Efficient One-Pot Strategy for the Highly Regioselective Metal-Free Synthesis of 1,4-Disubstituted-1,2,3-Triazoles†

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SUPORTING INFORMATION

Computational Details:

All DFT calculations were performed with Gaussian 09 suit of programs using a ultrafine grid.[1] Full optimization were conducted in DMSO medium with the polarizable continuum model (IEF-PCM),[2] employing the B3LYP[3] functional with standard 6-31+G(d,p) basis set. Frequency calculations at 295.15 K (1 atm) ensured that the stationary points represent either minima (no imaginary frequency) or transition states (single imaginary frequency) on the potential-energy surface, furnishing also the zero-point vibrational energies, the thermal and entropic correction from which the Gibbs free energies were determined. To refine the electronic energy, single-point calculations were performed at the B3LYP/6-311+G(d,p) level of theory with IEF-PCM in DMSO employing the B3LYP/6-31+G(d,p) geometries. The IRC calculations were done using the first-order Euler integration for the predictor step along with the Hessian-based Predictor-Corrector integrator (HPC) corrector step, including the "recorrect=test" corrector step Gaussian keyword.[4] In the distortion/interaction model were considered the the Gibbs free energies.

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[1] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2013**.
[2] Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327.
[3] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
[4] (a) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Phys.*, **2004**, *120*, 9918. (b) Hratchian, H. P.; Schlegel, H. B. *J. Chem. Theory and Comput.* **2005**, *1*, 61.

Discussion:

To explore the nature of regioselectivity in 1,3-dipolar cycloaddition reaction with PhN_3 (**2a**) and the vinylogous carbanion (**A**) in DMSO, we have performed DFT (B3LYP) calculations. First, we have computed both concerted and stepwise mechanism for the PhN_3 and the simple model vinylogous carbanion, as can be seen in Figure S1. We also used a simple amidine as a model for DBU basis.

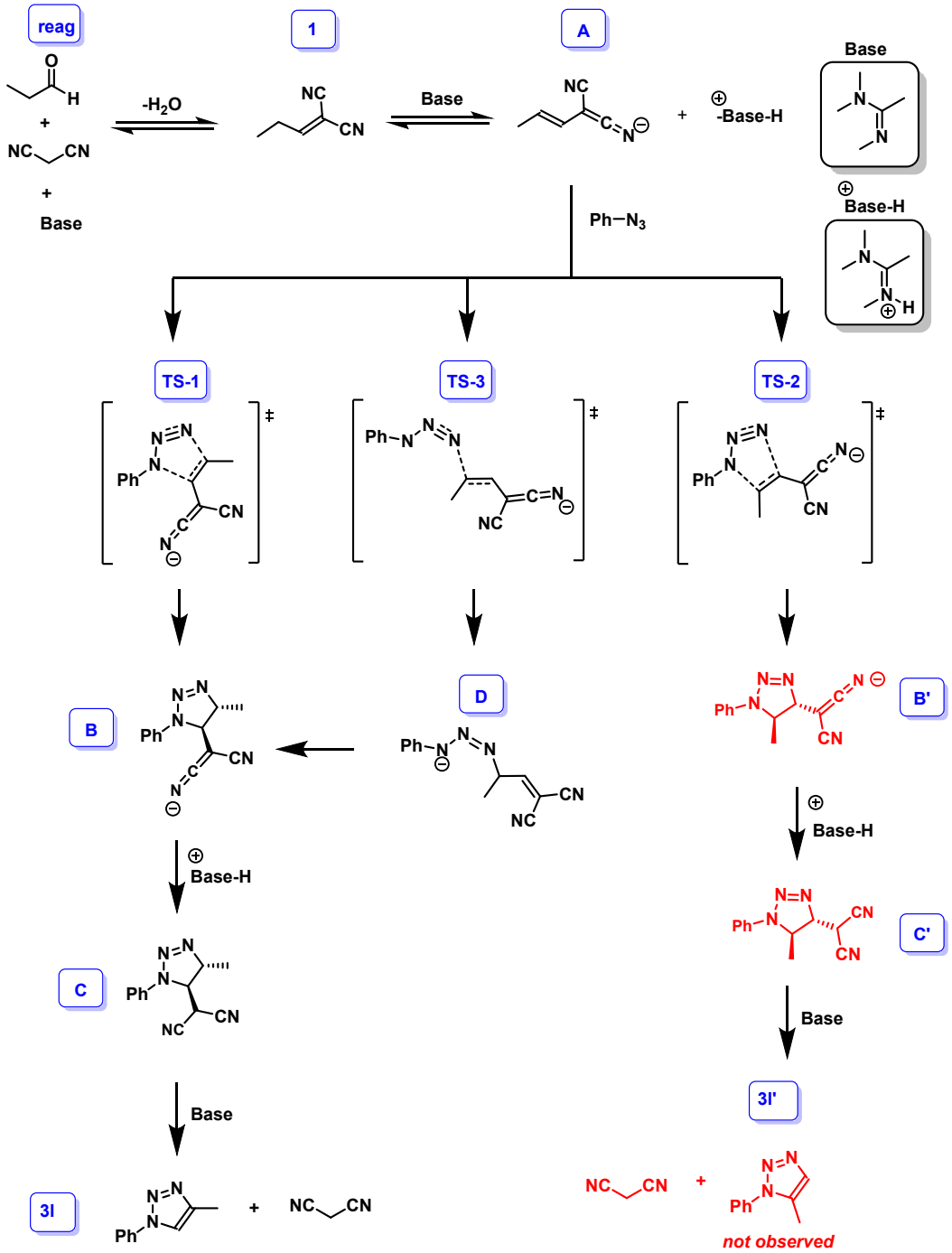

Figure S1. Concerted and stepwise mechanism of cycloadditions of PhN_3 to vinylogous carbanion.

