Supporting Information

Photoswitchable Diazocine-based Estrogen Receptor Agonists Stabilization of the Active Form Inside the Receptor

Julia Ewert [1,†], Linda Heintze [2,†], Mireia Jordà-Redondo [3], Jan-Simon von Glasenapp [1], Santi Nonell [3], Götz Bucher [4], Christian Peifer [2,*] and Rainer Herges [1,*]

[1] Otto-Diels-Institute of Organic Chemistry, Christian-Albrechts-University of Kiel, 24098 Kiel, Germany
[2] Institute of Pharmacy, Christian-Albrechts-University of Kiel, 24118 Kiel, Germany
[3] IQS School of Engineering, University Ramon Llull, 08017 Barcelona, Spain
[4] Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom
* Correspondence: cpeifer@pharmazie.uni-kiel.de (C.P.); rherges@oc.uni-kiel.de (R.H.)
† These authors contributed equally to this work.

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1. Analytical equipment

NMR spectroscopy

NMR spectra were recorded in deuterated solvents from Deutero GmbH, VWR Chemicals and Sigma Aldrich. The solvents reference signals are summarized in table 1.

Table 1. Reference signals of the deuterated solvents for ^{1}H-NMR and ^{13}C-NMR.

solvent	degree of deuteration	^{1}H signal (ppm)	^{13}C signal (ppm)
aceton-d_6	99.9 %	2.05 (qui)	29.84 (sep)
acetonitril-d_3	99.8 %	1.94 (qui)	1.32 (sep)
chloroform-d_1	99.8 %	7.26 (s)	77.16 (t)
deuteriumoxide	99.9 %	4.79 (s)	/
dimethylsulfoxide-d_6	99.8 %	2.50 (qui)	39.52 (sep)

NMR measurements were performed on Bruker ARX300 (^{1}H-NMR: 300.0 MHz, only used for photochemical characterisation measurements), on Bruker Avance Neo 500 (^{1}H-NMR: 500.1 MHz, ^{13}C-NMR: 125.8 MHz) and on Bruker Avance 600 (^{1}H-NMR: 600.1 MHz, ^{13}C-NMR: 150.9 MHz).

NMR determinations of the composition of PSS at different concentrations of CD were recorded on Bruker Avance 200MHz DPX and Bruker Avance III 400MHz spectrometers. Samples were irradiated inside a home-built photoreactor equipped with high power LEDs (405 nm) and air cooling.

Mass spectrometry

High resolution mass spectra were recorded using the following devices:

HR-ESI and HR-APCI: Thermo Scientific Q Exactive Plus MS; Hybrid Quadrupol-Orbitrap

HR-EI: AccuTOF GCv 4G (Joel) with ionization energy of 70 eV

IR spectroscopy

Infrared spectra were measured with a 1600 Series FT-IR spectrometer from Perkin-Elmer with an A531-G Golden-Gate-Diamond-ATR-unit. Table 2 shows the abbreviations used to describe the signal intensities.

Table 2. Abbreviations for the signal intensities.

signal intensity	abbreviation
weak	w
medium	m
strong	s

Melting Point

Melting points were measured in melting point tubes using Melting Point B-560 (Büchi).

UV/Vis spectroscopy

UV/VIS spectra were measured with a Lambda 14 (thermostat form Büchi) and a Lambda 650 UV spectrometer from Perkin-Elmer. Quartz cuvettes of 10 mm optical path length were used.

Chromatography

Column chromatography purifications were performed on silica gel from Merck with a particle size 0.040-0.063 mm. For thin layer chromatography Alugram® Xtra SIL/UV_{254} pre-coated sheets (0.2 mm particle size) from Macherey Nagel were used.

Flash-Chromatography

Flash column chromatography purifications were performed on a Biotage® type Isolera one. Biotage® Ultra cartridges (Biotage®, HP-SphereTM, particle diameter: 25 µm, cartridges sizes: 10 g, 25 g, 50 g and 100 g) and Interchim puriFlash® cartridges (Interchim®, SIHP, particle diameter: 30 µm, cartridges sizes: F0012, F0025 and F0040) were used.

Light sources

For irradiation different custom-built light sources with a wavelength of 385nm, 405 nm and 530 nm were used (Sahlmann Photochemistry Solutions & in-house built).

385 nm: 12 x Nichia NCSU034A, FWHM = 9 nm, P(opt) = 12 x 340 mW,

530 nm: 16 x Luxeon LXML-PM01-0080, FWHM = 33 nm, P(opt) = 16 x 200 mW

UV-Vis Nanosecond Laser flash photolysis

The kinetics of the *E*→*Z* back isomerization of compounds **3** and **4** were determined using a home-built nanosecond laser flash photolysis system described in details elsewhere.[1] Briefly, a Q-switched pulsed Nd:YAG laser (Surelite I-10, Continuum, Santa Clara, CA), emitting 5-ns pulses at 355 nm, 10 mJ/pulse, and operating at 1 Hz repetition rate, was used to excite the samples in air-saturated solutions. Transient absorption was monitored at 500 nm using a white-light beam probe produced by a CW 75 W Xe lamp (Photon Technology International (PTI), Notthingham, NJ) in a right-angles geometry, which was then passed though a dual-grating monochromator (mod. 101, PTI) and detected with a Hamamatsu R928 photomultiplier appropriately wired. The signal was fed to a WaveSurfer 454 oscilloscope (TeledyneLecroy, Chestnut Ridge, NY) for digitizing and averaging and finally transferred to a PC for data storage and analysis. The transient decays obeyed first-order kinetics whose lifetime was obtained using a custom-written data fitting software based on the Lavenverg-Marquardt algorithm. Activation parameters were obtained from Eyring plots of the decay rate constants measured at different temperatures using a Peltier-controlled cuvette holder (TLC50, Quantum Northwest, Liberty Lake, WA).

2. Molecular Modelling

The software package Maestro DrugDiscoverySuite (Maestro Version 12.6.144, MMshare Version 5.2.144, Release 2020-4, Platform Windows-x64), Schrödinger LLC (New York, USA) was used for molecular modeling studies. Calculations were run on a DELL laptop. The protein structure 1ERE of the RCSB protein data bank (PDB) was used as estrogen receptor model. The protein structure was prepared with the Protein Preparation Wizard. Bond orders were adjusted, hydrogen atoms were added, disulfide bonds were optimized and water molecules within a distance > 5 Å to heteroatoms

were deleted and H-bonding within the protein structure was optimized using the standard protocol in Glide. The geometry of the protein was improved in a simplified, restricted optimization using OPLS3e force field. In the process, heavy atoms within RMSD of 0.3 Å were converged. Receptor Grids were created using the tool Glide. Geometries of diazocines structures were optimized using LigPrep. Binding modes were calculated with the tool Glide using Standard Precision (SP) mode.

3. Syntheses

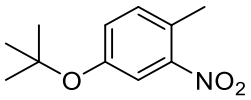
3.1 Synthesis of difunctionalised diazocines

Syntheses of *tert*-butoxy nitrotoluenes 8-10

General procedure

Under nitrogen atmosphere the benzyl alcohol or nitrophenol substrate was mixed with isobutene (8 % in dichloromethane) and 100 µL concentrated sulfuric acid. After stirring at room temperature, the mixture was diluted with saturated potassium carbonate. The organic layer was separated and washed with potassium carbonate. The aqueous layer was extracted with dichloromethane and the combined organic layers were dried over magnesium sulfate. The solvent was removed under reduced pressure after the addition of few drops of triethylamine.

Synthesis of 4-(*tert*-butoxy)-1-methyl-2-nitrobenzene (8)



tert-Butoxy nitrotoluene **8** was prepared from 4-methyl-3-nitrophenol (6.00 g, 39.2 mmol) dissolved in 120 mL isobutene (8 % in dichloromethane) and 100 µL concentrated sulfuric acid according to the general procedure. After 3 h of stirring at room temperature the reaction mixture was purified according to the procedure described above. The target compound was obtained as a yellow liquid (6.91 g, 33.0 mmol, 84 %).

R_f= 0.58 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 7.56 (d, ^4J = 2.6 Hz, 1 H, *H*-3), 7.38 (d, ^3J = 8.5 Hz, 1 H, *H*-6), 7.27 (dd, ^3J = 8.5 Hz, ^4J = 2.6 Hz, 1 H, *H*-5), 2.50 (s, 3 H, -CH_3), 1.38 (s, 9 H, -C-CH_3) ppm.

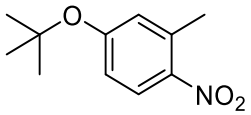
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 155.4 (*C*-2), 150.6 (*C*-4), 133.9 (*C*-6), 129.6 (*C*-5), 128.2 (*C*-1), 120.0 (*C*-3), 80.3 (-*C*-CH_3), 28.9 (-C-*C*H_3), 19.4 (-*C*H_3) ppm.

IR: $\tilde{\nu}$= 2978 (m), 2934 (w), 1620 (w), 1523 (s), 1493 (m), 1454 (w), 1392 (w), 1366 (m), 1340 (m),1278 (m), 1241 (m), 1161 (s), 1035 (w), 956 (m), 899 (m), 860 (m), 832 (m), 813 (m), 781 (w), 760 (w), 695 (w), 674 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 209 (34) $[M]^{+\bullet}$, 153 (90) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{11}H_{15}NO_3$ *m*/*z*= calc.: 209.1052, found: 209.1048.

Synthesis of 4-(*tert*-butoxy)-2-methyl-1-nitrobenzene (9)



tert-Butoxy nitrotoluene **9** was prepared from 3-methyl-4-nitrophenol (5.00 g, 32.7 mmol) dissolved in 80 mL isobutene (8 % in dichloromethane) and 100 µL concentrated sulfuric acid according to the general procedure. However, after 1 h stirring at room temperature another amount of 70 mL isobutene and 100 µL concentrated sulfuric acid was added. After 4.5 h the reaction mixture was purified according to the procedure described above. The target compound was obtained as a yellow liquid (5.18 g, 24.7 mmol, 76 %).

R_f= 0.60 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 8.00 (d, ^3J = 8.8 Hz, 1 H, *H*-6), 7.06-7.03 (m, 2 H, *H*-5, *H*-3), 2.57 (s, 3 H, -CH_3), 1.45 (s, 9 H, C-CH_3) ppm.

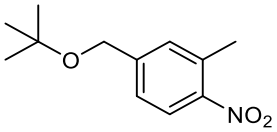
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 161.3 (*C*-4), 146.5 (*C*-1), 136.6 (*C*-2), 127.3 (*C*-6), 126.1 (*C*-3), 120.4 (*C*-5), 80.8 (-*C*-CH_3), 29.0 (-C-*C*H_3), 20.9 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2979 (m), 2936 (w), 1608 (w), 1577 (m), 1509 (s), 1483 (m), 1393 (w), 1368 (m), 1338 (m), 1295 (m), 1247 (m), 1154 (s), 1078 (m), 1019 (w), 967 (m), 897 (w), 871 (w), 828 (m), 762 (m), 723 (w), 694 (w), 652 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 209 (3) $[M]^{+\bullet}$, 153 (46) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{11}H_{15}NO_3$ *m*/*z*= calc.: 209.1052, found: 209.1054.

Synthesis of 4-(*tert*-butoxy methyl)-2-methyl-1-nitrobenzene (10)



tert-Butoxy nitrotoluene **10** was prepared from (3-methyl-4-nitrophenyl) methanol (5.00 g, 29.9 mmol) dissolved in 100 mL isobutene (8 % in dichloromethane) and 100 µL concentrated sulfuric acid according to the general procedure. After 19.5 h of stirring at room temperature the reaction mixture was purified according to the procedure described above, but the organic layer was washed with 1 M sodium hydroxide solution. The target compound was obtained as a yellow liquid (6.16 g, 27.6 mmol, 92 %).

R_f= 0.83 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 7.95 (d, ^3J = 7.9 Hz, 1 H, *H*-6), 7.41-7.44 (m, 2 H, *H*-3, *H*-5), 4.56 (s, 2 H, Ar-CH_2), 2.57 (s, 3 H, -CH_3), 1.28 (s, 9 H, C-CH_3) ppm.

^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 149.0 (*C*-1), 147.4 (-*C*-CH_2), 134.0 (*C*-2), 131.6 (*C*-3), 126.1 (*C*-5), 125.3 (*C*-6), 74.1 (-*C*-CH_3), 63.5 (-C-*C*H_2) 27.9 (-C-*C*H_3), 20.3 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2974 (m), 2935 (w), 1614 (w), 1591 (w), 1517 (s), 1471 (w), 1388 (w), 1364 (w), 1341 (s), 1237 (w), 1192 (s), 1162 (w), 1090 (m), 1033 (w), 938 (w), 891 (m), 836 (s), 749 (s), 689 (w), 646 (w), 581 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 224 (7) $[M+H]^+$, 208 (34) $[M-CH_3]^+$, 150 (100) $[M-C_4H_9O]^+$.

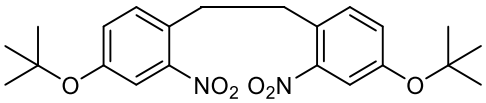
MS (EI, HR, 70 eV): $C_{12}H_{18}NO_3$ *m/z*= calc.: 224.1287, found: 224.1289.

Syntheses of difunctionalised *tert*-butoxy-di-nitrophenyl diazocine precursors 11-15

General procedure

Under nitrogen atmosphere the *tert*-butoxy protected benzyl alcohol or nitrophenol substrate was dissolved in dry tetrahydrofuran and cooled to – 5 °C. Thereafter potassium butoxide was added and the reaction mixture was stirred for 45 s, followed by the addition of bromine. After stirring for further 10 min at room temperature the reaction mixture was diluted with saturated sodium thiosulfate solution. The organic layer was separated and washed with saturated sodium chloride solution. The aqueous layer was extracted with dichloromethane and the combined organic layers were dried over magnesium sulfate followed by removal of the solvent. The crude product was purified by flash column chromatography on silica.

Synthesis of 1,2-bis(4-(*tert*-butoxy)-2-nitrophenyl) ethane (11)



According to the general procedure 4-(*tert*-butoxy)-1-methyl-2-nitrobenzene (**8**, 0.81 g, 3.87 mmol) reacted in the presence of potassium butoxide (434 mg, 3.87 mmol) and bromine (0.20 mL, 3.87 mmol) to the desired product. After purification using flash column chromatography on silica (*n*-pentane/ dichloromethane gradient, 12 % DCM → 100 % DCM) the product was obtained as a beige solid (337 mg, 0.81 mmol, 42 %).

melting point: 125 °C

R_f= 0.31 (*n*-pentane/ dichloromethane 1:1).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, TMS): δ = 7.57 (d, ^4J = 2.4 Hz, 2 H, *H*-3), 7.25 (d, ^3J = 8.4 Hz, 2 H, *H*-6), 7.15 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 2 H, *H*-5), 3.18 (s, 4 H, -CH_2), 1.36 (s, 18 H, -CH_3) ppm.

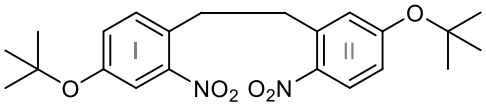
^{13}C-NMR (125 MHz, $CDCl_3$, 298 K, TMS): δ = 154.5 (*C*-4), 149.1 (*C*-2), 132.7 (*C*-6), 130.6 (*C*-1), 128.9 (*C*-5), 119.6 (*C*-3), 80.0 (-*C*-CH_3), 33.9 (-*C*H_2), 28.7 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2975 (m), 2252 (w), 1614 (w), 1519 (s), 1493 (s), 1457 (w), 1390 (w), 1365 (m), 1344 (s), 1261 (m), 1237 (m), 1160 (s), 1067 (w), 1034 (w), 955 (m), 901 (m), 857 (m), 838 (m), 809 (m), 763 (w), 743 (w), 693 (w), 634 (w), 520 (w), 477 (w) cm^{-1}.

MS (APCI): *m/z* (%) = 416 (47) [M], 417 (10) $[M+H]^+$.

MS (APCI): $C_{22}H_{28}N_2O_6$ *m/z*= calc.: 416.1953, found: 416.1941.

Synthesis of 4-(*tert*-butoxy)-2-(4-(*tert*-butoxy)-2-nitrophenethyl)-1-nitrobenzene (12)



According to the general procedure 4-(*tert*-butoxy)-1-methyl-2-nitrobenzene (**8**, 2.14 g, 10.2 mmol) reacted with 4-(*tert*-butoxy)-2-methyl-1-nitrobenzene (**9**, 2.57 g, 12.3 mmol) in the presence of potassium butoxide (2.53 g, 22.5 mmol) and bromine (1.2 mL, 22.5 mmol). After purification using flash column chromatography on silica (*n*-pentane/ dichloromethane gradient, 5 % DCM → 100 % DCM) the product **12** and the by-product **13** could be obtained in one fraction with a ratio of 46 %: 53 % (determined by ^{1}H-NMR spectroscopy). The dimers **12** and **13** could be separated by repeated recrystallisation from cold acetone. The product was obtained as a beige solid (1.07 g, 2.58 mmol, 25 %).

melting point: 78 °C

R_f= 0.36 (*n*-pentane/ dichloromethane 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 7.99 (m_c, 1 H, Ar^{II}-*H*-6), 7.54 (d, ^4J = 2.4 Hz, 1 H, Ar^{I}-*H*-3), 7.35 (d, ^4J = 8.4 Hz, 1 H, Ar^{I}-*H*-6), 7.29 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1 H, Ar^{I}-*H*-5), 7.07 (m_c, 1 H, Ar^{II}-*H*-3), 6.95 (dd, ^3J = 9.8 Hz, ^4J = 2.6 Hz, 1 H, Ar^{II}-*H*-5), 3.25 (m_c, 4 H, Ar^{I}-CH_2, Ar^{II}-CH_2), 1.43 (s, 9 H, Ar^{II}-CH_3), 1.39 (s, 9 H, Ar^{I}-CH_3) ppm.

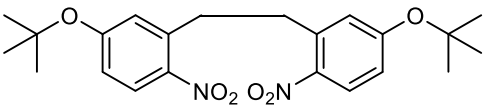
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 161.3 (Ar^{II}-*C*-4), 155.7 (Ar^{I}-*C*-4), 150.4 (Ar^{I}-*C*-2), 144.2 (Ar^{II}-*C*-1), 139.0 (Ar^{II}-*C*-2), 133.5 (Ar^{I}-*C*-6), 130.6 (Ar^{I}-*C*-1), 129.4 (Ar^{I}-*C*-5), 127.7 (Ar^{II}-*C*-6), 125.5 (Ar^{II}-*C*-5), 121.00 (Ar^{II}-*C*-3), 119.9 (Ar^{I}-*C*-3), 80.9 (Ar^{II}-*C*-CH_3), 80.4 (Ar^{I}-*C*-CH_3), 35.1 (Ar^{I}-*C*H_2), 33.7 (Ar^{II}-*C*H_2), 29.0 (Ar^{II}-*C*H_3), 28.9 (Ar^{I}-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2976 (w), 1701 (w), 1608 (m), 1572 (m), 1526 (m), 1503 (s), 1416 (w), 1393 (w), 1367 (m), 1338 (m), 1317 (w), 1297 (w), 1273 (w), 1260 (w), 1237 (w), 1161 (s), 1077 (m), 973 (m), 959 (m), 908 (w), 875 (m), 824 (m), 759 (w), 693 (w), 634 (w), 528 (w), 464 (w), 411 (m) cm^{-1}.

MS (APCI): *m/z* (%) = 416 (48) [M].

MS (APCI): $C_{22}H_{28}N_2O_6$ *m/z*= calc.: 416.1953, found: 416.1941.

Synthesis of 1,2-Bis(5-(*tert*-Butoxy)-2-nitrophenyl) ethane (13)



According to the general procedure 4-(*tert*-butoxy)-2-methyl-1-nitrobenzene (**9**, 2.88 g, 13.8 mmol) reacted in the presence of potassium butoxide (1.55 g, 13.8 mmol) and bromine (0.71 mL, 13.8 mmol) forming the desired product. After purification using flash column chromatography on silica (cyclohexane/ ethyl acetate gradient, 3 % EE → 40 % EE) the product was obtained as a beige solid (1.89 g, 4.53 mmol, 66 %).

melting point: 150 °C

R_f= 0.36 (*n*-pentane/ dichloromethane 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 8.00 (d, ^3J = 8.9 Hz, 2 H, *H*-3), 7.07 (dd, ^3J = 8.9 Hz, ^4J = 2.7 Hz, 2 H, *H*-4), 6.96 (d, ^4J = 2.7 Hz, 2 H, *H*-6), 3.31 (s, 4 H, -CH_2), 1.42 (s, 18 H, -CH_3) ppm.

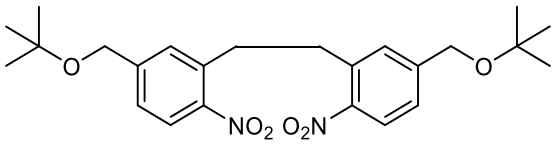
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 161.3 (*C*-5), 142.9 (*C*-2), 139.0 (*C*-1), 127.7 (*C*-3), 125.5 (*C*-6), 121.0 (C-4), 80.9 (-*C*-CH_3), 34.9 (-*C*H_2), 29.1 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2973 (w), 2160 (w), 1980 (w), 1606 (m), 1575 (m), 1505 (s), 1482 (m), 1417 (w), 1390 (w), 1365 (m), 1344 (s), 1293 (m), 1260 (m), 1158 (s), 1076 (m), 1031 (w), 979 (m), 886 (s), 830 (m), 816 (m), 765 (m), 756 (m), 704 (w), 660 (m), 606 (w), 580 (w), 546 (w), 506 (w), 487 (w), 448 (m), 414 (w) cm^{-1}.

MS (APCI): *m*/*z* (%) = 416 (9) [M], 359 (56) [M-C_4H_9].

MS (APCI): $C_{22}H_{28}N_2O_6$ *m*/*z*= calc.: 416.1953, found: 416.1941.

Synthesis of 1,2-bis (5-(*tert*-butoxy methyl)-2-nitrophenyl) ethane (14)



According to the general procedure 4-(*tert*-butoxy methyl)-2-methyl-1-nitrobenzene (**10**, 478 mg, 2.14 mmol) reacted in the presence of potassium butoxide (288 mg, 2.57 mmol) and bromine (0.13 mL, 2.57 mmol) to the desired product. After purification using flash column chromatography on silica (cyclohexane/ ethyl acetate gradient, 6 % EE → 40 % EE) the product was obtained as a beige solid (234 mg g, 0.53 mmol, 50 %).

melting point: 132 °C

R_f= 0.52 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (600 MHz, $CO(CD_3)_2$, 300 K): δ = 7.95 (d, ^3J = 8.1 Hz ,2 H, *H*-3), 7.46 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 2 H, *H*-4), 7.41 (d, ^4J = 1.7 Hz, 2 H, *H*-6), 4.56 (s, 4H, Ar-CH_2-O*t*Bu), 3.27 (s, 4 H, Ar-CH_2), 1.28 (s, 18 H, CH_3) ppm.

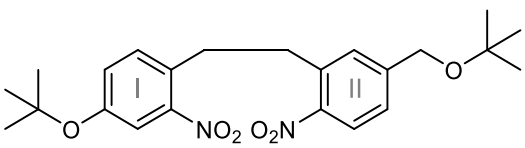
^{13}C-NMR (150 MHz, $CO(CD_3)_2$, 300 K): δ = 149.0 (*C*-2), 147.6 (*C*-5), 136.4 (*C*-1), 131.1 (*C*-6), 126.7 (*C*-4), 125.5 (*C*-3), 74.2 (-*C*-CH_3), 63.4 (Ar-*C*H_2-O*t*Bu), 34.7 (Ar-*C*H_2), 27.9 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2975 (m), 2166 (w), 2045 (w), 1612 (w), 1589 (m), 1514 (s), 1463 (m), 1365 (w), 1344 (s), 1235 (m), 1190 (s), 1087 (s), 1066 (m), 1028 (m), 940 (w), 901 (s), 885 (s), 832 (s), 757 (s), 703 (s), 649 (w), 574 (w) cm^{-1}.

MS (APCI): *m*/*z* (%) = 444 (20) [M].

MS (APCI): $C_{24}H_{32}N_2O_6$ *m*/*z*= calc.: 444.2266, found: 444.2251.

Synthesis of 4-(*tert*-butoxy)-1-(5-(*tert*-butoxymethyl)-2-nitrophenethyl)-2-nitrobenzene (15)



According to the general procedure 4-(*tert*-butoxy methyl)-2-methyl-1-nitrobenzene (**10**, 2.13 g, 9.56 mmol) reacted with 4-(*tert*-butoxy)-1-methyl-2-nitrobenzene (**8**, 2.00 g, 9.56 mmol) in the presence

of potassium butoxide (2.36 g, 21.0 mmol) and bromine (1.08 mL, 21.0 mmol). After purification using flash column chromatography on silica (*n*-pentane/ dichloromethane gradient, 10 % DCM → 100 % DCM) the product was obtained as a beige solid (683 mg, 1.59 mmol, 17 %). In addition, the by-products **11** (364 mg, 0.87 mmol, 18 %, R_f= 0.30 (*n*-pentane/ dichloromethane 1:1)) and **14** (327 mg, 0.74 mmol, 15 %, R_f= 0.07 (*n*-pentane/ dichloromethane 1:1)) could be obtained.

melting point: 69.4 °C

R_f= 0.21 (*n*-pentane/ dichloromethane 1:1).

^{1}H-NMR (600 MHz, $CO(CD_3)_2$, 300 K): δ = 7.93 (d, ^3J = 8.3 Hz, 1 H, Ar^{II}-*H*-3), 7.55 (d, ^4J = 2.6 Hz, 1 H, Ar^{I}-*H*-3), 7.46 (d, ^3J = 8.3 Hz, 1 H, Ar^{II}-*H*-4), 7.40 (s, 1 H, Ar^{II}-*H*-6), 7.33 (d,^3J = 8.4 Hz , 1H, Ar^{I}-*H*-6), 7.28 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1 H, Ar^{I}-*H*-5), 4.55 (s, 2 H, Ar^{II}-*C*H_2-O*t*Bu), 3.23 (m_c, 4 H, Ar^{I}-CH_2, Ar^{II}-CH_2), 1.39 (s, 9 H, Ar^{I}-CH_3), 1.28 (s, 9 H, Ar^{II}-CH_3) ppm.

^{13}C-NMR (150 MHz, $CO(CD_3)_2$, 300 K): δ = 155.6 (Ar^{I}-*C*-4), 150.4 (Ar^{I}-*C*-2), 150.0 (Ar^{II}-*C*-1), 147.6 (Ar^{II}-*C*-5), 136.4 (Ar^{II}-*C*-1), 133.5 (Ar^{I}-*C*-6), 131.1 (Ar^{II}-*C*-6), 130.6 (Ar^{I}-*C*-1), 129.5 (Ar^{I}-*C*-5), 126.6 (Ar^{II}-*C*-4), 125.5 (Ar^{II}-*C*-3), 120.0 (Ar^{I}-*C*-3), 80.4 (Ar^{I}-*C*-CH_3), 74.3 (Ar^{II}-*C*-CH_3), 63.4 (Ar^{II}-*C*H_2-O*t*Bu), 34.6 (Ar^{II}-*C*H_2), 34.0 (Ar^{I}-*C*H_2), 28.9 (Ar^{I}-*C*H_3), 27.9 (Ar^{II}-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2975 (m), 2251 (w), 1721 (w), 1613 (w), 1589 (w), 1519 (s), 1493 (m), 1459 (w), 1390 (w), 1365 (m), 1342 (s), 1241 (m), 1192 (m), 1161 (s), 1091 (m), 1024 (w), 958 (m), 897 (m), 835 (m), 756 (w), 699 (w), 646 (w), 596 (w), 515 (w) cm^{-1}.

MS (APCI): *m*/*z* (%) = 431 (6) $[M+H]^+$.

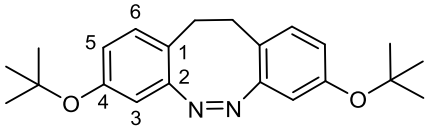
MS (APCI): $C_{23}H_{31}N_2O_6$ *m*/*z*= calc.: 431.2177, found: 431.2174.

Syntheses of *tert*-butoxy diazocines 16-20

General procedure

The *tert*-butoxy-di-nitrophenyl ethanes **11**-**15** (diazocine precursors) were suspended in ethanol and water in the presence of $Ba(OH)_2$ 8 H_2O and heated under reflux. Zinc powder was added, and after reaction the solution was filtrated trough celite. The solvent was evaporated under reduced pressure and the obtained crude product was taken up in ethyl acetate and washed with water. The combined organic layers were dried over magnesium sulfate followed by removal of the solvent. The residue was dissolved in 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ was added. Air was led trough the solution overnight. After neutralisation with 1 M HCl, and extraction with dichloromethane, the combined organic layers were dried in vacuo. The obtained crude product was purified using flash column chromatography on silica.

Synthesis of (*Z*)-3,8-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (16)



According to the general procedure 1,2-bis(4-(*tert*-butoxy)-2-nitrophenyl) ethane (**11**, 325 mg, 0.78 mmol) and $Ba(OH)_2$ 8 H_2O (738 mg, 2.34 mmol) was suspended in 67 mL ethanol and 25 mL water and heated under reflux. Zinc powder (1.02 g, 15.6 mmol) was added, and after 2.5 h the reaction mixture

was purified according to the procedure described above. The residue was dissolved in 110 mL 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ (6.3 mg) was added. Air was led trough the solution overnight. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 6 % EE → 50 % EE) the product was obtained as a yellow solid (64.8 mg, 0.18 mmol, 23 %).

Melting point: 95.4 °C

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 6.94 (d, ^3J = 8.4 Hz, 2 H, *H*-6), 6.65 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 2 H, *H*-5), 6.43 (d, ^4J = 2.4 Hz, 2 H, *H*-3), 2.80-2.78 (m, 4 H, -CH_2), 1.22 (s, 18 H, -CH_3) ppm.

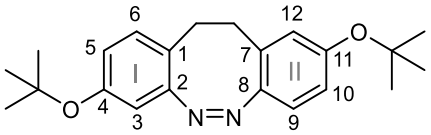
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 157.1 (*C*-2), 155.1 (*C*-4), 131.1 (*C*-6), 124.0 (*C*-1), 123.1 (*C*-5), 114.2 (*C*-3), 80.0 (-*C*-CH_3), 31.5 (-*C*H_2), 29.0 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2974 (m), 1601 (m), 1565 (w), 1485 (s), 1391 (w), 1364 (m), 1252 (m), 1163 (s), 1079 (w), 953 (s), 886 (m), 855 (m), 822 (m), 769 (w), 645 (m), 568 (w), 506 (m), 463 (m), 420 (m), 404 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 352 (15) $[M]^{+\bullet}$, 240 (37) $[M\text{-}C_8H_{18}]^+$.

MS (EI, HR, 70 eV): $C_{22}H_{28}N_2O_2$ *m/z*= calc.: 352.2151, found: 352.2149.

Synthesis of (*Z*)-2,8-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (17)



According to the general procedure 4-(*tert*-butoxy)-2-(4-(*tert*-butoxy)-2-nitrophenethyl)-1-nitrobenzene (**12**, 574 mg, 1.38 mmol) and $Ba(OH)_2$ 8 H_2O (1.96 g, 6.20 mmol) was suspended in 118 mL ethanol and 65 mL water and heated under reflux. Zinc powder (2.17 g, 33.1 mmol) was added, and after 2 h the reaction mixture was purified according to the procedure described above. But after removing the solvent the obtained residue was taken up in dichloromethane and filtered. The filtrate was dried in vacuo and the crude product was dissolved in 200 mL 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ (11 mg) was added. Air was led trough the solution overnight. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 6 % EE → 60 % EE) the product was obtained as a yellow solid (107 mg, 0.30 mmol, 22 %).

Melting point: 111 °C

R_f= 0.64 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 6.92 (d, ^3J = 8.3 Hz, 1 H, *H*-6), 6.77 (dd, ^3J = 8.5 Hz, ^4J = 2.3 Hz, 1 H, *H*-10), 6.69 (d, ^3J = 8.5 Hz, 1 H, *H*-9), 6.66 (d, ^4J = 2.3 Hz, 1 H, *H*-12), 6.62 (dd, ^3J = 8.3 Hz, ^4J = 2.3 Hz, 1 H, *H*-5), 6.35 (d, ^4J = 2.3 Hz, 1 H, *H*-3), 2.83-2.76 (m, 4 H, -CH_2), 1.20 (s, 9 H, Ar^{II}-CH_3), 1.19 (s, 9 H, Ar^{I}-CH_3) ppm.

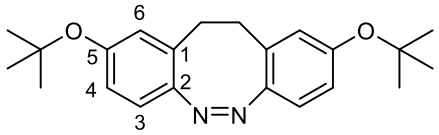
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 157.4 (*C*-4), 155.0 (*C*-2), 154.9 (*C*-11), 152.7 (*C*-8), 130.8 (*C*-6), 130.5 (*C*-7), 125.9 (*C*-12), 124.4 (*C*-1), 123.1 (*C*-5), 122.7 (*C*-10), 119.6 (*C*-9), 114.4 (*C*-3), 79.1 (Ar^{I}-*C*-CH_3), 78.9 (Ar^{II}-*C*-CH_3), 32.2 (Ar^{II}-*C*H_2), 31.3 (Ar^{I}-*C*H_2), 29.0 (Ar^{II}-*C*H_3), 28.9 (Ar^{I}-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2975 (m), 2931 (w), 1599 (m), 1568 (w), 1482 (m), 1391 (m), 1366 (m), 1243 (m), 1158 (s), 1147 (s), 1200 (w), 1083 (w), 1000 (w), 940 (m), 910 (m), 874 (m), 849 (m), 822 (m), 767 (m), 740 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 352 (13) $[M]^{+\bullet}$, 240 (7) $[M\text{-}C_8H_{18}]^+$.

MS (EI, HR, 70 eV): $C_{22}H_{28}N_2O_2$ *m/z*= calc.: 352.2151, found: 352.2145.

Synthesis of (*Z*)-2,9-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (18)



According to the general procedure 1,2-Bis(5-(*tert*-Butoxy)-2-nitrophenyl) ethane (**13**, 1.89 g, 4.53 mmol) and $Ba(OH)_2$ 8 H_2O (6.43 g, 20.4 mmol) was suspended in 370 mL ethanol and 180 mL water and heated under reflux. Zinc powder (7.26 g, 111 mmol) was added, and after 5 h the reaction mixture was purified according to the procedure described above. The residue was dissolved in 400 mL 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ (6.3 mg) was added. Air was led trough the solution overnight. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 3 % EE → 40 % EE) the product was obtained as a yellow solid (562 mg, 1.59 mmol, 35 %).

Melting point: 187 °C

R_f= 0.64 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 6.78 (dd, ^3J = 8.5 Hz, ^4J = 2.6 Hz, 2 H, *H*-4), 6.71-6.69 (m, 4 H, *H*-6, *H*-3), 2.81 (s, 4 H, -CH_2), 1.21 (s, 18 H, -CH_3) ppm.

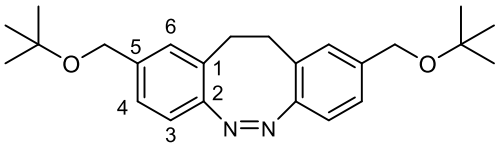
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 155.0 (*C*-5), 152.6 (*C*-2), 130.2 (*C*-1), 125.6 (*C*-3), 122.8 (*C*-4), 120.1 (*C*-6), 78.8 (*C*-CH_3), 32.1 (-*C*H_2), 27.5 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2974 (w), 1600 (m), 1482 (m), 1390 (w), 1365 (m), 1255 (m), 1149 (s), 1103 (w), 1001 (m), 962 (m), 935 (w), 904 (m), 859 (m), 829 (m), 768 (w), 619 (w), 548 (w), 474 (w), 456 (w), 434 (w), 417 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 352 (38) $[M]^{+\bullet}$, 296 (13) $[M\text{-}C_4H_9]^+$, 240 (73) $[M\text{-}C_8H_{18}]^+$.

MS (EI, HR, 70 eV): $C_{22}H_{28}N_2O_2$ *m/z*= calc.: 352.2151, found: 352.2149.

Synthesis of (*Z*)-2,9-bis(*tert*-butoxymethyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (19)



According to the general procedure 1,2-bis (5-(*tert*-butoxy methyl)-2-nitrophenyl) ethane (**14**, 271 mg, 0.61 mmol) and $Ba(OH)_2$ 8 H_2O (577 mg, 1.83 mmol) was suspended in 50 mL ethanol and 25 mL water and heated under reflux. Zinc powder (798 mg, 12.2 mmol) was added, and after 2 h the reaction mixture was purified according to the procedure described above. The residue was dissolved in 250 mL 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ (30 mg) was added. Air was led trough the solution overnight. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 40 % EE) the product was obtained as a yellow solid (152 mg, 0.34 mmol, 56 %).

Melting point: 167 °C

R_f= 0.41 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 7.13 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 2 H, *H*-4), 7.05 (d, ^4J = 1.7 Hz, 2 H, *H*-6), 6.78 (d, ^3J = 8.1 Hz, 2 H, *H*-3), 4.32 (s, 4 H, -*C*H_2-O*t*Bu), 2.86 (s, 4 H, -CH_2), 1.21 (s, 18 H, -CH_3) ppm.

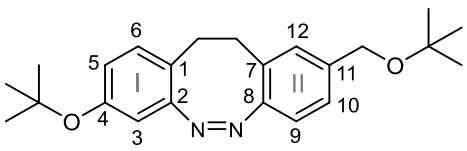
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 155.6 (*C*-2), 140.1 (*C*-5), 129.3 (*C*-6), 128.7 (*C*-1), 126.5 (*C*-4), 119.5 (*C*-3), 73.7 (-*C*-CH_3), 63.9 (Ar-*C*H_2-O*t*Bu), 32.3 (-*C*H_2), 27.9 (-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2969 (m), 1469 (m), 1387 (m), 1362 (s), 1103 (s), 1070 (s), 884 (s), 826 (s), 804 (m), 767 (m), 632 (w), 534 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 380 (87) $[M]^{+\bullet}$, 323 (5) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{24}H_{32}N_2O_2$ *m*/*z*= calc.: 380.2464, found: 380.2460.

Synthesis of (*Z*)-8-(*tert*-butoxy)-2-(*tert*-butoxymethyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (20)



According to the general procedure 4-(*tert*-butoxy)-1-(5-(*tert*-butoxymethyl)-2-nitrophenethyl)-2-nitrobenzene (**15**, 126 mg, 0.29 mmol) and $Ba(OH)_2$ 8 H_2O (277 mg, 0.88 mmol) was suspended in 25 mL ethanol and 10 mL water and heated under reflux. Zinc powder (383 mg, 5.86 mmol) was added, and after 15.5 h the reaction mixture was purified according to the procedure described above. The residue was dissolved in 100 mL 0.1 M methanolic sodium hydroxide solution and $CuCl_2$ (25 mg) was added. Air was led trough the solution overnight. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 6 % EE → 30 % EE) the product was obtained as a yellow solid (32.8 mg, 90.0 µmol, 31 %).

Melting point: 115 °C

R_f= 0.53 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 7.13 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz 1 H, *H*-10), 7.02 (d, ^4J = 1.0 Hz , 1 H, *H*-12), 6.94 (d, ^3J = 8.0 Hz, 1 H, *H*-6), 6.75 (d, ^3J = 8.0 Hz, 1 H, *H*-9), 6.64 (dd, ^3J = 8.0 Hz , ^4J = 2.6 Hz, 1 H, *H*-5), 6.41 (d, ^4J = 2.6 Hz, 1 H, *H*-3), 4.32 (s, 2 H, -CH_2O*t*Bu), 2.83-2.77 (m, 4 H, -CH_2), 1.23 (s, 9 H, Ar^I-CH_3), 1.20 (s, 9 H, Ar^{II}-CH_3) ppm.

^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 157.2 (*C*-2), 155.6 (*C*-8), 155.1 (*C*-4), 140.1 (*C*-11), 131.0 (*C*-6), 129.3 (*C*-12), 128.9 (*C*-7), 126.3 (*C*-10), 123.9 (*C*-1), 123.0 (*C*-5), 119.1 (*C*-9), 114.4 (*C*-3), 79.1 (Ar^{I}-*C*-CH_3), 73.7 (Ar^{II}-*C*-CH_3), 63.9 (-*C*H_2-O*t*Bu), 32.3 (Ar^{II}-*C*H_2), 31.5 (Ar^{I}-*C*H_2), 29.0 (Ar^{I}-*C*H_3), 27.9 (Ar^{II}-*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2972 (m), 2930 (m), 2179 (w), 1697 (w), 1604 (m), 1570 (w), 1488 (s), 1389 (m), 1365 (s), 1245 (m), 1196 (s), 1164 (s), 1093 (s), 953 (m), 930 (m), 871 (s), 851 (m), 807 (s), 768 (w), 651 (w), 620 (m), 595 (m), 560 (w), 522 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 366 (20) $[M]^{+\bullet}$, 310 (14) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{23}H_{30}N_2O_2$ *m*/*z*= calc.: 366.2307, found: 366.2304.

Syntheses of difunctionalised hydroxy/ benzyl alcohol diazocines 1 and 3-6

General procedure

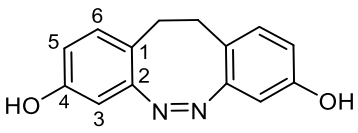
Deprotection using $TiCl_4$:

Under nitrogen atmosphere the *tert*-butoxy diazocine was dissolved in dry dichloromethane and cooled to 0 °C. $TiCl_4$ (3 eq.) was added, and after further stirring at 0 °C for 1 min the reaction mixture was diluted with saturated potassium carbonate solution. The organic phase was separated and the aqueous phase was neutralised with concentrated hydrochloric acid. After extraction with dichloromethane and ethyl acetate the combined organic layers were dried over magnesium sulfate followed by removal of the solvent. The crude product was purified using flash column chromatography on silica.

Deprotection using trifluoroacetic acid:

The *tert*-butoxy diazocine was dissolved in dichloromethane and trifluoroacetic acid was added. After a few hours, the reaction mixture was diluted with saturated potassium carbonate solution and the organic phase was separated. The aqueous phase was neutralised with concentrated hydrochloric acid and extracted with dichloromethane and ethyl acetate. The combined organic layers were dried over magnesium sulfate followed by removal of the solvent. The residue was purified using flash column chromatography on silica.

Synthesis of (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-3,8-diol (1)



Starting from (*Z*)-3,8-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**16**, 155 mg, 0.44 mmol) dissolved in 29 mL dichloromethane, TFA (1.1 mL) was added according to the general procedure using trifluoroacetic acid. The reaction mixture was stirred for 2 h. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 60 % EE) the product was obtained as a yellow solid (48 mg, 0.20 mmol, 46 %).

melting point: 194 °C

R_f= 0.42 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 8.39 (s, 1 H, O*H*), 6.85 (d, ^3J = 8.2 Hz, 2 H, *H*-6), 6.50 (dd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, 2 H, *H*-5), 6.27 (d, ^4J = 2.6 Hz, 2 H, *H*-3), 2.72 (m_c, 4 H, -CH_2) ppm.

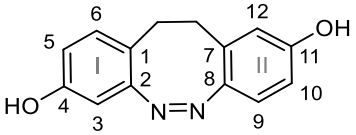
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 157.5 (*C*-2), 156.8 (*C*-4), 131.7 (*C*-6), 120.1 (*C*-1), 114.8 (*C*-5), 105.9 (*C*-3), 31.5 (-*C*H_2) ppm.

IR: $\tilde{\nu}$ = 3340 (m), 2946 (w), 2896 (w), 2591 (w), 1610 (m), 1587 (m), 1499 (m), 1440 (m), 1362 (w), 1270 (s), 1231 (s), 1135 (m), 934 (m), 903 (m), 799 (s), 740 (m), 716 (m), 676 (w), 620 (m), 552 (w), 525 (m), 505 (m), 489 (s), 451 (m), 410 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 240 (88) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{14}H_{12}N_2O_2$ m/z= calc.: 240.0894, found: 240.0898.

Syntheses of (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol (3)



Starting from (*Z*)-2,8-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**17**, 107 mg, 0.30 mmol) dissolved in 20 mL dry dichloromethane, $TiCl_4$ (99.9 µL, 0.91 mmol) was added according to the general procedure using $TiCl_4$. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 80 % EE) the product was obtained as a green, yellow solid (61.6 mg, 0.26 mmol, 86 %).

melting point: 200 °C

***R*$_f$**= 0.18 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (600 MHz, DMSO, 300 K, TMS): δ = 9.47 (s, 1 H, Ar^I-O*H*), 9.43 (s, 1 H, Ar^{II}-O*H*), 6.86 (d, ^3J = 8.3 Hz, 1 H, *H*-6), 6.68 (d, ^3J = 8.5 Hz, 1 H, *H*-9), 6.55 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz, 1 H, *H*-10), 6.44 (dd, ^3J = 8.3 Hz, ^4J = 2.5 Hz, 1 H, *H*-5), 6.41 (d, ^4J = 2.5 Hz, 1 H, *H*-12), 6.14 (d, ^4J = 2.5 Hz, 1 H, *H*-3), 2.64 (m_c, 4 H, -CH_2) ppm.

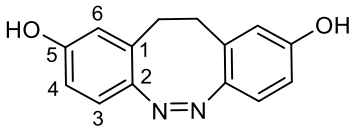
^{13}C-NMR (150 MHz, DMSO, 300 K, TMS): δ = 156.1 (*C*-11), 156.0 (*C*-4), 155.7 (*C*-2), 147.5 (*C*-8), 130.7 (*C*-6), 130.5 (*C*-7), 120.5 (*C*-9), 118.4 (*C*-1), 115.8 (*C*-12), 114.0 (*C*-5), 113.3 (*C*-10), 104.8 (*C*-3), 31.6 (Ar^{II}-*C*H_2), 29.9 (Ar^I-*C*H_2) ppm.

IR: $\tilde{\nu}$ = 3368 (m), 3037 (w), 2938 (w), 2697 (w), 1705 (w), 1607 (m), 1580 (s), 1499 (m), 1474 (m), 1439 (w), 1423 (w), 1364 (m), 1333 (w), 1292 (s), 1247 (s), 1211 (s), 1188 (m), 1154 (s), 1107 (m), 1046 (w), 1002 (w), 945 (w), 927 (m), 901 (m), 884 (m), 851 (m), 818 (s), 753 (w), 735 (w), 714 (w), 682 (w) cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 240 (64) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{14}H_{12}N_2O_2$ *m/z*= calc.: 240.0896, found: 240.0899.

Syntheses of (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,9-diol (4)



Starting from (*Z*)-2,9-di-*tert*-butoxy-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**18**, 427 mg, 1.21 mmol) dissolved in 105 mL dichloromethane, TFA (4.0 mL) was added according to the general procedure using trifluoroacetic acid. The reaction mixture was stirred for 5 h. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 100 % EE) the product was obtained as a green, yellow solid (243 mg, 1.01 mmol, 84 %).

melting point: 173 °C

R_f= 0.36 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 8.32 (s, 2 H, O*H*), 6.67 (d, ^3J = 8.4 Hz, 2 H, *H*-3), 6.63 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 2 H, *H*-4), 6.54 (d, ^4J = 2.4 Hz, 2 H, *H*-6), 2.75 (s, 4 H, -CH_2) ppm.

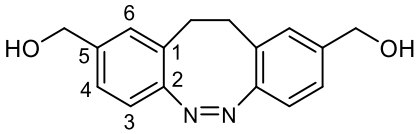
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 156.8 (*C*-5), 149.6 (*C*-2), 130.8 (*C*-1), 121.6 (*C*-3), 116.5 (*C*-6), 114.3 (*C*-4), 32.4 (-*C*H_2) ppm.

IR: $\tilde{\nu}$ = 1602 (m), 1563 (m), 1495 (m), 1445 (m), 1366 (w), 1339 (w), 1293 (m), 1230 (s), 1153 (m), 1102 (m), 1040 (w), 954 (w), 914 (w), 892 (w), 863 (m), 822 (m), 750 (w), 714 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 240 (94) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{14}H_{12}N_2O_2$ m/z= calc.: 240.0899, found: 240.0895.

Synthesis of (*Z*)-(11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,9-diyl)dimethanol (5)



Starting from (*Z*)-2,9-bis(*tert*-butoxymethyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**19**, 26 mg, 68.0 µmol) dissolved in 5 mL dry dichloromethane, $TiCl_4$ (22.4 µL, 0.20 mmol) was added according to the general procedure using $TiCl_4$. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 20 % EE → 80 % EE) the product was obtained as a yellow solid (13 mg, 49.0 µmol, 72 %).

melting point: 153 °C

R_f= 0.12 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, CD_3CN, 298 K, TMS): δ = 7.12 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2 H, *H*-4), 7.03 (s, 2 H, *H*-6), 6.80 (d, ^3J = 7.9 Hz, 2 H, *H*-3), 4.44 (d, ^3J = 5.7 Hz, 4 H, -CH_2-OH), 3.15 (t, ^3J = 5.7 Hz, 2 H, O*H*), 2.85 (m_c, 4 H, -CH_2) ppm.

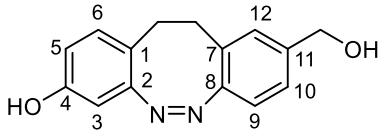
^{13}C-NMR (125 MHz, CD_3CN, 298 K, TMS): δ = 155.6 (*C*-2), 142.1 (*C*-5), 129.4 (*C*-1), 129.1 (*C*-6), 126.1 (*C*-4), 119.8 (*C*-3), 64.0 (-*C*H_2-OH), 32.3 (-*C*H_2) ppm.

IR: $\tilde{\nu}$ = 3284 (m), 2931 (w), 2876 (w), 2360 (w), 2174 (w), 2146 (w), 2134 (w), 2038 (w), 2013 (w), 1751 (w), 1654 (w), 1523 (w), 1483 (w), 1457 (m), 1415 (m), 1364 (m), 1206 (w), 1182 (w), 1150 (m), 1100 (w), 1022 (s), 995 (s), 960 (m), 915 (m), 892 (m), 838 (m), 814 (s), 754 (m), 734 (m), 718 (w), 699 (w), 675 (s), 604 (w), 575 (w), 533 (m), 509 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 268 (32) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{16}H_{16}N_2O_2$ *m*/*z*= calc.: 268.1212, found: 268.1209.

Synthesis of (*Z*)-9-(hydroxymethyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocin-3-ol (6)



Starting from (*Z*)-8-(*tert*-butoxy)-2-(*tert*-butoxymethyl)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**20**, 131 mg, 0.36 mmol) dissolved in 25 mL dry dichloromethane, $TiCl_4$ (117 µL, 1.07 mmol) was added according to the general procedure using $TiCl_4$. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 30 % EE → 80 % EE) the product was obtained as a yellow solid (66.5 mg, 0.26 mmol, 73 %).

melting point: 177 °C

R_f= 0.24 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (600 MHz, $CO(CD_3)_2$, 300 K, TMS): δ = 8.40 (s, 1 H, Ar-O*H*), 7.15 (d, ^3J = 8.2 Hz, 1 H, *H*-10), 7.03 (s, 1 H, *H*-12), 6.88 (d, ^3J = 8.2 Hz, 1 H, *H*-6), 6.77 (d, ^3J = 8.2 Hz, 1 H, *H*-9), 6.51 (dd, ^3J = 8.2 Hz , ^4J = 2.5 Hz, 1 H, *H*-5), 6.28 (d, ^4J = 2.5 Hz, 1 H, *H*-3), 4.50 (d, 2 H, ^3J = 5.6 Hz, -CH_2OH), 4.12 (t, 1 H, ^3J = 5.6 Hz, -CH_2-O*H*), 2.81-2.71 (m, 4 H, -CH_2) ppm.

^{13}C-NMR (150 MHz, $CO(CD_3)_2$, 300 K, TMS): δ = 157.6 (*C*-2), 156.9 (*C*-4), 155.5 (*C*-8), 142.1 (*C*-11), 131.6 (*C*-6), 129.0 (*C*-7), 128.8 (*C*-12), 125.6 (*C*-10), 119.8 (*C*-1), 119.4 (*C*-9), 114.9 (*C*-5), 106.0 (*C*-3), 64.0 (-*C*H_2-OH), 32.7 (-*C*H_2-Ar-CH_2OH), 31.2 (Ar^I-*C*H_2) ppm.

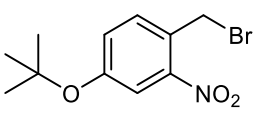
IR: $\tilde{\nu}$ = 3221 (s), 2934 (w), 1999 (w), 1610 (s), 1499 (m), 1453 (s), 1278 (m), 1240 (s), 1170 (w), 1141 (w), 1104 (w), 1025 (s), 908 (m), 847 (w), 807 (s), 726 (w), 622 (w), 584 (w), 532 (w), 508 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 254 (66) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{15}H_{14}N_2O_2$ m/z= calc.: 254.1055, found: 254.1052.

3.2 Syntheses of monofunctionalised diazocines

Synthesis of 1-(bromomethyl)-4-(*tert*-butoxy)-2-nitrobenzene



4-(*tert*-butoxy)-1-methyl-2-nitrobenzene (1.00 g, 4.78 mmol) was dissolved in 7.0 mL carbon tetrachloride and *N*-bromosuccinimide (938 mg, 5.27 mmol) and DBPO (36.0 mg, 0.15 mmol) were added. The reaction mixture was heated under reflux and after 2.5 h a further amount of DBPO (40.0 mg) was added. After 7.5 h the solution was cooled to room temperature and after stirring for further 13 h it was filtrated through celite. The solvent was removed under reduced pressure and the residue was purified using flash column chromatography on silica (cyclohexane/ ethyl acetate, 0 % EE → 20 % EE). The product was obtained as a yellow liquid (851 mg, 2.95 mmol, 62 %).

R_f= 0.51 (cyclohexane/ ethyl acetate 3:1).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K, TMS): δ = 7.65 (d, ^4J = 2.6 Hz, 1 H, *H*-3), 7.44 (d, ^3J = 8.4 Hz, 1 H, *H*-6), 7.20 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1 H, *H*-5), 4.80 (s, 2 H, -CH_2), 1.42 (s, 9 H, -CH_3) ppm.

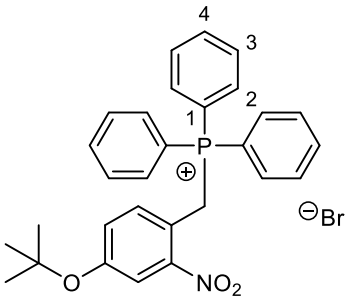
^{13}C-NMR (125 MHz, $CDCl_3$, 298 K, TMS): δ = 156.7 (*C*-4), 148.1 (*C*-2), 133.0 (*C*-6), 128.2 (*C*-5), 126.7 (*C*-1), 119.5 (*C*-3), 80.6 (*C*-CH_3), 29.0 (-CH_2), 28.7 (-CH_3) ppm.

IR: $\tilde{\nu}$ = 2978 (m), 1765 (w), 1616 (m), 1527 (s), 1495 (m), 1439 (m), 1393 (w), 1368 (m), 1338 (m), 1342 (m), 1295 (w), 1245 (m), 1223 (m), 1157 (s), 1112 (w), 1062 (w), 1033 (w), 997 (w), 960 (m), 902 (m), 861 (m), 839 (m), 816 (m), 795 (w), 762 (w), 703 (w), 622 (m), 458 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 287 (2) $[M]^{+\bullet}$, 231 (7) $[M\text{-}C_4H_9]^+$, 153 (10) $[M\text{-}C_4H_9Br]^+$.

MS (EI, HR, 70 eV): $C_{11}H_{14}NO_3Br$ *m*/*z*= calc.: 287.0157, found: 287.0155.

Synthesis of (4-(*tert*-butoxy)-2-nitrobenzyl) triphenylphosphonium bromide (21)



Under nitrogen atmosphere 1-(bromomethyl)-4-(*tert*-butoxy)-2-nitrobenzene (3.78 g, 13.1 mmol) was dissolved in 200 mL dry acetone and heated under reflux. Triphenylphosphine (6.88 g, 26.2 mmol) was added, and after 2 h the precipitated colorless solid was filtered off. After recrystallisation from ethyl acetate the product was obtained (5.22 g, 9.48 mmol, 72 %).

melting point: 212 °C

^{1}H-NMR (500 MHz, DMSO, 298 K): δ = 7.92 (m_c, 3 H, *H*-4), 7.74 (m_c, 6 H, *H*-2), 7.65-7.61 (m, 6 H, *H*-3), 7.52 (d, ^4J = 2.5 Hz, 1 H, *H*-3), 7.38 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz, 1 H, *H*-5), 7.32 (dd, ^3J = 8.5 Hz, ^5J = 2.5 Hz, 1 H, *H*-6), 5.38 (d, ^2J = 14.7 Hz, 2 H, -CH_2), 1.34 (s, 9 H, -CH_3) ppm.

^{13}C-NMR (125 MHz, DMSO, 298 K): δ = 156.1 (*C*-4), 148.5 (*C*-2), 135.2 (d, $^{4}J_{CP}$ = 2.9 Hz, *C*-4), 133.7 (d, $^{3}J_{CP}$ = 9.3 Hz, *C*-3), 133.9 (*C*-6), 130.2 (d, $^{2}J_{CP}$ = 12.8 Hz, *C*-2), 129.0 (*C*-5), 119.8 (*C*-3), 117.3 (d, $^{1}J_{CP}$ = 86.3 Hz, *C*-1), 80.5 (*C*-CH_3), 28.1 (-*C*H3), 26.2 (-*C*H_2) ppm.

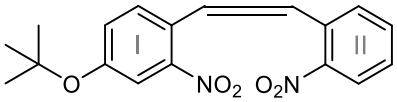
^{31}P-NMR (202.5 MHz, DMSO, 300 K): δ = 23.4 ppm.

IR: $\tilde{\nu}$ = 3049 (w), 2982 (w), 2844 (w), 2777 (w), 2033 (w), 1583 (w), 1528 (s), 1482 (m), 1431 (m), 1396 (w), 1373 (m), 1339 (m), 1304 (w), 1241 (m), 1156 (s), 1108 (s), 1027 (w), 996 (w), 963 (m), 921 (m), 865 (m), 836 (m), 752 (s), 715 (m), 690 (s) cm^{-1}.

MS (ESI, pos): *m*/*z* (%) = 470 (100) $[M]^+$.

MS (ESI, HR, pos): $C_{29}H_{29}O_3NP$ *m*/*z*= calc.: 470.1880, found: 470.1879.

Synthesis of 4-(*tert*-butoxy)-2-nitro-1-(2-nitrostyryl) benzene (22)



Under nitrogen atmosphere (4-(*tert*-butoxy)-2-nitrobenzyl) triphenylphosphonium bromide (**21**, 1.00 g, 1.82 mmol) was suspended in 120 mL dry tetrahydrofuran and heated under reflux. Potassium tert-butoxide (204 mg, 1.82 mmol) was added, and after 10 min the reaction mixture was cooled to 50 °C. After adding 2-nitrobenzaldehyde (275 mg, 1.82 mmol) and stirring for further 2 h the solution was washed with water (30 mL). It was extracted with diethyl ether (3x 100 mL) and the combined organic layers were dried in vacuo. The crude product was purified using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 80 % EE). The product was obtained as a yellow oil (494 mg, 1.44 mmol, 79 %).

***R*$_f$**= 0.67 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ = 8.05 (dd, ^{3}J = 8.0 Hz , ^{4}J = 1.5 Hz, 1 H, Ar^{II}-*H*-3), 7.68 (d, ^{4}J = 2.3 Hz, 1 H, Ar^{I}-*H*-3), 7.34 (m_c, 1 H, Ar^{II}-*H*-5), 7.30 (m_c, 1 H, Ar^{II}-*H*-4), 7.05 (s, 2 H, C*H*), 7.03 (dd, ^{3}J = 8.0 Hz , ^{4}J = 1.7 Hz, 1 H, Ar^{II}-*H*-6), 6.92 (dd, ^{3}J = 8.5 Hz , ^{4}J = 2.3 Hz, 1 H, Ar^{I}-*H*-5), 6.88 (d, ^{3}J = 8.5 Hz, 1 H, Ar^{I}-*H*-6), 1.36 (s, 9 H, CH_3) ppm.

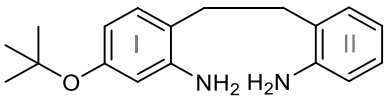
^{13}C-NMR (125 MHz, $CDCl_3$, 298 K): δ = 155.6 (Ar^{I}-*C*-4), 148.3 (Ar^{I}-*C*-2), 148.3 (Ar^{II}-*C*-2), 133.0 (Ar^{II}-*C*-4), 132.8 (Ar^{I}-*C*-6), 132.7 (Ar^{II}-*C*-1), 132.5 (Ar^{II}-*C*-6), 128.7 (Ar^{I}-*C*H), 128.3 (Ar^{II}-*C*-5), 128.2 (Ar^{II}-*C*H), 128.4 (Ar^{I}-*C*-5), 126.8 (Ar^{I}-*C*-1), 124.7 (Ar^{II}-*C*-3), 118.8 (Ar^{I}-*C*-3), 88.3 (*C*-CH_3), 28.7 (*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2978 (w), 2932 (w), 1606 (w), 1571 (w), 1554 (w), 1519 (s), 1492 (w), 1393 (w), 1367 (w), 1341 (s), 1249 (m), 1159 (s), 959 (m), 900 (w), 857 (m), 832 (w), 812 (w), 787 (w), 761 (w), 746 (w), 705 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 342 (2) $[M]^+$, 286 (15) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{18}H_{18}N_2O_5$ *m*/*z*= calc.: 342.1216, found: 342.1199.

