Electronic Supplementary Information for Dalton Transactions

Intramolecular hydroamination/cyclisation of aminoallenes mediated by a cationic zirconocene catalyst: A computational mechanistic study

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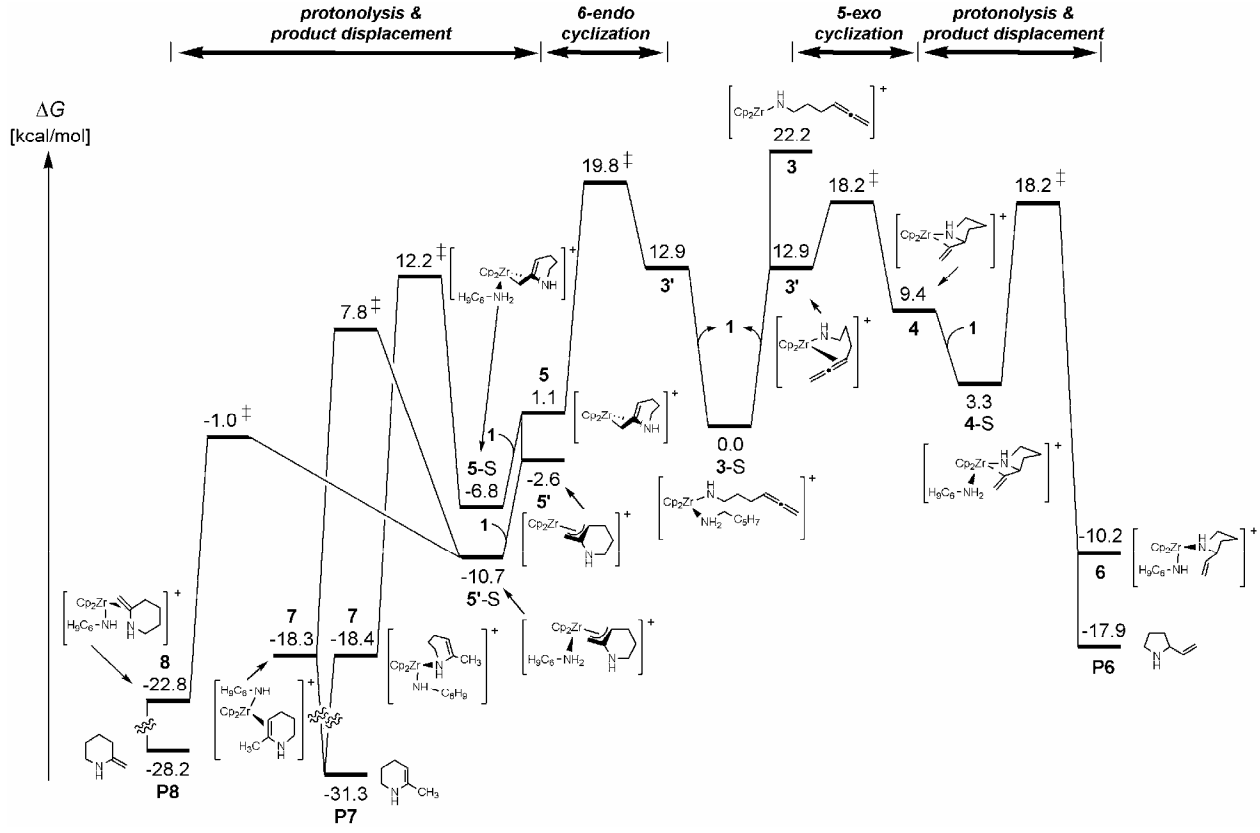
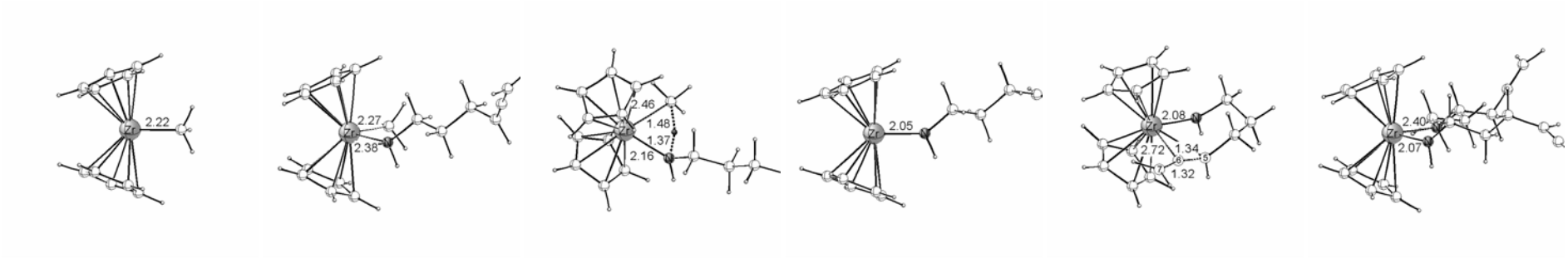


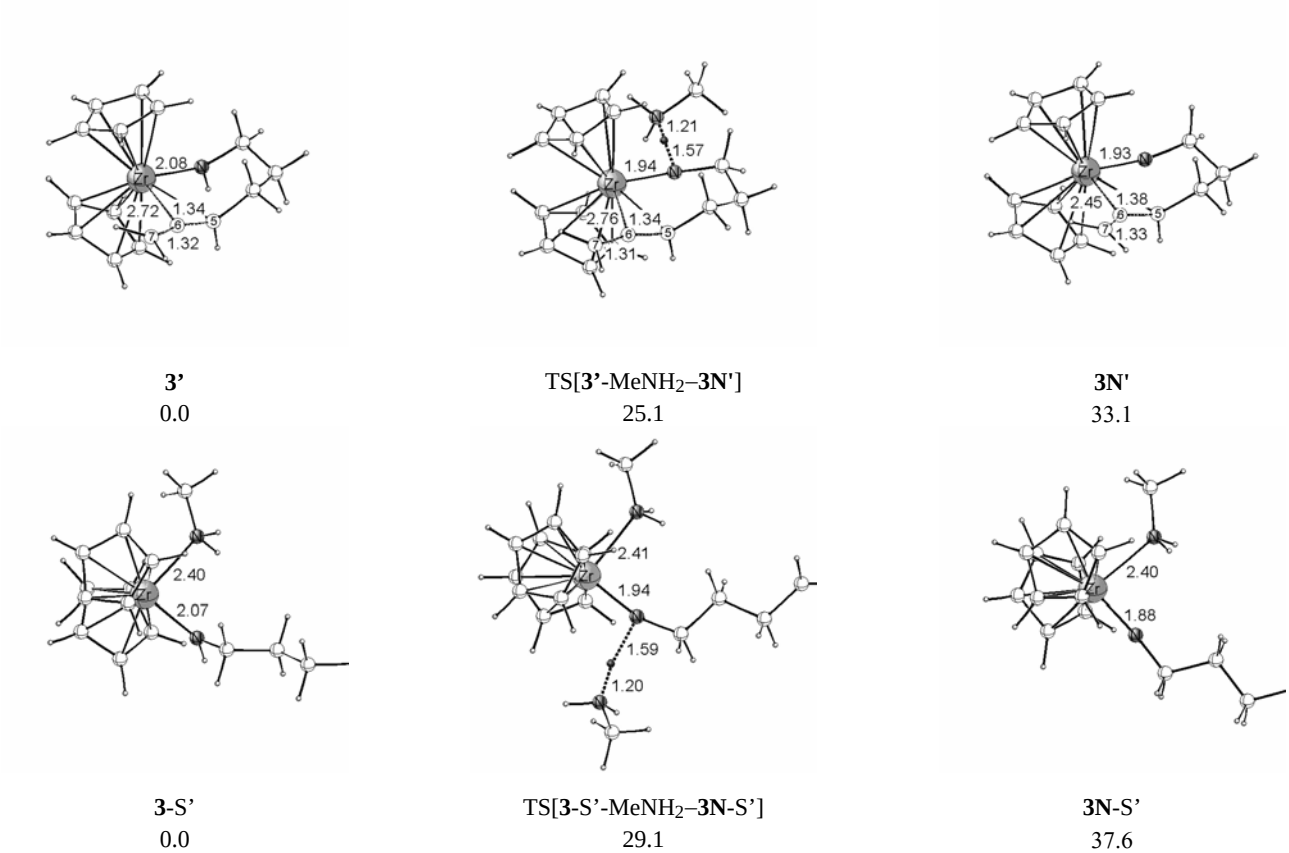
Scheme S1 Condensed Gibbs free-energy profile of the intramolecular hydroamination/cyclisation of 4,5-hexadien-1-ylamine **1** mediated by the cationic $[Cp_2ZrCH_3]^+$ precatalyst **2**[a]

[a] Cycloamine expulsion through **6**/**7**/**8** + **1** → **3**-S + **P6**/**P7**/**P8** is included.



2 **2**-S TS[**1**+**2**→**3**+CH_4] **3** **3'** **3**-S

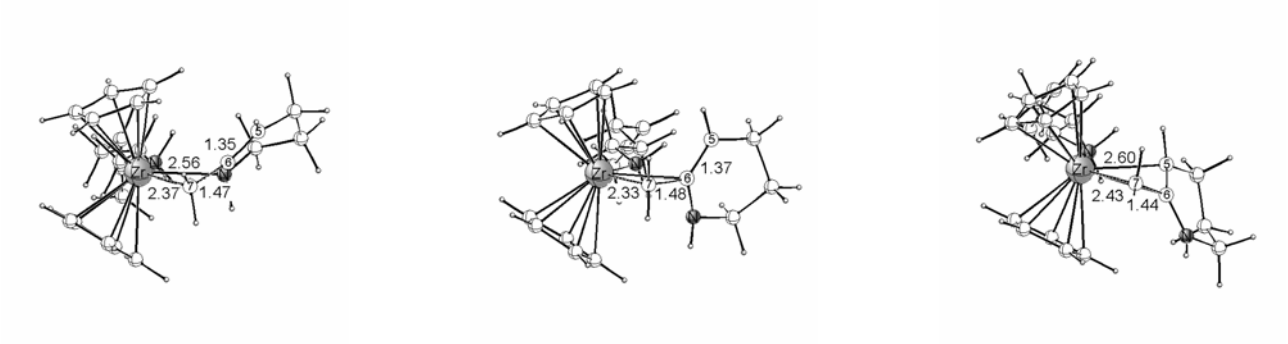
Fig. S1 Selected structural parameters (Å) of the optimised structures of key species for **1** + **2** → **3**⇄**3'** + CH_4 activation of precatalyst **2** through protonolytic cleavage of the Zr–Me bond by aminoallene substrate **1**. The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species.