The computed transition structures, are shown in Figure S2a. In addition, the free energy profile for the catalytic cycle of PhN_3 to vinylogous carbanion are represented in Figure S2b.

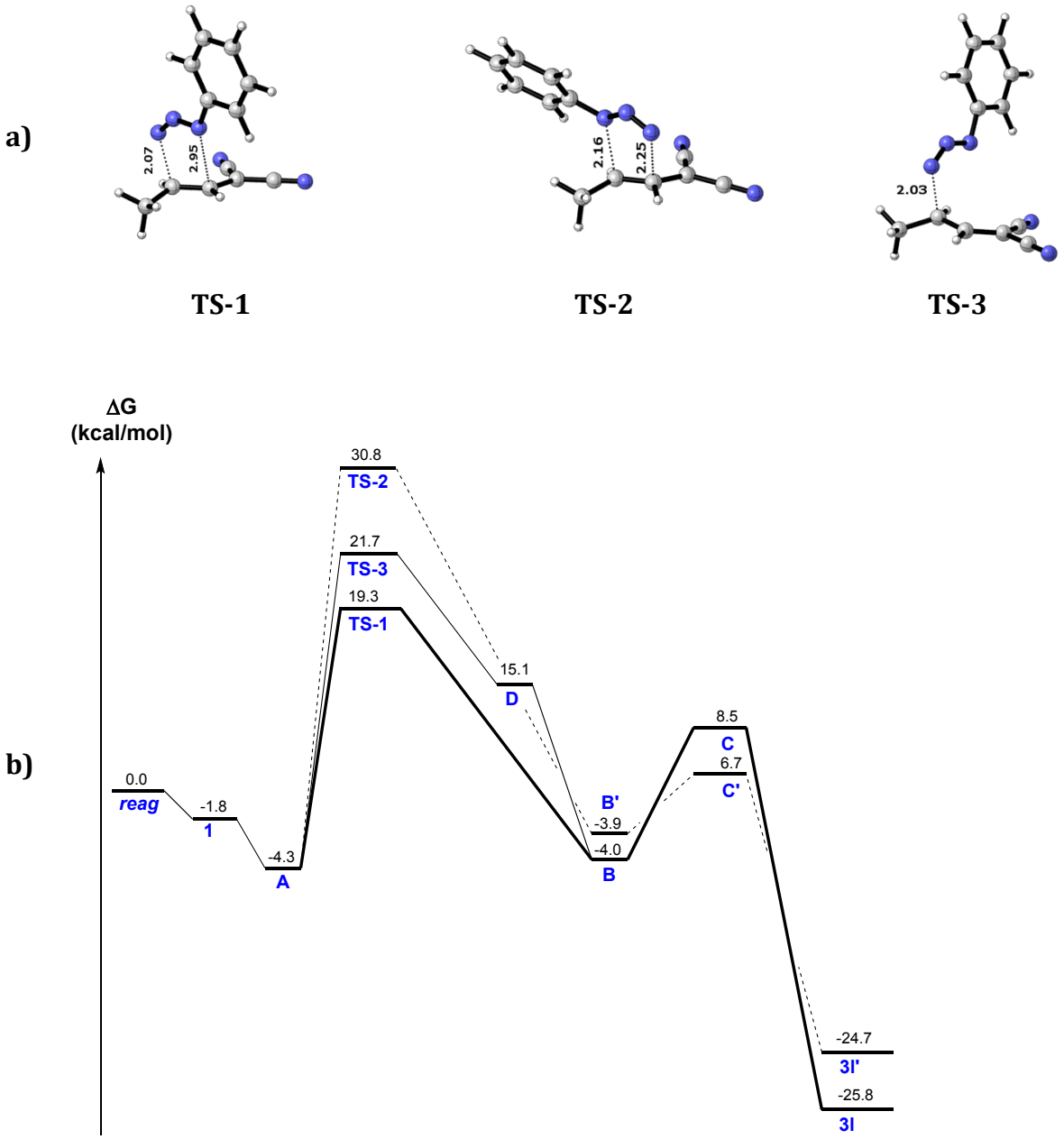

Figure S2. (a) Computed transition structures. (b) Free energy profile for the catalytic cycle of PhN_3 to vinylogous carbanion. All stationary points are represented at B3LYP/6-311+G(d,p)// B3LYP/6-31+G(d,p) level of theory with IEF-PCM: DMSO.

