Supporting Information

From Intra- to Intermolecular Hydrogen Bond with the Surrounding: Steady-State and Time-Resolved Behaviours

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≠ Equal contributions

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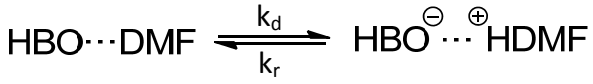
Reversible Model 1:1

Reversible reaction



t=0	C	
t=t	C-x	x
t=335 min	$C-x_{eq}$	x_{eq}

Where *C* is the HBO concentration at t=0, x_{eq} is the anion concentration when the equilibrium is reached (at t=335 min) and k_d and k_r are the direct and reverse constants, respectively.

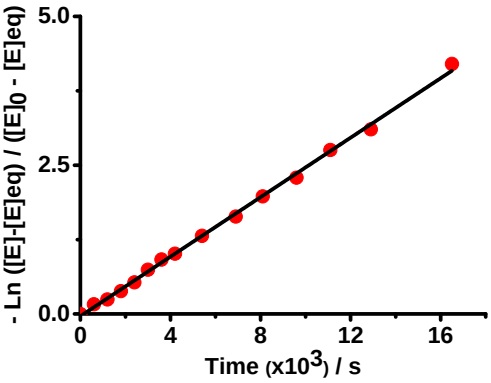
To calculate the concentrations, it was necessary to know the value of the molar extinction coefficient (ε) of enol form, $\varepsilon_{330} = 1.37 \times 10^{-4}\ M^{-1}\ cm^{-1}$.

In this way, the concentrations were calculated following the Lambert Beer equation:

$$C(t) = \frac{A(t)_{330}}{b\varepsilon_{330}} \qquad (1)$$

Based on reversible first order reaction model1, the $\ln\frac{[E]_t-[E]_o}{[E]_o-[E]_{eq}}$, versus time was represented to obtain the values of the constants (k_d and k_r). $[E]_t$ is the concentration of the enol form for each time, $[E]_0$ the initial concentration and $[E]_{eq}$ the concentration at t = 335 min.

$$ln\frac{[E]_t - [E]_o}{[E]_o - [E]_{eq}} = (k_d + k_r)t$$



$$slope = k_d + k_r = (2.50 \pm 0.03)\ x\ 10^{-4}\ s^{-1}$$

Taking into account the slope value and the equation obtained through the steady state approximation,[1] the direct and reverse constant were calculated;

$$k_d\left(\frac{[E]_0}{[E]_0 - [E]_{eq}}\right) = k_r + k_d$$

where $[E]_0$=1.673x10^{-4} M and $[E]_{eq}$=1.479x10^{-4} M

Thus,

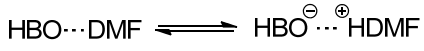
$$k_d = (3.09 \pm 0.02)\ x\ 10^{-5} s^{-1}$$

$$k_r = 2.499x10^{-4} - k_d = (2.19 \pm 0.01)\ x\ 10^{-4}\ s^{-1}$$

Finally, the equilibrium constant $K_{eq} = k_d/k_r = 0.14 \pm 0.01$.

Calculation of the different constants ΔG, ΔH y ΔS

Equilibrium system



t=0	C	
t=t	C-x	x
t=335 min	$C-x_{eq}$	x_{eq}

$$\Delta G^o = -RTLnK_{eq}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

where R= 8.314 J/K mol

Thus,

$$-RTLnK_{eq} = \Delta H^o - T\Delta S^o$$

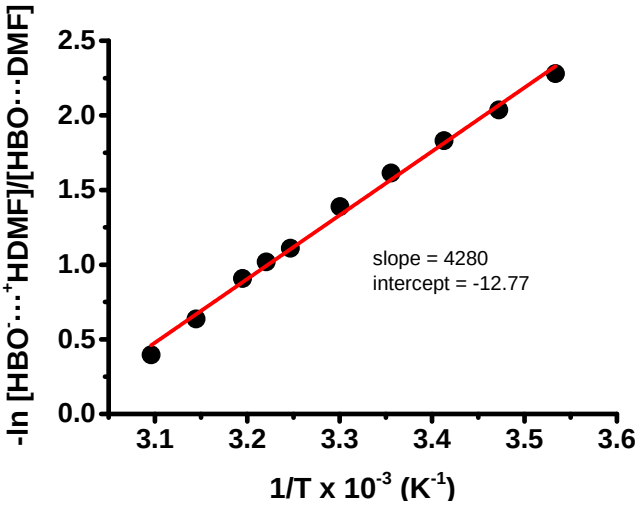
$$-LnK_{eq} = \frac{\Delta H^o}{RT} - \frac{\Delta S^o}{R}$$

Where $K_{eq} = \frac{[HBO^- \cdots {}^+\mathbf{HDMF}]}{[HBO \cdots \mathbf{DMF}]}$

So,

$$-Ln\frac{[HBO^- \cdots {}^+\mathbf{HDMF}]}{[HBO \cdots \mathbf{DMF}]} = \frac{\Delta H^o}{R}\frac{1}{T} - \frac{\Delta S^o}{R}$$

To calculate the concentrations we used the absorbance and the molar extinction coefficient (ε) at 330 and 400 nm for enol and anion form ($\varepsilon_{enol}(330) = 1.37 \times 10^{-4}$ M^{-1} cm^{-1}, $\varepsilon_{anion}(400) = 2.12 \times 10^{-4}$ M^{-1} cm^{-1}) (equation 1). The ε values were calculated at 298 K.



$$\text{slope} = 4280 = \frac{\Delta H^o}{R}$$

$$\mathbf{\Delta H^o = 35.58 \pm 0.01\ kJ/mol}$$

$$\text{intercept} = -12.77 = -\frac{\Delta S^o}{R}$$

$$\mathbf{\Delta S^o = 106.1 \pm 0.3\ J/molK}$$

Therefore,

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\mathbf{\Delta G^o_{(298\ K)} = 3.96 \pm 0.02\ kJ/mol}$$

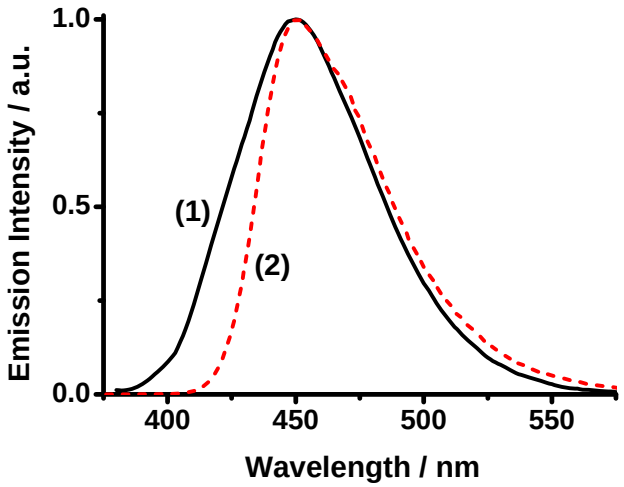


Figure S1. Normalized fluorescence spectra (upon excitation at 370 nm) of HBO in (1) pure DMF and (2) DMF/KOH solutions.

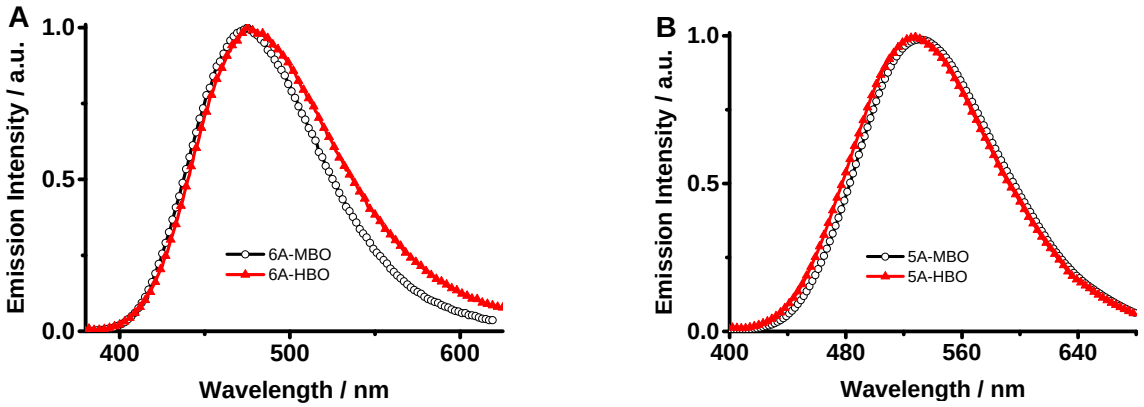


Figure S2. Normalized fluorescence spectra (upon excitation at 370 nm) of (A) 6A-MBO and 6A-HBO, (B) 5A-MBO and 5A-HBO in neutral water solutions.

