Supplementary information

The mechanism of the photochromic transformation of spirorhodamines.

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Contents

A) Absorption and emission spectra in ethanol and in TFA 4.1 mM.

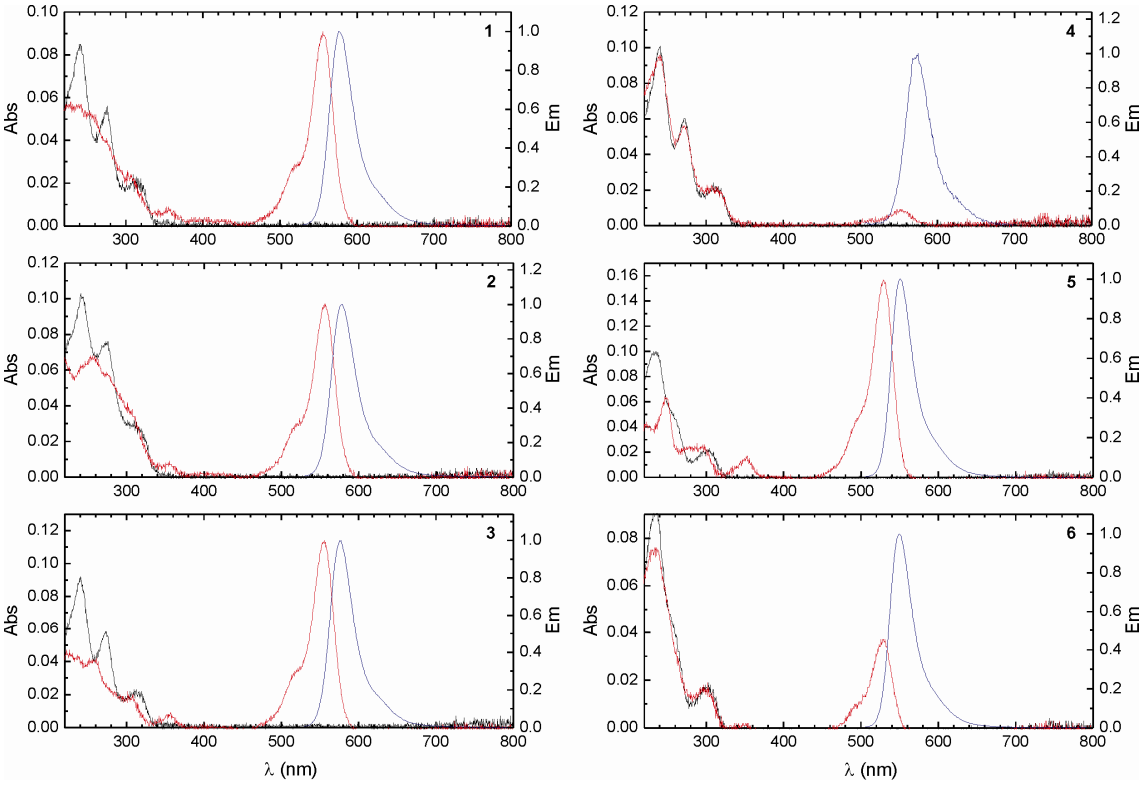


Figure S1. Absorption spectra of compounds 1–6 (2.3 μM) in ethanol (black lines) and in 4.1 mM TFA (red lines), and emission of the TFA solutions (blue lines).

B) Selected kinetics decays with the corresponding fits to a monoexponential function and the residuals.

