Supplementary information for:

Computational Electrochemistry Study of Derivatives of Anthraquinone and Phenanthraquinone Analogues: the Substitution Effect

Zhen Wang,[a] Anyang Li, [a,*] Lei Gou,[b] Jingzheng Ren,[c] Gaohong Zhai [a,*]

[a] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry, Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China*

[b] *School of materials science and engineering, Chang'an university, Xi'an, 710061, China*

[c] *Department of Technology and Innovation, University of Southern Denmark, Campusvej 55 5230 Odense M Danmark*

* Corresponding author, email address: liay@nwu.edu.cn, zgh@nwu.edu.cn.

Due to the cell resistance in measurements or lack of a better description for electrolyte solvent in calculations, the calculated redox potentials are not directly equal to experimental values.[1-3] In order to predict the redox potentials of new molecules, it is necessary to find the correlation between computational and experimental values. Figure S1 lists twelve carbonyl based organic molecules, which are all candidates as cathode materials for rechargeable Li-ion batteries. Since density functional theory (DFT) methods are supposed to be reliable in electrochemical theoretical studies, seven different functionals including B3LYP, B98, PBE1PBE, BHandHLYP, mPW1PW91, ωB97XD and M06 are used to calculate redox potentials. Figure 2 and Figure S2 show the linear correlation between calculated and measured values.

Figure S3a-d present the stable geometries of all the 96 mono-substitution quinone derivatives with electron-withdrawing groups after Li binding. In addition to bind with carbonyl

groups of the quinone derivatives,[4] Li atom has significant interaction with the N, O or F atom of the substituent for some derivatives.

Table S1a-b give the nuclear independent chemical shift (NICS) values of each ring of the mono-substituted derivatives for both delithiation and lithiation states. The positive values of center rings change to negative during the reduction process for all the derivatives.

Figure S1 Structures of 12 molecules have been studied in this work, used to verify the computational method. The capital letters are corresponding to Figure 2 and Figure S2.

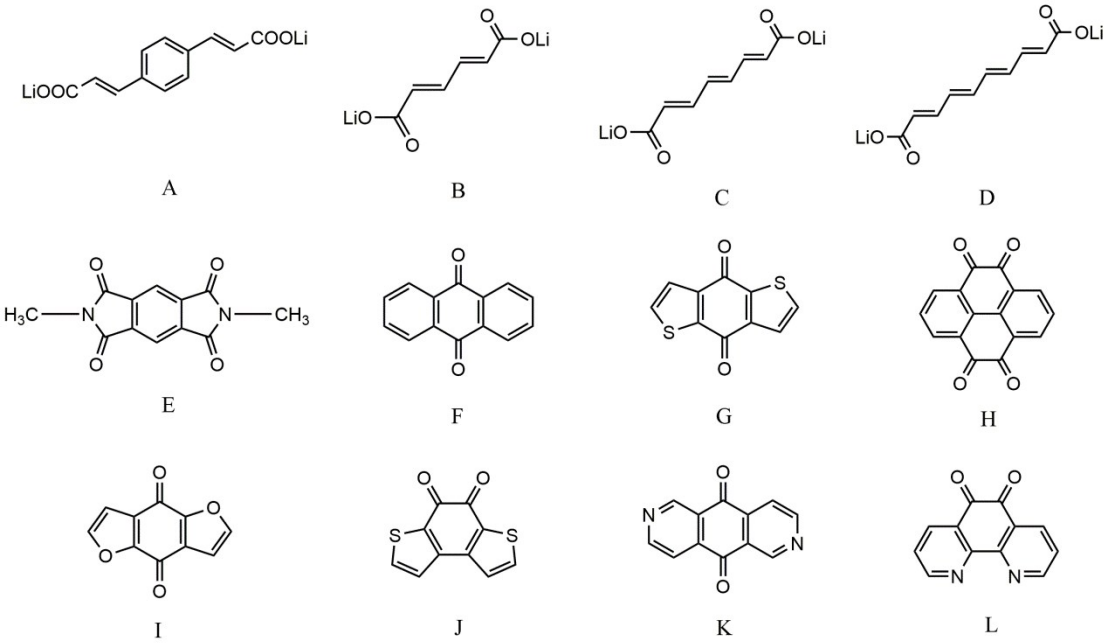

Figure S2 The fitting lines of calculated redox potentials (*vs* Li/Li^+) to experimental values by using six different functionals (B98, PBE1PBE, BHandHLYP, mPW1PW91, ωB97XD and M06)