Calculation of pKa

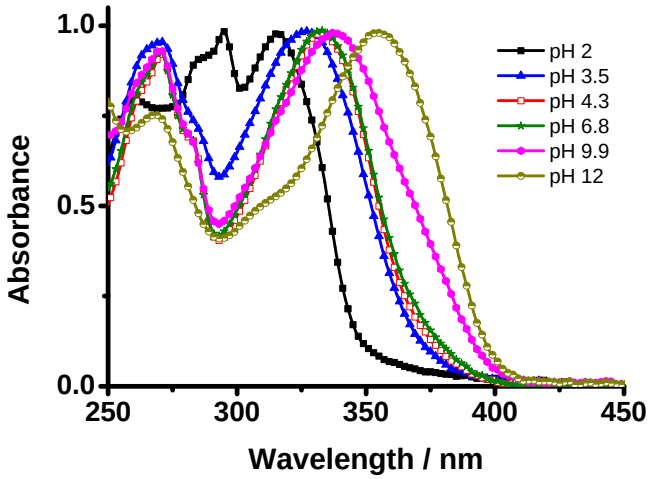


Figure S3. Normalized UV-visible absorption spectra 5A-HBO in different pH solutions.

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) and pKa (-OH of the phenyl ring) in 5A-HBO, absorption intensities (A) were taken at 315, 330 and 355 nm, respectively.

Calculation of pKa*

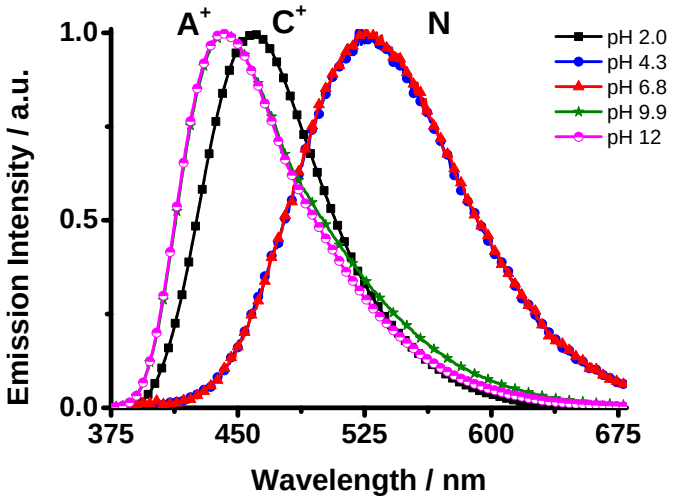


Figure S4. Normalized Fluorescence spectra 5A-HBO, respectively, in different pH solutions and upon excitation at 330 nm.

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

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

For 5A-HBO in water solutions we got:

pKa (-NH^+) = 4.2 ± 0.2; pKa* (-NH^+) = 7.76 ± 0.1

pKa (-OH) = 10.15 ± 0.13; pKa* (-OH) = 5.02 ± 0.1

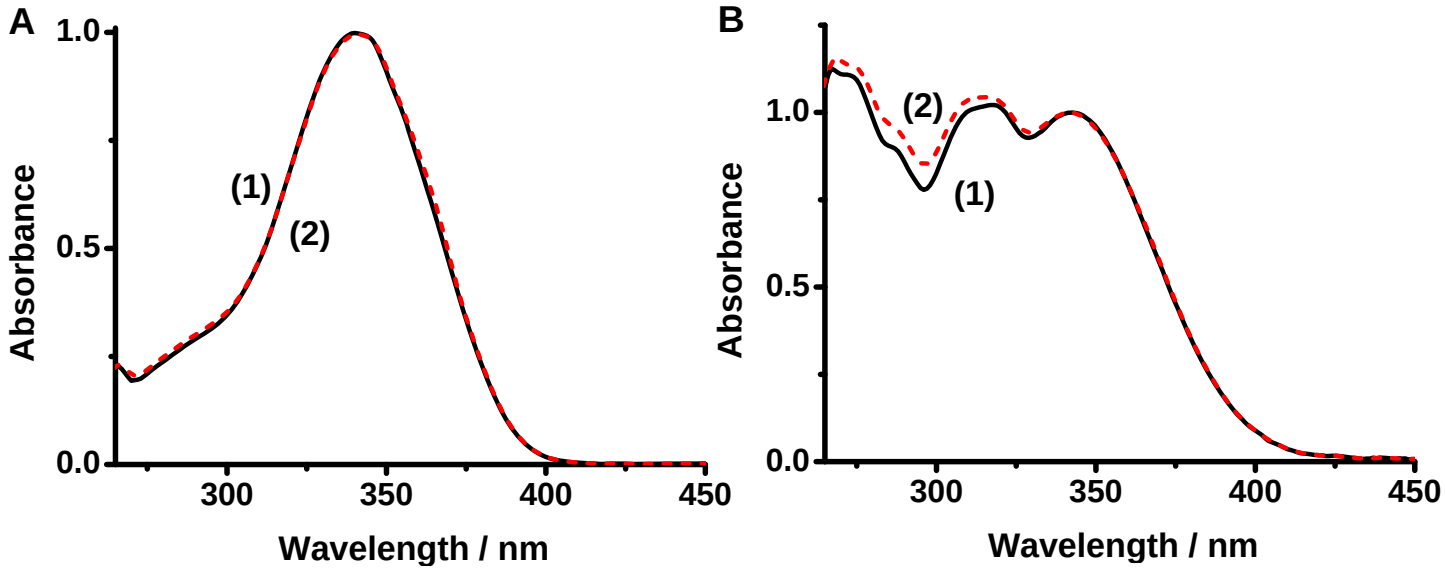


Figure S5. Normalized UV-visible absorption spectra of (A) 6A-MBO and (B) 5A-MBO in (1) pure DMF and (2) DMF/KOH solutions.

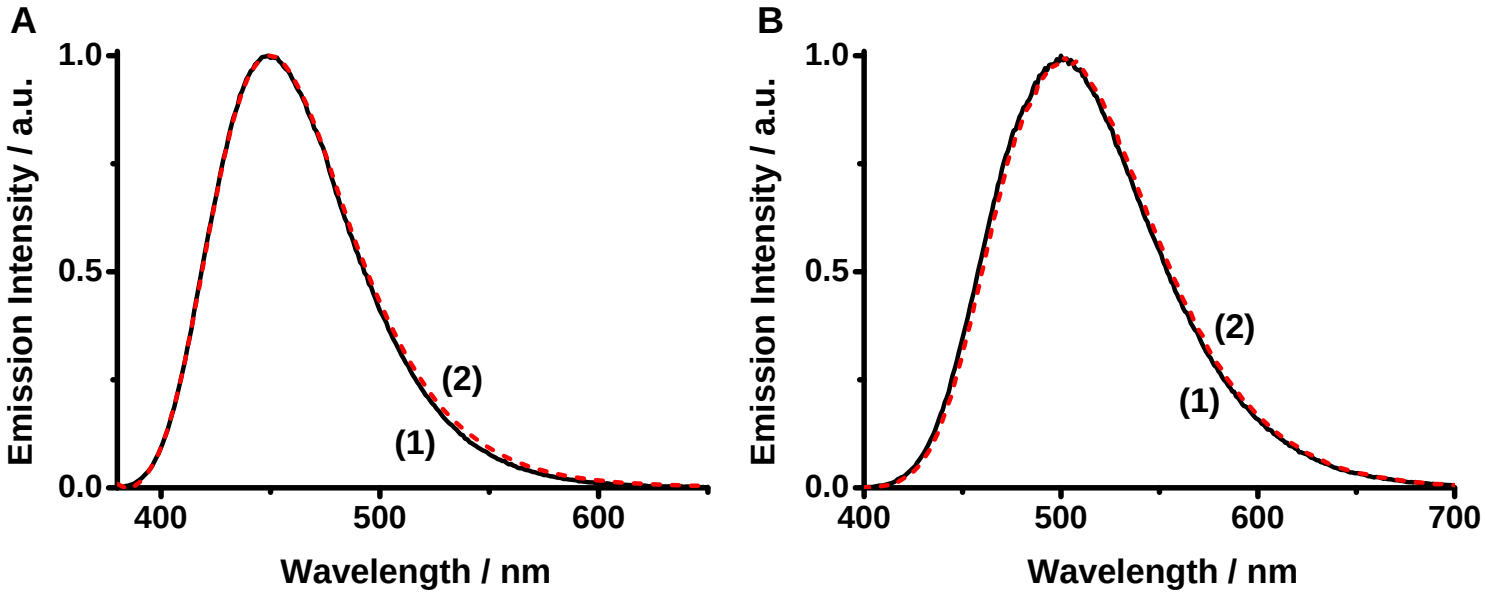


Figure S6. Normalized fluorescence spectra (upon excitation at 370 nm) of (A) 6A-MBO and (B) 5A-MBO in (1) pure DMF and (2) in DMF/KOH solutions.

