Supporting information

Combining *in situ* electrochemistry, *operando* XRD & Raman and density functional theory to investigate the fundamentals of Li_2CO_3 formation in supercapacitor

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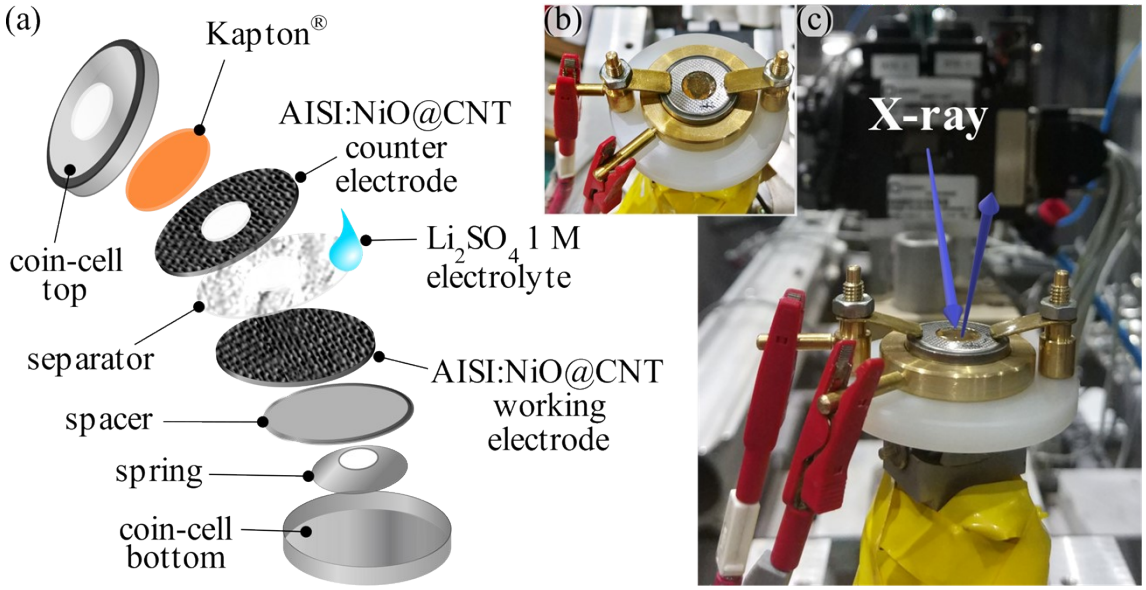

Figure S1. Measurements under dynamic polarization conditions: a) coin cell set up; b) top view of the coin cell installed in metallic adapter and positioned on the sample stage at the XPD beamline. There is a hole on the center of the coin cell which is covered with with a Kapton® foil to be transparent to the income and outcome x-ray and; c) a lateral view of the coin cell and the exhibiting the electrical contacts.

