Dynamic Stereoisomerization in Inherently Chiral Bimetallic [2]Catenanes

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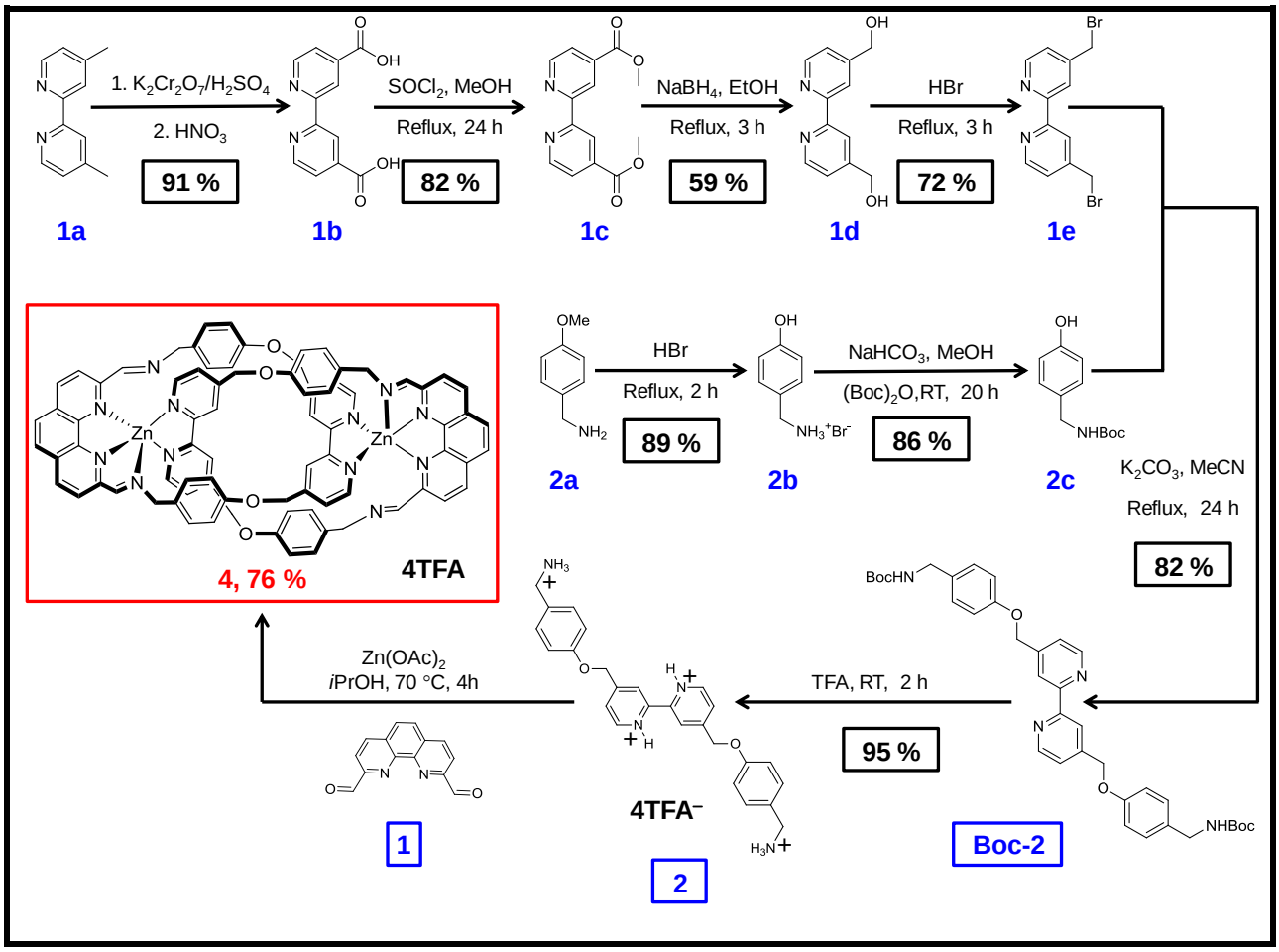
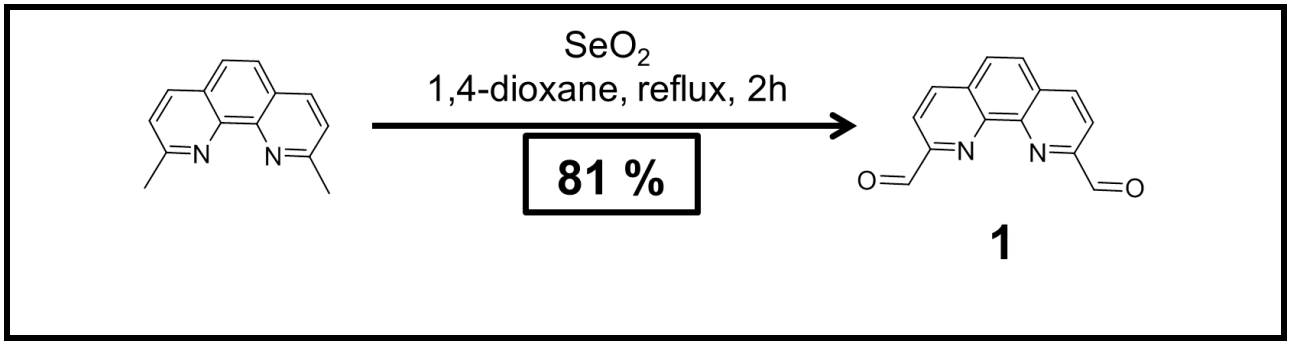
1. General materials and methods

All reagents and starting materials were purchased from Sigma-Aldrich and used without further purification. The diamino bipyridine (DAB) ligand, **2**, was synthesized as reported earlier.[1] The new chiral DAB ligand, **3**, and 2,9-diformyl-1,10-phenanthroline ligand, **1**, were synthesized as described in the synthesis section. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). The plates were inspected with UV light. Column chromatography was performed on silica gel 60F (Merck 9385, 0.040–0.063 mm). Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance 600 spectrometer, with working frequencies of 600 and 500 MHz for ^{1}H, and 151.0 MHz for ^{13}C nuclei, respectively. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvents (CD_3CN: δ = 1.94 ppm, CD_3OD: δ = 3.31 ppm).[2] All ^{13}C spectra were recorded with the simultaneous decoupling of proton nuclei. Coupling constant values (*J*) are given in hertz (Hz), the multiplicity is abbreviated in the following way: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), qt (quintet), sx (sextet), m (multiplet). A wide signal is preceded by br (broad). High resolution mass spectrometry (HRMS) analyses were performed using an Agilent 6540 UHA Accurate Mass Q-TOF / LC - MS-spectrometer in the positive mode and an acetonitrile/water gradient on a C-18 column. Circular dichroism spectra were measured at room temperature using a Chirascan CD Spectrometer from Applied Photophysics.

2. Synthetic strategy employed in the preparation of the the [2]catenanes, 4

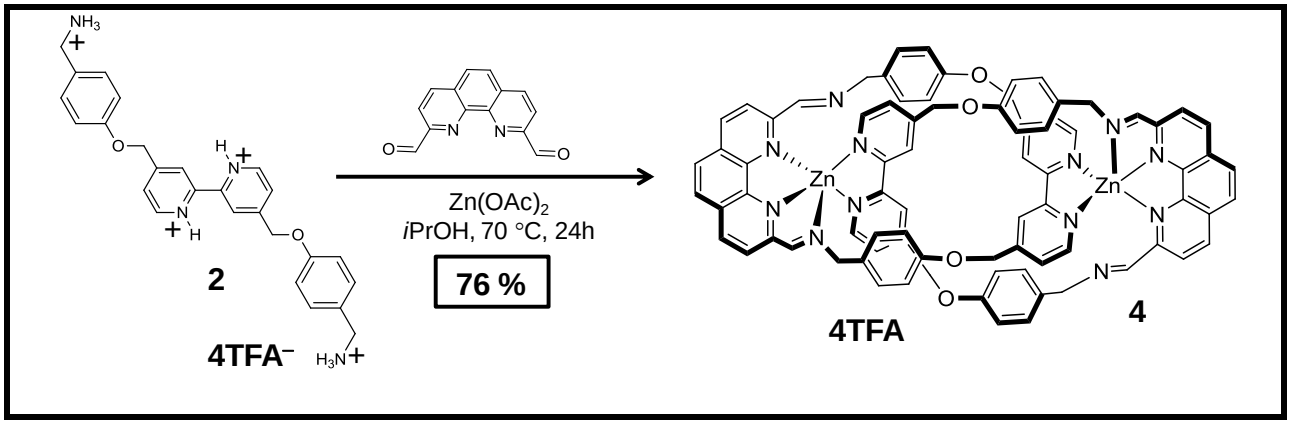


3: Synthesis of 2,9-diformyl 1, 10-phenanthroline, 1



2,9-diformyl-1,10-phenanthroline (**1**) was synthesized as described in the literature from 2,9-dimethyl-1,10-phenanthroline using selenium dioxide oxidation.[3] A mixture of 2,9-dimethyl-1,10-phenanthroline (3.0 g, 14.4 mmol) and selenium dioxide (7.5 g, 67.6 mmol) in dioxane with 4% water (200 ml) was heated under reflux for 2 hours, after which the hot reaction mixture was filtered through a bed of Celite. Yellow crystals of **1** precipitated from the filtrate upon cooling to 0 °C. The crystals were collected by filtration and purified by recrystallization from hot dioxane. Yield: 2.8 g, 81%; ^{1}H NMR (600 MHz, DMSO-d6, 25 °C): δ 8.30 (s, 2H, Ar-*H*), 8.32 (d, 2H, *J* = 8.4 Hz, Ar-*H*), 8.80 (d, 2H, *J* = 6.0 Hz, Ar-*H*), 10.37 (s, 2H, Ar-*H*); ^{13}C NMR (75 MHz, DMSO-d6, 25 °C): δ 120.6, 129.7, 131.9, 138.9, 145.7, 152.6, 194.2.

4: Synthesis of Zinc Phenanthroline 2-Catenane, 4



Freshly deprotected **2** (0.22 g, 0.25 mmol) was stirred with diformyl-1,10-phenanthroline (0.059 g, 0.25 mmol) and zinc acetate (0.055 g, 0.25 mmol) in 15 ml of isopropanol. The reaction mixture was refluxed at 65 °C for 20 h. After 2-3 h, a pale yellow solid started to precipitate, and after 20 h, the reaction mixture was cooled to room temperature. The pale yellow precipitate was filtered and dried under vacuum for 2 h to give **4**. Yield: 0.174 g, 76%; ^{1}H NMR (600 MHz, ACN-d3, 25 °C): δ 4.58 (s, 8H, Ar-CH_2), 4.99 (s, 8H, Ar-CH_2), 6.46 (s, 8H, Ar-*H*), 6.78 (s, 8H, Ar-*H*), 7.11 (d, 4H, *J* = 8.4 Hz, Ar-*H*), 7.36 (s, 4H, Ar-*H*), 7.40 (d, 4H, *J* = 8.4 Hz, Ar-*H*), 7.54 (brs, 4H, Ar-*H*), 8.41 (s, 4H, Ar-*H*), 8.50 (d, 4H, *J* = 7.8 Hz, Ar-*H*), 9.03 (d, 4H, *J* = 4.8 Hz, Ar-*H*); ^{13}C NMR (125 MHz, ACN-d4, 25 °C): δ 62.1, 67.8, 114.9, 115.8, 116.7 (q, $^{2}J_{C\text{-}F}$ = 275 Hz, TFA), 120.6, 124.6, 127.3, 128.5, 130.9, 131.1, 132.4, 141.4, 147.1, 148.6, 149.3, 151.6, 157.4, 158.3 (q, $^{3}J_{C\text{-}F}$ = 33 Hz. TFA); MS (ESI-HRMS): m/z Calcd for $(C_{84}H_{64}F_6N_{12}O_8Zn_2)^{2+}$: 805.1723 $(M^+–2TFA+ 2H)^{2+}$, found: 805.1618, $(M^+–2TFA+ 2H)^{2+}$, m/z Calcd for $(C_{82}H_{64}F_3N_{12}O_6Zn_2)^{3+}$: 499.1196 $(M^+–3TFA+ 3H)^{3+}$, found: 499.1130 $(M^+–3TFA+ 3H)^{3+}$, m/z Calcd for $(C_{80}H_{64}N_{12}O_4Zn_2)^{4+}$: 346.093 $(M^+–3TFA+ 4H)^{4+}$, found: 346.089 $(M^+–3TFA+ 4H)^{4+}$.

The ^{1}H NMR spectrum of **4** in CD_3CN is presented in Figure S1. All the assignments have been made based on ^{1}H–^{1}H gradient-selected double-quantum filtered phase-sensitive COSY, recorded in CD_3CN at 298 K. Some of the key correlation peaks are labeled in the spectrum.

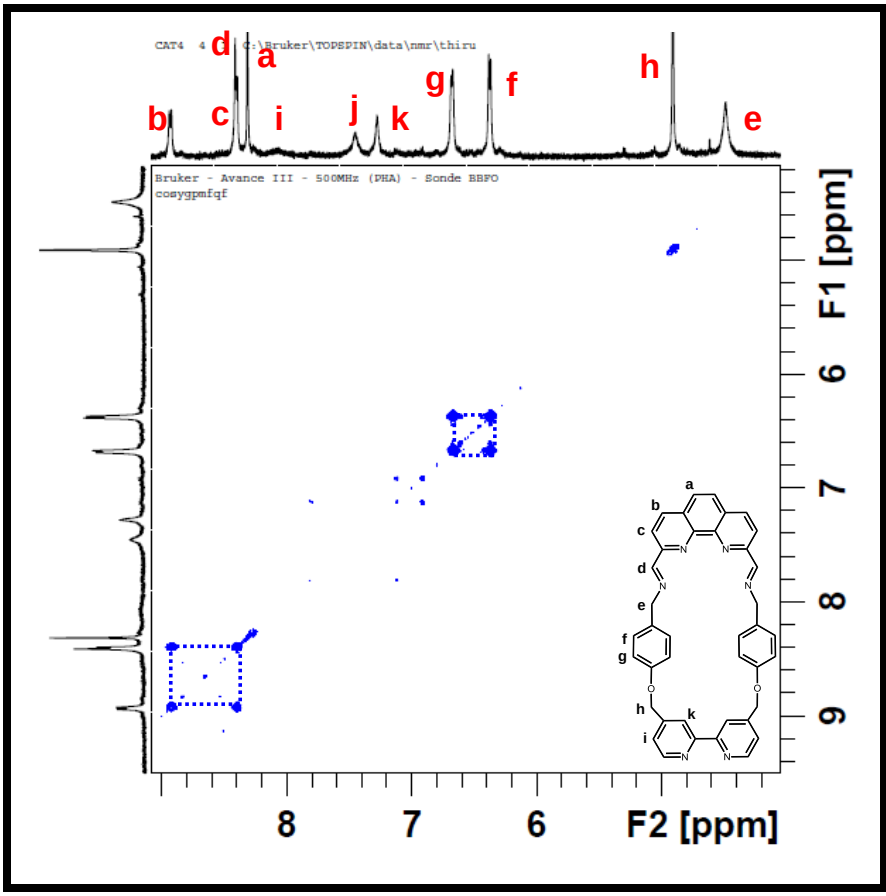


Figure S1.1. ^{1}H–^{1}H Gradient-selected double-quantum filtered phase-sensitive COSY NMR of **4** in CD_3CN at 298 K (500 MHz).

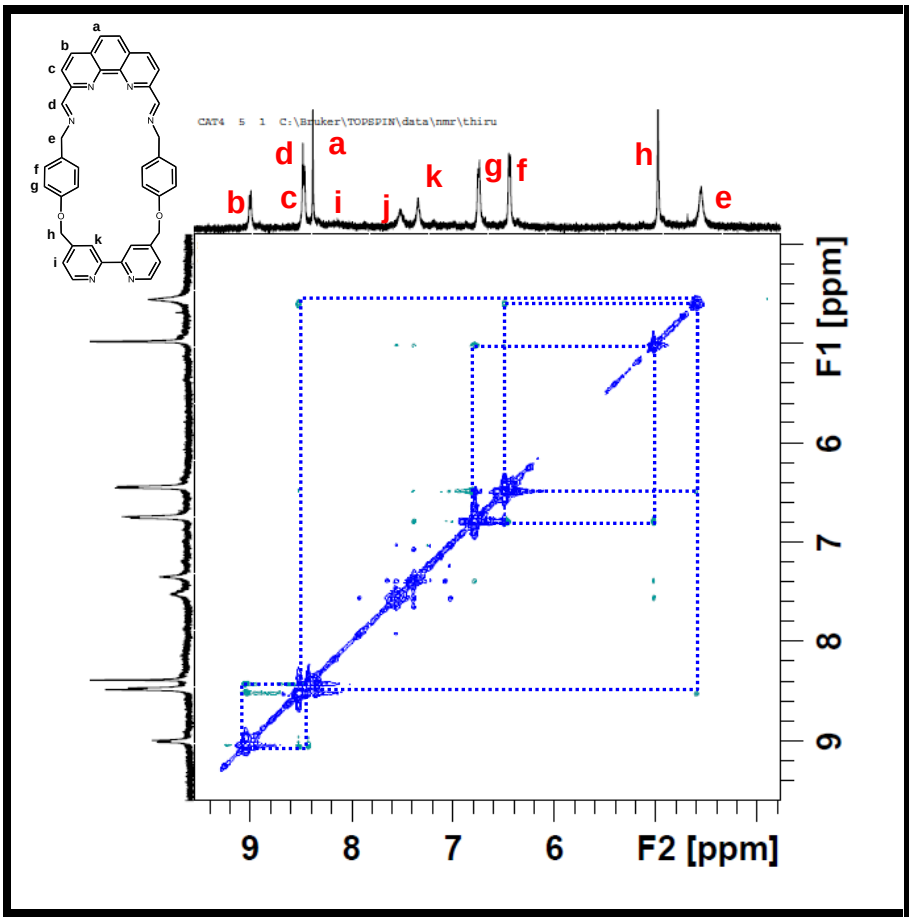


Figure S1.2. $^{1}H–^{1}H$ gradient-selected NOESY of **4** in CD_3CN at 298 K (500 MHz).

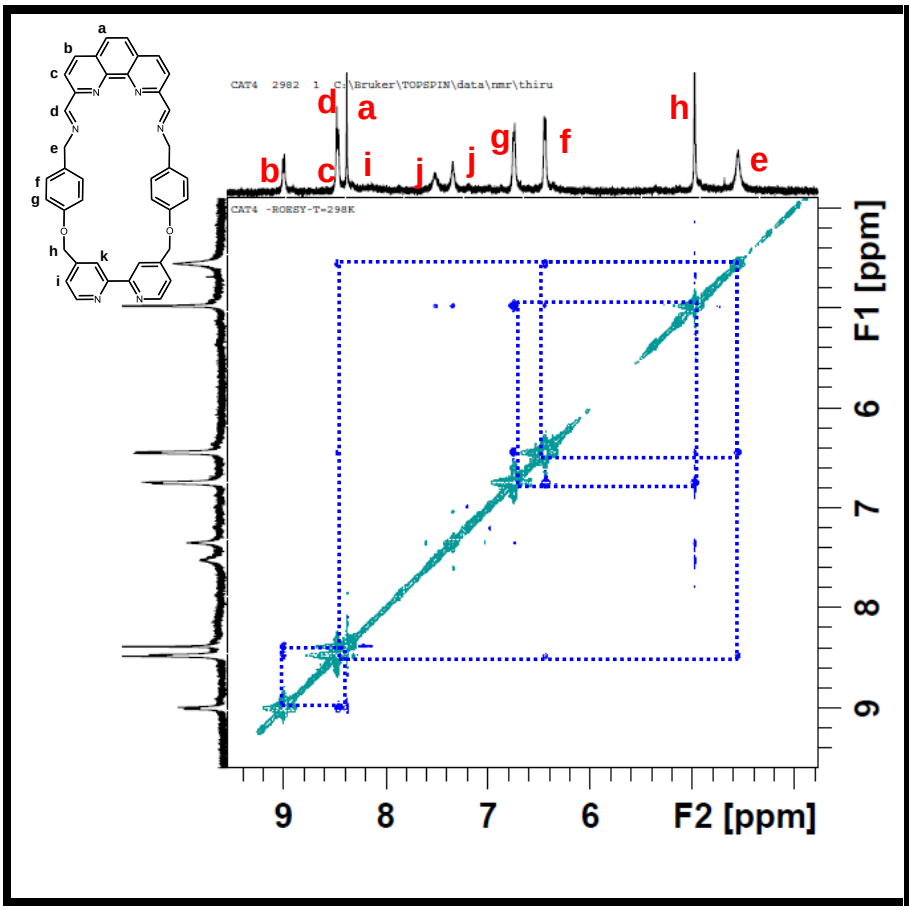


Figure S1.3. $^{1}H–^{1}H$ gradient-selected ROESY of **4** in CD_3CN at 298 K (500 MHz).

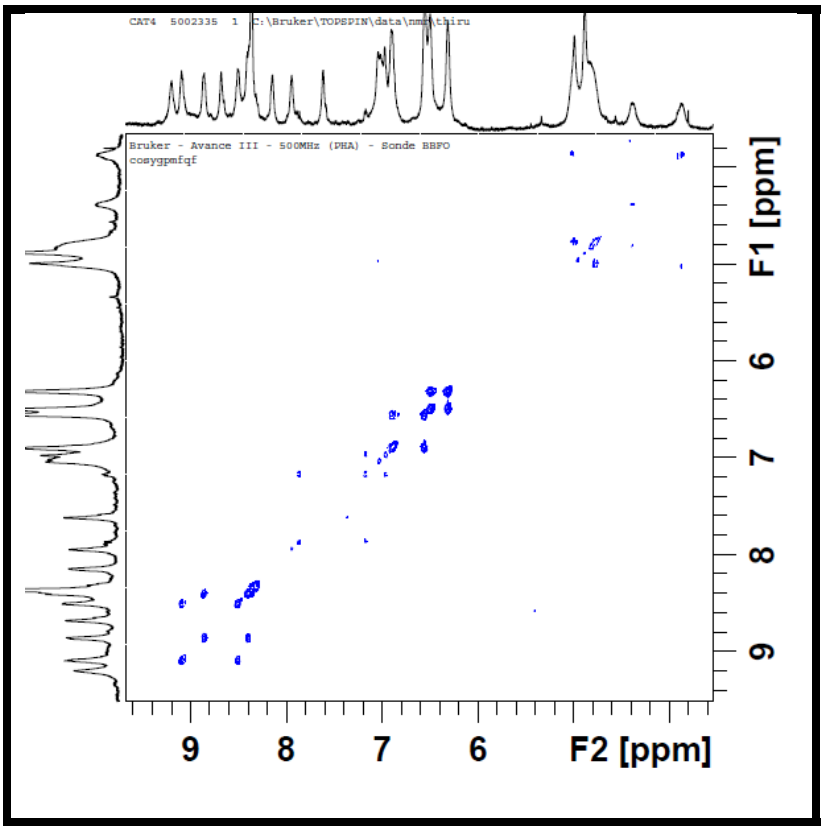


Figure S1.4. ^{1}H–^{1}H Gradient-selected double-quantum filtered phase-sensitive COSY NMR of **4** in CD_3CN at 233 K (500 MHz).