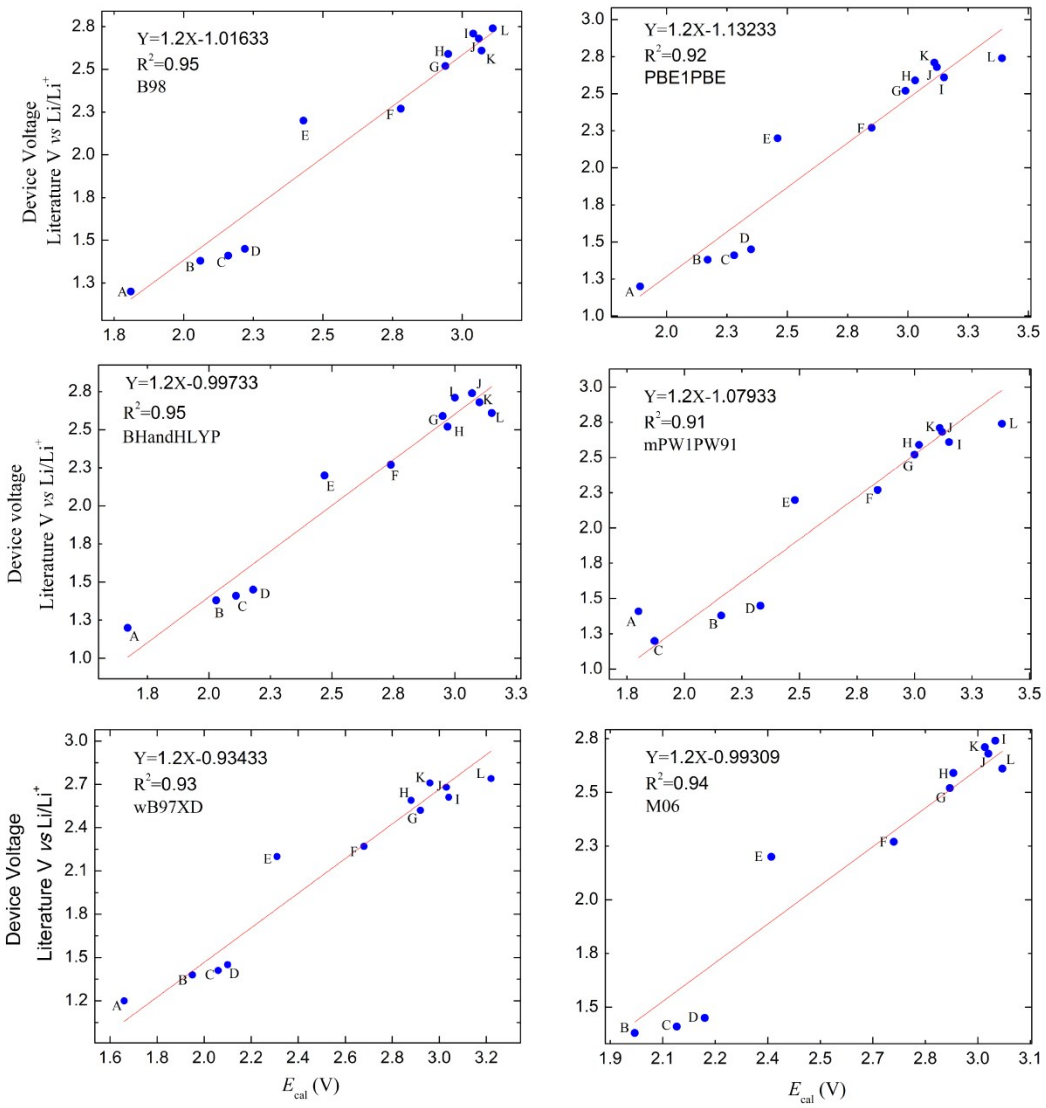

Figure S3a Optimized geometries of lithiated BDTD and BFFD mono-substitution derivatives with six different electron-withdrawing groups (F, CN, COOH, PO_3H_2, SO_3H and NO_2)

