

## Supporting Information

### **2-Azahetaryl-2-(oxoindolin-2-ylidenes)acetonitriles as colorimetric probes for Zn: synthesis and optical properties**

Dedicated to Prof. Olga A. Zaporozhets in memoriam.

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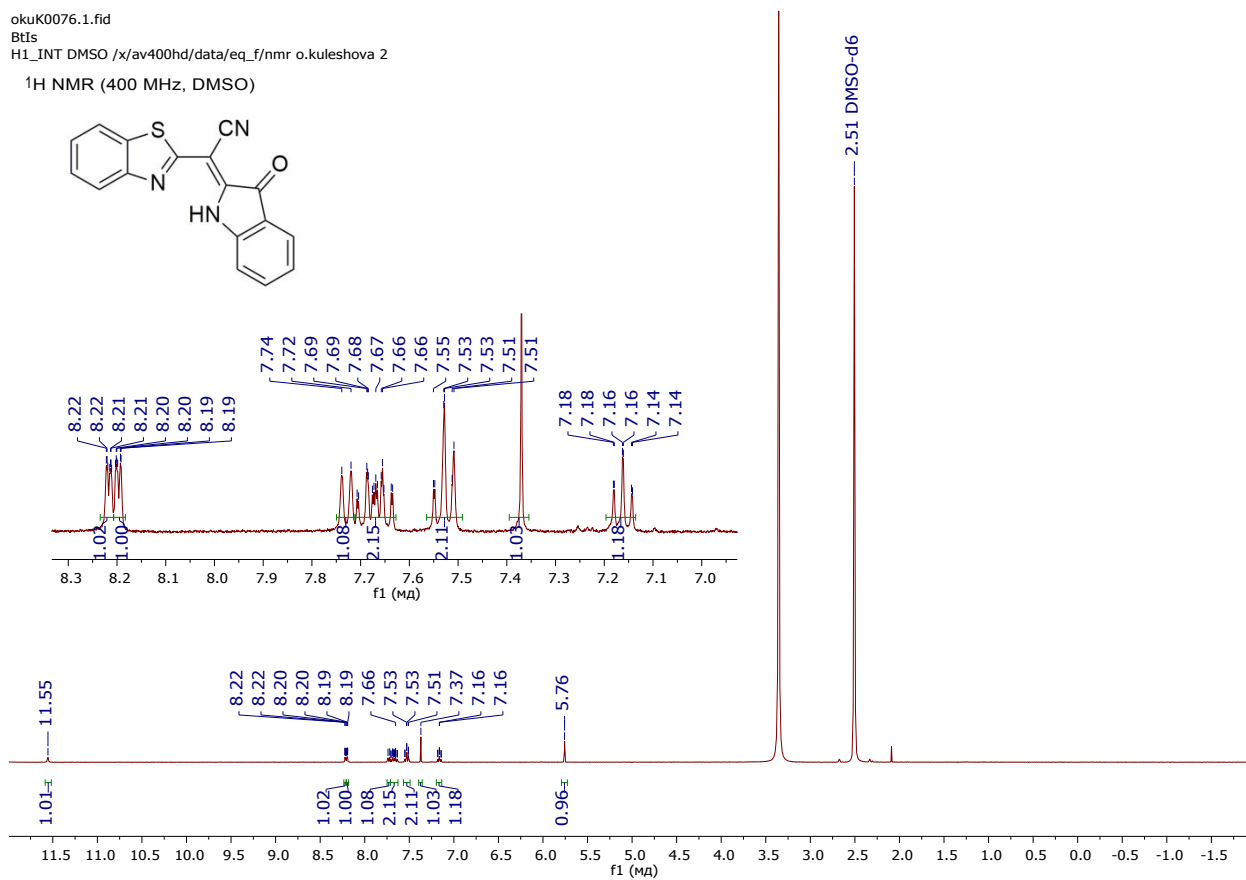
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## 1. $^1\text{H}$ , $^{13}\text{C}$ Data

**Figure S1.**  $^1\text{H}$ -NMR spectra of the compound (Z)-2-(benzo[d]thiazol-2-yl)-2-(3-oxoindolin-2-ylidene)acetonitrile (**3a**), Solvent:  $\text{DSMO-}d_6$



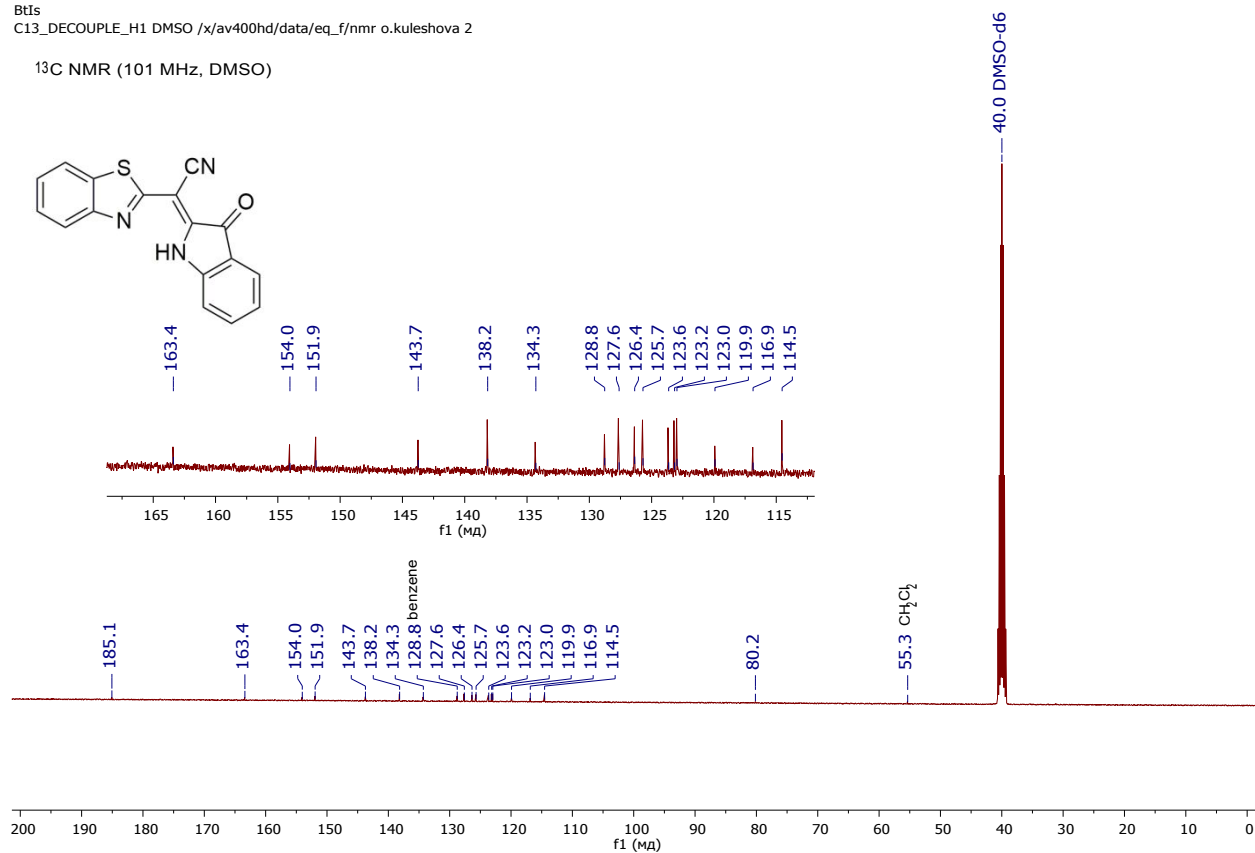
**Figure S2.**  $^{13}\text{C}$ -NMR spectra of the compound (Z)-2-(benzo[d]thiazol-2-yl)-2-(3-oxoindolin-2-ylidene)acetonitrile (**3a**)