Synthesis of 2-(2-aminophenethyl)-5-(*tert*-butoxy) aniline (23)



In a baffled flask 4-(*tert*-butoxy)-2-nitro-1-(2-nitrostyryl) benzene (**22**, 913 mg, 2.67 mmol) was dissolved in 300 mL ethanol. It was carefully evacuated and flooded with nitrogen three times. Under nitrogen counter current Pd/C was added followed by an additional evacuation and flooding with hydrogen. After stirring for 15 h at room temperature the solution was filtered through celite and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 100 % EE) and the product was obtained as a yellow solid (303 mg, 1.07 mmol, 75 %).

melting point: 78.5 °C

R_f= 0.4 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 7.01 (dd, ^3J = 7.5 Hz , ^4J = 1.5 Hz, 1 H, Ar^{II}-*H*-6), 6.93 (m_c, 1 H, Ar^{II}-*H*-5), 6.88 (d, ^3J = 8.0 Hz, 1 H, Ar^{I}-*H*-3), 6.69 (dd, ^3J = 7.7 Hz , ^4J = 1.2 Hz, 1 H, Ar^{II}-*H*-3), 6.57 (m_c, 1 H, Ar^{II}-*H*-4), 6.40 (d, ^4J = 2.3 Hz, 1 H, Ar^{I}-*H*-6), 6.23 (dd, ^3J = 8.0 Hz , ^4J = 2.4 Hz, 1 H, Ar^{I}-*H*-4), 4.42 (bs, 4 H, NH_2), 2.86 (s, 9 H, CH_3), 2.74 (m_c, 4 H, CH_2) ppm.

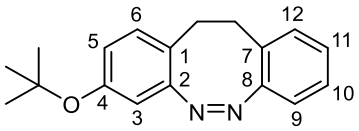
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 155.6 (Ar^{I}-*C*-5), 147.2 (Ar^{I}-*C*-1), 146.7 (Ar^{II}-*C*-2), 130.1 (Ar^{II}-*C*-6), 130.0 (Ar^{I}-*C*-3), 127.5 (Ar^{II}-*C*-5), 126.8 (Ar^{II}-*C*-1), 121.8 (Ar^{I}-*C*-2), 118.2 (Ar^{II}-*C*-4), 116.0 (Ar^{II}-*C*-3), 113.9 (Ar^{I}-*C*-4), 111.7 (Ar^{I}-*C*-6), 77.7 (*C*-CH_3), 31.4 (Ar^{II}-*C*H_2), 30.8 (Ar^{I}-*C*H_2), 29.2 (*C*H_3) ppm.

IR: $\tilde{\nu}$ = 3423 (w), 3350 (w), 3227 (w), 3031 (w), 2976 (w), 2933 (w), 2863 (w), 1619 (m), 1605 (m), 1575 (m), 1498 (s), 1456 (m), 1388 (m), 1365 (m), 1283 (m), 1260 (w), 1154 (s), 1136 (w), 1078 (w), 1035 (w), 991 (m), 971 (m), 886 (s), 867 (w), 851 (w), 822 (w), 806 (w), 775 (w), 749 (s), 685 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 284 (4) $[M]^{+\bullet}$, 228 (3) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{18}H_{24}N_2O$ *m*/*z*= calc.: 284.1889, found: 284.1889.

Synthesis of (*Z*)-3-(*tert*-butoxy)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (24)



2-(2-Aminophenethyl)-5-(*tert*-butoxy) aniline (**23**, 261 mg, 0.92 mmol) was dissolved in 10 mL dichloromethane, and oxone (1.13 g, 1.83 mmol) dissolved in 10 mL water was added. After stirring for 2.5 h the phases were separated and the aqueous layer was extracted with dichloromethane (2 x 50.0 mL). The combined organic layers were dried in vacuo, and the residue was dissolved in 5 mL dichloromethane and 5 mL acetic acid. After stirring for further 14 h the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography on silica (cyclohexane/ ethyl acetate, 6 % EE → 50 % EE). The product was obtained as a yellow solid (125 mg, 0.45 mmol, 49 %).

melting point: 81.6 °C

R_f= 0.64 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 7.15 (m_c, 1 H, *H*-10), 7.00-7.05 (m, 2 H, *H*-11, *H*-12) 6.92 (d, ^3J = 8.2 Hz, 1 H, *H*-6), 6.78 (dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz, 1 H, *H*-9), 6.63 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1 H, *H*-5), 6.39 (d, ^4J = 2.4 Hz, 1 H, *H*-3), 2.82 (m_c, 4 H, CH_2), 1.21 (s, 9 H, CH_3) ppm.

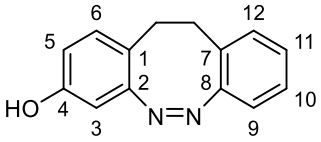
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K, TMS): δ = 157.1 (*C*-2), 156.8 (*C*-8), 155.1 (*C*-4), 131.1 (*C*-6), 130.6 (*C*-12), 129.4 (*C*-7), 127.7 (*C*-11), 127.5 (*C*-10), 123.9 (*C*-1), 123.1 (*C*-5), 119.0 (*C*-9), 114.4 (*C*-3), 79.1 (*C*-CH_3), 32.0 (Ar-*C*H_2), 31.5 (O*t*Bu-Ar-*C*H_2), 29.0 (*C*H_3) ppm.

IR: $\tilde{\nu}$ = 2985 (w), 2937 (w), 1606 (m), 1560 (m), 1489 (s), 1460 (m), 1444 (w), 1393 (m), 1368 (m), 1290 (m), 1244 (m), 1173 (s), 1147 (m), 1102 (m), 1082 (m), 1035 (w), 973 (m), 944 (m), 918 (m), 862 (m), 847 (m), 808 (s), 781 (w), 754 (s), 728 (w), 705 (w) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 280 (20) $[M]^+$, 224 (44) $[M\text{-}C_4H_9]^+$.

MS (EI, HR, 70 eV): $C_{18}H_{20}N_2O$ *m*/*z*= calc.: 280.1576, found: 280.1572.

Synthesis of (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocin-3-ol (2)



Under nitrogen atmosphere (*Z*)-3-(*tert*-butoxy)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine (**24**, 75.0 mg, 0.27 mmol) was dissolved in 15.0 mL dichloromethane, cooled to 0 °C and treated with $TiCl_4$ (87.5 µL, 0.80 mmol). After 1 min stirring at 0 °C the reaction mixture was diluted with saturated potassium carbonate solution. The organic phase was separated and the aqueous phase was neutralised with 1 M hydrochloric acid. It was extracted with ethyl acetate (2 x 30.0 mL) and the combined organic layers were dried over magnesium sulfate followed by removal the solvent. The residue was purified using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE → 80 % EE) and the product was obtained as a yellow solid (46.4 mg, 0.21 mmol, 78 %).

melting point: 121 °C

R_f= 0.49 (cyclohexane/ ethyl acetate 1:1).

^{1}H-NMR (600 MHz, $CO(CD_3)_2$, 300 K, TMS): δ = 8.39 (s, 1 H, O*H*), 7.16 (m_c, 1 H, *H*-10), 7.00-7.06 (m, 2 H, *H*-11, *H*-12), 6.85 (d, ^3J = 8.3 Hz, 1 H, *H*-6), 6.79 (d, ^3J = 8.0 Hz, 1 H, *H*-9), 6.49 (dd, ^3J = 8.3 Hz, ^4J = 2.5 Hz, 1 H, *H*-5), 6.27 (d, ^4J = 2.5 Hz, 1 H, *H*-3), 2.72-2.80 (m, 4 H, CH_2) ppm.

^{13}C-NMR (150 MHz, $CO(CD_3)_2$, 300 K, TMS): δ = 157.6 (*C*-2), 156.9 (*C*-4), 156.7 (*C*-8), 131.7 (*C*-6), 130.7 (*C*-12), 129.4 (*C*-7), 127.7 (*C*-11), 127.4 (*C*-10), 119.8 (*C*-1), 119.3 (*C*-9), 114.9 (*C*-5), 105.9 (*C*-3), 32.3 (-*C*H_2), 31.3 (HO-Ar-*C*H_2) ppm.

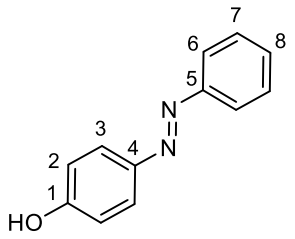
IR: $\tilde{\nu}$ = 3215 (w), 2925 (w), 2161 (w), 1609 (m), 1582 (m), 1498 (m), 1441 (m), 1275 (m), 1232 (m), 1168 (w), 1140 (w), 1102 (w), 1083 (w), 946 (w), 911 (w), 879 (w), 843 (w), 815 (w), 754 (s) cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 224 (61) $[M]^{+\bullet}$.

MS (EI, HR, 70 eV): $C_{14}H_{12}N_2O$ *m*/*z*= calc.: 224.0950, found: 224.0947.

3.3 Syntheses of hydroxy azobenzenes

Synthesis of (*E*)-4-(phenyldiazenyl)phenol



In a three-necked flask aniline (1.00 g, 10.7 mmol) was dissolved in 21 mL water and treated with 2.7 mL concentrated hydrochloric acid. The solution was cooled to 0 °C and $NaNO_2$ (1.10 g, 16.1 mmol) dissolved in 3.5 mL water was added dropwise. After 15 min stirring at 0 °C the reaction mixture was diluted with 35 mL cold ethanol.

In a separate flask, phenol (1.00 g, 10.7 mmol) was dissolved in 5 mL ethanol under addition of potassium hydroxide (1.10 g, 20.3 mmol). The solution was cooled to 0 °C and was slowly added to the diazonium solution. After 17 h of stirring at room temperature the solution was acidified with 1 M hydrochloric acid. The precipitated solid was filtered off and washed with water. After recrystallisation from methanol/water the product was obtained as an orange solid (870 mg, 4.39 mmol, 41 %).

melting point: 155 °C

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 9.11 (s, 1 H, O*H*), 7.87 (m_c, 4 H, *H*-6, *H*-3), 7.55 (m_c, 2 H, *H*-7), 7.47-7.51 (m, 1 H, *H*-8), 7.03 (m_c, 2 H, *H*-2) ppm.

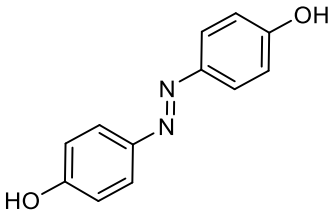
^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 161.6 (*C*-1), 153.6 (*C*-5), 147.2 (*C*-4), 131.2 (*C*-8), 130.0 (*C*-7), 125.8 (*C*-3), 123.2 (*C*-6), 116.7 (*C*-2) ppm.

IR: $\tilde{\nu}$ = 3095 (m), 1896 (w), 1584 (s), 1506 (s), 1471 (m), 1455 (s), 1414 (s), 1378 (m), 1273 (s), 1218 (s), 1138 (s), 1022 (w), 999 (m), 917 (m), 836 (s), 807 (w), 791 (m), 764 (s), 719 (s), 679 (s), 643 (m), 545 (s), 531 (s) cm^{-1}.

MS (ESI, neg): *m*/*z* (%) = 197 (100) $[M-H]^-$.

MS (ESI, HR, neg): $C_{12}H_9ON_2$ *m*/*z*= calc.: 197.0720, found: 197.0714.

Synthesis of (*E*)-4,4'-(diazene-1,2-diyl) diphenol



In a three-necked flask 4-aminophenol (1.00 g, 9.16 mmol) was dissolved in 18 mL of water and treated with 2.3 mL concentrated hydrochloric acid. The solution was cooled to 0 °C and $NaNO_2$ (943 mg, 13.7 mmol) dissolved in 3.0 mL water was added dropwise. After 15 min stirring at 0 °C the reaction mixture was diluted with 29 mL cooled ethanol.

In a separate flask, phenol (862 mg, 9.16 mmol) was dissolved in 4.3 mL ethanol under addition of potassium hydroxide (977 mg, 17.4 mmol). The solution was cooled to 0 °C and was slowly added to the diazonium solution. After 25 h of stirring at room temperature the solution was acidified with 1 M hydrochloric acid and extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried over magnesium sulfate, and the solvent was removed under reduced pressure. After purification using column chromatography on silica (cyclohexane/ ethyl acetate; 1:1) and recrystallisation from acetone/water the product could be obtained as a dark red solid (34.8 mg, 0.16 mmol, 2 %).

melting point: 204 °C

^{1}H-NMR (500 MHz, $CO(CD_3)_2$, 298 K): δ = 7.79 (m_c, 4 H, *H*-3), 6.99 (m_c, 4 H, *H*-2) ppm.

^{13}C-NMR (125 MHz, $CO(CD_3)_2$, 298 K): δ = 160.8 (*C*-1), 147.2 (*C*-4), 125.2 (*C*-3), 116.6 (*C*-2) ppm.

IR: $\tilde{\nu}$ = 3182 (m), 2352 (w), 2012 (w), 1589 (s), 1506 (m), 1476 (s), 1428 (m), 1384 (m), 1249 (s), 1153 (s), 1104 (m), 830 (s), 772 (w), 646 (w), 530 (s) cm^{-1}.

MS (ESI, pos): *m/z* (%) = 215 (71) $[M+H]^+$.

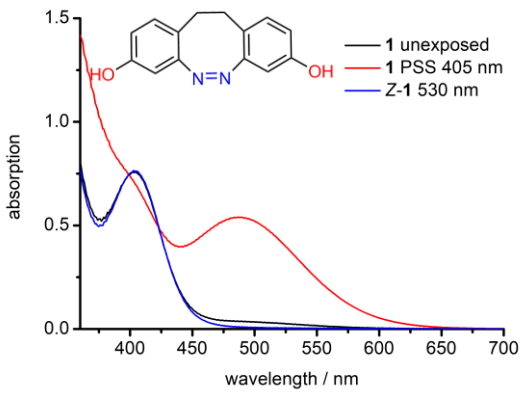
MS (ESI, HR, pos): $C_{12}H_{11}O_2N_2$ *m/z*= calc.: 215.0815, found: 215.0815

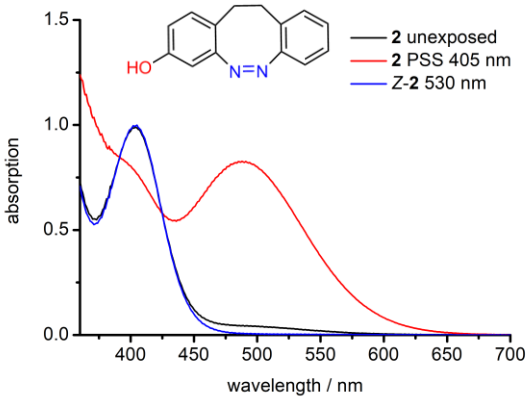
4. Photochemical Characterisation

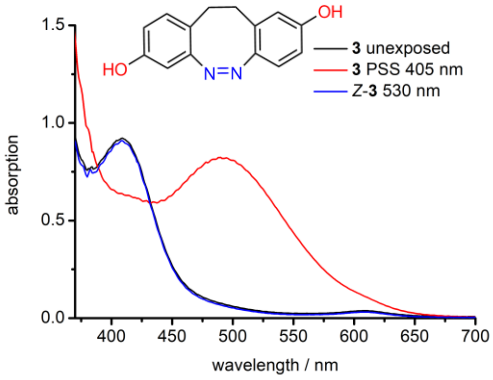
4.1 UV/Vis Measurements

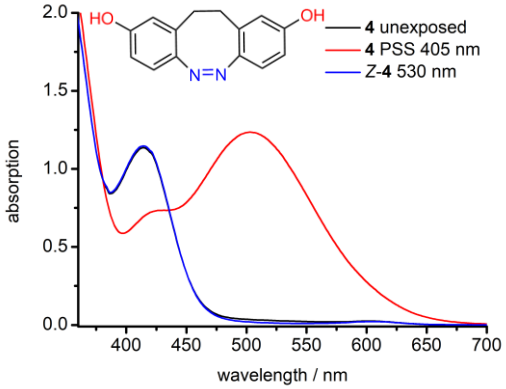
UV/Vis spectra of hydroxy and benzyl alcohol diazocines

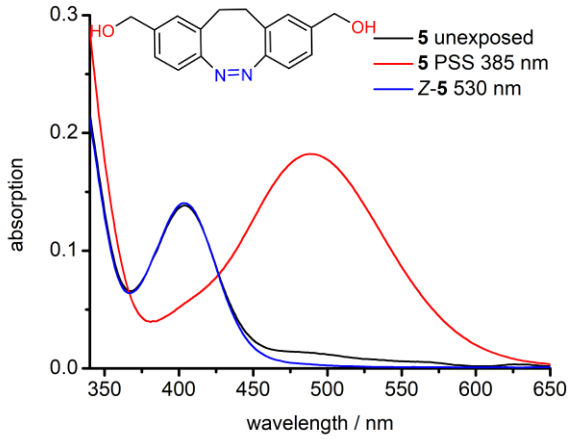
UV/Vis spectra of the unexposed samples (black) and after irradiation with 385/ 405 nm (red) were recorded in DMSO and in aqueous solution (H_2O 98 %; DMSO 2 %). Additionally, UV/Vis spectra after back isomerisation with 530 nm (blue) are presented.

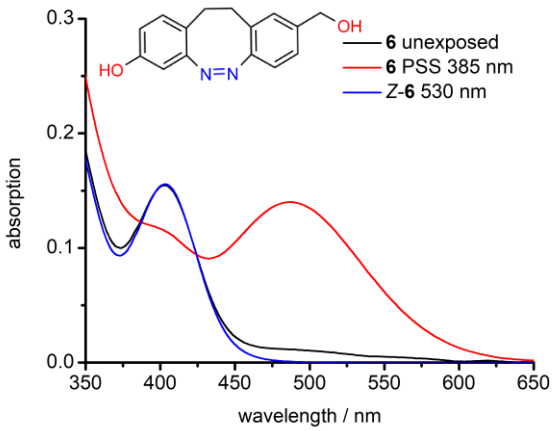


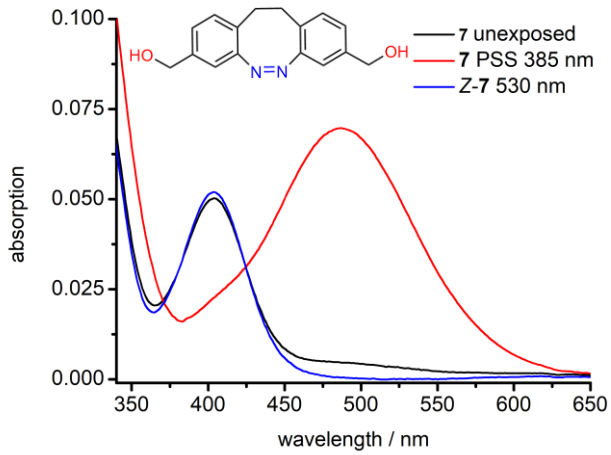








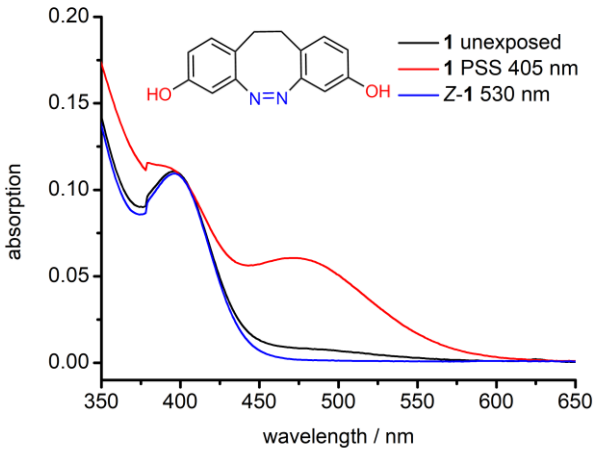


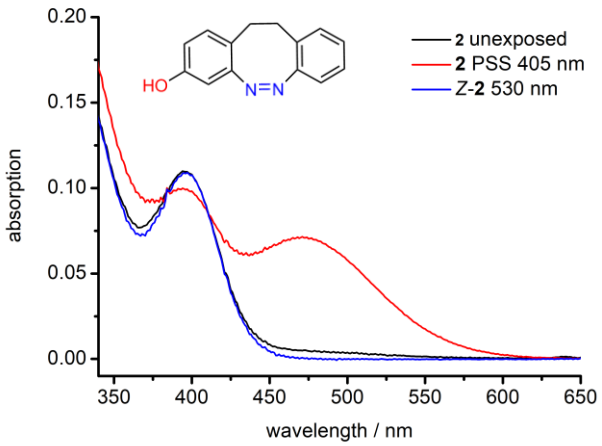


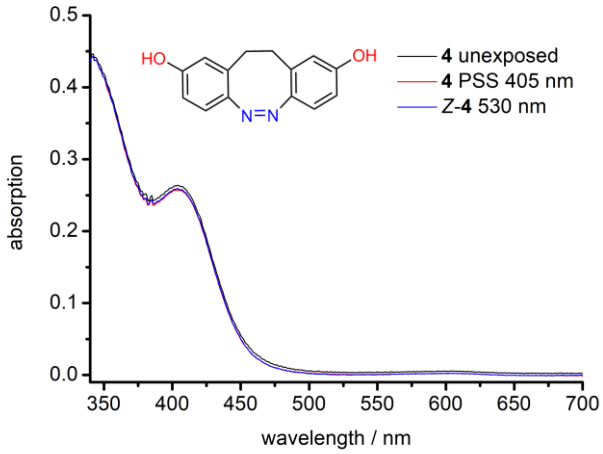
Supplementary figure 1. UV/Vis spectra of compound **1**-**7** recorded at 25 °C in pure DMSO solution. The unexposed sample is plotted in black, the spectra of the *Z* configuration in blue and the spectra of the PSS (405 nm or 385 nm) between *Z*/*E* in red.

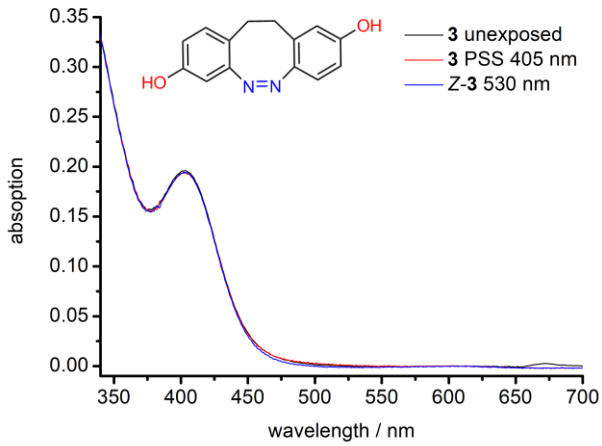
Compared to DMSO in water the n-π* absorption maxima of the *E* and *Z* isomers are shifted hypsochromically. Due to the solvent-dependent shift in the absorption maxima the optimal excitation wavelengths were recorded in DMSO and water.

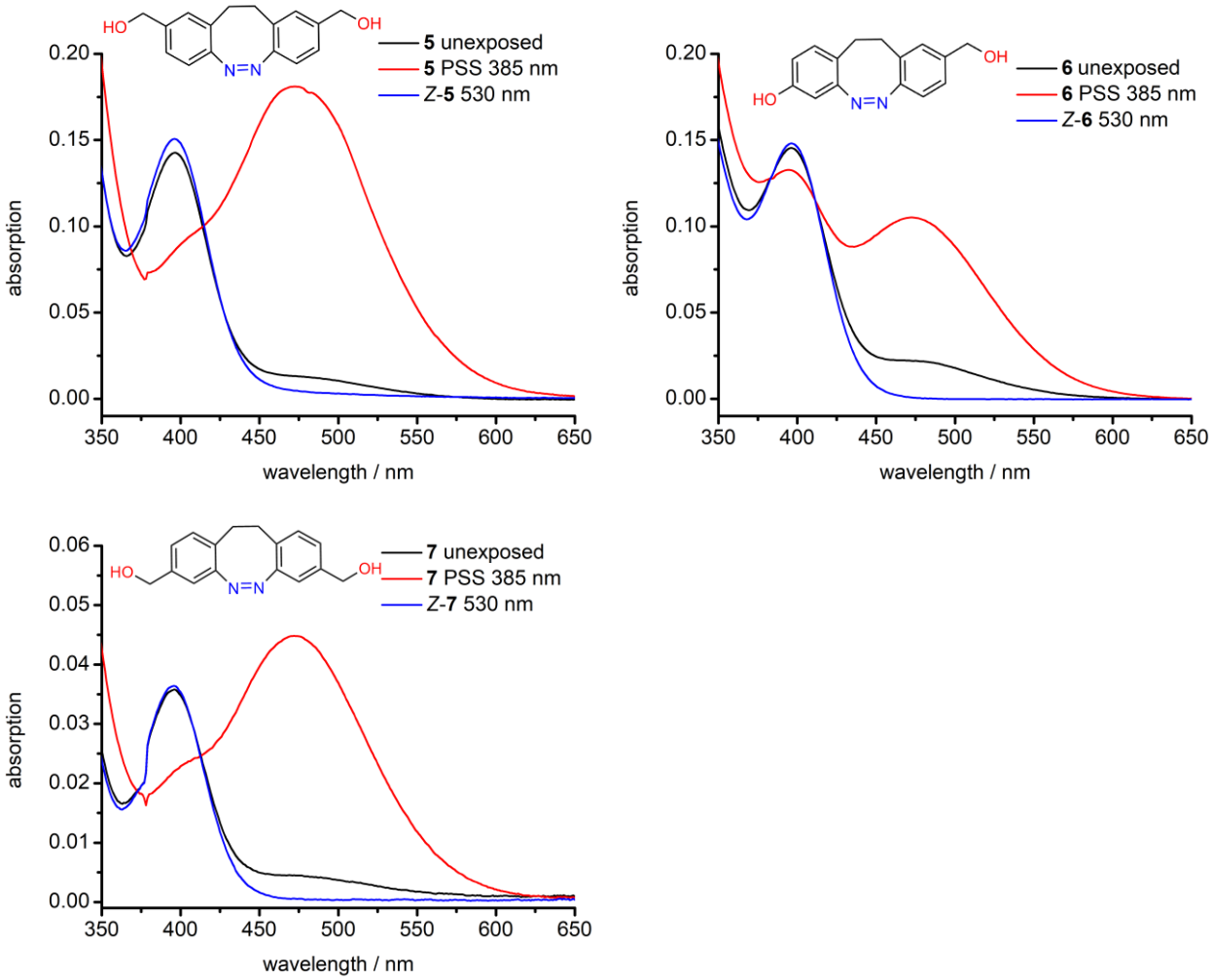
Figure 2 shows the UV/Vis spectra of the hydroxy and benzyl alcohol diazocines in aqueous solution (H_2O 98 %; DMSO 2 %).







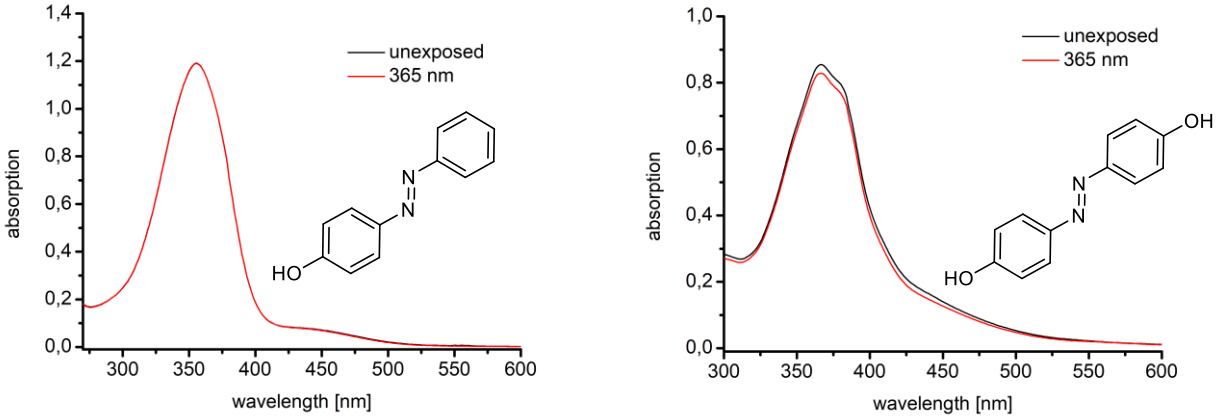




Supplementary figure 2. UV/Vis spectra of compound **1**-**7** recorded at 25 °C in aqueous solution (H_2O 98 %; DMSO 2 %; 200 µM). The unexposed sample is plotted in black, the spectra of the *Z* configuration in blue and the spectra of the PSS between *Z*/*E* in red. The *para*-hydroxy diazocines **3** and **4** show no detectable switching.

UV/Vis spectra of hydroxy azobenzenes

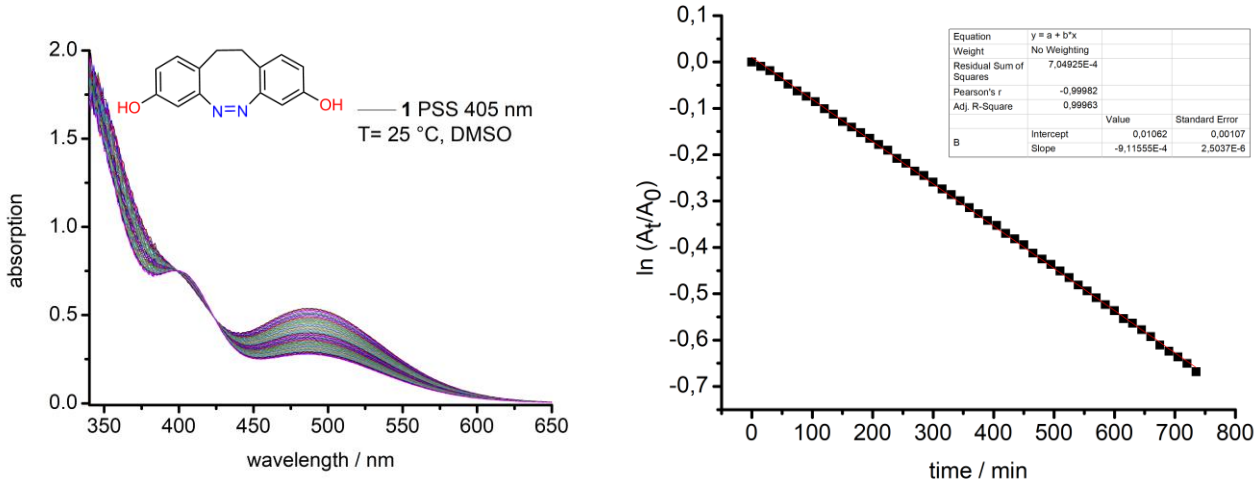
UV/Vis spectra of the hydroxy azobenzenes were recorded in DMSO at 25 °C (50 µM). In black the unexposed samples and in red the irradiated samples with 365 nm are display. Due to the *para*-hydroxy group and the azo hydrazone tautomerism no switching in DMSO was detectable. [2–6]



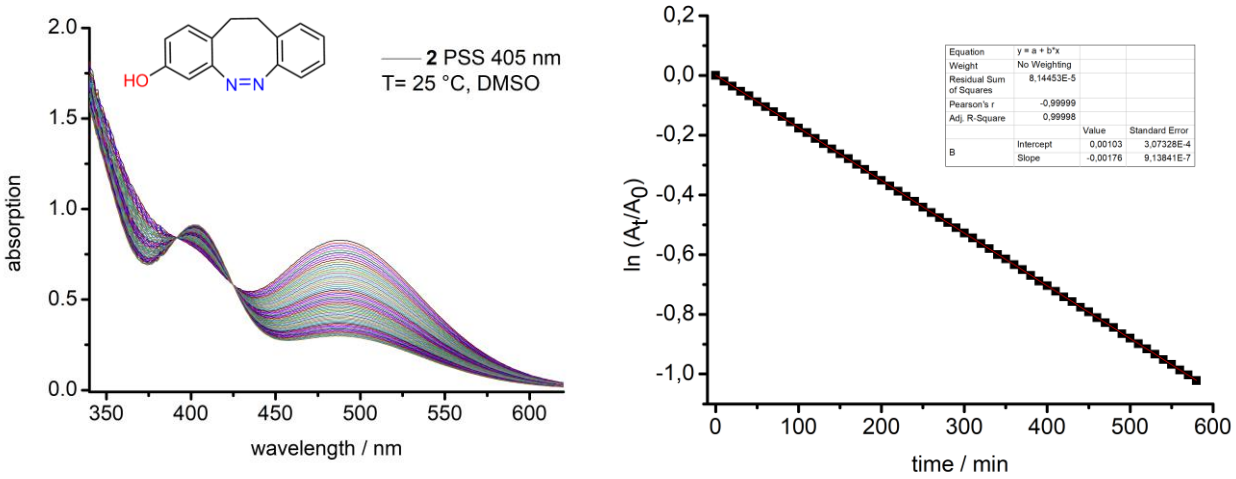
Supplementary figure 3. UV/Vis spectra of hydroxy azobenzenes recorded at 25 °C in DMSO (50 µM). The unexposed sample is plotted in black and the irradiated sample with 365 nm in red.

4.2 Thermal half-lives

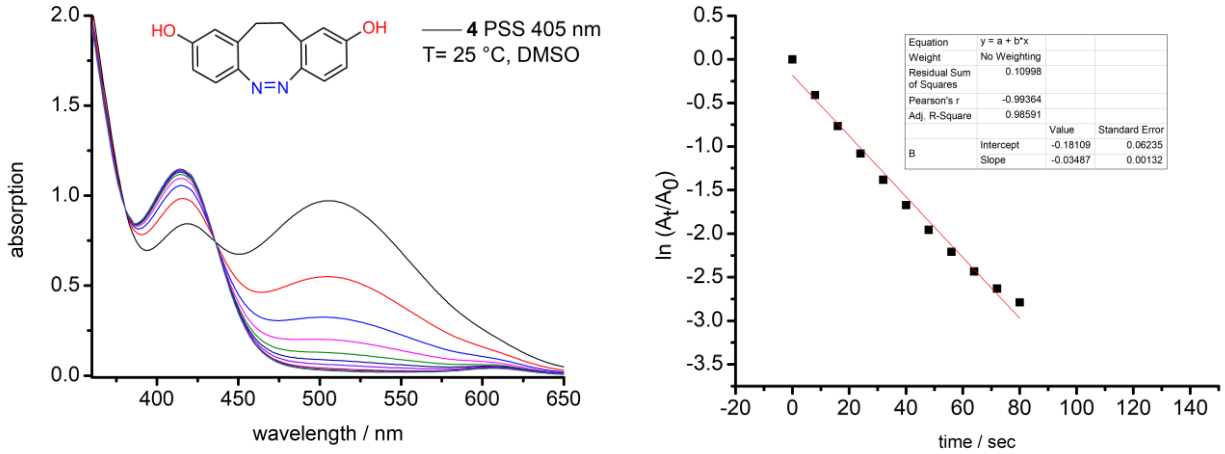
Thermal half-lives in DMSO



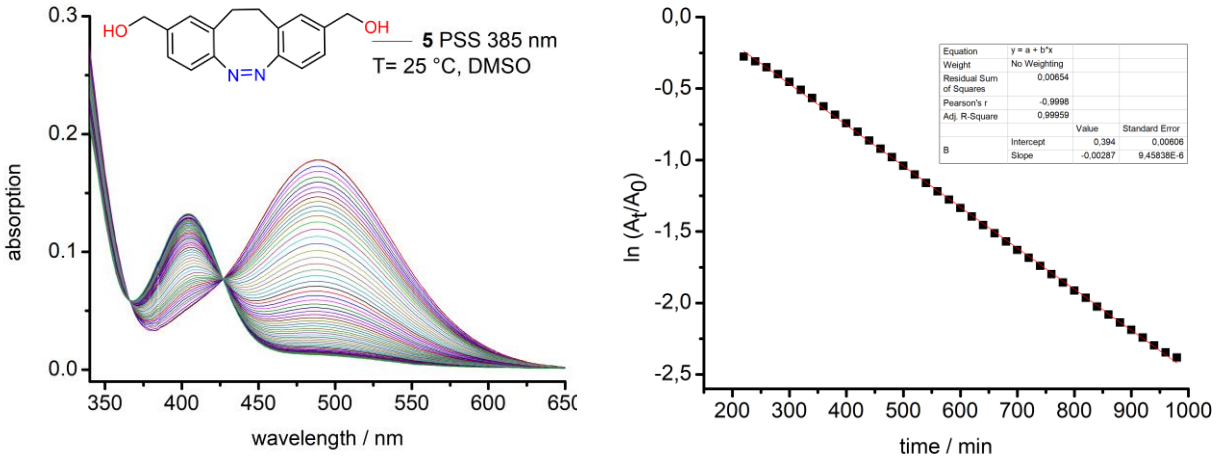
Supplementary figure 4. Left: UV/Vis spectra of compound **1** in 15 min interval at 25 °C in DMSO (1.7 mM). Right: Linear fit of the decrease in absorption at 497 nm for first-order kinetics (-k= -9.1156*10^{-4} min^{-1}; $t_{1/2}$=12.7 h).



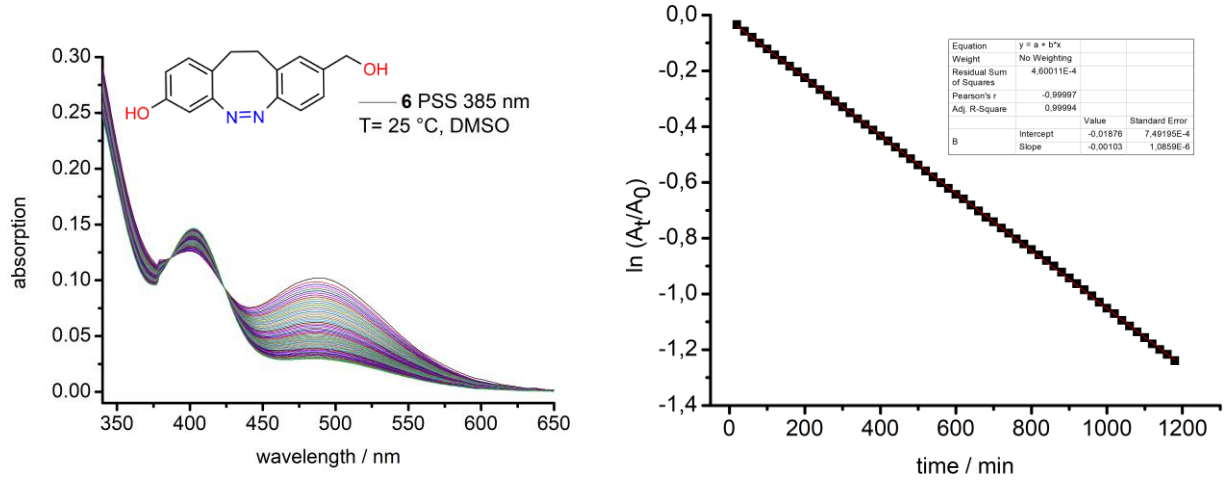
Supplementary figure 5. Left: UV/Vis spectra of compound **2** in 10 min interval at 25 °C in DMSO (1.0 mM). Right: Linear fit of the decrease in absorption at 489 nm for first-order kinetics (-k= -0.00176 min^{-1}; $t_{1/2}$=6.6 h).



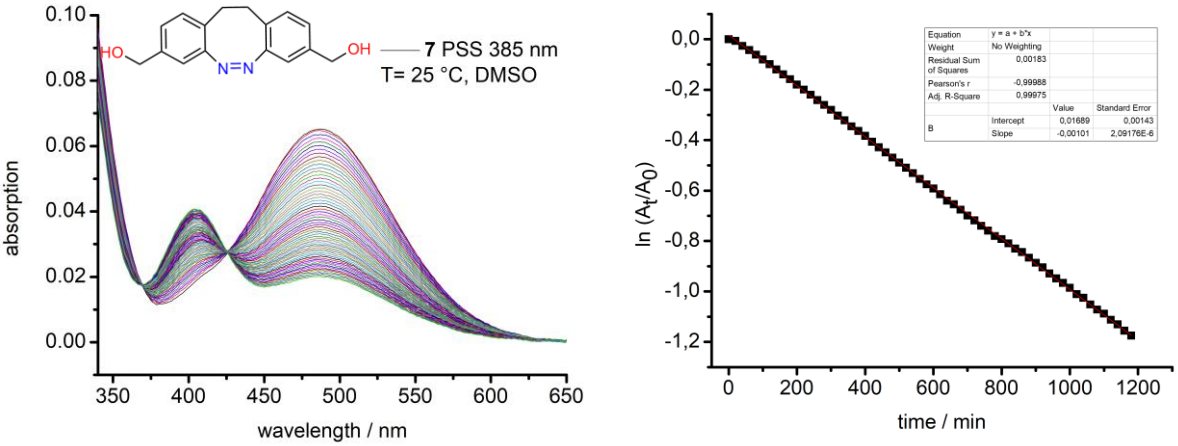
Supplementary figure 6. Left: UV/Vis spectra of compound **4** in 8 s interval at 25 °C in dry DMSO (1.0 mM). Right: Linear fit of the decrease in absorption at 505 nm for first-order kinetics (-k= -0.03487 s^{-1}; $t_{1/2}$=19.9 s).



Supplementary figure 7. Left: UV/Vis spectra of compound **5** in 20 min interval at 25 °C in DMSO (200 µM). Right: Linear fit of the decrease in absorption at 489 nm for first-order kinetics (-k= -0.00287 min^{-1}; $t_{1/2}$= 4.0 h).

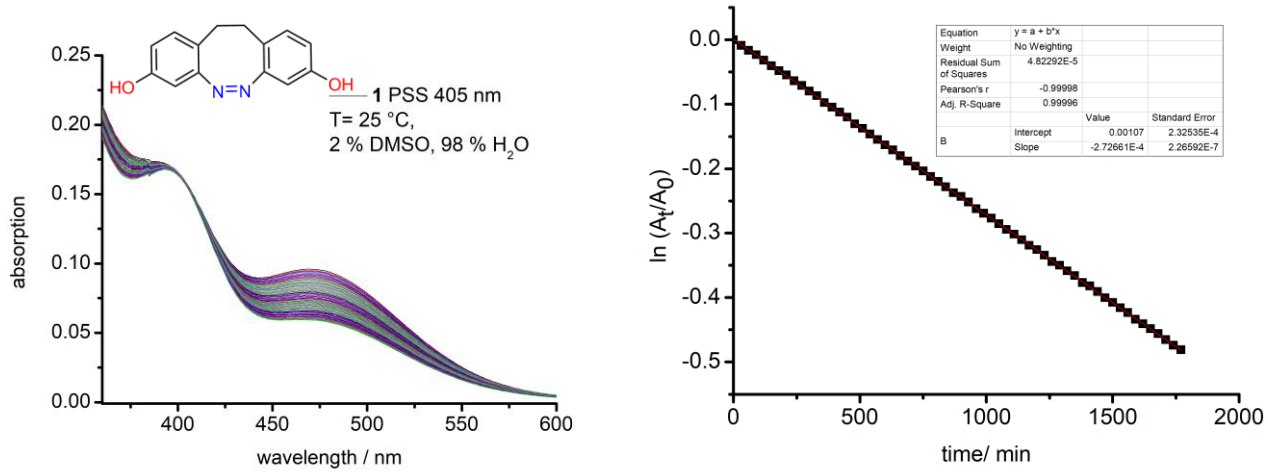


Supplementary figure 8. Left: UV/Vis spectra of compound **6** in 20 min interval at 25 °C in DMSO (200 µM). Right: Linear fit of the decrease in absorption at 486 nm for first-order kinetics (-k= -0.00103 min^{-1}; $t_{1/2}$= 11.2 h).

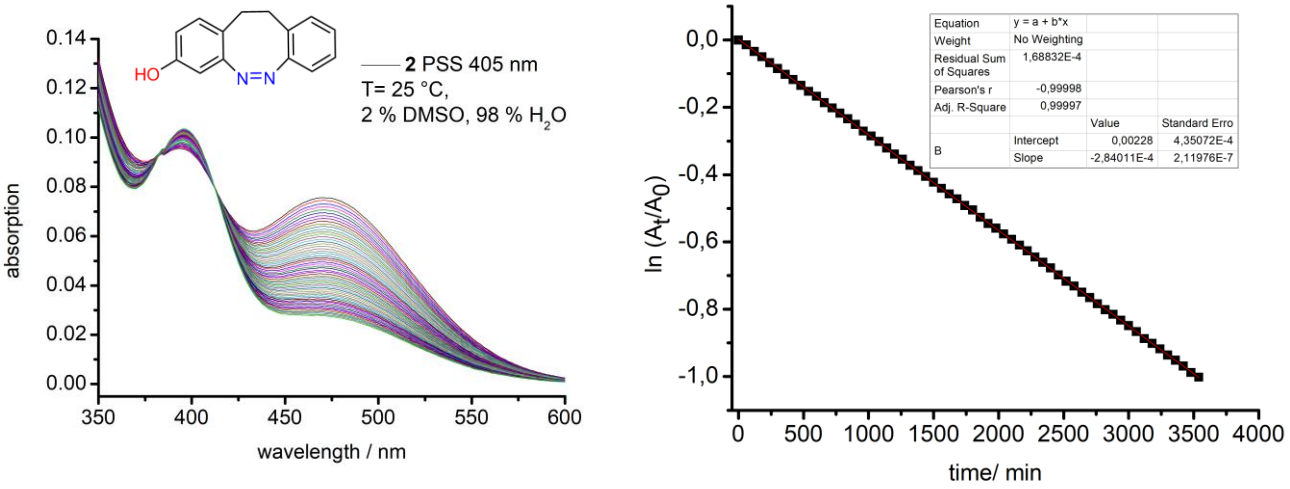


Supplementary figure 9. Left: UV/Vis spectra of compound **7** in 20 min interval at 25 °C in DMSO (200 µM). Right: Linear fit of the decrease in absorption at 487 nm for first-order kinetics (-k= -0.00101 min^{-1}; $t_{1/2}$=11.4 h).

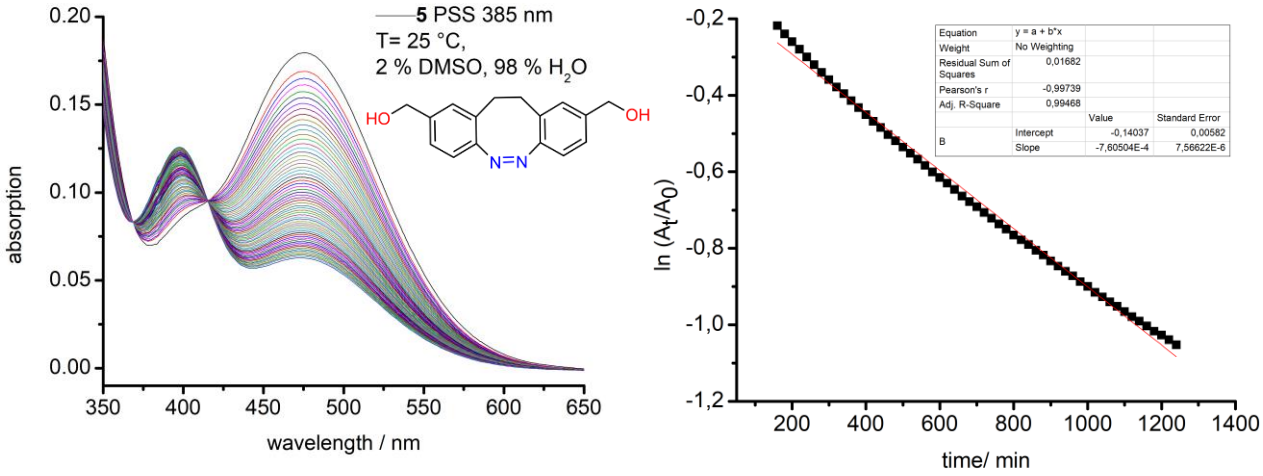
Thermal half-lives in water at 25 °C



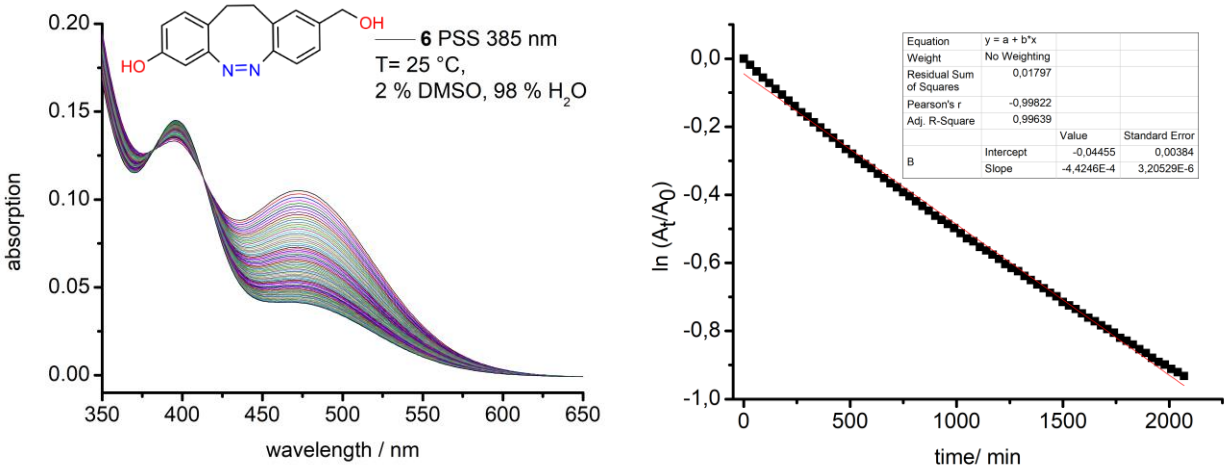
Supplementary figure 10. Left: UV/Vis spectra of compound **1** in 30 min interval at 25 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 470 nm for first-order kinetics (-k= -2.7266*10^{-4} min^{-1}; $t_{1/2}$= 42.4 h).



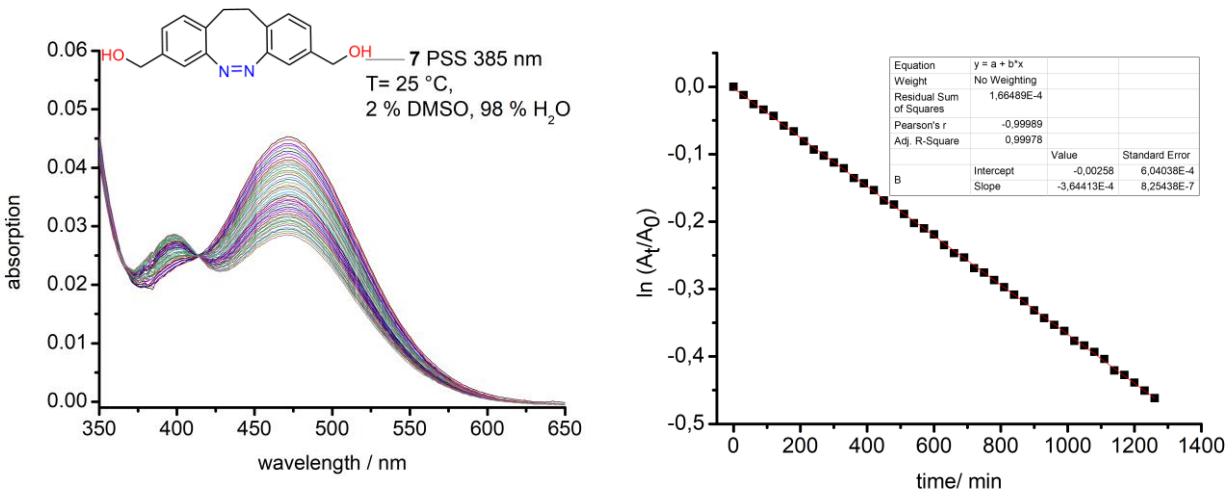
Supplementary figure 11. Left: UV/Vis spectra of compound **2** in 60 min interval at 25 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 471 nm for first-order kinetics (-k= -2.84011*10^{-4} min^{-1}; $t_{1/2}$= 40.7 h)



Supplementary figure 12. Left: UV/Vis spectra of compound **5** in 20 min interval at 25 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 476 nm for first-order kinetics (-k= -7.60504*10^{-4} min^{-1}; $t_{1/2}$= 15.2 h).

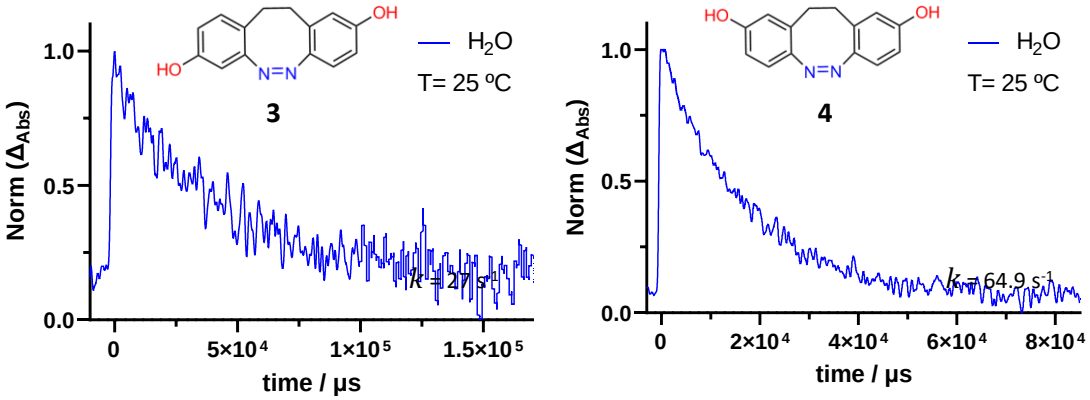


Supplementary figure 13. Left: UV/Vis spectra of compound **6** in 30 min interval at 25 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 472 nm for first-order kinetics (-k= -4.4246*10^{-4} min^{-1}; $t_{1/2}$= 26.1 h).



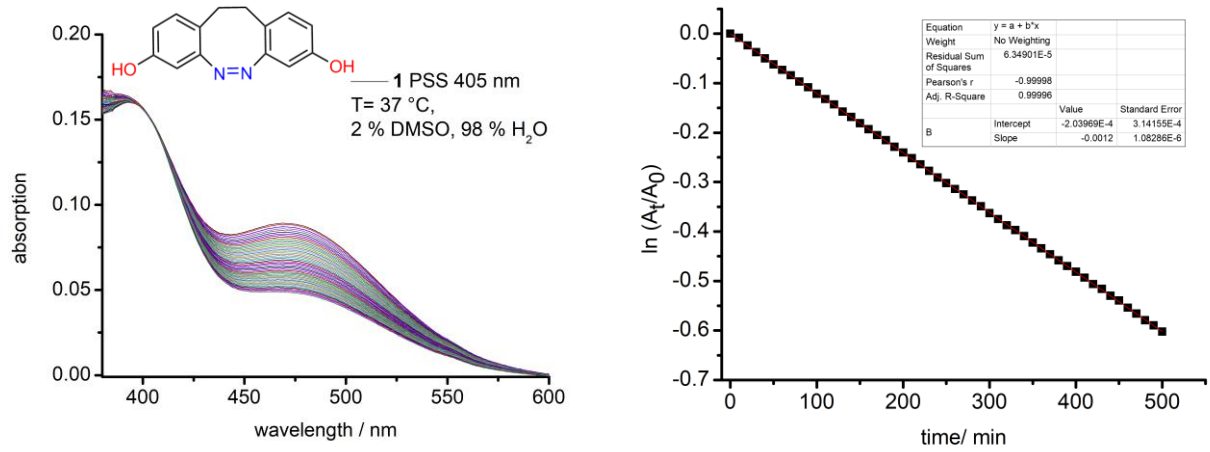
Supplementary figure 14. Left: UV/Vis spectra of compound **7** in 30 min interval at 25 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 471 nm for first-order kinetics (-k= -3.64413*10^{-4} min^{-1}; $t_{1/2}$= 31.7 h)

The isomerization rates of compound **3** and **4** were determined by nanosecond laser flash photolysis.

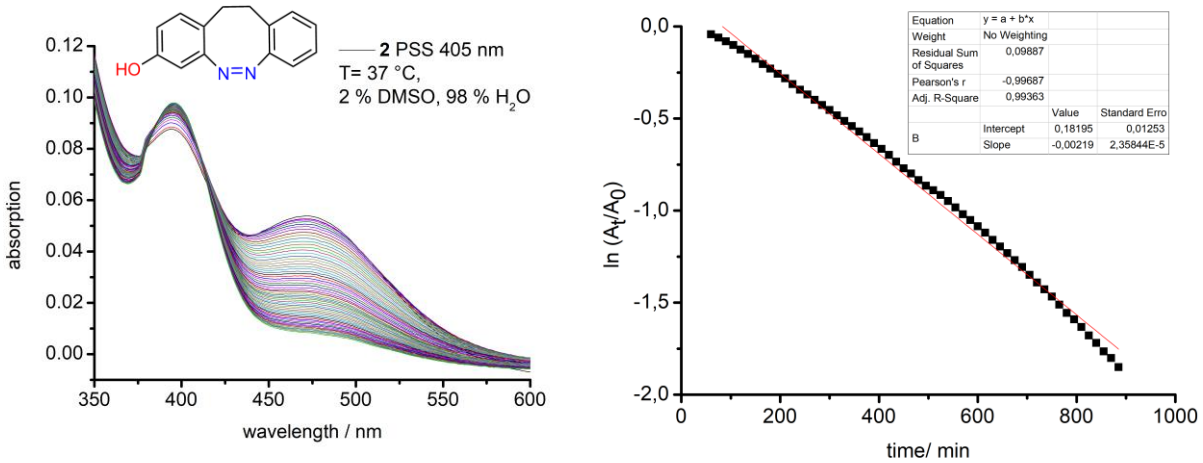


Supplementary figure 15. Transient absorption decay and rate constant (k) of compounds **3** (420 µM; left) and **4** (420 µM; right) recorded at 25 °C in aqueous solution H_2O 98 %; DMSO 2 %. λ_{exc} = 355 nm; λ_{obs} = 500 nm.

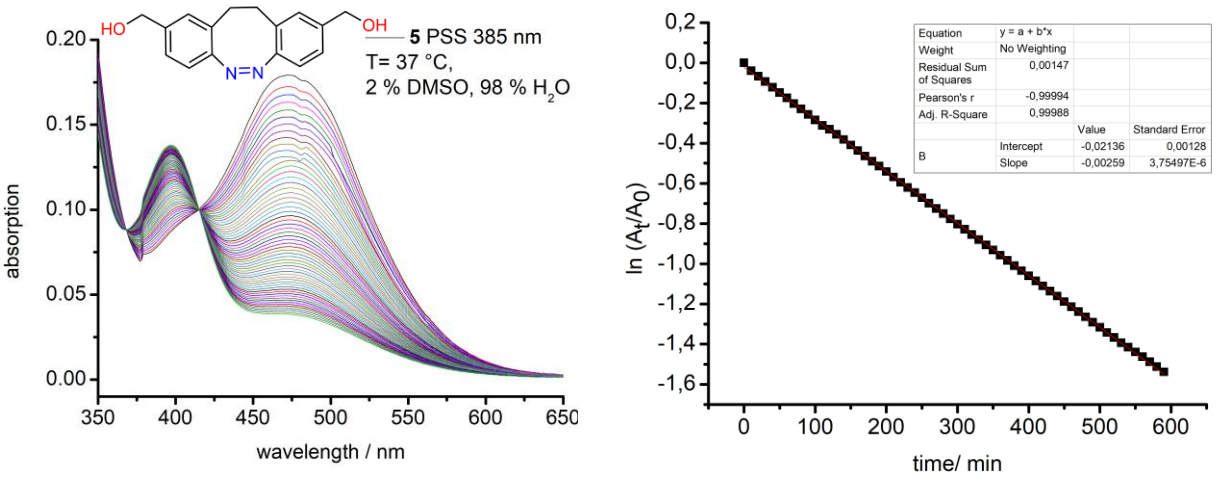
Thermal half-lives in water at 37 °C



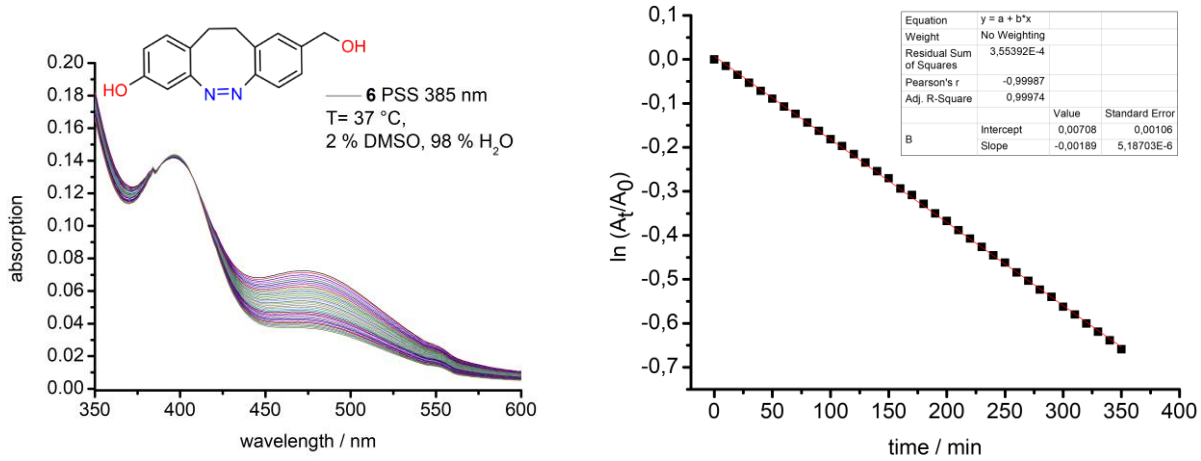
Supplementary figure 16. Left: UV/Vis spectra of **1** in 10 min interval at 37 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 470 nm for first-order kinetics (-k= -0.0012 min^{-1}; $t_{1/2}$= 9.6 h).



