Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Mechanistic Understanding of Methane to Methanol Conversion on Graphene-Stabilized Single-Atom Iron Centers

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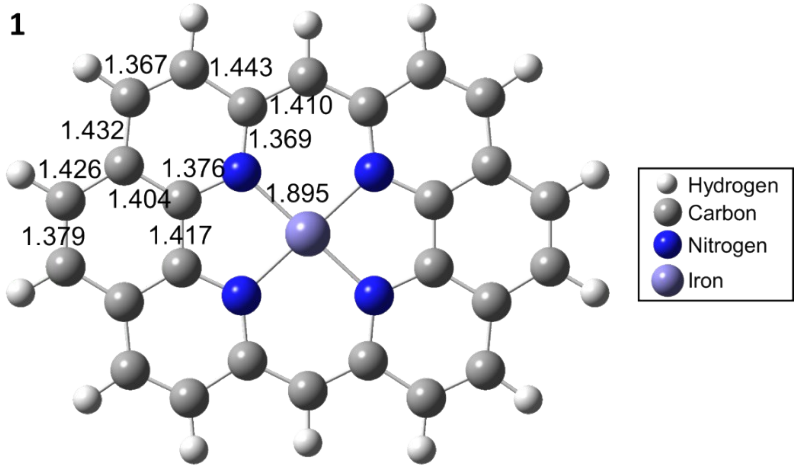

Figure S1. Optimized FeN_4/GN catalyst structure in the ground spin state (triplet) with each bond length shown in Å.

Active site formation

Formation energy profiles of 5 different active centers (mono-oxo, di-oxo, mono-hydroxy, di-hydroxy, and hydroxy(oxo)) from the bare FeN_4/GN catalyst at different spin states are shown in Figure S2. The ground spin state for the FeN_4/GN is triplet as it exhibits lower energy than that of structures in singlet and quintet states by 1.34 and 0.74 eV, respectively. After an initial oxidation, which is highly exothermic in triplet (-1.71 eV), the Fe center can be further oxidized (forming a di-oxo center) or hydroxylated (hydroxy(oxo) center), where the former is endothermic (0.30 eV) while the latter is slightly exothermic (-0.07 eV). Between the isoenergetic triplet and quintet di-oxo FeN_4/GN structures, the triplet one is chosen as a reference in the reaction pathways investigation (in consistency with the mono-oxo case). Also, the hydroxy(oxo) catalysts are at the same energy level in doublet and quartet, and the lower spin state (doublet) is considered as a ground state. The hydroxy(oxo) centers can also be formed by initial hydroxylation followed by oxidation, but not presented here since oxidation is preferred as an initial step. Two consecutive exothermic hydroxylations on the Fe center leads to mono-hydroxy (quartet) and di-hydroxy center (triplet).

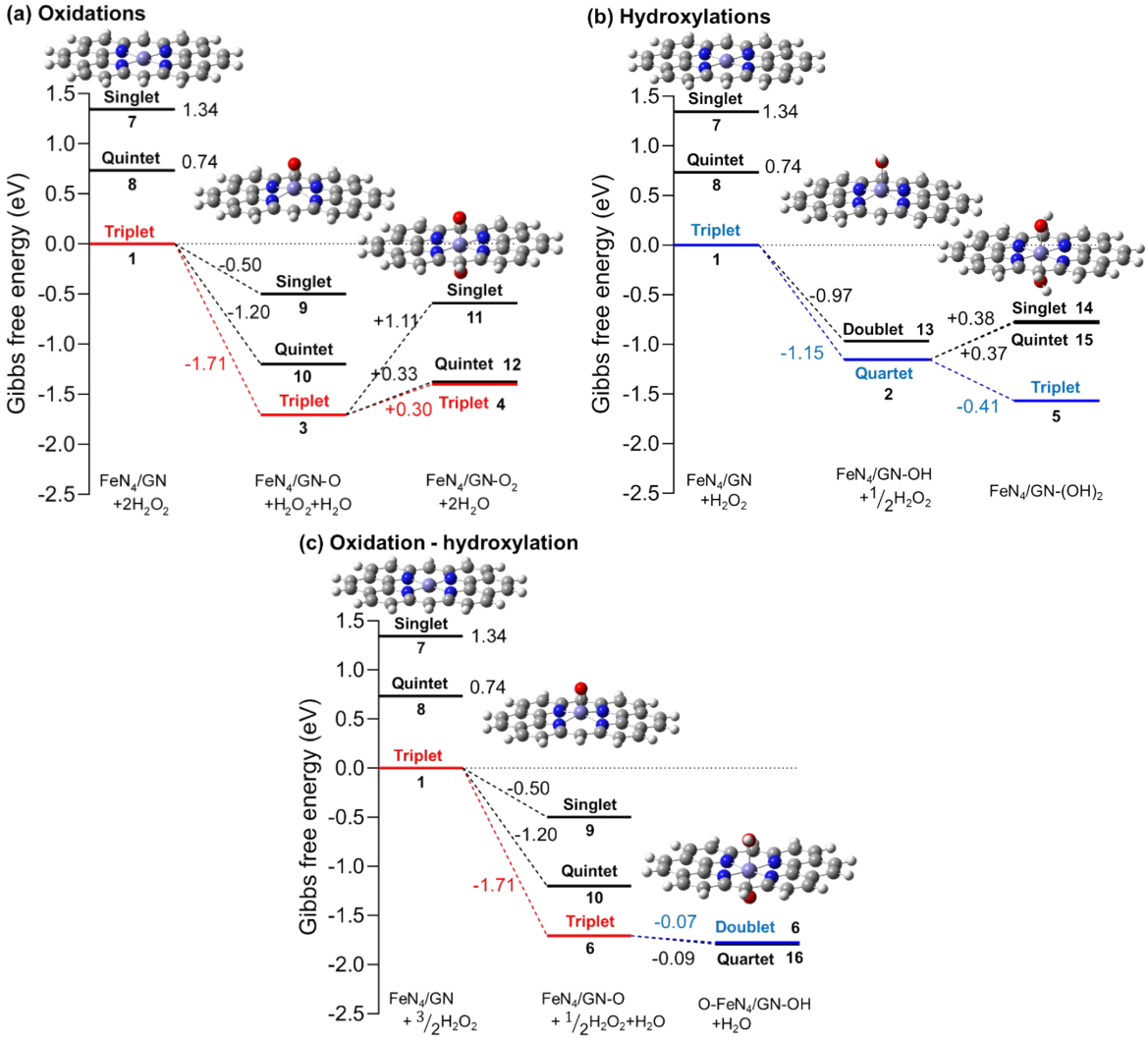

Figure S2. Detailed free energy profiles of formation of various active centers by (a) oxidation, (b) hydroxylation, and (c) initial oxidation followed by hydroxylation. The ground states are highlighted with colors, where red and blue stand for oxidation and hydroxylation steps, respectively.

Triplet di-oxo FeN_4/GN

The methane conversion to methanol on the di-oxo catalyst in the triplet spin state following path 1c is presented in Figure S3. The initially produced methyl radical via homolytic C-H activation by the reactive O site (TS 1) is stabilized by one of the N atoms surrounding the Fe center with a reaction barrier that is comparable to that of the first C-H cleavage (0.75 eV, TS 6). The methyl group bonded on N then reacts with the hydroxyl ligand to produce methanol. The energy barrier for this step is significantly high (1.34 eV, TS 7) as the strong C-N bond stabilizes the intermediate, which makes this pathway unfavorable. After the methanol desorption, the remaining steps are the same as in path 1a (steps 19-3-20-TS3-21-4).

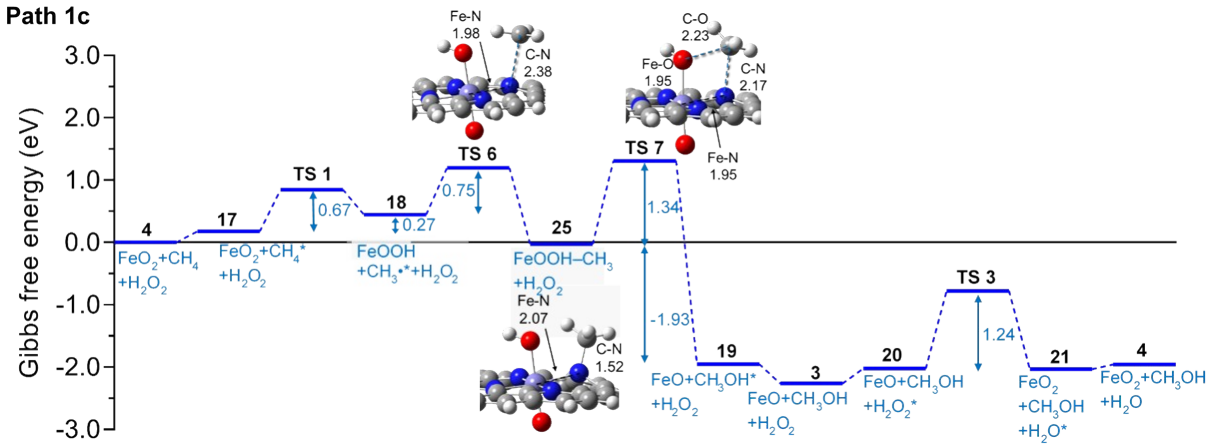

Figure S3. Detailed free energy profile of methane conversion to methanol by the di-oxo FeN_4/GN catalyst (triplet state) following path 1c. "Fe" on the profiles stands for FeN_4/GN catalyst structure, and "TS" represents a transition state. Asterisk (*) denotes adsorbed species on the catalyst surface. The first four steps are identical with those in path 1a and 1b. Select interatomic distances (in Å) are shown on the molecular structures.

