

Appendix A: Supplementary Material for

## **Hydrophobic Model Systems for Oil Film Photooxidation:**

### **Part II: Direct and Indirect Pathways Controlled by Oxygen and Molecular Structure**

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## Section A1 Quantum yield calculation and literature values

### Text A1.1. Quantum yield calculation

The integrated irradiance for the nitrate actinometer is to determine by (Eq. (1)):

$$E = \frac{-1}{2.303 \times \phi_{SA} \times \epsilon_{SA}} \ln \left[ \frac{\phi_{NO_3^-} \times \epsilon_{NO_3^-} \times [NO_3^-]_1}{\phi_{NO_3^-} \times \epsilon_{NO_3^-} \times [NO_3^-]_0} - \frac{f(\epsilon_{NO_3^-}) \times \phi_{NO_3^-} \times [SA]_1}{f(\epsilon_{NO_3^-}) \times \phi_{NO_3^-} \times [SA]_0} \right] \quad (1)$$

Then, the quantum yield could be calculated with Eq. (2):

$$\phi_{model} = \frac{k_{model}}{1000} \cdot \frac{l}{\sum E_{\lambda} (1 - 10^{-\epsilon_{\lambda} [model]_0 \Delta \lambda})} \cdot [model]_0 \quad (2)$$

where  $\phi_{SA}$  (mol SA degraded per mol photons absorbed by SA) and  $\epsilon_{SA}$  ( $\text{cm}^2 \text{mol}^{-1}$ ) represent the mean quantum yield and molar absorption coefficient of SA, respectively, over the SA degradation response band. Similarly,  $\phi_{SA}$  (mol SA formed per mol photons absorbed by nitrate) and  $\epsilon_{SA}$  ( $\text{cm}^2 \text{mol}^{-1}$ ) refer to the mean quantum yield and molar absorption coefficient for nitrate over the nitrate actinometer response band.

$[NO_3^-]$  is the initial concentration of nitrate ( $\text{mol L}^{-1}$ ), while  $[SA]_0$  and  $[SA]_1$  are the initial and final concentrations of salicylic acid ( $\text{mol L}^{-1}$ ) in the actinometric solution after irradiation. The correction factor  $f$  accounts for differences in spectral overlap between nitrate absorption and SA formation, specifically the fraction of available irradiance within the SA degradation bandwidth relative to that within the nitrate actinometer response band. This correction ensures accurate photon flux determination even when SA absorbance is non-negligible. In Eq. (2),  $\epsilon_{\lambda}$  and  $L_{\lambda}$  are the molar absorptivity and the irradiance at a specific wavelength, respectively.  $\rho_{\lambda}$  is

the relative spectral photon irradiance determined by Equation (4) where  $\Delta\lambda$  is 1 nm and the summation is from 280 to 400 nm. The molar absorptivity of model compounds and  $\text{NO}_3^-$  were measured using a UV spectrophotometer. The irradiance data in the solar simulator was measured by the spectrometer.

**Table A1.1** Literature-reported quantum yields for the direct photolysis of PAHs

<b>Compound</b>	<b>Ring number</b>	<b>Quantum yield in toluene (<math>10^{-5}</math>)</b>	<b>Quantum yield in water (<math>10^{-3}</math>)</b>
naphthalene	2	N/A	$15 \pm 1(313 \text{ nm})^1$
phenanthrene	3	N/A	$10 \pm 1.6(313 \text{ nm})^1$ $3.0 \pm 0.2(366 \text{ nm})^1$
anthracene	3	N/A	$1(1(313 \text{ nm})^1, 1(aerated)(350 \text{ nm})^2, 12(\text{degassed})(350 \text{ nm})^2, 182-0.241(254 \text{ nm})^3, 96(254 \text{ nm})^4$
9 methyl anthracene	3	N/A	$7.5 \pm 0.5(313 \text{ nm})^1$
benzo[a]anthracene	4	$6.2 \pm 0.4(366 \text{ nm})^5$	$3.3 \pm 0.1(313 \text{ nm}, 366 \text{ nm})^6$
chrysene	4	$6.7 \pm 0.2(>300 \text{ nm})^5$	$2.8 \pm 0.7(313 \text{ nm})^1$
pyrene	4	N/A	$2.0 \pm 0.3(313 \text{ nm})^7$ $2.2 \pm 0.3(366 \text{ nm})^7$
benzo[a]pyrene	5	$3.4 \pm 0.3(366 \text{ nm})^5$	$0.89(313 \text{ nm})^6$ $0.54(366 \text{ nm})^6$
benzo[e]pyrene	5	$5.5 \pm 0.2(>300 \text{ nm})^5$	N/A

## Section A2 Apparent quantum yield calculations

### Text A2.1. Apparent quantum yield calculations

The light absorption rate is calculated with the equation below.

$$Ra = \sum_{280nm}^{400nm} I_{\lambda} (1 - 10^{-a_{\lambda,SEN} l})$$

Where Ra is the photosensitizer light absorption rate.  $I_{\lambda}$  is the spectral irradiance.

The  $a_{\lambda,SEN}$  is represented as the light attenuation coefficient for photosensitizers (the measured absorbance for a given wavelength when the cuvette path length is 1 cm)

The apparent quantum yield in the different photosensitizer present in the solution is calculated by the equation.

$$\varphi_{apparent} = \frac{k_{model}}{1000} \cdot \frac{l}{\sum E_{\lambda} (1 - 10^{-\epsilon_{\lambda} l [photosensitizer]_0}) \Delta\lambda} \cdot [model]_0$$

**Table A2.1** The apparent quantum yield of ANT and 9MA by the light absorption rates in the reaction with photosensitizers (BaP, MBaP, PYR and MPYR only in present of tetracene)

Photosensitizer	$\varphi_{apparent}$					
	ANT	9MA	BaP	MBaP	PYR	MPYR
Phenaleone	$6.90 \times 10^{-4}$	$3.96 \times 10^{-4}$	N/A	N/A	N/A	N/A
Tetracene	$3.10 \times 10^{-3}$	$2.41 \times 10^{-3}$	$3.17 \times 10^{-3}$	$4.91 \times 10^{-3}$	$1.12 \times 10^{-3}$	$3.16 \times 10^{-3}$
Naphthol	$1.77 \times 10^{-3}$	$1.17 \times 10^{-3}$	N/A	N/A	N/A	N/A
Xanthone	$1.52 \times 10^{-3}$	$6.94 \times 10^{-4}$	N/A	N/A	N/A	N/A
Anthraquinone	$1.96 \times 10^{-3}$	$9.67 \times 10^{-4}$	N/A	N/A	N/A	N/A

## Section A3 Analytical Methods

### Text A3.1 UV-Vis method

Visible ultraviolet (UV-Vis) absorption spectra of Butylbenzene, Indane, naphthalene, 2-ethylnaphthlene, phenanthrene, anthracene, 9-methyl-anthracene, butyl cyclohexane, decalin, hexadecane, squalene, phenalenone, tetracene, naphthol, xanthone, and anthraquinone were obtained using an Agilent 1601UV-PC dual beam spectrophotometer from 200–800 nm in 1-cm quartz cuvettes, with a scan speed of 2400 nm min<sup>-1</sup> and a 1.0 nm interval.

### Text A3.2 Oxygen measurement

The partial pressure of oxygen (pO<sub>2</sub>, in hPa) was measured using the FireSting-O<sub>2</sub> fiber-optic oxygen meter (PyroScience), equipped with the solvent-resistant probe tip OXSOLV-PT. The sensor was calibrated using a two-point method: ambient air as the high-oxygen reference and a 1% sodium sulfite solution in water as the zero-oxygen reference. The saturated oxygen concentration in air-saturated solvent can be calculated as below:

$$C_{O_2} = \frac{P_{O_2}}{P_N} \alpha \frac{M_{O_2}}{V_{O_2}}$$

Where:

C<sub>O<sub>2</sub></sub>: saturated oxygen concentration

P<sub>O<sub>2</sub></sub>: partial pressure of oxygen

P<sub>N</sub>: atmospheric pressure

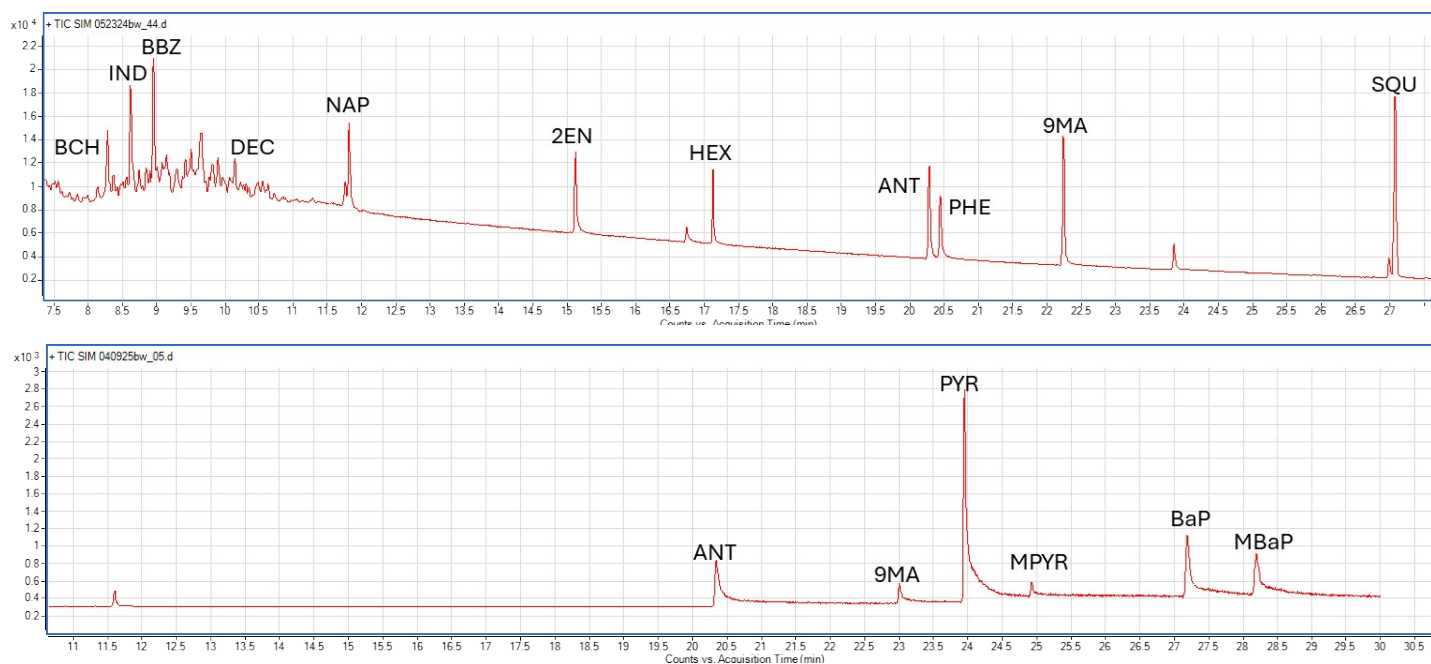
α: absorption coefficient for solvents (α<sub>toluene</sub> = 21.49; α<sub>hexane</sub> = 89.91)

M<sub>O<sub>2</sub></sub>: molar mass of oxygen (32 g/l)

V<sub>O<sub>2</sub></sub>: molar volume of oxygen (22.414 l/mol)

**Table A3.3** Monitored m/z values and chromatographic retention times for target compounds.

Compounds	m/z	Retention time
ANT	178	20.37
9MA	192	21.9
PYR	202	20
MPYR	212	23.945
BaP	255	27.195
MBaP	262	28.19
HEX	57	17.1
BCH	83	8.211
BBZ	91	8.88
IND	117	8.551
NAP	128	11.751
DEC	138	9.84
PHE	178	20.218
SQU	57	24.8
2EN	141	15.006



**Figure A3.4.** Representative SIM chromatogram of target PAHs.

## Section A4 Oxygen and solvent effect on photolysis

**Table A4.1:** ANT and 9MA direct photolysis first order reaction rate constant in

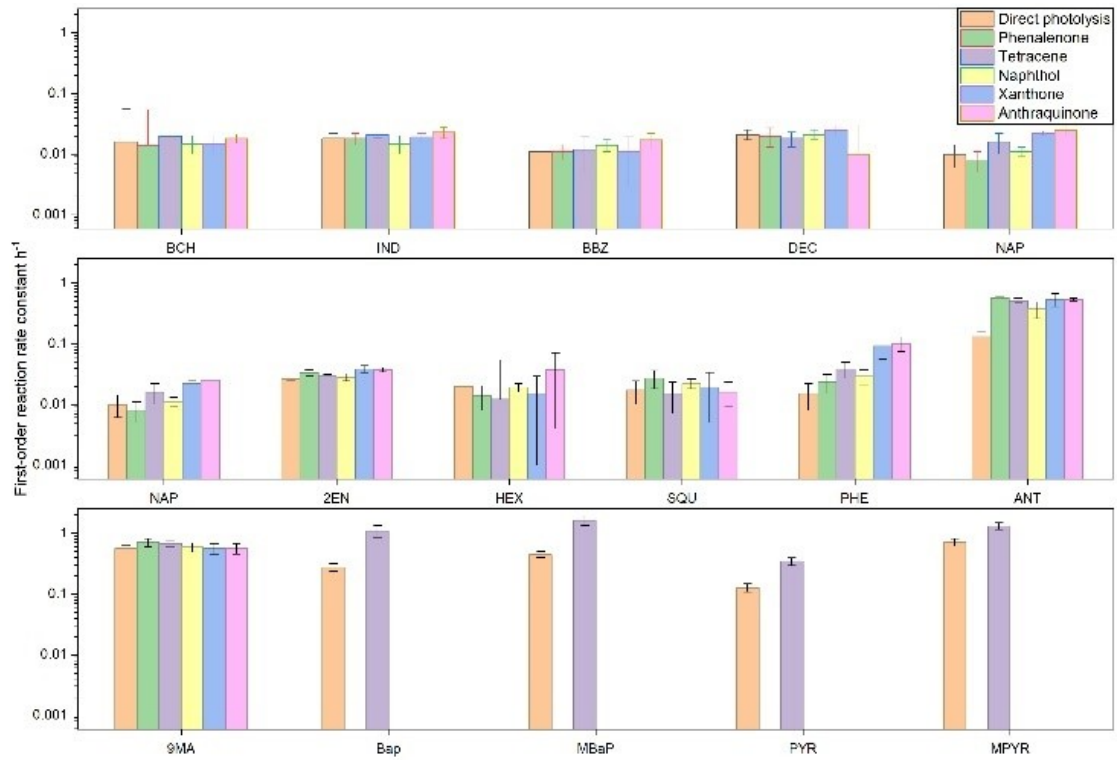
Compounds	$k/h^{-1}$			
	toluene		hexane	
	Air-saturated	N <sub>2</sub> -purging	Air-saturated	N <sub>2</sub> -purging
ANT	0.13±0.03	0.13±0.014	0.11±0.051	0.10±0.025
9MA	0.56±0.075	0.62±0.094	0.57±0.042	0.67±0.078

toluene and hexane in the presence and absence of oxygen

**Table A4.2:** Model compounds indirect photolysis first order reaction rate constant in toluene in the presence and absence of oxygen

Compounds	Sensitizer	$k/h^{-1}$		Relative Removal rate
		Air-saturated	N <sub>2</sub> -purging	Air-saturated
ANT	Phenalenone	0.59±0.02	0.48±0.066	4.38
	Tetracene	0.51±0.049	0.33±0.019	3.92
	Naphthol	0.37±0.11	0.32±0.1	2.85
	Xanthone	0.53±0.13	0.29±0.12	4.08
	Anthraquinone	0.52±0.1	0.48±0.1	4.08
9MA	Phenalenone	0.7±0.11	1.03±0.25	1.23
	Tetracene	0.68±0.078	0.54±0.27	1.19
	Naphthol	0.59±0.1	0.58±0.14	1.04
	Xanthone	0.54±0.11	0.52±0.17	0.98
	Anthraquinone	0.56±0.11	0.45±0.19	0.98
BaP	Tetracene	0.89±0.11	1.064±0.11	3.3
MBaP	Tetracene	1.4±0.19	1.29±0.11	3.1
PYR	Tetracene	0.34±0.052	0.32±0.03	2.62
MPYR	Tetracene	1.31±0.17	0.99±0.006	1.85
BCH	Phenalenone	0.014±0.004	n.a.	0.88
	Tetracene	0.02±0.004	n.a.	1.25
	Naphthol	0.015±0.005	n.a.	0.94
	Xanthone	0.015±0.003	n.a.	0.94
	Anthraquinone	0.018±0.004	n.a.	1.12
IND	Phenalenone	0.018±0.004	n.a.	1
	Tetracene	0.021±0.003	n.a.	1.17
	Naphthol	0.015±0.005	n.a.	0.83
	Xanthone	0.019±0.003	n.a.	1.06
	Anthraquinone	0.023±0.005	n.a.	1.28
	Phenalenone	0.011±0.003	n.a.	1

	Tetracene	0.012±0.007	n.a.	1.09
	Naphthol	0.014±0.003	n.a.	1.27
	Xanthone	0.011±0.002	n.a.	1
	Anthraquinone	0.017±0.005	n.a.	1.55
DEC	Phenalenone	0.02±0.004	n.a.	0.95
	Tetracene	0.023±0.007	n.a.	0.86
	Naphthol	0.018±0.005	n.a.	1
	Xanthone	0.02±0.004	n.a.	1.19
	Anthraquinone	0.025±0.005	n.a.	0.48
NAP	Phenalenone	0.008±0.003	n.a.	0.8
	Tetracene	0.016±0.006	n.a.	1.6
	Naphthol	0.011±0.002	n.a.	1.1
	Xanthone	0.022±0.002	n.a.	2.2
	Anthraquinone	0.025±0.005	n.a.	2.5
2EN	Phenalenone	0.033±0.004	n.a.	1.27
	Tetracene	0.029±0.002	n.a.	1.12
	Naphthol	0.028±0.004	n.a.	1.08
	Xanthone	0.038±0.005	n.a.	1.46
	Anthraquinone	0.037±0.003	n.a.	1.42
HEX	Phenalenone	0.014±0.006	n.a.	0.7
	Tetracene	0.012±0.009	n.a.	0.6
	Naphthol	0.019±0.003	n.a.	0.95
	Xanthone	0.003±0.003	n.a.	0.75
	Anthraquinone	0.008±0.007	n.a.	1.85
SQU	Phenalenone	0.02±0.004	n.a.	1.59
	Tetracene	0.015±0.008	n.a.	0.88
	Naphthol	0.022±0.004	n.a.	1.29
	Xanthone	0.038±0.005	n.a.	1.12
	Anthraquinone	0.016±0.01	n.a.	0.94
PHE	Phenalenone	0.016±0.01	n.a.	1.53
	Tetracene	0.038±0.011	n.a.	2.53
	Naphthol	0.029±0.008	n.a.	1.93
	Xanthone	0.091±0.01	n.a.	6.07
	Anthraquinone	0.1±0.008	n.a.	6.67



