Electronic Supplementary Material (ESI)

Experimental and theoretical study of bidirectional photoswitching behavior of the 5,5'-diphenylhydantoin Schiff bases: synthesis, crystal structure and kinetics approaches

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NMR spectra

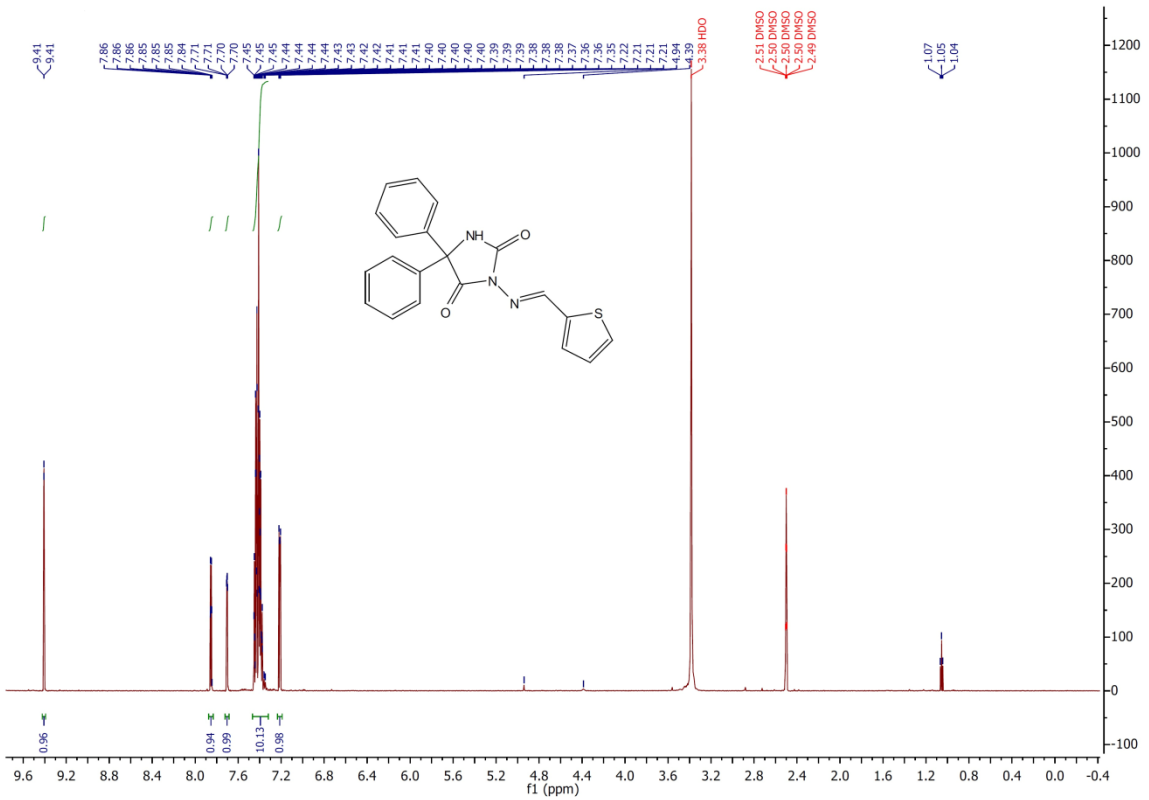

Figure S1. *[1]H-NMR spectrum of* **SB1**

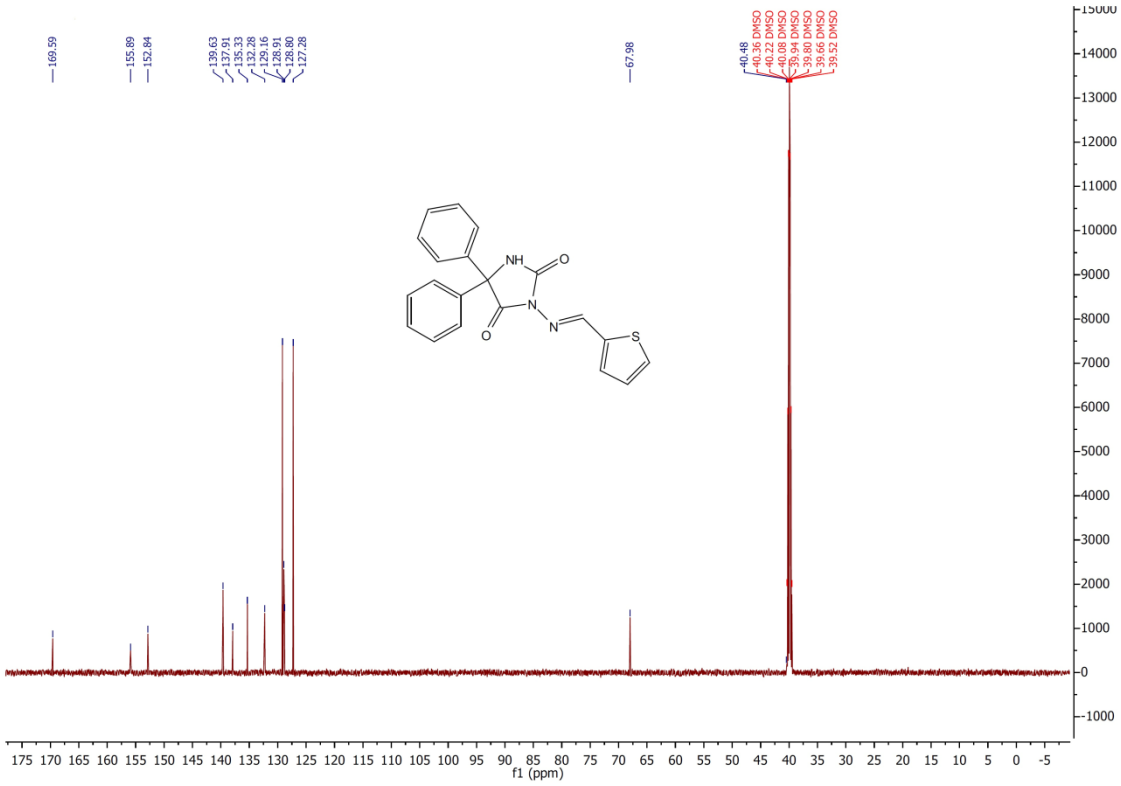

Figure S2. *[13]C-NMR spectrum of* **SB1**

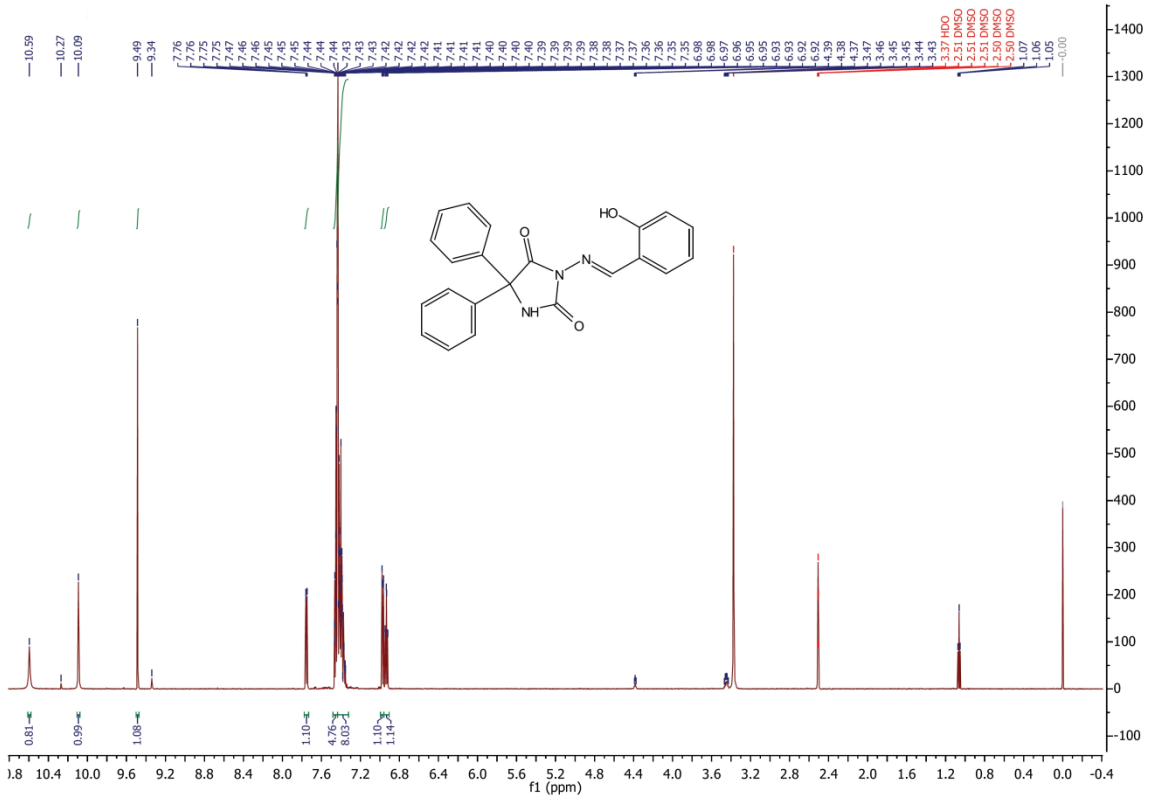

Figure S3*.*[1]*H-NMR spectrum of* **SB2**