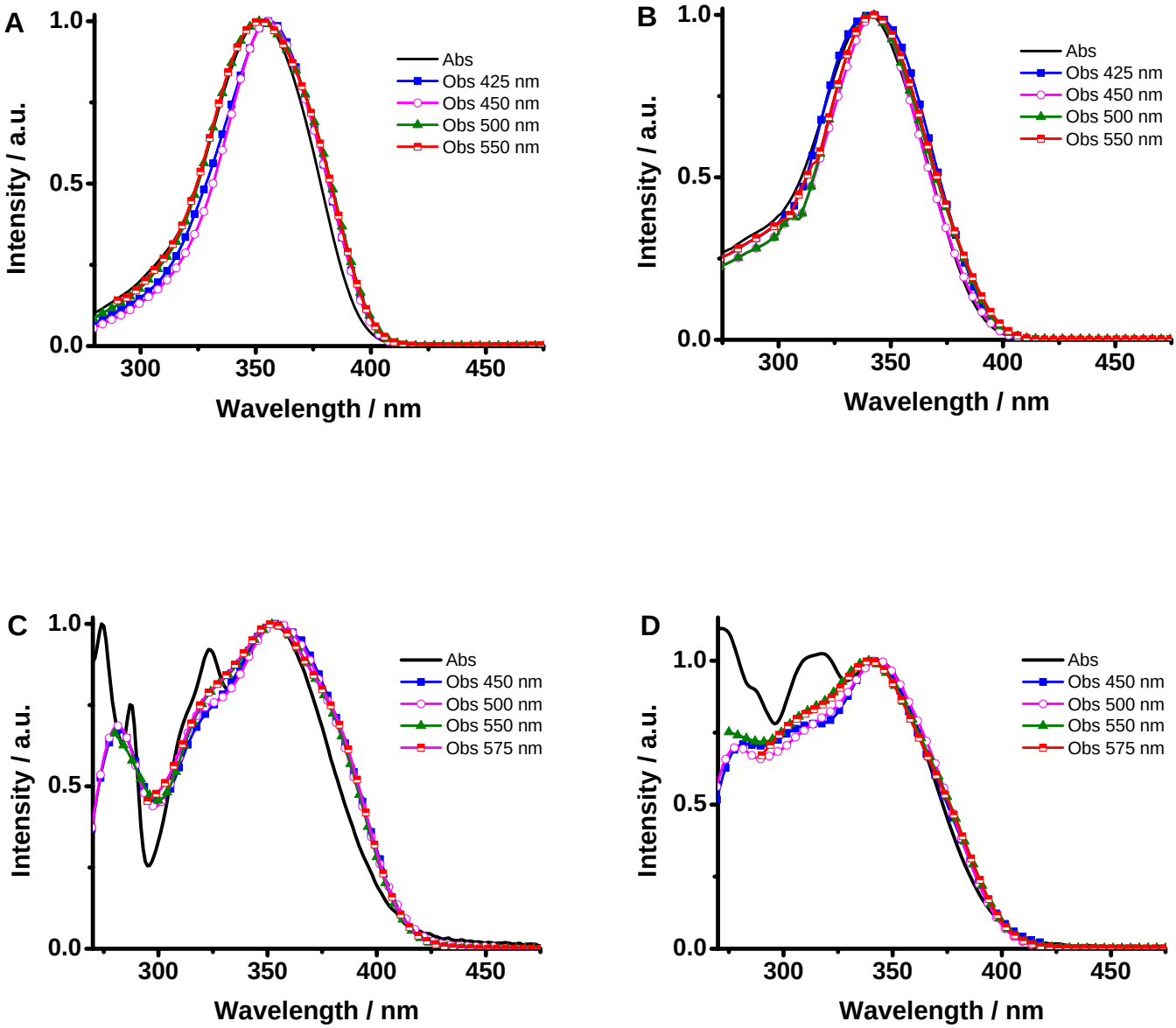


Figure S7. Excitation fluorescence and absorption spectra of (A) 6A-HBO, (B) 6A-MBO, (C) 5A-HBO and (D) 5A-MBO in DMF solutions. The observation wavelengths are shown in the inset.

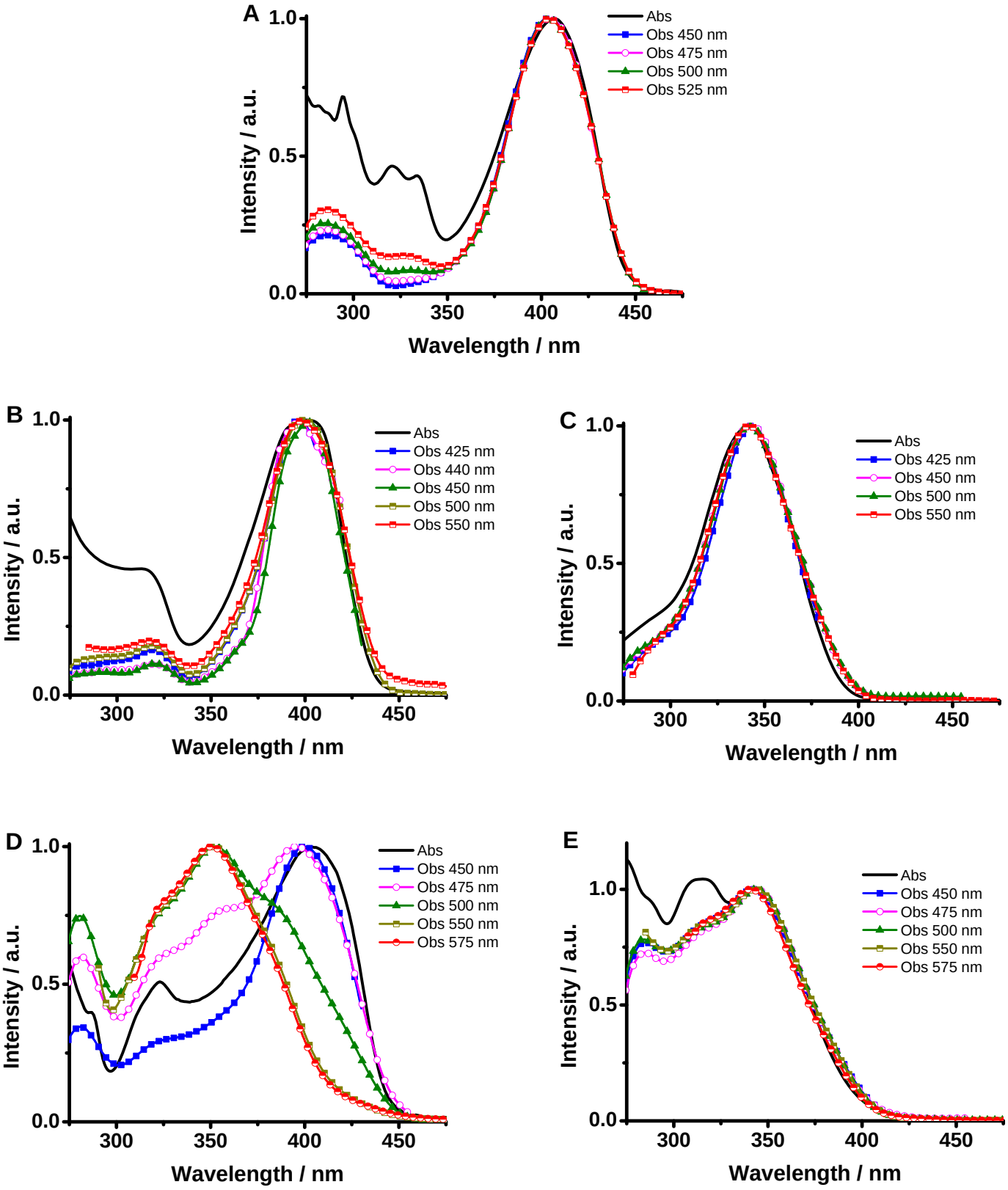


Figure S8. Excitation fluorescence and absorption spectra of (A) HBO, (B) 6A-HBO, (C) 6A-MBO, (D) 5A-HBO and (E) 5A-MBO in DMF/KOH solutions. The observation wavelengths are shown in the inset.

