

Supporting Information

New insights into the structure and catalytic performance of alizarin-zirconium hybrids for Meerwein–Ponndorf–Verley reductions: first-principles approach

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Characterization

Scanning electron microscope (SEM) images were acquired on a Hitachi S-4800 Scanning Electron Microscope with an energy dispersive spectrometer (EDS) unit.

Transmission electron microscope (TEM) images were acquired on a JEM-2100plus Microscope operating at 200 kV.

Fourier transform infrared spectra (FT-IR) was collected on a Boman FTLA200-104.

X-ray diffraction (XRD) pattern was measured on XRD spectrometer (D8, Bruker AXS, Germany) with Cu K α radiation source over the 2θ range of 5-90°.

The X-ray photoelectron spectroscopy (XPS) measurement was carried out on an Axis supra spectrometer. N₂ adsorption-desorption isotherms were obtained using the Micromeritics ASAP 2020 (USA) surface area analyzer. The thermal property of solid samples was examined by thermogravimetry (TG) analysis on a Mettler-Toledo TGA-1100SF instrument under N₂ in a flow rate of 30 mL/min at a programmed temperature range of 50–700 °C with a heating ramp of 10 °C/min.

Diffuse reflectance UV–vis (UV–vis DRS) spectra of catalysts were measured on an UV–vis-near infrared light spectrophotometer (UV-3600 plus) with BaSO₄ as a reference.

Temperature-programmed reduction (TPR) and temperature programmed desorption (TPD) were performed on a BELCAT-B catalyst analyser connected with TCD. In detail, 95 mg of each vacuum-dried catalyst was heated was first heated at 323 K at a rate of 10 K min⁻¹ in a flow of 10 % H₂/N₂ (30 mL min⁻¹) for H₂-TPR. For CO₂-and NH₃-TPD (temperature programmed desorption) testing, 95 mg of each vacuum-dried sample was first heated at 423 K for 2 h in a flow of Ar, and then the catalyst was kept at 423 K for 2 h. After that, the temperature was decreased to 323K. 10 vol % CO₂/Ar or 10 vol % NH₃/Ar (50 mL min⁻¹) was adsorbed for 0.5 h, until the acid sites were saturated with CO₂ or NH₃. The adsorbed CO₂ or NH₃ was removed by a flow of Ar (50 cm³ min⁻¹). When the baseline was stable, the temperature was increased from 323 K to 573 K at a rate of 10 K min⁻¹.

Molar ratios of Lewis and Brønsted acid sites of the samples were measured by pyridine adsorption FT-IR fitted with a NEXUS 670 FT-IR spectrometer, based on the characteristic peak position and integral area in the wavenumber range of 1400-1700 cm⁻¹.

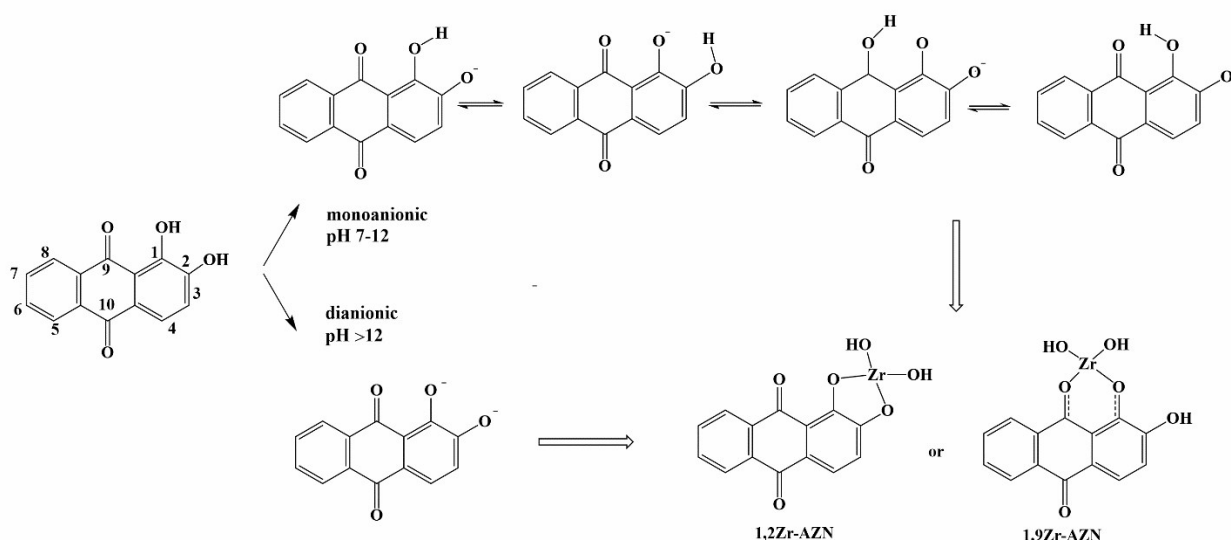


Fig. S1 Alizarin deprotonation and complexation paths in alkali media.