Among the concerted transition states, **TS-1** was the lowest in energy and furnished the only observed regioisomer (**3l**) in the reaction, presenting the highly

asynchronicity, and energy barrier of 23.5 kcal.mol^{-1} (Figure S2). **TS-2**, that leads the unobserved regioisomer (**3l'**), is disfavored by 11.6 kcal.mol^{-1}. These energy barriers are in the same order of magnitude of 1,3-dipolar cycloadditons of phenyl azides with electron rich enamines, as previously reported by Houk and coworkers.[5] Moreover, the **TS-3** related to the first step of the stepwise mechanism leading to observed regioisomer (**3l**) is disfavored by 2.4 kcal.mol^{-1} in energy, resulting in a zwitterionic intermediate **D**. We are not able in characterize the ring closure to the intermediate **D**. Similar problem was faced by Houk and coworkers.[5]

Due to the high asynchronicity observed in **TS-1**, we investigate the intrinsic reaction coordinate (IRC) from **A** ⇨ **TS-1** ⇨ **B**. We observed in this process a very flat potential energy surface (Figure S3) in which the forward IRC from **TS-1** terminates at **I-A**, that is not a stationary point since its optimization leads to **B** (Figure S3, IRC-1). The same result was obtained changing the algorithm (GS2 and HPC without EulerPC), or the step size along the reaction path (7 and 5) on Gaussian 09. Thus, it was not possible to trace the whole process using a single set of IRC calculations. To analyze the reaction path from **I-A** to **B**, it was allowed **I-A** to proceed downhill on the potential energy surface using the keyword "IRC=downhill" in Gaussian 09 (IRC-2).

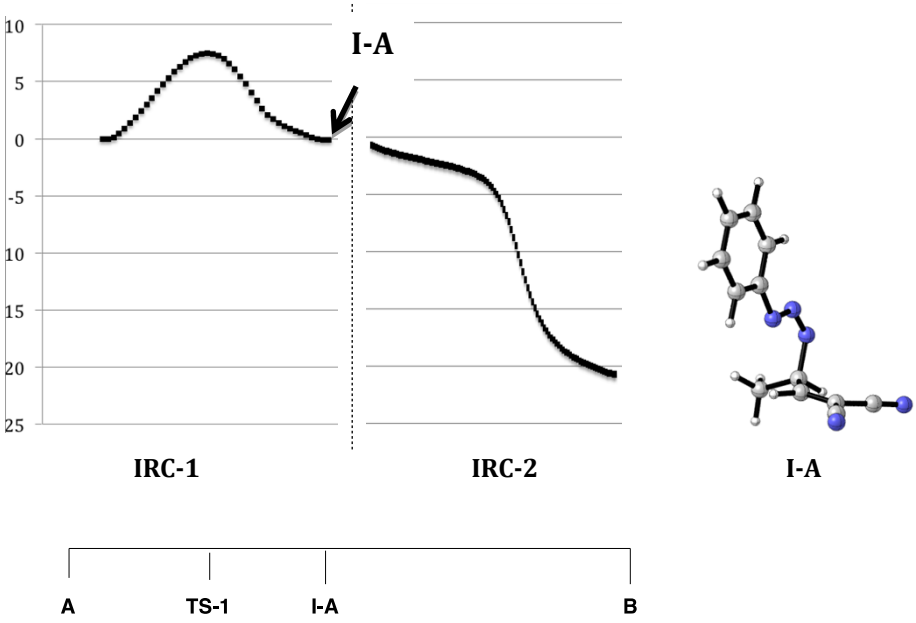

Figure S3. IRC obtained for the process from **A** ⇨ **TS-1** ⇨ **B**. The units of IRC are [amu$^{1/2}$ bohr] and Energy (kcal mol^{-1}) on x- and y-axis, respectively.

[5] Lopez, S. A.; Munk, M. E.; Houk, K. N. *J. Org. Chem.* **2013**, *78*, 1576.

We have examined the regioselectivity applying the general distortion/interaction theory proposed by Houk and Ess.[6] The distortion/interaction model divides the activation energy ($\Delta E^{\ddagger}$) of a 1,3-dipolar reaction in two parts: the energy required to distort the fragments (dipole and dipolarophile) ($\Delta E_d^{\ddagger}$), and the interaction energy ($\Delta E_i^{\ddagger}$) between them. The activation energy is $\Delta E^{\ddagger} = \Delta E_d^{\ddagger} + \Delta E_i^{\ddagger}$. The relationship between $\Delta E^{\ddagger}$, $\Delta E_d^{\ddagger}$, and $\Delta E_i^{\ddagger}$ of the reaction components on the reaction studied in this work can be visualized on the Figure S4.

