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

SUPPORTING INFORMATION for

Synthesis of Glycoluril-Tetrathiafulvalene Molecular Clips for Electron-Deficient Neutral Guests through a Straightforward Diels-Alder Strategy

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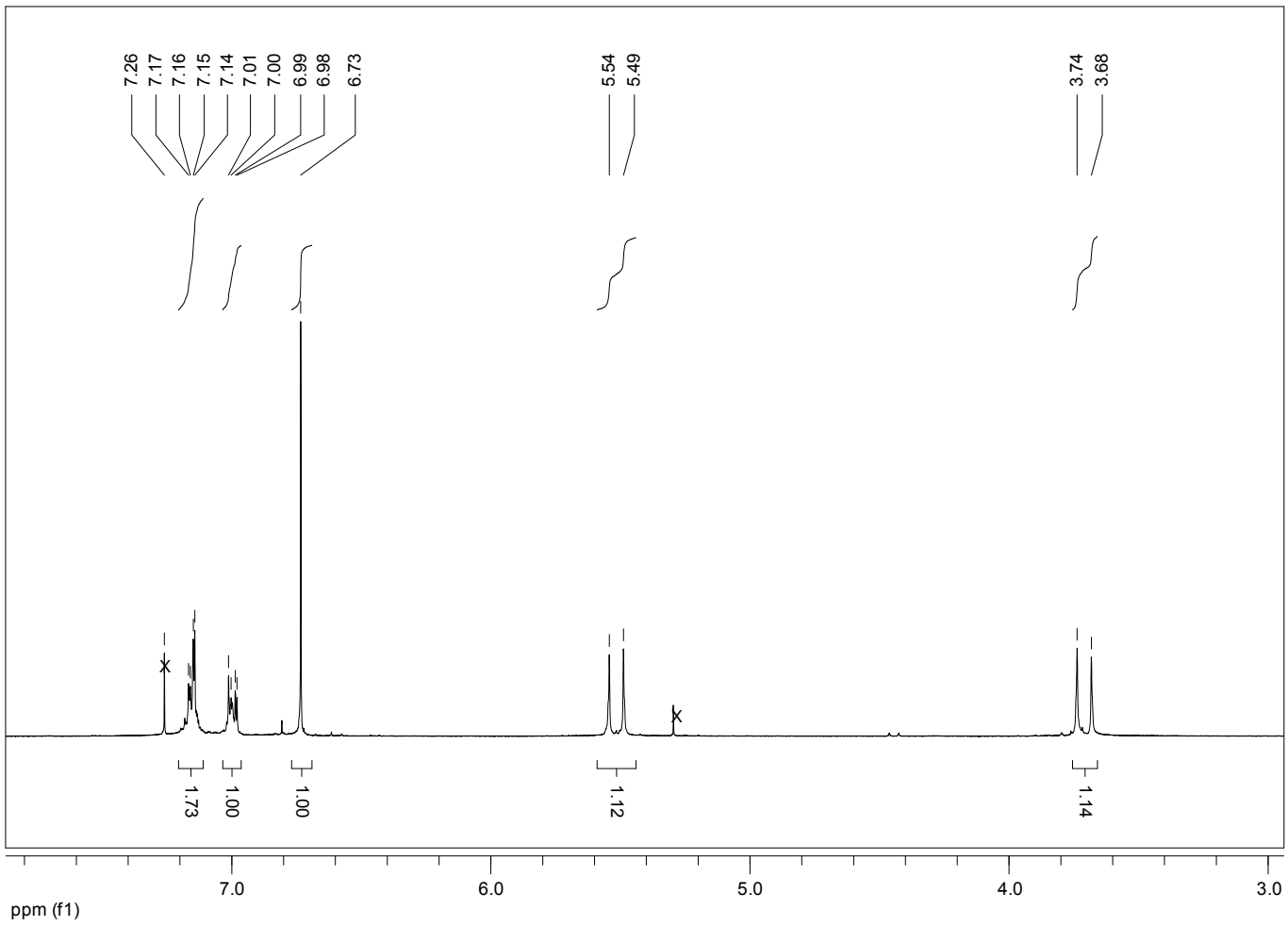
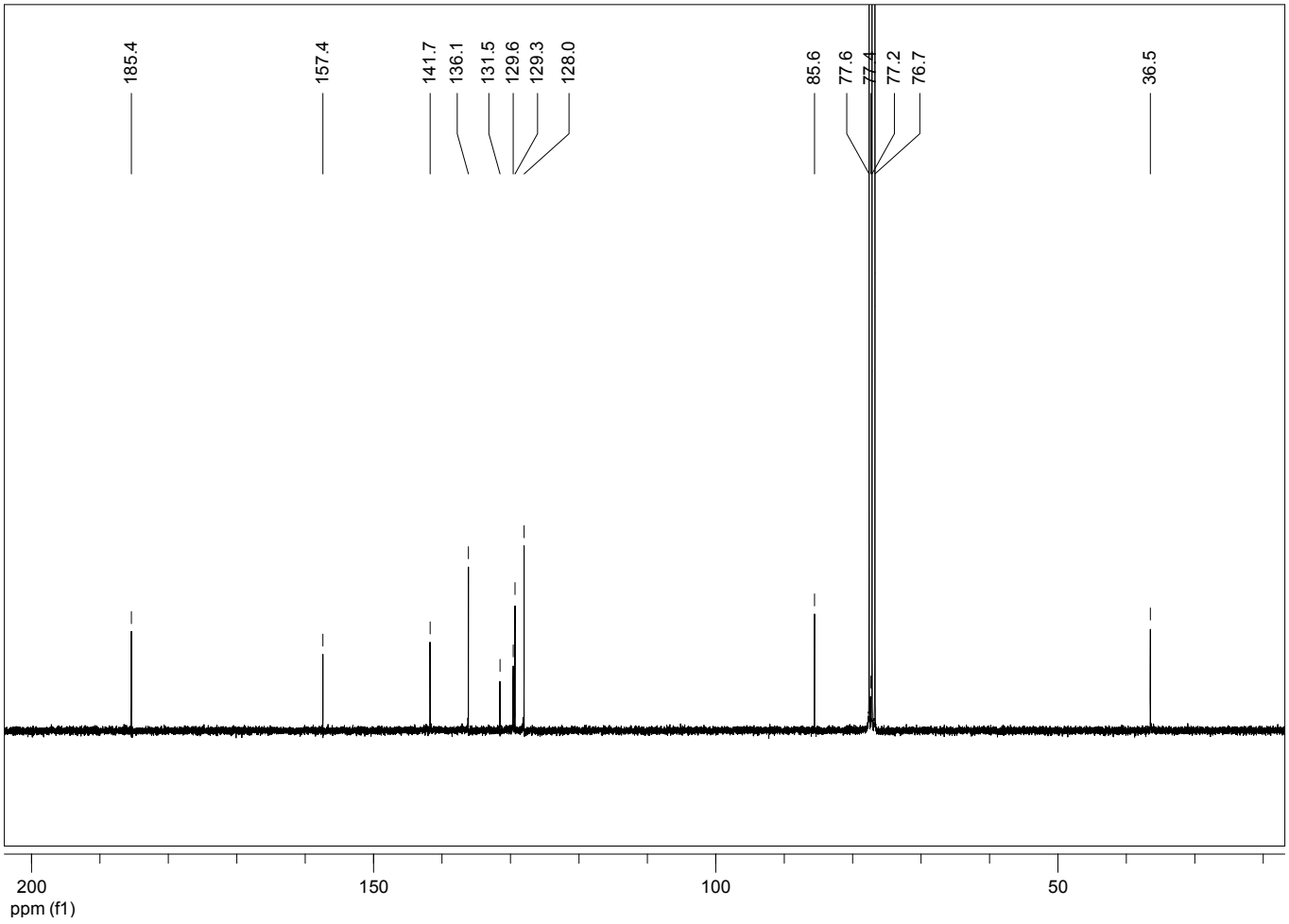
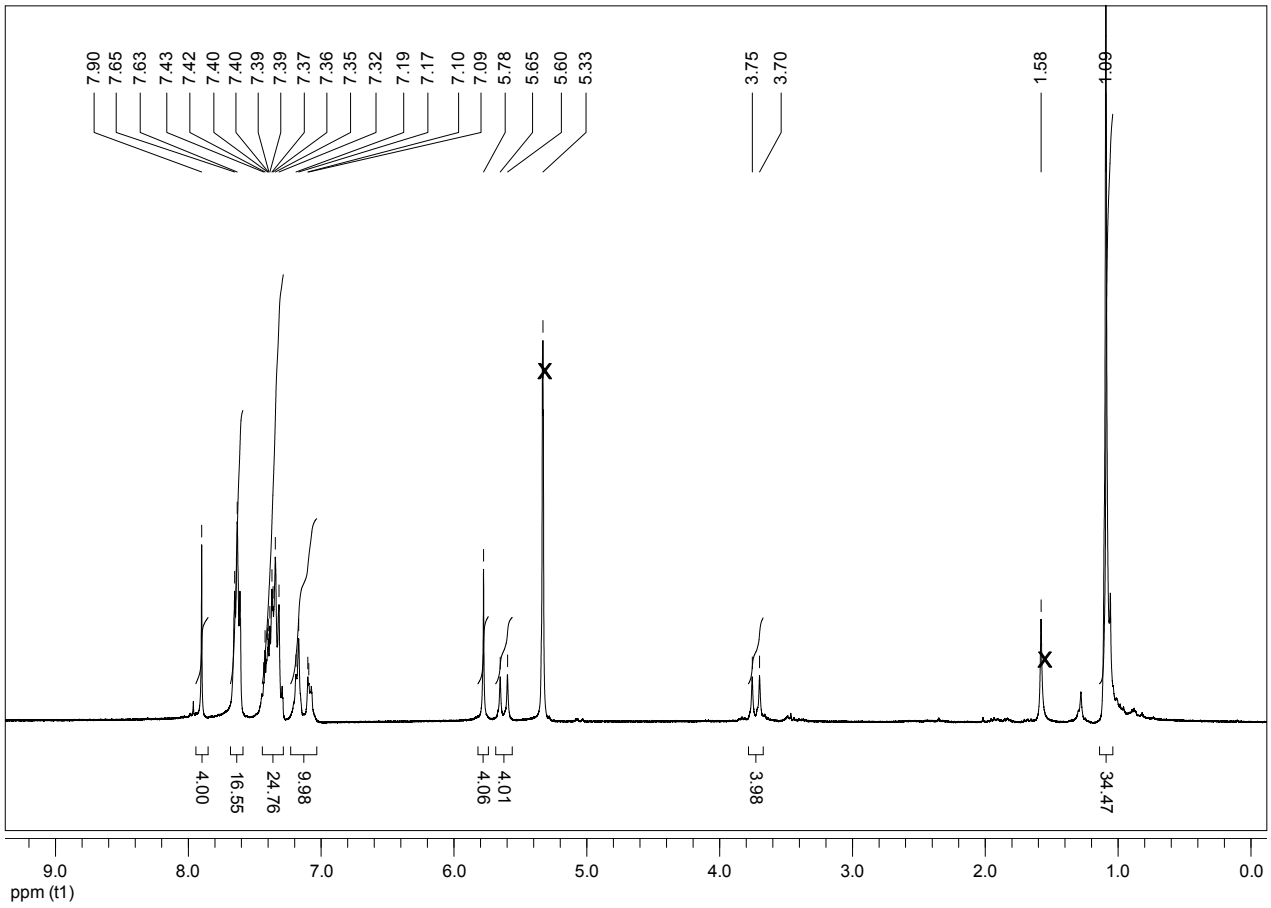
^{1}H NMR spectrum of compound 5 ($CDCl_3$, 300 MHz) :

