

Supplementary Information for

**Photochemical oxidation of phenols and anilines mediated by
phenoxy radicals in aqueous solution**

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Abbreviations

2-AN	2-acetonaphthone
4-CN-PhOH	4-cyanophenol
4-CN-PhO ⁻	4-cyanophenoxyde ion
4-CN-PhO [•]	4-cyanophenoxy radical
CBBP	4-carboxybenzophenone
CDOM	chromophoric dissolved organic matter
³ CDOM*	excited triplet states of CDOM
DMOP	3,4-dimethoxyphenol
DOM	dissolved organic matter
<i>E</i> _{red,1} ⁰	standard one-electron reduction potential (unit: V vs. SHE)
<i>f</i> _{R-PhO_{ep}⁻}	fraction of electron-poor phenoxide ion (R-PhO _{ep} ⁻) present in solution
HPLC	high-performance liquid chromatography
<i>k</i> ^{obs}	pseudo-first-order rate constants for the transformation of a TC
<i>k</i> ^{obs} _{3²-AN*,TC}	contribution of the direct reaction of TC with ³ 2-AN* to <i>k</i> ^{obs} (see Eq. (6))
<i>k</i> _x ^{obs}	<i>k</i> ^{obs} for [TC] ₀ = <i>x</i> μM
<i>k</i> _{x,control} ^{obs}	<i>k</i> ^{obs} _{x,control} determined in the absence of photosensitizer
<i>k</i> _{x,Sens} ^{obs}	<i>k</i> ^{obs} _{x,Sens} determined in the absence of electron-poor phenol
<i>k</i> _{R-PhO_{ep}[•]} ^{obs,c}	corrected <i>k</i> ^{obs} (= <i>k</i> _{0.1} ^{obs} - <i>k</i> _{0.1,control} ^{obs} - <i>k</i> _{5.0,Sens} ^{obs}), representing the contribution of the electron-poor phenoxy radical (R-PhO _{ep} [•]) to the transformation of TC
<i>k</i> _{X,Q} ^q	second-order rate constant for the quenching of a reactive species X by a quencher Q
LLPO	long-lived photooxidants
SHE	standard hydrogen electrode
PPRI	photochemically produced reactive intermediates
R-PhOH _{ep}	model electron-poor phenol
R-PhO _{ep} ⁻	model electron-poor phenoxide ion
R-PhO _{ep} [•]	model electron-poor phenoxy radical
Sens	photosensitizer
³ Sens*	excited triplet state of a photosensitizer (Sens), e.g., ³ 2-AN*, ³ CBBP*
TC	target compound
TMP	2,4,6-trimethylphenol
<i>β</i> _{4-CN-PhO[•],TC} ^r	inverse proportionality factor used to characterize the contribution of reaction of TC with 4-CN-PhO [•] to <i>k</i> ^{obs} (see Eq. (6))

Text S1: Materials and solutions.

Irradiation experiments

The following chemicals were obtained from common commercial sources and used as received: 2,4,6-trimethylphenol (TMP, Ega Chemie, 99 %); 3,4-dimethoxyphenol (DMOP; Alfa Aesar, 98%); aniline (Sigma Aldrich, $\geq 99.5\%$); methylaniline (Sigma Aldrich, 99.6 %); 3,5-dichlorophenol (Riedel de Haën, pestanal); 2,6-dichlorophenol (Sigma Aldrich, 99%); 4-hydroxybenzoic acid (Sigma Aldrich, $\geq 99\%$); 4-hydroxyacetophenone (Sigma Aldrich, 99%); 4-cyanophenol (4-CN-PhOH, Fluka, $> 97\%$); 2-acetonaphthone (2-AN, Sigma Aldrich, 99 %), and 4-carboxybenzophenone (Sigma Aldrich, 99%).

Stock solutions of all target compounds (100 or 500 μM) and the model electron-poor phenols (500 μM) were prepared in ultrapure water. Phosphate buffer stock solutions (50 mM, pH 7.76) were prepared in ultrapure water using $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ (Sigma Aldrich/Merck, $\geq 98.5\%$) and $\text{NaH}_2\text{PO}_4 \times \text{H}_2\text{O}$ (Merck, for analysis).

Laser flash photolysis (1)

The following chemicals were obtained from common commercial sources and used as received: 2,4,6-trimethylphenol (TMP, Acros organics, 99%); aniline (Sigma Aldrich, $\geq 99.5\%$); methylaniline (Alfa Aesar $> 99\%$); 3,5-dichlorophenol (Sigma Aldrich, analytical standard); 4-hydroxyacetophenone (Acros organics, 98%); 4-cyanophenol (Acros organics, 99%), 2-acetonaphthone (Fluka, $> 98\%$), $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ (Sigma Aldrich/Merck, $\geq 98.5\%$), $\text{NaH}_2\text{PO}_4 \times \text{H}_2\text{O}$ (Merck, for analysis) and boric acid (Fisher Scientific, electrophoresis grade). Water was obtained from a Merck Millipore Milli-Q Direct purification system with a Merck Quantum ® TEX polishing cartridge.

Laser flash photolysis (2)

The following chemicals were obtained from common commercial sources and used as received: 2,4,6-trimethylphenol (Merck, 97%); 4-cyanophenol (TCI, 98%), 2-acetonaphthone (Sigma Aldrich, 99%), $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ (Sigma Aldrich/Merck, $\geq 98.5\%$) and $\text{NaH}_2\text{PO}_4 \times \text{H}_2\text{O}$ (Sigma Aldrich, $> 99\%$). Water was obtained from an Aqua Osmotic 02A purification system.

Text S2: Calculation of photon fluence rates

The photon fluence rate is calculated based on equation (S1) (Canonica et al. 2008), the photon irradiance spectra ((Leresche et al. 2016), Table S1) taking in consideration the effect of the filter solution, and by including the quantum yield calculations of the *p*-nitroanisole/pyridin actinometer (S2) by (Laszakovits et al. 2017) :

$$E_p^\circ(334\text{-}436 \text{ nm}) = \frac{k_{P,PNA}}{2.303 * \Phi_{PNA} * \sum_{\lambda=334 \text{ nm}}^{436 \text{ nm}} (f_{p,\lambda}^f * \varepsilon_{PNA,\lambda})} \quad (\text{S1})$$

E_p° is the photon fluence rate (in einstein $\text{m}^{-2} \text{ s}^{-1}$) in the wavelength range of 290-400 nm, relevant in the current study, $k_{P,PNA}$ (in s^{-1}) is the observed transformation rate constant of *p*-nitroanisole, Φ_{PNA} is the quantum yield of the *p*-nitroanisole/pyridine system (in mol einstein $^{-1}$), $f_{p,\lambda}$ is the emission spectrum of the lamp based on the photon flux and normalized to the wavelength interval (i.e. $\sum_{\lambda=334 \text{ nm}}^{436 \text{ nm}} f_{p,\lambda} = 1$), $f_{p,\lambda}^f$ is adjusted for the filter solution, and $\varepsilon_{PNA,\lambda}$ is the molar absorption coefficient of *p*-nitroanisole at the wavelength λ (in $\text{m}^2 \text{ mol}^{-1}$).

$$\Phi_{PNA} = 0.29[\text{pyr}] + 0.00029 \quad (\text{S2})$$

Here:

$$[\text{pyr}] = 10 \text{ mM}$$

$$\Phi_{PNA} = 0.00319 \text{ mol einstein}^{-1}$$

$$k_{P,PNA}^{\max} = 3.7 \times 10^{-3} \text{ s}^{-1}$$

$$k_{P,PNA}^{\min} = 2.9 \times 10^{-3} \text{ s}^{-1}$$

Calculation

$$\begin{aligned} \sum_{\lambda=334 \text{ nm}}^{436 \text{ nm}} (f_{p,\lambda}^f * \varepsilon_{PNA,\lambda}) &= (f_{p,334.2}^f * \varepsilon_{PNA,334.2}) + (f_{p,365.4}^f * \varepsilon_{PNA,365.4}) + \\ &\quad (f_{p,404.7-407.8}^f * \varepsilon_{PNA,404.7-407.8}) + (f_{p,435.8}^f * \varepsilon_{PNA,435.8}) \end{aligned}$$

$$\sum_{\lambda=334 \text{ nm}}^{436 \text{ nm}} (f_{p,\lambda}^f * \varepsilon_{PNA,\lambda}) = 90.7 \text{ m}^2 \text{ mol}^{-1}$$

Results

$$E_p^{\max}(334\text{-}436 \text{ nm}) = 5.6 \times 10^{-3} \text{ einstein m}^{-2} \text{ s}^{-1}$$

$$E_p^{\min}(334\text{-}436 \text{ nm}) = 4.4 \times 10^{-3} \text{ einstein m}^{-2} \text{ s}^{-1}$$

Table S1: Normalized emission of the lamp, $f_{p,\lambda}$, and corrected for the transmittance of the filter solution, $T_{\text{filter},\lambda}$, resulting in $f_{p,\lambda}^f$ and *p*-nitroanisol molar extinction coefficient, $\varepsilon_{PNA,\lambda}$, employed to calculate the photon fluence rate for the medium-pressure Hg lamp system, data from (Leresche et al. 2016).

λ / nm	$f_{p,\lambda}$	$T_{\text{filter},\lambda}^*$	$f_{p,\lambda}^f$	$\varepsilon_{PNA,\lambda} / \text{m}^2 \text{ mol}^{-1}$
334.2	0.011	0.568	0.006	854
365.4	0.365	0.992	0.374	221
404.7-407.8	0.204	0.994	0.209	6
435.8	0.396	0.996	0.408	4

*Transmittance of the filter solution (0.15 M NaNO₃) with a path length of 2.5 cm

Text S3: Details of HPLC analyses and pH measurements

An Agilent 1100 HPLC system, equipped with a quaternary low-pressure mixing gradient pump, a photodiode array detector, and a fluorescence detector (Agilent 1200 series) was used. Compound concentrations $> 0.5 \mu\text{M}$ were analyzed with a photodiode array detector, compound concentrations $< 0.5 \mu\text{M}$ were analyzed with a fluorescence detector, as typically higher sensitivity could be achieved with the fluorescence detector. Mostly, duplicate injections of 100 μL samples were performed, in some cases of a second duplicate injection, the injection volume was 50 μL . All compounds were analyzed on a reverse-phase C₁₈ column (COSMOSIL 5C18-MS-II packed column, pore size 120 Å, particle size 5 μm , internal diameter 3.0 mm, length 100 mm) with a column oven temperature of 25 °C, a flow rate of 0.5 mL min⁻¹. Mean deviations of measured concentrations were typically $< 5 \%$.

Mixtures of acetonitrile (Fisher Scientific, LC/MS grade), water and buffer (10 mM H₃PO₄ in ultrapure water, pH 2.1) were employed as eluents.

