Supporting Information

for

Excited state dynamics of homoleptic Zn(II)dipyrrin complexes and their application in photocatalysis

Julia Leier[a], Pascal Rauthe [a], Roberta Tabone[b], Claudia Bizzarri[b,]*, and Andreas-Neil Unterreiner [a]*

1. **Sample preparation**

1.1. **Synthesis of the ligands**.

In a 2-neck round bottom flask, equipped with an air-condenser and a Dean-Stark Apparatus, under an argon atmosphere, **1** (0.3 g, 1 mmol, 1 equiv.) and 2-naphthaldehyde (1 g, 6.4 mmol, 6.4 equiv.) were dissolved in 10 mL of dry toluene. Then 0.5 mL of piperidine and 0.5 mL of glacial acetic acid were added. The solution was refluxed for 8 hours. After this time, the reaction was quenched by addition of water(20 mL) and the organic phase was separated. The aqueous layer was extracted several times with dichloromethane (DCM). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by flashchromatography on silica gel (DCM/Cyclohexane) giving the product **3** as a purple solid, (20% yield) and the product **L4** as dark-red solid (26%yield), which were recrystallized from DCM/MeOH.
2: ^{1}HNMR ($CDCl_3$,300 MHz) δ = 14.28(bs, 1H), 7.91–7.79(m, 8H),7.69(d,J=7.3 Hz, 2H), 7.53–7.28(m, 8H), 6.96(s, 2H), 6.42(s, 2H),2.36(s, 3H), 2.16(s, 6H), 1.42 ppm(s, 6H).
L4: ^{1}HNMR ($CDCl_3$,300 MHz) δ = 7.90–7.72(m, 5H), 7.53–7.40(m, 2H), 7.25(d,J=1.6 Hz, 2H),6.93(s, 2H), 6.40(s, 1H), 5.91(s, 1H), 2.44(s, 3H), 2.34(s, 3H), 2.13(s, 6H), 1.37(s, 3H), 1.33 ppm(s, 3H)

1.2. **Synthesis of the complexes 3 and 4.**

The dipyrrin **2** for complex M1 and **L4** for complex **4** was dissolved in 15 ml of dichloromethane. A solution of anhydrous zinc acetate (0.5 equiv.) in 5 ml of methanol was added, and the reaction mixture was stirred overnight. A dark blue precipitate was collected after the solvent was removed by a rotary evaporator. The solid was recrystallized from dichloromethane/ cold methanol, yielding a dark blue powder in the case of **3** and a a dark brown powder for **4** (75- 90%).
3: ^{1}HNMR ($CDCl_3$,500 MHz) δ =7.74 (dd, *J*=25.6, 5.9 Hz, 4H), 7.64–7.58 (m, 2H), 7.56 (s, 2H), 7.48–7.37 (m, 4H), 7.37–7.30 (m, 2H), 7.21 (dd, *J*=16.1, 2.6 Hz, 2H), 7.08 (dd, *J*=16.1, 4.8 Hz, 2H), 6.88–6.72 (m, 3H), 2.33 (s, 3H), 1.92 (d, *J*=4.5 Hz, 6H), 1.51 ppm (d, *J* = 4.1 Hz, 6H); ^{13}CNMR ($CDCl_3$, 126 MHz) δ = 156.5, 144.0, 143.1, 138.5, 137.9, 136.3, 135.8, 135.1, 133.7, 133.1, 133.0, 128.9, 128.2, 128.1, 127.8, 127.6, 126.3, 126.0, 123.9, 122.7, 118.6, 21.4, 19.8, 15.6 ppm. HRMS(MALDI): m/z calcd for $C_{88}H_{74}N_4Zn^+$: 1252.9680[M^+]; found:1252.1520.
4: ^{1}HNMR ($CDCl_3$,500 MHz) δ = 7.78–7.63 (m, 4H), 7.55 (d, *J*=8.6 Hz, 2H), 7.49(s, 2H), 7.43–7.34 (m, 4H), 7.25–7.18 (m,4H), 7.09 (d, *J*=16.1 Hz, 2H), 6.96 (d, *J*=10.2 Hz, 4H), 6.68 (s, 2H), 5.93 (s, 2H), 2.38 (s, 6H), 2.16 (s, 6H), 2.13 (s, 6H), 2.03 (s, 6H), 1.56 (s, 6H), 1.31 ppm (s, 6H); ^{13}CNMR ($CDCl_3$,126 MHz) δ = 158.48; 154.14; 144.51; 143.17; 142.52; 137.68; 136.59; 136.10; 135.97; 135.73; 135.17; 133.61; 132.88;130.97; 128.92; 128.85; 128.00; 127.95; 127.57; 126.90; 126.07; 125.66; 123.37; 123.14; 121.11; 116.79; (77.30, 77.24, 77.04,$CDCl_3$); 21.30; 19.75; 19.63; 16.38; 15.31; 14.95 ppm. HRMS(MALDI):m/z calcd for $C_{66}H_{62}N_4Zn^+$: 976.6300 [M^+]; found:976.9426

