An Isosteric Triaza Analogue of a Polycyclic Aromatic Hydrocarbon Monkey Saddle

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1 General Remarks

Materials: All used reagents and solvents were purchased from abcr, Acros Organics, Carbolution, Carl Roth, Deutero, Fisher Scientific, Honeywell, Sigma-Aldrich, Grüssing, Merck, TCI or VWR Chemicals and used without further purification, if not mentioned otherwise. Anhydrous tetrahydrofuran was dispensed from a Solvent Purification System MB SPS-800. Water was degassed by bubbling Argon through it for two hours, tetrahydrofuran was degassed by three times freeze-thaw pumping. If not mentioned otherwise, all reactions were performed under standard conditions (25°C, 1013 mbar). Inert conditions were achieved by evacuating the flasks, bake out and flooding with Argon (three cycles). Complete removal of solvents was achieved by applying high vacuum (1 · 10⁻¹ mbar).

Thin layer and flash column chromatography Analytical Thin Layer Chromatography was performed with POLYGRAM® SIL G/UV₂₅₄ gel plates sold by Macherey-Nagel. Detection was accomplished using UV-light (254 nm). Flash column chromatography was accomplished using Silica gel 60 (40–63 μm / 230–400 mesh ASTM) purchased from Macherey-Nagel.

Chiral high-performance liquid chromatography (HPLC) Analytical chiral HPLC was performed on a Shimadzu LC-40 Nexera HPLC-System and semi-preparative chiral HPLC was performed on an Agilent 1200 series HPLC system. Both systems use Chiralpak® IE columns from Daicel.

Nuclear magnetic resonance (NMR) All reported NMR spectra were recorded on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Fourier 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) or Bruker Avance III 600 (600 MHz). Chemical shifts (δ) are given in parts per million (ppm) and coupling constants in Hertz (Hz). All spectra were calibrated relative to traces of less-deuterated solvent (CDCl₃: 7.26 ppm / 77.16 ppm, CD₂Cl₂: 5.32 ppm / 53.84 ppm). The following abbreviations were used for °H NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). All ¹³C NMR spectra were measured with °H decoupling.
Mass spectrometry (MS) MS experiments were performed on a Bruker AutoFlex Speed time-of-flight spectrometer (MALDI-MS), a JEOL AccuTOF GCx time-of-flight spectrometer (EI-MS) or on a Bruker ApexQe hybrid 9.4 T FT-ICR spectrometer (ESI-, DART-, MALDI-MS). For MALDI-MS experiments DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methylpropenylidene)-malononitrile) was used as matrix. All measurements were performed by the mass spectrometry division of the University of Heidelberg under the supervision of Dr. Jürgen H. Gross.

Infrared spectroscopy (IR) IR spectra were recorded on a ZnSe ATR crystal using a Bruker Tensor 27 spectrometer. The following abbreviations were used to indicate the absorption intensity: vw (very weak), w (weak), m (medium), s (strong), vs (very strong).

Elemental analysis Elemental analysis were performed in the Microanalytical laboratory of the University of Heidelberg with a Vario EL Element Analyzer.

UV/vis and fluorescence spectroscopy UV/vis spectra were recorded with a Jasco V-730 spectrometer and fluorescence spectra with a Jasco FP-8300 spectrometer.

CD spectroscopy CD spectra were recorded with a Jasco J-1500 CD spectrometer.

Melting points The non-corrected melting points were determined with a Büchi Melting Point B-545.

X-ray crystal structure analysis X-ray crystal structure analyses were recorded with a Bruker APEX-II Quazar diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at 200 K or with a Stoe Stadivari using Cu-Kα radiation (λ = 1.54178 Å) at 100 K. Intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[52] or X-Area LANA 1.70.0.0[53] based on the Laue symmetry of the reciprocal space (μ, Tmin, Tmax). The structures were solved with SHELXT-2014 (Sheldrick 2014)[54] and refined against F2 with a Full-matrix least-squares algorithm using the SHELXL-2018/1 software.[55]

Computational Details All quantumchemical calculations were performed by employing the Gaussian09 program package.[56] The theoretical approach is based on Kohn-Scham density functional methodologies[57] using the B3LYP[58] functional. As basis set the triple-ζ-basis (6-311G(d,p))[59] was used. The geometries of the regarded species were fully optimized using ultra-tight convergence criteria of the representative computational method. Ground states were confirmed by using frequency calculations to not exhibit any imaginary frequency. Prediction of excited state properties[510] and electronic circular dichroism (ECD) analysis[511] were performed using time-depended DFT methods with the B3LYP or BHandHLYP functional, as implemented in Gaussian 09, Rev. D.01, and convoluted with GaussSum.[512] NICS(0) and NICS(1) values were calculated from the optimized geometries by adding a ghost atom in the centroid or 1 Å above/below of the corresponding ring and performing a single-point calculation based on Hartree-Fock methods[513] using the augmented double-ζ-basis (6-31+G(d))[59, 514] with the GIAO method.[515] Ring-current analysis was accomplished by performing a single-point calculation with the CSGT method[515a, 516] on the HF/6-31+G(d) level and using the AICD program package of the Herges group.[517]
2 Experimental Procedures

Scheme S1: Compounds S1-S3 and 3 were synthesised as reported in our previous paper.\[S18\]

2.1 4,9,14-Tribromo-1,6,11-tris(hexyloxy)-5H-diindenoph1,2-a:1’,2’-c]fluorene-5,10,15-trione (4)

Tribrromotruxene 3 (880 mg, 1.00 mmol) was added to a solution of potassium carbonate (829 mg, 6.00 mmol) in DMF (100 mL). The flask was equipped with an oxygen balloon and the atmosphere exchanged three times. Then the mixture was stirred at 40°C for 96 hours. After cooling down to room temperature, the solvent was removed \textit{in vacuo}, the residue re-dissolved in DCM (50 mL) and eluted through a short plug of silica until the eluent was colorless (approx. 400 mL). The solvent was evaporated, methanol (10 mL) was added and the mixture ultrasonicated for 20 minutes. The suspension was cooled to 0°C, the precipitate filtered off and washed with cold methanol (3×5 mL). After drying in an air-stream, truxenone 4 was isolated as yellow powder in 62% yield (570 mg, 619 μmol).\[mp. 211–213°C; \textit{^1}H NMR\]
Aniline boronic acid hydrochloride S4 (624 mg, 3.60 mmol), Pd2(dbad)2 (18.3 mg, 20.0 μmol), t-Bu3PHBF4 (23.2 mg, 80.0 μmol) and potassium carbonate (1.16 g, 8.40 mmol) were suspended in degassed THF/water (3.0 mL, 1:1 V/V) and stirred under argon for five minutes. Bromotruxenone 4 (369 mg, 400 μmol) was added and the mixture stirred for 48 hours at 80°C. After cooling to room temperature, the phases were separated and the aqueous phase extracted with ethyl acetate (2×10 mL). From the combined organic phases the solvent was evaporated in vacuo, the residue suspended in methanol (5 mL), the dark red precipitate filtered off and dried under air. The dark red powder was dissolved in chloroform (12 mL), acetic acid (1.2 mL) was added and the mixture was stirred at 80°C overnight. After cooling down to room temperature DCM (20 mL) was added, the phases separated, the organic phase washed with saturated sodium carbonate solution (30 mL) and the combined aqueous phases reextracted with DCM (3×20 mL). The combined organic phases were dried over Na2SO4, filtered and the solvent was removed in vacuo. The residue was further purified via flash column chromatography (SiO2, PE/toluene 1:5; Rf = 0.33) to give 161 mg (45%) of 2 as yellow-orange powder. mp. 135-137°C (decomp.) 1H NMR (CD2Cl2, 400 MHz) δ (ppm) 7.44 (d, 3J = 8.5 Hz, 3H, H-3/11/19), 7.31 (td, 3J = 7.7 Hz, 4J = 1.3 Hz, 3H, H-6/14/22), 7.13 (td, 3J = 7.5 Hz, 4J = 1.5 Hz 3H, H-5/13/21), 7.09 (d, 3J = 8.6 Hz, 3H, H-2/10/18), 6.89 (dd, 3J = 8.0 Hz, 4J = 1.3 Hz, 6H, H-4/7/12/15/20/23), 4.28 (dt, 3J = 9.6 Hz, 4J = 6.1 Hz, 3H, H-1’), 4.14 (dt, 3J = 9.6 Hz, 4J = 6.9 Hz, 3H, H-1”), 4.17-4.11 (m, 3H, H-1”), 1.90 - 1.74 (m, 6H, H-2”), 1.61 - 1.43 (m, 6H, H-3”), 1.36 - 1.29 (m, 12H, H-4’/5’), 0.86 (t, 3J = 7.1 Hz, 9H, H-6’); 13C NMR (CD2Cl2, 100 MHz) δ (ppm) 153.9 (C-1/6/11), 144.6 (C-4a/9a/14a), 144.4 (C-4b/9b/14b), 141.1 (C-3/8/13), 135.8 (C-4c/9c/14c), 126.1 (C-5a/10a/15a), 117.9 (C-2/7/12), 112.4 (C-4/9/14), 69.9 (C-1”), 31.6 (C-5”), 29.1 (C-2”), 25.6 (C-3”), 22.7 (C-4”), 14.2 (C-6’); IR (ATR, FT) ν (cm⁻¹) 2951 (w), 2930 (m), 2870 (w), 2858 (w), 1709 (s), 1597 (m), 1583 (m), 1566 (s), 1462 (s), 1375 (m), 1354 (w), 1281 (vs), 1219 (m), 1169 (s), 1121 (s), 1074 (m), 1036 (m), 961 (m), 919 (m), 818 (m), 795 (m), 762 (w), 721 (m), 640 (vw); UV/vis (dichloromethane) λmax (lg ε) 305 nm (4.67), 400 nm (4.29), 436 nm (3.81) (sh); MS (HR-DART+) m/z calculated for [M+H]+: 919.0839, found: 919.0839; Elem. Anal. calculated for C45H45Br3O6·2/3 MeOH: C 58.17%, H 5.10%, found: C 58.13%, H 5.19%.