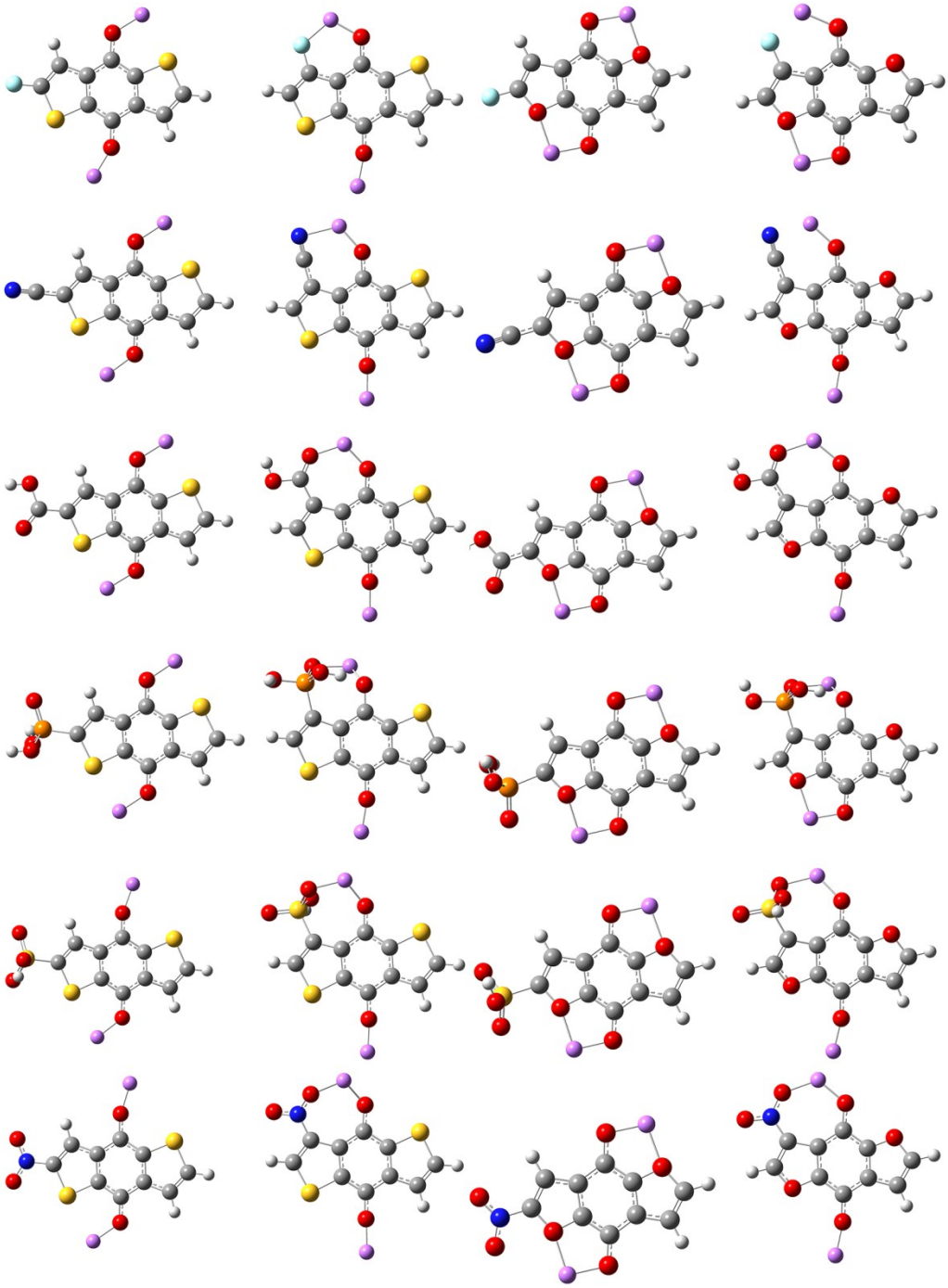

Figure S3b Optimized geometries of lithiated PID mono-substitution derivatives with six different electron-withdrawing groups (F, CN, COOH, PO_3H_2, SO_3H and NO_2)

