

Ewert, J., Heintze, L., Jordà-Redondo, M., von Glasenapp, J.-S., Nonell, S., <u>Bucher, G.</u>, Peifer, C. and Herges, R. (2022) Photoswitchable diazocine-based estrogen receptor agonists: stabilization of the active form inside the receptor. *Journal of the American Chemical Society*, 144(33), pp. 15059-15071. (doi: <u>10.1021/jacs.2c03649</u>)

Supplemental Material

There may be differences between this version and the published version. You are advised to consult the published version if you wish to cite from it.

https://eprints.gla.ac.uk/277285/

Deposited on 25 August 2022

Enlighten – Research publications by members of the University of Glasgow <u>http://eprints.gla.ac.uk</u>

Supporting Information

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

Julia Ewert^{1,†}, Linda Heintze^{2,†}, Mireia Jordà-Redondo³, Jan-Simon von Glasenapp¹, Santi Nonell³, Götz Bucher⁴, 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.

Table of Contents

1.	Analytical equipment	2		
2.	Molecular Modelling	3		
3.	Syntheses	4		
3.1	Synthesis of difunctionalised diazocines	4		
3.2	Syntheses of monofunctionalised diazocines	16		
3.3	Syntheses of hydroxy azobenzenes	21		
4.	Photochemical Characterisation	23		
4.1	UV/Vis Measurements	23		
4.2	Thermal half-lives	26		
4.3 NMR switching experiments and photostationary states41				
5.	Kinetic studies of the thermal relaxation process by Laser flash-photolysis	53		
6.	Biological Evaluation	55		
7.	Properties and characterization of the cell incubator lamps	61		
8.	Computational Details	64		
9.	NMR determination of the composition of PSS at different concentrations of CD	129		

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.

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)

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

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

signal intensity	abbreviation
weak	w
medium	m
strong	S

 Table 2. Abbreviations for the signal intensities.

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/UV₂₅₄ 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 μ m, cartridges sizes: 10 g, 25 g, 50 g and 100 g) and Interchim puriFlash[®] cartridges (Interchim[®], SIHP, particle diameter: 30 μ m, 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 $E \rightarrow Z$ 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 μ L 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 μ L 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(CD₃)₂, 298 K, TMS): δ = 7.56 (d, ⁴*J* = 2.6 Hz, 1 H, *H*-3), 7.38 (d, ³*J* = 8.5 Hz, 1 H, *H*-6), 7.27 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.6 Hz, 1 H, *H*-5), 2.50 (s, 3 H, -CH₃), 1.38 (s, 9 H, -C-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 28.9 (-*C*-CH₃), 19.4 (-CH₃) 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]⁺⁺, 153 (90) [M-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₁₁H₁₅NO₃ *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 μ L concentrated sulfuric acid according to the general procedure. However, after 1 h stirring at room temperature another amount of 70 mL isobutene and 100 μ L 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(CD₃)₂, 298 K, TMS): δ = 8.00 (d, ³*J* = 8.8 Hz, 1 H, *H*-6), 7.06-7.03 (m, 2 H, *H*-5, *H*-3), 2.57 (s, 3 H, -CH₃), 1.45 (s, 9 H, C-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 29.0 (-*C*-CH₃), 20.9 (-*C*H₃) 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]⁺⁺, 153 (46) [M-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₁₁H₁₅NO₃ *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 μ L 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(CD₃)₂, 298 K): δ = 7.95 (d, ³*J* = 7.9 Hz, 1 H, *H*-6), 7.41-7.44 (m, 2 H, *H*-3, *H*-5), 4.56 (s, 2 H, Ar-CH₂), 2.57 (s, 3 H, -CH₃), 1.28 (s, 9 H, C-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)₂, 298 K): δ = 149.0 (*C*-1), 147.4 (-*C*-CH₂), 134.0 (*C*-2), 131.6 (*C*-3), 126.1 (*C*-5), 125.3 (*C*-6), 74.1 (-*C*-CH₃), 63.5 (-*C*-CH₂) 27.9 (-*C*-CH₃), 20.3 (-*C*H₃) 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-CH₃]⁺, 150 (100) [M-C₄H₉O]⁺.

MS (EI, HR, 70 eV): C₁₂H₁₈NO₃ *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 \rightarrow 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, CDCl₃, 298 K, TMS): δ = 7.57 (d, ⁴*J* = 2.4 Hz, 2 H, *H*-3), 7.25 (d, ³*J* = 8.4 Hz, 2 H, *H*-6), 7.15 (dd, ³*J* = 8.4 Hz, ⁴*J* = 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, CDCl₃, 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*-CH₃), 33.9 (-CH₂), 28.7 (-CH₃) ppm.

IR: $\tilde{v} = 2975$ (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): C₂₂H₂₈N₂O₆ *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 \rightarrow 100 % DCM) the product **12** and the by-product **13** could be obtained in one fraction with a ratio of 46 %: 53 % (determined by ¹H-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(CD₃)₂, 298 K, TMS): δ = 7.99 (m_c, 1 H, Ar^{II}-*H*-6), 7.54 (d, ⁴*J* = 2.4 Hz, 1 H, Ar^I-*H*-3), 7.35 (d, ⁴*J* = 8.4 Hz, 1 H, Ar^I-*H*-6), 7.29 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 1 H, Ar^I-*H*-5), 7.07 (m_c, 1 H, Ar^{II}-*H*-3), 6.95 (dd, ³*J* = 9.8 Hz, ⁴*J* = 2.6 Hz, 1 H, Ar^{II}-*H*-5), 3.25 (m_c, 4 H, Ar^I-CH₂, Ar^{II}-CH₂), 1.43 (s, 9 H, Ar^{II}-CH₃), 1.39 (s, 9 H, Ar^I-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 80.4 (Ar^I-*C*-CH₃), 35.1 (Ar^{II}-*C*H₂), 33.7 (Ar^{II}-*C*H₂), 29.0 (Ar^{II}-*C*H₃), 28.9 (Ar^I-*C*H₃) 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): C₂₂H₂₈N₂O₆ *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 \rightarrow 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(CD₃)₂, 298 K, TMS): δ = 8.00 (d, ³*J* = 8.9 Hz, 2 H, *H*-3), 7.07 (dd, ³*J* = 8.9 Hz, ⁴*J* = 2.7 Hz, 2 H, *H*-4), 6.96 (d, ⁴*J* = 2.7 Hz, 2 H, *H*-6), 3.31 (s, 4 H, -CH₂), 1.42 (s, 18 H, -CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 34.9 (-*C*H₂), 29.1 (-*C*H₃) 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-C₄H₉].

MS (APCI): C₂₂H₂₈N₂O₆ *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 \rightarrow 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(CD₃)₂, 300 K): δ = 7.95 (d, ³*J* = 8.1 Hz ,2 H, *H*-3), 7.46 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.7 Hz, 2 H, *H*-4), 7.41 (d, ⁴*J* = 1.7 Hz, 2 H, *H*-6), 4.56 (s, 4H, Ar-CH₂-OtBu), 3.27 (s, 4 H, Ar-CH₂), 1.28 (s, 18 H, CH₃) ppm.

¹³**C-NMR** (150 MHz, CO(CD₃)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*-CH₃), 63.4 (Ar-CH₂-OtBu), 34.7 (Ar-CH₂), 27.9 (-*C*H₃) 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): C₂₄H₃₂N₂O₆ *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 \rightarrow 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(CD₃)₂, 300 K): δ = 7.93 (d, ³*J* = 8.3 Hz, 1 H, Ar^{II}-*H*-3), 7.55 (d, ⁴*J* = 2.6 Hz, 1 H, Ar^I-*H*-3), 7.46 (d, ³*J* = 8.3 Hz, 1 H, Ar^{II}-*H*-4), 7.40 (s, 1 H, Ar^{II}-*H*-6), 7.33 (d, ³*J* = 8.4 Hz, 1 H, Ar^I-*H*-6), 7.28 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.6 Hz, 1 H, Ar^{II}-*H*-5), 4.55 (s, 2 H, Ar^{II}-*C*H₂-OtBu), 3.23 (m_c, 4 H, Ar^I-*C*H₂, Ar^{II}-*C*H₂), 1.39 (s, 9 H, Ar^{II}-*C*H₃), 1.28 (s, 9 H, Ar^{II}-*C*H₃) ppm.

¹³**C-NMR** (150 MHz, CO(CD₃)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*-CH₃), 74.3 (Ar^{II}-*C*-CH₃), 63.4 (Ar^{II}-*C*H₂-OtBu), 34.6 (Ar^{II}-*C*H₂), 34.0 (Ar^I-*C*H₂), 28.9 (Ar^{II}-*C*H₃), 27.9 (Ar^{II}-*C*H₃) 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): C₂₃H₃₁N₂O₆ *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 H₂O 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 CuCl₂ 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 H₂O (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 CuCl₂ (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, $6 \% EE \rightarrow 50 \% EE$) 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(CD₃)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, -CH₂), 1.22 (s, 18 H, -CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 31.5 (-*C*H₂), 29.0 (-*C*H₃) ppm.

IR: $\tilde{v} = 2974$ (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]^{+*}, 240 (37) [M-C₈H₁₈]⁺.

MS (EI, HR, 70 eV): C₂₂H₂₈N₂O₂ *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)-1nitrobenzene (**12**, 574 mg, 1.38 mmol) and Ba(OH)₂ 8 H₂O (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 CuCl₂ (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 \rightarrow 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(CD₃)₂, 298 K): δ = 6.92 (d, ³*J* = 8.3 Hz, 1 H, *H*-6), 6.77 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.3 Hz, 1 H, *H*-10), 6.69 (d, ³*J* = 8.5 Hz, 1 H, *H*-9), 6.66 (d, ⁴*J* = 2.3 Hz, 1 H, *H*-12), 6.62 (dd, ³*J* = 8.3 Hz, ⁴*J* = 2.3 Hz, 1 H, *H*-5), 6.35 (d, ⁴*J* = 2.3 Hz, 1 H, *H*-3), 2.83-2.76 (m, 4 H, -CH₂), 1.20 (s, 9 H, Ar^{II}-CH₃), 1.19 (s, 9 H, Ar^I-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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-CH₃), 78.9 (Ar^{II}-C-CH₃), 32.2 (Ar^{II}-CH₂), 31.3 (Ar^I-CH₂), 29.0 (Ar^{II}-CH₃), 28.9 (Ar^{II}-CH₃) ppm.

IR: $\tilde{v} = 2975$ (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]^{+*}, 240 (7) [M-C₈H₁₈]⁺.

MS (EI, HR, 70 eV): C₂₂H₂₈N₂O₂ *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 H₂O (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 CuCl₂ (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 \rightarrow 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(CD₃)₂, 298 K, TMS): δ = 6.78 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.6 Hz, 2 H, *H*-4), 6.71-6.69 (m, 4 H, *H*-6, *H*-3), 2.81 (s, 4 H, -CH₂), 1.21 (s, 18 H, -CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 32.1 (-*C*H₂), 27.5 (-*C*H₃) 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]⁺⁺, 296 (13) [M-C₄H₉]⁺, 240 (73) [M-C₈H₁₈]⁺.

MS (EI, HR, 70 eV): C₂₂H₂₈N₂O₂ *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 H₂O (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 CuCl₂ (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 \rightarrow 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(CD₃)₂, 298 K): δ = 7.13 (dd, ³*J* = 8.1 Hz, ⁴*J* = 1.7 Hz, 2 H, *H*-4), 7.05 (d, ⁴*J* = 1.7 Hz, 2 H, *H*-6), 6.78 (d, ³*J* = 8.1 Hz, 2 H, *H*-3), 4.32 (s, 4 H, -*C*H₂-OtBu), 2.86 (s, 4 H, -*C*H₂), 1.21 (s, 18 H, -*C*H₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 63.9 (Ar-CH₂-OtBu), 32.3 (-*C*H₂), 27.9 (-*C*H₃) ppm.

IR: $\tilde{v} = 2969$ (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]^{+*}, 323 (5) [M-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₂₄H₃₂N₂O₂ *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 H₂O (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 CuCl₂ (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 \rightarrow 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(CD₃)₂, 298 K): δ = 7.13 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz 1 H, *H*-10), 7.02 (d, ⁴*J* = 1.0 Hz , 1 H, *H*-12), 6.94 (d, ³*J* = 8.0 Hz, 1 H, *H*-6), 6.75 (d, ³*J* = 8.0 Hz, 1 H, *H*-9), 6.64 (dd, ³*J* = 8.0 Hz, ⁴*J* = 2.6 Hz, 1 H, *H*-5), 6.41 (d, ⁴*J* = 2.6 Hz, 1 H, *H*-3), 4.32 (s, 2 H, -CH₂OtBu), 2.83-2.77 (m, 4 H, -CH₂), 1.23 (s, 9 H, Ar^{II}-CH₃), 1.20 (s, 9 H, Ar^{II}-CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 73.7 (Ar^{II}-*C*-CH₃), 63.9 (-CH₂-OtBu), 32.3 (Ar^{II}-CH₂), 31.5 (Ar^I-CH₂), 29.0 (Ar^I-CH₃), 27.9 (Ar^{II}-CH₃) 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]⁺⁺, 310 (14) [M-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₂₃H₃₀N₂O₂ *m*/*z*= calc.: 366.2307, found: 366.2304.

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

General procedure

Deprotection using TiCl₄:

Under nitrogen atmosphere the *tert*-butoxy diazocine was dissolved in dry dichloromethane and cooled to 0 °C. TiCl₄ (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 \rightarrow 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(CD₃)₂, 298 K, TMS): δ = 8.39 (s, 1 H, OH), 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, -CH₂) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*H₂) ppm.

IR: $\tilde{v} = 3340$ (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]^{+*}.

MS (EI, HR, 70 eV): C₁₄H₁₂N₂O₂ 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, TiCl₄ (99.9 μ L, 0.91 mmol) was added according to the general procedure using TiCl₄. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 12 % EE \rightarrow 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-OH), 9.43 (s, 1 H, Ar^{II}-OH), 6.86 (d, ³*J* = 8.3 Hz, 1 H, *H*-6), 6.68 (d, ³*J* = 8.5 Hz, 1 H, *H*-9), 6.55 (dd, ³*J* = 8.5 Hz, ⁴*J* = 2.5 Hz, 1 H, *H*-10), 6.44 (dd, ³*J* = 8.3 Hz, ⁴*J* = 2.5 Hz, 1 H, *H*-5), 6.41 (d, ⁴*J* = 2.5 Hz, 1 H, *H*-12), 6.14 (d, ⁴*J* = 2.5 Hz, 1 H, *H*-3), 2.64 (m_c, 4 H, - CH₂) 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*H₂), 29.9 (Ar^I-*C*H₂) 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]^{+*}.

MS (EI, HR, 70 eV): C₁₄H₁₂N₂O₂ *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 \rightarrow 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(CD₃)₂, 298 K, TMS): δ = 8.32 (s, 2 H, O*H*), 6.67 (d, ³*J* = 8.4 Hz, 2 H, *H*-3), 6.63 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.4 Hz, 2 H, *H*-4), 6.54 (d, ⁴*J* = 2.4 Hz, 2 H, *H*-6), 2.75 (s, 4 H, -C*H*₂) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*H₂) ppm.

IR: $\tilde{v} = 1602$ (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]^{+*}.

MS (EI, HR, 70 eV): C₁₄H₁₂N₂O₂ 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 μ mol) dissolved in 5 mL dry dichloromethane, TiCl₄ (22.4 μ L, 0.20 mmol) was added according to the general procedure using TiCl₄. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 20 % EE \rightarrow 80 % EE) the product was obtained as a yellow solid (13 mg, 49.0 μ mol, 72 %).

melting point: 153 °C

*R*_f= 0.12 (cyclohexane/ ethyl acetate 1:1).

¹**H-NMR** (500 MHz, CD₃CN, 298 K, TMS): δ = 7.12 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.5 Hz, 2 H, *H*-4), 7.03 (s, 2 H, *H*-6), 6.80 (d, ³*J* = 7.9 Hz, 2 H, *H*-3), 4.44 (d, ³*J* = 5.7 Hz, 4 H, -CH₂-OH), 3.15 (t, ³*J* = 5.7 Hz, 2 H, OH), 2.85 (m_c, 4 H, -CH₂) ppm.

¹³**C-NMR** (125 MHz, CD₃CN, 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 (-CH₂-OH), 32.3 (-CH₂) 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]^{+*}.

MS (EI, HR, 70 eV): C₁₆H₁₆N₂O₂ *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, TiCl₄ (117 μ L, 1.07 mmol) was added according to the general procedure using TiCl₄. After work-up and purification using flash column chromatography on silica (cyclohexane/ ethyl acetate, 30 % EE \rightarrow 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(CD₃)₂, 300 K, TMS): δ = 8.40 (s, 1 H, Ar-O*H*), 7.15 (d, ³*J* = 8.2 Hz, 1 H, *H*-10), 7.03 (s, 1 H, *H*-12), 6.88 (d, ³*J* = 8.2 Hz, 1 H, *H*-6), 6.77 (d, ³*J* = 8.2 Hz, 1 H, *H*-9), 6.51 (dd, ³*J* = 8.2 Hz, ⁴*J* = 2.5 Hz, 1 H, *H*-5), 6.28 (d, ⁴*J* = 2.5 Hz, 1 H, *H*-3), 4.50 (d, 2 H, ³*J* = 5.6 Hz, -CH₂OH), 4.12 (t, 1 H, ³*J* = 5.6 Hz, -CH₂OH), 2.81-2.71 (m, 4 H, -CH₂) ppm.

¹³**C-NMR** (150 MHz, CO(CD₃)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*H₂-OH), 32.7 (-*C*H₂-Ar-CH₂OH), 31.2 (Ar^I-CH₂) ppm.

IR: \tilde{v} = 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]^{+*}.

MS (EI, HR, 70 eV): C₁₅H₁₄N₂O₂ m/z= calc.: 254.1055, found: 254.1052.

3.2 Syntheses of monofunctionalised diazocines

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

Br

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 \rightarrow 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, CDCl₃, 298 K, TMS): δ = 7.65 (d, ⁴*J* = 2.6 Hz, 1 H, *H*-3), 7.44 (d, ³*J* = 8.4 Hz, 1 H, *H*-6), 7.20 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.6 Hz, 1 H, *H*-5), 4.80 (s, 2 H, -CH₂), 1.42 (s, 9 H, -CH₃) ppm.

¹³**C-NMR** (125 MHz, CDCl₃, 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*-CH₃), 29.0 (-*C*H₂), 28.7 (-*C*H₃) 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]⁺⁺, 231 (7) [M-C₄H₉]⁺, 153 (10) [M-C₄H₉Br]⁺.

MS (EI, HR, 70 eV): C₁₁H₁₄NO₃Br *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, -CH₂), 1.34 (s, 9 H, -CH₃) 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*-CH₃), 28.1 (-CH₃), 26.2 (-CH₂) 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): $C_{29}H_{29}O_{3}NP m/z$ = 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 \rightarrow 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, CDCl₃, 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^{II}-*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^{II}-*H*-5), 6.88 (d, ³*J* = 8.5 Hz, 1 H, Ar^I-*H*-6), 1.36 (s, 9 H, C*H*₃) ppm.

¹³**C-NMR** (125 MHz, CDCl₃, 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*-CH₃), 28.7 (CH₃) 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-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₁₈H₁₈N₂O₅ *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 \rightarrow 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(CD₃)₂, 298 K, TMS): δ = 7.01 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1 H, Ar^{II}-*H*-6), 6.93 (m_c, 1 H, Ar^{II}-*H*-5), 6.88 (d, ³*J* = 8.0 Hz, 1 H, Ar^I-*H*-3), 6.69 (dd, ³*J* = 7.7 Hz, ⁴*J* = 1.2 Hz, 1 H, Ar^{II}-*H*-3), 6.57 (m_c, 1 H, Ar^{II}-*H*-4), 6.40 (d, ⁴*J* = 2.3 Hz, 1 H, Ar^I-*H*-6), 6.23 (dd, ³*J* = 8.0 Hz, ⁴*J* = 2.4 Hz, 1 H, Ar^I-*H*-4), 4.42 (bs, 4 H, NH₂), 2.86 (s, 9 H, CH₃), 2.74 (m_c, 4 H, CH₂) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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-CH₃), 31.4 (Ar^{II}-CH₂), 30.8 (Ar^I-CH₂), 29.2 (CH₃) 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]^{+*}, 228 (3) [M-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₁₈H₂₄N₂O *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 \rightarrow 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(CD₃)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, ³*J* = 8.2 Hz, 1 H, *H*-6), 6.78 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 1 H, *H*-9), 6.63 (dd, ³*J* = 8.2 Hz, ⁴*J* = 2.4 Hz, 1 H, *H*-5), 6.39 (d, ⁴*J* = 2.4 Hz, 1 H, *H*-3), 2.82 (m_c, 4 H, CH₂), 1.21 (s, 9 H, CH₃) ppm.

¹³**C-NMR** (125 MHz, CO(CD₃)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*-CH₃), 32.0 (Ar-CH₂), 31.5 (OtBu-Ar-CH₂), 29.0 (CH₃) ppm.

IR: $\tilde{v} = 2985$ (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-C₄H₉]⁺.

MS (EI, HR, 70 eV): C₁₈H₂₀N₂O *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 TiCl₄ (87.5 μ L, 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 \rightarrow 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(CD₃)₂, 300 K, TMS): δ = 8.39 (s, 1 H, OH), 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, CH₂) ppm.

¹³**C-NMR** (150 MHz, CO(CD₃)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*+2), 31.3 (HO-Ar-*C*H₂) 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]^{+*}.

MS (EI, HR, 70 eV): C₁₄H₁₂N₂O *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 $^{\circ}$ C and NaNO₂ (1.10 g, 16.1 mmol) dissolved in 3.5 mL water was added dropwise. After 15 min stirring at 0 $^{\circ}$ 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(CD₃)₂, 298 K): δ = 9.11 (s, 1 H, OH), 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(CD₃)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): C₁₂H₉ON₂ *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 NaNO₂ (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(CD₃)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(CD₃)₂, 298 K): *δ* = 160.8 (*C*-1), 147.2 (*C*-4), 125.2 (*C*-3), 116.6 (*C*-2) ppm.

IR: $\tilde{v} = 3182$ (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): C₁₂H₁₁O₂N₂ *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 $n-\pi^*$ 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 (H₂O 98 %; DMSO 2 %; 200 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M; left) and **4** (420 μ M; right) recorded at 25 °C in aqueous solution H₂O 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M). 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 μ M; left) and **4** (420 μ M; right) recorded at 37 °C in aqueous solution H₂O 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 μ M) 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 μ M) in presence of (2hydroxypropyl)- 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 μ M) 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 μ M) 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 μ M) 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 μ M) 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 (H₂O 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 (H₂O 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. ¹H-NMR spectra of compound **1** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 33. ¹H-NMR spectrum of the photostationary state of compound **1** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 34. ¹H-NMR spectra of compound **2** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 35. ¹H-NMR spectrum of the photostationary state of compound **2** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 36. ¹H-NMR spectra of compound **4** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 37. ¹H-NMR spectrum of the photostationary state of compound **4** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 38. ¹H-NMR spectra of compound **3** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 39. ¹H-NMR spectrum of the photostationary state of compound **3** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 40. ¹H-NMR spectra of compound **7** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 41. ¹H-NMR spectrum of the photostationary state of compound **7** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 42. ¹H-NMR spectra of compound **5** measured in DMSO-d₆ at 298 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 43. ¹H-NMR spectrum of the photostationary state of compound **5** measured in DMSO-d₆ at 298 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 44. ¹H-NMR spectra of compound **6** measured in DMSO-d₆ at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 45. ¹H-NMR spectrum of the photostationary state of compound **6** measured in DMSO-d₆ at 300 K. Integrals of the *E* and *Z* isomers are display in red.

NMR switching experiments and photostationary states in aqueous solution



8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0

Supplementary figure 46. ¹H-NMR spectra of compound **1** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 47. ¹H-NMR spectrum of the photostationary state of compound **1** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Integrals of the *E* and *Z* isomers are display in green.



Supplementary figure 48. ¹H-NMR spectra of compound **2** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Spectra after irradiation with 405 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 49. ¹H-NMR spectrum of the photostationary state of compound **2** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 50. ¹H-NMR spectra of compound **7** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 51. ¹H-NMR spectrum of the photostationary state of compound **7** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 52. ¹H-NMR spectra of compound **5** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 298 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 53. ¹H-NMR spectrum of the photostationary state of compound **5** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 298 K. Integrals of the *E* and *Z* isomers are display in red.



Supplementary figure 54. ¹H-NMR spectra of compound **6** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) at 300 K. Spectra after irradiation with 385 nm plotted in green and after irradiation with 530 nm plotted in blue.



Supplementary figure 55. ¹H-NMR spectrum of the photostationary state of compound **6** measured in aqueous solution (90 % D_2O ; 10 % DMSO-d₆) 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 μ M) recorded at 25 °C (left) and 37 °C (right) in aqueous solution H₂O 98 %; DMSO 2 % (blue) or D₂O 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 (H₂O 98 %; DMSO 2 % and D₂O 98 %; DMSO 2 %).

Compound 3	∆ <i>H</i> [‡] / kJ·mol⁻¹	ΔS^{\dagger} / J·K ⁻¹ mol ⁻¹ ·
H ₂ O	31.3 ± 0.4	-112.7 ± 1.0
D ₂ O	32.7 ± 1.3	-114.7 ± 2.6



Supplementary figure 57. Top: Transient absorption decays of compound **4** (420 μ M) recorded at 25 °C (left) and 37 °C (right) in aqueous solution H₂O 98 %; DMSO 2 % (blue) or D₂O 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 (H₂O 98 %; DMSO 2 % and D₂O 98 %; DMSO 2 %).

Compound 4	∆ <i>H</i> [‡] / kJ·mol⁻¹	ΔS^{\dagger} / J·K ⁻¹ mol ⁻¹ ·
H ₂ O	30.9 ± 0.1	-106.7 ± 0.7
D ₂ O	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 % CO₂ in a humidified atmosphere. Prior to transient transfection, cells were seeded into culture flasks at a density of 1.2×10^5 cells / cm² 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 McDonnell⁷) and 62.5 ng Renilla normalization plasmid per 10⁶ 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 96well plates (4 * 10⁴ 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 μ M - 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 EC₅₀ values were performed using GraphPad Prism® (v. 7.03, GraphPad Software, San Diego, CA, USA). Additionally, the maximum relative activity (at 100 μ M) 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. EC₅₀ = 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, $EC_{50} = 5.4 \pm 0.7 \mu$ M, max. relative activity: $123.4 \pm 46.4 \%$). (b) Disubstituted hydroxy azobenzene, unirradiated (*E*-isomer, dark, red circles, $EC_{50} = 1.8 \pm 0.8 \mu$ M, max. relative activity: $87.9 \pm 4.3 \%$). The highest concentrations (100 μ M and 33 μ M) 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 \pm SD. EC₅₀-values are means of biological replicates \pm 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, EC₅₀ = 19.8 pM) *vs.* irradiated at 405 nm every 3 h with 50 % power for 1 min (blue triangles, EC₅₀ = 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, EC₅₀ = 15.1 pM) *vs.* irradiated at 405 nm every 30 min with 50 % power for 1 min (blue triangles, EC₅₀ = 37.2 pM). (b) β -Estradiol, unirradiated (red circles, EC₅₀ = 16.3 pM) *vs.* irradiated at 405 nm every 30 min with 25 % power for 3 min (blue triangles, EC₅₀ = 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, EC₅₀ = 8.06 pM) *vs.* irradiated at 385 nm every 3 h with 50 % power for 3 min (blue triangles, EC₅₀ = 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, EC₅₀ 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). (b) Asymmetrical diazocine **6**, 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, EC₅₀ 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 μ M in ddH₂O containing 2 % DMSO and a volume of 110 μ l 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 μ l 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 μ M in ddH₂O 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 μ M in ddH₂O 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 μ M in ddH₂O 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 highenergy 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 = $0.0 \text{ kcal mol}^{-1}$). 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*-**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.