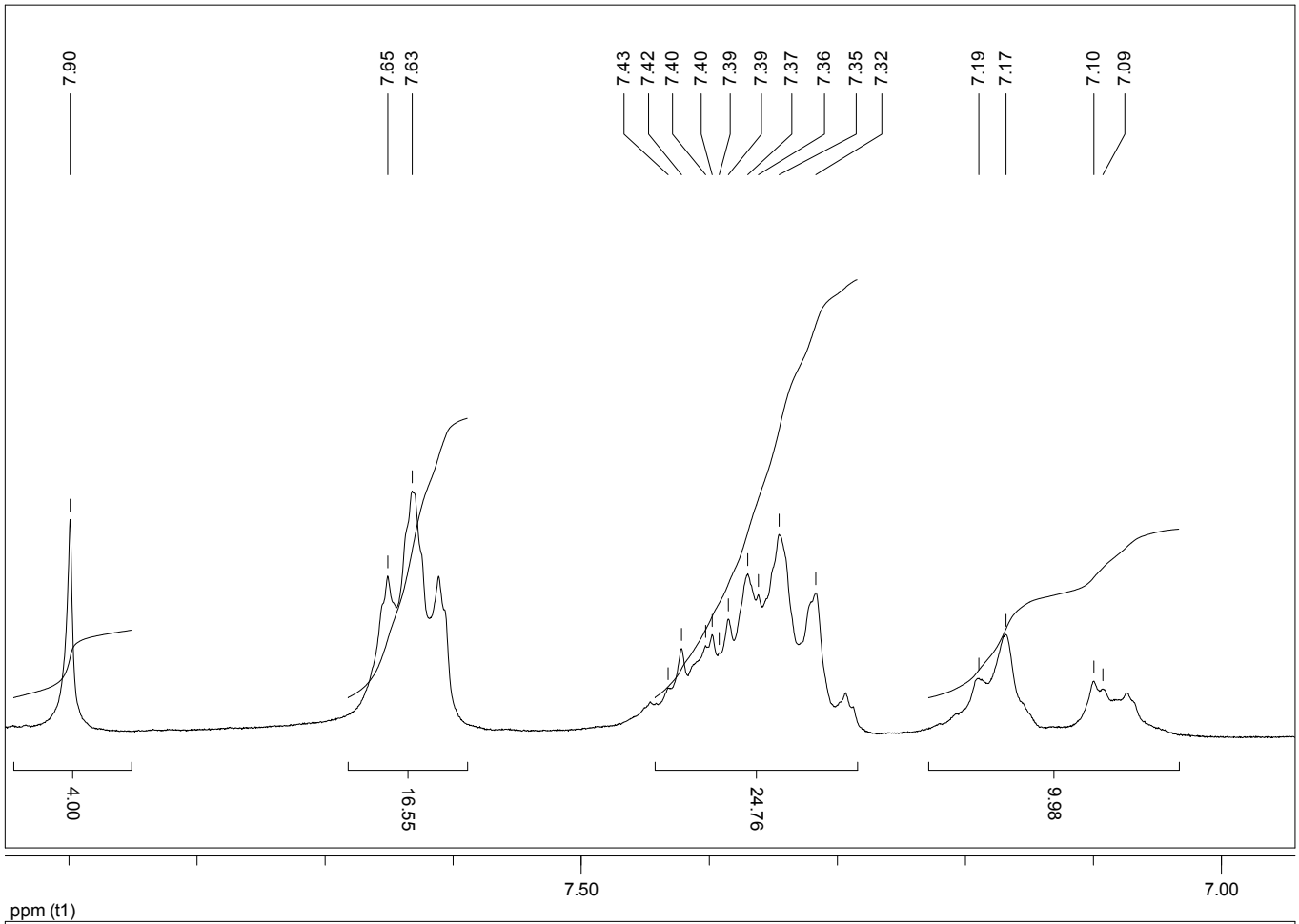


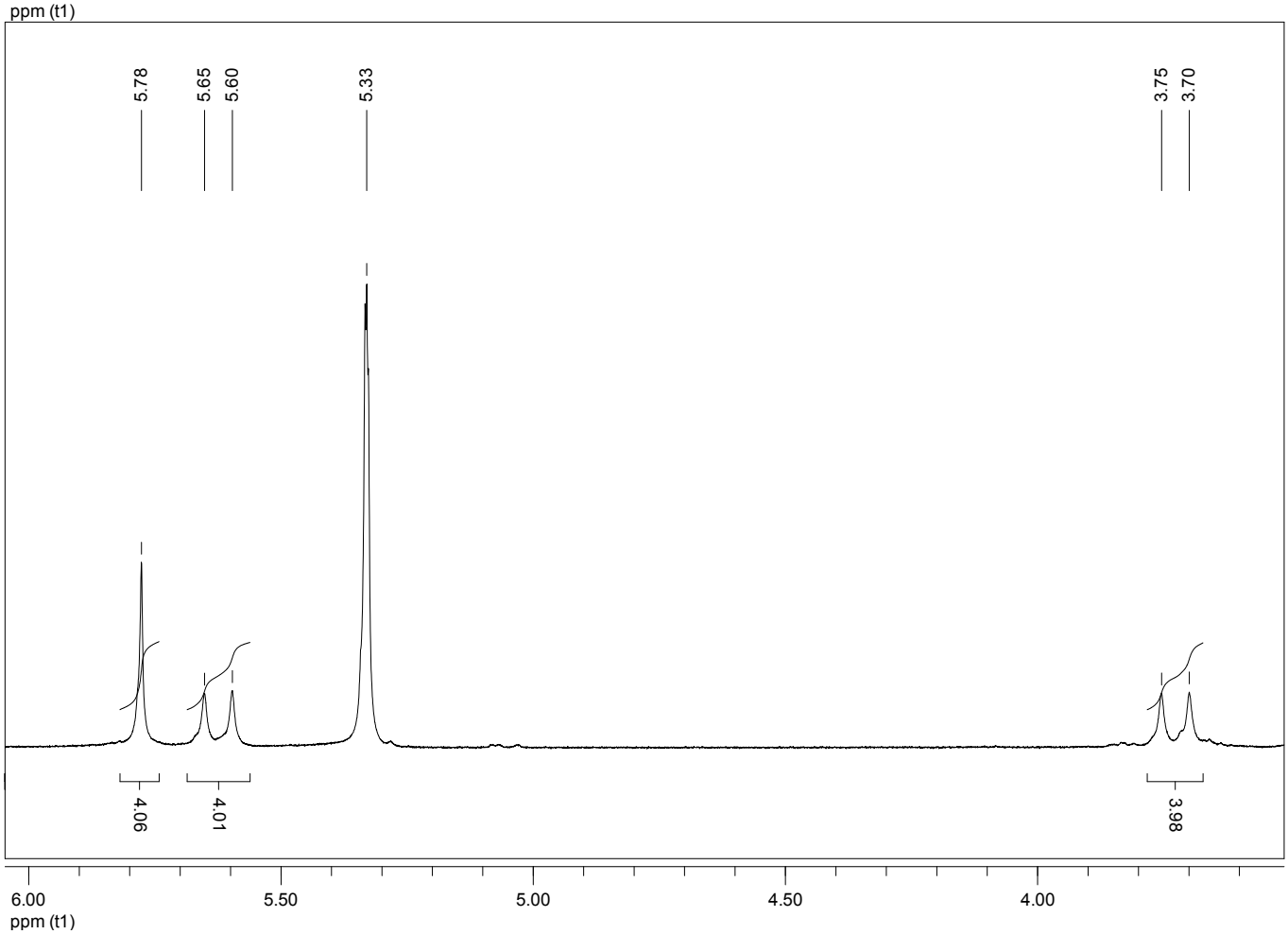
^{13}C NMR spectrum of compound 5 ($CDCl_3$, 300 MHz) :



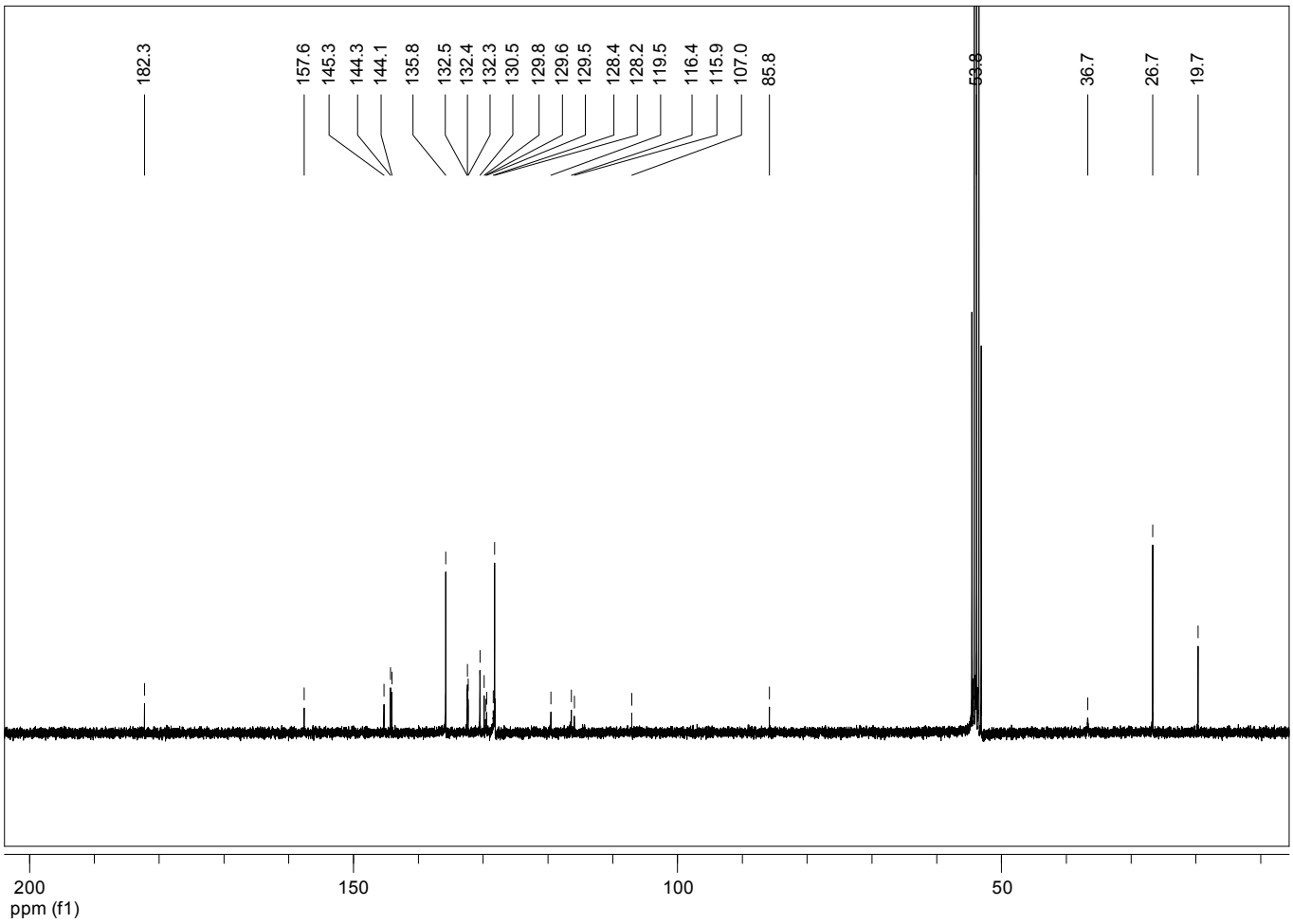
^{1}H NMR spectrum of molecular clip 1 (CD_2Cl_2, 300 MHz) :



