Supplementary Materials: Electronic Supplementary Information (ESI)

7-Dialkylaminocoumarin Oximates: Small Molecule Fluorescent "Turn-on" Chemosensors for Low-Level Water Content in Aprotic Organic Solvents

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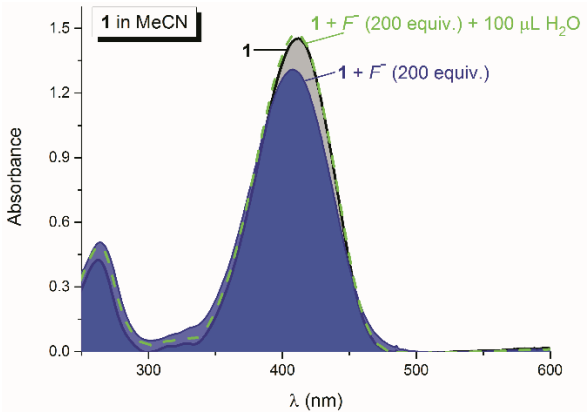


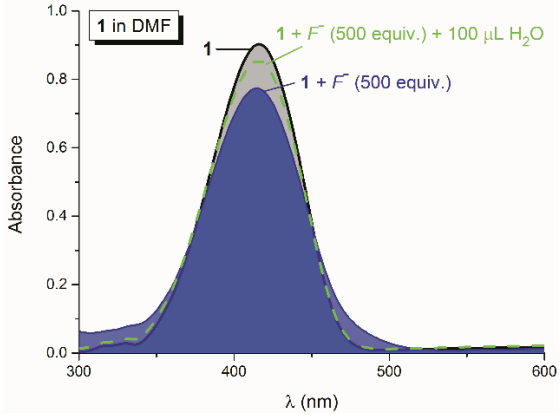
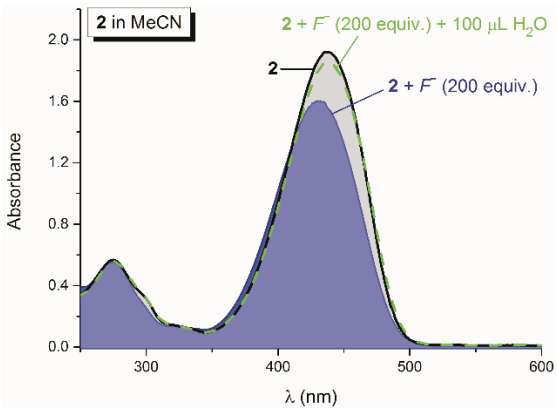


Fig. S1. (left) Evolution of the absorption spectrum of 7-dimethylaminocoumarin oxime **1** in MeCN after F^- anion and subsequent water addition (5×10^{-5} mol L^{-1} **1** + 1×10^{-2} mol L^{-1} TBA^+F^-; T = 298.15 K).

Fig. S2. (right) Evolution of the absorption spectrum of 7-dimethylaminocoumarin oxime **1** in DMF after F^- anion and subsequent water addition (2×10^{-5} mol L^{-1} **1** + 1×10^{-2} mol L^{-1} TBA^+F^-; T = 298.15 K).



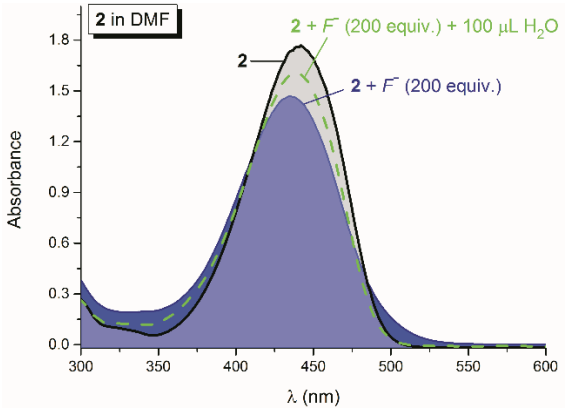
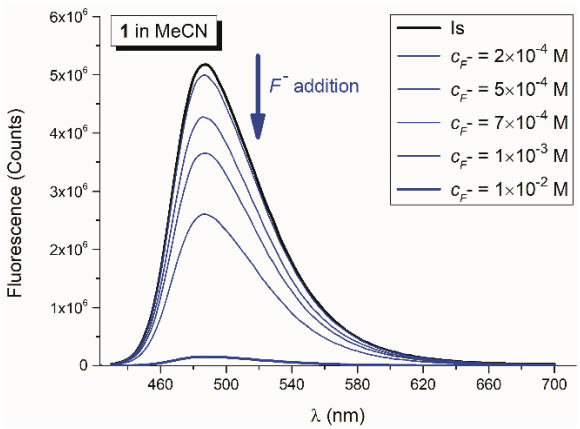


Fig. S3. (left) Evolution of the absorption spectrum of 7-coumarin oxime **2** in MeCN after F^- anion and subsequent water addition (5×10^{-5} mol L^{-1} **1** + 1×10^{-2} mol L^{-1} TBA^+F^-; T = 298.15 K).

Fig. S4. (right) Evolution of the absorption spectrum of coumarin oxime **2** in DMF after F^- anion and subsequent water addition (5×10^{-5} mol L^{-1} **1** + 1×10^{-2} mol L^{-1} TBA^+F^-; T = 298.15 K).



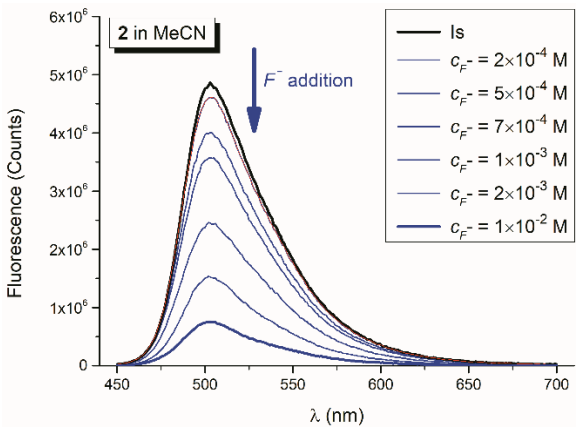


Fig. S5. (left) Evolution of the emission spectrum of 7-coumarin oxime **1** in MeCN during **1** solution titration with TBA^+F^- (5×10^{-5} mol L^{-1} **1**; Is – initial state; T = 298.15 K; M = mol dm^{-3}).

Fig. S6. (right) Evolution of the emission spectrum of coumarin oxime **2** in MeCN during **2** solution titration with TBA^+F^- (5×10^{-5} mol L^{-1} **2**; Is – initial state; T = 298.15 K; M = mol dm^{-3}).

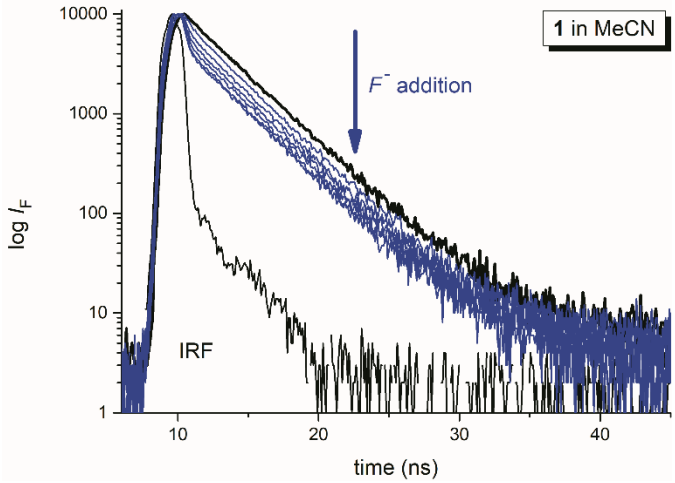


Fig. S7. (right) Evolution of fluorescence decay of 7-coumarin oxime **1** in MeCN during **1** solution titration with TBA^+F^- (5×10^{-5} mol L^{-1} **1**; T = 298.15 K).