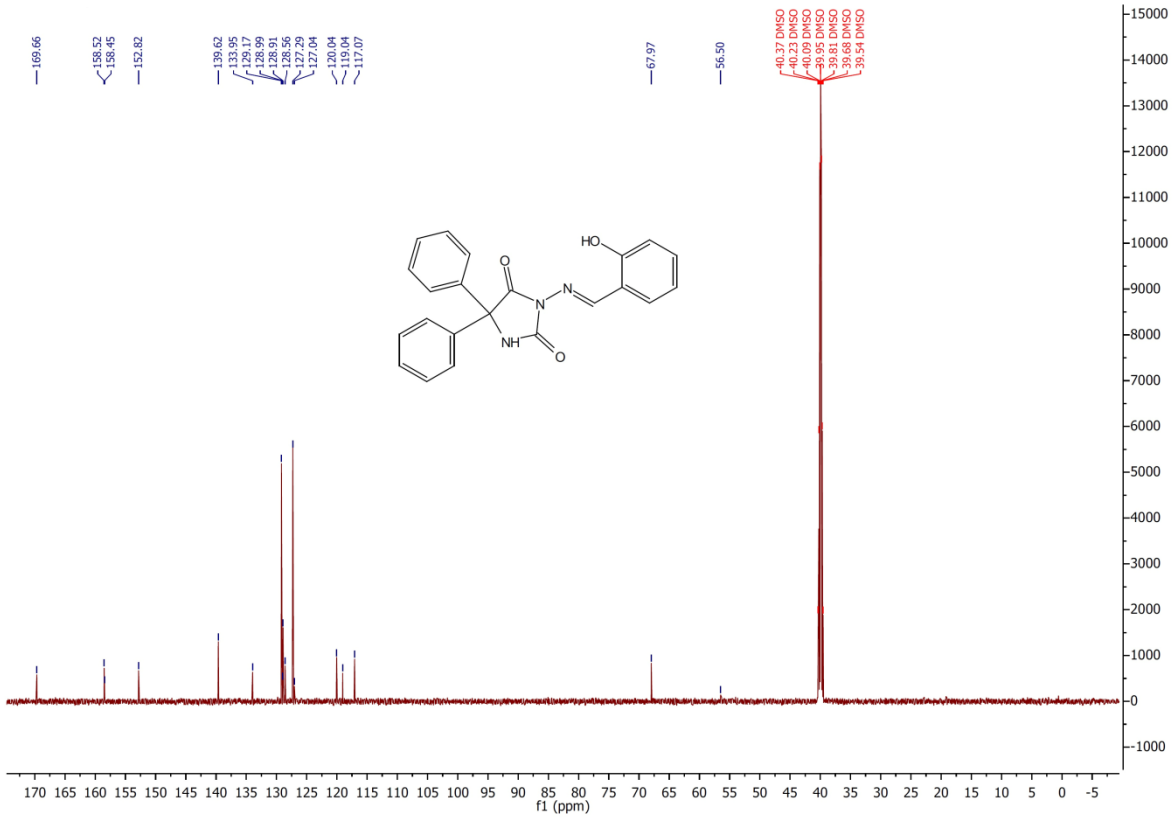

Figure S4*.*[13]*C-NMR spectrum of* **SB2**

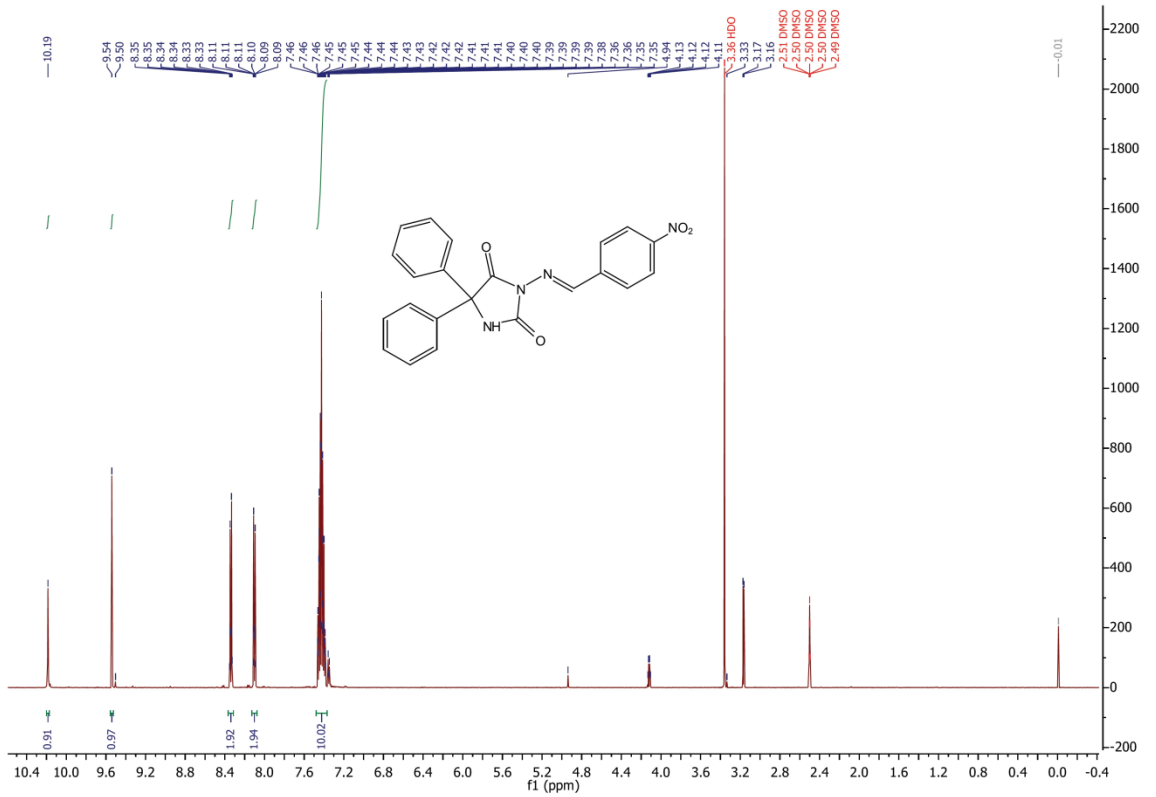

Figure S5. *^{1}H-NMR spectrum of* **SB3**

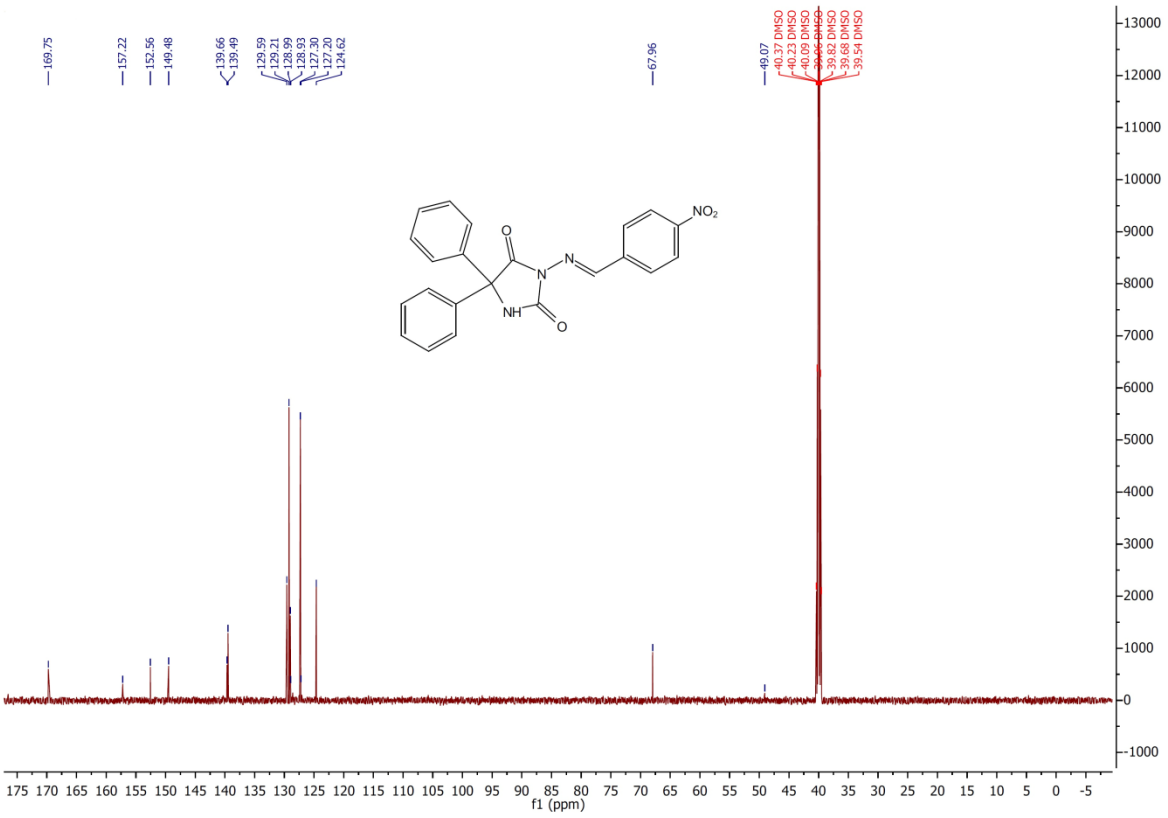

Figure S6. *^{13}C-NMR spectrum of* **SB3**