2. Photooxidation tests

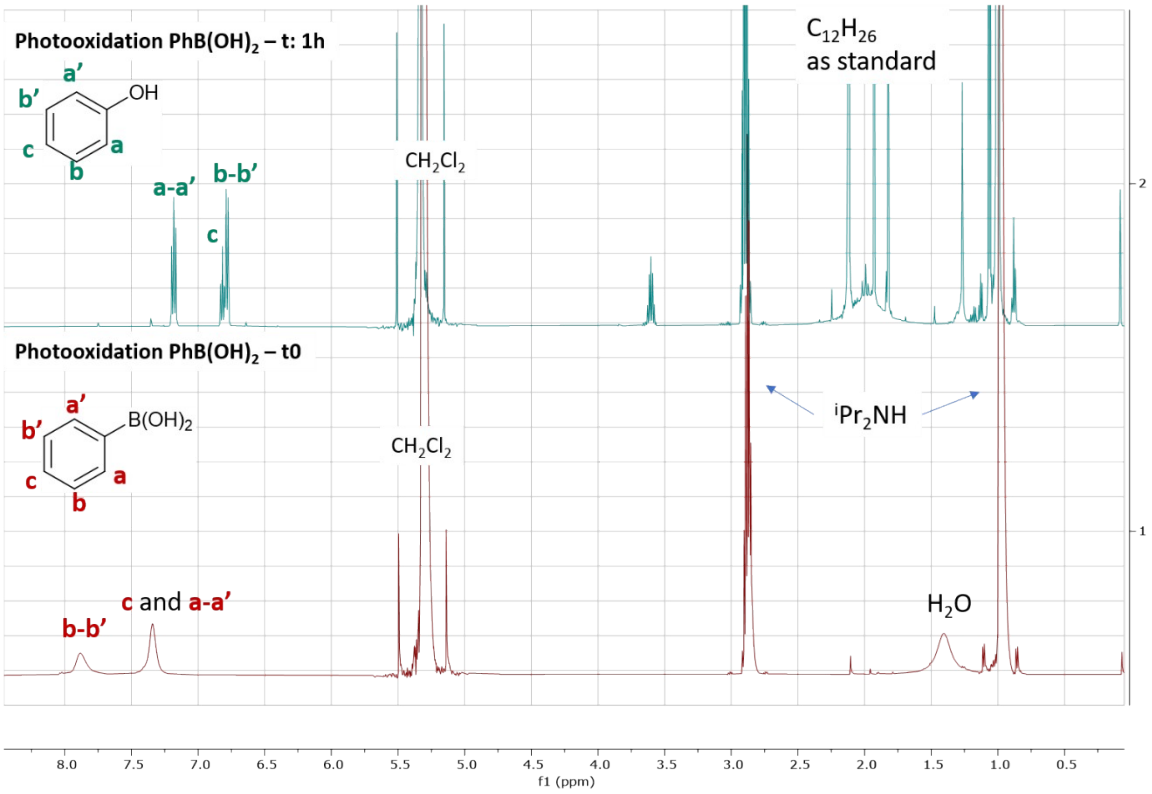

Figure S1. 1H NMR monitoring of the photo-driven hydroxylation of phenyl boronic acid in DCM, employing **3** as photocatalyst.

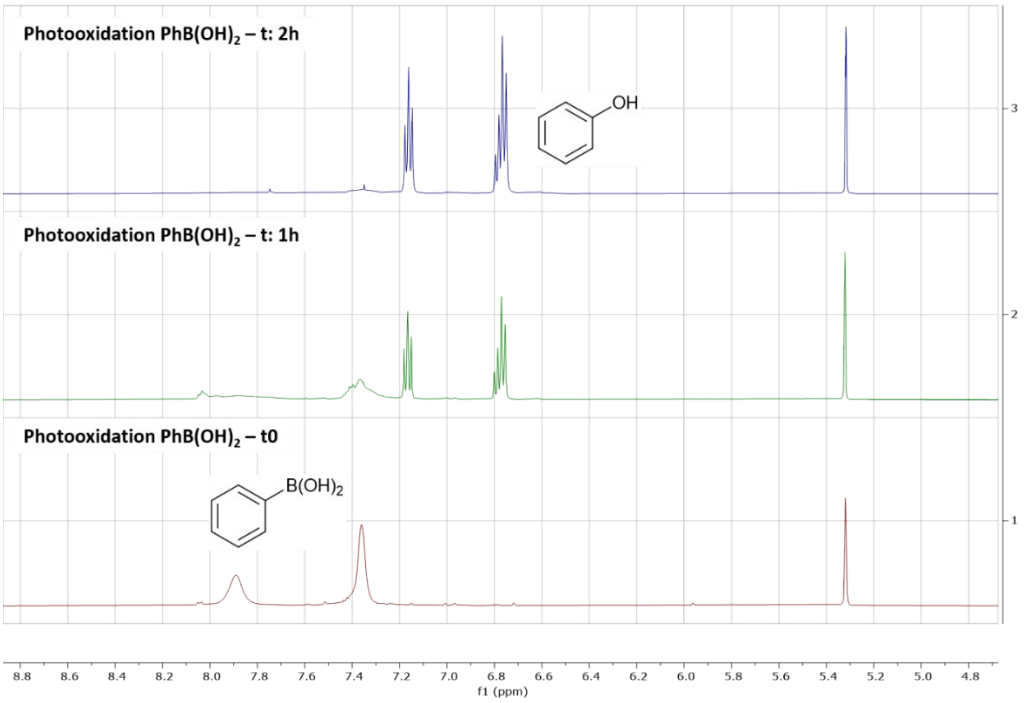

Figure S2. 1H NMR monitoring of the photo-driven hydroxylation of phenyl boronic acid in DCM, employing **4** as photocatalyst. It is evident how the starting material is still present after one hour of irradiation. The reaction is completed after 2 hours.