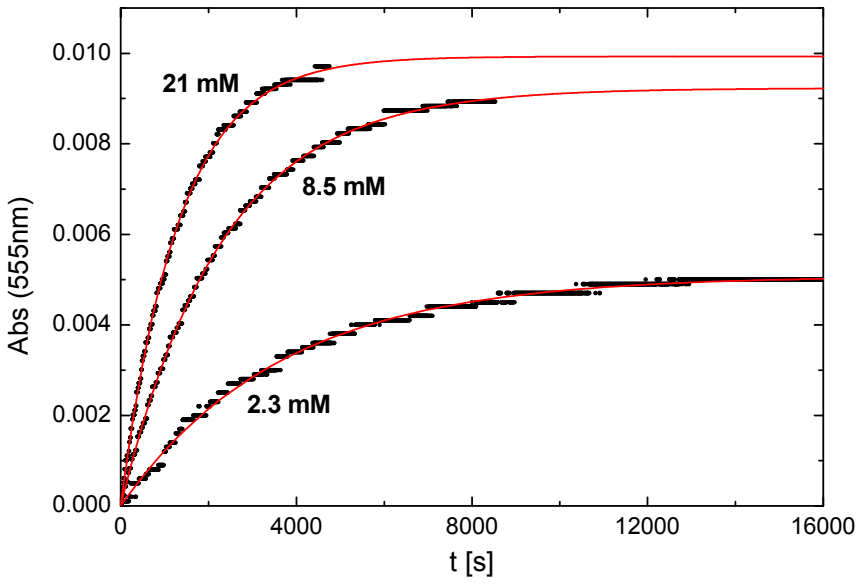


Figure S2. Dark kinetics for compound **4** after a TFA addition to a final concentration of (from bottom to top) 2.3 mM, 8.5 mM and 21 mM, and the corresponding fitted functions (red lines). The extent of the reaction was followed by the absorption at 555 nm.

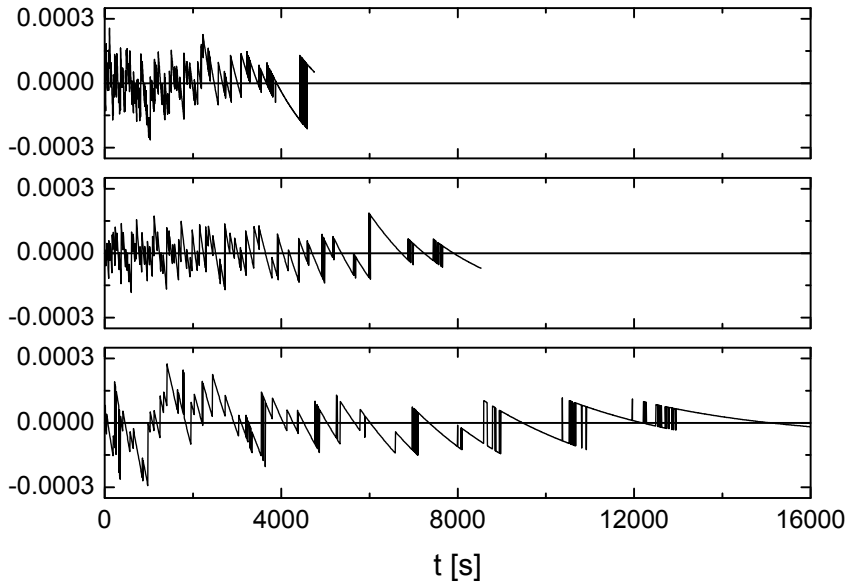


Figure S3. Residuals for the exponential fits to the decays shown in figure S2.