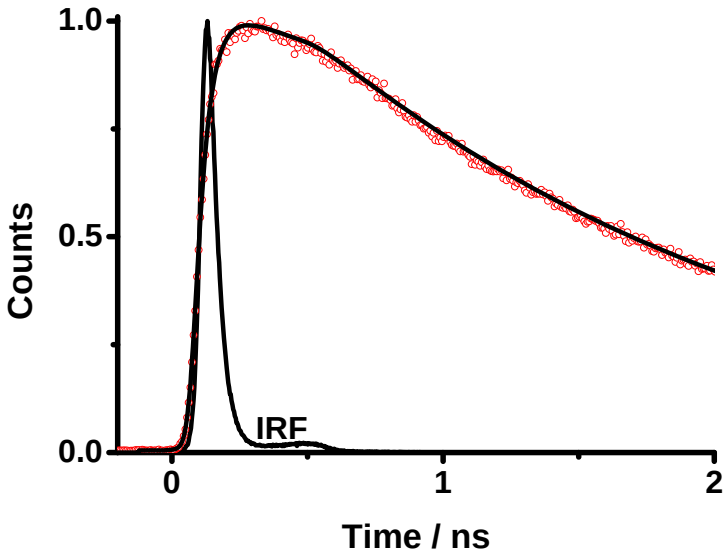


Figure S9. Magic-angle emission decay of 6A-HBO in DMF solution exciting at 371 nm and observing at 550 nm. The solid lines are from the best-fit using multiexponential functions and the IRF is the instrumental response function.

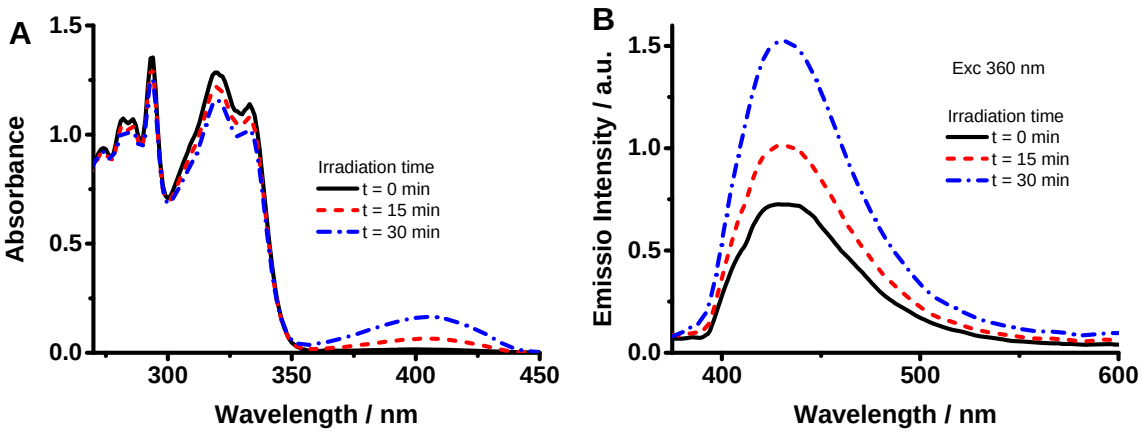


Figure S10. UV-visible absorption and fluorescence spectra of HBO in a DMF solution upon fs-pulse irradiation (λexc=360 nm) at 10 mW and 80 MHz.

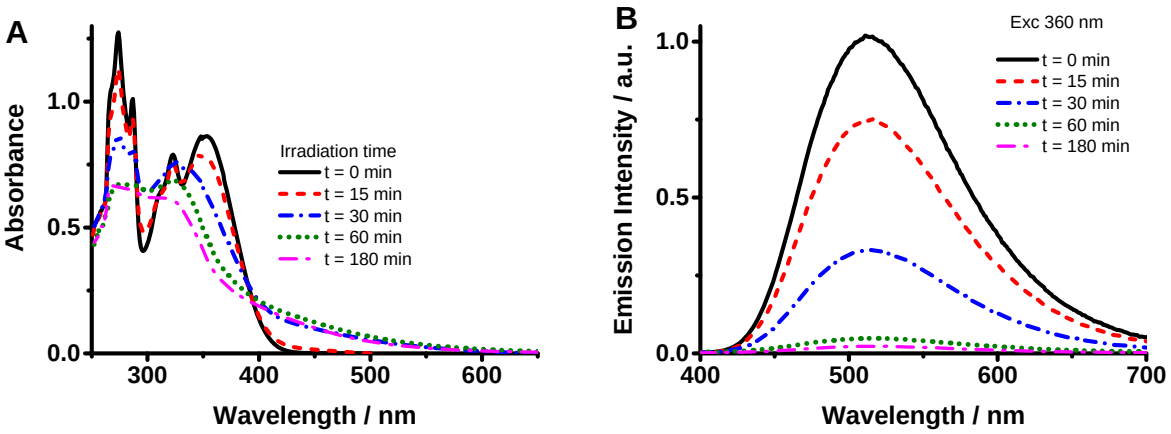


Figure S11. UV-visible absorption and fluorescence spectra of 5A-HBO in a DMF solution upon fs-pulse irradiation (λexc=360 nm) at 10 mW and 80 MHz.

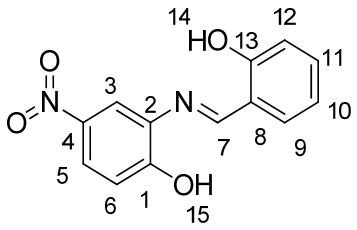
Synthesis y characterization of the different molecules (5A-MBO, 5A-HBO)

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)* Synthesis of Nitro-imines**

*(*E*)-2-(2-hydroxybenzyliden)amino-4-nitrophenol* (**HBA-4NP**)



To an ice-cooled solution of 2-amino-4-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-hydroxybenzaldehyde (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-4-nitrophenol was filtered, recrystallized from ethanol and dried *in vacuo* (50ºC/0.1 mmHg - 6 hours) yielding (2.42 g, 94%).

M. p.: 239-240 ºC (Lit.[3] 228-231ºC).

Elemental analysis: Calc. for $C_{13}H_{10}N_2O_4$: C, 60.41%; H, 3.87%; N, 10.84%.
Found: C, 60.17%; H, 4.03%; N, 10.71%.

IR ν (cm^{-1}): 3087, 3058 (C-H, arom); 2383(NH); 1628 (C=N); 1524, 1338 (NO_2); 1142, 1108 (C-O)

^{1}H-NMR (DMSO-*d6*) δ = 13.20 (s, 1H, OH_{14}); 10.25 (s, 1H, OH_{15}); 9.10 (s, 1H, HC=N, H-7); 8.25 (d, 1H, H-3, $J_{H3,H5}$=2.82 Hz); 8.07 (dd, 1H, H-5, J_{H5-H6}= 8.20 Hz); 7.69 (dd, 1H, H-9, J_{H9-H10}= 7.61Hz, J_{H9-H11}= 1.75Hz); 7.43 (dd, 1H, H-11, $J_{H10-H11}$= 8.10 Hz, $J_{H11-H12}$= 8.20 Hz); 7.12 (d, 1H, H-6); 6.94 (dd, 1H, H-10); 6.92 (d, 1H, H-12).

^{13}C-NMR (DMSO-*d6*) δ = 164.41 (C7); 160.57 (C13); 157.82 (C1); 140.16 (C2); 135.73 (C4); 133.57 (C11); 132.79 (C9); 123.76 (C5); 119.38 (C8); 119.09 (C10); 116.71 (C12); 116.34 (C6); 115.37 (C3).

Mass spectra (m/z, %): 258 (M^+, 100); 257 (M^+-1, 51); 241 (M^+-OH, 12); 211 (M^+-H-NO_2,45); 165 (25).