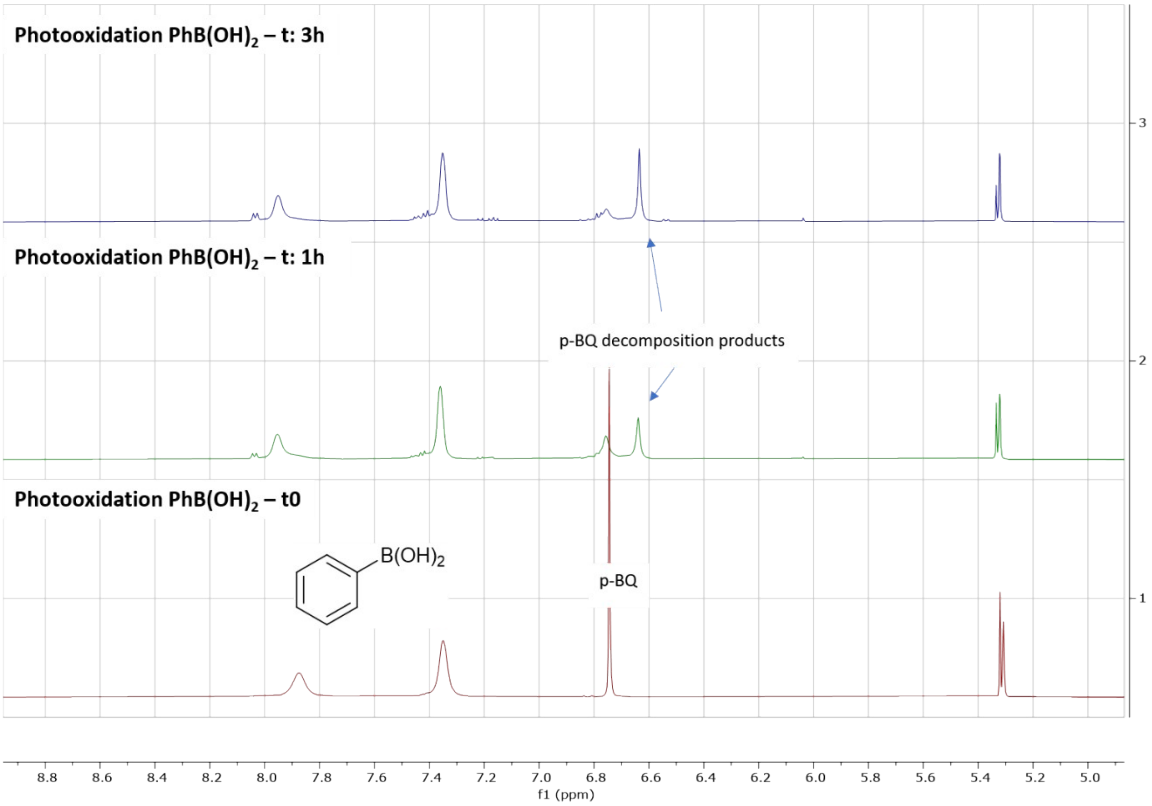

Figure S3. 1H NMR monitoring of the photo-driven hydroxylation of phenyl boronic acid in DCM with **3**, after the addition of five equivalents of para-benzoquinone (p-BQ). In the spectra, no formation of phenol could be detected.

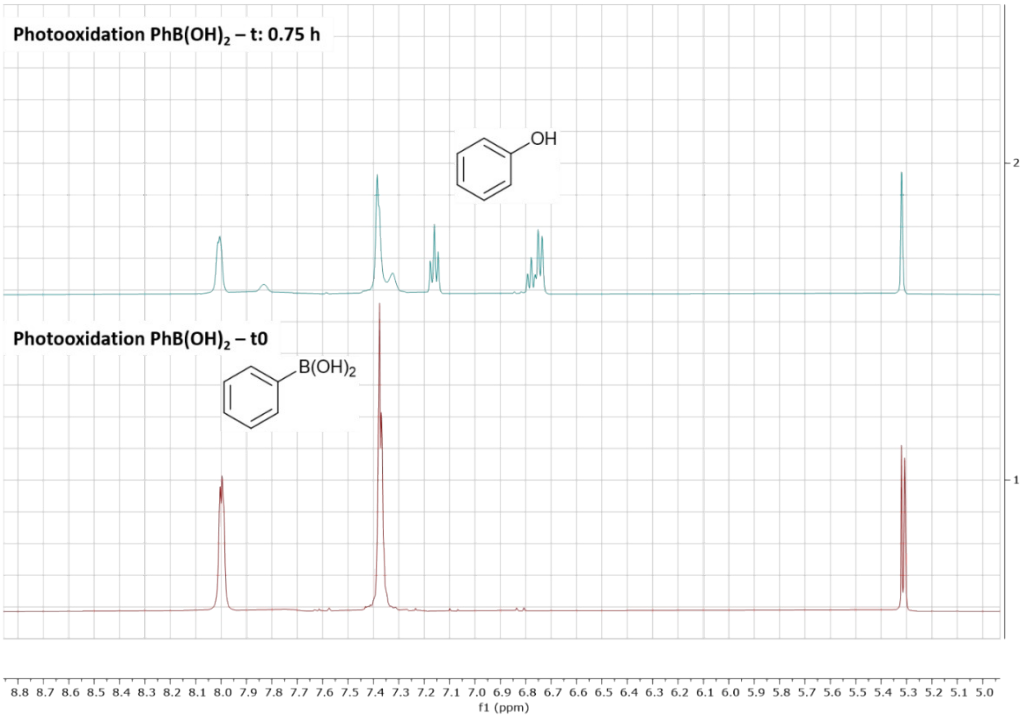

Figure S4. 1H NMR monitoring of the photo-driven hydroxylation of phenyl boronic acid in DCM with **3**, after addition of five equivalents of DABCO. The formation of the phenol could be detected (top spectrum).

