

Supporting Information

Heterodiazocines: Synthesis and Photochromic Properties, Trans to Cis Switching within the Bio-optical Window

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I. Analytical equipment

NMR spectroscopy

NMR spectra were measured in deuterated solvents (Deutero). To reference the NMR spectra the following solvent signals were used:

solvent	degree of deuteration	¹ H signal	¹³ C signal
acetone-d ₆	99.8 %	2.05 (quintet)	29.84 (septet)
chloroform-d ₁	99.8 %	7.26 (s)	77.16 (triplet)
DMSO-d ₆	99.8 %	2.60 (quintet)	39.52 (septet)

NMR measurements were performed with a Bruker DRX 500 (¹H NMR: 500 MHz, ¹³C-NMR: 125 MHz) and a Bruker AV 600 (¹H NMR: 600 MHz, ¹³C NMR: 150 MHz).

Melting point

Melting points were measured with a Melting Point B-540 (Büchi) in melting point tubes.

Mass spectrometry

The high resolution (HR-EI) mass spectra were measured with an AccuTOF GCv 4G (Joel) with ionization energy of 70 eV.

IR spectroscopy

Infrared spectra were measured on a Perkin-Elmer 1600 Series FT-IR spectrometer with an A531-G Golden-Gate-Diamond-ATR-unit. Signals were abbreviated with w, m, s for weak, medium and strong signal intensity. Broad signals are additionally abbreviated with br.

UV-Vis spectroscopy

UV-Vis spectra were measured with a Cary3000 (Agilent Technologies) and with a Lambda 14 spectrometer (Perkin-Elmer) with a (Büchi) thermostat. Quartz cuvettes of 1 cm optical path length were used.

Chromatography stationary phases

For column chromatography purifications silica gel (Merck, particle size 0.040-0.063 mm) was used. R_f values were determined by thin layer chromatography on Polygeram® SilG/UV254 (Macherey Nagel, 0.2 mm particle size).

Light source

UV/vis and ^1H NMR:

The irradiation of the samples was performed with LEDs with a wavelength of 385 nm, 405 nm, 525 nm and 660 nm from Sahlmann Photochemical Solutions.

Movie

The irradiation of the samples was performed with LEDs with a wavelength of 385 nm, 530 nm and 630 nm from Sahlmann Photochemical Solutions.

Ultrasound generator

The synthesis with ultrasound was performed with a high energy Branson Sonifier 450 (450 W).

II. DFT calculations

II.1 Relative Energies and Solvent Correction

Geometry optimizations were carried out at the B3LYP/6-31G* level of density functional theory using Gaussian 09 D01. The calculated energies show that the three investigated diazocines are more stable in the *cis* configuration. However, the *trans* isomer of diazocines **1**, **2** and **3** can adopt two conformations (twist and chair, Figure S1, top). For diazocines **1** and **2** the *trans*-twist form is lower in energy than the *trans*-chair conformation by roughly 2.50 kcal/mol. Hence, the *trans*-twist conformation is predicted to be the predominant species in solution. Contrary to this, the two *trans* conformers of diazocine **3** are isoenergetic according to our calculations. To account for solvent effects a solvent correction for tetrahydrofuran (THF, Figure S1, middle) and acetonitrile (ACN, Figure S1, right) was performed on the optimized structures of Diazocines **1**, **2** and **3**. It is noteworthy that the solvent corrected energies do not differ significantly from the uncorrected values (Figure S1, left).

Table S1. Calculated (B3LYP/6-31G*) energies of the *cis*-isomer and the two *trans*-conformations of the investigated diazocines **1**, **2** and **3** relative to the *cis* isomer without and with solvent correction.

compound	solvent correction	E_{abs} [Hartree]	E_{rel} [kcal/mol]
1 <i>cis</i>	-	-650.16138410	0.00
1 <i>trans</i> -twist	-	-650.14927140	7.60
1 <i>trans</i> -chair	-	-650.14468650	10.48
2 <i>cis</i>	-	-686.05501300	0.00
2 <i>trans</i> -twist	-	-686.03507610	12.51
2 <i>trans</i> -chair	-	-686.03051040	15.38
3 <i>cis</i>	-	-1009.03156460	0.00
3 <i>trans</i> -twist	-	-1009.02336720	5.14
3 <i>trans</i> -chair	-	-1009.02345900	5.09
1 <i>cis</i>	THF	-650.16753400	0.00
1 <i>trans</i> -twist	THF	-650.15427810	8.32
1 <i>trans</i> -chair	THF	-650.14976950	11.15
2 <i>cis</i>	THF	-686.06140660	0.00
2 <i>trans</i> -twist	THF	-686.04117320	12.70
2 <i>trans</i> -chair	THF	-686.03628370	15.76
3 <i>cis</i>	THF	-1009.03846370	0.00
3 <i>trans</i> -twist	THF	-1009.02968340	5.51
3 <i>trans</i> -chair	THF	-1009.02926110	5.77
1 <i>cis</i>	ACN	-650.16892570	0.00
1 <i>trans</i> -twist	ACN	-650.15545570	8.45
1 <i>trans</i> -chair	ACN	-650.15097120	11.27
2 <i>cis</i>	ACN	-686.06277100	0.00
2 <i>trans</i> -twist	ACN	-686.04257660	12.67
2 <i>trans</i> -chair	ACN	-686.03761580	15.79
3 <i>cis</i>	ACN	-1009.03999590	0.00
3 <i>trans</i> -twist	ACN	-1009.03115180	5.55
3 <i>trans</i> -chair	ACN	-1009.03059080	5.90

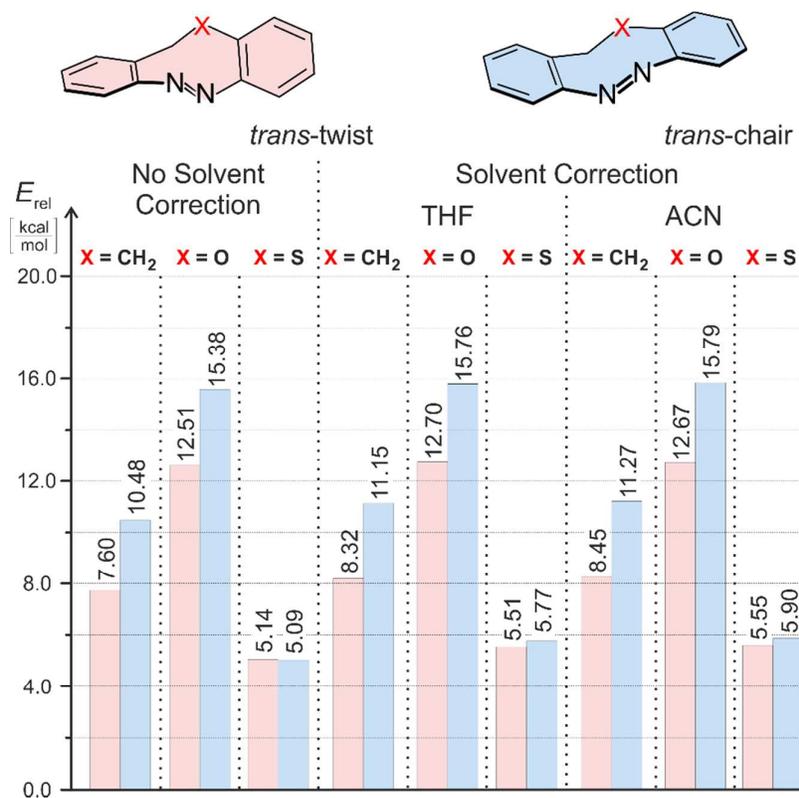


Figure S1. Bar diagram representing the relative energies (E_{rel}) of the *trans-twist* and *trans-chair* conformers of diazocines **1**, **2** and **3** relative to the respective *cis* configuration calculated at the B3LYP/6-31G* level of theory (left). Additionally, the energy values obtained after a solvent correction for tetrahydrofuran (middle) and acetonitrile (right) are provided.

II.2 Ring Strain

The standard synthetic procedures to prepare diazocines only proceed in low yields. To find the reason for the inefficient ring closure reaction we calculated the ring strain energies of diazocines **1**, **2** and **3** at the B3LYP/6-31G* level of density functional theory using an isodesmic reaction approach. According to our calculations the ring strain amounts to more than 16 kcal mol⁻¹ (see Figure S2) which explains why polymer formation is the main reaction pathway during the reductive azo coupling reaction.

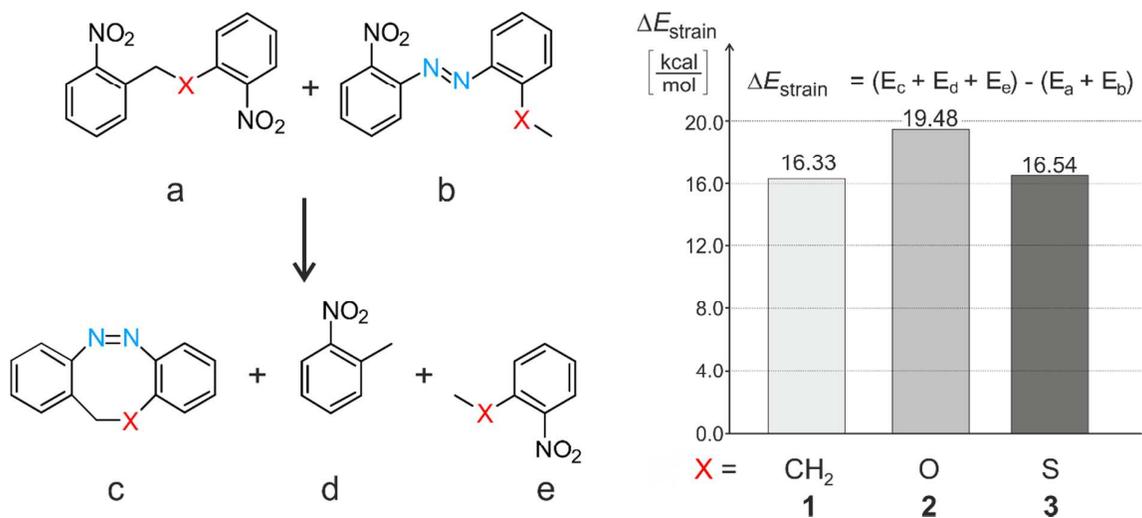


Figure S2. Left: Isodesmic reaction defining the ring strain energy of the diazocines **1**, **2**, and **3**. Right: bar energy diagram of the calculated (B3LYP/6-31G*) ring strain energies of the diazocines **1**, **2** and **3**.

II.3 Calculated UV Spectra

TD-DFT calculations were performed at the B3LYP/6-31G* level of theory using Gaussian 09.D01.² Note that all structures in Figure S2 are chiral, however, only one enantiomer is considered. The measured UV-vis spectrum of the parent diazocine **1** exhibits absorption maxima at $\lambda_{\text{max}} = 404$ nm for the *cis* isomer and at $\lambda_{\text{max}} = 490$ nm in the *trans* form. The respective calculated $n\text{-}\pi^*$ transitions (see Table S2) of **1** are at 433 nm (*cis*) and 533 nm (*trans*-twist). According to our calculations the *trans*-chair is 2.9 kcal/mol less stable than the *trans*-twist conformation and therefore should not contribute to the UV/vis spectrum. As compared to the experiment, theory predicts the $n\text{-}\pi^*$ absorptions at higher wavelengths but the distance between the $n\text{-}\pi^*$ absorption in *cis* and *trans* isomers as well as the oscillator strength of the $n\text{-}\pi^*$ transitions are in good agreement with the experimental results. Hence we assume that this level of theory is suitable to give a semi quantitative estimation of the photochromic properties of the hetero diazocines **2** and **3** (Figure S3).

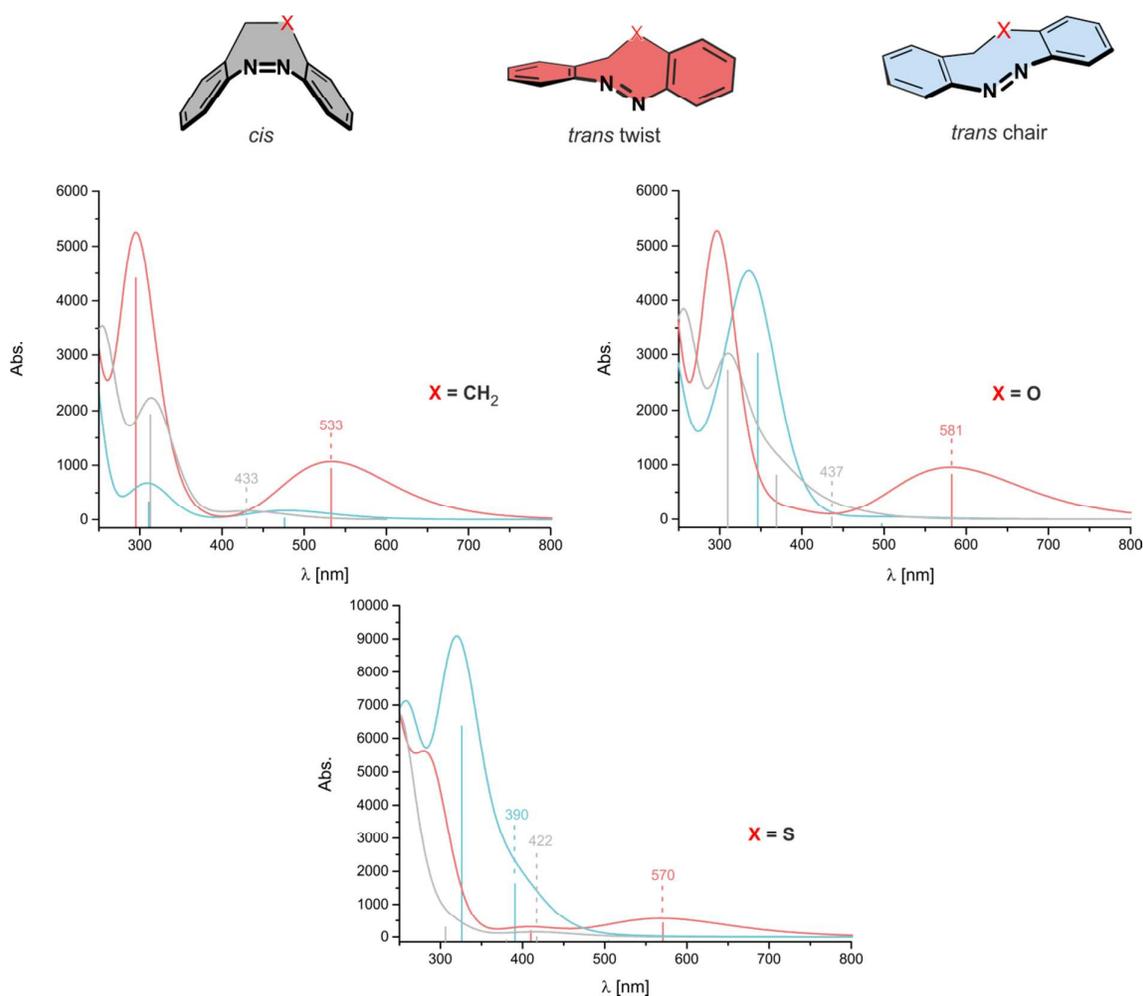


Figure S3. Calculated (TD-B3LYP/6-31G*) UV-vis spectra of the *cis* isomer (black line) and the *trans* twist (red) and *trans* chair conformation (blue) of the parent diazocine **1** (top left) and its oxygen (**2**, top right) and sulfur analogue (**3**, bottom). The bars in the corresponding color which are proportional to the oscillator strength represent the $n\text{-}\pi^*$ transitions. The UV spectra are simulated by an overlay of Gaussian functions with a half-width of 0.333 eV.

