Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

An Abnormally Slow Proton Transfer Reaction in a Simple HBO Derivative due to Ultrafast Intramolecular-Charge Transfer Events

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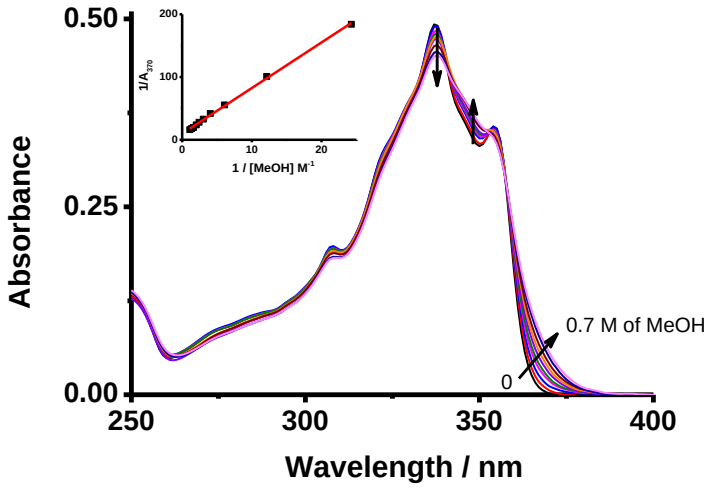


Figure S1. Absorption spectra of 6A-HBO ($8x10^{-6}$ M) in n-heptane (black spectrum) and in the presence of different concentrations of MeOH (0.04; 0.08; 0.16; 0.24; 0.32; 0.40; 0.50; 0.60; 0.70 M) . The inset shows the best linear fit assuming a 1:1 6A-HBO/MeOH complex using a Benesi-Hildebrand model.[1]

Supposing a 1:1 stoichiometric of the 6A-HBO/MeOH complex following the reaction:

$$\text{6A-HBO} + \text{MeOH} \underset{}{\overset{K_e}{\rightleftharpoons}} \text{6A-HBO/MeOH}$$

the Benesi-Hildebrand analysis can be appliqued when [MeOH]>>[6A-HBO] to get the equilibrium constant, K_e.

Our analysis involves the measurement of absorbance intensity at 370 nm (A_{370}) of the 6A-HBO/MeOH complex in function of addition of MeOH (M). The equation defined for a 1:1 complex is the following:

$$\frac{1}{A_{370}} = \frac{1}{\varepsilon_{370}[6AHBO]_0 K_e}\frac{1}{[MeOH]} + \frac{1}{\varepsilon_{370}[6AHBO]_0}$$

Where $y = 1/A_{370}$, $x = 1/[MeOH]$ (M^{-1}) and ε_{370} is the molar absorption coefficient at 370 nm.

A linear plot of "y" vs "x" gives a intercept = $1/\varepsilon[6A\text{-}HBO]_0$ and a slope = $1/\varepsilon[6A\text{-}HBO]_0K_e$. The ratio intercept/slope gives a K_e value of 1.4±0.2 M^{-1} at 293 K.

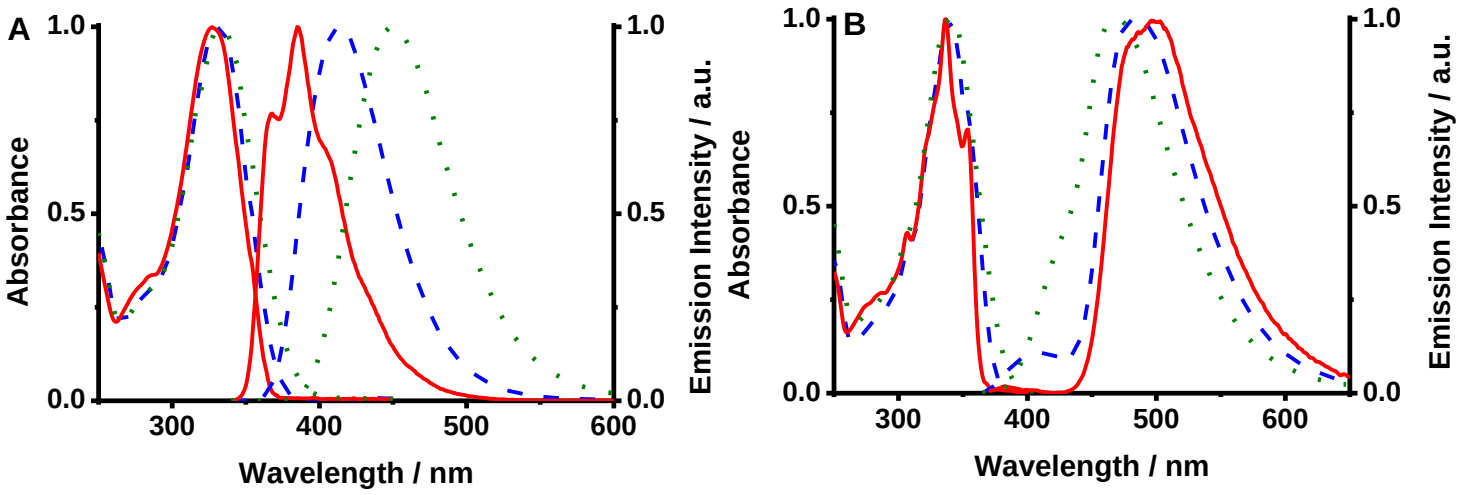


Figure S2. Normalized UV-visible absorption and fluorescence spectra of (A) 6A-MBO and (B) 6A-HBO in n-heptane (solid line), dicloromethane (DCM) (dashed line) and methanol (MeOH) (dotted line), upon excitation at 330 nm.

Calculation of pKb and pKa

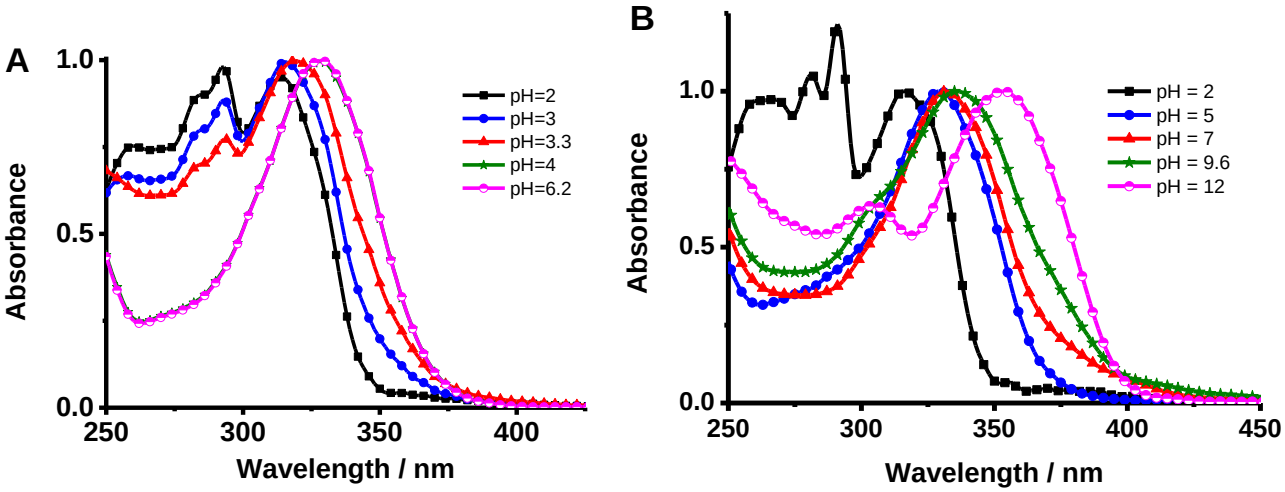


Figure S3. Normalized UV-visible absorption spectra (A) of 6A-MBO and (B) 6A-HBO in different pH solutions.

We calculated the pK_a of the species using:

$$pKa = pH + \log r \qquad \textbf{Eq.S1}$$

$$r = \frac{A - A_N}{A_I - A} \qquad \textbf{Eq.S2}$$

$\mathbf{A_N}$**:** Absoption intensity of the neutral specie (at pH 7).

$\mathbf{A_I}$**:** Absoption intensity of the ionic specie (cationic or anionic, at pH 2 and 12, respectively).

To get the values of pKa (-NH^+ of the benzoxazole ring) in 6A-MBO and 6A-HBO, and pKa (-OH of the phenyl ring) in 6A-HBO, absorption intensity (A) were taken at 295 nm, 316 nm and 360 nm, respectively.

Calculation of pKb* and pKa*

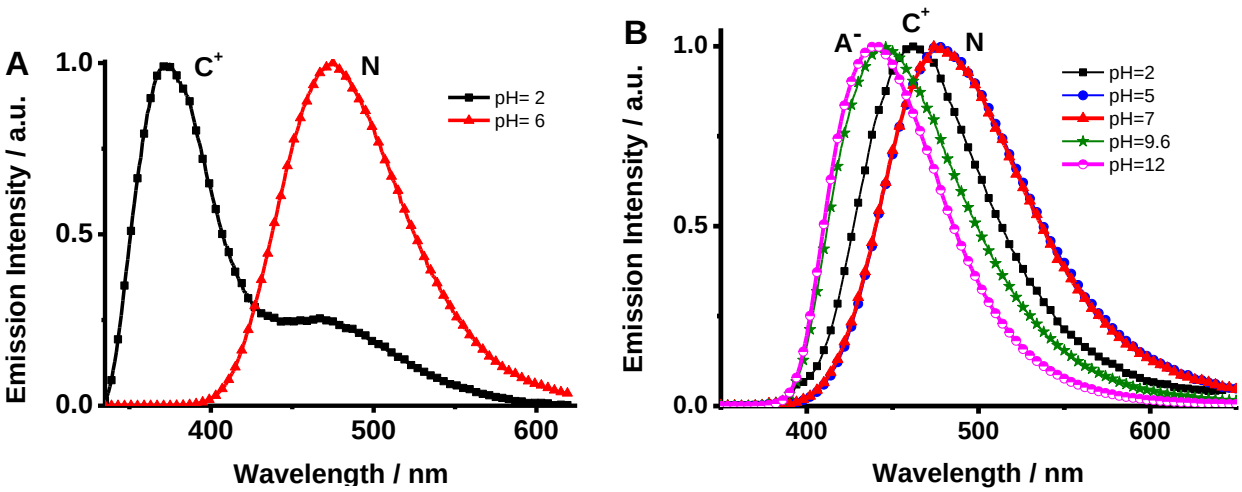


Figure S4. Normalized Fluorescence spectra (A) of 6A-MBO and (B) 6A-HBO, respectively, in different pH solutions and upon excitation at 335 nm.