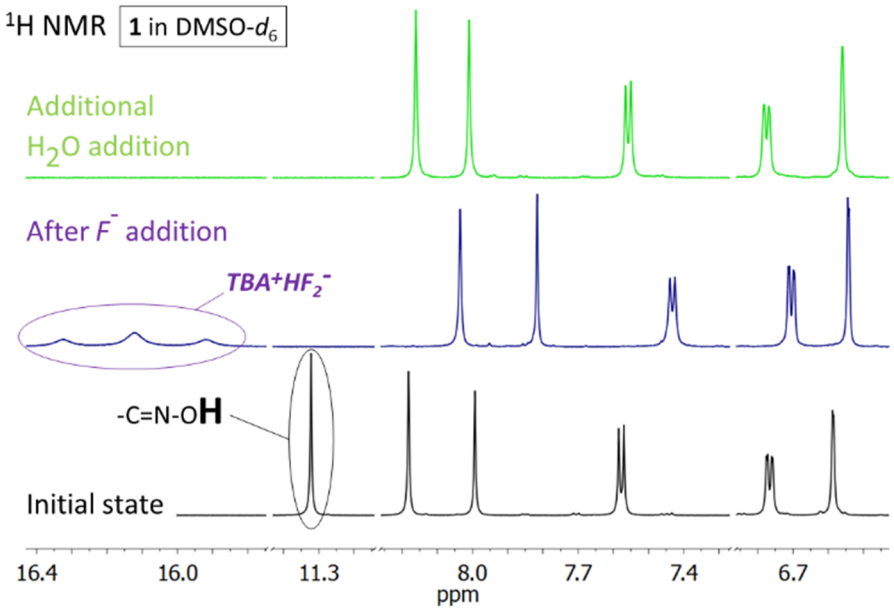


Fig. S8. ^{1}H NMR spectrum of 7-dimethylaminocoumarin oxime **1** in DMSO-d_6 before and after F^- anion (TBA^+F^-) and subsequent water addition ($c_1 = 5\times10^{-4}$ mol L^{-1}; $c_{F^-} = 1\times10^{-1}$ mol L^{-1}; 4% (v/v) of water; T = 298.15 K).

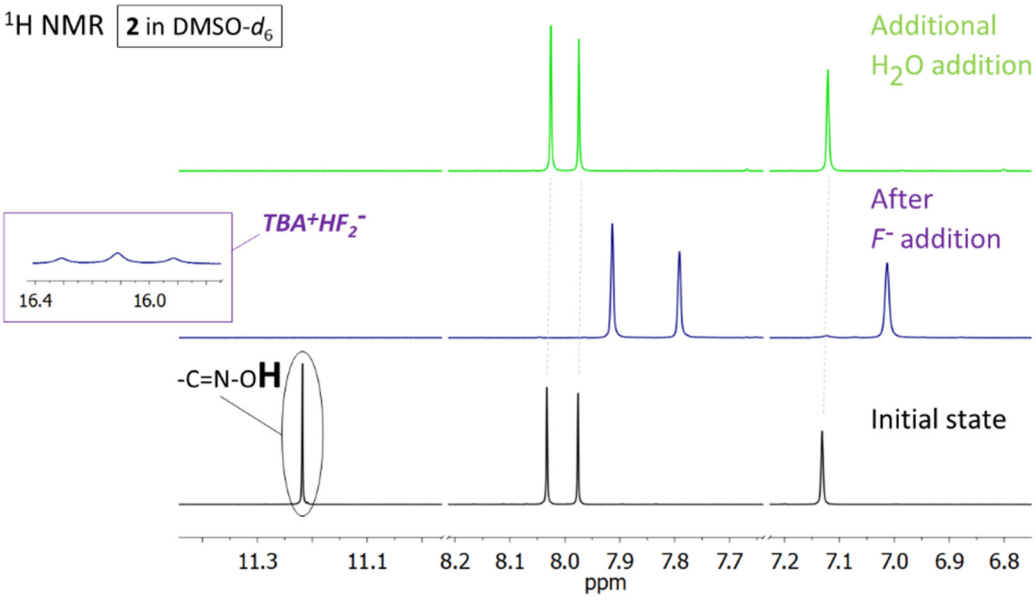


Fig. S9. ^{1}H NMR spectrum of coumarin oxime **2** in DMSO-d_6 before and after F^- anion (TBA^+F^-) and subsequent water addition ($c_2 = 5\times10^{-4}$ mol L^{-1}; $c_{F^-} = 1\times10^{-1}$ mol L^{-1}; 4% (v/v) of water; T = 298.15 K).

Table S1. Relative Gibbs free energy (ΔG) of oxime **1**/oximate **1** stable conformers calculated at the M06-2X/6-311+G(2d,p) level of theory in vacuum on geometries optimized at M06-2X/6-31+G(d,p) level of theory (calculated in Gaussian 09).

Conformer	ΔG (kJ mol^{-1})
oxime I	0
oxime II	2
oxime III	16
oxime IV	23
oxime V	40
oximate VI	0
oximate VII	6
oximate VIII	33
oximate IX	59