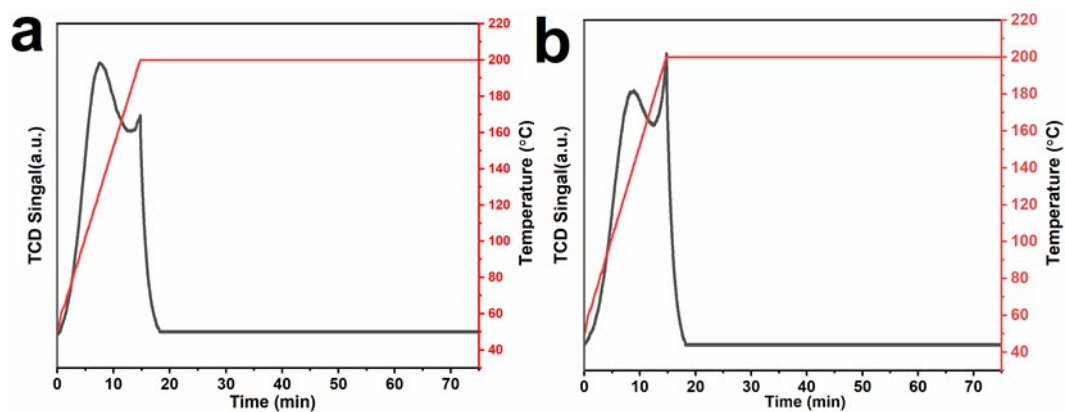


Fig. S2 (a) NH_3 -TPD and (b) CO_2 -TPD spectra for Zr-AZN

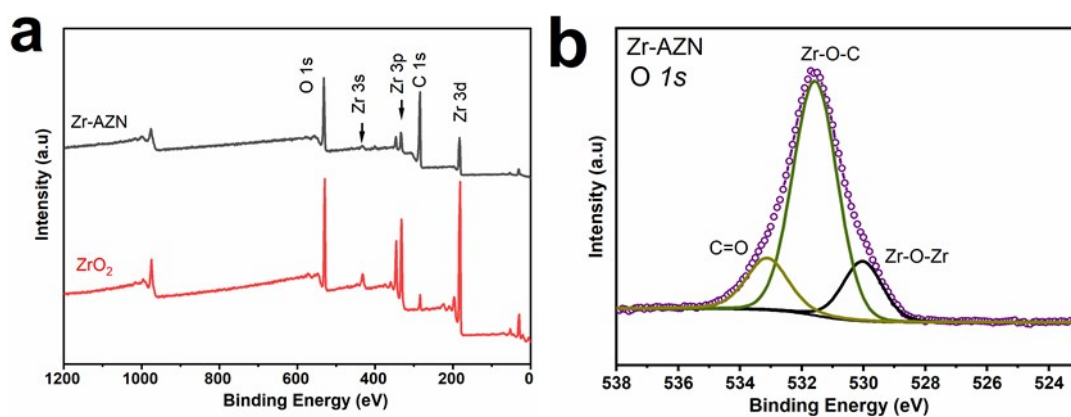


Fig. S3 XPS survey spectra of Zr-AZN and ZrO_2 (a) and O 1s core energy levels (b), charge referenced to adventitious C1s peak at 284.8eV

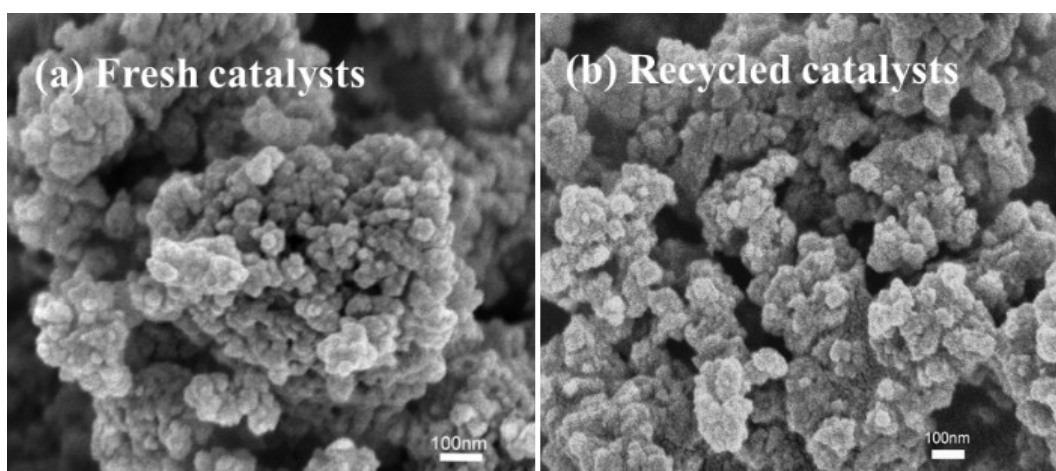


Fig. S4 SEM images of fresh (a) and recovered (b) Zr-AZN catalyst

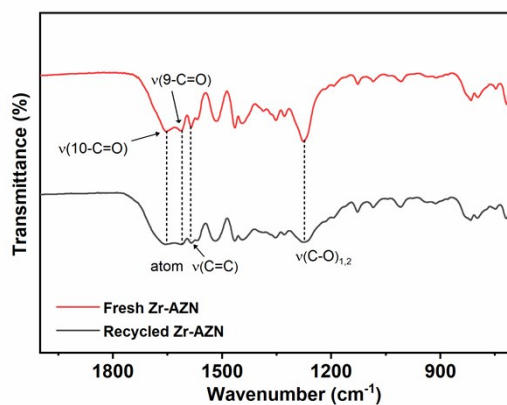


Fig. S5 Analyses of fresh and recovered Zr-LS catalyst after six cycles: FT-IR spectra.