Table S2a. HPLC methods for the analyses of individual compounds

Compound	Eluent composition (%)			Retention time (min)	Absorption wavelength / nm (Photodiode array detector)	Excitation/Emission wavelength / nm (Fluorescence detector)
	water	acetonitrile	buffer			
2-acetonaphthone	-	70	30	2.4	242	-
aniline	70	30	-	3.2	242	232/343
4-benzoylbenzoic acid	-	50	50	2.8	242	-
3,5-dichlorophenol	-	60	40	2.9	220	-
3,4-dimethoxyphenol	-	25	75	2.6	220	230/325
4-methylaniline	60	40	-	3.0	242	232/343

Table S2b. HPLC methods for the analyses of multiple compounds in mixtures, isocratic methods

Compound	Eluent composition (%)			Retention time (min)	Absorption wavelength / nm (Photodiode array detector)	Excitation/Emission wavelength / nm (Fluorescence detector)
	water	acetonitrile	buffer ^b			
3,4-dimethoxyphenol	25	75		2.7	220	230/325
4-cyanophenol	25	75		4.0	220	-
3,4-dimethoxyphenol	10	90		8.0	220	230/325
4-hydroxyacetophenone	10	90		10.5	220	-
3,4-dimethoxyphenol	22	78		3.0	220	230/325
4-hydroxybenzoic acid	22	78		2.2	220	-
2,4,6-trimethylphenol	40	60		7.7	220	230/325
4-cyanophenol	40	60		2.3	220	-
2-acetonaphthone	40	60		9.2	242	-
2,6-dichlorophenol	40	60		5.8	220	-
3,5-dichlorophenol	60	40		9.3	220	
4-hydroxyacetophenone	60	40		2.0	220	-

Table S2c. Retention times for the analyses of multiple compounds in mixtures with the gradient method. Time course of the gradient method (acetonitrile (ACN)/buffer): 0.0 min (start), 25% ACN; 3.8 min, 25% ACN; 6.8 min, 70% ACN; 8.8 min, 70% ACN; 10.2 min, 25% ACN; 12 min (stop), 15% ACN.

Compound	Retention time (min)
3,4-dimethoxyphenol	2.6
2,6-dichlorophenol	8.8
4-cyanophenol	3.8
2-acetonaphthone	9.5

Text S4: Compound Characterization

Calculation of fraction of deprotonated phenol, at a given pH:

$$f_{\text{PhO}^-} (\%) = \frac{\text{PhO}^-}{\text{PhOH}} \times 100 = \frac{100}{1+10^{\text{p}K_a - \text{pH}}} \quad (\text{S3})$$

Calculation of the reduction potential of protonated phenol form ($E_{\text{red},1}^0(\text{PhOH}^{+}/\text{PhOH}^-)$)

$$E_{\text{red},1}^0(\text{PhOH}^{+}/\text{PhOH}^-) = E_{\text{red},1}^0(\text{PhO}^+/\text{PhO}^-) + 2.303RT ((\text{p}K_a(\text{PhOH}^-) - \text{p}K_a(\text{PhOH}^{+})) / F) \quad (\text{S4})$$

Table S3a. Selected chemical properties of target compounds. (1)

Compound	Structure	$E_{\text{red},1}^0$ ($\text{PhO}^+/\text{PhO}^-$) /V vs SHE	$E_{\text{red},1}^0$ ($\text{PhOH}^{+}/\text{PhOH}^-$) /V vs SHE	$\text{p}K_a$ (PhOH)	$\text{p}K_a$ (PhOH^{+})	f_{PhO^-} (%) ^a
2,4,6-trimethylphenol (TMP)		0.49 ^b	1.22 ^c	10.9 ^d	-1.5 ^c	0
3,4-dimethoxyphenol (DMOP)		0.50 ^e	1.17 ^c	9.9 ^c	-1.5 ^c	1

^a(calculations based on eq. S1) ^b(Jonsson et al. 1993b) ^c(Canonica et al. 2000) ^d(Dean 1999)

^e(Jovanovic et al. 1991)

Table S3b. Selected chemical properties of target compounds. (2)

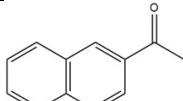
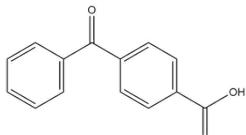
Compound	Structure	$E_{\text{red},1}^0$ (PhNH [•] / PhNH ⁻) /V vs SHE	$E_{\text{red},1}^0$ (PhNH ₂ ^{•+} /PhN H ₂) /V vs SHE	pK _a (PhNH ₂)
Aniline (A)		n. a.	1.02 ^a	4.6 ^b
4-methylaniline (MA)		n. a.	0.92 ^a	5.1 ^b

^a(Jonsson et al. 1994) ^b(Dean 1999)**Table S3c. Selected chemical properties of electron-poor phenols.**

Compound	Structure	$E_{\text{red},1}^0$ (PhO [•] / PhO ⁻) /V vs SHE	$E_{\text{red},1}^0$ ^a (PhOH ^{•+} / PhOH ⁻) /V vs SHE	pK _a (PhOH) ^b	pK _a (PhOH ^{•+})	f_{PhO^-} ^a (%)
2,6-dichlorophenol		0.85 ^c	1.37	6.8	-2.0 ^d	94
4-hydroxybenzoic acid		0.90 ^c	1.56	4.6 (1) 9.2 (2)	-2.0 ^d	6
4-hydroxyacetophenone		1.00 ^c	1.59	8.1	-1.86 ^f	44
3,5-dichlorophenol		1.06 ^c	1.66	8.2	-2.0 ^d	39
4-cyanophenol (4-CN- PhOH/CNP)		1.12 ^c	1.71	8.0	-2.0 ^d	50

^a(calculations based on eq. S1,2) ^b(Dean 1999) ^c(calculated based on (Jonsson et al. 1993a) with $\sigma_m^+(Cl)=0.40$, $\sigma_o^+(Cl)=0.07$, $\sigma_p^+(Cl)=0.11$ (Dean 1999)) ^d(estimations based on structurally similar phenols in (Holton and Murphy 1979)) ^e(Lind et al. 1990) ^f(Holton and Murphy 1979)

Table S3d. Selected chemical properties of photosensitizers.

Compound	Structure	$E_{\text{red},1}^0$ /V vs SHE	Triplet State Energy, $E_{0,0}$ /eV	Triplet state reduction potential, E_{red}^* /V vs SHE
2-acetonaphthone (2-AN)		-1.48 ^a	2.58 ^b	1.1 ^c /1.34 ^d
4-carboxybenzophenone (CBBP)		-1.13 ^e	286 kJ mol ⁻¹ ^e	1.84 ^f

^a(Barwise et al. 1978) ^b(Murov et al. 1993) ^c(Canonica et al. 2000) ^d(Loeff et al. 1993) ^e(Hurley et al. 1988) ^f(McNeill and Canonica 2016)

Table S4a. Rate constants, k^{obs} , for the transformation of target compounds, TC (initial concentration 0.1 or 5.0 μM) in a model system with 2-acetonaphthone (1.5 μM) and electron poor phenol ($\text{R-PhOH}_{\text{ep}}$, 5 μM) at pH 8.

TC	R-PhOH _{ep} ^a	$k_{0.1}^{\text{obs}}$ ^b / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{0.1,\text{control}}^{\text{obs}}$ ^c / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ [*] / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{5.0}^{\text{obs}}$ / s^{-1} ([TC] ₀ = 5 μM)	$k_{5.0,\text{control}}^{\text{obs}}$ ^c / s^{-1} ([TC] ₀ = 5 μM)
TMP	-	$(1.5 \pm 0.2) \times 10^{-4}$	No TC transformed		$k_{5.0,\text{Sens}}^{\text{obs}} = (2.107 \pm 0.001) \times 10^{-4}$	$(3.9 \pm 0.1) \times 10^{-6}$
	2.6Cl2P	$(1.40 \pm 0.02) \times 10^{-3}$	No TC transformed	$(1.19 \pm 0.02) \times 10^{-3}$	$(3.1 \pm 0.5) \times 10^{-4}$	No TC transformed
	Hba	$(9 \pm 1) \times 10^{-4}$	$(7.6 \pm 0.8) \times 10^{-5}$	$(6 \pm 1) \times 10^{-4}$	$(2.7 \pm 0.5) \times 10^{-4}$	No TC transformed
	AcP	$(5.2 \pm 0.2) \times 10^{-3}$	$(9 \pm 1) \times 10^{-5}$	$(4.9 \pm 0.2) \times 10^{-3}$	$(4.2 \pm 0.1) \times 10^{-4}$	$(2.571 \pm 0.005) \times 10^{-5}$
	3.5Cl2P	$(6.9 \pm 0.4) \times 10^{-3}$	$(9.2 \pm 0.2) \times 10^{-5}$	$(6.6 \pm 0.4) \times 10^{-3}$	$(4.16 \pm 0.09) \times 10^{-4}$	No TC transformed
	CNP	$(9.5 \pm 0.2) \times 10^{-3}$	$(9 \pm 2) \times 10^{-5}$	$(9.2 \pm 0.2) \times 10^{-3}$	$(4.4 \pm 0.1) \times 10^{-4}$	$(6.0 \pm 0.5) \times 10^{-6}$
	Average				$(3.4 \pm 0.9) \times 10^{-4}$	
DMOP	-	$(3 \pm 1) \times 10^{-3}$	$(2 \pm 1) \times 10^{-4}$		$k_{5.0,\text{Sens}}^{\text{obs}} = (9.0 \pm 0.2) \times 10^{-4}$	No TC transformed
	2.6Cl2P	$(1.6 \pm 0.6) \times 10^{-2}$	No TC transformed	$(1.6 \pm 0.6) \times 10^{-2}$	$(1.06 \pm 0.02) \times 10^{-3}$	No TC transformed
	Hba	$(2.7 \pm 0.7) \times 10^{-3}$	$(5.9 \pm 0.5) \times 10^{-4}$	$(1.2 \pm 0.7) \times 10^{-3}$	$(8.7 \pm 0.6) \times 10^{-4}$	No TC tranformed
	AcP	$(2.8 \pm 0.4) \times 10^{-2}$	$(1.8 \pm 0.1) \times 10^{-3}$	$(2.5 \pm 0.4) \times 10^{-2}$	$(8.69 \pm 0.02) \times 10^{-4}$	$(2.7 \pm 0.4) \times 10^{-5}$
	3.5Cl2P	$(2.4 \pm 0.2) \times 10^{-2}$	$(2.1 \pm 0.2) \times 10^{-4}$	$(2.3 \pm 0.2) \times 10^{-2}$	$(8.8 \pm 0.2) \times 10^{-4}$	No TC transformed
	CNP	$(2.3 \pm 0.4) \times 10^{-2}$	$(6 \pm 1) \times 10^{-4}$	$(2.2 \pm 0.4) \times 10^{-2}$	$(9.71 \pm 0.02) \times 10^{-4}$	No TC transformed
	Average				$(9.3 \pm 0.7) \times 10^{-4}$	
Aniline	-	$(1.0 \pm 0.2) \times 10^{-4}$	$(6 \pm 2) \times 10^{-6}$		$k_{5.0,\text{Sens}}^{\text{obs}} = (7.0 \pm 0.7) \times 10^{-4}$	$5.3 \pm 0.4 \times 10^{-4}$
	CNP	$(1.6 \pm 0.2) \times 10^{-3}$	No TC transformed		$(8.3 \pm 0.3) \times 10^{-4}$	$(5.4 \pm 0.4) \times 10^{-4}$
	Average				$(6.7 \pm 0.1) \times 10^{-4}$	

^a In the Tables 4a-4g the following abbreviations are employed: 2,6Cl2P is 2,6-dichlorophenol, Hba is 4-hydroxybenzoic acid, AcP is 4-hydroxyacetophenone, 3,5Cl2P is 3,5-dichlorophenol, CNP is 4-cyanophenol.

^b In the Tables 4a-4g the following descriptors for rate constants are employed: $k_{0.1}^{\text{obs}}$ and $k_{5.0}^{\text{obs}}$ are the pseudo-first-order transformation rate constants of DMOP, in aqueous solution with 2-acetonaphthone (1.5 μM) and electron poor phenol ($\text{R-PhOH}_{\text{ep}}$, 5 μM), with $[\text{DMOP}]_0=0.1 \mu\text{M}$ and $[\text{DMOP}]_0=5.0 \mu\text{M}$, respectively; $k_{0.1,\text{control}}^{\text{obs}}*$ and $k_{5.0,\text{control}}^{\text{obs}}$ are the pseudo-first-order transformation rate constant of DMOP in aqueous solution of electron poor phenol ($\text{R-PhOH}_{\text{ep}}$, 5 μM); $k_{5.0,\text{Sens}}^{\text{obs}}$ is $k_{5.0}^{\text{obs}}$ without added phenol; $k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}} = k_{0.1}^{\text{obs}} - k_{0.1,\text{control}}^{\text{obs}} + k_{5.0,\text{Sens}}^{\text{obs}}$

^cwithout Sensitizer

Table S4b. Rate constants, k^{obs} , for the transformation of DMOP (initial concentration 0.1 or 5.0 μM) in a model system with CBBP (0.5 μM) and electron poor phenol ($\text{R-PhOH}_{\text{ep}}$, 5 μM) at pH 8. Abbreviations and descriptors for rate constants are as in Table S4a.