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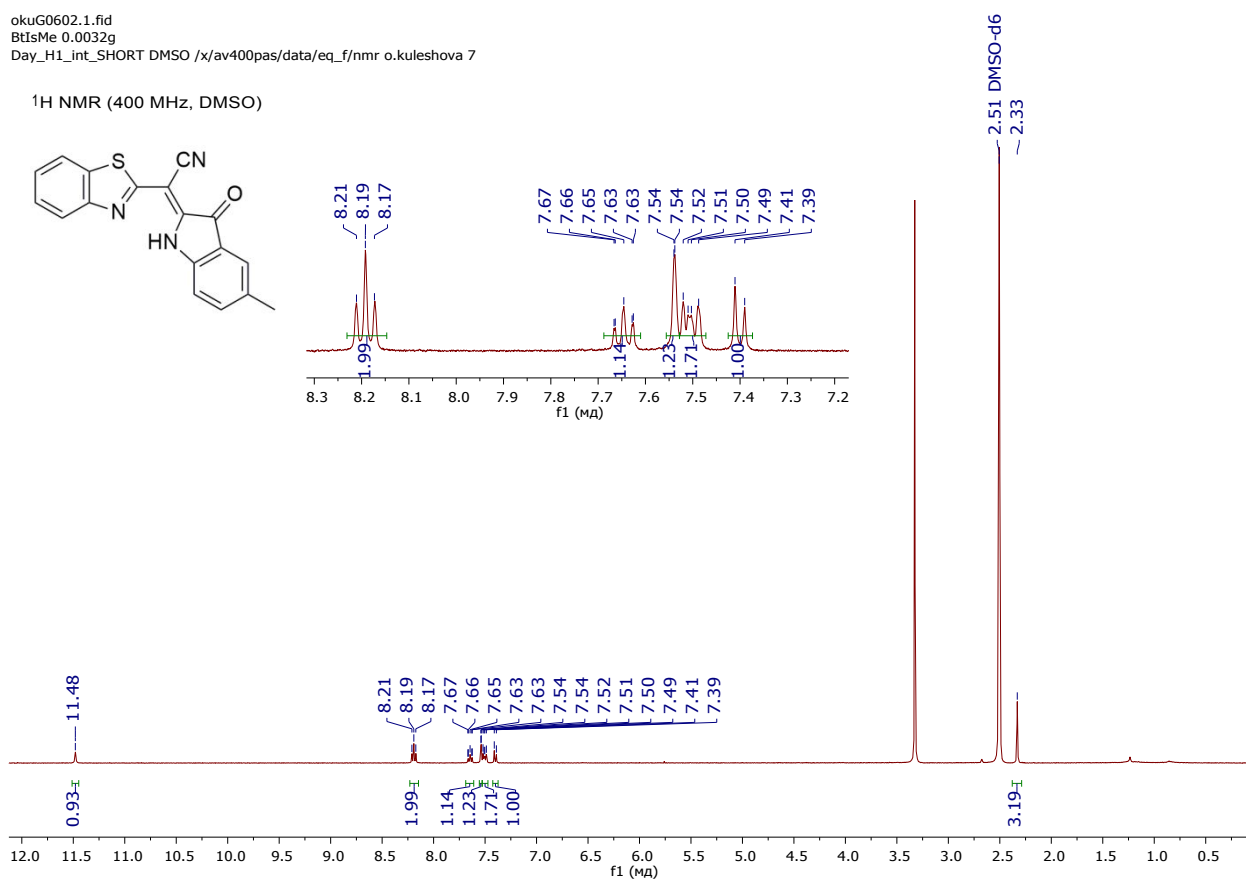
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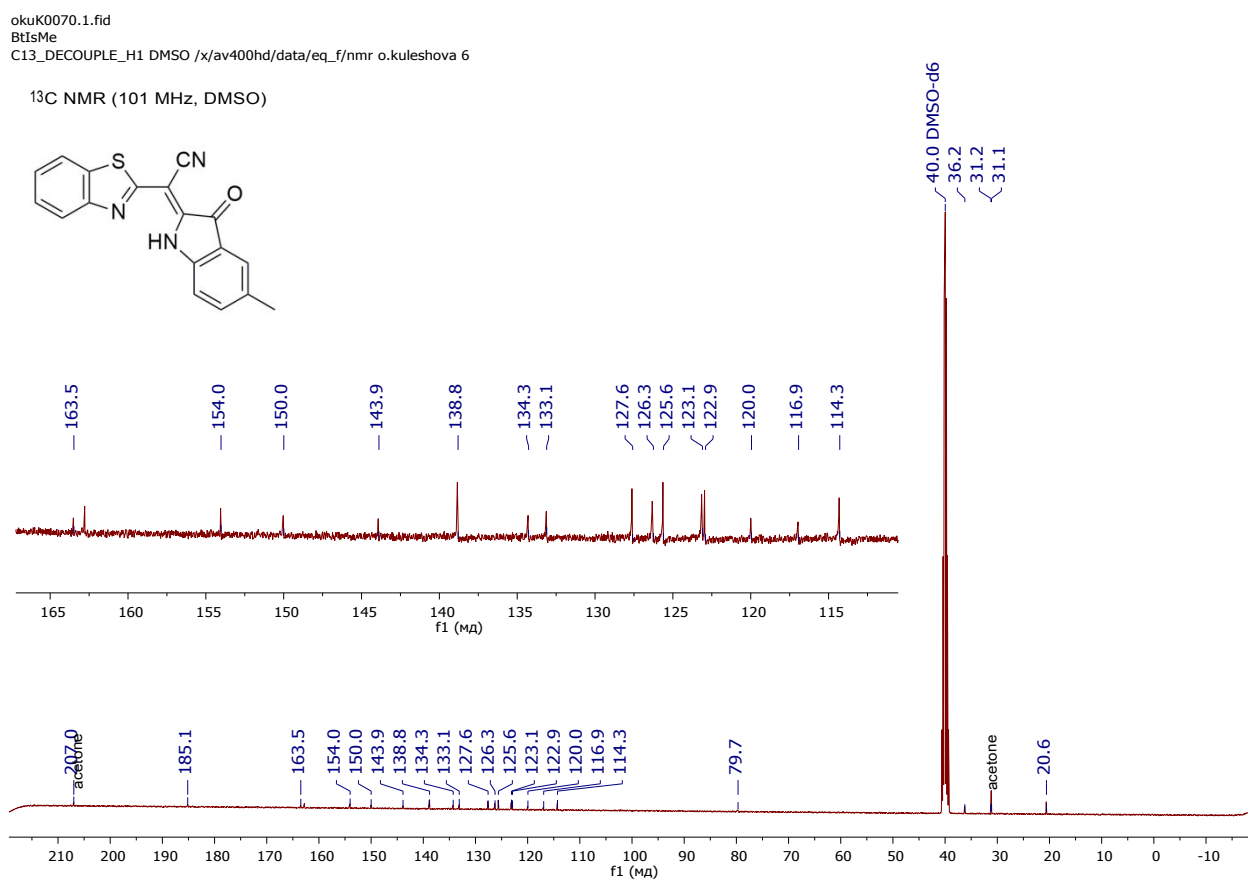
$^{13}\text{C}$  NMR (101 MHz, DMSO)



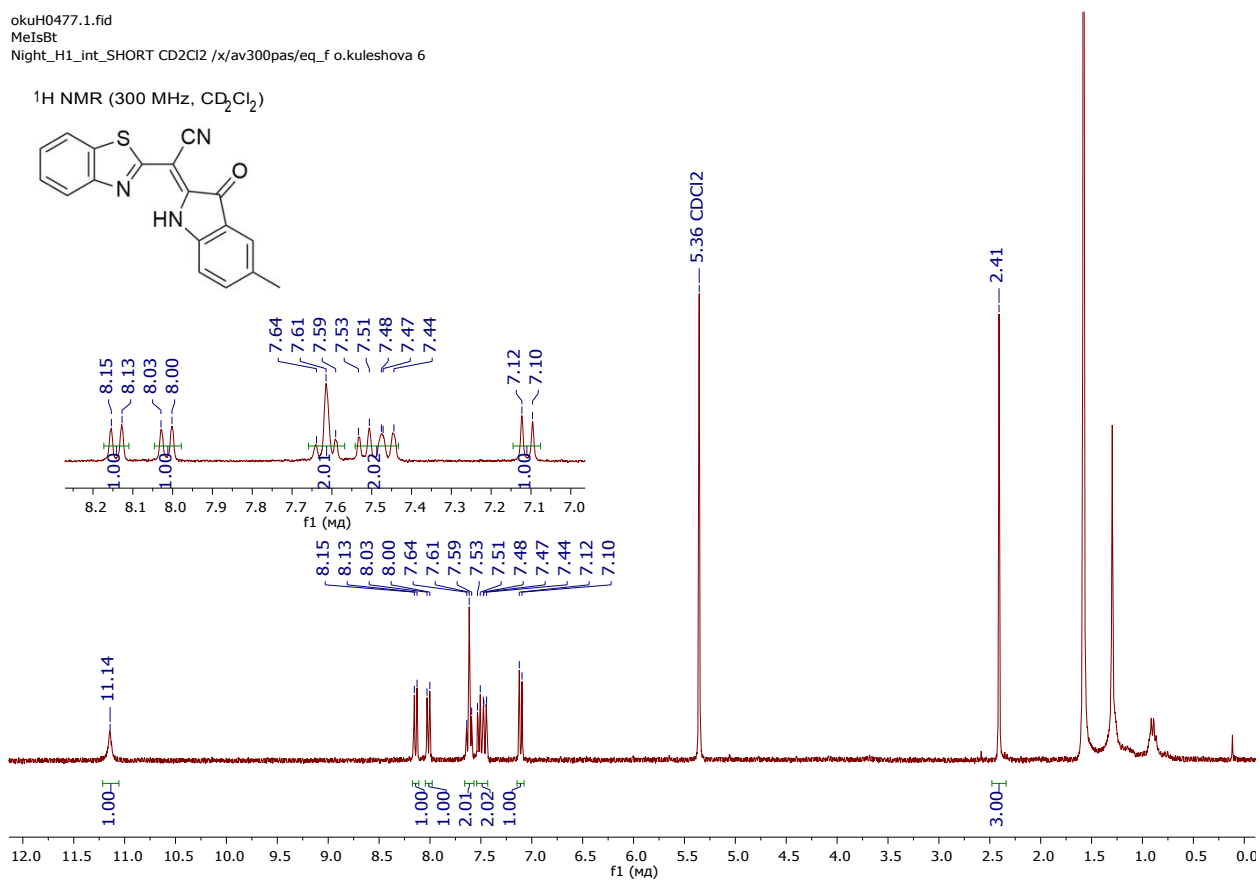
**Figure S3.**  $^1\text{H-NMR}$  spectra of the compound (*Z*)-2-(benzo[*d*]thiazol-2-yl)-2-(5-methyl-3-oxoindolin-2-ylidene)acetonitrile (**3b**), Solvent:  $\text{DMSO-}d_6$



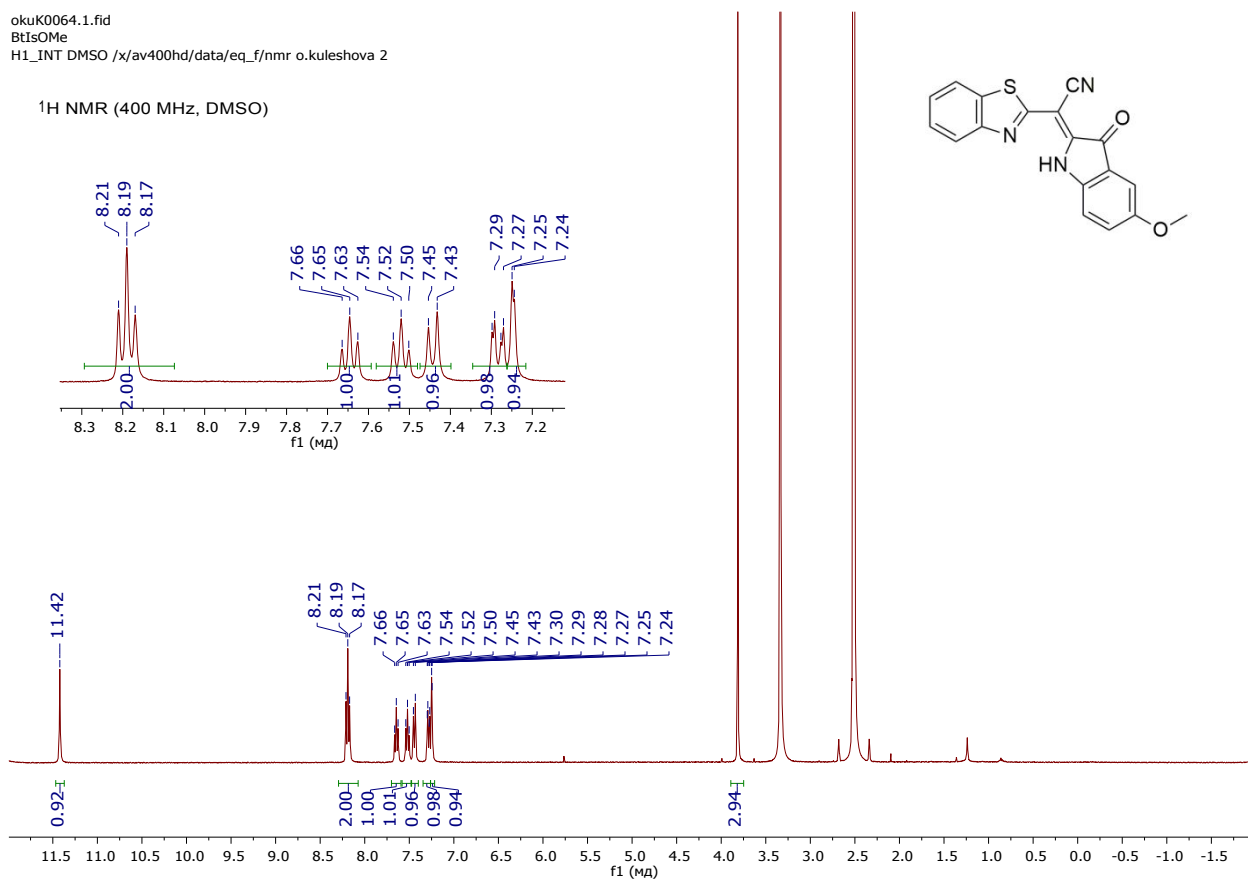
**Figure S4.**  $^{13}\text{C}$ -NMR spectra of the compound (*Z*)-2-(benzo[*d*]thiazol-2-yl)-2-(5-methyl-3-oxoindolin-2-ylidene)acetonitrile (**3b**), Solvent:  $\text{DMSO-}d_6$