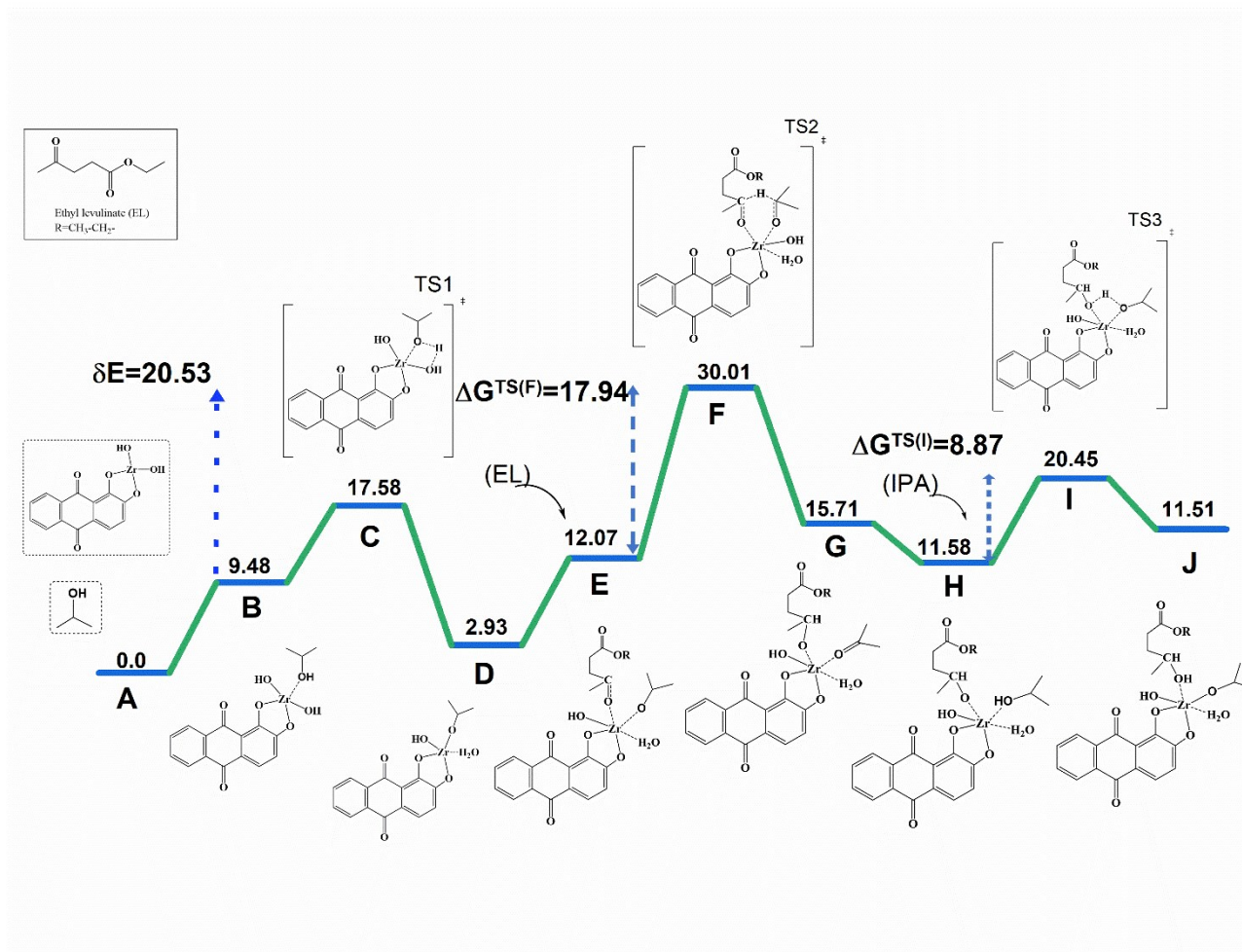


Fig. S6 Computed free energy for the liquid phase hydrogenation of EL to 4-HPE by Zr-AZN in IPA medium. The free energy/enthalpy corrections and solvation energies were computed at the B3LYP level of theory. All energies are referenced to Zr-AZN and EL in solution (A) and reported in kcal/mol. Note that an implicit solvation model for IPA is used in all steps, and an explicit IPA molecule is added at step D→E, in addition to the implicit solvation model.

Table S1 physicochemical properties of the prepared catalysts

Sample	Textural properties			Basicity (mmol/g) ^d	Acidity (mmol/g) ^d	Base/acid ratio
	S _{BET} (m ² g ⁻¹) ^a	V _p (cm ³ g ⁻¹) ^b	D _{mean} (nm) ^c			
Zr-AZN	98.7	0.43	6.4	0.79	0.58	1:0.73
UiO-66(Zr)	882	0.38	1.1	0.68	0.39	1:0.57
ZrO ₂	25	0.06	0.6	0.18	0.11	1:0.61
Zr-AZN ^e	87.3	0.22	6.9	0.75	0.54	1:0.71

^a BET surface area was obtained from N₂ adsorption isotherm.

^b Volume of pores was estimated from BJH absorption cumulative volume of pores.

^c Average pore size was estimated from the adsorption average pore diameter.

^d Basicity and acidity of the catalysts were determined by CO₂-and NH₃-TPD, respectively, with a programmed temperature: heating from 50 to 200 °C at a rate of 10 °C/min and then kept at 200 °C for 60 min gas desorption.

^e Recovered Zr-AZN in the sixth cycle.

**Optimized XYZ coordinates of Transition State (TS) structures;
TS for the intra-molecular hydrogen transfer of Ethyl Levulinate (Fig.6, Fig.7 and Fig.8 of the
main text)**

Zr-AZN_{1,2}(TS1)

C	5.90628600	-2.42763400	-0.16836400
C	4.52229300	-2.32855800	-0.08949800
C	3.89936300	-1.07644700	-0.10690000
C	4.68406800	0.08322800	-0.20639600
C	6.07630400	-0.02410900	-0.28899700
C	6.68619700	-1.27215000	-0.26914500
C	2.40356500	-1.01390400	-0.01749800
C	4.05446100	1.43319500	-0.22195900
C	2.58277800	1.50481500	-0.10202300
C	1.77796300	0.32685300	-0.00634100
C	0.38581700	0.48684700	0.10681000
C	-0.18241800	1.80007000	0.14346800
C	0.61824800	2.92823400	0.04238700
C	1.99767300	2.76854500	-0.08149500
H	6.38032500	-3.40216100	-0.15133700
H	3.90212800	-3.21236100	-0.01205600
H	6.66054600	0.88398300	-0.36644800
H	7.76550400	-1.34893900	-0.33095700
H	0.16400900	3.91181600	0.06496700
H	2.64514200	3.63217000	-0.16014000
O	-0.51606500	-0.48742700	0.18717700
O	1.76191100	-2.05569300	0.04767100
O	-1.50790500	1.82198600	0.27887300
Zr	-2.54272900	0.00166200	0.43483200
O	-2.69503900	-0.18249900	2.39045900
H	-2.09438700	0.00802100	3.11636500
O	-2.67738200	-2.14810600	-0.09097300
H	-1.93469100	-2.56575000	-0.53960900
O	4.74919800	2.44147300	-0.32602500
C	-6.37337300	-1.17254200	-0.12477000
H	-7.43960400	-1.13582500	-0.36430200
H	-6.21728700	-0.65820400	0.82851000
H	-6.08874000	-2.22051800	-0.00237900
C	-5.55331200	-0.51354700	-1.23149600
H	-5.73107800	-1.04861200	-2.17181200
C	-5.90090200	0.95616500	-1.43207100
H	-5.74144100	1.52206100	-0.50896800
H	-5.28249500	1.39247400	-2.21985400
H	-6.94981900	1.06542700	-1.71960900
O	-4.14719600	-0.63503900	-0.95885900
H	-3.57919500	-1.68199500	-0.75651700

Zr-AZN_{1,2}(TS2)

C	-7.15742300	-3.14178600	1.27747100
C	-5.81658500	-2.79196000	1.17320100
C	-5.43758900	-1.62933100	0.49407100
C	-6.42404300	-0.81538600	-0.08449900
C	-7.77191700	-1.17436300	0.02337600
C	-8.13877000	-2.33060400	0.70062300
C	-3.97907000	-1.28860700	0.40611400
C	-6.05633100	0.43172600	-0.81381000
C	-4.62489800	0.77951500	-0.89337300
C	-3.61390600	-0.04717600	-0.30727000
C	-2.27253000	0.35811600	-0.42867600
C	-1.94450300	1.58104600	-1.11245400
C	-2.94933300	2.36111600	-1.67283300
C	-4.27759400	1.95243800	-1.55971700
H	-7.44140000	-4.04425800	1.80642200
H	-5.04209300	-3.40755700	1.61251600
H	-8.51487600	-0.53134000	-0.43118400
H	-9.18475600	-2.60291300	0.78141200
H	-2.68579700	3.27697600	-2.18927700
H	-5.07258100	2.54789400	-1.99005600
O	-1.21513800	-0.28339900	0.04067100
O	-3.15819700	-2.03833200	0.92434300
O	-0.65158500	1.88434400	-1.14883500
Zr	0.72066400	0.53172400	-0.23534800
O	1.25098300	-0.49932200	-1.85141600
H	0.72250000	-0.85460100	-2.57129100
O	-6.93086000	1.13291700	-1.32078100
C	4.40473600	2.77903800	-0.63120900
H	5.29635700	2.95627400	-0.02765700
H	4.25632400	3.64610400	-1.28317800
H	4.55097500	1.90303500	-1.26183300
C	3.16165300	2.62199000	0.23221000
H	3.53128800	1.66516700	1.08420400
C	2.87954500	3.78103400	1.17574000
H	2.64000900	4.65834600	0.56595400
H	2.02380800	3.56433200	1.81338000
H	3.74944200	4.01986300	1.78963200
O	2.12057900	2.09734800	-0.37189100
C	3.03065700	1.04178600	3.15685100
H	3.87307100	1.62457500	3.53246400
H	2.88346900	0.18423700	3.82137000
H	2.12451900	1.64511100	3.17180400
C	3.29914000	0.50532100	1.76034800
C	4.63332800	-0.22686800	1.61112400
H	5.44928100	0.45246400	1.86945700