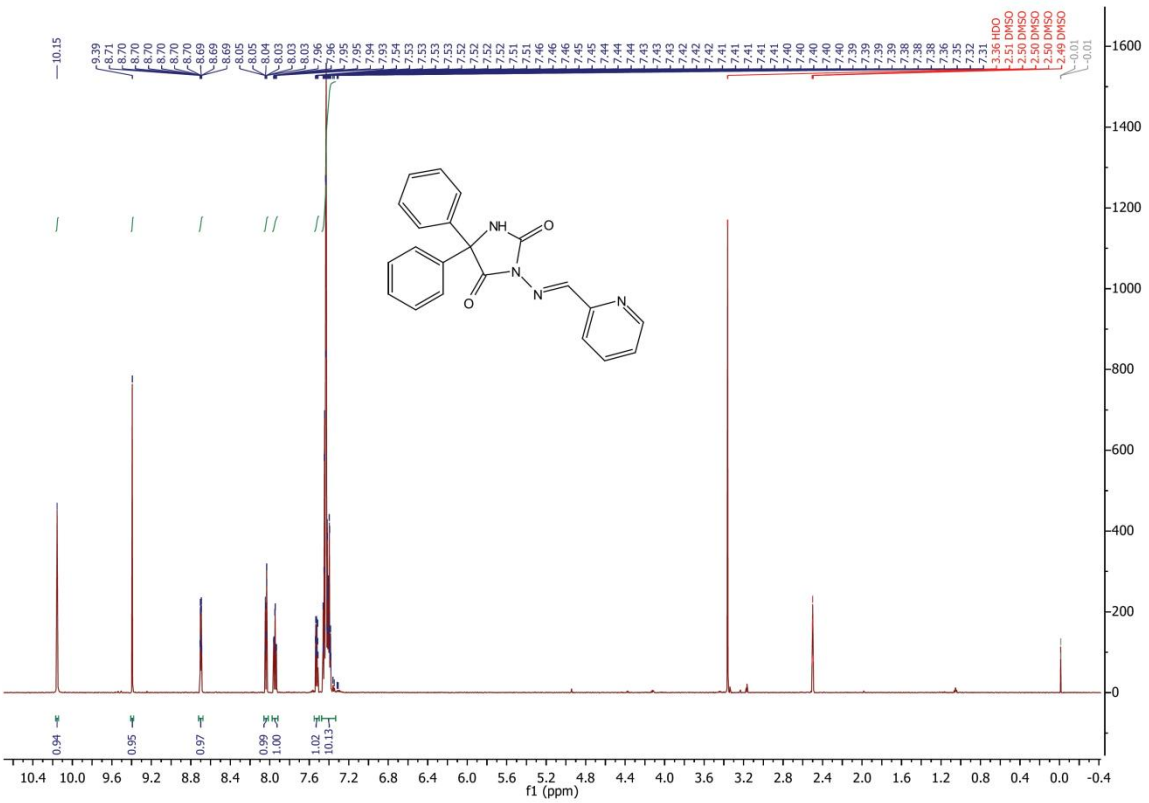

Figure S7*.*[1]*H-NMR spectrum of* **SB4**

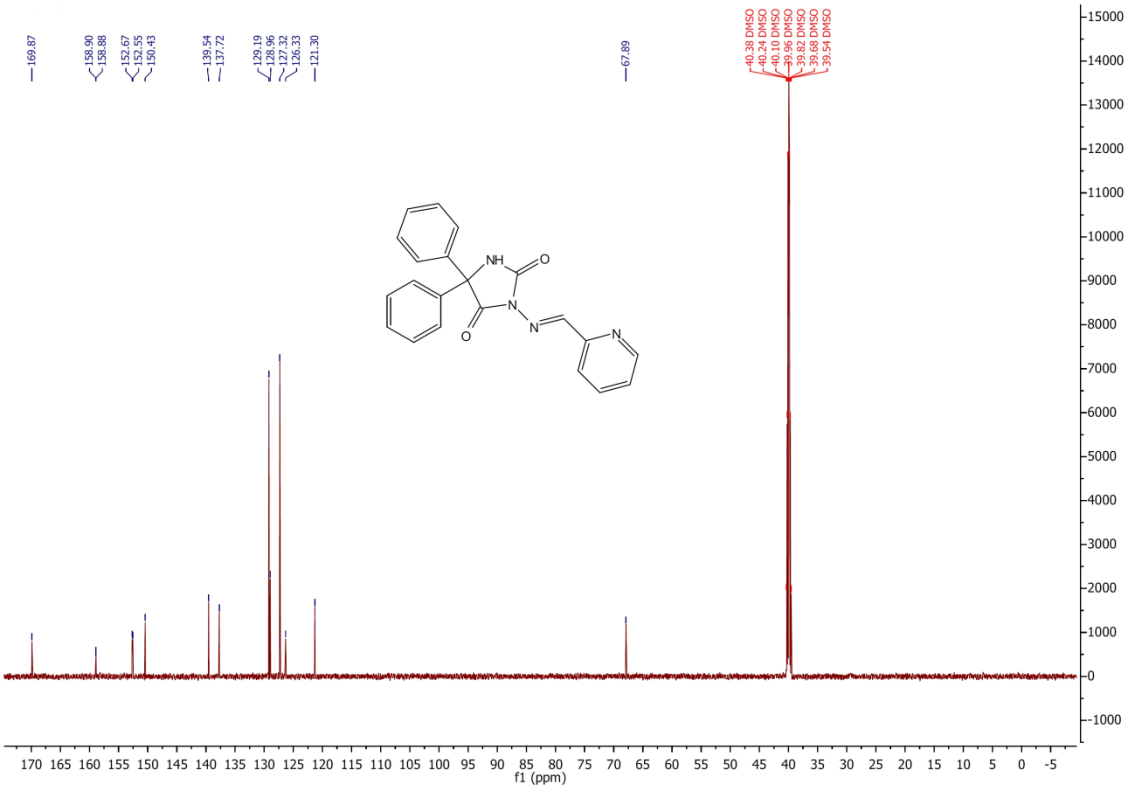

Figure S8*.*[13]*C-NMR spectrum of* **SB4**

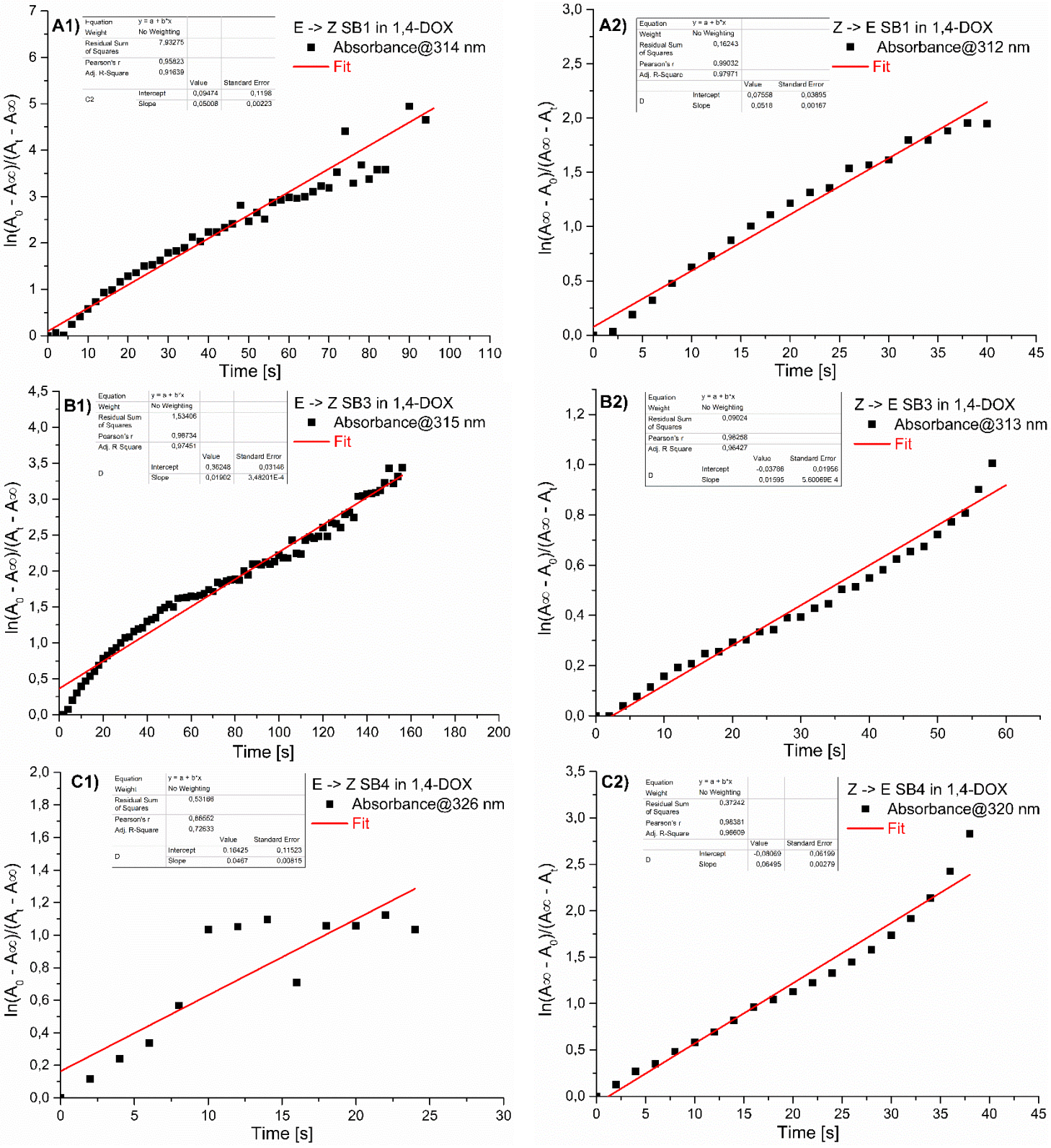

Figure S9. *First-order plots for the E/Z photoisomerization