Pictogram

The mechanistic details of palladium-catalyzed esterification of methanol to methyl formate have been studied by DFT calculations. A two-step mechanism and four proposed potential reaction pathways have been fully characterized.

Highlights

- Detailed mechanistic of palladium-catalyzed esterification of methanol to methyl formate
- A two-step mechanism and four possible esterification pathways have been fully characterized
- Each oxidation step proceeds via a deprotonation followed by a β -H transfer.
- Initial hydrogen-bonding path is the most favorable for the deprotonation step.
- Spatial distribution of the molecular orbital of the catalyst actively affects its catalytic activity

Computational Mechanistic Study on Oxidative Esterification of Alcohols to Esters Catalyzed by Palladium Complex

Wei Hu^a, Jing Li^a, Suwen deng^a, Jianyin Huang^b, Xueyi Le^a, Wenxu Zheng^{a,*}

^a College of Science, South China Agricultural University, Guangzhou 510642, China

^b Environmental Future Center, Griffith University, Gold Coast campus, Queensland 4215, Australia

*Corresponding Author

E-mail address: wzheng@scau.edu.cn; Tel.: +86 2085280325; Fax: +86 2085285026

Abstract: Mechanistic details of palladium-catalyzed oxidative esterification of methanol to methyl formate have been studied by density functional theory (DFT) calculations without using system simplification. A two-step mechanism involving oxidation of methanol to formaldehyde and further oxidation of formaldehyde to methyl formate and four potential reaction pathways for the later step have been proposed and fully characterized. This mechanistic study provides evidence that each oxidation step proceeds via a deprotonation followed by β -H transfer. The results indicate that methoxymethanol oxidation is the most favorable pathway kinetically and thermodynamically in the formation of methyl formate. Comparative studies on the structural and electronic properties of three Pd complexes indicate that the acetate and the acetonitrile ligands play key ligand-accelerated catalytic roles in the reactions, that is, the former acts as a nucleophilic site to facilitate the deprotonation and the latter provides a coordination site to facilitate the β -H transfer.

Keywords: DFT; Palladium; oxidative esterification; alcohols; esters; mechanisms.

1. Introduction

Esterification is one of the most important reactions in synthetic organic chemistry [1]. Although many methods for the synthesis of esters have been developed, the transition metal-catalyzed oxidative esterification of alcohols to esters is considered the most efficient one, without using corresponding acid or acid-derivative [1-3]. Moreover, development of highly active catalysts for alcohols oxidation in high conversion yield at low temperature still remains a challenge. Recently, direct oxidative esterification reactions have attracted much attention and have been intensively studied [3-11]. This class of catalytic reactions is considered in a two-step mechanism: the transition metal-catalyzed tandem oxidation of alcohol to aldehyde followed by an oxidative esterification [6, 11, 12]. Although the mechanistic studies of these catalytic reactions are now underway, the relative mechanisms are still unknown [6, 11, 12].

Based on the first report of ligand-accelerated catalysis with $\text{Pd}(\text{OAc})_2$ and pyridine [13], Conley et al. (2007) prepared a novel complex $[(\text{dmp})\text{Pd}(\mu\text{-OAc})]_2(\text{OTf})_2$ (**1**) (OTf = trifluoromethylsulfonate; dmp = 2,9-dimethyl-1,10-phenanthroline) [14], which exhibited a very fast initial rate for alcohol oxidation to esters in air at room temperature. Moreover, catalytic oxidation of methanol to methyl formate (**MF**) with **1** has 82% conversion at 50°C by using dry acetonitrile (CH_3CN) as solvent and benzoquinone (**BQ**) as terminal oxidant (see Scheme 1). In addition, experimental study on the catalytic mechanism of this reaction was carried out in 2009 [15], which provided sufficient information for theoretical studies. Therefore, we choose this system as a model to investigate the mechanism of oxidative esterification of alcohols to esters catalyzed by the transition metal complexes.

From the experimental results [15], Pearson et al. (2009) proposed the mechanism for methyl formate synthesis from methanol catalyzed by complex **1** as a two-step process, which consists of β -H elimination of Pd-OMe to generate formaldehyde (CH_2O) (step I) and formation of methyl formate from formaldehyde (step II) (see Scheme 1). Meanwhile, four reaction pathways for step II were proposed and verified, namely formic acid formation pathway (**A**), CO insertion pathway (**B**), disproportionation reaction pathway (**C**), and methoxymethanol (**MM**) oxidation pathway (**D**). Based on the experimental results [15], Pearson et al. confirmed that step II should carry out through pathway **D**. However, details for all the four pathways and the reasons why pathway **D** was the most favorable pathway were not entirely known. Previously, oxidation of alcohol using catalysts $[(\text{dmp})\text{Pd}(\text{OAc})_2]$ (**cat2**) and $[(\text{dmp})\text{Pd}(\text{CH}_3\text{CN})_2]^{2+}$ (**cat3**) was studied experimentally [14]. The results showed that **cat2** was not effective, while **cat3** was slightly effective. Up to now, it is not known which features of catalysts are the fundamental factors affecting on the catalytic performance and how they work in the catalytic oxidation process.

Although there are some reports concerned with theoretical mechanism of complex-catalyzed alcohols oxidation to aldehydes [16-23] and mechanism of acetate assisted deprotonation [24-27], the mechanism of alcohols oxidative esterification to esters is still not available yet. To provide a better insight into the above issues, we performed a thorough computational study on the catalytic mechanism of oxidative esterification of methanol using DFT calculations. Mechanisms mentioned above were modified and improved by referring to other mechanistic reports [16-31] and computational evidence.

2. Computational Details

The geometries for all the reactants, products, intermediates and transition states were fully optimized with the hybrid HF-DFT method B3LYP [32, 33]. The double- ζ quality LANL2DZ [34] basis set was used for Pd atom and 6-31G(d,p) basis set was used for C, H, N and O atoms in all the optimizations in the gas phase. This basis set is denoted as BSI throughout this paper. Frequency analyses were performed to notarize each structure being a minimum (without imaginary vibration) or a transition state (with only one imaginary vibration) at the same level.

Single-point calculations for refining energetic results were performed at B3LYP/BSII level (BSII represents the basis set combination of LanL2DZ for Pd and 6-311++G(d,p) for other atoms) with solvation effects. The solvation effects of acetonitrile (experimentally used) were simulated by the integral equation formulation of the polarized continuum model (PCM) [35, 36] using united atom Hartree-Fock (UAHF) [37] radii in gas phase geometries. Enthalpies and Gibbs free energies for all complexes in solvation were obtained via thermal corrections to single-point energies calculated by PCM model. The correction values were afforded by the gas phase B3LYP/BSI frequencies calculations at 298.15 K and 1 atm. We selected a few stationary points to optimize the PCM model at B3LYP/BSII level. The energetic results from these optimization calculations agree with the B3LYP/BSII//B3LYP/BSI values, which implies that the calculation method in our paper is reliable (see SI1 in the Supporting Information). As the DFT functionals poorly describe dispersion effects, dispersion correction for reaction heat and free energy barrier were estimated using the DFT-D3 program developed by Grimme and co-workers.[38] Influence of the functional on the free energy

barriers and the reaction heat of all pathways are given in SI2. The B3LYP-D3 free energies were used throughout the discussions. Moreover, natural bond orbital (NBO) analyses [39] were performed at the B3LYP/BSII level to calculate the atomic NBO charges (Q) and Wiberg bond indices (WBI). All calculations were carried out using Gaussian03 program [40].

3. Results and Discussions

According to the experimental work [15], catalytic cycle starts from intermediate **2** (in Scheme 1). This intermediate was reduced in the process of oxidation of methanol and then was oxidized by benzoquinone in the catalytic cycle. According to the proposed mechanism by Pearson [15] and the theoretical studies for oxidation of methanol to formaldehyde [30], we proposed a mechanism for stepwise oxidation of methanol to methyl formate. The overall scheme including step I and step II (involving pathway **A-D**) is given in scheme 2. The details of each step and pathway along with the corresponding free energy profiles are given separately in the following discussion. The optimized structures for the stationary points are given in SI3. Moreover, the optimized structures of **1** and **cat2** are in good agreement with the X-ray structures [14, 41] (see **SI4**), supporting the suitability of the employed computational level.

3.1. Step I: Oxidation of MeOH to CH₂O

3.1.1. Deprotonation of MeOH

Some of previous mechanism studies of dehydrogenation of methanol [29, 30] proposed that the methoxide anion (MeO⁻) was formed spontaneously by the deprotonation of MeOH.

However, we believe that this reaction is less likely to occur under the acidic condition (the laboratory environment) without catalyst. Although a few studies have presented the deprotonation of alcohol, the correlative transition states have not been located yet [28]. Therefore, we first investigated the mechanism of the deprotonation of MeOH to generate the palladium methoxide with the catalyst in step I.

The energetic results for the formation of palladium methoxide are given in Figure 1. We adopt two possible paths proposed by Privalov et al [28], where the substrate may coordinate to Pd center either by direct coordination with replacement of CH₃CN from the coordination site or via initial hydrogen-bonding to the coordinated acetate (see SI5). For the direct coordination path, the MeOH substitutes the CH₃CN ligand in **2** to give complex **3a** via **TS2-3a** ($\Delta G^\ddagger = 15.0$ kcal/mol). Then, the attraction between the hydroxyl hydrogen and the terminal oxygen atom of acetate affords **3** via **TS3a-3** overcoming a small barrier of 5.0 kcal/mol. In comparison with the above reaction sequence, a reversed process was considered. In this process, a hydrogen-bonding was formed firstly and then CH₃CN was substituted. The attack of oxygen atom of MeOH on the Pd center leads to the formation of a six-membered ring complex **3** via **TS1** along with the hydroxide hydrogen transfer from methanol to **2**. The barrier for this path is not high, just 11.1 kcal/mol. Moreover, there is a hydrogen-bonding complex **2H** prior to the **TS1**. The free energy of **2H** is 3.2 kcal/mol higher than that of the **2**, but the favorable binding enthalpy (-7.3 kcal/mol) indicates that the hydrogen-bond is beneficial to this step by pulling the substrate and catalyst together. Both the two paths are exergonic (-5.1 kcal/mol) owing to the formation of a highly stable six-membered ring. Moreover, the results show that the initial hydrogen-bonding path is kinetically more

favorable by 3.9 kcal/mol than the direct coordination path.

After the formation of complex **3**, one molecule of CH₃CN attacks the Pd center and binds to it by expelling the acetate group, meanwhile, the hydroxyl hydrogen transfers to the terminal oxygen atom of the acetate from MeOH through the transition state **TS2** ($\Delta G^\ddagger = 17.6$ kcal/mol). The resulting hydrogen-bonding complex **4H** undergoes dissociation to give palladium methoxide complex **4**. In the above proton transfer process, the opening of the stable six-membered ring (**3**→**TS2**→**4H**) needs comparatively high energy barriers. To search for other path, we explored the possibility that the acetate is directly substituted by the methanol in **2H** (see SI5). As shown in Figure 1, the **4H** can alternatively be formed by the substitution of oxygen atom of methanol for oxygen atom of acetate in **2H** via a six-centered transition state **TS2H-4H**. This process has an energy barrier of 16.6 kcal/mol. According to the above discussion of the deprotonation of MeOH, all three paths are energetically possible. **TS2** is more favored than **TS2H-4H** by +4.1 kcal/mol in free energy. [42] Therefore, the initial hydrogen-bonding path (**2**→**2H**→**TS1**→**3**→**TS2**→**4H**) is most favorable.

As shown in Figure 2, the NBO charges for some selected atoms of complex **2** shows that the O1 atom carries a relatively larger negative charge (-0.702) than the O2 atom (-0.653). Theoretically, the O1 atom could nucleophilically attack the hydroxyl hydrogen of methanol to form the hydrogen-bonding complex more easily than the O2 atom. But in fact, it is failed when we try to search the corresponding reaction path, in which the hydroxyl hydrogen transfers to the O1 atom. The four-membered ring intermediate and the corresponding transition state cannot be obtained. This can be explained by the reason that the six-centered transition state is more stable than the four-centered one.

3.1.2. β -H elimination from Pd-OMe

The β -H elimination takes place in intermediate **4** in three steps: (1) Agostic interaction between one of the methoxyl hydrogens and Pd center along with the leaving of CH_3CN ligand gives the four-numbered ring complex **5** with the barrier of 11.6 kcal/mol (via **TS3**); (2) Strong interaction between the Pd center and the hydride leads to Pd-H bond shortening and C-H bond breaking, which gives the complex **6** by only overcoming a small barrier of 3.7 kcal/mol (via **TS4**); (3) Formaldehyde is replaced by the solvent molecule. The intermediate **7** is easily oxidized by benzoquinone [15, 43] to form species **2**, which completes the catalytic cycle of step I.

In the first cycle (step I), the β -H elimination (**TS3**) is the rate-determining step and the total energy barrier is 22.7 kcal/mol from **3**. Overall, the process of step I is exergonic by 2.5 kcal/mol.

3.2. Step II: Further Oxidation of CH_2O

3.2.1. The pathway A, B and C

The first possible reaction pathway of the step II proposed by Pearson [15] is formic acid synthesis. However, experimental results provided no evidence for the buildup of labeled formic acid under standard conditions. In addition, we know nothing about the further detail of the mechanism. With reference to the relative reports [44-46], we therefore propose the conceivable mechanism involving a water molecule addition as shown in Figure S3, although the experiment is carried out under anhydrous conditions. This detailed mechanism is very helpful to us in understanding the experiments of alcohol/aldehyde oxidation to acid/ester [44, 45, 47, 48]. The second possible reaction pathway is CO insertion. CO formation is a

prerequisite for this pathway. The reaction mechanism of CO formation (see Figure S5) was studied to avoid catalyst poisoning caused by the strong affinity of CO to the catalysts on the heterogeneous electrode in the methanol fuel cell¹⁹. Previous experimental results [15] reveals that oxidation of CH₃OH under CO atmosphere has no detectable incorporation of CO into methyl formate. We therefore studied the reaction mechanism of methanol oxidation to form methyl formate in the presence of CO (see Figure S5). Moreover, the experiment studies [15] offered a strong argument against that the methyl formate was generated by the disproportionation of formaldehyde in neither Tishchenko (pathway **CT**) nor Cannizzaro type (pathway **CC**). The detailed mechanisms of pathways A, B and C were investigated. We hope this study could provide a reference for this kind of reaction through the pathway A, B or C [44-52]. These pathways A, B and C are shown in supporting information (see SI6).

3.2.2. Pathway D: Oxidation of Methoxymethanol to Methyl Formate

During the catalytic cycle, addition of small amounts of acid [15] could catalyze the formation of methoxymethanol at early reaction times. Then the methoxymethanol intermediate disappeared at later time. With reference to the mechanism of CH₂O formation in step I, we proposed two paths for the oxidation of methoxymethanol to methyl formate: initial hydrogen-bonding path and direct substitution path. The calculated potential energy profiles for these two paths are illustrated in Figure 3.

As shown in Figure 3, for the initial hydrogen-bonding path, the formation of methyl formate starts with the substitution of methoxymethanol for CH₃CN from a hydrogen-bonding complex **d1H**. The substitution reaction leads to **d2** via **TSd1**. Then further substitution reaction forms **d3H** via **TSd2**, and the subsequent hydrogen-bonding

breaking in this complex forms **d3**. **TSd2** is more favored than **TSd1H-d3H** by +4.6 kcal/mol in free energy. Similar to the case in step I, the initial hydrogen-bonding path ($\Delta G^\ddagger = 14.2$ kcal/mol, via **TSd2**) is more kinetically favorable than the direct substitution path ($\Delta G^\ddagger = 19.5$ kcal/mol, via **TSd1H-d3H**).

After deprotonation, a concerted reaction via **TSd3** ($\Delta G^\ddagger = 11.8$ kcal/mol) results in β -H transfer of Pd-OCH₂OCH₃, and leads to **ct2** containing methyl formate. Being different from the process **4**→**6** in step I, the corresponding four-membered ring intermediate is not observed. This may be ascribed to the steric hindrance effect of the side chain of methoxymethanol. This step is strongly exergonic ($\Delta G = -16.2$ kcal/mol) and irreversible. Then a substitution reaction forms complex **d5** and product methyl formate.

4. Further Discussion

4.1. Reaction Kinetics and Pathways

In step II, four pathways reveal four different mechanistic processes as well four rate-determining steps. Their rate-determining steps and energy barriers are respectively: substitution of HOAc by CH₃CN via **TSa3** and 21.5 kcal/mol in pathway **A**; hydrogen proton migration between two ligands via **TSb8** and 40.1 kcal/mol in pathway **B**; CH₂O addition via **TSct1** and 47.4 kcal/mol in pathway **CT**; substitution of HOAc by CH₂O via **TScc2** and 26.9 kcal/mol in pathway **CC**; substitution of methyl formate by CH₃CN via **TSd3** and 18.4 kcal/mol in pathway **D**. Moreover, the heat of formation of methyl formate respectively are: -19.1 kcal/mol for pathway **A**, -1.1 kcal/mol for pathway **B**, -18.2 kcal/mol for pathway **CT**, -12.2 kcal/mol for pathway **CC** and -19.4 kcal/mol for pathway **D**. Obviously, the above

results reveal that the oxidation of methoxymethanol to methyl formate (pathway **D**) is the most kinetically and thermodynamically favorable pathway for methyl formate formation catalyzed by $[(\text{dmp})\text{Pd}(\mu\text{-OAc})]_2(\text{OTf})_2$. This is completely consistent with the experimental results [15] of Pearson et al.