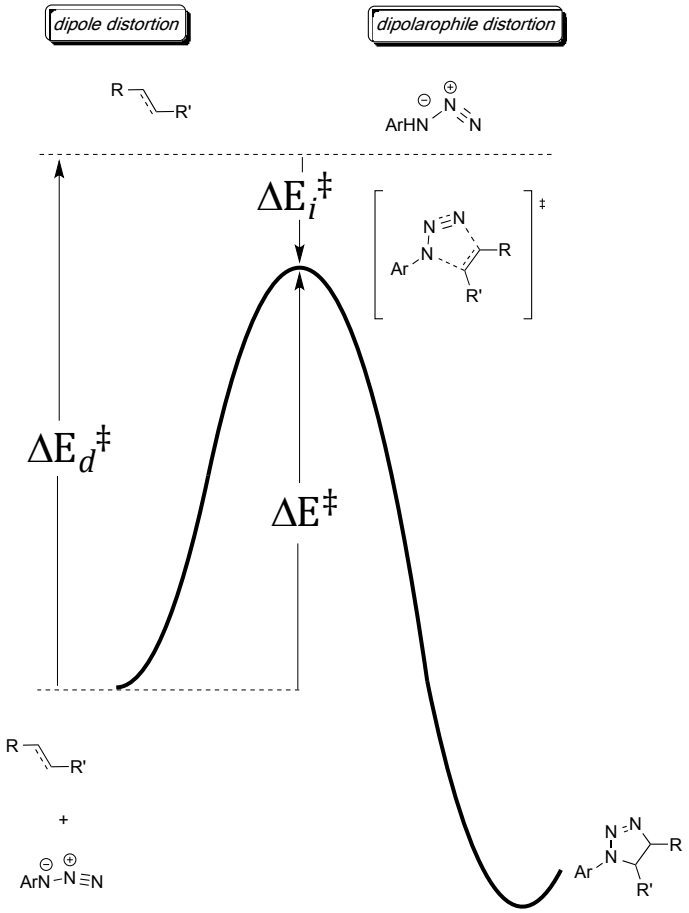

Figure S4. Relation between $\Delta E^{\ddagger}$, $\Delta E_d^{\ddagger}$, and $\Delta E_i^{\ddagger}$ of the reaction components on the reaction studied in this work.

The distortion/interaction energy of **TS-1** and **TS-2** are depicted on Table S1.

[6] (a) Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 10646. (b) Ess, D. H.; Houk, K. N. *J. Am. Chem. Soc.* **2008**, *130*, 10187.

Table S1. B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d,p) IEF-PCM (DMSO) Free Energies: Electronic activation ($\Delta E^{\ddagger}$), distortion ($\Delta E_d^{\ddagger}$), and interaction energies ($\Delta E_i^{\ddagger}$) for the reaction between PhN_3 and vinylogous carbanion. Energies in kcal mol^{-1}.

	$\Delta E^{\ddagger}$	$\Delta E_d^{\ddagger}$ (total)	$\Delta E_d^{\ddagger}$ (azide)	$\Delta E_d^{\ddagger}$ (dipolarophile)	$\Delta E_i^{\ddagger}$
TS-1	23.5	69.3	66.7	2.6	–45.8
TS-2	35.1	70.4	65.6	4.8	–35.2

Analyzing the Table S1, we observe that the $\Delta\Delta E_d^{\ddagger}$ (total) between **TS-1** and **TS-2** is very small (1.1 kcal mol^{-1}). We can conclude that the exclusive formation of **3l** arises from the more favorable HOMO-LUMO interaction, in which the $\Delta\Delta E_i^{\ddagger}$ is 10.6 kcal mol^{-1}. As described previously by FMO theories of cycloaddition reactions, the regioselectivity are driven by the match between the largest HOMO-LUMO coefficients. In Figure S5, we can see that this reaction proceeds by an inverse electron-demand. The LUMO of the azide has the largest coefficient on the N terminus, bonding to nucleophilic γ carbon of vinylogous carbanion with the largest HOMO.

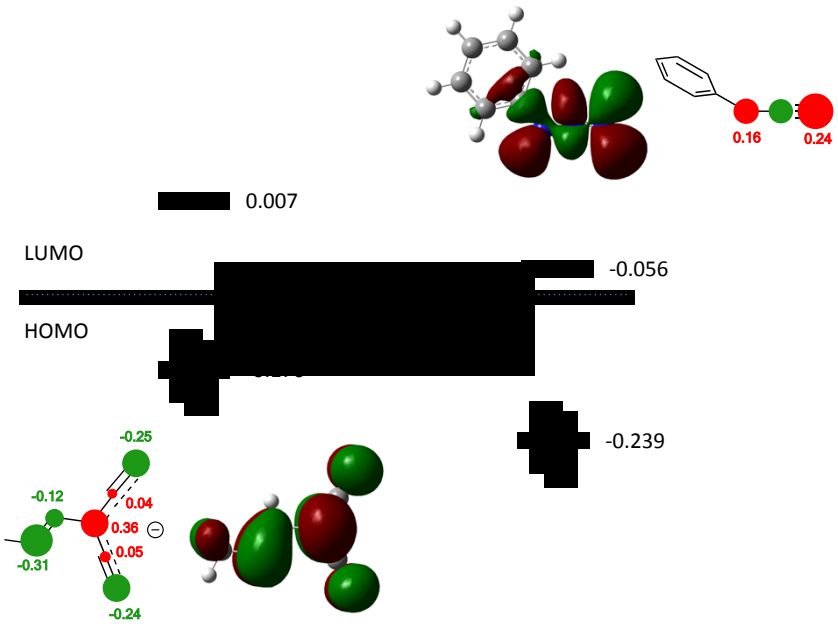

Figure S5. FMO diagram for the reaction between PhN_3 and vinylogous carbanion.