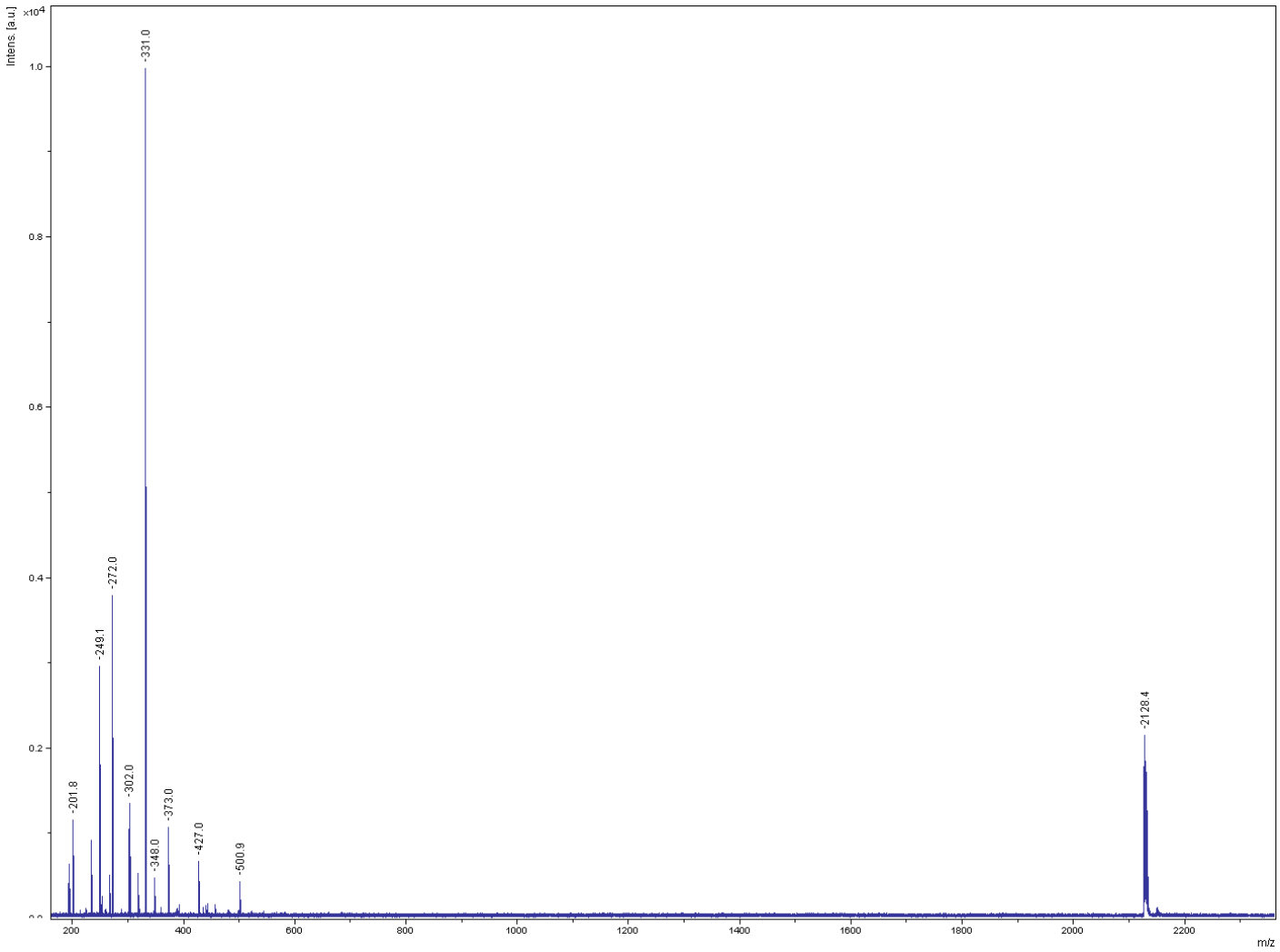

7.90
7.65
7.63
7.43
7.42
7.40
7.40
7.39
7.39
7.37
7.36
7.35
7.32
7.19
7.17
7.10
7.09
4.00
16.55
24.76
9.98
7.50
7.00
ppm (t1)