Singlet di-oxo FeN_4/GN

The methane conversion to methanol on the di-oxo catalyst in the singlet spin state was investigated as presented in Figure S4. This is a concerted mechanism because the methane activation and methanol production occur simultaneously via a single step, as the primary C-H bond of CH_4 is elongated while the active O forms bonds with both of C and H (TS 8). Thereafter, the produced methanol is desorbed, and the active O site is regenerated by H_2O_2 (TS 9). The reaction barrier of this step (1.18 eV) is comparable with that of the same step found on the di-oxo center in the triplet spin state (1.24 eV, TS 3). The high energy barrier for the CH_4 activation (1.38 eV, TS 8) makes the concerted pathway unfavorable, as also reported by Cui et al.[1]

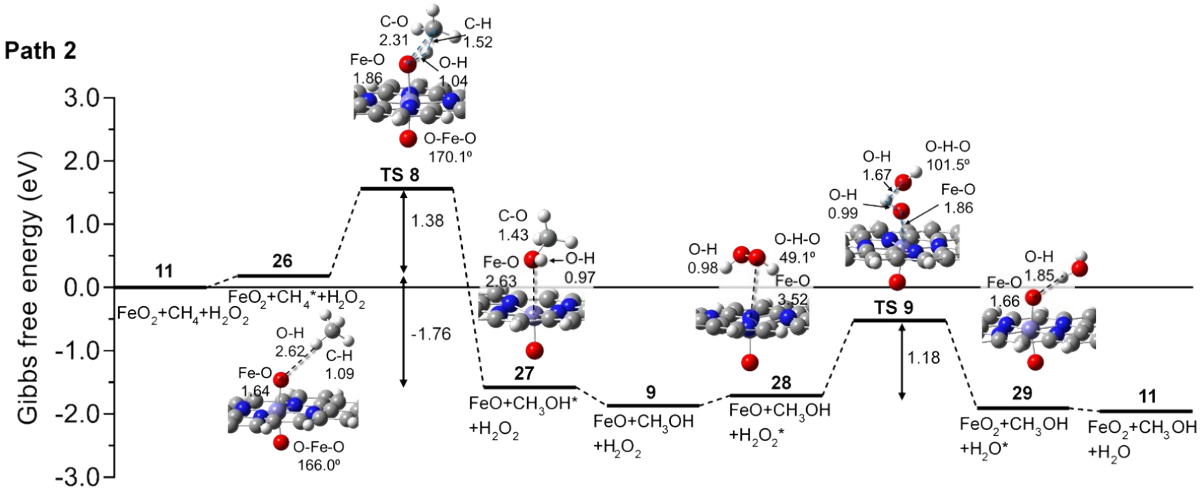

Figure S4. Detailed free energy profile of methane conversion to methanol by the di-oxo FeN_4/GN catalyst (singlet state). Select interatomic distances (in Å) are shown on the molecular structures.

Doublet hydroxy(oxo) FeN_4/GN

The methane conversion to methanol on the di-oxo catalyst in the doublet spin state via a concerted mechanism was identified as presented. Mechanistically, this pathway is identical to path 2 (singlet di-oxo catalyst, Figure S4). The high energy barrier for the CH_4 activation (1.76 eV, TS 23) makes the pathway unfavorable

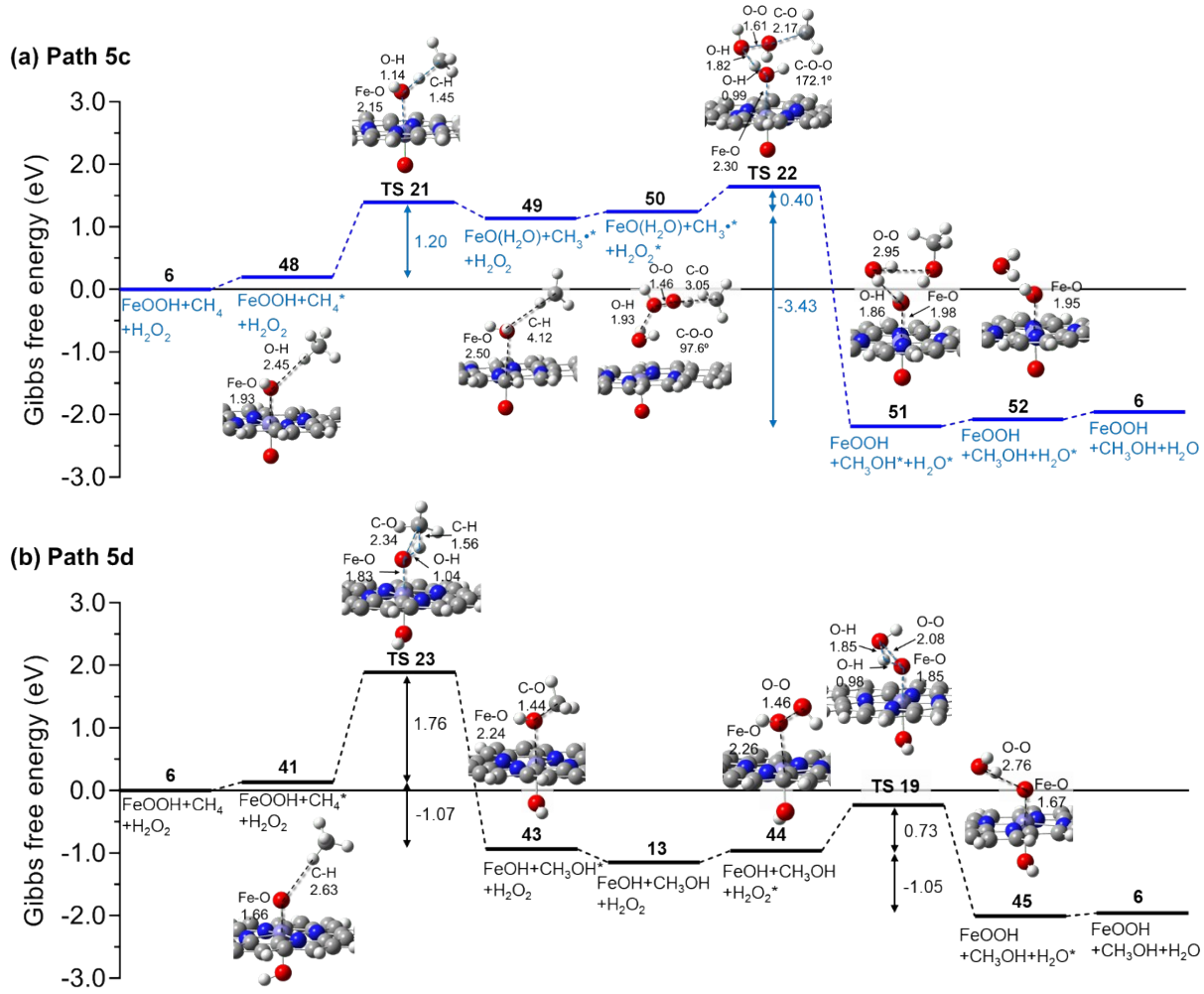

Figure S5. Detailed free energy profile of methane conversion to methanol by the hydroxy(oxo) FeN_4/GN catalyst (doublet state) following (a) path 5c and (b) path 5d. Select interatomic distances (in Å) are shown on the molecular structures.

Solvent effects

The solvent effects on three important pathways on the di-oxo and mono-oxo centers, i.e., path 1a, 1b, and 4, were investigated as presented in Figure S6. The computational detail and discussion regarding the results are found in the main manuscript.