2.2 8,16,24-Triaza-1,9,17-tris(hexyloxy)-16a,24a-dihydro-8aH-bis(benzo[4,5]-cycloocta[1,2,3-cd]indenoo)[2,2a,3,4-sab:2’,2a’,3’,4’-cde]benzo[5,6]-cycloocta[1,2,3,4-def]fluorene (2)
(ppm) 166.2 (C-8a/16a/24a), 156.4 (C-1/9/17), 149.8 (C-7a/15a/23a), 147.7 (C-8d/16d/24d), 144.5 (C-8c/16c/24c), 135.5 (C-3/11/19), 134.7 (C-4/12/20), 132.5 (Cq), 131.1 (C-3a/11a/19a), 131.0 (C-3b/11b/19b), 128.9 (Cq), 128.5 (C-6/14/22), 126.2 (C-7/15/23), 125.4 (C-5/13/21), 116.5 (C-2/10/18), 69.9 (C-1'), 31.9 (C-5'), 29.6 (C-2'), 26.0 (C-3'), 23.0 (C-4'), 14.2 (C-6'); IR (ATR, FT) $\tilde{\nu}$ (cm$^{-1}$) 3057 (vw), 2920 (m), 2853 (m), 1645 (m), 1582 (s), 1562 (m), 1502 (m), 1464 (s), 1431 (w), 1379 (w), 1350 (w), 1281 (s), 1248 (m), 1207 (w), 1169 (m), 1119 (m), 1094 (m), 1063 (m), 1043 (w), 1005 (m), 943 (w), 926 (w), 883 (w), 812 (s), 791 (w), 756 (vs), 727 (m), 700 (m), 640 (w); UV/vis (dichloromethane) $\lambda_{\text{max}}$ (lg $\varepsilon$) 273 nm (4.80), 316 nm (4.43), 414 nm (4.13); MS (HR-DART$^+$) $m/z$ calculated for [M+H]$^+$: 904.4473, found: 904.4482.

3 Spectra

3.1 $^1$H NMR and $^{13}$C NMR spectra

![NMR spectra diagram]

Figure S1: $^1$H NMR spectrum of 4 (CDCl$_3$, 600 MHz, 300 K).
Figure S2: $^{13}$C NMR spectrum of 4 (CDCl$_3$, 150 MHz, 300 K).

Figure S3: $^1$H NMR spectrum of 2 (CD$_2$Cl$_2$, 400 MHz, 300 K).
Figure S4: $^{13}$C NMR spectrum of 2 (CD$_2$Cl$_2$, 100 MHz, 300 K).

3.2 2D NMR Spectra

Figure S5: $^1$H,$^1$H-COSY spectrum of 4 (CDCl$_3$, 600 MHz, 300 K).
Figure S6: $^1$H,$^{13}$C-HSQC spectrum of 4 (CDCl$_3$, 600 MHz, 150 MHz, 300 K).

Figure S7: $^1$H,$^{13}$C-HMBC spectrum of 4 (CDCl$_3$, 600 MHz, 150 MHz, 300 K).
Figure S8: $^1$H,$^1$H-COSY spectrum of 2 (CD$_2$Cl$_2$, 400 MHz, 300 K).

Figure S9: $^1$H,$^1$H-NOESY spectrum of 2 (CD$_2$Cl$_2$, 400 MHz, 300 K).
Figure S10: $^1$H, $^{13}$C-HSQC spectrum of 2 (CD$_2$Cl$_2$, 400 MHz, 100 MHz, 300 K).

Figure S11: $^1$H, $^{13}$C-HMBC spectrum of 2 (CD$_2$Cl$_2$, 400 MHz, 100 MHz, 300 K).
3.3 IR spectra

Figure S12: FT-IR spectrum of 4 (ATR, ZnSe).

Figure S13: FT-IR spectrum of 2 (ATR, ZnSe).
3.4 Mass Spectra

Figure S14: HR DART-MS of compound 4.

Figure S15: HR MALDI-MS of compound 2.
3.5 UV/vis Spectra

Figure S16: UV/vis spectrum of 4 in DCM.

Figure S17: UV/vis spectrum of 2 in DCM.
Figure S18: UV/vis spectrum of 2 in n-heptane.

Figure S19: UV/vis spectrum of 2 in DCM (black, solid line), with triethylamine (orange dotted line) and with TFA (red, solid line).
Figure S20: UV/vis spectrum of 1 in DCM (black, solid line), with triethylamine (orange dotted line) and with TFA (red, dotted line).

3.6 HPLC-Chromatograms

Figure S21: Analytical chromatograms of the racemic mixture of 2 (top) and from the both separated enantiomers (IE column, n-heptane/i-PrOH 70:30, 1.0 mL min⁻¹, 254 nm).
3.7 CD Spectra

The g-values were calculated following eq. (1), dividing the absorption of the CD spectra through the absorption of the UV/vis spectrum, for each wavelength.$^{[S19]}$

\[
g_{\text{abs}} = \frac{\Delta \varepsilon_{\text{nm}}}{\varepsilon_{\text{nm}}} \quad (1)
\]

The Aza Monkey Saddle 2 has the most positive g-value at 290 nm with \(g_{\text{abs}} = 3.41 \times 10^{-3}\), corresponding with the maximum in the CD spectrum at 288 nm and the most negative at 343 nm with \(g_{\text{abs}} = -2.70 \times 10^{-3}\) corresponding to minimum at 338 nm.

Figure S22: CD spectrum of 2 (n-heptane).
4  Crystallographic Data

4.1  4,9,14-Tribromo-1,6,11-tris(hexyloxy)-5H-diindeno[1,2-a:1’,2’-c]fluorene-5,10,15-trione (4)

Crystals suitable for X-ray diffraction were obtained by diffusion of n-hexane into a solution of 4 in chloroform at room temperature.

CCDC 1994481
Empirical formula  C₅₅H₄₅Br₃O₆
Formula weight  921.54
Temperature  200(2) K
Wavelength  1.54178 Å
Crystal system  orthorhombic
Space group  Pbca
Z  8
Unit cell dimensions
\[ a = 19.3949(4) \text{ Å} \quad \alpha = 90 \text{ deg.} \]
\[ b = 14.4594(3) \text{ Å} \quad \beta = 90 \text{ deg.} \]
\[ c = 28.3431(8) \text{ Å} \quad \gamma = 90 \text{ deg.} \]
Volume  7948.5(3) Å³
Density (calculated)  1.54 g/cm³
Absorption coefficient  4.16 mm⁻¹
Crystal shape  brick
Crystal size  0.160 x 0.130 x 0.115 mm³
Crystal colour  yellow
Theta range for data collection  3.9 to 72.0 deg.
Index ranges  -17≤h≤23, -17≤k≤13, -34≤l≤26
Reflections collected  30156
Independent reflections  7495 (R(int) = 0.0150)
Observed reflections  6688 (I > 2σ(I))
Absorption correction  Semi-empirical from equivalents
Max. and min. transmission 1.38 and 0.76
Refinement method Full-matrix least-squares on F²
Data/restraints/parameters 7495 / 663 / 553
Goodness-of-fit on F² 1.06
Final R indices (I>2sigma(I)) R1 = 0.030, wR2 = 0.069
Largest diff. peak and hole 0.57 and -0.51 eÅ⁻³

4.2 8,16,24-Triaza-1,9,17-tris(hexyloxy)-16a,24a-dihydro-8aH-bis(benzo[4,5]-cycloocta[1,2,3-cd]indeno)[2,2a,3,4-sab:2',2a',3',4'-cd]benzo[5,6]-cycloocta[1,2,3,4-def]fluorene (2)

Crystals suitable for X-ray diffraction were obtained by diffusion of n-pentane into a solution of 2 in methyl tert-butyl ether at room temperature.
5 Kinetic studies of the racemisation process

As we showed for the hydrocarbon monkey saddle 1, four enantiomers of the molecule are possible, which can interconvert by a stepwise mechanism.\cite{S18} Figure S23 shows the determination of the stereodescriptors for 2 according to the three chiral biaryl axes.

