Experimental and Computational Evidence of non-MEP Pathways in the Fragmentation and Rearrangement of Bicyclo[3.3.1] heptane Diazonium Ions

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Abstract

Oxadiazoles have been utilized to release norbornyl-related carbocations by photoactivation in protic polar media. The product formation has been monitored by ¹H NMR and the experimentally observed product ratios were analyzed in comparison to expected product ratios based on minimum energy pathway calculations (MEP) and molecular dynamics simulations (MDs). Viewing all aspects together the results deliver the strong indication of non-MEP situations playing a major role in the product formation from fenchyl and bornyl diazonium ions. The valley-ridge inflection points have been further localized by projected frequency analysis. The here described observation supplements the computational studies by the groups of Tantillo as well as Weitman and Major in the closely related field of reaction path bifurcations in the rearrangements of norbornyl related carbo cations.

Introduction.

Secondary carbocations imbedded in bicyclo[2.2.1]heptane frameworks pose a longstanding fascination for physical organic chemists. The controversial discussion of their true electronic structure is well known.¹ The now proven charge delocalization via sigma bonds leading to the term non-classical carbo cations shape not only the molecular structure but also their reactivity.² For instance, the stabilization achieved by the charge delocalization within the norbornyl cation via the C6-C1 bond creates a driving force and enhances solvolysis rates of *endo*-isomers of norbornyl tosylates by factors of around 1000.³ Besides these established characteristics, the discussion of a potential link between non-classical carbo cations and certain non-MEP reaction pathways like reaction path bifurcations (BIFs) is currently ongoing. Computational evidence has been provided mainly by the groups of Major⁴

¹ Robert A. Moss "The 2-norbornyl cation: a retrospective", *J. Phys. Org. Chem.* **2017**, 27, 374–379

² Scholz, F.; Himmel, D.; Heinemann, F. W.; Schleyer, P. v. R.; Meyer, K.; Krossing, I. "Crystal Structure Determination of the Nonclassical 2-Norbornyl Cation", *Science* **2013**, 341, 62 – 64.

³ T. W. Bentley, C. T. Bowen, D. H. Morten, and Paul v. R. Schleyer *J. Am. Chem. Soc.* **1981**, 103, 5466–5475.

⁴ [a] Major, D. T.; Weitman, M., 'Electrostatically guided dynamics--the root of fidelity in a promiscuous terpene synthase?', *J. Am. Chem. Soc.* **2012**, 134, 19454-19462 and references cited therein. [b] Weitman, M. Major, D. T., 'Challenges posed to bornyl diphosphate synthase: diverging reaction mechanisms in monoterpenes', *J. Am. Chem. Soc.* **2010**, 132, 6349–6360.

and Tantillo.⁵ However, a link to experimental data has not been established yet.

Here, we present experimental evidence for reaction path bifurcations being related to non-classical carbo cationic structures and their direct cationic precursors. The impact of subtle changes in the substitution pattern on the occurrence of BIFs is exemplified by carbo cations featuring fenchyl and bornyl frameworks.

To follow the onward reaction of rather short-lived species like carbo cations a photochemical release is mandatory. However, the photochemical generation of carbo cations is usually a stepwise process whereas a direct photon-induced heterolytic bond cleavage is mostly unknown. Instead homolytic bond cleavage yielding radicals as direct predecessors of the ion pair is a common mechanistic scenario. Mandatory for a clean 'ionic' follow-up chemistry is a fast single electron transfer (SET) due to strong spin-orbit coupling as for instance described for the heavy alkyl halogenides (iodides and bromides)⁶. An alternative access to carbo cations via photo activation starts with a charged precursor like phosphonium⁷ or diazonium salts⁸ (this work). The latter can be generated *in situ* via the photofragmentation of oxadiazoles to diazo alkanes (Scheme 1).

Scheme 1 Postulated mechanism of photo fragmentation leading to carbenes (in aprotic media) and to carbocations (protic media). The rate of fragmentation of **1-N** to diazo **2-N** has been determined in ACN and HFIP by time-resolved infrared spectroscopy (TRIR, see Figure 1).

The generation of the diazo alkane accompanied by release of acetyl methyl ester as the stoichiometric side product (Scheme 1) can be followed by time-resolved infrared spectroscopy (TRIR, Figure 1)): Femtosecond photo-excitation and subsequent probing of vibrational resonances probes the diazo

⁵ Recent reviews: [a] Hare, S. R.; Tantillo, D. J., " *Beilstein J. Org. Chem.* **2016**, *12*, 377–390. [b] Tantillo, D. J. *Chem. Soc. Rev.* **2010**, *39*, 2847 – 2854. [c] Hong, Y J., Tantillo, D. J. *Nature Chemistry* **2009**, *1*, 384–389.

⁶ Kropp, Paul J.; Adkins, Rick L., 'Photochemistry of alkyl halides. 12. Bromides vs. iodides', *J. Am. Chem. Soc.* **1991**, *113*, 2709–2717.