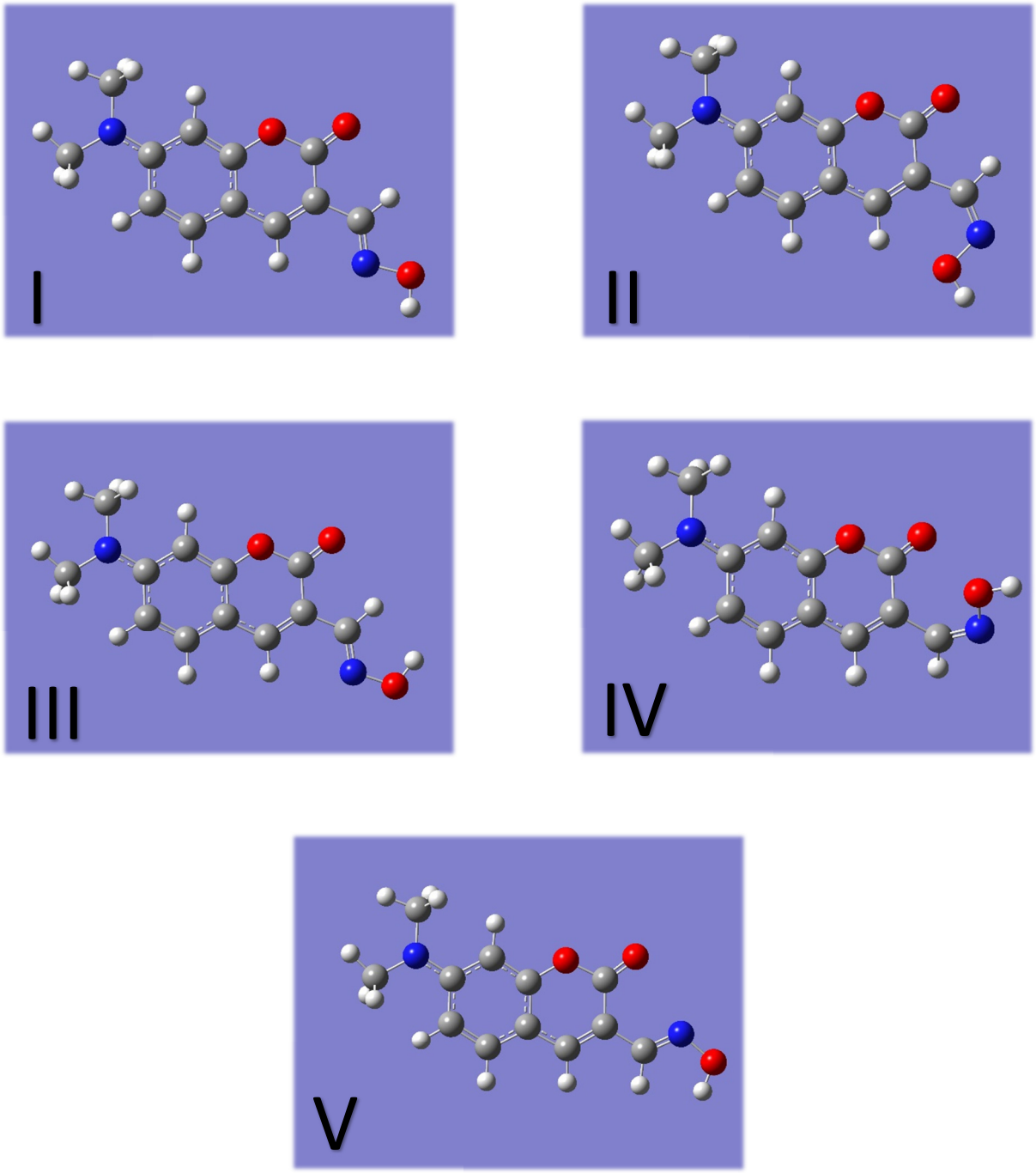


Fig. S10. Geometries of oxime **1** stable conformers optimized at the M06-2X/6-31+G(d,p) level of theory (calculated in Gaussian 09).

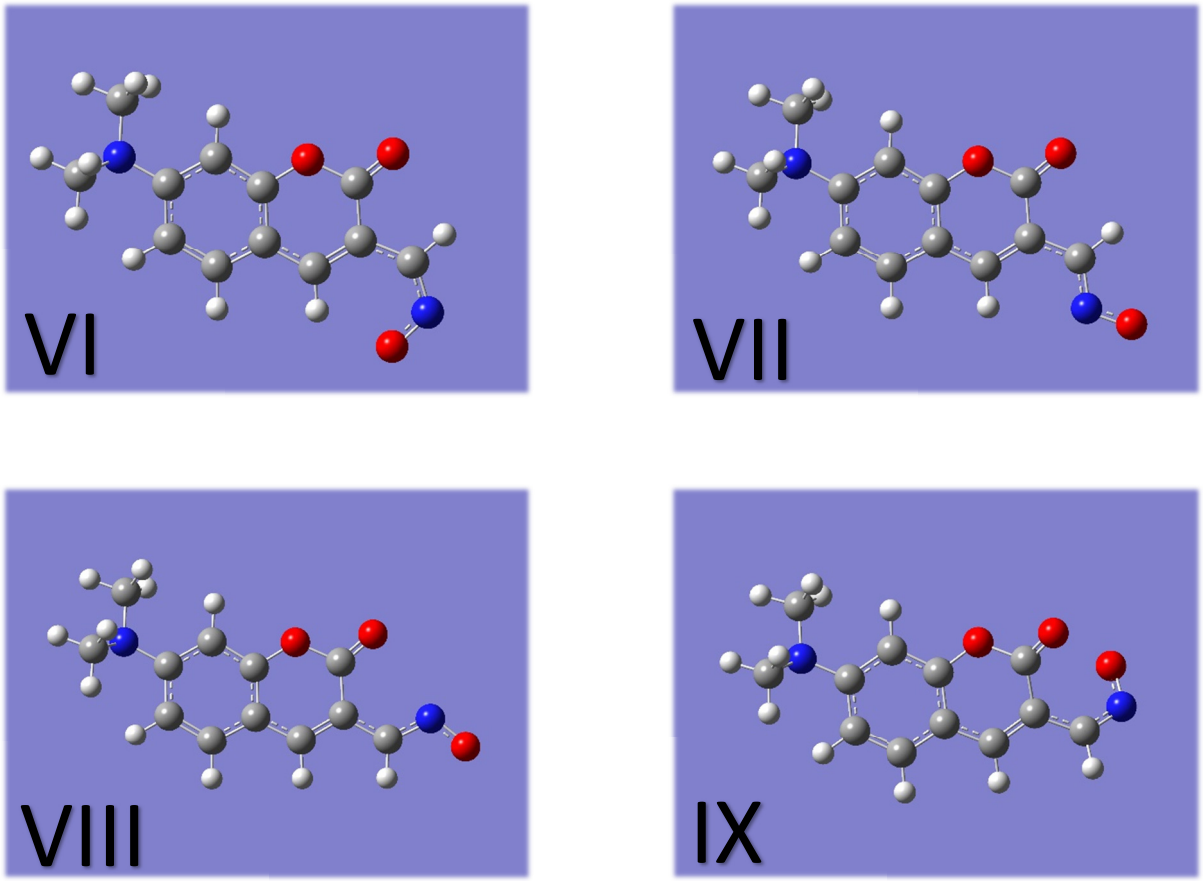
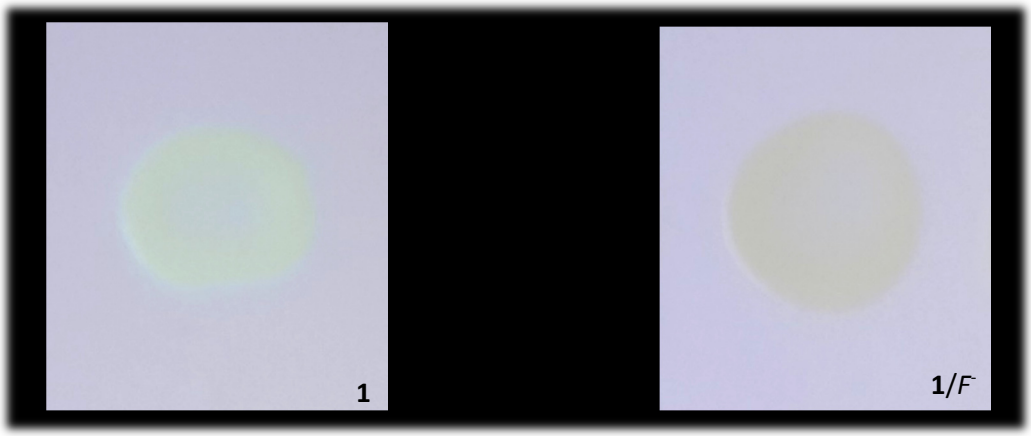


Fig. S10. Geometries of oximate **1** stable conformers optimized at the M06-2X/6-31+G(d,p) level of theory (calculated in Gaussian 09).

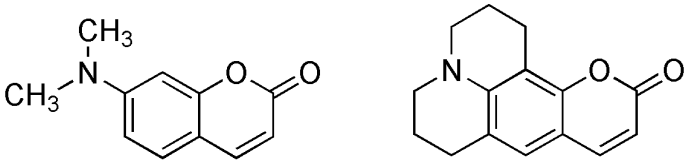


$\Phi_F = 0.80$ $\Phi_F = 0.20$

Fig. S11. Poly (propylene carbonate) thin polymer films of pure 7-dimethylaminocoumarin oxime **1** and two-component 7-dimethylaminocoumarin oxime **1**/F^- system on teflon plate (TBA^+F^- addition to chloroform solution of polycarbonate and oxime **1**; $\lambda_{EX} = \lambda_A$; Φ_F were determined using integrating sphere; poly (propylene carbonate) was purchased from Sigma-Aldrich, St. Louis, MO, USA, Mn ~ 50,000 by GPC).

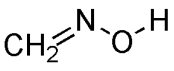
Table S2. Calculated HOMO and LUMO orbital energy of compounds **3-6** at the M06-2X/6-31+G(d,p) level in vacuum (calculated in Gaussian 09).