![Figure S23: (S\_a,S\_a,S\_a)-2 with one of the three chiral biaryl units highlighted in orange with the biaryl axis in blue (left side). The determination of the stereodescriptor follows the rules for axially chiral compounds.]

The same calculations and measurements were also done for the aza monkey saddle 2. A planar transition state was not considered this time. The results of the DFT calculations differ from the hydrocarbon congener 1 (Figure S24). The first transition state, which is the rate determining step for 1, is equally high for both congeners (102 and 103 kJ mol\(^{-1}\)), but the second transition state turns out to be 12 kJ mol\(^{-1}\) higher for the aza monkey saddle 2, making this here the rate determining barrier.

The determination of the inversion barrier was conducted via CD spectroscopy. A 25 \(\mu\)M solution of the (\(R_a\)\(_a\)\(_a\)\(_a\)) was heated at different temperatures and the CD spectra recorded over time (Figure S25 to Figure S30). All measurements were repeated three times and averaged. The typical measurement time per spectrum is about 3 minutes. The time course of the signal at 250 nm is shown in Figure S31. The data were fitted according a first-order kinetics using an Arrhenius plot (Figure S32). In contrast to the hydrocarbon monkey saddle 1, the enantiomers of 2 are more stable at room temperature. Over 24 h no decay could be
observed. Using the other kinetic data, a half-life at 25°C of 162 days was calculated. At 70°C, the half-life of 2 is 67 times longer than of 1.

The with the Arrhenius equation calculated activation barrier of 113±6 kJ mol\(^{-1}\) fits well to the DFT value of 112 kJ mol\(^{-1}\).

Table S1: Kinetic data for the racemisation of 2 from the CD time course measurements in comparison to the hydrocarbon Monkey Saddle 1. Kinetic data for 1 were earlier published.\(^{[S18]}\)

| No. | temperature | Aza Monkey Saddle 2 | Monkey Saddle 1 |
|-----|-------------|---------------------|-----------------|
|     |             | \(k_e\) [10\(^{-3}\) s\(^{-1}\)] | \(t_{1/2}\) | \(k_e\) [10\(^{-3}\) s\(^{-1}\)] | \(t_{1/2}\) |
| 1   | 25°C        | 162 d\(^a\)        | 0.0083 ± 0.0004 | 23 ± 1 h |
| 2   | 50°C        | 0.0016 ± 0.0001    | 123 ± 6 h       | 0.1999 ± 0.0013 | 57.8 ± 0.4 min |
| 3   | 60°C        | 0.0102 ± 0.0001    | 18.9 ± 0.1 h    | 0.6966 ± 0.0161 | 16.6 ± 0.4 min |
| 4   | 70°C        | 0.0250 ± 0.0002    | 7.7 ± 0.1 h     | 1.6800 ± 0.0922 | 6.9 ± 0.4 min |
| 5   | 85°C        | 0.0983 ± 0.0023    | 118 ± 3 min     | -                | -               |
| 6   | 100°C       | 0.4118 ± 0.0025    | 28.1 ± 0.2 min  | -                | -               |

\(^a\) Calculated from kinetic data.

Figure S24: Comparison between the calculated inversion barriers for the racemisation process (red: CH-MS 1, black: aza-MS 2). The first barrier between the \((S_a,S_a,S_a)\) and the \((S_a,S_a,R_a)\) enantiomer is for both Monkey Saddles equally high, but the middle barrier between \((S_a,S_a,R_a)\) and \((R_a,R_a,S_a)\) is for the Aza Monkey Saddle 2 significantly higher.
Figure S25: Change of the CD spectra of 2 at 25°C over time (n-heptane).

Figure S26: Change of the CD spectra of 2 at 50°C over time (n-heptane).
Figure S27: Change of the CD spectra of 2 at 60°C over time (n-heptane).

Figure S28: Change of the CD spectra of 2 at 70°C over time (n-heptane).
Figure S29: Change of the CD spectra of 2 at 85°C over time (n-heptane).

Figure S30: Change of the CD spectra of 2 at 100°C over time (n-heptane).
Figure S31: Time course of CD signal of 2 at 250 nm over time at different temperatures (red square: 25°C, yellow circle: 50°C, green triangle: 60°C, bright blue inversed triangle: 70°C, blue diamond: 85°C, purple left triangle: 100°C).

Figure S32: Arrhenius plot for the racemisation of 2. The data were fitted using a linear equation, as shown in the graph. Following the Arrhenius equation \( \ln(k) = -\frac{E_A}{R} \cdot \frac{1}{T} \), the activation energy is calculated by \( E_A = -b \cdot R \), where \( R \) is the gas constant.
6 Computational Details

6.1 Frontier Molecular Orbital analysis

All possible C₃-symmetric aza monkey saddles were investigated by their frontier molecular orbitals, as shown in Figure S33, using DFT methods (B3LYP/6-311G(d,p)).

![Energy levels and Frontier Molecular Orbitals](image)

Figure S33: DFT (B3LYP/6-311G(d,p)) analysis of the frontier molecular orbitals of 1, 2 and all other possible C₃-symmetrical Aza Monkey Saddles.

6.2 TD-DFT calculations

The absorption spectrum was reproduced using TD-DFT methods (B3LYP/6-311G(d,p)). Even if the overall shape of the spectrum fits only partially, the most prominent peaks are reproduced, as shown in Figure S34.

![Absorption spectra](image)

Figure S34: Comparison between the calculated absorption spectrum applying TD-DFT methods (B3LYP/6-311G(d,p)) (black, solid line) and the experimental spectrum (red, dotted line) of 2. Both spectra are recorded/calculated in/for DCM. The UV correction is 9 nm.
The assignment of the enantiomers was performed using the calculated ECD spectrum, shown in Figure S35. The best congruence between the shapes of the experimental and calculated spectra was achieved by using the BHandHLYP functional and the 6-311G(d,p) basis set. Not only the first maximum, which is used to assign the enantiomers,\(^{[520]}\) fits but also the rest of the spectrum is reproduced. The in red shown experimental CD spectrum was assigned to be the (S\(_a\)S\(_a\)S\(_a\)) enantiomer of 2.

Figure S35: Comparison between the experimental CD spectra for both enantiomers of 2 (top, (S\(_a\)S\(_a\)S\(_a\)): red, (R\(_a\)R\(_a\)R\(_a\)): black) and calculated ECD spectrum (BHandHLYP/6-311G(d,p), \(\sigma = 0.6\) eV) for the (S\(_a\)S\(_a\)S\(_a\)) enantiomer of compound 2. The assignment of the absolute configuration was accomplished by comparing experimental and simulated spectra.
6.2 NICS values and AICD calculations

To investigate the overall aromaticity and the difference between the both sides of the monkey saddles, we calculated the NICS(0) and NICS(1) values for 2 and compared them with the earlier reported values of the hydrocarbon monkey saddle 1,[18] which we extended for the NICS(1) values. For the splitting of the NICS(1) values we followed the suggestions of Lipiński and coworkers.[21]

As shown in Table S2, the overall trends for the different rings in the aza monkey saddle 2 are the same as in the parent structure 1. The six-membered rings A, C and E show an aromatic character, as indicated by negative NICS(0) and NICS(1)av values. In comparison between 1 and 2, the NICS values for the central ring A are smaller for 2. On the other hand are the five-membered ring B slightly more positive for the aza monkey saddle 2. The NICS(0) values for the five- and eight-membered rings B and D are for both structures positive, which means that there tend to be slightly antiaromatic. But the corresponding NICS(1)av values, which are less influenced by the σ electrons, are nearly zero and so the rings have mainly non-aromatic character. This is also displayed by the the NICS(1)bia values. For the six-membered rings A, C and E these values are quite small for both 1 and 2, but the rings B and D show large values between 3.4 and 4.7. This indicates a bigger influence of non-aromatic anisotropy effects on the NICS(0) values.