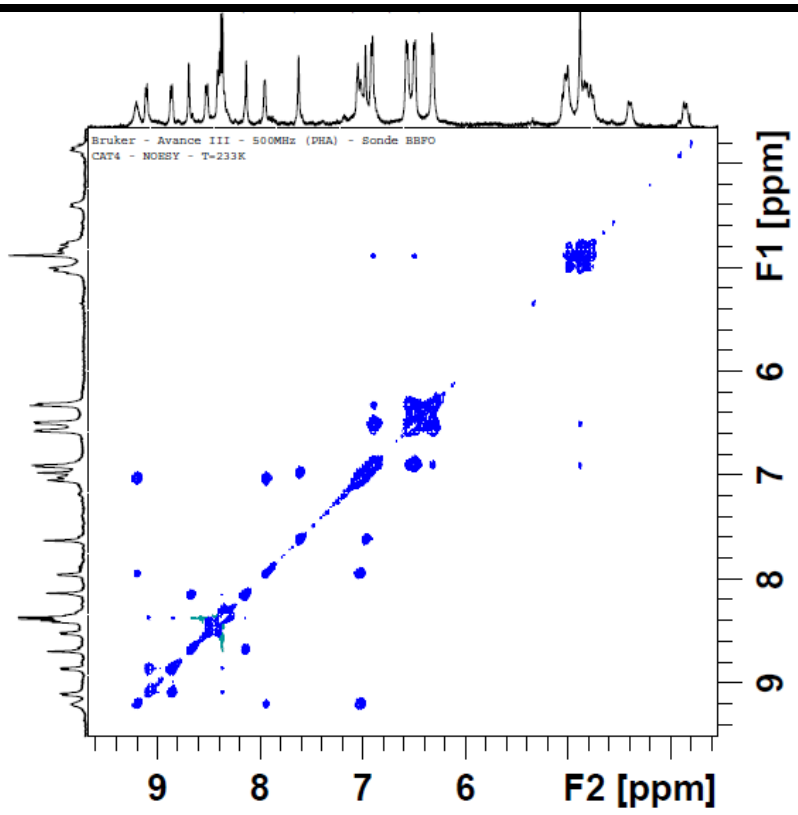


Figure S1.5. $^{1}H–^{1}H$ gradient-selected NOESY of **4** in CD_3CN at 298 K (500 MHz).

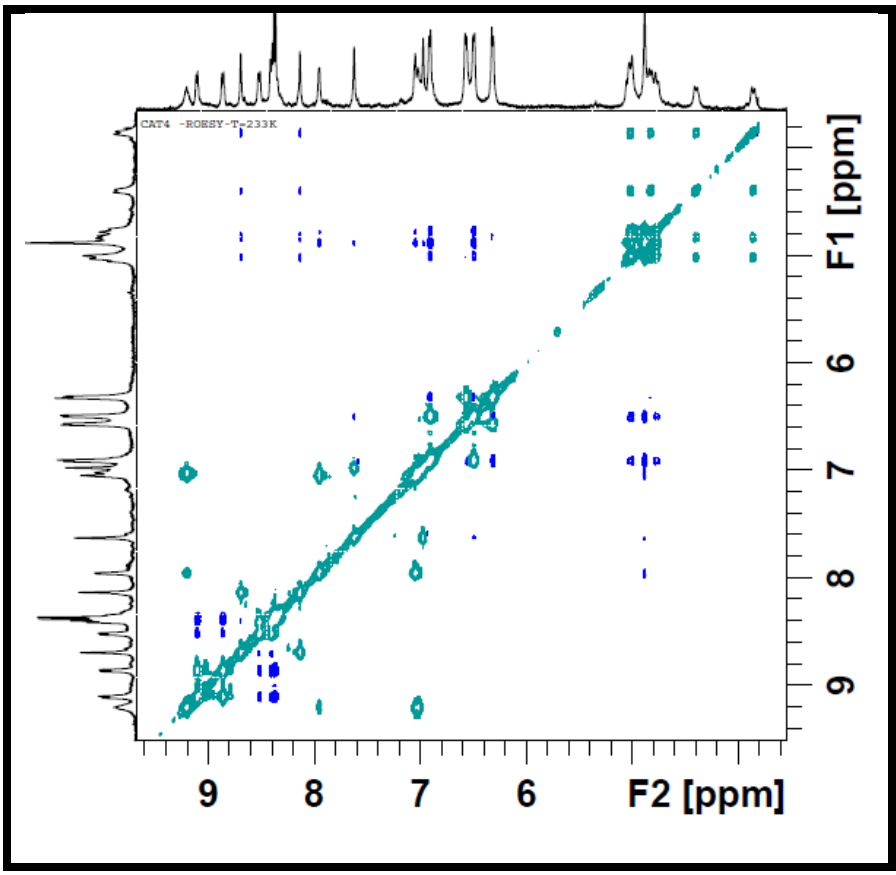
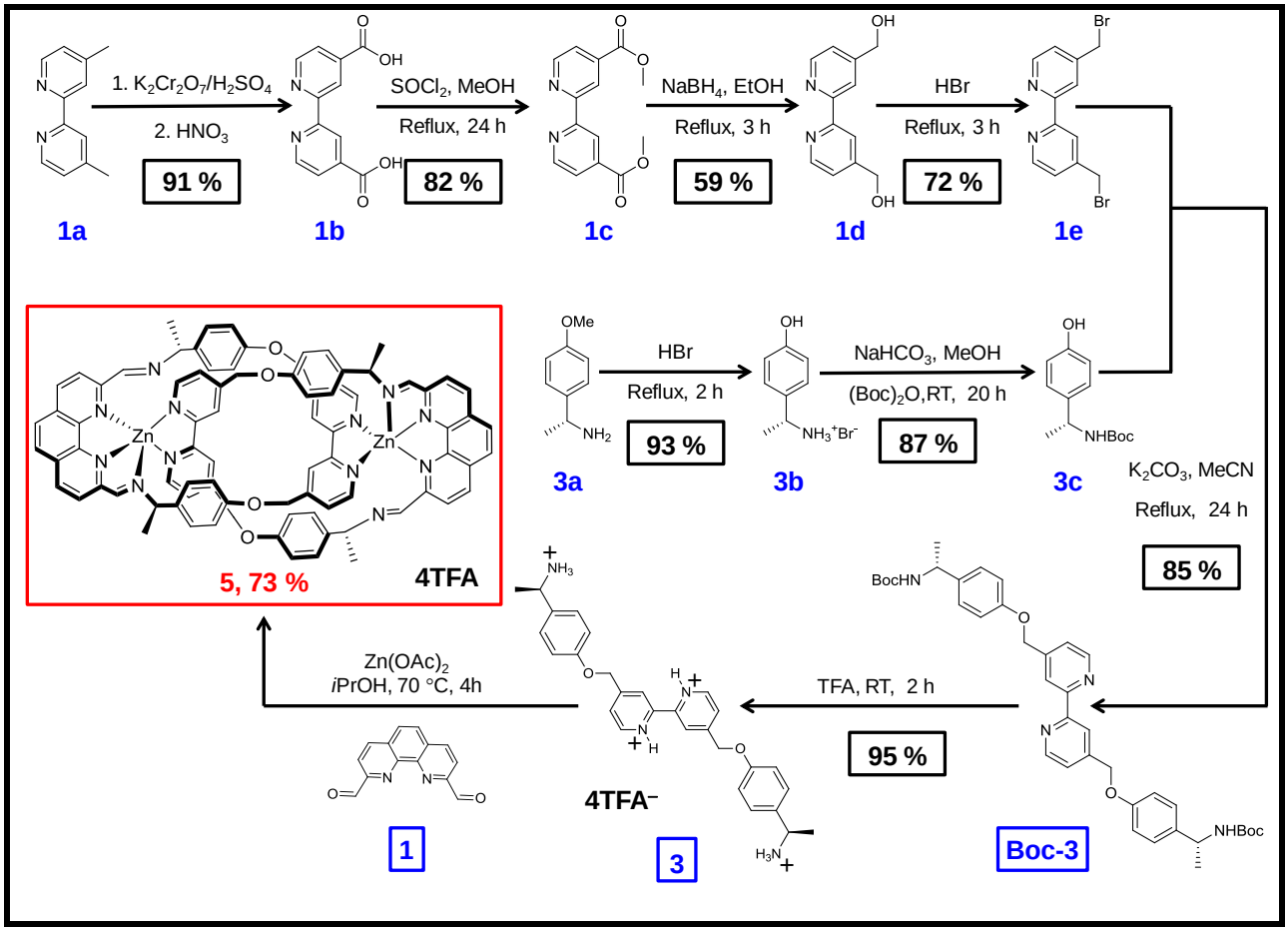
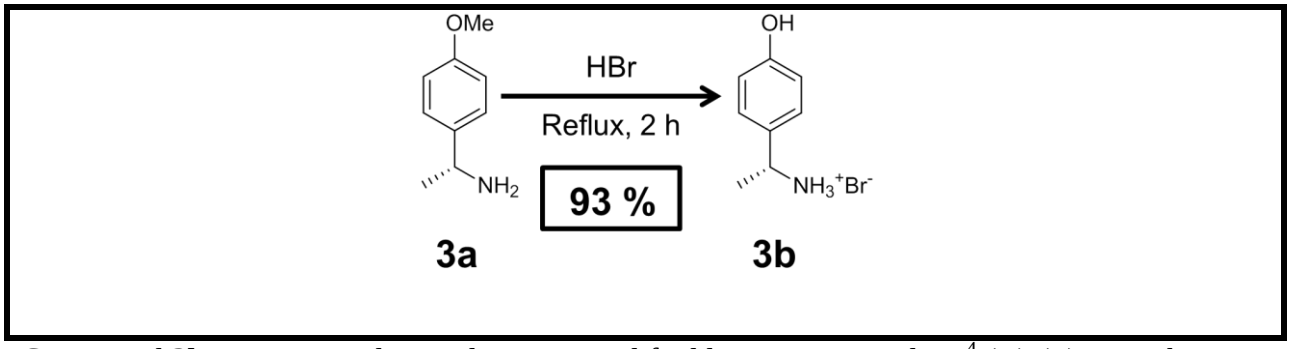


Figure S1.6. $^{1}H–^{1}H$ gradient-selected ROESY of **4** in CD_3CN at 233 K (500 MHz).

5. Synthetic strategy employed in the preparation of the chiral [2]catenanes, 5

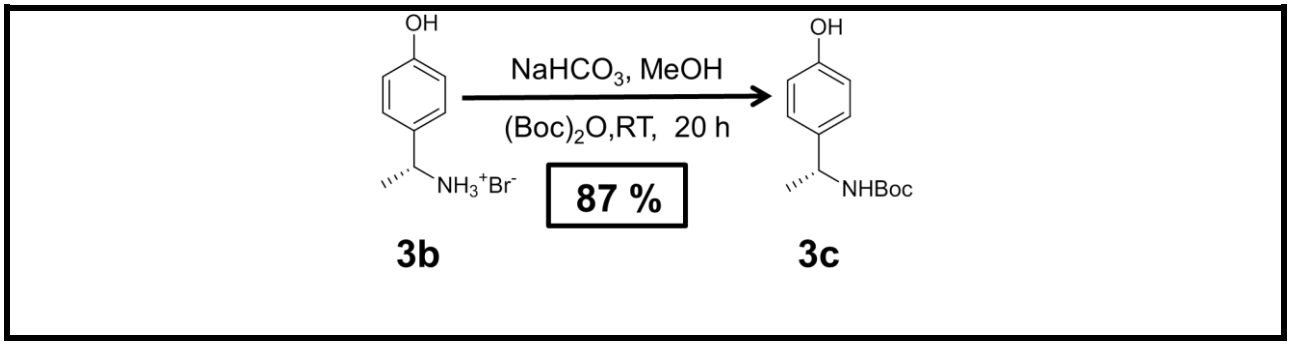


6. Synthesis of (R)-(+)-1-(4-hydroxyphenyl)ethanaminium bromide, 3b



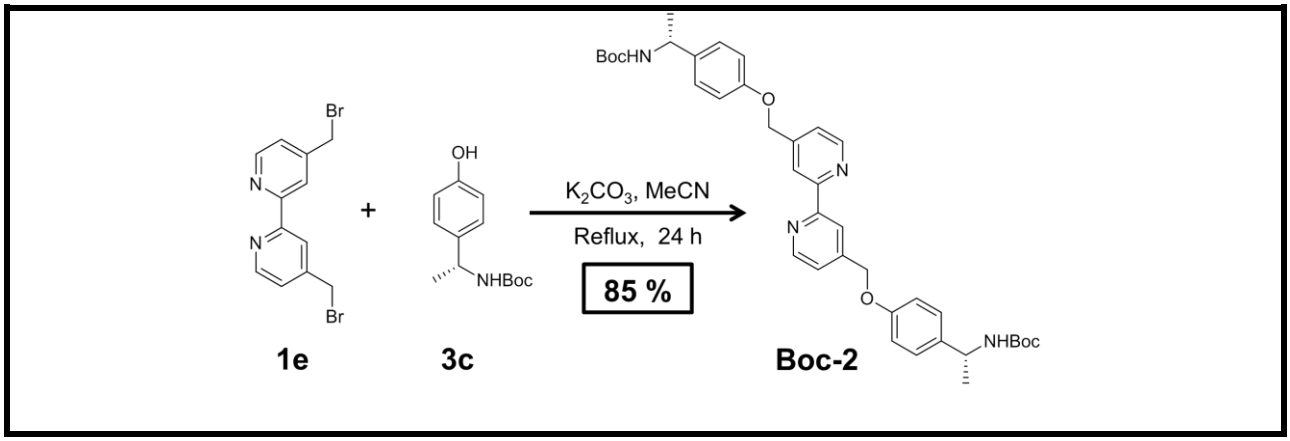
Compound **3b** was prepared according to a modified literature procedure.[4] (R)-(+)-4-Methoxy-α-methylbenzylamine (4 ml, 25 mmol) was added dropwise with stirring to 62% HBr (6 mL) in a two-necked 100-mL round-bottomed flask fitted with a condenser. The mixture was then stirred at reflux for 2 h, before being cooled down to room temperature and concentrated to dryness, affording an off white solid. MeCN (15 mL) was added to this residue and the product was collected by filtration and dried under vacuum. Yield: 5.04 g, 93%; ^{1}H NMR (600 MHz, D_2O, 25 °C): δ 1.49 (d, 3H, *J* = 6.6 Hz -C*H*$_3$), 4.36 (brs, 1H, -C*H*), 6.81 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.23 (d, *J* = 8.1 Hz, 2H, Ar-*H*); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ 19.1, 50.5, 115.8, 128.4, 129.5, 156.0.

7. Synthesis of (R)-(+)-tert-butyl (1-(4-hydroxyphenyl)ethyl)carbamate, 3c



Di-*tert*-butyl dicarbonate (2.7 g, 12.4 mmol) was added with stirring under an atmosphere of argon to a solution of **3b** (2.5 g, 11.6 mmol) and $NaHCO_3$ (3.95 g, 47.2 mmol) in MeOH (60 mL) in a 200-mL round-bottom flask. After 20 h of stirring at room temperature, the solvents were removed under reduced pressure, and the oily residue was purified by column chromatography [SiO_2, EtOAc:hexanes (1:4)] to afford **3c** as a colorless oil[4-8]. Yield: 2.39 g, 87 %; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 1.44 (s, 12H, -C*H*$_3$), 4.72 (brs, 1H, Ar-C*H*), 4.89 (brs, 1H, -N*H*), 6.73 (d, 2H, *J* = 8.1 Hz, Ar-*H*), 7.09 (d, 2H, *J* = 7.2 Hz, Ar-*H*), 7.53 (brs, 1H, -O*H*); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 22.7, 28.3, 28.4, 49.7, 79.8, 115.4, 127.0, 135.4, 155.3.

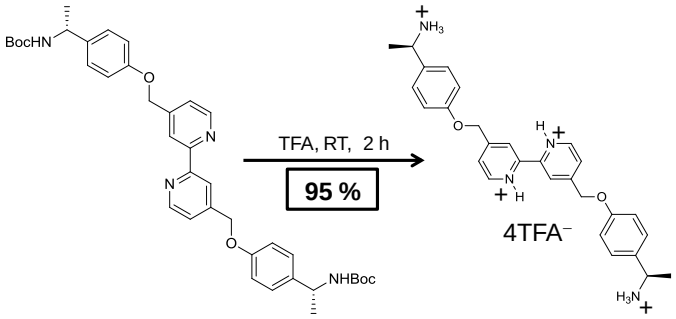
8. Synthesis of di-tert-butyl ((1R,1'R)-((([2,2'-bipyridine]-4,4'-diylbis(methylene))bis(oxy))bis(4,1-phenylene))bis(ethane-1,1-diyl))dicarbamate, Boc-2



4,4'-Bis(bromomethyl)-2,2'-bipyridine (1.2 gm, 3.5 mmol) was added with stirring to a solution of **3c** (1.68 g, 7.1 mmol) and anhydrous K_2CO_3 (1.95 g, 14 mmol) in anhydrous acetonitrile (30 mL) under argon atmosphere in a 100-mL round-bottom flask. The reaction mixture was refluxed at 65 °C for 20 h. Thereafter, the solvents were removed under reduced pressure, poured into water and extracted with ethyl acetate (3 × 50 ml). The organic layer was dried over sodium sulfate and reduced to dryness. The solid was recrystallized using CH_2Cl_2 and EtOAc (2:3 ratio)

Compound Boc-**2** was collected by filtration as a light yellow powder and dried under vacuum.[6] Yield: 1.95 g, 85 %; ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 1.43 (s, 18H, -CH_3), 1.70 (s, 6H, -CH_3), 4.50 (s, 2H, Ar-C*H*), 4.77 (brs, 2H, -N*H*), 5.18 (s, 4H, Ar-CH_2), 6.93 (d, 4H, *J* = 8.7 Hz, Ar-*H*), 7.26 (d, 4H, *J* = 8.7 Hz, Ar-*H*), 7.43 (d, 2H, *J* = 5.1 Hz, Ar-*H*), 8.47 (s, 2H, Ar-*H*), 8.69 (d, 2H, *J* = 3.0 Hz, Ar-*H*); ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 22.6, 30.7, 30.9, 49.6, 68.5, 79.4, 114.9, 115.4, 119.0, 121.1, 121.7, 123.8, 127.2, 137.0, 147.5, 149.6, 149.7, 155.1, 155.8, 156.1, 157.3; MS (ESI-HRMS): m/z Calcd for $C_{38}H_{47}N_4O_6$: 655.3490 $[M + H]^+$, found: 655.3423 $[M + H]^+$.

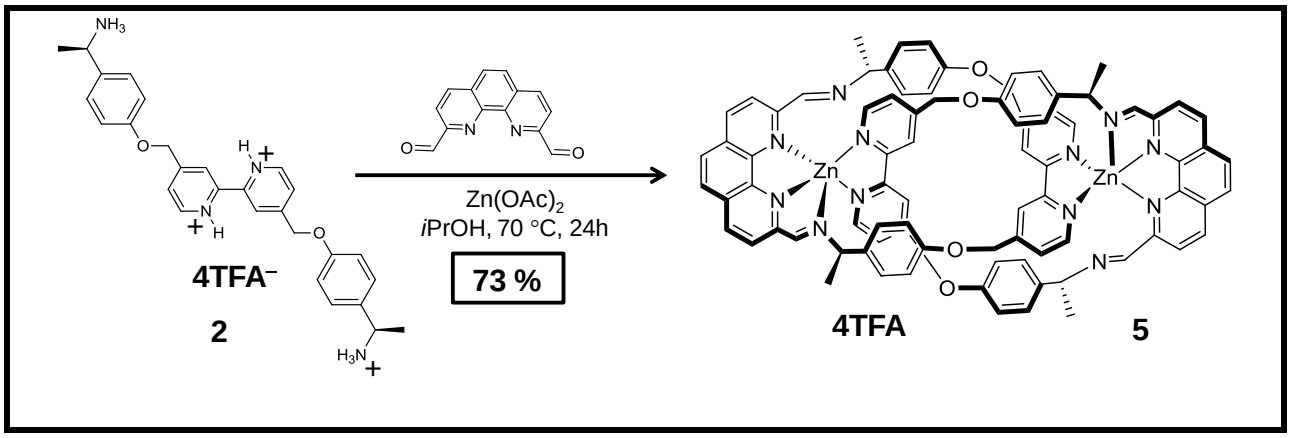
9. Synthesis of 4,4'-bis((4-((R)-1-ammonioethyl)phenoxy)methyl)-[2,2'-bipyridine]-1,1'-diium trifluoroacetate, 2-4H·4TFA



The Boc-protecting groups in the asymmetric ligand Boc-**2** (0.327 g, 0.500 mmol) were removed by the addition of trifluoroacetic acid to compound Boc-**2**.[4-8] The reaction mixture was stirred in ambient temperature for 2 h. After completion of the reaction, trifluoroacetic acid was removed completely under reduced pressure, and methanol (3 × 10 ml) was added and removed under reduced pressure. Lastly, dichloromethane (1 × 10 ml) was added and removed under reduced

pressure. The isolated pink solid was dried under vacuum for 6 h. Yield: 0.455 g, 95 %; ^{1}H NMR (600 MHz, MeOH –d4, 25 °C): δ 1.62 (d, 6H, *J* = 6.9 Hz, Ar-C*H*$_3$), 4.41 (ABq, 2H, *J* = 6.8 Hz, Ar-C*H*), 5.40 (s, 4H, Ar-C*H*$_2$), 7.17 (d, 4H, *J* = 8.8 Hz, Ar-*H*), 7.44 (d, 4H, *J* = 8.7 Hz, Ar-*H*), 7.77 (d, 2H, *J* = 5.0 Hz, Ar-*H*), 8.60 (s, 2H, Ar-*H*), 8.77 (d, 2H, *J* = 5.3 Hz, Ar-*H*); ^{13}C NMR (75 MHz, MeOD-d4, 25 °C): δ 20.5, 49.3, 69.1, 116.6, 117.2 (q, $^{2}J_{C\text{-}F}$ = 283 Hz, TFA), 121.3, 124.5, 129.4, 132.5, 149.1, 150.9, 152.7, 153.2, 160.1 (q, $^{3}J_{C\text{-}F}$ = 34 Hz, TFA) ; MS (ESI-HRMS): m/z Calcd for $C_{28}H_{31}N_4O_2$: 455.2447 $[M + H]^+$, found: 455.2419 $[M + H]^+$.