**Figure A4.3** The photolysis of target compounds in the absence and presence of photosensitizers\*

\*A logarithmic scale was applied to improve readability given the wide range of rate constants

Section A5 Singlet oxygen quantum yield and triplet state reduction potential of photosensitizers and PAHs

**Table A5.1** Singlet oxygen quantum yield and triplet state reduction potential of photosensitizers and PAHs

photosensitizers	Quantum yield of $^1\text{O}_2$	$E^{0*} (^3\text{S}^*/\text{S}^-)^f$
Phenalenone	0.95 <sup>a</sup>	1.03
Tetracene	0.68-0.86 <sup>b</sup>	n.a.
Xanthone	0.27 <sup>c</sup>	1.96
AQ	0.62 <sup>d</sup>	2.23
PHE	0.33 <sup>e</sup>	0.46
NAP	0.5 <sup>e</sup>	0.37
ANT	0.61 <sup>e</sup>	0.15

a:<sup>8</sup>; b:<sup>9-11</sup>; c:<sup>12</sup>; d:<sup>13</sup>; e:<sup>14</sup>; f<sup>15</sup>

**Table A5.2** The second-order reaction rate constant of singlet oxygen with HCs ( $k_r$  M<sup>-1</sup> s<sup>-1</sup>)

Compound	$k_r(^1\text{O}_2)$ M <sup>-1</sup> s <sup>-1</sup>
NAP	$5.2 \times 10^8$ <sup>16</sup>
ANT	$1.2 \times 10^4$ - $5.4 \times 10^5$ <sup>17-20</sup>
9MA	$2 \times 10^6$ - $9.6 \times 10^7$ <sup>17, 20, 21</sup>
Toluene	$3.9 \times 10^3$ (CCl <sub>4</sub> as solvent) <sup>22</sup>
BAP	$7.5 \times 10^5$ <sup>5</sup>
Tetracene	$5 \times 10^6$ - $5.2 \times 10^8$ <sup>11, 16, 20, 23-25</sup>

Section A6 The spectral incident photon flux of the lamps and the UV-Vis absorption Spectra of compounds

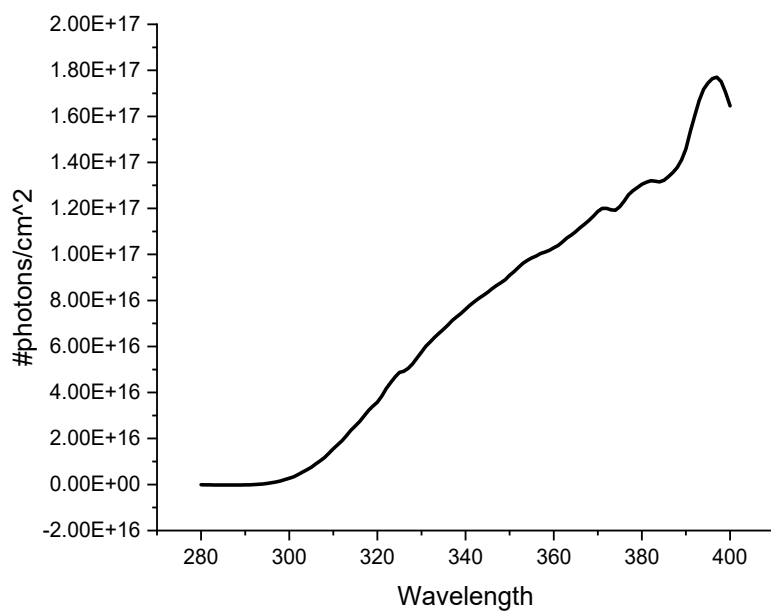


Figure A6.1 The spectral incident photon flux of the lamps

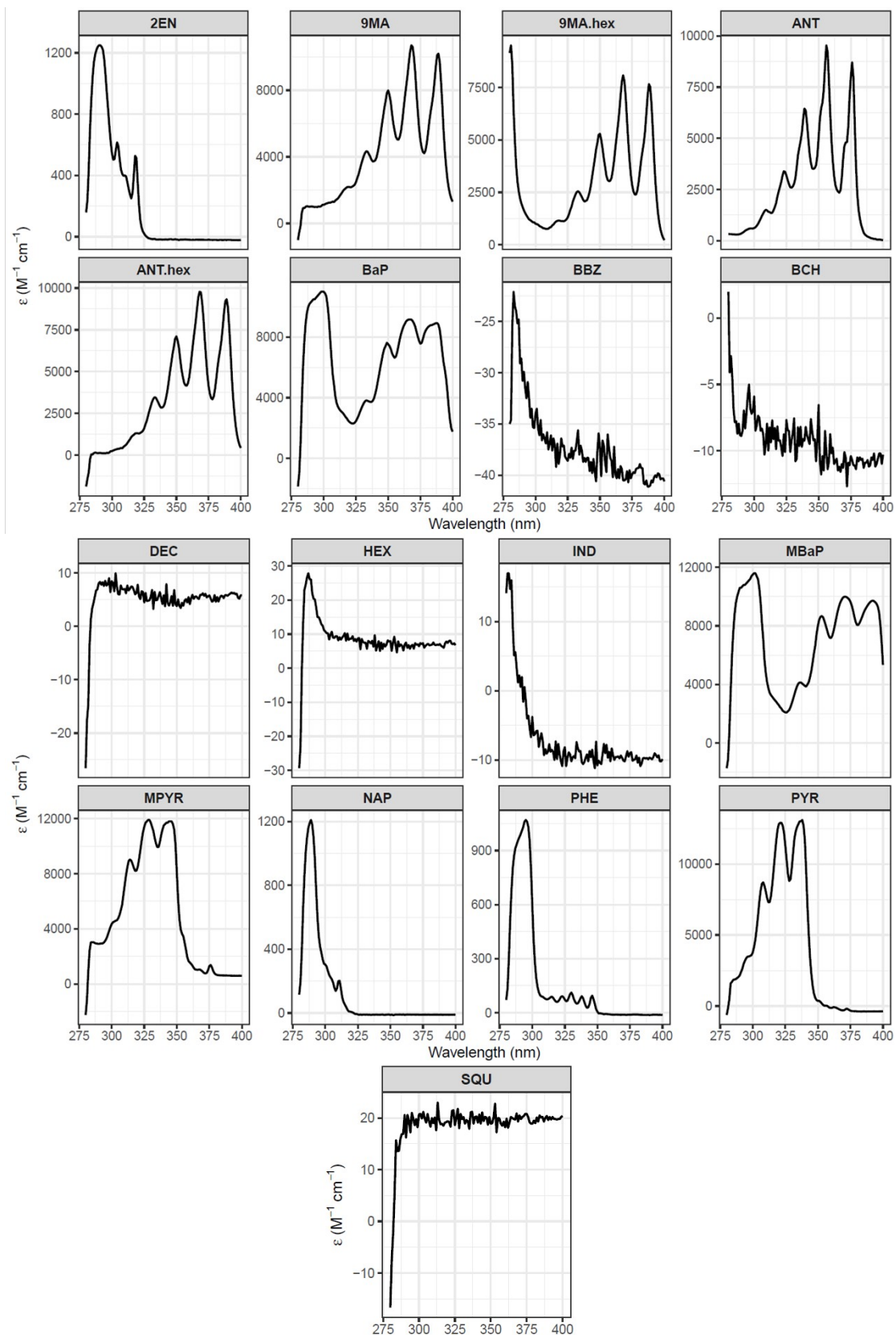


Figure A6.2 The UV-Vis absorption Spectra (280-400 nm) \*

\* All compounds were investigated in toluene, unless otherwise noted.

## Section A7 Kinetics data for model compounds

**Table A7.1** Dark Control and direct photolysis of hydrocarbon mixtures<sup>#</sup>

Corresponding kinetic plots are shown in Fig. 1.

