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Submitted date: 14/05/2020 • Posted date: 15/05/2020

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Citation information: Shende, Vikram V.; Khatri, Yogan; Newmister, Sean A.; Sanders, Jacob N.; Lindovska, Petra; Yu, Fengan; et al. (2020): Structure and Function of NzeB, a Versatile C–C and C–N Bond Forming Diketopiperazine Dimerase. ChemRxiv. Preprint. <https://doi.org/10.26434/chemrxiv.12307439.v1>

This report details the discovery and characterization of a versatile bacterial cytochrome P450, NzeB, which catalyzes the dimerization of diketopiperazines via enzymatic C–H functionalization. This includes the first high-resolution crystal structure of a diketopiperazine dimerase, which along with active site via mutagenesis and quantum mechanical calculations, provides insight into the selectivity and mechanism of these enzymes.

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Structure and Function of NzeB, a Versatile C–C and C–N Bond Forming Diketopiperazine Dimerase

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KEYWORDS cytochrome P450, diketopiperazine, diketopiperazine dimers, natural product biosynthesis, C–H functionalization

ABSTRACT: The dimeric diketopiperazine (DKPs) alkaloids are a diverse family of natural products (NPs) whose unique structural architectures and biological activities have inspired the development of new synthetic methodology to access these molecules. However, catalyst-controlled methods that enable the selective formation of constitutional and stereoisomeric dimers from a single monomer are lacking. To resolve this long-standing synthetic challenge, we sought to characterize the biosynthetic enzymes that assemble these NPs for application in biocatalytic syntheses. Genome mining enabled identification of the cytochrome P450, NzeB (derived from *Streptomyces* sp. NRRL F-5053), which catalyzes both intermolecular carbon–carbon (C–C) and carbon–nitrogen (C–N) bond formation, generating all currently known DKP dimer scaffolds isolated from bacterial sources. To identify the molecular basis for the flexible site-, stereo-, and chemoselectivity of NzeB, we obtained high-resolution crystal structures (1.5Å) of the protein in complex with native and non-native substrates. This, to our knowledge, represents the first crystal structure of an oxidase catalyzing direct, intermolecular C–H amination. Site-directed mutagenesis was employed to assess the role individual active site residues play in guiding selective DKP dimerization. Finally, computational approaches were employed to evaluate plausible mechanisms regarding NzeB function and its ability to catalyze both C–C and C–N bond formation. These results provide a structural and computational rationale for the catalytic versatility of NzeB, as well as new insights into variables that control selectivity of CYP450 diketopiperazine dimerases.

The tryptophan-linked dimeric diketopiperazine (DKP) alkaloids are a family of over 50 natural products isolated from bacteria, fungi, and plants.^{1–4} Their dimerization modes encompass an array of stereo- and regiochemical connectivities, and potent biological activity of these natural products elicited the development and application of effective methods for their total synthesis.^{3–5} In particular, biomimetic strategies enabled access to *C*₂-symmetrical dimers, such as (–)-ditryptophenaline (**2**, Figure 1), wherein two identical monomers are coupled at a late-stage resulting in highly convergent and efficient syntheses.^{6, 7} However, the chemical synthesis of structurally challenging non-symmetrical DKP dimers such as (+)-naseaezines A (**1**) and B (**2**),^{8, 9} (–)-naseaezine C (**4**),^{10, 11} and the related alkaloid (–)-aspergilazine A (**5**),^{10, 12} continues to inspire the development of new synthetic routes.^{4, 9, 13–16} The synthesis of structurally complex non-symmetrical dimeric DKPs requires independent synthesis of appropriately substituted precursors to allow selective formation of a key C–C or C–N bond that adjoin the two subunits.^{9, 17, 18} Seeking to develop an efficient approach towards DKP dimer assembly, we envisioned a process wherein the site- and stereochemical outcome of dimerization would be dictated by the biocatalyst, and a single DKP monomer could dimerized selectively to a variety of site- and stereo-isomeric products.

While dozens of fungal dimeric diketopiperazine natural products have been reported since the isolation of **2**,^{1–4, 6} fungal biosynthetic gene clusters (BGCs) responsible for dimerization of DKPs have only recently been identified, and have been limited to biosynthesis of *C*₂ symmetrical dimers.¹⁹ Characterization of these BGCs identified cytochromes P450 that mediate the oxidative convergence of two DKP monomers to generate *C*₂ symmetrical dimers, validating long-standing hypotheses proposed in isolation, characterization, and total syntheses of these molecules.¹⁹ While the majority of DKP dimers have been isolated from fungi, marine actinomycetes have recently emerged as a new source for non-symmetrical dimeric DKP natural products. Notably, bacterial DKP dimers display coupling patterns distinct from their fungal counterparts, with the exception of **4**, a rare example of a secondary metabolite isolated from both fungal and bacterial sources.^{8, 10, 11} Contemporaneous efforts to identify DKP dimer biosynthetic gene clusters from bacteria have led to the recent identification of gene clusters for dimers **3** (*nasc*)²⁰ (*Streptomyces* sp. CMB-MQ030), and the (+)-naseaezines A (**1**) and B (**2**) (*nas*) and (–)-aspergilazine A (**5**) gene clusters (*Streptomyces* sp. NRRL-S1868).²¹ While functional characterization of these BGCs have provided insight into the biogenesis of these natural products, the molecular basis for the selective formation of non-symmetrical dimers by these P450s has remained elusive.

Herein, we report the identification of NzeB, a versatile P450 that catalyzes both C–C and C–N bond formation through bioinformatics and sequence similarity network (SSN) analysis. Structural and functional characterization of NzeB provides the first insights into the molecular basis of selectivity displayed by the DKP dimerizing class of P450s. Quantum mechanics (QM) calculations were performed to elucidate plausible mechanisms for NzeB catalyzed C–C and C–N dimerization.

Figure 1. A: Representative examples of substrate controlled, biomimetic total syntheses of dimeric diketopiperazine natural products. B: Current work describing the molecular basis for catalyst-controlled NzeB mediated assembly of isomeric dimers.

Identification of the *nzn* gene cluster. Previous studies by Tian *et al.* identified a gene cluster (*nasc*) from *Streptomyces* sp. CMB-MQ030 composed of a cyclodipeptide synthase (CDPS), *nascA*, and P450, *nascB*, which mediates assembly of cryptic diketopiperazine dimer (–)-naseasezine C (**4**).²⁰ Our independent sequencing and annotation of the *Streptomyces* sp. CMB-MQ030 genome (Supplementary Information, Table S1) identified an additional operon, *nzn*, also composed of a CDPS and P450, each with high sequence homology to *nasc* counterparts (*NznA/NascB* = 61%, *NznB/NascB* = 68%). Given the high sequence homology to the *nasc* gene cluster, we hypothesized P450 NznB catalyzes formation of the site- and stereoisomeric (+)-naseasezines A (**1**) and B (**2**),

the original dimeric DKP natural products isolated from this strain. To assess NznB as the (+)-naseasezines A and B synthase as well as evaluate relative catalytic activities, both recombinant proteins (*NznB* and *NascB*) were subjected to dimerization conditions with predicted native substrate breviaamide F (**6**). Homodimerization reactions demonstrated *NznB* catalyzes formation of **6** into **2**, albeit in modest total turnover number (TTN), 145 TTN, relative to the conversion of **6** to **4** by *NascB*, >500 TTN (Figure 2).²²

Figure 2. Products (–)-naseasezine C (**4**) and (+)-naseasezine B (**2**) formed from homodimerizations of **6** catalyzed by *NascB* and *NznB*.

To confirm the structure of (–)-naseasezine C (**4**), as well as resolve a discrepancy in the literature regarding its connectivity,^{10, 11} the first total synthesis of (–)-naseasezine C (**4**) was performed, using the undirected Friedel-Crafts methodology described in the first generation total synthesis of (+)-naseasezines A and B (Scheme 1).⁹ This route was provided dimers with connectivities at both C5 and C6, encompassing the constitutional isomers proposed in both isolation reports. Detailed analysis of key HMBC correlations confirmed both the stereochemical configuration of the dimerization axis and connectivity of (–)-naseasezine C (**4**) at C5, as well as its C6 constitutional isomer, which we name (–)-isonaseasezine C (**11**) based on previous precedent.⁹

Scheme 1. Total synthesis of (–)-naseasezine C (**4**) and (–)-iso-naseasezine C (**11**)

^aReagents and conditions: (a), AgSbF₆, EtNO₂, (–)-**9**:(–)-**10** = 1:1.4, 40%. (b) H₂/Pd/C, EtOH, (80% for (–)-**4** and 84% for (–)-**11**).

Discovery and functional characterization of NzeB. Given the divergent site- and stereoselectivities displayed by *NascB* and *NznB*, we reasoned that comparative sequence analysis may uncover regions conferring selectivity to the dimerization cascade. Therefore,

we sought to identify additional DKP dimerases through sequence similarity network (SSN) analysis.²³ Using NascB and NznB as *in silico* probes, along with known DKP functionalizing P450s from the thaxtomin (**12**),²⁴ pulcherrimic acid (**13**),²⁵ guanitryptmycin (**14**),²⁶⁻²⁹ bicyclomycin (**15**),^{30, 31} and mycocyclosin (**16**)^{32, 33} BGCs, we mined the NCBI database to identify candidate DKP dimerases. The resulting sequences were assembled into a SSN, which revealed a series of nodes clustered with NascB and NznB. From these data we identified a BGC, *nze*, consisting of a CDPS (NzeA) and P450 (NzeB) pair with high sequence homology to the *nasc* and *nzn* operons (Figure 3).

Figure 3. Sequence similarity network with clusters representing characterized DKP functionalizing P450s (clusters of unknown function and orphan nodes omitted for clarity).

Heterologous expression of CDPS, NzeA, and analysis of its product profile identified **6** as the sole DKP metabolite (Supporting Information, Supplementary Figure 8). Subsequent NzeB-catalyzed homodimerization of **6** resulted in formation of three dimeric products; (-)-naseaeazine C (**4**) as the major product, and two minor products, (+)-naseaeazine B (**2**) and unknown dimer **5** (Figure 4). Scale up and NMR characterization revealed **5** to be C-

N linked dimer (-)-aspergilazine A. This product distribution exemplifies the versatility of NzeB, as it is able to form site- and stereoisomeric Csp³-Csp² linked dimeric products **2**, and **4**, as well as display variant chemoselectivity in the formation of Csp²-Nsp² linked **5** (Figure 1b).^{10, 12, 14, 15} The multifunctional nature of NzeB enables assembly of all currently known bacterial-derived DKP dimer scaffolds from a single biocatalyst.

Figure 4. Products formed and HPLC traces from homodimerization of **6** by NzeB.

Crystal structure of NzeB. Given the catalytic flexibility displayed by NzeB, we sought to identify the molecular basis for this versatility using X-ray crystallography. We obtained high-resolution (1.5 Å) crystal structures of NzeB both in the presence and absence of native substrate **6** (Figure 5, Supporting Information Supplementary Figure 21). NzeB shares highest structural homology with DKP functionalizing cytochrome P450, CYP121, which catalyzes oxidative intramolecular C-C bond formation to generate mycocyclosin (30% Sequence ID, 2.4 Å RMSD, 45.8 Z-score).³⁴ NzeB adopts the prototypical triangular prism P450 fold, with only minor structural rearrangement between the ligand-bound and ligand-free forms (0.45 Å RMSD). Notably, both ligand-free and substrate bound structures of NzeB display electron density for the conserved axial water 3 Å from the heme-iron.

The active site of the ligand bound crystal structure of NzeB contains two units of **6**, with each substrate occupying a discrete pocket in the active site. The DKP core and tryptophan side chain of the first substrate (Figure 5, *light pink*) are “sandwiched” by Gln68 and Phe391, forcing the DKP to adopt a concave architecture. The concave pose of this substrate is suggestive of the pyrroloindoline scaffold in the C-C linked dimeric products **2** and **4** and as such we named this site the “cyclization site.” The proline side chain of the second substrate (Figure 5, *mint green*) is encapsulated by predominately hydrophobic residues (Gln75, Glu76, Phe177, Phe390, Phe391) and binds in an extended pose. This extended conformation positions the indole atoms that undergo C-H functionalization to form the dimeric axis (C5 for **4** and C6 for **2** and **5**) proximal to the iron center of the heme cofactor; therefore, we named this the “dimerization site.”

Figure 5. Active site of NzeB with concave substrate (light pink) bound in the “cyclization site” and extended substrate (mint green) bound in the “dimerization site.”

Inspection of this complex revealed close packing of the substrate proline side chain in the dimerization site compared to the relatively open cavity surrounding the proline side chain in the cyclization site (Supporting Information, Supplementary Figure 22).

Figure 7. Heterodimerization reaction of NzeB with substrates **6** and **17**, HPLC traces from heterodimerization reactions and structure of heterodimer **18**.

We reasoned that the more open cyclization site could selectively accommodate non-native substrates with bulkier side chains. We hypothesized that reactions involving heterodimerization of the larger substrate and the native DKP **6** would show pyrroloindoline

ring formation in the larger substrate due to selective binding in the putative cyclization site.

To confirm the roles of the cyclization and dimerization sites, non-native DKP substrates with bulky side chains in place of proline were synthesized and screened for their heterodimerization capacity with native substrate **6** (Supporting Information, Supplementary Figure 12). Although a variety of these substrates were capable of forming heterodimers with **6**, only heterodimerizations with *cyclo*(L-Trp-L-Trp) (**17**) resulted in the exclusive formation of a single heterodimeric product (Figure 7). Suppression of homodimeric product formation in the presence of **11** and formation of a single heterodimer suggested that each substrate bound selectively and preferentially to a single DKP binding site.

This biocatalytic union of substrates **6** and **17** was performed on preparative scale and the structure of product **18** was determined. This result suggests that binding of **17** is limited to the cyclization site. We obtained a crystal structure of a mixed-ligand complex of NzeB with **17** binding in the cyclization site and **6** in the dimerization site, confirming our assignment of the functional roles of each of these active site pockets (Figure 8).

Figure 8. Crystal structure of NzeB heterocomplex with diketopiperazine **17** (yellow) bound in the cyclization site and diketopiperazine **6** (green) bound in the dimerization site, with omit map ($F_o - F_c$) displayed as blue mesh.

Site-directed mutagenesis of NzeB. To identify key residues that control chemoselectivity in the NzeB catalyzed dimerization cascade, we examined the conservation of amino acid residues in both the cyclization and dimerization sites between NzeB, NascB and NznB. As (–)-naseaezine C (**4**) is the major product of the NzeB and the exclusive product of NascB, we began our analysis by comparing the active sites of these two homologs. A single residue variation exists in the active sites of NascB and NzeB, (NascB: Ala 287, NzeB: Ser 287). In the ligand-bound structures of NzeB, Ser287 forms a hydrogen bond with the proline carbonyl of the substrate in the dimerization site (Figure 5). NzeB variant NzeB_{S287A} was generated and homodimerization reactions of **6** with this mutant protein

Figure 9. Computed mechanistic pathways for the formation of radical cyclized pyrroloindoline intermediate (R-III) via indole N-H abstraction (left) and DKP N-H abstraction (right).

resulted in exclusive formation of (–)-nasaseazine C (4) (Figure 10). Functionally, this mutation completely reconstituted the specificity of NzeB and pinpointed Ser287 as a key determinant of dimerase selectivity.

Figure 10. Homodimerization reactions of NzeB variants with 6 and corresponding HPLC traces.

To examine the generality of remodeling active sites to recapitulate selectivity, we compared the active site residues of (+)-nasaseazine B (2) synthase, NznB, to NzeB. This revealed a single active site variation (NznB: Met68, NzeB: Gln68), located in the cyclization site. To assess the consequence of this variation, NzeB_{Q68M} was constructed and subjected to homodimerization reactions with 6. Rather than exclusive formation of 2, homodimerization reactions of 6 with NzeB_{Q68M} generated dimers 2, 4 and 5, as well as a new metabolite, 11 (Figure 10). Scale up and characterization of this product revealed its identity as the C6 constitutional isomer of 2, (–)-isonaseazine C (11) based on comparison to synthetic standard (Scheme 1).⁹

To further profile the role of active site residues in controlling selectivity in the C–C/C–N bond-forming cascade, we performed alanine scanning mutagenesis on residues within 5 Å of either substrate. The resulting variants (S287A, Q75A, E76A, Q75A/E76A, F177A, E317A, F390A, F391A and F390A/F391A) were profiled for catalytic activity and selectivity against native substrate 6 (Supporting Information, Supplementary Figure 13). All functional variants from this experiment displayed the same product profile as NzeB_{Q68M}, formation of 2, 4, 5 and 13, and differed only in the relative distributions of dimers. Given the increased formation of 13 across a variety of active site variants at various positions within the NzeB active site, we hypothesize that 13 results from loss of selectivity during the dimerization cascade.

NzeB dimerization mechanism and quantum mechanics (QM) calculations. The first biomimetic total synthesis of the (+)-nasaseazines proposed two alternative biosynthetic mechanisms for DKP dimer formation.⁹ Both mechanisms involved oxidative formation of a pyrroloindoline radical, but diverged on formation of the intermolecular C–C bond. The first mechanism proposed directed pyrroloindoline radical coupling to a second DKP followed by oxidative re-aromatization to afford the non-symmetrical DKP scaffold. The second involved oxidation of the pyrroloindoline radical to a tertiary, benzylic cation followed by electrophilic

Figure 11. A: Computed radical dimerization pathways to generate (–)-naseezazine C model **PDT_{C-C}** and B: Transition state and product free energies for both radical C–C bond formation at indole positions C2–C7 for **PDT_{C-C}**. C: Computed cationic dimerization pathways to generate **PDT_{C-C}** and D: Transition state and product free energies for cationic C–C bond formation at indole positions C2–C7 for **PDT_{C-C}**.

aromatic substitution (EAS) to form the C–C bond. The reaction was completed by re-aromatization via deprotonation of the resulting Wheland intermediate to forge the dimeric axis. To shed light on the viability of these proposed mechanisms for intermolecular C–C bond formation, as well as the intermolecular C–N bond formation to give **5** (catalyzed by NzeB), we turned to quantum mechanical (QM) calculations.

Given the proximity and orientation of the substrate in the cyclization site relative to the heme iron, we propose that the dimerization cascade is initiated by the oxidation of the substrate occupying the cyclization site. The mechanistic pathways (Figure 9) compare two possible modes for oxidative formation of the cyclized pyrroloindoline radical: hydrogen abstraction of 1) the proximal indole N–H bond or 2) the diketopiperazine N–H bond starting from separated brevianamide **6** and P450 iron-oxo (Compound I). While indole N–H abstraction has a lower free energy barrier (path 1, 11.5 kcal/mol) than DKP N–H abstraction (path 2, 20.3 kcal/mol), both pathways are energetically plausible and subsequent steps have equal or higher free energy barriers. Furthermore, the diketopiperazyl radical (**R-II**) can cyclize directly to the pyrroloindoline radical (**R-III**) with a free energy barrier of 20.7 kcal/mol, while cyclization of the indolyl radical (**R-I**) would need to be accompanied by the net movement of a hydrogen atom from the DKP ni-

trogen to the indole nitrogen. A unique feature of the active site of NzeB is the hydrogen bonding of the DKP N–H to a heme propionate. We considered the heme propionate as a possible hydrogen relay to enable cyclization of indolyl radical (**R-I**), however calculations using acetate as a surrogate for the heme propionate gave a large free energy barrier (30.8 kcal/mol). Furthermore, there is an overall absence of participant residues (both side chain and backbone atoms) in the active site to catalyze this proton transfer. Single electron oxidation of indole to give a radical carbocation was also considered (Supporting Information, Supplementary Figure 23), however given the high energy radical cation intermediate (41.2 kcal/mol) we did not pursue this pathway further. In both depicted N–H abstraction pathways, a significant contribution to the overall free energy barrier is the formation of a pre-complex (**PC**) between the heme iron-oxo species and the substrate N–H bond to be abstracted (Figure 9, **PC-I** and **PC-II**). Compared to separated starting materials (diketopiperazine **6** and the heme iron-oxo), the free energy for the formation of the **PC** for indole N–H abstraction (**PC-I**) and the **PC** for DKP N–H abstraction (**PC-2**) are 5.3 kcal/mol and 9.2 kcal/mol, respectively. However, as evidenced by the crystal structure of NzeB, both DKP substrates are oriented to facilitate **PC** formation substantially lowering the free

Figure 12. A. Computed dimerization pathways for the formation of (–)-aspergilazine A (**5**): radical dimerization pathway and demonstration that a cationic pathway is thermodynamically unfavorable. B. Transition state and product free energies for radical C–N bond formation at indole positions C2–C7 for (–)-aspergilazine A (**5**) model PDT_{C-N}.

energy barrier for the entire transformation.

Following cyclization to the pyrroloindoline radical (Figure 11, **R-III**), formation of the C–C bond with a second unit of **6** (modeled as 3-methylindole) may occur through either a radical-mediated, or a cationic Friedel-Crafts mechanism. The depicted energetic landscape of both dimerization mechanisms lead to formation of (–)-naseseazine C (**4**) (Figure 11), however, analogous computations of the pathway leading to the formation of (+)-naseseazine B (**2**) (Supporting Information), were qualitatively similar and led to the same conclusions. In the radical-mediated mechanism, C–C bond formation is the rate-determining step with a free energy barrier of 24.3 kcal/mol, while in the cationic mechanism the C–C bond formation barrier of 20.3 kcal/mol falls slightly below the preceding cyclization. Both mechanisms remain viable given that these computations are performed on a model system in the absence of active site residues, and that the computed barriers are relatively close. However, NzeB lacks any side chains, backbone amides, or water molecules at an appropriate location in the active site to act as a general base for deprotonation of Wheland intermediate (**C-IV**) generated in the cationic Friedel-Crafts pathway. Furthermore, alanine mutants of distal acidic/basic residues in the active site (Q78, Q75, E76, E317), which could act to re-aromatize the Wheland intermediate (**C-IV**) are still catalytically competent for dimerization (Supporting Information, Supplementary Figure S13). However, re-aromatization of intermediate (**R-IV**) via H-atom abstraction by the iron(IV)-hydroxo (Compound II) is likely to be facile given the proximity of C5 and C6 to the heme co-factor. Alternatively, localization of C5 and C6 to the heme may also allow a single electron oxidation of intermediate **R-IV** to intermediate **C-IV** by Compound II followed by deprotonation and re-aromatization of **C-IV** by the resulting iron(III)-hydroxo species.

In addition to catalyzing intermolecular C–C bond formation, NzeB also catalyzes the intermolecular C–N bond formation to generate (–)-aspergilazine A (**5**). Given the viability of both a radical and cationic dimerization mechanism for NzeB catalyzed C–C bond formation, we also compared the energetic landscapes of radical and cationic pathways for C–N bond formation starting from the uncyclized indolyl radical (Figure 11). In the radical-

mediated pathway, the rate-limiting C–N bond formation has a thermodynamically plausible free energy barrier of 21.7 kcal/mol. In contrast, a potential cationic pathway would require oxidizing the indolyl radical (**R-V**) to a cation (**C-V**), which is thermodynamically demanding (45.5 kcal/mol). Given that the oxidation needed to access a cationic pathway is so highly unfavorable, quantum mechanical computations clearly support a radical-mediated pathway in the case of C–N bond formation.

The C–C bond forming cascade catalyzed by NzeB results in the formation of two C–C linked dimers **2** and **4**, as well as the C–N bond linked dimer **5**. Computations were performed to examine the innate selectivity for cation and radical mechanisms for intermolecular C–C bond formation (Figure 11B & 11D), and analogous computations were performed for radical C–N bond formation (Figure 12B). For all computations relating to C–C and C–N bond formation, regardless of radical or cation mechanism, the observed dimerization site selectivity displayed by NzeB does not coincide with either the transition states or products that are lowest in free energy. Thus, these computations suggest that DKP-dimerization is catalyst-controlled rather than driven by the innate reactivity of the DKP substrates, with NzeB guiding the selective intermolecular C–C and intramolecular C–N bond formation.

Discussion

Biosynthesis of the tryptophan-linked dimeric DKP alkaloids reveal Nature's ability to build molecular complexity from simple and abundant building blocks captured from primary metabolism. The production of DKP dimers from both fungal and bacterial origin indicates the biological utility of this natural product scaffold. Characterized fungal systems utilize non-ribosomal peptide synthetases (NRPS) to generate DKP monomers, while bacterial pathways generate the same monomers via CDPSSs. Characterization of CDPSS-associated gene clusters has decrypted the biosynthetic pathways for known natural products such as bicyclomycin,^{30, 31} albonoursin,³⁵ and the drimentines.³⁶ Furthermore, these investigations have also identified new classes of natural products as well as unique DKP tailoring reactions including dehydrogenation,³⁵ C–H hydroxylation,^{30, 31} C–, O–, and N–methylation,³⁷ prenylation and cyclization of terpenes,³⁶ and oxidative coupling with purine nucle-

obases.²⁶⁻²⁹ P450-mediated diketo-piperazine dimerization further expands the repertoire of tailoring events found in CDPS-associated pathways.

The isolation of isomeric DKP dimers from a single organism is relatively common, which suggested two biosynthetic postulates; 1) a single dimerase with low selectivity enabled the assembly of isomeric products, or 2) a discrete dimerase was required for each coupling mode. Our results demonstrate there is no general axiom for bacterial biosynthesis of DKP dimers. P450s NascB and NznB from *Streptomyces* sp. CMB-MQ030 each catalyze a site- and stereoselective dimerization of **6** resulting in (–)-naseaezine C (**4**) and (+)-naseaezine B (**2**), respectively. By contrast, NzeB catalyzes both known bacterial C–C bond forming dimerization modes generating **2** and **4**, while also displaying chemodivergent reactivity in the formation of C–N bond linked dimer, (–)-aspergilazine A (**5**). While “multifunctional” bacterial P450s are well known,³⁸ this typically refers to the ability for a P450 to perform multiple monooxygenase reactions, such as hydroxylations at multiple sites,³⁹ hydroxylation and epoxidation activity,⁴⁰ hydroxylation with continued reaction to higher oxidation states, or a combination of these processes. NzeB differs from these enzymes in its ability to mediate formation of site- and stereoisomeric C–C linked products **1** and **2**, and also catalyzes direct Csp²–H amination in the formation of **5**. Recently, multiple reports have disclosed engineered enzymes capable of performing inter- and intramolecular C–H amination.^{41, 42} However this transformation is relatively rare in nature with few examples in the literature,^{43, 44} and to our knowledge, NzeB represents the first structurally characterized, wild-type P450 to catalyze intermolecular Csp²–H amination.

We were able to obtain multiple high-resolution crystal structures, including NzeB ligand free, and in complex with select native and non-native substrates. Our biosynthetic hypotheses for the C–C bonded dimers **2** and **4** were supported by direct observation of the NzeB-DKP complex, with the enzyme possessing two distinct binding sites to pre-organize substrates for diastereoselective cyclization as well as site-selective C–C bond formation. Synthesis and screening of non-native substrates for their selective heterodimerization enabled validation of the cyclization and dimerization sites. Moreover, we were able to capture a complex of NzeB with sterically differentiated ligands, brevianamide F (**6**) and *cyclo*(L-Trp-L-Trp) (**17**), which unambiguously confirmed our assignment of roles to each DKP binding site. The connectivity and configuration of the dimerization axis of heterodimeric product **18** is identical to that of the NzeB minor product (+)-naseaezine B (**2**), and is consistent with the binding mode of the two monomeric precursors (Figure 8). We hypothesize this is due to the markedly larger side chain of **17** which occupies the additional channel in the cyclization site wherein the native substrates may occupy during catalysis in order for both substrate and enzyme to undergo the conformational changes necessary to access either the (–)-naseaezine C or (–)-aspergilazine A scaffolds. Notably, all other structurally characterized DKP functionalizing CYP450s (CYP121,³³ CypX,²⁵ and TxtC²⁴) bind DKPs in the analogous position of the active site, which corresponds to the cyclization site of NzeB. The dimerization site of NzeB is a previously unobserved pocket for DKPs in P450s and accounts for an approximate doubling of the active site volume of NzeB (832 Å³) relative to other DKP binding CYP450s.⁴⁵ Previous efforts in the characterization of NascB demonstrated that in heterodimerization reactions the bulky substrates undergo cyclization to form pyrroloindoline functionality.²⁰

Our structural investigations of NzeB and assignment of the role of the dimerization site provides a structural basis for this phenomenon. Furthermore, identifying the sidechains in the dimerization site that encapsulate the proline moiety of its substrate paves the way to reshaping this binding pocket. Engineering DKP dimerases to enable coupling of DKPs with larger side chains may enable formation of products similar to those isolated from fungi.⁴⁶⁻⁴⁸

Mutagenesis of the active site of NzeB provided further insight into how NzeB guides the site- and stereoselective formation of C–C and C–N bonds. Comparison of the active site residues of NzeB to NascB and NznB, identified that each possessed a single, active site variation (NzeB: Ser287, NascB: Ala287). To examine the role of this active site variation in selectivity the NzeB_{S287A} variant was generated and homodimerization reactions with native substrate **6**, NzeB_{S287A} exclusively generates (–)-naseaezine C (**4**) completely reconstituting the selectivity of NascB with a single substitution. Given this result, we reasoned that through homologous substitution of the active site variation between NznB and NzeB, located in the cyclization site (NzeB: Gln68 vs NznB: Met68) would provide access to a surrogate of NznB. The prospect of engineering the dimerization selectivity of NzeB to recapitulate that of NznB is particularly attractive, as wildtype NznB has low TTN relative to NascB and NzeB (Figure 2). However, counter to the results from NzeB_{S287A}, dimerization reactions with NzeB_{Q68M} did not recapitulate the observed NznB selectivity, rather led to the formation of previously unobserved dimer (–)-isonaseaezine C (**11**).

These results demonstrate that the selectivity of a given DKP dimerase cannot be reconstituted simply by interchanging active site residues, and therefore the selectivity of NzeB and its homologues must also be determined by residues outside the active site motif. Thus, we propose that the observed crystal structure represents one of many catalytically relevant conformations, and that the active site must undergo conformational remodeling during catalysis, with the selectivity of the dimerization reaction being influenced by a combination of residues both inside and outside of the active site. This is best represented by the discrepancy between the conformation of substrates in the ligand bound crystal structure of NzeB and the observed product distribution from the dimerization reaction. In the ligand-bound structure of NzeB, both substrates are apparently pre-organized toward formation of (+)-naseaezine B (**2**), despite this dimer being a minor product. To access conformations that would lead to the major product, diketopiperazine dimer **4**, the orientation of substrate in the cyclization site would require inversion from a concave to convex posture. Furthermore, in spin-shift binding assays of NzeB,⁴⁹ substrate **6** was able to displace the water molecules axial to the heme to induce a low- to high-spin transition of the heme iron indicative of direct binding to the active site (Supporting Information, Supplementary Figure 10). However, this axial water is present in both the ligand-bound and ligand-free crystal structures at high-occupancy, suggesting that solution-phase dynamics provide access to currently unobserved conformations. In addition, it is well-precedented that binding of electron transport proteins alters the architecture of cytochromes P450 during catalysis.⁵⁰ Given these factors we propose residues and regions distal to the active site are influencing selectivity and catalysis, and efforts to identify them in bacterial DKP dimerases are currently underway.

Finally, quantum mechanical computations provided new insights into NzeB's ability to catalyze formation of C–C and C–N bonds. Relative to C–O bond forming P450s, far fewer C–C bond forming

P450s have been structurally characterized; examples include both intramolecular such as StaP (PDB: 2Z3U)⁵¹ and CYP121 (PDB: 3G5H),³³ as well as intermolecular such as CYP158A1/CYP158A2 (PDB: 1T93, 2D09),^{52, 53} and recently the intramolecular C–N bond forming indolactam cytochrome P450 (PDB: 6J82).⁵⁴ A common feature among the characterized intra- and intermolecular C–C/C–N bond forming P450s is that one of the reactive atoms participating in C–C/C–N coupling is proximal to the heme iron while the second reactive atom is distal, and oxidation of this distal atom is facilitated by a basic amino acid residue or water via proton-coupled electron transfer (PCET).^{55, 56} However, unique to the structure of NzeB, reactive atoms from both ligands are positioned within 4 Å of the axial water ligand, indicating the possibility for direct oxidation of both ligands catalyzed by the heme without intervention of neighboring residues or solvent (Figure 5). Regardless of mechanism, they indicate that a major role of NzeB is to orient substrates for reaction with the heme iron oxo species. By facilitating the formation of a pre-complex, NzeB can reduce the free energy barrier for the overall transformation by up to 5 to 10 kcal/mol. Previous investigations into the mechanism for C–C bond formation excluded a cationic mechanism due to reactivity of electron poor substrates.²⁰ However, the utilization of electronically differentiated substrates for mechanistic studies such as Hammett plots is well represented in the literature, including enzymatic electrophilic aromatic substitution (EAS) type reactions.⁵⁷ Our computations demonstrate that both radical-mediated and cationic pathways are thermodynamically plausible for the formation of C–C bonds, with rate-determining transition states of comparable free energies. While there are residues present in the active site that could be positioned for deprotonation of Wheland intermediates, their distance appears too great from the appropriate carbon atoms, and mutation of these residues to alanine does not prevent dimerization. Given the lack of residues or active site water molecules necessary to deprotonate Wheland intermediates generated from a cationic pathway dimerization, and the localization of reactive atoms from both substrates proximal to the heme iron, we propose that C–C bond forming dimerization modes likely also proceed via a radical-mediated mechanism. However, re-aromatization of the C–C bond formed radical intermediate may occur through either concerted HAT or stepwise PCET by Compound II. In contrast, computations relating to formation of the intermolecular C–N bond in (–)-aspergilazine A (**5**) demonstrate that the cationic pathway is thermodynamically prohibitive and the radical-mediated mechanism is strongly favored. To examine the site selectivity of NzeB we also explored computationally the innate selectivity for C–C and C–N bond forming dimerizations. These computations demonstrate that regardless of cationic or radical mechanism, NzeB overrides the innate selectivity for C–C and C–N bond formation and the connectivity of the product dimers **2**, **4**, and **5** are the result of a catalyst-controlled dimerization, rather than the reactivity of the diketopiperazine substrates themselves. Further analysis is required to unambiguously exclude other mechanisms for C–C and C–N bond formation and is currently underway.

Conclusion

In conclusion, we identified and characterized the chemically versatile cytochrome P450, NzeB, capable of generating both (+)- and (–)-naseesazine frameworks as well as the non-cyclized Csp²–Nsp² linked (–)-aspergilazine dimeric scaffold. To gain insight into the molecular basis for its versatility, we obtained the first high-

resolution crystal structure of a DKP dimerizing P450 in complex with select native and non-native substrates. This structural information revealed a previously unrecognized DKP binding site compared to other reported crystal structures of DKP functionalizing P450s.^{24, 25, 33} NzeB is distinguished from the flaviolin dimerase, in its relatively close binding of DKP substrates proximal (within 4 Å) to the heme cofactor. Site directed mutagenesis of NzeB demonstrated that active site residues are not the sole drivers of site-, stereo- and chemoselectivity. Tandem structural, biochemical, and computational approaches explored the viability of cationic and radical mechanisms in intermolecular C–C bond formation, and provided evidence for a likely radical mechanism for intermolecular C–N bond formation. The structural, biochemical, and computational characterization of NzeB provides the first insight into the molecular basis for DKP dimerization. This new information opens the door to engineering NzeB and its functional homologs for improved total turnover number, broadened substrate scope, and new non-natural dimerization modes furthering our efforts towards a catalyst controlled method for DKP dimerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Full experimental and computational details, NMR spectra, tables, and figures. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the NSF CCI Center for Selective C–H Functionalization (CHE-1700982), NIH grant R35 GM118101 and the Hans W. Vahlteich Professorship (to D.H.S.). M.M. also acknowledges financial support by NIH grant GM089732. We are grateful to Dr. Robert J. Capon for providing *Streptomyces* sp. CMB MQ-030 under a materials transfer agreement. J.N.S. acknowledges support from the National Institutes of Health for award F32 GM122218. Computational resources were provided by the UCLA Institute for Digital Research and Education (IDRE) and by the San Diego Supercomputing Center (SDSC) through XSEDE (ACI-1548562).

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“Structure and Function of NzeB, a Versatile C–C and C–N Bond Forming Diketopiperazine Dimerase”

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Supporting Information

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Instrumentation

All UV-Visible spectra were acquired using a single beam Molecular Devices Spectra Max M5 spectrophotometer, with a 1cm quartz cuvette. Analytical HPLC data was acquired using a Shimadzu HPLC system comprised of two LC-20AD_{XR} pumps, a SIL-20AC_{XR} autosampler, and a SPD-M20A diode array detector. Preparatory HPLC was performed using a Beckman Coulter stack comprised of a System Gold 125 solvent module, 168 detector, and SC100 fraction collector. ¹H NMR spectra were recorded on Varian 600 MHz spectrometers and are reported relative to residual solvent peak (CD₂HOD: δ 3.31). ¹³C NMR spectra were reported relative to residual solvent peaks (CD₂HOD: δ 49.0).

Streptomyces sp. CMBMQ-030 genomic DNA sequencing

The genomic DNA of *Streptomyces* sp. CMB-MQ030 was extracted and purified as prescribed using the Promega Wizard® Genomic DNA Purification Kit. The genomic DNA (2x250 bp paired-end) was sequenced using Illumina HiSeq 2500 sequencing system at University of Michigan DNA Sequencing Core. Briefly, the genomic DNA sample was first sheared to approximately 500 nucleotide average fragment size, then Illumina-compatible sequencing libraries were prepared from those fragments on an Apollo 324 robotic workstation (WaferGen Biosystems), using the Kapa HTP Library Preparation Kit (KAPABiosystem) according to the manufacturer's protocols. Subsequent libraries were sequenced on an Illumina HiSeq 2000, obtaining paired-end sequence data with 100 nucleotide reads at each end, as per recommended protocols from Illumina, Inc. The generated next-generation sequencing data were then *de novo* assembled using Velvet 1.2.10.

Supplementary Table 1. Summary of genome assembly dataset and parameters

Genome	Number of reads	k-mer	Coverage cutoff	N50	Number of contigs
<i>Streptomyces</i> sp. (CMB-MQ030)	33,263,004	51	10	66,868	591

Cloning of NascA, NascB, and NznA

The PCR primers were designed to introduce an *NdeI* restriction site at the 5' end of the fragment and a *HindIII* restriction site 3' end, respectively. The coding sequences were amplified from the genomic DNA of *Streptomyces* sp. CMB-MQ030 using primers for the associated target gene. The expression constructs were designed in pET28b vector cloning at *NdeI* and *HindIII* restriction sites for NascA, NznA and NascB. NznB+09 and NzeB were cloned into pET28b using Quickchange mutagenesis. The nucleotide sequences were confirmed by automated sequencing (University of Michigan DNA Sequencing Core).

Supplementary Table 2. Primers used in cloning NascA, NascB, NznA, NznB, and extending codon optimized sequence of NznB

Gene	Primer	Rest. Site	5'→3'
NascA	Forward	<i>NdeI</i>	CCAACCcatatgGTGAACACTTCCCTCGCTGCGGTGGCCGGC
NascA	Reverse	<i>HindIII</i>	CCAACCaaagcttGCGTTCGGCCGCCCGGTCCCGCAGCAGGAT
NascB	Forward	<i>NdeI</i>	CCAACCcatatgGTGACCACCACCGCCACGCTGACCTACCCC
NascB	Reverse	<i>HindIII</i>	CCAACCaaagctt CCAGGTGGCGGGAAGCGCCCGCGGACGGCG
NznA	Forward	<i>NdeI</i>	CCAACCcatatgATGGCCACACACGCCTCCGCACCCGCACCC
NznA	Reverse	<i>HindIII</i>	CCAACCaaagcttCTGCTGCGTCACGCGGTCCTTGAGGAG
NznB (CO) +09	Forward		GTGGATCCGTATACCAAAGAATGCCGTACCGTGACCACCGC GCCGGTTCCGCT
NznB (CO) +19	Forward		GTGATTTCGTCCGCAGCCGCATCGTAGCCCGGTGGATCCGTA TACCAAAGAATGCCGTACCGTGACCACCGCGCCGGTTCCGC T
NzeB	Forward		ctgagaatctctacttccaaggcgtagcGTGACCACCACCACCGCCACG CTGACCT
NzeB	Reverse		cctttcgggctttgttagcagccggtatcTCACCAGGTGGCGGGGATCGCCC GC

Codon optimized sequence for NznB

ACCACCGCGCCGGTTCCGCTGACCTTCCCGTTTCACGATTGGAGCCAAGAGCTGAGCCCGCACCATGAG
CGTCTGCGTGAAGCGGATGCGCCGGTGTGCCCGGTGGTTAGCGAGTACACCGGTGACCGTCTGTGGCT
GGTTACCCGTTATGCGACCGCGAAGCGTCTGCTGGAAGATCGTCGTTTCAGCAGCACCGCGGCGATGGC
GCCGGGTGCGCCGCGTCAGGAGCCGGTGGAACTGCGTGCGCCGGGCACCACCGGTGATGGTGTGAGC
GTTCTGCGTGAGGCGGGTCTGCGTACCGTTTTTACCGAAGGTCTGGGTCCGCGTGCGGCGCGTCGTCAC
GGTAAATGGCTGCGTGATCGTGCGGACACCCTGCTGCGTGATGTGGCGGAGTGCGAAGGTCCGGTTGAT
CTGGCGGCGGACTTTGCGCAGCCGCTGGCGGTGGCGATGACCAGCCGTGTTCTGCTGGGTGAACTGAG
CACCGAGGAAGCGGCGCTGCTGCGTGATCGTACCGATCTGGCGCTGCAGTTTTGCGGTGCGACCGCGG
AGGAACAACGTGGTGGCCTGATCGATATTCACCGTTTCTTTACCGCGCATGCGCGTCTGCTGGCGGATG
GTCCGGGTGACCACCTGCTGAAGCGTCTGGCGGAGGCGCCGGCGGAAAACGGTCCGCTGGGTGATGCG
GCGCTGAGCGAAATTGCGGCGCTGCTGCTGATTGCGGGTTTCCCGACCAGCAGCGGCTTTCTGTGCGGT
GCGCTGATCACCTGCTGCGTCACCCGAGGCGGTGGGCCGTCTGCGTCGTGATCCGGAACCTGATTCC
GGACGCGGTTGAGGAACTGCTGCGTCATACCCCGCTGAGCACCGGTGCGGCGAAACGTATGGCGACCG
AGGACGCGGATATCGACGGCGTGCGTATTCGTGCGTGGTGGCGATGGTTAGCCTGGAAGCGGCG
AACCACGATCCGGACGCGTTTCGACGATCCGGATAGCTTTCGTCCGGAACGTCAAGGTCCGGGTACCTG
GGTTTTGGCCACGGTCCGAACCTTTTGGCCGGTAACCGTCTGGCGCGTTGCCTGATTGATGCGATGGTG
CGTGCGGTTGCGCGTCTCGGGTCTGCACCTGACCGTTGGTCCGGAGGAAATCCGTTGGCACGAAGG
CCTGTTCTTTCGTGCTCCGAAGGCGATTCCGGCGAGCTGG

Overexpression and analysis of CDPs NascA/NznA.

The expression of CDPs was performed by transforming the plasmid into the competent cell *E. coli* strain C41(DE3) and selected on Luria-Bertani (LB) medium plates containing 50 µg/mL kanamycin. A single colony was grown overnight in 5 mL LB broth containing the same concentration of the antibiotics. The main culture was prepared by inoculating 1% of each overnight culture into a 2 L baffled flask containing 1 L of LB containing 50 µg/mL kanamycin. The cultures were incubated at 37°C and 250 rpm for 3-4 h until the absorbance $A_{590\text{nm}} = 0.6$. The expression of CDPs was induced by the addition of 1 mM isopropyl β-D-1-thiogalactopyranoside (IPTG). The cultures were incubated further at 18°C for 18 h shaking at 180 rpm. Cells were harvested by centrifugation at 5000×g at 4°C for 15 min and a 1 mL aliquot of the supernatant was extracted with 1 mL CHCl_3 (3x). The organic extracts were dried and solvents were removed *en vacuo*. Residue was resuspended in 100 µL of HPLC grade methanol for HPLC analysis in which the samples were resolved using a linear gradient of 5-100% acetonitrile: water (0.1% formic acid) over 30 min (1.5 mL/min flow rate) on a Phenomenex Luna 5µ C-18(2) 100A, 250 × 4.60mm 5 micron column.

Supplementary Figure 1. HPLC traces for NascA/NznA Expression Extractions

Supplementary Figure 2. HPLC/MS Analysis of Diketopiperazine 6 Isolated From CDPS Culture

Exact Mass: 284.1394

Supplementary Figure 3. ^1H NMR characterization of purified DKP 6 from NascA CDPS overexpression

^1H NMR (599 MHz, $\text{DMSO}-d_6$) δ 10.83 (s, 1H), 7.73 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 2.2 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 1.94 (dtd, J = 9.8, 6.9, 2.7 Hz, 1H), 1.66 (ddd, J = 19.1, 9.1, 5.6 Hz, 1H), 1.59 (ddp, J = 12.2, 8.4, 4.6, 4.1 Hz, 1H), 1.35 (dtd, J = 12.1, 10.3, 7.8 Hz, 1H).