H	4.63753900	-1.00820900	2.37976500
C	4.86506600	-0.87292000	0.24946000
H	5.01411900	-0.13584800	-0.54076300
H	3.98826600	-1.45812800	-0.04383600
O	2.27811400	-0.00434400	1.12212500
C	6.05217000	-1.81172900	0.25053200
O	6.59599200	-2.25550600	1.23707500
O	6.42403000	-2.11474700	-1.00336500
C	7.52965300	-3.04766800	-1.15543600
H	8.40593300	-2.63057100	-0.65525300
H	7.26558300	-3.98271500	-0.65747700
C	7.76057800	-3.23994700	-2.63918200
H	8.01653200	-2.29352100	-3.12050100
H	8.58671600	-3.93823400	-2.79359800
H	6.87064700	-3.64835100	-3.12293500
O	-0.03482800	1.88102800	1.71722900
H	-0.55553100	1.43122100	2.39493600
H	-0.56081800	2.64307900	1.44224200

Zr-AZN_{1,2}(TS3)

C	-7.74874500	-2.30248900	-0.57258500
C	-6.37272200	-2.26295600	-0.38200200
C	-5.69063700	-1.04191000	-0.39075700
C	-6.40747900	0.14790400	-0.59377800
C	-7.79269700	0.10065500	-0.78223500
C	-8.46159300	-1.11701100	-0.77257000
C	-4.20593700	-1.04362000	-0.17990900
C	-5.71289900	1.46661000	-0.61403500
C	-4.24822600	1.47076300	-0.42918800
C	-3.51311800	0.26202100	-0.21807500
C	-2.12096900	0.35795600	-0.05280100
C	-1.47135000	1.63530700	-0.10221200
C	-2.21099600	2.79375800	-0.30617000
C	-3.59241900	2.69941800	-0.46733600
H	-8.26847800	-3.25359400	-0.56604100
H	-5.80379900	-3.17030200	-0.22456300
H	-8.32436600	1.03110400	-0.93558700
H	-9.53484300	-1.14703900	-0.92055600
H	-1.70535200	3.75168400	-0.33883100
H	-4.18733900	3.58934900	-0.62751200
O	-1.28036300	-0.64675500	0.15906800
O	-3.62835300	-2.10824300	0.01168100
O	-0.15306300	1.60581500	0.07136400
Zr	0.78275000	-0.27260600	0.34116800
O	1.30928800	-0.76776700	-1.49631400
H	0.89936600	-0.98318400	-2.33718000

O	-6.35386500	2.50218700	-0.78306600
H	3.98205200	-2.42748000	2.19609600
C	2.47822900	-3.65263700	1.27766700
H	3.10775700	-4.54448400	1.22339300
H	1.81730600	-3.64771000	0.40532700
H	1.86255900	-3.72138200	2.17756800
C	3.33190100	-2.38844100	1.31199700
C	4.21001900	-2.25786400	0.06173600
H	4.78423100	-3.18164800	-0.05572700
H	3.56281800	-2.16956700	-0.81606400
C	5.17224000	-1.07171900	0.11620300
H	5.82421800	-1.13749600	0.99547700
H	4.63672900	-0.12383000	0.20873400
O	2.47321900	-1.24980200	1.48403100
C	6.06900600	-0.96533700	-1.09754500
O	6.16188900	-1.78482600	-1.98356700
O	6.77487800	0.18012200	-1.07070000
C	7.69404000	0.41502400	-2.17146700
H	8.40921100	-0.40920300	-2.21085000
H	7.12619100	0.41755900	-3.10413700
C	8.37419500	1.74421200	-1.91899800
H	8.92973000	1.72584600	-0.97873300
H	9.07629400	1.95726500	-2.72873000
H	7.64329400	2.55476700	-1.87656400
C	2.82388700	3.25913600	0.36881900
H	3.18244200	4.23812100	0.69878600
H	1.81231900	3.36814600	-0.02677000
H	3.47762400	2.90604800	-0.43225800
C	2.82844400	2.27494100	1.53284100
H	3.85701300	2.15332400	1.89132000
C	1.94900200	2.72293400	2.69668900
H	0.91681900	2.85353600	2.36454200
H	1.96599700	1.98407100	3.50136000
H	2.31068100	3.67373500	3.09833500
O	2.42124000	0.97743600	1.05655300
H	2.81872900	-0.06539400	1.45646300
O	0.06889500	-0.36614900	2.60737400
H	0.69196500	-0.84426200	3.17139900
H	-0.81833400	-0.68979500	2.80746600

Zr-AZN_{1,9}(TS1)

Zr	1.94383300	-0.66925300	0.56546400
C	-2.81189900	-3.31251400	-0.57130900
C	-3.55562200	-2.14335200	-0.59155300
C	-2.97280600	-0.90226300	-0.31141800
C	-1.57835100	-0.82675800	0.00816000

C	-0.82315200	-2.03014500	0.00347300
C	-1.44737200	-3.25455500	-0.27946400
C	-3.80794500	0.30497900	-0.36576100
C	-0.98935200	0.43666600	0.32805900
C	-1.76583200	1.63874500	0.27796700
C	-3.14404600	1.58734100	-0.07117400
C	-3.88251400	2.77877100	-0.13783100
H	-4.92888000	2.71084400	-0.40894500
C	-3.29073000	4.00075800	0.13206800
C	-1.92965600	4.05458400	0.48507100
C	-1.18019100	2.89736000	0.55946900
H	-3.26210500	-4.27404300	-0.78724300
H	-4.61144500	-2.16530100	-0.82853900
H	-3.87213400	4.91346400	0.07200000
H	-1.46557600	5.01113200	0.69778300
H	-0.13302700	2.93474200	0.82919800
O	0.29297900	0.52733700	0.67876800
O	0.50118000	-2.09255900	0.24344900
O	-5.01534100	0.25407600	-0.65242100
O	2.48744100	-0.92643500	2.46071400
H	1.96169000	-1.01263900	3.26125200
O	3.10928400	-1.68535400	-1.06129800
H	2.66639400	-2.19017800	-1.75090600
O	-0.70242600	-4.38915500	-0.27173500
H	0.20305100	-4.11809200	-0.04927900
C	4.52615000	2.04890200	-2.12705400
H	5.29513800	2.82394300	-2.06871100
H	3.68034800	2.43988600	-2.69939400
H	4.94416400	1.19446000	-2.66506500
C	4.07611800	1.63940300	-0.72929200
H	4.93763700	1.23943800	-0.17917900
C	3.47485300	2.79520700	0.06108700
H	2.61343400	3.21208000	-0.46813000
H	3.14498400	2.46096400	1.04866600
H	4.21329300	3.58879700	0.20090800
O	3.09447000	0.59060700	-0.84372100
H	3.33311100	-0.50629300	-1.27599800