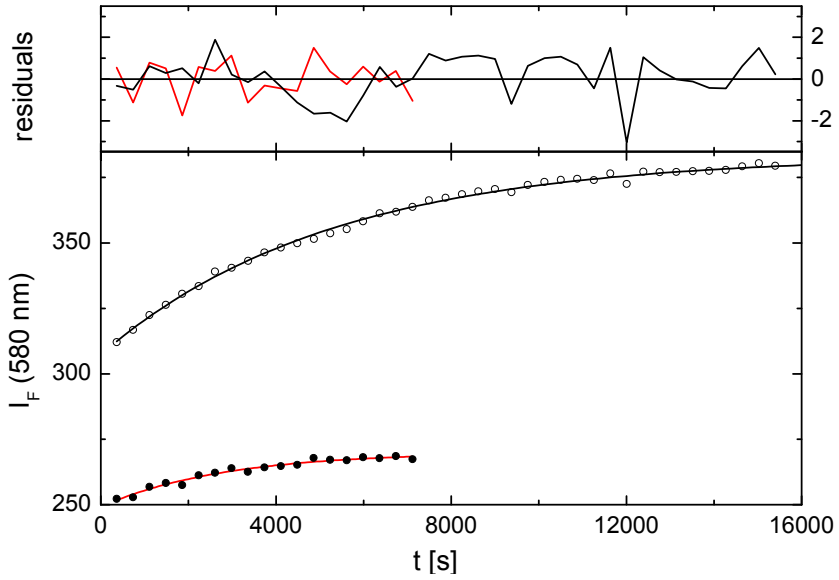


Figure S4. Kinetics under continuous irradiation with 315 nm light for compound **3** at a TFA concentration of 3.5 mM (whollow circles, black lines) and 7.8 mM (filled circles, red lines). Excitation was performed at 520 nm and fluorescence intensity was detected at 580 nm.

C) Lifetimes of the exponential decays for every compound at different TFA concentrations.

Compound 1

[TFA] /M	τ_{H+} / s	k_{H+} / s^{-1}	[TFA] /M	τ_{PH} / s	k_{PH} / s^{-1}	[TFA] /M	τ_{Th} / s	k_{Th} / s^{-1}
1.1E-02	1.8E+02	5.6E-03	7.6E-03	1.4E+02	7.3E-03	3.6E-03	1.0E+03	9.6E-04
7.6E-03	2.8E+02	3.6E-03	3.6E-03	3.2E+02	3.1E-03	3.0E-03	1.1E+03	9.5E-04
3.6E-03	5.8E+02	1.7E-03	3.0E-03	4.7E+02	2.1E-03	1.8E-03	2.2E+03	4.6E-04
3.0E-03	7.2E+02	1.4E-03	1.8E-03	6.9E+02	1.4E-03	9.7E-04	5.9E+03	1.7E-04
1.8E-03	1.7E+03	6.0E-04	9.7E-04	1.9E+03	5.3E-04	6.4E-04	7.3E+03	1.4E-04
9.7E-04	4.1E+03	2.4E-04	6.4E-04	2.0E+03	5.0E-04	3.6E-04	1.1E+04	9.2E-05
6.4E-04	6.4E+03	1.6E-04	3.6E-04	3.4E+03	3.0E-04			
3.6E-04	1.3E+04	7.9E-05						

Compound 2

[TFA] /M	τ_{H+} / s	k_{H+} / s^{-1}	[TFA] /M	τ_{PH} / s	k_{PH} / s^{-1}	[TFA] /M	τ_{Th} / s	k_{Th} / s^{-1}
8.5E-03	2.8E+02	3.5E-03	3.5E-03	7.2E+02	1.4E-03	3.5E-03	1.7E+03	6.0E-04
6.3E-03	3.0E+02	3.3E-03	1.4E-03	1.7E+03	5.8E-04	1.4E-03	3.1E+03	3.3E-04
4.2E-03	5.0E+02	2.0E-03	8.8E-04	2.8E+03	3.6E-04	8.8E-04	4.3E+03	2.3E-04
2.1E-03	1.1E+03	9.3E-04	5.3E-04	3.7E+03	2.7E-04	3.5E-04	5.7E+03	1.8E-04
8.5E-04	3.4E+03	2.9E-04	1.7E-04	5.5E+03	1.8E-04	8.7E-05	8.6E+03	1.2E-04
8.5E-04	3.8E+03	2.6E-04	1.0E-04	8.9E+03	1.1E-04			
8.5E-04	3.9E+03	2.6E-04						
7.4E-04	2.5E+03	4.0E-04						
7.4E-04	2.9E+03	3.4E-04						
4.9E-04	3.0E+03	3.4E-04						
4.9E-04	3.0E+03	3.4E-04						
8.5E-05	1.1E+04	8.8E-05						
8.5E-05	1.1E+04	9.2E-05						
8.5E-06	8.1E+03	1.2E-04						