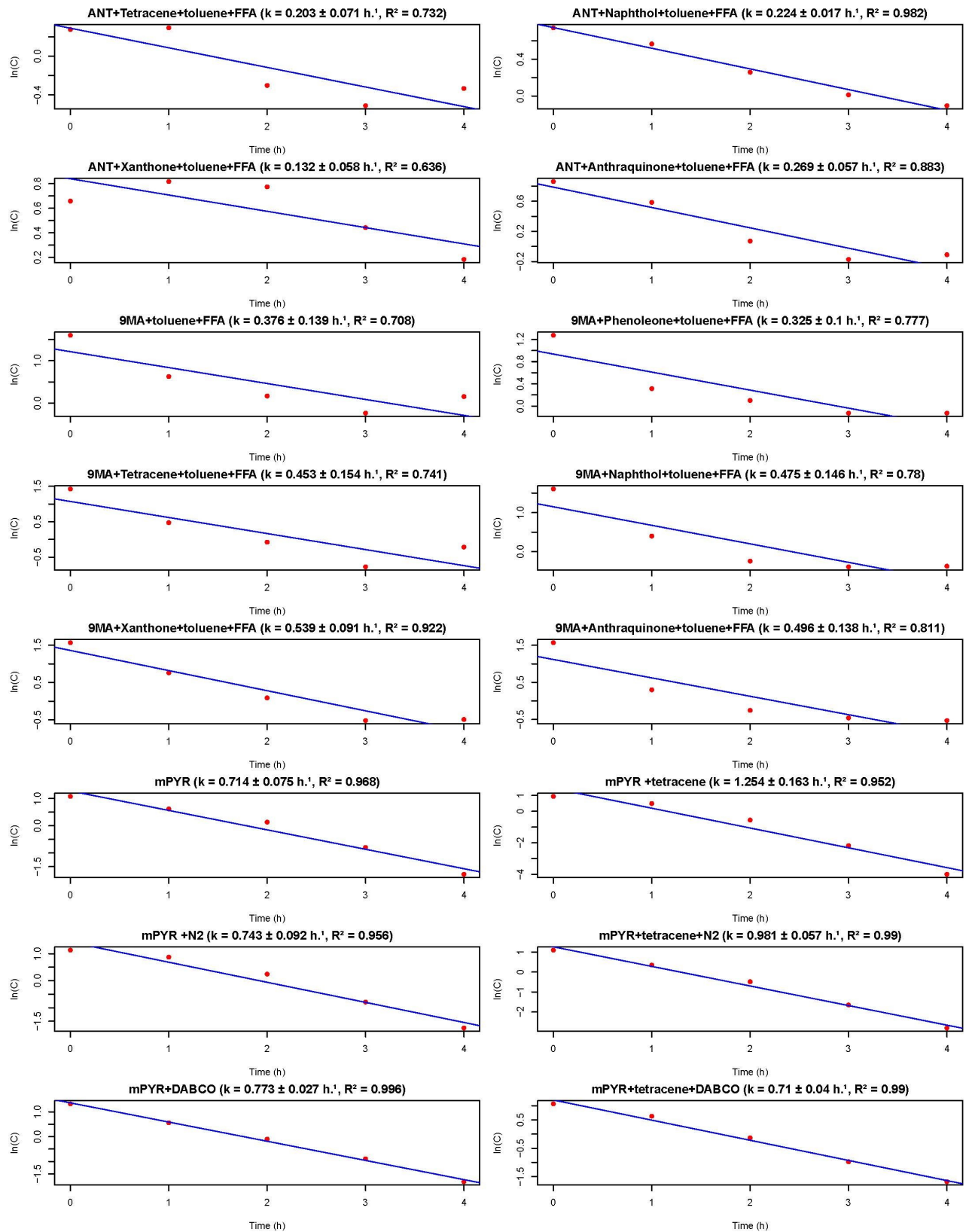
Compounds	CAS number	First-order	First-order	p-value	Quantum yield
		reaction rate constant (h <sup>-1</sup> , Dark control)	reaction rate constant (h <sup>-1</sup> )		
BCH	1678-93-9	(0.7 ± 2.0) × 10 <sup>-3</sup>	0.016 ± 0.039*	0.0025	not calculated
IND	496-11-7	(0.7 ± 2.0) × 10 <sup>-3</sup>	0.018 ± 0.004 *	0.0016	not calculated
BBZ	104-51-8	(1.3 ± 2.0) × 10 <sup>-3</sup>	0.011 ± 0.004 *	0.033	not calculated
DEC	91-17-8	(1.4 ± 1.0) × 10 <sup>-3</sup>	0.021 ± 0.004 *	0.0006	not calculated
NAP	91-20-3	(0.6 ± 3.0) × 10 <sup>-3</sup>	0.01 ± 0.004 *	0.046	not calculated
2EN	939-27-5	(2.7 ± 3.0) × 10 <sup>-3</sup>	0.026 ± 0.002 *	0.000002	not calculated
HEX	544-76-3	(2.0 ± 2.0) × 10 <sup>-3</sup>	0.02 ± 0.005 *	0.005	not calculated
SQU	111-02-4	(2.8 ± 3.0) × 10 <sup>-3</sup>	0.017 ± 0.007 *	0.039	not calculated
PHE	85-01-8	(0.4 ± 4.0) × 10 <sup>-3</sup>	0.015 ± 0.007 (n.s.)	0.152	not calculated
ANT (Toluene as solvent)	120-12-7	(1.2 ± 3.0) × 10 <sup>-3</sup>	0.13 ± 0.03*	0.022	(6.21 ± 0.91) × 10 <sup>-5</sup>
9MA (Toluene as solvent)	779-02-2	(3.9 ± 2.0) × 10 <sup>-3</sup>	0.56 ± 0.075*	0.005	(1.08 ± 0.1) × 10 <sup>-4</sup>
ANT (Hexane as solvent)	120-12-7	Not measured	0.11 ± 0.051 *	0.12	(4 ± 1.86) × 10 <sup>-5</sup>
9MA (Hexane as solvent)	779-02-2	Not measured	0.57 ± 0.041*	0.0008	(1.98 ± 0.14) × 10 <sup>-4</sup>
BaP	50-32-8	Not measured	0.27 ± 0.045 *	0.009	(2.56 ± 0.43) × 10 <sup>-5</sup>
MBaP	63041-77-0	Not measured	0.45 ± 0.051 *	0.003	(3.84 ± 0.44) × 10 <sup>-5</sup>
PYR	129-00-0	Not measured	0.13 ± 0.024 *	0.014	(1.0 ± 0.2) × 10 <sup>-5</sup>
MPYR	2381-21-7	Not measured	0.71 ± 0.078 *	0.003	(8.64 ± 0.1) × 10 <sup>-5</sup>

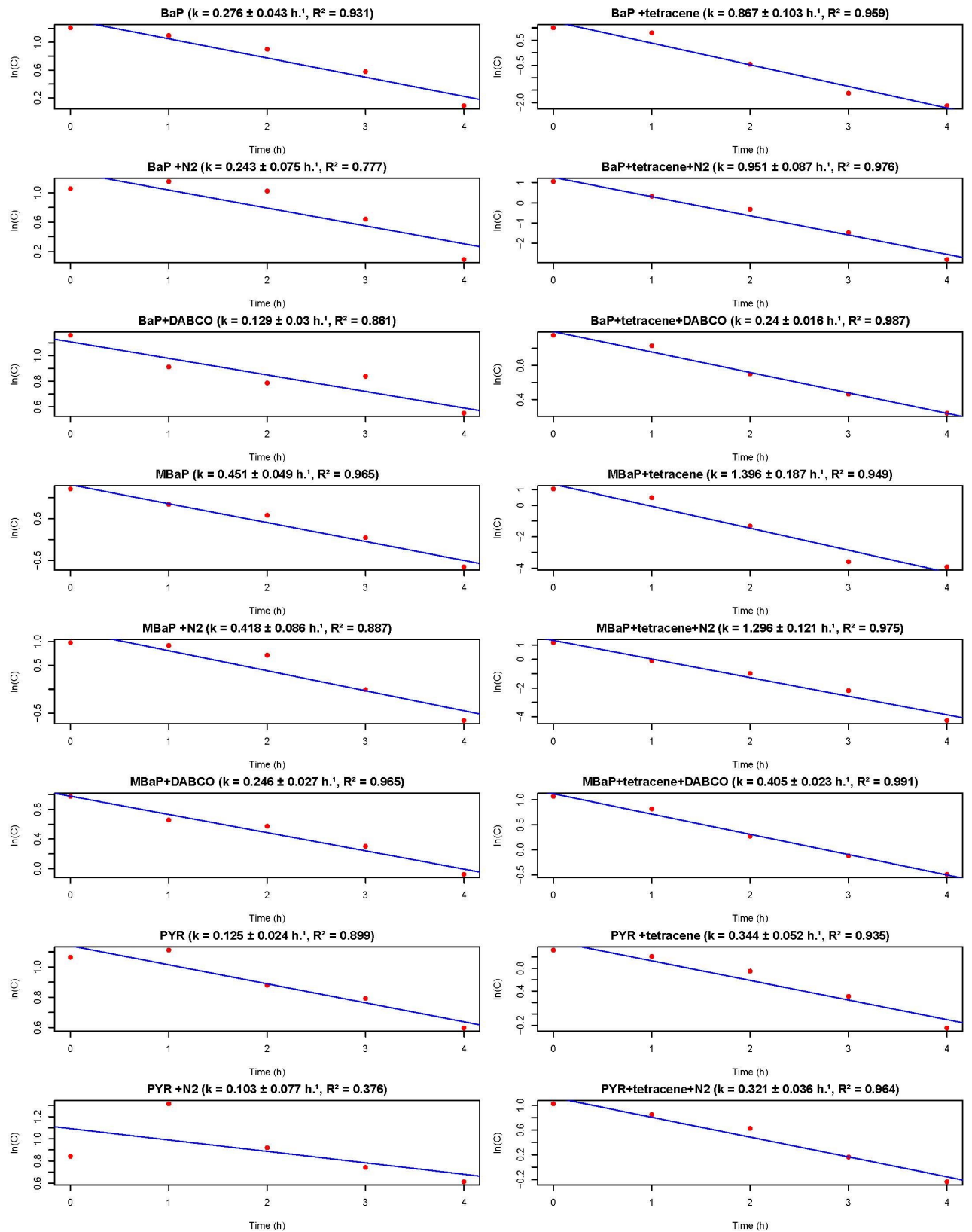
<sup>#</sup> All compounds were investigated in toluene, unless otherwise noted.

