

Supporting information for
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Isotope Fractionation Associated with the Indirect Photolysis of Substituted Anilines in Aqueous Solution

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Contents

S1 Chemicals	2
S2 Tables	2
S2.1 Reaction rate constants	2
S3 Figures	3
S3.1 Kinetics and isotope fractionation associated with the transformation of aniline, 4-Cl-aniline, and 4-OCH ₃ -aniline by ³ AQDS*	3
S3.2 Kinetics and isotope fractionation associated with the transformation of aniline, 4-CH ₃ -, and 4-OCH ₃ -aniline by ³ MB*	4
S4 Product analysis	5
S4.1 Indirect Phototransformation of 4-CH ₃ -aniline by ³ AQDS*	5
S4.2 Indirect Phototransformation of aniline by ³ AQDS*	6
S4.3 Indirect Phototransformation of 4-Cl-aniline by ³ AQDS*	8

S1 Chemicals

Chemicals and gases were purchased from various manufacturers and used without further treatment. A list of compound names, purities, and suppliers follows. Aniline ($\geq 99.5\%$), *p*-toluidine (99.6%), 4-chloroaniline (98%), *p*-anisidine ($\geq 99\%$), methylene blue (certified by the Biological Stain Commission) and potassium phosphate monobasic ($>99\%$) were purchased from Sigma-Aldrich (Buchs SG, Switzerland); anthraquinone-1,5-disulfonic acid disodium salt (98%) was from ABCR GmbH & CO. KG (Karlsruhe, Deutschland); hydrochloric acid (32%) and sodium hydroxide (98%), sodium chloride ($>99\%$) were from Merck (Dietikon, Switzerland); methanol (for HPLC gradient) from Acros Organics (Geel, Belgium). All aqueous solutions were prepared in nanopure water (18.2 M Ω -cm, Barnstead NANOpure Diamond Water Purification System).

The carrier and reference gas for GC and GC/IRMS included helium (He, 99.999%), N₂ (99.9999%), CO₂ (99.999%), H₂ (99.999%), synthetic air (20 \pm 1% O₂ in N₂, 99.9995%), O₂ (99.9995%) and, N₂ (99.9995%) from Carbagas (Rümlang, Switzerland). All aqueous solutions were prepared in nanopure water (18.2 M Ω -cm, Barnstead NANOpure Diamond Water Purification System).

S2 Tables

S2.1 Reaction rate constants

Table S1 Pseudo-first order reaction rate constants for the indirect photolysis of aniline and 4-Cl-, 4-CH₃-, 4-OCH₃-aniline, by excited triplet states of 9,10-anthraquinone-1,5-disulfonate (³AQDS*) and methylene blue (³MB*). Uncertainties are 95% confidence intervals.

Compound	pH	$k_{\text{obs}}/\text{h}^{-1}$
³ AQDS*		
aniline	7.0	0.6 ± 0.2
4-Cl-aniline	7.0	1.7 ± 0.3
4-CH ₃ -aniline	7.0	1.6 ± 0.6
4-OCH ₃ -aniline	7.5	0.14 ± 0.02
³ MB*		
aniline	7.0	31 ± 6
4-Cl-aniline	7.0	34 ± 3
4-CH ₃ -aniline	7.0	n.d.
4-OCH ₃ -aniline	7.5	n.d.

S3 Figures

S3.1 Kinetics and isotope fractionation associated with the transformation of aniline, 4-Cl-aniline, and 4-OCH₃-aniline by ³AQDS*