 $k = K_{B}T/h \times \exp(-\Delta H^{\dagger}/RT) \times \exp(\Delta S^{\dagger}/R)$ (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 $\tau = 283$ s, for *E*-**4** $\tau = 632$ 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 energy and enthalpy of activation as obtained by M06-2X/cc-pVTZ, into the Eyring equation,¹ the lifetime of **1** is obtained as $\tau = 42$ d, for **2**: $\tau = 58$ 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 hydrogenbonded 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 eightmembered 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 ($\Delta U_{dim} = -11.7 \text{ kcal mol}^{-1}$ for *E*-**3** and -12.1 kcal mol}^{-1} for *E*-**4**). The barrier of the twofold hydrogen atom transfer is moderate (*E*-**3** \rightarrow *E*-**3b**: $\Delta U^{\ddagger} = 14.5 \text{ kcal mol}^{-1}$, *E*-**4** \rightarrow *E*-**4b**: $\Delta U^{\ddagger} = 12.9 \text{ kcal mol}^{-1}$), both values are relative to the free solvated monomers). Relative to the free solvated monomers, the reaction is slightly exothermic, with $\Delta U_{H} = -2.6 \text{ kcal mol}^{-1}$ for *E*-**3** \rightarrow *E*-**3b**, and $\Delta U_{H} = -3.7 \text{ kcal mol}^{-1}$ for *E*-**4** \rightarrow *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 $\tau = 14.8$ 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 ($\tau = 59$ 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.

- 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 $\Delta U^{\ddagger} = 25.4$ kcal mol⁻¹. At the same level of theory, the calculated enthalpy of activation is $\Delta H^{\ddagger} = 19.9$ kcal mol⁻¹, resulting in a correction of 5.5 kcal mol⁻¹. Applied to the value obtained by DLPNO-CCSD(T) ($\Delta U^{\ddagger} = 26.2$ 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 NHflip 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(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/ccpVTZ)

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	
T	5.206083000	-1.965518000	-0.706767000	
	$(-2x) \cdot -800 = 5646004$			
E (MUC	(-2X): -800.3646004	: //mn6_2x), _799 2	222326615633	
ы (рыг	NO CCOD(1)/CC PV12	7/1100 ZX). 755.2	.52550015055	
E-Dia	zocine E-3, twist	conformer 4, opti	lmized geometry	(M06-2X/cc-
pVTZ)	,	, 1	<u> </u>	、
- ,				
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	

0	4.130234000	0.431243000	0.190929000
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(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)

3.322119000	2.027576000	-0.098257000
3.044508000	0.982387000	-0.033033000
2.587136000	-1.767307000	-0.457206000
1.760366000	0.596800000	-0.072661000
4.182407000	0.035556000	-0.060879000
3.856869000	-1.361732000	-0.407448000
1.499789000	-0.868042000	-0.076719000
4.691998000	-2.025217000	-0.583489000
2.308504000	-2.795750000	-0.645312000
0.696949000	1.617327000	-0.483901000
	3.322119000 3.044508000 2.587136000 1.760366000 4.182407000 3.856869000 1.499789000 4.691998000 2.308504000 0.696949000	3.3221190002.0275760003.0445080000.9823870002.587136000-1.7673070001.7603660000.5968000004.1824070000.0355560003.856869000-1.3617320001.499789000-0.8680420004.691998000-2.0252170002.308504000-2.7957500000.6969490001.617327000

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

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

Transition state for NH flip of *E*-Diazocine quinone hydrazone tautomer $E-\mathbf{3b}$, 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(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(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(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	5-2X): -800.5769266		
E(DLE	NO-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)

2.161738000	1.239541000	-2.419028000
2.168476000	0.671922000	-1.496277000
2.229255000	-0.766006000	0.867059000
1.447384000	1.150082000	-0.406664000
2.891265000	-0.505736000	-1.431479000
2.917207000	-1.229914000	-0.244509000
1.484945000	0.399272000	0.763668000
	2.161738000 2.168476000 2.229255000 1.447384000 2.891265000 2.917207000 1.484945000	2.1617380001.2395410002.1684760000.6719220002.229255000-0.7660060001.4473840001.1500820002.891265000-0.5057360002.917207000-1.2299140001.4849450000.399272000

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	0.054005000
1 7	-3.394705000	-1 105027000	-1 120561000
י ר	-3.300140000	-1.193027000	-1.120301000
l G	-3.708395000	-0.743403000	-0.010303000
0	-5.081892000	-0.363239000	0.079621000
6	-7.578255000	0.747899000	0.18209/000
6	-5.191686000	1.1006/95000	-0.1/0539000
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
5	0.1,0002000	T.001720000	0.110/120000

5.998633000	-2.238024000	-0.555245000
6.620750000	2.590392000	0.313822000
-1.774850000	0.648210000	1.774091000
-1.155151000	-1.925351000	1.721953000
1.155151000	-1.925351000	-1.721953000
1.774850000	0.648210000	-1.774091000
2.414452000	0.058266000	-1.334831000
-2.414452000	0.058266000	1.334831000
-8.572831000	1.167834000	0.226068000
8.572831000	1.167833000	-0.226069000
-8.530060000	-1.333955000	0.720809000
-8.290973000	-2.252197000	0.870478000
8.530060000	-1.333955000	-0.720808000
8.290973000	-2.252197000	-0.870477000
	5.998633000 6.620750000 -1.774850000 -1.155151000 1.155151000 2.414452000 -2.414452000 -8.572831000 8.572831000 -8.530060000 8.530060000 8.290973000	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

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, $\pi\text{-}$ 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 1/1//7000
⊥ 1	-2 952024000	-2 596194000	1 740601000
	-2.852024000	-2.390184000	1.740091000
1	-4.149/18000	-1.927524000	0.1/4343000
1	-4.644487000	-2.868530000	0.413165000
1	-3.582776000	-2.107223000	-0./41503000
1	-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 7	3 476170000	0 654437000	0.324029000
6	4 964005000	0.427571000	0.425509000
C C	7 52500000	0.437371000	0.273393000
C C	7.555606000	-0.139133000	-0.010063000
0	5.225661000	-0.885018000	0.021967000
6	5.792862000	1.460762000	0.358050000
6	7.137842000	1.155181000	0.204378000
6	6.583282000	-1.1601/4000	-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

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 1/2/28000
G	0.103400000	5 220227000	-0.142420000
0	-0.520038000	5.329237000	1 100000
0	1 124280000	7 102051000	-1.100200000
6	1.134380000	7.102951000	-1.00//50000
6	-0.645165000	6.705341000	0.55/512000
1	2.043832000	5.340893000	-1.832339000
1	-1.391/6/000	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	0.112120000
6	-1 288914000	-5 732046000	-1 166266000
6	-1 134380000	-7 102051000	-1 007750000
6	1.134300000 0 645165000	-6 7053/1000	1.007750000
1	-2 042022000	-5.240002000	
⊥ 1	-2.043032000	-3.340893000	-1.032339UUU
\perp	T.3AT/0/000	-/.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
÷	-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	-1 969205000	1 675368000	0.234330000
1	-2 727049000	2 745635000	-0 257672000
5	-0 557227000	-1 408490000	-0 520921000
1	-0.147318000	-1 087144000	-1 /81539000
1	-0 949516000	-2 413084000	-0 679112000
5	0.629455000	-1 542135000	0.079112000
1	0.02940000	-2 567737000	0.40000000
⊥ 1	0.245512000	-1 402354000	1 500027000
1 7	-0.355935000	1 350454000	-0.426873000
י ר	-0.333933000	1 022142000	-0.420073000
r G	1 664170000	1.033142000	0.379301000
6	1.6641/9000	0.760970000	0.34/98/000
6	4.18125/000	-0.241623000	-0.088429000
6	1.82/809000	-0.626954000	0.289824000
6	2.716475000	1.63/66/000	0.196292000
6	3.990828000	1.130/61000	-0.016/61000
6	3.105183000	-1.114430000	0.05/362000
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/ccpVTZ)

9238000 8350000 8545000 4875000 7591000
8350000 8545000 4875000 7591000
8545000 4875000 7591000
4875000 7591000
7591000
7316000
0463000
8224000
7817000
3846000
5476000
7399000
7643000
7942000
8196000
6137000
6720000
6813000
4662000
8019000
0099000
1366000
8763000
5646000
6354000
2082000
8111000
5627000
5102000
3151000

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/ccpVTZ)

-4.060943000 1.018469000 -0.4013	335000
--------------------------------------	--------

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

4.937654000	1.600357000	0.646565000
2.657384000	2.525756000	1.007991000
0.584072000	-1.405063000	-0.518425000
0.949672000	-2.429055000	-0.591076000
0.198697000	-1.150535000	-1.506702000
5.418581000	-0.854678000	-0.290708000
6.112347000	-0.237135000	-0.045543000
-4.945412000	1.614275000	-0.638181000
-5.476256000	-0.723827000	0.241279000
-5.448159000	-1.618677000	0.589461000
	4.937654000 2.657384000 0.584072000 0.949672000 0.198697000 5.418581000 6.112347000 -4.945412000 -5.476256000 -5.448159000	4.9376540001.6003570002.6573840002.5257560000.584072000-1.4050630000.949672000-2.4290550000.198697000-1.1505350005.418581000-0.8546780006.112347000-0.237135000-4.9454120001.614275000-5.476256000-0.723827000-5.448159000-1.618677000

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(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	0.96200000	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(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(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(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

-3.802224000	2.704378000	0.575390000
3.314498000	0.955376000	-2.343715000
3.771123000	2.264239000	-0.058366000
4.153335000	2.523257000	-0.900786000
	-3.802224000 3.314498000 3.771123000 4.153335000	-3.8022240002.7043780003.3144980000.9553760003.7711230002.2642390004.1533350002.523257000

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
T T	2.342403000	0 612487000	0.000/71000
0	2.308/80000	0.012487000	1 50510000
0	2.012628000	-0.517851000	-1.595123000
6	1.549157000	-0.497842000	0.///165000
6	2.986623000	1.1/3425000	-0.200993000
6	2.808699000	0.60/406000	-1.45/522000
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
2	3 768819000	2 268044000	0 004558000
1	1 1 1 2 5 9 5 0 0 0	2 559069000	
1	4.143363000	2.556066000	-0.031030000

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 (MO6-2X/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
-	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 59606000
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	0.507270000
7	3 391270000	1 402169000	-1 059748000
, 7	3 700322000	0 911/19000	0 031826000
6	5 073451000	0.536747000	0.051020000
6	7 563516000	-0 601005000	0.132303000
6	5 188997000	-0.839536000	-0.088101000
6	6 153317000	1 334723000	0.000101000
6	7 416039000	0 756593000	0.515552000
6	6 457132000	-1 391610000	-0 032287000
1	6 017372000	2 393474000	0.032207000
⊥ 1	8 281906000	1 363602000	0.017294000
⊥ 1	6.201900000	-2 446064000	-0.219755000
⊥ ○	9,772506000	-2.440004000	-0.210755000
0	0.772300000	-1.225291000	0.519580000
⊥ ○	9.457540000	-0.387387000	1 702222000
0	-1.140149000	-0.401400000 2 112076000	-1 720050000
⊥ 1	-1.140140000 1.140140000	2.112075000 2.112075000	-1.720050000
⊥ 0	1.752015000	2.113U/3UUU	1 702222000
0 1	T. / JZUTJUUU	-U.401401UUU	1 2E0C0E000
⊥ 1	2.39/406000	0.121544000	1.350605000
\perp	-2.39/406000	0.121343000	-1.330003000

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	0 078/13000
т Т	2 072260000	-2.037275000	0.070413000
1	3.972309000	-2.0373730000	1 001006000
⊥ 1	4 268708000	-1.835594000	1.901990000
T C	4.208/98000	-3.080218000	0.717561000
b 1	2.515897000	-1.918180000	0.290533000
1	2.073934000	-2.913169000	0.335039000
Ţ	2.555879000	-1.65/33/000	-0.769606000
8	-1.970685000	-0.967158000	1.9638/0000
1	-2.5856/9000	-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(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(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(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	-0.70JJ0J000	2 017202000	1 000225000
1	-5.5/01/5000	-2.017293000	1 122270000
	-7.086809000	1.462255000	-1.1323/9000
0	-4.386166000	1.469550000	-1.0469/8000
1	-4.103944000	2.295982000	-0.389007000
	-4.954250000	1.918242000	-1.861109000
6	-3.100908000	0.853358000	-1.6531/9000
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
1	3 098817000	-0 852543000	-1 660172000
1	2 904632000	-1 35/185000	-2 607525000
⊥ 1	2.251102000	1.334103000	_1 011700000
⊥ ○	J. E70221000	1 001245000	-1.911/09000
0	-1.378231000	-1.991343000	-1.191303000
1	-2.992327000	-0.983836000	-0.100457000
⊥ 1	7.020041UUU	1.722000000	1 607017000
⊥ ⊥		-1./23808000	1.00/81/000
0 1	-8.944816000	0.014200000	0.0951/3000
⊥ ∩	-9.145085000	0.129356000	-0.514288000
ರ 1	8.921631000	-0.11348/000	0.001820000
\bot	9.438123000	0.506553000	0.523206000

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 xtb¹⁹ and the GFN2-xtb method.²⁰ The resulting structures were refined using ORCA¹⁵ at the ω B97X-D3²¹/def2-SVP²² level of theory with Grimme's dispersion correction²³ as well as an auxiliary basis set²⁴ and the RIJCOSX approximation for Coulomb and HF Exchange²⁵. 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 ω B97X-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 $E \rightarrow Z$ 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 toolkit²⁶. 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 21²⁷, as well as the GAFF2 forcefield²⁸. 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 backisomerization 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

#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 ENRGY = 5:071.094177386979 Input = w697X-03 def2.5VP def2/1 D32ERO RUCOSX OPT C 148042243540408 22.70378711612064 6.45080839830643 H 0.795253540427199 23 33158444416216 7.0211630839830643 H 1.2969724655446 21 6625259835505 6.752735557748504 C 11534099095398 22.88772218336619 4.97067320921330 H 0.442347752802 23.68519448234052 4.03735362797898 H 0.442347752902 23.685139145164 4.5655998681346 C 2.32393625852138 22.286536448234952 4.03735362797898 H 1.30567315725902 23.685139163767 4.36593446402284 C 1.82514079083585 32.117373882533919 2.61053374161194 H 1.10469715100752787 24.39201524423878 24.47760488921938 C 1.0751907952787 24.39201524423878 24.4776048921938 C 1.0751907952787 24.39201524423878 24.4776048921938 C 1.075190795121802 24.52759209501595 3.3570198322070 C -2.89114655388911 23.6259030337365 5.42208159148910 H -3.33386063833191 2.07786713829730 6.24744175496674