3' 0.0 | TS[**3'**-$MeNH_2$–**3N'**] 25.1 | **3N'** 33.1

3-S' 0.0 | TS[**3**-S'-$MeNH_2$–**3N**-S'] 29.1 | **3N**-S' 37.6

Fig. S2 Selected structural parameters (Å) of the optimised structures of key species for the transformation of the amidoallene–Zr complex into the imidoallene-Zr complex via **3'** + $MeNH_2$ → **3N'** + $MeNH_3^+$ (top) and **3**-S' + $MeNH_2$ → **3N**-S' + $MeNH_3^+$ (bottom), respectively, together with relative free energies (kcal mol^{-1}). The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amido-/imidoallene moiety is displayed in a truncated fashion for several of the species.

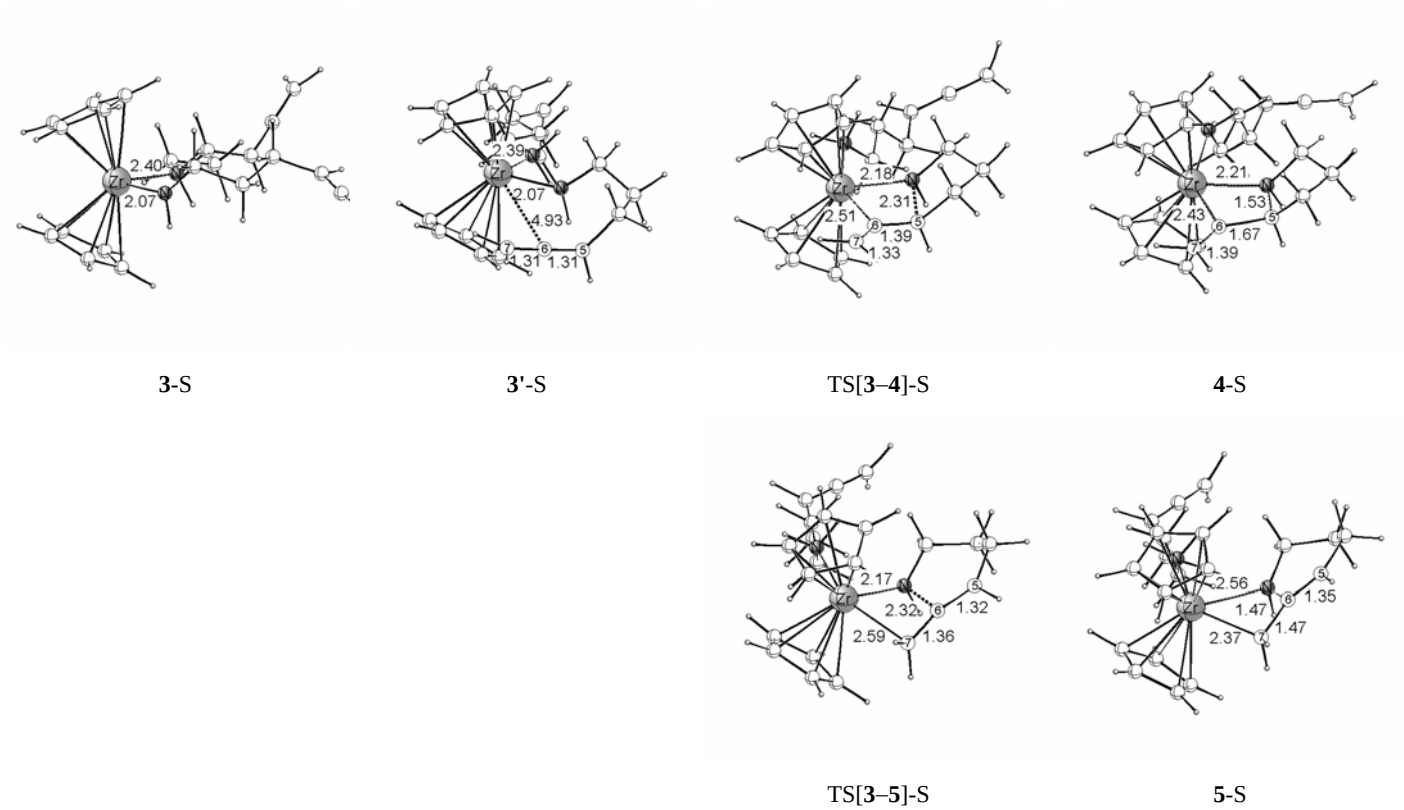


5-S
0.0

TS[**5**–**5'**]-S
2.0

5'-S
–4.7

Fig. S3 Selected structural parameters (Å) of the optimised structures of key species for **5** ⇄ **5'** interconversion to be assisted by aminoallene substrate **1**, together with relative free energies (kcal mol^{-1}). The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species.



3-S

3'-S

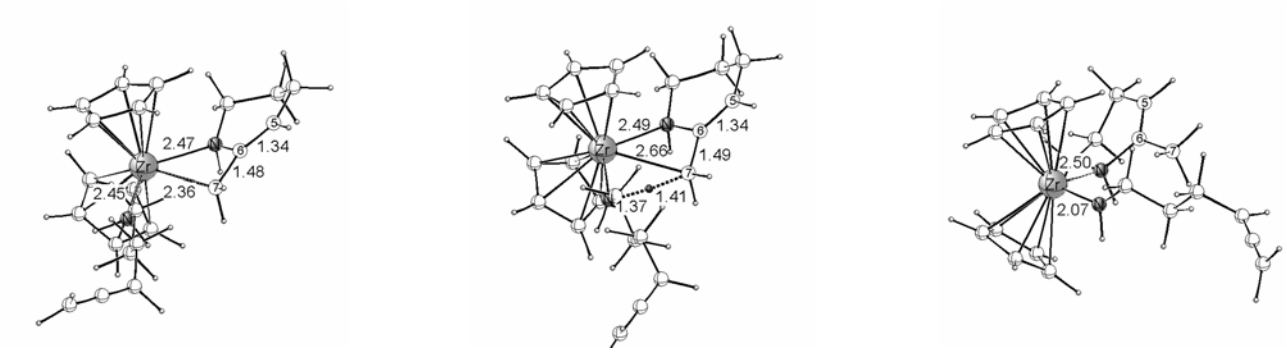
TS[**3**–**4**]-S

4-S

TS[**3**–**5**]-S

5-S

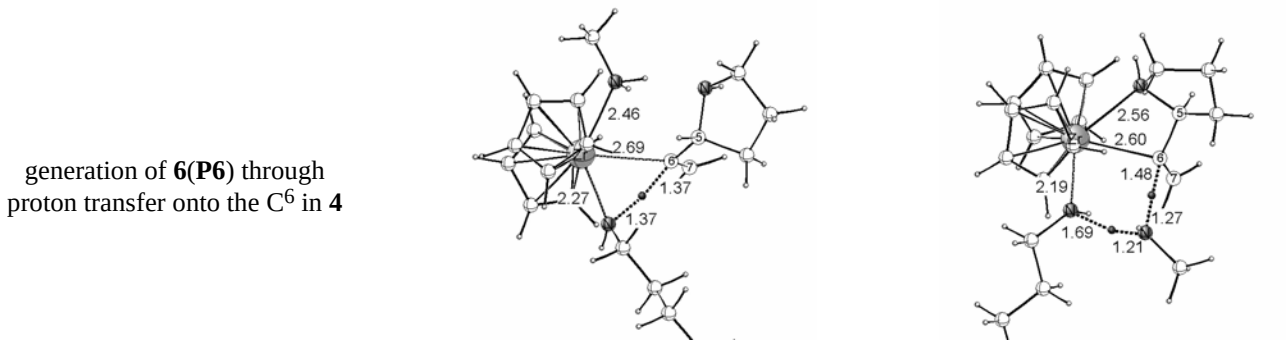
Fig. S4 Selected structural parameters (Å) of the optimised structures of key species for regioisomeric 5-*exo* (top) and 6-*endo* (bottom) pathways for cyclisation to be assisted by aminoallene substrate **1**. The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species.



5-S TS[**5**-S–**7**] **7**

Fig. S5 Selected structural parameters (Å) of the optimised structures of key species for proton transfer onto the C^7 carbon atom of the azacycle–Zr intermediate **5** by aminoallene substrate **1** affording the cycloamine-amido–Zr compound **7**. The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species.

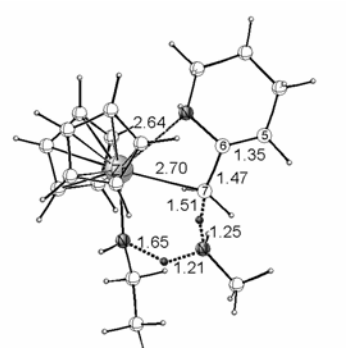
generation of **6**(**P6**) through proton transfer onto the C^6 in **4**



TS[**4**-S–**6**]-$MeNH_2$ TS[**4**-S-$MeNH_2$–**6**]

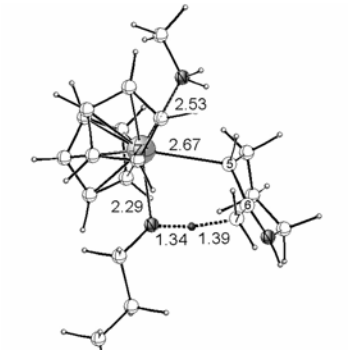
Fig. S6 Selected structural parameters (Å) of the optimised transition-state structures for protonolysis of the azacycle–Zr intermediate **4** by aminoallene substrate **1** affording the cycloamine-amido–Zr compound **6** to be assisted by additive aminoallene substrate. The methylamine model substrate **S'** is acting either as a coordinated spectator ligand (left) or as a 'proton shuttle' (right). The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species.