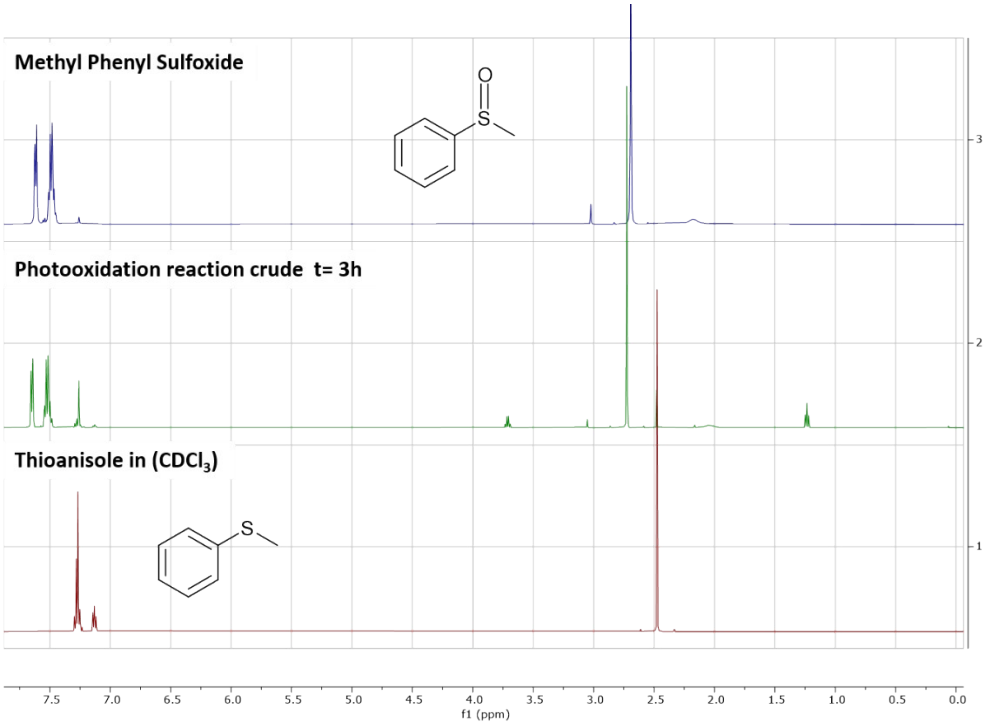

Figure S5. 1H NMR in CDCl3 of the starting material (bottom) and the crude of photo-driven oxidation (middle) performed in EtOH with **3** as photocataylst, after 3 h. The formation of the sulfoxide is well visible, as well as a small amount of unreacted thioanisole. The isolated product is shown in the top spectrum.

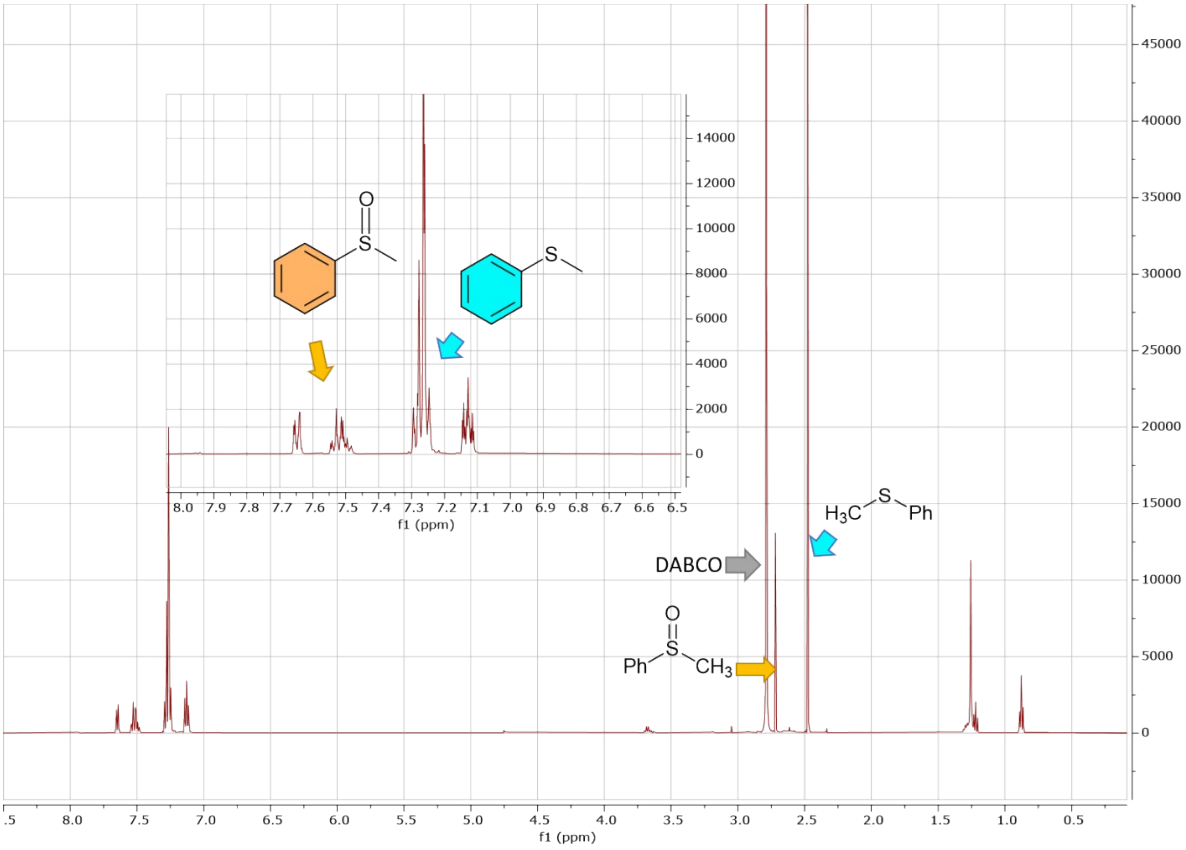

Figure S6. 1H NMR in CDCl3 of the crude of the photooxidation of thioanisole with **3** after 4 h in the presence of DABCO. The formation of the sulfoxide is corresponds to 8.8%.