Table S2: Calculated NICS(0) and NICS(1) values for the Aza Monkey Saddle 2 and the Monkey Saddle 1 on the HF/6-31+G(d) level of theory (GIAO method). The different NICS(1) values are calculated following the suggestions of Lipiński and coworkers.[21] The picture on the right side shows from which side NICS(+1) and NICS(-1) values were defined.

| Ring | NICS(0) | NICS(-1) | NICS(+1) | NICS(1)av | NICS(1)diff | NICS(1)as | NICS(1)bia |
|------|---------|----------|----------|-----------|-------------|-----------|------------|
| A    | -5.6    | -4.4     | -8.6     | -6.5      | -4.3        | 1.0       | 0.9        |
| B    | 4.5     | 0.4      | -0.8     | -0.2      | -1.2        | -2.9      | 4.7        |
| C    | -9.0    | -9.5     | -8.9     | -9.2      | 0.5         | -0.1      | 0.2        |
| D    | 4.8     | 1.1      | 0.4      | 0.8       | -0.7        | 0.6       | 4.0        |
| E    | -9.1    | -9.9     | -10.0    | -10.0     | -0.1        | 0.0       | 0.9        |

Aza Monkey Saddle (X = CH, N) 2
The difference between both sides of the monkey saddles is only visible for the inner rings A and B. The NICS(1)_{diff} values are -4.3 for A and -1.2 for B for the Aza Monkey Saddle. In 1 the values are slightly larger (-5.4 and -2.0, respectively). For the other rings C-E NICS(1)_{diff} is in smaller than ±1.

The results of the NICS calculations are supported by the ring current analysis (AICD). The results are shown in Figure S36 and are for both structures nearly identical. The six-membered rings have an clockwise ring current, as expected for aromatic rings, which fits to the negative NICS(0) and NICS(1)_{av} values. The five- and eight-membered rings, where the NICS(1)_{av} values tend to be non-aromatic, are completely delocalized, but no main direction of the ring current can be observed. This supports the non-aromatic character.

### Table

| Ring | NICS(0) | NICS(-1) | NICS(+1) | NICS(1)_{av} | NICS(1)_{diff} | NICS(1)_{as} | NICS(1)_{bia} |
|------|---------|----------|----------|-------------|---------------|-------------|-------------|
| A    | -7.2    | -5.2     | -10.7    | -7.9        | -5.4          | 1.0         | 0.8         |
| B    | 1.7     | -0.7     | -2.7     | -1.7        | -2.0          | 2.8         | 3.4         |
| C    | -9.5    | -9.9     | -9.2     | -9.5        | 0.7           | -0.1        | 0.0         |
| D    | 5.4     | 2.0      | 1.2      | 1.6         | -0.8          | -0.4        | 3.8         |
| E    | -8.7    | -9.8     | -10.3    | -10.1       | -0.6          | 0.1         | 1.4         |

Figure S36: AICD analysis of both monkey saddles (the magnetic field points out of the paper plane). As the large arrows indicate, is the ring current in the six-membered rings clockwise, as expected for aromatic rings. For the five- and eight-membered rings is no uniform direction of the ring current visible. This indicates a non-aromatic character.
### 6.3 xyz coordinates of computed geometries

**($S_a$,$S_a$,$S_a$) enantiomer of 2**

| atom  | x     | y     | z     |
|-------|-------|-------|-------|
| C1    | -1.3888 | 0.2285 | 0.4717 |
| C2    | -0.8727 | -1.1043 | 0.4824 |
| C3    | 0.4965  | -1.3169 | 0.4715 |
| C4    | 1.3927  | -0.2036 | 0.4824 |
| C5    | 0.8923  | 1.0885  | 0.4715 |
| C6    | -0.5200 | 1.3080  | 0.4826 |
| C7    | 2.7281  | -0.6923 | 0.0239 |
| N8    | 3.9158  | -0.2431 | 0.1367 |
| C9    | 4.3598  | 0.8081  | 0.9448 |
| C10   | 3.9467  | 2.1523  | 0.9073 |
| C11   | 2.8991  | 2.7228  | 0.0164 |
| C12   | 1.5537  | 2.3293  | 0.0142 |
| C13   | -0.7645 | 2.7087  | 0.0239 |
| N14   | -1.7473 | 3.5127  | 0.1369 |
| C15   | -2.8793 | 3.3716  | 0.9456 |
| C16   | -3.8370 | 2.3418  | 0.9085 |
| C17   | -3.8077 | 1.1495  | 0.0174 |
| C18   | -2.7942 | 0.1810  | 0.0146 |
| C19   | -1.9636 | -2.0163 | 0.0236 |
| N20   | -2.1686 | -3.2695 | 0.1362 |
| C21   | -1.4805 | -4.1796 | 0.9445 |
| C22   | -0.1098 | -4.4940 | 0.9074 |
| C23   | 0.9083  | -3.8721 | 0.0167 |
| C24   | 1.2404  | -2.5103 | 0.0144 |
| C25   | 3.1987  | 3.8962  | -0.6929 |
| C26   | 2.2283  | 4.6820  | -1.3062 |
| C27   | 0.8707  | 4.3659  | -1.1630 |
| C28   | 0.5487  | 3.1851  | -0.4771 |
| C29   | 1.7748  | -4.7184 | -0.6923 |
| C30   | 2.9408  | -4.2711 | -1.3053 |
| C31   | 3.3459  | -2.9374 | -1.1622 |
| C32   | 2.4841  | -2.0679 | -0.4768 |
| C33   | -4.9740 | 0.8222  | -0.6914 |
| C34   | -5.1695 | -0.4109 | -1.3049 |
| C35   | -4.2168 | -1.4285 | -1.1625 |
| C36   | -3.0329 | -1.1171 | -0.4770 |
| C37   | -3.0792 | 4.4601  | 1.8174 |
| C38   | -4.1594 | 4.5154  | 2.6822 |
| C39   | -5.1044 | 3.4914  | 2.6630 |
| C40   | -4.9393 | 2.4347  | 1.7789 |
| C41   | 5.4029  | 0.4374  | 1.8163 |
| C42   | 5.9912  | 1.3456  | 2.6804 |
| C43   | 5.5768  | 2.6760  | 2.6608 |
| atom  | x     | y     | z     |
| C44   | 4.5787  | 3.0609 | 1.7770 |
| C45   | -2.3232 | -4.8974 | 1.8159 |
| C46   | -1.8312 | -5.8609 | 2.6803 |
| C47   | -0.4718 | -6.1673 | 2.6610 |
| C48   | 0.3609  | -5.4955 | 1.7774 |
| O49   | -0.1420 | 5.1083  | -1.6575 |
| C50   | -1.1729 | 6.9337  | -2.7676 |
| C51   | 0.1521  | 6.3214  | -2.3569 |
| O52   | -4.3535 | -2.6765 | -1.6574 |
| C53   | -5.5515 | -3.0282 | -2.3563 |
| C54   | 4.4953  | -2.4319 | -1.6565 |
| C55   | 6.5922  | -2.4525 | -2.7656 |
| O56   | 5.3992  | -3.2935 | -2.3550 |
| O57   | -5.1492 | -4.4816 | -2.7679 |
| H58   | 4.2340  | 4.2114  | -0.7529 |
| H59   | 2.5357  | 5.5588  | -1.8591 |
| C60   | 1.5302  | -5.7727 | -0.7521 |
| C66   | 3.5465  | -4.9759 | -1.8579 |
| C62   | -5.7647 | 1.5612  | -0.7509 |
| H63   | -6.0827 | -0.5830 | -1.8574 |
| H64   | -2.3500 | 5.2602  | 1.7841 |
| H65   | -4.2712 | 5.3584  | 3.3549 |
| H66   | -5.9623 | 3.5161  | 3.3249 |
| H67   | -5.6680 | 1.6325  | 1.7685 |
| H68   | 5.7312  | -0.5941 | 1.7833 |
| H69   | 6.7774  | 1.0212  | 3.3529 |
| H70   | 6.0274  | 3.4070  | 3.3221 |
| H71   | 4.2484  | 4.0931  | 1.7663 |
| H72   | -3.3807 | -4.6660 | 1.7826 |
| H73   | -2.5053 | -6.3795 | 3.3527 |
| H74   | -0.0643 | -6.9229 | 3.3226 |
| H75   | 1.4199  | -5.7255 | 1.7670 |
| H76   | -1.0032 | 7.8693  | -3.3069 |
| H77   | -1.7245 | 6.2513  | -3.4171 |
| H78   | -1.7864 | 7.1411  | -1.8891 |
| H79   | 0.7128  | 6.9991  | -1.7018 |
| H80   | 0.7722  | 6.1024  | -3.2349 |
| H81   | -6.4184 | -2.8820 | -1.7007 |
| H82   | -5.6724 | -2.3813 | -3.2339 |
| H83   | 6.2774  | -1.6340 | -3.4157 |
| H84   | 7.0781  | -2.0244 | -1.8871 |
| H85   | 7.3179  | -3.0676 | -3.3042 |
| H86   | 5.7053  | -4.1177 | -1.6993 |
| atom | x       | y       | z       |
|------|---------|---------|---------|
| H87  | 4.8998  | -3.7214 | -3.2330 |
| H88  | -6.3146 | -4.8023 | -3.3069 |