Supplementary Figure 4. ^{13}C NMR characterization of purified DKP 6 from NascA CDPS overexpression¹

^{13}C NMR (151 MHz, dms) δ 169.43, 165.92, 136.37, 127.77, 124.82, 121.30, 119.08, 118.65, 111.65, 109.70, 58.85, 55.66, 45.03, 28.11, 26.23, 22.31.

Supplementary Figure 5. HPLC/MS Analysis of Diketopiperazine SI-01 Isolated From CDPS Culture

SI-01
Exact Mass: 258.1237

Supplementary Figure 6. ^1H NMR characterization of purified DKP SI-01 from NznA expression.

^1H NMR (599 MHz, $\text{DMSO}-d_6$) δ 10.87 (s, 1H), 8.00 (s, 1H), 7.89 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 4.08 (d, J = 2.7 Hz, 1H), 3.56 (dd, J = 7.0, 2.0 Hz, 1H), 3.32 (s, 1H), 3.21 (dd, J = 14.4, 4.1 Hz, 1H), 2.98 (dd, J = 14.4, 4.6 Hz, 1H), 2.47 (t, J = 1.9 Hz, 1H), 0.38 (d, J = 7.0 Hz, 3H).

Supplementary Figure 7. ^{13}C NMR characterization of purified DKP SI-01 from NznA expression.

^{13}C NMR (151 MHz, dmso) δ 168.14, 167.16, 136.20, 128.22, 124.98, 121.22, 119.40, 118.80, 111.51, 108.91, 55.82, 50.20, 29.27, 19.98.

Supplementary Figure 8. HPLC trace for NzeB CDPS overexpression

General procedure for overexpression, purification and spectral characterization of cytochrome P450s

The expression of P450s was performed by transforming the plasmid into the competent cell *E. coli* strain C41(DE3) and selected on Luria-Bertani (LB) medium plates containing 50 µg/mL kanamycin. A single colony was grown overnight in LB broth containing the same concentration of the antibiotics. The main culture was prepared by inoculating 1% of each overnight culture into a 2 L baffled flask containing 500 ml of Terrific Broth (TB) containing 50 µg/mL kanamycin. The cultures were incubated at 37°C and 250 rpm for 3-4 h unless the absorbance $A_{590\text{nm}} = 1$. The expression was induced by the addition of 0.8 mM isopropyl β-D-1-thiogalactopyranoside (IPTG) and 1.0 mM delta-5-aminolevulinic acid (w/v). The cultures were incubated further for 36 h, 28°C at 160 rpm. Cells were harvested by centrifugation at 5000×g at 4°C for 10 min and the cell pellet was stored at –80°C until purification of the protein.

The cell pellet was resuspended in 5% culture volume of lysis buffer (50 mM Tris, pH 7.4 containing 50 mM NaCl, 2% glycerol, 0.5 mM EDTA, 10 mM beta-mercaptoethanol and 1mM phenylmethane sulfonyl fluoride (PMSF) and disrupted by sonication. The cell lysate was centrifugated (35,000 rpm for 35 min) and filtered (0.2 µM Millipore filter). The soluble His₆-tagged NasB was purified by affinity chromatography using Ni-NTA (Qiagen) column and the collected fractions were analyzed by SDS-PAGE. The suitable red fractions were pooled and dialyzed at 4°C three times using 50 mM Tris, pH 7.4 containing 10% glycerol, 50 mM NaCl and 1 mM dithiothreitol (DTT) against a total of 6 L buffer.

Supplementary Figure 9. UV-Visible spectra of NzeB

UV-Vis spectra for the purified NzeB was recorded at room temperature in buffer (50 mM Tris-HCl buffer, pH 7.4 containing 5% glycerol) was used for the spectral measurements of the oxidized and reduced form. NzeB was reduced by the addition of a small amount of sodium dithionite. The concentration of the P450s was estimated by CO-difference spectra, assuming $\epsilon(459-490) = 91 \text{ mM}^{-1} \text{ cm}^{-1}$ according to the method of Omura and Sato .

The UV-Vis spectra of oxidized (blue line), sodium dithionite reduced (red line) and CO-bound (green line) of purified NzeB are shown. The inset showed the SDS-PAGE of NzeB purification, Lane 1: marker (SeeBlue Plus2, Novex), 2-5: purified NzeB fractions

Supplementary Figure 10. Spin shift titrations with NzeB and brevianamide F (**6**)

The spin-state shift caused by binding of **6** with NzeB was assayed at room temperature under aerobic conditions using an UV-Vis spectrophotometer. The high-spin spectrum of NzeB (5 μM) was obtained by adding 10 to 100 μM of **6**.

The overlaid difference spectra obtained by subtracting the spectrum for ligand-free NzeB from the successive spectra for substrate-bound accumulated during the titration between 10 and 100 μM **6** are shown. The Soret band maximum is gradually shifted from 417 nm to 393 nm during the addition of increasing concentrations of **6**.

General reaction conditions for analytical scale P450 reactions

The conversion of DKPs by P450s were carried out with the heterologous redox electron partners Fdx and FdR from *S. olerecea*. A protein ratio of P450: Fdx: FdR of 10: 20: 6 was used. The *in vitro* reaction mixture included 50 mM Tris-HCl, pH 7.4, 10 μ M P450, 20 μ M Fdx and 6 μ M FdR at the end volume of 250 μ L. 3mM of DKP dissolved in DMSO was added, followed by 1 unit of glucose-6-phosphate dehydrogenase (from *S. cerevisiae* and a 500 mM glucose-6-phosphate. The reaction was initiated by adding NADPH (1 mM). Two of the control reactions including all the contents except for NADPH or P450 were used as controls. The reaction was incubated at 30°C for 1 h agitating at 600 rpm in a thermoshaker (Multi-thermoshaker, Benchmark). The conversion was stopped by adding an equal volume of chloroform and was extracted with chloroform for 3 times. The samples were dried under a stream of nitrogen and the residue was resuspended in 100 μ L of HPLC grade methanol and analyzed by HPLC in which the reaction mixture was resolved using a linear gradient of 5-100% acetonitrile: water (0.1% formic acid) over 30 min (1.5 mL/min flow rate) on a Phenomenex Luna 5 μ C-18(2) 100A, 250 $\times$ 4.60mm 5 micron column.

General reaction conditions for preparatory scale P450 reactions

Large scale reaction were performed in 10mL volumes with reaction conditions as described above. After 2 hours, reactions were quenched with 30mL of methanol, transferred to a 50mL conical tube and vortexed on the highest setting for 1 minute. This mixture was then passed through a column of Celite © followed by 20mL of methanol to wash the filter cake. Water and solvents were removed *en vacuo*, and residue was resuspended in HPLC grade methanol with sonication. Insoluble particulates were removed via filtration through 0.2 μ m syringe filter and products were directly purified by preparatory-HPLC.

Prep-Scale Synthesis of (–)-naseseazine C (4)

Procedure above was followed with DKP **6**, as a substrate and NascB as P450. The filtered solution was then purified via preparative HPLC (Luna preparative HPLC column, C18, 5 μ m, 21.2 $\times$ 250 mm;) using gradient of 5% to 100% acetonitrile in water containing 0.1% formic acid at the flow of 7.0 mL/min for 60 min. The retention time (t_R) of **4** was 31.2 min. The product fractions were pooled, solvent was removed *en vacuo*, to give 8 mg of (–)-naseseazine C which was used for detailed NMR characterization without any further purification.

Prep-Scale Synthesis of (+)-naseseazine B (2)

Procedure above was followed with DKP **6**, as a substrate and NznB+09 as P450. The filtered solution was then purified via preparative HPLC (Luna preparative HPLC column, C18, 5 μ m, 21.2 $\times$ 250 mm;) using gradient of 5% to 100% acetonitrile in water containing 0.1% formic acid at the flow of 7.0 mL/min for 60 min. The retention time (t_R) of **2** was 34.1 min. The product fractions were pooled, solvent was removed *en vacuo*, to give 11 mg of (+)-naseseazine B which was used for detailed NMR characterization without any further purification.

Prep-Scale Synthesis of (–)-aspergilazine A (5)

Procedure above was followed with DKP **6**, as a substrate and NzeB as P450. The filtered solution was then purified via preparative HPLC (Luna preparative HPLC column, C18, 5 μ m, 21.2 $\times$ 250 mm;) using gradient of 5% to 100% acetonitrile in water containing 0.1% formic acid at the flow of 7.0 mL/min for 60 min. The retention time (t_R) of **5** was 36.6 min. The product fractions were pooled, solvent was removed *en vacuo*, to give 2 mg of (+)-naseseazine B, 6 mg of (–)-naseseazine C, and 3 mg of (–)-aspergilazine A which was used for detailed NMR characterization without any further purification.

Prep-Scale Synthesis of 18

Procedure above was followed with DKPs **6** and **17**, as a substrates and NzeB as P450. The filtered solution was then purified via preparative HPLC (Luna preparative HPLC column, C18, 5 μ m, 21.2 $\times$ 250 mm;) using gradient of 5% to 100% acetonitrile in water containing 0.1% formic acid at the flow of 7.0 mL/min for 60 min. The retention time (t_R) of **18** was 42.1 min. The product fractions were pooled, solvent was removed *en vacuo*, to give approximately 1 mg of **18** which was used for detailed NMR characterization without any further purification.

Supplementary Figure 11. HPLC/MS traces with extraction ion chromatograms (EIC) for analytical scale heterodimerization of SI-01 and DKP 6 to form (–)-naseseazine A catalyzed by NznB.

Supplementary Figure 12. HPLC traces from NzeB catalyzed heterodimerizations.

All heterodimerizations of DKP **6** with DKPS **SI-02-SI-04** show formation of (–)-naseseazine C (**4**) with the heterodimerization of **6** with *cyclo*(L-Trp-L-Trp) (**17**) giving the least formation of **4**.

Supplementary Figure 13. HPLC traces from NzeB alanine scanning mutants.

Supplementary Figure 14. ^1H NMR spectra for isolated (–)-aspergilazine A (5) from NzeB scale up reaction

^1H NMR (599 MHz, $\text{DMSO}-d_6$) δ 11.05 (s, 1H), 7.97 (s, 1H), 7.85 (s, 1H), 7.71 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.43 (s, 1H), 7.41 (d, J = 1.9 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.10 (d, J = 2.0 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 4.37 (t, J = 5.4 Hz, 1H), 4.33 (t, J = 5.3 Hz, 1H), 4.09 – 4.03 (m, 2H), 3.35 (tdd, J = 19.4, 9.6, 6.3 Hz, 3H), 3.30 – 3.20 (m, 3H), 3.15 – 3.09 (m, 2H), 1.96 (dtt, J = 14.0, 6.9, 3.5 Hz, 2H), 1.75 – 1.51 (m, 4H), 1.36 (ddtd, J = 18.1, 12.4, 10.2, 7.8 Hz, 2H).

Supplementary Figure 15. ^{13}C NMR spectra for isolated (–)-aspergilazine A (5) from NzeB scale up reaction

^{13}C NMR (151 MHz, DMSO- d_6) δ 169.54, 169.47, 165.88, 165.84, 136.49, 136.01, 133.45, 128.94, 128.76, 128.54, 126.49, 126.17, 122.45, 119.82, 115.63, 111.38, 110.12, 107.09, 58.88, 55.68, 55.59, 45.05, 28.14, 26.20, 22.31, 22.28.

Supplementary Figure 16. ^1H NMR spectra for **18** isolated from NzeB scale up

^1H NMR (599 MHz, $\text{DMSO}-d_6$) δ 10.80 (s, 2H), 8.26 (s, 1H), 7.88 (s, 1H), 7.70 (s, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.41 (s, 1H), 7.19 (dd, J = 17.9, 8.2 Hz, 2H), 7.15 (d, J = 2.2 Hz, 1H), 7.12 (d, J = 2.3 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.86 (t, J = 7.4 Hz, 1H), 6.76 (dd, J = 8.5, 1.7 Hz, 1H), 6.63 (s, 1H), 6.58 (d, J = 7.8 Hz, 1H), 6.55 (t, J = 7.4 Hz, 1H), 5.49 (s, 1H), 4.38 (d, J = 5.1 Hz, 1H), 4.29 (t, J = 5.5 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.92 (dd, J = 11.8, 5.5 Hz, 1H), 3.37 (dt, J = 11.7, 7.9 Hz, 1H), 3.27 (ddd, J = 12.2, 8.8, 3.9 Hz, 1H), 3.23 – 3.17 (m, 3H), 3.02 (dd, J = 15.0, 6.0 Hz, 1H), 2.81 (dd, J = 12.2, 5.6 Hz, 1H), 2.09 (t, J = 11.9 Hz, 1H), 2.04 – 1.95 (m, 1H), 1.73 – 1.58 (m, 2H), 1.53 – 1.42 (m, 1H).

Supplementary Figure 17. ^{13}C NMR spectra for **18** isolated from NzeB scale up

^{13}C NMR (151 MHz, dms) δ 169.64, 168.30, 166.01, 165.70, 164.76, 150.07, 136.29, 135.14, 134.50, 133.07, 128.45, 127.79, 127.40, 125.08, 124.71, 124.24, 121.22, 119.53, 119.08, 118.63, 118.31, 114.97, 111.94, 111.57, 110.00, 109.45, 109.39, 82.00, 59.02, 58.91, 58.83, 55.68, 55.45, 49.04, 45.09, 41.43, 28.11, 26.83, 25.86, 22.40.

Supplementary Figure 18. gHSQCAD spectra for **18** isolated from NzeB scale up

Supplementary Figure 19. gHMBCAD spectra for **18** isolated from NzeB scale up

Supplementary Figure 20. gCOSY spectra for **18** isolated from NzeB scale up

Supplementary Table 3. Cytochromes P450 used to generate sequence similarity network (SSN)

P450	Organism	Accession	Natural Product	Reference
NascB	<i>Streptomyces</i> <i>sp.</i> CMB-MQ030	AWF71596.1	(–)-naseseazine C	Nat. Commun. 2018, 4428
P450NB5737	<i>S. purpureus</i> (NRRL B-5737)	WP_019889608	guanitrypmycin C3-1	<i>Org. Lett.</i> 2018 , 4921
TxtC	<i>S. scabies</i>	6F0C_A	thaxtomin A	<i>JACS</i> 2019 , 216
CypX	<i>B. subtilis</i>	WP_148962661. 1	pulcherrimic acid	Biochemistry, 2010, 7282
BcmD	<i>S.</i> <i>sapporonensis</i>	AXQ04975.1	bicyclomycin	<i>ACIEE</i> 2018 , 719
CYP121	<i>M. tuberculosis</i>	P9WPP7.1	mycocyclosin	J. Biol. Chem. 2003, 5141

Process of crystallization

Crystallization of NzeB.

Single, diffraction quality crystals of the *NzeB* complexes were grown by sitting drop vapor diffusion at 20 °C by mixing 2 μ L of 8 mg/mL protein containing 1 mM DKP substrate and 0.2% DMSO with 2 μ L of a well solution containing 23% PEG 3350, 100 mM DL-malic acid, 2.5% ethylene glycol. Equimolar concentrations of substrate (0.5 mM) were used for the *NzeB*-6·17 complex. Sitting droplets were nucleated after 4 h from an earlier spontaneous crystallization using a cat whisker. Single crystals grew after 48 hours. 8 μ L of a cryoprotecting solution containing 10 mM Tris pH 7.5, 2 % glycerol, 23% PEG 3350, 100 mM DL-malic acid, 18% ethylene glycol, 1 mM DKP substrate, 0.2% DMSO was added directly to the sitting drops and the crystals were harvested using nylon loops and vitrified by rapid plunging into liquid nitrogen. *NzeB* crystallized in space group *P* 1 with unit cell dimensions of $a = 56.1$ Å, $b = 56.3$ Å, $c = 58.8$ Å, $\alpha = 91.1^\circ$, $\beta = 92.9^\circ$, $\gamma = 100.1^\circ$ and two chains in the asymmetric unit.

Data collection and processing.

X-ray data were collected at 100 K on beamline 23ID-B at the National Institute for General Medical Sciences (NIGMS) and National Cancer Institute (NCI) Structural Biology Facility at the Advanced Photon Source in Argonne, IL, USA. Diffraction data were integrated and scaled using XDS.¹ Data collection statistics are given in Supplementary Table 2.

Molecular replacement, model building and refinement.

The structure of NascB-F5053 was solved using Phenix MR-Rosetta.² This resulted in an initial model that could be extended by alternating cycles of manual building in Coot³ and least-squares refinement with Phenix.⁴ Final models were validated using MolProbity.⁵

Supplementary Table 4. Data Collection Statistics

	NzeB in complex with 6	NzeB in complex with 6 and 17	NzeB ligand free
Wavelength (Å)	1.03	1.03	0.826
Resolution range (Å)	40.83 - 1.49 (1.54 - 1.49)	41.22 - 1.48 (1.53 - 1.48)	39.13 - 1.498 (1.55 - 1.50)
Space group	P 1	P 1	P 2 ₁
Unit cell	56.12, 56.28, 58.78 Å 91.13, 92.93, 100.10°	56.07, 56.13, 58.48 Å 91.36, 93.04, 101.10°	55.71, 55.81, 56.10 Å 90, 101.92, 90°
Total reflections	382537 (31077)	324387 (4806)	359895 (35646)
Unique reflections	109037 (10046)	94423 (2902)	54058 (5282)
Multiplicity	3.5 (3.1)	3.4 (1.7)	6.7 (6.7)
Completeness (%)	94.48 (87.34)	80.96 (24.95)	99.66 (97.45)
Mean I/sigma(I)	16.78 (2.39)	20.64 (1.81)	14.45 (1.35)
Wilson B-factor (Å ²)	19.96	22.24	23.40
R-merge	0.039 (0.361)	0.030 (0.287)	0.056 (1.013)
R-meas	0.046 (0.439)	0.036 (0.398)	0.061 (1.097)
CC1/2	0.998 (0.85)	0.999 (0.851)	0.999 (0.743)
Reflections used in refinement	109025 (10043)	94401 (2902)	54024 (5279)
R-work	0.168 (0.287)	0.192 (0.333)	0.188 (0.292)
R-free	0.211 (0.340)	0.234 (0.410)	0.219 (0.307)
Number of atoms (total):	6989	6995	3441
macromolecules	6108	6079	3021
ligands	190	196	55
solvent	691	720	365
Protein residues	798	793	392
RMS(bonds)	0.005	0.007	0.006
RMS(angles)	0.91	1.23	0.84
Ramachandran favored (%)	97.21	97.56	97.91
Ramachandran allowed (%)	2.79	2.44	2.09
Ramachandran outliers (%)	0.00	0.00	0.00
Average B-factor (Å ²)	27.51	28.55	31.52
macromolecules	26.79	28.07	30.84
ligands	19.50	22.09	25.73
solvent	36.01	34.38	37.97

Supplementary Figure 21. Comparison of A) NzeB substrate bound, and B) substrate free active sites.

Supplementary Figure 22. NzeB Active site showing A) steric packing in dimerization site, b) open channel in cyclization site, C) and the view from 180° rotation.

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Computational Methods

Conformational searches were performed using the Schrödinger MacroModel¹ software package to identify low-energy conformers for quantum mechanical calculations. All quantum mechanical calculations were performed using the Gaussian 09² software package. Structures were optimized at the UB3LYP^{3,4}/LanL2DZ(Fe)⁵/6-31G(d) level of theory using the CPCM⁶⁻⁸ solvent model for diethyl ether, which is intended to model the environment of the enzyme active site; frequency calculations were used to confirm the presence of local minima (no imaginary frequencies) and transition states (one imaginary frequency). Thermochemistry corrections to obtain enthalpies and free energies were computed at 298 K and 1 M, with Truhlar corrections⁹ applied to all frequencies below 100 cm⁻¹. To obtain more accurate energetics, single-point energy calculations were performed on the optimized structures at the UB3LYP^{3,4}/LanL2DZ(Fe)⁵/6-311++G(2d,2p) level of theory using Grimme's D3(BJ) dispersion correction^{10,11} and the CPCM⁶⁻⁸ solvent model for diethyl ether. For all iron-containing species, all possible spin states were computed separately; the spin state with the lowest free energy is reported and used in the computed reaction pathways.

Supplementary Table 5: Optimized Quantum Mechanical Energies and Geometries

Structure	Single-Point Energy (Hartree) UB3LYP/ 6-311++G(2d,2p) CPCM diethylether solvent D3-BJ dispersion correction	Enthalpy Correction (Hartree) UB3LYP/6-31G(d) CPCM diethylether solvent	Gibbs Free Energy Correction (Hartree) UB3LYP/6-31G(d) CPCM diethylether solvent
Compound 6	-935.064995353	0.332193	0.267005
Compound PC-I	-2560.69811814	0.675898	0.552976
Transition State from PC-I to R-I	-2560.68200451	0.668580	0.548785
Compound R-I	-934.408484774	0.318396	0.252323
Compound PC-II	-2560.69111264	0.675486	0.550891
Transition State from PC-II to R-II	-2560.66865641	0.668467	0.549941
Compound R-II	-934.378337774	0.317810	0.251336
Transition State from R-II to R-III	-934.375022742	0.317227	0.254810
Compound R-III	-934.406015167	0.319252	0.257416
3-methylindole	-403.297212617	0.166766	0.125308
Transition State from R-III to R-IV	-1337.68979078	0.486702	0.403190
Compound R-IV	-1337.70558024	0.488372	0.406134
Compound PDT_{C-C}	-1337.15954501	0.479009	0.398229
Compound C-III	-934.228902694	0.321380	0.260447
Transition State from C-III to C-IV	-1337.54044714	0.489605	0.408473
Compound C-IV	-1337.55215821	0.491575	0.410726
Compound R-V	-934.408292246	0.318638	0.253313
Transition State from R-V to R-VI	-1337.69321370	0.486722	0.403322
Compound R-VI	-1337.70428197	0.488290	0.400752
Compound PDT_{C-N}	-1337.15657933	0.478377	0.394108
Compound C-V	-934.179753468	0.319454	0.254095
Iron-Oxo Quartet	-1625.60979018	0.341464	0.266017
Iron-Hydroxo Triplet	-1626.26453700	0.352745	0.277069
Iron-Aqua Doublet	-1626.92110182	0.365210	0.288026
Iron-Hydroxo Doublet Anion	-1626.42321553	0.351663	0.276113
Figure 11B Radical C2 TS	-1337.69755972	0.486871	0.403638
Figure 11B Radical C2 Product	-1337.72340783	0.489309	0.407811
Figure 11B Radical C3 TS	-1337.69205782	0.486851	0.405608
Figure 11B Radical C3 Product	-1337.70825431	0.488798	0.408087
Figure 11B Radical C4 TS	-1337.69550474	0.487160	0.405177
Figure 11B Radical C4 Product	-1337.71350934	0.489101	0.407451
Figure 11B Radical C5 TS	-1337.68979078	0.486702	0.403190
Figure 11B Radical C5 Product	-1337.70558024	0.488372	0.406134
Figure 11B Radical C6 TS	-1337.69174411	0.486788	0.403349
Figure 11B Radical C6 Product	-1337.70914756	0.488422	0.405258
Figure 11B Radical C7 TS	-1337.69379606	0.486938	0.404223
Figure 11B Radical C7 Product	-1337.71560829	0.489107	0.407992
Figure 11D Cation C2 TS	-1337.53832625	0.489255	0.407257
Figure 11D Cation C2 Product	-1337.56124772	0.491742	0.410737
Figure 11D Cation C3 TS	-1337.54174717	0.489798	0.408678
Figure 11D Cation C3 Product	-1337.56290761	0.492522	0.413750

Figure 11D Cation C4 TS	-1337.53534315	0.489690	0.408765
Figure 11D Cation C4 Product	-1337.54696654	0.492005	0.412079
Figure 11D Cation C5 TS	-1337.54044714	0.489605	0.408473
Figure 11D Cation C5 Product	-1337.55215821	0.491575	0.410726
Figure 11D Cation C6 TS	-1337.53368503	0.489370	0.406633
Figure 11D Cation C6 Product	-1337.55077701	0.491474	0.409790
Figure 11D Cation C7 TS	-1337.53365020	0.489592	0.407774
Figure 11D Cation C7 Product	-1337.55229112	0.491566	0.411883
Figure 12B Radical C2 TS	-1337.69951164	0.486587	0.402050
Figure 12B Radical C2 Product	-1337.72283996	0.488652	0.402337
Figure 12B Radical C3 TS	-1337.69039795	0.486633	0.404156
Figure 12B Radical C3 Product	-1337.69932417	0.488295	0.403578
Figure 12B Radical C4 TS	-1337.69014921	0.486500	0.401321
Figure 12B Radical C4 Product	-1337.71217497	0.488517	0.401914
Figure 12B Radical C5 TS	-1337.68944354	0.486708	0.404293
Figure 12B Radical C5 Product	-1337.69958304	0.488216	0.400754
Figure 12B Radical C6 TS	-1337.69321370	0.486722	0.403322
Figure 12B Radical C6 Product	-1337.70428197	0.488290	0.400752
Figure 12B Radical C7 TS	-1337.68740315	0.486476	0.401229
Figure 12B Radical C7 Product	-1337.70835455	0.488657	0.402298
Compound SI-6	-935.062969833	0.332324	0.268187
Compound SI-PC-I	-2560.69153790	0.675829	0.551602
TS from SI-PC-I to SI-R-I	-2560.67865279	0.668912	0.547686
Compound SI-R-I	-934.408292246	0.318638	0.253313
Compound SI-PC-II	-2560.69492543	0.676111	0.552240
TS from SI-PC-II to SI-R-II	-2560.66886329	0.668918	0.548679
Compound SI-R-II	-934.380566351	0.317339	0.251457
TS from SI-R-II to SI-R-III	-934.378935128	0.317125	0.255510
Compound SI-R-III	-934.402373050	0.319158	0.257062
TS from SI-R-III to SI-R-IV	-1337.68947287	0.487089	0.404197
Compound SI-R-IV	-1337.70630293	0.488419	0.405430
Compound SI-PDT_{c-c}	-1337.15713807	0.479196	0.399406
Compound SI-C-III	-934.227258143	0.321166	0.259968
TS from SI-C-III to SI-C-IV	-1337.53149035	0.489508	0.407077
Compound SI-C-IV	-1337.54947128	0.491664	0.410192
Figure S23B Radical C2 TS	-1337.69720677	0.486790	0.403187
Figure S23B Radical C2 Product	-1337.72387603	0.489129	0.407753
Figure S23B Radical C3 TS	-1337.69024969	0.486815	0.406062
Figure S23B Radical C3 Product	-1337.70583195	0.488790	0.407690
Figure S23B Radical C4 TS	-1337.69238834	0.487192	0.405409
Figure S23B Radical C4 Product	-1337.71039565	0.488908	0.407710
Figure S23B Radical C5 TS	-1337.68710983	0.486895	0.403027
Figure S23B Radical C5 Product	-1337.70169171	0.488268	0.405240
Figure S23B Radical C6 TS	-1337.68947287	0.487089	0.404197
Figure S23B Radical C6 Product	-1337.70630293	0.488419	0.405430
Figure S23B Radical C7 TS	-1337.69515416	0.487005	0.404216
Figure S23B Radical C7 Product	-1337.71296380	0.488933	0.406893
Figure S23D Cation C2 TS	-1337.53901559	0.489064	0.406499
Figure S23D Cation C2 Product	-1337.56397314	0.491670	0.411416
Figure S23D Cation C3 TS	-1337.54056391	0.489799	0.410016
Figure S23D Cation C3 Product	-1337.56254502	0.492561	0.414297
Figure S23D Cation C4 TS	-1337.53295258	0.489870	0.409363

Figure S23D Cation C4 Product	-1337.54486276	0.491909	0.412625
Figure S23D Cation C5 TS	-1337.53078689	0.489548	0.407453
Figure S23D Cation C5 Product	-1337.54732307	0.491534	0.410373
Figure S23D Cation C6 TS	-1337.53149035	0.489508	0.407077
Figure S23D Cation C6 Product	-1337.54947128	0.491664	0.410192
Figure S23D Cation C7 TS	-1337.53688422	0.489745	0.408768
Figure S23D Cation C7 Product	-1337.54891315	0.491855	0.410992
Compound 6 Radical Cation	-934.841312043	0.332396	0.265895
Iron-Oxo Anion Triplet	-1625.76714766	0.340805	0.266113

Compound **6**

O 1

N	-3.499289	1.573570	-1.088827
C	1.839291	-1.196192	-0.541564
O	1.826066	-2.204846	-1.249758
C	0.556139	-0.411010	-0.221570
C	-5.029522	0.477437	0.591361
C	3.030029	0.481835	0.883470
C	4.482290	0.949079	0.719319
C	5.247060	-0.376807	0.556634
C	4.296107	-1.267749	-0.264702
C	1.970015	1.520484	0.536979
C	-0.483945	-0.581218	-1.349833
C	-1.795276	0.089217	-1.056838
C	-2.259600	1.261651	-1.608940
C	-3.868917	0.603390	-0.181298
C	-2.815166	-0.352831	-0.133412
C	-2.948156	-1.465888	0.717596
C	-4.099105	-1.595235	1.485973
C	-5.128482	-0.631631	1.424408
N	0.848386	1.009082	-0.026565
N	2.965631	-0.703387	0.015475
O	2.130102	2.715542	0.776148
H	-4.050301	2.379233	-1.344403
H	0.136445	-0.835920	0.704576
H	-5.823219	1.217901	0.540913
H	2.854238	0.186240	1.931134
H	4.820264	1.545090	1.569466
H	4.567959	1.564711	-0.182763
H	5.429127	-0.827695	1.538699
H	6.214910	-0.249410	0.064775
H	4.335977	-2.322526	0.023834
H	4.493268	-1.209952	-1.341471
H	-0.615877	-1.656822	-1.501350
H	-0.054730	-0.182839	-2.276257
H	-1.805210	1.896742	-2.357757
H	-2.165671	-2.218741	0.770625
H	-4.211946	-2.451727	2.145046
H	-6.016453	-0.759741	2.037384
H	0.082201	1.657848	-0.179663

Compound **PC-I**

O 4

N	-0.596448	1.739290	-1.534251
C	-6.297386	0.017667	-0.842924
O	-6.959349	0.271436	-1.850792
C	-4.919265	0.650980	-0.599685
C	-0.440828	4.164207	-0.860686
C	-5.986782	-1.152197	1.353302
C	-6.538474	-2.534975	1.726270
C	-8.011209	-2.437386	1.288243
C	-7.971361	-1.597063	-0.002778
C	-4.477612	-1.083105	1.162991
C	-4.211008	0.972500	-1.937796
C	-2.845647	1.566283	-1.741575

C	-1.643315	0.895236	-1.828221
C	-1.101174	2.984314	-1.228719
C	-2.519932	2.918625	-1.355579
C	-3.279769	4.078241	-1.110589
C	-2.626155	5.249747	-0.745722
C	-1.220088	5.290688	-0.619355
N	-4.069035	-0.230024	0.200717
N	-6.725305	-0.823292	0.124869
O	-3.706031	-1.747724	1.862120
H	0.376016	1.440389	-1.432970
H	-5.082677	1.596314	-0.058431
H	0.641680	4.196268	-0.771460
H	-6.240300	-0.429680	2.146679
H	-6.413756	-2.753915	2.788743
H	-6.009787	-3.306060	1.155146
H	-8.596579	-1.918981	2.056020
H	-8.469333	-3.416352	1.125056
H	-8.831287	-0.928556	-0.108017
H	-7.919982	-2.217351	-0.905058
H	-4.868160	1.646328	-2.495555
H	-4.139734	0.046438	-2.519582
H	-1.453402	-0.136177	-2.095880
H	-4.362676	4.061509	-1.208600
H	-3.203368	6.150625	-0.554901
H	-0.737571	6.221287	-0.332628
H	-3.066796	-0.097832	0.096012
Fe	2.698903	-0.358968	-0.034310
N	3.709959	-1.370786	-1.459031
N	1.160416	-1.647815	-0.218547
N	4.373503	0.689376	0.372216
N	1.812282	0.443477	1.586758
C	4.952458	-1.073420	-1.959394
C	-0.010933	-1.643015	0.494156
C	3.230708	-2.402761	-2.231846
C	1.026875	-2.644594	-1.151045
C	5.541406	0.707364	-0.366327
C	0.543208	0.179976	2.052269
C	4.523504	1.666170	1.333597
C	2.292255	1.463535	2.367179
C	5.267568	-1.939232	-3.068861
C	-0.907608	-2.660263	0.001433
C	4.200933	-2.769115	-3.233895
C	-0.260048	-3.283480	-1.023142
C	6.447649	1.694575	0.163457
C	0.224115	1.054708	3.153004
C	5.820971	2.284227	1.218017
C	1.310011	1.852899	3.348350
H	6.192387	-1.906306	-3.630102
H	-1.891581	-2.846697	0.411917
H	4.064950	-3.559828	-3.960304
H	-0.602979	-4.102725	-1.641881
H	7.433361	1.897108	-0.234897
H	-0.712248	1.041121	3.695466
H	6.183772	3.073327	1.863856
H	1.452913	2.632905	4.084941

C	5.806708	-0.095443	-1.461884
C	-0.309839	-0.793917	1.554543
C	3.558668	2.031086	2.259988
C	1.990300	-3.005665	-2.086647
H	6.763308	0.033025	-1.957923
H	-1.285266	-0.910393	2.018369
H	3.807964	2.828703	2.952438
H	1.747310	-3.817396	-2.764801
O	2.081031	0.735586	-1.077832
S	4.000270	-1.995224	1.498491
C	3.902696	-1.437322	3.226359
H	2.866539	-1.367596	3.565672
H	4.459664	-2.139863	3.853112
H	4.369427	-0.449315	3.319768

Transition State from **PC-I** to **R-I**

O 4

N	-0.336737	1.089292	-1.372406
C	-6.282375	0.092394	-1.127643
O	-6.745613	0.279307	-2.253627
C	-4.842179	0.499024	-0.761109
C	-0.082569	3.554161	-0.962505
C	-6.468963	-0.681512	1.242359
C	-7.359104	-1.814134	1.772270
C	-8.713984	-1.519201	1.103141
C	-8.342418	-1.002519	-0.299341
C	-4.972452	-0.968396	1.261612
C	-3.955735	0.531748	-2.027225
C	-2.587327	1.072905	-1.766223
C	-1.385240	0.321217	-1.678930
C	-0.799405	2.403951	-1.254509
C	-2.203731	2.430086	-1.495880
C	-2.892044	3.652359	-1.442625
C	-2.172220	4.816843	-1.146873
C	-0.792856	4.768888	-0.909551
N	-4.282207	-0.420394	0.230042
N	-6.981989	-0.467629	-0.119460
O	-4.449819	-1.629255	2.158155
H	0.872119	0.709942	-1.255216
H	-4.885276	1.517918	-0.344813
H	0.987308	3.520863	-0.781662
H	-6.626873	0.226673	1.847160
H	-7.405227	-1.822615	2.863099
H	-6.959374	-2.778732	1.441175
H	-9.245742	-0.740119	1.660843
H	-9.362570	-2.397741	1.056513
H	-9.016501	-0.222449	-0.665465
H	-8.319935	-1.803041	-1.047816
H	-4.487480	1.144466	-2.762309
H	-3.893390	-0.481860	-2.437434
H	-1.269344	-0.745838	-1.826849
H	-3.960393	3.703908	-1.633859
H	-2.690469	5.769954	-1.103656
H	-0.256411	5.685549	-0.683219
H	-3.272538	-0.522202	0.265552

Fe	2.746783	-0.411197	0.079566
N	3.311397	-1.980796	-1.068114
N	1.020824	-1.372572	0.515138
N	4.530733	0.476025	-0.247502
N	2.262572	1.055009	1.368535
C	4.491209	-2.107276	-1.754011
C	0.043576	-0.951774	1.379418
C	2.560501	-3.083438	-1.387508
C	0.578916	-2.555962	-0.019020
C	5.539705	0.013102	-1.054752
C	1.111322	1.150490	2.107861
C	4.935887	1.702947	0.209228
C	2.969813	2.208445	1.606692
C	4.492469	-3.333171	-2.517269
C	-1.053157	-1.891657	1.389423
C	3.293319	-3.937343	-2.292364
C	-0.720873	-2.884112	0.513567
C	6.618263	0.972796	-1.097790
C	1.098300	2.389771	2.847049
C	6.242525	2.022718	-0.317129
C	2.247950	3.048947	2.530977
H	5.311459	-3.666985	-3.141359
H	-1.956187	-1.794180	1.980779
H	2.922150	-4.873026	-2.690471
H	-1.286449	-3.769528	0.252470
H	7.533094	0.842815	-1.661600
H	0.301703	2.700226	3.510936
H	6.785138	2.934567	-0.102879
H	2.594024	4.011762	2.884550
C	5.533003	-1.187431	-1.750670
C	0.080563	0.217669	2.128705
C	4.208854	2.523293	1.064324
C	1.284006	-3.354262	-0.912739
H	6.405996	-1.420640	-2.351815
H	-0.769660	0.427322	2.769784
H	4.651597	3.473493	1.345097
H	0.807875	-4.269531	-1.249246
O	2.038638	0.402233	-1.241610
S	3.789555	-1.664610	1.855711
C	4.483422	-0.501372	3.087377
H	3.702724	0.114871	3.540846
H	4.965857	-1.095724	3.869873
H	5.233899	0.152763	2.633894

Compound **R-I**

O 2

N	3.546705	-1.709327	-1.054497
C	-1.770616	1.170224	-0.535921
O	-1.700518	2.182332	-1.235014
C	-0.524194	0.322154	-0.214274
C	5.042110	-0.504590	0.559450
C	-3.045978	-0.458726	0.870851
C	-4.515304	-0.861219	0.688192
C	-5.219236	0.498570	0.529315
C	-4.222062	1.354406	-0.274464

C	-2.029734	-1.541771	0.534706
C	0.514329	0.468437	-1.351653
C	1.834196	-0.149151	-1.031519
C	2.356200	-1.393326	-1.534595
C	3.884711	-0.648683	-0.182242
C	2.854690	0.336174	-0.141039
C	3.000655	1.478120	0.651952
C	4.177595	1.623339	1.405494
C	5.178032	0.650570	1.361276
N	-0.880263	-1.084387	-0.027777
N	-2.920240	0.726107	0.009228
O	-2.238901	-2.726276	0.779449
H	-0.084251	0.726633	0.710841
H	5.824291	-1.257066	0.524336
H	-2.869745	-0.174490	1.921348
H	-4.887035	-1.448373	1.530187
H	-4.618304	-1.465007	-0.219947
H	-5.392435	0.948604	1.513245
H	-6.185938	0.417420	0.025792
H	-4.214950	2.406303	0.026361
H	-4.411368	1.317254	-1.353308
H	0.621839	1.542913	-1.532267
H	0.096066	0.025252	-2.262020
H	1.850526	-2.035814	-2.250407
H	2.231602	2.245346	0.686934
H	4.310226	2.503663	2.027218
H	6.080352	0.783244	1.951261
H	-0.151292	-1.778242	-0.156905

Compound PC-II

0 4

N	-1.081610	3.574209	-0.367355
C	-4.828508	-1.149960	-0.914314
O	-5.533899	-0.916569	-1.898068
C	-3.788991	-0.146194	-0.375655
C	-2.503315	5.301087	0.802224
C	-4.090212	-2.589002	0.981454
C	-4.153208	-4.119975	1.071138
C	-5.565358	-4.437310	0.546092
C	-5.790792	-3.409935	-0.578320
C	-2.682751	-2.007974	0.859103
C	-3.383093	0.869615	-1.460637
C	-2.691026	2.087988	-0.920902
C	-1.346592	2.367578	-0.983335
C	-2.258739	4.106340	0.114688
C	-3.301821	3.194624	-0.220817
C	-4.622831	3.512460	0.146590
C	-4.869562	4.698582	0.829846
C	-3.819262	5.582916	1.156644
N	-2.616331	-0.858230	0.145078
N	-4.914524	-2.291578	-0.199439
O	-1.716390	-2.557472	1.386847
H	-0.160371	3.978104	-0.266311
H	-4.278730	0.406373	0.442936
H	-1.694789	5.983956	1.049285

H	-4.549691	-2.143610	1.879584
H	-3.977048	-4.479351	2.087230
H	-3.385861	-4.554511	0.421408
H	-6.304170	-4.289377	1.342072
H	-5.662989	-5.465548	0.187722
H	-6.829517	-3.074904	-0.656851
H	-5.489545	-3.794480	-1.560204
H	-4.302966	1.144690	-1.986283
H	-2.746499	0.359645	-2.193737
H	-0.544500	1.782463	-1.409180
H	-5.442277	2.842604	-0.102611
H	-5.886534	4.951748	1.117529
H	-4.041944	6.502124	1.691865
H	-1.699861	-0.415139	0.079551
Fe	2.098308	-0.293750	-0.086056
N	2.380291	-0.311707	-2.085102
N	2.144331	-2.308562	-0.066360
N	2.372321	1.707237	-0.083003
N	2.168517	-0.295910	1.927106
C	2.479199	0.775729	-2.915957
C	2.008865	-3.129074	1.024204
C	2.381265	-1.409693	-2.904159
C	2.179781	-3.141935	-1.160350
C	2.469478	2.528168	-1.182959
C	2.033858	-1.388753	2.761682
C	2.343381	2.538639	1.006300
C	2.190130	0.806509	2.755913
C	2.547440	0.352026	-4.293198
C	1.960915	-4.510913	0.612121
C	2.488075	-1.008496	-4.285768
C	2.071592	-4.519375	-0.743974
C	2.507587	3.910322	-0.772226
C	1.993709	-0.961279	4.137466
C	2.427866	3.916902	0.590348
C	2.094157	0.395672	4.135039
H	2.632824	1.021093	-5.139646
H	1.860643	-5.349915	1.288277
H	2.514152	-1.691718	-5.124758
H	2.081077	-5.366957	-1.416950
H	2.595824	4.751421	-1.447946
H	1.899034	-1.629504	4.983490
H	2.439103	4.764393	1.263702
H	2.097091	1.074079	4.978360
C	2.522218	2.101441	-2.502769
C	1.945703	-2.705591	2.346456
C	2.267085	2.124002	2.333481
C	2.297162	-2.731854	-2.478967
H	2.602051	2.863007	-3.271868
H	1.831470	-3.466370	3.111470
H	2.260522	2.894585	3.097638
H	2.314545	-3.503140	-3.242232
O	0.475589	-0.191946	-0.199320
S	4.643118	-0.622798	0.386079
C	5.389542	0.950848	0.908600
H	4.925309	1.283363	1.844986

H	6.455336	0.788974	1.094717
H	5.251367	1.729051	0.154304

Transition State from **PC-II** to **R-II**

O 4

N	-0.318459	3.592617	-1.955506
C	-4.297482	-0.431363	-0.107857
O	-5.206214	0.390622	0.062278
C	-2.866211	0.051773	-0.406019
C	-1.047106	5.483346	-0.441509
C	-3.494523	-2.784155	-0.345897
C	-4.238724	-3.750085	-1.277739
C	-5.653577	-3.765115	-0.663870
C	-5.866164	-2.330908	-0.119314
C	-2.152716	-2.239268	-0.830166
C	-2.953008	1.004022	-1.683391
C	-2.047600	2.181106	-1.618713
C	-0.849447	2.370649	-2.283529
C	-1.153790	4.232012	-1.053332
C	-2.255162	3.363693	-0.819048
C	-3.270087	3.766380	0.067880
C	-3.164367	5.009036	0.686853
C	-2.067143	5.857687	0.433321
N	-1.852991	-0.947307	-0.595680
N	-4.508309	-1.760540	-0.078755
O	-1.341776	-3.056153	-1.299106
H	0.572040	3.940552	-2.280247
H	-2.584572	0.695945	0.436749
H	-0.205287	6.141314	-0.638726
H	-3.267563	-3.313055	0.594450
H	-3.769687	-4.735519	-1.311988
H	-4.255290	-3.340370	-2.294514
H	-5.695601	-4.489253	0.157164
H	-6.425471	-4.041564	-1.387143
H	-6.326126	-2.324391	0.874813
H	-6.484195	-1.708995	-0.774007
H	-3.990979	1.346846	-1.735864
H	-2.749725	0.392638	-2.567176
H	-0.330880	1.708149	-2.961447
H	-4.114210	3.110934	0.266831
H	-3.939513	5.334485	1.375126
H	-2.014632	6.824100	0.927098
H	-0.402264	-0.593587	-0.782707
Fe	1.805219	-0.484530	0.243709
N	3.082580	-1.452543	-0.989664
N	1.089034	-2.256601	0.870031
N	2.658453	1.274836	-0.251045
N	0.618346	0.473256	1.562763
C	4.020515	-0.881111	-1.813016
C	0.109613	-2.458977	1.805651
C	3.165611	-2.802187	-1.200892
C	1.457774	-3.505289	0.429138
C	3.654813	1.473291	-1.173867
C	-0.318726	-0.097371	2.384964
C	2.296146	2.522510	0.191694