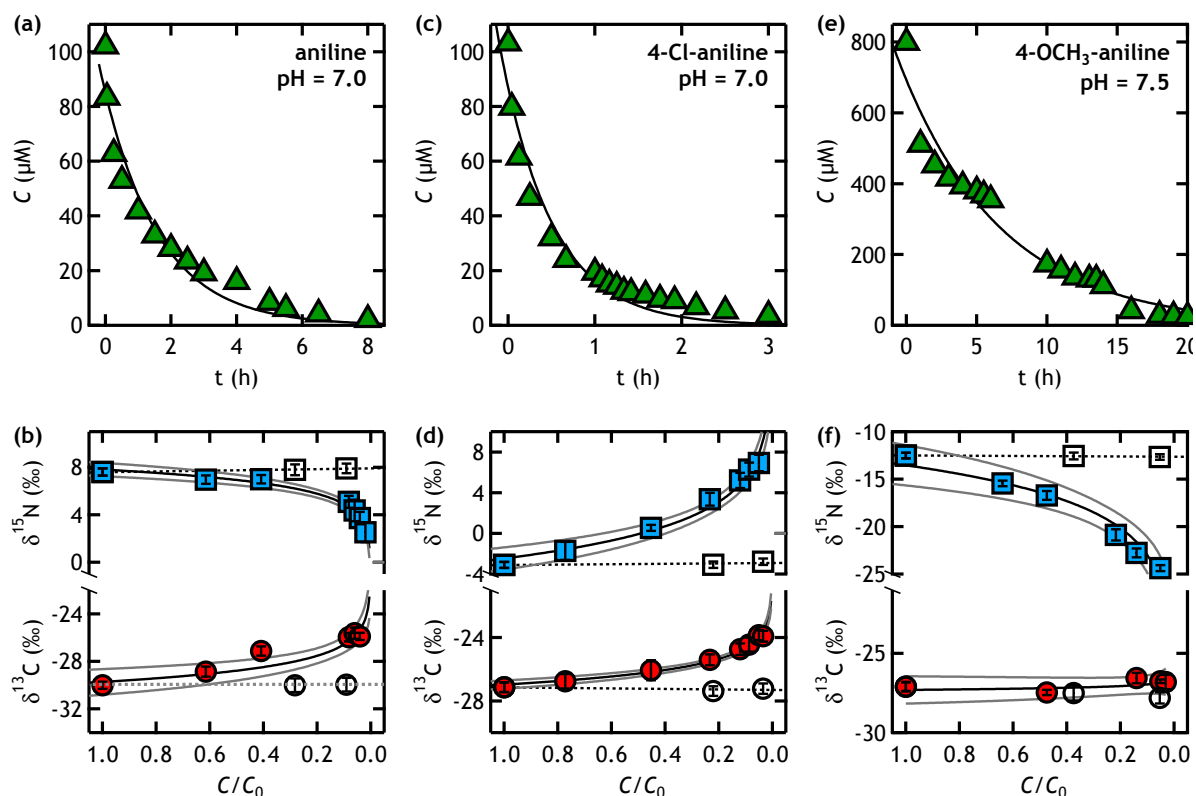


Figure S1 Transformation of aniline (panels a,b), 4-Cl-aniline (panels c,d) and 4-OCH₃-aniline (panels e, f) by excited triplet states of 9,10-anthraquinone-1,5-disulfonate (³AQDS*). Total AQDS concentration was 1.0 mM. Panels (a), (c), and (e) illustrate substrate disappearance. The solid lines were calculated using pseudo-first-order decay kinetics. Panels (b), (d), and (f): C and N isotope signatures ($\delta^{13}\text{C}$, circles, $\delta^{15}\text{N}$, squares) vs. fraction of remaining substrate (C/C_0). Uncertainties of data points are standard deviations of triplicate measurements. Solid lines were calculated with eq. 1; gray lines are 95% confidence intervals. Control experiments were treated identically but reactors did not contain photosensitizers (empty symbols, dotted lines).

S3.2 Kinetics and isotope fractionation associated with the transformation of aniline, 4-CH₃-, and 4-OCH₃-aniline by ³MB*