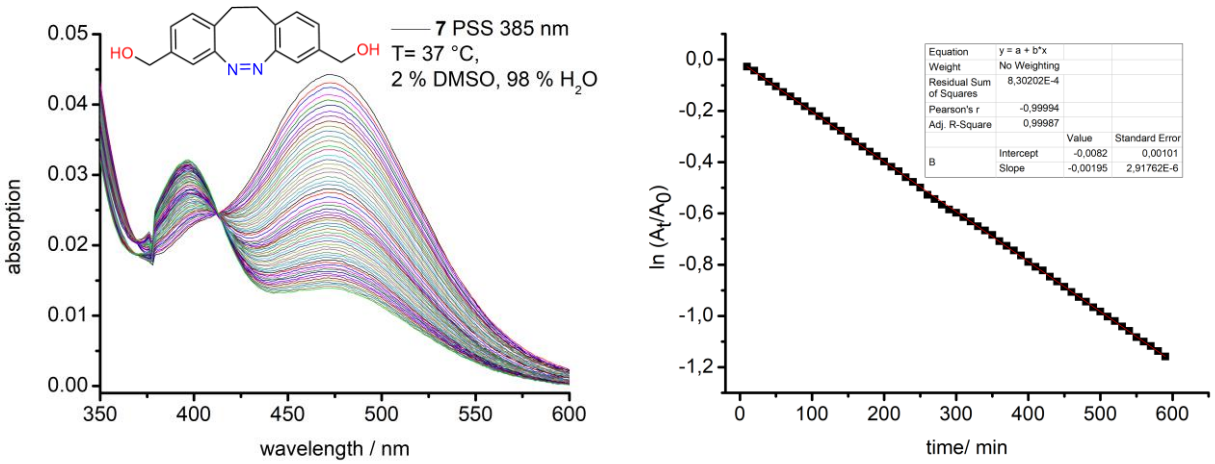
Supplementary figure 17. Left: UV/Vis spectra of compound **2** in 15 min interval at 37 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 471 nm for first-order kinetics (-k= -0.00219 min^{-1}; $t_{1/2}$= 5.3 h).



Supplementary figure 18. Left: UV/Vis spectra of compound **5** in 10 min interval at 37 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 472 nm for first-order kinetics (-k= -0.00259 min^{-1}; $t_{1/2}$= 4.5 h)

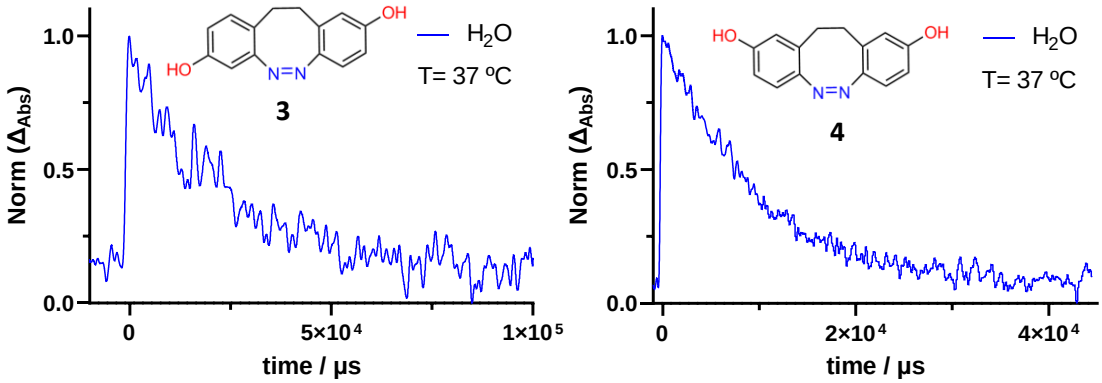


Supplementary figure 19. Left: UV/Vis spectra of compound **6** in 10 min interval at 37 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 472 nm for first-order kinetics (-k= -0.00189 min^{-1}; $t_{1/2}$= 6.1 h).



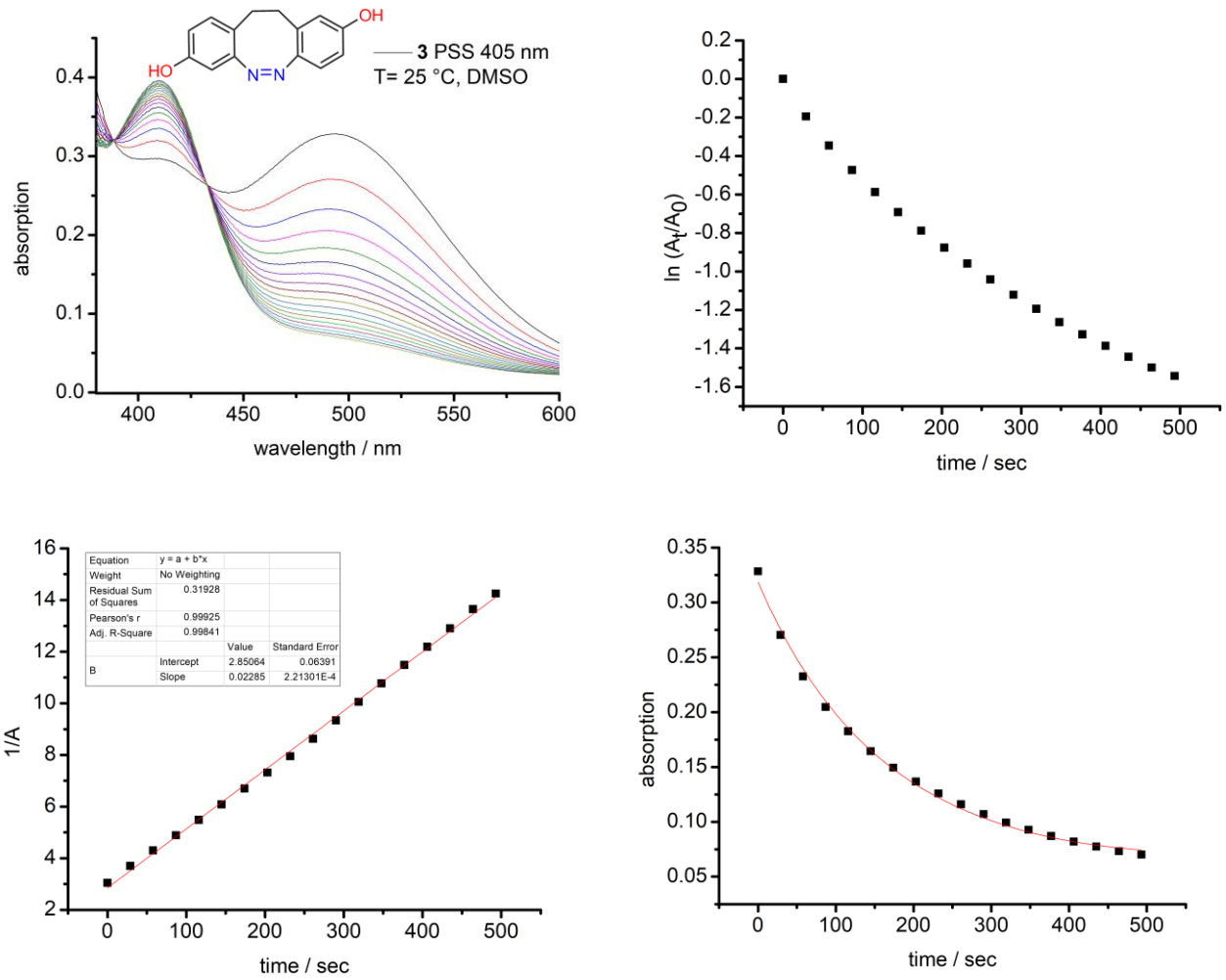
Supplementary figure 20. Left: UV/Vis spectra of compound **7** in 10 min interval at 37 °C in aqueous solution (200 µM). Right: Linear fit of the decrease in absorption at 472 nm for first-order kinetics (-k= -0.00195 min^{-1}; $t_{1/2}$= 5.9 h).

The isomerization rates of compound **3** and **4** in water at 37 °C were determined by nanosecond laser flash photolysis.



Supplementary figure 21. Left: Transient absorption decay and rate constant (k) of compounds **3** (420 µM; left) and **4** (420 µM; right) recorded at 37 °C in aqueous solution H_2O 98 %; DMSO 2 %. λ_{exc} = 355 nm; λ_{obs} = 500 nm.

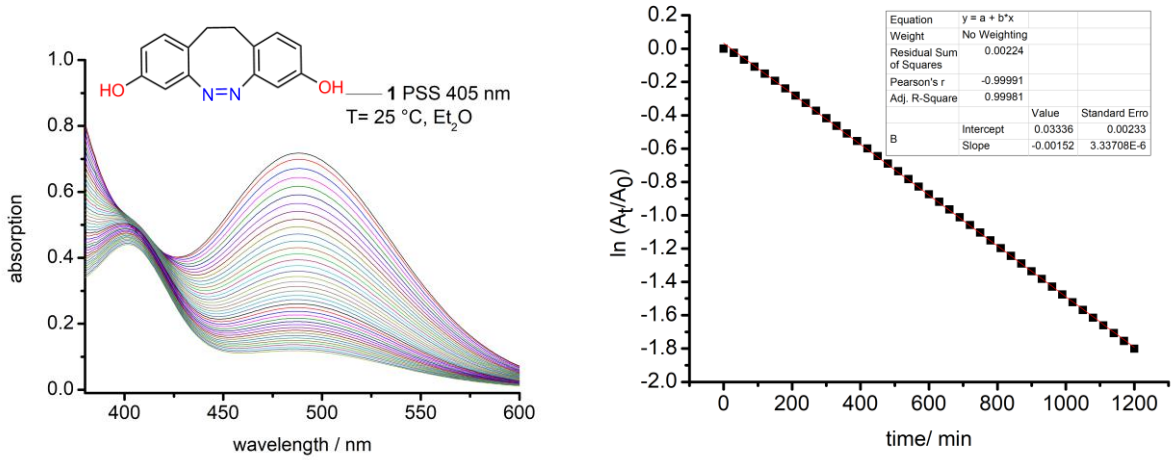
Switching behaviour of *para*-hydroxydiazocine 3 in DMSO and determination of the half-life



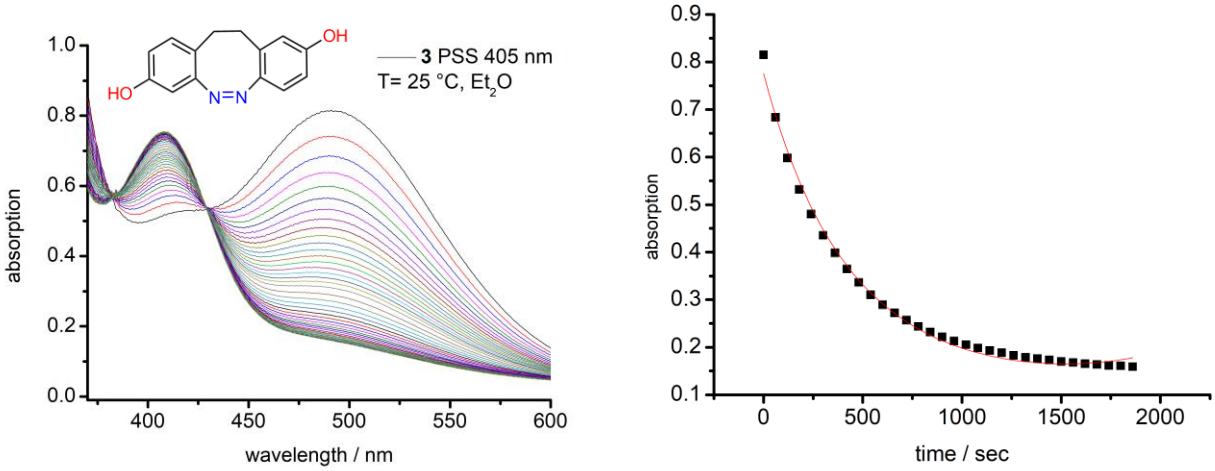
Supplementary figure 22. Top left: UV/Vis spectra of compound **3** in 29 s interval at 25 °C in dry DMSO (0.5 mM). Top right: The first-order kinetic fit shows strong deviations from a linear straight line. Bottom left: A linear fit for a kinetic second order was possible. Bottom right: Decrease in absorption at 494 nm versus time was plotted. Determination of the half-life when half of the absorption maximum is reached ($A_{1/2}$ = 0.16423; time= 2.4 min)

Thermal half-lives of dihydroxy diazocines 1, 3 and 4 in diethyl ether

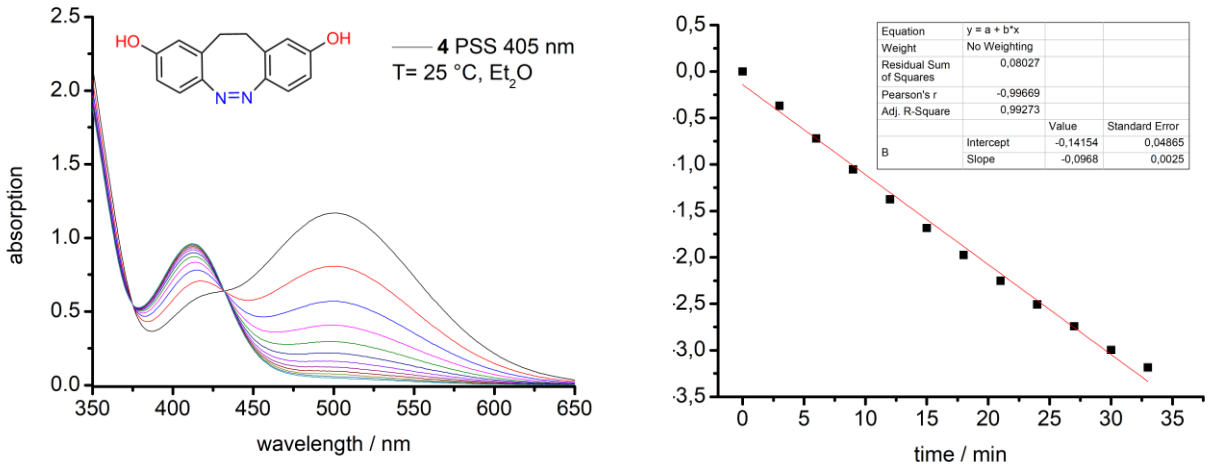
To investigate the switching properties as a function of the environment the thermal back isomerisation of compound **1**, **3** and **4** was also recorded in a non-polar solvent (Et_2O).



Supplementary figure 23. Left: UV/Vis spectra of compound **1** in 30 min interval at 25 °C in diethyl ether (1.0 mM). Right: Linear fit of the decrease in absorption at 488 nm for first-order kinetics (-k= -0.00152 min^{-1}; $t_{1/2}$= 7.6 h).



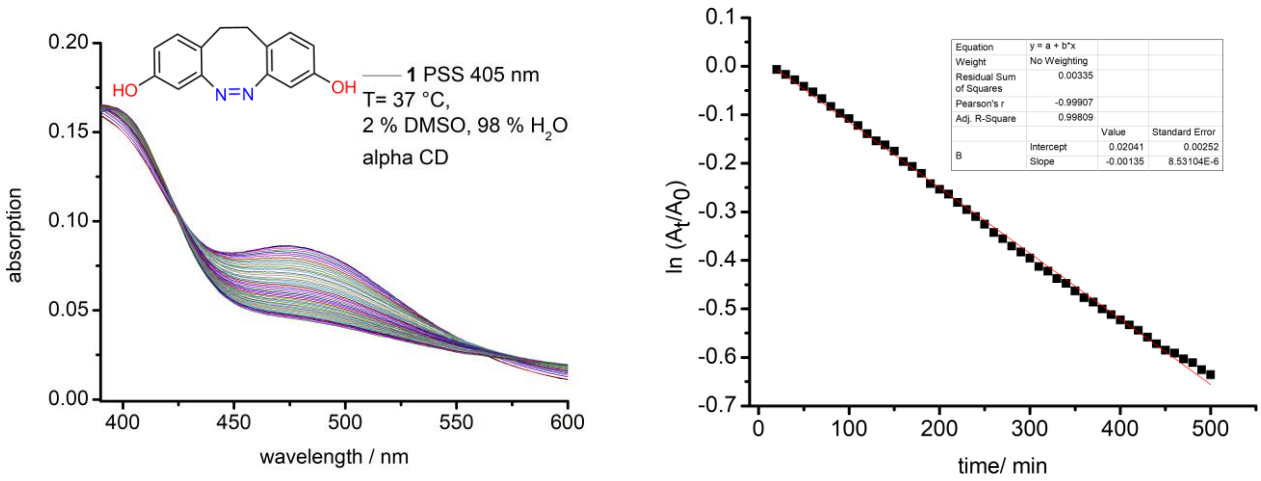
Supplementary figure 24. Left: UV/Vis spectra of compound **3** in 60 s interval at 25 °C in diethyl ether (1.0 mM). Right: A first-order kinetic fit was not possible so decrease in absorption at 491 nm versus time was plotted. Determination of the half-life when half of the absorption maximum is reached ($A_{1/2}$ = 0.4076; time= 6.0 min)



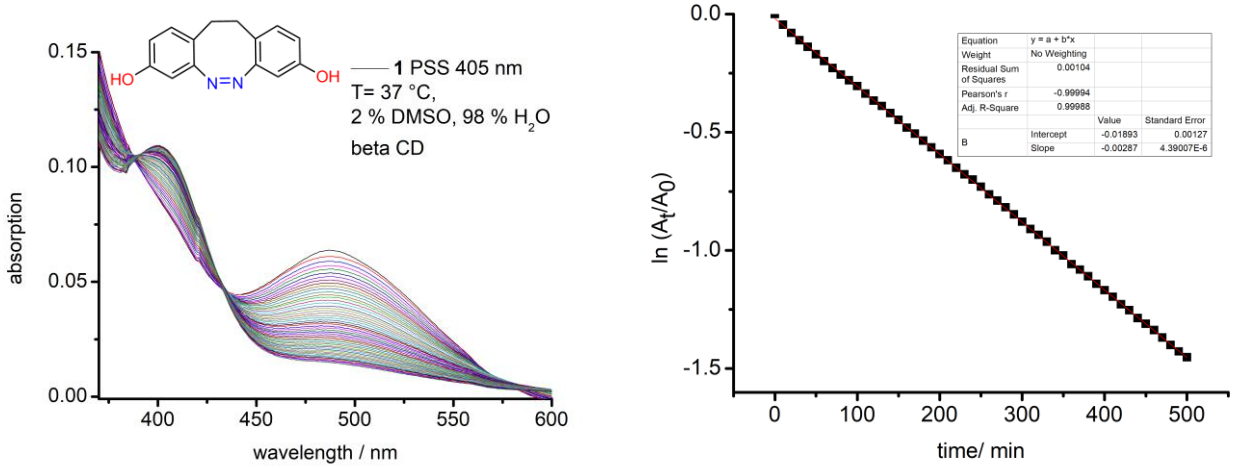
Supplementary figure 25. Left: UV/Vis spectra of compound **4** in 3 min interval at 25 °C in diethyl ether (1.0 mM). Right: Linear fit of the decrease in absorption at 501 nm for first-order kinetics (-k= -0.0968 min^{-1}; $t_{1/2}$= 7.2 min).

Thermal half-lives of dihydroxy diazocines 1, 3 and 4 in the presence of (2-hydroxypropyl)-cyclodextrin

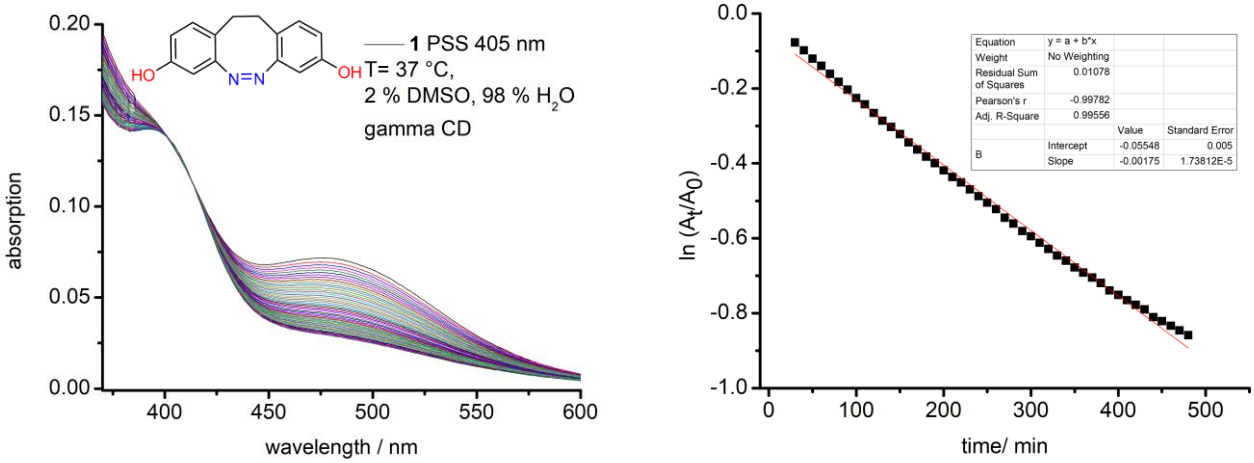
The half-lives ($t_{1/2}$) of the *E* isomer of phenol-type diazocine **1** in the presence of (2-hydroxypropyl)-cyclodextrin was determined by UV/Vis spectroscopy. Measurements of the diazocine **1** (185 µM) and 2-hydroxypropyl)-cyclodextrin (278 mM, 1500-fold excess) were performed in water (2% DMSO and 98% water) at 37 °C.



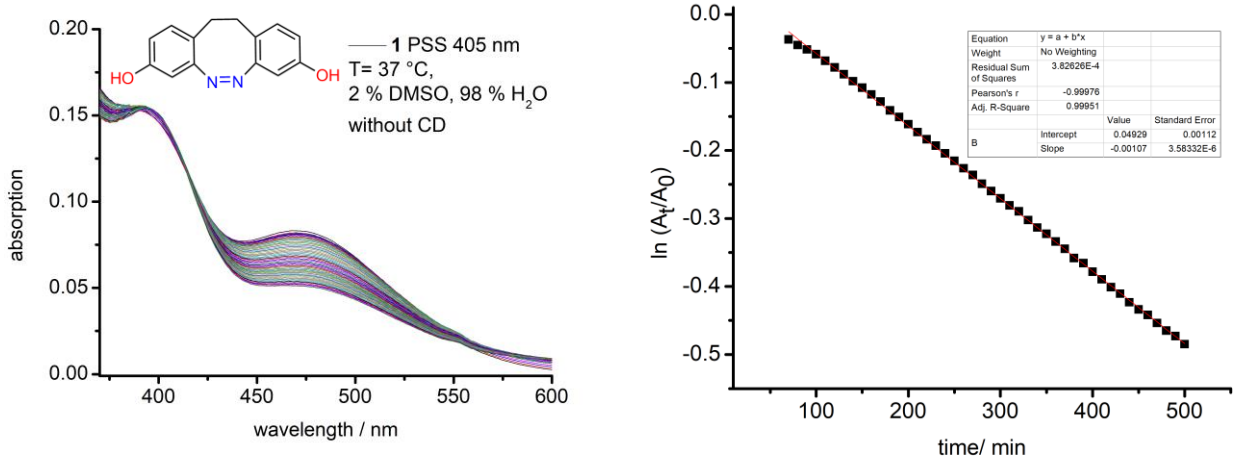
Supplementary figure 26. Left: UV/Vis spectra of compound **1** (185 µM) in presence of (2-hydroxypropyl)-α-cyclodextrin (278 mM, 1500-fold excess) in 10 min interval at 37 °C. Right: Linear fit of the decrease in absorption at 474 nm for first-order kinetics (-k= -0.00135 min^{-1}; $t_{1/2}$= 8.6 h).



Supplementary figure 27. Left: UV/Vis spectra of compound **1** (185 µM) in presence of (2-hydroxypropyl)-β-cyclodextrin (278 mM, 1500-fold excess) in 10 min interval at 37 °C. Right: Linear fit of the decrease in absorption at 487 nm for first-order kinetics (-k= -0.00287 min^{-1}; $t_{1/2}$= 4.0 h).

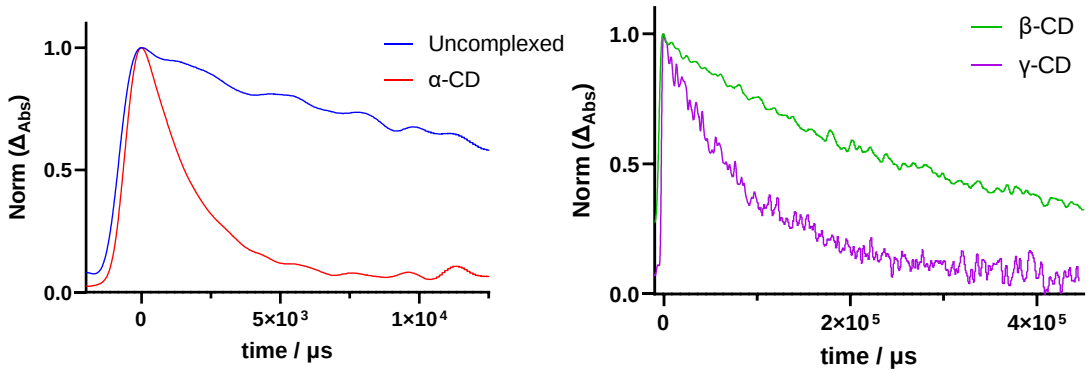


Supplementary figure 28. Left: UV/Vis spectra of compound **1** (185 µM) in presence of (2-hydroxypropyl)-γ-cyclodextrin (278 mM, 1500-fold excess) in 10 min interval at 37 °C. Right: Linear fit of the decrease in absorption at 477 nm for first-order kinetics (-k= -0.00175 min^{-1}; $t_{1/2}$= 6.6 h).

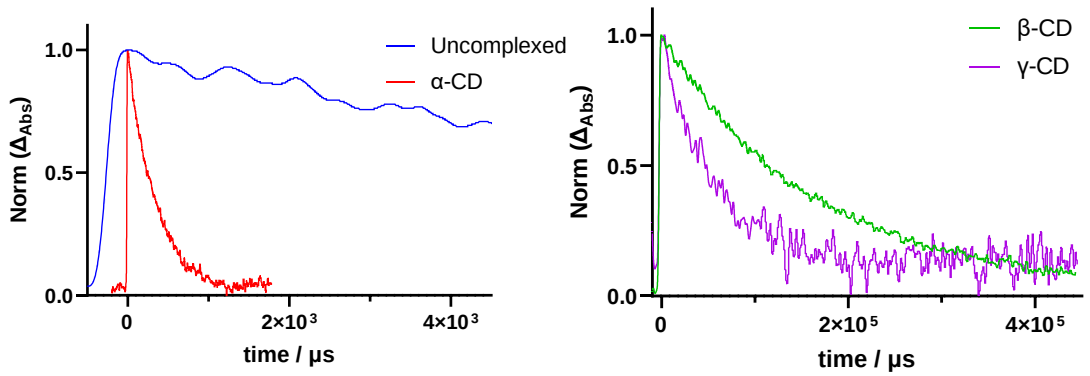


Supplementary figure 29. Left: UV/Vis spectra of compound **1** (185 µM) in water without cyclodextrin in 10 min interval at 37 °C. Right: Linear fit of the decrease in absorption at 470 nm for first-order kinetics (-k= -0.00107 min^{-1}; $t_{1/2}$= 10.8 h).

The kinetic of the reisomerization of diazocines **3** and **4** (185 µM) in the presence of (2-hydroxypropyl)-α/β -cyclodextrin (278 mM, 1500-fold excess) and (2-hydroxypropyl)-γ-cyclodextrin (151 mM, 820-fold excess) were measured by laser flash photolysis.



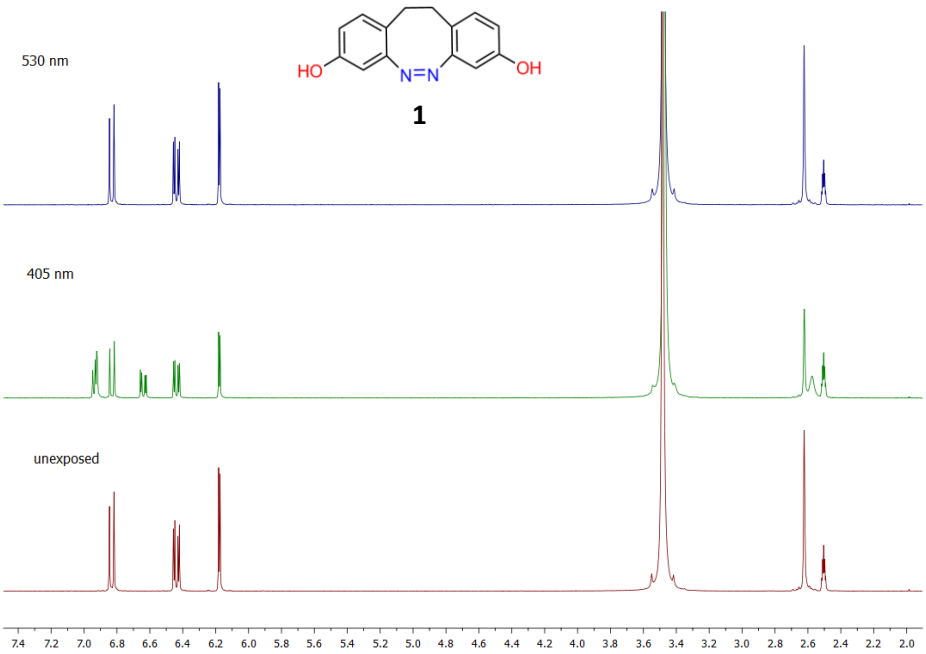
Supplementary figure 30. Transient absorption decay of compound **3** recorded at 37 °C in aqueous solution (H_2O 98 %; DMSO 2 %; 185 µM). λ_{exc} = 355 nm; λ_{obs} = 500 nm. The uncomplexed sample is plotted in blue, the transient spectra of the compound **3** in presence of (2-hydroxypropyl)-α-cyclodextrin (278 mM, 1500-fold excess) is plotted in red, in presence of (2-hydroxypropyl)-β-cyclodextrin (278 mM, 1500-fold excess) in green and in the presence of (2-hydroxypropyl)-γ-cyclodextrin (151 mM, 820-fold excess) in purple.



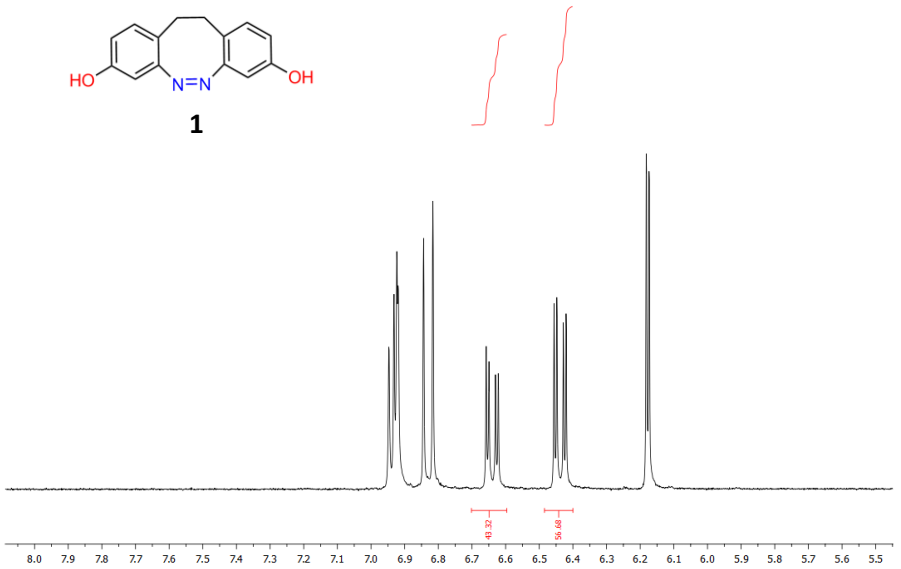
Supplementary figure 31. Transient absorption decay of compound **4** recorded at 37 °C in aqueous solution (H_2O 98 %; DMSO 2 %; 185 µM). λ_{exc} = 355 nm; λ_{obs} = 500 nm. The uncomplexed sample is plotted in blue, the transient spectra of the compound **4** in presence of (2-hydroxypropyl)-α-cyclodextrin (278 mM, 1500-fold excess) is plotted in red, in presence of (2-hydroxypropyl)-β-cyclodextrin (278 mM, 1500-fold excess) in green and in the presence of (2-hydroxypropyl)-γ-cyclodextrin (278 mM, 1500-fold excess) in purple.

4.3 NMR switching experiments and photostationary states

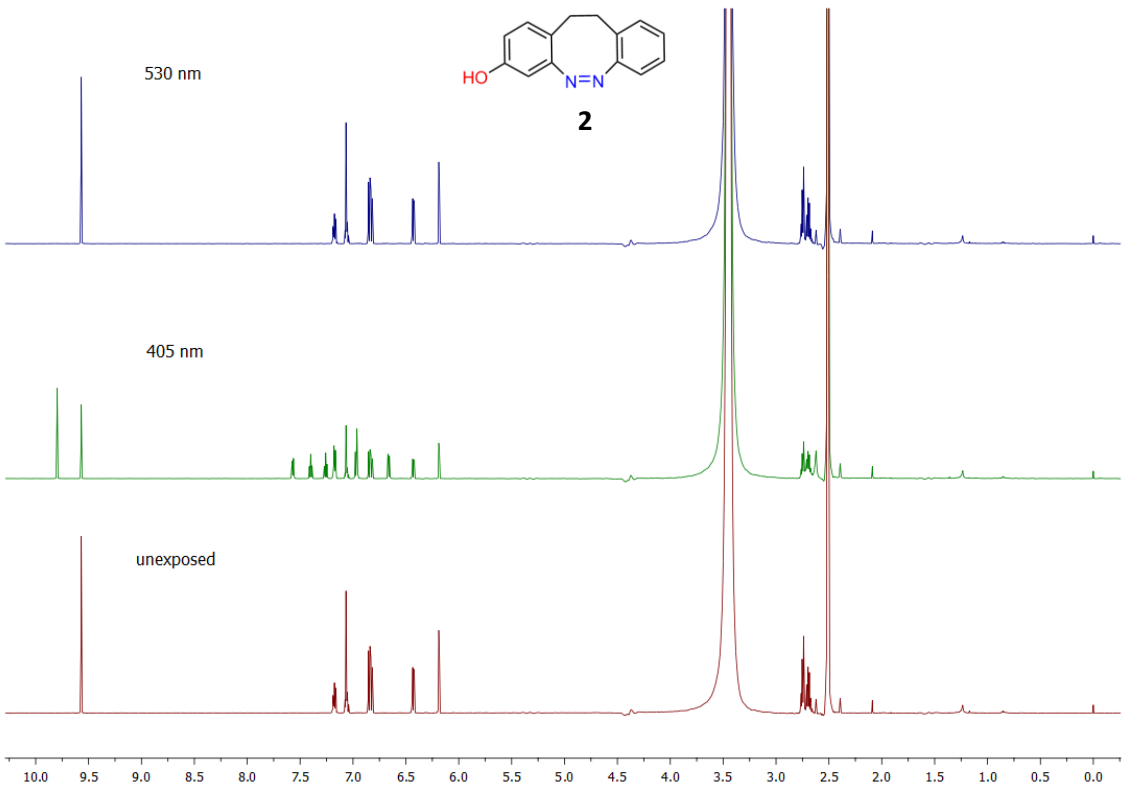
NMR switching experiments and photostationary states in DMSO



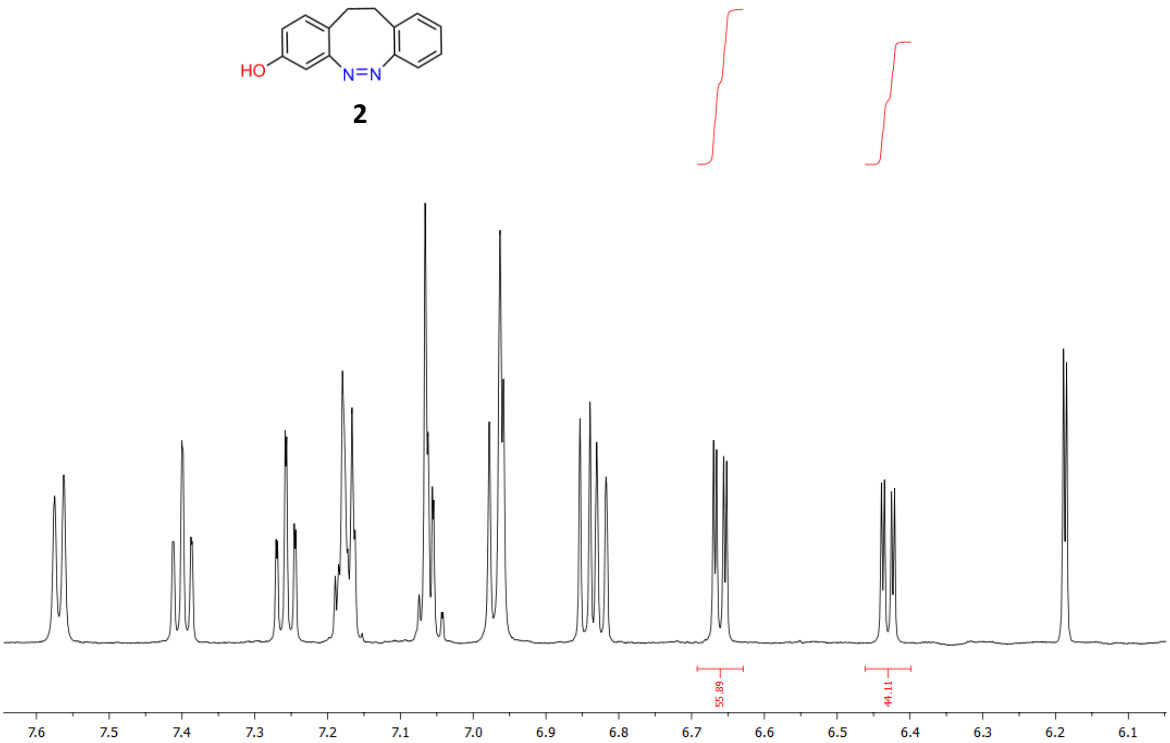
Supplementary figure 32. ^{1}H-NMR spectra of compound **1** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



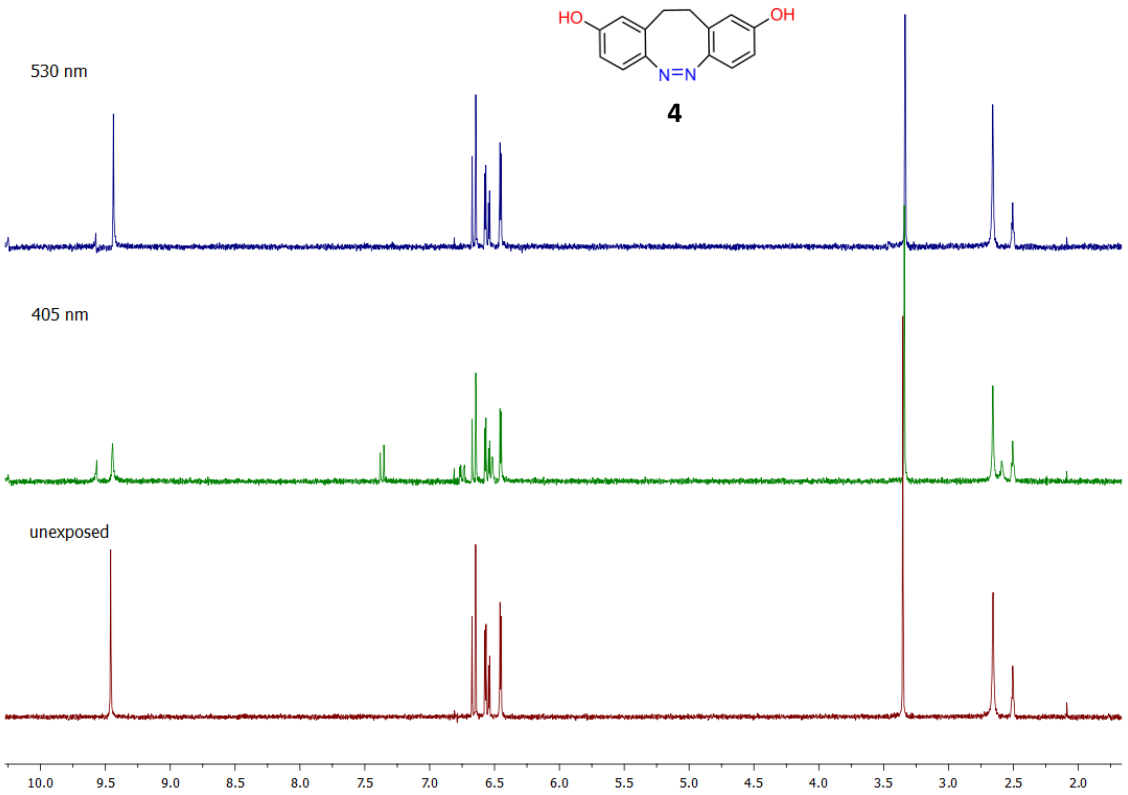
Supplementary figure 33. ^{1}H-NMR spectrum of the photostationary state of compound **1** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.



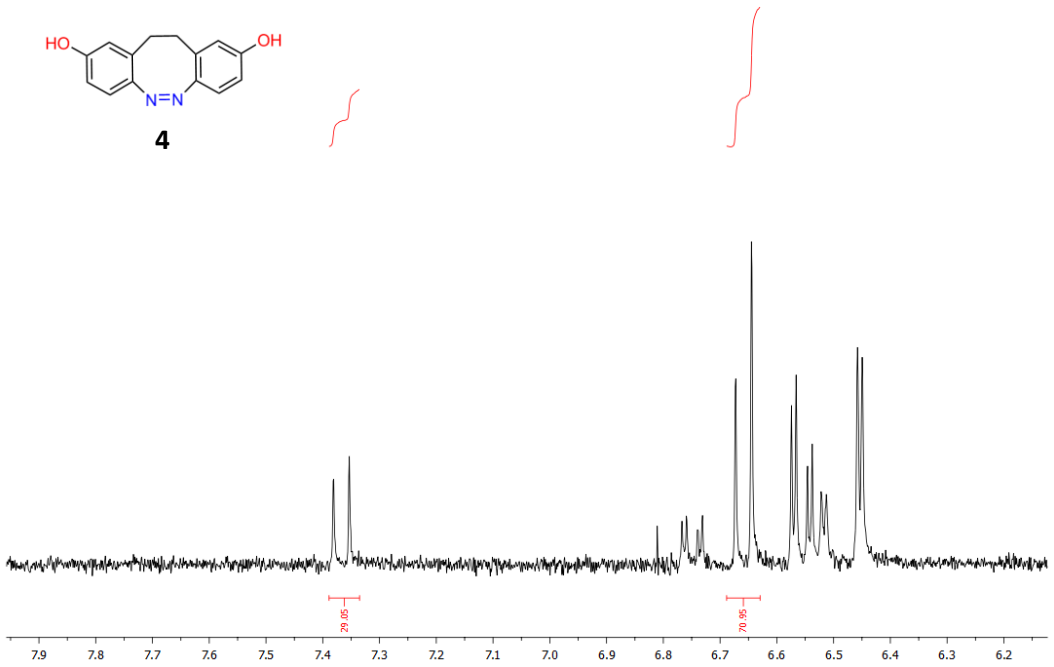
Supplementary figure 34. ^{1}H-NMR spectra of compound **2** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



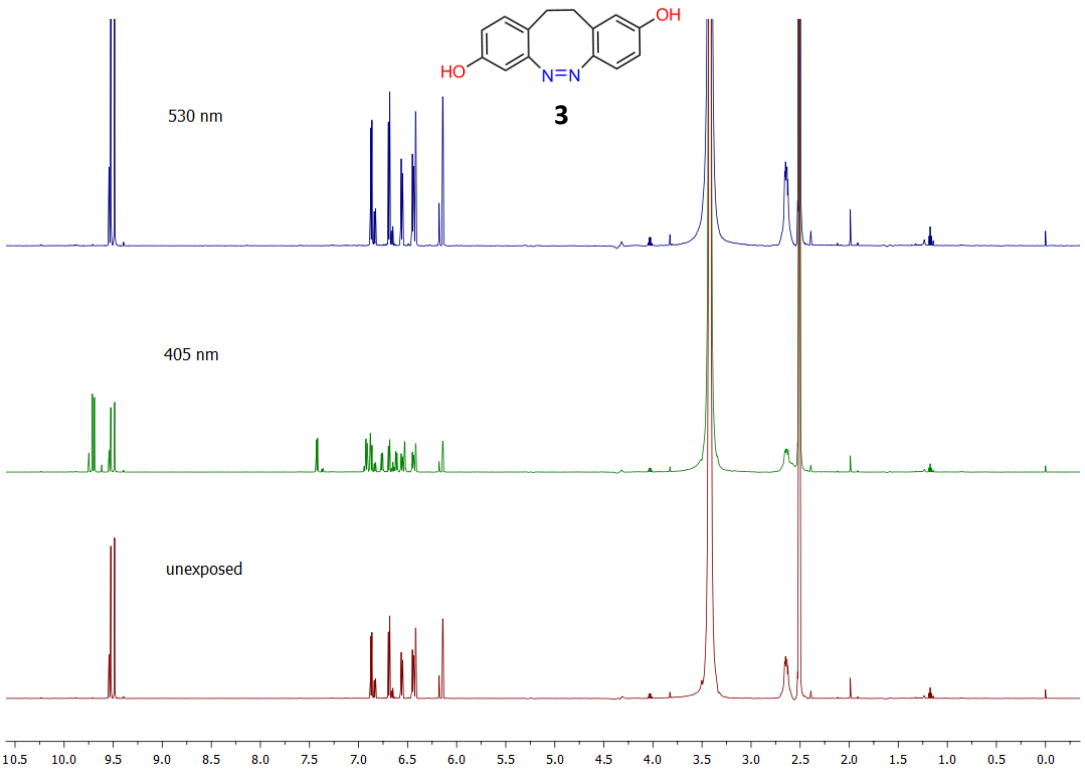
Supplementary figure 35. ^{1}H-NMR spectrum of the photostationary state of compound **2** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.



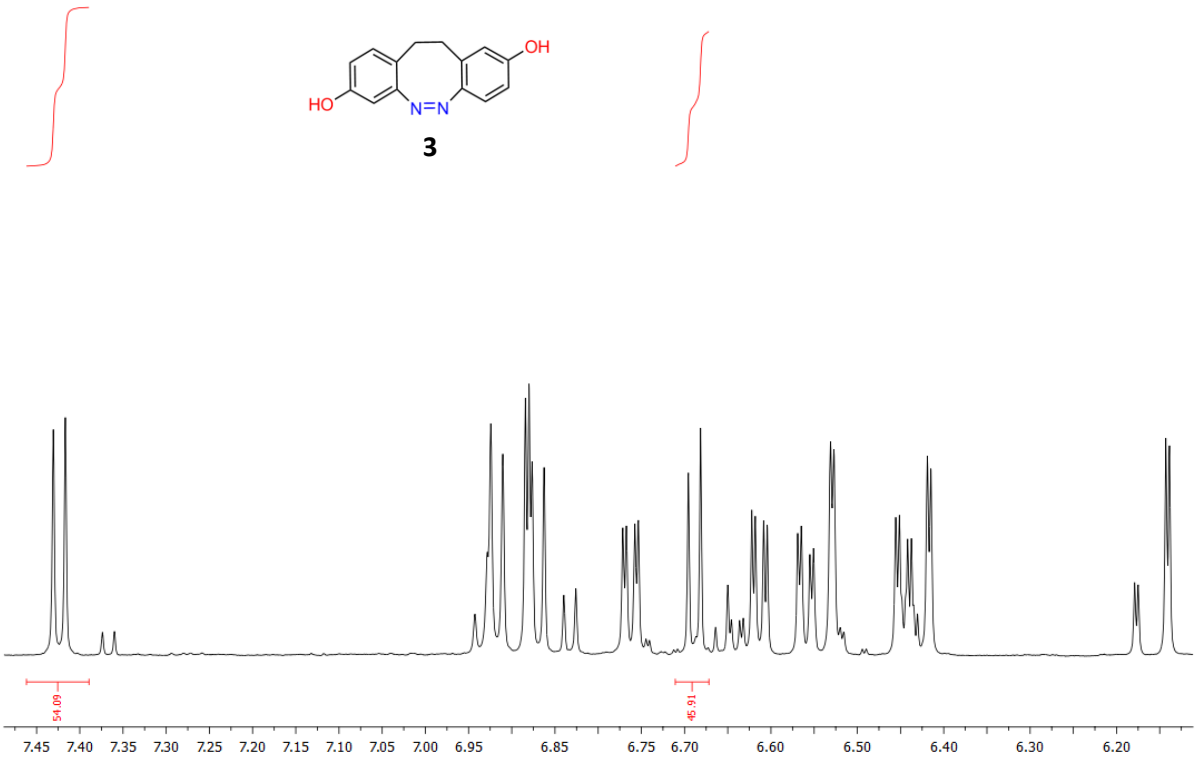
Supplementary figure 36. ^{1}H-NMR spectra of compound **4** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



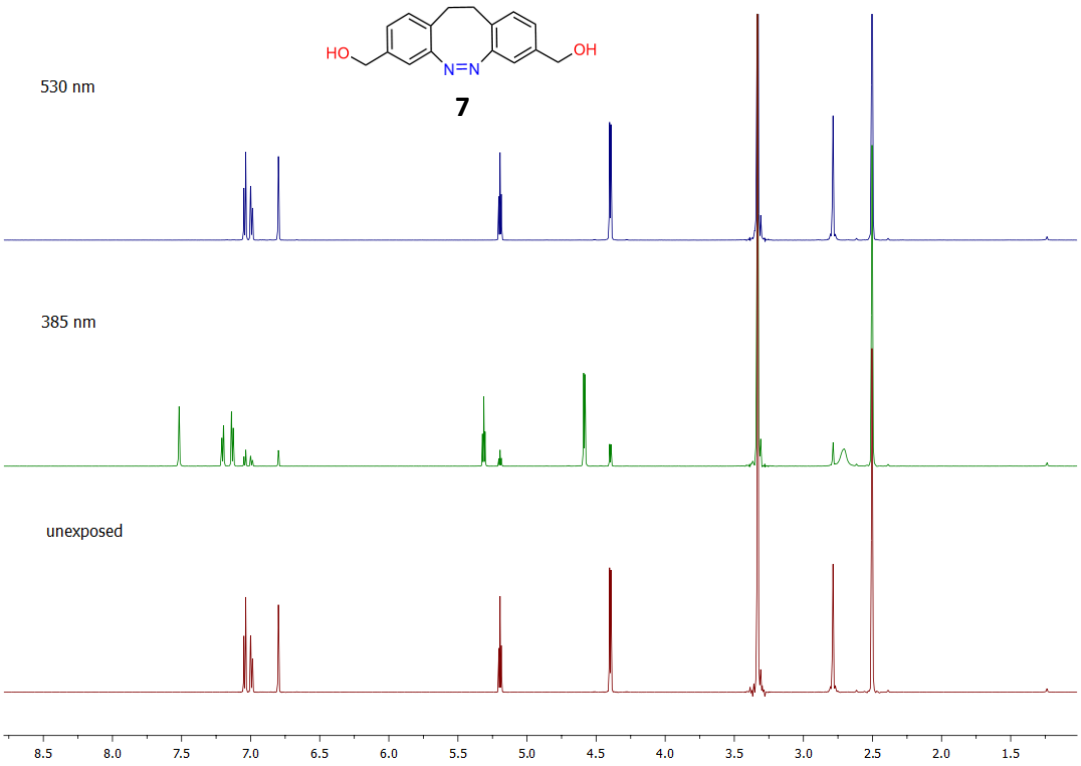
Supplementary figure 37. ^{1}H-NMR spectrum of the photostationary state of compound **4** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.



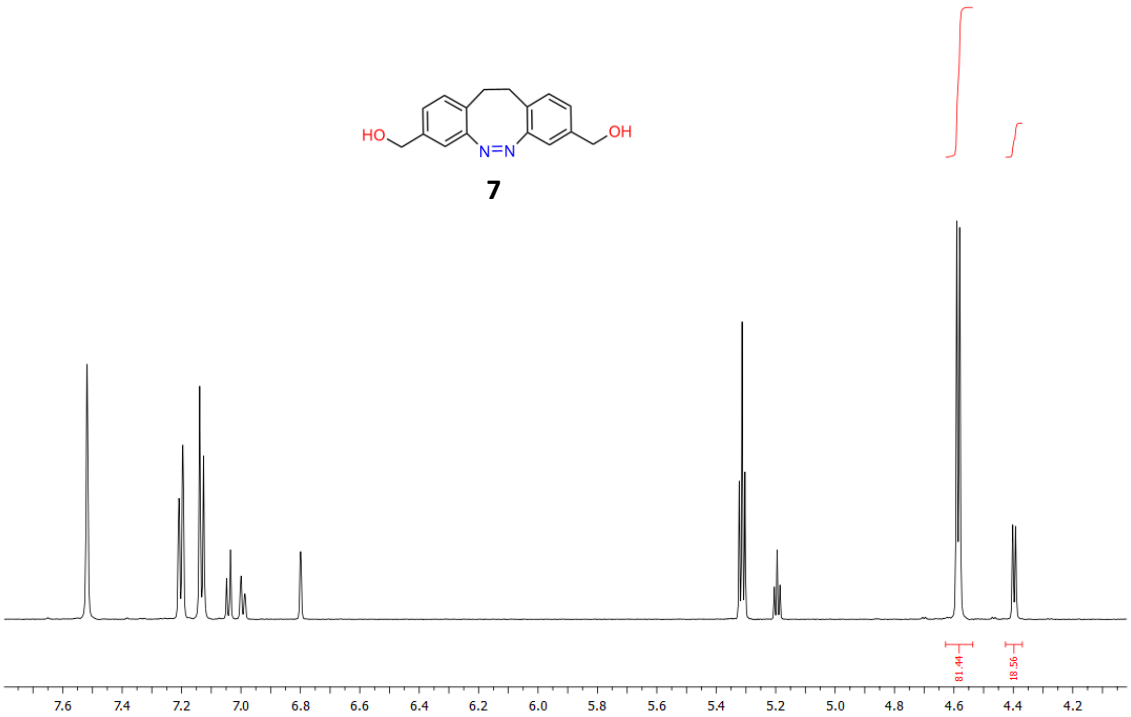
Supplementary figure 38. ^{1}H-NMR spectra of compound **3** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



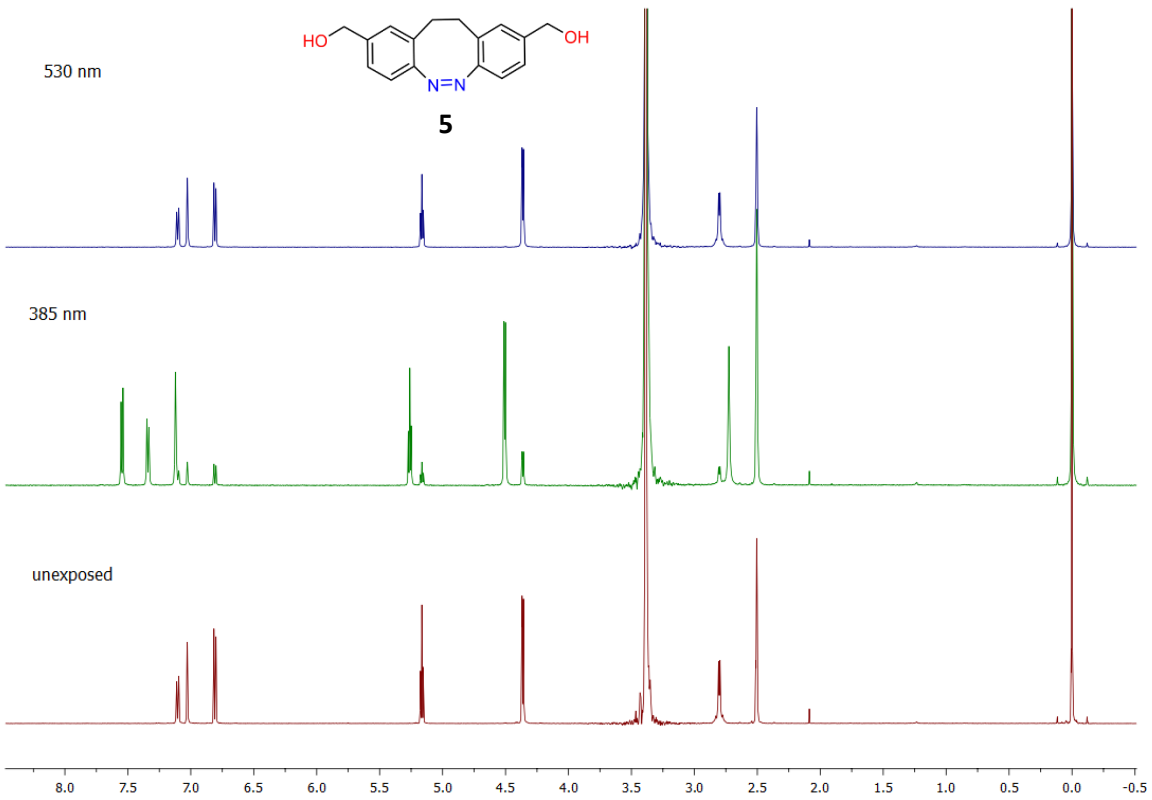
Supplementary figure 39. ^{1}H-NMR spectrum of the photostationary state of compound **3** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.