**Figure S5.**  $^1\text{H-NMR}$  spectra of the compound (*Z*)-2-(benzo[*d*]thiazol-2-yl)-2-(5-methyl-3-oxoindolin-2-ylidene)acetonitrile (**3b**), Solvent  $\text{CD}_2\text{Cl}_2$

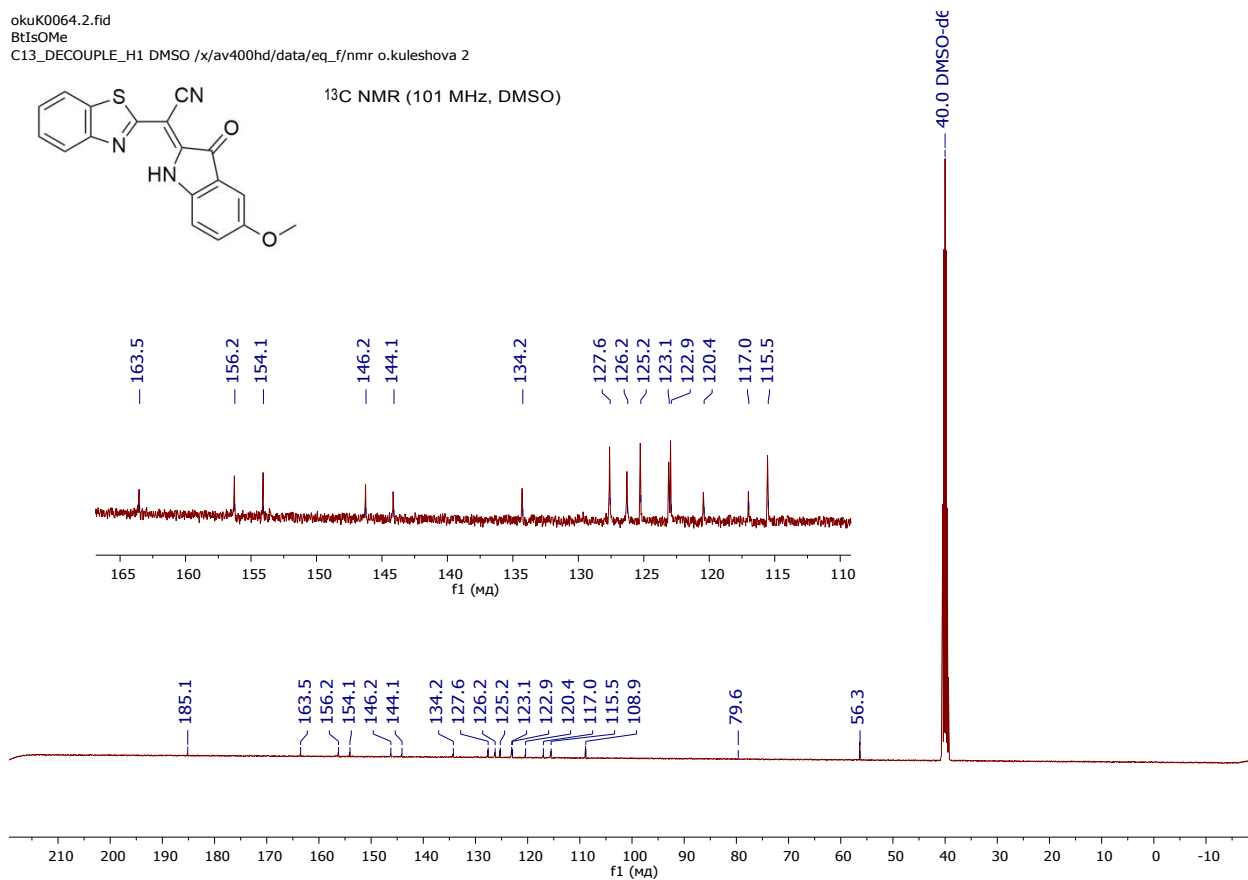


**Figure S6.**  $^1\text{H-NMR}$  spectra of the compound (Z)-2-(benzo[d]thiazol-2-yl)-2-(5-methoxy-3-oxoindolin-2-ylidene)acetonitrile (**3c**), Solvent:  $\text{DMSO-}d_6$





**Figure S7.**  $^{13}\text{C}$ -NMR spectra of the compound (*Z*)-2-(benzo[*d*]thiazol-2-yl)-2-(5-methoxy-3-oxoindolin-2-ylidene)acetonitrile (**3c**), Solvent:  $\text{DMSO-}d_6$



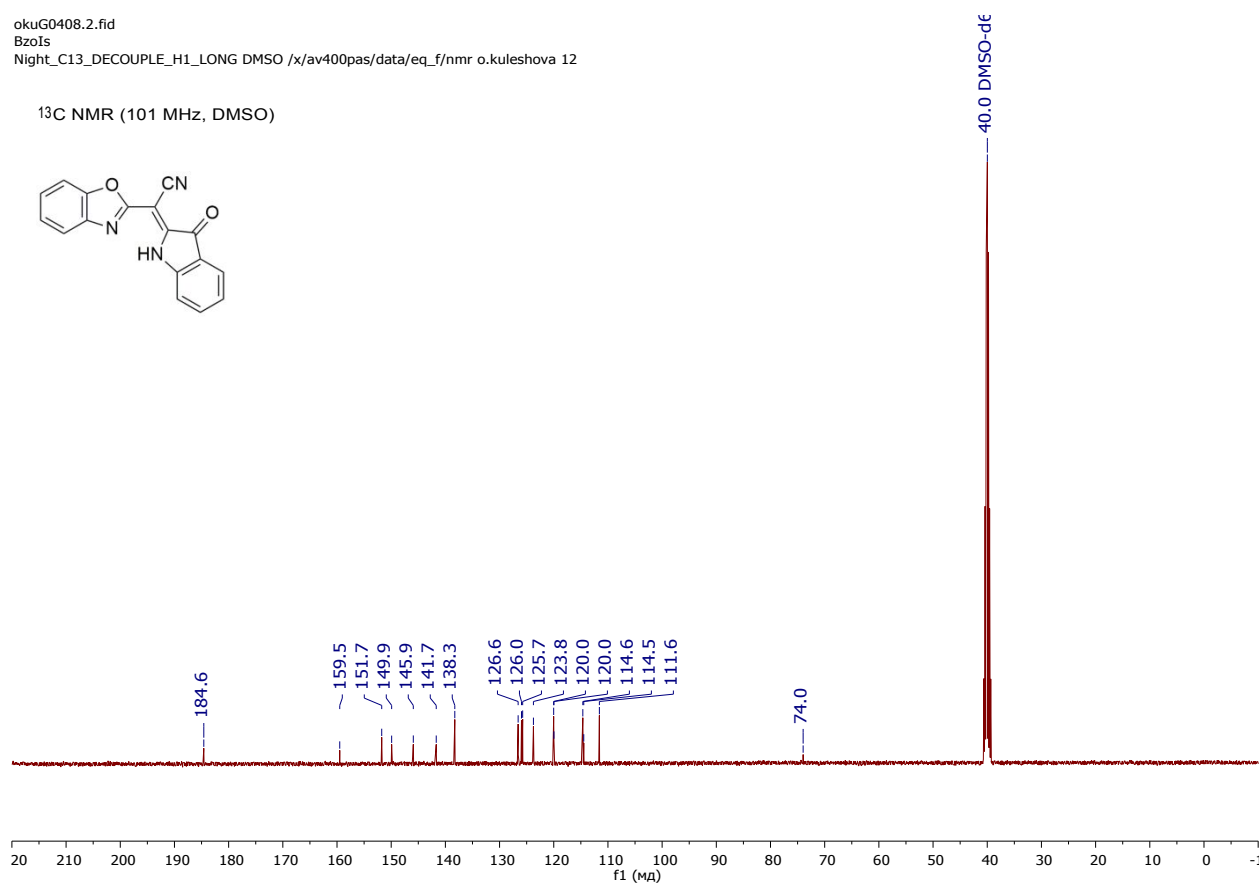


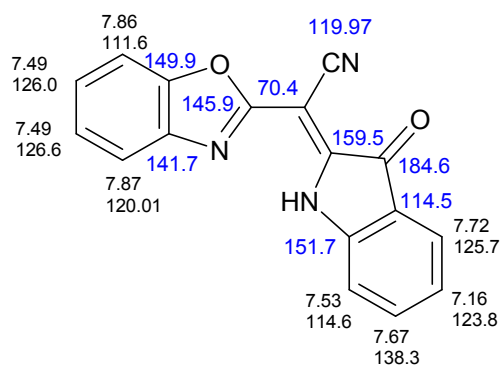
**Figure S9.**  $^{13}\text{C}$ -NMR spectra of the compound (Z)-2-(benzo[d]oxazol-2-yl)-2-(3-oxoindolin-2-ylidene)acetonitrile (**4**), Solvent:  $\text{DMSO-}d_6$