Compd	**3**	**4**	**5**	**6**
LUMO (kJ mol^{-1})	-77	-75	8	343
HOMO (kJ mol^{-1})	-664	-645	-903	-91



3

4



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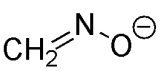

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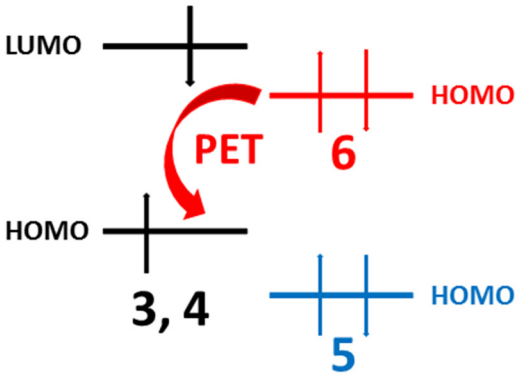


Scheme S1. Molecular structure of compounds **4-6** and scheme of possible intramolecular photoinduced electron transfer (PET).

Table S3. Natural bond orbital (NBO) analysis of oximate **1**.

NATURAL BOND ORBITAL ANALYSIS:

(Occupancy) Bond orbital/ Coefficients/ Hybrids

(1.99179) BD (1) C 14 - N 16

(41.69%) 0.6457* C 14 s(32.72%)p 2.05(67.21%)d 0.00(0.08%)

0.0000 0.5708 -0.0372 0.0032 -0.0005

0.4757 -0.0724 0.0058 -0.0018 -0.6622

0.0402 0.0050 0.0018 -0.0197 -0.0006

0.0005 0.0000 -0.0144 -0.0124 0.0003

-0.0008 0.0017 -0.0003 -0.0057 -0.0033

-0.0192 -0.0002

(58.31%) 0.7636* N 16 s(38.37%)p 1.60(61.31%)d 0.01(0.33%)

0.0001 0.6182 -0.0368 0.0132 -0.0001

-0.4918 -0.0131 0.0098 0.0018 0.6082

-0.0215 -0.0163 0.0030 0.0156 -0.0018

-0.0006 0.0003 -0.0488 -0.0018 -0.0005

-0.0003 0.0005 -0.0001 0.0077 -0.0017

-0.0290 0.0015

(1.80211) BD (2) C 14 - N 16

(56.09%) 0.7489* C 14 s(0.00%)p 1.00(99.97%)d 0.00(0.03%)

0.0000 -0.0005 0.0000 -0.0001 0.0000

-0.0411 -0.0021 -0.0007 -0.0002 -0.0597

-0.0030 -0.0009 -0.0004 0.9958 0.0503

0.0158 0.0063 -0.0001 0.0005 0.0082

-0.0020 -0.0108 -0.0081 -0.0010 -0.0004

-0.0005 -0.0010

(43.91%) 0.6626* N 16 s(0.00%)p 1.00(99.72%)d 0.00(0.28%)

0.0000 0.0002 -0.0001 0.0001 0.0000

-0.0424 0.0001 -0.0004 0.0002 -0.0600

0.0000 -0.0007 0.0003 0.9958 -0.0012

0.0116 -0.0046 0.0026 -0.0003 -0.0508

0.0013 0.0117 0.0053 0.0028 0.0003

-0.0025 0.0007

(1.99247) BD (1) N 16 - O 17

(45.02%) 0.6710* N 16 s(25.25%)p 2.95(74.43%)d 0.01(0.33%)

-0.0001 -0.4957 0.0815 0.0120 0.0003

0.3461 0.0040 -0.0098 -0.0043 0.7817

-0.0965 0.0066 -0.0020 0.0620 -0.0057

0.0000 -0.0003 -0.0426 -0.0076 -0.0046

-0.0002 -0.0061 -0.0009 0.0119 0.0081

0.0336 0.0010

(54.98%) 0.7415* O 17 s(26.03%)p 2.84(73.87%)d 0.00(0.10%)
-0.0001 -0.5057 0.0673 0.0022 0.0000
-0.3496 0.0290 -0.0047 -0.0003 -0.7808
 0.0447 0.0059 -0.0030 -0.0625 0.0039
 0.0001 -0.0002 -0.0200 -0.0032 -0.0014
-0.0003 -0.0035 -0.0007 0.0191 0.0039
 0.0138 0.0032

(1.95729) LP (1) N 16 s(37.02%)p 1.70(62.82%)d 0.00(0.16%)
-0.0003 0.6063 0.0512 -0.0035 0.0002
 0.7898 0.0452 0.0035 0.0047 0.0275
 0.0159 0.0052 -0.0017 0.0352 0.0029
 0.0005 0.0001 -0.0060 0.0039 -0.0034
 0.0007 -0.0010 -0.0001 -0.0295 0.0069
 0.0243 -0.0018

(1.98593) LP (1) O 17 s(74.14%)p 0.35(25.85%)d 0.00(0.00%)
-0.0002 0.8608 0.0221 0.0012 0.0000
-0.2601 0.0081 0.0062 -0.0002 -0.4350
 0.0103 0.0007 -0.0030 -0.0376 0.0009
 0.0003 -0.0002 -0.0042 -0.0010 -0.0004
-0.0001 -0.0008 -0.0002 0.0029 0.0013
 0.0039 0.0010

(1.96420) LP (2) O 17 s(0.27%)p99.99(99.70%)d 0.11(0.03%)
-0.0001 0.0512 -0.0040 -0.0092 0.0000
 0.8975 0.0094 -0.0120 -0.0017 -0.4369
-0.0135 -0.0056 -0.0009 0.0122 -0.0003
-0.0007 -0.0001 0.0133 -0.0019 0.0012
-0.0002 -0.0001 -0.0001 0.0111 -0.0014
 0.0005 0.0010

(1.53924) LP (3) O 17 s(0.00%)p 1.00(99.91%)d 0.00(0.09%)
 0.0000 -0.0001 0.0001 0.0000 0.0000
-0.0430 -0.0009 -0.0005 0.0001 -0.0605
-0.0013 -0.0008 0.0001 0.9964 0.0224
 0.0151 -0.0020 -0.0017 0.0002 0.0084
-0.0005 0.0277 -0.0038 0.0013 -0.0002
 0.0036 -0.0005