There is an overlap of the $n-\pi^*$ transition of the *cis* and *trans* twist isomer in the oxygen derivative **2**, which explains the incomplete conversion of the *cis* to the *trans* isomer upon irradiation with 385 nm. The $n-\pi^*$ transition of the *trans* twist isomer is bathochromically shifted with respect to the parent system which is also in agreement with experiment. This also applies for the sulfur analogue **3** in which the distance of the $n-\pi^*$ transitions of *cis* and *trans-twist* increases to 148 nm. However, according to the calculations the *trans-twist* and *trans-chair* conformations of the sulfur bridged azobenzene **3** are almost isoenergetic. Therefore, both *trans* conformations have to be included in the prediction of the UV/vis spectrum. The *chair* conformer of **3** exhibits a $n-\pi^*$ transition with a high oscillator strength ($f = 0.0430$) at 390 nm resulting in a substantial overlap with the transition of the *cis* isomer (422 nm). Hence, the percentage of the *trans* isomer in the photostationary state of **3** upon irradiation with 405 nm is predicted to be lower in comparison to the parent system **1** and the oxygen analogue **2**. So, we conclude that any measure (e.g. substitution) which disfavors the *trans* chair conformation would improve the photochromic properties of the sulfur bridged diazocine. Generally it can be stated that the *trans* twist conformations are responsible for the unusually bathochromic $n-\pi^*$ absorptions of heterodiazocines **2** and **3**.

Table S2. Calculated (TD-B3LYP/6-31G*) $n-\pi^*$ transitions and oscillator strengths (f) of the *cis*, *trans* twist and *trans* chair configurations of the diazocines **1**, **2** and **3**. Experimental absorption wavelengths are given as λ_{\max} .

compound	isomer/conform.	calc. λ [nm]	f	exp. λ_{\max} [nm]
1 (CH ₂)	<i>trans-twist</i>	533	0.0264	490
		294	0.1148	
	<i>trans-chair</i>	478	0.0041	
		318	0.0115	
	<i>cis</i>	433	0.0038	404
		317	0.0507	
2 (O)	<i>trans-twist</i>	581	0.0236	522
		497	0.0011	
	<i>trans-chair</i>	346	0.0776	
		437	0.0045	
	<i>cis</i>	367	0.0232	404
		311	0.0701	
3 (S)	<i>trans-twist</i>	570	0.0139	523
		408	0.0075	
	<i>trans-chair</i>	504	0.0009	
		390	0.0430	
	<i>cis</i>	326	0.1607	
		422	0.0033	
		379	0.0008	396
		312	0.0107	

II.4 Barriers of the Thermal *Trans* to *Cis* Isomerization

The transition states of the thermal *trans* to *cis* isomerization of diazocine **1**, **2** and **3** were optimized at the B3LYP/6-31G* level of density functional theory. The energy barrier for the isomerization process decreases in the order **3** (20.84 kcal/mol) > **1** (19.87 kcal/mol) > **2** (17.28 kcal/mol). It is noteworthy that the calculated barrier of diazocine **2** is in very good agreement with the experimentally derived value (17.01 ± 0.11 kcal/mol). Furthermore, the order of the calculated energy barriers are qualitatively in very good agreement with the thermal half-lives which decrease in the order **3** (3.5 d) > **1** (4.5 h) > **2** (89 sec).

Table S3. Calculated (B3LYP/6-31G*) energies of the *trans*-twist and *cis* isomer of the diazocines **1**, **2** and **3** as well as the respective transition states. The barriers of the thermal *trans* to *cis* isomerization are provided for all compounds.

compound	E_{abs} [Hartree]	E_{rel} [kcal/mol]	$E_{\text{A,exp}}$ [kcal/mol]
1 <i>trans</i> twist	-650.14927140	0.00	no exp. value
1 transition state	-650.11760920	19.87	
1 <i>cis</i>	-650.16138410	-7.60	
2 <i>trans</i> twist	-686.03507610	0.00	17.01 ± 0.11
2 transition state	-686.00754340	17.28	
2 <i>cis</i>	-686.05501300	-12.51	
3 <i>trans</i> twist	-1009.02336720	0.00	no exp. value
3 transition state	-1008.99016300	20.84	
3 <i>cis</i>	-1009.03156460	-5.14	

II.5 XYZ Coordinates of the B3LYP/6-31G* Optimized Structures of 1, 2 and 3

II.5.1 Parent Diazocine (X = CH₂) (1)

trans-twist

E_{B3LYP/6-31G*} = -650.1492714 Hartree

NImag = 0

C	0.583470	1.549820	0.525660
H	0.168850	1.333220	1.517200
H	0.957570	2.578820	0.581860
C	-4.231370	0.383960	-0.202230
C	-3.100260	1.163680	-0.456600
C	-1.808450	0.661250	-0.268850
C	-1.701310	-0.669420	0.198820
C	-2.819900	-1.440830	0.507780
C	-4.092570	-0.918450	0.281270
C	1.808480	0.661250	0.268800
N	-0.366280	-1.045040	0.511330
N	0.366230	-1.044820	-0.511380
C	1.701330	-0.669420	-0.198880
C	3.100270	1.163700	0.456570
C	4.231380	0.383970	0.202190
C	4.092580	-0.918440	-0.281250
C	2.819900	-1.440850	-0.507760
H	-5.221130	0.801980	-0.363940
H	-3.223340	2.186270	-0.806910
H	-2.684240	-2.444820	0.898840
H	-4.971170	-1.521670	0.492300
H	3.223340	2.186280	0.806900
H	5.221150	0.801990	0.363900
H	4.971170	-1.521690	-0.492250
H	2.684290	-2.444870	-0.898760
C	-0.583490	1.549930	-0.525560
H	-0.168890	1.333620	-1.517160
H	-0.957640	2.578920	-0.581460

trans-chair

E_{B3LYP/6-31G*} = -650.1446865 Hartree

NImag = 1 (-73 Hz)

C	4.052970	-0.994450	-0.097320
C	2.788010	-1.543450	0.130500
C	1.699650	-0.689780	0.245090
C	4.205970	0.388610	-0.189080
C	3.099270	1.230750	-0.042160
C	1.819130	0.715930	0.182890
C	0.628770	1.634070	0.473060
C	-0.628400	1.633610	-0.473430
C	-1.818840	0.715690	-0.182770
C	-1.699800	-0.690080	-0.244920
C	-3.098860	1.230890	0.042160
C	-4.205820	0.389100	0.189100
C	-4.053270	-0.994010	0.097320
C	-2.788480	-1.543390	-0.130510
N	0.343690	-1.058420	0.523640
N	-0.344020	-1.059570	-0.523340
H	4.913100	-1.649280	-0.206390
H	2.643750	-2.617520	0.198030
H	5.188720	0.816760	-0.365980
H	3.233350	2.308980	-0.097090
H	0.284900	1.445110	1.498310
H	1.018890	2.658460	0.467120
H	-0.284430	1.443880	-1.498510
H	-1.018570	2.657980	-0.468360
H	-3.232640	2.309160	0.096950
H	-5.188430	0.817560	0.365990
H	-4.913600	-1.648560	0.206340
H	-2.644570	-2.617510	-0.198110

cis

$E_{\text{B3LYP/6-31G}^*} = -650.1613841$ Hartree

NImag = 0

C	0.82786	1.80316	1.05208
H	0.78594	1.51621	2.1079
H	1.37882	2.74941	1.00999
C	-3.17058	0.07164	-1.46035
C	-2.32132	1.07111	-0.99507
C	-1.42218	0.86776	0.0652
C	-1.40423	-0.4137	0.64943
C	-2.2912	-1.41029	0.21471
C	-3.1551	-1.18327	-0.84967
C	1.57066	0.74452	0.27476
N	-0.62602	-0.82391	1.80059
N	0.61193	-0.97243	1.75627
C	1.38376	-0.61064	0.59658
C	2.45528	1.05577	-0.76358
C	3.1248	0.05535	-1.46832
C	2.93707	-1.28504	-1.12212
C	2.08698	-1.618	-0.07011
H	-3.84448	0.27437	-2.288
H	-2.34667	2.05106	-1.46653
H	-2.27734	-2.36758	0.72758
H	-3.81717	-1.97443	-1.19003
H	2.61896	2.10027	-1.02027
H	3.80285	0.32141	-2.27442
H	3.46474	-2.06869	-1.65864
H	1.95339	-2.65088	0.23792
C	-0.60689	2.06326	0.52986
H	-1.16366	2.59735	1.31352
H	-0.54621	2.75608	-0.31733

**Transition state of thermal *trans* to *cis*
isomerization**

$E_{\text{B3LYP/6-31G}^*} = -650.11760920$ Hartree

NImag = 1 (-455 Hz)

C	-4.21221	-0.68764	0.05872
C	-3.01850	-1.36541	0.28203
C	-1.78488	-0.72355	0.12089
C	-1.71250	0.64356	-0.24475
C	-2.93258	1.30420	-0.43588
C	-4.16442	0.65930	-0.30045
N	-0.66191	-1.57022	0.46050
N	0.45642	-1.16541	0.11485
C	1.69769	-0.68668	0.01636
C	2.80321	-1.44217	-0.44546
C	4.05486	-0.84346	-0.51591
C	4.24387	0.47347	-0.07985
C	3.15166	1.22060	0.37544
C	1.86812	0.68330	0.38771
C	0.62172	1.46349	0.71922
H	4.90029	-1.41882	-0.88423
H	2.64873	-2.47273	-0.74823
H	5.23323	0.92062	-0.10776
H	3.29517	2.25529	0.68087
H	-3.00211	-2.40757	0.58781
H	-5.16457	-1.19701	0.17483
H	-5.08292	1.21536	-0.46840
H	0.89595	2.50446	0.92226
H	0.14839	1.09039	1.63709
H	-2.91591	2.35819	-0.70466
C	-0.42820	1.42901	-0.45339
H	0.07784	1.07065	-1.35699
H	-0.72264	2.46247	-0.66813

II.5.2 Oxygen-Diazocine (X = O) (2)

trans-twist

$E_{\text{B3LYP/6-31G}^*} = -686.0350761$ Hartree

NImag = 0

C	0.469660	1.463050	0.527200
H	0.052590	1.225130	1.510480
H	0.753710	2.520130	0.536140
C	-4.125770	0.495780	-0.308610
C	-2.949180	1.220110	-0.514740
C	-1.713390	0.636070	-0.239980
C	-1.676610	-0.697270	0.240480
C	-2.852590	-1.395150	0.498630
C	-4.081900	-0.802900	0.203980
C	1.736530	0.639530	0.249560
N	-0.354440	-1.094420	0.581470
N	0.371440	-1.155950	-0.448500
C	1.690440	-0.710500	-0.171320
C	2.993450	1.230950	0.388240
C	4.163550	0.508210	0.137550
C	4.089940	-0.815580	-0.299400
C	2.846880	-1.421580	-0.483040
H	-5.082710	0.958760	-0.532550
H	-2.970140	2.239010	-0.888660
H	-2.795010	-2.404610	0.894850
H	-5.001630	-1.354360	0.375560
H	3.061470	2.273310	0.692300
H	5.130300	0.988380	0.259270
H	4.998470	-1.371910	-0.512180
H	2.765580	-2.443220	-0.841560
O	-0.572230	1.377190	-0.474470

trans-chair

$E_{\text{B3LYP/6-31G}^*} = -686.0305104$ Hartree

NImag = 0

C	0.567250	1.604580	0.455740
H	0.229360	1.464020	1.487220
H	0.828480	2.657420	0.309560
C	-4.097540	0.589450	0.044780
C	-2.902100	1.305410	-0.036590
C	-1.679020	0.636550	-0.129370
C	-1.688770	-0.787910	-0.143350
C	-2.888370	-1.496160	-0.118060
C	-4.094720	-0.807700	0.000220
C	1.798280	0.745460	0.190120
N	-0.401130	-1.365130	-0.326540
N	0.321590	-0.923460	0.603050
C	1.680010	-0.659100	0.292790
C	3.049240	1.274590	-0.121680
C	4.153970	0.430270	-0.286090
C	4.010450	-0.951780	-0.160830
C	2.759840	-1.512870	0.122180
H	-5.038120	1.127370	0.125220
H	-2.897730	2.390950	-0.050900
H	-2.860850	-2.580950	-0.162130
H	-5.029540	-1.358190	0.051720
H	3.166190	2.350740	-0.228420
H	5.127320	0.855040	-0.514440
H	4.871340	-1.601230	-0.293950
H	2.627110	-2.586820	0.207230
O	-0.559740	1.384630	-0.440730

cis $E_{\text{B3LYP/6-31G}^*} = -686.0550130$ Hartree

NImag = 0

C	0.633890	1.404790	1.385290
H	0.444770	0.858180	2.315340
H	1.078010	2.369030	1.641610
C	-3.339270	0.508460	-1.249740
C	-2.393020	1.322670	-0.645930
C	-1.412670	0.801560	0.216430
C	-1.398260	-0.588010	0.469580
C	-2.403940	-1.385130	-0.110740
C	-3.345460	-0.865370	-0.985840
C	1.535320	0.635800	0.457960
N	-0.590530	-1.361700	1.394580
N	0.646820	-1.499570	1.313440
C	1.454010	-0.762850	0.390340
C	2.459180	1.292850	-0.363740
C	3.273780	0.578810	-1.239440
C	3.191190	-0.817140	-1.284550
C	2.305510	-1.490720	-0.449780
H	-4.077890	0.945960	-1.915550
H	-2.377320	2.393960	-0.819820
H	-2.409950	-2.439180	0.151140
H	-4.088250	-1.515880	-1.437290
H	2.531870	2.376790	-0.314110
H	3.980500	1.104430	-1.875080
H	3.832300	-1.379890	-1.957310
H	2.252350	-2.575190	-0.441100
O	-0.615240	1.759550	0.769620

Transition state of thermal *trans* to *cis* isomerization $E_{\text{B3LYP/6-31G}^*} = -686.00754340$ Hartree

NImag = 1 (-528 Hz)

C	-4.147310	-0.636550	-0.067930
C	-3.000190	-1.315200	0.324740
C	-1.740950	-0.709650	0.236910
C	-1.626500	0.643280	-0.178390
C	-2.794110	1.317820	-0.554800
C	-4.034030	0.682640	-0.520050
N	-0.619800	-1.508170	0.657210
N	0.436690	-1.205200	0.082770
C	1.679530	-0.733210	-0.016890
C	2.800200	-1.422780	-0.525920
C	4.020880	-0.759180	-0.599450
C	4.162420	0.558610	-0.151100
C	3.042880	1.244610	0.332500
C	1.792720	0.638740	0.373800
C	0.534180	1.343350	0.794820
O	-0.467860	1.358750	-0.267820
H	4.883810	-1.289710	-0.993930
H	2.692430	-2.450680	-0.855250
H	5.127880	1.052650	-0.195980
H	3.136590	2.281940	0.648750
H	-3.038400	-2.339950	0.683720
H	-5.117070	-1.122340	-0.020720
H	-4.920920	1.231290	-0.825430
H	0.743940	2.394750	1.012680
H	0.079180	0.898130	1.688960
H	-2.701160	2.352530	-0.869700