Finally, distortion energy also reinforces the preference on regiosselectivity, because the unfavorable transition state presented the higher distortion energy ($\Delta E_d^{\ddagger}$).

Table S1. Energies (Hartree) obtained for the concerted and stepwise mechanism of cycloadditions of PhN_3 to vinylogous carbanion.

	B3LYP/6-31+G(d,p)		B3LYP/ 6-311+G(d,p)	
	E (Hartree)	**Gibbs Free Energy Correction (Hartree)**	***Single-point* (Hartree)**	**Negative Frequencies (cm^{-1})**
aldehyde	-193.169762037	0.056903	-193.213573500	-
malonitrile	-225.003872899	0.016966	-225.056238359	-
base	-307.267106589	0.136505	-307.328470723	-
base-H^+	-307.743174014	0.152122	-307.804031092	-
H_2O	-76.442198260	0.002900	-76.466280921	-
PhN_3	-395.865111253	0.071308	-395.947174606	-
1	-341.734477179	0.072474	-341.807831468	-
A	-341.263808437	0.059425	-341.338857202	-
TS-1	-737.113388298	0.150151	-737.267947121	-290.10
TS-2	-737.095977221	0.151306	-737.250634695	-347.57
TS-3	-737.110261913	0.150649	-737.264489646	-320.82
B	-737.161132727	0.157952	-737.312785374	-
C	-737.614375363	0.170258	-737.765113073	-
D	-737.125767106	0.154013	-737.278400957	-
B'	-737.160725266	0.157626	-737.312380073	-
C'	-737.618683637	0.171501	-737.769279405	-
3l	-512.641844072	0.130521	-512.740720792	-
3l'	-512.640718300	0.131182	-512.739702800	-

CARTESIAN COORDINATES

aldehyde

C	1.43102800	-0.52734900	0.00000300
H	1.24754800	-1.14523700	-0.88390100
H	1.24769100	-1.14518900	0.88397100
H	2.48538500	-0.23700600	-0.00009000
C	0.54046100	0.71276700	0.00004200
H	0.73899200	1.35706400	0.86975900
H	0.73885900	1.35702500	-0.86973500
C	-0.93835300	0.44428100	0.00018100
H	-1.58057500	1.34828200	-0.00015200
O	-1.45255800	-0.66294600	-0.00010800

malonitrile

C	-3.00494400	1.11718800	0.04329900
H	-2.63006100	0.08727400	0.02698500
H	-2.63027400	1.61729700	-0.85740500
C	-2.48108200	1.80329800	1.23157300
N	-2.04771700	2.34040500	2.16330300
C	-4.47313600	1.09861800	0.01199100
N	-5.63154300	1.07397000	-0.03146100

base

N	3.93993800	-2.45237400	-0.43872600
C	3.34819100	-3.75030500	-0.09857100
H	3.03369700	-4.27731400	-1.01242400
H	4.07824300	-4.37773800	0.42441200
H	2.47368800	-3.63261900	0.53589200
C	4.97438000	-2.57564400	-1.46480000
H	4.56833700	-2.86443200	-2.44703800
H	5.53315700	-1.64513500	-1.57163000
H	5.67869300	-3.35201900	-1.15088800
C	3.15055500	-1.29407500	-0.38373800
N	2.45012100	-0.91106600	0.63138500
C	2.54612800	-1.59092100	1.91587200
H	2.42633500	-0.84257400	2.70697000
H	1.73900200	-2.32290300	2.05543400
H	3.50369200	-2.10959900	2.06759400
C	3.15202300	-0.39513300	-1.60368000
H	2.39103900	0.37491000	-1.47443800
H	4.11947300	0.10347200	-1.72976100
H	2.95241800	-0.95654100	-2.52273300

base-H^+

N	3.79509400	-2.48616700	-0.64784500
H	1.90839100	-0.17594000	0.53144700
C	3.45249200	-3.73992900	0.04608000

H	3.47294900	-4.53873400	-0.69829100
H	4.17617800	-3.97319300	0.83092500
H	2.44864600	-3.69111600	0.45879700
C	4.80537000	-2.65546700	-1.70608400
H	4.35378400	-3.10222400	-2.59756100
H	5.27255900	-1.70794500	-1.96254800
H	5.57838000	-3.32564500	-1.32572400
C	3.16751200	-1.32801300	-0.46727900
N	2.42587800	-1.04109300	0.60449600
C	2.41885500	-1.64725300	1.94223100
H	2.25066100	-0.84220400	2.65864700
H	1.62261700	-2.38651300	2.05386800
H	3.38404500	-2.10307500	2.15792500
C	3.28148700	-0.24416000	-1.50587200
H	2.50870800	0.51016900	-1.35186800
H	4.25182800	0.25561500	-1.42071000
H	3.18469900	-0.64723800	-2.51490500