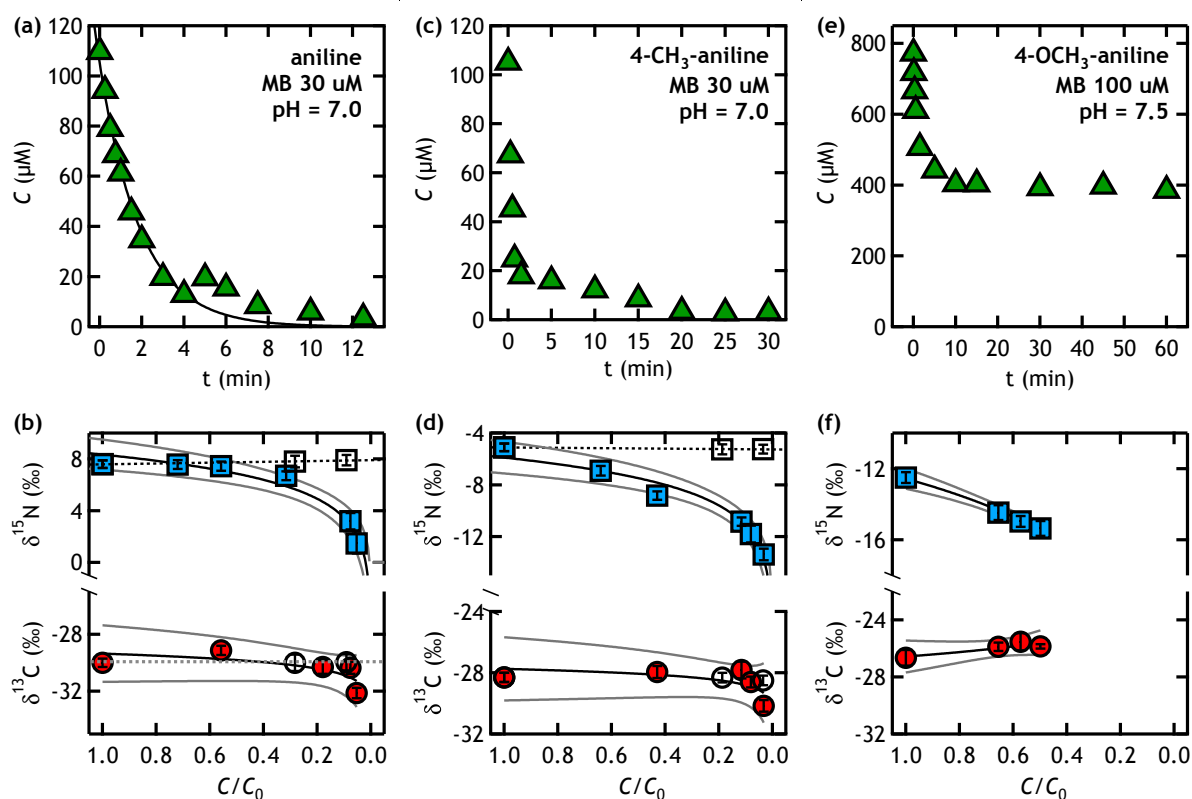


Figure S2 Transformation of aniline (panels a,b), 4-CH₃-aniline (panels c,d) and 4-OCH₃-aniline (panels e, f) by excited triplet states of methylene blue (³MB*). Panels (a), (c), and (e) illustrate substrate disappearance. The solid line in panel (a) was calculated using pseudo-first-order decay kinetics. Panels (b), (d), and (f): C and N isotope signatures ($\delta^{13}\text{C}$, circles, $\delta^{15}\text{N}$, squares) vs. fraction of remaining substrate (C/C_0). Uncertainties of data points are standard deviations of triplicate measurements. Solid lines were calculated with eq. 1; gray lines are 95% confidence intervals. Control experiments were treated identically but reactors did not contain photosensitizers (empty symbols, dotted lines).

