

Supporting Information for:

Small, electron-donating substituents give CO₂ activation by permethylpentalene zirconium amido complexes the upper hand: A DFT study of distortion and interaction

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Table of contents:

Section S1	Benchmarking results.	S2
	Table S1. Geometric values from calculations at various levels of theory.	
	Figure S1. Key for benchmarking data.	
	Table S2. Comparison of metrical parameters for optimizations with PCM and SMD solvent models.	
	Figure S2. Reaction energetics for solvated 1a and TS1a .	
Section S2	IRC endpoints for TS1a and TS1b .	S3
	Figure S3	
Section S3	Distortion-interaction analysis of TS1c-d .	S4
	Figure S4	
Section S4	1a-b and TS1a-b HOMO visualizations and bonding analysis.	S5
	Figure S5	
Section S5	Partial charges and metrical parameters.	S5
	Table S3. Metrical parameters of TS1c-d .	
	Table S4. Comparison of nitrogen bonding across substituents.	
Section S6	Sample input file for TS1a optimization.	S6
Section S7	Coordinates of optimized geometries.	S9

Section S1. Benchmarking Results

Table S1. Bond distances [\AA] and angles [$^\circ$] from calculations of **1a** at various levels of theory. The best combination was assessed using a combination of agreement with literature values and literature precedent. Most model chemistries reasonably agree with literature values, and values highlighted in gray showed closest agreement. A key for atom labels is shown in Figure S1.

Functional	PBE (def2-ECP) with D3		B3LYP (def2-ECP) with D3		wb97xd (def2-ECP)	
Basis set*	6-31G(d,p)	cc-pVDZ	6-31G(d,p)	cc-pVDZ	6-31G(d,p)	<i>Literature¹</i>
Zr-N	2.155	2.154	2.146	2.145	2.146	2.136
Zr-Ct1	2.242	2.242	2.268	2.268	2.257	2.28
Zr-Ct2	2.141	2.139	2.143	2.147	2.118	2.1326
Zr-Ct3	2.140	2.142	2.146	2.143	2.115	2.1254
N-Zr-Ct1	103.70	103.40	103.75	103.47	103.68	103.77
C1-N-C2	110.46	110.47	110.57	110.52	110.49	112.5

*The reactive nitrogen and CO_2 atoms (see Figure S1) were modeled with additional diffuse functions corresponding the underlying basis set (eg. cc-pVDZ \rightarrow aug-cc-pVDZ).

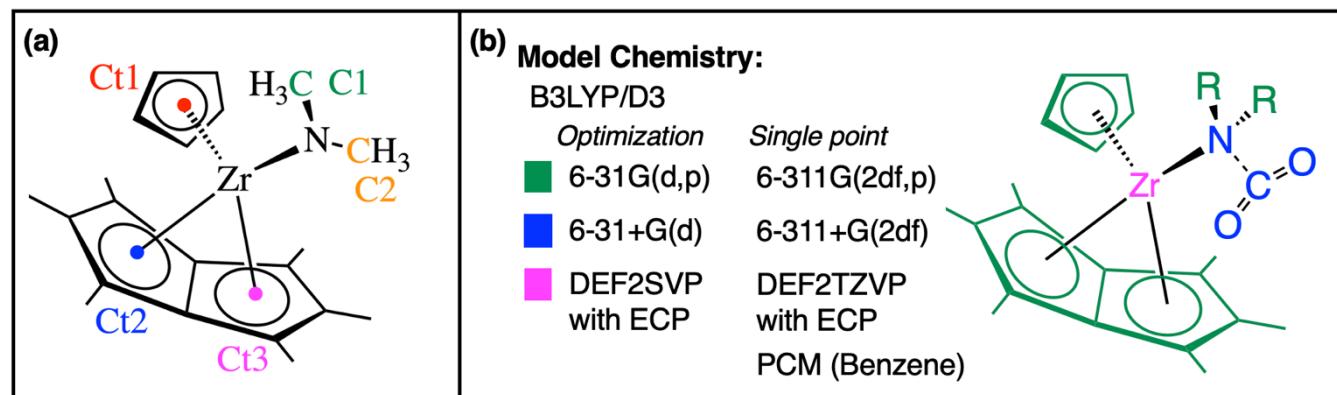


Figure S1. (a) Labeled key to interpret the benchmarking data. For example, bond “Zr-Ct1” is the bond length from the zirconium (IV) to the center of the cyclopentadienyl. (b) Schematic of the model chemistry ultimately used for calculations.

The total angle around N reported in crystallographic studies of complexes **1a** and **1b** are 351.2° and 357.4° respectively.¹ Computations give values of 351.7° and 357.1° respectively, indicating that the correct bonding nature of the amido group is captured well by the computational method.

Table S2. Comparison of metrical parameters for optimizations with PCM and SMD solvent models. The values were very similar to those from gas phase optimizations (Table S1).

Coord.	1a PCM	1a SMD	TS1a PCM	TS1a SMD
Zr-N (\AA)	2.148	2.153	2.25	2.232
C-N-C ($^\circ$)	110.3	110.5	106.6	108.2
N-CO ₂ (\AA)			2.355	2.46
C-O(1) (\AA)			1.183	1.179
C-O(2) (\AA)			1.185	1.18
Zr-O ₂ (\AA)			3.53	3.798
O-C-O $^\circ$			159.87	163.29

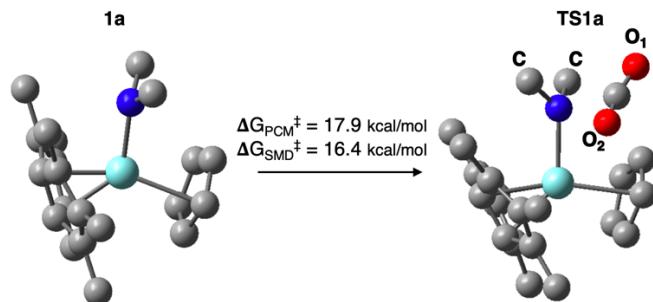


Figure S2. Free energy barriers for **1a** calculated from optimizations with each solvent method differ by 1.5 kcal/mol, and it was concluded that the choice of solvent model has only a minor impact on the reaction energetics. The distortion and interaction energies computed for structures optimized in PCM were 19.1 and -13.5 kcal/mol, which were very close to the values of 19.8 and -13.9 kcal/mol determined using single point calculations in solvent with structures optimized in vacuum. The electronic energy values computed for the structures optimized in SMD were slightly lower in magnitude, with a distortion energy of 14.1 and an interaction energy of -11.2. These results validated the use of gas phase optimizations paired with single point solvent energies as described in the main text. Hydrogen atoms have been omitted for clarity.

Section S2. IRC endpoints for Me and Ph

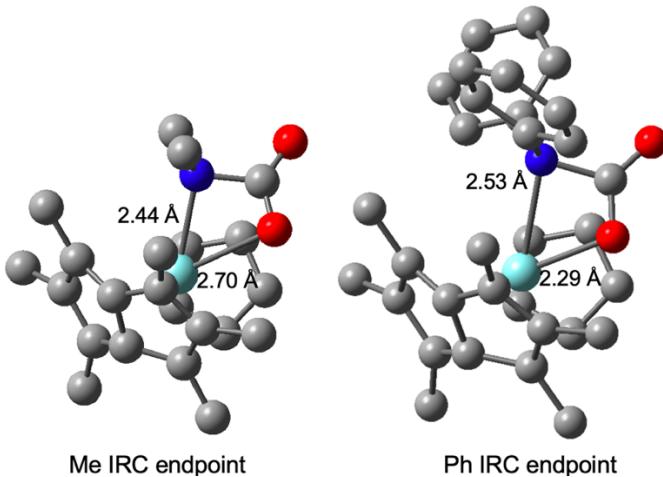


Figure S3. Structures at the termination point for intrinsic reaction coordinate (IRC) calculations of **TS1a** (Me) and **TS1b** (Ph) are analogous. However, while geometry optimizations of the Me endpoint led to the η^2 N- and O-bound intermediate **2a**, careful optimization of the Ph endpoint does not lead to **2b**, but the final η^2 O-bound intermediate **3b**. While these two endpoints are analogous, the Ph endpoint has a longer Zr-N bond distance (2.53 Å vs 2.44 Å) and a shorter Zr-O distance (2.29 Å vs 2.70 Å), indicating that coordination of the amido nitrogen is less favorable. This could be due to a combination of steric repulsion between the phenyl rings and permethylpentalenyl ligand as well as decreased nitrogen nucleophilicity due to the electron-withdrawing phenyl substituents. Hydrogen atoms have been omitted for clarity.