⁷ [a] Ammer, J.; Sailer, C. F.; Riedle, E.; Mayr, H. 'Photolytic generation of benzhydryl cations and radicals from quaternary phosphonium salts: how highly reactive carbocations survive their first nanoseconds' *J. Am. Chem. Soc.* **2012**, *134*, 11481–11494. [b] Peranovich, T. M. S.; Marcondes, M. E. R.; Toscano, V. G. 'Photochemistry of Phosphonium Salts-Photolysis of 9-(Antryl)methyl Triphenylphosphonium Chloride' *Phosphorus, Sulfur, and Silicon and the Related Elements* **1990**, *54*, 314.

⁸ [a] John Paul Pezacki, Brian D. Wagner, Calvin S. Q. Lew, John Warkentin, and Janusz Luszytk, 'Δ³-1,3,4-Oxadiazolines: Photochemical Precursors to Diazoalkanes and sec-Alkanediazonium Ions in Acidic Solution', *J. Am. Chem. Soc.* **1997**, *119*, 1789 – 1790. [b] John Paul Pezacki, Deepak Shukla, Janusz Luszytk, and John Warkentin 'Lifetimes of Dialkylcarbocations Derived from Alkanediazonium Ions in Solution: Cyclohexadienyl Cations as Kinetic Probes for Cation Reactivity' *J. Am. Chem. Soc.* **1999**, *121*, 6589 – 6598.

alkane and the methyl ester which exhibit characteristic stretching vibrations of the diazo and the carbonyl group, respectively (Fig. 1A). The formation of these vibrational resonances is occurring on picosecond-timescales (Fig. 1B,C; see SI for experimental details). While intramolecular vibrational energy relaxation (IVR) and solvation influence the absorption strength at early times, the formation time constants of the spectroscopic signals provide an upper bound for the fragmentation process which is complete at 20 ps after photo-excitation. Product absorption thermalizes on tens of picoseconds and reaches a constant level after ~ 60 ps in acetonitrile (ACN) and in hexafluoroisopropanol (HFIP) after ~ 100 ps. The absence of signal decay at 200 ps delay suggests a primary product lifetime of at least 1 ns.

Figure 1 Results of femtosecond infrared spectroscopy with 267-nm excitation of **1-N** in HFIP and ACN monitoring the formation of **2-N**. Absorption lineshapes of the carbonyl of the acetyl methyl ester and the diazo stretching vibration 60 ps of **2-N** after 267-nm excitation (A). Time evolution of the lineshape area the carbonyl (B) and diazo (C) stretching vibrations in HFIP (blue) and ACN (red) solution. The lines are fits of a sequential rate equation model (see supporting information for details).

In protic polar media (alcohols, acidic additives) diazo alkanes can be protonated to yield diazonium salts that are believed to fragment spontaneously to carbo cations and dinitrogen. The advantage of oxadiazole in the mechanistic study of carbo cations is the irreversible formation of the desired product as re-trapping by the leaving group is inhibited (N₂). In addition, the potential impact on differences in reactivity of different diastereomers is levelled by the long lifetime of the diazo-intermediate. Also, the oxadiazoles as such are stable compounds (storage at -20 °C for month) and synthesized easily in two steps.

Extensive computational analysis of the underlying potential energy surfaces for the diazonium ion fragmentation and subsequent skeletal rearrangements of the fenchyl and bornyl frameworks complete the picture and provide a rational for the observed product ratios.

Methods. Oxadiazolines of norbornanone, fenchone and norcamphor were prepared according to Warkentin and co-worker.⁹ *Endo*- and *exo*-diastereomers of **N** (Table 1) were separated by solvolysis in wet ACN with 0.8 eq TFA, leaving one set of *endo*-diastereomers, **B** and **F** were used as the original diastereomeric mixture, since kinetics of the photochemical fragmentation confirmed same rate constants for all diastereomers.

Analysis of product ratios was done in two different approaches: on a preparative scale, reactions were run in de-aerated quartz cuvettes and on an analytical scale in quartz NMR tubes equipped with a Young's tap using deuterated solvents. Reaction solutions were irradiated with UVB lamps (6 Watt, 12 lamps) in a Rayonett reactor for different time intervals and subsequently analyzed by ¹H NMR. To enable an unambiguous assignment of structures to spectral features a set of reference substance were synthesized.

Computational Details. All calculations presented herein were performed with the Gaussian09.D02 and .E02 program package.¹⁰ Geometry optimisations of stationary points were performed using different density functionals without (B3LYP, M062X)^{11, 12} and with short-range dispersion correction in conjunction with the 6-31G*, 6-31+G(d,p) or 6-311+G** basis sets¹³. The choice of level of theory was guided by latest publications on related structures.¹⁴ Further details on the progression and initial conditions of the BOMD simulations can be found in the SI.

Results & Discussion.

Product scope/ kinetics. In acetonitrile (ACN) the diazo fragmentation proceeds via the carbene pathway to form tricyclene (**4-N**, blue box, Figure 2) or its methylated derivatives (**4-F**, **4-B**) as one of the main products. The diazo compounds **2** are unusually stable (calculated barrier of thermally active N₂-extrusion: $\Delta G^\ddagger_{\text{N}} = 28.9$ kcal/mol, see SI for TRIR data) and can be observed by ¹H NMR-spectroscopy of irradiated samples in ACN. Subsequent optimization of the reaction conditions led to the favorite choice of HFIP as solvent and proton source.¹⁵ Here, the diazo protonation became competitive to the de-azation of the diazo **2-N** (ratio 2 : 1 ionic : carbene path) or even the unique reaction path (**2-F**, **2-B**). According to the calculated barrier for N₂-extrusion out of the diazoniumion the process is now barrier-free ($\Delta G^\ddagger_{\text{endo-N-N}_2^+} = 1.3$ kcal/mol; $\Delta G^\ddagger_{\text{exo-N-N}_2^+} = 2.1$ kcal/mol).