Zr-AZN_{1,9}(TS2)

Zr	-0.32316900	-1.74477100	0.92240400
C	1.25722400	3.65293400	1.16671000
C	2.51269800	3.40355800	0.63490000
C	2.91892300	2.10528700	0.30471700
C	2.02674300	1.00075600	0.51222900
C	0.74649300	1.26523200	1.07625100
C	0.38265900	2.58820500	1.38285800

C	4.26315300	1.90812800	-0.25147400
C	2.43609100	-0.32556300	0.15794600
C	3.74617300	-0.55463200	-0.38350900
C	4.64848400	0.52728100	-0.58100200
C	5.92847500	0.27145200	-1.10092400
H	6.59466500	1.11428400	-1.23843000
C	6.32371800	-1.01389400	-1.42474600
C	5.43145000	-2.08695000	-1.23518300
C	4.16844600	-1.86313200	-0.72596500
H	0.93896500	4.65686100	1.42217300
H	3.21121400	4.21217200	0.46343900
H	7.31511300	-1.19642800	-1.82332400
H	5.73890300	-3.09515900	-1.49016500
H	3.47888400	-2.68383100	-0.57826600
O	1.64124000	-1.36752600	0.32473600
O	-0.18154500	0.33736100	1.35017500
O	5.04480800	2.85951700	-0.43522200
O	-0.02895900	-3.59191600	1.62527600
H	0.37736800	-3.93510700	2.42516300
O	-0.77033100	-1.41769700	3.22011200
H	-0.96034800	-0.49821100	3.44638900
O	-0.85495400	2.81145300	1.90684400
H	-1.26234900	1.93303300	1.98732700
C	-1.81044900	-1.71534800	-3.14917000
H	-2.78757100	-1.77327400	-3.63073900
H	-1.06339000	-2.11205900	-3.84451500
H	-1.55958400	-0.67670200	-2.93950700
C	-1.75827300	-2.55127400	-1.88085800
H	-2.83940500	-2.09135300	-1.21216100
C	-2.10849600	-4.01992800	-2.04630700
H	-1.31919400	-4.48612100	-2.64488400
H	-2.14259600	-4.52497700	-1.08101900
H	-3.05699200	-4.15261100	-2.56839800
O	-0.77082800	-2.28706300	-1.06150100
H	-1.36140600	-1.98482600	3.72988800
C	-4.40689700	-2.81891100	0.16223400
H	-5.08068800	-2.96628300	-0.68321200
H	-5.00787800	-2.56231700	1.04020400
H	-3.87501400	-3.74616800	0.37409900
C	-3.42977600	-1.68030100	-0.08905100
C	-4.09242200	-0.36684100	-0.51533500
H	-4.71200900	-0.54072400	-1.39862800
H	-4.78298700	-0.10824800	0.29553600
C	-3.13785100	0.80357300	-0.73428400
H	-2.65343700	0.77070700	-1.71087400
H	-2.33196400	0.78084400	0.00621700

O	-2.43611900	-1.58797000	0.76037300
C	-3.81377900	2.15001100	-0.58752200
O	-4.88347300	2.34686400	-0.05535700
O	-3.04625500	3.12496600	-1.09824900
C	-3.52268600	4.49031200	-0.94167200
H	-4.50344400	4.57251600	-1.41396500
H	-3.63750800	4.69395900	0.12481800
C	-2.50220000	5.40410400	-1.58601300
H	-2.39419300	5.18098900	-2.64971900
H	-2.82546200	6.44291500	-1.48404800
H	-1.52701700	5.29868700	-1.10601400

Zr-AZN_{1,9}(TS3)

Zr	-0.32316900	-1.74477100	0.92240400
C	1.25722400	3.65293400	1.16671000
C	2.51269800	3.40355800	0.63490000
C	2.91892300	2.10528700	0.30471700
C	2.02674300	1.00075600	0.51222900
C	0.74649300	1.26523200	1.07625100
C	0.38265900	2.58820500	1.38285800
C	4.26315300	1.90812800	-0.25147400
C	2.43609100	-0.32556300	0.15794600
C	3.74617300	-0.55463200	-0.38350900
C	4.64848400	0.52728100	-0.58100200
C	5.92847500	0.27145200	-1.10092400
H	6.59466500	1.11428400	-1.23843000
C	6.32371800	-1.01389400	-1.42474600
C	5.43145000	-2.08695000	-1.23518300
C	4.16844600	-1.86313200	-0.72596500
H	0.93896500	4.65686100	1.42217300
H	3.21121400	4.21217200	0.46343900
H	7.31511300	-1.19642800	-1.82332400
H	5.73890300	-3.09515900	-1.49016500
H	3.47888400	-2.68383100	-0.57826600
O	1.64124000	-1.36752600	0.32473600
O	-0.18154500	0.33736100	1.35017500
O	5.04480800	2.85951700	-0.43522200
O	-0.02895900	-3.59191600	1.62527600
H	0.37736800	-3.93510700	2.42516300
O	-0.77033100	-1.41769700	3.22011200
H	-0.96034800	-0.49821100	3.44638900
O	-0.85495400	2.81145300	1.90684400
H	-1.26234900	1.93303300	1.98732700
C	-1.81044900	-1.71534800	-3.14917000
H	-2.78757100	-1.77327400	-3.63073900
H	-1.06339000	-2.11205900	-3.84451500

H	-1.55958400	-0.67670200	-2.93950700
C	-1.75827300	-2.55127400	-1.88085800
H	-2.83940500	-2.09135300	-1.21216100
C	-2.10849600	-4.01992800	-2.04630700
H	-1.31919400	-4.48612100	-2.64488400
H	-2.14259600	-4.52497700	-1.08101900
H	-3.05699200	-4.15261100	-2.56839800
O	-0.77082800	-2.28706300	-1.06150100
H	-1.36140600	-1.98482600	3.72988800
C	-4.40689700	-2.81891100	0.16223400
H	-5.08068800	-2.96628300	-0.68321200
H	-5.00787800	-2.56231700	1.04020400
H	-3.87501400	-3.74616800	0.37409900
C	-3.42977600	-1.68030100	-0.08905100
C	-4.09242200	-0.36684100	-0.51533500
H	-4.71200900	-0.54072400	-1.39862800
H	-4.78298700	-0.10824800	0.29553600
C	-3.13785100	0.80357300	-0.73428400
H	-2.65343700	0.77070700	-1.71087400
H	-2.33196400	0.78084400	0.00621700
O	-2.43611900	-1.58797000	0.76037300
C	-3.81377900	2.15001100	-0.58752200
O	-4.88347300	2.34686400	-0.05535700
O	-3.04625500	3.12496600	-1.09824900
C	-3.52268600	4.49031200	-0.94167200
H	-4.50344400	4.57251600	-1.41396500
H	-3.63750800	4.69395900	0.12481800
C	-2.50220000	5.40410400	-1.58601300
H	-2.39419300	5.18098900	-2.64971900
H	-2.82546200	6.44291500	-1.48404800
H	-1.52701700	5.29868700	-1.10601400
Sn _{1,2} (TS1)			
C	6.11547100	-2.07838700	-0.53417100
C	4.73734300	-2.11425000	-0.35827700
C	4.01055800	-0.92756300	-0.21951100
C	4.68416400	0.30315900	-0.25912300
C	6.07114100	0.33203400	-0.43679500
C	6.78476800	-0.85209500	-0.57380700
C	2.52587400	-1.01166300	-0.03389100
C	3.93932500	1.58348600	-0.11453400
C	2.47205600	1.50880100	0.07062600
C	1.78180600	0.26388300	0.11351700
C	0.38675200	0.27404500	0.29373400
C	-0.30524900	1.51960400	0.42696000
C	0.39591600	2.71881300	0.38044400
C	1.77444900	2.70655000	0.20393500