Section S3. Distortion-interaction analysis of TS1c-d

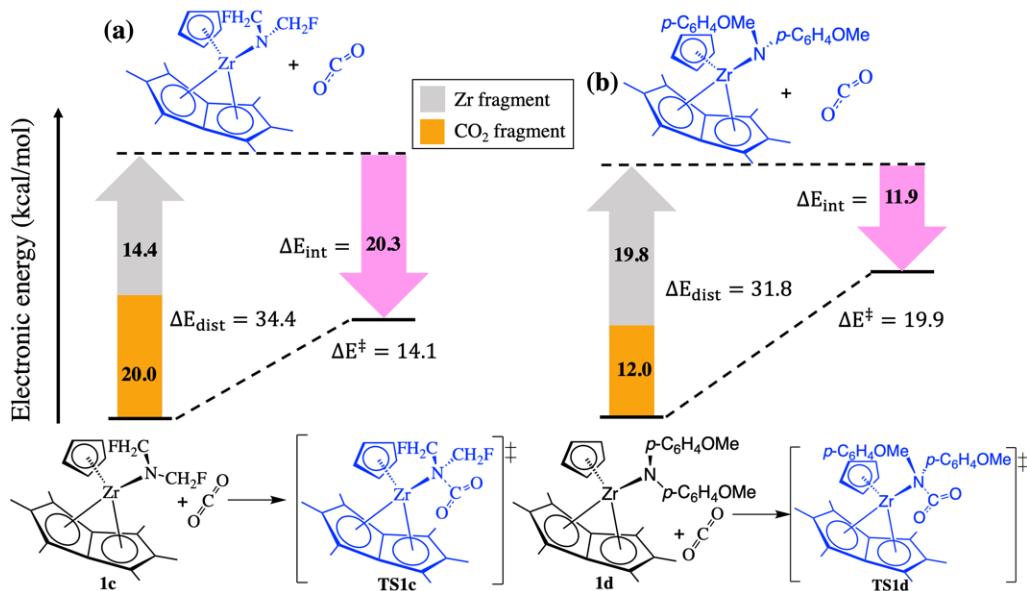


Figure S4. Distortion-interaction diagram for (a) **TS1c** and (b) **TS1d**. The distortion energy of **TS1c** is 34.4 kcal/mol, 14.6 kcal/mol greater than its sterically similar partner **TS1a**. The much greater relative contribution of the CO₂ fragment (20.0 kcal/mol vs. 8.4 kcal/mol) indicates that the electron-withdrawing nature of CH₂F shifts the TS coordinate later along the PES such that greater distortion is observed. The distortion energy of **TS1d** is 31.8 kcal/mol, 5.1 kcal/mol less than Ph substituted **TS1b**. The reduced distortion energy is not steric, as both substituents have similar steric profiles, but a result of the earlier TS of the more electron donating 4-C₆H₄OMe substituent. Concretely, we observe that the contribution of the Zr fragment to the distortion energy for 4-C₆H₄OMe (19.8 kcal/mol) is 4.5 kcal/mol lower than for Ph (24.3 kcal/mol, in main text), indicating that electron-donating groups stabilize the deformed aromatic ring. The shifts in TS location can be seen clearly in Figure 6.

Section S4. 1a-b and TS1a-b HOMO visualizations and bonding analysis

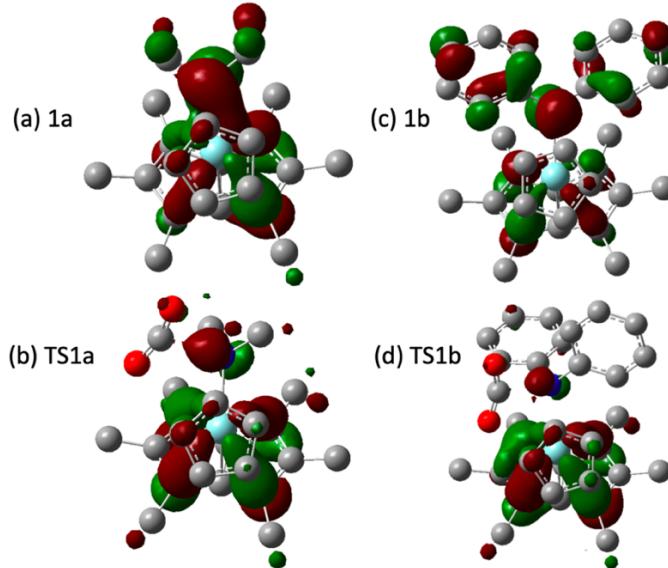


Figure S5. HOMO visualizations of (a) **1a**, (b) **TS1a**, (c) **1b**, (d) **TS1b** using an isovalue of 0.04. The nitrogen lone pair p-orbital contributes significantly to the HOMO in both **1** starting structures, with delocalization into the aromatic ring for **1b**. From **1** to **TS1**, the nitrogen p-orbital retains a similar lobe structure to interact with the CO₂ carbon, however, the orbital density around the nitrogen substituents is diminished. For **TS1b**, this corresponds to a loss of aromaticity and a large energetic penalty for forming the activated complex.

Section S5. Partial charges and metrical parameters

Table S3. Metrical parameters of **TS1c** and **TS1d**.

Parameter	TS1c	TS1d
Zr–N (Å)	2.40	2.37
C–N–C (°)	110.7	109.2
N–C(O ₂) (Å)	1.96	2.23
C–O1 (Å)	1.20	1.18
C–O2 (Å)	1.21	1.20
Zr–O2 (Å)	3.02	2.75
O–C–O (°)	148.4	155.3

Table S4. Comparison of nitrogen bonding across substituents in **TS1a-d**.²

Substituent	σ_{meta}	σ_{para}	Zr–N (Å)	C–N (Å)
Me (TS1a)	-0.07	-0.17	2.252	2.307
4-C ₆ H ₄ OMe (TS1d)	0.05	-0.08	2.367	2.234
Ph (TS1b)	0.06	-0.01	2.380	2.215
CFH ₂ (TS1c)	0.12	0.11	2.394	2.053

The Zr–N bond length increases and the C–N (CO₂ carbon) bond length decreases down the series of more electron-withdrawing substituents. The trend in Zr–N bond lengths indicate that the interaction of the amide with Zr is decreased through impaired nucleophilicity at N; the trend in C–N bond length shows that the degree of lateness in the TS is increased for more electron-withdrawing substituents.²

Section S6. Sample input file for TS1a optimization

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C 0.51555200 -2.18033100 -0.71885200
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H	0.66668700	3.06657500	-0.97240800
C	2.70075800	0.61901100	-1.54722400
N	1.74196100	0.62857100	0.66338700
O	1.85980700	1.19629000	-2.14808600
O	3.70128600	0.04909400	-1.29076400
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C	2.32651400	1.90663900	1.08098800
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6-31+G(d)

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Zr 0

def2svp

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def2tzvp

Zr 0
def2tzvp

Section 7. Coordinates of optimized geometries

Coordinates of 1a.

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H	0.01083000	-2.98184800	1.19280200
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C	-0.20651800	0.23021000	2.99377100
H	-1.77855400	-1.33724800	2.77591000
H	0.70061200	2.23422600	2.63378800
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H	-0.10855400	-3.74362400	-1.30091900
H	0.79987400	-3.17713500	-2.70438900

H	1.44296200	-2.93550400	-1.06931800
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H	2.80939000	3.21717300	-1.55766300
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H	3.41608700	2.12649200	-0.30773800
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Coordinates of **1b**.