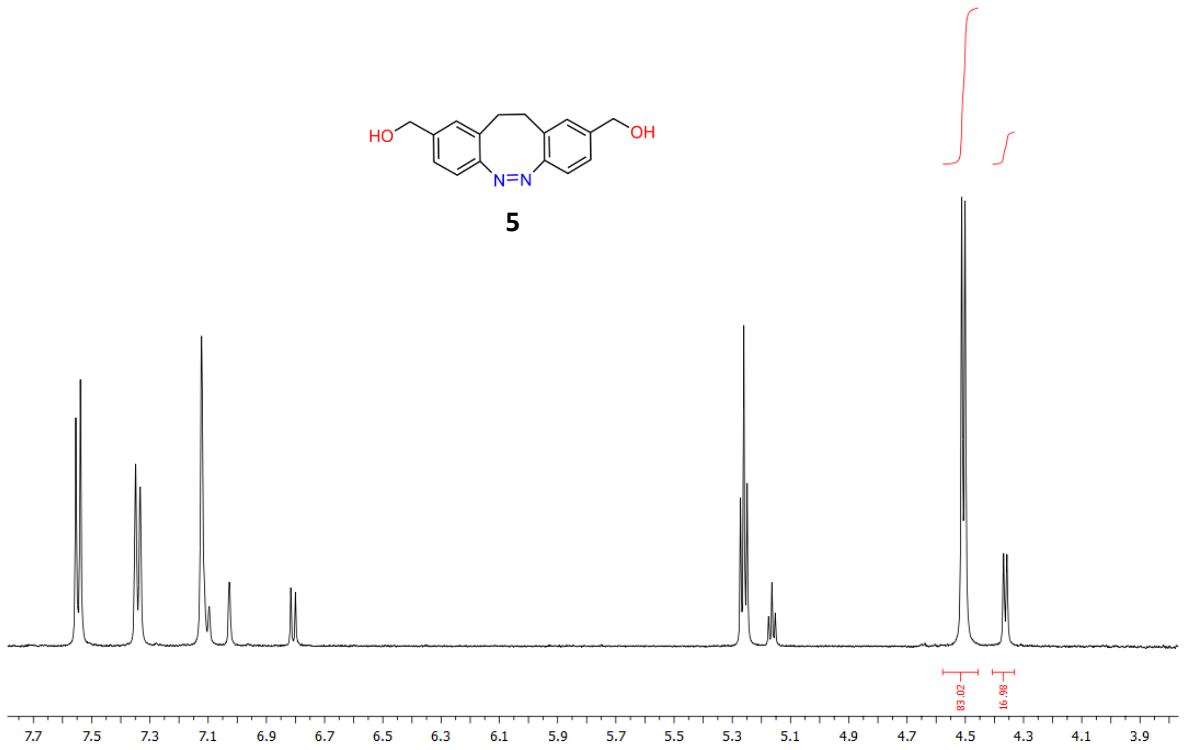
Supplementary figure 40. ^{1}H-NMR spectra of compound **7** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



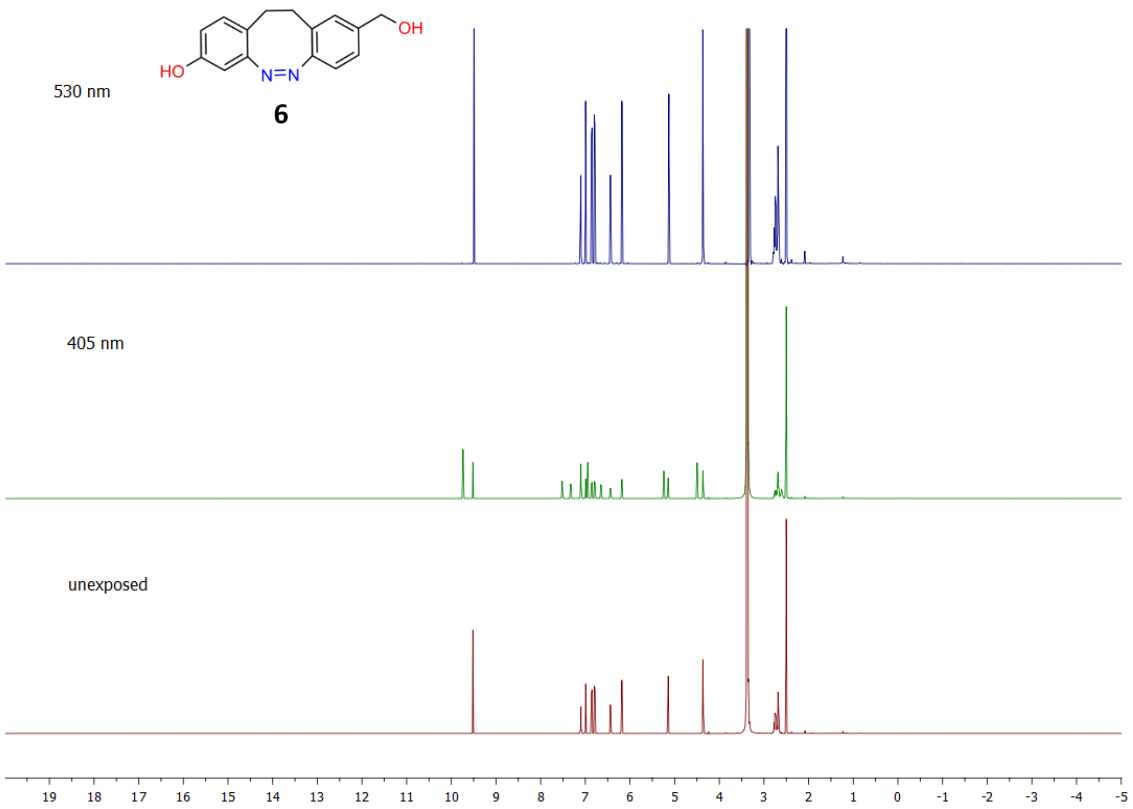
Supplementary figure 41. ^{1}H-NMR spectrum of the photostationary state of compound **7** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.



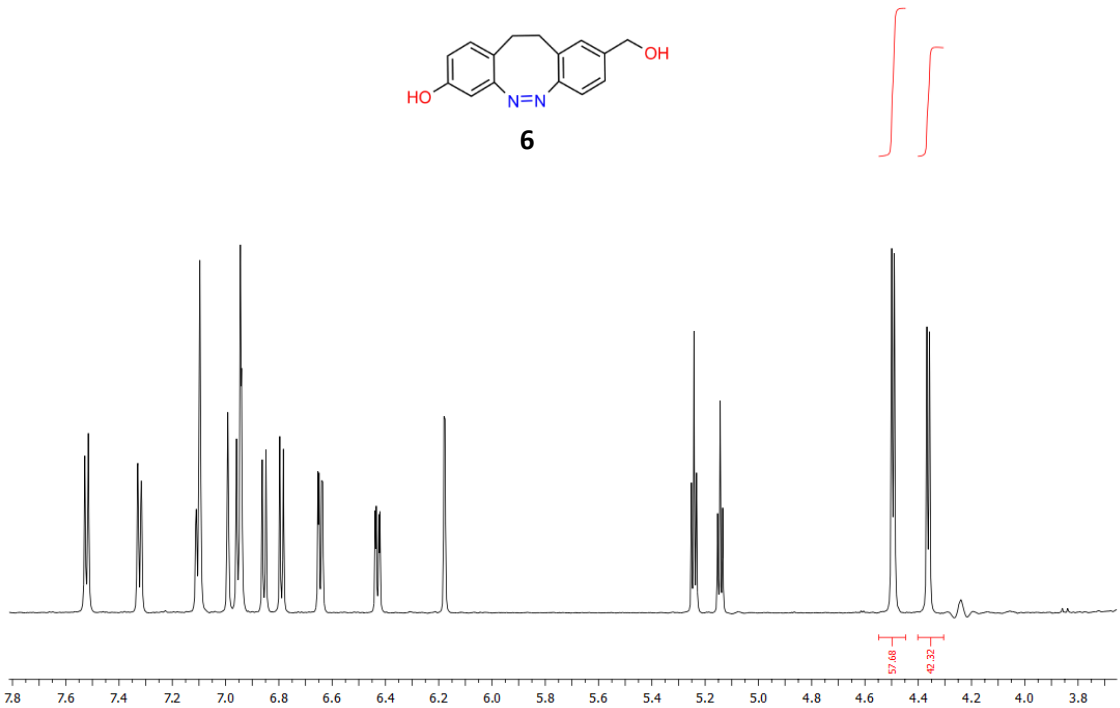
Supplementary figure 42. ^{1}H-NMR spectra of compound **5** measured in DMSO-d_6 at 298 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 43. ^{1}H-NMR spectrum of the photostationary state of compound **5** measured in DMSO-d_6 at 298 K. Integrals of the *E* and *Z* isomers are display in red.

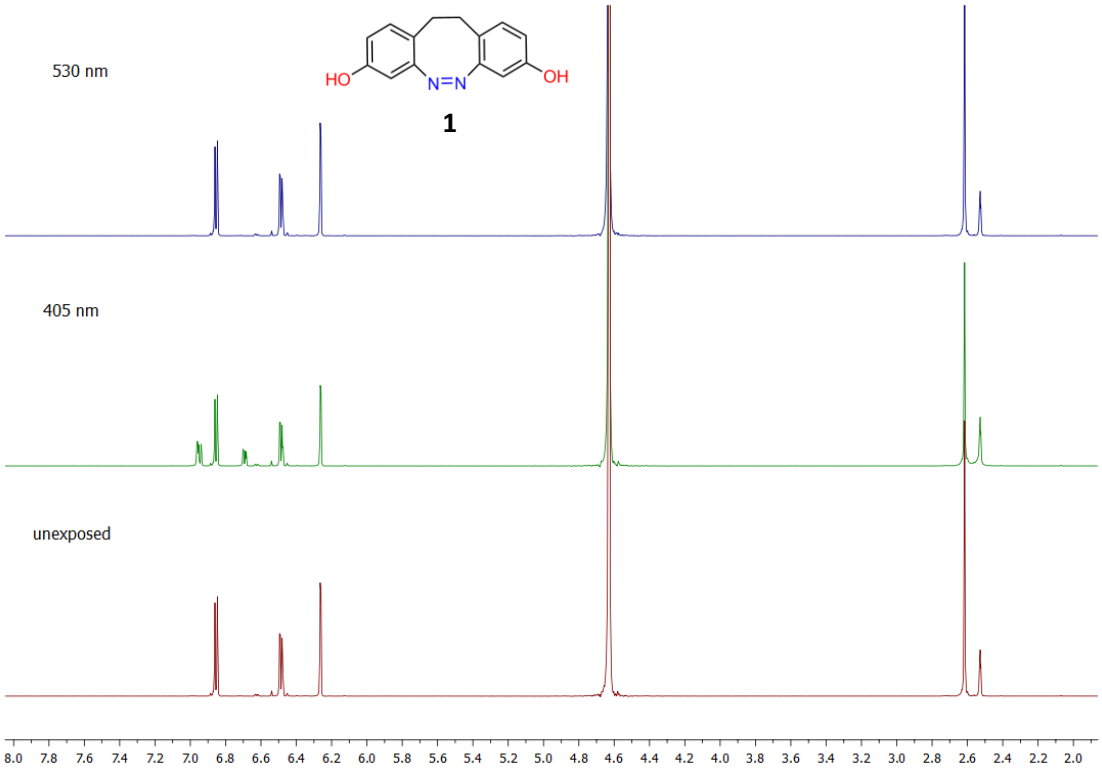


Supplementary figure 44. ^{1}H-NMR spectra of compound **6** measured in DMSO-d_6 at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.

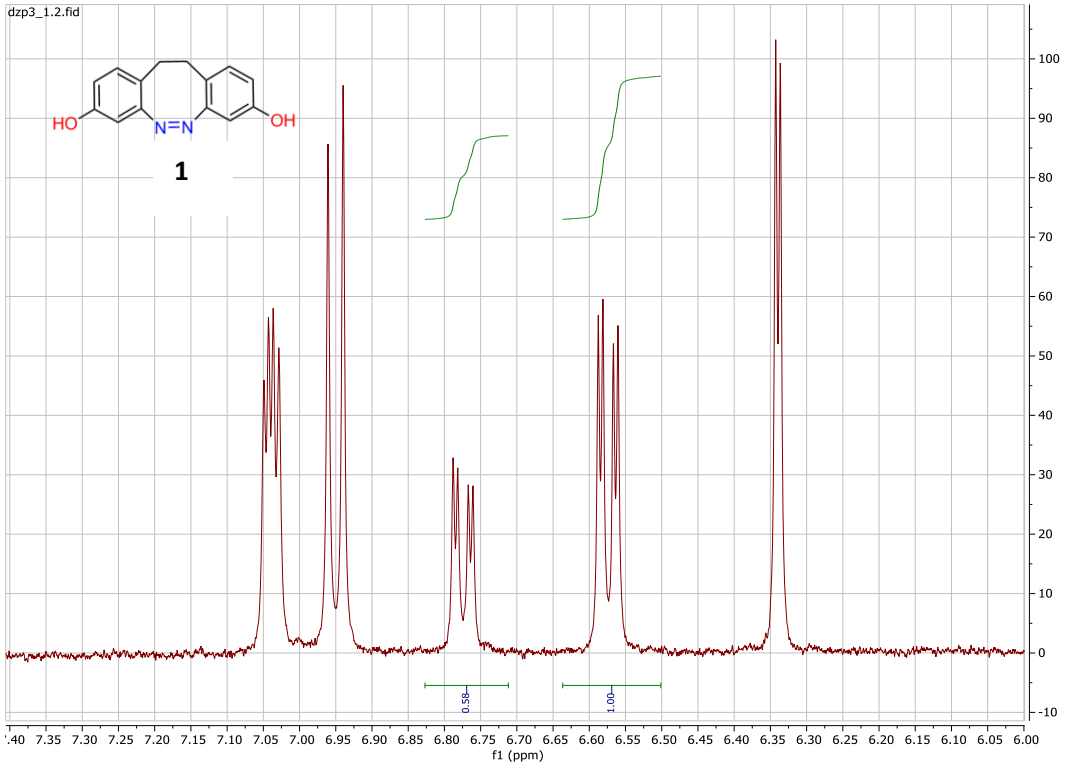


Supplementary figure 45. ^{1}H-NMR spectrum of the photostationary state of compound **6** measured in DMSO-d_6 at 300 K. Integrals of the *E* and *Z* isomers are display in red.

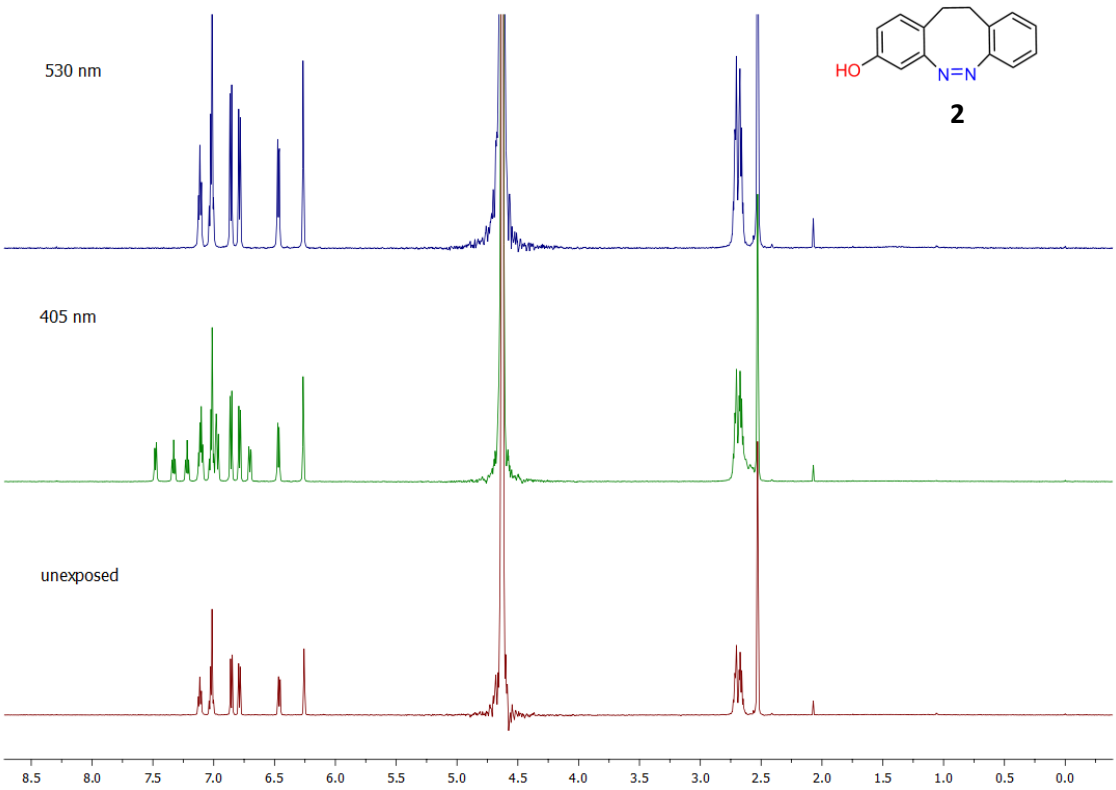
NMR switching experiments and photostationary states in aqueous solution



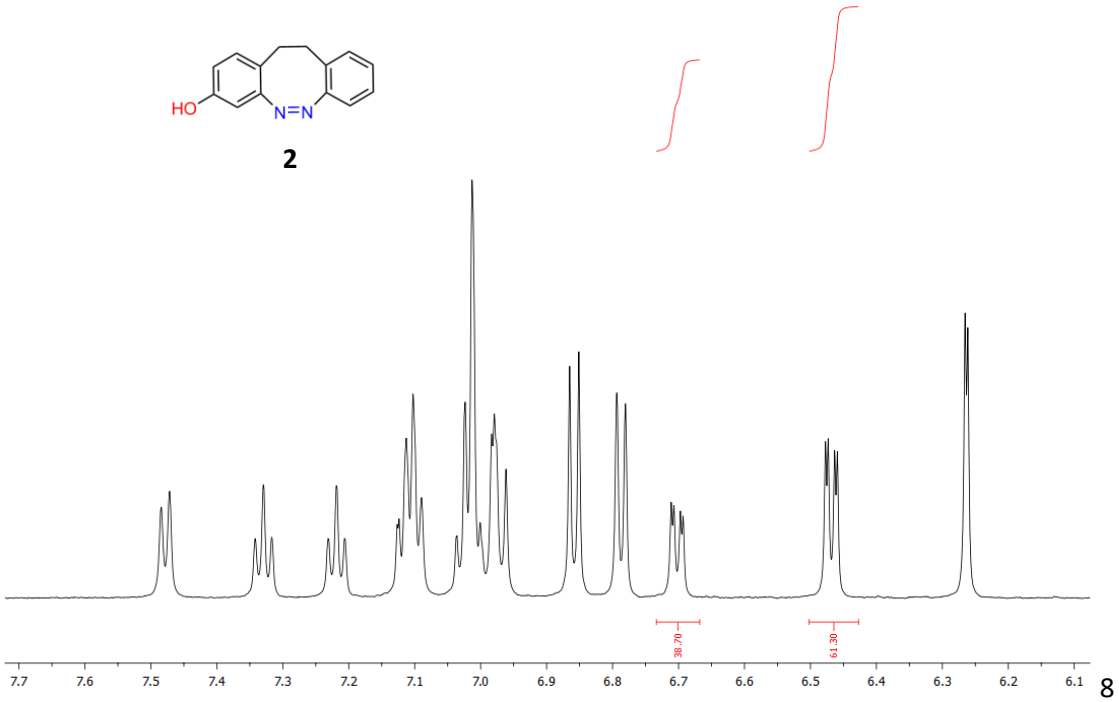
Supplementary figure 46. ^{1}H-NMR spectra of compound **1** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



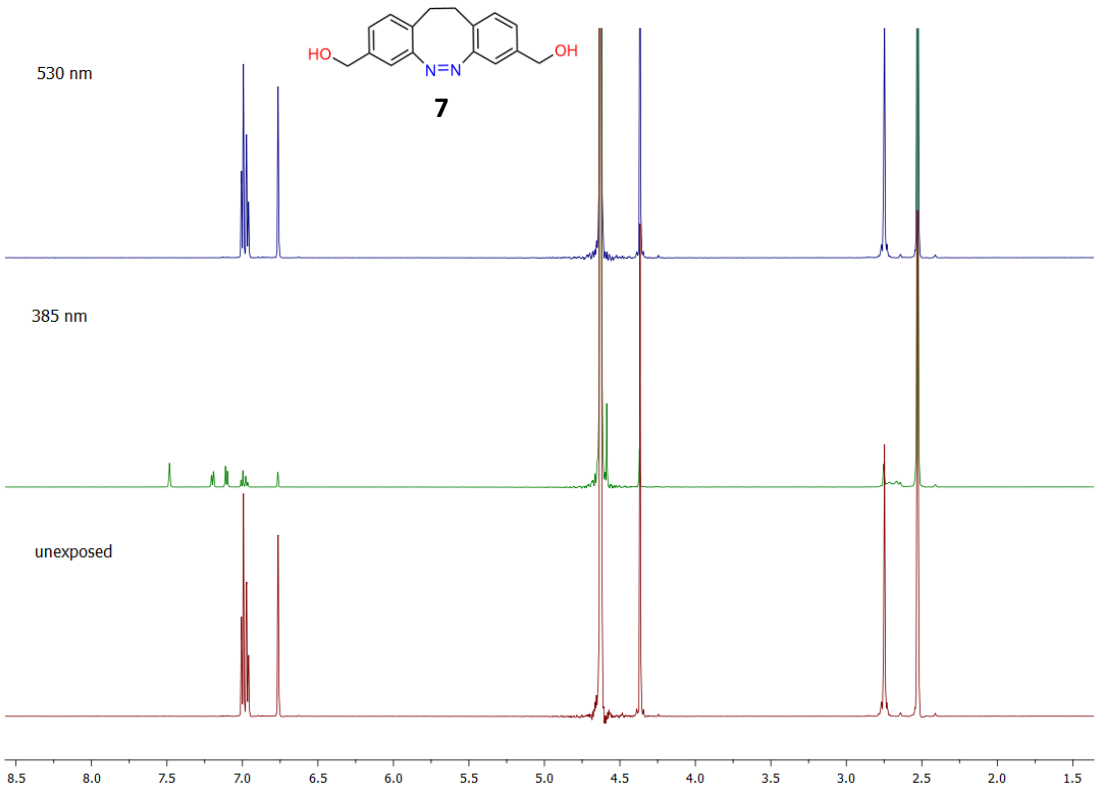
Supplementary figure 47. ^{1}H-NMR spectrum of the photostationary state of compound **1** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Integrals of the *E* and *Z* isomers are display in green.



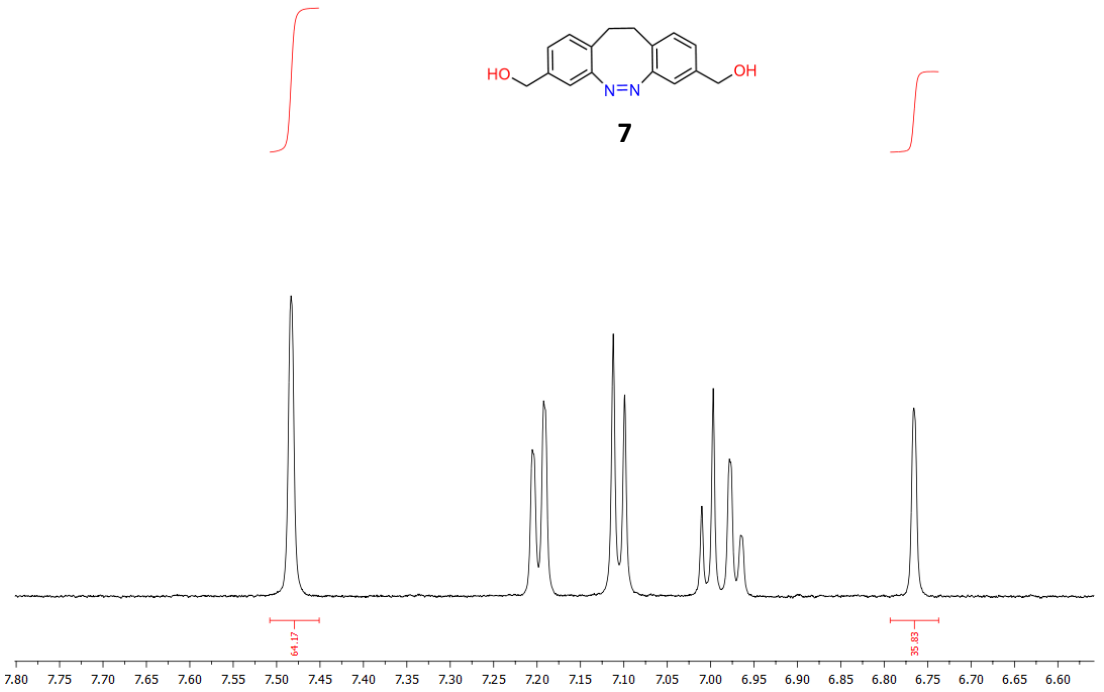
Supplementary figure 48. ^{1}H-NMR spectra of compound **2** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



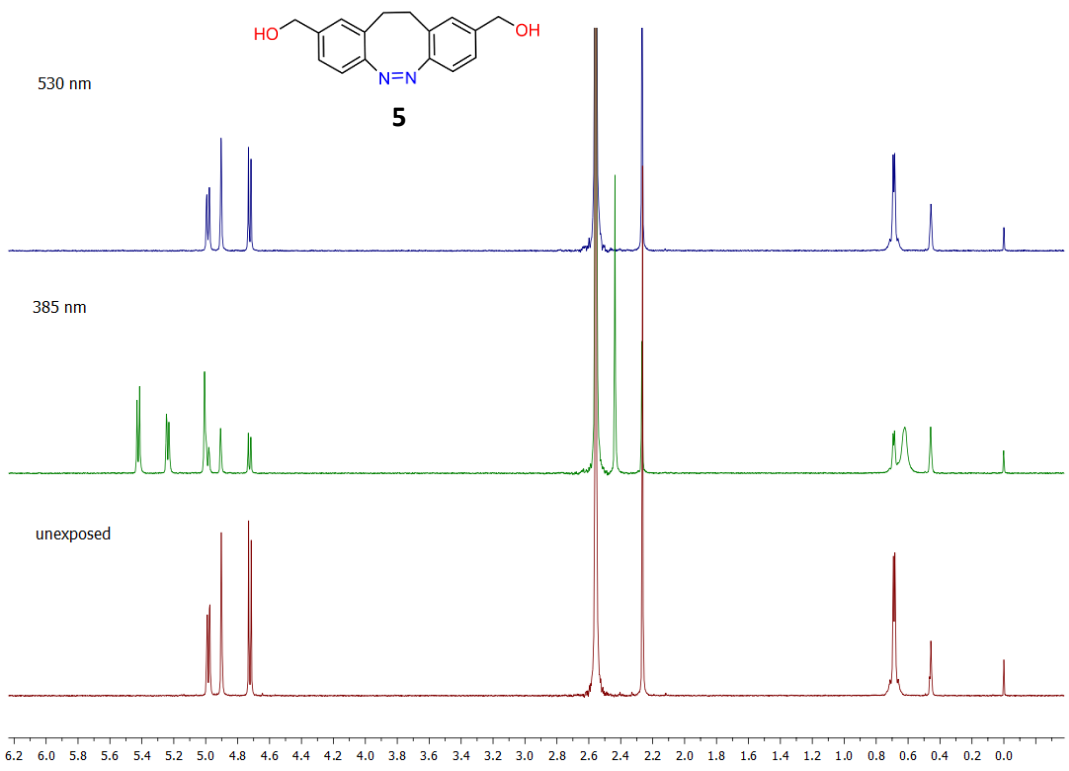
Supplementary figure 49. ^{1}H-NMR spectrum of the photostationary state of compound **2** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Integrals of the *E* and *Z* isomers are display in red.



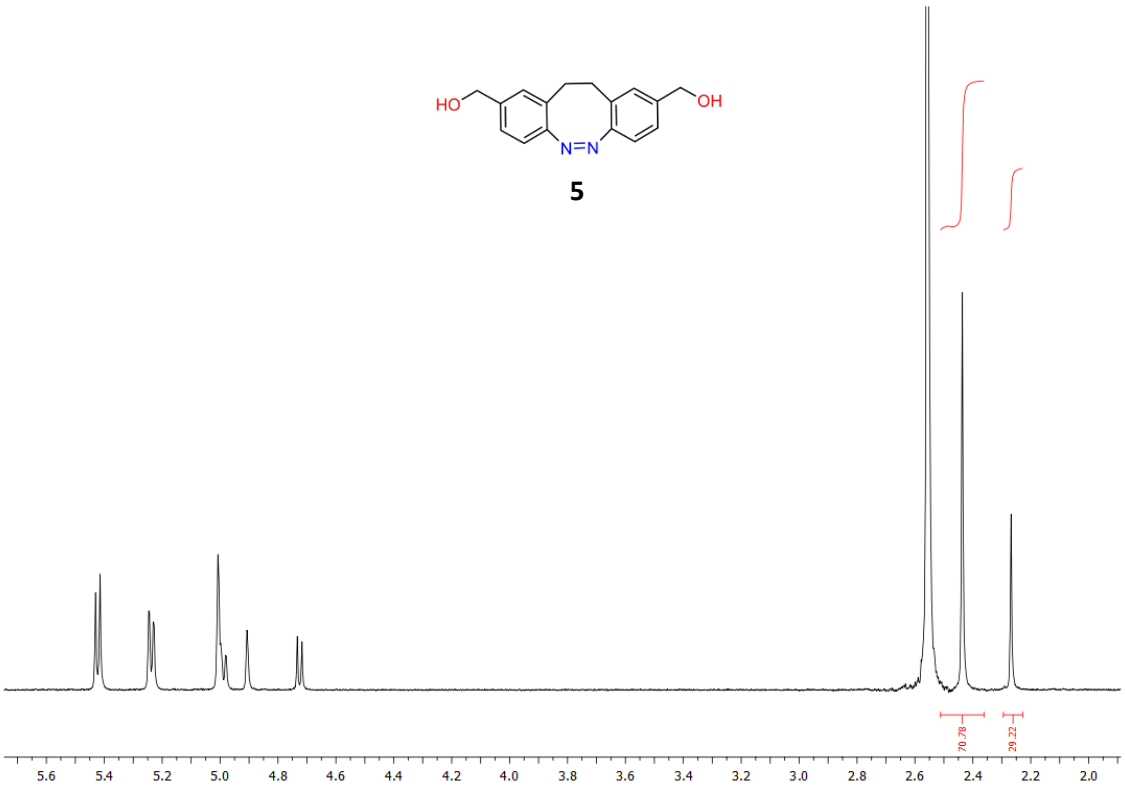
Supplementary figure 50. ^{1}H-NMR spectra of compound **7** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



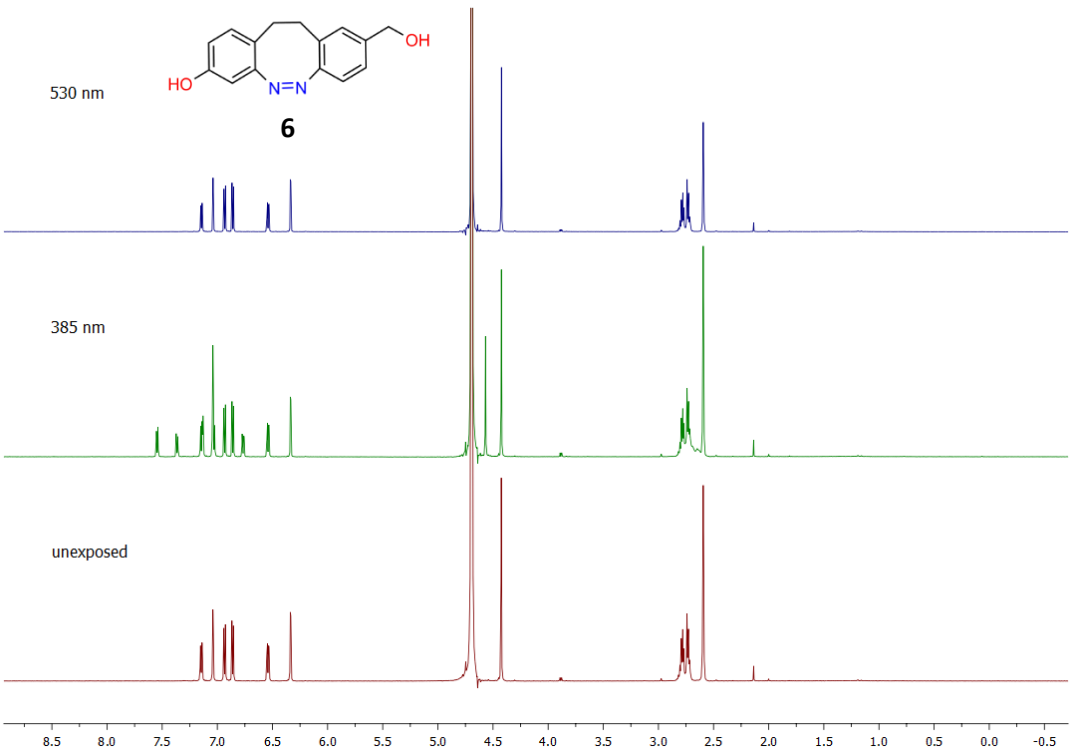
Supplementary figure 51. ^{1}H-NMR spectrum of the photostationary state of compound **7** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Integrals of the *E* and *Z* isomers are display in red.



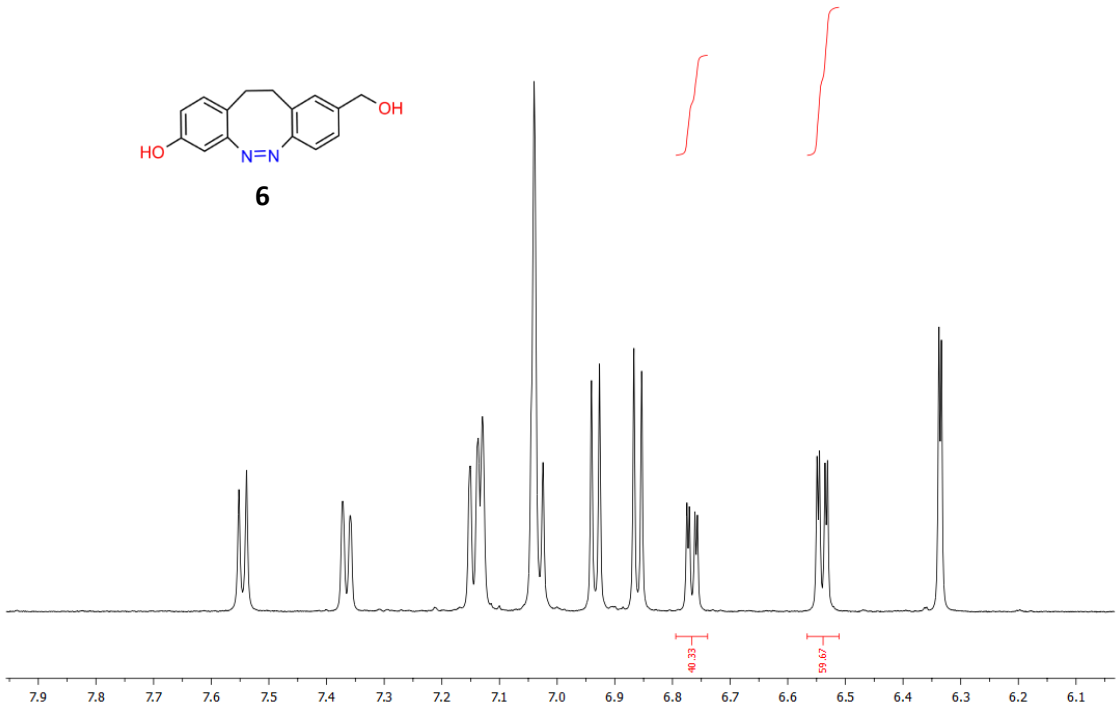
Supplementary figure 52. ^{1}H-NMR spectra of compound **5** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 298 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 53. ^{1}H-NMR spectrum of the photostationary state of compound **5** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 298 K. Integrals of the *E* and *Z* isomers are display in red.

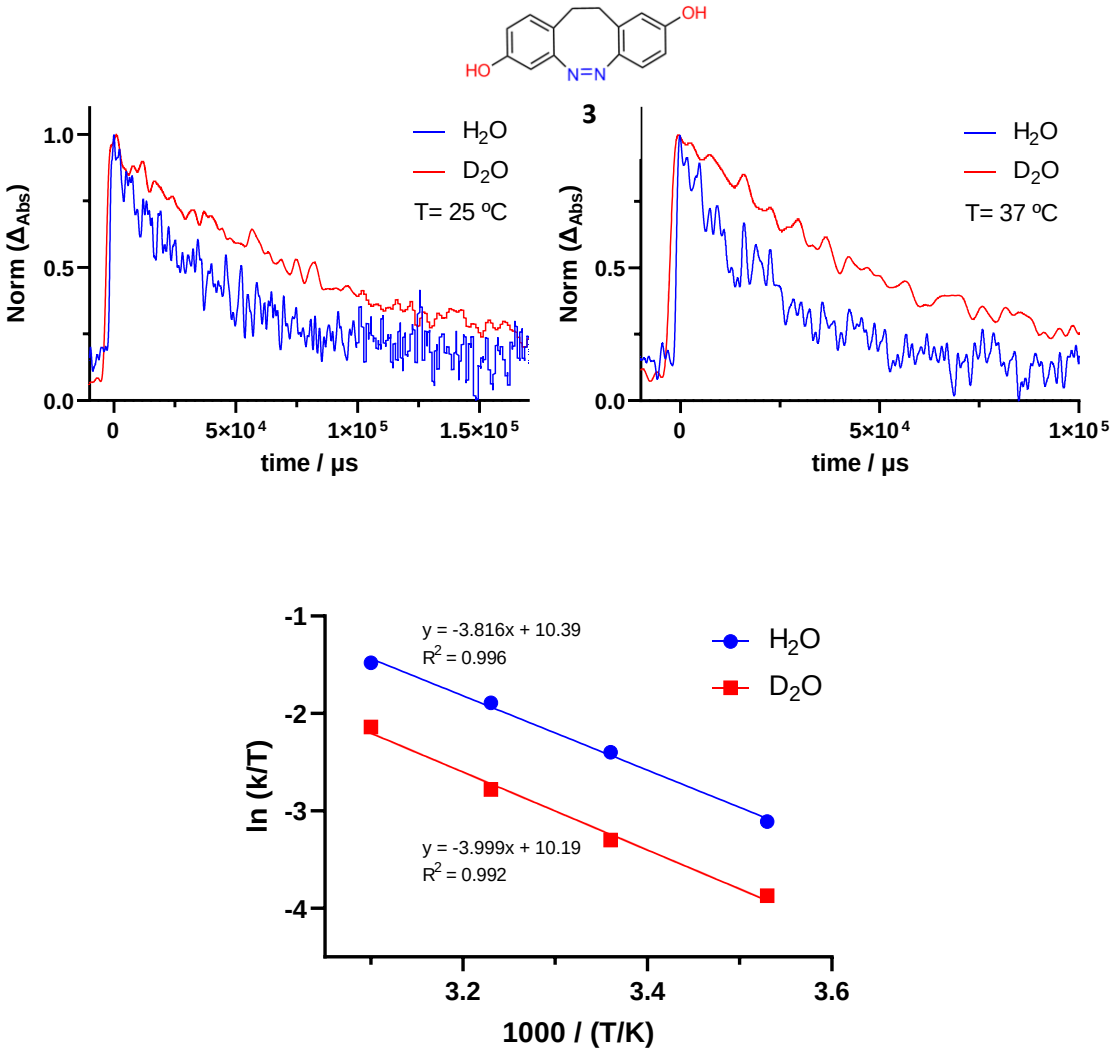


Supplementary figure 54. ^{1}H-NMR spectra of compound **6** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 55. ^{1}H-NMR spectrum of the photostationary state of compound **6** measured in aqueous solution (90 % D_2O; 10 % DMSO-d_6) at 300 K. Integrals of the *E* and *Z* isomers are display in red.

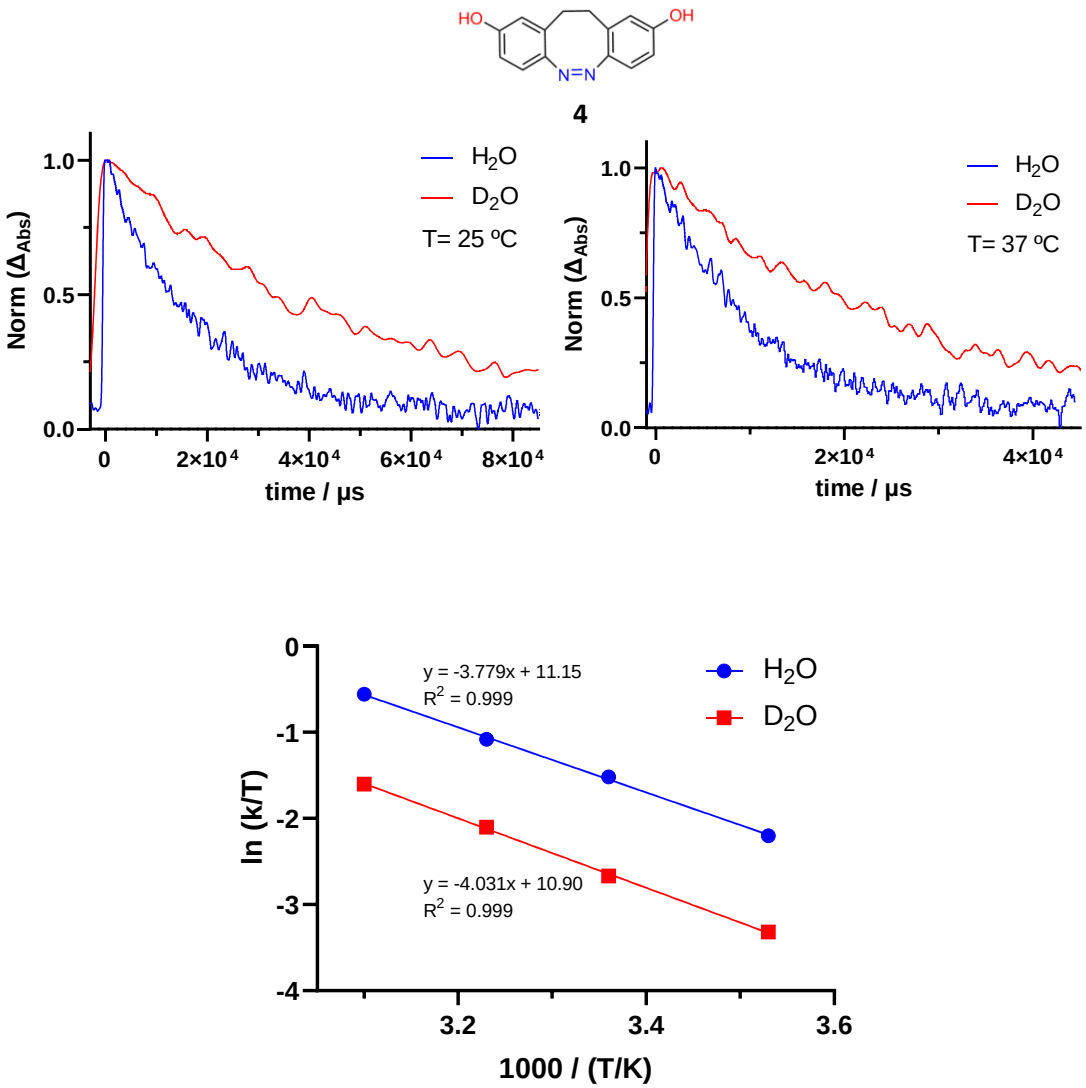
5. Kinetic studies of the thermal relaxation process by Laser flash-photolysis



Supplementary figure 56. Top: Transient absorption decays of compound **3** (420 µM) recorded at 25 °C (left) and 37 °C (right) in aqueous solution H_2O 98 %; DMSO 2 % (blue) or D_2O 98 %; DMSO 2 % (red). λ_{exc} = 355 nm; λ_{obs} = 500 nm. Bottom: Eyring plots for the *trans*-to-cis thermal isomerization.

Supplementary Table 3. Activation parameters derived from the Eyring plots for the *trans*-to-cis thermal isomerization of compound **3** in aqueous solutions (H_2O 98 %; DMSO 2 % and D_2O 98 %; DMSO 2 %).

Compound 3	$\Delta H^{\ddagger}$ / kJ·mol^{-1}	$\Delta S^{\ddagger}$ / J·K^{-1} mol^{-1}·
H_2O	31.3 ± 0.4	-112.7 ± 1.0
D_2O	32.7 ± 1.3	-114.7 ± 2.6



Supplementary figure 57. Top: Transient absorption decays of compound **4** (420 µM) recorded at 25 °C (left) and 37 °C (right) in aqueous solution H_2O 98 %; DMSO 2 % (blue) or D_2O 98 %; DMSO 2 % (red). λ_{exc} = 355 nm; λ_{obs} = 500 nm. Bottom: Eyring plots for the *trans*-to-*cis* thermal isomerization

Supplementary Table 4. Activation parameters derived from the Eyring plots for the *trans*-to-cis thermal isomerization of compound **4** in aqueous solutions (H_2O 98 %; DMSO 2 % and D_2O 98 %; DMSO 2 %).

Compound 4	$\Delta H^{\ddagger}$ / kJ·mol^{-1}	$\Delta S^{\ddagger}$ / J·K^{-1} mol^{-1}·
H_2O	30.9 ± 0.1	-106.7 ± 0.7
D_2O	33.0 ± 0.8	-108.8 ± 0.4

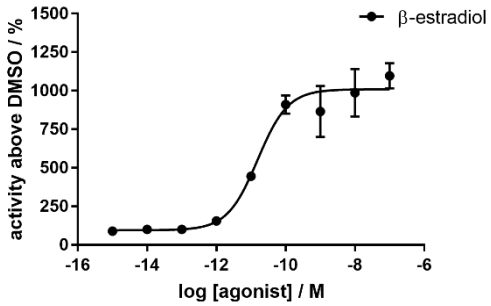
6. Biological Evaluation

Methodology Luciferase Reporter Gene Assay in MCF-7

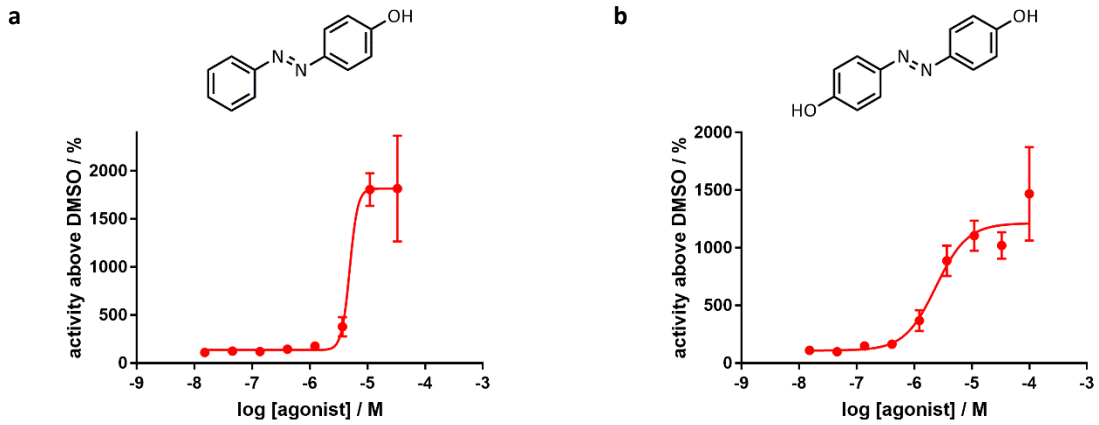
For determination of estrogenic activities, a luciferase reporter gene assay was performed comparable to methods published previously.[7–11] MCF-7 cells (CLS Cell Lines Service, Eppenheim, Germany) were grown in DMEM, high glucose with 10 % FBS (ThermoFisher, Waltham, MA, USA) at 37 °C and 5 % CO_2 in a humidified atmosphere. Prior to transient transfection, cells were seeded into culture flasks at a density of 1.2 * 10^5 cells / cm^2 with DMEM containing only 2 % FBS and were allowed to adhere for 1-2 h. Co-transfection in bulk was conducted using 1187.5 ng firefly plasmid (3X ERE TATA luc, Addgene, Watertown, MA, USA, #11354, was a gift from Donald McDonnell[7]) and 62.5 ng *Renilla* normalization plasmid per 10^6 cells. Lipofectamine 2000™ (ThermoFisher) was used as transfection reagent (3 µl per 1 µg DNA). Approx. 20 h post-transfection cells were harvested and reseeded on 96-well plates (4 * 10^4 cells / well) with hormone-free medium (phenolred-free DMEM containing 10 % charcoal-stripped FBS, ThermoFisher). Approx. 3 h later, test compounds were added to the cells with a final DMSO concentration of 1 %. Compound handling took place under light exclusion. Each compound was tested in nine concentrations together with DMSO alone as a vehicle control in triplicates. For reference β-estradiol (Sigma-Aldrich, St. Louis, MO, USA) final test concentrations were 100 nM - 1 fM in 1:10 dilution steps, for diazocines (and hydroxy azobenzenes) 100 µM - 15 nM in 1:3 dilutions. When required, irradiation of the compounds was performed in DMSO before adding this solution to the cells as well as during the 15-hour incubation with the cells, mostly every 3 h. Therefore, custom-made lamps for the cell incubator were used, which were controlled by a timer. Irradiation was conducted at 405 nm every 3 h for 1 min at 50 % power or every 30 min for 3 min at 25 % power or at 385 nm every 3 h for 3 min at 50 % power. In case of back-switching to the *Z*-isomer, the cell assay was additionally irradiated at 525 nm (approx. 10 min after the irradiation at 405 nm or 385 nm) using a custom-made 96-well plate lamp (16 × 380 mW Nichia NCSG219B-V1 LEDs in the distance of the wells, dimmable, Sahlmann Photochemical Solutions, Bad Segeberg, Germany). Thereby, every well was irradiated for 20 s at 5 % power. Irradiation tolerance of the cell assay was verified by performing dose-response analysis of reference β-estradiol with and without irradiation. After 15 h incubation, both luciferase activities of the cell lysates were evaluated using Dual-Luciferase© Reporter Assay (Promega, Madison, WI, USA) according to the manufacturer's protocol. Luminescence was measured with a TECAN Spark® Microplate Reader (Tecan, Männedorf, Switzerland). For each well, measured firefly signals were divided by *Renilla* signals for normalization of transfection efficiency and cell number. Estrogenic activities were calculated in percent of DMSO control without compound and plotted against logarithm of compound concentrations. Data points represent average of triplicate determinations with standard deviation as error bars. If appropriated, sigmoidal fitting (*log(agonist) vs. response – variable slope*) and calculation of EC_{50} values were performed using GraphPad Prism® (v. 7.03, GraphPad Software, San Diego, CA, USA). Additionally, the maximum relative activity (at 100 µM) was calculated in relation to the maximum activity of reference β-estradiol (top plateau of the dose-response curve) in the respective assay as a percentage. Each experiment was repeated independently at least three times unless otherwise stated.

To investigate an antagonistic effect, test substances were incubated together with β-estradiol in the described reporter gene assay. For this purpose, the respective final concentrations of estradiol as well as of the respective diazocine or reference indicated above were used in the corresponding dilution series with a total of 1 % DMSO. Raloxifene hydrochloride (Cayman Chemical, Ann Arbor, MI, USA) was used as a positive control for an antagonistic effect.

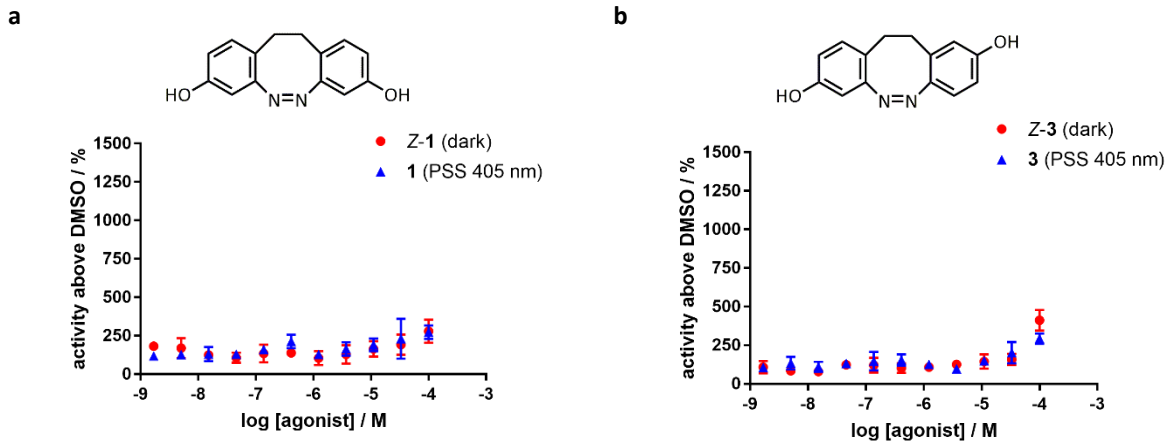
Additional Reporter Gene Assay Results



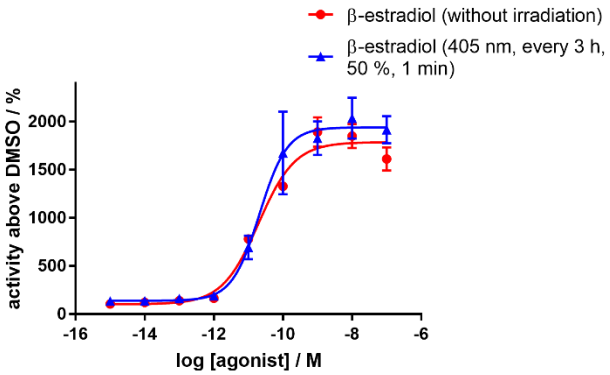
Supplementary figure 58. Exemplary dose-response curve of reference β-estradiol in a cell-based reporter gene assay. EC_{50} = 15.6 pM. Data points are means of technical triplicates ± SD.



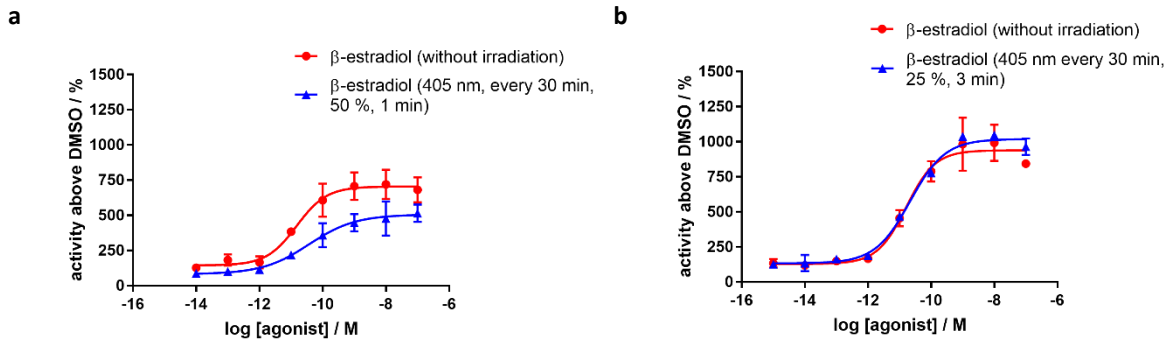
Supplementary figure 59. Estrogenic activities of mono- and disubstituted *para*-hydroxy azobenzenes in a cell-based reporter gene assay. (**a**) Monosubstituted hydroxy azobenzene, unirradiated (*E*-isomer, dark, red circles, EC_{50} = 5.4 ± 0.7 µM, max. relative activity: 123.4 ± 46.4 %). (**b**) Disubstituted hydroxy azobenzene, unirradiated (*E*-isomer, dark, red circles, EC_{50} = 1.8 ± 0.8 µM, max. relative activity: 87.9 ± 4.3 %). The highest concentrations (100 µM and 33 µM) were in part highly toxic for the cells, therefore the evaluation was only possible to a limited extent. Dose-response curves are one representative example from two independent cell assays. Data points are means of technical triplicates ± SD. EC_{50}-values are means of biological replicates ± SD.



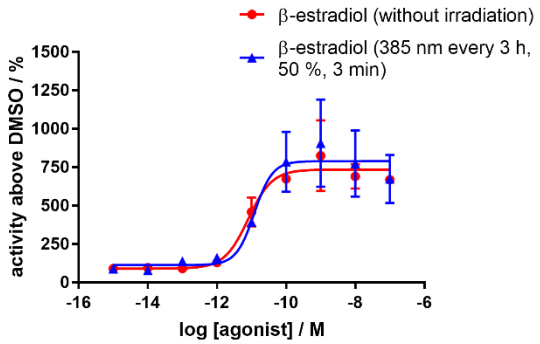
Supplementary figure 60. Estrogenic activities of hydroxy diazcoines **1** and **3** in a cell-based reporter gene assay after one-time irradiation of the compounds before addition to the cell assay. (**a**) Diazocine **1**, unirradiated (*Z*-**1**, dark, red circles) *vs*. one-time irradiated at 405 nm (PSS 405 nm, blue triangles). (**b**) Diazocine **3**, unirradiated (*Z*-**3**, dark, red circles) *vs*. one-time irradiated at 405 nm (PSS 405 nm, blue triangles). Representative for all hydroxy diazocines **1-7** no increase in estrogenic activity could be detected after only one-time irradiation. Data points are means of technical triplicates ± SD.



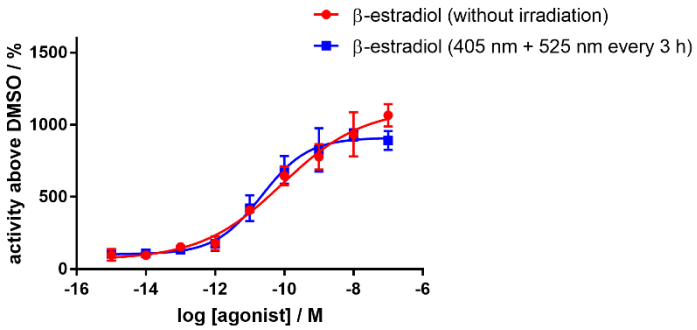
Supplementary figure 61. Irradiation tolerance of the cell-based reporter gene assay. Estrogenic activity of reference β-estradiol with and without irradiation. β-Estradiol, unirradiated (red circles, EC_{50} = 19.8 pM) *vs*. irradiated at 405 nm every 3 h with 50 % power for 1 min (blue triangles, EC_{50} = 21.0 pM). Dose-response curves are one representative example from at least two independent cell assays. Data points are means of technical triplicates ± SD.



Supplementary figure 62. Irradiation tolerance of the cell-based reporter gene assay. Estrogenic activity of reference β-estradiol with and without irradiation. (**a**) β-Estradiol, unirradiated (red circles, EC_{50} = 15.1 pM) *vs*. irradiated at 405 nm every 30 min with 50 % power for 1 min (blue triangles, EC_{50} = 37.2 pM). (**b**) β-Estradiol, unirradiated (red circles, EC_{50} = 16.3 pM) *vs*. irradiated at 405 nm every 30 min with 25 % power for 3 min (blue triangles, EC_{50} = 28.5 pM). Irradiation at 405 nm every 30 min was only tolerated by the cell assay when the irradiation was performed with an intensity of 25 % for 3 min each (b). Irradiation at 405 nm with 50 % power for 1 min every 30 min was not tolerated (see clearly flatter blue curve in a). Data points are means of technical triplicates ± SD.

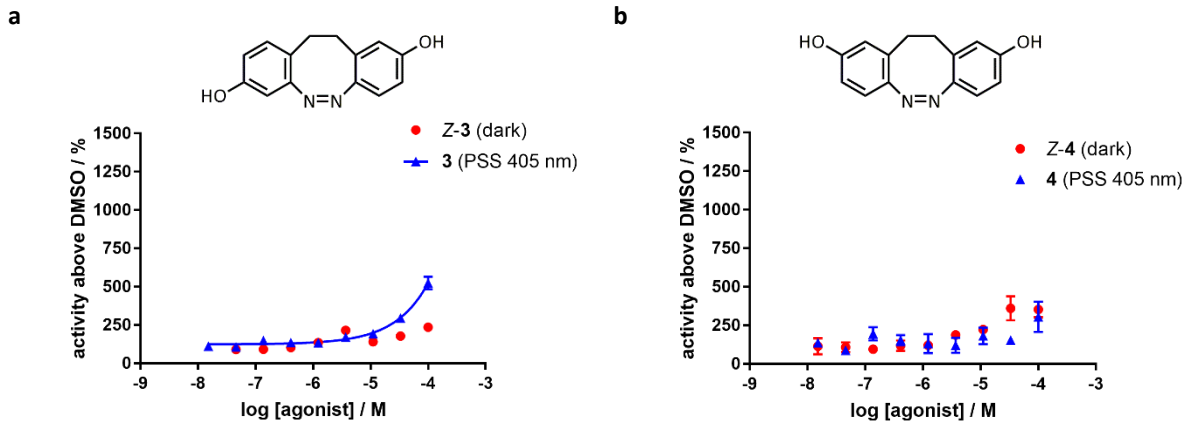


Supplementary figure 63. Irradiation tolerance of the cell-based reporter gene assay. Estrogenic activity of reference β-estradiol with and without irradiation. β-Estradiol, unirradiated (red circles, EC_{50} = 8.06 pM) *vs*. irradiated at 385 nm every 3 h with 50 % power for 3 min (blue triangles, EC_{50} = 12.1 pM). Dose-response curves are one representative example from at least two independent cell assays. Data points are means of technical triplicates ± SD.

