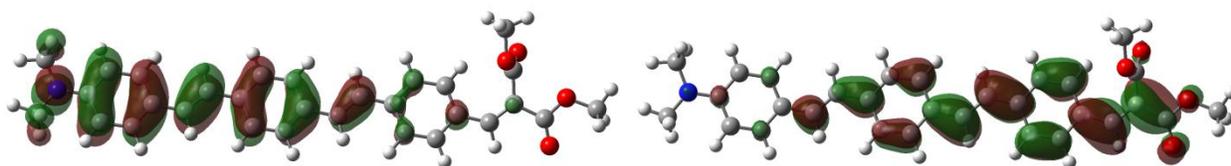
**Figure S1.** Enlargement of <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>) for molecular modules **8** (A), **9** (B).



**Figure S2.** UV/Vis spectra of **7-9** (MeCN, 2.1 – 8.2 × 10<sup>-5</sup> M.).

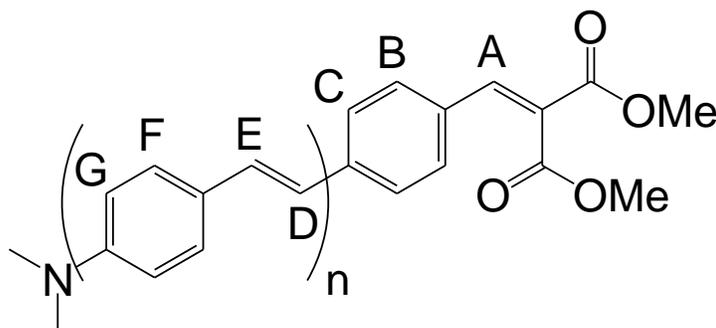


**Figure S3.** Lippert-Mataga plot of **8**. The Stokes shift  $\Delta\nu$  is reported as a function of the orientation polarizability of the solvents (from left to right: toluene, chloroform, tetrahydrofuran, dichloromethane, dimethylformamide, acetonitrile). Absorption (blue) and emission (red) maxima are reported on the right scale.



**Figure S4.** Plots of the LC-BLYP/6-311++G\*\* HOMO (left) and LUMO (right) of compound **9**. Isosurfaces value 0.02 a.u.

**Table S1.** Selected  $^1\text{H}$  NMR chemical shifts for molecular modules **7-9** (300 MHz,  $\text{CDCl}_3$ ).<sup>a</sup>



Entry	Compound	A	B, C	D,E (J)	F, G	COOMe
1	<b>7</b>	7.68	7.32, 6.63	b	b	3.88, 3.82
2	<b>8</b>	7.77	7.49, 7.40	7.14, 6.90 (16 Hz)	7.44, 6.73	3.90, 3.87
3	<b>9</b>	7.78	7.55-7.43	7.20 (D), 7.09 (E), 7.10 (D'), 6.93 (E') (16 Hz)	7.54, 6.74	3.90, 3.87

a) Concentrations were in the range 5-10 mM (300 MHz). b) Not applicable.