H	6.67077100	-3.00294800	-0.64089700
H	4.20239000	-3.05461400	-0.32566500
H	6.56927300	1.29275000	-0.46470700
H	7.85936300	-0.82421600	-0.71133600
H	-0.15045800	3.64839000	0.48376600
H	2.33192500	3.63316600	0.16663900
O	-0.35285700	-0.84622100	0.34564400
O	1.98313200	-2.10813800	-0.01147800
O	-1.63635000	1.49855600	0.59839000
O	-3.32399700	-0.68313200	2.32870200
H	-3.16753900	0.07224000	2.91087300
O	-2.92086300	-2.34384400	-0.19212700
H	-2.22700900	-2.83050200	-0.65570300
O	4.53103600	2.65837400	-0.14893400
C	-4.73208000	1.83099100	-1.27698300
H	-5.68174800	2.36826200	-1.33667700
H	-4.16508200	2.02162600	-2.19183200
H	-4.16729100	2.23084600	-0.43178700
C	-4.98794100	0.34082400	-1.11382900
H	-5.55109500	0.15846700	-0.19290900
C	-5.72387100	-0.27749000	-2.29362600
H	-5.15825300	-0.12908800	-3.21703500
H	-5.87566700	-1.34870700	-2.14242200
H	-6.70423500	0.19200800	-2.40663300
O	-3.70270500	-0.34363100	-1.00000300
H	-3.55679000	-1.55067000	-0.88487400
Sn	-2.34861200	-0.44514400	0.62063300
Sn _{1,2} (TS2)			
C	-7.52113400	-0.81813700	0.97895300
C	-6.20688700	-1.21429900	0.76180900
C	-5.23728300	-0.27904000	0.38569700
C	-5.60195700	1.06755500	0.22913900
C	-6.92663500	1.45920100	0.44942400
C	-7.88281900	0.52281600	0.82217200
C	-3.83110100	-0.74957700	0.15955200
C	-4.59482400	2.09075900	-0.16946100
C	-3.21024300	1.63291300	-0.39885200
C	-2.83333700	0.26392700	-0.24485600
C	-1.49488300	-0.09932800	-0.48501500
C	-0.53901100	0.90216600	-0.87604300
C	-0.93877600	2.22632500	-1.01225100
C	-2.26421100	2.58158500	-0.77563700
H	-8.26555000	-1.55033900	1.26964900
H	-5.90834400	-2.24825300	0.87787700
H	-7.18393400	2.50305900	0.32221700
H	-8.90774400	0.83224800	0.99091100

H	-0.20327900	2.96659500	-1.30409400
H	-2.58338100	3.61024300	-0.88202500
O	-1.03792000	-1.33930400	-0.37380900
O	-3.56557300	-1.93725700	0.31554300
O	0.72041200	0.52088400	-1.09651300
O	1.02107300	-2.25376500	-2.66062400
H	0.55013700	-3.09609200	-2.64124200
O	0.03413700	-3.69267900	-0.38272900
H	-0.84782700	-3.39152200	-0.10496800
O	-4.92287500	3.26861500	-0.29820700
C	2.71265200	-1.00534500	3.15164600
H	3.72879100	-1.11869400	3.53063500
H	2.01745000	-1.31314300	3.93928600
H	2.51535300	0.03881900	2.91489700
C	2.46060500	-1.89233900	1.94415300
H	3.47985600	-1.51391800	1.14890900
C	2.76639400	-3.36749300	2.12965600
H	1.99158300	-3.78298000	2.78157900
H	2.73937700	-3.90898700	1.18329400
H	3.73541500	-3.52508700	2.60333800
O	1.36880200	-1.59279200	1.27078700
H	0.35101000	-4.29822100	0.29867400
C	5.07993100	-2.38473100	-0.06230600
H	5.74692900	-2.37596400	0.80100500
H	5.67976300	-2.23075000	-0.96405600
H	4.59478800	-3.35677700	-0.14382500
C	4.05229100	-1.26313800	0.00575800
C	4.66113800	0.12257600	0.24443500
H	5.25935900	0.10081700	1.15869900
H	5.36987000	0.27436600	-0.57730800
C	3.67638800	1.28726600	0.26050600
H	3.07971900	1.31814200	1.17381700
H	2.95867500	1.19947900	-0.56014900
O	3.10027500	-1.33929000	-0.90951600
C	4.36786800	2.62421300	0.10671400
O	5.50611500	2.78827100	-0.27234200
O	3.53877300	3.63122400	0.42576200
C	4.05615600	4.98229900	0.27501500
H	4.95007600	5.08215500	0.89373400
H	4.34518500	5.12839900	-0.76769200
C	2.96198200	5.93831600	0.69982900
H	2.68038000	5.77140300	1.74182000
H	3.31634700	6.96717400	0.60042000
H	2.07440700	5.81910600	0.07475600
Sn	1.00712000	-1.52207000	-0.79974400

Sn_{1,2}(TS3)