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$^{13}\text{C}$  NMR (101 MHz, DMSO)





**Figure S10.** The NMR chemical shifts of **4** found by 2D experiments (COSY, HMQC, HMBC)

**Table S1.** The full list of heteronuclear correlations  $^1\text{H}$ – $^{13}\text{C}$ , founded for compound **4** in HMQC and HMBC spectra (Solvent:  $\text{DMSO-}d_6$ )

$^1\text{H}$	Position of cross peaks in $^{13}\text{C}$ dimension	
	HMQC	HMBC
7.16	123.8	114.6, 125.7, 138.2, 151.7, 184.6
7.49	126.0	120.01, 149.9
7.49	126.6	111.6, 141.7
7.53	114.6	123.8, 151.7
7.67	138.3	151.7, 125.7, 114.6
7.72	125.7	138.3, 151.7, 184.6
7.86	111.6	141.7, 126.6
7.87	120.01	149.9, 126.0
11.37	–	119.97, 145.9, 151.7, 184.6

**Figure S11.** COSY NMR spectrum of the compound **4**, Solvent: DMSO-*d*<sub>6</sub>

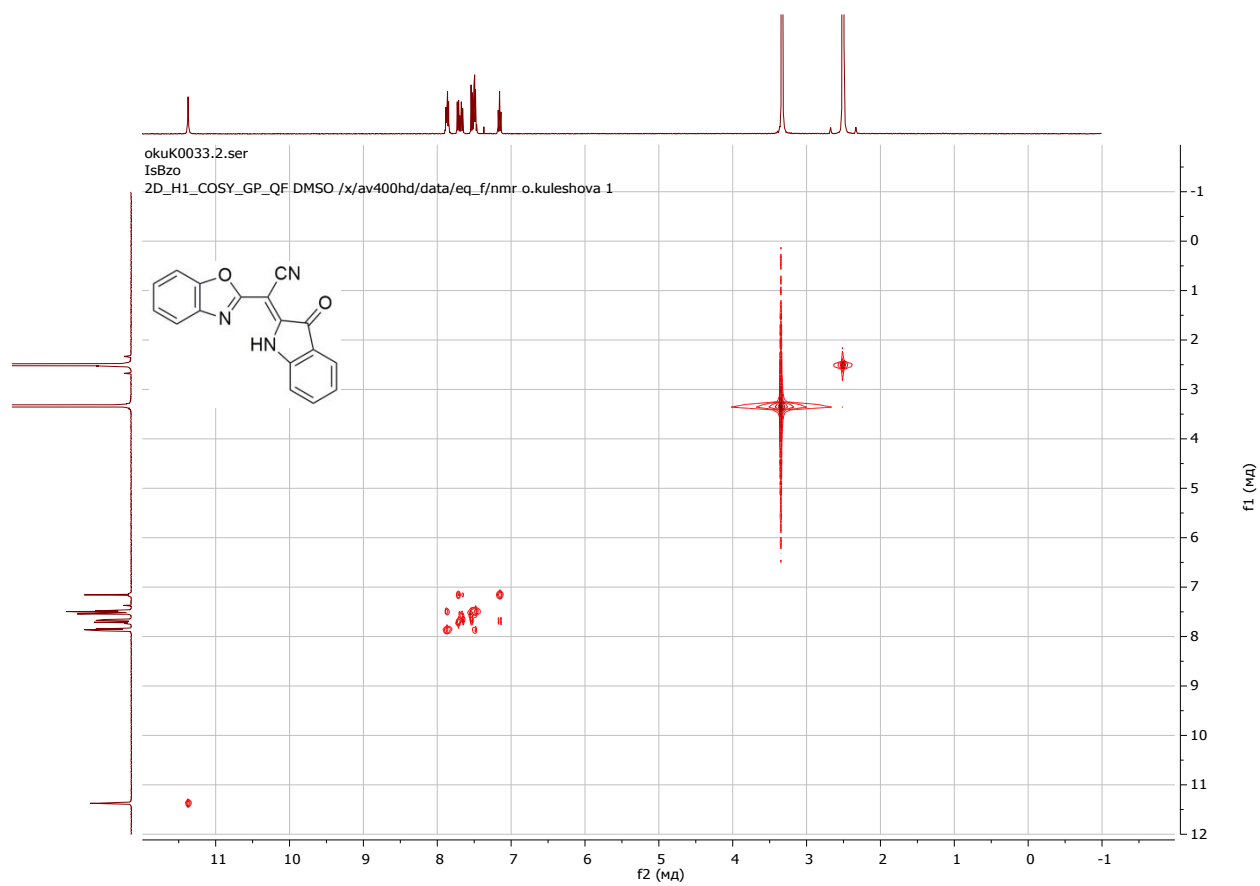


Figure S12. HMQC NMR spectrum of the compound 4, Solvent: DMSO- $d_6$

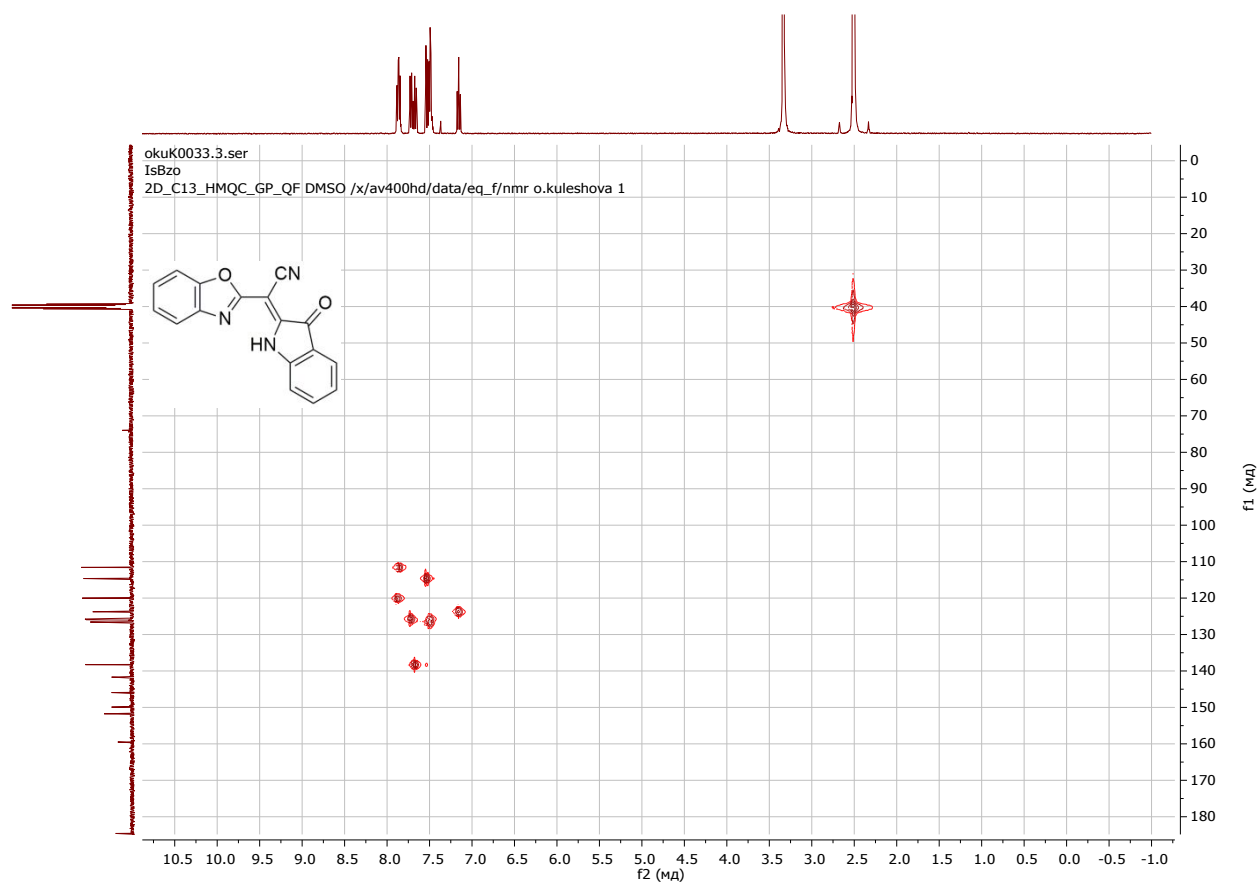
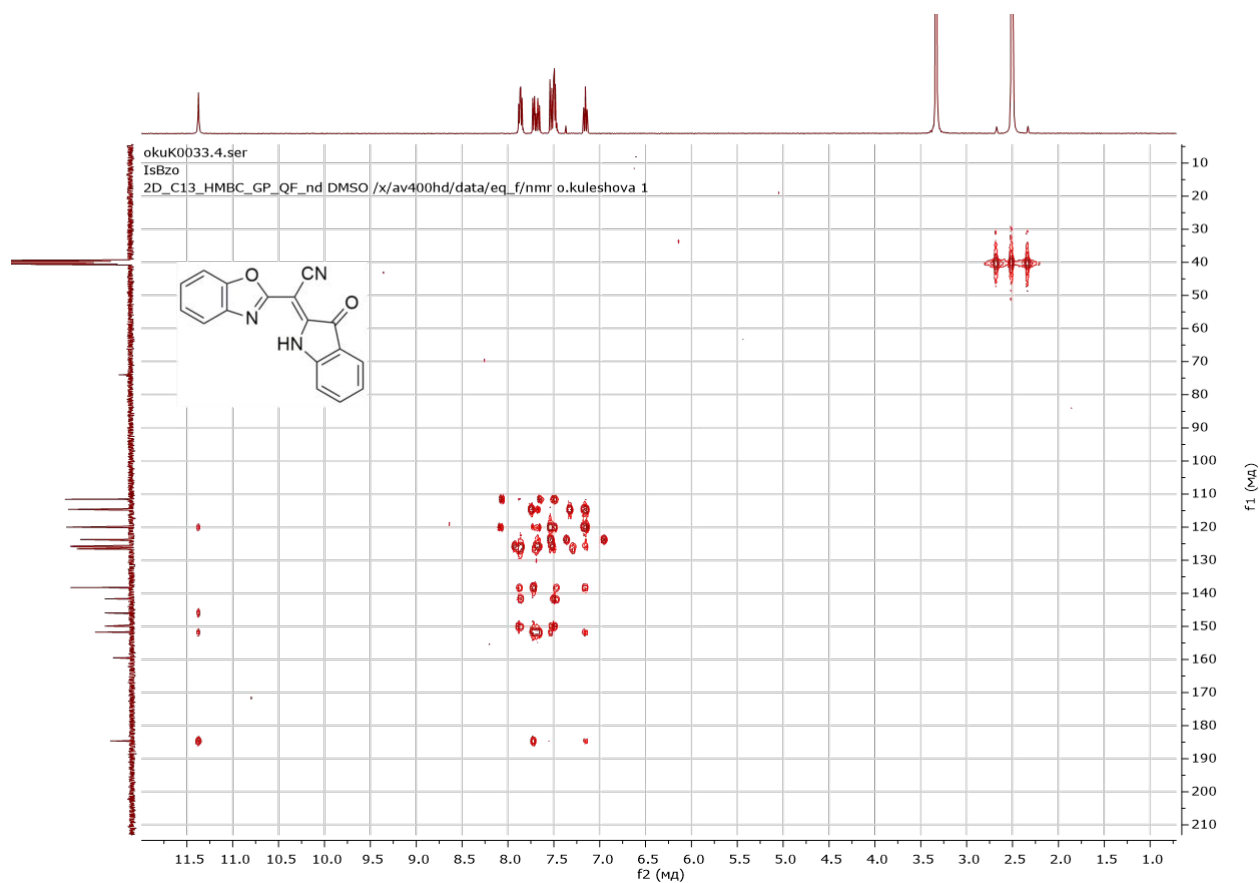
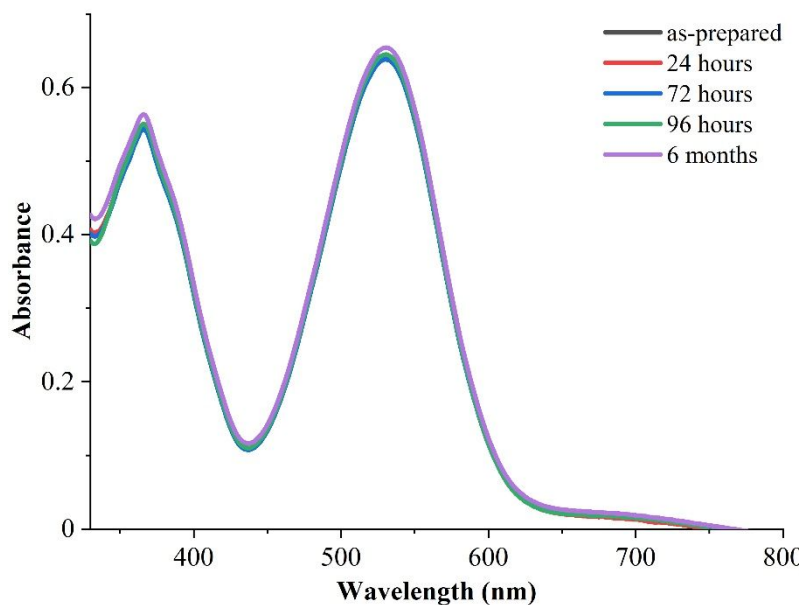