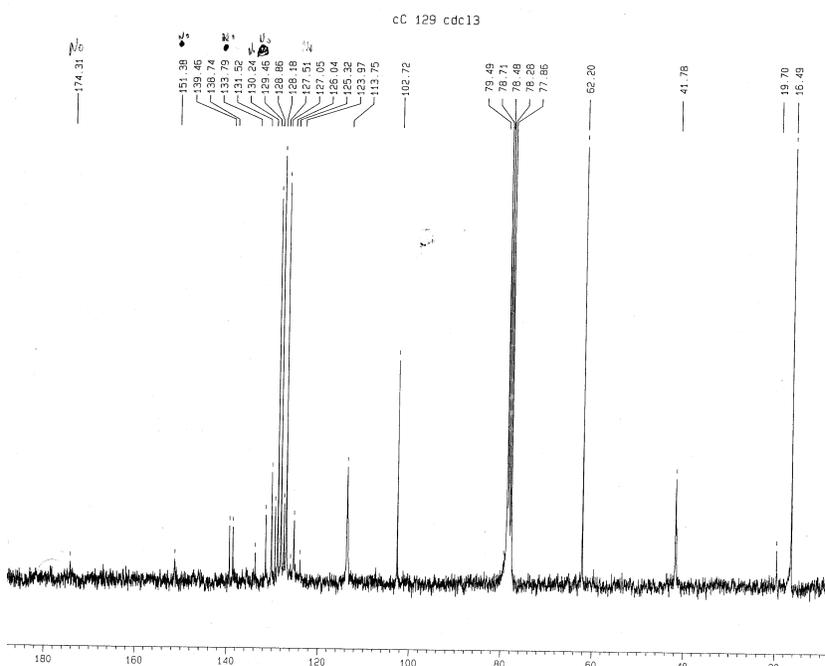
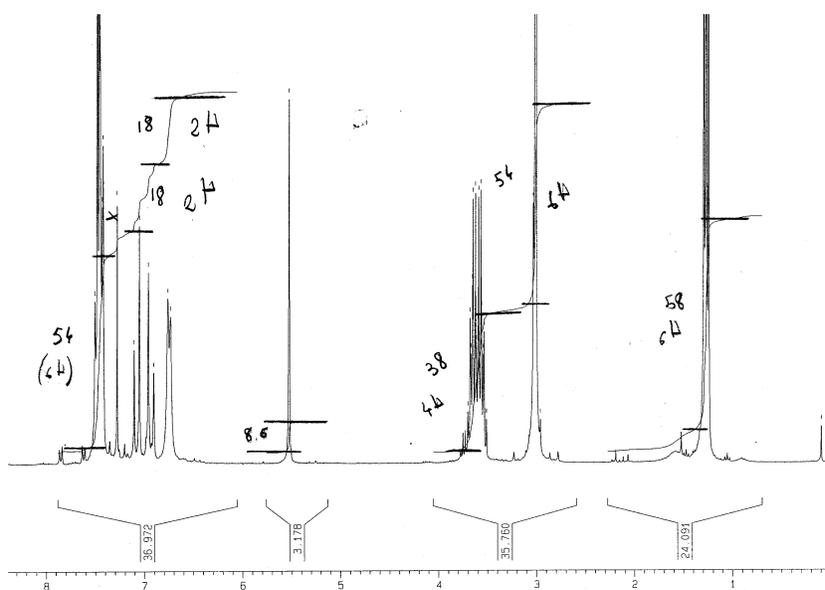
**Table S2.** Computed ground state dipole moments ( $\mu$ ), electronic transitions ( $\lambda_{\text{max}}$ ) and dynamic hyperpolarizabilities ( $\beta_{\text{dyn}}$ ) of compounds **7-9**, along with the associated oscillator strengths ( $f$ ), the transition dipole moments ( $\mu_{\text{eg}}$ ), and the excited state dipole moments ( $\mu_e$ ).<sup>a</sup>