⁹ Bekhazi, M.; Risbood, P. A.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105* (17), 5675–5679.

¹⁰ Gaussian09.D02 & E02 Version, for full citation see SI.

¹¹ B3: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; LYP: Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

¹² Zhao, Y., Truhlar, D.G. *Theor Chem Account* **2008**, *120*, 215–241.

¹³ 6-31G: [a] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724; 6-311: [b] Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-54. [c] McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639-48.

¹⁴ [a] Hong, Y., Tantillo, D. Biosynthetic consequences of multiple sequential post-transition-state bifurcations. *Nature Chem* **6**, 104–111 (2014). [b] Y. J. Hong, D. J. Tantillo, 'Quantum chemical dissection of the classic terpinyl/pinyl/bornyl/camphyl cation conundrum—the role of pyrophosphate in manipulating pathways to monoterpenes', *Org. Biomol. Chem.* **2010**, *8*, 4589 – 4600.

¹⁵ See SI: Addition of TFA (0.2 - 16 eq) to a solution of **N** in ACN-d₃ should lead to a protonation of the diazo intermediate, but according to the product ratios (1 : 1) the ionic pathway (red & grey boxes. Table 1) is not yet favored over the carbene path.

Figure 1 Experimentally observed products under continuous irradiation (UVB, Rayonett, quartz NMR tube, 60 min): **2**, **4** major products in ACN, **2**, **4**, **5** in ACN with 1 eq TFA, **6-8** major products in HFIP and **6-10** major products in HFIP with 10 eq TMB.

The fragmentation of the heterocycle and formation of the different terpenoid structures occurs quantitatively based on the occurrence of 91-98% of the stoichiometric side product methyl acetate (¹H NMR data & TRIR data) and is independent of the solvent and protic additives within the error margin of the measured rate constants. Moreover, the different diastereomers are consumed with similar rate constants. Ps-time-resolved IR spectroscopy (ps-TRIR) could show that **2** is formed within 2 ps and hence presumably within one step after the electronic excitation and that **2** is a rather long-lived species even in HFIP (minimum life time of 50 ps).¹⁶ Hence, the chemistry related to the carbo cation formation out of the diazo compounds is independent of the configuration of the starting materials **N**, **B**, and **F**.

With fenchyl and bornyl carbon frameworks rearrangement products are expected to occur and indeed are observed in form of the corresponding alkenes or the TMB-trapping¹⁷ product (Scheme 2). The formation of the rearrangement products is on average at 61% independent of the presence of TMB.¹⁸

Table 1 Summary of *in situ*-NMR studies of product ratios (C2-C6 products: trapping or elimination products of α-F⁺ or C⁺; C2-C7 products: trapping or elimination products of P⁺, T⁺, Phe⁺). See Schemes 2 and 3 for structures.

#	prec.	TMB	C2-C6 products [%] ^a	C2-C7 products [%] ^a	sum [%]	ratio C2-C6 : C2-C7
1	1-F	-	54	5	59	11:1
2	1-B	-	56	0	56	Quant. C2-C6
3	1-F	4 eq	49	22	61	2:1
4	1-B	4 eq	61	5	66	12:1

^a Measured in HFIP-*d*2 under irradiation with UVB-lamps in quartz NMR-tubes under inert atmosphere.

¹⁶ For further details and results of kinetics and transient absorption spectroscopy see SI.

¹⁷ TMB-trapping: Steenken, S.; Ashokkumar, M.; Maruthamuthu, P.; McClelland, R. A., , Making Photochemically Generated Phenyl Cations Visible by Addition to Aromatics: Production of Phenylcyclohexadienyl Cations and Their Reactions with Bases/Nucleophiles', *J. Am. Chem. Soc.* **1998**, *120*, 11925–11931.

¹⁸ The remaining 39% could not be identified.

Two experimental observations can be made: First, in general the C2-C6 rearrangement products are preferred over C2-C7 ones for both **F** and **B**, independent of the absence or presence of TMB and with **F** is providing lower selectivities than **B**. Second, in presence of TMB one sees for both **F** and **B** higher amounts of the C2-C7 rearrangement products than without TMB, i.e. a decrease in C2-C6-selectivity. The latter observation is quite likely due to the trapping of the phenandryl cation **Phe**⁺ by the very good nucleophile TMB (Scheme 2 and 3) before it can revert back to the thermodynamic sink of the PES, i.e. **α-F**⁺ or **C**⁺ (C2-C6 products). This assumption is corroborated by the relative barrier heights of the associated elementary steps of the cationic rearrangements summarized in Scheme 3.¹⁹

To find a rational of the experimentally determined selectivities the reaction coordinates of the dissociation of the *endo*- and *exo*-isomers of the **B-N₂**⁺ and the **F-N₂**⁺ have been analyzed in detail (Scheme 2).