H_2O

O	-1.66085600	2.14586600	0.00000000
H	-0.69492700	2.18415200	0.00000000
H	-1.94720000	3.06917100	0.00000000

Ph-N_3

N	-0.12804600	0.13942900	0.32514200
N	0.66192300	0.15390700	-0.62485900
N	1.47901600	0.24693200	-1.41617900
C	-1.36531900	-0.55107300	0.17734400
C	-2.21635700	-0.52561400	1.29052300
C	-1.74610000	-1.22685100	-0.99106500
C	-3.44882200	-1.17670000	1.23198700
H	-1.90389700	0.00212800	2.18578500
C	-2.98303300	-1.87431100	-1.03568200
H	-1.09026600	-1.25020900	-1.85617800
C	-3.83862700	-1.85334400	0.07049000
H	-4.10513800	-1.15421300	2.09667300
H	-3.27559300	-2.39648600	-1.94172000
H	-4.79827500	-2.35872900	0.02778000

1

C	2.85307400	-0.57459000	0.57117200
H	2.95546800	-1.66365700	0.53842400
H	2.54480200	-0.28702600	1.58050600
H	3.83362900	-0.13354900	0.37258400
C	1.84053600	-0.07582000	-0.48083100
H	1.76838900	1.01511200	-0.45863900
H	2.20257200	-0.35879700	-1.47942100
C	0.50133200	-0.70318900	-0.30644700
H	0.46000100	-1.79047000	-0.32322000

C	-0.67367600	-0.04789600	-0.12170000
C	-1.90972200	-0.76254200	0.03531700
N	-2.91294300	-1.33781300	0.16248500
C	-0.76348200	1.38553100	-0.07395300
N	-0.85184000	2.54475400	-0.03207600

A

C	-0.70033600	-0.05971200	0.00016600
C	-1.78019700	-0.95419900	-0.00187300
N	-2.67822600	-1.71763800	-0.00358600
C	-0.99148100	1.31264000	0.00316200
N	-1.20171100	2.47140000	0.00566900
C	0.67732800	-0.55173800	-0.00098100
H	0.75571000	-1.64015300	-0.00315500
C	1.81845000	0.17133700	0.00024800
H	1.75567400	1.25933900	0.00215800
C	3.20604500	-0.43584600	-0.00027000
H	3.97247200	0.34532900	-0.00987100
H	3.39229800	-1.05665900	0.88622300
H	3.38489000	-1.07149300	-0.87764200

TS-1

C	0.68273300	-0.85092600	0.84206700
C	-0.65178200	-1.17868600	0.60786200
H	0.91423600	0.17145600	1.12754600
H	-0.89282900	-2.23708100	0.53602500
C	-1.77101400	-0.28699200	1.09403400
H	-2.66328300	-0.39786300	0.46920600
H	-2.05988100	-0.54309500	2.12228100
H	-1.47513000	0.76698200	1.08254100
N	-0.88749900	-0.98788200	-1.44701800
N	-0.34160400	-0.04134300	-1.91832000
N	0.44410800	0.89739700	-1.51830000
C	1.80115200	-1.72037900	0.73026000
C	1.66525300	-3.08627400	0.38930900
C	3.11232200	-1.23787000	0.94360600
N	4.19597400	-0.82793800	1.12463400
N	1.53840800	-4.21769800	0.11087100
C	0.83811200	1.82850000	-2.49842900
C	0.44400700	1.79905600	-3.85232400
C	1.69451000	2.86050800	-2.06767600
C	0.89882000	2.77629400	-4.73928400
H	-0.21571500	1.01050000	-4.20074000
C	2.14338900	3.83231800	-2.96258900
H	2.00026800	2.88595800	-1.02571000
C	1.75026600	3.79989200	-4.30597400
H	0.58400600	2.73609700	-5.77886300
H	2.80398900	4.61864200	-2.60745400
H	2.10019400	4.55653700	-5.00165200

TS-2

C	0.74283600	-0.79798500	0.78546400
C	-0.57392400	-1.27555300	0.84316300
H	0.92472600	0.20852200	1.14792100
H	-0.72194100	-2.34882800	0.91851800
C	-1.69297100	-0.40839500	1.35522500
H	-2.66125900	-0.70733300	0.94326600
H	-1.76600900	-0.49449000	2.44820500
H	-1.52395800	0.64623000	1.11565500
N	-0.32125800	-0.41572500	-1.71746800
N	0.55439900	0.20844400	-1.21400000
C	1.92322300	-1.64925000	0.68106600
C	1.83320200	-3.02210900	0.40276600
C	3.20650400	-1.09653600	0.81391600
N	4.27521800	-0.61748500	0.93628300
N	1.74136500	-4.17424500	0.17922100
N	-1.05790900	-1.37512500	-1.26321300
C	-2.32092500	-1.61651100	-1.82939400
C	-2.99943100	-2.77255000	-1.40018200
C	-2.94440200	-0.75907000	-2.75783800
C	-4.27719900	-3.05745400	-1.88304400
H	-2.51711300	-3.43927700	-0.69244200
C	-4.21511600	-1.06559300	-3.24629000
H	-2.42558000	0.13160000	-3.09725900
C	-4.89319900	-2.21038400	-2.81120300
H	-4.78824000	-3.95213700	-1.53901800
H	-4.67964200	-0.40014100	-3.96870300
H	-5.88350900	-2.43993500	-3.19217200