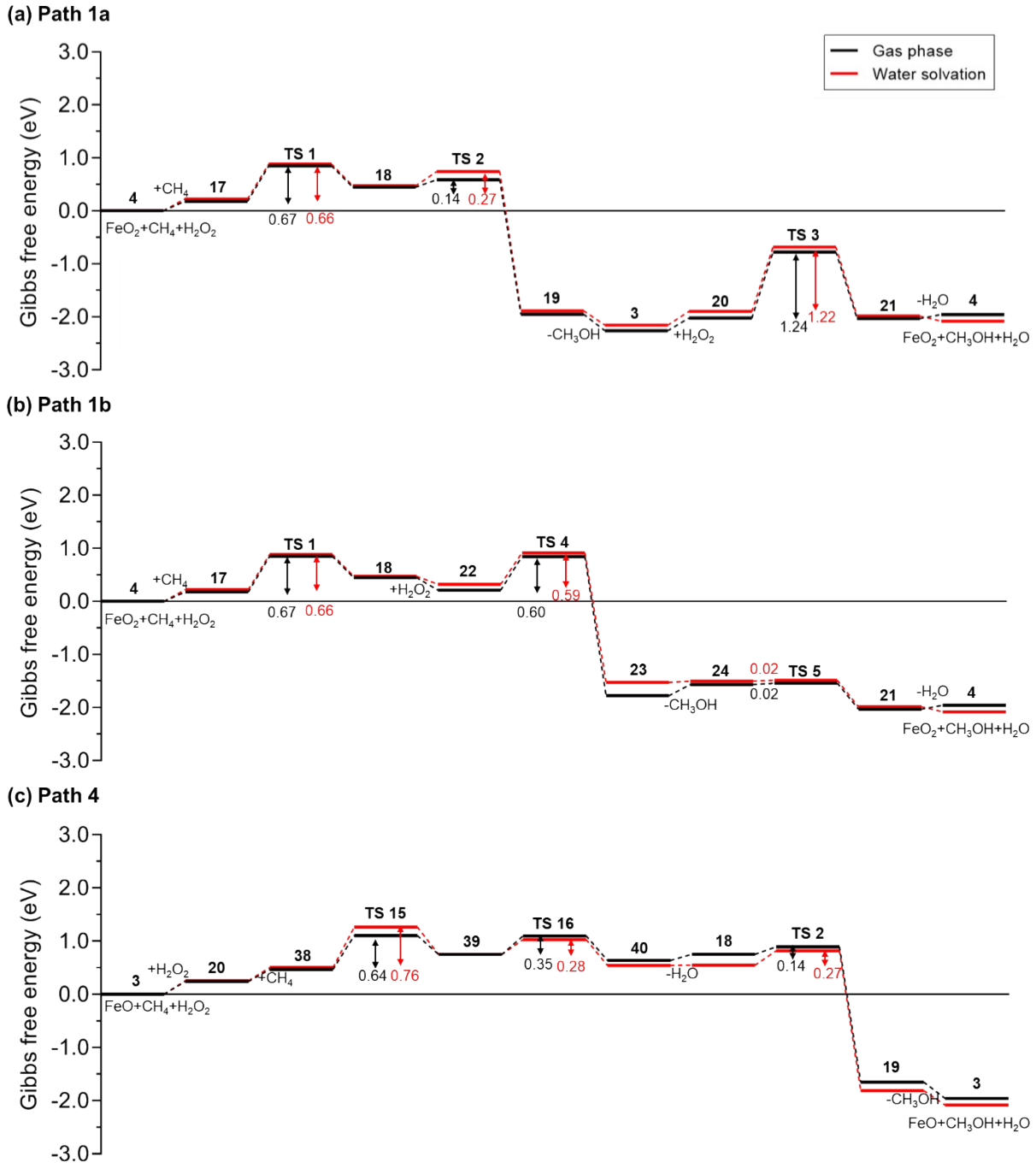

Figure S6. Free energy profiles of methane conversion to methanol by the di-oxo and mono-oxo FeN_4/GN catalysts on the gas phase (black) and in the presence of water solvent (red), following (a) path 1a and (b) path 1b, and (c) path 4

Validation of energy profiles with different DFT methods

In order to validate our DFT calculations at the B3LYP/6-31G(d) level of theory, we investigated three important pathways (path 1a, 1b, and 4) with a different functional using the same basis set (M062X[2]/6-31G(d)). The global hybrid Minnesota functional with a high percentage of Hartree-Fock exchange (M062X, 54 HF%) has been shown to describe the main-group chemistry and account for dispersion interactions accurately[2,3]. In path 1a, the activation energy for the C-H cleavage of an adsorbed CH_4 molecule becomes negligible (0.02 eV, TS 1), but it does not alter the overall energy penalty for C-H activation as the adsorption energy of methane significantly rises (0.75 eV). With the M062X functional, the barrier for the oxygen site recovery on the di-oxo catalyst increases (2.44 eV, TS 3), which makes the pathway more unlikely. The adsorption, intermediate and TS state energies in path 1b and 4 slightly change as well, so that these pathways become energetically slightly more demanding than the ones calculated with B3LYP. However, overall the results of Figure S7 demonstrate that the choice of functional (B3LYP vs. M062X) does not change the mechanistic scenarios and reactivity interpretation.

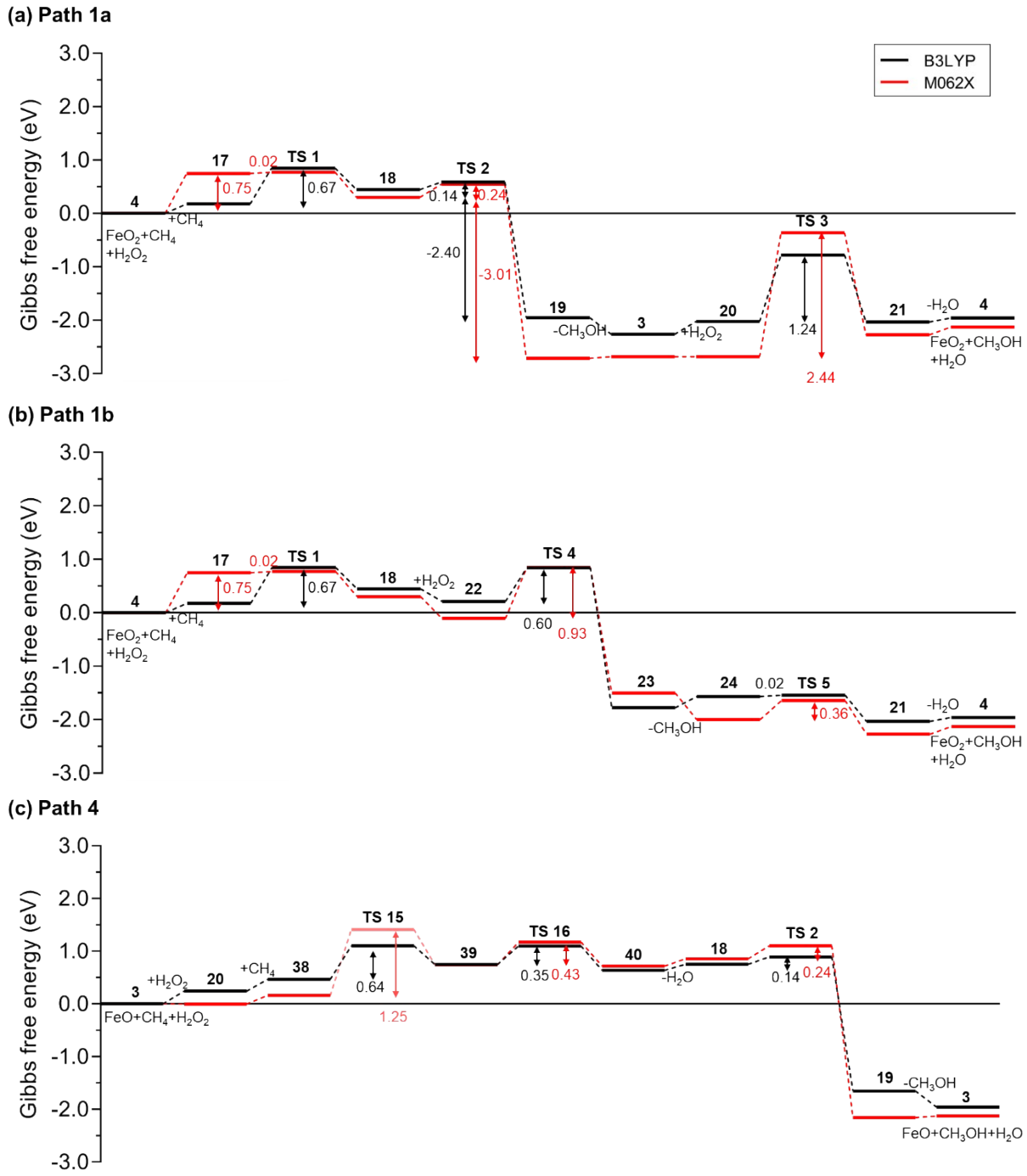

Figure S7. Free energy profiles of methane conversion to methanol by the di-oxo and mono-oxo FeN_4/GN catalysts in the gas phase following (a) path 1a, (b) path 1b, and (c) path 4, at the M062X/6-31g(d) level of theory (red) projected against the profiles calculated with B3LYP/6-31g(d) (black). The TS 15 at panel (c) was very difficult to be located at the M062X level and the energy value was obtained with partial optimization.

Structural Information

In this section, we provide the detailed information of the optimized structures of path 1b (H_2O_2-mediated mechanism on the di-oxo center) and path 4 (Fenton-type mechanism on the mono-oxo center). The order follows the order of reactions as presented in Figure 2(b) and Figure 3(c). The repeated structures are omitted for clarity. The number of imaginary frequencies is 1 if the structure is a transition state (TS), and 0 otherwise.

Path 1b

4
Electronic energy = -2632.297059 Hartree
Gibbs free energy = -2632.003731 Hartree
Charge = 0 Multiplicity = 3
Geometry =

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C	-1.28111600	2.65735800	-0.02884400
C	-2.48642400	3.44460400	0.00891600
C	-3.72318000	2.85560700	0.04635800
C	-3.84777000	1.43320000	0.05100800
H	-2.39366200	4.52637900	0.01010000
H	-4.61968100	3.46993000	0.07533100
C	-2.48640700	-3.44461200	0.00923900
C	-1.28109700	-2.65736400	-0.02866500
C	-2.62869200	-0.71909200	0.00769000
C	-3.84776100	-1.43320900	0.05116000
C	-3.72316100	-2.85562200	0.04668000
H	-2.39363400	-4.52638700	0.01053300
H	-4.61965800	-3.46994300	0.07577500
C	2.62869200	0.71909200	0.00768500
C	3.84776000	1.43321000	0.05114000
C	3.72316000	2.85562300	0.04661000
C	2.48640600	3.44461100	0.00913900
C	1.28109600	2.65736400	-0.02874300
H	4.61965600	3.46994700	0.07569000
H	2.39363400	4.52638600	0.01039600
C	2.48642500	-3.44460600	0.00905400
C	3.72318100	-2.85560600	0.04648600
C	3.84777000	-1.43319800	0.05108500
C	2.62868900	-0.71908000	0.00768300
C	1.28111800	-2.65735900	-0.02875000
H	2.39366200	-4.52638000	0.01028100
H	4.61968200	-3.46992500	0.07549200
Fe	0.00000000	0.00000000	-0.11324600
C	0.00000500	-3.26902100	-0.04340700
C	-0.00000400	3.26901900	-0.04351300
H	0.00001400	-4.35462100	-0.03799500
H	-0.00001300	4.35461900	-0.03814200
N	1.42128700	-1.31046300	-0.03608300
N	-1.42127800	-1.31046500	-0.03606900
N	-1.42128500	1.31045900	-0.03612300
N	1.42127600	1.31046200	-0.03610000
C	5.05843800	0.69188800	0.09270500
C	5.05844200	-0.69187200	0.09268700
H	6.00167600	-1.23083400	0.12564700
C	-5.05844200	0.69187400	0.09262300
C	-5.05844000	-0.69188600	0.09269100
H	6.00166700	1.23085600	0.12570100
H	-6.00167600	1.23083800	0.12555500
H	-6.00166900	-1.23085200	0.12569700
O	0.00000200	-0.00000900	-1.77941200
O	-0.00000300	0.00001000	1.70775900