н	-1.82781092829676	23.74396817732692	5.67733706483981
C	-3.01593126514518	22.80006251980123	4.15340341786436
с	-2.25958987028160	23.41248180826054	2.97399373537184
н	-2.52145711173144	24.48244728664669	2.89249338570817
н	-2.19072772409806	21.67061890790903	1.75693226610805
C	-4.09145298470055	22.60804605763456	1.49033221603457
c	-4.75655989872280	22.00996366587852	2.72657308558202
H C	-5.85092349826218 -4.42750361250687	22.09529785496603 19.21582890639885	2.63497147634789 5.47887854781901
н	-3.80099415301717	20.09406415563822	5.26377231575482
H	-5.28543990328900	19.56302068254705	6.08975040698081 4.15775493114730
н	-4.17242692861306	18.09039741837234	3.69241607581147
С	-5.42761474468227	19.77071735659773 20.31479672727232	3.17196648844225
C	-5.89271251357194	19.09231145341229	1.88623723628153
H C	-5.02419447005595 -6.98626208741788	18.54482293385014 18.08448962853089	1.47053921420614 2.19712292388314
Ĥ	-7.86408297032260	18.65615895513387	2.55775041115422
С	-6.56743680492454 -7.44514943069484	17.14713395730353 16.58180794089325	3.32903711870847 3.68758612317317
С	-5.52763475001657	15.15033481347608	5.79007302993637
н	-6.06027164391393 -6.25550372752158	14.29140875316433 15.94275985682009	6.23534266599973 5.58558600455848
с	-4.86323527832473	14.66294653018822	4.50598474050857
н С	-5.63279894457550	14.91743599103227	4.4104/432/8566/ 3.20965518701642
Н	-6.68231747048192	14.57868306788268	3.31068966910524
н	-4.03673683325656	14.69194931354233	1.81921020323330
С	-4.74659839198126	12.74231823564930	2.30091810296020
c	-3.97323010077063	12.65105985221171	3.62451257581748
H C	-3.83785899916857 -1.66953223377862	11.59729721193018	3.91648355791776
н	-1.09439596181075	11.80376675911790	6.76958371860737
н С	-2.61634359548183 -0.87185998049151	12.28256050046258 12.44647643392591	5.97813782354277 4.74655804140889
н	-0.70768247945087	13.49030282098318	5.05704302289732
C H	-1.5/322062155598 -1.84705789418510	12.46160605464642 11.43056061547586	5.383/9214232757 3.10067021150373
c	-0.66050080829809	13.03120255571690	2.31590394637000
н С	0.66948687672869	12.28916162566063	2.31933955684866
H	0.47156743553850	11.22232081924110	2.10300214019488
ч	2.19861456027984	11.79033290830716	3.79276952237402
C	1.72502659153175	14.44989892434918	6.93888811195729
н	0.79100501541717	13.97657197112471	6.60583252197831
C	2.41046117141585	15.08737412187442	5.74332815527875
с	2.69233105289199	14.07235490570106	4.63279899074021
H C	3.17911122773741	13.19090937927922	5.08786226576120
н	3.07725062359836	15.52634229693421	3.11524839517704
С	4.87970818111768	15.17718432655738	4.23152124332637
c	4.49805795436289	16.18651758710447	5.31646269346175
H C	5.39541758821818 3.42108848295773	16.50858784149325 18.97373243913125	5.87201588586008 7.14468762321538
Ĥ	3.10391724292897	17.91589388133494	7.11974041378843
н С	4.40054427509487 3.58351815373436	19.03407824404625 19.46429936773395	7.65633974269372 5.72622219286650
Н	2.58176689648298	19.54254993987643	5.26943854780013
н	4.44586088822735 5.46572042740458	18.49571102723192	4.83645362534326 5.26339827495860
C	4.53030549173425	19.18973208315213	3.45140403315093
c	5.05206816502850	20.61521488722981	3.55600045540588
	6 00124222002222	20 57040535950533	0.0000047070000
С	4.21707168251216	21 42548414259678	3.92225847973009 4.55588702339318
СН	4.21707168251216 4.68553369503471	21.42548414259678 22.40263394421855	4.55588702339318 4.76025058101157
с Н О Н	4.21707168251216 4.68553369503471 2.80573518223137 3.28648292167713	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166	3.92225847973009 4.55588702339318 4.76025058101157 6.77646315981002 6.86447495864524
СНОНОН	4.21707168251216 4.68553369503471 2.80573518223137 3.28648292167713 2.97581993465511 3.59939242727111	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 23.13328688877376 22.43090714625454	3.9222584/973009 4.55588702339318 4.76025058101157 6.77646315981002 6.86447495864524 1.70837732509889 1.97131739855046
снононо:	4.21707168251216 4.68553369503471 2.80573518223137 3.28648292167713 2.97581993465511 3.59939242722111 0.50163298249435	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 23.13328688877376 22.43099714625454 24.506399533229627	3.92225847973009 4.55588702339318 4.76025058101157 6.77646315981002 6.86447495864524 1.70837732509889 1.97131739855946 1.19647386170667
гснонононо	0.051947230532 4.21707168251216 4.68553369503471 2.80573518223137 3.28648292167713 2.97581993465511 3.59939242722111 0.50163298249435 1.13272922076477 0.46974851896558	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 23.13328688877376 22.43099714625454 24.50639953929627 24.19926441907666 24.14103070724508	3.3222584/9/3009 4.55588702339318 4.76025058101157 6.77646315981002 6.86447495864524 1.70837732509889 1.97131739855946 1.19647386170667 0.53258706515054 4.79385283303552
- С - С - С - С - С - С - С - С - С - С	0.5134723931216 4.68553369503471 2.80573518223137 3.28648292167713 2.97581993465511 3.59939242722111 0.50163298249435 1.13272922076477 0.46974851896558 -0.87226727221238	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 22.43099714625454 24.50639953929627 24.19926441907666 24.14103070724508 23.25632214180538	3.3222584/9/3009 4.55588702339318 4.76025058101157 6.87646315981002 6.86447495864524 1.7083773250888 1.9713173885594 1.19647386170667 0.53258706515054 4.79385283303552 3.15506526578888 5.2473791076698
п С н О н О н О н О О О н	0.031447303142 4.68553369503471 2.80575318223137 3.28648292167713 2.97581993465511 0.50163298249435 1.13272922076477 0.46974851896558 -0.8722672722138	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 23.13328688877376 22.43099714625454 24.50639953929627 24.19926441907666 23.25632214180538 24.90769517288885 24.90769517288885	3.9222584/97/3002 4.5558870/30339318 4.76025058101157 6.77646315981002 6.86447495864524 1.70837732509889 1.97313739855946 1.19647386170667 0.53258706515054 4.7938528303552 3.15506526578988 5.24772281056888
	0.031947263251216 4.68553369503471 2.80575318223137 3.28648292167713 2.97581993465511 0.50163298249435 1.13272922076477 0.46974851896558 -0.8722672722138 -3.43310096766219 4.33335158402312 -2.07706292722133	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 22.31332688877376 22.43099714625454 42.50339953929627 24.19926441907666 24.14103070724508 23.25652214180538 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 24.90769517288885 25.90562502693581	3.9222584/97/3002 4.55588/02339318 4.76025058101157 6.7764513981002 6.86447495864524 1.19647386170667 0.53258706515054 4.79385283303552 3.15506526578988 5.24772281056888 5.24772281056888
пононорононо	0.51347253310 4.68553369503471 2.80573512823137 3.28648292167713 3.5993924722111 0.50163298249435 1.13272922076477 0.46974851896558 -3.43310096766219 -3.4335154802312 -2.07706292722133 -1.15019683538951	21.42548414259678 22.40263394421855 23.03610391265943 22.20202581879166 22.31332688877376 22.43099714625454 24.19926441907666 24.14103070724508 23.25632214180538 24.90769517288885 24.9769517288885 23.356625026995620 23.35662502693581 23.35662502693581 23.5862502693581 23.58626261582745	3.9222584/9/3002 4.555887020339318 4.76025058101157 6.7764513981002 6.86447495864524 1.1964738617066 1.1964738617065 0.53258706515054 4.79385283303552 3.15506526578988 5.24772281056888 4.93203090457537 0.55261928159547 0.73048849778064 0.3551695655208
- СНОНОНОНОООНОНОНО	0.0017473002130 4.86553306903471 2.08773518223137 3.28648292167713 3.29848292167713 3.2993924722111 0.50163298249435 1.3272922076477 0.46974851896558 4.33535158402312 2.077062392722123 1.15019683530951 4.41089818215402 3.81775822355400	11.425.4841.4259678 22.40263394421855 23.03610391765943 22.20202581879166 23.13322688877376 22.43099714625454 42.50639953929627 24.490927441807366 23.25632214180538 24.7418202724508 23.2565220693581 23.3662520693581 23.3662520693581 23.3662520693581 23.3662520693581 23.3662520693581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366276083581 23.366275083581 23.366276085885 23.366276885885 23.3662768858858 23.3662768858858 23.36627688588588 23.36627688588588 23.36627688588588 23.367888588588858	3.9222584/97/3002 4.55588/702339318 4.76025058101157 6.77646315981002 6.86447495864524 1.97131739855946 1.97131739855946 1.97131739855946 1.973528706515054 4.9335283706576578988 4.93203909457537 0.55261928159547 0.73048849778064 0.35716965565208 0.34998935358515
с нонононоо нононоо	0.031741002112 4.6653330650471 2.0657351223137 3.28648222167713 3.29848222167713 3.2993824722111 3.5993924722113 1.327922076477 4.3253548248435 0.8722672722123 4.34310096766219 4.3435158402315 4.3431096766219 4.345354584244598185 4.34512542254402 4.341758222554402 4.34827580424114	11.4258414425677 22.40263394421857 22.40263394421857 22.305610391265943 22.20202581879166 22.4303971462544 23.450539953395627 24.409371462544 24.30539953395627 24.41913070724508 23.25652214180336 24.3076951728885 24.3783292996620 23.3565250693581 23.3565250693581 23.3565250780313 23.3565250780313 21.1803036441841 22.751722254678913 21.1803036441841 22.751722254678913	32422384773609 455588702339318 476025055101157 6.8644749568524 17083732509880 13731730855946 1394733610667 0.5325570551504 4793822833052 315506525678888 49320390457537 0.532545798155547 0.532545798155547 0.53254593155547 0.53254293155547 0.53254293155547 0.53469849778064 0.33716695555208 0.33716695555208
с нонононоонононоо н	0.031741002112 4.6655330650471 2.06575518223137 3.28648292167713 3.29848292167713 3.29848292167713 3.5993924722111 3.5993924722111 3.5993924722112 4.3755158402312 2.07706292722132 4.330106766219 4.3355158402312 4.41089818215400 4.388278004818215400 4.388278004818215400 4.38827800442114 3.62886522213463	21.4254841425675 22.4025394421855 23.03610931265943 22.2002531942185 23.032501931265943 23.200225812959436 23.1332868887376 43.1932641907566 43.1410307074508 43.19926414007566 43.1410307074508 43.2552214180538 43.076951728885 23.5552214180538 43.076951728885 23.5552214180538 43.076951728885 23.5552214180538 43.076951728885 23.5552214180538 43.076951728885 23.5552214180538 43.076951728885 23.5552214180538 43.076951728855 23.555221480538 43.076951728855 23.55522099650 23.555221480538 23.555221480538 24.076951728855 23.555221480538 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769517288557 24.0769577 24.0769577 24.076957724.076577 24.076757 24.07675777577770	32225881773003 45568702339318 476025054101157 657645315801022 63647149350455 1974631581002 63647149350455 197413738617067 4793825394 53258705515564 47938252303555 234772281155687 4792822330355 234772281155687 47928253305555560 47928253305555560 479282533055717322 63269297378064 33571669555500 33708657577322 614429348196031 2437285555555
снононоронононороно:	4.21707168252116 4.6555336900471 2.80557358023157 2.975518223157 2.9758192345571 3.559892347272111 3.559892347272111 3.559892347272111 3.579822076477 4.3353154802515 4.33531548025122128 3.43510548538951215402 3.81775522255400 4.34625240598189 4.36286522213463 4.1286768938229	21.4254814255671 22.4025394412855 23.0361039125594 22.200253195166 23.133286887736 23.40097144725454 24.5009505295275 24.1092641007666 24.141097074508 24.5092209520 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221089550 23.555221084579 20.57572212546379 20.5757221264579 20.5757221264579 20.5757221264579 20.5757221264579	392223831973009 455588702339318 476025058101157 6364519391002 63644749564524 1197137385596 1197137385596 1197137385596 1197137385596 1197137385596 1197137385596 1197137385596 1197137385596 119713786570 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119647386 119648786 119648786 119648786 119648786 1196486 1196
с с н о н о н о н о о о н о н о н о н о	4.21707142852126 4.65553369050471 2.8057338020167713 2.8758318221317 2.97581993465511 0.50163298249435 3.95939242722111 0.50163298249435 0.48724677221238 3.43310096766219 2.07706429722138 3.43310096766219 2.15102982315180 3.4310096766219 2.15102982315180 3.81775822355400 3.81775822355400 3.81775822355400 3.81775822355400 4.19826768936289 4.19826768894812 5.70006883033967 4.13956746894812	21.42548/41425675 22.402633942421855 22.402633942421855 22.00261391265943 22.20022518105166 23.1332862877376 43.599539539252 43.599539539526 24.3410307074506 24.3410307074506 24.3410307074506 23.35632214180538 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 21.35652720123 21.13396557013 22.1150305441845 21.13396557013 22.150222548799 0.6739211492659 20.53515667061387 17.3202555202212	32223834793409 435588702339318 476025058101157 637645139391002 63644749564524 119947380102 63644749564524 1199473801706570 139473801706570 139473801706570 139473801706570 13947380170657 2311505657088 4392090457537 2477228105688 4392090457537 2487259055520 33571665555208 33571665555208 33571665555208 3357169555520 335716955520 33571655520 33571655520 33571655520 33571655520 33571655520 33571655520 33571655520 33571655520 33571655520 33571655520 33571755775 3357175775775775775775775775775775757575
гонононооонононооононононо	4.21707146251216 4.6555336050471 2.8057354020167713 2.8758218272137 2.97581993465511 0.5016329249435 3.59939242722111 0.5016329249435 0.8722672722123 4.343310096766219 4.33535154802312 2.0770629272133 4.310096766319 4.4109818215400 4.410828240598182 4.41089818215400 4.4282554002411 4.36288652213446 4.43822554002411 4.36288652213446 4.41287678936289 4.41287678936289 4.41287678936289 4.41287678936289 4.731653244680481 7.731653244680481 7.7416530411595	21.42548/41425675 22.40024394424855 23.0361039126594 23.0361039126594 23.133268887736 23.200225818979166 23.133268887736 43.5992541907666 43.14103070724508 43.35632214180538 44.9076951728885 23.35632214180538 24.9076951728885 23.5562550069351 23.3565250069351 23.3565250069351 23.3565250069351 23.3565250069351 23.3565250029351 23.3565250029351 23.3565250029351 23.3565270252424 19.9673972854841 23.5551567051387 17.3202555002171 17.32032552021214	33222383173303 43558870233318 43558870233318 4360256870133318 10358870233318 1035887023318 1035873351705 1373173855346 1395473385170657 1395325870551554 4729382823303552 13550525657888 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105687 3.3520592855525 3.38602555250 0.35458297385 3.4632938535851 3.86025555520 0.34598935335851 3.8602556551 0.34598935335851 3.8602556551 0.3459843535851 3.863254555520 0.3459843535851 3.863254555520 0.345984354565530 0.3459843542431105 1.0704064713398
	4.21707146251216 4.6555336905471 2.8057354502457 2.805735452457 2.97581993465511 0.50163293494355 1.3272922076477 0.46974851895558 4.33535154802312 2.0770629272123 4.33535154802312 2.0770629272133 4.31009818215400 4.33535154802312 4.4089818215400 4.335255402312 4.4089818215400 4.335255402312 4.4089818215400 4.335255402312 4.4089818215400 4.335255402312 4.4089818215400 4.335255402312 4.4089312355402 4.40852221345 4.335255402312 4.335255402312 4.33525240312 4.33525240312 5.70008630330574 7.3165352460982 5.59504027687240	$\label{eq:2} 12.4254841425677 \\ 22.40024394421855 \\ 23.03610391265944 \\ 22.2002581894766 \\ 23.1332808887736 \\ 23.200258189593592527 \\ 24.309714025454 \\ 24.50639953925257 \\ 24.309714025454 \\ 24.30952414007666 \\ 24.3410307074508 \\ 24.35525214180538 \\ 24.90769517288857 \\ 23.5562254180538 \\ 24.90769517288857 \\ 23.5562550693587 \\ 23.5562550693587 \\ 23.5562550693587 \\ 23.556255069387 \\ 23.5555567061387 \\ 17.202555202212 \\ 20.535515667061387 \\ 17.202555202212 \\ 20.535515667061387 \\ 17.202555202212 \\ 17.94653641313177 \\ 17.848103833200 \\ 25.857567061387 \\ 17.2625552002157 \\ 25.857567061387 \\ 17.262555202212 \\ 24.887300175750 \\ 25.855567061387 \\ 17.262555202212 \\ 24.88832004377 \\ 25.855567061387 \\ 25.855567001387 \\ 25.8555670000000000000000000000000000000000$	3222381/73009 435588702339318 476025954101157 677464319584023 677464319584023 677464319584023 677464319584023 677464319584023 677464319584023 677464319585402 11967137385196 7325870561556 47793528233355 11556555657888 5.2477228105688 5.24772281056878 5.24772281056878 5.247722810568788 5.247722810568788 5.247722810568788 5.2477228105687533 0.5265870877322 6.3429383535851 3.86025586671257 6.3378855765530 0.9454535284310 0.95455525685 0.95455528582 0.9454535284310 0.9545552528 0.945453284310 0.954551241176 1.0704067413398 0.34221716189574 4.22437513925146
гототототоототототототототото	4.21707148512116 4.8555336902471 2.805753369024771 3.2057531822317 2.97581993465511 0.5015329349345511 0.501532934934551 0.4507485199558 4.335551549312 2.0770639722131 4.335551549312 2.0770639722134 4.335551549312 4.41099818215400 4.4108948124540 4.4108948124540 4.4108948124540 4.412876789396289 4.41387548934285 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.4139544893428 4.41395448 4.4128764893428 4.41395448 4.4128764893428 4.41395448 4.4128764893428 4.41395448 4.4128764893428 4.41395448 4.4128764893428 4.41395448 4.41395448 4.4128764893428 4.41395448 4.412876	21.4254841425675 22.40253944241855 23.03610931265941 23.2002531942694 23.200253195491 23.200253195495 23.200253195495 23.200253195495295 23.20025419407666 24.1410307072458 24.3097142059529025 23.25622714180538 24.0976951728885 23.35622714180538 24.077823129299650 23.3562520695351 23.3962561582745 21.183039554760313 23.962561482745 21.183039554760313 23.962561482745 21.183039554760313 23.9562561482745 21.1840395441841 22.517222548799 20.35315667661387 77.3202552022124 20.35315667661387 77.3465564133177 77.7846384313177 77.7846384313177	3.9225981793009 4.76625687039318 4.76025058101157 0.6364749364524 0.77646315981002 6.3644749364524 0.1791373250989 1.971373250989 1.971373250989 1.971373250989 1.971373250989 1.971373250989 1.95135017564 0.79382303955 1.9512501855 0.720482072105688 0.3271605555708 0.3271615771722 0.32716158574 0.32716158574 0.32717121 0.32027171158574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171189574 0.32227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198574 0.3227171198575 0.32271711971717200500
	4.217071428521124 4.85553369050471 2.80573380201471 2.80573380201471 2.97581993465511 0.5016329249435 3.9939342722111 0.5016329249435 0.48724672722138 3.4331006766219 2.07706429722138 3.4331006766219 4.31039518215400 4.328521240591150 4.38521240591150 4.3852120442114 4.36284629211346 4.36284629211346 4.36284639211346 4.36284639211346 4.36284639211346 4.362845201441 5.55994027687240 4.386212404598151 5.55994027687240 4.36626419936574 3.8112407589761 3.8112407589761 3.8112407589761	21.42548/41425675 22.402633942424855 22.002610391265943 22.20022518/0166 23.133268287736 24.309274425454 24.5063995392527 24.3092744209766 24.1410307074508 24.30765122899620 23.3565274180558 24.907691728885 24.907691728885 24.907691728885 24.907691728885 24.907691728885 24.907691728885 24.907691728885 24.907691728885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.90769172885 24.9076917285 24.9	34223891/93009 455082702393151 47746415581002 455082702393151 47746415581002 47745173250988 56447495854624 170837732509889 13924373855946 1392473851965 5245725215554 472938282330355 2.3477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.247723815921536 5.24723920571762 5.258576855500 9.34528576855500 9.34528576855500 9.34528576855500 9.34528576855500 9.34528576855500 9.3452877481376 2.8473430231340 5.3429253545 2.8473430231355545 2.8473430231355545 2.84734302313555
	4.21707146251216 4.65553360501471 4.865553360501471 2.8057351822137 2.97581993465511 3.95893242722111 0.5016329249435 3.95993242722111 0.5016329249435 0.8722672722123 4.33535158402312 2.0770629272133 4.33535158402312 4.4109818215400 4.40882840598189 4.41089818215400 4.40882840598189 4.4108746894821 4.408842840598189 4.41287678930289 4.412876789 4.412876789 4.412876789 4.412876787878 4.412876787787878 4.4128767877878787878787878	21.42548/41425677 22.40263394241855 23.0361039126594 23.0361039126594 23.133268887736 23.20022518305879166 23.133268887736 24.309714627545 24.309714627545 24.30953392527 23.256221480538 24.9076951728885 23.256221480538 24.9076951728885 23.5562550695178 23.5562550695178 23.5562550695178 23.5562550695178 23.5562550695178 23.5562550695178 23.556250676138 23.556250676138 23.555156766138 23.555156766138 23.55515676138 23.55156766138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515676138 23.5515670138 23.5515676138 23.5515670138 23.5515670138 23.5515670138 23.5515670138 23.5515670138 23.5715672429788003 23.5715672429788003 25.707552692715 25.707526927875 25.70752692785 25.707526927875 25.70752692785	33222383173303 332223817330318 47602263101150 47602263101150 5056474703584521 170837732509889 1973173855346 1196473855346 1196473855346 1196473855346 1396473855346 1396473855346 139647385385 139728105687 139728105687 139728105687 139728105687 139728105685 139728105685 1397281555520 1397281555520 1397281555520 1397281555520 1397281555520 149239335851 107046541395145 139728451035745 10704541395745 107
понононорононоронононорононононононон	4.21707146251216 4.655533460051471 4.86553346002167713 3.28648292167713 3.28648292167713 3.297881993465511 0.50163298249435 3.99939242722111 0.50163298249435 4.3292076477 0.46974851198558 4.33535158402312 2.07706292722133 4.33535158402312 2.07068918215400 4.40089818215400 4.40089818215400 4.362882652213463 4.362882652213463 4.362882652213463 4.362882652213463 4.36282652213463 4.36282652213463 4.36282652213463 4.3628264593623 4.4287645893629 4.4296746894821 4.287678293629 4.5026746894821 4.50264693651 4.50264663261 4.50264664264 4.50264664264 4.50264664264 4.50264664264 4.50264664 4.50264664264 4.50264664 4.50264664 4.50264664 4.50264664 4.50264664 4.50264664 4.50264664 4.50264664 4.50264664 4.502646464 4.5026464 4.5026464 4.502646464 4.502646464 4.502646464 4.50264646464 4.50264646464646464646464646464646464646464	$\label{eq:2} 12.4254841425675 \\ 22.402633942442855 \\ 22.402633942442855 \\ 22.6025318428575 \\ 22.2002581829576 \\ 22.2002581829576 \\ 22.2002581829576 \\ 22.2002581829576 \\ 22.2002581829576 \\ 22.2002581829576 \\ 22.200258182955 \\ 22.200258182955 \\ 22.200258259520 \\ 22.2005825520629551 \\ 22.200582552062955 \\ 22.2005825520629551 \\ 22.200582552062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.200582555062955 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555069555 \\ 22.20058555005555065555 \\ 22.20058555005555005555005555 \\ 22.20059555005555005555005555005555005555005555005555$	3222383/73009 435588702339318 47602595101157 677464738584023 677464738584023 677464738584023 677464738584023 67746473854023 67746473854023 67746473854023 119671373855462 119671378655402 053258705675888 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.247722810568788 5.247722810568788 5.247722810568788 5.247722810568788 5.247722810568788 5.247722810568788 5.24772810577322 6.1462393358515 3.8602558562 0.34598935358515 3.8602558562 0.34598435358515 3.378855765530 0.345215169574 4.2243716109574 4.2243751395546 7.35668120556
с и с н о н о н о н о н о н о н о н о н о н	4.21707148251214 4.65553346902147 4.86553346902146713 2.875534802415713 2.87581993465511 4.97581993465511 4.975829824935 4.375922076477 0.4697485198558 4.33535154802312 2.0770629722123 4.3353515490312 2.0770629722133 4.3353515490312 4.099818215400 4.33553515490312 4.099818215400 4.38822800442114 3.67886522213463 4.38822800442114 3.67886522213463 4.3882280442114 3.6788652213463 4.3882280442114 3.6788522213463 4.3882280442114 3.6788522213463 4.3882280442114 3.6788652213463 4.3882280442114 3.6788652213463 4.3882280442114 3.6788652213463 4.3882280442114 3.678652213463 4.3882280442114 3.678652213463 4.3882280442114 3.678652213463 4.388228044214 4.388228044214 4.388228044214 4.388228044214 4.3892642936424 4.38926423244433 4.6662642936574 4.666264294574574574 4.666264294574574574574574574574574574574574574574	21.42548/41425675 22.40263394242855 23.03610391265943 22.20022518421855 23.03610391265943 23.13232882887736 23.13232882887736 23.13292641300766 24.1410307074508 24.309764126354 24.309764126354 24.30765128885 25.30576512885 25.30576550 25.30576500 25.3057650000000000000000000000000000000000	3.92225897/3.9309 4.7558870239318 4.76025054101157 0.6364749354524 0.774643159341002 0.6364749354524 1.971471382170667 4.793822030955 2.325257055554 4.7923822030555 1.555555555 4.32525270555564 4.325282030555 1.5505555556 4.327224105688 8.2477224105688 8.2477224105688 8.2477224105688 8.2477224105685 8.326555556 4.32724105771722 6.3429847585550 0.9454532835555 1.3926555556 0.94545328348196031 0.342217413175 1.070467413798 0.342217413175 1.07046741398574 4.42847513025165 0.3926215555 1.2905663734565 0.895643125555 1.2905663734565
	4.21707146255124 4.65553369051471 4.865553369051471 2.8057531802137 2.97581993465511 3.93939242722111 0.5016329249435 3.93939242722111 0.5016329249435 4.32535158402312 2.0770629272133 4.33535158402312 2.0770629272133 3.43310096766219 4.408918215400 4.408918215400 3.81775921255400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.408918215400 4.4089182400 4.408918215400 4.408918215400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.4089182400 4.408918400 4.40891824000 4.40891824000000000000000000000000000000000000	21.42548/41425675 22.402633942424855 22.03610391265943 22.020251810591265 23.133208287736 23.133208287736 24.309714623454 24.30952402576 24.3141302765 24.3192641200726 24.314130307074508 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.3076951728885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 24.307695172885 25.30755202212 27.47552022 27.47552022 27.47552022 27.47552022 27.47552022 27.47552022 2	332223831/3303 33222381/330315 4 7746415381102 5 65447403584524 1 7083773250988 1 7083773250988 1 7083773250988 1 7083773250988 1 7083773250988 1 7083773250988 2 737228105688 2 737228105688 2 737228105688 2 737228105688 2 737228105688 2 737228105688 2 737228105688 2 737281057808 3 802057808 3 8020578 3 8020
	4.21707146251216 4.65553360501471 4.865553360501471 2.80752518223137 2.97581993465511 3.95983242722111 0.5016329249435 3.95993242722111 0.5016329249435 0.8722672722123 4.343531508405212 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.41089818215400 4.3535158402312 4.41089818215400 4.3535158402312 4.41085420598135 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.3535158402312 4.355560520342334 5.35990427872400 4.3555605625155 3.209748502652515 3.209748502652515 3.2097485026552034 4.35556056250155 3.2097485026552034 4.35556056250155 3.209748502665203 3.20974850265503 3.209748504503 3.20974575040420140305505055055055055055055055055055055055	21.42548141425677 22.40263394241855 23.0361039126594 23.0361039126594 23.133268887736 23.20022518305879166 23.133268887736 24.30971462754 24.30973462754 24.30953392527 23.2562214180538 24.9076951728885 23.2562214180538 24.9076951728885 23.35622514180538 24.9076951728885 23.35622514180538 24.9076951728885 23.3562551282745 21.3395255478031 23.3562551282745 21.3395255478031 23.3562551282745 21.3395255478031 23.3562551282745 21.3395255478031 23.3562551282745 21.33952551282745 21.33952551282745 21.33952551282745 21.3395255129212 21.33952555129212 21.33952555129212 21.33952555129212 21.33952555129212 21.339525552121 21.339525524212 21.339525524212 21.339525524212 21.339525524212 21.33952554212 21.3292524349936204 23.272123222434995612 23.2721322254349 23.2721322254349 23.2721322254349 23.2721322254349 23.2721322254349 23.2721322254349 23.2721322254349 23.2721322254349	33222383173303 332223817330318 47602263101150 47602263101150 50564747035845124 170837732509889 1906474703585462 170837732509889 119647385346 1196473855346 1196473855346 139647385384 13964738548 13964738548 13964738548 13964738548 13964738548 13964738548 13964738548 13964738548 13964738548 139647385 139764853555555 1397648530854 10954654530 1095465450 1095465450 1095465450 1095465450 1095465450 10954555555 1095465450 10954555555 10954555555 10954555555 10954555555 109545555555 109545555555 109545555555 109545555555 109545555555 109545555555 109545555555 1095455555 10954555555 10954555555 10954555555 1095455555 10954555555 109545555 1095455555 109545555 1095455555 1095
с и о н о н о н о н о н о н о н о н о н о	4.21707146251216 4.65553360501471 4.865553360501471 2.8057351822317 2.97581993465511 2.97581993465511 3.975824222111 0.50163208249435 3.95939242722113 0.50163208249435 0.45274282195558 4.41098818215400 4.33535158402312 2.0770629272133 4.31039818215400 4.4089818215400 4.4089818215400 4.4089818215400 4.4089818215400 4.4089818215400 4.4089818215400 4.40858240598183 4.41089818215400 4.40854240598183 4.4089818215400 4.40854240598183 4.4089818215400 4.40854240598183 4.4089818215400 4.40854240598183 4.4089818215400 4.4085440930574 4.4085440930574 4.5056449385574 4.5056449385574 4.505646938574 4.5056457035711 3.20974850265521 3.20974850265521 3.20974850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.2094850265521 3.209485026521 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.2094850455520 3.209485045550 3.209485555600 3.209485555600 3.2	21.42548/41425671 22.40263394/241855 23.0361039126594 23.0361039126594 23.03261897166 23.133268887736 23.032879716 23.1332808887736 24.30971426254 24.30971426254 24.309702408 23.25632214180538 24.9076951728885 23.25632214180538 24.9076951728885 23.25632214180538 24.9076951728885 23.25632214180538 24.9076951728885 23.2563251480538 24.9076951728885 23.2563251480538 24.9076951728885 23.55625060518 23.356525060518 23.55625060518 23.55656061887 17.32052592232 19.967536418413117 17.878108333204 15.26757540824715 15.26757540824715 15.26757540824715 15.26757540824715 15.26757540824715 15.26757540824715 15.26757540824715 15.271127285489 13.2721372925489 13.2721372925489 13.2721372925489 13.2721372925489	33222383173303 436258870333318 43605263101157 67464793584021 637464793584021 637464793584021 637464793584021 637464793584021 637487733651067 13963738510667 139637385106 6325870567888 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105687 4328257656530 0.3459893535851 3.86025586071257 1.3286556520 0.3459893535851 3.86025565530 0.345983535851 3.86025565530 0.34521655530 0.34221716189574 4.22847340213740 6.7356832841165 1.13165954 4.473841055555 0.8362717422 6.14623515555 1.131659574 4.42847340213740 6.7356832815555 1.131659574 4.428475135555 1.131659574 4.47351455555 1.13165576 4.47351455555 1.131655764 4.4735145555 2.781683764057578 2.78168475789 3.4477850756439 2.7816877644 2.7816875685 3.4477850756439 2.781687764 2.78177777777777777777777777777777777777
с и то но	4.217071462512164 4.215707146255146 4.65553346902167713 2.9578518223137 2.97581993465511 0.50163293464355 3.95939242722111 0.50163298249435 0.8722672221218 3.43310096766219 0.8722672221238 3.43310096766219 4.33535158402312 2.0770629272133 3.43310096766219 4.33535158402312 4.400828240598189 4.41028745893628 4.43652213463 3.8172582255402 4.4382280042114 3.6288652213463 3.8382580442114 3.6288652213463 4.382280442114 3.6288652213463 3.8375546893623 4.4395746894821 4.362852431461 3.628652213463 3.8375546493657 4.4382524044114 3.628652213463 3.81122047359761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8642320342143 4.605642935761 3.8644233242143 4.605642935761 3.8644233242143 4.605642935761 3.8644233242143 4.605642935761 3.864423777337 5.864433203421343 4.60564247771337 5.86443139113920	21.42548/41425675 22.40263394242855 23.03610391265943 22.402633942421855 23.03610391265943 23.1632241855 23.163224185516 23.163224180538 24.309764126354 24.309764126354 24.3097691728885 24.307691728885 24.307691728885 24.307691728885 24.307691728885 24.307691728885 24.307691728885 24.307691728885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 24.30769172885 25.307670137 27.3172255520212 27.517222548799 20.673921492650 25.5172512885489 20.53515667061387 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.52824027985401 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.5284029854074 25.528402986401 25.5284	322238317330318 47602505101157 67663139318 47602505101157 63663791250500 6366379125050 197117308170667 4793825304 1991137308170667 4793825304 635258705515564 47938252330555 2.367228105685 2.367228105685 2.367228105685 2.367228105685 2.367228105685 2.367228105685 2.367228105717322 6.142393835851 3.86025586617257 1.320845852833 3.8602586617257 1.320845852833 3.8602585651 2.3378855768530 0.945435285555 1.28056653734566 0.8376482515555 1.280566373456 0.8375428555009 4.4733438159501 1.219355560495 4.4734348159531 1.219355560495 4.4734348159531 1.219355560495 4.4734348159531 1.2193555560495 4.4734348159531 1.2193555560495 4.4734348159531 2.338363444845753 2.338363444845753 3.4478640554633 3.4478640545433 3.4478640545433 3.4478640545433 3.4478640545433 3.447864054433 3.447864054433 3.44786405444343 3.44786405444343 3.44786405444343 3.44786405444343 3.44786405444434
сототототоро тоторотототоротототоронототоро	4.21707146255124 4.218077146255124 4.8655534690514671 4.8655534690514671 4.8655534690514671 4.8655534690514671 4.8655534690514671 4.95893462722111 0.5016329249435 3.93939242722111 0.5016329249435 4.33535158402312 2.07706429722133 4.33535158402312 2.07706429722133 3.43310096766219 4.33535158402312 4.33535158402312 4.33535158402312 4.33535158402312 4.33535158402312 4.33535158402312 4.33545158402312 4.3355458402312 4.33545158402312 4.3355458402312 4.335454202121453 4.3355458402312 4.33545400862 4.335454202121453 4.3355464088231 4.335454202121453 4.3355464088231 4.335454202124453 4.3354542024589514 3.21074450265521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.20074450165521 3.2007445016521 3.2007445016552 3.2007445016552 3.2007455 3.2007455 3.2007455 3.2007455 3.2007455 3.200745	21.425441425567 22.40263344242855 22.0361039126594 22.40263344242855 22.0361039126594 22.1323268287736 22.1323268287736 22.1323268271480538 24.30974426345 24.30974426345 24.30955329257 23.3563221480538 24.9076951728885 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9562761382745 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572751429528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.9572754459528245 23.95727545459528245 23.95727545459528245 23.95727545459528245 23.95727545459528245 23.95727545459528245 23.9572754545952824552 23.957275454595282452 23.957275454595282452 23.957275454595282452 23.957275454595282452 23.957275454595282452 23.957275454595282452 23.957275454595282452 23.95727545454545454545454545454545454545454	332223831/3303 33222381/33031 4 7746415581002 5 6544740584524 1 7083773250989 5 65447405854524 1 7083773250989 1 7083773250989 1 7083773250989 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70974847598 2 8472321056885 2 847232105685520 1 7094884778064 0 357166555208 0 342921074078064 0 357246555208 0 3429217431176 0 3459283258451 0 345928325146 1 7074064747398 0 34221716189574 0 345632251465 2 8473430213746 0 34564552538325146 2 8473430213746 0 34563525544 2 8473430213746 0 34564555208 0 34221716189574 0 34254551255546 2 8473430251346 0 3456455528325146 2 8473434457548 3 44735143457548 3 4473514367546 2 847344457548 3 4473514367546 2 847344457548 3 4473514367546 2 731444857548 3 44735144657548 3 44735144657548 3 44735144657548 3 44735144657548 3 44735144657548 3 44735144657548 3 44735144657548 3 4473844657548 3 4473844657548 3 4473844857548 3 44738484857548 3 44738484857548 3 447384857548 3 4473857548857548 3 4473857548857548 3 447385754857548 3 4473857548859771 3 447585757888289771 3 45584859971 3 45584859971 3 4558485971 3 45584859971 3 4558485971 3 4558569857 3 555856955 3 5558588595971
	4.21707146255124 4.6555336050146 1.4555336050146 1.4555336050146 1.4555336050146 1.4555336050146 1.4555336050146 1.45553360514 1.455534221411 0.5016329249435 3.59393242722111 0.5016329249435 4.41095818215400 4.41085818215400 4.41085818215400 4.41085818215400 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.4108548240598189 4.410854840598189 4.410854840598189 4.410854840598189 4.4108548405840134 4.1174749390141159 4.4128749390141159 4.412874939014159 4.412874939014159 4.412874939014159 4.41287439014159 4.555454203421343 5.19741848046863850 1.4111444111039 0.6381214297397683 1.416448411039 0.638151143408960 1.47557397080391 4.2554640377970565	21.42548141425677 22.40263394241855 23.0361039126594 23.0361039126594 23.133268887736 23.20022518305879166 23.133268887736 24.30971462545 24.30971462545 24.3097342614907666 24.14103070724508 24.3076951728885 24.3076951728885 23.5562214180538 24.3076951728885 23.55622514180538 24.3076951728885 23.55622514180538 24.3076951728885 23.5562251282745 21.183036541841 23.5562251221221487 23.5562251282745 21.183036541841 23.5762714926529 23.2562251292124 23.2562251282745 21.3097654113177 23.255525022121 21.747310833204 15.282047984011 55.2097526982715 15.1585112268831 55.2097526982715 15.1585112268831 23.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.272132725489 33.2721372548893307 31.3759734881413 31.4759734881413 31.475973488143	33222383173303 332223817330318 347602563101150 347602563101150 347602563101150 347602563101150 347602563101150 3478351765 34783517657 34793173855946 1196473385346 1196473385346 119647385346 119647385346 12967373173210 38602555208 386025555208 38602555208 38602555208 38602555208 38602555208 38602555208 38602555208 38602555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555208 386025555508 38605555508 386055555605