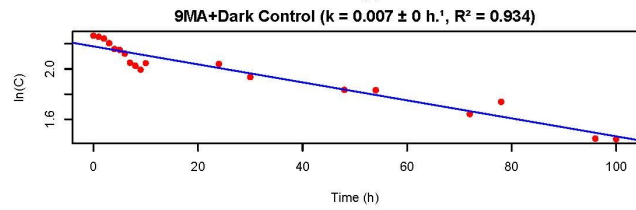
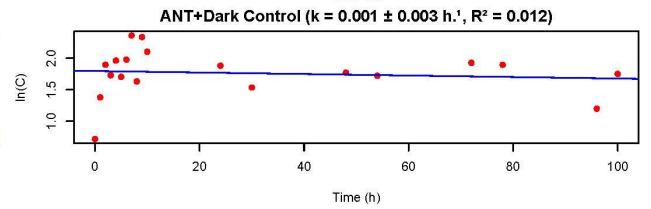
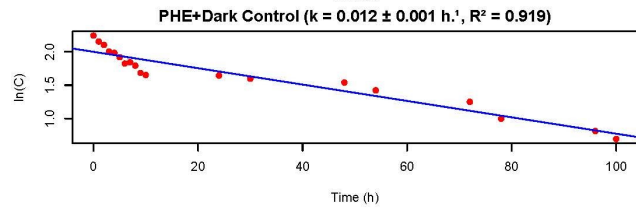
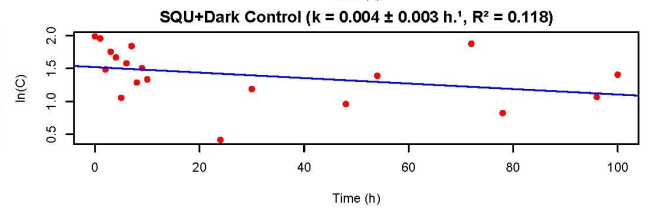
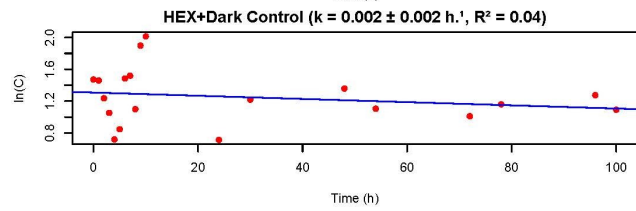
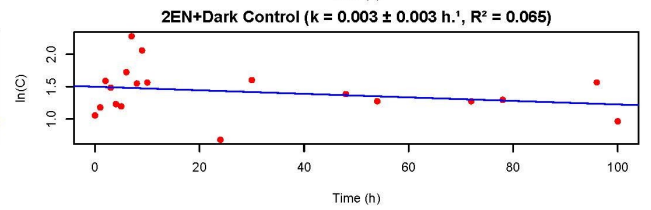
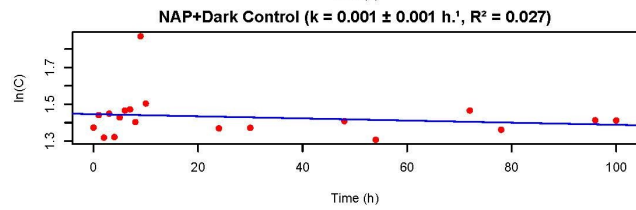
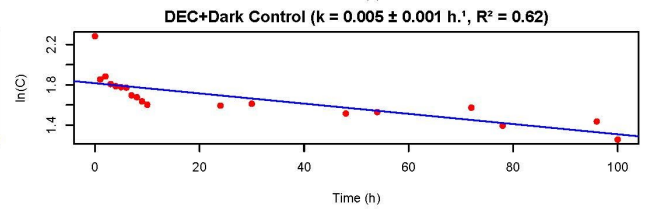
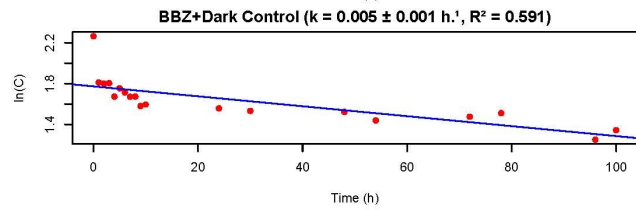
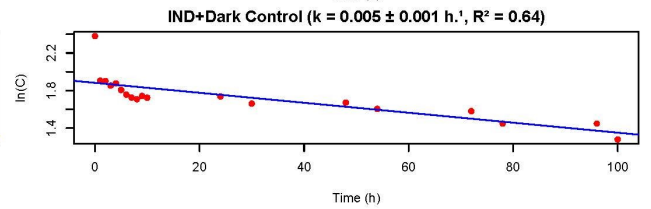
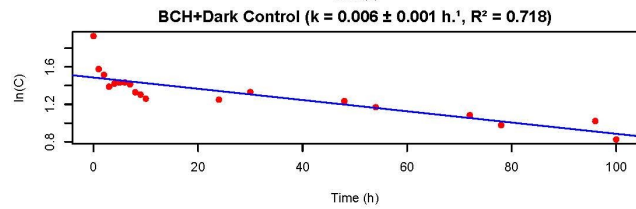
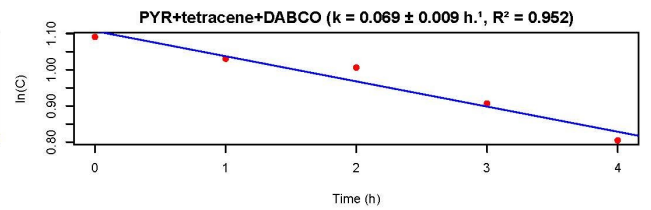
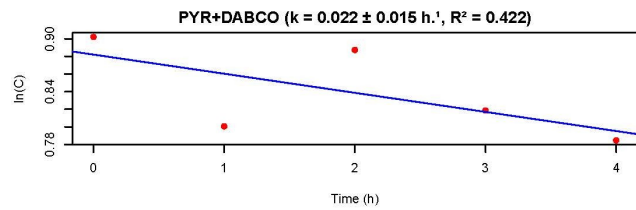
n.s. = not significant (p ≥ 0.05), \* = significant degradation (p < 0.05)

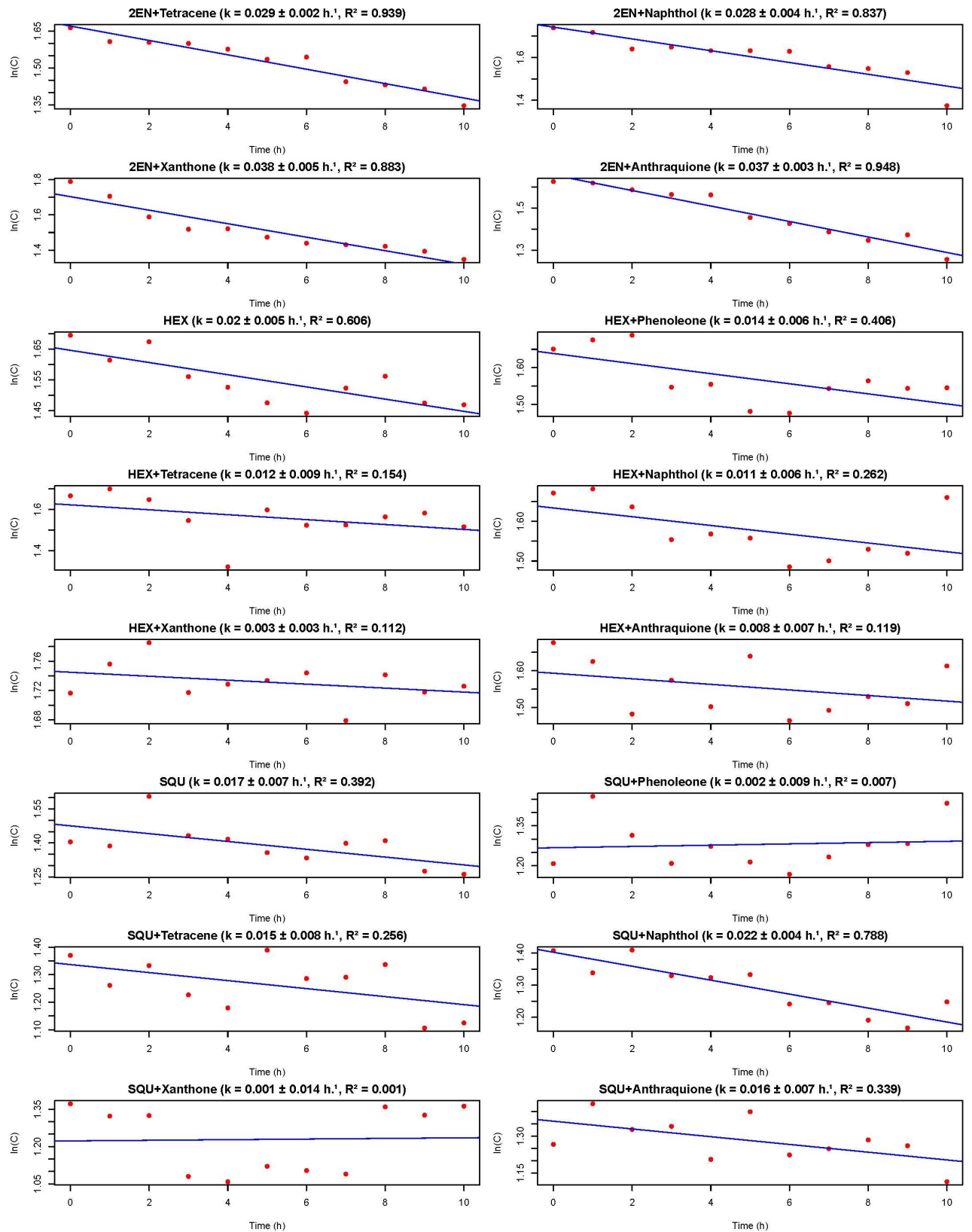
**Table A7.2** Quencher effect on ANT and 9MA indirect photolysis