II.5.3 Sulfur-Diazocine (X = S) (3)

trans-twist

$E_{\text{B3LYP/6-31G}^*} = -1009.0233672$ Hartree

NImag = 0

C	0.776490	1.449660	0.761490
H	0.302970	1.139860	1.693480
H	1.172930	2.456950	0.922860
C	-4.280540	0.098760	-0.205640
C	-3.217650	0.986590	-0.386650
C	-1.900220	0.570560	-0.168110
C	-1.677920	-0.759580	0.249610
C	-2.738800	-1.629460	0.483050
C	-4.044790	-1.205010	0.233080
C	1.932700	0.535620	0.364880
N	-0.317310	-1.041260	0.571940
N	0.408890	-1.130590	-0.448330
C	1.751320	-0.762780	-0.166910
C	3.247270	0.996020	0.493290
C	4.336940	0.199190	0.134300
C	4.129460	-1.072490	-0.403050
C	2.830110	-1.542790	-0.582370
H	-5.296720	0.438160	-0.385380
H	-3.408830	2.011240	-0.692890
H	-2.532170	-2.635750	0.835270
H	-4.874070	-1.888370	0.391410
H	3.422280	1.996670	0.881910
H	5.346380	0.582180	0.254700
H	4.974590	-1.688080	-0.697570
H	2.638820	-2.515850	-1.024710
S	-0.578330	1.757520	-0.492880

trans-chair

$E_{\text{B3LYP/6-31G}^*} = -1009.0234590$ Hartree

NImag = 0

C	0.973680	1.697760	0.613490
H	0.599150	1.582990	1.632550
H	1.359330	2.717030	0.501720
C	-4.242860	0.257120	0.105480
C	-3.115960	1.079570	0.057310
C	-1.826420	0.538100	-0.053440
C	-1.709160	-0.884960	-0.085410
C	-2.844240	-1.698430	-0.080970
C	-4.110740	-1.131820	0.031650
C	2.061930	0.688580	0.310610
N	-0.415530	-1.445620	-0.209510
N	0.335830	-0.768120	0.537640
C	1.713320	-0.680400	0.286850
C	3.382060	1.034290	0.022450
C	4.330770	0.037460	-0.232620
C	3.965060	-1.311380	-0.235080
C	2.640530	-1.681120	0.007090
H	-5.228490	0.706640	0.189160
H	-3.231630	2.158490	0.086670
H	-2.708960	-2.774510	-0.137170
H	-4.989980	-1.768850	0.063360
H	3.676550	2.080920	0.007090
H	5.361220	0.316980	-0.433840
H	4.710870	-2.075360	-0.436430
H	2.326720	-2.720120	-0.009000
S	-0.539040	1.725210	-0.515350

cis

$E_{\text{B3LYP/6-31G}^*} = -1009.0315646$ Hartree

NImag = 0

C	1.058910	2.000580	0.478000
H	1.138000	2.102700	1.562830
H	1.572720	2.846390	0.013940
C	-3.011880	-0.724630	-1.436860
C	-2.298740	0.458800	-1.264200
C	-1.447260	0.644550	-0.162550
C	-1.318060	-0.407400	0.763370
C	-2.046830	-1.590070	0.594700
C	-2.880790	-1.757330	-0.506730
C	1.649840	0.701560	0.019870
N	-0.569070	-0.311350	1.996840
N	0.674970	-0.374850	2.001650
C	1.412610	-0.466210	0.762930
C	2.456650	0.607770	-1.119930
C	3.021600	-0.608160	-1.501870
C	2.795210	-1.752850	-0.733880
C	2.003910	-1.680860	0.411190
H	-3.663610	-0.839820	-2.298140
H	-2.389810	1.261050	-1.990230
H	-1.952480	-2.368930	1.345880
H	-3.430780	-2.685650	-0.631320
H	2.642170	1.502480	-1.709300
H	3.646360	-0.660160	-2.388810
H	3.240660	-2.701230	-1.020910
H	1.832210	-2.556830	1.029530
S	-0.734230	2.271800	0.017060

**Transition state of thermal *trans* to *cis*
isomerization**

$E_{\text{B3LYP/6-31G}^*} = -1008.99016300$ Hartree

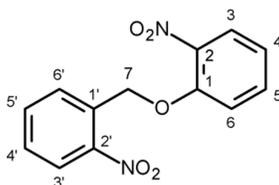
NImag = 1 (-435 Hz)

C	4.198290	0.920420	0.043830
C	2.973150	1.510780	0.326660
C	1.770760	0.801200	0.192030
C	1.792950	-0.564750	-0.178150
C	3.043300	-1.151410	-0.432880
C	4.227060	-0.419630	-0.348120
N	0.626850	1.626720	0.515810
N	-0.496760	1.253200	0.164050
C	-1.735900	0.784350	0.024880
C	-2.781980	1.532270	-0.570860
C	-4.049110	0.974730	-0.666740
C	-4.321490	-0.291550	-0.131380
C	-3.290760	-1.031310	0.452540
C	-1.989090	-0.536470	0.503350
C	-0.821540	-1.342990	0.964760
S	0.396220	-1.644490	-0.437960
H	-4.845880	1.546860	-1.134800
H	-2.568820	2.526120	-0.950240
H	-5.325380	-0.702110	-0.181170
H	-3.491430	-2.028400	0.839680
H	2.898610	2.546520	0.645150
H	5.117930	1.490140	0.138040
H	5.173180	-0.908560	-0.563880
H	-1.130070	-2.339800	1.290630
H	-0.251760	-0.887200	1.780320
H	3.079540	-2.204870	-0.694990

III. Syntheses

III. 1 Synthesis of 1-nitro-2-((2'-nitrobenzyl)oxy)benzene (**6**)

2-Nitrophenol (**5**, 800 mg, 5.75 mmol), 2-nitrobenzylbromide (**4**, 1.49 g, 6.88 mmol), potassium phosphate (2.30 g, 8.63 mmol) and tetra-*n*-butylammonium bromide (TBAB) (940 mg, 2.90 mmol) were stirred in 30 mL of water at room temperature for 16 h. The suspension was diluted with water and extracted with 250 mL dichloromethane. The combined organic layers were dried over sodium sulfate. The solution was evaporated and recrystallized from ethanol to obtain colorless crystals (**6**, 1.47 g 5.36 mmol, 93 %).



melting point: 156 °C (154 °C)²

¹H-NMR (500 MHz, acetone-*d*₆, 300 K): δ = 8.22 (dd, ³*J* = 8.2 Hz, ⁴*J* = 1.2 Hz, 1 H, *H*-3'), 8.01 (d, ³*J* = 7.9 Hz, 1 H, *H*-6'), 7.94 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.7 Hz, 1 H, *H*-6), 7.87 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.2 Hz, 1 H, *H*-5'), 7.70 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.7 Hz, 1 H, *H*-4), 7.67 (t, ³*J* = 7.8 Hz, 1 H, *H*-4'), 7.49 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.0 Hz, 1 H, *H*-3), 7.21 (ddd, ³*J* = 7.8 Hz, ³*J* = 7.3 Hz, ⁴*J* = 1.1 Hz, 1 H, *H*-5), 5.73 (s, 2 H, *H*-7) ppm.

¹³C-NMR (125 MHz, acetone-*d*₆, 300 K): δ = 152.04 (*C*-2), 148.16 (*C*-2'), 141.05 (*C*-1), 135.35(*C*-4), 135.12 (*C*-5'), 133.24 (*C*-1'), 129.92 (*C*-4'), 129.63 (*C*-6'), 126.25 (*C*-6), 125.83 (*C*-3'), 122.10 (*C*-5), 116.18 (*C*-3), 68.80 (*C*-7) ppm.

IR (ATR): $\tilde{\nu}$ = 3115 (w), 3089 (w), 1604 (m), 1515 (s), 1339 (s), 1248 (s), 1153 (m), 1024 (m), 865(m), 727 (s), 665 (m), 617 (w), 525 (w) cm⁻¹.

MS (EI, 70 eV): *m/z* = 274.06 [*M*]⁺, 152.06 [*M*-C₆H₄NO₂]⁺, 136.04 [*M*-C₆H₄NO₃]⁺.

MS (HR) (EI, 70 eV): *m/z* = calc.: 274.05897, found: 274.05894.

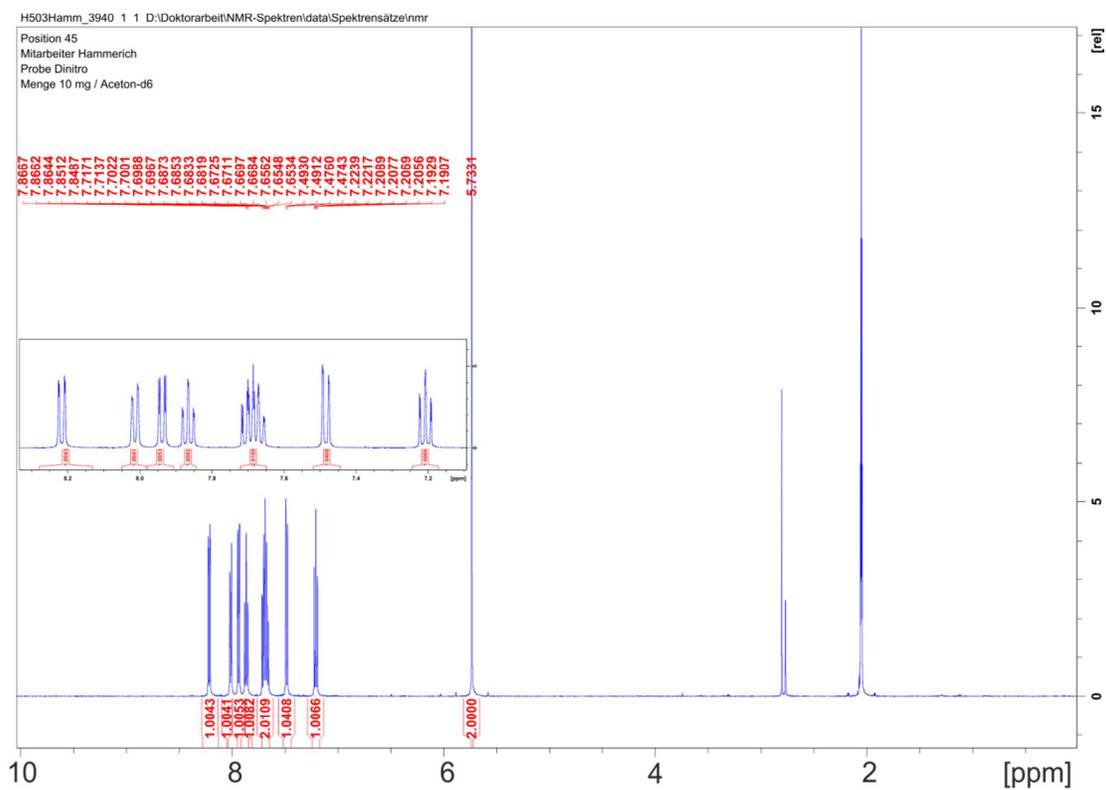


Figure S3: ^1H -NMR spectrum of compound 6.

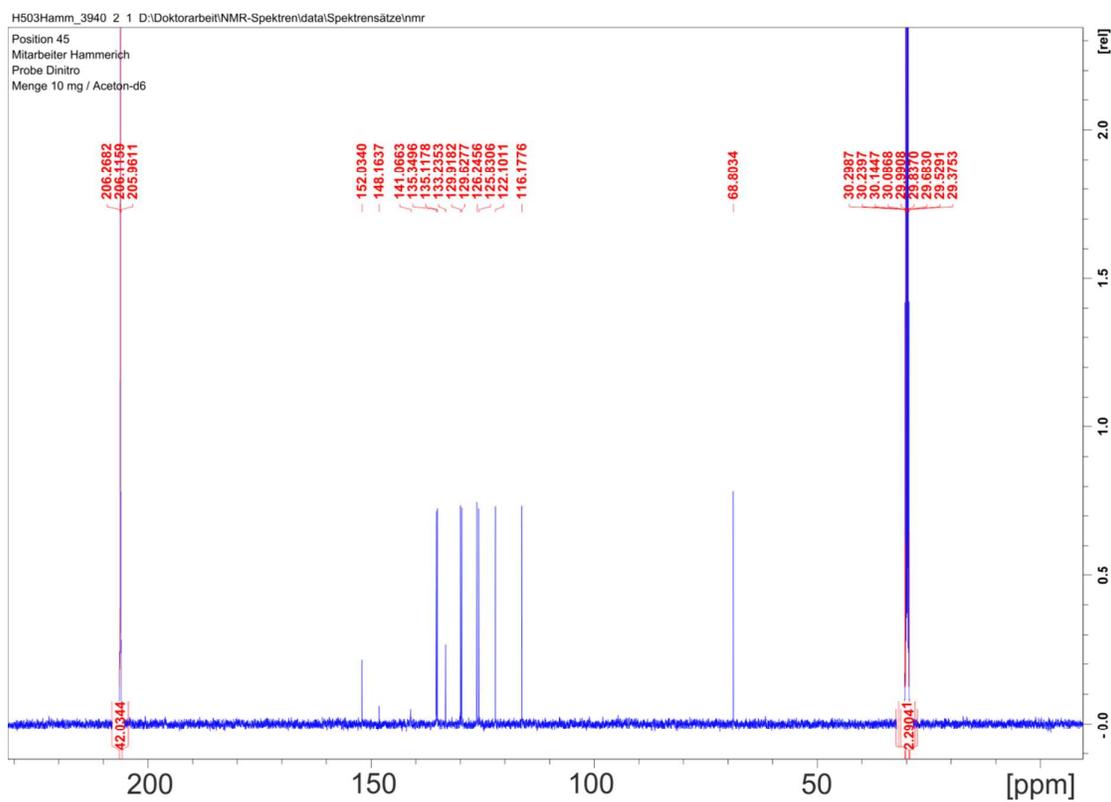
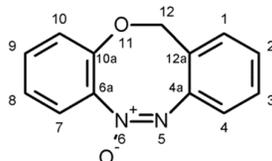


Figure S4: ^{13}C -NMR spectrum of compound 6.

III.2. Synthesis of 12*H*-dibenzo[*b,f*][1,4,5]oxadiazocine-6-oxide (**9 b**)

To a solution of triethylamine (22 mL), methanol (50 mL), formic acid (1 mL) and water (14 mL) were added 1-nitro-2-((2'-nitobenzyl)oxy)benzene (**6**, 100 mg, 364 μmol) and lead powder (350 mg, 1.69 mmol) and the suspension was treated with ultrasound (450 W) for 5 h. After the first and second hour another portion lead (350 mg, 1.69 mmol) was added. The reaction mixture was filtrated and reduced in vacuo. The residue was extracted with dichloromethane, dried over magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography (0.040–0.063 mm, dichloromethane, R_f : 0.29) to obtain of a yellow solid (**7a/b**, 36 mg, 160 μmol , 44 %). As a side product the diazocine could be obtained as a yellow solid (**9**, 7 mg, 32 μmol , 9 %).



melting point: 141 °C.

$^1\text{H-NMR}$ (600 MHz, DMSO-d_6 : CDCl_3 (1:1), 300 K, TMS): 7.40 (t, $^3J = 7.6$ Hz, 1 H, *H*-8), 7.36 (d, $^3J = 7.5$ Hz, 1 H, *H*-10), 7.26 (m, 2 H, *H*-3,9), 7.21 (d, $^3J = 8.2$ Hz, 1 H, *H*-1), 7.13 (dd, $^3J = 8.2$ Hz, 1 H, *H*-7), 7.01 (t, $^3J = 7.5$ Hz, 1 H, *H*-2), 6.94 (d, $^3J = 8.3$ Hz, 1 H, *H*-4), 5.27 (d, $^3J = 12.3$ Hz, 1 H, *H*-12), 5.13 (d, $^3J = 12.3$ Hz, 1 H, *H*-12) ppm.

$^{13}\text{C-NMR}$ (125 MHz, DMSO-d_6 : CDCl_3 (1:1), 300 K, TMS): 145.32 (*C*-6a), 144.44 (*C*-4a), 139.66 (*C*-12a), 130.17 (*C*-3), 129.45 (*C*-10), 128.83 (*C*-8), 126.44 (*C*-9), 124.12 (*C*-10a), 122.01(*C*-1,2), 120.15 (*C*-7), 120.07 (*C*-4), 69.28 (*C*-12) ppm.

$^{15}\text{N-NMR}$ (600 MHz, DMSO-d_6 : CDCl_3 (1:1), 300 K, TMS): $\delta = 363.6$ (s, 1 N, *N*-6), 342.3 (s, 1 N, *N*-5) ppm.

IR (ATR): $\tilde{\nu} = 3037$ (w), 2828 (w), 2887 (w), 1597 (w), 1468 (s), 1443 (s), 1343 (m), 1225 (m), 1195 (m), 981 (m), 765 (s), 678 (w), 639 (w), 611 (m) cm^{-1} .

MS (EI, 70 eV): $m/z = 226.07$ [M] $^+$, 196.07 [$\text{M}-\text{CH}_2\text{O}$] $^+$, 181.07 [$\text{M}-\text{CHO}_2$] $^+$, 141.07, 120.04 [$\text{M}-\text{C}_7\text{H}_6\text{O}$] $^+$.