To calculate pK_a^* (at S_1) we used the following equation[2], where ν_{AH+}, ν_{A-} and ν_{AH} are the frecuency of the 0-0 transition (cm^{-1}) of the cationic, anionic and neutral forms, respectively. The term 2.4 x 10^{-3} is for T=293K.

$$pK_a^* - pK_a = 2.4x10^{-3}(\nu_{AH+/A-} - \nu_{AH}) \qquad \textbf{Eq.S3}$$

For 6A-MBO in water solutions we got:

pKa (-NH^+)=3.47±0.2; pKa* (-NH^+)=17±0.15

For 6A-HBO in water solutions we got:

pKa (-NH^+)=3.45±0.12; pKa* (-NH^+)=5.02±0.1

pKa (-OH)=10.11±0.15; pKa* (-OH)=2.45±0.11

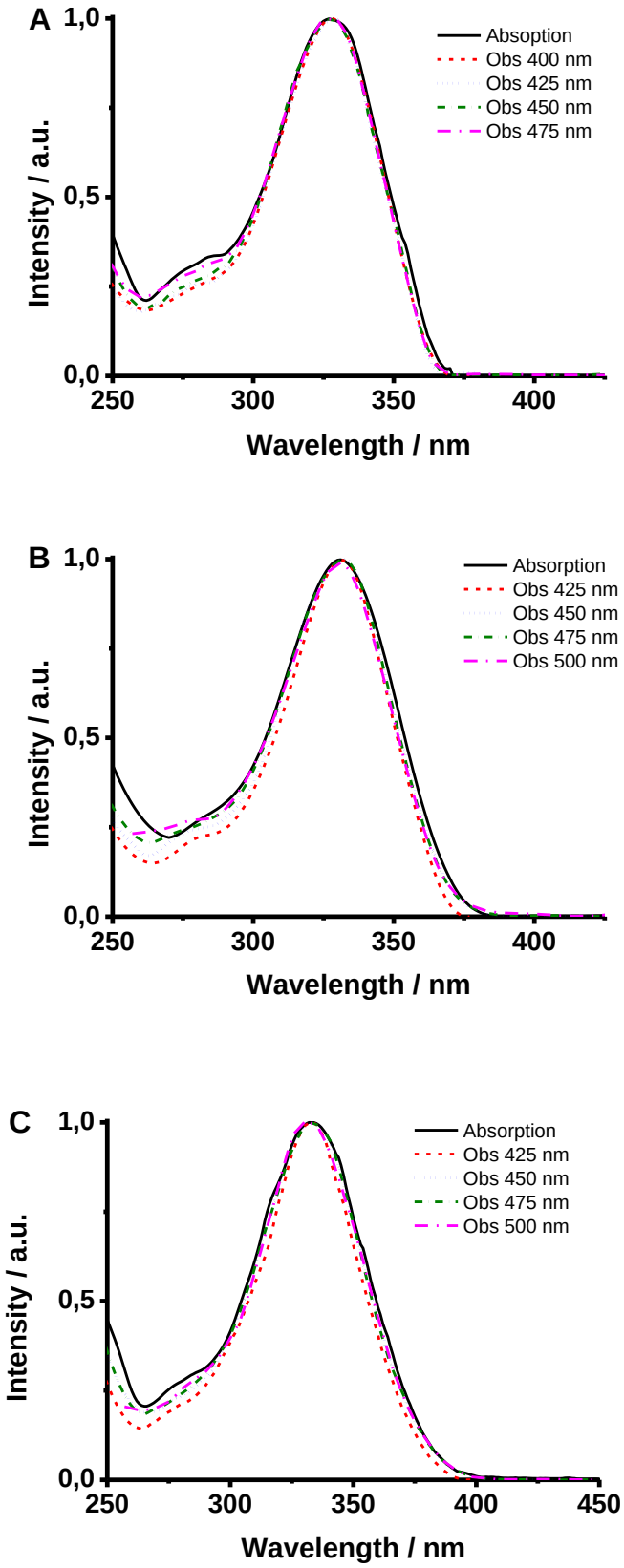


Figure S5. Excitation fluorescence and absorption spectra of 6A-MBO in (A) n-heptane, (B) DCM, and (C) MeOH, solutions. The observation wavelengths are shown in the inset.

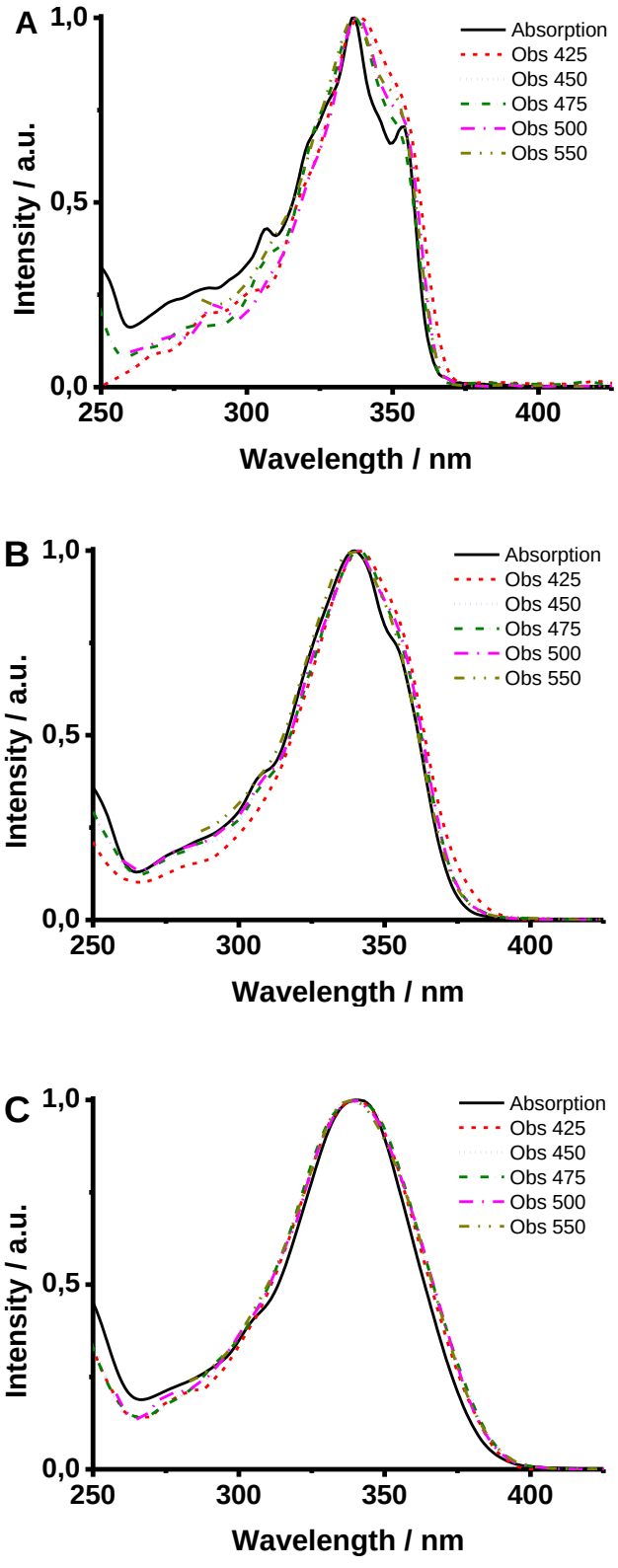


Figure S6. Excitation fluorescence and absorption spectra of 6A-HBO in (A) n-heptane, (B) DCM, and (C) MeOH, solutions. The observation wavelengths are shown in the inset.

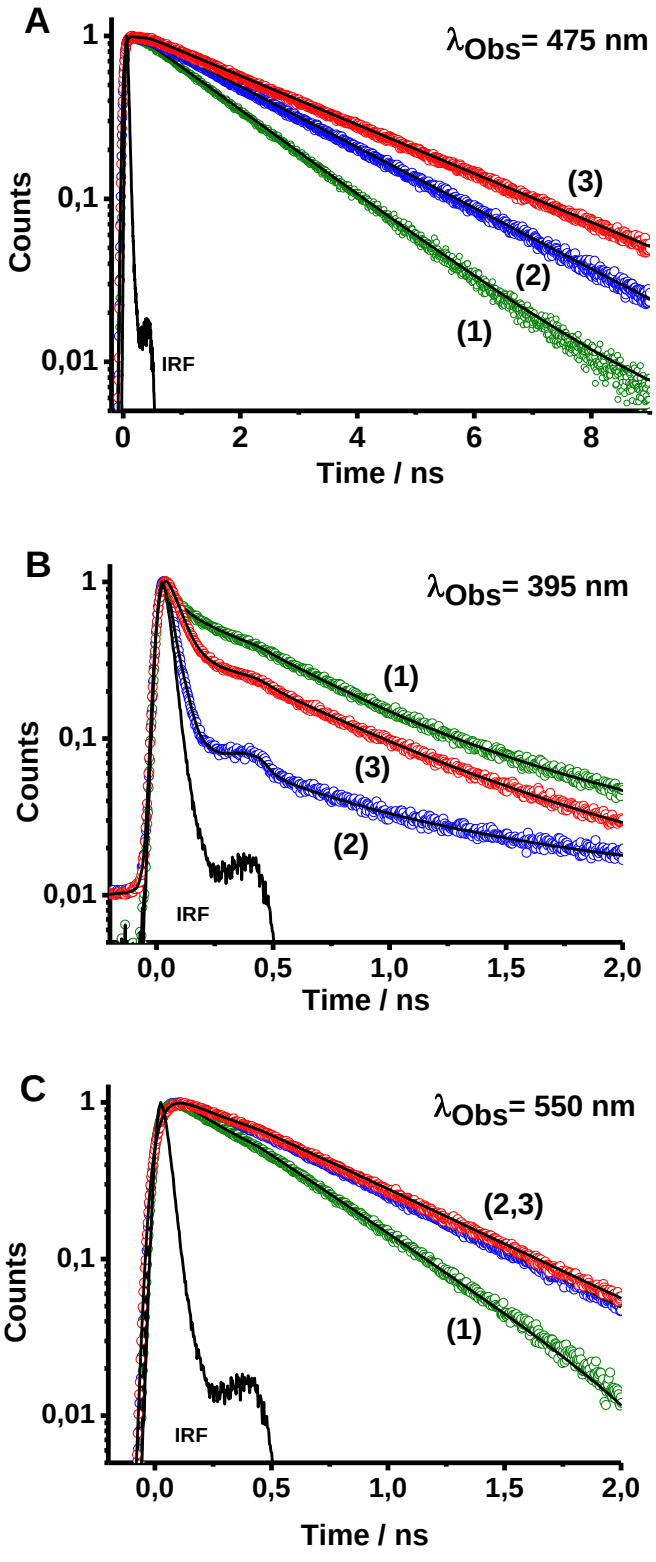


Figure S7. Magic-angle emission decays of (A) 6A-MBO, (B) and (C) 6A-HBO in (1) n-heptane, (2) DCM, and (3) MeOH solutions. The wavelength of observation is indicated as inset. The samples were excited at 371 nm. The solid lines are from the best-fit using a multiexponential function.