S4 Product analysis

S4.1 Indirect Phototransformation of 4-CH₃-aniline by ³AQDS*

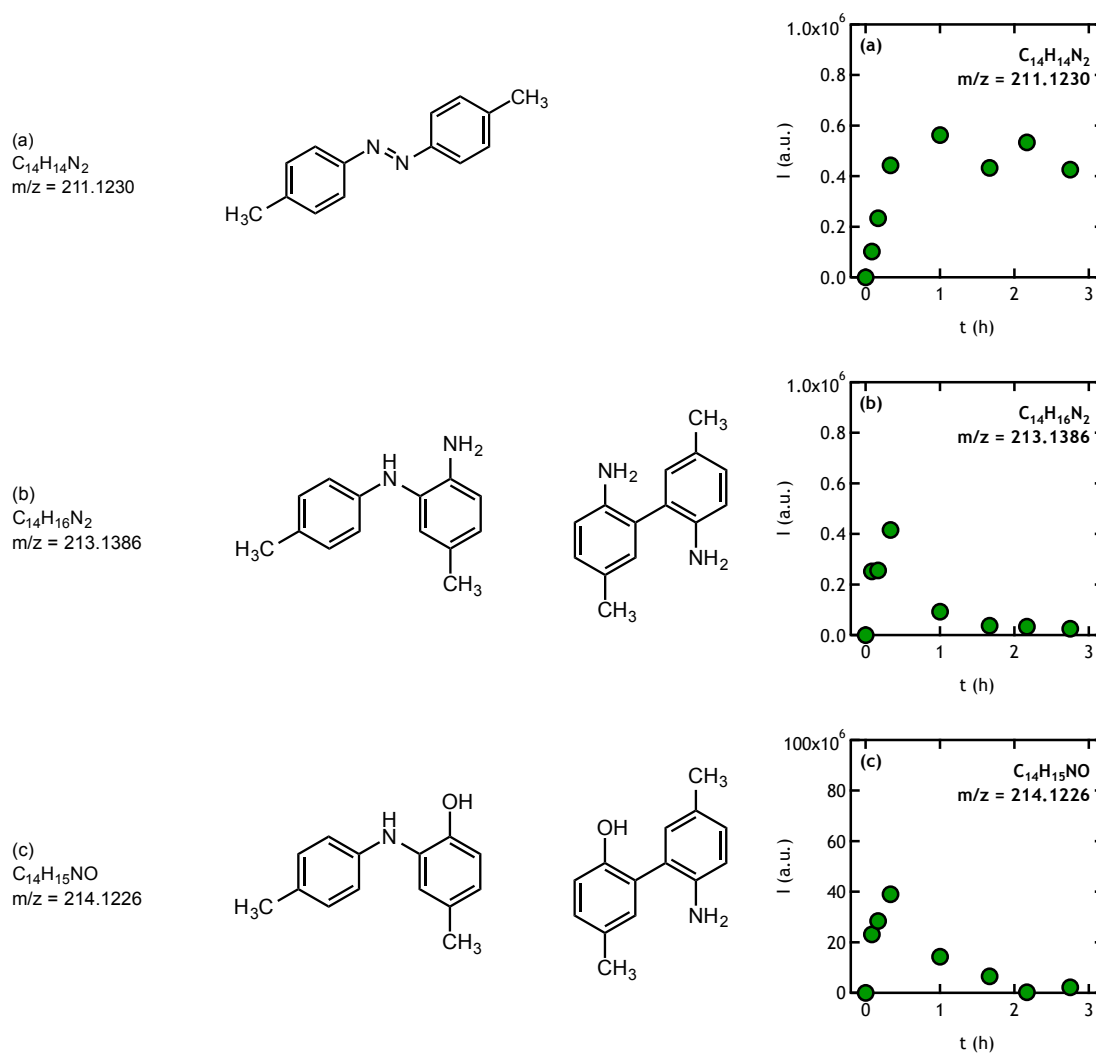
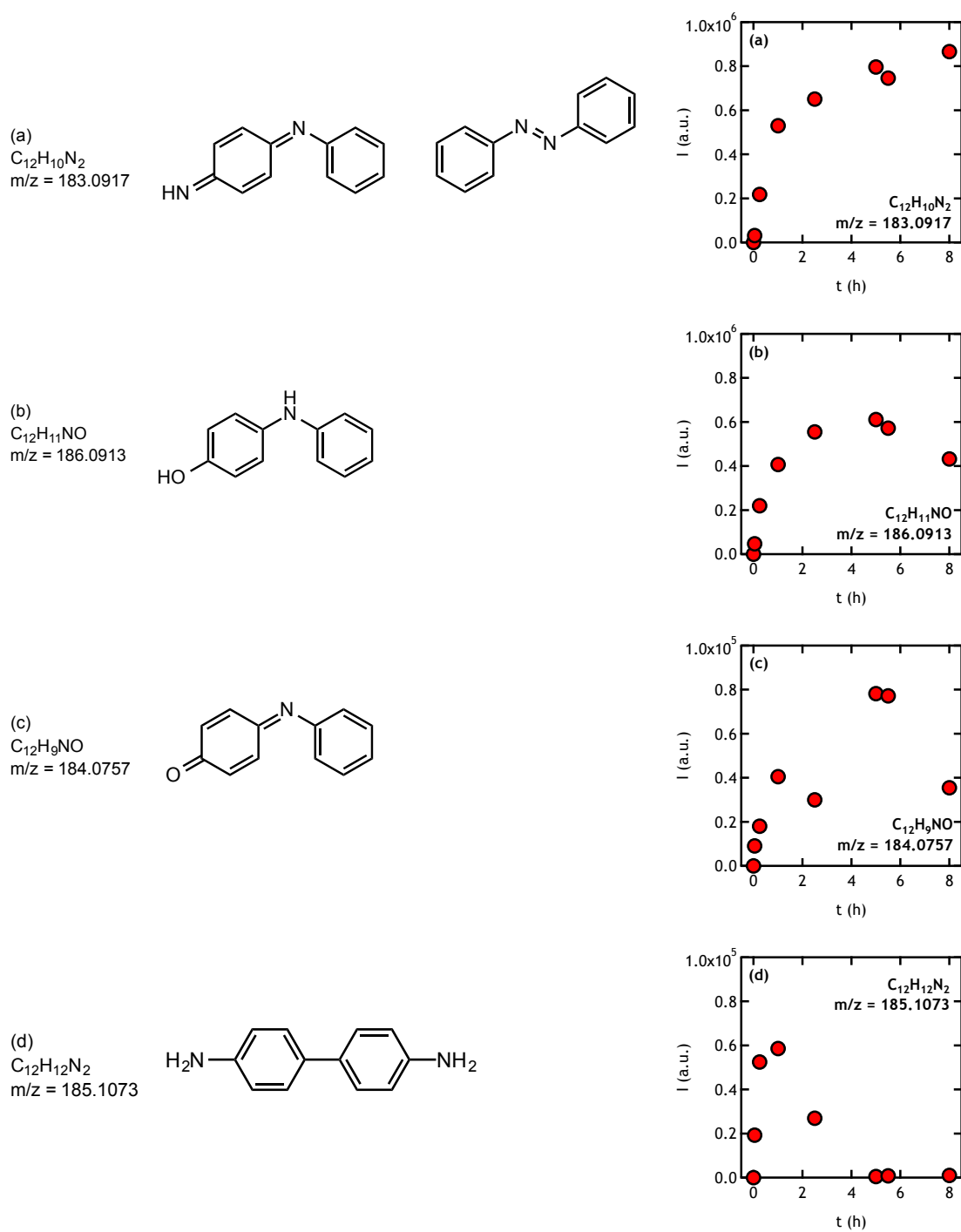