MS (HR) (EI, 70 eV): $[m/z] = \text{calc.}: 226.07423$, found: 226.07381

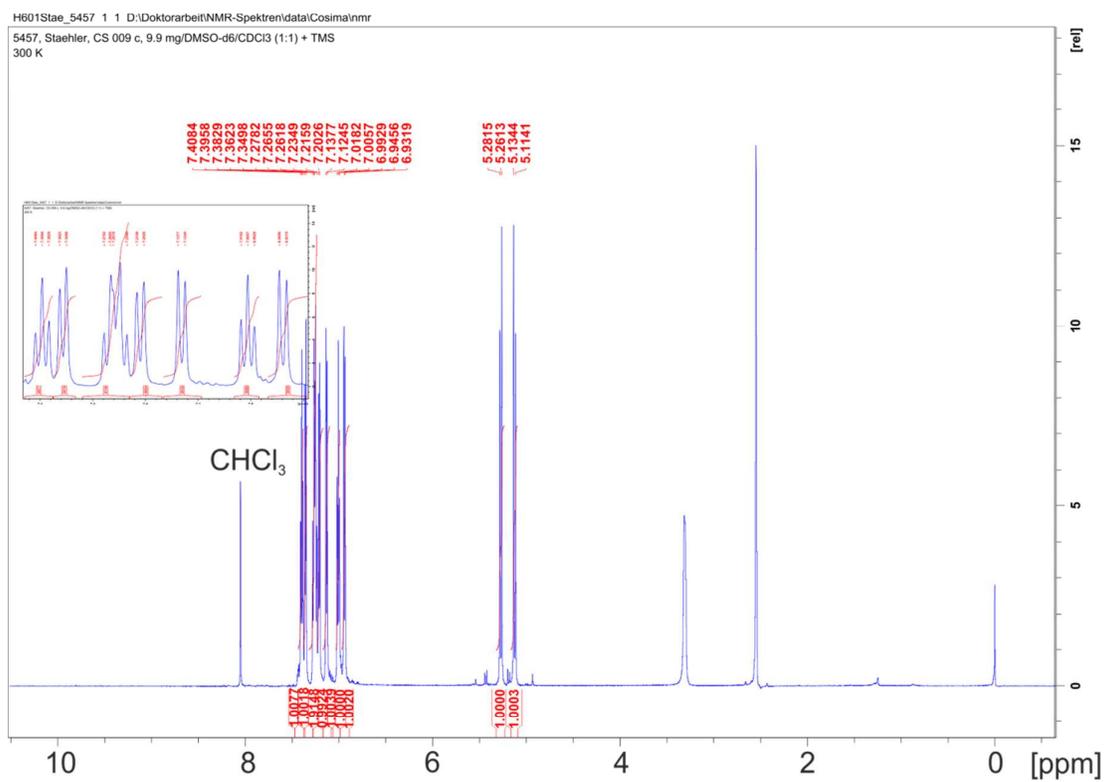


Figure S5: ¹H-NMR spectrum of compound **7b**.

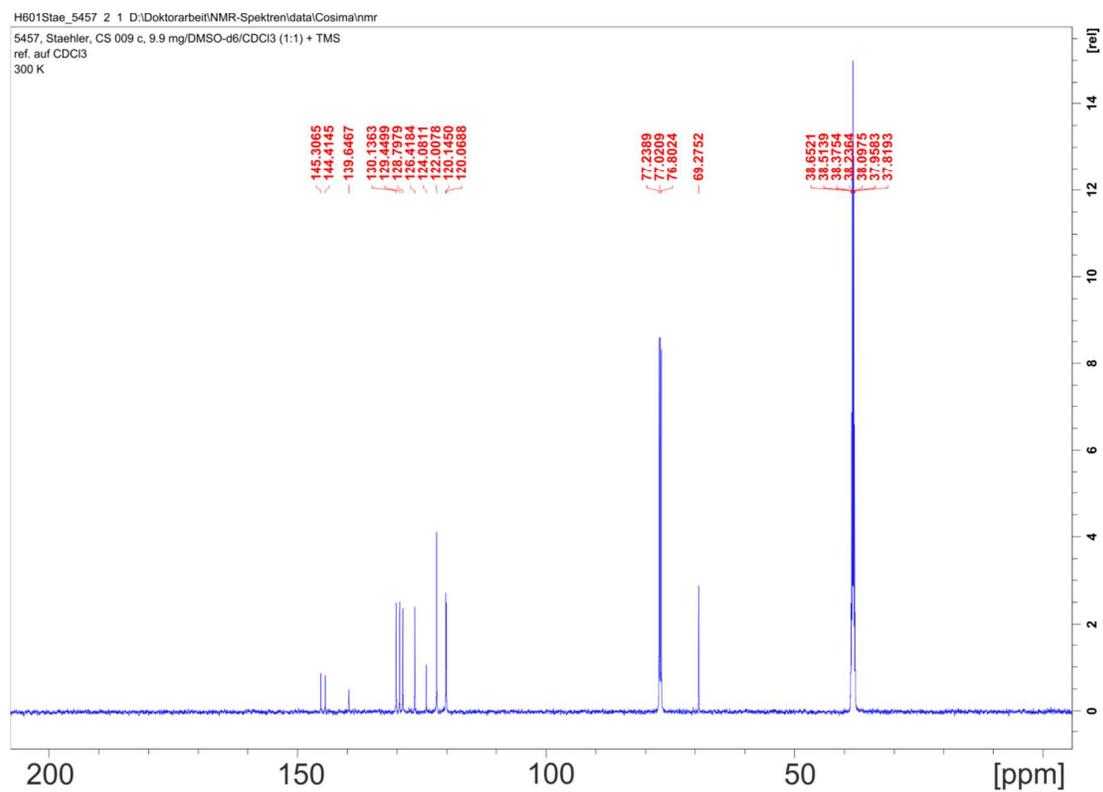
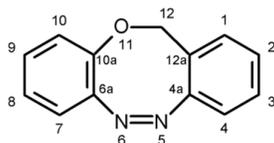


Figure S6: ¹³C-NMR spectrum of compound **7b**.

III.3 Synthesis of 12*H*-dibenzo[*b,f*][1,4,5]oxadiazocine (2)

12*H*-dibenzo[*b,f*][1,4,5]oxadiazocine-6-oxid (**9a/b**, 89.0 mg, 390 μmol) was dissolved under a nitrogen atmosphere in THF (5 mL) and triphenylphosphine (521 mg, 1.99 mmol) and molybdenum(VI)dichloride dioxide (18.0 mg, 91.0 μmol) were added. The solution was refluxed for 3 h, the solvent was evaporated and the residue was purified by column chromatography (0.040–0.063 mm, dichloromethane, R_f : 0.65) to obtain of a yellow solid (34 mg, 163 μmol , 42 %).



melting point: 106 °C

$^1\text{H-NMR}$ (500 MHz, acetone- d_6 , 300 K): δ = 7.47–7.41 (m, 2 H, *H*-1,3), 7.30 (td, 3J = 7.5 Hz, 4J = 1.2 Hz, 1 H, *H*-2), 7.20 (dd, 3J = 7.9 Hz, 4J = 1.1 Hz, 1 H, *H*-4), 7.09 (td, 3J = 7.7 Hz, 4J = 1.8 Hz, 1 H, *H*-9), 6.98 (td, 3J = 7.6 Hz, 4J = 1.3 Hz, 1 H, *H*-8), 6.91 (dd, 3J = 8.0 Hz, 4J = 1.8 Hz, 1 H, *H*-7), 6.87 (dd, 3J = 8.2 Hz, 4J = 1.3 Hz, 1 H, *H*-10), 4.97 (s, 2 H, *H*-12) ppm.

$^{13}\text{C-NMR}$ (125 MHz, acetone- d_6 , 300 K): δ = 157.87 (*C*-4a), 147.26 (*C*-6a), 144.12 (*C*-10a), 133.21(*C*-3), 130.64 (*C*-1), 129.74 (*C*-9), 129.12 (*C*-2), 123.17 (*C*-8), 123.00 (*C*-7), 122.71 (*C*-12a), 122.13 (*C*-10), 120.81 (*C*-4), 71.94 (*C*-12) ppm.

IR (ATR): $\tilde{\nu}$ = 2908 (w), 1596 (w), 1523 (w), 1465 (m), 1434 (m), 1202 (m), 989 (m), 764 (s) cm^{-1} .

UV/Vis (acetonitrile): $\lambda(\lg \epsilon)$ = 398 (2.72) nm.

MS (EI, 70 eV): m/z = 210.08 [M] $^+$, 181.06 [$\text{M}-\text{CH}_2\text{O}$] $^+$, 152.06 [$\text{M}-\text{CH}_2\text{N}_2\text{O}$] $^+$, 90.04 [$\text{M}-\text{C}_7\text{H}_6\text{NO}$] $^+$.

MS (HR) (EI, 70 eV): $[m/z]$ = calc.: 210.07931, found: 210.07923.

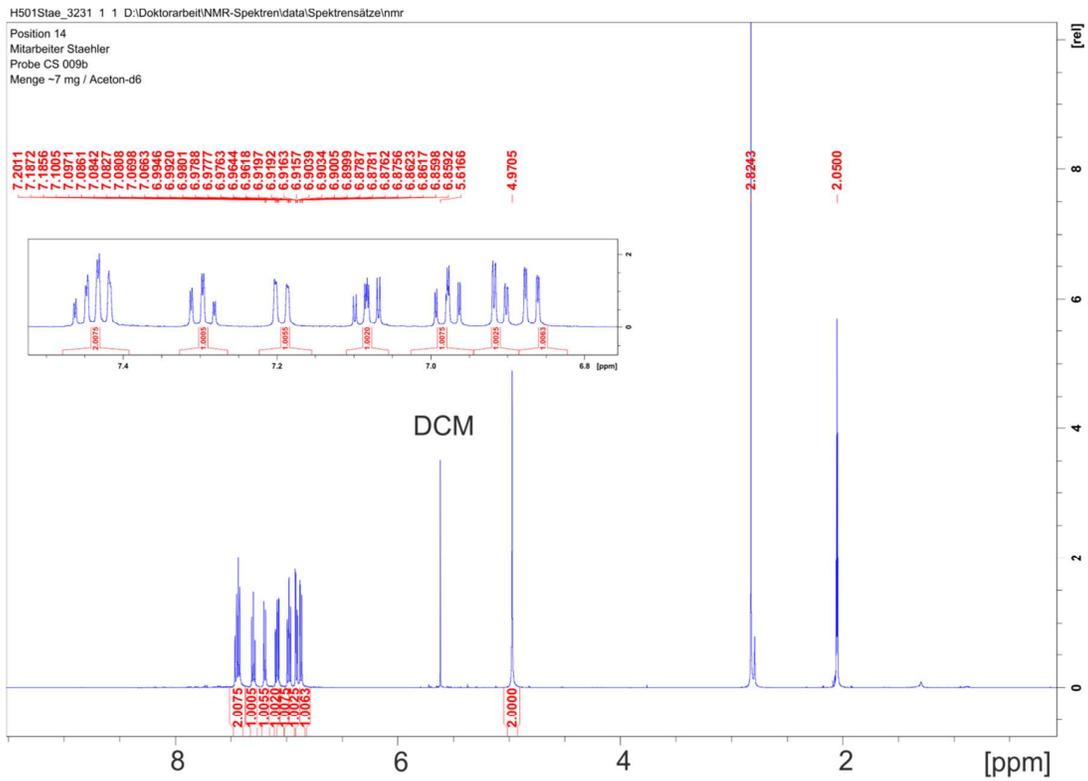


Figure S7: ^1H -NMR spectrum of compound 2.

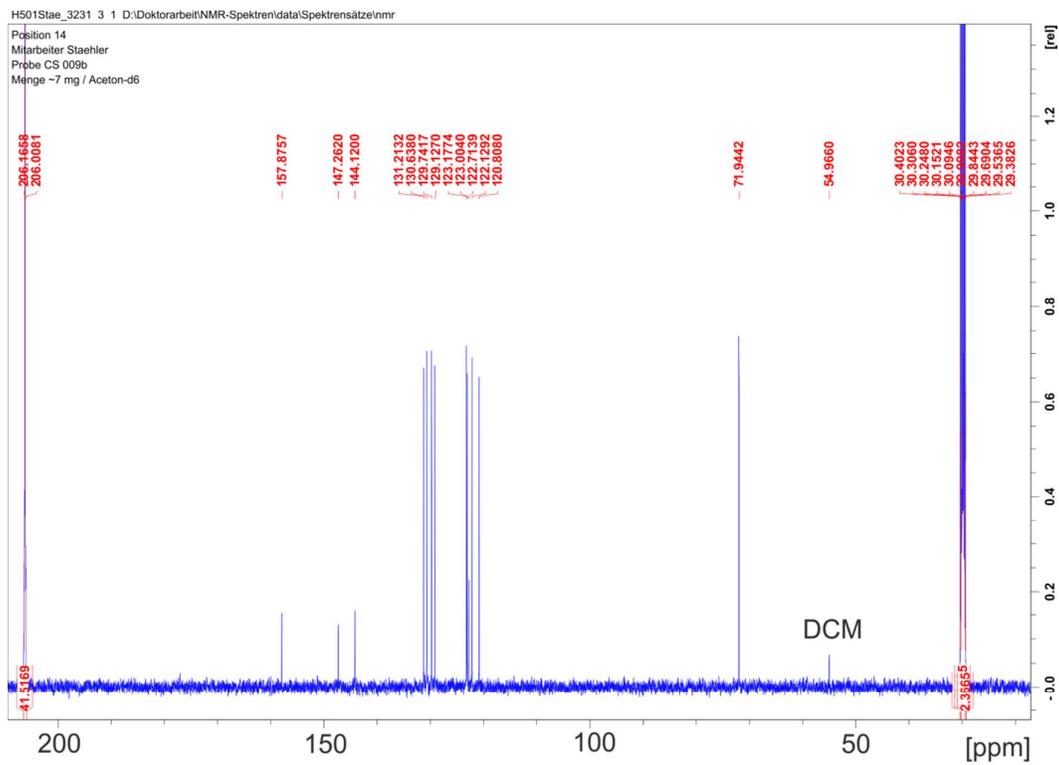
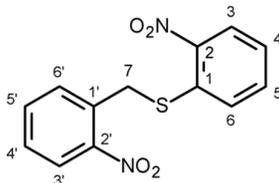


Figure S8: ^{13}C -NMR spectrum of compound 2.

III.4 Synthesis of 2'-nitrobenzyl-2-nitrophenyl-sulfide (6)

Bis(2-nitrophenyl)disulfide (7, 2.00 g, 6.48 mmol) was suspended in THF (40 mL) under nitrogen atmosphere, sodium borohydride (1.22 mg, 32.4 mmol) was added to this suspension (solution turns immediately red) and heated up to 60 °C 1 h. To this solution 2-nitrobenzylbromide (4, 2.80 g, 13.0 mmol) was added and stirred 16 h at room temperature (solution turns yellow). The reaction mixture was carefully poured on ice water. The precipitated solid was filtered and washed with water and methanol. The product was obtained as a yellow solid (1.69 g, 5.85 mmol, 45 %).



melting point: 165.6 °C

¹H-NMR (500 MHz, acetone-d₆, 300 K): δ = 8.18 (dd, ³J = 8.2 Hz, ⁴J = 1.3 Hz, 1 H, *H*-3), 8.07 (dd, ³J = 8.2 Hz, ⁴J = 1.2 Hz, 1 H, *H*-3'), 7.77-7.69 (m, 4H, *H*-5, 5', 6, 6'), 7.61 (m_c, 1 H, *H*-4'), 7.47 (ddd, ³J = 8.2 Hz, ³J = 8.3 Hz, ⁴J = 1.6 Hz, 1 H, *H*-4), 4.71 (s, 2 H, *H*-7) ppm.

¹³C-NMR (125 MHz, acetone-d₆, 300 K): δ = 150.13 (C-2'), 147.94 (C-2), 136.26 (C-1), 134.79 (C-5), 134.47 (C-5'), 133.35 (C-6), 131.78 (C-1'), 130.11 (C-4'), 129.26 (C-6'), 126.81 (C-4), 126.54 (C-3), 126.16 (C-3'), 35.17 (C-7) ppm.

IR (ATR): $\tilde{\nu}$ = 3118.33 (w), 1596.24 (w), 1565.58 (m), 1527.51 (m), 1505.15 (s), 1428.01 (m), 1334.40 (s), 1308.91 (s), 1256.71 (m), 1231.44 (m), 1168.31 (w), 1106.66 (m), 1061.87 (w), 1045.75 (m), 954.13 (w), 858.20 (m), 782.28 (s), 734.90 (s), 712.24 (s), 653.32 (s) cm⁻¹.