Compound 3

[TFA] /M	τ_{H+} / s	k_{H+} / s^{-1}	[TFA] /M	τ_{PH} / s	k_{PH} / s^{-1}	[TFA] /M	τ_{Th} / s	k_{Th} / s^{-1}
8.8E-02	4.4E+02	2.3E-03	1.1E-02	2.2E+03	4.6E-04	8.8E-02	6.5E+02	1.5E-03
4.4E-02	7.4E+02	1.3E-03	7.7E-03	2.8E+03	3.6E-04	4.4E-02	7.4E+02	1.3E-03
2.2E-02	2.4E+03	4.2E-04	5.0E-03	3.9E+03	2.6E-04	2.2E-02	2.9E+03	3.4E-04
1.5E-02	3.7E+03	2.7E-04	3.5E-03	5.3E+03	1.9E-04	1.1E-02	6.2E+03	1.6E-04
7.7E-03	4.9E+03	2.0E-04				9.2E-03	9.2E+03	1.1E-04
3.5E-03	2.2E+04	4.6E-05				3.5E-03	2.2E+04	4.5E-05

Compound 4

[TFA] /M	τ_{H+} / s	k_{H+} / s^{-1}	[TFA] /M	τ_{PH} / s	k_{PH} / s^{-1}	[TFA] /M	τ_{Th} / s	k_{Th} / s^{-1}
2.1E-02	1.3E+03	7.6E-04	2.1E-02	1.2E+03	8.2E-04	1.4E-02	1.7E+03	5.8E-04
1.4E-02	1.8E+03	5.7E-04	1.8E-02	1.3E+03	7.6E-04	1.2E-02	1.9E+03	5.4E-04
1.4E-02	1.7E+03	5.8E-04	1.4E-02	1.5E+03	6.6E-04	7.1E-03	2.2E+03	4.6E-04
8.5E-03	2.3E+03	4.3E-04	4.2E-03	1.9E+03	5.3E-04	6.1E-03	2.3E+03	4.4E-04
2.4E-03	3.7E+03	2.7E-04						

Compound 5

[TFA]/M	τ_{H+} / s	k_{H+} / s^{-1}	[TFA]/M	τ_{PH} / s	k_{PH} / s^{-1}	[TFA]/M	τ_{Th} / s	k_{Th} / s^{-1}
7.7E-02	4.7E+01	2.1E-02	7.9E-03	1.3E+03	7.6E-04	8.2E-03	3.6E+02	2.7E-03
3.9E-02	1.3E+02	8.0E-03	6.2E-03	1.6E+03	6.1E-04	6.2E-03	4.7E+02	2.1E-03
1.3E-02	2.0E+02	4.9E-03	3.9E-03	2.7E+03	3.7E-04	3.9E-03	9.1E+02	1.1E-03
8.2E-03	7.0E+02	1.4E-03	2.1E-03	5.8E+03	1.7E-04	2.1E-03	1.5E+03	6.6E-04
4.1E-03	2.0E+03	4.9E-04						
2.0E-03	6.0E+03	1.7E-04						
8.4E-04	1.2E+04	8.1E-05						

Compound 6

[TFA]/M	τ_{H+} / s	k_{H+} / s^{-1}
2.4E-02	3.0E+03	3.3E-04
1.7E-02	3.2E+03	3.1E-04
1.4E-02	4.0E+03	2.5E-04
7.1E-03	4.3E+03	2.3E-04
2.4E-03	5.3E+03	1.9E-04

D) Derivation of Equations 1, 2, and 3a

The equilibrium constant for the proton assisted ring opening is:

$$K_{eq} = \frac{[OFH^+]}{[SF].[H^+]} \qquad \text{(S1)}$$

Considering the mass balance

$$C_0 = [SF] + [OFH^+] \qquad \text{(S2)}$$

And the relation between the concentrations of the two isomers and the respective values of the absorbance measured at the UV maximum for SF, and at the maximum in the visible for OFH^+, we can write the concentrations as:

$$C_0 = A_0^{UV} \Big/ \varepsilon_{SF}^{UV}$$
$$[OFH^+] = A_\infty^{VIS} \Big/ \varepsilon_{OFH^+}^{VIS} \qquad \text{(S3)}$$