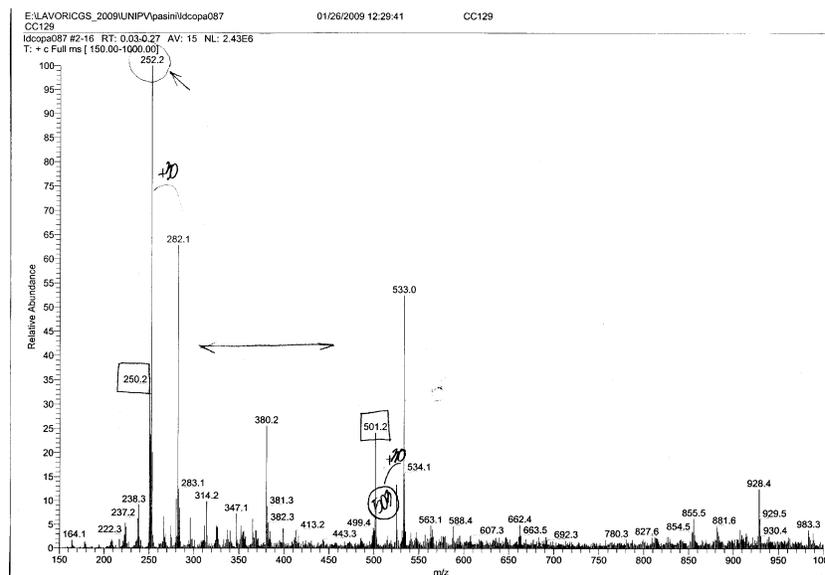
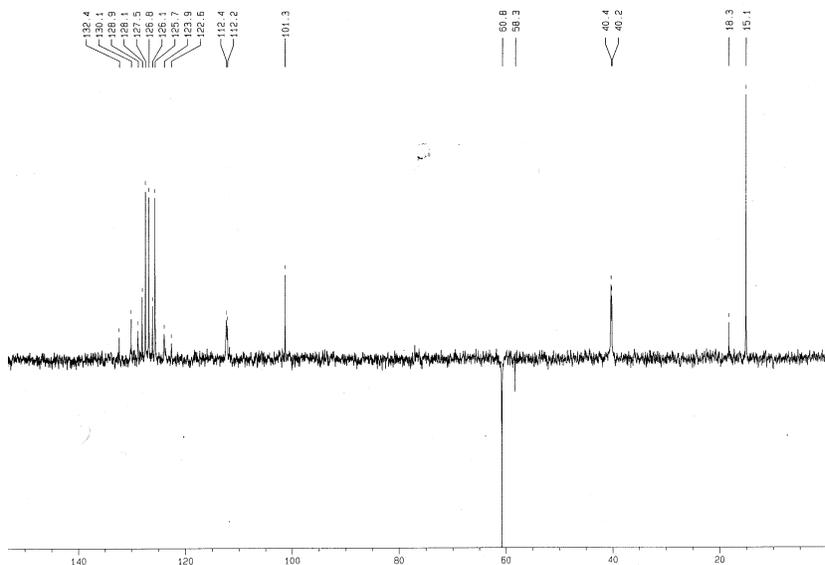
Compound	$\mu$ (D)	$\lambda_{\text{max}}$ (nm)	Assignment	$f$	$\mu_{\text{eg}}$ (D)	$\mu_e$ (D)	$\mu\beta_{\text{vec,dyn}}$ ( $\times 10^{-48}$ esu)
<b>7</b>	7.7	371	HOMO→LUMO	1.1	9.4	15.5	986
<b>8</b>	9.1	491	HOMO→LUMO	1.6	12.8	28.8	8227
<b>9</b>	9.6	537	HOMO→LUMO	1.9	14.7	41.2	17556

<sup>a</sup>Calculations in  $\text{CHCl}_3$  at DFT/6-311++G\*\*, TD-DFT/6-311++G\*\* and CPKS/6-311++G\*\* levels using the PBE0 functional. The hyperpolarizability values include the 1/2 factor to be compared with the experimental results.