с с н о н о н о н о о о н о н о о о о н о н о н о о о н о н о н о н о о о н о н о н о о о н о н о н о о о н о н о н о и о и	21707146251216 24057346004 2405735402437 24057351822317 247581993465511 2595824222111 05016329249435 35993242722111 05016329249435 243730129272413 243730129272413 243730129272413 243730129272413 243730129272413 243730542924 243730542924213 243730542924213 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 2440828240598182 244086822013463 2440828240598182 244082409818215400 2440824049141 245082405419365744 244082904141591 254404074514 244082904141591 24408240419365744 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 24408268220154 244082824059818 2440828405988 2440828405988 24408284088888 24408284088888 24408284088888 24408284088888 24408284088888 24408284088888 24408284088888 24408408488888 24408408488888 24408488888 24408488888 24408488888 244084888888 244084888888 24408488888 24408488888 244084888888 2	21.42548/41425671 22.40263394241855 23.0361039126594 23.0361039126594 23.03261039126594 23.03268887736 23.03268887736 24.309714625454 24.5063995392927 24.309714625454 24.30970340591728885 24.3070591728885 23.5562214180538 24.9070591728885 23.5562214180538 24.9070591728885 23.5562250059351 23.3565250059351 23.3565250059351 23.3565250059351 23.3562550059351 23.356250059351 23.356250059351 23.356250059351 23.355560501387 23.35555002135 23.555560501387 23.35555002135 23.55556051387 24.37003715750 23.55556051387 24.37003715750 23.55556051387 24.37003715750 23.55556051387 24.320329985015705 23.55556051387 23.5555002125 23.55555002125 23.5555500	332235817/3403 4356870233318 4356870233318 43602568101157 437682568101157 437682568101157 43768256810115 43768274341 1964733651065 1954733651065 43798326535 5325870551554 4379832583355 5325870551554 432233054555555 4322231024555555 4322231024555555 4322231024555555 43223231024555555 43223254555555 43225555555 4322555555 432555555 432555555 43255555 4325555555 432555555 4325555555 4325555555 432555555 4325555555 4325555555 4325555555 4325555555 4325555555 43255555555 4325555555555
с с н о н о н о н о о о н о н о н о о о н о н о н о о о о н о н о н о о о о н о н о н о о о о н о н о н о н о и о и	4.21707148251214 4.217071482551340 4.8655334690514671 4.8655334690514671 4.8655334690514671 3.28648292167713 3.28548292167713 3.297849346511 3.2978429221110 5.05162392849435 3.43310069766219 4.3353154802312 2.07706297221238 3.43310096766219 4.3353154802312 2.0770629722138 3.43310096766219 4.38527522355402 4.3827522355402 4.3827522355402 4.3827522355402 4.382752355402 4.382752355402 4.382752355402 4.382752355402 4.382752355402 4.382752355402 4.382752355402 4.382752355402 4.38275245512 4.3825525402 4.3827527525552 4.5656425204450 4.052545930547 3.811204755754 4.052545930547 3.811204755754 4.052545930547 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755776052 3.811204755778052 3.83055788855528 4.55128755787855 4.55128755787855 4.55128755787855 4.5512875787855 4.5512875787855 4.551287577875 4.5512875787855 4.55128757578555 4.551287577855572 4.551287577855572 4.552287578785572 4.552287578785572 4.5512875787855728 4.5512875787855728 4.5512875787855728 4.5512875787855728 4.5512875787855728 4.551287578785578 4.551287578785578 4.551287578785578 4.551287578785578 4.	21.42548/1425675 22.4026339424285 23.03610391265943 23.03610391265943 23.036210391265943 23.036210391265943 23.2020251879166 23.133286887736 24.30974425454 24.309744267454 24.30975421480538 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.307691278885 24.30769127887 24.30769278778 24.30769278278 25.30725782785 25.30725782785 25.30725782785 25.30725782785 25.30725782785 25.30725782785 25.30725782785 25.307257827857 25.307257872785 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727875 25.3072578727857727857 25.30725787278577277857772777577777757777777	3.322.53817/3.039 3.322.53817/3.039318 4.7602.5054101157 6.77645315801023 6.77645315801024 6.77645315801024 6.77645315801024 6.77645315801024 6.77845315801024 6.7784531801024 6.7784573861024 7.938258304 7.938258304 7.938258304 7.938258304 7.938258304 7.93825830 7.9326 7.932632 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.9326 7.932 7.9326 7.932 7.9326 7.932 7.9326 7.932 7.932 7.9326 7.932 7.93 7.93 7.932 7.93 7.93 7.93 7.93 7.93 7.93 7.93 7.93
с н о н о н о н о о о н о н о н о н о н	4.21707146255124 4.218707146255124 4.2655533690514671 4.2655533690514671 3.28645232167713 3.288442322167713 3.297841993465511 3.2978429221411 0.5016329249435 3.43310086766219 4.243535158402312 2.077062927212138 4.33535158402312 2.0770629272133 3.43310086766219 4.40386748918215400 4.4038748918215400 4.404797588 4.403474978958 4.403474978958 4.403474978958 4.40347497858 4.40347497858 4.40347497858 4.40347497858 4.404797858 4.404797858 4.40347497858 4.404797858 4.404789788 4.403478978860538 4.403478978860538 4.4034784958 4.403478978860538 4.4034784958 4.403478978860538 4.4034784958 4.4034784958 4.4034784958 4.4034784958 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.404789588 4.4044789588 4.40	21.425441425567 22.402633442442855 22.03610391265943 22.0022518421855 22.03610391265943 22.002251810391265943 22.002251810391265943 22.103925412625454 24.103926412005766 24.14103070724508 24.3095421480538 24.30769517288855 24.30769517288855 23.35622514180538 24.30769517288855 23.3562524180538 24.30769517288855 23.35625420493541 23.35625420493541 23.35625420493541 23.3562542043954 23.3562542043954 23.3562542043954 23.3562542043954 23.3562542043954 23.3562542043954 23.3562542043954 23.3562542043954 23.3562562542 23.3562542043954 23.3562542243 23.3562542343 23.3562542343 23.3572542443954 23.3572542443 23.3572542443 24.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.3572542443 23.35725424443 23.3572542443 23.3572542443 23.3572542443 23.35725424443 23.357254244443 23.3572542444443 23.3572542444444444444444444444444444444444	332223831/3303 33222381/33031 4 774641581020 5 6547470358546 1 7083773250989 5 6547470358546 1 7083773250989 1 7083773250989 1 7083773250989 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 7097317385594 1 7097317385594 1 7097317385594 1 7097317385594 1 7097317385594 1 7097317385594 1 7097317385594 1 7097317317 1 70974847739 1 7097494 1 7097494 1 7097494 1 7097494 1 7097494 1 709749 1 709
с с н о н о н о н о о о н о н о н о н о	21707142852124 218077341282534 28057345024 28057354122137 297581923457 297581923457 297581923457 297581923457 29758292493 35939242722111 0.5016329224935 3.4331006766219 2.0770629272133 3.43310096766219 2.0770629272133 3.4310096766219 2.0770629272133 3.43758240598182 4.40082818215400 4.40082818215400 4.40082818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818215400 4.40085818315400 4.40085818315400 4.40085818315400 4.40085818315400 4.40085818315400 4.40085818315400 4.50520545703571 3.209748502655703571 1.20110484111039 0.6381511048401039 0.6381511048401039 0.6381511048401039 0.6381511048401039 0.5381511048401039 0.5381511048401039 0.5381511048401039 0.5381511048401039 0.5381511048401039 0.5381511048401039 0.5381511048401039 0.53815110480561 0.3375088055797885 5.7727045415287	21.42548/41425675 22.4026339424855 23.0361039126594 23.0361039126594 23.03268887736 23.03268887736 23.03268887736 23.03268887736 24.3403974462545 24.30974462545 24.30973407565 24.3410307074508 23.2563274180538 24.3076951728885 23.563274180538 24.3076951728885 23.563274180538 24.3076951728885 23.563274180538 24.3076951728885 23.563274180538 24.3076951728885 23.563274180538 24.3076951728885 21.180303641841 22.751722344799 23.56527419255 23.5632745 23.5632745 23.5632745 23.5632745 23.5632745 23.5632745 23.563574584 23.5727547439525 23.5727547439525 23.572754743952 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547439525 23.5727547454752 23.5727547454752 23.572754745475475 23.572754745475475 23.57275475475475475 23.57275475475475475475 23.5727547547547547547547547547547547547547547	33222383173303 332223817330318 347602563103115 347602563103115 347602563103115 347602563103115 34760256310315 34762551554 47938258365 34773250885 3477282105685 3477282105685 347025025757 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 34802555250 348025555250 34802555525 34802555525 34802555525 34802555525 34802555525 34802555525 34802555525 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 34802555555 3480255555 34802555555 348025555 348025555 34
с н о н о н о н о о о н о н о н о н о н	21707146251214 2405734624514 24057345045 250574521457 2475874521457 2475874574 2475874574 2475874574 2475874574 2475874574 2475874574 2475874574 2475747574 247574757574 2475747574 247574757574 2475747574 2475747574 2475747574 2475747575775757 2475747574757577 24757475744129775757 24757475744129775757 24757475747575775757 247574757577575775757757577575775757757	21.42548/4142567 22.40263394241855 23.0361039126594 23.0361039126594 23.03268887736 23.032879166 23.133268887736 24.30971462545 24.309714625454 24.5063995392927 23.3563221480538 24.9076951728885 23.3563221480538 24.9076951728885 23.3563221480538 24.9076951728885 23.3563221480538 24.9076951728885 23.35632540951728885 23.35632540951728 23.35632540951728885 23.35632540951728885 23.35632540951728885 23.35632641841 23.3563254180258 23.35632641841 23.551546761387 17.32032553202124 19.96739214926529 18.2873903175750 19.463344131177 17.075149265292234 19.9673923553021215 5.3097526902375 5.3097526902375 5.309725902375 5.31443005548411 5.2390405566733 13.14297374881413 1.7779141690226 13.7773145839307 13.1425973488143 13.1779734881435 13.14267925566373 13.14269295566373 13.14269295666373 13.1426929566873 13.14	32223831/330318 32558870/330318 47602595101150 47602595101150 47602595101150 4760259510150 47703173855946 11964739855946 11964739855946 11964739855946 4793825830 5235870551554 4793825833555 1255057657888 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105685 5.247728105685 5.247728105685 5.247728105685 5.247728105685 5.247728105685 5.247728105685 5.247728105685 5.247728105685 5.24772810578 5.2472810578 5.2472810578 5.2472810578 5.2472810578 5.2472810578 5.2472810578 5.2472810578 5.2472810578 5.247381382 5.2751877824 5.2453815784207 5.25581778228 5.2558177827 5.25581778
с н о н о н о н о о о н о н о н о о о н о н о о о о н о н о н о о о н о н о н о о о н о н о н о о о н о н о о о н о н о о о н о н о и о о о н о н	4.217071482551246 4.2150714825534690451 4.8655534690451 4.8655534690451 4.8655534690451 3.97824822167713 3.978248293465511 3.9793242722113 0.5016329249435 3.9893242722113 0.87226727221238 3.43310069766219 4.33553158402312 2.07706237221238 3.43310069766219 4.33553158402312 4.33553158402312 4.33553158402312 4.33553158402312 4.33553158405812 4.3825200442114 4.382528058139 4.3825200442114 4.3625840593129 4.3825200442114 4.3625840593129 4.3825200442114 4.3625840593129 4.3825200442114 4.3625840593129 4.3825200442114 4.3625641939514 3.8112047589764028 4.38252044214 4.105243054124 4.10524305452 4.10524305452 4.10524305452 4.10524305452 4.10524311155 3.89275654122287 4.2052431205552 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275654412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.2034310057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 3.89275564412287 4.203431057305 4	21.42548/41425675 22.402633942424855 22.402633942424855 22.402633942424855 22.402639424242855 22.402639165945 22.40295744263454 23.5029244180558 24.30976425454 24.30976425454 24.30976425454 24.30976951288885 24.3076951288885 24.307695128885 24.3076512885 24.3076512885 25.30755029512 25.30755029512 25.30755029512 25.307550295025 25.307550295025 25.307550295025 25.307550295025 25.307550295025 25.30755029505 25.30755029505 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.30755025025 25.3075502505 25.3075500505050505050505050505050505050505	3422384/73009 3422384/73009 345000000000000000000000000000000000000
г C H O H O H O H O O O H O H O H O H O H	21707142825124 21807531822137 28057351822137 2875821827317 2875821827317 2875821827317 2875821827317 2875821827317 287582182137 287582722111 0.5016329249435 3.43310086766219 2.0770629272133 3.43310086766219 2.0770629272133 3.43310086766219 4.4088618215400 4.4088618200 4.4086618200 7.31532404086 5.59940027087280 4.40864000 7.31532404008 5.59940027087280 4.315400700155 5.32097485006531 3.3275082661959 3.83076861528 5.7727305416297 3.830768616281 5.5381104200960 3.8387268615819 3.830768616288 5.7727305416297 3.830768166733 3.83877691911553 3.83877691911553 3.8387769191555 3.83987165416287 3.4301310871387 3.838771911555 3.83987165416287 3.83016733 3.83877691911553 3.83877691911553 3.8387769191555 3.830457183777 3.43031006733 3.8387791911553 3.8387791911553 3.8387769191555 3.8304571897177 3.5302007303 3.8387791911553 3.8387769191555 3.830457183777 3.53230007303 3.8387791911553 3.8387791	21.42548/41425675 22.402633942421855 22.03610391265943 22.402633942421855 22.03610391265943 22.40263942421855 22.03025180597166 23.1332808887736 24.309714625454 24.3097241625454 24.3097241625454 24.3097241625454 24.309724180538 24.30769517288855 23.5562214180538 24.30769517288855 23.556226182745 21.1830355478031 23.5562214180538 24.30724121480558 23.5562214180538 24.30725121480558 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55627214180538 23.55727214180558 23.55727214180558 23.55727214180558 23.57727214180558 23.57727214180558 23.57727214180558 23.57727214180558 23.57727214180558 23.57727214180558 23.577272418916124 23.57727414916232 23.57725438916124 23.57725438916124 23.57721418052825021 23.57721418052825021 23.577214180558451 23.177273045841437 23.57721418052825661 23.577214180558451 23.577213941805126 23.58812475805365 25.581127568331054 23.581272758035155 25.5812757803515525.58127578035155 25.58127578035155 25.58127578035155 25.58127578035155 25.5812757803515525.58125	33222383173430 3322238173430 4 774641581020 5 6544740584524 1 7083773250989 5 65447405854524 1 7083773250989 1 7083773250989 1 7083773250989 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70973173855946 1 70972815565 2 70728159859 2 70728159859 2 70728159859 2 70972815985 2 70972815985 2 70972815985 2 70972815985 2 7097281595 2 7098281295 2 7097281295 2 709881295 2 7097281295 2 709728129 2 709728150 2 709728150 2 70
г С H O H O H O U O O H O H O H O H O H O H	21707142851214 218077341822514 28057341822137 28057351822137 297581923457 297581923457 297581923457 297581923457 29758292493 23535158402312 2.0770629221213 2.0770629222133 2.33331508918215402 2.0770629222133 2.1519168358245 2.0770629222133 2.1519168358245 2.0770629222133 2.151916835245 2.07706292213 2.15191682255402 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.07706292213 2.077062921213 2.077062921213 2.079062921213 2.079062921213 2.07907492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.12007492024 2.120077001225 2.099473130159 0.63815110408401 2.12006473330159 0.63815110408401 2.1200647333012998 2.354077700125 2.359078860538 2.35979885053 2.359797885 5.7727204411297 2.433931002393 3.638779191153 3.83927564162287 2.433931002393 3.638779191155 3.83927564162287 2.4339310295337 5.1330112798095 5.3239100295337 5.1330112798095 5.3239100295337 5.133011279809	21.42548/4142567/ 22.4026339424855 23.0361039126594 23.0361039126594 23.03268887736 23.03268887736 23.03268887736 23.03268887736 24.30974462545 24.30974462545 24.30973462545 24.30973462545 24.30953952925 23.565221480538 24.3076951288885 23.565221480538 24.3076951288885 21.3052054841841 22.751272254879 23.5652264182745 21.83055547841841 23.5522264541841 23.562255202212 21.960305441841 23.56255202412 21.960305441841 23.552255202212 21.960305441841 23.55255202212 21.960305441841 23.55255202212 21.960305441841 23.55255202212 21.960305441841 23.5520522212 21.96035554131177 25.205255202212 21.9645544131177 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9645544131377 25.205255202212 21.9745454413137 25.205255202212 21.974545441312 25.205250545141 21.7773414905256 21.377734788814183 21.2072525489 21.80727375 21.655114416891564 21.86511227808356 21.65811227808356 21.865112268531054 21.86511227808356	332235817/3303 332235817/330318 347602563101150 347602563101150 347602563101150 347602563101150 347602563101150 3476256310150 3475317355085 34773250885 3477282105688 347782657888 3477282105685 3480257821055525 34802558270 34802565210 34802555520 34802555210 34802555520 348025555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 348025555520 348025555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555520 34802555555 34802555555 3480255555 3480255555 34802555555 3480255555 3
	217071462512146 24057346024 2805735402437 280573518223137 297581923437 297581923457 297581923457 297581923457 297581923457 297581923457 29758292425 20770629272123 243535158402312 2.0770629272133 2.0770629272133 2.0770629272133 2.15109453538951 4.4109818215400 4.40828240598183 4.41089818215400 4.40828240598183 4.41089682213443 3.628652213443 4.40858240598183 4.41287678996289 4.438272804411591 4.63825240443 4.1287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.41287678996289 4.4128778996289 4.5126727978 3.2097482078575 3.209748078557 3.209748078557 3.209748078557 3.209471315581496 4.638272797954416297 5.83138671315564146287 3.46382845002457 2.463813102477 2.46383110247 2.46383110247 2.46383110247 2.46383110247 2.46383110247 2.46383110247 2.46383110247 2.46383110247 2.4638311155611496 3.4638221444111037 3.4638245900431 3.463845900431 3.46384545900431 3.46384545900431 3.4638454500431 3	21.42548/41425675 22.40263394242855 23.03610391265943 22.402633942421855 23.03610391265943 23.036210391265943 23.136221430514262545 23.1362214180538 24.3097641263545 24.3097641263545 24.3097641263545 24.3097651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.307651728885 24.30765172885 24.307651728885 24.30765172885 24.30765172885 24.30765172885 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577313 25.307577373 25.3075777373 25.3075777373 25.3075777373 25.3075777373 25.3075777373 25.3075777373 25.3075777373 25.3075777773 25.307577777757 25.3075777777777 25.30757777777777777777777777777777777777	32223831/330318 32558870/330318 47602595101150 47602595101150 47602595101150 47602595101150 476025951056 4793825830 4793825830 4793825830 4793825830 524570551556 4793825830 524570551556 47938258335 52477228105688 52477228105688 52477228105688 52477228105688 52477228105688 52477228105688 52477228105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 5247728105685 524772810578 524738105782 524738105782 52582774715105574 57536282611565 5258277421550 525827742155 525827742155 5259370266 5259517562261 5255817562261 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 575379900168155 57537900168155 57537900168155 57537900168155 57537900168155 57537900168155 57537900168155 57537900168155 5753790000000000000000000000000000000000
г С H O H O H O H O H O H O H O H O H O H	4.217071462551246 4.215071462551246 4.655533690541 4.655533690542 3.28648292167713 3.287581822137 3.297581993465511 3.297581293455 3.29738129355 4.215282224345 3.43310069766219 4.3353515840312 4.2170522212138 3.43310069766219 4.3353515840312 4.2170582722138 4.3353515840312 4.3105981251540 4.382520042114 4.3825212460862 4.1286748938125 4.328220042114 4.38252124669842 4.32825201421 4.328520042114 4.38252004214 4.38252004214 4.3852004200424	21.425441425657 22.40263344242855 22.40263344242855 22.40263344242855 22.40263142424545 22.40263142424545 22.4020521420576 23.1332828887736 24.30972442057 23.35632714180538 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.9076951728885 24.907695172885 24.9076951728885 24.907695172885 24.907695172885 24.907695172885 24.907695172885 24.907695172885 24.90769517287 24.907695170757 24.9076951728	3422384/07300 3422384/07300 3425082702393135 457646415581002 56844749584524 170837732509889 19947732509889 19947732509889 19947732509889 199477385798657888 5.24772281056888 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.247728105655200 5.242728105655200 5.242728105655200 5.242728105655200 5.242728105655200 5.242728105655200 5.242292748115 5.24273430233745 5.2427810575603 5.422193027456 5.422193027456 5.24219402073875 5.247191057425 5.247319402073875 5.247319402073875 5.247319402073875 5.247319402073875 5.247319402073875 5.247319402073815 5.247319402073815 5.247319402073815 5.247319402028150 3.29340400738155 5.247319402028150 3.29340400273875 5.247319402028150 3.29340400273875 5.247319402028150 3.29340400273875 5.247319402028150 3.2934040028155 5.247319402028150 3.2934040028155 5.247319404023 1.74518374977084 5.247319402028150 3.2934040028155 5.253599313274 5.253599313224 5.253599313274 5.253599313224 5.253599313274 5.253599313224 5.253599313224 5.253599313224 5.253599313224 5.253599312274 5.253599312274 5.253599312274 5.253599312274 5.25359931207678 5.2555931207678 5.2555931207678 5.2555931207678 5.2555931207678 5.2555931207678 5.255595768 5.255595768 5.255595768 5.25
п С н О н О н О н О н О н О н О н О н О н	21707142825124 21807531822137 28057351822137 287581822137 287581822137 287581822137 287581822137 287581822137 287582722111 0.5016329249435 3.5939342722111 0.5016329249435 2.0770629272133 3.43310096766219 2.0770629272133 3.43310096766219 2.0770629272133 3.437582255402 4.408818215402 4.408818215402 4.408282042114 3.6387752392820 3.17552225340 4.408282042114 3.6387752392820 3.17552225402 4.4082824053818 3.6387752392820 4.4082824053818 3.6387752392820 4.4082624053818 3.6387752392820 4.408262405381 3.638742042114 3.638742042115 3.5394042115 3.5394042115 3.5394042115 3.5394042115 3.20974820455035 1.14110484111039 3.23560475930831 4.5212935204480 4.5212875279885 5.772704555708571 3.3150427701625 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.320944802655015 3.3209448026559885 5.772704551581496 5.83830107030 3.8387768461287 5.238310026733 3.8387768416228 5.238310026537 3.533310926533 5.23843543057722 3.838375846028 5.2384354305732 3.83875654162287 2.4638393102752 5.2384304305733 3.83875654162287 2.46383931027572 5.2384304305733 3.838776846228 5.238330077725 5.238310295537 5.3330045732 5.2383102455746537 5.33330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 3.838776846228 5.238330045733 5.2384350377223 5.234355077223 5.2	21.425441425567 22.402633942441425557 22.402633942442855 22.030510391265943 22.402633942442855 22.0302518597166 23.1332805887736 24.309714625454 24.505995302567 24.3192041900766 24.1410307074508 24.309741480538 24.3076951728885 23.3555274180538 24.3076951728885 23.3555274180538 24.3076951728885 23.3555274180538 23.3555274180538 23.3555274180538 23.3555274180538 23.3555274813 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.35552748137 23.3555274213 23.3555274213 23.3555274213 23.3555274213 23.3555748313 23.375757439523222 23.355567615387 23.375757439523222 23.35556761387 23.375757439523222 23.35556761387 23.375757439523222 23.35556761387 23.375757439523222 23.35556761387 23.375757439523222 23.3556761387 23.37757143852292 23.355757317457 23.37575743955232 23.37575743955232 23.37575743955232 23.37575743955232 23.3757574395535 23.37771143452297 23.377573139443617 23.37773143852395 23.377314385235 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.37731434535 23.3773145355 23.3773145355 23.3773145355 23.3773145355 23.375355 23.375355	332223831/330331 33222381/330331 435588702333318 435588702333318 435588702333318 135588702333318 13558512351 170837732509889 137931738855846 13964738855846 1396473885386 13964738238233355 23677228105688 23677228105688 23677228105688 23677228105688 23677228105688 23677228105688 23677228105689 23678273281598 23678257888 23677228105689 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 23678257888 2367825788 23678257888 23678257888 2367825788 2367825788 2367825788 2367825788 236785788 236785788 236785788 236785788 236785788 236785788 236785788 236785788 236785788 236785788 23678578 236785788 236857788 23678578 236785788 23678578 23678578 23678578 23678578 23678578 23678578 23678578 23678578 23678578578 23678578578 23678778 23678578 23678578 23678578578 236787778 2367777777777777777777777777777
п С н О н О н О 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 1 0 0 0 1 0 1 0 0 0 1 0 1 0 0 0 0 0 1 0 1 0 0 0 0 1 0 1 0 0 0 0 0 1 0 1 0 0 0 0 1 0 0 0 0 0 1 0 1 0 0 0 0 1 0	21107146251214 21077342751422137 21075351822137 21075351822137 217581923457 217581923457 217581923457 21758293242722111 0.5016329249435 2132792207647 0.46974451895558 4.31301006766219 4.33535154802312 2.0770629272133 4.3100956219 4.335351548240598189 4.41089818215400 4.335351548240598189 4.41089818215400 4.335351548240598189 4.41089818215400 4.335351548240598189 4.410874893428 4.410874893428 4.410874893428 4.4128767839428 4.410874893428 4.4128767839428 4.410874893428 4.4128767839428 4.410974893428 4.4128767839428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.41287474893428 4.4128748428 4.4128748428 4.4128748428 4.41287484411039 4.5128474397458 4.512887597885 5.77272464116297 3.3638749191553 3.363877491555 3.3638749416287 4.4338317694772 4.538381902452 4.538317694772 4.5383317694772 4	21.42548/41425677 22.40263394241855 23.0361039126594 23.0361039126594 23.03621039126594 23.03621039126594 23.20022518025879166 23.133268887736 24.309714025454 24.309734025454 24.309539529257 23.3562214180538 24.3076951288885 23.3562214180538 24.3076951288885 23.35622514180538 24.3076951288885 21.305265520929520 23.3565250293521 23.3562550299520 23.35652502929520 23.35652502929520 23.35652502929520 23.35652502929520 23.35652502929520 23.35652502929520 23.35652502929520 23.35652502929520 23.356525029212 23.356525029212 23.356525029212 23.356552029212 23.356552029212 23.356552029212 23.356552029212 23.356552029212 23.356555029212 23.356555029212 23.356555029212 23.3565541313177 23.25255202212 23.3565541313177 23.2721327295489 23.2721327295489 23.2721327295489 23.2721327295489 23.270134849137 23.2582928292952 23.35630938839307 23.357237254881413 23.529348814489 23.2721327295489 23.2721327295489 23.2721327295489 23.2721327295489 23.2721327295489 23.2721327285489 23.2721327285489 23.2721327285489 23.2721327285489 23.2721327285489 23.2721327285489 23.2721232725489 23.2721327285489 23.2721232725489 23.272132725489 23.2721232725489 23.27212725489 23.27212725489 23.27272575567 23.275678 23.2727575678 23.2727575678 23.	332235817/3303 332235817/330318 35588702339318 47602563101150 5658474305845124 57687732509889 1956474305854524 19567732509889 1957732509889 5287728105685 5287728105685 52872705578988 5287728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 52872728105685 528728105717322 61429373105717322 61429373105717322 61429373105717322 61429373105717322 6142937310571732 614293713105916 614293713105916 614293713105916 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 614293713105716 61429371105717522 61429371105716 61429371105716 61429371105717522 614293711056010555555 715113477537 717114513706758 72114377334455595115374 6143773143487558 72114377334462857622 721534059311257776225 7313493011115 71745133407578 72114377337462867022 721535955115374 7214347753842755 731379011115 72145633482755 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 731379011115 7313790111115 7313790111115 7313790111115 7313790111115 7313790111115 7313790111115 7313790111115 7313790111115 731379011115 7313790111115 7313790111115 7313790111111111111111111111111111111111
п С н О н О н О 0 0 0 1 0 1 0 1 0 0 0 0 1 0 1 0 0 0 0	4.217071482551246 4.215071482551467 4.865533690547 4.865533690547 3.28648292167713 3.28648292167713 3.2978493465511 3.2978429324645 3.2993462722113 0.5016329249435 3.4331006766219 4.335315840312 2.0770629722133 3.4331006766219 4.335315840312 4.3382520042114 4.38528200442114 4.38528200442114 4.38528200442114 4.38528200442114 4.3852820044214 4.3852820044214 4.3852820044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.385280044214 4.3852800421580142 4.3813807380391 4.551491049805 5.381390713880558 4.551287597854 5.3233002983377 5.32331002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.3233002985377 5.32333002985377 5.323300298537	21.42548(4142567) 22.402633942(42457) 22.402633942(42457) 22.402633942(42457) 22.402633942(42457) 22.4026374(425454) 22.4030714625454 24.30370746505 24.30370746505 24.30370746505 24.30370746505 24.30370746505 24.30595309530 24.30595309530 24.30595128885 24.307651298855 24.30765128885 25.3056506137 25.3075502522221 21.368511126883304 16.282797820437 21.32725550221 21.34881413 11.7773148915112 25.2499501617905 31.2721327254890 11.3575174890514112 25.2499501617905 31.27213272543905 11.3575174890514112 25.2499501617905 31.27213272543905 11.3575174881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.7773144905124881413 11.77731449052495687313 13.582149295687313 13.582149295687313 13.582149295687313 13.582149295687313 13.582149295687313 13.582149295687313 13.582149295687313 13.582149295687313 13.58214929568731 13.58214945442481558 13.582144944544248584441 13.585644441 15	332223831/3303 332223831/3303 355087023331315 47746415581002 565447439584524 170837732509889 56447439585946 1394738579465782 13973173865946 13947385794657828 5.247722810568 5.24722810569 5.248728105782 2.8537390571722 2.8537390571722 2.8537390571722 2.8537390571722 2.853739057172 2.853739057172 2.853739057172 2.853790571292 2.853790571292514 5.24234310253505 5.42239322462 5.2561756203 5.422393246259 5.422393246259 5.422393246259 5.422393246259 5.422393246259 5.4223932464537 1.2458159640971 7.53269113026671522 2.155590511302467 5.255617762261 4.653745811046977 5.255617762261 4.05394454202373457 5.3537950112034 5.35379501203457 5.3537950120345 5.35379570012354 5.3537950120345 5.353795012034 5.3539457120347 5.353950120347 5.35
с нононононононононононононононононононо	4.217071462551246 4.212071462551246 4.655533690542 4.655533690542 3.28648292167713 3.28848292167713 3.297581993465511 3.29758129346551 3.2973842122111 0.5016329249435 3.43310006766219 4.3125351840312 2.0770629722133 3.43310006766219 4.3125351840312 4.3125351840312 4.3125321204211 4.3125321204211 4.3125321242 3.4331006766219 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.328220042114 4.3283220042114 4.3283220042114 4.3282320042114 4.328220042114 4.3282320042114 4.3282320042114 4.3282320042114 4.3282320042114 4.3282320042114 4.3282320042114 4.3282320042124 4.3282310045733 3.3593826023 3.3593826023 3.3593826023 4.3293431004752 4.32931907677135 5.23931007512 4.331367771355 5.32931007512 4.331367771355 5.33300793315 5.2344213027577223 3.369377846023 4.333531932100757 5.323910757 5.323957 5.323910757	21.425441425557 22.402633942424355 22.402633942424355 22.402633942424355 22.402633942424355 22.40263942424545 42.50259559529527 42.50259559529527 42.50259559529527 42.502595529527 42.502595529527 42.50259527 42.5025274180558 42.50259527 42.50259527 42.502572458 42.502572458 42.50257245 42.50257242 42.50257245 42.50257242 42.5025	3.322.338.107.3409 3.322.338.107.3409 4.5558970.23931315 4.5558970.23931315 4.5558970.23931315 4.5558970.23931315 4.5558970.23931315 4.575873855846 1.9647.33855846 1.9647.33855846 1.9647.33855846 1.9547.3382385345 3.86025587888 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.24772281056885 5.2477228105685 5.24772281056885 5.24772281056885 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.247228105685 5.2472855 5.2472855556685
п С н О н О н О 0 0 0 н О н О н О 0 0 0 н 0 н	21707142825124 21807531822137 28057351822137 28057351822137 287581822137 287581822137 287581822137 287581822137 287582722111 0.5016329249435 3.59393942722111 0.5016329249435 3.4331006766219 2.0770629272138 3.43310096766219 2.0770629272138 3.43310096766219 2.0770629272138 3.151592825402312 3.151592825402312 3.151592825402312 3.151592825402312 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.151592824053818 3.15159282405381 3.15159282405381 3.15159282405381 3.15159282405381 3.15159282405381 3.151592701625 3.2097485026520 3.151140409100 3.3556068250155 3.2097485026550 3.2097485026550 3.35114040980 3.3556068250155 3.2097485026551 3.3575938260480 3.3556082594653 3.3575938260459 3.35560759393 3.359378860528 3.359378	21.425441425567 22.4026339424412555 22.0361039126594 22.4026339424421855 22.0361039126594 22.4026394424855 22.0302518405879166 23.1332808887736 24.1992641900766 24.1410307074508 24.309574265454 24.309574265454 24.309574265454 23.3555274180538 24.30769517288854 23.3555274180538 24.30769517288854 21.183035641841 27.7721215467795 21.183035547641341 27.7327213467795 20.3555547641341 27.7327213467795 20.3555547641341 27.7327213467795 20.3575564761377 15.3555167615387 21.323055202212 17.3465643131177 15.26253202312 15.28254641341377 15.28254202378 20.3551566761387 15.28240785641313177 15.28255202212 17.3465643131177 15.28255202212 15.3555112266333 15.2824079864011 15.2824079864011 15.2824079864011 15.2824079864011 15.2824979566313 13.7070116345297 13.37073014348197 13.37073014348197 13.37073014348197 13.37073014384197 13.37073014384197 13.37073014384197 13.37073014384197 13.37073014384197 13.37073014384197 13.36521730733515 15.5831127508335 15.583112578035 15.583112578035 15.583112578035 15.583112578035 15.583112578035 15.583112578035 15.583112578035 15.583112578035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.583102758035 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.58310275805315 15.5831027580555 15.58310575805755 15.58310575805755 15.58310575805755 15.58310575805755 15.58310575805755 15.58310575805755 15.58310575805755 15.583105758057554 15.5831057558057554 15.5831057558057554 15.5831057554575547555 15.585555555555555555	33223381/330331 3322381/330331 3332351 343538070233331 347054153811005 34558070233331 347054153811005 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705425 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 34705455 347054555 347054555 34705455555 3470545555 34705455555 347
C H O H O H O H O H O H O H O H O H O H	21107146251214 2107734275146 21075351822137 21075351822137 217581923457 217581923457 217581923457 217581923457 217582322445 2175923457 2175923457 2175925457 2175924557 2175924557 217592457 2175924557 2175924557 21759	21.42548/4142567/ 22.4026339424855 23.0361039126594 23.0361039126594 23.03621039126594 23.03621039126594 23.133208887736 23.133208887736 24.309714025454 24.309734025454 24.309539529527 23.3563271480538 24.30795128885 23.3563271480538 24.30795128885 23.3563271480538 24.30795128885 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 23.3563271480538 24.3079521480538 24.3079521480538 24.3079521480538 24.3079524999620 23.3565520212 27.3563554781 23.35635502721 27.357518033204 23.257535202212 27.34554541313177 25.2095256292149 25.20927254399 25.2092725439 25.20926554073 25.2092725439 25.2092725439 25.2092725439 25.2092725459 25.209272554128 25.209272554128 25.209272554128 25.2092725459 25.2092725459 25.209272554128 25.209272554128 25.209272554128 25.209272554128 25.2092725459 25.2092725459 25.2092725459 25.2092725459 25.2092725459 25.209272554128 25.2092725459 25.20927255459 25.20927255459 25.20927255459 25.20927255459 25.20927255459 25.209272555459 25.209272555459 25.20927555459 25.20927555457 25.20927555547 25.20927555	332235817/330318 332235817/330318 35558070.333318 47602563101150 5556870.333318 47602563101150 5756870551554 47703528551554 479382583055555 5258770551554 4793825830555555 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105688 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.2477228105685 5.24772810577282 6.1429373105726 6.3786565630 0.345652717322 6.1429373105726 6.378656530 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.345653028310 0.3456130485758 0.338364946347 7.711344857588 3.4478530756430 0.338364946347 7.711344857588 3.447845075881596407 7.21134778324628 7.721144857588 3.24484578991107872 1.2448857881596407 7.21134778324628 7.711344857588 3.244284751994077 6.2552677612261 1.21985576655465 3.293440776758 3.26447031269155 2.5447411164403778 3.26447031269155 2.5447411164403778 3.264471134845778 3.26447134484877891107872 2.2644757877602 7.2113477783446287782 2.2644757877602 7.2113477783446287782 2.2644757877602 7.2113477783446287782 2.2644757877602 7.2113477783446287782 2.2644757877602 7.2113477783446287782 2.26447774444857788 2.264477877864778 2.26447774444857788 2.264477877444857788 2.2644777444857788 2.2644777444857788 2.2644777444857788 2.2644777444857788 2.2644777444857889107872 2.2644777444857889107872 2.26447747444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.264477444857889107872 2.2644774448578890778 2.26447744484578897780 2.26447744484578897774 2.25444448778877
C H O H O H O H O O O H O H O H O H O H	217071482551246 240071482551246 2465533690542 2465533690542 2465533690542 2465533690542 24758318223137 237581222317 237582222511 0.5016329249435 2475831895538 24353154804312 2.077642722133 3.431006766219 2.11501663338663 4.383515840312 2.0776282255180 4.38325280442114 4.38252820042114 4.38252820042114 4.3825280042114 4.3825280042114 4.382540680812 5.70940680333674 4.1826748094812 5.70940678936289 4.19267480468082 4.0562641993574 4.0562641993574 4.0562641993574 4.0562641993574 4.0562641993574 4.0562641930579 4.38424807703152 5.319407936031 2.720654572673071 1.9761684663830 0.831287703052 0.8311491040991503 3.8903	21.42548(4142567) 22.402633942(424257) 22.402633942(42185) 22.402633942(42185) 22.402633942(42185) 22.40263942(42185) 23.15322(42185) 23.15322(4180538) 24.3097(4261485) 24.3097(421855) 24.3097(42185) 24.3097(421855)	33223381/3303 3322381/3303 3422381/3303131 34255027023331315 34255027023331315 34255027023331315 34255027023331315 34255027023331315 34255027023331315 34255270251554 4723825823303552 3427228105688 5.247722810568 5.247728105678 5.24722810568 5.24722810555520 5.245281057 5.24528305 5.24528105 5.2452192514 5.25581762026 5.25581762261 5.25581762000000000000000000000000000000000000