C	0.524598	1.829397	1.761219
C	4.703983	-1.899973	-2.573309
C	-0.138916	-3.870008	1.972559
C	4.172889	-3.094155	-2.192417
C	0.699559	-4.518991	1.119103
C	3.938226	2.880021	-1.305458
C	-1.020969	0.923493	3.124164
C	3.093490	3.532406	-0.456448
C	-0.497003	2.119823	2.737185
H	5.486387	-1.706462	-3.295649
H	-0.864265	-4.288712	2.658107
H	4.426972	-4.088633	-2.535690
H	0.805301	-5.583049	0.952783
H	4.687823	3.296686	-1.965755
H	-1.807527	0.730688	3.842110
H	3.009192	4.595590	-0.271192
H	-0.767514	3.114880	3.065235
C	4.293761	0.475648	-1.902035
C	-0.565822	-1.460008	2.497664
C	1.300922	2.789314	1.125432
C	2.416156	-3.767794	-0.536455
H	5.066640	0.784943	-2.598322
H	-1.335297	-1.770807	3.196852
H	1.114446	3.828106	1.375762
H	2.597631	-4.806384	-0.792699
O	0.619764	-0.338817	-1.011237
S	3.387000	-0.787264	2.002265
C	3.843603	0.832576	2.717955
H	2.966448	1.358701	3.104442
H	4.524823	0.632626	3.551211
H	4.351737	1.467818	1.988249

Compound **R-II**

O 2

N	-3.068676	-1.986608	0.268667
C	1.838962	1.398401	-0.301609
O	1.665946	2.577640	-0.004289
C	0.607305	0.512059	-0.646042
C	-5.137800	-0.593746	-0.114142
C	3.302596	-0.630996	-0.568764
C	4.365301	-1.002555	0.470677
C	5.224630	0.276227	0.523773
C	4.222516	1.436392	0.328523
C	2.003218	-1.437622	-0.538494
C	-0.245983	0.385108	0.668259
C	-1.548222	-0.334046	0.482195
C	-1.738989	-1.696167	0.487635
C	-3.774508	-0.811637	0.116757
C	-2.841906	0.258006	0.241774
C	-3.309897	1.580292	0.126310
C	-4.662564	1.800740	-0.104274
C	-5.567869	0.724173	-0.223784
N	0.969604	-0.774322	-1.162743
N	3.044276	0.790955	-0.282924
O	1.931957	-2.580584	-0.110472

H	-3.461429	-2.915562	0.235496
H	0.012047	1.046565	-1.392574
H	-5.833050	-1.423954	-0.204905
H	3.722580	-0.730006	-1.581282
H	4.930613	-1.891192	0.182063
H	3.883172	-1.198629	1.434275
H	5.955036	0.268919	-0.292160
H	5.776547	0.371921	1.462192
H	4.610832	2.226962	-0.321113
H	3.916338	1.898715	1.272026
H	-0.411680	1.410421	1.013361
H	0.369993	-0.115847	1.424901
H	-1.014399	-2.489144	0.615845
H	-2.624391	2.419496	0.215250
H	-5.032882	2.818356	-0.195049
H	-6.619731	0.928568	-0.403999

Transition State from R-II to R-III

O 2

N	-2.338248	-1.782052	0.475069
C	1.933448	1.512669	-0.181575
O	2.058894	2.702385	0.125154
C	0.537341	0.908657	-0.369460
C	-4.622182	-1.106776	-0.355875
C	2.890735	-0.756604	-0.645921
C	4.074481	-1.346518	0.129538
C	5.143821	-0.246858	-0.009728
C	4.348934	1.074951	0.039727
C	1.509286	-1.360924	-0.325239
C	-0.365050	1.277650	0.852540
C	-1.488169	0.289379	0.821722
C	-1.219449	-1.105681	0.872291
C	-3.334571	-0.883138	0.124791
C	-2.815449	0.431926	0.331866
C	-3.627429	1.545450	0.025327
C	-4.912735	1.325481	-0.448249
C	-5.404278	0.015046	-0.634552
N	0.470139	-0.538664	-0.518892
N	2.979812	0.675706	-0.327892
O	1.433628	-2.562620	-0.030201
H	-2.427303	-2.787993	0.464407
H	0.099071	1.383704	-1.258702
H	-5.002807	-2.111645	-0.511650
H	3.052683	-0.903312	-1.725400
H	4.389042	-2.311920	-0.272224
H	3.790374	-1.490144	1.178012
H	5.654658	-0.342403	-0.974357
H	5.904913	-0.293345	0.773848
H	4.734002	1.830673	-0.652713
H	4.331330	1.522036	1.039683
H	-0.705282	2.312834	0.785343
H	0.214037	1.178042	1.778839
H	-0.428730	-1.638618	1.377713
H	-3.252609	2.555097	0.166886
H	-5.553270	2.170459	-0.682559

H	-6.414612	-0.124762	-1.007942
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Compound R-III

O 2

N	-1.825839	-1.536027	0.207325
C	1.975028	1.532017	-0.131974
O	2.210570	2.711006	0.136743
C	0.547036	1.018466	-0.335224
C	-4.258316	-1.392632	-0.397436
C	2.670484	-0.827879	-0.577819
C	3.948188	-1.524530	-0.091778
C	5.039840	-0.475963	-0.371066
C	4.361042	0.868827	-0.056935
C	1.381177	-1.311158	0.085301
C	-0.528403	1.796064	0.475666
C	-1.547686	0.728873	0.721137
C	-0.874169	-0.617174	0.825944
C	-3.038255	-0.875192	0.024054
C	-2.866484	0.530932	0.258928
C	-3.938795	1.410550	-0.002590
C	-5.155799	0.886643	-0.430077
C	-5.317060	-0.498095	-0.613139
N	0.395058	-0.382956	0.116466
N	2.933692	0.593060	-0.285417
O	1.249026	-2.450859	0.530648
H	-1.823790	-2.498270	0.521265
H	0.312492	1.089499	-1.407576
H	-4.383988	-2.457226	-0.573881
H	2.555439	-0.969950	-1.664638
H	4.117559	-2.473966	-0.604246
H	3.865125	-1.729827	0.980713
H	5.333211	-0.510276	-1.426391
H	5.939257	-0.631425	0.230411
H	4.700409	1.686883	-0.699142
H	4.510663	1.177494	0.984630
H	-0.915425	2.650057	-0.084502
H	-0.074420	2.180189	1.398402
H	-0.631596	-0.957224	1.843486
H	-3.817520	2.479030	0.153321
H	-5.993234	1.552469	-0.618361
H	-6.278311	-0.885672	-0.939195

3-methylindole

O 1

N	0.632687	1.814318	0.000440
C	-1.790518	1.108332	0.000038
C	2.641172	-1.314436	0.000037
C	1.608295	-0.226725	-0.000164
C	1.834240	1.127603	-0.000085
C	-0.405047	0.907751	0.000049
C	0.174859	-0.393770	-0.000045
C	-0.675624	-1.514387	0.000006
C	-2.052337	-1.319799	-0.000023
C	-2.603782	-0.020530	-0.000047
H	0.536398	2.818369	-0.001853

H	-2.214783	2.108908	0.000084
H	2.550605	-1.962805	-0.881613
H	3.653333	-0.896375	0.000588
H	2.771096	1.668609	-0.000155
H	-0.261497	-2.519740	0.000054
H	-2.717631	-2.179206	-0.000028
H	-3.683712	0.100979	-0.000093
H	2.549839	-1.963186	0.881338

Transition State from **R-III** to **R-IV**

O 2

N	-5.566010	0.067828	-0.750328
C	-3.454605	0.700912	-1.990373
C	-4.832501	-3.102094	1.047864
C	-4.862720	-1.840573	0.238460
C	-5.927209	-0.991043	0.067570
C	-4.252694	-0.077585	-1.125277
C	-3.766090	-1.271044	-0.515001
C	-2.448732	-1.672261	-0.752188
C	-1.566897	-0.813989	-1.490162
C	-2.154795	0.306253	-2.202178
H	-6.176279	0.822785	-1.025463
H	-3.867343	1.568247	-2.499427
H	-4.064844	-3.062957	1.832136
H	-5.796425	-3.281852	1.535252
H	-6.929326	-1.051219	0.470160
H	-2.068121	-2.601321	-0.336045
H	-0.719156	-1.296211	-1.977442
H	-1.526915	0.877519	-2.879386
H	-4.605915	-3.979222	0.427063
N	0.370239	2.191987	-0.782233
C	3.033387	-1.588206	0.786701
O	2.865040	-2.775631	1.068131
C	1.886553	-0.574303	0.794455
C	-0.928421	3.435362	0.975946
C	4.450511	0.349733	0.084470
C	5.747855	0.295457	-0.733970
C	6.529909	-0.847469	-0.062876
C	5.448422	-1.877127	0.310084
C	3.250176	0.937567	-0.657262
C	0.495758	-1.170169	0.492859
C	-0.249851	-0.002293	-0.133561
C	0.783946	0.807292	-0.931227
C	-0.479647	2.290720	0.321110
C	-0.896340	0.998166	0.725834
C	-1.777322	0.862332	1.800922
C	-2.236110	2.008060	2.462871
C	-1.813846	3.277280	2.051555
N	2.057237	0.441918	-0.260771
N	4.233375	-1.060095	0.456805
O	3.369234	1.804301	-1.526856
H	1.075567	2.898458	-0.953090
H	1.873819	-0.086820	1.781145
H	-0.594050	4.422834	0.669273
H	4.605929	0.956180	0.991746

H	6.278617	1.249778	-0.724339
H	5.511617	0.050567	-1.775019
H	7.026897	-0.481508	0.842661
H	7.296375	-1.275343	-0.714376
H	5.663680	-2.414495	1.238490
H	5.293505	-2.623200	-0.478554
H	0.015751	-1.549716	1.396973
H	0.606425	-2.008434	-0.205451
H	0.881116	0.552887	-1.991896
H	-2.101273	-0.123659	2.122621
H	-2.918971	1.910454	3.302204
H	-2.171186	4.159557	2.576477

Compound **R-IV**

O 2

N	-5.707588	-0.106556	-0.984684
C	-3.514493	0.747008	-1.934977
C	-4.888469	-3.070003	1.101239
C	-4.944779	-1.862661	0.215120
C	-6.064454	-1.160100	-0.159222
C	-4.344925	-0.109478	-1.157341
C	-3.817546	-1.201966	-0.414240
C	-2.448342	-1.453522	-0.410841
C	-1.486476	-0.564979	-1.162549
C	-2.173712	0.531195	-1.950510
H	-6.350730	0.555945	-1.391436
H	-3.952497	1.553633	-2.518845
H	-4.265773	-2.894119	1.988841
H	-5.887756	-3.353622	1.447858
H	-7.101804	-1.324991	0.098605
H	-2.045811	-2.311287	0.120373
H	-0.918361	-1.191505	-1.880610
H	-1.538564	1.179253	-2.547167
H	-4.458452	-3.936931	0.581580
N	0.440190	2.192594	-0.853279
C	2.945619	-1.604629	0.806795
O	2.746688	-2.765072	1.168401
C	1.826344	-0.562040	0.744898
C	-0.594181	3.503371	1.028183
C	4.411405	0.243809	-0.024422
C	5.697867	0.098899	-0.849304
C	6.454800	-1.018436	-0.109762
C	5.349277	-1.989588	0.342068
C	3.223802	0.825641	-0.789041
C	0.434089	-1.139490	0.474653
C	-0.340452	0.004862	-0.222402
C	0.758799	0.783485	-1.023731
C	-0.305836	2.334251	0.323546
C	-0.819854	1.090218	0.732157
C	-1.636557	1.010413	1.853518
C	-1.936942	2.178235	2.571118
C	-1.416667	3.407428	2.157253
N	2.019981	0.369075	-0.376936
N	4.157585	-1.131678	0.440048
O	3.362002	1.657868	-1.688826

H	1.204444	2.833371	-1.036675
H	1.828609	-0.007655	1.695942
H	-0.189497	4.460917	0.711799
H	4.595711	0.901995	0.840492
H	6.254623	1.036435	-0.908040
H	5.443984	-0.208518	-1.869469
H	6.972483	-0.606876	0.764048
H	7.201326	-1.510890	-0.738279
H	5.558649	-2.466591	1.304176
H	5.166973	-2.784081	-0.391378
H	-0.049433	-1.474747	1.393645
H	0.523382	-2.003791	-0.193005
H	0.816040	0.530400	-2.085830
H	-2.038898	0.053708	2.175041
H	-2.571343	2.124434	3.451162
H	-1.647894	4.307559	2.721269

Compound PDT_{c-c}

0 1

N	-5.659156	-1.125029	-1.454404
C	-3.636937	0.287975	-2.002739
C	-4.842626	-2.913365	1.701484
C	-4.913807	-2.080493	0.456239
C	-5.964187	-1.998092	-0.424986
C	-4.393358	-0.620818	-1.254922
C	-3.891169	-1.202051	-0.058515
C	-2.598926	-0.858948	0.378889
C	-1.828157	0.039517	-0.358017
C	-2.367123	0.609054	-1.541098
H	-4.025603	0.731838	-2.915406
H	-4.691284	-2.295760	2.596717
H	-5.765336	-3.484911	1.846327
H	-6.922195	-2.500063	-0.401743
H	-2.212353	-1.301169	1.292335
H	-1.770426	1.321956	-2.102336
H	-4.010942	-3.629420	1.665855
N	0.593831	2.105467	-1.321278
C	2.647188	-1.472023	1.206004
O	2.320724	-2.379984	1.971345
C	1.743132	-0.267752	0.930557
C	0.275050	4.133009	0.138959
C	4.222796	-0.371656	-0.394160
C	5.272186	-1.061090	-1.277193
C	5.947897	-2.042169	-0.302816
C	4.797800	-2.540030	0.590544
C	3.031205	0.210497	-1.152344
C	0.246864	-0.561871	1.054812
C	-0.437501	0.466807	0.120186
C	0.602250	0.676218	-1.040318
C	0.173294	2.774577	-0.163366
C	-0.467513	1.882785	0.712514
C	-1.032749	2.345307	1.893174
C	-0.937517	3.708236	2.211029
C	-0.287126	4.585870	1.338651
N	1.870299	0.193038	-0.459589

N	3.823864	-1.437645	0.542030
O	3.135572	0.674322	-2.290391
H	1.409454	2.446032	-1.819171
H	2.032769	0.539380	1.620800
H	0.776938	4.820272	-0.536656
H	4.691019	0.457025	0.161800
H	5.965118	-0.345365	-1.724354
H	4.769942	-1.598617	-2.088684
H	6.693005	-1.515607	0.304226
H	6.455068	-2.864431	-0.814194
H	5.104382	-2.735901	1.622326
H	4.333054	-3.453703	0.201257
H	-0.094246	-0.486164	2.089249
H	0.048146	-1.579994	0.707569
H	0.390496	0.106782	-1.947355
H	-1.542012	1.660460	2.567340
H	-1.369184	4.080411	3.135596
H	-0.213885	5.640391	1.591944
H	-6.269967	-0.895924	-2.223785

Compound C-III

1 1

N	-1.843818	-1.512494	0.257149
C	2.006729	1.529724	-0.091016
O	2.224830	2.683849	0.272329
C	0.587546	1.062692	-0.442791
C	-4.287649	-1.445226	-0.199211
C	2.679528	-0.823946	-0.609120
C	3.924232	-1.572061	-0.113030
C	5.040947	-0.524621	-0.271163
C	4.368761	0.804905	0.108496
C	1.361142	-1.300584	-0.007939
C	-0.524615	1.849467	0.315826
C	-1.532267	0.775006	0.511678
C	-0.844548	-0.543404	0.707564
C	-3.020865	-0.894400	0.093849
C	-2.845435	0.556468	0.198926
C	-3.945640	1.432272	-0.082730
C	-5.152305	0.871457	-0.383810
C	-5.313006	-0.557853	-0.432423
N	0.367371	-0.360285	-0.057767
N	2.951094	0.577184	-0.227982
O	1.171001	-2.411728	0.469505
H	-1.729771	-2.508472	0.409070
H	0.442911	1.175059	-1.524728
H	-4.435437	-2.517515	-0.257474
H	2.595197	-0.906573	-1.704048
H	4.103346	-2.486239	-0.682695
H	3.789617	-1.847788	0.937837
H	5.381101	-0.489612	-1.311892
H	5.908373	-0.738371	0.357889
H	4.754814	1.663651	-0.446997
H	4.456646	1.026179	1.178362
H	-0.898201	2.702369	-0.250986
H	-0.125932	2.219624	1.268502

H	-0.625059	-0.772373	1.762091
H	-3.811293	2.507028	-0.026894
H	-6.014871	1.496611	-0.586205
H	-6.295957	-0.950760	-0.674931

Transition State from C-III to C-IV

1 1

N	-5.209632	0.262283	-0.586504
C	-3.203395	0.840413	-1.976389
C	-4.627184	-3.106813	0.887129
C	-4.614109	-1.782017	0.187942
C	-5.597134	-0.833208	0.186381
C	-3.976616	0.047186	-1.101810
C	-3.546267	-1.243534	-0.632385
C	-2.301151	-1.707898	-1.016250
C	-1.454746	-0.860671	-1.786322
C	-1.968702	0.359614	-2.342749
H	-5.777610	1.083321	-0.746843
H	-3.585522	1.780169	-2.362403
H	-3.799807	-3.193684	1.602521
H	-5.561637	-3.249195	1.437454
H	-6.561623	-0.834086	0.674360
H	-1.941769	-2.682704	-0.699706
H	-0.577471	-1.302144	-2.248819
H	-1.352023	0.925162	-3.032984
H	-4.526682	-3.936026	0.176185
N	0.212167	2.155357	-0.599177
C	3.064318	-1.597984	0.666610
O	2.941516	-2.816807	0.780964
C	1.864309	-0.652221	0.798628
C	-1.371289	3.180726	1.038707
C	4.373960	0.491170	0.248974
C	5.701164	0.624974	-0.510089
C	6.525615	-0.557286	0.029508
C	5.497739	-1.688511	0.199805
C	3.162285	1.087500	-0.463797
C	0.515217	-1.300054	0.400845
C	-0.245062	-0.095669	-0.107465
C	0.745076	0.829190	-0.832893
C	-0.741248	2.118853	0.373120
C	-1.049099	0.759509	0.704185
C	-1.973371	0.475660	1.734178
C	-2.581684	1.527568	2.395690
C	-2.282206	2.863342	2.037875
N	1.982266	0.503264	-0.116804
N	4.232324	-0.967634	0.425187
O	3.227386	2.015536	-1.264898
H	0.721965	2.979367	-0.886630
H	1.813658	-0.299732	1.838190
H	-1.139534	4.211872	0.793522
H	4.449869	0.981310	1.232721
H	6.171736	1.595531	-0.340323
H	5.519506	0.519766	-1.584766
H	6.963572	-0.299222	1.000007
H	7.340634	-0.842364	-0.640232

H	5.713278	-2.349326	1.043872
H	5.407519	-2.308657	-0.699634
H	0.031034	-1.787954	1.247248
H	0.690544	-2.048660	-0.375847
H	0.887564	0.661779	-1.902258
H	-2.193115	-0.551810	2.003906
H	-3.290257	1.334059	3.193926
H	-2.773446	3.671477	2.572534

Compound C-IV

1 1

N	-5.647849	-0.163982	-1.064375
C	-3.500934	0.740552	-1.956776
C	-4.894590	-3.074322	1.141437
C	-4.942774	-1.893042	0.225743
C	-6.037991	-1.219164	-0.210976
C	-4.324256	-0.131559	-1.192630
C	-3.798900	-1.219538	-0.384328
C	-2.456582	-1.414697	-0.332673
C	-1.518574	-0.539144	-1.089870
C	-2.160947	0.538712	-1.905149
H	-6.294610	0.473339	-1.515326
H	-3.939724	1.530300	-2.557389
H	-4.317288	-2.850763	2.046276
H	-5.901210	-3.371654	1.446142
H	-7.086674	-1.376641	-0.005002
H	-2.035003	-2.228748	0.249905
H	-1.003861	-1.209824	-1.804330
H	-1.499965	1.188129	-2.468717
H	-4.418714	-3.933438	0.654255
N	0.411151	2.171135	-0.902376
C	2.930070	-1.608562	0.817419
O	2.713867	-2.766109	1.176857
C	1.821497	-0.550925	0.777156
C	-0.570374	3.548170	0.963059
C	4.396394	0.225560	-0.041922
C	5.677309	0.072355	-0.874022
C	6.431205	-1.050119	-0.139169
C	5.322973	-2.015876	0.315540
C	3.204720	0.803108	-0.802065
C	0.421922	-1.128088	0.538595
C	-0.343655	0.013358	-0.170655
C	0.746260	0.759845	-1.015439
C	-0.300573	2.356339	0.289966
C	-0.805694	1.130001	0.756669
C	-1.594022	1.084204	1.900962
C	-1.873019	2.274665	2.585310
C	-1.361803	3.488679	2.114921
N	1.999859	0.370399	-0.353815
N	4.138339	-1.147837	0.431055
O	3.324239	1.606783	-1.726776
H	1.163233	2.810349	-1.137089
H	1.846015	0.006585	1.725035
H	-0.173798	4.493987	0.605835
H	4.585667	0.887280	0.818737

H	6.239544	1.006379	-0.934107
H	5.416362	-0.232292	-1.893098
H	6.955170	-0.643242	0.732794
H	7.171380	-1.545374	-0.772529
H	5.535184	-2.500659	1.272690
H	5.126546	-2.802344	-0.422599
H	-0.048612	-1.432863	1.475099
H	0.499505	-2.011127	-0.104720
H	0.800100	0.467323	-2.067675
H	-1.982723	0.140223	2.275221
H	-2.480487	2.252143	3.484775
H	-1.577357	4.406476	2.655127

Compound R-V

0 2

N	-3.049957	1.767668	-0.938990
C	1.226975	-0.379821	1.350606
O	0.668817	-1.205515	2.078688
C	0.891815	1.119025	1.446887
C	-3.937156	-0.528659	-1.404071
C	2.951727	0.232762	-0.356465
C	3.358945	-0.614142	-1.568735
C	3.598159	-1.999161	-0.939197
C	2.528685	-2.114275	0.165686
C	2.191476	1.510604	-0.674993
C	-0.590898	1.344209	1.848498
C	-1.600186	1.142981	0.761433
C	-2.163567	2.189106	-0.058441
C	-3.128193	0.370188	-0.735631
C	-2.247992	-0.055782	0.304737
C	-2.194798	-1.406082	0.671805
C	-3.019767	-2.316515	-0.008681
C	-3.873622	-1.888708	-1.027255
N	1.213738	1.831963	0.211707
N	2.173231	-0.713534	0.453780
O	2.474247	2.204186	-1.647704
H	1.499014	1.511817	2.277799
H	-4.604721	-0.196304	-2.193602
H	3.855768	0.535333	0.197462
H	4.236716	-0.209331	-2.076008
H	2.532376	-0.644972	-2.286978
H	4.599817	-2.040306	-0.497273
H	3.522188	-2.811683	-1.666205
H	2.895304	-2.612983	1.068029
H	1.631644	-2.646631	-0.168840
H	-0.676916	2.370569	2.224488
H	-0.783836	0.667611	2.685956
H	-1.913981	3.244200	0.022986
H	-1.518446	-1.741265	1.451010
H	-2.991264	-3.368044	0.261809
H	-4.502380	-2.611211	-1.539980
H	0.765510	2.726764	0.048899

Transition State from R-V to R-VI

0 2

N	1.628868	2.371470	0.385167
C	-3.057800	-0.383152	1.292029
O	-3.737536	0.514829	1.793887
C	-1.622581	-0.692437	1.759793
C	0.332875	3.860637	-1.181784
C	-2.761023	-2.328535	-0.245852
C	-3.469395	-2.577941	-1.583383
C	-4.936073	-2.242684	-1.256950
C	-4.846998	-1.048538	-0.289576
C	-1.277190	-2.000168	-0.342929
C	-0.921317	0.532525	2.415086
C	-0.165289	1.417839	1.465689
C	1.205666	1.451723	1.325502
C	0.465431	2.904003	-0.169023
C	-0.678346	2.370905	0.497738
C	-1.957553	2.836098	0.159862
C	-2.081661	3.786109	-0.854961
C	-0.950282	4.288995	-1.522441
N	-0.813341	-1.233708	0.663127
N	-3.519814	-1.205633	0.327785
O	-0.579786	-2.430606	-1.271574
H	-1.728718	-1.460371	2.541819
H	1.205318	4.268784	-1.685649
H	-2.859558	-3.216158	0.400716
H	-3.326397	-3.600416	-1.939099
H	-3.069333	-1.895647	-2.340699
H	-5.413539	-3.093734	-0.758530
H	-5.523112	-2.005611	-2.147886
H	-5.627882	-1.051486	0.476472
H	-4.892440	-0.084966	-0.810284
H	-0.223341	0.150971	3.168011
H	-1.706800	1.077960	2.947712
H	1.941598	0.872288	1.872365
H	-2.834709	2.460448	0.678417
H	-3.068542	4.149615	-1.130270
H	-1.075982	5.029132	-2.308464
H	0.141219	-0.893382	0.590969
N	2.283452	-2.063674	-1.021218
C	2.276500	0.423216	-1.356496
C	5.321341	-2.829177	0.988720
C	4.184181	-2.233125	0.212777
C	3.120222	-2.922849	-0.355244
C	2.766582	-0.773905	-0.864981
C	3.968233	-0.860003	-0.091867
C	4.673715	0.341163	0.210390
C	4.167951	1.544587	-0.201453
C	2.904802	1.638663	-0.916648
H	1.322837	-2.282504	-1.301820
H	1.389518	0.466976	-1.980630
H	5.196008	-3.910690	1.101922
H	6.285879	-2.656927	0.493982
H	2.906609	-3.983242	-0.326546
H	5.612699	0.297331	0.756450
H	4.690834	2.468077	0.027645
H	2.774659	2.511858	-1.546851

H 5.395658 -2.394980 1.993737

Compound **R-VI**

O 2

N -1.872034 1.532076 0.088560
C 3.904836 0.046474 1.075030
O 4.234756 0.472665 2.183532
C 2.611276 0.503892 0.380565
C -1.833326 3.853849 -0.921656
C 4.304828 -1.365469 -0.952649
C 5.047536 -2.707464 -0.994375
C 6.325048 -2.411468 -0.188406
C 5.857411 -1.466262 0.934344
C 2.800764 -1.450830 -1.183020
C 1.552130 0.926563 1.422215
C 0.280963 1.435015 0.805328
C -0.913249 0.757743 0.713912
C -1.293603 2.739717 -0.263177
C 0.061044 2.716963 0.181557
C 0.871115 3.847261 -0.030497
C 0.334044 4.953610 -0.677650
C -1.005066 4.953460 -1.120870
N 2.073148 -0.556684 -0.470996
N 4.645378 -0.842134 0.378803
O 2.310969 -2.258975 -1.969424
H 2.863928 1.383060 -0.234113
H -2.861533 3.868290 -1.270650
H 4.709000 -0.696438 -1.730346
H 5.243779 -3.036362 -2.016867
H 4.441387 -3.475111 -0.500989
H 7.059909 -1.904450 -0.823843
H 6.794989 -3.315586 0.207356
H 6.599003 -0.704592 1.193825
H 5.597840 -2.003950 1.853703
H 2.016525 1.686760 2.057616
H 1.340032 0.065068 2.065603
H -1.173397 -0.226946 1.078554
H 1.903813 3.857574 0.309654
H 0.951440 5.831622 -0.847058
H -1.399643 5.829534 -1.628406
H 1.077749 -0.519606 -0.670269
N -5.051880 -1.572970 1.855717
C -3.921373 0.466496 0.953583
C -5.072142 -4.083306 -0.885284
C -4.925682 -2.897371 0.023114
C -5.359011 -2.814429 1.339577
C -4.407755 -0.818460 0.887212
C -4.324024 -1.647306 -0.280162
C -3.699024 -1.112289 -1.456058
C -3.203792 0.148626 -1.459186
C -3.244329 1.066678 -0.252288
H -5.259518 -1.265457 2.793862
H -4.002912 1.074702 1.849323
H -4.097973 -4.451834 -1.230855
H -5.577097 -4.909750 -0.375069

H -5.866236 -3.553292 1.944514

H -3.625863 -1.726528 -2.350738

H -2.728537 0.556357 -2.347430

H -3.769090 1.993874 -0.530962

H -5.657401 -3.838633 -1.780837

Compound **PDT_{C-N}**

O 1

N 1.356808 0.707155 0.573365
C -4.081042 0.336718 0.949207
O -4.341482 1.528507 1.137207
C -3.008470 -0.408945 1.766030
C 1.096272 2.383042 -1.305989
C -4.510119 -1.867295 -0.146330
C -5.062732 -2.108654 -1.555841
C -6.245956 -1.125921 -1.631076
C -5.763561 0.113109 -0.853560
C -3.043113 -2.235749 0.048003
C -1.917459 0.538487 2.333466
C -0.748562 0.826435 1.431506
C 0.494137 0.254674 1.560531
C 0.660142 1.614018 -0.219437
C -0.665674 1.710617 0.291072
C -1.570271 2.595368 -0.325835
C -1.141789 3.349713 -1.411588
C 0.179071 3.246737 -1.894550
N -2.411833 -1.496753 0.992314
N -4.740787 -0.427444 0.056384
O -2.502081 -3.137109 -0.588784
H -3.545340 -0.826325 2.633463
H 2.115685 2.313803 -1.670960
H -5.095666 -2.444063 0.588558
H -5.353094 -3.149981 -1.710331
H -4.295071 -1.857647 -2.295472
H -7.124714 -1.558408 -1.139529
H -6.526649 -0.880333 -2.658555
H -6.559636 0.605398 -0.286949
H -5.305253 0.864485 -1.506958
H -1.537527 0.087060 3.256466
H -2.434722 1.460446 2.616301
H 0.847396 -0.461960 2.290180
H -2.586256 2.680368 0.046491
H -1.833111 4.035049 -1.894955
H 0.489639 3.855495 -2.739530
H -1.416606 -1.660170 1.099554
N 5.259044 -0.997053 -1.940452
C 3.187533 -0.137795 -0.799451
C 7.916480 -1.150499 0.656990
C 6.682845 -0.992579 -0.181149
C 6.548326 -1.273608 -1.518287
C 4.527773 -0.528064 -0.873914
C 5.395085 -0.512776 0.256543
C 4.882918 -0.072616 1.489204
C 3.559723 0.339613 1.571412
C 2.716672 0.303755 0.436455

H	4.913928	-1.125835	-2.879716
H	2.528304	-0.191921	-1.659576
H	7.754077	-1.842854	1.493444
H	8.749271	-1.539320	0.062038
H	7.279620	-1.655734	-2.217705
H	5.516089	-0.040955	2.371856
H	3.159007	0.709255	2.510163
H	8.237153	-0.195091	1.092582

Compound C-V

1 1

N	2.390732	-1.819704	-1.422595
C	-1.008776	0.551870	1.251532
O	-0.197445	1.319865	1.779028
C	-0.945713	-0.960549	1.542905
C	3.836111	0.234091	-1.555774
C	-3.002929	0.089168	-0.185243
C	-3.345418	0.815108	-1.493051
C	-3.234871	2.295983	-1.084955
C	-2.061525	2.340070	-0.085488
C	-2.579796	-1.362179	-0.323993
C	0.545899	-1.380014	1.793450
C	1.424478	-1.216982	0.619718
C	1.542912	-2.192876	-0.530695
C	2.909647	-0.559881	-0.953304
C	2.313732	-0.191979	0.296969
C	2.667406	1.015553	0.947923
C	3.618429	1.835931	0.332323
C	4.186644	1.453287	-0.881786
N	-1.550420	-1.760995	0.489326
N	-1.966607	0.949522	0.402982
O	-3.151157	-2.130201	-1.084283
H	-1.445616	-1.134175	2.507029
H	4.297364	-0.029133	-2.500840
H	-3.887882	0.084951	0.470995
H	-4.333305	0.539465	-1.865838
H	-2.605326	0.560458	-2.259565
H	-4.158645	2.618336	-0.593097
H	-3.064821	2.955626	-1.939090
H	-2.230382	3.026922	0.748602
H	-1.111989	2.612101	-0.558233
H	0.539869	-2.435455	2.093546
H	0.897858	-0.772637	2.628174
H	0.983796	-3.119325	-0.605294
H	2.195807	1.295638	1.882198
H	3.915654	2.768208	0.798024
H	4.926974	2.099349	-1.343953
H	-1.443865	-2.768993	0.548216

Iron-Oxo Quartet FeO_quartet

0 4

Fe	0.089141	0.036057	-0.377911
N	1.819494	-0.979714	-0.146250
N	-0.917496	-1.709275	-0.274068
N	1.083957	1.774351	-0.133367

N	-1.657172	1.037712	-0.294031
C	3.081401	-0.442680	-0.039450
C	-2.283740	-1.880043	-0.331182
C	1.995090	-2.338860	-0.207619
C	-0.378864	-2.980953	-0.309906
C	2.440098	1.939745	-0.026959
C	-2.917859	0.504666	-0.369167
C	0.552637	3.037947	-0.164823
C	-1.825001	2.402919	-0.311109
C	4.071808	-1.491461	-0.023063
C	-2.610089	-3.284464	-0.372069
C	3.397629	-2.668854	-0.134568
C	-1.431248	-3.964519	-0.364664
C	2.774252	3.342623	0.015773
C	-3.906480	1.553781	-0.424663
C	1.599634	4.026212	-0.073553
C	-3.227094	2.733367	-0.389255
H	5.138437	-1.328178	0.061663
H	-3.617167	-3.679288	-0.410096
H	3.794198	-3.675647	-0.157896
H	-1.269081	-5.034293	-0.392542
H	3.779796	3.733563	0.102573
H	-4.974948	1.389913	-0.480023
H	1.437863	5.096418	-0.073688
H	-3.621023	3.741304	-0.409414
C	3.374694	0.911083	0.028832
C	-3.216766	-0.854725	-0.375471
C	-0.802078	3.337879	-0.250908
C	0.973072	-3.277374	-0.299936
H	4.419583	1.191446	0.116024
H	-4.263773	-1.135122	-0.431928
H	-1.081791	4.386473	-0.266560
H	1.257039	-4.323926	-0.342683
O	0.174206	0.077727	-2.000977
S	-0.029871	-0.377906	2.210114
C	-1.717070	-0.057908	2.807120
H	-2.414815	-0.741276	2.308018
H	-1.755821	-0.254933	3.882505
H	-2.027517	0.968924	2.599579

Iron-Hydroxo Triplet

0 3

Fe	0.057031	0.006037	-0.226647
N	0.974394	-1.797923	-0.242753
N	-1.731268	-0.907687	-0.220318
N	1.856372	0.908100	-0.084704
N	-0.852320	1.799772	-0.277175
C	2.329800	-2.034563	-0.206678
C	-2.960752	-0.301749	-0.339972
C	0.367226	-3.032337	-0.203144
C	-1.968581	-2.262094	-0.209979
C	3.088172	0.302557	-0.085169
C	-2.199602	2.037186	-0.378754
C	2.088668	2.262332	-0.048308
C	-0.244044	3.029094	-0.224220

C	2.580119	-3.454499	-0.182363
C	-3.998864	-1.300172	-0.375981
C	1.366010	-4.071634	-0.175489
C	-3.385332	-2.513778	-0.289586
C	4.126445	1.301639	-0.022854
C	-2.448488	3.458318	-0.407465
C	3.507320	2.514797	0.003547
C	-1.237045	4.072641	-0.307636
H	3.565438	-3.902074	-0.160285
H	-5.055580	-1.082119	-0.462645
H	1.147003	-5.131360	-0.149657
H	-3.833148	-3.499210	-0.293325
H	5.186599	1.083695	-0.008209
H	-3.429966	3.907778	-0.487049
H	3.953478	3.500219	0.041649
H	-1.015958	5.132094	-0.290082
C	3.319890	-1.065283	-0.147197
C	-3.189691	1.064480	-0.417758
C	1.120128	3.254418	-0.104192
C	-1.000845	-3.257576	-0.181502
H	4.351412	-1.401018	-0.128845
H	-4.218904	1.396951	-0.503597
H	1.456901	4.285330	-0.071754
H	-1.340819	-4.287758	-0.163832
O	0.105832	0.052682	-2.029855
S	0.134786	0.070941	2.082629
C	-1.551017	-0.093903	2.771846
H	-1.987130	-1.064516	2.525644
H	-1.465322	-0.001876	3.858606
H	-2.198792	0.701402	2.395289
H	0.411430	-0.826094	-2.320515

Iron-Aqua Doublet

0 2

Fe	-0.061810	-0.012974	-0.108940
N	-1.440696	1.471790	-0.171790
N	1.426825	1.340160	-0.271464
N	-1.567654	-1.350895	-0.149754
N	1.297105	-1.480332	-0.269235
C	-2.811606	1.352528	-0.123321
C	2.780244	1.098135	-0.365256
C	-1.176848	2.822091	-0.121987
C	1.290574	2.709063	-0.215092
C	-2.919623	-1.107179	-0.115452
C	2.663493	-1.361298	-0.376448
C	-1.428734	-2.716964	-0.114451
C	1.036251	-2.828918	-0.228404
C	-3.424222	2.657030	-0.063240
C	3.509577	2.342040	-0.374909
C	-2.411019	3.567883	-0.059073
C	2.586833	3.340253	-0.276853
C	-3.651620	-2.351266	-0.067339
C	3.277292	-2.667368	-0.409065
C	-2.726705	-3.350030	-0.063671
C	2.268486	-3.577279	-0.312873

H	-4.491511	2.834722	-0.025654
H	4.586746	2.423825	-0.447020
H	-2.475562	4.647925	-0.018730
H	2.751516	4.410129	-0.254024
H	-4.731062	-2.429621	-0.039679
H	4.341759	-2.845496	-0.494230
H	-2.888531	-4.420111	-0.034299
H	2.333066	-4.658000	-0.304806
C	-3.508948	0.151165	-0.110512
C	3.362852	-0.161422	-0.429642
C	-0.224180	-3.408337	-0.145828
C	0.086616	3.400029	-0.138759
H	-4.592712	0.199035	-0.073877
H	4.444266	-0.212462	-0.508450
H	-0.271881	-4.492591	-0.120154
H	0.137795	4.483815	-0.100804
O	-0.145349	0.032792	-2.296283
S	-0.085960	-0.034935	2.133451
C	1.638559	0.015887	2.746327
H	2.132588	0.951395	2.472574
H	1.591581	-0.054151	3.837830
H	2.222347	-0.824329	2.363104
H	-0.898807	0.632536	-2.442733
H	0.640921	0.566030	-2.510789

Iron-Hydroxo Doublet Anion

-1 2

Fe	0.064821	-0.001115	-0.221145
N	1.585262	-1.345021	-0.150582
N	-1.305723	-1.489454	-0.267154
N	1.446338	1.486933	-0.159251
N	-1.443693	1.345391	-0.276697
C	2.931596	-1.096136	-0.097124
C	-2.665785	-1.371806	-0.365284
C	1.443391	-2.708095	-0.142425
C	-1.032427	-2.830214	-0.254517
C	2.810444	1.370747	-0.105622
C	-2.786159	1.094913	-0.373573
C	1.172035	2.829343	-0.161717
C	-1.303741	2.706417	-0.270540
C	3.667576	-2.341348	-0.056227
C	-3.278135	-2.683455	-0.407602
C	2.743649	-3.342022	-0.083157
C	-2.263598	-3.589312	-0.336544
C	3.421566	2.682362	-0.074348
C	-3.524068	2.339897	-0.421777
C	2.404506	3.587718	-0.107798
C	-2.603301	3.341178	-0.355152
H	4.747013	-2.419808	-0.011309
H	-4.343201	-2.866275	-0.482376
H	2.907871	-4.412600	-0.065784
H	-2.322694	-4.670947	-0.342212
H	4.488240	2.865889	-0.030976
H	-4.601947	2.417145	-0.496777
H	2.463382	4.669324	-0.098415

H	-2.767940	4.411805	-0.365729
C	3.512974	0.169140	-0.078506
C	-3.365870	-0.169537	-0.418899
C	-0.096751	3.399739	-0.211639
C	0.236567	-3.400673	-0.190315
H	4.596912	0.222512	-0.034853
H	-4.448002	-0.222606	-0.497209
H	-0.150258	4.484860	-0.211157
H	0.290072	-4.485778	-0.183511
O	0.110636	-0.002976	-2.069830
S	0.066238	-0.018863	2.182733
C	-1.665805	0.046371	2.792667
H	-2.255038	-0.791062	2.406404
H	-1.659807	-0.008823	3.886918
H	-2.159557	0.977055	2.495720
H	1.057433	-0.012378	-2.287687

Figure 11B Radical C2 TS

O 2

N	2.035711	-0.920612	1.727039
C	2.372037	-3.391249	1.368746
C	4.189336	0.763761	-0.802561
C	3.379826	-0.147172	0.065864
C	2.436656	0.243184	1.056341
C	2.556205	-2.033040	1.103180
C	3.406556	-1.572232	0.050721
C	4.089040	-2.522830	-0.737597
C	3.912805	-3.875255	-0.469107
C	3.063223	-4.304924	0.571702
H	1.420774	-0.942104	2.525591
H	1.719648	-3.725291	2.170809
H	3.880152	0.715524	-1.856614
H	4.103793	1.805800	-0.482330
H	2.487971	1.165416	1.623048
H	4.742380	-2.200202	-1.543980
H	4.433374	-4.615938	-1.070007
H	2.944094	-5.368648	0.758460
H	5.252058	0.488585	-0.776539
N	-0.479438	2.379289	1.571440
C	-2.034364	-1.179002	-1.412882
O	-1.542500	-2.038164	-2.145616
C	-1.280255	0.095175	-1.026703
C	0.104475	4.583270	0.515677
C	-3.876945	-0.259676	0.007742
C	-4.967803	-1.054993	0.738210
C	-5.430459	-2.063763	-0.328185
C	-4.139614	-2.442450	-1.075697
C	-2.829692	0.381147	0.918333
C	0.258567	-0.047518	-0.992025
C	0.664288	0.984132	0.038824
C	-0.432701	1.004446	1.109015
C	0.124195	3.194242	0.613673
C	0.838169	2.393779	-0.317131
C	1.528179	3.014941	-1.364245
C	1.513452	4.410286	-1.468951

C	0.811586	5.182611	-0.535799
N	-1.615213	0.530045	0.344067
N	-3.278971	-1.263776	-0.891117
O	-3.083078	0.745757	2.069219
H	-1.326120	2.675432	2.041597
H	-1.560198	0.882542	-1.742760
H	-0.454851	5.185472	1.226517
H	-4.335783	0.547580	-0.586220
H	-5.770313	-0.410498	1.103314
H	-4.528169	-1.568296	1.600071
H	-6.135602	-1.585006	-1.017051
H	-5.926492	-2.937394	0.102781
H	-4.297250	-2.639222	-2.140295
H	-3.650451	-3.323245	-0.642657
H	0.700225	0.126688	-1.975135
H	0.523813	-1.062237	-0.677391
H	-0.304464	0.327653	1.959040
H	2.061144	2.419589	-2.100161
H	2.045030	4.895835	-2.282438
H	0.804682	6.265389	-0.629336

Figure 11B Radical C2 Product

O 2

N	2.021897	-0.812981	1.380367
C	3.475741	-2.854607	1.436932
C	3.688043	1.336042	-1.270884
C	3.175283	0.298457	-0.326469
C	2.050322	0.485176	0.678402
C	3.074558	-1.614212	0.958229
C	3.747670	-0.973253	-0.128925
C	4.826988	-1.641481	-0.755068
C	5.221157	-2.889476	-0.278958
C	4.560355	-3.488268	0.807315
H	1.800037	-0.806017	2.367699
H	2.964921	-3.323651	2.273540
H	3.195911	1.301554	-2.254875
H	3.547794	2.349416	-0.880310
H	2.298025	1.295207	1.385644
H	5.347447	-1.180416	-1.590059
H	6.052401	-3.406840	-0.750372
H	4.888869	-4.459622	1.166566
H	4.759246	1.189607	-1.454013
N	-0.628700	1.996562	1.787857
C	-2.056025	-1.345315	-1.463782
O	-1.549091	-2.096623	-2.297401
C	-1.359476	-0.072008	-0.975772
C	-0.605075	4.291176	0.765246
C	-3.879092	-0.678104	0.111844
C	-4.896036	-1.600332	0.798199
C	-5.351679	-2.521613	-0.347142
C	-4.074839	-2.755885	-1.173090
C	-2.829214	-0.074632	1.043769
C	0.172643	-0.127145	-1.018184
C	0.620261	0.830730	0.102279
C	-0.476397	0.673631	1.207300

C	-0.298999	2.930872	0.798768
C	0.441997	2.316146	-0.229516
C	0.840931	3.070035	-1.327861
C	0.535405	4.438275	-1.379740
C	-0.173014	5.038487	-0.336083
N	-1.646763	0.190966	0.444607
N	-3.270546	-1.552544	-0.907423
O	-3.054254	0.163914	2.232917
H	-1.481104	2.132029	2.320891
H	-1.724799	0.766542	-1.587790
H	-1.178719	4.753052	1.564048
H	-4.403600	0.158402	-0.378316
H	-5.713580	-1.039776	1.256362
H	-4.394655	-2.172258	1.586202
H	-6.105989	-2.014621	-0.959471
H	-5.786580	-3.458450	0.010712
H	-4.264819	-2.860542	-2.245344
H	-3.523013	-3.644316	-0.843321
H	0.560456	0.157519	-1.998437
H	0.513263	-1.143496	-0.799963
H	-0.252525	-0.057497	1.984089
H	1.371184	2.609648	-2.155130
H	0.845026	5.027509	-2.237875
H	-0.408703	6.098494	-0.383328