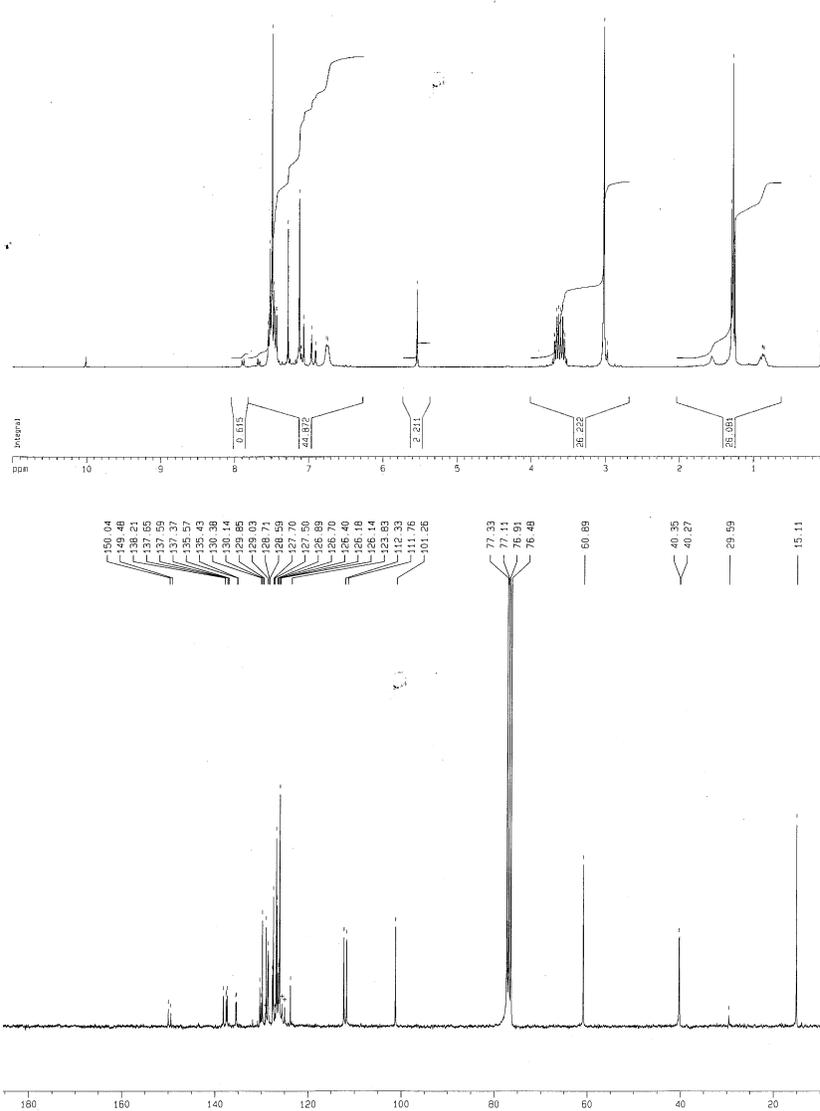
## Copies of NMR and Mass spectra

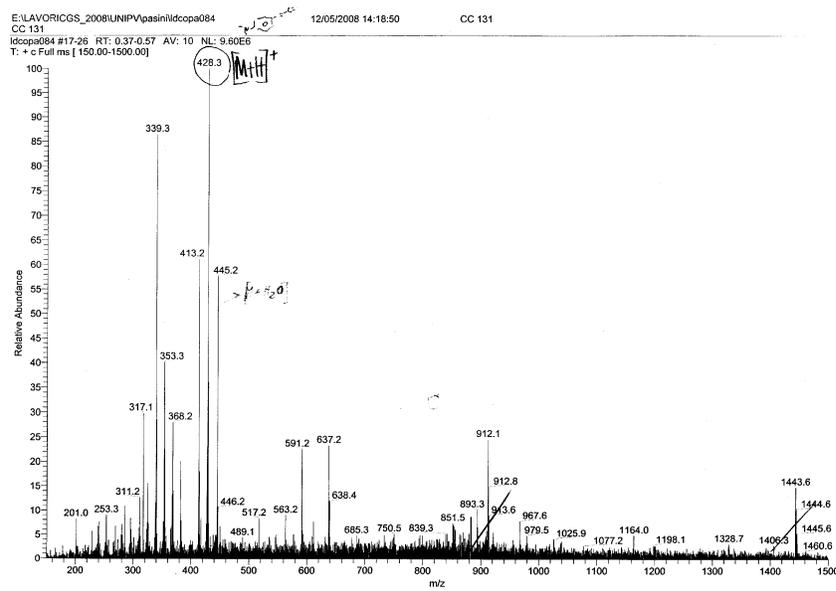
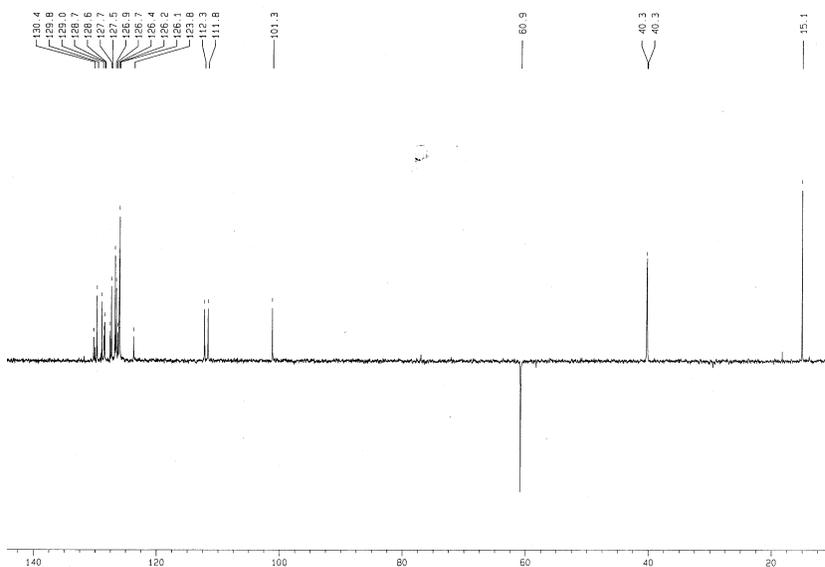
Compound 2.