С	-1.24574538654062	16.06674115766689	6.22476238134199
С	-0.58178717456837	17.12583098775756	6.83976127962861
С	-0.08308940893471	18.16439176111895	6.05856279541042
н	-1.94903333881002	15.20258490592498	4.38878713622474
н	-2.11695961986065	19.79393435559953	-0.42856902956915
н	-0.61165396811361	21.48832132435594	-1.45607650666086
С	-1.74780819206036	18.34039974860914	1.86826193804775
н	-2.47919993961712	18.03137218579617	1.10632971142340
н	-2.33104239185051	18.92000731434964	2.60391530005556
н	2.39552686153573	20.57708599534020	1.48397942787341
н	0.42871156142704	19.00659500608961	6.53079990501017
0	1.72100283007793	22.17182462354434	-0.55813852899840
н	2.39100966915681	22.43221492358659	0.10293900977295
н	-0.48472665436570	17.16305446994329	7.92871934298863
0	-1.78291724436410	15.02859735950184	6.93499719178178
н	-1.59751348919816	15.14359438436607	7.87324278794662

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

177 EN	JERGV = -5071 137888	202838 Input = w897¥-	D3 def2-SVP def2/I D37EBO BUCOSX OPT
C	1.49122449274576	22.70785682019121	6.89907510849217
Н	0.78779131865464	23.31746783009261	7.49272604372450
н С	1.07457478723720	22.87671013238704	5.42904775348233
H	0.41019154215098	22.03952292432556	5.15950640170952
С	2.26397344121416	22.85548725351064	4.47306545901402 4.84775495754101
C	1.85766773597261	23.21637514363463	3.05530191388295
н	1.18621549117846	22.41387080748121	2.70929465283350
н	1.64014917043477	25.34707685110985	3.34563783236196
С	-0.13429641679034	24.31683351654937	3.99173170567569
н С	-3.24305957439663	23.95027715833892	4.03423599311914 5.31047531759337
H	-3.95979315333313	23.56312324985706	6.05918893637619
H C	-2.24905993308922	23.98200831638907	5.78149317427256 4 13728531579119
н	-2.92437496384104	21.98212737533150	4.49567912473528
C	-2.19945867555766	23.40071155970205	3.06534551283870
С	-2.33470275403255	22.53668611989756	1.81956135369150
Н	-2.08291547930777	21.49581810488495	2.10019510244271
С	-3.78158970001232 -4.06457988484302	22.54192859952766 23.57853679757950	1.36038843958558 1.09697832722834
С	-4.68615551456473	22.09668231030035	2.50713549103023
H	-5.74394782544758	22.16507773772894	2.20997000406728
н	-3.95399893638660	20.15517930752016	5.35947193939285
Н	-5.60750782412841	19.76447234884438	5.89115558865861
н	-4.09380086502418	18.31004576286070	4.0508/1/8509181 3.67134018047371
С	-5.41340515743348	19.87798847125733	3.03153284850886
H C	-6.31634883729472 -5.72724153848926	20.40155472943520	3.40053305193312
Ĥ	-4.80792119597270	18.68065557730819	1.35868608357400
C	-6.79229089643087	18.12397653449527	1.92871105477725
С	-6.33983815804187	17.16455615586730	3.03025621532108
Н	-7.14603049638731	16.45768367620141	3.28915690843280
C H	-4.72001447816268 -5.57650518440151	14.86/25805608682 14.23627253048726	5.39399080432550
н	-5.05548662354210	15.92036888461439	5.12394218498341
С	-4.29755927810612 -3.28267291981208	14.53374411228805	3.69202024660372
c	-5.16659774002377	15.08582406522963	2.56810012568174
н	-6.18803040933358	14.66461525797659	2.64008303283618
н	-3.55504469903621	15.24037033727273	1.23124301318918
С	-4.24736207577814	13.22143413842720	1.11374737164012
н С	-5.21442415229370 -3.58114393956225	12.70542192017081 12.70939736232564	0.99306525842426 2.40230244585164
Ĥ	-3.57846084222184	11.60770426609239	2.43122122813272
C	-1.94857681159586	11.75294900675263	5.15968865576128
н	-2.92700517891574	12.23315658711532	5.04563133054433
C	-0.91927322664361	12.45504227585147	4.28879072070374
н С	-0.86519963429305	12.36667337717890	4.57251703146380 2.78097285095708
н	-1.44675520650570	11.31634321761711	2.53269596092606
С	-0.01518305614511	12.80864917822302	1.96042904022397 2.15856122100530
c	1.22444757059822	12.03614033602891	2.38682842612148
Н	1.02925102859637	10.95937349252323	2.23827599432118
н	2.28799953224746	11.67278559736886	4.25355721139294
С	1.49381022957996	14.06326163118356	7.10832825281765
н	1.06273200310266 0.66567535359721	14.74773626715216	7.86257778273334 6.62081077578601
С	2.23110806311032	14.88901152151011	6.06763969566669
H	1.57425254575218	15.68938175428633	5.68514821214169 4.89792194801979
н	3.24784230762171	13.15568334874109	5.31482478752848
C	3.66777121385317	14.81484490411487	4.01169349185746
н С	4.79287340561192	15.42854116531183	4.82708045930218
Н	5.37284028114090	14.61366846564437	5.29316007201103
С	4.18/25/9634/442	16.25164609736019	5.97596841955215 6.64762395808721
С	4.05780295578653	19.40453728191441	7.61383969591992
н	3.60876105514143	18.43707278046833	7.90237871363555 7.76970500924390
c	3.77149691078628	19.65579066607814	6.15411681933226
H C	2.68410676106445	19.82538341299387 18.52341736291099	6.05844715291042 5.19238906957130
н	5.23946215638835	18.34810223827737	5.24134206754746
C	3.77187108981604	18.97823440435476	3.78185359602343
С	4.50056154598867	20.27791780630746	3.46575844732391
Н	5.59179002235224	20.10696144865338	3.53037571929944
н	4.69248232488260	22.25002573159814	4.32551453255546 4.38189473102275
0	2.80661102305756	23.09943671161056	7.16978570732831
н 0	3.30919681101273 2.94589628895036	22.30033485079830	7.38647234664153 2.18406219229449
Ĥ	3.34066538907513	22.48218742391664	2.03744200345383
0	0.53402430115779	24.69577590000790	1.71503320073816
0	0.34771488891839	24.09576062830239	5.27706002190501
0	-0.89939432938205	23.21666217676408	3.56847128330135
н	-4.41267174784603	25.19770641765040	4.44297653632492
0	-1.53046767389253	22.96114953365359	0.75364151287596
н О	-0.77585602762397 -3.97196058818383	23.47811452740837 21.69079047406354	0.25423809135767
н	-3.27955714219180	21.89227203590708	-0.38808773559794
0	-4.52592278417078 -4.35529862400665	22.95854716163458 20.78881872355737	3.59836401790900 2.85988698244066
0	-4.13908810786672	18.33789972661061	6.26001339452231
H O	-4.81556729253674 -6.20660408775565	17.66456529362737 20.06604352787803	6.40611276651128 0.72523322625820
н	-5.44702874209395	20.52764171120335	0.32895667877232
0	-7.02711574574247	17.38737291629609	0.75599354477756
0	-6.05534440566957	17.88244244652196	4.19899842817331
0	-5.21323719567155	16.49562715151256	2.58084625141371
н	-2.93615793263185	15.18145354255040	5.78576890415260
0	-5.31393567085549	15.16283864748928	0.14648930810449
н 0	-3.45596122446657	12.90697999429610	0.00561132324362
Н	-2.52465737226864	12.99770717096531	0.26609012836046
υ	-4.20/4262843/392	13.12011094609060	3.34301060114022

0	-2.27506429802051	13.20288420439604	2.39298891646002
0	-2.07221742802125	10.39884786958965	4.81047173581794
н	-1.19599240582145	10.00861637246685	4.90758485202391
0	-0.29049483968723	12.60889759238330	0.59533885519230
н	0.56484040268219	12.61410233118031	0.14408073014567
0	2.32168155131343	12.37810665756954	1.59481995187105
Ĥ	2.85548080753180	13.06806068354254	2.03020719040611
0	0.31417452592585	11.80409576386521	4.58993615680274
ò	1 63491053969292	13 62159438487066	4 10750357714438
ŏ	2.33683931916786	13.10555022353903	7.68658080559496
н	3 09952642778903	13 58597729798055	8 02915753488391
0	4 17245896859519	13.94725174213825	3.02220420198603
н	4.93164384190499	14.38250614155100	2.61330756581026
0	5.67822886864161	16.14101035319966	4.01072985789122
Ĥ	5.17121879245227	16.79699917528708	3.49033919741820
0	3 34813262700153	15 46171383952047	6 74825858299877
õ	3 44470101645292	17 34499375830772	5 49473550687671
õ	3 47870880249834	20 47755602629622	8 32229314890041
н	3 73098890654449	20.43537871952186	9 24828843085985
~	A 06062957476937	10 07757962761796	2 7950029622906
ŭ	2 72595772440720	17 57060090970901	2 51001100005101
	A 1577A6505A1626	20 76017206274257	2.515011555505151
	4.13774035341030	20.70317300274237	1.57210564026641
	4.24200203337999	20.05409747519192	1.3/310304020041 5 7004070732C0410
	4.47595012100250	20.82978044484085	5./0040/0/209410
	2.76192445010159	21.55456510290060	4.45776929406509
	0.0/5/9232/82456	19.65584477675597	0.318/5213459289
н	0.70931999746482	19.82102/22528//0	-0.56945613461765
н	-0.67042857643109	20.46393355141234	0.30440927838930
С	-1.23515521906739	18.9931//4988/4/3	4.61392649721485
С	-0.51664150394320	19.73582640859951	3.68238233380823
С	0.31996921443689	19.11390509155212	2.75792344587933
С	0.46425675815299	17.72436653062713	2.85247203493497
С	-0.24278888304739	16.95438181086049	3.77257402123433
С	-1.14888667811382	17.59605428485646	4.62510933891550
С	-0.66269442882910	18.34219836008250	0.14165475436688
Ν	1.46537873982484	17.11329375755582	2.01179258079684
Ν	1.23358748653759	16.83236971020145	0.82873721171001
С	-0.07621802686966	17.06701306083052	0.28913825548770
С	-1.99522660500723	18.39179192652180	-0.27221660113051
С	-2.72312925571292	17.23595533731127	-0.57435175830665
С	-2.07680237519902	15.99517873687875	-0.54944821319403
С	-0.76159073838815	15.92018225840294	-0.11526538713697
н	-0.62581974190361	20.82356813478636	3.65829997960676
н	-2.50594250232830	19.35629313640952	-0.33187498077357
н	-1.88138217217994	19.49493001912675	5.33732068459910
С	0.93917598680787	19.81996645545996	1.58537659956840
н	1.95502590610132	19.44090983345124	1.40852899928964
н	1.05872991078815	20.88858336469273	1.79385257790619
н	-0.27683061301655	14.94446890741131	-0.04126891933900
н	-0.11611386811879	15.86959237963377	3.80588399895214
0	-1.92103670557673	16.85549560430290	5.45345187888243
н	-2.62099608765078	17.42289150781768	5.84261543977220
н	-2.61787811237922	15.08805537934448	-0.83146927742745
0	-4.02750258388880	17.35502217678193	-0.87441823712692
н	-4.45782454671163	16.47927190714012	-0.77469383139008

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

198			
EN	IERGY = -5681.278144	114335 Input = wB97X-	D3 def2-SVP def2/J D3ZERO RIJCOSX OPT
0	8.21240504903062	25.05621827676585	5.85207327583254
0	9.86835517785385	23.16973000110755	7.25864713083231
н	10.56714440747783	23.59988423115185	7.77689882700294
0	7.37664791667849	24.10322145160823	9.74006164700133
н	4.94913450717635	24.76863394931664	10.12108435552057
0	9.67334905088439	24.12167210992235	9.80916476706134
0	12.36829148808340	24.10805852749393	9.36151561179608
н 0	13.25131430908285	24.49629586179534 24.39682344324530	9.40883468613937
н	13.87716054055060	25.06980478067474	12.45317502654034
0	10.94070199479189	22.74096416841170	12.95347121981399
0	8.98410386251659	21.14275193042909	11.47422820662579
ö	11.74115944355289	24.84975246653426	13.40879251400533
0	14.02990591296981	26.06088650022958	14.24676423476615
н	14.67482945138769	26.72429967213370	14.52584192611592
н	13.40159907918904	27.93874020393849 28.74838963902896	16.05509176988988
0	10.76989890198687	25.95169979658850	16.75122367288090
0	10.08314411681913	23.14788626602525	15.63325520302414
н	10.36219677011351	22.78493091276743	14.77976162889521
ō	12.63354829270249	30.35771460461111	15.68729844425793
н	12.98891421499889	31.23634162632460	15.49501674804752
0	11.67335754549135	32.92720028055902	16.23641617121232
н 0	11.11062979811574	32.99934197793624	15.436/122111423/ 18.36381622761197
ō	10.06968760192682	28.46963607152072	19.71297142036391
н	10.13426599970529	29.35665555923067	20.08684101774834
0	8.85785315230647	32.10227675181417	16.60399153578046
н	9.94382358119821 9.81394674066282	32.9552/0915/3290 32.01827282409102	13.87127977550767
0	8.47024844554185	34.78827066444663	12.65887457252874
н	9.30590648858312	34.34630060939413	12.46334518917934
0	6.80224743526693	35.02907749134922	15.86739807521740
н	7.67416462347877	35.77734391435092	17.94562117887124
0	6.11041260627520	34.09435641984508	13.85969089388853
0	5.16479098353197	36.54359221681074	12.52057801759516
н 0	3.20621127563850	37.04508837403141	10.51824308093145
н	3.66128533392359	35.37590715869641	9.88679193989350
0	2.72161468542685	33.27875631128438	12.93250536304756
О	3.453411/4/58531	32.79899432954167	15.65835827764257
ö	3.23157424803198	33.22885471544781	10.69353318691750
0	3.68349654122764	34.31742319261578	8.06787012749576
н	2.83555366966484	34.74781487889388	7.89774560540024
н	4.17730487467192	33.13385245799855	6.01303641763857
0	1.59068924671029	30.80483756904626	8.52071825927291
0	-0.10767549969461	32.24518488262770	10.44216741735179
н	-0.83///398986261	32.15498897778723	11.05954911476901
ő	6.22837668130013	31.10632168382672	7.43170503535992
н	5.59795248217906	31.51706111206687	6.81916859381130
0	8.21610684656281	29.12822729952704	6.58877232962421
н 0	8.48345958994367 5.12221207768962	28.44628205196359 27.20885670391640	7.22024039722332 6.37943314894202
0	2.44253462724398	27.84687508766599	5.80059658778406
н	3.08158629750094	27.50411033351474	5.16436479738487
0	7.03471725952907	27.04202146699537	7.68435630811861
н	6.21444987936909	25.14753176457256	7.58375007704896
С	8.36448406606592	25.05671002702238	7.24823634614771
н	9.21815224039900	25.69598092418591	7.54751369621180
C, h	8.63290191267870 7.85696609752422	23.03078275536713	7.73330484790869
c	8.53965671174754	23.50075683650494	9.25314186005179
н	8.50699820297913	22.44174971041875	9.54893377100341
C	7.31623892317693	25.49136963310668	9.43146611818889
н С	8.2/4015030/9937	25.96422468718208	9.69415334289622
н	6.60618734070111	25.98665448246429	11.37046547673892
н	6.32946986518546	27.23351790293708	10.13534829347562
C H	10.52724939802552	23.37118959490858	10.65050396240960
c	11.83560806702540	24.13957739656959	10.65862874633119
н	11.60926356559025	25.18187730054782	10.95591577003237
C	12.80829759860691	23.61208828882316	11.70548570981241
н	13.10014655499/83	22.36360//1019/81	11.4303002034100

С	12.08488802338832	23.55007870025952	13.04613034881668
н	12.72748941904734	23.08781996760569	13.81278329257605
н	9.64337719952028	24.25636755980748	12.38741180877685
С	8.73839814479646	22.33705377472954	12.17459570186833
Н	8.56839604948469	22.15567509061457	13.25170065771074
c	11.87237560840687	25.22605531293847	14.76502865322002
н	12.31167694426430	24.39176476550338	15.33859670363447
c	12.79927186014699	26.41965942621895	14.82930080905989
С	12.33/64/553861/1 12.96675786928906	26.84561450691492	16.28306671139683
н	13.44115699302324	26.01049934391166	16.82605621565340
С	10.52762024122558	25.56669069900206	15.40668356889530
С	9.52811089580672	24.41059474463724	15.40556083624482
н	8.80441046930929	24.62113506415247	16.20834593100275
н	8.96725129999747	24.44377595973108	14.45339861057132
С	10.93784035155026	29.3/8/8/44//1498	17.06412411093691
c	11.32681173752697	30.54455359654953	16.18392821588984
н	10.60690917598953	30.60151205376786	15.34630480992330
C	9.83646962340682	31.97780470425445	17.60025808860965
c	9.54362227971961	29.61530300236565	17.65305587142547
н	8.80592402850654	29.64719535753066	16.83160704914533
C	9.14913262715168	28.54707848081466	18.65646496836921
н	9.13010386877732	27.56665678230485	18.15743143859732
С	8.57390008142872	33.39443855255701	16.11629339338888
н	9.27517488904576	34.13077161748613	16.54585052241413
н	7.91744806244412	32.68502450983029	14.23596342312809
С	8.34833495663995	34.75799497779753	14.05072227184194
н	8.99965557306598	35.52019566521662	14.52366581654582
C H	6.60680859804008	35.06377685643726 36.07283993345334	14.46647470789051
c	7.14109378647044	33.79496840862246	16.49077425311551
Н	6.45861861140572	32.99453003140542	16.15565061866479
C H	0.95759273523393 5.89584061482951	34.00325828814436 34.25061367804334	17.98109379478852
н	7.17898818498370	33.06155964236633	18.50590003511370
С	4.77288432270727	34.40892128918853	13.55487525064664
н	4.29268745379491	34.93036730532635	14.40231658772496
н	5.29077001802644	34.72842713129876	11.52352446896050
С	3.23968310243921	35.32724333594337	11.77312439428220
н	2.66151225392259	35.95781696417357	12.46743455217309
н	1.51025518043694	34.01862798304314	11.50990891344048
C	4.07643451486320	33.06417357945615	13.32712693583315
н	4.60901818235545	32.52648236515118	12.52480710408125
С	4.05346145473892	32.17672641002856 31.23096547126678	14.55409429040928 14.28040853086563
н	5.08982197653725	31.92936533248983	14.82494743685203
С	2.50108226190094	32.80800773930054	9.56850833793059
H C	1.61/65/9920/21/	33.45478595509770	9.41169766228829
Ĥ	4.42011040352427	32.53605576832897	8.65004867820562
С	2.94218828671950	32.20003388518552	7.15989918294178
н	2.00341562428608	32.65795367445000	6.78959275214974
н	2.17621378256904	30.20987529195061	6.68921642877023
С	2.00843870424638	31.36694646310279	9.75728128431741
н	2.84409426217543	30.78190086921212	10.16780752017638
н	0.45991985080416	30.24941634314699	10.68480293198199
н	1.28573254199735	31.42203803664932	11.75933568195136
C	4.52802513708834	29.37901346861815	7.18987098635074
c	5.99585725560940	29.72653525569796	7.43947734698210
н	6.28569381427433	29.36039857543230	8.43947276085783
С	6.83941925990232	28.96568486219016	6.40680317618973 5.40248130655388
c	6.48997096907125	27.47050470968989	6.45798674905038
н	6.95188702187271	26.92304562357896	5.62509746745881
C	4.31207212768897	27.87377609058747	7.34027783954332
c	2.88286543747555	27.44514059266449	7.07163202294224
н	2.82087629623549	26.34887012492991	7.20381527067102
н С	2.2188///0550445 11.58259171405634	27.90924266692437 27.07063117848039	16.91098794712556
Ĥ	11.67081435747047	27.22994216008707	17.99763606205510
C	11.24423726055891	31.83441147298509	16.99500139785270
С	11.94370929680224 8 37816996049275	31.74902180776423	17.84479118216433
Ĥ	9.14109043309284	32.15859384419191	10.46156869035442
н	8.14462909866942	31.25505001748176	9.32466131023284
c	4.59178896022263	28.95416870616742	11.15464/3/55/118 10.80525453237605
c	6.26816380631534	30.66187121484727	11.59117641421604
C	6.57257208391264	29.98368206214278	12.78046544367496
c	5.90966624773918	28.82388996508390	13.1/340109108097
č	8.98980425406042	30.05502567639046	10.85919533810887
Ν	7.56219225527108	30.56716872914161	13.63408067672162
N C	8./5//35/2551585 9.17665843934914	30.50731656199288 29.69901109074247	13.3236308/971522
č	9.41661797373972	29.13600914606443	9.89802944841315
C	9.99713487182393	27.91105545588161	10.24098842818341
c	10.20617945693580	2/.59812478125697 28 51048798619129	11.58763844246850
ñ	4.98692212918248	30.62588503594925	9.87100852527369
Н	9.26650874822999	29.37446696817920	8.84291261167816
H C	3.81/88111515969	28.54580347622395 31.82961163727029	10.49858149364339
ñ	7.33802177401377	32.50328014574271	11.96407244817304
Н	6.50365620608444	32.43541893076802	10.42778315843924
H	9.98525824364880	28.30342844380064 28.30962957465205	13.62047556201803
0	4.42283756540407	27.06544706780461	12.63208705839389
н	4.18697289812249	26.61166406302453	11.80572728926296
н	10.83265/7/406371	20.002/0110555569 27.07618569091768	11.89267409796412 9.22795192251674
н	10.52554267711663	26.18428010514402	9.54989361092689

