Supporting Information

Simulated Mechanism for Palladium-Catalyzed, Directed γ-Arylation of Piperidine

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1. Description of Automated Reaction Path Discovery Tools (ZStruct)

The reaction simulation methods developed by the Zimmerman group were used to investigate possible elementary reaction steps in Pd-catalyzed directed C-H functionalization of piperidine. This technique, named ZStruct,[1] takes a pair of reactants as input and combinatorially generates driving coordinates and starting structures for use in reaction path searches using quantum chemistry. As an example of how this method is used to find reaction paths **Figure S1** shows two reactants (an aldehyde and an ene) that are converted into a graph representation describing their connectivity. The graph is then changed systematically based on feasible changes in connectivity (breaking connections shown in red, making connections shown in green). The connectivity changes defined in the new graphs are used as driving coordinates for possible elementary steps. The single-ended Growing String Method (SSM)[2] is then used to calculate the kinetic and thermodynamic information of single elementary steps. This is done by

locating minimum energy pathways with exact transition states that connect the starting structures to minimum energy intermediates found by SSM.

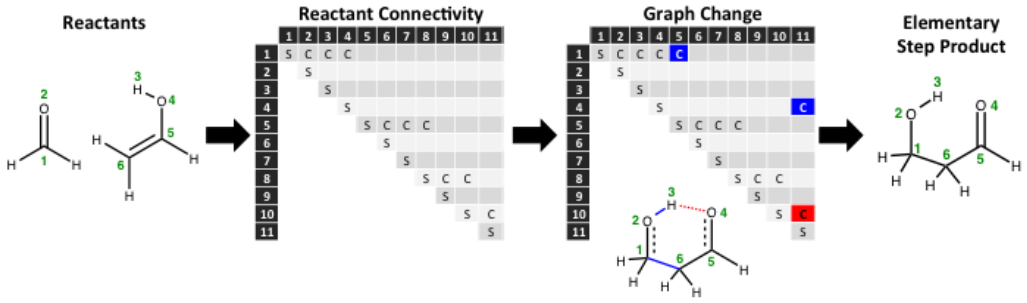
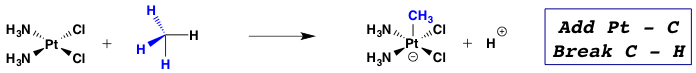
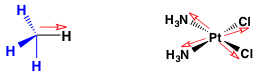


Figure S1: Example of graph representation based elementary step reaction search using ZStruct.

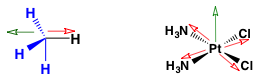
Once the driving coordinates are generated ZStruct aligns reactants (for intermolecular reactions) based on the add and break moves designated in the driving coordinates. This process is shown in **Figure S2**. If the driving coordinates include a transition metal, then the number of alignments generated is dependent upon the geometry of the metal center, which is identified by ZStruct. For example if the metal center is a square planar then alignments above and below the plane of the metal center will be generated for each set of driving coordinates containing an add move at the transition metal center, **Figure S2**.



Step 1: Create vector in direction of bond breaking
No break – vectors in direction of coordinated atoms



Step 2: Average vectors from step 1. Generate vector opposite to average.



Step 3: Align vectors generated in step 2.
Transition Metal – Multiple Alignments Generated

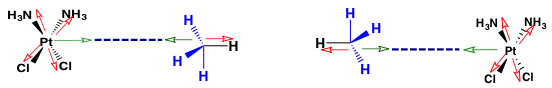


Figure S2: Example of alignment of bimolecular reactions using ZStruct

2. *Example of Reaction Exploration Using ZStruct*

Due to limited reports of computational investigations of oxidative addition of aryl-iodides with Pd(II) to generate high valent Pd(IV) automated reaction path discovery tools (ZStruct) was applied to investigate the oxidative addition step of the catalytic cycle for piperidine γ-arylation. As shown in **Figure S3**, four atoms were chosen as being "reactive" in the graph representation of reactant connectivity, structure **1** in **Figure S3**. These reactive atoms were used to systematically generate possible driving coordinates for elementary steps. This choice of reactive atoms led to 250 potential elementary steps being generated via ZStruct and evaluated using SSM to provide insight into how oxidative addition of PhI to Pd would occur. Of the 250 potential elementary steps 65 of them successfully produced reaction pathways and transition states via SSM. Of these 65 successful pathway searches the most favorable was found to lead to I-Pd coordination prior to oxidative addition, structure **2** in **Figure S3**. The other high barrier pathways were considered to be uncompetitive, and further exploration based on those elementary steps was not pursued.

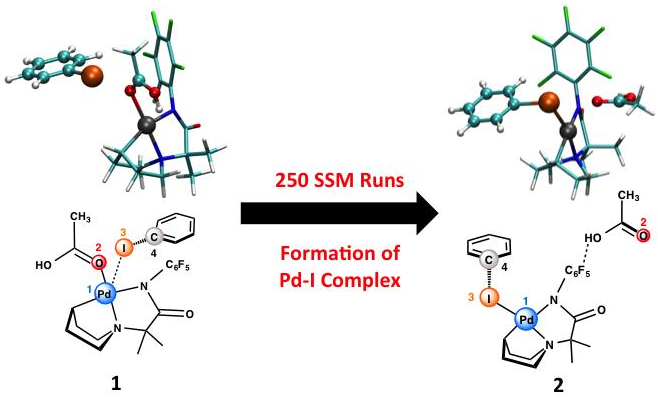


Figure S3: Example of using ZStruct to explore PhI coordination to Pd, and the lowest barrier intermediate identified.

3. Number of Gradients Used for GSM Optimization During Reaction Path Exploration

Table S1: Number of gradients used for GSM optimization steps during reaction path exploration for elementary steps connecting intermediates for piperidine arylation using the B3LYP functional with LANL2DZ on all elements with an ECP on Pd.

Elementary Step (Intermediates Connected)	Number of Gradients Used for GSM Optimization
2 to 3	429
3 to 4	501
4 to 5	212
5 to 7	516
4 to 6	1409
6 to 7	233
8 to 9	190
11 to 12	201
12 to 13	127
14 to 15	1842
16 to 17	1027

4. Alternative Reaction Pathways

a. C-H Activation Including Free Acetic Acid

C-H activation beginning from **5s**, which includes free acetic acid, was explored to ensure that the free acetic acid does not participate in the C-H activation transition state. The overall pathway was identical to the C-H activation pathway starting from **5**. The same one-step process was found, involving piperidine isomerization from a chair to a boat conformation as the O of the κ^2-acetate ligand closest to C_γ-H dissociates from Pd. As the κ^2-acetate O dissociates, Pd facilitates the proton transfer from C_γ to the newly deligated O, **TS-5s-7s**, and then the newly formed OH group rotates out of the square plane of Pd to avoid steric interactions, **Figure S4**. This process results in intermediate **7s**, which is identical to **7**, in which Pd is bound to N_{DG}, N_{Pip}, C_γ and a κ^1acetic acid ligand, except that a free acetic acid molecule is present. The barrier to C-H activation is 36.0 kcal/mol, **TS-5s-7s**, and leads uphill 22.3 kcal/mol to **7s.**

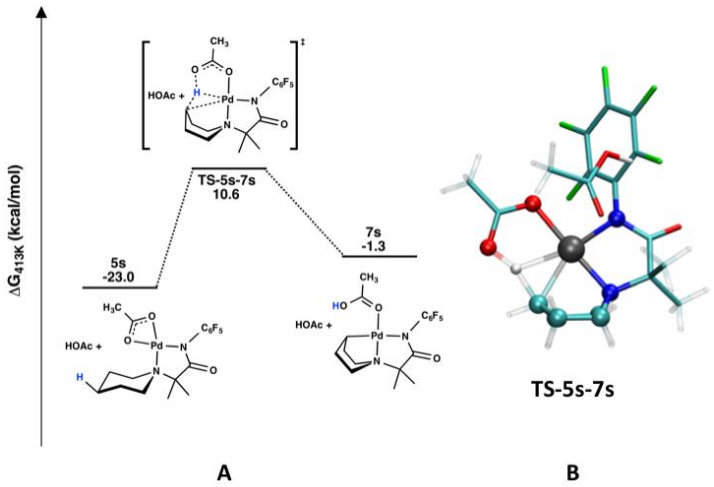


Figure S4: (A) Alternative C-H activation pathway starting from **5s.** (B) 3D rendering of **TS-5s-7s**. Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

b. *Two-step C-H Activation Pathway*

A two-step pathway for C-H activation involving a chair to boat isomerization followed by C-H activation from the boat intermediate was investigated, **Figure S5**. Starting from **5** the chair to boat isomerization can occur through **TS-5-5boat**, **Figure S5**, with a barrier of 11.6 kcal/mol. This leads to **5boat,** which still has Pd bound to a κ^2-acetate ligand, N_{DG}, and N_{Pip} with the piperidine ring in a twisted-boat conformation and is uphill 7.7 kcal/mol from **5**. The difference between **5** and **5boat** comes solely from the isomerization of the piperidine ring from a chair to twisted-boat conformation, which puts the γ-C-H bond in closer proximity to the Pd center. From **5boat** C-H activation is found to occur through a CMD mechanism in which a Pd-O bond closest to the γ–C-H bond breaks, allowing Pd to coordinate to the γ–carbon and hydrogen. This coordination enables Pd to facilitate the proton transfer to the newly un-ligated O. Once the proton transfer is complete the newly formed κ^1-acetic acid ligand rotates out of the square plane of the Pd to avoid steric interactions between the OH and the Pd- γ–carbon bond. The barrier to this step is 34.2 kcal/mol (**TS-5boat-7, Figure S5**) and results in **7**, which is uphill 23.8 kcal/mol from **5.**

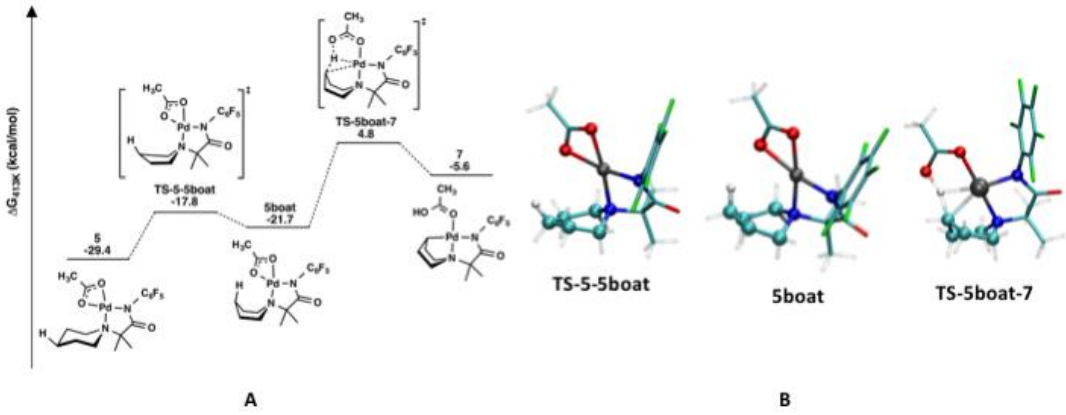


Figure S5: (A) Alternative two-step C-H activation pathway starting from **5** leading to **7** through a boat intermediate, **5boat**. (B) 3D renderings of **TS-5-5boat, 5boat, and TS-5boat-7** structures. Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

c. Comparison of Alpha, Beta and Gamma Carbon C-H Activation

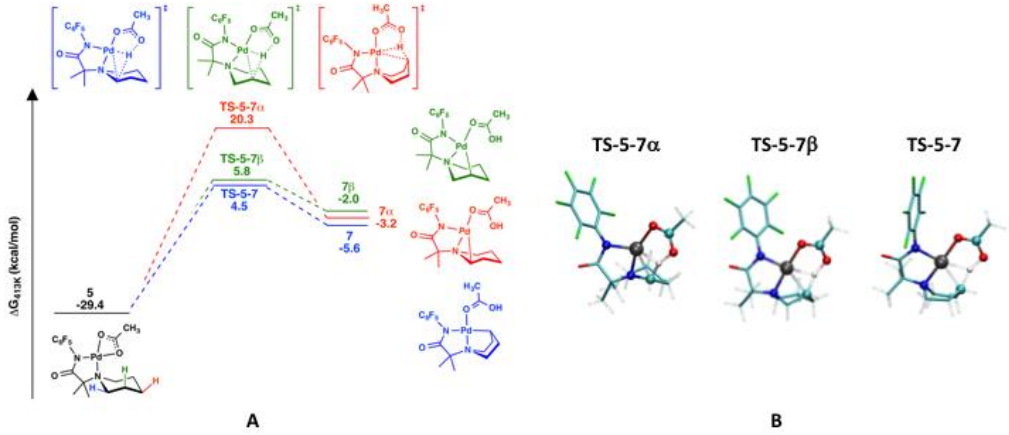


Figure S6: (A) Pathways for α-, β-, and *γ*-carbon C-H activation. (B) 3D renderings of **TS-5-7*α*, TS-5-7β and TS-5-7*γ*** structures. Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

Mechanisms for C-H activation at the α-, β-, and *γ*-carbons have been compared to determine the kinetic difference in reactivity, **Figure S6**. From **5** C-H activation at each site can occur through a concerted metallation deprotonation mechanism where an O atom of the κ^2-acetate ligand on Pd dissociates

and abstracts the proton from the carbon being activated. Activation of the α-carbon has the highest barrier of 49.7 kcal/mol through **TS-5-7α**. The α-activated intermediate, **7α**, is 2.4 kcal/mol higher in energy than the γ-activated intermediate, **7**. The high activation barrier makes C-H activation at the α-carbon infeasible starting from **5**. In contrast, activation at the β-carbon has a barrier of 35.2 kcal/mol through **TS-5-7β**. This barrier is only 1.3 kcal/mol above that of γ-carbon activation, and the β-activated intermediate that forms, **7β**, is 3.6 kcal/mol higher in energy than the γ-activated intermediate, **7**. The activation barriers and difference in energy between activated intermediates supports the proposal that α- and β-carbon activation are unfavorable compared to γ-carbon activation from **5**.

d. PhI Coordination: Pd-I vs Pd-π Complex Formation

From **7** PhI can coordinate to Pd through either iodine or the Ph group through the formation of a Pd-π-complex, **Figure S7**. The first pathway investigated leads to Pd-I coordination. This pathway begins with PhI addition to **7** leading downhill 2.1 kcal/mol to **8** through the addition of PhI to intermediate **7**. From **8** PhI coordination to Pd through iodine causes the displacement of acetic acid with a barrier of 8.5 kcal/mol from **7** through **TS-8-9** leading to intermediate **9,** which is 0.9 kcal/mol downhill from **7**.

Alternatively the addition of PhI to **7** can also lead to **8a**, which is uphill 5.7 kcal/mol from **7**. From **8a** the Ph group can form a Pd-π complex, which also causes the displacement of acetic acid. This reaction has a barrier of 10.9 kcal/mol through **TS-8a-9a** leading to **9a**, which is uphill 3.7 kcal/mol from **7**. The 2.4 kcal/mol difference in activation barriers between these two pathways as well as the thermodynamic preference for Pd-I coordination over Pd-π complexation suggests that the Pd-I coordination pathway is operable rather than the Pd-π complex formation pathway. These results lead to further reaction path exploration only proceeding from **9**.

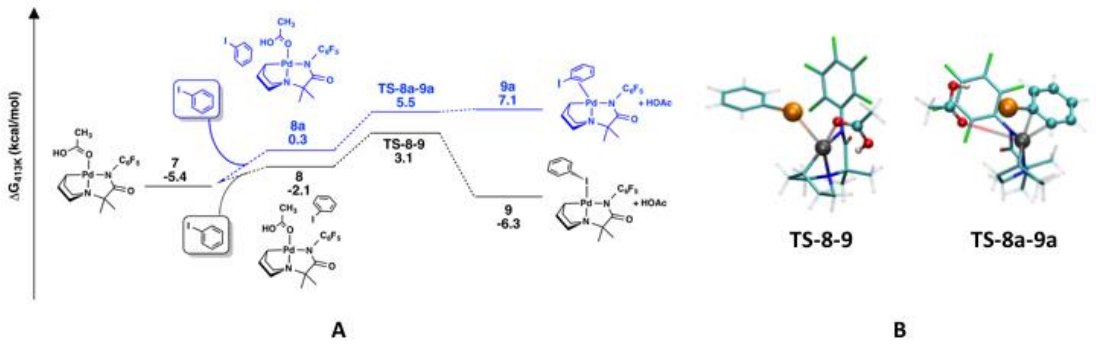


Figure S7: (A) Reaction pathway for Pd-I coordination verses Pd-π complex formation. (B) 3D renderings of the transition state structures for Pd-I coordination, **TS-8-9**, and Pd-π complex formation, **TS-8a-9a**. Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

e. Oxidative Addition without CsOAc

From **9**, oxidative addition without CsOAc was examined. First, the removal of acetic acid from **9** leads to **10s,** which is downhill from **9** by 1.8 kcal/mol. From **10s** an oxidative addition pathway, shown in **Figure S8**, was found where Ph adds into the axial position on Pd *cis* to C_γ while iodine remains in the equatorial position, leading to **11s** through **TS-10s-11s**. The barrier for this pathway is 19.1 kcal/mol above **10s**, but 40.4 kcal/mol above **5** (**Figure 4**), which is the lowest energy intermediate prior to this step. This makes oxidative addition to form the high valent Pd(IV) intermediate energetically infeasible without CsOAc. Intermediate **11s** is 3.0 kcal/mol downhill from **10s** and has square pyramidal Pd(IV) center bound to C_γ, C_{Ph}, iodine, N_{DG} and N_{Pip}. This structure is identical to intermediate **12**, from **Figure 10**, which forms through oxidative addition after acetic acid sequestration by Cs-acetate.

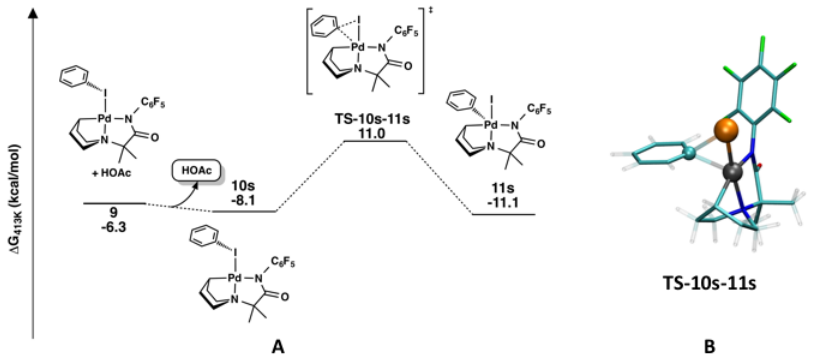


Figure S8: (A) Oxidative addition pathway without acetic acid sequestration. (B) 3D structure of the oxidative addition transition state **TS-10s-11s**. Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

f. Oxidative Addition and Reductive Elimination with Acetate or Acetic Acid Coordinated to Pd

Additional coordination of acetate or acetic acid to Pd prior to or following oxidative addition can result in 4 structures (**11-OAc, 11-OAcH, 12-OAc, 12-OAcH** in **Figure S9**) where the additional ligand is bound to Pd in addition to the aryl-iodide. From these four structures only **12-OAc** lead to a stable structure where the additional acetate ligand remained bound to Pd. From **12-OAc** the pathway for reductive elimination was investigated, **Figure S10**. Reductive elimination from **12-OAc** was found to have a barrier of 32.1 kcal/mol, 63.3 kcal/mol above the lowest energy intermediate, **5**, prior to this step. The barrier makes reductive elimination from **12-OAc** an energetically infeasible pathway.

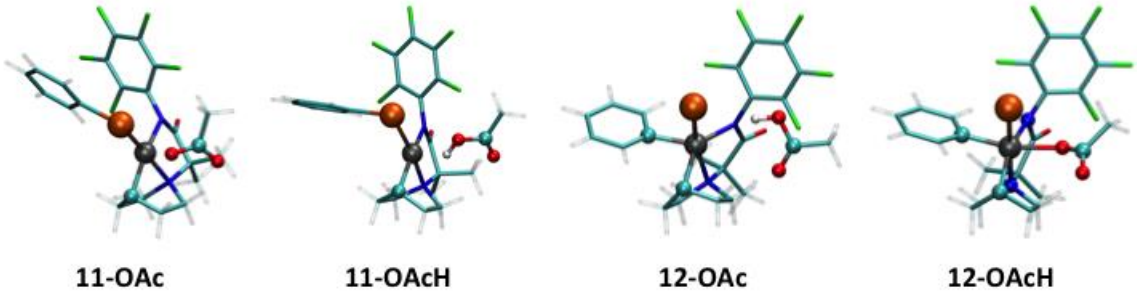


Figure S9: Optimized structures for pre and post oxidative addition intermediates with acetate or acetic acid coordinated to Pd.

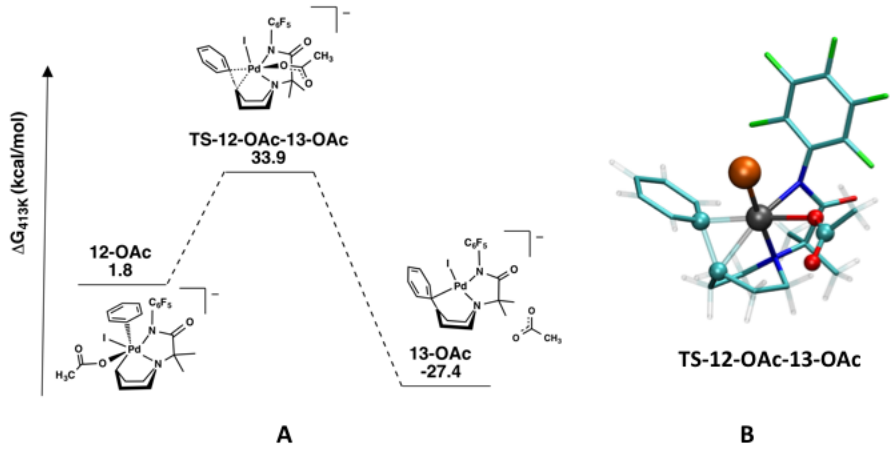


Figure S10: (A) Reaction pathway for reductive elimination from **12-OAc**. (B) 3D rendering of **TS-12-OAc-13-OAc.** Energies are referenced to separate reactants (i.e. **1** from **Figure 4,** main paper).

g. *Acetic Acid Assisted Iodine Abstraction Without Cesium*

Iodine abstraction with acetic acid assistance, but without the inclusion of a Cs cation, was investigated to assess the importance of the Cs cation in making iodine abstraction energetically feasible. Starting from **16**, acetic acid-assisted iodine abstraction can occur in the two-step process shown in **Figure S11**. First, acetic acid must replace Cs-OAcH, leading from **16** uphill 26.7 kcal/mol to **16s1**, immediately making this pathway energetically unfavorable. From **16s1** a ligand swap reaction between acetic acid and iodine can occur through **TS-16s1-17s1** with a barrier of 49.9 kcal/mol above **16** to form **17s1**, which is uphill 35.7 kcal/mol from **16**. This pathway leads to a free iodine anion and a square planar Pd center bound to κ^1-acetic acid, κ^1-acetate, N_{DG}, and $N_{Pip.}$ The high energy profile indicates the importance of having the Cs cation participate in iodine abstraction, so that it can coordinate to the iodine anion and generate CsI.

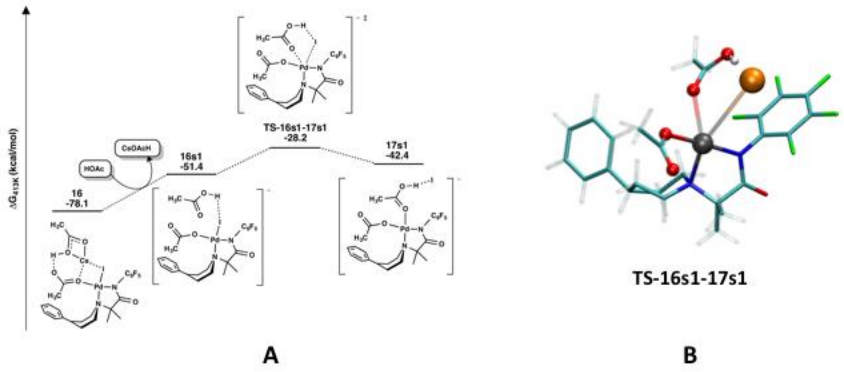


Figure S11: (A) Iodine abstraction pathway without the Cs cation but with HOAc rebinding to Pd. (B) 3D structure of the iodine abstraction transition state **TS-16s1-17s1**. Energies are referenced to separate reactants (i.e. **1** from **Figure 4**).

h. *Iodine Abstraction without Cs-OAcH*

Iodine abstraction without the assistance of Cs-OAcH was investigated to determine its affect on the barrier to iodine abstraction. Without the assistance of Cs-OAcH, iodine abstraction can occur in through a single ligand swap step (**Figure S12**) where the free O of the κ^1-acetate ligand rebinds to Pd, forcing iodine to dissociate from the metal center through **TS-16s2-17s2**. Without the presence of the Cs cation the iodine anion is left without a counter ion, which ultimately increases the energy of this step. The initial removal of Cs-OAcH from **16** leads uphill 14.5 kcal/mol to **16s2**. From **16s2** the barrier to form **17s2** is 28.6 kcal/mol above **16** through **TS-16s2-17s2**, which makes it feasible, but unlikely to occur in competition with the pathway leading from **16** to **17** through **TS-16-17** (**Figure 16**), which has a barrier of 17.7 kcal/mol above **16** (**TS-16-17, Figure 17**). The high energy for these steps helps establish the importance of having the Cs cation participate in iodine abstraction.

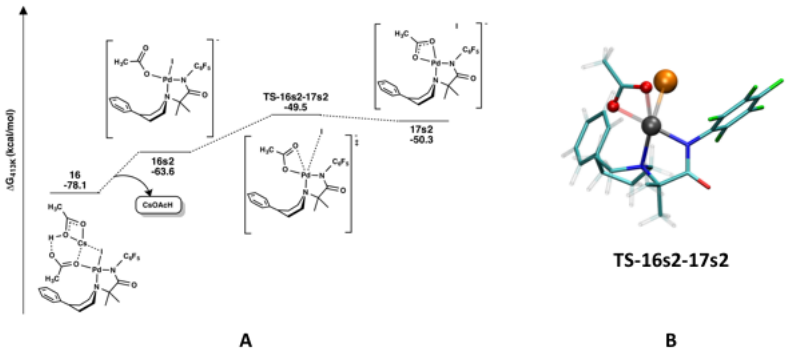


Figure S12: (A) Iodine abstraction pathway without any additives. (B) 3D structure of the iodine abstraction transition state **TS-16s2-17s2**. Energies are referenced to separate reactants (i.e. **1** from **Figure 4**).

5. Natural Bond Orbital Data for N_{DG},N_{Pip} versus O_{DG},N_{Pip} Coordination to Pd

Table S2: Natural Bond Orbital Analysis for Pd coordinated to either N_{DG},N_{Pip} or O_{DG},N_{Pip}.

Bond	Atom	AO Contribution (%)	s-Orbital Contribution (%)	p-Orbital Contribution (%)	d-Orbital Contribution (%)
N_{DG}-Pd	N_{DG}	72.47	19.67	80.33	0.00
	Pd	27.53	9.73	0.06	90.21
O_{DG}-Pd	O_{DG}	83.17	8.92	91.08	0.00
	Pd	16.83	45.18	0.70	54.12

The thermodynamic difference of 15.7 kcal/mol favoring Pd-N_{DG},N_{Pip} coordination over Pd-O_{DG},N_{Pip} coordination can be further explained by the bonding differences between N_{DG}-Pd and O_{DG}-Pd, **Table S2**. The N_{DG}-Pd bond is composed of more even contributions from the N_{DG} and Pd orbitals (72.47% and 27.53% respectively) in comparison to the O_{DG}-Pd bond (83.17% O_{DG} and 16.83% Pd). In addition, the p-d orbital overlap differences between N_{DG} and O_{DG} coordinated to Pd could further explain the greater stability of Pd-N_{DG},N_{Pip} coordination. The N_{DG}-Pd bond is composed of 19.67% N_{DG} s-orbital and 80.33% N_{DG} p-orbital interacting with 9.73% Pd s-orbital and 90.21% Pd d-orbital interactions. In contrast, the O_{DG}-Pd bond is composed of 8.29% O_{DG} s-borbital and 91.08% O_{DG} p-orbital interactions with 45.18% Pd

s-orbital, 0.70% Pd p-orbital and 54.12% Pd d-orbital interactions. The greater involvement of Pd orbitals in the N_{DG}-Pd bond and the significant reduction in p-d orbital overlap between O_{DG} and Pd in comparison to N_{DG} and Pd can explain the greater stability of the N_{DG},N_{Pip} chelation mode.

6. Dispersion Correction Impact on C-H Activation Energetics and Structures

To check the reliability of the B3LYP functional for optimizations and reaction path exploration single point energies using three other functionals were examined in the C-H activation step for the model system and the real system (intermediates **5, TS-5-7**, **7, 5'**, **TS-5'-7'**, **7'**). Specifically PBE, B3LYP, ωB97X-D, and M06-2X. were used to run gas-phase and solvent corrected single point energy calculations for the C-H activation intermediates. We expect to see similar energetics from B3LYP, M06-2X and ωB97X-D functionals but an underestimated activation barrier with the GGA functional, PBE. In addition these same C-H activation intermediates and transition states have been optimized using B3LYP and ωB97X-D to see how dispersion corrections effect optimizations.

a. Gas- and Solvent-Phase Energies

The energies of the C-H activation intermediates and transition state for the model system (**5**, **TS-5-7**), and the real system (**7**, **5'**, **TS-5'-7',** and **7'**) were calculated using the PBE, B3LYP, M06-2X and ωB97X-D density functionals with the LANL2TZ(f) basis set and ECP on Pd and 6-311++G** basis set on all main group elements in both the gas- and solvent-phase, and the results can be found in **Tables S3, S4, S5**, and **S6**. The activation barriers for C-H activation were found to be within 1 kcal/mol of one another using B3LYP, M06-2X and ωB97X-D, with barriers between 38.1-39.1 kcal/mol for the model system and 38.2-39.4 kcal/mol for the real system, respectively, in the gas-phase. In the solvent phase, the barriers were still within 1 kcal/mol, ranging from 37.1-38.0 kcal/mol in the model system and 36.8-37.9 kcal/mol in the real system. As expected, the PBE functional underestimated the barriers for the model and real system in the gas-phase at 31.2 and 31.9 kcal/mol and the solvent-phase barriers at 30.0 and 30.2 kcal/mol. This shows that the use of a dispersion corrected functional (ωB97X-D) versus a non-dispersion corrected functional (B3LYP) has little impact on calculating the activation barrier for the reaction.

In addition, the thermodynamics of the reaction were also found to have little variance with respect to the functional chosen, as the energy of reaction for the model and real system ranged from 22.7-

26.1 kcal/mol and 20.3-23.7 kcal/mol, respectively, in the gas-phase. Similarly, the solvent phase thermodynamics of the reaction were 21.1-24.6 kcal/mol and 18.4-22.0 kcal/mol for the model and real system, respectively.

Table S3: Gas phase enthalpies of the structures 5, TS-5-7, and 7 using various functionals. LANL2TZ(f) basis set with LANL2TZ(f) ECP was used on Pd, while 6-311++G** was used on all main group elements.

Functional	5 (Hartrees)	TS-5-7 (Hartrees)	7 (Hartrees)	E_a (kcal/mol)	E_{rxn} (kcal/mol)
PBE	-1619.184644	-1619.13501	-1619.148423	31.2	22.7
B3LYP	-1620.839231	-1620.77833	-1620.797674	38.2	26.1
ωB97X-D	-1620.368434	1620.307773	-1620.327864	38.1	25.5
M06-2X	-1620.157362	-1620.095131	-1620.119208	39.1	24.0

Table S4: Gas phase enthalpies of the structures 5', TS-5'-7', and 7' using various functionals. LANL2TZ(f) basis set with LANL2TZ(f) ECP was used on Pd, while 6-311++G** was used on all main group elements.

Functional	5' (Hartrees)	TS-5'-7' (Hartrees)	7' (Hartrees)	E_a (kcal/mol)	E_{rxn} (kcal/mol)
PBE	-1974.641696	-1974.590826	-1974.609394	31.9	20.3
B3LYP	-1976.691449	-1976.628646	-1976.653669	39.4	23.7
ωB97X-D	-1976.125353	-1976.063768	-1976.089155	38.7	22.7
M06-2X	-1975.881549	-1975.819552	-1975.84816	38.9	21.0

Table S5: Solvated enthalpies of the structures 5, TS-5-7, and 7 using various functionals. LANL2TZ(f) basis set with LANL2TZ(f) ECP was used on Pd, while 6-311++G** was used on all main group elements.

Functional	5 (Hartrees)	TS-5-7 (Hartrees)	7 (Hartrees)	E_a (kcal/mol)	E_{rxn} (kcal/mol)
PBE	-1619.2302537	-1619.1824004	-1619.1966954	30.0	21.1
B3LYP	-1620.0578100	-1619.9986559	-1620.0186513	37.1	24.6
ωB97X-D	-1620.420491	-1620.361419	-1620.382578	37.1	23.8
M062X	-1620.200299	-1620.139672	-1620.164763	38.0	22.3

Table S6: Solvated enthalpies of the structures 5', TS-5'-7', and 7' using various functionals. LANL2TZ(f) basis set with LANL2TZ(f) ECP was used on Pd, while 6-311++G** was used on all main group elements.

Functional	5'	TS-5'-7'	7'	E_a	E_{rxn}

	(Hartrees)	(Hartrees)	(Hartrees)	(kcal/mol)	(kcal/mol)
PBE	-1974.692773	-1974.644594	-1974.663399	30.2	18.4
B3LYP	-1975.736102	-1975.675712	-1975.701069	37.9	22.0
ωB97X-D	-1976.180376	-1976.121733	-1976.147466	36.8	20.7
M062X	-1975.928218	-1975.868213	-1975.897928	37.7	19.0

b. Optimized Structures, Key Bond Lengths and Energies

The structures of C-H activation intermediates and transition state for the model system (**5**, **TS-5-7**), and the real system (**7**, **5'**, **TS-5'-7'**, and **7'**) were optimized using the B3LYP and ωB97X-D density functionals with the LANL2DZ basis set and ECP on all elements. The structures can be found in **Figure S13** and **S14** and the key bond lengths and energies can be found in **Tables S7**, **S8**, **S9**, and **S10**. The use of a dispersion versus non-dispersion corrected functional appeared to have little impact on the structure optimization for the rate-limiting C-H activation intermediates and transition states in the model and real system. In addition changing the functional did not change the key features of the transition state structures **TS-5-7** and **TS-5'-7'**, which involve proton transfer from carbon to oxygen facilitated by Pd.

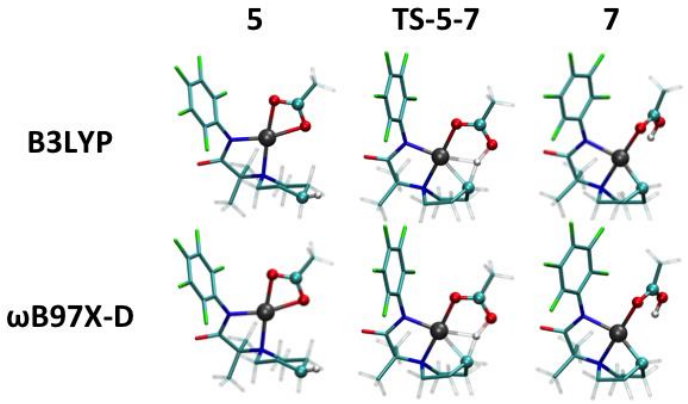


Figure S13: 3D renderings of optimized structures for **5, TS-5-7,** and **7** using B3LYP and ω97X-D.

Table S7: Key bond lengths in Å for gas phase optimized structures of **5, TS-5-7,** and **7** using B3LYP and ωB97X-D with LANL2DZ basis set on all atoms and the LANL2DZ ECP on Pd.

Key Bond Length (Å)	Functional	5	TS-5-7	7
Pd-C	**B3LYP**	4.006	2.300	2.085
	ωB97X-D	3.958	2.257	2.067
Pd-O	**B3LYP**	2.198	2.961	3.142
	ωB97X-D	2.182	2.930	3.178

C-H	**B3LYP**	1.096	1.486	3.344
	ωB97X-D	1.094	1.477	3.109
O-H	**B3LYP**	4.200	1.277	0.997
	ωB97X-D	4.142	1.273	0.987

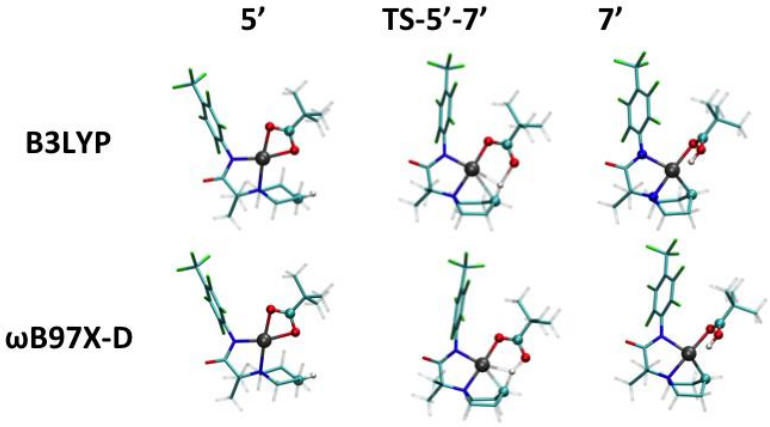


Figure S14 3D renderings of optimized structures for **5', TS-5'-7', 7'** using B3LYP and ωB97X-D.

Table S8: Key bond lengths for gas phase optimized structures of **5', TS-5'-7',** and **7'** using B3LYP and ωB97X-D with LANL2DZ basis set on all atoms and the LANL2DZ ECP on Pd.

Key Bond Length (Å)	**Functional**	**5'**	**TS-5'-7'**	**7'**
Pd-C	**B3LYP**	4.016	2.28706	2.084
	ωB97X-D	3.966	2.250	2.062
Pd-O	**B3LYP**	2.176	2.94597	3.127
	ωB97X-D	1.094	1.462	3.323
C-H	**B3LYP**	1.096	1.47219	3.418
	ωB97X-D	1.094	1.462	3.323
O-H	**B3LYP**	4.167	1.29960	0.996
	ωB97X-D	4.123	1.290	0.988

The gas phase energies of the optimized structures for C-H activation leads to the same conclusion as above: the functional has little impact on the activation barrier and energy of reaction found for the C-H activation step, even when using a smaller basis set, LANL2DZ with ECP on Pd. The activation barriers for the real and model system were found to be 38.4 and 37.4 kcal/mol using B3LYP and 37.7 and 35.6

kcal/mol using ωB97X-D. The energy of reaction for the optimized structures were found to be 28.8 and 26.0 kcal/mol using B3LYP and 27.7 and 24.4 kcal/mol using ωB97X-D respectively.

Table S9: Gas-phase enthalpies of the re-optimized structures of 5, TS-5-7, 7 using B3LYP and ωB97X-D with LANL2DZ basis set on all atoms and the LANL2DZ ECP on Pd.

Functional	5 (Hartrees)	TS-5-7 (Hartrees)	7 (Hartrees)	E_a (kcal/mol)	E_{rxn} (kcal/mol)
B3LYP	-1620.009124	-1619.948006	-1619.963306	38.4	28.8
ωB97X-D	-1619.562935	-1619.502937	-1619.518833	37.7	27.7

Table S10: Gas-phase enthalpies of the re-optimized structures of 5', TS-5'-7', 7' using B3LYP and ωB97X-D with the LANL2DZ basis set on all elements and LANL2DZ ECP for Pd.

Functional	5' (Hartrees)	TS-5'-7' (Hartrees)	7' (Hartrees)	E_a (kcal/mol)	E_{rxn} (kcal/mol)
B3LYP	-1975.674782	-1975.615123	-1975.633434	37.4	26.0
ωB97X-D	-1975.139256	-1975.0826	-1975.100383	35.6	24.4

7. Tables for Bond Lengths of Structures During C-H Activation Featured in Figures 8 and 9

Table S11: Bond lengths during C-H Activation. C-H and O-H bond lengths featured in **Figure 8** and **Figure 9** of the main text for the conversion from **5** to **7** through **TS-5-7**. All bond lengths are in Å.

	5	5-7a	5-7b	5-7c	5-7d	5-7e	5-7f	TS-5-7	5-7g	5-7h	7
C-H Bond Length (Å)	1.096	1.096	1.096	1.093	1.091	1.094	1.138	1.485	2.215	2.766	3.330
O-H Bond Length (Å)	4.200	3.652	3.119	2.660	2.360	2.188	1.966	1.279	1.007	0.998	0.996

Table S12: Bond lengths during C-H Activation. Pd-C and Pd-O bond lengths features in **Figure 8** and **Figure 9** of the main text for the conversion of **5** to **7** through **TS-5-7**. All bond lengths are in Å.

	5	5-7a	5-7b	5-7c	5-7d	5-7e	5-7f	TS-5-7	5-7g	5-7h	7
Pd-C Bond Length (Å)	4.006	3.810	3.623	3.440	3.301	3.049	2.592	2.279	2.138	2.096	2.085

Pd-H Bond Length (Å)	2.198	2.199	2.201	2.202	2.219	2.463	2.895	2.944	3.134	3.171	3.145

8. Energetic Differences Between High and Low Spin States for Intermediates 15 and 16

Table S13: Energies for structures **15** and **16** in the singlet (low spin) and triplet (high spin) states, and their energies referenced to the lowest energy structure. [a]Energies reported are enthalpies calculated in the gas phase enthalpies[3]. [b]Energies are Gibbs free energies calculated in solvent[4,5]

Geometry (structure)	**Spin State**	**Energy (hartrees)**	**ΔE (kcal/mol)**
Square Planar (16)[a]	singlet	-2111.438676	0.0
Square Planar (16)[a]	triplet	-2111.371125	42.4
Tetradedral (15)[a]	singlet	-2111.397954	25.6
Tetradedral (15)[a]	triplet	-2111.365756	45.8
Square Planar (16)[b]	singlet	-2111.531667	0.0
Tetradedral (15)[b]	singlet	-2111.496421	22.1

The barrierless isomerization of structure **15** to structure **16** can be attributed to the thermodynamic stability of the singlet square planar complex in comparison to the singlet tetrahedral complex, which lies 25.6 kcal/mol uphill in energy. This stability is extended to the difference in energy between the singlet at triplet states of the square planar and tetrahedral complexes in which the square planar singlet complex lies 42.4 and 45.8 kcal/mol downhill in energy from the triplet square planar and tetrahedral complexes respectively, **Table S13**.

Solvent, and frequency corrections are shown to have minimal impact on changing the energetics between the singlet square planar and tetrahedral complexes in comparison to the gas phase. The smaller energetic difference between the square planar and tetrahedral complexes **15** and **16** are expected to translate to the differences in energy between the singlet and triplet states, as evident in the gas phase energies. Overall the singlet square planar state is the lowest energy state, and the thermodynamic difference in energy between the varying spin states and geometries suggests that only the square planar singlet structure should exist in-situ.

9. Solvated Entropy Corrections

Method for calculating reaction free energies

The gas phase entropy is given by

$$-S(g) = ((G(g)-H(g))/T) \text{ where } G(g) = E(g) + G_{corr} \text{ and } H(g) = E(g) + H_{corr}$$

For solvent phase entities entropy S(l) is derived by scaling the gas phase entropy S(g) by a factor of 0.5:

$$S(l) = 0.50 \times S(g)$$

$$G(l) = H(l) - TS(l) = E(l) + H_{corr} - 0.50xTS(g)$$

10. Vibrational Entropy Corrections

Corrections made to low entropies of stationary points and transition state structures.

All entropies below 50 cm^{-1} were replaced by 50 cm^{-1} and the vibrational entropy of the structure was corrected to account for these changes. In transition state structures, the highest magnitude imaginary frequency, corresponding to the TS mode, was left unchanged by these corrections.

Entropy corrections and transition state frequency for each structure

- Free Substrate ($PipCONHC_6F_5$-chair)
  - 17.72, 29.24, 40.94 replaced with 50 cm^{-1}
- Free Substrate ($PipCONHC_6F_5$boat)
  - 20.10, 32.41, 42.18 replaced with 50 cm^{-1}
- Pd-Acetate
  - All frequencies above 50 cm^{-1}
- Acetic Acid Dimer
  - All frequencies above 50 cm^{-1}
- Acetic Acid Monomer
  - All frequencies above 50 cm^{-1}
- Acetate Anion
  - 27.23 cm^{-1} replaced with 50 cm^{-1}
- PhI
  - All frequencies above 50 cm^{-1}
- CsOAc
  - Imaginary frequency: i15.66 (Me group rotation) replaced with 50 cm^{-1}
  - All other frequencies above 50 cm^{-1}
- CsOAc-HOAc
  - 27.69, 47.95 cm^{-1} replaced with 50 cm^{-1}
- Free Product ($PhPipCONHC_6F_5$-chair)
  - 15.49, 18.86, 23.86, 34.83, 48.20 replaced with 50 cm^{-1}
- N_{DG},N_{Pip} Chelated Structure
  - Imaginary frequency: i38.62 (Me group rotation) replaced with 50 cm^{-1}

    - 21.68, 23.40, 33.35, 44.55 replaced with 50 cm^{-1}
- O_{DG},N_{Pip} Chelated Structure
    - 14.46, 17.80, 27.84, 44.89, 46.68 replaced with 50 cm^{-1}
- Pd(OAc)(HOAc)-Substrate
    - 25.60, 28.90, 35.46, 45.55 replaced with 50 cm-^{1}
- Pd(OAc)(HOAc)-Product
    - Imaginary frequency: i10.42 (Arene ring rotation) replaced with 50 cm^{-1}
    - 13.16, 19.87, 30.25, 32.80, 33.36, 39.69, 44.28 replaced with 50 cm^{-1}
- Alpha CMD
    - Imaginary frequency: i17.32 (Me group rotation) replaced with 50 cm^{-1}
    - 21.88, 29.05, 32.97, 45.21 replaced with 50 cm^{-1}
- Beta CMD
    - 27.84, 30.27, 39.17, 47.53 replaced with 50 cm^{-1}
- Gamma CMD (same as structure 7)
    - 22.72, 34.46, 40.62 replaced with 50 cm^{-1}
- Free Substrate (PipCONHC$_7$F$_7$-chair)
    - 20.70, 22.76, 26.97, 36.96 replaced with 50 cm^{-1}
- Pd-Pivalate
    - 18.41, 26.12, 30.90, 49.39 replaced with 50 cm^{-1}
- Pivalic Acid Dimer
    - 10.82, 30.61, 35.24 replaced with 50 cm^{-1}

- 1 – separate reactants
    - See free structures
- 2
    - 11.14, 18.64, 30.26, 31.18, 41.54, 46.18 replaced with 50 cm^{-1}
- TS-2-3
    - i110.08 = TS frequency
    - Imaginary frequencies: i53.34, i28.19 (Me group rotations) replaced with 50 cm^{-1}
    - 13.58, 18.12, 32.91, 33.76, 43.67, 47.13 replaced with 50 cm^{-1}
- 3
    - 23.36, 25.54, 31.86, 34.04, 44.37, 48.28 replaced with 50 cm^{-1}
- TS-3-4
    - i70.37 = TS frequency
    - Imaginary frequency: i19.33 (Arene ring rotation) replaced with 50 cm^{-1}
    - 19.41, 35.77, 42.31 replaced with 50 cm^{-1}
- 4
    - 21.98, 25.91, 30.61, 32.93, 35.3, 43.05 replaced with 50 cm^{-1}
- TS-4-5
    - i31.99 = TS frequency
    - 18.63, 26.98, 28.85, 35.16, 46.05 replaced with 50 cm^{-1}
- 5 (with HOAc)
    - 13.30, 21.06, 31.58, 34.91 45.33, 48.88 replaced with 50 cm^{-1}
- 5 (without HOAc)
    - Imaginary frequency: i38.62 (Me group rotation) replaced with 50 cm^{-1}
    - 21.68, 23.40, 33.35, 44.55 replaced with 50 cm^{-1}
- TS-4-6
    - i137.60 = TS frequency
    - Imaginary frequency: i6.07 (Arene ring rotation) replaced with 50 cm^{-1}
    - 18.82, 26.37, 36.70, 45.12 replaced with 50 cm^{-1}
- 6
    - Imaginary frequency: i18.86 (Me group rotation) replaced with 50 cm^{-1}
    - 24.17, 33.01, 35.84, 45.03, 49.63 replaced with 50 cm^{-1}
- TS-6-7
    - i1289.72 = C-H activation TS frequency

- 24.50, 27.37, 37.55, 40.34, 49.85 replaced with 50 cm^{-1}
- TS-5-7
  - i1219.12 = C-H activation TS frequency
  - 13.80, 23.87, 33.68, 49.34 replaced with 50 cm^{-1}
- 7 (with HOAc)
  - 19.56, 22.10, 30.30, 33.53, 35.47 replaced with 50 cm^{-1}
- 7 (without HOAc)
  - 22.72, 34.46, 40.62 replaced with 50 cm^{-1}
- 5exp
  - 18.56, 22.34, 26.21, 27.68, 35.75, 36.02 replaced with 50 cm^{-1}
- TS-5exp-7exp
  - i1260.82 = C-H activation TS frequency
  - 10.40, 19.69, 22.94, 28.54, 36.51, 42.63 replaced with 50 cm^{-1}
- 7exp
  - 9.27, 16.45, 31.25, 35.96, 38.86, 47.55 replaced with 50 cm^{-1}

- 8
  - 19.11, 27.52, 28.32, 30.98, 35.89, 37.46, 44.72 replaced with 50 cm^{-1}
- TS-8-9
  - i66.7 = TS frequency
  - 12.44, 29.06, 31.74, 35.36, 36.29, 42.81 replaced with 50 cm^{-1}
- 9
  - 11.92, 24.14, 27.36, 30.85, 31.49, 40.9, 47.85 replaced by 50 cm^{-1}
- 10
  - 33.14 replaced with 50 cm^{-1}
- 11
  - 16.94, 24.64, 25.53, 31.69, 36.09 replaced with 50 cm^{-1}
- TS-11-12
  - i163.68 = TS frequency
  - 16.99, 28.25, 32.3, 44.64 cm^{-1} replaced with 50 cm^{-1}
- 12
  - 15.71, 21.91, 33.05, 42.84 replaced with 50 cm^{-1}
- TS-12-13
    - i280.02 = TS frequency
  - 14.48, 22.85, 35.04, 41.26 replaced with 50 cm^{-1}
- 13
  - 11.18, 22.5, 36.79, 43.74 replaced with 50 cm^{-1}
- 14
  - 2.00, 15.43, 19.12, 20.89, 27,.85, 29.06, 37.28, 44.44 replaced with 50 cm^{-1}
- TS-14-15
  - i40.81 = TS frequency
  - 8.05, 15.84, 16.96, 21.76, 25.28, 26.39, 31.88, 33.51, 37.01, 44.10, 48.73 replaced with 50 cm^{-1}
- 15
  - Imaginary frequency: i17.98 (Substrate wobble) replaced with 50 cm^{-1}
  - 7.53, 9.04, 20.47, 22.15, 29.43, 30.79, 35.08, 38.38, 39.94, 46.36 replaced with 50 cm^{-1}
- 16
  - 5.27, 10.57, 16.81, 22.08, 27.19, 27.82, 31.79, 34.89, 37.4, 44.77, 45.18 replaced with 50 cm^{-1}
- TS-16-17
  - i190.9 = TS frequency
  - 12.32, 16.14, 17.19, 18.51, 21.46, 35.53, 41.38, 42.69, 49.53 replace with 50 cm^{-1}
- 17
  - 12.5, 16.04, 23.38, 30.76, 32.79, 36.19, 37.2, 42.39, 43.95 replaced with 50 cm^{-1}

- 18
    - 25.60,28.9,35.46,45.55 replaced with 50 cm^{-1}
- 19
    - Imaginary frequency: i10.42 (Arene ring rotation) replaced with 50 cm^{-1}
    - 13.16, 19.87, 30.25, 32.80, 33.36, 39.69, 44.28 replaced with 50 cm^{-1}
- 20 (Prod-chair + Pd-acetate)
    - See separate Prod-chair & Pd-acetate structures frequency corrections above.

SI Structures

- 5s
    - 21.99, 25.88, 30.59, 32.91, 35.9, 43.02 replaced with 50 cm^{-1}
- TS-5s-7s
    - 1197.67i = C-H activation TS frequency
    - Imaginary frequencies: i44.83 (Me group rotation) i25.22 (acetate wobble) replaced with 50 cm^{-1}
    - 14.49, 25.94, 33.32, 38.14, 46.52 replaced with 50 cm^{-1}
- 7s
    - 19.56, 22.10, 30.30, 33.53, 35.47 replaced with 50 cm^{-1}
- 5
    - See structure 5 frequency corrections above.
- TS-5-5boat
    - i223.22 = Isomerization TS frequency
    - Imaginary frequency: i44.93 (Me group rotation) replaced with 50 cm^{-1}
    - 11.2, 30.53, 33.68, 47.99 replaced with 50 cm^{-1}
- 5boat
    - Imaginary frequency: i47.00 (Me group rotation) replaced with 50 cm^{-1}
    - 15.34, 30.03, 35.19, 46.92 replaced with 50 cm^{-1}
- TS-5boat-7
    - i1252.25 = C-H activation TS frequency
    - Imaginary frequency: i77.76 (Me group rotation) replaced with 50 cm^{-1}
    - 20.56, 23.54, 36.91 replaced with 50 cm^{-1}
- 7
    - See structure 7 frequency corrections above.
- 5
    - See structure 5 frequency corrections above.
- TS-5-7α
    - i1450.15 = C-H activation TS frequency
    - 17.02, 24.48, 29.40, 35.09 replaced with 50 cm^{-1}
- TS-5-7β
    - i1275.58 = C-H activation TS frequency
    - 20.66, 32.17, 35.43, 49.17 replaced with 50 cm^{-1}
- TS-5-7
    - See structure TS-5-7 frequency corrections above.
- 7α
    - See structure Alpha CMD frequency corrections above.
- 7β
    - See structure Beta CMD frequency correcttions above.
- 7
    - See structure 7 frequency corrections above.
- 8
    - See structure 8 frequency corrections above
- 8a
    - 25.49 32.07, 39.84 replaced with 50 cm^{-1}
- TS-8-9
    - See structure TS-8-9 frequency corrections above

- TS-8a-9a
  - i83.30 = Pi complex formation TS frequency
  - Imaginary frequency i51.36 (Me group wobble) replaced with 50 cm^{-1}
  - Imaginary frequency i43.17 (Me group wobble) replaced with 50 cm^{-1}
  - Imaginary frequency i25.06 (acetate rocking) replaced with 50 cm^{-1}
  - Imaginary frequency i15.87 (acetate rocking) replaced with 50 cm^{-1}
  - 15.66, 24.24, 31.22, 35.92, 38.45, 45.83 replaced with 50 cm^{-1}
- 9
  - See structure 9 frequency corrections above
- 9a
  - Imaginary Frequency i71.19 (Me group wobble) replaces with 50 cm^{-1}
  - 10.34, 17.97, 30.20, 32.80, 35.49, 40.79, 48.77 replaced with 50 cm^{-1}
- 10s
  - See structure 11 frequency corrections above.
- TS-10s-11s
  - See structure TS-11-12 frequency corrections above.
- 11s
  - See structure 12 frequency corrections above.
- 12-OAc
  - 25.49, 32.07, 39.84 replaced with 50 cm^{-1}
- TS-12-OAc-13-OAc
  - i323.92 = C-C coupling TS frequency
  - Imaginary frequency 49.86 (substrate wobble) replaced with 50 cm^{-1}
  - 16.36, 26.56, 32.04, 36.3, 48.43 replaced with 50 cm^{-1}
- 13-OAc
  - 27.14, 36.22, 38.09, 48.54 replaced with 50 cm^{-1}
- 16s1
  - 19.11, 24.46, 32.02, 33.65, 36.46, 40.73, 47.73 replaced with 50 cm^{-1}
- TS-16s1-17s1
  - i48.77 = TS frequency
  - Imaginary frequency: i12.48 (Phenyl/CsOAcH wobble) replaced with 50 cm^{-1}
  - 5.98 17.31, 21.45, 25.64, 33.64, 35.82, 44.77 – replace with 50cm^{-1}
- 17s1
  - 9.75, 14.36, 18.87, 26.14, 30.52, 32.25, 26.07, 38.93, 47.69 replaced with 50 cm^{-1}
- 16s2
  - 16.42, 20.51, 24.58, 27.8, 34.67, 36.99, 48.15 replaced with 50 cm^{-1}
- TS-16s2-17s2
  - i57.01 = TS frequency
  - Imaginary frequency: i7.11 (Substrate wobble) replaced with 50 cm^{-1}
  - 13.57, 22.84, 32.01, 35.93, 37.31, 45.42 replaced with 50 cm^{-1}
- 17s2
  - 13.51, 21.1, 27.16, 29.95, 37.13, 40.82, 47.03 replaced with 50 cm^{-1}

11. XYZ Coordinates and Energies for All Structures

Free Substrate (PipCONHC_6F_5-chair)
Total free energy in solvent: -1265.743067
40

C	-4.64054860	2.20651846	1.34037785
N	-4.82283667	1.86896006	-0.09787452
C	-4.21527053	0.55473466	-0.41641748
C	-4.87041352	-0.55232893	0.42704230
H	-3.12407756	0.56127689	-0.22538714
H	-4.36368296	0.33565494	-1.47422077
C	-5.31422598	1.15598674	2.23530803

H	-5.07595917	3.19358782	1.52435755
H	-3.56759593	2.26335085	1.59789700
N	-6.89276610	3.44506671	-0.45583059
C	-4.55158403	3.01060472	-1.03257824
C	-5.71368052	4.02912251	-0.88190457
C	-4.61379337	2.54582291	-2.51138525
C	-3.20671519	3.72919679	-0.78445185
O	-5.61018867	5.22330166	-1.20998773
C	-8.12724022	4.09540913	-0.36011977
C	-9.26857797	3.50859709	-0.92336742
C	-8.29628188	5.31517023	0.31073149
C	-9.53949321	5.94031478	0.36459298
C	-10.65387124	5.33865990	-0.21235816
C	-10.51867342	4.10913463	-0.85126623
F	-9.67910192	7.13704771	1.02630382
F	-11.88367915	5.94729612	-0.14061875
F	-11.61388853	3.50187549	-1.41914732
F	-9.13875337	2.29549336	-1.57107820
F	-7.24038211	5.89379760	0.97112190
H	-2.37524856	3.03031889	-0.92870252
H	-3.14548212	4.14428099	0.22490841
H	-3.09750010	4.55847581	-1.48684633
H	-3.73209850	1.95564794	-2.77831229
H	-4.63480125	3.42887810	-3.15625908
H	-5.51306270	1.95168910	-2.70470715
C	-4.76869782	-0.25101088	1.93277936
H	-6.39946012	1.17882653	2.06342349
H	-5.14874681	1.41832841	3.28802278
H	-4.39278908	-1.51251359	0.19365983
H	-5.92654328	-0.63406665	0.13613719
H	-5.30946385	-1.00806677	2.51377839
H	-3.71442271	-0.30538904	2.24357386
H	-6.81138125	2.44083833	-0.29176486

Free Substrate (PipCONHC$_6$F$_5$-boat)
Total free energy in solvent: -1265.7319682148
40

C	-4.44248425	2.33099587	1.42570928
N	-4.61689287	1.92065920	0.00286796
C	-3.96583241	0.61435281	-0.24712934
C	-4.78066798	-0.50508138	0.45077238
H	-2.92501711	0.61581130	0.12466103
H	-3.91852658	0.42109143	-1.31799659
C	-4.62765249	1.12042061	2.37737419
H	-5.18268893	3.10811543	1.64643121
H	-3.44697517	2.77219208	1.59566505
N	-6.80580496	3.33757056	-0.39150789
C	-4.45231323	3.02701393	-0.99003521
C	-5.66432487	3.98474388	-0.82966521
C	-4.55880176	2.48608402	-2.44190956
C	-3.14216782	3.83308600	-0.84899763
O	-5.63070209	5.18277327	-1.15682282
C	-8.06822364	3.92720134	-0.26675602
C	-9.19127473	3.30188906	-0.82467403
C	-8.27899051	5.12580473	0.42980772
C	-9.54599103	5.69709455	0.51330283

C	-10.64187548	5.05899137	-0.06002095
C	-10.46433490	3.84811009	-0.72376741
F	-9.72621998	6.87434260	1.19938830
F	-11.89483217	5.61432195	0.03746720
F	-11.54165033	3.20703753	-1.28865778
F	-9.02035804	2.10791991	-1.49720585
F	-7.23735672	5.73403419	1.08638171
H	-2.28028745	3.16576122	-0.96054452
H	-3.07225010	4.34218491	0.11551703
H	-3.09664647	4.60284112	-1.62292161
H	-3.64381894	1.96461398	-2.73826419
H	-4.69734758	3.32800031	-3.12652787
H	-5.40908300	1.80501064	-2.55116583
C	-5.48335579	0.02320566	1.72474107
H	-5.07491751	1.46342595	3.31764121
H	-3.64772329	0.69756910	2.63648843
H	-4.10218159	-1.32996813	0.70587837
H	-5.52775056	-0.90863860	-0.24345570
H	-6.46676786	0.43494472	1.46528594
H	-5.66251941	-0.79721622	2.42963782
H	-6.66734043	2.34286898	-0.21444271

Pd-Acetate
Total free energy in solvent: -583.725678

15			
Pd	-0.59383466	0.97243554	-0.01367325
O	-2.41278039	2.03512538	-0.10033808
C	-3.09098212	0.91919612	-0.02561941
C	-4.57558780	0.89287422	-0.00031947
H	-4.92952331	1.09696562	1.01770523
H	-4.93930078	-0.09030685	-0.30431774
H	-4.97585360	1.66937597	-0.65678182
O	-2.37026272	-0.16888210	0.05126848
O	1.18315034	2.11403733	-0.07590560
C	1.90329366	1.02635759	0.00393466
O	1.22460736	-0.09004395	0.07449046
C	3.38832794	1.05297266	0.00807015
H	3.74513360	2.08372254	0.00368343
H	3.77071928	0.52741758	-0.87384488
H	3.76746320	0.52947233	0.89164784

Acetic Acid Dimer
Total free energy in solvent: -458.207813

16			
O	-1.98989203	-1.31597072	0.16150003
C	-0.82895576	-0.84128924	0.07932781
O	0.27563196	-1.59810812	0.03672308
C	-0.55677850	0.63076424	0.02628737
H	-1.49552851	1.18323821	0.05231793
H	-0.00118853	0.87619223	-0.88473311
H	0.07080494	0.91955462	0.87616211
H	0.08846540	-2.60023393	0.08939850
C	-1.48688673	-4.61925671	0.31885549
O	-0.32833593	-4.14627979	0.20297392
O	-2.59195316	-3.86268488	0.35219242
C	-1.75594211	-6.08820430	0.43406379

H	-0.81990227	-6.64382296	0.38657126
H	-2.42321965	-6.40714790	-0.37315864
H	-2.26873262	-6.29821338	1.37868748
H	-2.40800649	-2.86163736	0.27301056

Acetic Acid Monomer
Total free energy in solvent: -229.0957852802
8
Step 5

O	-1.99890573	-0.70525672	0.00000000
C	-0.87271532	-0.20341518	0.00000000
O	0.27348899	-0.97753366	0.00000000
C	-0.54398309	1.25913095	-0.00000000
H	-1.46587800	1.84005371	0.00000000
H	0.05462206	1.50990544	-0.88168624
H	0.05462206	1.50990544	0.88168624
H	0.03678903	-1.93059998	0.00000000

Acetate Anion
Total free energy in solvent: -228.6212823531
7
Step 6

O	-1.43798821	4.49565243	-0.22187906
C	-1.13420066	4.24729529	0.99868037
O	-0.69784017	3.15446422	1.51106176
C	-1.31697783	5.42706995	2.00893138
H	-1.67936047	6.32820820	1.50180941
H	-0.36062975	5.64436716	2.50618188
H	-2.02837291	5.13764275	2.79590426

PhI
Total free energy in solvent: -243.0139382
12

C	-4.81092703	3.14562646	0.00239324
C	-4.85562393	1.74500040	-0.00431502
C	-3.58231219	3.81547195	0.00199684
C	-2.39052070	3.08232167	-0.00501329
C	-2.41997423	1.68143970	-0.01174399
C	-3.65560560	1.02835204	-0.01134224
I	-3.70913671	-1.12583623	-0.02240446
H	-5.80896946	1.22917839	-0.00407595
H	-3.55377024	4.90012065	0.00710419
H	-5.73952341	3.70758011	0.00789391
H	-1.49576709	1.11549694	-0.01724698
H	-1.43337942	3.59415792	-0.00537624

CsOAc
Total free energy in solvent: -248.4541855139 A.U.
8

Cs	-4.44468501	-3.74648959	1.17166753
O	-3.66632306	-4.08561220	-1.64979784
C	-4.35032470	-5.17241156	-1.79195832
O	-5.04849137	-5.72539507	-0.85643641
C	-4.30751076	-5.85784141	-3.15763642
H	-4.48973170	-5.12495489	-3.95098169
H	-5.04530494	-6.66107080	-3.21026962

H	-3.30731846	-6.27723448	-3.32640723

CsOAc-HOAc
Total free energy in solvent: -477.5798046820
16

O	-0.06598901	3.19350241	2.26741770
O	0.10717302	2.50954560	0.08935991
C	-0.58476799	2.83298890	1.17951717
C	-2.07891680	2.72195212	0.99547187
H	1.18985095	2.58899164	0.17996166
H	-2.34569960	1.69002908	0.74296192
H	-2.39864804	3.35065036	0.15796825
H	-2.59509081	3.02495977	1.90712961
Cs	2.74793205	3.50509963	3.33941509
O	2.52645518	2.76420609	0.45070356
C	3.26802472	3.74653768	-0.01967933
O	4.06230374	4.40996195	0.71275686
C	3.13872594	4.05625952	-1.50143709
H	2.08335510	4.17095116	-1.77331401
H	3.53350853	3.21726685	-2.08683740
H	3.69085301	4.96316726	-1.75245579

Free Product (PhPipCONHC$_6$F$_5$-chair)
Total free energy in solvent: -1496.77711
50

N	-5.92876040	3.10009466	-0.81486298
C	-5.17236277	2.46420638	0.29017279
C	-6.68006100	2.08498148	-1.60093450
C	-5.20773001	4.10747904	-1.66072275
C	-6.27542242	5.03887375	-2.29368628
N	-7.42395240	5.14397248	-1.52988287
O	-6.07124804	5.69504744	-3.32926829
C	-8.48643379	6.01079187	-1.81078415
C	-9.11417271	6.04737216	-3.06368658
C	-8.97232251	6.87588537	-0.82158575
C	-10.01774220	7.75772541	-1.06592772
C	-10.59982638	7.80129332	-2.32993751
C	-10.14431795	6.94552712	-3.32847460
F	-8.74687562	5.15670564	-4.04252064
F	-10.73790901	6.96629933	-4.56803384
F	-10.46518772	8.59762372	-0.07319587
F	-8.39065227	6.84906064	0.43041886
C	-4.32798854	5.04103101	-0.78927600
C	-4.34120981	3.49092954	-2.78070273
C	-7.67826307	1.32893412	-0.71392901
C	-6.12509111	1.70651792	1.22872770
C	-6.95783925	0.64484223	0.47298173
H	-4.65140728	3.23436441	0.86100187
H	-4.40629173	1.76485949	-0.09721954
H	-5.98966712	1.35622600	-2.06327712
H	-7.21068773	2.59335034	-2.41233776
H	-4.89202197	5.43626664	0.06161981
H	-3.99292473	5.88104354	-1.40426762
H	-3.43975826	4.52021553	-0.42049754
H	-4.93559868	2.88171454	-3.46654167
H	-3.55193554	2.86693637	-2.34694668

H	-3.87750404	4.28630461	-3.36877853
H	-8.20517214	0.57848760	-1.31630234
H	-8.43630446	2.02712919	-0.33430595
H	-6.80007497	2.43089963	1.70275539
H	-5.54452915	1.22990208	2.02817977
H	-6.25145076	-0.08458538	0.04643665
C	-7.90554439	-0.11773658	1.38787216
C	-8.90861805	0.54528863	2.11885282
C	-7.79182939	-1.51119983	1.52691410
C	-9.76758161	-0.16411581	2.96404364
H	-9.01894014	1.62254830	2.03120059
C	-9.64089832	-1.55260833	3.09394540
H	-10.53400452	0.36563124	3.52164125
C	-8.64979593	-2.22506263	2.37124759
H	-7.02220677	-2.03901352	0.96957268
H	-10.30707601	-2.10237307	3.75129056
H	-8.54285189	-3.30145526	2.46444194
H	-7.40685370	4.57340956	-0.68439394
F	-11.62627172	8.67778809	-2.58601651

N,N chelated substrate
Total free energy in solvent: -1620.4204909147
47

N	0.710080	-1.183610	0.733421
C	0.539561	-2.687851	0.777849
C	2.067602	-0.839483	0.136755
C	0.524524	-0.515039	2.121905
C	0.370076	0.999761	1.858762
N	-0.285936	1.267083	0.691378
O	0.756389	1.856759	2.683822
C	-0.526142	2.574960	0.247476
C	-1.821909	3.106231	0.221674
C	0.507049	3.376710	-0.256207
C	0.270379	4.651441	-0.754092
C	-1.029959	5.151205	-0.771728
C	-2.078694	4.375241	-0.286596
F	-2.869666	2.360574	0.707551
F	-3.362160	4.869916	-0.304712
F	-1.276481	6.407492	-1.271890
F	1.305420	5.413954	-1.245674
F	1.793196	2.876835	-0.279605
C	-0.785838	-1.005464	2.783127
C	1.703973	-0.757176	3.079337
C	2.254582	-1.445477	-1.258311
C	0.756013	-3.354960	-0.588788
C	2.111066	-2.976034	-1.211450
Pd	-0.755631	-0.271025	-0.495073
O	-2.185713	0.517144	-1.867216
O	-1.603838	-1.623081	-2.006760
C	-2.320775	-0.637719	-2.464458
C	-3.252726	-0.805089	-3.617427
H	-0.465888	-2.896525	1.143060
H	1.261839	-3.085175	1.505568
H	2.839010	-1.239856	0.806284
H	2.153115	0.248675	0.116782
H	-1.627673	-0.967049	2.085072

H	-1.013298	-0.344358	3.624793
H	-0.685418	-2.022648	3.174248
H	2.626100	-0.285867	2.734940
H	1.877446	-1.825264	3.243440
H	1.457825	-0.294112	4.037702
H	3.247459	-1.155050	-1.623702
H	1.518658	-1.019604	-1.952816
H	-0.054892	-3.074013	-1.267922
H	0.689854	-4.440292	-0.438997
H	2.932860	-3.400879	-0.615049
H	2.195597	-3.400616	-2.218377
H	-4.267521	-0.522261	-3.318698
H	-3.243960	-1.839108	-3.964424
H	-2.955557	-0.139295	-4.434975

O,N chelated substrate
Total free energy in solvent: -1620.3962645805
47

C	2.26931914	0.16863950	1.55611653
N	2.14204789	-0.26497805	0.10379061
C	3.23962660	-1.24963727	-0.23546536
C	3.28494721	-2.44923370	0.72428056
H	4.19499875	-0.70743802	-0.20362885
H	3.07334219	-1.59506742	-1.25594348
C	2.24290492	-1.02243024	2.51938867
H	1.45551472	0.86685314	1.76165059
H	3.22174641	0.70134345	1.66674802
Pd	0.20657148	-1.07934463	-0.11414325
O	-0.24016764	0.87425640	-0.27546214
C	2.12470912	0.97413844	-0.85102985
C	0.79001544	1.67165449	-0.56450832
C	2.09628868	0.50296375	-2.32656953
C	3.31846573	1.91949039	-0.64008986
N	0.72477466	2.96218628	-0.65702392
C	-0.48108110	3.66340849	-0.58200325
C	-1.53123430	3.47663885	-1.49613832
C	-0.63777512	4.69930981	0.35134519
C	-1.78052312	5.49065218	0.38737779
C	-2.80542678	5.27724392	-0.52941159
C	-2.67724422	4.26201806	-1.47330735
F	-1.90099928	6.48853751	1.33006000
F	-3.68407786	4.04801930	-2.38897463
F	-1.41980938	2.48929111	-2.45426913
F	0.35554015	4.92677197	1.28251301
C	-1.05243234	-3.26955950	-0.14024047
C	-1.77995041	-4.56946208	-0.16091859
O	0.24852254	-3.21477455	0.01889139
H	4.27099319	1.41660213	-0.83494352
H	3.33228824	2.36256468	0.35690738
H	3.21500795	2.74856087	-1.34345187
H	3.07003399	0.11757907	-2.64175646
H	1.85355310	1.36446389	-2.95511234
H	1.33245977	-0.26266767	-2.49412896
O	-1.66253185	-2.13181869	-0.28366856
C	3.37379612	-2.01389342	2.19694263
H	1.27106149	-1.53006757	2.46174969

H	2.34163639	-0.63407237	3.54069228
H	4.15573129	-3.05832389	0.44925505
H	2.39678829	-3.06976758	0.57349927
H	3.31097031	-2.89056198	2.85176336
H	4.34628747	-1.53793701	2.39378207
H	-2.85200496	-4.39777684	-0.26470857
H	-1.58032196	-5.12546104	0.76115835
H	-1.42321487	-5.18127894	-0.99671088
F	-3.93663805	6.06259480	-0.50294339

TS-5α-7α
Total free energy in solvent: -1620.335365
47
-1619.925515 -1620.007696 -1619.950292
N 0.780146 -1.297191 0.650928
C -0.367933 -2.082561 1.238356
C 1.516213 -1.882723 -0.488843
C 1.405843 -0.300198 1.666483
C 0.363782 0.868892 1.843498
N -0.353335 1.186786 0.714292
O 0.267946 1.429972 2.957237
C -1.256470 2.252853 0.707093
C -2.581048 2.043414 0.293046
C -0.896439 3.573148 1.021105
C -1.809999 4.618944 0.944758
C -3.115273 4.376562 0.526348
C -3.498520 3.081412 0.188846
F -2.987987 0.761827 -0.031216
F -4.790015 2.829422 -0.220297
F -4.018693 5.411282 0.437051
F -1.423067 5.900808 1.264410
F 0.401931 3.856312 1.378631
C 1.666895 -0.973452 3.023786
C 2.727586 0.296512 1.139215
C 1.219822 -3.319601 -0.967318
C -1.017374 -3.012507 0.218277
C 0.022350 -4.019917 -0.287999
Pd 0.186505 -0.088179 -0.847298
O -0.139583 0.559189 -2.841303
O 1.569280 -0.916437 -3.209723
C 0.686990 -0.062222 -3.629542
C 0.589371 0.213185 -5.106544
H -1.073285 -1.349459 1.635584
H 0.026719 -2.676612 2.069304
H 0.747251 -1.262029 3.534121
H 2.165920 -0.249924 3.671694
H 2.313841 -1.849958 2.904985
H 2.626026 0.738087 0.144250
H 3.528537 -0.450762 1.127855
H 3.024178 1.093987 1.826602
H -1.450952 -2.432624 -0.606215
H -1.846437 -3.533289 0.712211
H 1.055318 -3.265199 -2.048955
H -0.257355 -0.343708 -5.523804
H 1.501748 -0.100191 -5.614357
H 0.400431 1.275900 -5.274695

H 0.385827 -4.609990 0.564795
H -0.434508 -4.728291 -0.986388
H 1.463304 -1.152013 -1.765440
H 2.581040 -1.671116 -0.393259
H 2.124828 -3.923401 -0.827137

AlphaCMD (**7α)**
Total free energy in solvent: -1620.3751854932
47

N	0.80471776	-0.95372599	0.58262115
C	0.24489224	-2.15105355	1.30339003
C	1.48999921	-1.14564330	-0.63160709
C	0.95673539	0.28831758	1.47980450
C	-0.48913747	0.77578976	1.84288085
N	-1.35438890	0.80280806	0.78502320
O	-0.73455558	1.10312444	3.03128092
C	-2.59853197	1.39470358	0.91404403
C	-3.73682700	0.77603138	0.36572113
C	-2.83531818	2.66831003	1.48222010
C	-4.10346782	3.23485918	1.52975112
C	-5.20046345	2.57191078	0.98374613
C	-5.00728918	1.33281300	0.38228224
F	-3.58561464	-0.47234769	-0.26787311
F	-6.07044688	0.66017040	-0.18182946
F	-6.45540001	3.14092797	1.02186652
F	-4.27960025	4.48056169	2.09200669
F	-1.77573394	3.41579143	1.94767913
C	1.73880579	-0.06766283	2.75552117
C	1.88095836	-2.52503191	-1.14774864
C	-0.01465012	-3.32241473	0.35740021
C	1.29164116	-3.71234389	-0.35073756
Pd	-0.45717284	-0.33621129	-0.99587188
O	-1.00405773	-0.05939762	-3.09477915
O	-3.27933911	-0.33292429	-3.00680307
C	-2.12354900	-0.09415516	-3.65782566
C	-2.30566282	0.12386305	-5.12589899
H	-0.66782913	-1.82172456	1.80487547
H	0.96894190	-2.45643765	2.06705749
H	2.71693650	-0.49252410	2.50193478
H	1.19090444	-0.75671749	3.39946441
H	1.88850238	0.84437663	3.33698013
H	2.97909728	-2.59738899	-1.15333252
H	1.57324052	-2.58124879	-2.19835836
H	-0.79227969	-3.05508950	-0.36968968
H	-0.39655030	-4.16243616	0.95017193
H	2.01283843	-4.03801307	0.41172041
H	1.13222810	-4.56678142	-1.01712407
H	-2.99024703	0.96110371	-5.29536476
H	-2.76033244	-0.76279907	-5.58010185
H	-1.34270468	0.32827727	-5.59220881
H	-3.20164090	-0.44876048	-2.02479750
H	2.16829973	-0.34337311	-0.90034243
C	1.67664594	1.43453914	0.74133456
H	1.17703974	1.69065903	-0.19688381
H	2.72764240	1.19221507	0.54782994
H	1.64905378	2.31589346	1.38883016

TS-5β-7β
Total free energy in solvent: -1620.360329

47
-1619.944200 -1619.956514 -1620.007696
N 1.029279 -1.398399 0.946436
C 0.014932 -2.438671 1.355156
C 2.107527 -2.085152 0.123132
C 1.369291 -0.359677 2.028976
C 0.261762 0.739732 1.964162
N -0.167281 1.025120 0.690049
O -0.118275 1.316110 3.006868
C -1.011983 2.106300 0.428614
C -2.202342 1.929608 -0.292385
C -0.690203 3.424025 0.796258
C -1.521651 4.494653 0.491072
C -2.694407 4.283745 -0.229279
C -3.030210 2.994151 -0.628731
F -2.576392 0.656535 -0.685887
F -4.186994 2.774667 -1.343812
F -3.513271 5.343275 -0.547122
F -1.173927 5.771952 0.869444
F 0.497142 3.675544 1.446581
C 1.435440 -0.980400 3.431632
C 2.711296 0.341832 1.717326
C 1.376260 -2.386710 -1.221195
C -0.598711 -3.173408 0.142773
C 0.430633 -3.578836 -0.937907
Pd 0.419027 -0.362107 -0.691725
O -0.009871 0.643796 -2.484787
O -0.174872 -1.473258 -3.278688
C -0.306114 -0.188548 -3.431688
C -0.833860 0.345882 -4.729295
H -0.772760 -1.938021 1.924366
H 0.522917 -3.152054 2.018366
H 0.488152 -1.428801 3.736686
H 1.649536 -0.183790 4.147359
H 2.228765 -1.734220 3.488876
H 2.736968 0.749024 0.701225
H 3.559493 -0.333468 1.866115
H 2.821358 1.178423 2.412471
H -1.357971 -2.527581 -0.316171
H -1.120358 -4.061608 0.520853
H 0.448952 -1.744483 -2.161126
H -1.879434 0.644727 -4.592378
H -0.781242 -0.415501 -5.507408
H -0.272617 1.236045 -5.023240
H 1.024959 -4.442231 -0.596015
H -0.100777 -3.891461 -1.843255
H 2.964264 -1.425602 0.001007
H 2.433972 -3.009975 0.625497
H 2.106228 -2.581478 -2.013801

BetaCMD (7β)
Total free energy in solvent: 1620.3765669847

47

N	1.11585199	-1.47903119	1.04106869
C	0.07830826	-2.50520527	1.41475562
C	2.25571328	-2.19369208	0.31135819
C	1.36462365	-0.39692566	2.10272315
C	0.21185197	0.65871826	1.97368845
N	-0.13330190	0.94858958	0.67880201
O	-0.26484863	1.18628708	3.00635580
C	-0.96284591	2.01882195	0.36258376
C	-2.02649913	1.85859599	-0.54204858
C	-0.73115229	3.33766519	0.80188549
C	-1.51355320	4.40705233	0.38049129
C	-2.54348867	4.20785478	-0.53567581
C	-2.78773510	2.92255957	-1.00615272
F	-2.33483819	0.59163162	-1.02614672
F	-3.77951571	2.69984667	-1.94377647
F	-3.29701745	5.27078642	-0.98384837
F	-1.24346112	5.68094434	0.83088803
F	0.34059951	3.59860568	1.62743306
C	1.40678314	-0.98584361	3.52022096
C	2.68428793	0.35426986	1.81897281
C	1.55739858	-2.38985203	-1.04959192
C	-0.49833115	-3.22775638	0.17603769
C	0.56991326	-3.55805796	-0.90034129
Pd	0.59679756	-0.51193288	-0.67832014
O	0.10412368	0.51071210	-2.50314082
O	-0.67683295	-1.40139862	-3.44753183
C	-0.56191088	-0.05840567	-3.40556062
C	-1.30474640	0.68601721	-4.46017742
H	-0.72476744	-1.99782329	1.95394043
H	0.55477460	-3.22519213	2.09543229
H	0.46062312	-1.44722270	3.80833134
H	1.58653954	-0.17338870	4.22739096
H	2.21305003	-1.72281281	3.61172249
H	2.72603670	0.72680284	0.79112603
H	3.55753706	-0.27548967	2.02016496
H	2.72916061	1.21801427	2.48880410
H	-1.26606768	-2.58237965	-0.26954323
H	-1.00134643	-4.14253119	0.51430397
H	-0.17758836	-1.80679561	-2.68525310
H	-2.20279716	1.12045708	-4.00182776
H	-1.60269646	0.02585497	-5.27401421
H	-0.69277765	1.50957707	-4.83509319
H	1.12472500	-4.46672831	-0.60248545
H	0.06659718	-3.80864245	-1.84444525
H	3.12321555	-1.53967982	0.25074106
H	2.53351084	-3.12145677	0.84140434
H	2.24124683	-2.46880042	-1.89748212

GammaCMD
See structure 7

Free Substrate (PipCONHC$_7$F$_7$-chair)
Total free energy in solvent: -1503.5606321614
43

C	-4.62671289	2.17469670	1.33948079

N	-4.81062533	1.86426176	-0.10526854
C	-4.22173862	0.54537062	-0.44371327
C	-4.89264284	-0.56564167	0.38176735
H	-3.13089692	0.53452557	-0.25230008
H	-4.37238011	0.34487745	-1.50482846
C	-5.31883854	1.11968965	2.21471050
H	-5.04640741	3.16548345	1.53932032
H	-3.55373012	2.20996624	1.59970035
N	-6.85201711	3.47701423	-0.43821183
C	-4.51554707	3.01572922	-1.01926987
C	-5.66064658	4.05115159	-0.85835356
C	-4.57747300	2.57718768	-2.50636027
C	-3.16104411	3.70981907	-0.75289608
O	-5.54234036	5.24362136	-1.18123814
C	-8.07814760	4.12596953	-0.32996313
C	-9.23699196	3.49725828	-0.80358544
C	-8.24307067	5.38164014	0.27402792
C	-9.49462908	5.98055159	0.33092730
C	-10.64796972	5.36319969	-0.16947398
C	-10.49131902	4.08708870	-0.72389529
F	-9.59524718	7.20951982	0.94238003
C	-11.96221679	6.06608240	-0.03410832
F	-11.55726878	3.37710956	-1.22561303
F	-9.11626105	2.24286464	-1.37173166
F	-7.18322980	6.00947671	0.87897621
H	-2.34045123	3.00006714	-0.90449880
H	-3.09828872	4.10707295	0.26354490
H	-3.03426448	4.54859314	-1.44099025
H	-3.70288616	1.97924387	-2.77875786
H	-4.58276542	3.47104227	-3.13631761
H	-5.48355748	1.99853644	-2.71457469
C	-4.78985944	-0.28913991	1.89213948
H	-6.40285189	1.15925722	2.03850111
H	-5.15455470	1.36324804	3.27204457
H	-4.42680855	-1.52784841	0.13378554
H	-5.94925844	-0.62978877	0.08831676
H	-5.34123625	-1.04814245	2.46028602
H	-3.73713597	-0.36082575	2.20439968
H	-6.78196234	2.46566680	-0.30776735
F	-12.99627976	5.40866600	-0.67339465
F	-11.90971702	7.35081535	-0.56365901
F	-12.33041948	6.19988206	1.30363233

Pd-pivalate
Total free energy in solvent: -819.6097592455
33

Pd	-0.52667201	1.01205629	-0.01590359
O	-2.35669750	2.04677527	0.03588900
C	-3.02608590	0.92137281	-0.02186296
C	-4.53319390	0.89088810	-0.00117037
C	-4.98974154	1.39768291	1.39718567
C	-5.04031120	-0.54400715	-0.24630388
C	-5.05539333	1.85709405	-1.09701322
O	-2.28600533	-0.15571271	-0.07668884
O	1.23729919	2.17717436	0.04080601
C	1.97294895	1.09757016	-0.01320255

O	1.29923171	-0.02601906	-0.06632353
C	3.48010957	1.11677234	-0.01214116
C	3.99400446	2.56932285	0.01072183
C	3.97153397	0.38051558	-1.28834228
C	3.96361935	0.34609551	1.24808057
H	-4.67821950	2.87078506	-0.93493575
H	-6.14996798	1.87978008	-1.06906288
H	-4.74460955	1.52785735	-2.09478619
H	-4.63091751	0.73497065	2.19249251
H	-6.08429831	1.41640583	1.43318802
H	-4.61309051	2.40714758	1.58582493
H	-4.66295670	-1.23392698	0.51422378
H	-4.72025573	-0.91805370	-1.22404109
H	-6.13531342	-0.55412238	-0.21358458
H	3.64871222	3.12642907	-0.86560816
H	5.08956972	2.56764032	0.01289263
H	3.64467912	3.09997391	0.90160781
H	3.65903992	0.91129515	-2.19447538
H	3.57596262	-0.63841368	-1.32864159
H	5.06592623	0.33398827	-1.27855580
H	3.64325874	0.85194514	2.16557704
H	5.05811819	0.30126309	1.24533188
H	3.56969595	-0.67428605	1.25669209

Pivalic acid dimer
Total free energy in solvent: -694.0899782392
34

O	-2.06914720	-1.34689963	0.24205161
C	-0.91170743	-0.86963207	0.11770091
O	0.18250539	-1.64104530	0.04889704
C	-0.62819180	0.62495218	0.04316716
C	-1.95241237	1.41135528	0.07115325
C	0.14694662	0.91899713	-1.26833186
C	0.25374139	1.01040341	1.26210706
H	-0.01344316	-2.64155030	0.11055663
C	-1.58545826	-4.65797129	0.35084112
O	-0.42870277	-4.18141537	0.21779300
O	-2.67857735	-3.88587412	0.42882811
C	-1.86884287	-6.15225118	0.43376668
C	-0.54770980	-6.94043887	0.35849134
C	-2.79725593	-6.53898733	-0.74877392
C	-2.59304717	-6.44176216	1.77583230
H	-2.48301003	-2.88559769	0.36281220
H	-0.44676549	0.64572490	-2.14826975
H	1.08752956	0.36308524	-1.29793022
H	0.36724745	1.99073694	-1.32622782
H	1.19435025	0.45325863	1.25267055
H	-0.26505878	0.80555802	2.20564813
H	0.47777895	2.08222535	1.22223503
H	-2.58947430	1.14779205	-0.77905192
H	-1.74158663	2.48561783	0.02695503
H	-2.51944544	1.20500279	0.98403922
H	-0.01548129	-6.73582728	-0.57544132
H	-0.75802186	-8.01434481	0.41195730
H	0.11969208	-6.67562750	1.18439015
H	-1.96463905	-6.16723714	2.63103697

H	-2.81201467	-7.51317702	1.84563848
H	-3.53181753	-5.88540080	1.84158466
H	-2.31113677	-6.34585598	-1.71208371
H	-3.73194921	-5.97336226	-0.71046673
H	-3.02863451	-7.60855163	-0.69280670

Tetrahedral complex
Total free energy in solvent: -2111.9663603556
67

N	0.412235	-1.573927	-0.674342
C	0.744205	-0.623922	-1.797147
C	1.548196	-2.587917	-0.469530
C	-0.956583	-2.228152	-0.794860
C	-1.268601	-2.892591	0.564781
N	-0.634295	-2.328802	1.645536
O	-2.103344	-3.822760	0.645994
C	-0.883465	-2.835971	2.930360
C	-1.466145	-2.037380	3.921252
C	-0.534895	-4.143677	3.291504
C	-0.762653	-4.634124	4.571837
C	-1.335425	-3.811009	5.537604
C	-1.676588	-2.501846	5.211592
F	-1.790938	-0.723255	3.633252
F	-2.218929	-1.669574	6.167761
F	-1.549399	-4.283805	6.811791
F	-0.406546	-5.922953	4.897636
F	0.084106	-4.956341	2.368229
C	-2.034386	-1.145785	-1.036011
C	-1.040739	-3.292253	-1.905502
C	2.365782	-2.846683	-1.742777
C	2.245575	-0.316867	-1.821767
C	3.076734	-1.563063	-2.256160
Pd	0.373753	-0.616073	1.331491
O	0.488539	1.507582	0.960961
O	1.902380	2.577764	-0.483299
C	0.738202	2.342046	-0.010666
C	-0.448945	3.099887	-0.581700
H	0.157783	0.282449	-1.659345
H	0.441803	-1.073244	-2.753073
H	1.108070	-3.505404	-0.072883
H	2.196673	-2.189278	0.314261
H	-1.941979	-0.329617	-0.311398
H	-3.021391	-1.602421	-0.917023
H	-1.969136	-0.737543	-2.049446
H	-0.315429	-4.096654	-1.761498
H	-0.897647	-2.850296	-2.896249
H	-2.033236	-3.746333	-1.860653
H	1.714982	-3.241160	-2.530372
H	3.094264	-3.638482	-1.531991
H	2.563143	0.022347	-0.831269
H	2.433014	0.523360	-2.496416
H	3.069060	-1.602480	-3.354991
H	2.955243	2.668247	0.674015
H	-0.955303	2.489273	-1.339428
H	-0.116480	4.024562	-1.056516
H	-1.181611	3.310940	0.202179

C	6.679997	-0.282859	-2.185639
C	5.354862	-0.519972	-2.562399
C	7.210926	-0.914418	-1.054267
C	6.405154	-1.782178	-0.310806
C	5.079561	-2.019855	-0.693304
C	4.531986	-1.391772	-1.824159
I	1.948504	-0.841650	3.642744
H	4.951721	-0.027554	-3.445371
H	8.240124	-0.733139	-0.757616
H	7.297497	0.389297	-2.775243
H	4.477939	-2.690025	-0.091504
H	6.803481	-2.275633	0.570718
Cs	1.301238	2.832647	3.928182
O	3.262344	2.973327	1.603952
C	3.801948	4.214006	1.725376
O	3.771513	4.773798	2.835674
C	4.410012	4.810328	0.479616
H	3.713995	4.723911	-0.361595
H	5.316493	4.255309	0.212005
H	4.666964	5.855293	0.652741

Square Planar complex
Total free energy in solvent: -2112.0046810196
67

N	0.72321399	-1.33854808	-0.71570499
C	1.02984397	-0.40996408	-1.87348541
C	1.53083518	-2.63713613	-0.82290634
C	-0.78638113	-1.58751027	-0.55124460
C	-1.00259042	-2.24228786	0.83075643
N	-0.04335539	-1.93650154	1.75463500
O	-2.00853947	-2.96008386	1.05329316
C	-0.20233500	-2.38459449	3.07386776
C	-1.17365598	-1.83135560	3.91013981
C	0.68041357	-3.29575080	3.66439441
C	0.62480345	-3.60188217	5.02200201
C	-0.32511668	-2.99125204	5.83656824
C	-1.22317357	-2.09457872	5.26904715
F	-2.04827755	-0.88066932	3.40220519
F	-2.10633330	-1.37132419	6.06593982
F	-0.35984205	-3.24633140	7.18826856
F	1.52214499	-4.48781888	5.56973774
F	1.66784308	-3.87096678	2.90005076
C	-1.54049601	-0.23579013	-0.54822271
C	-1.38075526	-2.50674553	-1.63454500
C	1.90590660	-3.02063856	-2.25950745
C	2.48344450	-0.54249845	-2.33341069
C	2.76794067	-1.92626182	-2.97530460
Pd	1.31634368	-0.51535013	1.20351083
O	2.63965138	0.87546015	0.41749508
O	1.35413235	2.76191643	0.63727730
C	2.43093406	2.15783228	0.31839618
C	3.59854127	2.95453494	-0.22811008
H	0.82023588	0.60778808	-1.54618880
H	0.35395622	-0.64653638	-2.70694400
H	0.95354495	-3.42520769	-0.33717176
H	2.43547089	-2.50619176	-0.22635892

H	-1.06776286	0.48226261	0.12895241
H	-2.56510476	-0.41322596	-0.20864541
H	-1.58574522	0.19974269	-1.55125132
H	-0.91893643	-3.49676870	-1.63425343
H	-1.29442595	-2.06630591	-2.63248336
H	-2.43863642	-2.65166866	-1.40422240
H	1.00138013	-3.21525729	-2.84526149
H	2.45973537	-3.96576036	-2.22041458
H	3.13622027	-0.35709476	-1.47626247
H	2.69480841	0.25248032	-3.05932371
H	2.43025893	-1.88834929	-4.01976745
H	0.35562028	2.89325708	1.76249534
H	4.37446974	3.02535897	0.54377634
H	3.27524656	3.95862356	-0.50642144
H	4.04202842	2.44637017	-1.08877911
C	6.22308125	-2.97521176	-4.26268454
C	4.86631764	-2.63578802	-4.21192751
C	6.99502900	-2.95082935	-3.09649495
C	6.39940157	-2.58416128	-1.88364516
C	5.04401595	-2.24212421	-1.83715425
C	4.25470238	-2.26405064	-3.00244735
I	2.10140336	0.27156215	3.70410551
H	4.27212966	-2.65710184	-5.12198533
H	8.04808680	-3.21165878	-3.13111953
H	6.67414200	-3.25616065	-5.20957004
H	4.60839238	-1.94947925	-0.88682796
H	6.98917979	-2.56001586	-0.97257068
Cs	-1.44742635	1.72817901	5.08964727
O	-0.26815262	3.12207823	2.54920109
C	-0.04330917	4.29630522	3.18537633
O	-0.67904465	4.54739794	4.22882805
C	1.00260599	5.21011006	2.60485639
H	0.86016858	5.33071197	1.52801114
H	1.99399378	4.76355745	2.74491165
H	0.96369033	6.17493592	3.10970084

Intermediates

1 (separate reactants)

See free structures listed above for PipCONHC$_6$F5, Pd-acetate, PhI, CsOAc

2
Total free energy in solvent: -1849.483602
55

N	-6.647104	3.023995	-0.996170
C	-6.596773	1.868207	-0.069882
C	-6.501017	2.575321	-2.411227
C	-5.816548	4.227249	-0.651849
C	-6.461834	5.445322	-1.363974
N	-7.827401	5.311744	-1.522220
O	-5.819667	6.454827	-1.710874
C	-8.666735	6.244660	-2.139286
C	-9.567651	5.829346	-3.128822
C	-8.680413	7.605749	-1.801413
C	-9.511238	8.505128	-2.465258

C -10.384795 8.062541 -3.454604
C -10.416017 6.710750 -3.782293
F -9.590103 4.491576 -3.495932
F -11.274190 6.248933 -4.754869
F -11.215971 8.949093 -4.093894
F -9.500770 9.832967 -2.111789
F -7.896188 8.072682 -0.775514
C -5.897378 4.544504 0.864248
C -4.336735 4.108385 -1.077537
C -7.645682 1.631873 -2.798681
C -7.730682 0.877074 -0.388055
C -7.690085 0.415647 -1.856648
Pd -6.605233 5.297086 -5.573921
O -5.569652 7.100253 -5.253903
O -4.775508 5.172846 -4.532296
O -8.491329 5.469261 -6.479102
O -7.711824 3.502291 -5.846546
C -4.639268 6.476908 -4.578416
C -8.703526 4.182387 -6.356867
C -3.551046 7.190746 -3.875050
C -9.993323 3.562996 -6.748112
H -6.706623 2.222463 0.955990
H -5.623866 1.343937 -0.139413
H -5.534847 2.062526 -2.562473
H -6.501659 3.453265 -3.061546
H -6.932507 4.526392 1.219185
H -5.487672 5.543515 1.040703
H -5.306645 3.832080 1.447988
H -4.232394 4.038863 -2.162757
H -3.888850 3.221442 -0.615803
H -3.780231 4.989072 -0.746870
H -7.514115 1.321569 -3.841574
H -8.593817 2.183418 -2.749330
H -8.691190 1.369307 -0.181905
H -7.654406 0.017295 0.290339
H -6.793192 -0.201362 -2.019192
H -8.555987 -0.219589 -2.081610
H -3.884566 7.361046 -2.843874
H -3.354726 8.152328 -4.353012
H -2.646094 6.579210 -3.852505
H -10.793224 4.005665 -6.145200
H -9.960230 2.484539 -6.589368
H -10.210720 3.780784 -7.798721
H -8.148111 4.358108 -1.332434

TS-2-3
Total free energy in solvent: -1849.461889
55
N -6.631946 2.964537 -1.250882
C -7.150090 1.661554 -0.773614
C -5.360871 2.803589 -2.006500
C -6.615627 4.106817 -0.298155
C -6.700421 5.413860 -1.125026
N -7.682044 5.388973 -2.153939
O -6.087403 6.446892 -0.834141
C -8.453949 6.542491 -2.433392

C -9.848502 6.480810 -2.315112
C -7.901927 7.758097 -2.858240
C -8.707097 8.868232 -3.102199
C -10.087237 8.784493 -2.949677
C -10.663041 7.576333 -2.566952
F -10.427153 5.284245 -1.928180
F -12.026079 7.475519 -2.417585
F -10.877216 9.881222 -3.189314
F -8.139548 10.045051 -3.528529
F -6.564453 7.850798 -3.166488
C -7.894079 4.119004 0.585371
C -5.373719 4.159023 0.619111
C -5.543765 1.880827 -3.218128
C -7.384112 0.712420 -1.962274
C -6.099335 0.513892 -2.784585
Pd -6.850775 5.108457 -4.682417
O -5.559525 6.125387 -6.095863
O -4.815770 5.225389 -4.216959
O -8.701752 5.036001 -5.515046
O -8.649826 3.354996 -4.045442
C -4.550929 5.921881 -5.297776
C -9.268235 3.963696 -4.978456
C -3.193271 6.458592 -5.568274
C -10.601714 3.543434 -5.509708
H -8.099683 1.815256 -0.254668
H -6.451204 1.186550 -0.056019
H -4.573211 2.380228 -1.355504
H -5.016888 3.787820 -2.338320
H -8.803441 3.997531 -0.010288
H -7.954934 5.072197 1.120856
H -7.853295 3.323501 1.333697
H -4.455411 4.316085 0.048674
H -5.288381 3.218307 1.173753
H -5.458977 4.981387 1.333480
H -4.578486 1.768570 -3.726878
H -6.240648 2.346867 -3.926658
H -8.162035 1.147556 -2.601407
H -7.754085 -0.247874 -1.582328
H -5.347879 -0.009913 -2.172826
H -6.296689 -0.119232 -3.659080
H -3.065265 7.408710 -5.036516
H -3.063727 6.638079 -6.636822
H -2.435154 5.763118 -5.202018
H -11.331770 4.348838 -5.374429
H -10.942968 2.647626 -4.989770
H -10.528239 3.345536 -6.584225
H -8.141646 4.483264 -2.280660

3
Total free energy in solvent: -1849.482958
55
N -6.57308991 3.04723782 -1.54761750
C -7.15175162 1.69012501 -1.39424308
C -5.12689321 2.99722193 -1.89303730
C -6.90395860 4.05891263 -0.49958211
C -6.95422990 5.45060188 -1.16740439

N	-7.86329524	5.57184656	-2.31908577
O	-6.38609857	6.45279837	-0.73961597
C	-8.54679465	6.84351455	-2.39288151
C	-9.85125894	6.96224407	-1.89887936
C	-7.94489111	7.99914331	-2.89933200
C	-8.62662489	9.21138605	-2.94998069
C	-9.93059237	9.29726838	-2.47348462
C	-10.54627476	8.16613102	-1.94766492
F	-10.46504306	5.87025847	-1.32662966
F	-11.82889663	8.24266682	-1.46214919
F	-10.60676100	10.48957778	-2.52488634
F	-8.01429284	10.32191118	-3.47594897
F	-6.67019910	7.95519417	-3.40932192
C	-8.32026980	3.82807121	0.10182321
C	-5.88899724	4.10682578	0.66869120
C	-4.88111507	2.19507993	-3.17782589
C	-6.94847751	0.86074083	-2.67201539
C	-5.46489614	0.77771735	-3.06560403
Pd	-6.88248751	5.14121930	-4.19814224
O	-5.57273516	4.90971272	-5.87018955
O	-4.83535541	5.67221831	-3.92241708
O	-8.61339191	4.49265557	-5.03977227
O	-9.62825282	3.73085766	-3.13701884
C	-4.57364357	5.37324981	-5.16906320
C	-9.56449522	3.83523501	-4.39874915
C	-3.22388539	5.58163348	-5.75836707
C	-10.60758168	3.21514834	-5.29609536
H	-8.22130145	1.77475513	-1.20476190
H	-6.69510414	1.15244762	-0.53849212
H	-4.54525893	2.53471202	-1.07348009
H	-4.75767538	4.01877975	-2.02451108
H	-9.08582214	3.67988999	-0.66170092
H	-8.60319394	4.69158548	0.71246693
H	-8.30323977	2.95201857	0.75573973
H	-4.89998584	4.43291396	0.34175910
H	-5.80649721	3.11020609	1.11457128
H	-6.22572144	4.80487789	1.43979333
H	-3.80040009	2.15752701	-3.36880637
H	-5.34504846	2.71370330	-4.02638864
H	-7.52239412	1.32838716	-3.48208303
H	-7.36569667	-0.14181720	-2.51128415
H	-4.91272634	0.21209075	-2.29929255
H	-5.34592931	0.23348381	-4.01080795
H	-3.15021098	6.60375098	-6.14974230
H	-3.06051750	4.88549308	-6.58362133
H	-2.45541477	5.45611223	-4.99225969
H	-11.10687570	3.99590627	-5.87922756
H	-11.33994397	2.67711871	-4.69396101
H	-10.12841321	2.53442384	-6.00637846
H	-8.53906383	4.75754924	-2.42196828

TS-3-4
Total free energy in solvent: -1849.470444
55
N -6.468080 3.204868 -1.669346
C -7.066543 1.841756 -1.812927

C -4.969278 3.144117 -1.745035
C -6.983599 3.998421 -0.470177
C -7.355580 5.441021 -0.880436
N -8.016199 5.611472 -2.120374
O -7.228475 6.385143 -0.079314
C -8.523174 6.936095 -2.332469
C -9.887047 7.213513 -2.183356
C -7.698717 8.019229 -2.668313
C -8.207047 9.294025 -2.887146
C -9.572168 9.528972 -2.752232
C -10.415644 8.482659 -2.396814
F -10.750880 6.206275 -1.801595
F -11.766149 8.703317 -2.252889
F -10.082953 10.784295 -2.973030
F -7.367131 10.325435 -3.233077
F -6.345584 7.823601 -2.804742
C -8.303912 3.417660 0.124869
C -5.971465 4.074126 0.700731
C -4.458465 2.395536 -2.985910
C -6.596446 1.124796 -3.084689
C -5.067985 0.992302 -3.107086
Pd -7.026717 4.909458 -3.794352
O -5.848477 4.455011 -5.455196
O -4.825913 5.684193 -3.903140
O -8.880520 4.398727 -4.818254
O -9.919583 3.806382 -2.885669
C -4.801304 5.163209 -5.080126
C -9.811977 3.788434 -4.212820
C -3.660110 5.361450 -6.021789
C -10.856703 3.016219 -4.951327
H -8.151757 1.934734 -1.838937
H -6.804329 1.213277 -0.941082
H -4.569823 2.638117 -0.851114
H -4.589375 4.167763 -1.761083
H -9.112179 3.340117 -0.604071
H -8.635414 4.087854 0.923283
H -8.131973 2.431161 0.563825
H -5.043152 4.572775 0.418244
H -5.740766 3.070922 1.072631
H -6.413333 4.656520 1.510695
H -3.363839 2.345817 -2.920018
H -4.706583 2.959220 -3.887763
H -6.925306 1.692406 -3.966250
H -7.082663 0.141463 -3.128320
H -4.737857 0.358585 -2.270235
H -4.731654 0.506122 -4.030668
H -3.817673 6.284162 -6.593611
H -3.596034 4.529633 -6.726678
H -2.726679 5.465068 -5.463824
H -11.489045 3.711576 -5.514750
H -11.476710 2.448549 -4.258286
H -10.377537 2.350744 -5.674381
H -9.252683 4.472267 -2.452272

4
Total free energy in solvent: -1849.520775

55

N	-6.299039	3.380943	-1.596642
C	-5.828093	1.945176	-1.764120
C	-5.109062	4.292924	-1.324939
C	-7.350267	3.500356	-0.446002
C	-7.907640	4.940290	-0.512592
N	-8.136648	5.386093	-1.802049
O	-8.121163	5.612734	0.517050
C	-8.410934	6.765036	-1.982753
C	-9.647115	7.317774	-1.624107
C	-7.459451	7.638247	-2.524129
C	-7.730111	8.988136	-2.725164
C	-8.970829	9.504735	-2.360617
C	-9.933716	8.665388	-1.806257
F	-10.621212	6.488996	-1.107596
F	-11.163542	9.169940	-1.453275
F	-9.245127	10.837230	-2.551769
F	-6.774353	9.817742	-3.261468
F	-6.210984	7.154223	-2.860132
C	-8.505377	2.498261	-0.674181
C	-6.753539	3.264679	0.955373
C	-4.035371	4.187506	-2.409783
C	-4.634243	1.762666	-2.715681
C	-3.484577	2.751894	-2.460077
Pd	-7.357323	4.171622	-3.263940
O	-6.797880	2.809179	-4.686852
O	-5.445863	4.423440	-5.572164
O	-8.682865	4.882051	-4.803951
O	-10.527300	4.728152	-3.457269
C	-6.027514	3.317239	-5.659750
C	-9.934140	4.857423	-4.656897
C	-5.927100	2.435836	-6.886412
C	-10.877053	4.995578	-5.805993
H	-6.673691	1.363016	-2.131491
H	-5.558008	1.579709	-0.765060
H	-4.676540	3.995687	-0.362145
H	-5.487861	5.311436	-1.241901
H	-8.862787	2.511777	-1.707854
H	-9.337993	2.766767	-0.015172
H	-8.197766	1.477321	-0.424869
H	-6.021520	4.024560	1.231166
H	-6.302106	2.272834	1.040835
H	-7.565004	3.337419	1.683400
H	-3.240117	4.903221	-2.165818
H	-4.446637	4.477684	-3.384392
H	-4.992952	1.867640	-3.740428
H	-4.287199	0.727707	-2.596440
H	-2.981797	2.517379	-1.507853
H	-2.730456	2.656391	-3.250358
H	-6.840597	2.539997	-7.482865
H	-5.835575	1.383695	-6.604873
H	-5.074104	2.743151	-7.493640
H	-10.989771	6.058016	-6.054922
H	-11.856804	4.594852	-5.547876
H	-10.467294	4.488323	-6.681678
H	-9.886224	4.765783	-2.689841

TS-4-5
Total free energy in solvent: -1849.519857
55
N -6.244866 3.397727 -1.541751
C -5.82011 1.949296 -1.714886
C -5.016942 4.283392 -1.368291
C -7.217389 3.557625 -0.330863
C -7.770021 4.999894 -0.386474
N -7.907777 5.480533 -1.661214
O -8.074105 5.626019 0.654431
C -8.317745 6.812173 -1.852142
C -9.660904 7.186776 -1.738274
C -7.406235 7.826328 -2.171905
C -7.812658 9.14124 -2.375852
C -9.158796 9.476361 -2.251411
C -10.092168 8.492629 -1.932302
F -10.597958 6.199963 -1.459672
F -11.424336 8.816481 -1.824419
F -9.567268 10.77257 -2.452966
F -6.893753 10.113405 -2.691788
F -6.066465 7.51962 -2.280133
C -8.40719 2.578073 -0.471584
C -6.544953 3.335378 1.037146
C -4.02068 4.131827 -2.520176
C -4.694311 1.72217 -2.737428
C -3.506763 2.684634 -2.579705
Pd -7.376479 4.198777 -3.151631
O -7.042964 2.745994 -4.562356
O -5.59027 4.133213 -5.656353
O -8.599425 5.075894 -4.693804
O -10.756751 4.87396 -3.935482
C -6.296082 3.099809 -5.61618
C -9.834478 5.055011 -4.903635
C -6.371629 2.118628 -6.770634
C -10.426514 5.234868 -6.262309
H -6.700363 1.383555 -2.019981
H -5.497362 1.593326 -0.727737
H -4.524032 3.988984 -0.433478
H -5.36641 5.31091 -1.276172
H -8.827877 2.59703 -1.481941
H -9.186199 2.877523 0.236425
H -8.112581 1.552069 -0.232111
H -5.755849 4.060623 1.242147
H -6.144496 2.322586 1.13546
H -7.307751 3.483303 1.8049
H -3.195636 4.833688 -2.345096
H -4.48638 4.407148 -3.474939
H -5.115421 1.819202 -3.738055
H -4.366111 0.680122 -2.624195
H -2.942954 2.454695 -1.662095
H -2.814727 2.556033 -3.419694
H -7.386222 2.109165 -7.184966
H -6.153807 1.102946 -6.424632
H -5.663625 2.40825 -7.548544
H -11.135192 6.06865 -6.257669
H -10.985963 4.334058 -6.537597

H -9.634759 5.414619 -6.98812
H -10.400535 4.857102 -3.016079

5 (with HOAc)
Total free energy in solvent: -1849.522793
55

N	-6.12906511	3.28422388	-1.38091996
C	-5.92746772	1.79839526	-1.60116146
C	-4.81023210	3.93925668	-1.00652811
C	-7.22617798	3.58106848	-0.31775628
C	-7.59055328	5.07329593	-0.46563212
N	-7.48401301	5.52783242	-1.75376665
O	-7.97660356	5.75777100	0.50725552
C	-7.87453936	6.82063537	-2.11642389
C	-9.17698835	7.29887410	-1.92006462
C	-6.97845162	7.69125426	-2.75415185
C	-7.35830334	8.95855237	-3.17927868
C	-8.65644676	9.40624845	-2.94975900
C	-9.57095903	8.57016908	-2.31419292
F	-10.13089059	6.45506736	-1.36482504
F	-10.86137401	8.99559679	-2.10415938
F	-9.03662885	10.66231195	-3.35739485
F	-6.45236789	9.77947380	-3.81019428
F	-5.68030444	7.27668773	-2.97507570
C	-8.50718752	2.76674207	-0.61710975
C	-6.76372877	3.30236827	1.12285927
C	-3.71840988	3.69165196	-2.05237887
C	-4.79760672	1.48034605	-2.59338551
C	-3.47795350	2.18342874	-2.23213211
Pd	-6.80272865	4.24426271	-3.13683127
O	-6.19043085	3.17197748	-4.93883243
O	-7.33002904	5.07769154	-5.04782212
O	-10.01751358	3.29093163	-3.65490018
O	-11.03200733	5.33884685	-3.79515947
C	-6.73462100	4.09646119	-5.67376546
C	-10.53235358	4.18488855	-4.33975231
C	-6.70628128	4.03056893	-7.16478609
C	-10.66880328	4.17492110	-5.83164291
H	-6.86990096	1.38970011	-1.96521396
H	-5.70809540	1.34806532	-0.62238229
H	-4.48110063	3.52032924	-0.04718993
H	-5.00384024	5.00506149	-0.87568305
H	-8.83241944	2.86554107	-1.65662830
H	-9.30656422	3.15536854	0.02201518
H	-8.37375742	1.70885826	-0.37137586
H	-5.94753146	3.95469517	1.43877677
H	-6.46738457	2.25726825	1.25683377
H	-7.60484704	3.51081778	1.78801647
H	-2.80502912	4.19657509	-1.71386755
H	-4.00292394	4.14783161	-3.00884352
H	-5.10632668	1.77093597	-3.60149553
H	-4.66498784	0.39074572	-2.59853636
H	-3.06918786	1.76662868	-1.29884999
H	-2.73173131	2.00405625	-3.01460313
H	-7.58009490	3.47421377	-7.52568800
H	-5.80925112	3.50564377	-7.50011440

H	-6.73964908	5.03614106	-7.58931475
H	-9.92420040	4.85991253	-6.25287371
H	-11.65807361	4.52775494	-6.13267002
H	-10.49175240	3.16770264	-6.21008005
H	-10.88006142	5.39334772	-2.82395131

5 (without HOAc)
Total free energy in solvent: -1620.420491
47

N	0.710080	-1.183610	0.733421
C	0.539561	-2.687851	0.777849
C	2.067602	-0.839483	0.136755
C	0.524524	-0.515039	2.121905
C	0.370076	0.999761	1.858762
N	-0.285936	1.267083	0.691378
O	0.756389	1.856759	2.683822
C	-0.526142	2.574960	0.247476
C	-1.821909	3.106231	0.221674
C	0.507049	3.376710	-0.256207
C	0.270379	4.651441	-0.754092
C	-1.029959	5.151205	-0.771728
C	-2.078694	4.375241	-0.286596
F	-2.869666	2.360574	0.707551
F	-3.362160	4.869916	-0.304712
F	-1.276481	6.407492	-1.271890
F	1.305420	5.413954	-1.245674
F	1.793196	2.876835	-0.279605
C	-0.785838	-1.005464	2.783127
C	1.703973	-0.757176	3.079337
C	2.254582	-1.445477	-1.258311
C	0.756013	-3.354960	-0.588788
C	2.111066	-2.976034	-1.211450
Pd	-0.755631	-0.271025	-0.495073
O	-2.185713	0.517144	-1.867216
O	-1.603838	-1.623081	-2.006760
C	-2.320775	-0.637719	-2.464458
C	-3.252726	-0.805089	-3.617427
H	-0.465888	-2.896525	1.143060
H	1.261839	-3.085175	1.505568
H	2.839010	-1.239856	0.806284
H	2.153115	0.248675	0.116782
H	-1.627673	-0.967049	2.085072
H	-1.013298	-0.344358	3.624793
H	-0.685418	-2.022648	3.174248
H	2.626100	-0.285867	2.734940
H	1.877446	-1.825264	3.243440
H	1.457825	-0.294112	4.037702
H	3.247459	-1.155050	-1.623702
H	1.518658	-1.019604	-1.952816
H	-0.054892	-3.074013	-1.267922
H	0.689854	-4.440292	-0.438997
H	2.932860	-3.400879	-0.615049
H	2.195597	-3.400616	-2.218377
H	-4.267521	-0.522261	-3.318698
H	-3.243960	-1.839108	-3.964424
H	-2.955557	-0.139295	-4.434975

TS-4-6
Total free energy in solvent: -1849.507553
55
N -6.217989 3.417298 -1.483385
C -5.711905 2.027494 -1.786591
C -5.029260 4.275974 -1.083898
C -7.302291 3.455916 -0.372633
C -7.884444 4.893589 -0.391676
N -7.841741 5.484909 -1.629597
O -8.352847 5.420597 0.641872
C -8.294875 6.802215 -1.799442
C -9.657563 7.122278 -1.759180
C -7.403709 7.851576 -2.057800
C -7.844959 9.154319 -2.266257
C -9.206707 9.439997 -2.208912
C -10.119703 8.418278 -1.954916
F -10.571838 6.103554 -1.558023
F -11.467416 8.694453 -1.918883
F -9.650461 10.724552 -2.412697
F -6.944506 10.162920 -2.519332
F -6.050942 7.590976 -2.103725
C -8.432889 2.452339 -0.691554
C -6.744656 3.159719 1.032543
C -4.100011 4.565037 -2.258582
C -4.453791 1.985907 -2.702930
C -3.809664 3.331539 -3.156077
Pd -7.221798 4.254174 -3.128735
O -7.042498 2.653347 -4.405273
O -5.546164 3.499027 -5.925140
O -8.252604 5.248260 -4.725060
O -10.399555 4.702142 -4.148351
C -6.383194 2.642295 -5.567372
C -9.472890 5.176887 -5.006796
C -6.750452 1.458320 -6.449686
C -10.032203 5.647269 -6.307717
H -6.526676 1.476526 -2.253261
H -5.477233 1.564690 -0.820297
H -4.494356 3.731789 -0.295097
H -5.410028 5.208584 -0.666978
H -8.765573 2.536934 -1.730500
H -9.281604 2.661956 -0.033233
H -8.111929 1.422187 -0.512730
H -5.966256 3.864399 1.331332
H -6.356787 2.139165 1.105616
H -7.564974 3.274905 1.745209
H -3.171120 4.974804 -1.840464
H -4.545080 5.361912 -2.864808
H -4.724860 1.433822 -3.606470
H -3.698748 1.381848 -2.185569
H -2.728297 3.176688 -3.227554
H -4.162957 3.581666 -4.159845
H -7.744097 1.617768 -6.885178
H -6.795013 0.536087 -5.863173
H -6.021050 1.360617 -7.255182
H -10.373924 6.684336 -6.201796
H -10.892128 5.039124 -6.594289

H -9.257364 5.612907 -7.074158
H -10.036469 4.485935 -3.255943

6
Total free energy in solvent: -1849.51868
55
N -6.26355909 3.48742148 -1.65041071
C -5.84835788 2.05699479 -1.99903368
C -5.03041823 4.39329844 -1.55902890
C -7.13615377 3.59824953 -0.37051004
C -7.63205182 5.06041423 -0.33045759
N -7.91489850 5.55284759 -1.57564692
O -7.80823819 5.67513561 0.74427012
C -8.37334711 6.86688888 -1.75614302
C -9.69516215 7.13658105 -2.12787615
C -7.51100532 7.96664299 -1.64649923
C -7.93463837 9.26645670 -1.89671825
C -9.25152798 9.49723743 -2.28756671
C -10.13057347 8.42595433 -2.40908956
F -10.60221135 6.10475928 -2.24860753
F -11.42784681 8.63935884 -2.82596229
F -9.67567296 10.77455941 -2.56559519
F -7.05832656 10.32129895 -1.78465850
F -6.19002020 7.75249869 -1.30996708
C -8.38861358 2.69115444 -0.47474649
C -6.38905707 3.25183607 0.92693097
C -4.02106212 4.06255820 -2.65741542
C -4.38401536 1.75178558 -1.64438323
C -3.41878487 2.64681883 -2.45905750
Pd -7.51031287 4.35260708 -3.14304083
O -7.44539055 3.02523415 -4.81801052
O -5.24412729 2.58440611 -5.22735933
O -8.81319391 5.51175531 -4.35982447
O -9.58690765 3.84907259 -5.70787937
C -6.43817435 2.52730717 -5.56824292
C -9.65424547 5.06820002 -5.21359644
C -6.89842244 1.87111170 -6.85353892
C -10.76352883 5.94786331 -5.69562380
H -5.97367172 1.94019476 -3.07306194
H -6.53303554 1.37351096 -1.49788023
H -4.56741894 4.24560038 -0.57863365
H -5.37320527 5.42472393 -1.61396083
H -8.87918120 2.78029608 -1.44796428
H -9.09956616 3.00191068 0.29734475
H -8.14616613 1.63936240 -0.29392267
H -5.54772144 3.91650183 1.13024987
H -6.04281989 2.21421706 0.91837761
H -7.08924142 3.37911308 1.75647801
H -3.23671975 4.82846652 -2.64502422
H -4.51110014 4.11157363 -3.63440687
H -4.19999372 0.69248617 -1.86162299
H -4.21717552 1.87868609 -0.56759659
H -2.45231150 2.70391013 -1.94314521
H -3.24290323 2.19907666 -3.44191821
H -7.44018627 2.59107038 -7.47727265
H -7.58592068 1.04739143 -6.63226887

H	-6.03590869	1.49131040	-7.40139152
H	-11.26638022	6.40143957	-4.83679540
H	-11.47196671	5.37602891	-6.29418114
H	-10.34921378	6.76058452	-6.30336668
H	-8.69828392	3.33654868	-5.37218680

TS-6-7
Total free energy in solvent: -1849.457675
55

N	-6.120703	3.515819	-1.253778
C	-5.773318	2.104420	-1.682701
C	-4.838923	4.304199	-1.043251
C	-7.134290	3.606942	-0.100786
C	-7.809612	4.997263	-0.182685
N	-7.968458	5.465015	-1.462119
O	-8.226636	5.565976	0.851291
C	-8.470483	6.758310	-1.666849
C	-9.634135	6.985872	-2.411298
C	-7.780068	7.896859	-1.218054
C	-8.229526	9.184081	-1.478840
C	-9.385369	9.373369	-2.236319
C	-10.081152	8.266756	-2.709537
F	-10.349176	5.911708	-2.906180
F	-11.200159	8.437110	-3.499335
F	-9.821817	10.643010	-2.528317
F	-7.524832	10.275027	-1.023715
F	-6.596324	7.733132	-0.527899
C	-8.260526	2.562443	-0.284250
C	-6.462524	3.420226	1.267684
C	-4.219452	4.562850	-2.443649
C	-4.792170	2.164431	-2.873637
C	-4.830200	3.577742	-3.478665
Pd	-6.891831	4.472254	-2.912222
O	-8.170011	1.985094	-4.902001
O	-6.147905	2.791033	-5.567674
O	-7.711814	5.582947	-4.512813
O	-9.288734	4.152483	-5.367335
C	-7.098368	1.899759	-5.604652
C	-8.724137	5.329770	-5.246984
C	-6.922944	0.731442	-6.541233
C	-9.371880	6.436414	-6.024748
H	-6.699158	1.620981	-1.989184
H	-5.357723	1.564127	-0.821538
H	-4.170971	3.724592	-0.394410
H	-5.093247	5.239349	-0.539681
H	-8.693323	2.609347	-1.287662
H	-9.050889	2.791762	0.437166
H	-7.908200	1.546101	-0.085012
H	-5.682332	4.162175	1.452307
H	-6.039128	2.415263	1.368995
H	-7.223492	3.563872	2.038160
H	-3.129440	4.412844	-2.404733
H	-4.385939	5.603564	-2.741092
H	-5.066309	1.409934	-3.614942
H	-3.766514	1.934398	-2.547463
H	-4.239316	3.637652	-4.400076

H -5.934765 3.461276 -4.450854
H -7.573768 0.868983 -7.413966
H -7.239411 -0.190773 -6.045255
H -5.889711 0.651738 -6.878700
H -10.120872 6.925232 -5.391426
H -9.879964 6.034921 -6.902006
H -8.627333 7.179555 -6.315178
H -8.813485 3.285741 -4.982977

TS-5-7
Total free energy in solvent: -1620.361419
47
N 0.985237 -1.293060 1.004654
C 0.713284 -2.780297 1.130066
C 2.348486 -1.172063 0.347244
C 0.782970 -0.456754 2.281211
C 0.465626 1.008583 1.869815
N -0.257548 1.121102 0.711834
O 0.763335 1.952806 2.636290
C -0.637674 2.377855 0.221135
C -1.986347 2.664038 -0.022795
C 0.296294 3.361132 -0.138430
C -0.092586 4.579303 -0.683092
C -1.443048 4.834495 -0.910921
C -2.390557 3.869260 -0.584891
F -2.946552 1.729770 0.297349
F -3.726883 4.113839 -0.816176
F -1.837217 6.032496 -1.461505
F 0.850331 5.522672 -1.026557
F 1.641769 3.101970 0.015284
C -0.467815 -0.934842 3.058763
C 2.018182 -0.505393 3.194074
C 2.211602 -1.675932 -1.119103
C 0.432377 -3.365799 -0.272222
C 0.834174 -2.358062 -1.368310
Pd -0.185552 -0.505308 -0.517989
O -1.375522 0.315635 -2.050348
O -1.319846 -1.767368 -2.924345
C -1.790826 -0.555199 -2.909971
C -2.847670 -0.163532 -3.899214
H -0.129948 -2.940454 1.795415
H 1.600381 -3.239980 1.585517
H 3.060368 -1.781249 0.916788
H 2.672770 -0.129789 0.389914
H -1.335120 -1.034180 2.398549
H -0.702914 -0.174970 3.809858
H -0.291380 -1.877500 3.584887
H 2.907601 -0.099613 2.706365
H 2.223469 -1.529553 3.525290
H 1.824520 0.118335 4.070401
H 3.038574 -2.359240 -1.365660
H 2.304804 -0.819169 -1.797447
H -0.640548 -3.573888 -0.365912
H 0.949098 -4.331150 -0.390496
H 0.912674 -2.880779 -2.333059
H -0.375143 -1.852963 -2.066951

H	-3.810614	-0.086063	-3.381675
H	-2.925305	-0.907958	-4.690504
H	-2.621508	0.820370	-4.318603

7 (with HOAc)
Total free energy in solvent: -1849.487877

55			
N	-6.31003818	3.29882366	-1.04008320
C	-6.56410077	1.83833612	-1.36059646
C	-4.82425231	3.48351814	-0.77356011
C	-7.23164997	3.92643253	0.02843066
C	-7.39775621	5.44462787	-0.27888654
N	-7.47307018	5.74179531	-1.61451988
O	-7.57241501	6.25246112	0.66480173
C	-7.66657948	7.06422147	-2.02186348
C	-8.74363429	7.40144150	-2.85043744
C	-6.76475405	8.10207956	-1.73061855
C	-6.94091628	9.39183917	-2.21735207
C	-8.02665731	9.68506550	-3.03939626
C	-8.93199968	8.67914537	-3.36203791
F	-9.68382715	6.42483550	-3.17697635
F	-10.00884684	8.95336062	-4.17764726
F	-8.19583736	10.95693687	-3.54029117
F	-6.02900171	10.37935903	-1.91624252
F	-5.64056618	7.82678433	-0.98236205
C	-8.65849056	3.33193404	-0.04859062
C	-6.67271342	3.72641692	1.44733923
C	-4.06248073	3.19705653	-2.09869704
C	-5.79789812	1.48253571	-2.66330792
C	-5.08618382	2.75215094	-3.16805878
Pd	-6.47964057	4.32138853	-2.83057082
O	-6.67196193	3.45499905	-5.85059495
O	-6.66642884	5.40153482	-4.68613146
O	-9.58974244	2.44211686	-3.32665930
O	-9.69180045	4.16407453	-4.83813926
C	-6.82721668	4.79240977	-5.77672338
C	-9.72075263	2.83542072	-4.49274925
C	-7.23532515	5.46019438	-7.04167999
C	-9.89534946	1.95587798	-5.69558956
H	-7.63306659	1.70696827	-1.50608612
H	-6.24150672	1.22819100	-0.50513667
H	-4.52103954	2.80879948	0.03659683
H	-4.67375501	4.51301566	-0.44298200
H	-9.05656835	3.34261630	-1.06585932
H	-9.30571105	3.94913473	0.58218849
H	-8.69247463	2.30991274	0.34321884
H	-5.70810222	4.21706938	1.59317695
H	-6.57685594	2.66155002	1.68710624
H	-7.36829437	4.18581385	2.15233448
H	-3.30670909	2.40967091	-1.94213927
H	-3.52998415	4.09738143	-2.42239741
H	-6.50490888	1.09170756	-3.40407859
H	-5.06304143	0.68268213	-2.47135896
H	-4.59402797	2.60608626	-4.13729829
H	-6.41421025	3.10694777	-4.94469116
H	-8.31981646	5.33691925	-7.15337253

H	-6.74762072	4.99597967	-7.90103767
H	-7.00622271	6.52479483	-6.99449713
H	-9.01198313	2.03987851	-6.33821073
H	-10.76193308	2.27894513	-6.27960231
H	-10.02201919	0.92068562	-5.37902080
H	-9.60827778	4.77034706	-4.06324290

7 (without HOAc)
Total free energy in solvent: -1620.382578
47

N	1.134672	-1.359383	0.972653
C	0.907802	-2.858176	1.062293
C	2.537615	-1.140162	0.415774
C	0.794279	-0.540815	2.232155
C	0.403683	0.917539	1.824155
N	-0.249492	1.019594	0.626203
O	0.587229	1.842857	2.651830
C	-0.634564	2.260526	0.122346
C	-1.909081	2.419138	-0.445061
C	0.227466	3.367911	0.000347
C	-0.171110	4.553612	-0.607430
C	-1.443311	4.666820	-1.162738
C	-2.309234	3.581289	-1.089513
F	-2.809587	1.361705	-0.405537
F	-3.562610	3.646388	-1.670620
F	-1.829345	5.828491	-1.795351
F	0.709115	5.608992	-0.707774
F	1.534504	3.263239	0.424992
C	-0.463226	-1.109464	2.933875
C	1.966879	-0.516079	3.226443
C	2.555455	-1.691719	-1.043223
C	0.884228	-3.433810	-0.379453
C	1.163167	-2.284453	-1.358762
Pd	0.045624	-0.673775	-0.647373
O	-0.988072	0.028982	-2.392707
O	-2.733076	-1.360387	-1.950141
C	-2.168531	-0.339326	-2.626421
C	-3.053506	0.329791	-3.619306
H	-0.042834	-3.035725	1.558643
H	1.704092	-3.296615	1.680000
H	3.264121	-1.645847	1.063726
H	2.736354	-0.067028	0.440109
H	-1.292529	-1.231246	2.230543
H	-0.772276	-0.386759	3.694517
H	-0.261129	-2.059672	3.438363
H	2.857794	-0.043650	2.806947
H	2.218847	-1.527384	3.566305
H	1.667606	0.084589	4.087375
H	3.339884	-2.459480	-1.152485
H	2.801083	-0.883355	-1.740209
H	-0.089521	-3.894299	-0.579730
H	1.639102	-4.231656	-0.485741
H	1.042282	-2.562619	-2.408591
H	-2.110416	-1.690377	-1.245598
H	-3.559126	1.163172	-3.113891
H	-3.812290	-0.357899	-3.994105

H -2.458019 0.736529 -4.437834

Energies are gas phase LANL2DZ/B3LYP in kcal/mol relative to structure 5 for the individual structures from 5 to 7 as follows:

5
47
N 0.710080 -1.183610 0.733421
C 0.539561 -2.687851 0.777849
C 2.067602 -0.839483 0.136755
C 0.524524 -0.515039 2.121905
C 0.370076 0.999761 1.858762
N -0.285936 1.267083 0.691378
O 0.756389 1.856759 2.683822
C -0.526142 2.574960 0.247476
C -1.821909 3.106231 0.221674
C 0.507049 3.376710 -0.256207
C 0.270379 4.651441 -0.754092
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5-7a
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H	-0.723736	-2.076572	3.175343
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5-7c
47
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5-7d
47
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5-7e
47
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5-7f
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47
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5-7g
47
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5-7h
47
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C 0.849329 -2.861606 1.111035
C 2.518376 -1.231787 0.385502
C 0.855328 -0.519212 2.243630
C 0.492005 0.945646 1.828698
N -0.189885 1.049223 0.647670
O 0.715131 1.872360 2.644352
C -0.613590 2.281137 0.154112
C -1.910384 2.407490 -0.373069
C 0.218705 3.408228 0.009309
C -0.229530 4.587301 -0.578376
C -1.522218 4.670713 -1.089166
C -2.358633 3.564125 -0.995016
F -2.783029 1.330174 -0.311726
F -3.632283 3.607048 -1.529578
F -1.960107 5.827571 -1.698552
F 0.618557 5.665043 -0.700053
F 1.539601 3.335823 0.394680
C -0.397744 -1.035016 2.994041
C 2.061890 -0.519439 3.196173
C 2.455040 -1.781287 -1.072666
C 0.721839 -3.448953 -0.319300
C 1.032415 -2.332343 -1.329333
Pd 0.016063 -0.649985 -0.602238
O -1.014631 0.173423 -2.290712
O -2.331423 -1.668346 -2.474581
C -2.018521 -0.394584 -2.792353
C -2.955790 0.290132 -3.725400
H -0.070087 -3.005390 1.670302
H 1.671791 -3.318741 1.678718
H 3.231441 -1.786365 1.009358
H 2.788552 -0.173486 0.405671
H -1.248395 -1.152605 2.315735
H -0.666876 -0.284670 3.743324
H -0.207494 -1.976446 3.518301
H 2.953199 -0.088012 2.736102
H 2.290200 -1.533541 3.544854

H 1.816109 0.105803 4.056817
H 3.220598 -2.559913 -1.228342
H 2.676656 -0.971372 -1.776682
H -0.294727 -3.833468 -0.465611
H 1.402378 -4.307729 -0.447930
H 0.899470 -2.646504 -2.369370
H -1.672784 -2.020701 -1.813485
H -3.576518 0.980219 -3.137318
H -3.598227 -0.425692 -4.236560
H -2.392586 0.887897 -4.446272

7
47
28.756213
N 1.134672 -1.359383 0.972653
C 0.907802 -2.858176 1.062293
C 2.537615 -1.140162 0.415774
C 0.794279 -0.540815 2.232155
C 0.403683 0.917539 1.824155
N -0.249492 1.019594 0.626203
O 0.587229 1.842857 2.651830
C -0.634564 2.260526 0.122346
C -1.909081 2.419138 -0.445061
C 0.227466 3.367911 0.000347
C -0.171110 4.553612 -0.607430
C -1.443311 4.666820 -1.162738
C -2.309234 3.581289 -1.089513
F -2.809587 1.361705 -0.405537
F -3.562610 3.646388 -1.670620
F -1.829345 5.828491 -1.795351
F 0.709115 5.608992 -0.707774
F 1.534504 3.263239 0.424992
C -0.463226 -1.109464 2.933875
C 1.966879 -0.516079 3.226443
C 2.555455 -1.691719 -1.043223
C 0.884228 -3.433810 -0.379453
C 1.163167 -2.284453 -1.358762
Pd 0.045624 -0.673775 -0.647373
O -0.988072 0.028982 -2.392707
O -2.733076 -1.360387 -1.950141
C -2.168531 -0.339326 -2.626421
C -3.053506 0.329791 -3.619306
H -0.042834 -3.035725 1.558643
H 1.704092 -3.296615 1.680000
H 3.264121 -1.645847 1.063726
H 2.736354 -0.067028 0.440109
H -1.292529 -1.231246 2.230543
H -0.772276 -0.386759 3.694517
H -0.261129 -2.059672 3.438363
H 2.857794 -0.043650 2.806947
H 2.218847 -1.527384 3.566305
H 1.667606 0.084589 4.087375
H 3.339884 -2.459480 -1.152485
H 2.801083 -0.883355 -1.740209
H -0.089521 -3.894299 -0.579730
H 1.639102 -4.231656 -0.485741

H 1.042282 -2.562619 -2.408591
H -2.110416 -1.690377 -1.245598
H -3.559126 1.163172 -3.113891
H -3.812290 -0.357899 -3.994105
H -2.458019 0.736529 -4.437834

8
Total free energy in solvent: -1863.406703
59
N -1.700992 -0.957117 -0.632303
C -2.760733 -0.016201 -1.176942
C -0.923150 -1.513002 -1.820461
C -2.179601 -2.006075 0.387034
C -0.993235 -2.400676 1.325308
N -0.142127 -1.373043 1.631926
O -0.971849 -3.553196 1.822224
C 0.981874 -1.604168 2.423463
C 1.320085 -0.705513 3.447076
C 1.919861 -2.625428 2.177480
C 3.083848 -2.753406 2.924161
C 3.386047 -1.839091 3.929130
C 2.495267 -0.801359 4.180408
F 0.472510 0.360214 3.722757
F 2.786362 0.150174 5.140004
F 4.558085 -1.946225 4.644774
F 3.999540 -3.740865 2.607243
F 1.741445 -3.473443 1.106136
C -3.253945 -1.404061 1.325518
C -2.744333 -3.257812 -0.304926
C -0.177696 -0.318866 -2.492029
C -2.045838 1.206984 -1.811639
C -0.531437 0.972677 -1.721073
Pd -0.210423 0.220456 0.196311
O 1.379422 1.461740 0.955462
O -0.135471 2.796086 1.997858
C 1.129106 2.394072 1.764741
C 2.174554 3.094877 2.558879
H -3.395352 0.298812 -0.353093
H -3.381804 -0.564783 -1.899687
H -1.622453 -2.007038 -2.506007
H -0.223175 -2.259991 -1.439717
H -2.922064 -0.451441 1.749274
H -3.405367 -2.105277 2.151169
H -4.215326 -1.270119 0.819451
H -2.005167 -3.747019 -0.943182
H -3.631410 -3.014328 -0.900676
H -3.017160 -3.977031 0.469526
H -0.473689 -0.229811 -3.550943
H 0.902051 -0.497649 -2.475313
H -2.334243 2.123444 -1.284550
H -2.359799 1.331864 -2.862089
H 0.067224 1.834667 -2.024947
H -0.776687 2.206379 1.513789
H 2.268684 2.578908 3.523555
H 1.889120 4.129806 2.752618
H 3.134610 3.043975 2.044491

C 7.401067 -1.962262 -2.389925
C 6.360521 -1.100474 -2.019890
C 7.612108 -3.155489 -1.690332
C 6.777959 -3.488810 -0.617843
C 5.732521 -2.636699 -0.237027
C 5.536847 -1.447079 -0.944735
I 3.944613 -0.121373 -0.367162
H 6.199439 -0.175502 -2.561351
H 8.419880 -3.820189 -1.978807
H 8.043093 -1.695311 -3.223556
H 5.094862 -2.910429 0.594749
H 6.933259 -4.412489 -0.069546

TS-8-9
Total free energy in solvent: -1863.397463
59
N -0.87963163 -1.05209043 -0.71204656
C -1.76130589 -0.00263440 -1.36511095
C -0.19229603 -1.82629493 -1.82784526
C -1.52242502 -1.92993740 0.37722740
C -0.45145213 -2.31281740 1.45077244
N 0.45664808 -1.33026329 1.73868311
O -0.57859426 -3.40427759 2.06092738
C 1.37330185 -1.54663370 2.77602045
C 1.44322796 -0.66656155 3.86632657
C 2.32009296 -2.58360666 2.76687610
C 3.26922253 -2.73902530 3.76951031
C 3.30849318 -1.84133799 4.83292009
C 2.39168869 -0.79619415 4.87405481
F 0.53250102 0.37323138 3.96366345
F 2.41987846 0.10423432 5.91830010
F 4.25506313 -1.97641758 5.82429954
F 4.18928059 -3.76297613 3.70408187
F 2.35814514 -3.45626250 1.69183351
C -2.60627322 -1.15234824 1.16197588
C -2.15602860 -3.20126825 -0.21477822
C 0.71181576 -0.83163211 -2.61307772
C -0.83891718 1.05550907 -2.02664803
C 0.60806780 0.55140615 -1.94062754
Pd 0.80403482 -0.03882020 0.04457125
O 1.70971369 2.03176061 1.52196536
O -0.53905580 2.24257471 1.78890054
C 0.74578753 2.58020920 2.09105884
C 0.85217026 3.61626214 3.16263365
H -2.38774586 0.45515655 -0.60349886
H -2.41795851 -0.49888213 -2.09421471
H -0.95674965 -2.29014804 -2.46428761
H 0.39973762 -2.61675426 -1.36396064
H -2.23336918 -0.19734585 1.54202111
H -2.88510851 -1.76262381 2.02567865
H -3.50795575 -0.98579702 0.56404021
H -1.41978758 -3.85308608 -0.68921381
H -2.93854883 -2.95177903 -0.94074523
H -2.59817819 -3.77275571 0.60293470
H 0.39608592 -0.77498445 -3.66853973
H 1.74659769 -1.18948718 -2.60834867

H	-0.94730034	2.01934343	-1.51572587
H	-1.13486815	1.22028781	-3.07678213
H	1.34477530	1.27197503	-2.30263425
H	-0.53213033	1.44911243	1.18401448
H	0.72155103	3.11832342	4.13080504
H	0.06510628	4.36612291	3.05945884
H	1.83674388	4.08349133	3.13495907
C	5.87412405	-1.89999999	-3.16748380
C	5.35623963	-0.89338799	-2.34190533
C	5.61421427	-3.24605696	-2.88710004
C	4.83528569	-3.58826675	-1.77625380
C	4.31116328	-2.59268956	-0.93974119
C	4.58046055	-1.25269699	-1.23526244
I	3.80533216	0.29636999	0.03652175
H	5.56127229	0.14854838	-2.55915127
H	6.01831392	-4.02267643	-3.52803497
H	6.47921504	-1.62605901	-4.02579488
H	3.71289599	-2.86909955	-0.07981947
H	4.63314859	-4.62988526	-1.54860353

9

Total free energy in solvent: -1863.4125151665

59

N	-0.92209314	-1.17313754	-0.68729652
C	-1.45138933	-0.18152976	-1.69948327
C	-0.50190318	-2.43221913	-1.42678746
C	-1.78320370	-1.42744943	0.55972652
C	-0.80648050	-1.90209902	1.67810883
N	0.27109042	-1.05912784	1.92795660
O	-1.03001303	-2.97057491	2.29182264
C	1.22645931	-1.57289815	2.84501015
C	1.36972193	-1.06424670	4.14101558
C	2.11857567	-2.59238978	2.48353206
C	3.11617267	-3.05351420	3.33058957
C	3.23361728	-2.51790927	4.61002504
C	2.35576145	-1.51765334	5.01273352
F	0.51036413	-0.08019531	4.58499586
F	2.45767530	-0.98595055	6.27854244
F	4.21583011	-2.96702872	5.46271363
F	3.99808388	-4.02326716	2.90263124
F	2.05666350	-3.12223809	1.19933955
C	-2.48601840	-0.13551488	1.03133682
C	-2.84885892	-2.50854548	0.30303101
C	0.70060455	-2.06507466	-2.34049871
C	-0.26616818	0.24836496	-2.60524663
C	0.97534005	-0.55656989	-2.19922230
Pd	0.98560812	-0.45329014	-0.12465253
O	2.19647493	1.90545238	2.38258836
O	-0.07314491	1.61842476	2.34171904
C	1.04330005	2.35060976	2.54902780
C	0.74461911	3.75133494	3.00361008
H	-1.85292887	0.67593864	-1.16403432
H	-2.26826003	-0.65034064	-2.26713746
H	-1.35825821	-2.81513467	-1.99714453
H	-0.22177653	-3.17726458	-0.67974783
H	-1.81370401	0.72158536	1.09042886

H	-2.88468270	-0.30903893	2.03589845
H	-3.33210669	0.11234064	0.38134353
H	-2.40902755	-3.48250180	0.08526292
H	-3.51175808	-2.21207956	-0.51805202
H	-3.45154079	-2.63182862	1.20594039
H	0.48277655	-2.32111474	-3.39123181
H	1.58347745	-2.64082962	-2.04520586
H	-0.08271828	1.32234242	-2.49552464
H	-0.50818053	0.06971076	-3.66673789
H	1.88861202	-0.23482239	-2.70355356
H	0.08575810	0.61455950	2.18018905
H	0.30854892	3.72259617	4.00829045
H	0.00720385	4.21525242	2.34164900
H	1.66175881	4.33995900	3.02056832
C	5.79205641	-0.90902246	-3.31186394
C	5.13283701	-0.13392786	-2.34827895
C	5.86145908	-2.29913649	-3.17020953
C	5.27083938	-2.91821904	-2.06240485
C	4.60948556	-2.15499123	-1.09095576
C	4.54877364	-0.76611374	-1.24679634
I	3.55473017	0.42040142	0.24607480
H	5.08141542	0.94354497	-2.45801204
H	6.37358268	-2.89633104	-3.91734267
H	6.24794464	-0.42191663	-4.16787850
H	4.14761921	-2.64160811	-0.23933662
H	5.32315321	-3.99583202	-1.94588754

8a
Total free energy in solvent: -1863.403724
59
14.265132
N -0.897265 0.448622 1.718369
C -0.739389 1.410090 2.869744
C -1.392400 1.213788 0.506975
C -1.655565 -0.843389 2.011481
C -1.314275 -1.830234 0.859937
N 0.008906 -1.854835 0.512895
O -2.221780 -2.548169 0.367683
C 0.354068 -2.520939 -0.667560
C 1.304036 -3.552971 -0.698572
C -0.157175 -2.118729 -1.918015
C 0.263619 -2.677334 -3.114584
C 1.257310 -3.649783 -3.098625
C 1.778490 -4.092578 -1.890382
F 1.811838 -4.054674 0.487106
F 2.759504 -5.062059 -1.874676
F 1.765014 -4.132828 -4.302921
F -0.264183 -2.263896 -4.314879
F -1.077728 -1.087354 -1.969478
C -1.161253 -1.479505 3.330101
C -3.172831 -0.604879 2.079625
C -0.205334 2.072238 0.002338
C 0.298442 2.478184 2.443775
C 0.880311 2.066441 1.088061
Pd 1.129677 -0.014815 1.171356
O 1.970979 -0.448701 -4.742300

O 2.773800 -2.075126 -6.148316
C 2.472607 -0.776674 -5.823290
C 2.831686 0.167204 -6.934991
H -0.371203 0.848557 3.726666
H -1.714303 1.846228 3.132200
H -2.255859 1.826426 0.798206
H -1.713672 0.496120 -0.248044
H -0.069783 -1.549170 3.350778
H -1.566637 -2.494174 3.391893
H -1.512374 -0.928233 4.208920
H -3.568674 -0.218760 1.137856
H -3.423832 0.087486 2.891474
H -3.670076 -1.559830 2.261790
H -0.524303 3.104796 -0.217115
H 0.184976 1.655090 -0.932900
H 1.080385 2.565214 3.205246
H -0.171353 3.472320 2.358516
H 1.780766 2.612246 0.799410
H 2.488056 -2.714400 -5.455890
H 2.661772 -0.303175 -7.905426
H 3.892463 0.438596 -6.874901
H 2.238013 1.078010 -6.842116
C 3.825408 -2.353465 2.149285
C 3.684406 -1.778195 0.896892
C 3.734112 -1.564969 3.319044
C 3.498919 -0.202956 3.225740
C 3.333003 0.416123 1.953705
C 3.406004 -0.388080 0.781228
I 3.761834 0.539782 -1.145691
H 3.781386 -2.383438 0.005537
H 3.871132 -2.028913 4.290185
H 4.005623 -3.419476 2.225909
H 3.365438 1.495483 1.887662
H 3.473588 0.417730 4.115970

TS-8a-9a
Total free energy in solvent: -1863.383958
59
-1862.903364 -1862.937599 -1862.914866
N -0.748821 0.470274 1.466620
C -0.414888 1.385150 2.622437
C -1.360374 1.298601 0.350992
C -1.500617 -0.812286 1.816861
C -1.278261 -1.830986 0.662978
N 0.002084 -1.889366 0.177146
O -2.232219 -2.574126 0.316145
C 0.202559 -2.701453 -0.941887
C 1.164514 -3.723104 -0.964028
C -0.516014 -2.518261 -2.142641
C -0.312885 -3.309324 -3.264617
C 0.646265 -4.319937 -3.243080
C 1.393170 -4.518038 -2.086281
F 1.901676 -3.994873 0.177047
F 2.341341 -5.519768 -2.040778
F 0.866813 -5.096228 -4.358980
F -1.028165 -3.077645 -4.419226

F -1.432088 -1.491248 -2.227877
C -0.919133 -1.459283 3.095409
C -3.003473 -0.545644 2.009433
C -0.219770 2.159201 -0.256865
C 0.596909 2.441187 2.113753
C 0.995406 2.068039 0.682416
Pd 1.140266 -0.009821 0.618825
O 1.618869 0.017154 -2.803388
O 2.795170 -1.706926 -3.735454
C 2.261528 -0.437833 -3.755790
C 2.608039 0.291241 -5.016151
H 0.039447 0.779151 3.403107
H -1.339034 1.831152 3.018523
H -2.172463 1.911507 0.765523
H -1.781380 0.613559 -0.386856
H 0.168389 -1.557035 3.032200
H -1.345439 -2.462709 3.187605
H -1.188320 -0.899775 3.997643
H -3.471338 -0.160262 1.101015
H -3.173264 0.156695 2.833503
H -3.496594 -1.491817 2.239832
H -0.540820 3.207405 -0.383966
H 0.044021 1.780586 -1.251081
H 1.469404 2.468772 2.774778
H 0.152282 3.450806 2.127776
H 1.877216 2.595110 0.312146
H 2.570197 -2.167866 -2.897219
H 2.510109 -0.365219 -5.883577
H 3.653164 0.617957 -4.962184
H 1.966479 1.165749 -5.122978
C 3.582645 -2.171682 1.872307
C 3.704971 -1.419341 0.690136
C 3.591293 -1.540178 3.117347
C 3.688398 -0.142904 3.196766
C 3.806022 0.620423 2.031564
C 3.834262 -0.022661 0.775659
I 4.523742 1.113817 -0.926227
H 3.747618 -1.919665 -0.268057
H 3.522235 -2.132629 4.023748
H 3.480434 -3.246739 1.802445
H 3.927051 1.694775 2.093229

H 3.688025 0.354207 4.161470

9a
Total free energy in solvent: -1863.404718
59
Step 55

N	-1.12570662	0.48047267	2.19300601
C	-1.01231900	1.02774087	3.59855860
C	-1.56881162	1.61007867	1.27932424
C	-1.92224972	-0.81552075	2.03642496
C	-1.41755276	-1.55821427	0.76894830
N	-0.05951307	-1.52612029	0.58293865
O	-2.23757941	-2.22725199	0.08915490
C	0.43025856	-2.28257666	-0.49109460

C	1.30125810	-3.36009144	-0.28398362
C	0.09950523	-1.99560334	-1.82758439
C	0.58606837	-2.75045412	-2.88507936
C	1.43649503	-3.82080879	-2.63571807
C	1.81390849	-4.11651794	-1.33415516
F	1.69213455	-3.68688113	1.00023478
F	2.70204890	-5.14270571	-1.08423595
F	1.93578816	-4.56576703	-3.69884563
F	0.26921673	-2.43327912	-4.19046760
F	-0.70359306	-0.91026133	-2.10586749
C	-1.64047173	-1.78104931	3.21276918
C	-3.43338274	-0.54694505	1.93774179
C	-0.43795010	2.67740105	1.26627215
C	0.15163887	2.04789560	3.62893867
C	0.69059480	2.20189774	2.20301532
Pd	0.85907160	0.24795068	1.46874633
O	3.55238197	-1.94781179	-4.07296342
O	2.81597709	-3.00494807	-5.95571565
C	3.43894421	-1.97694195	-5.30736039
C	3.95109749	-0.93508005	-6.25479837
H	-0.81294593	0.20400357	4.27882591
H	-1.97468112	1.47913168	3.88009909
H	-2.52096206	2.01784814	1.64345980
H	-1.73047706	1.18556764	0.28642886
H	-0.56524932	-1.90081641	3.37428125
H	-2.05216157	-2.75952259	2.94888465
H	-2.12516671	-1.45550806	4.13896731
H	-3.69247461	0.03069849	1.04781337
H	-3.79961955	-0.02517804	2.82973584
H	-3.94969013	-1.50461129	1.84988163
H	-0.82580948	3.65582650	1.59673563
H	-0.06582483	2.81144973	0.24471982
H	0.93818067	1.69882593	4.30705715
H	-0.19414958	3.02074424	4.01788139
H	1.57841706	2.83953322	2.15894207
H	2.44975061	-3.65698908	-5.31356974
H	3.12541802	-0.54507757	-6.85839909
H	4.67716821	-1.37911101	-6.94354264
H	4.41566442	-0.12494218	-5.69302539
C	3.94292418	-1.63624729	-0.01653436
C	3.67768640	-0.80006181	-1.12447667
C	3.74433142	-1.19004248	1.28516959
C	3.28445403	0.12754149	1.51488634
C	3.01068713	0.97627274	0.41243263
C	3.20947692	0.48644870	-0.89621568
I	2.81869782	1.80786999	-2.54868063
H	3.82653179	-1.16949171	-2.13348061
H	3.95463138	-1.84134591	2.12567420
H	4.29879094	-2.64573348	-0.19475454
H	2.80437101	2.02620827	0.56606500
H	3.29109562	0.53816942	2.51941962

10
Total free energy in solvent: -2111.916698
67

N	-1.14583857	-1.71459417	-1.05163802

C	-1.95836949	-1.01267546	-2.12101353
C	-0.25360369	-2.73435414	-1.74491330
C	-1.90234893	-2.26359212	0.16736637
C	-0.93702218	-2.25749011	1.39674997
N	-0.17055118	-1.12734296	1.52038003
O	-0.98427763	-3.20804795	2.21697027
C	0.74108943	-1.07100131	2.59027917
C	0.59902468	-0.14544204	3.63045619
C	1.91087218	-1.84644741	2.61666210
C	2.88011665	-1.70817785	3.60075760
C	2.70760144	-0.76479933	4.61061228
C	1.56029962	0.02080304	4.61968232
F	-0.53639985	0.65034643	3.67940086
F	1.39747914	0.98456325	5.59428683
F	3.67297404	-0.59689182	5.57751761
F	4.02429656	-2.47531120	3.56538855
F	2.15107531	-2.73357606	1.57632220
C	-3.09019199	-1.34953776	0.54517396
C	-2.43176941	-3.68660144	-0.08311928
C	0.70277459	-1.96006962	-2.69689939
C	-0.99230725	-0.11834499	-2.94338836
C	0.44631375	-0.45035186	-2.52506332
Pd	0.36684453	-0.36946929	-0.44684977
O	1.45026747	2.70282789	2.02156637
O	1.74326217	4.87683811	2.65462821
C	2.08305159	3.60570083	2.65736739
C	3.27720500	3.25827325	3.51312592
H	-2.72627240	-0.40870553	-1.64325235
H	-2.45793624	-1.77103865	-2.74049841
H	-0.88322843	-3.45643828	-2.28055321
H	0.30149818	-3.26704762	-0.97027389
H	-2.78684681	-0.30124017	0.59565436
H	-3.44517598	-1.64766762	1.53624564
H	-3.92483290	-1.44983880	-0.15608021
H	-1.62503562	-4.40921271	-0.21649964
H	-3.08954099	-3.71058676	-0.95963602
H	-2.99727992	-4.00897985	0.79317465
H	0.52936062	-2.26090449	-3.74421304
H	1.74180506	-2.20904973	-2.46233921
H	-1.21179061	0.93979127	-2.76348044
H	-1.13417630	-0.29300484	-4.02305500
H	1.19511680	0.17578416	-3.01413131
H	0.77486519	5.13956459	2.08819342
H	3.92136142	2.54445375	2.99154034
H	2.92516706	2.77533944	4.43301346
H	3.84019168	4.15337497	3.77821530
C	5.20530981	-0.30321114	-3.43503844
C	4.39690016	0.47427684	-2.59381674
C	5.48705033	-1.63444428	-3.10983015
C	4.95559027	-2.19585503	-1.94241295
C	4.14353712	-1.43038379	-1.09477138
C	3.87569748	-0.09949483	-1.43129934
I	2.68658850	1.09003305	-0.08536720
H	4.18771341	1.50813606	-2.84454719
H	6.11817985	-2.23077826	-3.76049714
H	5.61303144	0.13679000	-4.33936259

H	3.72208375	-1.86808290	-0.19674913
H	5.17221080	-3.22735386	-1.68340475
Cs	-1.57699917	2.52029734	1.41968741
O	-0.35253966	5.24463625	1.50433095
C	-0.50253301	5.52904893	0.21996325
O	-1.38875594	4.97162917	-0.48642746
C	0.44337722	6.55864986	-0.36828660
H	1.48197141	6.28817791	-0.14533541
H	0.25739820	7.53543834	0.09358664
H	0.30059923	6.63410824	-1.44714343

11
Total free energy in solvent: -1634.3036428981
51

N	-1.00849195	-1.12514336	-0.76865061
C	-1.74583273	-0.05242395	-1.54207561
C	-0.54697563	-2.17985773	-1.75763943
C	-1.69901336	-1.67328568	0.48657423
C	-0.61241244	-2.21288343	1.47016928
N	0.51526192	-1.43810948	1.55291563
O	-0.88275306	-3.20654625	2.18973789
C	1.51116515	-1.79485188	2.46600680
C	2.01218175	-0.84987733	3.37571848
C	2.13822191	-3.05356002	2.47940727
C	3.14710046	-3.37390649	3.37993923
C	3.59291114	-2.42036105	4.29069601
C	3.03004919	-1.14762951	4.27454222
F	1.49859896	0.43326239	3.36584929
F	3.48395984	-0.18697931	5.15311046
F	4.59651392	-2.72690166	5.18398820
F	3.73357539	-4.62190117	3.35343404
F	1.81080086	-3.98185122	1.50673871
C	-2.41448618	-0.53560569	1.25452792
C	-2.70653241	-2.78212858	0.14481134
C	0.48158533	-1.50699248	-2.71585654
C	-0.71795776	0.68689291	-2.44040290
C	0.63388119	-0.02552855	-2.30689237
Pd	0.85776952	-0.31441740	-0.25617734
H	-2.19607619	0.63718315	-0.83335600
H	-2.54985540	-0.52464430	-2.12499414
H	-1.41808241	-2.57895450	-2.29357905
H	-0.09092140	-2.98890803	-1.18349703
H	-1.74851390	0.31923894	1.40239508
H	-2.69397253	-0.91987565	2.23992467
H	-3.33166630	-0.21308437	0.75079014
H	-2.22890296	-3.64476621	-0.32513271
H	-3.49916714	-2.40459996	-0.51138250
H	-3.15374408	-3.13933153	1.07432639
H	0.14195780	-1.58719549	-3.76274143
H	1.44292717	-2.02853377	-2.65452385
H	-0.63566177	1.73357923	-2.12796631
H	-1.05759095	0.69236475	-3.49026428
H	1.44796984	0.48428768	-2.82779213
C	6.19578859	-1.38403326	-2.56780419
C	5.46632124	-0.39292715	-1.89671749
C	5.92942636	-2.73729250	-2.33386937

C	4.93032650	-3.10666007	-1.42620487
C	4.19182086	-2.12927159	-0.74448055
C	4.47651145	-0.78493591	-0.99451318
I	3.36682940	0.74899149	0.05084242
H	5.67107562	0.65516613	-2.07983197
H	6.49747236	-3.50005140	-2.85557319
H	6.96842643	-1.09075765	-3.27098019
H	3.41712174	-2.42742670	-0.04836067
H	4.71986868	-4.15408440	-1.23759581

TS-11-12
Total free energy in solvent: -1634.2736644464
51

N	-0.548767	-1.105108	-0.905713
C	-1.282116	0.110844	-1.448511
C	-0.143298	-1.962144	-2.084426
C	-1.232130	-1.844256	0.255340
C	-0.168106	-2.384266	1.266460
N	0.915869	-1.565387	1.466591
O	-0.457578	-3.398697	1.946900
C	1.735868	-1.799679	2.581151
C	1.971428	-0.754087	3.491206
C	2.389054	-3.012536	2.856931
C	3.213357	-3.179160	3.965742
C	3.419957	-2.120952	4.843482
C	2.799624	-0.899768	4.596533
F	1.350336	0.462432	3.297850
F	3.001195	0.157942	5.457014
F	4.241445	-2.275380	5.938213
F	3.846533	-4.384777	4.184917
F	2.287916	-4.066121	1.966058
C	-2.080038	-0.875098	1.119830
C	-2.130558	-2.988566	-0.243130
C	0.782015	-1.099406	-2.985814
C	-0.250966	1.025652	-2.152120
C	1.054207	0.243731	-2.283849
Pd	1.389315	-0.373523	-0.292957
H	-1.750335	0.637444	-0.622810
H	-2.075954	-0.232934	-2.127279
H	-1.041576	-2.301140	-2.617500
H	0.383240	-2.837574	-1.699541
H	-1.502184	0.002618	1.422706
H	-2.366314	-1.412741	2.028235
H	-2.998798	-0.566718	0.611470
H	-1.570754	-3.753809	-0.785322
H	-2.936234	-2.607251	-0.881219
H	-2.567818	-3.478272	0.628550
H	0.305128	-0.911784	-3.961422
H	1.709954	-1.637993	-3.184910
H	-0.101653	1.945218	-1.575937
H	-0.616407	1.328019	-3.147851
H	1.866576	0.822106	-2.721775
C	4.673934	-1.757856	-3.024750
C	4.010244	-0.774956	-2.280484
C	4.743000	-3.078242	-2.560035
C	4.165801	-3.408551	-1.331508

C 3.506493 -2.433421 -0.561017
C 3.401485 -1.138199 -1.072763
I 3.569782 1.013777 0.396776
H 3.991670 0.247579 -2.632101
H 5.259315 -3.834678 -3.141437
H 5.148623 -1.479140 -3.959152
H 3.089141 -2.713887 0.391759
H 4.222095 -4.421851 -0.946218

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Total free energy in solvent -1634.3095661444
51
N -0.24982218 -1.16044470 -0.71034941
C -0.61257522 0.27273962 -0.33472086
C -0.34261075 -1.30851187 -2.20335770
C -0.94067635 -2.18853856 0.16795391
C -0.30986262 -2.05067547 1.58355391
N 0.94945620 -1.49920094 1.60923351
O -0.94584116 -2.45624329 2.58263911
C 1.55826959 -1.30330538 2.86522570
C 1.59895539 -0.03164067 3.44294986
C 2.20830863 -2.33483577 3.54972685
C 2.87510787 -2.11081305 4.74861233
C 2.90022519 -0.83138963 5.29747945
C 2.26243310 0.21555802 4.63853908
F 0.97981877 1.02103402 2.79022345
F 2.29070254 1.48506463 5.17103895
F 3.56072298 -0.60048611 6.48173163
F 3.51425233 -3.14544159 5.39257633
F 2.21880644 -3.60052979 3.00569495
C -2.46207358 -1.95738307 0.25340789
C -0.66897661 -3.61939060 -0.33817764
C 0.61691670 -0.25325031 -2.81278310
C 0.56314383 1.18454612 -0.75850344
C 1.45334159 0.36964855 -1.68883872
Pd 1.88700502 -1.15948456 -0.27437020
H -0.76080343 0.32029936 0.74269581
H -1.55234195 0.53487318 -0.83519251
H -1.38233015 -1.17628519 -2.53160659
H -0.01474473 -2.31432145 -2.46524861
H -2.71270715 -0.96413804 0.63279840
H -2.87287025 -2.68255018 0.95942413
H -2.93893883 -2.10213662 -0.72252065
H 0.39527666 -3.78602205 -0.51458598
H -1.22231506 -3.83359409 -1.25827834
H -1.00321179 -4.32200446 0.43016317
H 0.04851976 0.55572036 -3.29914982
H 1.24065365 -0.71359782 -3.57816083
H 1.10891853 1.52908574 0.12383613
H 0.20160037 2.08048583 -1.28781033
H 2.37955968 0.85486352 -1.98970676
C 4.21199329 -2.33657383 -3.86841968
C 3.58553539 -1.49865639 -2.93395494
C 4.18628280 -3.72597520 -3.70647461
C 3.54953721 -4.27834689 -2.59116305
C 2.92405162 -3.44473056 -1.65048121

C	2.91334401	-2.05580827	-1.84141672
I	4.32830855	-0.51901294	0.60995664
H	3.65883842	-0.42539097	-3.06435196
H	4.67618145	-4.36928007	-4.43000127
H	4.73226686	-1.89456077	-4.71286007
H	2.48879109	-3.88944398	-0.76101992
H	3.54858629	-5.35246882	-2.43379327

TS-12-13
Total free energy in solvent: -1634.2961822224
51

N	-0.245710	-1.310111	-0.674520
C	-0.470539	0.175775	-0.487519
C	-0.463675	-1.648229	-2.124113
C	-0.991965	-2.180166	0.329474
C	-0.346043	-1.948275	1.719318
N	0.964143	-1.546073	1.707132
O	-1.012811	-2.173181	2.756556
C	1.592415	-1.331229	2.952378
C	1.627882	-0.055331	3.521133
C	2.238233	-2.360099	3.643393
C	2.907459	-2.126627	4.839217
C	2.931103	-0.843615	5.378626
C	2.290886	0.199302	4.714713
F	1.009433	0.990340	2.862111
F	2.318352	1.471337	5.241261
F	3.592118	-0.604576	6.560645
F	3.546186	-3.156175	5.491814
F	2.240385	-3.631008	3.115554
C	-2.491778	-1.838136	0.395285
C	-0.807410	-3.677990	0.003563
C	0.416218	-0.727224	-3.006037
C	0.717978	0.897454	-1.159042
C	1.476662	-0.064729	-2.121246
Pd	1.868197	-1.303119	-0.126988
H	-0.499343	0.385978	0.581084
H	-1.431974	0.459922	-0.933427
H	-1.528971	-1.533217	-2.366645
H	-0.194225	-2.690113	-2.279571
H	-2.664813	-0.787434	0.641097
H	-2.937414	-2.430704	1.197169
H	-2.997609	-2.077217	-0.546336
H	0.253021	-3.933633	-0.084798
H	-1.338340	-3.970781	-0.907616
H	-1.221889	-4.256014	0.834064
H	-0.195733	0.074434	-3.445212
H	0.852159	-1.296267	-3.828281
H	1.381494	1.345646	-0.415568
H	0.354050	1.719897	-1.798033
H	2.232069	0.505278	-2.650866
C	4.756975	-1.926157	-3.477412
C	3.939620	-1.133246	-2.668419
C	4.441673	-3.272800	-3.696738
C	3.305097	-3.821353	-3.096076
C	2.469218	-3.025191	-2.300652
C	2.779018	-1.667307	-2.078769

I 4.345829 -0.791300 0.810990
H 4.226503 -0.107101 -2.471743
H 5.081168 -3.889261 -4.319990
H 5.646741 -1.493239 -3.923247
H 1.611929 -3.488662 -1.829755
H 3.066497 -4.871420 -3.231836
13
Total free energy in solvent: -1634.3786420550
51
N -0.198033 -1.478494 -0.724238
C -0.207682 0.031095 -0.641037
C -0.659218 -1.890778 -2.098465
C -1.055312 -2.139117 0.375497
C -0.357327 -1.876438 1.724547
N 1.008701 -1.829673 1.670632
O -1.023640 -1.764028 2.780455
C 1.703377 -1.564732 2.871247
C 2.056262 -0.258296 3.219070
C 2.065505 -2.586035 3.754214
C 2.770522 -2.320671 4.922090
C 3.119416 -1.010089 5.236670
C 2.764961 0.026915 4.379057
F 1.713868 0.778722 2.371313
F 3.110705 1.324103 4.687791
F 3.816779 -0.740899 6.390200
F 3.127870 -3.344970 5.768353
F 1.749927 -3.888392 3.445930
C -2.491414 -1.583019 0.438334
C -1.095819 -3.672468 0.168124
C -0.036135 -1.022338 -3.215426
C 0.881271 0.646695 -1.548284
C 1.225542 -0.253609 -2.776588
Pd 1.858471 -1.986425 -0.166657
H -0.038890 0.314581 0.398458
H -1.201355 0.388448 -0.940866
H -1.751308 -1.796481 -2.138055
H -0.425984 -2.947764 -2.225911
H -2.514281 -0.502164 0.600272
H -2.982393 -2.038444 1.301219
H -3.067142 -1.825956 -0.459935
H -0.091004 -4.081149 0.020448
H -1.732519 -3.951431 -0.677709
H -1.515379 -4.130286 1.068902
H -0.772884 -0.281733 -3.550056
H 0.186448 -1.651861 -4.085066
H 1.785214 0.845234 -0.964605
H 0.511458 1.615549 -1.906743
H 1.487149 0.419534 -3.603914
C 4.902646 -1.244683 -2.790467
C 3.733391 -0.502661 -2.690559
C 4.860521 -2.652124 -2.771309
C 3.642139 -3.297693 -2.631311
C 2.443419 -2.552378 -2.528562
C 2.467532 -1.133191 -2.583404
I 4.360306 -2.269662 0.787630
H 3.777924 0.581761 -2.729594

H 5.778609 -3.224659 -2.848963
H 5.856425 -0.735431 -2.888270
H 1.509877 -3.093569 -2.604317
H 3.592931 -4.380983 -2.606286

12-OAc
Total free energy in solvent: -1862.930773

58
0.000000
C -2.145245 -0.297888 1.036900
N -0.935396 0.629693 1.005427
C -0.394787 0.752114 2.410840
C 0.060835 -0.643131 2.902115
H -1.171841 1.192003 3.054089
H 0.459053 1.423043 2.387591
C -1.692721 -1.697009 1.533886
H -2.510541 -0.378170 0.014418
H -2.910704 0.148339 1.684032
Pd 0.449686 -0.714203 -0.033004
N 0.170178 0.937457 -1.584440
C -1.167079 1.960919 0.267880
C -0.764074 1.862938 -1.241385
C -0.323122 3.119405 0.860107
C -2.649836 2.395612 0.341941
O -1.254199 2.737088 -2.012271
C 0.377841 0.667650 -2.935251
C 1.678260 0.537247 -3.453079
C -0.665844 0.405751 -3.847304
C -0.424318 0.041560 -5.165375
C 0.878107 -0.079686 -5.638109
C 1.932705 0.169802 -4.768819
F -1.485206 -0.235124 -6.010830
F 1.119018 -0.444877 -6.951274
F 3.235058 0.071144 -5.224072
F 2.765588 0.793677 -2.639566
F -1.981814 0.457794 -3.442037
C -1.603215 -2.708113 -1.671015
C -1.707181 -2.967518 -3.168308
O -1.128185 -1.513594 -1.360334
H -2.963278 2.551407 1.381529
H -3.318965 1.676411 -0.132739
H -2.743881 3.331557 -0.210587
H -0.661118 3.395052 1.865132
H -0.468389 3.979463 0.200512
H 0.743145 2.892672 0.889898
O -1.968638 -3.596090 -0.851874
C -0.183761 -1.655741 1.778941
H -1.952679 -2.468490 0.804261
H -2.189861 -1.938974 2.490096
H -0.532232 -0.956619 3.777134
H 1.101537 -0.598816 3.220691
H 0.296487 -2.626262 1.901792
C 4.158732 -0.137171 2.231071
C 2.969633 -0.675213 1.720282
C 4.606880 1.118582 1.804233

C 3.865563 1.817713 0.847664
C 2.673733 1.280417 0.333627
C 2.198647 0.042213 0.789672
I 2.020960 -2.701143 -1.022505
H 2.668485 -1.669829 2.026722
H 5.532331 1.533403 2.194230
H 4.740725 -0.713475 2.945823
H 2.141620 1.799019 -0.450498
H 4.216691 2.777860 0.478275
H -2.156335 -2.109834 -3.676994
H -2.291431 -3.871298 -3.355819
H -0.693989 -3.102480 -3.566360

TS-12-OAc-13-OAc
Total free energy in solvent: -1862.874099
58
-1862.347329 -1862.411113 -1862.441193
C -1.885316 -0.324869 1.325909
N -0.938509 0.786656 0.930824
C -0.366263 1.357453 2.211530
C 0.299842 0.279493 3.095099
H -1.186791 1.850380 2.753568
H 0.363236 2.118601 1.957404
C -1.043428 -1.450124 1.984733
H -2.353785 -0.703267 0.420159
H -2.652485 0.065032 2.010318
Pd 0.393476 -0.703391 -0.146584
N -0.045190 1.087076 -1.767196
C -1.529992 1.893813 0.021850
C -1.218136 1.689128 -1.499056
C -0.898693 3.286763 0.309136
C -3.054066 2.014120 0.224767
O -1.981877 2.294698 -2.309736
C 0.380443 0.880396 -3.064346
C 1.749322 1.078082 -3.351798
C -0.397583 0.400073 -4.143327
C 0.155152 0.152559 -5.395911
C 1.509237 0.362544 -5.634781
C 2.309298 0.824199 -4.594709
F -0.646135 -0.318862 -6.423279
F 2.053737 0.111497 -6.884439
F 3.659662 1.044241 -4.813568
F 2.584077 1.550075 -2.350796
F -1.738270 0.119630 -3.991015
C -1.812526 -2.567840 -1.445243
C -2.175567 -3.111006 -2.819943
O -1.223085 -1.387076 -1.480791
H -3.300301 2.292427 1.257223
H -3.577057 1.091590 -0.036010
H -3.411558 2.786713 -0.458280
H -1.160339 3.681476 1.296798
H -1.300827 3.965144 -0.447182
H 0.188261 3.268043 0.189132
O -2.073482 -3.228660 -0.398317
C 0.431365 -1.001896 2.275177

H -1.118728 -2.355874 1.373669
H -1.460426 -1.685132 2.981291
H -0.334410 0.058369 3.966360
H 1.262170 0.638434 3.468382
H 0.924089 -1.817682 2.799855
C 4.314332 -1.260084 1.724536
C 2.956313 -1.546168 1.592205
C 4.787205 0.040387 1.501619
C 3.885496 1.044734 1.137587
C 2.517103 0.768986 1.033524
C 2.016476 -0.539288 1.259093
I 1.819996 -2.618680 -1.461346
H 2.614561 -2.565743 1.730201
H 5.846123 0.262396 1.595612
H 5.005431 -2.055992 1.984234
H 1.861058 1.554281 0.684114
H 4.243101 2.044819 0.909701
H -2.563720 -2.309948 -3.452554
H -2.895042 -3.928545 -2.733343
H -1.256634 -3.483723 -3.287850

13-OAc
Total free energy in solvent: -1862.976465
58
-18.875184
C -1.729996 -0.078831 1.188641
N -0.816095 1.083512 0.842792
C -0.341345 1.731439 2.125924
C 0.027990 0.721662 3.231417
H -1.145640 2.382185 2.495116
H 0.505623 2.369838 1.878478
C -1.000763 -1.186074 1.994714
H -2.079531 -0.511073 0.248376
H -2.569173 0.322281 1.772866
Pd 0.723959 0.121136 -0.353110
N -0.128266 1.245431 -1.880649
C -1.491396 2.144717 -0.060497
C -1.333775 1.790510 -1.556616
C -0.759886 3.515049 0.044666
C -2.980058 2.341790 0.273876
O -2.187624 2.212769 -2.379888
C 0.193793 1.118375 -3.242541
C 1.326767 1.772521 -3.745413
C -0.556952 0.359254 -4.153878
C -0.180282 0.250111 -5.488890
C 0.960404 0.896588 -5.951843
C 1.718963 1.660223 -5.072345
F -0.937404 -0.501970 -6.367474
F 1.333623 0.787860 -7.278452
F 2.852811 2.308988 -5.526463
F 2.098110 2.541498 -2.899387
F -1.675955 -0.317675 -3.743425
C -0.692872 -3.104737 -0.940030
C -0.777773 -3.919169 -2.233004
O -0.900925 -1.829556 -1.057522
H -3.122112 2.665897 1.311408

H -3.561733 1.435128 0.098201
H -3.371997 3.108431 -0.397164
H -0.919644 4.007941 1.007866
H -1.173091 4.160842 -0.735575
H 0.310531 3.401578 -0.146361
O -0.389013 -3.716374 0.146529
C 0.293231 -0.692657 2.692880
H -0.788049 -2.040168 1.340865
H -1.692637 -1.534406 2.775298
H -0.805216 0.643232 3.941407
H 0.886089 1.104504 3.797531
H 0.451727 -1.339176 3.569068
C 3.367961 -2.391788 1.247011
C 2.034765 -2.144390 1.552932
C 4.303448 -1.344030 1.221521
C 3.883226 -0.035943 1.447244
C 2.541469 0.225800 1.766599
C 1.597927 -0.829146 1.878474
I 2.580745 -1.034714 -1.989134
H 1.302152 -2.946786 1.513035
H 5.342185 -1.547944 0.980380
H 3.679036 -3.401380 0.999888
H 2.256894 1.241895 2.006493
H 4.584565 0.788767 1.367553
H -1.603857 -3.559744 -2.854401
H -0.891494 -4.985558 -2.017897
H 0.151605 -3.764682 -2.797622

14
Total free energy in solvent: -2111.99437
67
N 0.73447826 -2.57504167 -1.46636818
C 0.18214314 -1.17449382 -1.61021870
C 1.52155323 -2.92016946 -2.70402032
C -0.36984038 -3.61690804 -1.17562962
C -0.89635449 -3.31526821 0.24102739
N 0.06067858 -2.85236420 1.10343439
O -2.09750922 -3.49336466 0.54512177
C -0.29485011 -2.51754067 2.41835888
C -0.13791111 -1.20693870 2.87375016
C -0.73984011 -3.46213445 3.35264938
C -0.99273066 -3.11555518 4.67611921
C -0.77799369 -1.80872206 5.10899556
C -0.33160278 -0.85608033 4.20086161
F 0.32175054 -0.23421348 1.99509512
F -0.03331301 0.43150237 4.62032264
F -0.98049353 -1.46860411 6.42539318
F -1.41486782 -4.06583630 5.57478122
F -0.86305800 -4.77538053 2.97545437
C -1.53800391 -3.54288327 -2.17401337
C 0.22770338 -5.04313614 -1.16752698
C 2.38709710 -1.73474072 -3.18810834
C 1.30623351 -0.12170141 -1.55843277
C 2.66119972 -0.67477108 -2.10200991
Pd 1.93947813 -2.59722962 0.34602450
O 0.63543672 3.53502628 2.25115947

O	1.03866635	4.06358924	0.06112274
C	0.28302782	4.05540932	1.16622891
C	-1.04672848	4.74216089	0.98335079
H	-0.53276254	-1.00828758	-0.80368891
H	-0.35702185	-1.11521824	-2.56440818
H	0.81883157	-3.20661946	-3.49623882
H	2.12611339	-3.79743079	-2.47683267
H	-2.02629061	-2.56635024	-2.16839139
H	-2.28892732	-4.27214947	-1.86221856
H	-1.21934475	-3.78358145	-3.19261765
H	1.11669256	-5.09795312	-0.53182639
H	0.47902529	-5.38264065	-2.17718113
H	-0.52180241	-5.72766247	-0.75952132
H	1.87411979	-1.22854939	-4.01472928
H	3.32843718	-2.11758661	-3.59791837
H	1.43967454	0.23206065	-0.53300208
H	0.99402466	0.74426788	-2.15289629
H	3.17437030	0.16021904	-2.59647906
H	1.98843299	3.58534509	0.16560312
H	-1.58965549	4.28927174	0.14743206
H	-0.88838173	5.79639697	0.73172643
H	-1.63677213	4.66554193	1.89707305
C	5.25534890	-0.35777489	0.65848584
C	4.17158016	-0.09756163	-0.17371143
C	5.79848867	-1.65546057	0.74200976
C	5.23166455	-2.68701612	0.00833677
C	4.13550993	-2.43625001	-0.85523678
C	3.61489209	-1.11842017	-0.98672452
I	3.07966290	-3.04208402	2.77719707
H	3.78101992	0.91716988	-0.23201463
H	6.64576818	-1.84921473	1.39041005
H	5.67847317	0.46612743	1.22581003
H	3.85189539	-3.21684566	-1.55084541
H	5.62196874	-3.69587775	0.08382092
Cs	2.70790158	1.54601060	3.28368469
O	3.19889184	2.87572642	0.42398148
C	4.29064005	3.43406289	0.90304353
O	5.03992001	2.85185596	1.74742602
C	4.62868604	4.82728710	0.40007671
H	3.74487129	5.47272329	0.44819601
H	4.93244787	4.77286360	-0.65247308
H	5.44227809	5.25833758	0.98507831

TS-14-15
Total free energy in solvent: -2111.957248
67

N	0.96833942	-1.65953603	-0.48252504
C	1.47395209	-0.54490980	-1.37768615
C	1.76879488	-2.95143170	-0.68746637
C	-0.55187037	-1.85963211	-0.55205722
C	-0.96146772	-2.55894600	0.75493880
N	-0.20934353	-2.19154119	1.85147048
O	-1.95308945	-3.31364748	0.82535560
C	-0.46807860	-2.76378258	3.10799926
C	-0.94301038	-1.99478297	4.17622673
C	-0.23827277	-4.12480757	3.35694382

C	-0.47931880	-4.69359025	4.60121859
C	-0.94508374	-3.89682536	5.64541361
C	-1.16987417	-2.53888557	5.43285146
F	-1.16434713	-0.64060285	3.99933611
F	-1.62029641	-1.74236784	6.46032285
F	-1.17967813	-4.44833871	6.87937494
F	-0.25295002	-6.03212158	4.81142017
F	0.25828639	-4.91344364	2.34460318
C	-1.28121459	-0.49603263	-0.58093014
C	-0.99842801	-2.69540276	-1.76333276
C	2.40241311	-3.04611138	-2.07930523
C	2.99365626	-0.62483254	-1.53770175
C	3.41605225	-1.88042245	-2.35137331
Pd	1.46033706	-1.13624236	1.51199842
O	-0.45381903	2.49852308	0.28352129
O	1.31219276	3.66866622	-0.58119562
C	0.11014636	3.14671290	-0.65530563
C	-0.60597643	3.37193819	-1.97479161
H	1.16815836	0.40500607	-0.93598311
H	0.98720200	-0.63279040	-2.35796850
H	1.10610879	-3.79146771	-0.47222415
H	2.55648375	-2.97671547	0.07068875
H	-0.90288645	0.21183722	0.15859129
H	-2.34248568	-0.67459957	-0.38236042
H	-1.20468282	-0.02428984	-1.56507793
H	-0.55141560	-3.69127807	-1.78559635
H	-0.77498830	-2.17732388	-2.70093705
H	-2.07982126	-2.83463287	-1.69024415
H	1.61859520	-3.04204093	-2.84558003
H	2.91364978	-4.01165570	-2.15853541
H	3.47129366	-0.62538553	-0.54852120
H	3.34704186	0.28520005	-2.03405771
H	3.32373637	-1.62607923	-3.41524096
H	1.81287504	3.70498461	0.58835207
H	0.04063750	3.08701029	-2.81107418
H	-0.82658795	4.43923173	-2.09246677
H	-1.53932795	2.80704530	-2.00605866
C	7.05133987	-2.87426422	-3.04009908
C	5.72128891	-2.47831416	-3.21696440
C	7.55476381	-3.08323362	-1.75178960
C	6.71946315	-2.89023807	-0.64555405
C	5.39081153	-2.49191175	-0.82603850
C	4.86914870	-2.28159810	-2.11637011
I	2.65164642	-0.55984187	3.81453663
H	5.33848619	-2.31497597	-4.22102684
H	8.58678922	-3.38708357	-1.60988964
H	7.69162665	-3.01472805	-3.90532852
H	4.77126758	-2.33699564	0.05224023
H	7.10131101	-3.04389874	0.35877880
Cs	-0.08786264	2.38531947	3.37561327
O	2.06261191	3.76009339	1.71642709
C	2.01643653	4.94194250	2.33955320
O	1.59785693	5.03647033	3.51921631
C	2.49683215	6.14155658	1.55164716
H	2.26747556	7.06283101	2.08822673
H	2.03339112	6.15272457	0.55911694

H	3.58074381	6.06973879	1.40272941

15
Total free energy in solvent: -2111.96636
67

N	0.72369920	-1.34146982	-0.70434605
C	1.02418098	-0.40940032	-1.86117678
C	1.53777450	-2.63569193	-0.81369810
C	-0.78519830	-1.59705462	-0.54118766
C	-1.00149927	-2.25285830	0.84010019
N	-0.04951563	-1.93765287	1.76798383
O	-2.00293383	-2.97797798	1.05942180
C	-0.21657681	-2.37825081	3.08863749
C	-1.20004624	-1.82647007	3.91155824
C	0.66779736	-3.27835452	3.69344402
C	0.60221912	-3.57504787	5.05267629
C	-0.36119824	-2.96715804	5.85332086
C	-1.26094637	-2.08130952	5.27153563
F	-2.07632539	-0.88537348	3.38826805
F	-2.15724338	-1.36066919	6.05606115
F	-0.40726933	-3.21207477	7.20652888
F	1.50256034	-4.44832000	5.61578085
F	1.66928587	-3.84726500	2.94305042
C	-1.54493821	-0.24822925	-0.53834815
C	-1.37609649	-2.51783674	-1.62515151
C	1.90966853	-3.01881112	-2.25112937
C	2.47524436	-0.53738837	-2.33012865
C	2.76330001	-1.92087338	-2.97163045
Pd	1.31484280	-0.52071594	1.21829102
O	2.65687068	0.85363773	0.43614781
O	1.39371985	2.75972930	0.61816127
C	2.46340279	2.13643657	0.31189421
C	3.63475390	2.90206720	-0.27078438
H	0.81448914	0.60729624	-1.53030489
H	0.34404964	-0.64429178	-2.69163775
H	0.96675747	-3.42646745	-0.32458565
H	2.44419853	-2.49832843	-0.22127319
H	-1.07065186	0.47406879	0.13326674
H	-2.56677939	-0.42869137	-0.19169242
H	-1.59791023	0.18287621	-1.54294963
H	-0.91536113	-3.50829727	-1.62138999
H	-1.28613455	-2.08016011	-2.62390921
H	-2.43498055	-2.66120399	-1.39864057
H	1.00378333	-3.21898061	-2.83301136
H	2.46842322	-3.96109135	-2.21237165
H	3.13306460	-0.34801798	-1.47764678
H	2.67766088	0.25701102	-3.05926645
H	2.42206337	-1.88730979	-4.01522124
H	0.38992712	2.88158300	1.74066510
H	4.49978031	2.80426195	0.39413831
H	3.37795563	3.95510241	-0.39069013
H	3.92100282	2.47710356	-1.23817358
C	6.22048610	-2.95480908	-4.26738984
C	4.86176069	-2.62367757	-4.21302479
C	6.99667873	-2.92090617	-3.10419989
C	6.40341645	-2.55197283	-1.89088821

C	5.04603410	-2.21785118	-1.84098570
C	4.25227719	-2.24999567	-3.00306474
I	2.07778604	0.27709721	3.72064234
H	4.26426904	-2.65375872	-5.12070340
H	8.05093458	-3.17679591	-3.14118409
H	6.66940364	-3.23612852	-5.21516844
H	4.61200131	-1.92166349	-0.89106062
H	6.99672350	-2.52008738	-0.98224193
Cs	-1.49747429	1.74053126	5.05645569
O	-0.24404632	3.10962541	2.52010768
C	-0.03338348	4.28632882	3.15544854
O	-0.68520188	4.53845149	4.18891091
C	1.02210429	5.20190122	2.59504976
H	0.96663621	5.24756191	1.50520968
H	2.01324698	4.80602586	2.84911150
H	0.91138897	6.19371940	3.03321794

16
Total free energy in solvent: -2112.0046808509
67

N	0.723214	-1.338548	-0.715705
C	1.029844	-0.409964	-1.873485
C	1.530835	-2.637136	-0.822906
C	-0.786381	-1.587510	-0.551245
C	-1.002590	-2.242288	0.830756
N	-0.043355	-1.936502	1.754635
O	-2.008539	-2.960084	1.053293
C	-0.202335	-2.384594	3.073868
C	-1.173656	-1.831356	3.910140
C	0.680414	-3.295751	3.664394
C	0.624803	-3.601882	5.022002
C	-0.325117	-2.991252	5.836568
C	-1.223174	-2.094579	5.269047
F	-2.048278	-0.880669	3.402205
F	-2.106333	-1.371324	6.065940
F	-0.359842	-3.246331	7.188269
F	1.522145	-4.487819	5.569738
F	1.667843	-3.870967	2.900051
C	-1.540496	-0.235790	-0.548223
C	-1.380755	-2.506746	-1.634545
C	1.905907	-3.020639	-2.259507
C	2.483445	-0.542498	-2.333411
C	2.767941	-1.926262	-2.975305
Pd	1.316344	-0.515350	1.203511
O	2.639651	0.875460	0.417495
O	1.354132	2.761916	0.637277
C	2.430934	2.157832	0.318396
C	3.598541	2.954535	-0.228110
H	0.820236	0.607788	-1.546189
H	0.353956	-0.646536	-2.706944
H	0.953545	-3.425208	-0.337172
H	2.435471	-2.506192	-0.226359
H	-1.067763	0.482263	0.128952
H	-2.565105	-0.413226	-0.208645
H	-1.585745	0.199743	-1.551251
H	-0.918936	-3.496769	-1.634253

H -1.294426 -2.066306 -2.632483
H -2.438636 -2.651669 -1.404222
H 1.001380 -3.215257 -2.845261
H 2.459735 -3.965760 -2.220415
H 3.136220 -0.357095 -1.476262
H 2.694808 0.252480 -3.059324
H 2.430259 -1.888349 -4.019767
H 0.355620 2.893257 1.762495
H 4.374470 3.025359 0.543776
H 3.275247 3.958624 -0.506421
H 4.042028 2.446370 -1.088779
C 6.223081 -2.975212 -4.262685
C 4.866318 -2.635788 -4.211928
C 6.995029 -2.950829 -3.096495
C 6.399402 -2.584161 -1.883645
C 5.044016 -2.242124 -1.837154
C 4.254702 -2.264051 -3.002447
I 2.101403 0.271562 3.704106
H 4.272130 -2.657102 -5.121985
H 8.048087 -3.211659 -3.131120
H 6.674142 -3.256161 -5.209570
H 4.608392 -1.949479 -0.886828
H 6.989180 -2.560016 -0.972571
Cs -1.447426 1.728179 5.089647
O -0.268153 3.122078 2.549201
C -0.043309 4.296305 3.185376
O -0.679045 4.547398 4.228828
C 1.002606 5.210110 2.604856
H 0.860169 5.330712 1.528011
H 1.993994 4.763557 2.744912
H 0.963690 6.174936 3.109701

TS-16-17
Total free energy in solvent: -2111.9772137287
67
N 0.54236956 -1.11223077 -0.56475149
C 0.94264781 -0.36806775 -1.83944269
C 1.60307377 -2.14650910 -0.17490749
C -0.89840918 -1.66718737 -0.63531858
C -1.34638594 -1.99925859 0.80023283
N -0.81110289 -1.17017103 1.74906525
O -2.18005867 -2.90161984 1.03848529
C -1.27939454 -1.23306298 3.07169371
C -2.49250616 -0.63946807 3.44859413
C -0.54085689 -1.84952490 4.08438859
C -0.95263288 -1.85052594 5.40996391
C -2.15862805 -1.24898529 5.75568856
C -2.93403591 -0.64531911 4.76818429
F -3.26120160 -0.01759315 2.49501563
F -4.12279259 -0.04427007 5.10782840
F -2.57593964 -1.24133253 7.06441107
F -0.15717506 -2.42677283 6.38097960
F 0.66305845 -2.46491522 3.77503257
C -1.86509873 -0.56488397 -1.13990400
C -1.02264812 -2.92006026 -1.51594334
C 2.24449745 -2.95383516 -1.32222195

C	2.40692667	-0.58447840	-2.22818901
C	2.65032487	-2.07625170	-2.55502219
Pd	0.51932540	0.19377430	1.12804362
O	2.01861676	1.41403850	0.26633933
O	1.64880722	3.52276587	1.06054893
C	2.36701401	2.63037874	0.38896252
C	3.63697022	3.11678450	-0.21925813
H	0.72146500	0.68873264	-1.69632756
H	0.31333819	-0.74424662	-2.65332369
H	1.14853005	-2.80037173	0.57339668
H	2.39613878	-1.57639020	0.31505324
H	-1.74549762	0.36141071	-0.56938117
H	-2.88950996	-0.92124664	-0.99730449
H	-1.72667341	-0.35596874	-2.20412768
H	-0.47058711	-3.76531480	-1.10251901
H	-0.68696566	-2.73177857	-2.54011739
H	-2.07521901	-3.21191959	-1.54059794
H	1.60010169	-3.77516572	-1.64587680
H	3.14362702	-3.41202493	-0.89351939
H	3.07807777	-0.22737582	-1.44156125
H	2.61073612	0.02278257	-3.11883826
H	1.96656186	-2.32997842	-3.37894739
H	0.82019517	3.13014359	1.53212690
H	4.47324259	2.56287971	0.23314313
H	3.75604317	4.18851018	-0.06580264
H	3.65197237	2.88203519	-1.28801532
C	5.56923815	-3.22785495	-4.75592059
C	4.27465611	-2.96245523	-4.29414554
C	6.67580983	-2.88427824	-3.97167611
C	6.47823830	-2.27461685	-2.72636109
C	5.18456247	-2.01174419	-2.26444460
C	4.06520369	-2.35432186	-3.04516931
I	5.76590887	-0.10883435	1.31012931
H	3.41855816	-3.23115033	-4.90867603
H	7.68133439	-3.08719796	-4.32723556
H	5.71082093	-3.70002209	-5.72362493
H	5.06729837	-1.53017580	-1.29585508
H	7.32523015	-1.99583892	-2.10785353
Cs	3.44480296	-0.94360278	4.11080699
O	-0.16145504	2.29306493	2.38299013
C	0.34488929	1.86666439	3.50379154
O	1.00935625	0.76770517	3.53087769
C	0.15644580	2.69366701	4.75127067
H	0.46234845	2.14304028	5.64208330
H	-0.89016793	2.99781552	4.84040222
H	0.75427346	3.60980155	4.67364621

17
Total free energy in solvent: -2111.9944668893
67

N	0.46005100	-1.06566571	-0.92341889
C	0.81855490	-0.30722195	-2.19510181
C	1.31796966	-2.33246248	-0.79427478
C	-1.06216091	-1.35395861	-0.83292557
C	-1.34240388	-1.83943482	0.60501666

N	-0.55057464	-1.23040520	1.54238377
O	-2.22576723	-2.68643705	0.86031280
C	-0.71249892	-1.48977162	2.90494784
C	-1.90336594	-1.23758140	3.60540368
C	0.37170800	-1.93234066	3.66816316
C	0.31953315	-2.05227823	5.04830376
C	-0.87487440	-1.80774993	5.71705634
C	-1.99321372	-1.41243559	4.98412587
F	-2.99515595	-0.74788514	2.93234663
F	-3.17116226	-1.14778932	5.64039073
F	-0.94523158	-1.93046300	7.08409037
F	1.47367859	-2.37249349	5.74799157
F	1.57770043	-2.20868415	3.03691570
C	-1.85387988	-0.04025744	-1.04295846
C	-1.55037025	-2.42043477	-1.82585106
C	1.76137918	-2.91491809	-2.13990988
C	2.29448020	-0.46368271	-2.57480483
C	2.67806371	-1.92485886	-2.93262793
Pd	0.86225745	0.03400601	0.85488283
O	2.42343069	1.18655343	0.03537874
O	1.97299966	3.38988669	0.45642927
C	2.74097716	2.42310969	-0.00957940
C	4.05140317	2.83254711	-0.58444550
H	0.57090980	0.74238874	-2.03219938
H	0.18350245	-0.68130989	-3.00697478
H	0.75116313	-3.05440307	-0.20324173
H	2.20500851	-2.06210237	-0.21635652
H	-1.48758674	0.76072662	-0.39250055
H	-2.90323549	-0.22500953	-0.79454207
H	-1.80835063	0.29312754	-2.08346061
H	-1.04792482	-3.37913420	-1.68546851
H	-1.43448104	-2.09582564	-2.86376785
H	-2.61172693	-2.59121900	-1.63113483
H	0.89106586	-3.18307570	-2.74783278
H	2.30380237	-3.84658082	-1.94354588
H	2.90400672	-0.09081521	-1.75165347
H	2.49651231	0.19207786	-3.43082370
H	2.46317659	-2.08264277	-3.99807139
H	1.13615450	3.11706675	1.01688290
H	4.84970075	2.50470119	0.10441890
H	4.09563690	3.91257151	-0.71820630
H	4.23151464	2.31464859	-1.53012515
C	6.16948825	-3.39709063	-3.47962549
C	4.82182309	-3.06290818	-3.64598017
C	6.88849610	-2.89063098	-2.39022985
C	6.25058575	-2.05135195	-1.47040798
C	4.89927452	-1.72425695	-1.63790847
C	4.16373850	-2.22230362	-2.72914535
I	6.55718663	0.72481939	1.75799882
H	4.27355620	-3.45208820	-4.50068566
H	7.93769019	-3.13865323	-2.26447958
H	6.65794660	-4.04256393	-4.20356955
H	4.44662772	-1.05790695	-0.91044632
H	6.79111420	-1.62827082	-0.62910381
Cs	3.84463097	-0.27819309	4.07843112
O	0.15790957	2.85576714	2.12004754

C	0.47643323	2.01968975	3.02068938
O	1.08955677	0.87813632	2.77330821
C	0.18921129	2.33771401	4.46956569
H	-0.74124590	2.90496476	4.54037173
H	0.98935519	2.97374669	4.86986186
H	0.12221883	1.42968820	5.07160293

18
Total free energy in solvent: -2080.5605954577
65

N	-0.06632852	-0.82854913	-0.70002168
C	-0.15110565	0.27310260	-1.74483170
C	0.68372819	-2.05133787	-1.25871131
C	-1.46292141	-1.19676090	-0.13821942
C	-1.22265987	-2.07406625	1.10745566
N	-0.05689143	-1.78339919	1.75577862
O	-2.05324127	-2.93501739	1.47793716
C	0.31968331	-2.48472304	2.91235714
C	-0.04509715	-2.04460814	4.18956017
C	1.12823140	-3.62418013	2.83274061
C	1.55921212	-4.30028940	3.96830670
C	1.17932165	-3.83923362	5.22605034
C	0.37669236	-2.70665966	5.33738411
F	-0.82037346	-0.91742395	4.32038010
F	0.01314072	-2.24645496	6.58278483
F	1.60347370	-4.49690145	6.35676870
F	2.35990132	-5.41491767	3.85803927
F	1.52719846	-4.08003788	1.59292805
C	-2.19556431	0.08991224	0.31034832
C	-2.34086300	-1.97411537	-1.13383594
C	0.61572252	-2.15126284	-2.78541545
C	1.12194477	0.33261992	-2.59133619
C	1.29322350	-0.92582198	-3.48530889
Pd	1.05715965	-0.28862947	1.01478360
O	2.17363970	-0.18049884	2.83598397
O	3.97931117	0.99023524	2.07663982
C	3.33834639	0.30734319	3.00777827
C	4.04797264	0.14027696	4.31368131
H	-0.30969873	1.21199255	-1.21788029
H	-1.01708707	0.06895318	-2.38641797
H	0.28680368	-2.94028054	-0.76639356
H	1.72626111	-1.96486385	-0.94740338
H	-1.54771458	0.73774239	0.90763233
H	-3.05747117	-0.19890381	0.91904245
H	-2.56027231	0.65913903	-0.54959643
H	-1.88219688	-2.91426246	-1.44759716
H	-2.58646307	-1.37561338	-2.01571523
H	-3.26815796	-2.23332606	-0.61745720
H	-0.42686169	-2.22904011	-3.10963993
H	1.11128241	-3.07983925	-3.08994110
H	1.97666077	0.45907208	-1.92191374
H	1.08400142	1.23399319	-3.21424755
H	0.74415834	-0.75507651	-4.42065111
H	3.37220578	1.16811286	1.21500852
H	4.02280072	1.08832352	4.86388802
H	5.09695799	-0.11182146	4.13922680

H	3.56218480	-0.62990806	4.91222826
C	4.35839389	-1.86639503	-5.58200754
C	3.05014742	-1.55660337	-5.19663554
C	5.39338237	-1.83056119	-4.64108903
C	5.10687204	-1.47875056	-3.31766622
C	3.79704950	-1.16617501	-2.93611669
C	2.74426584	-1.20431071	-3.86971507
H	2.25227566	-1.58531601	-5.93440171
H	6.41024603	-2.06941723	-4.93572292
H	4.56837350	-2.13123774	-6.61373362
H	3.60774963	-0.88281514	-1.90515778
H	5.90274737	-1.44346235	-2.57992585
O	2.26803390	1.31767218	0.32574375
C	1.78466600	2.55969641	0.07001107
O	0.57062336	2.79826021	-0.05001572
C	2.85602008	3.61796083	-0.07232804
H	3.52397645	3.36868362	-0.90423299
H	3.46835211	3.66653743	0.83526079
H	2.39305382	4.58837933	-0.25227480

19

Total free energy in solvent: -1849.5343240915

55

C	-4.50289973	3.21972082	1.08371749
N	-4.68359239	2.23596428	-0.06627571
C	-3.51614024	1.26778516	-0.10134402
C	-3.24122460	0.59441816	1.25251498
H	-2.63022385	1.83786184	-0.41306840
H	-3.74594285	0.51304706	-0.85076379
C	-4.32090903	2.52224803	2.43309945
H	-5.37124400	3.87808660	1.09595781
H	-3.60805507	3.81771333	0.87277384
N	-7.12647695	3.12170503	-0.52604253
C	-4.86040952	2.99480943	-1.41441740
C	-6.19556678	3.76350764	-1.30176768
C	-4.97516266	1.98373701	-2.58021236
C	-3.72816266	3.99432686	-1.71288156
O	-6.37630768	4.85630326	-1.88158409
C	-8.42478422	3.62187710	-0.38018987
C	-9.26812835	3.86839197	-1.47421381
C	-8.96250661	3.84084115	0.89476753
C	-10.26545965	4.28323779	1.08243184
C	-11.06940658	4.54599674	-0.02336628
C	-10.56487062	4.34145813	-1.30467179
F	-10.76191692	4.46802064	2.35480142
F	-11.36409437	4.57886327	-2.39956623
F	-8.82552738	3.60264173	-2.74799422
F	-8.18351431	3.58240120	2.00825173
H	-2.75992512	3.49378820	-1.80262619
H	-3.66053796	4.79034267	-0.96892607
H	-3.96033256	4.47627169	-2.66535388
H	-3.99437840	1.58661948	-2.85784818
H	-5.38765478	2.50486499	-3.44959039
H	-5.62752325	1.14285311	-2.33003099
C	-3.08981793	1.60402802	2.40176487
H	-5.22188341	1.94549513	2.68086663

H	-4.21668227	3.29792914	3.20213010
H	-2.33145189	-0.00883341	1.13870124
H	-4.06043936	-0.08999509	1.48726315
H	-2.97415205	1.07726675	3.35639365
H	-2.18322533	2.21078166	2.25857746
Pd	-6.58796886	1.32084846	0.19251317
O	-8.64493369	0.81686293	0.49808576
C	-9.11800178	-0.07314762	1.27890665
O	-8.36898159	-0.98476779	1.87176255
C	-10.58158101	-0.12096914	1.58241131
O	-6.16886905	-0.67334851	0.79928255
C	-5.66705981	-1.58885503	-0.06765372
O	-5.11446171	-1.27165996	-1.13543628
C	-5.82118068	-3.02066825	0.39497367
H	-7.35260364	-0.94452347	1.54433450
F	-12.35824423	4.99524920	0.15024823
H	-11.11808848	0.61163044	0.98064815
H	-10.73867934	0.09114734	2.64586591
H	-10.96843301	-1.12587173	1.38964752
H	-5.42826451	-3.69756680	-0.36383709
H	-6.87627244	-3.24986667	0.58203110
H	-5.28281479	-3.17208997	1.33719828

20 (Prod-chair + Pd-acetate)
Total free energy in solvent = product chair + Pd-acetate = -2080.502788
For xyz coordinates see xyz coordinates in the free substrate section above for $PhPipCONHC_6F_5$ and Pd-acetate.

SI structures

5s
Total free energy in solvent: -1849.520775
55

N	-6.299039	3.380943	-1.596642
C	-5.828093	1.945176	-1.764120
C	-5.109062	4.292924	-1.324939
C	-7.350267	3.500356	-0.446002
C	-7.907640	4.940290	-0.512592
N	-8.136648	5.386093	-1.802049
O	-8.121163	5.612734	0.517050
C	-8.410934	6.765036	-1.982753
C	-9.647115	7.317774	-1.624107
C	-7.459451	7.638247	-2.524129
C	-7.730111	8.988136	-2.725164
C	-8.970829	9.504735	-2.360617
C	-9.933716	8.665388	-1.806257
F	-10.621212	6.488996	-1.107596
F	-11.163542	9.169940	-1.453275
F	-9.245127	10.837230	-2.551769
F	-6.774353	9.817742	-3.261468
F	-6.210984	7.154223	-2.860132
C	-8.505377	2.498261	-0.674181
C	-6.753539	3.264679	0.955373
C	-4.035371	4.187506	-2.409783
C	-4.634243	1.762666	-2.715681
C	-3.484577	2.751894	-2.460077

Pd -7.357323 4.171622 -3.263940
O -6.797880 2.809179 -4.686852
O -5.445863 4.423440 -5.572164
O -8.682865 4.882051 -4.803951
O -10.527300 4.728152 -3.457269
C -6.027514 3.317239 -5.659750
C -9.934140 4.857423 -4.656897
C -5.927100 2.435836 -6.886412
C -10.877053 4.995578 -5.805993
H -6.673691 1.363016 -2.131491
H -5.558008 1.579709 -0.765060
H -4.676540 3.995687 -0.362145
H -5.487861 5.311436 -1.241901
H -8.862787 2.511777 -1.707854
H -9.337993 2.766767 -0.015172
H -8.197766 1.477321 -0.424869
H -6.021520 4.024560 1.231166
H -6.302106 2.272834 1.040835
H -7.565004 3.337419 1.683400
H -3.240117 4.903221 -2.165818
H -4.446637 4.477684 -3.384392
H -4.992952 1.867640 -3.740428
H -4.287199 0.727707 -2.596440
H -2.981797 2.517379 -1.507853
H -2.730456 2.656391 -3.250358
H -6.840597 2.539997 -7.482865
H -5.835575 1.383695 -6.604873
H -5.074104 2.743151 -7.493640
H -10.989771 6.058016 -6.054922
H -11.856804 4.594852 -5.547876
H -10.467294 4.488323 -6.681678
H -9.886224 4.765783 -2.689841

TS-5s-7s
Total free energy in solvent: -1849.46018
55
N -6.217769 3.190995 -1.039718
C -6.324894 1.699694 -1.302610
C -4.756008 3.448965 -0.721225
C -7.230452 3.775179 -0.033613
C -7.491360 5.260204 -0.393920
N -7.392469 5.553716 -1.730485
O -7.852503 6.067688 0.493282
C -7.820668 6.797446 -2.207611
C -9.163458 7.192448 -2.133003
C -6.947110 7.684733 -2.850265
C -7.389181 8.882328 -3.401372
C -8.729315 9.243654 -3.299712
C -9.624144 8.391044 -2.658084
F -10.085257 6.322340 -1.556860
F -10.954637 8.730430 -2.567650
F -9.169013 10.431430 -3.837291
F -6.501864 9.721420 -4.038369
F -5.607945 7.367223 -2.948342
C -8.612893 3.085888 -0.159346
C -6.732208 3.651453 1.416190

C -3.938614 3.223715 -2.021660
C -5.696125 1.391293 -2.678411
C -4.794434 2.558555 -3.134966
Pd -6.382004 4.182593 -2.867015
O -5.280772 3.587086 -5.584469
O -6.668025 5.151410 -4.725793
O -9.820655 2.810057 -3.345547
O -10.691434 4.866331 -3.868907
C -6.068732 4.611821 -5.731817
C -10.190713 3.634546 -4.192515
C -6.307663 5.141241 -7.114304
C -10.129491 3.448747 -5.679657
H -7.365552 1.391812 -1.268936
H -5.784767 1.187028 -0.495557
H -4.449823 2.751058 0.067272
H -4.644150 4.466233 -0.343756
H -8.964190 3.034209 -1.193477
H -9.328074 3.683892 0.414131
H -8.603570 2.081794 0.275679
H -5.786959 4.173684 1.584508
H -6.617700 2.600015 1.703322
H -7.473603 4.117408 2.068791
H -3.029756 2.640459 -1.807712
H -3.596866 4.197057 -2.392964
H -6.498998 1.280337 -3.415012
H -5.161729 0.430438 -2.644952
H -4.086769 2.184918 -3.890948
H -5.225781 3.257799 -4.375591
H -7.059354 4.513868 -7.609969
H -5.390305 5.088749 -7.706277
H -6.678394 6.166239 -7.073056
H -9.399406 4.160889 -6.079335
H -11.096513 3.674117 -6.136725
H -9.824899 2.429235 -5.915928
H -10.661327 5.058611 -2.903594

7s
Total free energy in solvent: -1849.487877
55
N -6.31003818 3.29882366 -1.04008320
C -6.56410077 1.83833612 -1.36059646
C -4.82425231 3.48351814 -0.77356011
C -7.23164997 3.92643253 0.02843066
C -7.39775621 5.44462787 -0.27888654
N -7.47307018 5.74179531 -1.61451988
O -7.57241501 6.25246112 0.66480173
C -7.66657948 7.06422147 -2.02186348
C -8.74363429 7.40144150 -2.85043744
C -6.76475405 8.10207956 -1.73061855
C -6.94091628 9.39183917 -2.21735207
C -8.02665731 9.68506550 -3.03939626
C -8.93199968 8.67914537 -3.36203791
F -9.68382715 6.42483550 -3.17697635
F -10.00884684 8.95336062 -4.17764726
F -8.19583736 10.95693687 -3.54029117
F -6.02900171 10.37935903 -1.91624252

F	-5.64056618	7.82678433	-0.98236205
C	-8.65849056	3.33193404	-0.04859062
C	-6.67271342	3.72641692	1.44733923
C	-4.06248073	3.19705653	-2.09869704
C	-5.79789812	1.48253571	-2.66330792
C	-5.08618382	2.75215094	-3.16805878
Pd	-6.47964057	4.32138853	-2.83057082
O	-6.67196193	3.45499905	-5.85059495
O	-6.66642884	5.40153482	-4.68613146
O	-9.58974244	2.44211686	-3.32665930
O	-9.69180045	4.16407453	-4.83813926
C	-6.82721668	4.79240977	-5.77672338
C	-9.72075263	2.83542072	-4.49274925
C	-7.23532515	5.46019438	-7.04167999
C	-9.89534946	1.95587798	-5.69558956
H	-7.63306659	1.70696827	-1.50608612
H	-6.24150672	1.22819100	-0.50513667
H	-4.52103954	2.80879948	0.03659683
H	-4.67375501	4.51301566	-0.44298200
H	-9.05656835	3.34261630	-1.06585932
H	-9.30571105	3.94913473	0.58218849
H	-8.69247463	2.30991274	0.34321884
H	-5.70810222	4.21706938	1.59317695
H	-6.57685594	2.66155002	1.68710624
H	-7.36829437	4.18581385	2.15233448
H	-3.30670909	2.40967091	-1.94213927
H	-3.52998415	4.09738143	-2.42239741
H	-6.50490888	1.09170756	-3.40407859
H	-5.06304143	0.68268213	-2.47135896
H	-4.59402797	2.60608626	-4.13729829
H	-6.41421025	3.10694777	-4.94469116
H	-8.31981646	5.33691925	-7.15337253
H	-6.74762072	4.99597967	-7.90103767
H	-7.00622271	6.52479483	-6.99449713
H	-9.01198313	2.03987851	-6.33821073
H	-10.76193308	2.27894513	-6.27960231
H	-10.02201919	0.92068562	-5.37902080
H	-9.60827778	4.77034706	-4.06324290

5
See structure 5

TS-5-5boat
Total free energy in solvent: -1620.4055577319

47			
C	1.83546483	0.19304098	1.36760372
N	1.53895931	-0.32118217	-0.02604134
C	2.33787174	-1.58027485	-0.24970232
C	2.24641361	-2.63035030	0.89417499
H	3.38231739	-1.27045474	-0.38726862
H	1.99538085	-2.02235433	-1.18501053
C	1.24553314	-0.71937545	2.44143413
H	1.41968791	1.19881758	1.45719163
H	2.92654549	0.25703932	1.47256886
Pd	-0.51924582	-0.72133076	-0.20687853
N	-0.50653627	1.24359349	-0.59636142

C	1.82118661	0.76947845	-1.09402343
C	0.68622942	1.80881754	-0.94903769
C	1.73036906	0.16747024	-2.51554967
C	3.18431422	1.45590588	-0.91043907
O	0.86586840	3.02077789	-1.20234240
C	-1.66356612	2.01393324	-0.40939063
C	-2.71357562	1.98448948	-1.33606722
C	-1.83932434	2.80104844	0.73659339
C	-2.99957486	3.53390302	0.95175880
C	-4.02841718	3.48243746	0.01371895
C	-3.88646776	2.70364046	-1.13117578
F	-3.14712795	4.29517153	2.08885637
F	-4.90204603	2.65785301	-2.05802033
F	-2.58524125	1.23335415	-2.48049823
F	-0.83893629	2.83493219	1.68638933
C	-2.19602283	-2.62096424	-0.08404868
C	-3.19614647	-3.72702548	-0.02756080
O	-0.92195122	-2.84116446	0.09920056
H	4.01226815	0.74816241	-1.01932928
H	3.26919316	1.96929061	0.04887246
H	3.27555200	2.22119906	-1.68465186
H	2.59721790	-0.46064803	-2.74247209
H	1.71498392	0.99142544	-3.23543532
H	0.81441190	-0.41637098	-2.64852183
O	-2.55460798	-1.38914005	-0.31733282
C	1.54215836	-2.23012854	2.22911168
H	0.16179623	-0.55533663	2.47556109
H	1.63645104	-0.38271973	3.40979424
H	3.27290821	-2.94549988	1.11419841
H	1.72883355	-3.50836524	0.49942215
H	0.59410916	-2.77246341	2.28051784
H	2.15542460	-2.59858336	3.05907891
H	-4.19975875	-3.33924866	-0.20608032
H	-3.15688804	-4.21481916	0.95227600
H	-2.95440688	-4.48458957	-0.78065656
F	-5.18334151	4.19722715	0.22195128

5boat
Total free energy in solvent: -1620.4119676898
47
C	1.699006	0.134319	1.421227
N	1.495479	-0.392551	0.011457
C	2.267047	-1.694947	-0.186405
C	2.603520	-2.406312	1.138846
H	3.193394	-1.471142	-0.724924
H	1.653230	-2.340843	-0.818187
C	1.132993	-0.828046	2.479067
H	1.214628	1.109864	1.486974
H	2.774698	0.274090	1.577539
Pd	-0.571062	-0.715748	-0.240361
N	-0.478635	1.252394	-0.607865
C	1.837230	0.684166	-1.051095
C	0.743393	1.770462	-0.932076
C	1.740981	0.079718	-2.471900
C	3.224735	1.309333	-0.842730
O	0.979017	2.974054	-1.178651

C -1.612588 2.061555 -0.452321
C -2.658156 2.031938 -1.384071
C -1.774786 2.885466 0.669340
C -2.916838 3.653621 0.855960
C -3.942220 3.600169 -0.085789
C -3.814223 2.784547 -1.206432
F -3.050653 4.450411 1.970197
F -4.826365 2.735167 -2.136695
F -2.543463 1.242462 -2.504261
F -0.780287 2.917882 1.625608
C -2.307106 -2.565147 -0.171360
C -3.337326 -3.643533 -0.129563
O -1.040054 -2.822568 0.021867
H 4.023070 0.567908 -0.952145
H 3.318791 1.803193 0.126208
H 3.358933 2.081601 -1.603606
H 2.538919 -0.645065 -2.658493
H 1.847794 0.891954 -3.197244
H 0.772767 -0.401098 -2.639911
O -2.627377 -1.322519 -0.396448
C 1.452360 -2.312524 2.154040
H 0.049411 -0.686692 2.562852
H 1.566868 -0.537769 3.444389
H 3.519253 -1.981358 1.571416
H 2.827507 -3.454019 0.907082
H 0.567285 -2.799902 1.732663
H 1.716900 -2.854370 3.068957
H -4.327391 -3.229007 -0.322583
H -3.325159 -4.130718 0.851351
H -3.104598 -4.408276 -0.878057
F -5.080926 4.347883 0.096135

TS-5boat-7
Total free energy in solvent: -1620.3635294592
47
C 2.148778 0.078261 1.483617
N 1.834659 -0.234514 0.031515
C 2.504624 -1.535166 -0.363109
C 2.161710 -2.629593 0.672688
H 3.587752 -1.372913 -0.458602
H 2.108382 -1.811117 -1.339014
C 1.413711 -0.967702 2.372565
H 1.799134 1.090403 1.692019
H 3.235423 0.045447 1.625839
Pd -0.169465 -0.678598 0.190421
N -0.386393 1.182398 -0.618586
C 2.032786 0.929788 -0.955469
C 0.781641 1.849652 -0.882322
C 2.075062 0.413903 -2.414997
C 3.312472 1.722673 -0.650825
O 0.878364 3.065775 -1.163754
C -1.603699 1.874230 -0.533956
C -2.667209 1.556337 -1.387985
C -1.848621 2.838437 0.454224
C -3.078891 3.473312 0.573819
C -4.117249 3.135053 -0.290819

C -3.910010 2.169002 -1.270851
F -3.285469 4.414598 1.556942
F -4.934387 1.828433 -2.125498
F -2.488707 0.612956 -2.375663
F -0.852351 3.144968 1.357924
C -2.361359 -2.501797 0.342766
C -3.738632 -3.075936 0.199141
O -1.353430 -3.303172 0.536224
H 4.201237 1.088543 -0.742025
H 3.293655 2.175274 0.343130
H 3.384738 2.540127 -1.371828
H 3.000723 -0.128559 -2.631061
H 2.033906 1.286462 -3.072575
H 1.212964 -0.220002 -2.643802
O -2.202602 -1.218404 0.302037
C 0.950821 -2.182163 1.513057
H 0.564191 -0.499410 2.881262
H 2.099192 -1.322153 3.157797
H 3.017663 -2.792965 1.346432
H 1.978082 -3.578625 0.159508
H -0.312001 -2.589882 0.820680
H 0.641428 -2.977148 2.205665
H -4.279758 -2.963967 1.146173
H -3.684505 -4.135338 -0.051686
H -4.292873 -2.527249 -0.565830
F -5.343452 3.749164 -0.172792

7
see structure 7

5’
Total free energy in solvent: -1976.180376
56
C 2.802391 0.591758 0.214561
N 1.941973 0.108935 -0.943325
C 2.466805 -1.218540 -1.448409
C 2.583755 -2.274634 -0.337671
H 3.453496 -1.040787 -1.900220
H 1.790847 -1.570494 -2.227819
C 2.869512 -0.431354 1.352645
H 2.390083 1.540739 0.560868
H 3.815261 0.768097 -0.168034
Pd -0.045778 -0.061568 -0.222190
N 0.014205 1.894833 -0.630797
C 1.847290 1.191631 -2.053559
C 0.998597 2.342058 -1.464050
C 1.085922 0.638270 -3.281232
C 3.217255 1.730784 -2.497636
O 1.182624 3.534639 -1.793543
C -0.876931 2.761418 0.017850
C -2.217941 2.853801 -0.375878
C -0.483897 3.507969 1.136529
C -1.375552 4.314242 1.832060
C -2.704734 4.381277 1.420121
C -3.127238 3.647700 0.315313
F -0.960596 5.031434 2.931214

F -3.596939 5.168750 2.107634
F -4.440131 3.714527 -0.089951
F -2.654210 2.141606 -1.468199
F 0.822259 3.421839 1.574267
C -1.763335 -1.697002 0.688590
C -2.800975 -2.662945 1.221342
C -2.190437 -3.395242 2.446322
C -3.105228 -3.696461 0.102374
C -4.082991 -1.909191 1.623556
O -0.579327 -2.108034 0.320615
H 3.843277 0.938015 -2.918638
H 3.753931 2.229323 -1.688754
H 3.041920 2.485057 -3.268045
H 1.699908 -0.058491 -3.860222
H 0.832398 1.480045 -3.932683
H 0.155278 0.143993 -2.986487
O -1.994391 -0.417161 0.565928
C 3.423297 -1.775095 0.850783
H 1.870826 -0.574122 1.785451
H 3.505915 -0.016641 2.144265
H 3.034976 -3.171579 -0.781323
H 1.582801 -2.553421 0.006032
H 3.415948 -2.519052 1.655931
H 4.472675 -1.647272 0.544341
H -1.267666 -3.911523 2.166865
H -2.907071 -4.132327 2.825089
H -1.964911 -2.690628 3.255046
H -3.543091 -3.206894 -0.775033
H -3.821613 -4.437574 0.474416
H -2.192589 -4.214711 -0.206369
H -4.521107 -1.387447 0.767453
H -3.876242 -1.163709 2.397645
H -4.820499 -2.618841 2.014962

TS-5'-7'
Total free energy in solvent: -1976.121733
56
C 3.268623 0.392996 0.046856
N 2.385442 0.227833 -1.175643
C 2.907742 -1.000029 -1.896771
C 2.510234 -2.258020 -1.090632
H 3.997374 -0.899427 -1.976717
H 2.495147 -1.040053 -2.900905
C 2.942840 -0.772689 1.022484
H 3.073994 1.367093 0.499615
H 4.314507 0.363623 -0.280709
Pd 0.587785 -0.253936 -0.246858
N 0.111644 1.673129 -0.716624
C 2.181924 1.490606 -2.030028
C 1.093927 2.379643 -1.359101
C 1.597821 1.125605 -3.417976
C 3.487695 2.279668 -2.208903
O 1.100561 3.618556 -1.539716
C -0.964803 2.312966 -0.091100
C -2.280213 1.933164 -0.392910
C -0.798981 3.260695 0.930538

C	-1.883867	3.825312	1.591532
C	-3.177615	3.422974	1.271374
C	-3.372462	2.464617	0.281495
F	-1.683859	4.757857	2.586151
F	-4.255056	3.964600	1.934545
F	-4.647108	2.038198	-0.024031
F	-2.510083	0.991825	-1.372565
F	0.472656	3.615362	1.326317
C	-1.378924	-1.900638	1.101743
C	-2.727157	-2.365961	1.642951
C	-2.503488	-2.962889	3.056473
C	-3.256046	-3.470952	0.688032
C	-3.722816	-1.191574	1.706009
O	-0.394489	-2.751252	1.043983
H	4.236673	1.682633	-2.741038
H	3.904934	2.615488	-1.256668
H	3.267910	3.177714	-2.790210
H	2.354159	0.693997	-4.080555
H	1.239980	2.049191	-3.882178
H	0.746676	0.443515	-3.330389
O	-1.227665	-0.683702	0.700489
C	2.077869	-1.878361	0.342267
H	2.372853	-0.366503	1.866162
H	3.867838	-1.188451	1.449221
H	3.326351	-2.995625	-1.102329
H	1.656952	-2.732050	-1.588974
H	0.657415	-2.164601	0.627744
H	2.164441	-2.763278	0.991203
H	-1.795154	-3.795557	3.020998
H	-3.457684	-3.327578	3.452820
H	-2.117127	-2.203885	3.746811
H	-3.422201	-3.073469	-0.319702
H	-4.211923	-3.849817	1.066762
H	-2.547412	-4.301825	0.625898
H	-3.873330	-0.738458	0.722091
H	-3.366083	-0.409654	2.384045
H	-4.688953	-1.551870	2.075842

7’

Total free energy in solvent: -1976.147466

59			
C	3.20884845	0.72199230	1.61624712
N	2.97374504	0.21083922	0.20149899
C	3.85331888	-1.00904765	0.00032430
C	3.35506341	-2.12711789	0.95466676
H	4.89829322	-0.72554804	0.18895541
H	3.76913580	-1.32711421	-1.03596582
C	2.67389199	-0.36241165	2.60046478
H	2.66729609	1.66392001	1.72317268
H	4.27954556	0.92053892	1.75080232
Pd	1.03007054	-0.47849663	0.41530428
N	0.57767066	1.33259446	-0.65643929
C	3.03781052	1.28751383	-0.89560191
C	1.69559119	2.08519251	-0.91832088
C	3.14629426	0.63799020	-2.29603702
C	4.21995386	2.24616562	-0.67727007

O	1.70859887	3.27957897	-1.29880461
C	-0.67387472	1.92523401	-0.60611527
C	-1.77567449	1.29550889	-1.20727915
C	-0.97407575	3.09358513	0.12447294
C	-2.26001592	3.60302885	0.18903539
C	-3.34926265	2.97559486	-0.43395539
C	-3.06842559	1.78914372	-1.12310218
F	-2.47579727	4.74740535	0.92888923
C	-4.70832627	3.57337887	-0.29830089
F	-4.06502225	1.05836007	-1.74544401
F	-1.57221264	0.11566923	-1.90994146
F	0.01566557	3.70967204	0.85941937
C	-1.41039529	-2.17695591	0.04495359
C	-2.81989932	-2.72199085	0.16200320
C	-2.72281779	-4.23543003	0.50257687
C	-3.53796524	-2.53495151	-1.20443297
C	-3.57937389	-1.96946738	1.27196102
O	-0.64735696	-2.76541742	-0.90188599
H	5.17196186	1.70350486	-0.68737981
H	4.13240149	2.80320896	0.25829895
H	4.22193232	2.98389790	-1.48203677
H	4.13837355	0.21287930	-2.47832332
H	2.97720621	1.42150217	-3.04009021
H	2.38097383	-0.13082850	-2.43709737
O	-0.94063545	-1.25786150	0.76732812
C	2.18012086	-1.56823205	1.76942386
H	1.85854168	0.05394925	3.20132770
H	3.46722513	-0.66977182	3.30223093
H	4.17024731	-2.45656866	1.62122763
H	3.05204871	-3.00640847	0.37556899
H	0.24706049	-2.32947543	-0.94422401
H	1.65776164	-2.32049665	2.36495495
H	-2.18972293	-4.78223216	-0.27966243
H	-3.73434282	-4.64537363	0.59063046
H	-2.20844386	-4.39573203	1.45733458
H	-3.60513120	-1.47819346	-1.47605401
H	-4.55406229	-2.93503274	-1.12445600
H	-3.01198380	-3.06677014	-2.00161150
H	-3.65365974	-0.90143928	1.04796790
H	-3.08348678	-2.07744213	2.24145660
H	-4.59300057	-2.37513111	1.35230142
F	-5.67498123	2.89482430	-1.02152224
F	-4.73711149	4.89628099	-0.73313228
F	-5.13958980	3.58798415	1.02968756

10s

See structure 10

TS-10s-11s

See structure TS-11-12

11s

See structure 12

*Pathway 10s-TS-10s-11s-11s is the same oxidative addition pathway was that shown in the main paper, however the energetics do not include the thermodynamic stability associated with the CsOAc-HOAc cluster that can form.

16s1
Total free energy in solvent: -2092.1427687787
66

O	0.62749171	1.13538207	-1.69329390
C	-0.19385274	1.10256135	-0.76567058
O	-0.18969735	0.16245008	0.21898650
C	-1.31934791	2.08131715	-0.57287606
H	-1.20824585	2.57074075	0.39918504
H	-2.27898316	1.55398265	-0.56873404
H	-1.30450568	2.82365786	-1.37137882
H	0.57169849	-0.47784724	0.18606535
N	4.87787912	1.46734851	-0.64981989
C	5.86150202	1.04267046	-1.72110230
C	3.76260154	2.33492690	-1.23219711
C	5.56754340	2.09401274	0.56824953
C	4.51965076	2.16848683	1.70092812
N	3.60862834	1.15600400	1.68685987
O	4.56382863	3.08938551	2.56082227
C	2.57519104	1.18009687	2.63848459
C	2.63512120	0.44189075	3.82655426
C	1.41688713	1.93541281	2.42642431
C	0.35502535	1.93602612	3.32004469
C	0.43793133	1.18233733	4.48524438
C	1.58327581	0.43328198	4.73650203
F	3.75326078	-0.30478577	4.10622980
F	1.66873186	-0.31049223	5.89629892
F	-0.60691497	1.18015934	5.38774273
F	-0.78244382	2.67818918	3.05334404
F	1.30060223	2.69332928	1.27241264
C	6.72358578	1.17576212	1.03617847
C	6.10515291	3.51292102	0.30032576
C	4.17062442	3.14755565	-2.47171672
C	5.16175548	0.88385528	-3.07285834
C	4.70643877	2.25615697	-3.64139569
Pd	3.82454179	-0.23793717	0.19806178
O	4.14959241	-1.53503169	-1.37279741
O	6.28588855	-2.06160064	-0.72026099
C	5.23548270	-2.29412635	-1.37674326
C	5.10624424	-3.52352348	-2.26028081
H	6.31413728	0.10614641	-1.39664197
H	6.65213772	1.80365443	-1.80311598
H	3.39633508	2.98865868	-0.43842964
H	2.93472715	1.67157296	-1.48528169
H	6.41739486	0.12572037	1.05180564
H	7.02284390	1.47753218	2.04499147
H	7.59347895	1.27194886	0.37803536
H	5.30328496	4.21605930	0.06247185
H	6.84373989	3.51710671	-0.50748714
H	6.57898834	3.87324447	1.21640952
H	4.92943619	3.89178658	-2.20543751
H	3.28759439	3.70840852	-2.80089602
H	4.31258911	0.20419521	-2.95254038
H	5.84950758	0.39972961	-3.77756823
H	5.59884213	2.75373525	-4.04862240
H	4.43991838	-4.23840442	-1.76268896
H	6.08435207	-3.98433290	-2.41366785

H	4.64972140	-3.26214131	-3.21962276
C	3.28786722	2.13127448	-7.20147187
C	4.15508858	2.31072944	-6.11734761
C	1.96868059	1.72220113	-6.98036114
C	1.52975330	1.49558747	-5.66988823
C	2.39744852	1.67319874	-4.58687937
C	3.72797800	2.08576830	-4.79706166
I	2.27350499	-2.20998737	1.28399876
H	5.18000917	2.62869520	-6.29470881
H	1.29105907	1.58040152	-7.81749150
H	3.64208811	2.31170075	-8.21283611
H	2.02415865	1.48485577	-3.58531999
H	0.50902513	1.17563569	-5.48295695

TS-16s1-17s1
Total free energy in solvent: -2092.1029789670
66

O	1.077293	-0.356295	-0.678075
C	-0.080841	-0.071940	-0.317403
O	-0.659983	-0.582793	0.791221
C	-0.979942	0.897465	-1.036119
H	-0.933433	1.860625	-0.517452
H	-2.015461	0.549443	-1.013801
H	-0.639596	1.028476	-2.065060
H	-0.046198	-1.213976	1.302225
N	4.949420	1.501713	-0.779778
C	5.920677	0.987588	-1.823361
C	3.984234	2.532389	-1.375046
C	5.664736	1.999367	0.489636
C	4.578777	2.183574	1.571899
N	3.530124	1.321949	1.456179
O	4.705302	3.059677	2.467298
C	2.478881	1.415087	2.387105
C	2.608529	0.977229	3.712710
C	1.258568	1.995509	2.030127
C	0.192875	2.093373	2.915366
C	0.347965	1.640800	4.220339
C	1.560464	1.085320	4.619012
F	3.796338	0.433918	4.133476
F	1.710917	0.650178	5.917348
F	-0.693725	1.747388	5.117611
F	-0.997813	2.668004	2.514515
F	1.097120	2.499397	0.747643
C	6.667706	0.925562	0.972759
C	6.394366	3.343195	0.285387
C	4.566192	3.284109	-2.580339
C	5.262293	0.913969	-3.201161
C	4.939699	2.326216	-3.763899
Pd	3.632259	-0.051578	-0.046179
O	3.827610	-1.447127	-1.528975
O	5.918187	-2.101901	-0.860148
C	4.844425	-2.300759	-1.488746
C	4.596998	-3.574859	-2.272574
H	6.256700	0.003799	-1.494337
H	6.784063	1.667090	-1.863041
H	3.692298	3.212707	-0.573078

H 3.078103 2.000736 -1.670571
H 6.234868 -0.078367 0.934390
H 6.946668 1.152660 2.006199
H 7.577356 0.932328 0.363327
H 5.702232 4.155497 0.050930
H 7.156397 3.274392 -0.496935
H 6.878516 3.604284 1.228925
H 5.453610 3.848327 -2.274234
H 3.825426 4.021003 -2.913337
H 4.362457 0.297698 -3.121691
H 5.935572 0.385466 -3.887038
H 5.857945 2.727266 -4.215687
H 3.875738 -4.190367 -1.722436
H 5.529849 -4.129657 -2.391709
H 4.157820 -3.346331 -3.248171
C 3.133420 2.970878 -7.086757
C 4.104903 2.960202 -6.079515
C 1.913475 2.314758 -6.890932
C 1.676682 1.646582 -5.683588
C 2.650015 1.637498 -4.679864
C 3.880306 2.297433 -4.860621
I 1.557145 -2.538202 2.520444
H 5.051441 3.470525 -6.238498
H 1.157886 2.318733 -7.671104
H 3.331111 3.486611 -8.022379
H 2.460982 1.097914 -3.757910
H 0.737366 1.126190 -5.523412

17s1
Total free energy in solvent: -2092.1285844155
66
O 1.82845858 -0.75528670 0.79875740
C 0.68289770 -1.07565562 0.34547233
O -0.18802718 -1.73384380 1.08014294
C 0.21368893 -0.70278379 -1.02913406
H 0.04320405 0.38072169 -1.04979921
H -0.71584180 -1.22027732 -1.26506389
H 1.00086351 -0.93728188 -1.75103280
H 0.05877592 -1.91267665 2.09171547
N 4.86485889 1.64042063 -0.85999795
C 5.79249219 0.97851629 -1.86421935
C 4.10598505 2.80841250 -1.49956947
C 5.61399632 2.05975473 0.42889157
C 4.53637325 2.43057132 1.47691481
N 3.39968986 1.68860494 1.36535448
O 4.75162727 3.32347936 2.33375203
C 2.37060324 1.79073041 2.31232954
C 2.57274995 1.54919762 3.67892040
C 1.06112513 2.08396419 1.91488119
C 0.00570527 2.13934303 2.81498294
C 0.24247341 1.91456722 4.16668548
C 1.53209235 1.61941647 4.59717239
F 3.82802241 1.20892452 4.12632389
F 1.76932042 1.38694904 5.93031322
F -0.79211993 1.98802378 5.06880282
F -1.26875790 2.43508013 2.37315244

F	0.79545148	2.30482363	0.56754820
C	6.41476278	0.85263260	0.97117796
C	6.55327127	3.26036969	0.22515546
C	4.83535691	3.43557262	-2.69472130
C	5.17462268	0.97819175	-3.26417398
C	5.08221680	2.40987401	-3.85523515
Pd	3.34955625	0.33435180	-0.14289926
O	3.26014132	-1.04839097	-1.70135584
O	5.24480966	-2.05910372	-1.15830391
C	4.14358910	-2.04272427	-1.76268475
C	3.70535928	-3.19567592	-2.64929384
H	5.96905796	-0.04011073	-1.52051755
H	6.74407061	1.52623935	-1.87591711
H	3.91056908	3.54418436	-0.71754122
H	3.13396282	2.43117313	-1.82204271
H	5.81121823	-0.05899645	0.97593015
H	6.72220144	1.07382601	1.99787796
H	7.31514840	0.66848361	0.37607443
H	6.01724378	4.15380921	-0.10411534
H	7.35479704	3.03241412	-0.48393431
H	6.99517644	3.50080241	1.19478222
H	5.79450580	3.85497451	-2.37300527
H	4.23281887	4.27682296	-3.05726030
H	4.19135127	0.50414649	-3.20192459
H	5.78257437	0.34175044	-3.91868780
H	6.05997305	2.65794345	-4.29089130
H	2.89875852	-3.74790020	-2.15246788
H	4.54451566	-3.87102945	-2.82503898
H	3.31274920	-2.82139579	-3.59982509
C	3.48681794	3.31268542	-7.22236694
C	4.41403726	3.15248500	-6.18687433
C	2.17457750	2.85412225	-7.06472965
C	1.80334596	2.23192727	-5.86695104
C	2.73419891	2.06957069	-4.83539078
C	4.05669497	2.53175688	-4.97669208
I	0.23954779	-2.23215953	4.31243745
H	5.43224003	3.51098678	-6.31639535
H	1.45137911	2.97527758	-7.86538829
H	3.78990052	3.79192186	-8.14882026
H	2.42548460	1.56981043	-3.92301044
H	0.78904446	1.86756365	-5.73485779

16s2
Total free energy in solvent: -1863.0367009419
58

N	0.718876	-1.268150	-0.769498
C	1.012526	-0.383416	-1.962669
C	1.471677	-2.594095	-0.860981
C	-0.792041	-1.457160	-0.543265
C	-0.971479	-2.095173	0.855878
N	-0.007426	-1.750764	1.752618
O	-1.946376	-2.859228	1.090655
C	-0.066588	-2.279407	3.050984
C	-1.045328	-1.889826	3.974436
C	0.891863	-3.197634	3.494490
C	0.895147	-3.690970	4.793541

C -0.089784 -3.285709 5.687285
C -1.063929 -2.382665 5.273481
F -1.999464 -0.971469 3.603088
F -2.036974 -1.974438 6.165167
F -0.102757 -3.780559 6.977147
F 1.857696 -4.596057 5.198083
F 1.876762 -3.624740 2.625456
C -1.494943 -0.078587 -0.544750
C -1.455134 -2.374690 -1.589644
C 1.817443 -2.991387 -2.301130
C 2.465740 -0.535518 -2.420519
C 2.756555 -1.948225 -2.996364
Pd 1.373995 -0.379417 1.115724
O 2.745047 0.964077 0.343727
O 1.152664 2.466006 -0.349574
C 2.335849 2.165576 -0.036706
C 3.447990 3.201558 -0.058875
H 0.813370 0.645279 -1.661931
H 0.334795 -0.652660 -2.787071
H 0.866675 -3.359911 -0.372477
H 2.381505 -2.500673 -0.265733
H -0.937988 0.656511 0.042467
H -2.494166 -0.198527 -0.114309
H -1.604389 0.307547 -1.564096
H -1.017861 -3.376551 -1.596963
H -1.397304 -1.945801 -2.595177
H -2.505406 -2.491699 -1.313218
H 0.894927 -3.087152 -2.884280
H 2.291445 -3.980113 -2.291159
H 3.112688 -0.303870 -1.570005
H 2.675453 0.227105 -3.181198
H 2.488526 -1.946194 -4.062512
H 3.721518 3.436914 0.976453
H 3.109678 4.109299 -0.563011
H 4.339842 2.800612 -0.550707
C 6.189815 -3.340631 -3.980679
C 4.856426 -2.920551 -4.032353
C 6.924491 -3.191766 -2.799208
C 6.314650 -2.615391 -1.678867
C 4.982053 -2.192393 -1.734848
C 4.227198 -2.344188 -2.913844
I 2.023260 0.571052 3.579630
H 4.290265 -3.037457 -4.953631
H 7.960126 -3.515495 -2.752673
H 6.652770 -3.779788 -4.860120
H 4.540110 -1.733213 -0.856686
H 6.875674 -2.489111 -0.757763

TS-16s2-17s2
Total free energy in solvent: -1863.0097706801
58
N 0.559196 -1.387280 -1.028508
C 0.889326 -0.585231 -2.263715
C 1.387935 -2.674422 -0.954918
C -0.939773 -1.624157 -0.820978
C -1.111693 -2.098588 0.645668

N -0.202602 -1.548377 1.492526
O -2.042118 -2.881896 0.970147
C -0.144432 -1.919195 2.844898
C -0.706723 -1.118005 3.846517
C 0.542124 -3.070189 3.255241
C 0.696102 -3.389546 4.597452
C 0.145166 -2.562669 5.570942
C -0.561564 -1.426165 5.195179
F -1.416189 0.010833 3.501448
F -1.127458 -0.620081 6.163544
F 0.287726 -2.876334 6.907812
F 1.386791 -4.521655 4.975088
F 1.068800 -3.915103 2.306616
C -1.717666 -0.297937 -0.976823
C -1.523441 -2.678477 -1.779353
C 1.850941 -3.166604 -2.332129
C 2.380363 -0.691612 -2.598101
C 2.766598 -2.125760 -3.060570
Pd 1.124467 -0.233141 0.718428
O 2.299855 1.345848 -0.052418
O 1.416222 1.742718 1.968277
C 2.238527 2.077008 1.043249
C 3.184523 3.230455 1.189890
H 0.624647 0.454554 -2.064224
H 0.279869 -0.942638 -3.107255
H 0.792184 -3.428281 -0.439087
H 2.248898 -2.476266 -0.312772
H -1.264070 0.491188 -0.367955
H -2.743108 -0.457517 -0.631088
H -1.755818 0.026412 -2.022300
H -1.014713 -3.639486 -1.691161
H -1.478136 -2.340331 -2.821147
H -2.566200 -2.845153 -1.502674
H 0.982375 -3.391201 -2.963806
H 2.392071 -4.110920 -2.197968
H 2.952233 -0.384383 -1.718211
H 2.619083 0.031871 -3.388432
H 2.543410 -2.202816 -4.134787
H 4.167776 2.828813 1.462325
H 2.845243 3.904085 1.980117
H 3.286594 3.768931 0.243501
C 6.344704 -3.251154 -3.860804
C 4.986226 -2.936840 -3.986005
C 6.996417 -3.060506 -2.637318
C 6.279996 -2.553640 -1.547524
C 4.923965 -2.235123 -1.674610
C 4.254371 -2.424723 -2.898337
I 3.879192 -1.292446 2.227652
H 4.485699 -3.087376 -4.939631
H 8.050409 -3.303519 -2.534844
H 6.889884 -3.642259 -4.715314
H 4.408665 -1.843744 -0.801523
H 6.763404 -2.401474 -0.588069

17s2
Total free energy in solvent: -1863.0141981195

58
N 0.532378 -1.404636 -1.037942
C 0.879148 -0.627833 -2.289243
C 1.418722 -2.650658 -0.893175
C -0.967632 -1.708778 -0.887326
C -1.174531 -2.132435 0.589822
N -0.353472 -1.462166 1.437484
O -2.055767 -2.967846 0.915539
C -0.266746 -1.750803 2.806700
C -0.717235 -0.840957 3.770976
C 0.379842 -2.906923 3.265963
C 0.583441 -3.141644 4.618698
C 0.140472 -2.211030 5.553509
C -0.512618 -1.059052 5.129351
F -1.383324 0.298855 3.377901
F -0.968753 -0.147331 6.060803
F 0.334352 -2.437112 6.901077
F 1.221505 -4.285628 5.044943
F 0.823903 -3.835759 2.353259
C -1.801044 -0.428623 -1.130629
C -1.456287 -2.826409 -1.822411
C 1.910604 -3.198152 -2.239130
C 2.377952 -0.722889 -2.585258
C 2.764586 -2.155391 -3.041315
Pd 0.985892 -0.185888 0.631262
O 2.281518 1.426337 0.014343
O 1.417995 1.366254 2.069169
C 2.264790 1.896809 1.235471
C 3.229815 2.948168 1.668743
H 0.582214 0.409350 -2.129383
H 0.298530 -1.026625 -3.135010
H 0.850430 -3.397749 -0.336538
H 2.264854 -2.374957 -0.256619
H -1.434963 0.400414 -0.517342
H -2.838565 -0.634820 -0.848066
H -1.787231 -0.132248 -2.184726
H -0.902335 -3.756112 -1.676753
H -1.390516 -2.526120 -2.873661
H -2.500411 -3.036489 -1.576306
H 1.059173 -3.517227 -2.852333
H 2.507989 -4.095103 -2.040849
H 2.935166 -0.424609 -1.691429
H 2.635902 0.002274 -3.366990
H 2.478348 -2.253232 -4.098770
H 4.161497 2.444996 1.958974
H 2.841368 3.489759 2.533457
H 3.446787 3.634630 0.846143
C 6.335104 -3.131202 -4.041095
C 4.965834 -2.847762 -4.100944
C 7.025107 -2.994206 -2.831815
C 6.337480 -2.567955 -1.688819
C 4.970541 -2.278351 -1.749950
C 4.263207 -2.419860 -2.959462
I 4.206091 -1.520131 2.121769
H 4.433148 -2.960676 -5.043023
H 8.086727 -3.217622 -2.780349

H 6.858311 -3.459262 -4.935042
H 4.479974 -1.951099 -0.835066
H 6.847006 -2.457987 -0.736426

5 – B3LYP functional and LANL2DZ basis set and ECP
Total gas phase energy: -1620.00912395426
47
Step 2
N 0.70989569 -1.18361332 0.73335963
C 0.53926191 -2.68785824 0.77771942
C 2.06741065 -0.83947753 0.13691539
C 0.52441205 -0.51504847 2.12198351
C 0.36972715 0.99976174 1.85882511
N -0.28666159 1.26704857 0.69161656
O 0.75631335 1.85679941 2.68369760
C -0.52649185 2.57494241 0.24757491
C -1.82219927 3.10631927 0.22119425
C 0.50699483 3.37654799 -0.25575544
C 0.27066090 4.65134266 -0.75366834
C -1.02960483 5.15124059 -0.77180759
C -2.07862295 4.37536147 -0.28714700
F -2.87024527 2.36073901 0.70655140
F -3.36204407 4.87011818 -0.30593638
F -1.27582609 6.40751987 -1.27213047
F 1.30597450 5.41370993 -1.24492402
F 1.79308826 2.87650694 -0.27884838
C -0.78560410 -1.00578165 2.78371210
C 1.70429124 -0.75690132 3.07885049
C 2.25460235 -1.44535433 -1.25819863
C 0.75597114 -3.35487819 -0.58891896
C 2.11109883 -2.97591536 -1.21140012
Pd -0.75573741 -0.27099129 -0.49508599
O -2.18589236 0.51696708 -1.86716906
O -1.60365500 -1.62315439 -2.00681152
C -2.32077525 -0.63790601 -2.46447765
C -3.25279004 -0.80516687 -3.61738499
H -0.46631216 -2.89643899 1.14264185
H 1.26130131 -3.08522547 1.50563075
H 2.83880480 -1.23989204 0.80647111
H 2.15298485 0.24867593 0.11704288
H -1.62786721 -0.96686564 2.08620949
H -1.01253321 -0.34519633 3.62594503
H -0.68505013 -2.02320508 3.17416528
H 2.62619836 -0.28552982 2.73393056
H 1.87799307 -1.82493805 3.24302542
H 1.45853897 -0.29372333 4.03726933
H 3.24751147 -1.15489095 -1.62345665
H 1.51874372 -1.01948174 -1.95277906
H -0.05487324 -3.07390550 -1.26812447
H 0.68983613 -4.44022443 -0.43921975
H 2.93284078 -3.40075045 -0.61491949
H 2.19574262 -3.40049469 -2.21831801
H -4.26777663 -0.52351729 -3.31818198
H -3.24322699 -1.83888635 -3.96526425
H -2.95641129 -0.13838694 -4.43440485

TS-5-7 – B3LYP functional and LANL2DZ basis set and ECP
Total gas phase energy: -1619.94800647991
47
Step 63

N	0.95888895	-1.31285784	1.00424611
C	0.50619505	-2.74426344	1.18144970
C	2.31910217	-1.30536395	0.33474174
C	0.85852937	-0.42277410	2.26382125
C	0.54119866	1.03290505	1.82084880
N	-0.25124181	1.11502419	0.70634471
O	0.88863308	1.99636600	2.54089229
C	-0.70494063	2.35891704	0.24166907
C	-2.07745793	2.62149026	0.14631748
C	0.16655104	3.35349895	-0.22415143
C	-0.30032867	4.56026968	-0.73145154
C	-1.67085068	4.79265819	-0.81029029
C	-2.56145407	3.81592851	-0.37545902
F	-2.98202493	1.67485781	0.57429483
F	-3.91871668	4.03827968	-0.46136436
F	-2.14184354	5.98075667	-1.32082210
F	0.58363234	5.51713782	-1.17924549
F	1.52496847	3.12000787	-0.21443473
C	-0.34326602	-0.83833255	3.14789748
C	2.14516236	-0.46559997	3.10329300
C	2.17297912	-1.87302707	-1.10541802
C	0.41860514	-3.43982988	-0.20092473
C	0.75152851	-2.44732959	-1.32927548
Pd	-0.20927885	-0.52628740	-0.50566175
O	-1.39233846	0.33336505	-2.01633245
O	-1.15638726	-1.64554088	-3.07795525
C	-1.65909285	-0.44981267	-3.00887940
C	-2.56145797	0.03580566	-4.10345043
H	-0.47046838	-2.72581902	1.65780034
H	1.20965914	-3.25433820	1.85415798
H	3.01352138	-1.90188095	0.93957232
H	2.67603640	-0.27407527	0.31788748
H	-1.27404386	-0.86724165	2.57453664
H	-0.45305520	-0.07736672	3.92555949
H	-0.17762655	-1.80140418	3.64029882
H	3.01658600	-0.10345214	2.55410657
H	2.34476727	-1.47842677	3.47049938
H	2.01371507	0.20081935	3.95827563
H	2.91702924	-2.66947495	-1.26118883
H	2.38848355	-1.08845437	-1.83837087
H	-0.58202833	-3.86224734	-0.34052481
H	1.12679378	-4.28205198	-0.23846629
H	0.76707060	-2.99752488	-2.28272868
H	-0.36793260	-1.83723267	-2.09204374
H	-3.51136506	0.36980228	-3.67478289
H	-2.73670589	-0.75456314	-4.83236600
H	-2.10592749	0.90023753	-4.59839554

7 – B3LYP functional and LANL2DZ basis set and ECP
Total gas phase
energy: -1619.96330568397
47

Step 6

N	1.13323737	-1.35875665	0.97185186
C	0.91046068	-2.85833772	1.05814787
C	2.53639865	-1.13337279	0.41834831
C	0.78820771	-0.54329338	2.23235604
C	0.39277625	0.91410976	1.82584627
N	-0.25968464	1.01598450	0.62724102
O	0.57348332	1.83921132	2.65431331
C	-0.63851610	2.25807175	0.12122116
C	-1.91156789	2.42422982	-0.44727456
C	0.23094187	3.35949030	-0.00270360
C	-0.15880116	4.54643264	-0.61359266
C	-1.42984345	4.66712450	-1.16993385
C	-2.30331763	3.58776204	-1.09445274
F	-2.81986400	1.37344937	-0.40619119
F	-3.55590495	3.66029503	-1.67617645
F	-1.80761344	5.82987713	-1.80551535
F	0.72942212	5.59480282	-0.71663777
F	1.53737647	3.24630952	0.42205470
C	-0.46591007	-1.11765625	2.93529662
C	1.96147660	-0.51596489	3.22582331
C	2.55864414	-1.68001894	-1.04243956
C	0.89551443	-3.43210552	-0.38459321
C	1.16967388	-2.27912344	-1.36094650
Pd	0.04387079	-0.67500461	-0.64819213
O	-0.99212031	0.02250707	-2.39385417
O	-2.74200912	-1.35446718	-1.93258761
C	-2.17549534	-0.34153081	-2.61953072
C	-3.06216235	0.32466242	-3.61285207
H	-0.04262339	-3.03908023	1.54851154
H	1.70441411	-3.29582724	1.67957546
H	3.26336309	-1.63917917	1.06579375
H	2.73189899	-0.05975056	0.44747644
H	-1.29658300	-1.24214165	2.23407947
H	-0.77562612	-0.39693293	3.69751162
H	-0.25865982	-2.06754002	3.43826154
H	2.84721665	-0.03059568	2.81040660
H	2.22318803	-1.52818140	3.55540297
H	1.65772593	0.07290444	4.09326785
H	3.34690137	-2.44365700	-1.15282899
H	2.80137728	-0.86859224	-1.73694232
H	-0.07482012	-3.89826486	-0.58843377
H	1.65597118	-4.22467588	-0.49014438
H	1.05136903	-2.55552477	-2.41153260
H	-2.11785137	-1.68190645	-1.22815430
H	-3.55863828	1.16616637	-3.11192132
H	-3.82797273	-0.36135945	-3.97622618
H	-2.46932666	0.71945493	-4.43912971

5 – ωB97X-d functional and LANL2DZ basis set and ECP
Total gas phase energy: -1619.56293469966
47
Step 14

N	0.70689494	-1.18069031	0.74235944
C	0.53725657	-2.67307198	0.78349238
C	2.05899833	-0.84014255	0.16247147

C	0.52218022	-0.52236038	2.11858764
C	0.37886339	0.98861926	1.86063221
N	-0.26003802	1.25071184	0.69039553
O	0.75608844	1.84028563	2.68555993
C	-0.51366472	2.55158911	0.24730015
C	-1.80488796	3.07769909	0.26172573
C	0.49741996	3.33506859	-0.30924290
C	0.24208721	4.59332905	-0.82875907
C	-1.05475540	5.09032991	-0.80999362
C	-2.08090216	4.33040327	-0.26612537
F	-2.82545773	2.34396077	0.79924664
F	-3.35829718	4.82174329	-0.25166561
F	-1.32101604	6.32602687	-1.33155300
F	1.25310087	5.33830213	-1.37414285
F	1.77434895	2.83518499	-0.36517374
C	-0.79433186	-0.99418487	2.76735366
C	1.69000861	-0.77743645	3.07637148
C	2.23846916	-1.42031314	-1.23858229
C	0.74933817	-3.33100631	-0.58264686
C	2.09610618	-2.94614365	-1.20794033
Pd	-0.72681455	-0.26715106	-0.48578374
O	-2.12244461	0.54169489	-1.85386992
O	-1.57593816	-1.59642536	-1.99523764
C	-2.27185818	-0.60427149	-2.45070476
C	-3.20861069	-0.74909465	-3.59737228
H	-0.46781319	-2.88941472	1.14570881
H	1.26170839	-3.07283606	1.50700209
H	2.82700894	-1.26261977	0.82204924
H	2.15564621	0.24711543	0.16228203
H	-1.62620432	-0.94947738	2.05762282
H	-1.02376927	-0.32242596	3.59890437
H	-0.70955408	-2.00892923	3.16587346
H	2.61574131	-0.30963797	2.73864826
H	1.85269985	-1.84871562	3.22851843
H	1.44078246	-0.32340907	4.03740260
H	3.22672692	-1.12339643	-1.60618727
H	1.49783226	-0.98779859	-1.92355860
H	-0.06326236	-3.04894748	-1.25911677
H	0.68882817	-4.41617105	-0.44165629
H	2.92198465	-3.37751640	-0.62399856
H	2.16611150	-3.35699794	-2.21991653
H	-4.22625339	-0.52589665	-3.26286933
H	-3.16693967	-1.76108523	-3.99818426
H	-2.95342011	-0.02449534	-4.37522780

TS-5-7 – ωB97X-d functional and LANL2DZ basis set and ECP
Total gas phase energy: -1619.50293702403
47
Step 45

N	0.96466126	-1.29727256	0.99641867
C	0.53271843	-2.72621344	1.14823685
C	2.32602747	-1.25881580	0.35861761
C	0.82939042	-0.43664013	2.25009557
C	0.54888934	1.02165747	1.81543194
N	-0.22670883	1.10962748	0.69790492
O	0.90401787	1.97413381	2.53539060

C	-0.66313451	2.34974125	0.22519137
C	-2.02675770	2.62087988	0.11814460
C	0.22335578	3.31952978	-0.24575380
C	-0.22490118	4.52224733	-0.76878993
C	-1.58836724	4.76810342	-0.85825770
C	-2.49218107	3.81108559	-0.41924678
F	-2.93620058	1.68986374	0.54629991
F	-3.83874542	4.04727787	-0.51721690
F	-2.04010656	5.94972812	-1.38295633
F	0.66744741	5.45947841	-1.21955539
F	1.56976956	3.06304932	-0.22465712
C	-0.41616118	-0.83786443	3.06704406
C	2.07202396	-0.51657272	3.13893485
C	2.20155227	-1.77449493	-1.09726034
C	0.49943842	-3.40300905	-0.23931627
C	0.79428219	-2.37317652	-1.33836475
Pd	-0.17831949	-0.51203937	-0.51065296
O	-1.35648769	0.34195066	-2.00676582
O	-1.23378330	-1.67523271	-2.98320866
C	-1.70345128	-0.47250917	-2.94032734
C	-2.68468359	-0.02117436	-3.97199524
H	-0.46311003	-2.72962278	1.58356797
H	1.21771625	-3.23297440	1.84087013
H	3.00953816	-1.87590857	0.95362411
H	2.68174910	-0.22686948	0.38119283
H	-1.31363075	-0.85119628	2.44156317
H	-0.55996532	-0.07897996	3.84041165
H	-0.28814719	-1.80473879	3.56180285
H	2.97098161	-0.15511526	2.63619120
H	2.23613834	-1.54087268	3.49008584
H	1.91164353	0.13425245	4.00053144
H	2.95872882	-2.55028114	-1.27868689
H	2.40070703	-0.96258726	-1.80340995
H	-0.47887319	-3.86534005	-0.39889674
H	1.24834608	-4.20648804	-0.28556117
H	0.83053065	-2.89343009	-2.30667534
H	-0.37820502	-1.83041398	-2.05336611
H	-3.66479958	0.10317382	-3.50103659
H	-2.76016166	-0.75493623	-4.77261579
H	-2.38296858	0.95054378	-4.36845124

7 – ωB97X-d functional and LANL2DZ basis set and ECP
energy: -1619.51883326169
47
Step 15

N	1.14965889	-1.36694151	0.98086254
C	0.78434459	-2.82331630	1.09181045
C	2.56204295	-1.27934587	0.45302196
C	0.86354220	-0.50681171	2.20889386
C	0.52981603	0.95389809	1.77655269
N	-0.14516640	1.03947249	0.59886108
O	0.75480132	1.88665963	2.57579885
C	-0.62036612	2.24746706	0.10895214
C	-1.93006382	2.30953713	-0.38038500
C	0.15985401	3.39687050	-0.07544735
C	-0.35141066	4.54248323	-0.67012604

C	-1.65567314	4.56469685	-1.14481535
C	-2.44361969	3.43219738	-1.00436297
F	-2.74671207	1.20073226	-0.27576528
F	-3.72758789	3.41657963	-1.49898088
F	-2.15672297	5.68480881	-1.75550739
F	0.44452799	5.64559272	-0.83525210
F	1.48269797	3.38219046	0.27757222
C	-0.42111567	-0.98301507	2.91982553
C	2.02974701	-0.52377849	3.19973641
C	2.55588213	-1.82030342	-1.00296658
C	0.78278346	-3.43088072	-0.33094307
C	1.12849893	-2.31246752	-1.32390514
Pd	0.12415331	-0.63942531	-0.64144479
O	-0.88274338	0.14306874	-2.35301460
O	-2.54358402	-1.38423018	-2.19874714
C	-2.02584262	-0.24597860	-2.68095601
C	-2.91660609	0.53062427	-3.57826875
H	-0.20908267	-2.89194634	1.52635510
H	1.49410765	-3.32115232	1.76666238
H	3.22335236	-1.85808595	1.10911384
H	2.87049025	-0.23246138	0.48510355
H	-1.25327277	-1.06075613	2.21368955
H	-0.68149500	-0.22942933	3.66741574
H	-0.27716889	-1.93552091	3.43822610
H	2.94605971	-0.11543735	2.76898149
H	2.22048896	-1.54047551	3.56077011
H	1.76743109	0.11418123	4.04503522
H	3.28519789	-2.63762506	-1.11297432
H	2.85362682	-1.02762859	-1.69649916
H	-0.19919050	-3.86430509	-0.54794053
H	1.51648523	-4.24889317	-0.40329436
H	1.01521439	-2.61534332	-2.36759194
H	-1.93039579	-1.80705967	-1.55094680
H	-3.54811490	1.17184907	-2.95311703
H	-3.56129933	-0.12648192	-4.16095312
H	-2.31757275	1.16619118	-4.22903515

5’ – B3LYP functional and LANL2DZ basis set and ECP
Total gas phase energy: -1975.674782
59
Step 2

C	2.56374832	0.53152991	1.39110976
N	2.39308695	0.04000941	-0.03971336
C	3.22426967	-1.20722299	-0.25669763
C	2.93817661	-2.30659904	0.77837849
H	4.28230545	-0.91184079	-0.21211521
H	3.01349808	-1.57655853	-1.26046491
C	2.20056632	-0.54391375	2.41930170
H	1.94574378	1.42391653	1.50740766
H	3.61522033	0.81244115	1.52972525
Pd	0.32482626	-0.33250757	-0.31548049
N	0.37593588	1.63992950	-0.66782393
C	2.72399693	1.16699726	-1.05643198
C	1.59060666	2.20931892	-0.93205271
C	2.68978981	0.61370063	-2.50184739
C	4.08027888	1.84477443	-0.79910581

O	1.78652607	3.42703007	-1.13617050
C	-0.78271935	2.40273232	-0.49410354
C	-1.86355789	2.28798044	-1.37367280
C	-0.94716356	3.25877769	0.60372245
C	-2.12165580	3.96533598	0.79940255
C	-3.20621053	3.84817240	-0.08213123
C	-3.05228197	2.98367810	-1.17220292
F	-2.22598336	4.78209652	1.90486656
C	-4.45314642	4.62326917	0.20859992
F	-4.05704030	2.79613388	-2.09364169
F	-1.75471343	1.46635330	-2.47053481
F	0.07174849	3.36869454	1.52696536
C	-1.45184943	-2.13807634	-0.17925824
C	-2.52425811	-3.19802215	-0.04704329
C	-2.48698747	-3.71971606	1.41640220
C	-2.18420660	-4.35758793	-1.02005796
C	-3.90949714	-2.60654713	-0.37193000
O	-0.18859028	-2.42308250	-0.00117349
H	4.90886307	1.13314537	-0.86939345
H	4.11724736	2.35523940	0.16472479
H	4.21619995	2.61321705	-1.56364222
H	3.57734532	0.01396330	-2.72577108
H	2.67799785	1.46286835	-3.19187301
H	1.79186469	0.01523040	-2.68483564
O	-1.72647596	-0.89022875	-0.45059121
C	3.06963478	-1.79756508	2.22414143
H	1.13800165	-0.80395530	2.32922259
H	2.34417088	-0.11890096	3.42035376
H	3.64437431	-3.12582788	0.59166217
H	1.93227531	-2.70562938	0.61744823
H	2.77159651	-2.58387200	2.92722291
H	4.11968723	-1.55295050	2.44488598
H	-1.50250372	-4.13113371	1.65776110
H	-3.23867349	-4.50650936	1.54191279
H	-2.71292290	-2.91585435	2.12640241
H	-2.22319762	-4.01961058	-2.06179415
H	-2.91325307	-5.16587160	-0.89530086
H	-1.18383087	-4.75199266	-0.82030894
H	-3.94553037	-2.22166895	-1.39568212
H	-4.15774157	-1.78108511	0.30210499
H	-4.67342534	-3.38475961	-0.26512747
F	-5.43291335	4.46312325	-0.75280199
F	-4.19547996	5.98822512	0.30061956
F	-5.01377858	4.24120315	1.42643345

TS-5’-7’ – B3LYP functional and LANL2DZ basis set and ECP
energy: -1975.615123
59
Step 103

C	3.16082396	0.44124717	1.49391595
N	2.90811665	0.17653940	0.02079213
C	3.69210415	-1.05013148	-0.39499928
C	3.23360458	-2.27234012	0.44211056
H	4.76360377	-0.84211378	-0.26578712
H	3.50126109	-1.22518638	-1.45067357
C	2.56800469	-0.73621901	2.32158949

H	2.67532322	1.38552170	1.74715985
H	4.24025334	0.55026523	1.65502816
Pd	0.92498300	-0.39510864	0.09867531
N	0.60870550	1.44768914	-0.72799164
C	3.06083095	1.41107414	-0.89437810
C	1.73219177	2.22237966	-0.86909237
C	3.23805300	0.98703644	-2.37327111
C	4.24004953	2.30315621	-0.47634619
O	1.74307935	3.44907969	-1.11187145
C	-0.67255585	2.00175853	-0.72183050
C	-1.67517200	1.46393700	-1.53857000
C	-1.07026937	3.01368675	0.16634986
C	-2.38030886	3.46494273	0.21496469
C	-3.37858335	2.93118039	-0.61226136
C	-2.99362269	1.89271014	-1.46945706
F	-2.70029885	4.43904080	1.13742514
C	-4.79213295	3.39164691	-0.46740375
F	-3.91003539	1.24755219	-2.27500387
F	-1.36378005	0.44921202	-2.41737889
F	-0.15979210	3.52008634	1.06754240
C	-1.34550578	-2.12398774	0.52646712
C	-2.78431659	-2.62493401	0.45064467
C	-2.88183364	-4.07800766	0.95238467
C	-3.23544167	-2.53501826	-1.03395383
C	-3.66762697	-1.69104794	1.31961113
O	-0.38430883	-2.90541173	0.91283959
H	5.19495211	1.77824310	-0.58724721
H	4.14794786	2.67104459	0.54770754
H	4.23887291	3.17999022	-1.12728268
H	4.21495028	0.52856303	-2.55329081
H	3.17492416	1.89206176	-2.98388110
H	2.44332844	0.30856422	-2.69651892
O	-1.09901945	-0.89916160	0.18299807
C	2.08749668	-1.88049388	1.39206167
H	1.74549425	-0.37475083	2.94718099
H	3.33928766	-1.12758776	3.00289425
H	4.07805745	-2.65678883	1.03432133
H	2.92127259	-3.08130774	-0.22666967
H	0.72486141	-2.22963236	0.95768472
H	1.85004850	-2.74380040	2.03208604
H	-2.24336230	-4.74317811	0.36367752
H	-3.91828465	-4.42293221	0.86735219
H	-2.57329264	-4.15966350	1.99933762
H	-3.14810533	-1.51425172	-1.41463723
H	-4.28106796	-2.85266161	-1.11208644
H	-2.63099765	-3.19359820	-1.66836749
H	-3.61829168	-0.66027785	0.95885803
H	-3.34900618	-1.70832455	2.36836251
H	-4.70847445	-2.02924390	1.27488217
F	-5.58545551	3.04796092	-1.54929128
F	-4.87871954	4.77139529	-0.33236552
F	-5.39602760	2.84104607	0.66579307

7’ – B3LYP functional and LANL2DZ basis set and ECP
Total gas phase energy: -1975.633434
59

Step 11

C	3.20884845	0.72199231	1.61624712
N	2.97374504	0.21083922	0.20149899
C	3.85331888	-1.00904766	0.00032430
C	3.35506341	-2.12711789	0.95466676
H	4.89829322	-0.72554804	0.18895540
H	3.76913579	-1.32711421	-1.03596582
C	2.67389200	-0.36241165	2.60046479
H	2.66729609	1.66392001	1.72317268
H	4.27954556	0.92053892	1.75080232
Pd	1.03007054	-0.47849663	0.41530428
N	0.57767066	1.33259446	-0.65643929
C	3.03781052	1.28751383	-0.89560191
C	1.69559119	2.08519251	-0.91832088
C	3.14629425	0.63799020	-2.29603702
C	4.21995386	2.24616562	-0.67727007
O	1.70859887	3.27957898	-1.29880461
C	-0.67387472	1.92523401	-0.60611527
C	-1.77567449	1.29550889	-1.20727916
C	-0.97407575	3.09358513	0.12447294
C	-2.26001593	3.60302885	0.18903539
C	-3.34926265	2.97559486	-0.43395540
C	-3.06842559	1.78914372	-1.12310219
F	-2.47579727	4.74740535	0.92888923
C	-4.70832627	3.57337887	-0.29830090
F	-4.06502225	1.05836008	-1.74544403
F	-1.57221264	0.11566924	-1.90994146
F	0.01566557	3.70967203	0.85941938
C	-1.41039529	-2.17695591	0.04495359
C	-2.81989931	-2.72199085	0.16200320
C	-2.72281778	-4.23543003	0.50257686
C	-3.53796524	-2.53495151	-1.20443296
C	-3.57937389	-1.96946739	1.27196103
O	-0.64735696	-2.76541742	-0.90188599
H	5.17196186	1.70350485	-0.68737981
H	4.13240149	2.80320896	0.25829894
H	4.22193232	2.98389790	-1.48203677
H	4.13837355	0.21287930	-2.47832332
H	2.97720620	1.42150216	-3.04009021
H	2.38097383	-0.13082850	-2.43709736
O	-0.94063545	-1.25786150	0.76732812
C	2.18012086	-1.56823205	1.76942386
H	1.85854168	0.05394925	3.20132770
H	3.46722514	-0.66977182	3.30223093
H	4.17024730	-2.45656866	1.62122763
H	3.05204871	-3.00640847	0.37556900
H	0.24706049	-2.32947543	-0.94422402
H	1.65776164	-2.32049664	2.36495495
H	-2.18972293	-4.78223216	-0.27966245
H	-3.73434281	-4.64537364	0.59063046
H	-2.20844385	-4.39573204	1.45733457
H	-3.60513121	-1.47819345	-1.47605400
H	-4.55406229	-2.93503274	-1.12445599
H	-3.01198381	-3.06677013	-2.00161150
H	-3.65365973	-0.90143929	1.04796792
H	-3.08348677	-2.07744214	2.24145661

H	-4.59300057	-2.37513112	1.35230143
F	-5.67498123	2.89482431	-1.02152225
F	-4.73711148	4.89628100	-0.73313229
F	-5.13958980	3.58798415	1.02968755

5’ – ωB97X-d functional and LANL2DZ basis set and ECP
Total gas phase energy: -1975.13925550961
59
Step 14

C	2.59456190	0.54187598	1.36482133
N	2.38881388	0.04290169	-0.04518034
C	3.19963011	-1.20403674	-0.26625915
C	2.91807642	-2.28983613	0.77731364
H	4.26069376	-0.91958334	-0.23987856
H	2.96701665	-1.58450565	-1.26103237
C	2.21933303	-0.50964925	2.40521330
H	2.00640945	1.45383535	1.48496057
H	3.65649097	0.79069055	1.48353570
Pd	0.33897993	-0.32341704	-0.27418557
N	0.38731971	1.61974532	-0.64720653
C	2.71151074	1.14938180	-1.06229641
C	1.58571908	2.19102192	-0.93967282
C	2.66254277	0.59034907	-2.49771216
C	4.06586893	1.82345820	-0.82134488
O	1.77267925	3.40157282	-1.15624715
C	-0.77592778	2.37196788	-0.48517087
C	-1.80602725	2.31522430	-1.41893761
C	-0.98734490	3.14738586	0.65511299
C	-2.16853883	3.83729771	0.84535517
C	-3.20398701	3.78120128	-0.09170794
C	-3.00121466	2.99595666	-1.22592900
F	-2.32678946	4.57597283	1.98888353
C	-4.46088321	4.54299710	0.19214894
F	-3.95994423	2.87061959	-2.19444965
F	-1.64277717	1.57039599	-2.55333967
F	-0.01085997	3.19795397	1.61697710
C	-1.44038980	-2.09718834	-0.12233181
C	-2.51786298	-3.14684476	-0.02172210
C	-2.50571747	-3.69021881	1.42596346
C	-2.16813555	-4.28414003	-1.00720042
C	-3.88719463	-2.54024024	-0.35752038
O	-0.18919337	-2.39549843	0.06205089
H	4.88514955	1.10004634	-0.86939765
H	4.10179742	2.35673021	0.12942583
H	4.21320908	2.56860799	-1.60532485
H	3.54767921	-0.01126803	-2.72283669
H	2.64247727	1.43228467	-3.19513699
H	1.76225399	-0.00887814	-2.66685836
O	-1.70292928	-0.85250344	-0.38665934
C	3.06877366	-1.77095054	2.21182730
H	1.15284953	-0.75700875	2.33009631
H	2.37818754	-0.07838684	3.39942174
H	3.61909633	-3.11117547	0.59016821
H	1.90831285	-2.68551945	0.63315197
H	2.77387395	-2.54637928	2.92569968
H	4.12268931	-1.53067544	2.41526467

H	-1.52736400	-4.11045498	1.67568070
H	-3.26310812	-4.47444538	1.52581344
H	-2.73910602	-2.89753177	2.14493972
H	-2.16533709	-3.91712464	-2.03875321
H	-2.91866953	-5.07716890	-0.92563290
H	-1.18381341	-4.70271192	-0.78136419
H	-3.89819147	-2.13010036	-1.37091282
H	-4.14048269	-1.73256309	0.33469943
H	-4.65595647	-3.31651111	-0.28365065
F	-5.38956450	4.46221233	-0.81749766
F	-4.19932249	5.88705414	0.39128812
F	-5.07536793	4.07777172	1.34353895

TS-5'-7' – ωB97X-d functional and LANL2DZ basis set and ECP
Total gas phase energy: -1975.08260020473
59
Step 102

C	3.20576785	0.29781543	1.43409804
N	2.91158054	0.18836555	-0.03880555
C	3.68011882	-0.97163801	-0.60018281
C	3.21883664	-2.27550921	0.08958231
H	4.75320804	-0.78489580	-0.45757311
H	3.48232838	-1.02478919	-1.66744606
C	2.63229478	-0.95494620	2.14520799
H	2.73729408	1.21295745	1.80216706
H	4.29030834	0.38276432	1.56953409
Pd	0.94813592	-0.38695692	0.02385860
N	0.62059618	1.51147217	-0.59550086
C	3.04147977	1.49929830	-0.81136978
C	1.72904126	2.30586530	-0.64128947
C	3.13313808	1.24135149	-2.33015957
C	4.25180041	2.31626851	-0.35659675
O	1.73609948	3.54856834	-0.70327975
C	-0.66950828	2.02826549	-0.54373299
C	-1.62894372	1.58131650	-1.45177714
C	-1.11162423	2.88090017	0.47007710
C	-2.43433984	3.27469984	0.55038870
C	-3.39252076	2.83113523	-0.36420788
C	-2.95932268	1.95329729	-1.35789824
F	-2.81025849	4.09467525	1.58407662
C	-4.81645564	3.24022131	-0.17702109
F	-3.83082781	1.41527953	-2.27060069
F	-1.26100569	0.71387828	-2.44620887
F	-0.23597341	3.27728043	1.44604184
C	-1.35013252	-2.06090460	0.40170930
C	-2.78810599	-2.53967835	0.35450225
C	-3.15539945	-3.09743153	1.74674717
C	-2.86066974	-3.67003383	-0.69897233
C	-3.72849876	-1.38883711	-0.03358430
O	-0.41279958	-2.88481412	0.73721790
H	5.18046144	1.75523492	-0.50667118
H	4.18154099	2.62771204	0.68731479
H	4.29112286	3.22965717	-0.95301902
H	4.10282172	0.82564736	-2.61826132
H	3.02039472	2.20459966	-2.83440189
H	2.32561547	0.58658810	-2.67069800

O	-1.06684631	-0.84477989	0.09543615
C	2.10916750	-1.97931364	1.11027141
H	1.83573546	-0.66525566	2.83701971
H	3.42199662	-1.42789765	2.74610487
H	4.06908294	-2.74606951	0.60281659
H	2.86568092	-2.98720367	-0.66213689
H	0.72082688	-2.27023511	0.75612529
H	1.89688756	-2.90857034	1.65973535
H	-2.47616289	-3.90649791	2.02825949
H	-4.17879404	-3.48474948	1.72402976
H	-3.10291701	-2.31362030	2.50998859
H	-2.60661702	-3.29035286	-1.69442692
H	-3.88013846	-4.06703221	-0.73046773
H	-2.17118300	-4.47922452	-0.44462582
H	-3.46922968	-0.97729455	-1.01261967
H	-3.68404560	-0.57708319	0.69915705
H	-4.75688460	-1.76175322	-0.07229780
F	-5.62175051	2.90783170	-1.24178502
F	-4.93725851	4.60635041	0.00084889
F	-5.36835643	2.63952110	0.94609158

7’– ωB97X-d functional and LANL2DZ basis set and ECP
Total gas phase energy: -1975.10038277338
59
Step 17

C	3.19287487	0.76658434	1.57450798
N	2.97203026	0.21643956	0.18564939
C	3.85901660	-0.98618532	0.01489023
C	3.38133185	-2.07811080	1.00158969
H	4.90087987	-0.68182595	0.18498854
H	3.77309015	-1.34259014	-1.00853140
C	2.65951021	-0.28787027	2.58311066
H	2.64641562	1.70942586	1.65137883
H	4.26173329	0.97339122	1.70956238
Pd	1.04839570	-0.47558256	0.40706104
N	0.58551219	1.28049966	-0.69194381
C	3.02515823	1.25680087	-0.92569885
C	1.68612307	2.04576958	-0.95153662
C	3.11383450	0.57831586	-2.30689298
C	4.20466275	2.21463614	-0.74089561
O	1.68461071	3.23732054	-1.32022284
C	-0.66706905	1.84957114	-0.58910716
C	-1.77132750	1.22606826	-1.17734455
C	-0.95291858	2.96696145	0.21014405
C	-2.24044965	3.44445087	0.35136444
C	-3.33640957	2.82426170	-0.25580174
C	-3.06545179	1.68689420	-1.01755626
F	-2.44790020	4.54151479	1.14846011
C	-4.69595155	3.39996121	-0.04638141
F	-4.06855039	0.97183430	-1.62859849
F	-1.56939683	0.09062728	-1.93510364
F	0.05484718	3.55600285	0.92894154
C	-1.39355552	-2.13366047	0.01839792
C	-2.82567323	-2.60919234	0.05082407
C	-2.82187795	-4.05333844	0.61054276
C	-3.38601268	-2.60521371	-1.39016529

C	-3.66120805	-1.68593753	0.94846058
O	-0.59219665	-2.81321557	-0.81703967
H	5.15432588	1.66869561	-0.73283689
H	4.11550958	2.80054127	0.17624819
H	4.21009007	2.92692158	-1.56747451
H	4.10469188	0.15281197	-2.49107002
H	2.93058812	1.34325387	-3.06588584
H	2.34723729	-0.19473160	-2.41619051
O	-0.93963856	-1.20356664	0.72485119
C	2.18373770	-1.51721626	1.77794746
H	1.83311121	0.13881334	3.16028849
H	3.44520491	-0.56974649	3.30007167
H	4.19062257	-2.35839731	1.69320418
H	3.10329380	-2.98269417	0.45135219
H	0.32272356	-2.44044935	-0.81547654
H	1.67596514	-2.26079863	2.39566204
H	-2.21907616	-4.71409535	-0.01751268
H	-3.84939789	-4.42823165	0.62844222
H	-2.42940443	-4.07822802	1.63260356
H	-3.40342761	-1.59228945	-1.79743598
H	-4.41080607	-2.98802303	-1.37028767
H	-2.78470339	-3.23914886	-2.04551145
H	-3.67382662	-0.66581428	0.55682056
H	-3.27099675	-1.65848873	1.96909616
H	-4.69083272	-2.05442447	0.97466515
F	-5.68303446	2.71840872	-0.72275335
F	-4.75872901	4.71761385	-0.46834353
F	-5.05730492	3.39467547	1.29247303

12. References

1. (a) Dewyer, A. L.; Zimmerman, P. M. *Org. Biomol. Chem.* **2017,** 15, 501-504. (b) Zimmerman, P. M. *J. Comput. Chem.* **2013,** 34, 1385−1392. (c) Zimmerman, P. M. *Mol. Simul.* **2015,** 41, 43−54.
2. Zimmerman, P. M. *J. Comput. Chem.* **2015,** 36, 601-611.
3. Gas phase enthalpies were calculated using DFT with restricted B3LYP and LANL2DZ basis set with an ECP on Pd, Cs and iodine.
4. Gibbs free energies were calculated using DFT with restricted ωB97X-D and LANL2TZ(f) basis set with an ECP on Pd, uncontracted LANL2DZ basis set with an ECP on Cs and iodine, and 6-311++G** basis set on all main group elements. Solvent corrections were made using an SMD solvent model with tert-butanol as the solvent.
5. Thermodynamic corrections to the enthalpy, H, and gas phase entropy $S_{(g)}$ at catalytic conditions (413 K, 1 atm) were computed for all structures. See sections 6 and 7 of the SI for more details