4.2. Roles of the Acid and the Catalyst

As mentioned in the pathway **D**, addition of acid can catalyze the formation of essential intermediate methoxymethanol which will form product by further catalytic oxidation. Therefore, small amount of acid are needed for pathway **D**. However, addition of acid can suppress the spontaneous deprotonation of alcohol. So it is unfavorable to the deprotonation of MeOH in step I and methoxymethanol in pathway **D**. As a complement, the catalyst complex **2** can catalyze deprotonation of the substrates, and further catalyze the oxidation of the intermediates to the products. Moreover, it is noteworthy that step I and pathway **D** have a similar catalytic reaction mechanism.

We observed several possible paths for the decomposition of MeOH (methoxymethanol) using complex **2** as the catalyst in step I (pathway **D**). In the most kinetically favorable pathway for deprotonation, the essential intermediate **4** (**d3**) can be obtained by the addition of MeOH (methoxymethanol) to **2** and the transfer of hydroxyl hydrogen in MeOH (methoxymethanol) to acetate ligand. After deprotonation, the subsequent steps consist of the transfer of $\beta\text{-H}$ to the Pd center and the substitution of CH_2O (methyl formate) by CH_3CN . As mentioned above, the key role of complex **2** in the reaction can be briefly described as the catalysis of deprotonation (**2** $\rightarrow$ **4** and **d1** $\rightarrow$ **d3**) and $\beta\text{-H}$ transfer (**4** $\rightarrow$ **6** and **d3** $\rightarrow$ **ct2**). In addition, the total barriers energy of 22.7 kcal/mol in step I and 18.4 kcal/mol in step II show

that the catalytic reactions can proceed experimentally.

4.3. Structural and Electronic Properties of Complex 2

In the catalytic process, the donation of hydroxyl hydrogen to one of the oxygen atoms of the acetate ligand and the subsequent transfer of β -H to Pd center lead to the leaving of CH_3CN from the Pd center. To show the reason why the catalyst has a good catalytic effect on the oxidative dehydrogenation of methanol, we have examined the structural and electronic properties of the complex **2**. As shown in Figure 4, the HOMO of **2** is mainly localized on the O atoms (p_z orbital) of acetate and Pd center (d_z orbital). This indicates that in the deprotonation step the O atoms can act as a nucleophile to attack the electron deficient hydroxyl hydrogen, facilitating the hydrogen proton transfer. The acetate acts as an electron donor to accept protons. Moreover, the LUMO of **2** is mainly localized on the Pd atom ($d_{x^2-y^2}$ orbital). This shows that in β -H transfer step the Pd atoms can act as electrophile to attract hydride ions, facilitating the hydride ion transfer. This indicates that the active sites of **2** are located at O atoms and Pd center. Furthermore, as shown in Figure 2, an NBO charge analysis also shows that the O2 atom carries a secondary larger negative charge ($Q = -0.653$) and the Pd center carries a most positive charge ($Q = 0.890$). So O2 atom attacks the hydroxyl hydrogen and the Pd center attracts the hydride ion more easily than the other atoms in **2**.

In addition, the acetonitrile ligand in **2** plays two distinct roles in the process of catalytic oxidation of methanol to methyl formate. The first one is that it can act as an excellent leaving group due to the loose binding between the $\text{N}_{\text{CH}_3\text{CN}}$ atom and the Pd center since the Pd-N bond (WBI = 0.304) is relatively weaker than the Pd-O1 bond (WBI = 0.442). The

second one is that it is a good substituent used to replace other ligands because its long linear structure is less steric hindrance to its neighbored methyl group of dmp ligand. As an example shown in Figure S4, the acetonitrile can substitute CO ligand better than water and formaldehyde.

4.4. Comparisons of Different Catalysts

For deeper understanding the three catalysts (complex **2**, **cat2** and **cat3**, see Figure S2), properties of the latter two catalysts and the corresponding catalytic mechanism were calculated.

As shown in Figure 4 and compared with the frontier molecular orbitals of **2**, the HOMO of **cat2** is also mainly localized on the oxygen atoms of two coordinated acetates. However, its LUMO is mainly contributed from the dmp moiety rather than the Pd center. Moreover, **cat2** is unable to afford an open coordination site or a good leaving group owing to the strong binding between the acetate oxygen and the Pd center. Because of these features, **cat2** could catalyze the deprotonation of alcohols only through the direct substitution path. To further testify the above results, we studied the key steps for the oxidation of methanol catalyzed by **cat2**. As shown in Figure 5, the deprotonation in the direct substitution path is a kinetically favorable process with an energy barrier of 16.2 kcal/mol (via **cat2TSa**). The corresponding transition states for the other two paths (initial hydrogen-bonding path and direct coordination path) in deprotonation step can not be located. It is noteworthy that the β -H transfer is changed into an endergonic process compared with the corresponding process catalyzed by complex **2**. In addition, the corresponding transition state **cat2TSb** can not be located because the acetate ligand is hardly substituted by the transferred β -H. We believe that the assumed

cat2TSb is extremely unstable, which leads to a high energy barrier. Therefore, the catalyst **cat2** has no catalytic effect on the methanol oxidation, which is consistent with the experimental results.

Again, compared with the frontier molecular orbitals of **2**, the LUMO of **cat3** is also mainly localized on the Pd center, but its HOMO is mainly contributed from dmp moiety. Therefore, **cat3** is able to catalyze β -H transfer through the same process (**4**→**7**) catalyzed by complex **2**, while the deprotonation can not be carried out due to the lack of a nucleophilic site. However, the spontaneous deprotonation of methanol in solution can proceed slowly, which results that **cat3** is slightly effective for methanol oxidation. These results agree with the experimental observation. All the above results further confirm the importance of CH₃CN and acetate ligand.

5. Conclusions

We have reported a DFT/B3LYP study on the palladium-catalyzed selective oxidation of methanol to methyl formate reaction. It is a systematic investigation on the transition metal-catalyzed oxidative esterification of alcohols to esters using theoretical methods. The calculations show that the oxidation reactions consist of two steps, the oxidative dehydrogenation of methanol to formaldehyde and the further oxidative esterification of formaldehyde to methyl formate. For the later step, four possible esterification pathways with different mechanisms have been considered in the calculations. As shown in the complete catalytic cycle (Scheme 3), the methoxymethanol oxidation pathway shows a kinetically and thermodynamically favorable. Each oxidation step proceeds with a deprotonation followed by

a β -H transfer, and the deprotonation can be accomplished through several processes in which the initial hydrogen-bonding path is most favorable. The acid plays a determinate role in the formation of methyl formate since it can act as a co-catalyst to promote the conversion of formaldehyde to methoxymethanol.

The studies on the structural and electronic properties of three catalysts (complex **2**, **cat2** and **cat3**) reveal that the spatial distribution of HOMO and LUMO of the catalyst significantly affects its catalytic activity. The HOMO should be localized on the acetate ligand to facilitate the deprotonation, while the LUMO should be localized on the Pd center to facilitate the β -H transfer. Comparative studies on these catalysts demonstrate that an acetate ligand and an excellent leaving group CH_3CN are two key factors ensuring the rapid dehydrogenation of alcohols.

In summary, this computational study provides a better understanding of the experimental results obtained by Person et al [14, 15]. And this study is expected to provide a useful reference for this type of catalytic reaction (oxidative esterification of alcohols/aldehyde).

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Appendix A. Supporting information

Supplementary data related to this article can be found online at

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Schemes

Scheme 1. The oxidative esterification of methanol to methyl formate catalyzed by $[(\text{dmp})\text{Pd}(\text{OAc})(\text{CH}_3\text{CN})]^+$ (**2**)

Scheme 2. Overview of the investigated mechanisms for the formation of methyl formate from methanol.

Scheme 3. A complete catalytic cycle of Pd-catalyzed oxidation of CH_3OH to HCOOCH_3 .

For the sake of clarity, trivial stationary points are omitted.

Figures

Figure 1. Free-energy profile (in kcal/mol) for step I and there path for the deprotonation of methanol.

Enthalpy values (in kcal/mol) are listed in the square brackets.

Figure 2. The NBO charges (in parentheses) for some selected atoms and the WBIs for some selected bonds (in square brackets) of complex **2**.

Figure 3. Mechanism and free-energy profile (in kcal/mol) for pathway **D**. Enthalpy values (in kcal/mol) are listed in the square brackets.

Figure 4. Spatial distribution of the HOMO (left) and the LUMO (right) for three catalysts (complex **2**, **cat2** and **cat3**).

Figure 5. (A) Potential energy profiles calculated for the deprotonation and β -H transfer catalyzed by **cat2**. The free energies are given in kcal/mol and enthalpy values (in kcal/mol) are listed in the square brackets.

(B) Optimized structures for the stationary points, together with the key bond lengths ($\text{\AA}$). The H atoms in the dmp ligand are omitted for clarity.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Computational Mechanistic Study on Oxidative Esterification of Alcohols to Esters Catalyzed by Palladium Complex

Wei Hu^a, Jing Li^a, Suwen deng^a, Jianyin Huang^b, Xueyi Le^a, Wenxu Zheng^{a,*}

^a College of Science, South China Agricultural University, Guangzhou 510642, China

^b Environmental Future Center, Griffith University, Gold Coast campus, Queensland 4215, Australia

Supporting Information

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SI1. Energetic results for some selected stationary points.

Table S1. Reaction free energies of B3LYP/BSII (PCM) optimization and B3LYP/BSII//B3LYP/BSI calculations for some selected stationary points (in kcal/mol).

	B3LYP/BSII (PCM)	B3LYP/BSII//B3LYP/BSI
2+ MeOH→ 2H	7.3	8.8
2+ MeOH→ TS1	14.9	17.4
2+ MeOH→ TS2-3a	19.2	21.2
2+ MeOH→ TS2H-4H	22.2	23.9

SI2. Free energy barriers and reaction heat

Table S2. Free energy barriers (in kcal/mol) for each elementary reaction and the reaction heat (in kcal/mol) of overall reaction for each pathway.

		B3LYP	B3LYP-D3 ^a
<i>Step I</i>	2+ HOCH ₃ →TS2-3a	21.2	15.0
	2+ HOCH ₃ →TS1	17.4	11.1
	2+ HOCH ₃ →TS2H-4H	23.9	16.6
	3a→TS3a-3	2.1	2.1
	3+ CH ₃ CN→TS2	21.3	17.6
	4→TS3	10.6	11.6
	5→TS4	4.0	3.6
	6+ CH ₃ CN→TS5	14.1	10.8
	reaction heat	-8.1	-2.5
<i>Pathway A</i>	2+ CH ₂ O→TSa1	20.6	15.7
	a1+ H ₂ O→TSa2	11.5	5.0
	a2+ CH ₃ CN→TSa3	11.5	8.2
	a3→TSa4	10.8	11.7
	a4+ CH ₃ CN→TSa5	15.0	11.8
	reaction heat	-23.9	-19.1
<i>CO formation</i>	6→TSb1	16.5	15.9
	b1→TSb2	5.6	5.4
	b2→TSb3	3.3	3.5
	b3+ CH ₃ CN→TSb4	23.4	20.4
	reaction heat	-8.9	-3.1
<i>Pathway B</i>	3+ CO→TSb5	22.6	19.4
	4+ CO→TSb5'	17.0	13.9
	b4→TSb6	4.1	4.3
	b5→TSb7	10.6	10.6
	b6+ HOAc→TSb8	36.9	30.9
	b7+ CH ₃ CN→TSb9	16.1	11.1
	reaction heat	-0.1	-1.1
<i>pathway CT</i>	a1+ CH ₂ O→TSct1	52.6	47.4
	6+ CH ₂ O→TSct2	51.8	49.2
	ct2+ CH ₃ CN→TSct3	15.6	16.2
	reaction heat	-25.1	-20.7
<i>pathway CC</i>	a1+ HOCH ₃ →TScc1	9.9	4.0
	cc1+ CH ₂ O→TScc2	23.5	17.4
	cc2→TScc3	6.6	7.2
	cc3+ CH ₃ CN→TScc4	17.2	13.8
	reaction heat	-12.3	-12.2

	2+MM→TSd1	21.0	12.9
	2+MM→TSd1H-d3H	27.1	19.5
<i>pathway D</i>	d2+ CH ₃ CN→TSd2	18.8	14.2
	d3→TSd3	12.0	12.2
	reaction heat	-25.7	-19.4

^a the dispersion contribution was computed independently and added to the B3LYP results

SI3. Optimized structures for the stationary points

Figure S1. Optimized structures for the stationary points, together with the key bond lengths (Å) and angles (°). The H atoms in the dmp ligand are omitted for clarity

SI4. Optimized structures of catalysts

Figure S2. Optimized structures of the $[(\text{dmp})\text{Pd}(\mu\text{-OAc})_2]^{2+}$ (**1**), $(\text{dmp})\text{Pd}(\text{OAc})_2$ (**cat2**) and $[(\text{dmp})\text{Pd}(\text{CH}_3\text{CN})_2]^{2+}$ (**cat3**), together with the key bond lengths (in angstroms) and angles (in degree). The corresponding parameters from the crystal structure are given in parentheses. All H atoms are omitted for clarity.

SI5. Possible mechanisms for the deprotonation of MeOH

Scheme S1. Three possible mechanisms for the deprotonation of MeOH

initial hydrogen-bonding path:

direct substitution path:

SI6. mechanisms for pathway A, B and C

Pathway A: Formation of HCOOH by Addition of H₂O

Figure S3. Mechanism and free-energy profile (in kcal/mol) for pathway **A**. Enthalpy values (in kcal/mol) are listed in the square brackets.

Figure S3 shows the calculated free energy profile for the pathway **A**. The HCOOH formation reaction starts with the substitution of CH₃CN ligand in complex **2** by CH₂O. This process needs to overcome an energy barrier of 15.7 kcal/mol (via **TSa1**) to afford **a1**. Then the addition of a water molecule to the intermediate **a1** leads to **a2** via a low-energy transition state **TSa2** ($\Delta G^\ddagger = 4.9$ kcal/mol). After via **TSa3**, the acetic acid is replaced by CH₃CN to afford **a3**. Then, the transfer of a β -H and the departure of CH₃CN ligand occur simultaneously and result in the formation of **a4** via the transition state **TSa4**. Finally, the free HCOOH is generated through

another substitution reaction via **TSa5**. The last two downhill processes have modest activation barriers (11.7 kcal/mol and 11.8 kcal/mol, respectively) and are consecutive highly exergonic (18.3 kcal/mol and 8.3 kcal/mol, respectively). The energy profile indicates that the rate-limiting step is **TSa** with an activation energy of 21.5 kcal/mol. Note that **TSa3** is the rate-determining step and the total energy barrier is +21.5 kcal/mol

Pathway B: Formation of Methyl Formate by CO Insertion

Formation of CO by Oxidative Dehydrogenation of CH_2O

Figure S4. Mechanism and free-energy profile (in kcal/mol) for CO formation. Enthalpy values (in kcal/mol) are listed in the square brackets.

As mentioned in step I, the CH_2O in **6** can be substituted by CH_3CN to give **7**. Alternatively, the CH_2O can also be retained in **6** to afford CO by oxidative dehydrogenation. Originally, we considered that the dehydrogenation could be completed by the two successive β -hydrogen eliminations in the intermediate **6**, like the process of **4**→**6** in step I. Unfortunately, the corresponding intermediates and transition states of this process cannot be found. This may be

due to the absence of an open coordination site on the metal complex or a substitutable ligand for the transferred hydride, which is an important prerequisite for β -hydrogen elimination. Therefore, we discuss another mechanism here, and the free energy profile for the generation of CO is shown in Figure S4. To form the important intermediate **b1** for the dehydrogenation, CH₂O ligand in **6** has to coordinate to the Pd center by one hydrogen atom through a four-centered transition state **TSb1**. This process has an energy barrier of 15.9 kcal/mol and is highly endergonic (14.6 kcal/mol). Thus the process **6**→**TS5**→**7** is more kinetically and thermodynamically favorable than the process **6**→**TSb1**→**b1**. This is agreement with the fact that no CO is observed but CH₂O is detected. Subsequently, the coordinated hydrogen of CH₂O transfers to the hydride along with the coordination of CH₂O carbon to the Pd center, leading to the η^2 -H₂ complex **b2** via **TSb2** ($\Delta G^\ddagger = 5.4$ kcal/mol). Following the three-centered transition state **TSb3**, an α -H replaces the H₂ to afford **b3**. The energy values show that the α -H transfer is easy and irreversible with a low barrier of 3.5 kcal/mol and a large energy release of 23.1 kcal/mol. Finally, three possible substitution patterns for the decooordination of CO in **b3** can be found. As can be seen from Figure S4, the most favorable pattern is substitution of CO by CH₃CN via **TSb4**, which requires a relatively lower energy barrier than other two patterns.

CO Insertion mechanism

Firstly, the insertion of CO to the six-membered ring complex **3** gives **b4** via **TSb5** ($\Delta G^\ddagger = 19.3$ kcal/mol). Then a three-membered ring intermediate **b5** is formed by the interaction of carbonyl carbon and methoxyl oxygen via **TSb6** with a low energy barrier of 4.3 kcal/mol. Our calculations indicate that the interaction between the p-type lone pair electrons of methoxyl oxygen and the empty d orbital of Pd leads to the stable η^2 -coordination complex **b5** in the CO insertion process. The coordinated ester group in **b5** rotates around the Pd-C bond via **TSb7** to

give the π -coordinated palladium-ester complex **b6** by only overcoming a small rotational barrier of 10.7 kcal/mol. Subsequently, intermediate **b7**, a complex involving methyl formate, is formed by the concerted protonation and substitution reaction. This process is completed via transition state **TSb8**, from which the hydrogen of HOAc is donated to the coordinated carbon and the acetate replaces the oxygen to coordinate to the Pd center. The rate limiting step of this pathway is found to be the ester protonation (**TSb8**) with a total energy barrier 40.1 kcal/mol (from **b5**). This implies that this process cannot be completed under the experimental conditions.