Eq. S1 can be rearranged as:

$$\frac{1}{K_{eq}.[H^+]} = \frac{C_0}{[OFH^+]} - 1 = \frac{A_0^{UV} \Big/ \varepsilon_{SF}^{UV}}{A_\infty^{VIS} \Big/ \varepsilon_{OFH^+}^{VIS}} - 1 \qquad \text{(S4)}$$

This can be rearranged to Eq 1 in the text upon multiplication by

$$A^0 = A_0^{UV} \frac{\varepsilon_{SF}^{UV}}{\varepsilon_{OFH^+}^{VIS}} \qquad \text{(S5)}$$

According to the kinetic scheme 5, the rate of formation of OFH^+ is:

$$\left(\frac{d[OFH^+]}{dt}\right)_{Th} = k_3.[SFH^+] - k_4.[OFH^+] \qquad \text{(S6)}$$

Considering that i) the protonation step is at equilibrium:

$$[SFH^+] = \frac{k_1.[SF].[H^+]}{k_2} \qquad \text{(S7)}$$

and ii) the mass balance (Eq. S3), Eq. S6can be rewritten as:

$$\left(\frac{d[OFH^+]}{dt}\right)_{Th} = \left(\frac{k_3.k_1.[H^+]}{k_2} + k_4\right).[SF] - k_4.C_0 \qquad \text{(S8)}$$

This is identical to Eq. 2 of the text. Upon making the substitution

$$\begin{aligned} u &= \left(\frac{k_3.k_1.[H^+]}{k_2} + k_4\right).[SF] - k_4.C_0 \\ du &= \left(\frac{k_3.k_1.[H^+]}{k_2} + k_4\right).d[SF] = -\left(\frac{k_3.k_1.[H^+]}{k_2} + k_4\right).d[OFH^+] \end{aligned} \qquad \text{(S9)}$$

Eq. S9 can be rearranged to

$$d(\ln u) = -\left(\frac{k_3.k_1.[H^+]}{k_2} + k_4\right).dt \qquad \text{(S10)}$$

Eq. S10 can be readily integrated to Eq. 3a of the text with the condition that the initial concentration of OFH^+ is zero.