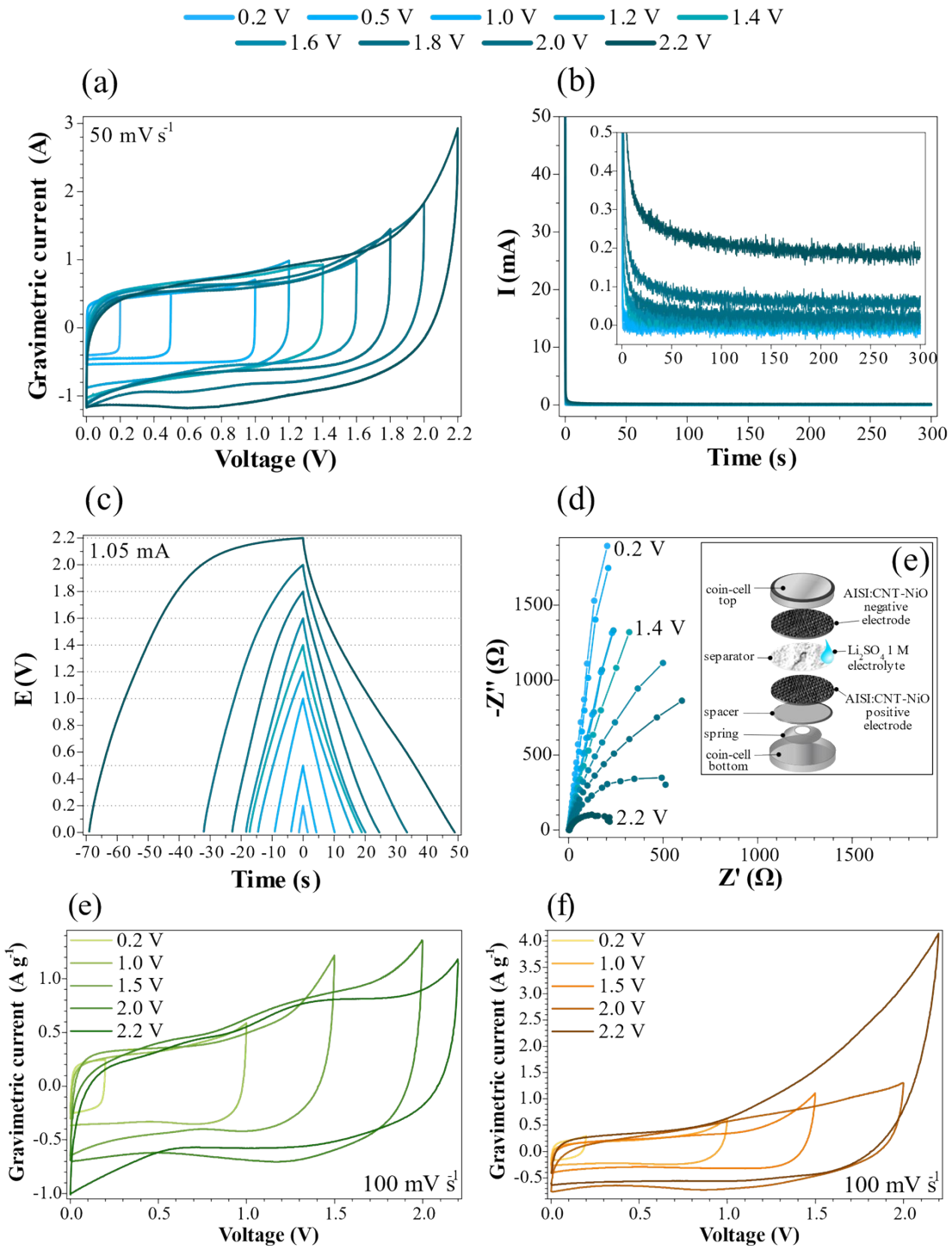

Figure S2. Electrochemical data from symmetric coin cell filled with a 1 M Li_2SO_4 aqueous solution (a) Voltammetric curves up to 2.2 V; (b) chronoamperometry from 0.2 V to 2.2 V; (c) galvanostatic charge/discharge curves up to 2.2 V; (d) electrochemical impedance spectroscopy at constant cell voltages from 0.2V to 2.2V in steps of 0.4V and; (e) Coin cell set up for electrochemical measurements. (e) Cyclic voltamograms for MWCNT and (f) for NiO@MWCNT.

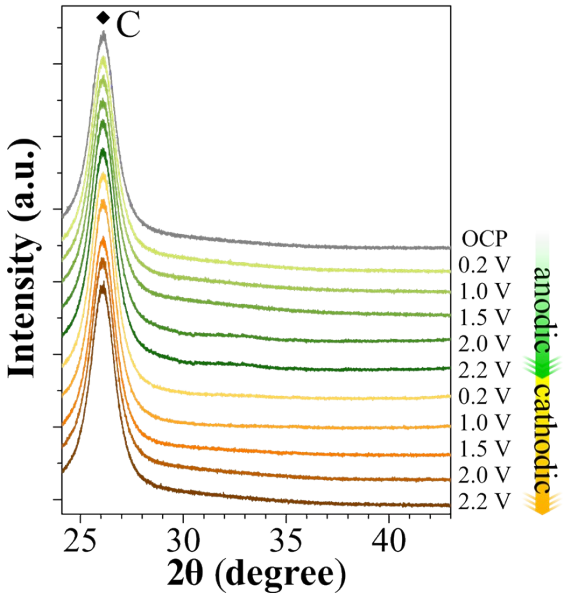

Figure S3. *Operando* XRD from MWCNTs electrodes in the coin cell. All XRD diffraction patterns were obtained under constant voltage during anodic polarization for MWCNTs anode (positive pole) green lines and MWCNTs cathode (negative pole) orange lines.