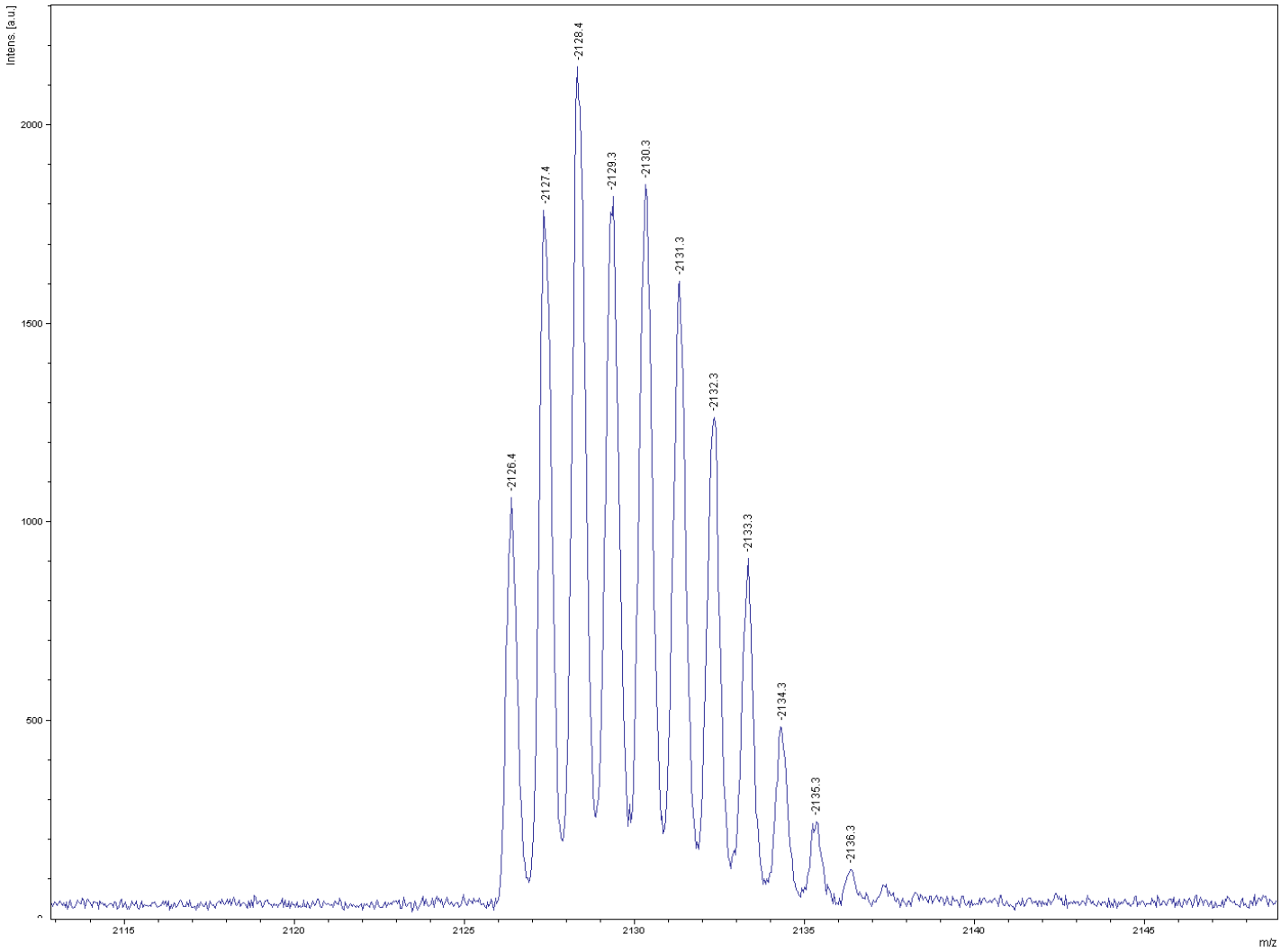

5.78
5.65
5.60
5.33
3.75
3.70
4.09
4.01
3.98
6.00
5.50
5.00
4.50
4.00
ppm (t1)

^{13}C NMR spectrum of molecular clip 1 (CD_2Cl_2, 300 MHz) :



MALDI-TOF spectrum of molecular clip 1 (Dithranol as the matrix) :

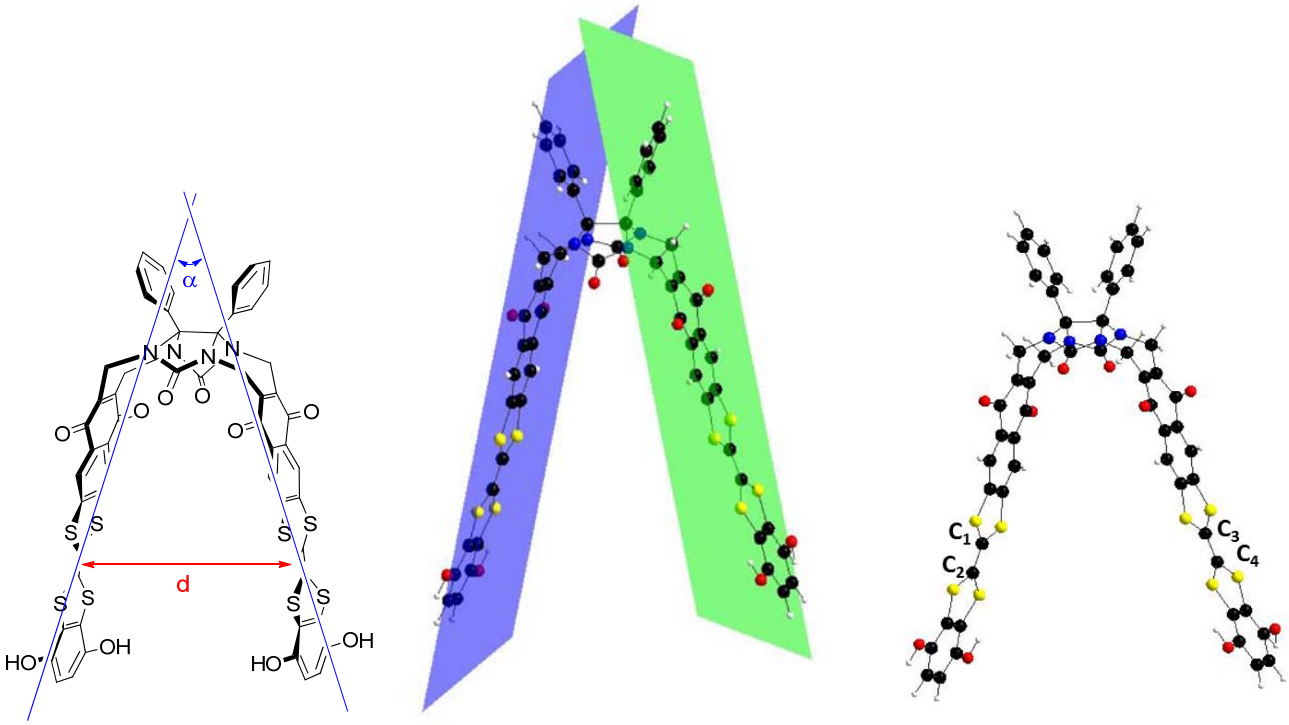



Intens. [a.u.]
2000
1500
1000
500
0
-2126.4
-2127.4
-2128.4
-2129.3
-2130.3
-2131.3
-2132.3
-2133.3
-2134.3
-2135.3
-2136.3
2115
2120
2125
2130
2135
2140
2145
m/z

Theoretical calculations :

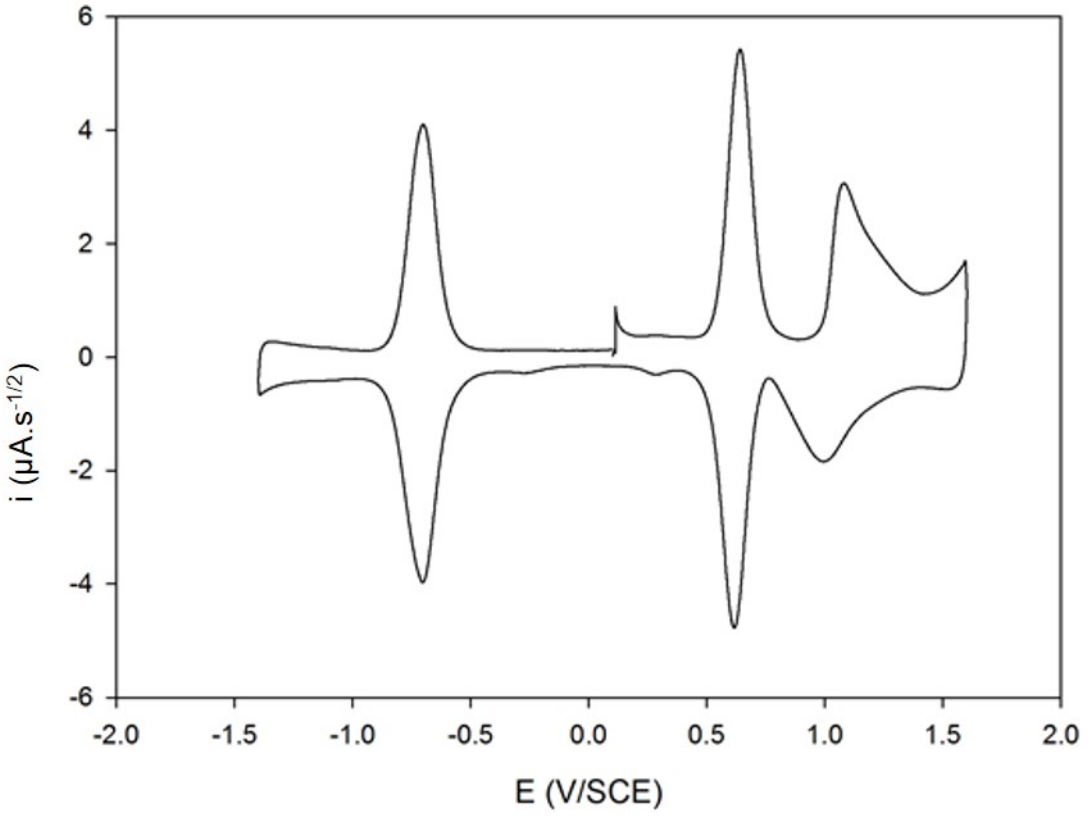
Theoretical calculations were realized using semi-empirical AM1 method on molecular clip **1** without silylated groups on the hydroquinone moieties for simplification.

