Thiophene-benzoquinones: synthesis, crystal structures and preliminary coordination chemistry of derived anilate ligands

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SUPPORTING INFORMATION

X-Ray structures

Compound **2a**

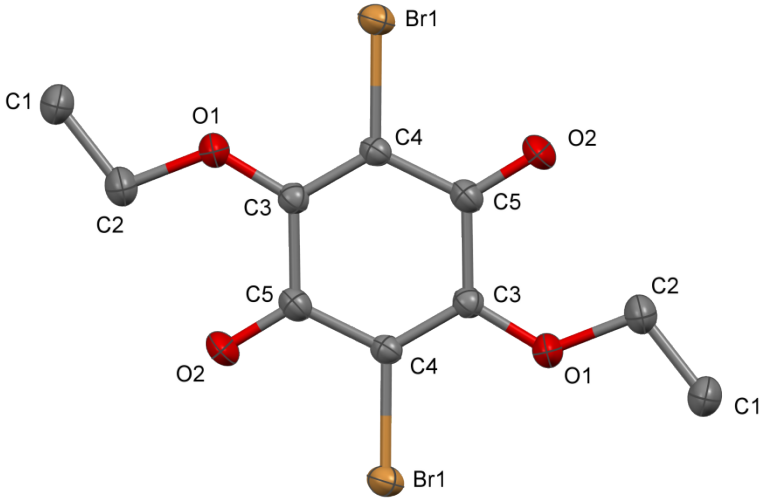


Figure S1 Ortep drawing of **2a** with thermal ellipsoids at 30% probability level.

Table S1 Summary of X-ray crystallographic data for **2a**.

	2a
Empirical formula	$C_{10}H_{10}Br_2O_4$
Formula weight	354.00
Crystal size, mm	0.2 x 0.05 x 0.02
Crystal system	Monoclinic
Space group	*P21/a*
a, Å	8.9370(11)
b, Å	5.0321(2)
c, Å	13.3138(12)
α, deg.	90
β, deg.	96.958(8)
γ, deg.	90
V, Å^3	594.34(9)
Z	2
T, K	293(2)
ρ (calc), Mg/m^3	1.978
μ, mm^{-1}	6.815
θ range, deg.	4.33 to 26.98 deg
GooF	1.091
*R*1	0.0357
*wR*2	0.0568

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{½}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Compound **4a**

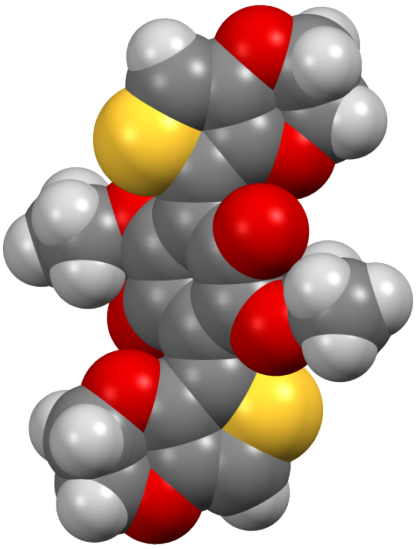


Figure S2 Molecular structure for the compound **4a** in space filling model; the steric hindrance between the 3,4-ethylenedioxy group and the benzoquinone moiety is highlighted.

Compound **4b**

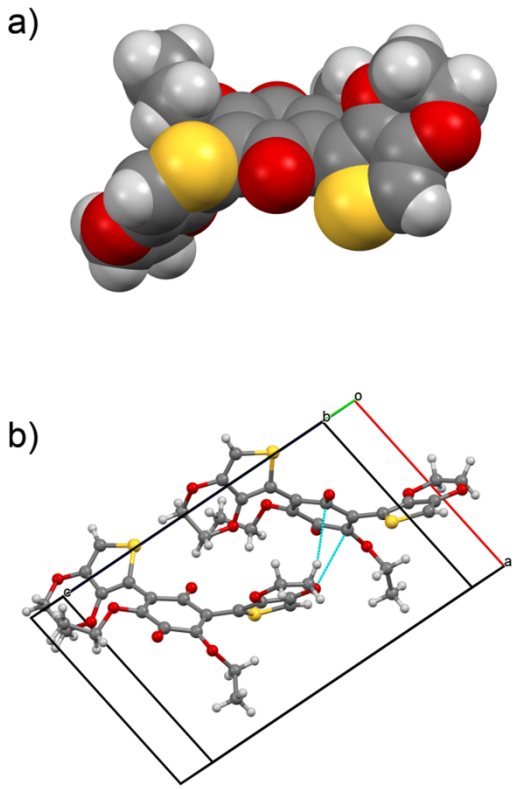


Figure S3 a) Molecular structure for the compound **4b** in space filling model; b) Stacking interactions between the 3,4-etylenedioxy fragment and the benzoquinone ring for **4b**: O7···C3 3.19 Å; C18–H···C1 2.86 Å.

Table S2 Selected bond distances (Å) of the benzoquinone ring for compounds **3a**, **3b**, **4a**, and **4b**.

Bond	**3a**	**3b**		**4a**	**4b**
C=O	1.223(4)	1.218(4)	1.223(4)	1.222(2)	1.226(5)
		1.227(4)	1.219(4)		1.223(4)
C=C	1.359(4)	1.352(5)	1.368(5)	1.359(2)	1.345(5)
		1.346(5)	1.347(5)		1.343(5)
C–O	1.334(4)	1.361(4)	1.361(4)	1.342(2)	1.342(4)
		1.344(4)	1.342(4)		1.352(4)
C–C	1.479(4)	1.482(5)	1.489(5)	1.475(2)	1.484(5)
		1.500(5)	1.471(5)		1.495(5)
	1.501(4)	1.481(5)	1.505(5)	1.499(2)	1.481(5)
		1.500(5)	1.488(5)		1.489(5)

Theoretical calculations

Computational details

Program and version: Gaussian09 A02; GaussSum 2.2.4; MolIV3D

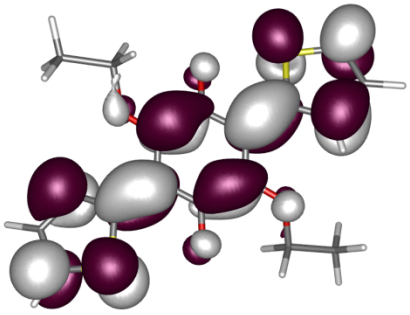
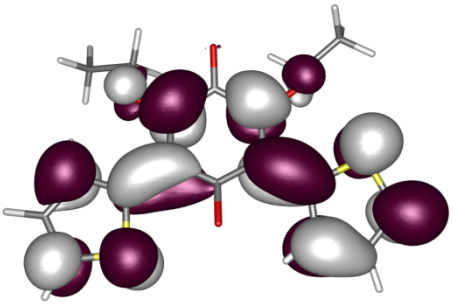
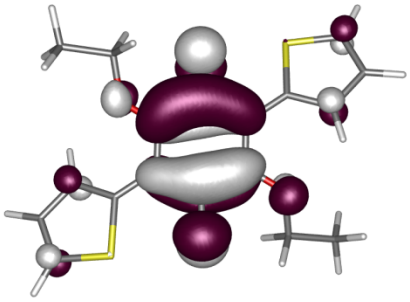
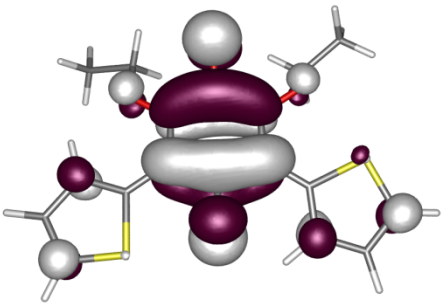
Property n°1: geometry and electronic structure of fundamental state