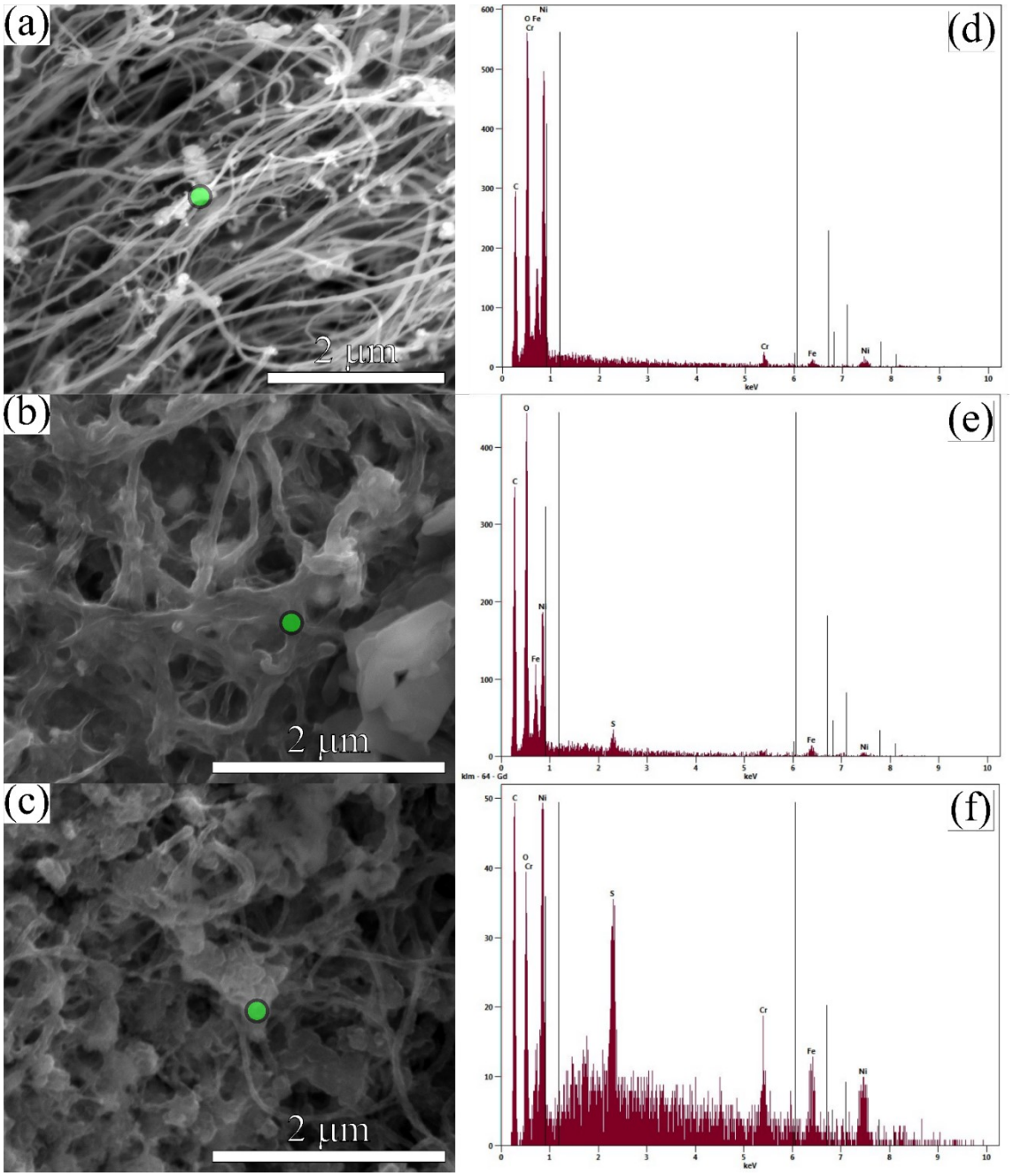

Figure S4. SEM data from (a) Pristine NiO@MWCNT electrode; electrodes after chronoamperometry of 30 min. (b) positive; (c) negative. EDS data from (d) Pristine NiO@MWCNT electrode; electrodes after chronoamperometry of 2.0 hours. (e) positive; (f) negative.