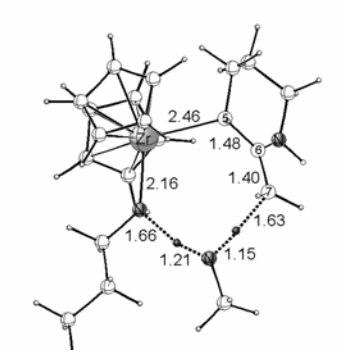
generation of **7**(**P7**) through proton transfer onto the C^7 in **5**



TS[**5**-S–**7**]-$MeNH_2$ | TS[**5**-S-$MeNH_2$–**7**]

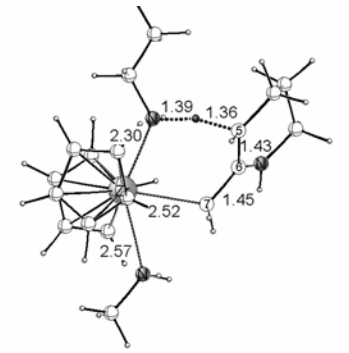
generation of **7**(**P7**) through proton transfer onto the C^7 in **5'**

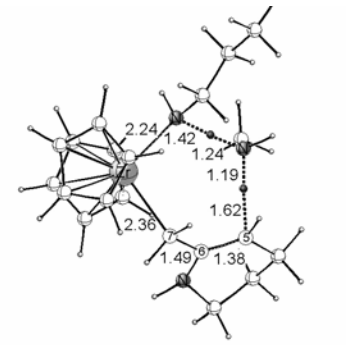




TS[**5'**-S–**7**]-$MeNH_2$ | TS[**5'**-S-$MeNH_2$–**7**]

generation of **8**(**P8**) through proton transfer onto the C^5 in **5'**





TS[**5'**-S–**8**]-$MeNH_2$ | TS[**5'**-S-$MeNH_2$–**8**]

Fig. S7 Selected structural parameters (Å) of the optimised transition-state structures for protonolysis of the azacycle–Zr intermediates **5** ⇄ **5'** by aminoallene substrate **1** affording the cycloamine-amido–Zr compound **7**, **8** along alternative pathways that are assisted by additive aminoallene substrate. The methylamine model substrate **S'** is acting either as a coordinated spectator ligand (left) or as a 'proton shuttle' (right). The cutoff for drawing Zr–C bonds was arbitrarily set to 2.8 Å. Please note that the amino-/amidoallene moiety is displayed in a truncated fashion for several of the species. We have not been able to locate TS[**5**-S–**7**]-$MeNH_2$.

Table S1 Enthalpies and free energies of activation and reaction for protonolysis of the azacycle–Zr intermediates **4** and **5** by aminoallene substrate **1** to afford the cycloamine-amido–Zr compounds **6**–**8** along various regioisomeric paths for proton transfer[a-c]

proton transfer pathway	**4**/**5**-S[d]	TS	product[d]
5-*exo* precursor **4**			2-vinyl-pyrrolidine
H-trf onto C^6 of **4**	–15.0/*–6.1* (**4**-S)	–0.2/*8.8* ($\Delta S^{\ddagger}$=–30.1 eu)[f]	–27.5/*–19.6* (**6**)
6-*endo* precursor **5**, **5'**			6-methyl-tetrahydropyridine
H-trf onto C^7 of **5**	–16.5/*–7.9* (**5**-S)	2.2/*11.1* ($\Delta S^{\ddagger}$=–30.0 eu)[f]	–27.6/*–19.5* (**7** η^1-N)
H-trf onto C^7 of **5'**	–20.5/*–11.8* (**5'**-S)	–2.1/*6.7* ($\Delta S^{\ddagger}$=–29.4 eu)[f]	–27.3/*–19.4* (**7** η^1-C^5)
			2-methylene-piperidine
H-trf onto C^5 of **5'**	–22.3/*–13.5* (**5'**-S)[e]	–10.7/*–2.1* ($\Delta S^{\ddagger}$=–28.8 eu)[f]	–31.9/*–23.9* (**8** η^1-C^7)

	aminoallene substrate-assisted process[g]
proton transfer pathway	TS
5-*exo* precursor **4**	
H-trf onto C^6 of **4**[h]	6.4/*3.3* ($\Delta S^{\ddagger}$=–56.5 eu)[f]
H-trf onto C^6 of **4**[i]	7.5/*24.1* ($\Delta S^{\ddagger}$=–55.9 eu)[f]
6-*endo* precursor **5**, **5'**	
H-trf onto C^7 of **5**[h]	9.9/*26.6* ($\Delta S^{\ddagger}$=–56.0 eu)[f]
H-trf onto C^7 of **5'**[h]	–1.1/*15.7* ($\Delta S^{\ddagger}$=–56.4 eu)[f]
H-trf onto C^5 of **5'**[h]	–12.2/*5.2* ($\Delta S^{\ddagger}$=–55.3 eu)[f]
H-trf onto C^7 of **5**[i]	–/–
H-trf onto C^7 of **5'**[i]	–0.2/*17.1* ($\Delta S^{\ddagger}$=–58.0 eu)[f]
H-trf onto C^5 of **5'**[i]	–7.7/*9.7* ($\Delta S^{\ddagger}$=–58.2 eu)[f]

[a] See Scheme 1. [b] Total barriers, reaction energies and activation entropies are relative to {**4** + **1**} and {**5** + **1**} for protonation of 5-*exo* and 6-*endo* cyclisation intermediate, respectively. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 3, S4, S5, ESI) for description of the various isomers of the amine adducts **4**-S, **5**-S, **5'**-S and of the cycloamine-amido–Zr product species **6**–**8**. [e] The precursor amine-adduct species is not identical with the related one reported in Table 2. [f] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}. [g] The process to be assisted by an additionally coordinating aminoallene molecule has been investigated with methylamine ($MeNH_2$, S') as the substrate. Total barriers, reaction energies and activation entropies are relative to {**4** + **1** + $MeNH_2$} and {**5** + **1** + $MeNH_2$}, respectively. [h] The additive substrate acts as a 'proton shuttle' (Figs S6, S7, ESI, right). [i] The additive substrate acts as a Zr-coordinated spectator ligand (Figs. S6, S7, ESI, left).

I. Computational Details

All calculations have been performed with the program package TURBOMOLE[1] using density functional theory (DFT). The local exchange-correlation potential by Slater[2a,b] and Vosko et al.[2c] was augmented with gradient-corrected functionals for electron exchange according to Becke[2d] and correlation according to Perdew[2e] in a self-consistent fashion. This gradient-corrected density functional is usually termed BP86 in the literature. In was shown in previous benchmark computational studies that the BP86 functional provides results for C–C bond formation in excellent agreement with the best wave function-based methods available today.[3] The suitability of the BP86 functional for the reliable determination of the kinetic balance between various elementary processes in the Group 4 metal-assisted selective ethylene oligomerisation has been demonstrated.[4] Furthermore, the appropriateness of the BP86 functional for the reliable exploration of the Group 4 metal-mediated hydroamination has been substantiated (see below), thereby allowing to draw mechanistic conclusions having substantial predictive value. In view of the fact that all species investigated in this study show a large HOMO–LUMO gap, a spin-restricted formalism was used for all the calculations.

For Zr we used the Stuttgart–Dresden quasirelativistic effective core potential (SDD) with the associate (8s7p6d)/[6s5p3d] valence basis set contracted according to a (311111/22111/411) scheme.[5] All other elements were represented by Ahlrichs' split-valence SV(P) basis set[6a] with polarisation functions on heavy main group atoms, but not on hydrogen (BS-A); *viz*. for carbon and nitrogen a 7s/4p/1d set contracted to (511/31/1) and for hydrogen a 4s set contracted to (31). The geometry optimisation and the saddle-point search were carried out by utilising analytical/numerical gradients/Hessians according to standard algorithms. No symmetry constraints were imposed in any case. This level of basis-set quality has been identified as a reliable tool for the assessment of structural parameters and vibrational frequencies.[7] The stationary points were identified exactly by the curvature of the potential-energy surface at these points corresponding to the eigenvalues of the Hessian. All reported transition states possess exactly one negative Hessian eigenvalue, while all other stationary points exhibit exclusively positive eigenvalues. Each transition state was further confirmed by following its imaginary vibrational mode downhill on both sides, yielding to the reactant and product minima presented on the reaction profile for the individual steps. The many isomers that are possible for each of the investigated species were carefully explored. The reaction and activation enthalpies and free energies (ΔH, $\Delta H^{\ddagger}$ and ΔG, $\Delta G^{\ddagger}$ at 298 K and 1 atm) were evaluated according to standard textbook procedures[8] using computed harmonic frequencies. To obtain more accurate energy profiles, all key species were fully located by employing a more accurate basis set (BS-B), consisting of the aforementioned basis set for Zr and of Ahlrichs' valence triple-ζ TZVP basis set[7b] with polarisation functions on all other atoms; *viz*. for carbon and nitrogen a 11s/6p/1d set contracted to (62111/411/1) and for hydrogen a 5s/1p set contracted to (311/1).

It has been explicitly scrutinized for each of the individual steps in Scheme 1 whether a specific substrate species, which are always present in excess,[9] is likely to facilitate the elementary process. Furthermore, the influence of nonspecific solute–solvent interactions[10] on the energy profile of individual steps has been estimated for benzene[9] (dielectric constant $\varepsilon = 2.247$ at 298 K)[11] by employing the conductor-like screening

model (COSMO) due to Klamt and Schüürmann[12] as implemented in TURBOMOLE.[13] Nonelectrostatic contributions to solvation were not considered. The solvation effects were included selfconsistently in the calculations, and all key species were fully optimized including solvation at the BP86/BS-B level. The optimised atomic COSMO radii (r_H = 1.3 Å, r_C = 2.0 Å, r_N = 1.83 Å)[14] have been used, in combination with the radius of 2.22 Å for Zr.

Energetics (BP86/BS-B) on the ΔH(298 K) surface were reported as ΔE + zero point energy correction at 0 K + thermal motion corrections at 298 K. The Gibbs free-energies were obtained as $\Delta G_{298} = \Delta H_{298} - T\Delta S$ at 298 K and 1 atm. The $T\Delta S$ contribution of about 11–13 kcal mol^{-1} (under standard conditions) calculated for aminoallene substrate coordination in gas phase certainly does not reflect the real entropic cost for substrate association/dissociation processes under actual catalytic conditions.[9] The difference in the reaction entropy for the Cp_2ZrR + **1** → Cp_2ZrR–**1** substrate uptake process taking place in the gas and condensed phases is mainly due to the substrate solvation, since the solvation entropies of the Cp_2ZrR compound and the Cp_2ZrR–**1** adduct can be regarded as being similar. The solvation entropy of ethylene is about 16 eu in typical aromatic hydrocarbon solvents,[16] which can reasonably be adopted as a rough estimate for aminoallenes as well. This reduces the entropic costs for substrate complexation by about 4.8 kcal mol^{-1} (298.15 K); thus to about two-thirds of the gas-phase value. This estimation agrees reasonably well with the findings of a recent theoretical study, where it was shown that for polar solvents the entropies in solution decrease to nearly half of the gas-phase value.[17] Therefore, the solvation entropy for substrate association and dissociation was approximated as being two-thirds of its gas-phase value, which the author considers as a reliable estimate of the entropy contribution in the condensed phase.