Figure S5. Mechanism and free-energy profile (in kcal/mol) for pathway **B**. Enthalpy values (in kcal/mol) are listed in the square brackets.

Pathway C: Disproportionation Reaction

Pathway CT: Tishchenko Type Disproportionation Mechanism

We observed two paths for the Tishchenko type disproportionation mechanism (pathway **CT**), and the potential-energy surfaces of these two paths are shown in Figure S6. As shown in the

figure, these two paths begin with **a1** and **6**, which respectively contains a methoxyl and a hydride as an ancillary ligand. Moreover, these two parallel paths are similar in the energy barriers and the reaction processes. Firstly, the oxygen atom of free CH_2O attacks carbon atom of CH_2O ligand simultaneously with intramolecular 1,3-hydrogen migration. This concerted reaction leads to the complex (**b7** or **ct2**) containing methyl formate via the four-centered transition state **TSct1** or **TSct2**. Then the CH_3CN replaces the methyl formate via **TSb9** or **TSct3**. This mechanism only needs two reaction steps to generate methyl formate with two continuous exergonic stages. It seems to be simple and easy in comparison with other mechanisms with multi-step reactions. Nevertheless, the predicted barriers of disproportionation process, 47.4 kcal/mol for **TSct1** and 49.2 kcal/mol for **TSct2**, are too high to be crossed at the ambient temperature.

Figure S6. Mechanism and free-energy profiles (in kcal/mol) for pathway **CT**. Enthalpy values (in kcal/mol) are listed in the square brackets. Two paths begin from **a1** (dashed line) and **6** (solid line), respectively.

Pathway CC: Cannizzaro Type Disproportionation Mechanism

We characterized another disproportionation process denoted as pathway **CC**, which is performed according to the Cannizzaro reaction mechanism. The correlative reaction mechanism and energy profile are illustrated in Figure S7. The reaction is initiated by the addition reaction of methanol with **a1** via TScc1. From the resulting complex **cc1**, an important intermediate for the following hydride transfer could be formed by a substitution reaction via a barrier of 17.4 kcal/mol (**TScc2**). The interligand hydride transfer in **cc2** gives **cc3** containing methoxyl and methyl formate via **TScc3**. The energies of **TScc3** and **cc3** in the transfer step, relative to **cc2**, 7.2 and -23.0 kcal/mol, respectively, indicates that the transfer of a hydride is kinetically and thermodynamically accessible. The substitution reaction in **cc3** affords the product methyl formate. The relatively high total energy barrier 26.9 kcal/mol restrain this Cannizzaro type reaction. total energy barrier 40.2 kcal/mol (from **b5**)

Figure S7. Mechanism and free-energy profile (in kcal/mol) for pathway **CC**. Enthalpy values (in kcal/mol) are listed in the square brackets.

SI7. The Cartesian coordinates of all the structures.

Table S4. Cartesian coordinates of all optimized geometries reported in this study

2				C	-1.846515	-3.460454	0.079290
C	-3.122908	2.804927	0.450663	C	-0.690275	-2.665325	0.289548
C	-2.032659	3.463068	-0.067673	N	-0.765020	-1.334261	0.146712
C	-3.114252	1.393172	0.524381	C	0.588828	-3.330987	0.697446
C	-1.937715	0.736216	0.099003	C	0.301249	3.420657	0.930050
C	-0.880770	2.747180	-0.478904	Pd	0.755893	0.073698	-0.043715
N	-0.834944	1.416210	-0.350559	H	-4.243935	3.287682	-0.109569
C	-4.234403	0.618913	0.969005	H	-2.157285	4.462088	0.552641
C	-4.200700	-0.743451	0.922743	H	-5.406670	1.083826	-0.605806
C	-3.045508	-1.432353	0.429195	H	-5.290677	-1.383126	-0.715592
C	-1.902038	-0.694626	0.053001	H	-3.932213	-3.505178	-0.411379
C	-2.990019	-2.834496	0.255035	H	-1.752294	-4.535556	0.181974
C	-1.878631	-3.399322	-0.321766	H	1.148227	-2.711929	1.400796
C	-0.757502	-2.609335	-0.686398	H	1.223368	-3.503409	-0.175731
N	-0.767265	-1.291922	-0.438676	H	0.366640	-4.293565	1.162961
C	0.400679	-3.264909	-1.377880	H	0.969588	2.772508	1.497685
C	0.279737	3.491233	-1.073630	H	0.027133	4.277298	1.550047
Pd	0.799739	0.073158	-0.410917	H	0.846522	3.802245	0.060287
H	-4.000930	3.355644	0.774917	N	2.238016	1.459000	-0.427863
H	-2.035724	4.542097	-0.174859	C	3.244984	1.990636	-0.619317
H	-5.118750	1.139934	1.321851	C	4.522868	2.650421	-0.838623
H	-5.058245	-1.329668	1.237547	H	4.442381	3.716112	-0.607245
H	-3.838713	-3.447626	0.543326	H	4.829594	2.530681	-1.881427
H	-1.836425	-4.465220	-0.516046	H	5.274823	2.196799	-0.186126
H	1.131243	-3.634142	-0.653253	O	2.135327	-1.265126	-0.630963
H	0.923947	-2.570577	-2.033066	C	3.167390	-1.382895	0.188100
H	0.035577	-4.116008	-1.958189	O	3.266958	-0.800558	1.261186
H	0.973792	3.814287	-0.290612	C	4.214269	-2.356399	-0.329942
H	-0.077524	4.386573	-1.587792	H	4.355743	-2.253924	-1.407958
H	0.829044	2.870820	-1.782005	H	3.882089	-3.382037	-0.135994
N	2.360312	1.400934	-0.170604	H	5.153438	-2.193374	0.200085
C	3.350501	1.868907	0.195564				
C	4.598496	2.437489	0.679332	2H			
H	4.471390	3.501011	0.898905	C	3.325661	-2.842846	-0.124911
H	5.381430	2.315914	-0.074323	C	2.112456	-3.440277	0.120068
H	4.890547	1.912426	1.593857	C	3.397179	-1.435449	-0.240709
O	2.223902	-1.341952	-0.339821	C	2.180341	-0.723723	-0.152025
C	2.797222	-1.465179	0.847849	C	0.921105	-2.673520	0.195678
O	2.519488	-0.786987	1.828867	N	0.971007	-1.349018	0.005741
C	3.841787	-2.571081	0.872499	C	4.625342	-0.716388	-0.402817
H	4.425795	-2.590114	-0.050139	C	4.638493	0.646998	-0.401838
H	3.341427	-3.540730	0.969569	C	3.426348	1.391732	-0.232006
H	4.492378	-2.433041	1.736879	C	2.194061	0.707324	-0.138793
				C	3.389500	2.799127	-0.110385
2'				C	2.193431	3.422366	0.151653
C	-3.311927	2.742227	0.005357	C	0.986057	2.684121	0.246646
C	-2.155853	3.394326	0.363864	N	0.998985	1.358027	0.049491
C	-3.293232	1.340237	-0.174399	C	-0.282565	3.403656	0.594269
C	-2.047024	0.690896	-0.023857	C	-0.381162	-3.348556	0.508342
C	-0.935516	2.686703	0.499713	Pd	-0.576183	0.034435	-0.307207
N	-0.890753	1.370955	0.260080	H	4.232518	-3.436008	-0.197079
C	-4.463806	0.566051	-0.461138	H	2.041634	-4.512890	0.261848
C	-4.399543	-0.794476	-0.521935	H	5.547633	-1.279712	-0.503681
C	-3.161959	-1.481088	-0.299420	H	5.571450	1.192382	-0.503055
C	-1.979930	-0.738081	-0.086846	H	4.308623	3.371991	-0.190371
C	-3.054268	-2.889388	-0.240067	H	2.149027	4.495709	0.297200

H	-0.900887	2.805026	1.265234
H	-0.868394	3.603685	-0.306112
H	-0.044872	4.353012	1.078346
H	-1.032759	-2.693203	1.092828
H	-0.189977	-4.266742	1.069051
H	-0.895628	-3.631394	-0.416267
N	-2.054881	-1.258212	-0.970565
C	-3.043281	-1.755693	-1.299040
C	-4.298613	-2.378249	-1.689977
H	-4.281511	-3.443750	-1.444729
H	-4.457948	-2.257553	-2.765003
H	-5.117801	-1.898458	-1.146326
O	-1.869562	1.480660	-0.865044
C	-3.032786	1.570283	-0.267593
O	-3.412484	0.875094	0.678173
C	-3.907839	2.673967	-0.837795
H	-3.764174	2.781307	-1.914443
H	-3.635272	3.624014	-0.364918
H	-4.953240	2.467504	-0.604998
O	-1.922093	-0.928534	2.150374
C	-1.906451	-0.594959	3.531471
H	-2.529790	-0.317055	1.684981
H	-2.887985	-0.743035	4.001599
H	-1.189569	-1.255338	4.027156
H	-1.592982	0.443691	3.708126

TS2-3a

C	3.289436	-2.787067	0.248400
C	2.085067	-3.448451	0.207807
C	3.319082	-1.384508	0.090176
C	2.079228	-0.728415	-0.097960
C	0.872221	-2.741681	0.020232
N	0.888926	-1.407895	-0.125864
C	4.530765	-0.622388	0.106239
C	4.504576	0.726236	-0.086140
C	3.266807	1.410769	-0.308557
C	2.050875	0.689413	-0.293140
C	3.192623	2.797381	-0.571281
C	1.973319	3.362703	-0.845039
C	0.783859	2.588441	-0.821130
N	0.834128	1.289501	-0.502908
C	-0.504242	3.262697	-1.185499
C	-0.425932	-3.491523	-0.016367
Pd	-0.735347	-0.095280	-0.136493
H	4.217457	-3.331289	0.396860
H	2.040332	-4.525420	0.321535
H	5.469414	-1.143570	0.265562
H	5.422788	1.305152	-0.085574
H	4.099778	3.394171	-0.580304
H	1.891291	4.416005	-1.089736
H	-0.864194	3.852703	-0.335618
H	-1.276324	2.546945	-1.458076
H	-0.329259	3.953570	-2.014865
H	-1.140062	-3.062647	0.690409
H	-0.259558	-4.542199	0.226920
H	-0.870023	-3.432669	-1.014022
N	-2.429290	-1.375800	-1.124362
C	-3.359761	-1.606694	-1.773278
C	-4.531984	-1.900099	-2.588602
H	-4.229058	-2.092335	-3.621566
H	-5.216766	-1.047701	-2.571606
H	-5.049180	-2.781264	-2.199073
O	-2.292929	1.158152	0.037295

C	-2.254206	1.977884	1.074973
O	-1.299540	2.087286	1.836517
C	-3.525250	2.800232	1.213451
H	-3.499934	3.355211	2.151560
H	-4.410020	2.158743	1.178577
H	-3.604105	3.502381	0.377173
O	-1.807260	-1.253642	1.879342
C	-1.357343	-0.930899	3.210856
H	-2.681607	-0.862954	1.747623
H	-2.033891	-1.358775	3.958687
H	-0.374284	-1.390573	3.326087
H	-1.270170	0.150186	3.343979

3a

O	1.871413	-2.380748	0.098940
C	1.940521	-2.863872	-1.275166
H	2.748490	-2.030435	0.346650
H	2.641907	-3.700646	-1.313039
H	2.243306	-2.059233	-1.948071
H	0.941236	-3.211297	-1.533713
C	-3.830971	-1.604654	-0.379358
C	-3.035984	-2.630074	0.072844
C	-3.309726	-0.290209	-0.434899
C	-1.958679	-0.121215	-0.060150
C	-1.683930	-2.398157	0.434731
N	-1.161337	-1.171783	0.318700
C	-4.083040	0.852665	-0.816166
C	-3.545503	2.105333	-0.761633
C	-2.198617	2.307720	-0.318885
C	-1.396826	1.191512	0.003246
C	-1.618929	3.586774	-0.147949
C	-0.350340	3.687869	0.365995
C	0.411447	2.531057	0.678190
N	-0.102636	1.316104	0.450260
C	1.771054	2.709595	1.284309
C	-0.866641	-3.535552	0.976226
Pd	0.837109	-0.531591	0.383955
O	2.781482	0.042563	0.406984
C	3.210208	0.491215	-0.771680
C	4.674116	0.888734	-0.756976
O	2.495179	0.569160	-1.762290
H	-4.862076	-1.787400	-0.667143
H	-3.427298	-3.637398	0.165915
H	-5.111189	0.703853	-1.130320
H	-4.137649	2.973863	-1.031986
H	-2.191109	4.475786	-0.395862
H	0.099750	4.657639	0.547627
H	2.479704	3.050071	0.520628
H	2.155676	1.790222	1.718078
H	1.721949	3.490277	2.049075
H	-1.407019	-4.002535	1.806170
H	0.110507	-3.214012	1.328356
H	-0.727821	-4.310764	0.214183
H	4.972598	1.222485	-1.750572
H	5.295727	0.043641	-0.446477
H	4.840564	1.688590	-0.029298

TS3a-3

C	3.720644	-1.749994	0.359813
C	2.904948	-2.701044	-0.206287
C	3.254810	-0.420012	0.493921
C	1.926422	-0.166208	0.089735
C	1.578350	-2.382849	-0.596931

N 1.098256 -1.152466 -0.382992
 C 4.062719 0.662391 0.970542
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 C 2.276269 2.234421 0.461465
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 N 0.169709 1.383618 -0.440452
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 Pd -0.870296 -0.421720 -0.377878
 O -2.720366 0.383883 -0.339765
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 H 2.379179 4.396489 0.607795
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 H -2.290203 2.159462 -1.211122
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 H -0.283312 -3.096858 -1.444923
 H 1.187636 -3.592539 -2.297244
 H -5.300787 0.857550 1.621705
 H -4.403374 2.204640 0.884879
 H -5.199636 1.027451 -0.161104
 H -1.851901 -2.346745 2.064244
 H -2.163276 -3.909327 1.220160
 H -0.523378 -3.209740 1.218942

TS1

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 C 3.402080 -1.460540 -0.228836
 C 2.207588 -0.718406 -0.077359
 C 0.924750 -2.655909 0.297333
 N 0.998683 -1.322537 0.168807
 C 4.635359 -0.780898 -0.485008
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 C 3.489875 2.768351 -0.379429
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 N 1.080988 1.405041 0.041940
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 C -0.380804 -3.345632 0.555275
 Pd -0.565249 0.033043 0.088146
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 H 2.005226 -4.517297 0.276446
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 H 5.612048 1.097915 -0.740230
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 H 2.302133 4.525790 -0.094204
 H -0.691392 3.070045 1.227650

H -0.792404 3.590133 -0.442873
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 H -0.203695 -4.266244 1.116720
 H -0.839846 -3.622023 -0.400598
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 H -4.447019 -1.555699 -3.236064
 H -5.024724 -1.318137 -1.562491
 O -1.933743 1.477449 -0.247092
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 H -2.822925 -0.867830 3.643733
 H -1.049533 -0.909654 3.521457
 H -1.928705 0.588736 3.130671

TS2H-4H

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 C 3.645508 1.208658 0.083090
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 C 1.309679 2.719377 0.384609
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 H -3.947712 -0.698239 3.215686
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 H -1.029978 -0.877345 -3.384378
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 H -2.742359 -1.352183 -3.340778

3

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 H -4.803956 2.110070 -0.615968
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 H -2.636389 -3.309118 1.666194
 H -0.974231 -2.710284 1.914488

TS2

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 C 4.002232 -2.122178 0.217131
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 N -1.969147 0.967021 1.557255
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 H -4.119094 2.756558 3.034197
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4H

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 C -3.668494 -0.989139 -0.027631
 C -2.349983 -0.484807 0.016928
 C -3.821649 -2.394020 0.027167
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 C -1.409006 -2.622055 0.248389
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 C 0.790238 3.124362 0.730997
 Pd 0.480013 -0.153813 -0.324796
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 C 3.442994 -0.436683 1.712652

O	3.779383	-1.265174	0.728348
C	4.537568	-0.275042	2.739000
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C	1.711899	-2.047952	-2.183253
H	-3.801862	3.891725	0.323481
H	-1.462429	4.633698	0.711235
H	-5.418285	1.953386	-0.026257
H	-5.777264	-0.488941	-0.153105
H	-4.814702	-2.830634	-0.024721
H	-2.806174	-4.261252	0.285424
H	-0.414030	-4.518734	0.184076
H	0.686318	-3.101325	0.160550
H	-0.144180	-3.577231	1.652491
H	1.393797	2.318771	1.153698
H	1.266497	3.475286	-0.190922
H	0.772999	3.964429	1.429945
H	5.497408	-0.087700	2.250547
H	4.291482	0.535537	3.424072
H	4.641250	-1.207375	3.303556
H	2.445386	-2.858692	-2.290396
H	0.738325	-2.426331	-2.526322
H	2.999679	-1.410532	0.109226
H	2.013579	-1.226165	-2.848346
N	2.007562	1.006850	-1.186507
C	2.969059	1.403123	-1.689813
C	4.188247	1.898667	-2.312807
H	4.082092	1.890457	-3.401136
H	4.390950	2.920338	-1.979784
H	5.026895	1.256424	-2.028616