Figure 11B Radical C3 TS

O 2

N	1.839883	-2.633470	1.532976
C	3.492027	-3.344098	-0.234524
C	2.591438	0.876978	2.235670
C	2.155020	-0.351744	1.458445
C	1.502361	-1.434502	2.123310
C	2.814221	-2.424904	0.569462
C	3.089023	-1.035329	0.531812
C	4.111959	-0.570329	-0.298739
C	4.809425	-1.481030	-1.097377
C	4.493161	-2.849822	-1.070929
H	1.437641	-3.529077	1.768168
H	3.259837	-4.404780	-0.199240
H	2.887521	1.689315	1.566225
H	1.787932	1.249816	2.877810
H	0.797672	-1.405069	2.941892
H	4.363939	0.485654	-0.324688
H	5.607927	-1.128216	-1.744005
H	5.044675	-3.539788	-1.703837
H	3.450043	0.634201	2.873558
N	-0.266893	2.391172	1.215343
C	-2.301233	-1.352517	-1.152531
O	-1.956889	-2.434305	-1.631132
C	-1.316991	-0.203124	-0.920506
C	0.810074	4.128833	-0.246056
C	-3.997217	0.208870	-0.184103
C	-5.300985	-0.167547	0.533070
C	-5.890870	-1.259731	-0.376613
C	-4.662769	-2.050947	-0.860146

C	-2.913375	0.796265	0.720554
C	0.143305	-0.637826	-0.680726
C	0.700853	0.474392	0.194302
C	-0.457701	0.955743	1.084086
C	0.555552	2.826334	0.174214
C	1.172925	1.711173	-0.449840
C	2.043836	1.923960	-1.523597
C	2.307594	3.232078	-1.950336
C	1.698620	4.319356	-1.314873
N	-1.653396	0.546363	0.303697
N	-3.573210	-1.064580	-0.794504
O	-3.178219	1.455580	1.729583
H	-1.082752	2.930917	1.478728
H	-1.367966	0.467138	-1.792297
H	0.322051	4.974807	0.230694
H	-4.204427	0.950434	-0.972875
H	-5.960550	0.693035	0.663026
H	-5.067988	-0.567989	1.525538
H	-6.401815	-0.801868	-1.231279
H	-6.612488	-1.897384	0.140825
H	-4.769085	-2.437407	-1.878142
H	-4.429759	-2.898583	-0.204314
H	0.685205	-0.754768	-1.621031
H	0.147450	-1.602195	-0.164722
H	-0.531050	0.489819	2.071215
H	2.503897	1.081234	-2.031654
H	2.981453	3.401257	-2.785645
H	1.905266	5.329701	-1.658309

Figure 11B Radical C3 Product

O 2

N	2.161406	-2.553138	1.589048
C	3.987615	-3.136642	-0.029161
C	2.564915	0.842287	2.098101
C	1.952142	-0.223774	1.158170
C	1.433696	-1.422899	1.939771
C	3.086421	-2.272960	0.598340
C	3.042404	-0.891966	0.306572
C	3.976169	-0.361955	-0.576248
C	4.897998	-1.211365	-1.209054
C	4.890081	-2.584459	-0.942566
H	1.987209	-3.477400	1.955555
H	3.998785	-4.198624	0.199725
H	2.988301	1.675172	1.526966
H	1.812886	1.249474	2.781242
H	0.981400	-1.375383	2.923297
H	4.006007	0.704473	-0.773827
H	5.622632	-0.797338	-1.904159
H	5.605121	-3.234531	-1.440082
H	3.366367	0.393486	2.693216
N	-0.323586	2.244481	1.395226
C	-2.246010	-1.337030	-1.249517
O	-1.880554	-2.349385	-1.848358
C	-1.285549	-0.196774	-0.900482
C	0.460821	4.099452	-0.105727

C	-3.970786	0.064898	-0.103156
C	-5.246928	-0.427214	0.594132
C	-5.822270	-1.437199	-0.414569
C	-4.581698	-2.129516	-1.006346
C	-2.891477	0.596809	0.838490
C	0.169930	-0.632461	-0.702492
C	0.761520	0.398408	0.286776
C	-0.451285	0.808704	1.193984
C	0.377228	2.768431	0.303338
C	1.056117	1.743134	-0.383417
C	1.787406	2.053693	-1.525603
C	1.879403	3.387553	-1.951231
C	1.226549	4.396590	-1.239091
N	-1.628352	0.415473	0.393146
N	-3.519912	-1.123041	-0.850388
O	-3.161443	1.160334	1.902322
H	-1.171656	2.709542	1.700683
H	-1.353797	0.557753	-1.699032
H	-0.068178	4.881749	0.431761
H	-4.219052	0.876393	-0.806624
H	-5.929909	0.392947	0.825132
H	-4.980990	-0.920362	1.535310
H	-6.369630	-0.909692	-1.203969
H	-6.509071	-2.151304	0.047276
H	-4.699387	-2.402852	-2.059150
H	-4.308225	-3.037015	-0.454747
H	0.715499	-0.666167	-1.647182
H	0.190473	-1.633027	-0.261932
H	-0.503294	0.295303	2.154811
H	2.273418	1.271758	-2.100988
H	2.450444	3.631533	-2.842316
H	1.297264	5.427609	-1.575999

Figure 11B Radical C4 TS

O 2

N	1.620635	-4.001210	0.629230
C	2.220096	-3.150934	-1.665412
C	2.447052	-1.289044	3.023908
C	2.137057	-2.168932	1.845743
C	1.707880	-3.480784	1.902941
C	2.012995	-3.042757	-0.280583
C	2.316723	-1.867312	0.453662
C	2.715423	-0.676594	-0.254214
C	3.075616	-0.862760	-1.634217
C	2.780541	-2.039245	-2.316459
H	1.370546	-4.952881	0.405647
H	2.006109	-4.071093	-2.200993
H	3.527632	-1.113459	3.115482
H	1.973948	-0.303156	2.947642
H	1.467843	-4.089735	2.763819
H	3.247593	0.087841	0.305776
H	3.527212	-0.032211	-2.169301
H	3.008859	-2.111203	-3.376812
H	2.110394	-1.752856	3.957095
N	0.663978	1.696845	1.638795

C	-2.436458	-0.261094	-1.592535
O	-2.384917	-0.960078	-2.605491
C	-1.258223	0.596067	-1.124085
C	1.676579	3.913617	1.017803
C	-3.599933	0.641960	0.428299
C	-4.749711	-0.011105	1.207509
C	-5.693186	-0.491863	0.090445
C	-4.745558	-0.964550	-1.025845
C	-2.260251	0.672878	1.165038
C	0.132812	0.067574	-1.530985
C	1.028871	0.596874	-0.427276
C	0.205790	0.554501	0.864929
C	1.290380	2.597295	0.774909
C	1.543028	1.971917	-0.472553
C	2.196773	2.685614	-1.481079
C	2.590307	4.007793	-1.243653
C	2.331049	4.610550	-0.007039
N	-1.184320	0.650036	0.348741
N	-3.529995	-0.166889	-0.802652
O	-2.179521	0.734392	2.394643
H	0.040445	2.030865	2.364086
H	-1.399122	1.611528	-1.525046
H	1.468278	4.390115	1.971855
H	-3.861415	1.682854	0.176904
H	-5.220877	0.685999	1.903698
H	-4.363263	-0.856925	1.786016
H	-6.307268	0.342344	-0.267512
H	-6.368471	-1.286259	0.419016
H	-5.138578	-0.790389	-2.031914
H	-4.503945	-2.031053	-0.941975
H	0.420460	0.414935	-2.524714
H	0.121289	-1.026742	-1.546593
H	0.284900	-0.365873	1.447391
H	2.386169	2.223722	-2.446689
H	3.094306	4.570155	-2.024547
H	2.636453	5.639491	0.164146

Figure 11B Radical C4 Product

O 2

N	2.339850	-3.871873	0.285473
C	3.077094	-2.534350	-1.705250
C	1.876747	-1.511342	3.099210
C	2.065900	-2.205459	1.774932
C	2.066670	-3.585487	1.599105
C	2.554862	-2.696746	-0.403707
C	2.343935	-1.633887	0.498713
C	2.486395	-0.203790	0.034136
C	3.299653	-0.143072	-1.243021
C	3.492699	-1.226772	-2.062895
H	2.473944	-4.798775	-0.091312
H	3.249502	-3.382704	-2.359777
H	0.830039	-1.503755	3.430702
H	2.454888	-2.008916	3.886351
H	1.899658	-4.375727	2.317741
H	2.985331	0.390146	0.814203

H	3.673344	0.829744	-1.545461
H	4.011680	-1.088257	-3.008901
H	2.207308	-0.468982	3.054755
N	0.418714	1.710266	1.767619
C	-2.242272	-0.541080	-1.636418
O	-2.064050	-1.250178	-2.627615
C	-1.165280	0.404467	-1.096929
C	0.989047	4.055466	1.055934
C	-3.617383	0.310075	0.269551
C	-4.774272	-0.410326	0.975202
C	-5.594185	-0.976580	-0.197936
C	-4.533720	-1.398127	-1.230293
C	-2.343792	0.447253	1.103456
C	0.273889	-0.042680	-1.378492
C	1.096526	0.555259	-0.218894
C	0.129640	0.508015	1.003518
C	0.889023	2.677067	0.869209
C	1.308950	2.066162	-0.327968
C	1.815159	2.848950	-1.359884
C	1.918767	4.237845	-1.188042
C	1.512881	4.827289	0.011783
N	-1.208670	0.489864	0.372104
N	-3.397548	-0.511597	-0.934640
O	-2.362333	0.529836	2.334625
H	-0.297051	1.972439	2.436927
H	-1.344590	1.399831	-1.531387
H	0.657930	4.518922	1.981252
H	-3.931051	1.325376	-0.023322
H	-5.344458	0.262901	1.618843
H	-4.374286	-1.216397	1.599465
H	-6.237171	-0.195378	-0.619114
H	-6.234299	-1.812055	0.097488
H	-4.861523	-1.268733	-2.266021
H	-4.224360	-2.442953	-1.106223
H	0.618807	0.295770	-2.356543
H	0.332821	-1.134743	-1.362420
H	0.219781	-0.375793	1.629515
H	2.115236	2.397240	-2.301419
H	2.309495	4.853914	-1.992683
H	1.592068	5.904108	0.137229

Figure 11B Radical C5 TS

0 2

N	-5.566010	0.067828	-0.750328
C	-3.454605	0.700912	-1.990373
C	-4.832501	-3.102094	1.047864
C	-4.862720	-1.840573	0.238460
C	-5.927209	-0.991043	0.067570
C	-4.252694	-0.077585	-1.125277
C	-3.766090	-1.271044	-0.515001
C	-2.448732	-1.672261	-0.752188
C	-1.566897	-0.813989	-1.490162
C	-2.154795	0.306253	-2.202178
H	-6.176279	0.822785	-1.025463
H	-3.867343	1.568247	-2.499427

H	-4.064844	-3.062957	1.832136
H	-5.796425	-3.281852	1.535252
H	-6.929326	-1.051219	0.470160
H	-2.068121	-2.601321	-0.336045
H	-0.719156	-1.296211	-1.977442
H	-1.526915	0.877519	-2.879386
H	-4.605915	-3.979222	0.427063
N	0.370239	2.191987	-0.782233
C	3.033387	-1.588206	0.786701
O	2.865040	-2.775631	1.068131
C	1.886553	-0.574303	0.794455
C	-0.928421	3.435362	0.975946
C	4.450511	0.349733	0.084470
C	5.747855	0.295457	-0.733970
C	6.529909	-0.847469	-0.062876
C	5.448422	-1.877127	0.310084
C	3.250176	0.937567	-0.657262
C	0.495758	-1.170169	0.492859
C	-0.249851	-0.002293	-0.133561
C	0.783946	0.807292	-0.931227
C	-0.479647	2.290720	0.321110
C	-0.896340	0.998166	0.725834
C	-1.777322	0.862332	1.800922
C	-2.236110	2.008060	2.462871
C	-1.813846	3.277280	2.051555
N	2.057237	0.441918	-0.260771
N	4.233375	-1.060095	0.456805
O	3.369234	1.804301	-1.526856
H	1.075567	2.898458	-0.953090
H	1.873819	-0.086820	1.781145
H	-0.594050	4.422834	0.669273
H	4.605929	0.956180	0.991746
H	6.278617	1.249778	-0.724339
H	5.511617	0.050567	-1.775019
H	7.026897	-0.481508	0.842661
H	7.296375	-1.275343	-0.714376
H	5.663680	-2.414495	1.238490
H	5.293505	-2.623200	-0.478554
H	0.015751	-1.549716	1.396973
H	0.606425	-2.008434	-0.205451
H	0.881116	0.552887	-1.991896
H	-2.101273	-0.123659	2.122621
H	-2.918971	1.910454	3.302204
H	-2.171186	4.159557	2.576477

Figure 11B Radical C5 Product

0 2

N	-5.707588	-0.106556	-0.984684
C	-3.514493	0.747008	-1.934977
C	-4.888469	-3.070003	1.101239
C	-4.944779	-1.862661	0.215120
C	-6.064454	-1.160100	-0.159222
C	-4.344925	-0.109478	-1.157341
C	-3.817546	-1.201966	-0.414240
C	-2.448342	-1.453522	-0.410841

C	-1.486476	-0.564979	-1.162549
C	-2.173712	0.531195	-1.950510
H	-6.350730	0.555945	-1.391436
H	-3.952497	1.553633	-2.518845
H	-4.265773	-2.894119	1.988841
H	-5.887756	-3.353622	1.447858
H	-7.101804	-1.324991	0.098605
H	-2.045811	-2.311287	0.120373
H	-0.918361	-1.191505	-1.880610
H	-1.538564	1.179253	-2.547167
H	-4.458452	-3.936931	0.581580
N	0.440190	2.192594	-0.853279
C	2.945619	-1.604629	0.806795
O	2.746688	-2.765072	1.168401
C	1.826344	-0.562040	0.744898
C	-0.594181	3.503371	1.028183
C	4.411405	0.243809	-0.024422
C	5.697867	0.098899	-0.849304
C	6.454800	-1.018436	-0.109762
C	5.349277	-1.989588	0.342068
C	3.223802	0.825641	-0.789041
C	0.434089	-1.139490	0.474653
C	-0.340452	0.004862	-0.222402
C	0.758799	0.783485	-1.023731
C	-0.305836	2.334251	0.323546
C	-0.819854	1.090218	0.732157
C	-1.636557	1.010413	1.853518
C	-1.936942	2.178235	2.571118
C	-1.416667	3.407428	2.157253
N	2.019981	0.369075	-0.376936
N	4.157585	-1.131678	0.440048
O	3.362002	1.657868	-1.688826
H	1.204444	2.833371	-1.036675
H	1.828609	-0.007655	1.695942
H	-0.189497	4.460917	0.711799
H	4.595711	0.901995	0.840492
H	6.254623	1.036435	-0.908040
H	5.443984	-0.208518	-1.869469
H	6.972483	-0.606876	0.764048
H	7.201326	-1.510890	-0.738279
H	5.558649	-2.466591	1.304176
H	5.166973	-2.784081	-0.391378
H	-0.049433	-1.474747	1.393645
H	0.523382	-2.003791	-0.193005
H	0.816040	0.530400	-2.085830
H	-2.038898	0.053708	2.175041
H	-2.571343	2.124434	3.451162
H	-1.647894	4.307559	2.721269

Figure 11B Radical C6 TS

0 2

N	2.477549	-3.282471	-1.302257
C	2.166737	-0.851400	-1.866568
C	4.390644	-3.390378	1.883507
C	3.633059	-3.060107	0.631191

C	3.097775	-3.958546	-0.268890
C	2.591307	-1.922643	-1.088909
C	3.325192	-1.755535	0.125707
C	3.637505	-0.436012	0.549181
C	3.197071	0.636479	-0.186334
C	2.351196	0.475059	-1.356326
H	1.997614	-3.716455	-2.076185
H	1.687045	-1.011808	-2.827452
H	3.892192	-2.992834	2.777141
H	4.486321	-4.473549	2.011726
H	3.113068	-5.039917	-0.252860
H	4.239408	-0.278233	1.440938
H	3.438027	1.646188	0.132858
H	2.387242	1.275975	-2.092673
H	5.403599	-2.967323	1.869482
N	0.455305	1.530548	1.615077
C	-2.854646	-0.328476	-1.434265
O	-2.938866	-0.623425	-2.627473
C	-1.833216	0.682897	-0.907818
C	0.736354	4.028340	1.615968
C	-3.538558	-0.537764	0.961090
C	-4.203914	-1.746818	1.633697
C	-5.293517	-2.146752	0.623219
C	-4.642629	-1.903015	-0.749574
C	-2.089852	-0.284999	1.380758
C	-0.547084	0.796266	-1.752134
C	0.499723	1.208446	-0.730807
C	0.119804	0.546313	0.599983
C	0.611636	2.776056	1.016175
C	0.668703	2.627853	-0.393237
C	0.866592	3.750732	-1.200279
C	0.998397	5.011138	-0.604483
C	0.932013	5.142145	0.787656
N	-1.331592	0.291925	0.422648
N	-3.650307	-0.852311	-0.475225
O	-1.667490	-0.566948	2.504686
H	0.020613	1.432517	2.523769
H	-2.328604	1.663890	-0.846167
H	0.677656	4.139695	2.695229
H	-4.109326	0.377601	1.187919
H	-4.597700	-1.500191	2.621990
H	-3.466595	-2.547704	1.754548
H	-6.170829	-1.500748	0.741411
H	-5.622880	-3.182192	0.743170
H	-5.351856	-1.570319	-1.513249
H	-4.133691	-2.795669	-1.132953
H	-0.660973	1.516232	-2.565777
H	-0.324026	-0.181050	-2.190973
H	0.611758	-0.406465	0.815146
H	0.906104	3.649845	-2.282554
H	1.148160	5.890243	-1.224737
H	1.030097	6.125732	1.239796

Figure 11B Radical C6 Product

0 2

N	3.212186	-3.043001	-0.990506
C	2.002355	-0.922575	-1.536790
C	5.820712	-2.174360	1.511190
C	4.697764	-2.239450	0.516986
C	4.257976	-3.373054	-0.149783
C	2.943116	-1.687385	-0.881253
C	3.880748	-1.166297	0.066564
C	3.852760	0.242500	0.335240
C	2.941450	1.043375	-0.269118
C	1.880453	0.551684	-1.233564
H	2.708484	-3.693159	-1.574506
H	1.367510	-1.365541	-2.297109
H	5.476279	-1.818550	2.490707
H	6.274623	-3.159887	1.657876
H	4.615723	-4.391570	-0.087667
H	4.579720	0.672219	1.021341
H	2.944071	2.108937	-0.061099
H	1.999145	1.117619	-2.177998
H	6.613890	-1.489565	1.184292
N	0.234056	1.384904	1.607731
C	-2.974968	-0.585873	-1.411653
O	-3.080069	-0.861515	-2.607656
C	-1.947857	0.420880	-0.887118
C	0.086470	3.896370	1.535100
C	-3.613374	-0.836475	0.991838
C	-4.245857	-2.067142	1.657341
C	-5.353808	-2.461514	0.664735
C	-4.737469	-2.184752	-0.717943
C	-2.165382	-0.560197	1.395006
C	-0.685152	0.540830	-1.745891
C	0.421688	0.975253	-0.753845
C	0.007659	0.343774	0.615290
C	0.193099	2.625632	0.967619
C	0.336938	2.461398	-0.422371
C	0.390248	3.571826	-1.255276
C	0.287784	4.855761	-0.698078
C	0.134898	5.006629	0.683001
N	-1.417817	0.007188	0.421718
N	-3.748103	-1.130209	-0.446160
O	-1.735033	-0.815426	2.522157
H	-0.245544	1.259048	2.491864
H	-2.445769	1.398608	-0.797920
H	-0.032445	4.021379	2.607840
H	-4.196824	0.064106	1.244584
H	-4.618713	-1.844582	2.659263
H	-3.496011	-2.860900	1.744036
H	-6.235403	-1.828202	0.815147
H	-5.668324	-3.502816	0.772749
H	-5.467592	-1.843948	-1.457965
H	-4.229312	-3.064517	-1.130742
H	-0.812822	1.256302	-2.561407
H	-0.468810	-0.433801	-2.187807
H	0.552111	-0.564787	0.879051
H	0.500144	3.452460	-2.330980
H	0.322016	5.730326	-1.341140

H	0.048921	6.003156	1.108717
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Figure 11B Radical C7 TS
O 2

N	-2.892314	0.454058	-1.848977
C	-1.664756	-1.556181	-0.917054
C	-6.416100	0.240288	-0.687096
C	-4.957892	0.094171	-1.006261
C	-4.180383	0.954574	-1.741089
C	-2.810016	-0.723807	-1.148817
C	-4.089200	-0.987566	-0.606192
C	-4.288594	-2.157098	0.159709
C	-3.206635	-3.024440	0.353660
C	-1.953171	-2.766865	-0.203632
H	-2.086921	1.003447	-2.124869
H	-0.893341	-1.602786	-1.684137
H	-6.595894	0.242032	0.395973
H	-6.815600	1.176655	-1.090529
H	-4.444339	1.889337	-2.216999
H	-5.263719	-2.387556	0.579917
H	-3.353924	-3.941201	0.919202
H	-1.158631	-3.497593	-0.083118
H	-7.011613	-0.581723	-1.106241
N	-0.172638	1.747898	-0.744439
C	3.321457	-1.319006	0.793663
O	3.410660	-2.493549	1.153293
C	2.014226	-0.528146	0.893300
C	-1.427957	2.960829	1.072083
C	4.256405	0.787461	-0.176567
C	5.452465	0.920950	-1.129165
C	6.501724	-0.010902	-0.497375
C	5.679816	-1.196780	0.036970
C	2.895953	1.076692	-0.810771
C	0.731562	-1.384358	0.812287
C	-0.277104	-0.419688	0.217891
C	0.491782	0.451433	-0.785599
C	-0.864157	1.837437	0.475521
C	-0.974520	0.553459	1.063036
C	-1.677332	0.400940	2.261425
C	-2.250963	1.524802	2.866136
C	-2.123897	2.788270	2.276763
N	1.868063	0.413577	-0.234477
N	4.355297	-0.607980	0.290270
O	2.752416	1.860843	-1.751761
H	0.389294	2.533510	-1.054504
H	2.026187	0.029442	1.841697
H	-1.327223	3.944636	0.621803
H	4.376808	1.476154	0.675490
H	5.789500	1.955636	-1.220978
H	5.164855	0.569692	-2.125814
H	7.007172	0.498220	0.331084
H	7.267033	-0.330041	-1.209671
H	6.087935	-1.629386	0.955182
H	5.586588	-2.003715	-0.699815
H	0.437285	-1.767581	1.791111

H	0.912609	-2.242642	0.155853
H	0.533996	0.083953	-1.816376
H	-1.773466	-0.579632	2.720230
H	-2.795332	1.416949	3.799954
H	-2.568985	3.654157	2.759705

Figure 11B Radical C7 Product
0 2

N	-2.749404	0.588212	-1.668534
C	-1.565597	-1.344318	-0.448539
C	-6.417170	0.076139	-1.457907
C	-4.918690	0.058967	-1.384589
C	-4.052147	0.974734	-1.932147
C	-2.758327	-0.553932	-0.912675
C	-4.097646	-0.925722	-0.723321
C	-4.424894	-2.085244	0.034263
C	-3.365106	-2.827857	0.596351
C	-2.041640	-2.496403	0.412502
H	-1.936926	1.194460	-1.762016
H	-1.064385	-1.785654	-1.336005
H	-6.874014	0.097266	-0.459625
H	-6.773922	0.956491	-2.003054
H	-4.253869	1.876710	-2.493605
H	-5.457615	-2.378185	0.195308
H	-3.599647	-3.704781	1.196455
H	-1.275981	-3.136302	0.839368
H	-6.813512	-0.811619	-1.968691
N	-0.221474	1.738705	-0.636559
C	3.265009	-1.345483	0.722345
O	3.375754	-2.501592	1.131233
C	1.955479	-0.559142	0.829930
C	-1.122259	2.970459	1.371492
C	4.148882	0.722686	-0.370206
C	5.299978	0.817075	-1.381510
C	6.381296	-0.080969	-0.754566
C	5.591017	-1.243769	-0.129188
C	2.761873	0.995064	-0.949245
C	0.692749	-1.423211	0.815087
C	-0.410198	-0.503686	0.234456
C	0.364911	0.407509	-0.780747
C	-0.742152	1.826195	0.673436
C	-0.914196	0.543540	1.218969
C	-1.487118	0.394305	2.476986
C	-1.874960	1.536094	3.192069
C	-1.688762	2.807414	2.641416
N	1.763706	0.321535	-0.331895
N	4.273137	-0.651105	0.149561
O	2.572698	1.778927	-1.881969
H	0.378404	2.489460	-0.965938
H	1.994204	0.040806	1.751782
H	-0.982075	3.959768	0.944851
H	4.308826	1.446651	0.445510
H	5.626227	1.847740	-1.535312
H	4.970707	0.418476	-2.347076
H	6.920408	0.468277	0.025620

H	7.115785	-0.430237	-1.484844
H	6.040158	-1.627900	0.791395
H	5.473071	-2.086643	-0.820606
H	0.447227	-1.796289	1.810569
H	0.853750	-2.287814	0.162045
H	0.309191	0.082203	-1.823156
H	-1.632271	-0.594540	2.903601
H	-2.318336	1.431485	4.177981
H	-1.986750	3.687377	3.205323

Figure 11D Cation C2 TS
1 1

N	1.501309	-1.347979	1.780037
C	1.512447	-3.761497	1.061592
C	4.287954	0.271535	-0.064632
C	3.196383	-0.595981	0.464102
C	2.200847	-0.213198	1.396802
C	1.941693	-2.427959	1.053326
C	3.001857	-1.978597	0.206975
C	3.645507	-2.903280	-0.649772
C	3.225392	-4.218768	-0.636694
C	2.169474	-4.639827	0.212388
H	0.806079	-1.386188	2.511643
H	0.705626	-4.093279	1.707043
H	4.479147	0.083232	-1.126610
H	4.069154	1.332748	0.072551
H	2.228907	0.648161	2.050799
H	4.455409	-2.582645	-1.297907
H	3.704572	-4.947439	-1.282749
H	1.866686	-5.682568	0.195750
H	5.222711	0.059943	0.472086
N	-0.140728	2.607873	1.308266
C	-2.153191	-0.987562	-1.305574
O	-1.758441	-1.992945	-1.894588
C	-1.231037	0.212866	-1.058207
C	1.109938	4.511145	0.289322
C	-3.868491	0.359024	-0.080314
C	-5.094182	-0.163580	0.681296
C	-5.669498	-1.221125	-0.277595
C	-4.428616	-1.884146	-0.898948
C	-2.760705	0.929862	0.801917
C	0.268358	-0.165997	-0.955231
C	0.772445	0.886741	-0.007661
C	-0.330496	1.203187	1.016424
C	0.755344	3.162176	0.450316
C	1.323677	2.145385	-0.387144
C	2.200913	2.509504	-1.435413
C	2.533155	3.840359	-1.598411
C	1.997368	4.823959	-0.729361
N	-1.522401	0.861332	0.238639
N	-3.404759	-0.826399	-0.827838
O	-2.951750	1.420239	1.910785
H	-0.731847	3.107768	1.956862
H	-1.373910	0.933694	-1.875078
H	0.686293	5.280500	0.926062

H	-4.169516	1.151529	-0.783799
H	-5.798755	0.636247	0.917963
H	-4.771723	-0.620473	1.622696
H	-6.266515	-0.736990	-1.058230
H	-6.309295	-1.946177	0.231333
H	-4.576814	-2.199618	-1.935332
H	-4.090653	-2.755727	-0.326372
H	0.764122	-0.141847	-1.925878
H	0.354804	-1.176941	-0.547304
H	-0.333060	0.632262	1.946815
H	2.603795	1.751569	-2.099368
H	3.204606	4.142205	-2.395050
H	2.278544	5.862536	-0.878243

Figure 11D Cation C2 Product

1 1

N	1.951542	-1.052607	1.314640
C	3.289477	-3.138505	1.097434
C	3.855563	1.499039	-0.695683
C	3.253263	0.310277	-0.032086
C	1.995487	0.313038	0.800080
C	2.967209	-1.784065	0.852851
C	3.799507	-0.956172	0.005730
C	4.978029	-1.510591	-0.590868
C	5.270753	-2.822686	-0.348182
C	4.425384	-3.624314	0.492814
H	1.249585	-1.393810	1.957627
H	2.667717	-3.759710	1.732119
H	3.595585	1.515810	-1.761963
H	3.512257	2.435856	-0.256262
H	2.140954	1.006621	1.642475
H	5.609921	-0.897258	-1.224109
H	6.150728	-3.280008	-0.787126
H	4.703122	-4.661149	0.657945
H	4.947068	1.452533	-0.635366
N	-0.547363	2.039664	1.738912
C	-2.135124	-1.349285	-1.397643
O	-1.639880	-2.177932	-2.161835
C	-1.379458	-0.086422	-0.968517
C	-0.371422	4.277740	0.603476
C	-3.952377	-0.485322	0.086085
C	-5.050285	-1.300084	0.784206
C	-5.526611	-2.256004	-0.323898
C	-4.241751	-2.618995	-1.087857
C	-2.888918	0.091466	1.018151
C	0.148331	-0.243963	-0.980420
C	0.623207	0.722042	0.122290
C	-0.505346	0.688709	1.210097
C	-0.149918	2.905206	0.714133
C	0.558144	2.196241	-0.274011
C	0.995296	2.853726	-1.420334
C	0.772836	4.230135	-1.548259
C	0.106596	4.930086	-0.536809
N	-1.678199	0.268238	0.429766
N	-3.371937	-1.451294	-0.866898

O	-3.106889	0.385451	2.193067
H	-1.377775	2.262593	2.277487
H	-1.681928	0.735331	-1.633339
H	-0.917946	4.818523	1.370274
H	-4.400640	0.358171	-0.463149
H	-5.844392	-0.662356	1.177857
H	-4.615570	-1.855097	1.622223
H	-6.226196	-1.739943	-0.990753
H	-6.032391	-3.140595	0.071087
H	-4.402066	-2.777387	-2.157969
H	-3.756871	-3.515825	-0.684401
H	0.571278	-0.005307	-1.957886
H	0.410389	-1.278995	-0.745058
H	-0.367159	-0.014679	2.035004
H	1.487398	2.312693	-2.223039
H	1.109249	4.750536	-2.439409
H	-0.063710	5.997519	-0.645747

Figure 11D Cation C3 TS

1 1

N	1.502823	-2.495214	1.567613
C	3.068634	-3.503374	-0.146769
C	2.707532	0.904036	2.192691
C	2.222280	-0.346666	1.511318
C	1.341861	-1.280837	2.112585
C	2.542659	-2.472284	0.627468
C	3.039807	-1.150849	0.597189
C	4.144184	-0.859441	-0.211850
C	4.689199	-1.883313	-0.987658
C	4.154196	-3.183201	-0.961960
H	0.944719	-3.308828	1.799336
H	2.662955	-4.509379	-0.111606
H	3.020163	1.657160	1.462723
H	1.939059	1.344219	2.834156
H	0.610398	-1.118461	2.892657
H	4.576110	0.136074	-0.230072
H	5.547870	-1.675543	-1.618789
H	4.600793	-3.956820	-1.578742
H	3.577475	0.671487	2.817738
N	-0.204073	2.508775	1.000737
C	-2.358858	-1.329471	-1.080285
O	-2.016551	-2.455754	-1.439328
C	-1.357661	-0.170491	-0.984121
C	1.219011	4.097056	-0.298961
C	-4.016307	0.346984	-0.250625
C	-5.336727	0.073783	0.483187
C	-5.939725	-1.095504	-0.315749
C	-4.725739	-1.959466	-0.694398
C	-2.920175	0.973751	0.609427
C	0.100312	-0.630703	-0.740406
C	0.644988	0.507298	0.086560
C	-0.487154	1.087385	0.957775
C	0.765579	2.830294	0.100673
C	1.308391	1.640656	-0.482282
C	2.279113	1.735060	-1.503687

C	2.718834	2.986690	-1.896098
C	2.193555	4.151028	-1.286227
N	-1.660614	0.695274	0.174425
N	-3.618441	-0.988527	-0.738477
O	-3.138966	1.674139	1.593820
H	-0.841471	3.160367	1.436087
H	-1.412284	0.414715	-1.912563
H	0.809820	5.000948	0.139923
H	-4.189386	1.020985	-1.104638
H	-5.978187	0.956950	0.510131
H	-5.125756	-0.222552	1.515995
H	-6.429764	-0.720306	-1.220909
H	-6.680648	-1.658886	0.256790
H	-4.830470	-2.458985	-1.661372
H	-4.508813	-2.725696	0.059239
H	0.642069	-0.767069	-1.676528
H	0.085056	-1.586983	-0.213586
H	-0.587057	0.703866	1.973944
H	2.669789	0.837138	-1.970413
H	3.463090	3.083547	-2.679336
H	2.554010	5.122288	-1.612959

Figure 11D Cation C3 Product

1	1		
N	2.179513	-2.543992	1.473199
C	4.140154	-3.043660	-0.036436
C	2.470277	0.742183	2.181264
C	1.939014	-0.265376	1.120859
C	1.478722	-1.510343	1.825871
C	3.184610	-2.209827	0.526538
C	3.086601	-0.832676	0.287164
C	4.043078	-0.238789	-0.530320
C	5.020347	-1.052677	-1.118891
C	5.064564	-2.432959	-0.886717
H	2.035935	-3.482754	1.842409
H	4.175552	-4.106343	0.178381
H	2.852917	1.623539	1.660691
H	1.679053	1.060250	2.862449
H	0.678934	-1.602073	2.550422
H	4.047535	0.829844	-0.707406
H	5.765866	-0.598673	-1.764054
H	5.834689	-3.034672	-1.357836
H	3.285869	0.297531	2.757521
N	-0.302737	2.197058	1.410000
C	-2.307586	-1.351369	-1.230663
O	-1.946534	-2.382760	-1.798233
C	-1.329188	-0.217033	-0.904300
C	0.509883	4.042366	-0.090040
C	-4.002037	0.102914	-0.107344
C	-5.299059	-0.345969	0.580704
C	-5.888891	-1.354118	-0.421414
C	-4.661092	-2.090354	-0.984429
C	-2.915527	0.607572	0.839979
C	0.118571	-0.682850	-0.716630
C	0.723236	0.339994	0.275239

C	-0.477606	0.770154	1.195545
C	0.400588	2.712317	0.317260
C	1.049408	1.678814	-0.383868
C	1.772403	1.969987	-1.538036
C	1.887167	3.300735	-1.959017
C	1.267412	4.321815	-1.231271
N	-1.651905	0.404801	0.388939
N	-3.575770	-1.104728	-0.840756
O	-3.161080	1.166434	1.908748
H	-1.129655	2.684035	1.739100
H	-1.388497	0.531353	-1.707864
H	0.005911	4.835266	0.454547
H	-4.216793	0.915690	-0.819594
H	-5.962178	0.495571	0.790865
H	-5.058363	-0.832676	1.531869
H	-6.409834	-0.823867	-1.226330
H	-6.601510	-2.040961	0.041965
H	-4.772877	-2.383446	-2.032107
H	-4.414323	-2.990266	-0.408660
H	0.662022	-0.717100	-1.662036
H	0.112671	-1.697521	-0.305162
H	-0.549477	0.264597	2.161421
H	2.227703	1.178907	-2.125993
H	2.447715	3.535982	-2.858273
H	1.358038	5.351296	-1.566411

Figure 11D Cation C4 TS

1	1		
N	0.892592	-4.090827	0.529078
C	1.777601	-3.249487	-1.664431
C	2.018955	-1.670858	3.109006
C	1.638789	-2.416412	1.862048
C	0.977610	-3.642429	1.812839
C	1.505138	-3.178773	-0.305179
C	1.961217	-2.102077	0.513988
C	2.599192	-0.983953	-0.116549
C	2.961887	-1.132875	-1.495952
C	2.532515	-2.212026	-2.250864
H	0.475488	-4.966373	0.243408
H	1.445933	-4.093877	-2.261628
H	3.098008	-1.743778	3.294257
H	1.778683	-0.603335	3.048373
H	0.578811	-4.230334	2.628357
H	3.183952	-0.310370	0.500948
H	3.548987	-0.349503	-1.964127
H	2.780881	-2.270329	-3.305071
H	1.503908	-2.082405	3.981687
N	0.877277	1.634879	1.617970
C	-2.382668	-0.022189	-1.613931
O	-2.369497	-0.762710	-2.596614
C	-1.138988	0.759152	-1.172129
C	2.252593	3.653000	1.067768
C	-3.466295	1.038283	0.374059
C	-4.680223	0.525629	1.160966
C	-5.652649	0.091806	0.049634

C	-4.743264	-0.512439	-1.033525
C	-2.136050	0.951946	1.120530
C	0.194203	0.087720	-1.573359
C	1.106517	0.527238	-0.451602
C	0.278622	0.566843	0.843150
C	1.664338	2.408851	0.802674
C	1.839407	1.771535	-0.461240
C	2.601426	2.395657	-1.466521
C	3.179385	3.627205	-1.203173
C	3.004446	4.240982	0.057713
N	-1.056540	0.847374	0.299980
N	-3.462614	0.187713	-0.832449
O	-2.036173	0.985581	2.344621
H	0.386834	1.992808	2.427448
H	-1.192480	1.768660	-1.603507
H	2.116861	4.142278	2.026787
H	-3.617183	2.091681	0.089283
H	-5.090898	1.291741	1.821788
H	-4.381381	-0.328306	1.777853
H	-6.181823	0.964177	-0.349233
H	-6.401637	-0.622250	0.400857
H	-5.109518	-0.348997	-2.050759
H	-4.594019	-1.590177	-0.898215
H	0.536205	0.414023	-2.555652
H	0.061352	-0.997003	-1.598591
H	0.239111	-0.356026	1.423676
H	2.728410	1.922409	-2.435738
H	3.767317	4.127582	-1.965340
H	3.466323	5.206774	0.241523

Figure 11D Cation C4 Product

1 1

N	2.499813	-3.824961	0.324475
C	3.240414	-2.474241	-1.628323
C	1.887050	-1.440664	3.087033
C	2.117435	-2.110956	1.761675
C	2.179529	-3.516193	1.589501
C	2.690420	-2.646430	-0.383976
C	2.400054	-1.561244	0.508659
C	2.491217	-0.157926	-0.000060
C	3.235531	-0.069695	-1.295293
C	3.540679	-1.145604	-2.069769
H	2.642710	-4.761672	-0.032626
H	3.494956	-3.325280	-2.253717
H	0.883857	-1.646843	3.477791
H	2.604844	-1.809441	3.827986
H	2.026842	-4.290485	2.329839
H	2.978562	0.478424	0.749469
H	3.472110	0.927466	-1.649524
H	4.029522	-1.013981	-3.028695
H	2.003283	-0.356717	3.016504
N	0.418483	1.663886	1.763658
C	-2.251115	-0.616107	-1.626793
O	-2.046003	-1.355735	-2.589684
C	-1.197493	0.376585	-1.121254

C	0.930396	4.033836	1.089736
C	-3.629823	0.262390	0.261565
C	-4.788755	-0.440914	0.980792
C	-5.597000	-1.049603	-0.179118
C	-4.526932	-1.502278	-1.187023
C	-2.355250	0.412965	1.091204
C	0.248118	-0.042681	-1.419201
C	1.057218	0.571821	-0.260453
C	0.109213	0.485756	0.974583
C	0.850327	2.657944	0.877039
C	1.246130	2.082563	-0.345845
C	1.703295	2.894887	-1.380464
C	1.783943	4.278602	-1.180719
C	1.406325	4.833864	0.046531
N	-1.224347	0.485088	0.346354
N	-3.402703	-0.588546	-0.923013
O	-2.352352	0.477456	2.320872
H	-0.273033	1.900120	2.467776
H	-1.408249	1.357324	-1.571951
H	0.619382	4.471833	2.033510
H	-3.938922	1.270974	-0.056546
H	-5.367264	0.250911	1.596478
H	-4.390612	-1.223584	1.635052
H	-6.239261	-0.286367	-0.632418
H	-6.235637	-1.877045	0.140149
H	-4.847910	-1.419442	-2.229189
H	-4.205314	-2.536578	-1.015837
H	0.575917	0.311442	-2.397865
H	0.319473	-1.134482	-1.417442
H	0.200347	-0.412917	1.579446
H	1.973907	2.475251	-2.345928
H	2.132890	4.920296	-1.983649
H	1.470196	5.908690	0.191401

Figure 11D Cation C5 TS

1 1

N	-5.209632	0.262283	-0.586504
C	-3.203395	0.840413	-1.976389
C	-4.627184	-3.106813	0.887129
C	-4.614109	-1.782017	0.187942
C	-5.597134	-0.833208	0.186381
C	-3.976616	0.047186	-1.101810
C	-3.546267	-1.243534	-0.632385
C	-2.301151	-1.707898	-1.016250
C	-1.454746	-0.860671	-1.786322
C	-1.968702	0.359614	-2.342749
H	-5.777610	1.083321	-0.746843
H	-3.585522	1.780169	-2.362403
H	-3.799807	-3.193684	1.602521
H	-5.561637	-3.249195	1.437454
H	-6.561623	-0.834086	0.674360
H	-1.941769	-2.682704	-0.699706
H	-0.577471	-1.302144	-2.248819
H	-1.352023	0.925162	-3.032984
H	-4.526682	-3.936026	0.176185

N	0.212167	2.155357	-0.599177
C	3.064318	-1.597984	0.666610
O	2.941516	-2.816807	0.780964
C	1.864309	-0.652221	0.798628
C	-1.371289	3.180726	1.038707
C	4.373960	0.491170	0.248974
C	5.701164	0.624974	-0.510089
C	6.525615	-0.557286	0.029508
C	5.497739	-1.688511	0.199805
C	3.162285	1.087500	-0.463797
C	0.515217	-1.300054	0.400845
C	-0.245062	-0.095669	-0.107465
C	0.745076	0.829190	-0.832893
C	-0.741248	2.118853	0.373120
C	-1.049099	0.759509	0.704185
C	-1.973371	0.475660	1.734178
C	-2.581684	1.527568	2.395690
C	-2.282206	2.863342	2.037875
N	1.982266	0.503264	-0.116804
N	4.232324	-0.967634	0.425187
O	3.227386	2.015536	-1.264898
H	0.721965	2.979367	-0.886630
H	1.813658	-0.299732	1.838190
H	-1.139534	4.211872	0.793522
H	4.449869	0.981310	1.232721
H	6.171736	1.595531	-0.340323
H	5.519506	0.519766	-1.584766
H	6.963572	-0.299222	1.000007
H	7.340634	-0.842364	-0.640232
H	5.713278	-2.349326	1.043872
H	5.407519	-2.308657	-0.699634
H	0.031034	-1.787954	1.247248
H	0.690544	-2.048660	-0.375847
H	0.887564	0.661779	-1.902258
H	-2.193115	-0.551810	2.003906
H	-3.290257	1.334059	3.193926
H	-2.773446	3.671477	2.572534

Figure 11D Cation C5 Product

1 1

N	-5.647849	-0.163982	-1.064375
C	-3.500934	0.740552	-1.956776
C	-4.894590	-3.074322	1.141437
C	-4.942774	-1.893042	0.225743
C	-6.037991	-1.219164	-0.210976
C	-4.324256	-0.131559	-1.192630
C	-3.798900	-1.219538	-0.384328
C	-2.456582	-1.414697	-0.332673
C	-1.518574	-0.539144	-1.089870
C	-2.160947	0.538712	-1.905149
H	-6.294610	0.473339	-1.515326
H	-3.939724	1.530300	-2.557389
H	-4.317288	-2.850763	2.046276
H	-5.901210	-3.371654	1.446142
H	-7.086674	-1.376641	-0.005002