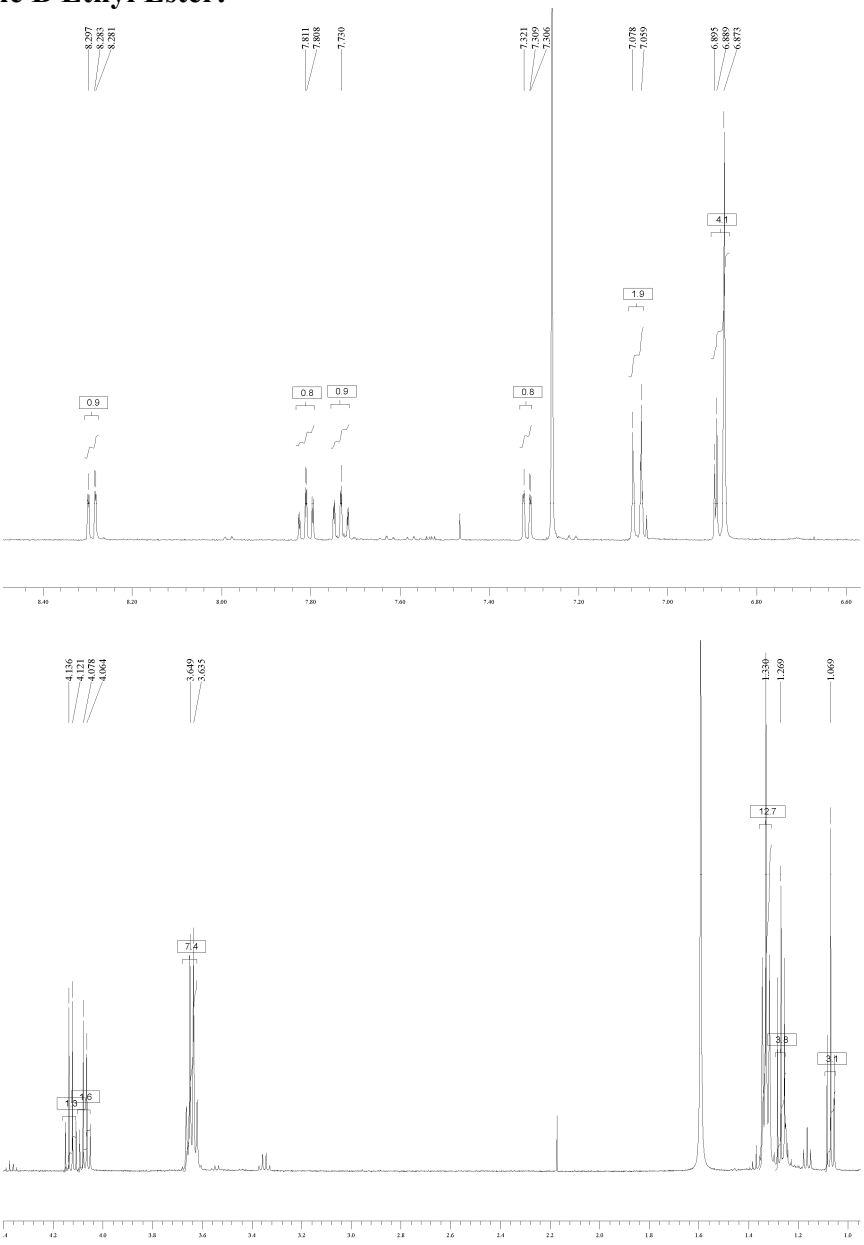
E) Parameters of the linear fits for kinetic constants as a function of proton concentration.

Note that errors in the intercept are of the order of 0.001; therefore negative values for $k_{0,i}$, which are physically inconsistent, represent values that are too small to be measured by our method, and thus they are zero within the experimental error.