Scheme 2 Summary of product ratios based on MEP-pathways & MD-Pathways (% numbers) and experimentally observed product selectivity (bold % numbers) for the fragmentation and rearrangement of diazonium ions in dependence of their *endo*- or *exo*-configuration.

¹⁹ That indeed the carbocation is trapped by TMB was shown by the transient absorption spectrum of the corresponding cyclohexadienylcation using a ns-pump-probe set-up. See SI for the transient absorption spectrum.

The IRC-product in case of both *endo*- and *exo*-isomers of $\mathbf{F-N_2^+}$ is the C2-C6 rearrangement product, i.e. the α -fenchyl cation, $\alpha\text{-F}^+$ (Scheme 2, left side).

In case of $\mathbf{B-N_2^+}$ the IRC products depend on the configuration at C2: *endo*- $\mathbf{B-N_2^+}$ is linked directly to the C2-C7 rearrangement product, i.e. the pinyl cation, $\mathbf{P}^+$, whereas the *exo*- $\mathbf{B-N_2^+}$ leads to C2-C6 rearrangement, i.e. camphyl cation $\mathbf{C}^+$ (Scheme 2, right side).

Scheme 3 Reaction coordinate diagram of the free carbocations in black the common intermediates of both branches of $\mathbf{F}^+$ (blue lines) and $\mathbf{B}^+$ (red lines). The preceding steps (black line) are identical for both isomers $\mathbf{F}^+$ and $\mathbf{B}^+$. The data shown was calculated at M06-2X/6-311+G**.

Based on the IRC calculations the expectation would be that fragmentation of either *endo*- or *exo*- $\mathbf{F-N_2^+}$ would lead to $\alpha\text{-F}^+$ selectively and hence one would observe in the NMR the corresponding elimination product α -fenchene or trapping products (HFIP ether, TMB adduct). This expectation is only valid of course, as long as the barrier (18.7 kcal/mol) for reverting back to the pinyl cation is higher than the barriers for elimination or trapping. This can be assumed with some confidence as HFIP - though not a good nucleophile - is abundant as a solvent and secondly the alcoholate stays in close proximity (ion pair) after proton transfer, so both formation of the alkene or the ether within the ion pair is facilitated and not slowed down by diffusion.²⁰ In presence of TMB, this assumption is even more reliable as TMB is a very good nucleophile and captures cations with rate constants close to the diffusion controlled limit.¹⁷

However, the MEP prediction of only $\alpha\text{-F}^+$ derivatives (C2-C6 rearrangement products, Table 1) is an obvious contradiction to the experimental observation of 11 : 1 C2-C6 : C2-C7 (without TMB) or 2 : 1 (with TMB) product ratios.²¹ Based on the special nature of the closely related fenchyl cation $\mathbf{F}^+$, being part of a bifurcating PES (Scheme 3) we therefore analyzed also the molecular dynamics of the $\mathbf{F-N_2^+}$ -fragmentation in respect to off-MEP behavior (vide infra).

The IRC analysis of the $\mathbf{B-N_2^+}$ delivered a more complicated picture (Scheme 2, right): Here, the *exo*-isomer leads via the MEP to $\mathbf{C}^+$ and similarly to the case of $\alpha\text{-F}^+$, $\mathbf{C}^+$ can be assumed to be formed irreversibly under the reaction conditions. Hence, for 100% *exo*- $\mathbf{B-N_2^+}$ one would expect to see only

²⁰ This is based on a) MD simulations with HOAc that protonation and subsequent trapping or deprotonation by the acetate as a close to barrier-free process. B) preliminary *in situ* NMR studies indicating significant and specific H-bonding between HFIP and precursor 1.

²¹ It was ensured that the final products are not photochemically active under irradiation with UVB light.

camphene or trapping products of $\mathbf{C}^+$ (C2-C6 product). On the contrary, the *endo*- $\mathbf{B-N_2}^+$ leads to the pinyl cation $\mathbf{P}^+$ as the IRC-product. Comparing the barriers around $\mathbf{P}^+$ (Scheme 3) it is apparent that the formation of the terpinyl cation $\mathbf{T}^+$ and onwards to the phenandyl cation, $\mathbf{Ph}^+$ is almost a barrier-free process ($\Delta G_{T-P}^\ddagger=4.0$ kcal/mol and $\Delta G_{T-Ph}^\ddagger=2.6$ kcal/mol). Since $\mathbf{Ph}^+$ is significantly more stable than $\mathbf{P}^+$ (–14.0 kcal/mol, ΔG) the lifetime should be sufficiently long to allow for the trapping by TMB in the experiment. The barriers towards the camphyl cation ($\mathbf{C}^+$) on the one hand and the α -fenchyl cation ($\alpha\text{-}\mathbf{F}^+$) on the other are somewhat higher, but still low (8.1 kcal/mol and 9.6 kcal/mol respectively) and accessible under the reaction conditions.