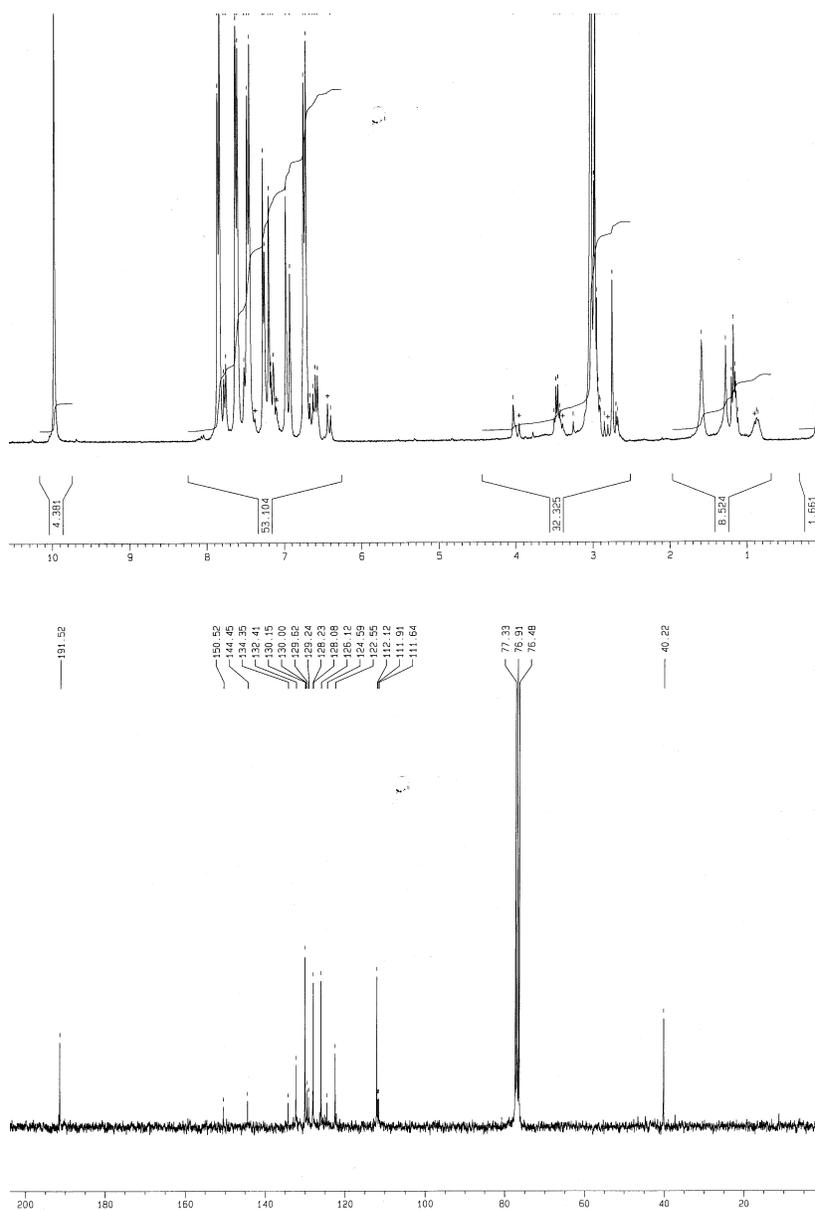


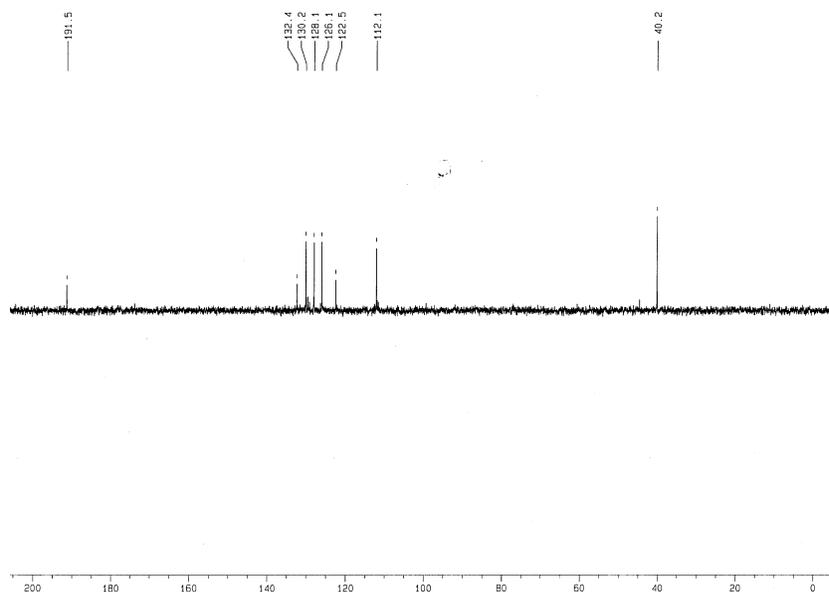