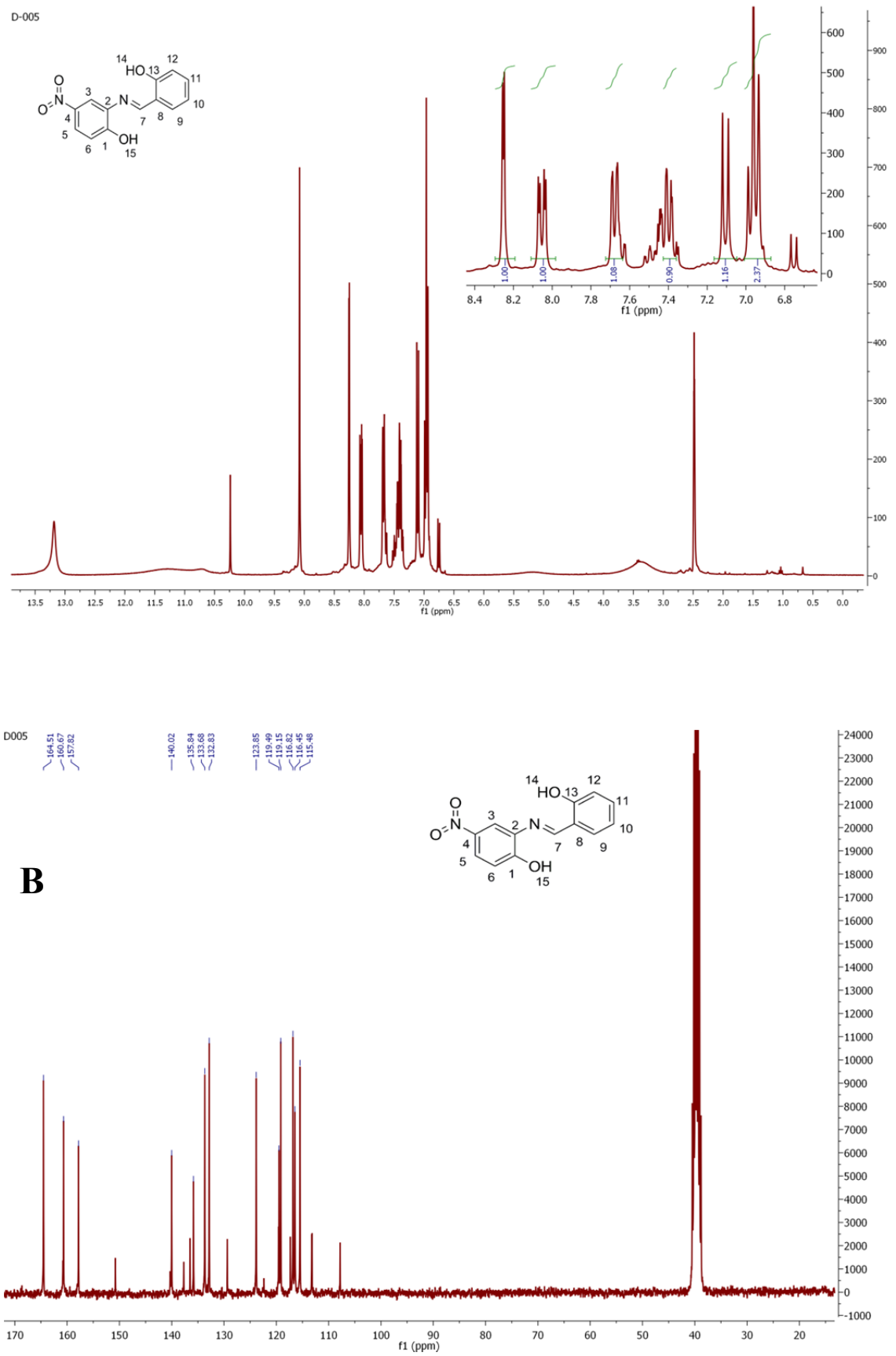
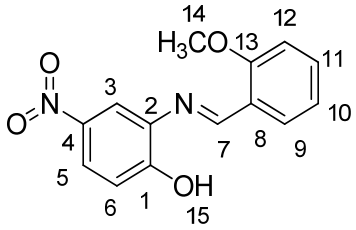


Figure S12. ^{1}H (A) and ^{13}C (B) NMR spectra of HBA-4NP in DMSO-d_6.

*(*E*)-2-((2-methoxybenzyliden)amino-4-nitrophenol* (**MBA-4NP**)



To an ice-cooled solution of 2-amino-4-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-methoxy-benzaldehyde (1.34 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 green precipitated (*E*)-2-(2-methoxybenzyliden)amino-4-nitrophenol was filtered, recrystallized from ethanol and dried *in vacuo* (50ºC/0.1 mmHg - 6 hours) yielding (2.6 g, 95%).

m. p.: 160-167 ºC.

Elemental analysis: Calc. for $C_{14}H_{12}N_2O_4$: C, 61.76%; H, 4.44%; N, 10.29%.
Found: C, 61.87%; H, 4.43%; N, 10.18%.

IR (KBr) ν (cm^{-1}): 3085 (C-H, arom); 1628, (C=N); 1525, 1335 (NO_2); 1249, 1159, 1024 (C-O)

^{1}H-NMR ($CDCl_3$) δ = 9.27 (s, 1H, HC=N, H-7); 8.25 (d, 1H, H-3, J_{H3-H5}=2.57 Hz); 8.13 (m, 1H, H-9), 8.15 (dd, 1H, H-5, J_{H5-H6}=8.97 Hz); 7.51 (ddd, 1H, H-11, $J_{H10-H11}$= 7.33, Hz, $J_{H11-H12}$= 8.51, Hz, J_{H11-H9}= 1.79Hz); 7.07 (d, 1H, H-6); 7.07 (dd, 1H, H-10, J_{H10-H9} =7.7 Hz); 7.01 (d, 1H, H-12); 3,45 (s, 3H, H-14).

^{13}C-NMR (CDCl3) δ = 160.1 (C1); 157.8 (C13); 156.3 (C7); 141.1 (C2); 136.1 (C4); 134.2 (C11); 127.5 (C9); 124.2 (C5); 123.4 (C8); 120.9 (C10); 114.6 (C6); 112.1 (C3); 111.4 (C12); 55.6 (C14).

Mass spectra (m/z, %): 272 (M^+, 57);

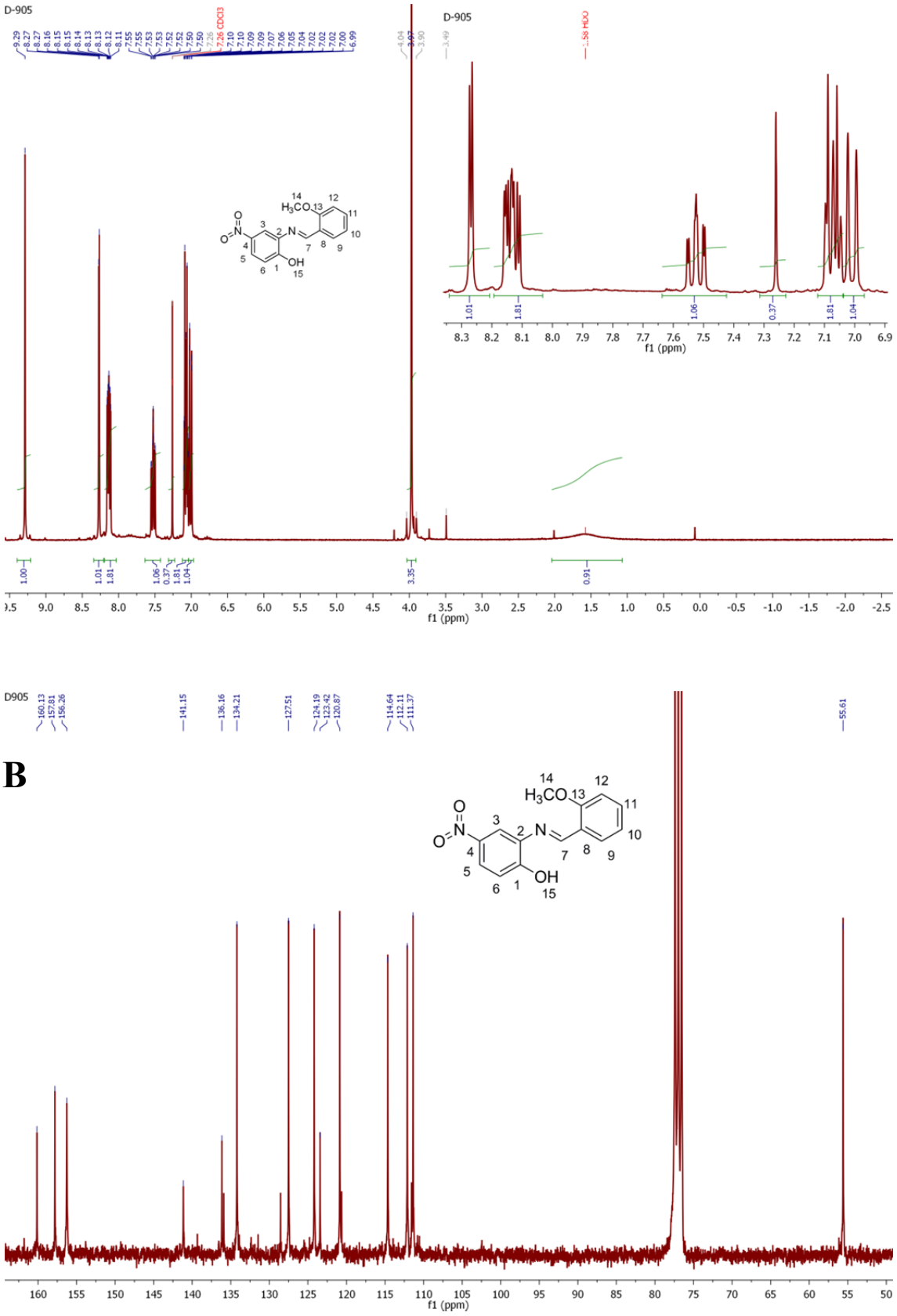
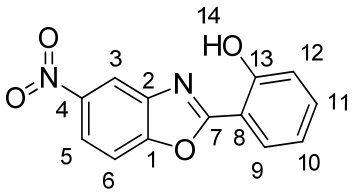


Figure S13. ^{1}H (A) and ^{13}C (B) NMR spectra of MBA-4NP in DMSO-d_6.

b) Nitro and aminobenzoxazoles

5-nitro-2-(2-hydroxyphenyl)benzoxazole (**5NO$_2$-HBO**)



Method A: A mixture of (*E*)-2-(2-hydroxybenzyliden)amino-4-nitrophenol (268 mg, 1 mmol) and 2,3-dichloro-5,6-dicyano-1,4-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 6-nitro-2-(2-hydroxyphenyl)benzoxazole (143 mg, 56% yield).