Figure S13. HMBC NMR spectrum of the compound **4**, Solvent: DMSO-*d*<sub>6</sub>



## 2. Photostability test

The photostability test was performed for the studied dyes in DMSO as a control for the absorbance of a diluted solution of the appropriate concentration. Dye **3b** was used as an example.



**Figure S14.** Absorption spectra of dye **3b** in DMSO as-prepared and after 24, 72, 96 h and 6 months of storage.  $C_{3b} = 50 \mu\text{mol}\cdot\text{L}^{-1}$

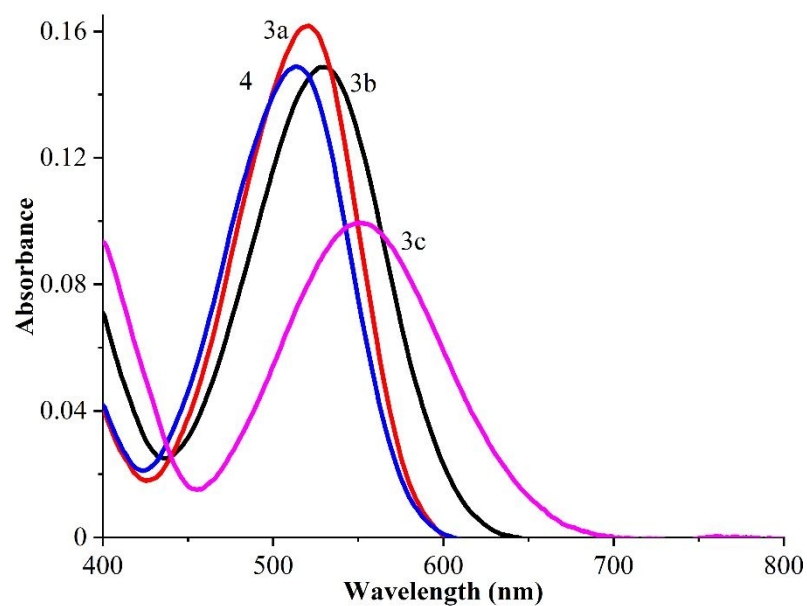
## 3. Absorption properties of probe **3a-c**, **4** and **3b-Zn<sup>2+</sup>**, **4-Zn<sup>2+</sup>** in H<sub>2</sub>O/DMSO solutions.

The molar absorption coefficient ( $\epsilon$ ,  $\text{mol}^{-1}\text{Lcm}^{-1}$ ) was calculated according the Beer-Lambert law using value of the absorbance of solution at the appropriate wavelength of UV-Vis spectra.

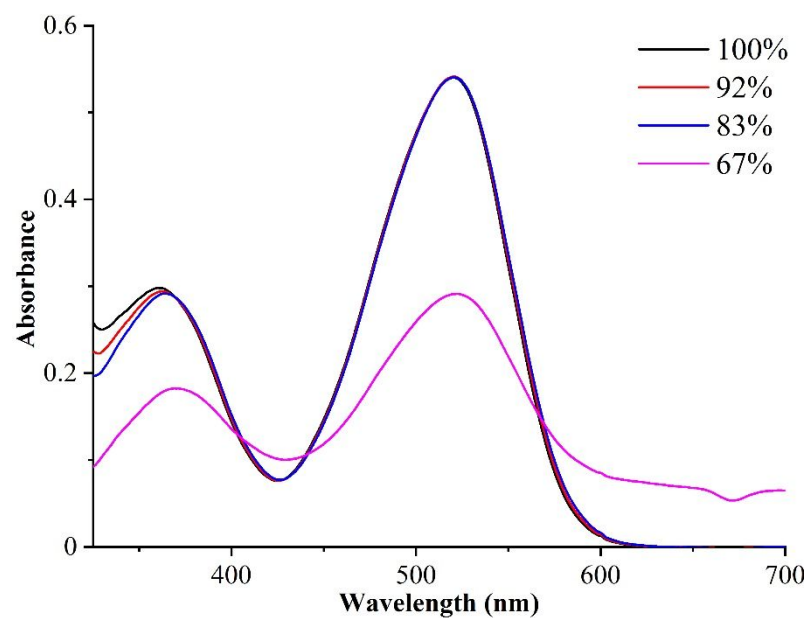
**Table S2.** Molar absorption coefficient of dyes **3a**, **3b** and **4** in DMSO and H<sub>2</sub>O/DMSO

Dye	$\lambda_{\text{max}}$ , nm	$\epsilon_{\text{max}}$ (DMSO), $10^4$	$\epsilon_{\text{max}}, 10^4$			$\Delta\epsilon_{\text{max}}, \%$		
			H <sub>2</sub> O/DMSO, v/v					
			1/11	1/5	1/2	1/11	1/5	1/2
<b>3a</b>	520	1.48	1.59	1.59	<b>0.85</b>	7.4	7.4	<b>-42.6</b>
<b>3b</b>	530	1.38	1.46	1.43	1.44	5.8	3.6	4.3
<b>4</b>	515	1.66	1.59	1.59	1.53	-4.2	-4.2	-7.8

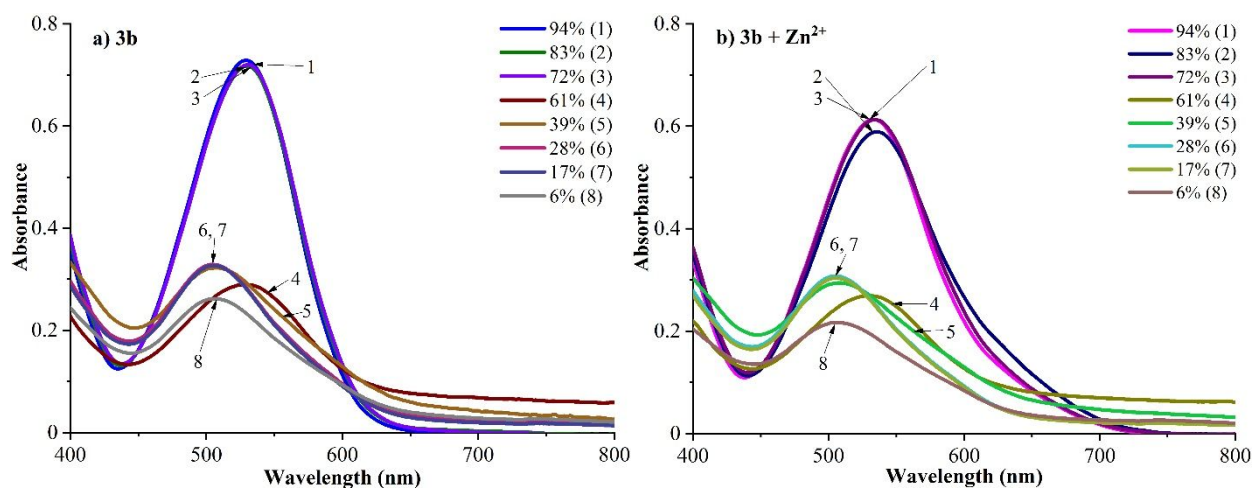




**Figure S15.** Absorption spectra of dye **3a-c** and **4** in H<sub>2</sub>O/ DMSO (1/5, v/v). C = 10 μmol·L<sup>-1</sup>