4

C	-2.130479	3.395928	-0.224934
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C	-2.508167	2.036433	-0.301330
C	-1.505884	1.072354	-0.038601
C	0.112287	2.710460	0.386963
N	-0.216136	1.419185	0.265606
C	-3.843553	1.613137	-0.598463
C	-4.174083	0.291445	-0.572988
C	-3.194166	-0.702812	-0.252306
C	-1.853202	-0.321274	-0.021056
C	-3.506111	-2.075216	-0.118301
C	-2.529463	-2.952188	0.283194
C	-1.196741	-2.516108	0.504048
N	-0.873245	-1.231594	0.292172
C	-0.191704	-3.511765	1.004636
C	1.506003	3.089231	0.798018
Pd	1.017849	-0.337899	0.137744
N	2.919208	0.463307	-0.116209
C	4.059267	0.615167	-0.227662
C	5.495987	0.806394	-0.363125
O	1.972933	-2.041187	-0.103652
C	2.147129	-2.398751	-1.451153
H	-2.865319	4.169883	-0.426106
H	-0.543234	4.760196	0.234944
H	-4.590293	2.368306	-0.822671
H	-5.190840	-0.030272	-0.775317
H	-4.521076	-2.416943	-0.298806
H	-2.757118	-4.000050	0.444345
H	0.283497	-4.039366	0.172376
H	0.604268	-3.037437	1.573353
H	-0.706892	-4.252072	1.622715
H	2.174525	3.095765	-0.069210

H	1.512992	4.090571	1.233594
H	1.905358	2.382453	1.527194
H	5.848285	1.531791	0.375556
H	6.006415	-0.147062	-0.199570
H	5.731519	1.171576	-1.366689
H	2.702090	-3.349251	-1.458915
H	2.739314	-1.670539	-2.029057
H	1.198002	-2.566219	-1.988091

TS3

C	2.336739	3.189742	-0.010022
C	1.082230	3.576142	0.407728
C	2.616289	1.820172	-0.217351
C	1.562160	0.907162	0.017921
C	0.070264	2.612566	0.626890
N	0.324383	1.314509	0.424542
C	3.893466	1.327915	-0.641470
C	4.100843	-0.008242	-0.814916
C	3.050198	-0.954846	-0.578876
C	1.778317	-0.498732	-0.163436
C	3.212729	-2.349337	-0.738254
C	2.151984	-3.188358	-0.491030
C	0.895863	-2.675980	-0.078678
N	0.735243	-1.353879	0.078145
C	-0.249366	-3.606357	0.176088
C	-1.298529	3.013173	1.097401
Pd	-0.994526	-0.295885	0.664941
O	-2.274515	-1.743123	1.047475
C	-3.141680	-0.898017	1.690598
H	3.115205	3.928092	-0.178200
H	0.852063	4.621908	0.577005
H	4.692630	2.040544	-0.819409
H	5.069138	-0.380843	-1.134154
H	4.172856	-2.747009	-1.053718
H	2.255787	-4.261142	-0.606468
H	-0.649099	-3.468750	1.183261
H	-1.077965	-3.396394	-0.506537
H	0.066037	-4.642306	0.044978
H	-1.497469	2.599223	2.092716
H	-1.386521	4.098980	1.161698
H	-2.064682	2.635637	0.413863
H	-4.114722	-0.788018	1.190456
H	-2.709046	0.181443	1.644676
H	-3.250207	-1.098609	2.765870
N	-2.791670	0.736022	-1.131153
C	-3.445713	0.688655	-2.087885
C	-4.273536	0.629874	-3.287753
H	-3.716496	1.012593	-4.147243
H	-4.568206	-0.404080	-3.487297
H	-5.174214	1.234678	-3.151072

5

C	2.995867	-2.301695	-0.000079
C	1.923953	-3.167376	0.000078
C	2.770860	-0.906672	-0.000104
C	1.424939	-0.474520	0.000053
C	0.599583	-2.671690	0.000195
N	0.376424	-1.351388	0.000173
C	3.822906	0.066793	-0.000294
C	3.537970	1.400264	-0.000317
C	2.181414	1.864096	-0.000139
C	1.125252	0.926295	0.000069
C	1.824415	3.231939	-0.000162

C	0.496025	3.588297	0.000087
C	-0.524366	2.603990	0.000355
N	-0.190536	1.305068	0.000296
C	-1.967011	3.006863	0.000665
C	-0.575478	-3.608601	0.000487
Pd	-1.462369	-0.354563	0.000002
H	4.012913	-2.682391	-0.000204
H	2.078937	-4.240164	0.000099
H	4.851399	-0.279816	-0.000426
H	4.335950	2.136027	-0.000467
H	2.601095	3.991001	-0.000363
H	0.202893	4.631785	0.000100
H	-2.484835	2.603866	0.875268
H	-2.484601	2.605908	-0.875037
H	-2.058312	4.093644	0.001877
H	-1.196399	-3.452232	0.889139
H	-0.244886	-4.648307	-0.001150
H	-1.198613	-3.450092	-0.886205
O	-3.304031	0.401184	-0.000867
C	-3.754730	-0.870035	-0.000527
H	-4.263569	-1.198936	-0.917774
H	-2.778099	-1.614897	-0.000494
H	-4.263460	-1.198416	0.916970

TS4

C	1.796484	3.286480	0.001641
C	0.466978	3.635764	0.006781
C	2.160408	1.921156	-0.001015
C	1.109745	0.971088	0.001390
C	-0.536185	2.636039	0.008623
N	-0.205567	1.339176	0.005414
C	3.524628	1.486829	-0.005994
C	3.829378	0.160164	-0.007898
C	2.792874	-0.828690	-0.004636
C	1.432590	-0.432924	-0.000104
C	3.070670	-2.212141	-0.005572
C	2.033959	-3.114584	-0.001233
C	0.691280	-2.671766	0.003482
N	0.414301	-1.357033	0.003497
C	-0.413894	-3.688851	0.008411
C	-1.986510	3.024292	0.014558
Pd	-1.450002	-0.471190	0.000861
O	-3.441154	0.372624	-0.065786
C	-4.154931	-0.632844	0.022730
H	2.571310	4.047512	-0.000196
H	0.166812	4.677426	0.009274
H	4.308843	2.237299	-0.008200
H	4.861847	-0.174392	-0.011725
H	4.101860	-2.552620	-0.009412
H	2.227789	-4.180619	-0.001421
H	-0.002129	-4.699438	0.018536
H	-1.050317	-3.565873	0.889713
H	-1.043864	-3.581685	-0.879697
H	-2.094046	4.109947	0.017839
H	-2.500856	2.624976	-0.863768
H	-2.493333	2.621259	0.895779
H	-4.341212	-1.123361	0.990502
H	-4.688080	-1.024639	-0.858792
H	-2.161283	-1.837091	-0.011103

6

C	1.574581	3.399868	-0.001453
C	0.223866	3.655091	0.006179

C	2.032962	2.063872	-0.004221
C	1.051876	1.040346	-0.000042
C	-0.703089	2.585339	0.010093
N	-0.285583	1.314667	0.005970
C	3.425364	1.731436	-0.010294
C	3.825467	0.430973	-0.010759
C	2.863485	-0.630332	-0.005237
C	1.476648	-0.338091	-0.000607
C	3.246380	-1.988098	-0.003617
C	2.281683	-2.966239	0.003353
C	0.909195	-2.626730	0.007612
N	0.530857	-1.336742	0.004623
C	-0.110513	-3.729943	0.015553
C	-2.178138	2.871105	0.019320
Pd	-1.403762	-0.615624	-0.000418
O	-3.411634	0.066740	-0.019542
C	-4.455696	-0.573911	-0.017661
H	2.294519	4.213033	-0.004697
H	-0.149187	4.672996	0.009413
H	4.152325	2.537526	-0.014037
H	4.879422	0.171881	-0.014891
H	4.300738	-2.248207	-0.007299
H	2.556276	-4.014391	0.005608
H	0.383616	-4.703029	0.024006
H	-0.753338	-3.658770	0.897555
H	-0.751058	-3.673307	-0.869275
H	-2.362182	3.946511	0.029900
H	-2.663053	2.444648	-0.862974
H	-2.654857	2.428777	0.898267
H	-4.467593	-1.671126	-0.002062
H	-5.413617	-0.035479	-0.032011
H	-1.987225	-2.019891	-0.005400

TS5

C	2.149756	3.321973	0.201726
C	0.824658	3.639619	0.013156
C	2.546853	1.966769	0.236130
C	1.534418	0.990025	0.060826
C	-0.135962	2.613580	-0.154175
N	0.227866	1.327515	-0.134993
C	3.905716	1.565243	0.443043
C	4.239072	0.246312	0.484694
C	3.240730	-0.768803	0.321355
C	1.887458	-0.408266	0.101737
C	3.550682	-2.144135	0.374427
C	2.547399	-3.071331	0.222208
C	1.212924	-2.658847	0.001555
N	0.904897	-1.354284	-0.063401
C	0.140203	-3.697396	-0.162263
C	-1.586153	2.948213	-0.355984
Pd	-0.973158	-0.504753	-0.442600
O	-2.551613	0.314429	-1.959553
C	-3.365495	-0.300247	-2.625306
H	2.895447	4.101347	0.329576
H	0.499069	4.673596	-0.010277
H	4.661657	2.334150	0.569170
H	5.267123	-0.062944	0.645253
H	4.577227	-2.457521	0.539748
H	2.762568	-4.132620	0.266651
H	0.550461	-4.699056	-0.020674
H	-0.664252	-3.540518	0.561666
H	-0.300690	-3.639995	-1.162337
H	-1.752072	4.024130	-0.277683

H	-1.926933	2.608831	-1.337960
H	-2.202604	2.436601	0.388620
H	-3.495288	-1.389566	-2.529197
H	-4.003395	0.227455	-3.353080
H	-1.612294	-1.861832	-0.660907
N	-2.919045	-0.030654	1.093438
C	-3.649157	-0.123771	1.989176
C	-4.569405	-0.237973	3.115633
H	-5.431336	0.417584	2.964127
H	-4.920647	-1.269322	3.208579
H	-4.064044	0.049047	4.041828

7

C	1.636448	3.463710	0.001221
C	0.273741	3.647553	-0.003220
C	2.164669	2.154058	0.002591
C	1.239021	1.079506	-0.000048
C	-0.592945	2.529391	-0.005754
N	-0.110331	1.282843	-0.003772
C	3.572867	1.895149	0.006057
C	4.040618	0.617538	0.006210
C	3.136032	-0.493343	0.002979
C	1.735679	-0.275447	0.000406
C	3.590127	-1.829026	0.002123
C	2.677382	-2.855891	-0.001732
C	1.289255	-2.586459	-0.003937
N	0.841886	-1.319063	-0.002291
C	0.325534	-3.739089	-0.008131
C	-2.082233	2.730423	-0.011165
Pd	-1.145216	-0.705551	0.000453
H	2.312429	4.313796	0.003253
H	-0.152161	4.644489	-0.004904
H	4.256480	2.738373	0.008281
H	5.106878	0.414523	0.008560
H	4.656762	-2.033131	0.004117
H	3.006105	-3.888428	-0.002993
H	-0.318369	-3.710468	0.875753
H	-0.320175	-3.702642	-0.890342
H	0.865867	-4.687390	-0.012769
H	-2.331673	3.792875	-0.019676
H	-2.529806	2.261454	-0.892137
H	-2.534620	2.274870	0.874420
H	-1.654328	-2.134011	0.005317
N	-3.150408	-0.315776	0.005834
C	-4.305607	-0.267090	0.006001
C	-5.760243	-0.203687	0.006751
H	-6.095553	0.733554	-0.446149
H	-6.165596	-1.042862	-0.565862
H	-6.132393	-0.259469	1.033761

TSa1

C	-3.519478	-2.552253	-0.353398
C	-2.355289	-3.273755	-0.463416
C	-3.458019	-1.161968	-0.114366
C	-2.172828	-0.578633	-0.009222
C	-1.092686	-2.642133	-0.347215
N	-1.026154	-1.318533	-0.132875
C	-4.624407	-0.344566	0.026259
C	-4.508341	0.989573	0.274381
C	-3.220375	1.602914	0.397864
C	-2.047512	0.824830	0.247329
C	-3.055392	2.976624	0.678605
C	-1.788408	3.487399	0.807097

C	-0.645506	2.663102	0.644059
N	-0.786837	1.360592	0.355741
C	0.709279	3.285659	0.786646
C	0.155792	-3.466744	-0.444416
Pd	0.683903	-0.150720	-0.024510
H	-4.485696	-3.039539	-0.445039
H	-2.379972	-4.342609	-0.641670
H	-5.599887	-0.811783	-0.064091
H	-5.389922	1.612536	0.387741
H	-3.928102	3.611423	0.799573
H	-1.633811	4.535691	1.035377
H	1.133842	3.474659	-0.205554
H	1.396488	2.631080	1.321326
H	0.627435	4.241152	1.307708
H	0.883056	-3.013987	-1.118872
H	-0.086090	-4.472024	-0.793032
H	0.632391	-3.542432	0.537254
N	2.012425	-1.640786	1.402613
C	2.892125	-1.886167	2.115026
C	4.002376	-2.195833	3.007808
H	3.626074	-2.439007	4.005172
H	4.669695	-1.332558	3.080034
H	4.566379	-3.049227	2.621569
O	2.368306	0.925437	0.116499
C	2.821316	1.579469	-0.923133
O	2.239095	1.680338	-2.008468
C	4.181131	2.212095	-0.680437
H	4.952549	1.441016	-0.781783
H	4.255208	2.624275	0.328165
H	4.361155	2.986771	-1.426552
O	1.850336	-1.187414	-1.863570
C	1.787525	-0.502961	-2.880803
H	2.652596	-0.424572	-3.556804
H	0.861329	-0.013448	-3.209096

al

C	-3.769414	-1.675433	-0.481265
C	-2.978589	-2.689694	0.004389
C	-3.264653	-0.354721	-0.517956
C	-1.929658	-0.168459	-0.096047
C	-1.645186	-2.439363	0.416558
N	-1.132996	-1.206938	0.315957
C	-4.042107	0.779049	-0.920368
C	-3.530236	2.040393	-0.834236
C	-2.203984	2.261379	-0.339659
C	-1.392611	1.154925	-0.008663
C	-1.656719	3.546778	-0.118198
C	-0.416556	3.661946	0.461171
C	0.356867	2.515088	0.779388
N	-0.117777	1.297457	0.483137
C	1.671673	2.696549	1.478756
C	-0.824087	-3.561514	0.983455
Pd	0.863269	-0.522043	0.373164
O	2.698015	0.295153	0.298404
C	3.185821	0.398645	-0.921137
O	2.616500	-0.029697	-1.926344
C	4.524657	1.110268	-0.979221
H	-4.786816	-1.872489	-0.805999
H	-3.361622	-3.700918	0.086371
H	-5.055532	0.615442	-1.272740
H	-4.128474	2.901203	-1.115601
H	-2.235451	4.430128	-0.371263
H	-0.001832	4.636515	0.693832

H	2.470972	2.906929	0.762103
H	1.961552	1.810176	2.038781
H	1.597411	3.552004	2.155580
H	-1.472346	-4.245729	1.536534
H	-0.044067	-3.195102	1.649755
H	-0.346875	-4.139892	0.185027
H	5.119863	0.696395	-1.795077
H	5.064125	1.038444	-0.033659
H	4.352173	2.169573	-1.200297
O	1.786251	-2.424584	0.164067
C	2.495102	-2.782700	-0.773876
H	2.708572	-2.109408	-1.613637
H	2.915354	-3.798714	-0.746444

TSa2

C	3.768781	-2.009768	0.543469
C	2.874465	-2.957813	0.107769
C	3.399896	-0.645094	0.522426
C	2.083483	-0.345850	0.108976
C	1.564596	-2.599684	-0.304555
N	1.178468	-1.317561	-0.242982
C	4.293929	0.423870	0.854434
C	3.912725	1.724995	0.702824
C	2.608326	2.053237	0.210578
C	1.683816	1.018288	-0.044525
C	2.188745	3.372584	-0.082592
C	0.953448	3.578105	-0.646416
C	0.065878	2.495080	-0.876363
N	0.421685	1.256686	-0.524679
C	-1.242358	2.758592	-1.560330
C	0.649240	-3.664193	-0.832442
Pd	-0.729720	-0.470158	-0.280261
O	-2.637110	0.385788	-0.051089
C	-2.812568	1.340816	0.889666
O	-1.882995	1.877203	1.453165
C	-4.268277	1.688300	1.133767
O	-1.669640	-2.252477	-0.034029
C	-2.763798	-2.365547	0.669694
H	-3.140956	-3.393551	0.727707
H	-2.810982	-1.842786	1.636283
O	-3.946224	-1.619885	-0.160547
H	-4.797058	-1.645407	0.308569
H	4.765499	-2.294212	0.867616
H	3.154641	-4.004361	0.063673
H	5.291235	0.176069	1.203883
H	4.600933	2.533317	0.928883
H	2.858224	4.206017	0.108382
H	0.629427	4.574490	-0.926611
H	-1.052446	3.265998	-2.512175
H	-1.795963	1.842081	-1.752253
H	-1.857863	3.427824	-0.951411
H	0.042961	-4.090699	-0.028650
H	-0.040192	-3.267635	-1.576544
H	1.246027	-4.465294	-1.274815
H	-4.332970	2.483477	1.875455
H	-4.745757	2.007945	0.202528
H	-4.817055	0.814682	1.502548
H	-3.505841	-0.595085	-0.175709

a2

C	-3.726127	-2.057320	-0.604387
C	-2.829913	-2.988403	-0.138463
C	-3.379603	-0.686719	-0.579904

C	-2.079435	-0.363915	-0.133924
C	-1.536399	-2.609242	0.307410
N	-1.168832	-1.321384	0.244961
C	-4.283403	0.365344	-0.938673
C	-3.930336	1.673822	-0.781985
C	-2.645329	2.026419	-0.257068
C	-1.709449	1.008750	0.025868
C	-2.255849	3.354215	0.041524
C	-1.039395	3.584673	0.636653
C	-0.141852	2.516683	0.896131
N	-0.465845	1.271505	0.538826
C	1.143455	2.796817	1.616890
C	-0.626943	-3.658879	0.872740
Pd	0.723563	-0.452139	0.330892
O	2.671697	0.455683	0.074686
C	2.936621	1.412069	-0.889617
O	2.048467	2.109504	-1.301914
C	4.390170	1.493872	-1.283264
O	1.649857	-2.208472	0.127962
C	2.745480	-2.348168	-0.644991
H	2.989187	-3.416814	-0.742492
H	2.658876	-1.897662	-1.650024
O	3.896937	-1.699320	0.025476
H	4.727670	-1.949116	-0.405547
H	-4.709068	-2.359065	-0.953974
H	-3.095013	-4.038885	-0.094781
H	-5.266821	0.098175	-1.312431
H	-4.627248	2.468571	-1.028606
H	-2.934862	4.174835	-0.170297
H	-0.740912	4.587962	0.920695
H	0.923655	3.320781	2.553097
H	1.688550	1.883476	1.848023
H	1.780622	3.451776	1.015560
H	0.008963	-4.084078	0.091897
H	0.037297	-3.248856	1.631878
H	-1.231233	-4.460918	1.303403
H	4.501254	2.211139	-2.095149
H	4.990528	1.814327	-0.425368
H	4.762087	0.514793	-1.599491
H	3.369497	-0.302180	0.126753

TSa3

C	3.714097	2.448116	-0.547178
C	2.624864	3.281388	-0.528266
C	3.537533	1.072561	-0.278171
C	2.217649	0.621213	-0.034793
C	1.321684	2.776016	-0.282730
N	1.132600	1.465605	-0.075467
C	4.631078	0.150871	-0.227914
C	4.423091	-1.158434	0.085965
C	3.106600	-1.637635	0.375106
C	2.003701	-0.755008	0.304350
C	2.844393	-2.974269	0.754135
C	1.560014	-3.352877	1.051386
C	0.488963	-2.428102	0.958392
N	0.725645	-1.165392	0.583258
C	-0.899769	-2.901123	1.262071
C	0.180678	3.750910	-0.260922
Pd	-0.677700	0.317602	0.157153
O	-2.152541	-1.124984	-1.174278
C	-1.751928	-1.997517	-2.148236
O	-0.809830	-2.727123	-1.951495
C	-2.595903	-1.990522	-3.402898

O	-1.991561	1.750853	-0.261005
C	-2.406909	1.900560	-1.549082
H	-2.801112	2.920135	-1.682052
H	-1.627339	1.716582	-2.303257
O	-3.465510	0.969040	-1.925777
H	-4.236585	1.172372	-1.375290
H	4.709506	2.834604	-0.745210
H	2.736147	4.346284	-0.700536
H	5.629906	0.521460	-0.435779
H	5.251979	-1.857638	0.133468
H	3.663346	-3.684732	0.816677
H	1.334916	-4.368946	1.355451
H	-0.871693	-3.639938	2.067439
H	-1.561649	-2.085550	1.543427
H	-1.303260	-3.384281	0.366930
H	-0.151620	3.963438	-1.284782
H	-0.675540	3.366775	0.287606
H	0.520267	4.697291	0.168199
H	-2.093864	-2.571659	-4.175387
H	-3.567854	-2.448503	-3.188285
H	-2.784948	-0.971934	-3.752706
H	-2.817851	-0.447898	-1.502566
N	-2.130092	0.084272	2.182913
C	-2.750794	0.435299	3.096106
C	-3.534619	0.876632	4.244155
H	-3.860844	1.909872	4.096910
H	-4.415246	0.239539	4.363556
H	-2.930537	0.820881	5.153803

a3

C	-2.322901	3.376619	-0.378601
C	-1.064590	3.785233	-0.003734
C	-2.634021	1.998500	-0.389737
C	-1.594476	1.100011	-0.051035
C	-0.066705	2.835759	0.324226
N	-0.329610	1.525467	0.260001
C	-3.938576	1.493239	-0.694003
C	-4.203477	0.159584	-0.600747
C	-3.186055	-0.764787	-0.198666
C	-1.873047	-0.304154	0.043014
C	-3.434043	-2.141265	0.010558
C	-2.426389	-2.940387	0.487120
C	-1.121763	-2.425972	0.714786
N	-0.858353	-1.141279	0.438766
C	-0.085992	-3.345471	1.284828
C	1.292180	3.307614	0.756016
Pd	0.981793	-0.164558	0.247234
N	2.825547	0.734365	-0.060931
C	3.949436	0.968414	-0.192148
C	5.365885	1.264714	-0.350821
O	2.062696	-1.824267	0.154171
C	2.284509	-2.306346	-1.107701
O	1.060143	-2.771855	-1.680479
H	-3.087737	4.102332	-0.639090
H	-0.816577	4.839395	0.050572
H	-4.715302	2.195963	-0.978587
H	-5.197466	-0.223984	-0.808737
H	-4.425515	-2.544255	-0.174045
H	-2.603960	-3.987976	0.703066
H	0.408846	-3.882325	0.470766
H	0.684582	-2.807364	1.831511
H	-0.575605	-4.071561	1.939509
H	1.975853	3.350927	-0.098375

H	1.223956	4.312441	1.178572
H	1.721967	2.638373	1.502649
H	5.632044	2.147228	0.237682
H	5.957123	0.412354	-0.003935
H	5.592260	1.453561	-1.403954
H	2.994433	-3.147079	-0.992770
H	2.741962	-1.558375	-1.785615
H	1.241008	-3.088726	-2.576495

TSa4

C	2.936568	-2.915942	0.107954
C	1.718553	-3.480595	-0.198930
C	3.051398	-1.511701	0.214932
C	1.876953	-0.753301	0.002447
C	0.579610	-2.667085	-0.404342
N	0.678811	-1.337114	-0.294456
C	4.279357	-0.838527	0.518872
C	4.325264	0.521342	0.601884
C	3.148903	1.312978	0.390010
C	1.922445	0.676389	0.091227
C	3.138839	2.723744	0.465709
C	1.963267	3.405918	0.257417
C	0.760303	2.714884	-0.034410
N	0.763901	1.377017	-0.116448
C	-0.512212	3.475741	-0.248148
C	-0.751006	-3.268601	-0.752644
Pd	-0.851618	0.061175	-0.515673
O	-2.323456	1.328465	-0.939870
C	-3.178357	0.393165	-1.380555
O	-4.311829	0.247611	-0.575108
H	3.811498	-3.539859	0.264897
H	1.613289	-4.555602	-0.290499
H	5.172326	-1.434171	0.679928
H	5.256177	1.030566	0.830814
H	4.057772	3.257455	0.689715
H	1.933441	4.488054	0.313336
H	-0.345083	4.543651	-0.101453
H	-0.902610	3.307796	-1.255149
H	-1.290499	3.134723	0.438991
H	-1.496003	-3.001701	0.002477
H	-1.100278	-2.894874	-1.721845
H	-0.681193	-4.355792	-0.814505
H	-3.447345	0.510868	-2.445069
H	-2.569803	-0.626381	-1.360946
N	-2.202194	-1.071616	1.423566
C	-3.151830	-0.734902	1.999750
C	-4.347972	-0.294718	2.704064
H	-4.962534	-1.155619	2.981338
H	-4.075025	0.253026	3.609974
H	-4.917847	0.358603	2.037937
H	-5.043694	-0.074149	-1.119206

a4

C	3.496272	-1.992769	-0.000603
C	2.529989	-2.969398	0.000125
C	3.114949	-0.634739	-0.000682
C	1.728323	-0.340797	-0.000134
C	1.158125	-2.627717	0.000678
N	0.780589	-1.337689	0.000431
C	4.078037	0.425584	-0.001235
C	3.679221	1.726458	-0.001127
C	2.287202	2.060506	-0.000474
C	1.305185	1.038105	-0.000044

C	1.829739	3.396855	-0.000185
C	0.479295	3.652699	0.000544
C	-0.449572	2.583962	0.000911
N	-0.032023	1.313073	0.000556
C	-1.923652	2.872048	0.001788
C	0.136730	-3.729469	0.001561
Pd	-1.151061	-0.612184	0.000206
O	-3.155458	0.086141	-0.000159
C	-4.191093	-0.568137	-0.001950
O	-5.351149	0.055011	-0.001376
H	4.550297	-2.254251	-0.001058
H	2.802950	-4.018005	0.000301
H	5.131736	0.165351	-0.001700
H	4.407068	2.531798	-0.001501
H	2.550279	4.209526	-0.000508
H	0.106834	4.670827	0.000835
H	-2.105230	3.947954	0.001951
H	-2.407181	2.436856	-0.876700
H	-2.406085	2.436804	0.880875
H	-0.505081	-3.662988	0.884641
H	-0.504838	-3.664604	-0.881834
H	0.629435	-4.703381	0.002493
H	-4.204715	-1.665307	-0.003994
H	-1.743986	-2.014627	0.000024
H	-6.092284	-0.571527	-0.002980

TSa5

C	2.240659	3.364519	0.092848
C	0.894065	3.644556	0.075051
C	2.676707	2.021177	0.067241
C	1.677971	1.016692	0.012725
C	-0.051814	2.592194	0.025229
N	0.348226	1.317106	-0.011370
C	4.061460	1.657974	0.099072
C	4.434253	0.349029	0.087200
C	3.452150	-0.693526	0.038968
C	2.072305	-0.370954	-0.006782
C	3.804651	-2.059439	0.037575
C	2.816481	-3.014258	0.000096
C	1.454213	-2.638965	-0.049341
N	1.103452	-1.343642	-0.060891
C	0.398552	-3.706802	-0.090345
C	-1.524192	2.886268	0.016107
Pd	-0.830839	-0.544555	-0.186102
O	-2.597852	0.268287	-1.500614
C	-3.378315	-0.357881	-2.189261
H	2.974488	4.164457	0.130959
H	0.539196	4.668825	0.099699
H	4.805482	2.447674	0.136596
H	5.482556	0.068672	0.115664
H	4.852135	-2.344178	0.070814
H	3.065120	-4.069162	0.005621
H	0.850896	-4.697375	-0.012759
H	-0.313162	-3.578565	0.729870
H	-0.165759	-3.653895	-1.026549
H	-1.707612	3.957006	0.121750
H	-1.983698	2.536187	-0.911982
H	-2.022650	2.356021	0.832466
H	-3.386081	-1.457247	-2.240666
H	-1.458697	-1.916053	-0.345010
O	-4.283434	0.269960	-2.931794
N	-2.568183	-0.147277	1.569114
C	-3.200515	-0.225481	2.537347

C	-3.997792	-0.319623	3.755729
H	-4.801630	0.421365	3.736271
H	-4.437432	-1.317302	3.839258
H	-3.367392	-0.136218	4.630140
H	-4.826377	-0.362862	-3.426935

TSb1

C	-3.858278	-0.856486	0.047420
O	-3.848565	-0.207185	1.070400
C	1.140923	3.532996	0.022658
C	-0.228155	3.620768	-0.074130
C	1.762941	2.263403	0.055226
C	0.918611	1.128707	-0.010070
C	-1.014394	2.445039	-0.138148
N	-0.438823	1.239209	-0.099763
C	3.181842	2.097025	0.149163
C	3.733465	0.852201	0.171544
C	2.908729	-0.317391	0.102151
C	1.501033	-0.187731	0.013649
C	3.444249	-1.623297	0.117083
C	2.601816	-2.707006	0.043991
C	1.200960	-2.529938	-0.043079
N	0.682579	-1.291322	-0.053939
C	0.311858	-3.737377	-0.121554
C	-2.507582	2.525031	-0.271207
Pd	-1.321240	-0.765922	-0.131157
H	1.751930	4.429422	0.073651
H	-0.722802	4.585048	-0.102129
H	3.807337	2.982593	0.200703
H	4.808611	0.721405	0.241243
H	4.519239	-1.761612	0.184509
H	2.995712	-3.716320	0.051785
H	-0.369480	-3.772573	0.734221
H	-0.292490	-3.714853	-1.033340
H	0.907936	-4.651361	-0.124564
H	-3.001769	1.825264	0.408460
H	-2.866722	3.532492	-0.053687
H	-2.808262	2.282249	-1.298059
H	-3.320243	-0.488225	-0.885450
H	-1.723217	-2.235499	-0.164165
H	-4.414612	-1.799035	-0.075405

b1

C	-3.766536	-1.054565	0.412649
O	-4.068938	-0.265178	1.256882
C	0.832913	3.600381	0.025585
C	-0.532935	3.568002	-0.134024
C	1.561543	2.390471	0.087052
C	0.823587	1.185746	-0.012222
C	-1.208918	2.328153	-0.228747
N	-0.533412	1.176442	-0.158506
C	2.984806	2.350811	0.238710
C	3.644106	1.160247	0.279634
C	2.930076	-0.077332	0.172845
C	1.520657	-0.073997	0.031142
C	3.579821	-1.330117	0.200492
C	2.841922	-2.484270	0.087075
C	1.435220	-2.432074	-0.052529
N	0.807709	-1.245054	-0.073888
C	0.661758	-3.713407	-0.175491
C	-2.697371	2.277005	-0.418477
Pd	-1.236954	-0.905307	-0.218359
H	1.360207	4.546841	0.101032

H	-1.107881	4.485333	-0.189401
H	3.525973	3.288422	0.317213
H	4.723048	1.125118	0.391677
H	4.659554	-1.371962	0.308988
H	3.324896	-3.454053	0.103092
H	-0.049024	-3.817611	0.649920
H	0.096012	-3.736582	-1.111579
H	1.337502	-4.570026	-0.158455
H	-3.171620	1.688887	0.373234
H	-3.129495	3.278839	-0.404295
H	-2.942823	1.819963	-1.383952
H	-3.063238	-0.738054	-0.477730
H	-1.520824	-2.400864	-0.287424
H	-4.174856	-2.068734	0.301715

TSb2

C	-3.457190	-0.880228	0.240786
O	-3.818821	-0.654939	1.352000
C	0.540515	3.630079	0.029039
C	-0.808093	3.490583	-0.195359
C	1.354662	2.479053	0.109416
C	0.716553	1.220340	-0.015738
C	-1.383572	2.203651	-0.315576
N	-0.635211	1.098600	-0.199421
C	2.773563	2.553614	0.292710
C	3.532077	1.423481	0.319823
C	2.925320	0.135030	0.168737
C	1.521253	0.026291	0.016515
C	3.673590	-1.062390	0.152750
C	3.031405	-2.266452	-0.020111
C	1.624757	-2.314071	-0.159554
N	0.903778	-1.184607	-0.127096
C	0.936909	-3.637756	-0.341947
C	-2.856043	2.081419	-0.585914
Pd	-1.222937	-1.029508	-0.085119
H	0.989477	4.614055	0.127136
H	-1.449083	4.360083	-0.286301
H	3.230919	3.532243	0.398850
H	4.608462	1.478498	0.447817
H	4.752735	-1.021725	0.267762
H	3.591240	-3.193995	-0.049482
H	0.354964	-3.896981	0.549582
H	0.255900	-3.609388	-1.197018
H	1.666483	-4.432091	-0.508217
H	-3.405649	1.833844	0.328058
H	-3.255691	3.023944	-0.964707
H	-3.050137	1.309732	-1.335645
H	-2.540918	-2.000885	0.077135
H	-1.525393	-2.577563	0.032506
H	-4.051878	-0.716730	-0.675852

b2

C	-2.953991	-1.316563	0.553017
O	-3.257111	-0.863014	1.612244
C	-0.357140	3.575053	-0.019472
C	-1.611616	3.129098	-0.356749
C	0.699708	2.647804	0.119715
C	0.392990	1.274091	-0.043257
C	-1.862619	1.744767	-0.503823
N	-0.889034	0.847028	-0.295728
C	2.044841	3.061846	0.386571
C	3.056000	2.151948	0.437672
C	2.793948	0.761420	0.220653

C	1.468481	0.310246	-0.002280
C	3.820765	-0.209839	0.198323
C	3.512206	-1.524909	-0.060432
C	2.166620	-1.906091	-0.276276
N	1.181603	-1.005007	-0.226131
C	1.825252	-3.343405	-0.562912
C	-3.234581	1.300191	-0.925874
Pd	-1.043920	-1.289383	-0.010299
H	-0.160329	4.635250	0.109678
H	-2.426563	3.825994	-0.517372
H	2.240531	4.119673	0.530823
H	4.077772	2.465854	0.626518
H	4.848901	0.095287	0.369773
H	4.288757	-2.280361	-0.104216
H	1.460738	-3.846100	0.341036
H	1.053840	-3.417176	-1.333510
H	2.705753	-3.889978	-0.905883
H	-3.898984	1.188323	-0.062886
H	-3.680733	2.049953	-1.583916
H	-3.193160	0.355239	-1.471165
H	-1.152817	-3.094362	-0.201288
H	-1.030607	-3.010072	0.583319
H	-3.669048	-1.809891	-0.141348

TSb3

C	-3.174301	-1.104628	0.116991
O	-4.069514	-0.571239	0.673829
C	0.473215	3.629167	0.053000
C	-0.874581	3.472197	-0.157777
C	1.306734	2.490876	0.112646
C	0.692105	1.218673	-0.008595
C	-1.436161	2.178505	-0.278439
N	-0.666123	1.086368	-0.169554
C	2.726976	2.598029	0.268045
C	3.516150	1.488824	0.267643
C	2.937722	0.188829	0.114607
C	1.533081	0.043846	-0.005936
C	3.717508	-0.990298	0.064192
C	3.107200	-2.210038	-0.113390
C	1.698257	-2.282154	-0.221480
N	0.949252	-1.179531	-0.151157
C	1.015614	-3.609788	-0.402982
C	-2.905955	2.043027	-0.544864
Pd	-1.256819	-1.015461	0.023443
H	0.909029	4.618934	0.152396
H	-1.529779	4.332008	-0.237487
H	3.160031	3.587783	0.373498
H	4.593217	1.571863	0.373471
H	4.797590	-0.919273	0.153637
H	3.690781	-3.122180	-0.172956
H	0.846584	-4.095527	0.566093
H	0.051171	-3.493473	-0.904763
H	1.631928	-4.286472	-1.000077
H	-3.447366	1.739338	0.355149
H	-3.318609	2.995070	-0.882682
H	-3.092660	1.293460	-1.318015
H	-1.321638	-2.883955	1.391790
H	-1.322832	-2.267031	1.831628
H	-3.260931	-2.067672	-0.487681

b3

C	-3.278917	-0.681665	-0.001101
O	-4.416574	-0.671106	-0.001901

C	1.016172	3.552460	-0.000095
C	-0.358228	3.601554	0.000501
C	1.671696	2.301162	-0.000312
C	0.857147	1.141994	0.000018
C	-1.114647	2.406031	0.000815
N	-0.508020	1.212664	0.000505
C	3.098551	2.178668	-0.000793
C	3.688744	0.951957	-0.000836
C	2.895671	-0.241086	-0.000408
C	1.482282	-0.156146	-0.000045
C	3.469237	-1.531360	-0.000277
C	2.655474	-2.639516	0.000260
C	1.248377	-2.498674	0.000578
N	0.689946	-1.276933	0.000346
C	0.385208	-3.728481	0.001180
C	-2.616556	2.471138	0.001473
Pd	-1.370596	-0.818889	-0.000059
H	1.604038	4.465644	-0.000355
H	-0.879249	4.552026	0.000742
H	3.697338	3.083925	-0.001090
H	4.769690	0.854504	-0.001163
H	4.550043	-1.637760	-0.000556
H	3.078624	-3.637023	0.000444
H	1.001210	-4.629128	0.002087
H	-0.258452	-3.751955	0.885902
H	-0.257732	-3.753295	-0.884042
H	-3.028424	1.982194	-0.886934
H	-3.027736	1.980587	0.889297
H	-2.960182	3.506594	0.002512
H	-1.783903	-2.296919	-0.000635

TSb4

C	-1.962438	3.411671	0.010585
C	-0.632238	3.663958	0.256047
C	-2.404317	2.080546	-0.156802
C	-1.427254	1.056468	-0.073661
C	0.291326	2.594992	0.328491
N	-0.110322	1.331793	0.154529
C	-3.776979	1.746718	-0.392593
C	-4.160974	0.447666	-0.525869
C	-3.202714	-0.614063	-0.434905
C	-1.833253	-0.320187	-0.216220
C	-3.568290	-1.972118	-0.551235
C	-2.604173	-2.946671	-0.444360
C	-1.250993	-2.597333	-0.228209
N	-0.888193	-1.310496	-0.125290
C	-0.214549	-3.678705	-0.116220
C	1.744119	2.856654	0.606662
Pd	1.077038	-0.533847	0.151975
H	-2.679931	4.224958	-0.048296
H	-0.276084	4.678046	0.398264
H	-4.503499	2.550690	-0.457223
H	-5.201117	0.190418	-0.699719
H	-4.608238	-2.235509	-0.719918
H	-2.864932	-3.995524	-0.525354
H	-0.675536	-4.665438	-0.187689
H	0.527644	-3.584408	-0.915487
H	0.314702	-3.611719	0.839094
H	1.917941	3.913452	0.816357
H	2.084402	2.267855	1.463914
H	2.358003	2.565276	-0.250425
H	1.696338	-1.910443	0.054879
N	2.982233	0.043910	-0.868504

C	3.982256	0.119673	-1.446171
C	5.241545	0.218521	-2.173052
H	5.070461	0.666867	-3.155669
H	5.948468	0.838205	-1.614466
H	5.670367	-0.778641	-2.306431
C	1.868748	-0.604983	2.277681
O	1.906538	-1.223800	3.233897

TSb4w

C	-1.586935	3.422212	0.092435
C	-0.234601	3.667828	0.042826
C	-2.058999	2.090747	0.064897
C	-1.089781	1.060901	-0.028058
C	0.681805	2.592465	-0.042362
N	0.248087	1.328068	-0.087159
C	-3.451640	1.764812	0.132904
C	-3.860004	0.466412	0.122254
C	-2.907857	-0.600874	0.038451
C	-1.522451	-0.313959	-0.046890
C	-3.295423	-1.957700	0.041139
C	-2.335738	-2.939184	-0.030233
C	-0.965457	-2.601995	-0.119564
N	-0.584691	-1.314624	-0.135556
C	0.057805	-3.698542	-0.198910
C	2.161002	2.853078	-0.059156
Pd	1.361554	-0.569104	-0.317088
H	-2.297932	4.240637	0.157774
H	0.147310	4.682115	0.070303
H	-4.172413	2.573798	0.198501
H	-4.914043	0.213974	0.179960
H	-4.348518	-2.214948	0.105025
H	-2.613081	-3.986723	-0.021722
H	-0.420742	-4.676170	-0.119473
H	0.597494	-3.654694	-1.150290
H	0.792391	-3.605060	0.606027
H	2.367353	3.919720	-0.162130
H	2.614489	2.510359	0.878505
H	2.648061	2.314155	-0.874262
H	1.925543	-1.963008	-0.533010
C	2.688678	-0.496472	1.623990
O	2.507351	-0.825793	2.700136
O	3.279290	0.118566	-1.426275
H	4.055246	-0.136050	-0.906532
H	3.368066	-0.333977	-2.276868

TSb4f

C	-2.018922	3.290016	0.054256
C	-0.692164	3.648633	0.108884
C	-2.373152	1.924139	-0.016759
C	-1.315884	0.980838	-0.045452
C	0.315878	2.655426	0.082707
N	-0.005080	1.360006	-0.006352
C	-3.734167	1.480495	-0.049943
C	-4.028745	0.152234	-0.093197
C	-2.985647	-0.830016	-0.110091
C	-1.627488	-0.425700	-0.097295
C	-3.254803	-2.215143	-0.134034
C	-2.211875	-3.110691	-0.133596
C	-0.872708	-2.656636	-0.124693
N	-0.603488	-1.341736	-0.117843
C	0.245060	-3.659716	-0.124589
C	1.765654	3.038659	0.167053
Pd	1.280539	-0.427940	-0.181623

H	-2.799445	4.045012	0.073535
H	-0.400793	4.690739	0.175346
H	-4.524084	2.224834	-0.033232
H	-5.058950	-0.189026	-0.111555
H	-4.283845	-2.561896	-0.145996
H	-2.398087	-4.178203	-0.142412
H	-0.150269	-4.674975	-0.060815
H	0.837154	-3.576654	-1.041625
H	0.916463	-3.493550	0.722545
H	1.876467	4.117926	0.283193
H	2.242226	2.546486	1.021001
H	2.306332	2.723079	-0.728626
H	1.974409	-1.764977	-0.372745
C	4.132610	-0.061149	-1.589284
C	2.405835	-0.327330	1.936465
O	2.265171	-0.857708	2.935018
O	3.123460	0.476082	-1.162049
H	4.303869	-1.143640	-1.493088
H	4.907810	0.540850	-2.087824

TSb5

C	2.816998	3.187385	-0.085250
C	1.519678	3.626599	-0.174728
C	3.080185	1.799675	-0.050488
C	1.967540	0.925399	-0.092158
C	0.440426	2.708155	-0.204936
N	0.675584	1.388753	-0.153472
C	4.406385	1.265632	0.003809
C	4.613840	-0.080541	-0.029288
C	3.510215	-0.986752	-0.118866
C	2.185727	-0.489998	-0.118658
C	3.679170	-2.385718	-0.237664
C	2.576116	-3.182357	-0.405192
C	1.266934	-2.631396	-0.406152
N	1.090918	-1.318324	-0.202308
C	0.118677	-3.549207	-0.705739
C	-0.959990	3.240757	-0.267405
Pd	-0.691234	-0.188646	0.128481
O	-1.899212	-1.727885	0.528304
C	-1.793312	-2.320832	1.809787
H	3.642687	3.892108	-0.054358
H	1.292888	4.685777	-0.220389
H	5.241980	1.956413	0.054846
H	5.619158	-0.489105	-0.006460
H	4.678688	-2.810075	-0.226221
H	2.677806	-4.252595	-0.549117
H	0.137783	-4.415534	-0.036297
H	-0.842045	-3.048396	-0.619139
H	0.242670	-3.935065	-1.724686
H	-1.636871	2.566396	-0.788634
H	-1.347064	3.393444	0.748402
H	-0.963155	4.216119	-0.759292
H	-2.446794	-3.202928	1.821690
H	-0.768596	-2.656743	2.016526
H	-2.109332	-1.651624	2.621341
O	-2.616120	0.733953	-0.908391
C	-3.710429	0.174351	-1.118161
O	-4.019986	-0.999169	-0.638528
C	-4.776949	0.814455	-1.961890
H	-3.221519	-1.363710	-0.107925
H	-5.730352	0.799656	-1.427280
H	-4.500372	1.835380	-2.221497
H	-4.909097	0.226207	-2.875647

C	-1.887239	0.972095	2.011327
O	-2.708560	1.232197	2.749160

TSb5'

C	-2.382282	3.244252	0.107421
C	-1.118540	3.584520	0.530571
C	-2.685065	1.895135	-0.179033
C	-1.640838	0.948069	-0.033563
C	-0.113938	2.596685	0.653671
N	-0.380133	1.319164	0.349518
C	-3.987348	1.465858	-0.591127
C	-4.242909	0.146783	-0.811900
C	-3.219607	-0.839103	-0.631911
C	-1.910912	-0.447176	-0.257761
C	-3.460003	-2.221359	-0.793300
C	-2.447992	-3.115426	-0.545393
C	-1.158073	-2.667588	-0.160554
N	-0.904361	-1.355497	-0.057343
C	-0.097280	-3.683164	0.142694
C	1.248576	2.973255	1.163299
Pd	0.999950	-0.296536	0.187657
O	2.076384	-1.874817	-0.220561
C	3.358864	-1.922705	0.339566
H	-3.154621	4.000545	0.002491
H	-0.871991	4.611505	0.775169
H	-4.765802	2.212348	-0.713205
H	-5.231444	-0.184171	-1.114755
H	-4.446690	-2.564639	-1.090152
H	-2.617042	-4.182628	-0.633720
H	-0.546031	-4.674602	0.226077
H	0.667183	-3.692939	-0.637145
H	0.421166	-3.439702	1.071716
H	1.376486	4.057182	1.149320
H	1.369936	2.638317	2.200096
H	2.041279	2.513530	0.572088
H	3.967288	-1.032617	0.118919
H	3.350870	-2.073905	1.431771
H	3.866734	-2.787203	-0.113821
N	2.502984	0.855228	-1.117509
C	3.209027	1.117786	-1.996729
C	4.104269	1.440456	-3.100265
H	4.173173	0.585693	-3.779053
H	3.723239	2.304320	-3.651656
H	5.101591	1.672413	-2.716361
C	1.608977	-0.201533	2.445941
O	1.255864	-0.368123	3.515260

b4

C	-2.586365	-2.877395	-0.068421
C	-1.391414	-3.453224	0.282522
C	-2.670941	-1.470289	-0.194440
C	-1.481031	-0.733219	-0.001938
C	-0.227715	-2.662383	0.474388
N	-0.278157	-1.336738	0.277032
C	-3.897313	-0.786530	-0.475644
C	-3.945701	0.575242	-0.504379
C	-2.768516	1.351256	-0.255591
C	-1.531780	0.700258	-0.032021
C	-2.775362	2.762812	-0.194338
C	-1.615355	3.436988	0.108623
C	-0.406601	2.731671	0.318236
N	-0.377179	1.396074	0.216798
C	0.845686	3.488821	0.659441

C	1.024294	-3.322575	0.967233
Pd	1.301565	0.087660	0.097778
O	2.850803	-1.167622	-0.116350
C	3.001371	-1.682300	-1.427648
C	2.842545	1.246193	-0.176495
O	3.811406	1.811697	-0.353027
H	-3.473049	-3.485036	-0.223567
H	-1.311165	-4.524861	0.427743
H	-4.792176	-1.376818	-0.645656
H	-4.879008	1.094317	-0.697743
H	-3.701609	3.303413	-0.365118
H	-1.607411	4.517740	0.192174
H	1.481358	3.614549	-0.224476
H	1.419449	2.976448	1.435184
H	0.598299	4.487874	1.022983
H	0.904695	-3.534454	2.037713
H	1.902751	-2.692908	0.830552
H	1.172347	-4.284117	0.467705
H	2.126956	-2.259220	-1.764495
H	3.863853	-2.361634	-1.392994
H	3.217584	-0.907574	-2.176760

TSb6

C	2.717821	2.866171	-0.003737
C	1.491654	3.470022	0.137746
C	2.798834	1.455004	-0.073289
C	1.582619	0.739238	-0.008368
C	0.305485	2.694440	0.193513
N	0.368727	1.360963	0.104194
C	4.036262	0.743285	-0.190171
C	4.055058	-0.619474	-0.221742
C	2.838779	-1.371787	-0.135893
C	1.601547	-0.693576	-0.035386
C	2.802117	-2.783663	-0.135588
C	1.594093	-3.433027	-0.028519
C	0.385357	-2.703853	0.071379
N	0.408219	-1.362220	0.058651
C	-0.919197	-3.436555	0.194416
C	-1.022672	3.376579	0.343573
Pd	-1.230888	-0.063110	0.097308
O	-3.089351	0.868043	0.180958
C	-3.681313	1.386223	-1.023280
C	-2.929057	-0.963072	0.100771
O	-3.863222	-1.637354	0.076854
H	3.626447	3.459200	-0.050685
H	1.408474	4.548878	0.210270
H	4.959270	1.311543	-0.246992
H	4.992842	-1.159419	-0.305177
H	3.727804	-3.346219	-0.212907
H	1.546987	-4.515665	-0.017435
H	-1.561816	-3.243140	-0.669571
H	-1.459118	-3.128560	1.094073
H	-0.747702	-4.512243	0.252196
H	-0.932239	4.227018	1.024584
H	-1.791183	2.699330	0.716109
H	-1.351472	3.775134	-0.624123
H	-2.959287	1.947895	-1.623755
H	-4.483717	2.057989	-0.702197
H	-4.116812	0.588871	-1.635491

b5

C	-3.190972	-2.525267	-0.129637
C	-2.083614	-3.317741	0.066736

C	-3.052816	-1.117034	-0.174165
C	-1.747171	-0.595113	-0.019227
C	-0.805093	-2.725561	0.212385
N	-0.663338	-1.400550	0.162894
C	-4.157891	-0.225599	-0.355367
C	-3.964171	1.123359	-0.353858
C	-2.656498	1.681560	-0.173810
C	-1.537401	0.827940	-0.024993
C	-2.424644	3.073909	-0.116260
C	-1.154289	3.540456	0.118501
C	-0.066454	2.644692	0.265348
N	-0.265986	1.322185	0.153511
C	1.297883	3.183788	0.563537
C	0.418223	-3.577103	0.405569
Pd	1.167220	-0.222976	0.108029
O	3.416598	-0.758190	0.017845
C	4.701349	-1.139324	-0.572134
C	2.959251	0.509050	-0.195528
O	3.581107	1.460652	-0.560099
H	-4.175644	-2.969020	-0.243979
H	-2.173310	-4.397673	0.112979
H	-5.151179	-0.643767	-0.484468
H	-4.800826	1.803353	-0.479543
H	-3.255649	3.762762	-0.235963
H	-0.958572	4.603480	0.197894
H	1.961597	3.093691	-0.300116
H	1.760168	2.629537	1.384373
H	1.234495	4.236217	0.844058
H	0.217357	-4.394105	1.104170
H	1.256005	-2.992154	0.794061
H	0.724307	-4.029592	-0.545165
H	4.555542	-1.377958	-1.626953
H	5.036085	-2.011907	-0.015176
H	5.386963	-0.299184	-0.454873

TSb7

C	-3.748673	-1.826465	-0.024348
C	-2.853268	-2.868455	0.055465
C	-3.281808	-0.490376	-0.042314
C	-1.880600	-0.293947	0.017901
C	-1.465459	-2.598645	0.108974
N	-1.015672	-1.343765	0.087263
C	-4.159464	0.638001	-0.110439
C	-3.656867	1.903760	-0.099309
C	-2.245073	2.136984	-0.019850
C	-1.342475	1.045153	0.025732
C	-1.699288	3.438656	0.032673
C	-0.341292	3.601175	0.156305
C	0.517488	2.475796	0.199467
N	0.016683	1.237261	0.106248
C	1.994028	2.690379	0.358924
C	-0.457145	-3.712565	0.164204
H	-4.816906	-2.017598	-0.067993
H	-3.195383	-3.897385	0.077397
H	-5.229675	0.465212	-0.164619
H	-4.318206	2.763426	-0.142614
H	-2.360067	4.299567	-0.007286
H	0.096927	4.590226	0.223943
H	2.508142	2.568064	-0.598988
H	2.414147	1.973743	1.069328
H	2.193056	3.698708	0.726272
H	-0.252414	-4.097730	-0.841872
H	-0.822519	-4.548155	0.766721

H	0.487822	-3.369798	0.600092
Pd	1.050369	-0.669376	-0.048127
O	3.649335	-0.569121	0.610240
C	5.098079	-0.568913	0.391168
C	2.902837	-0.125037	-0.401676
O	3.274049	0.338192	-1.449428
H	5.346008	-1.258347	-0.417321
H	5.527386	-0.899655	1.334262
H	5.424428	0.440965	0.138197

b6

C	2.717821	2.866171	-0.003737
C	1.491654	3.470022	0.137746
C	2.798834	1.455004	-0.073289
C	1.582619	0.739238	-0.008368
C	0.305485	2.694440	0.193513
N	0.368727	1.360963	0.104194
C	4.036262	0.743285	-0.190171
C	4.055058	-0.619474	-0.221742
C	2.838779	-1.371787	-0.135893
C	1.601547	-0.693576	-0.035386
C	2.802117	-2.783663	-0.135588
C	1.594093	-3.433027	-0.028519
C	0.385357	-2.703853	0.071379
N	0.408219	-1.362220	0.058651
C	-0.919197	-3.436555	0.194416
C	-1.022672	3.376579	0.343573
Pd	-1.230888	-0.063110	0.097308
O	-3.089351	0.868043	0.180958
C	-3.681313	1.386223	-1.023280
C	-2.929057	-0.963072	0.100771
O	-3.863222	-1.637354	0.076854
H	3.626447	3.459200	-0.050685
H	1.408474	4.548878	0.210270
H	4.959270	1.311543	-0.246992
H	4.992842	-1.159419	-0.305177
H	3.727804	-3.346219	-0.212907
H	1.546987	-4.515665	-0.017435
H	-1.561816	-3.243140	-0.669571
H	-1.459118	-3.128560	1.094073
H	-0.747702	-4.512243	0.252196
H	-0.932239	4.227018	1.024584
H	-1.791183	2.699330	0.716109
H	-1.351472	3.775134	-0.624123
H	-2.959287	1.947895	-1.623755
H	-4.483717	2.057989	-0.702197
H	-4.116812	0.588871	-1.635491

TSb8

C	3.066231	-2.928324	-0.503947
C	1.816765	-3.371994	-0.866624
C	3.252334	-1.569983	-0.155942
C	2.107067	-0.742535	-0.160557
C	0.704083	-2.494538	-0.850530
N	0.862526	-1.225680	-0.461452
C	4.527923	-1.006562	0.170046
C	4.651186	0.324461	0.437774
C	3.511805	1.192282	0.394766
C	2.233830	0.658549	0.106368
C	3.593066	2.585019	0.615143
C	2.455970	3.351388	0.521365
C	1.201540	2.762267	0.223819
N	1.108125	1.438702	0.035079

C	-0.016833	3.630291	0.119864
C	-0.638218	-2.993923	-1.301066
Pd	-0.622571	0.185600	-0.131766
C	-3.001785	0.903210	-0.602781
O	-4.107078	1.520418	-0.954167
C	-4.243373	2.951400	-0.695545
O	-2.083636	1.577471	-0.051941
H	3.916751	-3.603539	-0.506938
H	1.659654	-4.399481	-1.176324
H	5.395269	-1.658791	0.187846
H	5.619124	0.753987	0.676100
H	4.552134	3.039631	0.845011
H	2.497029	4.424140	0.671601
H	-0.554070	3.438646	-0.811107
H	-0.713259	3.426808	0.937785
H	0.268041	4.682704	0.157761
H	-1.075341	-3.654198	-0.545637
H	-1.336002	-2.180012	-1.496032
H	-0.520352	-3.578479	-2.218328
H	-3.478454	3.502976	-1.245276
H	-4.152364	3.146286	0.374520
H	-5.237326	3.212308	-1.053039
O	-1.695959	-1.456859	1.166826
C	-2.831392	-1.954633	1.132525
O	-3.727628	-1.648182	0.220210
C	-3.292006	-2.970744	2.138935
H	-3.399362	-0.838823	-0.298886
H	-4.061889	-2.520221	2.773846
H	-3.753588	-3.819771	1.627282
H	-2.457038	-3.299493	2.756552

b7

C	-3.716052	2.406762	0.133209
C	-2.620452	3.166618	-0.197734
C	-3.582987	1.002879	0.233412
C	-2.290230	0.466653	0.046582
C	-1.342968	2.575745	-0.376447
N	-1.192778	1.256555	-0.194490
C	-4.685842	0.120588	0.474104
C	-4.513493	-1.231848	0.457806
C	-3.225440	-1.801812	0.196746
C	-2.109383	-0.952983	0.022431
C	-2.999876	-3.191109	0.067368
C	-1.746357	-3.644375	-0.269033
C	-0.665963	-2.742235	-0.437185
N	-0.851923	-1.429920	-0.245748
C	0.677400	-3.267798	-0.850831
C	-0.192993	3.440197	-0.796911
Pd	0.533287	0.138685	0.055845
O	1.615653	1.705791	0.704771
C	2.644956	2.074278	-0.018963
O	2.966543	1.546003	-1.086626
C	3.444869	3.207611	0.599403
C	3.293763	-1.088133	0.170050
O	2.123607	-1.151625	0.564516
O	4.139034	-2.009524	0.553089
C	5.516973	-1.917453	0.108462
H	-4.687530	2.868409	0.282894
H	-2.710087	4.238619	-0.332888
H	-5.666365	0.552544	0.647517
H	-5.353594	-1.899818	0.619341
H	-3.823093	-3.886001	0.204397
H	-1.561032	-4.702374	-0.416679

H	1.324339	-3.412899	0.019178
H	1.174435	-2.572414	-1.529614
H	0.560097	-4.228987	-1.355392
H	0.513794	2.889334	-1.418135
H	0.343311	3.814991	0.079173
H	-0.571225	4.297585	-1.358505
H	4.201299	2.783811	1.269334
H	2.815347	3.871329	1.194794
H	3.956410	3.763335	-0.187869
H	3.642153	-0.285864	-0.493864
H	5.652420	-1.075274	-0.574746
H	6.139240	-1.793657	0.995198
H	5.757519	-2.855303	-0.392173

TSb9

C	3.540542	2.617986	-0.996113
C	2.327955	3.217168	-1.225820
C	3.577850	1.258535	-0.613996
C	2.338012	0.597607	-0.448967
C	1.113482	2.504971	-1.047740
N	1.133677	1.231760	-0.633374
C	4.801213	0.541308	-0.416048
C	4.788688	-0.784871	-0.104403
C	3.550329	-1.489195	0.034516
C	2.326763	-0.795989	-0.121233
C	3.477801	-2.871691	0.313046
C	2.249734	-3.480491	0.407360
C	1.052180	-2.739130	0.249730
N	1.113556	-1.421023	0.002331
C	-0.270077	-3.435247	0.359828
C	-0.174349	3.211807	-1.342235
Pd	-0.460924	-0.069012	-0.054297
O	-2.018492	1.197417	-0.092814
C	-2.146916	2.076343	0.883072
O	-1.293621	2.307027	1.733647
C	-3.487050	2.795907	0.843634
H	4.468260	3.167197	-1.126316
H	2.271426	4.249724	-1.551834
H	5.738692	1.075778	-0.533206
H	5.715422	-1.332844	0.033536
H	4.392581	-3.442847	0.441212
H	2.171759	-4.542981	0.606639
H	-0.856915	-3.013628	1.179751
H	-0.858234	-3.301730	-0.550226
H	-0.118533	-4.500677	0.538795
H	-0.015477	3.954817	-2.127279
H	-0.954881	2.515666	-1.642616
H	-0.516794	3.738580	-0.444750
H	-3.495803	3.594500	1.585833
H	-3.673865	3.209378	-0.151375
H	-4.295223	2.090163	1.061924
O	-2.089132	-1.525348	-1.141320
C	-3.207716	-1.141679	-1.439296
O	-4.038102	-1.922550	-2.108676
C	-5.348677	-1.420085	-2.439116
H	-3.575367	-0.139634	-1.172417
H	-6.085640	-2.084794	-1.986050
H	-5.449610	-1.437665	-3.525246
H	-5.486983	-0.400204	-2.067699
N	-1.293709	-0.848902	2.108141
C	-1.403125	-0.300023	3.124822
C	-1.541387	0.427118	4.378769
H	-1.522795	1.495907	4.146640

H	-2.485942	0.169850	4.865688
H	-0.714982	0.182716	5.051422

TSct1

C	-3.164132	-3.000006	-0.060183
C	-1.964020	-3.503610	-0.502487
C	-3.289063	-1.613068	0.184008
C	-2.127510	-0.827256	0.015007
C	-0.832163	-2.663404	-0.659971
N	-0.919789	-1.364043	-0.346791
C	-4.521834	-0.981862	0.549554
C	-4.600240	0.374179	0.667538
C	-3.453017	1.199026	0.429303
C	-2.208599	0.596811	0.138759
C	-3.498021	2.611413	0.431715
C	-2.369720	3.322680	0.101588
C	-1.146064	2.665506	-0.184713
N	-1.073413	1.328836	-0.112133
C	0.046620	3.479158	-0.585564
C	0.442239	-3.236790	-1.206891
Pd	0.588040	0.067699	-0.041943
O	2.035730	-1.384474	0.332747
C	3.278395	-1.151698	0.240554
O	4.167011	-2.364266	0.513106
C	4.483479	-1.853866	1.678137
O	1.914541	1.496956	0.505290
C	2.836510	1.793711	-0.386671
C	3.726621	2.954937	0.023798
O	2.977184	1.203251	-1.457756
H	-4.025038	-3.649357	0.068715
H	-1.860805	-4.555094	-0.746275
H	-5.397450	-1.603767	0.706579
H	-5.539866	0.855083	0.920453
H	-4.428996	3.121246	0.661265
H	-2.392891	4.405267	0.050355
H	-0.275715	4.465660	-0.924060
H	0.724689	3.601541	0.262605
H	0.599823	2.989327	-1.389620
H	0.215028	-4.108218	-1.825050
H	0.977576	-2.500987	-1.808177
H	1.110319	-3.550137	-0.400343
H	3.758407	-0.713394	-0.646875
H	3.759168	-0.436809	1.095826
H	5.541616	-1.757667	1.939757
H	3.732469	-1.803473	2.470121
H	4.711094	2.840067	-0.432957
H	3.291079	3.885286	-0.357204
H	3.809477	3.040836	1.108773

TSct2

C	-2.790006	2.973647	0.043108
C	-1.537512	3.540559	0.054777
C	-2.920230	1.567399	0.027831
C	-1.725052	0.804052	0.019143
C	-0.385326	2.718472	0.045805
N	-0.491345	1.386074	0.023612
C	-4.194932	0.915734	0.024402
C	-4.276770	-0.442314	0.020147
C	-3.091744	-1.247399	0.017962
C	-1.812132	-0.637215	0.012754
C	-3.145178	-2.657012	0.023316
C	-1.977054	-3.380226	0.028349
C	-0.723916	-2.725592	0.020639

N	-0.657481	-1.383521	0.008134
C	0.529324	-3.554022	0.026974
C	0.983486	3.336819	0.062443
Pd	1.060850	-0.227666	-0.059261
H	-3.681799	3.593630	0.048709
H	-1.415064	4.617712	0.071064
H	-5.091647	1.527603	0.027785
H	-5.240008	-0.942619	0.020229
H	-4.108963	-3.157526	0.026474
H	-1.996509	-4.463625	0.037210
H	0.282828	-4.616306	0.075277
H	1.117776	-3.373727	-0.877446
H	1.158003	-3.300682	0.885061
H	0.916690	4.424697	0.117504
H	1.560295	2.974219	0.917415
H	1.542152	3.062668	-0.836303
H	1.962064	-1.444753	-0.120657
O	2.834319	0.923620	-0.170009
C	3.953191	0.532412	-0.563786
H	4.287633	0.471593	-1.607128
H	4.912286	1.157119	-0.089454
O	4.498326	-0.853462	-0.074225
C	5.297536	-0.175463	0.717105
H	4.895640	0.289084	1.622578
H	6.378043	-0.344670	0.653510

ct2

C	-2.870464	2.918588	0.132834
C	-1.630886	3.512665	0.101425
C	-2.970906	1.509970	0.109951
C	-1.761006	0.773267	0.044778
C	-0.462638	2.715966	0.040778
N	-0.540758	1.381951	0.007069
C	-4.230010	0.830037	0.154496
C	-4.282050	-0.529525	0.145218
C	-3.080769	-1.308018	0.087073
C	-1.816815	-0.669166	0.028203
C	-3.101947	-2.718572	0.088869
C	-1.918677	-3.415192	0.041226
C	-0.682220	-2.732374	-0.021615
N	-0.647358	-1.389228	-0.035237
C	0.588662	-3.531768	-0.072460
C	0.892739	3.363814	0.018132
Pd	1.035623	-0.195248	-0.197801
H	-3.774353	3.518972	0.179547
H	-1.531144	4.592018	0.124031
H	-5.139057	1.421669	0.199837
H	-5.233136	-1.051136	0.183702
H	-4.053040	-3.240997	0.132460
H	-1.913296	-4.498746	0.048831
H	0.370432	-4.598234	0.008648
H	1.119258	-3.356014	-1.013113
H	1.258894	-3.247055	0.743057
H	0.805189	4.449133	0.091160
H	1.502301	3.005888	0.852856
H	1.427302	3.115252	-0.902438
H	1.955700	-1.390368	-0.346921
O	2.772759	0.991048	-0.493277
C	3.945211	0.742376	-0.224818
O	4.326120	-0.339778	0.402537
C	5.738190	-0.548411	0.664621
H	4.734179	1.451558	-0.512014
H	5.856614	-0.644895	1.743795

H	6.027697	-1.473807	0.166687
H	6.335072	0.287013	0.289546

TSct3

C	-2.953548	-2.826883	-1.011758
C	-1.692564	-3.374331	-1.066895
C	-3.115336	-1.479653	-0.619688
C	-1.940656	-0.749594	-0.306450
C	-0.562026	-2.588294	-0.739501
N	-0.699982	-1.308906	-0.378450
C	-4.398899	-0.851203	-0.529276
C	-4.507768	0.446864	-0.135148
C	-3.343535	1.213357	0.198184
C	-2.055237	0.627403	0.112732
C	-3.424517	2.556626	0.621534
C	-2.272766	3.238196	0.935736
C	-1.012226	2.606139	0.831983
N	-0.917930	1.331177	0.424334
C	0.229330	3.375696	1.182047
C	0.819432	-3.176171	-0.780955
Pd	0.837494	0.201871	0.159121
H	-3.828506	-3.419801	-1.262489
H	-1.548030	-4.408248	-1.359911
H	-5.281182	-1.432503	-0.779028
H	-5.478814	0.926764	-0.062556
H	-4.394884	3.038256	0.698062
H	-2.312082	4.269444	1.267079
H	-0.023174	4.386315	1.508994
H	0.780697	2.874535	1.982978
H	0.896603	3.441437	0.317427
H	0.789895	-4.221778	-1.092936
H	1.460089	-2.616164	-1.466537
H	1.287685	-3.112034	0.205856
H	1.726438	1.364661	0.530019
O	2.628981	-0.505556	-1.189538
C	3.328758	0.185760	-1.907502
O	3.178700	1.493553	-2.020133
C	4.064999	2.223436	-2.897136
H	4.138623	-0.250584	-2.514619
H	3.449930	2.737968	-3.636288
H	4.611122	2.948834	-2.292632
H	4.767328	1.551507	-3.399004
N	2.164824	-1.123584	1.800866
C	2.702491	-1.462234	2.770107
C	3.380607	-1.891243	3.988776
H	4.049166	-2.728747	3.771531
H	3.969010	-1.066114	4.399374
H	2.646280	-2.207819	4.734516

TScc1

C	3.694214	-2.414744	0.568021
C	2.693473	-3.247487	0.129139
C	3.494579	-1.015694	0.541054
C	2.227022	-0.558498	0.117903
C	1.440201	-2.733325	-0.293695
N	1.212525	-1.413136	-0.239995
C	4.511711	-0.064761	0.877605
C	4.295091	1.273098	0.723438
C	3.043551	1.758588	0.224461
C	1.999823	0.845196	-0.037165
C	2.791420	3.119947	-0.067428
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 H -5.655744 -2.084469 0.116623
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cc1

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 C 1.279041 -2.765314 -0.239486
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TSec2

C -3.248994 3.021659 0.193618
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TSec3

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H	1.877925	4.189299	2.767264
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H	1.441616	2.661098	3.580348
O	2.304939	-1.024603	-1.490060
C	3.296407	-0.462734	-1.980477
O	3.616372	0.784361	-1.735255
C	4.230901	-1.168197	-2.926050
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H	5.262422	-1.056248	-2.581632
H	3.968742	-2.222295	-3.006387
H	4.166760	-0.696826	-3.911878
N	1.778647	-1.055970	1.645875
C	2.376537	-1.418850	2.569487
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H	2.454189	-2.193153	4.522210

d3H

C	3.635509	2.923703	0.181518
C	2.443906	3.610621	0.183276
C	3.630574	1.520583	0.014516
C	2.368865	0.891578	-0.091909
C	1.210959	2.923010	0.068602
N	1.189970	1.588175	-0.024776
C	4.822942	0.732922	-0.083894
C	4.752965	-0.603399	-0.346089
C	3.488113	-1.251432	-0.526641
C	2.296886	-0.513232	-0.359685
C	3.352921	-2.605963	-0.910776
C	2.102611	-3.111460	-1.166591
C	0.935017	-2.321938	-0.987626
N	1.054128	-1.068724	-0.529192
C	-0.398279	-2.896092	-1.351631
C	-0.074188	3.698436	0.039095
Pd	-0.404628	0.214473	0.206045
O	-1.765226	-1.225416	0.553643
C	-1.741794	-1.781431	1.815319
N	-1.890626	1.415842	1.018776
C	-2.955323	1.753453	1.315910
C	-4.314286	2.144453	1.654836
O	-0.573476	-2.567833	1.968688
C	-0.491680	-3.179583	3.246493
H	4.579937	3.451282	0.277381
H	2.427276	4.691414	0.267724
H	5.782732	1.226760	0.030185
H	5.657072	-1.195659	-0.446877
H	4.238741	-3.221345	-1.037906
H	1.977750	-4.129864	-1.516853
H	-0.259766	-3.670289	-2.110481
H	-0.861471	-3.343446	-0.469067
H	-1.068626	-2.123040	-1.727866
H	-0.788845	3.244223	-0.649370
H	-0.530257	3.729670	1.033925
H	0.115977	4.726879	-0.274843
H	-1.774315	-1.023874	2.624043
H	-2.639633	-2.422600	1.907390
H	-4.484482	2.030481	2.728891
H	-4.493112	3.184718	1.369432

H	-4.998277	1.490918	1.104079
H	-1.331692	-3.867422	3.422953
H	0.439932	-3.747256	3.273998
H	-0.476875	-2.433159	4.055045
O	-2.332442	0.018041	-2.276225
C	-3.512308	-0.039569	-1.964596
O	-3.933988	-0.466476	-0.764847
C	-4.649722	0.344847	-2.878794
H	-3.137122	-0.793092	-0.249537
H	-5.351726	1.008224	-2.366129
H	-4.259479	0.825024	-3.775331
H	-5.206218	-0.554915	-3.160597

d3

C	-2.856655	3.057468	-0.692993
C	-1.688350	3.688097	-0.335243
C	-2.959807	1.654423	-0.562344
C	-1.812883	0.963324	-0.104341
C	-0.574885	2.939728	0.117348
N	-0.638424	1.605087	0.189418
C	-4.162261	0.929167	-0.841279
C	-4.230222	-0.412714	-0.612793
C	-3.103450	-1.126591	-0.091279
C	-1.883748	-0.450075	0.131593
C	-3.152072	-2.496790	0.254799
C	-2.056067	-3.082349	0.835437
C	-0.852418	-2.355759	1.038934
N	-0.772212	-1.079767	0.636759
C	0.285835	-3.045568	1.725755
C	0.680711	3.654496	0.527507
Pd	0.908640	0.142242	0.395536
N	2.611039	1.274916	0.051752
C	3.695163	1.658469	-0.060949
C	5.061129	2.143258	-0.196170
O	2.227446	-1.334703	0.506023
C	2.581880	-1.890222	-0.693552
O	1.483629	-2.588182	-1.273821
C	1.818777	-3.202461	-2.507123
H	-3.709373	3.628395	-1.048532
H	-1.601180	4.767510	-0.389779
H	-5.022561	1.473551	-1.217616
H	-5.147396	-0.961524	-0.802331
H	-4.064680	-3.062110	0.090235
H	-2.084580	-4.117962	1.155257
H	0.898459	-3.562890	0.982487
H	0.934802	-2.346010	2.247295
H	-0.114399	-3.782221	2.427480
H	1.386347	3.706561	-0.308260
H	0.448237	4.677540	0.831023
H	1.171832	3.142659	1.356361
H	5.176251	3.091486	0.336354
H	5.751364	1.408723	0.228657
H	5.301765	2.292543	-1.252481
H	3.401760	-2.604753	-0.481926
H	2.956562	-1.151613	-1.433002
H	0.920330	-3.698829	-2.878519
H	2.613748	-3.953337	-2.386118
H	2.149790	-2.464832	-3.254174

Tsd3

C	-3.068096	2.983028	0.087229
C	-1.821690	3.520841	-0.144485
C	-3.225227	1.580427	0.153681

C	-2.062206	0.794688	-0.019178
C	-0.695854	2.681068	-0.312921
N	-0.835636	1.352020	-0.242034
C	-4.484655	0.935339	0.379345
C	-4.571386	-0.424233	0.425344
C	-3.407621	-1.243316	0.252032
C	-2.150500	-0.635027	0.031517
C	-3.440421	-2.655173	0.290964
C	-2.275244	-3.365555	0.122857
C	-1.040367	-2.702408	-0.089648
N	-1.002402	-1.363253	-0.135553
C	0.219315	-3.495280	-0.258847
C	0.666420	3.253422	-0.577517
Pd	0.667453	-0.082085	-0.420919
O	2.122093	-1.385357	-0.794474
C	3.008635	-0.477338	-1.230240
O	4.136544	-0.365733	-0.420525
C	5.148773	0.477410	-0.967428
H	-3.933098	3.626965	0.215791
H	-1.683350	4.594376	-0.203729
H	-5.368130	1.552001	0.510908
H	-5.525993	-0.912450	0.594720
H	-4.383874	-3.167552	0.454819
H	-2.278193	-4.449182	0.150832
H	0.010483	-4.562331	-0.171358
H	0.679595	-3.295424	-1.229562
H	0.961790	-3.211777	0.491542
H	1.364158	2.946488	0.206947
H	1.054796	2.893655	-1.537038
H	0.628711	4.343320	-0.614305
H	3.293968	-0.609297	-2.291460
H	2.441763	0.566927	-1.226202
H	6.015995	0.396259	-0.311394
H	5.435457	0.156215	-1.977246
H	4.822787	1.526286	-1.003286
N	1.988813	0.945677	1.573503
C	2.868976	0.486300	2.174975
C	3.975434	-0.108725	2.911402
H	4.659128	0.669265	3.262185
H	3.600688	-0.666479	3.773775
H	4.510239	-0.786566	2.240404

TSd1H-d3H

Pd	0.356940	-0.480332	0.080695
N	-0.887717	1.047909	0.606537
N	-1.491133	-1.506395	-0.046697
C	-0.548531	2.268364	1.052090
C	-1.556502	3.262478	1.177497
C	-2.866866	3.000691	0.867084
C	-3.235367	1.700593	0.450855
C	-2.202405	0.745551	0.340276
C	-2.520732	-0.602123	-0.002778
C	-3.867372	-0.970337	-0.229009
C	-4.124114	-2.333844	-0.492620
C	-3.083589	-3.232637	-0.476941
C	-1.753259	-2.805706	-0.240509
C	-4.585769	1.315139	0.169796
C	-4.891744	0.027565	-0.158693
C	0.857559	2.606910	1.423745
C	-0.649639	-3.821132	-0.194882
N	1.654425	-1.921863	-0.587669
C	2.695879	-2.328798	-0.878629
C	4.030525	-2.795318	-1.214369

H	-1.254893	4.242476	1.528681
H	-3.625350	3.772393	0.959433
H	-5.141003	-2.664946	-0.681032
H	-3.262476	-4.289196	-0.640985
H	-5.363687	2.068783	0.240579
H	-5.917713	-0.266527	-0.355854
H	1.357170	1.751067	1.878415
H	0.857217	3.454523	2.112436
H	1.410479	2.884668	0.520103
H	0.036101	-3.615248	0.629171
H	-0.072435	-3.809348	-1.124383
H	-1.066839	-4.821621	-0.067263
H	4.246445	-3.734834	-0.698370
H	4.122951	-2.943940	-2.293552
H	4.731890	-2.022286	-0.883160
O	2.080430	-0.248667	1.776036
C	3.324144	-0.157390	1.555646
C	4.268746	-0.392387	2.723410
O	3.848622	0.146084	0.432824
H	4.504864	0.575338	3.179533
H	5.207445	-0.828003	2.375069
H	3.804609	-1.024318	3.481609
O	1.931828	0.846249	-0.914863
C	1.990840	1.613677	-2.066842
O	1.489909	2.905223	-1.783278
C	1.584884	3.781937	-2.894957
H	2.840431	0.623420	-0.397801
H	1.381910	1.150768	-2.862445
H	3.036700	1.682325	-2.414917
H	1.172118	4.743035	-2.583981
H	1.010443	3.410301	-3.756793
H	2.628888	3.928344	-3.208432

cat2

Pd	-0.798214	0.048426	-0.096678
O	-2.266372	-1.343494	0.011915
O	-1.220746	-2.314985	1.767056
O	-2.299806	1.267723	0.509711
O	-2.900934	1.524520	-1.651906
N	0.863300	-1.218448	-0.479169
N	0.777074	1.471996	-0.073041
C	0.896755	-2.507480	-0.829053
C	2.107946	-3.242468	-0.743475
C	3.266634	-2.643569	-0.318076
C	3.259735	-1.263914	-0.012323
C	2.023187	-0.586036	-0.118743
C	1.977292	0.834856	0.095252
C	3.170798	1.528163	0.408695
C	3.087438	2.932827	0.526146
C	1.887141	3.558609	0.293379
C	0.723767	2.809445	-0.017788
C	4.438434	-0.542870	0.363058
C	4.395816	0.803737	0.565802
C	-0.331194	-3.201771	-1.335946
C	-0.563727	3.520768	-0.293922
C	-2.195273	-2.160857	1.032639
C	-3.487574	-2.947761	1.234213
C	-3.132136	1.602121	-0.446744
C	-4.457792	2.132741	0.087949
H	2.092051	-4.291224	-1.020105
H	4.191810	-3.207460	-0.238812
H	3.976807	3.505161	0.774755

H	1.805041	4.638686	0.343128
H	5.370197	-1.091193	0.465222
H	5.292595	1.354766	0.833100
H	-1.113660	-2.495533	-1.604532
H	-0.068833	-3.825431	-2.196436
H	-0.725621	-3.857628	-0.552543
H	-1.082469	3.069825	-1.143667
H	-1.233987	3.426302	0.565014
H	-0.374824	4.578822	-0.489553
H	-3.317300	-3.772008	1.928680
H	-4.249944	-2.280582	1.649574
H	-3.869546	-3.323076	0.281004
H	-5.007178	2.633952	-0.710397
H	-5.051120	1.290694	0.459248
H	-4.299411	2.814144	0.928391

cat2H

Pd	-0.800825	0.050877	-0.343755
O	-2.265679	-1.358229	-0.225021
O	-2.291051	1.275869	0.278956
O	-2.932912	1.518016	-1.872655
N	0.838098	-1.232159	-0.738151
N	0.775972	1.459126	-0.348168
C	0.856641	-2.523733	-1.083222
C	2.060649	-3.268446	-1.003306
C	3.227570	-2.675328	-0.588935
C	3.234849	-1.295280	-0.289561
C	2.004455	-0.607624	-0.388241
C	1.969966	0.812939	-0.179672
C	3.169201	1.497644	0.124726
C	3.097315	2.902619	0.239070
C	1.900753	3.537617	0.010113
C	0.731459	2.796483	-0.294983
C	4.422041	-0.582578	0.076631
C	4.390048	0.763976	0.276875
C	-0.385624	-3.206103	-1.577343
C	-0.552650	3.516851	-0.566957
C	-2.348643	-2.050212	0.870446
C	-3.630684	-2.869229	0.962158
C	-3.138268	1.612267	-0.664580
C	-4.445120	2.167241	-0.108314
O	-1.514786	-2.089055	1.785217
H	2.035173	-4.318195	-1.275448
H	4.148403	-3.246809	-0.513509
H	3.992099	3.468705	0.482617
H	1.826834	4.618369	0.058325
H	5.349927	-1.137985	0.175222
H	5.292131	1.309106	0.538393
H	-1.140764	-2.491518	-1.897106
H	-0.127067	-3.878603	-2.401108
H	-0.821938	-3.814571	-0.777430
H	-1.083491	3.063402	-1.407539
H	-1.214627	3.439358	0.299998
H	-0.355532	4.570953	-0.775613
H	-3.528589	-3.642016	1.725408
H	-4.454503	-2.203054	1.239474
H	-3.881331	-3.312429	-0.004732
H	-5.008281	2.658591	-0.903081
H	-5.039205	1.340535	0.294993
H	-4.258398	2.864030	0.713490
O	0.663390	-0.528130	2.439956
C	0.176716	0.376387	3.411817
H	-0.087503	-1.104640	2.178541

H	0.997459	1.047774	3.689057
H	-0.655200	0.991439	3.037314
H	-0.161871	-0.132271	4.327769

cat2TSa

Pd	-0.471070	0.024527	0.301035
O	-1.964010	1.300838	0.709564
O	-2.413910	1.918924	-1.421638
N	1.100469	-1.341098	0.070146
N	1.171892	1.396462	0.039553
C	1.024028	-2.682544	0.040380
C	2.205366	-3.456421	-0.094577
C	3.435539	-2.859323	-0.205459
C	3.524146	-1.451376	-0.198310
C	2.316085	-0.723901	-0.061356
C	2.354549	0.712351	-0.072307
C	3.604734	1.366736	-0.209264
C	3.601192	2.777075	-0.223759
C	2.407094	3.444723	-0.116971
C	1.184399	2.738544	0.010543
C	4.769414	-0.758505	-0.326528
C	4.808349	0.601962	-0.330040
C	-0.295955	-3.373776	0.130252
C	-0.092508	3.509774	0.094636
C	-2.736180	1.776563	-0.247118
C	-4.120651	2.141840	0.269886
H	2.108335	-4.535979	-0.108106
H	4.339487	-3.453637	-0.305401
H	4.538685	3.316841	-0.323081
H	2.373404	4.528217	-0.130647
H	5.679119	-1.343498	-0.423637
H	5.750153	1.133314	-0.429535
H	-0.937128	-3.024540	-0.685945
H	-0.161299	-4.456078	0.081767
H	-0.817228	-3.093279	1.049000
H	-0.735229	3.256798	-0.755223
H	-0.650199	3.238045	0.993356
H	0.111429	4.582421	0.095656
H	-4.618536	2.804582	-0.439797
H	-4.688811	1.210779	0.364098
H	-4.068939	2.607655	1.257401
O	-1.810278	-1.200466	-1.353676
C	-3.063199	-1.260115	-1.181581
C	-3.938683	-1.245675	-2.427728
O	-3.645187	-1.294611	-0.051903
H	-4.940190	-1.621914	-2.210366
H	-4.010035	-0.207722	-2.770167
H	-3.474404	-1.826550	-3.228298
O	-1.811586	-1.294905	1.644166
C	-2.208246	-0.746521	2.894614
H	-2.629942	-1.301335	0.977455
H	-1.379684	-0.853587	3.602968
H	-2.469279	0.312909	2.801419
H	-3.074093	-1.295944	3.287575

cat2a

Pd	-0.902119	-0.402139	0.092610
O	-2.702533	0.426867	0.584157
O	-3.216036	0.484041	-1.615435
N	1.038528	-1.257012	-0.254107
N	0.309377	1.375590	-0.099221
C	1.378517	-2.533262	-0.490328
C	2.734572	-2.940462	-0.399972

C 3.724466 -2.031976 -0.117258
 C 3.389321 -0.669305 0.041946
 C 2.017831 -0.325452 -0.043217
 C 1.633782 1.061378 0.038724
 C 2.637818 2.046583 0.208087
 C 2.223041 3.395938 0.220399
 C 0.895091 3.694159 0.036684
 C -0.062827 2.662446 -0.132279
 C 4.372185 0.348624 0.260720
 C 4.009825 1.658796 0.340609
 C 0.327829 -3.514576 -0.899203
 C -1.500250 3.013562 -0.355202
 C -3.530389 0.526829 -0.426728
 C -4.978105 0.724937 0.012269
 O -1.832101 -2.127368 0.424956
 C -2.340566 -2.276778 1.724025
 H 2.969079 -3.986074 -0.566375
 H 4.763124 -2.341902 -0.040980
 H 2.959676 4.182964 0.356390
 H 0.554271 4.723362 0.016056
 H 5.413645 0.052591 0.345855
 H 4.754677 2.434609 0.491575
 H 0.040527 -3.319657 -1.940296
 H 0.704070 -4.537830 -0.832495
 H -0.578011 -3.368063 -0.297006
 H -1.910228 2.443736 -1.193778
 H -2.093858 2.736976 0.520690
 H -1.606246 4.084274 -0.543506
 H -5.580451 1.065680 -0.831273
 H -5.373998 -0.231342 0.370493
 H -5.045209 1.436019 0.840322
 H -1.554705 -2.438808 2.485516
 H -2.950387 -1.418599 2.038226
 H -2.991352 -3.166587 1.728743

cat3

C -2.968111 -2.821516 -0.271786
 C -1.842711 -3.413405 0.253054
 C -3.002192 -1.415983 -0.438529
 C -1.823585 -0.710271 -0.121192
 C -0.684583 -2.654652 0.562807
 N -0.675213 -1.338129 0.307398
 C -4.162377 -0.682882 -0.851174
 C -4.162341 0.683048 -0.851180
 C -3.002117 1.416088 -0.438534
 C -1.823551 0.710313 -0.121188
 C -2.967959 2.821621 -0.271799
 C -1.842537 3.413449 0.253062
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 N -0.675153 1.338110 0.307424
 C 0.483329 3.337266 1.211775
 C 0.483214 -3.337366 1.211640
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 H -1.821132 -4.479046 0.453545
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 H -5.053514 1.234978 -1.132135
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 H -1.820904 4.479090 0.453556
 H 1.069843 3.893616 0.472977
 H 1.132778 2.633770 1.731223
 H 0.112267 4.065124 1.938382
 H 1.069775 -3.893538 0.472744

H 0.112170 -4.065381 1.938096
 H 1.132620 -2.633936 1.731236
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