Method used: OPT in DFT (functional: PBE0); basis set: 6-311++G(3df,2pd) (1708 primitives gaussians); solvatation: one test PCM solvent = acetonitrile

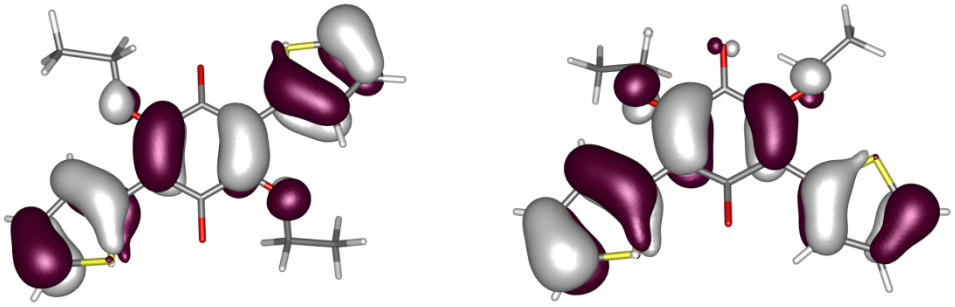
Property n°3: excited states, UV visible absorption

Method used: TD-DFT same details as 1; solvatation: one test Non equilibrium LR-PCM solvent = acetonitrile

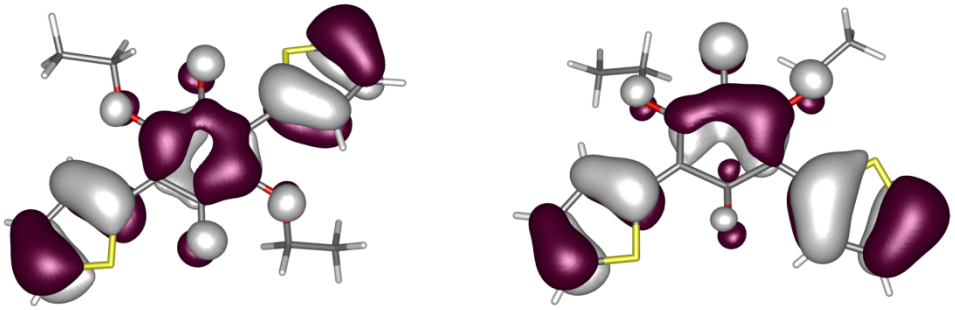
Table S3 Frontier orbitals plots for **3a** and **3b** with an isovalue chosen to represent 35% of the function.

MO	**3a**	**3b**
LUMO+1		
LUMO		

HOMO



HOMO-1



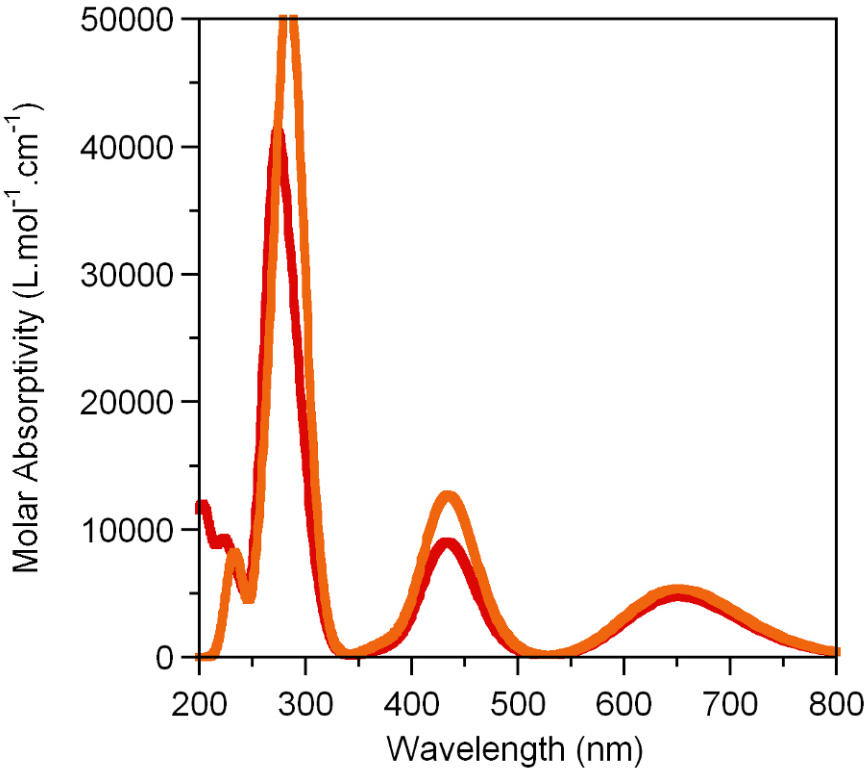
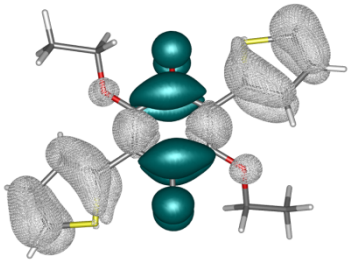
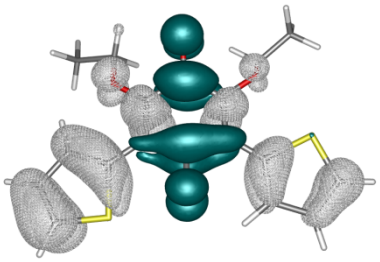
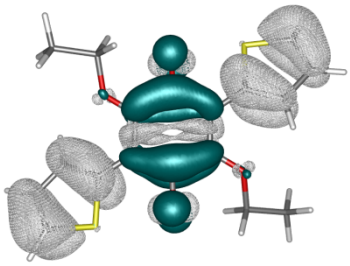
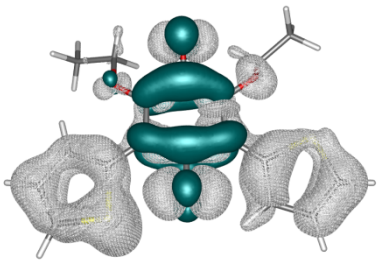
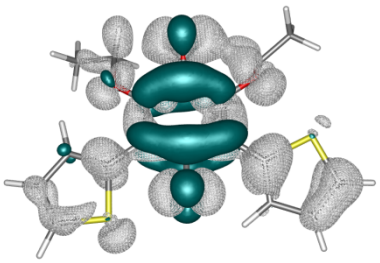
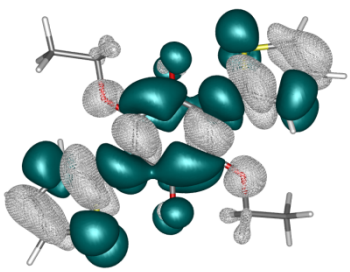
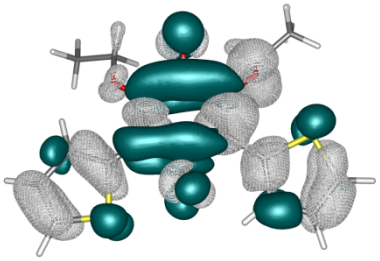
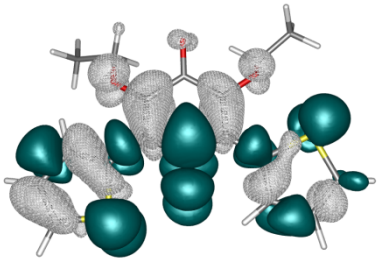
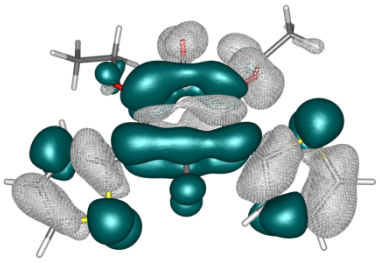
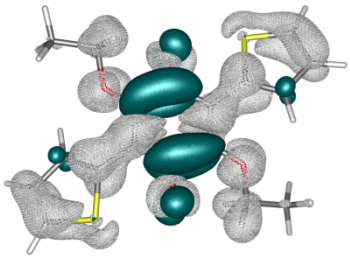
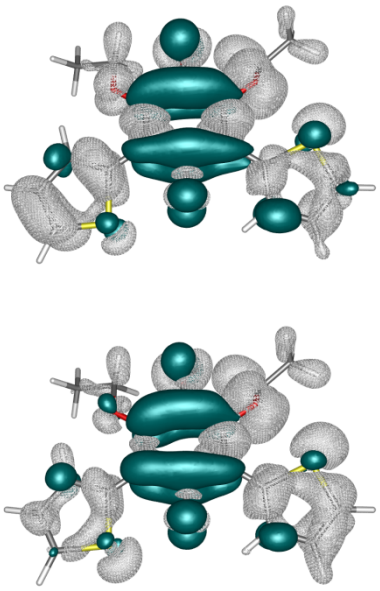