MS (EI, 70 eV): *m/z* = 290.04 [M]⁺, 155.00 [C₆H₄NO₂S]⁺, 136.04 [C₇H₆NO₂]⁺.

MS (HR) (EI, 70 eV): [*m/z*] = calc.: 290.03613, found: 290.03624.

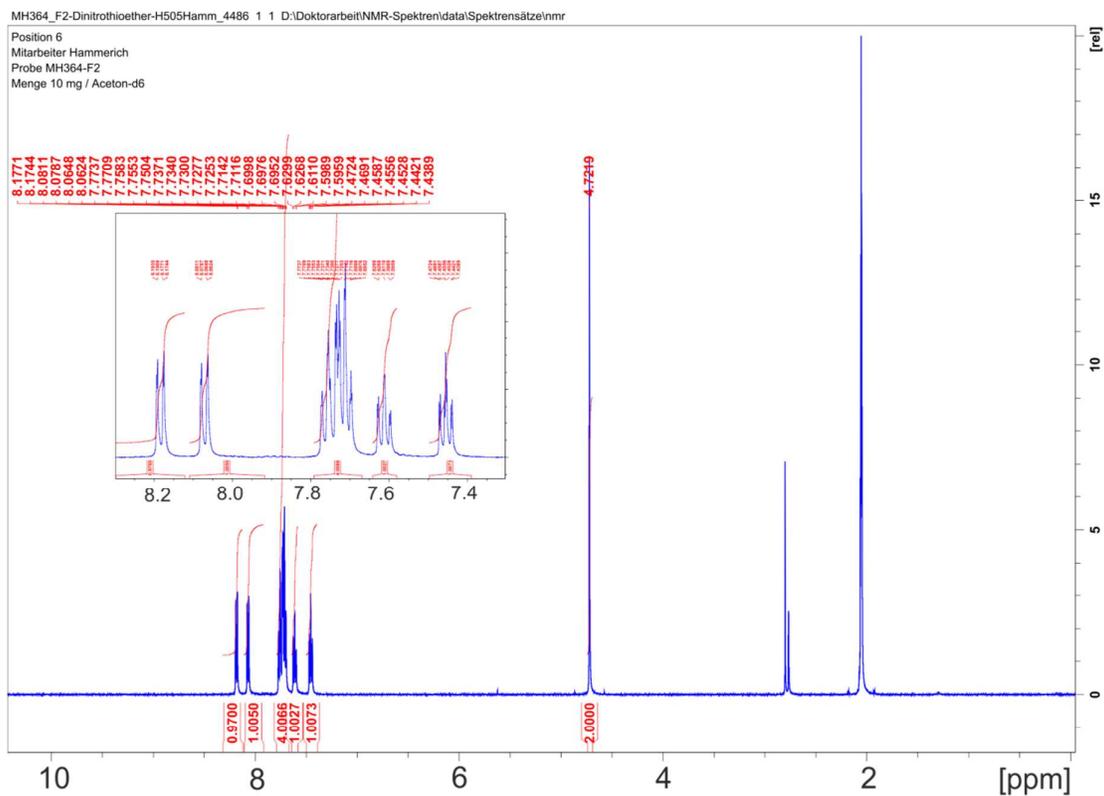


Figure S9: ^1H -NMR spectrum of compound **8**.

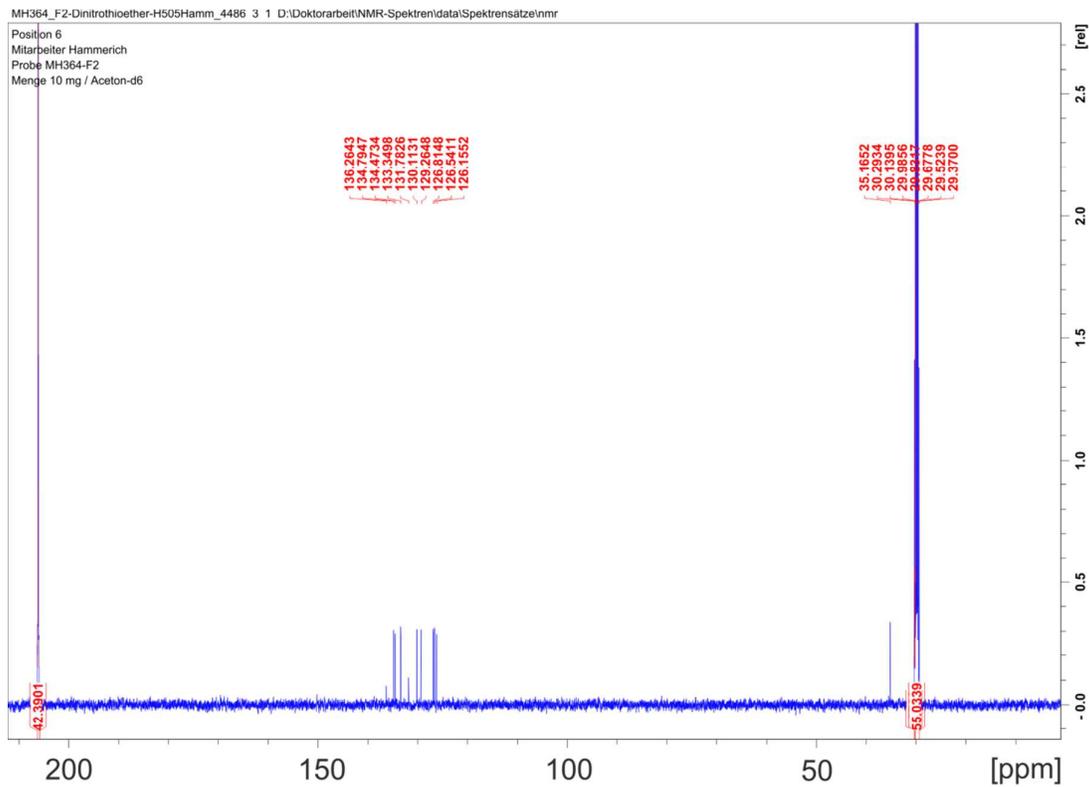
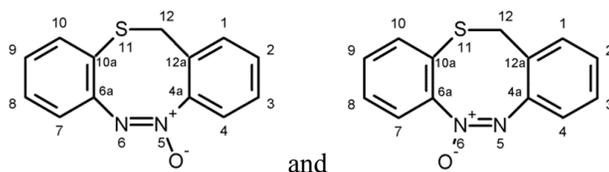


Figure S10: ^{13}C -NMR spectrum of compound **8**.

III.5 Synthesis of 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine-6-oxide (10b) and 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine-5-oxide (10a)

To a solution of triethylamine (22 mL), methanol (50 mL), formic acid (1 mL) and water (14 mL), 2'-nitrobenzyl-2-nitrophenyl-sulfide (**6**, 100 mg, 344 μmol) and lead powder (350 mg, 1.69 mmol) were added, and the solution was treated with ultrasound (450W) for 5 h. After the first and second hour an additional portion of lead (350 mg, 1.69 mmol) was added. The reaction mixture was filtrated and reduced in vacuo. The residue was extracted with dichloromethane, dried over magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography (0.040–0.063 mm, dichloromethane, R_f : 0.29) to obtain a mixture of the regioisomers of both azoxy compounds (27 mg, 110 μmol , 32 %) as a yellow solid. As a side product the diazocine could be obtained as a yellow solid (9 mg, 41 μmol , 12 %).

The azoxy compounds were used for the next synthetic step as a mixture of regioisomers.



melting point: 129.9 °C

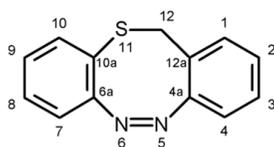
MS (EI, 70 eV): m/z = 242.04 (X) $[\text{M}]^+$, 225.04 (100), 184.03, 136.02.

MS (HR) (EI, 70 eV): $[m/z]$ = calc.: 242.05138, found: 242.05127.

IR (ATR): $\tilde{\nu}$ = 3280.52 (m), 3242.53 (m), 3507.86 (m), 1603.56 (w), 1568.61 (s), 1448.77 (s), 1347.71 (m), 1194.35 (w), 1131.15 (w), 1034.00 (w), 924.48 (m), 880.93 (m), 854.04 (m), 809.66 (m), 760.89 (s), 743.84 (s), 743.84 (s), 723.04 (m), 692.78 (m), 660.14 (m), 610.84 (m), 583.58 (m), 564.12 (m), 504.93 (m) cm^{-1} .

II.6 Synthesis of 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine (3)

A mixture of 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine-6-oxide and 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine-5-oxide (**10b/10a**, 50 mg, 206 μmol) and lead shots (341 mg, 1.65 mmol) were placed in a ball mill with 20 balls and were shaken for 4 h with 40 Hz. The black powder was extracted with dichloromethane. The solvent was evaporated and the crude product was purified by column chromatography (0.040–0.063 mm, dichloromethane). The product was obtained as a yellow solid (26 mg, 115 μmol , 56 %).



melting point: 112.9 °C

¹H-NMR (500 MHz, acetone-*d*₆, 300 K): δ = 7.52–7.20 (m, 3 H, *H*-1, *H*-3, *H*-8), 7.12 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.3 Hz, 1 H, *H*-2), 7.10 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.2 Hz, 1 H, *H*-10), 6.99 (ddd, ³*J* = 7.5 Hz, ³*J* = 7.8 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-9), 6.78 (dd, ³*J* = 7.6 Hz, ⁴*J* = 0.7 Hz, 1 H, *H*-4), 6.76 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-7), 3.98 (d, ²*J* = 11.6 Hz, 1 H, *H*-12), 3.84 (d, ²*J* = 11.6 Hz, 1 H, *H*-12) ppm.

¹³C-NMR (125 MHz, acetone-*d*₆, 300 K): δ = 158.30 (*C*-6a), 158.58 (*C*-4a), 134.28 (*C*-10), 130.31 (*C*-1), 129.27 (*C*-3), 128.80 (*C*-8), 128.29 (*C*-2), 127.86 (*C*-9), 124.97 (*C*-12a), 122.94 (*C*-10a), 120.16, (*C*-7) 117.81 (*C*-4), 35.12 (*C*-12) ppm.

IR (ATR): $\tilde{\nu}$ = 2923.65 (m), 1517.7(w), 1476.23 (m), 1454.55 (m), 1260.02 (m), 1155.28 (m), 1087.98 (m), 1064.49 (m), 1030.39 (m), 954.58 (m), 915.22 (m), 892.30 (s), 801.76 (m), 768.92 (s), 734.28 (s), 691.15 (s), 659.16 (s), 578.66 (m) cm^{-1} .

UV/Vis (acetonitrile): $\lambda(\lg \epsilon)$ = 398 (2.61) nm.

MS (EI, 70 eV): *m/z* = 226.05 (100) [*M*]⁺, 199.04 (X) 165.07 (X).

MS (HR) (EI, 70 eV): [*m/z*] = calc.: 226.05647, found: 226.05602.

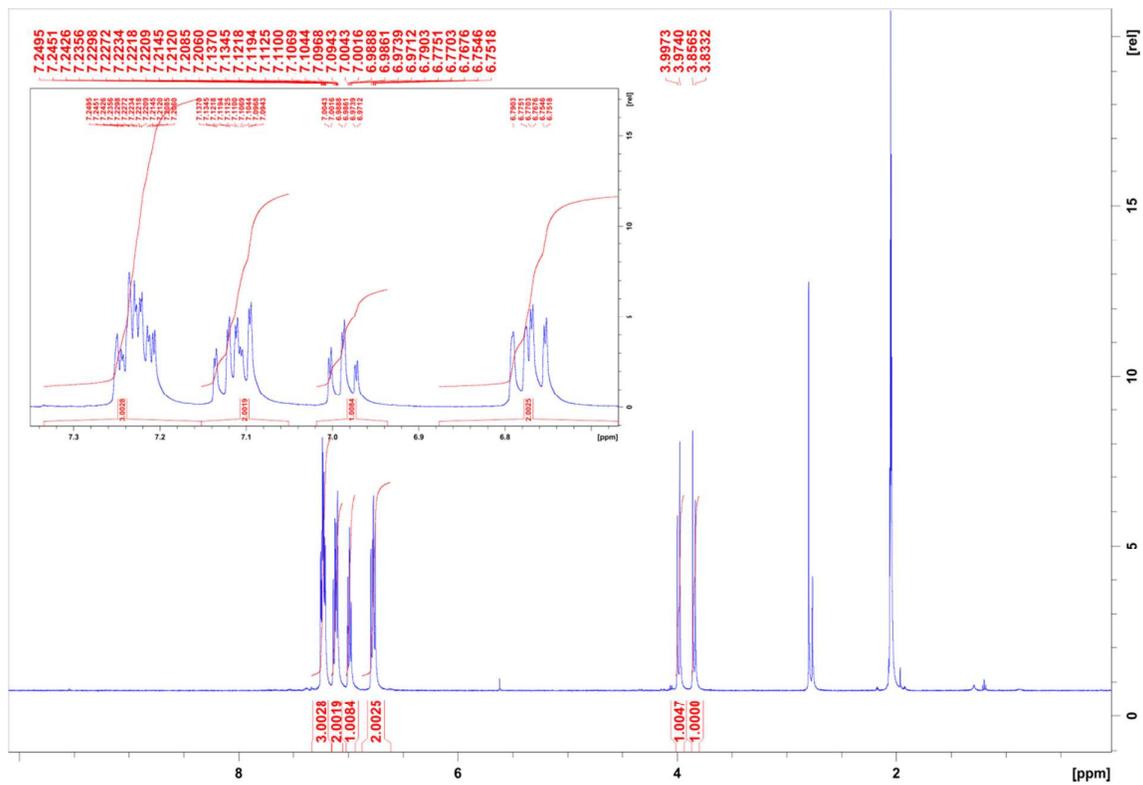


Figure S11: ¹H-NMR spectrum of compound 3

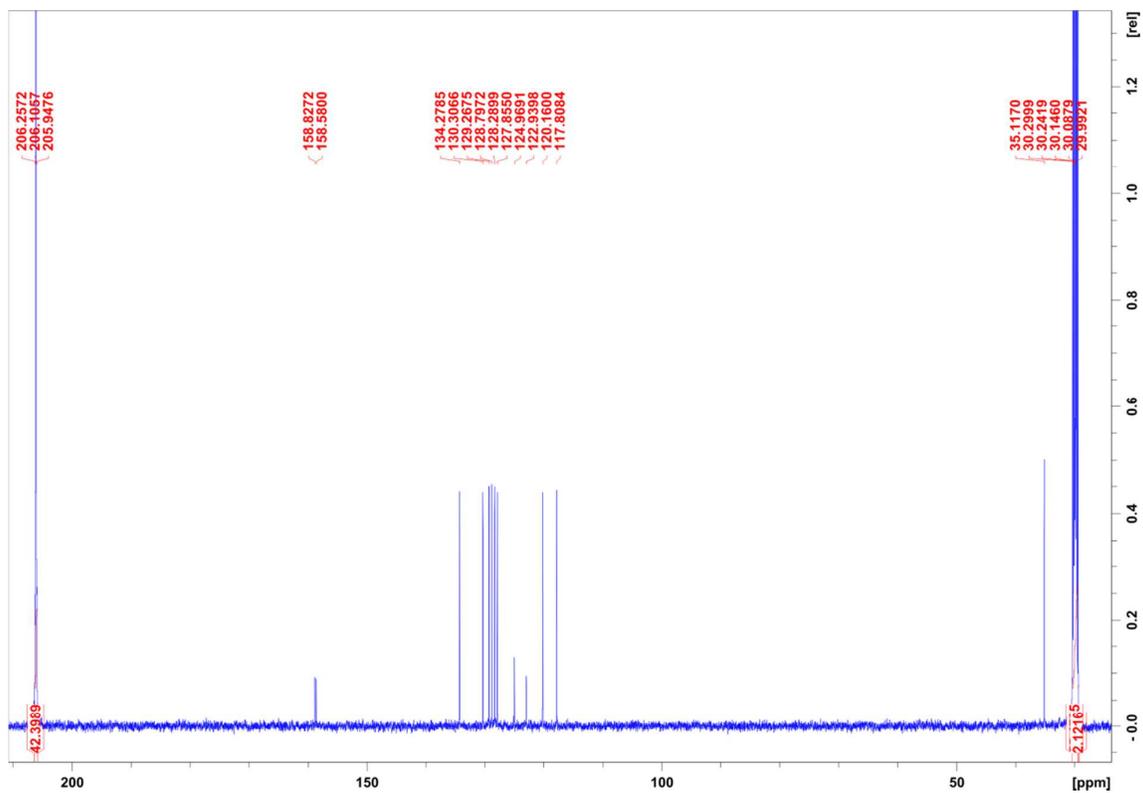


Figure S12: ¹³C-NMR spectrum of compound 3

IV. ¹H- NMR measurements

IV.1 ¹H-NMR measurements of O-diazocine **2** at 198 K

As the rate of the back isomerization (*cis* → *trans*) of O-diazocine **2** is fast at room temperature, investigations of the photo switching can only be performed at low temperatures. Therefore, the sample was cooled within the NMR spectrometer to 198 K. Upon cooling of *cis*-**2** we observe coalescence of the methylene protons in the bridge. We attribute the splitting of the singlet at 4.97 ppm into two doublets to the freezing of the ring inversion of the boat conformation leading to the separation of the signals for the pseudo equatorial and pseudo axial protons.