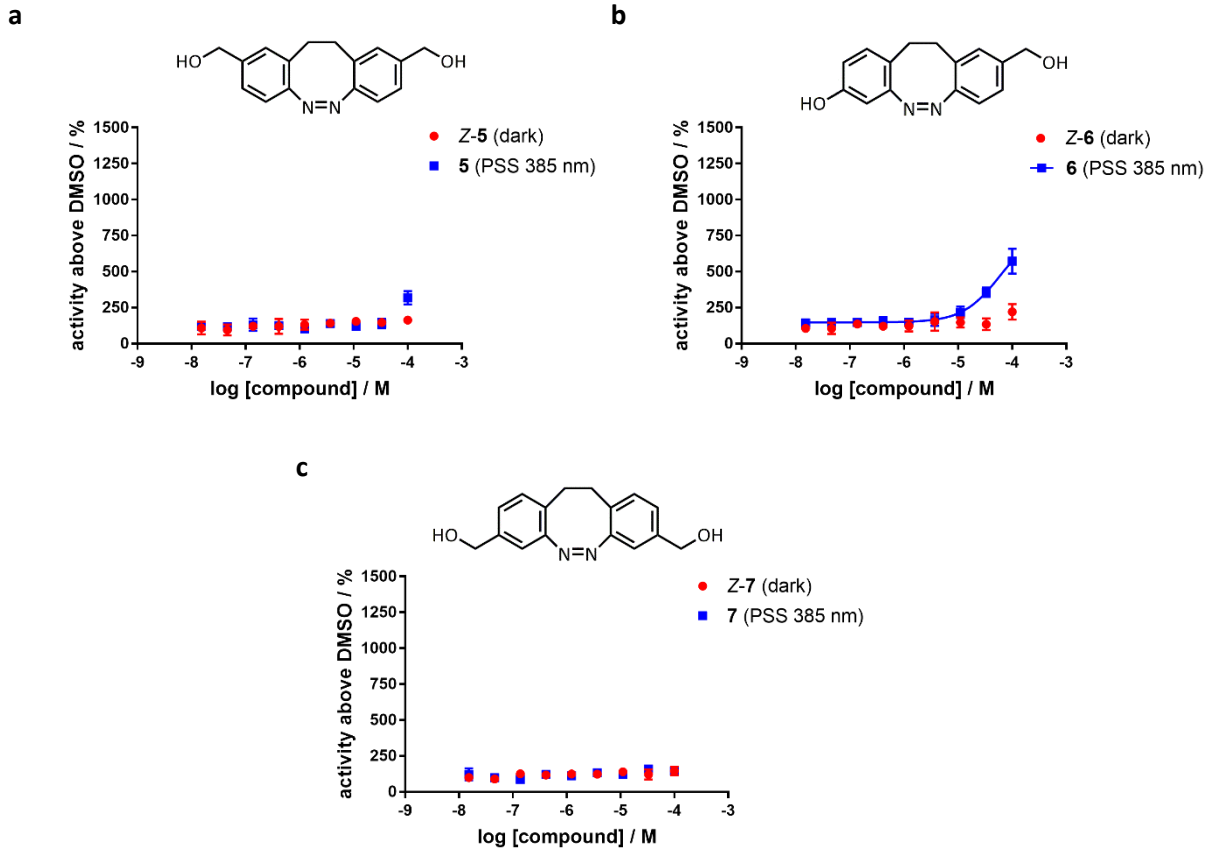


Supplementary figure 64. Irradiation tolerance of the cell-based reporter gene assay. Estrogenic activity of reference β-estradiol with and without irradiation. β-Estradiol, unirradiated (red circles,

EC_{50} = 85.9 pM) *vs*. irradiated at 405 nm and 525 nm every 3 h (blue squares, EC_{50} = 21.9 pM). Data points are means of technical triplicates ± SD.

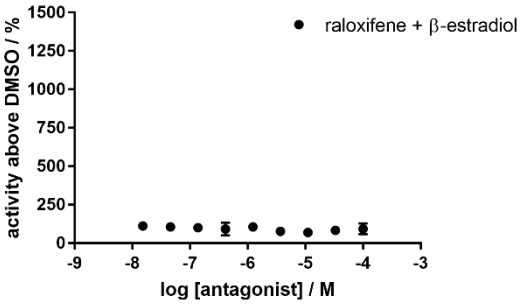


Supplementary figure 65. Estrogenic activities of diazocines **3** and **4** in a cell-based reporter gene assay after irradiation every 30 min. (**a**) Diazocine **3**, unirradiated (*Z*-**3**, dark, red circles, max. relative activity: 23.3 %) *vs*. irradiated at 405 nm every 30 min (PSS 405 nm, blue triangles, EC_{50} cannot be determined reliably, max. relative activity: 51.7 %). (**b**) Diazocine **4**, unirradiated (*Z*-**4**, dark, red circles) *vs*. irradiated at 405 nm every 30 min (PSS 405 nm, blue triangles). Data points are means of technical triplicates ± SD.

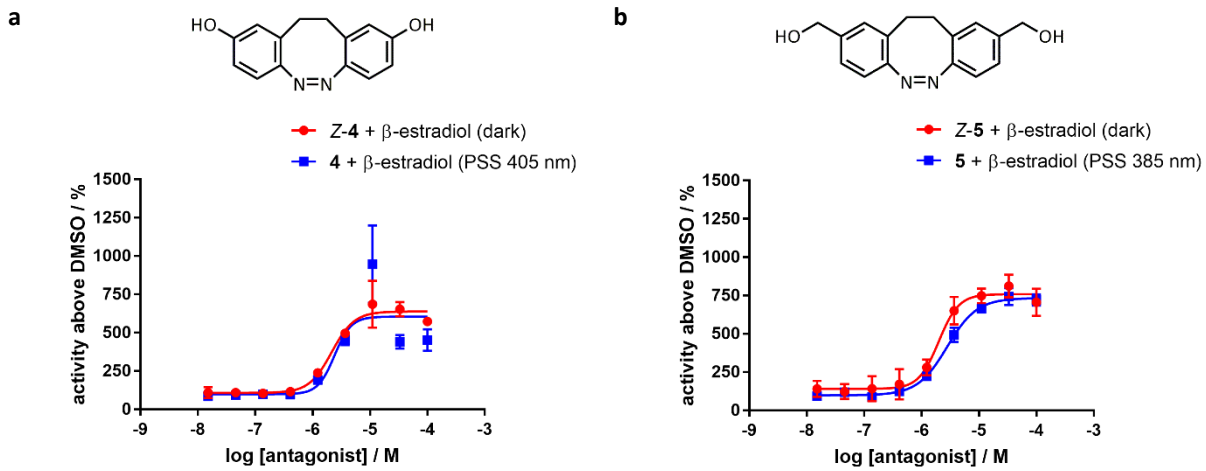


Supplementary figure 66. Estrogenic activities of benzyl alcohol diazocines **5**, **6** and **7** in a cell-based reporter gene assay. (**a**) *para*-disubstituted diazocine **5**, unirradiated (dark, red circles) *vs.* irradiated at 385 nm every 3 h (PSS 385 nm, blue squares). (**b**) Asymmetrical diazocine **6**, unirradiated (dark, red circles) *vs.* irradiated at 385 nm every 3 h (PSS 385 nm, blue squares, EC_{50} cannot be determined

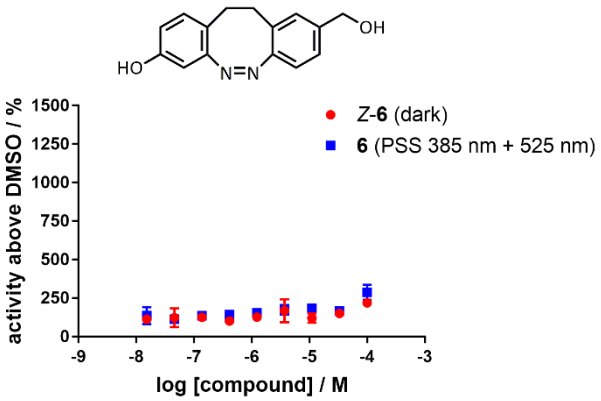
reliably). (**c**) *meta*-Disubstituted diazocine **7**, unirradiated (dark, red circles) *vs.* irradiated at 385 nm every 3 h (PSS 385 nm, blue squares). Dose-response curves are one representative example from three independent cell assays. Data points are means of technical triplicates ± SD.



Supplementary figure 67. Antiestrogenic activity of reference antagonist raloxifene in a cell-based reporter gene assay. Raloxifene was used together with the reference agonist β-estradiol. The estrogenic activity of β-estradiol is completely extinguished by raloxifene. Dose-response curves are one representative example from at least two independent cell assays. Data points are means of technical triplicates ± SD.



Supplementary figure 68. Antiestrogenic activity of *para*-substituted diazocines **4** and **5** in a cell-based reporter gene assay. (**a**) Diazocine **4** with β-estradiol, unirradiated (*Z*-**4**, dark, red circles) *vs*. irradiated at 405 nm every 3 h (PSS 405 nm, blue triangles). (**b**) Diazocine **5** with β-estradiol, unirradiated (*Z*-**5**, dark, red circles) *vs*. irradiated at 385 nm every 3 h (PSS 385 nm, blue triangles). Both diazocines are not able to reduce the estrogenic activity of β-estradiol. Data points are means of technical triplicates ± SD.

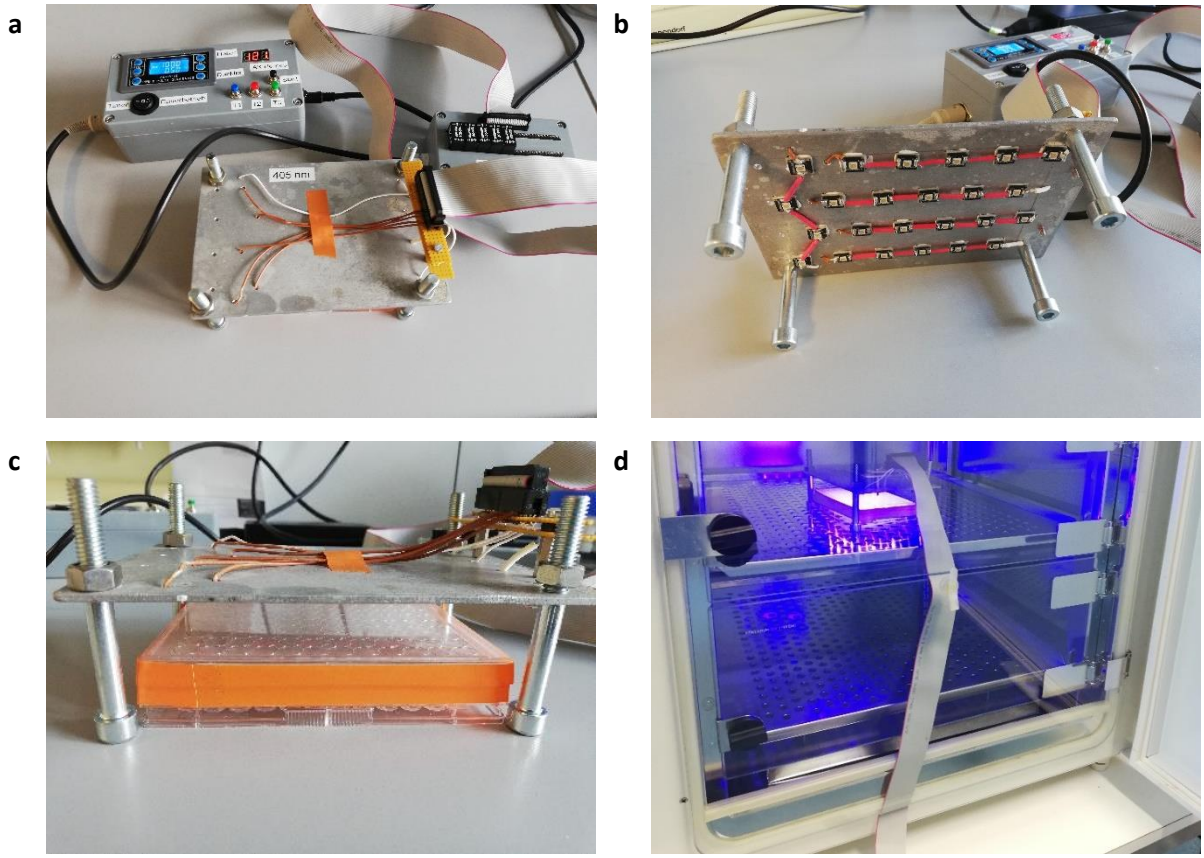


Supplementary figure 69. Estrogenic activities of diazocine **6** during an irradiation scheme including photochemically enforced back-isomerization with 525 nm (green light) in a cell-based reporter gene assay. Diazocine **6**, unirradiated (*Z*-**6**, dark, red circles) *vs*. irradiated at 385 nm and 525 nm (approx. 10 min later) every 3 h (PSS 385 nm + 525 nm, blue squares). Dose-response curves are one representative example from two independent cell assays. Data points are means of technical triplicates ± SD.

7. Properties and characterization of the cell incubator lamps

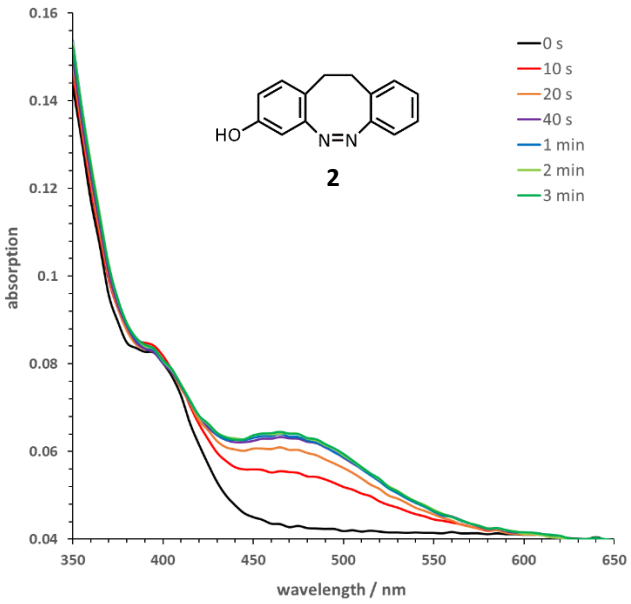
For irradiation of the cell assay inside the cell incubator a custom-made lamp was used. The set-up of both lamps (405 nm and 385 nm) is analogous and shown in supplementary figure 64. 24 LEDs (Nichia NCSU275(T)-U405, 370 mW and U385, 350 mW, respectively) are fixed with regular spacing from below on a plate that can be placed over a microtiter plate. A ribbon cable allows the cable to pass through the door seals of the cell incubator. Irradiation cycles as well as irradiation intensity can be adjusted via a connected, programmable timer. A double lid with diffuser foil in between was used for the microtiter plates to distribute the light as evenly as possible.

To determine the required intensity and duration of irradiation to switch the diazocines into the PSS, UV/Vis-spectra of the diazocines were recorded after irradiation with different parameters. Therefore, conditions as similar as possible to the cell assay were chosen. Diazocine solutions were placed in a 96-well plate with a concentration of 200 µM in ddH_2O containing 2 % DMSO and a volume of 110 µl per well. Exemplary for hydroxy diazocines **1-4**, diazocine **2** was irradiated at 405 nm. On the one hand irradiation was performed with 50 % power for 0 s, 10 s, 20 s, 40 s, 1 min, 2 min and 3 min and on the other hand with 25 % power for 0 s, 1 min, 2 min, 3 min and 5 min. Exemplary for benzyl alcohol diazocines **5-7**, diazocine **5** was irradiated at 385 nm. Irradiation was performed with 50 % power for 0 s, 1 min, 2 min, 3 min and 5 min. After each irradiation period, 100 µl of the compound solution was transferred to a new 96-well plate for subsequent absorbance measurement. The entire procedure took place under controlled light conditions. UV/Vis-spectra were measured in the range of 350 nm - 650 nm on a TECAN Spark® microplate reader (Tecan, Männedorf, Switzerland).



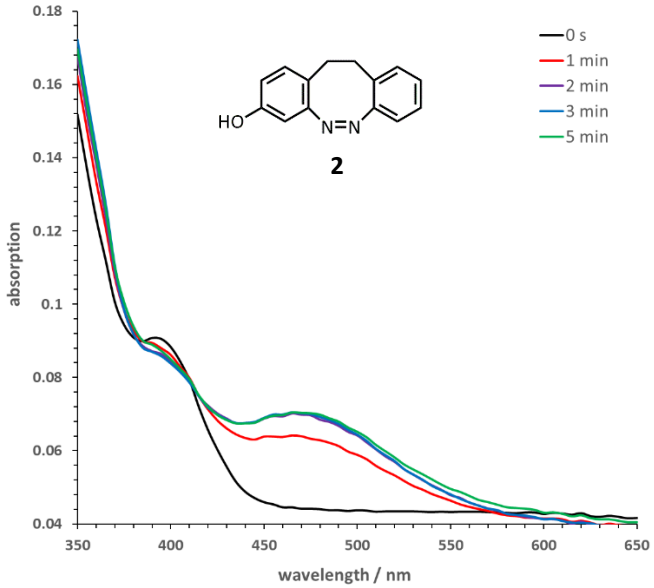
Supplementary figure 70. Set-up of the cell incubator lamp. (**a**) Overview of irradiation unit, ribbon cable and control element with timer. (**b**) LEDs on the underside of the irradiation unit plate. (**c**) The irradiation unit stands above a 96-well plate, which is used for the cell assays. A diffuser foil is integrated in the double lid of the 96-well plate. (**d**) Irradiation of the cell assay plate in the cell incubator. A ribbon cable allows the cable to pass through the door seals.

UV/Vis-spectra

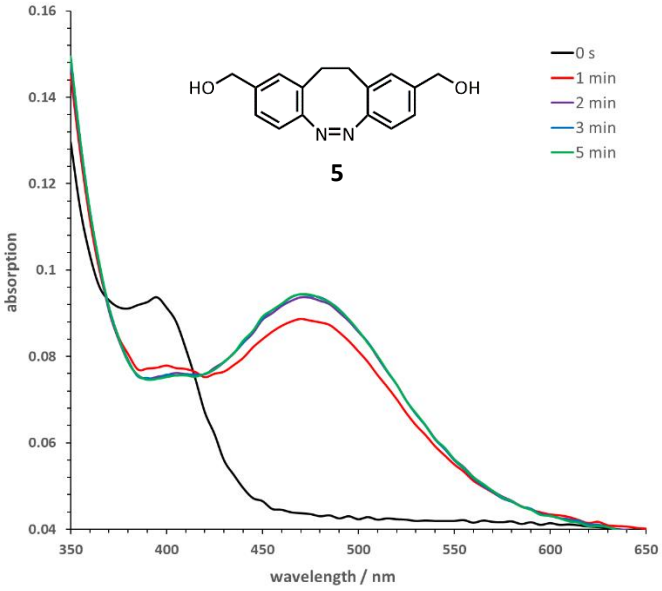


Supplementary figure 71. UV/Vis-spectra of hydroxy diazocine **2** (200 µM in ddH_2O with 2 % DMSO) after irradiation using the 405 nm cell incubator lamp under conditions similar to the cell assay. UV/Vis-spectra were recorded after 0 s, 10 s, 20 s, 40 s, 1 min, 2 min and 3 min irradiation with 50 % power.

An irradiation time of 1 min in the described set-up with 50 % power was determined to be sufficient for switching the diazocine into the PSS.



Supplementary figure 72. UV/Vis-spectra of hydroxy diazocine **2** (200 µM in ddH_2O with 2 % DMSO) after irradiation using the 405 nm cell incubator lamp under conditions similar to the cell assay. UV/Vis-spectra were recorded after 0 s, 1 min, 2 min, 3 min and 5 min irradiation with 25 % power. An irradiation time of 3 min in the described set-up with 25 % power was determined to be sufficient for switching the diazocine into the PSS.



Supplementary figure 73. UV/Vis-spectra of benzyl alcohol diazocine **5** (200 µM in ddH_2O with 2 % DMSO) after irradiation using the 385 nm cell incubator lamp under conditions similar to the cell assay. UV/VIS-spectra were recorded after 0 s, 1 min, 2 min, 3 min and 5 min irradiation with 50 % power. An irradiation time of 3 min in the described set-up with 50 % power was determined to be sufficient for switching the diazocine into the PSS.

8. Computational Details

8.1 Calculation mechanism studies of the thermal *E*-*Z* isomerization of 3 and 4

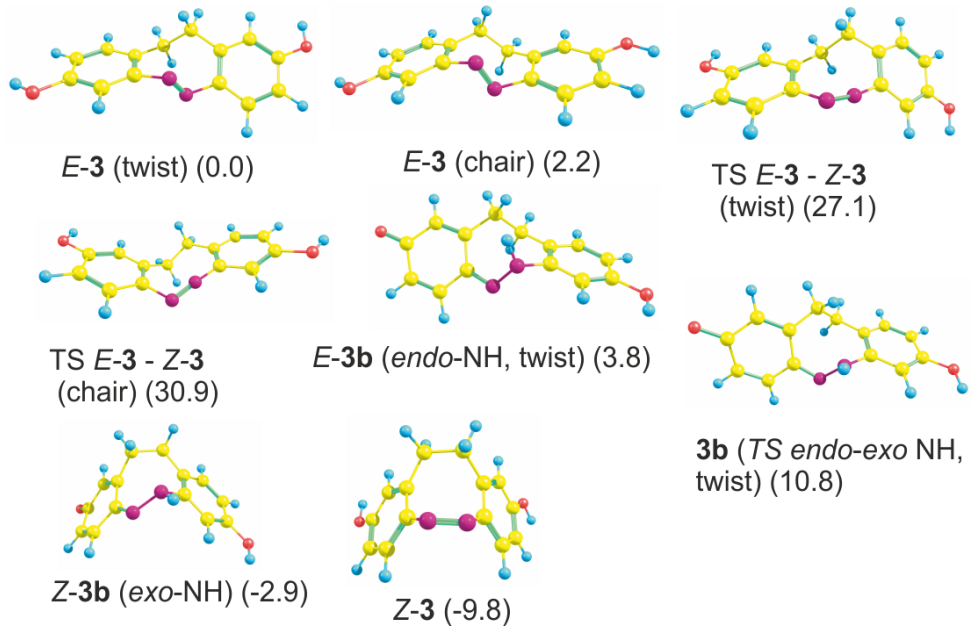
All geometry optimizations and frequency calculations were performed employing Gaussian09 Rev. E.01.[12] Geometry optimizations were generally performed at the M06-2X/cc-pVTZ[13,14] level of theory. All stationary points were characterized as minima or transition structures by performing a vibrational analysis. Single point energy calculations at the DLPNO-CCSD(T)/cc-pVTZ(cc-pVTZ(C))//M06-2X/cc-pVTZ level of theory were performed employing ORCA 4.2.1.[15–17] In these DLPNO-CCSD(T) single point energy calculations, the influence of solvation by DMSO was accounted for employing the CPCM method.[18]

Calculations on the *E*-dihydroxydiazocine **3** gave two possible conformations of the eight-membered ring, twist and chair. The twist conformer was found to be lower in energy (by ca. 2.2 kcal mol-1) than the chair conformer. The electronic energies of the TS (linear C-N-N unit, inversion at N) for direct *E*-*Z* interconversion of *E*-**3** were calculated to be substantial (for the twist conformer: 27.1 kcal mol-1), which is in agreement with the kinetics of the slow and direct isomerization process. A quinone hydrazone tautomer was calculated to be 6.7 kcal mol^{-1} higher in energy than *E*-**3** (*E*-**3b**, N-H endo) or roughly equal (*Z*-**3b**: +0.1 kcal mol^{-1}, N-H exo) to *E*-**3**. Flipping of the N-H proton from endo to exo position is coupled with rotation around the C-N(H)-N=C dihedral, thus resulting in the conversion from *E*-**3b** to *Z*-**3b**. The electronic energy for this N-H flipping is calculated (DLPNO-CCSD(T)) to be 10.8 kcal mol^{-1} (twist conformer). The resulting N-H (exo) quinone hydrazone **3**-exo intermediate assumes the boat conformation of the final *Z*-dihydroxydiazocine *Z*-**3**. The latter is predicted (DLPNO-CCSD(T)) to be lower in electronic energy than *E*-**3** by 9.8 kcal mol-1. At ambient temperature therefore formation of the quinone hydrazone tautomer **3b**, if it can be formed via a proton transfer reaction, appears to be a viable possibility for the rapid relaxation of *E*-**3** to *Z*-**3**, whereas direct *E*-**Z** interconversion suffers from a large barrier that would correspond to a lifetime of *E*-**3** of the order of days.

Figure 6 (main text) summarizes the results. To convert *E*-**3** into *Z*-**3**, the reaction has to go via a high-energy transition state TS *E*-**3**/*Z*-**3**. Alternatively, in a protic solvent where a solvent-mediated 1,7-H shift is feasible, the reaction can proceed via s-*E* quinone hydrazone *E*-**3b** and the transition state for the N-H exo-endo flip (TS *E*-**3b** / *Z*-**3b**) to s-Z-quinone hydra-zone *Z*-**3b**. The latter would then be converted into *Z*-**3** via another solvent-mediated 1,7-hydrogen shift.

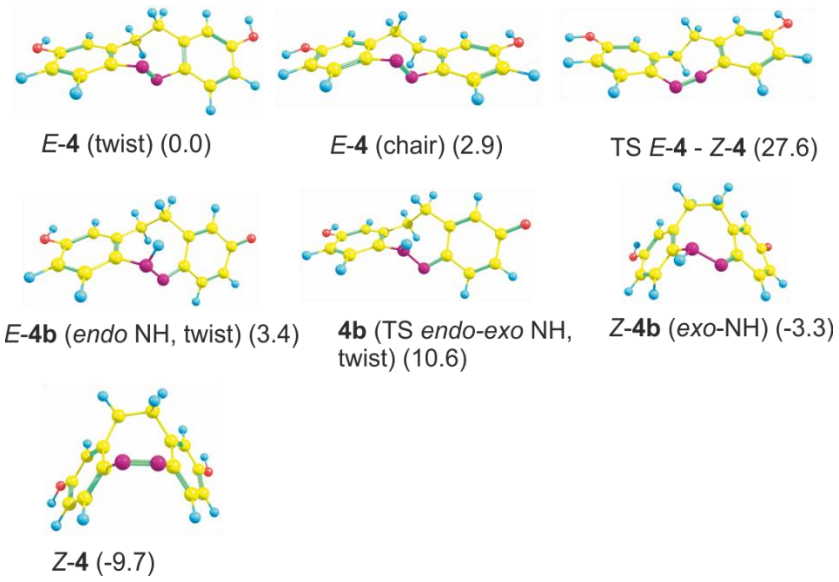
As mentioned above, the *E* dihydroxydiazocine *E*-**3** (asymmetric) has two possible conformations of the eight-membered ring, one twist conformer, and one chair conformer. Given that the presence of two hydroxy groups results in four different conformers for each conformer of the eight-membered ring, there are eight conformers of *E*-**3**. However, for the isolated molecules, the orientation of the hydroxy groups has almost no influence on the energy (differences are of the order of 0.0-0.3 kcal mol^{-1}, but typically 0.1 kcal mol^{-1}), so that this factor can likely be ignored (this also applies to *E*-**4**, see below). The chair conformer of *E*-**3** was calculated (DLPNO-CCSD(T)) to be 2.2-2.5 kcal mol^{-1} higher in energy than the twist conformer (reference value = 0.0 kcal mol^{-1}). The electronic energies of the TS (linear C-N-N unit) for direct *E*-*Z* interconversion of *E*-**3** were calculated to be substantial (for the twistboat conformer: 27.1 kcal mol^{-1} if the linear CNN unit was *meta* to a hydroxy group, and 28.8 kcal mol^{-1} if it was *para* to a hydroxy group; for the chair conformer: 30.9 kcal mol^{-1}). A quinone hydrazone tautomer *E*-**3b** was calculated to be 6.7 kcal mol^{-1} higher in energy than *E*-**3** (N-H *endo*) or roughly equal (+0.1 kcal mol^{-1}, N-H *exo*) to *E*-**3**. Flipping of the N-H proton from *endo* to *exo* position is coupled with rotation around the C-N(H)-N=C dihedral. The electronic energy for this N-H flipping is calculated (DLPNO-CCSD(T)) to be 16.9 kcal mol^{-1} (boat conformer) or 10.8 kcal mol^{-1} (twist conformer). The resulting N-H (*exo*) quinone hydrazone 3-*exo* intermediate therefore assumes the boat conformation

of the final *Z* dihydroxydiazocine *Z*-**3**. The latter is predicted (DLPNO-CCSD(T)) to be lower in electronic energy than *E*-**3** by 9.8 kcal mol^{-1}. At ambient temperature therefore formation of the quinone hydrazone tautomer *E*-**3b**, if it can be formed via a proton transfer reaction, appears to be a viable possibility for relaxation of *E*-**3** to *Z*-**3**, whereas direct *E*-*Z* interconversion suffers from a large barrier that would correspond to a lifetime of *E*-**3** of the order of tens of days (see below). Figure 74 summarizes the results on **3**.



Supplementary figure 74: Calculated structures (M06-2X/cc-pVTZ) of stationary points in the relaxation of **1** to **4**. In brackets: electronic energies [kcal mol^{-1}], calculated at the DLPNO-CCSD(T)(CPCM,DMSO)/cc-pVTZ//M06-2X/cc-pVTZ level of theory, relative to the lowest energy conformer of **1** = 0.0 kcal mol^{-1}.

Similar results were obtained with symmetric *E* dihydroxydiazocine *E*-**4**. Here, the chair conformer of *E*-**4** was calculated (DLPNO-CCSD(T)) to be 2.9 kcal mol^{-1} higher in energy than the twist conformer (reference value = 0.0 kcal mol^{-1}). The electronic energy of the transition state (linear C-N-N unit, twist conformation) for direct *E*-*Z* interconversion is 27.6 kcal mol^{-1}. Attempts to locate a TS from the chair conformer of *E*-**4** converged to the same TS with twist conformation. The electronic energy of its quinone hydrazone tautomer was higher than the lowest-energy conformer of *E*-**4** by 3.4 kcal mol^{-1} (*E*-**4b** NH *endo*, twist) or 7.0 kcal mol-1 (*E*-**4b** NH *endo*, chair), or lower in energy by 3.3 kcal mol^{-1} (*Z*-**4b** NH *exo*, twist) or 0.4 kcal mol^{-1} (*Z*-**4b** NH *exo*, chair). The TS for the exo-endo flip in **4b** is calculated (DLPNO-CCSD(T)) as 10.6 kcal mol^{-1} (twist) or 16.7 kcal mol^{-1} (chair) above *E*-**4**. As in the case of the isomeric quinone hydrazone **3b**, the *endo*-*exo* NH flip of **4b** is accompanied by a rotation around the central C-N(H)-N=C dihedral, converting the s-*E* conformation of the quinone hydrazone to the more stable s-*Z* conformation. This reaction therefore again constitutes a viable path for conversion of *E*-**4** into *Z*-diazocine *Z*-**4**, provided **4b** can be formed from *E*-**4** via proton transfer. The barrier for direct conversion of *E*-**4** into *Z*-**4**, on the other hand, is quite substantial. *Z*-Diazocine *Z*-**4** is calculated to be 9.7 kcal mol^{-1} lower in energy than *E*-**4**. Figure 75 summarizes the results on *E*-**4**.

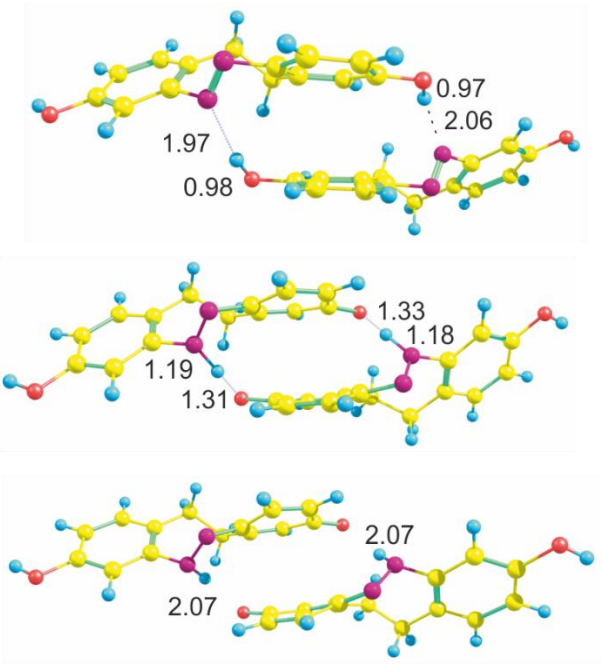


Supplementary figure 75: Calculated structures (M06-2X/cc-pVTZ) of stationary points in the relaxation of *E*-**4** to *Z*-**4**. In brackets: electronic energies [kcal mol^{-1}], calculated at the DLPNO-CCSD(T)(CPCM,DMSO)/cc-pVTZ//M06-2X/cc-pVTZ level of theory, relative to the lowest energy conformer of *E*-**4** = 0.0 kcal mol^{-1}.

$$k = K_B T/h \times \exp(-\Delta H^{\ddagger}/RT) \times \exp(\Delta S^{\ddagger}/R) \qquad \text{(equation SI 1)}$$

Entering the calculated (M06-2X/cc-pVTZ) enthalpies and entropies and of activation for the *trans* to *cis* isomerization of *E*-**3** and *E*-**4** into the Eyring equation (eq. SI 1), the estimated lifetime of *E*-**3** is obtained as τ = 283 s, for *E*-**4** τ = 632 s. However, compared to the coupled cluster single point energy calculations detailed above, the values obtained by DFT are significantly (by ca. 5 kcal mol^{-1}) smaller (electronic energy of activation: $\Delta U^{\ddagger}$ = 21.5 kcal mol^{-1} for **1**, 22.4 kcal mol^{-1} for **2**). Entering the larger electronic energies of activation obtained by DLPNO-CCSD(T), corrected for the difference between electronic energy and enthalpy of activation as obtained by M06-2X/cc-pVTZ, into the Eyring equation,[1] the lifetime of **1** is obtained as τ = 42 d, for **2**: τ = 58 d. If the DLPNO-CCSD(T) energies of activation are assumed to be accurate, the conclusion therefore has to be that the direct *E*-*Z* isomerization should be considerably slower than the reaction kinetic observed experimentally, and that another mechanism has to be operational.

Experimental evidence indicated a higher order decay for *E* dihydroxydibenzodiazocines *E*-**3** in DMSO solution. We therefore also investigated a mechanism involving tautomerization of **3** and **4** into the quinone hydrazone tautomers **3b** and **4b**, via a concerted twofold hydrogen transfer via hydrogen-bonded π-dimers of *E*-**3** and *E*-**4**. Figure 76 shows the π-dimer of asymmetric *E*-dihydroxydibenzodiazocine *E*-**3**, the transition state for concerted twofold hydrogen transfer, and the π-dimer of the quinone hydrazone tautomer *E*-**3b** (NH *endo*). The twist conformers of the eight-membered ring again are more stable in the π-dimer than the chair conformers (for *E*-**3**, by 4.9 kcal mol^{-1}, corresponding to roughly twice the energy difference of the monomer). For that reason, the following discussion will focus on the twist conformers only. All energy values are based on DLPNO-CCSD(T)/cc-pVTZ(C)(CPCM, DMSO)//M06-2X/cc-pVTZ single point energy calculations.



Supplementary figure 76: Top: π-dimer of *E* dihydroxydiazocine *E*-**3** (twist). Middle: transition state for concerted twofold hydrogen transfer. Bottom: π-dimer of quinone hydrazone tautomer *E*-**3b** (NH *endo*). All geometries M06-2X/cc-pVTZ. Distances in Å.

Dimer formation is significantly exothermic (ΔU_{dim} = -11.7 kcal mol^{-1} for *E*-**3** and -12.1 kcal mol^{-1} for *E*-**4**). The barrier of the twofold hydrogen atom transfer is moderate (*E*-**3** → *E*-**3b**: $\Delta U^{‡}$ = 14.5 kcal mol^{-1}, *E*-**4** → *E*-**4b**: $\Delta U^{‡}$ = 12.9 kcal mol^{-1}), both values are relative to the free solvated monomers). Relative to the free solvated monomers, the reaction is slightly exothermic, with ΔU_H = -2.6 kcal mol^{-1} for *E*-**3** → *E*-**3b**, and ΔU_H = -3.7 kcal mol^{-1} for *E*-**4** → *E*-**4b**.

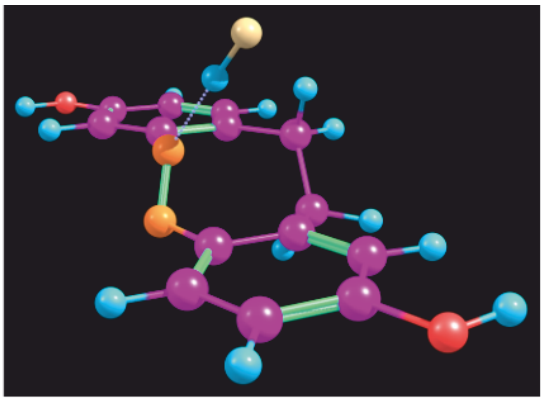
The calculated (M06-2X/cc-pVTZ) enthalpies and entropies of activation, entered into the Eyring equation (eq. 1), translate into a lifetime at *T* = 298 K of τ = 14.8 min for *E*-**3**. Given that the barriers calculated at coupled cluster level are somewhat higher than the DFT barriers, the lifetimes could also be slightly longer (τ = 59 min for *E*-**3**).[2] The twofold hydrogen transfer reaction results in formation of a quinone hydrazone conformer *E*-**3b** retaining an s-*E* stereochemistry around the newly formed N-N bond. Inversion of the N-H proton results in a huge change of molecular geometry en route to *Z*-**3b**, which is reflected in a very long reaction coordinate (c.f. Figure 79). The tweezer shape of *Z*-**3b** is similar to the shape of *Z*-**3**, and it does not lend itself to formation of a doubly hydrogen-bonded π-dimer. Hence, the tautomerization of *Z*-**3b** back to *Z*-**3** needs to proceed via non-concerted intermolecular hydrogen transfer, presumably involving ion pairs.

1) For *E*-**3** and *E*-**4**, the enthalpy of activation (M06-2X/cc-pVTZ) is smaller than the electronic energy of activation (same level of theory) by 1.0 or 1.1 kcal mol^{-1}. Hence, instead of the calculated (DLPNO-CCSD(T)) electronic energies of activation (27.1 or 27.6 kcal mol^{-1}), we used the corrected values 26.1 and 26.5 kcal mol^{-1}, respectively, for *E*-**3** and *E*-**4**.
2) At the M06-2X/cc-pVTZ level of theory, the calculated electronic energy activation for the twofold H-transfer in the π-dimer of twist-*E*-**3** is $\Delta U^{‡}$ = 25.4 kcal mol^{-1}. At the same level of theory, the calculated enthalpy of activation is $\Delta H^{‡}$ = 19.9 kcal mol^{-1}, resulting in a correction of 5.5 kcal mol^{-1}. Applied to the value obtained by DLPNO-CCSD(T) ($\Delta U^{‡}$ = 26.2 kcal mol^{-1}), a

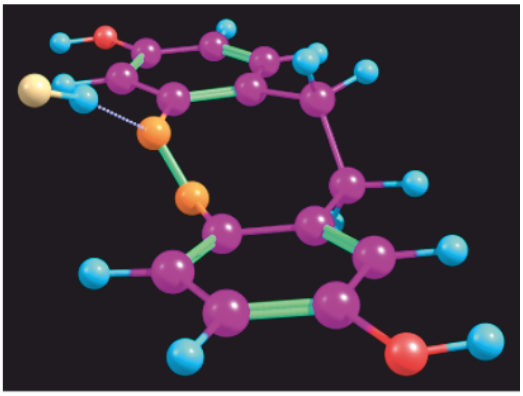
corrected value of 20.7 kcal mol^{-1} ensues. Entered into eq. 1, along with the entropy of activation as calculated by DFT, a value of τ = 59 min results.

A plot of the HOMO of *E*-**3** and an electrostatic potential map (electrostatic potential mapped onto an electron density isosurface) clearly indicate that the electron density of the nitrogen lone pair accepting the incoming proton points inward, resulting in a preference for *endo* protonation (Figure 77, see SI). This is in agreement with the fact that an acid-base complex of *E*-**3** (chair conformer) with one molecule of hydrogen fluoride as a model acid hydrogen-bonded to the nitrogen accepting the proton is significantly (2.0 kcal mol^{-1}, DLPNO-CCSD(T)) lower in energy when the HF molecule is in *endo* position than when it is bound *exo* (Figure 78, see SI). In case of the twist conformer of *E*-**3**, the *exo*-complex with HF is not even a minimum structure at the M06-2X/cc-pVTZ level of theory. Finally, an intrinsic reaction coordinate (IRC) calculation on the NH-flip of one of the conformers of *E*-**3b** indicates that the energy gradient in vicinity of the transition state is steeper when the NH is *endo* than when it is *exo* (see Figure 79). This also indicates a kinetic preference for *endo* protonation. Having a less steep gradient for the exothermic half of a reaction coordinate is unusual. It is due to the fact that the reaction initially proceeds towards a series of points on the reaction coordinate that resemble **E**-*3b* with an *exo*-NH proton. The latter, however, is not a minimum structure and only later on the reaction coordinate relaxes to the more stable *Z*-**3b**.

Supplementary figure 77: Left: Overlay of an electrostatic potential map (electrostatic potential mapped onto an electron isodensity surface) and the molecular structure of *E*-**3**. Red color in the electrostatic potential map indicates strong attraction to a positive probe charge. Calculated at the M06-2X/6-31G(d) level of theory. Right: HOMO of *E*-**3**, calculated at the M06-2X/cc-pVTZ level of theory.



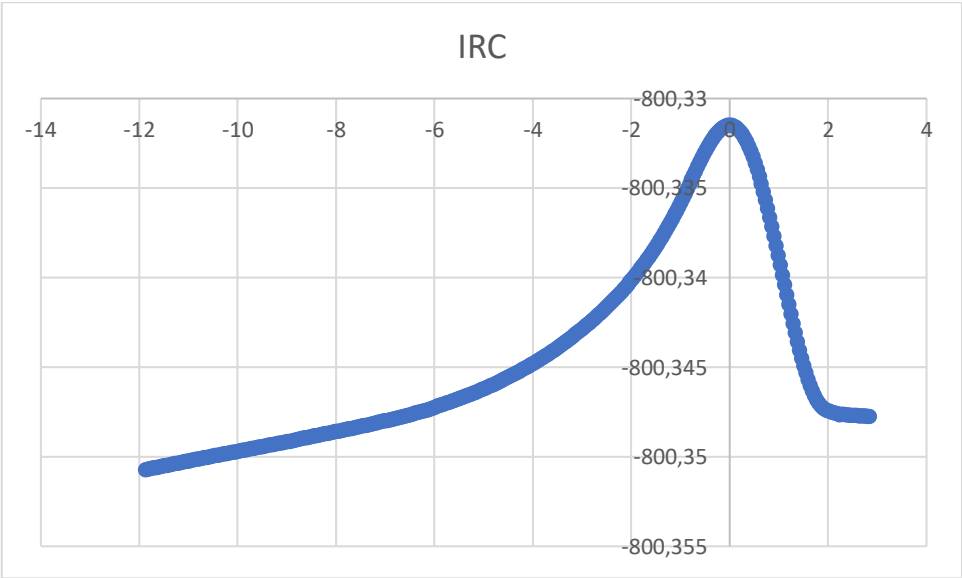
-899.588033



-899.584824

DLPNO-CCSD(T)/cc-pVTZ(DMSO)//M06-2X/cc-pVTZ

Supplementary figure 78: Left: hydrogen-bonded complex of *E*-**3** (chair) with HF (*endo*). Right: hydrogen-bonded complex of *E*-**3** (chair) with HF (*exo*). Optimized geometries (M06-2X/cc-pVTZ). The electronic energies (in Hartrees) given are single point energies at the DLPNO-CCSD(T)/cc-pVTZ (DMSO)//M06-2X/cc-pVTZ level of theory.



Supplementary figure 79: Intrinsic Reaction Coordinate (IRC) calculation (M06-2X/cc-pVDZ) on the NH-flip of *E*-**3b** (chair). Positive values of the reaction coordinate correspond to an *endo* NH proton, negative values to an *exo* NH proton. Energies in Hartrees.

Cartesian coordinates (in Å) and electronic energies (in Hartrees) of stationary points optimized
Note: all minimum structures have been calculated to have exactly zero imaginary frequencies, and all transition structures optimized have been calculated to have exactly one imaginary frequency.

E-Diazocine *E*-**3**, chair conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	-3.379590000	1.990077000	0.082422000
6	-3.144021000	0.930953000	0.079924000
6	-2.594309000	-1.787444000	0.151158000
6	-1.826753000	0.523010000	0.245813000
6	-4.170208000	0.002867000	-0.071136000
6	-3.899738000	-1.357756000	-0.027111000
6	-1.580930000	-0.856873000	0.253874000
1	-4.715503000	-2.057967000	-0.134268000
1	-2.361260000	-2.842475000	0.187409000
6	-0.734158000	1.539625000	0.568540000
1	-0.311917000	1.274757000	1.540907000
1	-1.239638000	2.495797000	0.704377000
6	0.449422000	1.789567000	-0.420406000
1	0.707378000	2.846323000	-0.345560000
1	0.090405000	1.624368000	-1.438109000
7	-0.189470000	-1.141164000	0.450662000
7	0.425149000	-0.835952000	-0.574470000
6	1.753882000	-0.384416000	-0.320795000
6	4.134920000	0.890204000	0.137433000
6	1.739956000	1.010402000	-0.219309000
6	2.895725000	-1.146775000	-0.214337000
6	4.102802000	-0.492042000	0.017163000
6	2.962603000	1.623708000	0.020605000
1	2.845200000	-2.225085000	-0.297068000
1	3.003775000	2.702111000	0.113384000
1	5.084361000	1.372847000	0.318990000
8	5.278799000	-1.164507000	0.140194000
1	5.125063000	-2.107589000	0.041797000
8	-5.467228000	0.379324000	-0.246763000
1	-5.525751000	1.337933000	-0.263571000

E(M06-2X): -800.5601168
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228603057762

E-Diazocine *E*-**3**, chair conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	-3.381797000	1.994111000	0.081759000
6	-3.146952000	0.934799000	0.080677000
6	-2.597888000	-1.784067000	0.151922000
6	-1.830280000	0.525807000	0.248549000
6	-4.173237000	0.007014000	-0.071327000
6	-3.903020000	-1.353584000	-0.027684000
6	-1.584739000	-0.853731000	0.257519000
1	-4.718787000	-2.053565000	-0.136434000
1	-2.365111000	-2.839152000	0.187558000
6	-0.735365000	1.540400000	0.567559000
1	-0.314010000	1.279190000	1.541266000

1	-1.237214000	2.499301000	0.697690000
6	0.448491000	1.779435000	-0.423649000
1	0.708923000	2.836237000	-0.357653000
1	0.088442000	1.606872000	-1.439776000
7	-0.193260000	-1.135606000	0.457519000
7	0.423529000	-0.849580000	-0.571445000
6	1.753221000	-0.399561000	-0.319660000
6	4.130830000	0.874778000	0.133449000
6	1.737947000	0.999406000	-0.218923000
6	2.891263000	-1.162486000	-0.217147000
6	4.098716000	-0.506813000	0.012242000
6	2.957280000	1.612772000	0.018097000
1	2.862785000	-2.239157000	-0.298475000
1	3.000422000	2.691118000	0.109688000
1	5.073616000	1.376820000	0.313395000
8	5.213270000	-1.279261000	0.114569000
1	5.976555000	-0.721145000	0.284523000
8	-5.470173000	0.384014000	-0.248420000
1	-5.528088000	1.342634000	-0.264996000

E(M06-2X): -800.5602936
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228826248459

E-Diazocine *E*-**3**, chair conformer 3, optimized geometry (M06-2X/cc-pVTZ)

1	-3.396738000	2.006128000	0.072892000
6	-3.143236000	0.954058000	0.080124000
6	-2.594800000	-1.770014000	0.155901000
6	-1.832436000	0.541544000	0.254925000
6	-4.170117000	0.025908000	-0.074240000
6	-3.901417000	-1.333810000	-0.028559000
6	-1.585707000	-0.841243000	0.266874000
1	-4.705848000	-2.050717000	-0.138474000
1	-2.364789000	-2.825624000	0.191059000
6	-0.733176000	1.552289000	0.568395000
1	-0.312919000	1.296390000	1.543952000
1	-1.230948000	2.514111000	0.689459000
6	0.450561000	1.775137000	-0.426643000
1	0.715018000	2.831502000	-0.372372000
1	0.087785000	1.594456000	-1.440450000
7	-0.193555000	-1.116949000	0.471507000
7	0.424887000	-0.861104000	-0.564117000
6	1.754197000	-0.406096000	-0.315435000
6	4.132990000	0.869730000	0.127036000
6	1.738581000	0.993161000	-0.218654000
6	2.893019000	-1.168320000	-0.215506000
6	4.100892000	-0.512120000	0.009451000
6	2.959003000	1.606998000	0.012342000
1	2.864792000	-2.245159000	-0.294775000
1	3.002246000	2.685664000	0.099880000
1	5.076081000	1.372558000	0.303219000
8	5.215961000	-1.284209000	0.110950000
1	5.979357000	-0.725314000	0.277789000
8	-5.427708000	0.518872000	-0.251334000
1	-6.049509000	-0.208261000	-0.336891000

E(M06-2X): -800.5604904
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228959202558

E-Diazocine *E*-**3**, chair conformer 4, optimized geometry (M06-2X/cc-pVTZ)

1	-3.395603000	2.002053000	0.072678000
6	-3.141021000	0.950252000	0.079030000
6	-2.590843000	-1.773139000	0.155451000
6	-1.829577000	0.539273000	0.252675000
6	-4.167383000	0.021373000	-0.074673000
6	-3.897881000	-1.338234000	-0.028374000
6	-1.582037000	-0.843688000	0.264200000
1	-4.701921000	-2.055734000	-0.137105000
1	-2.360213000	-2.828612000	0.191382000
6	-0.732755000	1.552220000	0.569369000
1	-0.312085000	1.293725000	1.544094000
1	-1.233982000	2.511674000	0.694678000
6	0.451115000	1.784309000	-0.423446000
1	0.713333000	2.840749000	-0.361612000
1	0.089529000	1.609869000	-1.438770000
7	-0.189712000	-1.120393000	0.466849000
7	0.427104000	-0.849579000	-0.566272000
6	1.755141000	-0.391795000	-0.315622000
6	4.137061000	0.885664000	0.130374000
6	1.740209000	1.003332000	-0.218293000
6	2.898322000	-1.152746000	-0.212641000
6	4.105619000	-0.496844000	0.013772000
6	2.963833000	1.617747000	0.014678000
1	2.848709000	-2.231261000	-0.293445000
1	3.004600000	2.696522000	0.103071000
1	5.086620000	1.369666000	0.307665000
8	5.282481000	-1.168434000	0.134922000
1	5.128863000	-2.111740000	0.038740000
8	-5.425158000	0.513477000	-0.251066000
1	-6.046991000	-0.213797000	-0.335268000

E(M06-2X): -800.5602512
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228744021964

E-Diazocine *E*-**3**, twist conformer 1, optimized geometry (M06-2X/cc-pVTZ)

6	4.144408000	-0.467362000	-0.195165000
6	2.933219000	-1.113643000	-0.411662000
6	1.766383000	-0.434228000	-0.135049000
6	4.160342000	0.847718000	0.249708000
6	2.965265000	1.516383000	0.483980000
6	1.736356000	0.898918000	0.305659000
6	0.428215000	1.639307000	0.568096000
6	-1.838412000	0.511361000	-0.213592000
6	-1.604269000	-0.780460000	0.278786000
6	-3.161913000	0.881635000	-0.419280000
6	-4.206617000	0.002172000	-0.156150000

6	-3.949152000	-1.262676000	0.358704000
6	-2.640951000	-1.640090000	0.598950000
7	0.461992000	-0.914437000	-0.431705000
7	-0.237078000	-1.037133000	0.580909000
1	2.917601000	-2.129508000	-0.778772000
1	5.106043000	1.353796000	0.401150000
1	2.996340000	2.546818000	0.816220000
1	0.039465000	1.354308000	1.547359000
1	0.684436000	2.696265000	0.642882000
1	-3.386198000	1.878678000	-0.783850000
1	-4.778472000	-1.921210000	0.572387000
1	-2.414173000	-2.610824000	1.017672000
6	-0.719572000	1.517748000	-0.480125000
1	-1.199910000	2.494477000	-0.542567000
1	-0.289303000	1.328652000	-1.464179000
8	-5.508209000	0.340994000	-0.362356000
1	-5.557386000	1.228988000	-0.725541000
8	5.280784000	-1.170851000	-0.447816000
1	6.046736000	-0.621291000	-0.262969000

E(M06-2X): -800.5645455
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232530394986

E-Diazocine *E*-**3**, twist conformer 2, optimized geometry (M06-2X/cc-pVTZ)

6	4.144975000	-0.475079000	-0.190752000
6	2.932526000	-1.119008000	-0.406532000
6	1.766923000	-0.435953000	-0.133289000
6	4.163358000	0.841410000	0.249766000
6	2.969595000	1.513692000	0.480250000
6	1.739149000	0.898786000	0.302905000
6	0.432925000	1.644619000	0.559984000
6	-1.837944000	0.522389000	-0.218745000
6	-1.605228000	-0.771946000	0.278131000
6	-3.155890000	0.897930000	-0.427042000
6	-4.203452000	0.021269000	-0.162030000
6	-3.949876000	-1.242758000	0.354178000
6	-2.640733000	-1.627650000	0.597616000
7	0.462235000	-0.916069000	-0.429552000
7	-0.238374000	-1.027974000	0.583097000
1	2.914787000	-2.135930000	-0.770627000
1	5.110041000	1.345907000	0.400456000
1	3.002761000	2.545322000	0.808496000
1	0.042606000	1.366570000	1.540608000
1	0.692410000	2.701113000	0.629339000
1	-3.397365000	1.886836000	-0.794332000
1	-4.769822000	-1.914983000	0.575105000
1	-2.418910000	-2.598641000	1.018178000
6	-0.713608000	1.521228000	-0.489295000
1	-1.190269000	2.498706000	-0.561010000
1	-0.282440000	1.321909000	-1.470969000
8	-5.464364000	0.469824000	-0.408999000
1	-6.100459000	-0.210811000	-0.174550000
8	5.280156000	-1.182098000	-0.439683000
1	6.046981000	-0.633069000	-0.256922000

E(M06-2X): -800.5646492
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232391964346

E-Diazocine *E*-**3**, twist conformer 3, optimized geometry (M06-2X/cc-pVTZ)

6	4.150889000	-0.458849000	-0.186052000
6	2.940512000	-1.105893000	-0.398850000
6	1.768196000	-0.427750000	-0.124366000
6	4.165534000	0.859202000	0.252648000
6	2.971064000	1.523711000	0.480934000
6	1.738191000	0.904562000	0.306177000
6	0.431448000	1.653062000	0.554357000
6	-1.836524000	0.520919000	-0.221673000
6	-1.602072000	-0.769968000	0.283200000
6	-3.154791000	0.892601000	-0.434318000
6	-4.201061000	0.015490000	-0.165441000
6	-3.945743000	-1.244833000	0.358923000
6	-2.636177000	-1.625801000	0.606615000
7	0.467880000	-0.919593000	-0.420870000
7	-0.234853000	-1.017678000	0.592281000
1	2.903771000	-2.125372000	-0.762080000
1	5.118068000	1.348807000	0.395680000
1	2.999537000	2.556624000	0.805801000
1	0.039529000	1.387583000	1.537743000
1	0.691619000	2.710088000	0.611285000
1	-3.397546000	1.878845000	-0.807857000
1	-4.764718000	-1.917167000	0.583057000
1	-2.413441000	-2.593626000	1.033934000
6	-0.712891000	1.519489000	-0.496008000
1	-1.190902000	2.495579000	-0.576561000
1	-0.278755000	1.313645000	-1.475113000
8	-5.462359000	0.460042000	-0.417089000
1	-6.097794000	-0.219632000	-0.178102000
8	5.349097000	-1.065619000	-0.402632000
1	5.206083000	-1.965518000	-0.706767000

E(M06-2X): -800.5646004
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232336615633

E-Diazocine *E*-**3**, twist conformer 4, optimized geometry (M06-2X/cc-pVTZ)

6	4.150254000	-0.451243000	-0.190523000
6	2.941102000	-1.100631000	-0.403819000
6	1.767637000	-0.426021000	-0.126017000
6	4.162529000	0.865517000	0.252169000
6	2.966822000	1.526511000	0.484240000
6	1.735461000	0.904764000	0.308855000
6	0.426818000	1.647839000	0.562668000
6	-1.836991000	0.510024000	-0.216209000
6	-1.601105000	-0.778417000	0.284003000
6	-3.160815000	0.876445000	-0.426287000
6	-4.204174000	-0.003581000	-0.159571000

6	-3.944943000	-1.264835000	0.363215000
6	-2.636370000	-1.638313000	0.607803000
7	0.467563000	-0.917813000	-0.422947000
7	-0.233567000	-1.026882000	0.590334000
1	2.906384000	-2.119141000	-0.769912000
1	5.114155000	1.356712000	0.395712000
1	2.993278000	2.558293000	0.812908000
1	0.036598000	1.375279000	1.544804000
1	0.683722000	2.705390000	0.625109000
1	-3.386369000	1.870899000	-0.797057000
1	-4.773331000	-1.923598000	0.579787000
1	-2.408668000	-2.605946000	1.033149000
6	-0.718915000	1.516243000	-0.486505000
1	-1.200674000	2.491645000	-0.557510000
1	-0.285841000	1.320843000	-1.468182000
8	-5.506066000	0.331144000	-0.369873000
1	-5.556861000	1.217567000	-0.736694000
8	5.349486000	-1.054454000	-0.410446000
1	5.208416000	-1.954405000	-0.715393000

E(M06-2X): -800.5645372
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232489130947

Transition state for direct conversion of *E*-**3** into *Z*-**3**, chair conformer, optimized geometry (M06-2X/cc-pVTZ)

6	3.876890000	-1.234415000	-0.460303000
6	2.704085000	-1.790686000	0.009563000
6	1.654191000	-0.981913000	0.420470000
6	4.007709000	0.150116000	-0.468393000
6	2.979913000	0.954581000	0.010334000
6	1.782176000	0.410110000	0.461126000
6	0.739565000	1.324766000	1.067179000
6	-1.675223000	1.030031000	0.089960000
6	-1.700627000	-0.377637000	0.190372000
6	-2.882302000	1.674462000	-0.148994000
6	-4.056626000	0.981570000	-0.392932000
6	-4.050584000	-0.409910000	-0.368124000
6	-2.892657000	-1.089027000	-0.038813000
7	0.439857000	-1.624096000	0.858485000
7	-0.563057000	-1.020608000	0.495493000
1	2.570394000	-2.863889000	0.045383000
1	3.125537000	2.029432000	0.056340000
1	0.298368000	0.849356000	1.944134000
1	1.274329000	2.203806000	1.429947000
1	-2.894524000	2.756522000	-0.201154000
1	-2.878620000	-2.167174000	0.054866000
6	-0.388376000	1.817866000	0.133525000
1	-0.644344000	2.839797000	0.415737000
1	0.010617000	1.877952000	-0.883528000
1	-4.979866000	1.496378000	-0.616746000
8	-5.223829000	-1.047324000	-0.632159000
1	-5.093011000	-1.997635000	-0.580018000
1	4.697897000	-1.842729000	-0.811457000
8	5.178500000	0.665654000	-0.927479000
1	5.149447000	1.624998000	-0.884073000

E(M06-2X): -800.5233539
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.183369437287

Transition state for direct conversion of *E*-**3** into *Z*-**3**, twist conformer, optimized geometry (M06-2X/cc-pVTZ)

6	-0.534382000	1.392691000	-0.261683000
1	0.033292000	1.106559000	-1.149128000
1	-0.931737000	2.386804000	-0.464328000
6	4.121169000	0.933659000	-0.015888000
6	2.980957000	1.538631000	0.503347000
6	1.779113000	0.867566000	0.591423000
6	1.752035000	-0.497697000	0.203664000
6	2.883011000	-1.120177000	-0.336702000
6	4.049665000	-0.383852000	-0.458219000
6	-1.725054000	0.468180000	-0.125922000
7	0.580863000	-1.104265000	0.381185000
7	-0.483768000	-1.523007000	0.796703000
6	-1.672814000	-0.860041000	0.323106000
6	-2.977597000	0.964657000	-0.466734000
6	-4.128555000	0.186016000	-0.390270000
6	-4.059567000	-1.122493000	0.071633000
6	-2.829846000	-1.621740000	0.443271000
1	3.022656000	2.578656000	0.804734000
1	2.858329000	-2.154425000	-0.643903000
1	-3.062689000	1.993154000	-0.801698000
1	-2.728837000	-2.625342000	0.834831000
6	0.460825000	1.495503000	0.936234000
1	0.619183000	2.544766000	1.181168000
1	0.013656000	1.033695000	1.820372000
1	5.048104000	1.485929000	-0.101344000
8	5.123481000	-1.021393000	-1.002824000
1	5.878756000	-0.428036000	-0.998013000
1	-4.964033000	-1.708941000	0.141632000
8	-5.347658000	0.666145000	-0.738663000
1	-5.266686000	1.574657000	-1.041214000

E(M06-2X): -800.5303136
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.189361516159

E-Diazocine quinone hydrazone tautomer *E*-**3b** (NH *endo*), chair conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	3.322119000	2.027576000	-0.098257000
6	3.044508000	0.982387000	-0.033033000
6	2.587136000	-1.767307000	-0.457206000
6	1.760366000	0.596800000	-0.072661000
6	4.182407000	0.035556000	-0.060879000
6	3.856869000	-1.361732000	-0.407448000
6	1.499789000	-0.868042000	-0.076719000
1	4.691998000	-2.025217000	-0.583489000
1	2.308504000	-2.795750000	-0.645312000
6	0.696949000	1.617327000	-0.483901000