TC	R-PhOH _{ep}	$k_{0,1}^{\text{obs}}$ / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{0,1, \text{control}}^{\text{obs}}$ / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ / s^{-1} ([TC] ₀ = 0.1 μM)	$k_{5,0}^{\text{obs}}$ / s^{-1} ([TC] ₀ = 5 μM)	$k_{5,0, \text{control}}^{\text{obs}}$ / s^{-1} ([TC] ₀ = 5 μM)
DMOP	-	$(1.2 \pm 0.4) \times 10^{-4}$	$(2 \pm 1) \times 10^{-4}$		$(6 \pm 1) \times 10^{-5}$	No TC transformed
	2.6Cl2P	$(1.1 \pm 0.2) \times 10^{-3}$	No TC transformed	$(1.1 \pm 0.2) \times 10^{-3}$	$(1 \pm 0.2) \times 10^{-4}$	No TC transformed
	Hba	$(1.67 \pm 0.05) \times 10^{-3}$	$(5.9 \pm 0.5) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-3}$	$(6.6 \pm 0.8) \times 10^{-5}$	No TC tranformed
	AcP	$(6.0 \pm 0.3) \times 10^{-3}$	$(1.8 \pm 0.1) \times 10^{-3}$	$(4.1 \pm 0.4) \times 10^{-3}$	$(8.1 \pm 0.8) \times 10^{-5}$	$(2.7 \pm 0.4) \times 10^{-5}$
	3.5Cl2P	$(4.3 \pm 0.5) \times 10^{-3}$	$(2.1 \pm 0.2) \times 10^{-4}$	$(4.0 \pm 0.6) \times 10^{-3}$	$(9.9 \pm 0.7) \times 10^{-5}$	No TC transformed
	CNP	$(6.5 \pm 0.6) \times 10^{-3}$	$(6 \pm 1) \times 10^{-4}$	$(5.9 \pm 0.7) \times 10^{-3}$	$(3 \pm 2) \times 10^{-5}$	No TC transformed
	Average				$(1.2 \pm 0.5) \times 10^{-5}$	

*without Sensitizer, values are the same as in Table S3a.

Table S4c. Ratios of rate constants, $k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$, for the transformation of DMOP and TMP (initial concentration 0.1 μM) in a model system with CBBP (0.5 μM) or 2-AN (1.5 μM) and electron-poor phenol ($\text{R-PhOH}_{\text{ep}}$, 5 μM) at pH 8. Abbreviations and descriptors for rate constants are as in Table S4a.

R-PhOH _{ep}	$(k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}} \cdot (\text{Sens} = 2\text{-AN}) / k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}} \cdot (\text{Sens} = \text{CBBP}))$	$(k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}} \cdot (\text{TC} = \text{DMOP}) / k_{\text{R-PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}} \cdot (\text{TC} = \text{TMP}))$
2.6Cl2P	15 ± 8	13 ± 5
Hba	1 ± 1	2 ± 2
AcP	6 ± 2	5 ± 1
3.5Cl2P	6 ± 1	3.5 ± 0.6
CNP	4 ± 1	2.4 ± 0.5

Table S4d. Rate constants, k^{obs} , for the transformation of target compounds, TC (initial concentration range from 0.1 to 5.0 μM) in a model system with 2-acetonaphthone (1.5 μM) and electron poor phenol (4-cyanophenol, 5 μM) at pH 8. Abbreviations and descriptors for rate constants are as in Table S4a.

TC	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{TC}]_0 = 0.1 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{TC}]_0 = 0.25 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{TC}]_0 = 0.5 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{TC}]_0 = 1 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN,CNP})$ / s^{-1} ($[\text{TC}]_0 = 2.5 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN,CNP})$ / s^{-1} ($[\text{TC}]_0 = 5 \mu\text{M}$)
TMP	$(9.5 \pm 0.2) \times 10^{-3}$	$(4.932 \pm 0.008) \times 10^{-3}$	$(2.53 \pm 0.06) \times 10^{-3}$	$(1.02 \pm 0.07) \times 10^{-3}$	$(4.9 \pm 0.5) \times 10^{-4}$	$(4.4 \pm 0.1) \times 10^{-4}$
DMOP*	$(2.3 \pm 0.4) \times 10^{-2}$	$(4.4 \pm 0.3) \times 10^{-3}$	$(3.2 \pm 0.2) \times 10^{-3}$	$(1.4 \pm 0.2) \times 10^{-3}$	$(1.0 \pm 0.3) \times 10^{-3}$	$(9.71 \pm 0.02) \times 10^{-4}$
Aniline	$(1.6 \pm 0.2) \times 10^{-3}$	$(1.3 \pm 0.3) \times 10^{-3}$	$(1.04 \pm 0.09) \times 10^{-3}$	$(8.4 \pm 0.2) \times 10^{-4}$	$(7.6 \pm 0.3) \times 10^{-4}$	$(6.75 \pm 0.03) \times 10^{-4}$

*already published in (Remke et al. 2021)

Table S4e. Rate constants, k^{obs} , for the transformation of target compounds, TC (initial concentration range 0.1 or 5.0 μM) in a model system with 2-acetonaphthone (0.5 μM) and electron poor phenol (4-cyanophenol, concentrations ranging from 1 to 10 μM) at pH 8. Abbreviations and descriptors for rate constants are as in Table S4a.

TC	[TC] ₀ / μM	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{CNP}] = 0 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{CNP}] = 2.5 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{CNP}] = 5 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} ($[\text{CNP}] = 10 \mu\text{M}$)	$k^{\text{obs}}(2\text{-AN, CNP})$ / s^{-1} Average ($[\text{CNP}] = 0\text{-}10 \mu\text{M}$)
DMOP	5	$(3.125 \pm 0.004) \times 10^{-4}$	$(3.1 \pm 0.2) \times 10^{-4}$	$(3.10 \pm 0.02) \times 10^{-4}$	$(2.98 \pm 0.03) \times 10^{-4}$	$(3.06 \pm 0.05) \times 10^{-4}$
	0.1	$(5.6 \pm 0.4) \times 10^{-4}$	$(1.37 \pm 0.03) \times 10^{-3}$	$(3.45 \pm 0.06) \times 10^{-3}$	$(8 \pm 1) \times 10^{-3}$	
MA	5	$(3.285 \pm 0.006) \times 10^{-4}$	$(3.0 \pm 0.1) \times 10^{-4}$	$(3.2 \pm 0.2) \times 10^{-4}$	$(3.57 \pm 0.06) \times 10^{-4}$	$(3.3 \pm 0.2) \times 10^{-4}$
	0.1	$(7.4 \pm 0.9) \times 10^{-5}$	$(3.6 \pm 0.2) \times 10^{-4}$	$(6.2 \pm 0.2) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-4}$	

Table S4f. Fitting results for the linear correlations shown in the main paper in Fig. 4.:
(a) for $k_{R-\text{PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ • (TC = DMOP, Sens= 2-AN) and $E_{\text{red},1}^0$; (b) for $k_{R-\text{PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ • (Sens = 2-AN)/ $k_{R-\text{PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ • (Sens = CBBP) and $f_{\text{PhO}^{\bullet}}$ and $E_{\text{red},1}^0$ and (c) $k_{R-\text{PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ • (TC = DMOP)/ $k_{R-\text{PhO}_{\text{ep}}^{\bullet}}^{\text{obs,c}}$ • (TC = TMP)) and $E_{\text{red},1}^0$. Descriptors for rate constants are as in Table S4a.

Linear Regression, details	(a)	(b)	(c)*
Equation	$y = a + bx$	$y = a + bx$	$y = a + bx$
Intercept	-0.0149 ± 0.003	-1 ± 2	47 ± 6
Slope	0.0184 ± 0.003	0.15 ± 0.03	-41 ± 6
Residual sum of squares	1.24×10^{-6}	12.64	2.89
Pearson's r	0.97	0.94	-0.98
R-Square (COD)	0.93	0.88	0.96
Adj. R-Square	0.91	0.84	0.94

* without the data of 4-hydroxybenzoic acid

Table S4g. Pseudo-first-order rate constants, k^{obs} , determined for the phototransformation of target compounds, TC (initial concentration: 0.1 or 5.0 μM) in aqueous solutions (pH 8.0) containing 2-acetonaphthone (1.5 μM) and 4-cyanophenol (CNP, concentrations ranging from 0 to 10 μM).

TC	[TC] ₀ / μM	$k^{\text{obs}} / \text{s}^{-1}$ blank (without 2-acetonaphthone)	$k^{\text{obs}} / \text{s}^{-1}$ ([CNP] = 0 μM)	$k^{\text{obs}} / \text{s}^{-1}$ ([CNP] = 1 μM)	$k^{\text{obs}} / \text{s}^{-1}$ ([CNP] = 2.5 μM)	$k^{\text{obs}} / \text{s}^{-1}$ ([CNP] = 5 μM)	$k^{\text{obs}} / \text{s}^{-1}$ ([CNP] = 10 μM)	$k^{\text{obs}} / \text{s}^{-1}$ Average ([CNP] = 0-10 μM)
TMP	5	$(3.9 \pm 0.1) \times 10^{-6}$	$(2.107 \pm 0.001) \times 10^{-4}$	$(1.839 \pm 0.008) \times 10^{-4}$	$(2.36 \pm 0.09) \times 10^{-4}$	$(4.4 \pm 0.1) \times 10^{-4}$	$(7.5 \pm 0.08) \times 10^{-4}$	$(4 \pm 2) \times 10^{-4}$
	0.1	$< 1 \times 10^{-5}$	$(1.5 \pm 0.2) \times 10^{-4}$	$(1.7 \pm 0.1) \times 10^{-3}$	$(4.0 \pm 0.4) \times 10^{-3}$	$(9.5 \pm 0.2) \times 10^{-3}$	$(2.4 \pm 0.4) \times 10^{-2}$	
DMOP	5	$< 1 \times 10^{-5}$	$(9.1 \pm 0.2) \times 10^{-4}$	/	$(8.7 \pm 0.1) \times 10^{-4}$	$(9.71 \pm 0.02) \times 10^{-4}$	$(1.04 \pm 0.03) \times 10^{-3}$	$(9.5 \pm 0.6) \times 10^{-4}$
	0.1	$(2 \pm 1) \times 10^{-4}$	$(1.8 \pm 0.1) \times 10^{-3}$	/	$(6.4 \pm 0.7) \times 10^{-3}$	$(2.3 \pm 0.4) \times 10^{-2}$	$(4.13 \pm 0.05) \times 10^{-2}$	
Aniline	5	$(9 \pm 2) \times 10^{-5}$	$(7.0 \pm 0.7) \times 10^{-4}$	$(6.6 \pm 0.5) \times 10^{-4}$	$(6.92 \pm 0.08) \times 10^{-4}$	$(8.3 \pm 0.3) \times 10^{-4}$	$(6.75 \pm 0.04) \times 10^{-4}$	$(7.1 \pm 0.6) \times 10^{-4}$
	0.1	$(6 \pm 2) \times 10^{-6}$	$(1.0 \pm 0.2) \times 10^{-4}$	$(4.7 \pm 0.1) \times 10^{-4}$	$(1.10 \pm 0.04) \times 10^{-3}$	$(1.6 \pm 0.2) \times 10^{-3}$	$(2.60 \pm 0.01) \times 10^{-3}$	