H	-2.035003	-2.228748	0.249905
H	-1.003861	-1.209824	-1.804330
H	-1.499965	1.188129	-2.468717
H	-4.418714	-3.933438	0.654255
N	0.411151	2.171135	-0.902376
C	2.930070	-1.608562	0.817419
O	2.713867	-2.766109	1.176857
C	1.821497	-0.550925	0.777156
C	-0.570374	3.548170	0.963059
C	4.396394	0.225560	-0.041922
C	5.677309	0.072355	-0.874022
C	6.431205	-1.050119	-0.139169
C	5.322973	-2.015876	0.315540
C	3.204720	0.803108	-0.802065
C	0.421922	-1.128088	0.538595
C	-0.343655	0.013358	-0.170655
C	0.746260	0.759845	-1.015439
C	-0.300573	2.356339	0.289966
C	-0.805694	1.130001	0.756669
C	-1.594022	1.084204	1.900962
C	-1.873019	2.274665	2.585310
C	-1.361803	3.488679	2.114921
N	1.999859	0.370399	-0.353815
N	4.138339	-1.147837	0.431055
O	3.324239	1.606783	-1.726776
H	1.163233	2.810349	-1.137089
H	1.846015	0.006585	1.725035
H	-0.173798	4.493987	0.605835
H	4.585667	0.887280	0.818737
H	6.239544	1.006379	-0.934107
H	5.416362	-0.232292	-1.893098
H	6.955170	-0.643242	0.732794
H	7.171380	-1.545374	-0.772529
H	5.535184	-2.500659	1.272690
H	5.126546	-2.802344	-0.422599
H	-0.048612	-1.432863	1.475099
H	0.499505	-2.011127	-0.104720
H	0.800100	0.467323	-2.067675
H	-1.982723	0.140223	2.275221
H	-2.480487	2.252143	3.484775
H	-1.577357	4.406476	2.655127

Figure 11D Cation C6 TS

1 1

N	1.379894	-3.637013	-1.373907
C	1.821328	-1.235931	-1.944873
C	3.139838	-4.283304	1.837828
C	2.536687	-3.741532	0.576205
C	1.760788	-4.442501	-0.338054
C	1.898664	-2.372763	-1.170144
C	2.642216	-2.421301	0.061929
C	3.320239	-1.254113	0.498758
C	3.220312	-0.104315	-0.246637
C	2.415827	-0.043266	-1.442852
H	0.812567	-3.924355	-2.159092

H	1.316476	-1.239775	-2.905585
H	2.770154	-3.748907	2.721254
H	2.898096	-5.342637	1.963479
H	1.457412	-5.480661	-0.313096
H	3.913588	-1.274587	1.407704
H	3.732973	0.796623	0.074403
H	2.628675	0.743028	-2.160472
H	4.232254	-4.187711	1.833871
N	0.856189	1.366652	1.603421
C	-2.840085	0.402586	-1.391288
O	-3.000248	0.208750	-2.595803
C	-1.621545	1.162492	-0.851927
C	1.912636	3.628959	1.704735
C	-3.479274	0.169408	1.016139
C	-4.358255	-0.921963	1.642260
C	-5.533341	-1.025757	0.653863
C	-4.885486	-0.829530	-0.727306
C	-2.000253	0.091164	1.387074
C	-0.370407	1.043793	-1.755959
C	0.741080	1.168523	-0.732113
C	0.284477	0.518083	0.577509
C	1.381873	2.497805	1.063005
C	1.317859	2.428317	-0.364505
C	1.768525	3.510759	-1.147381
C	2.283517	4.625237	-0.510648
C	2.355020	4.671782	0.903838
N	-1.170401	0.601116	0.437855
N	-3.691223	-0.017702	-0.432439
O	-1.587841	-0.370302	2.447562
H	0.725152	1.182685	2.587708
H	-1.895665	2.219484	-0.727410
H	1.964765	3.685832	2.786908
H	-3.839473	1.164888	1.321077
H	-4.666397	-0.664652	2.657624
H	-3.797401	-1.861530	1.686459
H	-6.257926	-0.226641	0.845105
H	-6.061040	-1.979895	0.726558
H	-5.531074	-0.310172	-1.440897
H	-4.576453	-1.778114	-1.181795
H	-0.336606	1.825350	-2.515943
H	-0.388192	0.075090	-2.254470
H	0.586660	-0.521057	0.734806
H	1.718772	3.463195	-2.231372
H	2.637675	5.470995	-1.090336
H	2.765062	5.558780	1.378192

Figure 11D Cation C6 Product

1 1

N	3.408693	-3.005977	-0.939452
C	2.053440	-0.970920	-1.398005
C	6.033981	-1.979417	1.484378
C	4.882407	-2.082431	0.529516
C	4.474648	-3.245005	-0.154230
C	3.052001	-1.664323	-0.808390
C	3.996354	-1.078262	0.124837

C	3.878330	0.310349	0.440239
C	2.882710	1.037455	-0.125871
C	1.887275	0.481015	-1.098684
H	2.941379	-3.690966	-1.519809
H	1.389910	-1.447578	-2.110866
H	5.697763	-1.661297	2.477523
H	6.538637	-2.942927	1.593274
H	4.911716	-4.234404	-0.106518
H	4.578348	0.769932	1.130242
H	2.785547	2.091581	0.107871
H	2.065656	1.000661	-2.060092
H	6.773451	-1.249310	1.136897
N	0.177992	1.414163	1.598650
C	-2.947730	-0.723520	-1.426272
O	-2.970913	-1.104816	-2.596910
C	-1.961199	0.341614	-0.934745
C	-0.004084	3.919403	1.407065
C	-3.708189	-0.778640	0.953976
C	-4.381505	-1.948959	1.685247
C	-5.431333	-2.432229	0.668820
C	-4.738131	-2.273312	-0.695260
C	-2.278180	-0.480786	1.401304
C	-0.662961	0.405913	-1.748730
C	0.391645	0.900705	-0.731137
C	-0.069004	0.335500	0.653666
C	0.125706	2.624596	0.902021
C	0.291895	2.399057	-0.476163
C	0.347437	3.467312	-1.364956
C	0.220086	4.771137	-0.869504
C	0.044457	4.984904	0.502525
N	-1.491079	0.036762	0.425616
N	-3.769180	-1.189200	-0.461872
O	-1.880476	-0.675783	2.549978
H	-0.295920	1.327302	2.491272
H	-2.470952	1.315998	-0.947957
H	-0.139409	4.094207	2.470280
H	-4.294332	0.142794	1.100847
H	-4.811618	-1.640823	2.640351
H	-3.639679	-2.729683	1.884632
H	-6.320705	-1.793942	0.714074
H	-5.749956	-3.462009	0.848926
H	-5.424521	-2.003515	-1.502847
H	-4.203194	-3.180952	-0.999167
H	-0.750634	1.075766	-2.606406
H	-0.445116	-0.592752	-2.132576
H	0.438414	-0.574915	0.980758
H	0.477162	3.299686	-2.431696
H	0.252632	5.615199	-1.551273
H	-0.058778	5.999543	0.877244

Figure 11D Cation C7 TS

1 1

N	2.280527	-2.430600	-0.931170
C	1.526461	-0.246925	-1.968903
C	5.685665	-1.855176	0.455900

C	4.328822	-1.825683	-0.178965
C	3.425651	-2.851075	-0.256926
C	2.424075	-1.133962	-1.302518
C	3.711355	-0.709713	-0.860570
C	4.146175	0.568985	-1.209667
C	3.345302	1.396359	-2.027616
C	2.092932	0.981654	-2.441052
H	1.502917	-3.033486	-1.163716
H	0.662988	-0.656668	-2.484142
H	5.766952	-1.118077	1.264067
H	5.896967	-2.841173	0.879499
H	3.497545	-3.868199	0.101155
H	5.124753	0.919562	-0.892927
H	3.727998	2.362159	-2.340229
H	1.487444	1.621811	-3.074637
H	6.474117	-1.626574	-0.271407
N	0.457191	-0.677336	1.534374
C	-3.333659	1.031083	-0.999722
O	-3.515206	1.630097	-2.058927
C	-1.992434	1.096934	-0.259325
C	1.807259	0.915391	2.905820
C	-4.038186	-0.481810	0.864416
C	-5.127443	-1.562265	0.819308
C	-6.287508	-0.847164	0.104583
C	-5.596595	0.021019	-0.960840
C	-2.609768	-1.012227	0.954397
C	-0.781985	1.323424	-1.193798
C	0.326495	0.625171	-0.425850
C	-0.279496	-0.597365	0.291387
C	1.153196	0.479215	1.746535
C	1.117987	1.293231	0.572653
C	1.722880	2.567453	0.582827
C	2.355196	3.002700	1.736577
C	2.399206	2.173307	2.878585
N	-1.679922	-0.182304	0.408211
N	-4.263954	0.273090	-0.383489
O	-2.310573	-2.079180	1.484118
H	0.171910	-1.319850	2.260588
H	-2.045275	1.904235	0.484451
H	1.830820	0.300537	3.799432
H	-4.196449	0.176254	1.733695
H	-5.387168	-1.921897	1.816952
H	-4.771336	-2.415537	0.232579
H	-6.830416	-0.211149	0.812316
H	-7.003803	-1.544135	-0.337192
H	-6.111736	0.966069	-1.153748
H	-5.484594	-0.502820	-1.917222
H	-0.582640	2.383334	-1.353907
H	-0.985565	0.861384	-2.163017
H	-0.231335	-1.554047	-0.233335
H	1.682849	3.199503	-0.297894
H	2.820976	3.981943	1.766712
H	2.901917	2.534176	3.771489

1	1		
N	2.749700	-0.468795	-1.547095
C	1.592525	1.327498	-0.154347
C	6.406364	0.244425	-1.669374
C	4.924449	0.167590	-1.472298
C	4.060745	-0.757167	-1.974022
C	2.743545	0.614003	-0.780510
C	4.104266	1.068322	-0.678683
C	4.397929	2.116414	0.162444
C	3.363176	2.772813	0.907461
C	2.064278	2.392673	0.793658
H	1.925055	-1.077314	-1.676379
H	1.151343	1.931965	-0.975306
H	6.939175	0.178365	-0.713454
H	6.755324	-0.572298	-2.306646
H	4.239617	-1.619020	-2.600147
H	5.425334	2.447914	0.287924
H	3.635246	3.588748	1.568136
H	1.300348	2.931396	1.343285
H	6.697293	1.190156	-2.141385
N	0.256657	-1.647046	-0.822564
C	-3.257592	1.263236	0.855727
O	-3.353866	2.366216	1.393103
C	-1.965406	0.440536	0.916788
C	1.070996	-3.166938	1.025488
C	-4.130186	-0.641440	-0.509682
C	-5.252719	-0.596298	-1.556262
C	-6.339607	0.238340	-0.855758
C	-5.552727	1.308992	-0.080875
C	-2.730289	-0.856891	-1.078391
C	-0.696574	1.287321	1.054336
C	0.406003	0.437873	0.377242
C	-0.346400	-0.311137	-0.778093
C	0.720655	-1.931091	0.487494
C	0.880510	-0.743772	1.216879
C	1.407970	-0.776876	2.503855
C	1.764632	-2.012301	3.057834
C	1.592613	-3.190423	2.323442
N	-1.741598	-0.293066	-0.337691
N	-4.252686	0.662711	0.169464
O	-2.508360	-1.500115	-2.103882
H	-0.334473	-2.338269	-1.278023
H	-2.046197	-0.265894	1.755708
H	0.941533	-4.083435	0.457590
H	-4.319547	-1.455875	0.208030
H	-5.587558	-1.596251	-1.839229
H	-4.890930	-0.091867	-2.458538
H	-6.904904	-0.389756	-0.158342
H	-7.049968	0.680701	-1.558523
H	-6.023143	1.595817	0.863712
H	-5.398133	2.220285	-0.670389
H	-0.473009	1.509723	2.099212
H	-0.839783	2.237928	0.529832
H	-0.274273	0.160374	-1.762371
H	1.533813	0.136146	3.080211

Figure 11D Cation C7 Product

H	2.169476	-2.055530	4.064145
H	1.866728	-4.143663	2.766266

Figure 12B Radical C2 TS

O 2

N	4.285907	0.772804	-0.045631
C	4.904886	-1.463709	0.939753
C	1.469529	0.110404	-2.380628
C	2.550238	0.084548	-1.350602
C	3.239943	1.226885	-0.829705
C	4.163016	-0.595537	0.144350
C	3.086290	-1.050405	-0.677592
C	2.757418	-2.423324	-0.682793
C	3.500216	-3.291740	0.108649
C	4.561557	-2.818625	0.906902
H	4.837990	1.381602	0.541294
H	5.720551	-1.105536	1.561000
H	0.714476	-0.658991	-2.184188
H	0.975050	1.085893	-2.410189
H	3.338919	2.175989	-1.335927
H	1.917062	-2.782318	-1.269093
H	3.258450	-4.350618	0.119602
H	5.123970	-3.520648	1.516120
H	1.875202	-0.083637	-3.384559
N	1.900103	2.052854	0.488820
C	-3.055961	-0.224053	1.311536
O	-3.636908	0.741877	1.813652
C	-1.672326	-0.696355	1.799011
C	0.794488	3.733603	-1.021766
C	-2.962811	-2.173453	-0.248316
C	-3.668698	-2.312616	-1.602416
C	-5.092964	-1.814363	-1.296583
C	-4.887071	-0.660721	-0.297782
C	-1.446904	-2.022192	-0.316033
C	-0.847828	0.444949	2.458193
C	-0.001896	1.258278	1.520533
C	1.367320	1.151193	1.389046
C	0.807731	2.724924	-0.050634
C	-0.398600	2.294215	0.583206
C	-1.612984	2.910760	0.253512
C	-1.617812	3.910544	-0.722115
C	-0.429857	4.314052	-1.356968
N	-0.915689	-1.334846	0.720086
N	-3.596364	-0.978734	0.333756
O	-0.782020	-2.505692	-1.234822
H	-1.879921	-1.437204	2.587625
H	1.714280	4.064125	-1.497954
H	-3.179875	-3.053384	0.379399
H	-3.639213	-3.337774	-1.977676
H	-3.175517	-1.668264	-2.337771
H	-5.678547	-2.614449	-0.829816
H	-5.628260	-1.489480	-2.192531
H	-5.676873	-0.594657	0.456434
H	-4.816637	0.314138	-0.794203
H	-0.192695	-0.012638	3.207540

H	-1.570835	1.065841	2.996706
H	2.026677	0.485201	1.935393
H	-2.533542	2.614188	0.747398
H	-2.555362	4.390831	-0.990725
H	-0.463113	5.096279	-2.110883
H	0.079974	-1.142087	0.672604

Figure 12B Radical C2 Product

O 2

N	3.844035	1.208031	0.392991
C	5.979825	0.026852	0.966909
C	2.066650	-1.142762	-1.962229
C	3.000126	-0.435724	-1.039688
C	2.768026	0.991404	-0.574977
C	4.750605	0.158412	0.336072
C	4.213103	-0.884897	-0.491898
C	4.940639	-2.091698	-0.628897
C	6.169757	-2.220855	0.011042
C	6.688163	-1.174479	0.794231
H	4.172928	2.153139	0.544434
H	6.381942	0.827225	1.581875
H	1.117781	-1.413151	-1.474894
H	1.803963	-0.516444	-2.826407
H	2.842330	1.695276	-1.417127
H	4.548778	-2.899226	-1.241099
H	6.739514	-3.139437	-0.098750
H	7.652607	-1.294885	1.279722
H	2.512054	-2.067489	-2.342193
N	1.444723	1.226250	0.007224
C	-3.533280	-0.129704	1.363734
O	-3.985056	0.915990	1.839997
C	-2.247140	-0.766567	1.917209
C	0.510642	3.056465	-1.474559
C	-3.702065	-2.090105	-0.187034
C	-4.305053	-2.080432	-1.596318
C	-5.644268	-1.351322	-1.382075
C	-5.332222	-0.274670	-0.324546
C	-2.190230	-2.251469	-0.120179
C	-1.233719	0.305783	2.411996
C	-0.362705	0.908528	1.344848
C	0.925800	0.515953	1.074252
C	0.475985	2.114281	-0.437185
C	-0.676918	1.941487	0.383658
C	-1.807780	2.746514	0.150780
C	-1.771287	3.682244	-0.876068
C	-0.623890	3.833911	-1.681141
N	-1.611115	-1.664085	0.954180
N	-4.142951	-0.800601	0.366916
O	-1.562198	-2.898852	-0.956976
H	-2.562383	-1.338462	2.804027
H	1.387585	3.186355	-2.101654
H	-4.143306	-2.914172	0.397482
H	-4.419285	-3.088082	-2.001271
H	-3.651645	-1.515131	-2.269430
H	-6.393717	-2.050965	-0.995428

H	-6.040334	-0.915881	-2.303065
H	-6.151085	-0.115730	0.383671
H	-5.086018	0.694771	-0.772079
H	-0.592224	-0.171965	3.161121
H	-1.823171	1.067385	2.930569
H	1.543313	-0.213996	1.581086
H	-2.695993	2.624565	0.762416
H	-2.639825	4.307915	-1.064014
H	-0.622314	4.572646	-2.478131
H	-0.598896	-1.721430	0.978165

Figure 12B Radical C3 TS

O 2

N	-1.367504	-2.194245	-1.417445
C	-0.989037	-2.879502	0.973255
C	-4.437493	-0.173647	-1.409041
C	-3.024797	-0.611376	-1.096303
C	-2.266328	-1.386171	-2.056654
C	-1.600025	-2.150108	-0.045200
C	-2.676354	-1.267717	0.194065
C	-3.199069	-1.167409	1.483573
C	-2.610847	-1.907692	2.514168
C	-1.508852	-2.738778	2.262411
H	-0.493810	-2.539001	-1.813588
H	-0.157926	-3.545046	0.763001
H	-4.480924	0.313878	-2.387122
H	-2.268920	-1.295329	-3.133111
H	-4.053648	-0.531918	1.692058
H	-3.011317	-1.837459	3.521220
H	-1.062355	-3.298924	3.079357
H	-5.108143	-1.040940	-1.421154
N	-2.128709	1.056529	-1.067112
C	2.982124	1.195665	-0.255042
O	3.150924	2.296986	0.272868
C	2.426933	1.084905	-1.682423
C	-2.623481	2.069911	1.195555
C	3.209738	-1.303534	-0.236116
C	3.024921	-2.207772	0.987990
C	3.907436	-1.516631	2.044072
C	3.737519	-0.009930	1.763954
C	2.131030	-1.394779	-1.302253
C	1.335834	2.160024	-1.956246
C	0.001701	1.892822	-1.317166
C	-1.008121	1.139953	-1.869889
C	-1.822735	1.775768	0.083028
C	-0.504623	2.323189	-0.033321
C	-0.000810	3.146953	0.986492
C	-0.796395	3.410324	2.098568
C	-2.097520	2.880335	2.199075
N	1.906496	-0.252401	-1.982111
N	3.294394	0.036407	0.359950
O	1.553682	-2.460824	-1.552065
H	3.271986	1.302780	-2.353019
H	-3.639157	1.695538	1.269980
H	4.163484	-1.550864	-0.731696

H	3.317304	-3.240285	0.785432
H	1.972841	-2.200978	1.291750
H	4.954342	-1.809143	1.906416
H	3.621919	-1.776101	3.066655
H	4.663649	0.558148	1.895163
H	2.970837	0.453162	2.394533
H	1.215897	2.220678	-3.045393
H	1.757207	3.114781	-1.630032
H	-1.011410	0.662208	-2.841853
H	1.000340	3.560597	0.908708
H	-0.414439	4.043563	2.895535
H	-2.706362	3.115062	3.068594
H	1.190629	-0.312012	-2.697214
H	-4.806097	0.535473	-0.662920

Figure 12B Radical C3 Product

O 2

N	4.312527	1.164820	-1.750030
C	4.542382	2.792893	0.148514
C	4.272968	-1.869107	-0.314840
C	3.342897	-0.665966	-0.606490
C	3.715606	-0.069375	-1.953026
C	4.183567	1.574510	-0.430173
C	3.604522	0.531754	0.320371
C	3.382529	0.712228	1.680089
C	3.737655	1.929878	2.279454
C	4.311985	2.953330	1.517530
H	4.609874	1.772308	-2.500012
H	4.982995	3.588816	-0.445067
H	4.087569	-2.668154	-1.040586
H	3.992059	-0.661481	-2.817333
H	2.925877	-0.068848	2.279010
H	3.561862	2.078037	3.340732
H	4.581626	3.892306	1.993452
H	5.312712	-1.543372	-0.413251
N	1.909026	-1.103912	-0.600893
C	-3.580380	-0.585581	-0.867267
O	-3.876331	-1.783690	-0.851375
C	-2.487219	-0.012732	-1.790841
C	1.621370	-2.396346	1.585685
C	-3.936443	1.785607	-0.173889
C	-4.518354	2.297934	1.148973
C	-5.732023	1.376386	1.367507
C	-5.263573	0.002504	0.855260
C	-2.448482	2.055463	-0.380635
C	-1.441295	-1.073918	-2.227519
C	-0.248495	-1.251616	-1.328071
C	1.006845	-0.761254	-1.593018
C	1.214377	-1.830056	0.365258
C	-0.141860	-1.947265	-0.071061
C	-1.067940	-2.663125	0.710433
C	-0.650200	-3.231219	1.906279
C	0.682336	-3.091263	2.340230
N	-1.839889	1.149772	-1.184398
N	-4.217062	0.340336	-0.122523

O	-1.874691	3.016219	0.127380
H	-3.019281	0.300436	-2.704074
H	2.635330	-2.304512	1.953866
H	-4.477184	2.238695	-1.021203
H	-4.781510	3.356652	1.098508
H	-3.777790	2.171160	1.945698
H	-6.581887	1.727721	0.771497
H	-6.051070	1.337284	2.412298
H	-6.059219	-0.578240	0.379285
H	-4.830885	-0.613805	1.652177
H	-1.081470	-0.788848	-3.222082
H	-1.993269	-2.011971	-2.343116
H	1.353218	-0.199463	-2.448999
H	-2.096900	-2.755239	0.376850
H	-1.357434	-3.784974	2.518139
H	0.989424	-3.533306	3.284327
H	-0.832258	1.226309	-1.275306
H	4.146923	-2.276845	0.689539

Figure 12B Radical C4 TS

O 2

N	4.667825	-2.445472	0.666480
C	2.510785	-2.607687	-0.629545
C	5.838701	1.059626	0.315739
C	5.151211	-0.272539	0.286677
C	5.574211	-1.438945	0.902173
C	3.640375	-1.957338	-0.113353
C	3.924487	-0.593911	-0.367220
C	2.988180	0.192686	-1.126304
C	1.916536	-0.528038	-1.760699
C	1.657648	-1.861398	-1.464770
H	4.758690	-3.397934	0.988548
H	2.310627	-3.653187	-0.414748
H	5.179257	1.835282	0.723065
H	6.743096	1.025635	0.931393
H	6.459963	-1.622455	1.494680
H	3.350839	1.094784	-1.606459
H	1.248796	0.017521	-2.419827
H	0.776622	-2.340489	-1.881092
H	6.133009	1.385504	-0.690404
N	2.011978	1.289791	0.226097
C	-3.297860	0.201890	1.322863
O	-3.607835	1.293846	1.806634
C	-2.026045	-0.561626	1.742974
C	1.241373	3.154316	-1.283442
C	-3.753772	-1.782222	-0.121037
C	-4.587890	-1.830645	-1.406617
C	-5.836833	-1.010097	-1.036187
C	-5.297520	0.119500	-0.139765
C	-2.251249	-1.965704	-0.315441
C	-0.931699	0.367254	2.337892
C	0.030014	0.956845	1.346365
C	1.332070	0.540058	1.161819
C	1.073311	2.187611	-0.288031
C	-0.165707	2.046320	0.404955

C	-1.226791	2.913528	0.112320
C	-1.053609	3.874225	-0.886909
C	0.163073	3.990345	-1.580817
N	-1.500012	-1.362346	0.635679
N	-4.064230	-0.450390	0.425479
O	-1.787059	-2.618313	-1.250351
H	-2.347662	-1.232525	2.555940
H	2.186663	3.258655	-1.809853
H	-4.096956	-2.561475	0.579417
H	-4.815942	-2.854686	-1.709958
H	-4.030143	-1.353436	-2.219223
H	-6.541412	-1.631858	-0.472312
H	-6.362727	-0.621792	-1.912285
H	-5.987886	0.406794	0.658893
H	-5.052029	1.023147	-0.710022
H	-0.360437	-0.220160	3.064764
H	-1.465976	1.142846	2.895954
H	1.847984	-0.257606	1.684792
H	-2.166054	2.836112	0.651808
H	-1.871703	4.548122	-1.128492
H	0.270089	4.746879	-2.353846
H	-0.494468	-1.363339	0.491029

Figure 12B Radical C4 Product

O 2

N	-5.664623	-1.505061	-1.029016
C	-4.368672	-2.663947	0.790844
C	-4.419887	1.980691	-1.204769
C	-4.727947	0.539967	-0.915334
C	-5.680310	-0.238864	-1.561069
C	-4.712176	-1.572098	-0.033050
C	-4.112972	-0.302844	0.049099
C	-3.031184	-0.018188	1.054972
C	-2.730438	-1.231637	1.912520
C	-3.356860	-2.441867	1.760379
H	-6.267628	-2.263727	-1.311314
H	-4.852887	-3.629634	0.690682
H	-3.409096	2.105693	-1.612315
H	-5.126640	2.395317	-1.930903
H	-6.361902	0.021451	-2.358742
H	-3.345675	0.811811	1.705652
H	-1.956314	-1.103708	2.664113
H	-3.068601	-3.267153	2.407145
H	-4.474801	2.596057	-0.297900
N	-1.789741	0.484416	0.412421
C	3.393620	0.344507	-1.347710
O	3.465095	1.496649	-1.784438
C	2.231320	-0.602238	-1.704169
C	-1.223812	2.477230	1.864067
C	4.332610	-1.601017	-0.094206
C	5.275344	-1.562910	1.114369
C	6.320372	-0.511983	0.698067
C	5.511263	0.544794	-0.076421
C	2.914950	-2.080519	0.201039
C	0.933324	0.153318	-2.095743

C	0.014689	0.537153	-0.967951
C	-1.152935	-0.120099	-0.652716
C	-1.017638	1.556089	0.826795
C	0.124026	1.627022	-0.026285
C	1.056577	2.663538	0.166518
C	0.846140	3.580391	1.189606
C	-0.281156	3.485790	2.031692
N	1.978813	-1.561253	-0.629573
N	4.344965	-0.206656	-0.567627
O	2.663851	-2.878057	1.101978
H	2.565680	-1.141356	-2.605725
H	-2.085993	2.413384	2.521170
H	4.749977	-2.261047	-0.872583
H	5.706895	-2.542765	1.329361
H	4.719080	-1.236283	1.999369
H	7.068926	-0.966963	0.039579
H	6.847681	-0.078715	1.551943
H	6.062741	0.986029	-0.912011
H	5.169527	1.363459	0.567636
H	0.378782	-0.488271	-2.789357
H	1.255473	1.033307	-2.661079
H	-1.609187	-0.973697	-1.136602
H	1.930300	2.733343	-0.473805
H	1.561889	4.383038	1.347257
H	-0.417801	4.212953	2.827751
H	1.012613	-1.785057	-0.416345

Figure 12B Radical C5 TS

O 2

N	2.236957	-2.686931	-0.632466
C	1.662316	-0.537246	-1.806753
C	5.349938	-2.070473	1.316957
C	4.115946	-2.049460	0.466848
C	3.252491	-3.087456	0.228532
C	2.410568	-1.366402	-0.937084
C	3.581404	-0.909011	-0.254254
C	3.937526	0.431557	-0.348215
C	3.039670	1.346157	-1.018425
C	2.022659	0.780644	-1.898485
H	1.350145	-3.163662	-0.785830
H	0.843812	-0.948408	-2.389519
H	5.305035	-1.313997	2.111241
H	5.483653	-3.047084	1.793139
H	3.277292	-4.101529	0.603968
H	4.811525	0.825544	0.162060
H	3.469106	2.294703	-1.325653
H	1.481145	1.452229	-2.555576
H	6.253039	-1.860268	0.728982
N	1.960608	2.109903	0.357242
C	-2.974004	-0.093844	1.145800
O	-3.541887	0.951474	1.467915
C	-1.644284	-0.545738	1.777681
C	0.930305	3.987277	-0.977513
C	-2.883660	-2.268070	-0.080182
C	-3.515865	-2.602079	-1.437524

C	-4.929010	-2.004766	-1.309200
C	-4.724587	-0.710885	-0.499341
C	-1.361511	-2.200277	-0.072351
C	-0.815116	0.622665	2.374895
C	0.046884	1.399294	1.417846
C	1.397278	1.193408	1.220057
C	0.903479	2.914969	-0.080944
C	-0.301627	2.526955	0.574555
C	-1.481075	3.250658	0.341551
C	-1.448412	4.318537	-0.554812
C	-0.257617	4.680861	-1.211021
N	-0.852886	-1.333306	0.826877
N	-3.486179	-0.967808	0.253559
O	-0.680593	-2.901086	-0.831779
H	-1.928352	-1.190209	2.625048
H	1.851388	4.277271	-1.476651
H	-3.183297	-3.022686	0.666032
H	-3.514204	-3.675363	-1.638395
H	-2.951180	-2.106398	-2.234258
H	-5.578810	-2.693502	-0.757736
H	-5.394798	-1.811538	-2.278889
H	-5.550542	-0.493560	0.184413
H	-4.582697	0.166053	-1.141459
H	-0.173164	0.192527	3.152049
H	-1.535604	1.273704	2.879268
H	2.026523	0.448653	1.692590
H	-2.402677	2.968679	0.841261
H	-2.356996	4.883006	-0.749056
H	-0.260697	5.517253	-1.905227
H	0.148515	-1.171179	0.800912

Figure 12B Radical C5 Product

O 2

N	5.506655	-2.301124	-0.650018
C	3.545351	-1.266604	-1.878345
C	6.429878	0.039847	2.085015
C	5.862558	-0.717985	0.923464
C	6.285557	-1.928739	0.435252
C	4.563612	-1.333758	-0.884671
C	4.748456	-0.308469	0.088363
C	3.925819	0.810659	0.093502
C	2.814537	0.958433	-0.916385
C	2.723145	-0.186013	-1.907288
H	5.622609	-3.151216	-1.181692
H	3.430391	-2.069815	-2.602325
H	5.677161	0.207157	2.866920
H	7.266291	-0.501085	2.539509
H	7.090237	-2.567059	0.773611
H	4.047396	1.608546	0.820172
H	2.960071	1.897331	-1.473934
H	1.936779	-0.111247	-2.653080
H	6.797690	1.029614	1.783326
N	1.503990	1.157945	-0.238449
C	-3.558733	-0.109837	1.391811
O	-3.835493	0.941624	1.975884

C	-2.247248	-0.875291	1.651735
C	0.595669	3.201242	-1.421947
C	-4.136018	-1.997886	-0.139140
C	-5.056816	-1.949772	-1.364346
C	-6.273965	-1.162691	-0.845196
C	-5.671872	-0.106857	0.100799
C	-2.654085	-2.185315	-0.447633
C	-1.104437	0.042465	2.163789
C	-0.271165	0.722511	1.112251
C	0.989247	0.321244	0.731795
C	0.558185	2.129579	-0.518074
C	-0.572571	1.891435	0.319406
C	-1.671223	2.768703	0.248509
C	-1.628937	3.834126	-0.642792
C	-0.507461	4.046295	-1.471375
N	-1.827909	-1.628994	0.470768
N	-4.394810	-0.706843	0.519015
O	-2.261537	-2.803357	-1.435163
H	-2.480053	-1.575876	2.470192
H	1.452498	3.374983	-2.066152
H	-4.442412	-2.822146	0.526025
H	-5.308627	-2.948160	-1.728207
H	-4.555490	-1.410372	-2.174982
H	-6.941639	-1.828766	-0.287101
H	-6.856379	-0.706389	-1.649864
H	-6.300724	0.102934	0.971260
H	-5.475340	0.845076	-0.406007
H	-0.443711	-0.573112	2.784064
H	-1.578175	0.772816	2.826931
H	1.589154	-0.497945	1.106271
H	-2.539446	2.602706	0.878637
H	-2.473186	4.515819	-0.705582
H	-0.502968	4.885061	-2.162460
H	-0.836276	-1.655808	0.258488

Figure 12B Radical C6 TS

O 2

N	1.628868	2.371470	0.385167
C	-3.057800	-0.383152	1.292029
O	-3.737536	0.514829	1.793887
C	-1.622581	-0.692437	1.759793
C	0.332875	3.860637	-1.181784
C	-2.761023	-2.328535	-0.245852
C	-3.469395	-2.577941	-1.583383
C	-4.936073	-2.242684	-1.256950
C	-4.846998	-1.048538	-0.289576
C	-1.277190	-2.000168	-0.342929
C	-0.921317	0.532525	2.415086
C	-0.165289	1.417839	1.465689
C	1.205666	1.451723	1.325502
C	0.465431	2.904003	-0.169023
C	-0.678346	2.370905	0.497738
C	-1.957553	2.836098	0.159862
C	-2.081661	3.786109	-0.854961
C	-0.950282	4.288995	-1.522441

N	-0.813341	-1.233708	0.663127
N	-3.519814	-1.205633	0.327785
O	-0.579786	-2.430606	-1.271574
H	-1.728718	-1.460371	2.541819
H	1.205318	4.268784	-1.685649
H	-2.859558	-3.216158	0.400716
H	-3.326397	-3.600416	-1.939099
H	-3.069333	-1.895647	-2.340699
H	-5.413539	-3.093734	-0.758530
H	-5.523112	-2.005611	-2.147886
H	-5.627882	-1.051486	0.476472
H	-4.892440	-0.084966	-0.810284
H	-0.223341	0.150971	3.168011
H	-1.706800	1.077960	2.947712
H	1.941598	0.872288	1.872365
H	-2.834709	2.460448	0.678417
H	-3.068542	4.149615	-1.130270
H	-1.075982	5.029132	-2.308464
H	0.141219	-0.893382	0.590969
N	2.283452	-2.063674	-1.021218
C	2.276500	0.423216	-1.356496
C	5.321341	-2.829177	0.988720
C	4.184181	-2.233125	0.212777
C	3.120222	-2.922849	-0.355244
C	2.766582	-0.773905	-0.864981
C	3.968233	-0.860003	-0.091867
C	4.673715	0.341163	0.210390
C	4.167951	1.544587	-0.201453
C	2.904802	1.638663	-0.916648
H	1.322837	-2.282504	-1.301820
H	1.389518	0.466976	-1.980630
H	5.196008	-3.910690	1.101922
H	6.285879	-2.656927	0.493982
H	2.906609	-3.983242	-0.326546
H	5.612699	0.297331	0.756450
H	4.690834	2.468077	0.027645
H	2.774659	2.511858	-1.546851
H	5.395658	-2.394980	1.993737

Figure 12B Radical C6 Product

O 2

N	1.436848	1.622912	0.112574
C	-3.604476	-0.172117	1.222682
O	-4.097955	0.886551	1.621131
C	-2.255581	-0.702578	1.745995
C	0.459894	3.367009	-1.436960
C	-3.697515	-2.288584	-0.099461
C	-4.442957	-2.532692	-1.416833
C	-5.814839	-1.883871	-1.157035
C	-5.492909	-0.637326	-0.312355
C	-2.175687	-2.273281	-0.205508
C	-1.331034	0.422865	2.284649
C	-0.445533	1.096732	1.272594
C	0.895642	0.834058	1.108268
C	0.426845	2.412550	-0.410078

C	-0.772964	2.115816	0.302999
C	-1.950070	2.817288	-0.019682
C	-1.913237	3.768918	-1.031877
C	-0.720741	4.038381	-1.735338
N	-1.571193	-1.505695	0.733230
N	-4.219617	-0.983465	0.338954
O	-1.567735	-2.916477	-1.058735
H	-2.511187	-1.340614	2.607608
H	1.371383	3.582601	-1.986652
H	-3.971852	-3.064270	0.634448
H	-4.504921	-3.594936	-1.662792
H	-3.915578	-2.026417	-2.232287
H	-6.451545	-2.568739	-0.585669
H	-6.343498	-1.628614	-2.079131
H	-6.257677	-0.411617	0.436791
H	-5.353255	0.259258	-0.927638
H	-0.695921	-0.019308	3.060005
H	-1.988623	1.143410	2.780611
H	1.532551	0.152188	1.656451
H	-2.872099	2.603165	0.511838
H	-2.817433	4.314260	-1.289613
H	-0.722161	4.784083	-2.525947
H	-0.568118	-1.385495	0.639808
N	4.218573	-1.871805	-1.583379
C	2.976331	0.276843	-1.272523
C	6.743454	-2.045623	1.138391
C	5.649742	-1.716506	0.164408
C	5.249077	-2.495512	-0.912561
C	3.921427	-0.670948	-0.956805
C	4.822370	-0.561871	0.153096
C	4.734396	0.597223	0.994207
C	3.815143	1.562243	0.747877
C	2.828369	1.500281	-0.399410
H	3.747171	-2.238856	-2.396416
H	2.305881	0.170741	-2.120004
H	6.366437	-2.104350	2.167401
H	7.206416	-3.008473	0.899794
H	5.628546	-3.450553	-1.248835
H	5.416107	0.701721	1.835383
H	3.746935	2.440518	1.384119
H	2.959564	2.405961	-1.011627
H	7.535235	-1.285673	1.131104

Figure 12B Radical C7 TS

0 2

N	-2.628234	-0.497297	1.886417
C	-3.844699	0.303962	-0.181696
C	-1.497132	-3.974606	1.227141
C	-2.069454	-2.589328	1.243453
C	-1.976295	-1.662915	2.253534
C	-3.143138	-0.642738	0.628298
C	-2.815957	-1.949175	0.186024
C	-3.275365	-2.379946	-1.071805
C	-4.066239	-1.507232	-1.845761
C	-4.383104	-0.230805	-1.405833

H	-2.617827	0.364504	2.414395
H	-4.382883	1.112494	0.299795
H	-0.659403	-4.040840	0.523207
H	-1.121136	-4.254568	2.216604
H	-1.502167	-1.740486	3.222042
H	-3.048219	-3.378542	-1.433994
H	-4.457837	-1.853008	-2.798484
H	-5.008589	0.416078	-2.013023
H	-2.246966	-4.718987	0.931414
N	-2.461876	1.623527	-0.803679
C	3.084488	0.894715	-0.916491
O	3.347774	2.098162	-0.850916
C	1.999625	0.323760	-1.850563
C	-2.217282	2.895311	1.356540
C	3.508165	-1.494246	-0.344652
C	4.132065	-2.061124	0.936776
C	5.323878	-1.118183	1.182846
C	4.807108	0.267435	0.755765
C	2.023053	-1.795283	-0.534278
C	0.950620	1.375452	-2.292540
C	-0.244749	1.572437	-1.401017
C	-1.527179	1.155518	-1.699769
C	-1.744752	2.276043	0.192721
C	-0.358873	2.307834	-0.153470
C	0.540471	3.006610	0.663752
C	0.064016	3.612645	1.828252
C	-1.297171	3.553547	2.175311
N	1.367041	-0.852556	-1.251847
N	3.753313	-0.047396	-0.221174
O	1.499291	-2.810137	-0.077969
H	2.538657	0.019676	-2.762982
H	-3.274923	2.884547	1.609841
H	4.041094	-1.887636	-1.226202
H	4.423352	-3.107441	0.823008
H	3.405132	-1.999420	1.753508
H	6.170831	-1.412135	0.552616
H	5.662838	-1.127101	2.222048
H	5.576956	0.896452	0.299105
H	4.372567	0.826083	1.593241
H	0.589209	1.076258	-3.282398
H	1.503684	2.311553	-2.423163
H	-1.851245	0.582232	-2.561182
H	1.590288	3.070812	0.393925
H	0.755801	4.147051	2.474397
H	-1.641530	4.038742	3.084861
H	0.361500	-0.952577	-1.344759

Figure 12B Radical C7 Product

0 2

N	-2.852943	-0.675510	1.620853
C	-3.219138	1.210708	-0.070840
C	-4.910853	-3.600901	0.644288
C	-4.185744	-2.298677	0.815185
C	-3.298911	-1.972362	1.814342
C	-3.433299	-0.159537	0.497792

C	-4.278641	-1.137875	-0.038404
C	-5.019761	-0.864899	-1.222400
C	-4.868436	0.403072	-1.830887
C	-4.042682	1.380836	-1.327382
H	-2.163471	-0.208317	2.192710
H	-3.524420	1.979235	0.657362
H	-4.678300	-4.072443	-0.319379
H	-4.637501	-4.309005	1.433370
H	-2.942706	-2.557190	2.650663
H	-5.679523	-1.609766	-1.655532
H	-5.430641	0.617392	-2.736967
H	-3.957455	2.343463	-1.823140
H	-6.000275	-3.469381	0.679706
N	-1.786180	1.504046	-0.321203
C	3.524201	0.336283	-1.055599
O	3.949637	1.491988	-1.138358
C	2.304591	-0.153416	-1.860631
C	-1.177034	2.840207	1.739334
C	3.676003	-2.016308	-0.231743
C	4.281470	-2.502391	1.090403
C	5.602406	-1.715662	1.169875
C	5.259779	-0.334894	0.580443
C	2.158813	-2.137288	-0.336187
C	1.343586	0.997734	-2.260946
C	0.276911	1.356260	-1.262260
C	-1.049148	1.008750	-1.379670
C	-0.923864	2.176390	0.529853
C	0.383930	2.113655	-0.036532
C	1.445236	2.756457	0.628005
C	1.191937	3.419766	1.823026
C	-0.104942	3.458178	2.374747
N	1.591697	-1.213855	-1.149741
N	4.112529	-0.611541	-0.298999
O	1.525565	-3.008363	0.256209
H	2.721722	-0.556356	-2.797982
H	-2.172696	2.882196	2.171467
H	4.111639	-2.581208	-1.072375
H	4.419972	-3.585515	1.104761
H	3.613727	-2.235370	1.916358
H	6.368017	-2.204715	0.557073
H	5.989493	-1.640944	2.189401
H	6.081441	0.109138	0.010585
H	4.960381	0.385355	1.350822
H	0.854010	0.706083	-3.196415
H	1.980598	1.858465	-2.487008
H	-1.546984	0.459104	-2.167598
H	2.446722	2.722601	0.210710
H	2.006028	3.917027	2.343788
H	-0.273527	3.981446	3.312112
H	0.577978	-1.206794	-1.186534

Compound SI-6

O 1

N	-3.411545	1.506824	-0.600124
C	1.358177	-0.248240	1.359732

O	0.933925	-1.082974	2.164039
C	0.823028	1.195582	1.318693
C	-3.998417	-0.847060	-1.280641
C	2.945599	0.480348	-0.427680
C	3.579456	-0.396553	-1.514122
C	4.050463	-1.629507	-0.721584
C	2.956197	-1.842449	0.341574
C	1.912163	1.485608	-0.923507
C	-0.632012	1.312448	1.846299
C	-1.729816	1.067741	0.847147
C	-2.486681	2.057690	0.261036
C	-3.279619	0.134434	-0.587631
C	-2.224383	-0.183751	0.315383
C	-1.900592	-1.538844	0.522785
C	-2.614339	-2.515452	-0.161952
C	-3.651366	-2.174342	-1.056257
N	0.944798	1.772342	-0.019162
N	2.352438	-0.507877	0.487718
O	1.976136	1.996010	-2.039887
H	-4.090602	2.027075	-1.135132
H	1.458503	1.758574	2.021697
H	-4.798876	-0.579752	-1.965306
H	3.731268	1.048551	0.097580
H	4.387958	0.117843	-2.037783
H	2.817025	-0.669696	-2.251358
H	5.009386	-1.418559	-0.234994
H	4.184679	-2.511838	-1.352667
H	3.348472	-2.193769	1.300695
H	2.187887	-2.552612	0.014878
H	-0.752821	2.323525	2.250832
H	-0.703840	0.619364	2.690162
H	-2.448788	3.128955	0.409946
H	-1.099900	-1.808675	1.204075
H	-2.371032	-3.563439	-0.007429
H	-4.189824	-2.961729	-1.576910
H	0.203031	2.386955	-0.336186

Compound SI-PC-I

O 4

H	0.156796	0.114742	0.205381
Fe	-2.998491	-0.235894	0.008038
N	-3.474594	-2.190562	0.184175
N	-2.222544	-0.595080	-1.817988
N	-4.078481	0.149371	1.666905
N	-2.792431	1.742806	-0.306468
C	-4.067139	-2.802783	1.259344
C	-1.642011	0.318113	-2.660525
C	-3.139187	-3.201730	-0.686097
C	-2.059578	-1.817107	-2.418291
C	-4.604047	-0.776450	2.547968
C	-2.123730	2.346625	-1.347260
C	-4.288463	1.381361	2.249504
C	-3.150039	2.755235	0.545957
C	-4.110441	-4.231010	1.063532
C	-1.101164	-0.342825	-3.821983