TS-3

C	-0.80023700	-1.00230900	0.18445900
C	0.34516700	-1.25405400	0.94781800
H	-1.27121300	-1.86246700	-0.29094700
H	0.77626000	-0.41181500	1.48768400
C	0.55786300	-2.61980000	1.55886000
H	1.61663100	-2.79297300	1.77472300
H	0.00377400	-2.72253400	2.50094600
H	0.21668100	-3.41148100	0.88267000
N	1.72195900	-1.43426400	-0.52679700
N	2.38796800	-0.45038700	-0.68853800
N	2.39574600	0.76925400	-0.25574100
C	-1.41982300	0.23586800	-0.08842400
C	-1.05181500	1.43934000	0.56188700
C	-2.49514400	0.31452800	-1.00840700
N	-3.38695100	0.37256700	-1.76557200
N	-0.76411000	2.43043800	1.11405800
C	3.48265100	1.54220700	-0.71042500
C	4.50791000	1.08725300	-1.56672100

C	3.53045200	2.87557200	-0.25701800
C	5.54134400	1.94431700	-1.94872900
H	4.48702500	0.06422700	-1.92901100
C	4.56799500	3.72456800	-0.64412500
H	2.74307300	3.23064700	0.40164500
C	5.58339300	3.26782400	-1.49319300
H	6.32089500	1.57333500	-2.60936200
H	4.58222800	4.74861200	-0.28051000
H	6.39022400	3.92906200	-1.79467800

B

C	-0.06919200	0.36424800	0.30431800
C	-1.55884000	0.16178400	0.69947500
H	0.48755700	0.80770900	1.13530000
H	-1.84037300	-0.89229000	0.60747500
C	-1.91105400	0.66044400	2.10261900
H	-2.98273000	0.54860900	2.29201800
H	-1.36568300	0.08020100	2.85406800
H	-1.64598100	1.71660100	2.21964800
N	-2.33703500	0.91991500	-0.31572000
N	-1.56507600	1.58193200	-1.05685900
N	-0.25639800	1.39962800	-0.75566500
C	0.66922000	-0.87334700	-0.15822600
C	0.13469500	-1.67989000	-1.16766800
C	1.90114500	-1.21305700	0.40387100
N	2.93819600	-1.47795300	0.89968100
N	-0.34246900	-2.33857400	-2.02086200
C	0.73880800	2.10171700	-1.45391700
C	2.07332000	2.05319300	-1.01283100
C	0.41872700	2.87215400	-2.58932900
C	3.06273400	2.76533500	-1.69559500
H	2.34595000	1.46543000	-0.14512200
C	1.41824700	3.57976000	-3.25606300
H	-0.60542000	2.91287900	-2.93857500
C	2.74745800	3.53331900	-2.81927300
H	4.08739000	2.71479400	-1.33857000
H	1.15238600	4.16958400	-4.12882600
H	3.52068900	4.08394800	-3.34591200

C

C	0.00683000	0.30889800	0.28666200
C	-1.44690400	0.17706100	0.80271800
H	0.69363100	0.64658000	1.06350800
H	-1.76999900	-0.86679300	0.85104600
C	-1.70122000	0.85161100	2.15289000
H	-2.76754800	0.81727100	2.39063900
H	-1.15253400	0.32887400	2.94195100
H	-1.38146600	1.89801400	2.13498700
N	-2.25459500	0.85838700	-0.25065400

N	-1.50986700	1.48821700	-1.03476800
N	-0.17970100	1.30431800	-0.76153000
C	0.79260400	2.11265200	-1.40464700
C	1.96192800	2.48846500	-0.72877900
C	0.57150500	2.55150500	-2.71956800
C	2.90848500	3.28793100	-1.37364300
H	2.14037200	2.16820600	0.29175700
C	1.51636400	3.36617500	-3.34424000
H	-0.33058100	2.25360800	-3.24116300
C	2.69141200	3.73436900	-2.67990400
H	3.81324800	3.56862700	-0.84305700
H	1.33679600	3.70194800	-4.36118600
H	3.42811900	4.35927200	-3.17481500
C	0.52956100	-1.06040300	-0.30815200
H	-0.19800400	-1.40452000	-1.05494900
C	1.83685700	-0.97147000	-0.98121500
N	2.86339100	-0.93181300	-1.51953100
C	0.60058800	-2.07979800	0.75328500
N	0.63513400	-2.86372800	1.60754700

D

C	-0.73597200	-0.65536500	0.74751800
C	0.70968600	-0.80616300	1.05928800
H	-1.26755100	-1.58006400	0.53012200
H	1.16663800	0.17197500	1.24305000
C	0.92026800	-1.74097300	2.25643000
H	1.99371400	-1.88246800	2.41808600
H	0.48128600	-1.32319400	3.16834900
H	0.47093500	-2.72211200	2.06940600
N	1.33535000	-1.47233800	-0.13951900
N	1.70802000	-0.72009400	-1.12173300
N	1.46182200	0.56426200	-1.10427000
C	-1.45765400	0.50043100	0.66512000
C	-0.91686200	1.78780700	0.98554100
C	-2.83748500	0.47974000	0.27935100
N	-3.96053700	0.46066500	-0.03083200
N	-0.51703100	2.84586300	1.26255100
C	2.00577200	1.25311700	-2.20148500
C	2.81820900	0.69188300	-3.21662700
C	1.71777500	2.63418000	-2.28168700
C	3.30483100	1.48368300	-4.25788900
H	3.06188000	-0.36360100	-3.17700600
C	2.20954600	3.41852000	-3.32572300
H	1.09999200	3.07618700	-1.50488800
C	3.00847400	2.85174100	-4.32689900
H	3.92670400	1.02708600	-5.02467700
H	1.96772200	4.47809200	-3.35740400
H	3.39328100	3.46060100	-5.13986400