Figure S4 Comparison between simulated absorption spectra of **3b** in solution (non-equilibrium LR-PCM) (orange line) and in gas phase (red line).

Table S4 One-electron density difference between the ES and GS. The isocontour value is set to represent 75% of the electron. The solid turquoise (white grid) zones indicate increase (decrease) of density upon electronic transition.

Excitation (Osc. Str.)	**3a**	Excitation (Osc. Str.)	**3b**
$S_0 \rightarrow S_1$ (0.000)		$S_0 \rightarrow S_1$ (0.066)	
$S_0 \rightarrow S_2$ (0.122)		$S_0 \rightarrow S_2$ (0.050) + $S_0 \rightarrow S_4$ (0.050)	 
$S_0 \rightarrow S_8$ (0.612)		$S_0 \rightarrow S_8$ (0.088) + $S_0 \rightarrow S_{10}$ (0.410) + $S_0 \rightarrow S_{12}$ (0.071)	 

			
$S_0 \rightarrow S_9$ (0.308)		$S_0 \rightarrow S_9$ (0.161) + $S_0 \rightarrow S_{11}$ (0.122)	

Compound 3a

Table of major excitations with transitions

Excitation	Wavelength (nm)	Energy (eV)	Oscillator strength	Transitions
$S_0 \rightarrow S_1$	676	1.83	0.000	99% HOMO → LUMO
$S_0 \rightarrow S_2$	463	2.68	0.122	90% HOMO-1 → LUMO 6% HOMO-5 → LUMO
$S_0 \rightarrow S_3$	431	2.88	0.000	69% HOMO-4 → LUMO -26% HOMO-3 → LUMO 3% HOMO-6 → LUMO
$S_0 \rightarrow S_4$	408	3.04	0.012	53% HOMO-5 → LUMO -40% HOMO-2 → LUMO -4% HOMO-1 → LUMO
$S_0 \rightarrow S_5$	400	3.10	0.007	59% HOMO-2 → LUMO 37% HOMO-5 → LUMO
$S_0 \rightarrow S_8$	312	3.98	0.612	82% HOMO → LUMO+1 -15% HOMO-7 → LUMO
$S_0 \rightarrow S_9$	284	4.37	0.308	76% HOMO-7 → LUMO 13% HOMO → LUMO+1 3% HOMO-9 → LUMO 2% HOMO-1 → LUMO
$S_0 \rightarrow S_{13}$	244	5.08	0.044	84% HOMO-3 → LUMO+1 5% HOMO-9 → LUMO -5% HOMO-4 → LUMO+1
$S_0 \rightarrow S_{16}$	237	5.24	0.054	55% HOMO-9 → LUMO -21% HOMO-4 → LUMO+1 -8% HOMO-3 → LUMO+1 6% HOMO-11 → LUMO 3% HOMO-12 → LUMO
$S_0 \rightarrow S_{21}$	224	5.53	0.027	72% HOMO → LUMO+5 -13% HOMO → LUMO+7 4% HOMO → LUMO+4 -3% HOMO-1 → LUMO+3 2% HOMO-1 → LUMO+6
$S_0 \rightarrow S_{24}$	222	5.57	0.108	66% HOMO → LUMO+7 12% HOMO → LUMO+5 5% HOMO → LUMO+4 -3% HOMO-12 → LUMO -3% HOMO-9 → LUMO
$S_0 \rightarrow S_{30}$	212	5.86	0.058	52% HOMO-12 → LUMO -21% HOMO-6 → LUMO+1 -7% HOMO → LUMO+11 4% HOMO → LUMO+9 3% HOMO → LUMO+7
$S_0 \rightarrow S_{32}$	210	5.91	0.022	53% HOMO → LUMO+11 28% HOMO → LUMO+9 5% HOMO-12 → LUMO 3% HOMO-2 → LUMO+2
$S_0 \rightarrow S_{37}$	203	6.10	0.034	60% HOMO-6 → LUMO+1 -13% HOMO → LUMO+11 6% HOMO → LUMO+9 5% HOMO-12 → LUMO
$S_0 \rightarrow S_{39}$	201	6.15	0.030	48% HOMO → LUMO+14 -24% HOMO-2 → LUMO+2 -8% HOMO-1 → LUMO+6 4% HOMO → LUMO+11 -3% HOMO → LUMO+22 2% HOMO-6 → LUMO+1
$S_0 \rightarrow S_{41}$	201	6.17	0.038	19% HOMO-2 → LUMO+2 19% HOMO → LUMO+16 -15% HOMO-1 → LUMO+6 10% HOMO-1 → LUMO+8 9% HOMO → LUMO+14 7% HOMO-1 → LUMO+3 -5% HOMO → LUMO+11 4% HOMO → LUMO+13 4% HOMO → LUMO+17
$S_0 \rightarrow S_{45}$	197	6.29	0.090	24% HOMO-2 → LUMO+2 19% HOMO → LUMO+14 -13% HOMO-1 → LUMO+8 -12% HOMO → LUMO+13 -6% HOMO-2 → LUMO+3 6% HOMO-1 → LUMO+6 -5% HOMO → LUMO+17
$S_0 \rightarrow S_{50}$	192	6.46	0.035	23% HOMO-5 → LUMO+2 20% HOMO → LUMO+16 -18% HOMO → LUMO+17 15% HOMO-4 → LUMO+7 -4% HOMO-3 → LUMO+7 -3% HOMO-8 → LUMO+1 -3% HOMO → LUMO+14