Figure S3 Molecular structure of possible reaction products from the indirect phototransformation of 4-CH₃-aniline by ³AQDS* at pH = 7.0 (total AQDS = 1mM). Concentration dynamics of reaction products are shown as signal areas of the investigated m/z -ratio vs. irradiation time.

S4.2 Indirect Phototransformation of aniline by $^3\text{AQDS}^*$



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(e)
 $C_{18}H_{15}N_3$
 $m/z = 274.1339$

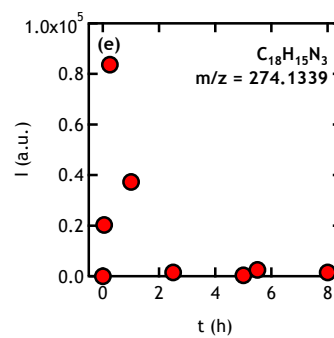
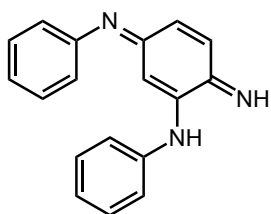


Figure S4 Molecular structure of possible reaction products from the indirect phototransformation of aniline by $^3AQDS^*$ at pH = 7.0 (total AQDS = 1mM). Concentration dynamics of reaction products are shown as signal areas of the investigated m/z -ratio vs. irradiation time.