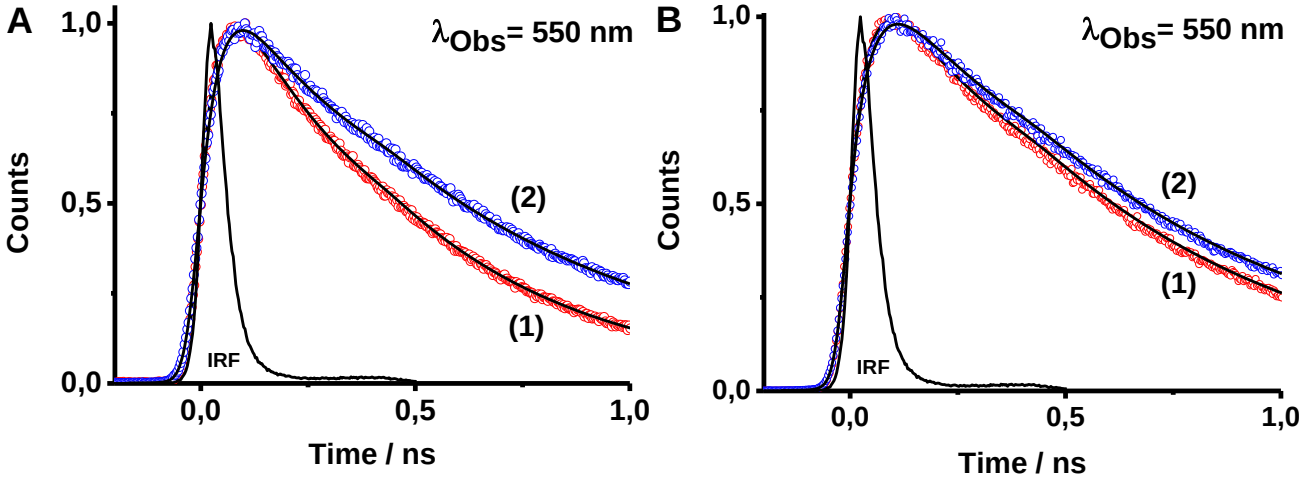


Figure S8. Magic-angle emission decays of (1) 6A-HBO and (2) deuterated 6A-DBO in (A) n-heptane and (B) DCM-d_2 solutions. The samples were excited at 371 nm and observed as indicated in the insets. The solid lines are from the best-fit using multiexponential functions.

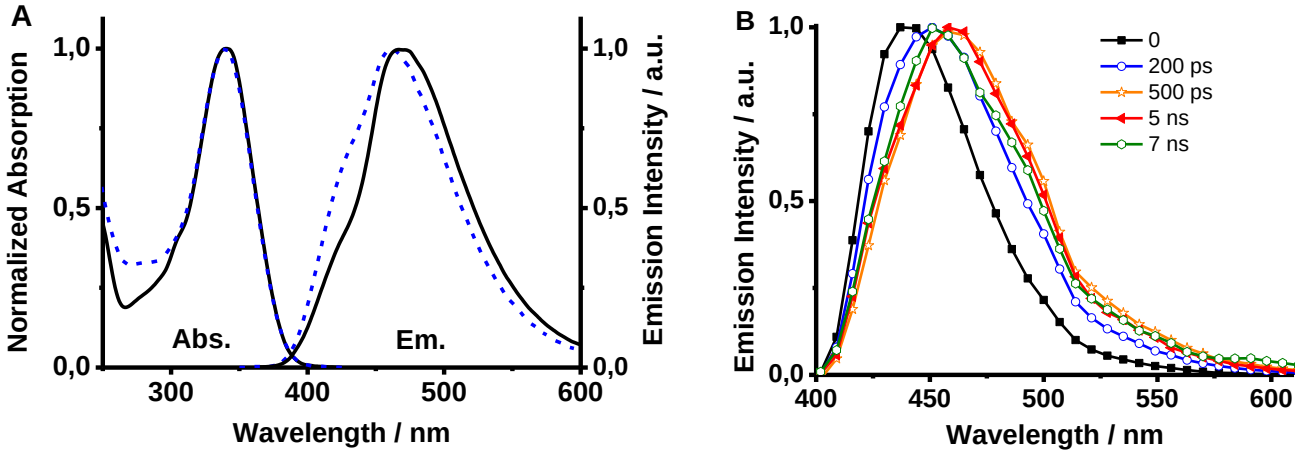


Figure S9. (A) Normalized UV-visible absorption and fluorescence spectra of 6A-HBO (solid line) and deuterated 6A-DBO (dashed line) in MeOH and CD_3OD solutions, respectively. (B) Normalized (to the maximum of intensity) magic-angle time-resolved emission spectra of 6A-DBO in CD_3OD gated at the indicated delay times after excitation at 371 nm. The inset gives the gating time of the spectra.

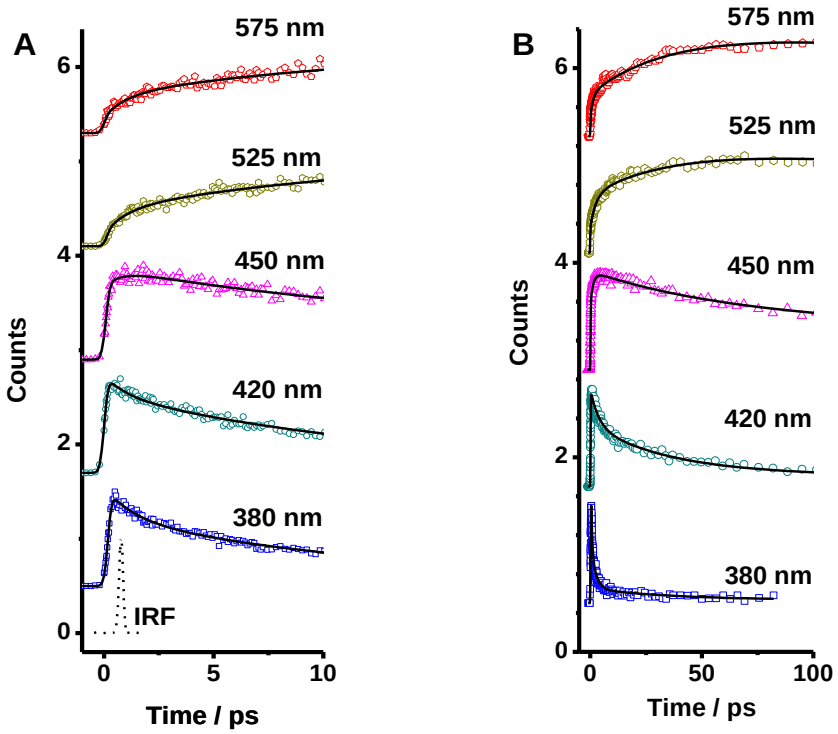


Figure S10. Magic-angle fs-emission transients of 6A-HBO in (A) DCM and (B) MeOH. The samples were excited at 350 nm and the wavelengths of observation are indicated in the insets. The solid lines are from the best multiexponential fits.

Table S1. Values of time constants (τ_i), normalized (to 100) pre-exponential factors (a_i) and fractional contributions ($c_i = \tau_i a_i$) obtained from the fit of the emission decays of 6A-MBO in different solutions upon excitation at 370 nm and observation as indicated.

6A-MBO in n-Heptane

λ_{obs}	τ_1 / ns	a_1	c_1
400	1.65	100	100
425	1.65	100	100
450	1.65	100	100
475	1.65	100	100

6A-MBO in DCM

λ_{obs}	τ_1 / ns	a_1	c_1
395	2.3	100	100
400	2.3	100	100
410	2.3	100	100
430	2.3	100	100
450	2.3	100	100
475	2.3	100	100
500	2.3	100	100

6A-MBO in MeOH

λ_{obs}	τ_1 / ns	a_1	c_1
395	2.9	100	100
400	2.9	100	100
425	2.9	100	100
450	2.9	100	100
475	2.9	100	100
500	2.9	100	100
550	2.9	100	100

Table S2. Values of time constants (τ_i), normalized (to 100) pre-exponential factors (a_i) and fractional contributions ($c_i = \tau_i a_i$) obtained from the fit of the emission ps-ns decays of 6A-HBO in different solutions upon excitation at 371 nm and observation as indicated. The negative sign for a_1 (c_1) indicates a rising component in the emission signal.