Method B: To a solution of (*E*)-2-(2-hydroxybenzyliden)amino-4-nitrophenol (1 g, 3.8 mmol) and phenylboronic acid (47.2 mg, 0.38 mmol) in methanol (60 ml), potassium cyanide was added (252 mg, 3.8 mmol) and reaction mixture was stirred at room temperature 14-20 h. The reaction mixture was concentrated under reduced pressured to 30 ml and cooled. The product was filtered to obtain 6-nitro-2-(2-hydroxyphenyl)benzoxazole (854 mg, 86% yield) practically pure.

m. p.: 195-205 ºC.

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

Found: C, 60.75%; H, 3.40%; N, 11.03%.

IR ν (cm^{-1}): 3014 (C-H, arom); 1628 (C=N); 1530, 1348 (NO_2); 1487 (CC arom.), 1236 (C-O), 1045, 808, 758.

^{1}H-NMR (DMSO-*d6*) δ = 10.81 (s, 1H, OH_{14}); 8.68 (d, 1H, H-3, $J_{H3,H5}$=2.21 Hz); 8.34 (dd, 1H, H-5, J_{H5-H6}= 8.96 Hz); 8,06 (d, 1H, H-6); 8.03 (dd, 1H, H-9, J_{H9-H10}= 7.71 Hz, J_{H9-H11}= 1.62 Hz); 7.55 (ddd, 1H, H-11, $J_{H11-H12}$= 8,33 Hz, $J_{H10-H11}$= 8,35 Hz); 7,14 (dd 1H, H-12, $J_{H10-H12}$= 0.73 Hz);); 7.09 (dd, 1H, H-10).

^{13}C-NMR (DMSO-*d6*) δ = 165.53 (C7); 158.35 (C13); 153.24 (C2); 146.64 (C5); 140.90 (C1); 135.03 (C11); 128.33 (C9); 121.85 (C4); 120.41 (C10); 117.80 (C12); 115.53 (C6); 112.11 (C3); 110.70 (C8).

Mass spectra (m/z, %): 256 (M^+, 100); 210 (M^+-NO_2, 41); 182 (10).

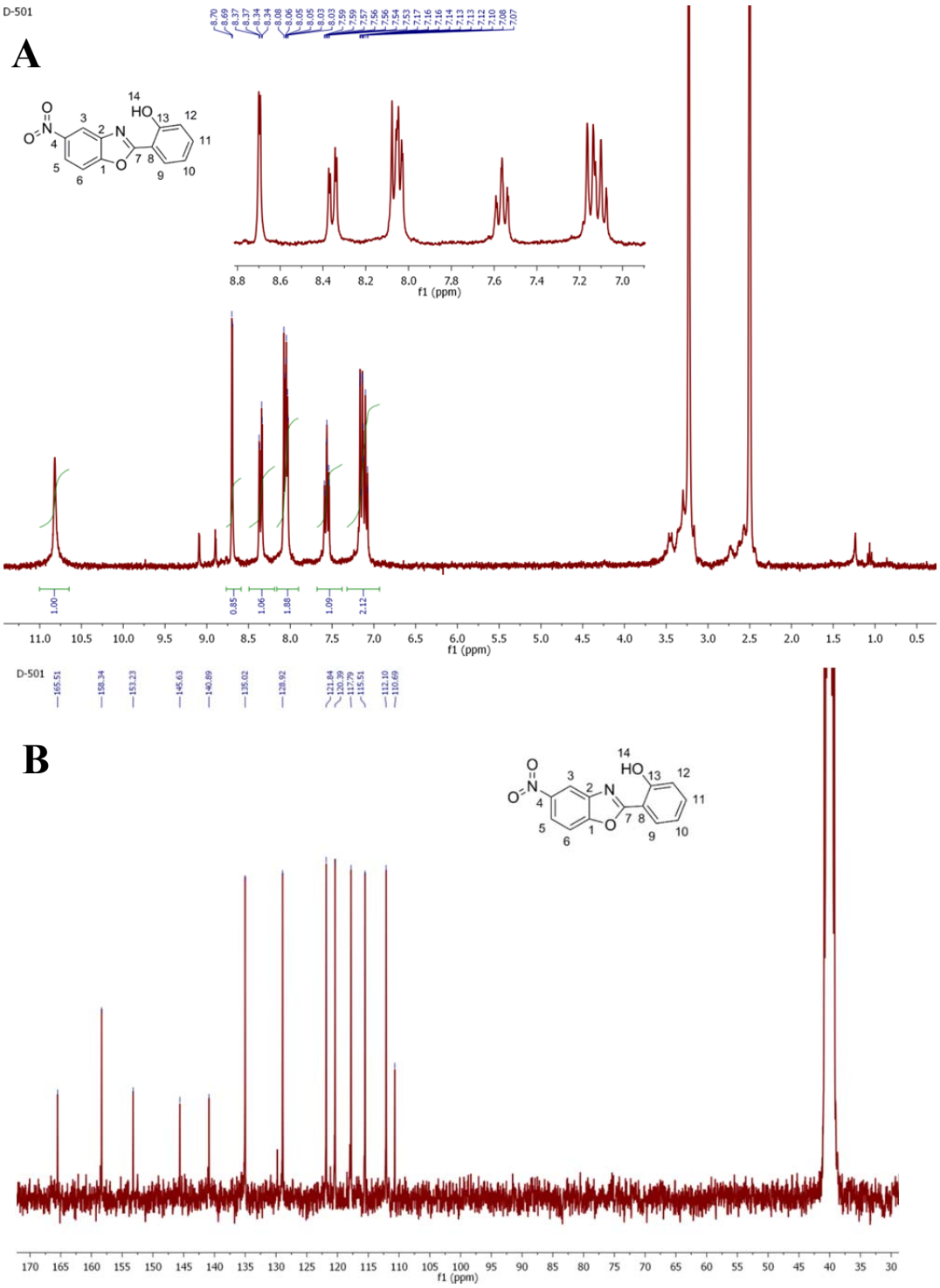
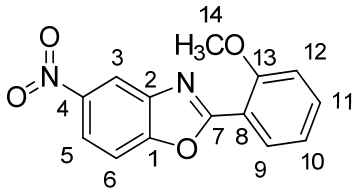


Figure S14. ^{1}H (A) and ^{13}C (B) NMR spectra of 5NO_2-HBO in DMSO-d_6.

5-nitro-2-(2-methoxyphenyl)benzoxazole **(5NO_2-MBO)**



Method A: A mixture of (E)-2-(2-hydroxybenzyliden)amino-4-nitrophenol (268 mg, 1 mmol) and 2,3-dichloro-5,6-dicyano-1,4-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 6-nitro-2-(2-hydroxyphenyl)benzoxazole (143 mg, 56% yield).

M. p.: 154-157 ºC

Elemental analysis: Calc. for $C_{14}H_{10}N_2O_4$: C, 62.22%; H, 3.73%; N, 10.37%.
Found: C, 62.10%; H, 3.86%; N, 10.31%.

IR ν (cm^{-1}): 3104 (C-H, arom); 1601 (C=N); 1527, 1344 (NO_2); 1481 (CC arom.), 1255 (C-O), 1017, 826, 751.

^{1}H-NMR (DMSO-*d6*) δ = 8.67 (d, 1H, H-3, $J_{H3,H5}$=2.36 Hz); 8.32 (dd, 1H, H-5, J_{H5-H6}= 8.96 Hz); 8.06 (dd, 1H, H-9, J_{H9-H10}= 7.8 Hz, J_{H9-H11}= 1.8 Hz); 8,03 (d, 1H, H-6); 7.65 (ddd, 1H, H-11, $J_{H11-H12}$= 8,35 Hz, $J_{H10-H11}$= 7.4 Hz); 7,31 (dd, 1H, H-12, $J_{H10-H12}$= 0.8 Hz);); 7.17 (dd, 1H, H-10).