### Compound 3.



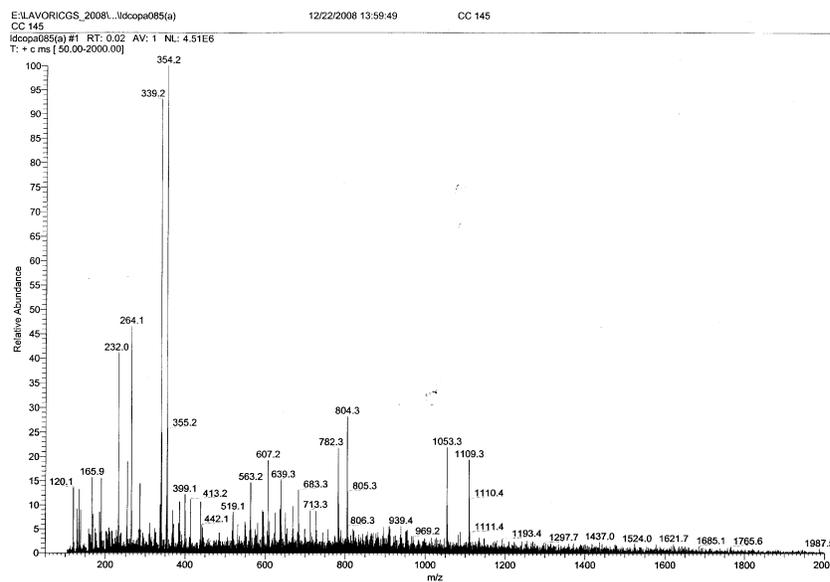
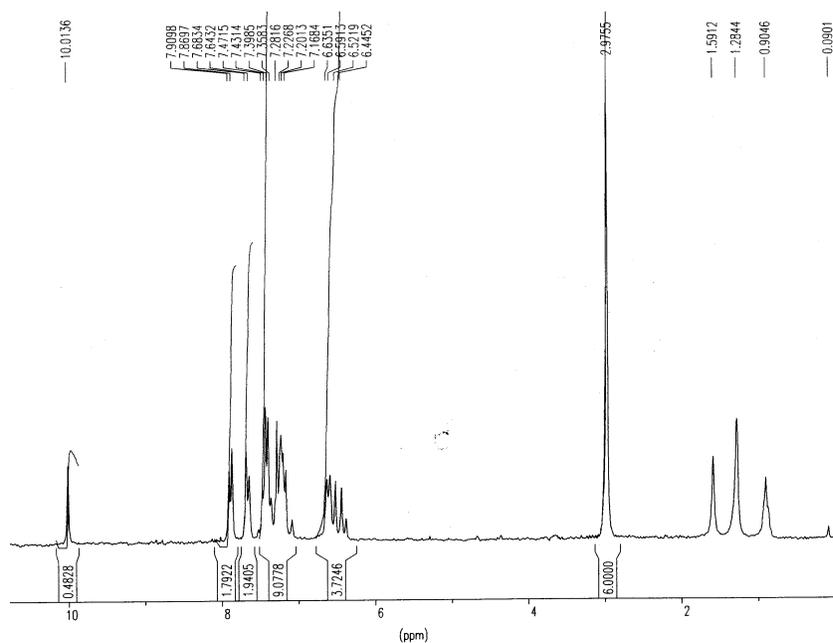