The effect of the counterion was neglected in the present study. Considering the size of the used perfluoroaryl borane activator[9] this would be too resource demanding and virtually impractical having the mechanistic diversity of aminoallene IHC in mind. Although its influence cannot be excluded *a priori*, the cationic catalyst model investigated herein may provide a realistic description of the title process.

II. Reaction energetics obtained with different computational approaches. An legitimate question one may ask is about the confidence one can have in the competence of approximate DFT calculations (*viz*. the variation of the computed energy profile of individual elementary steps depending on the employed exchange-correlation functional, provided that a basis set of appropriate quality - like BS-B used herein - is employed) for the elucidation of the salient mechanistic aspects of the investigated class of reaction. To settle this question, the gas phase Gibbs free-energy profile of relevant elementary steps was computed by employing the BP86[2] and B3LYP[18,19] exchange-correlation functionals. Thus, the two DFT methods that are used most frequently to study organometallic reactions were considered. Tables S2–S4 and S5–S7 summarise the energetics for relevant steps that were computed at BP86/BS-B and B3LYP/BS-B levels of approximation, respectively. These profiles were obtained from key species that are fully optimised at the respective DFT level, following the methodology described in the Computational Details section. The free-energies were approximated by employing the zero-point energy corrections and the thermal motion and entropy contributions calculated by using the BP86 functional.

The two probed computational methods predict the same fine mechanistic aspects. (1) Precatalyst activation is a facile and strongly exergonic, thus irreversible process. (2) The two methods predict energy profiles for individual ring closure pathways that are very similar. (3) Of the two regioisomeric pathways, 5-*exo* cyclisation is favourable kinetically. The $\Delta\Delta G^{\ddagger}$ gap amounts to 1.2/1.5 kcal mol^{-1} at the BP86/B3LYP levels, thus being in almost quantitative agreement. (4) Proton transfer onto the allylic C^5 carbon centre in **5'** is the favourable pathway for protonolysis of the six-membered azacycle intermediate. All other alternative pathways are seen to be distinctly less favourable kinetically. (5) Protonolysis is kinetically most demanding for formation of five-membered cycloamines, whilst cyclisation has the highest barrier of all viable steps along the branch that generates six-membered cycloamines. (6) The **P6**:**P7'** product distribution is regulated by the kinetics of ring closure, whilst protonolysis is not likely affecting the reaction outcome.

Thus, both DFT methods can be considered to be equally competent for the reliable determination of the energetics for the Group 4 metal-mediated IHC of aminoallenes, providing results of comparable accuracy. Overall, the computational methodology chosen in the present study has been demonstrated to allow us to draw mechanistic conclusions having substantial predictive value.

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Table S2 Enthalpies and free energies of activation and reaction (BP86, gas phase) for protonolysis of precatalyst **2** by aminoallene substrate **1**[a-c]

protonolysis pathway	substrate encounter complex	TS	products[d]
1 + **2** → **3** + CH_4	–40.1/*–31.7* (**2**-S)	–21.4/*–12.4* ($\Delta S^{\ddagger}$=–30.1 eu)[e]	–38.5/*–36.8* (**3**) –52.8/*–48.6* (**3'**)

[a] See Scheme 1. [b] Total barriers and reaction energies are relative to the respective precursor species. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 1, S1, ESI) for description of isomers **3**, **3'**. [e] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Table S3 Enthalpies and free energies of activation and reaction (BP86, gas phase) for cyclisation of **3** through alternative regioisomeric 5-*exo* and 6-*endo* paths[a-c]

cyclisation pathway	precursor[d]	TS	product[e]
5-*exo*	14.3/*11.8* (**3**) 0.0/*0.0* (**3'**)	4.3/*5.6* ($\Delta S^{\ddagger}$=–4.4 eu)[f]	–3.4/*–2.8* (**4**)
6-*endo*	14.3/*11.0* (**3**) 0.0/*0.0* (**3'**)	5.4/*6.8* ($\Delta S^{\ddagger}$=–4.4 eu)[f]	–12.4/*–11.3* (**5**) –16.3/*–15.4* (**5'**)

[a] See Scheme 1. [b] Total barriers, reaction energies and activation entropies are relative to the thermodynamically favourable isomer **3'** with a chelating allene functionality. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 1, S1, ESI) for description of isomers **3**, **3'**. [e] See Scheme 1 for description of the azacyclic cyclisation products. [f] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Table S4 Enthalpies and free energies of activation and reaction (BP86, gas phase) for protonolysis of the azacycle–Zr intermediates **4** and **5** by aminoallene substrate **1** to afford the cycloamine-amido–Zr compounds **6**–**8** along various regioisomeric paths for proton transfer[a-c]

Proton transfer pathway	**4**/**5**-S[d]	TS	product[d]
5-*exo* precursor **4**			2-vinyl-pyrrolidine
H-trf onto C^6 of **4**	–14.7/*–5.9* (**4**-S)	1.2/*10.2* ($\Delta S^{\ddagger}$=–30.1 eu)[f]	–27.9/*–19.9* (**6**)
6-*endo* precursor **5**, **5'**			6-methyl-tetrahydropyridine
H-trf onto C^7 of **5**	–15.8/*–7.2* (**5**-S)	2.2/*11.2* ($\Delta S^{\ddagger}$=–30.0 eu)[f]	–27.7/*–19.6* (**7** η^1-N)
H-trf onto C^7 of **5'**	–20.2/*–11.5* (**5'**-S)	–2.3/*6.5* ($\Delta S^{\ddagger}$=–29.4 eu)[f]	–27.5/*–20.0* (**7** η^1-C^5)
			2-methylene-piperidine
H-trf onto C^5 of **5'**	–22.0/*–13.3* (**5'**-S)[e]	–10.9/*–2.4* ($\Delta S^{\ddagger}$=–28.8 eu)[f]	–31.5/*–23.5* (**8**)

[a] See Scheme 1. [b] Total barriers, reaction energies and activation entropies are relative to {**4** + **1**} and {**5** + **1**} for protonation of 5-*exo* and 6-*endo* cyclisation intermediate, respectively. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs 2, S4, S5, ESI) for description of the various isomers of the amine adducts **4**-S, **5**-S, **5'**-S and of the cycloamine-amido–Zr product species **6**–**8**. [e] The precursor amine-adduct species is not identical with the related one reported in Table 2. [f] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Table S5 Enthalpies and free energies of activation and reaction (B3LYP, gas phase) for protonolysis of precatalyst **2** by aminoallene substrate **1**[a-c]

protonolysis pathway	substrate encounter complex	TS	products[d]
1 + **2** → **3** + CH_4	–40.3/*–32.0* (**2**-S)	–15.7/*–6.8* ($\Delta S^{\ddagger}$=–30.1 eu)[e]	–38.6/*–36.9* (**3**) –48.8/*–44.7* (**3'**)

[a] See Scheme 1. [b] Total barriers and reaction energies are relative to the respective precursor species. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 1, S1, ESI) for description of isomers **3**, **3'**. [e] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Table S6 Enthalpies and free energies of activation and reaction (B3LYP, gas phase) for cyclisation of **3** through alternative regioisomeric 5-*exo* and 6-*endo* paths[a-c]

cyclisation pathway	Precursor[d]	TS	product[e]
5-*exo*	10.2/*7.8* (**3**) 0.0/*0.0* (**3'**)	6.1/*7.4* ($\Delta S^{\ddagger}$=–4.4 eu)[f]	–4.7/*–4.1* (**4**)
6-*endo*	10.2/*7.8* (**3**) 0.0/*0.0* (**3'**)	7.6/*8.9* ($\Delta S^{\ddagger}$=–4.4 eu)[f]	–12.8/*–11.7* (**5**) –16.2/*–15.3* (**5'**)

[a] See Scheme 1. [b] Total barriers, reaction energies and activation entropies are relative to the thermodynamically favourable isomer **3'** with a chelating allene functionality. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 1, S1, ESI) for description of isomers **3**, **3'**. [e] See Scheme 1 for description of the azacyclic cyclisation products. [f] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Table S7 Enthalpies and free energies of activation and reaction (B3LYP, gas phase) for protonolysis of the azacycle–Zr intermediates **4** and **5** by aminoallene substrate **1** to afford the cycloamine-amido–Zr compounds **6**–**8** along various regioisomeric paths for proton transfer[a-c]

proton transfer pathway	**4**/**5**-S[d]	TS	Product[d]
5-*exo* precursor **4**			2-vinyl-pyrrolidine
H-trf onto C^6 of **4**	–14.0/*–5.2* (**4**-S)	3.6/*12.5* ($\Delta S^{\ddagger}$=–30.1 eu)[f]	–27.8/*–19.9* (**6**)
6-*endo* precursor **5**, **5'**			6-methyl-tetrahydropyridine
H-trf onto C^7 of **5**	–15.5/*–6.9* (**5**-S)	4.3/*13.3* ($\Delta S^{\ddagger}$=–30.0 eu)[f]	–27.8/*–19.7* (**7** η^1-N)
H-trf onto C^7 of **5'**	–18.5/*–9.8* (**5'**-S)	–1.2/*7.6* ($\Delta S^{\ddagger}$=–29.4 eu)[f]	–26.3/*–18.4* (**7** η^1-C^5)
	–20.3/*–11.5* (**5'**-S)[e]		2-methylene-piperidine
H-trf onto C^5 of **5'**		–10.0/*–1.4* ($\Delta S^{\ddagger}$=–28.8 eu)[f]	–25.4/*–16.7* (**8**)

[a] See Scheme 1. [b] Total barriers, reaction energies and activation entropies are relative to {**4** + **1**} and {**5** + **1**} for protonation of 5-*exo* and 6-*endo* cyclisation intermediate, respectively. [c] Enthalpies and free energies of activation ($\Delta H^{\ddagger}/\Delta G^{\ddagger}$) and reaction ($\Delta H/\Delta G$) are given in kilocalories per mole; numbers in italic type are the Gibbs free energies. [d] See the text (or Figs. 2, S4, S5, ESI) for description of the various isomers of the amine adducts **4**-S, **5**-S, **5'**-S and of the cycloamine-amido–Zr product species **6**–**8**. [e] The precursor amine-adduct species is not identical with the related one reported in Table S3. [f] The activation entropy is given in entropic units ≡ cal mol^{-1} K^{-1}.

Cartesian coordinates (in Å) of optimised structures of key species of the investigated elementary steps.