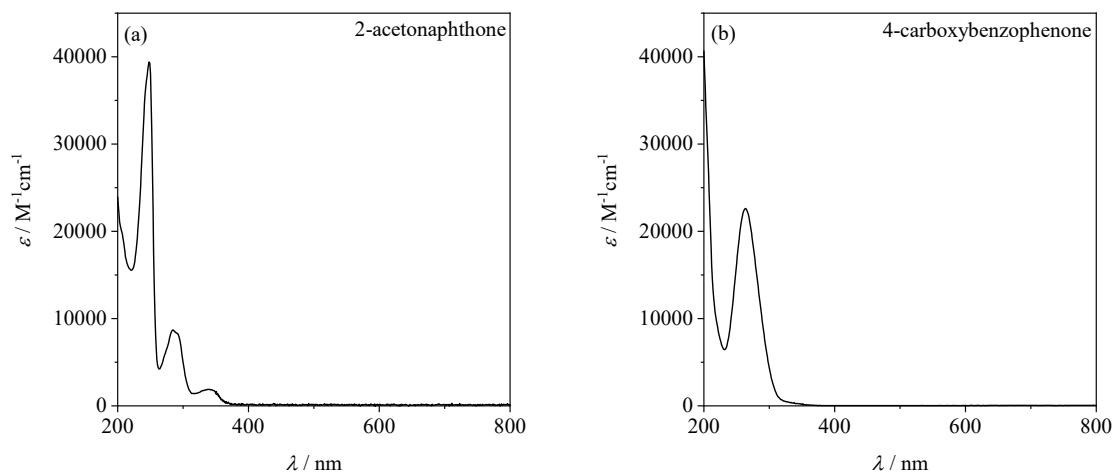


Fig. S1: UV-visible absorption spectra of the selected photosensitizers, represented by molar absorption coefficients ε for (a) 2-acetonaphthone and (b) 4-carboxybenzophenone.

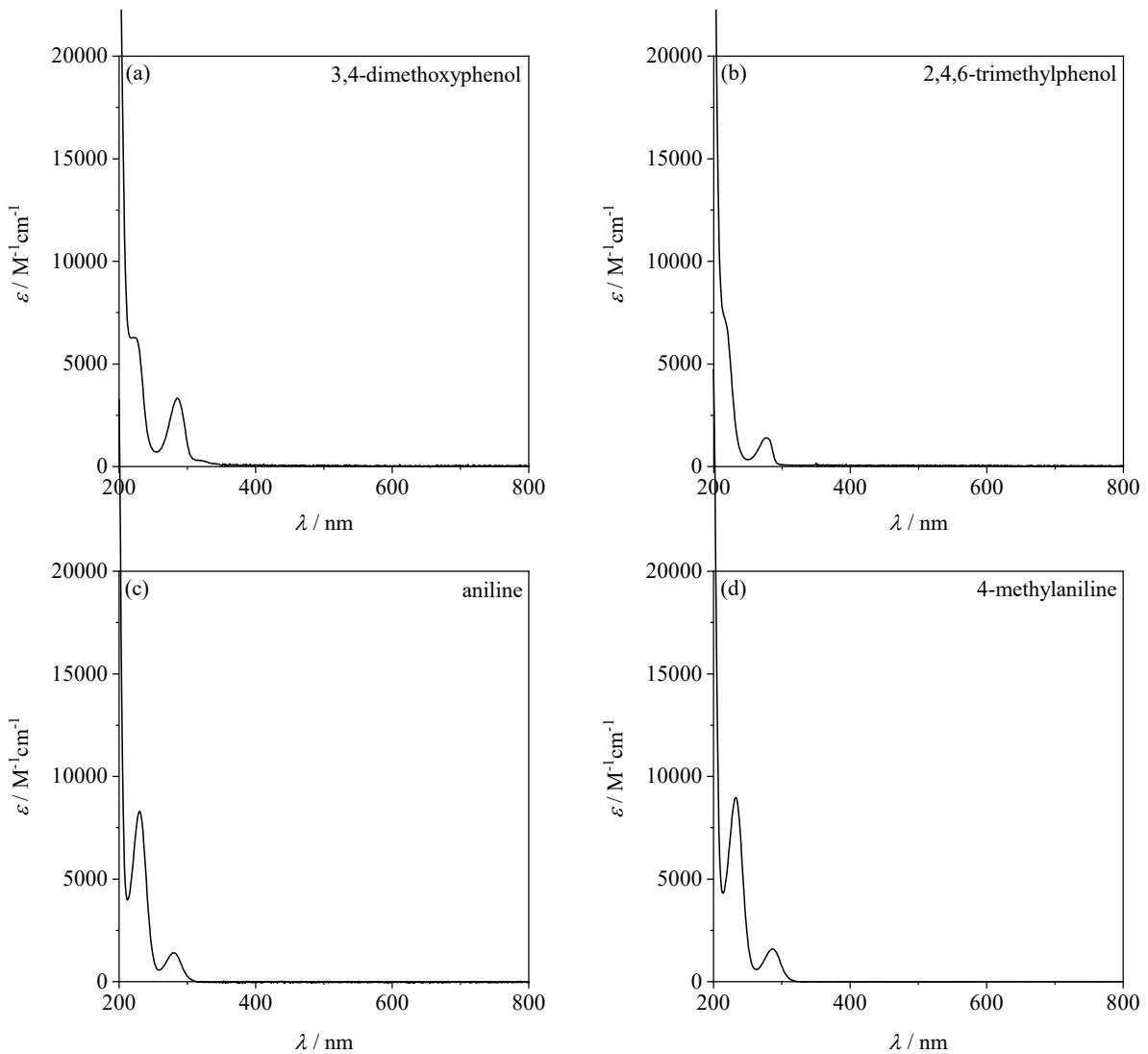


Fig. S2: UV-visible absorption spectra of the selected probe compounds, represented by molar absorption coefficients. (a) 3,4-dimethoxyphenol, (b) 2,4,6-trimethylphenol, (c) aniline, (d) 4-methylaniline.

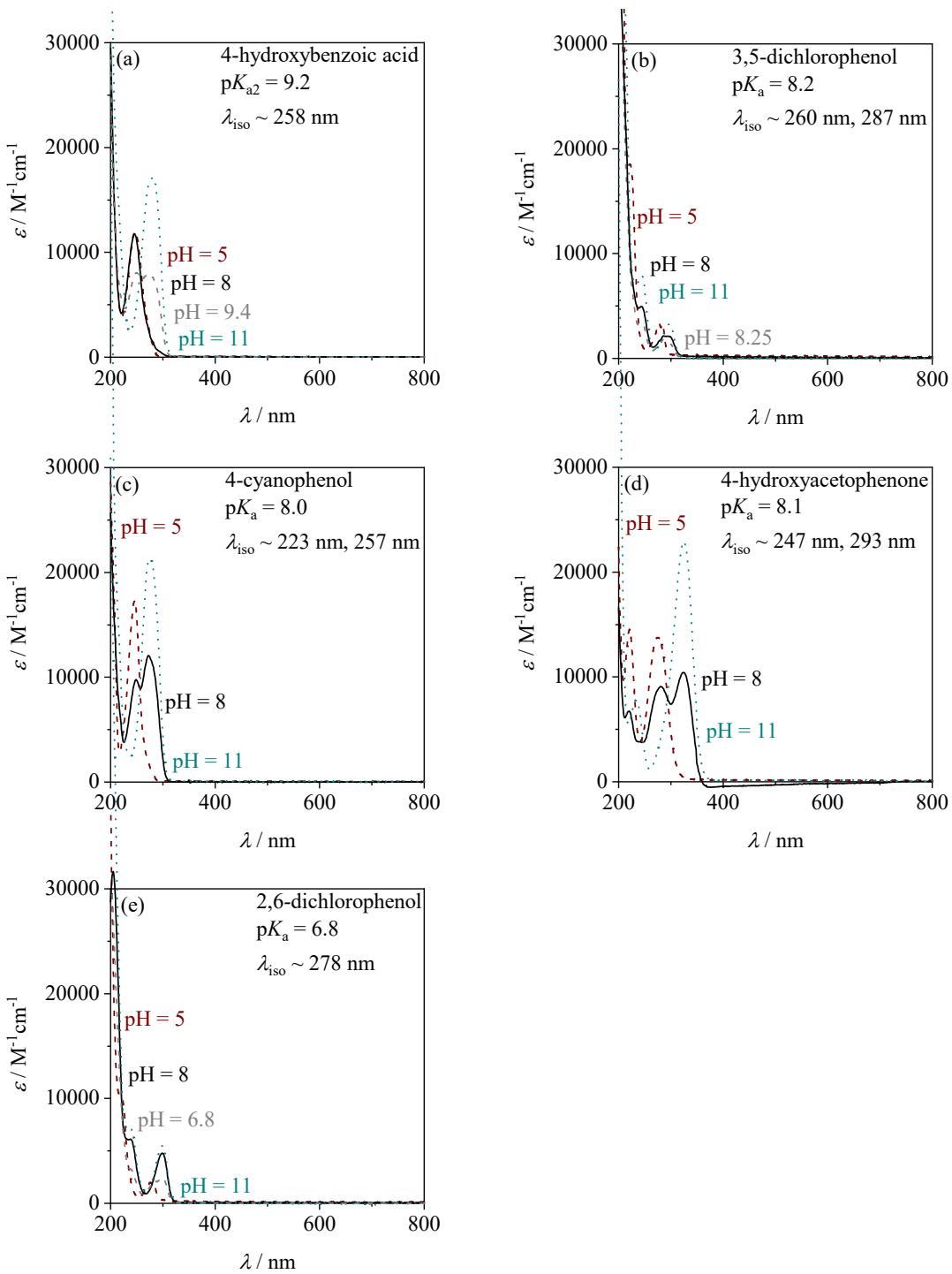


Fig. S3: UV-visible absorption spectra of the selected electron-poor phenols at various pH values, represented by molar absorption coefficients. (a) 4-hydroxybenzoic acid, (b) 3,5-dichlorophenol, (c) 4-cyanophenol, (d) 4-hydroxyacetophenone, (e) 2,6-dichlorophenol. The wavelengths of isosbestic points are indicated as λ_{iso} .

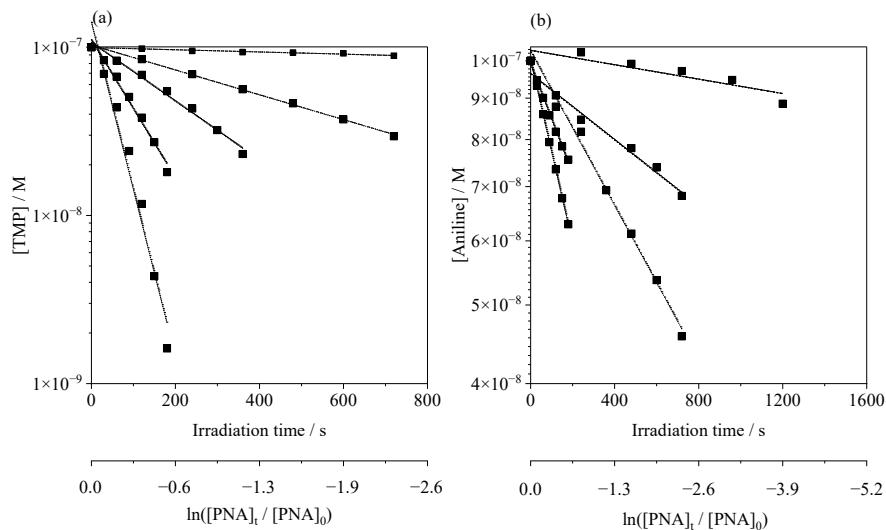


Fig. S4: Phototransformation kinetics of (a) 2,4,6-trimethylphenol (TMP, $[TMP]_0=0.1 \mu\text{M}$) and (b) aniline ($[aniline]_0=0.1 \mu\text{M}$) in aqueous solutions of 2-acetonaphthone ($1.5 \mu\text{M}$) buffered at pH 8 and containing various concentrations of 4-cyanophenol (0-10 μM). Results of duplicate measurements and linear fits of the logarithmic concentration data versus irradiation time are shown. Secondary x-axis is an additional time indicator provided as the decay of *p*-nitroanisole in the *p*-nitroanisole/pyridine actinometer within the given irradiation time.