10. Synthesis of Zinc Phenanthroline Asymmetric 2-Catenane, 5



The freshly deprotected diamino asymmetric ligand **2** (0.23 g, 0.25 mmol) was stirred with 2,9-diformyl-1,10-Phenanthorline (0.059 g, 0.25 mmol) and zinc acetate (0.055 g, 0.25 mmol) in 15ml of isopropanol. The reaction mixture was refluxed about for 20 h. After completion of the reaction, the pale yellow solid, **5**, was filtered off. Yield: 0.172 g, 73%. ^{1}H NMR (600 MHz, MeOH-d4, 25 °C): δ 1.59 (dd, 12H, *J* = 7.2 Hz, Ar-*H*), 3.73 (ABq, 4H, *J* = 6.6 Hz, Ar-*H*), 5.10 (ABq, 8H, *J* = 7.6 Hz, Ar-C*H*$_2$), 6.43 (dd, 8H, *J* = 2.8 Hz, Ar-*H*), 6.75 (d, 4H, *J* = 5.2 Hz, Ar-*H*), 7.26 (ABq, 8H, *J* = 12 Hz, Ar-*H*), 7.95 (brs, 4H, Ar-*H*), 8.15 (dd, 4H, *J* = 2.6 Hz, Ar-*H*), 8.41 (d,

4H, *J* = 9.6 Hz, Ar-*H*), 8.64 (dd, 4H, *J* = 5.7 Hz, Ar-*H*), 9.26 (s, 4H, Ar-*H*), 9.61 (s, 4H, Ar-*H*); ^{13}C NMR (125 MHz, MeOH-d4, 25 °C): δ ; MS (ESI-HRMS): m/z Calcd for $(C_{88}H_{72}F_6N_{12}O_8Zn_2)^{2+}$: 833.2036 $(M^+–2TFA+ 2H)^{2+}$, found: 833.1950, $(M^+–2TFA+ 2H)^{2+}$, m/z Calcd for $(C_{86}H_{72}F_3N_{12}O_6Zn_2)^{3+}$: 517.8072 $(M^+–3TFA+ 3H)^{3+}$, found 517.8436 $(M^+–3TFA+ 3H)^{3+}$.

The ^{1}H NMR spectra of **5** in CD_3OD is presented in Figure S2. All the assignments have been made based on ^{1}H–^{1}H gradient-selected double-quantum filtered phase-sensitive COSY, recorded in CD_3OD at 298 K. Some of the key correlation peaks are labeled in the spectrum.

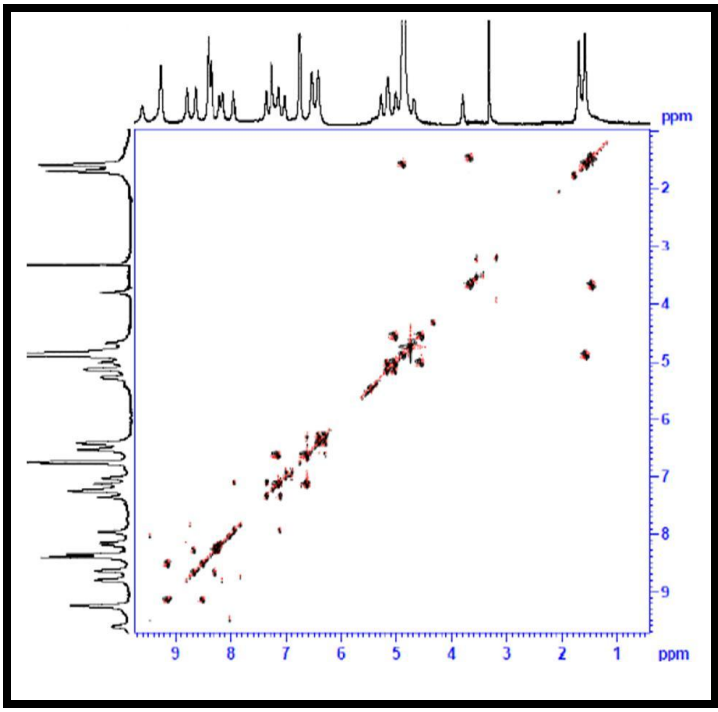


Figure S2. ^{1}H–^{1}H Gradient-selected double-quantum filtered phase-sensitive COSY NMR of **5** in CD_3OD at 298 K (600 MHz).

11. High resolution mass spectrometry (HRMS)

High resolution mass spectrometry (HRMS) analyses were performed using an Agilent 6540 UHA Accurate Mass Q-TOF / LC - MS-spectrometer in the positive mode and an acetonitrile/water gradient on a C-18 column. Figure S3

High resolution electrospray ionization-mass spectrometry of 4 dissolved in MeOH revealed three major peaks with maxima at *m/z* 805.162, 499.113, and 346.089, which correspond to $[4•2TFA]^{2+}$, $[4•TFA]^{3+}$, and $[4]^{4+}$, respectively. Two major peaks were observed in the case of 5 with maxima at *m/z* 833.195 and 517.844, and correspond to $[5•2TFA]^{2+}$ and $[5•TFA]^{3+}$, respectively. The isotopic distribution patterns of the assigned sets of peaks were in full agreement with the patterns predicted for the corresponding formulas (see bloew).

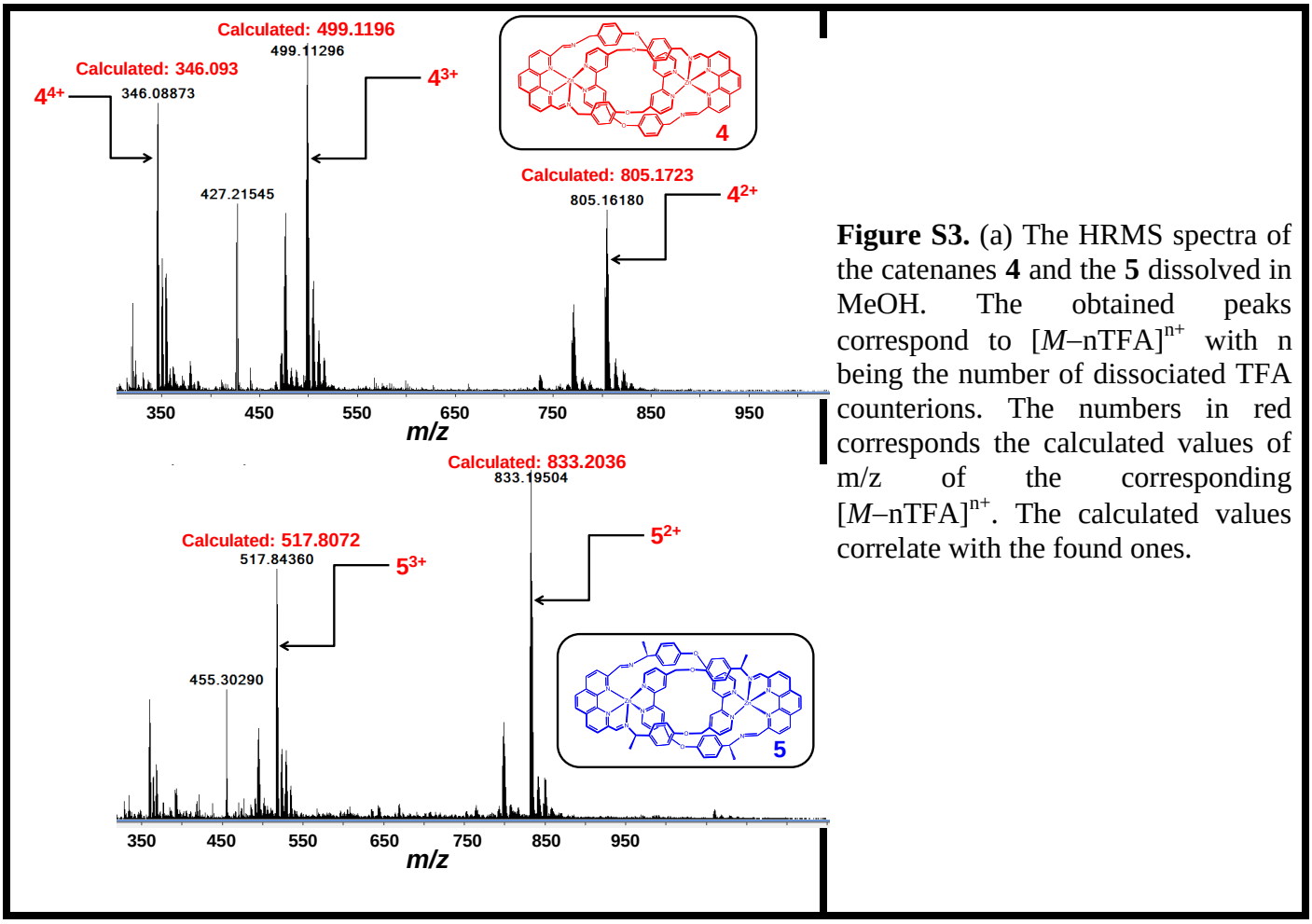


Figure S3. (a) The HRMS spectra of the catenanes **4** and the **5** dissolved in MeOH. The obtained peaks correspond to $[M–nTFA]^{n+}$ with n being the number of dissociated TFA counterions. The numbers in red corresponds the calculated values of m/z of the corresponding $[M–nTFA]^{n+}$. The calculated values correlate with the found ones.

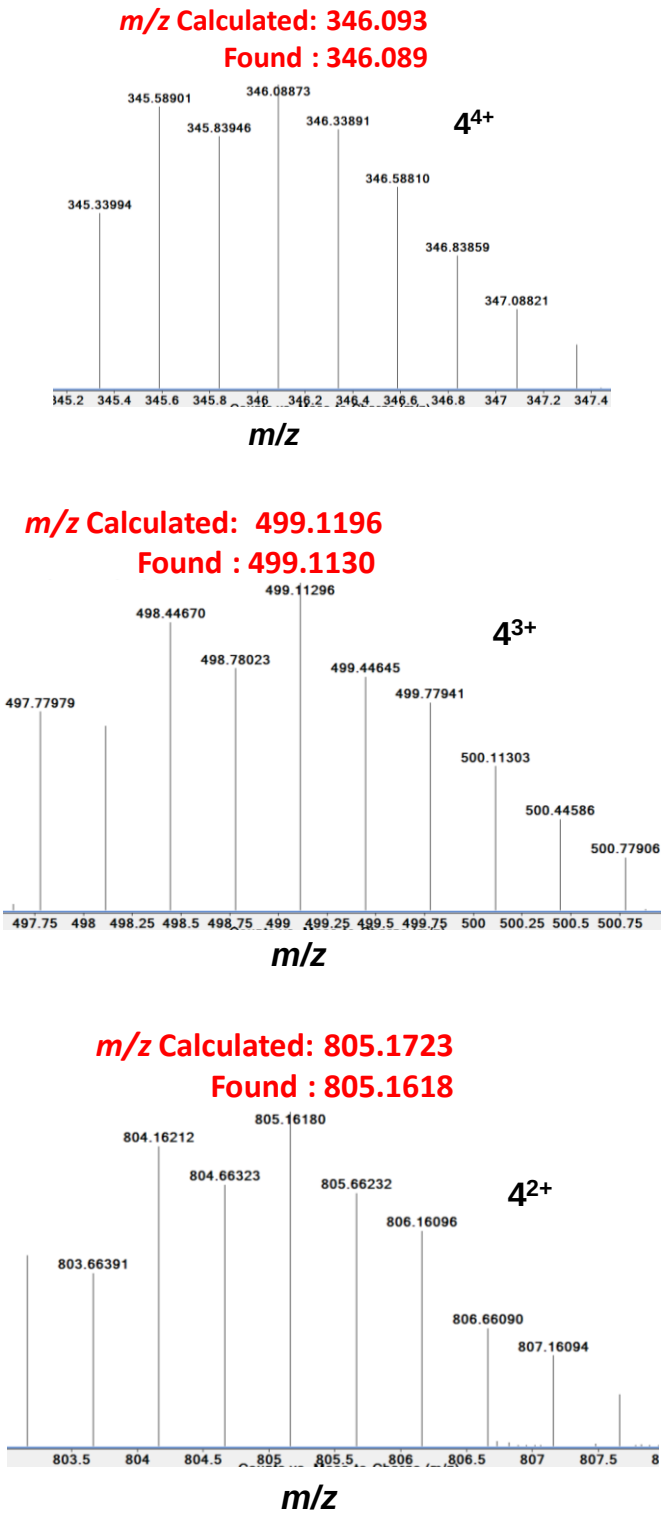


Figure S3. (b) Isotopic distribution pattern of Catenane (**4**)

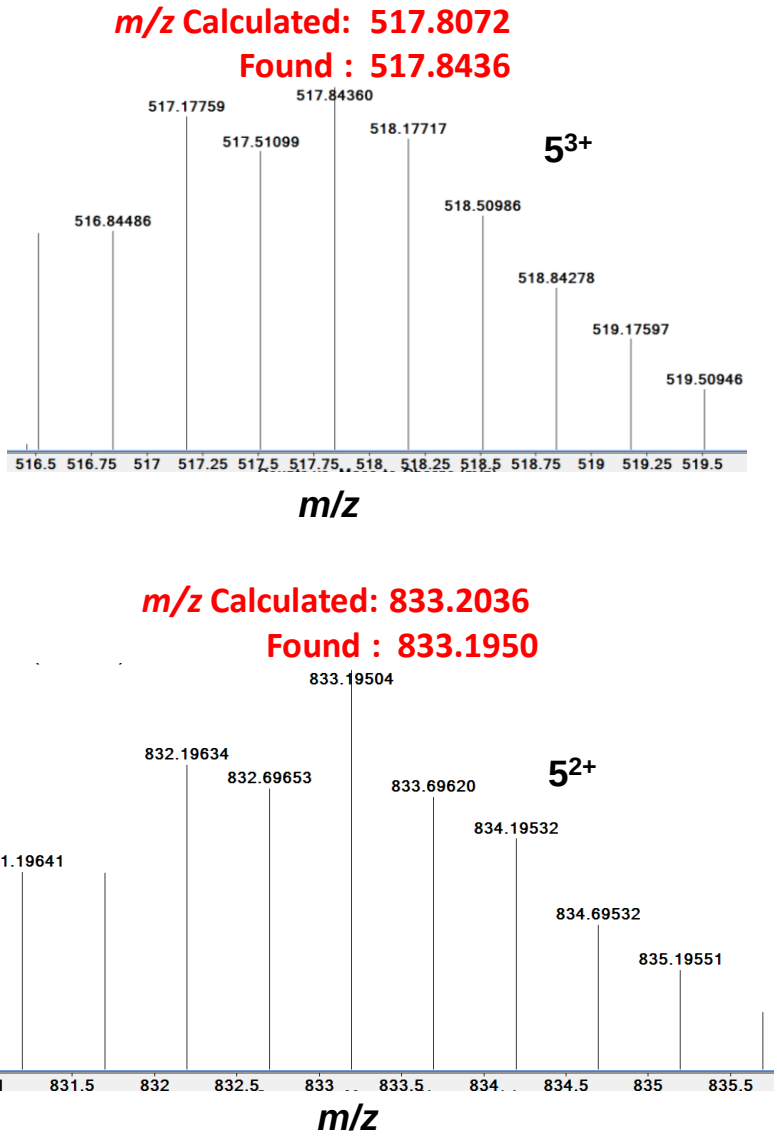


Figure S3. (c) Isotopic distribution pattern of Catenane (**5**)

12. ^{1}H NMR DOSY

Diffusion-ordered-spectroscopy DOSY was employed to determine the diffusion coefficient of **4**, and **5** in CD_3CN and CD_3OD at room temperature.

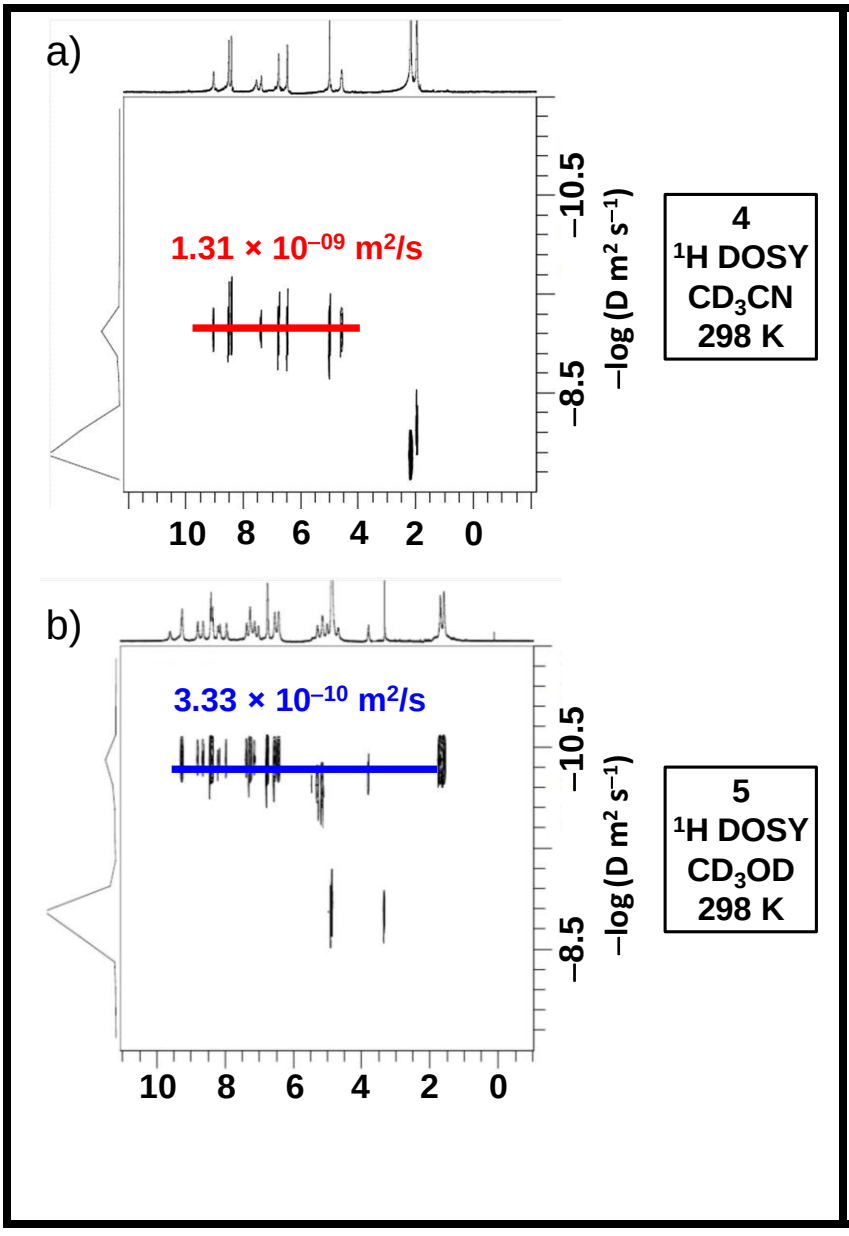


Figure S4. ^{1}H NMR DOSY NMR of Catenane **4** and the **5** dissolved in CD3CN and CD3OD recorded at 298k

13. Crystallographic characterization

All crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Single crystals of both catenanes **4** and **5** were grown at room temperature by slow vapor diffusion of *n-butyl ether* into trifluoroethanol solutions of the catenanes over the course of a week. X-ray diffraction data were collected at 100 K on a Bruker APEX II DUO diffractometer. Data reduction was perfomed with the Bruker Apex suite whereas crystal solution and refinement was obtained by direct methods using SHELL-X software via the X-seed interface. Residual electron density was "squeezed" out of the reflection intensity files with the PLATON suite.

CCDC 993838-993839

Summary of Data CCDC 993838

Compound Name: Formula: C84 H60 F6 N12 O8 Zn2 2+,2(C2 F3 O2 1-)

Unit Cell Parameters: a 8.1943(5) b 26.8625(17) c 42.167(3) P21/n

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Summary of Data CCDC 993839

Compound Name:

Formula: C88 H68 F6 N12 O8 Zn2 1+,C2 F3 O2 1-,3(C2 H1 F3 O1)

Unit Cell Parameters: a 43.874(4) b 8.3311(9) c 29.743(3) C2

Crystal data for **4**: $C_{88}H_{60}F_{12}N_{12}O_{12}Zn_2$, M = 1836.22, colourless needle, 0.500 × 0.300 × 0.200 mm^3, , space group $P2_1/n$ (No. 14), V = 9281.7(10) $Å^3$, Z = 4, D_c = 1.314 g/cm^3, F_{000} = 3744, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 38.0°, 37890 reflections collected, 6894 unique (R_{int} = 0.0752). The structure was solved and refined using the programs and SHELXL-2013 (Sheldrick, 2013) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Final *GooF* = 1.047, *R1* = 0.0928, *wR2* = 0.2499, *R* indices based on 5066 reflections with I I > 2(I) (refinement on F^2), 1067 parameters, 102 restraints. Lp and absorption corrections applied, μ = 0.604 mm^{-1}.

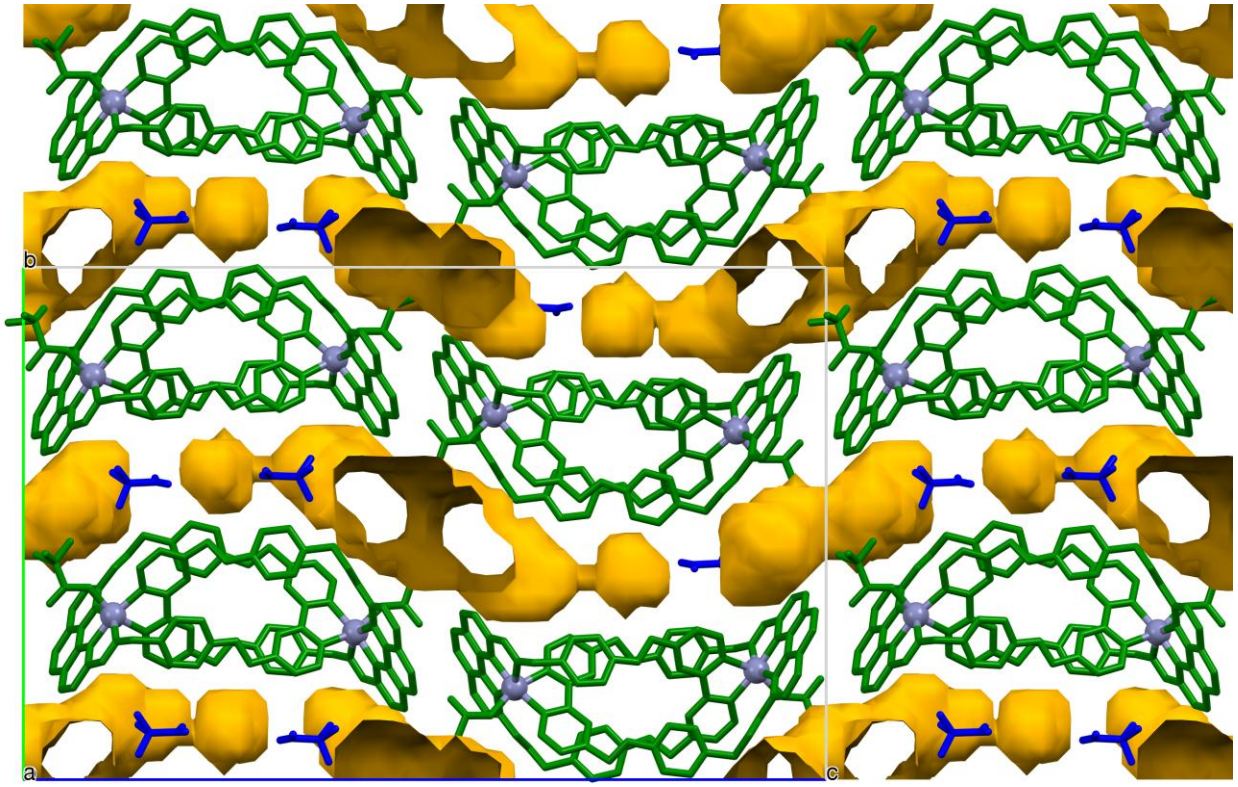


Figure S5. Crystal structure packing of [2]catenane (**4**) with voids

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) C__c_p21np
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE

FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.
No syntax errors found. CIF dictionary Interpreting this report

Datablock: C__c_p21np

Bond precision: C-C = 0.0194 A Wavelength=0.71073
Cell: a=8.1943(5) b=26.8625(17) c=42.167(3)
alpha=90 beta=90.213(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	9281.7(10)	9281.7(10)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C84 H60 F6 N12 O8 Zn2, 2(C2 F3 O2)	?
Sum formula	C88 H60 F12 N12 O12 Zn2	C88 H60 F12 N12 O12 Zn2
Mr	1836.26	1836.22
Dx,g cm-3	1.314	1.314
Z	4	4
Mu (mm-1)	0.604	0.604
F000	3744.0	3744.0
F000’	3748.35	
h,k,lmax	7,24,38	7,23,38
Nref	7484	6894
Tmin,Tmax	0.805,0.886	
Tmin’	0.739	

Correction method= Not given
Data completeness= 0.921 Theta(max)= 18.993
R(reflections)= 0.0928(5066) wR2(reflections)= 0.2648(6894)
S = 1.047 Npar= Npar =1067

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level A

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4579
PLAT058_ALERT_1_A Maximum Transmission Factor Missing ..... ?
PLAT059_ALERT_1_A Minimum Transmission Factor Missing ..... ?
PLAT211_ALERT_2_A ADP of Atom N9 is N.P.D. or (nearly) 2D ... Please Check
PLAT213_ALERT_2_A Atom C5 has ADP max/min Ratio ..... 14.6 prolat
PLAT213_ALERT_2_A Atom C27 has ADP max/min Ratio ..... 8.7 prolat
PLAT213_ALERT_2_A Atom C56 has ADP max/min Ratio ..... 5.6 oblate
PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure ! Info

Alert level B

REFNR01_ALERT_3_B Ratio of reflections to parameters is < 8 for a centrosymmetric structure
sine(theta)/lambda 0.4579
Proportion of unique data used 1.0000
Ratio reflections to parameters 6.4611
Crystal system given = monoclinic
PLAT019_ALERT_1_B _diffrn_measured_fraction_theta_full/_max < 1.0 0.446 Why ?