Zr	0.05057000	0.10192200	0.47106200
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C	0.05327100	-0.51044200	-1.77180400
C	0.51440500	1.72536100	-1.31518400
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N	1.00586900	-1.78668200	1.20659300
C	1.48310300	-0.38046500	-1.68253300
C	-0.88926700	-1.51697500	-1.36329300
C	1.74687900	0.98385700	-1.42129500
C	-2.03459300	-0.83220900	-0.89563700
C	-1.01924800	1.98033100	1.78975500
C	0.37691800	2.17285800	1.92312200
C	-1.36268500	0.78297600	2.48398600
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C	0.90099000	1.09935500	2.68752300
H	0.94265900	2.99757800	1.51374300
C	-0.17975800	0.25033500	3.04356700
H	-2.35782400	0.36546600	2.57050100
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H	-0.09253500	-0.67116400	3.60112800
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H	-3.67975400	1.52353600	-1.61794900
H	-3.48993500	1.44809800	0.13373300
H	-2.56034200	2.61781600	-0.81201800
C	-3.31226200	-1.47801100	-0.45006200
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H	3.89977800	0.87999100	-1.25351300
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H	0.38435500	3.67163600	-2.23047300
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H	1.28016800	3.65175500	-0.71219000
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C	-1.07705700	-2.93785600	1.80561000
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C	-1.82858700	-4.10985600	1.91306300
H	-1.54200300	-1.98298600	2.02280900
C	-1.24743500	-5.35054800	1.65406500
H	0.57285400	-6.35986200	1.08484700
H	-2.87102100	-4.04847200	2.21423300
H	-1.83037300	-6.26202400	1.74025100
C	2.23987800	-1.69817200	1.86650300
C	3.23911900	-0.82058900	1.39448400
C	2.50830500	-2.38496800	3.07404800
C	4.42992100	-0.62757200	2.09152900
H	3.06753200	-0.28585700	0.47178800
C	3.70466600	-2.19486900	3.75890100
H	1.76231700	-3.06205600	3.47442100
C	4.67840700	-1.31278500	3.28131700
H	5.17210800	0.05833200	1.69112800
H	3.87227600	-2.73493800	4.68707200
H	5.60783900	-1.16745800	3.82235000

Coordinates of **1c.**

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C	-0.55425600	0.71750500	-1.69181100
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C	0.09284200	1.89536600	-1.16313300
C	-1.79377400	0.06875600	-1.34440600
N	1.40594700	-1.42333600	1.15830400
C	1.73656100	0.24567200	-1.43162500
C	-0.16056800	-1.59984100	-1.55424800
C	1.49673500	1.58469900	-1.05199800
C	-1.53015700	-1.34402400	-1.29473800
C	2.67240000	-1.02439200	1.61530800
C	0.98888400	-2.68124900	1.62621300
H	3.08624100	-0.23098700	0.98979300
H	3.37586600	-1.86868300	1.67637500
H	1.81731100	-3.40505300	1.66568900
H	0.17341900	-3.07727200	1.01327400
C	-2.17666500	0.55578500	1.79549100
C	-1.46360800	1.77392100	1.68824700
C	-1.40044700	-0.34378000	2.57380300
H	-3.14162600	0.34846000	1.35688900
C	-0.24903300	1.63328900	2.42662500
H	-1.79358700	2.66047900	1.16853400
C	-0.22543700	0.33844000	2.98671600
H	-1.64498500	-1.36510800	2.82740400
H	0.51409200	2.39224700	2.54468100
H	0.58730600	-0.09552000	3.54446200
C	-3.15375700	0.70420700	-1.31248100
H	-3.53136500	0.86057400	-2.33063300
H	-3.88262700	0.07856500	-0.79112200
H	-3.14100400	1.67928900	-0.81860000
C	-2.57918200	-2.38847500	-1.04930300
H	-3.10265500	-2.64326800	-1.97915800
H	-2.14714100	-3.30946900	-0.65094300
H	-3.33200600	-2.04100900	-0.33674400
C	0.50471700	-2.93720000	-1.66697600
H	-0.12568600	-3.73967900	-1.27679000
H	0.72025200	-3.17262400	-2.71607800
H	1.44957300	-2.95581300	-1.11941700
C	3.06224800	-0.43895300	-1.56248500
H	3.30493500	-0.58647100	-2.62152800
H	3.87210300	0.14728800	-1.12254500
H	3.05528500	-1.42127200	-1.08512300
C	2.53951800	2.58668500	-0.65154200

H	2.83919800	3.20178600	-1.50945500
H	2.16350900	3.26609800	0.11822300
H	3.43853500	2.10558800	-0.25930200
C	-0.46999400	3.28564800	-1.06927400
H	-0.18213200	3.88310500	-1.94409800
H	-1.56103100	3.27325200	-1.03403400
H	-0.11174900	3.81730700	-0.18238700
F	0.46581400	-2.65860600	2.95919100
F	2.66941600	-0.46361900	2.93726600

Coordinates of **1d.**

Zr	0.12758600	0.03336000	0.40093100
C	-0.33200000	0.60717200	-1.75157700
C	0.26899700	-0.71964900	-1.79517300
C	0.72707700	1.53735900	-1.45404500
C	-1.66228200	0.44554800	-1.21263800
N	1.00291800	-1.80395400	1.30722600
C	1.69139000	-0.59573700	-1.62216000
C	-0.71022300	-1.68982100	-1.38435400
C	1.95441900	0.78019300	-1.43008000
C	-1.87503500	-0.96714700	-1.03726200
C	-1.00870400	2.00192000	1.52453300
C	0.37740200	2.19552100	1.73522900
C	-1.40689400	0.85299800	2.26955700
H	-1.65535300	2.62800700	0.93019000
C	0.84180000	1.17047900	2.59887100
H	0.97584900	2.98932000	1.31149400
C	-0.26727300	0.35172500	2.93767800
H	-2.40934300	0.44686900	2.31795000
H	1.85692100	1.02977800	2.93909500
H	-0.22371800	-0.53312700	3.55636500
C	-2.76088600	1.46971600	-1.16311900
H	-3.43638200	1.35556300	-2.02087700
H	-3.37103100	1.38056800	-0.25879300
H	-2.36289900	2.48566700	-1.20165400
C	-3.18620800	-1.57224800	-0.63316600
H	-3.84678000	-1.67525700	-1.50363000
H	-3.05265100	-2.56227600	-0.19441500
H	-3.70962300	-0.94601500	0.09551800
C	-0.57209100	-3.17783900	-1.47490100
H	-1.22386000	-3.69750000	-0.77173900
H	-0.83275400	-3.51255200	-2.48747200

H	0.45007300	-3.49781900	-1.27312100
C	2.66525700	-1.73507900	-1.63651700
H	2.58012500	-2.30290500	-2.56925200
H	3.69834500	-1.39150100	-1.55042400
H	2.47067300	-2.41914800	-0.80407300
C	3.30807100	1.41195600	-1.28197500
H	3.57352400	1.96829900	-2.18914300
H	3.33435500	2.12086600	-0.44838100
H	4.09004400	0.66966500	-1.11021700
C	0.64382600	3.03637300	-1.46926100
H	0.67710900	3.42351800	-2.49583600
H	-0.28315500	3.39875100	-1.01720700
H	1.47621600	3.49204100	-0.92588500
C	0.24602300	-2.97102400	1.54376000
C	0.81644100	-4.24997300	1.41896000
C	-1.12346900	-2.91219800	1.86125500
C	0.06352700	-5.41269300	1.57156500
H	1.87361500	-4.32606100	1.18395900
C	-1.89239800	-4.06480500	1.99592600
H	-1.59659700	-1.94571900	1.99263900
C	-1.30678200	-5.32663800	1.85025400
H	0.54894800	-6.37427200	1.45424600
H	-2.95015600	-4.00775000	2.23227000
C	2.18142800	-1.67218800	2.06335900
C	3.24104900	-0.86087500	1.60278700
C	2.33469900	-2.23863700	3.34487700
C	4.36833000	-0.61378800	2.37604500
H	3.16665100	-0.41332600	0.62239200
C	3.47094700	-2.00863200	4.12193400
H	1.54523800	-2.86605100	3.74331000
C	4.49798800	-1.18671800	3.64595500
H	5.17180600	0.01419400	2.00411600
H	3.53460100	-2.46767800	5.10163700
O	5.65067100	-0.89235700	4.32932000
O	-2.14244300	-6.40138200	2.00409600
C	5.80277100	-1.44895100	5.62019300
H	5.80341200	-2.54720400	5.59302000
H	6.76762100	-1.09996900	5.99222200
H	5.01084400	-1.11440100	6.30414200
C	-1.58236200	-7.69264900	1.85841700
H	-0.79635500	-7.88152800	2.60185700
H	-2.39952900	-8.39884400	2.01422000