Solvent	λ_{Obs}/nm	τ_1 / ps	A_1	a_1	c_1	τ_2 / ps	A_2	a_2	c_2	τ_3 / ns	A_3	a_3	c_3
n-Heptane	395	-	-	-	-	420	1180	75	46	1.5	387	25	54
	400	-	-	-	-	420	1321	78	51	1.5	358	22	49
	410	-	-	-	-	420	1580	82	57	1.5	334	18	43
	430	-	-	-	-	420	2104	94	83	1.5	122	6	17
	450	-	-	-	-	420	2402	98	92	1.5	56	2	8
	475	-	-	-	-	420	2510	98	94	1.5	48	2	6
	500	-	-	-	-	420	2642	100	100	-	-		-
	550	-	-	-	-	420	2651	100	100	-	-		-
DCM	395	14	5650	98	63	600	44	1	21	1.7	12	1	16
	410	14	6334	98	58	600	61	1	23	1.7	19	1	20
	430	14	4820	76	9	600	1609	23	85	1.7	25	1	6
	450	14	2530	58	4	600	1723	42	96	-	-	-	-
	475	14	-600	(-)100	(-)100	600	1801	100	100	-	-	-	-
	500	14	-1760	(-)100	(-)100	600	1904	100	100	-	-	-	-
	525	14	-2680	(-)100	(-)100	600	1915	100	100	-	-	-	-
	550	14	-3004	(-)100	(-)100	600	1920	100	100	-	-	-	-
MeOH	395	35	4252	85	24	615	786	15	76	-		-	-
	410	35	4213	85	25	615	754	15	75	-		-	-
	430	35	3954	79	20	615	1035	21	80	-		-	-
	450	35	3124	70	12	615	1358	30	88	-		-	-
	475	35	793	32	3	615	1630	68	97	-		-	-
	500	35	-218	(-)100	(-)100	615	1690	100	100	-		-	-
	550	35	-422	(-)100	(-)100	615	1799	100	100	-		-	-
CD_3OD	410	200	1680	71	30	780	550	23	38	2.4	154	6	32
	430	200	1518	70	32	780	578	27	49	2.4	55	3	19
	450	200	895	45	15	780	1016	50	66	2.4	73	5	19
	475	200	-30	(-)100	(-)100	780	1693	95	86	2.4	85	5	14
	500	200	-776	(-)100	(-)100	780	2193	96	89	2.4	87	4	11
	525	200	-1277	(-)100	(-)100	780	2467	96	89	2.4	91	4	11
	550	200	-1602	(-)100	(-)100	780	2580	97	90	2.4	91	3	10

Table S3. Values of time constants (τ_i) and normalized (to 100) pre-exponential factors (a_i) of the functions used in fitting the fs-emission transients of 6A-MBO in different solutions, upon excitation at 350 nm and observation as indicated.

Solvent	λ_{Obs}/nm	τ_1 / fs	a_1	τ_2 / ps	a_2	τ_3 / ns	a_3
n-Heptane	380	140	-100	1.0	17	1.65	83
	400	140	-100	1.0	10	1.65	90
	410	140	-100	1.0	8	1.65	92
	420	140	-100	-	-	1.65	100
	430	-	-	-	-	1.65	100
	440	-	-	-	-	1.65	100
	450	-	-	-	-	1.65	100
DCM	380	140	-100	1.0	48	2.3	52
	400	150	-100	1.0	23	2.3	77
	410	160	-100	1.0	15	2.3	85
	420	160	-90	1.0	-10	2.3	100
	430	-	-	1.0	-100	2.3	100
	440	-	-	1.0	-100	2.3	100
	450	-	-	1.0	-100	2.3	100
	475	-	-	1.1	-100	2.3	100
	500	-	-	1.1	-100	2.3	100
	525	-	-	1.1	-100	2.3	100
MeOH	370	280	39	2.0	49	2.9	12
	380	280	35	2.0	43	2.9	22
	400	-	-	2.3	50	2.9	50
	410	-	-	3.9	38	2.9	62
	420	-	-	0.6	-100	2.9	100
	430	-	-	1.1	-100	2.9	100
	440	-	-	2.0	-100	2.9	100
	450	-	-	3.6	-100	2.9	100
	475	-	-	3.6	-100	2.9	100
	500	-	-	4.3	-100	2.9	100
	525	-	-	5.0	-100	2.9	100
	550	-	-	5.5	-100	2.9	100

Table S4. Values of time constants (τi) and normalized (to 100) pre-exponential factors (ai) of the functions used in fitting the fs-emission transients of 6A-HBO in different solutions, upon excitation at 350 nm and observation as indicated.

Solvent	λ_{Obs}/nm	τ_1 / fs	a_1	τ_2 / ps	a_2	τ_3 / ps	a_3	τ_4 / ps	a_4
n-Heptane	395	140	-100	1.2	99	-	-	600*	1
	410	140	-100	1.2	98	-	-	600*	2
	420	140	-100	1.2	98	-	-	600*	2
	430	-	-	1.1	95	-	-	600*	5
	440	-	-	1.2	92	-	-	600*	8
	450	-	-	1.2	62	-	-	600*	38
	475	-	-	1.1	-100	-	-	420	100
	500	-	-	1.1	-100	-	-	420	100
	525	-	-	1.1	-100	-	-	420	100
	550	-	-	1.2	-100	-	-	420	100
	600	-	-	1.2	-100	-	-	420	100
DCM	395	140	-100	1.0	31	14	67	600	2
	410	140	-100	1.0	16	14	82	600	2
	420	140	-93	0.9	-7	14	96	600	4
	430	-	-	0.9	-100	14	90	600	10
	440	-	-	1.0	-100	14	85	600	15
	450	-	-	1.0	-100	14	65	600	35
	475	-	-	1.1	-56	14	-44	600	100
	500	-	-	1.1	-28	14	-72	600	100
	525	-	-	1.1	-24	14	-76	600	100
	550	-	-	1.1	-24	14	-76	600	100
	600	-	-	1.2	-20	14	-80	600	100
MeOH	380	250	55	2.1	38	35	10	615	2
	400	-	-	2.1	47	35	47	615	6
	410	-	-	2.1	33	34	54	615	12
	420	-	-	2.1	10	36	69	615	21
	430	-	-	0.8	-100	35	70	615	30
	440	-	-	1.8	-100	35	60	615	40
	450	-	-	2.0	-100	35	30	615	70
	475	-	-	2.0	-70	8.6	-30	615	100
	500	-	-	2.1	-46	35	-54	615	100
	525	-	-	2.1	-33	35	-67	615	100
	550	-	-	2.1	-22	35	-78	615	100
	600	-	-	2.1	-15	35	-85	615	100

*Value obtained from a combination of the two components observed in TCSPC measurements.

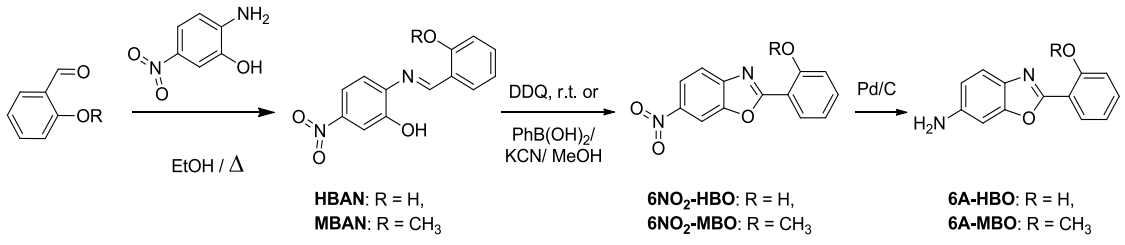
Synthesis y characterization of the different molecules (6A-MBO, 6A-HBO, 6A-DBO and 6A-DMBO)

General Remarks

Solvents were carefully degassed before use. 2-hydroxybenzaldehyde was purchased from Fluka and distilled under reduced pressure before used, 2-amino-4-nitrophenol, 2-amino-5-nitrophenol, 2-methoxybenzaldehyde, phenylboronic acid and Pd/C (10%) were purchased from Aldrich. ^{1}H-NMR and ^{13}C-NMR spectra were recorded in deuterated solvents at 300 and 75 MHz, respectively, using the proton signal of the trace of undeuterated solvent or the carbon signal of the deuterated solvent as internal reference ($CDCl_3$:7.26 (H), 77.0 (C) ppm; DMSO-d6: 2.50 (H), 39.5 (C) ppm). δ values are reported in ppm and coupling constants are given in Hz. The assignment of chemical shifts is based on standard NMR experiments (^{1}H, ^{13}C-DEPT, ^{1}H, ^{1}H-COSY, gHSQC, gHMBC). Abbreviations: s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets). IR spectra were recorded on Perkin-Elmer 681 and FT-Spectrum One spectrometers. Low resolution mass spectra were recorded by electron impact (EI) (70 eV) in a Hewlett-Packard 5973 spectrometer in the direct injection mode. Elemental analysis was performed with a Heraeus CHN-O-RAPID instrument. Melting points were determined on a Reichert hot-stage microscope and are uncorrected.

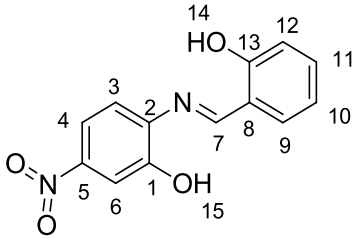
A general scheme (reactions) for the synthesis of the compounds is the following:

Scheme S1



a) Synthesis of Nitro-imines

*(*E*)-2-((2-hydroxybenzyliden)amino-5-nitrophenol* (**HBAN**)



To an ice-cooled solution of 2-amino-5-nitrophenol (1,54 g, 10 mmol) in dry ethanol (50 ml) containing a drop of formic acid was added drop-wise and efficient stirring 2-hydroxy-benzaldehyde (1.22 g, 10 mmol) in dry ethanol (10 ml). After addition was completed the reaction mixture was maintained 10 minutes at 0ºC and 16 hours at room temperature with stirring. The deep-red precipitated (*E*)-2-(2-hydroxybenzyliden)amino-5-nitrophenol was filtered, recrystallized from ethanol and dried *in vacuo* (50ºC/0.1 mmHg - 6 hours) yielding (2.48 g, 96%).

M. p.:227-229 ºC (Lit.[3] 220ºC).

Elemental analysis: Calc. for $C_{13}H_{10}N_2O_4$: C, 60.41%; H, 3.87%; N, 10.84%.

Found: C, 60.08%; H, 3.95%; N, 10.88%.

IR (KBr) ν (cm^{-1}): 3089 (C-H, arom); 2536 (OH); 1622 (C=N); 1522, 1345 (NO_2); 1216, 1142, 1077 (C-O)

^{1}H-NMR(DMSO-*d6*) δ = 13.03 (s, 1H, OH_{14}); 10.72 (s, 1H, OH_{15}); 9.02 (s, 1H, HC=N, H7); 7.78 (dd, 1H, H-4, $J_{H3,H4}$=9,4 Hz; $J_{H3,H6}$=2.3 Hz); 7.76 (d, 1H, H-6); 7.69 (dd, 1H, H-9, J_{H9-H10}= 7.78 Hz, J_{H9-H11}= 1.30Hz)); 7.54 (dd, 1H, H-3); 7.45 (ddd, 1H, H-11, $J_{H11-H12}$=7.82 Hz, $J_{H10-H11}$= 7.90Hz); 7.01 (dd, 1H, H-10); 6.98 (dd, 1H, H-12).