Compound 3b

Table of major excitations with transitions

Excitation	Wavelength (nm)	Energy (eV)	Oscillator strength	Transitions
$S_0 \rightarrow S_1$	652	1.90	0.066	98% HOMO → LUMO
$S_0 \rightarrow S_2$	440	2.82	0.050	44% HOMO-1 → LUMO, -30% HOMO-5 → LUMO, -11% HOMO-2 → LUMO, 8% HOMO-4 → LUMO, -3% HOMO-3 → LUMO
$S_0 \rightarrow S_3$	432	2.87	0.026	35% HOMO-2 → LUMO, 28% HOMO-4 → LUMO, 16% HOMO-1 → LUMO, 13% HOMO-5 → LUMO, 3% HOMO-3 → LUMO
$S_0 \rightarrow S_4$	429	2.89	0.050	49% HOMO-4 → LUMO, -34% HOMO-1 → LUMO, -10% HOMO-5 → LUMO
$S_0 \rightarrow S_5$	395	3.14	0.003	50% HOMO-2 → LUMO, -23% HOMO-5 → LUMO, -20% HOMO-3 → LUMO, -5% HOMO-4 → LUMO
$S_0 \rightarrow S_7$	306	4.05	0.041	79% HOMO-6 → LUMO, 9% HOMO-7 → LUMO, 7% HOMO → LUMO+1, -2% HOMO-4 → LUMO
$S_0 \rightarrow S_8$	293	4.23	0.088	48% HOMO-7 → LUMO, -45% HOMO → LUMO+1
$S_0 \rightarrow S_9$	288	4.30	0.161	37% HOMO → LUMO+1, 27% HOMO-8 → LUMO, 20% HOMO-7 → LUMO, -12% HOMO-6 → LUMO
$S_0 \rightarrow S_{10}$	274	4.53	0.410	88% HOMO → LUMO+2, 7% HOMO-1 → LUMO+1
$S_0 \rightarrow S_{11}$	263	4.71	0.122	43% HOMO-8 → LUMO, 24% HOMO-1 → LUMO+1, -13% HOMO-7 → LUMO, -5% HOMO → LUMO+1, 3% HOMO-9 → LUMO, 3% HOMO-6 → LUMO
$S_0 \rightarrow S_{12}$	261	4.76	0.071	66% HOMO-1 → LUMO+1, -15% HOMO-8 → LUMO, -8% HOMO → LUMO+2, 4% HOMO-7 → LUMO
$S_0 \rightarrow S_{17}$	234	5.31	0.021	72% HOMO-3 → LUMO+1, -5% HOMO-1 → LUMO+2, -4% HOMO-2 → LUMO+1, 2% HOMO-5 → LUMO+1, 2% HOMO-3 → LUMO+2
$S_0 \rightarrow S_{23}$	224	5.54	0.043	48% HOMO → LUMO+6, -22% HOMO-5 → LUMO+1, 7% HOMO-3 → LUMO+1, 4% HOMO → LUMO+7, 3% HOMO → LUMO+5
$S_0 \rightarrow S_{26}$	219	5.66	0.020	74% HOMO → LUMO+7, -5% HOMO → LUMO+6, 3% HOMO → LUMO+3, -2% HOMO → LUMO+8
$S_0 \rightarrow S_{34}$	207	6.00	0.053	23% HOMO → LUMO+10, 15% HOMO-3 → LUMO+2, 9% HOMO-2 → LUMO+2, -9% HOMO → LUMO+9, 7% HOMO → LUMO+11, -6% HOMO-4 → LUMO+2, 6% HOMO-1 → LUMO+4, 5% HOMO-13 → LUMO, -5% HOMO-6 → LUMO+1, -3% HOMO-5 → LUMO+2
$S_0 \rightarrow S_{42}$	199	6.23	0.041	35% HOMO-6 → LUMO+1, -14% HOMO → LUMO+13, -8% HOMO → LUMO+14, -5% HOMO-14 → LUMO, -4% HOMO-7 → LUMO+1, 4% HOMO-1 → LUMO+5, 4% HOMO → LUMO+10, 4% HOMO → LUMO+11, -2% HOMO-13 → LUMO
$S_0 \rightarrow S_{49}$	193	6.42	0.028	37% HOMO-7 → LUMO+1, 18% HOMO-1 → LUMO+7, 6% HOMO-15 → LUMO, -5% HOMO → LUMO+15, -5% HOMO → LUMO+16, 3% HOMO-8 → LUMO+1, 3% HOMO-6 → LUMO+1, -3% HOMO-1 → LUMO+6

Electrochemical studies. Cyclic voltammetry was carried out on a BioLogic potentiostat model SP-150, using a three-electrode cell equipped with a platinum millielectrode with a surface area of 0.126 cm^2, an Ag/Ag^+ pseudoreference and a platinum-wire as counterelectrode. The experiments were performed at room temperature (25 °C), in dry and Nitrogen-degassed CH_3CN solution containing 0.1 mol dm^{-3} $[(n\text{-}Bu)_4N]PF_6$ as supporting electrolyte, at 100 mV s^{-1} scan rate. All the voltamograms were corrected for the half-wave potential of the ferrocene-ferrocenium couple as internal standard (0.42 V under these conditions).

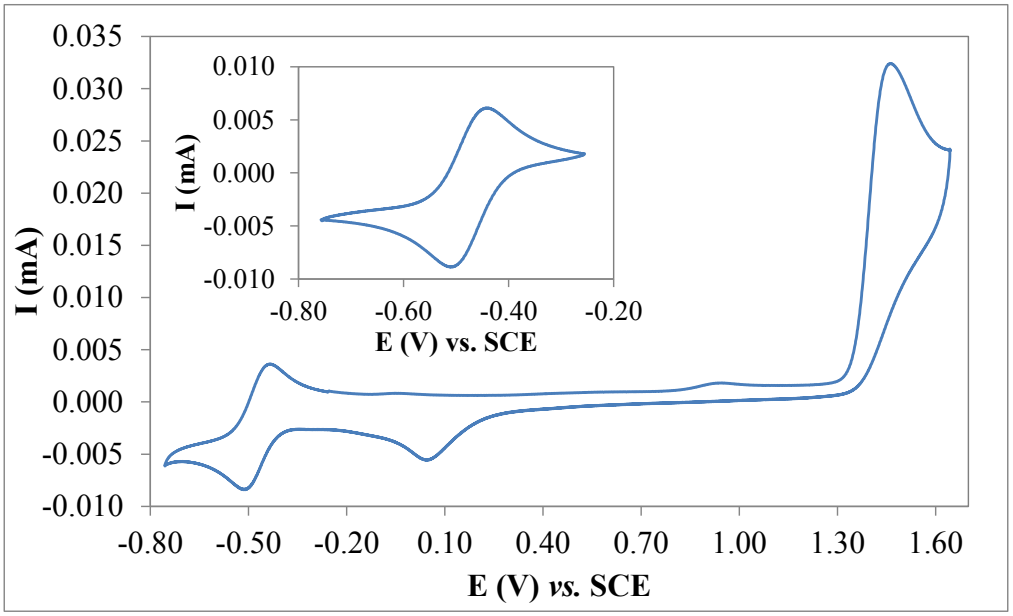


Figure S5 Cyclic voltammogram (-0.80 - 1.60 V) for **3a** (CH_3CN, 0.1 mol dm^{-3} $[(n\text{-}Bu)_4N]PF_6$, 100 mV s^{-1}). Inset shows the reversible reduction peak.

Table S5 Cyclic Voltammetry data for compounds **3a,b** and **4a,b**.

Redox Potential (*vs* SCE)	**3a**	**3b**	**4a**	**4b**
E_{ox}	+1.46	+1.47	+1.37	+1.32
$E_{½red}$	-0.47	-0.48	-0.55	-0.54

X-Ray structure of complex 7

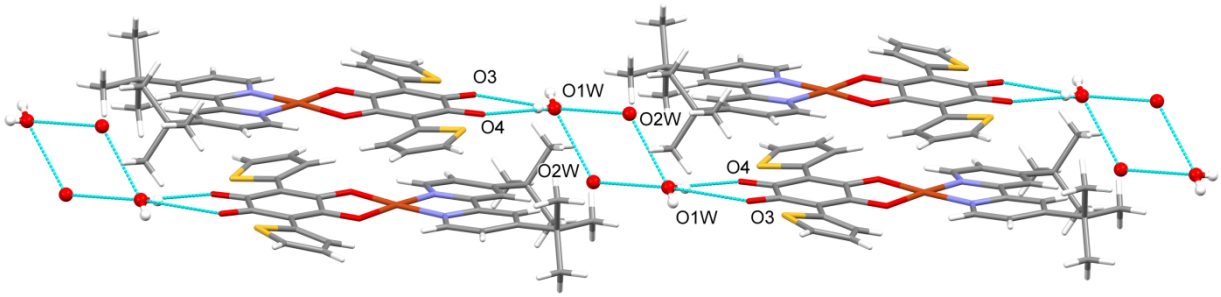


Figure S6 Hydrogen bonding intermolecular interactions between crystallization water molecules and pairs of metal complexes. (Å): O3···O1w 3.04, O4···O1w 2.79, O1w···O2w 2.84, O1w···O2w 2.86.