S4.3 Indirect Phototransformation of 4-Cl-aniline by $^3\text{AQDS}^*$

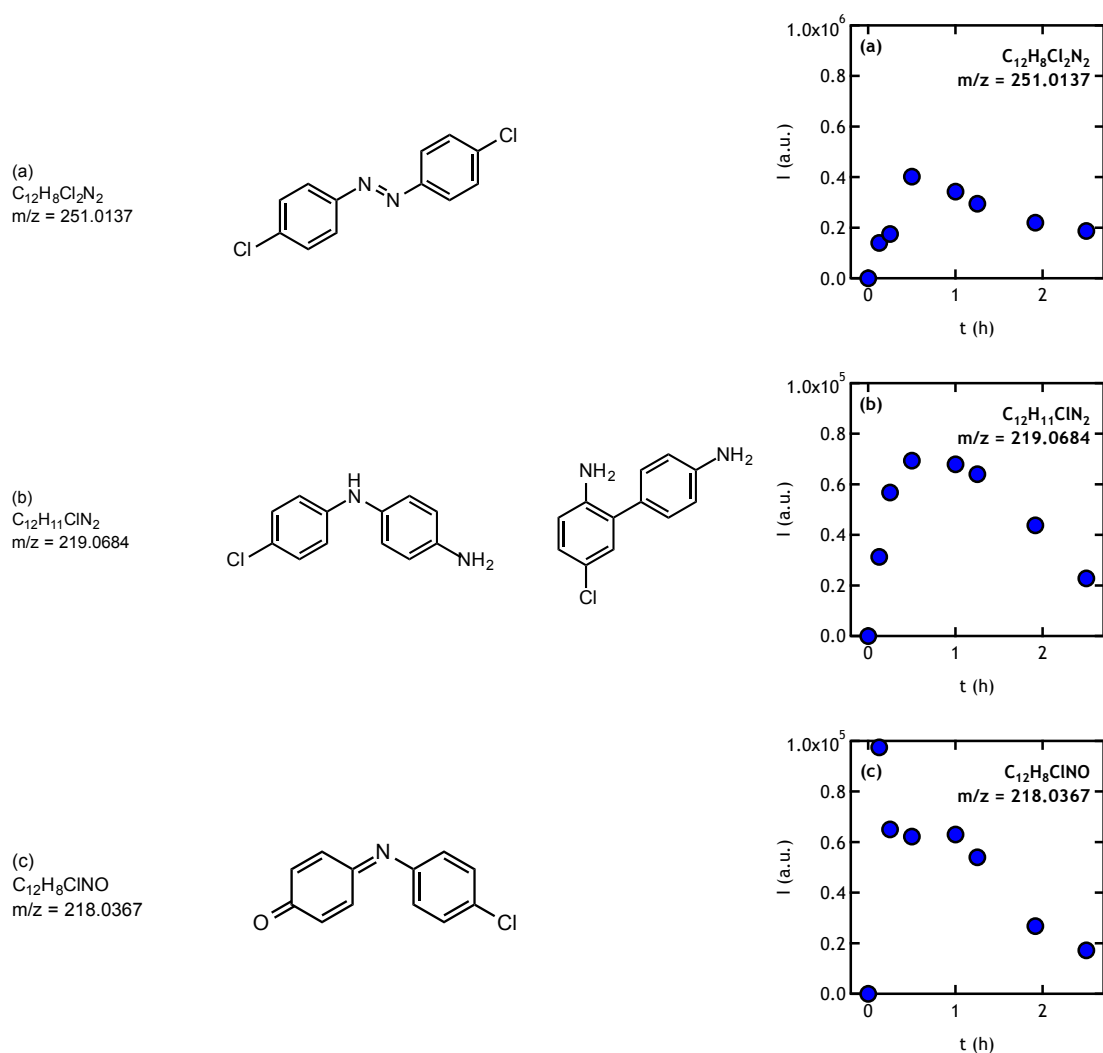


Figure S5 Molecular structure of possible reaction products from the indirect phototransformation of 4-Cl-aniline by $^3\text{AQDS}^*$ at $\text{pH} = 7.0$ (total AQDS = 1mM). Concentration dynamics of reaction products are shown as signal areas of the investigated m/z -ratio vs. irradiation time.