^{13}C-NMR (DMSO-*d6*) δ = 165.54 (C7); 158.38 (C13); 153.82 (C1); 144.92 and 141.70 (C2 and C4); 134.29 (C11); 131.33 (C9); 121.25 (C5); 120.81 (C10); 115.62 (C3); 114.23 (C8); 112.93 (C12); 111 (C8).

Mass spectra (m/z, %): 270 (M^+, 100); 241 (M^++2-CH_3O, 45); 223 (M^+-1-NO_2, 10).

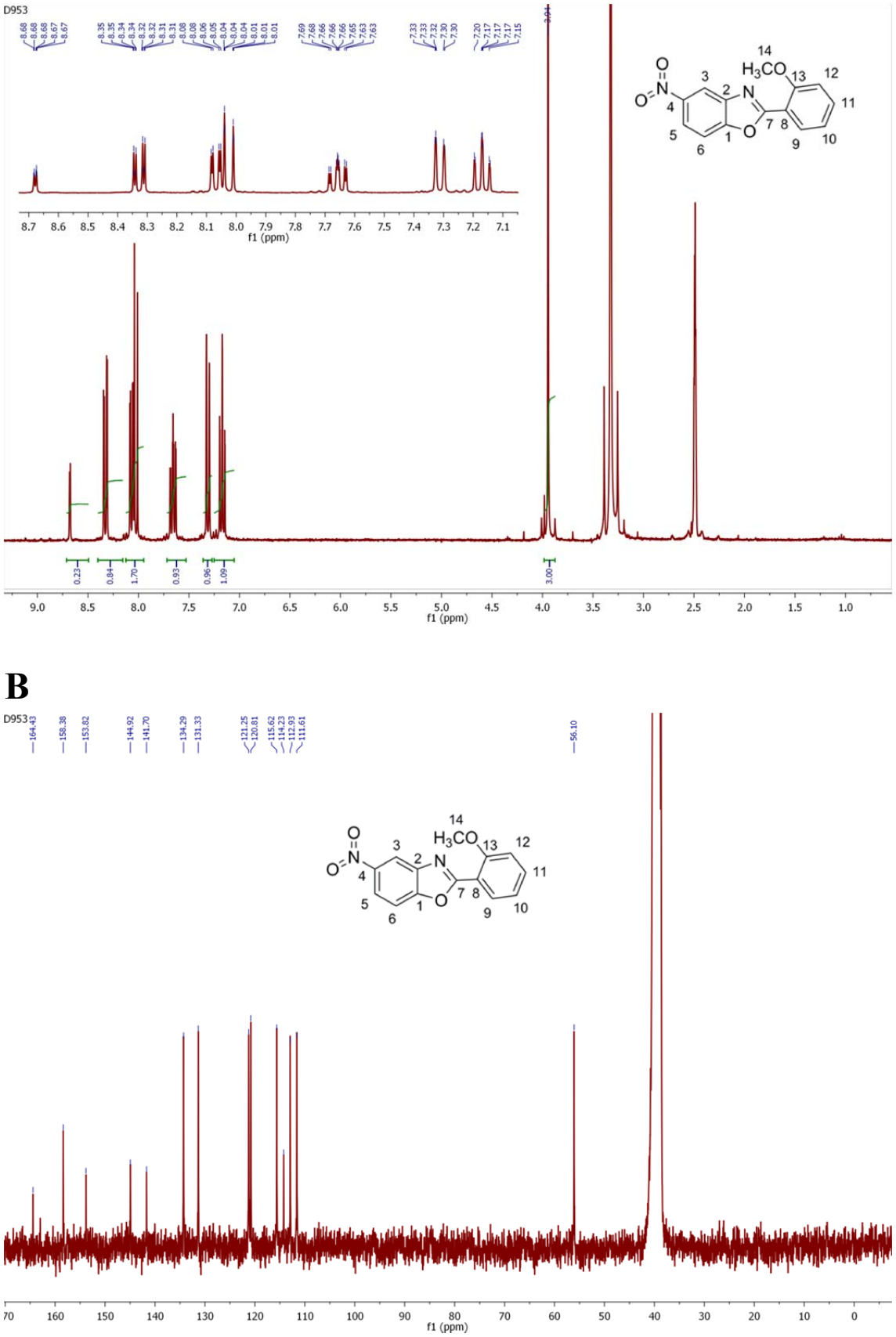
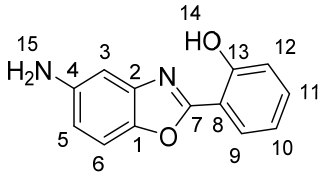


Figure S15. ^{1}H (A) and ^{13}C (B) NMR spectra of $5NO_2$-MBO in DMSO-d_6.

5-amino-2-(2-hydroxyphenyl)benzoxazole **(5A-HBO)**



To a solution of 5-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 5-amino-2-(2-hydroxyphenyl)benzoxazole (226 mg, 100%).

m. p.: 175-180 ºC

Elemental analysis: Calc. for $C_{13}H_{10}N_2O_2$: C, 69.02%; H, 4.46%; N, 12.38%.
Found: C, 68.86%; H, 4.32%; N, 12.65%.

IR ν (cm^{-1}): 3437 (O-H); 3325, 3213 (NH2); 3010 (C-H, arom); 1632, 1597 (C=N); 1542, 1487 (CC arom.), 1261,1187, 800, 752.

^{1}H-NMR ($CDCl_3$) δ = 11.50 (broad s, 1H, OH_{14}); 7.99 (dd, 1H, H-9, $J_{H9,H10}$=7.88 Hz, $J_{H9,H11}$=1.60 Hz); 7.42 (ddd, 1H, H-11, $J_{H10-H11}$= 8.63 Hz, $J_{H11-H12}$= 8.63 Hz); 7.37 (dd, 1H, H-6, J_{H5-H6}= 8.62 Hz); 7.12 (d, 1H, H-5, J_{H3-H5}= 0.70 Hz); 7.00 (ddd, 1H, H-10); 6.98 (d, 1H, H-3); 6.73 (dd, 1H, H-12, $J_{H10-H12}$= 2.29 Hz): 3.75 (broad s, 2H, NH_2).

^{13}C-NMR ($CDCl_3$) δ = 163.31 (C7); 158.63 (C13); 143.34 (C1); 143.13 (C4); 141.15 (C2); 133.23 (C11); 126.94 (C9); 119.43 (C3); 117.35 (C5); 113.78 (C12); 110.91 (C8); 110.70 (C6); 104.24 (C10).