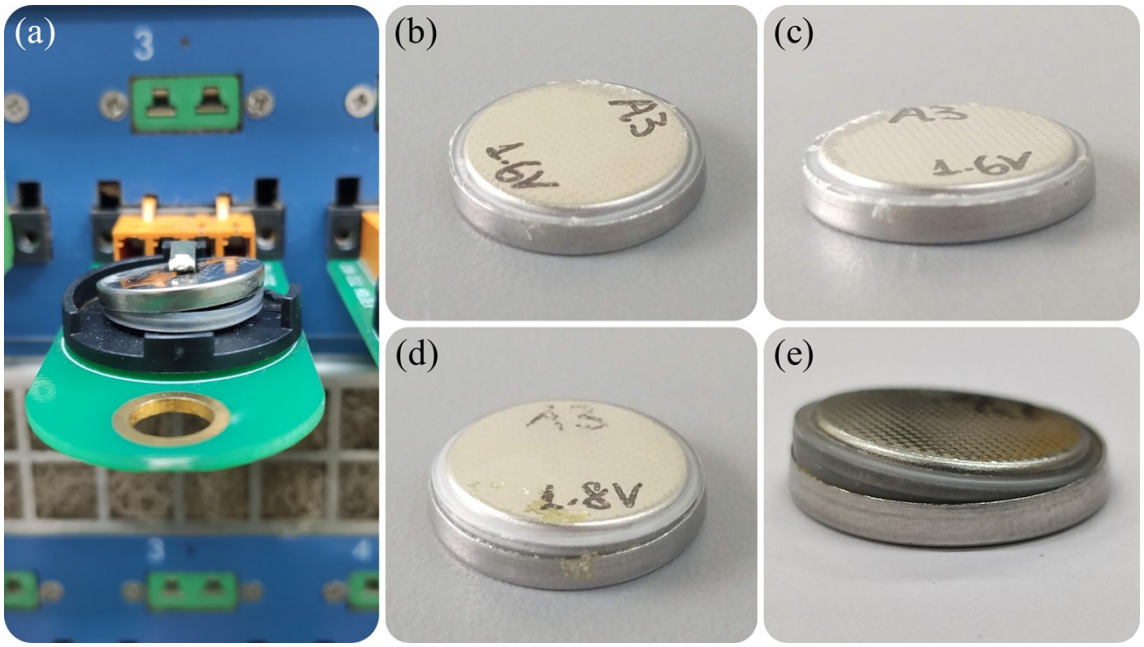

Figure S5. Coin cell used for electrochemical analysis: a) open-up coin cell after abusive regime of voltage applied; b) & c) undamaged coin cell under 1.6 V voltage; d) & e) damaged coin cell under 1.8 V voltage.