PLAT088_ALERT_3_B Poor Data / Parameter Ratio ..... 6.46 Note
PLAT234_ALERT_4_B Large Hirshfeld Difference C5 -- C6 .. 0.26 Ang.
PLAT234_ALERT_4_B Large Hirshfeld Difference C37 -- C40 .. 0.29 Ang.
PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.0194 Ang.
PLAT911_ALERT_3_B Missing # FCF Refl Between THmin & STh/L= 0.458 569 Why ?

Alert level C

RFACR01_ALERT_3_C The value of the weighted R factor is > 0.25
Weighted R factor given 0.265
PLAT084_ALERT_3_C High wR2 Value (i.e. > 0.25) ..... 0.26 Why ?
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent 14
PLAT213_ALERT_2_C Atom F5A has ADP max/min Ratio ..... 3.4 prolat
PLAT213_ALERT_2_C Atom F5B has ADP max/min Ratio ..... 4.0 prolat
PLAT213_ALERT_2_C Atom F7A has ADP max/min Ratio ..... 3.3 prolat
PLAT213_ALERT_2_C Atom N4 has ADP max/min Ratio ..... 3.3 oblate
PLAT213_ALERT_2_C Atom N5 has ADP max/min Ratio ..... 3.7 prolat
PLAT213_ALERT_2_C Atom C18 has ADP max/min Ratio ..... 3.9 prolat
PLAT213_ALERT_2_C Atom C54 has ADP max/min Ratio ..... 3.5 oblate
PLAT213_ALERT_2_C Atom C57 has ADP max/min Ratio ..... 3.5 prolat
PLAT213_ALERT_2_C Atom C77 has ADP max/min Ratio ..... 3.7 prolat
PLAT213_ALERT_2_C Atom C80 has ADP max/min Ratio ..... 3.4 prolat
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 4.0 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for C2A -- C4A .. 6.3 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for C18 -- C19 .. 5.5 su
PLAT234_ALERT_4_C Large Hirshfeld Difference O1A -- C2A .. 0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O2 -- C84 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O3A -- C2A .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1 -- C12 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N4 -- C75 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N4 -- C77 .. 0.25 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N5 -- C52 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N5 -- C53 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N7 -- C28 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N7 -- C32 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N9 -- C14 .. 0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N10 -- C40 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N11 -- C64 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C2 -- C6 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C6 -- C7 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C7 -- C8 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C11 -- C12 .. 0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 -- C21 .. 0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C22 -- C23 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C23 -- C24 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C26 -- C27 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C28 -- C29 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C29 -- C30 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C30 -- C33 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C35 -- C36 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C51 -- C59 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C56 -- C57 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C57 -- C58 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C58 -- C59 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C59 -- C60 .. 0.23 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C73 -- C74 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C76 -- C77 .. 0.24 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C77 -- C78 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C79 -- C80 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C80 -- C81 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C80 -- C83 .. 0.23 Ang.

```
PLAT234_ALERT_4_C Large Hirshfeld Difference C81 -- C82 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C85 -- C86 .. 0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C88 -- C89 .. 0.19 Ang.
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... Zn2 Check
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C14 Check
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C33 Check
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C68 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... N9 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C2A Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C2B Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C19 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C30 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C69 Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C4C Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C4D Check
PLAT334_ALERT_2_C Small Average Benzene C-C Dist. C84 -C89 1.37 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ...... 9.735 Check
PLAT906_ALERT_3_C Large K value in the Analysis of Variance ...... 2.324 Check
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 1 Note
PLAT918_ALERT_3_C Reflection(s) with I(obs) much smaller I(calc) . 2 Check
PLAT975_ALERT_2_C Check Calcd Residual Density 0.92A From O1D 0.63 eA-3
Alert level G
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 28 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 2 Why ?
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.15 Why ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 50.15 Why ?
PLAT242_ALERT_2_G Low Ueq as Compared to Neighbors for ..... C4A Check
PLAT242_ALERT_2_G Low Ueq as Compared to Neighbors for ..... C4B Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2 Note
C2 F3 O2
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............. 102 Note
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) still 56 %
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ....... Please Check
8 ALERT level A = Most likely a serious problem - resolve or explain
7 ALERT level B = A potentially serious problem, consider carefully
73 ALERT level C = Check. Ensure it is not caused by an omission or oversight
10 ALERT level G = General information/check it is not something unexpected
3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
36 ALERT type 2 Indicator that the structure model may be wrong or deficient
14 ALERT type 3 Indicator that the structure quality may be low
44 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check
```

Crystal data for 5: $C_{96}H_{68}F_{18}N_{12}O_{13}Zn_2$, M = 2070.36, Colourless needle, 0.020 × 0.020 ×0.120 mm^3, monoclinic, space group *C2* (No. 5), V = 10212.0(18) $Å^3$, Z = 4, D_c = 1.347 g/cm^3, F_{000} = 4216, CuKa radiation, l = 1.54178 Å, T = 100(2) K, 2 $Theta_{max}$ = 46.74º, 20566 reflections collected, 8688 unique (R_{int} = 0.0360). Final *GooF* = 1.043, *R1* = 0.0693, *wR2* = 0.1899, *R* indices based on 8191 reflections with I I > 2(I) (refinement on F^2), 1180 parameters, 37

restraints. Lp and absorption corrections applied, m = 1.420 $mm^{-1,}$ Absolute structure parameter 0.05(4).

One trifluoroacetate counter anion could not be found and three trifluoroethanol solvent molecules are refined isotropically. This still leaves two large voids in the structure, one that forms channels running in the direction of the b-axis and one that almost makes channels running in the direction of the a-axis. The solvent/counter anion disorder in these voids could not be resolved so SQUEEZE (Spek, A.L. (2003). J. Appl. Cryst. 36, 7-13. Spek, A.L. (2009). Acta Cryst. D65, 148-155.) was used. Approximately five trifluoroacetate/trifluoroethanol molecules (~50/55 electrons, volume ~70 $Å^3$) could fit in the voids per asymmetric unit, but the electron density in the voids (~70 electrons per ~370/460 $Å^3$ void) does not amount to this much.

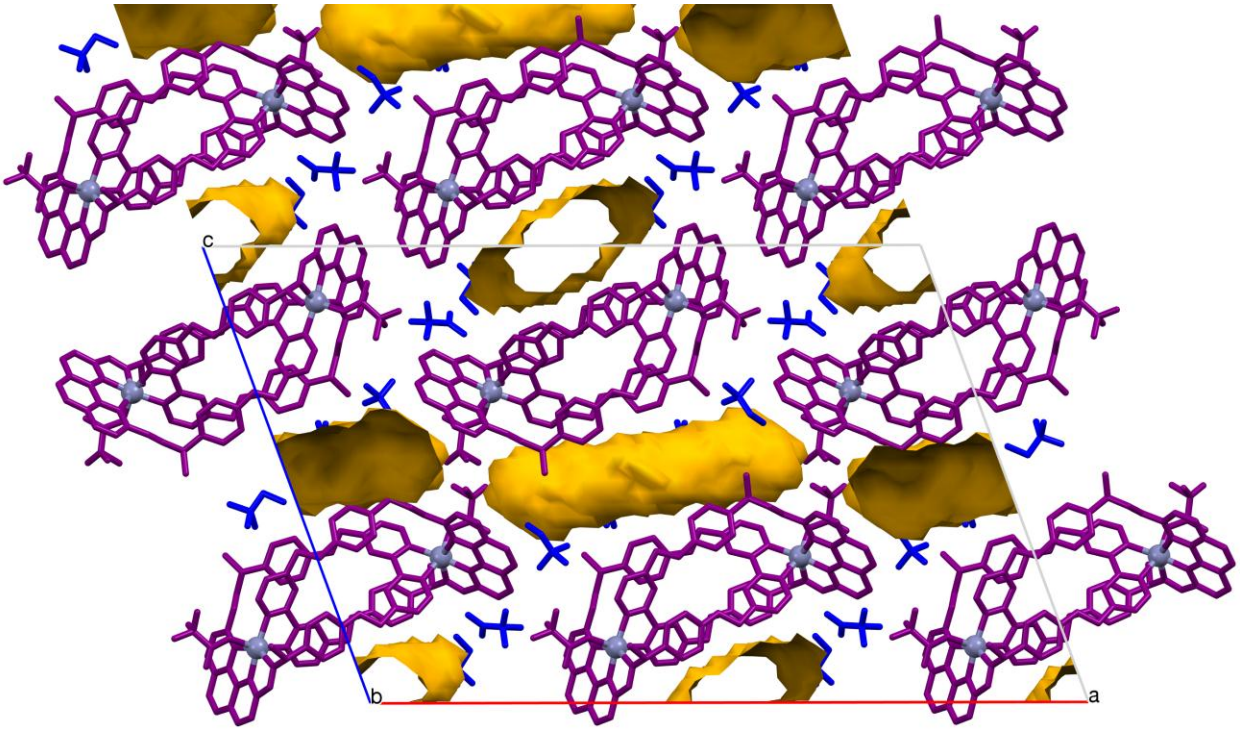


Figure S6. Crystal structure packing of [2]catenane (**5**) with voids

CheckCIF/PLATON report

Structure factors have been supplied for datablock(s) ekn026s_sq_d

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: ekn026s_sq_d

```
Bond precision: C-C = 0.0145 A Wavelength=1.54178
Cell: a=43.874(4) b=8.3311(9) c=29.743(3)
alpha=90 beta=110.065(6) gamma=90
Temperature: 100 K
Calculated Reported
Volume 10211.8(18) 10212.0(18)
Space group C 2 C2
Hall group C 2y ?
Moiety formula
C88 H68 F6 N12 O8 Zn2, C2
F3 O2, 3(C2 F3 O)
C84 H68 N12 O4 Zn2, 3 C2
F3 O2, 3 C2 F3 O
Sum formula C96 H68 F18 N12 O13 Zn2 C96 H68 F18 N12 O13 Zn2
Mr 2070.41 2070.36
Dx,g cm-3 1.347 1.347
Z 4 4
Mu (mm-1) 1.420 1.420
F000 4216.0 4216.0
F000' 4219.09
h,k,lmax 41,7,28 41,7,28
Nref 8987[ 4923] 8688
Tmin,Tmax 0.966,0.972 0.848,0.972
Tmin' 0.843
Correction method= MULTI-SCAN
Data completeness= 1.76/0.97 Theta(max)= 46.740
R(reflections)= 0.0693( 8191) wR2(reflections)= 0.1931( 8688)
S = 1.043 Npar= Npar =1180
```

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level.**

Click on the hyperlinks for more details of the test.

Alert level A

```
THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4723
PLAT213_ALERT_2_A Atom C27 has ADP max/min Ratio ..... 9.0 oblate
```

Alert level B

```
REFNR01_ALERT_3_B Ratio of reflections to parameters is < 8 for a
non-centrosymmetric structure, where ZMAX > 18
sine(theta)/lambda 0.4723
Proportion of unique data used 1.0000
Ratio reflections to parameters 7.3627
PLAT035_ALERT_1_B No _chemical_absolute_configuration info given . Please Do !
PLAT090_ALERT_3_B Poor Data / Parameter Ratio (Zmax > 18) ........ 4.06 Note
```

PLAT213_ALERT_2_B Atom C67 has ADP max/min Ratio ..... 4.5 oblate
PLAT782_ALERT_2_B Unusual geometry for C-CO2 moiety involving .. C300
PLAT934_ALERT_3_B Number of (Iobs-Icalc)/SigmaW > 10 Outliers .... 3 Check

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without
a literature citation. This should be contained in the
_exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.974 Note
PLAT202_ALERT_3_C Isotropic non-H Atoms in Anion/Solvent 18
PLAT213_ALERT_2_C Atom C10 has ADP max/min Ratio ..... 3.3 oblate
PLAT213_ALERT_2_C Atom C62 has ADP max/min Ratio ..... 3.2 oblate
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) Range 3.7 Ratio
PLAT230_ALERT_2_C Hirshfeld Test Diff for F4 -- C100 .. 5.6 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for F6 -- C100 .. 5.1 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for N4 -- C75 .. 6.0 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for N5 -- C53 .. 5.1 su
PLAT234_ALERT_4_C Large Hirshfeld Difference F1 -- C200 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F3 -- C200 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O4 -- C34 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1 -- C12 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N3 -- C82 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N5 -- C52 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N10 -- C40 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N12 -- C92 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C1 -- C9 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C10 -- C11 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C16 -- C21 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C17 -- C18 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C20 -- C21 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C24 -- C25 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C34 -- C35 .. 0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C35 -- C36 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C36 -- C37 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C40 -- C41 .. 0.18 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C53 -- C54 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C53 -- C92 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C55 -- C56 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C58 -- C59 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C59 -- C60 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C66 -- C67 .. 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C68 -- C69 .. 0.19 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C69 -- C70 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C70 -- C71 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C79 -- C80 .. 0.16 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference F8 -- C301 .. 0.20 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O30 -- C300 .. 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C300 -- C301 .. 0.18 Ang.
PLAT241_ALERT_2_C High Ueq as Compared to Neighbors for ..... C68 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C40 Check
PLAT242_ALERT_2_C Low Ueq as Compared to Neighbors for ..... C101 Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C501 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C300 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 3.7 Note
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ..... O40 Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ..... O50 Check
PLAT309_ALERT_2_C Single Bonded Oxygen (C-O > 1.3 Ang) ..... O60 Check
PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0145 Ang.
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.472 127 Why ?

PLAT918_ALERT_3_C Reflection(s) with I(obs) much smaller I(calc) . 5 Check

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 18 Note
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF Please Do !
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.15 Why ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large. 35.26 Why ?
PLAT128_ALERT_4_G Alternate Setting for Input Space-Group C2 I2 Note
PLAT242_ALERT_2_G Low Ueq as Compared to Neighbors for ..... C100 Check
PLAT242_ALERT_2_G Low Ueq as Compared to Neighbors for ..... C200 Check
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C301 Check
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C400 Check
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C500 Check
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of C601 Check
PLAT335_ALERT_2_G Check Large C6 Ring C-C Range C1 -C9 0.17 Ang.
PLAT344_ALERT_2_G Check sp? Angle Range in Solvent/Ion for ... C401
PLAT344_ALERT_2_G Check sp? Angle Range in Solvent/Ion for ... C501
PLAT344_ALERT_2_G Check sp? Angle Range in Solvent/Ion for ... C600
PLAT606_ALERT_4_G VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 2 Do !
N4 -ZN1 -N1 -C1 -79.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 7 Do !
N4 -ZN1 -N1 -C12 104.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 31 Do !
N1 -ZN1 -N4 -C77 -11.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 36 Do !
N1 -ZN1 -N4 -C75 169.50 1.70 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 43 Do !
N7 -ZN2 -N5 -C52 -81.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 48 Do !
N7 -ZN2 -N5 -C53 106.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 62 Do !
N5 -ZN2 -N7 -C28 -12.00 2.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 67 Do !
N5 -ZN2 -N7 -C32 170.80 1.70 1.555 1.555 1.555 1.555
PLAT791_ALERT_4_G The Model has Chirality at C14 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C40 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C64 ..... R Verify
PLAT791_ALERT_4_G The Model has Chirality at C90 ..... R Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 37 Note
PLAT869_ALERT_4_G ALERTS Related to the use of SQUEEZE Suppressed ! Info
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) still 91 %
PLAT910_ALERT_3_G Missing # of FCF Reflections Below Th(Min) ..... 1 Why ?
PLAT961_ALERT_5_G Dataset Contains no Negative Intensities ..... Please Check
2 **ALERT level A** = Most likely a serious problem - resolve or explain
6 **ALERT level B** = A potentially serious problem, consider carefully
53 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
35 **ALERT level G** = General information/check it is not something unexpected
4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
26 ALERT type 2 Indicator that the structure model may be wrong or deficient
12 ALERT type 3 Indicator that the structure quality may be low
52 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

14. Circular dichroism studies of precursor ligands (2, 3) and [2]catenanes (4^{2+} and 5^{2+})

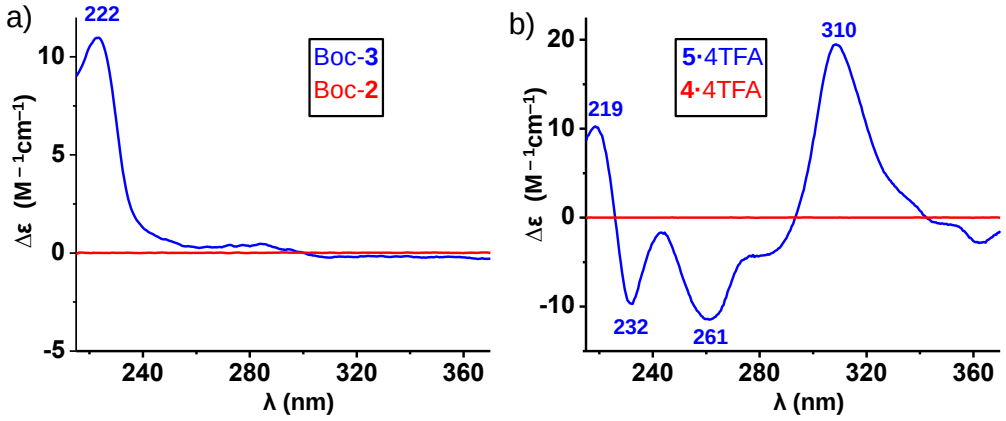


Figure S7. Circular dichroism (CD) spectra of (a) ligand precursors Boc-2 and Boc-3 (0.02 μM in MeOH at 298 K) and (b) catenanes 4 and 5 (8 μM in MeOH at 298 K).

As expected, both the achiral precursor ligand, Boc-**2**, and the corresponding racemic mixture of helical [2]catenanes, **4**, show no optical activity (Figure S7a and S7b). The CD spectrum of the chiral ligand Boc-**3** is optically active below 250 nm and has a λ_{max} = 222 nm that can be attributed to n→π* transitions on the carbamate moieties close to the stereogenic carbon atoms (Figure S7a). The spectrum of catenane **5** shows Cotton effects at λ_{max} = 219 nm and λ_{min} = 232 nm, which are in the same range as absorptions seen in the spectrum of Boc-**3** and most likely arise directly from the four stereogenic centres of the catenane's component ligands (Figure S7b). The optical activity of **5** seen at lower energies (λ_{min} = 261 nm and λ_{max} = 310 nm) is due to the two stereogenic metal centers and the fact that **5** exists at room temperature as a quasi-single stereoisomer and not a racemic mixture of enantiomers. The positive Cotton effect observed at 310 nm arises from π→π* transitions of the aromatic moieties. A very similar pattern

was observed in the CD spectra of chiral Borromean rings.[9] Because the latter structure lacks phenanthroline moieties, it can be surmised that the signal at 310 nm in the spectrum of **5** is due to $\pi \rightarrow \pi^*$ transitions of the bipyridyl groups.

15. Computational details

All calculations were performed employing Gaussian 09 package (Revision A.01).[10] Initial calculations on the [**4**•2TFA]$^{2+}$ system and the corresponding trefoil knot resulting from the assembly of **1**, **2** and Zn^{2+} were performed using the PM6 semiempirical MO method,[11] which has been shown to provide more accurate results than the classical PM3 and AM1 semiempirical methods for Zn complexes.[12] Density functional theory (DFT) calculations were carried out using the hybrid BHandHLYP functional (BH&HLYP).[13] Full geometry optimizations of the [**4**•2TFA]$^{2+}$ and [**5**•2TFA]$^{2+}$ systems were performed in vacuo without symmetry constraint. Due to the large size of these systems, in these calculations we used a mixed basis set comprising the 6-31G(d) basis set for Zn, N and O, and the smaller 3-21G basis set for C, H and F. The default values for the integration grid (75 radial shells and 302 angular points) and the SCF energy convergence criteria (10^{-8}) were used in all calculations. The stationary points found on the potential energy surfaces as a result of geometry optimizations were tested to represent energy minima rather than saddle points via frequency analysis. The interconversion between the P-(C,C) and P-(C,A) stereoisomers of [**4**•2TFA]$^{2+}$ was investigated by means of the synchronous transit-guided quasi-Newton method.[14] The nature of the saddle points (one imaginary frequency) was characterized by frequency analysis. The relative free energies of the two energy minima and the free energy barrier for their interconversion include non-potential-energy contributions (zero point energies and thermal terms) obtained through frequency analysis.

Recently, we reported the synthesis of a diaminobipyridine (DAB) ligand, 2, that, in a 1:1:1 combination with diformylpyridine (DFP) and zinc(II) acetate, simultaneously produces three topologically non-trivial structures: a [2]catenane (22%), a trefoil knot (56%) and a Solomon link (trace amounts).[1] When DFP is replaced by 2,9-diformyl-1,10-phenanthroline (1), bimetallic [2]catenanes (4 and 5) are formed exclusively and in higher yield and no trefoil knot nor Solomon link are observed. In order to support our experimental results, PM6 calculations were performed and show that the formation of the trefoil knot is energetically less favorable with a larger heat formation compared to the [2]catenane (Figure S8).