^{13}C-NMR (DMSO-*d6*) δ = 164.88 (C7); 160.67 (C13); 151.15 (C1); 145.86 (C5); 142.02 (C2); 133.94 (C11); 132.65 (C9); 120.57 (C8); 119.39 (C3); 119.14 (C10); 116.81 (C12); 115.05 (C4); 110.78 (C10).

Mass spectra (m/z, %): 258 (M^+, 100); 257 (M^+-1, 56); 241 (M^+-OH, 16); 211 (M^+-H-NO_2, 35).

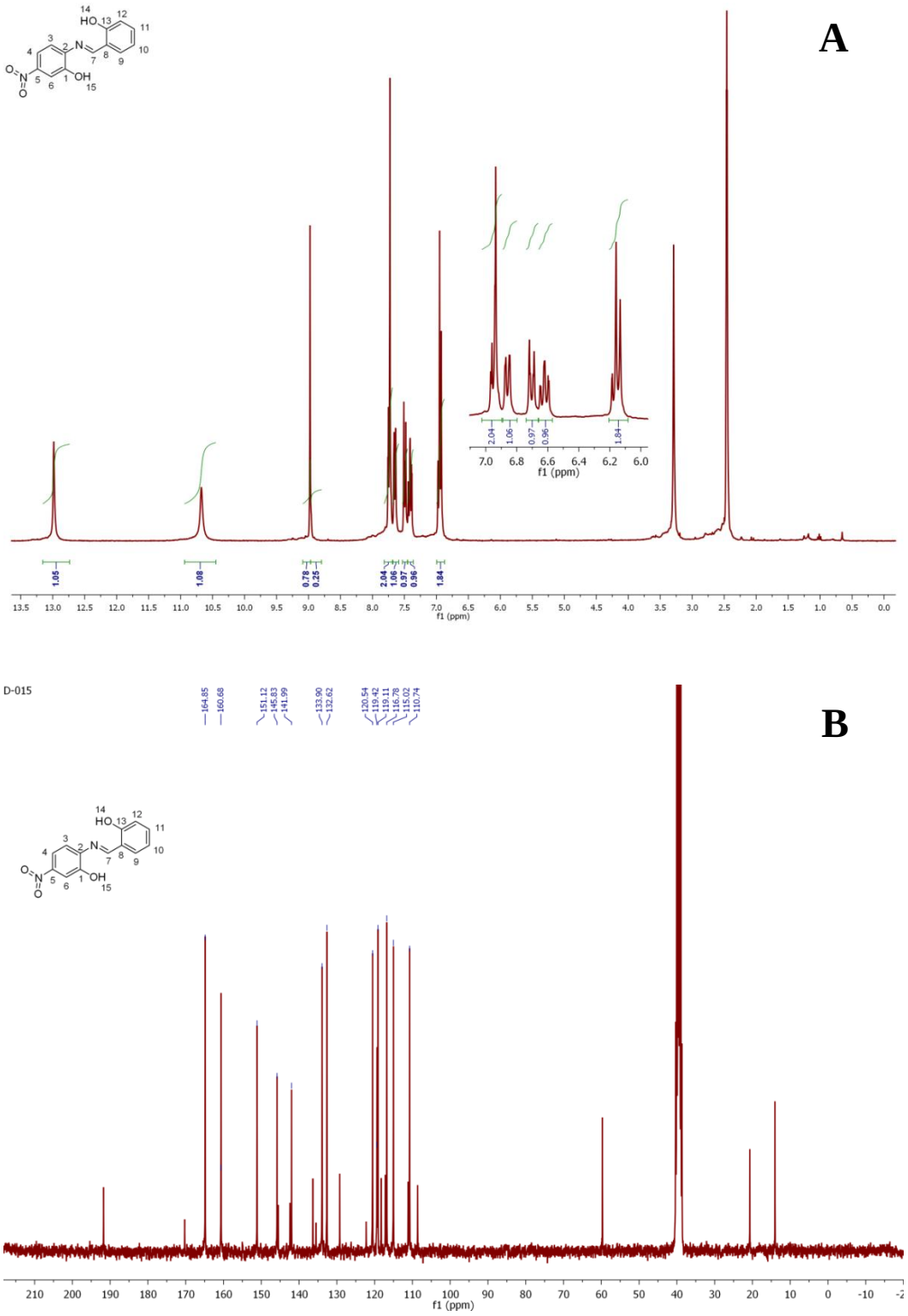
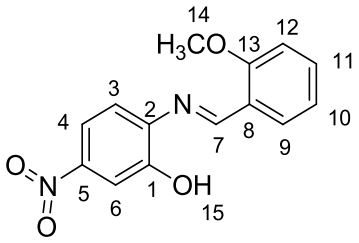


Figure S11. ^{1}H (A) and ^{13}C (B) NMR spectra of HBAN in DMSO-d6**.**

*(*E*)-2-((2-methoxybenzyliden)amino-5-nitrophenol* (**MBAN**)



To an ice-cooled solution of 2-amino-5-nitrophenol (308 mg, 2 mmol) in dry ethanol (20 ml) containing a drop of formic acid was added drop-wise and efficient stirring 2-methoxy-benzaldehyde (272 mg, 2 mmol) in dry ethanol (10 ml). After addition was completed the reaction mixture was maintained 10 minutes at 0ºC and 16 hours at room temperature with stirring. The green precipitated (*E*)-2-((2-methoxybenzyliden)amino-5-nitrophenol was filtered, recrystallized from toluene and dried *in vacuo* (50ºC/0.1 mmHg - 6 hours) yielding (190 mg, 70%).

M. p.:165-170 ºC.

Elemental analysis: Calc. for $C_{14}H_{12}N_2O_4$: C, 61.76%; H, 4.44%; N, 10.29%.

Found: C, 61.80%; H, 4.44%; N, 10.43%.

IR (KBr) ν (cm^{-1}): 3381, 3307 (OH); 3108 (C-H, arom); 1621 (C=N); 1514, 1337 (NO_2); 1216, 1142, 1077 (C-O).

^{1}H-NMR(DMSO-*d6*) δ = 10.36 (d, 1H, J_{H7-H9} = 0.8 Hz, HC=N, H7); 10.05 (s, 1H, OH_{15}); 7.7-7.6 (m, 2H, H-12 and H10); 7.59 (dd, 1H, H-4, J_{H4-H3} = 8.8 Hz, J_{H4-H6} = 2.6 Hz); 7.47 (d, 1H, H-6); 7.22 (ddd, 1H, H-9, J_{H9-H10}= 8.3 Hz, J_{H9-H11}= 0.5 Hz); 7.07 (ddd, 1H, H-11, J_{H9-H11}=7.47 Hz); 6.59 (d, 1H, H-3); 3.9 (s, 3H, H-14).

^{13}C-NMR (DMSO-*d6*) δ = 189.1 (C7); 161.5 (C13); 158.1 (C1); 145.6 (C5); 136.5 (C12 or C10); 135.5 (C2); 127.8 (C12 or C10); 124.1 (C8); 120.6 (C11); 118.3 (4); 112.7 (C9); 111.18 (C3); 108.66 (C6); 55.86 (C14).

Mass spectra (m/z, %): 272 (M^+, 54); 271 (M+-H, 8); 257 (M^+-CH_3, 2); 241 (M^+-OCH_3, 2); 225 (M^+-H-NO_2, 10); 211 (12), 154 (26), 119 (100).

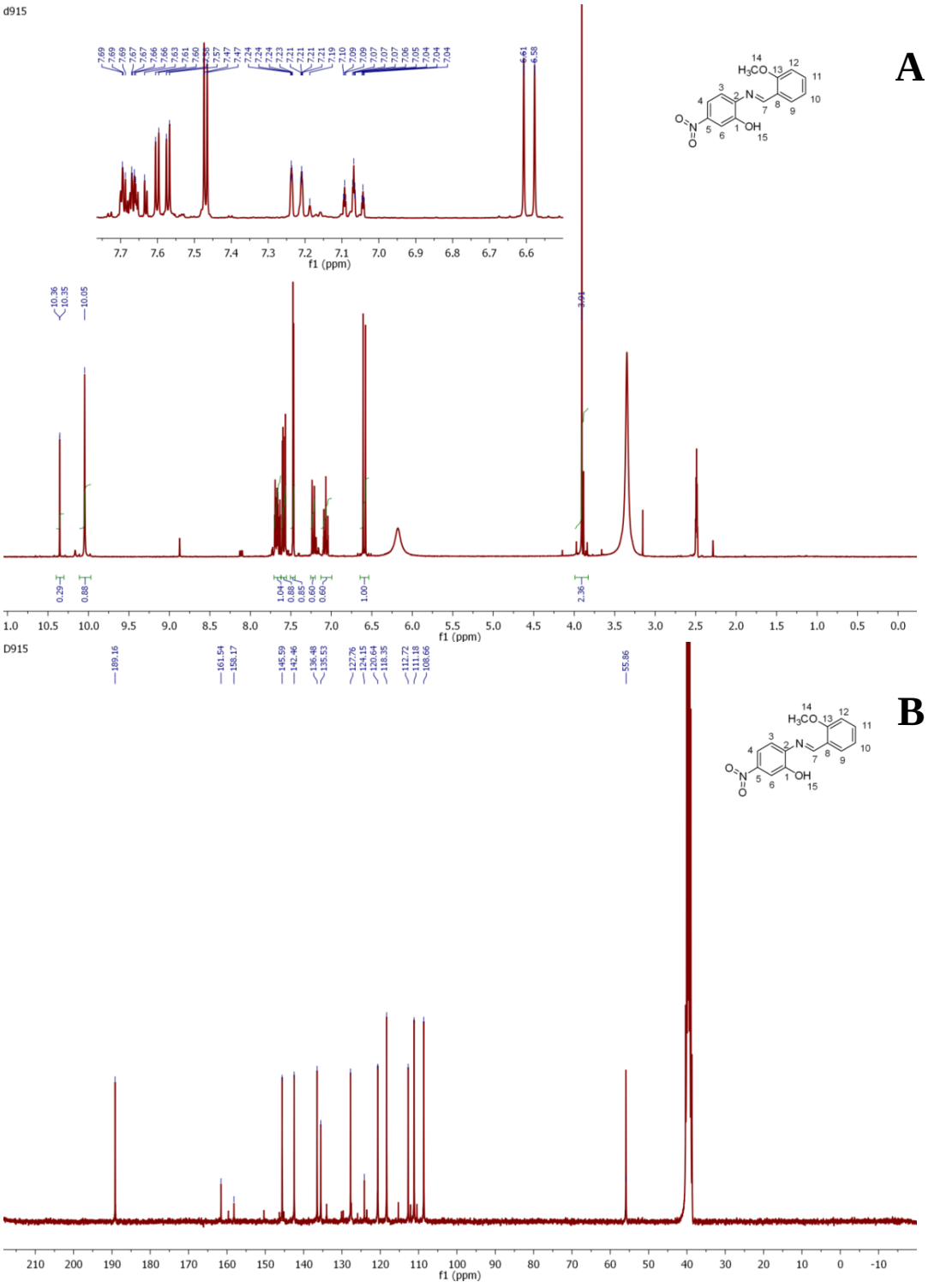
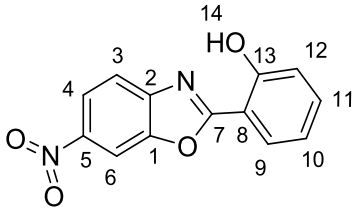