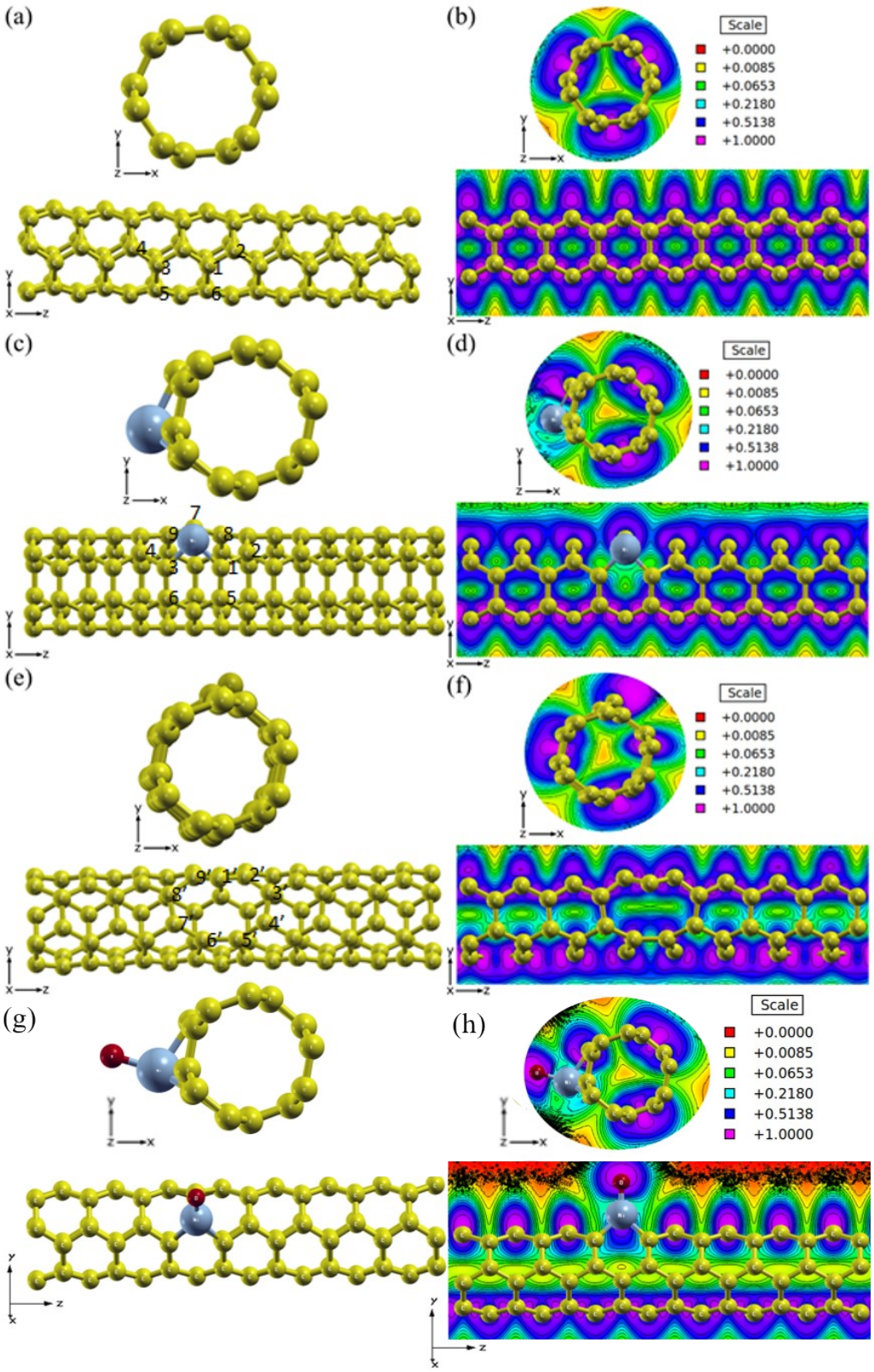

Figure S6. DFT calculation for SWCNT: a) relaxed; b) ELF. Ni-doped SWCNT: c) relaxed; d) ELF. SWCNT with vacancy: e) relaxed; f) ELF. NiO-doped SWCNT: g) relaxed; h) ELF.

Table S1. Elemental analysis via EDS of electrodes

Element	Pristine electrode		Positive electrode		Negative electrode	
	Weight (%)	Atom (%)	Weight (%)	Atom (%)	Weight (%)	Atom (%)
C_K	8.732	22.952	17.284	35.075	10.645	29.281
O_K	18.729	36.959	26.484	40.346	9.342	19.29
S_K	-	-	1.991	1.514	8.697	8.962
Fe_L	24.313	13.745	25.724	11.227	17.031	10.075
Ni_L	42.333	22.765	28.516	11.838	28.892	16.258
Cr_K	5.893	3.578	-	-	25.393	16.134

Table S2. Bond lengths armchair single wall carbon nanotubes

Distance (Å)	**SWCNT (CNT)**	**Ni-doped SWCNT (CNT_Ni)**	**NiO-doped SWCNT (CNT_NiO)**	**SWCNT with vacancy (CNT_v0)**	**Ni-doped SWCNT with vacancy (CNT_Ni_v0)**
C1 – C2	1.4215	1.4496	1.4313	-	1.4458
C1 – C5	1.4392	1.4042	1.4077	-	1.4001
C3 – C4	1.4213	1.4490	1.4311	-	1.4397
C3 – C6	1.4398	1.4044	1.4073	-	1.4072
C7 – C8	1.4217	1.4043	1.3914	-	1.3866
C7 – C9	1.4216	1.4040	1.3911	-	1.4014
C1 – Ni	1.4217	1.7848	1.8467	-	1.7991
C3 – Ni	1.4216	1.7853	1.8446	-	1.7887
C7 – Ni	1.4394	1.8999	1.8446	-	1.9036
C1’ – C2’	1.4215	1.4246	1.4231	1.3689	1.3573

C2’ – C3’	1.4217	1.4199	1.4193	1.4517	1.4595
C3’ – C4’	1.4394	1.4336	1.4349	1.4320	1.4338
C4’ – C5’	1.4217	1.4250	1.4210	1.5425	1.5422
C5’ – C6’	2.4355	2.4454	2.4365	1.5707	1.5906
C6’ – C7’	1.4216	1.4159	1.4186	1.5427	1.5330
C7’ – C8’	1.4398	-	-	1.4321	1.4390
C8’ – C9’	1.4216	-	-	1.4519	1.4441
C9’ – C1’	1.4217	-	-	1.3688	1.3563