Again, the IRC-prediction of the product ratio is different to the experimental one. However, since for the bornyl-framework the MEP-selectivity is dependent on the *endo*-/ *exo*-configuration of the diazoniumion, and this very ratio can only be predicted based on computed relative stabilities (2:1 in favour of the *endo*-configuration), the following discussion of the MD results will focus mainly on the fenchyl-system. BOMD simulations were started at the transition state of the N_2 -extrusion of either *endo*- or *exo*-isomers of $\mathbf{F-N_2}^+$ and $\mathbf{B-N_2}^+$ and the results are summarized in Table 2. Based on the relative stabilities of *endo*- vs. *exo*-isomers one can calculate the numbers of expected product ratios for a mixture of *endo*- and *exo*- $\mathbf{F-N_2}^+$ and $\mathbf{B-N_2}^+$.

Table 2 Comparison of predicted product ratios and experimentally observed ones.

#		MD C2-C6 vs. C2-C7	MD rel. stab. C2-C6 vs. C2-C7	MEP C2-C6 vs. C2-C7	MEP rel. stab. C2-C6 vs. C2-C7	exp. ^c C2-C6 vs. C2-C7
1	<i>exo</i> - $\mathbf{F-N_2}^+$	1:0	2:1 ^a	1:0	1:0 ^a	2:1
2	<i>endo</i> - $\mathbf{F-N_2}^+$	1:8		1:0		
3	<i>exo</i> - $\mathbf{B-N_2}^+$	1:0	1:2.0 ^b	1:0	1:2.3 ^b	12:1
4	<i>endo</i> - $\mathbf{B-N_2}^+$	1:9		0:1		

^c relative stability *endo*- vs. *exo*-isomer: + 0.3 kcal/mol, i.e. *endo* : *exo* = 1: 1.7. ^b relative stability *endo*- vs. *exo*-isomer: –0.5 kcal/mol, i.e. *endo* : *exo* = 2.3: 1. ^c with 4 eq TMB.

By comparison of the MD- predicted product ratios (C2-C6 vs C2-C7) with the experimental ones, one can see, that the numbers fit amazingly well for the fenchyl system $\mathbf{F-N_2}^+$ whereas the MEP-predictions were suggesting 100% formation of C2-C6 products only.

For the bornyl-case the results are not matching exactly, but even though the absolute numbers do not fit, the MD simulations show a deterioration of the predicted MEP-selectivities towards the observed preference of C2-C6 products. Overall, the reduced selectivities as observed in the MDS are down to the trajectories that bifurcate to the non-MEP-products (Table 1, Scheme 2) and thereby provide a rational for the lower than expected experimental product selectivity.

To further test the hypothesis of a reaction path bifurcation we aimed at a better understanding of the topology of the PES describing the fragmentation and skeletal rearrangements. Therefore, relaxed scans of the PESs of the diazoniumions were conducted, driving the geometric parameters $r(\text{C2-N}_2)$ (fragmentation) and $r(\text{C2-C6})$ simultaneously. As a third computational analysis tool for identifying valley ridge inflection points – the prerequisite for reaction path bifurcations – the frequencies of structures along the IRC associated to $\mathbf{F-N_2}^+\text{-TS}$ and $\mathbf{B-N_2}^+\text{-TS}$ were projected and analyzed. This approach, though being again a PES analysis avoids the bias introduced by scanning the PES by using simple specified reaction coordinates.

The *endo*- $\mathbf{F-N_2}^+$ ion is part of a PES that clearly features a bifurcation if plotted as shown in Figure 2. The *endo*- $\mathbf{F-N_2}^+\text{-TS}$ (fragmentation TS) is associated with the MEP towards the fenchyl cation $\mathbf{F}^+$ that resides close to the valley-ridge inflection point (VRI). The 2nd transition state belongs to the

interconversion of the pinyl cation (P^+) and the $\alpha\text{-F}^+$. The structure-related analysis of the BOMD simulations revealed that the trajectories diverge in proximity to the diazoniumion-fragmentation TS and either led to the $\alpha\text{-F}^+$ (major path) or to P^+ without any re-crossing and no interconversion between $\alpha\text{-F}^+$ and P^+ on the simulation time scales (Scheme 2, top left).

Figure 2 3D plots of the PESs scans generated by driving the N_2 -C bond length and the C2-C6 bond length simultaneously.

The additional analysis by using projected frequencies support the BOMD results and allowed for a better structural characterization of the valley-ridge inflection points (**VRT-I** and **VRT-II**, Figure 4). The VRI point is defined by the change in sign of the projected frequency from positive to negative. Only **VRT-I** is of importance for the skeletal rearrangement of the carbon framework as the imaginary frequency here shows the necessary wagging movement to shorten the C2-C6 distance. **VRT-II** on the other hand only shows the rotation of the N_2 in relation to the carbocation.

Figure 3 The projected frequencies along the IRC for *endo-F-N₂⁺* (top) and *endo-B-N₂⁺* (bottom) indicate that close by the TS of the N₂ release there is a valley ridge inflection point (VRT).

Changing the stereochemistry of the **F-N₂⁺** from *endo*- to *exo*-isomer provides a very different picture. Here a clear MEP towards the α -fenchyl (cation **12**) is present. This MD simulations led quantitatively to the α -F⁺ (Table 2) and also the frequency analysis along the IRC-path indicate ‘standard’ MEP behavior (see SI for details).