(S$_a$S$_a$R$_a$) enantiomer of 2

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C1   | -0.0113 | 1.4062  | -0.0831 |
| C2   | 1.2128  | 0.6825  | -0.1675 |
| C3   | 1.1928  | -0.7004 | -0.0471 |
| C4   | -0.0327 | -1.3973 | -0.1738 |
| C5   | -1.2118 | -0.6912 | -0.3758 |
| C6   | -1.2180 | 0.7210  | -0.1780 |
| C7   | 0.1603  | -2.7649 | 0.3832  |
| N8   | -0.4154 | -3.8894 | 0.2087  |
| O8   | -1.2112 | -4.2554 | -0.8878 |
| C10  | -2.3183 | -3.6038 | -1.4758 |
| C11  | -3.0806 | -2.4265 | -0.9619 |
| C12  | -2.5836 | -1.1568 | -0.6237 |
| C13  | 2.3279  | 1.6465  | -0.3020 |
| N14  | 3.5846  | 1.5363  | -0.4938 |
| C15  | 4.4537  | 0.4780  | -0.7325 |
| C16  | 4.5057  | -0.8308 | -0.1865 |
| C17  | 3.5668  | -1.4915 | 0.7695  |
| C18  | 2.1797  | -1.5926 | 0.5913  |
| C19  | -2.6390 | 1.1634  | -0.1479 |
| N20  | -3.2516 | 2.2069  | 0.2583  |
| C21  | -2.8941 | 3.3036  | 1.0305  |
| C22  | -1.7066 | 4.0730  | 1.0713  |
| C23  | -0.4894 | 3.9863  | 0.2099  |
| C24  | 0.3046  | 2.8507  | -0.0367 |
| C25  | 0.0900  | 5.2140  | -0.1570 |
| C26  | 1.4078  | 5.3495  | -0.5720 |
| C27  | 2.2596  | 4.2386  | -0.5729 |
| C28  | 1.6838  | 2.9831  | -0.3049 |
| C29  | 4.1084  | -2.3437 | 1.7482  |
| C30  | 3.3674  | -3.3198 | 2.4079  |
| C31  | 2.0341  | -3.5571 | 2.0457  |
| C32  | 1.4524  | -2.6779 | 1.1221  |
| C33  | -4.4817 | -2.5344 | -1.0025 |
| C34  | -5.3382 | -1.4535 | -0.8417 |
| C35  | -4.8262 | -0.1646 | -0.6478 |
| C36  | -3.4328 | -0.0357 | -0.5184 |
| C37  | -3.9546 | 3.6502  | 1.9004  |
| C38  | -3.8518 | 4.6458  | 2.8551  |
| C39  | -2.6629 | 5.3617  | 2.9456  |
| C40  | -1.6304 | 5.0737  | 2.0638  |
| C41  | -0.7615 | -5.4694 | -1.4481 |
| C42  | -1.2940 | -5.9949 | -2.6128 |
| C43  | -2.3349 | -5.3194 | -3.2427 |
| C44  | -2.8327 | -4.1600 | -2.6663 |
| C45  | 5.4704  | 0.8706  | -1.6345 |
| C46  | 6.4737  | 0.0185  | -2.0586 |
| C47  | 6.5157  | -1.2735 | -1.5442 |
| C48  | 5.5504  | -1.6689 | -0.6288 |
| C49  | -5.5963 | 0.9430  | -0.5778 |
| C50  | -7.5898 | 2.2255  | -0.7239 |
| C51  | -7.0087 | 0.8256  | -0.7758 |
| C52  | 3.5816  | 4.3112  | -0.8379 |
| C53  | 5.6599  | 5.3707  | -1.2891 |
| C54  | 4.1741  | 5.5913  | -1.0808 |
| C55  | 1.2646  | -4.5448 | 2.5494  |
| C56  | 0.7439  | -6.4565 | 3.8552  |
| C57  | 1.8266  | -5.4567 | 3.4983  |
| C58  | -0.5153 | 6.1092  | -0.0800 |
| C59  | 1.7736  | 6.3303  | -0.8406 |
| C60  | 5.1621  | -2.2530 | 1.9853  |
| C61  | 3.8494  | -3.9202 | 3.1669  |
| C62  | -4.9176 | -3.5079 | -1.1912 |
| C63  | -6.4045 | -1.6214 | -0.8978 |
| C64  | -4.8617 | 3.0704  | 1.7913  |
| C65  | -4.6851 | 4.8588  | 3.5149  |
| C66  | -2.5340 | 6.1389  | 3.6902  |
| C67  | -0.7053 | 5.6279  | 2.1569  |
| C68  | 0.0474  | -5.9687 | -0.9302 |
| C69  | -0.9007 | -6.9188 | -3.0216 |
| C70  | -2.7647 | -5.6927 | -4.1651 |
| C71  | -3.6468 | -3.6419 | -3.1579 |
| C72  | 5.4209  | 1.8931  | -1.9852 |
| C73  | 7.2182  | 0.3619  | -2.7678 |
| C74  | 7.2864  | -1.9716 | -1.8503 |
| C75  | 5.5759  | -2.6862 | -0.2594 |
| C76  | -8.6702 | 2.1883  | -0.8863 |
| C77  | -7.1415 | 2.8542  | -1.4954 |
| C78  | -7.4003 | 2.6871  | 0.2470  |
| C79  | -7.4433 | 0.1920  | 0.0070  |
| C80  | -7.2083 | 0.3556  | -1.7464 |
| C81  | 6.1603  | 6.3285  | -1.4546 |
| C82  | 5.8375  | 4.7333  | -2.1576 |
| atom | x      | y      | z      | atom | x      | y      | z      |
|------|--------|--------|--------|------|--------|--------|--------|
| H83  | 6.1018 | 4.8915 | -0.4137 | H87  | 0.4117 | -6.9942 | 2.9654 |
| H84  | 3.9933 | 6.2499 | -0.2227 | H88  | -0.1185 | -5.9473 | 4.2897 |
| H85  | 3.7194 | 6.0505 | -1.9669 | H89  | 2.1612 | -4.9072 | 4.3866 |
| H86  | 1.1251 | -7.1797| 4.5809  | H90  | 2.6968 | -5.9582 | 3.0576 |

### Aza Monkey Saddle S4

| atom | x      | y      | z      | atom | x      | y      | z      |
|------|--------|--------|--------|------|--------|--------|--------|
| C1   | -1.1976| 0.7444 | -0.3628| C40  | -5.3634| 1.5010 | -1.7873|
| C2   | 0.0650 | 1.4122 | -0.3456| C41  | 3.8444 | -4.1900| -1.5982|
| C3   | 1.2436 | 0.6649 | -0.3628| C42  | 3.6841 | -5.2678| -2.4555|
| C4   | 1.1907 | -0.7624| -0.3456| C43  | 2.4337 | -5.8691| -2.5616|
| C5   | -0.0458| -1.4095| -0.3627| C44  | 1.3821 | -5.3952| -1.7871|
| C6   | -1.2554| -0.6500| -0.3457| C45  | 1.7062 | 5.4242 | -1.5988|
| C7   | 2.5162 | -1.2723| 0.0625 | C46  | 2.7196 | 5.8242 | -2.4563|
| C8   | 3.1234 | -2.4755| -0.0625| C47  | 3.8656 | 5.0420 | -2.5625|
| C9   | 2.7769 | -3.6658| -0.8423| C48  | 3.9811 | 3.8944 | -1.7880|
| C10  | 1.5275 | -4.3100| -0.9046| C49  | -3.4717| -3.9808| 1.5157 |
| C11  | 0.3423 | -4.0080| -0.0559| C50  | -5.3571| -4.8981| 2.6468 |
| C12  | -0.3734| -2.7975| 0.0006 | C51  | -3.9463| -5.1786| 2.1688 |
| C13  | -0.1562| 2.8151 | 0.0624 | C52  | -1.7118| 4.9965 | 1.5165 |
| C14  | 0.5822 | 3.9425 | -0.0629| C53  | -1.5638| 7.0879 | 2.6476 |
| C15  | 1.7861 | 4.2376 | -0.8428| C54  | -2.5119| 6.0062 | 2.1699 |
| C16  | 2.9687 | 3.4777 | -0.9053| C55  | 5.1834 | -1.0157| 1.5161 |
| C17  | 3.3000 | 2.3004 | -0.0565| C56  | 6.9210 | -2.1894| 2.6469 |
| C18  | 2.6094 | 1.0753 | 0.0003 | C57  | 6.4582 | -0.8276| 2.1689 |
| C19  | -2.3599| -1.5429| 0.0621 | C58  | 4.1390 | -2.5001| 0.3125 |
| C20  | -3.7054| -1.4673| -0.0634| C59  | 0.0956 | 4.8344 | 0.3121 |
| C21  | -4.5630| -0.5719| -0.8430| C60  | -4.2345| -2.3347| 0.3112 |
| C22  | -4.4962| 0.8322 | -0.9050| C61  | -5.3614| 2.7971 | 0.6277 |
| C23  | -3.6421| 1.7075 | -0.0561| C62  | 5.1034 | 3.2446 | 0.6270 |
| C24  | -2.2359| 1.7220 | 0.0005 | C63  | 0.2581 | -6.0418| 0.6278 |
| C25  | -4.2770| 2.7797 | 0.5814 | C64  | -5.6244| -2.3129| -1.5148|
| C26  | -3.6602| 3.8211 | 1.1502 | C65  | -7.1403| -1.1022| -3.0348|
| C27  | -2.3447| 3.9038 | 1.0348 | C66  | -6.9466| 1.3816 | -3.2322|
| C28  | -1.5790| 2.8830 | 0.4437 | C67  | -5.2914| 2.5793 | -1.8626|
| C29  | 4.5461 | 2.3141 | 0.5807 | C68  | 4.8154 | -3.7144| -1.5137|
| C30  | 5.1397 | 1.2593 | 1.1495 | C69  | 4.5252 | -5.6322| -3.0342|
| C31  | 4.5535 | 0.0787 | 1.0344 | C70  | 2.7273 | -6.7063| -3.2322|
| C32  | 3.2864 | -0.0741| 0.4437 | C71  | 0.4122 | -5.8720| -1.8628|
| C33  | -0.2690| -5.0940| 0.5815 | C72  | 0.8087 | 6.0273 | -1.5142|
| C34  | -1.4795| -5.0806| 1.1499 | C73  | 2.6145 | 6.7348 | -3.0350|
| C35  | -2.2088| -3.9826| 1.0344 | C74  | 4.6687 | 5.3251 | -3.2332|
| C36  | -1.7074| -2.8091| 0.4435 | C75  | 4.8789 | 3.2929 | -1.8637|
| C37  | -5.5508| -1.2341| -1.5990| C76  | -5.7528| -5.7757| 3.1646 |
| C38  | -6.4042| -0.5562| -2.4561| C77  | -5.3724| -4.0535| 3.3389 |
| C39  | -6.2997| 0.8274 | -2.5618| C78  | -6.0185| -4.6690| 1.8080 |
Aza Monkey Saddle S5