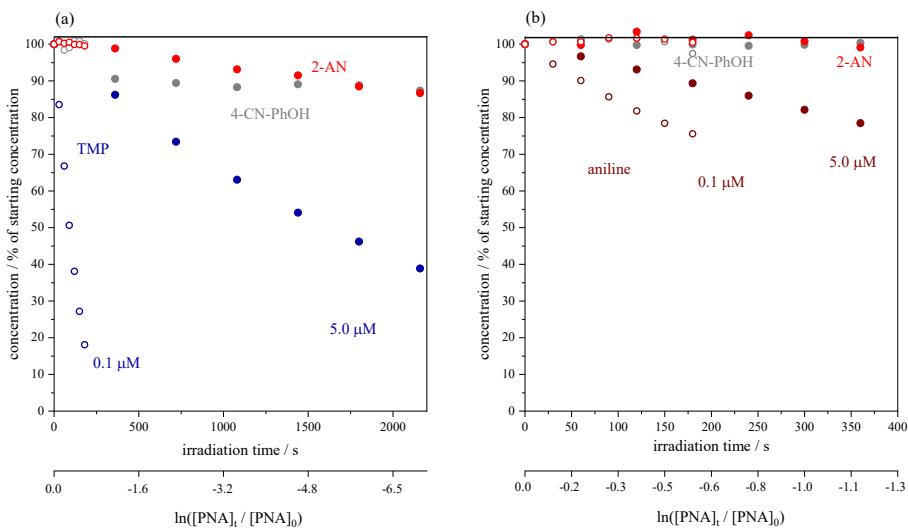


Fig. S5: Phototransformation kinetics of (a) 2,4,6-trimethylphenol (TMP, $[TMP]_0=0.1 \mu\text{M}$) and (b) aniline ($[aniline]_0=0.1 \mu\text{M}$) in aqueous solutions of 2-acetonaphthone ($1.5 \mu\text{M}$) and 4-cyanophenol ($5 \mu\text{M}$), buffered at pH 8. Results of duplicate measurements and linear fits of the logarithmic concentration data versus irradiation time are shown. Secondary x-axis is an additional time indicator provided as the decay of *p*-nitroanisole in the *p*-nitroanisole/pyridine actinometer within the given irradiation time.

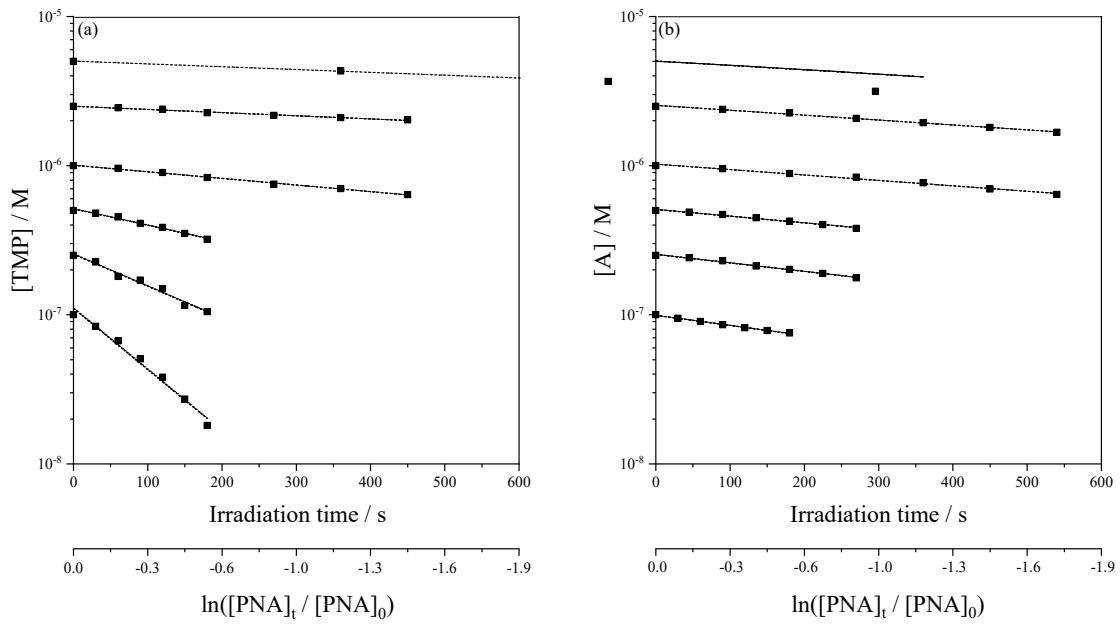


Fig. S6: Phototransformation kinetics of probe compounds employed at various initial concentrations (between 0.1 and 5 μM): (a) 2,4,6-trimethylphenol (TMP) and (b) aniline concentrations with irradiation time in aqueous solutions of 2-acetonaphthone (1.5 μM) and 4-cyanophenol (5 μM), buffered at pH 8. Results of duplicate measurements and linear fits of the concentration changes as a function of the irradiation time are shown. The secondary x-axis is an additional time indicator provided as the decay of *p*-nitroanisole in the *p*-nitroanisole/pyridine actinometer for the given irradiation time.

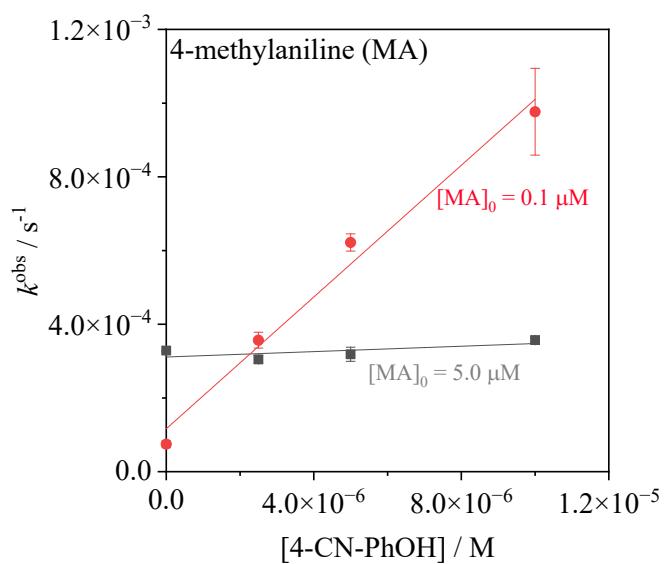


Fig. S7: Pseudo-first-order rate constants, k^{obs} , determined for the transformation of 4-methylaniline in irradiated aqueous solution buffered at pH 8 containing 2-acetonaphthone (0.5 μM) and for varying concentrations of 4-cyanophenol (0–10 μM). Error bars indicate mean deviations of duplicate measurements.

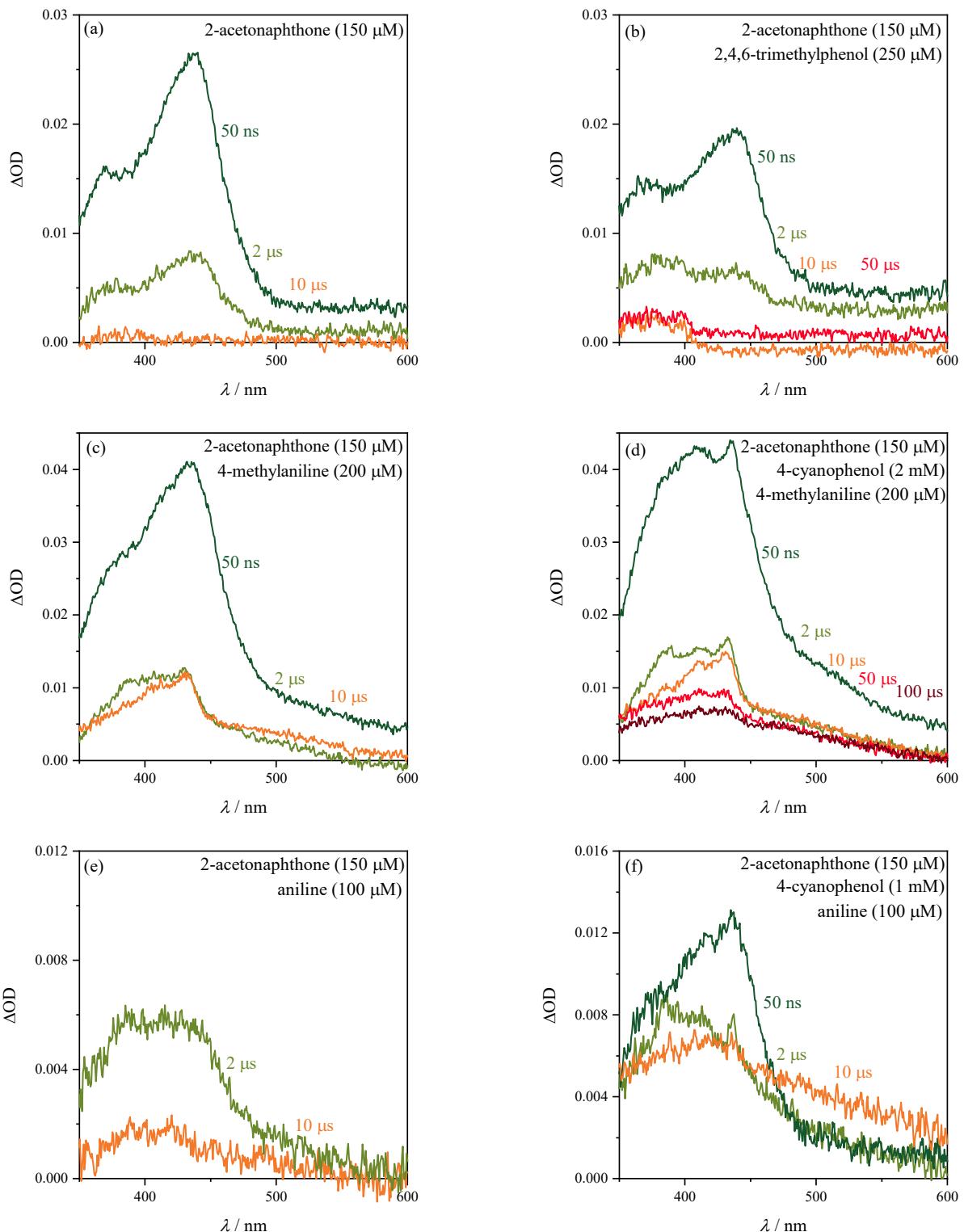


Fig. S8: Transient absorption spectra of various aqueous solutions obtained using LFP-1 (composition of samples and time delays after the laser pulse indicated in the graphs). Excitation wavelength was 355 nm. All solutions were buffered at pH 8.0 with 20 mM phosphate buffer.

Table S5: Compilation of the wavelength of absorption maxima and of measurement of the observed transients in the laser flash photolysis experiments with combinations of 2-acetonaphthone (2-AN), 4-cyanophenol (4-CN-PhOH), 2,4,6-trimethylphenol (TMP), aniline (A), 4-methylaniline (4-MA).