The angle α defining the tapering cavity of the clip was determined to be close to 31° taking into account the two mean planes of the TTF-naphthoquinone arms. From these two planes, the distance (d = 9.73 Å) was calculated as an average of the distances between both TTF central double bonds, *i.e.* the average of the distances C1-C3 (9.35 Å) and C2-C4 (10.12 Å).



Cyclic voltammetry of molecular clip 1 :

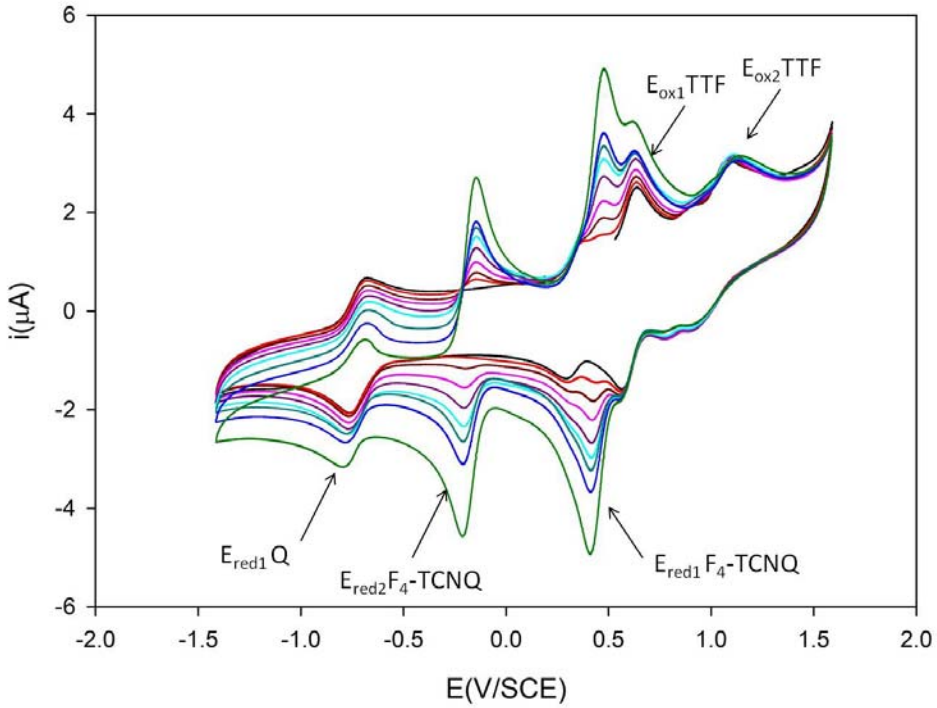
Cyclic voltammetry were carried out in a three-electrode cell equipped with a platinum millielectrode as working electrode, a platinum wire counter electrode and a silver wire in a 0.01 M solution of $AgNO_3$ in CH_3CN as a reference electrode. The electrolytic media involved a 0.1 M solution of tetrabutylammonium-hexafluorophosphate (TBAHP - puriss quality) in CH_3CN. The ferrocene/ferricinium couple (Fc/Fc^+) was used as internal reference and the potentials were expressed versus a saturated calomel electrode (SCE) as a reference. All experiments were performed in a glove box containing dry, oxygen-free (< 1 ppm) argon, at room temperature. Electrochemical experiments were carried out with an EGG PAR 273A potentiostat.



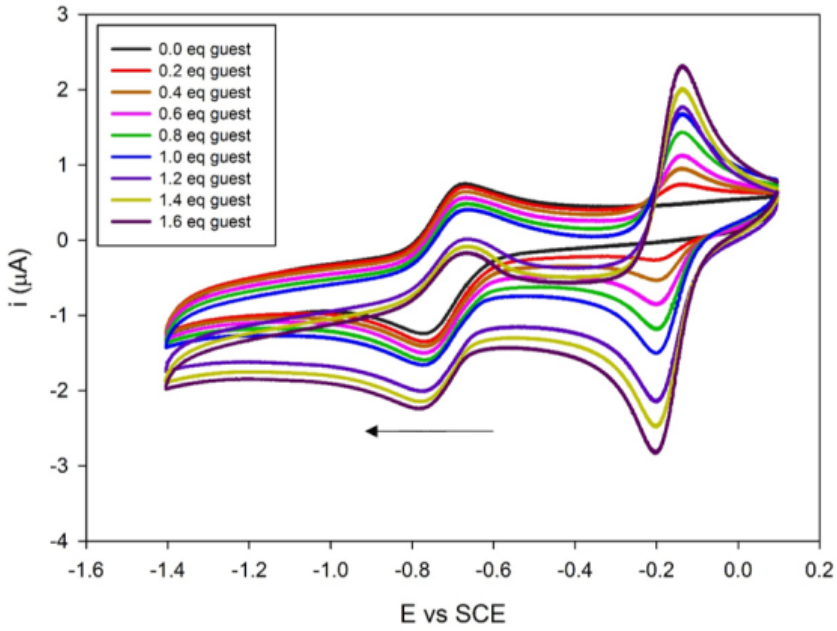
Deconvoluted cyclic voltamogramm for molecular clip **1** : 5.10^{-4} M in CH_2Cl_2/CH_3CN (9/1) in Bu_4NPF_6 0.1M. Pt as the working and counter electrode, Ag/Ag^+ reference electrode, scan rate 100 $mV.s^{-1}$. Values are given *vs* SCE, the couple Fc/Fc^+ ($E° = + 0.405$ V *vs* SCE) being used as an internal reference.[1]

[1] (a) G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461. (b) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

Cyclic voltammetry of the molecular clip 1 titration with F_4-TCNQ :