H -1.16260900 -7.84289100 0.85465800

Coordinates of **TS1a.**

Zr	-0.42138100	0.23975300	0.17134200
C	-0.45827400	-2.11056900	0.35028800
C	-1.70926400	-1.60549200	-0.21004800
C	0.51555200	-2.18033100	-0.71885200
C	-0.45696300	-1.83974000	1.76241600
C	-2.46908400	-1.03023100	0.86993000
C	-1.43586600	-1.18474000	-1.56205400
C	1.84757900	-2.87959000	-0.71661400
C	-0.08659600	-1.61276000	-1.85336700
C	0.45412600	-2.38658300	2.82495300
C	-1.68560500	-1.17713400	2.04983500
C	-3.91582600	-0.62563100	0.85609700
C	-2.42521500	-0.77796900	-2.61673200
H	2.06060400	-3.32584700	0.25644900
H	1.84235800	-3.69763900	-1.44733000
H	2.68072500	-2.21929300	-0.97189400
C	0.53559300	-1.53977400	-3.21501600
H	1.37626900	-2.79137600	2.40921000
H	-0.04657100	-3.20479800	3.35952100
H	0.72786000	-1.63303500	3.56831500
C	-2.14601500	-0.81043100	3.42924100
H	-4.10203500	0.31939500	1.37638500
H	-4.29292300	-0.52876300	-0.16368600
H	-4.52943400	-1.38893800	1.35122900
H	-1.96477800	-0.13489500	-3.37250800
H	-2.82878800	-1.65468900	-3.14044300
H	-3.27432200	-0.23573200	-2.19580000
H	0.37085900	-0.56488400	-3.68140400
H	0.10113900	-2.29998400	-3.87706000
H	1.61352500	-1.71132200	-3.17608300
H	-2.86577900	0.01209500	3.40895200
H	-1.30966600	-0.51395200	4.06794800
H	-2.64039900	-1.66275200	3.91372200
C	-2.34815500	1.79651600	-0.37981700
C	-1.92631900	2.16343600	0.92597700
C	-1.31732400	2.14645800	-1.28799000
H	-3.29758700	1.35986400	-0.63976400
C	-0.63592000	2.72554200	0.82418900
H	-2.48775400	2.02130600	1.83936800

C	-0.26271200	2.72091800	-0.55064100
H	-1.33064700	1.98859500	-2.35722000
H	-0.04077000	3.09419000	1.64665000
H	0.66668700	3.06657500	-0.97240800
C	2.70075800	0.61901100	-1.54722400
N	1.74196100	0.62857100	0.66338700
O	1.85980700	1.19629000	-2.14808600
O	3.70128600	0.04909400	-1.29076400
C	2.50451900	-0.38676300	1.38356600
C	2.32651400	1.90663900	1.08098800
H	2.40095100	-0.27525100	2.47583800
H	3.57676200	-0.31306100	1.14848000
H	2.18483100	-1.38596200	1.11999900
H	2.11940500	2.13701500	2.14153300
H	3.42308600	1.87394100	0.97990800
H	1.97468300	2.74442000	0.48336200

Coordinates of **TS1b.**

Zr	1.29282300	0.04321400	-0.05997900
C	2.69825300	-1.41348300	-1.10049100
C	1.36285200	-1.87253200	-1.42235000
C	2.92954800	-1.73336500	0.29204500
C	2.96356300	-0.26056000	-1.91739100
N	-1.05241600	0.09860000	0.34030600
C	0.88946200	-2.70766600	-0.33911900
C	0.78561400	-0.98206200	-2.38318700
C	1.84013300	-2.61430100	0.68159200
C	1.79187500	-0.01648100	-2.69188000
C	1.32819400	2.64750500	-0.07104000
C	2.64539500	2.21274200	-0.32168400
C	1.02010000	2.34418700	1.28507200
H	0.68966100	3.17812800	-0.75900600
C	3.13769500	1.58563000	0.85348400
H	3.18830600	2.36103000	-1.23914400
C	2.13770100	1.70607100	1.85383300
H	0.08308800	2.56709700	1.77362600
H	4.12162800	1.16343900	0.99195300
H	2.21081500	1.32127900	2.86059200
C	-0.47299500	0.13339000	2.47823200
O	0.52150300	-0.53510100	2.37895200
O	-1.28955900	0.75164500	3.05899700
C	-1.69707500	1.29970400	-0.12166800

C	-1.38316100	1.86430600	-1.36504900
C	-2.69507300	1.91660300	0.65183700
C	-2.00825100	3.03050400	-1.80928500
H	-0.63822000	1.37932300	-1.98230100
C	-3.31405700	3.08486400	0.21178200
H	-2.97707700	1.47200800	1.59709600
C	-2.97292300	3.65302000	-1.01811700
H	-1.74443700	3.44457600	-2.77870300
H	-4.07304600	3.55156800	0.83309600
H	-3.46103400	4.56099700	-1.35848200
C	-1.99783600	-0.98485100	0.35392100
C	-2.01935300	-1.97108900	1.35755700
C	-2.99406200	-1.07090100	-0.64147000
C	-2.98453800	-2.97602600	1.36780800
H	-1.26418300	-1.98691400	2.13023300
C	-3.94780200	-2.08653300	-0.63669500
H	-3.02682300	-0.31874700	-1.41978000
C	-3.95710400	-3.04978400	0.37242800
H	-2.96674700	-3.71136000	2.16749100
H	-4.69359600	-2.11507800	-1.42685400
H	-4.70733700	-3.83449400	0.38515500
C	1.66607000	1.05377000	-3.73609300
H	2.10895800	0.73151600	-4.68822400
H	0.61994600	1.30205600	-3.93424200
H	2.17476700	1.97541900	-3.43667600
C	4.31344600	0.35926500	-2.13497800
H	4.94942100	-0.33367900	-2.69871500
H	4.25547900	1.28360700	-2.71507800
H	4.83329700	0.58139700	-1.19927900
C	-0.52302200	-1.15916600	-3.09290700
H	-0.94166700	-0.21001400	-3.43593800
H	-0.39430000	-1.79755300	-3.97651100
H	-1.26580100	-1.62942300	-2.44892900
C	-0.24257600	-3.68035000	-0.45092800
H	-1.14174300	-3.23755500	-0.87995200
H	0.06563800	-4.50292300	-1.11002000
H	-0.51616900	-4.11031400	0.51185900
C	1.80169400	-3.33088400	1.99484800
H	2.52759100	-4.15411400	2.01279200
H	2.05139600	-2.65487100	2.81706800
H	0.81399500	-3.75020500	2.19702800
C	4.22374700	-1.64253600	1.05392800

H	4.06220700	-1.35488600	2.09757500
H	4.75028200	-2.60624400	1.05894500
H	4.89863700	-0.91035900	0.60626000

Coordinates of **TS1c.**

Zr	-0.42764800	0.22508200	0.09541500
C	-0.47033300	-2.11453600	0.30537300
C	-1.72976100	-1.60431800	-0.22196200
C	0.48676400	-2.16111200	-0.77939000
C	-0.43399000	-1.85711500	1.71874600
C	-2.43824000	-0.98745600	0.87321200
C	-1.49265600	-1.20394200	-1.58828500
C	1.84492400	-2.80819500	-0.79019400
C	-0.15366900	-1.62645700	-1.91016500
C	0.47473300	-2.45882900	2.75079900
C	-1.62841700	-1.15568900	2.03651000
C	-3.88091700	-0.56784100	0.90231400
C	-2.51052500	-0.81217600	-2.62129300
H	2.08545400	-3.24856000	0.17892200
H	1.87029600	-3.62288100	-1.52325600
H	2.65194700	-2.11808100	-1.05551100
C	0.43825000	-1.54932700	-3.28315100
H	1.36171500	-2.90958300	2.30361600
H	-0.05944700	-3.26187400	3.27485300
H	0.80954400	-1.73275600	3.49045400
C	-2.03080000	-0.76331800	3.42629800
H	-4.04030400	0.38359200	1.41839500
H	-4.29144300	-0.47857400	-0.10489300
H	-4.48212400	-1.32126300	1.42605100
H	-2.08533200	-0.14166900	-3.37352700
H	-2.88751600	-1.69617900	-3.15158100
H	-3.37296000	-0.31100600	-2.17874700
H	0.23260300	-0.58462800	-3.75370800
H	0.01309900	-2.33043400	-3.92669400
H	1.52136900	-1.67972400	-3.26328700
H	-2.74358300	0.06521800	3.42052200
H	-1.16409800	-0.46272400	4.02061100
H	-2.51111500	-1.60363800	3.94450600
C	-2.33094900	1.78241400	-0.48374900
C	-1.91828100	2.17205100	0.81869700
C	-1.29348500	2.12005900	-1.39046500
H	-3.28043100	1.34633100	-0.74457200