B'

C	-0.016331	0.192274	0.107553
C	-1.467897	0.015191	0.632607
H	0.636991	0.561196	0.904646
H	-1.807093	-1.013649	0.481663
N	-2.290205	0.880816	-0.289440
N	-1.546963	1.552219	-1.046376
N	-0.224437	1.258349	-0.889202
C	0.754877	2.036858	-1.524856
C	2.102585	1.933027	-1.135655
C	0.406800	2.927605	-2.560057
C	3.077591	2.706427	-1.771202
H	2.396703	1.260275	-0.338753
C	1.391929	3.694709	-3.179773
H	-0.627627	3.012386	-2.868881
C	2.734416	3.592278	-2.795143
H	4.112233	2.611884	-1.454280
H	1.104538	4.376361	-3.975375
H	3.495900	4.190520	-3.285555
C	0.560435	-1.085102	-0.509835
H	1.552854	-0.920220	-0.937740
H	0.648121	-1.854881	0.263947
H	-0.098270	-1.461145	-1.299277
C	-1.708965	0.380472	2.078599
C	-1.232829	1.591671	2.591334
N	-0.805510	2.611320	3.000509
C	-2.514235	-0.426845	2.886345
N	-3.185687	-1.128376	3.555579

C'

C	-0.043548	0.121264	0.087214
C	-1.496289	-0.081140	0.568485
H	0.623795	0.399700	0.907740
H	-1.825510	-1.117311	0.465315
C	-1.747125	0.373380	2.048437
H	-1.422459	1.416578	2.157587
N	-2.318963	0.789198	-0.313611
N	-1.560886	1.525963	-1.004045
N	-0.255935	1.291450	-0.797950
C	0.732550	2.049552	-1.463752
C	2.064964	1.992201	-1.026207
C	0.390942	2.869714	-2.553168
C	3.043219	2.748649	-1.676489
H	2.346154	1.372067	-0.182845
C	1.378195	3.624968	-3.184894
H	-0.635435	2.911003	-2.896232
C	2.709256	3.570079	-2.755585
H	4.069972	2.694018	-1.327534
H	1.102438	4.255290	-4.025140

H	3.472711	4.156930	-3.256347
C	0.514474	-1.086468	-0.671116
H	1.499813	-0.869813	-1.089851
H	0.612990	-1.932544	0.015471
H	-0.155638	-1.373927	-1.486850
C	-0.965547	-0.438849	2.997078
N	-0.324549	-1.079700	3.720821
C	-3.178163	0.314544	2.395959
N	-4.303754	0.267109	2.670777

3l

C	-2.72228400	0.16053600	0.07081500
C	-1.51117200	0.77901900	0.30499400
N	-0.57025500	-0.13991100	-0.05017700
H	-1.25931700	1.74840100	0.70428100
C	0.85179000	-0.02426600	-0.01293400
C	1.62595200	-1.14869800	0.29250500
C	1.45208700	1.20959000	-0.28449900
C	3.01673000	-1.03040900	0.32204600
H	1.14197800	-2.09390200	0.50874800
C	2.84376800	1.31756900	-0.23605200
H	0.84473500	2.07010500	-0.54406700
C	3.62922600	0.20024600	0.06324200
H	3.62018100	-1.90104900	0.55925000
H	3.31128600	2.27454500	-0.44546500
H	4.71076000	0.28765700	0.09422700
N	-1.16505800	-1.27483000	-0.48715600
N	-2.45925100	-1.09249600	-0.41266600
C	-4.11478300	0.66586600	0.27707900
H	-4.66527800	0.02471300	0.97322200
H	-4.10122500	1.67972600	0.68376500
H	-4.66906000	0.68375100	-0.66714700

3l'

C	0.793203	1.116765	-0.246870
C	2.149145	1.220380	0.003748
N	0.312806	2.349886	0.094062
H	2.917227	0.471160	-0.119740
C	-1.033144	2.836943	0.072545
C	-1.593380	3.335961	1.252574
C	-1.759408	2.826848	-1.121815
C	-2.899728	3.829450	1.232312
H	-1.011754	3.331787	2.167931
C	-3.069992	3.310775	-1.127600
H	-1.303619	2.459373	-2.034876
C	-3.640576	3.813482	0.045943
H	-3.339329	4.218546	2.145371
H	-3.638339	3.304232	-2.052341
H	-4.657669	4.192900	0.035628

N	1.317572	3.158734	0.532268
N	2.425457	2.468577	0.472683
C	-0.036838	-0.025927	-0.731972
H	-0.938384	-0.149947	-0.124493
H	-0.349589	0.109266	-1.772242
H	0.547538	-0.946465	-0.674442