2

Zr	0,0000	0,0000	0,0000
C	0,2769	-2,5096	-0,1463
C	0,1532	-2,1905	1,2334
C	-1,1520	-1,6547	1,4436
C	-1,8462	-1,6761	0,1924
C	-0,9617	-2,2010	-0,7851
H	1,1517	-2,9452	-0,6245
H	0,9109	-2,3446	1,9961
H	-1,5748	-1,3641	2,4015
H	-2,8793	-1,3809	0,0286
H	-1,1939	-2,3585	-1,8379
C	-1,8463	1,6752	0,2195
C	-1,1259	1,6626	1,4557
C	0,1741	2,1981	1,2147
C	0,2689	2,5064	-0,1699
C	-0,9831	2,1932	-0,7801
H	-2,8821	1,3776	0,0795
H	-1,5282	1,3784	2,4244
H	0,9468	2,3589	1,9605
H	1,1332	2,9393	-0,6693
H	-1,2375	2,3424	-1,8289
C	2,1774	-0,0049	0,4395
H	2,2885	-0,0324	-0,6888
H	2,6966	-0,8919	0,8169
H	2,7013	0,8955	0,7765

2-S

Zr	0,0000	0,0000	0,0000
C	-0,3395	-2,0803	-1,4336
C	0,1851	-2,5537	-0,2033
C	-0,7805	-2,3058	0,8159
C	-1,8956	-1,6655	0,2194
C	-1,6198	-1,5160	-1,1734
H	0,1432	-2,1508	-2,4034
H	1,1395	-3,0613	-0,0772
H	-0,7003	-2,5951	1,8621
H	-2,8145	-1,3797	0,7239
H	-2,2982	-1,1077	-1,9174
C	-1,7980	1,6020	0,7598
C	-0,5967	2,1192	1,3124
C	0,2361	2,5459	0,2398
C	-0,4534	2,3066	-0,9775
C	-1,7082	1,7160	-0,6601
H	-2,6542	1,2359	1,3198
H	-0,3743	2,2124	2,3733
H	1,2175	3,0047	0,3304
H	-0,0915	2,5459	-1,9730
H	-2,4880	1,4544	-1,3697
C	1,6524	0,1685	-1,5411
N	1,4333	-0,3088	1,8748
C	2,6039	0,6182	2,0874
C	3,5009	0,1879	3,2478
C	4,6775	1,1618	3,4650
C	5,5875	0,7173	4,5886
C	5,7647	1,3836	5,7047
C	5,9536	2,0545	6,8114
H	6,7457	2,8033	6,8944
H	2,9081	0,1291	4,1763
H	0,8813	-0,3265	2,7423
H	4,2926	2,1692	3,6835
H	5,2623	1,2348	2,5312
H	1,8050	-1,2638	1,7952
H	6,1329	-0,2232	4,4443
H	2,1961	1,6226	2,2630
H	3,1677	0,6512	1,1447
H	3,8950	-0,8249	3,0554
H	5,3362	1,8839	7,6972
H	1,3310	0,2406	-2,5924
H	2,2987	-0,7239	-1,4779
H	2,2631	1,0637	-1,3403

TS_{prot}-precat

Zr	0,0000	0,0000	0,0000
C	-0,5985	-1,8882	-1,5989
C	0,0270	-2,5039	-0,4769
C	-0,8143	-2,3197	0,6543
C	-1,9501	-1,5712	0,2396
C	-1,8188	-1,3113	-1,1586
H	-0,2188	-1,8839	-2,6172
H	0,9639	-3,0555	-0,4996
H	-0,6323	-2,6925	1,6596
H	-2,7961	-1,2956	0,8637
H	-2,5453	-0,8006	-1,7852
C	-1,4830	1,6662	1,1603
C	-0,1524	2,0899	1,4368
C	0,4422	2,4983	0,2136
C	-0,5274	2,3498	-0,8209
C	-1,7181	1,8449	-0,2361
H	-2,2120	1,3304	1,8939
H	0,3183	2,1053	2,4163
H	1,4462	2,8948	0,0871
H	-0,3885	2,6109	-1,8675
H	-2,6555	1,6586	-0,7534
C	1,8898	0,1398	-1,5746
N	1,7494	-0,4599	1,1839
C	2,7131	0,3275	1,9895
C	4,1339	-0,2445	1,9581
C	5,1068	0,5700	2,8329
C	6,5133	0,0134	2,8043
C	7,1377	-0,4722	3,8509
C	7,7621	-0,9419	4,9001
H	8,3724	-0,2950	5,5358
H	4,1176	-1,2877	2,3172
H	1,9229	-1,4568	1,3418
H	4,7445	0,5920	3,8719
H	5,1238	1,6154	2,4767
H	1,9869	-0,2342	-0,1482
H	7,0345	0,0254	1,8392
H	2,3482	0,3622	3,0300
H	2,7133	1,3618	1,6168
H	4,5011	-0,2718	0,9183
H	7,7064	-1,9985	5,1748
H	1,1781	0,4457	-2,3612
H	2,3888	-0,7617	-1,9550
H	2,6243	0,9550	-1,5125

3

Zr	0,0000	0,0000	0,0000
C	0,2502	-2,4760	-0,4139
C	0,1263	-2,3123	0,9929
C	-1,1826	-1,8097	1,2645
C	-1,8802	-1,7056	0,0239
C	-0,9924	-2,0959	-1,0119
H	1,1154	-2,8672	-0,9440
H	0,8834	-2,5460	1,7374
H	-1,6012	-1,6194	2,2500
H	-2,9129	-1,3926	-0,1045
H	-1,2290	-2,1402	-2,0739
C	-1,9419	1,6189	0,2035
C	-1,1658	1,7267	1,3961
C	0,1007	2,2825	1,0476
C	0,1206	2,4818	-0,3607
C	-1,1447	2,0690	-0,8809
H	-2,9689	1,2690	0,1397
H	-1,5069	1,4954	2,4027
H	0,9023	2,5211	1,7417
H	0,9347	2,9133	-0,9376
H	-1,4577	2,1276	-1,9223
N	2,0437	-0,0007	0,1990
C	3,1608	0,9512	0,2993
H	3,6496	0,8298	1,2829
H	2,7690	1,9764	0,2607
C	4,2037	0,7499	-0,8114
H	3,7157	0,8708	-1,7928
H	4,5880	-0,2830	-0,7747
C	5,3867	1,7293	-0,6869
H	5,8872	1,5894	0,2826
H	5,0038	2,7652	-0,7040
C	6,3932	1,5554	-1,8028
C	7,6311	1,1561	-1,6308
C	8,8693	0,7719	-1,4560
H	9,1513	-0,2837	-1,4850
H	6,0511	1,7798	-2,8206
H	2,4471	-0,9430	0,2425
H	9,6708	1,4951	-1,2836

3’

Zr	0,8470	-0,2188	0,1644
C	1,1825	-2,7225	-0,2388
C	0,4061	-2,6152	0,9491
C	-0,8494	-2,0462	0,6045
C	-0,8513	-1,8060	-0,8005
C	0,4051	-2,2262	-1,3218
H	2,1771	-3,1557	-0,3090
H	0,7079	-2,9349	1,9428
H	-1,6764	-1,8622	1,2856
H	-1,6851	-1,4220	-1,3811
H	0,7013	-2,1974	-2,3674
C	-0,7377	1,4386	-0,8763
C	-1,1570	1,3259	0,4845
C	-0,1317	1,8612	1,3016
C	0,9178	2,3229	0,4495
C	0,5339	2,0784	-0,8923
H	-1,3184	1,1588	-1,7512
H	-2,1054	0,9204	0,8276
H	-0,1560	1,9584	2,3826
H	1,8154	2,8399	0,7771
H	1,1048	2,3262	-1,7831
N	2,6673	-0,1376	-0,8295
C	3,7483	0,8445	-0,8321
C	4,7072	0,6025	0,3533
C	4,0028	0,6594	1,7148
C	2,9702	-0,4176	1,9562
C	1,8513	-0,3020	2,6855
C	1,0359	-0,2583	3,7170
H	-0,0414	-0,1098	3,6438
H	4,3161	0,7946	-1,7754
H	5,5070	1,3583	0,3273
H	5,1987	-0,3768	0,2314
H	4,7658	0,5032	2,5004
H	3,0126	-1,0156	-1,2253
H	3,5730	1,6527	1,9079
H	3,3279	1,8569	-0,7582
H	3,2590	-1,4300	1,6450
H	1,4434	-0,3920	4,7250

3-S

Zr	0,0000	0,0000	0,0000
C	0,3008	-2,5433	-0,0941
C	-0,5733	-2,2683	0,9938
C	-1,7772	-1,7268	0,4623
C	-1,6537	-1,6843	-0,9584
C	-0,3729	-2,1895	-1,2979
H	1,2857	-2,9994	-0,0246
H	-0,3721	-2,4581	2,0448
H	-2,6580	-1,4489	1,0346
H	-2,4181	-1,3563	-1,6579
H	0,0074	-2,3292	-2,3070
C	-2,0204	1,5478	-0,2421
C	-1,6388	1,5572	1,1316
C	-0,3759	2,2028	1,2322
C	0,0474	2,5483	-0,0761
C	-0,9771	2,1462	-0,9896
H	-2,9535	1,1615	-0,6430
H	-2,2381	1,2003	1,9653
H	0,1624	2,3958	2,1551
H	0,9568	3,0877	-0,3307
H	-0,9853	2,3170	-2,0625
N	1,6081	-0,1102	1,2996
C	2,5008	0,8076	2,0215
H	2,2110	0,8510	3,0887
H	2,3802	1,8246	1,6193
C	3,9765	0,3927	1,9277
H	4,2816	0,3598	0,8677
H	4,0960	-0,6314	2,3204
C	4,9076	1,3386	2,7099
H	4,6258	1,3429	3,7735
H	4,7712	2,3703	2,3390
C	6,3643	0,9541	2,5764
C	7,1186	0,5369	3,5652
C	7,8730	0,1347	4,5555
H	7,9581	-0,9229	4,8183
H	6,8074	1,0273	1,5753
H	1,8580	-1,0638	1,5776
N	1,5125	0,2059	-1,8455
H	2,0661	-0,6581	-1,7988
H	2,1732	0,9390	-1,5621
C	1,1348	0,4440	-3,2781
C	2,3218	0,3562	-4,2388
C	1,9073	0,6090	-5,7021
C	3,0726	0,4810	-6,6585
C	3,5505	1,4659	-7,3813
C	4,0185	2,4434	-8,1136
H	4,8173	3,0973	-7,7542
H	1,4656	1,6123	-5,7970
H	1,1239	-0,1156	-5,9862
H	0,3622	-0,2912	-3,5449
H	3,5398	-0,5077	-6,7425
H	2,7900	-0,6401	-4,1571
H	3,0909	1,0922	-3,9504
H	0,6678	1,4364	-3,3321
H	8,4538	0,8422	5,1533
H	3,6345	2,6356	-9,1189