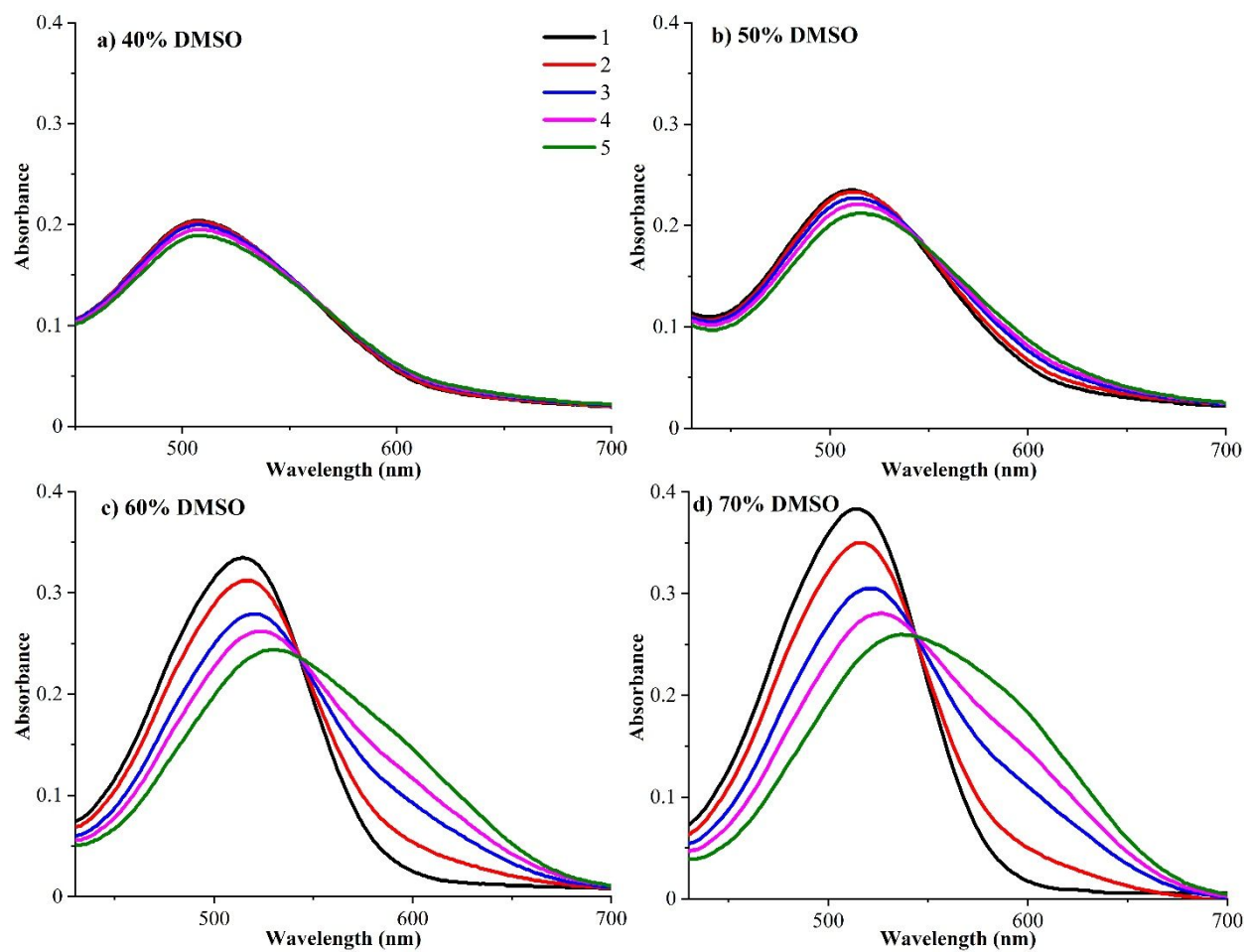
**Figure S16.** Absorption spectra of dye **3a** in DMSO and H<sub>2</sub>O/ DMSO. % (v/v) DMSO is shown in the inset. C<sub>3a</sub> = 34 μmol·L<sup>-1</sup>



**Figure S17.** Absorption spectra of dye **3b** in Tris-buffer (pH 7.2) / DMSO without (a) and in the presence of  $50 \mu\text{mol}\cdot\text{L}^{-1}$   $\text{Zn}^{2+}$  (b). % (v/v) DMSO is shown in the insets.  $C_{3b} = 50 \mu\text{mol}\cdot\text{L}^{-1}$ .

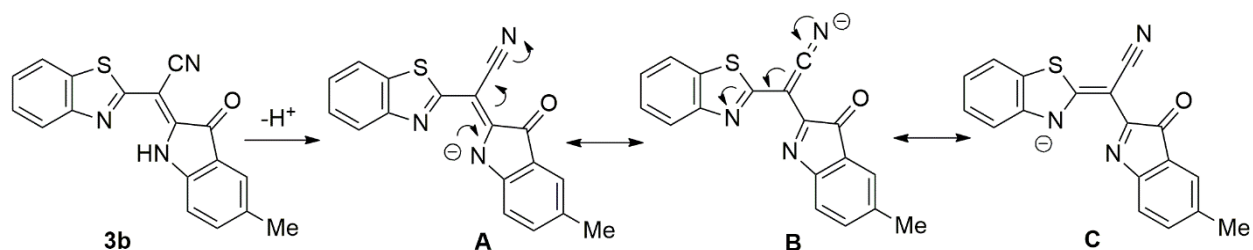
**Table S3.** The influence of water on the absorbance of dye **3b** and **3b-Zn<sup>2+</sup>** in solutions with different ratio  $\text{H}_2\text{O}$  (Tris-buffer, pH 7.2) / DMSO.  $C_{3b} = C(\text{Zn}^{2+}) = 50 \mu\text{mol}\cdot\text{L}^{-1}$ . Sample volume – 3.00 ml.  $\Delta A_{640} = A_{640}(3b) - A_{640}(3b+\text{Zn}^{2+})$

№	V (DMSO), ml	V (H <sub>2</sub> O), ml	% DMSO	A <sub>640</sub>		ΔA <sub>640</sub>
				3b	3b+Zn <sup>2+</sup>	
1	2.83	0.17	94	0.0088	0.102	0.0932
2	<b>2.50</b>	<b>0.50</b>	<b>83</b>	<b>0.0154</b>	<b>0.1405</b>	<b>0.1251</b>
3	2.17	0.83	72	0.0159	0.1082	0.0923
4	1.84	1.16	61	0.081	0.0854	0.0044
5	1.17	1.83	39	0.0673	0.0727	0.0054
6	0.85	2.15	28	0.0389	0.0389	0
7	0.50	2.50	17	0.0349	0.0372	0.0023
8	0.18	2.82	6	0.0452	0.0408	-0.0044

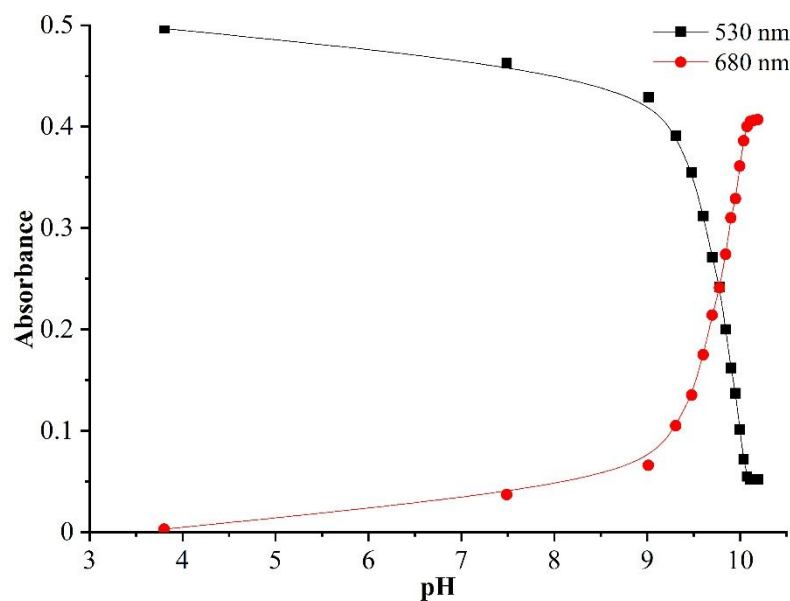


**Figure S18.** Absorption spectra of dye 4 without (1) and in the presence of different amount of Zn<sup>2+</sup> (2-5),  $C_4 = 25.0 \mu\text{mol}\cdot\text{L}^{-1}$ , Tris-buffer (pH 7.2)/DMSO with different %, v/v of DMSO.  $C(\text{Zn}^{2+}), \mu\text{mol}\cdot\text{L}^{-1} : 0$  (1), 5.0 (2), 15.0 (3), 24.0 (4), 43.0 (5).

#### 4. Deprotonation studies



**Scheme S1.** Possible way of negative charge delocalization upon deprotonation of **3b**



**Figure S19.** Spectrophotometric titration plots at the absorption maxima of dye **3b** in H<sub>2</sub>O/DMSO (1/5, v/v). pH corresponds to the calculated concentration of H<sup>+</sup> in the aqueous part of the sample (0.5 ml). Black line corresponds to the absorption of neutral form; red line – absorption of anionic form of the dye.

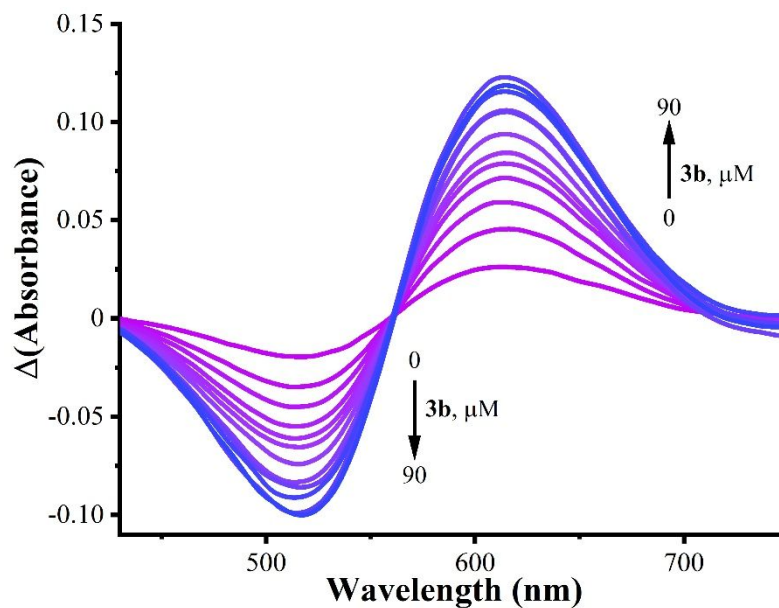
**Table S4.** Calculation data of the ionization constant of dye **3b** in H<sub>2</sub>O/DMSO solutions.