17

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Gibbs free energy = -2672.487640 Hartree
Charge = 0 Multiplicity = 3
Geometry =

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C	3.83638000	2.85387400	0.11222400
C	3.95954700	1.43130900	0.12423700
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H	4.73002800	3.46757800	0.19381700
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C	1.39911400	-2.65726300	-0.11164900
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C	3.83239700	-2.85752500	0.10705000
H	2.50623600	-4.52713300	-0.01077700
H	4.72518500	-3.47262100	0.18757300
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C	-3.72269600	1.43706000	-0.32740900
C	-3.59705400	2.85928400	-0.32208900
C	-2.35980600	3.44735200	-0.28723000
C	-1.15493500	2.65925700	-0.25661900
H	-4.49330000	3.47426500	-0.34265200
H	-2.26650900	4.52901800	-0.27828200
C	-2.36453000	-3.44178200	-0.29420700
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C	-3.72466000	-1.42955300	-0.33023700
C	-2.50478900	-0.71616100	-0.30448300
C	-1.15860600	-2.65537400	-0.26195900
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H	-4.49805900	-3.46567700	-0.34972900
Fe	0.12708700	0.00109300	-0.27046900
C	0.12081900	-3.26789100	-0.20248200
C	0.12532500	3.26991800	-0.19617200
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H	0.12571900	4.35549500	-0.18980000
N	-1.29718800	-1.30834600	-0.27732300
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N	1.54225400	1.31030800	-0.10551600
N	-1.29537900	1.31243600	-0.27456800
O	0.01527900	-0.00057800	1.55431800
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C	-4.93530800	-0.68733900	-0.35569400
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C	5.16413400	-0.69478300	0.23497000
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H	-3.78463000	-0.11157100	3.09121900
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TS 1

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Gibbs free energy = -2672.463054 Hartree
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Geometry =

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C	-3.84583900	-1.35878100	-0.15325000
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H	-4.61880800	3.53517900	0.13711200
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C	3.84577900	-1.35826500	-0.15359700
C	3.72228700	-2.77801000	-0.25130300
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C	1.27827800	-2.57856700	-0.30227100
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C	1.28110800	2.72706000	-0.02310400
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O	-0.00018900	0.14171700	-1.88748100
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C	5.05777200	0.76141400	0.00569800
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C	-5.05809100	0.76073700	0.00618500
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H	-6.00156500	1.29692700	0.06596300
H	0.00126000	-0.82292700	2.23205000
C	0.00334200	-1.94434200	3.00845800
H	0.00144300	-1.52831100	4.01530100
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18

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C	3.91948000	1.46790900	0.06142800
H	2.42746300	4.53785600	-0.10204400
H	4.66286800	3.51499300	0.09185500
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C	1.41093500	-2.65910900	-0.06399000
C	2.73144200	-0.70116700	-0.00068900
C	3.95510000	-1.39675100	0.11857600
C	3.84951800	-2.82119500	0.13625300
H	2.54597400	-4.51067600	0.06384500
H	4.75150100	-3.42221700	0.22123900
C	-2.53456500	0.66512500	-0.28827400
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C	-1.21287400	2.61719700	-0.29281100
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H	-2.34552900	4.47368400	-0.32632500
C	-2.34232000	-3.49442200	-0.18947800
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C	-2.51710300	-0.77155400	-0.25463600
C	-1.14474000	-2.69340000	-0.18673600
H	-2.23679000	-4.57477000	-0.16428100
H	-4.47553300	-3.54588800	-0.22166600
Fe	0.10524100	-0.02098100	-0.28529300
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C	0.05988800	3.24632400	-0.25657500
H	0.15477200	-4.37430200	-0.09986500
H	0.04566500	4.33188000	-0.26471200
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N	1.50243700	1.30758600	-0.15632200
N	-1.33301300	1.26952100	-0.29282700
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O	0.18754000	-0.06373300	-1.93961700
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C	-4.94796900	-0.77366700	-0.27924800
C	5.13603900	0.74500200	0.18093700
C	5.15277000	-0.63826200	0.20686600
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H	-5.88485800	-1.32470100	-0.27861100
H	6.06912700	1.29743700	0.25385600
H	6.09963700	-1.16409600	0.29825500
C	-2.62252600	0.54550600	3.71289500
H	-3.49483200	-0.08157600	3.56411300
H	-2.61597800	1.23897000	4.54642100
H	-1.76922500	0.47830600	3.04257700
H	-0.00437600	-0.83034600	2.00881400

22

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Gibbs free energy = -2824.015073 Hartree
Charge = 0 Multiplicity = 3
Geometry =

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C	-2.36023500	-3.16887900	-1.04257700
C	-3.56432700	-2.51661800	-1.09637000
C	-3.62267200	-1.09889100	-0.96075300
H	-2.31596400	-4.24969200	-1.13314500
H	-4.48452100	-3.07824300	-1.23485400
C	-2.04811300	3.67114300	-0.31804800
C	-0.88309900	2.82472000	-0.29000700
C	-2.31348500	0.97177800	-0.62189200
C	-3.49249900	1.74693200	-0.65456500
C	-3.30428700	3.15305400	-0.49405300
H	-1.90745400	4.74082300	-0.19611400
H	-4.16850500	3.81252400	-0.51169400
C	2.83090800	-0.75891900	-0.14720200
C	3.99866100	-1.54670100	-0.02087300
C	3.80831100	-2.95259200	-0.18129400
C	2.55994400	-3.46009200	-0.42967700
C	1.41038900	-2.60076800	-0.54171200
H	4.66281900	-3.61964100	-0.09970100
H	2.41459600	-4.52998000	-0.54307800
C	2.88106200	3.38417900	0.27687200
C	4.07342200	2.72266300	0.40285900
C	4.13079400	1.30045200	0.27366400
C	2.89673900	0.66869400	0.00444500
C	1.65262100	2.67828000	0.01013800
H	2.83939300	4.46435600	0.37888600
H	4.98654400	3.27709000	0.60494200
Fe	0.27832100	0.12230400	-0.52990200
C	0.41476700	3.36141500	-0.08765000
C	0.11474900	-3.13190300	-0.77376400
H	0.46292300	4.43947800	0.02984100
H	0.06284100	-4.21184700	-0.87092200
N	1.73084000	1.33069700	-0.12185200
N	-1.08243600	1.49167900	-0.44655500
N	-1.20175000	-1.10413500	-0.74569500
N	1.61296700	-1.26948800	-0.40433000
O	0.07196200	-0.11342000	1.40425200
O	0.47931700	0.29121600	-2.15728600
C	5.22672200	-0.88729500	0.24864500
C	5.28975100	0.48808900	0.38948900
C	-4.79396000	-0.29735500	-0.98821100
C	-4.73050000	1.07627500	-0.84228300
H	6.13101800	-1.48203700	0.34642500
H	6.24447800	0.96505800	0.59552200
H	-5.75715000	-0.78180300	-1.12378100
H	-5.64466500	1.66373400	-0.86767200
C	-2.20542500	-0.78704900	5.46765600
H	-1.78668400	0.15669500	5.79815800
H	-3.01156700	-1.23401300	6.03815600
H	-1.73349300	-1.34261200	4.66284100
H	-0.10664900	0.74329600	1.82078300
O	-2.93846100	-0.59635300	2.33594900
H	-3.02050200	-0.45442200	3.30077000
O	-1.88562300	-1.60341400	2.31123600
H	-1.10927700	-1.04109900	1.97472700

TS 4

Electronic energy = -2824.381013 Hartree
Gibbs free energy = -2824.026072 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.52302500	-0.36324900	-0.57220900
C	-1.23302600	-2.32050100	-0.87807900
C	-2.46331900	-3.05154200	-1.05197200
C	-3.68133200	-2.42858300	-0.98019000
C	-3.76238400	-1.02318700	-0.72756400
H	-2.40326900	-4.11852400	-1.24054500
H	-4.59508500	-3.00053200	-1.11434100
C	-2.25167700	3.73281600	0.15210200
C	-1.07129100	2.91429600	0.04833800
C	-2.48003000	1.04933800	-0.31824700
C	-3.67487100	1.79865700	-0.22569700
C	-3.50610900	3.19659900	0.02006200
H	-2.12542100	4.79392500	0.34015300
H	-4.38216400	3.83364200	0.10177900
C	2.72568700	-0.57135300	-0.29950200
C	3.91638000	-1.33011900	-0.32054100
C	3.75036800	-2.72510200	-0.58522400
C	2.50088000	-3.24892600	-0.79029900
C	1.32238400	-2.42134900	-0.74533500
H	4.62429800	-3.36932600	-0.62191300
H	2.37650800	-4.30853200	-0.98836000
C	2.70968500	3.53478400	0.41486000
C	3.92430400	2.89855500	0.41574500
C	4.00492800	1.49181900	0.17955600
C	2.77075900	0.84290200	-0.05326800
C	1.48727300	2.81349800	0.17459100
H	2.64878200	4.60219200	0.59995700
H	4.83444900	3.46239500	0.59940700
Fe	0.13268200	0.26162200	-0.45012700
C	0.22653900	3.47006800	0.19923100
C	0.02664600	-2.97349700	-0.93490300
H	0.25904700	4.53787900	0.38831600
H	-0.00462200	-4.03812600	-1.14341300
N	1.58387700	1.48226900	-0.05959800
N	-1.24982400	1.58871100	-0.18493400
N	-1.32981800	-0.98722500	-0.65098800
N	1.50099600	-1.09950600	-0.50410800
O	0.05576100	-0.06868100	1.47997200
O	0.21866800	0.55012300	-2.07763800
C	5.14499100	-0.65589100	-0.08607900
C	5.18840400	0.70653400	0.15650400
C	-4.94985400	-0.25014500	-0.62646300
C	-4.90812100	1.11312000	-0.38488500
H	6.06689600	-1.23014200	-0.09820600
H	6.14341800	1.19255700	0.33355400
H	-5.90877900	-0.74653400	-0.74401700
H	-5.83385800	1.67665900	-0.31446900
C	-2.65362900	-1.21487800	3.34744000
H	-2.20776800	-0.36750900	3.85636600
H	-3.14520700	-1.02885700	2.39962200
H	-3.04810500	-2.01293900	3.96444500
H	-0.32410000	0.70318400	1.92679000
O	-0.90950700	-2.18639300	2.72988300
H	-0.53050300	-1.37828500	2.25028400
O	0.30503800	-3.20540500	2.40410200
H	-0.03390200	-3.52019600	1.54689500