C	-0.63123300	2.73844900	0.71859700
H	-2.48268300	2.04347100	1.73183100
C	-0.24751900	2.71012700	-0.65257100
H	-1.29665800	1.94183100	-2.45659300
H	-0.03729100	3.10101100	1.54244000
H	0.68159100	3.06112100	-1.07310300
C	2.63479900	0.56364400	-1.12194200
N	1.83866000	0.59490400	0.77063400
O	1.67660200	0.79708200	-1.80996700
O	3.79943400	0.33810900	-1.00290900
C	2.58655500	-0.39852200	1.49124200
C	2.31618000	1.89387200	1.17255400
H	3.66311100	-0.26983100	1.32804400
H	2.28304000	-1.39645800	1.19562300
H	3.40320600	1.87994800	1.31922200
H	2.05427000	2.65436600	0.43790500
F	1.76145500	2.31144700	2.39696500
F	2.39010800	-0.28961100	2.87754900

Coordinates of **TS1d**.

Zr	1.36083800	0.03397900	-0.02547600
C	2.77516300	-1.32108100	-1.18252200
C	1.44015100	-1.75799800	-1.54282400
C	3.00885300	-1.75477600	0.17788900
C	3.03329600	-0.09929300	-1.89473800
N	-0.96816000	0.04491700	0.39817200
C	0.96598400	-2.67098000	-0.52542800
C	0.86109600	-0.79284500	-2.42857200
C	1.91734500	-2.65666100	0.50052900
C	1.85962500	0.20393700	-2.64584600
C	1.39832800	2.62540200	0.25314500
C	2.71307500	2.22078800	-0.05654900
C	1.09669800	2.16207400	1.56370500
H	0.75283300	3.22851000	-0.36518900
C	3.21200500	1.46106300	1.03381500
H	3.24759400	2.46789000	-0.95795600
C	2.21524900	1.45503600	2.04545100
H	0.16265500	2.32867000	2.07927000
H	4.19441600	1.02142800	1.11357600
H	2.29251000	0.95313600	2.99907800
C	-0.44949000	-0.11639300	2.56534000
O	0.52234900	-0.80912400	2.45146400

O	-1.27135500	0.48757700	3.15834900
C	-1.61334400	1.28140300	0.03512200
C	-1.28667200	1.96367100	-1.13866300
C	-2.64032500	1.82132800	0.83421400
C	-1.90414000	3.16739800	-1.49660900
H	-0.52633200	1.55041100	-1.78942200
C	-3.26135200	3.01416000	0.49481600
H	-2.94645800	1.29167400	1.72669400
C	-2.89416900	3.70399600	-0.67038000
H	-1.61283100	3.65818200	-2.41755400
H	-4.04365700	3.43403100	1.11835900
C	-1.91853000	-1.03583600	0.28672500
C	-2.01289700	-2.08498500	1.21189200
C	-2.85539900	-1.05123700	-0.76997800
C	-2.97137600	-3.09611700	1.09733300
H	-1.31746000	-2.16100000	2.03553800
C	-3.80407400	-2.05527700	-0.90242800
H	-2.84250400	-0.24750100	-1.49511000
C	-3.87495500	-3.09335900	0.03430900
H	-2.99123200	-3.87773600	1.84716600
H	-4.51141400	-2.04701400	-1.72526500
C	1.72704400	1.35800800	-3.59477800
H	2.18048600	1.12219600	-4.56571900
H	0.67929600	1.60784900	-3.77952200
H	2.22219100	2.25604800	-3.21371000
C	4.37632200	0.55110900	-2.05738900
H	5.01512600	-0.07553100	-2.69122400
H	4.30527800	1.52763400	-2.54268400
H	4.89969100	0.68415700	-1.10705100
C	-0.43545900	-0.91402900	-3.17161600
H	-0.91043800	0.05563800	-3.34117600
H	-0.27009600	-1.37260900	-4.15513000
H	-1.14734400	-1.53569900	-2.63040300
C	-0.16915300	-3.63006300	-0.70113800
H	-1.06390100	-3.15856600	-1.10770800
H	0.13803300	-4.41455300	-1.40552200
H	-0.44921700	-4.11390200	0.23378300
C	1.88074600	-3.47814800	1.75115700
H	2.58405400	-4.31857300	1.68588200
H	2.16149100	-2.88017100	2.62202900
H	0.88542400	-3.88672100	1.93626300
C	4.30448200	-1.72828800	0.94210900

H	4.14848100	-1.50782600	2.00287000
H	4.81908800	-2.69648400	0.88262800
H	4.98756300	-0.97692900	0.54104200
O	-4.84725800	-4.03217900	-0.17350800
O	-3.56399600	4.86984200	-0.91196700
C	-3.22210700	5.59446700	-2.07917700
H	-3.41729900	5.01242300	-2.98966000
H	-3.85280300	6.48460900	-2.08078600
H	-2.16701100	5.89893100	-2.07195500
C	-4.94400500	-5.09059400	0.76168700
H	-5.16490300	-4.72057700	1.77156200
H	-5.76640100	-5.72256600	0.42308400
H	-4.02175000	-5.68608500	0.79645100

Coordinates of **2a**.

Zr	-0.27019500	0.18760100	-0.08759900
C	-0.52628100	-2.07570400	0.29993400
C	-1.77393600	-1.57536900	-0.25502200
C	0.42556100	-2.15590100	-0.79066700
C	-0.47968100	-1.65831800	1.67653400
C	-2.57984600	-1.06038900	0.83249900
C	-1.55790200	-1.25997300	-1.64589000
C	1.77833900	-2.81173300	-0.80992900
C	-0.22937100	-1.69879400	-1.95513700
C	0.45452600	-2.13792000	2.75364600
C	-1.78975500	-1.11425700	1.98051500
C	-4.01971000	-0.64070900	0.77058000
C	-2.57890000	-0.83460500	-2.66219500
H	2.05232200	-3.19663400	0.17414700
H	1.76693400	-3.67176200	-1.49108600
H	2.57395600	-2.14639700	-1.16115400
C	0.41581400	-1.65810900	-3.30515800
H	1.38765100	-2.52301400	2.34380200
H	-0.00599800	-2.95611400	3.32399700
H	0.70231000	-1.34915500	3.47144700
C	-2.21757400	-0.71498200	3.35977000
H	-4.19964500	0.33306400	1.23899700
H	-4.37769000	-0.58756600	-0.25922000
H	-4.65712700	-1.36637400	1.29049500
H	-2.13908800	-0.19139000	-3.42930600
H	-3.01527800	-1.70348700	-3.17120600
H	-3.40150400	-0.28274600	-2.20469700

H	-0.25216700	-1.24462100	-4.06330300
H	0.70378700	-2.66651100	-3.62601400
H	1.32019500	-1.04221900	-3.27761100
H	-3.15123300	-0.14672900	3.34564500
H	-1.45623700	-0.10127900	3.85368800
H	-2.37938700	-1.59476300	3.99618500
C	-2.25901300	1.76604200	-0.41697800
C	-1.85812500	2.00637100	0.91875200
C	-1.24037200	2.26103700	-1.27904900
H	-3.19291700	1.32996200	-0.73122800
C	-0.58370500	2.61377800	0.88803100
H	-2.40822400	1.73922900	1.80878300
C	-0.21833900	2.79859300	-0.47612400
H	-1.24225500	2.21629100	-2.35966600
H	-0.01806200	2.92813900	1.75342000
H	0.70352000	3.21861000	-0.84948000
C	2.48889900	0.54655300	-0.79124400
N	2.14282700	0.51812100	0.67665600
O	1.40694800	0.68537100	-1.46912300
O	3.64450300	0.44340500	-1.16331200
C	2.95731800	-0.47970100	1.40229000
C	2.49895600	1.84267600	1.25353000
H	2.69307100	-0.44105800	2.45986700
H	4.02255500	-0.26012300	1.27632000
H	2.76123900	-1.47568300	1.02278100
H	2.11625200	1.90013000	2.27518200
H	3.58877100	1.96145100	1.26555800
H	2.06873300	2.64737700	0.66462000