Figure S12. ^{1}H (A) and ^{13}C (B) NMR spectra of MBAN in DMSO-d6**.**

b) Nitro and aminobenzoxazoles

6-nitro-2-(2-hydroxyphenyl)benzoxazole (**6NO2-HBO**)



Method A: A mixture of (*E*)-2-(2-hydroxybenzyliden)amino-5-nitrophenol (268 mg, 1 mmol) and 2,3-dichloro-5,6-dicyano1,4-benzoquinone (295 mg, 1.3 mmol) in dioxane (40 ml) was stirred at room temperature overnight. After reaction was complete (TLC-Heptane/ Ethyl acetate, 2:1) solvent was evaporated at reduced pressure and residue was chromatographed with heptane/ethyl acetate (2:1) for obtaining 5-nitro-2-(2-hydroxyphenyl)benzoxazole (123 mg, 48% yield).

Method B: To a solution of (*E*)-2-((2-hydroxybenzyliden)amino-4-nitrophenol (400 mg, 1.2 mmol) and phenylboronic acid (14.5 mg, 0.12 mmol) in methanol (40 ml), potassium cyanide was added (77 mg, 1.2 mmol) and reaction mixture was stirred at room temperature 14-20 h. The reaction mixture was concentrated under reduced pressured to 20 ml and cooled. The product was filtered to obtain 5-nitro-2-(2-hydroxyphenyl)benzoxazole (326 mg, 82% yield) practically pure.

m. p.: 170-195 ºC

Elemental analysis: Calc. for $C_{13}H_8N_2O_4$: C, 60.94%; H, 3.15%; N, 10.93%.

Found: C, 60.80%; H, 3.10%; N, 10.96%.

IR ν (cm^{-1}): 3111 (C-H, arom); 1632, 1610 (C=N); 1524, 1347 (NO_2); 1545, 1487 (CC arom.), 1238 (C-O), 1060, 808, 760.

^{1}H-NMR (DMSO-*d6*) δ = 10.82 (s, 1H, OH_{14}); 8.70 (d, 1H, H-3, J_{H3-H4}=2.13 Hz); 8.34 (dd, 1H, H-5, J_{H4-H6}= 8.79 Hz); 8.05 (dd, 1H, H-9, J_{H9-H10}= 8.30 Hz, J_{H9-H11}= 1.51 Hz); 8,03 (d, 1H, H-6); 7.58 (ddd, 1H, H-11, $J_{H11-H12}$= 8.27 Hz, $J_{H10-H11}$= 8.30 Hz); 7,15 (d, 1H, H-12, $J_{H10-H12}$= 0.70 Hz); 7.11 (dd, 1H, H-10).

^{13}C-NMR (DMSO-*d6*) δ = 166.34 (C7); 157.92 (C13); 148.22 (C2); 145.11 (C1); 144.61 (C4); 134.53 (C11); 128.24 (C9); 121.84 (C6); 120.61 (C5); 119.71 (C10); 117.10 (C12); 110.15 (C8); 106.90 (C3).

Mass spectra (m/z, %): 256 (M^+, 100); 210 (M^+-NO_2, 10); 182 (38).

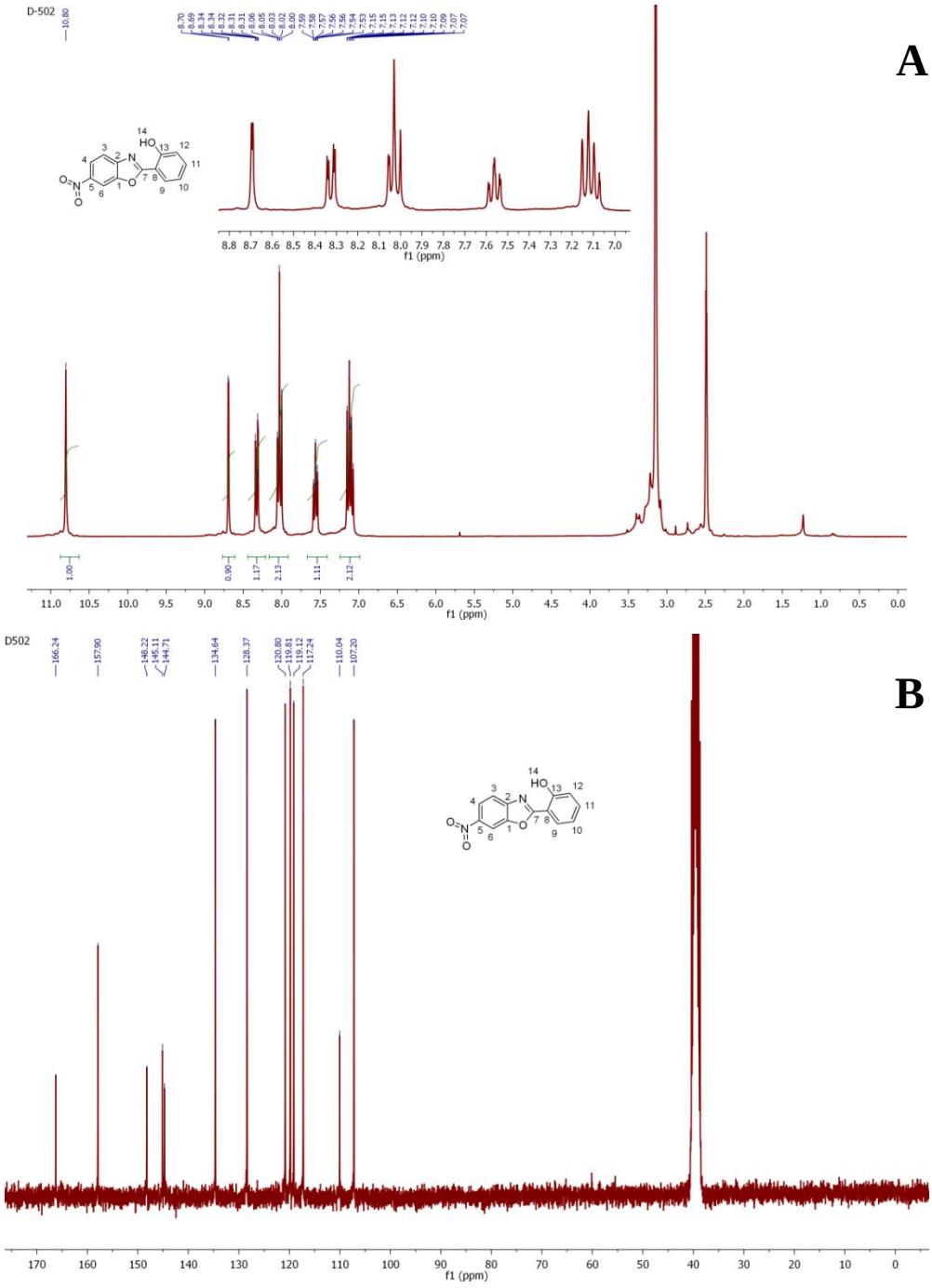
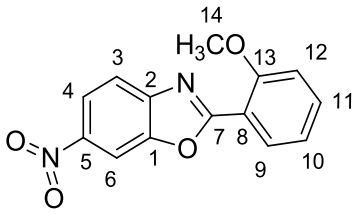


Figure S13. ^{1}H (A) and ^{13}C (B) NMR spectra of 6NO2-HBO in DMSO-d6**.**

6-nitro-2-(2-methoxyphenyl)benzoxazole (**6NO2-MBO**)



Method A: A mixture of (E)-2-((2-methoxybenzyliden)amino-5-nitrophenol (100 mg, 0.37 mmol) and 2,3-dichloro-5,6-dicyano1,4-benzoquinone (88 mg, 0.39 mmol) in dioxane (10 ml) was stirred at room temperature overnight. After reaction was complete (TLC-Heptane/ Ethyl acetate, 2:1) solvent was evaporated at reduced pressure and residue was chromatographed with heptane/ethyl acetate (5:1) for obtaining-nitro-2-(2-hydroxyphenyl)benzoxazole (50 mg, 51% yield).

Method B: To a solution of (*E*)-2-((2-methoxybenzyliden)amino-5-nitrophenol (1.3 mg, 5 mmol) and phenylboronic acid (124 mg, 1.0 mmol) in methanol (60 ml), potassium cyanide was added (652 mg, 5 mmol) and reaction mixture was stirred at room temperature 14-20 h. The reaction mixture was concentrated under reduced pressured to 8-10 ml and cooled. The product was filtered and recrystallized from methanol and dried in vacuo (50ºC/0.1 mmHg - 6 hours) yielding 5-nitro-2-(2-methoxyphenyl)benzoxazole (425 mg, 31.5% yield).

m. p.: 160-166 ºC.

Elemental analysis: Calc. for $C_{14}H_{10}N_2O_4$: C, 62.22%; H, 3.73%; N, 10.37%.
Found: C, 62.20%; H, 3.76%; N, 10.26%.

IR ν (cm^{-1}): 3111 (C-H, arom); 1600 (C=N); 1530, 1345 (NO_2); 1547, 1496 (CC arom.), 1250 (C-O), 1059, 1015, 757.