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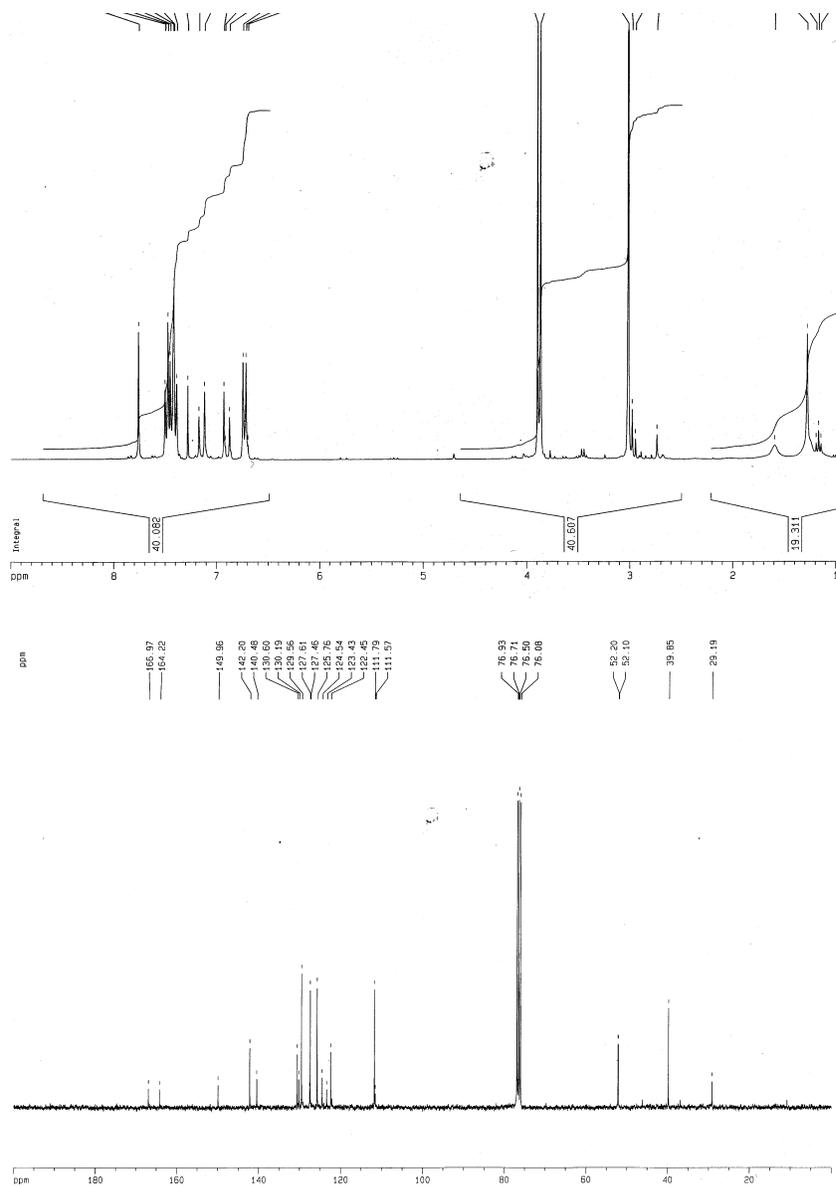