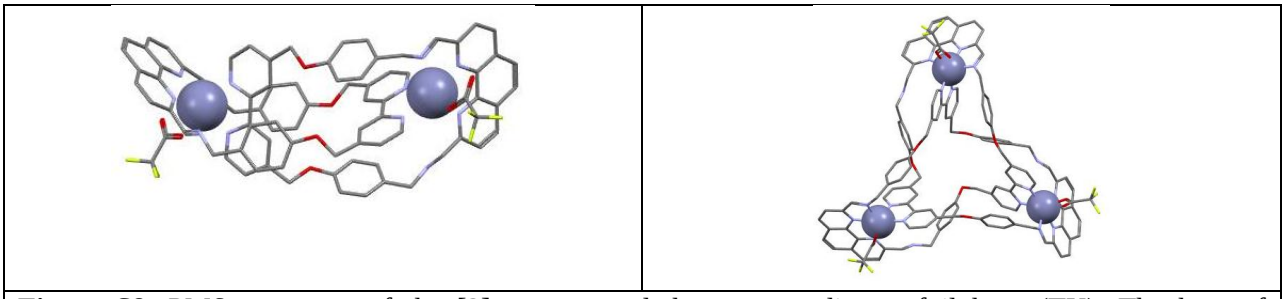


Figure S8. PM6 structures of the [2]catenane and the correponding trefoil knot (TK). The heat of formation per mol of Zn calculated for the TK is 10.8 kcal·mol^{-1} more positive than that obtained for the [2]catenane, which is in line with a higher stability of the latter.

DFT calculations performed with the aid of the BH&HLYP functional predict that the $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$)/$\vec{\Lambda}$-($\vec{\lambda}$,$\vec{\lambda}$) enantiomeric pair is the most stable, with the $\vec{\Lambda}$-($\vec{\delta}$,$\vec{\delta}$)/$\vec{\Delta}$-($\vec{\lambda}$,$\vec{\lambda}$) and $\vec{\Lambda}$-($\vec{\lambda}$,$\vec{\delta}$) /$\vec{\Delta}$-($\vec{\delta}$,$\vec{\lambda}$) enantiomeric pairs being 1.6 kcal mol^{-1} and 0.4 kcal mol^{-1} less stable, respectively (Figure S9). These relative energies are in line with the structure observed in the solid state. In the crystal structure, the $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$) and $\vec{\Lambda}$-($\vec{\lambda}$,$\vec{\lambda}$) enantiomers are arranged in sheets parallel to the (1 1 0) plane. In each enantiomer, the absolute configuration of the two zinc cations is the same. The two

enantiomers pack in a head to tail fashion in successive layers along the c axis. Solvent and counter ions fill the gaps between catenanes.

In contrast, **5** exists in the solid state as just a single stereoisomer, $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$). It packs in a polar space group in a head to head motif forming capsule-like supramolecular adducts that contain – and are held together by – counter ions and solvent molecules.

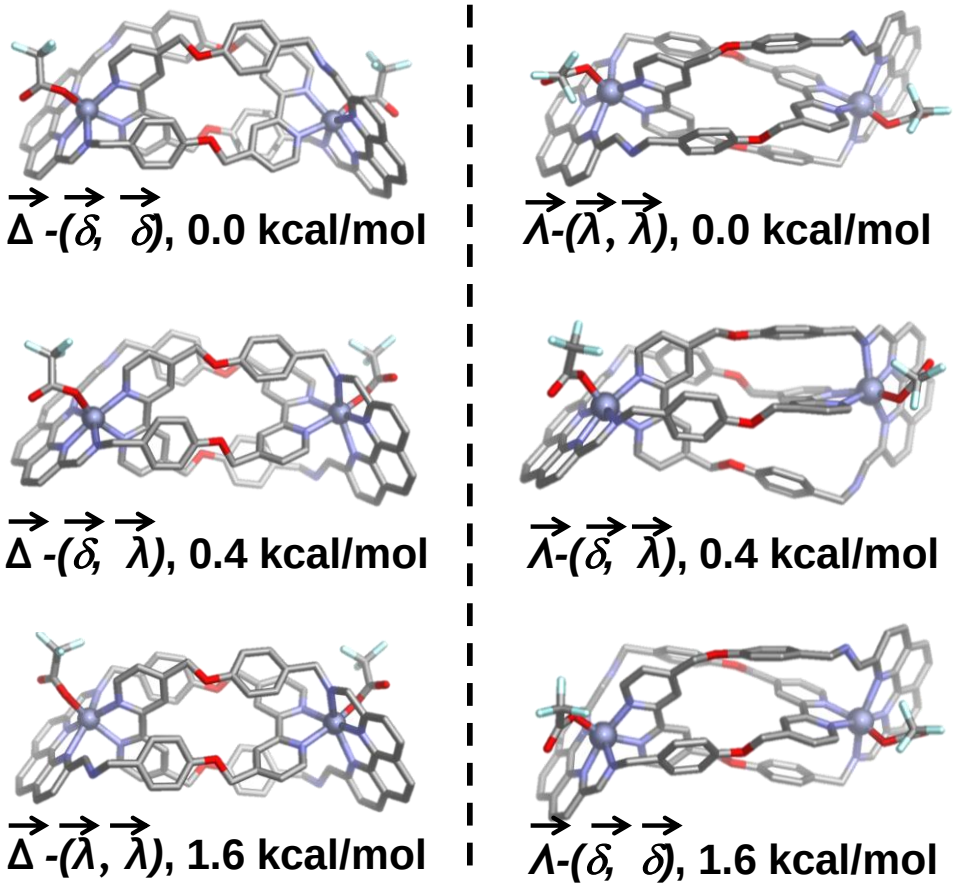


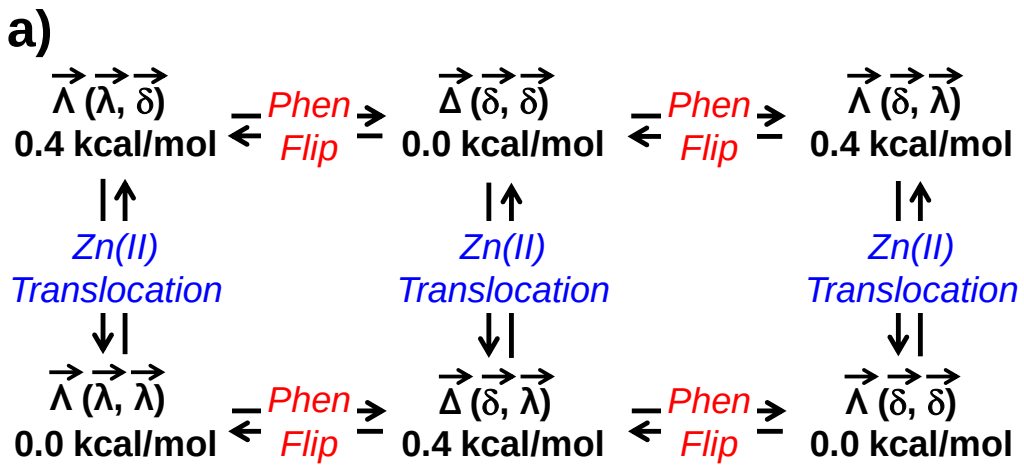
Figure S9. Structures and relative energies of the six major stereoisomers of catenane **4** obtained with DFT calculations.

At the molecular level, a more detailed picture of the dynamics of **4** was obtained using DFT calculations (Figure S10). A careful inspection of the minimum energy geometries obtained for **4**

reveals that the $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$) isomer can interconvert to the $\vec{\Lambda}$-($\vec{\delta}$,$\vec{\delta}$) form through a $\vec{\Delta}$-($\vec{\delta}$,$\vec{\lambda}$) intermediate following i) a translocation of one of the Zn ions between imine nitrogens and ii) a flip ("phen flip" in Figure S10) of the phenanthroline ring coordinated to the translocated Zn^{2+} ion. Each phen flip is accompanied by the decoordination of a triflate ion from one side of a zinc complex and recoordination to the other side. This latter process causes a change of the configuration at the Zn center bound to the flipping phenanathroline unit. The translocation of the second Zn ion followed by a phen flip yields the starting $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$) isomer, the overall process involving a shuttling of the two zinc cations between imine nitrogens. Overall, this mechanism is expected to average the chemical environments of proton nuclei of the two sides of the cavity of the catenane, and is consistent with the VT ^{1}H NMR spectra described above. Alternatively, the translocation of a Zn ion of the $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$) form followed by a phen flip at the opposite end of the catenane results in enantiomerization to give the Λ-($\vec{\lambda}$,$\vec{\lambda}$) form. A second translocation and phen flip (at the opposite end of the cavity) can give the starting $\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$) form. Thus, both of these pathways, which are illustrated in Figure S10a, are consistent with the NMR spectral data.

The translocation process was further investigated using DFT. According to our calculations the translocation of a Zn ion is a two-step mechanism involving the decoordination of one of the imine nitrogen atoms to give a five-coordinate intermediate and subsequent coordination of the other imine nitrogen atom of the same ligand strand (Figure S10b). The activation free energy for this process, as estimated from the energy of the transition state with the highest energy, amounts to only 10.9 kcal mol^{-1}, which is in reasonable agreement with the values obtained from VT ^{1}H NMR spectroscopy. Interestingly, the translocation of the second Zn ion to give the Λ-($\vec{\lambda}$,$\vec{\lambda}$) isomer proceeds through a transition state with nearly identical energy, indicating that the

dynamic processes occurring at one end of the cavity do not significantly distort the coordination environment around the other Zn ion. These results suggest that Zn translocation represents the rate limiting step for the interconversion processes experienced by **4**.



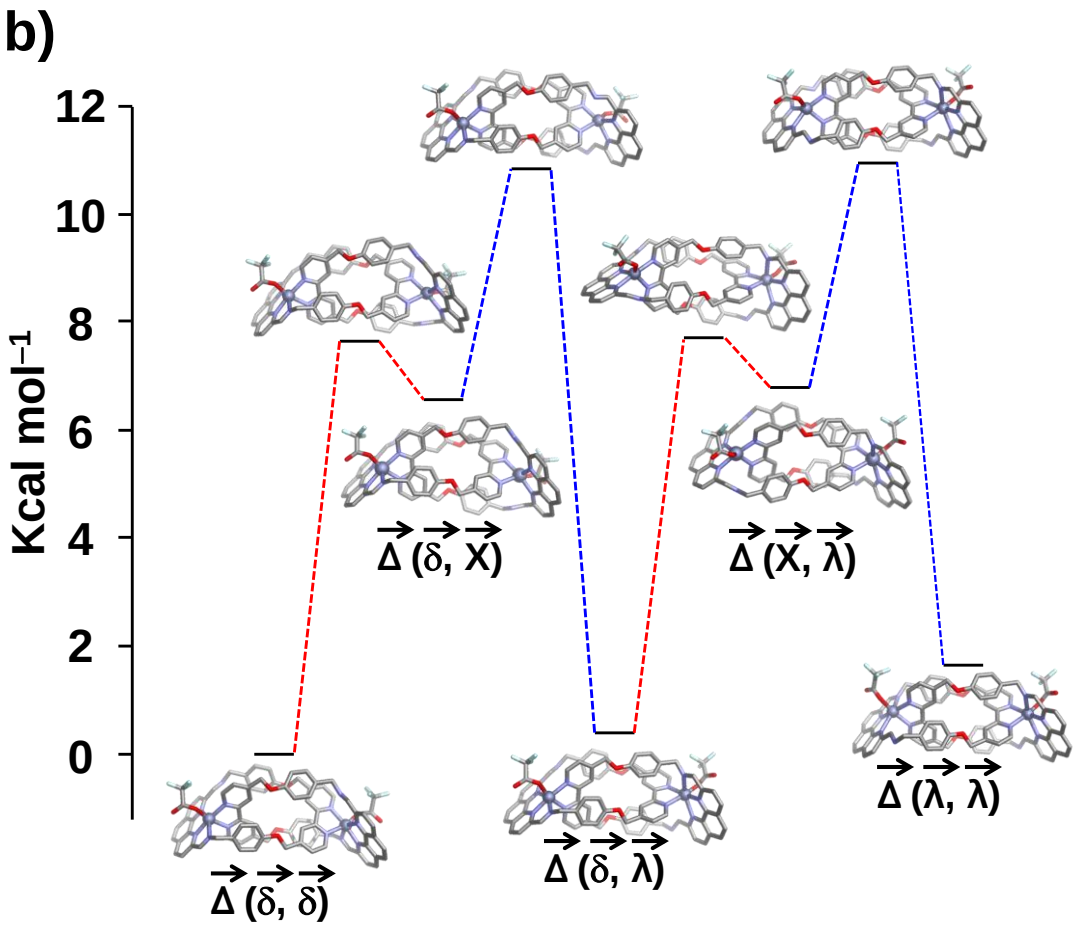


Figure S10. a) Interconversion pathways observed in solutions of **4** and relative free energies of the different isomers obtained with DFT calculations for $[\mathbf{4}\bullet 2TFA]^{2+}$ (BH&HLYP/6-31G(d)/3-21G). The same pathway can be described for **5**. b) In vacuo relative free energies of minima, intermediates, and transition states involved in the translocation of the two Zn^{2+} ions in $[4\bullet 2TFA]^{2+}$. The translocation process is a four-step process involving the rupture of a N_{imine}–zinc bond (red dotted lines) to give the five-coordinate species P-(C,X), followed by the formation of a N_{imine}–zinc bond with the nitrogen atom on the opposite side of the coordination cage to give the Δ-($\vec{\delta}$,$\vec{\lambda}$) intermediate (blue dotted lines). An analogous two-step process affecting

the second Zn^{2+} ion results in the formation of Δ-($\vec{\lambda}$,$\vec{\lambda}$). X indicates a five-coordinate zinc(II) cation.results demonstrate that slowing the exchange processes leads, effectively, to a loss of symmetry (for example, loss of two-fold symmetry within the macrocycles) and therefore an increased number of signals.

$\vec{\Delta}$-($\vec{\lambda}$, $\vec{\lambda}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (0 Imaginary Frequencies)

	Coordinates (Angstroms)		
	X	Y	Z
O	7.52641600	1.32573200	-1.16400400
C	8.28071200	2.24487900	-0.70615900
O	9.07487500	2.22568100	0.20132900
C	7.97984100	3.58460500	-1.38691000
F	6.87304400	4.13478000	-0.76629000
F	7.61378600	3.42159200	-2.68714000
F	8.97653000	4.47113700	-1.31050700
O	-7.52651400	1.32650800	1.16351600
C	-8.27937000	2.24667400	0.70534100
O	-9.07295200	2.22864800	-0.20267700
C	-7.97740400	3.58586300	1.38666300
F	-7.61339600	3.42217900	2.68736800
F	-8.97255000	4.47399300	1.30890100
F	-6.86880400	4.13432800	0.76763100
Zn	6.45170000	0.19460600	-0.00432400
N	-4.79580700	-1.04794700	-0.59226600
C	-4.89789000	-2.09308400	-1.40517700
H	-5.89222400	-2.36517900	-1.70829300
C	-3.79893700	-2.79072400	-1.87524500
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C	-2.44323800	-1.34349900	-0.56360700
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C	-1.26871700	-3.01659800	-1.98362500
H	-0.77396600	-3.59229000	-1.20106000
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E(RBHandHLYP) = -8628.9413216 Hartree
Zero-point correction = 1.361361
Thermal correction to Energy = 1.450386
Thermal correction to Enthalpy = 1.451330
Thermal correction to Gibbs Free Energy = 1.229888

Sum of electronic and zero-point Energies = -8627.579960
Sum of electronic and thermal Energies = -8627.490936
Sum of electronic and thermal Enthalpies = -8627.489992
Sum of electronic and thermal Free Energies = -8627.711433

$\vec{\Delta}$-($\vec{X}$,$\vec{\lambda}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (0 Imaginary Frequencies)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.83805500	1.26946100	0.48802400
C	-8.59465900	1.98429400	-0.24644200
O	-9.29720200	1.67994900	-1.17832600
C	-8.43584700	3.46930400	0.09800800
F	-7.26396800	3.91783100	-0.48642700
F	-8.26104100	3.66290200	1.43343900
F	-9.43484000	4.24070000	-0.33966100
O	6.65894400	-0.52773200	-2.53034300
C	7.75575000	-0.26242100	-3.12140600
O	8.46612100	-0.95906400	-3.79585500
C	8.15345600	1.21018500	-2.90724600
F	7.42246400	2.05220400	-3.69257900
F	9.44869900	1.47148000	-3.06814000
F	7.80258000	1.56933700	-1.59831400
Zn	-6.51524200	0.04342600	-0.25004600
N	4.88185600	-0.99614700	0.56553500
C	5.02067300	-2.01387200	1.40976400
H	5.96824600	-2.51730400	1.39432000
C	4.00533500	-2.43367200	2.25034500
H	4.17101100	-3.26294900	2.91209300
C	2.79257800	-1.76606600	2.21372700
C	2.65290300	-0.71008000	1.33052500
H	1.72881600	-0.17452600	1.30034600
C	3.70774100	-0.36053900	0.51096500
C	1.61204500	-2.19151000	3.05412400
H	1.08896700	-2.98810400	2.52360000
H	1.93722500	-2.56742400	4.02162200
O	0.78118700	-1.05981400	3.20622100
C	-0.52083300	-1.21111800	3.58790500
C	-1.13247500	-2.41251700	3.92063800
H	-0.57976200	-3.33266000	3.93652700
C	-2.47528000	-2.42296300	4.27768100
H	-2.94239800	-3.35497200	4.54087200
C	-3.21776800	-1.25230200	4.30897200
C	-2.58772300	-0.05937200	3.97803600
H	-3.14028300	0.86275400	4.00407800
C	-1.25594500	-0.03360500	3.62335000

H	-0.77437100	0.89358500	3.37728500
C	-4.67562800	-1.23742400	4.72180500
H	-4.77443500	-1.62470100	5.73270200
H	-5.02918800	-0.20576300	4.71895600
N	-5.48528900	-2.08354000	3.85609500
C	-6.14701200	-1.52381400	2.94474700
H	-6.13137800	-0.45485400	2.74578300
C	-7.04679600	-2.32008400	2.07975600
C	-7.61730700	-3.50671300	2.57390000
H	-7.34825300	-3.82898300	3.56018600
C	-8.51070000	-4.19240700	1.80164100
H	-8.98552600	-5.08531400	2.16597400
C	-8.81670100	-3.71442500	0.51595200
C	-8.16098300	-2.54965300	0.09767100
N	-7.31236700	-1.85385000	0.87464300
C	-9.75250300	-4.35446000	-0.35856700
H	-10.25772600	-5.23463100	-0.00439800
C	-10.00902900	-3.86684900	-1.59121700
H	-10.72330900	-4.34763400	-2.23416200
C	-9.32864100	-2.70513600	-2.07168200
C	-8.39920200	-2.06313000	-1.23613900
N	-7.69693200	-1.00661300	-1.63564700
C	-7.88872600	-0.49844400	-2.83367400
C	-8.80567000	-1.04839500	-3.73204600
H	-8.94742700	-0.60230200	-4.69804300
C	-9.52203400	-2.15551800	-3.34809100
H	-10.23451800	-2.60339300	-4.01670200
C	-7.08522900	0.69925900	-3.14371700
H	-7.24007700	1.16374900	-4.11005400
N	-6.27487500	1.15203800	-2.28757200
C	-5.55520300	2.37698200	-2.61282600
H	-5.89456100	3.12851800	-1.90764100
H	-5.81990100	2.71601100	-3.61649100
C	-4.05152700	2.21500800	-2.51742300
C	-3.42963000	0.99589000	-2.76293800
H	-4.02449400	0.13129500	-2.99349100
C	-2.05723500	0.87513900	-2.69834300
H	-1.57168000	-0.06878700	-2.86182900
C	-1.26694100	1.98325900	-2.41299200
C	-1.87133600	3.21655100	-2.21007300
H	-1.28754000	4.09904500	-2.02988600
C	-3.25569700	3.31792400	-2.24951700
H	-3.71408100	4.27680200	-2.07949100
O	0.07020100	1.73644500	-2.33467300
C	0.97444600	2.82232800	-2.20095300
H	0.68175800	3.47725000	-1.38209500
H	1.02512500	3.39603000	-3.12279300
C	2.31060900	2.21109100	-1.86177400
C	3.48164800	2.54008700	-2.52191600

H	3.48784400	3.23945900	-3.33656200
C	4.66022400	1.92259100	-2.13812400
H	5.57726300	2.12229500	-2.65656600
N	4.71228900	1.03859900	-1.14536000
C	3.58512600	0.70192000	-0.51642900
C	2.36910100	1.26684200	-0.85154200
H	1.46583100	0.96598800	-0.36409800
Zn	6.41658600	-0.16884200	-0.61107300
N	-4.70486600	-1.09877600	-0.41564500
C	-3.60738600	-0.55465100	0.11367600
C	-2.39981900	-1.23010300	0.13372300
H	-1.53725500	-0.79804100	0.59921300
C	-2.31436500	-2.48332400	-0.44933700
C	-3.45492200	-3.03115400	-1.01147500
C	-4.63121000	-2.30721300	-0.95825100
H	-5.54266000	-2.70224600	-1.36851800
C	-0.99706100	-3.21030900	-0.46928800
H	-0.70203100	-3.45747900	0.55075400
H	-1.07997700	-4.12957900	-1.04359600
O	-0.05576800	-2.33120500	-1.06294000
C	1.18406000	-2.83401400	-1.34139200
C	1.64630100	-4.06469000	-0.90122600
H	1.02900900	-4.71450700	-0.31117900
C	2.92516700	-4.47841800	-1.24581300
H	3.27215900	-5.44016200	-0.91131600
C	3.75347500	-3.68424700	-2.01850100
C	3.28088500	-2.44690500	-2.44798000
H	3.91642300	-1.81577800	-3.04604900
C	2.00771400	-2.02610200	-2.11904600
H	1.62544700	-1.08204100	-2.46061800
C	5.14532900	-4.14829900	-2.37783000
H	5.17439200	-5.23535400	-2.34221300
H	5.40347100	-3.83437200	-3.38990400
N	6.10571500	-3.66073200	-1.39485900
C	7.18685500	-3.19174100	-1.82936200
H	7.46631800	-3.10379500	-2.87344600
C	8.19055500	-2.72888300	-0.82524900
C	9.32285200	-3.51457000	-0.56362900
H	9.49105200	-4.40101600	-1.14406100
C	10.17124300	-3.15158600	0.44411100
H	11.03149500	-3.75044100	0.68279400
C	9.91155700	-1.98412200	1.18189700
C	8.79565300	-1.22588900	0.80568400
N	7.94884300	-1.61071500	-0.16742600
C	8.52283400	0.01766600	1.47651300
N	7.52706100	0.79304000	1.00124000
C	7.29081800	1.94924500	1.59868300
C	7.99586100	2.37051300	2.73623300
H	7.72920400	3.30808400	3.18211600