Transient	$\lambda_{\max}^{\text{Lit.}} / \text{nm}$		$\lambda_{\max}^{\text{obs}} / \text{nm}$	$\lambda_{\text{meas}} / \text{nm}$
			/ nm	/ nm
³ 2-AN*	440 (Bryce and Wells 1963, Canonica et al. 2000)		440 380	440/ 450
AN•-	440, <400 (Bryce and Wells 1963)		380	/
4-CN-PhO•	436 (Bronner and Wenger 2012, Lind et al. 1990)		436	436
TMP•	395 (Wenk et al. 2013)		395	/
MA•/	410 (Jonsson et al. 1994)		410	/
MA• ⁺	440 (Jonsson et al. 1994)			/
A•/	420 (Qin et al. 1985)		420	/
A•+	400 (Qin et al. 1985)			/
e ⁻ (hyd.)	600-700 (Hart and Boag 1962)		650	/
O ₂ ^{•-}	240		/	/

Text S5: Kintecus Simulations

The software Kintecus[©] (Ianni 2017) was employed to simulate the kinetic traces obtained by laser flash photolysis with the aim to verify the set of assumed reactions. To determine the second-order quenching rate constant of the 4-cyanophenoxy radical by TMP, samples consisting of aqueous solutions of 2-acetonaphthone, 4-cyanophenol and 2,4,6-trimethylphenol were analyzed. A system of equations was used to build a kinetic model (Table S6). The descriptor _{deact} indicates the deactivated form of transient species, e.g. the ground state or the transformation products of the respective transient. The reaction of oxygen with 2-AN^{•-} leading to O₂^{•-} was neglected, as O₂^{•-} is of minor importance for the transient species of interest.

Table S6: Overview of reactions and rate constants in the kinetic model. Initial concentrations used in the model were: [³2-AN*]₀ = 1.5 × 10⁻⁴ M, [4-CN-PhO^{•-}]₀ = 5 × 10⁻⁴ M, [TMP]₀ = 1 × 10⁻⁴ M.

Reaction	Rate constant	Notes and references
³ 2-AN* → 2-AN	$k_{^3\text{2-AN}^*}^{\text{d},0} = 6.4 \times 10^5 \text{ s}^{-1}$	(Canonica et al. 2000)
³ 2-AN* + 4-CN-PhO ^{•-} → 2-AN ^{•-} + 4-CN-PhO [•]	$k_{^3\text{2-AN}^*,\text{4-CN-PhO}^{\bullet-}}^{\text{q}} = 6.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	(extrapolated based on measurements in this study)
³ 2-AN* + TMP → 2-AN ^{•-} + TMP [•] + H ⁺	$k_{^3\text{2-AN}^*,\text{TMP}}^{\text{q}} = 7.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	(Canonica et al. 2000)
4-CN-PhO [•] + TMP → 4-CN-PhO ^{•-} + TMP [•] + H ⁺	$k_{^4\text{CN-PhO}^{\bullet},\text{TMP}}^{\text{q}} = 4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	(measured in this study, average value)
4-CN-PhO [•] → 4-CN-PhO [•] _{deact}	$k_{^4\text{CN-PhO}^{\bullet}}^{\text{d},0} = 2.2 \times 10^4 \text{ s}^{-1}$	(estimated based on measurements in this study)
TMP [•] → TMP [•] _{deact}	$k_{\text{TMP}^{\bullet}}^{\text{d},0} = 2.1 \times 10^4 \text{ s}^{-1}$	(estimated based on measurements in this study)

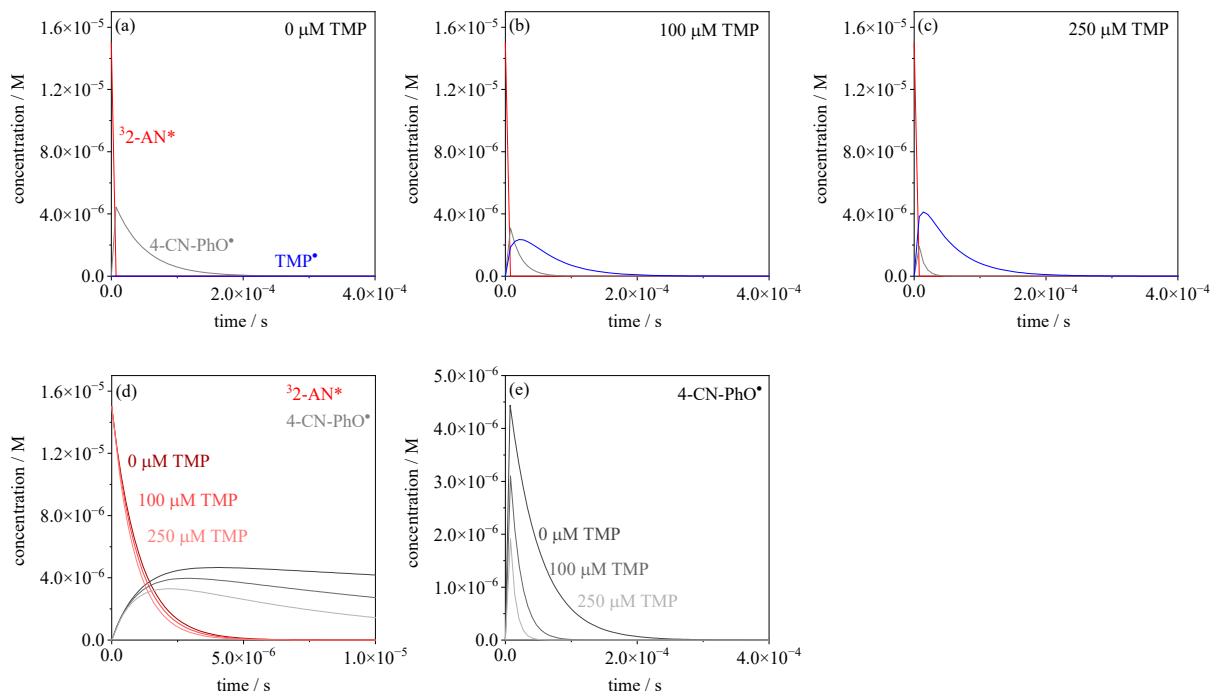


Fig. S9: Simulated concentration regime of transients in LFP measurements obtained by applying kinetic modeling using the Kintecus[©] software.

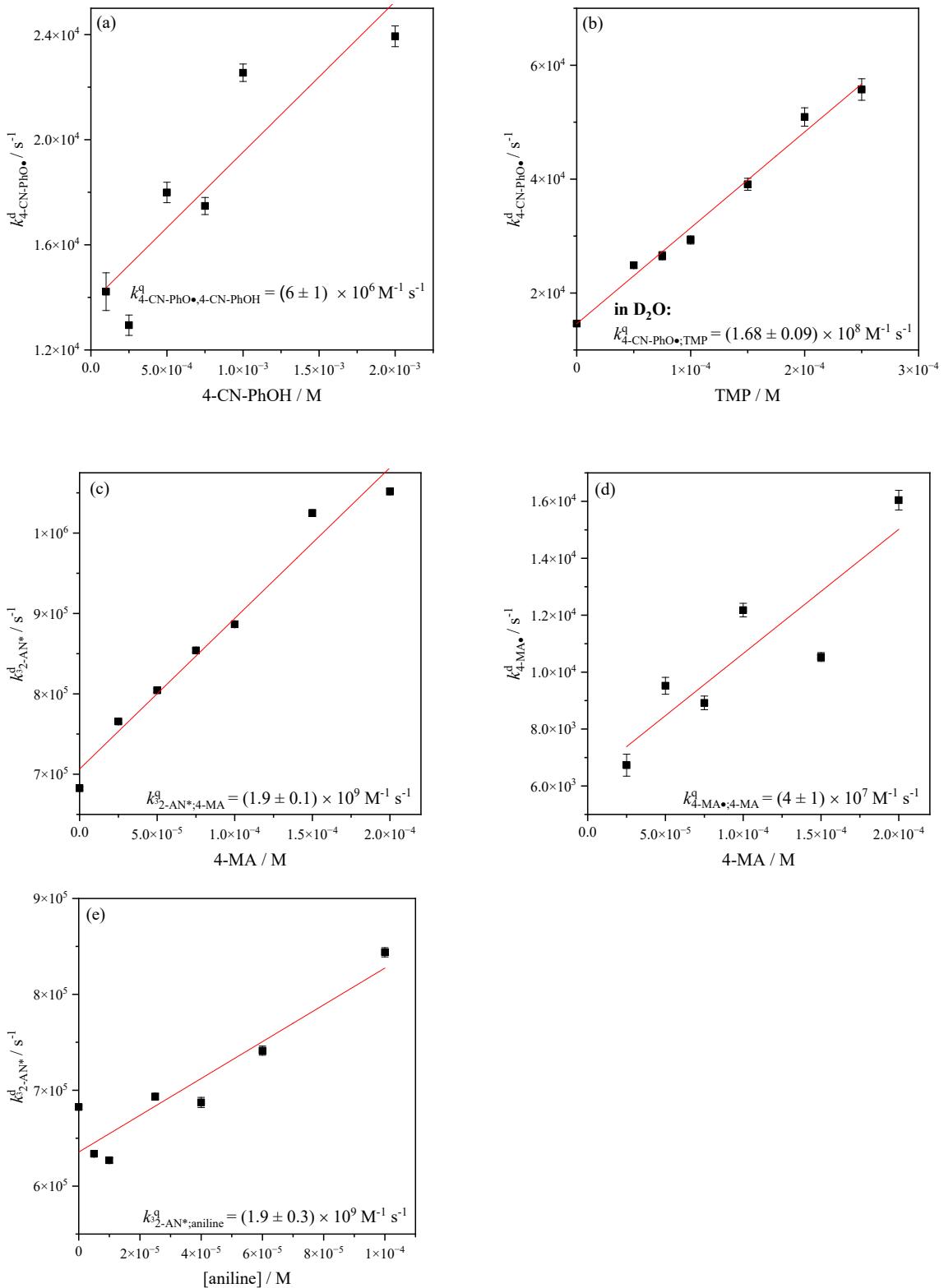


Fig. S10: Plots of determined first-order decay rate constants as functions of the quencher concentrations used to determine second-order quenching rate constants for the following reactive species–quencher pairs: (a) 4-CN-PhO \bullet with 4-cyanophenol, (b) 4-CN-PhO \bullet with 2,4,6-trimethylphenol in D₂O, (c) ³2-AN * with 4-methylaniline, (d) 4-methylaniline radical cation with 4-methylaniline, and (e) ³2-AN * with aniline.