| atom | x    | y    | z    |
|------|------|------|------|
| C1   | 0.1588 | -1.4020 | -0.3232 |
| C2   | -1.1458 | -0.8232 | -0.3136 |
| C3   | -1.2934 | 0.5634 | -0.3235 |
| C4   | -0.1400 | 1.4039 | -0.3134 |
| C5   | 1.1347 | 0.8384 | -0.3233 |
| C6   | 1.2859 | -0.5807 | -0.3132 |
| C7   | -0.5594 | 2.7655 | 0.0639 |
| C8   | 0.0092 | 3.9802 | -0.1088 |
| C9   | 1.1707 | 4.4137 | -0.8918 |
| C10  | 2.4596 | 3.8555 | -0.8924 |
| C11  | 2.9539 | 2.7445 | -0.0203 |
| C12  | 2.4318 | 1.4392 | 0.0316 |
| C13  | -2.1155 | -1.8672 | 0.0635 |
| C14  | -3.4517 | -1.9820 | -0.1092 |
| C15  | -4.4079 | -1.1926 | -0.8920 |
| C16  | -4.5689 | 0.2027 | -0.8923 |
| C17  | -3.8537 | 1.1860 | -0.0201 |
| C18  | -2.4622 | 1.3864 | 0.0315 |
| C19  | 2.6748 | -0.8983 | 0.0641 |
| C20  | 3.4424 | -1.9982 | -0.1082 |
| C21  | 3.2371 | -3.2211 | -0.8908 |
| C22  | 2.1092 | -4.0582 | -0.8913 |
| C23  | 0.8997 | -3.9304 | -0.0196 |
| C24  | 0.0304 | -2.8256 | 0.0318 |
| N25  | 0.5435 | -5.0859 | 0.5595 |
| N26  | -0.6524 | -5.2238 | 1.1301 |
| N27  | -1.6525 | -4.2513 | 1.0482 |
| C28  | -1.2995 | -3.0332 | 0.4536 |
| N29  | -4.6764 | 2.0720 | 0.5591 |
| C30  | -4.1979 | 3.1763 | 1.1304 |
| C31  | -2.8556 | 3.5561 | 1.0489 |
| C32  | -1.9771 | 2.6417 | 0.4541 |
| N33  | 4.1327 | 3.0141 | 0.5585 |
| C34  | 4.8502 | 2.0476 | 1.1295 |
| C35  | 4.5080 | 0.6952 | 1.0482 |
| C36  | 3.2766 | 0.3915 | 0.4539 |
| C37  | 4.3398 | -3.5758 | -1.6952 |

S31
| atom  | x    | y    | z    |
|-------|------|------|------|
| H75   | -5.6812 | 1.8375 | -1.7055 |
| H76   | 8.0428  | -1.1325 | 3.1979 |
| H77   | 6.4372  | -1.8811 | 3.2835 |
| H78   | 7.3667  | -1.9453 | 1.7762 |
| H79   | 7.1756  | 0.5454  | 1.5480 |
| H80   | 6.2629  | 0.6156  | 3.0705 |
| H81   | -5.0031 | -6.3968 | 3.1991 |
| H82   | -4.8487 | -4.6320 | 3.2832 |

### Aza Monkey Saddle S6

| atom  | x    | y    | z    |
|-------|------|------|------|
| C1    | 0.8803 | 1.1050 | 0.3495 |
| C2    | -0.5349 | 1.3048 | 0.3398 |
| C3    | -1.3970 | 0.2098 | 0.3497 |
| C4    | -0.8625 | -1.1157 | 0.3395 |
| C5    | 0.5168  | -1.3148 | 0.3494 |
| C6    | 1.3975  | -0.1892 | 0.3395 |
| C7    | -1.9399 | -2.0421 | -0.0573 |
| C8    | -2.1001 | -3.3707 | 0.1256 |
| C9    | -1.3546 | -4.3257 | 0.9484 |
| C10   | 0.0337  | -4.5521 | 0.9551 |
| C11   | 1.0358  | -3.8932 | 0.0643 |
| C12   | 1.2975  | -2.5152 | -0.0169 |
| C13   | 2.7386  | -0.6589 | -0.0570 |
| C14   | 3.9692  | -0.1334 | 0.1263 |
| C15   | 4.4234  | 0.9900  | 0.9488 |
| C16   | 3.9254  | 2.3057  | 0.9548 |
| C17   | 2.8536  | 2.8437  | 0.0638 |
| C18   | 1.5294  | 2.3812  | -0.0170 |
| C19   | -0.7988 | 2.7011  | -0.0566 |
| C20   | -1.8690 | 3.5041  | 0.1271 |
| C21   | -3.0687 | 3.3356  | 0.9500 |
| C22   | -3.9590 | 2.2465  | 0.9562 |
| C23   | -3.8895 | 1.0496  | 0.0649 |
| C24   | -2.8269 | 0.1340  | -0.0167 |
| C25   | 1.9595  | -4.7532 | -0.5427 |
| C26   | 3.1138  | -4.2999 | -1.1675 |
| C27   | 3.4552  | -2.9478 | -1.0924 |
| C28   | 2.5570  | -2.0640 | -0.4755 |
| C29   | -5.0961 | 0.6799  | -0.5422 |
| C30   | -5.2806 | -0.5462 | -1.1675 |
| C31   | -4.2803 | -1.5179 | -1.0928 |
| C32   | -3.0658 | -1.1822 | -0.4758 |
| C33   | 3.1365  | 4.0734  | -0.5436 |
| C34   | 2.1666  | 4.8462  | -1.1685 |
| C35   | 0.8250  | 4.4658  | -1.0929 |

| atom  | x    | y    | z    |
|-------|------|------|------|
| H83   | -5.3688 | -5.4061 | 1.7764 |
| H84   | -3.1162 | -6.4863 | 1.5498 |
| H85   | -2.5994 | -5.7295 | 3.0716 |
| H86   | -3.0392 | 7.5296  | 3.2016 |
| H87   | -1.5882 | 6.5132  | 3.2859 |
| H88   | -1.9976 | 7.3517  | 1.7794 |
| H89   | -4.0594 | 5.9412  | 1.5505 |
| H90   | -3.6635 | 5.1144  | 3.0722 |