TS[**3**–**4**]

Zr	0,0000	0,0000	0,0000
C	-0,9656	-2,2414	0,7625
C	-2,0477	-1,4585	0,2805
C	-1,8706	-1,2757	-1,1245
C	-0,6761	-1,9428	-1,5064
C	-0,1115	-2,5301	-0,3395
H	-0,8250	-2,5760	1,7853
H	-2,8873	-1,1003	0,8705
H	-2,5531	-0,7582	-1,7925
H	-0,2787	-2,0062	-2,5167
H	0,7811	-3,1503	-0,3031
C	-1,1876	1,9550	-1,0682
C	-1,7001	1,8569	0,2613
C	-0,6493	2,1689	1,1617
C	0,5119	2,4696	0,3921
C	0,1752	2,3494	-0,9821
H	-1,7537	1,8158	-1,9854
H	-2,7245	1,6155	0,5327
H	-0,7190	2,2017	2,2449
H	1,4711	2,7823	0,7957
H	0,8333	2,5341	-1,8277
N	2,0062	-0,2834	-0,7308
C	3,1850	0,5607	-0,9575
C	4,2503	0,2318	0,1004
C	3,5143	0,2190	1,4442
C	2,2860	-0,6466	1,3817
C	1,0690	-0,3390	2,0472
C	0,7487	-0,2506	3,3420
H	1,4676	-0,4746	4,1375
H	3,5677	0,3872	-1,9755
H	5,0685	0,9650	0,0872
H	4,6926	-0,7565	-0,1035
H	4,1557	-0,2121	2,2337
H	2,2169	-1,2325	-1,0534
H	3,2457	1,2342	1,7679
H	2,8927	1,6158	-0,8834
H	2,4803	-1,7065	1,1754
H	-0,2543	0,0246	3,6724

4

Zr	0,0000	0,0000	0,0000
C	-0,1217	-2,5363	0,3083
C	-1,4383	-2,0329	0,5000
C	-1,8967	-1,5109	-0,7410
C	-0,8539	-1,6616	-1,6971
C	0,2405	-2,3053	-1,0470
H	0,4822	-3,0265	1,0655
H	-2,0020	-2,0690	1,4291
H	-2,8799	-1,0911	-0,9345
H	-0,9058	-1,3867	-2,7483
H	1,1622	-2,6264	-1,5284
C	-1,3978	1,8172	-1,0379
C	-1,9392	1,5841	0,2635
C	-0,9799	2,0050	1,2233
C	0,1536	2,4976	0,5197
C	-0,1065	2,3887	-0,8741
H	-1,9014	1,6333	-1,9836
H	-2,9293	1,1927	0,4825
H	-1,0913	1,9722	2,3029
H	1,0451	2,9160	0,9799
H	0,5543	2,7044	-1,6792
N	2,3135	-0,0274	-0,2308
C	3,2833	1,0860	-0,5270
C	4,3633	0,9606	0,5500
C	3,5483	0,5974	1,7992
C	2,4556	-0,3717	1,2942
C	1,0791	-0,2734	1,9479
C	0,9085	-0,3456	3,2734
H	1,7386	-0,4745	3,9791
H	3,6488	0,9838	-1,5567
H	4,9364	1,8892	0,6703
H	5,0740	0,1600	0,2940
H	4,1510	0,1275	2,5863
H	2,6270	-0,8471	-0,7549
H	3,0760	1,4909	2,2327
H	2,7601	2,0465	-0,4430
H	2,8159	-1,4118	1,3327
H	-0,0823	-0,2880	3,7302

TS[**3**–**5**]

Zr	0,0000	0,0000	0,0000
C	0,0509	-2,5502	-0,1744
C	-1,0907	-2,2272	0,6186
C	-2,0157	-1,5395	-0,2060
C	-1,4448	-1,4234	-1,5096
C	-0,1787	-2,0710	-1,4903
H	0,9213	-3,1091	0,1627
H	-1,2432	-2,4927	1,6612
H	-2,9999	-1,1896	0,0928
H	-1,9233	-0,9856	-2,3813
H	0,4859	-2,1827	-2,3434
C	-1,3915	1,8487	-1,0049
C	-1,8499	1,6982	0,3385
C	-0,8042	2,1057	1,2069
C	0,3045	2,5015	0,4054
C	-0,0651	2,3543	-0,9603
H	-1,9737	1,6618	-1,9029
H	-2,8412	1,3737	0,6431
H	-0,8568	2,1440	2,2915
H	1,2493	2,8879	0,7786
H	0,5483	2,6000	-1,8232
N	2,0135	-0,0192	-0,6741
C	3,0187	0,9117	-1,2038
C	4,4257	0,5540	-0,7230
C	4,6159	0,7868	0,7745
C	3,5187	0,3050	1,6836
C	2,2590	-0,0549	1,5225
C	1,0494	-0,3924	2,1226
H	0,9073	-1,4384	2,4056
H	2,9752	0,8723	-2,3060
H	5,1624	1,1526	-1,2782
H	4,6326	-0,4998	-0,9736
H	5,5561	0,3222	1,1088
H	2,3455	-0,9721	-0,8612
H	4,7491	1,8661	0,9734
H	2,7546	1,9352	-0,9043
H	0,6526	0,3337	2,8382
H	3,8020	0,2546	2,7463

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Zr	0,0000	0,0000	0,0000
C	0,1265	-2,5637	-0,0209
C	-0,8096	-2,2017	0,9853
C	-1,9179	-1,5808	0,3449
C	-1,6634	-1,5571	-1,0595
C	-0,4005	-2,1723	-1,2817
H	1,0673	-3,0830	0,1472
H	-0,7066	-2,3867	2,0510
H	-2,8216	-1,2274	0,8340
H	-2,3370	-1,1863	-1,8275
H	0,0650	-2,3352	-2,2518
C	-0,7034	2,1812	-1,0783
C	-1,8544	1,6692	-0,4207
C	-1,6034	1,6852	0,9816
C	-0,3009	2,2174	1,1934
C	0,2548	2,5233	-0,0807
H	-0,5919	2,3207	-2,1519
H	-2,7733	1,3456	-0,9015
H	-2,3004	1,3800	1,7586
H	0,1679	2,3963	2,1558
H	1,2265	2,9763	-0,2525
N	2,2304	-0,0762	-0,7710
C	2,8682	0,6689	-1,9009
C	4,3260	1,0057	-1,5918
C	4,4064	1,8756	-0,3320
C	3,5103	1,3617	0,7579
C	2,5726	0,4041	0,5931
C	1,6447	-0,1792	1,5983
H	1,6769	0,3521	2,5538
H	2,7653	0,0519	-2,8034
H	4,7729	1,5185	-2,4549
H	4,8949	0,0735	-1,4451
H	5,4423	1,9117	0,0408
H	2,4833	-1,0696	-0,8421
H	4,1530	2,9258	-0,5693
H	2,2917	1,5912	-2,0599
H	1,8386	-1,2472	1,7749
H	3,6576	1,7470	1,7694

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Zr	0,0000	0,0000	0,0000
C	-0,1121	-2,4530	0,6024
C	-1,4205	-1,9248	0,7930
C	-1,9376	-1,5592	-0,4818
C	-0,9423	-1,8351	-1,4569
C	0,1854	-2,3937	-0,7884
H	0,5268	-2,8628	1,3782
H	-1,9484	-1,8498	1,7411
H	-2,9251	-1,1502	-0,6760
H	-1,0376	-1,6767	-2,5293
H	1,0918	-2,7533	-1,2650
C	-0,3770	2,3307	-0,9859
C	-1,6483	1,7125	-0,8166
C	-1,8801	1,5640	0,5837
C	-0,7506	2,0868	1,2737
C	0,1747	2,5576	0,3036
H	0,0788	2,6047	-1,9347
H	-2,3420	1,4508	-1,6117
H	-2,7813	1,1667	1,0437
H	-0,6286	2,1399	2,3530
H	1,1289	3,0348	0,5141
N	3,2787	-1,6806	0,3696
C	4,0431	-2,1741	-0,7894
C	4,2702	-1,0557	-1,8052
C	2,9457	-0,3448	-2,1366
C	2,2836	0,1515	-0,8562
C	2,5682	-0,5366	0,3736
C	1,8130	-0,1173	1,5389
H	1,8796	-0,7524	2,4273
H	4,9999	-2,5659	-0,4164
H	4,7241	-1,4849	-2,7090
H	4,9857	-0,3276	-1,3929
H	3,1280	0,4972	-2,8180
H	3,3967	-2,1660	1,2555
H	2,2913	-1,0422	-2,6850
H	3,5068	-3,0189	-1,2548
H	1,9441	0,9405	1,7865
H	2,2934	1,2391	-0,7220

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Zr	0,0000	0,0000	0,0000
C	0,2592	-2,2308	-1,3133
C	-0,3078	-2,5739	-0,0672
C	-1,6173	-2,0022	-0,0159
C	-1,8491	-1,3197	-1,2346
C	-0,6760	-1,4250	-2,0295
H	1,2318	-2,5622	-1,6695
H	0,1576	-3,1969	0,6903
H	-2,3438	-2,1314	0,7823
H	-2,7698	-0,8159	-1,5138
H	-0,5494	-1,0314	-3,0354
C	-1,4890	1,8213	-1,0467
C	-1,8194	1,7793	0,3361
C	-0,6920	2,2602	1,0645
C	0,3423	2,5482	0,1466
C	-0,1534	2,2746	-1,1652
H	-2,1486	1,5673	-1,8710
H	-2,7896	1,5134	0,7501
H	-0,6387	2,4128	2,1398
H	1,3190	2,9462	0,4043
H	0,3784	2,4333	-2,0981
N	2,0925	0,1189	-1,3035
C	2,8656	1,2834	-1,8430
C	4,3319	0,8879	-1,6487
C	4,3206	0,2522	-0,2481
C	2,9352	-0,4404	-0,1453
C	2,0642	-0,2025	1,0623
C	2,5842	-0,0731	2,2926
H	3,6600	-0,1423	2,5034
H	2,6326	2,1772	-1,2497
H	4,6348	0,1576	-2,4155
H	5,0099	1,7482	-1,7226
H	4,3986	1,0302	0,5250
H	2,0657	-0,5738	-2,0558
H	5,1461	-0,4536	-0,0948
H	2,5783	1,4737	-2,8852
H	3,0395	-1,5247	-0,3171
H	1,9803	0,1159	3,1877
N	-0,5887	-0,3874	2,3354
H	0,0050	0,3131	2,7954
H	-1,5494	-0,0631	2,4959
C	-0,4042	-1,6718	3,0853
C	-0,6534	-1,5279	4,5881
C	-0,4604	-2,8601	5,3399
C	-0,7509	-2,7331	6,8192
C	0,1424	-2,8841	7,7676
C	1,0313	-3,0499	8,7134
H	1,2074	-4,0301	9,1640
H	-1,1329	-3,6210	4,9044
H	0,5683	-3,2224	5,1980
H	0,6207	-2,0118	2,8885
H	-1,7843	-2,4975	7,1031
H	0,0329	-0,7750	5,0115
H	-1,6780	-1,1546	4,7613
H	-1,0924	-2,4137	2,6571
H	1,6211	-2,2137	9,0981