As it became apparent from the analysis above, the observed product ratios in the bornyl framework are only qualitatively described correctly by the MDs simulations as these predict a diminished selectivity. Again, the *exo-B-N₂⁺* – like the *exo-F-N₂⁺* – seems to follow the MEP, whereas the *endo*-isomer shows interesting deviations from it. Although the scanned PES (Figure 3b) indicates rather MEP behavior the projected frequencies along the IRC suggest a BIF possible based on the existence of a VRI (Figure 4).

Conclusion. The combination of experimental determination of product ratios, spectroscopic characterization of intermediates by NMR, TRIR and TRUV on time-scales from min to ps and an in-depth computational analysis beyond stationary point calculations and minimum energy pathways, led to the identification of reaction path bifurcations and the characterization of the associated valley ridge inflection points in the fragmentation and rearrangement processes of bicyclic-diazonium ions. It was shown that the configuration of the diazonium ions (*endo*- vs. *exo*) determines the presence or absence of VRI points and thereby the impact of dynamically controlled product selectivity. The control of the diazoniumion configuration may hence in future deliver a handle to invoke the dynamic control at will and steer the product selectivity to the desired product.

Supporting Information

Experimental and Computational Evidence of non-MEP Pathways in the Fragmentation and Rearrangement of Bicyclo[3.3.1] heptane Diazonium Ions

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1. Synthesis

1.1 General methods

All moisture and air sensitive reactions were conducted in flame-dried glass ware under nitrogen atmosphere. The solutions for the kinetic measurements were degassed using the freeze-pump -thaw method. Commercially available chemicals, if not stated otherwise, were used as purchased without further purification. Solvents were distilled prior to use. Anhydrous solvents were distilled according to standard procedures or bought. Column chromatography was conducted with silica gel 60 by Fluka. For TLC, silica gel 60 F₂₅₄ coated alumina plates by Macherey-Nagel were used. NMR spectra were measured on Bruker FOURIER 300, Bruker AVANCE 400, Bruker DRX 500 and Bruker AVANCEIII 600 spectrometers and referenced to the residual solvent peak. Characterization of signals: s = singlet ; d = doublet ; t = triplet ; dd = doublet of doublets ; ddd = doublet of doublets of doublets ; dddd = doublet of doublets of doublets of doublets ; dt = doublet of triplets ; ddt = doublet of doublets of triplets ; q = quartet ; dq = doublet of quartets ; ddq = doublet of doublets of quartets ; sept = septet ; m = multiplet. Mass spectrometry was conducted on a VG 70 S for EI spectra and on an Agilent 6224 ESI-TOF for ESI mass spectra. Infrared spectra were measured on an Alpha Platinum ATR-IR spectrometer by Bruker. The static photolysis experiments were conducted with a Rayonet RPR-100 photochemical reactor using RPR2537A (UV-C), RPR3000A (UV-B) or RPR3500A (UV-A) lamps. Samples were either prepared in standard quartz cuvettes (d = 1 cm) or in quartz NMR tubes with Young seal.

1.2 General procedure for the synthesis of *N*-acetyl hydrazones

A solution of the ketone (10 mmol, 1 eq), acetyl hydrazine (11.5 mmol, 1.15 eq) and acetic acid (0.02 mL/mmol) in ethanol (1 mL/mmol) was heated to reflux. After cooling down, the solvent was mostly evaporated and the reaction mixture then heated to 120 °C for three hours. The obtained crude product was recrystallized from acetone or directly used in the following synthesis.²²

Norcamphor-*N*-acetyl hydrazone (11-N)

Synthesis according to general procedure with heating for 30 minutes. The crude product was used without further purification.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 8.95 (s, 0.95H, N-H), 2.73-2.86 (m, 1H, H-4), 2.51-2.63 (m, 1H, H-1), 1.59-2.26 (m + s (2.20, 3H, H-9) + s (2.19), 11.5H), 1.19-1.54 (m, 5.5H). ¹³C-NMR (CDCl₃, 100 MHz): δ [ppm] = 173.8 (C=O, C-8), 164.1 (C-2), 44.4 (C-7), 38.8 (C-1), 35.9 (C-4), 35.4 (C-3), 27.7 (C-6), 27.0 (C-5), 20.4 (C-9).

Camphor-*N*-acetyl hydrazone (11-B)

Synthesis according to general procedure with heating for 5 h at 90 °C in a pressure tube. The crude product was recrystallized from acetone to yield 9.5 g (46 mmol, 77 %) of a colorless crystalline solid.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 9.28 (s, 1H, N-H), 8.36 (s, 1H, N-H), 2.20-2.40 (m + s (2.25, 3H, H12), 4.69H), 1.95-2.11 (m + s (2.04), 5.02H), 1.64-1.95 (m, 5.90H), 1.33-1.49 (m, 1.19H), 1.15-1.28 (m, 1.35H), 0.88-1.12 (m + s (0.99, H-8) + s (0.93, H-10), 7.95H), 0.68-0.85 (m + s (0.74, H-9), 3.85H). ¹³C-NMR (CDCl₃, 100 MHz): δ [ppm] = 173.5 (C-2), 167.6 (C=O, C-11), 52.7 (C-1), 48.0 (C-7), 44.2 (C-4), 33.4 (C-3), 32.7 (C-6), 27.4 (C-5), 20.8 (C-12), 19.6 (C-8), 18.8 (C-10), 11.2 (C-9).