C32

S32
### Aza Monkey Saddle S7

| atom  | x      | y     | z     |
|-------|--------|-------|-------|
| H71   | -2.1503| -6.7077| 3.2667|
| H72   | 0.3470 | -9.4166| 3.1765|
| H73   | -2.7337| 5.2921 | 1.7753|
| H74   | -4.7333| 5.2144 | 3.2697|
| H75   | -6.1846| 3.1687 | 3.1786|
| H76   | 7.3902 | -3.0060| -3.3261|
| H77   | 6.3295 | -1.6409| -3.4124|
| H78   | 7.2139 | -1.9977| -1.9192|
| H79   | 5.8692 | -4.0931| -1.6186|
| H80   | 5.0017 | -3.7552| -3.1311|

| atom  | x      | y     | z     |
|-------|--------|-------|-------|
| C     | 0.2734 | -1.3851| -0.3463|
| C2    | -1.0764| -0.9142| -0.3340|
| C3    | -1.3362| 0.4558 | -0.3464|
| C4    | -0.2535| 1.3893 | -0.3337|
| C5    | 1.0628 | 0.9293 | -0.3464|
| C6    | 1.3299 | -0.4751| -0.3336|
| C7    | 2.3048 | 1.6368 | 0.0210|
| C8    | 3.2170 | 0.6661 | 0.4872|
| C9    | 2.7395 | -0.6693| 0.0706|
| C10   | -2.5698| 1.1776 | 0.0214|
| C11   | -2.1850| 2.4528 | 0.4877|
| C12   | -0.7900| 2.7071 | 0.0705|
| C13   | 0.2649 | -2.8144| 0.0214|
| C14   | -1.0321| -3.1188| 0.4871|
| C15   | -1.9496| -2.0377| 0.0698|
| C16   | 2.6874 | 2.9870 | 0.0584|
| C17   | 3.8820 | 3.3407 | 0.5831|
| C18   | 4.7093 | 2.4105 | 1.2052|
| C19   | 4.4142 | 1.0492 | 1.1142|
| C20   | -3.9304| 0.8339 | -0.0575|
| C21   | -4.8337| 1.6913 | 0.5849|
| C22   | -4.4414| 2.8726 | 1.2074|
| C23   | -3.1151| 3.2978 | 1.1156|
| C24   | 1.2430 | -3.8208| -0.0568|
| C25   | 0.9518 | -5.0319| 0.5854|
| C26   | -0.2677| -5.2829| 1.2071|
| C27   | -1.2992| -4.3468| 1.1147|
| C28   | 5.2200 | 0.0648 | 1.6015|
| C29   | 6.4110 | 0.4227 | 2.3129|
| C30   | 7.0686 | -0.8615| 2.7793|
| O31   | -2.6651| 4.4877 | 1.6032|
| C32   | -3.5700| 5.3393 | 2.3163|
| C33   | -2.7864| 6.5504 | 2.7835|

| atom  | x      | y     | z     |
|-------|--------|-------|-------|
| O34   | -2.5549| -4.5522| 1.6013|
| C35   | -2.8407| -5.7621| 2.3135|
| C36   | -4.2820| -5.6894| 2.7788|
| C37   | 2.4256 | -3.8081| -0.9584|
| C38   | 3.6023 | -1.6948| -0.1044|
| C39   | 3.4878 | -2.8940| -0.9361|
| C40   | 4.5784 | -3.1540| -1.7850|
| C41   | 4.5564 | -4.2412| -2.6427|
| C42   | 5.3288 | -5.0942| -2.7103|
| C43   | 2.5105 | -4.8661| -1.8841|
| C44   | -0.3335| 3.9670 | -0.1052|
| C45   | 0.7619 | 4.4671 | -0.9377|
| C46   | 2.0846 | 4.0042 | -0.9603|
| C47   | 0.4412 | 5.5409 | -1.7872|
| C48   | 1.3934 | 6.0650 | -2.6456|
| C49   | 2.6459 | 5.6017 | -2.7134|
| C50   | 2.9579 | 4.6063 | -1.8868|
| C51   | -3.2690| -2.2722| -0.1062|
| C52   | -4.2498| -1.5731| -0.9382|
| C53   | -4.5103| -0.1962| -0.9599|
| C54   | -5.4685| 0.2598 | -1.8859|
| N55   | -6.1747| -0.5076| -2.7129|
| C56   | -5.9497| -1.8240| -2.6460|
| C57   | -5.0195| -2.3871| -1.7881|
| C58   | 4.1828 | 4.3819 | 0.5814|
| C59   | 5.6025 | 2.7535 | 1.7079|
| H60   | -5.8857| 1.4312 | 0.5836|
| H61   | -5.1848| 3.4744 | 1.7108|
| H62   | 1.7031 | -5.8128| 0.5846|
| H63   | -0.4176| -6.2275| 1.7104|
| H64   | 7.0788 | 0.9898 | 1.6538|
| H65   | 6.1485 | 1.0593 | 3.1657|
| H66   | 7.9746 | -0.6318| 3.3459|

S33
| atom | x     | y     | z     |
|------|-------|-------|-------|
| H67  | 6.3917| -1.4281| 3.4216|
| H68  | 7.3449| -1.4884| 1.9289|
| H69  | -4.3956| 5.6347| 1.6582|
| H70  | -3.9893| 4.7927| 3.1689|
| H71  | -3.4379| 7.2195| 3.3513|
| H72  | -1.9567| 6.2468| 3.4248|
| H73  | -2.3822| 7.1041| 1.9334|
| H74  | -2.6828| -6.6245| 1.6552|
| H75  | -2.1588| -5.8521| 3.1669|
| H76  | -4.5363| -6.5883| 3.3460|
| H77  | -4.4350| -4.8193| 3.4202|
| H78  | -4.9625| -5.6160| 1.9279|

| atom | x     | y     | z     |
|------|-------|-------|-------|
| H79  | 4.6082| -1.5166| 0.2526|
| H80  | 5.4349| -2.4893| -1.7752|
| H81  | 5.3944| -4.4393| -3.3051|
| H82  | 1.6837| -5.5677| -1.9476|
| H83  | -0.9907| 4.7492| 0.2518|
| H84  | -0.5627| 5.9502| -1.7773|
| H85  | 1.1456| 6.8893| -3.3085|
| H86  | 3.9789| 4.2410| -1.9506|
| H87  | -3.6178| -3.2326| 0.2503|
| H88  | -5.6627| 1.3267| -1.9488|
| H89  | -6.5397| -2.4503| -3.3093|
| H90  | -4.8720| -3.4612| -1.7790|

**Aza Monkey Saddle S8**

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C1   | 1.1047| -0.8793| 0.3427|
| C2   | 1.3070| 0.5353| 0.3277|
| C3   | 0.2091| 1.3964| 0.3427|
| C4   | -1.1170| 0.8643| 0.3279|
| C5   | -1.3139| -0.5171| 0.3426|
| C6   | -0.1900| -1.3995| 0.3277|
| C7   | -2.0417| 1.9466| -0.0692|
| C8   | -3.3705| 2.1198| 0.1111|
| C9   | -4.3272| 1.3736| 0.9255|
| C10  | -4.5232| -0.0145| 0.9618|
| C11  | -3.8909| -1.0222| 0.0672|
| C12  | -2.5146| -1.2960| -0.0180|
| C13  | -0.6650| -2.7414| -0.0695|
| C14  | -0.1507| -3.9788| 0.1110|
| C15  | 0.9736| -4.4343| 0.9256|
| C16  | 2.2738| -3.9098| 0.9626|
| C17  | 2.8308| -2.8585| 0.0682|
| C18  | 2.3797| -1.5297| -0.0176|
| C19  | 2.7065| 0.7948| -0.0695|
| C20  | 3.5210| 1.8590| 0.1104|
| C21  | 3.3535| 3.0606| 0.9249|
| C22  | 2.2493| 3.9244| 0.9619|
| C23  | 1.0601| 3.8808| 0.0677|
| C24  | 0.1349| 2.8258| -0.0176|
| C25  | -4.7557| -1.9251| -0.5656|
| C26  | -4.3093| -3.0847| -1.1908|
| C27  | -2.9631| -3.4443| -1.1034|
| C28  | -2.0724| -2.5551| -0.4790|
| C29  | 0.7104| 5.0814| -0.5646|
| C30  | -0.5172| 5.2747| -1.1895|
| C31  | -1.5016| 4.2886| -1.1023|