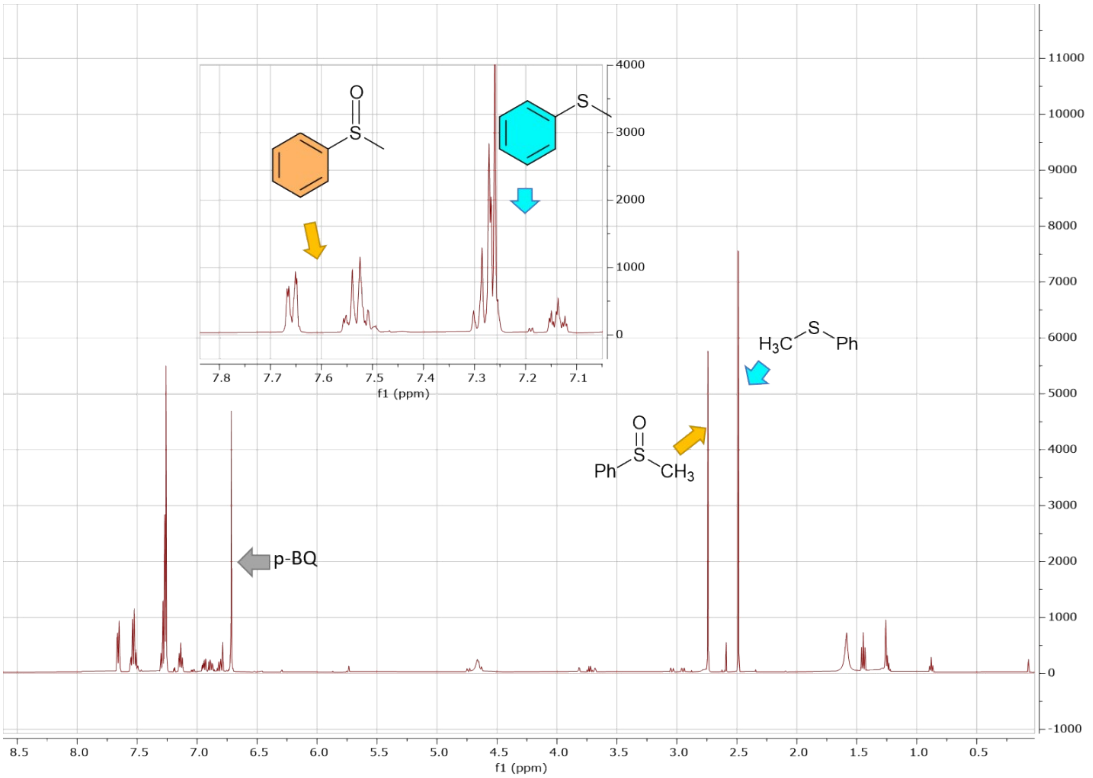

Figure S7. 1H NMR in CDCl3 of the crude of the photooxidation of thioanisole with **3** after 4 h in the presence of p-BQ. The formation of the sulfoxide is corresponds to 24 %.

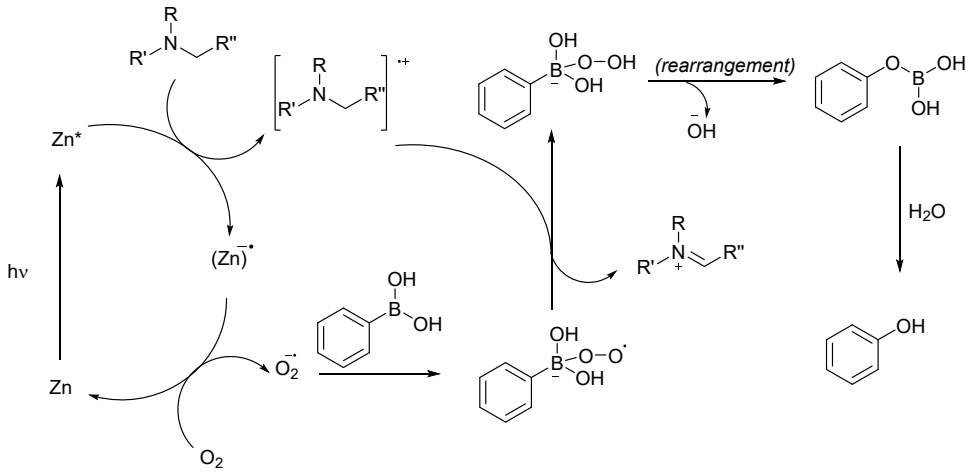

Figure S8. Proposed mechanism of the photocatalytic oxidation of phenyl boronic acid to phenol upon photocatalysis with Zn(II) bis(dipyrrinato) complexes.

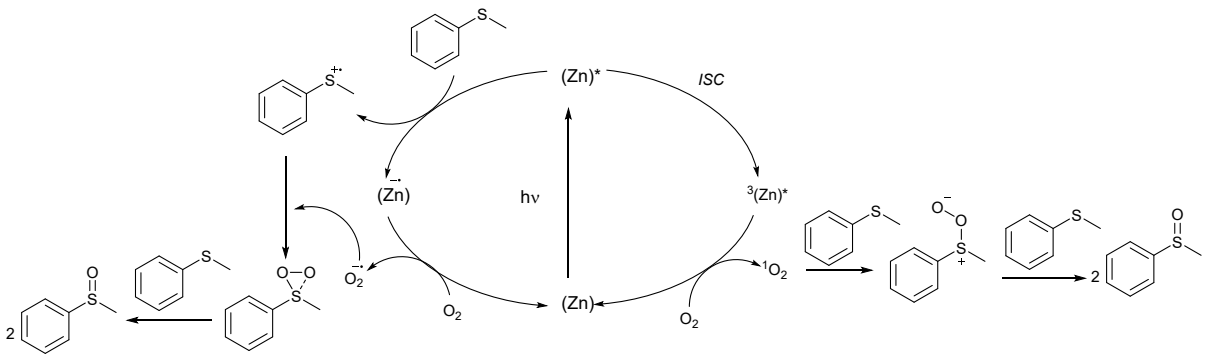

Figure S9. Proposed mechanism of the photocatalytic oxidation of thioanisole to methyl phenylsulfoxide upon photocatalysis with Zn(II) bis(dipyrrinato) complexes.