^{1}H-NMR (DMSO-*d6*) δ = 8.71 (dd, 1H, H-6, J_{H6-H4}=2.3 Hz, J_{H6-H3} = 0.5 Hz); 8.31 (dd, 1H, H-4, J_{H4-H3}= 8.8 Hz); 8.09 (ddd, 1H, H-9, J_{H9-H10} = 7.8 Hz, J_{H9-H11}=1.8 Hz, J_{H9-H12} = 0.4 Hz); 8.02 (dd, 1H, H-3); 7.67 (ddd, 1H, H-11, $J_{H11-H10}$ = 7.3 Hz, $J_{H11-H12}$ =8.5 Hz); 7.32 (ddd, 1H, H-12, $J_{H12-H10}$ = 1 Hz); 7.18 (ddd, 1H, H-10).

^{13}C-NMR (DMSO-*d6*) δ = 166.94 (C7); 158.5 (C13); 149.3 (C1); 146.7 (C2); 144.63 (C5); 134.54 (C11); 131.42 (C9); 120.83 (C10); 120.69 (C4); 119.85 (C3); 114.22 (C8); 113.00 (C12); 107.48 (C6), 56.11 (C14).

Mass spectra (m/z, %): 270 (M^+, 100); 21 (M^++2-CH_3O, 43); 223 (M^++2-NO_2, 7); 165 (28).

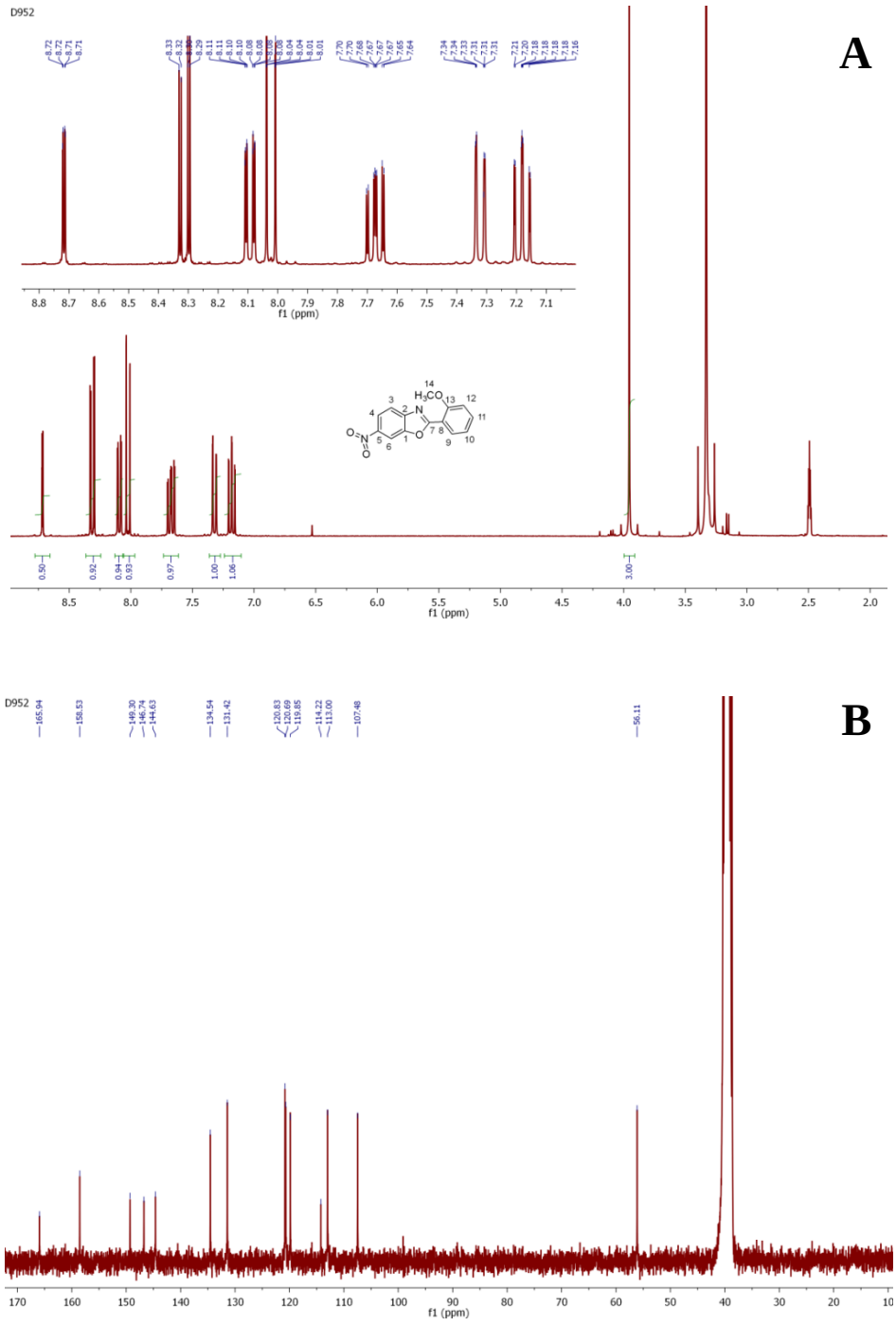
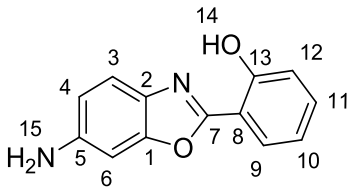


Figure S14. ^{1}H (A) and ^{13}C (B) NMR spectra of 6NO2-MBO in DMSO-d6**.**

6-amino-2-(2-hydroxyphenyl)benzoxazole **(6A-HBO)**



To a solution of 6-nitro-2-(2-hydroxyphenyl)benzoxazole (256 mg, 1 mmol) in THF (15 ml) was added a dispersion of Pd/C(10%) (15 mg) in THF (1 ml) and efficiently stirred in dihydrogen atmosphere (1.1 bar) for 4 hours. After reduction was completed (TLC-Heptane-Ethyl acetate, 2:1) reaction mixture was filtered on celite and solvent evaporated under reduced pressure to obtain 6-amino-2-(2-hydroxyphenyl)benzoxazole (226 mg, 100%).

M. p.: 175-190 ºC

Elemental analysis: Calc. for $C_{13}H_{10}N_2O_2$: C, 69.02%; H, 4.46%; N, 12.38%.
Found: C, 68.90%; H, 4.61%; N, 12.15%.

IR ν (cm^{-1}): 3430 (O-H); 3319, 3191 (NH_2); 3071 (C-H, arom); 1634, 1604 (C=N); 1497, 1488 (CC arom.), 1257, 1241, 1148, 747.

^{1}H-NMR ($CDCl_3$) δ = 11.40 (broad s, 1H, OH_{14}); 7.96 (dd, 1H, H-9, $J_{H9,H10}$=7.85 Hz, $J_{H9,H11}$=1.51 Hz); 7.48 (d, 1H, H-3, J_{H3-H4}= 8.46 Hz); 7.48 (ddd, 1H, H-11, $J_{H10-H11}$= 7.81 Hz, $J_{H11-H12}$= 8.47 Hz); 7.11 (d, 1H, H-4, J_{H3-H5}= 0.45 Hz); 6.99 (ddd, 1H, H-10); 6.98 (d, 1H, H-3); 6.72 (dd, 1H, H-12, $J_{H10-H12}$= 2.10 Hz): 3.87 (broad s, 2H, NH_2).

^{13}C-NMR ($CDCl_3$) δ = 161.08 (C7); 158.14 (C13); 150.62 (C1); 146.31 (C5); 132.66 (C11); 132.55 (C2); 126.61 (C9); 119.49 (C3); 119.40 (C10); 117.20 (C4); 113.41 (C12); 111.13 (C8); 96.47 (C6).

Mass spectra (m/z, %): 226 (M^+, 100), 197 (15), 169 (12).

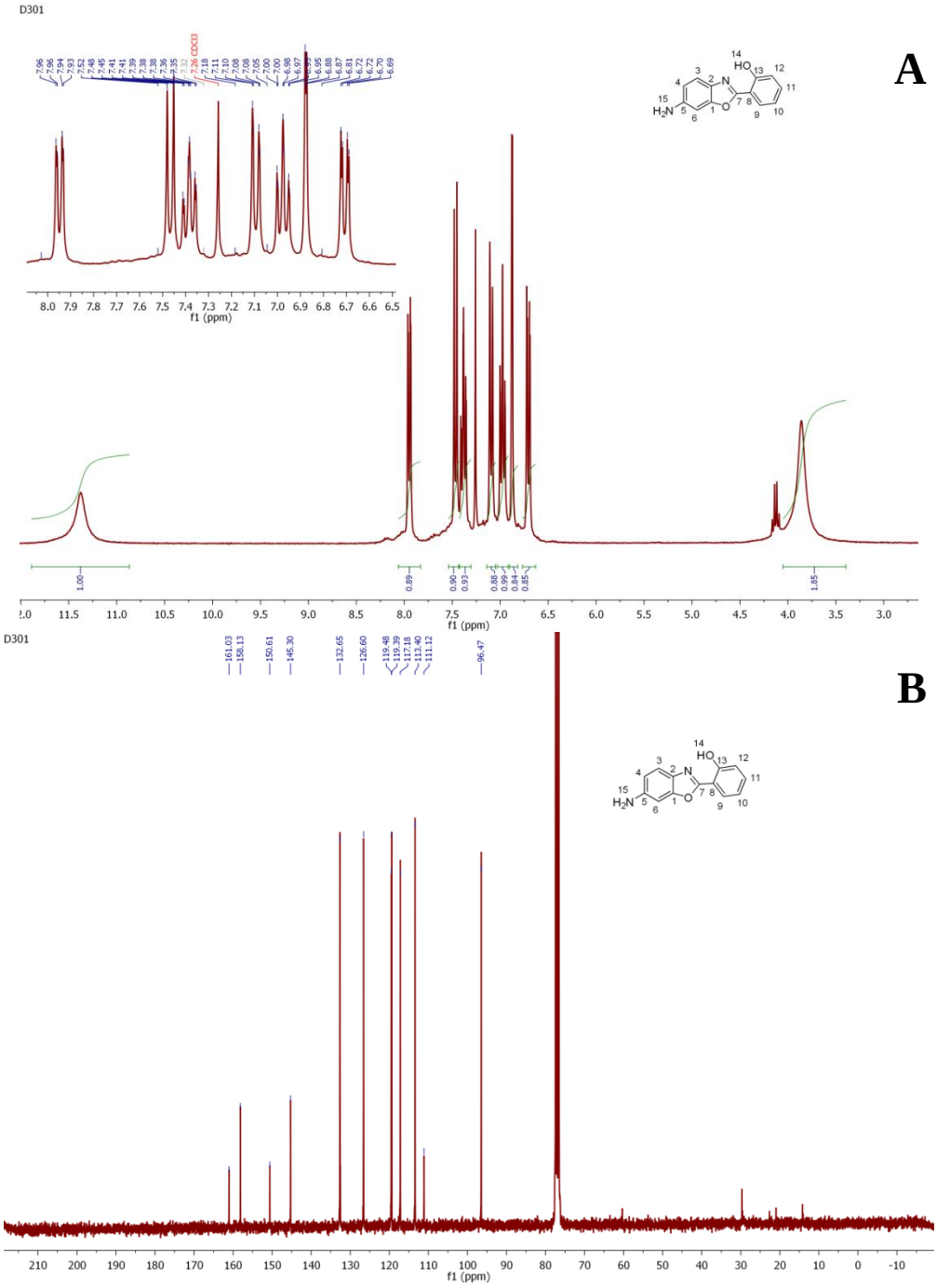
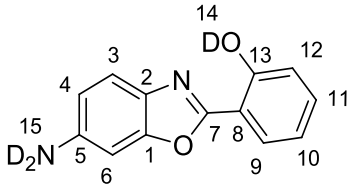