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C32  | -1.1767| 3.0725| -0.4784|
| C33  | 4.0455| -3.1561| -0.5638|
| C34  | 4.8267| -2.1898| -1.1890|
| C35  | 4.4648| -0.8442| -1.1024|
| C36  | 3.2491| -0.5173| -0.4786|
| C37  | 0.7012| -5.5477| 1.7480|
| N38  | 1.5491| -6.1028| 2.6067|
| C39  | 2.7666| -5.5537| 2.6769|
| C40  | 3.1631| -4.4872| 1.8832|
| C41  | -5.1553| 2.1660| 1.7481|
| N42  | -6.0602| 1.7089| 2.6063|
| C43  | -6.1937| 0.3800| 2.6758|
| C44  | -5.4682| -0.4964| 1.8818|
| C45  | 4.4541| 3.3815| 1.7470|
| N46  | 4.5111| 4.3936| 2.6053|
| C47  | 3.4269| 5.1736| 2.6756|
| C48  | 2.3048| 4.9835| 1.8821|
| O49  | -2.4585| -4.6111| -1.5918|
| C50  | -2.4840| -6.6808| -2.7657|
| C51  | -3.3241| -5.5083| -2.2978|
| O52  | 5.2231| 0.1761| -1.5908|
| C53  | 6.4332| -0.1250| -2.2963|
| O54  | -2.7644| 4.4351| -1.5905|
| C55  | -4.5445| 5.4920| -2.7638|
| C56  | -3.1090| 5.6335| -2.2961|
| C57  | 7.0286| 1.1887| -2.7643|
| H58  | -3.7570| 3.0689| -0.2370|
| H59  | -0.7793| -4.7880| -0.2372|
| H60  | 4.5360| 1.7191| -0.2380|
| H61  | -5.8193| -1.7174| -0.5570|
| H62  | -5.0241| -3.7222| -1.6915|

S34
| atom  | x     | y     | z     |
|-------|-------|-------|-------|
| H63   | 1.4219| 5.8987| -0.5557|
| H64   | -0.7121| 6.2127| -1.6897|
| H65   | 4.3975| -4.1809| -0.5546|
| H66   | 5.7365| -2.4902| -1.6891|
| H67   | -0.2862| -6.0005| 1.6950|
| H68   | 3.4571| -5.9972| 3.3888|
| H69   | -5.0535| 3.2475| 1.6957|
| H70   | -6.9233| 0.0035| 3.3872|
| H71   | 5.3399| 2.7528| 1.6940|
| H72   | 3.6460| 5.9935| 3.3872|
| H73   | -3.1046| -7.3828| -3.3283|
| H74   | -1.6736| -6.3385| -3.4121|
| H75   | -2.0488| -7.2113| -1.9161|
| H76   | -4.1305| -5.8422| -1.6343|

| atom  | x     | y     | z     |
|-------|-------|-------|-------|
| H77   | -3.7743| -4.9856| -3.1497|
| H78   | 7.1254| -0.6562| -1.6325|
| H79   | 6.2059| -0.7765| -3.1481|
| H80   | -4.6532| 4.6192| -3.4105|
| H81   | -5.2213| 5.3800| -1.9142|
| H82   | -4.8424| 6.3806| -3.3260|
| H83   | -2.9950| 6.4986| -1.6324|
| H84   | -2.4314| 5.7623| -3.1480|
| H85   | 7.9472| 1.0021| -3.3264|
| H86   | 6.3273| 1.7191| -3.4113|
| H87   | 7.2699| 1.8311| -1.9149|
| H88   | 4.1699| -4.0978| 1.9719|
| H89   | 1.4644| 5.6608| 1.9708|
| H90   | -5.6346| -1.5630| 1.9699|

### Aza Monkey Saddle S9

| atom  | x     | y     | z     |
|-------|-------|-------|-------|
| C1    | -0.9797| 1.0154| 0.3381|
| C2    | -1.3661| -0.3610| 0.3220|
| C3    | -0.3896| -1.3562| 0.3381|
| C4    | 0.9956| -1.0026| 0.3223|
| C5    | 1.3693| 0.3407| 0.3382|
| C6    | 0.3705| 1.3635| 0.3222|
| C7    | 1.7698| -2.1958| -0.0836|
| C8    | 3.0665| -2.5426| 0.0756|
| C9    | 4.1181| -1.9463| 0.9063|
| C10   | 4.4714| -0.5878| 0.9688|
| C11   | 3.9851| 0.4951| 0.6969|
| C12   | 2.6604| 0.9541| -0.0212|
| C13   | 1.0167| 2.6305| -0.0840|
| C14   | 0.6688| 3.9268| 0.0749|
| C15   | -0.3731| 4.5395| 0.9060|
| C16   | -1.7263| 4.1662| 0.9690|
| C17   | -2.4214| 3.2037| 0.0700|
| C18   | -2.1565| 1.8270| -0.0210|
| C19   | -2.7865| -0.4347| 0.0842|
| C20   | -3.7352| -1.3843| 0.0744|
| C21   | -3.7450| -2.5932| 0.9050|
| C22   | -2.7451| -3.5785| 0.9681|
| C23   | -1.5637| -3.6989| 0.0693|
| C24   | -0.5038| -2.7811| -0.0212|
| C25   | 4.9654| 1.2731| -0.5607|
| C26   | 4.6811| 2.4839| -1.1847|
| C27   | 3.3941| 3.0202| -1.1069|
| C28   | 2.3895| 2.2583| -0.4876|
| C29   | -1.3799| -4.9368| -0.5608|

| atom  | x     | y     | z     |
|-------|-------|-------|-------|
| C30   | -0.1890| -5.2962| -1.1844|
| C31   | 0.9190| -4.4498| -1.1062|
| C32   | 0.7612| -3.1987| -0.4872|
| C33   | -3.5853| 3.6638| 0.5600|
| C34   | -4.4920| 2.8123| -1.1838|
| C35   | -4.3130| 1.4295| -1.1063|
| C36   | -3.1506| 0.9403| -0.4874|
| N37   | 0.1236| 5.5641| 1.6307|
| C38   | -0.6592| 6.1848| 2.5064|
| C39   | -1.9919| 5.8386| 2.7071|
| C40   | -2.5218| 4.8307| 1.9148|
| N41   | 4.7572| -2.8886| 1.6313|
| C42   | 5.6863| -2.5206| 2.5068|
| C43   | 6.0527| -1.1933| 2.7069|
| C44   | 5.4447| -0.2307| 1.9143|
| N45   | -4.8810| -2.6757| 1.6294|
| C46   | -5.0273| -3.6644| 2.5048|
| C47   | -4.0610| -4.6453| 2.7054|
| C48   | -2.9229| -4.5999| 1.9134|
| O49   | 3.0515| 4.2407| -1.6015|
| C50   | 3.3746| 6.3239| -2.7001|
| C51   | 4.0448| 5.0390| -2.2535|
| O52   | -5.1987| 0.5227| -1.6008|
| C53   | -6.3871| 0.9839| -2.2522|
| O54   | 2.1474| -4.7633| -1.6004|
| C55   | 3.7903| -6.0848| -2.6986|
| C56   | 2.3423| -6.0227| -2.2525|
| C57   | -7.1651| -0.2389| -2.6985|
| H58   | 3.3357| -3.5356| -0.2538|

S35
| atom | x    | y    | z    | atom | x    | y    | z    |
|------|------|------|------|------|------|------|------|
| H59  | 1.394| 4.656| -0.2547 |
| H60  | -4.7297| -1.1209| -0.2551 |
| H61  | 5.9916| 0.9242| -0.5490 |
| H62  | 5.4775| 3.0211| -1.6803 |
| H63  | -2.1.952| -5.6511| -0.5494 |
| H64  | -0.1218| -6.2544| -1.6799 |
| H65  | -3.7963| 4.7270| -0.5481 |
| H66  | -5.3555| 3.2334| -1.6791 |
| H67  | -2.5976| 6.3546| 3.4424 |
| H68  | 6.8026| -0.9264| 3.4420 |
| H69  | -4.2052| -5.4282| 3.4404 |
| H70  | 4.0954| 6.9592| -3.2214 |
| H71  | 2.5469| 6.1086| -3.3787 |
| H72  | 2.9843| 6.8752| -1.8423 |
| H73  | 4.8672| 5.2454| -1.5584 |
| H74  | 4.4500| 4.4902| -3.1119 |
| H75  | -6.9767| 1.5928| -1.5568 |
| H76  | -6.1148| 1.6092| -3.1108 |
| H77  | 4.0179| -5.2603| -3.3772 |
| H78  | 4.4626| -6.0223| -1.8405 |
| H79  | 3.9802| -7.0267| -3.2197 |
| H80  | 2.1.097| -6.8382| -1.5575 |
| H81  | 1.6647| -6.0991| -3.1112 |
| H82  | -8.0759| 0.0678| -3.2192 |
| H83  | -6.5651| -0.8480| -3.3775 |
| H84  | -7.4469| -0.8526| -1.8406 |
| H85  | -3.5630| 4.5473| 2.0159 |
| H86  | -2.1569| -5.3599| 2.0146 |
| H87  | 5.7199| 0.8128| 2.0150 |
| H88  | 6.1619| -3.3220| 3.0663 |
| H89  | -5.9593| -3.6756| 3.0638 |
| H90  | -0.2028| 6.9974| 3.0658 |

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