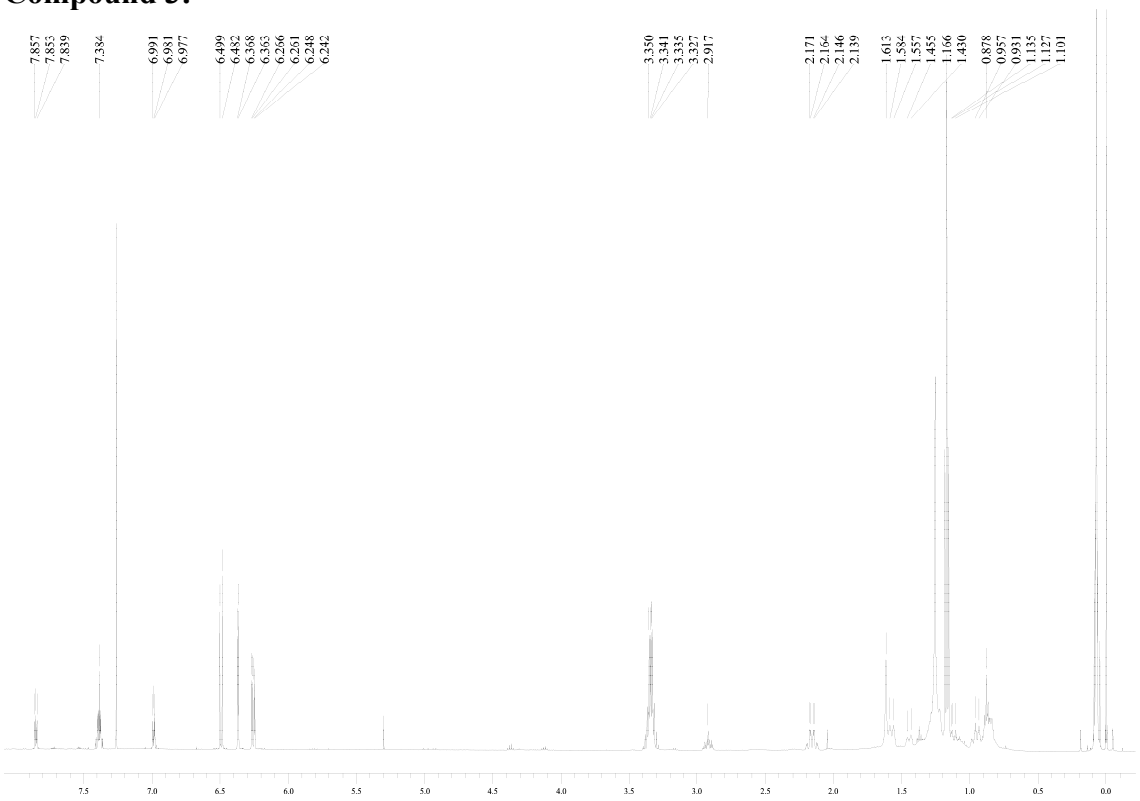
Comp.	$k_{H^+} = k_{0,H^+} + k_{slope,H^+} \times [H^+]$		$k_{PH} = k_{0,PH} + k_{slope,PH} \times [H^+]$		$k_{Th} = k_{0,Th} + k_{slope,Th} \times [H^+]$	
	k_{0,H^+} / s^{-1}	k_{slope,H^+} / s^{-1} M^{-1}	$k_{0,PH}$ / s^{-1}	$k_{slope,PH}$ / s^{-1} M^{-1}	$k_{0,Th}$ / s^{-1}	$k_{slope,Th}$ / s^{-1} M^{-1}
1	– 2.0 E-4	0.51	– 3.0 E-4	0.98	– 6.0 E-5	0.30
2	+ 4.0 E-5	0.45	+ 7.0 E-5	0.37	+ 1.0 E-4	0.14
3	– 3.0 E-5	0.03	+ 6.0 E-5	0.04	+ 5.0 E-5	0.019
4	+ 2.0 E-4	0.03	+ 4.0 E-4	0.017	+ 3.0 E-4	0.017
5	– 4.0 E-4	0.27	– 4.0 E-5	0.10	– 2.0 E-4	0.36
6	+ 2.0 E-4	0.007	n.d.	n.d.	n.d.	n.d.

F) ^{1}H NMR (500 mHz) of prepared compounds.