Coordinates of **3a.**

Zr	-0.25486800	0.09246100	0.37679700
C	-0.35026000	1.10437100	-1.67430700
C	-0.20085800	-0.32838600	-1.88462700
C	0.91016300	1.60706700	-1.17743400
C	-1.72942500	1.35220200	-1.32349900
C	1.18576400	-0.67001700	-1.63796300
C	-1.45446600	-0.95724400	-1.56861900
C	1.84351300	0.51215800	-1.25683200
C	-2.38188300	0.09897900	-1.28682900
C	-2.07861000	1.19354000	1.82830500
C	-1.01332800	2.12570300	1.72742500
C	-1.62553500	0.09110000	2.58856200

H	-3.05603500	1.29186700	1.38025700
C	0.08876000	1.60797600	2.46261000
H	-1.04527500	3.07554900	1.21482100
C	-0.29303100	0.36315400	3.00229500
H	-2.19333700	-0.79990900	2.82148800
H	1.06088200	2.07231900	2.56163000
H	0.34267300	-0.29941200	3.57066300
C	-2.39241200	2.69277400	-1.19505800
H	-2.94019400	2.94532400	-2.11181600
H	-3.11142500	2.73153900	-0.37106700
H	-1.65983400	3.48573100	-1.03419500
C	-3.84552900	-0.10312000	-1.02856300
H	-4.38587400	-0.29733000	-1.96351600
H	-4.02571300	-0.95588600	-0.36695000
H	-4.29923600	0.77870900	-0.56961400
C	-1.79597800	-2.41410000	-1.68074900
H	-2.76470600	-2.62784200	-1.22146200
H	-1.85175200	-2.72863600	-2.73047300
H	-1.05402300	-3.03679500	-1.17656900
C	1.80460300	-2.02593200	-1.80094500
H	1.10549000	-2.81652200	-1.52063700
H	2.10375700	-2.20589000	-2.84122900
H	2.69740600	-2.13520200	-1.17909400
C	3.29740200	0.63813200	-0.92255700
H	3.84873200	1.11262600	-1.74440500
H	3.44534100	1.25034100	-0.02859200
H	3.75007500	-0.33567700	-0.72957000
C	1.29447600	3.03787100	-0.92525900
H	1.64710100	3.52846100	-1.84234200
H	0.45375600	3.62393000	-0.54772000
H	2.09898100	3.10884000	-0.18747000
N	1.82148300	-3.08268300	1.77865200
C	1.25024800	-4.40526900	1.59028100
C	3.20844600	-3.00829200	2.20428500
H	0.19639700	-4.30590000	1.33752500
H	1.34877600	-4.98718100	2.51335700
H	1.76414000	-4.94527700	0.78301100
H	3.33760900	-3.54231000	3.15228500
H	3.87391600	-3.46228400	1.45703900
H	3.48228100	-1.96302100	2.33667600
C	1.17939800	-1.97009700	1.32928500
O	-0.01759300	-2.07330000	0.84643600

O 1.72143100 -0.82077400 1.38164200

Coordinates of **3b.**

Zr	-0.58780400	0.22346900	0.34626200
C	-0.09760600	1.25629800	-1.62859900
C	-0.66792600	-0.05421800	-1.93930600
C	1.23448600	1.03810200	-1.09763700
C	-1.18805600	2.12474000	-1.22885700
C	0.37005400	-1.05475200	-1.74063500
C	-2.08490000	-0.00844900	-1.65798100
C	1.51698300	-0.37330900	-1.27229000
C	-2.38367900	1.34551700	-1.27118300
C	-1.39797700	2.13465400	1.80730400
C	0.01417500	2.05959600	2.00291400
C	-1.98529000	0.95804000	2.35059000
H	-1.93339300	2.94861100	1.32557600
C	0.28961000	0.85675700	2.72308800
H	0.74710300	2.80663000	1.69913900
C	-0.93517100	0.18215800	2.93537700
H	-3.04671000	0.70911800	2.34916600
H	1.27529400	0.47919700	2.99292300
H	-1.04816000	-0.79239400	3.40954000
C	-1.08987900	3.60787900	-1.01211100
H	-0.86615400	4.12093100	-1.96408300
H	-2.03210100	4.03264100	-0.63166200
H	-0.28988100	3.88089000	-0.30407500
C	-3.76252600	1.86224900	-0.97974100
H	-4.26455100	2.20496200	-1.90241400
H	-4.39861800	1.08240800	-0.53201700
H	-3.74284200	2.71502600	-0.28278800
C	-3.08319200	-1.10976700	-1.87020800
H	-4.04106500	-0.88399900	-1.37651600
H	-3.29114400	-1.25437900	-2.94555400
H	-2.72268400	-2.06397700	-1.45813300
C	0.23852200	-2.52208100	-2.02582800
H	-0.63431700	-2.96186100	-1.51588600
H	0.10731800	-2.70371600	-3.10696900
H	1.12891100	-3.08162000	-1.70012100
C	2.84681300	-0.98271500	-0.94187200
H	3.66300900	-0.46164100	-1.47193600
H	3.05444300	-0.91832200	0.13960000
H	2.89100800	-2.04502500	-1.22452900

C	2.27780500	2.07076300	-0.76528200
H	2.94510400	2.26238000	-1.62687600
H	1.82223000	3.03365000	-0.49007100
H	2.91480300	1.74822300	0.07465700
N	-0.39724200	-3.69485300	1.47703000
C	-0.36444400	-2.34852300	1.12473400
O	-1.43905100	-1.81788200	0.62179100
O	0.68273300	-1.64469700	1.28617300
C	-1.59563400	-4.46145200	1.29345800
C	-1.52308900	-5.67683900	0.58974100
C	-2.82489500	-4.02542100	1.81728500
C	-2.67657700	-6.44985500	0.40983500
H	-0.55817500	-6.00778900	0.19556900
C	-3.97567100	-4.79855500	1.62080300
H	-2.87179700	-3.07793600	2.35801000
C	-3.90752600	-6.01179000	0.91998000
H	-2.61285100	-7.39410600	-0.13864600
H	-4.93080800	-4.45219000	2.02617700
H	-4.80865100	-6.61410800	0.77467600
C	0.76514000	-4.35902200	1.98578300
C	2.03090800	-4.17724800	1.40047700
C	0.61903300	-5.23207600	3.07974900
C	3.13880100	-4.85882600	1.91881400
H	2.13994100	-3.49281400	0.55858900
C	1.73108000	-5.91786800	3.58196400
H	-0.37013100	-5.36995400	3.52500300
C	2.99675000	-5.73187700	3.00694600
H	4.12071500	-4.70938500	1.46005400
H	1.60683500	-6.59409800	4.43275800
H	3.86561200	-6.26471800	3.40320900

Coordinates of **TS1a IRC Endpoint**

Zr	0.16316600	0.27533100	0.07108500
C	1.52805400	-1.14208200	-1.07833900
C	0.17509100	-1.60865100	-1.32824900
C	1.85455300	-1.46468700	0.29175800
C	1.74619400	0.02690300	-1.89468800
C	-0.24018000	-2.39675900	-0.18449400
C	-0.45249500	-0.69472500	-2.24194900
C	3.20136400	-1.38360900	0.95548200
C	0.76894000	-2.28357000	0.78146900
C	3.07670600	0.66363400	-2.17057600
C	0.53675900	0.27868400	-2.59198900
C	-1.37104700	-3.38059800	-0.13555400