Figure S15. ^{1}H (A) and ^{13}C (B) NMR spectra of 6A-HBO in DMSO-d6**.**

6-amino-2-(2-hydroxyphenyl)benzoxazol-d_3 **(6A-DBO)**



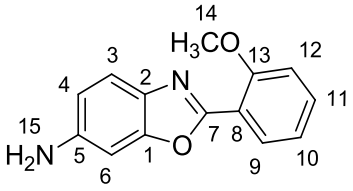
A solution of 6-amino-2-(2-hydroxyphenyl)benzoxazol (113 mg, 0.5 mmol) in methanol-d_4 was stirred at 70 ºC for 2 hours and concentrated under reduced pressure; this process have been repeated for three times and 6-amino-2-(2-hydroxyphenyl)benzoxazol-d_3 was dried (10^{-4} bar; 4 h).

IR ν (cm^{-1}): 3071 (C-H, arom); 2430, 2400 (O-D, ND_2); 1634, 1604 (C=N); 1497, 1488 (CC arom.), 1257, 1241, 1148, 747.

^{1}H-NMR ($CDCl_3$) δ = 7.96 (dd, 1H, H-9, $J_{H9,H10}$=7.85 Hz, $J_{H9,H11}$=1.51 Hz); 7.48 (d, 1H, H-3, J_{H3-H4}= 8.46 Hz); 7.48 (ddd, 1H, H-11, $J_{H10-H11}$= 7.81 Hz, $J_{H11-H12}$= 8.47 Hz); 7.11 (d, 1H, H-4, J_{H3-H5}= 0.45 Hz); 6.99 (ddd, 1H, H-10); 6.98 (d, 1H, H-3); 6.72 (dd, 1H, H-12, $J_{H10-H12}$= 2.10 Hz).

Mass spectra (m/z, %): 230 (M^++1, 12); 229 (M+, 85); 228 (M^+-1, 100); 227 (M^+-2, 45).

6-amino-2-(2-methoxyphenyl)benzoxazole **(6A-MBO)**



To a solution of 6-nitro-2-(2-methoxyphenyl)benzoxazole (272 mg, 1 mmol) in THF (15 ml) was added a dispersion of Pd/C(10%) (15 mg) in THF (1 ml) and efficiently stirred in dihydrogen atmosphere (1.1 bar) for 4 hours. After reduction was completed (TLC-Heptane-Ethyl acetate, 2:1) reaction mixture was filtered on celite and solvent evaporated under reduced pressure to obtain 6-amino-2-(2-methoxyphenyl)benzoxazole (234 mg, 100%).

m. p.: 150-152 ºC

Elemental analysis: Calc. for $C_{14}H_{12}N_2O_2$: C, 69.99%; H, 5.03%; N, 11.66%.
Found: C, 70.43%; H, 5.38%; N, 10.43%.

IR ν (cm^{-1}): 3319, 3211 (NH_2); 3051 (C-H, arom); 1631, 1602 (C=N); 1493, 1469 (CC arom.), 1259, 1228, 1147, 765.

^{1}H-NMR ($CDCl_3$) δ = 8.09 (dd, 1H, H-12, $J_{H12-H11}$ = 8.2, Hz, $J_{H12-H10}$=1.8 Hz); 7.60 (dd, 1H, H-3, J_{H3-H4}= 8.4 Hz, J_{H3-H6} = 0.6 Hz); 7.48 (ddd, 1H, H-11, $J_{H11-H10}$= 7.4 Hz, J_{H11-H9}= 1.8 Hz); 7.10 (ddd, 1H, H-10, J_{H10-H9}= 7.6 Hz); 7.08 (d, 1H, H-9); 6.99 (s, 2H, NH_2); 6.94 (dd, 1H, H-6, J_{H6-H4}= 2.10 Hz); 6.75 (dd, 1H, H4); 4.02 (s, 1H, H-14).

^{13}C-NMR ($CDCl_3$) δ = 159.6 (C7), 158.1 (C13); 151.49 (C5); 144.09 (C1); 135.75 (C2); 135.02 (C8); 132.14 (C11); 130.80 (C12); 120.65 (C10); 120.48 (C3); 113.25 (C4); 111.96 (C9); 97.12 (C6); 56.19 (C14).

Mass spectra (m/z, %): 240 (M^+, 100); 211 (M^+-2-CH_3O, 26); 197 (20).

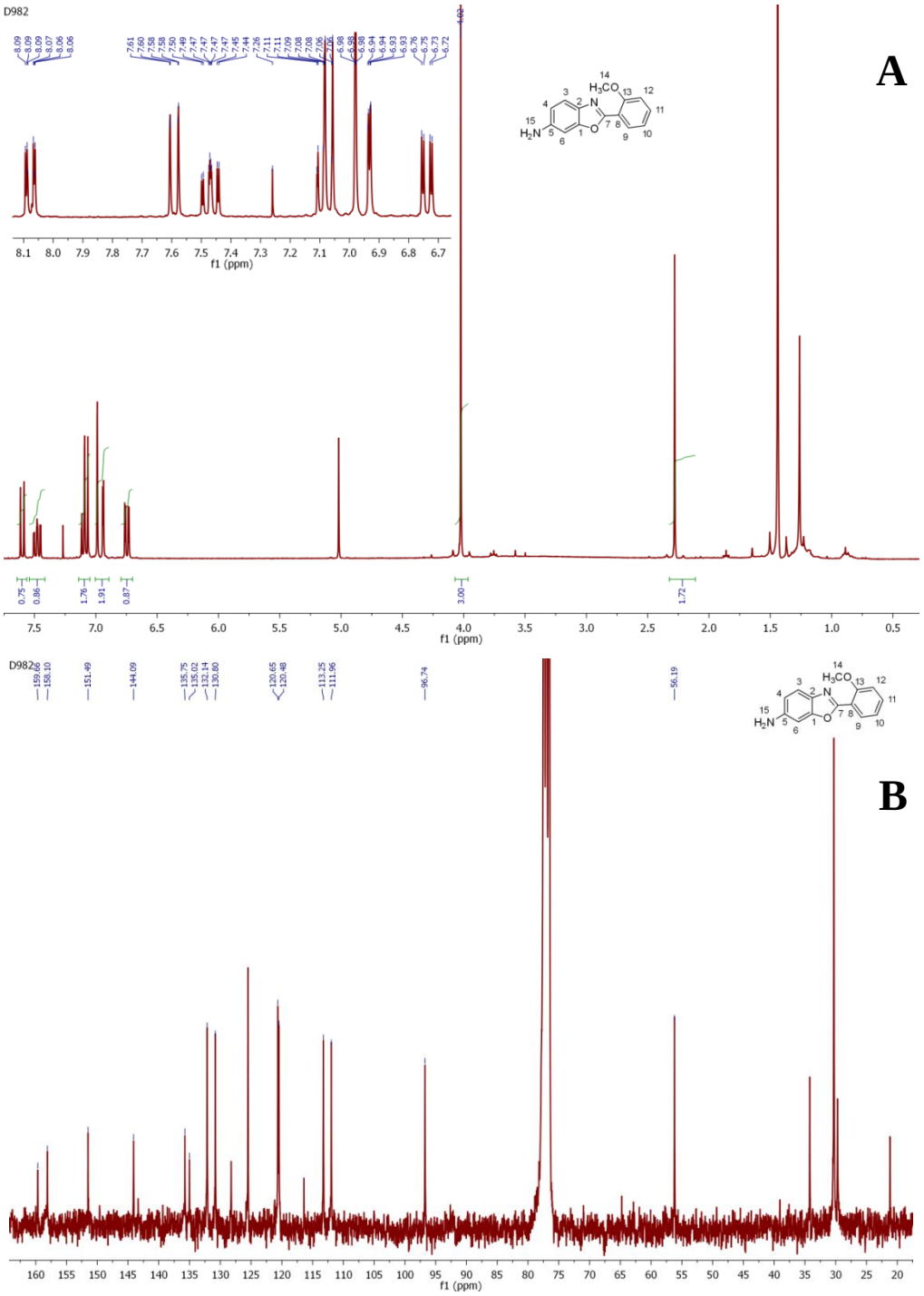
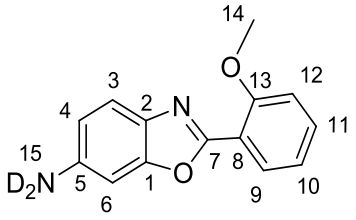


Figure S16. ^{1}H (A) and ^{13}C (B) NMR spectra of 6A-MBO in DMSO-d6**.**

6-amino-2-(2-methoxyphenyl)benzoxazol-d_2 **(6A-DMBO)**



A solution of 6-amino-2-(2-methoxyphenyl)benzoxazol (113 mg, 0.5 mmol) in methanol-d_4 was stirred at 70 ºC for 2 hours and concentrated under reduced pressure; this process have been repeated for three times and 6-amino-2-(2-hydroxyphenyl)benzoxazol-d_2 was dried (10^{-4} bar; 4 h).

IR ν (cm^{-1}): 3015 (C-H, arom); 2440, 2394 (O-D, ND_2); 1621, 1601 (C=N); 1497, 1492 (CC arom.), 1261, 1127, 766.

Mass spectra (m/z, %): 242 (M+, 99); 241 (M+-1, 100); 212 (M+-1-CH3O, 34); 198 (22)

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