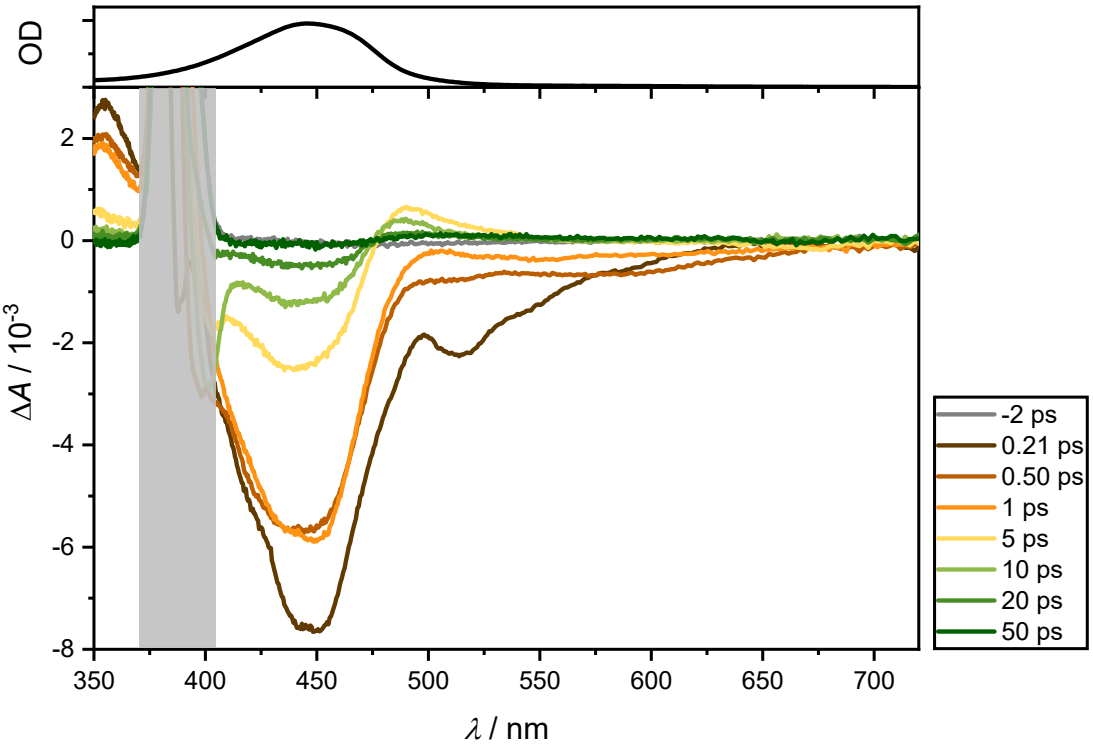

Figure S10. Transient absorption spectra of **1** in EtOH following excitation at 400 nm (OD = 0.19).

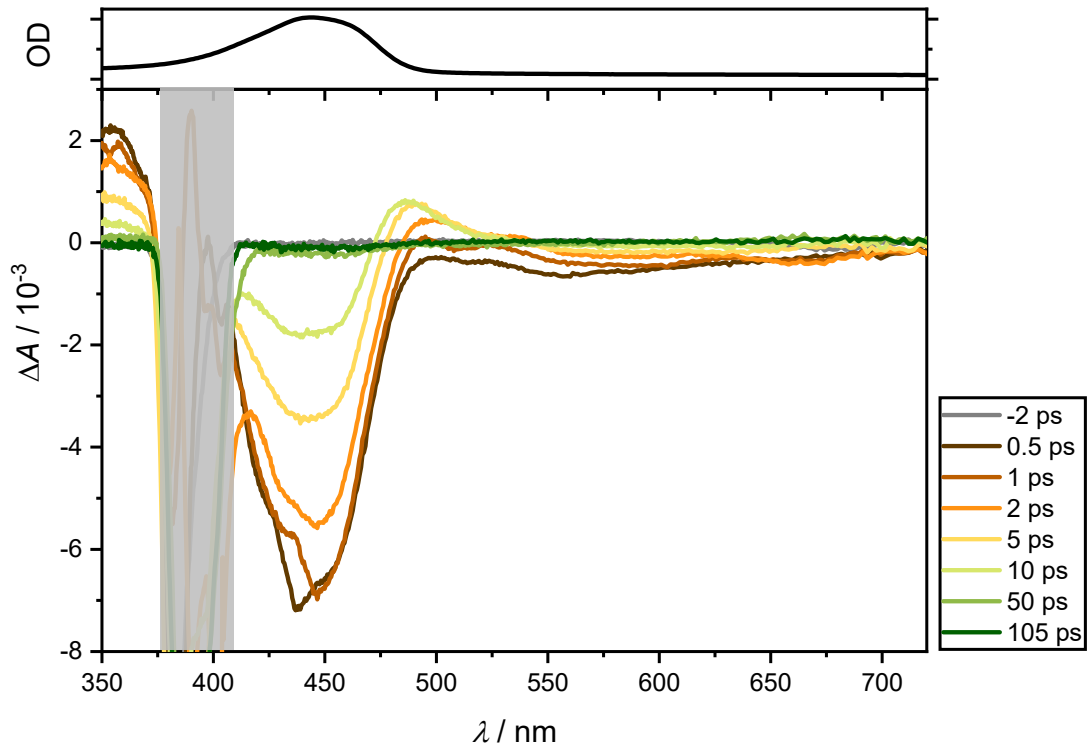

Figure S11. Transient absorption spectra of **1** in CHX following excitation at 400 nm (OD = 0.19).