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

198			
ΕN	ERGY = -5681.244414	073524 Input = wB97X-	D3 def2-SVP def2/J D3ZERO RIJCOSX OPT
0	9.00300595928369	27.23840077951341	6.20101047280159
н	9.86534660858873	27.63196689468834	6.37483710434068
0	10.96366483845300	25.81837057200791	7.75802919661113
н	11.37670825863128	25.29206401216773	8.46361384779303
0	7.96416839817420	23.76455646293930	8.09917725532754
0	5.61868090287227	23.39715018242766	6.58599391044056
н	6.40143085840070	22.83523301509974	6.54094674981501
0	9.18812598071712	24.88238932877245	9.70159087996911
0	11.84014438325147	24.06594049433868	9.92333195492289
н	12.74971116710970	23.93862332028342	10.22682392465416
0	12.87308957292344	23.65598965671755	12.51869092954653
н	13.05247492403690	24.57395724738682	12.80344047337648
0	9.25151331280598	23.60498291626941	13.10762459806807
0	7.05344748776136	23.00170498024806	11.29810396914851
н	6.11040930794145	22.82833034082805	11.34145593174179
0	10.78205591911503	25.06333729357907	13.92200979437336
0	13.36344298261154	26.18609017603453	13.56217624157343
н	14.04001443241366	26.87547414546106	13.53259743044606
0	14.15043859049428	28.01019953368539	15.55933528286287
н	13.69071338375227	28.84246590672257	15.77748209803140
0	11.71071528869177	25.95627558696344	17.33482887799666
0	11.18728050618097	23.14731643942387	16.75173682732984
н	10.78492121794590	22.35501282954882	17.11588366249710