NATURAL POPULATIONS: Natural atomic orbital occupancies

NAO	Atom	No	lang	Type(AO)	Occupancy	Energy
267	C	14	S	Cor(1S)	1.99925	-10.24859
268	C	14	S	Val(2S)	0.90734	-0.00475
269	C	14	S	Ryd(3S)	0.00358	1.34642
270	C	14	S	Ryd(4S)	0.00020	3.96174
271	C	14	S	Ryd(5S)	0.00002	18.57657
272	C	14	px	Val(2p)	0.99817	0.11896
273	C	14	px	Ryd(4p)	0.00933	1.05646
274	C	14	px	Ryd(3p)	0.00096	0.74087
275	C	14	px	Ryd(5p)	0.00022	3.33408
276	C	14	py	Val(2p)	1.05382	0.09989
277	C	14	py	Ryd(4p)	0.01086	1.22127
278	C	14	py	Ryd(3p)	0.00073	0.58982
279	C	14	py	Ryd(5p)	0.00019	3.52857
280	C	14	pz	Val(2p)	1.17544	0.03370
281	C	14	pz	Ryd(4p)	0.00853	0.67088
282	C	14	pz	Ryd(3p)	0.00031	0.44905
283	C	14	pz	Ryd(5p)	0.00011	2.99884
284	C	14	dxy	Ryd(3d)	0.00062	2.27965
285	C	14	dxy	Ryd(4d)	0.00045	3.66097
286	C	14	dxz	Ryd(3d)	0.00022	1.87841
287	C	14	dxz	Ryd(4d)	0.00012	2.98888
288	C	14	dyz	Ryd(3d)	0.00042	1.82525
289	C	14	dyz	Ryd(4d)	0.00022	2.84354
290	C	14	dx2y2	Ryd(3d)	0.00082	2.45311
291	C	14	dx2y2	Ryd(4d)	0.00036	3.60667
292	C	14	dz2	Ryd(3d)	0.00109	2.19609
293	C	14	dz2	Ryd(4d)	0.00025	3.28938
300	N	16	S	Cor(1S)	1.99943	-14.47317
301	N	16	S	Val(2S)	1.39728	-0.40799
302	N	16	S	Ryd(4S)	0.01707	1.49930
303	N	16	S	Ryd(3S)	0.00038	1.08834
304	N	16	S	Ryd(5S)	0.00000	35.39732
305	N	16	px	Val(2p)	1.61501	-0.09125
306	N	16	px	Ryd(4p)	0.00867	1.00117
307	N	16	px	Ryd(3p)	0.00045	0.78597
308	N	16	px	Ryd(5p)	0.00009	4.46133
309	N	16	py	Val(2p)	0.98289	0.02984
310	N	16	py	Ryd(4p)	0.01365	1.07899
311	N	16	py	Ryd(3p)	0.00160	0.75086
312	N	16	py	Ryd(5p)	0.00012	4.90360
313	N	16	pz	Val(2p)	1.00556	-0.01496
314	N	16	pz	Ryd(4p)	0.00028	0.81832
315	N	16	pz	Ryd(3p)	0.00017	0.65785

316	N	16	pz	Ryd(5p)	0.00002	4.05992
317	N	16	dxy	Ryd(3d)	0.00568	2.25703
318	N	16	dxy	Ryd(4d)	0.00011	5.23629
319	N	16	dxz	Ryd(3d)	0.00324	1.62841
320	N	16	dxz	Ryd(4d)	0.00003	4.83991
321	N	16	dyz	Ryd(3d)	0.00214	1.68757
322	N	16	dyz	Ryd(4d)	0.00005	4.89550
323	N	16	dx2y2	Ryd(3d)	0.00327	1.92797
324	N	16	dx2y2	Ryd(4d)	0.00028	5.16461
325	N	16	dz2	Ryd(3d)	0.00331	1.88476
326	N	16	dz2	Ryd(4d)	0.00003	5.00706
327	O	17	S	Cor(1S)	1.99985	-19.24327
328	O	17	S	Val(2S)	1.75899	-0.77893
329	O	17	S	Ryd(3S)	0.00800	1.14819
330	O	17	S	Ryd(4S)	0.00027	1.89363
331	O	17	S	Ryd(5S)	0.00000	49.85996
332	O	17	px	Val(2p)	1.85373	-0.15207
333	O	17	px	Ryd(3p)	0.00431	0.94000
334	O	17	px	Ryd(4p)	0.00070	1.32363
335	O	17	px	Ryd(5p)	0.00002	5.40781
336	O	17	py	Val(2p)	1.42646	-0.09848
337	O	17	py	Ryd(3p)	0.00468	0.86741
338	O	17	py	Ryd(4p)	0.00014	1.10333
339	O	17	py	Ryd(5p)	0.00005	5.46642
340	O	17	pz	Val(2p)	1.53569	-0.11073
341	O	17	pz	Ryd(3p)	0.00535	0.65018
342	O	17	pz	Ryd(4p)	0.00037	1.21267
343	O	17	pz	Ryd(5p)	0.00002	5.22447
344	O	17	dxy	Ryd(3d)	0.00095	2.86776
345	O	17	dxy	Ryd(4d)	0.00003	6.88415
346	O	17	dxz	Ryd(3d)	0.00015	2.58735
347	O	17	dxz	Ryd(4d)	0.00000	6.33266
348	O	17	dyz	Ryd(3d)	0.00133	2.69423
349	O	17	dyz	Ryd(4d)	0.00003	6.63320
350	O	17	dx2y2	Ryd(3d)	0.00077	2.87408
351	O	17	dx2y2	Ryd(4d)	0.00005	6.92107
352	O	17	dz2	Ryd(3d)	0.00028	2.72100
353	O	17	dz2	Ryd(4d)	0.00002	6.64220

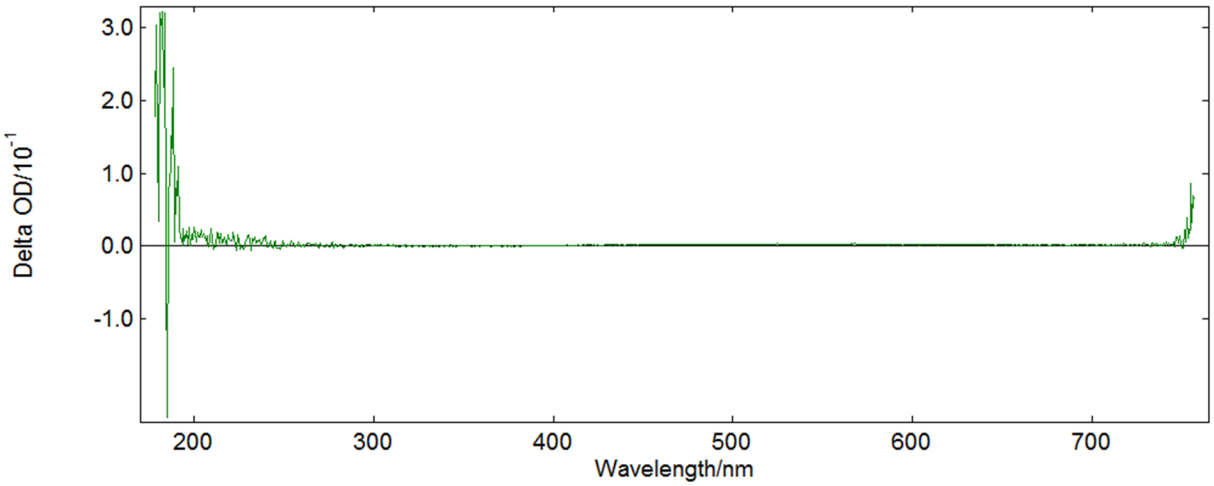
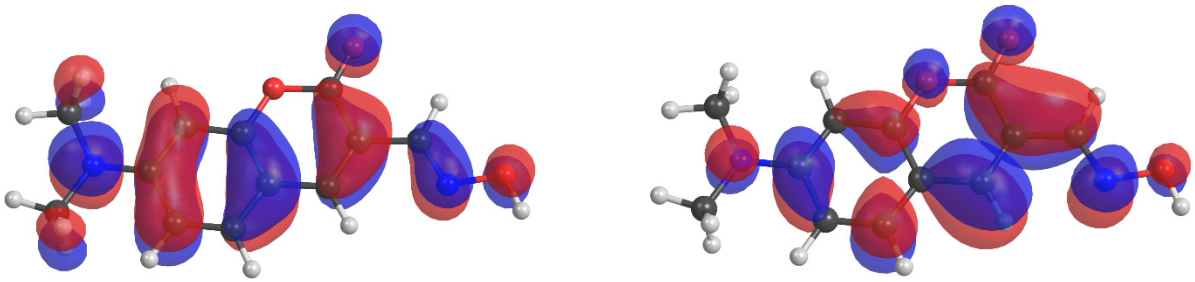


Fig. S12. Transient absorption spectrum of 7-dimethylaminocoumarin oxime **1**/F^- system in MeCN (Edinburgh Instruments Flash photolysis LP980-Spectrometer – nanosecond flash photolysis system; λ_{EX} = 355 nm; T = 298.15 K). Kinetic analysis of the transient absorption spectrum at different wavelength in the region of 200-700 nm does not confirm the presence of any transient decay above 5ns.