C	-1.76998900	-0.84810300	-2.94963500
H	3.12448300	-1.09156200	2.00697800
H	3.71038500	-2.35540600	0.92369200
H	3.85093500	-0.66419400	0.45315400
C	0.74542600	-2.91975900	2.13577300
H	3.66039300	0.82741200	-1.26077400
H	3.67180200	0.01211600	-2.82181300
H	2.97553300	1.62304000	-2.68426900
C	0.33572000	1.34978000	-3.62231400
H	-2.20100700	-3.10593700	-0.78763000
H	-1.01105700	-4.36052200	-0.47541200
H	-1.75793900	-3.51684200	0.87786100
H	-2.38367800	0.05753900	-2.90545300
H	-1.61172600	-1.07653100	-4.01124900
H	-2.35315600	-1.66945600	-2.53189800
H	1.32163100	-2.33262700	2.85417300
H	1.17538800	-3.92945600	2.10679100
H	-0.27389200	-2.98842400	2.52007600
H	0.92260100	2.24456200	-3.39753900
H	0.64111700	0.99988400	-4.61683800
H	-0.71420600	1.64686700	-3.68949800
N	-2.22850600	0.43653300	0.53928600
C	-2.93717000	1.61003100	-0.00713800
C	-3.09404900	-0.74780700	0.31544900
H	-3.03282900	1.48621000	-1.09035400
H	-2.38665300	2.52428900	0.19703400
H	-3.93034800	1.70077000	0.44377500
H	-3.17212100	-0.96765100	-0.74780700
H	-2.67383500	-1.59552100	0.84295100
H	-4.09743100	-0.54548800	0.71054500
C	0.25276000	2.85161700	0.16283900
C	1.57083400	2.39878300	-0.07086800
C	-0.10052800	2.47868800	1.49160000
H	-0.34263800	3.44260600	-0.52024900
C	2.00685900	1.69059100	1.08014100
H	2.14690800	2.58143900	-0.96162500
C	0.97004300	1.75867400	2.05014200
H	-1.03612000	2.68704200	1.98899400
H	2.97602700	1.23652600	1.21780800
H	0.96495800	1.28583500	3.02152600
C	-2.05594800	0.47308900	2.07700100
O	-2.82227400	1.18665200	2.71539900
O	-1.09228600	-0.27917900	2.39176000

Coordinates of **TS1b IRC Endpoint**

Zr	1.04532200	0.16984300	0.09538900
C	2.42400500	-1.26437900	-1.01208200
C	1.08366700	-1.71604500	-1.31540900
C	2.67885700	-1.59503600	0.37558300
C	2.69516100	-0.12297400	-1.85373400
N	-1.42142700	0.29421300	0.66333100

C	0.62472100	-2.55441500	-0.22530800
C	0.49500400	-0.80625900	-2.25125900
C	1.59102700	-2.47242300	0.77871800
C	1.52095900	0.13709400	-2.59834400
C	1.08871600	2.79580000	0.02638000
C	2.39309300	2.33722900	-0.23751300
C	0.79864600	2.52161400	1.39458300
H	0.45030200	3.32732400	-0.66213700
C	2.89134200	1.71543100	0.94224400
H	2.92374600	2.46381100	-1.16474100
C	1.90934400	1.87109000	1.95656600
H	-0.12324600	2.75879900	1.90517700
H	3.87150400	1.28140000	1.07155400
H	1.96385200	1.47367000	2.95954500
C	-0.91640200	0.33327500	2.12743900
O	0.19334000	-0.28960100	2.16787700
O	-1.57159100	0.87059900	2.99902600
C	-2.05514000	1.50954000	0.15485500
C	-1.69286800	1.96489100	-1.11373500
C	-3.05835400	2.16571000	0.87059800
C	-2.29544300	3.09959300	-1.65540600
H	-0.93130900	1.43081600	-1.66704600
C	-3.65334400	3.30479900	0.32788800
H	-3.35005100	1.78947800	1.84166000
C	-3.27377100	3.77843800	-0.92933900
H	-2.00071800	3.44715000	-2.64102300
H	-4.42323200	3.82153600	0.89242100
H	-3.74464500	4.66471200	-1.34315200
C	-2.33736200	-0.84387400	0.55000500
C	-2.39851600	-1.82345200	1.54919800
C	-3.21892800	-0.92253400	-0.53345000
C	-3.33547900	-2.85090400	1.46580200
H	-1.72250500	-1.79535400	2.39323500
C	-4.14674800	-1.96037800	-0.61252000
H	-3.20217700	-0.16124900	-1.30140000
C	-4.21728800	-2.92749900	0.38917200
H	-3.37172600	-3.59393900	2.25645200
H	-4.82532700	-1.99838100	-1.45919900
H	-4.95018700	-3.72575300	0.33312000
C	1.37275900	1.20486200	-3.64116700
H	1.76348700	0.87291400	-4.61138800
H	0.32358800	1.47366400	-3.79193200
H	1.91230700	2.11676900	-3.36841500
C	4.04541500	0.49115500	-2.07620000
H	4.68459400	-0.20798700	-2.62859500
H	3.98756700	1.40757300	-2.66897500
H	4.56198500	0.72589100	-1.14149500
C	-0.80202700	-0.99062600	-2.98510400
H	-1.27479300	-0.04012200	-3.24885000
H	-0.63592300	-1.53766600	-3.92221500
H	-1.51770100	-1.56107300	-2.39351500

C	-0.52707800	-3.50716200	-0.30970600
H	-1.42468700	-3.05289800	-0.73059400
H	-0.25020300	-4.34358400	-0.96498900
H	-0.79195300	-3.92169200	0.66261200
C	1.54333300	-3.14676800	2.11289100
H	2.32629500	-3.91047600	2.20137600
H	1.69494700	-2.41728100	2.91398800
H	0.57980900	-3.62994100	2.28569100
C	3.97709700	-1.50311000	1.12903400
H	3.81881000	-1.20485100	2.17016400
H	4.49988000	-2.46872100	1.14139000
H	4.65265100	-0.77757600	0.67138600

Coordinates of **1a** optimized in PCM benzene

Zr	-0.06955100	0.03299500	0.40262700
C	-0.56286200	0.71345000	-1.72591700
C	0.46237100	-0.32075800	-1.82718800
C	0.07915400	1.89533200	-1.20270400
C	-1.79533000	0.05430300	-1.37454900
N	1.36025300	-1.41409200	1.09101500
C	1.73168900	0.25121200	-1.45616100
C	-0.15375200	-1.60460300	-1.60912400
C	1.48193600	1.59200800	-1.08388100
C	-1.52333100	-1.35938800	-1.34858200
C	2.61872500	-1.02212500	1.68369900
C	0.89535200	-2.65439200	1.67213100
H	2.96661700	-0.06889400	1.27044400
H	3.41856000	-1.76328700	1.50258200
H	2.56060200	-0.89389600	2.78501100
H	1.61091200	-3.48255300	1.51897300
H	0.72627700	-2.58435100	2.76702000
H	-0.05402500	-2.96663900	1.22112500
C	-2.11860000	0.57488200	1.84169800
C	-1.39836300	1.78388600	1.70309000
C	-1.33558200	-0.31961700	2.62098600
H	-3.09619400	0.36970800	1.42990400
C	-0.16378100	1.64044100	2.40544200
H	-1.73187400	2.66650900	1.17924400
C	-0.14093800	0.35242600	2.98500100
H	-1.60461900	-1.32983700	2.89875000
H	0.60948600	2.39362500	2.48919400
H	0.66963400	-0.07092100	3.56152700
C	-3.15882400	0.67979400	-1.30605600
H	-3.57277400	0.83421200	-2.31072700
H	-3.86601300	0.04926100	-0.76053600
H	-3.13740800	1.65501600	-0.81231500
C	-2.56752500	-2.41110400	-1.11181200
H	-3.10630400	-2.64349100	-2.03895300
H	-2.12778300	-3.34128400	-0.74454500
H	-3.31043900	-2.08217500	-0.37980000
C	0.53252500	-2.93371600	-1.68484400

H	-0.11631100	-3.74344800	-1.34267700
H	0.83095000	-3.16291900	-2.71482900
H	1.42822300	-2.93698100	-1.05995300
C	3.05989700	-0.43681900	-1.52617200
H	3.37129100	-0.56789900	-2.56966300
H	3.84061500	0.13616600	-1.02080000
H	3.01255700	-1.42185000	-1.05897100
C	2.51715400	2.59952800	-0.67711800
H	2.81903000	3.21622000	-1.53322500
H	2.13333500	3.27832200	0.08979600
H	3.41684800	2.12177900	-0.28215100
C	-0.49717300	3.27916700	-1.09709100
H	-0.23499000	3.88141700	-1.97702900
H	-1.58724800	3.25556300	-1.03821000
H	-0.12549400	3.81515600	-0.21821700