1	0.300733000	1.268810000	-1.441744000
1	1.253907000	2.528497000	-0.698986000
6	-0.517817000	2.026682000	0.391151000
1	-0.802815000	3.030564000	0.077797000
1	-0.208634000	2.126757000	1.436182000
7	0.398617000	-1.438014000	0.276909000
7	-0.397699000	-0.649425000	1.082547000
6	-1.635031000	-0.216530000	0.547019000
6	-4.014816000	0.747711000	-0.456125000
6	-1.731403000	1.140219000	0.245613000
6	-2.684221000	-1.096356000	0.339762000
6	-3.877013000	-0.607777000	-0.174023000
6	-2.948178000	1.603789000	-0.245036000
1	-2.559641000	-2.143463000	0.585427000
1	-3.058412000	2.654343000	-0.483676000
8	5.324055000	0.411912000	0.104150000
1	0.120864000	0.132226000	1.463012000
1	-4.957107000	1.104909000	-0.845630000
8	-4.949381000	-1.409014000	-0.409152000
1	-4.732613000	-2.316721000	-0.180584000

E(M06-2X): -800.5503136
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.221905194908

E-Diazocine quinone hydrazone tautomer *E*-**3b** (NH *endo*), chair conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	3.317614000	2.032088000	-0.107670000
6	3.044842000	0.985888000	-0.038093000
6	2.599179000	-1.767543000	-0.449816000
6	1.762399000	0.594124000	-0.074799000
6	4.186975000	0.044211000	-0.063077000
6	3.867307000	-1.356041000	-0.401755000
6	1.507804000	-0.871416000	-0.075616000
1	4.705187000	-2.016956000	-0.574329000
1	2.325034000	-2.798078000	-0.633076000
6	0.693433000	1.608563000	-0.487263000
1	0.293574000	1.253122000	-1.441018000
1	1.246003000	2.520437000	-0.710422000
6	-0.518434000	2.019070000	0.391976000
1	-0.804147000	3.023292000	0.080261000
1	-0.205942000	2.118169000	1.436101000
7	0.405870000	-1.443111000	0.274484000
7	-0.391845000	-0.654334000	1.075371000
6	-1.634204000	-0.228987000	0.546542000
6	-4.015013000	0.735088000	-0.442629000
6	-1.732669000	1.132867000	0.249680000
6	-2.678040000	-1.110344000	0.340407000
6	-3.874222000	-0.620558000	-0.166418000
6	-2.947980000	1.596659000	-0.233915000
1	-2.571583000	-2.159695000	0.573509000
1	-3.061908000	2.647233000	-0.470344000
8	5.327204000	0.427201000	0.097966000
1	0.124445000	0.128297000	1.456374000
1	-4.954023000	1.112356000	-0.828617000
8	-4.880402000	-1.513381000	-0.360539000

1	-5.655102000	-1.058195000	-0.700505000

E(M06-2X): -800.5498962
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.221891244758

E-Diazocine quinone hydrazone tautomer *E*-**3b** (NH *endo*), twist conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	2.274614000	-2.395472000	1.396647000
6	2.591646000	-1.510195000	0.861339000
6	3.147372000	0.888944000	-0.498571000
6	1.536967000	-0.784069000	0.159433000
6	3.874873000	-1.165581000	0.738736000
6	4.257062000	0.024317000	-0.041965000
6	1.855656000	0.541468000	-0.415064000
1	4.679285000	-1.734259000	1.183849000
1	3.444305000	1.875330000	-0.834551000
7	0.386902000	-1.369984000	0.126457000
7	-0.486037000	-0.949128000	-0.850389000
6	-1.687951000	-0.344789000	-0.349077000
6	-4.012590000	0.823194000	0.556950000
6	-1.606230000	0.911011000	0.259864000
6	-2.888464000	-1.009015000	-0.510208000
6	-4.060844000	-0.425594000	-0.048057000
6	-2.797389000	1.475766000	0.700048000
1	-2.910996000	-1.976471000	-0.989970000
1	-2.777997000	2.451468000	1.169753000
1	-4.924798000	1.288252000	0.910989000
6	-0.298041000	1.643348000	0.478785000
1	0.156749000	1.293181000	1.409595000
1	-0.546370000	2.690969000	0.646022000
6	0.774168000	1.591132000	-0.636318000
1	1.292257000	2.549069000	-0.644750000
1	0.296516000	1.515825000	-1.615169000
8	-5.218106000	-1.115963000	-0.223112000
1	-5.953371000	-0.613741000	0.137726000
8	5.416179000	0.327745000	-0.238557000
1	-0.038244000	-0.364247000	-1.544628000

E(M06-2X): -800.5538824
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.226141679939

E-Diazocine quinone hydrazone tautomer *E*-**3b** (NH *endo*), twist conformer 2, optimized geometry (M06-2X/cc-pVTZ)

6	3.987994000	0.978597000	0.275030000
6	2.747105000	1.456086000	0.662482000
6	1.610428000	0.689773000	0.476233000
6	4.080148000	-0.284531000	-0.295442000
6	2.939050000	-1.058532000	-0.472979000
6	1.690851000	-0.583886000	-0.097010000
6	0.470243000	-1.447569000	-0.342048000
6	-1.819820000	-0.543893000	0.430939000
6	-1.616097000	0.786267000	-0.182808000
6	-3.071078000	-1.021689000	0.481318000

6	-4.244546000	-0.293114000	-0.047119000
6	-3.955564000	0.901735000	-0.859891000
6	-2.710410000	1.373109000	-0.950604000
7	0.335090000	1.191023000	0.895294000
7	-0.532260000	1.486435000	-0.131381000
1	2.642469000	2.433602000	1.111861000
1	3.049125000	-2.041212000	-0.912783000
1	0.027445000	-1.162626000	-1.300235000
1	0.823935000	-2.469683000	-0.469788000
1	-3.277757000	-2.021645000	0.843793000
1	-4.795913000	1.367316000	-1.355568000
1	-2.464796000	2.266644000	-1.509257000
6	-0.645111000	-1.465876000	0.731115000
1	-1.060673000	-2.472114000	0.759444000
1	-0.216019000	-1.305206000	1.721876000
8	-5.373580000	-0.707510000	0.120157000
1	4.878047000	1.578916000	0.417354000
8	5.262278000	-0.822523000	-0.694020000
1	5.975520000	-0.201899000	-0.522771000
1	-0.089939000	0.607108000	1.604277000

E(M06-2X): -800.5550568
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.226435354752

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**3b**, chair conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	3.264274000	2.055731000	-0.064457000
6	3.014333000	1.002332000	-0.025844000
6	2.658271000	-1.767855000	-0.486262000
6	1.746505000	0.579529000	-0.124260000
6	4.175790000	0.086277000	-0.007991000
6	3.908792000	-1.323404000	-0.377507000
6	1.535252000	-0.896920000	-0.122640000
1	4.773755000	-1.955775000	-0.522796000
1	2.415636000	-2.800759000	-0.697515000
6	0.658154000	1.554612000	-0.559908000
1	0.220218000	1.137682000	-1.471377000
1	1.194162000	2.452546000	-0.868626000
6	-0.510040000	2.005855000	0.355614000
1	-0.774697000	3.023146000	0.064736000
1	-0.160587000	2.058031000	1.387786000
7	0.449401000	-1.490530000	0.222071000
7	-0.345647000	-0.587433000	0.951786000
6	-1.627902000	-0.214180000	0.511040000
6	-4.048449000	0.759296000	-0.382648000
6	-1.745846000	1.147598000	0.238132000
6	-2.680970000	-1.095741000	0.316734000
6	-3.896281000	-0.601420000	-0.139641000
6	-2.979104000	1.620708000	-0.195395000
1	-2.542267000	-2.150752000	0.520034000
1	-3.104665000	2.674717000	-0.409827000
8	5.300561000	0.483854000	0.207960000
1	-0.113553000	-0.544989000	1.929663000

1	-5.006516000	1.118501000	-0.730746000
8	-4.975414000	-1.402326000	-0.356284000
1	-4.744242000	-2.314678000	-0.163838000

E(M06-2X): -800.5347321
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.205541399374

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**3b**, chair conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	3.261163000	2.059632000	-0.068961000
6	3.015041000	1.005399000	-0.028172000
6	2.668849000	-1.767220000	-0.482750000
6	1.748864000	0.577499000	-0.126046000
6	4.179703000	0.093529000	-0.007859000
6	3.917751000	-1.317980000	-0.373260000
6	1.542313000	-0.899399000	-0.123879000
1	4.785020000	-1.947859000	-0.515592000
1	2.429994000	-2.801465000	-0.691803000
6	0.656222000	1.547307000	-0.562825000
1	0.216524000	1.124841000	-1.470876000
1	1.188079000	2.445746000	-0.877300000
6	-0.510232000	1.998481000	0.355344000
1	-0.775402000	3.016357000	0.066726000
1	-0.158786000	2.048642000	1.386937000
7	0.455781000	-1.494681000	0.216389000
7	-0.339976000	-0.591945000	0.944396000
6	-1.626860000	-0.226109000	0.509270000
6	-4.047508000	0.745794000	-0.371669000
6	-1.746327000	1.140418000	0.239447000
6	-2.674319000	-1.109109000	0.318100000
6	-3.893171000	-0.614165000	-0.131737000
6	-2.977637000	1.613095000	-0.188222000
1	-2.554656000	-2.165503000	0.512224000
1	-3.106791000	2.666751000	-0.401867000
8	5.303114000	0.496140000	0.206694000
1	-0.107501000	-0.549503000	1.922290000
1	-5.002268000	1.124707000	-0.716505000
8	-4.904319000	-1.507853000	-0.308812000
1	-5.692515000	-1.047499000	-0.608269000

E(M06-2X): -800.5344648
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.205565478063

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**3b**, twist conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	2.465816000	-2.214630000	1.647516000
6	2.714939000	-1.387959000	0.995476000
6	3.087389000	0.880415000	-0.646373000
6	1.590624000	-0.755230000	0.303175000
6	3.970115000	-1.040050000	0.714094000
6	4.249835000	0.072620000	-0.219465000

6	1.819207000	0.523577000	-0.405045000
1	4.828803000	-1.544702000	1.134813000
1	3.329923000	1.834687000	-1.098311000
7	0.458164000	-1.360125000	0.406163000
7	-0.455369000	-0.972985000	-0.577408000
6	-1.676524000	-0.394458000	-0.222477000
6	-4.048709000	0.845757000	0.486412000
6	-1.624531000	0.857652000	0.396355000
6	-2.891219000	-1.006716000	-0.516139000
6	-4.078392000	-0.380459000	-0.168720000
6	-2.832405000	1.447026000	0.757975000
1	-2.893113000	-1.980930000	-0.990263000
1	-2.822265000	2.417824000	1.238194000
1	-4.983657000	1.315317000	0.756631000
6	-0.309619000	1.579142000	0.586901000
1	0.194091000	1.221173000	1.488942000
1	-0.538615000	2.628199000	0.770953000
6	0.678610000	1.503431000	-0.607051000
1	1.142090000	2.482080000	-0.730862000
1	0.130238000	1.298917000	-1.525084000
8	-5.297508000	-0.926393000	-0.427791000
1	-5.186435000	-1.773685000	-0.866599000
8	5.380748000	0.357779000	-0.552766000
1	-0.248278000	-1.272048000	-1.513471000

E(M06-2X): -800.5450277
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.215457117068

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**3b**, twist conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	2.483021000	-2.214927000	1.642602000
6	2.726219000	-1.385994000	0.991158000
6	3.084165000	0.886973000	-0.647752000
6	1.597194000	-0.755479000	0.305707000
6	3.979075000	-1.033624000	0.704064000
6	4.251153000	0.082131000	-0.227940000
6	1.818414000	0.524380000	-0.401836000
1	4.841300000	-1.536651000	1.119452000
1	3.321222000	1.843917000	-1.096955000
7	0.464260000	-1.359287000	0.415994000
7	-0.449195000	-0.979912000	-0.567975000
6	-1.675217000	-0.408122000	-0.219221000
6	-4.048464000	0.826372000	0.476900000
6	-1.626367000	0.844155000	0.408296000
6	-2.882265000	-1.018253000	-0.530409000
6	-4.072656000	-0.393341000	-0.188715000
6	-2.833215000	1.430604000	0.764050000
1	-2.901906000	-1.985371000	-1.012609000
1	-2.829196000	2.399191000	1.248642000
1	-4.977675000	1.311318000	0.750649000
6	-0.311823000	1.564928000	0.604858000
1	0.194479000	1.197405000	1.501345000
1	-0.540958000	2.611925000	0.800193000
6	0.672839000	1.501148000	-0.593342000

1	1.131896000	2.482460000	-0.712508000
1	0.121981000	1.300545000	-1.510812000
8	-5.231019000	-1.028289000	-0.514992000
1	-5.979281000	-0.515217000	-0.199234000
8	5.379869000	0.372639000	-0.564557000
1	-0.235443000	-1.270268000	-1.505413000

E(M06-2X): -800.5451121
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.215281322038

Z-Diazocine quinone hydrazone tautomer *Z*-**3b**, conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	-2.335716000	1.830102000	1.421007000
6	-2.320048000	0.903870000	0.858671000
6	-2.761137000	-1.313203000	-0.763962000
6	-1.461564000	0.743568000	-0.161973000
6	-3.388577000	-0.048741000	1.211844000
6	-3.623447000	-1.120240000	0.236059000
6	-1.518259000	-0.539739000	-0.900785000
1	-4.488451000	-1.750078000	0.389279000
1	-2.865710000	-2.135152000	-1.459343000
6	-0.734939000	1.982918000	-0.646221000
1	-0.556592000	2.616498000	0.223966000
1	-1.440178000	2.523230000	-1.283672000
6	0.573149000	1.801924000	-1.404412000
1	0.996395000	2.785628000	-1.607940000
1	0.389092000	1.319038000	-2.364770000
7	-0.653978000	-1.220227000	-1.582937000
7	0.662029000	-1.021180000	-1.695269000
6	1.518949000	-0.401760000	-0.739902000
6	3.299689000	0.750915000	1.032962000
6	1.533301000	0.981448000	-0.606785000
6	2.391207000	-1.208158000	-0.021036000
6	3.285975000	-0.629299000	0.866520000
6	2.426500000	1.537376000	0.299617000
1	2.376581000	-2.284160000	-0.130768000
1	2.453544000	2.613581000	0.418742000
8	-4.073206000	0.100046000	2.205825000
1	1.071490000	-1.840094000	-2.117356000
1	3.997710000	1.205649000	1.725139000
8	4.117596000	-1.461103000	1.546732000
1	4.665571000	-0.951217000	2.149117000

E(M06-2X): -800.5626014
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232350927692

Z-Diazocine quinone hydrazone tautomer *Z*-**3b**, conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	-2.331954000	1.756735000	1.508018000
6	-2.316332000	0.859917000	0.899910000
6	-2.757841000	-1.273319000	-0.831881000

6	-1.457310000	0.750752000	-0.127045000
6	-3.385338000	-0.109117000	1.204386000
6	-3.620968000	-1.129895000	0.175543000
6	-1.514064000	-0.495041000	-0.927892000
1	-4.487278000	-1.765030000	0.296033000
1	-2.862579000	-2.058938000	-1.568072000
6	-0.730867000	2.013008000	-0.549452000
1	-0.551154000	2.601838000	0.351313000
1	-1.437305000	2.584675000	-1.157529000
6	0.576233000	1.870896000	-1.318091000
1	0.997803000	2.863866000	-1.474393000
1	0.390963000	1.434682000	-2.300319000
7	-0.648948000	-1.141728000	-1.641092000
7	0.666952000	-0.933956000	-1.739785000
6	1.520079000	-0.357523000	-0.754801000
6	3.300766000	0.714586000	1.074049000
6	1.537500000	1.014591000	-0.560673000
6	2.390369000	-1.196694000	-0.063628000
6	3.282473000	-0.658747000	0.850804000
6	2.432434000	1.529360000	0.373402000
1	2.355322000	-2.266882000	-0.232930000
1	2.459371000	2.599579000	0.538224000
8	-4.069977000	-0.011122000	2.204493000
1	1.079829000	-1.724778000	-2.208979000
1	4.002666000	1.116914000	1.790235000
8	4.154947000	-1.421452000	1.560126000
1	4.035731000	-2.348927000	1.339795000

E(M06-2X): -800.5621813
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232283872020

Z-Diazocine *Z*-**3**, conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	2.144669000	1.078835000	-2.483633000
6	2.147626000	0.573912000	-1.525336000
6	2.197720000	-0.714702000	0.928497000
6	1.440405000	1.128376000	-0.468120000
6	2.855155000	-0.610456000	-1.383796000
6	2.875471000	-1.257637000	-0.154284000
6	1.474147000	0.450272000	0.750450000
1	3.399240000	-1.026687000	-2.222823000
1	2.240416000	-1.201264000	1.892599000
6	0.632668000	2.387283000	-0.590182000
1	0.736269000	2.970851000	0.323797000
6	-0.861294000	2.120129000	-0.870129000
1	-1.004042000	2.040208000	-1.947723000
1	-1.439157000	2.989654000	-0.547044000
7	0.857738000	1.054503000	1.900495000
7	-0.368037000	1.094820000	2.010281000
6	-1.222594000	0.433679000	1.047188000
6	-3.020489000	-0.968403000	-0.531721000
6	-1.903795000	-0.663887000	1.555681000
6	-1.465002000	0.877333000	-0.256516000
6	-2.369402000	0.151959000	-1.025301000
6	-2.787686000	-1.382376000	0.772106000
1	-2.581890000	0.457213000	-2.041391000

1	-3.297472000	-2.249361000	1.173787000
1	-1.725019000	-0.951286000	2.583080000
1	1.027036000	3.000309000	-1.400108000
8	3.554143000	-2.418242000	0.051779000
1	3.985951000	-2.687113000	-0.763152000
8	-3.879984000	-1.613271000	-1.366908000
1	-4.264753000	-2.367406000	-0.913011000

E(M06-2X): -800.5769266
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.240712418295

Z-Diazocine *Z*-**3**, conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	2.154944000	1.203583000	-2.434706000
6	2.162075000	0.647998000	-1.504758000
6	2.222254000	-0.760769000	0.876034000
6	1.446914000	1.143841000	-0.419151000
6	2.879138000	-0.532432000	-1.427228000
6	2.905536000	-1.241392000	-0.231272000
6	1.483290000	0.406752000	0.759897000
1	3.432504000	-0.915164000	-2.272588000
1	2.258190000	-1.280458000	1.825931000
6	0.631802000	2.402287000	-0.480139000
1	0.715666000	2.934232000	0.466770000
6	-0.852090000	2.136771000	-0.799287000
1	-0.969296000	2.077795000	-1.881442000
1	-1.441718000	2.997152000	-0.472674000
7	0.866477000	0.940218000	1.943370000
7	-0.359241000	0.982283000	2.054357000
6	-1.223957000	0.382438000	1.059986000
6	-3.051389000	-0.930283000	-0.564351000
6	-1.923954000	-0.722195000	1.528301000
6	-1.465156000	0.879668000	-0.225005000
6	-2.384169000	0.197670000	-1.016367000
6	-2.821343000	-1.397037000	0.722265000
1	-2.595254000	0.545058000	-2.019130000
1	-3.345017000	-2.269255000	1.093578000
1	-1.749167000	-1.048834000	2.544649000
1	1.032582000	3.063514000	-1.247975000
8	3.628526000	-2.392993000	-0.198033000
1	3.581666000	-2.779564000	0.680189000
8	-3.923673000	-1.528397000	-1.420080000
1	-4.318280000	-2.294341000	-0.995336000

E(M06-2X): -800.5770169
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.244469797139

Z-Diazocine *Z*-**3**, conformer 3, optimized geometry (M06-2X/cc-pVTZ)

1	2.161738000	1.239541000	-2.419028000
6	2.168476000	0.671922000	-1.496277000
6	2.229255000	-0.766006000	0.867059000
6	1.447384000	1.150082000	-0.406664000
6	2.891265000	-0.505736000	-1.431479000
6	2.917207000	-1.229914000	-0.244509000
6	1.484945000	0.399272000	0.763668000

1	3.449460000	-0.875001000	-2.279662000
1	2.265467000	-1.297151000	1.810551000
6	0.622197000	2.402271000	-0.456626000
1	0.692296000	2.922790000	0.497635000
6	-0.854975000	2.124493000	-0.791737000
1	-0.955456000	2.055807000	-1.875474000
1	-1.454583000	2.984082000	-0.481368000
7	0.865655000	0.917287000	1.952412000
7	-0.360060000	0.957302000	2.063311000
6	-1.226245000	0.366634000	1.065092000
6	-3.062940000	-0.939305000	-0.555031000
6	-1.931758000	-0.740064000	1.531808000
6	-1.467092000	0.868045000	-0.214309000
6	-2.394016000	0.187564000	-1.004499000
6	-2.831123000	-1.410829000	0.730677000
1	-2.593612000	0.555458000	-2.005341000
1	-3.364482000	-2.282217000	1.081749000
1	-1.754276000	-1.068433000	2.547199000
1	1.022020000	3.077556000	-1.212749000
8	3.645017000	-2.378376000	-0.224227000
1	3.591417000	-2.780996000	0.646420000
8	-3.960116000	-1.613476000	-1.323372000
1	-4.033849000	-1.189319000	-2.182228000

E(M06-2X): -800.5770134
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248152729851

Z-Diazocine *Z*-**3**, conformer 4, optimized geometry (M06-2X/cc-pVTZ)

1	2.148031000	1.114592000	-2.471710000
6	2.152517000	0.597775000	-1.519688000
6	2.208989000	-0.719068000	0.918961000
6	1.439491000	1.134150000	-0.457027000
6	2.868843000	-0.582800000	-1.391089000
6	2.892181000	-1.244308000	-0.169147000
6	1.476861000	0.442416000	0.753756000
1	3.418234000	-0.984529000	-2.233720000
1	2.254192000	-1.216544000	1.877346000
6	0.621173000	2.387278000	-0.566574000
1	0.711910000	2.959526000	0.355816000
6	-0.866701000	2.107565000	-0.860901000
1	-0.994051000	2.018367000	-1.940172000
1	-1.454488000	2.976019000	-0.552936000
7	0.857524000	1.030220000	1.910357000
7	-0.368230000	1.067162000	2.020355000
6	-1.224452000	0.415142000	1.052819000
6	-3.035812000	-0.976799000	-0.520691000
6	-1.909989000	-0.685728000	1.559040000
6	-1.468980000	0.865241000	-0.244305000
6	-2.383297000	0.142939000	-1.011197000
6	-2.797863000	-1.398400000	0.780896000
1	-2.586556000	0.470706000	-2.025176000
1	-3.316804000	-2.265883000	1.161964000
1	-1.726558000	-0.976673000	2.584689000
1	1.014262000	3.015472000	-1.365535000
8	3.579546000	-2.401521000	0.024581000

1	4.012744000	-2.659526000	-0.793111000
8	-3.922016000	-1.692009000	-1.265132000
1	-4.003988000	-1.297376000	-2.137147000

E(M06-2X): -800.5767473
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248103714174

E-Diazocine *E*-**3**, chair conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	-0.348471000	2.063288000	-1.752527000
6	-0.551282000	1.004097000	-1.658995000
6	-0.977765000	-1.736416000	-1.501303000
6	-1.847824000	0.545064000	-1.499124000
6	0.529540000	0.121707000	-1.686877000
6	0.311936000	-1.250370000	-1.656285000
6	-2.019324000	-0.844708000	-1.363673000
1	-1.166337000	-2.799429000	-1.436514000
6	-3.036237000	1.497662000	-1.642921000
1	-3.666012000	1.115660000	-2.450441000
1	-2.616921000	2.436951000	-2.002603000
6	-3.963777000	1.864186000	-0.441647000
1	-4.332524000	2.872158000	-0.634009000
1	-3.354705000	1.929075000	0.461445000
7	-3.386140000	-1.195027000	-1.120561000
7	-3.708395000	-0.743403000	-0.016583000
6	-5.081892000	-0.363259000	0.079621000
6	-7.578255000	0.747899000	0.182097000
6	-5.191686000	1.006795000	-0.170539000
6	-6.149498000	-1.180327000	0.380128000
6	-7.417007000	-0.607862000	0.433819000
6	-6.476602000	1.534920000	-0.118720000
1	-5.998633000	-2.238024000	0.555245000
1	-6.620750000	2.590392000	-0.313823000
1	0.348471000	2.063289000	1.752527000
6	0.551282000	1.004098000	1.658995000
6	0.977765000	-1.736415000	1.501303000
6	1.847824000	0.545065000	1.499124000
6	-0.529540000	0.121708000	1.686877000
6	-0.311936000	-1.250369000	1.656286000
6	2.019324000	-0.844708000	1.363674000
1	1.166337000	-2.799428000	1.436515000
6	3.036237000	1.497663000	1.642920000
1	3.666012000	1.115661000	2.450441000
1	2.616921000	2.436952000	2.002602000
6	3.963777000	1.864186000	0.441647000
1	4.332524000	2.872158000	0.634008000
1	3.354705000	1.929075000	-0.461446000
7	3.386140000	-1.195027000	1.120561000
7	3.708395000	-0.743404000	0.016583000
6	5.081892000	-0.363259000	-0.079621000
6	7.578255000	0.747899000	-0.182098000
6	5.191686000	1.006795000	0.170538000
6	6.149498000	-1.180327000	-0.380127000
6	7.417007000	-0.607862000	-0.433819000
6	6.476602000	1.534920000	0.118719000

1	5.998633000	-2.238024000	-0.555245000
1	6.620750000	2.590392000	0.313822000
8	-1.774850000	0.648210000	1.774091000
1	-1.155151000	-1.925351000	1.721953000
1	1.155151000	-1.925351000	-1.721953000
8	1.774850000	0.648210000	-1.774091000
1	2.414452000	0.058266000	-1.334831000
1	-2.414452000	0.058266000	1.334831000
1	-8.572831000	1.167834000	0.226068000
1	8.572831000	1.167833000	-0.226069000
8	-8.530060000	-1.333955000	0.720809000
1	-8.290973000	-2.252197000	0.870478000
8	8.530060000	-1.333955000	-0.720808000
1	8.290973000	-2.252197000	-0.870477000

E(M06-2X): -1601.1491992
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.476019

E-Diazocine *E*-**3**, twist conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	-1.313699000	1.183796000	-2.884550000
6	-0.976113000	0.358292000	-2.273063000
6	-0.172987000	-1.777085000	-0.692563000
6	-1.871584000	-0.280140000	-1.433559000
6	0.351435000	-0.032321000	-2.274799000
6	0.756581000	-1.095179000	-1.471802000
6	-1.501374000	-1.378762000	-0.642832000
1	1.080193000	0.479319000	-2.889183000
1	0.173186000	-2.618720000	-0.105683000
7	-3.270171000	-0.016546000	-1.381679000
7	-3.615107000	0.323806000	-0.242921000
6	-4.937319000	-0.103934000	0.065841000
6	-7.327662000	-1.167059000	0.877872000
6	-5.057966000	-1.502124000	0.087552000
6	-5.941229000	0.753299000	0.464818000
6	-7.159588000	0.211602000	0.854261000
6	-6.281897000	-2.002854000	0.509351000
1	-5.797783000	1.824391000	0.461740000
1	-6.426936000	-3.075171000	0.553076000
1	-8.272782000	-1.588329000	1.198427000
6	-3.915826000	-2.436248000	-0.303147000
1	-3.865991000	-2.520700000	-1.389628000
1	-4.194617000	-3.424644000	0.062344000
6	-2.490241000	-2.132451000	0.246350000
1	-2.021536000	-3.089970000	0.472215000
1	-2.583794000	-1.613565000	1.202836000
8	-8.143384000	1.078486000	1.211701000
1	-8.932658000	0.588610000	1.456787000
8	2.048456000	-1.510488000	-1.428265000
1	2.639508000	-0.734416000	-1.402089000
1	2.163755000	3.799793000	-1.309869000
6	1.563217000	3.122086000	-0.718762000
6	0.088490000	1.379825000	0.857084000
6	2.163965000	2.029287000	-0.115658000
6	0.198860000	3.302356000	-0.598726000

6	-0.546110000	2.410569000	0.169282000
6	1.452813000	1.158432000	0.725015000
1	-0.311958000	4.113808000	-1.096843000
1	-0.503123000	0.732211000	1.494517000
7	3.561472000	1.776337000	-0.146811000
7	3.794269000	0.635163000	-0.567773000
6	4.946570000	0.055940000	0.037050000
6	6.909930000	-1.294522000	1.386230000
6	4.759542000	-0.171016000	1.409263000
6	6.041983000	-0.395245000	-0.667860000
6	7.046521000	-1.060308000	0.024231000
6	5.773688000	-0.862027000	2.057278000
1	6.134125000	-0.228665000	-1.731404000
1	5.677699000	-1.071094000	3.115500000
1	7.686241000	-1.828552000	1.920661000
6	3.512890000	0.292772000	2.157943000
1	3.602410000	1.354993000	2.391732000
1	3.525515000	-0.226564000	3.116216000
6	2.116799000	0.032067000	1.517728000
1	1.431506000	-0.198692000	2.333494000
1	2.163835000	-0.870447000	0.905138000
8	8.131234000	-1.466413000	-0.686983000
1	8.750120000	-1.914324000	-0.104459000
8	-1.883523000	2.601917000	0.230543000
1	-2.339015000	1.776085000	0.461105000

E(M06-2X): -1601.1570582
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.483777245731

TS for twofold H-transfer, *E*-Diazocine *E*-**3**, chair conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	0.221921000	2.086850000	1.674017000
6	0.415869000	1.024974000	1.585914000
6	0.811310000	-1.732251000	1.700277000
6	1.690037000	0.557158000	1.413913000
6	-0.719714000	0.154321000	1.652652000
6	-0.456844000	-1.243507000	1.827386000
6	1.863442000	-0.866789000	1.356388000
1	1.016730000	-2.794191000	1.750418000
6	2.882614000	1.511473000	1.580753000
1	3.526727000	1.077817000	2.349818000
1	2.457781000	2.413879000	2.019864000
6	3.796798000	1.984910000	0.407139000
1	4.172008000	2.972480000	0.676979000
1	3.186138000	2.115933000	-0.486699000
7	3.091030000	-1.342870000	0.964663000
7	3.497430000	-0.609689000	0.008521000
6	4.860248000	-0.250997000	-0.102354000
6	7.387917000	0.793836000	-0.209717000
6	5.007283000	1.123630000	0.095700000
6	5.918526000	-1.109728000	-0.331128000
6	7.197679000	-0.571693000	-0.390644000
6	6.304715000	1.621785000	0.038789000
1	5.740789000	-2.170288000	-0.456963000
1	6.473879000	2.679526000	0.197133000

1	-0.202826000	1.928571000	-1.781299000
6	-0.401207000	0.878008000	-1.612720000
6	-0.779585000	-1.882081000	-1.466367000
6	-1.676882000	0.427114000	-1.411270000
6	0.722023000	0.005861000	-1.583484000
6	0.488501000	-1.399371000	-1.603059000
6	-1.843981000	-0.990391000	-1.238021000
1	-0.980312000	-2.943942000	-1.411860000
6	-2.863096000	1.368937000	-1.659936000
1	-3.508599000	0.880588000	-2.394139000
1	-2.431946000	2.231243000	-2.166620000
6	-3.770819000	1.934536000	-0.520609000
1	-4.118226000	2.914864000	-0.845319000
1	-3.162250000	2.090398000	0.371272000
7	-3.067819000	-1.453365000	-0.843475000
7	-3.530675000	-0.645212000	0.025848000
6	-4.886186000	-0.248513000	0.085365000
6	-7.393473000	0.830139000	0.071012000
6	-5.001963000	1.114936000	-0.185375000
6	-5.958497000	-1.086175000	0.324219000
6	-7.230227000	-0.529210000	0.320784000
6	-6.293980000	1.631969000	-0.186117000
1	-5.796427000	-2.139885000	0.511154000
1	-6.443667000	2.682811000	-0.398898000
8	1.914608000	0.494032000	-1.569324000
1	1.340485000	-2.060085000	-1.688437000
1	-1.298834000	-1.897398000	2.013750000
8	-1.905717000	0.612301000	1.581199000
1	-2.826660000	-0.048896000	0.631609000
1	2.680575000	-0.039555000	-0.788261000
1	8.393981000	1.185377000	-0.258478000
1	-8.394716000	1.236816000	0.074365000
8	8.299823000	-1.335070000	-0.621415000
1	8.042623000	-2.255337000	-0.720024000
8	-8.349707000	-1.262194000	0.555048000
1	-8.114036000	-2.179452000	0.716708000

E(M06-2X): -1601.1084015
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.432679534304

TS for twofold H-transfer, *E*-Diazocine *E*-**3**, twist conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	0.981596000	-1.633926000	2.779596000
6	0.757098000	-1.615534000	1.720956000
6	1.791632000	-1.278018000	0.827898000
6	-0.516036000	-1.772069000	1.257049000
6	1.596963000	-1.366867000	-0.584425000
6	0.326504000	-1.611429000	-1.028797000
6	-0.789039000	-1.671892000	-0.142219000
1	0.119689000	-1.716217000	-2.086553000
7	3.023734000	-0.914027000	1.297020000
1	-1.346904000	-1.940917000	1.929055000
8	-1.986809000	-1.645610000	-0.597808000
6	2.750545000	-1.323138000	-1.587096000
7	3.496660000	0.048829000	0.607914000

6	4.881383000	0.009850000	0.296846000
1	2.788340000	0.804419000	0.030024000
6	5.184970000	-0.986896000	-0.637506000
6	5.800526000	0.927386000	0.759585000
6	6.500929000	-1.045517000	-1.072842000
6	7.459281000	-0.156828000	-0.603918000
6	7.111805000	0.830655000	0.309253000
1	8.480435000	-0.222738000	-0.959663000
6	4.114011000	-1.934027000	-1.155678000
1	5.520936000	1.698009000	1.462912000
8	8.005797000	1.731883000	0.793975000
1	6.787111000	-1.795635000	-1.799432000
1	3.929924000	-2.714586000	-0.413565000
1	4.537466000	-2.439579000	-2.023027000
1	2.403599000	-1.893708000	-2.448342000
1	2.890578000	-0.300422000	-1.941653000
1	8.871522000	1.567853000	0.411028000
1	-2.788717000	-0.804015000	0.030223000
7	-3.496731000	-0.048804000	0.607973000
7	-3.023688000	0.914001000	1.297078000
6	-1.791592000	1.277912000	0.827933000
6	-0.757038000	1.615313000	1.721020000
1	-0.981535000	1.633653000	2.779658000
6	0.516106000	1.771765000	1.257118000
6	-1.596922000	1.366765000	-0.584393000
6	-0.326452000	1.611312000	-1.028741000
6	0.789043000	1.671698000	-0.142144000
1	-0.119609000	1.716087000	-2.086491000
1	1.346996000	1.940475000	1.929127000
8	1.986844000	1.645447000	-0.597789000
6	-2.750480000	1.323050000	-1.587083000
6	-4.881446000	-0.009764000	0.296827000
6	-5.184944000	0.986976000	-0.637548000
6	-5.800636000	-0.927231000	0.759597000
6	-6.500896000	1.045666000	-1.072899000
6	-7.459303000	0.157050000	-0.603957000
6	-7.111904000	-0.830432000	0.309249000
1	-8.480450000	0.223014000	-0.959713000
6	-4.113920000	1.934031000	-1.155717000
1	-5.521090000	-1.697851000	1.462945000
8	-8.005953000	-1.731586000	0.793986000
1	-6.787026000	1.795781000	-1.799512000
1	-3.929814000	2.714601000	-0.413619000
1	-4.537324000	2.439583000	-2.023089000
1	-2.403487000	1.893558000	-2.448350000
1	-2.890535000	0.300316000	-1.941585000
1	-8.871664000	-1.567536000	0.411015000

E(M06-2X): -1601.116524
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.441900494751

E-Diazocine quinone hydrazone tautomer *E*-**3b**, chair conformer, π-dimer, NH *endo*, optimized geometry (M06-2X/cc-pVTZ)

1	-0.641383000	-2.475648000	1.697957000
6	-0.709879000	-1.407192000	1.535667000

6	-0.763744000	1.400623000	1.667587000
6	-1.878724000	-0.821794000	1.217635000
6	0.529678000	-0.656058000	1.766396000
6	0.398530000	0.796242000	1.939799000
6	-1.879311000	0.654195000	1.109156000
1	-0.885989000	2.474669000	1.718542000
6	-3.169806000	-1.632227000	1.345490000
1	-3.746268000	-1.152137000	2.141447000
1	-2.852024000	-2.596184000	1.740691000
6	-4.149716000	-1.927524000	0.174343000
1	-4.644487000	-2.868530000	0.413165000
1	-3.582776000	-2.107223000	-0.741503000
7	-2.801524000	1.357282000	0.524629000
7	-3.476170000	0.654437000	-0.425310000
6	-4.864005000	0.437571000	-0.273593000
6	-7.535808000	-0.159135000	0.016083000
6	-5.225861000	-0.885018000	-0.021987000
6	-5.792862000	1.460762000	-0.358050000
6	-7.137841000	1.155181000	-0.204378000
6	-6.583282000	-1.160174000	0.106435000
1	-5.459969000	2.473595000	-0.547096000
1	-6.902166000	-2.177114000	0.298382000
1	0.641383000	-2.475648000	-1.697957000
6	0.709879000	-1.407192000	-1.535667000
6	0.763744000	1.400623000	-1.667587000
6	1.878724000	-0.821794000	-1.217635000
6	-0.529678000	-0.656058000	-1.766396000
6	-0.398530000	0.796242000	-1.939799000
6	1.879311000	0.654194000	-1.109156000
1	0.885989000	2.474669000	-1.718542000
6	3.169806000	-1.632228000	-1.345490000
1	3.746268000	-1.152137000	-2.141447000
1	2.852024000	-2.596184000	-1.740691000
6	4.149716000	-1.927524000	-0.174343000
1	4.644487000	-2.868530000	-0.413165000
1	3.582776000	-2.107223000	0.741503000
7	2.801524000	1.357282000	-0.524629000
7	3.476170000	0.654437000	0.425309000
6	4.864005000	0.437571000	0.273593000
6	7.535808000	-0.159135000	-0.016083000
6	5.225861000	-0.885018000	0.021987000
6	5.792862000	1.460762000	0.358050000
6	7.137842000	1.155181000	0.204378000
6	6.583282000	-1.160174000	-0.106435000
1	5.459969000	2.473595000	0.547095000
1	6.902166000	-2.177114000	-0.298382000
8	-1.613901000	-1.221009000	-1.858081000
1	-1.282718000	1.337123000	-2.249557000
1	1.282718000	1.337123000	2.249557000
8	1.613901000	-1.221009000	1.858081000
1	2.982026000	-0.173073000	0.750608000
1	-2.982026000	-0.173073000	-0.750608000
1	-8.589699000	-0.371831000	0.123143000
1	8.589699000	-0.371831000	-0.123143000
8	-8.111129000	2.103197000	-0.272442000
1	-7.713691000	2.964111000	-0.426588000
8	8.111129000	2.103197000	0.272441000

1	7.713691000	2.964111000	0.426588000

E(M06-2X): -1601.1294179
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.469207874990

E-diazocine quinone hydrazone tautomer *E*-**3b**, twist conformer, π-dimer, NH *endo*, optimized geometry (M06-2X/cc-pVTZ)

1	-1.692187000	0.975221000	-2.341138000
6	-1.632933000	0.828386000	-1.270608000
6	-1.480083000	0.720577000	1.530713000
6	-0.967856000	1.879450000	-0.517441000
6	-2.006583000	-0.313706000	-0.681305000
6	-1.835341000	-0.482013000	0.766693000
6	-1.032495000	1.847597000	0.952390000
1	-2.401297000	-1.156491000	-1.232629000
1	-1.613058000	0.652321000	2.603555000
7	-0.379585000	2.796433000	-1.224159000
7	0.633700000	3.457555000	-0.600793000
6	0.464784000	4.871501000	-0.467399000
6	0.163486000	7.588754000	-0.142428000
6	-0.520038000	5.329237000	0.413103000
6	1.288914000	5.732046000	-1.166266000
6	1.134380000	7.102951000	-1.007750000
6	-0.645165000	6.705341000	0.557512000
1	2.043832000	5.340893000	-1.832339000
1	-1.391767000	7.100603000	1.235259000
1	0.044220000	8.657441000	-0.009691000
6	-1.436110000	4.392348000	1.174050000
1	-2.274498000	4.111112000	0.530710000
1	-1.869807000	4.969388000	1.990213000
6	-0.828204000	3.104292000	1.782577000
1	-1.332883000	2.914748000	2.729352000
1	0.223037000	3.248477000	2.035946000
8	1.961882000	7.915461000	-1.717853000
1	1.758015000	8.833856000	-1.523260000
8	-2.006583000	-1.563043000	1.319252000
1	1.692187000	-0.975221000	-2.341138000
6	1.632933000	-0.828386000	-1.270608000
6	1.480083000	-0.720577000	1.530713000
6	0.967856000	-1.879450000	-0.517441000
6	2.006583000	0.313706000	-0.681305000
6	1.835341000	0.482013000	0.766693000
6	1.032495000	-1.847597000	0.952390000
1	2.401297000	1.156491000	-1.232629000
1	1.613058000	-0.652321000	2.603555000
7	0.379585000	-2.796433000	-1.224159000
7	-0.633700000	-3.457555000	-0.600793000
6	-0.464784000	-4.871501000	-0.467399000
6	-0.163486000	-7.588754000	-0.142428000
6	0.520038000	-5.329237000	0.413103000
6	-1.288914000	-5.732046000	-1.166266000
6	-1.134380000	-7.102951000	-1.007750000
6	0.645165000	-6.705341000	0.557512000
1	-2.043832000	-5.340893000	-1.832339000
1	1.391767000	-7.100603000	1.235259000

1	-0.044220000	-8.657441000	-0.009691000
6	1.436110000	-4.392348000	1.174050000
1	2.274498000	-4.111112000	0.530710000
1	1.869807000	-4.969388000	1.990213000
6	0.828204000	-3.104292000	1.782577000
1	1.332883000	-2.914748000	2.729352000
1	-0.223037000	-3.248477000	2.035946000
8	-1.961882000	-7.915461000	-1.717853000
1	-1.758015000	-8.833856000	-1.523260000
8	2.006583000	1.563043000	1.319252000
1	0.992989000	2.999296000	0.234436000
1	-0.992989000	-2.999296000	0.234436000

E(M06-2X): -1601.1367456
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.469207874990

E-Diazocine *E*-**3**, chair conformer, complex with HF (endo), optimized geometry (M06-2X/cc-pVTZ)

1	3.284413000	1.985212000	-0.336000000
6	3.062233000	0.923739000	-0.326950000
6	2.555636000	-1.803804000	-0.399215000
6	1.748346000	0.500364000	-0.471170000
6	4.102703000	0.010139000	-0.187866000
6	3.854461000	-1.356158000	-0.238350000
6	1.525706000	-0.886067000	-0.471734000
1	4.682632000	-2.043282000	-0.144802000
1	2.335230000	-2.861516000	-0.434033000
6	0.650859000	1.510258000	-0.814995000
1	0.211667000	1.203054000	-1.767543000
1	1.165743000	2.450743000	-1.009078000
6	-0.516733000	1.838756000	0.170373000
1	-0.782030000	2.882969000	0.004518000
1	-0.146021000	1.770797000	1.194597000
7	0.139790000	-1.219023000	-0.611501000
7	-0.453123000	-0.778674000	0.377209000
6	-1.796950000	-0.352873000	0.160726000
6	-4.200310000	0.867669000	-0.279828000
6	-1.803381000	1.038306000	0.037929000
6	-2.921943000	-1.142715000	0.076110000
6	-4.144003000	-0.513170000	-0.142103000
6	-3.041377000	1.624812000	-0.196142000
1	-2.846519000	-2.218320000	0.171722000
1	-3.103655000	2.699898000	-0.310038000
1	-5.161355000	1.330604000	-0.451854000
8	-5.310302000	-1.204212000	-0.235833000
1	-5.144546000	-2.143445000	-0.120687000
8	5.393149000	0.403269000	-0.027829000
1	5.436744000	1.361210000	0.031934000
9	0.754795000	0.076246000	2.620523000
1	0.353616000	-0.268263000	1.835187000

E(M06-2X): -901.0279141
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -899.588032519562

E-Diazocine *E*-**3**, chair conformer, complex with HF (exo), optimized geometry (M06-2X/cc-pVTZ)

1	-3.480992000	-2.238662000	0.309710000
6	-3.193025000	-1.230694000	0.030938000
6	-2.480852000	1.391078000	-0.610502000
6	-1.875298000	-0.955726000	-0.298394000
6	-4.152071000	-0.219453000	0.003123000
6	-3.799653000	1.086758000	-0.313693000
6	-1.553962000	0.368163000	-0.621688000
1	-4.564888000	1.849144000	-0.306523000
1	-2.174310000	2.406630000	-0.817147000
6	-0.773139000	-2.002800000	-0.250328000
1	-0.368440000	-2.145131000	-1.252795000
1	-1.232352000	-2.944822000	0.050280000
6	0.409363000	-1.720481000	0.738280000
1	0.705510000	-2.682897000	1.155385000
1	0.010963000	-1.143768000	1.577011000
7	-0.157044000	0.400354000	-0.852820000
7	0.554335000	0.993788000	-0.038444000
6	1.817047000	0.318839000	-0.004896000
6	4.134773000	-1.137513000	0.106544000
6	1.711014000	-1.051505000	0.286598000
6	3.020631000	0.972114000	-0.181922000
6	4.193128000	0.228922000	-0.140005000
6	2.913257000	-1.752019000	0.330064000
1	3.032600000	2.037335000	-0.376684000
1	2.896171000	-2.809835000	0.561108000
1	5.058470000	-1.697269000	0.141267000
8	5.417511000	0.783023000	-0.334929000
1	5.330044000	1.728841000	-0.479886000
8	-5.459081000	-0.458476000	0.292163000
1	-5.582099000	-1.388501000	0.498878000
9	-0.470094000	3.170247000	1.137659000
1	-0.075580000	2.367255000	0.836729000

E(M06-2X): -901.0254502
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -899.584824336351

E-Diazocine *E*-**3**, twist conformer, complex with HF (endo), optimized geometry (M06-2X/cc-pVTZ)

1	-2.395852000	-2.205615000	-1.788805000
6	-2.617441000	-1.352976000	-1.162263000
6	-3.125637000	0.880548000	0.404006000
6	-1.581170000	-0.594640000	-0.651170000
6	-3.923952000	-1.029314000	-0.840286000
6	-4.174025000	0.087345000	-0.050806000
6	-1.808006000	0.559162000	0.120682000
1	-4.745309000	-1.631675000	-1.207712000
1	-3.365611000	1.761907000	0.983664000
7	-0.216785000	-0.795021000	-0.998419000
7	0.483916000	-0.897955000	0.015152000
6	1.795909000	-0.367579000	-0.148733000
6	4.193239000	0.947143000	-0.224794000
6	1.770478000	1.027351000	-0.289830000

6	2.952981000	-1.102756000	-0.012069000
6	4.169342000	-0.433232000	-0.072735000
6	3.005283000	1.659661000	-0.319814000
1	2.927587000	-2.173387000	0.129403000
1	3.044936000	2.737227000	-0.419227000
1	5.142574000	1.467892000	-0.255088000
6	0.468105000	1.815251000	-0.391464000
1	0.086229000	1.753344000	-1.412433000
1	0.732437000	2.860810000	-0.235007000
6	-0.687380000	1.481867000	0.599645000
1	-1.169236000	2.425155000	0.854489000
1	-0.277686000	1.096527000	1.534522000
8	5.298170000	-1.181403000	0.033162000
1	6.070157000	-0.610855000	-0.006702000
8	-5.431645000	0.471774000	0.288290000
1	-6.070708000	-0.143761000	-0.080277000
9	-0.368575000	-1.128429000	2.535769000
1	-0.090821000	-1.120827000	1.630300000

E(M06-2X): -901.0323855
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -899.592426351149

E-Diazocine *E*-**4**, chair conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	-3.126784000	-2.172678000	-0.054825000
6	-3.025859000	-1.092418000	-0.067944000
6	-2.825596000	1.670725000	-0.197045000
6	-1.767421000	-0.524217000	-0.219528000
6	-4.164257000	-0.299800000	0.045410000
6	-4.068691000	1.083143000	-0.029158000
6	-1.697464000	0.877010000	-0.254358000
1	-4.969205000	1.675368000	0.045719000
1	-2.727049000	2.745635000	-0.257672000
6	-0.557227000	-1.408490000	-0.520921000
1	-0.147318000	-1.087144000	-1.481539000
1	-0.949516000	-2.413084000	-0.679112000
6	0.629455000	-1.542135000	0.488330000
1	0.993779000	-2.567737000	0.423049000
1	0.245512000	-1.402354000	1.500027000
7	-0.355935000	1.350454000	-0.426873000
7	0.284430000	1.033142000	0.579501000
6	1.664179000	0.760970000	0.347987000
6	4.181257000	-0.241623000	-0.088429000
6	1.827809000	-0.626954000	0.289824000
6	2.716475000	1.637667000	0.196292000
6	3.990828000	1.130761000	-0.016761000
6	3.105183000	-1.114430000	0.057362000
1	2.544403000	2.703830000	0.241416000
1	3.269695000	-2.185092000	-0.005112000
8	-5.405798000	-0.834761000	0.208173000
1	-5.342055000	-1.792296000	0.249597000
1	4.844014000	1.782886000	-0.136089000
8	5.450562000	-0.688394000	-0.304573000
1	5.454922000	-1.648500000	-0.329022000

E(M06-2X): -800.5591362
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.227971522292

E-Diazocine *E*-**4**, chair conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	-3.139653000	-2.184802000	-0.046163000
6	-3.019592000	-1.109462000	-0.066580000
6	-2.821684000	1.658636000	-0.200065000
6	-1.767365000	-0.538089000	-0.224569000
6	-4.158962000	-0.317123000	0.049206000
6	-4.065295000	1.064811000	-0.027314000
6	-1.697072000	0.866421000	-0.261956000
1	-4.957034000	1.674921000	0.048232000
1	-2.726540000	2.733770000	-0.260531000
6	-0.553866000	-1.417947000	-0.523123000
1	-0.145010000	-1.099404000	-1.485144000
1	-0.942862000	-2.424420000	-0.674947000
6	0.631909000	-1.540049000	0.488432000
1	0.999500000	-2.564815000	0.430556000
1	0.245682000	-1.395942000	1.498708000
7	-0.354353000	1.335932000	-0.438992000

7	0.284351000	1.039870000	0.574603000
6	1.664623000	0.765128000	0.344599000
6	4.183119000	-0.236717000	-0.084614000
6	1.828499000	-0.622865000	0.288038000
6	2.717101000	1.641962000	0.196142000
6	3.992195000	1.135563000	-0.014100000
6	3.106958000	-1.109589000	0.059728000
1	2.544819000	2.708119000	0.240855000
1	3.271995000	-2.180290000	-0.000615000
8	-5.346643000	-0.962415000	0.215238000
1	-6.057786000	-0.319036000	0.270803000
1	4.845335000	1.788025000	-0.131885000
8	5.453009000	-0.683488000	-0.297744000
1	5.457226000	-1.643607000	-0.322057000

E(M06-2X): -800.5593559
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228098006961

E-Diazocine *E*-**4**, chair conformer 3, optimized geometry (M06-2X/cc-pVTZ)

1	-3.146581000	-2.180011000	-0.049238000
6	-3.023746000	-1.104970000	-0.068350000
6	-2.818592000	1.662661000	-0.198545000
6	-1.769793000	-0.536963000	-0.224875000
6	-4.161116000	-0.309771000	0.047591000
6	-4.063925000	1.072014000	-0.027316000
6	-1.696068000	0.867503000	-0.260463000
1	-4.954152000	1.684333000	0.048224000
1	-2.720551000	2.737617000	-0.257817000
6	-0.558596000	-1.419870000	-0.523846000
1	-0.148609000	-1.101547000	-1.485476000
1	-0.950334000	-2.424950000	-0.677399000
6	0.626523000	-1.547589000	0.487643000
1	0.991783000	-2.572723000	0.427942000
1	0.241062000	-1.403370000	1.498196000
7	-0.352239000	1.334367000	-0.436137000
7	0.285680000	1.033924000	0.576720000
6	1.665042000	0.756968000	0.346813000
6	4.178329000	-0.256341000	-0.084662000
6	1.826747000	-0.635068000	0.288019000
6	2.716539000	1.629999000	0.200099000
6	3.992158000	1.115466000	-0.011366000
6	3.099175000	-1.127157000	0.058763000
1	2.549074000	2.696804000	0.245646000
1	3.281816000	-2.191832000	-0.006354000
8	-5.350637000	-0.952099000	0.212082000
1	-6.060041000	-0.306862000	0.268111000
1	4.837019000	1.783642000	-0.125627000
8	5.401480000	-0.819427000	-0.295102000
1	6.062623000	-0.128228000	-0.383151000

E(M06-2X): -800.5596098
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.228124241631
E-Diazocine *E*-**4**, chair conformer 4, optimized geometry (M06-2X/cc-pVTZ)

1	-3.133914000	-2.167891000	-0.057729000
6	-3.030095000	-1.087902000	-0.069691000
6	-2.822258000	1.674713000	-0.195595000
6	-1.769943000	-0.523247000	-0.220090000
6	-4.166384000	-0.292300000	0.043991000
6	-4.067116000	1.090455000	-0.028990000
6	-1.696361000	0.877892000	-0.253222000
1	-4.966047000	1.685057000	0.046047000
1	-2.720720000	2.749427000	-0.255019000
6	-0.562117000	-1.410623000	-0.521690000
1	-0.151120000	-1.089917000	-1.482069000
1	-0.957065000	-2.413915000	-0.681070000
6	0.623806000	-1.549185000	0.487592000
1	0.985872000	-2.575142000	0.421123000
1	0.240524000	-1.408783000	1.499460000
7	-0.353548000	1.348090000	-0.424792000
7	0.285892000	1.028242000	0.581413000
6	1.664680000	0.753240000	0.349933000
6	4.176392000	-0.261483000	-0.088299000
6	1.825793000	-0.638763000	0.289545000
6	2.716310000	1.625813000	0.200392000
6	3.991084000	1.110454000	-0.013771000
6	3.097049000	-1.131898000	0.056450000
1	2.549382000	2.692669000	0.246458000
1	3.278906000	-2.196587000	-0.010652000
8	-5.409419000	-0.824182000	0.205592000
1	-5.348034000	-1.781931000	0.245910000
1	4.836176000	1.778108000	-0.129365000
8	5.398723000	-0.825087000	-0.301622000
1	6.060162000	-0.134258000	-0.390525000

E(M06-2X): -800.5594725
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.227996979776

E-Diazocine *E*-**4**, twist conformer 1, optimized geometry (M06-2X/cc-pVTZ)

6	-4.061590000	1.030152000	-0.412909000
6	-2.791465000	1.542964000	-0.607126000
6	-1.684305000	0.787713000	-0.263514000
6	-4.206427000	-0.260328000	0.080928000
6	-3.086833000	-1.032567000	0.371704000
6	-1.803537000	-0.525475000	0.210705000
6	-0.589691000	-1.402674000	0.509911000
6	1.803537000	-0.525475000	-0.210704000
6	1.684305000	0.787714000	0.263514000
6	3.086833000	-1.032567000	-0.371704000
6	4.206426000	-0.260328000	-0.080928000
6	4.061591000	1.030151000	0.412909000
6	2.791465000	1.542964000	0.607126000
7	-0.335382000	1.161355000	-0.520394000
7	0.335382000	1.161356000	0.520394000
1	-2.653230000	2.537452000	-1.008148000
1	-3.219155000	-2.050521000	0.723296000
1	-0.204342000	-1.159581000	1.501010000

1	-0.958980000	-2.426423000	0.572092000
1	3.219156000	-2.050520000	-0.723298000
1	4.946333000	1.604326000	0.646877000
1	2.653230000	2.537452000	1.008148000
6	0.589691000	-1.402675000	-0.509908000
1	0.958980000	-2.426425000	-0.572087000
1	0.204342000	-1.159585000	-1.501008000
8	5.473573000	-0.731201000	-0.241095000
1	5.444348000	-1.623829000	-0.594808000
1	-4.946332000	1.604327000	-0.646877000
8	-5.473573000	-0.731202000	0.241092000
1	-5.444348000	-1.623828000	0.594808000

E(M06-2X): -800.5641442
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232699036412

E-Diazocine *E*-**4**, twist conformer 2, optimized geometry (M06-2X/cc-pVTZ)

6	4.060998000	1.011173000	0.406903000
6	2.790545000	1.531365000	0.605253000
6	1.684865000	0.779413000	0.263814000
6	4.201935000	-0.278163000	-0.088117000
6	3.079715000	-1.047721000	-0.379695000
6	1.802528000	-0.536233000	-0.214915000
6	0.584071000	-1.405060000	-0.518428000
6	-1.805686000	-0.525201000	0.209468000
6	-1.684595000	0.789947000	-0.259456000
6	-3.090078000	-1.030075000	0.368958000
6	-4.208410000	-0.254554000	0.082143000
6	-4.061628000	1.037619000	-0.406726000
6	-2.790603000	1.548498000	-0.599703000
7	0.336018000	1.151206000	0.524372000
7	-0.335796000	1.164756000	-0.515529000
1	2.657382000	2.525756000	1.007990000
1	3.229985000	-2.059270000	-0.733822000
1	0.198695000	-1.150525000	-1.506703000
1	0.949669000	-2.429053000	-0.591086000
1	-3.224189000	-2.049383000	0.715882000
1	-4.945413000	1.614273000	-0.638181000
1	-2.650533000	2.544127000	-0.997291000
6	-0.594177000	-1.407796000	0.502610000
1	-0.966570000	-2.430757000	0.558355000
1	-0.207951000	-1.172636000	1.495249000
8	-5.476252000	-0.723831000	0.241279000
1	-5.448153000	-1.618682000	0.589460000
1	4.937653000	1.600359000	0.646563000
8	5.418583000	-0.854678000	-0.290709000
1	6.112349000	-0.237140000	-0.045532000

E(M06-2X): -800.5643162
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232647724249
E-Diazocine *E*-**4**, twist conformer 3, optimized geometry (M06-2X/cc-pVTZ)

6	-4.060943000	1.018469000	-0.401335000

6	-2.789572000	1.536617000	-0.598569000
6	-1.685096000	0.781487000	-0.260008000
6	-4.203907000	-0.272342000	0.089355000
6	-3.083013000	-1.045170000	0.377268000
6	-1.804673000	-0.535982000	0.213809000
6	-0.588492000	-1.410249000	0.511219000
6	1.804672000	-0.535982000	-0.213809000
6	1.685097000	0.781489000	0.260007000
6	3.083011000	-1.045171000	-0.377267000
6	4.203907000	-0.272344000	-0.089355000
6	4.060944000	1.018467000	0.401336000
6	2.789574000	1.536616000	0.598570000
7	-0.336355000	1.154456000	-0.519647000
7	0.336357000	1.154464000	0.519645000
1	-2.654503000	2.532004000	-0.998244000
1	-3.235107000	-2.057949000	0.727029000
1	-0.202076000	-1.163649000	1.501068000
1	-0.957179000	-2.433534000	0.577483000
1	3.235104000	-2.057950000	-0.727027000
1	4.936603000	1.610073000	0.638659000
1	2.654505000	2.532004000	0.998245000
6	0.588492000	-1.410251000	-0.511217000
1	0.957180000	-2.433535000	-0.577476000
1	0.202076000	-1.163655000	-1.501067000
8	5.421555000	-0.847139000	-0.290691000
1	6.114195000	-0.228012000	-0.046368000
1	-4.936602000	1.610078000	-0.638654000
8	-5.421557000	-0.847138000	0.290693000
1	-6.114197000	-0.228027000	0.046327000

E(M06-2X): -800.5644221
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232464653949

E-Diazocine *E*-**4**, twist conformer 4, optimized geometry (M06-2X/cc-pVTZ)

6	-4.061627000	1.037620000	-0.406726000
6	-2.790602000	1.548498000	-0.599703000
6	-1.684595000	0.789945000	-0.259458000
6	-4.208409000	-0.254552000	0.082143000
6	-3.090080000	-1.030076000	0.368958000
6	-1.805688000	-0.525203000	0.209467000
6	-0.594178000	-1.407796000	0.502611000
6	1.802528000	-0.536233000	-0.214915000
6	1.684866000	0.779415000	0.263813000
6	3.079715000	-1.047722000	-0.379694000
6	4.201934000	-0.278164000	-0.088117000
6	4.060999000	1.011173000	0.406903000
6	2.790547000	1.531366000	0.605253000
7	-0.335793000	1.164745000	-0.515531000
7	0.336020000	1.151215000	0.524371000
1	-2.650529000	2.544127000	-0.997290000
1	-3.224193000	-2.049383000	0.715884000
1	-0.207952000	-1.172630000	1.495250000
1	-0.966568000	-2.430757000	0.558362000
1	3.229984000	-2.059271000	-0.733820000

1	4.937654000	1.600357000	0.646565000
1	2.657384000	2.525756000	1.007991000
6	0.584072000	-1.405063000	-0.518425000
1	0.949672000	-2.429055000	-0.591076000
1	0.198697000	-1.150535000	-1.506702000
8	5.418581000	-0.854678000	-0.290708000
1	6.112347000	-0.237135000	-0.045543000
1	-4.945412000	1.614275000	-0.638181000
8	-5.476256000	-0.723827000	0.241279000
1	-5.448159000	-1.618677000	0.589461000