23

Electronic energy = -2824.44748009 Hartree
Gibbs free energy = -2824.088183 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.39553000	-1.06234400	-0.38479500
C	-0.95613000	-2.89169500	-0.00099200
C	-2.12049800	-3.73290000	0.09813700
C	-3.38412900	-3.22383800	-0.04579300
C	-3.57850000	-1.83190100	-0.29432900
H	-1.97405100	-4.78989700	0.29802300
H	-4.24894500	-3.87732300	0.03553400
C	-2.45820200	3.04293300	-1.08726900
C	-1.21713300	2.33510700	-0.91428500
C	-2.46656500	0.35330900	-0.62657100
C	-3.71904300	0.98999500	-0.78363000
C	-3.66390200	2.39620900	-1.02607900
H	-2.41770400	4.11353600	-1.26131600
H	-4.58912900	2.95174300	-1.15585800
C	2.83570600	-0.73838100	-0.02498400
C	4.07986600	-1.35644600	0.23778100
C	4.02485000	-2.76384200	0.47423800
C	2.82552500	-3.42531900	0.44774700
C	1.59154400	-2.73285600	0.17895800
H	4.94393500	-3.30696400	0.67948700
H	2.78408300	-4.49402900	0.63448400
C	2.49011100	3.34820200	-0.75670500
C	3.74640900	2.85328500	-0.52587300
C	3.94030300	1.46245400	-0.26322100
C	2.76573900	0.67609900	-0.27153400
C	1.33102200	2.49297000	-0.74304900
H	2.34426100	4.40601200	-0.95272000
H	4.60613100	3.51853400	-0.53914900
Fe	0.19751900	-0.22028900	-0.48111700
C	0.02884200	3.01209200	-0.95545800
C	0.34891800	-3.41721700	0.17912400
H	-0.02554800	4.08123700	-1.13411100
H	0.40122300	-4.48296800	0.37883900
N	1.53642700	1.17470200	-0.50035000
N	-1.28803000	0.99977200	-0.69661100
N	-1.15896200	-1.57801400	-0.26062700
N	1.66660000	-1.40232700	-0.06092000
O	0.04095700	0.08217000	1.44894700
O	0.32897000	-0.47840100	-2.10390400
C	5.24420100	-0.54458700	0.24134100
C	5.17701300	0.81670900	-0.00184000
C	-4.82138700	-1.16949200	-0.45923500
C	-4.88941500	0.19321300	-0.69599300
H	6.20623300	-1.00943100	0.44039400
H	6.08681300	1.41120000	0.00698100
H	-5.73735400	-1.75047100	-0.39234600
H	-5.85813000	0.67112400	-0.81544100
C	-1.23695200	2.91301200	3.74959200
H	-2.17089400	3.15379300	4.28163800
H	-0.66961400	2.19453600	4.36138800
H	-0.64701000	3.83204100	3.67026900
H	-0.02952800	1.03560400	1.63925300
O	-1.47306200	2.44042500	2.43603000
H	-1.95764500	1.58543100	2.50869600
O	-2.30739700	-0.24010100	2.45129600
H	-1.32655600	-0.27650100	2.12390600

24

Electronic energy = -2708.70670876 Hartree
Gibbs free energy = -2708.394724 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.55409500	0.73765300	-0.17091000
C	-1.19992700	2.66824000	-0.15756100
C	-2.40041900	3.46094300	-0.13991400
C	-3.64089700	2.87698200	-0.14100900
C	-3.77038200	1.45674600	-0.15241000
H	-2.30228400	4.54211400	-0.12442200
H	-4.53524300	3.49501200	-0.12851500
C	-2.42556900	-3.42387900	-0.17874700
C	-1.21847000	-2.64107600	-0.18068300
C	-2.55908100	-0.69935000	-0.17655600
C	-3.77948900	-1.40911000	-0.17029300
C	-3.66094400	-2.83041100	-0.17538700
H	-2.33573500	-4.50580900	-0.17786100
H	-4.56000300	-3.44159200	-0.17206700
C	2.70068300	0.71770500	-0.04314200
C	3.92025700	1.42761100	0.04299600
C	3.79961600	2.85069400	0.04990300
C	2.56591700	3.44268400	-0.01343300
C	1.35982600	2.65912800	-0.09354400
H	4.69651400	3.46210600	0.11029900
H	2.47507000	4.52453200	-0.00083000
C	2.54306600	-3.44427900	-0.05462400
C	3.78023500	-2.86073500	0.01438400
C	3.91055000	-1.43796400	0.02559200
C	2.69614500	-0.71926400	-0.04891600
C	1.34059600	-2.65276400	-0.12028600
H	2.44568100	-4.52563200	-0.05862000
H	4.67329700	-3.47870200	0.06430700
Fe	0.07239600	0.01115300	-0.25633100
C	0.06007600	-3.25883300	-0.16387900
C	0.08357400	3.27579600	-0.13422100
H	0.05493000	-4.34431900	-0.15908500
H	0.08706800	4.36127500	-0.11596000
N	1.48578600	-1.30454900	-0.12046400
N	-1.35198400	-1.29203700	-0.18482700
N	-1.34398400	1.32213200	-0.18631900
N	1.49574700	1.31182300	-0.11793300
O	0.10538500	-0.00028100	-1.90581200
C	5.12650000	0.68256700	0.11331700
C	5.12172200	-0.70168000	0.10397400
C	-4.98430300	0.71946700	-0.14697500
C	-4.98821500	-0.66346000	-0.15682400
H	6.07013300	1.21797000	0.17716800
H	6.06183700	-1.24419400	0.15985300
H	-5.92627700	1.26140700	-0.13376900
H	-5.93359100	-1.19959400	-0.15112400
O	0.08396800	0.04357100	1.69680000
H	-0.15423300	-0.82059200	2.07069300
O	-1.95649600	-0.26717200	2.72368000
H	-1.52307800	0.53504600	3.06887900

TS 5

Electronic energy = -2708.70306636 Hartree
Gibbs free energy = -2708.393891 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.55900900	0.74916500	-0.16312600
C	-1.19411000	2.67314400	-0.12938100
C	-2.39247700	3.47001800	-0.11924100
C	-3.63581000	2.89226900	-0.13320800
C	-3.77236400	1.47241900	-0.15381700
H	-2.28988500	4.55072400	-0.10007600
H	-4.52694100	3.51503800	-0.12602600
C	-2.43668400	-3.41002200	-0.19431600
C	-1.22895300	-2.62836500	-0.18283200
C	-2.56810700	-0.68738200	-0.18058200
C	-3.78981300	-1.39492300	-0.18776400
C	-3.67213400	-2.81620800	-0.19863400
H	-2.34764900	-4.49200500	-0.19693200
H	-4.57129300	-3.42718500	-0.20531900
C	2.70650300	0.71546400	-0.05086900
C	3.92830900	1.42177400	0.02654800
C	3.80935200	2.84504100	0.04019600
C	2.57556600	3.43893700	-0.00756900
C	1.36685100	2.65803800	-0.07740100
H	4.70736700	3.45544700	0.09405500
H	2.48691800	4.52091000	0.01041900
C	2.53003700	-3.44411500	-0.06044900
C	3.77117900	-2.86725100	-0.00104500
C	3.90885600	-1.44543100	0.00662200
C	2.69702700	-0.72163600	-0.05973300
C	1.33128400	-2.64702300	-0.12030600
H	2.42708100	-4.52493500	-0.06076100
H	4.66103200	-3.49010300	0.04478500
Fe	0.06903900	0.01599600	-0.23301200
C	0.04835000	-3.24815000	-0.16441100
C	0.09099200	3.27622300	-0.10335200
H	0.04037300	-4.33367600	-0.16127900
H	0.09676900	4.36163000	-0.08111300
N	1.48387500	-1.30041100	-0.12454400
N	-1.36181300	-1.27989300	-0.18347400
N	-1.34562000	1.32720300	-0.15916300
N	1.50222100	1.31096200	-0.10961800
O	0.08857900	0.03225700	-1.89133500
C	5.13232400	0.67180200	0.08532800
C	5.12295400	-0.71266000	0.07537400
C	-4.98810500	0.73786200	-0.16416600
C	-4.99620300	-0.64542500	-0.18131500
H	6.07852200	1.20351200	0.14209000
H	6.06183100	-1.25796100	0.12399800
H	-5.92884600	1.28212400	-0.15760500
H	-5.94343500	-1.17824600	-0.18705500
O	0.14021600	-0.00120600	1.69502000
H	-0.64993000	-0.52956100	2.21660200
O	-1.85832200	-0.39747700	2.67530600
H	-1.72623700	0.33338500	3.30487200