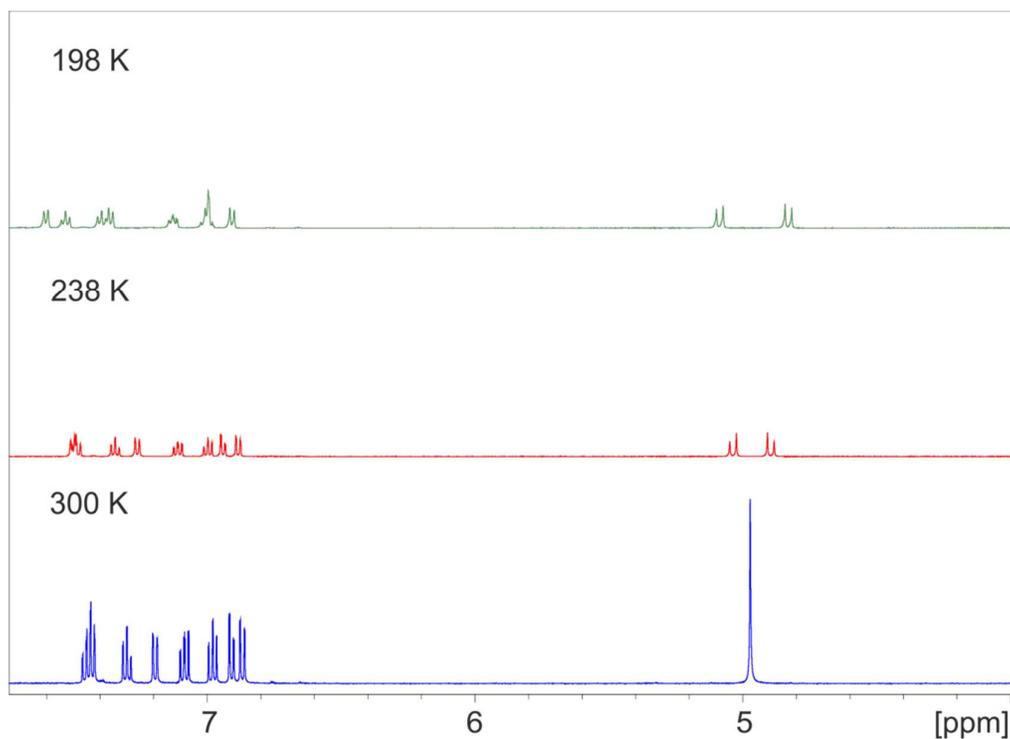


Figure S13: ¹H-NMR spectra of oxygen diazocine **2** upon lowering of the temperature from room temperature to 198 K. Ring inversion is fast at room temperature on the NMR time scale. The methylene protons appear as a sharp singlet. At lower temperatures the methylene protons split into two separate signals (doublets) for the pseudo equatorial and pseudo axial protons.

IV.2 Determination of the photostationary state of O-diazocine 2

^1H NMR spectra of compound **2** were measured in deuterated acetone at 198 K before and after irradiation with 385 nm for 15 min. The probe was irradiated outside the NMR spectrometer in an NMR tube at 195 K immersed in a quartz Dewar with acetone and dry ice. After irradiation the probe was transferred rapidly into the precooled spectrometer to avoid warming of the sample. According to integration of characteristic signals in the ^1H NMR spectrum the oxygen diazocine **2** is converted to the *trans* isomer with a yield of 80% (Figure S14 and S15).

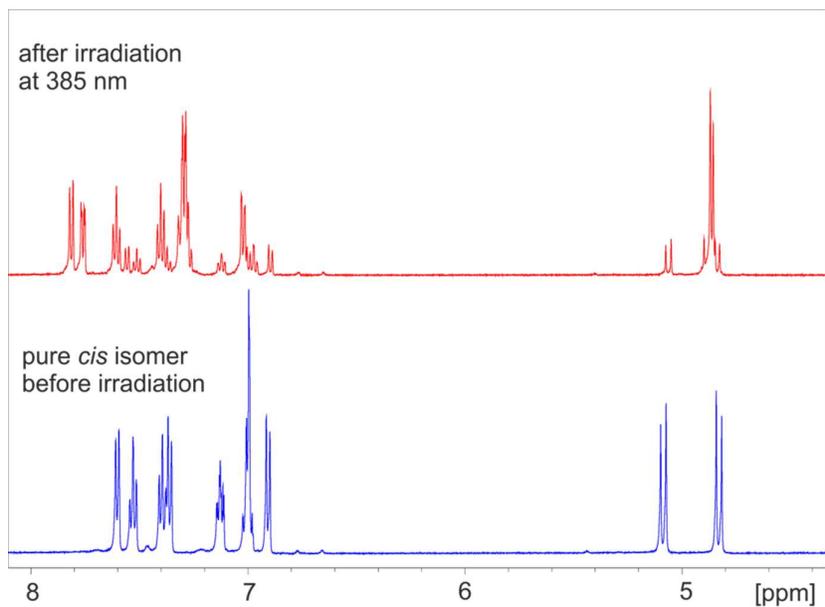


Figure S14: ^1H NMR spectra of oxygen diazocine **2** at 198 K before (blue) and after irradiation (red).

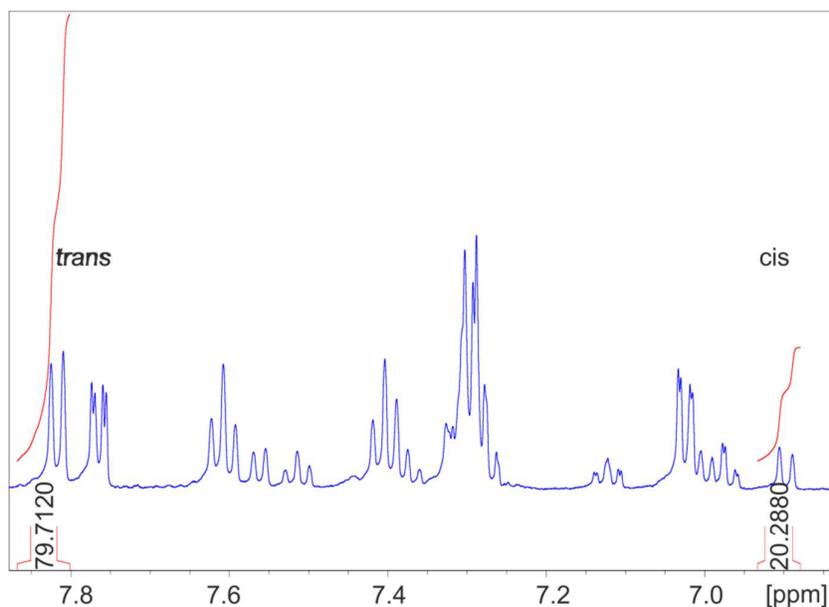


Figure S15: Aromatic region of the ^1H NMR spectrum of oxygen diazocine **2** at 198 K after irradiation.

IV.3 Kinetic measurements of the thermochemical *trans*->*cis* isomerization of O-diazocine **2**

¹H NMR spectra of compound **2** were measured in deuterated acetone at 278 K before and after irradiation with 385 nm (Nichia LED's) for 15 min (the probe was irradiated at 195 K with the NMR tube immersed in a quartz Dewar with acetone and dry ice outside the NMR spectrometer). Several spectra were recorded within a period of several half-lives (every fifth spectrum is shown in the graphic below, Figure S16 and Figure S17).

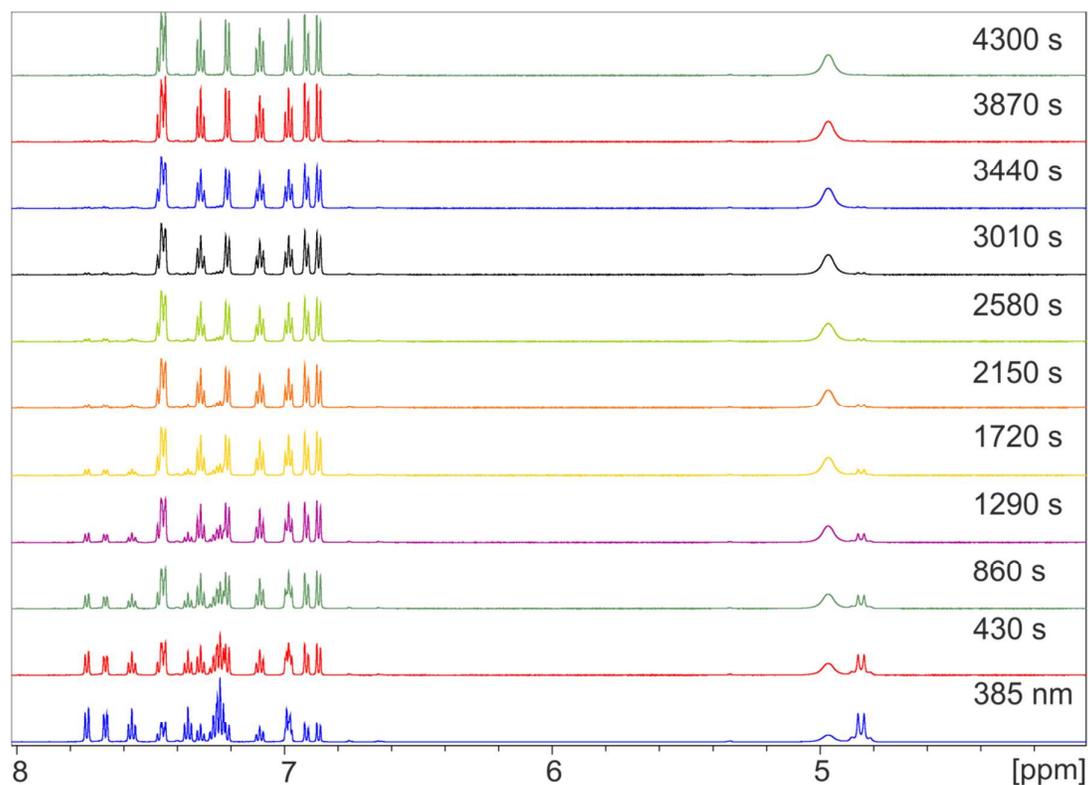


Figure S16: ¹H-NMR spectra of oxygen diazocine **2** after irradiation with 385 nm (directly after irradiation: blue spectrum at the bottom) and at regular time intervals after irradiation at 287 K.

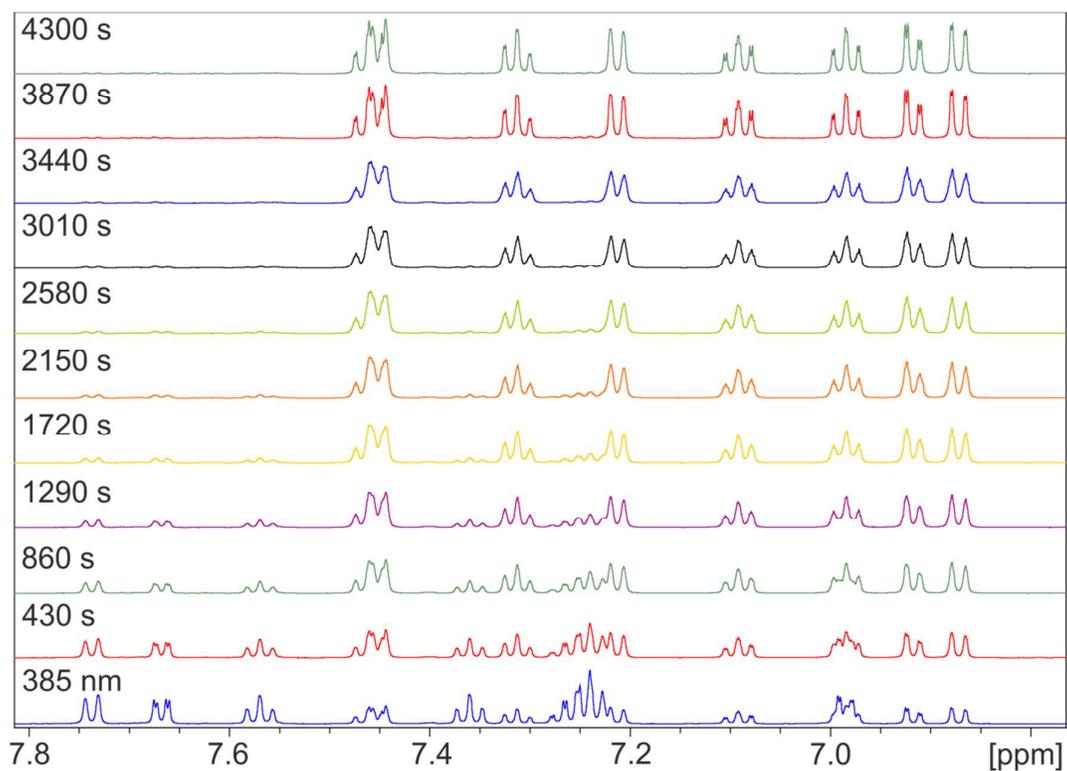


Figure S17: Aromatic region of the ^1H -NMR spectra of oxygen diazocine **2** after irradiation with 385 nm (directly after irradiation: blue spectrum at the bottom) and at regular time intervals after irradiation at 287 K.

IV.4 Thermal half-life of O-diazocine 2 determined with $^1\text{H-NMR}$ spectroscopy

To determine the half-life of compound 2 with $^1\text{H-NMR}$ spectroscopy the integrals of the *cis* and *trans* isomer were plotted as a function of time. The half-life was calculated with an exponential fit.

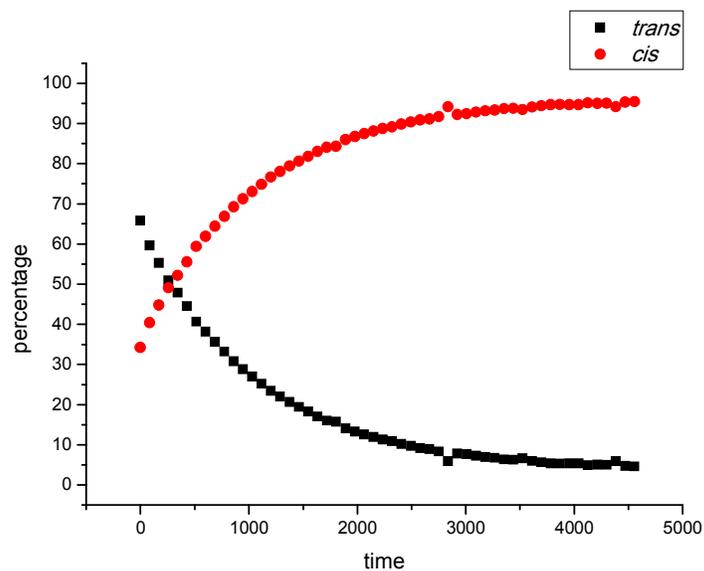


Figure S18: Percentage of *cis* and *trans* isomer of compound 2 plotted as a function of time.