Table S4. Excitation energies, oscillator strengths (*f*) and orbital contributions to corresponding electronic transitions from ground state (S_0) of studied coumarin oxime **1** (geometry was optimized at the M06-2X/6-31+G(d,p) level of theory and energies were calculated at the M06-2X/6-311+G(2d,p) level of theory).

7-dimethylaminocoumarin oxime 1					
Excited state	Orbital contributions		Energy [eV]	[nm]	Oscillator strength
T_1	HOMO-2 → LUMO HOMO-1 → LUMO HOMO → LUMO	(6%) (3%) (86%)	2.27	545	0.0000
S_1	HOMO → LUMO	(96%)	3.58	346	0.7375



HOMO **LUMO**

Fig. S13. Frontier molecular orbitals of 7-dimethylaminocoumarin oxime **1** (geometry was optimized at the M06-2X/6-31+G(d,p) level of theory and energies were calculated at the M06-2X/6-311+G(2d,p) level of theory).

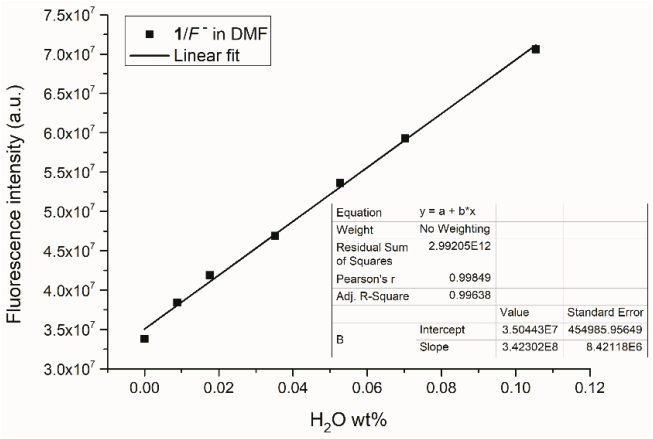


Fig. S14. Fluorescence intensity behaviour of studied two-component coumarin oxime sensor **1**/F^- in DMF during titration with water ($\lambda_{EX} = \lambda_{A(oxime)}$; $T = 298.15$ K).

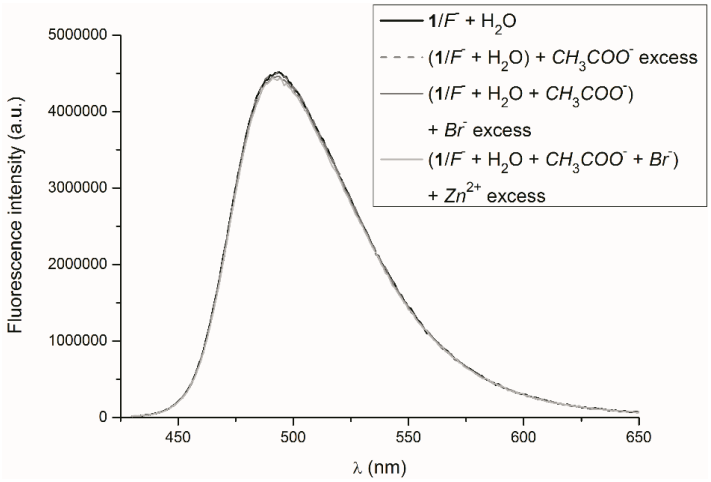


Fig. S15. Fluorescence spectrum of 7-dimethylaminocoumarin oxime **1**/F^- system in MeCN after 4 wt% water addition in the presence of various ion excess (~5×10^{-5} mol L^{-1} oxime + 1×10^{-2} mol L^{-1} TBA^+F; $\lambda_{EX} = \lambda_{A(oxime)}$; $T = 298.15$ K).

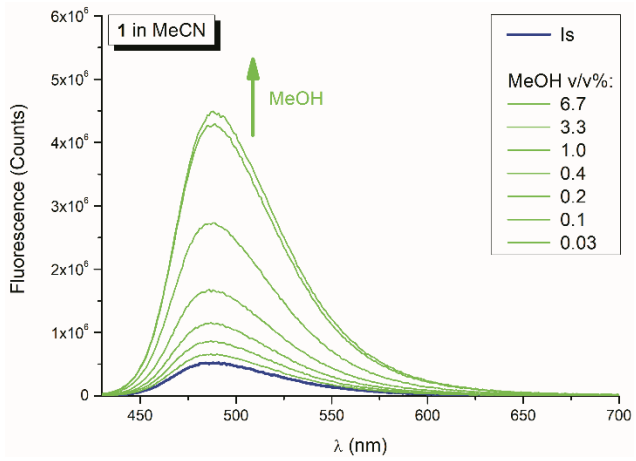


Fig. S16. Evolution of the emission spectrum of 7-dimethylaminocoumarin oxime **1**/F^- system in MeCN during **1**/F^- solution titration with methanol ($c_1 = 3\times10^{-5}$ mol L^{-1}; $c_{F^-} = 1\times10^{-2}$ mol L^{-1}; $\lambda_{EX} = 416$ nm; Is – initial state; $T = 298.15$ K).

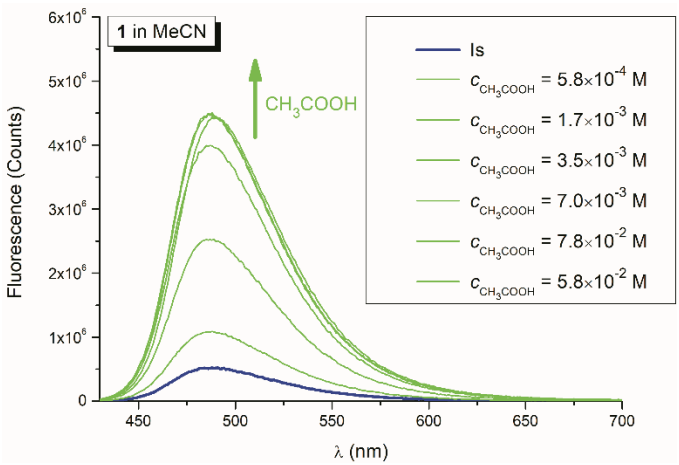


Fig. S17. Evolution of the emission spectrum of 7-dimethylaminocoumarin oxime **1**/F^- system in MeCN during **1**/F^- solution titration with acetic acid ($c_1 = 3\times10^{-5}$ mol L^{-1}; $c_{F^-} = 1\times10^{-2}$ mol L^{-1}; $\lambda_{EX} = 416$ nm; Is – initial state; $T = 298.15$ K; M = mol dm^{-3} = mol L^{-1}).