Fenchyl-*N*-acetyl hydrazone (11-F)

Synthesis according to general procedure with heating for 16 h at 90 °C in a pressure tube. Additionally, to heating to 120 °C, the crude mixture was heated in vacuum to remove an excess of fenchone. The

²² Synthesis according to Bekhazi, M.; Risbood, P. A.; Warkentin, J. *J. Am. Chem. Soc.* **1983**, *105*, 5675-5679.

crude product was recrystallized from acetone to yield 9.12 g (59.9 mmol, 58 %) of a colorless crystalline solid.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 8.83 (s, 1.2H, N-H), 8.30 (s, 0.8H, N-H), 2.22 (s, 3H, H-12), 1.88 (m, 1H, H-4), 1.74 („dt“, $\text{J} = 6.3$, 2.8 Hz, 1H, H-5_x), 1.69 – 1.51 (m, 3H, H-6_x, H-7_{syn}, H-5_n), 1.45 – 1.35 (m, 2H, H-6_n, H-7_{anti}), 1.31 (s, 3H, H-9), 1.23 (s, 3H, H-8), 1.20 (s, 3H, H-10). **¹³C-NMR** (CDCl₃, 75 MHz): δ [ppm] = 173.4 (C-11), 167.6 (C-2), 51.4 (C-1), 50.0 (C-4), 42.74 (C-3/C-7), 42.70 (C-3/C-7), 34.4 (C-6), 25.2 (C-5), 23.5 (C-9), 23.4 (C-10), 20.8 (C-12), 17.2 (C-8).

1.3 General procedure for the synthesis of 2-methoxy-2-methyl- Δ^3 -1,3,4-oxadiazolines

The synthesis was conducted according to a procedure published by Warkentin *et al.* [LIT]

Lead tetraacetate (4.44 g, 10 mmol, 1 eq) was suspended in dry methanol (10 mL) and cooled down to 0 °C. Then the *N*-acetyl hydrazone (10 mmol, 1 eq) was added and stirred until the yellow color of the solution disappeared (1 – 2 h). Potassium hydroxide (2 g, 36 mmol, 3.6 eq) was added and the reaction mixture stirred for 2 h at 0 °C. The solvent was evaporated and the precipitate extracted with dichloromethane and water. The organic phase was dried over magnesium sulfate and the solvent evaporated in vacuum. The crude mixture was purified by column chromatography, using PE/Et₂O mixtures as eluent.

Norbornyl- Δ^3 -1,3,4-oxadiazoline (1-N)

The synthesis was carried out according to the general procedure. The purification was carried out with PE/Et₂O 9:1 v/v as solvent mixture to yield 1.5 g (7.6 mmol, 34 %) of a colorless liquid. The oxadiazoline was isolated as a mixture of four diastereomers with the ratio of 1.0 : 1.3 : 1.2 : 1.2.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 3.13 (s, 0.64H/3H, -OCH₃, A), 3.05 (s, 0.80H/3H, -OCH₃, B), 2.99 (s, 0.79H/3H, -OCH₃, C), 2.95 (s, 0.75H/3H, -OCH₃, D), 2.44-2.53 (m, 1H, A+B+C+D, H-4), 2.18-2.36 (m, 1.53H), 2.06-2.18 (m, 0.26H), 1.82-2.06 (m, 1.65H), 1.40-1.82 (m, 8.55H, overlay with 1.62 (s, -CH₃), 1.58 (s, -CH₃) und 1.55 (s, 2x -CH₃)), 1.37 (dd, 0.37H, $\text{J}_{\text{H,H}} = 13.3$ Hz, $\text{J}_{\text{H,H}} = 3.8$ Hz, H-7_{syn}), 1.23 (dd, 0.38H, $\text{J}_{\text{H,H}} = 13.1$ Hz, $\text{J}_{\text{H,H}} = 3.8$ Hz, H-7_{anti}). **¹³C-NMR** (CDCl₃, 125 MHz): δ [ppm] = 133.1 (C_{quartA}, C-8), 132.7 (C_{quartB}, C-8), 132.6 (C_{quartC}, C-8), 132.3 (C_{quartD}, C-8), 127.5 (C_{quartA}, C-2), 127.4 (C_{quartB}, C-2), 127.21 (C_{quartC}, C-2), 127.15 (C_{quartD}, C-2), 50.3 (-OMe_A, C-10), 50.1 (-OMe_B, C-10), 49.97 (-OMe_C, C-10), 49.95 (-OMe_D, C-10), 48.3 (C1), 46.8 (C1), 46.2 (C1), 45.2 (C1), 43.3 (C3), 42.9 (C3), 40.5 (C-7), 40.0 (C-7), 39.0 (C-7), 38.8 (C-7), 38.2 (C-3), 38.1 (C-3), 37.0 (C-4), 36.7 (C-4), 36.4 (C-4), 36.3 (C-4), 28.8 (C-5), 28.6 (C-5), 28.3 (C-5), 28.2 (C-5), 23.4 (C-9), 23.2 (C-9), 23.1 (C-6), 23.04 (C-6), 23.02 (C-9), 22.92 (C-9), 22.7 (C-6), 22.5 (C-6).