and enol/keto tautomerization of SB's in 1,4-DOX as well as Z/E and keto/enol back relaxation in room temperature.*

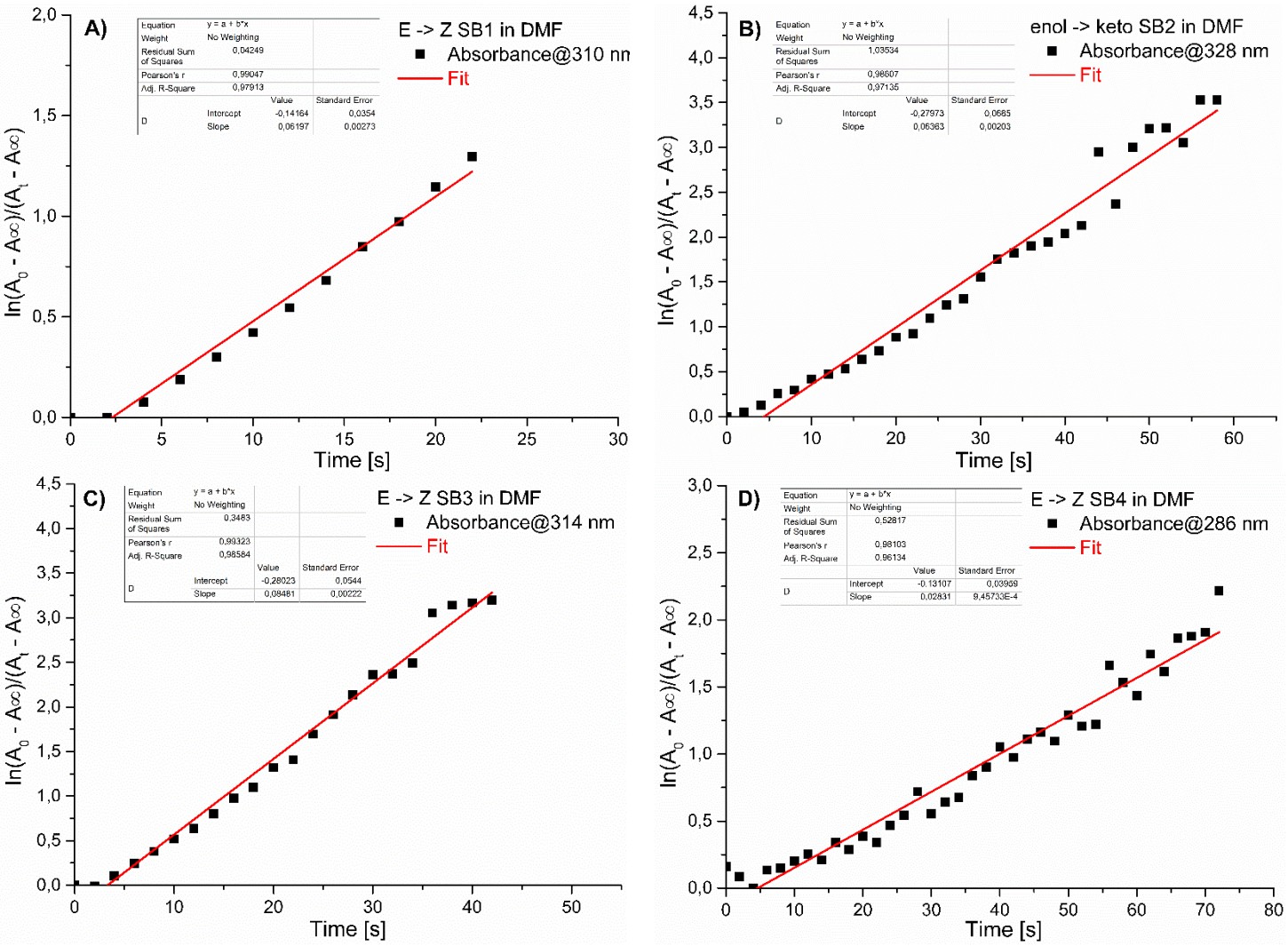

Figure S10. *First-order plots for the E/Z photoisomerization and enol/keto tautomerization of SB's in DMF.*