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

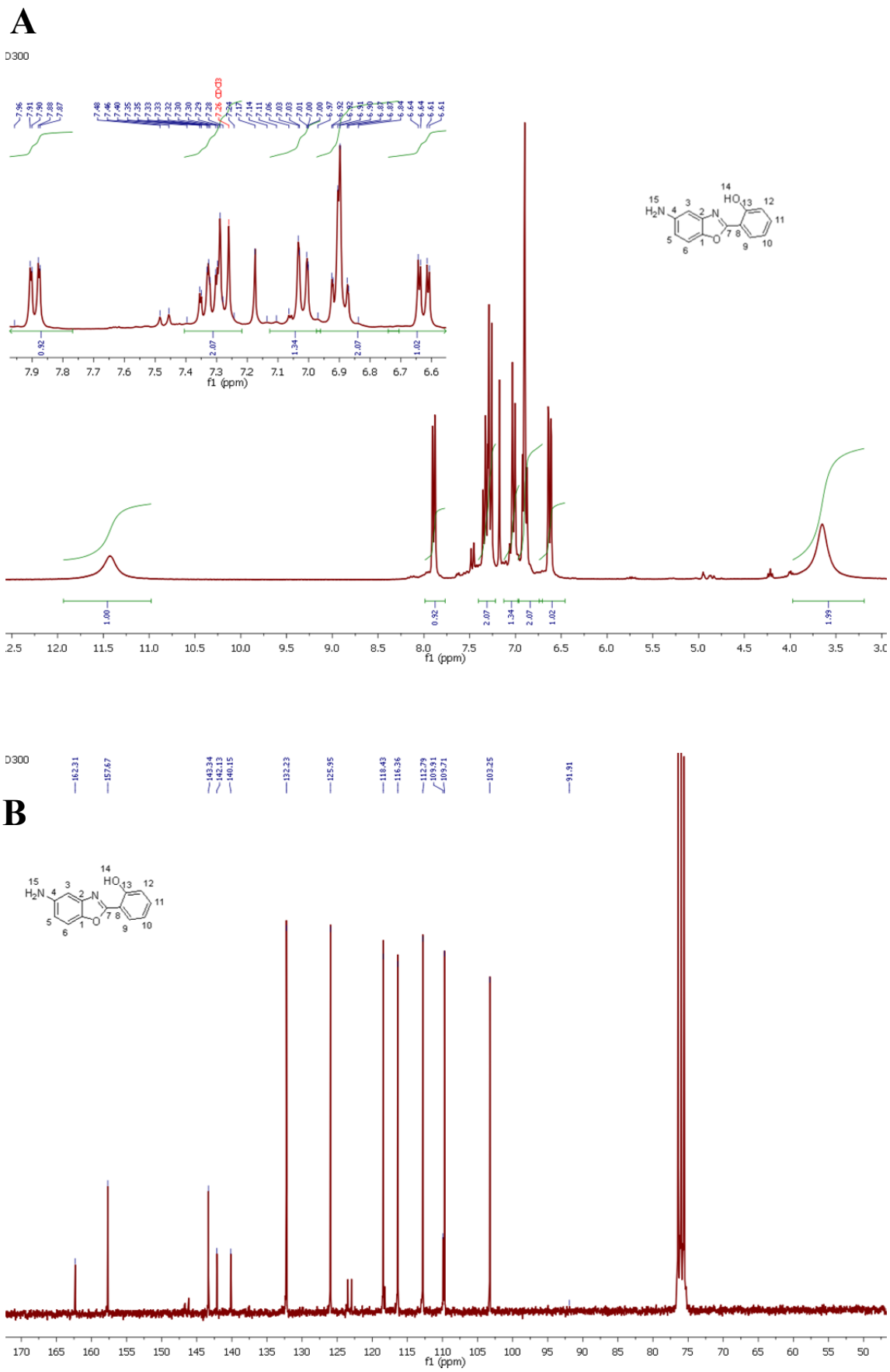
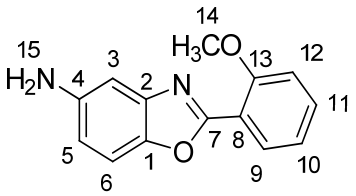


Figure S16. ^{1}H (A) and ^{13}C (B) NMR spectra of 5A-MBO in DMSO-d_6.

5-amino-2-(2-methoxyphenyl)benzoxazole **(5A-MBO)**



To a solution of 5-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 5-amino-2-(2-methoxyphenyl)benzoxazole (240 mg, 100%).

M. p.: 115-118 ºC.

Elemental analysis: Calc. for $C_{14}H_{12}N_2O_2$: C, 69.99%; H, 5.03%; N, 11.66%.
Found: C, 68.97%; H, 5.16%; N, 11.32%.

IR ν (cm^{-1}): 3317, 3215 (NH_2); 3073 (C-H, arom); 1601, 1584 (C=N); 1546, 1493 (CC arom.), 1260, 1194, 1032, 748.

^{1}H-NMR (DMSO-*d6*) δ = 7.95 (dd, 1H, H-9, J_{H9-H10}=7.8 Hz, J_{H9-H11}=1.80 Hz); 7.55 (ddd, 1H, H-11, $J_{H11-H12}$= 8.3 Hz, $J_{H11-H10}$= 7.3 Hz); 7.38 (dd, 1H, H-6, J_{H5-H6}= 8.7 Hz, J_{H3-H6}= 0.6 Hz); 7.24 (dd, 1H, H-12, $J_{H10-H12}$= 1 Hz); 7.10 (ddd, 1H, H-10); 6.86 (dd, 1H, H-3, J_{H3-H5}= 2.1 Hz); 6.65 (dd, 1H, H-5); 5.07 (broad s, 2H, NH_2); 3.90 (s, 3H, CH_3-O).

^{13}C-NMR (DMSO-*d6*) δ = 161.08 (C7); 157.78 (C13); 143.34 (C1); 146.34 (C4); 142.63 (C1); 142.26 (C2); 132.75 (C11); 130.8 (C9); 120.57 (C10); 115.95 (C8); 112.92 (C5); 112.67 (C12); 110.34 (C6); 102.53 (C3).

Mass spectra (m/z, %): 240 (M^+, 100), 223 (M^++1-NH_2, 10), 211 (M^++2-CH_3O).

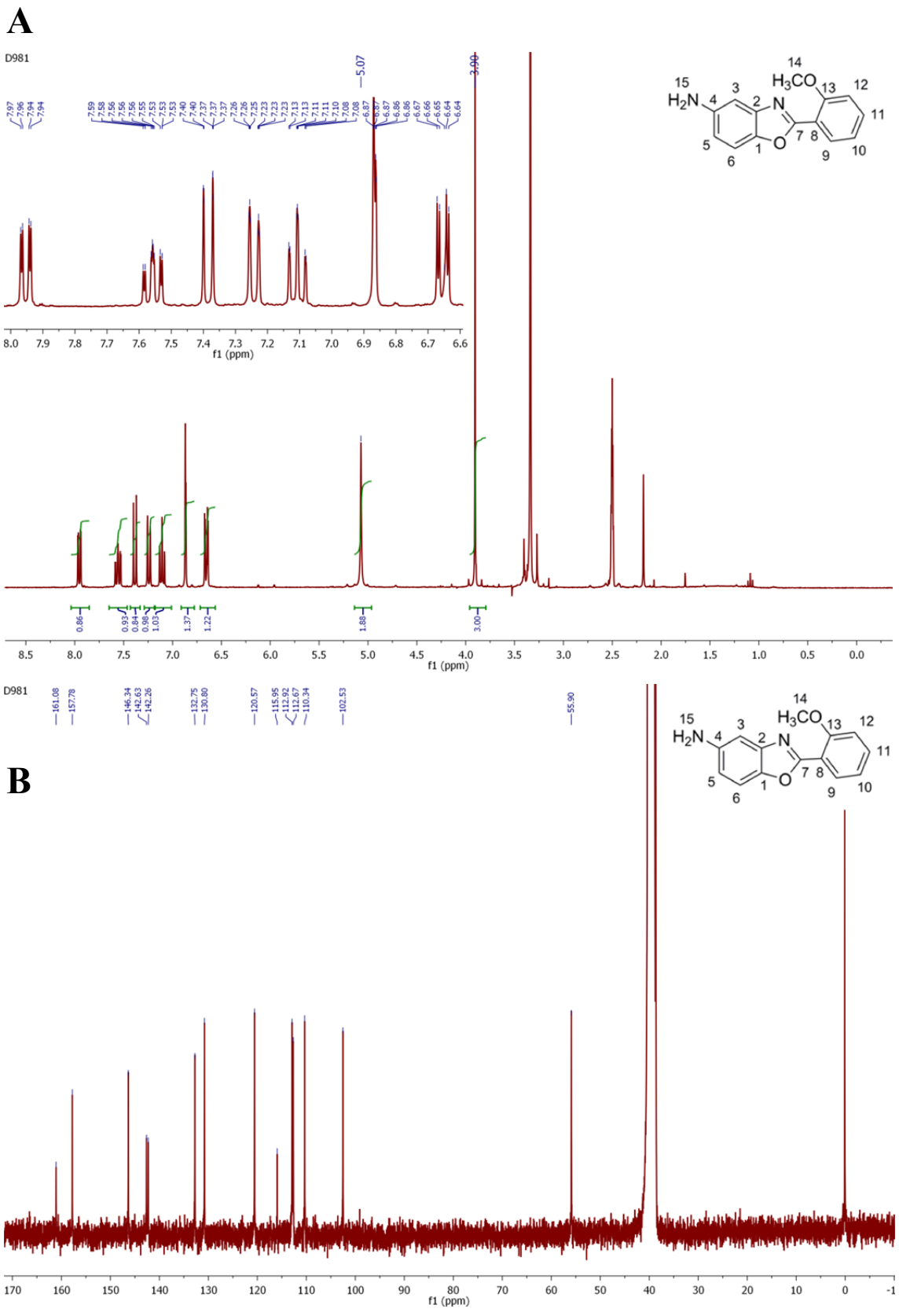


Figure S17. ^{1}H (A) and ^{13}C (B) NMR spectra of 5A-MBO in DMSO-d_6.

Acknowledgments

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References

1. K. J. Laidler, *Cinética de reacciones. Reacciones homogéneas en fase gaseosa*, 2º edn., Editorial Alhambra, S. A., 1971.
2. C. Albrecht, *Anal. Bioanal. Chem.*, 2008, **390**, 1223-1224.
3. V. Barba, D. Cuahutle, R. Santillan and N. Farfán, *Can. J. Chem.*, 2001, **79**, 1229-1237.