№	pH	$\lambda_1 = 530 \text{ nm}$		$\lambda_2 = 680 \text{ nm}$	
		A	pKa	A	pKa
1	10.15	0.463	-	0.037	-
2	12.70	0.429	13.44	0.066	13.43
3	13.19	0.391	13.69	0.105	13.66
4	13.48	0.355	13.81	0.135	13.79
5	13.69	0.312	13.83	0.175	13.81
6	13.85	0.271	13.83	0.214	13.81
7	13.98	0.242	13.85	0.241	13.82
8	14.09	0.200	13.79	0.274	13.78
9	14.18	0.162	13.70	0.310	13.68
10	14.27	0.137	13.64	0.329	13.64
11	14.34	0.101	13.44	0.361	13.44
12	14.41	0.072	-	0.386	-
13	14.48	0.055	-	0.400	-

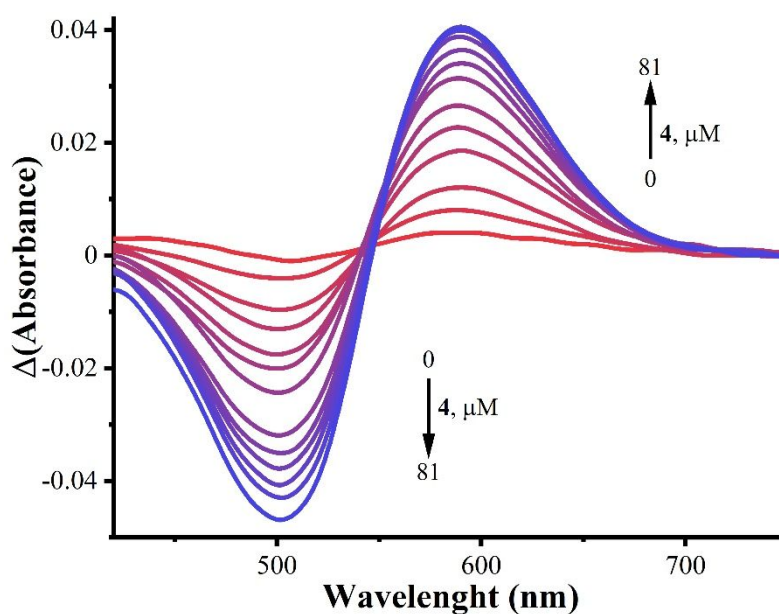
**Table S5.** Calculation data of the ionization constant of dye **4** in H<sub>2</sub>O/DMSO solutions.

№	pH	$\lambda_1 = 515 \text{ nm}$		$\lambda_2 = 645 \text{ nm}$	
		A	pKa	A	pKa
1	13.43	0.573	-	0.003	-
2	13.76	0.565	-	0.003	-
3	14.17	0.561	15.69	0.014	15.77
4	14.30	0.547	15.53	0.015	15.86
5	14.52	0.512	15.37	0.044	15.48
6	14.61	0.477	15.23	0.069	15.33
7	14.69	0.428	15.08	0.113	15.12
8	14.76	0.335	14.81	0.188	14.84
9	14.82	0.245	14.56	0.264	14.57
10	14.88	0.153	-	0.345	-
11	14.93	0.107	-	0.378	-

## 5. Complexation studies



**Figure S20.** Absorption spectra of different concentrations probe **3b** solutions in the presence of  $\text{Zn}^{2+}$ ,  $C(\text{Zn}^{2+}) = 10.0 \mu\text{mol}\cdot\text{L}^{-1}$ , Tris-buffer (pH 7.2)/DMSO (1/5, v/v)



**Figure S21.** Absorption spectra of different concentrations probe **4** solutions in the presence of  $\text{Zn}^{2+}$ ,  $C(\text{Zn}^{2+}) = 4.8 \mu\text{mol}\cdot\text{L}^{-1}$ , Tris-buffer (pH 7.2)/DMSO (1/3, v/v).

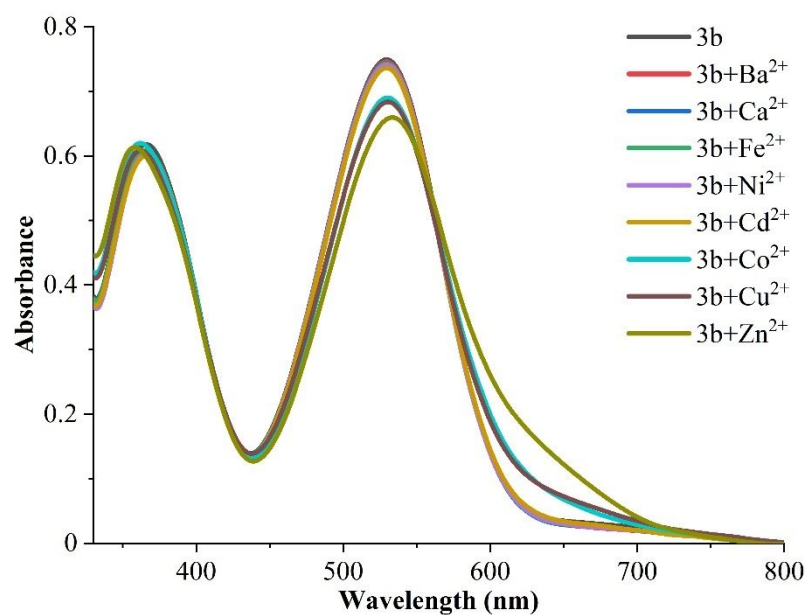
**Table S6.** Calculation data of the affinity constant of the  $\text{Zn}^{2+}$  complex with probe **3b** by the Bent-French method

№	$C_{3b}, \mu\text{mol}\cdot\text{L}^{-1}$	$\Delta A_{600}$	$\lg K^f$
1	2.04	0.010	10.26
2	2.63	0.013	10.28
3	3.13	0.015	10.25
4	3.78	0.018	10.26
5	4.61	0.022	10.28
6	5.12	0.025	10.31
7	5.88	0.027	10.28
8	6.36	0.029	10.28

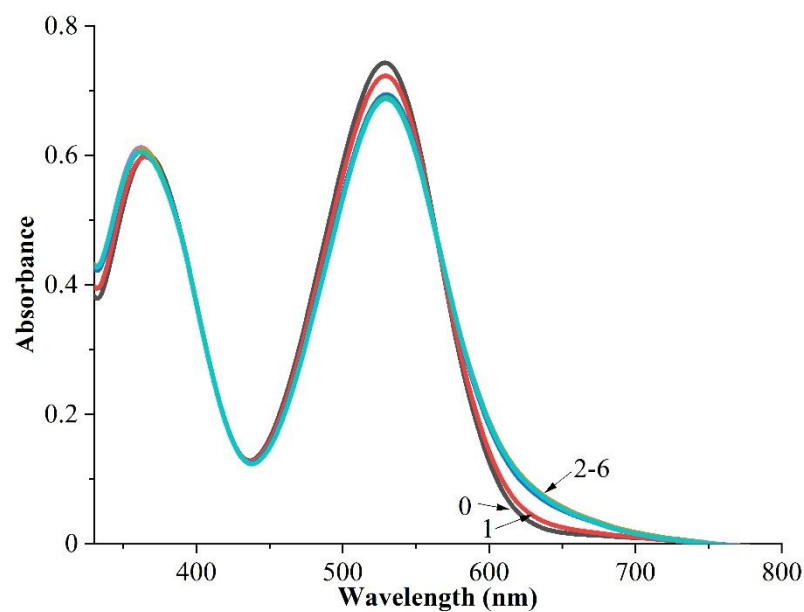
**Table S7.** Calculation data of the affinity constant of the  $\text{Zn}^{2+}$  complex with probe **4** by the Bent-French method

№	$C_4, \mu\text{mol}\cdot\text{L}^{-1}$	$\Delta A_{590}$	$\lg K^f$
1	1.1	0.009	12.77
2	1.4	0.010	12.69
3	1.7	0.011	12.55
4	2.0	0.012	12.49
5	2.5	0.013	12.41
6	3.0	0.014	12.32
7	3.4	0.015	12.28
8	4.0	0.016	12.22

## 6. Selectivity studies

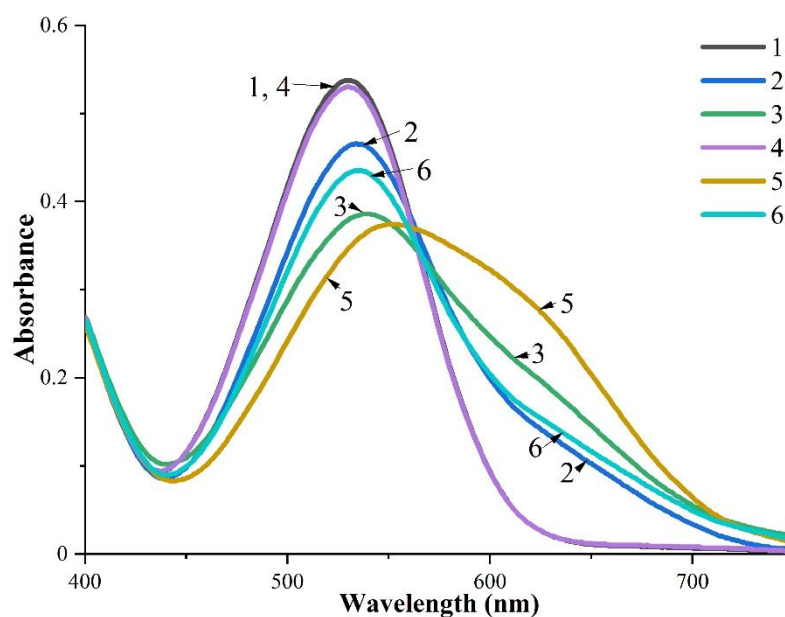


**Figure S22.** Absorption spectra of probe **3b** without and in the presence of different ions after 60 min prepared of solution. Tris-buffer (pH 7.2)/DMSO (1/5, v/v);  $C_{3b} = 50.0 \mu\text{mol}\cdot\text{L}^{-1}$ ; Concentration,  $\mu\text{mol}\cdot\text{L}^{-1}$ : 100 ( $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ); 10 ( $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ).