Electrochemistry

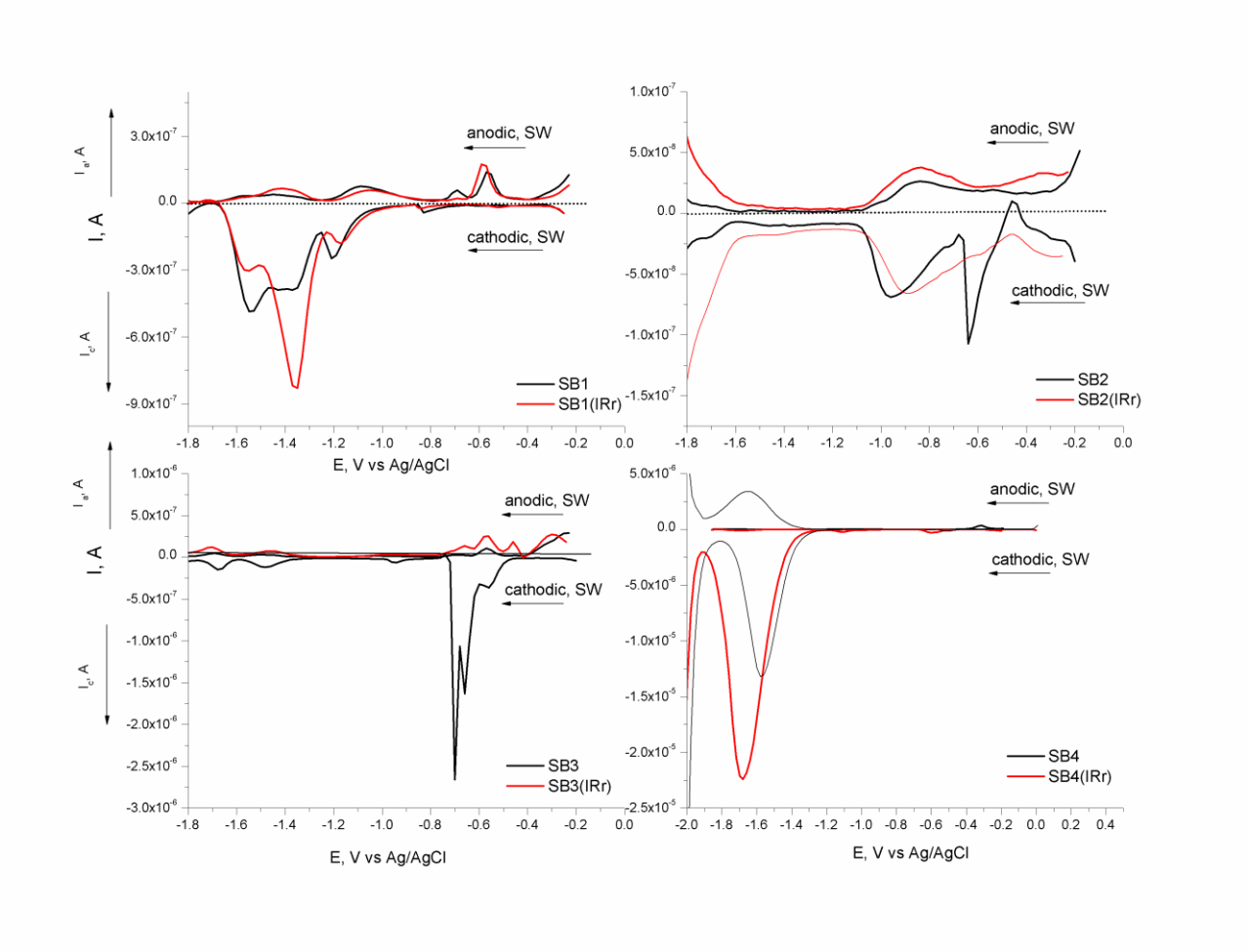

Figure S11. SWVs of 3-amino-5,5'-diphenylhydantoin Schiff bases before and after UV illumination with λ = 350 nm at pH 12.21 (LiOH/LiCl) and concentrations: **SB1**: 2.41×10^{-4}; **SB2**: 1.66×10^{-4}; **SB3**: 8.85×10^{-5}; **SB4**: 9.74×10^{-5} mol L^{-1} and frequency: 50Hz.