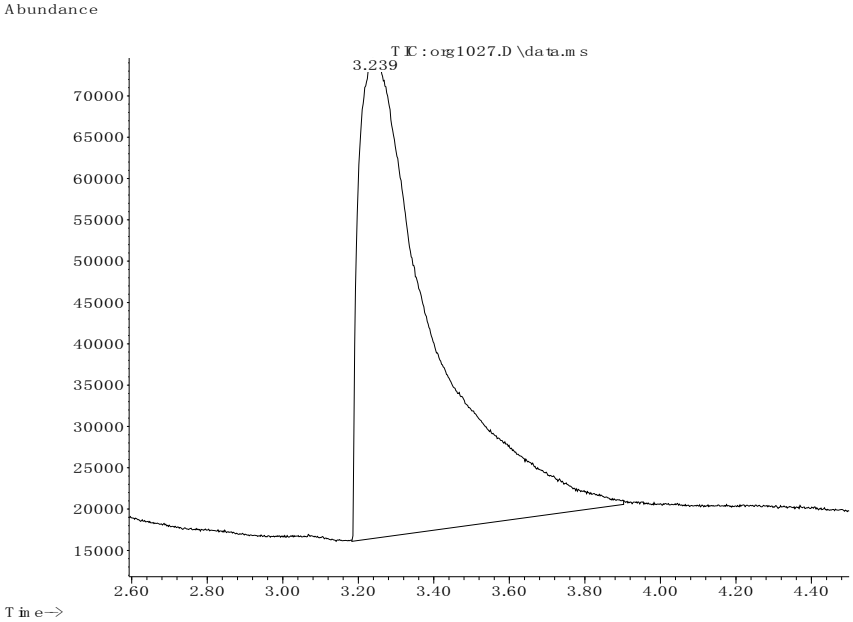


Fig. S18. GC-MS chromatogram of water analysis in MeCN in ionic liquid capillary column (0.4 v/v% of water; x-axis: time in seconds; capillary column coated with a 0.2 μm film thickness of ionic liquid SPB-IL100 as stationary phase was used).

Fig. S19. Coumarin oxime **1:** ^{1}H NMR, ^{13}C NMR.

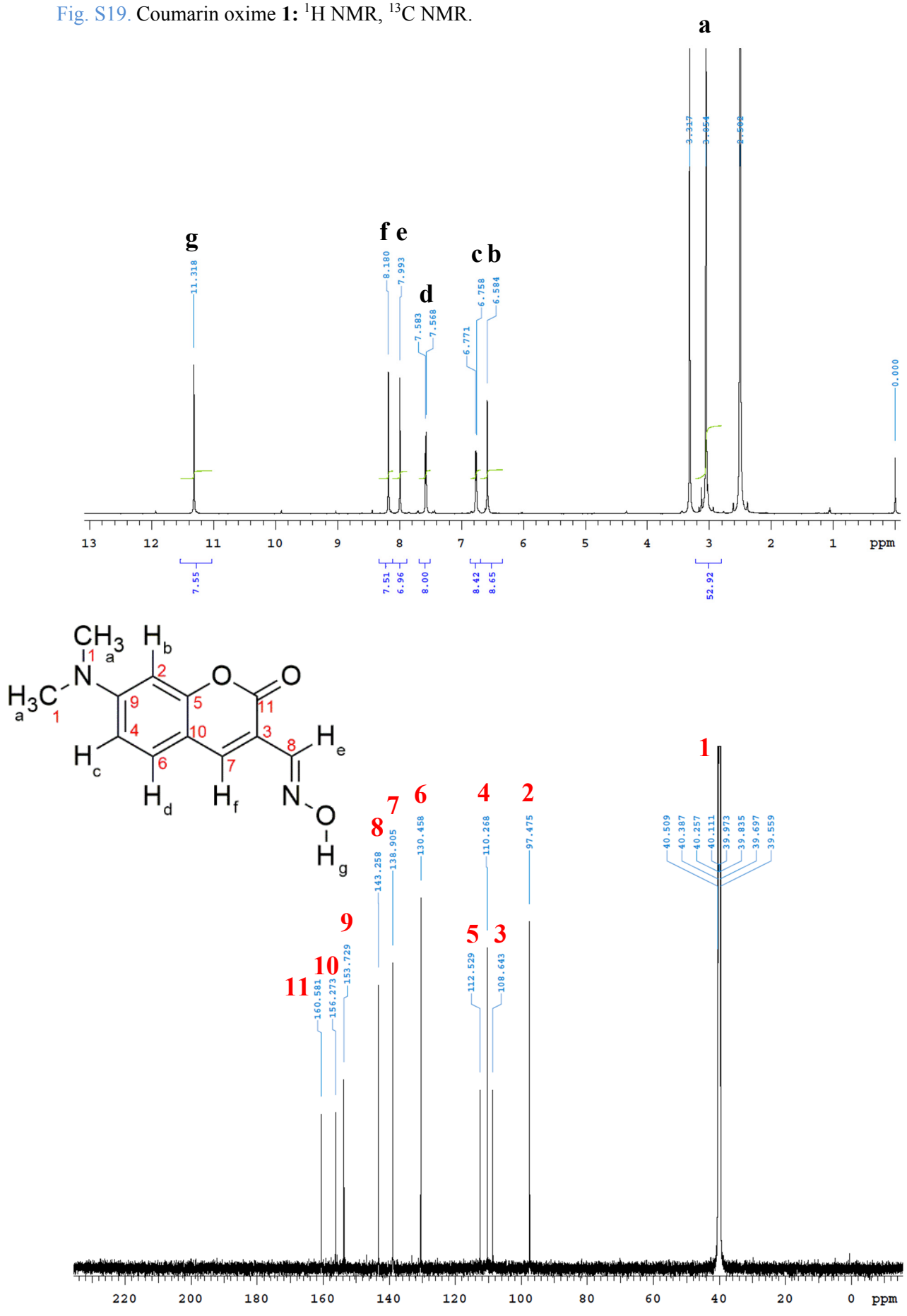
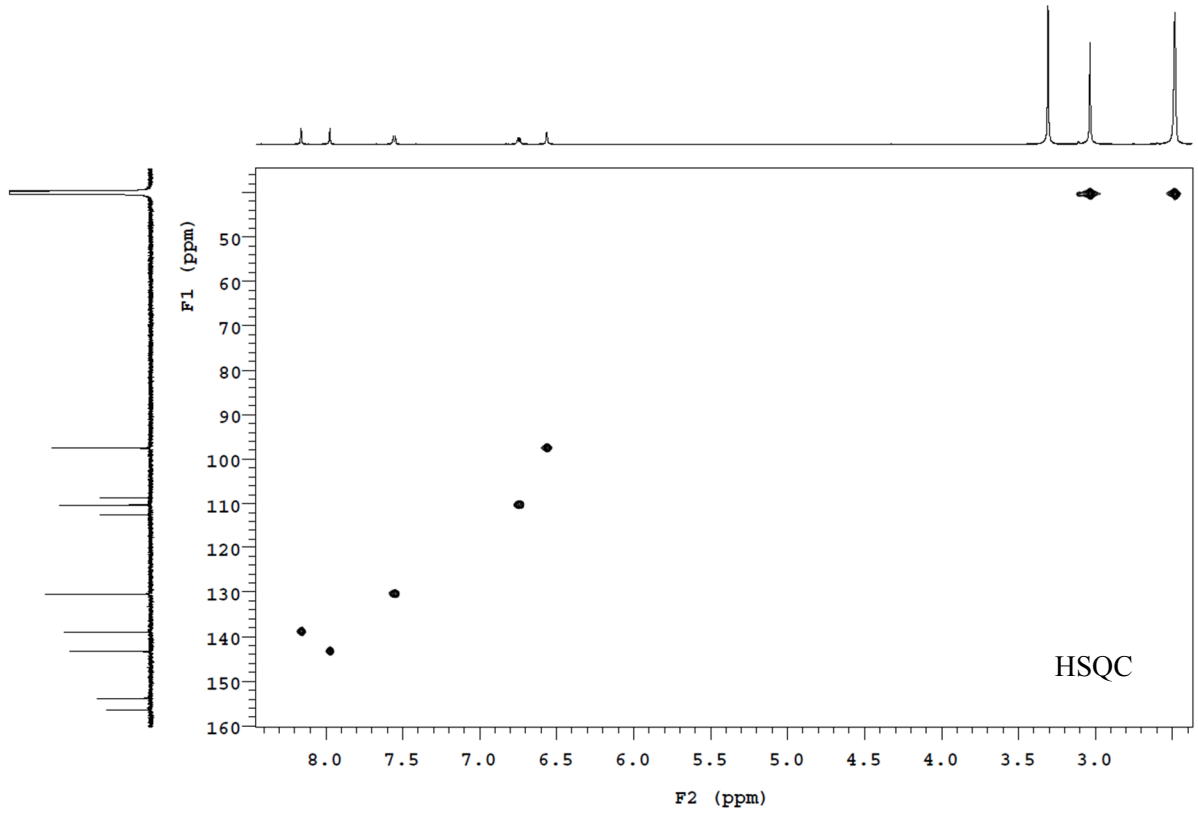


Fig. S19. Coumarin oxime **1:** 2D NMR spectra: HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation).