0	11.47694652242027 13.08606257851944	28.13828416213271 30.42029266069340	16.63723524623801 16.59026441086310
н О	13.39195517410149 11.76990820253094	31.31661392113365 32.89234909042352	16.39746087742025 16.94199349145474
н О	11.36413895236327 9.39114918777694	32.99612009269645 30.53751906527710	16.05947397642250 18.41746652397872
О Н	9.91923539578146 9.72389599422671	28.40482469901494 29.31275554563090	20.00493476480332 20.26604373959672
0	9.11483089719295 10.44901019871141	31.78571385823455 33.27186737238105	16.52712030454842 14.54497030792060
н О	10.66509056633033 8.76410665734997	33.53853362027741 34.65707604550538	13.64306299845562 12.78866463593147
H	8.14487935825026	35.27399487762894 34.39259303707113	12.36136022051212
0	7.37354652608108	33.82334552582094	18.52175939024400
0	6.26783198404817	33.79040143602542	13.58584867347980
н	6.51199647779343	36.57200964084243	11.02365748739435
н	4.74023561415676 5.00208617400015	35.44534389442997	9.03797661749430
0	2.81019079663485	33.60103586838216	11.88293417002022 14.58960061566896
н О	2.17962595806513 3.90222339036240	33.97258303658829 33.51380794812344	13.96150858712714 9.75231692898997
О Н	4.85222879575418 4.16754785712149	34.55508608891818 35.18624882431354	7.27205694196281 7.01350146445008
О Н	4.60821388117258 5.24518745024660	32.67889136157975 33.39561490779298	5.11255077461278 5.21813040381230
0 0	2.00063143767527 0.54844539700807	31.54266431915728 33.07003569304101	7.34422400098804 9.34955313374951
н О	-0.22327539455322 3.98990561163418	33.04145129893075 30.55652277148339	9.92061325036918 6.76052592633799
О Н	5.03803367610306 5.06874838368903	29.90496801535452 30.83685609481585	4.17940335584759 4.44181165063980
0 H	6.68341893792806 7.40110785727348	27.43760088481014 27.61812781983405	4.31022532729168 4.93852541007314
0	4.10902696982242	26.93912205261485 28.65022541711401	6.83875720647640 7.60145960845749
н	1.52836028659568	29.61080892288307	7.48974349570464
Ċ	7.32116521382437	25.79298566695806	7.00636076355408
c	8.69888374165364	26.37438379634561	7.26848739258115
C	9.72791291759303	25.26037868038032	8.22734782310192 7.42126625788056
C	9.22485802823097	24.72414858723210 24.25203625729309	6.45360522192647 8.45562607079284
н С	9.88967711980694 6.95616905951379	23.37518919714851 24.75992073772019	8.48601619588311 8.07523859487007
н С	6.90409939352465 5.64717163798969	25.26725930249210 24.03360007747154	9.05485026332381 7.83573079756649
H H	5.52362575659085 4.80948349841206	23.31476846061715 24.74536949313629	8.66740605369691 7.87078572213316
C H	9.60572212920432 9.43477912771886	24.10025947755664 23.03130984207986	10.79293687852240 10.57816344516659
С Н	11.07351964115176 11.19794370515771	24.35293652081500 25.41721330909795	11.07572387596412 11.35392645825375
С Н	11.51176275928852 11.37660964283207	23.48814216769533 22.43072864883928	12.24794772080427 11.96365663408270
С Н	10.59296575117100 10.79945121607383	23.75497514229355 23.02599623027527	13.45223499291547 14.25329545321874
C H	8.80257199308029 8.97590291433526	24.44536374546096 25.50512642428921	12.04682126474887 12.31210416128808
С Н	7.31204027360665	24.25337762523966 24.35545551613216	11.87654149457863 12.87352813465809
н	6.93612798100764 11.68524460958761	25.08553748102611 25.27124822591809	11.25147277932184 14.98556210998408
н	12.35733739096977	24.40518653479458	15.10423098216289
н	11.83816552713033	27.31628329882748	14.38459890153866
н	14.00645897446124	26.07701440279901	16.14565192622549
c	10.89148100400097	25.4/0402255/4595	10.26450907624619
н	10.09365012694258	26.20398398273768	16.07390107542480
H C H	10.09365012694258 10.24021034605972 9.83538526763454	26.20398398273768 24.18521093011300 24.36981082528633	16.07390107542480 16.75345724323270 17.76593018984391
нсннс	10.09365012694258 10.24021034605972 9.83538526763454 9.39222488327254 11.21836254419961	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789	16.07390107542480 16.75345724323270 17.76593018984391 16.07857903263388 17.46862919602621
нснснс	10.09365012694258 10.24021034605972 9.83538526763454 9.39222488327254 11.21836254419961 11.76521679398931 11.68779507331908	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789 29.14048700482963 30.49184627684068	16.07390107542480 16.75345724323270 17.76593018984391 16.07857903263388 17.46862919602621 18.42326810620506 16.75559220205496
нснснс	10.09365012694258 10.24021034605972 9.83538252765454 9.39222488327254 11.21836254419961 11.76521679398931 11.68779507331908 11.18521559995351 9.77692570614639	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789 29.14048700482963 30.49184627684068 30.53916151460506 31.70688420209264	16.07390107542480 16.75345724323270 17.7653018984391 16.07857903263388 17.46862919602621 18.42326810620506 16.75559220205496 15.77031896133730 17.76660476565095
нснснснс	10.09365012694258 10.24021034605972 9.3538526763454 9.39222488327254 11.21836254419961 11.76521679398931 11.68779507331908 11.18521559995351 9.7769257061669 9.45975642557405 9.71895561062075	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789 29.14048700482963 30.49184627684068 30.53916151460506 31.70688420209264 32.54005655207488 29.30620887020696	16.07390107542480 16.75345724323270 17.76593018984391 16.07857903263388 17.46862919602621 18.42326810620506 16.75559220205496 15.77031896133730 17.76660476565095 18.41354150535754 17.77723347647581
нснснснс нс	10.09365012694258 10.24021034605972 9.3538526763454 9.39222488327254 11.21836254419961 11.76521679389331 11.68779507331908 11.18521559995331 9.77692570614633 9.77692570614633 9.77592561052075 9.15290883921148 9.30367787753824	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789 29.24114562276789 29.24114562276789 30.49124672684068 30.53916151460506 31.70688420209264 29.30620887020696 29.20181034172329	16.07390107542480 16.73545774323270 17.76593018984391 16.07857903263388 17.46862396002621 18.4236810620561 15.77031896133730 17.76660476565095 18.4135415053754 17.77723347647581 16.83397937217536
нснснснснсн	10.09365012694258 10.24021034605972 9.83538526763454 9.39222488327254 11.21836254419961 11.76521679389391 11.8527159995351 9.7769257061639 9.4597564257405 9.71895561062075 9.71895561062075 9.71895561062075 9.15290883921148 9.30367787753824 8.2014427836247 9.6267883752852	26.20398398273768 24.18521093011300 24.36981082528633 23.95757078305212 29.24114562276789 29.24114562276789 29.24114562276784068 30.53916151460506 31.70688420209264 32.54005655207488 29.30820887020696 29.20181034172329 28.22123490321881 28.21507265396090 27.2450643828492	16.07390107542480 16.7334572432370 17.7659018984391 10.7085709263388 17.46652919602621 18.42326810620506 16.7555921002540 15.77031896103730 17.776660476565095 18.41354150535754 18.83415557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.8341557 18.834557 18.93457 18.834557 18.9345
нснснснснсннсн	10.0356012694258 10.2021034605972 9.83588256763454 9.3922248832754 11.285215673398931 11.285215673398931 11.1852155995551 9.77692570614639 9.245975642557405 9.215290683921148 9.3056778775324 8.20184427836247 9.305677877528692	26.20398398273768 24.18521093011300 23.95757078305212 29.34075707805276789 29.14045706482963 30.49184627684068 31.70688420209264 32.5400555207488 29.30620887020696 29.20181034172329 29.30620887020696 29.20181034172329 29.30620887020696 29.20181034172329 29.30620887020696 29.20181034172329 29.3062087020696 29.20181034172329 29.3062087020696 29.20181034172329 29.3062087020696 29.20181034172329 29.3062087020696 29.20181034172329 29.3062087020696 29.3052032949341 33.657553032949341	16.07390107542480 16.73345724323270 17.76539018984391 10.7085709253388 17.46652919602621 18.423268102620506 16.75559270205496 15.77031896103730 17.76650476565095 18.4334150535754 17.77723474647581 18.836690673631345 16.3152471255984 16.3152471255984
нсннснснснсннснс	10.035601264258 10.24021034605972 9.83588256763454 11.2188254673954 11.28254679957 9.392224882754 11.827159957351 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.37692570614639 9.30567787753824 8.2018447285247 9.04507139201208 8.6620841967338	26.20398398273768 24.18521093011300 24.3698108252863 39.95757078305212 39.3414562276789 30.43918427860482 30.33916151460506 31.706842000926 32.0620837020696 29.2016103417239 29.30620837020696 29.2016103417239 29.2012762596090 33.057155919188 33.057263924021881 28.2112740921881 28.21127459191883 33.26471559115891 33.264711589119883	16.07390107542480 16.7394572432270 17.7659018984391 10.78549724523270 18.4232681062506 16.755592102548 18.4232681062506 16.755592102548 17.766348062505 17.766348061505 17.76734846016 18.84208053216614 18.846906747581 18.84669075761145 16.1555471265984 16.31525471265984 16.5312276150643 14.6667149720853
ноннонононо ннононон	10.0365012694258 10.24021034065972 9.83368256763454 11.21826254419961 11.6521679398931 11.65721679398931 11.6572167938931 11.657215796133 9.7769257061459 9.7769257061459 9.7169257061459 9.7169257061459 9.0366778775824 8.2018447285247 9.0366778775824 8.2018447285247 9.04507139010208 8.66201417053824 8.6220843957338 8.462107699550571 9.39343701681803	16.0298398273768 24.18521093011300 24.395108225833 39.575078380511 29.34114562776789 30.4914462754082 30.33916131446276 30.33916131446276 30.33916131446276 30.33916131446276 30.33916131446276 30.365089702696 20.2013104477329 20.3667089702696 20.2013104477329 20.2012765396090 30.3672452403249341 30.3524612942642 30.35246214294 30.352461294542 30.35246214294 30.3524621424 30.3524621424 30.352462144 30.352462144 30.352462144 30.35246214 30.35246214	16.07390107542480 16.7394572432270 17.7559018984391 17.6659015986331 17.46652919502621 18.42326810620506 16.75559210205496 15.77031840620566 15.7703184053754 17.7773347647581 18.3435410535754 17.7773347647581 18.36560675671845 18.36560675671845 16.315267155084 16.53127275584 16.53267726538 14.35260611320868 14.37296513884
ноннононононнононон он	10.0350012694258 10.040211344605972 9.83538526763454 11.21836254619961 11.852155996351 11.6571579507331098 9.776925706146330 9.746925706146330 9.746925706146330 9.1895561062072 9.1520683921745 9.0357477753242 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.0314170753824 9.031417053854 9.031417053854 9.0345711681803 6.5580254422550	26.0298398273766 24.18521093011300 24.3998108222633 39.5757078050212 39.3408700422963 30.431462276780 30.33916151460506 31.706844202934 29.36248702599 30.02188702599 29.302188702599 30.02188702599 30.02188702599 30.02188702599 30.0218702599 30.0218702599 30.0218702599 30.0218702599 30.0218702599 30.0218702599 30.0217155919188 30.3966172990018 34.5729966919004 34.5729966919004 35.3966172990018	16.07390107542480 16.7394572432270 17.7659018984391 16.7384570263388 17.46652919602621 18.42326810620506 16.75559210205496 15.77031896102556 17.77031896103730 17.7660476565095 18.4335410545754 17.7773347647581 18.4325410545754 18.5327973217536 18.5422802316614 18.16242902316614 18.1632479754584 14.153405611320868 14.152405611320868 14.1296511399884
ноннононононнононононон	10.0356012694258 10.040211344665972 9.83538526763454 11.2186254619961 11.852159993531 11.657179507331098 9.776925706146330 9.776925706146330 9.71895561062075 9.1895561062075 9.1295561062075 9.129585172775324 9.0257187753245 9.025718725	26.20398398273768 24.18521093011300 24.3998108222633 39.5757078050212 39.3418462776708 30.4318462768042 30.4318462768042 30.533416131460506 31.7068487020964 29.360788702096 29.3018104477323 29.302188702096 29.30218477323 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.214564322847 20.21456432847 20.2145647	16.07390107542480 16.07394572423270 17.7659018984391 16.75345724523270 17.7659018984391 17.46652919602621 18.42326810620506 16.75559220205496 15.77031896103730 17.7660476565095 18.41354105635754 17.7773347467581 18.35690476513470 18.3569047651345 18.4228023216614 18.3669047651345 18.4228023216614 18.3669047651345 16.5132270553 14.15206611320868 14.1520651320868 14.12738442695889 16.251996334363984 16.2547599834435984
ноннононононнонононононон	10.03365012694258 10.043021034605972 9.83363526763454 11.21836254619961 11.65216793989331 11.6571579507331098 9.77692570614639 9.74692570614639 9.74692570614639 9.1495561062075 9.1295561062075 9.1295561062075 9.12957477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.0157477753824 9.015747753824 9.015747075824 9.015747075824 9.015747075824 9.015747075824 9.015747075824 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.01574707584 0.015747707584 0.01574707584 0.0157	26.20398398273768 24.18521093011300 24.3698108225833 39.9575707805212 39.34114562776790 30.33316151460206 30.33316151460206 31.7068482020924 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.306208702096 29.30620872090018 31.375326800866 33.32642129200018 31.375326800866 33.32642129200018 31.375326800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866 31.327526800866	16.07390107542480 16.0739407242480 16.7394572432370 17.7659018984391 17.6662919502621 18.42326810620506 16.75559220205496 15.7703189610255754 17.770340764513730 17.7660476565095 18.43324973717536 18.4326413545754 18.332973717536 18.432641354216514 18.3666927631345 16.75327125964 16.75327125964 16.75327125964 14.056172978983 14.0569965563076 14.2779844269889 14.24779844269889 14.24779844269889 16.25199633436598
ноннононононнонононононононно	10.0356012694258 10.04021034065972 9.8338526763454 11.21836254619961 11.65216793989331 11.657157907331098 9.77692570614639 9.77692570614639 9.7895561062075 9.1895561062075 9.1895561062075 9.189576124787753824 9.01597487753824 9.01597487753824 9.01597487753824 9.01597487753824 9.01597487753824 9.01597487753824 9.01597487753824 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775384 9.015974775584 9.01597477584 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.015974775874 9.0159747775874 9.0159747775874 9.015974777587474 9.015974777587474 9.01597	26.20398398273768 24.18521093011300 24.3698108225833 39.9575707805212 39.34114562776790 30.33916151460206 31.7068482020924 31.7068482020924 29.30218402560148 29.30218402560148 29.302184725902 29.20181034172329 28.2112490321831 29.3025403249341 33.824572590018 34.651883221347 35.30254032949341 33.82451392590018 34.32451392590018 34.324512950018 35.3266129209018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.32562129200018 35.3256212920018 35.3556212920018 35.3	16.07390107542480 16.07394572423270 17.7659018984391 16.75345724523270 17.7659018984391 17.46862919502621 18.42328810620506 16.75559220205496 15.770318961053754 17.7723487467581 18.43354105535754 17.7723487467581 18.432640145355754 18.332973727536 18.4328410535754 18.332973727536 18.43280423216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 18.3462403216614 19.3462408 10.44734462986580 10.427344669889 10.2510963141669889 10.2510963141669851 17.76954206181116 17.959320818116 17.9593218015116
ноннононононнонононононононнон с	10.0356012694258 10.03021034605972 9.8338526763454 11.21836254619961 11.6521679398931 11.6571679398931 11.65721679398931 11.657215796134308 9.77692570614639 9.78692570614639 9.1895561062075 9.1895561062075 9.1895561062075 9.1895561062075 9.129578372189 9.305778775324 9.305747775324 9.305747775324 9.305747775324 9.305747775324 9.30574775324 9.30574775324 0.658025422556 6.613243524556 6.613243524556 6.613243524555 5.577200368449 5.5772003684495 5.5772003684495 5.5772003684495 5.5772003684495 5.5772003684495 5.5772003684495 5.57720495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577203684495 5.577205684495 5.577205684495 5.577205684495 5.577205684495 5.	26.20398396273768 24.18521093011300 24.3698108222633 39.9575707805212 29.24114562276789 30.4319462758062 30.3316515460506 31.706842020926 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.30628702096 29.3062870290700000000000000000000000000000000	16.07390107542480 16.7334572432370 17.7659018984391 17.66623915902621 18.4232881062506 16.7555922020549 18.4232881062506 16.7555922020549 15.77031896125754 17.7772347647581 18.43354105535754 17.7772347647581 18.32690475216514 18.3420903216614 18.3420903216614 18.3420903216614 18.3420903216614 18.3420903216614 18.3420903216614 18.3420903216614 18.342641133490499 14.05671497290853 14.152047125984 14.15204611997290853 15.64767941839442 17.7678448530164 11.7678448530164 11.75684948530164 11.75684948530164 11.75684948530164 11.75684948530164 11.75684948530164 11.75684948530164 11.75684948530164 11.75684948530164 11.755682105111 12.9000031400511
ноннононононнононононононнононо	10.0385012694258 10.03021034065972 9.8338526763454 11.2836254619961 11.2832554673454 11.2832554613961 11.6872759057331086 9.77692570614639 9.77692570614639 9.7895561062075 9.71895561062075 9.71895561062075 9.5296883921148 9.30367787753824 9.30367787753824 9.303674278753824 9.303674278753824 9.4307439010208 8.62204845967318 8.304842783701681803 5.57720050884497 1.3367610448009 6.63295326956071 8.3344310014381 5.51672400708000 6.53426420373460 5.572400708000 6.53442913014381 5.51672400708000 6.53442913014381 5.51672400708000 6.53426421371450 5.5342042373460 5.5342042373460 5.5342042373460 5.5342042373453 5.5344242735453 5.5344242735453 5.5344242737453 5.534442737453 5.5344242737453 5.534442737453 5.5344242737453 5.5344242737453 5.5344242737453 5.5344242737453 5.5344242737453 5.5344242737453 5.5344242737453 5.5344242737453 5.53444242737453 5.53444242737453 5.53444242737453 5.53444242737453 5.5344424273745 5.5344424273745 5.5344424273745 5.5344424273745 5.53	26.20398398273768 24.18521093011300 24.385210182226831 35.977078285211 35.977078285211 35.977078285211 35.977078285211 35.977078285211 35.97707827864168 30.3391155146056 29.20111034172329 29.30620887020696 29.20121034172329 29.3062088702696 29.20121034172329 23.0620887026596090 29.2012103417239 31.0651126911988 31.0551205011004 31.396511269101004 31.396511269101004 31.396511269101004 31.396511269101004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.396511269011004 31.39511269011004 31.395126800868 31.31973326800868 31.31973326800868 31.31973356001004 31.3951268008564 31.3951268008564 31.395126800855420	16.07390107542480 16.07394704232370 17.7659018984391 17.7659018984391 17.6662391502621 18.4232881062506 16.75559220205496 18.4232881062506 17.77031896123730 17.7666047655095 18.4135415635754 17.7773347647581 18.842080123216514 18.842080123216514 18.842080123216514 18.842080123216514 18.342940123216514 18.342940123216514 18.342940123216514 18.342641132405145984 14.73945401579884 14.73945401579884 14.73945401579884 14.73945401579884 14.73945401579884 13.536477941839462 17.656649853064 17.656543250364 17.656543250364 17.656543250364 11.59915217447714 13.55189476665386
ноннононононнононононононнононононо	10.0385012694258 10.03021034605972 9.83385256783454 11.283265783454 11.2832654613961 11.1852167939393 11.1852167939393 11.1852167939393 9.45975642557405 9.15920683921148 9.45975642557405 9.15920683921148 8.201844976425745 9.03657787753824 8.20184427836247 9.04502139010208 8.46021490550571 9.04578245245914051 8.462345914051 6.65389536275576124 6.65389536269560 5.5772005084497 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538254269560 5.572400708000 6.6538535269560 5.572400708000 6.6538535269560 5.572400708000 6.6538535269560 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538535249540 5.572400708000 6.6538595421241 5.5744071840033 5.59448428737460 5.594484828737460 5.594484848737450 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737450 5.594484848737460 5.594484848737450 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.594484848737460 5.59448484848737460 5.594484848737460 5.59448484848737460 5.5944848484848484860 5.595484848484848660 5.59548484848484860 5.5944848484848484860 5.594484848484848484848484	26.20398398273768 24.3521093011300 24.36521093011300 24.36521093501130 24.3652109350113 23.3577078350511 23.34077684058 20.331151460505 23.254072684058 20.3311451460505 23.05287020696 23.05287020696 23.05287020696 23.05287020696 23.05287020696 23.05287020696 23.05287020696 23.05287020696 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.05287020697 23.0509785020677 23.340750500778 23.34059500778 23.4558300675716 25.5290267780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.529026780311 25.52	16.07390107542480 16.073954724323270 17.7659018984391 16.7384572453388 17.4685219502261 18.422361050266 18.422361050266 19.77031896133730 17.76604765055 18.41354150535754 18.84250821345655 18.43284150535754 18.84598023216614 18.84598023216614 18.36669675631345 16.15552471265984 16.3152541540643 14.6651997920953 14.15260611320865 14.1534553064 14.52519934345398 15.647794183942 15.518947665386 15.5518947665386 15.5518947665386 15.5518947665386 15.5518947665386 15.5518947665386 15.5915217447714 19.5028218919164 12.9100061408951 15.5518947665386 15.5518947665386 15.5518947665386 15.5915217447714 13.5518947665386 15.5518947665386 15.5915217447714 13.5518947665386 15.5518947665386 15.5915217447714 13.5518947665386 15.562229144477 15.5518947665386 15.562229144477 15.5518947665386 15.562229144477 15.5518947665386 15.562229144477 15.5518947665386 15.551894768 15.551894765386 15.551894765386 15.5518947655386
ноннононононнононононононнонононононон	10.0380012694258 10.030210340605972 9.83368526763454 11.21836254613961 11.6521679388331 11.6571679388331 11.6571679388331 11.6571679388331 11.6571679388331 11.6571679388332 9.4597564257405 9.15290683921148 9.4597564257405 9.15290683921148 9.0367787753824 8.2018442785647 9.04501314705386 8.6503141705386 8.6520549567338 8.4610769555671 1.169754573184025 5.5772000584497 1.6538954275400 6.65389542559560 5.5772000584497 1.65382542559560 5.5772000584497 5.5574200708000 6.65389542754007 1.65382542559560 5.5772000584497 1.65382542559560 5.5772000584497 5.5574200708000 6.5572500058497 1.653834532148053 5.59484928737460 6.05486961236115 5.57484928737460 5.594849428737460 5.59484948737460 5.594849428737460 5.594849428747460 5.594849428737460 5.59484948737460 5.59484948737460 5.59484948737460 5.59484487484874848487 5.59484484848	26.20398398273768 24.352103911300 24.3691108222633 33.9577078305111 33.357707830511 33.357707830511 33.357707830511 30.341846277580168 30.353115146050 29.2018103417329 30.650827020956 29.2018103417329 29.365082702056 29.2018103417329 29.365082702056 29.2018103417329 33.26711589119883 33.267230240314790 33.26711589119883 33.267230240314790 33.26711589119883 33.267230240314790 33.26711589119883 33.36672730240349 34.5729060019004 33.2672105805983 33.36672390018 33.3672390018 33.3672390018 33.3672390018 33.3672390018 33.3672390018 33.3672390018 33.3672390018 33.3672390018 3	16.07390107542480 16.073947042323270 17.7659018984391 16.73845703453388 17.4685219502621 18.42326810820506 18.42326810820506 19.7773347045781 18.42326810820506 19.77773347447581 18.36590675671345 18.36590675671345 18.36590675671345 16.1552471265984 14.65719379834 14.65671937983 14.1536043 14.6571937983 14.1536043 14.1537984 14.273844598342 14.1537984 14.27384459834 15.518947665386 15.51927515984 11.59915217347774 15.5518947665386 11.59915217347774 15.5518947665386 11.59915217347774 15.5518947665386 11.59915217347774 10.9770828256336 11.59915217347774 10.9770828256336 11.59915217347774 10.9770828256336 11.59915217347774 10.9770828256336 11.59915217347774 10.97728215543200 10.351184515077 10.9708826263315 11.59915217347774 10.97728215543200 10.351184515077 10.970882625831507 11.59915217347774 10.9772815543200 10.351184515077 10.9708826256336 11.59915217347774 10.9772815543200 10.351184515077 10.97088265315077 10.97088265315077 10.97088265315077 10.97088265315077 10.97088265315077 10.97088265315077 10.97088265315077 10.97088265531507 10.97088265531507 10.9708826531507 10.97088265531507 10.97088265531507 10.97088265531507 10.97088265531507 10.97088265531507 10.97088265531507 10.97088265553507 10.97088265531507 10.97088265531507 10.97088265531507 10.97082
ноннононононононононононнонононононон	10.0380012694258 10.030210340605972 9.83368526763454 11.21836254613961 11.28521679388331 11.687759073313062 9.4597564255405 9.4597564255405 9.4597564255405 9.4597564255405 9.15970883921148 2.0184427836247 9.0450718757824 8.20184497836247 9.045071814705388 8.601347531410705386 8.6023141705388 8.602645967338 8.46107699550571 9.1199364342873 9.045071810468069 6.557700058442755 6.5124533148051 7.1367510448069 5.577400708000 6.5577000584427553 5.598442873460 6.557200584425550 6.53742540718000 6.557200584425550 5.598442873460 5.577400788000 6.557200584427553 5.598442873460 5.5774200788000 6.557200584427553 5.598442873460 6.5527200584427553 5.598442873460 6.54724537453 5.598442873460 6.5486961236115 5.5784200788000 4.557213012387555 5.5984828737460 5.5984828737460 5.5984828737460 5.5984828737460 5.5984828737460 5.5984828737450 5.5984837550 5.5984828737450 5.5984828737450 5.598482873	26.20398398273768 24.18521093011300 24.3691108222683 39.5770783805112 39.34114562276784 39.577078340512 39.357707834053 30.4319467584063 30.4319467584063 30.4319467584063 30.4319467584063 30.4319467584063 30.3510514407029 29.30620827020996 29.2013103417239 29.3062082702096 29.2013103417239 29.30620827026959609 30.3626242924321 30.35264026997 30.366282492433101 33.366125900018 34.572966091004 34.572966091004 34.56298249231301 33.366125940018 34.56298249231301 33.366125940018 34.56298249231301 33.366125940018 34.56298249231301 33.366125900018 34.56298249231301 33.3661258400865 35.599062790312 31.510717568400865 34.31926400657516 35.599062790312 31.5597062790312 31.5597320274405719 33.24295420057516	16.07390107542480 16.07395472432270 17.7659018984391 16.738547924323270 18.47326842319502621 18.4732681025056 18.4732581200546 18.4732681025056 18.473581450555754 18.47354150555754 18.47354150555754 18.47354150555754 18.365696727631345 16.31552471265984 16.31552471265984 14.3666713979883 14.3560641320868 14.3627641320888 14.32508611320888 14.32508611320888 14.32508611320888 14.32508611320888 13.5392472653184 13.53182471658389 15.3518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947663386 1
ноннононононнононононононононононононо	10.0380012694258 10.03021034065972 9.8338526763454 11.21846254149961 11.25521679389331 11.65775907311098 9.4597564255405 9.4597564255405 9.4597564255405 9.1597064255405 9.1597064255405 9.1597064255405 9.1597064255405 9.1597064255405 9.1597064255405 9.1597064255405 9.1597064255405 8.6603114706386 8.6603147059550571 9.1597069550571 9.1597069550571 9.15970642542855 9.04302139010208 8.661324539148051 7.1367610468069 6.6334539148051 7.1367610468069 6.6334539148051 3.35062275759124 6.633453716048069 6.6334539148051 3.3506227877601 4.37121991035300 9.1482612341139 3.3506227877601 4.35212391248133 3.3506227877601 4.35212391248133 3.3506227877601 4.5521034076437 3.355335557559 5.594894373460 4.5521034076437 3.3506227877601 4.5521034076437 3.3506227877601 4.5521034076437 3.355335557557 3.5548354733759 3.5548354733759 3.55535555757 3.5548354733759 3.55535557575 3.5548354733759 3.55535557575 3.554835377513 3.55535557575 3.554835377513 3.55535557575 3.554835575375 3.554835575575 3.554835377531 3.55535557575 3.554835377531 3.55535557575 3.554835575575 3.5548530773137 3.55535557575 3.5548530773137 3.555355557575 3.554853575375 3.554835575575 3.554853575375 3.554853575375 3.554853575375 3.554853575575 3.554853575375 3.554853575575 3.554853575375 3.554853575575 3.554853755755 3.554853575575 3.554853755755 3.554854575575 3.5548547557557 3.5548547557557 3.55485475575757 3.5548575575757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.55485775757 3.5548577	26.20398398273768 24.3852103911300 24.38921031230 24.389210322363 39.5757078305121 39.34114562276784 30.339114562276784 30.3391155146050 29.2013105146050 29.2013105146050 29.2013105146050 29.2013103417239 29.36620837026956 29.2013103417239 29.36620837026956 29.2013103417239 29.36620837026956 29.2013103417239 29.36620837026956 29.2013103417239 29.3662083702695 29.2013103477239 23.26711589191883 23.3662172960018 34.56298264293101 33.136731356408968 35.3966172960018 34.36298258475661 35.59902873031 34.3153731356408968 34.31537841569098 34.31537841569098 34.31537841569098 34.342962790312 34.3429526790312 34.3429526790312 34.3429526790312 34.3429526790312 34.3429526790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.342952790312 34.34295269057316 35.5299262790312 34.342953651460 35.31178964716067 34.34727320744405719 32.234753361480 32.234753361480	16.073930107542480 16.73945724323270 17.76593018984391 16.73845724523270 17.86593018984391 16.7385702452056 16.7555327020548 15.770318623373 17.81354150555754 17.81354150555754 17.81354150555754 18.8452984052316614 18.8452984052316614 18.8452984052316614 18.8452984052316614 18.366696275613455 16.31525471265984 14.35206511320868 14.32506511320868 14.32506511320868 14.32506513208653026 14.32506513208653026 14.32506513208653026 14.32506513208653026 13.35518047665530 15.35518047665530 15.35518047665530 15.35518047665530 15.35518047665530 15.35518047665530 15.35518047665530 15.35518047665530 15.3551804766531
ноннононононноннонононононнонононононо	10.0380512694258 10.03021034065972 9.8338526763454 11.21836254619961 11.825125993531 11.657179507313082 9.76927465439 9.76927454543 9.76927454543 9.7692745454 9.7189556162454 9.718955616245425550 9.11293064242873 9.04302147065955071 9.0452042425769124 6.6528527569124 6.6528527569124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.6528532789124 6.5324327877601 4.57712005864497 3.3550327877601 4.57712005864497 3.3550327877601 4.5771200586497 3.3550327877601 4.5771200584497 3.3550327877601 4.5771200584497 3.3550327877601 4.5771200584497 3.3550327877601 4.5771200584497 3.3550327877601 4.5771207820247877601 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 4.57712078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5.5782078204 5	26.20398398273768 24.18521093011300 24.3698108222683 39.5757078305112 29.34114562276783 30.35757078305112 29.34114562276783 30.3511051440005 30.3511051440005 29.201310515440005 29.201310515440005 29.201310515440005 29.201310515440005 29.201310515440005 29.201310515440005 29.201310515440005 29.20131051540005 29.20131051540005 29.2013105142705 29.20150212881 28.2123400212881 28.2421390242381 23.36621290018 31.697812690987 31.697812690988 32.36928249233101 33.1375326408865 35.396617290018 31.835364075516 35.5990282932165 35.59902829351769 31.831159851769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.831159781769989 31.83115985417169 35.392627903212 31.7383940726905719 32.2475345611480 32.2497345611480 32.2497345611480	16.073930107542480 16.07394072423270 17.76593018984391 17.66652919602621 17.86593158020506 16.7555922020548 18.42326810620506 16.7555922020548 15.77031846133730 17.7666415055978 17.7664415055978 17.7664415055978 18.8669672761345 16.1555471265984 16.31527613485016 18.36669672761345 16.315276150643 14.665719979053 14.15206611320868 14.2738442695839 14.25694139342 14.4667199720853 14.15206611320868 14.2738442695839 16.25199633453984 14.2738442695889 16.25199633453984 12.91000614408951 13.5518947663386 11.5508273914477 15.66757345247713 15.56757813942 15.56757813942 15.56757813942 15.5675783942 13.851857697583942 15.613426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.513426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53426041943 15.53546040943 15.555464040943 15.55546040943 15.5554640494528828 15.55546040943
ноннононононнононон онононнонононононон	10.03805012694258 10.03021034065972 9.8338526763454 11.21836254619961 11.825125990351 11.825125990351 11.825125990351 11.825125990351 9.77621270614639 9.77621270614639 9.77621270614639 9.77825710614639 9.15390883921148 9.01892761267872 9.15390883921148 9.01892761267872692 9.01390578775782692 9.04392147065950731 9.04392147069550731 9.0439214905950731 9.0439214905950731 7.1367610468069 6.05307527509124 6.65389532769124 6.65389532769124 6.65389532769124 6.65389532769124 6.65389532769124 6.65389532769124 6.65389532769124 6.65389532769124 6.6538953278760 9.04392137460 6.054892137146 6.0548921341139 6.0548921	26.20398398273768 24.18521093011300 24.3698108222683 39.5757078305112 29.34114562276783 30.33114562276783 30.33114562276783 30.33114562276783 30.33114562276783 30.331145124000926 32.33607837002696 22.2013101514470239 31.05684009026 22.2013101514470239 31.05684009026 22.2013101514470239 31.05684009026 32.056287020696 32.05214520021881 32.0526402349341 33.0562402349341 33.056215950018 34.6512854783 32.6542842933101 33.1375326408868 33.0366175909018 31.8371585401785 33.0366175909018 31.8371585401785 33.0366175909018 31.8371585401785 33.036217590018 31.639158476405780 31.8311585401786 33.0362175909018 31.831547845786 33.036217590018 31.831547845786789 31.831547845786989 31.8315478457845789 31.8315478457845784 31.93953677401571 32.342724050713 31.743894072921 32.34272455611480 32.24473345611480 32.2447334561480 32.2447334561480 32.2447334561480 32.24473456405780 32.24473456405780 32.2447546405780 32.2447546405780 32.24473456405780 32.244754405780 32.24473456405780 32.244754405780 32.24473456405780 32.24473456405780 32.24473456405780 32.24473456405780 32.24473456405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.244754405780 32.24475445780 32.2447	16.07390107542480 16.07394072423270 17.7659018984391 16.738457024523270 17.7659018984391 17.46652919602621 18.42326810620506 16.755522020548 18.42326810620506 16.75552020549 17.7668470565095 18.4232681062056 18.423268107580 18.84208012316614 18.845980514560 18.845980514 16.11553471265984 16.3152471510643 14.35606132708984 14.3526014305985 14.3250661320868 14.3250661320868 14.3250661320868 14.325086138942 15.475743459883 15.25179983436398 15.25179983436398 15.25179983443598 15.2519963345398 15.25179715884 14.32696498553064 13.5518947663386 15.391297142915984 13.5518947663386 13.35189476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.3518476643386 13.351847664356 13.35184765757575757575757575757575757
ноннононононононононононононононононон	10.0380512694258 10.03021034065972 9.8338526763454 11.21836254619961 11.825125993531 11.857159907331098 9.77632750614639 9.77632750614639 9.77632750614639 9.77632750614639 9.73632750614639 9.13390883021148 9.0380578775824 9.03805127148 9.0365787757824 8.660314705886 8.6603147058950571 9.0450714075850 9.045074877580 8.66324539148053 7.1367610468069 6.6324539148051 7.1367610468069 6.6324539148051 7.1367610468069 6.6324539148051 7.1367610468069 5.57720050884497 6.632485317460 6.634867317465 5.57720050884497 5.57720050884497 5.57720050884497 5.57720050884497 5.57720050884497 5.5772005084497 5.57720507 5.57720507 5.57720507 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.5772057 5.57757 5.57757 5.5775757 5.577577 5.5775757 5.577577 5.577577577 5.	26.20398398273768 24.18521093011300 24.3698108222633 39.575078380211 29.34114562276783 39.35750783405212 29.34114562276783 39.3314048700482263 39.3314048700482263 39.3314048700482263 39.33140748700482263 39.331407482700482263 39.331407482700482263 39.331407482700482 39.3367024702459 39.3670387020596 29.2013103417239 29.3670387020596 29.2013103417239 29.3670387200596 39.36724726395070 39.3672472497453 30.56728429423 31.572157699899 31.89175895001 31.3955617269 31.692158950 31.69215269048 31.69215269048 31.69215269048 31.69215269048 31.69215269048 31.69215269048 31.69215269049 31.69215269049 31.69215269057 31.69215269049 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.69215269057 31.29215267 31.29215267	16.073930107542480 16.07394072423270 17.7659018984391 16.73845724523270 17.7659018984391 17.46652919602621 18.42326810620506 16.7555522020548 18.42326810620506 16.755552020549 17.76634961755 18.43354105405761 17.633773771755 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 18.3554014380515 14.3554074394159884 14.3554074394353 14.3554074395885 16.2519963343539 16.25199633435398 16.25199633453984 17.356847854139442 17.65654305611810 13.3518947665385 15.351297518314 13.5518947665385 13.3518947667385 13.3518947665385 13.3518947664385 13.3518947664385 13.3518947664385 13.3518947644385 13.3518947644385 13.3518447644585 13.351847644585 13
н с н н с н с н с н с н н с н с н с н с	10.0380512694258 10.03021034065972 9.8338526763454 11.21836254619961 11.825125993531 11.857155907331098 9.77632750614639 9.77632750614639 9.77632750614639 9.73632750614639 9.45395612570614639 9.45395612570614639 9.45395612570614639 9.45395612570614639 9.45395612761463 9.045972575726124 8.6603114706386 8.65207545761442873 9.04302139010208 8.6520147059550731 8.45207699550731 8.45207699550731 8.452107699550731 8.452104648059 6.653853269462 6.653853269462 6.653853269462 6.653853269462 3.3539532769612 3.3539532776012 4.65724937453 3.35395352769512 4.55724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.35724005884497 5.357240584497345 3.358353075175 3.358353075175 3.358353075175 3.358353075175 3.35824571488307 3.35223378246 5.3545854118830 5.3522495686188 3.4452121488036 2.45621234712931 5.57569641 3.30280755769641	26.20398398273768 24.3852103911300 24.3852103911300 24.3852103911300 24.3852103120 23.95751078305112 23.95751078305121 23.95751078305121 23.957510782052 23.957510782052 23.957510782052 23.957510782052 23.957510782052 23.95075207205596009 23.051037026596 23.051037026596 23.051037026596 23.051037026596 23.051037026596 23.0512697205396009 23.251105817983 23.2657126897589 23.2657126897589 23.2657126897589 23.2657126897589 23.265212697870 23.255712697870 23.255712697870 23.255712697870 23.255712697870 23.255712697870 23.265712697870 23.265712697870 23.265712697870 23.265712697870 23.265721267440 23.265721267440 23.265721267440 23.265721267440 23.265721267440 23.26521267405759 23.265212657589 23.265212657589 23.265240357581 23.265240357587581 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.2652405575758 23.26524055777778 23.26524055777778 23.26524055777778 23.26524055777778 23.2	16.0739407542480 16.0739407542480 16.7394572432270 17.7659018984391 17.46652919602621 18.42326810620506 16.7555522020548 18.42326810620506 16.755552020548 17.7631846133730 17.766407656095 18.433541054751 17.837377371753 18.3554014386016 18.84208023216614 18.36669027541345 16.1552471265984 16.352471265984 16.352471265984 16.352471265984 16.352471265984 16.352471265984 16.352671345 16.352471265984 16.352671345 16.35247265838 16.2519963343539 16.2519963345398 16.25199633453984 17.26564305611816 17.955627356147711 15.991521747714 15.99152777562193 15.991547714 15.9915277562193 15.991547714 15.9915477147714 15.9915477147714 15.9915477147714 15.9915477147714 15.9915477147714 15.9915477147714 15.9915477147774777777777777777777777777777
Н С Н Н С Н С Н С Н С Н Н С Н С Н С Н С	10.038012694258 10.03021034065972 9.8338326763454 11.2183254619961 11.283254619961 11.827155905331 9.7782527061433 9.7782527061433 9.7782527061433 9.7782527061433 9.78257061433 9.78257061433 9.78257061433 9.78257061433 9.78257061433 9.78257061433 9.78257061433 9.7825706143 9.7825706143 9.7825706143 9.0325706143 9.0325706143 9.0325706143 9.042678372692 8.66378372692 8.66378372692 9.0325769124 6.65389352695673 9.119396442873 9.04267433742657 9.04267433742657 9.042674337450 6.6538935269567 9.13267210468069 6.63246329148033 9.145561453017511 4.5571405307671 9.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 9.350223777061 2.3591448071333 3.3502237777061 2.359144807133 3.3502237777061 2.35144807133 3.3502237777061 2.35144807133 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.3502237777061 2.3514480713 3.35022377707060 3.350223777070715 3.35022377700715 3.35022377700715 3.35022377700715 3.35022377700715 3.35022377700715 3.350223772	26.20398398273768 24.18521093011300 24.3698108222633 39.5750782805212 39.341845072682 30.413456276789 30.4134627647805 30.4134627647805 30.4134627647805 30.413467764786 30.413467764786 30.41346776459 30.45747726539600 30.4571458191883 30.652640374054 30.4526403749341 30.452640374934 30.452640374934 31.457365403749 31.567128591988 31.657815769989 31.8671535144799 32.34411996507870 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56728542900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.56928242900 31.5692842900 31.5692842900 31.5692842900 31.5692842900 31.5692842900 31.5692842900 31.7638940079901 32.592964295978479990 31.29248263707291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.292482637007291 31.9451967069127	16.07390107542480 16.0739407242480 16.7394572423270 17.7659018984391 17.46652919602621 18.42326810620506 16.7555921020548 18.42326810620506 16.7555921020548 18.4232681053754 17.77031847647581 18.33210717536 18.33210717536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177536 18.33207177538 18.33207177538 18.34208023216614 18.3426902553164 14.322671375384 14.6657109720853 14.1290651320868 14.2773844295589 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345398 16.2510963345399 16.2510963345399 16.2510963345399 16.2510963345399 17.058892665386 17.05887801215 5.3526869285 3.556640913881 15.3528679033 7.70158878012155 5.8202800960560789 7.70158878012155 5.8202800960567
Н С Н Н С Н С Н С Н С Н С Н С Н С Н С Н	10.038012694258 10.03021034065972 9.83383256763454 11.21836254619961 11.285215990351 11.85715990733109 9.77892570614339 9.77892570614339 9.77892570614339 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.189561082075 9.1199964242873 9.04578327628672 8.66931147065865 8.669267525769124 6.65385352695607 7.1367610468069 6.63246329148051 7.1367610468069 6.63246329144051 3.5365235769124 6.65385352695607 1.3567610468069 5.57720005884497 5.3772005884497 5.3752005884497 5.35538535075175 2.345342671485314 5.35538535075175 2.345342671489334 4.555218307311 4.5552183075175 2.3453427576912 4.5552453075175 2.3453427576912 4.5552453075175 2.3453427576912 4.5552453075175 2.3453427576912 4.5552453075175 2.3453427576912 4.5552453075175 2.3453427576961 2.345524275696 2.3458671487340 2.345524275696 2.3458671487340 2.345524275696 2.3458671487340 2.345524275696 2.3458671487340 2.345524275696 2.3458671487340 2.345524275696 2.3458671487340 2.3455247249586158 2.3458671487340 2.3458671487340 2.3455247249586158 2.3458671487340 2.3455247249586158 2.3458671487340 2.3455247249586158 2.3458671487340 2.3455247249586158 2.3458671487340 2.3455247249586158 2.3458671487340 2.3455247249586158 2.3458671487340 2.345872724453586 2.3458671487340 2.345872724453586 2.3458671487340 2.345872724453586 2.3458671487340 2.345872724453586 2.3458671487340 2.345872724453586 2.3458671487340 2.345872734453586 2.345872734453586 2.345872734453586 2.345872734453586 2.3458723472445454147340 2.34597274453586 2.34587724453586	26.20398398273768 24.18521093011300 24.398108225833 39.575078380511 29.34114562776789 39.3404870408298 30.339161344627640082 30.33916134462764 30.3391613446276 30.3391613446276 30.36508702696 20.201310447239 30.36508702696 20.201310447239 30.365042726539609 20.201324272539609 30.365042726539609 30.365042726539609 30.365042726539609 30.365042726539609 30.365042726539609 30.365042726539609 30.365042726539609 30.365042726539609 30.3650427873 30.36504278739 30.36504278739 30.36504278739 30.36504278739 30.3650428759989 30.346042957891 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.342604297370 30.34262907212 30.3426290720	16.07390107542480 16.07394072423270 17.7659018984391 16.7384792432370 17.7659018984391 17.46652919602621 18.42326810620506 16.75559210205496 18.42326810635754 17.7723347647581 18.4332403127536 18.3660047565005 18.3620047565005 18.362004726510 18.362004726510 18.362004726510 18.362004726510 18.362004726510 18.362004726510 14.520072053 14.520072053 14.520072053 14.520072053 14.2500641320868 14.27738442695889 16.25109633436398 16.2510963345391 14.2506638510 15.2510963345391 13.5518947665385 11.5500229914477 13.5518947665385 13.5518947663385 13.551894767724454376 13.551894767724542320 13.551894767724542320 13.551894767724542320 13.5518477774447841 13.55189476742423474784
Н С Н Н С Н С Н С Н С Н С Н С Н С Н С Н	10.0380512694258 10.038012694258 10.24021034065972 9.83383256763454 11.283254619961 11.2852159903381 11.85715990733108 9.77892576014339 9.77892570614539 9.7892570614539 9.1895561062075 9.1895561062075 9.189561062075 9.189561062075 9.189561062075 9.11999642677338 8.6601245391470753824 9.04807199753824 9.04807199753824 9.048071995159751 9.048074995595751 9.048074995595751 9.048074995595751 9.1199916442873 9.0480719910020 8.66327525709124 6.6538535269560 6.632452510448053 9.3557420050884497 6.33443710448933483 3.954072482737824 6.6538535269560 4.6574482514453743 3.954082425769124 6.65385352695607 1.3557401058084497 6.33443710448073393 3.944521484873393 3.94562184307541 2.35538453075175 2.349344271848034 6.0548691236115 3.553845207578242 4.55244821377590 3.9448691339135 3.954621341535 3.95462134153 3.954621341537 3.934621488334 2.347342495814383 3.944521488334 2.347342495814383 3.944521488334 2.34734495814383 3.944521488334 2.34734495814383 3.944521488334 2.34734495814383 3.944521488334 2.347344958143833 3.944521488334 2.347344958143833 3.944521488334 2.347344958143833 3.9445214188334 3.9452734448334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.937374645334 3.9373746453454 3.9373746	26.20398398273768 24.352109311300 24.352109321300 24.352109321300 24.352109321300 24.352109321300 24.352109321300 24.352109321300 25.35707025300 25.3620522000264 25.261026322000264 25.261026322000264 25.261026322000264 25.261026322000264 25.261026322000264 25.261026322000264 25.261026322000264 25.26102632000262067 25.2640035101587 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.264005716 25.26400719 25.26400719 25.264005716 25.26400719	16.07390107542480 16.0739407242480 16.7394572423270 17.7659018984391 17.6662919602621 18.42326810620506 16.7555921020549 18.4232681062506 16.75559210205496 18.423268105554 17.7723347647581 18.433240327515 18.75804792053 18.75804792053 18.425804792053 14.15206511320868 14.65719792053 14.15206511320868 14.277384269589 16.25199633436398 16.2519963345394 13.5518947665386 11.559152177714 13.5518947665386 11.5591521747714 10.9709892643951 13.5518947665386 11.5591521747714 10.9709892645391 13.5518947665385 12.1599521747714 10.9709892645391 13.5518947665385 12.1599521747714 10.970892645391 13.5518947665386 12.1599521747714 10.970892645193146 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.5518947665386 13.55189476931481 13.5518947665386 13.5518942613831 13.518897801285 2.0124634489588 2.01246248212883 2.012462482988 2.012462482988 2.012462482988 2.012462482988 2.012462482988 2.012482138788 2.01248788 2.01248
Н С Н Н С Н С Н С Н С Н Н С Н С Н С Н С	10.0380012694258 10.030210340605972 9.83368526763454 11.21836254613961 11.21832634613961 11.218251679398398 11.118521679398398 11.118521679398398 11.1185216159938398 11.1185216526 9.45975642557405 9.15290683921148 2.0184427836247 9.15290683921148 2.0184427836247 9.0430214705382 8.660314705386 6.65285425405 5.577200508442873 9.043021490550571 9.13276104648050 6.652852629567 5.5727000584497 1.1327610448050 6.652852629567 5.57260058447 5.572640708000 6.652854212315 5.5948428737450 5.572400708000 6.6528542123151 5.5948428737450 5.572400708000 6.5324574575576124 5.572400708000 6.5324574575576124 5.572400708000 5.57269551123151 5.535455057575 5.53448421371591 5.535455057575 5.2311448033 3.545223787246 3.2219002595649 3.2312448475148731 4.5553555575757 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.5553555575757 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.555355557575 3.244886761487941 4.5553553575757 3.244886761487941 4.5553553575757 3.244886761487941 4.5553555757575 3.244886761487941 4.5553555757575 3.244886761487941 4.5553555757575 3.244886761487941 4.555355757575 3.244886761487941 4.555355757575 3.244886761487941 4.555355757575 3.244886761487941 4.555357577575 3.244886761487941 4.555357824645561 3.22192444556 3.24488671448535 3.24488671448535 3.24488671487941 4.55644558714944335 3.244886714489453 3.2448867144535 3.244886714489453 3.24488671448535 3.244886714489453 3.2448867144535 3.2448867144535 3.2448867144535 3.2448867144535 3.2448867144535 3.2448873746453 3.2448873746455 3.2448873746455 3.2448873746455 3.2448873746455 3.2448873746455 3.2448873746455 3.2448873744455 3.2448873744455 3.2448873744455 3.2448873744455 3.2448873744455 3.2448873744455 3.2448873744	26.20398398273768 24.352109311300 24.35210735211 24.35210735211 25.3577072835211 25.3577072835211 25.3577072835211 25.3577072835211 25.357707283521 25.357707283521 25.35770728372 25.3577228352 25.3577228352 25.3577228352 25.3577228352 25.3577228352 25.3577228352 25.3577228352 25.3577228352 25.357728352 25.357728352 25.357728352 25.357728352 25.357728352 25.357728352 25.3577283 25.357728352 25.3577283 25.3577728 25.3577728 25.3577728 25.3577773 25.3577773 25.3577773 27.3486234729 25.3577773 27.3486234729 27.3578457775 27.3486234729 27.3578457775 27.3486234729 27.3578457777 27.3486234729 27.3578457777 27.3486234729 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349662342257 27.349657425 27.349657422 27.349657422 27.349657422 27.349657422 27.349574237 27.349574237 27.349574237 27.349574237 27.349574325 27.345747372 27.34574325 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.34574775 27.345747757 27.345747757 27.345747757 27.345747757 27.345747757 27.345747757 27.345747757 27.345747757 27.345747757 27.3457477757 27.3457477757 27.345747757 27.345747757 27.345747757 27.345747757 27.3457477757 27.3457477757 27.34574777577757 27.345747	16.073930107542480 16.073940724232270 17.7659018984391 16.7384792433382 17.46862319502261 18.422361052066 18.422361052066 19.770131806133730 17.76604765050 18.41354150535754 18.8354150535754 18.835605273145 18.366596757631345 16.1552471265984 16.1552471265984 16.3525471265984 14.326661132086 14.36651927983 14.35249245335 14.35249245335 15.647574183942 15.54574436398 15.647574183942 15.5518947665386 11.55915217347714 15.5518947665386 11.55915217347714 15.5518947665386 11.55915217347714 15.5518947665386 11.55915217347714 15.5518947665386 11.55915217347714 15.5518947665386 11.55915217347714 15.5518947665386 15.56475912815164 15.5518947665386 15.56475912815164 15.5518947665386 15.5627593427 13.518165765392 13.61355789427 13.6134565761283 14.5379788506064 8.54566051208 15.642540718881 5.542540718881 5.542540718881 5.542540718881 5.5425470718881 5.5425470718881 5.5425470718881 5.5425470718881 5.5425470718881 5.5425470718881 5.5425470718881 5.5425470718881 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.54265470718878 5.542654771874 5.542654771878 5.542654771874 5.54265771875478 5.54
Н С Н Н С Н С Н С Н С Н Н С Н С Н С Н С	10.038012694258 10.030210340605972 9.83368256763454 11.21836254613961 11.25321679389331 11.65521679389331 11.65521679389331 11.65521679389331 11.65521679389331 11.65521679389331 11.6552167938321 9.4597564255405 9.15290883921148 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.03657887753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787753824 2.0365787758924 2.0365787758924 2.0365787758924 2.03787878484 2.0378787844 2.036578774 2.037878784 2.037878784 2.037878784 2.037878784 2.037878784 2.037878784 2.037878784 2.037878784 2.037878784 2.0388787784 2.0378784 2.0378787844 2.03787844 2.037878784 2.0	26.20398398273768 24.352109311300 24.3551078350213 24.3551078350213 23.557078350213 23.557078350213 23.557078350213 23.55076784058 20.33115146050 23.5507655207488 23.5507655207488 23.2507655207488 23.2507655207488 23.2507655207488 23.250726539609 23.2011034172329 23.267158911988 23.26725539609 23.26115941988 23.2621234021831 24.512960019004 24.512960019004 23.250765396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.250755396001 23.2507553000 23.2507553000 23.2507553000 23.2507553000 23.2507553000 23.2507553000 23.250755100 23.250755100 23.250950055510 23.2509500552075 23.250950755 23.2509500552075 23.2	16.073930107542480 16.073947042480 16.73945724323270 17.7659018984391 16.7384792433382 17.4660476203388 18.42236104205066 18.42236104205066 19.777334747581 18.4232610420506 18.423261777334747581 18.3659047561345 18.3659047561345 18.3659047561345 18.3659047561345 18.3659047561345 18.3659047561345 18.365904750483 14.159404132088 14.1594051320883 14.1594051320883 14.1594051320883 14.1594051320883 14.1594051320883 14.1595984 14.2773447581 15.5189476663386 11.59915217347774 15.55189476663386 11.59915217347774 15.55189476663386 11.59915217347714 10.97708282563364 11.59915217347714 10.97708282563364 11.59915217347714 10.9770828554329 11.59915217347774 10.977281554329 11.59915217347774 10.977281554329 11.59915217347774 10.977281554329 11.59915217347774 10.977281554329 11.59915217347774 10.977281554329 11.599152753 13.13456560694 8.554646983288 8.5569061023 6.359165576329 13.63265440583288 8.556906123789 13.63265440583288 8.558056120789 13.63265440583288 8.558056120789 13.6326544058328 13.5392887656120 8.54446189751921 13.6326544058328 13.5392845696132 13.5319476451208 13.5319476451208 13.53194776454793 13.5319476451208 13.5319476451208 13.5319476451208 13.5319476451208 13.5319476451208 13.53194764554718881 13.5328876551700 8.5428647883288 8.54286468348 8.54286468348 8.542864483388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.54286448388 8.544
н с н н с н с н с н с н н с н с н с н с	10.0380012694258 10.030210340605972 9.8336827254 11.21836254613961 11.6521679388331 11.6571679388331 11.6571679388331 11.6571679388331 11.6571679388331 11.6571679383331 11.657167937382 9.4597564257405 9.1529088392148 2.018442783647 9.1529088392148 2.018442783647 9.0520787757824 2.018442783647 9.0520784275805 5.577200584542 2.01844278364 2.01844278364 2.019407405556731 2.056785473148053 5.5772607544805 5.5772000584497 1.107074556731 2.598442873746 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.5772000584497 1.107074575695 5.577400758000 6.53849310014381 5.16725400758000 5.578400748000 3.5482541236115 3.5482541236115 3.5482541236115 3.54825412871391 3.548254148931 3.548254148931 3.548254148931 3.548254148931 3.548254149831 3.548254149831 3.54825445586168 3.00280755696616 3.00280755696616 3.0028075569661 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.0028075569561 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755696616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616 3.00280755695616	26.20398398273768 24.352109311300 24.3652109311300 24.3652109311300 24.3652109350211 23.3577078350211 23.3577078350211 23.357707835021 23.357707835021 23.357507835021 23.35750783502 23.35750783502 23.35750783502 23.35757078598500 23.25105475202 23.25070555207084 23.25070555207084 23.25070555207084 23.25070555207084 23.25070555207084 23.25070555207084 23.25070555207084 23.25070555207084 23.2507055207084 23.2507055207084 23.2507055207084 23.25070575510 23.250705755111837 23.2671250704 23.2505407555111857 23.265074750075751 23.26254777712805091 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254720074 23.26254721557 23.26254720074 23.26254721557 23.2625472075511837 23.26254721557 23.2625477172 23.26056755151 23.2425547715511857 23.25554302552075 23.242547715157 23.25554302552075 23.244455564420 23.25554302552075 23.24455564721 23.3460556472 23.3460556472 23.346055675151 23.2465564721 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721587 23.2465564721 23.2465656472 23.2465564721 24.2465564721 24.2465564721 25.2465656472 25.2465564721 25.2465564	16.073930107542480 16.073947042480 16.73945724323270 17.7659018984391 16.738479243388 17.4665219502621 18.42326810425066 19.7773347602506 19.7773347647581 19.7773347647581 19.8397937217536 18.84298003216614 18.8669627501345 16.1552471265984 14.6571937937217536 14.152467132085 14.152467132085 14.152471265984 14.6571937937217536 14.152471265984 14.52471265984 14.152471265984 14.152471265984 14.152471265984 14.1534996553026 14.152471265984 14.1534996553026 14.153471853042 15.15518947665386 11.599124738 15.518947665386 11.59912517347714 10.9770824263315 11.59912517347714 10.9770824263315 11.59912517347714 10.9770824263315 11.59912517347714 10.9770824263315 11.59912517347714 10.9770824263315 11.8551978 11.59912517347714 10.9770824263315 11.855077853044 15.518947665386 11.59912517347714 10.97708242631550789 7.4306195076953 13.8655767553944 13.85569605150789 7.4306195076953 13.86557475100 8.542640831288 5.53266408328 5.5326644831288 5.5326644831288 5.5326644831288 5.5326644831288 5.63266531718274 3.63265541128783 5.63266531718274 3.63265541128783 5.63266531718274 3.63265541128783 5.63266544831288 5.63266544834288 5.63266544834288 5.63266544834288 5.632665444834288 5.632665444834288 5.632665444834288 5.632665444834288 5.632665444834288 5.632665444834288 5.632665444834288 5.6326654483448 5.63266544483448 5.6326654448348 5.6326654448348 5.632
н с н н с н с н с н с н с н с н с н с н	10.0380012694258 10.038012694258 10.203210340605972 9.83385256763454 11.21846254613961 11.28521679388331 11.687759073310902 9.4597564255405 9.4597564255405 9.4597564255405 9.4597564255405 9.4597564255405 9.15920883921148 2.0184427836247 9.0430214705325 8.6603114706386 8.6603147053842873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.119396442873 9.043021490550571 9.1193964428737460 5.577600584425560 5.577600584425560 5.577600584425560 5.577600584425560 5.577600584425560 5.577605954148053 5.5984492737460 5.57840708000 6.5456961236115 5.5984892373460 5.578400786000 5.5784000000000000000000000000000000000000	26.20398398273768 24.3652103911300 24.36921031230 24.3692103223633 23.95770783805212 23.95770783805212 23.95770783805212 23.95770783805212 23.95770783805212 23.95707832078052 23.951155146950 23.251056552070269 23.251054752029 23.05028720269 23.251054752029 23.05028720269 23.2511259119883 23.2671265912690 23.2511259119883 23.2671269126907 23.2451043822492 23.265029249243101 23.2451045920507 23.2451045920507 23.2451045920507 23.25029262703121 23.2502926270312 23.2502926270312 23.2502926270312 23.25054126507 23.2502926270312 23.25054126507 23.2502926270312 23.25054126507 23.245124507 23.2651262707 23.245124507 23.2651262707 23.245124507 23.26521262707 23.245124507 23.255543025207 23.2452547777 23.246552311557 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.2465553755 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.246555375 23.2465553775 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537755 23.2455537	16.073930107542480 16.073947042323270 17.7659018984391 16.73847924323270 17.659018984391 17.46662319502621 18.4232681025056 18.4232681025056 18.4232681025056 18.4232681025056 18.4232681025056 18.4326871458 18.432697147581 18.8459973721753 18.845973721753 18.845973721753 18.845973721753 18.845973721753 18.845973721753 18.845973721753 18.845996553026 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15305411308984 14.2778444293946 15.312275150434 15.3518947665386 11.59912517147714 10.9772841550374 11.59912517147714 10.977284554304 11.59912517147714 10.977284554304 11.59912517147714 10.977284554304 11.59912517147714 10.977284554304 11.59912517147714 10.977284554307 10.8576873355479 13.8455764785394 14.53797985086004 14.53797985086004 14.53797985086004 14.5379785080004 14.5379785080004 14.5379785080004 14.5379785080004 14.5379785080004 15.59024108507700 15.444218075170 15.444218075170 15.425420718881 5.63865421018278 5.63865421018278 5.63865421018278 5.6386544138518 5.6386544185854418 5.6386544138518 5.6386544185854418 5.6386544185854418 5.6386544185854418 5.6386544185854418 5.63865441
н с н н с н с н с н с н с н с н с н с н	10.038012694258 10.030210340605972 9.83385256763454 11.21836254613961 11.28521679388331 11.685775907331308 9.3922248827254 11.21836254413961 11.685715907331308 9.4597564255405 9.4597564255405 9.15290883921148 2.0184427853247 9.043021842785324 9.043021842785324 9.043021842785324 9.043021842785324 9.04302189120 9.04592131001028 8.66031475246124 8.6034752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.6538752576124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.653875276124 6.6538752717824 8.25120430248955 5.5984802873460 0.6548696123217599 3.14852134032 3.35022237877601 4.371292035208649 3.2489207347643738 3.2552237872661 3.0282075769661 3.028275769621 3.028275769620 3.028275769664 3.028275769621 3.028275769621 3.028275769621 3.0282228988080 3.00222228988080 3.00222228988080 3.00222228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.0022228988080 3.002228988080 3.002228988080 3.002228988080 3.002228988080 3.0022228988080 3.002228988080 3.002228988080 3.0022289	26.20398398273768 24.38521093011300 24.3852109311300 24.3852109311300 24.38521073805212 29.34114562276784 29.35757078305121 29.34114562276784 20.3311551460506 29.20131051460506 29.20131034172329 29.0602887020696 29.2013103417239 29.0602887020696 29.2013103417239 29.0602887026596090 29.20130417563908 29.2123400212881 28.21527025596090 23.2451193911588 23.24611966097870 23.24611958191888 23.24611966097870 23.24611958191888 23.24611966097870 23.2461198916988 23.2461196607870 23.2461198916988 23.2461196607870 23.246194619867870 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.24619461986128 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.246294274805719 23.24754345674027 23.2494284274805719 23.249428427482719 23.249428427482719 24.249428427482719 24.2494284274827219 24.2494284274827219 24.24942842744274857 24.24942842744274857 24.24942842744274857 24.2494284274427455 24.2494284274427455 24.2494284274444474745 24.	16.073930107542480 16.0739407242480 16.73945724232270 17.76539018984391 17.468523915902621 18.43236810625056 16.7553927002548 18.43236810625056 16.7553927002548 17.7702347642530 17.7702347647581 17.7702347647581 18.36569627631455 16.3152471265984 16.3152471265984 16.3152471265984 16.3152471265984 16.3152471265984 14.362691270853 14.15206511320868 14.3206511320868 14.3206511320868 14.3206511320868 14.32076913483942 17.755381291511 15.518947665389 12.519943453924 12.5199476485381 15.5915217347714 10.5772281554230 10.3766873355479 15.5915217347714 10.5772281554230 10.3766873355479 15.5915217347714 10.5772281554230 10.3766873355479 15.5915217347714 10.5772281554230 10.3766873355479 15.5912517347714 10.5772281554230 10.3766873355479 15.5912517347714 10.5772281554230 10.31146150711 12.61797156621693 13.8455664693288 15.5902460505078 13.59857697583942 15.5302460505078 15.59024280718831 15.530247655770 13.8455564483288 5.630264097822443185 5.63026524108650 15.44618075470 15.44618075470 15.44618075470 15.44618075470 15.44618075470 15.44618075470 15.42620718818 15.59024086052 15.59024086052 15.59024086052 15.59024086052 15.59024086502 15.5912434 15.53024086524 15.59024086502 15.5912434 15.53024086524 15.5912434 15.53024086524 15.5912434 15.53024086524 15.5912434 15.54264432828 15.54264432828 15.54264432828 15.54264432828 15.54264432828 15.54264432828 15.5426443282 15.5426443282 15.5426443282 15.5426443282 15.5426443282 15.54264432828 15.5426443282 15.5426443282 15.54264432842 15.5426443282 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432 15.5426432
н с н н с н с н с н с н с н с н с н с н	10.038012694258 10.030210340605972 9.8338526763454 11.21846254619961 11.2552167938931 11.6557167938931 11.65571679389331 11.655716931530 9.4597564255405 9.4597564255405 9.4597564255405 9.4597564255405 9.4597564255405 9.15920883921148 9.036778775875428692 8.6603114706386 8.6603114706386 8.620845957148 9.036275475769124 6.6538954255405 9.119936442873 9.04302139010208 8.66324525769124 6.653895425560 6.6538552769124 6.6538552769124 6.6538554255505 7.1367610468069 6.6538552769124 6.653853524825550 5.5548492873460 6.6538552425550 5.5548492873460 6.05485621235115 5.5548492873460 5.554849373460 5.5548492873460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849873460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.554849373460 5.5548494373460 5.554849373460 5.554849373460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.554849473460 5.5548445454 5.5548445454 5.5548445454 5.5548445454 5.5548454545454 5.55484545454545454545454545454545454545	26.20398398273768 24.3652103911300 24.36921031200 24.36921031200 24.36921031200 24.369210322643 23.5570783805121 23.35750783805121 23.35750783805121 23.3575078305121 23.3507058405030 23.25105465050 23.25105465050 23.25105465702 23.251054257026 23.25105427026 23.25105427026 23.25105427026 23.25105427026 23.25105427026 23.2510542702 23.2520542702 23.2520542702 23.2520542702 23.25205427002 23.25205427255 23.252054272 23.25205427255 23.25205427255 23.25205427255	16.073930107542480 16.073947042480 16.73945724323270 17.76539018984391 17.46652319502621 18.4322681062506 16.7555927002548 18.4322681062506 16.7555927002548 17.7703149623376 17.7703149623376 17.7703147647581 18.842398013216614 18.84298023216614 18.8469062561345 16.1552471265984 16.1552471265984 16.352671345 15.3518074665388 11.59915217347714 10.9779282654335 11.59915217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9515217347714 10.9779285626331 15.9516374663385 11.59915217347714 10.9779285656335 11.59915217347714 10.9779285656335 11.59915217347714 10.9779285656335 11.59915217347714 10.9779285565331 15.9516756332 13.88557697583342 13.88557697583342 13.88557697583342 13.88557697583342 13.88557697583342 13.8855564463232 13.885556435557 13.985577707565213 13.88557677583342 13.8855767583342 13.8855767583342 13.88557675776775677677677677677777567777756777777
н с н н с н с н с н с н с н с н с н с н	10.038012694258 10.030210340605972 9.8338526763454 11.21846254419961 11.25521679389331 11.65775907331098 9.3922248827254 11.1852155993531 11.6577590731308 9.3922764255705 9.1529083921148 9.39367787758754255705 9.1529083921148 9.30367787758754255705 9.1529083921148 9.30367787758754255705 9.1529083921148 9.30367787758754255705 9.1529084297 9.0527825754124 6.65389532148053 7.1367610468059 6.63245219140515830 6.59802544225550 7.1367610468059 6.532452194025 5.5948908373760 6.632452148051 3.3502227877601 4.552103076437 3.5538535057155 5.594890373450 5.59489473350 5.59489473350 5.59489473350 5.59489473350 5.59489473450 2.40380744949483 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.40800744194833 2.4080744194833 2.4080074419483	26.20398398273768 24.3652103911300 24.36921031200 24.3692103120 24.3692103120 24.369210322643 23.95770738205212 23.95770738205212 23.957707382052 23.957707382052 23.957707382052 23.957707382052 23.957707382052 23.957707205396009 23.254103477229 23.0502872026956 23.20113417239 23.26712639200926 23.20113417239 23.2671263920927 23.2451043822492 23.2652042949341 23.2451043822492 23.2451043822492 23.2451043822492 23.2451043822492 23.2451043822492 23.2451043822492 23.2451043822492 23.2451043825492 23.2451043924 23.24521151897 23.24520392962 23.245204392921 23.245204392921 23.245204392921 23.245204392921 23.245204392921 23.245204392921 23.245204392921 23.245204392927 23.245204392927 23.245244057179 23.245244057179 23.245244057179 23.245244057199 23.245244057199 23.245244057199 23.245244057199 23.245244057199 23.245244057199 23.245244057199 23.245244057199 23.2452405715311389 23.2452405552422 29.200571531328 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.23055715511383 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305561772355 29.4755669312001 29.2305571551138 29.2305571551138 29.23055614292 29.2305571551138 29.23055614292 29.2305571551138 29.23055614292 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.2305571551138 29.230557155218 29.230557155218 29.230557155218 29.230557155218 29.230557155218 29.230557155218 29.230557155218 2	16.0739107542480 16.0739107542480 16.7394572432270 17.7659018984391 17.4665219502621 18.4232681062506 16.755532700548 18.4232681062506 16.75535754 17.4135415055754 17.4135415055754 17.8135415055754 18.8432981747581 18.84529817458016 18.84208023216614 18.3666962761345 16.1552471265984 16.1552471265984 14.656119279853 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.15206511320868 14.25784414389422 17.656842053181161 13.955810465181 15.951517347714 10.567822685380 11.590521891497 10.567823054135 13.591517347714 10.5772281554230 10.37056873554379 15.591517347714 10.5772281554230 10.37058826431 15.590521904477 10.5772281554230 10.37058326431 15.590521914477 10.5772281554230 10.37058326431 15.590521914477 10.5772281554230 10.37058326431 15.59052914477 10.5772281554230 10.3216837801215 15.382587697583342 15.383587697583342 15.38458448528 15.3935887865448 15.39358878858 15.29156444 15.3907682441381588 15.2202101544352 15.22021014306 15.2202211340669 15.220221343452 15.22024254343 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.22024254433 15.220242544
H C H H C H C H C H C H C H C H C H C H	10.038012694258 10.030210340605972 9.8338526763454 11.21846254419961 11.25516793498331 11.657179307311098 9.3922248827254 11.1852155993531 11.65715907313098 9.3922764255740 9.15320564255740 9.15320564255740 9.15320564255740 9.15320564255740 9.15320564255740 9.1532054255740 9.053074775754258 8.6603114706386 8.6520515769124 6.65383526956731 8.46124539148013 7.1367610468069 6.6324539148013 7.1367610468069 6.6324539148013 7.1367610468069 6.6324539148013 7.1367610468069 6.6324639148033 7.1367610468069 6.6324639148013 4.3721299105500 6.5346428733 3.550355505715 5.544630275479612 4.5512439127599 4.374521357546 4.37421990550649 4.37553945855 3.0922029586609 2.324594292580 6.0901431142899 4.8755613048615 3.0922029586059 2.3245290152864 4.6750549723953 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922295886059 3.0922239886059 3.0022999886059 3.0022999886059 3.002299	26.20398398273768 24.3652103911300 24.3692103120 24.3692103120 24.369210322643 23.9577078305121 29.34114562276782 20.331155146050 20.331165146050 20.331155146050 20.30115146050 20.30115146050 20.30115146050 20.30115146050 20.30115146050 20.30115146050 20.301207265396090 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.201103417239 20.362083702696 20.301103417239 20.36208276031 20.362082420 20.36208276031 20.3620827602777 20.36208777777 20.3620877777777777777777777777	16.0739107542480 16.0739107542480 16.7394572432370 17.76593018984391 17.4665219502621 18.4232681062506 16.755532200548 15.770318613373 17.8155532200548 15.7703184053754 15.7703184053754 15.77031840515 16.83579373737373 17.815540747581 16.83579373737373 16.8356987374581 16.835698737581 16.355471265984 16.355471265984 16.3526713455 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.352671345 16.35276713984 14.32738442695889 16.25199633436398 16.25199633436398 16.25199633453942 17.65643206118216 17.9563206118216 13.95052189159164 13.95052189159164 13.95052189159164 13.95052189159174 13.95052189159174 13.95052189159174 13.5932564355 13.854556405937 15.650229914477 10.677722815542320 10.970898264355 13.85455640393288 3.5650640393 15.3526050503789 7.70158878012155 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.820805500593 7.7015887801215 5.820805500513 5.8208051509789 3.9301205682288 3.9506051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 7.7015887801215 5.8208051509789 5.820808051509789 5.820808051509789 5.820808051509789