C	9.01477900	1.59816900	3.21307200
H	9.59386200	1.91036300	4.06311900
C	9.32759400	0.39290600	2.56374000
C	10.43105100	-0.42705200	2.95111800
H	11.03484000	-0.11012400	3.78165800
C	10.72508200	-1.55646400	2.27508500
H	11.57144400	-2.15855500	2.55081400
C	6.29145100	2.85468200	0.99083900
H	6.20757200	2.79339700	-0.08766700
N	5.63737400	3.65340600	1.70830300
C	4.70196400	4.53989900	1.04996700
H	4.81277600	4.51218300	-0.03767000
H	4.92009000	5.55045800	1.38996500
C	3.26361700	4.19878400	1.40361800
C	2.23996700	5.03097900	0.97993100
H	2.47282500	5.94514500	0.46096000
C	0.90897800	4.71901500	1.22069500
H	0.15013500	5.40929900	0.90680300
C	0.58987100	3.54542100	1.89181900
C	1.61320600	2.72907800	2.35804600
H	1.35864600	1.84519700	2.91353000
C	2.93237900	3.05456800	2.11708300
H	3.71155100	2.41693400	2.48941500
O	-0.67354400	3.09133000	2.13247500
C	-1.78389400	3.84330000	1.67632200
H	-1.56858800	4.30247500	0.71332000
H	-2.03627500	4.62121400	2.39205400
C	-2.93617800	2.89550100	1.46921000
C	-4.24479300	3.28155200	1.69613500
C	-5.27003900	2.41264400	1.35790000
H	-6.29750200	2.68114300	1.50204100
N	-5.03462900	1.21216500	0.83581700
C	-3.77251800	0.81234800	0.66462300
C	-2.69921400	1.62907800	0.95839400
H	-1.69421500	1.31054900	0.77860900
H	-4.48107900	4.24309500	2.11232300
H	-3.43647000	-3.99585000	-1.48217700

E(RBHandHLYP) = -8628.9344764 Hartree
Zero-point correction = 1.360945
Thermal correction to Energy = 1.449755
Thermal correction to Enthalpy = 1.450699
Thermal correction to Gibbs Free Energy = 1.231253
Sum of electronic and zero-point Energies = -8627.573532
Sum of electronic and thermal Energies = -8627.484722
Sum of electronic and thermal Enthalpies = -8627.483778
Sum of electronic and thermal Free Energies = -8627.703223

$\vec{\Delta}$-($\vec{\delta}$,$\vec{\lambda}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (0 Imaginary Frequencies)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.81945100	1.17055800	0.71689900
C	-8.56229700	1.99557200	0.09152300
O	-9.25654100	1.84170700	-0.88257600
C	-8.39529400	3.40992600	0.65750000
F	-7.21731200	3.93166400	0.15201200
F	-8.22618500	3.39753500	2.00754400
F	-9.38646700	4.24661000	0.33803300
O	7.23980800	0.39345700	-2.24852200
C	8.44519500	0.79801700	-2.12684000
O	9.45179200	0.18196800	-1.88998300
C	8.48944500	2.32569000	-2.19593800
F	7.60779000	2.80879900	-3.11754800
F	9.70343400	2.82871500	-2.44153900
F	8.06027300	2.81077000	-0.98076300
Zn	-6.50126900	0.05864000	-0.19145500
N	4.76023300	-1.36074700	0.43476400
C	4.87015200	-2.41752900	1.23298200
H	5.82320200	-2.91456400	1.23324300
C	3.83683400	-2.87107700	2.03142400
H	3.98385300	-3.72705600	2.66350800
C	2.63069900	-2.18768000	2.00528900
C	2.52228700	-1.08514700	1.17797100
H	1.60742200	-0.53326700	1.16560100
C	3.60150200	-0.70150400	0.39945200
C	1.43955400	-2.64475400	2.81431900
H	0.93881500	-3.44397700	2.26631200
H	1.75423000	-3.03077500	3.78169300
O	0.58489100	-1.53301300	2.97052000
C	-0.69890300	-1.71924200	3.40372000
C	-1.29480900	-2.94788200	3.65276100
H	-0.74293600	-3.86422200	3.56609700
C	-2.62586000	-2.99701200	4.04502600
H	-3.08272100	-3.95126000	4.23687000
C	-3.37207900	-1.83786200	4.19337800
C	-2.75432400	-0.61669500	3.95609600
H	-3.30831400	0.29666800	4.08050900
C	-1.43188100	-0.55249300	3.57074000
H	-0.95656400	0.39529200	3.40215400
C	-4.82701000	-1.87670400	4.61268600
H	-4.92731500	-2.40412600	5.55719600
H	-5.18019700	-0.85503400	4.75446000
N	-5.63355700	-2.58979900	3.62949800
C	-6.23028500	-1.90878400	2.75698300

H	-6.16889500	-0.82615000	2.67740200
C	-7.11061900	-2.57150600	1.76863300
C	-7.70895200	-3.80486200	2.08281100
H	-7.47370800	-4.25860400	3.02500900
C	-8.58467800	-4.36868700	1.19992200
H	-9.07866200	-5.29590900	1.42744300
C	-8.84959900	-3.71738300	-0.01724700
C	-8.17046700	-2.51619800	-0.25656400
N	-7.33351000	-1.94617400	0.62857100
C	-9.77020900	-4.21790700	-0.99291600
H	-10.29184600	-5.13238200	-0.77619300
C	-9.99483200	-3.55917200	-2.15003000
H	-10.69931600	-3.93632000	-2.86849700
C	-9.29577300	-2.34826500	-2.44697000
C	-8.37677900	-1.84302400	-1.51214300
N	-7.66246200	-0.74438200	-1.74126200
C	-7.83362200	-0.06227500	-2.85266900
C	-8.73802300	-0.46843500	-3.83653700
H	-8.86316700	0.11696400	-4.72755700
C	-9.46433000	-1.61597100	-3.63193900
H	-10.16786100	-1.95544000	-4.37024200
C	-7.02495400	1.16643700	-2.96860000
H	-7.17204100	1.77303000	-3.85403800
N	-6.22126700	1.48138400	-2.04698000
C	-5.49363300	2.73784800	-2.18156700
H	-5.80297600	3.36411900	-1.35148000
H	-5.78036100	3.24339000	-3.10605800
C	-3.98988500	2.54511400	-2.16312700
C	-3.40116300	1.36903900	-2.61410200
H	-4.02035200	0.55711200	-2.94911900
C	-2.03073900	1.21921700	-2.61884500
H	-1.57359500	0.30089400	-2.93609000
C	-1.20713500	2.25751300	-2.19646000
C	-1.77873600	3.45221900	-1.78018400
H	-1.16949700	4.28641000	-1.48789700
C	-3.16220600	3.58013000	-1.75540900
H	-3.59395400	4.50865900	-1.42377600
O	0.12567400	1.97993000	-2.22053100
C	1.06859500	2.97346900	-1.83699400
H	0.77715800	3.44824300	-0.90203100
H	1.16680300	3.72846500	-2.61241800
C	2.36577500	2.23168600	-1.62182800
C	3.53917400	2.53065300	-2.28976100
H	3.58938700	3.33296300	-3.00185100
C	4.66892300	1.76149400	-2.04137000
H	5.60500500	1.96026900	-2.53100100
N	4.65861100	0.74728800	-1.18020500
C	3.53184500	0.45535900	-0.52838500
C	2.37173300	1.17676900	-0.72429400

H	1.46878500	0.92708100	-0.20821300
Zn	6.33383600	-0.59121700	-0.84379900
N	-4.68473800	-1.05785300	-0.53567100
C	-3.57801200	-0.55755400	0.01667300
C	-2.35114800	-1.17997300	-0.13140100
H	-1.47514800	-0.78029800	0.33787700
C	-2.25546300	-2.32092900	-0.90883600
C	-3.40821500	-2.83028500	-1.48018800
C	-4.60352100	-2.17165000	-1.25267600
H	-5.52368400	-2.53864300	-1.66945700
C	-0.89421500	-2.91106600	-1.17187000
H	-0.38550400	-3.11428200	-0.23040800
H	-0.96955400	-3.83267300	-1.74330800
O	-0.20455000	-1.91321000	-1.90956600
C	1.09380000	-2.12884700	-2.25885900
C	1.84836100	-3.23150300	-1.88284600
H	1.42097400	-4.02431400	-1.29936700
C	3.17607600	-3.31811500	-2.27636800
H	3.75356900	-4.17713000	-1.98151900
C	3.76238300	-2.32301000	-3.04216400
C	2.98776000	-1.23491500	-3.42797200
H	3.42292700	-0.45749400	-4.03053700
C	1.66914800	-1.13387700	-3.04080500
H	1.07271700	-0.28390900	-3.31247900
C	5.21117400	-2.41892500	-3.45974700
H	5.39102600	-3.33191900	-4.02858500
H	5.45880400	-1.56913300	-4.09163900
N	6.09409500	-2.34088600	-2.30517300
C	7.00182900	-3.20628700	-2.17070400
H	7.13916200	-4.03384500	-2.85688600
C	7.96174100	-3.07452700	-1.05773800
C	8.99412200	-3.98701900	-0.83154600
H	9.11163900	-4.83905300	-1.47412200
C	9.85013700	-3.76515200	0.21967700
H	10.65283200	-4.45009000	0.42428300
C	9.68482300	-2.63185300	1.02902100
C	8.63210300	-1.75984700	0.69977800
N	7.79446600	-2.00942600	-0.30111500
C	8.42624800	-0.54836100	1.44989200
N	7.46346600	0.29648300	1.03440700
C	7.27108200	1.40310100	1.73106800
C	8.00833800	1.71126400	2.88702000
H	7.78115400	2.61997000	3.40805300
C	9.00168600	0.86812300	3.29276000
H	9.60193200	1.09401200	4.15531000
C	9.24869300	-0.30208900	2.55726600
C	10.29819200	-1.21909600	2.88530200
H	10.92163600	-0.99282600	3.73115000
C	10.51904500	-2.32727500	2.14816600

H	11.32237700	-2.99853100	2.39031000
C	6.26399600	2.37245700	1.24345200
H	6.12998400	2.41120200	0.17226100
N	5.66446900	3.12199700	2.05711400
C	4.73366000	4.08613500	1.51018500
H	4.80992600	4.14889700	0.42073700
H	4.99348500	5.05807300	1.92491300
C	3.29602500	3.76160000	1.87695700
C	2.29917300	4.68941700	1.62006600
H	2.55902000	5.66051700	1.23452200
C	0.96311100	4.40075000	1.86182800
H	0.22748700	5.16153900	1.68509100
C	0.61202500	3.15473600	2.36416500
C	1.60951300	2.23543700	2.66638500
H	1.32953100	1.29001500	3.09416800
C	2.93455000	2.53885000	2.42674800
H	3.69583200	1.82223300	2.67005100
O	-0.66384800	2.72411400	2.58726800
C	-1.75509700	3.54939900	2.22068200
H	-1.51802700	4.12960300	1.33108000
H	-2.00810200	4.22761600	3.03097100
C	-2.91378300	2.65077300	1.87527200
C	-4.22058400	2.98510600	2.17893300
C	-5.24497800	2.16889000	1.72505200
H	-6.27181300	2.40328200	1.92233800
N	-5.00965800	1.06486200	1.02141100
C	-3.74784300	0.70865800	0.76983000
C	-2.67753400	1.48247300	1.16848100
H	-1.67250500	1.20695100	0.92818300
H	-4.45670800	3.86776300	2.74343500
H	-3.38562200	-3.70951000	-2.09566500

E(RBHandHLYP) = -8628.944131 Hartree
Zero-point correction = 1.361005
Thermal correction to Energy = 1.449908
Thermal correction to Enthalpy = 1.450853
Thermal correction to Gibbs Free Energy = 1.230695
Sum of electronic and zero-point Energies = -8627.583126
Sum of electronic and thermal Energies = -8627.494223
Sum of electronic and thermal Enthalpies = -8627.493278
Sum of electronic and thermal Free Energies = -8627.713436

$\vec{\Delta}$-($\vec{\delta}$,$\vec{X}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (0 Imaginary Frequencies)

	Coordinates (Angstroms)		
	X	Y	Z

O	7.09558700	-0.23696100	-2.24274900
C	8.30112100	-0.00177500	-2.58411200
O	9.07891000	-0.67391300	-3.20692600
C	8.73937600	1.39020000	-2.09749200
F	8.23043800	1.57838000	-0.80857100
F	8.16261400	2.38254600	-2.83634400
F	10.05547200	1.58363200	-2.05411500
O	-7.53624600	0.68346700	1.86613300
C	-8.75654400	0.91692600	1.56946900
O	-9.69273100	0.16592500	1.47895700
C	-8.92576100	2.38703300	1.17876400
F	-8.17779700	3.20473500	1.97376800
F	-10.19277500	2.81238500	1.17849500
F	-8.42002700	2.54339800	-0.09385500
Zn	6.52711900	-0.21128600	-0.36178800
N	-4.71366100	-1.34665100	-0.20706000
C	-4.69350300	-2.56920400	-0.72489400
H	-5.62517800	-3.10494500	-0.71622200
C	-3.55155900	-3.14027500	-1.24562000
H	-3.58554100	-4.13244700	-1.65609200
C	-2.37316300	-2.40866100	-1.22341400
C	-2.39989300	-1.12852700	-0.70111300
H	-1.50065000	-0.54970800	-0.68992400
C	-3.59239400	-0.62557500	-0.20004300
C	-1.09119000	-3.04874200	-1.68509400
H	-0.75007000	-3.70713000	-0.88482600
H	-1.26741300	-3.65264600	-2.57364400
O	-0.12860600	-2.05126100	-1.94555000
C	1.14359700	-2.47623000	-2.22790200
C	1.56853900	-3.79220500	-2.11936200
H	0.89510400	-4.57948000	-1.84329400
C	2.88972700	-4.11155300	-2.39387300
H	3.20701700	-5.13603500	-2.31082500
C	3.79865500	-3.14379000	-2.78217100
C	3.35591800	-1.83005300	-2.90545700
H	4.04607300	-1.06644600	-3.22204500
C	2.04236800	-1.49639300	-2.63520600
H	1.69265700	-0.48640400	-2.74615100
C	5.23759900	-3.51503700	-3.05168900
H	5.28011600	-4.56384100	-3.33928100
H	5.64014500	-2.92272100	-3.87342500
N	6.03777700	-3.36266900	-1.83788500
C	7.23860000	-3.02422800	-1.98467200
H	7.72860100	-2.82021300	-2.93046100
C	8.08245600	-2.87776300	-0.76171400
C	9.07752200	-3.82286400	-0.47007500
H	9.26169300	-4.62186700	-1.16199200
C	9.77539000	-3.72079200	0.70117400
H	10.52565400	-4.44593500	0.95988700

C	9.50988100	-2.65404800	1.57757900
C	8.54373300	-1.72460700	1.17409100
N	7.83593000	-1.85813100	0.03796700
C	10.17653600	-2.48365100	2.82964300
H	10.90836900	-3.21327100	3.12459400
C	9.89010900	-1.43239500	3.62526100
H	10.38535300	-1.30800200	4.57085200
C	8.94372800	-0.44133000	3.22077200
C	8.28482600	-0.56672400	1.98840700
N	7.44839200	0.37482100	1.50718300
C	7.22761800	1.45595800	2.23601400
C	7.79012100	1.63434800	3.50875500
H	7.54683600	2.52466100	4.05395500
C	8.64990400	0.69253100	3.99622400
H	9.11994300	0.81753900	4.95480200
C	6.39706200	2.52946100	1.64546300
H	6.47944900	2.64110900	0.57089600
N	5.68099600	3.25431700	2.38112000
C	4.89044900	4.28938900	1.74808900
H	5.16966600	4.43286900	0.70093100
H	5.08202300	5.21721200	2.28398800
C	3.40479400	3.97027200	1.82281300
C	2.93522000	2.80716800	2.41963100
H	3.62957700	2.13106700	2.88084500
C	1.58735100	2.51324000	2.42899500
H	1.22156900	1.61284500	2.88746800
C	0.67350000	3.38143800	1.84418900
C	1.12467000	4.56626600	1.27752100
H	0.43786300	5.28265900	0.86817200
C	2.48473200	4.84693300	1.26916400
H	2.82220500	5.77105900	0.83139900
O	-0.62330900	2.96991700	1.87902900
C	-1.61608800	3.74181100	1.21577300
H	-1.28246300	4.02544400	0.21975100
H	-1.85605500	4.63359200	1.78852500
C	-2.81146000	2.83355000	1.08952800
C	-4.06209500	3.15912900	1.58007300
H	-4.24521100	4.09868200	2.06673200
C	-5.09248000	2.23889500	1.45063700
H	-6.08456800	2.44808200	1.80677100
N	-4.90882900	1.05246200	0.87845900
C	-3.70566700	0.73055300	0.39726700
C	-2.63910400	1.60147800	0.47864600
H	-1.67788700	1.33847900	0.08951000
Zn	-6.41822500	-0.47212200	0.77519100
N	4.77298100	-1.06580100	0.45561600
C	3.66983500	-0.32033800	0.34956700
C	2.48044300	-0.68487000	0.95387300
H	1.61431900	-0.06105600	0.89063800

C	2.41180500	-1.87457800	1.65714700
C	3.55535200	-2.65207800	1.74592700
C	4.71217900	-2.20740100	1.13359100
H	5.61340900	-2.78905900	1.16632700
C	1.09835400	-2.33901000	2.23736500
H	0.62643300	-2.99654600	1.50642900
H	1.25721200	-2.89541100	3.15875700
O	0.29760100	-1.19857300	2.47388600
C	-1.01640100	-1.36522200	2.80177900
C	-1.69439500	-2.57752500	2.79794800
H	-1.18999900	-3.49676000	2.57057600
C	-3.04574000	-2.60885900	3.11222000
H	-3.55865600	-3.55501500	3.11221800
C	-3.73456500	-1.45078800	3.43932600
C	-3.03633700	-0.24912400	3.46006900
H	-3.54699000	0.66019400	3.72361700
C	-1.69526700	-0.20170000	3.14245100
H	-1.16357300	0.73091700	3.14072500
C	-5.20205700	-1.49167300	3.80599700
H	-5.37441200	-2.21310800	4.60547900
H	-5.50693900	-0.51071900	4.16291700
N	-6.04219700	-1.78372800	2.65186200
C	-6.88570000	-2.71820800	2.73727900
H	-6.99155400	-3.34247500	3.61711600
C	-7.81246500	-2.96338400	1.61397400
C	-8.76495500	-3.98492100	1.61833800
H	-8.84758300	-4.64214600	2.46324500
C	-9.58765400	-4.12422000	0.52649900
H	-10.32703000	-4.90383100	0.49679000
C	-9.46901800	-3.24139100	-0.55709500
C	-8.50225200	-2.22791500	-0.44841200
N	-7.69565200	-2.12881900	0.60256000
C	-8.34323600	-1.25374600	-1.49661100
N	-7.46861700	-0.25047700	-1.29664500
C	-7.29482000	0.62405900	-2.27185300
C	-7.97010100	0.53170100	-3.50029800
H	-7.76374500	1.26685500	-4.25256700
C	-8.88657100	-0.46344300	-3.68876300
H	-9.44299200	-0.53628700	-4.60552900
C	-9.10926600	-1.39365700	-2.66079100
C	-10.07551400	-2.44691300	-2.75398600
H	-10.66437600	-2.51555000	-3.65055500
C	-10.26163700	-3.32219800	-1.74369900
H	-11.00290300	-4.09662300	-1.81693300
C	-6.38880500	1.77196800	-2.03042600
H	-6.40489700	2.17516800	-1.02705800
N	-5.71013200	2.25280400	-2.97441300
C	-4.90983000	3.42492900	-2.68491400
H	-5.13341500	3.83111000	-1.69429800

H	-5.16843100	4.17929100	-3.42599700
C	-3.41864400	3.14637600	-2.76628600
C	-2.52580800	4.19304300	-2.59636500
H	-2.89605500	5.19739600	-2.47916600
C	-1.15488400	3.97806100	-2.58295800
H	-0.49436800	4.81794500	-2.48129600
C	-0.66290800	2.68827300	-2.73417400
C	-1.54900200	1.63956900	-2.94961400
H	-1.15013700	0.65290200	-3.10084200
C	-2.91094300	1.86966200	-2.96764200
H	-3.58759400	1.05345100	-3.13696900
O	0.65438800	2.34206800	-2.67580700
C	1.61198700	3.33707400	-2.35416400
H	1.25444000	3.96999500	-1.54391600
H	1.83679200	3.95129100	-3.22204800
C	2.83560400	2.60475900	-1.87049200
C	4.11462100	2.91329200	-2.29709900
C	5.17693400	2.17360800	-1.80706000
H	6.17627500	2.35787500	-2.14851700
N	5.01233300	1.18423100	-0.93323000
C	3.78070000	0.87371000	-0.52381600
C	2.67266200	1.56721400	-0.96851300
H	1.68658600	1.29297600	-0.65800800
H	4.29293600	3.68836200	-3.01842600
H	3.55883300	-3.58642100	2.27521900

E(RBHandHLYP) = -8628.9333986 Hartree
Zero-point correction = 1.360359
Thermal correction to Energy = 1.449340
Thermal correction to Enthalpy = 1.450284
Thermal correction to Gibbs Free Energy = 1.229813
Sum of electronic and zero-point Energies = -8627.573040
Sum of electronic and thermal Energies = -8627.484058
Sum of electronic and thermal Enthalpies = -8627.483114
Sum of electronic and thermal Free Energies = -8627.703586

$\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (0 Imaginary Frequencies)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.56596100	0.44065100	1.90315400
C	-8.78334500	0.69915200	1.61651400
O	-9.70493400	-0.04301500	1.39537000
C	-8.96749200	2.20776100	1.43751900
F	-8.45598900	2.54646100	0.20349000
F	-8.23397100	2.91238900	2.34557200
F	-10.23949800	2.61509200	1.48772600

O	7.56604400	0.44003100	-1.90409800
C	8.78348000	0.69840800	-1.61748200
O	9.70507400	-0.04390400	-1.39685000
C	8.96771900	2.20693400	-1.43818900
F	8.23442700	2.91159000	-2.34657900
F	10.23981000	2.61411500	-1.48821400
F	8.45603900	2.54583100	-0.20445200
Zn	-6.42004000	-0.57814100	0.70806300
N	4.66653800	-1.33943500	0.31555200
C	4.60164000	-2.49846800	0.95962900
H	5.51110500	-3.06989800	1.00247700
C	3.44296000	-2.96636100	1.54944400
H	3.44537400	-3.90972800	2.06298600
C	2.29803400	-2.18945800	1.46861500
C	2.37192100	-0.97583800	0.80845600
H	1.50243700	-0.35559800	0.75736400
C	3.57170800	-0.58169000	0.23694100
C	0.98302200	-2.68028400	2.02165300
H	0.49687200	-3.27737600	1.24903300
H	1.14152400	-3.30726900	2.89658900
O	0.19436300	-1.55522200	2.34959000
C	-1.11867600	-1.74517000	2.67356200
C	-1.80318400	-2.94759300	2.55169300
H	-1.30602700	-3.84352300	2.23428000
C	-3.15420700	-3.00102400	2.86116000
H	-3.67441100	-3.93828000	2.76490900
C	-3.83540300	-1.87628200	3.29991400
C	-3.12936100	-0.68830800	3.44574300
H	-3.63392200	0.19303100	3.80013100
C	-1.78733300	-0.61841900	3.13484400
H	-1.24854900	0.30526500	3.23004500
C	-5.30985200	-1.94523500	3.63017600
H	-5.50688800	-2.75213700	4.33671100
H	-5.62075500	-1.00877100	4.08703600
N	-6.11187200	-2.10005000	2.42395300
C	-6.94210300	-3.04770100	2.36055800
H	-7.07145000	-3.77773800	3.15129400
C	-7.82069900	-3.15961900	1.17877800
C	-8.75797400	-4.18215000	1.01689700
H	-8.86251900	-4.94241800	1.76769300
C	-9.53889400	-4.18780300	-0.11369200
H	-10.26580900	-4.96399400	-0.27017700
C	-9.39646200	-3.17046300	-1.06867700
C	-8.44763000	-2.17059700	-0.79624400
N	-7.67795900	-2.20217300	0.28612300
C	-10.15208400	-3.10129600	-2.27969100
H	-10.87796100	-3.86805900	-2.47913100
C	-9.95325300	-2.09405700	-3.15559800
H	-10.51621400	-2.04733700	-4.07003700