^{1}H and ^{13}C NMR Spectra

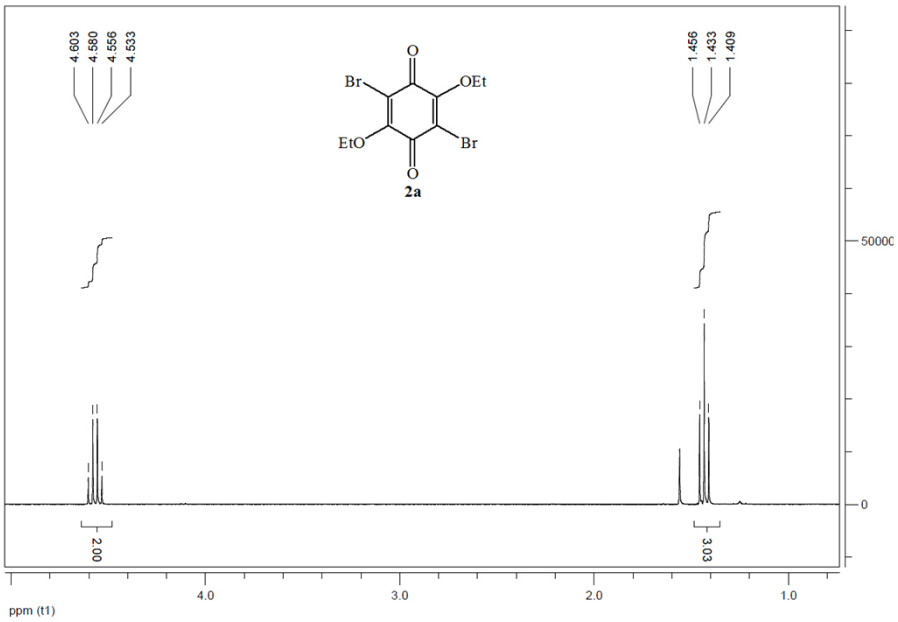


Figure S7 ^{1}H-NMR Spectrum of **2a**.

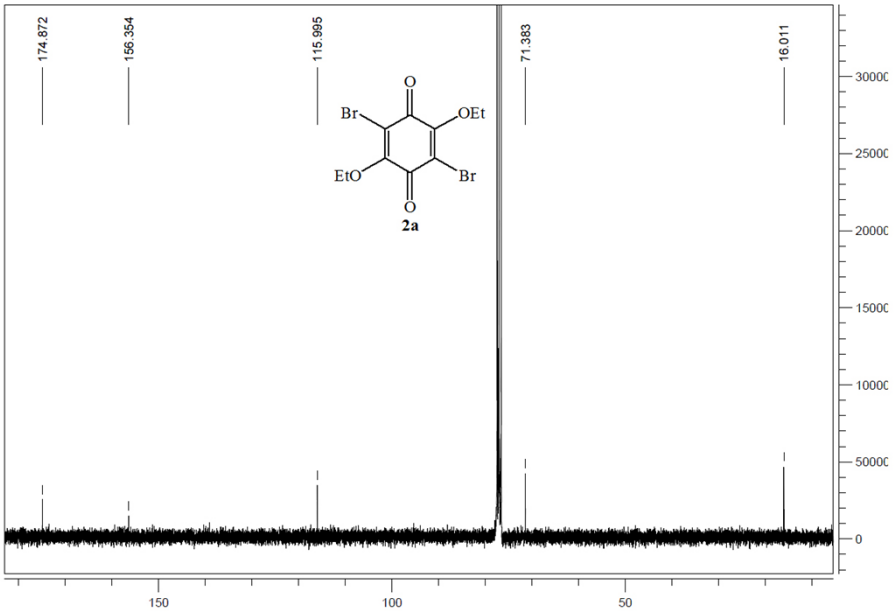


Figure S8 ^{13}C-NMR Spectrum of **2a**.

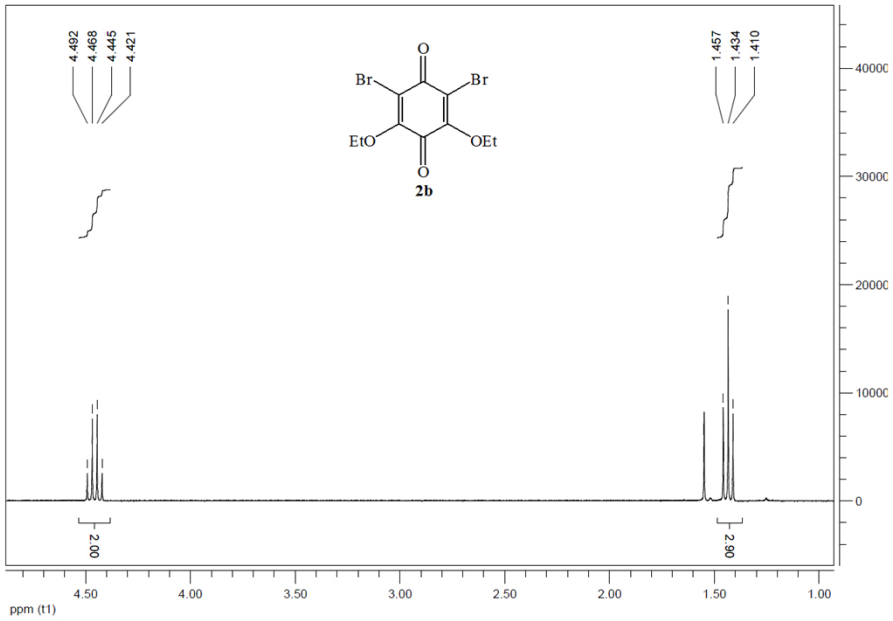


Figure S9 ^{1}H-NMR Spectrum of **2b**.

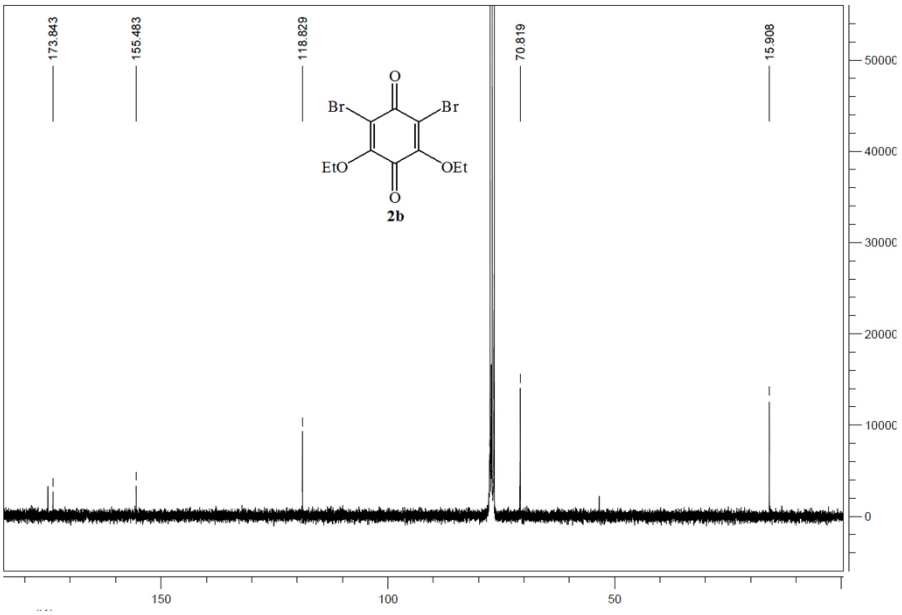


Figure S10 ^{13}C-NMR Spectrum of **2b**.