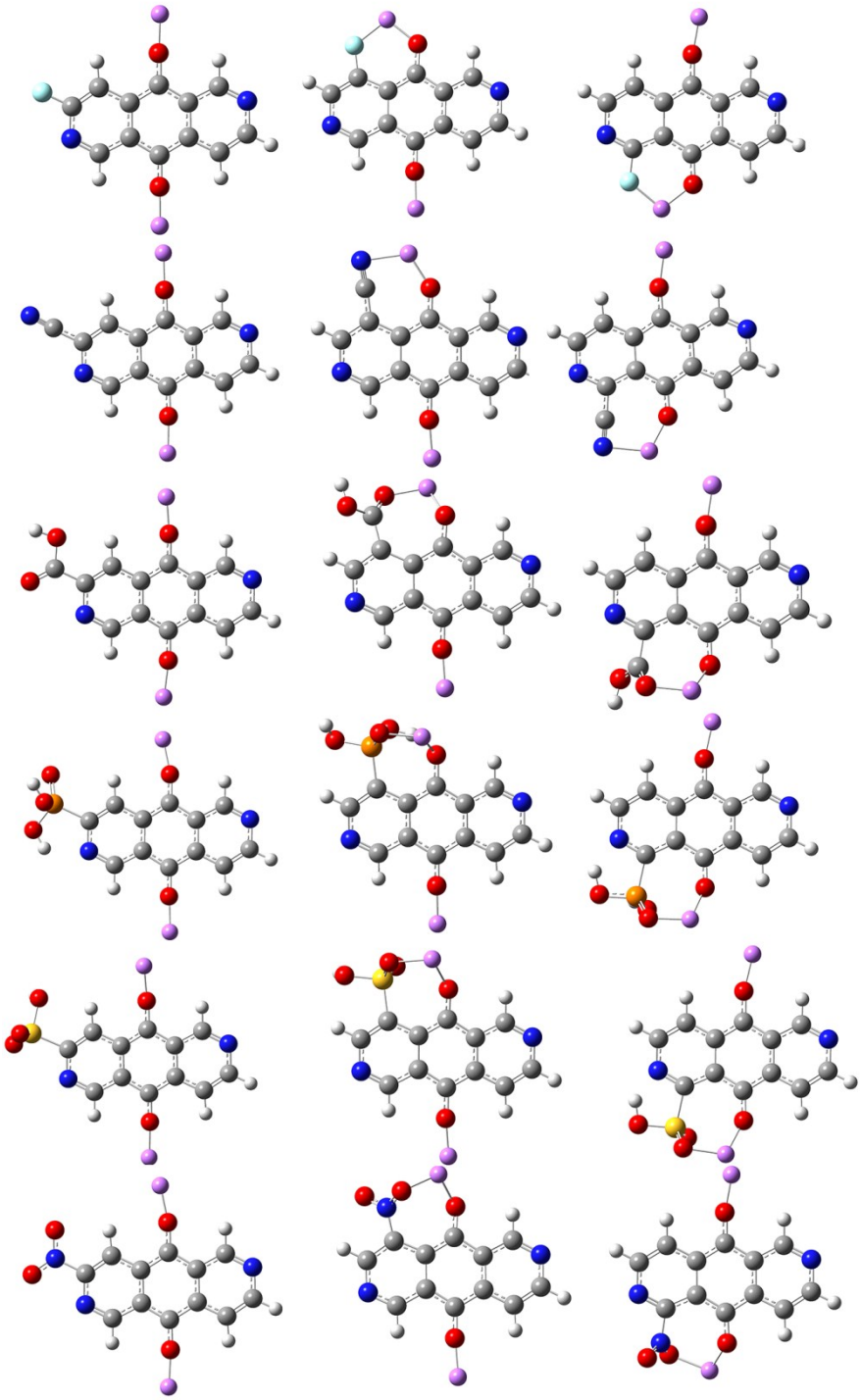

Figure S3c Optimized geometries of lithiated BDTQ and BDFD mono-substitution derivatives with six different electron-withdrawing groups (F, CN, COOH, PO_3H_2, SO_3H and NO_2)