E(M06-2X): -800.5643162
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.232647759917

Transition state for direct conversion of *E*-**4** (twist) to *Z*-**4**, lowest energy conformer, optimized geometry (M06-2X/cc-pVTZ)

6	3.921960000	-1.166739000	-0.509540000
6	2.718125000	-1.759472000	-0.178216000
6	1.643553000	-1.003963000	0.269934000
6	4.056439000	0.206148000	-0.350928000
6	2.997958000	0.957928000	0.146615000
6	1.777811000	0.375874000	0.463980000
6	0.696864000	1.256294000	1.037897000
6	-1.663123000	0.966009000	-0.016386000
6	-1.744924000	-0.430975000	0.226469000
6	-2.826859000	1.673830000	-0.266998000
6	-4.056261000	1.024229000	-0.337411000
6	-4.148560000	-0.350598000	-0.129416000
6	-3.007277000	-1.055245000	0.174375000
7	0.442857000	-1.753523000	0.523942000
7	-0.631674000	-1.137311000	0.513972000
1	2.574148000	-2.827691000	-0.274214000
1	3.155702000	2.017984000	0.301224000
1	0.197752000	0.776644000	1.880154000
1	1.177955000	2.148950000	1.439084000
1	-2.782721000	2.744297000	-0.438479000
1	-3.047612000	-2.117474000	0.371089000
6	-0.339221000	1.682124000	-0.030041000
1	-0.544532000	2.748763000	0.061695000
1	0.118175000	1.540005000	-1.012038000
1	4.750885000	-1.758045000	-0.879343000
8	5.209438000	0.865397000	-0.644715000
1	5.866284000	0.238251000	-0.958202000
1	-5.117068000	-0.825497000	-0.191078000
8	-5.204159000	1.688830000	-0.607474000
1	-5.020248000	2.624191000	-0.732589000

E(M06-2X): -800.5283791
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.188695147349
Quinone hydrazone tautomer *E*-**4b**, chair conformer 1 (NH *endo*), optimized geometry (M06-2X/cc-pVTZ)

1	-3.104645000	-2.220650000	0.044367000
6	-2.954049000	-1.147808000	0.031875000
6	-2.815436000	1.594431000	-0.608406000

6	-1.724585000	-0.614560000	-0.027724000
6	-4.194932000	-0.347725000	-0.078318000
6	-4.029715000	1.046323000	-0.533001000
6	-1.636447000	0.863737000	-0.151331000
1	-4.934068000	1.590644000	-0.766433000
1	-2.657083000	2.630518000	-0.877178000
6	-0.540727000	-1.525257000	-0.356503000
1	-0.171893000	-1.198419000	-1.332704000
1	-0.979474000	-2.510039000	-0.512170000
6	0.696029000	-1.725984000	0.557744000
1	1.097246000	-2.712899000	0.329754000
1	0.384922000	-1.772844000	1.605399000
7	-0.608802000	1.581432000	0.153186000
7	0.253085000	0.969649000	1.038046000
6	1.549045000	0.634620000	0.566216000
6	4.050560000	-0.143692000	-0.306965000
6	1.803523000	-0.718449000	0.358524000
6	2.522277000	1.592064000	0.325687000
6	3.771873000	1.206343000	-0.121904000
6	3.072037000	-1.099541000	-0.065127000
1	2.288729000	2.634263000	0.492775000
1	3.294844000	-2.149284000	-0.223257000
8	-5.287016000	-0.843401000	0.107716000
1	-0.183710000	0.176710000	1.491823000
1	4.548237000	1.930935000	-0.320929000
8	5.301443000	-0.471419000	-0.731833000
1	5.374771000	-1.424957000	-0.821738000

E(M06-2X): -800.5489977
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.221550157255

Quinone hydrazone tautomer *E*-**4b**, chair conformer 2 (NH *endo*), optimized geometry (M06-2X/cc-pVTZ)

1	-3.112659000	-2.215046000	0.036958000
6	-2.958290000	-1.142728000	0.027188000
6	-2.808751000	1.600654000	-0.605736000
6	-1.726720000	-0.613973000	-0.028927000
6	-4.196018000	-0.337953000	-0.083368000
6	-4.025049000	1.056711000	-0.534436000
6	-1.633309000	0.864526000	-0.147634000
1	-4.927034000	1.604714000	-0.768438000
1	-2.646086000	2.636872000	-0.871410000
6	-0.545562000	-1.528039000	-0.357772000
1	-0.174947000	-1.201277000	-1.333365000
1	-0.987286000	-2.511098000	-0.515539000
6	0.689765000	-1.734487000	0.556879000
1	1.088719000	-2.721746000	0.327793000
1	0.378458000	-1.780786000	1.604518000
7	-0.604915000	1.578714000	0.161984000
7	0.254774000	0.962000000	1.046532000
6	1.549741000	0.625004000	0.573166000
6	4.044982000	-0.163565000	-0.309520000
6	1.801261000	-0.731295000	0.358358000
6	2.523131000	1.578186000	0.336259000
6	3.772325000	1.185532000	-0.117426000

6	3.062849000	-1.117356000	-0.069140000
1	2.295812000	2.620895000	0.508198000
1	3.300398000	-2.159247000	-0.238655000
8	-5.290379000	-0.829694000	0.099580000
1	-0.184100000	0.167344000	1.495265000
1	4.539485000	1.925458000	-0.310337000
8	5.256791000	-0.611804000	-0.737831000
1	5.846809000	0.133607000	-0.875949000

E(M06-2X): -800.5493989
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.221489984216

Quinone hydrazone tautomer *E*-**4b**, twist conformer 1 (NH *endo*), optimized geometry (M06-2X/cc-pVTZ)

6	3.989835000	0.997280000	0.276439000
6	2.749018000	1.470111000	0.658185000
6	1.610676000	0.699584000	0.474553000
6	4.085385000	-0.268964000	-0.288486000
6	2.946507000	-1.046013000	-0.462623000
6	1.692600000	-0.574084000	-0.089691000
6	0.475393000	-1.443874000	-0.330066000
6	-1.817415000	-0.540868000	0.435225000
6	-1.616372000	0.785159000	-0.187654000
6	-3.067308000	-1.022096000	0.487446000
6	-4.242307000	-0.300400000	-0.047053000
6	-3.955790000	0.890364000	-0.866478000
6	-2.711698000	1.364380000	-0.959420000
7	0.333421000	1.201054000	0.887612000
7	-0.533001000	1.486817000	-0.141636000
1	2.640081000	2.449726000	1.102113000
1	3.038296000	-2.036576000	-0.895754000
1	0.031966000	-1.168045000	-1.290654000
1	0.831177000	-2.466632000	-0.449063000
1	-3.271525000	-2.020315000	0.856083000
1	-4.796952000	1.350903000	-1.365468000
1	-2.468167000	2.255135000	-1.523410000
6	-0.640553000	-1.457712000	0.742634000
1	-1.053588000	-2.464802000	0.777652000
1	-0.211909000	-1.288839000	1.732141000
8	-5.370152000	-0.717863000	0.120768000
1	4.887671000	1.583458000	0.407899000
8	5.321779000	-0.703381000	-0.646107000
1	5.260505000	-1.581228000	-1.031792000
1	-0.091343000	0.624872000	1.603052000

E(M06-2X): -800.5547387
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.227353351378
Quinone hydrazone tautomer *E*-**4b**, twist conformer 2 (NH *endo*), optimized geometry (M06-2X/cc-pVTZ)

6	3.987994000	0.978597000	0.275030000
6	2.747105000	1.456086000	0.662482000
6	1.610428000	0.689773000	0.476233000
6	4.080148000	-0.284531000	-0.295442000
6	2.939050000	-1.058532000	-0.472979000

6	1.690851000	-0.583886000	-0.097010000
6	0.470243000	-1.447569000	-0.342048000
6	-1.819820000	-0.543893000	0.430939000
6	-1.616097000	0.786267000	-0.182808000
6	-3.071078000	-1.021689000	0.481318000
6	-4.244546000	-0.293114000	-0.047119000
6	-3.955564000	0.901735000	-0.859891000
6	-2.710410000	1.373109000	-0.950604000
7	0.335090000	1.191023000	0.895294000
7	-0.532260000	1.486435000	-0.131381000
1	2.642469000	2.433602000	1.111861000
1	3.049125000	-2.041212000	-0.912783000
1	0.027445000	-1.162626000	-1.300235000
1	0.823935000	-2.469683000	-0.469788000
1	-3.277757000	-2.021645000	0.843793000
1	-4.795913000	1.367316000	-1.355568000
1	-2.464796000	2.266644000	-1.509257000
6	-0.645111000	-1.465876000	0.731115000
1	-1.060673000	-2.472114000	0.759444000
1	-0.216019000	-1.305206000	1.721876000
8	-5.373580000	-0.707510000	0.120157000
1	4.878047000	1.578916000	0.417354000
8	5.262278000	-0.822523000	-0.694020000
1	5.975520000	-0.201899000	-0.522771000
1	-0.089939000	0.607108000	1.604277000

E(M06-2X): -800.5550568
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.227284943828

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**4b**, chair conformer, optimized geometry (M06-2X/cc-pVTZ)

1	-3.047844000	-2.238922000	0.069048000
6	-2.924730000	-1.163019000	0.037773000
6	-2.891826000	1.590200000	-0.621019000
6	-1.715845000	-0.598596000	-0.088019000
6	-4.185787000	-0.390940000	-0.008188000
6	-4.082475000	1.010352000	-0.477323000
6	-1.677668000	0.886349000	-0.197424000
1	-5.014683000	1.524802000	-0.665714000
1	-2.771130000	2.626586000	-0.907069000
6	-0.514474000	-1.459335000	-0.461590000
1	-0.119554000	-1.046690000	-1.394291000
1	-0.934054000	-2.432369000	-0.718234000
6	0.685798000	-1.713346000	0.485796000
1	1.067377000	-2.711533000	0.268476000
1	0.334804000	-1.729936000	1.518461000
7	-0.663620000	1.621315000	0.090386000
7	0.214671000	0.885239000	0.904158000
6	1.542734000	0.626236000	0.521024000
6	4.083251000	-0.145295000	-0.245532000
6	1.817251000	-0.727468000	0.324430000
6	2.522288000	1.586865000	0.310900000
6	3.793860000	1.204751000	-0.079631000
6	3.099942000	-1.109110000	-0.044493000
1	2.278110000	2.631210000	0.450879000

1	3.335557000	-2.157581000	-0.193159000
8	-5.257981000	-0.902486000	0.235048000
1	-0.050174000	0.879434000	1.874431000
1	4.576170000	1.929785000	-0.252497000
8	5.351077000	-0.470324000	-0.616462000
1	5.429378000	-1.424039000	-0.701047000

E(M06-2X): -800.5350664
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.206147

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**4b**, twist conformer 1, optimized geometry (M06-2X/cc-pVTZ)

6	-3.996466000	0.956947000	-0.421590000
6	-2.741144000	1.445507000	-0.728727000
6	-1.599487000	0.712416000	-0.419907000
6	-4.110366000	-0.269876000	0.223173000
6	-2.974260000	-1.011032000	0.523229000
6	-1.709741000	-0.541770000	0.189006000
6	-0.483158000	-1.388655000	0.445988000
6	1.797707000	-0.538854000	-0.404840000
6	1.653799000	0.768820000	0.273031000
6	3.036950000	-1.024104000	-0.558318000
6	4.245606000	-0.329063000	-0.066938000
6	4.021377000	0.826523000	0.827697000
6	2.792013000	1.302831000	1.022419000
7	-0.304444000	1.142674000	-0.727567000
7	0.579445000	1.479841000	0.300270000
1	-2.630936000	2.411241000	-1.203738000
1	-3.079122000	-1.981313000	0.997529000
1	-0.010299000	-1.073102000	1.380091000
1	-0.819486000	-2.411335000	0.613019000
1	3.211189000	-2.005108000	-0.983805000
1	4.898229000	1.253448000	1.294511000
1	2.587141000	2.164144000	1.644406000
6	0.584145000	-1.408647000	-0.679335000
1	0.960721000	-2.427758000	-0.768303000
1	0.119230000	-1.162024000	-1.631921000
8	5.360591000	-0.735331000	-0.319614000
1	-4.894048000	1.511496000	-0.654493000
8	-5.363738000	-0.705196000	0.523393000
1	-5.313253000	-1.552411000	0.973461000
1	-0.031042000	1.433079000	-1.649229000

E(M06-2X): -800.5452129
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.215751192579

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer *E*-**4b**, twist conformer 2, optimized geometry (M06-2X/cc-pVTZ)

6	-3.995324000	0.938173000	-0.417339000
6	-2.739746000	1.432906000	-0.728904000
6	-1.599628000	0.704294000	-0.418865000

6	-4.105839000	-0.285802000	0.231459000
6	-2.967248000	-1.023154000	0.534635000
6	-1.708557000	-0.550070000	0.198059000
6	-0.478375000	-1.389978000	0.460517000
6	1.799765000	-0.542048000	-0.399879000
6	1.654783000	0.771096000	0.267624000
6	3.039863000	-1.025527000	-0.552000000
6	4.247957000	-0.324096000	-0.068435000
6	4.023113000	0.837473000	0.818392000
6	2.793234000	1.312878000	1.011413000
7	-0.305940000	1.134243000	-0.732919000
7	0.580465000	1.482002000	0.289827000
1	-2.634038000	2.397281000	-1.207449000
1	-3.090061000	-1.986402000	1.012465000
1	-0.006163000	-1.063446000	1.391108000
1	-0.812078000	-2.411399000	0.638146000
1	3.215408000	-2.009250000	-0.970597000
1	4.899934000	1.269315000	1.280728000
1	2.587545000	2.178296000	1.627388000
6	0.587659000	-1.416449000	-0.665777000
1	0.966229000	-2.435413000	-0.747371000
1	0.121607000	-1.178391000	-1.620028000
8	5.363415000	-0.728985000	-0.321153000
1	-4.885069000	1.505581000	-0.661835000
8	-5.306619000	-0.821959000	0.580301000
1	-6.014076000	-0.227234000	0.318237000
1	-0.035219000	1.416719000	-1.657729000

E(M06-2X): -800.545315
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.215707004322

Z-Diazocine quinone hydrazone tautomer *Z*-**4b**, optimized geometry (M06-2X/cc-pVTZ)

6	3.204511000	0.441778000	-1.231193000
6	2.253172000	1.335790000	-0.778265000
6	1.390792000	1.014534000	0.265717000
6	3.283468000	-0.812466000	-0.638674000
6	2.419644000	-1.140695000	0.394333000
6	1.473434000	-0.239116000	0.869588000
6	0.622592000	-0.664586000	2.038737000
6	-1.531169000	-0.078839000	0.813602000
6	-1.534168000	1.106636000	-0.063526000
6	-2.350067000	-1.096427000	0.513414000
6	-3.261342000	-1.094126000	-0.647038000
6	-3.380643000	0.181749000	-1.374726000
6	-2.595214000	1.214543000	-1.066319000
7	0.445380000	2.025911000	0.680517000
7	-0.725853000	2.109070000	-0.048735000
1	2.166162000	2.308509000	-1.246091000
1	2.501011000	-2.124862000	0.836733000
1	0.526863000	-1.750468000	1.994402000
1	1.157948000	-0.438566000	2.964354000
1	-2.425927000	-1.961823000	1.161491000
1	-4.123813000	0.226859000	-2.158614000
1	-2.643552000	2.157351000	-1.594673000

6	-0.777060000	-0.055078000	2.118202000
1	-1.353374000	-0.627266000	2.845326000
1	-0.720497000	0.968810000	2.478578000
8	-3.917849000	-2.072477000	-0.943236000
1	3.869410000	0.709457000	-2.042989000
8	4.181703000	-1.753588000	-1.028928000
1	4.707390000	-1.418406000	-1.759931000
1	0.883160000	2.931886000	0.593132000

E(M06-2X): -800.5671226
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.233330768498

Z-Diazocine *Z*-**4**, conformer 1, optimized geometry (M06-2X/cc-pVTZ)

1	2.534146000	1.096946000	1.844441000
6	2.369577000	0.639627000	0.874172000
6	2.009846000	-0.555856000	-1.594751000
6	1.549686000	-0.478510000	0.777190000
6	2.982018000	1.172237000	-0.252237000
6	2.801949000	0.571848000	-1.493458000
6	1.360994000	-1.056111000	-0.474341000
1	1.882561000	-1.055200000	-2.545690000
6	0.858043000	-1.064523000	1.973628000
1	0.826170000	-2.148501000	1.874594000
6	-0.567334000	-0.513899000	2.157786000
1	-0.507428000	0.433593000	2.693864000
1	-1.125802000	-1.197458000	2.802101000
7	0.615390000	-2.280177000	-0.590421000
7	-0.604201000	-2.295254000	-0.415287000
6	-1.359203000	-1.071843000	-0.235277000
6	-3.044536000	1.135430000	-0.171962000
6	-2.215552000	-0.799572000	-1.295612000
6	-1.368951000	-0.258746000	0.902218000
6	-2.221859000	0.841130000	0.903746000
6	-3.043433000	0.306715000	-1.285446000
1	-2.253938000	1.498013000	1.763052000
1	-3.689384000	0.516830000	-2.128972000
1	-2.218188000	-1.476336000	-2.139476000
1	1.429352000	-0.845217000	2.875258000
8	-3.834416000	2.239239000	-0.075512000
1	-4.350229000	2.337423000	-0.879935000
1	3.300314000	0.991495000	-2.355360000
8	3.783715000	2.270517000	-0.197567000
1	3.832230000	2.590820000	0.706775000

E(M06-2X): -800.5766665
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248092295171

Z-Diazocine *Z*-**4**, conformer 2, optimized geometry (M06-2X/cc-pVTZ)

1	2.536721000	1.172749000	1.801796000
6	2.374380000	0.674315000	0.851533000
6	2.021479000	-0.627239000	-1.564120000
6	1.548656000	-0.442774000	0.799169000
6	2.996219000	1.153081000	-0.293628000
6	2.818984000	0.499684000	-1.508273000

6	1.363966000	-1.074568000	-0.426327000
1	1.896685000	-1.167348000	-2.492823000
6	0.846437000	-0.970183000	2.016481000
1	0.804462000	-2.057065000	1.965693000
6	-0.573922000	-0.399035000	2.167497000
1	-0.504144000	0.578820000	2.645589000
1	-1.136840000	-1.037303000	2.853186000
7	0.615814000	-2.300501000	-0.491840000
7	-0.604146000	-2.306766000	-0.319340000
6	-1.361329000	-1.078043000	-0.195891000
6	-3.062215000	1.118332000	-0.242851000
6	-2.221762000	-0.859738000	-1.270432000
6	-1.374778000	-0.214326000	0.898895000
6	-2.238672000	0.880511000	0.844989000
6	-3.055092000	0.237162000	-1.316605000
1	-2.261135000	1.567681000	1.684246000
1	-3.706880000	0.419603000	-2.158614000
1	-2.218612000	-1.577245000	-2.080016000
1	1.414724000	-0.716144000	2.910963000
8	-3.899901000	2.188157000	-0.308256000
1	-3.817182000	2.713197000	0.491962000
1	3.324258000	0.878120000	-2.385085000
8	3.804423000	2.248021000	-0.282908000
1	3.855988000	2.603313000	0.608056000

E(M06-2X): -800.5764384
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248099762181

Z-Diazocine *Z*-**4**, conformer 3, optimized geometry (M06-2X/cc-pVTZ)

1	2.537174000	1.115858000	1.851973000
6	2.366399000	0.639958000	0.894871000
6	2.019515000	-0.572021000	-1.572579000
6	1.546018000	-0.473370000	0.795483000
6	2.989313000	1.163518000	-0.230835000
6	2.816075000	0.556422000	-1.468713000
6	1.362929000	-1.061179000	-0.455938000
1	1.898597000	-1.075370000	-2.522132000
6	0.839453000	-1.047640000	1.988778000
1	0.796940000	-2.131872000	1.897298000
6	-0.580590000	-0.479665000	2.153779000
1	-0.509937000	0.479898000	2.667203000
1	-1.148498000	-1.141150000	2.812821000
7	0.615009000	-2.284283000	-0.568097000
7	-0.605636000	-2.295855000	-0.400737000
6	-1.361634000	-1.071427000	-0.235344000
6	-3.054518000	1.130895000	-0.210813000
6	-2.218678000	-0.813732000	-1.303736000
6	-1.375557000	-0.246792000	0.889333000
6	-2.235193000	0.852445000	0.870603000
6	-3.048294000	0.286994000	-1.314137000
1	-2.257041000	1.510392000	1.732916000
1	-3.697849000	0.500294000	-2.150618000
1	-2.215967000	-1.503196000	-2.137360000
1	1.404258000	-0.825875000	2.893629000
8	-3.887414000	2.206079000	-0.241544000

1	-3.802224000	2.704378000	0.575390000
1	3.314498000	0.955376000	-2.343715000
8	3.771123000	2.264239000	-0.058366000
1	4.153335000	2.523257000	-0.900786000

E(M06-2X): -800.5768115
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248149622431

Z-Diazocine *Z*-**4**, conformer 4, optimized geometry (M06-2X/cc-pVTZ)

1	2.542485000	1.057328000	1.880824000
6	2.368780000	0.612487000	0.909471000
6	2.012628000	-0.517851000	-1.595123000
6	1.549157000	-0.497842000	0.777165000
6	2.986623000	1.173425000	-0.200993000
6	2.808699000	0.607406000	-1.457522000
6	1.361333000	-1.044149000	-0.492418000
1	1.888530000	-0.990212000	-2.560086000
6	0.849732000	-1.113380000	1.953978000
1	0.812902000	-2.194349000	1.827343000
6	-0.572849000	-0.558741000	2.144187000
1	-0.507762000	0.378611000	2.697052000
1	-1.137093000	-1.250339000	2.774771000
7	0.614306000	-2.263936000	-0.641939000
7	-0.605862000	-2.282155000	-0.471762000
6	-1.361139000	-1.063591000	-0.263175000
6	-3.047864000	1.140548000	-0.151141000
6	-2.218008000	-0.768684000	-1.317124000
6	-1.371473000	-0.276108000	0.892371000
6	-2.224934000	0.823143000	0.917673000
6	-3.046591000	0.336522000	-1.282658000
1	-2.256972000	1.460953000	1.791199000
1	-3.693454000	0.564278000	-2.120922000
1	-2.220839000	-1.427311000	-2.175238000
1	1.417575000	-0.918327000	2.863009000
8	-3.838623000	2.241390000	-0.030491000
1	-4.357747000	2.354173000	-0.830821000
1	3.303559000	1.035197000	-2.320867000
8	3.768819000	2.268044000	0.004558000
1	4.143585000	2.558068000	-0.831038000

E(M06-2X): -800.5767986
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -799.248223982909

E-Diazocine *E*-**4**, chair conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	-0.375327000	-1.870918000	1.744640000
6	-0.573805000	-0.811150000	1.647998000
6	-0.989900000	1.930708000	1.487449000
6	-1.866171000	-0.348154000	1.467795000
6	0.509326000	0.067936000	1.691340000
6	0.295829000	1.440916000	1.660632000
6	-2.032465000	1.042823000	1.330177000
1	-1.174700000	2.994300000	1.420888000

6	-3.058296000	-1.299399000	1.596060000
1	-3.706640000	-0.907219000	2.383647000
1	-2.647879000	-2.233281000	1.979016000
6	-3.958651000	-1.686702000	0.379721000
1	-4.317662000	-2.698589000	0.567275000
1	-3.336654000	-1.740646000	-0.514981000
7	-3.391270000	1.402168000	1.059749000
7	-3.700322000	0.911419000	-0.031825000
6	-5.073451000	0.536747000	-0.152363000
6	-7.563516000	-0.601005000	-0.273352000
6	-5.188997000	-0.839536000	0.088100000
6	-6.153317000	1.334723000	-0.447334000
6	-7.416039000	0.756593000	-0.515551000
6	-6.457132000	-1.391610000	0.032286000
1	-6.017372000	2.393474000	-0.617293000
1	-8.281906000	1.363602000	-0.749446000
1	-6.612799000	-2.446064000	0.218754000
8	-8.772506000	-1.225291000	-0.319380000
1	-9.457540000	-0.587587000	-0.535788000
1	0.375327000	-1.870917000	-1.744641000
6	0.573805000	-0.811149000	-1.647999000
6	0.989900000	1.930709000	-1.487448000
6	1.866171000	-0.348153000	-1.467795000
6	-0.509326000	0.067937000	-1.691339000
6	-0.295829000	1.440916000	-1.660631000
6	2.032465000	1.042824000	-1.330176000
1	1.174700000	2.994300000	-1.420887000
6	3.058296000	-1.299399000	-1.596060000
1	3.706640000	-0.907218000	-2.383647000
1	2.647879000	-2.233280000	-1.979016000
6	3.958651000	-1.686701000	-0.379721000
1	4.317662000	-2.698589000	-0.567276000
1	3.336654000	-1.740646000	0.514980000
7	3.391270000	1.402169000	-1.059748000
7	3.700322000	0.911419000	0.031826000
6	5.073451000	0.536747000	0.152363000
6	7.563516000	-0.601005000	0.273351000
6	5.188997000	-0.839536000	-0.088101000
6	6.153317000	1.334723000	0.447335000
6	7.416039000	0.756593000	0.515552000
6	6.457132000	-1.391610000	-0.032287000
1	6.017372000	2.393474000	0.617294000
1	8.281906000	1.363602000	0.749446000
1	6.612799000	-2.446064000	-0.218755000
8	8.772506000	-1.225291000	0.319380000
1	9.457540000	-0.587587000	0.535787000
8	-1.752015000	-0.461480000	-1.793322000
1	-1.140148000	2.113076000	-1.739858000
1	1.140148000	2.113075000	1.739859000
8	1.752015000	-0.461481000	1.793322000
1	2.397406000	0.121544000	1.350605000
1	-2.397406000	0.121545000	-1.350605000

E(M06-2X): -1601.14883657
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.475738899177

E-Diazocine *E*-**4**, twist conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	1.362625000	2.086344000	2.470256000
6	1.028404000	1.117927000	2.124254000
6	0.226296000	-1.382181000	1.219253000
6	1.906934000	0.292437000	1.446941000
6	-0.284894000	0.714715000	2.297278000
6	-0.690584000	-0.532925000	1.831880000
6	1.537353000	-0.984791000	1.000999000
1	-1.003728000	1.360710000	2.783454000
1	-0.117455000	-2.356406000	0.894491000
7	3.294906000	0.541795000	1.248376000
7	3.574202000	0.625958000	0.043876000
6	4.882210000	0.130936000	-0.217357000
6	7.273256000	-1.081284000	-0.828789000
6	5.061220000	-1.209743000	0.150173000
6	5.844742000	0.834373000	-0.921547000
6	7.057890000	0.238305000	-1.209849000
6	6.277193000	-1.798345000	-0.173989000
1	5.645408000	1.854716000	-1.219625000
1	6.450596000	-2.839106000	0.078413000
6	3.972369000	-2.037375000	0.830560000
1	3.977436000	-1.835594000	1.901996000
1	4.268798000	-3.080218000	0.717561000
6	2.515897000	-1.918180000	0.290533000
1	2.073934000	-2.913169000	0.335039000
1	2.555879000	-1.657337000	-0.769606000
8	-1.970685000	-0.967158000	1.963870000
1	-2.585679000	-0.241349000	1.740211000
1	-2.293753000	4.085619000	0.441122000
6	-1.681686000	3.298319000	0.022978000
6	-0.174528000	1.258882000	-1.103931000
6	-2.249408000	2.065979000	-0.252765000
6	-0.330133000	3.489149000	-0.194378000
6	0.432552000	2.456297000	-0.733795000
6	-1.522966000	1.032680000	-0.864374000
1	0.157782000	4.420141000	0.056278000
1	0.427302000	0.488125000	-1.572336000
7	-3.631838000	1.769552000	-0.114118000
7	-3.809504000	0.792318000	0.627891000
6	-4.937202000	0.021264000	0.224734000
6	-6.874386000	-1.702789000	-0.686456000
6	-4.791956000	-0.532705000	-1.058155000
6	-5.987482000	-0.316041000	1.054361000
6	-6.979392000	-1.165556000	0.590019000
6	-5.780929000	-1.400110000	-1.492829000
1	-6.038715000	0.099860000	2.051097000
1	-5.718246000	-1.867706000	-2.466633000
6	-3.583457000	-0.241984000	-1.945405000
1	-3.724716000	0.718487000	-2.442818000
1	-3.599100000	-0.994613000	-2.733129000
6	-2.165491000	-0.283415000	-1.300728000
1	-1.491985000	-0.713624000	-2.041895000
1	-2.171436000	-0.984686000	-0.463546000
8	1.757911000	2.672519000	-0.895452000
1	2.245371000	1.831698000	-0.907235000

1	-7.823133000	-1.419178000	1.219661000
1	7.840303000	0.767791000	-1.733669000
8	8.473913000	-1.634082000	-1.145419000
1	8.510458000	-2.538534000	-0.823355000
8	-7.802951000	-2.553952000	-1.198394000
1	-8.498748000	-2.700999000	-0.552451000

E(M06-2X): -1601.1576855
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.484712001321

TS for twofold H-transfer, *E*-Diazocine *E*-**4**, chair conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	0.204747000	-1.771760000	-1.721814000
6	0.406853000	-0.716739000	-1.588416000
6	0.803557000	2.042549000	-1.525914000
6	1.684320000	-0.265491000	-1.392834000
6	-0.711835000	0.161284000	-1.598402000
6	-0.467366000	1.562294000	-1.660210000
6	1.859703000	1.153481000	-1.265989000
1	1.008684000	3.104738000	-1.501915000
6	2.867758000	-1.222273000	-1.594909000
1	3.529456000	-0.761681000	-2.332541000
1	2.439785000	-2.096885000	-2.082695000
6	3.750283000	-1.762581000	-0.423731000
1	4.083249000	-2.761162000	-0.703431000
1	3.131107000	-1.867053000	0.468566000
7	3.094782000	1.613545000	-0.886069000
7	3.535828000	0.838056000	0.018727000
6	4.884235000	0.427978000	0.121266000
6	7.370272000	-0.712082000	0.197540000
6	4.990163000	-0.951628000	-0.099185000
6	5.976637000	1.236679000	0.351175000
6	7.235307000	0.657850000	0.395598000
6	6.256710000	-1.509044000	-0.057804000
1	5.842760000	2.298894000	0.498886000
1	8.110197000	1.266874000	0.585255000
1	6.406396000	-2.566420000	-0.230113000
8	8.576765000	-1.334338000	0.230891000
1	9.270010000	-0.693891000	0.411157000
1	-0.215594000	-1.818470000	1.730889000
6	-0.414881000	-0.760692000	1.610787000
6	-0.828508000	1.995127000	1.626811000
6	-1.691339000	-0.305863000	1.415774000
6	0.713536000	0.117991000	1.657168000
6	0.442573000	1.517738000	1.778280000
6	-1.873437000	1.112595000	1.313337000
1	-1.038893000	3.057169000	1.637156000
6	-2.879295000	-1.263001000	1.598102000
1	-3.539086000	-0.810022000	2.342225000
1	-2.455699000	-2.147298000	2.073387000
6	-3.769347000	-1.784947000	0.425847000
1	-4.126079000	-2.774621000	0.710471000
1	-3.148974000	-1.915190000	-0.461468000
7	-3.110878000	1.563064000	0.909957000
7	-3.504213000	0.803717000	-0.027336000

6	-4.859626000	0.421836000	-0.150879000
6	-7.362833000	-0.690755000	-0.267129000
6	-4.992022000	-0.954593000	0.079673000
6	-5.939889000	1.237528000	-0.413314000
6	-7.205651000	0.673548000	-0.479525000
6	-6.264571000	-1.497463000	0.020216000
1	-5.791755000	2.297263000	-0.566258000
1	-8.068854000	1.291339000	-0.694254000
1	-6.430773000	-2.551123000	0.201053000
8	-8.578498000	-1.298980000	-0.318474000
1	-9.257550000	-0.649035000	-0.516900000
8	1.904941000	-0.337030000	1.613235000
1	1.279704000	2.183339000	1.943799000
1	-1.313898000	2.225970000	-1.773422000
8	-1.908736000	-0.318318000	-1.578642000
1	-2.684273000	0.232255000	-0.793626000
1	2.813075000	0.279467000	0.652579000

E(M06-2X): -1601.1099338
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.434634465346

TS for twofold H-transfer, *E*-Diazocine *E*-**4**, twist conformer, π-dimer, optimized geometry (M06-2X/cc-pVTZ)

1	1.087950000	-1.605156000	2.894187000
6	0.863352000	-1.593419000	1.835197000
6	0.430534000	-1.600036000	-0.913748000
6	1.873438000	-1.182971000	0.946299000
6	-0.396906000	-1.833709000	1.369844000
6	-0.684857000	-1.737642000	-0.029850000
6	1.682809000	-1.280841000	-0.464834000
1	-1.212710000	-2.065935000	2.041844000
1	0.234326000	-1.716780000	-1.972540000
7	3.087050000	-0.743028000	1.408445000
7	3.485467000	0.256223000	0.724431000
6	4.868744000	0.295984000	0.413375000
6	7.464095000	0.259201000	-0.491801000
6	5.242085000	-0.689342000	-0.505971000
6	5.751812000	1.271545000	0.841334000
6	7.062151000	1.247976000	0.398831000
6	6.557776000	-0.693160000	-0.947519000
1	5.414518000	2.034285000	1.529192000
1	6.880332000	-1.438400000	-1.666902000
6	4.230583000	-1.700102000	-1.025098000
1	4.090806000	-2.482532000	-0.275708000
1	4.684766000	-2.186633000	-1.887728000
6	2.836401000	-1.167417000	-1.462638000
1	2.528988000	-1.756132000	-2.326800000
1	2.922308000	-0.138618000	-1.816366000
8	-1.878741000	-1.780603000	-0.478671000
1	-2.788801000	-0.915681000	0.180899000
1	-1.068659000	1.534169000	2.916242000
6	-0.845661000	1.537458000	1.857362000
6	-0.419987000	1.577523000	-0.893816000
6	-1.863475000	1.157935000	0.961543000
6	0.417606000	1.758673000	1.392878000

6	0.686386000	1.692693000	-0.006273000
6	-1.674958000	1.261859000	-0.450707000
1	1.241586000	1.957141000	2.064904000
1	-0.218143000	1.696752000	-1.950764000
7	-3.075896000	0.736818000	1.429974000
7	-3.505953000	-0.246061000	0.739014000
6	-4.886742000	-0.271099000	0.409887000
6	-7.470697000	-0.201408000	-0.512002000
6	-5.242041000	0.719088000	-0.514689000
6	-5.778429000	-1.233068000	0.838573000
6	-7.087042000	-1.192189000	0.384356000
6	-6.550726000	0.740594000	-0.964993000
1	-5.454141000	-1.998101000	1.529701000
1	-6.879460000	1.477909000	-1.685343000
6	-4.212216000	1.715243000	-1.023026000
1	-4.066895000	2.492547000	-0.269104000
1	-4.653861000	2.211735000	-1.885718000
6	-2.824402000	1.160297000	-1.452420000
1	-2.504599000	1.738686000	-2.318488000
1	-2.917587000	0.129332000	-1.798907000
8	1.885683000	1.746959000	-0.469920000
1	2.691851000	1.013667000	0.137225000
1	-7.805813000	-1.929322000	0.719448000
1	7.783107000	1.983591000	0.724353000
8	8.759682000	0.279816000	-0.902639000
1	8.919949000	-0.448362000	-1.508533000
8	-8.734934000	-0.110740000	-0.997963000
1	-9.275795000	-0.817271000	-0.635159000

E(M06-2X): -1601.1184814
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.444796272170

E-Diazocine quinone hydrazone tautomer *E*-**4b**, chair conformer, π-dimer, NH *endo*, optimized geometry (M06-2X/cc-pVTZ)

1	-0.639602000	-2.273006000	1.702015000
6	-0.708776000	-1.205189000	1.535772000
6	-0.772586000	1.602344000	1.660081000
6	-1.877843000	-0.621196000	1.213374000
6	0.527735000	-0.450810000	1.765334000
6	0.392551000	1.000866000	1.931895000
6	-1.885695000	0.852139000	1.108402000
1	-0.896388000	2.676374000	1.708863000
6	-3.170103000	-1.429056000	1.341867000
1	-3.755695000	-0.936472000	2.123237000
1	-2.858419000	-2.386636000	1.756521000
6	-4.133343000	-1.746334000	0.163316000
1	-4.615270000	-2.694773000	0.396928000
1	-3.556472000	-1.911882000	-0.748843000
7	-2.827002000	1.544868000	0.536416000
7	-3.479437000	0.844132000	-0.423775000
6	-4.870114000	0.607411000	-0.310925000
6	-7.537081000	-0.053824000	-0.087254000
6	-5.222189000	-0.720333000	-0.051591000
6	-5.827428000	1.595739000	-0.436974000
6	-7.168785000	1.266221000	-0.315923000

6	-6.567116000	-1.041823000	0.044046000
1	-5.519728000	2.613995000	-0.629258000
1	-7.929186000	2.031775000	-0.410596000
1	-6.885635000	-2.057517000	0.237844000
8	-8.838005000	-0.440051000	0.026424000
1	-9.411083000	0.323326000	-0.081042000
1	0.639602000	-2.273006000	-1.702016000
6	0.708776000	-1.205188000	-1.535772000
6	0.772586000	1.602345000	-1.660080000
6	1.877843000	-0.621195000	-1.213374000
6	-0.527735000	-0.450809000	-1.765334000
6	-0.392551000	1.000867000	-1.931894000
6	1.885696000	0.852140000	-1.108402000
1	0.896388000	2.676375000	-1.708862000
6	3.170103000	-1.429056000	-1.341867000
1	3.755695000	-0.936472000	-2.123237000
1	2.858419000	-2.386636000	-1.756522000
6	4.133343000	-1.746334000	-0.163316000
1	4.615270000	-2.694773000	-0.396928000
1	3.556472000	-1.911882000	0.748842000
7	2.827002000	1.544868000	-0.536415000
7	3.479437000	0.844132000	0.423776000
6	4.870114000	0.607411000	0.310926000
6	7.537081000	-0.053824000	0.087253000
6	5.222189000	-0.720333000	0.051590000
6	5.827428000	1.595739000	0.436974000
6	7.168785000	1.266221000	0.315923000
6	6.567116000	-1.041823000	-0.044047000
1	5.519728000	2.613994000	0.629259000
1	7.929186000	2.031775000	0.410597000
1	6.885635000	-2.057517000	-0.237845000
8	8.838005000	-0.440051000	-0.026425000
1	9.411083000	0.323326000	0.081041000
8	-1.614243000	-1.013217000	-1.862770000
1	-1.275349000	1.545722000	-2.238763000
1	1.275349000	1.545721000	2.238763000
8	1.614243000	-1.013218000	1.862770000
1	2.965340000	0.035298000	0.766662000
1	-2.965340000	0.035299000	-0.766661000

E(M06-2X): -1601.1283528
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.459005173977

E-Diazocine quinone hydrazone tautomer *E*-**4b**, twist conformer, π-dimer, NH *endo*, optimized geometry (M06-2X/cc-pVTZ)

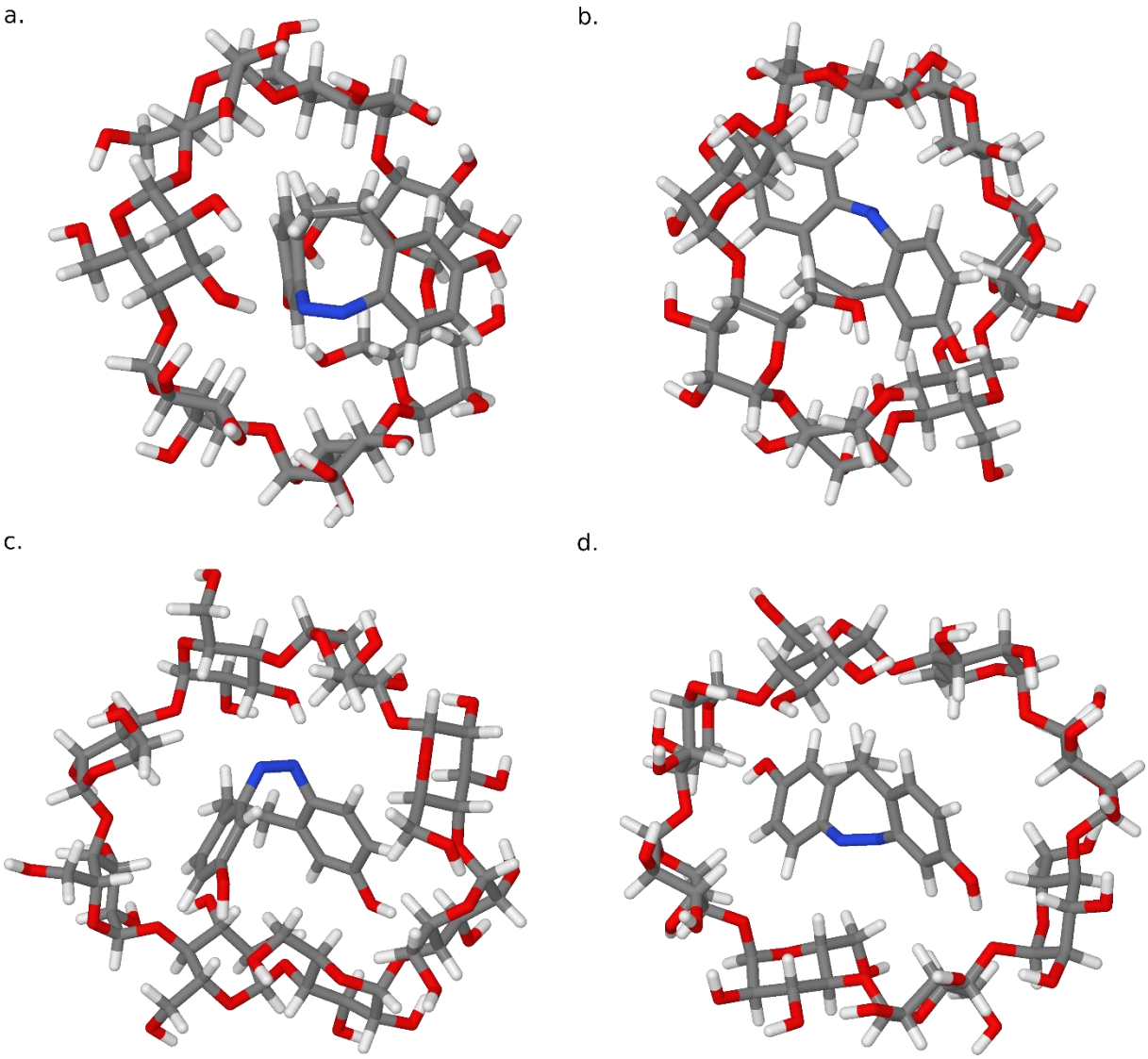
1	-0.966869000	1.692368000	2.471877000
6	-0.820711000	1.634109000	1.401168000
6	-0.712115000	1.486639000	-1.400459000
6	-1.876731000	0.980975000	0.646349000
6	0.325395000	1.998045000	0.812669000
6	0.492686000	1.830576000	-0.635573000
6	-1.842814000	1.047211000	-0.822319000
1	1.171609000	2.383176000	1.365558000
1	-0.642686000	1.620971000	-2.473043000
7	-2.804352000	0.400951000	1.348021000

7	-3.465955000	-0.605934000	0.717989000
6	-4.876135000	-0.436559000	0.573652000
6	-7.598079000	-0.109543000	0.231578000
6	-5.332726000	0.554736000	-0.296266000
6	-5.765978000	-1.256745000	1.249950000
6	-7.129369000	-1.098253000	1.088340000
6	-6.705585000	0.703715000	-0.456630000
1	-5.370173000	-2.017293000	1.908325000
1	-7.086809000	1.462255000	-1.132379000
6	-4.386166000	1.469550000	-1.046978000
1	-4.103944000	2.295982000	-0.389007000
1	-4.954250000	1.918242000	-1.861109000
6	-3.100908000	0.853358000	-1.653179000
1	-2.908173000	1.357874000	-2.599334000
1	-3.252813000	-0.196482000	-1.907038000
8	1.575114000	1.997328000	-1.187643000
1	2.994004000	0.978547000	-0.104301000
1	0.969457000	-1.703160000	2.465025000
6	0.821671000	-1.640953000	1.394773000
6	0.709580000	-1.484190000	-1.406273000
6	1.876799000	-0.985108000	0.640596000
6	-0.325212000	-2.002705000	0.806663000
6	-0.494390000	-1.829263000	-0.640702000
6	1.841452000	-1.047377000	-0.828537000
1	-1.170572000	-2.390118000	1.359283000
1	0.638641000	-1.615373000	-2.479140000
7	2.803755000	-0.406215000	1.343467000
7	3.466479000	0.602070000	0.715324000
6	4.876273000	0.430594000	0.569339000
6	7.596590000	0.099797000	0.217994000
6	5.333745000	-0.560134000	-0.306403000
6	5.764529000	1.246294000	1.246356000
6	7.130119000	1.084769000	1.079127000
6	6.702447000	-0.711136000	-0.471820000
1	5.371816000	2.005195000	1.908345000
1	7.100993000	-1.459976000	-1.143825000
6	4.384009000	-1.471700000	-1.056934000
1	4.101677000	-2.298261000	-0.399222000
1	4.951254000	-1.920139000	-1.871373000
6	3.098817000	-0.852543000	-1.660172000
1	2.904632000	-1.354185000	-2.607525000
1	3.251192000	0.197864000	-1.911709000
8	-1.578231000	-1.991345000	-1.191503000
1	-2.992327000	-0.983856000	-0.100457000
1	7.828641000	1.719656000	1.610073000
1	-7.840577000	-1.723808000	1.607817000
8	-8.944816000	0.014200000	0.095173000
1	-9.145085000	0.729356000	-0.514288000
8	8.921631000	-0.113487000	0.001820000
1	9.438123000	0.506553000	0.523206000

E(M06-2X): -1601.1389457
E(DLPNO-CCSD(T)/cc-pVTZ//M06-2X): -1598.479308858603

8.2 Calculations of diazocine 3 in the presence of cyclodextrins

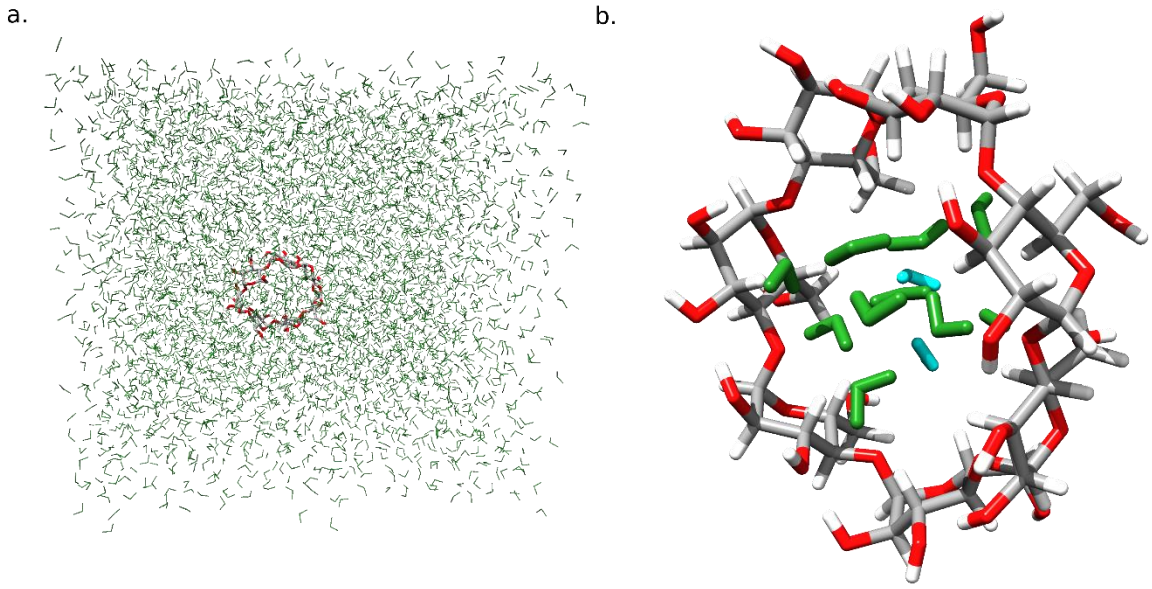
The structures of all diazocine **3**/cyclodextrin host/guest systems were obtained by geometry optimizations in two stages. Pre-optimizations were caried out with xtb[19] and the GFN2-xtb method.[20] The resulting structures were refined using ORCA[15] at the ωB97X-D3[21]/def2-SVP[22] level of theory with Grimme's dispersion correction[23] as well as an auxiliary basis set[24] and the RIJCOSX approximation for Coulomb and HF Exchange[25]. While it was possible to obtain geometries for the β- and γ- cyclodextrin inclusion compounds, no viable structure could be obtained for the system with α-cyclodextrin because its cavity is too small to accommodate the dihydroxy diazocines. The optimized geometries are displayed in Supplementary figure 80. The *.xyz files are listed at the end of this section.



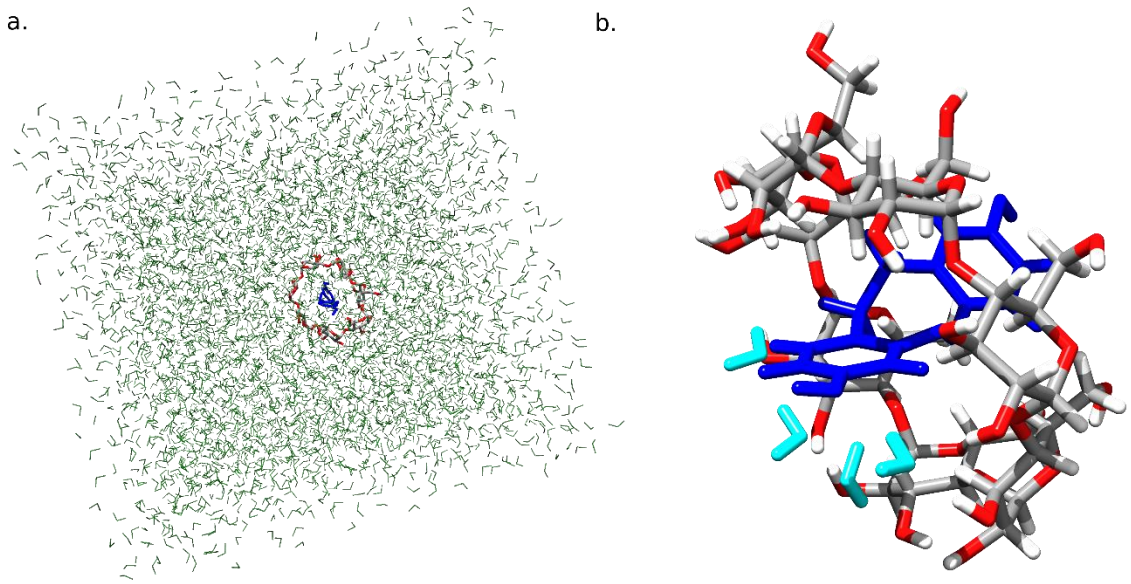
Supplementary figure 80. Geometries of the (*Z/E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol **(3)** complex with β- (**a** and **b**) and γ- cyclodextrine (**c** and **d**). Optimizations were carried out for *Z*-isomers (**a**, **c**) and *E*-isomers (**b**, **d**) at the ωB97X-D3/def2-SVP level of theory with D3 dispersion correction.

While high level DFT calculations provide an impression of the host/guest proportions, molecular dynamics (MD) calculations including explicit water molecules are necessary to provide more insight into the mechanism of the thermochemical back-isomerizations. Whereas the slow *E*→*Z* mechanism is well described in vacuo, and theoretically predicted activation barriers agree well with kinetic data from experiments, the fast tautomerization mechanism can only be operative in the presence of water

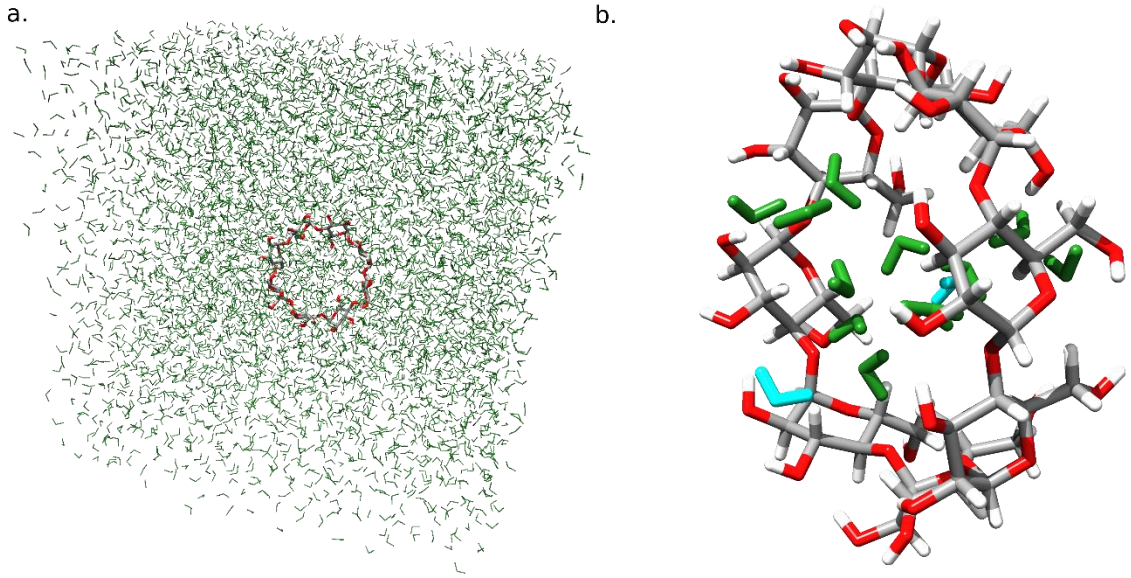
(or protic solvents). MD calculations should reveal if there is sufficient space available inside the cyclodextrin cavities for water to intrude and to support the tautomerization mechanism in a similar way as it operates in solution. Towards this end molecular dynamics (MD) simulations were performed utilizing the OpenMM toolkit[26]. Starting geometries of the host/guest structures of diazocine **3** in *E* configuration with β- and γ-cyclodextrin were taken from the above DFT calculations. Parameters for the individual molecules were assigned with the antechamber and tleap tool provided with Ambertools 21[27], as well as the GAFF2 forcefield[28]. An initial box with TIP3P water molecules was constructed with tleap providing at least 2 nm distance for each atom of the complex to a face of said box. The initial structure was first minimized and afterwards propagated for 500 ps at 300K with a friction of 1/ps. To achieve a realistic density within the periodic system a barostat was used (1 bar, 300K). The constructed systems for β- and γ- cyclodextrin and their corresponding host/guest systems with the *trans*-diazocine **3** after 500ps are shown below. The OpenMM simulation protocol used is provided below for more details.



Supplementary figure 81. MD calculation for β-cyclodextrin in a periodic TIP3P water-box after a simulation time of 500 ps at 300 K, 1bar. **(a)** Complete simulation-box. Water molecules are represented as wireframes. **(b)** β-Cyclodextrin with water molecules inside the cavity. Water molecules that are not within the ring cavity are removed for better visibility. Water molecules inside the cavity are colored in green to further improve visibility, water molecules that are located only partially within the cavity are colored in cyan. Under these boundary conditions of the simulation and after 500 ps simulation time, 11 water molecules are located within the cavity, counting partially included water molecules (cyan) as 0.5 water. The number of water molecules inside the cavity is in good agreement with experimental data.

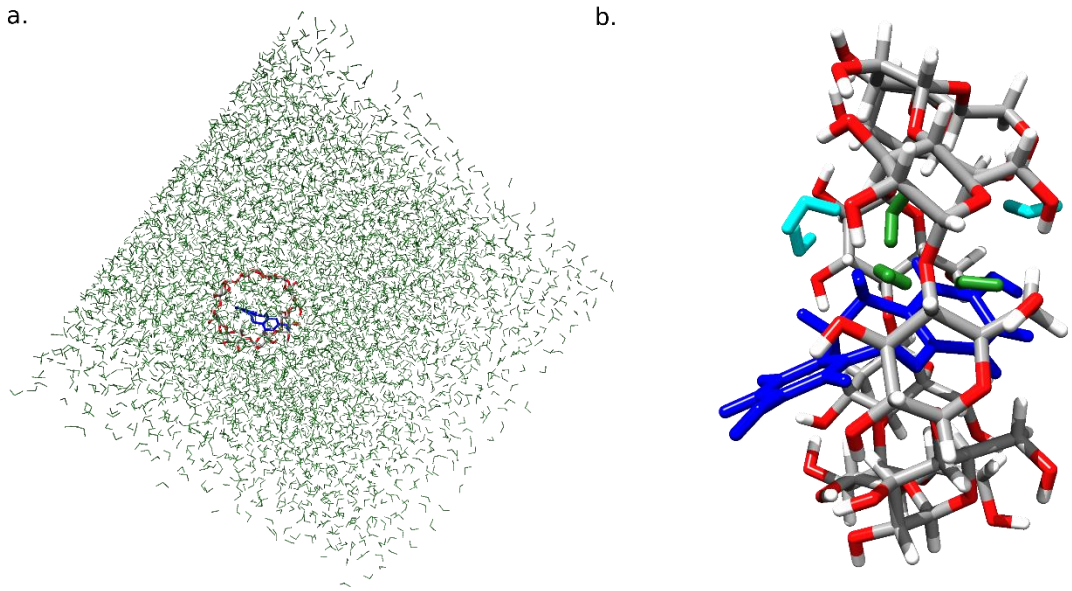


Supplementary figure 82. MD calculation for the complex of β-cyclodextrin including (*E*)-**3**. The MD calculation was performed in a periodic TIP3P water-box and the snapshots were taken after a trajectory propagation of 500 ps at 300 K, 1bar. **(a)** Complete simulation-box. Water molecules are represented as wireframes. **(b)** β-Cyclodextrin with water molecules at the brim and (*E*)-**3** (coloured in blue) inside the cavity. Water molecules that are not within the ring cavity are removed for better visibility. Water molecules that are located only partially within the cavity are colored in cyan. Under above boundary conditions of the simulation, 4 water molecules are present at the edge of the cavity and no water molecule is located inside the cavity. Since there is no water molecule interacting with the azo group, the fast tautomerization process is inhibited as long as the diazocine stays inside the cavity, and back-isomerization can only proceed via the slow nitrogen inversion process. This is in agreement with our experimental finding that the back-isomerization is drastically slowed down in the presence of β-cyclodextrin.



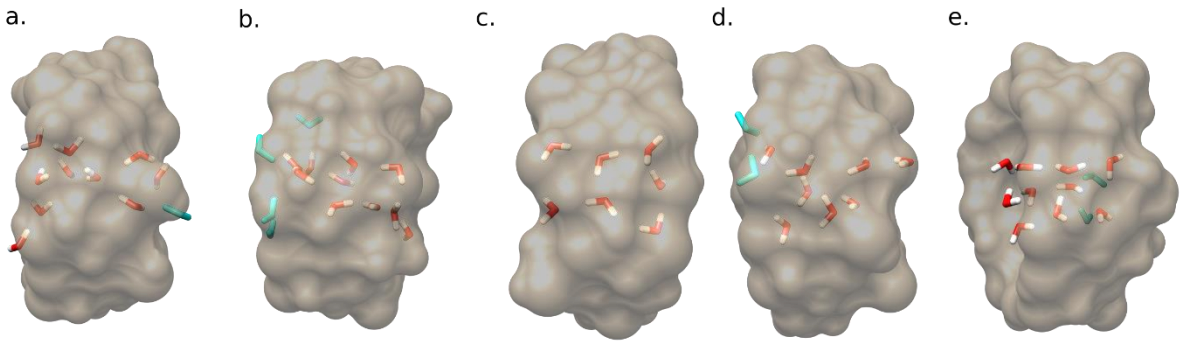
Supplementary figure 83. MD calculation for γ-cyclodextrin in a periodic TIP3P water-box after a simulation time of 500 ps at 300 K, 1bar. **(a)** Complete simulation-box. Water molecules are represented as wireframes. **(b)** β-Cyclodextrin with water molecules inside the cavity. Water molecules

that are not within the ring cavity are removed for better visibility. Water molecules inside the cavity are colored in green to further improve visibility, water molecules that are located only partially within the cavity are colored in cyan. Under these boundary conditions of the simulation and after 500 ps simulation time, 13 water molecules are located within the cavity, counting partially included water molecules (cyan) as 0.5 water.