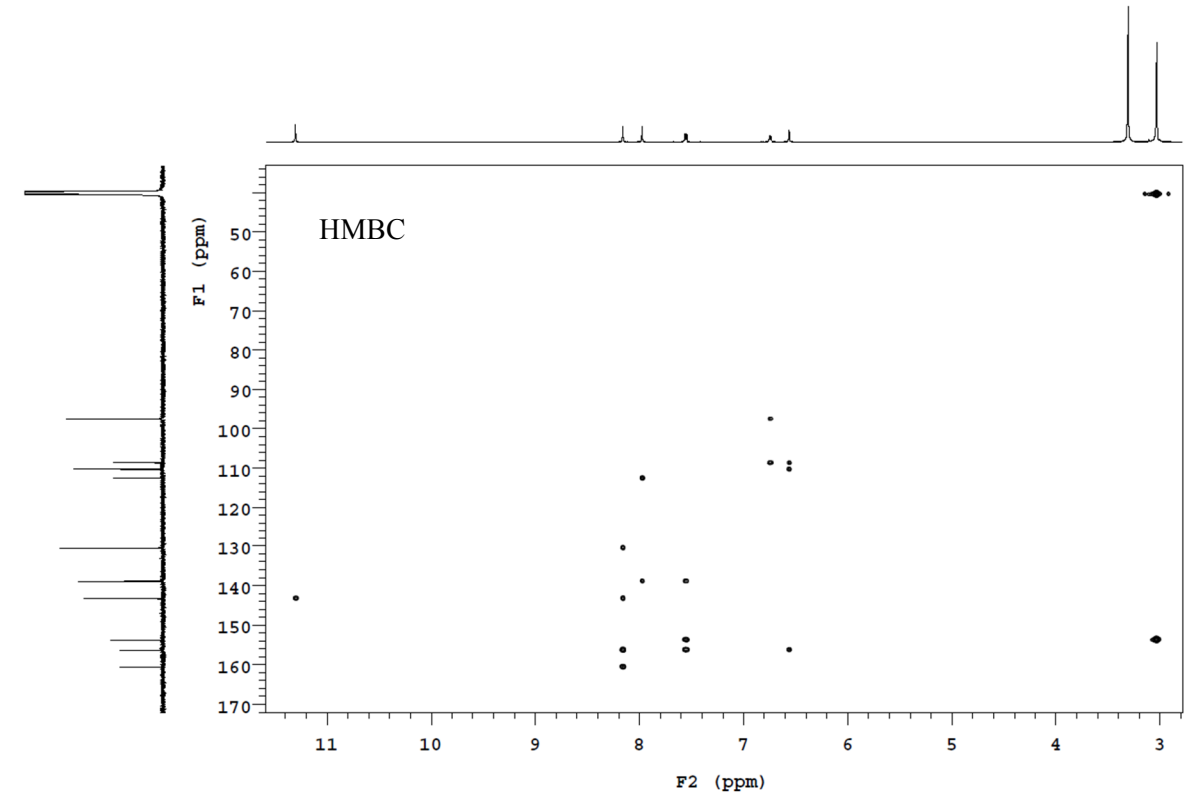


Fig. S20. Coumarin oxime **2:** ^{1}H NMR, ^{13}C NMR.

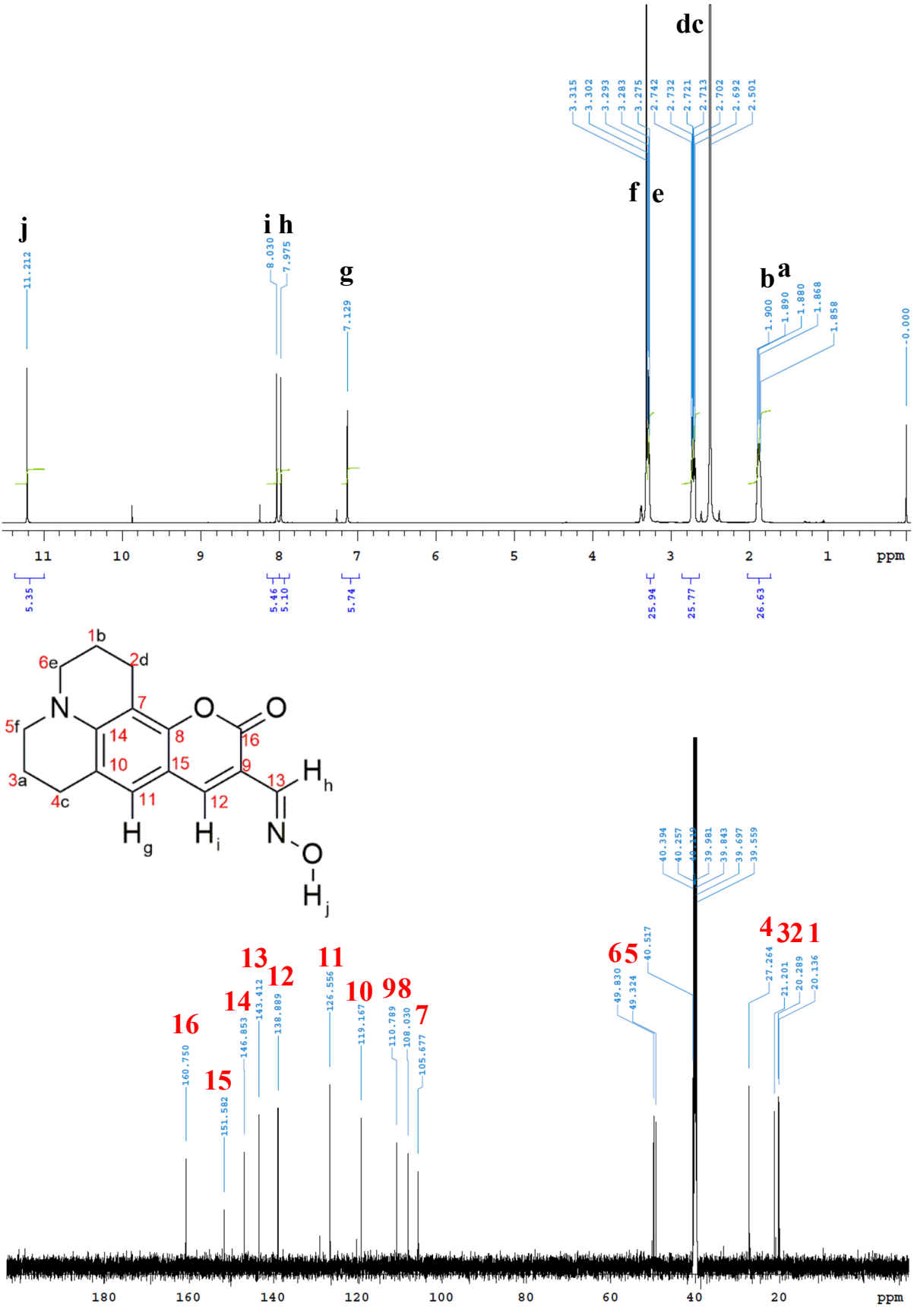


Fig. S20. Coumarin oxime **2:** 2D NMR spectra: HSQC (Heteronuclear Single Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Correlation).