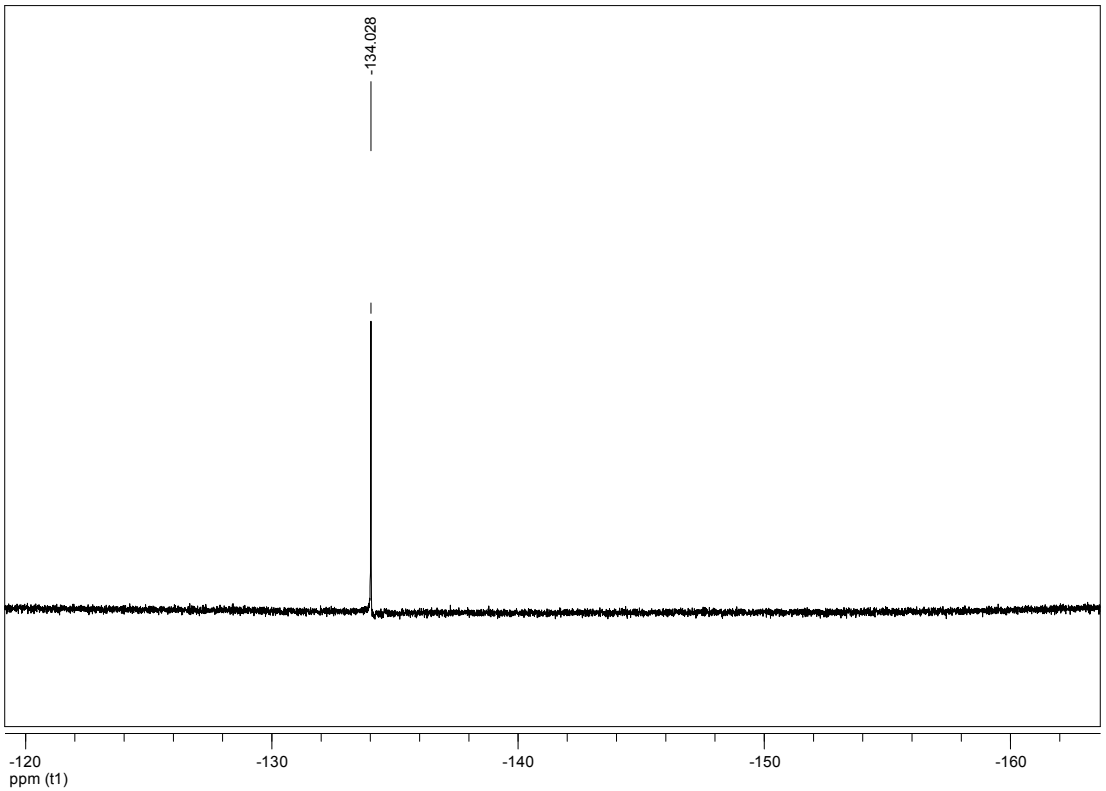


Cyclic voltamogramms of molecular clip **1** [$2.5.10^{-4}$ M in CH_2Cl_2/CH_3CN (9/1) in Bu_4NPF_6 0.1M] upon addition of F_4-TCNQ aliquots [10^{-2} M in CH_2Cl_2/CH_3CN (7/3)], scan rate : 100 $mV.s^{-1}$.

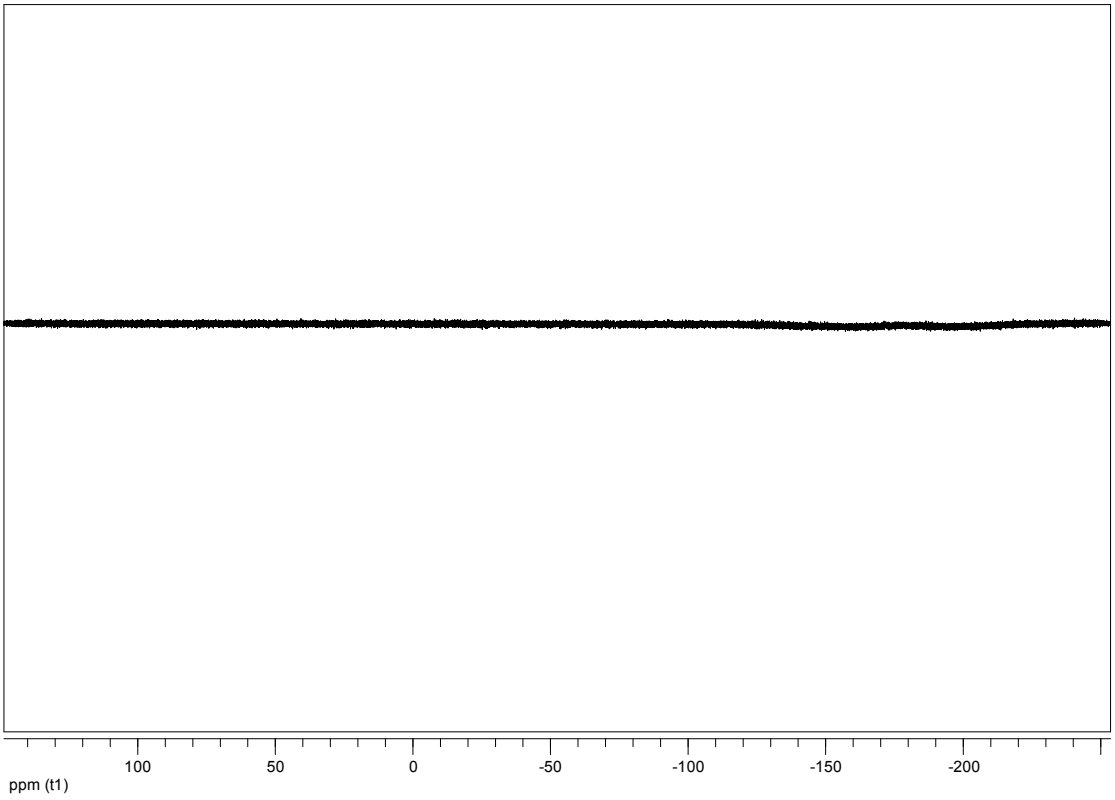


Cyclic voltamogramms of molecular clip **1** [$2.5.10^{-4}$ M in CH_2Cl_2/CH_3CN (9/1) in n-Bu_4NPF_6 0.1 M] upon addition of F_4-TCNQ aliquots [10^{-2} M in CH_2Cl_2/CH_3CN (7/3)], scan rate : 100 $mV.s^{-1}$. The two reduction waves correspond to the second reduction wave of F_4-TCNQ and the first reduction wave for quinone moiety at -0.22 V and -0.76 V *vs* SCE, respectively.

^{19}F NMR spectra (CD_2Cl_2) of F_4-TCNQ :



^{19}F NMR spectra (CD_2Cl_2) of F_4-TCNQ after its addition to the solution of molecular clip 1 in stoichiometry (1:1) :