C	-6.97533100	-3.14366000	0.36788500
C	-5.63174100	-2.79477800	0.43449500
C	-5.20905000	-1.52357500	0.03245600
C	-6.15453400	-0.60047100	-0.43989400
C	-7.50544300	-0.95767900	-0.50385500
C	-7.91570700	-2.22273300	-0.10245900
C	-3.74941800	-1.18902600	0.12151800
C	-5.73695700	0.75995700	-0.87524700
C	-4.29828100	1.09482700	-0.79597300
C	-3.32978700	0.16220000	-0.32037600
C	-1.97468300	0.55049100	-0.28002600
C	-1.60326100	1.87180100	-0.71086900
C	-2.57484300	2.75736000	-1.16320100
C	-3.90832000	2.36653700	-1.20584400
H	-7.29320400	-4.13136600	0.68111900
H	-4.89002000	-3.49520200	0.79608300
H	-8.21582000	-0.22815200	-0.87142700
H	-8.96350300	-2.49477200	-0.15434900
H	-2.26904300	3.74648900	-1.48252800
H	-4.66960500	3.04872100	-1.56072800
O	-0.99720400	-0.25434600	0.14412000
O	-2.96991800	-2.03060600	0.55079000
O	-0.31233600	2.23012700	-0.66775800
O	1.66037800	-0.19482100	-1.51904300
H	0.97081100	-0.67076700	-1.99850200
O	-6.56853400	1.56641600	-1.28413800
H	2.99671800	-1.64400100	2.77097700
C	1.12477000	-2.49182000	2.14426100
H	1.39441800	-3.52049400	2.39450600
H	0.46708800	-2.51263200	1.27065300
H	0.56805000	-2.06849800	2.98287100
C	2.37690600	-1.67090500	1.86715700
C	3.20468600	-2.22869600	0.70958200
H	3.41810500	-3.27849900	0.92927500
H	2.60753300	-2.20594400	-0.20570400
C	4.52044100	-1.48614800	0.48040800
H	5.10984000	-1.43855700	1.40393600
H	4.35204000	-0.45107400	0.17338400
O	1.98082100	-0.28840700	1.65923400
C	5.39277400	-2.13887300	-0.56969900
O	5.18647700	-3.21207100	-1.08993800
O	6.45784700	-1.36920200	-0.85473900
C	7.39827200	-1.88576600	-1.83546800
H	7.77318300	-2.84935900	-1.48435100
H	6.86580100	-2.04963100	-2.77448500
C	8.50713600	-0.86548800	-1.98328300

H	9.02239900	-0.70861600	-1.03305500
H	9.23683500	-1.22033700	-2.71515100
H	8.11249300	0.09253700	-2.32879000
C	2.78035200	3.81971900	-0.34159700
H	3.23759600	4.80798700	-0.25072900
H	1.69362800	3.93994600	-0.32700100
H	3.07117000	3.39412900	-1.30450700
C	3.24132200	2.92414900	0.79899000
H	4.32744100	2.79843300	0.73720900
C	2.87771500	3.45968100	2.17815500
H	1.79818800	3.58725400	2.27776100
H	3.22049000	2.77900500	2.96171300
H	3.36182900	4.42699500	2.33733200
O	2.71476200	1.58670900	0.59194300
H	2.71873600	0.63938600	1.36610200
O	0.14350900	1.59009900	2.17191100
H	0.49933700	0.97968900	2.83461300
H	-0.80712200	1.66081100	2.33063500
Sn	0.85552100	0.69345400	0.09162800
Zr-AZN _{1,2} (TS2'')			
C	6.10472000	2.08920800	1.44979400
C	4.72278900	1.94499500	1.42253700
C	4.12969700	0.94585400	0.64396900
C	4.94219200	0.08343400	-0.10908100
C	6.33249400	0.23350500	-0.07533500
C	6.91250500	1.23146100	0.69796100
C	2.63494900	0.82934500	0.63675400
C	4.34472100	-0.99317200	-0.94948900
C	2.87217900	-1.09210500	-0.98844400
C	2.03966800	-0.21364700	-0.22610200
C	0.64836600	-0.36406100	-0.33774500
C	0.09410900	-1.35605700	-1.20977800
C	0.92482700	-2.20559200	-1.92903100
C	2.30704000	-2.06542500	-1.80936000
H	6.55537700	2.86797100	2.05410700
H	4.08081000	2.59940000	1.99820900
H	6.93888900	-0.44238200	-0.66477300
H	7.99024600	1.34440300	0.71762800
H	0.48952400	-2.95464200	-2.58010900
H	2.97319000	-2.71094300	-2.36714700
O	-0.27818000	0.35324200	0.28683900
O	1.96887500	1.59313100	1.32659500
O	-1.23531000	-1.37012600	-1.27349200
Zr	-2.31038100	0.05846900	-0.14076400
O	-3.82794000	-0.57324600	-1.62947500
H	-3.51990400	-1.05234000	-2.40611800

O	5.06838700	-1.75556800	-1.58710800
C	-4.18937400	-2.96054600	1.94423000
H	-4.38891600	-3.68228200	2.74094500
H	-3.86490300	-3.50706000	1.05427000
H	-5.11972600	-2.43781900	1.71146500
C	-3.11307900	-1.97052000	2.38209900
H	-3.46430900	-1.43299900	3.27128500
C	-1.78189400	-2.64600300	2.70193000
H	-1.40870900	-3.18624200	1.82729500
H	-1.03566900	-1.90512600	2.99749300
H	-1.90374900	-3.35807400	3.52270800
O	-2.92725000	-0.99465500	1.36136200
C	-5.56579300	2.49880900	-0.42249600
H	-6.15333100	3.40961300	-0.27881000
H	-5.50211000	1.97808700	0.53828300
H	-6.10155100	1.85843000	-1.12764300
C	-4.17330900	2.84134200	-0.94730300
H	-4.27413800	3.36856800	-1.90316700
C	-3.38028700	3.71724100	0.01652800
H	-3.27166800	3.22514100	0.98882100
H	-2.38480800	3.92648100	-0.38189800
H	-3.89176300	4.66992200	0.17618100
O	-3.42806600	1.64124500	-1.22174100
H	-3.89081800	0.64254400	-1.71214200

Zr-AZN_{1,2}(TS3'')

C	5.91277200	3.30703600	1.82389300
C	4.67076400	2.71533300	1.62806600
C	4.53489200	1.61498200	0.77481900
C	5.66647200	1.11077300	0.11559400
C	6.91395900	1.71188200	0.31655700
C	7.03885600	2.80407000	1.16575500
C	3.17337000	1.00726700	0.59180500
C	5.55856700	-0.06104100	-0.79934400
C	4.22743600	-0.66348200	-0.97998500
C	3.06471700	-0.15497100	-0.31069300
C	1.83030500	-0.79558100	-0.54067900
C	1.76207400	-1.92880600	-1.42744600
C	2.90755400	-2.39519700	-2.06488000
C	4.12618400	-1.75962400	-1.83390600
H	6.00751500	4.15895300	2.48743900
H	3.78725800	3.09059000	2.12851600
H	7.77170000	1.30499900	-0.20400200
H	8.00801500	3.26514500	1.31766300
H	2.83660700	-3.24827300	-2.73036300
H	5.02827000	-2.11061600	-2.31885800
O	0.66782700	-0.46146300	-0.01630700