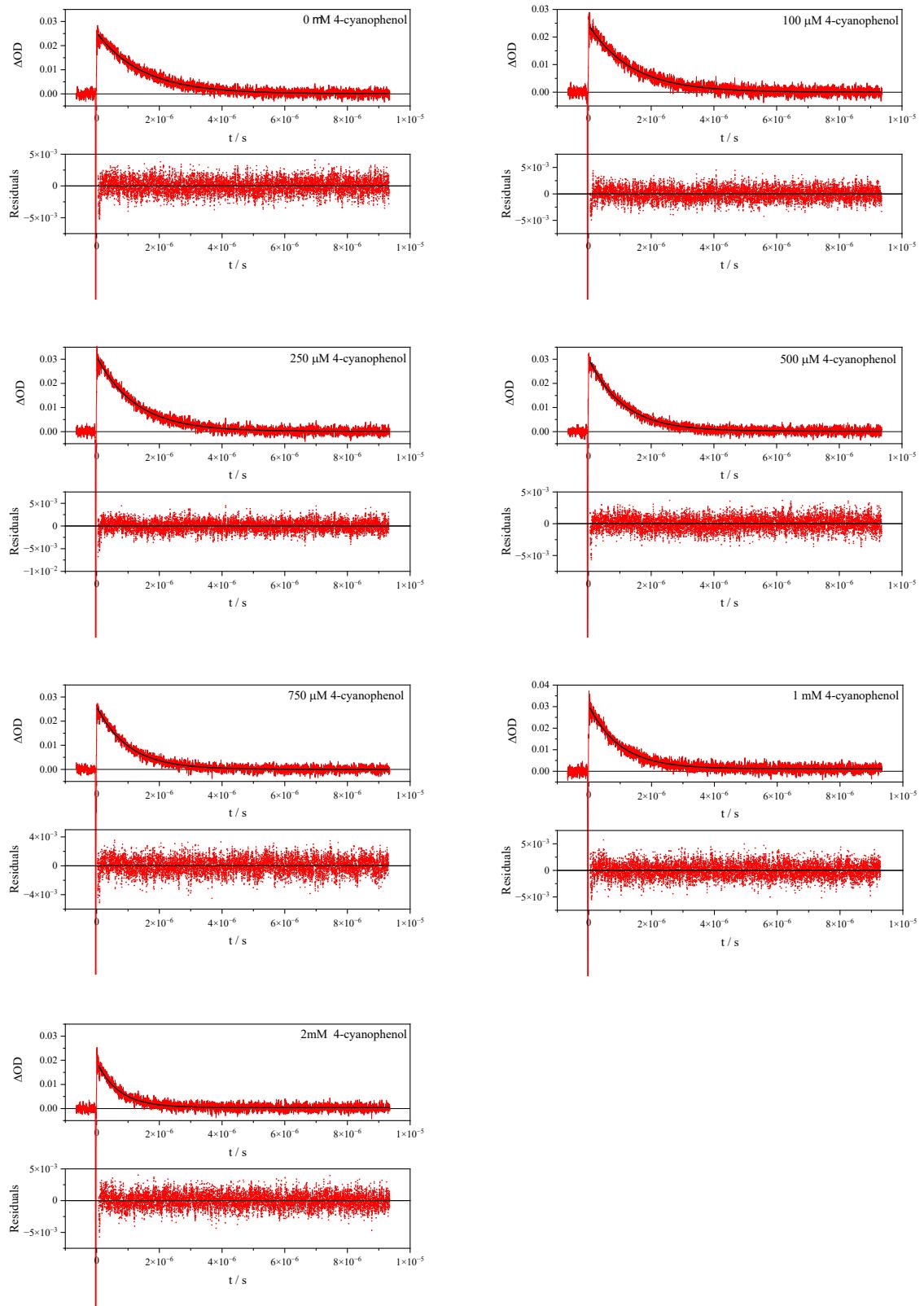


Fig. S11: Kinetic absorption traces at 450 nm of samples containing 2-acetonaphthone and varying amounts of 4-cyanophenol (0-2 mM, as indicated in the plots) with first-order fits, defining $k_{3_2-\text{AN}^*}^d$. Measurements performed with LFP-1.

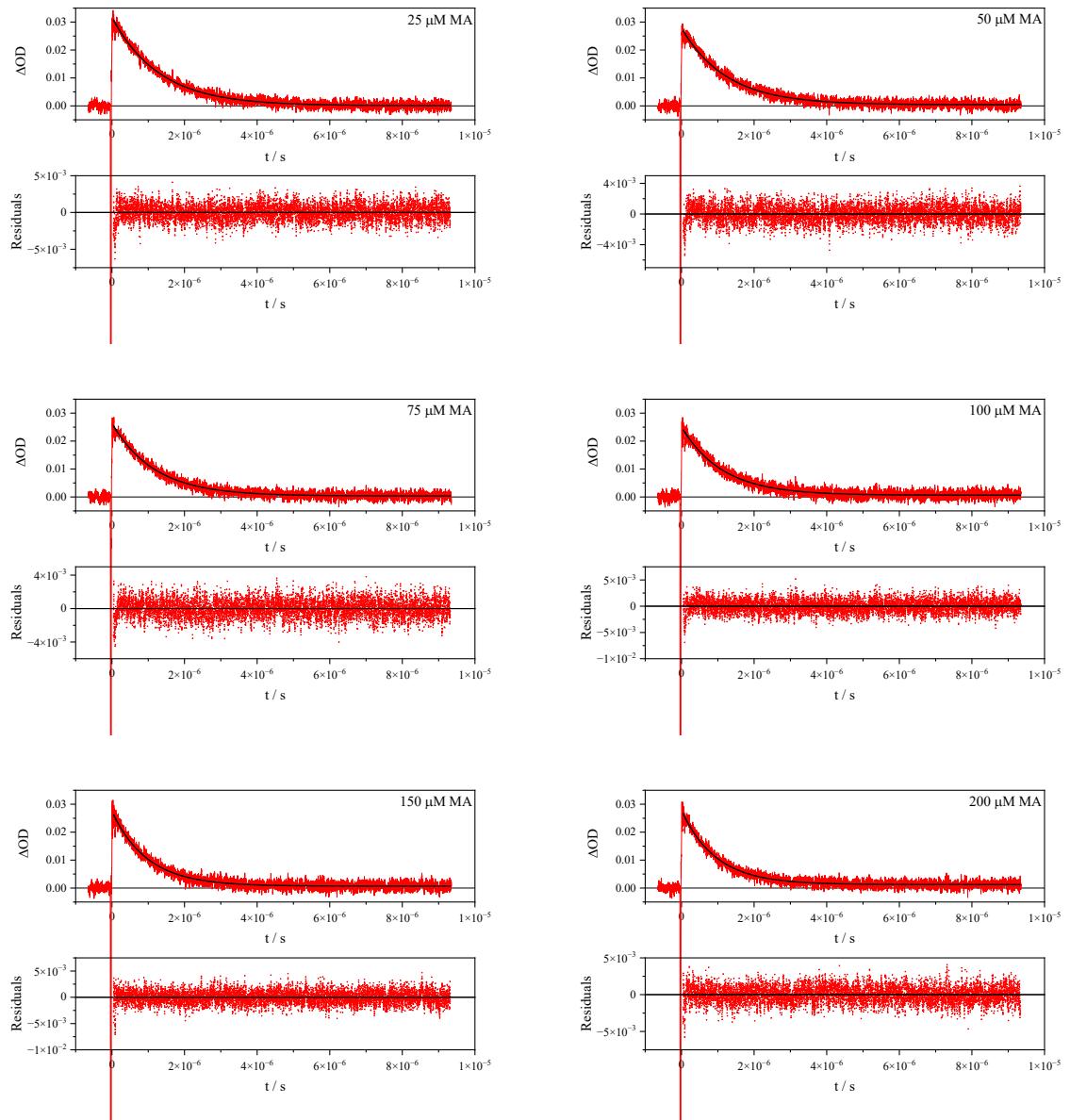


Fig. S12: Kinetic absorption traces at 450 nm of aqueous samples containing 2-acetonaphthone (150 μM) and varying amounts of 4-methylaniline (MA) with first-order fits, defining $k_{3_{2-\text{AN}^*}}^{\text{d}}$. Measurements performed with LFP-1.

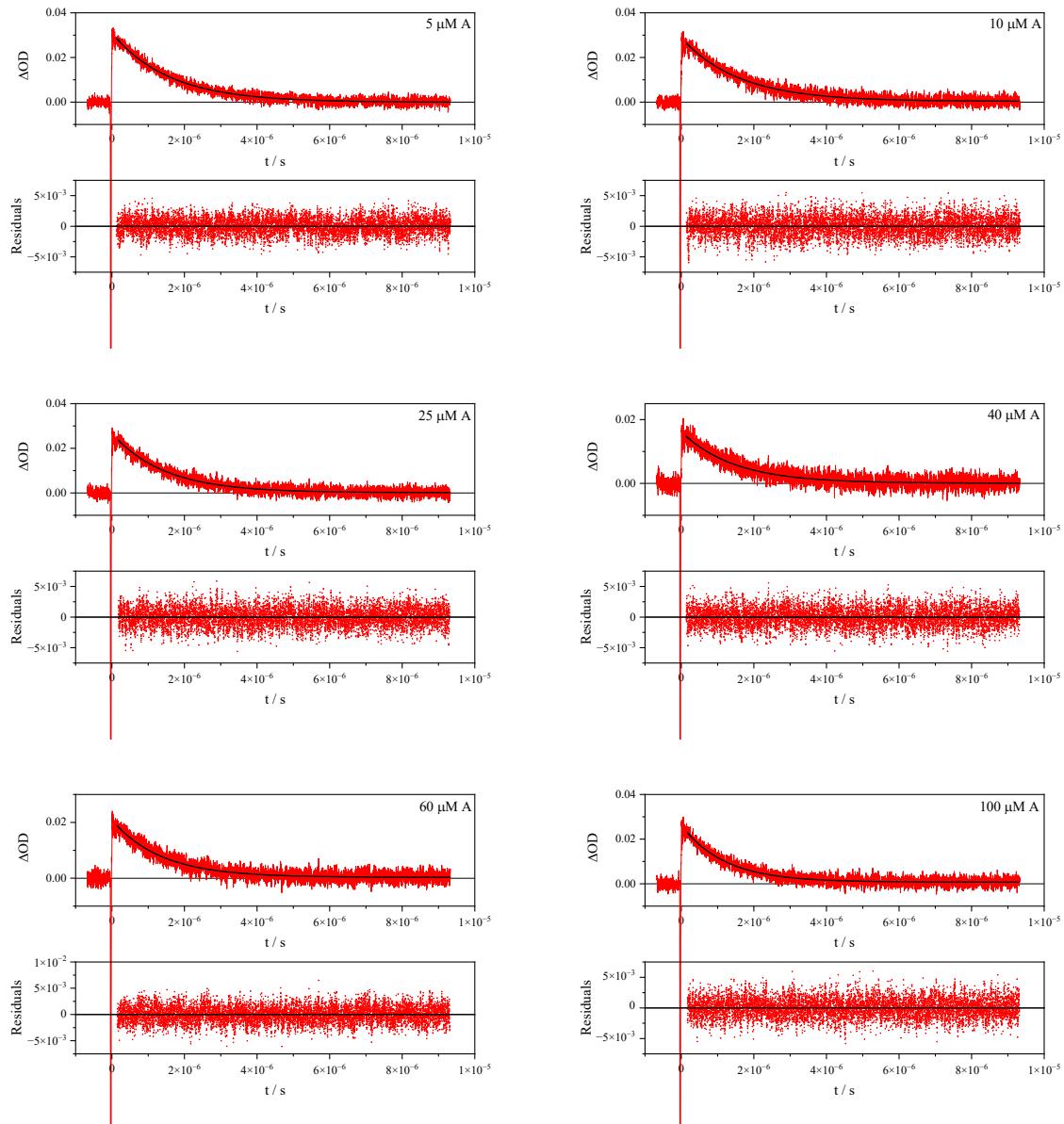


Fig. S13: Kinetic absorption traces at 440 nm of aqueous samples containing 2-acetonaphthone (150 mM) and varying amounts of aniline (A) with first-order fits used to determine $k_{3_{2-\text{AN}^*}}^d$. Measurements performed with LFP-1.