21

Electronic energy = -2708.72492475 Hartree
Gibbs free energy = -2708.411971 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.54102500	-0.68221500	-0.21212900
C	1.21078500	-2.63067000	-0.21194800
C	2.42087300	-3.40742200	-0.23648000
C	3.65344100	-2.80702700	-0.24894000
C	3.76544500	-1.38577400	-0.23359100
H	2.33715600	-4.48980700	-0.24131500
H	4.55537900	-3.41358400	-0.26449400
C	2.35827000	3.47875400	-0.15892900
C	1.15985800	2.68154200	-0.15328600
C	2.52762600	0.75509100	-0.18932900
C	3.73933000	1.48040800	-0.19666700
C	3.60105200	2.90046300	-0.18117500
H	2.25591200	4.55956000	-0.14629900
H	4.49203300	3.52348300	-0.18595600
C	-2.71741800	-0.72854800	-0.02598300
C	-3.92745500	-1.45524700	0.04872500
C	-3.78815000	-2.87679300	0.02975300
C	-2.54786100	-3.45321300	-0.05074300
C	-1.35092000	-2.65455300	-0.11971800
H	-4.67709000	-3.50044600	0.08201000
H	-2.44472200	-4.53394100	-0.06091100
C	-2.61219000	3.43539200	0.00389800
C	-3.84173000	2.83515600	0.07334500
C	-3.95429900	1.41103800	0.07023400
C	-2.73069900	0.70917400	-0.01694100
C	-1.40057600	2.65977000	-0.07731400
H	-2.52903100	4.51791900	0.01220500
H	-4.74216600	3.44128500	0.13466400
Fe	-0.09926500	0.01498600	-0.22535100
C	-0.12648000	3.28197600	-0.12202600
C	-0.06658000	-3.25328200	-0.18406200
H	-0.13493400	4.36743800	-0.10880200
H	-0.05690400	-4.33877700	-0.18830400
N	-1.53083000	1.31190700	-0.09513000
N	1.31359900	1.33499900	-0.17137700
N	1.33839000	-1.28269400	-0.20845200
N	-1.50560200	-1.30832100	-0.10985800
O	-0.14898900	0.03045600	-1.88157000
C	-5.14287800	-0.72631100	0.13312300
C	-5.15558800	0.65785200	0.14380700
C	4.96932800	-0.63333200	-0.23841000
C	4.95677600	0.74947900	-0.22087200
H	-6.07954000	-1.27441300	0.19140700
H	-6.10244900	1.18725800	0.21042600
H	5.91791100	-1.16337800	-0.25346300
H	5.89570200	1.29689200	-0.22461400
O	-0.06599000	-0.00115300	1.62231800
H	1.48301000	-0.32265400	2.44773500
O	2.39805300	-0.39417600	2.81524200
H	2.39123100	0.23102100	3.55457700

Path 4

3

Electronic energy = -2557.18459219 Hartree
Gibbs free energy = -2556.891710 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.61163900	0.70868700	-0.10333300
C	1.25611300	2.65158700	-0.03033500
C	2.46750000	3.43324800	-0.10674400
C	3.69912500	2.84861900	-0.18069700
C	3.81988700	1.42253600	-0.18847900
H	2.37045200	4.51466200	-0.10496800
H	4.59566000	3.46120900	-0.23686100
C	2.46750000	-3.43325400	-0.10655400
C	1.25611400	-2.65158800	-0.03018700
C	2.61163900	-0.70869300	-0.10329300
C	3.81988700	-1.42254700	-0.18839900
C	3.69912500	-2.84862900	-0.18053900
H	2.37045200	-4.51466700	-0.10471900
H	4.59566000	-3.46122200	-0.23667100
C	-2.61164000	0.70868700	-0.10337600
C	-3.81988400	1.42253800	-0.18853800
C	-3.69912100	2.84862100	-0.18075700
C	-2.46749700	3.43324900	-0.10678600
C	-1.25611300	2.65158700	-0.03035600
H	-4.59565500	3.46121000	-0.23693800
H	-2.37044800	4.51466300	-0.10501100
C	-2.46749600	-3.43325400	-0.10660000
C	-3.69912100	-2.84863100	-0.18060900
C	-3.81988400	-1.42255000	-0.18847000
C	-2.61163900	-0.70869300	-0.10334000
C	-1.25611200	-2.65158800	-0.03021000
H	-2.37044600	-4.51466800	-0.10476700
H	-4.59565300	-3.46122600	-0.23676100
Fe	-0.00000400	0.00001000	0.34322900
C	0.00000000	-3.28305000	0.00407900
C	0.00000000	3.28305100	0.00389800
H	0.00000000	-4.36777200	0.00260400
H	0.00000000	4.36777300	0.00236400
N	-1.37569200	-1.29254500	-0.02606400
N	1.37569200	-1.29254600	-0.02603800
N	1.37569100	1.29254500	-0.02611300
N	-1.37569300	1.29254500	-0.02613300
O	-0.00001500	0.00005500	1.95940500
C	-5.03631500	0.68979200	-0.27362400
C	-5.03631700	-0.68981000	-0.27360800
H	-5.97376600	-1.23560200	-0.34096900
C	5.03632000	0.68978900	-0.27354300
C	5.03632000	-0.68980400	-0.27350700
H	-5.97377400	1.23558400	-0.34106500
H	5.97379200	1.23558300	-0.34080300
H	5.97378900	-1.23560200	-0.34077600

20

Electronic energy = -2708.72649404 Hartree
Gibbs free energy = -2708.411484 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.64945600	-0.70892600	-0.08319200
C	1.28006700	-2.64153700	-0.17411200
C	2.48486500	-3.43215800	-0.12070100
C	3.72214500	-2.85431000	-0.05255100
C	3.85432300	-1.43106700	-0.02710900
H	2.38280300	-4.51294000	-0.13562600
H	4.61460200	-3.47426800	-0.01496600
C	2.53183100	3.43895300	-0.03928000
C	1.31366800	2.66750200	-0.10365700
C	2.65894100	0.71181400	-0.06513200
C	3.87295300	1.41563300	0.00397100
C	3.76018600	2.84197900	0.01095600
H	2.44566900	4.52127600	-0.03205900
H	4.66164800	3.44816800	0.05794800
C	-2.59564400	-0.67067900	-0.10812200
C	-3.80916900	-1.37636100	-0.12032000
C	-3.69381000	-2.80530600	-0.16678200
C	-2.46606400	-3.40152000	-0.20329200
C	-1.24142900	-2.63255600	-0.19141500
H	-4.59624400	-3.41163100	-0.17901900
H	-2.38153800	-4.48309000	-0.24736700
C	-2.42049200	3.47364500	-0.08539500
C	-3.65748900	2.89454900	-0.06548600
C	-3.79125400	1.46850700	-0.06947900
C	-2.58480500	0.74725800	-0.09018600
C	-1.20942300	2.68603500	-0.11517600
H	-2.31981100	4.55478000	-0.08611400
H	-4.55124600	3.51362000	-0.05051200
Fe	0.03627200	0.02342300	-0.41723200
C	0.05501300	3.30547800	-0.12166200
C	0.01087600	-3.26451100	-0.21997100
H	0.06286200	4.39018300	-0.11989200
H	0.00650300	-4.34871000	-0.25291200
N	-1.34448500	1.32861200	-0.10575400
N	1.43119200	1.31097200	-0.11588000
N	1.41544500	-1.28984800	-0.15768200
N	-1.35851600	-1.26961100	-0.11098900
O	0.01389000	0.03671100	-2.03141500
C	-5.02434300	-0.63629200	-0.09260900
C	-5.01545800	0.74330000	-0.06521200
H	-5.95196600	1.29438200	-0.04549400
C	5.07831500	-0.70567400	0.04793100
C	5.08705200	0.67235700	0.06215900
H	-5.96776600	-1.17578100	-0.09560800
H	6.01301000	-1.25808500	0.09578300
H	6.02896900	1.21137300	0.12114800
O	0.12455700	0.13330100	2.23552100
H	-0.30245100	1.00756900	2.28980200
O	-0.89274500	-0.70295700	2.85145300
H	-1.16106200	-1.21982900	2.06554000

38

Electronic energy = -2749.24695813 Hartree
Gibbs free energy = -2748.893727 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.81467700	-0.67201100	0.00165300
C	1.48845500	-2.62763100	-0.18832900
C	2.69650300	-3.39796100	-0.02625400
C	3.91418700	-2.79925300	0.14237300
C	4.02148900	-1.37394000	0.16643700
H	2.61326500	-4.48034600	-0.04079600
H	4.80978700	-3.40422600	0.26122800
C	2.63053600	3.47356700	-0.01527900
C	1.43426800	2.68184400	-0.17324300
C	2.80051000	0.74896400	0.00462400
C	3.99340100	1.47298700	0.16869800
C	3.85898400	2.89722400	0.14785500
H	2.52766300	4.55436500	-0.02903300
H	4.74380600	3.51837000	0.26427800
C	-2.40975200	-0.71966400	-0.44888100
C	-3.60753700	-1.44484300	-0.55202400
C	-3.46688000	-2.87199000	-0.58032500
C	-2.23107900	-3.44905400	-0.51812600
C	-1.02320500	-2.66053000	-0.41442200
H	-4.35622400	-3.49243400	-0.65931900
H	-2.12670000	-4.52933200	-0.54924300
C	-2.30046700	3.42751700	-0.46729900
C	-3.52605300	2.82878000	-0.53677500
C	-3.63725500	1.40053800	-0.53156700
C	-2.42218800	0.69860200	-0.44688300
C	-1.07865000	2.65962300	-0.38997300
H	-2.21662200	4.51005900	-0.47531500
H	-4.42761700	3.43318500	-0.60071300
Fe	0.22780100	0.01558500	-0.55629400
C	0.17201200	3.29928500	-0.30570600
C	0.23728700	-3.27188200	-0.33613800
H	0.16342100	4.38391800	-0.31889300
H	0.25306500	-4.35616000	-0.36142300
N	-1.19356000	1.30008900	-0.37143300
N	1.57320400	1.32779400	-0.15896200
N	1.60070100	-1.27393100	-0.17102900
N	-1.16735100	-1.29887400	-0.35163000
O	0.33814700	0.01166000	-2.16680100
C	-4.83241100	-0.72460300	-0.62842100
C	-4.84690100	0.65578100	-0.61614400
H	-5.79013200	1.19186400	-0.68024300
C	5.22329300	-0.62798100	0.33824700
C	5.20937700	0.75000200	0.33870900
H	-5.76407200	-1.27924100	-0.70238400
H	6.15893500	-1.16462900	0.47124500
H	6.13438500	1.30483800	0.47199200
O	0.09794500	0.12068300	2.07533000
H	-0.47350500	0.90461500	2.17290100
O	-0.74442600	-0.91423300	2.64843500
H	-1.01251400	-1.37229800	1.82580300
C	-4.10557300	0.36218900	3.55270900
H	-4.66431000	0.38284300	2.61297900
H	-4.62906400	-0.27080500	4.27480100
H	-3.10462500	-0.04075600	3.37510000
H	-4.02825200	1.37719400	3.95325200