C	-3.540646	-4.478082	-0.148008
C	-1.363745	-1.671439	-3.672769
C	-5.177734	-0.106419	3.687593
C	-2.067299	3.773025	-1.143658
C	-4.988367	1.228283	3.500794
C	-2.705897	4.027305	0.031916
H	-4.533443	-4.935121	1.768217
H	-0.594507	0.159842	-4.635577
H	-3.395086	-5.427904	-0.645993
H	-1.118095	-2.488763	-4.338308
H	-5.659137	-0.610381	4.515632
H	-1.597885	4.472442	-1.823081
H	-5.278933	2.048319	4.144559
H	-2.871894	4.979182	0.519431
C	-4.582733	-2.148845	2.372985
C	-1.589188	1.690709	-2.445518
C	-3.859081	2.594125	1.732910
C	-2.494582	-3.033127	-1.902144
H	-5.023357	-2.760310	3.153665
H	-1.091841	2.295557	-3.196783
H	-4.081166	3.488188	2.306612
H	-2.298181	-3.923565	-2.490749
O	-1.566668	-0.383353	0.779155
S	-5.413147	-0.140365	-0.931136
C	-5.971245	1.587188	-1.026737
H	-5.310977	2.184750	-1.659531
H	-6.991641	1.605509	-1.420412
H	-5.983127	2.024731	-0.021115
N	1.107021	0.348551	-0.089892
C	6.505686	0.008094	-0.840995
O	6.664471	1.055633	-1.474254
C	5.418407	-1.021853	-1.204157
C	1.388096	2.609570	0.981445
C	7.184461	-1.631286	0.916681
C	7.899187	-1.336052	2.240820
C	9.012132	-0.359621	1.818290
C	8.364261	0.505702	0.721335
C	5.729757	-2.072420	1.049228
C	4.220685	-0.395834	-1.968472
C	3.115686	0.181156	-1.126609
C	1.903657	-0.435347	-0.891361
C	1.786667	1.507429	0.212969
C	3.062705	1.442261	-0.421689
C	3.948204	2.528370	-0.274418
C	3.552314	3.623163	0.485807
C	2.285872	3.663617	1.109403
N	4.963669	-1.752639	-0.022020
N	7.297742	-0.356639	0.187986
O	5.311604	-2.674635	2.035919
H	5.906537	-1.721997	-1.901921
H	0.411769	2.636213	1.457757
H	7.723262	-2.421849	0.368520
H	8.276376	-2.244489	2.715388
H	7.198043	-0.858220	2.933183
H	9.861767	-0.914705	1.404683

H	9.382792	0.244539	2.650529
H	9.060415	0.790638	-0.073253
H	7.921044	1.424830	1.122308
H	3.796240	-1.179573	-2.606032
H	4.649350	0.361091	-2.632839
H	1.536536	-1.383130	-1.264351
H	4.926492	2.500548	-0.744185
H	4.229274	4.465391	0.605162
H	2.007562	4.533431	1.698896
H	3.969441	-1.937277	0.061203

TS from SI-PC-I to SI-R-I

0 4

H	0.212881	-0.095237	0.260839
Fe	2.755812	0.248505	-0.018954
N	3.073813	2.234834	0.209025
N	1.894495	0.612618	-1.814512
N	3.745924	-0.115029	1.701589
N	2.591814	-1.733687	-0.333383
C	3.705567	2.843470	1.261672
C	1.440768	-0.323620	-2.707577
C	2.632885	3.241688	-0.610806
C	1.613894	1.837898	-2.362039
C	4.277824	0.820746	2.552374
C	2.036436	-2.347116	-1.426516
C	3.930599	-1.332468	2.303013
C	2.932328	-2.736413	0.541210
C	3.673873	4.278390	1.096538
C	0.852443	0.329265	-3.852857
C	3.004603	4.525599	-0.062788
C	0.954884	1.671067	-3.635923
C	4.827519	0.171359	3.719975
C	2.039686	-3.779304	-1.245453
C	4.607783	-1.163546	3.567994
C	2.588500	-4.020393	-0.022055
H	4.107686	4.986413	1.791029
H	0.423745	-0.187245	-4.702229
H	2.776470	5.478977	-0.522069
H	0.632488	2.485499	-4.272199
H	5.309591	0.688136	4.540018
H	1.661069	-4.490757	-1.968216
H	4.874204	-1.973242	4.235320
H	2.758950	-4.971185	0.466712
C	4.273953	2.194235	2.350870
C	1.509632	-1.700771	-2.539342
C	3.542441	-2.559050	1.776030
C	1.942814	3.067812	-1.803464
H	4.735618	2.811822	3.114675
H	1.103629	-2.322119	-3.331271
H	3.754107	-3.447071	2.362995
H	1.659466	3.959674	-2.353184
O	1.258203	0.321697	0.786757
S	4.875395	0.265719	-1.175643
C	5.781432	-1.282407	-0.802588
H	5.235575	-2.161776	-1.154976

H	6.745971	-1.236476	-1.318420
H	5.964774	-1.386762	0.270695
N	-0.886881	-0.475613	-0.161706
C	-6.100032	-0.177158	-0.646909
O	-6.314447	-1.326261	-1.044886
C	-5.164180	0.766650	-1.422137
C	-1.090980	-2.681852	1.016169
C	-6.543099	1.722981	0.922303
C	-6.786999	1.597455	2.431666
C	-7.867430	0.501842	2.500588
C	-7.502421	-0.476694	1.365110
C	-5.227610	2.370521	0.520930
C	-4.015764	-0.019858	-2.110630
C	-2.917520	-0.496881	-1.209869
C	-1.692665	0.198096	-0.975773
C	-1.540376	-1.663124	0.195092
C	-2.812636	-1.706251	-0.446575
C	-3.644998	-2.822720	-0.252236
C	-3.193245	-3.858540	0.575941
C	-1.942584	-3.791203	1.199523
N	-4.631103	1.831615	-0.575473
N	-6.673486	0.336052	0.456742
O	-4.769363	3.330673	1.132889
H	-5.771496	1.197180	-2.233894
H	-0.119183	-2.633828	1.497020
H	-7.342078	2.337331	0.475455
H	-7.098529	2.544054	2.877360
H	-5.864761	1.272752	2.925922
H	-8.854930	0.938959	2.315968
H	-7.900919	0.003236	3.472560
H	-8.377817	-0.870731	0.839929
H	-6.911801	-1.329618	1.716414
H	-3.585814	0.632455	-2.879681
H	-4.486989	-0.864366	-2.620719
H	-1.384139	1.145522	-1.401398
H	-4.623661	-2.864105	-0.717478
H	-3.825404	-4.726403	0.737604
H	-1.616231	-4.606958	1.837732
H	-3.811043	2.330622	-0.902223

Compound SI-R-I

0 2

N	-3.049957	1.767668	-0.938990
C	1.226975	-0.379821	1.350606
O	0.668817	-1.205515	2.078688
C	0.891815	1.119025	1.446887
C	-3.937156	-0.528659	-1.404071
C	2.951727	0.232762	-0.356465
C	3.358945	-0.614142	-1.568735
C	3.598159	-1.999161	-0.939197
C	2.528685	-2.114275	0.165686
C	2.191476	1.510604	-0.674993
C	-0.590898	1.344209	1.848498
C	-1.600186	1.142981	0.761433
C	-2.163567	2.189106	-0.058441

C	-3.128193	0.370188	-0.735631
C	-2.247992	-0.055782	0.304737
C	-2.194798	-1.406082	0.671805
C	-3.019767	-2.316515	-0.008681
C	-3.873622	-1.888708	-1.027255
N	1.213738	1.831963	0.211707
N	2.173231	-0.713534	0.453780
O	2.474247	2.204186	-1.647704
H	1.499014	1.511817	2.277799
H	-4.604721	-0.196304	-2.193602
H	3.855768	0.535333	0.197462
H	4.236716	-0.209331	-2.076008
H	2.532376	-0.644972	-2.286978
H	4.599817	-2.040306	-0.497273
H	3.522188	-2.811683	-1.666205
H	2.895304	-2.612983	1.068029
H	1.631644	-2.646631	-0.168840
H	-0.676916	2.370569	2.224488
H	-0.783836	0.667611	2.685956
H	-1.913981	3.244200	0.022986
H	-1.518446	-1.741265	1.451010
H	-2.991264	-3.368044	0.261809
H	-4.502380	-2.611211	-1.539980
H	0.765510	2.726764	0.048899

Compound SI-PC-II

0 4

N	2.776823	-2.902193	-1.761432
C	3.906859	0.961732	1.432361
O	4.633907	0.451003	2.290953
C	2.443526	0.527270	1.299373
C	5.195672	-3.602081	-1.883743
C	3.532782	2.648665	-0.386444
C	4.526529	2.916383	-1.524176
C	5.834046	3.192586	-0.755828
C	5.774178	2.258427	0.473776
C	2.245204	1.943000	-0.779774
C	2.316617	-1.020417	1.402508
C	2.805609	-1.800963	0.212847
C	2.021531	-2.199354	-0.846039
C	4.077690	-2.982504	-1.311833
C	4.137548	-2.293111	-0.064876
C	5.370878	-2.238965	0.614233
C	6.482798	-2.854236	0.049027
C	6.397844	-3.529210	-1.187804
N	1.792775	1.009941	0.085140
N	4.348365	1.907141	0.579551
O	1.646077	2.272368	-1.806272
H	2.425542	-3.302117	-2.618368
H	1.925285	0.942518	2.177500
H	5.124965	-4.121352	-2.836012
H	3.229981	3.612421	0.056255
H	4.212553	3.746071	-2.160699
H	4.618321	2.019623	-2.147218
H	5.861786	4.238930	-0.431940

H	6.725581	3.010340	-1.361579
H	6.128291	2.741223	1.390665
H	6.353131	1.338900	0.338467
H	1.254746	-1.238712	1.563192
H	2.848360	-1.315989	2.311714
H	0.967240	-2.023808	-1.015201
H	5.449920	-1.702904	1.554511
H	7.437795	-2.814383	0.566853
H	7.285134	-3.999134	-1.603943
H	0.893260	0.580749	-0.150261
Fe	-2.316764	0.077543	0.009827
N	-2.689465	1.022754	-1.732504
N	-1.744423	1.827448	0.831512
N	-3.213099	-1.571878	-0.723594
N	-2.236046	-0.786790	1.828617
C	-3.116733	0.453929	-2.905415
C	-1.285613	2.026355	2.108761
C	-2.435659	2.342599	-2.025949
C	-1.620169	3.034990	0.195490
C	-3.582502	-1.799716	-2.035568
C	-1.704154	-0.242602	2.975609
C	-3.418860	-2.765692	-0.064402
C	-2.547789	-2.084806	2.140564
C	-3.133248	1.434561	-3.963028
C	-0.861552	3.393505	2.282887
C	-2.719416	2.609584	-3.414474
C	-1.075151	4.022519	1.093386
C	-4.052641	-3.152965	-2.190654
C	-1.690522	-1.222359	4.033637
C	-3.959153	-3.748506	-0.970313
C	-2.217254	-2.366436	3.515590
H	-3.435425	1.233167	-4.982519
H	-0.463360	3.801911	3.202695
H	-2.605304	3.575148	-3.889672
H	-0.886075	5.055037	0.830045
H	-4.406409	-3.574957	-3.122386
H	-1.326074	-1.039019	5.036092
H	-4.216552	-4.762302	-0.692168
H	-2.375327	-3.319809	4.002873
C	-3.516448	-0.869075	-3.057692
C	-1.257470	1.063569	3.111655
C	-3.114664	-3.007715	1.266338
C	-1.956645	3.285979	-1.130506
H	-3.830526	-1.186843	-4.046581
H	-0.867796	1.360747	4.080029
H	-3.316904	-4.001750	1.652079
H	-1.804748	4.294558	-1.500779
O	-0.800301	-0.368618	-0.400787
S	-4.825981	0.623891	0.373337
C	-5.470722	-0.325365	1.783660
H	-4.904321	-0.121263	2.695363
H	-6.524270	-0.067819	1.926835
H	-5.406894	-1.398018	1.563975

TS from **SI-PC-II** to **SI-R-II**

O 4			
N	2.868669	-2.928062	-1.953318
C	3.621599	1.017824	1.222748
O	4.489894	0.498841	1.931676
C	2.210243	0.409313	1.085576
C	5.306654	-3.571247	-1.997780
C	2.819526	2.845064	-0.271095
C	3.667652	3.543926	-1.342572
C	4.930516	3.948770	-0.557919
C	5.152893	2.795409	0.443649
C	1.729144	1.905295	-0.779699
C	2.254088	-1.131969	1.238413
C	2.801522	-1.871745	0.045305
C	2.064530	-2.265000	-1.053266
C	4.154826	-2.990954	-1.456348
C	4.150815	-2.328687	-0.193155
C	5.355940	-2.259554	0.533541
C	6.502441	-2.838574	0.000139
C	6.479943	-3.487951	-1.252481
N	1.493387	0.760749	-0.125260
N	3.830952	2.157811	0.537729
O	1.068883	2.258443	-1.782385
H	2.560068	-3.310608	-2.834475
H	1.647495	0.801762	1.955532
H	5.286068	-4.068911	-2.963764
H	2.312756	3.608412	0.343381
H	3.147536	4.391442	-1.793908
H	3.911683	2.830528	-2.137981
H	4.749413	4.884746	-0.017282
H	5.800028	4.102161	-1.202770
H	5.490681	3.143187	1.425589
H	5.880304	2.058147	0.086022
H	1.226526	-1.463619	1.423186
H	2.836817	-1.362043	2.134488
H	1.013110	-2.111086	-1.254293
H	5.385929	-1.734679	1.482404
H	7.436396	-2.786660	0.553833
H	7.393084	-3.928074	-1.644435
H	0.171342	0.046554	-0.396736
Fe	-2.237524	0.002843	0.045795
N	-2.657373	1.046801	-1.626583
N	-1.421310	1.670421	0.862033
N	-3.128449	-1.623699	-0.725794
N	-1.976109	-0.968611	1.791746
C	-3.295802	0.572216	-2.746433
C	-0.975913	1.825300	2.155099
C	-2.286066	2.330392	-1.915959
C	-1.258419	2.888306	0.257870
C	-3.704036	-1.734323	-1.964927
C	-1.416798	-0.473102	2.940514
C	-3.232456	-2.862628	-0.145476
C	-2.221532	-2.299368	2.033969
C	-3.339193	1.593811	-3.763185
C	-0.509555	3.173927	2.361755
C	-2.706249	2.684785	-3.248803

C	-0.680314	3.832687	1.181731
C	-4.186768	-3.076704	-2.172127
C	-1.323915	-1.507698	3.939273
C	-3.888165	-3.779887	-1.043658
C	-1.817547	-2.644832	3.372746
H	-3.790244	1.470445	-4.739083
H	-0.109847	3.549496	3.294635
H	-2.530500	3.646511	-3.712583
H	-0.454076	4.863908	0.944095
H	-4.682330	-3.419791	-3.070894
H	-0.922212	-1.367003	4.934217
H	-4.090240	-4.819559	-0.821373
H	-1.909301	-3.631864	3.806910
C	-3.795906	-0.712533	-2.904407
C	-0.966628	0.833425	3.123150
C	-2.796395	-3.187541	1.134301
C	-1.615953	3.190579	-1.050092
H	-4.277225	-0.946674	-3.848453
H	-0.569300	1.090650	4.099662
H	-2.936725	-4.211640	1.464787
H	-1.398308	4.190028	-1.409585
O	-0.708696	-0.527651	-0.580195
S	-4.346376	0.809579	0.771725
C	-5.039156	-0.304895	2.049446
H	-4.440599	-0.293232	2.963552
H	-6.043096	0.064705	2.281322
H	-5.120011	-1.330381	1.680053

Compound SI-R-II

O 2

N	2.644043	-1.781181	-1.140983
C	-1.130295	0.808909	0.799360
O	-0.283326	1.685774	0.916388
C	-0.917929	-0.637102	1.384117
C	4.381714	0.032908	-1.371507
C	-3.322762	-0.099010	0.076513
C	-4.134917	0.324925	-1.157262
C	-4.111774	1.862295	-1.064586
C	-2.709488	2.196369	-0.519161
C	-2.678551	-1.481357	0.004227
C	0.543061	-0.888083	1.793187
C	1.519784	-0.990193	0.652609
C	1.598576	-2.009132	-0.272380
C	3.276346	-0.604311	-0.796553
C	2.590200	-0.074818	0.333420
C	3.043337	1.136104	0.889126
C	4.143521	1.770833	0.324898
C	4.807152	1.225156	-0.794924
N	-1.380538	-1.611196	0.438871
N	-2.316731	0.965127	0.187870
O	-3.303049	-2.444474	-0.439334
H	2.896872	-2.379485	-1.913237
H	-1.556082	-0.647103	2.288131
H	4.889063	-0.388969	-2.235061
H	-3.971670	-0.095328	0.967502

H	-5.142356	-0.095347	-1.147955
H	-3.629067	-0.019938	-2.066013
H	-4.878412	2.205780	-0.361387
H	-4.300826	2.345534	-2.026451
H	-2.706319	3.050561	0.164191
H	-1.984916	2.399219	-1.315784
H	0.547744	-1.813649	2.381404
H	0.843356	-0.084002	2.470554
H	0.978621	-2.886849	-0.379164
H	2.527822	1.576402	1.737441
H	4.498472	2.706920	0.748002
H	5.663427	1.745647	-1.215417

TS from SI-R-II to SI-R-III

O 2

N	2.054588	-1.702855	-0.920267
C	-1.285375	0.527119	1.430980
O	-0.896443	1.486723	2.105933
C	-0.832201	-0.921629	1.700817
C	3.141042	0.408001	-1.773276
C	-2.587282	-0.472826	-0.440516
C	-3.056809	0.224715	-1.723386
C	-3.609956	1.566608	-1.209244
C	-2.660827	1.949133	-0.060258
C	-1.436582	-1.483161	-0.612862
C	0.584753	-0.934887	2.333706
C	1.508491	-0.972254	1.156546
C	1.423875	-2.059332	0.237002
C	2.496783	-0.389081	-0.832173
C	2.161418	0.089889	0.471328
C	2.474986	1.422340	0.814730
C	3.126193	2.216795	-0.118700
C	3.457796	1.714810	-1.394976
N	-0.745542	-1.775335	0.508010
N	-2.155522	0.651531	0.409468
O	-1.227853	-2.011393	-1.713728
H	2.124856	-2.289303	-1.739226
H	-1.560154	-1.353338	2.407149
H	3.384922	0.033421	-2.762814
H	-3.431780	-0.996424	0.035195
H	-3.796192	-0.368235	-2.266828
H	-2.197804	0.378683	-2.384721
H	-4.627634	1.432125	-0.825003
H	-3.645947	2.336580	-1.984868
H	-3.157964	2.485818	0.753694
H	-1.821869	2.567573	-0.402367
H	0.706991	-1.828549	2.955336
H	0.723044	-0.051847	2.958568
H	1.233769	-3.099462	0.444966
H	2.202206	1.815093	1.789175
H	3.380256	3.242796	0.130272
H	3.965163	2.361605	-2.104951

Compound SI-R-III

O 2

N	-1.634781	-1.658743	-0.712899
C	1.506274	1.567482	-0.154578
O	1.289192	2.670708	0.346353
C	0.755073	1.038723	-1.387324
C	-3.304927	-1.425570	1.142572
C	2.677383	-0.633732	-0.275697
C	3.411967	-1.374954	0.849997
C	4.199742	-0.253039	1.549491
C	3.250679	0.956017	1.502868
C	1.368101	-1.288041	-0.726507
C	-0.635159	1.703001	-1.624591
C	-1.597803	0.590322	-1.339798
C	-0.930233	-0.743561	-1.583446
C	-2.516513	-0.960855	0.094344
C	-2.538967	0.420425	-0.299025
C	-3.374652	1.321822	0.393154
C	-4.168361	0.849252	1.434670
C	-4.133360	-0.507518	1.803256
N	0.474856	-0.406728	-1.227093
N	2.439614	0.703610	0.301756
O	1.162150	-2.500586	-0.626376
H	-1.174033	-2.512178	-0.426085
H	1.408610	1.193394	-2.257627
H	-3.272493	-2.467841	1.446986
H	3.329629	-0.547663	-1.159799
H	4.046275	-2.176432	0.465264
H	2.679024	-1.822222	1.529485
H	5.116531	-0.031114	0.991515
H	4.485357	-0.511679	2.572487
H	3.769873	1.914922	1.417145
H	2.598707	1.005172	2.383523
H	-0.696716	2.068473	-2.657054
H	-0.758934	2.559516	-0.957255
H	-0.943585	-1.108738	-2.620713
H	-3.394087	2.371118	0.111483
H	-4.819868	1.533436	1.970662
H	-4.758319	-0.854737	2.621519

TS from **SI-R-III** to **SI-R-IV**

0 2

N	0.265708	0.489845	-1.431330
C	-3.102061	-0.299133	1.399508
O	-3.569103	0.553118	2.155126
C	-1.626946	-0.733673	1.418794
C	-0.303932	2.861026	-2.044520
C	-3.256682	-1.963198	-0.448991
C	-4.309087	-2.047212	-1.563253
C	-5.628170	-1.769166	-0.820289
C	-5.252241	-0.703634	0.222744
C	-1.859650	-1.542618	-0.916885
C	-0.658815	0.290992	2.059553
C	0.237476	0.763580	0.922416
C	0.185109	-0.276263	-0.201179
C	-0.049512	1.820228	-1.152825
C	-0.055024	2.034553	0.246374

C	-0.303496	3.312377	0.751533
C	-0.553996	4.364950	-0.137298
C	-0.554612	4.135698	-1.518381
N	-1.135600	-0.922788	0.040417
N	-3.829957	-0.971780	0.481196
O	-1.458994	-1.748919	-2.066965
H	-0.111076	0.036184	-2.256286
H	-1.583391	-1.690948	1.959163
H	-0.314333	2.688517	-3.117350
H	-3.161243	-2.938052	0.056518
H	-4.292303	-3.014701	-2.069735
H	-4.108421	-1.272667	-2.310731
H	-5.976438	-2.678506	-0.317294
H	-6.425347	-1.429515	-1.486781
H	-5.828344	-0.778003	1.149628
H	-5.371031	0.315547	-0.165134
H	-0.094538	-0.195297	2.859205
H	-1.231016	1.109055	2.503659
H	0.967053	-1.041636	-0.163663
H	-0.316232	3.486458	1.825023
H	-0.753941	5.361395	0.246319
H	-0.756964	4.958333	-2.199461
N	4.612971	0.341156	-1.222571
C	3.001693	1.230941	0.487554
C	5.364913	-3.165980	-0.245745
C	4.885589	-1.753666	-0.409610
C	5.248712	-0.871348	-1.406146
C	3.807945	0.267939	-0.101945
C	3.969451	-1.046907	0.435380
C	3.288990	-1.369186	1.637875
C	2.470190	-0.435282	2.228870
C	2.195451	0.850824	1.614223
H	4.686095	1.135361	-1.840357
H	2.917798	2.229792	0.070476
H	4.533512	-3.882529	-0.266057
H	6.059179	-3.441529	-1.046287
H	5.921990	-1.016140	-2.240212
H	3.444542	-2.336684	2.109677
H	1.995766	-0.670620	3.177130
H	1.897289	1.653397	2.287298
H	5.886538	-3.310882	0.709442

Compound **SI-R-IV**

0 2

N	0.098901	1.051300	-1.574953
C	-3.065573	-0.584440	1.445621
O	-3.536363	-0.054982	2.452857
C	-1.558598	-0.638766	1.176721
C	-0.102977	3.550690	-1.712833
C	-3.278238	-1.784768	-0.736549
C	-4.466217	-1.720217	-1.707018
C	-5.677065	-1.903360	-0.774946
C	-5.288394	-1.140623	0.504459
C	-2.005637	-1.099597	-1.230571
C	-0.767619	0.515645	1.809384

C	0.387181	0.857149	0.812919
C	0.063664	0.071998	-0.505960
C	0.068491	2.337354	-1.041991
C	0.303493	2.303019	0.343569
C	0.386173	3.484933	1.068556
C	0.226188	4.711746	0.406382
C	-0.020450	4.734052	-0.969459
N	-1.268575	-0.515932	-0.258831
N	-3.816917	-1.169769	0.487644
O	-1.689917	-1.100503	-2.424007
H	-0.416806	0.815927	-2.414236
H	-1.184677	-1.605931	1.548713
H	-0.293906	3.575357	-2.782212
H	-3.016797	-2.837888	-0.540819
H	-4.398846	-2.480233	-2.488047
H	-4.489185	-0.737588	-2.190666
H	-5.819775	-2.966234	-0.549416
H	-6.606690	-1.527118	-1.209823
H	-5.671148	-1.604733	1.418309
H	-5.631258	-0.099353	0.489796
H	-0.401506	0.248634	2.803109
H	-1.427869	1.376228	1.933279
H	0.770914	-0.739261	-0.706337
H	0.561846	3.463945	2.141964
H	0.287716	5.641520	0.964383
H	-0.152437	5.686520	-1.476646
N	4.827437	-0.008359	-0.944487
C	2.918302	0.852849	0.423305
C	5.141064	-3.633303	-0.185239
C	4.788338	-2.179008	-0.302936
C	5.424120	-1.244193	-1.105212
C	3.781910	-0.114483	-0.040617
C	3.749720	-1.484223	0.376989
C	2.773378	-1.867126	1.354234
C	1.887564	-0.960743	1.840349
C	1.818897	0.484585	1.389363
H	5.088543	0.832082	-1.437509
H	2.986814	1.882100	0.085806
H	4.306991	-4.280063	-0.486891
H	5.998766	-3.882851	-0.818355
H	6.260925	-1.369627	-1.778436
H	2.758423	-2.890319	1.724470
H	1.185055	-1.272397	2.608673
H	1.903544	1.126221	2.287369
H	5.399407	-3.906765	0.846009

Compound SI-PDT_{C-c}

0 1

N	-0.438727	0.477825	-1.938170
C	-2.844336	-0.568978	1.584112
O	-2.782404	0.067747	2.635303
C	-1.645382	-1.304830	0.960532
C	-0.928155	2.910736	-1.510061
C	-4.022475	-1.469358	-0.415412
C	-5.326405	-0.976539	-1.058309

C	-6.223145	-0.671484	0.155027
C	-5.254692	-0.091494	1.198913
C	-2.761785	-1.211069	-1.247230
C	-0.263357	-0.831207	1.436049
C	0.401925	-0.099049	0.235790
C	-0.331410	-0.655094	-1.037150
C	-0.494395	1.635187	-1.148104
C	-0.004895	1.371142	0.141423
C	0.051025	2.386785	1.087698
C	-0.380719	3.675178	0.738967
C	-0.862095	3.926691	-0.549036
N	-1.637367	-1.110858	-0.500239
N	-3.974078	-0.728873	0.860368
O	-2.792362	-1.090933	-2.475260
H	-1.142084	0.360033	-2.661409
H	-1.778140	-2.372384	1.190065
H	-1.313205	3.108633	-2.506587
H	-4.081035	-2.551904	-0.217190
H	-5.753592	-1.717960	-1.737065
H	-5.124951	-0.068661	-1.636075
H	-6.672689	-1.596175	0.534499
H	-7.034364	0.021582	-0.082760
H	-5.534285	-0.323943	2.230508
H	-5.159411	0.998039	1.113778
H	0.339814	-1.687996	1.741830
H	-0.369848	-0.174859	2.302573
H	0.180151	-1.489385	-1.522536
H	0.420133	2.188004	2.090967
H	-0.346015	4.474885	1.472992
H	-1.200853	4.925766	-0.811058
N	5.287597	1.266488	0.116899
C	2.829704	0.721944	0.179606
C	7.093687	-1.977626	-0.077088
C	6.132317	-0.829120	0.003164
C	6.442632	0.508538	0.044949
C	4.196669	0.425539	0.121799
C	4.693061	-0.904573	0.051214
C	3.760983	-1.957778	0.039219
C	2.405941	-1.666100	0.100428
C	1.919985	-0.333098	0.174107
H	2.490303	1.750850	0.225345
H	6.929921	-2.583607	-0.977961
H	8.129501	-1.623207	-0.100683
H	7.410997	0.990461	0.029169
H	4.093022	-2.991383	-0.018608
H	1.696742	-2.490085	0.088676
H	6.994076	-2.653529	0.782519
H	5.253870	2.274163	0.153016

Compound SI-C-III

1 1

N	-1.653726	-1.554632	-0.457652
C	1.744958	1.562715	-0.100231
O	1.638618	2.676386	0.408882
C	0.802434	1.074953	-1.212377

C	-3.770019	-1.468938	0.842437
C	2.770709	-0.708030	-0.344519
C	3.588057	-1.483869	0.699652
C	4.519506	-0.404333	1.277999
C	3.645765	0.859707	1.328363
C	1.394802	-1.301192	-0.645228
C	-0.572421	1.806822	-1.245228
C	-1.536262	0.702769	-0.979658
C	-0.911778	-0.627608	-1.292280
C	-2.720259	-0.934950	0.063988
C	-2.655577	0.500486	-0.219783
C	-3.621385	1.386893	0.361522
C	-4.615169	0.844769	1.123256
C	-4.683339	-0.574383	1.351158
N	0.473922	-0.352342	-0.976457
N	2.674684	0.646096	0.239742
O	1.132005	-2.496908	-0.591291
H	-1.505145	-2.556142	-0.493200
H	1.316747	1.184702	-2.175732
H	-3.837361	-2.532144	1.042767
H	3.320315	-0.665772	-1.298334
H	4.122081	-2.325160	0.253641
H	2.917386	-1.877840	1.470523
H	5.371984	-0.244943	0.608806
H	4.910962	-0.670994	2.262627
H	4.205211	1.783673	1.159792
H	3.109848	0.956902	2.279703
H	-0.748162	2.278716	-2.218935
H	-0.609577	2.590263	-0.483680
H	-1.050071	-0.923941	-2.345653
H	-3.562730	2.452737	0.170325
H	-5.375267	1.477656	1.567687
H	-5.495508	-0.952256	1.965084

TS from SI-C-III to SI-C-IV

1 1			
N	0.282788	0.644691	-1.446866
C	-3.035039	-0.389201	1.421128
O	-3.531108	0.407198	2.215769
C	-1.531379	-0.715268	1.398055
C	-0.269550	3.011137	-2.043863
C	-3.112645	-1.999073	-0.483448
C	-4.183456	-2.123295	-1.577146
C	-5.499021	-1.963915	-0.793860
C	-5.175577	-0.904735	0.271996
C	-1.759754	-1.474374	-0.968661
C	-0.636728	0.371172	2.049927
C	0.190495	0.889011	0.886202
C	0.220127	-0.147416	-0.237137
C	-0.018186	1.949740	-1.162944
C	-0.057927	2.147597	0.250339
C	-0.353364	3.418641	0.782611
C	-0.596875	4.464374	-0.090186
C	-0.552690	4.252805	-1.489209
N	-1.066862	-0.816354	-0.001759

N	-3.729250	-1.076520	0.490697
O	-1.346541	-1.626115	-2.116799
H	0.063298	0.197034	-2.328912
H	-1.390797	-1.677693	1.908673
H	-0.249759	2.864305	-3.118668
H	-2.936877	-2.979302	-0.011989
H	-4.109473	-3.071746	-2.112988
H	-4.058485	-1.313680	-2.303678
H	-5.768343	-2.910457	-0.312289
H	-6.333961	-1.662946	-1.431453
H	-5.719284	-1.047853	1.209713
H	-5.373795	0.114107	-0.081442
H	-0.037598	-0.066421	2.846452
H	-1.260423	1.155482	2.483610
H	1.042700	-0.869174	-0.197649
H	-0.386353	3.569928	1.857523
H	-0.827775	5.452743	0.292730
H	-0.754449	5.089075	-2.152370
N	4.420825	0.137988	-1.342505
C	2.951644	1.204971	0.387142
C	5.123178	-3.304831	-0.128381
C	4.678623	-1.892112	-0.363693
C	4.999878	-1.093182	-1.454821
C	3.701266	0.187841	-0.163676
C	3.855940	-1.090782	0.472363
C	3.234678	-1.307586	1.730636
C	2.494841	-0.296450	2.296499
C	2.275395	0.950977	1.616826
H	4.509435	0.887728	-2.014137
H	2.853375	2.168753	-0.102255
H	4.268135	-3.987492	-0.054004
H	5.760536	-3.656043	-0.944905
H	5.616076	-1.332193	-2.311271
H	3.370866	-2.250598	2.251348
H	2.063810	-0.436985	3.282400
H	1.971117	1.806099	2.212811
H	5.693454	-3.396254	0.803823

Compound SI-C-IV

1 1			
N	0.168642	0.394571	-1.466474
C	-3.072888	-0.431485	1.424746
O	-3.381382	0.357176	2.316885
C	-1.668132	-1.048162	1.294805
C	-0.641526	2.772177	-1.691039
C	-3.515386	-1.785976	-0.618621
C	-4.618686	-1.589365	-1.668184
C	-5.857771	-1.263766	-0.815443
C	-5.306373	-0.403603	0.333660
C	-2.101522	-1.468799	-1.111697
C	-0.555606	-0.271073	2.021804
C	0.352193	0.311056	0.910478
C	0.094140	-0.550155	-0.364885
C	-0.231841	1.646064	-0.976878
C	-0.112376	1.676774	0.422680

C	-0.388286	2.842772	1.128523
C	-0.798885	3.981136	0.423350
C	-0.923516	3.937355	-0.969907
N	-1.259926	-1.080984	-0.119984
N	-3.917616	-0.872197	0.469045
O	-1.773660	-1.547210	-2.296960
H	-0.245371	0.055398	-2.330422
H	-1.730707	-2.073238	1.686633
H	-0.742231	2.744607	-2.772042
H	-3.518144	-2.826036	-0.254411
H	-4.745298	-2.472641	-2.297613
H	-4.356684	-0.747306	-2.317050
H	-6.294573	-2.186115	-0.416554
H	-6.634128	-0.743444	-1.382000
H	-5.844700	-0.536664	1.276164
H	-5.311186	0.665698	0.090407
H	-0.017079	-0.941926	2.691280
H	-0.997211	0.517358	2.634675
H	0.800398	-1.372166	-0.512287
H	-0.302018	2.873679	2.211940
H	-1.028041	4.896268	0.960380
H	-1.250461	4.823887	-1.506250
N	4.779457	0.844622	-1.151920
C	2.714170	0.992737	0.227382
C	6.429390	-2.348788	-0.210321
C	5.543922	-1.148574	-0.366203
C	5.758958	-0.070808	-1.249783
C	3.862599	0.415356	-0.193826
C	4.352643	-0.851884	0.303651
C	3.599154	-1.529113	1.315608
C	2.451074	-0.974347	1.775609
C	1.902901	0.336331	1.294319
H	4.719801	1.701220	-1.687705
H	2.371589	1.940826	-0.173234
H	5.915727	-3.264608	-0.524454
H	7.334612	-2.248246	-0.814988
H	6.578373	0.069944	-1.943049
H	3.956770	-2.473638	1.712877
H	1.905312	-1.482826	2.561932
H	1.937171	1.026408	2.159582
H	6.734403	-2.483403	0.833155

Figure S23B Radical C2 TS

O 2

N	2.714778	-0.758670	1.803598
C	3.944439	-2.701281	0.772631
C	3.440973	2.172721	-0.375352
C	3.276231	0.843215	0.290893
C	2.468096	0.569027	1.427761
C	3.507543	-1.378260	0.861669
C	3.875989	-0.388977	-0.102480
C	4.717248	-0.762373	-1.171968
C	5.159781	-2.077524	-1.256967
C	4.776917	-3.036769	-0.296497
H	2.315984	-1.212909	2.610401

H	3.652981	-3.442190	1.512097
H	2.896273	2.223553	-1.327301
H	3.068620	2.984899	0.255797
H	2.249127	1.288281	2.208969
H	5.012467	-0.030086	-1.918835
H	5.808033	-2.375661	-2.076517
H	5.137357	-4.057695	-0.388453
H	4.497292	2.372197	-0.597641
N	0.237898	0.592625	-1.530339
C	-2.907903	-0.400917	1.474694
O	-3.284239	0.382243	2.346842
C	-1.451716	-0.875370	1.333131
C	-0.345976	3.014071	-1.872188
C	-3.263977	-1.865202	-0.510805
C	-4.400168	-1.801877	-1.540997
C	-5.648013	-1.567559	-0.671164
C	-5.156194	-0.628298	0.442965
C	-1.891573	-1.441454	-1.044418
C	-0.402941	0.059412	1.987616
C	0.384180	0.643635	0.827352
C	0.236410	-0.285853	-0.376624
C	-0.035763	1.893012	-1.105712
C	0.073350	1.972228	0.306369
C	-0.120897	3.199507	0.947371
C	-0.423074	4.332120	0.182392
C	-0.534593	4.235436	-1.210224
N	-1.073428	-0.942483	-0.091731
N	-3.727211	-0.956552	0.555517
O	-1.588171	-1.541287	-2.237306
H	-0.199164	0.223267	-2.367341
H	-1.399270	-1.880670	1.776458
H	-0.444551	2.943542	-2.952049
H	-3.169362	-2.888904	-0.113658
H	-4.456364	-2.710294	-2.144656
H	-4.229093	-0.958139	-2.217519
H	-5.989578	-2.514767	-0.238440
H	-6.480858	-1.137123	-1.233309
H	-5.660140	-0.786924	1.400823
H	-5.271793	0.428904	0.174379
H	0.220693	-0.525185	2.672244
H	-0.909953	0.826679	2.577619
H	1.003690	-1.060712	-0.475237
H	-0.051309	3.271986	2.030270
H	-0.578874	5.289279	0.671972
H	-0.777407	5.120568	-1.792375

Figure S23B Radical C2 Product

O 2

N	1.989245	-1.239008	1.313234
C	3.473386	-3.169335	0.716716
C	3.540872	1.671307	-0.564656
C	3.104180	0.371460	0.027350
C	2.010592	0.216728	1.068173
C	3.051171	-1.848357	0.654952
C	3.701829	-0.886102	-0.182984

C	4.780775	-1.309937	-0.996541
C	5.196149	-2.637831	-0.938317
C	4.557580	-3.557643	-0.089115
H	1.767606	-1.556833	2.248179
H	2.978469	-3.884855	1.367961
H	2.857418	2.025325	-1.348168
H	3.585354	2.465202	0.191765
H	2.289873	0.757330	1.991105
H	5.285297	-0.603088	-1.649460
H	6.027721	-2.967990	-1.555100
H	4.902858	-4.587232	-0.054931
H	4.535298	1.576800	-1.014210
N	0.054983	1.282895	-1.599473
C	-2.825086	-0.758997	1.480920
O	-3.163962	-0.402773	2.610191
C	-1.360601	-0.775411	1.035390
C	-0.075611	3.778144	-1.343442
C	-3.319260	-1.578969	-0.829262
C	-4.605521	-1.332591	-1.630673
C	-5.709313	-1.657777	-0.608692
C	-5.154541	-1.133735	0.728457
C	-2.085615	-0.844045	-1.348495
C	-0.482044	0.268094	1.739982
C	0.580212	0.729453	0.687629
C	0.091414	0.154869	-0.687664
C	0.123273	2.475322	-0.881381
C	0.510267	2.230003	0.447543
C	0.712971	3.287724	1.324982
C	0.529376	4.602623	0.870839
C	0.134092	4.835037	-0.449748
N	-1.229104	-0.431690	-0.386474
N	-3.695847	-1.169960	0.533679
O	-1.899690	-0.662650	-2.555131
H	-0.557035	1.185508	-2.400915
H	-0.961399	-1.786217	1.210227
H	-0.381662	3.966355	-2.368775
H	-3.076206	-2.654331	-0.842107
H	-4.651417	-1.947840	-2.531490
H	-4.650210	-0.281142	-1.934836
H	-5.861322	-2.741590	-0.553016
H	-6.668689	-1.199157	-0.861746
H	-5.442932	-1.748148	1.586592
H	-5.467528	-0.103657	0.935504
H	-0.030474	-0.141514	2.646563
H	-1.101879	1.113139	2.046043
H	0.741093	-0.634175	-1.079566
H	1.000551	3.103364	2.357720
H	0.686573	5.437210	1.547731
H	-0.016360	5.855066	-0.794077

Figure S23B Radical C3 TS

O 2

N	0.447129	-0.050752	-1.463984
C	-2.919196	0.064156	1.391562
O	-3.069446	0.981014	2.199269

C	-1.681680	-0.848689	1.358796
C	0.432169	2.417325	-1.926838
C	-3.624041	-1.350042	-0.533532
C	-4.653126	-1.027837	-1.626119
C	-5.798378	-0.360273	-0.843508
C	-5.080094	0.471348	0.231716
C	-2.167901	-1.383875	-1.012064
C	-0.423670	-0.261870	2.040114
C	0.532824	0.072416	0.904651
C	0.176172	-0.839192	-0.278918
C	0.459264	1.297197	-1.099579
C	0.516954	1.418296	0.311660
C	0.528380	2.693363	0.887576
C	0.505890	3.825073	0.063145
C	0.462844	3.684735	-1.328539
N	-1.276147	-1.106091	-0.035884
N	-3.831531	-0.272010	0.453051
O	-1.863848	-1.627522	-2.184545
H	-0.052308	-0.338151	-2.298742
H	-1.972600	-1.794855	1.839003
H	0.376462	2.311518	-3.007005
H	-3.851476	-2.325535	-0.073554
H	-4.964758	-1.921436	-2.171464
H	-4.211343	-0.331702	-2.346512
H	-6.425497	-1.123445	-0.368620
H	-6.442145	0.254647	-1.477976
H	-5.643138	0.557146	1.165626
H	-4.849992	1.486068	-0.116033
H	-0.000523	-1.012651	2.715608
H	-0.701616	0.611284	2.634449
H	0.703220	-1.796382	-0.313830
H	0.529356	2.810309	1.968158
H	0.510958	4.816278	0.507875
H	0.440197	4.569781	-1.959140
N	3.023256	-2.520003	0.761753
C	4.345167	-1.839888	-1.275953
C	2.595827	0.538547	2.718180
C	2.455057	-0.435447	1.562229
C	2.428802	-1.843286	1.805852
C	3.592786	-1.614714	-0.121489
C	3.315026	-0.312569	0.361432
C	3.842223	0.789425	-0.314993
C	4.611506	0.578233	-1.462746
C	4.850815	-0.721190	-1.939409
H	3.072101	-3.524513	0.675478
H	4.541509	-2.845915	-1.636235
H	2.443103	1.570813	2.393442
H	1.878381	0.321957	3.516206
H	1.992531	-2.384995	2.632677
H	3.655381	1.798087	0.041785
H	5.028020	1.428694	-1.995186
H	5.447623	-0.861390	-2.836713
H	3.602236	0.470984	3.149023

Figure S23B Radical C3 Product

O 2			
N	0.442596	0.602631	-1.589954
C	-3.028602	-0.247998	1.423820
O	-3.317107	0.319119	2.478258
C	-1.605899	-0.718472	1.104887
C	0.778510	3.085074	-1.621083
C	-3.598796	-1.165592	-0.829944
C	-4.720882	-0.679973	-1.759144
C	-5.926846	-0.573930	-0.809117
C	-5.323930	-0.061016	0.511068
C	-2.184661	-0.846851	-1.311103
C	-0.503301	0.086440	1.810536
C	0.673967	0.236666	0.788442
C	0.139993	-0.369504	-0.560733
C	0.688146	1.838582	-0.997502
C	0.888949	1.696262	0.387943
C	1.157671	2.821262	1.161748
C	1.257560	4.079353	0.549124
C	1.070580	4.201565	-0.830450
N	-1.305193	-0.565070	-0.323528
N	-3.926054	-0.517894	0.450625
O	-1.892059	-0.862442	-2.510668
H	-0.119223	0.536644	-2.430852
H	-1.529901	-1.780936	1.384798
H	0.618235	3.184245	-2.691149
H	-3.657708	-2.261141	-0.720071
H	-4.883545	-1.361988	-2.596083
H	-4.456806	0.301702	-2.167348
H	-6.373685	-1.563064	-0.657942
H	-6.707652	0.090338	-1.188506
H	-5.821477	-0.462918	1.398775
H	-5.345829	1.032798	0.582921
H	-0.198844	-0.416146	2.729582
H	-0.894146	1.065210	2.094497
H	0.586052	-1.338718	-0.802358
H	1.274154	2.737876	2.238752
H	1.470489	4.958049	1.150914
H	1.141970	5.179421	-1.299917
N	2.532660	-2.803257	0.853636
C	4.300414	-2.486202	-0.902060
C	2.575398	0.132571	2.545264
C	1.971222	-0.536751	1.283901
C	1.633878	-2.000294	1.549537
C	3.333605	-2.051525	0.007668
C	3.055322	-0.683295	0.207902
C	3.788820	0.268137	-0.490486
C	4.768980	-0.148962	-1.404633
C	5.013380	-1.511536	-1.606447
H	2.491810	-3.812027	0.837811
H	4.497850	-3.544313	-1.049953
H	2.948995	1.136265	2.322129
H	1.842098	0.208655	3.356133
H	1.227817	-2.373022	2.483603
H	3.603993	1.327259	-0.339603
H	5.339311	0.591432	-1.958020