TS[**4**-S–**6**]

Zr	0,0000	0,0000	0,0000
C	0,5496	-2,3182	-1,0016
C	-0,4811	-2,5302	-0,0535
C	-1,6508	-1,8630	-0,5104
C	-1,3433	-1,2564	-1,7612
C	0,0193	-1,5224	-2,0573
H	1,5560	-2,7235	-0,9321
H	-0,3837	-3,1153	0,8572
H	-2,6196	-1,8521	-0,0171
H	-2,0366	-0,7217	-2,4022
H	0,5411	-1,2122	-2,9600
C	-1,8292	1,6104	-0,7852
C	-1,7119	1,8160	0,6082
C	-0,4308	2,3873	0,8647
C	0,2325	2,5394	-0,3758
C	-0,6095	2,0252	-1,4002
H	-2,7092	1,2316	-1,2959
H	-2,4729	1,5938	1,3505
H	-0,0549	2,6998	1,8346
H	1,2062	2,9950	-0,5182
H	-0,4021	2,0291	-2,4678
N	2,3229	0,2831	-0,8647
C	2,9973	1,4130	-1,5980
C	3,7610	2,2192	-0,5156
C	3,4233	1,5358	0,8262
C	3,0704	0,0931	0,4346
C	2,1676	-0,6655	1,3660
C	2,6576	-1,6163	2,1779
H	3,7238	-1,8723	2,2115
H	2,2511	2,0058	-2,1400
H	4,8405	2,1741	-0,7101
H	3,4851	3,2824	-0,5184
H	2,5599	2,0109	1,3147
H	2,4300	-0,5664	-1,4221
H	4,2558	1,5582	1,5399
H	3,6912	0,9992	-2,3440
H	4,0082	-0,4628	0,2407
H	2,0163	-2,1690	2,8715
N	-0,4624	-0,5040	2,1300
H	-0,8834	-1,4215	2,2713
H	0,8575	-0,5679	1,8489
C	-0,6338	0,3150	3,3445
C	-0,6980	-0,5342	4,6181
C	-0,9134	0,3153	5,8855
C	-0,9534	-0,5244	7,1432
C	-2,0001	-0,6449	7,9246
C	-3,0423	-0,7531	8,7087
H	-3,1961	-0,0713	9,5495
H	-0,0934	1,0510	5,9699
H	-1,8496	0,8877	5,7986
H	-1,5474	0,9336	3,2775
H	-0,0372	-1,0673	7,4066
H	-1,5249	-1,2606	4,5314
H	0,2317	-1,1188	4,7157
H	0,2173	1,0141	3,4182
H	-3,7922	-1,5346	8,5598

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Zr	0,0000	0,0000	0,0000
C	0,2334	-2,5541	-0,2702
C	-0,6036	-2,3400	0,8566
C	-1,8068	-1,7337	0,4034
C	-1,7326	-1,6100	-1,0165
C	-0,4773	-2,1140	-1,4294
H	1,2049	-3,0441	-0,2599
H	-0,3794	-2,6036	1,8865
H	-2,6626	-1,4855	1,0245
H	-2,5124	-1,2213	-1,6661
H	-0,1418	-2,2035	-2,4605
C	-2,0273	1,4393	0,4313
C	-1,0432	1,8676	1,3639
C	0,0066	2,4894	0,6318
C	-0,3284	2,4461	-0,7457
C	-1,5805	1,7882	-0,8771
H	-2,9768	0,9726	0,6759
H	-1,0975	1,7642	2,4445
H	0,8855	2,9638	1,0574
H	0,2615	2,8742	-1,5510
H	-2,1264	1,6268	-1,8033
N	1,6627	0,0570	-1,7679
C	1,3146	0,5066	-3,1632
C	2,6131	0,3754	-3,9925
C	3,7440	0,2085	-2,9414
C	3,1009	0,5514	-1,5851
C	3,1256	2,0010	-1,1789
C	3,6692	3,0150	-1,8580
H	4,1566	2,8856	-2,8260
H	0,4782	-0,0921	-3,5442
H	2,7600	1,2658	-4,6162
H	2,5730	-0,4886	-4,6686
H	4,0981	-0,8318	-2,9182
H	1,7752	-0,9624	-1,8373
H	4,6209	0,8305	-3,1548
H	0,9864	1,5502	-3,1057
H	3,5253	-0,0423	-0,7612
H	3,6630	4,0283	-1,4549
N	1,3525	-0,1792	1,5552
H	1,6123	-1,1594	1,7072
H	2,6763	2,1984	-0,2017
C	1,9603	0,5920	2,6479
C	3,4799	0,3842	2,7496
C	4,1000	1,1432	3,9379
C	5,6022	0,9771	4,0074
C	6,2420	0,3854	4,9878
C	6,8782	-0,1932	5,9739
H	7,2271	0,3767	6,8391
H	3,8604	2,2175	3,8460
H	3,6494	0,7957	4,8796
H	1,4974	0,2982	3,6087
H	6,1857	1,3835	3,1718
H	3,6975	-0,6915	2,8605
H	3,9564	0,7079	1,8094
H	1,7422	1,6590	2,5071
H	7,0923	-1,2652	5,9672

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Zr	0,0000	0,0000	0,0000
C	0,3402	0,3237	-2,5300
C	-0,2024	-0,9694	-2,3646
C	-1,5270	-0,8269	-1,8494
C	-1,7963	0,5595	-1,7206
C	-0,6309	1,2753	-2,1076
H	1,3338	0,5377	-2,9061
H	0,2919	-1,9017	-2,6198
H	-2,2359	-1,6283	-1,6581
H	-2,7342	0,9938	-1,3895
H	-0,5200	2,3565	-2,1317
C	-1,6395	1,5679	1,1951
C	-2,0062	0,2450	1,5794
C	-0,9738	-0,2573	2,4203
C	0,0444	0,7186	2,5118
C	-0,3729	1,8562	1,7556
H	-2,2384	2,2536	0,6037
H	-2,9469	-0,2489	1,3481
H	-0,9813	-1,2123	2,9405
H	0,9502	0,6399	3,1074
H	0,1600	2,7983	1,6679
N	3,4382	0,1988	-1,5683
C	4,0222	1,4257	-2,1383
C	3,0441	2,5989	-2,0230
C	2,5277	2,7594	-0,5842
C	2,1315	1,4335	0,0435
C	2,7066	0,2202	-0,4253
C	2,2300	-0,9783	0,2081
H	2,5591	-1,9338	-0,2113
H	1,6860	3,4706	-0,5707
H	4,9638	1,6650	-1,6147
H	4,2711	1,2277	-3,1898
H	3,8515	-0,6881	-1,8408
H	2,2067	2,4507	-2,7197
H	3,5550	3,5171	-2,3458
H	3,3175	3,2253	0,0313
H	2,0495	1,4557	1,1304
H	2,3223	-0,9552	1,3011
N	-0,3279	-2,3930	0,5379
H	0,2492	-2,4998	1,3795
H	-1,2936	-2,4912	0,8712
C	-0,0362	-3,5659	-0,3456
C	-0,1318	-4,9074	0,3858
C	0,1818	-6,1025	-0,5364
C	0,0755	-7,4283	0,1846
C	1,0867	-8,2308	0,4162
C	2,0937	-9,0374	0,6361
H	2,3623	-9,8194	-0,0790
H	-0,5221	-6,0970	-1,3872
H	1,1935	-5,9944	-0,9558
H	0,9701	-3,4256	-0,7606
H	-0,9212	-7,7243	0,5331
H	0,5720	-4,9173	1,2352
H	-1,1436	-5,0263	0,8107
H	-0,7440	-3,5357	-1,1858
H	2,6950	-8,9681	1,5464

TS[**5'**-S–**7**]

Zr	0,0000	0,0000	0,0000
C	0,5256	-0,0431	-2,4898
C	-0,2002	-1,2328	-2,2353
C	-1,5222	-0,8748	-1,8463
C	-1,6167	0,5424	-1,8792
C	-0,3466	1,0602	-2,2577
H	1,5557	-0,0036	-2,8250
H	0,1833	-2,2416	-2,3512
H	-2,3292	-1,5623	-1,6030
H	-2,5073	1,1282	-1,6714
H	-0,1049	2,1123	-2,3918
C	-1,1296	1,9839	1,0741
C	-1,9932	0,8656	1,2806
C	-1,3497	-0,0237	2,1818
C	-0,0888	0,5360	2,5275
C	0,0416	1,7785	1,8534
H	-1,3525	2,8607	0,4713
H	-2,9899	0,7402	0,8670
H	-1,7645	-0,9554	2,5586
H	0,6372	0,1076	3,2149
H	0,8815	2,4626	1,9372
N	3,7710	-0,4893	-1,6175
C	4,1921	0,8277	-2,1335
C	3,2564	1,9480	-1,6851
C	2,9087	1,8308	-0,1970
C	2,4007	0,4233	0,1835
C	3,1689	-0,6853	-0,4121
C	3,1566	-1,9704	0,1785
H	3,7399	-2,7589	-0,3065
H	2,1762	2,6098	0,0609
H	5,2174	1,0323	-1,7783
H	4,2358	0,7695	-3,2306
H	4,3437	-1,2685	-1,9378
H	2,3421	1,9404	-2,2940
H	3,7508	2,9100	-1,8824
H	3,8098	2,0626	0,3990
H	2,4318	0,2978	1,2769
H	3,2592	-1,9725	1,2685
N	0,4604	-2,1063	0,6544
H	1,6589	-2,1796	0,3295
H	0,5153	-2,0836	1,6807
C	-0,2021	-3,4005	0,3069
C	0,2794	-4,5616	1,1817
C	-0,3870	-5,8977	0,8014
C	0,0331	-7,0310	1,7112
C	0,7023	-8,0897	1,3216
C	1,3586	-9,1520	0,9308
H	0,8371	-10,0510	0,5915
H	-1,4845	-5,7821	0,8529
H	-0,1413	-6,1548	-0,2398
H	0,0149	-3,6166	-0,7487
H	-0,2476	-6,9485	2,7684
H	1,3728	-4,6616	1,0951
H	0,0639	-4,3353	2,2415
H	-1,2957	-3,2957	0,3964
H	2,4512	-9,1854	0,9387