TS 15

Electronic energy = -2749.22011736 Hartree

Gibbs free energy = -2748.870267 Hartree

Charge = 0 Multiplicity = 3

Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.57823200	-0.67004600	-0.43365300
C	1.21810400	-2.60180400	-0.55760500
C	2.42364600	-3.38935700	-0.59685200
C	3.66194400	-2.80575800	-0.55413100
C	3.79124900	-1.38652200	-0.46361100
H	2.32707500	-4.46890800	-0.66019900
H	4.55690600	-3.42237600	-0.58504900
C	2.43914200	3.47524600	-0.15231600
C	1.22859900	2.69502800	-0.21417000
C	2.58005900	0.75751700	-0.34157000
C	3.79660900	1.46581500	-0.28052900
C	3.67447400	2.88604200	-0.18662800
H	2.34732100	4.55449700	-0.07680500
H	4.57250600	3.49720000	-0.13930300
C	-2.68520100	-0.66110100	-0.31605600
C	-3.89879200	-1.37447500	-0.31139800
C	-3.77526400	-2.79765200	-0.40358100
C	-2.54261300	-3.38422700	-0.48764200
C	-1.32898900	-2.60193000	-0.48845300
H	-4.67282900	-3.41123900	-0.40729600
H	-2.45196300	-4.46374100	-0.56085200
C	-2.52350000	3.48142100	-0.03865700
C	-3.76059400	2.89735100	-0.03128300
C	-3.89142900	1.47625100	-0.12665100
C	-2.68003500	0.76386700	-0.23047700
C	-1.31657400	2.69801300	-0.14968400
H	-2.42534100	4.56016000	0.03653400
H	-4.65432200	3.51122000	0.04949400
Fe	-0.05033200	0.06162800	-0.51861600
C	-0.04395300	3.31367300	-0.15052400
C	-0.06086900	-3.21683000	-0.57243400
H	-0.04062500	4.39632400	-0.07515800
H	-0.06291200	-4.30002200	-0.63834300
N	-1.45837900	1.35140200	-0.24278700
N	1.36361900	1.34932200	-0.31971500
N	1.35940900	-1.25522800	-0.48599600
N	-1.46351900	-1.25095900	-0.38418100
O	-0.11089400	0.15118900	-2.14581500
C	-5.11200400	-0.63873300	-0.21615000
C	-5.10811800	0.74020100	-0.12478000
H	-6.04785000	1.28097100	-0.04930900
C	5.00884000	-0.65290700	-0.40177500
C	5.01091700	0.72491500	-0.31295000
H	-6.05468300	-1.17960900	-0.21424900
H	5.94974900	-1.19639900	-0.42257500
H	5.95388100	1.26313000	-0.26379400
O	-0.10336600	-0.09749200	1.54258300
H	-0.19071100	-1.03658400	1.77401100
O	1.44474300	0.00365400	2.53692800
H	1.16447500	0.87409000	2.87126000
C	0.04869500	-1.10389200	5.62529900
H	-0.94429800	-0.65379300	5.71731300
H	-0.04294300	-2.19283200	5.67987800
H	0.49772500	-0.81962100	4.66895500
H	0.68022600	-0.75599800	6.44826700

39

Electronic energy = -2749.23428246 Hartree
Gibbs free energy = -2748.883334 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.43197200	-0.86579600	-0.40800500
C	1.03473900	-2.75182900	-0.20145600
C	2.21343700	-3.57541400	-0.18513200
C	3.46617600	-3.02872600	-0.27825200
C	3.62987200	-1.61647600	-0.39051100
H	2.08875700	-4.64929900	-0.08696400
H	4.34472100	-3.66833600	-0.25910500
C	2.40898300	3.29086700	-0.67241100
C	1.18055700	2.54478400	-0.57067900
C	2.47297100	0.56735400	-0.50369200
C	3.71093400	1.24117900	-0.59248800
C	3.62733400	2.66407700	-0.68331100
H	2.34778600	4.37280600	-0.73859100
H	4.54086700	3.24857700	-0.75799000
C	-2.80621300	-0.69091800	-0.01807500
C	-4.03703100	-1.36060300	0.17468800
C	-3.95153700	-2.78266700	0.26753600
C	-2.73736100	-3.41188700	0.17998500
C	-1.52007200	-2.66791100	-0.01267100
H	-4.85875300	-3.36365200	0.41279400
H	-2.67204000	-4.49269200	0.25868500
C	-2.54858600	3.45591900	-0.31601200
C	-3.79393100	2.91179100	-0.14713700
C	-3.95746700	1.49671700	-0.03229900
C	-2.76606500	0.74248800	-0.11539700
C	-1.36890300	2.63042700	-0.38411800
H	-2.42669700	4.53147200	-0.40044200
H	-4.66853100	3.55561600	-0.09747700
Fe	-0.17831300	-0.07196900	-0.40821600
C	-0.07837400	3.19782100	-0.52998200
C	-0.26126500	-3.32086600	-0.07751000
H	-0.04695800	4.28069600	-0.59764000
H	-0.28988200	-4.40202900	0.01572400
N	-1.54640500	1.28919000	-0.28127300
N	1.28080300	1.19457800	-0.49477700
N	1.20691900	-1.41692100	-0.33359100
N	-1.62274600	-1.32252200	-0.11698600
O	-0.30831700	-0.15768300	-2.04901500
C	-5.21971000	-0.57965000	0.25544400
C	-5.18067100	0.80023200	0.15349000
C	4.86053800	-0.91561100	-0.48391200
C	4.89917800	0.46393800	-0.58289300
H	-6.17171600	-1.08317900	0.40076100
H	-6.10326800	1.37114000	0.21819100
H	5.78806400	-1.48147800	-0.47107500
H	5.85733400	0.97246400	-0.64991600
O	-0.02937300	0.01988700	1.54094700
H	-0.01270900	0.94084700	1.84265200
O	2.10546400	-1.07032500	2.67326100
H	1.24118300	-0.68691700	2.29900900
C	2.20442100	2.32293200	3.74120500
H	2.35173500	2.88598800	2.81406100
H	1.24171700	2.59783100	4.18344200
H	2.22383800	1.24966000	3.53022000
H	3.00492900	2.57332400	4.44369900

TS 16

Electronic energy = -2749.21876137 Hartree

Gibbs free energy = -2748.870563 Hartree

Charge = 0 Multiplicity = 3

Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.55396200	-0.37058200	-0.45787300
C	1.30550300	-2.34488700	-0.75322600
C	2.54351700	-3.06380300	-0.88346700
C	3.75142000	-2.42347900	-0.79514400
C	3.80580600	-1.01720800	-0.56677500
H	2.50083000	-4.13630200	-1.04614700
H	4.67692200	-2.98520000	-0.89160000
C	2.20951300	3.72068800	0.24178400
C	1.04167000	2.88650000	0.11734500
C	2.48415700	1.04382200	-0.21640400
C	3.66645700	1.80636400	-0.09705100
C	3.47316800	3.20162400	0.13846700
H	2.06486400	4.78138200	0.42297700
H	4.33944400	3.85095500	0.23787100
C	-2.69123200	-0.66061000	-0.27109600
C	-3.87016700	-1.44148700	-0.29618200
C	-3.67507800	-2.83597900	-0.53256700
C	-2.41286200	-3.34019900	-0.70714400
C	-1.25300600	-2.48830200	-0.66454800
H	-4.53734500	-3.49702200	-0.56900800
H	-2.26465400	-4.40184900	-0.87948100
C	-2.75360200	3.44801200	0.41093800
C	-3.95612900	2.79298200	0.39422900
C	-4.01043800	1.38240400	0.17050900
C	-2.76148300	0.75481200	-0.03162400
C	-1.51106400	2.74675100	0.20455400
H	-2.71478100	4.51936200	0.58293300
H	-4.87994300	3.34383700	0.55268800
Fe	-0.11041900	0.21590700	-0.38397700
C	-0.26578700	3.42209300	0.24983900
C	0.05491100	-3.01745800	-0.82001800
H	-0.31802400	4.49080900	0.43270400
H	0.10914600	-4.08935700	-0.98345000
N	-1.58486200	1.40984500	-0.01376000
N	1.24571300	1.56538400	-0.11151300
N	1.37490500	-1.00834100	-0.56380800
N	-1.45895600	-1.16657900	-0.45832600
O	-0.18483100	0.49265700	-2.00946700
C	-5.11287900	-0.78669100	-0.08987700
C	-5.17981400	0.57755700	0.13376300
C	4.97980900	-0.22826800	-0.44397700
C	4.91225700	1.13485700	-0.21877000
H	-6.02583400	-1.37594000	-0.10907100
H	-6.14596400	1.05127900	0.28729200
H	5.94838300	-0.71416200	-0.52512600
H	5.82864100	1.71210700	-0.12745400
O	-0.03496500	-0.14479300	1.53191200
H	-0.01694800	0.68703800	2.02937000
O	2.07930500	-1.58379000	2.44697000
H	1.28454200	-1.04644400	2.15343300
C	0.68581200	-3.31938800	3.55792300
H	0.95241400	-3.33446900	4.61530500
H	-0.30191900	-2.90057900	3.36776100
H	1.51776500	-2.49104800	3.01074500
H	0.85314900	-4.27348700	3.05653100