O	2.22170100	1.49792100	1.19246000
O	0.56059800	-2.45237000	-1.56826400
Zr	-1.10666400	-1.58755500	-0.43724800
O	6.56131900	-0.49106800	-1.37143600
C	-1.05434500	-5.34810900	1.14576000
H	-0.96126700	-6.17877500	1.85085900
H	-0.27614900	-5.45142400	0.38413700
H	-2.02925100	-5.41922200	0.65751800
C	-0.91362100	-4.01014000	1.87098200
H	-1.70104200	-3.94018400	2.63387000
C	0.44397900	-3.85279800	2.55439200
H	1.25024600	-3.92135300	1.81848600
H	0.51125000	-2.88263000	3.05167000
H	0.58981100	-4.63615400	3.30350500
O	-1.11628300	-2.94682500	0.95832700
C	-5.38173600	-0.25998900	-0.84016100
H	-6.11163700	0.17082700	-0.15270300
H	-5.91586300	-0.91348600	-1.53815800
H	-4.90653600	0.53347500	-1.41633300
C	-4.33862200	-1.09627900	-0.11038800
H	-3.89919200	-0.22134600	0.82669100
C	-4.90545500	-2.20049800	0.77231600
H	-5.39874100	-2.93073500	0.12202500
H	-4.11087400	-2.71198200	1.31484200
H	-5.64615400	-1.81861900	1.47678400
O	-3.26379700	-1.38290900	-0.79230700
C	-3.01022700	-0.37382400	2.84554000
H	-3.99989000	-0.23751500	3.28529700
H	-2.26950100	0.06282000	3.52277000
H	-2.79261900	-1.43684400	2.74922300
C	-2.88549600	0.32918100	1.49878800
C	-3.27910200	1.81024300	1.53690900
H	-4.31386900	1.90387700	1.87654100
H	-2.66026300	2.27384900	2.31314000
C	-3.06292800	2.55603300	0.22496200
H	-3.77299000	2.25219400	-0.54651500
H	-2.06804800	2.32938800	-0.16995300
O	-1.83601700	0.03232200	0.78115300
C	-3.15504900	4.05780900	0.38254500
O	-3.14600400	4.65832000	1.43357800
O	-3.23116100	4.66142000	-0.81601200
C	-3.27956900	6.11482700	-0.81787300
H	-4.15145400	6.43364200	-0.24319700
H	-2.38550400	6.49254900	-0.31783900
C	-3.35537600	6.56537800	-2.26121100
H	-4.25186500	6.17310100	-2.74643800

H	-3.39220300	7.65664100	-2.30280200
H	-2.47966400	6.23006000	-2.82121400
O	-1.77111800	-3.13861900	-2.06693800
H	-2.52487800	-3.72323600	-1.92870000
H	-0.99772000	-3.66006400	-2.32549000
O	-1.26095200	-0.11058000	-2.31278700
H	-2.16787500	0.19026700	-2.45368500
H	-0.69025000	0.66626400	-2.35928000
Zr-AZN _{1,2} (TS4'')			
C	7.79935100	0.37571600	1.54218100
C	6.46012600	0.73416900	1.44606400
C	5.58437100	-0.00214300	0.64142300
C	6.06865600	-1.11127400	-0.07124400
C	7.41806400	-1.46568600	0.03068400
C	8.28041200	-0.72782400	0.83205600
C	4.14691000	0.41845200	0.56429900
C	5.16563300	-1.92264500	-0.93861100
C	3.75201200	-1.51361900	-1.01911100
C	3.25596100	-0.38165300	-0.29674200
C	1.89429000	-0.06087700	-0.42690800
C	1.03441800	-0.84989300	-1.26223600
C	1.54448400	-1.94312000	-1.95318600
C	2.89692200	-2.26325100	-1.82392000
H	8.47023100	0.95270400	2.16818100
H	6.06895800	1.58537700	1.98853100
H	7.76881100	-2.32423800	-0.52781100
H	9.32477000	-1.00820300	0.90612500
H	0.88665900	-2.53389800	-2.58013300
H	3.31056900	-3.11186200	-2.35381300
O	1.27491900	0.94191000	0.16298200
O	3.77175500	1.39514300	1.20900200
O	-0.22870000	-0.44629300	-1.30960100
Zr	-0.83077900	1.24099700	-0.14596900
O	5.60639000	-2.89258400	-1.55430500
C	-0.51719800	0.44303800	3.77300600
H	-0.44098000	-0.13133200	4.70032900
H	-0.97147400	1.41102200	4.00554700
H	0.49199200	0.61151200	3.39099200
C	-1.36280300	-0.31075700	2.74737900
H	-0.88528000	-1.27723200	2.54008200
C	-2.78693800	-0.56087500	3.23832700
H	-3.29409700	0.38788200	3.43580600
H	-3.36321600	-1.11486400	2.49449300
H	-2.77296100	-1.14413000	4.16332600
O	-1.39787800	0.41133200	1.52408300
H	-4.36137900	0.66748900	-2.42111600

C	-2.62754600	0.50215200	-3.68076100
H	-3.16610000	0.02774200	-4.50606400
H	-1.61530200	0.09380300	-3.64222500
H	-2.56755200	1.57369500	-3.88754700
C	-3.34754400	0.25044400	-2.35769600
C	-3.45300100	-1.24038100	-2.03066200
H	-3.94090600	-1.74667700	-2.86937000
H	-2.44399800	-1.64959900	-1.94663400
C	-4.23007100	-1.50530400	-0.74381900
H	-5.26001000	-1.13867800	-0.81579100
H	-3.77695100	-0.96151300	0.08955700
O	-2.69733600	0.93780600	-1.28092900
C	-4.28824200	-2.96610500	-0.36230900
O	-3.76396800	-3.87724000	-0.96287700
O	-5.01030300	-3.14239800	0.76186400
C	-5.15165900	-4.50577500	1.24402800
H	-5.58801300	-5.11248200	0.44802200
H	-4.15860100	-4.90159700	1.46690500
C	-6.03486100	-4.46671600	2.47334900
H	-7.01837400	-4.05639700	2.23378900
H	-6.17038700	-5.48011100	2.85913300
H	-5.58502000	-3.85783500	3.26064500
C	-3.36595500	5.12178800	-0.64777500
H	-3.80224300	5.95497900	-0.08965000
H	-4.13194100	4.71813000	-1.31706500
H	-2.54438800	5.50777000	-1.25587300
C	-2.86385100	4.03623400	0.30225500
H	-2.09128300	4.47166600	0.94705600
C	-3.97859200	3.46931300	1.17995700
H	-4.77102900	3.03535900	0.56216000
H	-3.59322600	2.69024500	1.84149900
H	-4.42061200	4.25655800	1.79693300
O	-2.23555700	2.99973600	-0.46122200
H	-2.83687100	2.09646800	-1.01620600
O	0.22952500	2.99784000	1.03693000
H	-0.08147000	3.30969600	1.89480300
H	1.11835400	2.61584800	1.15727900
O	-0.03595000	2.56882000	-1.96666400
H	-0.70892400	3.23982500	-2.14895500
H	0.29011100	2.22998000	-2.80846300