Table S2. Exponential fit of the *cis* and *trans* signal for the thermal back isomerization to the *cis* isomer.

Determined by increase of <i>cis</i> signal at 6.87 ppm	Determined by decrease of <i>trans</i> signal at 7.74ppm																																																								
<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Model</th> <th>Exponential</th> <th></th> <th></th> </tr> </thead> <tbody> <tr> <td>Equation</td> <td>$y = A1 \exp(-t/\tau1) + y0$</td> <td></td> <td></td> </tr> <tr> <td>Reduced Chi-S</td> <td>0.18211</td> <td></td> <td></td> </tr> <tr> <td>Adj. R-Square</td> <td>0.99929</td> <td></td> <td></td> </tr> <tr> <td>Integral 1</td> <td>y0</td> <td>Value</td> <td>Standard Error</td> </tr> <tr> <td>Integral 1</td> <td>A1</td> <td>-60.79545</td> <td>0.22921</td> </tr> <tr> <td>Integral 1</td> <td>t1</td> <td>1058.10383</td> <td>9.7045</td> </tr> </tbody> </table>	Model	Exponential			Equation	$y = A1 \exp(-t/\tau1) + y0$			Reduced Chi-S	0.18211			Adj. R-Square	0.99929			Integral 1	y0	Value	Standard Error	Integral 1	A1	-60.79545	0.22921	Integral 1	t1	1058.10383	9.7045	<table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>Model</th> <th>Exponential</th> <th></th> <th></th> </tr> </thead> <tbody> <tr> <td>Equation</td> <td>$y = A1 \exp(-t/\tau1) + y0$</td> <td></td> <td></td> </tr> <tr> <td>Reduced Chi-S</td> <td>0.18211</td> <td></td> <td></td> </tr> <tr> <td>Adj. R-Square</td> <td>0.99929</td> <td></td> <td></td> </tr> <tr> <td>Integral 1</td> <td>y0</td> <td>Value</td> <td>Standard Error</td> </tr> <tr> <td>Integral 1</td> <td>A1</td> <td>60.79545</td> <td>0.22921</td> </tr> <tr> <td>Integral 1</td> <td>t1</td> <td>1058.10383</td> <td>9.7045</td> </tr> </tbody> </table>	Model	Exponential			Equation	$y = A1 \exp(-t/\tau1) + y0$			Reduced Chi-S	0.18211			Adj. R-Square	0.99929			Integral 1	y0	Value	Standard Error	Integral 1	A1	60.79545	0.22921	Integral 1	t1	1058.10383	9.7045
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$k = 9.45 \pm 0.09 \cdot 10^{-4} \text{ mol/s}$	$k = 9.45 \pm 0.09 \cdot 10^{-4} \text{ mol/s}$																																																								
$t_{1/2} = 733 \pm 6 \text{ s} = 12.2 \pm 0.1 \text{ min}$	$t_{1/2} = 733 \pm 6 \text{ s} = 12.2 \pm 0.1 \text{ min}$																																																								

IV.5 Determination of the photostationary state of S-diazocine **3**

^1H NMR spectra of compound **3** were measured in deuterated acetone at 300 K before and after irradiation with 405 nm for 15 min. It could be shown, that the S-diazocine **3** is converted to the *trans* isomer with a yield of 70%.

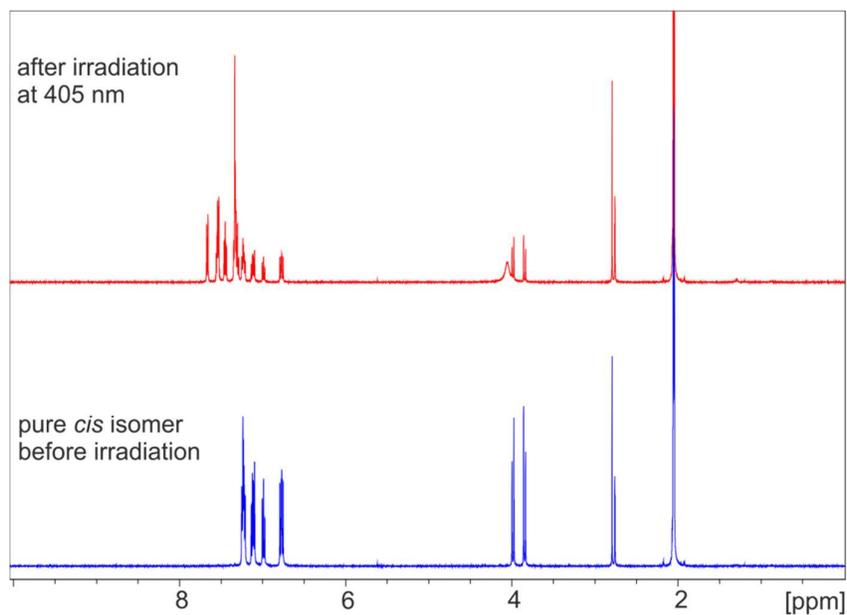


Figure S19: ^1H NMR spectra of S-diazocine **3** before (blue) and after irradiation (red).

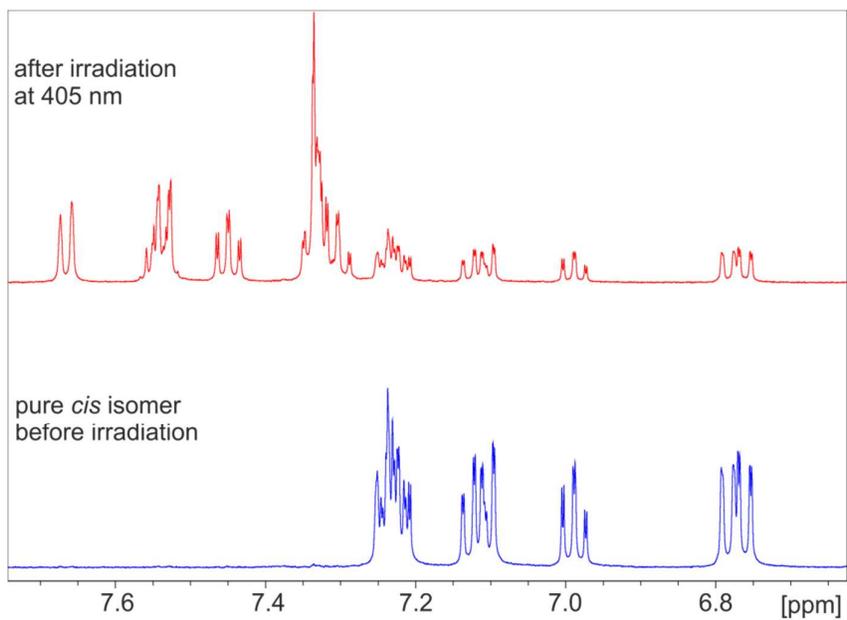


Figure S20: Aromatic regions of the ^1H NMR spectra of S-diazocine **3** before (blue) and after irradiation (red).

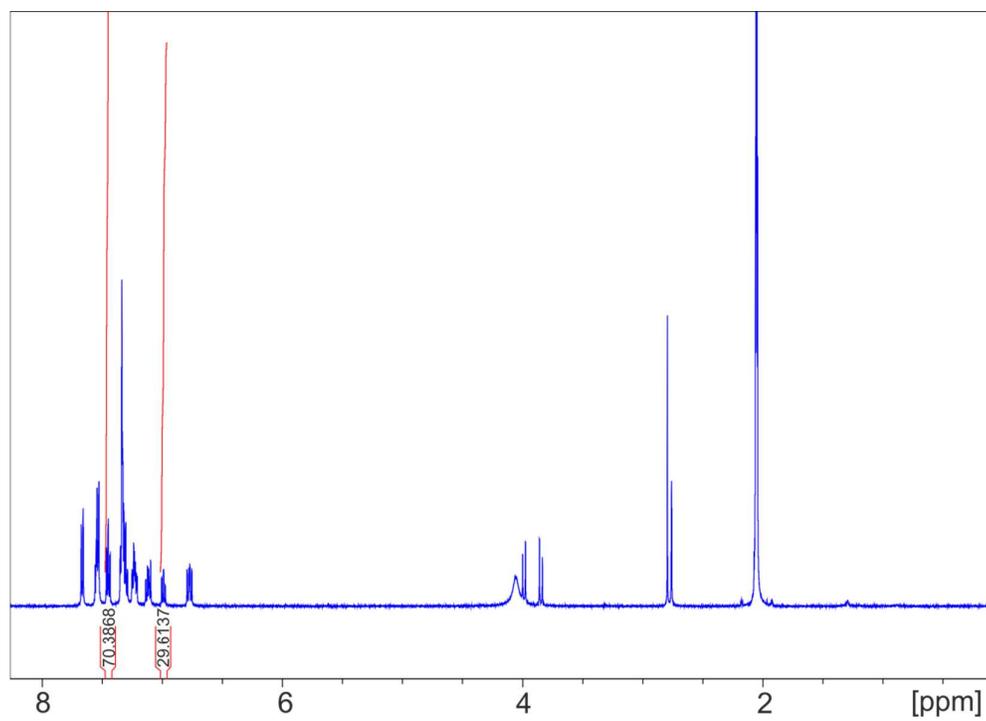


Figure S21: Photostationary state of S-diazocine **3** after irradiation with 405 nm (*trans*: 70% and *cis*: 30 %).

IV.6 Kinetic measurements of the thermochemical *trans*->*cis* isomerization of S-diazocine **3**

^1H NMR spectra of compound **3** were measured in deuterated acetone at 300 K before and after irradiation with 400 nm for 5 min. Several spectra were recorded over several half-lives (every fifth spectrum is shown in the graphic below).

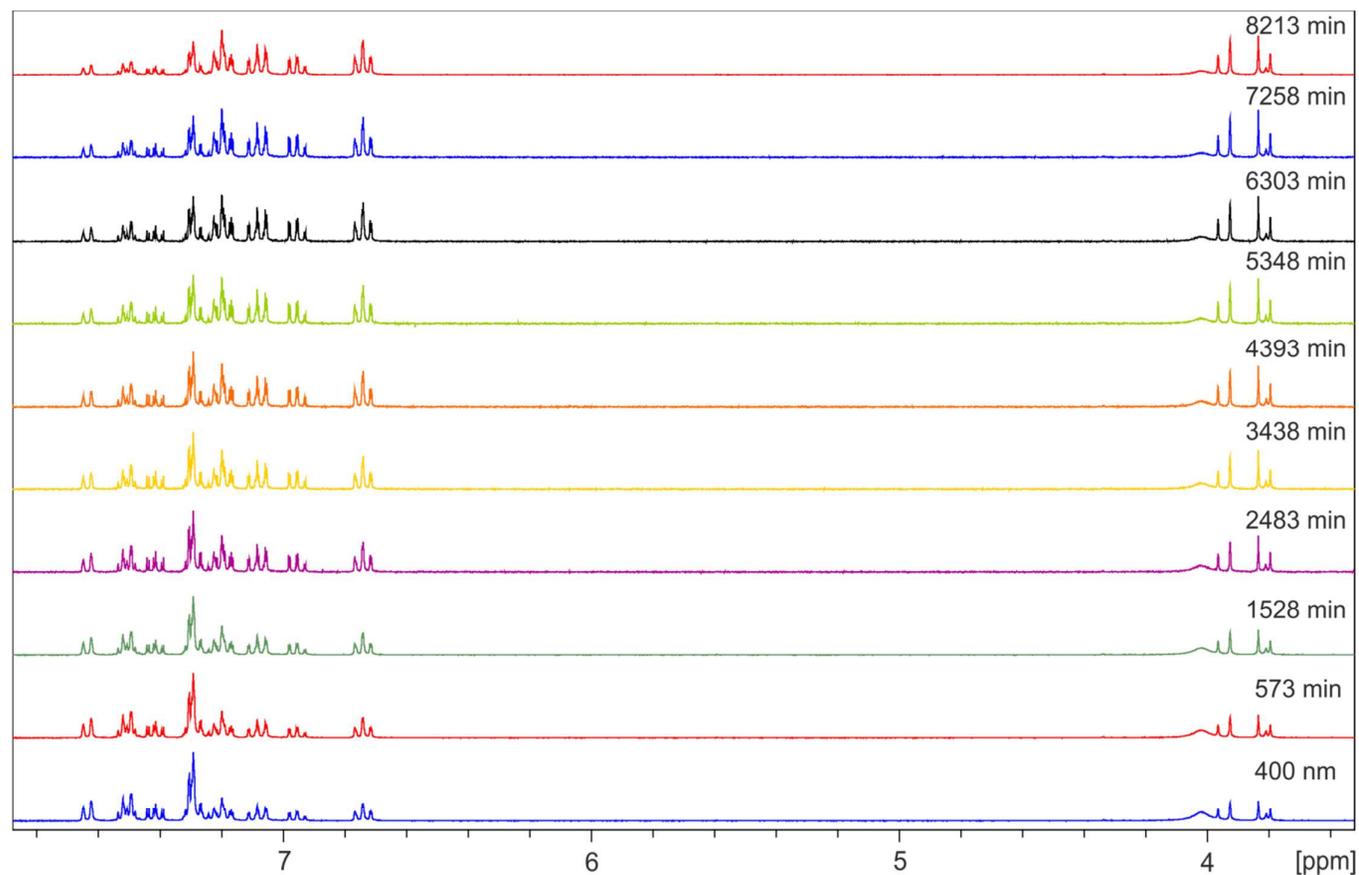


Figure S22: ^1H -NMR spectra of sulfur diazocine **3** after irradiation with 405 nm (blue spectrum at the bottom) and spectra measured after regular time intervals at 300 K.

IV.7 Half-life of S-diazocine 3 determined with ^1H NMR spectroscopy

To determine the thermal half-life of compound **3** with ^1H NMR spectroscopy the integrals of two aromatic signals for both isomers were plotted as a function of time. The half-life was calculated with an exponential fit.

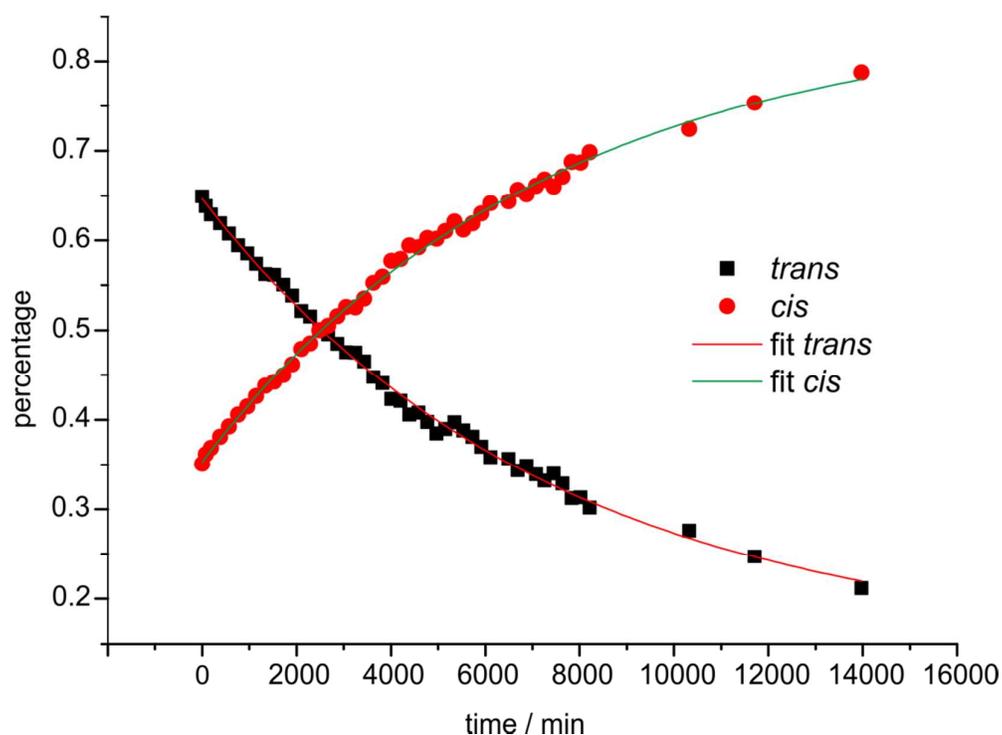


Figure S23: Percentage of *cis* and *trans* isomer of compound **3** plotted as a function of time.