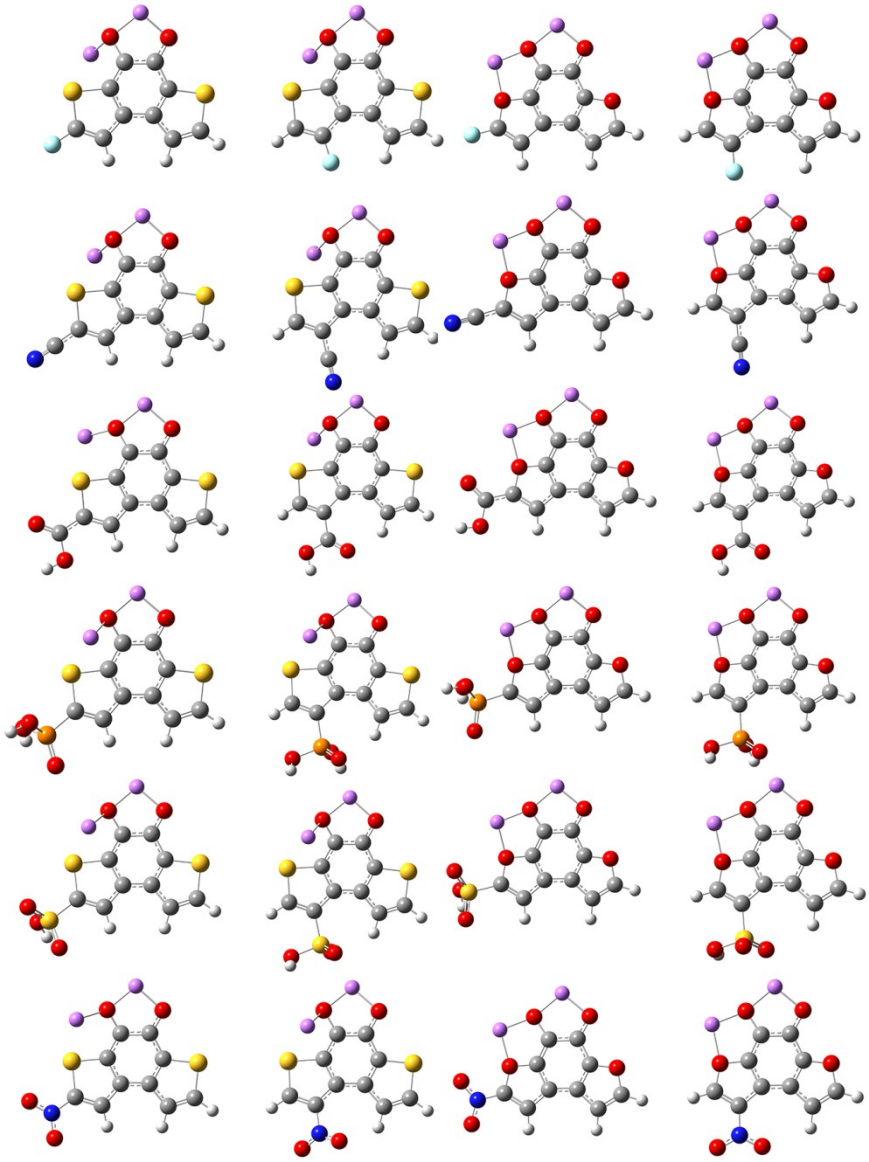

Figure S3d Optimized geometries of lithiated TQ and PhenQ mono-substitution derivatives with six different electron-withdrawing groups (F, CN, COOH, PO_3H_2, SO_3H and NO_2)