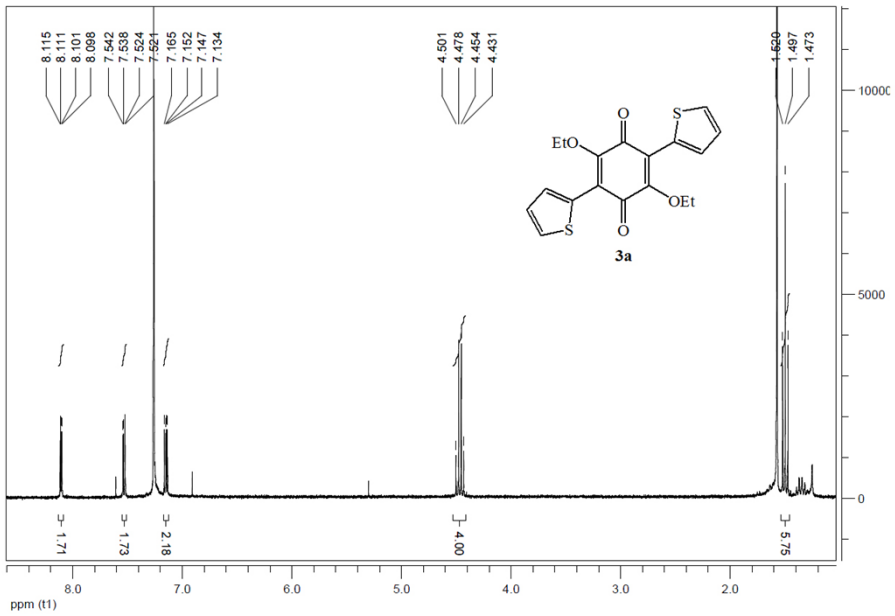


Figure S11 ^{1}H-NMR Spectrum of **3a**.

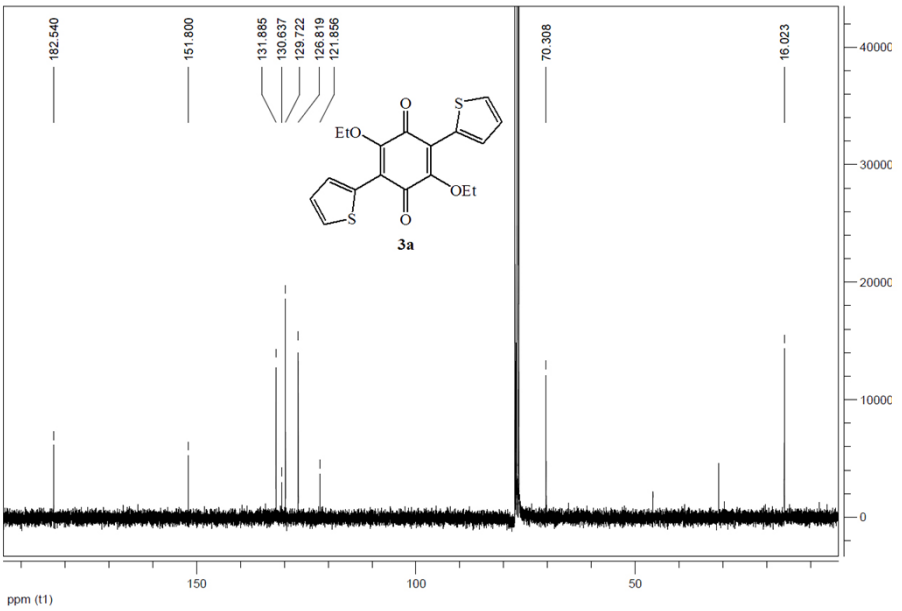


Figure S12 ^{13}C-NMR Spectrum of **3a**.

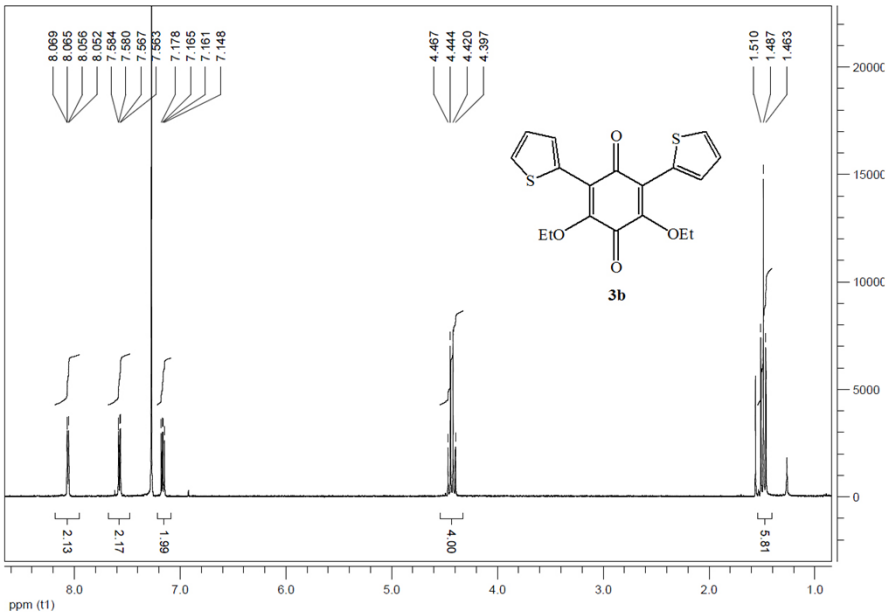


Figure S13 ^{1}H-NMR Spectrum of **3b**.

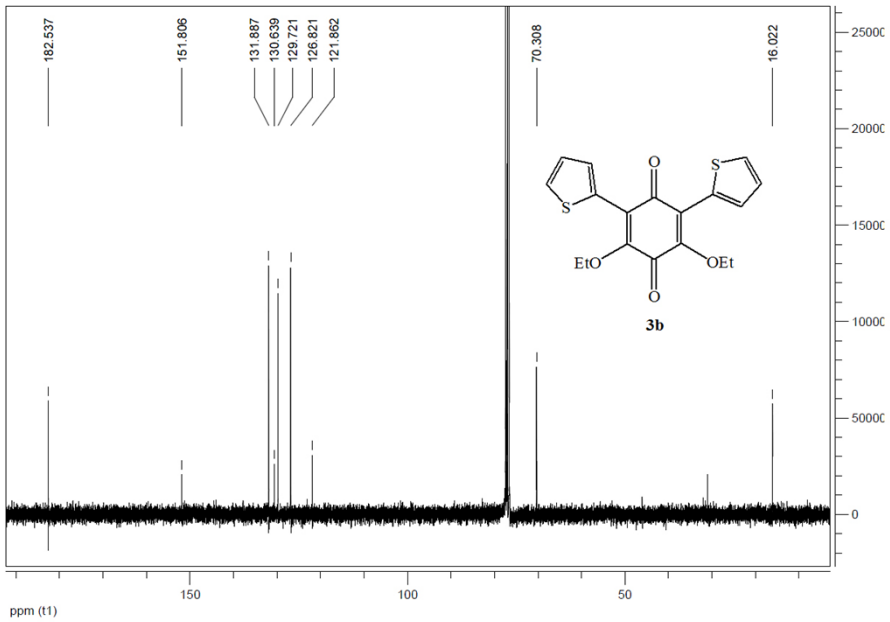


Figure S14 ^{13}C-NMR Spectrum of **3b**.