Table S3. Exponential fit of the *cis* and *trans* signal for the thermal back isomerization to the *cis* isomer.

Determined by increase of <i>cis</i> signal at 6.98 ppm	Determined by decrease of <i>trans</i> signal at 7.21 ppm
$k = 1.37 \pm 0.048 * 10^{-4}$ mol/min	$k = 1.36 \pm 0.054 * 10^{-4}$ mol/min
$t_{1/2} = 5050 \pm 161$ min = 84 ± 2.6 h	$t_{1/2} = 5093 \pm 190$ min = 85 ± 3.18 h

V. UV/vis switching experiment

V.1 UV/vis measurements of O-diazocine 2

A solution of O-diazocine **2** in THF was irradiated with 385 nm for 5 minutes and UV/vis spectra were recorded every two minutes at constant temperatures. The absorption maxima were plotted as a function of time and the reaction time constants were determined.

V.1.1 Temperature T = 262 K

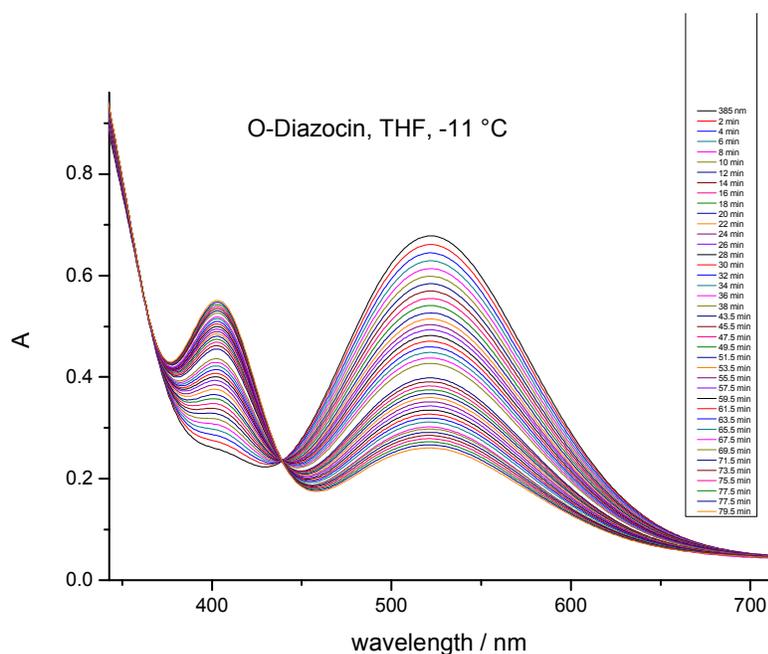


Figure S24: UV/Vis spectra of O-diazocine **2** after irradiation with 385 nm at 262 K.

Table S4. Exponential fit of the *cis* and *trans* signals for the thermal back isomerization at 262 K

absorption at 389 nm	absorption at 523 nm
$k = 2.39 \pm 0.03 \cdot 10^{-4} \text{ mol/s}$	$k = 2.24 \pm 0.03 \cdot 10^{-4} \text{ mol/s}$
$t_{1/2} = 2902 \pm 42 \text{ s} = 48.3 \pm 0.7 \text{ min}$	$t_{1/2} = 3096 \pm 42 \text{ s} = 51.6 \pm 0.7 \text{ min}$

V1.2 Temperature T = 273 K

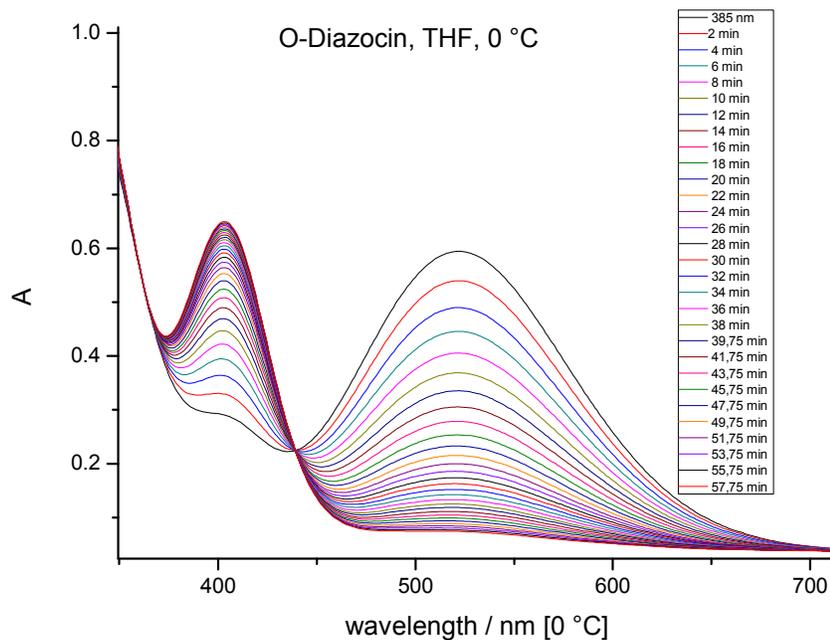


Figure S25: UV/Vis spectra of oxygen diazocine **2** after irradiation with 385 nm at 273 K.

Table S5. Exponential fit of the *cis* and *trans* signal for the thermal back isomerization at 273 K.

absorption at 389 nm	absorption at 523 nm
$k = 9.07 \pm 0.04 \cdot 10^{-4} \text{ mol/s}$	$k = 9.02 \pm 0.07 \cdot 10^{-4} \text{ mol/s}$
$t_{1/2} = 764 \pm 4 \text{ s} = 12.7 \pm 0.06 \text{ min}$	$t_{1/2} = 769 \pm 7 \text{ s} = 12.8 \pm 0.12 \text{ min}$

V1.3 Temperature T = 277 K

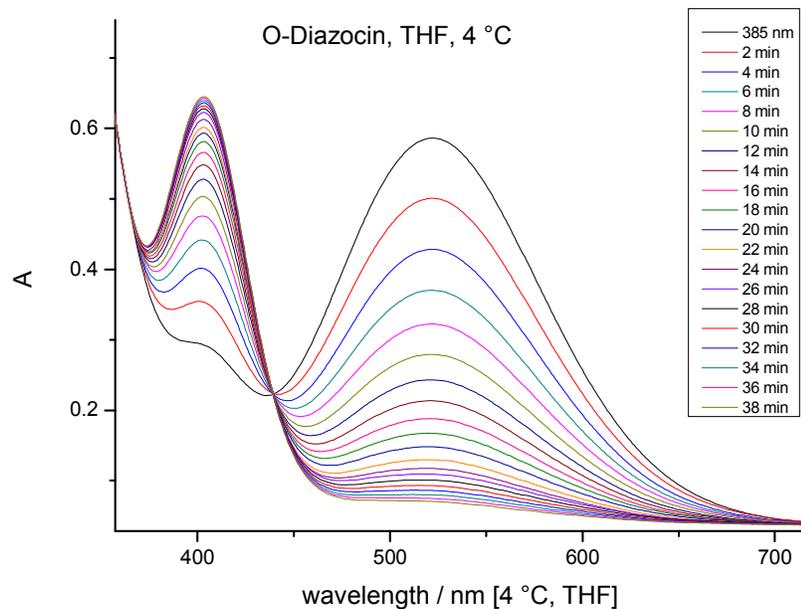


Figure S26: UV/Vis spectra of oxygen diazocine **2** after irradiation with 385 nm at 277 K.

Table S6. Exponential fit of the *cis* and *trans* signal for the thermal back isomerization at 277 K.

absorption at 389 nm	absorption at 523 nm
$k = 1.42 \pm 0.008 \cdot 10^{-3} \text{ mol/s}$	$k = 1.42 \pm 0.01 \cdot 10^{-3} \text{ mol/s}$
$t_{1/2} = 489 \pm 4 \text{ s} = 8.15 \pm 0.06 \text{ min}$	$t_{1/2} = 490 \pm 6 \text{ s} = 8.16 \pm 0.1 \text{ min}$

V1.4 Temperature T = 282 K

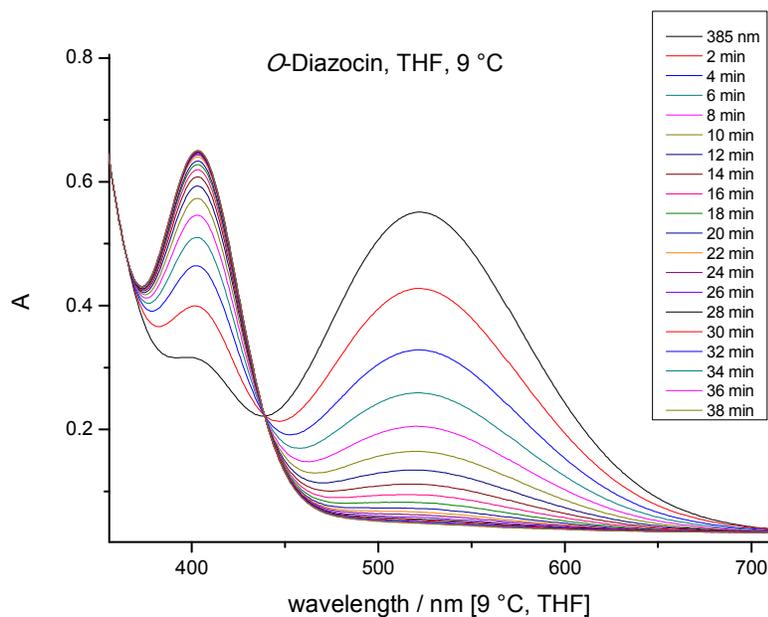


Figure S27: UV/Vis spectra of oxygen diazocine **2** after irradiation with 385 nm at 282 K.

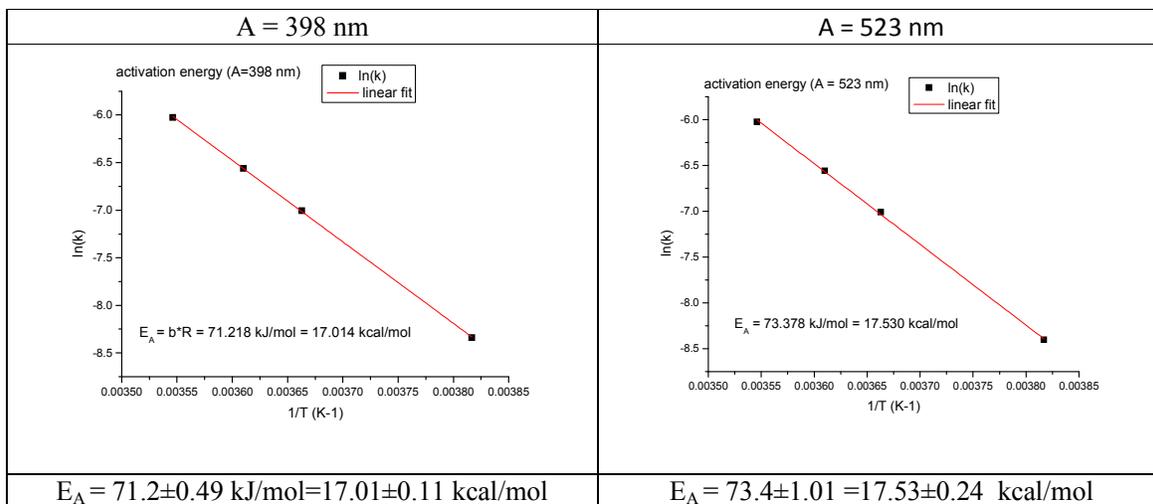
Table S7. Exponential fit of the *cis* and *trans* signal for the thermal back isomerization at 282 K.

absorption at 389 nm	absorption at 523 nm
$k = 2.42 \pm 0.009 \cdot 10^{-3} \text{ mol/s}$	$k = 2.42 \pm 0.009 \cdot 10^{-3} \text{ mol/s}$
$t_{1/2} = 287 \pm 2 \text{ s} = 4.78 \pm 0.03 \text{ min}$	$t_{1/2} = 286 \pm 2 \text{ s} = 4.77 \pm 0.03 \text{ min}$

V1.5 Experimental determination of activation energy of the oxygen diazocine 2

To determine the activation energy of the switching process the logarithm of the rate constants were plotted as a function of $1/T$.

Table S8. Arrhenius plots to determine the activation energy of the thermal back isomerization of the O-diazocine 2.



V.2 UV/Vis measurements of S-diazocine 3

A solution of sulfur diazocine **3** in THF was irradiated with 405 nm for 5 minutes at 293 K and UV/vis spectra were recorded every hour.

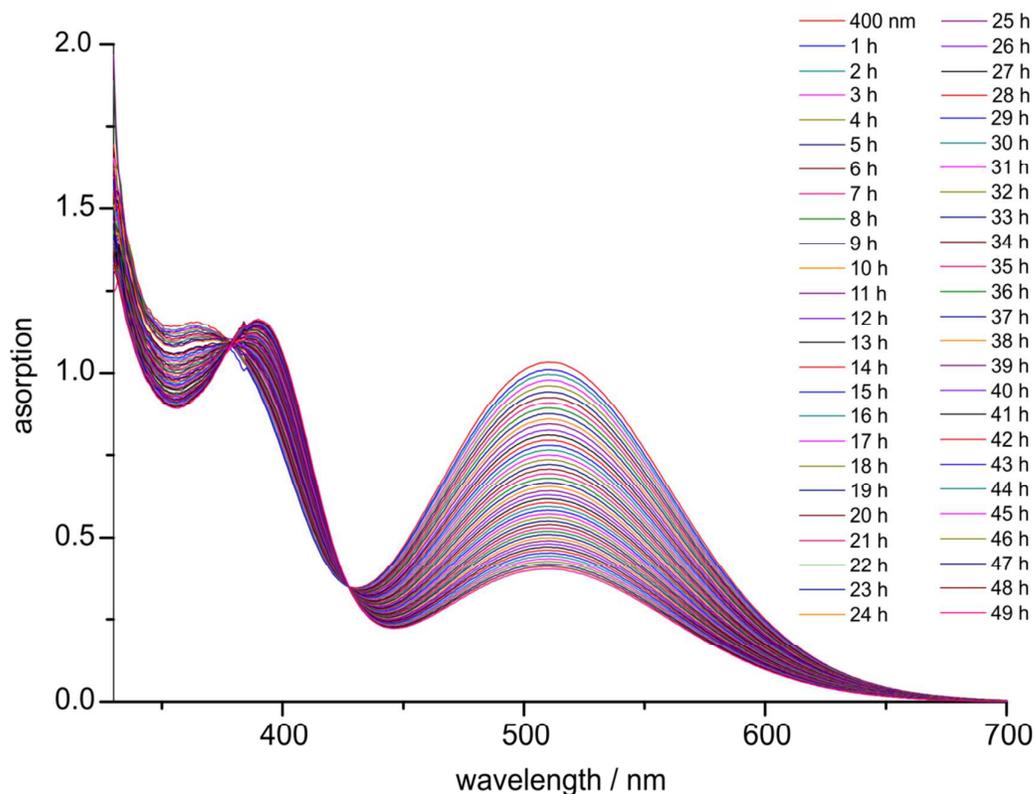


Figure S28: UV/Vis spectra of S-diazocine **3** after irradiation with 405 nm at 293 K.

References

- (1) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- (2) Lellmann, E.; Mayer, N. *Chem. Ber.* **1892**, *25*, 3583–3586.

VI.1 Brief outline of the movie

The movie is shown in real-time (no time-lapse!) The first part of the movie demonstrates that blue (385 nm) and green (530 nm) light don't penetrate the human skin while blood supported tissue is transparent to red light. Then the yellow *cis* isomer of the oxygen diazocine **2** is irradiated with 385 nm (LED light source) demonstrating the very rapid formation of the red *trans* isomer. By irradiation with green light (LED light source) the diazocine **2** isomerizes back to the yellow *cis* isomer within less than a second. The diazocine is switched a second time to the red *trans* isomer, to show the back isomerization to the *cis* configuration with red light.