40

Electronic energy = -2749.23677986 Hartree
Gibbs free energy = -2748.887461 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.60765600	0.53510200	-0.36123500
C	-1.27601000	2.45444900	-0.65310200
C	-2.48100100	3.23460200	-0.72305100
C	-3.71484000	2.65075900	-0.60723000
C	-3.82944100	1.24347500	-0.41015900
H	-2.39175100	4.30760500	-0.86169300
H	-4.61471200	3.25825000	-0.65762300
C	-2.43868900	-3.58633900	0.21550900
C	-1.23649800	-2.80568300	0.07184700
C	-2.59855700	-0.88703300	-0.15861900
C	-3.81162500	-1.59552800	-0.01811900
C	-3.67835200	-3.00468500	0.17224700
H	-2.33982000	-4.65760400	0.36184100
H	-4.57125900	-3.61463200	0.28462400
C	2.64870000	0.56901700	-0.35381100
C	3.86246600	1.29347200	-0.40020900
C	3.72718500	2.70166600	-0.59379300
C	2.48575400	3.26980600	-0.71176800
C	1.28794800	2.47328100	-0.65023800
H	4.61874000	3.32172500	-0.64334500
H	2.38347000	4.34149400	-0.85236300
C	2.53494800	-3.55551800	0.21496000
C	3.76651500	-2.95810500	0.17410000
C	3.88150100	-1.54591700	-0.01356200
C	2.65832100	-0.85433400	-0.15536500
C	1.32149700	-2.79056600	0.07068600
H	2.45011300	-4.62822700	0.35976600
H	4.66733700	-3.55643300	0.28584300
Fe	0.02591200	-0.18018300	-0.39954900
C	0.04713800	-3.40685700	0.14189300
C	0.00290700	3.06787600	-0.74789200
H	0.05346100	-4.48173500	0.29320200
H	-0.00455600	4.14509000	-0.88273900
N	1.45263500	-1.45315700	-0.11502800
N	-1.38399200	-1.47011200	-0.11280700
N	-1.40335500	1.11835900	-0.49281600
N	1.43661200	1.13815900	-0.48373500
O	0.02954500	-0.41344600	-2.03233900
C	5.07819600	0.57492000	-0.25478700
C	5.08646200	-0.79668600	-0.06946100
C	-5.03550500	0.50831500	-0.26562400
C	-5.02671900	-0.86207000	-0.07784200
H	6.01741900	1.12044700	-0.29023700
H	6.03317000	-1.31974300	0.03798800
H	-5.98151000	1.04183900	-0.30023000
H	-5.96644400	-1.39721900	0.03096800
O	0.03945600	0.12860800	1.53237700
H	-0.02162200	-0.71033400	2.01438400
O	-1.86974900	1.80459900	2.55712100
H	-1.21299500	1.14554800	2.21535900
C	1.24522800	2.31942400	3.88292700
H	0.93902700	2.15859200	4.91045600
H	1.03358800	1.57333200	3.12273600
H	-1.29734400	2.46184900	2.98165200
H	1.82541100	3.20303200	3.64132400

TS 2

Electronic energy = -2672.80013335 Hartree
Gibbs free energy = -2672.472568 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	-2.66217800	-0.71261400	-0.12316200
C	-1.29872300	-2.63706000	-0.22530100
C	-2.49704900	-3.43527800	-0.17684700
C	-3.73754000	-2.85898400	-0.10368200
C	-3.87295000	-1.43776000	-0.06742700
H	-2.39441600	-4.51602900	-0.19759200
H	-4.62828400	-3.48141300	-0.06850700
C	-2.55078400	3.44709900	-0.00371400
C	-1.33850600	2.67236500	-0.08983500
C	-2.67356200	0.72121200	-0.08075900
C	-3.89444100	1.42364400	0.00876500
C	-3.78118800	2.84744800	0.04294000
H	-2.46604400	4.52928000	0.02353900
H	-4.68181500	3.45313400	0.10742500
C	2.59193300	-0.67143400	-0.22246900
C	3.81613200	-1.37654200	-0.22439100
C	3.70224000	-2.79966500	-0.26460100
C	2.46932100	-3.39618700	-0.28980700
C	1.25690800	-2.61776500	-0.28050900
H	4.60370200	-3.40745300	-0.27264800
H	2.38380500	-4.47833200	-0.31578400
C	2.41881900	3.48726900	-0.11294100
C	3.65950000	2.90720400	-0.11466500
C	3.79442600	1.48516900	-0.14610100
C	2.58166600	0.76312400	-0.17790500
C	1.21637000	2.69316100	-0.14179700
H	2.31834200	4.56820700	-0.09024500
H	4.55222400	3.52750500	-0.09316900
Fe	-0.04364200	0.02800700	-0.29559100
C	-0.06611400	3.29741200	-0.11584300
C	-0.01676500	-3.24133200	-0.27956600
H	-0.07429500	4.38252900	-0.08727000
H	-0.00901500	-4.32671800	-0.29962700
N	1.36373700	1.34480700	-0.17294300
N	-1.46563000	1.32207400	-0.12399300
N	-1.44774300	-1.29113800	-0.20613000
N	1.38506200	-1.26958100	-0.25862700
O	-0.05371100	-0.04516800	1.64881500
O	-0.06228600	0.07812900	-1.94816600
C	5.02351300	-0.62832200	-0.18691400
C	5.01305400	0.75407400	-0.15079000
C	-5.09004600	-0.70917500	0.01885800
C	-5.10049700	0.67305000	0.05427400
H	5.97061900	-1.16154100	-0.18753900
H	5.95205700	1.30090000	-0.12524000
H	-6.02745400	-1.25782500	0.05870800
H	-6.04623800	1.20476800	0.11951200
C	1.10868700	-0.76004500	3.95537400
H	1.32434100	-1.68767200	3.44557400
H	1.85205500	0.02658700	3.98328100
H	0.13342900	-0.60329000	4.39516800
H	0.01832300	0.85196500	2.00930800

19

Electronic energy = -2672.90632768 Hartree
Gibbs free energy = -2672.566023 Hartree
Charge = 0 Multiplicity = 3
Geometry =

Element	Cartesian coordinate		
	x	y	z
C	2.60914000	0.66621600	-0.13510600
C	1.25536000	2.61636300	-0.23575300
C	2.47508800	3.39138900	-0.22827200
C	3.70569400	2.80000900	-0.17529900
C	3.82389500	1.37363900	-0.12271600
H	2.38712500	4.47302800	-0.26894500
H	4.60615100	3.40980900	-0.17489100
C	2.44356300	-3.48177900	-0.05158300
C	1.22972700	-2.69781000	-0.09392600
C	2.60297300	-0.75497900	-0.09268700
C	3.81043000	-1.47219600	-0.04848800
C	3.67888200	-2.89873800	-0.02870200
H	2.34655000	-4.56336100	-0.04242200
H	4.57399800	-3.51569700	-0.00006900
C	-2.63946000	0.69101600	-0.10482000
C	-3.84616700	1.41002500	-0.06722300
C	-3.71607400	2.83422900	-0.11497400
C	-2.48068900	3.41496900	-0.18564400
C	-1.27051100	2.62779300	-0.21709900
H	-4.61061200	3.45237100	-0.09518200
H	-2.38290400	4.49589400	-0.22168600
C	-2.51279300	-3.45643200	-0.01389700
C	-3.74304000	-2.86151300	0.02653300
C	-3.85979900	-1.43595500	0.00335300
C	-2.64627500	-0.73091600	-0.06953100
C	-1.29616900	-2.68268500	-0.08403700
H	-2.42479600	-4.53860900	0.00466200
H	-4.64320900	-3.46967000	0.07665400
Fe	-0.02188300	-0.03748400	-0.39898200
C	-0.03407600	-3.31847600	-0.09293700
C	-0.00349200	3.24962000	-0.26063500
H	-0.04019200	-4.40325700	-0.07935400
H	0.00114900	4.33382300	-0.29987900
N	-1.41969900	-1.32940700	-0.11258600
N	1.36605700	-1.34060200	-0.10076700
N	1.37955000	1.26134900	-0.18739800
N	-1.40703400	1.27517500	-0.17603500
O	-0.06091400	-0.06523200	2.09452000
O	-0.02039400	-0.08817600	-2.01292400
C	-5.06970100	0.68301900	0.01165800
C	-5.07646600	-0.69451600	0.04578800
C	5.04060800	0.63521800	-0.06635200
C	5.03425500	-0.74352400	-0.03185300
H	-6.00574800	1.23457400	0.04492600
H	-6.01774300	-1.23472000	0.10601300
H	5.98284700	1.17700700	-0.05426500
H	5.97141900	-1.29281100	0.00689200
C	0.46539500	0.96075300	2.93832500
H	0.22427500	0.76743300	3.99182300
H	1.55143600	1.06864300	2.82615600
H	-0.01288600	1.89072600	2.62780200
H	0.39863400	-0.89738300	2.28529700

References

1. X. Cui, H. Li, Y. Wang, Y. Hu, L. Hua, H. Li, X. Han, Q. Liu, F. Yang and L. He, *Chem*, 2018, **4**, 1902-1910.
2. Y. Zhao and D. G. Truhlar, *Accounts of Chemical Research*, 2008, **41**, 157-167.
3. M. Walker, A. J. Harvey, A. Sen and C. E. Dessent, *The Journal of Physical Chemistry A*, 2013, **117**, 12590-12600.