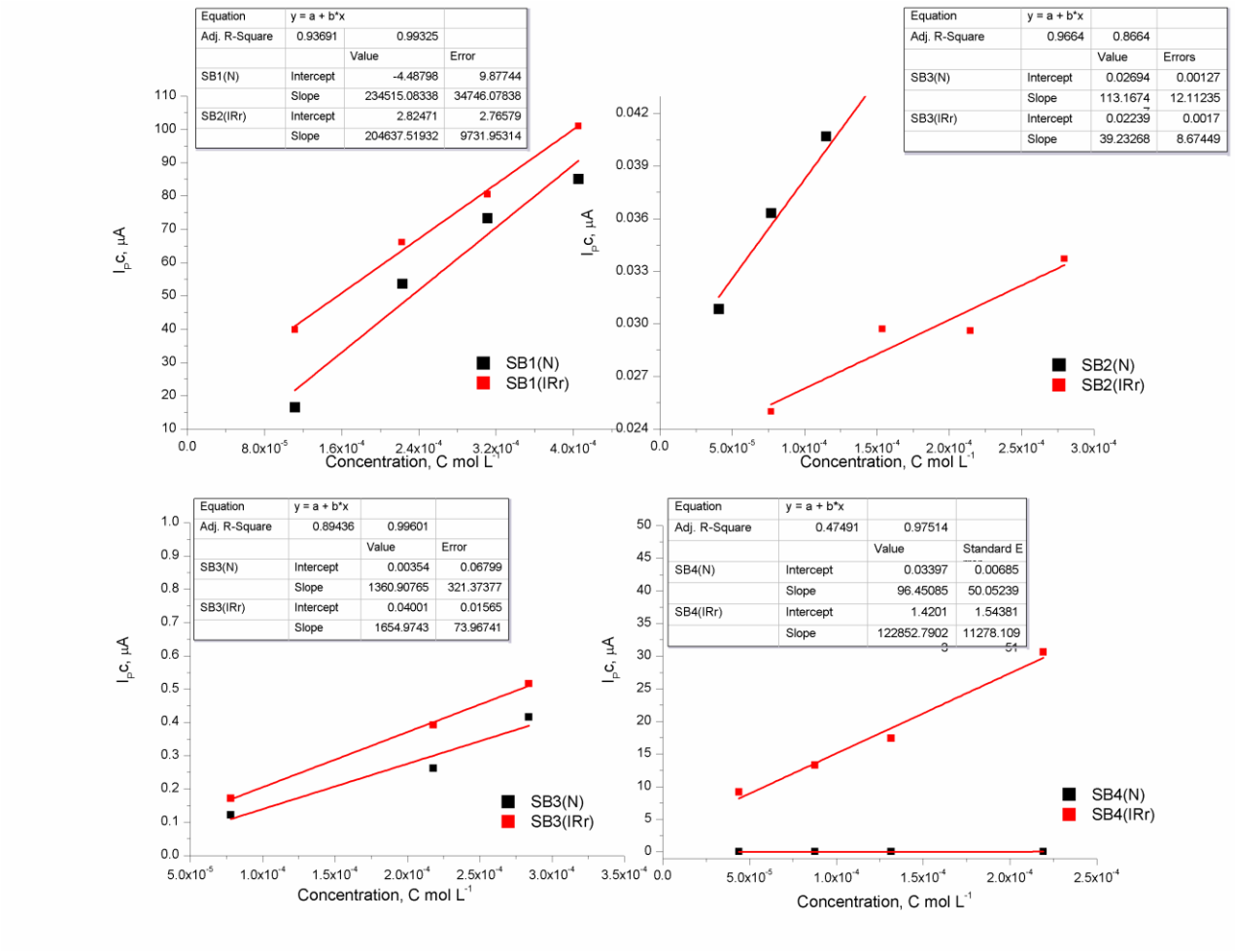

Figure S12. Plot of Ipc (µA) vs. different concentrations (mol L^{-1}) of 3-amino-5,5'-diphenylhydantoin Schiff bases before (**SB**) and after (**SB(IRr)**) UV illumination with λ = 350 nm and scan rate 100 mV s^{-1}

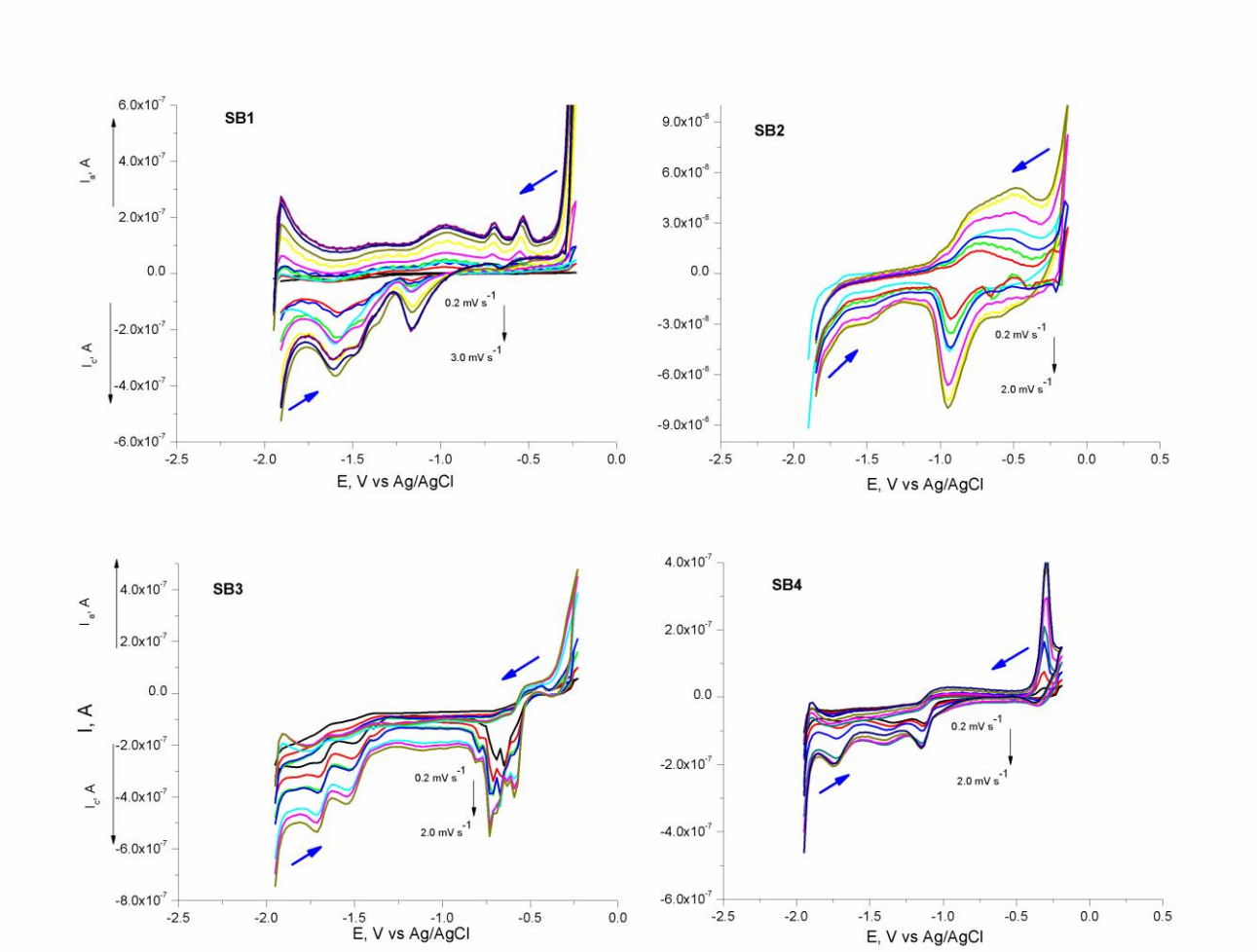

Figure S13. CVs of 3-amino-5,5'-diphenylhydantoin Schiff bases before UV illumination with λ = 350 nm at concentrations: **SB1**: 2.41×10^{-4}; **SB2**: 3.16×10^{-4}; **SB3**: 3.26×10^{-4}; **SB4**: 1.41×10^{-4} mol L^{-1} and different scan rate (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8 and 3.0 cm s^{-1}).