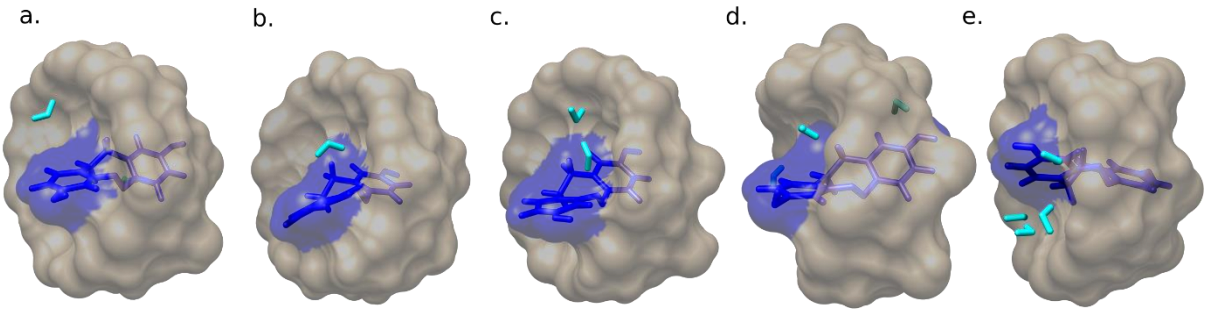
Supplementary figure 84. MD calculation for the complex of γ-cyclodextrin including (*E*)-**3**. The MD calculation was performed in a periodic TIP3P water-box and the snapshots were taken after a trajectory propagation of 500 ps at 300 K, 1bar. **(a)** Complete simulation-box. Water molecules are represented as wireframes. **(b)** β-Cyclodextrin with water molecules and (*E*)-**3** inside the cavity. Water molecules that are not within the ring cavity are removed for better visibility. Water molecules inside the cavity are in green and those located only partially within the cavity are colored in cyan. Under above boundary conditions of the simulation, 3 water molecules are completely inside the cavity and 3 water molecules are partially inside. Hence, the azo group is not fully protected from water and a tautomerization process might be hindered, but it may not be completely impossible.

For a statistical analysis, five snapshots (a-e) during each trajectory were recorded (see Supplementary figure 85).

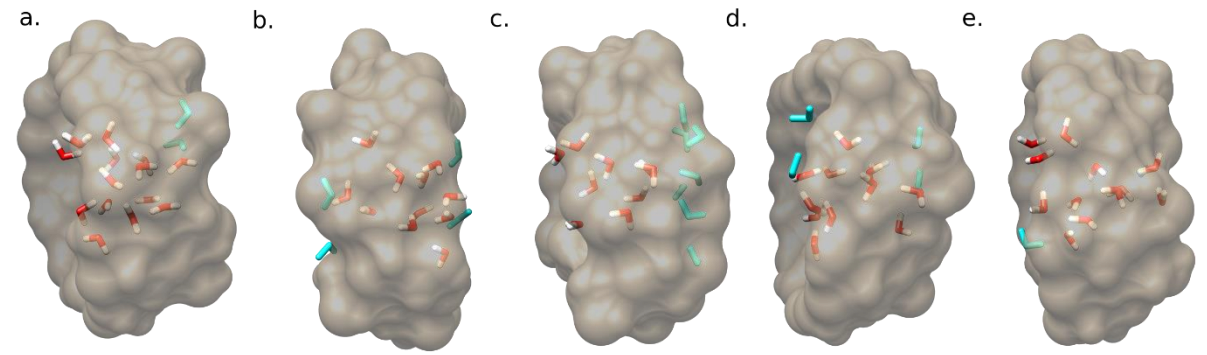


Supplementary figure 85. Snapshots during a molecular dynamic (MD) run of β-cyclodextrin in a periodic TIP3P water-box after propagation for **(a)** 100, **(b)** 200, **(c)** 300, **(d)** 400 and **(e)** 500 ps at 300 K, 1bar. Water molecules located inside the cyclodextrin are colored by element, while water molecules that lie only partially in the cyclodextrin cavity are colored cyan. Partial water molecules are

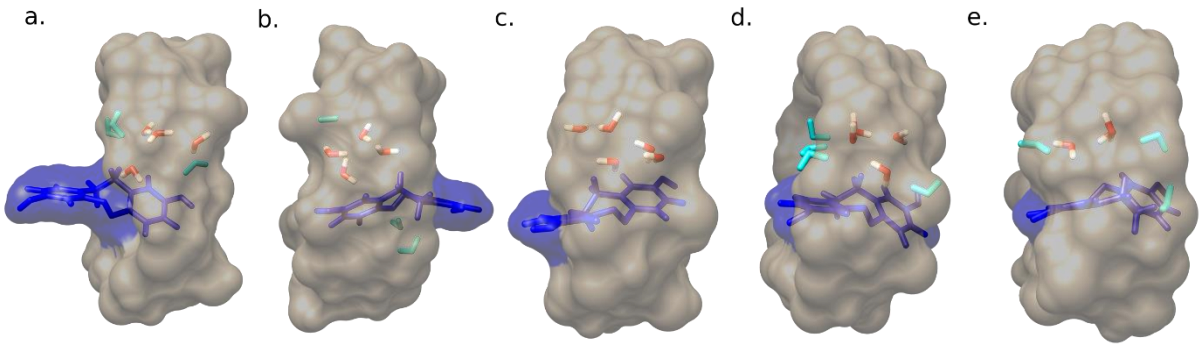
counted as 0.5 water. The numbers of water molecules present in the cyclodextrin cavity are: **(a)** 10.5, **(b)** 12, **(c)** 7, **(d)** 9, **(e)** 11.



Supplementary figure 86. Snapshots during an MD simulation for the complex of β-cyclodextrin and (*E*)- **3** in a periodic TIP3P water-box after propagation for **(a)** 100, **(b)** 200, **(c)** 300, **(d)** 400 and **(e)** 500 ps at 300 K, 1bar. Water molecules fully encapsulated by the cyclodextrin are colored by element, while water molecules that lie only partially in the cyclodextrin cavity are colored cyan. Partial water molecules were counted as 0.5 water. The numbers of water molecules present within the cyclodextrin cavity are: **(a)** 1, **(b)** 0.5, **(c)** 1, **(d)** 1.5, **(e)** 2. None of the water molecules in snapshots a-e is completely inside the cavity and in contact with the azo group of (*E*)- **3.**



Supplementary figure 87. MD system for γ-cyclodextrin in a periodic TIP3P water-box after propagation for **(a)** 100, **(b)** 200, **(c)** 300, **(d)** 400 and **(e)** 500 ps at 300 K, 1bar. Water molecules fully included in the cyclodextrin are colored by element, while water molecules that lie only partially in the cyclodextrin cavity are colored cyan. Partial water molecules are counted as 0.5 water. The numbers of water molecules present within the cyclodextrin cavity are: **(a)** 15, **(b)** 13, **(c)** 12.5, **(d)** 14, **(e)** 13.



Supplementary figure 88. MD system for γ-cyclodextrin/(*E*)-**3** host/guest system in a periodic TIP3P water-box after propagation for **(a)** 100, **(b)** 200, **(c)** 300, **(d)** 400 and **(e)** 500 ps at 300 K, 1bar. Water

molecules fully enveloped by the cyclodextrin are colored by element, while water molecules that lie only partially in the cyclodextrin cavity were colored cyan. Partial water molecules were counted as 0.5 water. The numbers of water molecules present within the cyclodextrin cavity are: **(a)** 5.5, **(b)** 4.5, **(c)** 5, **(d)** 6, **(e)** 4.5.

For β-cyclodextrin in water (Supplementary figure 85) an average of approx. 11 water (rounded from 10.63) molecules were present within the β-cyclodextrin cavity when excluding the structure at 300 ps (Supplementary figure 85 c) as an outlier. (approx. 10 water rounded from 9.9 when including c). For the β-cyclodextrin/(*E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol **(3)** complex an average of 1 water molecule (rounded down from 1.2) is present at the edge of the cyclodextrin cavity (Supplementary figure 86). It is, however, noteworthy that water molecules only enter the cavity partially.

In contrast γ-cyclodextrin exhibits a much larger cavity (Supplementary figure 80 c, d). An average of approx. 14 water (rounded from 13.5) molecules were present within the γ-cyclodextrin cavity (Supplementary figure 87). Assigning the inside/outside of the cavity attribute to water molecules becomes more challenging with larger ring sizes (due to increased flexibility). This led to an increased number of partially assigned water molecules. For the γ-cyclodextrin/(*E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol **(3)** host/guest system (Supplementary figure 76) at least 3 water molecules were present in every analyzed frame. Accounting for partial water molecules led to an average of 5 water molecules (rounded from 5.1) present within the cavity of the host/guest system.

The MD simulations clearly show the spatial dimensions of β- and γ-cyclodextrin and their capability to accommodate water in their cavities when a diazocine is bound at the same time. Water is present within the cavity of the γ-cyclodextrin/(*E*)-**3** host/guest system in every frame of the MD simulation while no water molecule could be observed fully included in the cavity of the β-cyclodextrin/(*E*)-**3** host/guest system.

Summing up: our molecular dynamics calculations predict a complete shutdown of the back-isomerization mechanism via the fast tautomerization process if the diazocine **3** is bound inside the cavity of β-cyclodextrin. Re-isomerization can only proceed either via the slow classical N-inversion process or by leaving the cavity. This agrees with the experimental finding that the back-isomerization dramatically slows down upon adding β-cyclodextrin to the solution of the diazocine (*E*)-**3**. γ-Cyclodextrin is less efficient in slowing down the reaction either because it allows water to enter the cavity or because the binding constant to the diazocine (*E*)-**3** is lower.

OpenMM simulation protocol:

```
from openmm.app import *
from openmm import *
from openmm.unit import *

from openff.toolkit.topology import Molecule

#load Aberfiles
print('Definition')
prmtop = AmberPrmtopFile('inputbox.prmtop')
inpcrd = AmberInpcrdFile('inputbox.inpcrd')
#define System from Amberfiles (prmtop contains topology and parameters)
system = prmtop.createSystem(nonbondedMethod=PME, nonbondedCutoff=1*nanometer,
    constraints=HBonds)

#Minimization
print('Starting minimization')
integrator = VerletIntegrator(0.001*picoseconds)
simulation = Simulation(prmtop.topology, system, integrator)
simulation.context.setPositions(inpcrd.positions)
```

```
simulation.context.setPeriodicBoxVectors(*inpcrd.boxVectors)
simulation.minimizeEnergy(maxIterations=100)
print('Saving to output_minimization.pdb')
positions = simulation.context.getState(getPositions=True).getPositions()
PDBFile.writeFile(simulation.topology, positions, open('output_minimization.pdb', 'w'))


#Propagate the System
time_step = 1 *femtoseconds  # simulation timestep
temperature = 300 * kelvin  # simulation temperature
friction = 1 / picosecond  # collision rate
integrator = LangevinIntegrator(temperature, friction, time_step)

# Length of the simulation.
num_steps = 500000  # number of integration steps to run

# Logging options.
trj_freq = 100  # number of steps per written trajectory frame
data_freq = 100  # number of steps per written simulation statistics

#Adding a barostat
barostat = MonteCarloBarostat(1, 300)
system.addForce(barostat)

# Set up an OpenMM simulation.
simulation = Simulation(prmtop.topology, system, integrator)

# Set the initial positions.
simulation.context.setPositions(positions)

#initial Periodic Box from Amberfile
simulation.context.setPeriodicBoxVectors(*inpcrd.boxVectors)

# Randomize the velocities from a Boltzmann distribution at a given temperature.
simulation.context.setVelocitiesToTemperature(temperature)

# Configure the output files.
pdb_reporter = PDBReporter("trajectory.pdb", trj_freq)
state_data_reporter = StateDataReporter(
   "data.csv",
   data_freq,
   step=True,
  potentialEnergy=True,
   temperature=True,
   density=True,
)
simulation.reporters.append(pdb_reporter)
simulation.reporters.append(state_data_reporter)

import time

print("Starting simulation")
start = time.process_time()

# Run the simulation
simulation.step(num_steps)

end = time.process_time()
print("Elapsed time %.2f seconds" % (end - start))
print("Done!")
```

Xyz file β-cyclodextrin/ (*Z*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol (3):

```
177
 ENERGY = -5071.094177386979 Input = wB97X-D3 def2-SVP def2/J D3ZERO RIJCOSX OPT
 C  1.48042243540408    22.70378711612064    6.45080839830643
 H  0.79525364927199    23.35184444416216    7.02116308234714
 H  1.26962784655446    21.66225269385605    6.73825527448504
 C  1.12634099085398    22.88772218336619    4.97067320921330
 H  0.44234747367488    22.07699919421664    4.66505986681346
 C  2.33293625852138    22.86536449329452    4.03735362797898
 H  3.05745315725920    23.62811389167679    4.36939484692284
 C  1.88214079083858    23.11737838233919    2.61053374161194
 H  1.19469972631640    22.29679878896470    2.35447974242393
 C  1.07619079527387    24.39201524428782    2.47760489821938
 H  1.71009379164101    25.26946983753133    2.70265852952732
 C -0.05886513218030    24.32378959091628    3.51177477542316
 H -0.62893771382329    25.26692198501959    3.53970198322070
 C -2.89114655886911    23.62590300337365    5.42208159148910
 H -3.38386063833191    23.07786713829730    6.24744175496674
```

H	-1.82781092829676	23.74396817732692	5.67733706483981
C	-3.01593126514518	22.80006251980123	4.15340341786436
H	-2.62073841346469	21.78182784256392	4.32349292307514
C	-2.25958987028160	23.41248180826054	2.97399373537184
H	-2.52145711173144	24.48244728664669	2.89249338570817
C	-2.59304217236930	22.69928006857261	1.67572124240354
H	-2.19072772409806	21.67061890790903	1.75693226610805
C	-4.09145298470055	22.60804605763456	1.49033221603457
H	-4.48635191265457	23.63543513307995	1.37609339053167
C	-4.75655989872280	22.00996366587852	2.72657308558202
H	-5.85092349826218	22.09529785496603	2.63497147634789
C	-4.42750361250687	19.21582890639885	5.47887854781901
H	-3.80099415301717	20.09406415563822	5.26377231575482
H	-5.28543990328900	19.56302068254705	6.08975040698081
C	-4.96873678902118	18.69873064162547	4.15775493114730
H	-4.17242692861306	18.09039741837234	3.69241607581147
C	-5.42761474468227	19.77071735659773	3.17196648844225
H	-6.27400332155848	20.31479672727232	3.63112323900921
C	-5.89271251357194	19.09231145341229	1.88623723628153
H	-5.02419447005595	18.54482293385014	1.47053921420614
C	-6.98626208741788	18.08448962853089	2.19712292388314
H	-7.86408297032260	18.65615895513387	2.55775041115422
C	-6.56743680492454	17.14713395730353	3.32903711870847
H	-7.44514943069484	16.58180794089325	3.68758612317317
C	-5.52763475001657	15.15033481347608	5.79007302993637
H	-6.06027164391393	14.29140875316433	6.23534266599973
H	-6.25550372752158	15.94275985682009	5.58558600455848
C	-4.86323527832473	14.66294653018822	4.50598474050857
H	-3.90505739563406	15.20095201033993	4.41047432785667
C	-5.63279894457550	14.91743599103227	3.20965518701642
H	-6.68231747048192	14.57868306788268	3.31068966910524
C	-5.02082191428297	14.20994940949506	2.00058330585188
H	-4.03673683325656	14.69194931354233	1.81921020323330
C	-4.74659839198126	12.74231823564930	2.30091810296020
H	-5.71147603417935	12.22383072924041	2.42851298495948
C	-3.97323010077063	12.65105985221171	3.62451257581748
H	-3.83785899916857	11.59729721193018	3.91648355791776
C	-1.66953223377862	11.74417000505344	5.82600647238089
H	-1.09439596181075	11.80376675911790	6.76958371860737
H	-2.61634359548183	12.28256050046258	5.97813782354277
C	-0.87185998049151	12.44647643392591	4.74655804140889
H	-0.70768247945087	13.49030282098318	5.05704302289732
C	-1.57322062155598	12.46160605464642	3.38379214232757
H	-1.84705789418510	11.43056061547586	3.10067021150373
C	-0.66050080829809	13.03120255571690	2.31590394637000
H	-0.45203637552810	14.08992461598417	2.55881788805801
C	0.66948687672869	12.28916162566063	2.31933955684866
H	0.47156743553850	11.22232081924110	2.10300214019488
C	1.25627647406926	12.35851799926580	3.72979998059529
H	2.19861456027984	11.79033290830716	3.79276952237402
C	1.72502659153175	14.44989892434918	6.93888811195729
H	1.45933314553351	15.25339248175368	7.65290858232651
H	0.79100501541717	13.97657197112471	6.60583252197831
C	2.41046117141585	15.08737412187442	5.74332815527875
H	1.78429588450280	15.90188145702502	5.33640947580302
C	2.69233105289199	14.07235490570106	4.63279899074021
H	3.17911122773741	13.19090937927922	5.08786226576120
C	3.60340505141022	14.67012142460426	3.57976967198123
H	3.07725062359836	15.52634229693421	3.11524839517704
C	4.87970818111768	15.17718432655738	4.23152124332637
H	5.38294993801392	14.32740698190445	4.72337212271190
C	4.49805795436289	16.18651758710447	5.31646269346175
H	5.39541758821818	16.50858784149325	5.87201588586008
C	3.42108848295773	18.97373243913125	7.14468762321538
H	3.10391724292897	17.91589388133494	7.11974041378843
H	4.40054427509487	19.03407824404625	7.65633974269372
C	3.58351815373436	19.46429936773395	5.72622219286650
H	2.58176689648298	19.54254993987643	5.26943854780013
C	4.44586088822735	18.56327642043473	4.83645362534326
H	5.46572042740458	18.49571102723192	5.26339827495860
C	4.53030549173425	19.18973208315213	3.45140403315093
H	3.50548486267616	19.19887379304197	3.03661163355041
C	5.05206816502850	20.61521488722981	3.55600045540588
H	6.09134223892332	20.57040535950533	3.92225847973009
C	4.21707168251216	21.42548414259678	4.55588702339318
H	4.68553369503471	22.40263394421855	4.76025058101157
O	2.80573518223137	23.03610391265943	6.77646315981002
H	3.28648292167713	22.20202581879166	6.86447495864524
O	2.97581993465511	23.13328688877376	1.70837732509889
H	3.59939242722111	22.43099714625454	1.97131739855946
O	0.50163298249435	24.50639953929627	1.19647386170667
H	1.13272922076477	24.19926441907666	0.53258706515054
O	0.46974851896558	24.14103070724508	4.79385283303552
O	-0.87226727221238	23.25632214180538	3.15506526578988
O	-3.43310096766219	24.90769517288885	5.24772281056888
H	-4.33535158402312	24.77832929999620	4.93203909457537
O	-2.07706292722133	23.35652502693581	0.55261928159547
H	-1.15019683538951	23.59626261582745	0.73048949778064
O	-4.41089818215402	21.83395554780313	0.35716965565208
H	-3.81775822355402	22.11803036441841	-0.34998935358515
O	-4.40882840598189	22.75172223648799	3.86025586617257
O	-4.38822800442114	20.67392114926629	2.86373905717322
O	-3.62886522213463	18.28773001717570	6.14429348196031
H	-4.12876789396289	17.47380952292234	6.33788567685630
O	-6.41936746894812	19.98759785854859	0.94545362843310
H	-5.70006830339674	20.53515667061387	0.58362717431176
O	-7.31653524460862	17.32025355202212	1.07040674173998
H	-7.41493901411591	17.94653641313177	0.34221716189574
O	-6.10223058101615	17.87810830833204	4.42847513925146
O	-5.59940276876240	16.28297382004337	2.84734309213740
O	-4.60626419936574	15.70975269828715	6.70046310396726
H	-3.81122047359761	15.15851112266833	6.75366382681566
O	-5.86433203421343	14.34813939263081	0.89764810359156
H	-6.11791373227421	15.28240297864011	0.84822825165556
O	-4.05566068250155	12.07715443916124	1.29056653734566
H	-3.20974850266532	12.52499501617905	1.12198559560495
O	-4.63662632044804	13.27213279254369	4.67731434857598
O	-2.72026545703671	13.27071161845297	3.44786307654039
O	-1.97616846863850	10.41894934736398	5.48219394284628
H	-1.14110484111039	9.982428245920 68	5.27819870107872
O	-1.29684713301159	12.93040858406745	1.06599136076678
H	-0.63812877173375	13.14430106548431	0.39386364946347
O	1.50213189120899	12.81376918393307	1.32479828229277
H	2.31540777001625	13.17597348881413	1.71688157984207
O	0.38151104308960	11.77791419602926	4.64887881950997
O	1.47757397080391	13.70730154384197	4.03594448909771
O	2.52464047979568	13.46679295668733	7.53269314331382
H	3.37503826619589	13.88240655866102	7.71761608405004
O	3.89035788660528	13.68763190443617	2.60918009783675
H	4.65128975297885	14.00652750723735	2.10507002889150
O	5.77273054316297	15.69194168916634	3.29034021736371
H	5.48304310967303	16.58111275808356	3.01368104496776
O	3.63878791911553	15.61830593938903	6.25256177632261
O	3.89275654162287	17.28598218925962	4.69201166534455
O	2.46389381902452	19.80106613363133	7.76114377793746
H	2.40215155681496	19.58247968531054	8.69479012669195
O	5.38139679183757	18.40830208047810	2.64745119644023
H	5.32931002995337	18.74278159851898	1.74518374067588
O	5.01303011279809	21.20172300783105	2.26421575977608
H	5.82342570572223	21.69512049615141	2.10485693384275
O	4.18382836609043	20.75372616124108	5.78379901018195
O	2.95264525646523	21.58663028750472	4.01979268672622
C	-1.21583317629171	17.03797785096887	2.53559953152374
H	-0.33139231907677	16.67522491235319	1.98855768585461
H	-1.98609677071959	16.26479542281951	2.39347682867082
C	-0.28819315682770	20.91028968424019	-0.58928580120181
C	-1.12505789434523	19.96533893385780	0.00008588646755
C	-0.76972095171297	19.28556491186196	1.16990912452335
C	0.51122649330576	19.56203902310900	1.67995191159303
C	1.40475898131289	20.41959758286793	1.05537246557830
C	0.97076943272524	21.16940580251541	-0.04270818828757
C	-0.91862639422767	17.06165332957482	4.03686435808140
N	0.80800641915038	18.81783035111280	2.85130753587474
N	0.09837740863637	19.18174302638383	3.80455270444072
C	-0.21982033212912	18.11126002649946	4.67558031716213
C	-1.40901754194815	16.03741703440796	4.84070553814171

C	-1.24574538654062	16.06674115766689	6.22476238134199
C	-0.58178717456837	17.12583098775756	6.83976127962861
C	-0.08308940893471	18.16439176111895	6.05856279541042
H	-1.94903333881002	15.20258490592498	4.38878713622474
H	-2.11695961986065	19.79393435559953	-0.42856902956915
H	-0.61165396811361	21.48832132435594	-1.45607650666086
C	-1.74780819206036	18.34039974860914	1.86826193804775
H	-2.47919993961712	18.03137218579617	1.10632971142340
H	-2.33104239185051	18.92000731434964	2.60391530005556
H	2.39552686153573	20.57708599534020	1.48397942787341
H	0.42871156142704	19.00659500608961	6.53079990501017
O	1.72100283007793	22.17182462354434	-0.55813852899840
H	2.39100966915681	22.43221492358659	0.10293900977295
H	-0.48472665436570	17.16305446994329	7.92871934298863
O	-1.78291724436410	15.02859735950184	6.93499719178178
H	-1.59751348919816	15.14359438436607	7.87324278794662

Xyz file β-cyclodextrin/ (*E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol (3):

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ENERGY = -5071.137888202838 Input = wB97X-D3 def2-SVP def2/J D3ZERO RIJCOSX OPT

C	1.49122449274576	22.70785682019121	6.89907510849217
H	0.78779131865464	23.31746783009261	7.49272604372450
H	1.33788352095056	21.65544263623192	7.18850452269694
C	1.07457478723720	22.87671013238704	5.42904775348233
H	0.41019154215098	22.03952292432556	5.15950640170952
C	2.26397344121416	22.85548725351064	4.47306545901402
H	3.03355752008314	23.54963134276209	4.84775495754101
C	1.85766773597261	23.21637514363463	3.05530191388295
H	1.18621549117846	22.41387080748121	2.70929465283350
C	1.03314126163288	24.48350127630397	3.01857248310087
H	1.64014917043477	25.34707685110985	3.34563783236196
O	-0.13429641679034	24.31683351654937	3.99173170567569
H	-0.75774181674054	25.22509013500120	4.03423599311914
C	-3.24305957439663	23.95027715833892	5.31047531759337
H	-3.95979315333313	23.56312324985706	6.05918893637619
H	-2.24905993308922	23.98200831638907	5.78149317427256
C	-3.21173874619266	22.98759316544269	4.13728531579119
H	-2.92437496384104	21.98212737533150	4.49567912473528
C	-2.19945867555766	23.40071155970205	3.06534551283870
H	-2.36658495128641	24.45935669175427	2.79854362065575
C	-2.33470275403255	22.53668611989756	1.81956135369150
H	-2.08291547930777	21.49581810488495	2.10019510244271
C	-3.78158970001232	22.54192859952766	1.36038843958558
H	-4.06457988484302	23.57853679757950	1.09697832722834
C	-4.68615551456473	22.09668231030035	2.50713549103023
H	-5.74394782544758	22.16507773772894	2.20997000406728
C	-4.69290019617886	19.34721722947792	5.43549623594380
H	-3.95399893638660	20.15517930752016	5.35947193939285
H	-5.60750782412841	19.76447234884438	5.89115558865861
C	-4.99761598633393	18.82048318510074	4.05087178509181
H	-4.09380086502418	18.31004576286070	3.67134018047371
C	-5.41340515743348	19.87798847125733	3.03153284850886
H	-6.31634883729472	20.40155472943520	3.40053305193312
C	-5.72724153848926	19.18618780498042	1.70594599017737
H	-4.80792119597270	18.68065557730819	1.35868608357400
C	-6.79229089643087	18.12397653449527	1.92871105477725
H	-7.72293440501813	18.61833838553200	2.26625665484691
C	-6.33983815804187	17.16455615586730	3.03025621532108
H	-7.14603049638731	16.45768367620141	3.28915690843280
C	-4.72001447816268	14.86725805608682	5.10903666569737
H	-5.57650518440151	14.23627253048726	5.39399080432550
H	-5.05548662354210	15.92036888461439	5.12394218498341
C	-4.29755927810612	14.53374411228805	3.69202024660372
H	-3.28267291981208	14.95158876003148	3.55466845860868
C	-5.16659774002377	15.08582406522963	2.56810012568174
H	-6.18803040933358	14.66461525797659	2.64008303283618
C	-4.52941078993209	14.72028902319564	1.23361388580862
H	-3.55504469903621	15.24037033727273	1.23124301318918
C	-4.24736207577814	13.22143413842720	1.11374737164012
H	-5.21442415229370	12.70542192017081	0.99306525842426
C	-3.58114393956225	12.70939736232564	2.40230244585164
H	-3.57846084222184	11.60770426609239	2.43122122813272
C	-1.94857681159586	11.75294900675263	5.15968865576128
H	-1.63876528768270	11.88233561076800	6.21359167781905
H	-2.92700517891574	12.23315658711532	5.04563133054433
C	-0.91927322664361	12.45504227585147	4.28879072070374
H	-0.86519963429305	13.52280907889138	4.57251703146380
C	-1.21033124543163	12.36667337717890	2.78097285095708
H	-1.44675520650570	11.31634321761711	2.53269596092606
C	-0.01518305614511	12.80864917822302	1.96042904022397
H	0.16381410116378	13.88374501932395	2.15856122100530
C	1.22444757059822	12.03614033602891	2.38682842612148
H	1.02925102859637	10.95937349252323	2.23827599432118
C	1.42771653011451	12.25472188256686	3.88513465276644
H	2.28799953224746	11.67278559736886	4.25355721139294
C	1.49381022957996	14.06326163118356	7.10832825281765
H	1.06273200310266	14.74773626715216	7.86257778273334
H	0.66567535359721	13.52926135742649	6.62081077578601
C	2.23110806311032	14.88901152151011	6.06763969566669
H	1.57425254575218	15.68938175428633	5.68514821214169
C	2.72321130520016	14.03356063695297	4.89792194801979
H	3.24784230762171	13.15568334874109	5.31482478752848
C	3.66777121385317	14.81484490411487	4.01169349185746
H	3.08457402913426	15.63064063577051	3.54537987240295
C	4.79287340561192	15.42854116531183	4.82708045930218
H	5.37284028114090	14.61366846564437	5.29316007201103
C	4.18725796347442	16.25164609736019	5.97596841955215
H	4.99147754357981	16.60195224575137	6.64762395808721
C	4.05780295578653	19.40453728191441	7.61383969591992
H	3.60876105514143	18.43707278046833	7.90237871363555
H	5.15155740597878	19.35450288827391	7.76970500924390
C	3.77149691078628	19.65579066607814	6.15411681933226
H	2.68410676106445	19.82538341299387	6.05844715291042
C	4.14957565237344	18.52341736281088	5.19238906957130
H	5.23946215638835	18.34810223827737	5.24134206754746
C	3.77187108981604	18.97823440435476	3.78185359602343
H	2.68972345783573	19.18463427657716	3.78099750974136
C	4.50056154598867	20.27791780630746	3.46575844732391
H	5.59179002235224	20.10696144865338	3.53037571929944
C	4.12630910727449	21.31609703322989	4.52551453255546
H	4.69248232488260	22.25002573159814	4.38189473102275
O	2.80661102305756	23.09943671161056	7.16978570732831
H	3.30919681101273	22.30033485079830	7.38647234664153
O	2.94589628895036	23.35958569790826	2.18406219229449
H	3.34066538907513	22.48218742391664	2.03744200345383
O	0.53402430115779	24.69577590000790	1.71503320073816
H	1.29458013145694	24.59810051152765	1.12506037816477
O	0.34771488891839	24.09576062830239	5.27706002190501
O	-0.89939432938205	23.21666217676408	3.56847128330135
O	-3.56589391767939	25.25159576772439	4.90120384677269
H	-4.41267174784603	25.19770641765040	4.44297653632492
O	-1.53046767389253	22.96114953365359	0.75364151287596
H	-0.77585602762397	23.47811452740837	1.09382997051581
O	-3.97196058818383	21.69079047406354	0.25423809135767
H	-3.27955714219180	21.89227203590708	-0.38808773559794
O	-4.52592278417078	22.95854716163458	3.59836401790900
O	-4.35529862400665	20.78881872355737	2.85988698244066
O	-4.13908810786672	18.33789972661061	6.26001339452231
H	-4.81556729253674	17.66456529362737	6.40611276651128
O	-6.20660408775565	20.06604352787803	0.72523322625820
H	-5.44702874209395	20.52764171120335	0.32895667877232
O	-7.02711574574247	17.38737291629609	0.75599354477756
H	-6.99494753366785	18.02233396858736	0.02602149772776
O	-6.05534440566957	17.88244244652196	4.19899842817331
O	-5.21323719567155	16.49562715151256	2.58084625141371
O	-3.69275134260429	14.62893583532311	6.03200458620173
H	-2.93615793263185	15.18145354255040	5.78576890415260
O	-5.31393567085549	15.16283864748928	0.14648930810449
H	-5.89716327525939	15.88582386528085	0.44986582366232
O	-3.45596122446657	12.90697999429610	0.00561132324362
H	-2.52465737226864	12.99770717096531	0.26609012836046
O	-4.26742828437392	13.12811094609060	3.54361080114622

O	-2.27506429802051	13.20288420439604	2.39298891646002
O	-2.07221742802125	10.39884786958965	4.81047173581794
H	-1.19599240582145	10.00861637246685	4.90758485202391
O	-0.29049483968723	12.60889759238330	0.59533885519230
H	0.56484040268219	12.61410233118031	0.14408073014567
O	2.32168155131343	12.37810665756954	1.59481995187105
H	2.85548080753180	13.06806068354254	2.03020719040611
O	0.31417452592585	11.80409576386521	4.58993615680274
O	1.63491053969292	13.62159438487066	4.10750357714438
O	2.33683931916786	13.10555022353903	7.68658080559496
H	3.09952642778903	13.58597729798055	8.02915753488391
O	4.17245896859519	13.94725174213825	3.02220420198603
H	4.93164384190499	14.38250614155100	2.61330756581026
O	5.67822886864161	16.14101035319966	4.01072985789122
H	5.17121879245227	16.79699917528708	3.49033919741820
O	3.34813262700153	15.46171383952047	6.74825858299877
O	3.44470101645292	17.34499375830772	5.49473550687671
O	3.47870880249834	20.47755602629622	8.32229314890041
H	3.73098890654449	20.43537871952186	9.24828843085985
O	4.06963857476827	18.02252863761786	2.78500288623806
H	3.23585723449739	17.57060989870891	2.51901199905191
O	4.15774659541636	20.76917306274257	2.19409041203920
H	4.24260265557999	20.03469747319192	1.57310564026641
O	4.47595012106256	20.82978644484085	5.78848787269418
O	2.76192443010139	21.53438316296086	4.43778929408569
C	0.07579232782456	19.65584477675597	0.31875213459289
H	0.70931999746482	19.82102722528770	-0.56945613461765
H	-0.67042857643109	20.46393355141234	0.30440927838930
C	-1.23515521906739	18.99317749887473	4.61392649721485
C	-0.51664150394320	19.73582640859951	3.68238233380823
C	0.31996921443689	19.11390509155212	2.75792344587933
C	0.46425675815299	17.72436653062713	2.85247203493497
C	-0.24278888304739	16.95438181086049	3.77257402123433
C	-1.14888667811382	17.59605428485646	4.62510933891550
C	-0.66269442882910	18.34219836008250	0.14165475436688
N	1.46537873982484	17.11329375755582	2.01179258079684
N	1.23358748653759	16.83236971020145	0.82873721171001
C	-0.07621802686966	17.06701306083052	0.28913825548770
C	-1.99522660500723	18.39179192652180	-0.27221660113051
C	-2.72312925571292	17.23595533731127	-0.57435175830665
C	-2.07680237519902	15.99517873687875	-0.54944821319403
C	-0.76159073838815	15.92018225840294	-0.11526538713697
H	-0.62581974190361	20.82356813478636	3.65829997960676
H	-2.50594250232830	19.35629313640952	-0.33187498077357
H	-1.88138217217994	19.49493001912675	5.33732068459910
C	0.93917598680787	19.81996645545996	1.58537659956840
H	1.95502590610132	19.44090983345124	1.40852899928964
H	1.05872991078815	20.88858336469273	1.79385257790619
H	-0.27683061301655	14.94446890741131	-0.04126891933900
H	-0.11611386811879	15.86959237963377	3.80588399895214
O	-1.92103670557673	16.85549560430290	5.45345187888243
H	-2.62099608765078	17.42289150781768	5.84261543977220
H	-2.61787811237922	15.08805537934448	-0.83146927742745
O	-4.02750258388880	17.35502217678193	-0.87441823712692
H	-4.45782454671163	16.47927190714012	-0.77469383139008

Xyz file γ-cyclodextrin/ (Z)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol (3):

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ENERGY = -5681.278144114335 Input = wB97X-D3 def2-SVP def2/J D3ZERO RIJCOSX OPT

O	8.21240504903062	25.05621827676585	5.85207327583254
H	8.98653291072160	24.60843016955270	5.48938104804321
O	9.86835517785385	23.16973000110755	7.25864713083231
H	10.56714440747783	23.59988423115185	7.77689882700294
O	7.37664791667849	24.10322145160823	9.74006164700133
O	4.96103730335021	25.73285397536226	10.12106435532037
H	4.94913450717635	24.76863394931664	10.15503752628904
O	9.67334905088439	24.12167210992235	9.80916476706134
O	12.36829148808340	24.10805852749393	9.36151561179608
H	13.25131430908285	24.49629586179534	9.40883468613937
O	13.96197006184069	24.39682344324530	11.75329253917229
H	13.87716054055060	25.06980478067474	12.45317502654034
O	10.94070199479189	22.74096416841170	12.95347121981399
O	8.98410386251659	21.14275193042909	11.47422820662579
H	8.30273665093048	20.50230562758679	11.69416089999261
O	11.74115944355289	24.84975246653426	13.40879251400533
O	14.02990591296981	26.06088650022958	14.24676423476615
H	14.67482945138769	26.72429967213370	14.52584192611592
O	13.82538764023352	27.93874020395849	16.40145160689986
H	13.40159907918904	28.74838963902896	16.05509176988988
O	10.76989890198687	25.95169979658850	16.75122367288090
O	10.08314411681913	23.14788626602525	15.63325520302414
H	10.36219677011351	22.78493091276743	14.77976162889521
O	10.97589006072633	28.18995756193376	16.30736826426595
O	12.63354829270249	30.35771460461111	15.68729844425793
H	12.98891421499889	31.23634162632460	15.49501674804752
O	11.67335754549135	32.92720028055902	16.23641617121232
H	11.11062979811574	32.99934197793624	15.43671221114237
O	9.53851161212383	30.85044954937269	18.36381622761197
O	10.06968760192682	28.46963607152072	19.71297142036391
H	10.13426599970529	29.35665555923067	20.08684101774834
O	8.85785315230647	32.10227675181417	16.60399153578046
O	9.94382358119821	32.95527091573290	14.12382712677298
H	9.81394674066282	32.01827282409102	13.87127977550767
O	8.47024844554185	34.78827066444663	12.65887457252874
H	9.30590648858312	34.34630060939413	12.46334518917934
O	6.80224743526693	35.02907749134922	15.86739807521740
O	7.82455702699693	34.98839704943254	18.47996623042334
H	7.67416462347877	35.77734391435092	17.94562117887124
O	6.11041260627520	34.09435641984508	13.85969089388853
O	5.16479098353197	36.54359221681074	12.52057801759516
H	5.02101588815332	37.04508837403141	11.70948687802551
O	3.20621127563850	35.95811635531111	10.51824308093145
H	3.66128533392359	35.37590715869641	9.88679193989350
O	2.72161468542685	33.27875631128438	12.93250536304756
O	3.45341174758531	32.79899432954167	15.65835827764257
H	2.57349144002107	33.07665666917165	15.38058103561301
O	3.23157424803198	33.22885471544781	10.69353318691750
O	3.68349654122764	34.31742319261578	8.06787012749576
H	2.83555366966484	34.74781487889388	7.89774560540024
O	3.92056664070170	32.21148335212261	6.14264624852072
H	4.17730487467192	33.13385245799855	6.01303641763857
O	1.59068924671029	30.80483756904626	8.52071825927291
O	-0.10767549969461	32.24518488262770	10.44216741735179
H	-0.83777398986261	32.15498897778723	11.05954911476901
O	3.69870982941237	30.08918584020864	8.08093606873689
O	6.22837668130013	31.10632168382672	7.43170503535992
H	5.59795248217906	31.51706111206687	6.81916859381130
O	8.21610684656281	29.12822729952704	6.58877232962421
H	8.48345958994367	28.44628205196359	7.22024039722332
O	5.12221207768962	27.20885670391640	6.37943314894202
O	2.44253462724398	27.84687508766599	5.80059658778406
H	3.08158629750094	27.50411033351474	5.16436479738487
O	7.03471725952907	27.04202146699537	7.68435630811861
C	7.13429925276467	25.65752178272757	7.92197078088801
H	6.21444987936909	25.14753176457256	7.58375007704896
C	8.36448406606592	25.05671002702238	7.24823634614771
H	9.21815224039900	25.69598092418591	7.54751369621180
C	8.63290191267870	23.63078275536713	7.73330484790869
H	7.85696609752422	22.98368591429046	7.29235212771436
C	8.53965671174754	23.50075683650494	9.25314186005179
H	8.50699820297913	22.44174971041875	9.54893377100341
C	7.31623892317693	25.49136963310668	9.43146611818889
H	8.27401503079937	25.96422468718208	9.69415334289622
C	6.29725112023356	26.15240971441198	10.32268786172114
H	6.60618734070111	25.98665448246429	11.37046547673892
H	6.32946986518546	27.23351790293708	10.13534829347562
C	10.52724939802552	23.37118959490858	10.65050396240960
H	10.69891551884288	22.36606419330705	10.22948982458349
C	11.83560806702540	24.13957739656959	10.65862874633119
H	11.60926356559025	25.18187730054782	10.95591577003237
C	12.80829759860691	23.61208828882316	11.70548570981241
H	13.10014853499783	22.58386771619781	11.43055652634183

C	12.08488802338832	23.55007870025952	13.04613034881668
H	12.72748941904734	23.08781996760569	13.81278329257605
C	9.94734605456252	23.24455075185412	12.06525641789296
H	9.64337719952028	24.25636755980748	12.38741180877685
C	8.73839814479646	22.33705377472954	12.17459570186833
H	8.56839604948469	22.15567509061457	13.25170065771074
H	7.85911998291502	22.87459561468046	11.77691994671400
C	11.87237560840687	25.22605531293847	14.76502865322002
H	12.31167694426430	24.39176476550338	15.33859670363447
C	12.79927186014699	26.41965942621895	14.82930080905989
H	12.33764755386171	27.25818192129306	14.27012067587007
C	12.96675786928906	26.84561450691492	16.28306671139683
H	13.44115699302324	26.01049934391166	16.82605621565340
C	10.52762024122558	25.56669069900206	15.40668356889530
H	10.06698457313916	26.41250417889318	14.86335362370297
C	9.52811089580672	24.41059474463724	15.40556083624482
H	8.80441046930929	24.62113506415247	16.20834593100275
H	8.96725129999747	24.44377595973108	14.45339861057132
C	10.93784035155026	29.37878744771498	17.06412411093691
H	11.66013938794833	29.31558816895015	17.89605180044744
C	11.32681173752697	30.54455359654953	16.18392821588984
H	10.60690917598953	30.60151205376786	15.34630480992330
C	9.83646962340682	31.97780470425445	17.60025808860965
H	9.80101866954578	32.84439530624883	18.28317910039441
C	9.54362227971961	29.61530300236565	17.65305587142547
H	8.80592402850654	29.64719535753066	16.83160704914533
C	9.14913262715168	28.54707848081466	18.65646496836921
H	8.12676568865832	28.76761324972124	19.01537039458726
H	9.13010386877732	27.56665678230485	18.15743143859732
C	8.57390008142872	33.39443855255701	16.11629339338888
H	9.27517488904576	34.13077161748613	16.54585052241413
C	8.68028915086030	33.38337129650822	14.60172722918978
H	7.91744806244412	32.68502450983029	14.23596342312809
C	8.34833495663995	34.75799497779753	14.05072227184194
H	8.99965557306598	35.52019566521662	14.52366581654582
C	6.90959735791969	35.06377685643726	14.46647470789051
H	6.60680859804008	36.07283993345334	14.15856436290570
C	7.14109378647044	33.79496840862246	16.49077425311551
H	6.45861861140572	32.99453003140542	16.15565061866479
C	6.95759273523393	34.00325828814436	17.98109379478852
H	5.89584061482951	34.25061362804334	18.16605338937914
H	7.17898818498370	33.06155964236633	18.50590003511370
C	4.77288432270727	34.40892128918853	13.55487525064664
H	4.29268745379491	34.93036730532635	14.40231658772496
C	4.67613026728610	35.24739926026984	12.28718674485530
H	5.29077001802644	34.72842713129876	11.52352446896050
C	3.23968310243921	35.32724333594337	11.77312439428220
H	2.66151225392259	35.95781696417357	12.46743455217309
C	2.59018765004906	33.94482334925012	11.71682889436706
H	1.51025518043694	34.01862798304314	11.50990891344048
C	4.07643451486320	33.06417357945615	13.32712693583315
H	4.60901818235545	32.52648236515118	12.52480710408125
C	4.05346145473892	32.17672641002856	14.55409429040928
H	3.54723964769570	31.23096547126678	14.28040853086563
H	5.08982197653725	31.92936533248983	14.82494743685203
C	2.50108226190094	32.80800773930054	9.56850833793059
H	1.61765799207217	33.45478595509770	9.41169766228829
C	3.43885552939457	32.95538676205322	8.38056293546664
H	4.42011040352427	32.53605576832897	8.65004867820562
C	2.94218828671950	32.20003388518552	7.15989918294178
H	2.00341562428608	32.65795367445000	6.78959275214974
C	2.58423320667339	30.76139830524065	7.55291078638272
H	2.17621378256904	30.20987529195061	6.68921642877023
C	2.00843870424638	31.36694646310279	9.75728128431741
H	2.84409426217543	30.78190086921212	10.16780752017638
C	0.86642303487102	31.27496971047381	10.74672204652459
H	0.45991985080416	30.24941634314699	10.68480293198199
H	1.28573254199735	31.42203803664932	11.75933568195136
C	4.52802513708834	29.37901346861815	7.18987098635074
H	4.27455879530435	29.65034928594753	6.14988242832775
C	5.99585725560940	29.72653525569796	7.43947734698210
H	6.28569381427433	29.36039857543230	8.43947276085783
C	6.83941925990232	28.96568486219016	6.40680317618973
H	6.58854295234985	29.34839972674610	5.40248130655388
C	6.48997096907125	27.47050470968989	6.45798674905038
H	6.95188702187271	26.92304562357896	5.62509746745881
C	4.31207212768897	27.87377609058747	7.34027783954332
H	4.58757362279972	27.55473052973629	8.36099271658401
C	2.88286543747555	27.44514059266449	7.07163202294224
H	2.82087629623549	26.34887012492991	7.20381527067102
H	2.21887770550445	27.90924266692437	7.81619550503322
C	11.58259171405634	27.07063117848039	16.91098794712556
H	11.67081435747047	27.22994216008707	17.99763606205510
C	11.24423726055891	31.83441147298509	16.99500139785270
H	11.94370929680224	31.74902180776423	17.84479118216433
C	8.37816996049275	31.36420402229205	10.39439598193299
H	9.14109043309284	32.15859384419191	10.46156869035442
H	8.14462909866942	31.25505001748176	9.32466131023284
C	4.59178896022263	28.95416870616742	11.15464737557118
C	5.25039073744727	30.12827169984968	10.80525453237605
C	6.26816380631534	30.66187121484727	11.59117641421604
C	6.57257208391264	29.98368206214278	12.78046544367496
C	5.90966624773918	28.82388996508390	13.17340109108097
C	4.94984600404526	28.26989966107755	12.32062234351215
C	8.98980425406042	30.05502567639046	10.85919533810887
N	7.56219225527108	30.56716872914161	13.63408067672162
N	8.75773572551585	30.50731656199288	13.32363087971522
C	9.17665843934914	29.69901109074247	12.20611846612663
C	9.41661797373972	29.13600914606443	9.89802944841315
C	9.99713487182393	27.91105545588161	10.24098842818341
C	10.20617945693580	27.59812478125697	11.58763844246850
C	9.81212718762580	28.51048798619129	12.55977294499881
H	4.98692212918248	30.62588503594925	9.87100852527369
H	9.26650874822999	29.37446696817920	8.84291261167816
H	3.81788111515969	28.54580347622395	10.49858149364339
C	7.09686198248196	31.82961163727029	11.12819343809140
H	7.33802177401377	32.50328014574271	11.96407244817304
H	6.50365620608444	32.43541893076802	10.42778315843924
H	9.98525824364880	28.30342844380064	13.62047556201803
H	6.17600943436637	28.30962957465205	14.09818451325938
O	4.42283756540407	27.06544706780461	12.63208705839389
H	4.18697289812249	26.61166406302453	11.80572728926296
H	10.68265777406371	26.66276110555569	11.89267409796412
O	10.33198032431294	27.07618569091768	9.22795192251674
H	10.52554267711663	26.18428010514402	9.54989361092689

Xyz file γ-cyclodextrin/ (*E*)-11,12-dihydrodibenzo[*c,g*][1,2]diazocine-2,8-diol (3):

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ENERGY = -5681.244414073524 Input = wB97X-D3 def2-SVP def2/J D3ZERO RIJCOSX OPT

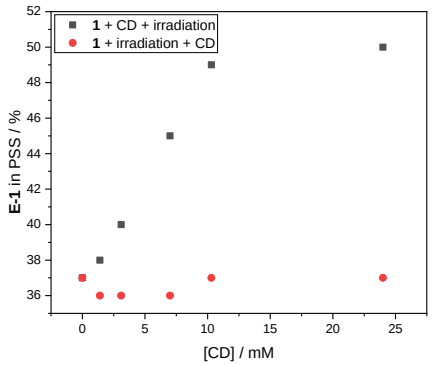
O	9.00300595928369	27.23840077951341	6.20101047280159
H	9.86534660858873	27.63196689468834	6.37483710434068
O	10.96366483845300	25.81837057200791	7.75802919661113
H	11.37670825863128	25.29206401216773	8.46361384779303
O	7.96416839817420	23.76455646293930	8.09917725532754
O	5.61868090287227	23.39715018242766	6.58599391044056
H	6.40143085840070	22.83523301509974	6.54094674981501
O	9.18812598071712	24.88238932877245	9.70159087996911
O	11.84014438325147	24.06594049433868	9.92333195492289
H	12.74971116710970	23.93862332028342	10.22682392465416
O	12.87308957292344	23.65598965671755	12.51869092954653
H	13.05247492403690	24.57395724738682	12.80344047337648
O	9.25151331280598	23.60498291626941	13.10762459808607
O	7.05344748776136	23.00170498024806	11.29810396914851
H	6.11040930794145	22.82833034082805	11.34145593174179
O	10.78205591911503	25.06333729357907	13.92200979437336
O	13.36344298261154	26.18609017603453	13.56217624157343
H	14.04001443241366	26.87547414546106	13.53259743044606
O	14.15043859049428	28.01019953368539	15.55933528286287
H	13.69071338375227	28.84246590672257	15.77748209803140
O	11.71071528869177	25.95627558696344	17.33482887799666
O	11.18728050618097	23.14731643942387	16.75173682732984
H	10.78492121794590	22.35501282954882	17.11588366249710

O	11.47694652242027	28.13828416213271	16.63723524623801
O	13.08606257851944	30.42029266069340	16.59026441086310
H	13.39195517410149	31.31661392113365	16.39746087742025
O	11.76990820253094	32.89234909042352	16.94199349145474
H	11.36413895236327	32.99612009269645	16.05947397642250
O	9.39114918777694	30.53751906527710	18.41746652397872
O	9.91923539578146	28.40482469901494	20.00493476480332
H	9.72389599422671	29.31275554563090	20.26604373959672
O	9.11483089719295	31.78571385823455	16.52712030454842
O	10.44901019871141	33.27186737238105	14.54497030792060
H	10.66509056633033	33.53853362027741	13.64306299845562
O	8.76410665734997	34.65707604550538	12.78866463593147
H	8.14487935825026	35.27399487762894	12.36136022051212
O	6.68121931393264	34.39259303707113	15.78101662892873
O	7.37354652608108	33.82334552582094	18.52175939024400
H	7.02134888844771	33.74716369010296	19.41202564266487
O	6.26783198404817	33.79040143602542	13.58584867347980
O	6.52209381107898	36.02595558891881	11.82296329746287
H	6.51199647779343	36.57200964084243	11.02365748739435
O	4.74023561415676	36.13841199209981	9.67141555319870
H	5.00208617400015	35.44534389442997	9.03797661749430
O	3.05461878443095	33.77018169639311	11.88293417002022
O	2.81019079663485	33.60103586838216	14.58960061566896
H	2.17962595806513	33.97258303658829	13.96150858712714
O	3.90222339036240	33.51380794812344	9.75231692898997
O	4.85222879575418	34.55508608891818	7.27205694196281
H	4.16754785712149	35.18624882431354	7.01350146445008
O	4.60821388117258	32.67889136157975	5.11255077461278
H	5.24518745024660	33.39561490779298	5.21813040381230
O	2.00063143767527	31.54266431915728	7.34422400098804
O	0.54844539700807	33.07003569304101	9.34955313374951
H	-0.22327539455322	33.04145129893075	9.92061325036918
O	3.98990561163418	30.55652277148339	6.76052592633799
O	5.03803367610306	29.90496801535452	4.17940335584759
H	5.06874838368903	30.83685609481585	4.44181165063980
O	6.68341893792806	27.43760088481014	4.31022532729168
H	7.40110785727348	27.61812781983405	4.93852541007314
O	4.10902696982242	26.93912205261485	6.83875720647640
O	1.56736399959630	28.65022541711401	7.60145960845749
H	1.52836028659568	29.61080892288307	7.48974349570464
O	6.39742505075494	26.86433704644768	6.98760325916700
C	7.32116521382437	25.79298566695806	7.00636076355408
H	7.33455169598690	25.30249286166431	6.01854682259125
C	8.69888374165364	26.37438379634561	7.26848739258115
H	8.68545215866400	26.92852056211037	8.22734782310192
C	9.72791291759303	25.26037868038032	7.42126625788056
H	9.79204693467507	24.72414858723210	6.45360522192647
C	9.22485802823097	24.25203625729309	8.45562607079284
H	9.88967711980694	23.37518919714851	8.48601619588311
C	6.95616905951379	24.75992073772019	8.07523859487007
H	6.90409939352465	25.26725930249210	9.05485026332381
C	5.64717163798969	24.03360007747154	7.83573079756649
H	5.52362575659085	23.31476846061715	8.66740605369691
H	4.80948349841206	24.74536949313629	7.87078572213316
C	9.60572212920432	24.10025947755664	10.79293687852240
H	9.43477912771886	23.03130984207986	10.57816344516659
C	11.07351964115176	24.35293652081500	11.07572387596412
H	11.19794370515771	25.41721330909795	11.35392645825375
C	11.51176275928852	23.48814216769533	12.24794772080427
H	11.37660964283207	22.43072864883928	11.96365663408270
C	10.59296575117100	23.75497514229355	13.45223499291547
H	10.79945121607383	23.02599623027527	14.25329545321874
C	8.80257199308029	24.44536374546096	12.04682126474887
H	8.97590291433526	25.50512642428921	12.31210416128808
C	7.31204027360665	24.25337762523966	11.87654149457863
H	6.84509178029545	24.35545551613216	12.87352813465809
H	6.93612798100764	25.08553748102611	11.25147277932184
C	11.68524460958761	25.27124822591809	14.98556210998408
H	12.35733739096977	24.40518653479458	15.10423098216289
C	12.52050276536028	26.49033463070336	14.65324462669151
H	11.83816552713033	27.31628329882748	14.38459890153866
C	13.34220389276239	26.91227889940711	15.86486249093242
H	14.00645897446124	26.07701440279901	16.14565192622549
C	10.89148106406697	25.47040225374395	16.28430907824819
H	10.09365012694258	26.20398398273768	16.07390107542480
C	10.24021034605972	24.18521093011300	16.75345724323270
H	9.83538526763454	24.36981082528633	17.76593018984391
H	9.39222488327254	23.95757078305212	16.07857903263388
C	11.21836254419961	29.24114562276789	17.46862919602621
H	11.76521679398931	29.14048700482963	18.42326810620506
C	11.68779507331908	30.49184627684068	16.75559220205496
H	11.18521559995351	30.53916151460506	15.77031896133730
C	9.77692570614639	31.70688420209264	17.76660476565095
H	9.45975642557405	32.54005655207488	18.41354150535754
C	9.71895561062075	29.30620887020696	17.77723347647581
H	9.15290883921148	29.20181034172329	16.83379737217536
C	9.30367787753824	28.22123490321881	18.75840149386016
H	8.20184427836247	28.21507265396090	18.84208023216614
H	9.62678837628692	27.24506438328492	18.36669627631345
C	8.66031147063886	33.05254032949341	16.11552471265984
H	9.11199364342873	33.84875351147990	16.73122761540643
C	9.04302139010208	33.26711589191883	14.66411934994099
H	8.62208459673338	32.44119996097870	14.06671997290853
C	8.46107699550571	34.57299660919004	14.15206611320868
H	8.93943701681803	35.39661729509018	14.71945401579884
C	6.95802544225650	34.66188312313479	14.44689966563026
H	6.61324539148051	35.69288249233101	14.27738442695889
C	7.13676104648069	33.13753268408868	16.25199633436398
H	6.69267525769124	32.32452105987589	15.64767941839442
C	6.66389536269560	32.95069968836825	17.67686498553064
H	5.57720050884497	33.15078175699899	17.69543206318116
H	6.83149310014381	31.89176395401778	17.95082189159164
C	5.16725400708000	34.34480898354263	12.91000061408951
H	4.66774495374539	35.09328962420030	13.55189476665386
C	5.59484928737460	34.98288584759641	11.59915217347714
H	6.05486961236115	34.19536300657516	10.97098926263913
C	4.37121991035309	35.52992627903121	10.87668733563479
H	3.91482621840332	36.31178964716067	11.50602229914477
C	3.35032237877601	34.40722302744449	10.67722815542320
H	2.39136498713393	34.79777128050091	10.30111461590171
C	4.15561853017311	33.23497264905719	12.61797156621693
H	4.65210340376437	32.43753436611480	12.03439520541355
C	3.55539535075175	32.64963363314936	13.88557697583942
H	2.94934521377599	31.76389940729921	13.61342606401943
H	4.37195233578246	32.30990329062067	14.53797985086084
C	3.22199032696649	33.26229403198021	8.54586446983288
H	2.46486761487941	34.04582511515879	8.35696051509789
C	4.25602128721931	33.27822657477179	7.43061950750953
H	5.07568954119639	32.59543029552075	7.70185887801215
C	3.64652181488036	32.79498629442257	6.12462540718881
H	2.83725495686168	33.49045978479999	5.82028609606062
C	3.00280795769961	31.42931915908159	6.35911665768292
H	2.49800794196483	31.07843263700721	5.44461807561700
C	2.49869319730716	31.91451967609127	8.62480524108690
H	3.23572736445358	31.16863193852877	8.96884188198858
C	1.34215811361135	31.93597515311833	9.60120636482958
H	0.77916916076749	30.99376387221587	9.46955427863604
H	1.75768920128208	31.95364505563442	10.62482139128783
C	4.00233835048858	29.23806591562292	6.23692835459483
H	3.09229258968069	29.06005715733236	5.63869539718924
C	5.22102934907650	29.12254177329515	5.32637426156444
H	6.09014391443733	29.47656689132081	5.90984441381598
C	5.45209510528663	27.66953250121173	4.92320282068287
H	4.67505497429863	27.41083537564545	4.18500976826431
C	5.27423721594320	26.72210929200731	6.12022105114306
H	5.23458031595926	25.68339875694793	5.76088511996846
C	4.00411831126899	28.24384952962456	7.38746862483522
H	4.87556135048615	28.44318048719400	8.03408163585974
C	2.75375458545457	28.32178108487034	8.26785309610031
H	2.62402897015388	27.32663869201611	8.72008087424603
H	2.96246834292760	29.02314835513645	9.09656825810595
C	12.37877994575451	27.14248571792657	17.02937935989614
H	12.92162774718775	27.44303149199364	17.94033720309946
C	11.29524800056033	31.72657436234713	17.54945237071353
H	11.77160645092197	31.67292190860582	18.54328629534584
C	5.95764399345665	29.64060000319560	14.33894944067795

H	5.05389597566972	29.44156985562708	13.74108459595929
H	5.646293250205 98	30.36070096061783	15.11188710614350
C	7.38363598507586	30.86468337674998	9.66952797262935
C	7.31302445552432	31.10527850645398	11.03946180047143
C	7.07551496441271	30.07329701029584	11.95455105271535
C	6.90678452243191	28.78457953990324	11.41483959474949
C	6.92106415880964	28.52230135892902	10.05115040508582
C	7.20049317446050	29.56976928952803	9.16517283769734
C	6.35356314949090	28.37008764494639	15.09278608775654
N	6.58708528866997	27.83052519896290	12.41376212796362
N	7.53965672342516	27.62356391710455	13.18227323607302
C	7.09844434459839	27.32666599071831	14.49620817368897
C	6.00657029364898	28.22707829016502	16.43360030590230
C	6.36451185958051	27.08547198685737	17.15877537597367
C	7.11688132322348	26.07818908588859	16.55173488656800
C	7.50821818339577	26.21498479662824	15.22098288944247
H	5.44973943497143	29.01118701344702	16.95274904874975
H	7.46665597885802	32.12170881318209	11.41953944050821
H	7.59109780643506	31.67201014292718	8.96405347787114
C	7.01854886090420	30.35643796904056	13.45588791963185
H	6.82016351639669	31.43465300066196	13.54334472571176
H	8.01459734789995	30.19901865037338	13.90456807780645
H	6.75484244078729	27.50738104212544	9.68378943739279
H	8.12861685309327	25.45542902404357	14.73720539048040
O	7.30298463764536	29.37960863273735	7.83949812410672
H	7.06365039966525	28.46599797354444	7.58784513509576
H	7.41047035089203	25.19391039225714	17.12520572746851
O	5.98065523301500	27.03163334914301	18.45566467231637
H	6.32404415299095	26.23151399878070	18.86542957973269

9. NMR determination of the composition of PSS at different concentrations of CD

Figure 89 shows that the fraction of *E*-**1** in PSS increases when the irradiation is performed in presence of the CD. In other words if irradiation of the sample with certain concentration of *Z*-**1** is done after the addition of CD to the sample, the degree of conversion of *Z*-**1** to *E*-**1** increases compared to samples that were irradiated without CD. This clearly indicates that the *Z*/*E* equilibrium is shifted to the *E* isomer in the presence of CD.



Supplementary figure 89. Fraction of *E*-**1** (total concentration of *E*/*Z*-1 1.7 mM) in the PSS depending on the concentration of CD (black squares) vs fraction of *E*-**1** (ca. 36 %) in samples that were irradiated without CD (red circles, deviation of values is due to the NMR integration error).

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