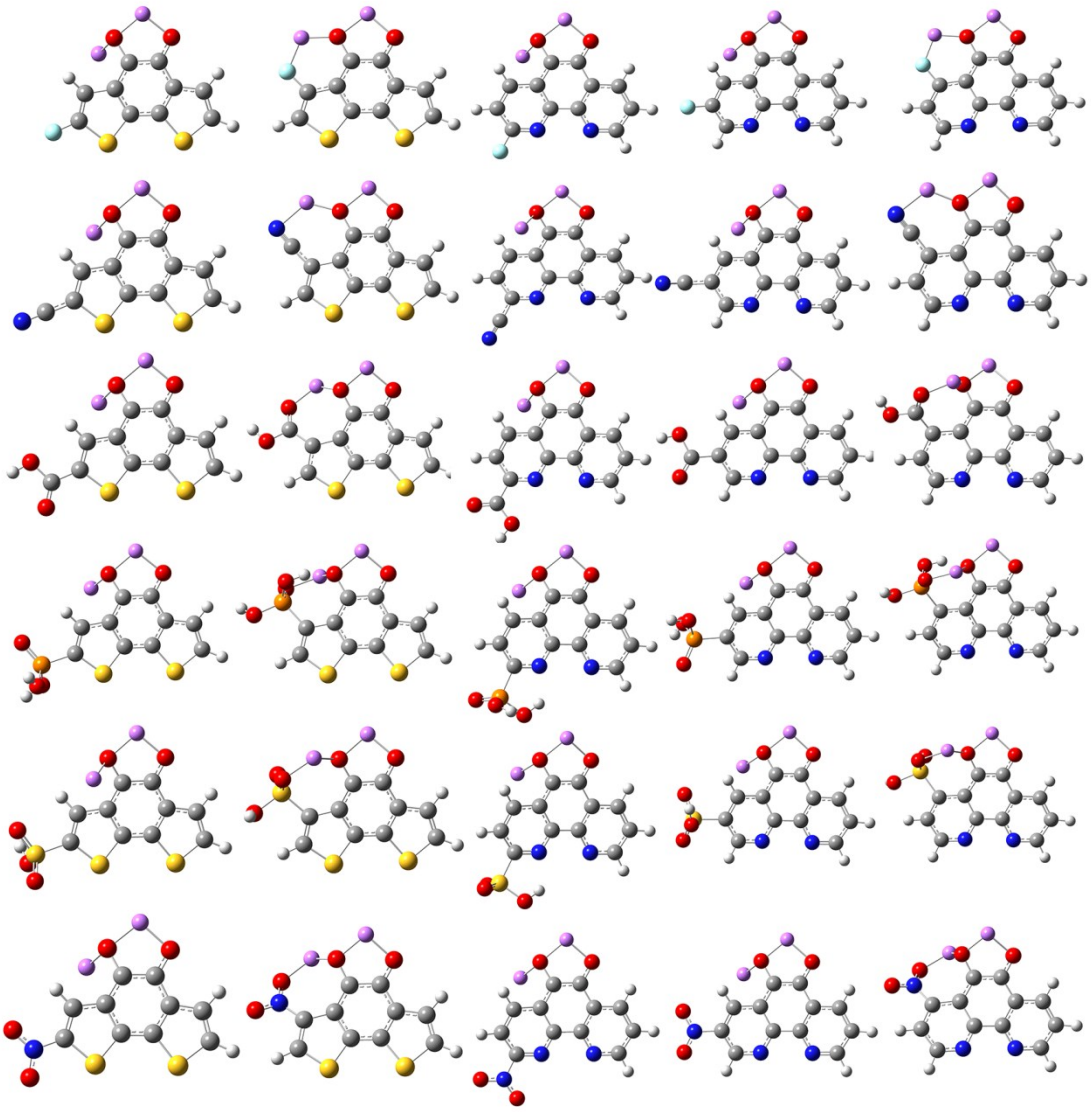

TABLE S1a NICS(1) values (in ppm) of mono-substitution derivatives of anthraquinone analogues. L, C and R indicate the left, center and right ring of each molecule.