Coordinates of **1a** optimized in SMD benzene

Zr	-0.05360300	0.04954600	0.41635400
C	-0.56678200	0.70099000	-1.72311800
C	0.46023900	-0.33046700	-1.81942300
C	0.07321400	1.89135500	-1.21567000
C	-1.79826700	0.03970900	-1.37491000
N	1.38120700	-1.40083900	1.10349800
C	1.73055800	0.24931900	-1.46300700
C	-0.15354300	-1.61515300	-1.60175600
C	1.47761200	1.59402400	-1.11110200
C	-1.52598500	-1.37339700	-1.34946100
C	2.62881900	-1.00156700	1.71194000
C	0.92176000	-2.65080800	1.66556100
H	2.96813800	-0.03656100	1.31718400
H	3.44245300	-1.72732900	1.52728500
H	2.56141300	-0.89005400	2.81480500
H	1.64967300	-3.47020700	1.51988500
H	0.73097300	-2.59647900	2.75808200
H	-0.01371600	-2.97378700	1.19348600
C	-2.12194700	0.63706100	1.85029700
C	-1.35172400	1.81930500	1.76185400
C	-1.39628400	-0.30866900	2.62595700
H	-3.09919000	0.48450500	1.41515800
C	-0.14169000	1.60463500	2.48591300
H	-1.63779700	2.72952800	1.25657100
C	-0.18304300	0.30128300	3.02951500
H	-1.71565200	-1.31300300	2.87238100
H	0.65710000	2.32431600	2.61666900
H	0.59612900	-0.16849100	3.61386500
C	-3.16183500	0.66423500	-1.30778500
H	-3.57877100	0.81205500	-2.31308300
H	-3.86926100	0.03791100	-0.75717400
H	-3.14117900	1.64401900	-0.82254900
C	-2.57418500	-2.42393500	-1.13116200
H	-3.12649500	-2.62266600	-2.05892600

H	-2.14020200	-3.37038000	-0.79957700
H	-3.30802200	-2.11369400	-0.38124300
C	0.53360700	-2.94265900	-1.69051300
H	-0.12180100	-3.76138700	-1.38306000
H	0.85356200	-3.14903300	-2.71951600
H	1.41954500	-2.96565300	-1.05190700
C	3.06099100	-0.43333600	-1.52984600
H	3.38098800	-0.55733400	-2.57236800
H	3.83844600	0.13812900	-1.01700000
H	3.01672400	-1.42261200	-1.07115800
C	2.51495700	2.61013200	-0.73151500
H	2.81602600	3.20623800	-1.60303600
H	2.13665300	3.31002900	0.01952200
H	3.41724800	2.14289800	-0.32859800
C	-0.50736900	3.27380500	-1.11796500
H	-0.27006900	3.86459100	-2.01345800
H	-1.59587200	3.24791100	-1.03232000
H	-0.11684500	3.82731200	-0.25812300

Coordinates of **TS1a** optimized in PCM benzene

Zr	1.33657300	0.02892600	-0.11793400
C	2.72259300	-1.41778000	-1.20551800
C	1.36483000	-1.88455900	-1.45656100
C	3.03618400	-1.72708000	0.17108300
C	2.93689600	-0.24877600	-2.01452800
C	0.92811600	-2.63875600	-0.30275800
C	0.74713800	-0.99297300	-2.40024100
C	4.38048100	-1.65175800	0.84032500
C	1.93688100	-2.51434900	0.67200200
C	4.25813700	0.41293900	-2.27791500
C	1.72252700	-0.01204400	-2.73276000
C	-0.19888300	-3.62762300	-0.25831000
C	-0.59466000	-1.13010700	-3.05782400
H	4.30042500	-1.38516000	1.89849100
H	4.89589400	-2.61973500	0.78838300
H	5.02752800	-0.91695500	0.35737000
C	1.92657100	-3.17539900	2.01741300
H	4.85130100	0.53637300	-1.36794400
H	4.85266300	-0.19631800	-2.96989300
H	4.14001600	1.39662100	-2.73956600
C	1.52262000	1.07521000	-3.74638400
H	-1.04854000	-3.32865200	-0.87195100
H	0.15668400	-4.59103600	-0.64716200
H	-0.55777700	-3.80421900	0.75835300
H	-1.13074600	-0.17827100	-3.10298800
H	-0.48763200	-1.49394300	-4.08785900
H	-1.22814500	-1.84002900	-2.52679200
H	2.46756200	-2.57966900	2.75686100
H	2.41072300	-4.15964400	1.97108600
H	0.90935100	-3.31887200	2.38738800
H	2.08902600	1.97482700	-3.49099400

H	1.85557300	0.74962000	-4.74006200
H	0.46889600	1.35319400	-3.82920900
N	-0.87610300	0.11413700	0.28325600
C	-1.59011300	1.24605800	-0.30563400
C	-1.81768600	-1.00083700	0.31957400
H	-1.96848800	1.01295800	-1.31507700
H	-0.95754200	2.12881100	-0.39236400
H	-2.46002700	1.52193800	0.31155200
H	-2.08025200	-1.37841800	-0.67962800
H	-1.41620400	-1.82552300	0.90307500
H	-2.76758100	-0.68814000	0.78610100
C	1.48507700	2.61186800	0.08758700
C	2.80892100	2.12904300	-0.07326600
C	1.02745000	2.20093000	1.36600500
H	0.95121100	3.23678800	-0.61550100
C	3.14855900	1.38232900	1.07916300
H	3.45000600	2.32383300	-0.91669700
C	2.03919100	1.42832000	1.97250000
H	0.05329400	2.41349200	1.77721500
H	4.09487600	0.90020500	1.26845600
H	1.98254500	0.94778200	2.93974600
C	-1.02480900	0.24422300	2.62975000
O	-1.80016800	1.13169200	2.73426700
O	-0.30093300	-0.64285400	2.93597300

Coordinates of **TS1a** optimized in SMD benzene

Zr	1.33889500	-0.03798000	-0.05028300
C	2.72038600	-1.36777400	-1.29154000
C	1.37217000	-1.90400400	-1.44810000
C	3.17491500	-1.72115900	0.03032400
C	2.79640700	-0.15211200	-2.05949100
C	1.02517100	-2.61962100	-0.24365200
C	0.66780900	-1.07816000	-2.39315400
C	4.56806300	-1.55464900	0.56248600
C	2.13813700	-2.50382600	0.63058500
C	4.02381600	0.64092900	-2.40721700
C	1.53854300	-0.02578800	-2.74633000
C	-0.11925100	-3.56805800	-0.04076600
C	-0.66412100	-1.34581000	-3.02738900
H	4.60850500	-1.66403400	1.64913000
H	5.23315100	-2.31854500	0.13854100
H	4.99593300	-0.58147600	0.30850700
C	2.23936400	-3.16297200	1.97366300
H	4.83966000	0.44336900	-1.70882400
H	4.38754400	0.37225800	-3.40828900
H	3.83865400	1.71992200	-2.41395400
C	1.23128500	1.03164100	-3.76376400
H	-0.98443300	-3.31059500	-0.65107300
H	0.18443700	-4.58608900	-0.32155700
H	-0.44379300	-3.60673900	1.00254900
H	-1.30484900	-0.46088400	-3.05179500

H	-0.53029500	-1.67432100	-4.06688900
H	-1.20455200	-2.13763600	-2.50880100
H	2.87596000	-2.59431300	2.65670700
H	2.67392100	-4.16739200	1.88310100
H	1.25982700	-3.27196100	2.44641900
H	1.75151600	1.96846600	-3.54475200
H	1.54929200	0.71263100	-4.76560200
H	0.15970900	1.24329400	-3.81506500
N	-0.87649700	0.12581800	0.16146800
C	-1.38951400	1.27235600	-0.57961300
C	-1.91624900	-0.89128500	0.20319100
H	-1.82244100	0.98860600	-1.55306000
H	-0.60671100	2.00985500	-0.78501100
H	-2.17913900	1.79752500	-0.01623300
H	-2.15336200	-1.31522700	-0.78420600
H	-1.63355500	-1.70865900	0.86354300
H	-2.86539300	-0.47195200	0.58544000
C	2.00283800	2.47276600	0.26949000
C	3.15822000	1.68379300	0.53510400
C	1.07564300	2.25178100	1.30968700
H	1.86805700	3.13549700	-0.57630800
C	2.93183300	0.97737000	1.73979100
H	4.06026600	1.65974000	-0.05500200
C	1.63928400	1.31496200	2.21329600
H	0.09226000	2.68940700	1.38588500
H	3.62724200	0.30738700	2.22321200
H	1.18744800	0.94032300	3.12014400
C	-1.35490900	0.51351700	2.54277800
O	-1.88307700	1.56325300	2.44838400
O	-0.92488400	-0.50123100	2.96377900

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