C	-9.00977200	-1.04942900	-2.89026300
C	-8.27469500	-1.06163700	-1.69818300
N	-7.42401500	-0.08235900	-1.33772400
C	-7.24937900	0.92609600	-2.17386300
C	-7.89582200	0.99739000	-3.41911600
H	-7.69008800	1.83675600	-4.05323600
C	-8.78389000	0.02101600	-3.77055600
H	-9.31773200	0.06839700	-4.70229900
C	-6.36868300	2.04084000	-1.75074000
H	-6.40157500	2.28778400	-0.69884400
N	-5.68546800	2.66551000	-2.60248800
C	-4.88981700	3.78020800	-2.13010100
H	-5.11684400	4.02778400	-1.08942700
H	-5.14448000	4.64058800	-2.74659100
C	-3.39944200	3.50991900	-2.25265700
C	-2.90702800	2.28336700	-2.67851200
H	-3.59327400	1.51650900	-2.98418500
C	-1.54850900	2.04122600	-2.71318100
H	-1.16572100	1.09059700	-3.03658900
C	-0.64802800	3.02748000	-2.32861500
C	-1.12428500	4.27238200	-1.93995800
H	-0.45164800	5.07220400	-1.69417200
C	-2.49368000	4.49973100	-1.90263400
H	-2.85168700	5.47053500	-1.60437500
O	0.66539100	2.66616300	-2.36653600
C	1.64503200	3.53858800	-1.81803600
H	1.29586200	3.97121200	-0.88278300
H	1.88946100	4.33167700	-2.51922500
C	2.84183700	2.66770100	-1.53273700
C	4.10393700	2.91779600	-2.03824700
H	4.30125200	3.77576500	-2.65315600
C	5.12778400	2.02465100	-1.75521300
H	6.12812100	2.17945700	-2.11626900
N	4.92742600	0.93078500	-1.02470900
C	3.71357200	0.68477100	-0.52678800
C	2.65423600	1.53906400	-0.75130900
H	1.68296500	1.33584000	-0.35188700
Zn	6.41978900	-0.57886500	-0.70946700
N	-4.66628700	-1.33941700	-0.31451500
C	-3.57158600	-0.58144300	-0.23635600
C	-2.37184200	-0.97556700	-0.80800200
H	-1.50252500	-0.35505200	-0.75748000
C	-2.29784300	-2.18945400	-1.46764000
C	-3.44262500	-2.96664800	-1.54789800
C	-4.60128900	-2.49872100	-0.95813000
H	-5.51065700	-3.07033200	-1.00055000
C	-0.98289100	-2.68038000	-2.02071300
H	-0.49689900	-3.27766700	-1.24813100
H	-1.14145500	-3.30723200	-2.89573300

O	-0.19402700	-1.55543500	-2.34849900
C	1.11892200	-1.74562800	-2.67270600
C	1.80329400	-2.94811500	-2.55062800
H	1.30608100	-3.84388700	-2.23286000
C	3.15425200	-3.00179500	-2.86028900
H	3.67436800	-3.93907900	-2.76384300
C	3.83551600	-1.87724500	-3.29945500
C	3.12960400	-0.68923200	-3.44551900
H	3.63420700	0.19195600	-3.80022700
C	1.78762900	-0.61909700	-3.13441700
H	1.24895700	0.30463600	-3.22976300
C	5.30992600	-1.94645600	-3.62979300
H	5.50689000	-2.75363100	-4.33602600
H	5.62093500	-1.01018700	-4.08697900
N	6.11193600	-2.10094800	-2.42350900
C	6.94214400	-3.04860300	-2.35968300
H	7.07148200	-3.77893900	-3.15013100
C	7.82063100	-3.16008500	-1.17775800
C	8.75771800	-4.18266600	-1.01525900
H	8.86230100	-4.94331600	-1.76566500
C	9.53845100	-4.18785300	0.11546200
H	10.26523600	-4.96406600	0.27245400
C	9.39600300	-3.17004000	1.06993000
C	8.44734100	-2.17014200	0.79689600
N	7.67789300	-2.20216000	-0.28560200
C	8.27440600	-1.06072900	1.69829800
N	7.42383400	-0.08155600	1.33730500
C	7.24932800	0.92728200	2.17300300
C	7.89578300	0.99912500	3.41824000
H	7.69012500	1.83883400	4.05192600
C	8.78368800	0.02281000	3.77020100
H	9.31749000	0.07054800	4.70194900
C	9.00941500	-1.04808500	2.89042900
C	9.95271300	-2.09272000	3.15636700
H	10.51557600	-2.04562800	4.07084800
C	10.15149300	-3.10042200	2.28099000
H	10.87722200	-3.86720600	2.48089100
C	6.36861400	2.04189700	1.74962500
H	6.40125000	2.28849200	0.69765000
N	5.68558400	2.66688100	2.60129400
C	4.88977300	3.78133300	2.12868000
H	5.11648500	4.02850100	1.08783700
H	5.14452200	4.64198900	2.74474200
C	3.39943000	3.51098900	2.25172400
C	2.49351400	4.50069600	1.90183800
H	2.85136200	5.47150900	1.60341800
C	1.12414000	4.27323500	1.93950400
H	0.45138900	5.07299000	1.69381600
C	0.64808000	3.02832400	2.32836000

C	1.54873100	2.04217300	2.71281100
H	1.16608700	1.09153900	3.03638400
C	2.90721200	2.28443400	2.67781000
H	3.59359600	1.51766100	2.98339100
O	-0.66529700	2.66689000	2.36654900
C	-1.64507200	3.53919000	1.81811900
H	-1.29598700	3.97185100	0.88284800
H	-1.88955400	4.33226000	2.51930700
C	-2.84181000	2.66822000	1.53283700
C	-4.10399400	2.91849400	2.03807200
C	-5.12784500	2.02537700	1.75501900
H	-6.12821100	2.18029900	2.11591800
N	-4.92745000	0.93138000	1.02472700
C	-3.71352600	0.68519300	0.52709700
C	-2.65413000	1.53941200	0.75169700
H	-1.68276800	1.33595300	0.35261200
H	-4.30136100	3.77659900	2.65277200
H	-3.44494000	-3.91024000	-2.06102500

E(RBHandHLYP) = -8628.94524643 Hartree
Zero-point correction = 1.361043
Thermal correction to Energy = 1.449833
Thermal correction to Enthalpy = 1.450778
Thermal correction to Gibbs Free Energy = 1.231208
Sum of electronic and zero-point Energies = -8627.584204
Sum of electronic and thermal Energies = -8627.495413
Sum of electronic and thermal Enthalpies = -8627.494469
Sum of electronic and thermal Free Energies = -8627.714038

TS-$\vec{\Delta}$-($\vec{\delta}$,$\vec{\delta}$)-$\vec{\Delta}$-($\vec{\delta}$,$\vec{X}$)-[-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (1 Imaginary Frequency)

	Coordinates (Angstroms)		
	X	Y	Z
O	7.15492300	-0.19450000	-2.22778700
C	8.37861900	0.02551900	-2.51323400
O	9.18304200	-0.66798900	-3.07561700
C	8.79391800	1.42463500	-2.03217200
F	8.29161700	1.60412900	-0.74324400
F	8.19121300	2.40244500	-2.77153100
F	10.10665600	1.64406100	-2.00194400
O	-7.55395000	0.65063900	1.87445000
C	-8.77311300	0.88631400	1.57486900
O	-9.70859000	0.13584000	1.47334200

C	-8.94151200	2.36001000	1.19746300
F	-8.20017600	3.17088400	2.00557500
F	-10.20899200	2.78385200	1.19247900
F	-8.42704400	2.52952900	-0.07007600
Zn	6.52315100	-0.25156900	-0.37088300
N	-4.71944500	-1.34676800	-0.21644300
C	-4.69246300	-2.56349100	-0.74736300
H	-5.62011500	-3.10623900	-0.74025200
C	-3.54866200	-3.12052800	-1.27987800
H	-3.57743100	-4.10832200	-1.70110500
C	-2.37617800	-2.37983500	-1.25633900
C	-2.41015400	-1.10590600	-0.71930900
H	-1.51595600	-0.51941000	-0.70832500
C	-3.60333300	-0.61776100	-0.20628500
C	-1.08945100	-2.99970000	-1.73279900
H	-0.72611100	-3.64994800	-0.93568600
H	-1.26524500	-3.60806900	-2.61830200
O	-0.15040600	-1.98340800	-2.00617600
C	1.13071000	-2.37738800	-2.29083000
C	1.59066100	-3.68140700	-2.17890600
H	0.93832600	-4.48510700	-1.89923100
C	2.91950900	-3.96619500	-2.45469600
H	3.26430600	-4.98156600	-2.36855300
C	3.80144000	-2.97538000	-2.84822800
C	3.32252400	-1.67528400	-2.97681600
H	3.99035200	-0.89472000	-3.29923100
C	2.00143400	-1.37556500	-2.70441200
H	1.62556200	-0.37514900	-2.81633400
C	5.24955600	-3.30626000	-3.11606100
H	5.31934800	-4.33927400	-3.45223100
H	5.64705200	-2.66777000	-3.90408200
N	6.04086000	-3.17443600	-1.89119100
C	7.28016200	-3.01979600	-2.02783500
H	7.80836100	-2.97123500	-2.97401600
C	8.11926900	-2.88033300	-0.80622000
C	9.14452600	-3.80025600	-0.53958500
H	9.35592100	-4.57352600	-1.25288100
C	9.83636600	-3.70940500	0.63621700
H	10.60652200	-4.41933400	0.87796500
C	9.54156300	-2.67123500	1.53715200
C	8.55327200	-1.75686300	1.15221300
N	7.84471300	-1.88700000	0.01732300
C	10.20395100	-2.50957100	2.79259800
H	10.95025500	-3.22929700	3.07532100
C	9.89678600	-1.47778000	3.60594800
H	10.38919500	-1.36020300	4.55389600
C	8.93508500	-0.49551900	3.21580300
C	8.27793300	-0.61375200	1.98195300
N	7.43374600	0.32498900	1.50941300

C	7.20338500	1.39673400	2.24887700
C	7.76041300	1.56497000	3.52552700
H	7.50850000	2.44734500	4.07966300
C	8.62765800	0.62556100	4.00445500
H	9.09481900	0.74430600	4.96523300
C	6.37191200	2.47324400	1.66536400
H	6.45521900	2.59223600	0.59161300
N	5.65714200	3.19485200	2.40558100
C	4.87035500	4.23664000	1.77912000
H	5.14498500	4.38039100	0.73070400
H	5.07158000	5.16193300	2.31590700
C	3.38299200	3.92833300	1.86134100
C	2.90947300	2.76003100	2.44456700
H	3.60239600	2.07254900	2.89084200
C	1.55976300	2.47497500	2.45878100
H	1.19110500	1.57024400	2.90625300
C	0.64813700	3.35766900	1.89254400
C	1.10357200	4.54729000	1.33955000
H	0.41888100	5.27393100	0.94497600
C	2.46541200	4.81903900	1.32631200
H	2.80630100	5.74708800	0.89963200
O	-0.65126700	2.95490700	1.93088100
C	-1.64110700	3.73397300	1.27159100
H	-1.30286100	4.02847800	0.28035500
H	-1.88400100	4.61926700	1.85303900
C	-2.83496500	2.82596400	1.13027300
C	-4.08666100	3.14068300	1.62508100
H	-4.27283100	4.07259300	2.12509000
C	-5.11405800	2.21898800	1.48239600
H	-6.10696200	2.42009700	1.84076600
N	-4.92632600	1.04117200	0.89397600
C	-3.72215200	0.73003000	0.40829000
C	-2.65867600	1.60340100	0.50168400
H	-1.69651300	1.34897200	0.10909700
Zn	-6.42879600	-0.48660700	0.77075700
N	4.76740300	-1.08917600	0.45866800
C	3.66607300	-0.34202800	0.35272400
C	2.47438100	-0.70812800	0.95262900
H	1.60777600	-0.08526600	0.88704300
C	2.40414400	-1.89869500	1.65395400
C	3.54815100	-2.67567200	1.74620500
C	4.70574100	-2.23074200	1.13592100
H	5.60788700	-2.81126700	1.16995400
C	1.08912100	-2.36644500	2.22816400
H	0.62102100	-3.02274200	1.49362200
H	1.24544300	-2.92548700	3.14840300
O	0.28469000	-1.22868000	2.46530200
C	-1.02954400	-1.40068500	2.79037900
C	-1.70500800	-2.61435000	2.77513500

H	-1.19854200	-3.53055200	2.54035600
C	-3.05661000	-2.65142700	3.08763800
H	-3.56735200	-3.59872400	3.07894600
C	-3.74840100	-1.49787400	3.42426000
C	-3.05282000	-0.29490900	3.45620700
H	-3.56564800	0.61092600	3.72744100
C	-1.71145800	-0.24172600	3.14039700
H	-1.18198000	0.69211200	3.14806100
C	-5.21618200	-1.54577800	3.78927500
H	-5.38807600	-2.27880600	4.57822600
H	-5.52262200	-0.57043900	4.16001000
N	-6.05503500	-1.82247200	2.63037100
C	-6.89804900	-2.75858100	2.70163100
H	-7.00492600	-3.39499200	3.57260300
C	-7.82239200	-2.98928600	1.57313400
C	-8.77486800	-4.01076900	1.56183500
H	-8.85979500	-4.67875600	2.39802700
C	-9.59461800	-4.13602100	0.46604500
H	-10.33394000	-4.91514400	0.42443700
C	-9.47297000	-3.23959400	-0.60599400
C	-8.50647100	-2.22767500	-0.48181700
N	-7.70297700	-2.14198200	0.57267500
C	-8.34403400	-1.24062100	-1.51745400
N	-7.46970300	-0.24015400	-1.30269100
C	-7.29169000	0.64551900	-2.26710400
C	-7.96282800	0.56791600	-3.49880100
H	-7.75330100	1.31142700	-4.24192500
C	-8.87961200	-0.42413500	-3.70184800
H	-9.43307500	-0.48574000	-4.62122500
C	-9.10634300	-1.36621800	-2.68570400
C	-10.07277600	-2.41781000	-2.79467500
H	-10.65896600	-2.47522200	-3.69378100
C	-10.26217400	-3.30542000	-1.79582000
H	-11.00347800	-4.07860400	-1.88080500
C	-6.38541600	1.79000200	-2.00957300
H	-6.40836300	2.18493800	-1.00305800
N	-5.69879100	2.27733000	-2.94445800
C	-4.89901100	3.44608500	-2.63994900
H	-5.12291900	3.83982400	-1.64438800
H	-5.15821700	4.20949800	-3.37157300
C	-3.40758200	3.16977800	-2.72544600
C	-2.51507500	4.21399300	-2.53900000
H	-2.88573900	5.21613600	-2.40519300
C	-1.14388500	3.99968000	-2.53047000
H	-0.48357600	4.83804500	-2.41560300
C	-0.65126100	2.71291100	-2.70359500
C	-1.53715700	1.66728900	-2.93455000
H	-1.13834600	0.68310000	-3.10124500
C	-2.89927300	1.89677000	-2.94764800

H	-3.57555600	1.08293900	-3.12949200
O	0.66644100	2.36655900	-2.65441000
C	1.62484400	3.35398700	-2.30945100
H	1.26645600	3.96893900	-1.48597500
H	1.85134900	3.98661500	-3.16348000
C	2.84621300	2.60701800	-1.84191200
C	4.12370100	2.89700500	-2.28561300
C	5.18188500	2.13960300	-1.81218700
H	6.18086600	2.31122500	-2.16211700
N	5.01245000	1.14889400	-0.94088900
C	3.78191300	0.85558700	-0.51542900
C	2.67957400	1.56964900	-0.94013100
H	1.69410800	1.31256800	-0.61351200
H	4.30391100	3.67219100	-3.00634200
H	3.55054500	-3.60949700	2.27650700

E(RBHandHLYP) = -8628.9333726 Hartree
Zero-point correction = 1.360134
Thermal correction to Energy = 1.448332
Thermal correction to Enthalpy = 1.449277
Thermal correction to Gibbs Free Energy = 1.231505
Sum of electronic and zero-point Energies = -8627.573238
Sum of electronic and thermal Energies = -8627.485040
Sum of electronic and thermal Enthalpies = -8627.484096
Sum of electronic and thermal Free Energies = -8627.701868

TS-$\vec{\Delta}$-($\vec{\delta}$,$\vec{X}$)-$\vec{\Delta}$-($\vec{\delta}$,$\vec{\lambda}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (1 Imaginary Frequency)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.35669300	0.35822600	1.86238500
C	-8.62798900	0.48691400	1.95875600
O	-9.47368500	-0.32680500	2.20801700
C	-9.03106600	1.93236200	1.63771600
F	-8.29098600	2.82482800	2.36010200
F	-10.32737200	2.19471500	1.81020000
F	-8.71014100	2.19298900	0.31709100
O	7.47517100	0.79475100	-1.92935600
C	8.69299600	1.07430100	-1.66429600
O	9.65534300	0.35637300	-1.57968100
C	8.81970700	2.55622100	-1.30429100
F	8.01663600	3.33148600	-2.08772200
F	10.06952700	3.02776800	-1.35214600
F	8.34965900	2.71532500	-0.01887500
Zn	-6.49291600	-0.06213400	0.16426900
N	4.77562900	-1.37368900	0.16101700

C	4.80750100	-2.59658200	0.67955500
H	5.74790600	-3.11342600	0.61956200
C	3.70914200	-3.19061700	1.26622500
H	3.78822100	-4.18141000	1.67400300
C	2.51901500	-2.47953700	1.31884200
C	2.49125200	-1.20304300	0.78907500
H	1.58430500	-0.63930400	0.83522500
C	3.63924500	-0.67919700	0.21320900
C	1.27908700	-3.11387600	1.89565800
H	0.92583800	-3.86795800	1.19117100
H	1.50878200	-3.60553700	2.83976800
O	0.30489600	-2.11100200	2.08133200
C	-0.94100200	-2.49613900	2.49728300
C	-1.37954100	-3.81091100	2.56335800
H	-0.73117900	-4.62970000	2.31893800
C	-2.67766600	-4.08242000	2.97073400
H	-3.00945200	-5.10408200	3.02162000
C	-3.54762700	-3.06282100	3.31742900
C	-3.09004600	-1.75043100	3.25794600
H	-3.74204300	-0.94418400	3.54641300
C	-1.80027900	-1.46570900	2.85680100
H	-1.43860600	-0.45412800	2.83818100
C	-4.97009500	-3.36104100	3.74250600
H	-4.98766900	-4.22898900	4.39488600
H	-5.36970700	-2.50806900	4.29153600
N	-5.77992000	-3.67422300	2.56839800
C	-6.51666700	-2.75225400	2.13402300
H	-6.59770600	-1.76139300	2.57337300
C	-7.37889400	-2.96618000	0.94773400
C	-8.05990800	-4.17604000	0.74188400
H	-7.90605900	-4.97776200	1.43677400
C	-8.91861800	-4.28493000	-0.31667400
H	-9.47231700	-5.19103200	-0.48412000
C	-9.10153500	-3.19159200	-1.18359400
C	-8.34621100	-2.04138900	-0.92276000
N	-7.50545600	-1.94887600	0.11799600
C	-10.01822100	-3.19861900	-2.27921000
H	-10.59314800	-4.08803900	-2.46160700
C	-10.17496900	-2.10561100	-3.05502300
H	-10.87828500	-2.10553900	-3.86755900
C	-9.41780600	-0.91678700	-2.81423400
C	-8.48683200	-0.88443300	-1.76800100
N	-7.72752900	0.20154700	-1.49936300
C	-7.88947900	1.29034600	-2.22587300
C	-8.81939300	1.35585800	-3.27203600
H	-8.92026300	2.26774700	-3.82828400
C	-9.57086200	0.25422600	-3.57357700
H	-10.28094000	0.27632900	-4.38031000
C	-7.05833600	2.49629600	-1.92927600

H	-7.58344200	3.32798900	-1.46837900
N	-5.85002900	2.50962500	-2.26734400
C	-5.09534900	3.74035700	-2.07712200
H	-5.44230500	4.30282800	-1.20936300
H	-5.27286700	4.35480100	-2.96122200
C	-3.60598500	3.47876000	-1.97795000
C	-3.04102100	2.35387300	-2.56949000
H	-3.67829000	1.64418700	-3.06184700
C	-1.68099700	2.14065600	-2.51969000
H	-1.24204800	1.26694500	-2.96417400
C	-0.84577500	3.05475500	-1.88547000
C	-1.39121500	4.19712700	-1.31849500
H	-0.76747700	4.94350900	-0.86361500
C	-2.76749300	4.39406600	-1.36369700
H	-3.17937800	5.28534900	-0.92205400
O	0.47339400	2.71631700	-1.87657100
C	1.41676600	3.55695400	-1.22515400
H	1.07128000	3.83171400	-0.23051700
H	1.59913900	4.45540100	-1.80870100
C	2.66640300	2.72164700	-1.09752100
C	3.89387900	3.10647900	-1.60401500
H	4.02360100	4.04949800	-2.10110000
C	4.97212500	2.24081300	-1.48038700
H	5.94727000	2.49691800	-1.85280100
N	4.85841700	1.05138800	-0.89575700
C	3.67904800	0.67458800	-0.39718500
C	2.56706800	1.48746400	-0.47555700
H	1.62285600	1.17458300	-0.08243000
Zn	6.43560500	-0.42186300	-0.83169500
N	-4.70714900	-1.01111200	-0.55772400
C	-3.58217100	-0.32933200	-0.32874400
C	-2.36166500	-0.74741600	-0.82786800
H	-1.47537000	-0.17037600	-0.66970600
C	-2.29209900	-1.90942800	-1.57633600
C	-3.46277200	-2.61311200	-1.80649600
C	-4.64411600	-2.12510700	-1.28029900
H	-5.57070400	-2.64329800	-1.44078700
C	-0.95760600	-2.39717100	-2.08416800
H	-0.47780700	-2.97335400	-1.29232200
H	-1.08598600	-3.03552600	-2.95545900
O	-0.18699900	-1.25583800	-2.40756900
C	1.12097800	-1.41704500	-2.76032100
C	1.82082600	-2.61513700	-2.70729200
H	1.33979100	-3.52765000	-2.41204700
C	3.16387300	-2.63988600	-3.05585700
H	3.69640300	-3.57425900	-3.01519700
C	3.82077000	-1.48873900	-3.46253800
C	3.10020200	-0.30235400	-3.53157700
H	3.58797600	0.60007900	-3.85514200