	M			MLi_2			M			MLi_2		
	L	C	R	L	C	R	L	C	R	L	C	R
	1-a						1-b					
H	-8.2	3.2	-8.2	-7.1	-10.6	-7.1						
F	-7.2	3.5	-8.3	-6.2	-10.3	-7.4	-8.2	3.0	-8.2	-7.0	-10.1	-7.7
CN	-8.5	3.0	-8.3	-7.0	-9.4	-7.5	-8.7	2.6	-8.3	-7.0	-10.8	-7.9
COOH	-7.9	3.0	-8.3	-6.4	-8.9	-7.4	-8.4	3.1	-8.4	-6.2	-10.4	-7.9
PO_3H_2	-8.3	3.1	-8.3	-6.8	-9.6	-7.4	-8.6	3.3	-8.1	-7.0	-10.2	-7.6
SO_3H	-8.0	2.8	-8.3	-6.2	-9.4	-7.7	-8.6	3.0	-8.3	-6.3	-10.1	-7.9
NO_2	-7.7	2.9	-8.4	-5.6	-6.3	-7.5	-8.4	2.9	-8.4	-5.3	-8.8	-8.0
	2-a						2-b					
H	-7.8	3.3	-7.8	-6.7	-11.0	-6.7						
F	-7.0	3.2	-7.8	-5.5	-10.9	-6.9	-7.9	2.6	-8.1	-6.5	-10.7	-7.0
CN	-8.0	2.6	-7.8	-6.7	-10.1	-6.9	-8.3	2.6	-8.1	-6.8	-10.8	-7.9
COOH	-7.7	2.7	-7.8	-6.8	-9.8	-6.7	-8.1	2.6	-8.1	-5.8	-10.5	-8.1
PO_3H_2	-8.0	2.8	-7.8	-7.1	-10.6	-6.8	-8.2	3.0	-8.0	-6.8	-10.5	-7.9
SO_3H	-8.0	2.7	-7.8	-6.7	-10.4	-7.0	-8.2	2.8	-8.1	-6.5	-10.7	-8.2
NO_2	-7.9	2.6	-7.8	-6.3	-7.7	-6.8	-8.0	2.3	-8.1	-4.4	-8.5	-8.2
	3-a						3-b					
H	-9.3	2.8	-9.3	-8.8	-11.0	-8.8						
F	-9.2	2.3	-9.3	-9.2	-11.0	-8.7	-9.5	2.1	-9.4	-7.9	-11.3	-9.3
CN	-9.5	2.1	-9.4	-7.3	-10.9	-9.5	-9.6	1.5	-9.4	-6.7	-11.3	-9.7
COOH	-9.6	2.1	-9.4	-7.4	-10.7	-9.2	-9.3	2.2	-9.2	-6.1	-10.4	-9.7
PO_3H_2	-9.6	1.9	-9.4	-7.2	-11.2	-9.5	-9.5	2.4	-9.3	-7.5	-11.2	-9.4
SO_3H	-9.9	1.8	-9.4	-7.6	-11.3	-9.4	-9.7	2.1	-9.2	-6.7	-11.1	-9.8
NO_2	-9.9	2.0	-9.3	-6.9	-9.6	-9.4	-9.6	1.8	-9.3	-6.0	-8.8	-9.8
	3-c											
F	-9.2	2.2	-9.4	-7.3	-11.1	-9.6						
CN	-9.8	1.5	-9.4	-7.3	-11.7	-9.7						
COOH	-9.5	2.0	-9.4	-7.4	-11.0	-9.5						
PO_3H_2	-9.8	2.3	-9.4	-6.8	-11.3	-9.8						
SO_3H	-9.7	1.8	-9.5	-6.1	-11.1	-10.2						
NO_2	-9.6	1.8	-9.4	-7.2	-10.5	-10.0						

TABLE S1b NICS(1) values (in ppm) of derivatives of phenanthraquinone analogues.