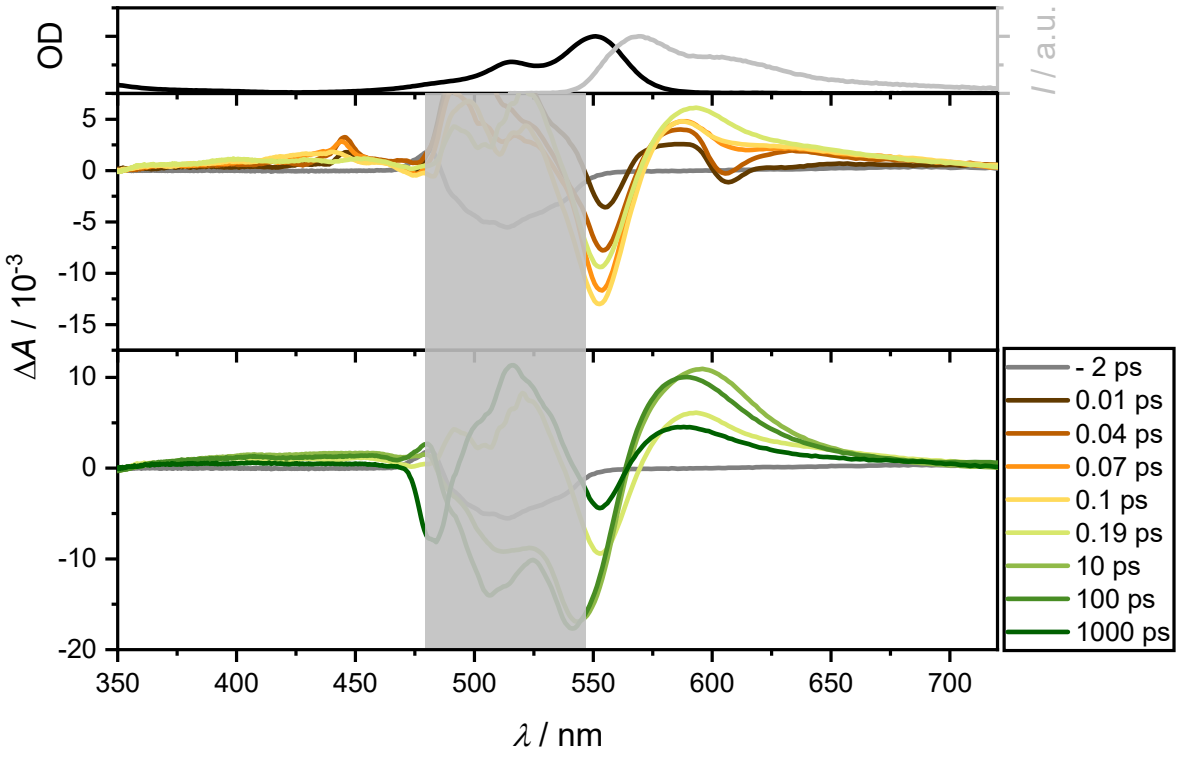

Figure S12. Transient absorption spectra of **4** in EtOH following excitation at 510 nm (OD = 0.14).

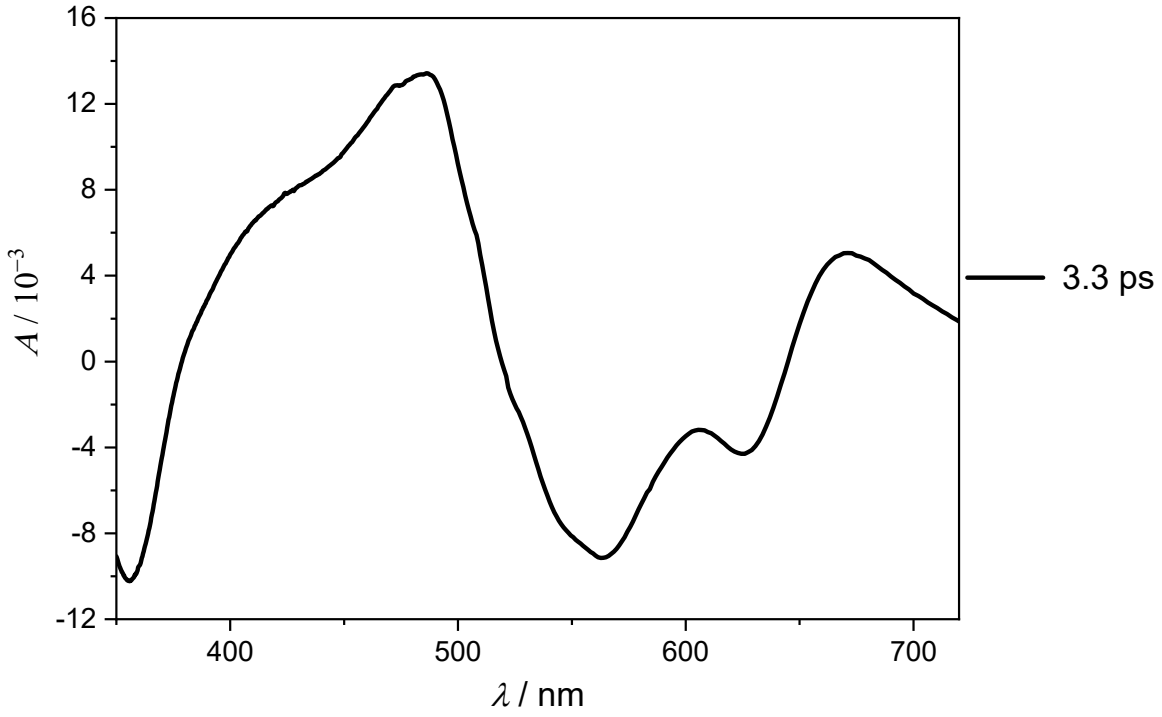

Figure S13. DADS of **2** in DCM.

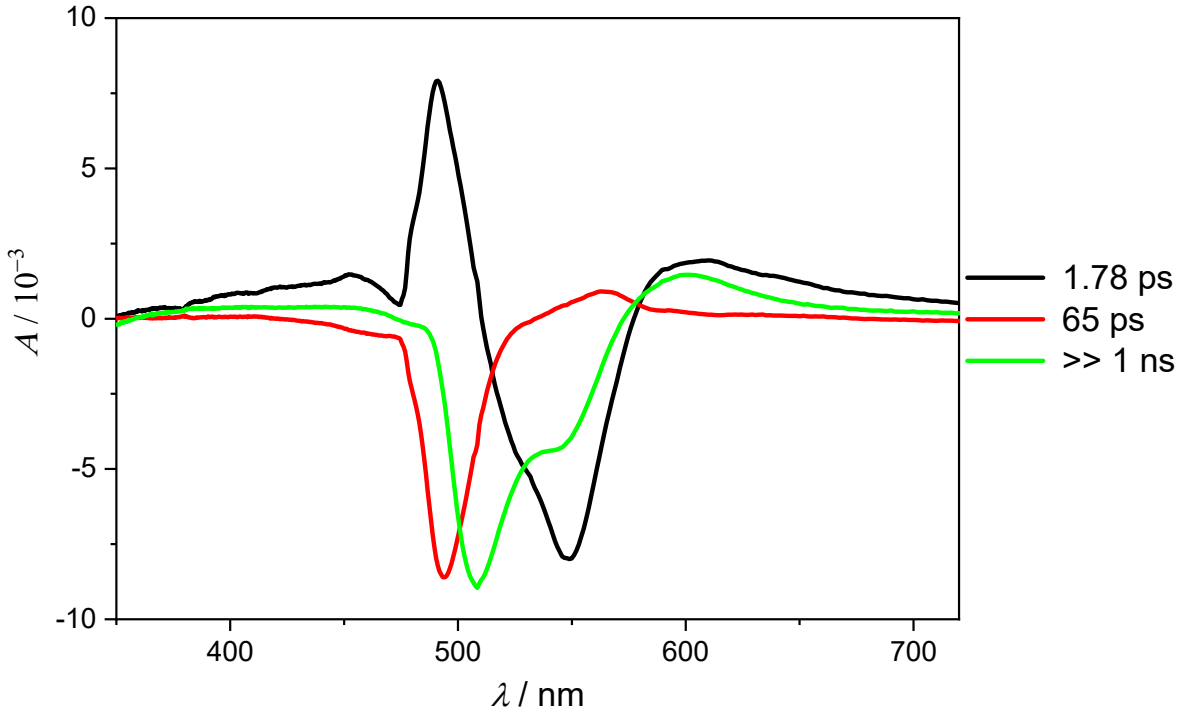

Figure S14. DADS of Zn complex **4** in DCM.