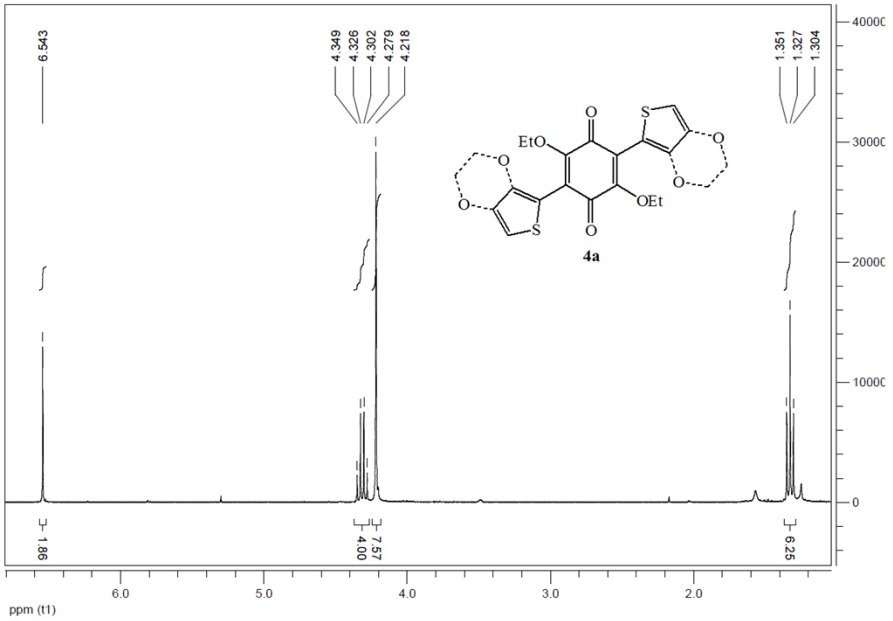


Figure S15 ^{1}H-NMR Spectrum of **4a**.

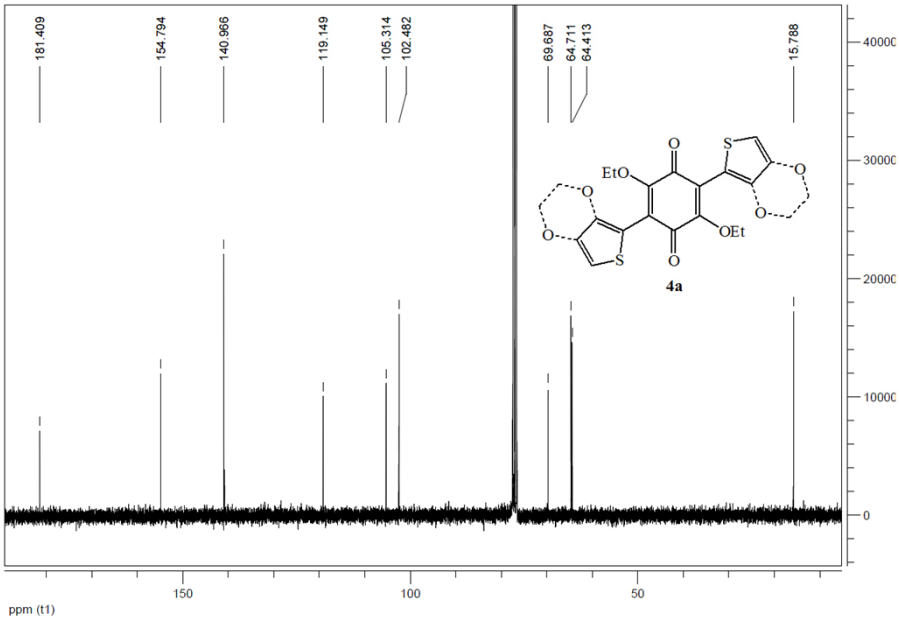


Figure S16 ^{13}C-NMR Spectrum of **4a**.

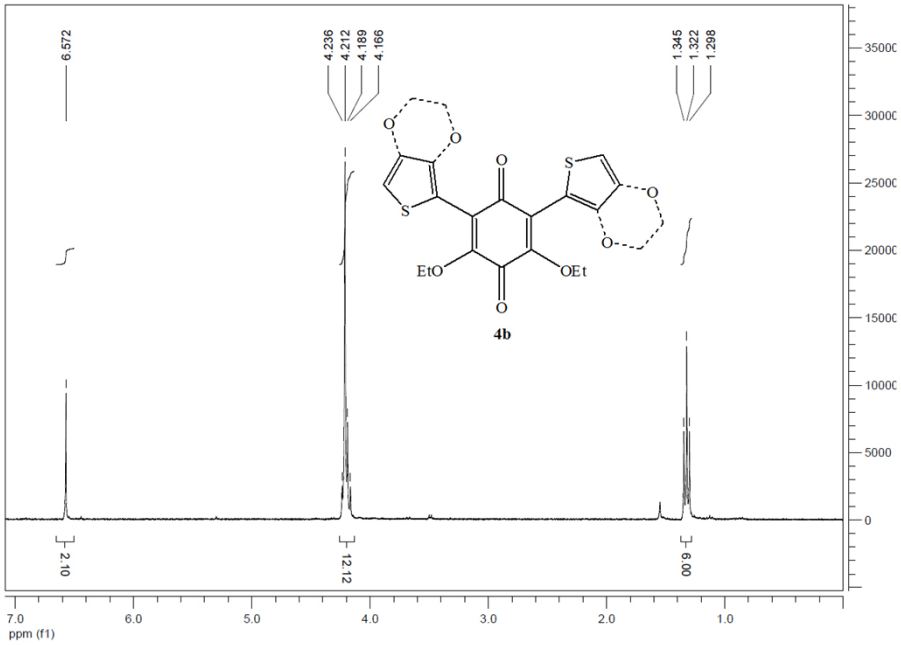


Figure S17 ^{1}H-NMR Spectrum of **4b**.

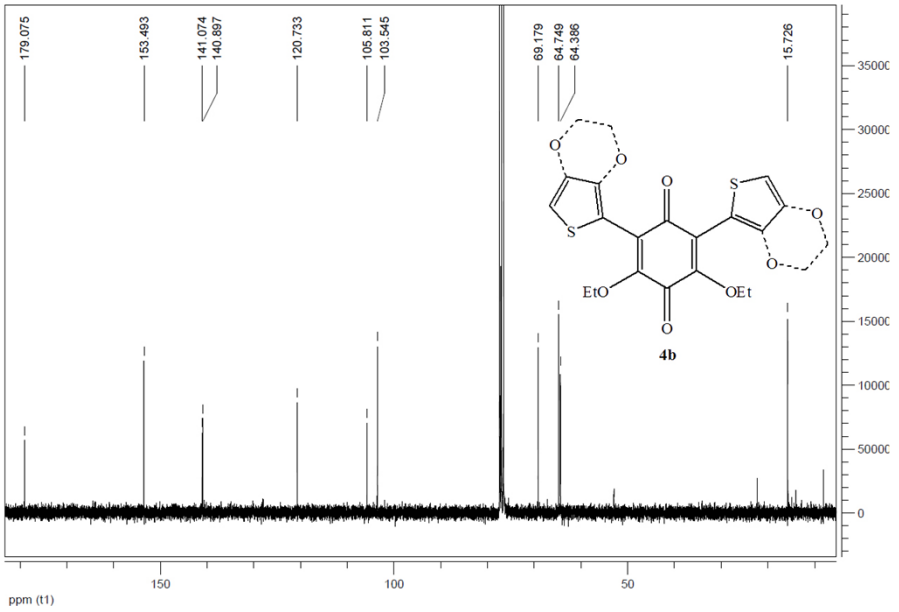


Figure S18 ^{13}C-NMR Spectrum of **4b**.