H	5.773491	-1.822721	-2.318388
H	3.416936	-0.465251	2.909292

Figure S23B Radical C4 TS

O 2			
N	4.424266	-2.387935	-0.475959
C	3.829139	-0.678768	-2.227623
C	3.570014	-0.895868	2.811526
C	3.761834	-1.267700	1.369207
C	4.373517	-2.414673	0.901565
C	3.870874	-1.208372	-0.927611
C	3.418715	-0.493148	0.209947
C	2.756752	0.777899	0.033154
C	2.884204	1.364187	-1.276345
C	3.348154	0.634221	-2.366135
H	4.873999	-3.081719	-1.054529
H	4.204861	-1.236537	-3.080288
H	2.512983	-0.770922	3.075051
H	3.985680	-1.664654	3.471261
H	4.786768	-3.248643	1.452181
H	2.747938	1.457244	0.882528
H	2.531591	2.379965	-1.425442
H	3.358867	1.097370	-3.349539
N	-0.357798	1.494762	-1.668088
C	-2.159326	-1.158956	1.376040
O	-2.162976	-0.887492	2.576758
C	-0.876004	-1.327171	0.545227
C	-1.067118	3.656173	-0.596666
C	-3.265338	-1.654156	-0.800889
C	-4.698325	-1.316620	-1.236205
C	-5.532464	-1.648771	0.014053
C	-4.636573	-1.216548	1.186741
C	-2.174469	-0.846766	-1.513142
C	0.379959	-0.651770	1.144703
C	0.672125	0.528246	0.234648
C	0.071165	0.212965	-1.141978
C	-0.476288	2.393858	-0.607098
C	0.145545	1.863390	0.548933
C	0.185985	2.619626	1.722579
C	-0.400903	3.890530	1.740413
C	-1.019562	4.397864	0.591460
N	-1.045890	-0.707738	-0.783066
N	-3.277668	-1.368299	0.646857
O	-2.339530	-0.363627	-2.637887
H	-1.077210	1.455556	-2.382079
H	-0.710920	-2.408486	0.429422
H	-1.555904	4.052243	-1.482637
H	-3.059256	-2.723719	-0.968918
H	-5.000693	-1.880290	-2.121499
H	-4.761491	-0.250784	-1.478499
H	-5.722245	-2.726957	0.065748
H	-6.499070	-1.138266	0.025124
H	-4.761781	-1.833040	2.081638
H	-4.805484	-0.171172	1.473151
H	1.207346	-1.366087	1.146789

H	0.181184	-0.351989	2.176408
H	0.743163	-0.291778	-1.842301
H	0.655124	2.219821	2.618542
H	-0.380090	4.483189	2.650543
H	-1.476373	5.383781	0.618164
H	4.071011	0.051272	3.050982

Figure S23B Radical C4 Product

O 2

N	0.429591	1.847117	-1.472722
C	-2.415722	-0.558557	1.366240
O	-2.556133	-0.519859	2.589808
C	-1.036369	-0.633979	0.712787
C	0.959831	4.131102	-0.579543
C	-3.311789	-0.588914	-0.969665
C	-4.609809	0.071985	-1.454506
C	-5.633458	-0.379319	-0.397447
C	-4.844692	-0.368508	0.925188
C	-2.026912	0.067444	-1.469099
C	0.065421	0.081498	1.502320
C	1.114058	0.552701	0.448042
C	0.359624	0.504398	-0.931188
C	0.895394	2.736861	-0.512551
C	1.392779	2.042567	0.604859
C	1.973186	2.736980	1.658052
C	2.056489	4.136882	1.598651
C	1.546913	4.818097	0.489617
N	-1.004338	0.051684	-0.586415
N	-3.447917	-0.544599	0.495228
O	-1.948271	0.555433	-2.600695
H	-0.272844	2.105200	-2.153858
H	-0.780719	-1.696406	0.578690
H	0.568745	4.666870	-1.440142
H	-3.284237	-1.637620	-1.309176
H	-4.869931	-0.232050	-2.470414
H	-4.490828	1.160988	-1.445471
H	-5.978583	-1.395307	-0.620109
H	-6.512517	0.269025	-0.355217
H	-5.140368	-1.168554	1.610655
H	-4.940779	0.582463	1.462020
H	0.497702	-0.551977	2.273595
H	-0.369058	0.948983	2.004822
H	0.790957	-0.213523	-1.634662
H	2.353011	2.205306	2.527855
H	2.510188	4.688718	2.416725
H	1.605630	5.902985	0.451149
N	2.237110	-3.722913	-0.951601
C	3.197737	-1.704071	-2.077442
C	1.481124	-2.842750	2.554984
C	1.812794	-2.863470	1.085847
C	1.821338	-4.023461	0.319736
C	2.538940	-2.379789	-1.026546
C	2.239320	-1.803624	0.226398
C	2.450248	-0.319516	0.441137
C	3.378898	0.244682	-0.615751

C	3.651610	-0.390425	-1.800823
H	2.408747	-4.397622	-1.682658
H	3.429284	-2.199806	-3.014666
H	0.422213	-2.637864	2.757524
H	1.708829	-3.812705	3.010419
H	1.572271	-5.037227	0.600879
H	2.887779	-0.148904	1.437860
H	3.754970	1.248708	-0.446791
H	4.254678	0.120049	-2.548351
H	2.067251	-2.086215	3.089210

Figure S23B Radical C5 TS

O 2

N	-0.101160	1.075050	-1.595294
C	-2.634826	-0.841903	1.480686
O	-3.027726	-0.244309	2.482553
C	-1.148922	-1.052269	1.143191
C	-1.143840	3.359616	-1.466511
C	-2.974536	-2.090830	-0.647401
C	-4.215547	-2.114021	-1.550507
C	-5.379202	-2.195177	-0.545996
C	-4.921748	-1.313823	0.627976
C	-1.762490	-1.364260	-1.240176
C	-0.179067	-0.064729	1.833040
C	0.365737	0.814962	0.715844
C	0.206899	0.056678	-0.608475
C	-0.541743	2.221640	-0.932756
C	-0.260862	2.120049	0.450754
C	-0.573972	3.181622	1.301847
C	-1.173034	4.331763	0.772882
C	-1.453912	4.413656	-0.595887
N	-0.925180	-0.865815	-0.303800
N	-3.456099	-1.409659	0.570012
O	-1.594514	-1.242881	-2.457900
H	-0.584483	0.747419	-2.424483
H	-0.903387	-2.087792	1.422180
H	-1.371981	3.426689	-2.526829
H	-2.664056	-3.119299	-0.401385
H	-4.193147	-2.947985	-2.255453
H	-4.259859	-1.185688	-2.129262
H	-5.513833	-3.228780	-0.207261
H	-6.328048	-1.855970	-0.969881
H	-5.287602	-1.657666	1.599832
H	-5.229233	-0.268010	0.504837
H	0.615116	-0.628748	2.329375
H	-0.714090	0.509146	2.593439
H	1.075180	-0.535146	-0.914242
H	-0.369075	3.111510	2.367662
H	-1.425709	5.160453	1.428234
H	-1.925214	5.308032	-0.995249
N	4.964346	-0.875054	-1.497722
C	3.665182	1.247005	-1.033154
C	4.468458	-3.085458	1.449847
C	4.499768	-2.018875	0.396870
C	5.184403	-2.047829	-0.792547

C	4.128358	-0.061665	-0.772783
C	3.803362	-0.750726	0.431810
C	2.982992	-0.127564	1.378388
C	2.357267	1.128773	1.069481
C	2.833059	1.835002	-0.111928
H	5.361869	-0.656211	-2.398983
H	3.975205	1.780143	-1.928220
H	3.445220	-3.433148	1.644847
H	5.063246	-3.954468	1.149868
H	5.818102	-2.821139	-1.205153
H	2.800044	-0.600818	2.338799
H	2.094523	1.756385	1.920948
H	2.467255	2.841954	-0.287431
H	4.867837	-2.724811	2.407226

Figure S23B Radical C5 Product

O 2

N	-0.119646	1.561815	-1.593199
C	-2.566201	-0.986770	1.471354
O	-2.933168	-0.710083	2.613940
C	-1.125206	-0.772092	1.000120
C	-0.637102	3.996132	-1.256340
C	-2.977170	-1.818510	-0.850751
C	-4.302269	-1.755607	-1.623986
C	-5.323195	-2.264699	-0.591097
C	-4.828200	-1.685967	0.746572
C	-1.883920	-0.887723	-1.371243
C	-0.394923	0.368412	1.723824
C	0.544111	1.032546	0.665291
C	0.121809	0.429676	-0.719717
C	-0.223348	2.728643	-0.839826
C	0.217889	2.507042	0.476507
C	0.266436	3.557694	1.383937
C	-0.135379	4.838958	0.976396
C	-0.585870	5.045234	-0.330731
N	-1.079422	-0.373706	-0.413784
N	-3.383874	-1.504345	0.528862
O	-1.757492	-0.647443	-2.575662
H	-0.724940	1.392185	-2.387333
H	-0.579287	-1.719172	1.134956
H	-0.987019	4.163551	-2.271307
H	-2.571036	-2.842574	-0.895829
H	-4.272245	-2.352491	-2.537757
H	-4.512438	-0.717494	-1.903564
H	-5.306588	-3.359902	-0.555162
H	-6.346269	-1.954030	-0.818353
H	-5.008144	-2.348846	1.598187
H	-5.285138	-0.716118	0.976168
H	0.149428	0.000561	2.596088
H	-1.129246	1.091080	2.085058
H	0.881610	-0.231545	-1.148905
H	0.601286	3.390224	2.405337
H	-0.102490	5.666817	1.678685
H	-0.904798	6.037662	-0.639278
N	4.877130	-1.518144	-1.253233

C	3.870665	0.770679	-0.813812
C	3.307284	-3.857672	1.168853
C	3.775887	-2.723282	0.309042
C	4.717496	-2.773547	-0.690004
C	4.036271	-0.631718	-0.626503
C	3.315358	-1.349403	0.368499
C	2.391184	-0.693061	1.177647
C	2.080935	0.773358	0.984825
C	2.968760	1.437387	-0.047111
H	5.511997	-1.295703	-2.005333
H	4.471528	1.300573	-1.549658
H	2.226988	-4.027615	1.064732
H	3.816646	-4.790674	0.905935
H	5.294901	-3.612757	-1.053355
H	1.888266	-1.229156	1.977190
H	2.224874	1.299173	1.948590
H	2.845495	2.508363	-0.176231
H	3.494781	-3.665491	2.233899

Figure S23B Radical C6 TS

O 2

N	0.265708	0.489845	-1.431330
C	-3.102061	-0.299133	1.399508
O	-3.569103	0.553118	2.155126
C	-1.626946	-0.733673	1.418794
C	-0.303932	2.861026	-2.044520
C	-3.256682	-1.963198	-0.448991
C	-4.309087	-2.047212	-1.563253
C	-5.628170	-1.769166	-0.820289
C	-5.252241	-0.703634	0.222744
C	-1.859650	-1.542618	-0.916885
C	-0.658815	0.290992	2.059553
C	0.237476	0.763580	0.922416
C	0.185109	-0.276263	-0.201179
C	-0.049512	1.820228	-1.152825
C	-0.055024	2.034553	0.246374
C	-0.303496	3.312377	0.751533
C	-0.553996	4.364950	-0.137298
C	-0.554612	4.135698	-1.518381
N	-1.135600	-0.922788	0.040417
N	-3.829957	-0.971780	0.481196
O	-1.458994	-1.748919	-2.066965
H	-0.111076	0.036184	-2.256286
H	-1.583391	-1.690948	1.959163
H	-0.314333	2.688517	-3.117350
H	-3.161243	-2.938052	0.056518
H	-4.292303	-3.014701	-2.069735
H	-4.108421	-1.272667	-2.310731
H	-5.976438	-2.678506	-0.317294
H	-6.425347	-1.429515	-1.486781
H	-5.828344	-0.778003	1.149628
H	-5.371031	0.315547	-0.165134
H	-0.094538	-0.195297	2.859205
H	-1.231016	1.109055	2.503659
H	0.967053	-1.041636	-0.163663

H	-0.316232	3.486458	1.825023
H	-0.753941	5.361395	0.246319
H	-0.756964	4.958333	-2.199461
N	4.612971	0.341156	-1.222571
C	3.001693	1.230941	0.487554
C	5.364913	-3.165980	-0.245745
C	4.885589	-1.753666	-0.409610
C	5.248712	-0.871348	-1.406146
C	3.807945	0.267939	-0.101945
C	3.969451	-1.046907	0.435380
C	3.288990	-1.369186	1.637875
C	2.470190	-0.435282	2.228870
C	2.195451	0.850824	1.614223
H	4.686095	1.135361	-1.840357
H	2.917798	2.229792	0.070476
H	4.533512	-3.882529	-0.266057
H	6.059179	-3.441529	-1.046287
H	5.921990	-1.016140	-2.240212
H	3.444542	-2.336684	2.109677
H	1.995766	-0.670620	3.177130
H	1.897289	1.653397	2.287298
H	5.886538	-3.310882	0.709442

Figure S23B Radical C6 Product

O 2

N	0.098901	1.051300	-1.574953
C	-3.065573	-0.584440	1.445621
O	-3.536363	-0.054982	2.452857
C	-1.558598	-0.638766	1.176721
C	-0.102977	3.550690	-1.712833
C	-3.278238	-1.784768	-0.736549
C	-4.466217	-1.720217	-1.707018
C	-5.677065	-1.903360	-0.774946
C	-5.288394	-1.140623	0.504459
C	-2.005637	-1.099597	-1.230571
C	-0.767619	0.515645	1.809384
C	0.387181	0.857149	0.812919
C	0.063664	0.071998	-0.505960
C	0.068491	2.337354	-1.041991
C	0.303493	2.303019	0.343569
C	0.386173	3.484933	1.068556
C	0.226188	4.711746	0.406382
C	-0.020450	4.734052	-0.969459
N	-1.268575	-0.515932	-0.258831
N	-3.816917	-1.169769	0.487644
O	-1.689917	-1.100503	-2.424007
H	-0.416806	0.815927	-2.414236
H	-1.184677	-1.605931	1.548713
H	-0.293906	3.575357	-2.782212
H	-3.016797	-2.837888	-0.540819
H	-4.398846	-2.480233	-2.488047
H	-4.489185	-0.737588	-2.190666
H	-5.819775	-2.966234	-0.549416
H	-6.606690	-1.527118	-1.209823
H	-5.671148	-1.604733	1.418309

H	-5.631258	-0.099353	0.489796
H	-0.401506	0.248634	2.803109
H	-1.427869	1.376228	1.933279
H	0.770914	-0.739261	-0.706337
H	0.561846	3.463945	2.141964
H	0.287716	5.641520	0.964383
H	-0.152437	5.686520	-1.476646
N	4.827437	-0.008359	-0.944487
C	2.918302	0.852849	0.423305
C	5.141064	-3.633303	-0.185239
C	4.788338	-2.179008	-0.302936
C	5.424120	-1.244193	-1.105212
C	3.781910	-0.114483	-0.040617
C	3.749720	-1.484223	0.376989
C	2.773378	-1.867126	1.354234
C	1.887564	-0.960743	1.840349
C	1.818897	0.484585	1.389363
H	5.088543	0.832082	-1.437509
H	2.986814	1.882100	0.085806
H	4.306991	-4.280063	-0.486891
H	5.998766	-3.882851	-0.818355
H	6.260925	-1.369627	-1.778436
H	2.758423	-2.890319	1.724470
H	1.185055	-1.272397	2.608673
H	1.903544	1.126221	2.287369
H	5.399407	-3.906765	0.846009

Figure S23B Radical C7 TS

O 2

N	0.386068	0.191715	-1.353244
C	-3.155271	-0.096339	1.348101
O	-3.382903	0.697709	2.260983
C	-1.871220	-0.937647	1.258417
C	0.545559	2.693855	-1.518248
C	-3.718300	-1.264691	-0.781020
C	-4.700371	-0.816118	-1.872342
C	-5.911273	-0.312555	-1.066863
C	-5.285908	0.370975	0.160883
C	-2.241739	-1.198831	-1.183830
C	-0.672352	-0.371159	2.058354
C	0.348614	0.039240	1.008488
C	0.051977	-0.728508	-0.282873
C	0.452514	1.482184	-0.835397
C	0.454896	1.435447	0.581617
C	0.571753	2.620238	1.315549
C	0.680576	3.839722	0.635385
C	0.664244	3.869736	-0.765316
N	-1.404904	-1.009076	-0.139889
N	-4.011812	-0.342560	0.332770
O	-1.874395	-1.297701	-2.358773
H	-0.058778	0.014665	-2.246798
H	-2.124534	-1.947175	1.614073
H	0.527980	2.726275	-2.604102
H	-3.938046	-2.300766	-0.476181
H	-4.944901	-1.626942	-2.561921

H	-4.250300	-0.004208	-2.452854
H	-6.531190	-1.158601	-0.748981
H	-6.545317	0.370099	-1.638681
H	-5.895747	0.285297	1.064977
H	-5.091386	1.436504	-0.012380
H	-0.287220	-1.143139	2.730313
H	-1.003585	0.471491	2.670054
H	0.588750	-1.675937	-0.396137
H	0.564379	2.596983	2.402858
H	0.767270	4.766195	1.195729
H	0.740351	4.822866	-1.282063
N	3.611321	1.071033	0.338382
C	2.235848	-0.545954	1.722043
C	5.582662	-0.930910	-2.090340
C	4.686470	-0.368282	-1.027344
C	4.502335	0.956822	-0.716133
C	3.193768	-0.177239	0.717077
C	3.853323	-1.114263	-0.114565
C	3.640290	-2.493985	0.096675
C	2.805008	-2.889492	1.149947
C	2.174155	-1.957958	1.976037
H	3.242430	1.939949	0.697934
H	2.093083	0.127752	2.565023
H	5.021293	-1.527583	-2.821324
H	6.093569	-0.132025	-2.637923
H	4.945505	1.840011	-1.155455
H	4.138162	-3.235562	-0.521835
H	2.674044	-3.949330	1.354639
H	1.588711	-2.311218	2.819861
H	6.353788	-1.589169	-1.668442

Figure S23B Radical C7 Product

0 2

N	-0.362704	0.719051	1.495497
C	3.201568	-0.191986	-1.382528
O	3.543373	0.383114	-2.416451
C	1.754289	-0.622229	-1.126212
C	-0.867000	3.177414	1.488855
C	3.663799	-1.163535	0.874552
C	4.766879	-0.727454	1.849619
C	6.007810	-0.642745	0.943242
C	5.466995	-0.090573	-0.387866
C	2.243270	-0.810785	1.310440
C	0.708820	0.252182	-1.833110
C	-0.526245	0.320983	-0.877039
C	-0.041465	-0.275710	0.491478
C	-0.672575	1.930152	0.889578
C	-0.852043	1.757400	-0.495193
C	-1.243049	2.828847	-1.290417
C	-1.457708	4.083574	-0.697873
C	-1.263088	4.246666	0.677283
N	1.404759	-0.500098	0.295569
N	4.054412	-0.504466	-0.382832
O	1.905802	-0.825772	2.497499
H	0.157343	0.672499	2.362990

H	1.651685	-1.671791	-1.443680
H	-0.720895	3.311786	2.556904
H	3.693599	-2.258234	0.746783
H	4.880726	-1.427762	2.679516
H	4.518201	0.254884	2.265795
H	6.430140	-1.642395	0.790885
H	6.794215	-0.008465	1.360424
H	5.982040	-0.493837	-1.264833
H	5.524902	1.003018	-0.440344
H	0.457222	-0.145135	-2.818855
H	1.123314	1.250401	-1.986550
H	-0.513643	-1.232882	0.735495
H	-1.373449	2.703287	-2.363136
H	-1.764204	4.926922	-1.309454
H	-1.420976	5.222280	1.129791
N	-3.683986	0.624760	-0.137445
C	-1.774837	-0.464792	-1.467583
C	-5.652408	-2.021817	1.553105
C	-4.699766	-1.157507	0.780485
C	-4.721926	0.213803	0.679632
C	-2.972690	-0.463597	-0.563089
C	-3.584898	-1.602708	-0.018820
C	-3.101294	-2.901509	-0.345515
C	-2.032672	-2.998430	-1.263092
C	-1.423379	-1.895110	-1.818288
H	-3.443338	1.585701	-0.335334
H	-2.012358	0.082394	-2.398127
H	-5.136082	-2.614338	2.320025
H	-6.411282	-1.415688	2.059158
H	-5.393928	0.936542	1.121045
H	-3.560672	-3.792950	0.069669
H	-1.687158	-3.986279	-1.561264
H	-0.637467	-2.042771	-2.552896
H	-6.177008	-2.733859	0.902216

Figure S23D Cation C2 TS

1 1

N	2.499976	-0.990244	1.891234
C	3.435639	-3.004202	0.701729
C	3.577696	1.963163	-0.087487
C	3.256661	0.622452	0.476312
C	2.484858	0.372334	1.636940
C	3.183815	-1.638333	0.889507
C	3.662650	-0.646611	-0.020789
C	4.413694	-1.049876	-1.150710
C	4.665976	-2.395706	-1.332210
C	4.180834	-3.360826	-0.412445
H	2.148343	-1.428841	2.730211
H	3.069611	-3.748908	1.401218
H	2.786096	2.314671	-0.766134
H	3.682843	2.716738	0.698181
H	2.282227	1.067139	2.440126
H	4.786431	-0.313016	-1.855637
H	5.243533	-2.727758	-2.189123
H	4.401283	-4.409897	-0.586235

H	4.506021	1.930707	-0.665024
N	0.339368	0.613424	-1.506113
C	-2.957120	-0.227594	1.460535
O	-3.345914	0.571139	2.310807
C	-1.490321	-0.680302	1.356446
C	0.188921	3.057604	-2.004183
C	-3.261675	-1.731434	-0.509760
C	-4.377587	-1.687293	-1.563881
C	-5.642378	-1.454917	-0.718666
C	-5.181472	-0.496940	0.392063
C	-1.880927	-1.322386	-1.025795
C	-0.476265	0.300241	2.003848
C	0.356178	0.773043	0.828151
C	0.238298	-0.215373	-0.326998
C	0.283667	1.929148	-1.169915
C	0.299375	2.070341	0.258264
C	0.197518	3.353005	0.844467
C	0.096952	4.453831	0.018286
C	0.095324	4.297870	-1.392938
N	-1.096746	-0.764613	-0.065130
N	-3.748167	-0.807273	0.534380
O	-1.520689	-1.473789	-2.190846
H	0.125153	0.232310	-2.418643
H	-1.412095	-1.670367	1.825868
H	0.173704	2.955172	-3.083959
H	-3.171765	-2.748738	-0.096719
H	-4.413595	-2.603043	-2.157298
H	-4.201745	-0.848667	-2.245604
H	-5.982819	-2.400018	-0.281454
H	-6.467575	-1.038923	-1.301773
H	-5.698058	-0.650937	1.343329
H	-5.301059	0.555521	0.109117
H	0.102851	-0.214479	2.771517
H	-1.007979	1.125549	2.481909
H	0.988024	-1.015051	-0.349455
H	0.202489	3.462863	1.924597
H	0.017104	5.449191	0.441983
H	0.010927	5.183501	-2.015901

Figure S23D Cation C2 Product

1 1

N	2.554474	-0.993042	1.452018
C	4.388018	-2.482461	0.672844
C	3.089784	2.228897	-0.414888
C	3.049797	0.848364	0.130171
C	2.068813	0.353374	1.168725
C	3.621427	-1.296542	0.706688
C	3.953371	-0.164193	-0.130867
C	5.081263	-0.240639	-1.009408
C	5.808749	-1.397695	-1.033949
C	5.457697	-2.506452	-0.193212
H	2.158041	-1.602516	2.154145
H	4.142860	-3.329899	1.303178
H	2.250551	2.403755	-1.098097
H	2.995072	2.969089	0.386605

H	2.179891	0.972384	2.070681
H	5.340179	0.601584	-1.641696
H	6.666616	-1.493142	-1.690514
H	6.069373	-3.402375	-0.244115
H	4.020306	2.410129	-0.956619
N	0.201303	0.498093	-1.561376
C	-2.862096	-0.470295	1.470715
O	-3.145377	0.297484	2.388906
C	-1.447947	-1.042775	1.260581
C	-0.597631	2.884222	-1.685506
C	-3.365621	-1.810403	-0.567264
C	-4.526508	-1.635075	-1.556591
C	-5.730150	-1.362993	-0.636809
C	-5.149118	-0.500952	0.496242
C	-1.989041	-1.441996	-1.125944
C	-0.327222	-0.240940	1.943590
C	0.530149	0.365805	0.800055
C	0.214994	-0.471319	-0.481314
C	-0.156425	1.738016	-1.020982
C	0.055982	1.743130	0.368491
C	-0.160867	2.896898	1.113405
C	-0.598835	4.053677	0.457157
C	-0.814006	4.038301	-0.926157
N	-1.109714	-1.041704	-0.171504
N	-3.740269	-0.924423	0.552994
O	-1.718038	-1.492948	-2.326384
H	-0.262455	0.175547	-2.405761
H	-1.459641	-2.074466	1.639507
H	-0.768665	2.878818	-2.757778
H	-3.317807	-2.854771	-0.218824
H	-4.656638	-2.513045	-2.192631
H	-4.325135	-0.775632	-2.204207
H	-6.115322	-2.304923	-0.230607
H	-6.551152	-0.861210	-1.154987
H	-5.633210	-0.666059	1.462777
H	-5.201891	0.570920	0.270966
H	0.251334	-0.897688	2.596930
H	-0.760742	0.537183	2.574921
H	0.926078	-1.274185	-0.693864
H	-0.006529	2.905454	2.189538
H	-0.780205	4.961182	1.024264
H	-1.161599	4.939391	-1.423547

Figure S23D Cation C3 TS

1 1

N	0.465649	-0.138262	-1.452311
C	-3.020731	0.326576	1.356612
O	-3.203100	1.312602	2.068231
C	-1.734805	-0.517213	1.417682
C	0.917941	2.188723	-2.235191
C	-3.657099	-1.302943	-0.423011
C	-4.683985	-1.118653	-1.550182
C	-5.862549	-0.432496	-0.836938
C	-5.191757	0.519451	0.166591
C	-2.200459	-1.348306	-0.888583

C	-0.514906	0.228332	2.018432
C	0.464403	0.304445	0.859299
C	0.116246	-0.753992	-0.192986
C	0.719866	1.188696	-1.270322
C	0.721316	1.503274	0.125782
C	0.871360	2.844648	0.544105
C	1.060790	3.826429	-0.411374
C	1.091250	3.490281	-1.786578
N	-1.326166	-0.899850	0.050486
N	-3.908309	-0.143382	0.456035
O	-1.857636	-1.743139	-2.001353
H	0.131458	-0.546035	-2.316022
H	-1.956116	-1.417662	2.007000
H	0.915255	1.951418	-3.293842
H	-3.858636	-2.237914	0.123981
H	-4.952221	-2.069050	-2.015908
H	-4.262654	-0.469502	-2.324727
H	-6.465525	-1.175771	-0.303697
H	-6.520796	0.099005	-1.528595
H	-5.763563	0.655743	1.088508
H	-5.002445	1.510051	-0.263478
H	-0.128918	-0.314982	2.881045
H	-0.820462	1.220435	2.357250
H	0.616851	-1.721997	-0.092429
H	0.820990	3.100735	1.597491
H	1.174430	4.863099	-0.112689
H	1.236255	4.281542	-2.516506
N	2.577521	-2.461500	1.181431
C	3.887169	-2.340304	-0.980407
C	2.722199	0.876824	2.671192
C	2.511641	-0.255501	1.700420
C	2.170742	-1.572405	2.100814
C	3.279159	-1.813713	0.155697
C	3.286820	-0.436714	0.469170
C	3.957051	0.450669	-0.378850
C	4.581997	-0.062780	-1.516762
C	4.542659	-1.435256	-1.816167
H	2.405385	-3.459031	1.228852
H	3.862553	-3.402349	-1.202848
H	2.698068	1.844330	2.163160
H	1.970723	0.880621	3.466324
H	1.648351	-1.899309	2.989581
H	4.000646	1.512261	-0.157387
H	5.112453	0.610051	-2.183652
H	5.038022	-1.801634	-2.709910
H	3.707026	0.782766	3.143309

Figure S23D Cation C3 Product

1 1

N	0.408224	0.073579	-1.522427
C	-2.854963	-0.160231	1.394091
O	-2.947450	0.639026	2.324355
C	-1.646641	-1.096461	1.203386
C	0.167977	2.575367	-1.580712
C	-3.636092	-1.281384	-0.686362

C	-4.683848	-0.796182	-1.698397
C	-5.792396	-0.214069	-0.802799
C	-5.028754	0.453764	0.352199
C	-2.195324	-1.276996	-1.205047
C	-0.373100	-0.658629	1.942914
C	0.628587	-0.200716	0.850406
C	0.162081	-0.898565	-0.475339
C	0.327620	1.345161	-0.942956
C	0.468944	1.262655	0.453579
C	0.431641	2.417180	1.231186
C	0.277238	3.658790	0.601542
C	0.151405	3.728808	-0.790044
N	-1.270552	-1.151827	-0.217895
N	-3.792486	-0.339967	0.440849
O	-1.912805	-1.360959	-2.401067
H	-0.111757	-0.101878	-2.377361
H	-1.957658	-2.093882	1.545079
H	0.052760	2.634447	-2.658907
H	-3.872662	-2.305143	-0.354322
H	-5.029841	-1.604305	-2.346227
H	-4.243594	-0.020490	-2.333215
H	-6.426825	-1.019266	-0.415907
H	-6.434772	0.493062	-1.333480
H	-5.565007	0.426276	1.304710
H	-4.780083	1.499417	0.134384
H	0.014316	-1.494854	2.529826
H	-0.614592	0.145234	2.641411
H	0.664440	-1.843185	-0.707420
H	0.497395	2.365827	2.314324
H	0.241478	4.565326	1.197410
H	0.024164	4.695768	-1.268856
N	3.279584	-2.442758	0.540731
C	4.888867	-1.437774	-1.126739
C	2.540973	0.089187	2.592622
C	2.140083	-0.547603	1.227210
C	2.338375	-2.033147	1.335847
C	3.846976	-1.379906	-0.211214
C	3.179343	-0.207039	0.162023
C	3.598298	0.998508	-0.391706
C	4.643688	0.974359	-1.323651
C	5.276941	-0.220747	-1.690378
H	3.584511	-3.412413	0.473612
H	5.378991	-2.370786	-1.384382
H	2.498669	1.176147	2.497745
H	1.869928	-0.224864	3.395512
H	1.818307	-2.727410	1.983821
H	3.130149	1.936965	-0.118850
H	4.973606	1.907201	-1.770033
H	6.085347	-0.201801	-2.413824
H	3.563858	-0.189119	2.859873

Figure S23D Cation C4 TS

1 1

N	4.298010	-2.367940	-0.688516
C	3.702047	-0.471728	-2.221449

C	3.637287	-1.177807	2.764684
C	3.736452	-1.404997	1.283685
C	4.283446	-2.526713	0.665769
C	3.776986	-1.129653	-0.999540
C	3.394066	-0.513970	0.228662
C	2.778545	0.781418	0.185041
C	2.811338	1.475802	-1.070741
C	3.232684	0.856090	-2.237761
H	4.676868	-3.032490	-1.349295
H	4.026271	-0.953745	-3.139256
H	2.614417	-0.953466	3.086130
H	3.971405	-2.061439	3.315923
H	4.681324	-3.424527	1.118914
H	2.762441	1.371969	1.095564
H	2.457115	2.500233	-1.105890
H	3.200367	1.395090	-3.178497
N	-0.281475	1.500890	-1.621422
C	-2.151410	-1.171284	1.371974
O	-2.167042	-0.906769	2.572814
C	-0.849374	-1.330833	0.566313
C	-1.013364	3.664088	-0.593382
C	-3.207514	-1.642838	-0.836442
C	-4.635041	-1.315598	-1.298308
C	-5.489627	-1.666255	-0.067181
C	-4.624080	-1.231463	1.126470
C	-2.112700	-0.817720	-1.518607
C	0.387259	-0.658168	1.210311
C	0.643383	0.535524	0.313311
C	0.120948	0.215207	-1.093667
C	-0.423678	2.393269	-0.585881
C	0.144561	1.857133	0.604630
C	0.123874	2.601471	1.798227
C	-0.459474	3.858361	1.789239
C	-1.019478	4.377460	0.599617
N	-0.996546	-0.682987	-0.754010
N	-3.250271	-1.369807	0.614741
O	-2.239637	-0.317039	-2.634664
H	-0.891608	1.506175	-2.431173
H	-0.669528	-2.406609	0.437006
H	-1.453632	4.072295	-1.497233
H	-2.984763	-2.707397	-1.011383
H	-4.912349	-1.876861	-2.192932
H	-4.705336	-0.248784	-1.533810
H	-5.668683	-2.746368	-0.026562
H	-6.460945	-1.165539	-0.073372
H	-4.760494	-1.853509	2.015213
H	-4.805602	-0.188482	1.412209
H	1.222869	-1.358884	1.210022
H	0.164645	-0.370105	2.239480
H	0.826279	-0.283454	-1.764244
H	0.554153	2.194952	2.708878
H	-0.493068	4.449936	2.698044
H	-1.474594	5.363491	0.619424
H	4.265045	-0.333897	3.076264

Figure S23D Cation C4 Product

1	1		
N	-0.182866	1.410408	-1.593239
C	-2.171310	-1.147479	1.284026
O	-2.217552	-0.852837	2.477387
C	-0.856208	-1.408184	0.528025
C	-1.279151	3.375353	-0.458066
C	-3.160174	-1.643646	-0.945902
C	-4.552477	-1.279286	-1.479906
C	-5.470461	-1.542119	-0.272495
C	-4.635725	-1.091128	0.937232
C	-2.002859	-0.886620	-1.604510
C	0.404548	-0.825887	1.184156
C	0.798439	0.397447	0.330407
C	0.227680	0.109735	-1.096243
C	-0.532405	2.196345	-0.489489
C	0.042927	1.667546	0.679076
C	-0.109367	2.321108	1.897820
C	-0.856630	3.503234	1.942752
C	-1.432733	4.017375	0.773893
N	-0.904941	-0.795233	-0.809541
N	-3.251060	-1.310477	0.490554
O	-2.076579	-0.394022	-2.731041
H	-0.809540	1.376116	-2.392315
H	-0.757019	-2.498779	0.432145
H	-1.727391	3.779576	-1.360752
H	-2.974522	-2.722758	-1.068476
H	-4.817957	-1.865850	-2.361981
H	-4.567438	-0.221498	-1.761553
H	-5.695005	-2.611774	-0.194460
H	-6.419585	-1.004535	-0.339966
H	-4.836011	-1.666168	1.845495
H	-4.784017	-0.029615	1.169471
H	1.188474	-1.580168	1.162550
H	0.200699	-0.562538	2.224040
H	0.926097	-0.367175	-1.789098
H	0.329621	1.917156	2.806771
H	-0.995829	4.019449	2.887448
H	-2.015023	4.933262	0.822954
N	4.788363	-1.875832	-0.746704
C	4.120484	0.172593	-1.991158
C	3.321271	-1.578913	2.637634
C	3.686650	-1.444832	1.186448
C	4.594253	-2.295230	0.515444
C	4.046945	-0.721827	-0.948790
C	3.309941	-0.471885	0.251853
C	2.402784	0.714959	0.319814
C	2.643956	1.683686	-0.797651
C	3.423966	1.411815	-1.883103
H	5.429374	-2.291651	-1.410695
H	4.736324	-0.031894	-2.862620
H	2.602951	-2.388307	2.810688
H	4.210732	-1.799914	3.236338
H	5.116615	-3.160867	0.900592
H	2.555121	1.231913	1.276855

H	2.120910	2.630937	-0.740153
H	3.523582	2.138830	-2.681408
H	2.879350	-0.655884	3.022261

Figure S23D Cation C5 TS

1 1

N	0.034211	1.419583	-1.553938
C	-2.595557	-0.899215	1.486292
O	-2.997112	-0.515287	2.583426
C	-1.115574	-0.824743	1.084020
C	-0.469252	3.864005	-1.423320
C	-2.917877	-1.845496	-0.806772
C	-4.194963	-1.789239	-1.658794
C	-5.293459	-2.173880	-0.652290
C	-4.851220	-1.509459	0.662720
C	-1.767698	-0.984009	-1.323921
C	-0.314013	0.259816	1.846706
C	0.381383	1.049315	0.742640
C	0.205039	0.343735	-0.606138
C	-0.123085	2.607672	-0.901368
C	0.104341	2.435434	0.497557
C	-0.027144	3.527469	1.378249
C	-0.365025	4.764652	0.859418
C	-0.580616	4.921468	-0.531523
N	-0.996334	-0.452549	-0.338401
N	-3.386165	-1.420616	0.525506
O	-1.559656	-0.794446	-2.520703
H	-0.308117	1.217663	-2.484368
H	-0.667110	-1.814715	1.250305
H	-0.647885	3.998504	-2.484960
H	-2.545671	-2.881761	-0.759982
H	-4.139812	-2.457698	-2.520147
H	-4.342463	-0.769124	-2.029109
H	-5.327410	-3.262091	-0.530179
H	-6.286180	-1.841188	-0.965251
H	-5.115199	-2.088315	1.552114
H	-5.265699	-0.501714	0.781745
H	0.360629	-0.192023	2.572253
H	-0.998713	0.905981	2.400369
H	1.035039	-0.305973	-0.907057
H	0.139067	3.397478	2.443694
H	-0.470222	5.621999	1.515655
H	-0.849737	5.902322	-0.912799
N	4.399680	-1.598593	-1.501512
C	3.701324	0.759485	-0.995383
C	3.398306	-3.706549	1.400610
C	3.688279	-2.656290	0.372771
C	4.317682	-2.819297	-0.828589
C	3.832431	-0.624353	-0.752889
C	3.355274	-1.247232	0.454646
C	2.747218	-0.459375	1.416868
C	2.516148	0.921574	1.155725
C	3.066017	1.513964	-0.037797
H	4.831063	-1.468101	-2.406814
H	4.093655	1.208688	-1.902077

H	2.322272	-3.790053	1.597413
H	3.755477	-4.686080	1.070177
H	4.725643	-3.711899	-1.281542
H	2.435817	-0.890903	2.363296
H	2.342284	1.570889	2.008838
H	2.945236	2.581638	-0.188259
H	3.884690	-3.477151	2.356679

Figure S23D Cation C5 Product

1 1

N	-0.103391	0.956113	-1.625212
C	-2.710496	-0.836337	1.463792
O	-2.995079	-0.248235	2.505963
C	-1.264673	-1.175376	1.055788
C	-1.213604	3.197802	-1.315998
C	-3.247293	-1.936327	-0.705668
C	-4.514375	-1.785633	-1.559668
C	-5.644248	-1.805854	-0.514655
C	-5.061392	-1.035641	0.681373
C	-1.989766	-1.308456	-1.312004
C	-0.186857	-0.332480	1.760244
C	0.470547	0.536266	0.657624
C	0.131917	-0.145293	-0.708097
C	-0.562189	2.045973	-0.873506
C	-0.222050	1.880673	0.479202
C	-0.514633	2.873286	1.408089
C	-1.165336	4.035669	0.975964
C	-1.508666	4.187247	-0.372316
N	-1.077159	-0.925599	-0.382897
N	-3.613900	-1.274075	0.562188
O	-1.836515	-1.156985	-2.525045
H	-0.609511	0.694943	-2.466453
H	-1.111800	-2.242722	1.269899
H	-1.484723	3.321952	-2.360231
H	-3.036808	-3.002569	-0.523489
H	-4.599819	-2.577808	-2.306402
H	-4.485120	-0.826724	-2.087262
H	-5.869537	-2.837504	-0.221985
H	-6.567889	-1.353141	-0.883857
H	-5.425435	-1.391087	1.649335
H	-5.263120	0.040543	0.619489
H	0.526401	-0.988806	2.260675
H	-0.651165	0.285791	2.531208
H	0.910502	-0.808724	-1.096428
H	-0.256716	2.750453	2.457331
H	-1.409552	4.816104	1.689829
H	-2.019649	5.089693	-0.696356
N	5.589065	-0.220951	-1.100628
C	3.794289	1.486289	-0.790491
C	4.803174	-3.167643	1.044612
C	4.900888	-1.885739	0.280477
C	5.868913	-1.508463	-0.594202
C	4.459141	0.250338	-0.577398
C	3.956516	-0.771852	0.324653
C	2.800321	-0.550817	1.002076

C	2.044199	0.725599	0.855390
C	2.634162	1.697850	-0.117362
H	6.174978	0.268690	-1.767181
H	4.199652	2.224283	-1.474893
H	3.881363	-3.707361	0.797459
H	5.649247	-3.821165	0.817125
H	6.756477	-2.028379	-0.924340
H	2.424275	-1.300720	1.690102
H	2.113034	1.216668	1.846835
H	2.098671	2.629977	-0.255181
H	4.795755	-2.985517	2.125744

Figure S23D Cation C6 TS

1 1

N	0.282788	0.644691	-1.446866
C	-3.035039	-0.389201	1.421128
O	-3.531108	0.407198	2.215769
C	-1.531379	-0.715268	1.398055
C	-0.269550	3.011137	-2.043863
C	-3.112645	-1.999073	-0.483448
C	-4.183456	-2.123295	-1.577146
C	-5.499021	-1.963915	-0.793860
C	-5.175577	-0.904735	0.271996
C	-1.759754	-1.474374	-0.968661
C	-0.636728	0.371172	2.049927
C	0.190495	0.889011	0.886202
C	0.220127	-0.147416	-0.237137
C	-0.018186	1.949740	-1.162944
C	-0.057927	2.147597	0.250339
C	-0.353364	3.418641	0.782611
C	-0.596875	4.464374	-0.090186
C	-0.552690	4.252805	-1.489209
N	-1.066862	-0.816354	-0.001759
N	-3.729250	-1.076520	0.490697
O	-1.346541	-1.626115	-2.116799
H	0.063298	0.197034	-2.328912
H	-1.390797	-1.677693	1.908673
H	-0.249759	2.864305	-3.118668
H	-2.936877	-2.979302	-0.011989
H	-4.109473	-3.071746	-2.112988
H	-4.058485	-1.313680	-2.303678
H	-5.768343	-2.910457	-0.312289
H	-6.333961	-1.662946	-1.431453
H	-5.719284	-1.047853	1.209713
H	-5.373795	0.114107	-0.081442
H	-0.037598	-0.066421	2.846452
H	-1.260423	1.155482	2.483610
H	1.042700	-0.869174	-0.197649
H	-0.386353	3.569928	1.857523
H	-0.827775	5.452743	0.292730
H	-0.754449	5.089075	-2.152370
N	4.420825	0.137988	-1.342505
C	2.951644	1.204971	0.387142
C	5.123178	-3.304831	-0.128381
C	4.678623	-1.892112	-0.363693

C	4.999878	-1.093182	-1.454821
C	3.701266	0.187841	-0.163676
C	3.855940	-1.090782	0.472363
C	3.234678	-1.307586	1.730636
C	2.494841	-0.296450	2.296499
C	2.275395	0.950977	1.616826
H	4.509435	0.887728	-2.014137
H	2.853375	2.168753	-0.102255
H	4.268135	-3.987492	-0.054004
H	5.760536	-3.656043	-0.944905
H	5.616076	-1.332193	-2.311271
H	3.370866	-2.250598	2.251348
H	2.063810	-0.436985	3.282400
H	1.971117	1.806099	2.212811
H	5.693454	-3.396254	0.803823

Figure S23D Cation C6 Product

1 1

N	0.168642	0.394571	-1.466474
C	-3.072888	-0.431485	1.424746
O	-3.381382	0.357176	2.316885
C	-1.668132	-1.048162	1.294805
C	-0.641526	2.772177	-1.691039
C	-3.515386	-1.785976	-0.618621
C	-4.618686	-1.589365	-1.668184
C	-5.857771	-1.263766	-0.815443
C	-5.306373	-0.403603	0.333660
C	-2.101522	-1.468799	-1.111697
C	-0.555606	-0.271073	2.021804
C	0.352193	0.311056	0.910478
C	0.094140	-0.550155	-0.364885
C	-0.231841	1.646064	-0.976878
C	-0.112376	1.676774	0.422680
C	-0.388286	2.842772	1.128523
C	-0.798885	3.981136	0.423350
C	-0.923516	3.937355	-0.969907
N	-1.259926	-1.080984	-0.119984
N	-3.917616	-0.872197	0.469045
O	-1.773660	-1.547210	-2.296960
H	-0.245371	0.055398	-2.330422
H	-1.730707	-2.073238	1.686633
H	-0.742231	2.744607	-2.772042
H	-3.518144	-2.826036	-0.254411
H	-4.745298	-2.472641	-2.297613
H	-4.356684	-0.747306	-2.317050
H	-6.294573	-2.186115	-0.416554
H	-6.634128	-0.743444	-1.382000
H	-5.844700	-0.536664	1.276164
H	-5.311186	0.665698	0.090407
H	-0.017079	-0.941926	2.691280
H	-0.997211	0.517358	2.634675
H	0.800398	-1.372166	-0.512287
H	-0.302018	2.873679	2.211940
H	-1.028041	4.896268	0.960380
H	-1.250461	4.823887	-1.506250

N	4.779457	0.844622	-1.151920
C	2.714170	0.992737	0.227382
C	6.429390	-2.348788	-0.210321
C	5.543922	-1.148574	-0.366203
C	5.758958	-0.070808	-1.249783
C	3.862599	0.415356	-0.193826
C	4.352643	-0.851884	0.303651
C	3.599154	-1.529113	1.315608
C	2.451074	-0.974347	1.775609
C	1.902901	0.336331	1.294319
H	4.719801	1.701220	-1.687705
H	2.371589	1.940826	-0.173234
H	5.915727	-3.264608	-0.524454
H	7.334612	-2.248246	-0.814988
H	6.578373	0.069944	-1.943049
H	3.956770	-2.473638	1.712877
H	1.905312	-1.482826	2.561932
H	1.937171	1.026408	2.159582
H	6.734403	-2.483403	0.833155