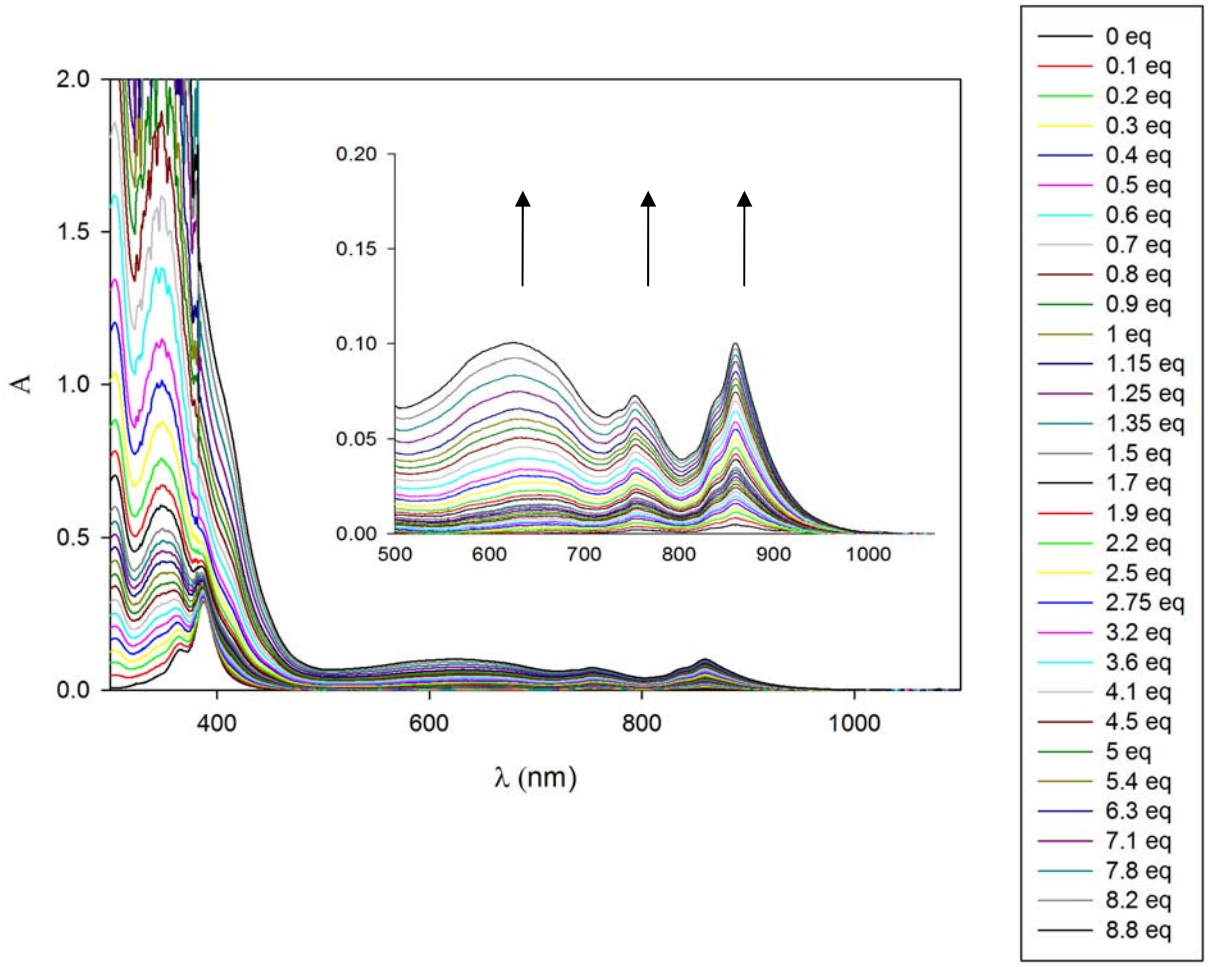
Determination of binding constants by UV-Visible titration :

UV-Visible titrations were performed in a quartz cell with 1 cm path length at room temperature in CH_2Cl_2. Mixing the molecular clip **1** (H) solution with F_4-TCNQ (G) solution immediately produced green - colored solution, and strong characteristic bands of TTF cation radical and F_4-TCNQ anion radical bands were detected at 625 nm (TTTF), 760 and 860 nm (F_4-TCNQ). Determination of the binding constants was performed using the absorbance of the band at 860 nm.

During the UV-Visible binding titration, the total guest concentration $[G]_0$ was kept constant, whereas the total host concentration $[H]_0$ was varied. Thus, the certain amount of host was dissolved in the stock solution of the guest with a concentration of $[G]_0$, followed by dilution of the sample with additional quantities of the same stock solution of the guest.

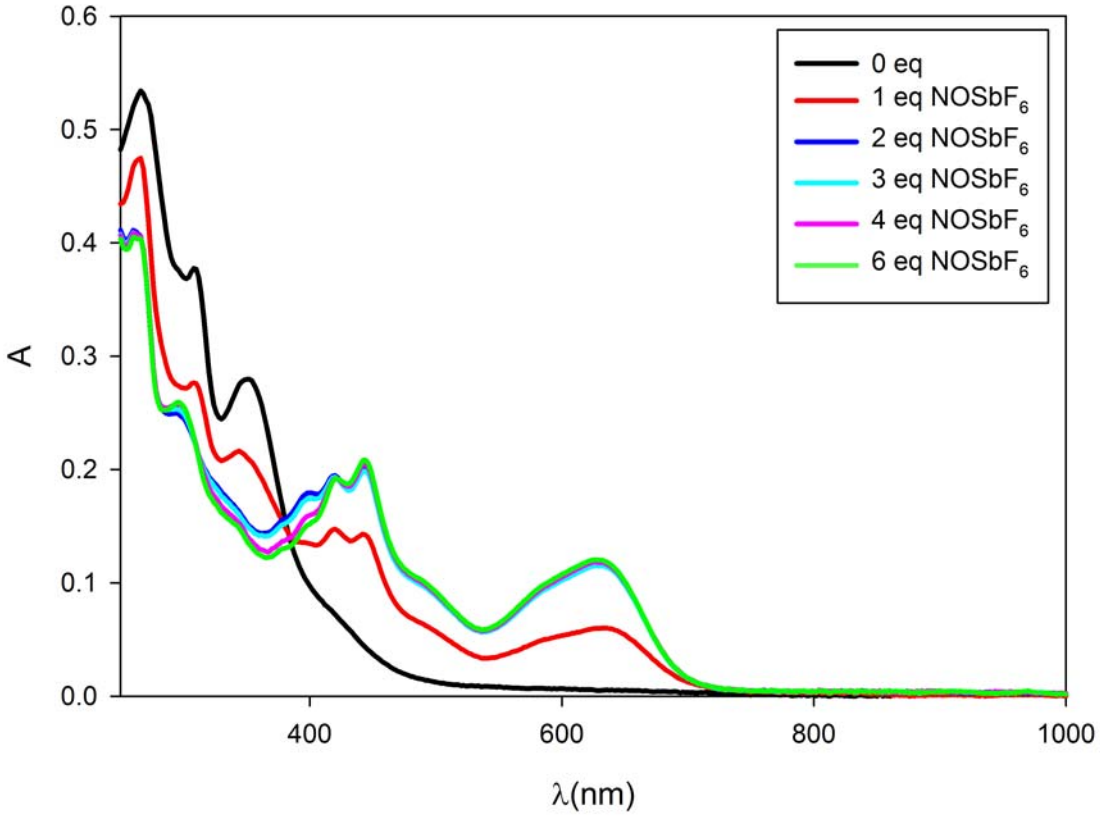
The following equation was used to determine the fit if the data to a 1:1 binding isotherm, after normalization of the guest concentration equal to 1.[1]

$$\Delta A_{obsd} = \varepsilon_C \left(\frac{[H]^\circ + [G]^\circ + \frac{1}{K_a}}{2} - \sqrt{\frac{\left([H]^\circ + [G]^\circ + \frac{1}{K_a}\right)^2}{4} - [G]^\circ \cdot [H]^\circ} \right)$$



UV-Visible absorption spectra of F_4-TCNQ (CH_2Cl_2, 10^{-5} M) upon titration with molecular clip **1** (CH_2Cl_2, 5. 10^{-4} M). Inset : enlargement of the absorption spectra between 500 and 1000 nm.

Chemical oxidation of molecular clip 1 followed by UV-Visible spectroscopy :



UV-Visible absorption spectra corresponding to the chemical oxidation of molecular clip **1** (10^{-5} M in CH_2Cl_2) using successive aliquot addition of $NOSbF_6$ (10^{-2} M in CH_2Cl_2 / CH_3CN 1 /1) used as oxidizing reagent

[1] Düker, M. H.; Schäfer, H.; Zeller, M.; Azov, V. A. *J. Org. Chem.* **2013**, *78*, 4905-4912.