**Figure S23.** Absorption spectra of probe **3b** without (0) and in the presence of  $10 \mu\text{mol}\cdot\text{L}^{-1}$   $\text{Co}^{2+}$  after 15 min (1), 30-60 min (2-6) of prepared.  $C_{3b} = 50.0 \mu\text{mol}\cdot\text{L}^{-1}$ , Tris-buffer (pH 7.2)/DMSO (1/5, v/v).





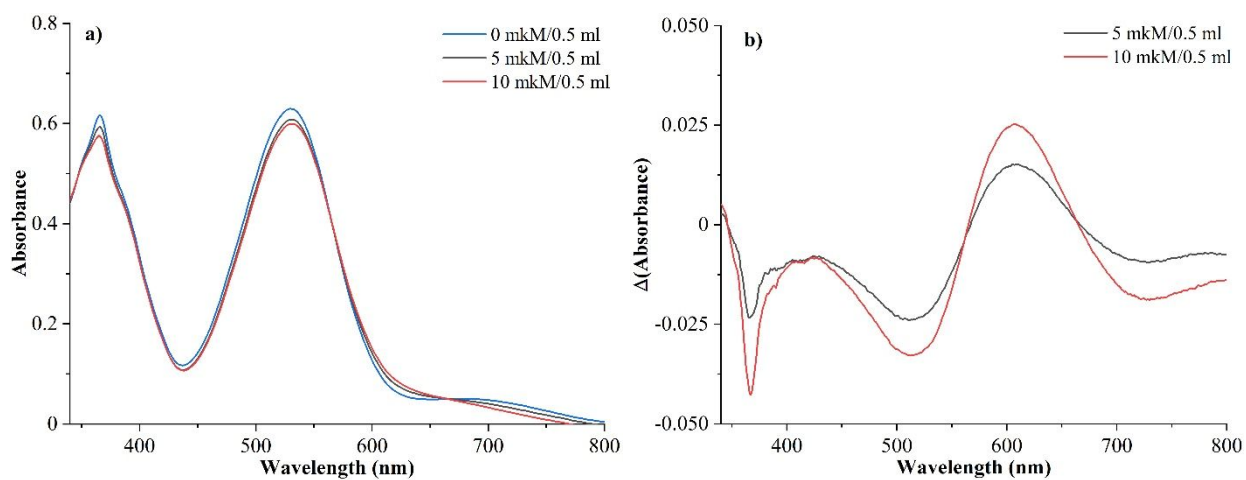
**Figure S24.** Absorption spectra of probe **3b** (1); **3b** with  $\text{Zn}^{2+}$  in the presence of  $\text{Na}_2\text{S}_2\text{O}_3$  (2); **3b** with  $\text{Cu}^{2+}$  without (3) and in the presence of  $\text{Na}_2\text{S}_2\text{O}_3$  (4); **3b** with  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  without (5) and in the presence of  $\text{Na}_2\text{S}_2\text{O}_3$  (6). Tris-buffer (pH 7.2)/DMSO (1/5, v/v);  $C_{3b} = 40.0 \mu\text{mol}\cdot\text{L}^{-1}$ ; Concentration of  $\text{Zn}^{2+} - 9.0 \mu\text{mol}\cdot\text{L}^{-1}$ ;  $\text{Cu}^{2+} - 20.0 \mu\text{mol}\cdot\text{L}^{-1}$ ;  $\text{Na}_2\text{S}_2\text{O}_3 - 1.0 \text{mmol}\cdot\text{L}^{-1}$ .

The thiosulfate ion is a well-known masking agent for  $\text{Cu}^{2+}$  due to the formation of complex compounds, particularly in the determination of  $\text{Zn}^{2+}$  with EDTA in the presence of  $\text{Cu}^{2+}$ .<sup>1,2</sup> Figure S24 shows the successful masking of  $20.0 \mu\text{mol}\cdot\text{L}^{-1}$   $\text{Cu}^{2+}$  by  $1.0 \text{mmol}\cdot\text{L}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  under optimal conditions for the complexation of probe **3b** with  $\text{Zn}^{2+}$ .

The initial 50-fold excess of thiosulfate ions allows us to predict the formation of  $\text{Cu}(\text{S}_2\text{O}_3)_n^{-(2n-1)}$  anionic complexes with  $n=1-3$  in the solution.<sup>3-5</sup>

## 7. Detecting of $\text{Zn}^{2+}$ in serum model solution

The model solutions of 2 times diluted pre-treated blood serum with  $5.0$  and  $10.0 \mu\text{mol}\cdot\text{L}^{-1}$   $\text{Zn}^{2+}$  were performed using Tris-buffer (pH=7.2) as a solvent. Concentration of components in each solution was as follows,  $\text{mmol}\cdot\text{L}^{-1}$ :  $\text{NaCl} - 120$ ,  $\text{KCl} - 2.4$ ,  $\text{CaCl}_2 - 1.5$ ,  $\text{MgCl}_2 - 0.6$ ,  $\text{CuSO}_4$ ,  $\text{FeSO}_4 - 0.005$ ,  $\text{Na}_2\text{S}_2\text{O}_3 - 1.0$ . Sample preparation:  $2.5 \text{ml}$  of  $40 \mu\text{mol}\cdot\text{L}^{-1}$  of probe **3b** solution in DMSO was mixed with  $0.5 \text{ml}$  of model solution. Spectrum of each sample in cuvette ( $1.00 \text{cm}$ ) was recorded at  $380-800 \text{nm}$  versus Tris-buffer (pH 7.2)/DMSO (1/5, v/v) as a blank solution. Figure S25 shows the absorption spectra. Concentration of  $\text{Zn}^{2+}$  in sample was calculated using equation:  $\Delta A_{600} = (0.005 \pm 0.002) + (0.0111 \pm 0.0002) \cdot C_{\text{Zn}}$ ,  $\mu\text{mol}\cdot\text{L}^{-1}$ , where  $\Delta A_{600} = A_{600}^i - A_{600}(\mathbf{3b})$ . The data obtained are listed in Table S8.



**Figure S25.** Absorption spectra of probe **3b** with spiked samples of serum model solution.  $C_{3b} = 40.0 \mu\text{mol}\cdot\text{L}^{-1}$ , Tris-buffer (pH 7.2)/DMSO (1/5, v/v): a) raw spectra; b) obtained as  $\Delta A_{\lambda} = A_{\lambda_i} - A_{\lambda_0}$ . Concentration of  $\text{Zn}^{2+}$  is shown in the insets.

**Table S8.** Recovery values of  $\text{Zn}^{2+}$  for spiked samples of serum model solution.  $n=3$

Added, $\mu\text{mol}\cdot\text{L}^{-1}$	Found, $\mu\text{mol}\cdot\text{L}^{-1}$	Recovery (%)	RSD, %
5.0	5.1	102.7	0.43
10.0	10.4	104.1	0.38

**Table S9.** Comparison of reported colorimetric probe with proposed for detection of Zn<sup>2+</sup> 6-12

Compound	$\lambda$ , nm	LOD, $\mu\text{mol} \cdot \text{L}^{-1}$	Object (Conditions)	Interfering ions (Masking agent)	References
Dithizone (1,5-Diphenylthiocarbazone)	538	0.2	Micellar solutions (pH 9, 0.05 M diethanolamine - HCl buffer with SDS)	Co <sup>2+</sup> , Pb <sup>2+</sup> , Cd <sup>2+</sup>	6
PAR (4-(2-Pyridylazo)resorcinol)	495	1.0	Metalloproteins (pH 7.4, 50 mM Hepes buffer with guanidine hydrochloride)	Cu <sup>2+</sup> , Ni <sup>2+</sup>	7
nitro-PAPS (3-[3-hydroxy-4-[(5-nitropyridin-2-yl)diazonyl]-N-propylanilino]propane-1-sulfonate)	574	0.15	Serum (pH 7.8-8.5, Tris-buffer)	Cu <sup>2+</sup> , Fe <sup>2+</sup> (CN <sup>-</sup> )	8
5-Br-PAPS (2-(5-Bromo-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]phenol)	560	15	Serum (0.5 M ammonium acetate/7.2×10 <sup>-3</sup> M salicylaldehyde oxime-1%(v/v) Triton X-100-0.5 M hydrochloric acid)	Fe <sup>2+</sup> , Cu <sup>2+</sup> (salicylaldehyde oxime, Na <sub>3</sub> Cit)	9
TCPP (5,10,15,20-tetrakis(4-carboxylphenyl)-porphyrin)	423	0.9	Natural waters and nutritional supplement (pH 9, Pb <sup>2+</sup> and 0.05 M borate buffer)	Fe <sup>3+</sup> (0.1% (w/v) NH <sub>2</sub> OH)	10
Xylenol orange (2,2',2'',2'''-{(1,1-Dioxo-2,1λ6-benzoxathiole-3,3(1H)-diyl)bis[(6-hydroxy-5-methyl-3,1-phenylene)methylenenitrilo]}tetraacetic acid)	580	0.6	Pharmaceuticals (pH = 5-6, Acetate buffer with 1 mM CDC; stability - 3 h; with CDC up to 7 days)	Al <sup>3+</sup> , Fe <sup>3+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , Pb <sup>2+</sup> (NaF, EDTA)	11
Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene monosodium salt)	620	0.2	Metalloproteins (pH = 8.5 - 9.5, urea; stability - 1-2 h)	Co <sup>2+</sup> in the presence of Cu <sup>2+</sup> , Cu <sup>2+</sup> (EDTA)	12
<b>3b</b> ((Z)-2-(benzo[d]thiazol-2-yl)-2-(5-methyl-3-oxoindolin-2-ylidene)acetonitrile)	600 640	0.5 0.4	Serum model solution (stripped of protein) (Tris-buffer (pH 7.2)/DMSO (1/5, v/v))	Co <sup>2+</sup> after 30 min of prepared, Cu <sup>2+</sup> (1.0 mM Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> )	This work

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