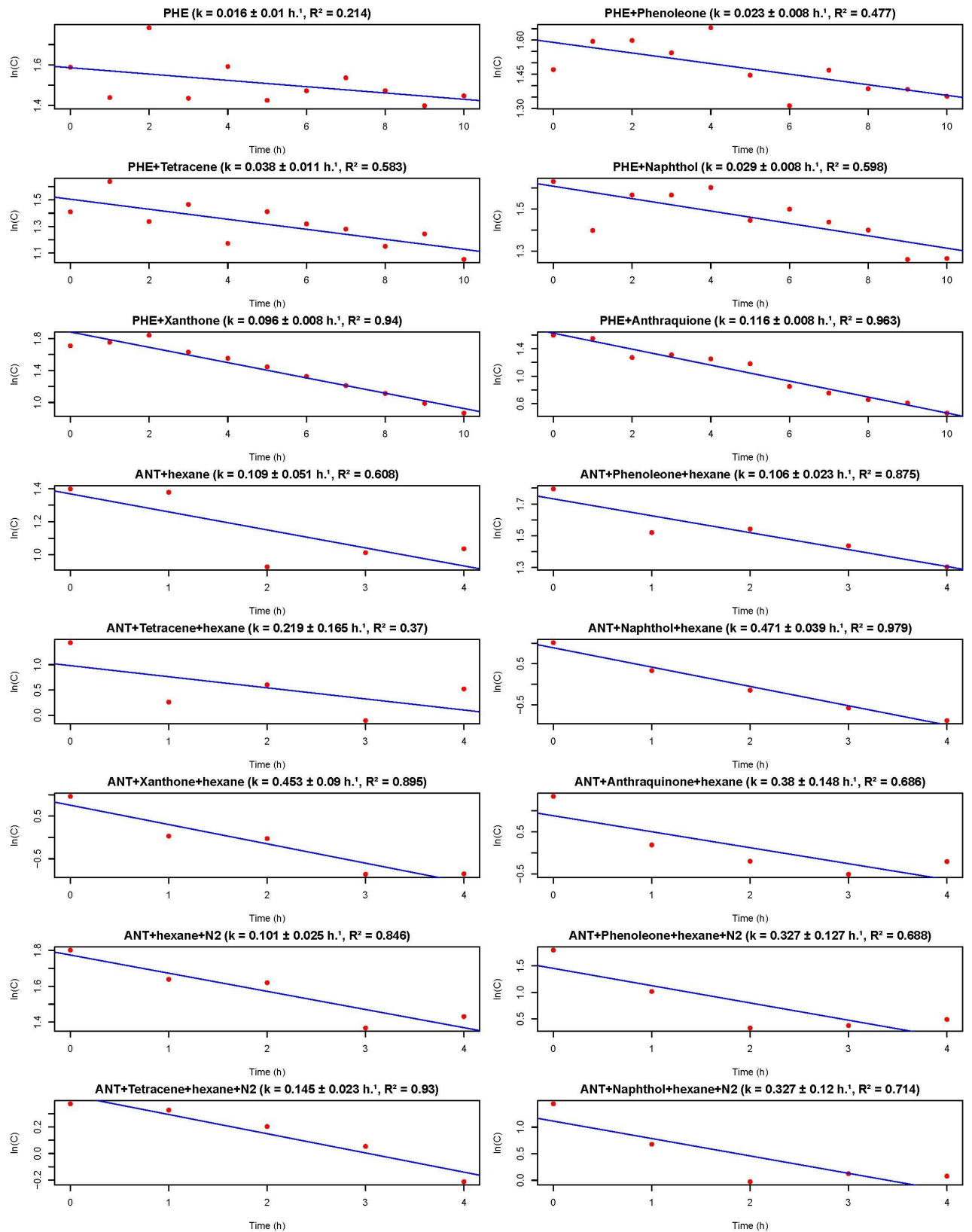
Compounds	Sensitizer	$k\ h^{-1}$			
		No quencher	50 $\mu$ M HDA	50 $\mu$ M DABCO	50 $\mu$ M FFA
<b>ANT</b>	Phenalenone	0.59±0.02	0.38±0.035	0.22±0.06	0.31±0.12
	Tetracene	0.51±0.049	0.60±0.085	0.17±0.036	0.20±0.071
	Naphthol	0.37±0.11	0.68±0.17	0.44±0.063	0.22±0.017
	Xanthone	0.53±0.13	0.65±0.54	0.42±0.13	0.13±0.058
	Anthraquinone	0.52±0.1	0.48±0.21	0.36±0.08	0.27±0.058
<b>9MA</b>	Phenalenone	0.7±0.11	1.07±0.35	0.96±0.11	0.32±0.1
	Tetracene	0.68±0.078	0.78±0.33	0.65±0.17	0.45±0.15
	Naphthol	0.59±0.1	0.71±0.17	0.42±0.076	0.48±0.15
	Xanthone	0.54±0.11	0.41±0.21	0.41±0.16	0.54±0.09
	Anthraquinone	0.56±0.11	0.36±0.21	0.41±0.09	0.50±0.14
<b>Bap</b>	Tetracene	0.89±0.11	n.a.	0.24±0.016	n.a.
<b>MBaP</b>	Tetracene	1.4±0.19	n.a.	0.41±0.023	n.a.
<b>PYR</b>	Tetracene	0.34±0.052	n.a.	0.07±0.009	n.a.
<b>MPYR</b>	Tetracene	1.31±0.17	n.a.	0.73±0.044	n.a.