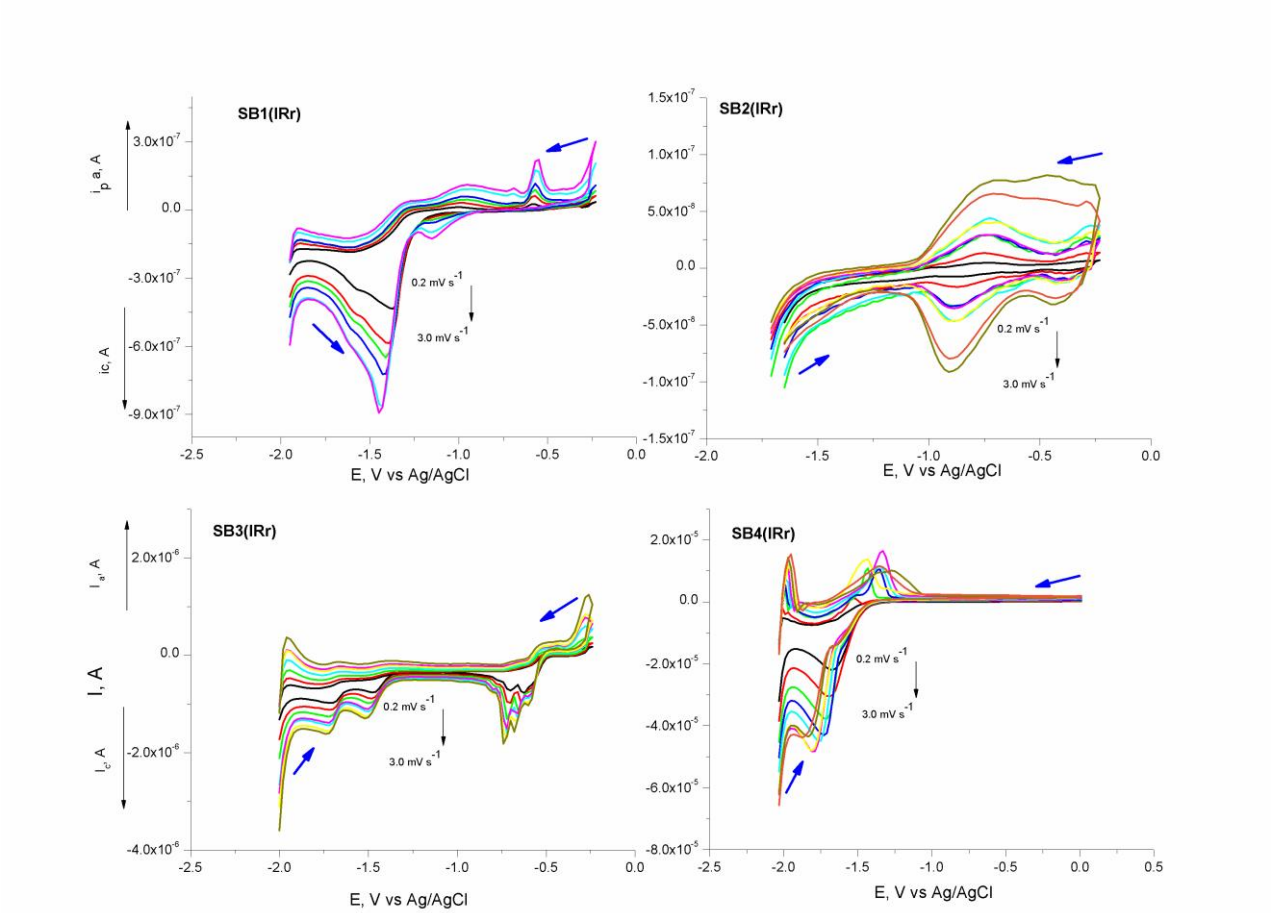

Figure S14. CVs of 3-amino-5,5'-diphenylhydantoin Schiff bases after UV illumination with λ = 350 nm at concentrations: **SB1**: 2.41×10^{-4}; **SB2**: 3.16×10^{-4}; **SB3**: 3.26×10^{-4}; **SB4**: 1.41×10^{-4} mol L^{-1} and different scan rate (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8 and 3.0 cm s^{-1}).

X-ray Diffraction

Table S1. Bond Lengths (Å) for **SB2, SB3** and **SB4** and calculated differences (Δ) between the molecules (only bolded values show substantial deviations, all other are comparable to the esd)

	SB2	Δ (SB2- SB3)	SB3	Δ (SB3- SB4)	SB4	Δ (SB2- SB4)
O1 C1	1.209(4)	-0.002	1.211(2)	-0.002	1.213(2)	-0.004
N3 N2	1.387(4)	0.000	1.387(2)	0.001	1.386(2)	0.001
N3 C10	1.273(5)	0.005	1.268(2)	0.005	1.263(2)	0.010
N2 C1	1.423(4)	0.004	1.419(2)	-0.001	1.420(2)	0.003
N2 C2	1.380(5)	0.006	1.374(2)	-0.011	1.385(2)	-0.005
N1 C1	1.330(5)	-0.007	1.337(2)	-0.004	1.341(2)	**-0.011**
N1 C3	1.459(4)	-0.001	1.460(2)	-0.001	1.461(2)	-0.002
O2 C2	1.214(4)	0.003	1.211(2)	0.010	1.201(2)	0.013
O16 C16	1.359(5)	-	-	-	-	-
C4A C3	1.537(5)	0.002	1.535(2)	0.006	1.529(3)	0.008
C4A C9A	1.382(5)	-0.002	1.384(3)	0.002	1.382(3)	0.000
C4A C5A	1.396(5)	0.008	1.388(3)	**0.014**	1.374(3)	0.022
C2 C3	1.538(5)	0.008	1.530(2)	-0.005	1.535(3)	0.003
C4 C3	1.515(5)	**-0.022**	1.537(2)	0.010	1.527(3)	**-0.012**
C4 C5	1.386(5)	-0.001	1.387(3)	0.011	1.376(3)	0.010
C4 C9	1.376(5)	-0.003	1.379(2)	0.000	1.379(3)	-0.003
C10 C11	1.444(5)	**-0.018**	1.462(3)	-0.008	1.470(3)	-0.026
C11 C16	1.389(6)	-0.001	1.390(3)	-	-	-
C11 C12	1.394(6)	0.007	1.387(3)	0.008	1.379(3)	0.015
C5 C6	1.387(6)	**0.011**	1.376(3)	**-0.010**	1.386(3)	0.001
C9 C8	1.379(5)	-0.002	1.381(3)	-0.003	1.384(3)	-0.005
C16 C15	1.386(6)	0.007	1.379(3)	-	-	-
C8 C7	1.365(5)	-0.002	1.367(3)	0.002	1.365(3)	0.000
C7 C6	1.364(6)	-0.013	1.377(3)	**0.015**	1.362(4)	0.002
C9A C8A	1.375(6)	-0.010	1.385(3)	0.004	1.381(4)	-0.006
C5A C6A	1.367(6)	**-0.014**	1.381(3)	-0.007	1.388(4)	**-0.021**
C12 C13	1.370(6)	-0.002	1.372(3)	-0.008	1.380(3)	-0.010
C13 C14	1.352(6)	**-0.027**	1.379(3)	**0.015**	1.364(3)	-0.012
C8A C7A	1.376(7)	0.007	1.369(3)	0.004	1.365(5)	**0.011**
C15 C14	1.366(6)	-0.004	1.370(3)	0.008	1.362(3)	0.004
C6A C7A	1.365(6)	-0.005	1.370(3)	**0.015**	1.355(5)	0.010
N14 C14	-	-	1.469(3)	-	-	-
N14 O14A	-	-	1.221(2)	-	-	-
N14 O14B	-	-	1.224(3)	-	-	-
N4 C11	-	-	-	-	1.338(2)	-
N4 C15	-	-	-	-	1.337(2)	-