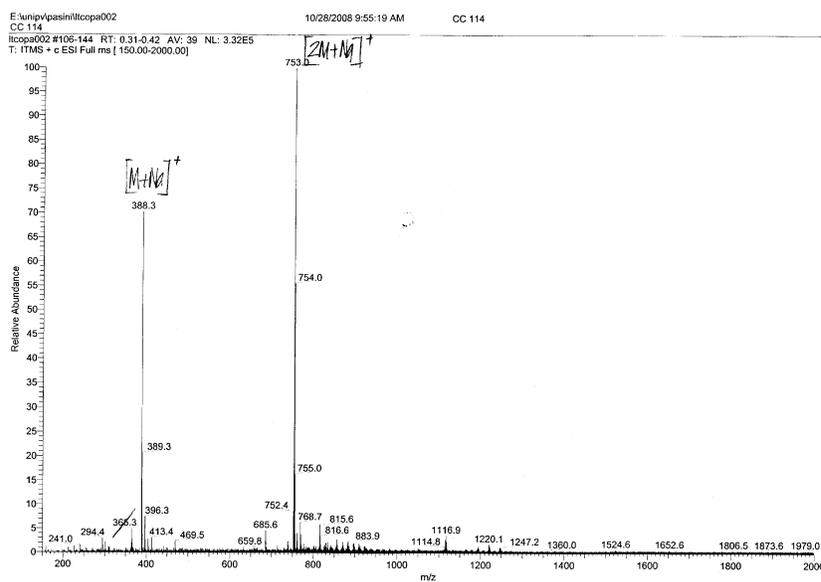
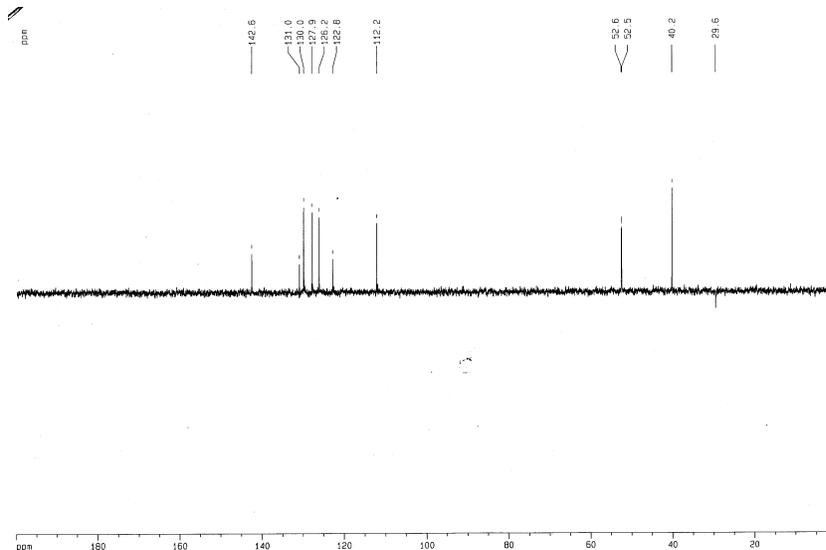


### Compound 6.



Compound 8.





### Compound 9