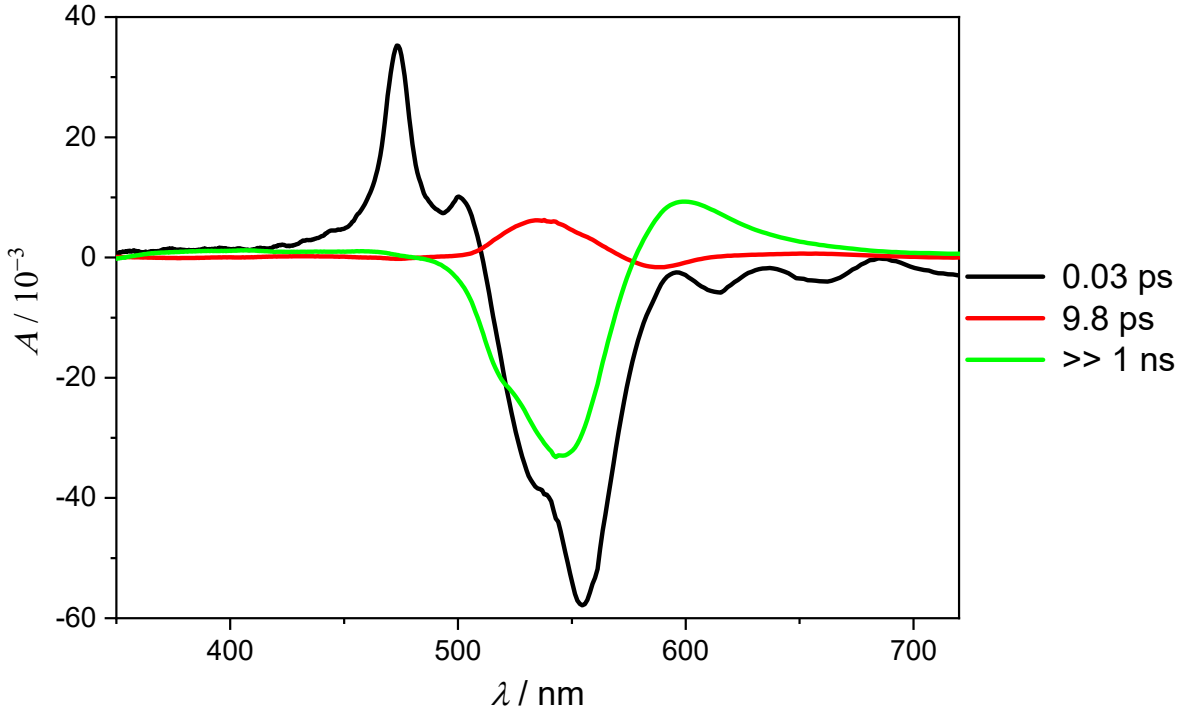

Figure S15. DADS of Zn complex **4** in EtOH.

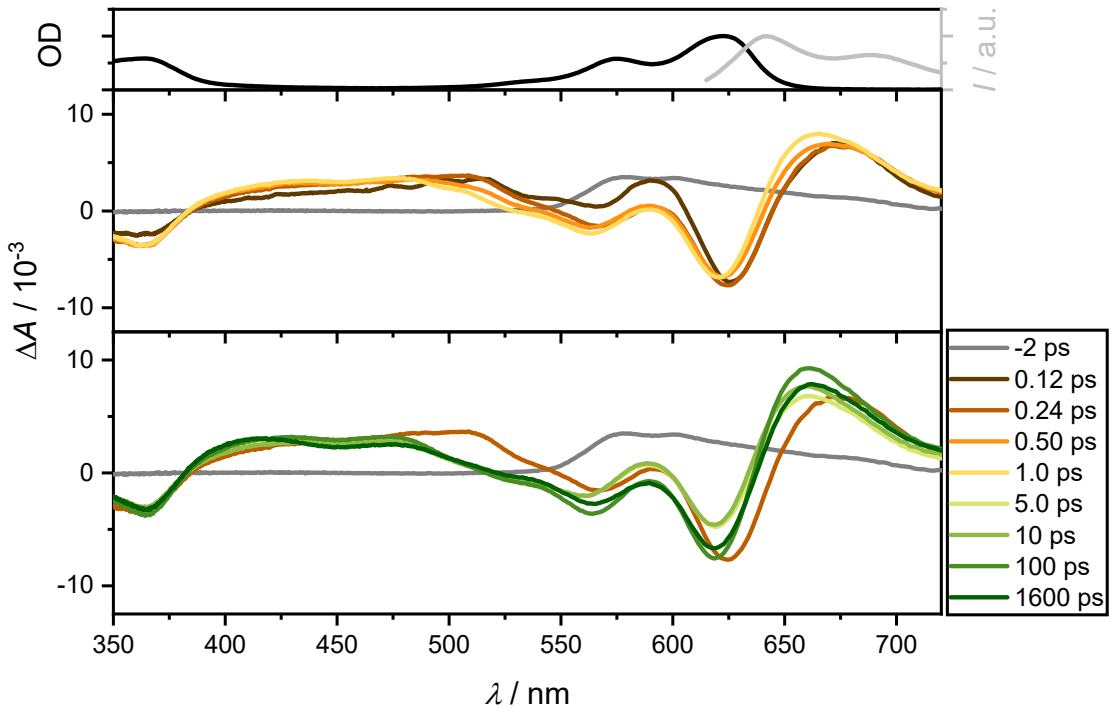

Figure S16. Transient absorption spectra of **3** in DCM following excitation at 510 nm (OD = 0.22).