C	1.76707300	-0.26185800	-3.18318300
H	1.21613400	0.65858200	-3.21368500
C	5.28230000	-1.52003700	-3.84879200
H	5.45800200	-2.26540100	-4.62527300
H	5.56832000	-0.54689100	-4.24106500
N	6.13498100	-1.76121500	-2.69267800
C	7.00783500	-2.66945700	-2.76185100
H	7.13321200	-3.30638400	-3.62987300
C	7.93991100	-2.86401400	-1.63397200
C	8.92696200	-3.85190700	-1.62301000
H	9.03385100	-4.51697100	-2.45900000
C	9.75121500	-3.94776400	-0.52807600
H	10.51720500	-4.70065800	-0.48598500
C	9.59909100	-3.05482100	0.54269900
C	8.59753400	-2.07670400	0.41926900
N	7.79030100	-2.01967500	-0.63462900
C	8.40496300	-1.09415100	1.45385900
N	7.49826700	-0.12238100	1.23999000
C	7.30305900	0.76378000	2.20075000
C	7.98351500	0.71247200	3.42896400
H	7.75761900	1.45507500	4.16815200
C	8.92839100	-0.25212700	3.63228200
H	9.48865000	-0.29346800	4.54866400
C	9.17726100	-1.19111500	2.61865000
C	10.17774000	-2.20999300	2.72754100
H	10.76840300	-2.24548500	3.62485000
C	10.39321800	-3.09293000	1.73013500
H	11.16001400	-3.84097600	1.81388200
C	6.36960500	1.88543700	1.94348700
H	6.36301800	2.26354100	0.93078300
N	5.69816700	2.37912000	2.88617200
C	4.87499000	3.53052200	2.58046700
H	5.06628800	3.90679000	1.57139400
H	5.14333500	4.31220900	3.28905500
C	3.39094300	3.23679000	2.71209700
C	2.48225800	4.27366200	2.56986000
H	2.83783400	5.28168700	2.44032300
C	1.11423300	4.04457500	2.60052400
H	0.44361900	4.87875600	2.52301600
C	0.64051700	2.74985100	2.76738800
C	1.54405800	1.71098200	2.95607400
H	1.16196300	0.72028500	3.12419600
C	2.90344400	1.95522300	2.93123700
H	3.59354900	1.14642100	3.08086600
O	-0.67486300	2.38948900	2.74963400
C	-1.65205700	3.36453300	2.43092300
H	-1.28772100	4.03609500	1.65546300
H	-1.91784700	3.94343200	3.31136500
C	-2.84531300	2.63202400	1.87711000

C	-4.14558200	3.01764400	2.14796300
C	-5.18745000	2.29581300	1.59037900
H	-6.20916200	2.52259500	1.82776800
N	-4.97579100	1.25632300	0.78755000
C	-3.72413300	0.88085100	0.51647000
C	-2.63693600	1.54285800	1.04810500
H	-1.63784300	1.21386500	0.85596400
H	-4.36070500	3.83985600	2.80433600
H	-3.46968600	-3.51570400	-2.38796900

E(RBHandHLYP) = -8628.9275556 Hartree
Zero-point correction = 1.360165
Thermal correction to Energy = 1.448427
Thermal correction to Enthalpy = 1.449372
Thermal correction to Gibbs Free Energy = 1.230762
Sum of electronic and zero-point Energies = -8627.567391
Sum of electronic and thermal Energies = -8627.479128
Sum of electronic and thermal Enthalpies = -8627.478184
Sum of electronic and thermal Free Energies = -8627.696793

TS-$\vec{\Delta}$-($\vec{\delta}$,$\vec{\lambda}$)-$\vec{\Delta}$-(X,$\vec{\lambda}$)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (1 Imaginary Frequency)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.90773900	1.25290300	0.37770000
C	-8.65526900	1.92455500	-0.40533500
O	-9.34542500	1.56794700	-1.32784000
C	-8.50278100	3.42651700	-0.14094200
F	-7.31506700	3.84078900	-0.71857000
F	-8.36302800	3.69521000	1.18578700
F	-9.48852400	4.17262600	-0.64709200
O	6.61108900	-0.70863200	-2.51206600
C	7.72231000	-0.67645200	-3.13571300
O	8.29565500	-1.53650100	-3.75013100
C	8.35101400	0.71752800	-3.01737300
F	7.56767100	1.66649900	-3.61278000
F	9.59410700	0.81987500	-3.48279200
F	8.35831300	1.06307800	-1.66933900
Zn	-6.54549300	0.01985300	-0.27399100
N	4.91258200	-0.94370100	0.71924500
C	5.06877300	-1.86573700	1.66329800
H	6.02865200	-2.34509400	1.70091200
C	4.05800800	-2.22065800	2.53815500
H	4.23679900	-2.97341800	3.28287400
C	2.82861100	-1.59228400	2.42300900
C	2.67380300	-0.62999700	1.44141300

H	1.73416700	-0.12998600	1.34756700
C	3.72985200	-0.33516900	0.60046200
C	1.64594800	-1.97401300	3.28167300
H	1.15609200	-2.82999700	2.81642100
H	1.96375600	-2.25223600	4.28396400
O	0.77941700	-0.85906000	3.32036300
C	-0.52654700	-1.01617800	3.68702100
C	-1.12658400	-2.21171100	4.06088800
H	-0.56062300	-3.12122300	4.12982300
C	-2.47652700	-2.22890800	4.39108400
H	-2.93350200	-3.15625600	4.68664000
C	-3.23805400	-1.07074000	4.35677700
C	-2.61946200	0.11669800	3.98646900
H	-3.18582800	1.03039100	3.96392900
C	-1.28146300	0.14901100	3.65651800
H	-0.81044200	1.07335900	3.38166900
C	-4.70283100	-1.05812300	4.74569000
H	-4.81220600	-1.40723300	5.76944500
H	-5.06680400	-0.03110200	4.69856100
N	-5.49317300	-1.94561300	3.90378300
C	-6.16848700	-1.42544800	2.97894200
H	-6.17366900	-0.36239800	2.74990800
C	-7.05749100	-2.26196200	2.14043700
C	-7.61817100	-3.43537300	2.67542600
H	-7.34927100	-3.71984500	3.67332600
C	-8.50358900	-4.15646100	1.92617300
H	-8.97166900	-5.03961200	2.32167200
C	-8.80918300	-3.72907000	0.62278000
C	-8.16212500	-2.57470700	0.16405100
N	-7.32458300	-1.84201400	0.91866400
C	-9.73491000	-4.40990600	-0.23161200
H	-10.23510600	-5.27996700	0.15334300
C	-9.98785100	-3.97250000	-1.48371600
H	-10.69427300	-4.48381900	-2.11160800
C	-9.31249700	-2.82575200	-2.00575000
C	-8.39434500	-2.14373500	-1.18991900
N	-7.69408300	-1.10134900	-1.62776100
C	-7.87665300	-0.64533300	-2.84792400
C	-8.78324000	-1.23718700	-3.72996200
H	-8.91842900	-0.83329700	-4.71526600
C	-9.49793200	-2.33060800	-3.30550900
H	-10.20236100	-2.80987500	-3.96076300
C	-7.07065600	0.53875400	-3.20241400
H	-7.21044800	0.95569700	-4.19245500
N	-6.27248300	1.03203700	-2.35708100
C	-5.54076900	2.23576900	-2.73154000
H	-5.88282800	3.02199100	-2.06679800
H	-5.79184200	2.52833400	-3.75318200
C	-4.03879600	2.06847900	-2.61245700

C	-3.42222700	0.83642300	-2.80136900
H	-4.01985700	-0.03405800	-3.00019500
C	-2.05107800	0.71069300	-2.72235400
H	-1.57029600	-0.24218500	-2.84197900
C	-1.25530900	1.82529900	-2.47984400
C	-1.85414400	3.06867200	-2.32822600
H	-1.26620900	3.95389500	-2.17685200
C	-3.23775700	3.17630900	-2.38216900
H	-3.69136000	4.14398200	-2.25402700
O	0.08025200	1.57389500	-2.38932000
C	0.99554800	2.65812700	-2.31871500
H	0.71758200	3.35393000	-1.52911800
H	1.03976600	3.18593900	-3.26777000
C	2.32754500	2.04141100	-1.96960500
C	3.47765000	2.24018800	-2.71407300
H	3.47337900	2.84711600	-3.59972500
C	4.64799600	1.61319800	-2.31460200
H	5.55727000	1.71208300	-2.87715800
N	4.70553900	0.84267000	-1.23233300
C	3.59740600	0.62437600	-0.52359000
C	2.39397000	1.21135100	-0.86311000
H	1.50468100	1.01799600	-0.30121400
Zn	6.41919500	-0.30479800	-0.60148400
N	-4.71967400	-1.10256100	-0.36015800
C	-3.64306000	-0.52310200	0.17385700
C	-2.42977300	-1.18286100	0.25509500
H	-1.58614100	-0.72231600	0.72833200
C	-2.31565800	-2.45797400	-0.27277900
C	-3.43365600	-3.04214000	-0.84284400
C	-4.61902900	-2.33111100	-0.85021400
H	-5.51545800	-2.75350000	-1.26643200
C	-0.98679800	-3.16166500	-0.23519100
H	-0.67331100	-3.29631300	0.79995700
H	-1.05711900	-4.13607200	-0.71208400
O	-0.07463100	-2.32722200	-0.93082400
C	1.18318400	-2.81344300	-1.14610700
C	1.68020000	-3.97625200	-0.57829700
H	1.07607300	-4.58489000	0.06675900
C	2.97762500	-4.37669000	-0.86444400
H	3.35122900	-5.28750700	-0.43040300
C	3.78913500	-3.63608100	-1.70486200
C	3.27955600	-2.46835200	-2.26731100
H	3.90256700	-1.88104400	-2.92042600
C	1.98895700	-2.06122600	-1.99550900
H	1.57919200	-1.16984100	-2.43301700
C	5.19841900	-4.08450900	-2.00019900
H	5.27182800	-5.15613900	-1.82275600
H	5.44666500	-3.89787200	-3.04431000
N	6.15124600	-3.41877500	-1.11305900

C	7.34506300	-3.36014100	-1.50045400
H	7.71590700	-3.75712300	-2.43864900
C	8.34875900	-2.71490300	-0.62079000
C	9.57000500	-3.35877700	-0.37711100
H	9.79817300	-4.26831200	-0.89902900
C	10.42856200	-2.83351400	0.54668100
H	11.35603900	-3.32438300	0.77960300
C	10.09238200	-1.63877600	1.20395300
C	8.89252200	-1.01491200	0.83046600
N	8.03668700	-1.56492300	-0.04855600
C	8.54658500	0.26091200	1.40432100
N	7.47425400	0.91818800	0.91437700
C	7.17431300	2.09777400	1.43388400
C	7.88951000	2.66076800	2.50295900
H	7.56709500	3.60944100	2.88374100
C	8.98493100	2.01121400	2.98831200
H	9.57350400	2.43397900	3.78213800
C	9.36521100	0.78603300	2.41767100
C	10.55169600	0.09655700	2.81290800
H	11.16003400	0.53179300	3.58447500
C	10.91573400	-1.05415000	2.21265900
H	11.82455900	-1.55702800	2.48824800
C	6.10011700	2.89584600	0.80561400
H	5.89416100	2.66926700	-0.23250300
N	5.51833000	3.80885300	1.44674000
C	4.53752200	4.60017700	0.73409100
H	4.60124600	4.44068500	-0.34630800
H	4.75758100	5.64611800	0.93669500
C	3.11836400	4.29692000	1.18167900
C	2.08676200	5.12978800	0.77908700
H	2.30765100	6.02773500	0.22775200
C	0.76398300	4.83716000	1.07900600
H	-0.00019900	5.52687900	0.77756500
C	0.46079800	3.68387800	1.79121300
C	1.49442600	2.87135500	2.24181200
H	1.25496500	2.00489300	2.83033000
C	2.80612100	3.17720600	1.94035100
H	3.59276700	2.53999900	2.29768800
O	-0.79714700	3.25004100	2.08959800
C	-1.91531700	3.96304000	1.59142600
H	-1.69375600	4.39362300	0.61684800
H	-2.19259400	4.75977500	2.27640000
C	-3.04818100	2.98914900	1.39912700
C	-4.36659100	3.36548300	1.58158000
C	-5.37227100	2.46961200	1.25614400
H	-6.40621400	2.72919900	1.36554200
N	-5.10870700	1.25234400	0.78937600
C	-3.83797900	0.86350700	0.66222300
C	-2.78243100	1.70689800	0.94511500

H	-1.76948300	1.39577600	0.80032200
H	-4.62482600	4.33957700	1.95317600
H	-3.39130700	-4.02514200	-1.27219800

E(RBHandHLYP) = -8628.9340904 Hartree
Zero-point correction = 1.360654
Thermal correction to Energy = 1.448750
Thermal correction to Enthalpy = 1.449694
Thermal correction to Gibbs Free Energy = 1.232329
Sum of electronic and zero-point Energies = -8627.573436
Sum of electronic and thermal Energies = -8627.485341
Sum of electronic and thermal Enthalpies = -8627.484397
Sum of electronic and thermal Free Energies = -8627.701761

TS-$\vec{\Delta}$-(X,$\vec{\lambda}$)-$\vec{\Delta}$-(λ,λ)-[**4**•2TFA]$^{2+}$, BH&HLYP/6-31G(d)/3-21G (1 Imaginary Frequency)

	Coordinates (Angstroms)		
	X	Y	Z
O	-7.76144600	1.39611300	0.67183700
C	-8.48495500	2.20756600	0.00774000
O	-9.20219200	2.01975100	-0.94362000
C	-8.25620700	3.64822900	0.47837800
F	-7.08403100	4.10224900	-0.10124900
F	-8.03601100	3.71393300	1.81910400
F	-9.23439100	4.49411900	0.14284900
O	6.99075100	0.36193400	-2.21111400
C	8.21320300	0.57345500	-2.53076800
O	9.06123300	-0.19099600	-2.89885400
C	8.55556100	2.05741100	-2.33824400
F	7.64329200	2.86192000	-2.96191100
F	9.78200300	2.39491900	-2.73959000
F	8.44031600	2.36600500	-0.99496900
Zn	-6.54079000	0.14299000	-0.18190900
N	4.81594300	-1.00029700	0.61575400
C	4.93346700	-2.04946400	1.42482400
H	5.91388400	-2.47894900	1.50958400
C	3.87022100	-2.57775500	2.13452100
H	4.02732700	-3.41821500	2.78405900
C	2.62368300	-1.99010900	1.99685400
C	2.50390900	-0.90393400	1.14855400
H	1.55620700	-0.42041800	1.05082700
C	3.61452900	-0.43336900	0.47496800
C	1.39931200	-2.49664900	2.72226800
H	0.89243200	-3.22588900	2.08887200
H	1.67358200	-2.97474400	3.65997100
O	0.57652400	-1.37082800	2.94859500

C	-0.70748100	-1.53518900	3.38330000
C	-1.32511500	-2.75128100	3.63980800
H	-0.79195600	-3.67795100	3.54126700
C	-2.64880900	-2.77134600	4.06133400
H	-3.12173500	-3.71520000	4.26552000
C	-3.36551100	-1.59572800	4.22763300
C	-2.72883500	-0.38837700	3.96925600
H	-3.26238300	0.53643100	4.09926500
C	-1.41477200	-0.35316700	3.55593200
H	-0.92461200	0.58191500	3.36273300
C	-4.80456600	-1.59490000	4.70067700
H	-4.87685400	-2.09107200	5.66458700
H	-5.13106300	-0.56230200	4.82591700
N	-5.66918700	-2.31800100	3.77658400
C	-6.27405600	-1.65393600	2.89654100
H	-6.17654900	-0.57905500	2.76272500
C	-7.21733100	-2.33155800	1.97852000
C	-7.85773100	-3.51373800	2.39186200
H	-7.61088100	-3.91540300	3.35443200
C	-8.78432800	-4.09445000	1.57480000
H	-9.31037600	-4.98159100	1.87771900
C	-9.05639700	-3.51491500	0.32361600
C	-8.33451600	-2.36329500	-0.01493600
N	-7.44979100	-1.77120900	0.80723100
C	-10.02174200	-4.04263700	-0.59230300
H	-10.57620300	-4.91524700	-0.29826700
C	-10.24472600	-3.46062600	-1.78987900
H	-10.98078300	-3.85738100	-2.46481400
C	-9.50014000	-2.30812100	-2.18964500
C	-8.54090000	-1.77444100	-1.31213700
N	-7.78468200	-0.72877400	-1.63708800
C	-7.94813300	-0.13061900	-2.79726900
C	-8.88839300	-0.57083400	-3.73158800
H	-9.00397900	-0.05208900	-4.66421500
C	-9.66077100	-1.66388600	-3.42541900
H	-10.39296000	-2.02801700	-4.12295700
C	-7.09590400	1.05053100	-3.02481200
H	-7.24727200	1.59691300	-3.94795300
N	-6.25666100	1.40387500	-2.15012200
C	-5.51266900	2.63368300	-2.39190700
H	-5.81561200	3.33153000	-1.61798000
H	-5.79561100	3.06203900	-3.35571000
C	-4.01057200	2.43868000	-2.35590300
C	-3.41551800	1.22120800	-2.66472300
H	-4.03036500	0.37323300	-2.90513600
C	-2.04277000	1.08011800	-2.65001400
H	-1.57882800	0.13466100	-2.86112900
C	-1.22684000	2.16651300	-2.35426500
C	-1.80675200	3.40081700	-2.09219700

H	-1.20663200	4.27172500	-1.91057800
C	-3.18955000	3.52088100	-2.07896500
H	-3.62750900	4.47996100	-1.86246200
O	0.10978900	1.90071300	-2.32661000
C	1.02887500	2.96270100	-2.12564700
H	0.71037400	3.60088600	-1.30337600
H	1.12735200	3.55969500	-3.02852600
C	2.34382700	2.33861300	-1.73353700
C	3.56119700	2.80112500	-2.20241500
H	3.61902200	3.60604100	-2.91082600
C	4.72425800	2.18319500	-1.77241500
H	5.68277700	2.47024100	-2.16067500
N	4.71003900	1.17643500	-0.90269800
C	3.54145700	0.72298000	-0.44878900
C	2.34048000	1.27396200	-0.84953400
H	1.40701600	0.87851400	-0.50904500
Zn	6.41181800	0.02273200	-0.38432600
N	-4.80396600	-1.08777600	-0.45913500
C	-3.65474700	-0.61508600	0.02749500
C	-2.47343900	-1.32671400	-0.08136500
H	-1.56245600	-0.94466300	0.33027600
C	-2.46956000	-2.54069500	-0.74671700
C	-3.66681200	-3.02328500	-1.24785400
C	-4.80994800	-2.26691600	-1.06930200
H	-5.75967700	-2.60843800	-1.43833800
C	-1.17119700	-3.28184900	-0.93018900
H	-0.88443100	-3.76262900	0.00539300
H	-1.27311200	-4.04290200	-1.69990800
O	-0.21097700	-2.30899600	-1.30762000
C	0.98371400	-2.74258400	-1.80941600
C	1.47874300	-4.03022600	-1.66386700
H	0.92018000	-4.78363800	-1.14135500
C	2.71180400	-4.35608800	-2.21017300
H	3.09004700	-5.35661500	-2.09891700
C	3.46105100	-3.41419700	-2.89625700
C	2.95269000	-2.12634500	-3.03019400
H	3.51281200	-1.38517700	-3.57333300
C	1.72394700	-1.79117100	-2.49861100
H	1.31486400	-0.80521100	-2.61990500
C	4.81755700	-3.76291100	-3.47073200
H	4.77440600	-4.72216100	-3.97715300
H	5.10835200	-3.00228100	-4.19502200
N	5.79255300	-3.87495000	-2.38870300
C	6.46704700	-2.84528900	-2.13114300
H	6.38964200	-1.89827300	-2.65809500
C	7.47302200	-2.86874600	-1.04461700
C	8.27106800	-4.00221000	-0.82179400
H	8.10713200	-4.87176300	-1.42682000
C	9.24514000	-3.95307400	0.13503400

H	9.88710900	-4.79711600	0.31122200
C	9.42878300	-2.77541900	0.88257500
C	8.55685500	-1.71093300	0.61875000
N	7.60229000	-1.77236200	-0.32277600
C	8.69470300	-0.47679300	1.34634900
N	7.82201700	0.52319800	1.08565900
C	7.98719500	1.68324500	1.69050300
C	9.02891700	1.91149500	2.59999100
H	9.12487200	2.87811800	3.05579400
C	9.89166700	0.89623500	2.90223700
H	10.68758200	1.04113500	3.61002400
C	9.74062600	-0.34806700	2.27054300
C	10.61282500	-1.45292200	2.51831700
H	11.40040900	-1.32850800	3.23878700
C	10.45813400	-2.62024400	1.85995100
H	11.11836700	-3.44755800	2.04566700
C	7.04301700	2.80457800	1.41515700
H	7.47136300	3.65901800	0.89792700
N	5.86540600	2.74699800	1.84508000
C	5.02802000	3.92797900	1.68809300
H	5.23029000	4.44562300	0.74955500
H	5.28758800	4.60738600	2.50150500
C	3.55268900	3.60534600	1.80075000
C	2.60934500	4.49751500	1.31936600
H	2.92811400	5.40711800	0.83954600
C	1.24818800	4.25662800	1.46053300
H	0.55046500	4.99318900	1.11093800
C	0.82087700	3.08869400	2.07642100
C	1.76288200	2.19984500	2.58258900
H	1.41944300	1.31089400	3.07855300
C	3.11066900	2.45942700	2.45151700
H	3.83164200	1.77036400	2.84832300
O	-0.47912300	2.70047500	2.22268300
C	-1.52126400	3.55522700	1.78557100
H	-1.26707800	4.01728400	0.83343900
H	-1.71112300	4.33314100	2.52042500
C	-2.74275000	2.70199100	1.55959900
C	-4.01791800	3.14251400	1.86405500
C	-5.10269600	2.35026300	1.51953200
H	-6.10680200	2.66352200	1.72455000
N	-4.95638600	1.17359800	0.91700000
C	-3.72602400	0.72050200	0.66734000
C	-2.59900700	1.45939900	0.96381000
H	-1.62073200	1.09990700	0.72397200
H	-4.18419200	4.08733000	2.34691400
H	-3.71665900	-3.95659800	-1.77626300

E(RBHandHLYP) = -8628.9267362 Hartree
Zero-point correction = 1.360293

```
Thermal correction to Energy = 1.448666
Thermal correction to Enthalpy = 1.449611
Thermal correction to Gibbs Free Energy = 1.230116
Sum of electronic and zero-point Energies = -8627.566443
Sum of electronic and thermal Energies = -8627.478070
Sum of electronic and thermal Enthalpies = -8627.477126
Sum of electronic and thermal Free Energies = -8627.696621
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