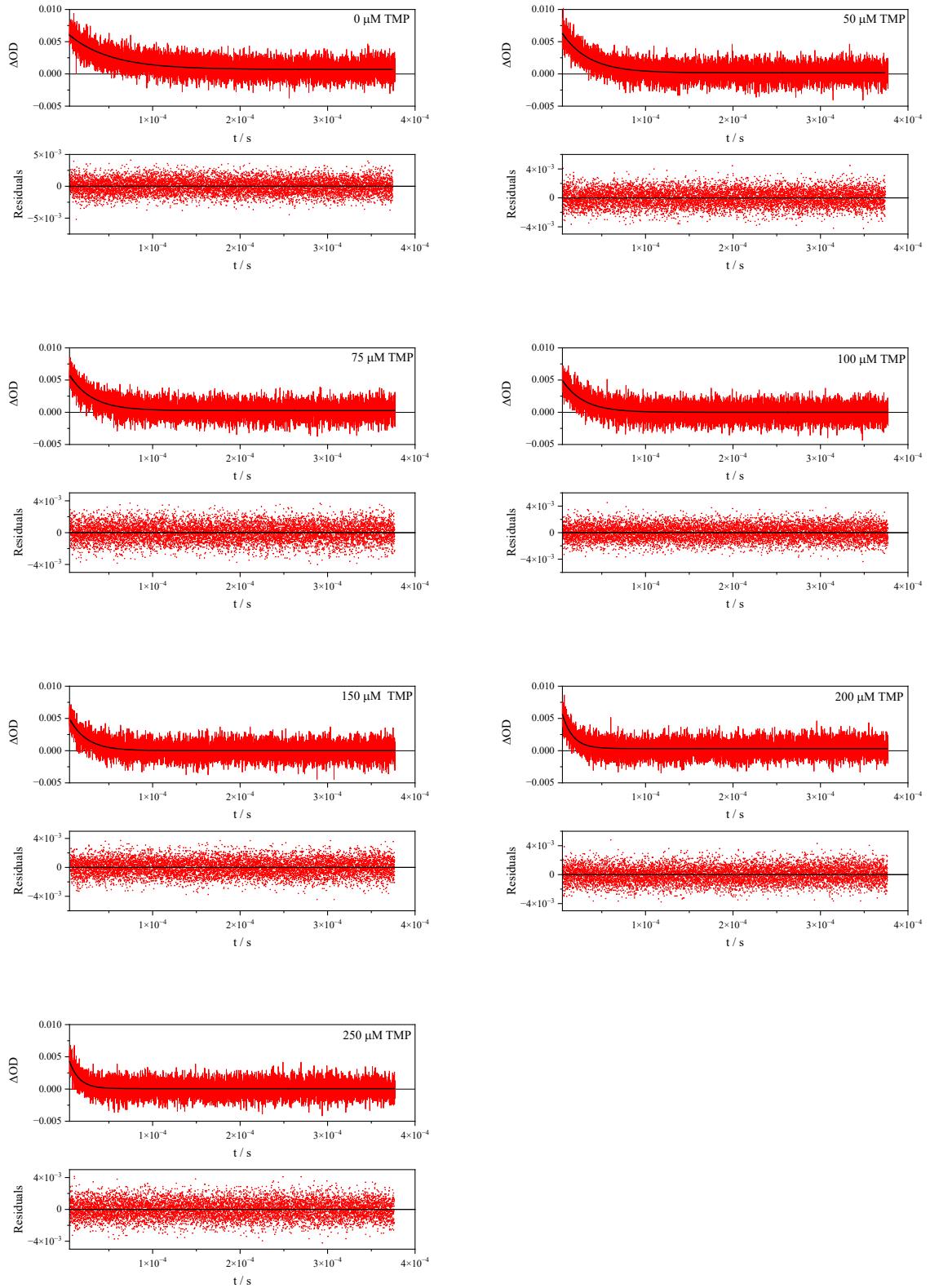


Fig. S14: Kinetic absorption traces at 436 nm of samples containing 2-acetonaphthone (150 μM), 4-cyanophenol (1 mM) and varying amounts of 2,4,6-trimethylphenol (TMP), with first-order fits used to determine $k_{4-\text{CN-PhO}\cdot}^d$. Measurements performed with LFP-1.

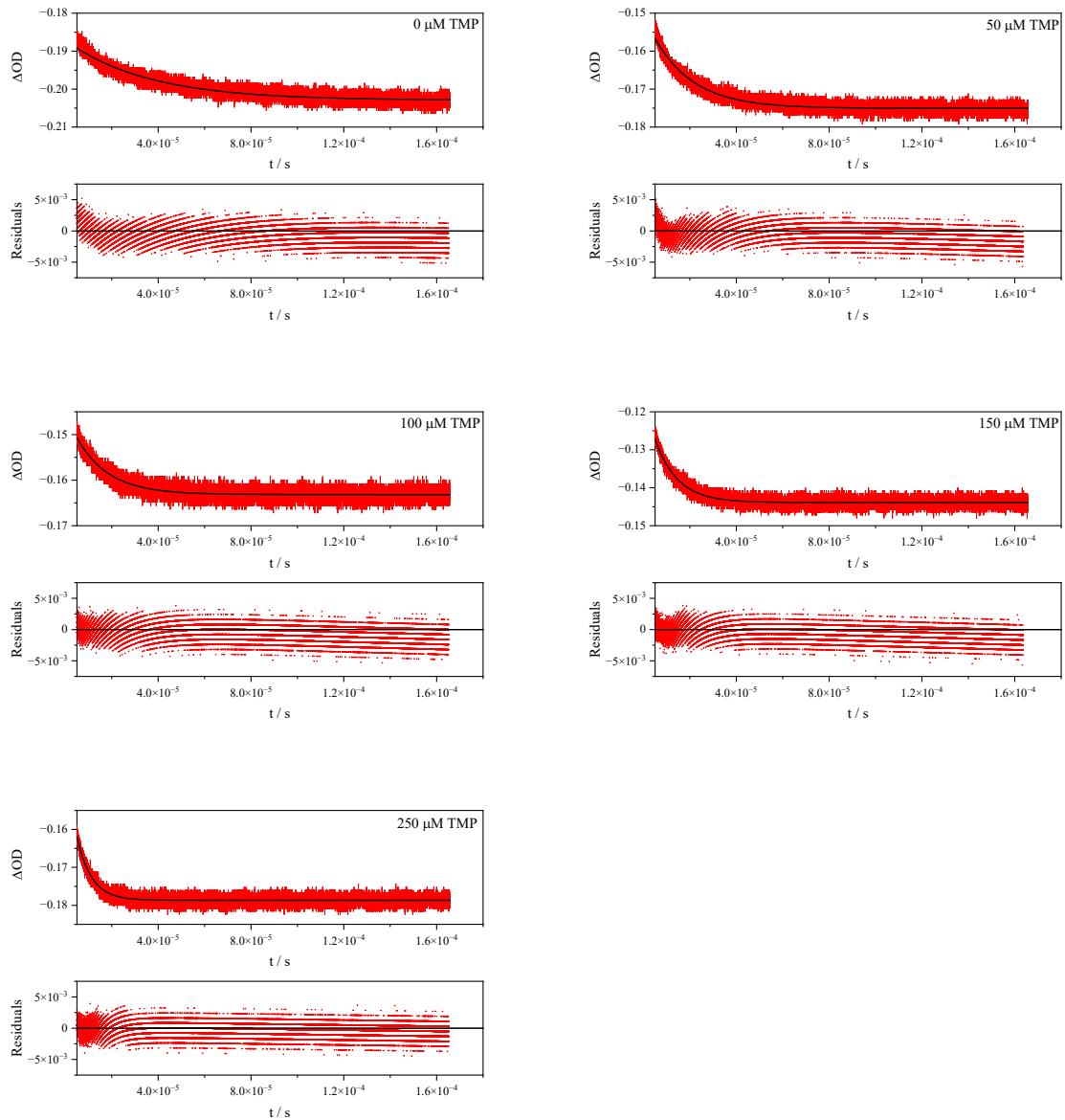


Fig. S15: Kinetic absorption traces at 436 nm of samples containing 2-acetonaphthone (150 μM), 4-cyanophenol (1 mM) and varying amounts of 2,4,6-trimethylphenol (TMP), with first-order fits used to determine $k_{4-\text{CN-PhO}\cdot}^{\text{d}}$. Measurements performed with LFP-2.

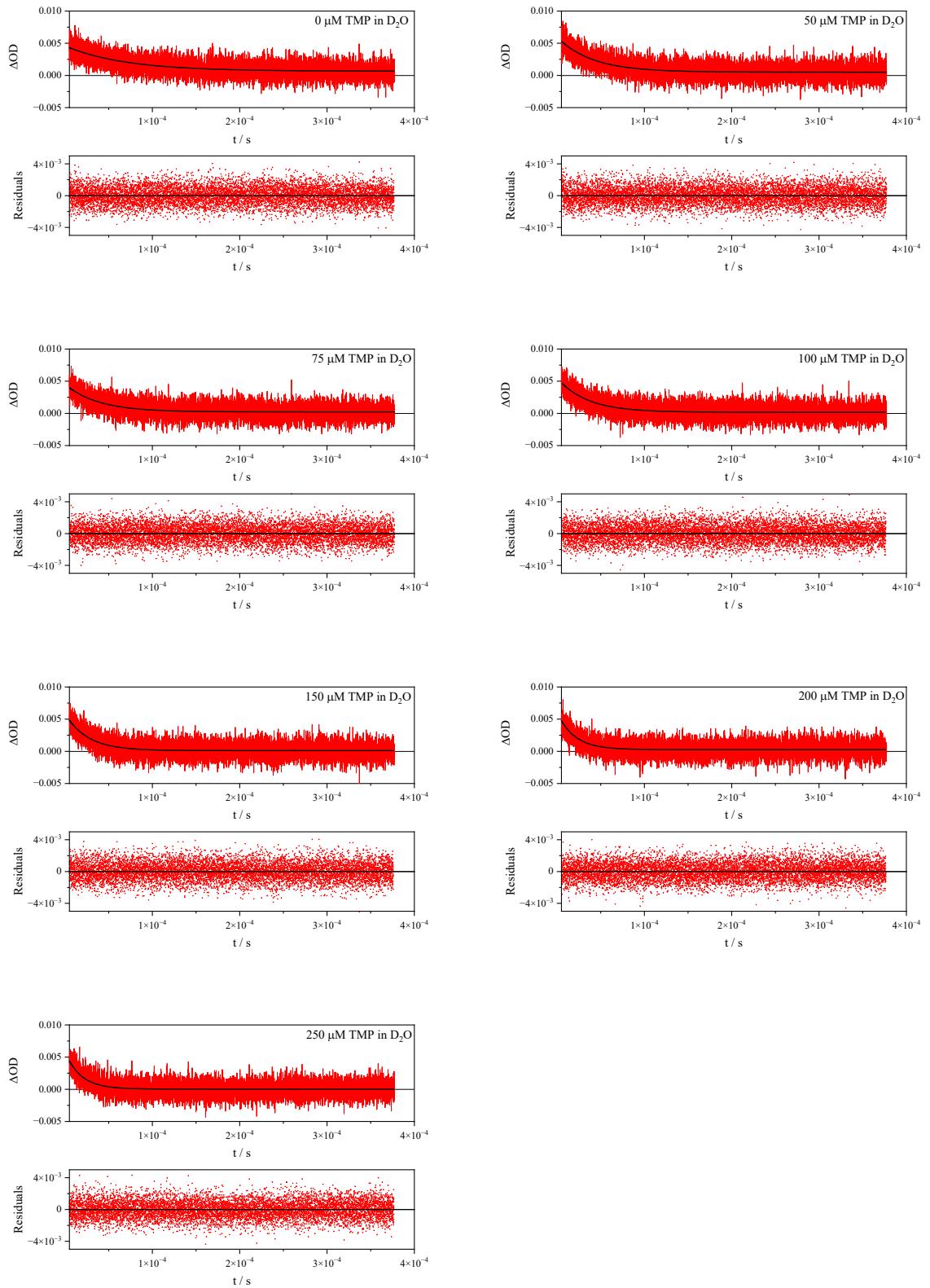


Fig. S16: Kinetic absorption traces at 436 nm of samples containing 2-acetonaphthone (150 μM), 4-cyanophenol (1 mM) and varying amounts of 2,4,6-trimethylphenol (TMP) in deuterated water, with first-order fits used to determine $k_{4-\text{CN}-\text{PhO}\cdot}^{\text{d}}$. Measurements performed with LFP-1.

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