н	5.05389597566972	29.44156985562708	13.74108459595929
н	5.64629325020598	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
С	6.90678452243191	28.78457953990324	11.41483959474949
C	6.92106415880964	28.52230135892902	10.05115040508582
C	7.20049317446050	29.56976928952803	9.16517283769734
С	6.35356314949090	28.37008764494639	15.09278608775654
N	6.58708528866997	27.83052519896290	12.41376212796362
Ν	7.53965672342516	27.62356391710455	13.18227323607302
С	7.09844434459839	27.32666599071831	14.49620817368897
С	6.00657029364898	28.22707829016502	16.43360030590230
C	6.36451185958051	27.08547198685737	17.15877537597367
С	7.11688132322348	26.07818908588859	16.55173488656800
C	7.50821818339577	26.21498479662824	15.22098288944247
н	5.44973943497143	29.01118701344702	16.95274904874975
н	7.46665597885802	32.12170881318209	11.41953944050821
н	7.59109780643506	31.67201014292718	8.96405347787114
C	7.01854886090420	30.35643796904056	13.45588791963185
н	6.82016351639669	31.43465300066196	13.54334472571176
н	8.01459734789995	30.19901865037338	13.90456807780645
н	6.75484244078729	27.50738104212544	9.68378943739279
н	8.12861685309327	25.45542902404357	14.73720539048040
0	7.30298463764536	29.37960863273735	7.83949812410672
н	7.06365039966525	28.46599797354444	7.58784513509576
Н	7.41047035089203	25.19391039225714	17.12520572746851
0	5.98065523301500	27.03163334914301	18.45566467231637
н	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).

References

(1) Bucher, G.; Bresolí-Obach, R.; Brosa, C.; Flors, C.; Luis, J. G.; Grillo, T. A.; Nonell, S. β-Phenyl quenching of 9-phenylphenalenones: a novel photocyclisation reaction with biological implications. *Phys. Chem. Chem. Phys.* **2014**, *16* (35), 18813–18820.

(2) Gabor, G.; Frei, Y.; Gegiou, D.; Kaganowitch, M.; Fischer, E. Tautomerism and Geometric Isomerism in Arylazo-Phenols and Naphthols. Part III. Orthohydroxy Derivatives and their Reversible Photochemical Reactions. *Isr. J. Chem.* **1967**, *5* (5), 193–211.

(3) Garcia-Amorós, J.; Sánchez-Ferrer, A.; Massad, W. A.; Nonell, S.; Velasco, D. Kinetic study of the fast thermal cis-to-trans isomerisation of para-, ortho- and polyhydroxyazobenzenes. *Phys. Chem. Chem. Phys.* **2010**, *12* (40), 13238–13242.

(4) Farrera, J.-A.; Canal, I.; Hidalgo-Fernández, P.; Pérez-García, M. L.; Huertas, O.; Luque, F. J. Towards a tunable tautomeric switch in azobenzene biomimetics: implications for the binding affinity

of 2-(4'-hydroxyphenylazo)benzoic acid to streptavidin. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2008**, *14* (7), 2277–2285.

(5) Ball, P.; Nicholls, C. H. Azo-hydrazone tautomerism of hydroxyazo compounds—a review. *Dyes Pigm.* **1982**, *3* (1), 5–26.

(6) Chen, X.-C.; Tao, T.; Wang, Y.-G.; Peng, Y.-X.; Huang, W.; Qian, H.-F. Azo-hydrazone tautomerism observed from UV-vis spectra by pH control and metal-ion complexation for two heterocyclic disperse yellow dyes. *Dalton Trans.* **2012**, *41* (36), 11107–11115.

(7) Hall, J. M.; McDonnell, D. P. The estrogen receptor beta-isoform (ERbeta) of the human estrogen receptor modulates ERalpha transcriptional activity and is a key regulator of the cellular response to estrogens and antiestrogens. *Endocrinology* **1999**, *140* (12), 5566–5578.

(8) Hall, J. M.; Korach, K. S. Analysis of the molecular mechanisms of human estrogen receptors alpha and beta reveals differential specificity in target promoter regulation by xenoestrogens. *J. Biol. Chem.* **2002**, *277* (46), 44455–44461.

(9) Kuznetsov, Y. V.; Levina, I. S.; Scherbakov, A. M.; Andreeva, O. E.; Fedyushkina, I. V.; Dmitrenok, A. S.; Shashkov, A. S.; Zavarzin, I. V. New estrogen receptor antagonists. 3,20-Dihydroxy-19norpregna-1,3,5(10)-trienes: Synthesis, molecular modeling, and biological evaluation. *Eur. J. Med. Chem.* **2018**, *143*, 670–682.

(10) Kwon, J.; Oh, K. S.; Cho, S.-Y.; Bang, M. A.; Kim, H. S.; Vaidya, B.; Kim, D. Estrogenic Activity of Hyperforin in MCF-7 Human Breast Cancer Cells Transfected with Estrogen Receptor. *Planta Med.* **2016**, *82* (16), 1425–1430.

(11) Sun, H.; Xu, X.-L.; Qu, J.-H.; Hong, X.; Wang, Y.-B.; Xu, L.-C.; Wang, X.-R. 4-Alkylphenols and related chemicals show similar effect on the function of human and rat estrogen receptor alpha in reporter gene assay. *Chemosphere* **2008**, *71* (3), 582–588.

(12) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G.
Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G.
Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D.
Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D.
Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R.
Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A.
Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N.
Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K.
Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian. Gaussian 09, Revision E.01. *Inc.* 2016 (Wallingford CT).

(13) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor Chem Account* **2008**, *120* (1-3), 215–241.

(14) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *The Journal of Chemical Physics* **1989**, *90* (2), 1007–1023.
(15) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **2020**, *152* (22), 224108.

(16) Liakos, D. G.; Neese, F. Is It Possible To Obtain Coupled Cluster Quality Energies at near Density Functional Theory Cost? Domain-Based Local Pair Natural Orbital Coupled Cluster vs Modern Density Functional Theory. *J. Chem. Theory Comput.* **2015**, *11* (9), 4054–4063.

(17) Demel, O.; Pittner, J.; Neese, F. A Local Pair Natural Orbital-Based Multireference Mukherjee's Coupled Cluster Method. *J. Chem. Theory Comput.* **2015**, *11* (7), 3104–3114.

(18) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102* (11), 1995–2001.

(19) Bannwarth, C.; Caldeweyher, E.; Ehlert, S.; Hansen, A.; Pracht, P.; Seibert, J.; Spicher, S.;
Grimme, S. Extended tight-binding quantum chemistry methods. *WIREs Comput. Mol. Sci.* 2021, *11*(2).

(20) Bannwarth, C.; Ehlert, S.; Grimme, S. GFN2-xTB-An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15* (3), 1652–1671.

(21) Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections. *J. Chem. Theory Comput.* **2013**, *9* (1), 263–272.

(22) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297–3305.

(23) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

(24) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057–1065.

(25) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree– Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. *Chem. Phys.* **2009**, *356* (1-3), 98–109.

(26) Eastman, P.; Swails, J.; Chodera, J. D.; McGibbon, R. T.; Zhao, Y.; Beauchamp, K. A.; Wang, L.-P.; Simmonett, A. C.; Harrigan, M. P.; Stern, C. D.; Wiewiora, R. P.; Brooks, B. R.; Pande, V. S. OpenMM 7: Rapid development of high performance algorithms for molecular dynamics. *PLoS Comput. Biol.* **2017**, *13* (7), e1005659.

(27) D.A. Case, H.M. Aktulga, K. Belfon, I.Y. Ben-Shalom, S.R. Brozell, D.S. Cerutti, T.E. Cheatham, III, G.A. Cisneros, V.W.D. Cruzeiro, T.A. Darden, R.E. Duke, G. Giambasu, M.K. Gilson, H. Gohlke, A.W. Goetz, R. Harris, S. Izadi, S.A. Izmailov, C. Jin, K. Kasavajhala, M.C. Kaymak, E. King, A. Kovalenko, T. Kurtzman, T.S. Lee, S. LeGrand, P. Li, C. Lin, J. Liu, T. Luchko, R. Luo, M. Machado, V. Man, M. Manathunga, K.M. Merz, Y. Miao, O. Mikhailovskii, G. Monard, H. Nguyen, K.A. O'Hearn, A. Onufriev, F. Pan, S. Pantano, R. Qi, A. Rahnamoun, D.R. Roe, A. Roitberg, C. Sagui, S. Schott-Verdugo, J. Shen, C.L. Simmerling, N.R. Skrynnikov, J. Smith, J. Swails, R.C. Walker, J. Wang, H. Wei, R.M. Wolf, X. Wu, Y. Xue, D.M. York, S. Zhao, and P.A. Kollman. Amber 2021, University of California, San Francisco, 2021. (28) Wang, J.; Wang, W.; Kollman, P. A.; Case, D. A. Automatic atom type and bond type perception in molecular mechanical calculations. *J. Mol. Graph.* 2006, *25* (2), 247–260.