	M			MLi_2			M			MLi_2		
	L	C	R	L	C	R	L	C	R	L	C	R
	4-a						4-b					
H	-7.0	5.1	-7.0	-7.0	-9.7	-7.0						
F	-6.3	4.6	-7.5	-5.5	-9.9	-7.8	-7.2	4.6	-7.4	-6.3	-9.6	-8.0
CN	-7.7	4.4	-7.4	-6.2	-8.8	-8.3	-7.7	4.5	-7.5	-6.8	-9.9	-8.1
COOH	-7.1	4.6	-7.2	-5.7	-8.2	-8.1	-7.5	4.8	-7.2	-6.6	-9.7	-8.1
PO_3H_2	-7.1	4.5	-7.3	-6.4	-9.3	-8.2	-7.4	5.0	-7.3	-6.6	-10.0	-8.3
SO_3H	-7.5	4.6	-7.3	-6.4	-9.1	-8.3	-7.6	4.8	-7.3	-6.6	-9.8	-8.2
NO_2	-7.0	4.4	-7.3	-5.3	-6.8	-8.3	-7.3	4.8	-7.3	-6.3	-9.7	-8.1
	5-a						5-b					
H	-7.0	4.7	-7.0	-6.8	-10.3	-6.8						
F	-6.0	4.2	-7.1	-5.5	-10.7	-7.8	-7.0	4.3	-7.3	-6.4	-10.5	-8.1
CN	-7.4	4.3	-7.1	-6.5	-9.5	-8.1	-7.4	4.2	-7.3	-6.5	-10.7	-8.2
COOH	-7.3	4.3	-7.1	-6.5	-9.1	-8.1	-7.1	4.6	-7.1	-6.2	-10.6	-8.1
PO_3H_2	-7.3	4.4	-7.1	-6.7	-9.9	-8.2	-7.4	4.6	-7.2	-6.5	-10.6	-8.1
SO_3H	-7.4	4.3	-7.2	-6.9	-9.7	-8.3	-7.3	4.3	-7.1	-6.2	-10.6	-8.0
NO_2	-7.2	4.1	-7.2	-5.4	-7.5	-8.1	-7.1	4.3	-7.2	-5.9	-10.4	-8.1
	6-a						6-b					
H	-6.8	5.5	-6.8	-7.1	-9.8	-7.1						
F	-6.1	5.4	-6.9	-5.9	-9.8	-7.4	-6.6	4.7	-7.1	-6.9	-9.9	-7.4
CN	-7.3	4.3	-7.3	-7.7	-9.9	-7.6	-7.4	4.6	-7.2	-7.0	-10.1	-7.4
COOH	-6.8	4.4	-7.3	-7.4	-9.6	-7.5	-7.0	4.4	-7.2	-6.7	-10.6	-7.3
PO_3H_2	-7.1	4.5	-7.3	-7.3	-10.0	-7.5	-7.0	5.1	-6.9	-7.3	-10.1	-7.6
SO_3H	-7.2	4.3	-7.3	-7.0	-9.9	-7.4	-7.2	4.8	-7.2	-6.8	-10.0	-7.5
NO_2	-6.4	4.0	-7.4	-6.7	-7.8	-6.9	-7.0	4.1	-7.4	-5.8	-9.4	-7.4
	7-a						7-b					
H	-7.7	4.3	-7.7	-9.9	-8.0	-9.9						
F	-7.8	3.6	-8.1	-9.8	-9.0	-10.3	-8.1	4.1	-7.8	-9.1	-7.9	-10.3
CN	-7.9	3.8	-8.1	-8.2	-8.0	-10.5	-7.9	3.7	-8.0	-8.7	-8.3	-10.5
COOH	-8.0	3.8	-8.0	-9.0	-8.1	-10.4	-7.9	3.8	-8.0	-9.4	-8.6	-10.3
PO_3H_2	-8.2	3.5	-8.1	-9.1	-9.0	-10.5	-8.1	3.7	-8.0	-9.6	-8.5	-10.5
SO_3H	-8.4	3.5	-8.2	-9.3	-9.0	-10.6	-8.1	3.6	-8.1	-9.1	-8.8	-10.5
NO_2	-8.5	3.8	-8.1	-8.5	-7.3	-10.3	-8.1	3.6	-8.1	-9.0	-8.3	-10.1
	7-c											
F	-7.8	3.6	-8.1	-9.8	-8.9	-10.4						
CN	-8.3	3.5	-8.1	-8.1	-8.0	-10.6						
COOH	-8.2	3.4	-8.1	-8.9	-6.8	-10.6						
PO_3H_2	-8.1	3.9	-8.0	-9.1	-8.0	-10.6						
SO_3H	-8.5	3.6	-8.1	-8.6	-8.3	-10.5						
NO_2	-8.2	3.5	-8.1	-7.9	-6.6	-10.1						

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