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Zr	0,0000	0,0000	0,0000
C	0,5919	0,5793	-2,4369
C	0,1769	-0,7807	-2,4270
C	-1,2026	-0,8165	-2,0870
C	-1,6314	0,5174	-1,8591
C	-0,5173	1,3845	-2,0764
H	1,5837	0,9318	-2,6994
H	0,7918	-1,6377	-2,6857
H	-1,8245	-1,7045	-2,0213
H	-2,6459	0,8251	-1,6257
H	-0,5326	2,4697	-2,0148
C	-0,5618	2,1036	1,3400
C	-1,7744	1,3739	1,1696
C	-1,6752	0,1697	1,9199
C	-0,4024	0,1553	2,5545
C	0,2762	1,3514	2,2050
H	-0,3447	3,0846	0,9246
H	-2,6468	1,7092	0,6177
H	-2,4481	-0,5885	2,0103
H	-0,0256	-0,6129	3,2255
H	1,2542	1,6518	2,5689
N	4,0329	0,1105	-1,6376
C	4,4518	1,5222	-1,7106
C	3,4388	2,4273	-1,0126
C	3,0141	1,8577	0,3472
C	2,5651	0,3958	0,2493
C	3,2608	-0,4135	-0,6711
C	3,2456	-1,9142	-0,6002
H	3,1544	-2,3713	-1,5969
H	2,2275	2,4985	0,7652
H	5,4453	1,6152	-1,2413
H	4,5631	1,7918	-2,7700
H	4,5015	-0,5389	-2,2659
H	2,5573	2,5631	-1,6550
H	3,8878	3,4220	-0,8850
H	3,8621	1,9259	1,0516
H	2,4130	-0,1210	1,2068
H	4,1952	-2,2644	-0,1648
N	-0,1053	-2,0226	0,4724
H	2,4202	-2,2666	0,0266
H	-0,3060	-2,1846	1,4631
C	-0,2062	-3,3225	-0,2054
C	0,3922	-4,4706	0,6201
C	0,2889	-5,8312	-0,0935
C	0,8217	-6,9680	0,7504
C	1,8612	-7,7056	0,4410
C	2,8897	-8,4516	0,1266
H	2,7702	-9,3721	-0,4508
H	-0,7692	-6,0298	-0,3385
H	0,8359	-5,7975	-1,0483
H	0,2990	-3,2682	-1,1814
H	0,2917	-7,1792	1,6874
H	1,4488	-4,2582	0,8495
H	-0,1317	-4,5274	1,5910
H	-1,2669	-3,5597	-0,4149
H	3,9041	-8,1917	0,4406

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Zr	0,0000	0,0000	0,0000
C	0,2945	-0,5086	-2,5154
C	-0,7373	-1,3634	-2,0327
C	-1,8341	-0,5523	-1,6458
C	-1,4878	0,8100	-1,8983
C	-0,1843	0,8258	-2,4551
H	1,2507	-0,8333	-2,9116
H	-0,7115	-2,4472	-2,0108
H	-2,7879	-0,9112	-1,2704
H	-2,1328	1,6722	-1,7486
H	0,3460	1,7053	-2,8124
C	-0,2047	0,9879	2,3861
C	-1,2045	1,6047	1,5692
C	-2,1582	0,6112	1,2327
C	-1,7281	-0,6245	1,7873
C	-0,5372	-0,3751	2,5277
H	0,6350	1,4855	2,8616
H	-1,2751	2,6621	1,3253
H	-3,0670	0,7702	0,6599
H	-2,2494	-1,5756	1,7176
H	0,0136	-1,1036	3,1154
N	2,5653	-2,4723	-1,1919
C	3,8751	-2,0862	-1,7332
C	4,0753	-0,5735	-1,6171
C	3,8183	-0,0931	-0,1799
C	2,4966	-0,6156	0,3496
C	2,0041	-1,8558	-0,1194
C	0,7301	-2,2784	0,4121
H	0,2707	-3,1603	-0,0418
H	3,8703	1,0081	-0,1413
H	4,6778	-2,6156	-1,1911
H	3,9229	-2,4056	-2,7835
H	2,1847	-3,3737	-1,4636
H	3,3966	-0,0613	-2,3176
H	5,0995	-0,3241	-1,9280
H	4,6428	-0,4360	0,4705
H	2,2925	-0,4298	1,4114
H	0,7221	-2,3462	1,5009
N	1,2828	2,0926	-0,2569
H	0,6568	2,7450	-0,7418
H	1,9937	1,8458	-0,9552
C	1,9737	2,8623	0,8264
C	2,8154	4,0253	0,2954
C	3,5161	4,8063	1,4252
C	4,3542	5,9507	0,8990
C	4,1183	7,2179	1,1414
C	3,8908	8,4813	1,3921
H	4,3381	8,9803	2,2555
H	4,1635	4,1149	1,9935
H	2,7669	5,1959	2,1307
H	1,2010	3,2364	1,5109
H	5,2170	5,6872	0,2745
H	2,1753	4,7187	-0,2762
H	3,5734	3,6424	-0,4099
H	2,5981	2,1575	1,3939
H	3,2557	9,0893	0,7422

TS[**5'**-S–**8**]

Zr	0,0000	0,0000	0,0000
C	0,6617	-0,2429	-2,4739
C	0,0165	-1,4569	-2,1101
C	-1,3388	-1,1636	-1,8043
C	-1,5359	0,2387	-1,9868
C	-0,3019	0,8015	-2,4110
H	1,7018	-0,1416	-2,7735
H	0,4679	-2,4451	-2,0933
H	-2,1033	-1,8844	-1,5276
H	-2,4766	0,7720	-1,8816
H	-0,1389	1,8452	-2,6699
C	-1,2845	1,2481	1,8148
C	-2,2047	0,3677	1,1876
C	-1,8052	-0,9695	1,4853
C	-0,6471	-0,9071	2,3080
C	-0,3157	0,4602	2,4998
H	-1,3310	2,3343	1,7972
H	-3,0849	0,6598	0,6218
H	-2,3273	-1,8754	1,1871
H	-0,1208	-1,7594	2,7291
H	0,5107	0,8386	3,0960
N	3,6578	-1,4282	-1,1377
C	4,9757	-1,0836	-1,6939
C	5,2827	0,3936	-1,4460
C	5,1209	0,7354	0,0416
C	3,7775	0,2583	0,5661
C	3,1706	-0,8862	0,0054
C	1,8852	-1,3781	0,5329
H	1,6636	-2,4087	0,2144
H	5,2304	1,8222	0,1851
H	5,7500	-1,7200	-1,2317
H	4,9602	-1,3115	-2,7689
H	3,1891	-2,2484	-1,5113
H	4,6019	1,0119	-2,0537
H	6,3037	0,6115	-1,7894
H	5,9446	0,2749	0,6151
H	3,6121	0,3723	1,6438
H	1,9205	-1,3592	1,6282
N	1,4805	1,6989	0,0148
H	1,5957	2,0244	-0,9527
H	2,5854	1,1021	0,2096
C	1,5170	2,9224	0,8752
C	2,5459	3,9494	0,3945
C	2,5404	5,2360	1,2420
C	3,5465	6,2529	0,7476
C	3,2311	7,4109	0,2177
C	2,9124	8,5700	-0,2992
H	2,8088	9,4627	0,3231
H	2,7681	4,9807	2,2918
H	1,5352	5,6842	1,2321
H	0,5218	3,3920	0,8950
H	4,6073	5,9884	0,8378
H	2,3289	4,2174	-0,6545
H	3,5523	3,5001	0,4036
H	1,7443	2,6035	1,9035
H	2,7486	8,6924	-1,3733

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Zr	0,0000	0,0000	0,0000
C	0,1241	-0,3540	-2,5383
C	-0,1588	-1,6348	-1,9799
C	-1,4452	-1,5868	-1,3896
C	-1,9639	-0,2717	-1,5794
C	-1,0014	0,4812	-2,3043
H	1,0181	-0,0830	-3,0941
H	0,4843	-2,5076	-2,0361
H	-1,9583	-2,4120	-0,9032
H	-2,9483	0,0756	-1,2804
H	-1,1201	1,5111	-2,6303
C	-0,8955	1,3456	1,9700
C	-1,9336	0,4624	1,5707
C	-1,5184	-0,8703	1,8676
C	-0,2223	-0,8057	2,4358
C	0,1717	0,5633	2,4878
H	-0,9215	2,4288	1,8962
H	-2,9004	0,7577	1,1729
H	-2,1074	-1,7712	1,7181
H	0,3576	-1,6505	2,7971
H	1,1033	0,9433	2,8999
N	3,1010	-2,6596	-1,3535
C	4,0642	-2,9543	-2,4354
C	4,7676	-1,6935	-2,9255
C	5,1893	-0,8332	-1,7322
C	3,9473	-0,4094	-0,9402
C	2,9978	-1,5428	-0,6291
C	2,0257	-1,4185	0,3953
H	1,5859	-2,3641	0,7362
H	5,7332	0,0600	-2,0670
H	4,7971	-3,6778	-2,0415
H	3,5149	-3,4512	-3,2479
H	2,5163	-3,4434	-1,0637
H	4,0974	-1,1183	-3,5844
H	5,6337	-1,9905	-3,5326
H	5,8776	-1,4003	-1,0851
H	4,2149	0,0753	0,0091
H	2,3654	-0,7889	1,2236
N	0,9669	1,7920	-0,4028
H	1,0446	1,9932	-1,4040
H	3,3777	0,3488	-1,5022
C	1,4269	2,9847	0,3214
C	2,8051	3,4783	-0,1423
C	3,2457	4,7661	0,5790
C	4,6304	5,2149	0,1678
C	4,8961	6,3287	-0,4722
C	5,1589	7,4475	-1,0981
H	5,3777	8,3682	-0,5507
H	3,2340	4,5918	1,6697
H	2,5244	5,5721	0,3772
H	0,6971	3,8071	0,1917
H	5,4644	4,5507	0,4279
H	2,7828	3,6683	-1,2292
H	3,5511	2,6838	0,0248
H	1,4657	2,7629	1,3971
H	5,1764	7,5034	-2,1896