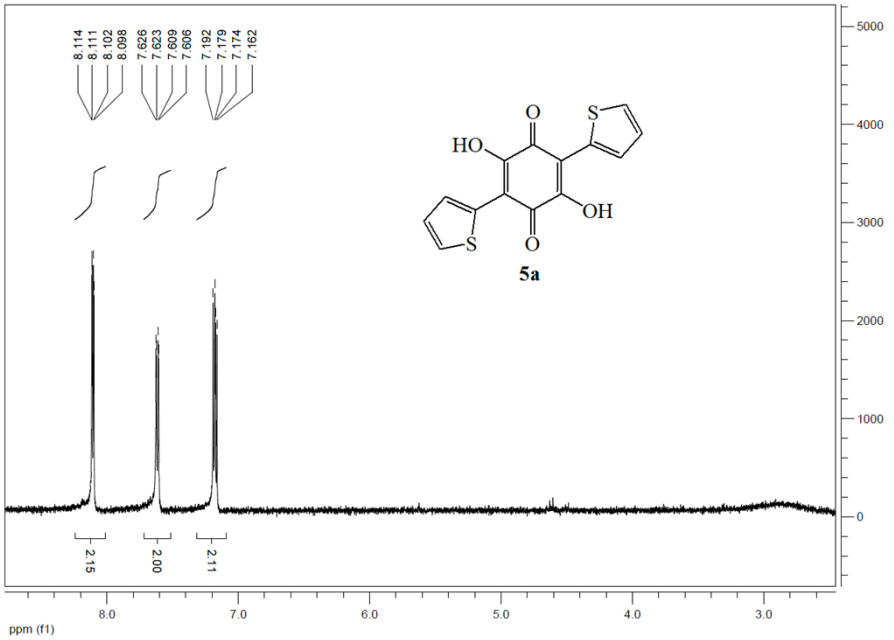


Figure S19 [1]H-NMR Spectrum of **5a**.

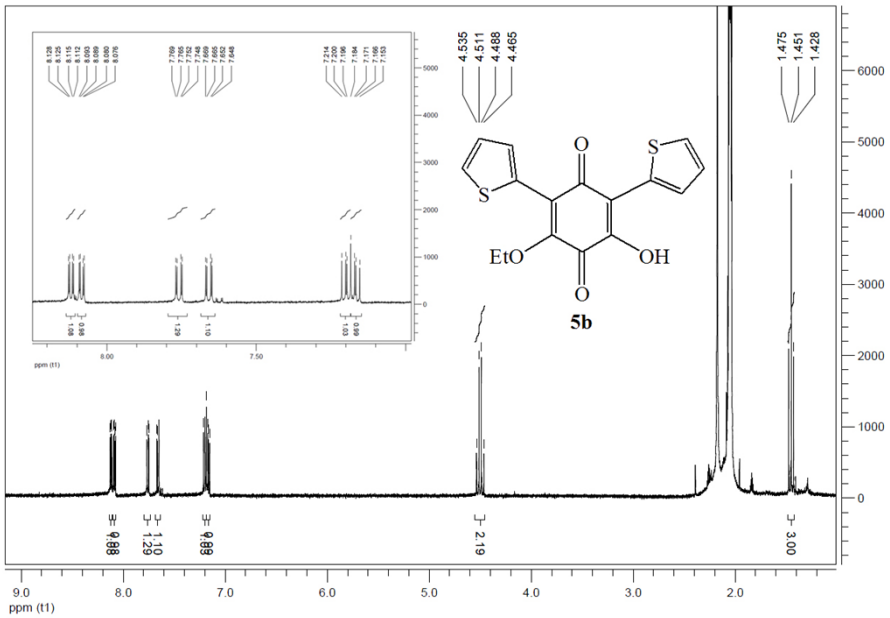


Figure S20 [1]H-NMR Spectrum of **5b**.

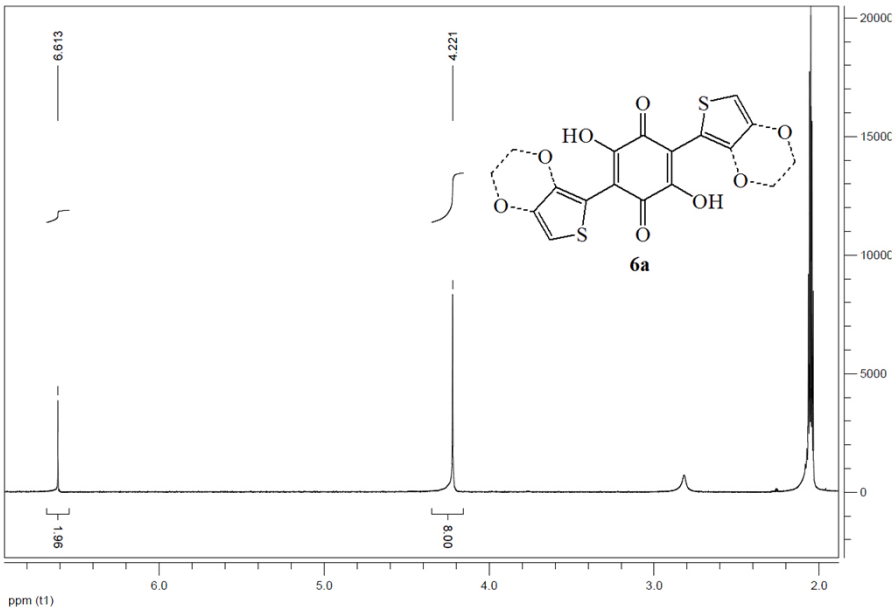


Figure S21 [1]H-NMR Spectrum of **6a**.

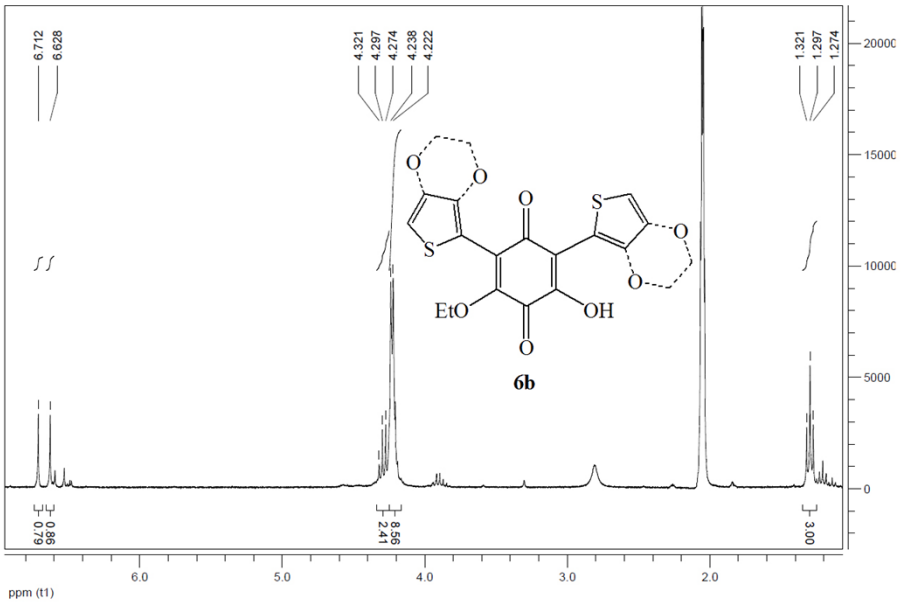


Figure S22 [1]H-NMR Spectrum of **6b**.