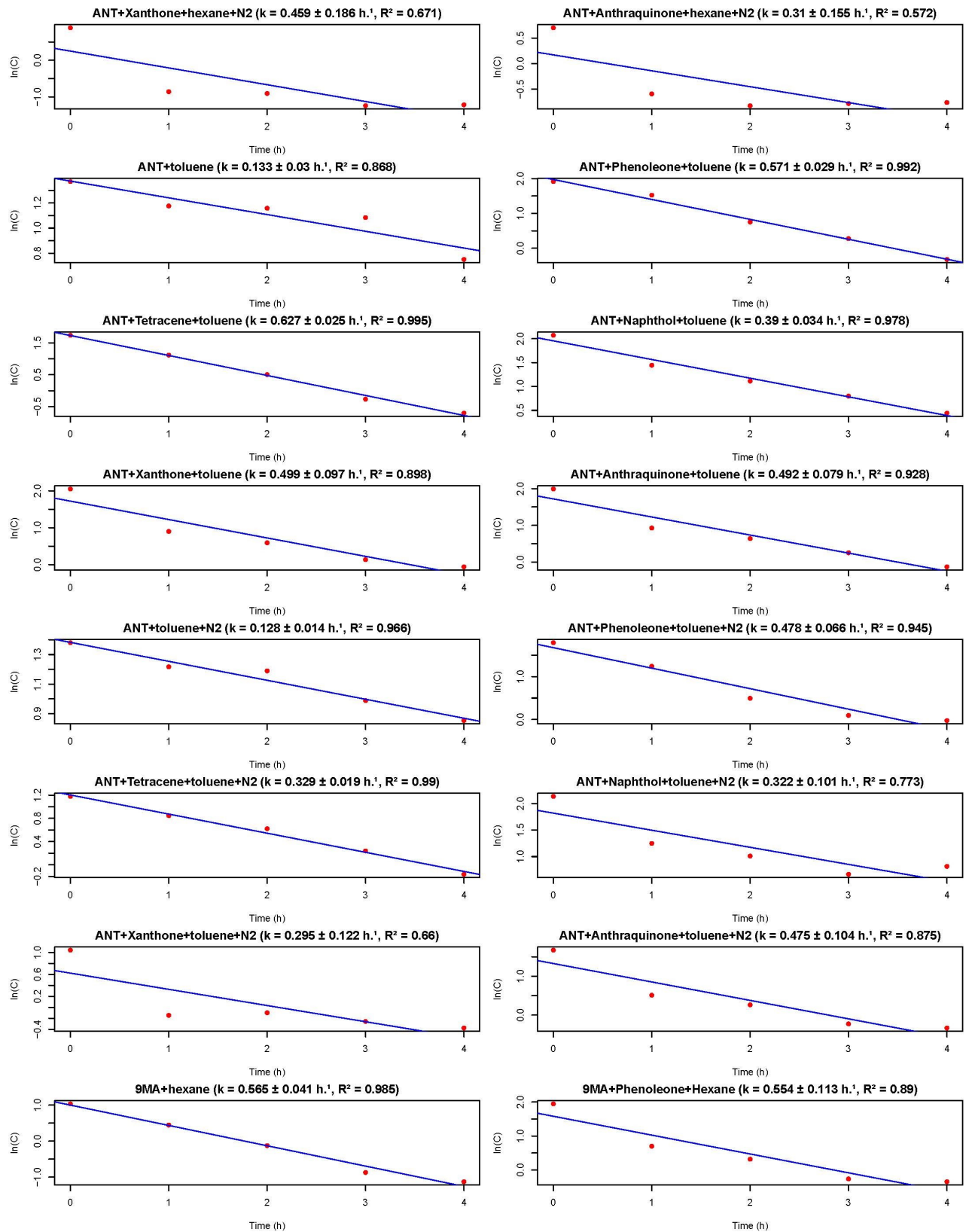


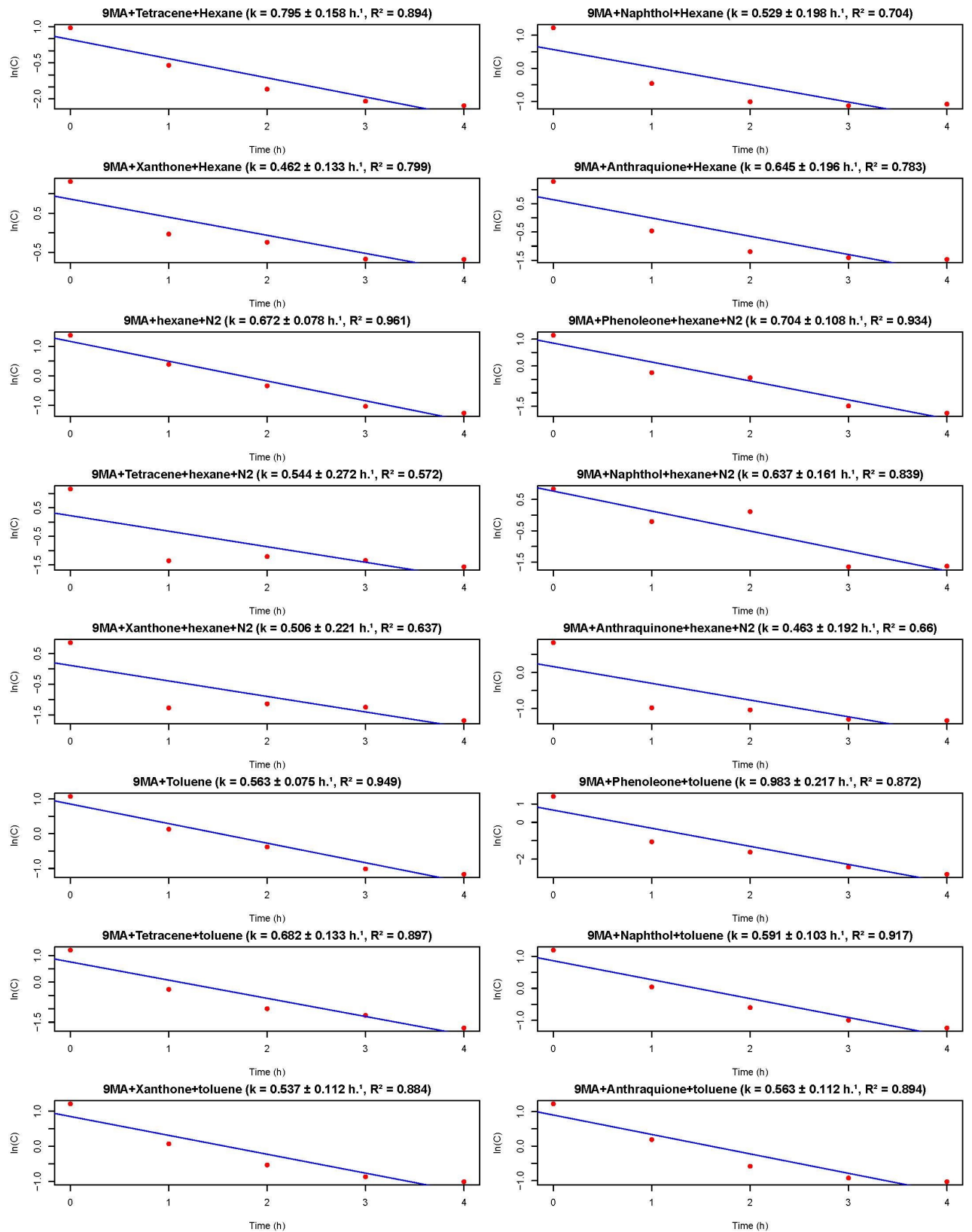


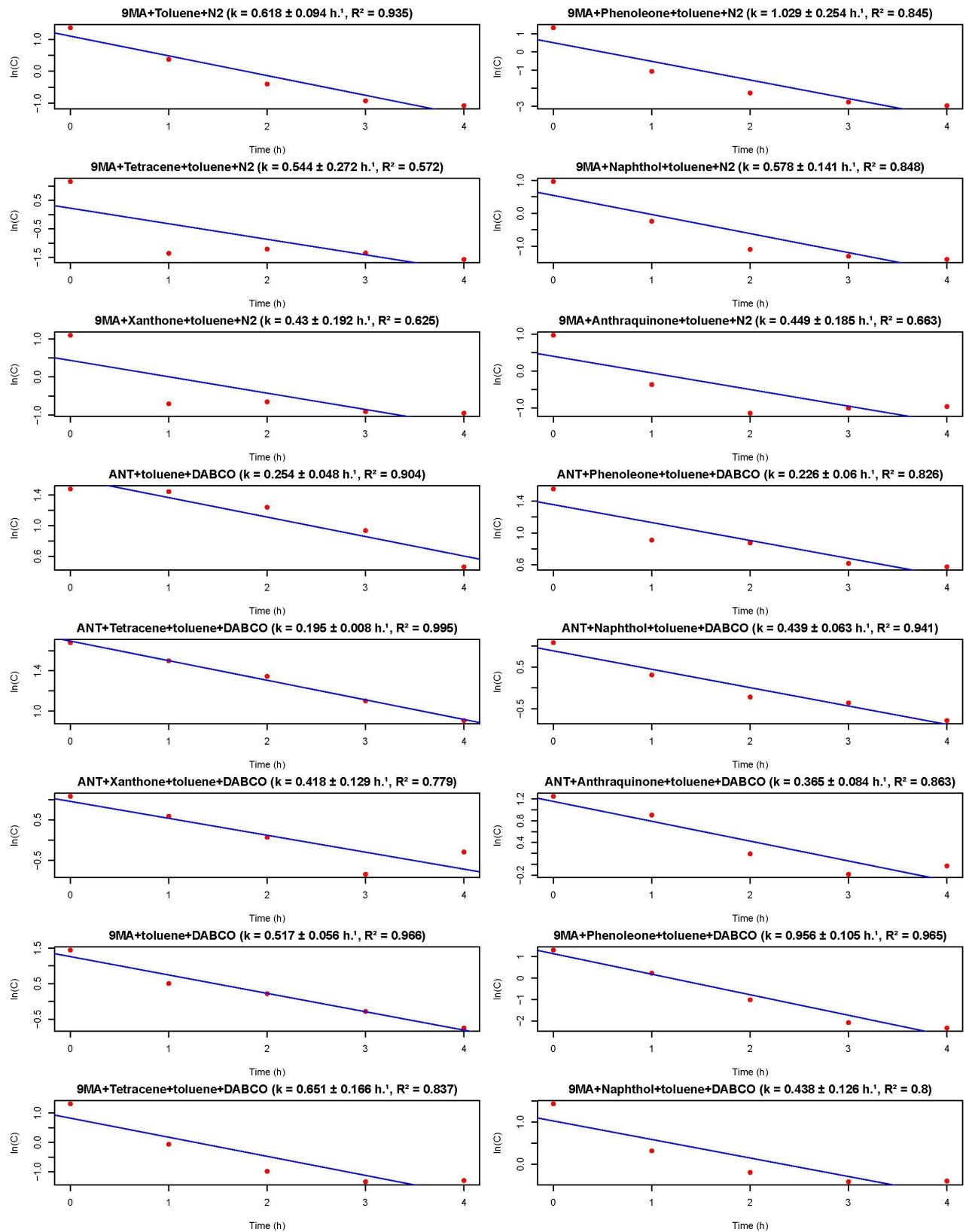


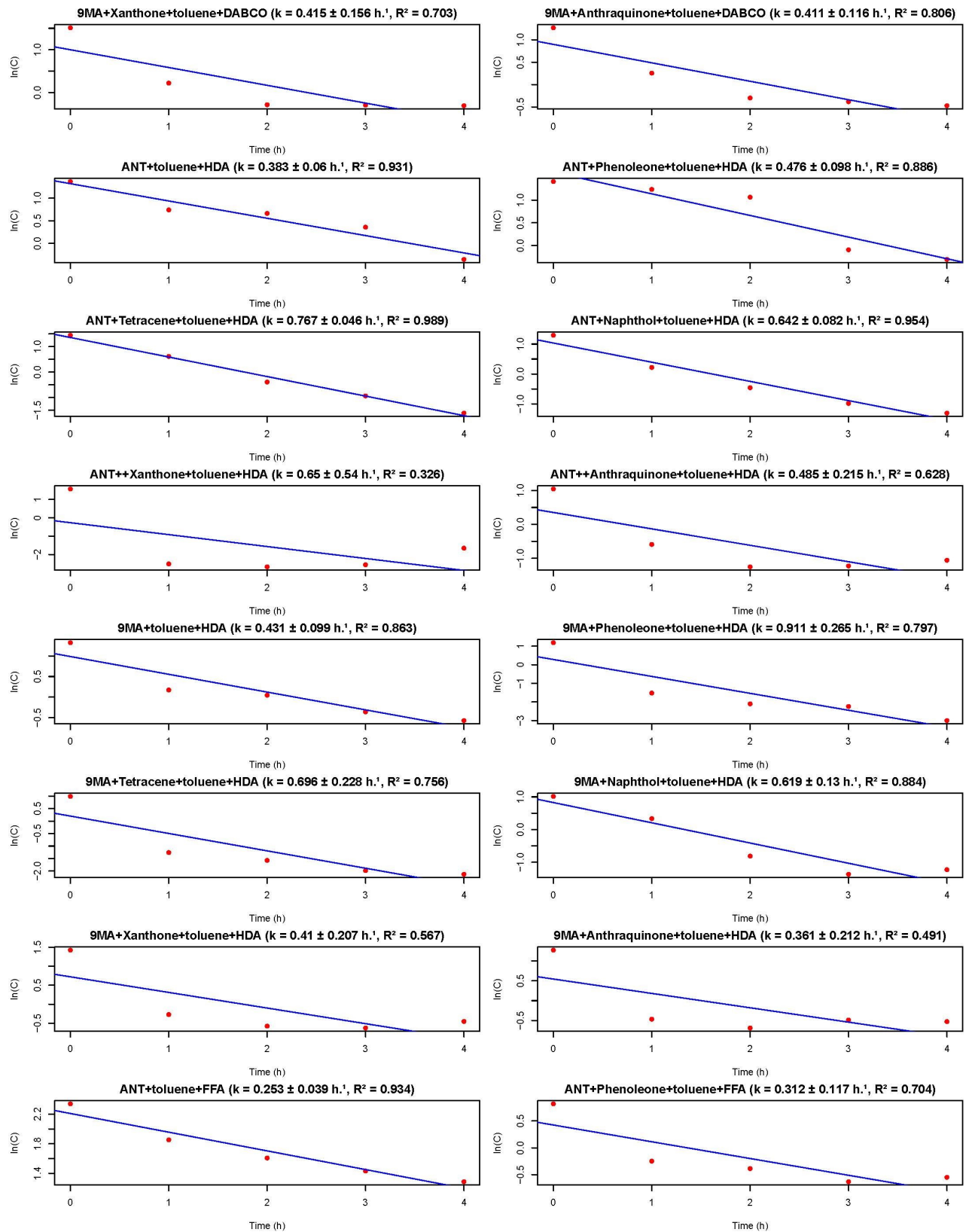


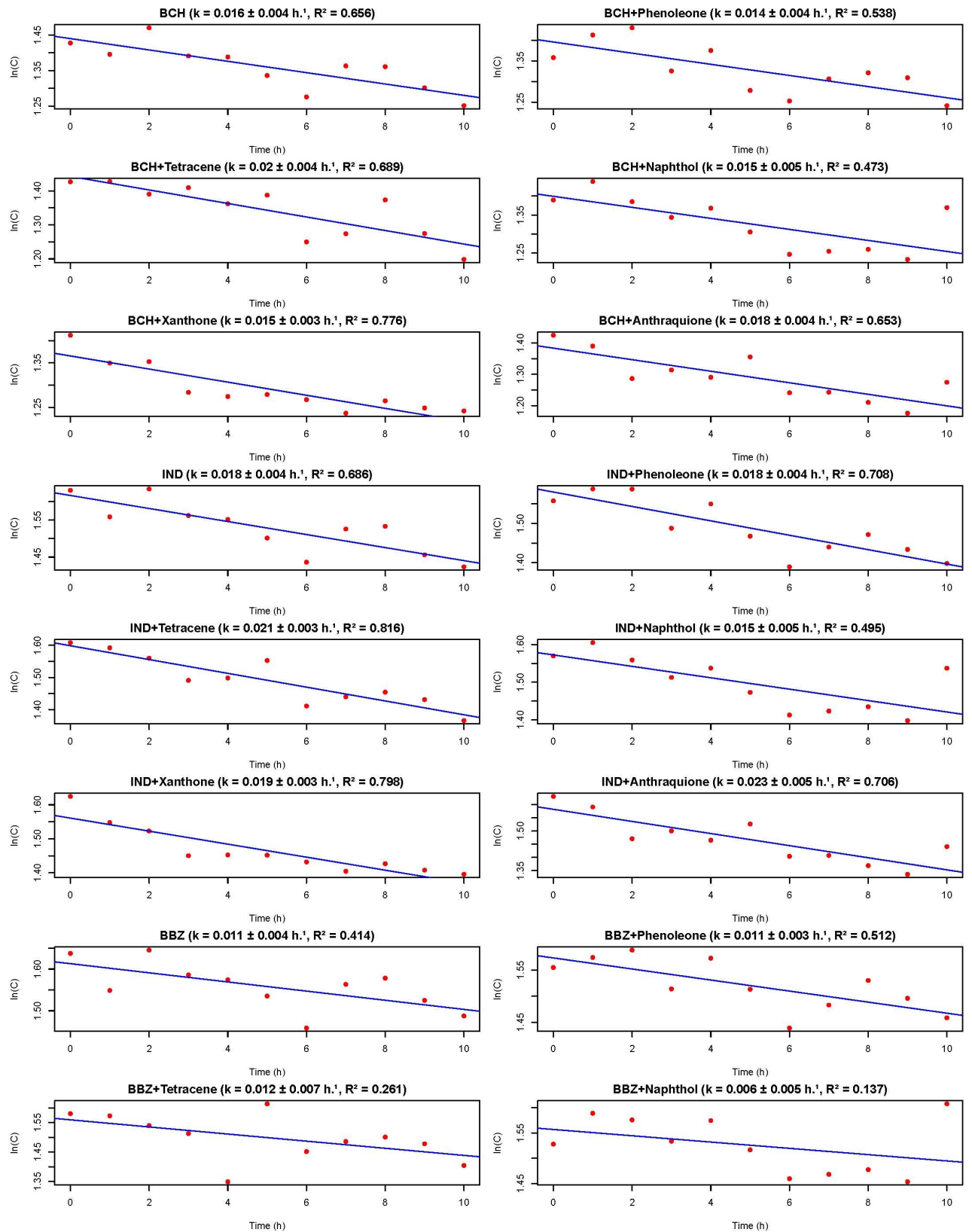


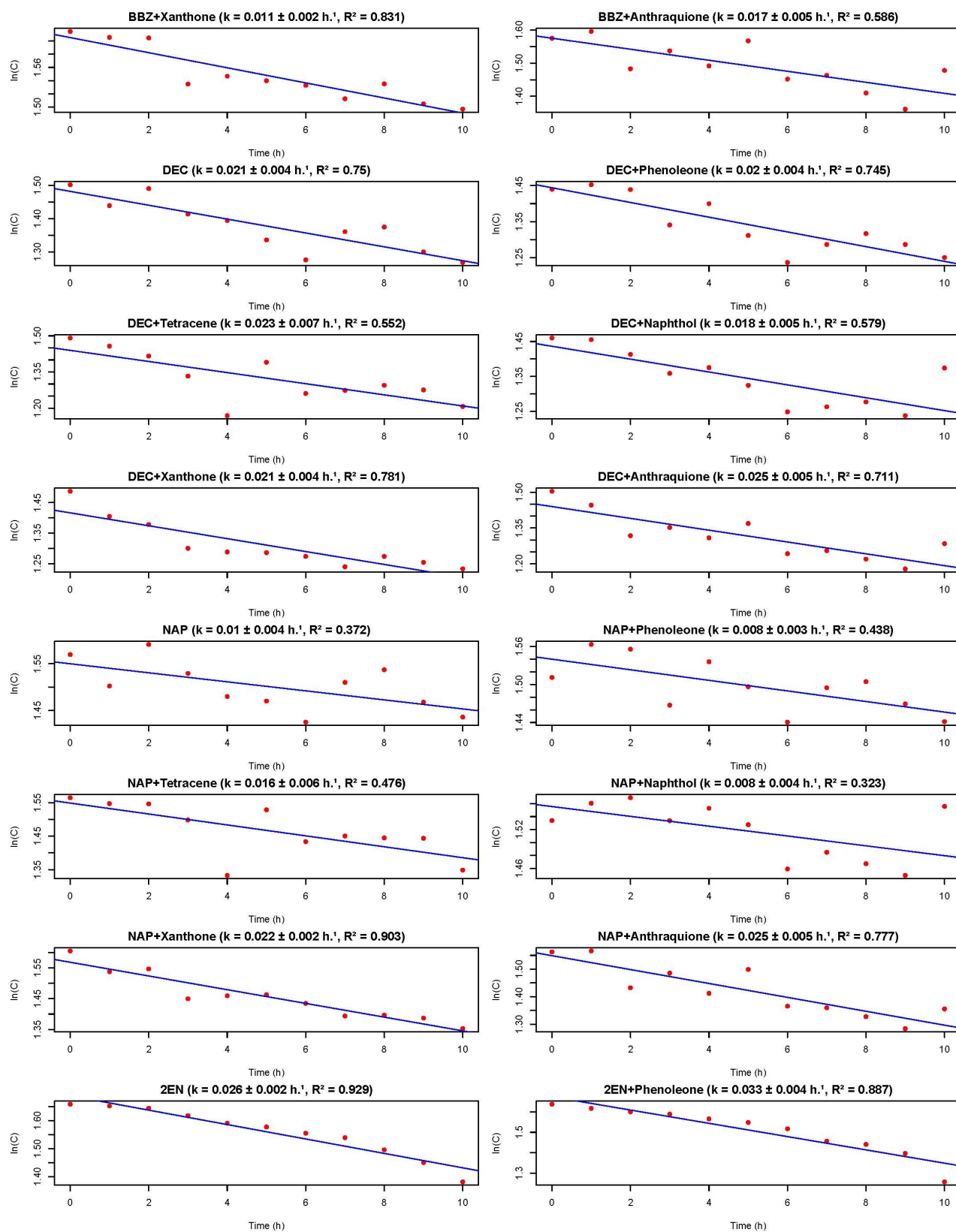












**Figure. A7.3** First-Order Kinetics of Compounds (95% Confidence Interval) \*

\*Unless otherwise noted, all experiments were conducted in air-saturated conditions.

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