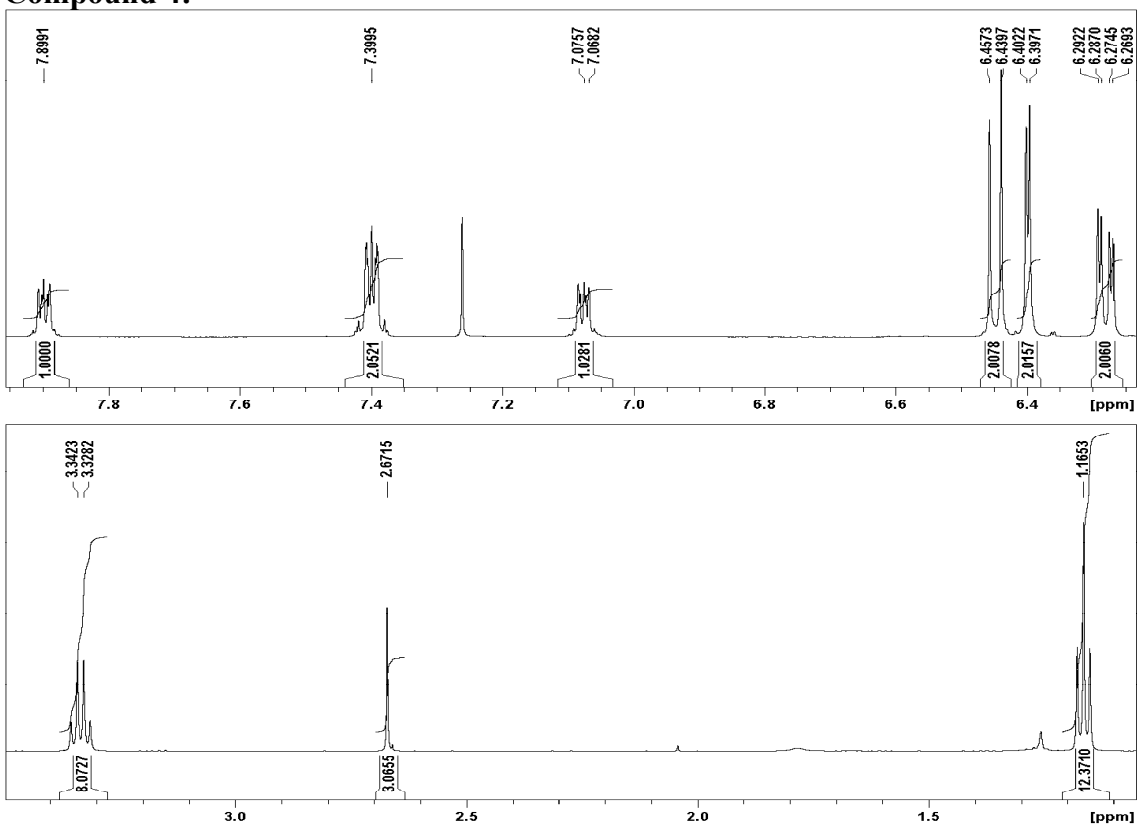
Rhodamine B Ethyl Ester:



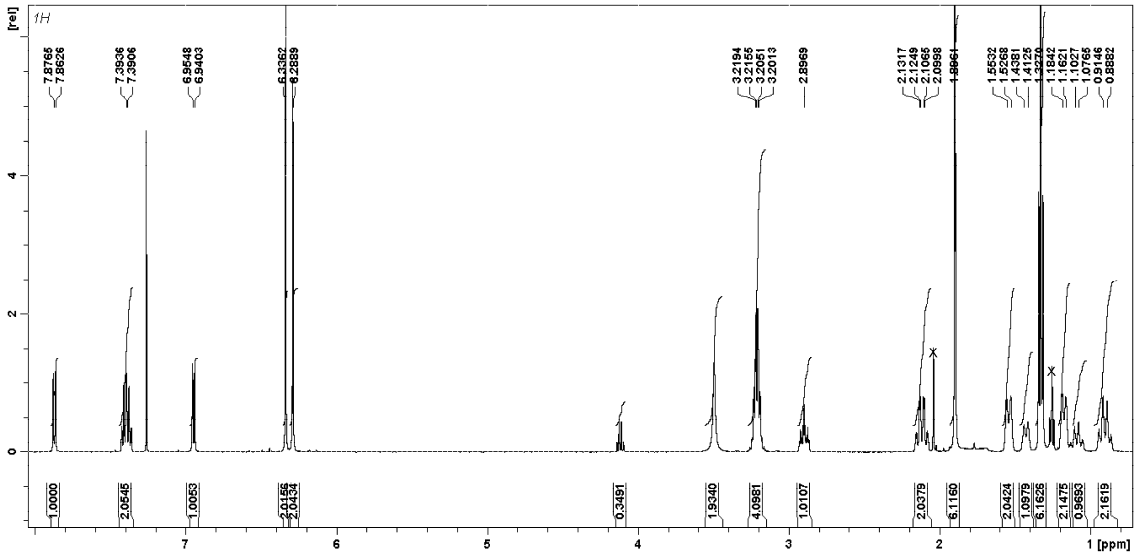
Compound 3:



Compound 4:



Compound 5:



Compound 6: