Guanidine-catalyzed Asymmetric Strecker Reaction: Modes of Activation and Origin of Stereoselectivity

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Dedicated to Professors Russell Boyd and Arvi Rauk

Abstract: Density functional theory (DFT) calculations were employed to study the catalytic mechanism, modes of activation and origin of enantioselectivity of guanidine-catalyzed asymmetric Strecker reaction of *N*-benzhydryl imine with hydrogen cyanide. Two types of bifunctional activation mode were identified, namely conventional bifunctional Brønsted acid activation and unconventional bifunctional Brønsted-Lewis acid activation. The lowest-energy transition states correspond to the conventional bifunctional mode of activation. The calculated enantiomeric excess (*ee*), based on eight lowest-energy C-C bond forming transition states via turnover frequency calculations, is in good accord with observed enantioselectivity. NCI (non-covalent interaction) analysis of the key transition states reveals extensive non-covalent interactions, include aromatic interactions and hydrogen bonds, between the guanidinium catalyst and substrates. Multiple C-H···π interactions between the phenyl groups of guanidine catalyst and the phenyl rings of *N*-benzhydryl imine are the key stabilizations in the most stable (*R*)-inducing transition state.

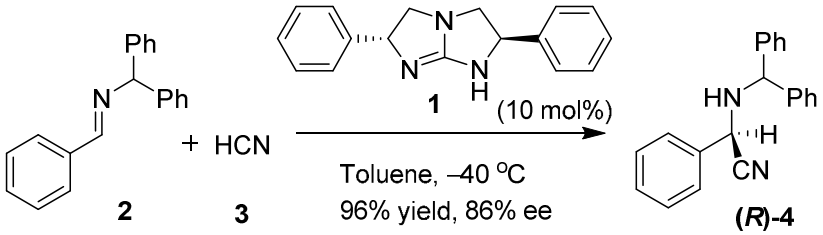
Key words: organocatalysis, Strecker reaction, mechanism, DFT, enantioselectivity, non-covalent interaction, turnover frequency.

Introduction

The classical Strecker synthesis of α-amino acids from aldehyde, ammonia and hydrogen cyanide was first reported in the year 1850[1] and even until today, its popularity still remains because of its direct, robust and economic access in the production of α-amino acids.[2] Recently, asymmetric Strecker reaction has attracted a great deal of attention in organic chemistry because enantiomerically pure α-amino acids play a prominent role in many important applications in

chemistry[3] and life sciences.[4] There are two approaches to achieve asymmetric Strecker reaction: nucleophilic addition of cyanide to chiral non-racemic imines and catalytic enantioselective cyanation of achiral imines.[5] The latter strategy turns out to be the method of choice in the last two decades.

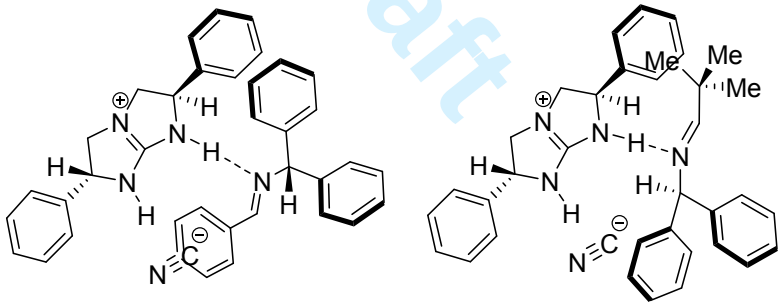
Scheme 1



Lipton et al. first reported a catalytic asymmetric Strecker reaction using cyclic dipeptide as catalyst.[6] The guanidine functional group in the catalyst is found to be critical for achieving high enantioselectivity with aromatic *N*-benzhydryl imines, but not with heteroaromatic and aliphatic derivatives. Subsequently, Grogan and Corey found that chiral C_2 symmetric bicyclic guanidine **1** could catalyze the Strecker reaction (Scheme 1) efficiently with good yield and high enantioselectivity.[7] This C_2 symmetric bicyclic guanidine catalyst surpasses the cyclic dipeptide as the reactions for aliphatic imines also worked well with better enantioselectivity. Interestingly, the Strecker products obtained from aliphatic imines have opposite absolute configuration compared to those derived from aromatic imines. Based on space-filling model of the hydrogen bond from aryl imine to the guanidine catalyst **1**, the authors postulated the existence of π···π stacking interaction between a phenyl group of the catalyst and one of the benzhydryl phenyl groups (Scheme 2).[7] In the pre-transition state assembly, the *si* face of the imine is blocked by other phenyl group of the benzhydryl moiety and this gives rise to the predominating (*R*)-

enantiomer of amino nitrile product. The opposite enantioselectivity coming from the aliphatic imines suggests that there is steric repulsion when the alkyl group from the imine comes into proximity with the guanidine core and distal phenyl group of the catalyst in the vacant quadrant of the guanidine catalyst. On the contrary, the aryl imine can experience van der Waals attraction. In 2003, Li and co-workers reported a DFT study of bicyclic guanidine-catalyzed Strecker reaction of HCN and methanimine.[8] The authors considered only a simple model system as they focused mainly on the rationalization of two competitive pathways to aminoacetonitrile product and they concluded that aminoisoacetonitrile may not form due to the instability of the product. Thus, the origin of stereoselectivity for the bicyclic guanidine (**1**) catalyzed addition of HCN to achiral *N*-benzhylimines remains an unresolved puzzle.

Scheme 2



Although there is great achievement in catalytic enantioselective Strecker reaction,[5] theoretical study on the catalytic mechanism is rather scarce.[9] To provide an in-depth mechanistic understanding of guanidine-catalyzed enantioselective Strecker reaction, we carried out a DFT study on the reaction in Scheme 1 because this guanidine-catalyzed reaction[7] represents a milestone in catalytic enantioselective Strecker reactions. We explored various possible activation modes of the bicyclic guanidine catalyst. The predicted enantiomeric excess

(*ee*) derived from several lowest-energy transition states (TS's) of various possible reaction pathways is in good accord with the observed enantioselectivity. Understanding the catalytic mechanism and its enantioselectivity in this reaction provides further insights into asymmetric Strecker reaction with other types of catalyst.

Computational Method

DFT calculations were performed with the Gaussian 09 programs.[10] All equilibrium structures and transition states were fully optimized using M06-2X density functional method[10] together with the standard 6-31G* basis set. The M06-2X functional was chosen in this study as it is better suited in handling kinetics, thermodynamics and non-covalent interactions.[11,12] Frequency calculations were performed on the M06-2X/6-31G* optimized geometries to confirm the nature of the stationary points as equilibrium structures (with all the real frequencies) or transition states (with only one imaginary frequency). The identities of all calculated TS's were confirmed by intrinsic reaction coordinate (IRC) calculations. The effect of solvation was evaluated by SMD implicit solvation model[13] through M06-2X/6-311+G** single-point energy calculation, based on the gas-phase M06-2X/6-31G* optimized geometry. Both electrostatic and non-electrostatic terms were included in the solvation calculations. Relative Gibbs free energies (ΔG) were computed at M06-2X/6-311+G**//M06-2X/6-31G* level in toluene solvent ($\varepsilon = 2.37$) at 233 K. The enantioselectivity of the catalytic reaction was predicted based on turnover frequency (TOF) calculations. The energetic span model of Kozuch and Shaik[14] was employed to evaluate the TOF of the catalytic cycles associated with various activation modes that are considered in this work. Non-covalent interaction plot (NCI)[15] is adopted for visualization of intra- and intermolecular non-covalent interactions. The NCI isosurfaces were calculated with

NCIplot[16] and visualized with Visual Molecular Dynamics (VMD) software.[17] In NCI plots, green represents weakly attractive while blue denotes strongly attractive.

Results and discussion

Catalytic cycle and various types of activation modes

The catalytic behaviour of the bicyclic guanidine **1** can be clearly captured in terms of the mechanistic cycle outlined in Scheme 3 for the conversion of *N*-benzhydryl imine **2** to amino nitriles **4**. The first step of the catalytic cycle involves deprotonation of hydrogen cyanide by the guanidine catalyst **1**. This is expected due to the high basicity of the bicyclic guanidine, of the order of a superbase. For comparison, a p*K*a value of 22 in THF has been reported for 1,5,7-triazabicyclo-[4.4.0]dec-5-ene.[18] Protonation of guanidine **1** generates a hydrogen-bonded guanidinium-cyanide complex **5** due to the strong electrostatic attraction between the guanidinium cation and cyanide anion. Subsequently, this ion-pair complex **5** serves as a hydrogen bond donor to *N*-benzhydryl imine **2** and a ternary pre-transition state complex **6** is formed before the C-C bond formation step. In the final step, the cyanide anion attacks the *N*-benzhydryl imine in **6** to yield the final product amino nitriles **4** and the catalyst returns to its original neutral form (**1**).

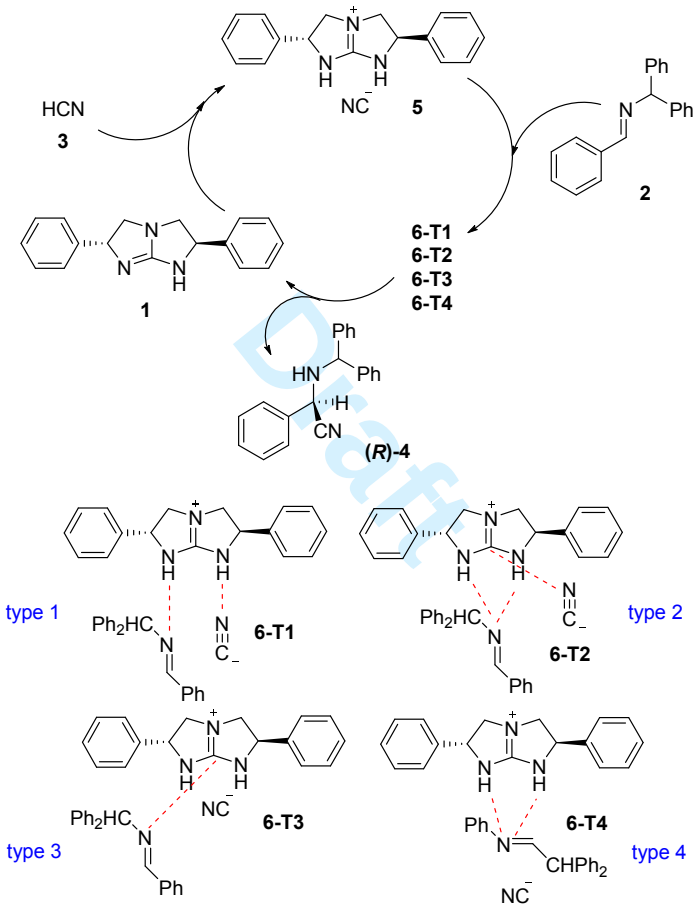
In Scheme 3, we propose four different types of reaction pathway (**T1** – **T4**) in the ternary complex **6**. Guanidine is a well-established bifunctional organocatalyst.[19] It can function as a Brønsted base and also a hydrogen bond donor (Lewis acid). In the bifunctional activation mode, the nucleophile is activated via deprotonation and the electrophile is activated via hydrogen bond. Type 1 pathway is referred as conventional bifunctional Brønsted acid activation mode[19] in which both cyanide anion and *N*-benzhydryl imine are hydrogen-bonded to the guanidinium

catalyst in a side by side manner to give rise to a pre-TS complex **6-T1** (Scheme 3). This activation mode is reminiscent to the well-established binding mode of bicyclic guanidine in asymmetric organocatalysis[19,20] and corresponds to the mechanism proposed by Grogan and Corey.[7] Type 2 and type 3 pathways are two possible electrophile-nucleophile arrangements of bifunctional Brønsted-Lewis acid activation mode.[21] Due to the strong electrophilicity of the central carbon in the bicyclic guanidinium ion and the existence of a vacant *p* orbital on this carbon,[21a,b] the cyanide anion may interact with this vacant *p* orbital of the central carbon in a face-on manner to form a ternary complex **6-T2** in type 2 pathway (Scheme 3). In this pathway, *N*-benzhydryl imine is hydrogen-bonded to the guanidinium catalyst. Similarly, in type 3 pathway, the cyanide anion is hydrogen-bonded to the bicyclic guanidinium ion and the nitrogen lone pair of *N*-benzhydryl imine can interact with the Lewis acidic central carbon of the guanidinium ion in a face-on manner to form complex **6-T3** (Scheme 3). We note that the terms "side-on" and "face-on" were adopted in previous computational studies on guanidine catalysis to describe the ternary pre-TS complexes and corresponding TS's.[20a,21b] Type 4 pathway corresponds to a monofunctional activation mode in which the guanidinium ion has interaction with *N*-benzhydryl imine only. Although the monofunctional activation pathway is less likely to occur in comparison with the bifunctional activation pathways because of its higher activation barrier, we still include it in our computational study for the purpose of complete understanding of the mechanistic pathways.

As can be seen from the computational results in the next section, the C-C bond formation step in the catalytic cycle actually controls the selectivity for the final stereoisomeric amino nitrile product. Therefore, the enantioselectivity of the guanidine-catalyzed asymmetric Strecker reaction can be determined by considering various possible C-C bond forming TS's leading to

the (*R*)- and (*S*)-products. In this work, we have systematically investigated all possible TS's generated from the four different reaction pathways mentioned above. All the relative energy values report subsequently correspond to Gibbs free energies (in kJ mol^{-1}) with respect to guanidine catalyst **1** + *N*-benzhydryl imine **2** + hydrogen cyanide **3**.

Scheme 3

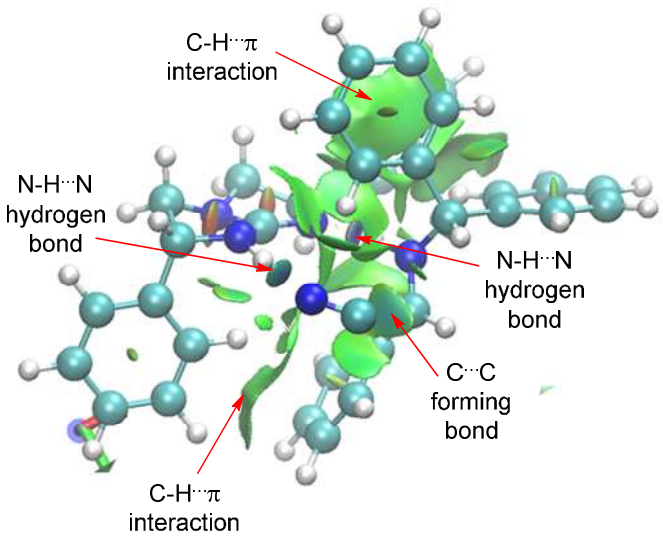


Bifunctional Brønsted acid activation mode

In the conventional bifunctional Brønsted acid activation mode, we have considered all possible orientations when both cyanide anion and *N*-benzhydryl imine are hydrogen-bonded to the catalyst in a side by side manner and successfully located ten different TS's for this C-C

bond formation step in type 1 pathway. Of the ten TS's, six lead to the formation of (*R*)-product while four yield the (*S*)-product (Fig. S1, Supplementary Material). The lowest-energy *R*- and *S*-inducing TS's (namely **6-T1-TS01-*R*** and **6-T1-TS02-*S***, respectively) associate with activation barriers of 58.3 and 64.4 kJ mol^{-1}, respectively. In type 1 pathway, the final process for the forming amino nitrile product **4** and regeneration of catalyst **1** from complex **6-T1** actually involves a series of intermediate steps in which the proton involved in hydrogen bonding between the catalyst and *N*-benzhydryl imine will transfer from the guanidine catalyst to the nitrogen atom in *N*-benzhydryl imine initially and the C-C bond formation will take place afterwards. This proton transfer step is predicted to have an energy barrier significantly lower than that of the C-C bond formation step. Thus, the C-C bond formation step remains the key step for controlling the enantioselectivity. For the lowest-energy transition state **6-T1-TS01-*R***, the proton transfer step is inhibited by an energy barrier of 39.1 kJ mol^{-1}. The C···C bond forming lengths in all the **6-T1** transition states are between 2.4 and 2.7 Å.

Fig. 1

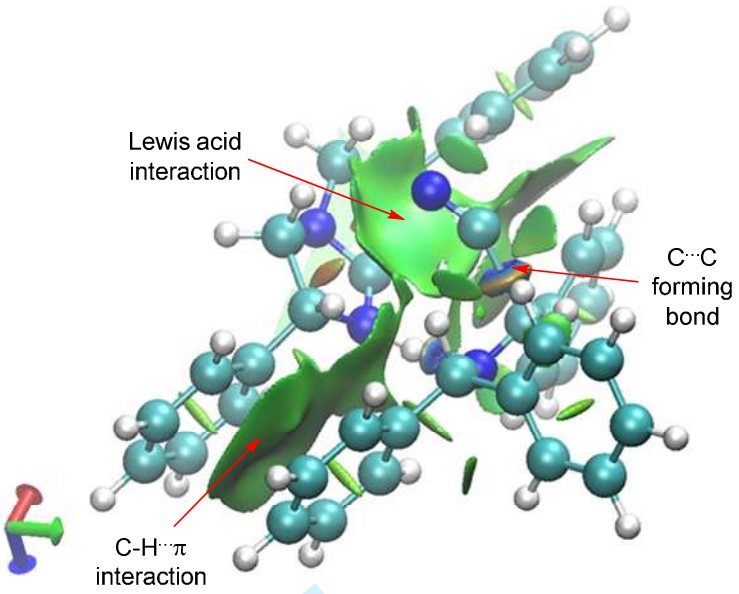


NCI analysis was used to understand non-covalent interactions between the substrates and catalyst. For the lowest-energy transition state **6-T1-TS01-*R***, NCI plot (Fig. 1) reveals that there are two C-H···π interactions between the phenyl groups of guanidine catalyst and the phenyl rings of *N*-benzhydryl imine. These non-covalent stabilizations provide extra stabilization to this TS over the others. The N-H···N hydrogen bonds and C···C bond forming bond are also evidenced in the NCI plot.

Bifunctional Brønsted-Lewis acid activation mode

Type 2 and type 3 pathways belong to bifunctional Brønsted-Lewis acid activation mode.[21] In type 2 pathway, *N*-benzhydryl imine forms hydrogen bond with the guanidinium catalyst and the cyanide anion interacts with the central carbon in the bicyclic guanidinium ion via "Lewis acid interaction".[21a,b] As a result, the cyanide anion positions on top of the guanidinium ion. In total, we found 17 different TS's for the C-C bond formation step (see Fig. S2, Supplementary Material), with seven of them lead to the formation of (*R*)-product and ten of them yield the (*S*)-product. The lowest-energy transition state (**6-T2-TS01-*S***) gives the (*S*)-product with an activation barrier of 80.5 kJ mol^{-1}. In contrast to type 1 pathway, the final step is a concerted process where the C-C bond formation and proton transfer from the catalyst to imine occur simultaneously. The C···C bond forming lengths in all the **6-T2** transition states (around 2.0 Å) are slightly shorter compared to those of **6-T1**. The NCI plot of the lowest-energy transition state **6-T2-TS01-*S*** (Fig. 2) clearly indicates π···π stacking interaction between a phenyl group of the guanidine catalyst and one of the benzhydryl phenyls, which provides the additional stability of this TS over the others. The "Lewis acid interaction" between the guanidinium catalyst and the nitrogen lone pair of cyanide ion is also observed in the NCI plot.

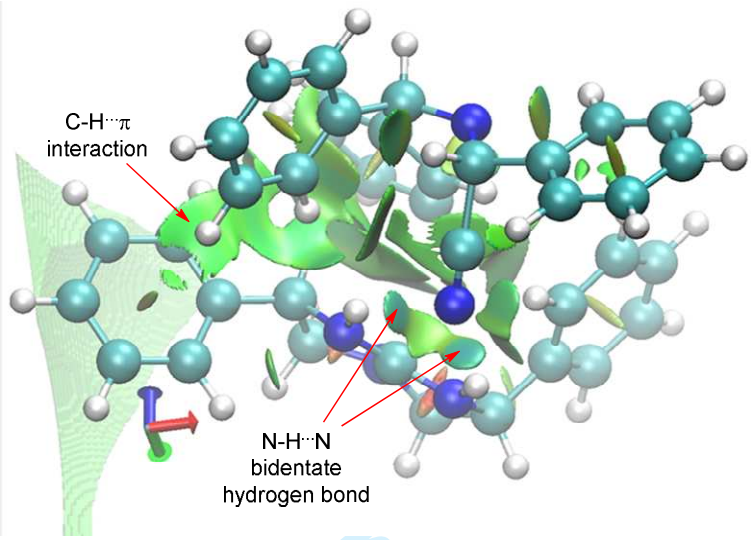
Fig. 2



Interestingly, there is only one transition state, namely **6-T3-TS01-*R***, leading to the (*R*)-product for type 3 pathway. It has a substantially higher barrier (156.3 kJ mol^{-1}) than those TS's from type 1 and type 2 pathways. Because *N*-benzhydryl imine is a relatively bulky molecule, it is unlikely that the nitrogen atom can interact with the Lewis acidic carbon due to the steric repulsion with a phenyl group of guanidine catalyst. This TS has a short C···C forming bond length of 1.69 Å. As in the case of type 1 pathway, the step leading to the formation of final product is a stepwise process in which the C-C bond formation occurs first and proton transfer follows afterwards. The NCI plot in Fig. 3 shows that **6-T3-TS01-*R*** has one C-H···π interaction between a phenyl group of guanidine catalyst and the phenyl ring of *N*-benzhydryl imine. However, this attractive interaction is not sufficient to provide net stabilization of the entire complex due to strong steric repulsion between the other phenyl group of guanidine catalyst and

the benzhydryl moiety of imine. The bidentate hydrogen bond between the two N-H protons of guanidinium and the nitrogen of cyanide ion is readily observed.

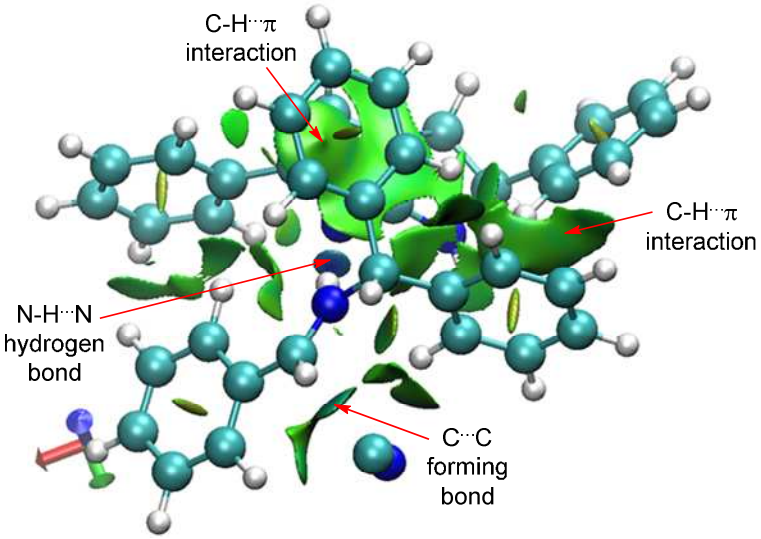
Fig. 3



Monofunctional activation mode

In the monofunctional activation mode (i.e. type 4 pathway), *N*-benzhydryl imine lies in between the guanidinium ion and cyanide anion so that the guanidinium ion forms hydrogen bond with the imine only while the cyanide anion is in the sense "bare" as it does not have any attractive interaction with the guanidinium ion and *N*-benzhydryl imine. We were able to locate only one TS (**6-T4-TS01-*R***), which has an energy barrier of 115.5 kJ mol^{-1} and it gives the (*R*)-product. In this case, the proton transfer from guanidinium ion to imine happens after the C-C bond formation step. Although there are two C-H···π interactions in **6-T4-TS01-*R*** (see NCI plot in Fig. 4), the bareness of the cyanide anion results in a higher activation barrier.

Fig. 4



Activation barriers and calculated enantioselectivity

The deprotonation of hydrogen cyanide by the guanidine catalyst forms a binary ion-pair complex in the first step of catalytic cycle (Scheme 3). *N*-benzhydryl imine in the next step comes in to interact with this binary complex to generate a ternary complex, which is the key pre-TS complex before the C-C bond formation takes place to yield the final product. The stereochemistry of the final product is controlled by the C-C bond forming TS. Transition state leading to either (*S*)- or (*R*)-product is indicated in the suffix of the TS label, e.g. **6-T1-TS01-*R***. Based on the relative energies of all the TS's discussed in the previous section, type 1 reaction pathway dominates. Thus, we took the eight lowest-energy C-C bond forming TS's for further evaluation of stereoselectivity. Type 1 pathway of the conventional bifunctional Brønsted acid activation mode is actually more favourable for the formation of both (*R*)- and (*S*)-products. In fact, all the eight lowest-energy TS's are associated with type 1 pathway. Fig. 5 shows the optimized geometries of selected binary and ternary complexes. The ternary complexes are

generally stable with respect to the binary ion-pair complex, with a binding free energy ranging from –1.3 to +9.4 kJ mol^{-1} in toluene solvent.

Fig. 5

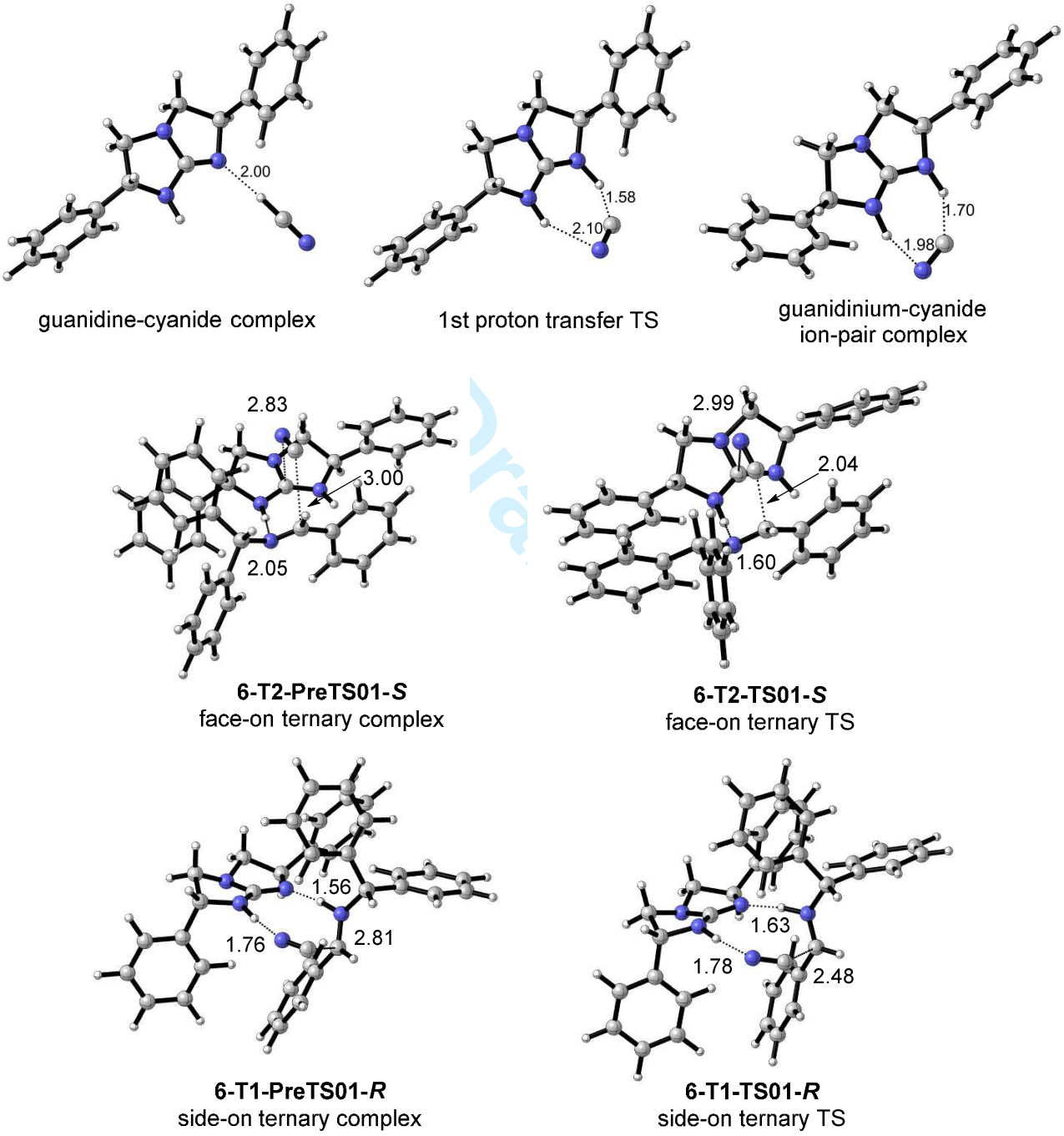


Table 1. C···C bond forming and hydrogen bond lengths (in Å) for the eight lowest-energy C-C bond forming transition states.

TS	N-H···N (cyanide)	C···C	N···H-N (imine)
6-T1-TS01-*R*	1.78	2.48	1.63
6-T1-TS02-*S*	1.85	2.50	1.64
6-T1-TS03-*R*	1.79	2.47	1.68
6-T1-TS04-*S*	1.85	2.52	1.61
6-T1-TS05-*R*	1.81	2.45	1.63
6-T1-TS06-*S*	1.87	2.47	1.62
6-T1-TS07-*R*	2.00	2.52	1.66
6-T1-TS08-*S*	1.88	2.44	1.68

Due to the asymmetry of the guanidine catalyst **1**, *N*-benzhydryl imine can approach the guanidinium-cyanide complex from either left or right side. This gives rise to different TS's and, hence, also different stereoisomeric products. In the eight lowest-energy C-C bond forming TS's, four of them lead to the (*R*)-product while another four yield the (*S*)-product. The optimized geometries of these eight TS's are depicted in Fig. 6 and the C···C bond forming and hydrogen bond lengths are summarized in Table 1. Interestingly, the hydrogen bond between the catalyst and cyanide (N-H···N = 1.78 – 2.00 Å) is significant weaker than that between the catalyst and *N*-benzhydryl imine (N···H-N = 1.61 – 1.68 Å). This can be attributed to the stronger negative charge on the nitrogen atom of *N*-benzhydryl imine.

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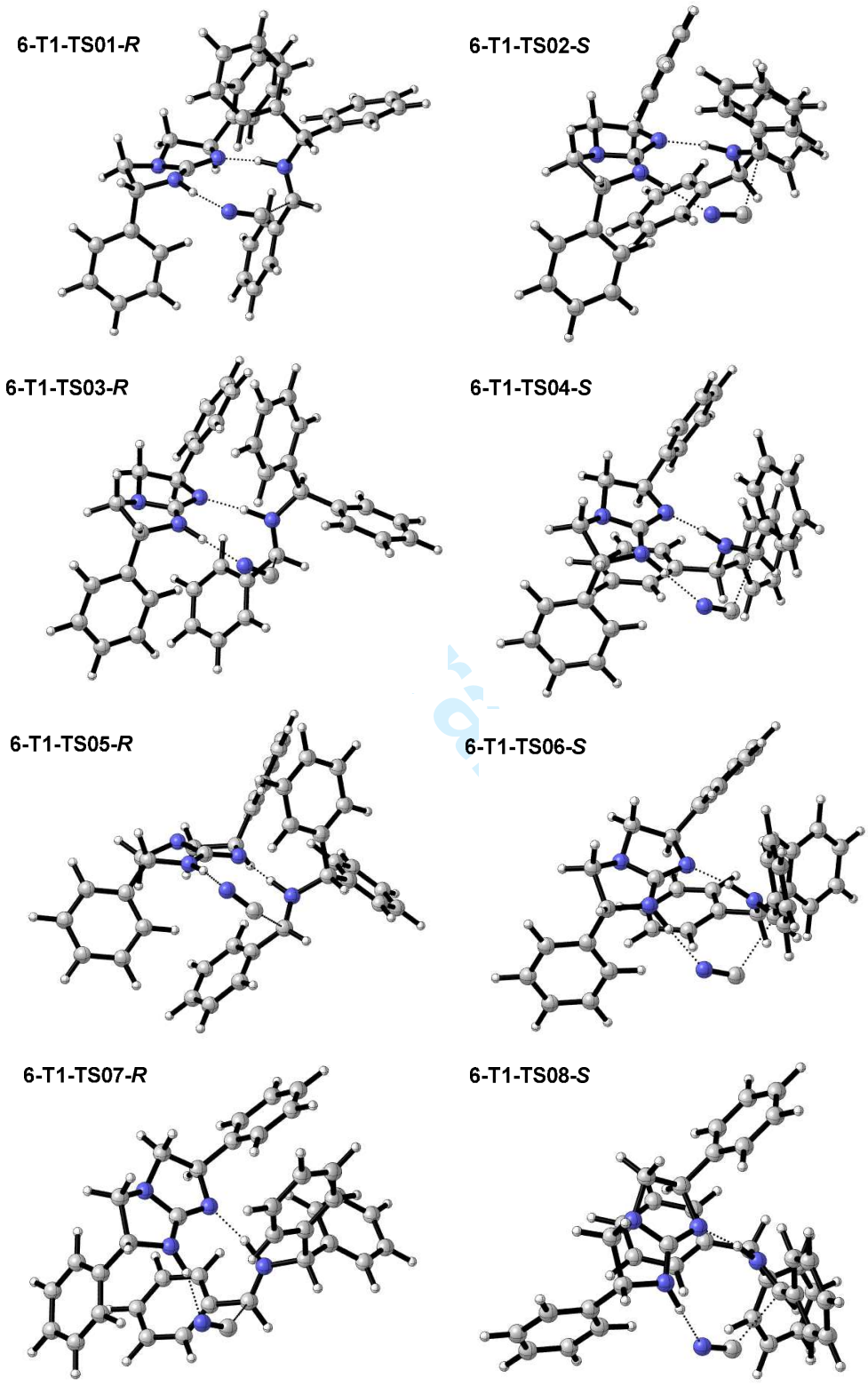
Fig. 6


6-T1-TS01-*R*
6-T1-TS02-*S*
6-T1-TS03-*R*
6-T1-TS04-*S*
6-T1-TS05-*R*
6-T1-TS06-*S*
6-T1-TS07-*R*
6-T1-TS08-*S*

The relative Gibbs free energies ($\Delta\Delta G^{\ddagger}_{233}$) of these TS's in the gas phase and toluene solvent are given in Table 2. The (*R*)- and (*S*)-inducing TS's take alternative order in terms of stability. The lowest-energy (*R*)- and (*S*)-inducing TS's are **6-T1-TS01-*R*** and **6-T1-TS02-*S***, respectively. **6-T1-TS01-*R*** has the lowest energy among all the eight TS's and this is in good accord with the experimental finding that the (*R*)-product is the preferred product.[7] **6-T1-TS01-*R*** has also the strongest N-H···N (cyanide) hydrogen bond. Therefore, the strength of N-H···N (cyanide) hydrogen bond may also be an important contribution factor to the relative stabilities of various TS's.

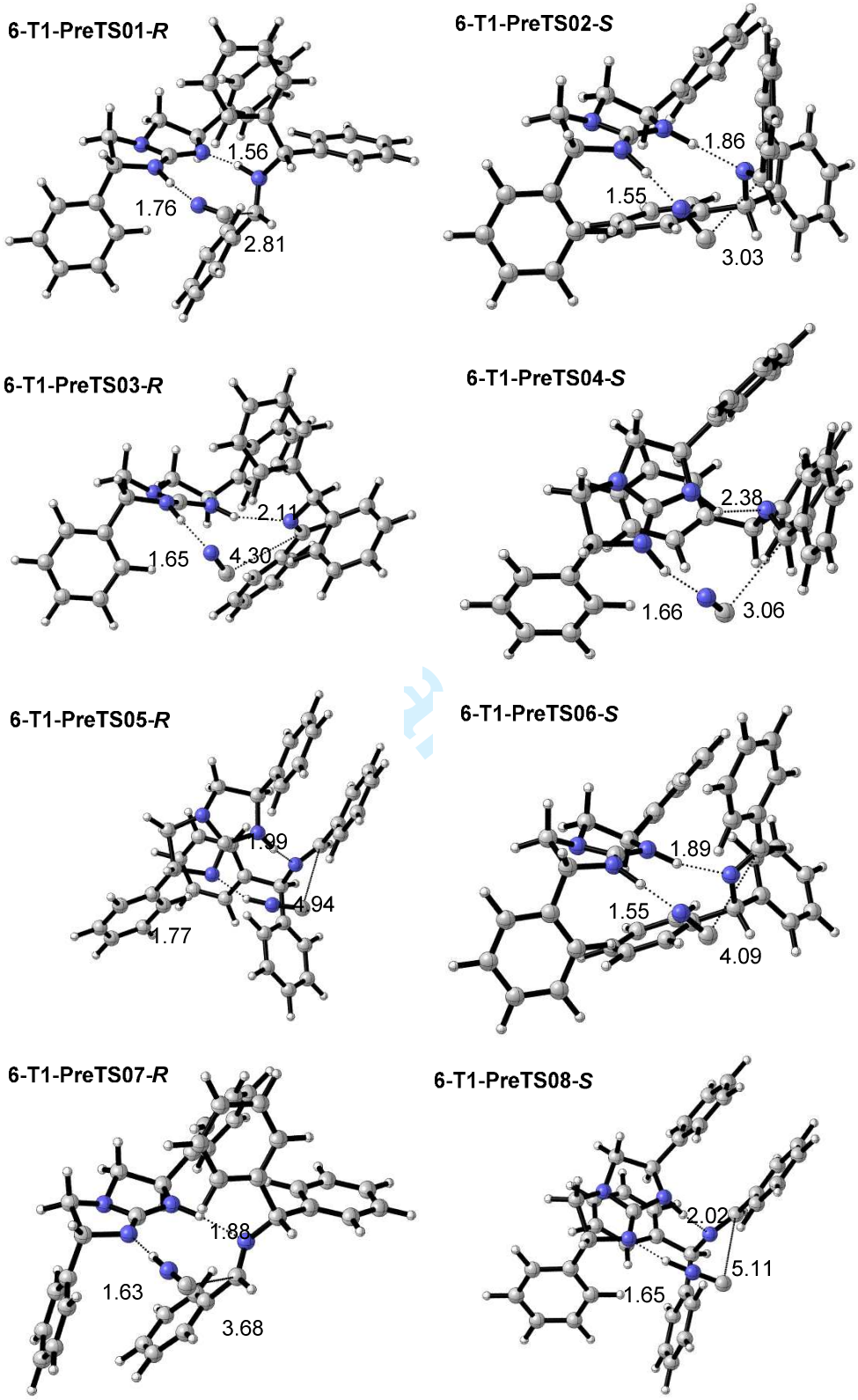
Table 2. Calculated relative energies ($\Delta\Delta H^{\ddagger}_{233}$ and $\Delta\Delta G^{\ddagger}_{233}$) and activation energies ($\Delta H^{\ddagger}_{233}$ and $\Delta G^{\ddagger}_{233}$) in the gas phase and toluene solvent.[a,b]

TS	$\Delta\Delta H^{\ddagger}_{233}$ gas phase	$\Delta\Delta G^{\ddagger}_{233}$ gas phase	$\Delta\Delta G^{\ddagger}_{233}$ toluene	$\Delta H^{\ddagger}_{233}$ gas phase	$\Delta G^{\ddagger}_{233}$ gas phase	$\Delta G^{\ddagger}_{233}$ toluene
6-T1-TS01-*R*	0.0	0.0	0.0	42.5	46.7	27.4
6-T1-TS02-*S*	8.2	8.7	6.3	35.8	39.2	41.2
6-T1-TS03-*R*	10.2	7.9	8.6	33.6	34.4	37.8
6-T1-TS04-*S*	7.4	8.4	9.0	33.8	39.3	41.8
6-T1-TS05-*R*	13.2	12.7	9.0	45.6	53.2	33.5
6-T1-TS06-*S*	6.7	9.4	10.8	31.3	35.9	43.1
6-T1-TS07-*R*	6.9	10.1	11.0	43.1	51.4	35.6
6-T1-TS08-*S*	16.8	13.2	15.8	63.3	60.0	39.9

[a] At M06-2X/6-311+G**// M06-2X/6-31G* level; SMD continuum model for the solvation calculations.

[b] Relative energies ($\Delta\Delta H^{\ddagger}_{233}$ and $\Delta\Delta G^{\ddagger}_{233}$) are with respect to the most stable transition state **6-T1-TS01-*R*** and activation barriers ($\Delta H^{\ddagger}_{233}$ and $\Delta G^{\ddagger}_{233}$) are with respect to the corresponding pre-TS complex.

Fig. 7


6-T1-PreTS01-*R*
1.56
1.76
2.81
6-T1-PreTS02-*S*
1.86
1.55
3.03
6-T1-PreTS03-*R*
2.11
1.65
4.30
6-T1-PreTS04-*S*
2.38
1.66
3.06
6-T1-PreTS05-*R*
1.99
4.94
1.77
6-T1-PreTS06-*S*
1.89
1.55
4.09
6-T1-PreTS07-*R*
1.88
1.63
3.68
6-T1-PreTS08-*S*
2.02
5.11
1.65

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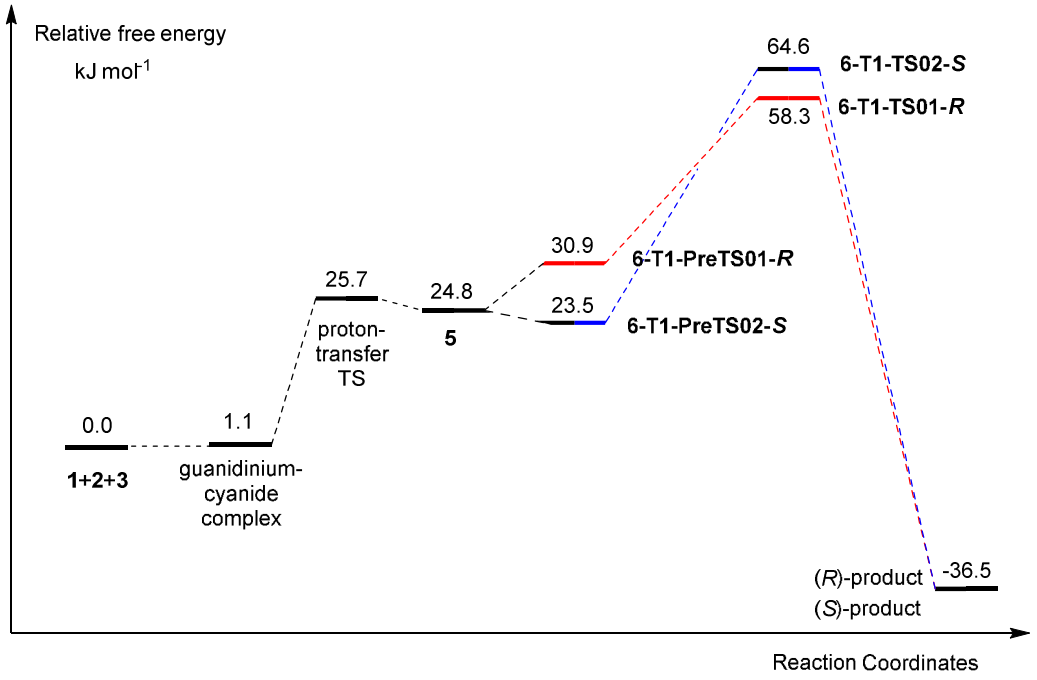
For each of the eight lowest-energy TS's, IRC method was used to locate the corresponding pre-TS complex. In all cases, the pre-TS complex resembles closely to the geometry of respective TS, with similar hydrogen bonding interactions (see Fig. 7). Table 2 also summarizes the absolute activation free energy ($\Delta G^{\ddagger}_{233}$), which is the Gibbs free energy difference between a particular pre-TS complex and its corresponding TS. The lowest activation free energies ($\Delta G^{\ddagger}_{233}$) for the (*R*)- and (*S*)-inducing TS's are 27.4 (**6-T1-TS01-*R***) and 39.9 (**6-T1-TS08-*S***) kJ mol^{-1}, respectively in toluene. The ternary pre-TS complexes play an essential role in assembling the substrates and also influencing the final outcome of stereoselectivity. Based on TOF calculations, using the energetic span model of Shaik and Kozuch,[14] and taking into consideration of all the eight TS's, the enantiomeric excess (*ee*) is predicted to be 90%, in close agreement with the observed value of 86%. A schematic potential energy diagram showing the lowest-energy pathways for the formation of (*R*)- and (*S*)-products is given in Fig. 8.

Fig. 8



Based on the lowest-energy TS (**6-T1-TS01-*R***) and it corresponding pre-TS complex (**6-T1-PreTS01-*R***), we can compare the pre-TS assembly proposed by Grogan and Corey.[7] Our calculations confirm the proposed mechanism via conventional bifunctional activation mode in which both substrates interact with the guanidinium via hydrogen bonds (Figs. 6 and 7). In terms of stereoselectivity, the authors pointed out correctly the importance of aromatic interaction. However, DFT calculations reveal a different type of aromatic interaction. The authors proposed π···π stacking between a guanidinium phenyl group and one of the phenyl groups of the benzhydryl moiety. On the other hands, the calculated TS and pre-TS complex indicate both guanidinium phenyl groups interact with two phenyl groups of *N*-benzhydryl imine via C-H···π interactions (Fig.1).

Conclusion

Bicyclic guanidine (**1**)-catalyzed asymmetric Strecker reaction of *N*-benzhydryl imine with hydrogen cyanide was studied at the M06-2X/6-311+G** level of theory together with the SMD solvation model in toluene solvent. This mechanistic study shed light into the possible activation modes and origin of enantioselectivity in this asymmetric Strecker reaction. Similar to other guanidine-catalyzed enantioselective reactions, there are two possible bifunctional activation modes of the bicyclic guanidinium catalyst **1**, namely conventional bifunctional Brønsted acid activation mode and unconventional bifunctional mode of Lewis and Brønsted acid activation, for the C-C bond formation step to yield the final amino nitrile product. We have successfully identified transition states corresponding to both types of bifunctional activation modes, with the conventional bifunctional activation mode found to be energetically more

favourable than the unconventional mode. Based on TOF calculations of the eight lowest-energy C-C bond forming TS's, the predicted enantiomeric excess is in good accord with the experimental observed enantioselectivity. Non-covalent interaction (NCI) analysis reveals extensive non-covalent interactions, namely aromatic interactions and hydrogen bonds, between the catalyst and substrates in the key TS's. In particular, multiple C-H···π interactions between the phenyl groups of the guanidinium catalyst and the phenyl groups of *N*-benzhydryl imine could be the basis for origin of enantioselectivity in this guanidine-catalyzed Strecker reaction. The understanding of the role of non-covalent interactions may provide useful insights for the design of other types of asymmetric catalyst for enantioselective Strecker reaction.

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2016-xxxx.

Acknowledgments

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Figure Captions

Scheme 1. Guanidine-catalyzed asymmetric Strecker reaction of *N*-benzhydryl imine with HCN.

Scheme 2. Pre-transition-state assemblies for the Strecker reactions of aromatic and aliphatic *N*-benzhydryl imine.

Scheme 3. Proposed catalytic cycle of guanidine-catalyzed asymmetric Strecker reaction of *N*-benzhydryl imine with HCN. Type 1 pathway corresponds to bifunctional Brønsted acid activation mode; types 2 and 3 pathways correspond to bifunctional Brønsted-Lewis acid activation mode; and type 4 pathway corresponds to monofunctional activation mode.

Fig. 1. NCI isosurface showing the non-covalent interactions in transition state **6-T1-TS01-*R***.

Fig. 2. NCI isosurface showing the non-covalent interactions in transition state **6-T2-TS01-*S***.

Fig. 3. NCI isosurface showing the non-covalent interactions in transition state **6-T3-TS01-*R***.

Fig. 4. NCI isosurface showing the non-covalent interactions in transition state **6-T4-TS01-*R***.

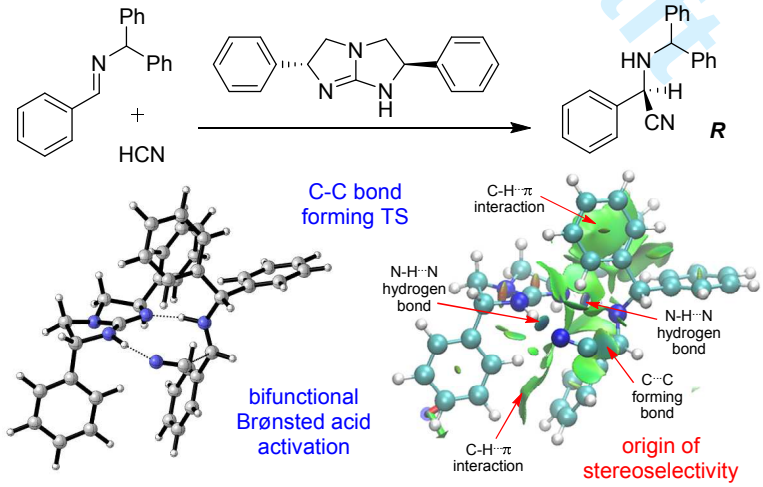
Fig. 5. Optimized (M06-2X/6-31G*) geometries of some binary and ternary complexes. The intermolecular interaction distances are given in Å.

Fig. 6. Optimized (M06-2X/6-31G*) geometries of the eight lowest-energy C-C bond forming TS's. The intermolecular interaction distances are given in Table 1.

Fig. 7. Optimized (M06-2X/6-31G*) geometries of the eight pre-transition states corresponding to the eight lowest C-C bond formation TS's. The intermolecular interaction distances are given in Å.

Fig.8. Potential energy diagram of the lowest-energy pathways for the formation of (*R*)- and (*S*)-products. Relative free energies (ΔG_{233}in toluene solvent) were calculated at M06-2X/6-311+G**// M06-2X/6-31G* level.

Graphical Abstract



1

Guanidine-catalyzed Asymmetric Strecker Reaction: Modes of Activation and Origin of Stereoselectivity

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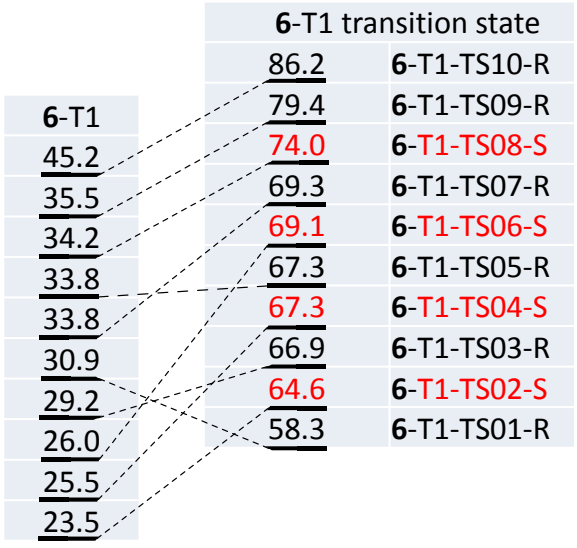
Supplementary Material

Figure S1. Potential energy diagram of C-C bond formation in type 1 pathway. Relative free energies (ΔG_{233} in toluene solvent) calculated at M06-2X/6-311+G**// M06-2X/6-31G* level.



2

Figure S2. Potential energy diagram of C-C bond formation in type 2 pathway. Relative free energies (ΔG_{233} in toluene solvent) calculated at M06-2X/6-311+G**// M06-2X/6-31G* level.

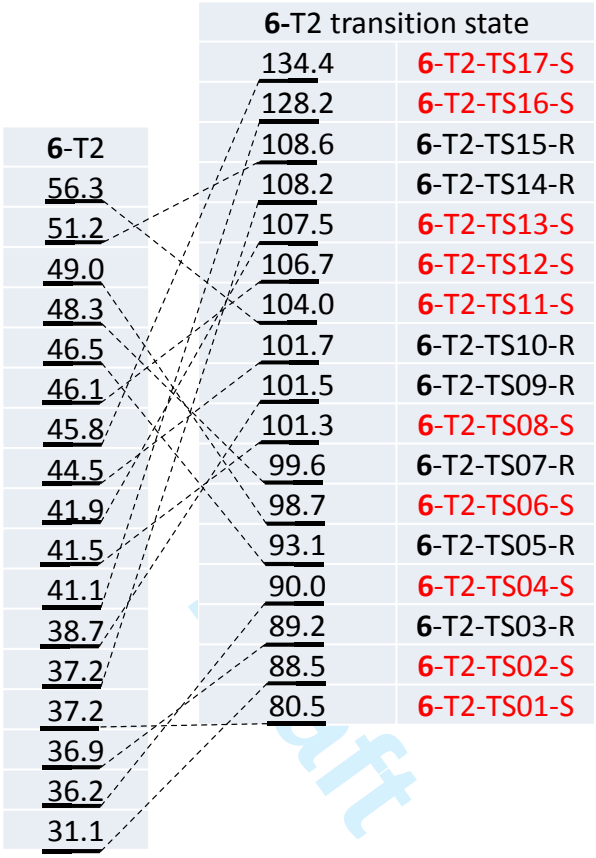


Table S1. Cartesian coordinates of the M06-2X/6-31G* optimized geometries of eight lowest-energy C-C bond forming transition structures and corresponding pre-TS complexes.

6-T1-PreTS01-*R*			
N	1.46400	0.60000	0.85600
C	0.39800	0.48700	0.12000
N	0.09800	-0.80100	-0.30200
N	-0.46200	1.37200	-0.39900
C	2.00000	-0.76200	0.99700
H	1.94500	1.92700	1.53000
C	-1.47200	0.65900	-1.17500
C	1.35100	-1.53400	-0.18500
C	-0.72900	-0.67000	-1.49000

6-T1-TS01-*R*			
N	1.32000	0.71700	0.66800
C	0.30000	0.53900	-0.11100
N	0.00000	-0.78100	-0.41600
N	-0.51600	1.37600	-0.77900
C	1.81500	-0.63400	0.97600
H	1.89000	2.04700	1.41200
C	-1.55100	0.58200	-1.43600
C	1.23200	-1.51300	-0.16300
C	-0.80800	-0.77000	-1.62200

3

H	-1.41900	-1.50800	-1.61000	H	-1.49700	-1.61600	-1.66700
H	1.19600	-2.59300	0.03200	H	1.05200	-2.54500	0.14400
H	-0.11000	-0.56600	-2.39500	H	-0.18200	-0.75000	-2.52800
H	1.96000	-1.43300	-1.09800	H	1.89600	-1.50200	-1.04400
H	-1.68600	1.20400	-2.10000	H	-1.80300	1.01900	-2.40700
H	1.63500	-1.20300	1.93900	H	1.37300	-0.97800	1.92600
C	3.50900	-0.75800	1.01700	C	3.31800	-0.65200	1.10700
C	4.22200	-0.08600	0.01900	C	4.11200	-0.02000	0.14400
C	4.20900	-1.36800	2.05800	C	3.93300	-1.25400	2.20500
C	5.61200	-0.04000	0.06000	C	5.49700	-0.01000	0.27400
H	3.68200	0.43400	-0.77200	H	3.63300	0.49300	-0.68900
C	5.60100	-1.31800	2.10400	C	5.32000	-1.24000	2.34000
H	3.65800	-1.87900	2.84400	H	3.31800	-1.73300	2.96500
C	6.30500	-0.65400	1.10300	C	6.10500	-0.61900	1.37100
H	6.15100	0.49400	-0.71600	H	6.10000	0.49400	-0.47500
H	6.13300	-1.79600	2.92200	H	5.78600	-1.71100	3.20100
H	7.38900	-0.60800	1.13800	H	7.18500	-0.60100	1.47600
C	-2.77200	0.42700	-0.42100	C	-2.81600	0.42400	-0.60500
C	-3.89400	-0.00400	-1.13300	C	-3.95100	-0.12000	-1.20900
C	-2.86800	0.60700	0.95700	C	-2.86500	0.77700	0.74300
C	-5.09400	-0.26100	-0.47900	C	-5.11700	-0.32100	-0.48000
H	-3.82700	-0.13300	-2.21200	H	-3.92000	-0.38600	-2.26500
C	-4.07100	0.35200	1.61200	C	-4.03500	0.57600	1.47300
H	-2.00600	0.95800	1.51900	H	-2.00000	1.22700	1.22500
C	-5.18400	-0.08300	0.90000	C	-5.16000	0.02600	0.86800
H	-5.96000	-0.59000	-1.04600	H	-5.99300	-0.74300	-0.96400
H	-4.13500	0.50000	2.68600	H	-4.06100	0.85800	2.52200
H	-6.12100	-0.27700	1.41400	H	-6.07100	-0.12500	1.44000
H	-0.57800	2.36100	-0.07000	H	-0.69300	2.34900	-0.45000
N	2.05600	2.95700	1.90700	N	2.10600	2.98500	1.91000
C	1.08700	3.44200	2.59500	C	1.21400	3.43200	2.72800
C	3.14200	3.80100	1.37600	C	3.18300	3.84300	1.39200
C	4.32900	3.70700	2.31500	C	4.38400	3.76800	2.31300
C	4.86800	2.45700	2.63600	C	4.87400	2.52400	2.72400
C	5.96200	2.36700	3.48800	C	5.99700	2.45100	3.53900
C	6.52800	3.52300	4.02700	C	6.64100	3.61700	3.95100
C	5.99500	4.76700	3.70900	C	6.15800	4.85600	3.54300
C	4.89600	4.85800	2.85500	C	5.03100	4.93000	2.72500
C	3.44700	3.38900	-0.06000	C	3.47800	3.44600	-0.05100
C	2.37700	3.20100	-0.94000	C	2.39800	3.29000	-0.92500
C	2.61200	2.81800	-2.25600	C	2.61600	2.90000	-2.24200
C	3.91800	2.65200	-2.71600	C	3.91400	2.69100	-2.70500
C	4.98500	2.87600	-1.85200	C	4.99200	2.87900	-1.84500
C	4.75200	3.23500	-0.52500	C	4.77600	3.25000	-0.51800
C	0.05800	2.60400	3.22000	C	0.22300	2.52500	3.33200

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C	0.35600	1.30700	3.65400
C	-0.62500	0.54600	4.28100
C	-1.89700	1.08000	4.48000
C	-2.19300	2.37500	4.05300
C	-1.21800	3.14200	3.42700
H	1.05100	4.51800	2.75300
H	2.75400	4.82900	1.37000
H	4.43700	1.55200	2.21000
H	6.37400	1.39000	3.72400
H	7.38300	3.45200	4.69200
H	6.42900	5.67000	4.12500
H	4.47900	5.83100	2.60600
H	1.36100	3.38200	-0.59600
H	1.77000	2.66500	-2.92500
H	4.10300	2.36300	-3.74700
H	6.00600	2.76700	-2.20700
H	5.59100	3.38600	0.14800
H	1.35900	0.91200	3.52200
H	-0.39400	-0.45700	4.62300
H	-2.66000	0.48600	4.97500
H	-3.18700	2.78500	4.20100
H	-1.43900	4.13300	3.04200
C	-0.27700	5.11500	0.80300
N	-0.59300	4.04600	0.42700
6-T1-PreTS02-*S*			
C	1.12600	-0.59400	2.94600
C	-0.01500	-0.65800	1.90100
C	1.73200	0.50300	1.04400
C	3.94500	0.91500	1.00200
C	3.53900	0.34300	2.39500
H	1.28800	-1.55400	3.43900
H	0.93200	0.18600	3.69900
H	4.50700	1.84500	1.12700
H	3.44000	1.14500	3.14100
N	0.40900	0.40500	0.97500
H	-0.16800	0.60800	0.14300
N	2.63200	1.22000	0.40900
H	0.04200	-1.62600	1.38600
H	4.23800	-0.41300	2.75500
N	2.23900	-0.22900	2.07600
H	2.43400	1.53800	-0.62600
C	4.76900	-0.06500	0.17800
C	5.97400	-0.54200	0.70400
C	4.37500	-0.47500	-1.09500

C	0.59000	1.20700	3.62400
C	-0.33100	0.33900	4.20000
C	-1.61500	0.78600	4.49700
C	-1.97500	2.10800	4.23000
C	-1.06100	2.97900	3.65000
H	1.31300	4.44600	3.10100
H	2.78100	4.86700	1.39400
H	4.37800	1.61100	2.39800
H	6.36900	1.47800	3.84800
H	7.51800	3.56000	4.58900
H	6.65400	5.76800	3.86100
H	4.65400	5.89700	2.40200
H	1.38700	3.48500	-0.57200
H	1.76500	2.76600	-2.90400
H	4.08600	2.39300	-3.73500
H	6.00700	2.73300	-2.20400
H	5.62100	3.37100	0.15300
H	1.60400	0.87500	3.41600
H	-0.04300	-0.68400	4.42400
H	-2.33700	0.10700	4.94100
H	-2.97500	2.45900	4.46400
H	-1.34000	3.99300	3.38400
C	-0.29100	4.61300	1.14300
N	-0.77800	3.96100	0.29800
6-T1-TS02-*S*			
C	1.30800	-1.27400	2.74000
C	0.13000	-1.19900	1.73100
C	1.68800	0.21600	1.09100
C	3.87800	0.85400	1.09800
C	3.57200	-0.01800	2.34900
H	1.54900	-2.29600	3.03800
H	1.10100	-0.66500	3.63600
H	4.39600	1.77100	1.39700
H	3.39500	0.61400	3.23400
N	0.40900	0.03600	0.97800
H	-0.67800	0.55600	-0.14000
N	2.52300	1.17500	0.64100
H	0.21800	-2.05800	1.05000
H	4.37000	-0.73200	2.56100
N	2.35000	-0.67400	1.91700
H	2.33100	1.60900	-0.28300
C	4.72800	0.11200	0.07600
C	6.01400	-0.29200	0.44500
C	4.27500	-0.16000	-1.21400

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C	6.76000	-1.43500	-0.01600
H	6.30800	-0.20700	1.68400
C	5.16500	-1.37000	-1.81600
H	3.46900	-0.08000	-1.54800
C	6.35100	-1.85800	-1.27900
H	7.69100	-1.79800	0.40700
H	4.84600	-1.67800	-2.80700
H	6.96200	-2.55500	-1.84500
C	-1.41300	-0.44500	2.41700
C	-1.86900	0.83300	2.74700
C	-2.27600	-1.53400	2.53600
C	-3.17900	1.01900	3.17800
H	-1.20100	1.68400	2.63300
C	-3.58300	-1.35000	2.97900
H	-1.92600	-2.52300	2.24900
C	-4.03800	-0.07300	3.29500
H	-3.53200	2.01700	3.41800
H	-4.25200	-2.20300	3.05500
H	-5.06200	0.07400	3.62700
N	-1.45600	0.59000	-1.20300
C	-1.21400	1.62300	-1.90700
C	-1.01900	2.93800	-1.26300
C	-0.31200	3.94900	-1.91600
C	-0.14400	5.18500	-1.30000
C	-0.68500	5.41900	-0.03800
C	-1.40000	4.41400	0.61200
C	-1.57000	3.17800	0.00000
C	1.53200	1.43100	-3.17300
N	1.96700	1.62900	-2.09800
C	-1.75900	-0.67000	-1.87700
C	-3.23700	-0.97400	-1.70900
C	-3.93000	-1.64600	-2.71500
C	-5.27000	-1.98500	-2.54800
C	-5.93000	-1.65600	-1.36700
C	-5.24300	-0.98400	-0.35800
C	-3.90500	-0.64300	-0.52600
C	-0.86400	-1.76600	-1.29300
C	-1.37200	-2.89300	-0.64800
C	-0.50900	-3.84900	-0.10700
C	0.86800	-3.67900	-0.19600
C	1.38400	-2.55500	-0.84300
C	0.52500	-1.61100	-1.39900
H	-1.14600	1.58100	-3.00000
H	0.13900	3.74200	-2.88200
H	0.41600	5.96700	-1.80500

C	6.82900	-0.97900	-0.44800
H	6.38500	-0.06200	1.44200
C	5.09500	-0.84800	-2.11000
H	3.30100	0.19500	-1.54100
C	6.36600	-1.26500	-1.73000
H	7.82500	-1.28700	-0.14400
H	4.73200	-1.04700	-3.11400
H	7.00000	-1.80000	-2.43200
C	-1.25600	-1.19500	2.32500
C	-1.79100	-0.02600	2.87400
C	-2.04200	-2.34800	2.29200
C	-3.08900	-0.01000	3.37500
H	-1.18700	0.87700	2.88400
C	-3.34000	-2.33600	2.79600
H	-1.63700	-3.25200	1.84500
C	-3.86800	-1.16600	3.33700
H	-3.49600	0.90800	3.79000
H	-3.94400	-3.23800	2.75700
H	-4.88300	-1.15200	3.72400
N	-1.31400	0.79100	-0.97500
C	-1.41500	2.00200	-1.40900
C	-1.10700	3.21000	-0.64400
C	-1.42500	4.43600	-1.23400
C	-1.18800	5.62400	-0.55400
C	-0.62300	5.58900	0.71800
C	-0.29500	4.36700	1.30600
C	-0.53600	3.17700	0.63300
C	0.73400	2.03600	-2.68200
N	1.66800	1.89700	-1.98200
C	-1.73500	-0.33600	-1.82900
C	-3.22000	-0.59000	-1.66500
C	-3.99900	-0.89000	-2.78100
C	-5.35400	-1.18100	-2.63700
C	-5.93600	-1.17500	-1.37300
C	-5.16000	-0.87700	-0.25400
C	-3.80800	-0.58400	-0.39700
C	-0.86100	-1.55500	-1.54400
C	-1.39400	-2.77800	-1.14300
C	-0.55200	-3.87000	-0.91800
C	0.82300	-3.73600	-1.07500
C	1.36000	-2.51000	-1.47200
C	0.52300	-1.42800	-1.71900
H	-1.91800	2.14300	-2.36300
H	-1.84200	4.45300	-2.23800
H	-1.43400	6.57300	-1.01800

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H	-0.55500	6.38700	0.43700
H	-1.83800	4.60000	1.59000
H	-2.14500	2.38900	0.47800
H	-1.53700	-0.58900	-2.95400
H	-3.41300	-1.90700	-3.63600
H	-5.79900	-2.50300	-3.34300
H	-6.97600	-1.91700	-1.23600
H	-5.74900	-0.72100	0.56700
H	-3.37100	-0.11600	0.26100
H	-2.44600	-3.03000	-0.56400
H	-0.92200	-4.72700	0.38300
H	1.54000	-4.41900	0.22800
H	2.45900	-2.41600	-0.91900
H	0.92700	-0.73500	-1.91000
6-T1-PreTS03-*R*			
N	-0.73200	0.54600	0.40900
C	-1.89000	0.06000	0.81800
N	-2.71700	1.02800	1.29900
N	-2.38400	-1.16000	0.95800
C	-0.72100	2.00700	0.59700
H	-0.02200	0.03600	-0.13500
C	-3.76200	-1.03200	1.45400
C	-1.90300	2.20000	1.58900
C	-3.70900	0.36600	2.13600
H	-4.67300	0.87600	2.10600
H	-2.44200	3.13100	1.41000
H	-3.35400	0.29100	3.17500
H	-1.54000	2.17900	2.62800
H	-3.95500	-1.80900	2.19900
H	-0.94800	2.49400	-0.36000
C	0.58400	2.53500	1.13800
C	1.26800	1.84800	2.14300
C	1.08900	3.74400	0.66200
C	2.45000	2.36900	2.66000
H	0.88800	0.89400	2.50600
C	2.27100	4.26500	1.18000
H	0.56500	4.26500	-0.13700
C	2.95400	3.57700	2.18000
H	2.97800	1.82200	3.43500
H	2.66100	5.20400	0.79800
H	3.87800	3.97900	2.58300
C	-4.81100	-1.10200	0.35600
C	-6.15800	-1.10900	0.72900
C	-4.47300	-1.14900	-0.99500

H	-0.43100	6.51500	1.25100
H	0.15600	4.34300	2.29300
H	-0.26500	2.22800	1.08600
H	-1.53100	-0.02000	-2.86200
H	-3.54100	-0.90000	-3.76700
H	-5.95300	-1.41100	-3.51300
H	-6.99300	-1.40000	-1.25900
H	-5.60300	-0.87200	0.73800
H	-3.20800	-0.35100	0.48000
H	-2.46500	-2.88800	-1.00700
H	-0.97800	-4.82200	-0.61500
H	1.47800	-4.58300	-0.89200
H	2.43400	-2.39500	-1.59000
H	0.93300	-0.46800	-2.03300
6-T1-TS03-*R*			
N	2.09300	0.34500	-0.49800
C	0.97200	-0.30600	-0.54100
N	0.97000	-1.55200	0.07200
N	-0.20900	-0.08200	-1.14600
C	3.02900	-0.53600	0.21800
H	2.36800	1.98200	-0.75000
C	-1.12900	-1.16200	-0.80100
C	2.37000	-1.94100	0.12600
C	-0.12900	-2.31100	-0.49800
H	-0.53500	-3.04000	0.20600
H	2.59900	-2.57700	0.98400
H	0.17500	-2.81900	-1.42700
H	2.68000	-2.45100	-0.80200
H	-1.74800	-1.41500	-1.66800
H	3.06800	-0.24900	1.28200
C	4.42600	-0.48400	-0.35200
C	4.61700	-0.33700	-1.72800
C	5.53800	-0.61100	0.48000
C	5.90400	-0.31800	-2.25800
H	3.75200	-0.22600	-2.37800
C	6.82600	-0.59900	-0.05000
H	5.39300	-0.71600	1.55400
C	7.01100	-0.45100	-1.42200
H	6.03800	-0.19500	-3.32900
H	7.68300	-0.69600	0.61000
H	8.01400	-0.43500	-1.83700
C	-2.03000	-0.84900	0.38500
C	-2.98900	-1.79200	0.76300
C	-1.93100	0.34400	1.09900

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C	-7.15900	-1.14900	-0.23400
H	-6.42500	-1.08800	1.78500
C	-5.48000	-1.19400	-1.95900
H	-3.43200	-1.18300	-1.30800
C	-6.81900	-1.19000	-1.58500
H	-8.20200	-1.15600	0.06900
H	-5.20700	-1.23900	-3.00800
H	-7.59800	-1.22800	-2.34100
H	-2.02900	-1.90400	0.28700
N	1.99500	-0.00600	-0.73600
C	2.40900	1.04100	-1.32400
C	2.98300	-0.80700	-0.01400
C	2.40300	-1.22500	1.32700
C	1.16500	-1.87100	1.37800
C	0.60000	-2.19800	2.60700
C	1.27500	-1.90600	3.79300
C	2.52700	-1.29900	3.74300
C	3.08600	-0.95900	2.51200
C	3.38200	-2.02600	-0.83700
C	4.61300	-2.63600	-0.58900
C	4.99200	-3.77300	-1.29500
C	4.13800	-4.31100	-2.25600
C	2.91000	-3.70600	-2.50200
C	2.52800	-2.56500	-1.79900
C	1.53100	1.89200	-2.14800
C	0.30700	1.41100	-2.63200
C	-0.51600	2.25700	-3.36900
C	-0.12400	3.56800	-3.64200
C	1.11000	4.03500	-3.19100
C	1.93600	3.19500	-2.45100
H	3.45700	1.36900	-1.23700
H	3.89200	-0.21200	0.17600
H	0.64300	-2.12200	0.45400
H	-0.36800	-2.69000	2.63400
H	0.83400	-2.16600	4.75100
H	3.06700	-1.08300	4.66100
H	4.05500	-0.46500	2.47200
H	5.27800	-2.21800	0.16500
H	5.95400	-4.23600	-1.09800
H	4.43200	-5.19800	-2.80900
H	2.23400	-4.12000	-3.24400
H	1.56300	-2.10500	-1.99700
H	0.01600	0.37300	-2.46000
H	-1.46200	1.88100	-3.74800
H	-0.76900	4.21900	-4.22400

C	-3.83100	-1.55800	1.84400
H	-3.08000	-2.71900	0.19900
C	-2.77900	0.58000	2.18000
H	-1.20900	1.10200	0.80400
C	-3.72500	-0.36500	2.55800
H	-4.57200	-2.30000	2.12500
H	-2.69600	1.51700	2.72300
H	-4.38500	-0.17400	3.39900
H	-0.55100	0.86400	-1.40200
N	2.40400	3.03700	-0.94600
C	1.60200	3.79800	-0.27500
C	3.22100	3.43500	-2.10900
C	3.05800	2.41500	-3.22200
C	1.84600	1.75700	-3.42700
C	1.73600	0.80100	-4.43500
C	2.82700	0.51100	-5.25100
C	4.03100	1.18800	-5.06300
C	4.14600	2.13400	-4.04900
C	2.96200	4.85900	-2.55900
C	3.92100	5.84400	-2.32100
C	3.70400	7.15600	-2.73400
C	2.51700	7.49100	-3.37800
C	1.55200	6.51200	-3.61000
C	1.77200	5.19800	-3.21100
C	1.05400	3.34800	1.02000
C	1.76200	2.42000	1.78900
C	1.26600	2.00700	3.02200
C	0.07400	2.53900	3.50300
C	-0.61600	3.49400	2.75600
C	-0.13400	3.89700	1.51800
H	1.51200	4.84000	-0.56200
H	4.26000	3.37400	-1.76000
H	0.98400	1.99000	-2.80500
H	0.79100	0.28600	-4.57400
H	2.73900	-0.23700	-6.03300
H	4.88400	0.97200	-5.70000
H	5.09200	2.64500	-3.88600
H	4.84500	5.58100	-1.81200
H	4.46000	7.91300	-2.55100
H	2.34300	8.51300	-3.69900
H	0.62200	6.77000	-4.10600
H	1.01100	4.44200	-3.37800
H	2.71200	2.03500	1.43100
H	1.81700	1.27700	3.60700
H	-0.31700	2.21200	4.46300

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H	1.42700	5.04800	-3.41800
H	2.89500	3.55500	-2.08400
N	-1.22100	-2.38800	-1.07000
C	-0.80100	-1.75000	-1.96500
6-T1-PreTS04-*S*			
C	1.32100	-1.01900	-2.58200
C	0.10900	-0.71200	-1.65500
C	1.94100	-1.22300	-0.39900
C	4.17700	-1.41100	-0.17900
C	3.78300	-1.47400	-1.68900
H	1.41700	-0.27200	-3.37100
H	1.24300	-2.02100	-3.02800
H	4.81600	-2.26100	0.07600
H	3.79000	-2.50800	-2.06000
N	0.61700	-1.18400	-0.35100
H	0.11500	-1.02600	0.52200
N	2.86900	-1.57400	0.47000
H	-0.04000	0.36900	-1.61000
H	4.43000	-0.85300	-2.31100
N	2.42500	-0.95200	-1.63200
H	2.60600	-1.44500	1.49500
C	4.88300	-0.11800	0.19800
C	6.08800	0.19000	-0.44000
C	4.38700	0.74500	1.17600
C	6.77900	1.35500	-0.12800
H	6.49500	-0.49100	-1.18600
C	5.08400	1.91300	1.48800
H	3.46500	0.51600	1.70800
C	6.27300	2.22400	0.83800
H	7.71200	1.58200	-0.63500
H	4.68700	2.57900	2.24800
H	6.81000	3.13400	1.08500
C	-1.18200	-1.38100	-2.05300
C	-1.28100	-2.77000	-2.13000
C	-2.30400	-0.59700	-2.31500
C	-2.48800	-3.36900	-2.47800
H	-0.42000	-3.38600	-1.88100
C	-3.51500	-1.19400	-2.65700
H	-2.22900	0.48400	-2.22000
C	-3.60800	-2.58100	-2.74000
H	-2.55900	-4.45100	-2.53200
H	-4.38600	-0.57500	-2.85300
H	-4.55100	-3.04900	-3.00300
N	-1.79800	0.33800	0.92900

H	-1.54300	3.91500	3.13400
H	-0.69000	4.59200	0.89800
N	-1.02600	2.55800	-1.74300
C	-0.55600	3.59400	-1.45600
6-T1-TS04-*S*			
C	1.34700	-1.49800	-2.65400
C	0.11600	-0.82200	-1.99200
C	1.55600	-1.33900	-0.40900
C	3.71300	-1.79000	0.19900
C	3.50500	-2.11600	-1.30400
H	1.66500	-0.98900	-3.56600
H	1.15700	-2.56100	-2.87500
H	4.19800	-2.63100	0.70500
H	3.32800	-3.19500	-1.44100
N	0.29100	-1.08800	-0.55100
H	-0.71200	-0.21000	0.35600
N	2.31900	-1.68400	0.64500
H	0.19200	0.26200	-2.16800
H	4.33900	-1.80500	-1.93300
N	2.30600	-1.34300	-1.57200
H	2.03300	-1.39800	1.59800
C	4.52100	-0.51600	0.44800
C	5.67200	-0.23300	-0.29300
C	4.14100	0.36800	1.46200
C	6.40200	0.93000	-0.05900
H	6.01500	-0.92100	-1.06200
C	4.87400	1.52900	1.69600
H	3.27000	0.16100	2.08000
C	5.99900	1.82100	0.93100
H	7.28600	1.13800	-0.65400
H	4.55400	2.20700	2.48200
H	6.56400	2.73100	1.11100
C	-1.24200	-1.29100	-2.45200
C	-1.60800	-2.63700	-2.34900
C	-2.18900	-0.36700	-2.89300
C	-2.89100	-3.04900	-2.69400
H	-0.88900	-3.35400	-1.96000
C	-3.47800	-0.77500	-3.23300
H	-1.91100	0.68400	-2.95300
C	-3.83100	-2.11800	-3.13600
H	-3.16300	-4.09800	-2.61300
H	-4.20600	-0.04400	-3.57200
H	-4.83400	-2.43900	-3.39900
N	-1.29100	0.43000	1.01600

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C	-1.71500	-0.32300	2.01500
C	-1.84800	-1.79400	2.03200
C	-1.30000	-2.51400	3.09900
C	-1.40400	-3.90000	3.12800
C	-2.06000	-4.57200	2.09900
C	-2.60600	-3.85700	1.03300
C	-2.49900	-2.47200	0.99500
C	1.06400	0.07200	3.22400
N	1.64000	-0.79400	2.67200
C	-1.66900	1.79200	1.03600
C	-3.01700	2.45800	0.82300
C	-4.06000	1.80900	0.16000
C	-5.27100	2.46500	-0.05600
C	-5.45200	3.77100	0.38700
C	-4.41400	4.42400	1.05000
C	-3.20500	3.77000	1.26300
C	-0.62700	2.23900	0.01300
C	0.72300	1.99900	0.29400
C	1.69900	2.27300	-0.66100
C	1.33800	2.79400	-1.90400
C	-0.00100	3.05700	-2.18000
C	-0.97900	2.78400	-1.22300
H	-1.50100	0.15900	2.97500
H	-0.76100	-1.97900	3.87600
H	-0.96900	-4.45700	3.95200
H	-2.14700	-5.65500	2.12700
H	-3.12000	-4.37700	0.23000
H	-2.92400	-1.90200	0.17300
H	-1.29600	2.07000	2.03600
H	-3.91800	0.78500	-0.17400
H	-6.07800	1.94800	-0.56800
H	-6.39800	4.27800	0.22300
H	-4.54800	5.44100	1.40500
H	-2.39300	4.28000	1.77700
H	0.99600	1.57100	1.25800
H	2.74400	2.07600	-0.43700
H	2.10100	3.00700	-2.64800
H	-0.29000	3.47900	-3.13800
H	-2.02300	2.99400	-1.44100
6-T1-PreTS05-*R*			
N	0.60700	1.40100	0.10100
C	-0.38200	0.63300	-0.21700
N	-0.39100	-0.64500	0.33500
N	-1.41900	0.77400	-1.05800

C	-1.74900	-0.10200	2.09800
C	-1.98100	-1.54300	2.21100
C	-1.92200	-2.15600	3.46600
C	-2.17900	-3.51500	3.57900
C	-2.50500	-4.26100	2.44500
C	-2.57200	-3.64900	1.19700
C	-2.31000	-2.28900	1.07500
C	0.38300	0.16000	3.42100
N	1.30500	-0.43400	3.00300
C	-1.09800	1.88800	0.94300
C	-2.42700	2.59700	0.78200
C	-3.45000	2.04100	0.01000
C	-4.64200	2.73400	-0.17900
C	-4.82300	3.98800	0.40000
C	-3.80500	4.54600	1.16900
C	-2.61300	3.85300	1.35900
C	-0.09200	2.20100	-0.15700
C	1.23600	1.80600	0.04000
C	2.18700	2.01700	-0.95300
C	1.82000	2.64400	-2.14600
C	0.50600	3.05700	-2.33800
C	-0.45200	2.83300	-1.34700
H	-2.10000	0.55800	2.88600
H	-1.62400	-1.56600	4.32700
H	-2.11600	-3.99800	4.54900
H	-2.70900	-5.32400	2.53900
H	-2.83500	-4.22400	0.31400
H	-2.38200	-1.80300	0.10600
H	-0.64500	2.16800	1.90700
H	-3.31000	1.06200	-0.44500
H	-5.43200	2.29200	-0.77900
H	-5.75400	4.52600	0.25400
H	-3.94100	5.52100	1.62700
H	-1.81700	4.28900	1.95800
H	1.50900	1.31200	0.97300
H	3.21200	1.69600	-0.79200
H	2.56300	2.81500	-2.91900
H	0.21900	3.55700	-3.25900
H	-1.47500	3.16300	-1.50000
6-T1-TS05-*R*			
N	0.63100	1.29500	0.23300
C	-0.45800	0.65100	-0.19800
N	-0.36900	-0.70600	0.09000
N	-1.49300	1.02400	-0.89100

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C	1.49200	0.57800	0.94300	C	1.58100	0.35100	0.81100
H	1.12300	2.98500	-0.15300	H	0.77000	2.32300	0.26400
C	-2.14100	-0.47800	-1.22000	C	-2.24100	-0.20200	-1.19400
C	0.99400	-0.88300	0.71800	C	1.04600	-0.99800	0.26000
C	-1.15400	-1.49500	-0.56500	C	-1.23400	-1.35500	-0.88300
H	-1.68300	-2.29100	-0.03600	H	-1.72000	-2.24500	-0.47700
H	1.08000	-1.50500	1.61200	H	1.22500	-1.82900	0.94700
H	-0.49800	-1.94100	-1.33000	H	-0.66200	-1.63100	-1.78500
H	1.55400	-1.35400	-0.10600	H	1.52400	-1.21800	-0.70900
H	-2.24900	-0.71200	-2.28700	H	-2.49300	-0.21600	-2.26300
H	1.35100	0.84600	2.00000	H	1.50100	0.35300	1.90800
C	2.95000	0.74500	0.58200	C	3.01800	0.60000	0.41300
C	3.32300	1.14900	-0.70100	C	3.35200	1.45900	-0.63300
C	3.94100	0.44400	1.51700	C	4.02700	-0.09700	1.08100
C	4.66900	1.25100	-1.04000	C	4.68600	1.61100	-1.00500
H	2.55200	1.39500	-1.42800	H	2.57700	2.02900	-1.13800
C	5.28700	0.53800	1.17600	C	5.35700	0.05000	0.70100
H	3.65500	0.14100	2.52200	H	3.76800	-0.75500	1.90800
C	5.65500	0.94300	-0.10500	C	5.68900	0.90600	-0.34600
H	4.94400	1.57800	-2.03900	H	4.93600	2.29300	-1.81300
H	6.05000	0.30500	1.91400	H	6.13400	-0.49600	1.22800
H	6.70400	1.02500	-0.36900	H	6.72700	1.03100	-0.63900
C	-3.52400	-0.47100	-0.59400	C	-3.54300	-0.32300	-0.41900
C	-4.48300	-1.37300	-1.06000	C	-4.44900	-1.32500	-0.77900
C	-3.85800	0.41400	0.43100	C	-3.87000	0.54600	0.62100
C	-5.75700	-1.40300	-0.50400	C	-5.65500	-1.47100	-0.10300
H	-4.22900	-2.05300	-1.87100	H	-4.20400	-1.99700	-1.60100
C	-5.13600	0.38500	0.98700	C	-5.08200	0.40200	1.29700
H	-3.12800	1.14100	0.77900	H	-3.18300	1.34500	0.88800
C	-6.08600	-0.52100	0.52400	C	-5.97400	-0.60400	0.94100
H	-6.49500	-2.10600	-0.87800	H	-6.34800	-2.25500	-0.39400
H	-5.38500	1.08500	1.77900	H	-5.32400	1.09100	2.10100
H	-7.08200	-0.53700	0.95600	H	-6.91700	-0.71100	1.46800
C	1.69400	5.11600	-0.45800	C	0.88900	4.81000	-0.77000
H	-1.59800	1.63400	-1.59200	H	-1.51200	2.46200	-1.66600
N	1.42200	3.99200	-0.27600	N	1.16800	4.08600	0.11100
N	-1.62700	3.30800	-2.40500	N	-1.51100	3.45700	-2.08200
C	-0.54800	3.84600	-2.80800	C	-0.45000	3.94400	-2.63400
C	-2.74500	4.15100	-1.98300	C	-2.74500	4.22400	-1.84400
C	-3.93600	3.78400	-2.85100	C	-3.77400	3.72300	-2.84400
C	-4.47500	4.69400	-3.75500	C	-4.15700	4.50400	-3.93100
C	-5.55400	4.33300	-4.56200	C	-5.05900	4.00600	-4.87000
C	-6.09700	3.05600	-4.46800	C	-5.57600	2.72200	-4.72800
C	-5.55900	2.13900	-3.56300	C	-5.19400	1.93600	-3.64000
C	-4.48500	2.50100	-2.76200	C	-4.29900	2.43500	-2.70200

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C	-3.01100	3.94500	-0.49000
C	-4.30100	4.02400	0.04100
C	-4.51000	3.86900	1.41000
C	-3.43800	3.62300	2.26400
C	-2.14900	3.54900	1.74100
C	-1.94000	3.71600	0.37500
C	0.59200	3.04800	-3.30500
C	0.43700	1.70400	-3.66400
C	1.52400	0.97600	-4.13100
C	2.77400	1.58400	-4.25200
C	2.93200	2.92400	-3.90600
C	1.84400	3.65400	-3.43800
H	-0.41400	4.93700	-2.80300
H	-2.50100	5.21400	-2.14800
H	-4.04900	5.69200	-3.83100
H	-5.96800	5.05200	-5.26200
H	-6.93900	2.77500	-5.09300
H	-5.98200	1.14200	-3.47500
H	-4.08100	1.79500	-2.03900
H	-5.14600	4.20000	-0.61600
H	-5.51900	3.93500	1.80700
H	-3.60500	3.49400	3.32900
H	-1.29800	3.36000	2.38900
H	-0.93200	3.66600	-0.01900
H	-0.54500	1.24700	-3.58900
H	1.39800	-0.06600	-4.41100
H	3.62200	1.01300	-4.61800
H	3.90300	3.40200	-3.99900
H	1.96900	4.69200	-3.13900
6-T1-PreTS06-*S*			
N	0.68100	0.65300	0.47300
C	1.98000	0.90500	0.54400
N	2.50100	0.59100	1.76200
N	2.84400	1.47700	-0.27000
C	0.28200	-0.03900	1.71000
H	0.14100	0.51700	-0.40300
C	4.15800	1.43100	0.38900
C	1.38400	0.44800	2.68800
C	3.74900	1.32800	1.88900
H	4.48400	0.78400	2.48400
H	1.58700	-0.28200	3.47300
H	3.57600	2.32300	2.32500
H	1.10900	1.41500	3.13700
H	4.69400	2.36700	0.20400

C	-3.17400	4.08900	-0.38700
C	-4.52400	4.07800	-0.03000
C	-4.89500	3.97900	1.30900
C	-3.92300	3.88800	2.30100
C	-2.57500	3.91200	1.94900
C	-2.20000	4.01900	0.61300
C	0.65500	3.09400	-3.11500
C	0.47100	1.72900	-3.34800
C	1.52400	0.95800	-3.83400
C	2.75100	1.55000	-4.11600
C	2.92700	2.92000	-3.91400
C	1.88900	3.68800	-3.40900
H	-0.46900	4.98500	-2.94000
H	-2.51000	5.27400	-2.06000
H	-3.75200	5.50600	-4.04500
H	-5.35700	4.62300	-5.71200
H	-6.28000	2.33500	-5.45800
H	-5.60200	0.93700	-3.51300
H	-4.02300	1.83600	-1.83600
H	-5.29000	4.13700	-0.79600
H	-5.94900	3.96700	1.57200
H	-4.21500	3.80600	3.34400
H	-1.80500	3.85300	2.71200
H	-1.14500	4.06500	0.35500
H	-0.49500	1.27100	-3.15900
H	1.37900	-0.10400	-4.00200
H	3.57200	0.94700	-4.49100
H	3.88300	3.38600	-4.13400
H	2.02900	4.74100	-3.18400
6-T1-TS06-*S*			
N	1.65500	0.77300	0.16600
C	0.50400	0.52500	-0.37900
N	-0.04000	-0.71800	-0.09700
N	-0.26800	1.19300	-1.25900
C	1.91900	-0.39200	1.03200
H	2.38800	2.16100	0.56100
C	-1.47000	0.39800	-1.52500
C	1.07200	-1.52000	0.38800
C	-0.96400	-1.02800	-1.17300
H	-1.76900	-1.68800	-0.84600
H	0.75700	-2.27800	1.10800
H	-0.44100	-1.48000	-2.03200
H	1.61600	-2.00200	-0.44200
H	-1.72200	0.45500	-2.59000

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H	0.39200	-1.12200	1.56800
C	-1.12600	0.27200	2.14700
C	-1.73000	1.49400	1.84800
C	-1.83200	-0.68200	2.88400
C	-3.03100	1.75200	2.27300
H	-1.18800	2.23300	1.26200
C	-3.12500	-0.41600	3.32500
H	-1.36900	-1.64400	3.08900
C	-3.72900	0.80100	3.01500
H	-3.49600	2.70000	2.01800
H	-3.66700	-1.16600	3.89200
H	-4.74300	1.00600	3.34600
C	5.00800	0.25300	-0.06300
C	6.25200	0.04900	0.53900
C	4.58600	-0.61800	-1.06800
C	7.05700	-1.02000	0.16200
H	6.59900	0.73600	1.30900
C	5.39700	-1.68800	-1.44800
H	3.63900	-0.45800	-1.58000
C	6.62700	-1.89600	-0.83300
H	8.02100	-1.16600	0.64000
H	5.06000	-2.35400	-2.23600
H	7.25300	-2.73100	-1.13100
H	2.62700	1.41800	-1.34300
N	-1.43500	0.09700	-1.35800
C	-2.29400	1.01100	-1.56600
C	-1.79900	-1.32000	-1.54200
C	-0.82900	-2.16700	-0.71100
C	0.53400	-2.08700	-1.02400
C	1.47300	-2.79900	-0.28400
C	1.06000	-3.62100	0.76700
C	-0.29400	-3.72300	1.06700
C	-1.23600	-2.99700	0.33300
C	-3.25600	-1.64000	-1.26700
C	-3.87300	-1.16500	-0.10400
C	-5.19300	-1.49300	0.17900
C	-5.91800	-2.29900	-0.69900
C	-5.31300	-2.77100	-1.85900
C	-3.98700	-2.44100	-2.14100
C	-1.95100	2.43500	-1.39800
C	-2.94400	3.32900	-0.98600
C	-2.62200	4.65600	-0.72000
C	-1.31100	5.09800	-0.88800
C	-0.32700	4.21700	-1.33500
C	-0.64100	2.88600	-1.59300

H	1.50600	-0.19400	2.03300
C	3.39400	-0.66900	1.16500
C	4.22200	-0.63900	0.03900
C	3.96100	-0.91100	2.41600
C	5.59500	-0.82900	0.16500
H	3.77600	-0.44300	-0.93400
C	5.33400	-1.11100	2.54500
H	3.32200	-0.91700	3.29500
C	6.15500	-1.06300	1.42200
H	6.23100	-0.79500	-0.71500
H	5.76500	-1.28500	3.52700
H	7.22600	-1.20800	1.52200
C	-2.68900	0.79900	-0.70300
C	-3.84200	0.01100	-0.77400
C	-2.70100	1.94400	0.09400
C	-4.97600	0.33800	-0.04000
H	-3.85600	-0.87000	-1.41400
C	-3.84100	2.27200	0.82900
H	-1.83800	2.60500	0.12000
C	-4.97500	1.47100	0.77300
H	-5.86100	-0.28900	-0.10200
H	-3.83500	3.16900	1.44200
H	-5.85900	1.73000	1.34800
H	-0.26800	2.22800	-1.26000
N	2.73500	3.13200	0.89700
C	2.88900	4.06400	0.01800
C	2.65300	3.43200	2.33300
C	1.67600	2.45900	2.98800
C	0.38300	2.36600	2.46000
C	-0.53000	1.46700	3.00000
C	-0.16900	0.67300	4.09100
C	1.10800	0.77900	4.63200
C	2.03400	1.66400	4.07600
C	4.04000	3.41400	2.94700
C	4.98400	2.46500	2.54700
C	6.23200	2.41900	3.15900
C	6.54900	3.32000	4.17400
C	5.61100	4.26600	4.57600
C	4.36100	4.31200	3.96400
C	3.14700	3.74600	-1.39300
C	2.79600	4.65000	-2.40100
C	3.10000	4.35700	-3.72300
C	3.75800	3.17000	-4.04500
C	4.11800	2.27500	-3.04200
C	3.81600	2.56200	-1.71500

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H	-3.33500	0.78600	-1.83000
H	-1.57800	-1.53900	-2.59600
H	0.85100	-1.44600	-1.84700
H	2.52800	-2.71600	-0.53000
H	1.79200	-4.18300	1.34000
H	-0.62700	-4.37000	1.87400
H	-2.28900	-3.08600	0.58100
H	-3.31100	-0.53100	0.57800
H	-5.65300	-1.11600	1.08900
H	-6.95100	-2.55300	-0.48000
H	-5.87200	-3.39400	-2.55000
H	-3.51700	-2.81100	-3.04800
H	-3.96300	2.97200	-0.85500
H	-3.39200	5.34600	-0.38800
H	-1.06000	6.13600	-0.68500
H	0.68800	4.56600	-1.49500
H	0.11000	2.20200	-1.98300
C	1.30200	0.29400	-3.36900
N	1.96800	0.96400	-2.66600

H	3.01900	5.08400	0.36700
H	2.23100	4.44400	2.41300
H	0.10800	2.98800	1.60800
H	-1.52200	1.38300	2.56400
H	-0.88500	-0.02500	4.51500
H	1.39200	0.17100	5.48500
H	3.03400	1.73200	4.49400
H	4.74400	1.75300	1.75900
H	6.95400	1.67400	2.83900
H	7.52500	3.28500	4.64900
H	5.85100	4.97300	5.36500
H	3.62600	5.04800	4.28100
H	2.24200	5.54400	-2.13500
H	2.81400	5.05100	-4.50700
H	3.99300	2.94600	-5.08100
H	4.64200	1.35700	-3.28900
H	4.11900	1.88400	-0.92200
C	0.54600	4.81200	-0.24300
N	-0.18100	4.00700	-0.69100

6-T1-PreTS07-*R*			
C	-0.63200	3.26000	-0.58700
C	0.30100	2.15200	-1.14100
C	-1.30000	1.23100	0.22600
C	-3.22600	1.41100	1.28500
C	-2.78700	2.82200	0.80700
H	-0.87500	4.01400	-1.33900
H	-0.16300	3.74700	0.28300
H	-3.44700	1.42500	2.35700
H	-2.32500	3.38300	1.63400
N	-0.06800	1.04000	-0.27500
H	0.39600	0.12500	-0.31000
N	-2.02800	0.56700	1.05900
H	0.01600	1.94200	-2.18400
H	-3.60600	3.41100	0.38900
N	-1.79100	2.46600	-0.19600
H	-2.02500	-0.89200	1.79600
C	-4.42400	0.81900	0.56300
C	-5.12900	-0.21400	1.18600
C	-4.81200	1.22400	-0.71500
C	-6.21000	-0.82100	0.55600
H	-4.81900	-0.54900	2.17400
C	-5.90300	0.62700	-1.34300
H	-4.25300	2.00000	-1.23000
C	-6.60600	-0.39500	-0.71100

6-T1-TS07-*R*			
C	-0.48900	3.19100	-0.81600
C	0.40800	2.01100	-1.28800
C	-1.09500	1.24200	0.12600
C	-3.06800	1.52300	1.27100
C	-2.57400	2.88200	0.71800
H	-0.75400	3.87600	-1.62400
H	0.00900	3.75100	-0.00700
H	-3.27100	1.59000	2.34400
H	-2.05700	3.44700	1.50800
N	0.05700	0.91800	-0.37000
H	0.57000	-0.64100	-0.09800
N	-1.87200	0.70000	1.06900
H	0.11200	1.74100	-2.31500
H	-3.38400	3.49300	0.31300
N	-1.63800	2.44700	-0.31300
H	-1.82500	-0.25000	1.44900
C	-4.28000	0.92000	0.58000
C	-4.95200	-0.12000	1.22900
C	-4.71400	1.33200	-0.68000
C	-6.06700	-0.71000	0.64200
H	-4.57600	-0.48200	2.18500
C	-5.83200	0.74100	-1.26700
H	-4.17300	2.10800	-1.21400
C	-6.51700	-0.27300	-0.60300

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H	-6.74700	-1.62100	1.05600
H	-6.20300	0.96000	-2.33300
H	-7.45800	-0.85800	-1.20100
C	1.78200	2.44000	-1.07800
C	2.46300	2.38700	0.14200
C	2.49500	2.70700	-2.24700
C	3.83600	2.60500	0.18500
H	1.92200	2.13900	1.05300
C	3.87000	2.92800	-2.20300
H	1.97100	2.72900	-3.20100
C	4.54300	2.87400	-0.98500
H	4.35400	2.54300	1.13700
H	4.41400	3.13100	-3.12000
H	5.61600	3.03200	-0.94900
N	0.97200	-1.65600	-0.13700
C	-0.02800	-2.44300	-0.13900
C	-1.21100	-2.15500	-0.97300
C	-1.10400	-1.30500	-2.08100
C	-2.23300	-0.97100	-2.81500
C	-3.47800	-1.48800	-2.45400
C	-3.58700	-2.35400	-1.36900
C	-2.45400	-2.69900	-0.63800
C	-2.00600	-2.81700	2.93900
N	-2.03400	-1.80400	2.35200
C	2.13800	-1.95400	0.68800
C	3.34900	-2.03700	-0.22400
C	4.16400	-3.16600	-0.23000
C	5.28600	-3.22400	-1.05600
C	5.59700	-2.15000	-1.88300
C	4.78300	-1.01600	-1.88200
C	3.66700	-0.96000	-1.05800
C	2.28700	-0.86600	1.75700
C	1.14700	-0.34200	2.36900
C	1.25100	0.63800	3.35100
C	2.50400	1.10200	3.74500
C	3.64700	0.57100	3.15200
C	3.54000	-0.40300	2.16100
H	-0.06400	-3.33800	0.49800
H	-0.12400	-0.92500	-2.35800
H	-2.14600	-0.31300	-3.67500
H	-4.36400	-1.21800	-3.02000
H	-4.55700	-2.74800	-1.08600
H	-2.53500	-3.35900	0.22000
H	2.01100	-2.92400	1.19600
H	3.92100	-4.00600	0.41600

H	-6.58600	-1.51100	1.15900
H	-6.16900	1.07800	-2.24300
H	-7.39500	-0.72500	-1.05600
C	1.89000	2.30100	-1.27200
C	2.58900	2.31000	-0.06100
C	2.58600	2.51900	-2.46100
C	3.96100	2.53900	-0.04700
H	2.05800	2.09700	0.86600
C	3.96000	2.75000	-2.44700
H	2.04800	2.49500	-3.40600
C	4.65000	2.75900	-1.23800
H	4.49300	2.53100	0.90000
H	4.49000	2.91500	-3.38100
H	5.72200	2.92900	-1.22400
N	0.72300	-1.65200	0.22500
C	-0.25700	-2.48800	0.11300
C	-1.38400	-2.17100	-0.78700
C	-1.13300	-1.42600	-1.94600
C	-2.17800	-1.09200	-2.80000
C	-3.47400	-1.50900	-2.50800
C	-3.72000	-2.28500	-1.37700
C	-2.68300	-2.61700	-0.51500
C	-1.53400	-2.33500	2.27900
N	-2.27900	-1.61700	2.83500
C	1.97300	-1.92400	0.94500
C	3.08200	-2.12900	-0.07000
C	3.86900	-3.27700	-0.05200
C	4.89500	-3.44100	-0.98200
C	5.13500	-2.45700	-1.93500
C	4.35000	-1.30400	-1.95600
C	3.33000	-1.14000	-1.02700
C	2.24400	-0.77900	1.91900
C	1.17700	-0.23600	2.64100
C	1.39300	0.81400	3.52700
C	2.67800	1.31800	3.72000
C	3.74700	0.75900	3.02500
C	3.53100	-0.28000	2.12100
H	-0.14200	-3.48200	0.52800
H	-0.11800	-1.12000	-2.17900
H	-1.97700	-0.50800	-3.69200
H	-4.29600	-1.23200	-3.16100
H	-4.73100	-2.60200	-1.14600
H	-2.87500	-3.16300	0.40100
H	1.81600	-2.85100	1.51200
H	3.68400	-4.04600	0.69400

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H	5.91400	-4.11000	-1.05200
H	6.47100	-2.19300	-2.52600
H	5.02100	-0.16900	-2.51900
H	3.04000	-0.07100	-1.04900
H	0.16400	-0.69600	2.07600
H	0.34700	1.03400	3.80400
H	2.59200	1.86600	4.51100
H	4.63000	0.91700	3.45900
H	4.43800	-0.79700	1.69500
6-T1-PreTS08-*S*			
N	0.68100	-0.83000	-0.80000
C	-0.48500	-1.36300	-1.25100
N	-0.72200	-2.58600	-0.66600
N	-1.32500	-0.97700	-2.15400
C	1.18000	-1.69200	0.28300
H	0.72100	0.17900	-0.63100
C	-2.35900	-2.02600	-2.18200
C	0.52300	-3.04900	-0.07900
C	-1.65100	-3.26600	-1.55100
H	-2.33200	-3.92000	-1.00200
H	0.36200	-3.66500	0.80900
H	-1.11600	-3.85000	-2.31600
H	1.13900	-3.60300	-0.80500
H	-2.64200	-2.23700	-3.21800
H	0.77000	-1.36500	1.24400
C	2.68300	-1.72200	0.38100
C	3.48400	-1.74700	-0.76300
C	3.28400	-1.74400	1.63900
C	4.86700	-1.81700	-0.64400
H	3.01400	-1.68600	-1.74100
C	4.67000	-1.81800	1.75800
H	2.65600	-1.70200	2.52600
C	5.46400	-1.86000	0.61500
H	5.48400	-1.82300	-1.53800
H	5.12900	-1.84000	2.74200
H	6.54500	-1.91200	0.70400
C	-3.60300	-1.60400	-1.40400
C	-4.60500	-2.53400	-1.11100
C	-3.77800	-0.28200	-0.99200
C	-5.73600	-2.16000	-0.39200
H	-4.50500	-3.56300	-1.45100
C	-4.90600	0.09400	-0.26500
H	-3.02200	0.45800	-1.23900
C	-5.88600	-0.84500	0.04200

H	5.50400	-4.34000	-0.96100
H	5.93200	-2.58600	-2.66100
H	4.53300	-0.52400	-2.68900
H	2.73400	-0.22900	-1.03500
H	0.17800	-0.65200	2.53400
H	0.55100	1.22800	4.07400
H	2.84700	2.13300	4.41600
H	4.75400	1.13400	3.18000
H	4.36900	-0.69300	1.56600
6-T1-TS08-*S*			
N	2.21200	0.52200	0.11900
C	1.16500	-0.17300	-0.19800
N	1.20000	-1.51500	0.14800
N	0.04200	0.10600	-0.89500
C	3.07200	-0.41000	0.87000
H	2.46400	2.15900	0.36700
C	-0.78200	-1.10200	-0.96300
C	2.60300	-1.81000	0.38800
C	0.29100	-2.20600	-0.74800
H	-0.12900	-3.10800	-0.29900
H	2.74500	-2.58800	1.14100
H	0.78600	-2.46200	-1.69900
H	3.11900	-2.10000	-0.54300
H	-1.22000	-1.19600	-1.96200
H	2.84200	-0.32500	1.94400
C	4.53800	-0.12400	0.66500
C	5.05200	0.05600	-0.62300
C	5.40000	-0.02900	1.75700
C	6.40400	0.32200	-0.81200
H	4.37600	-0.00500	-1.47200
C	6.75600	0.23300	1.57000
H	4.99700	-0.15800	2.75900
C	7.26000	0.41000	0.28500
H	6.79400	0.46300	-1.81600
H	7.41700	0.30200	2.42900
H	8.31500	0.61800	0.13700
C	-1.89200	-1.18000	0.07500
C	-2.71600	-2.30900	0.08300
C	-2.12000	-0.16800	1.00600
C	-3.73500	-2.44200	1.01900
H	-2.56000	-3.09300	-0.65600
C	-3.14300	-0.30100	1.94500
H	-1.53300	0.74600	0.97500
C	-3.94700	-1.43600	1.96000

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H	-6.50100	-2.89800	-0.17100		H	-4.36400	-3.32600	1.01200
H	-5.00600	1.12600	0.06100		H	-3.31500	0.49700	2.66100
H	-6.76400	-0.55500	0.61200		H	-4.74200	-1.53500	2.69300
H	-0.96400	0.42900	-2.93700		H	-0.37100	1.05100	-0.83400
N	0.94100	1.72500	0.65400		N	2.48600	3.18600	0.67400
C	2.16400	1.96200	0.90000		C	2.01900	4.07000	-0.14600
C	-0.06200	1.99000	1.68000		C	2.82900	3.40200	2.09000
C	-1.24500	2.73400	1.07700		C	2.42700	4.76600	2.61600
C	-1.39000	2.87900	-0.30100		C	1.08100	5.12200	2.74400
C	-2.52800	3.48800	-0.83000		C	0.73900	6.37200	3.24800
C	-3.52500	3.96400	0.01500		C	1.73200	7.26900	3.64300
C	-3.37800	3.83000	1.39700		C	3.07200	6.91700	3.52000
C	-2.24700	3.21600	1.92200		C	3.41600	5.67000	3.00200
C	-0.49700	0.65100	2.26900		C	2.29000	2.25700	2.93300
C	-1.50700	-0.09400	1.66200		C	1.03800	1.68900	2.68600
C	-1.84000	-1.36000	2.13600		C	0.60000	0.61900	3.46300
C	-1.16600	-1.89000	3.23400		C	1.39500	0.12800	4.49900
C	-0.16100	-1.14700	3.85500		C	2.63300	0.71000	4.76000
C	0.17400	0.11700	3.37100		C	3.08000	1.76700	3.97200
C	3.21600	1.75400	-0.11300		C	2.00700	3.82800	-1.59900
C	2.89200	1.69300	-1.47400		C	2.84800	2.86500	-2.16300
C	3.89500	1.51800	-2.41800		C	2.87600	2.69400	-3.54400
C	5.22500	1.40600	-2.01400		C	2.08100	3.49000	-4.36200
C	5.55200	1.47200	-0.66200		C	1.25200	4.46300	-3.80000
C	4.55000	1.65300	0.28600		C	1.21300	4.63200	-2.42500
H	2.49200	2.34500	1.87900		H	1.85800	5.07900	0.22000
H	0.37200	2.59600	2.49300		H	3.92500	3.33900	2.12900
H	-0.61800	2.51700	-0.96900		H	0.30400	4.43700	2.41400
H	-2.62000	3.58500	-1.90800		H	-0.30800	6.64600	3.33200
H	-4.41100	4.44000	-0.39500		H	1.45800	8.24100	4.04200
H	-4.14800	4.20300	2.06600		H	3.85000	7.61000	3.82300
H	-2.14500	3.09400	2.99900		H	4.46300	5.39600	2.90100
H	-2.03700	0.31500	0.80700		H	0.42300	2.06200	1.86700
H	-2.62100	-1.92500	1.63400		H	-0.36100	0.15900	3.24900
H	-1.42600	-2.87400	3.61400		H	1.05000	-0.70800	5.09900
H	0.35900	-1.55000	4.71900		H	3.25600	0.33600	5.56800
H	0.96400	0.69100	3.85000		H	4.05400	2.21300	4.16000
H	1.86100	1.81700	-1.79200		H	3.49000	2.26400	-1.52700
H	3.63600	1.48800	-3.47200		H	3.53000	1.94500	-3.97900
H	6.00800	1.27600	-2.75600		H	2.10600	3.35600	-5.43900
H	6.58700	1.38100	-0.34500		H	0.62700	5.08000	-4.43800
H	4.80100	1.70300	1.34300		H	0.53700	5.34700	-1.96700
C	-0.10400	2.36000	-3.65800		C	-0.39300	3.76700	0.04700
N	-0.57800	1.34800	-3.30800		N	-0.89000	2.72400	-0.15100