Figure S23D Cation C7 TS

1 1

N	-0.527346	0.146970	1.286103
C	3.172773	0.085885	-1.319558
O	3.454134	0.941467	-2.156795
C	1.845911	-0.692482	-1.341597
C	-0.923877	2.576526	1.723200
C	3.611477	-1.279184	0.724723
C	4.571094	-0.960291	1.880368
C	5.829806	-0.455489	1.153495
C	5.279595	0.352766	-0.033354
C	2.127851	-1.198525	1.086885
C	0.706530	0.016135	-2.119050
C	-0.350081	0.271807	-1.055321
C	-0.110613	-0.644707	0.148886
C	-0.700278	1.447219	0.915843
C	-0.605750	1.569557	-0.504236
C	-0.733025	2.834221	-1.116589
C	-0.954194	3.941951	-0.317899
C	-1.046213	3.803730	1.090295
N	1.338490	-0.849788	0.036835
N	3.977120	-0.282273	-0.301119
O	1.695424	-1.419724	2.216437
H	-0.276105	-0.155293	2.219116
H	2.045845	-1.679390	-1.780700
H	-0.989035	2.487699	2.802483
H	3.803394	-2.295378	0.344566
H	4.753631	-1.832904	2.510634
H	4.138383	-0.173717	2.507328
H	6.419676	-1.303320	0.788059
H	6.474122	0.148339	1.797224
H	5.913058	0.307119	-0.923392
H	5.126270	1.408887	0.217919
H	0.355244	-0.616615	-2.933232
H	1.076584	0.948040	-2.551477

H	-0.638048	-1.604183	0.132544
H	-0.655878	2.932906	-2.195503
H	-1.050607	4.926012	-0.764193
H	-1.213348	4.691352	1.693528
N	-3.615715	0.934179	-0.224470
C	-2.238938	-0.350496	-1.901063
C	-5.024906	-1.526235	2.188425
C	-4.349514	-0.751561	1.098394
C	-4.364471	0.601002	0.908829
C	-3.116791	-0.188985	-0.786158
C	-3.552848	-1.291776	0.014268
C	-3.198665	-2.579233	-0.372326
C	-2.431945	-2.775954	-1.545785
C	-2.005459	-1.703170	-2.308078
H	-3.513594	1.872212	-0.588496
H	-2.167527	0.435453	-2.647088
H	-4.300645	-2.095980	2.783297
H	-5.563613	-0.857947	2.866280
H	-4.854184	1.378417	1.477599
H	-3.520538	-3.438635	0.209189
H	-2.195766	-3.787703	-1.859102
H	-1.450000	-1.884123	-3.222397
H	-5.746441	-2.245078	1.781654

Figure S23D Cation C7 Product

1 1

N	-0.389877	0.143650	1.390111
C	3.050916	-0.226684	-1.355094
O	3.194813	0.508531	-2.330615
C	1.825902	-1.140236	-1.163382
C	-0.245296	2.655794	1.321071
C	3.724612	-1.198254	0.837609
C	4.716151	-0.631846	1.864067
C	5.873344	-0.120993	0.987129
C	5.176221	0.450943	-0.258074
C	2.259511	-1.164795	1.279453
C	0.591279	-0.735558	-1.987940
C	-0.469930	-0.264977	-0.962592
C	-0.061694	-0.881347	0.414251
C	-0.312212	1.381815	0.750978
C	-0.378341	1.215857	-0.644451
C	-0.391986	2.323415	-1.489445
C	-0.335968	3.605053	-0.927128
C	-0.260425	3.759227	0.464273
N	1.386110	-1.101225	0.241347
N	3.940743	-0.344539	-0.347884
O	1.915697	-1.178240	2.462180
H	0.062618	0.024631	2.291979
H	2.139437	-2.160216	-1.426563
H	-0.188021	2.784162	2.397611
H	3.979633	-2.243180	0.598366
H	5.023488	-1.384909	2.592571
H	4.243792	0.191911	2.408973
H	6.526924	-0.952840	0.701774
H	6.486921	0.627846	1.494201

H	5.762485	0.343997	-1.174863
H	4.922932	1.511468	-0.141186
H	0.247527	-1.582815	-2.582876
H	0.858476	0.063139	-2.683060
H	-0.557209	-1.822894	0.664650
H	-0.436619	2.202233	-2.568963
H	-0.337830	4.478838	-1.570818
H	-0.209199	4.757879	0.888586
N	-3.309709	1.174502	-0.279515
C	-1.964776	-0.678065	-1.402894
C	-6.045628	-0.332426	1.747708
C	-4.882094	0.032276	0.879481
C	-4.416610	1.276251	0.585506
C	-3.036144	-0.100200	-0.543591
C	-4.018303	-0.884573	0.153046
C	-4.022192	-2.250520	-0.008487
C	-3.064556	-2.885460	-0.866912
C	-2.119253	-2.163820	-1.522970
H	-2.782199	1.967708	-0.629816
H	-2.062438	-0.257351	-2.416648
H	-5.733746	-0.969782	2.583291
H	-6.515751	0.562907	2.162822
H	-4.761147	2.250887	0.898453
H	-4.761619	-2.862981	0.500353
H	-3.112304	-3.961739	-0.992615
H	-1.419111	-2.680493	-2.169513
H	-6.807154	-0.882706	1.182687

Compound 6 Radical Cation

1	2		
N	3.619127	1.673002	0.931523
C	-1.733273	-1.099358	0.570575
O	-1.580032	-2.071640	1.312202
C	-0.534835	-0.204420	0.182028
C	5.078210	0.312828	-0.611681
C	-3.137632	0.386325	-0.872211
C	-4.610126	0.742506	-0.627587
C	-5.248062	-0.635664	-0.374518
C	-4.176133	-1.421170	0.405296
C	-2.148826	1.522737	-0.668350
C	0.484949	-0.227703	1.351284
C	1.834238	0.285755	0.991920
C	2.402535	1.516279	1.450478
C	3.936560	0.574921	0.111790
C	2.821250	-0.304333	0.147473
C	2.878742	-1.511649	-0.579267
C	4.030813	-1.792945	-1.321724
C	5.106054	-0.901486	-1.340272
N	-0.957245	1.159996	-0.111026
N	-2.916782	-0.741228	0.045410
O	-2.399530	2.672308	-1.009656
H	4.226815	2.465868	1.109906
H	-0.061681	-0.659382	-0.701903
H	5.922524	0.993590	-0.629283
H	-3.011950	0.045210	-1.912663

H	-5.047387	1.275625	-1.473732
H	-4.690320	1.381850	0.258280
H	-5.458007	-1.132239	-1.328077
H	-6.187255	-0.569236	0.179932
H	-4.131840	-2.479203	0.131553
H	-4.313902	-1.360715	1.490264
H	0.548575	-1.276145	1.664838
H	0.070359	0.339949	2.189549
H	1.970350	2.249518	2.118082
H	2.052844	-2.215238	-0.559595
H	4.091014	-2.716637	-1.886685
H	5.990802	-1.139813	-1.921274
H	-0.256931	1.893523	-0.102324

Iron Oxo Anion Triplet

-1	3		
Fe	-0.073428	-0.001837	-0.310750
N	-1.285124	1.621577	-0.180319
N	1.550558	1.202948	-0.287649
N	-1.696456	-1.204347	-0.144644
N	1.140382	-1.622091	-0.276528
C	-2.653288	1.625993	-0.140660
C	2.861008	0.816128	-0.389064
C	-0.893012	2.933033	-0.183909
C	1.550140	2.572226	-0.278258
C	-3.008853	-0.817351	-0.108820
C	2.505740	-1.627396	-0.376674
C	-1.694549	-2.574003	-0.127759
C	0.748032	-2.933298	-0.248929
C	-3.145308	2.987235	-0.115666
C	3.719618	1.979164	-0.432436
C	-2.052645	3.798599	-0.140802
C	2.906279	3.069250	-0.359767
C	-3.868012	-1.980310	-0.060118
C	2.996351	-2.988679	-0.404731
C	-3.052198	-3.070631	-0.070422
C	1.905274	-3.799150	-0.322812
H	-4.192029	3.263174	-0.079544
H	4.799621	1.945343	-0.506726
H	-2.013474	4.880896	-0.131048
H	3.178594	4.117521	-0.364451
H	-4.949813	-1.945731	-0.021225
H	4.040958	-3.265924	-0.475557
H	-3.323941	-4.118684	-0.043185
H	1.866285	-4.881470	-0.313659
C	-3.464513	0.497224	-0.110210
C	3.314956	-0.497415	-0.436220
C	-0.565377	-3.384350	-0.172930
C	0.421338	3.383954	-0.223028
H	-4.538521	0.653658	-0.075410
H	4.386730	-0.653329	-0.515941
H	-0.722758	-4.458756	-0.156214
H	0.580286	4.458240	-0.221891
O	-0.140198	-0.004882	-1.957473
S	-0.077129	-0.034934	2.209741

C	1.657207	0.073177	2.813500
H	2.134832	1.007989	2.502419

H	1.660012	0.034311	3.908788
H	2.263352	-0.758495	2.439339

Supplementary Figure 23. Reaction coordinate diagrams for formation of (+)-naseseazine B (**2**), and single electron oxidation to radical cation.

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Chemistry

General Procedures:

All reactions were performed in oven-dried or flame-dried round-bottom flasks. The flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon. Gas-tight syringes with stainless steel needles or cannulae were used to transfer air- and moisture-sensitive liquids. Where necessary (so noted), reactions were performed in Schlenk tubes fitted with a PTFE stopcock. Flash column chromatography was performed as described by Still et al. using granular silica gel (60 Å pore size, 40–63 µm, 4–6% H₂O content, Zeochem). Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and an aqueous solution of ceric ammonium molybdate (CAM) followed by heating on a hot plate (~250 °C). Organic solutions were concentrated at 29–30 °C on rotary evaporators capable of achieving a minimum pressure of ~2 torr.

Materials:

Commercial reagents and solvents were used as received with the following exceptions: dichloromethane, acetonitrile, tetrahydrofuran, methanol, pyridine, toluene, and triethylamine were purchased from J.T. Baker (Cycletainer™) and were purified by the method of Grubbs et al. under positive argon pressure. Nitroethane was distilled over calcium hydride and stored over 4 Å molecular sieves. Silver hexafluoroantimonate was purchased from Strem Chemicals, Inc. All other solvents and chemicals were purchased from Sigma–Aldrich.

Instrumentation:

Proton nuclear magnetic resonance (1H NMR) spectra were recorded with Varian inverse probe INOVA-500 and Varian INOVA-500 spectrometers, or a Bruker AVANCE III 400 spectrometer. Chemical shifts are reported in parts per million on the δ scale, and are referenced from the residual protium in the NMR solvent (CHCl₃: δ 7.26, CD₃SOCD₂H: δ 2.50, CD₂HOD: δ 3.31). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant(s) in Hertz, integration, assignment]. Carbon-13 nuclear magnetic resonance (13C NMR) spectra were recorded with a Varian INOVA-500 spectrometer or a Bruker AVANCE III 400 spectrometer and are reported in parts per million on the δ scale, and are referenced from the carbon resonances of the solvent (CDCl₃: δ 77.16, DMSO-d₆: δ 39.52, CD₃OD: δ 49.00). Data are reported as follows: chemical shift (assignment). Data are reported as follows: chemical shift (assignment). Infrared data (IR) were obtained with a Perkin-Elmer 2000 FTIR, and are reported as follows: frequency of absorption (cm⁻¹), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Optical rotations were measured on a Jasco-1010 polarimeter. UV-Vis spectrophotometric data were acquired on a Varian Cary 50 Bio UV-Vis spectrophotometer. Preparative HPLC was performed on a Waters system with the 1525 Binary HPLC Pump, 2489 UV/Vis Detector, 3100 Mass Detector, System Fluidics Organizer, and 2767 Sample Manager components. We thank Liam P. Kelly for obtaining the mass spectrometric data at the Department of Chemistry's Instrumentation Facility, Massachusetts Institute of Technology. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics APEXIV 4.7 Tesla FT-ICR-MS using either an electrospray (ESI) or direct analysis in real time (DART) ionization source.

Positional Numbering System.

In assigning the ^1H and ^{13}C NMR data of all intermediates en route to our total syntheses of (–)-naseseazine C and (–)-iso-naseseazine C, we wished to employ a uniform numbering scheme. This numbering system is also consistent with that employed in the isolation papers of naseseazine C and iso-naseseazine B.^{1,2}

(–)-naseseazine C (**4**)

(–)-*iso*-naseseazine C (**11**)

Diketopiperazine bromide (-)-8: A sample of N-bromosuccinimide (641 mg, 3.60 mmol, 3.00 equiv) was added in one portion to a stirred suspension of diketopiperazine **7** (500 mg, 1.20 mmol, 1 equiv) in acetonitrile (60 mL). After 25 min, a solution of saturated aqueous sodium thiosulfate solution (30 mL) was added to the reaction mixture. After 10 min, the reaction mixture was diluted with ethyl acetate (30 mL), and washed with saturated aqueous sodium thiosulfate solution (30 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 30→35% ethyl acetate in hexanes), including a second chromatographic purification (eluent: 30→35% ethyl acetate in hexanes) to afford diketopiperazine bromide (-)-**8** (90.5 mg, 14.8%) as an off-white foam.

Structural assignments were made using additional information from gCOSY, HSQC, HMBC and nOe experiments. ¹H NMR (MHz, CDCl₃, 20 °C): δ 7.69 (app-br-s, 1H, C8H), 7.48 (app-d, J = 7.3 Hz, 2H, PhCbz-o-H), 7.43 (d, J = 7.7 Hz, 1H, C5H), 7.41–7.30 (m, 4H, C7H, PhCbz-m-H, PhCbz-p-H), 7.16 (app-t, J = 7.5 Hz, 1H, C6H), 6.57 (s, 1H, C2H), 5.43 (d, J = 12.2 Hz, 1H, PhCbzCHa), 5.31 (d, J = 12.3 Hz, 1H, PhCbzCHb), 4.04 (app-t, J = 8.2 Hz, 1H, C15H), 3.97 (dd, J = 5.9, 11.4 Hz, 1H, C11H), 3.62–3.45 (m, 2H, C19H), 3.35 (dd, J = 5.9, 13.2 Hz, 1H, C12Ha), 3.01 (dd, J = 11.0, 13.2 Hz, 1H, C12Hb), 2.35–2.23 (m, 1H, C17Ha), 2.25–2.14 (m, 1H, C17Hb), 2.10–1.97 (m, 1H, C18Ha), 1.95–1.80 (m, 1H, C18Hb). ¹³C NMR (100 MHz, CDCl₃, 20 °C): δ 165.8 (C16), 164.2 (C13), 153.0 (NC=OCbz), 141.4 (C9), 135.8 (PhCbz-i-C), 132.0 (C4), 131.2 (PhCbz), 128.7 (C7), 128.5 (PhCbz-o-C), 128.4 (PhCbz), 125.1 (C6), 123.9 (C5), 117.7 (C8), 83.3 (C2), 68.6, 60.4 (2C, C11, C15), 59.0 (C3), 45.6 (C19), 43.1 (C12), 27.8 (C17), 23.1 (C18). FTIR (thin film) cm⁻¹: 2957 (w), 2887 (w), 1716 (s), 1674 (s), 1329 (m). HRMS (ESI) (m/z): calc'd for C₂₄H₂₃BrN₃O₄ [M+H]⁺: 496.0866, found: 496.0858. [α]_D²⁴: -168 (c = 0.46, CH₂Cl₂). TLC (70% ethyl acetate in hexanes), R_f: 0.22 (UV, CAM).

meta-(-)-*N*ⁱⁿ,*N*ⁱⁿ-Dicarboxybenzyl iso-Naseseazine C (10) and para-(-)-*N*ⁱⁿ,*N*ⁱⁿ-Dicarboxybenzyl Naseseazine C (9): Diketopiperazine bromide (-)-8 (100 mg, 0.196 mmol, 1 equiv) and proline diketopiperazine 7 (245 mg, 0.588 mmol, 3.00 equiv) were azeotropically dried from anhydrous benzene (3 × 0.5 mL) and the residue was suspended in freshly distilled nitroethane (9.8 mL). Silver hexafluoroantimonate (202 mg, 0.588 mmol, 3.00 equiv) was then added as a solid in a single portion. After 4.5 h, the reaction mixture was diluted with dichloromethane (15 mL) and washed with a mixture of saturated aqueous sodium bicarbonate and saturated aqueous sodium thiosulfate (10:1 v/v, 15 mL). The resulting aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were dried over anhydrous sodium sulfate, were filtered, and were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 10→50% acetone in dichloromethane) to afford a regioisomeric mixture of (-)-10 and (-)-9 (65.6 mg, 40.1%, (-)-10:(-)-9, 1.4:1) as a white foam. Regioisomers (-)-10 and (-)-9 were separated for the purpose of full and independent characterization by preparative HPLC [Luna preparative HPLC column, C18, 5 μm, 21.2 × 250 mm; 7.0 mL/min; gradient, 5%→100% acetonitrile in water with 0.1% formic acid, 60 min; *t*_R((-)-10) = 48.3 min, *t*_R((-)-9) = 50.4 min]. Structural assignments were made using additional information from gCOSY, HSQC, HMBC and nOe experiments.

para-(-)-*N*ⁱⁿ,*N*ⁱⁿ-Dicarboxybenzyl Naseseazine C (9): ¹H NMR (500 MHz, CDCl₃, 20 °C): δ 7.99 (br-s, 1H, C₈H), 7.71 (br-s, 1H, C₈H), 7.53 (s, 1H, C₂H), 7.48–7.43 (m, 3H, C₅H, Ph_{Cbz}-H), 7.43–7.35 (m, 5H, Ph_{Cbz}-H), 7.34–7.26 (m, 4H, C₇H, Ph_{Cbz}-H), 7.22 (d, *J* = 7.4 Hz, 1H, C₅H), 7.10 (app-t, *J* = 7.5 Hz, 1H, C₆H), 7.04 (d, *J* = 8.8 Hz, 1H, C₇H), 6.61 (s, 1H, C₂H), 5.69 (s, 1H, N₁₀H), 5.42 (app-s, 2H, Ph_{Cbz}CH₂), 5.39 (d, *J* = 12.2 Hz, 1H, Ph_{Cbz}CH_a), 5.28 (d, *J* = 12.3 Hz, 1H, Ph_{Cbz}CH_b), 4.31 (dd, *J* = 3.5, 10.7 Hz, 1H, C₁₁H), 4.15 (dd, *J* = 5.8, 11.3 Hz, 1H, C₁₁H), 4.10 (app-q, *J* = 7.8 Hz, 2H, C₁₅H, C₁₅H), 3.69–3.47 (m, 5H, C₁₂H_a, C₁₉H, C₁₉H), 3.16 (dd, *J* = 5.8, 12.9 Hz, 1H, C₁₂H_a), 2.91–2.82 (m, 2H, C₁₂H_b, C₁₂H_b), 2.36–2.27 (m, 2H, C₁₇H), 2.27–2.11 (m, 1H, C₁₇H_a), 2.11–1.95 (m, 3H, C₁₇H_b, C₁₈H), 1.96–1.84 (m, 2H, C₁₈H). ¹³C NMR (125 MHz, CDCl₃, 20 °C): δ 169.5 (C₁₆), 166.0 (C₁₆), 165.4 (C₁₃), 164.9 (C₁₃), 153.1 (C_{Cbz}=O), 150.4 (C_{Cbz}=O), 141.5 (C₉), 136.6 (C₆), 136.1 (Ph_{Cbz}-*i*-C), 135.1 (C₄), 134.8 (2C, C₉, Ph_{Cbz}-*i*-C), 130.0 (C₄), 129.3 (C₇), 129.0 (2C, Ph_{Cbz}-C), 128.8 (Ph_{Cbz}-C), 128.6 (Ph_{Cbz}-C), 128.3 (2C, Ph_{Cbz}-C), 125.0 (C₂), 124.8 (C₆), 124.0 (C₅), 123.6 (C₇), 117.6 (C₈), 116.3 (C₈), 116.0 (C₃), 115.4 (C₅), 81.9 (C₂), 69.2 (Ph_{Cbz}-CH₂), 68.3 (Ph_{Cbz}-CH₂), 60.7 (C₁₁ or C₁₅), 60.6 (C₁₁ or C₁₅), 59.3 (C₁₅), 58.2 (C₃), 53.9 (C₁₁), 45.6 (C₁₉ or C₁₉), 45.5 (C₁₉ or C₁₉), 39.6 (C₁₂), 28.4 (C₁₇), 27.9 (C₁₇), 26.5 (C₁₂), 23.1 (C₁₈), 22.8 (C₁₈). FTIR (thin film) cm⁻¹: 3472 (br-m), 2956 (w), 1716 (s), 1668 (s), 1479 (m), 1401 (m). HRMS (ESI) (*m/z*): calc'd for C₄₈H₄₅N₆O₈ [M+H]⁺: 833.3293, found: 833.3286. [α]_D²⁴: -128 (c = 0.24, CH₂Cl₂). TLC (70% acetone in hexanes), R_f: 0.24 (UV, CAM).

meta-(-)-*N*ⁱⁿ,*N*ⁱⁿ-Dicarboxybenzyl iso-Naseseazine C (10): ¹H NMR (MHz, CDCl₃, 20 °C): δ 8.19 (br-s, 1H, C₈H), 7.73 (br-s, 1H, C₈H), 7.50 (s, 1H, C₂H), 7.48–7.38 (m, 6H, Ph_{Cbz}-H), 7.38–7.34 (m, 2H, C₅H, Ph_{Cbz}-H), 7.34–7.26 (m, 4H, C₇H, Ph_{Cbz}-H), 7.19 (d, *J* = 7.5 Hz, 1H, C₅H), 7.08 (d, *J* = 7.5 Hz, 1H, C₆H), 7.07–7.02 (m, 1H, C₆H), 6.64 (s, 1H, C₂H), 5.57 (s, 1H, N₁₀H), 5.41 (d, *J* = 12.3 Hz, 1H, Ph_{Cbz}CH_a), 5.39 (app-s, 2H, Ph_{Cbz}CH₂), 5.28 (d, *J* = 12.3 Hz, 1H, Ph_{Cbz}CH_b), 4.29 (dd, *J* = 2.9, 10.2 Hz, 1H, C₁₁H), 4.18–4.14 (m, 1H, C₁₁H), 4.14–4.08 (m, 1H, C₁₅H), 4.05 (app-t, *J* = 8.0 Hz, 1H, C₁₅H), 3.67–3.50 (m, 5H, C₁₂H_a, C₁₉H, C₁₉H), 3.15 (dd, *J* = 5.8, 12.9 Hz, 1H, C₁₂H_a), 2.92–2.81 (m, 2H, C₁₂H_b, C₁₂H_b), 2.37–2.28 (m, 2H), 2.27–2.15 (m, 1H, C₁₇H), 2.11–1.98 (m, 3H, C₁₇H_b, C₁₈H), 1.98–1.85 (m, 2H, C₁₈H). ¹³C NMR (MHz, CDCl₃, 20 °C): δ 169.4 (C₁₆), 166.0 (C₁₆), 165.4 (C₁₃), 165.0 (C₁₃), 153.1 (C_{Cbz}=O), 150.3 (C_{Cbz}=O), 141.5 (C₉), 138.8 (C₇), 136.2 (2C, C₄, Ph_{Cbz}-*i*-C), 134.9 (3C, C₄, C₉, Ph_{Cbz}-*i*-C), 129.3 (C₇), 129.0 (2C, Ph_{Cbz}-C), 128.8 (Ph_{Cbz}-C), 128.6 (Ph_{Cbz}-C),

128.3 (Ph_{Cbz}-C), 128.2 (Ph_{Cbz}-C), 124.8 (C_{2'}), 124.7 (C_{7'}), 124.0 (C₅), 121.1 (C₆), 119.5 (C_{5'}), 117.6 (C₈), 115.7 (C_{3'}), 113.0 (C_{8'}), 81.8 (C₂), 69.1 (Ph_{Cbz}-CH₂), 68.3 (Ph_{Cbz}-CH₂), 60.7 (C₁₁ or C_{15'}), 60.6 (C₁₁ or C_{15'}), 59.3 (C₁₅), 58.6 (C₃), 54.0 (C_{11'}), 45.6 (C₁₉ or C_{19'}), 45.5 (C₁₉ or C_{19'}), 39.4 (C₁₂), 28.4 (C_{17'}), 28.0 (C₁₇), 26.5 (C_{12'}), 23.1 (C_{18'}), 22.7 (C₁₈). FTIR (thin film) cm⁻¹: 3472 (br-m), 2955 (w), 1713 (s), 1667 (s), 1480 (m), 1398 (m). HRMS (ESI) (*m/z*): calc'd for C₄₈H₄₅N₆O₈ [M+H]⁺: 833.3293, found: 833.3278. [α]_D²⁴: -166 (*c* = 0.26, CHCl₃). TLC (70% acetone in hexanes), *R*_f 0.28 (UV, CAM).

(-)-Nasesezine C (4): Palladium on activated charcoal (3.3 mg, 3.1 μmol , 20 mol%) was added to a solution of para(-)-Nin,Nin'-dicarboxybenzyl nasesezine C (-)-**9** (12.9 mg, 30.4 μmol , 1 equiv) in degassed (N_2 stream, 5 min) ethanol (1.6 mL). A stream of hydrogen gas was passed through the heterogeneous mixture for 2 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring the reaction mixture at 22 $^\circ\text{C}$ for 21 h under an atmosphere of hydrogen gas, the solution was degassed (N_2 stream, 5 min) and filtered through Celite. The filter cake was washed with methanol (3×2 mL) and the combined filtrates were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 70 $\rightarrow$ 90% acetone in dichloromethane) to afford (-)-**4** (7.0 mg, 80%). Structural assignments were made using additional information from gCOSY, HSQC, HMBC and nOe experiments.

^1H NMR (MHz, CD_3OD , 20 $^\circ\text{C}$): δ 7.64 (d, J = 1.8 Hz, 1H, C5'H), 7.24 (d, J = 8.6 Hz, 1H, C8'H), 7.19 (d, J = 7.4 Hz, 1H, C5'H), 7.13 (dd, J = 1.9, 8.6 Hz, 1H, C7'H), 7.08 (s, 1H, C2'H), 7.06 (td, J = 1.2, 7.6 Hz, 1H, C7'H), 6.75 (td, J = 1.0, 7.5 Hz, 1H, C6'H), 6.71 (d, J = 8.1 Hz, 1H, C8'H), 5.70 (s, 1H, C2'H), 4.39 (td, J = 1.8, 4.9 Hz, 1H, C11'H), 4.31–4.23 (m, 2H, C11'H, C15'H), 3.97 (ddd, J = 1.9, 6.4, 10.9 Hz, 1H, C15'H), 3.54–3.47 (m, 2H, C19'H), 3.45–3.39 (m, 1H, C19'Ha), 3.28 (app-d, J = 5.2 Hz, 2H, C12'H), 3.26–3.21 (m, 1H, C19'Hb), 3.12 (dd, J = 6.1, 12.7 Hz, 1H, C12'Ha), 2.95–2.88 (m, 1H, C12'Hb), 2.33–2.25 (m, 1H, C17'Ha), 2.10–2.00 (m, 2H, C17'Hb, C18'Ha), 1.98–1.87 (m, 2H, C17'Ha, C18'Hb), 1.71–1.60 (m, 1H, C18'Ha), 1.48–1.40 (m, 1H, C18'Hb), 0.98–0.88 (m, 1H, C17'Hb). ^1H NMR (MHz, $\text{DMSO}-d_6$, 20 $^\circ\text{C}$): δ 10.84 (s, 1H, N1'H), 7.74 (s, 1H, N10'H), 7.63 (s, 1H, C5'H), 7.22 (d, J = 8.6 Hz, 1H, C8'H), 7.17 (s, 1H, C8'H), 7.16 (d, J = 8.7 Hz, 1H, C5'H), 7.03 (d, J = 8.6 Hz, 1H, C7'H), 6.98 (app-t, J = 7.7 Hz, 1H, C7'H), 6.65 (d, J = 8.6 Hz, C8H), 6.64 (s, 1H, N1H), 6.61 (app-t, J = 7.4 Hz, 1H, C6'H), 5.63 (s, 1H, C2'H), 4.35–4.27 (m, 2H, C11'H, C15'H), 4.16 (dd, J = 6.1, 11.4 Hz, 1H, C11'H), 4.09 (app-t, J = 8.4 Hz, 1H, C15'H), 3.45–3.33 (m, 3H, C19'H, C19'Ha), 3.33–3.23 (m, 1H, C19'Hb), 3.22 (dd, J = 4.8, 14.9 Hz, 1H, C12'Ha), 3.10–3.02 (m, 2H, C12'Ha, C12'Hb), 2.68 (app-t, J = 12.0 Hz, 1H, C12'Hb), 2.19–2.08 (m, 1H, C17'Ha), 2.04–1.97 (m, 1H, C17'Ha), 1.97–1.86 (m, 2H, C17'Hb, C18'Ha), 1.85–1.76 (m, 1H, C18'Hb), 1.75–1.68 (m, 1H, C18'Ha), 1.68–1.59 (m, 1H, C18'Hb), 1.53–1.42 (m, 1H, C17'Hb). ^{13}C NMR (MHz, CD_3OD , 20 $^\circ\text{C}$): δ 170.7 (C16'), 168.5 (C16), 168.0 (C13), 167.4 (C13'), 150.6 (C9), 136.9 (C9'), 135.3 (C6'), 134.2 (C4), 129.6 (C7), 128.5 (C4'), 126.2 (C2'), 125.2 (C5), 121.1 (C7'), 120.5 (C6), 116.3 (C5'), 112.6 (C8'), 111.1 (C8), 109.9 (C3'), 83.6 (C2), 61.9 (C15), 61.7 (C11), 60.8 (C3), 60.0 (C15'), 57.2 (C11'), 46.3 (C19), 46.0 (C19'), 41.1 (C12), 29.1 (2C, C12', C17'), 28.9 (C17), 23.8 (C18), 22.6 (C18'). ^{13}C NMR (MHz, $\text{DMSO}-d_6$, 20 $^\circ\text{C}$): δ 169.2 (C16'), 166.0 (C16), 165.6 (C13'), 165.3 (C13), 149.3 (C9), 134.8 (C9'), 134.1 (C6'), 133.0 (C4), 128.1 (C7), 127.1 (C4'), 124.8 (C2'), 123.8 (C5), 119.2 (C7'), 118.1 (C6), 114.6 (C5'), 111.4 (C8'), 109.6 (C3'), 109.5 (C8), 81.1 (C2), 60.1 (C11), 59.7 (C15), 58.7 (C3), 58.5 (C15'), 55.1 (C11'), 44.7 (2C, C19, C19'), 39.9 (C12), 27.7 (C17'), 27.4 (C17), 25.4 (C12'), 22.6 (C18), 22.0 (C18'). FTIR (thin film) cm^{-1} : 3310 (br-m), 2926 (m), 1661 (s), 1435 (s), 1301 (w), 1150 (w). HRMS (ESI) (m/z): calc'd for $\text{C}_{32}\text{H}_{33}\text{N}_6\text{O}_4$ [$\text{M}+\text{H}$] $^+$: 565.2558, found: 565.2551. $[\alpha]_{\text{D}}^{24}$: -180 (c = 0.16, CH_3OH). TLC (80% acetone in dichloromethane), R_f : 0.11 (UV, CAM).

(-)-iso-Naseseazine C (11): Palladium on activated charcoal (6.5 mg, 6.1 μ mol, 20.0 mol%) was added to a solution of meta(-)-Nin,Nin'-dicarboxybenzyl iso-naseseazine C **(-)-10** (25.2 mg, 30.3 μ mol, 1 equiv) in degassed (N_2 stream, 5 min) ethanol (3 mL). A stream of hydrogen gas was passed through the heterogeneous mixture for 2 min by discharge of a balloon equipped with a needle extending into the reaction mixture. After stirring the reaction mixture at 22 $^{\circ}$ C for 64 h under an atmosphere of hydrogen gas, the solution was degassed (N_2 stream, 5 min) and filtered over Celite. The filter cake was washed with methanol (3×2 mL) and the combined filtrates were concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: 70 $\rightarrow$ 90% acetone in dichloromethane) to afford **(-)-11** (14.3 mg, 83.6%). Structural assignments were made using additional information from gCOSY, HSQC, HMBC and nOe experiments.

1H NMR (MHz, CD_3OD , 20 $^{\circ}$ C): δ 7.49 (d, J = 8.4 Hz, 1H, C5'H), 7.31 (d, J = 1.6 Hz, 1H, C8'H), 7.11–7.01 (m, 2H, C5H, C6'H), 7.06 (s, 1H, C2'H), 7.05 (td, J = 1.1, 7.1 Hz, 1H, C7H), 6.72 (td, J = 1.0, 7.5 Hz, 1H, C6H), 6.70 (d, J = 7.7 Hz, 1H, C8H), 5.64 (s, 1H, C2H), 4.35 (td, J = 1.8, 5.0 Hz, 1H, C11'H), 4.21–4.15 (m, 2H, C11H, C15H), 3.92 (ddd, J = 1.9, 6.5, 11.0 Hz, 1H, C15'H), 3.54–3.44 (m, 2H, C19H), 3.44–3.37 (m, 1H, C19'Ha), 3.26 (app-d, J = 4.5 Hz, 2H, C12'H), 3.24–3.19 (m, 1H, C19'Hb), 3.05 (dd, J = 6.0, 12.6 Hz, 1H, C12Ha), 2.85–2.78 (m, 1H, C12Hb), 2.29–2.21 (m, 1H, C17Ha), 2.08–1.97 (m, 2H, C17Hb, C18Ha), 1.95–1.85 (m, 2H, C17'Ha, C18Hb), 1.67–1.56 (m, 1H, C18'Ha), 1.46–1.30 (m, 1H, C18'Hb), 0.96–0.86 (m, 1H, C17'Hb). 1H NMR (MHz, $DMSO-d_6$, 20 $^{\circ}$ C): δ 10.79 (d, J = 2.5 Hz, 1H, N1'H), 7.68 (s, 1H, N10'H), 7.50 (d, J = 8.4 Hz, 1H, C5'H), 7.23 (d, J = 1.6 Hz, 1H, C8'H), 7.17 (d, J = 7.4 Hz, 1H, C5H), 7.15 (d, J = 2.4 Hz, 1H, C2'H), 7.08 (dd, J = 1.8, 8.3 Hz, 1H, C6'H), 6.99 (app-t, J = 7.8 Hz, 1H, C7H), 6.65 (d, J = 4.7 Hz, 1H, C8H), 6.65 (s, 1H, N1H), 6.63 (d, J = 7.5 Hz, 1H, C6H), 5.56 (s, 1H, C2H), 4.31 (ddd, J = 1.8, 6.9, 9.1 Hz, 1H, C15H), 4.26 (app-t, J = 5.3 Hz, 1H, C11'H), 4.17 (ddd, J = 3.2, 6.6, 10.1 Hz, 1H, C11H), 4.05 (dd, J = 6.9, 9.7 Hz, 1H, C15'H), 3.45–3.30 (m, 3H, C19'Ha, C19H), 3.25 (td, J = 4.3, 7.7, 8.3 Hz, 1H, C19'Hb), 3.20 (app-dd, J = 4.9, 15.0 Hz, 1H, C12'Ha), 3.03 (app-ddd, J = 6.1, 13.8, 21.2 Hz, 2H, C12'Hb, C12Ha), 2.70–2.61 (m, 1H, C12Hb), 2.19–2.07 (m, 1H, C17'Ha), 2.01–1.86 (m, 3H, C17H, C18Ha), 1.86–1.73 (m, 1H, C18Hb), 1.73–1.63 (m, 1H, C18'Ha), 1.63–1.56 (m, 1H, C18'Hb), 1.46–1.35 (m, 1H, C17'Hb). ^{13}C NMR (MHz, CD_3OD , 20 $^{\circ}$ C): δ 170.8 (C16'), 168.5 (C16), 168.0 (C13), 167.4 (C13'), 150.6 (C9), 138.2 (C7'), 137.9 (C9'), 133.8 (C4), 129.7 (C7), 127.6 (C4'), 126.1 (C2'), 125.1 (C5), 120.4 (C5' or C6), 120.3 (C5' or C6), 118.0 (C6'), 111.1 (C8), 109.5 (C3'), 109.3 (C8'), 83.5 (C2), 61.8 (C11), 61.6 (C15), 60.7 (C3), 60.0 (C15'), 57.1 (C11'), 46.3 (C19), 46.0 (C19'), 40.9 (C12), 29.1 (C12' or C17'), 29.0 (C12' or C17'), 28.8 (C17), 23.8 (C18), 22.5 (C18'). ^{13}C NMR (MHz, $DMSO-d_6$, 20 $^{\circ}$ C): δ 169.1 (C16'), 166.1 (C16), 165.5 (C13'), 165.3 (C13), 149.4 (C9), 136.8 (C7'), 135.9 (C9'), 132.4 (C4), 128.2 (C7), 126.1 (C4'), 124.8 (C2'), 124.0 (C5), 119.0 (C5'), 118.1 (C6), 116.4 (C6'), 109.5 (C8), 109.2 (C3'), 108.0 (C8'), 81.5 (C2), 60.2 (C11), 59.6 (C15), 58.8 (C3), 58.4 (C15'), 55.2 (C11'), 44.8 (C19 or C19'), 44.6 (C19 or C19'), 39.9 (C12), 27.6 (C17'), 27.4 (C17), 25.7 (C12'), 22.6 (C18), 21.9 (C18'). FTIR (thin film) cm^{-1} : 3310 (br-m), 2955 (w), 1653 (s), 1457 (m), 1340 (w), 1056 (w). HRMS (ESI) (m/z): calc'd for $C_{32}H_{33}N_6O_4$ $[M+H]^+$: 565.2558, found: 565.2554. $[\alpha]_D^{24}$: -312 (c = 0.42, CH_3OH). TLC (80% acetone in dichloromethane), R_f : 0.11 (UV, CAM).

Supplementary Table 6. Comparison of our ^{13}C NMR data for (–)-naseseazine C (**4**) and (–)-iso-naseseazine C (**11**) with literature data (CD_3OD).¹

Assignment	Wang Report ¹ iso-naseseazine B ^{13}C NMR, 150 MHz, CD_3OD	This Work (–)-naseseazine C (4) ^{13}C NMR, 125 MHz, CD_3OD , 20 °C	This Work (–)-iso-naseseazine C (11) ^{13}C NMR, 125 MHz CD_3OD , 20 °C	Chemical Shift Difference $\Delta\delta = \delta(\text{–})\text{-naseseazine C (this work)} - \delta(\text{Wang report})^1$	Chemical Shift Difference $\Delta\delta = \delta(\text{–})\text{-iso-naseseazine C (this work)} - \delta(\text{Wang report})^1$
C2	83.6	83.6	83.5	0	–0.1
C3	60.8	60.8	60.7	0	–0.1
C4	134.2	134.2	133.8	0	–0.4
C5	125.2	125.2	125.1	0	–0.1
C6	120.5	120.5	120.4 or 120.3	0	–0.1 or –0.2
C7	129.7	129.6	129.7	–0.1	0
C8	111.2	111.1	111.1	–0.1	–0.1
C9	150.6	150.6	150.6	0	0
C11	62.0	61.9	61.8	–0.1	–0.2
C12	41.1	41.1	40.9	0	–0.2
C13	168.1	168.0	168.0	–0.1	–0.1
C15	61.7	61.9	61.6	0.2	–0.1
C16	168.6	168.5	168.5	–0.1	–0.1
C17	28.9	28.9	28.8	0	–0.1
C18	23.9	23.8	23.8	–0.1	–0.1
C19	46.4	46.3	46.3	–0.1	–0.1
C2'	126.3	126.2	126.1	–0.1	–0.2
C3'	109.8	109.9	109.5	0.1	–0.3
C4'	128.5	128.5	127.6	0	–0.9
C5'	112.6	116.3	120.4 or 120.3	3.7*	7.8 or 7.7
C6'	121.1	135.3	118.0	14.2	–3.1
C7'	135.3	121.1	138.2	–14.2	2.9
C8'	116.3	112.6	109.3	–3.7	–7.0
C9'	136.9	136.9	137.9	0	1.0
C11'	57.3	57.2	57.1	–0.1	–0.2
C12'	29.3	29.1	29.1 or 29.0	–0.2	–0.2 or –0.3
C13'	167.4	167.4	167.4	0	0
C15'	60.1	60.0	60.0	–0.1	0.1
C16'	170.7	170.7	170.8	0	0.1
C17'	29.1	29.1	29.1 or 29.0	0	0 or –0.1
C18'	22.5	22.6	22.5	0.1	0
C19'	46.03	46.0	46.0	0	0

The comparison of the ^1H and ^{13}C NMR chemical shifts of the reported isonaseseazine B with both synthetic regioisomers (–)-**4** and (–)-**11** in CD_3OD shows that the data for isonaseseazine B is most consistent with synthetic (–)-naseseazine C (**4**).

* Our assignment of these residues is supported by key HSQC and HMBC correlations

Supplementary Table 7. Comparison of our ^{13}C NMR data for (–)-naseeseazine C (4) and (–)-iso-naseeseazine C (11) with literature data (DMSO- d_6).²

Assignment	Carroll Report ² naseeseazine C 13C NMR, 200 MHz, DMSO- d_6	This Work (–)-naseeseazine C (4) 13C NMR, 125 MHz	This Work (–)-iso- naseeseazine C (11) 13C NMR, 125 MHz	Chemical Shift Difference $\Delta\delta = \delta$ (–)- naseeseazine C (this work) – δ (Carroll report) ² DMSO- d_6 , 20 °C	Chemical Shift Difference $\Delta\delta = \delta$ (–)-iso- naseeseazine C (this work) – δ (Carroll report) ² DMSO- d_6 , 20 °C
C2	81.1	81.1	81.5	0	–0.4
C3	59.7	58.7	58.8	–1.0*	0.9
C4	134.1	133	132.4	–1.1	1.7
C5	125.8	123.8	124	–2.0	1.8
C6	118.1	118.1	118.1	0	0
C7	128.1	128.1	128.2	0	–0.1
C8	111.4	109.5	109.5	–1.9	1.9
C9	149.3	149.3	149.4	0	–0.1
C11	60.1	60.1	60.2	0	–0.1
C12	40	39.9	39.9	–0.1	0.1
C13	165.3	165.3	165.3	0	0
C15	58.5	59.7	59.6	1.2	–1.1
C16	169.1	166	166.1	–3.1	3
C17	27.4	27.4	27.4	0	0
C18	22.5	22.6	22.6	0.1	–0.1
C19	44.7	44.7	44.8 or 44.6	0	0.1 or –0.1
C2'	124.8	124.8	124.8	0	0
C3'	109.6	109.6	109.2	0	0.4
C4'	127.1	127.1	126.1	0	1
C5'	114.6	114.6	119	0	–4.4
C6'	134.8	134.1	116.4	–0.7	18.4
C7'	119.2	119.2	136.8	0	–17.6
C8'	110.4	111.4	108	1.0	2.4
C9'	135.9	134.8	135.9	–1.1	0
C11'	55.1	55.1	55.2	0	–0.1
C12'	25.4	25.4	25.7	0	–0.3
C13'	166	165.6	165.5	–0.4	0.5
C15'	58.8	58.5	58.4	–0.3	0.4
C16'	165.6	169.2	169.1	3.6	–3.5
C17'	27.7	27.7	27.6	0	0.1
C18'	21.9	22	21.9	0.1	0
C19'	44.7	44.7	44.8 or 44.6	0	0.1 or –0.1

The comparison of the ^1H and ^{13}C NMR chemical shifts of the reported naseeseazine C with both synthetic regioisomers (–)-4 and (–)-11 in DMSO- d_6 shows that the data for naseeseazine C is most consistent with synthetic (–)-naseeseazine C (4).

* Our assignment of these residues is supported by key HSQC and HMBC correlations

Synthetic References:

1. Xiong, Z. Q.; Liu, Q. X.; Pan, Z. L.; Zhao, N.; Feng, Z. X.; Wang, Y., Diversity and bioprospecting of culturable actinomycetes from marine sediment of the Yellow Sea, China. *Arch. Microbiol.* 2015, 197 (2), 299-309.
2. Buedenbender, L.; Grkovic, T.; Duffy, S.; Kurtboke, D. I.; Avery, V. M.; Carroll, A. R., Nasesezazine C, a new anti-plasmodial dimeric diketopiperazine from a marine sediment derived *Streptomyces* sp. *Tet. Lett.* 2016, 57 (52), 5893-5895.

^1H NMR, 400 MHz, CDCl_3 , 20 °C

^{13}C NMR, 100 MHz, CDCl_3 , 20 °C

^{13}C NMR, 125 MHz, CDCl_3 , 20 $^\circ\text{C}$

^{13}C NMR, 125 MHz, DMSO-*d*₆, 20 °C

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