Solvolytic isomer separation of norbornyl- Δ^3 -1,3,4-oxadiazoline (*endo*-1-N)

1-N (2.44 g, 12.4 mmol, 1 eq) was solvated in non-anhydrous acetonitrile (10 mL, 0.8 mL/mmol) and trifluoro acetic acid (0.8 mL, 10.5 mmol, 0.8 eq) added. The reaction mixture was stirred for 2.25 h and acid and solvent were removed via distillation. The residue was extracted with dichloromethane and water. Purification via column chromatography with PE/Et₂O 9:1 v/v as eluent yielded 0.771 g (3.93 mmol, 32 %) of a colorless liquid.

OMe, C-10), 46.3 (C1), 45.3 (C1), 40.6 (C-7), 40.1 (C-7), 38.34 (C-3), 38.25 (C-3), 37.1 (C-4), 36.8 (C-4), 28.9 (C-5), 28.7 (C-5), 23.1 (C-9), 23.0 (C-6), 22.8 (C-9), 22.6 (C-6).

Bornyl- Δ^3 -1,3,4-oxadiazoline (1-B)

The synthesis was carried out according to the general procedure. The purification was carried out with a gradient ranging from PE/Et₂O 20:1 v/v to 13:1 v/v to yield 5.94 g (24.9 mmol, 46 %) of a colorless oily liquid. The oxadiazoline was isolated as a mixture of four diastereomers with the ratio of 1.0 : 2.1 : 3.8 : 2.7.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 3.28 (s, 0.30H/3H, -OCH₃, A), 3.26 (s, 0.64H/3H, -OCH₃, B), 2.99 (s, 1.14H/3H, -OCH₃, C), 2.94 (s, 0.82H/3H, -OCH₃, D), 2.59-2.66 (m, 0.14H, H-3_{aq} (A)), 2.48 (ddd, 0.42H, $^2J_{H,H}$ = 13.7 Hz, $^3J_{H,H}$ = 4.5 Hz, 3.1 Hz, H-3_{aq} (C)), 2.34-2.40 (m, 0.32H, H-3_{aq} (D)), 2.24 (ddd, 0.25H, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,H}$ = 4.4 Hz, 3.2 Hz, H-3_{aq} (B)), 1.95-2.07 (m, 0.94H), 1.79-1.95 (m, 2.36H), 1.68-1.72 (m, 1.97H, (s + s, 2x -CH₃)), 1.34-1.66 (m, 5.94H, overlay with 1.54 (s, -CH₃), 1.49 (s, -CH₃), 1.47 (s, -CH₃), 1.43 (s, -CH₃) und 1.41 (s, -CH₃)), 1.06 (s, 0.3H, -CH₃, (A)), 1.04 (s, 0.8H, -CH₃, (D)), 0.96-1.00 (m, 1.8H, overlay of 0.98 (s, -CH₃) und 0.99 (s, -CH₃)), 0.90-0.93 (m, 1.12H, (s + s, 2x -CH₃)), 0.73-0.77 (m, 0.94H, (s + s, 2x -CH₃), A+B), 0.61 (s, 0.8H, D), 0.57 (s, 1.16H, C). **¹³C-NMR** (CDCl₃, 75 MHz, DEPT): δ [ppm] = 129.2, 128.4, 125.6, 125.4, 55.1, 54.7, 51.0, 50.3, 50.1, 49.6, 45.6, 45.3, 41.0, 40.8, 30.9, 30.4, 27.4, 23.2, 21.0, 20.9, 20.3, 19.7. **¹³C-NMR** (125 MHz, CDCl₃, 25 °C): δ [ppm] = 133.31 (C_{quart}, C-11), 133.07 (C_{quart}, C-11), 130.68 (C_{quart}, C-11), 130.60 (C_{quart}, C-2), 130.34 (C_{quart}, C-2), 129.36 (C_{quart}, C-11), 128.19 (C_{quart}, C-2), 55.08 (C_{quart}, C-1), 54.68 (C_{quart}, C-1), 54.48 (C_{quart}, C-1), 54.33 (C_{quart}, C-1), 51.18 (-OMe, C-13), 50.94 (-OMe, C-13), 50.25 (-OMe, C-13), 50.09 (-OMe, C-13), 49.61 (C_{quart}, C-7), 49.57 (C_{quart}, C-7), 49.54 (C_{quart}, C-7), 49.47 (C_{quart}, C-7), 45.53 (C-4), 45.41 (C-4), 45.28 (C-4), 45.25 (C-4), 42.92 (C-5), 42.77 (C-5), 40.98 (C-3), 40.72 (C-3), 30.84 (C-3), 30.79 (C-3), 30.37 (C-5), 30.29 (C-5), 27.39 (C-6), 27.36 (C-6), 27.30 (C-6), 27.19 (C-6), 23.20 (C-12), 23.19 (C-12), 22.85 (C-12), 22.46 (C-12), 20.98 (C-10), 20.90 (C-9), 20.75 (C-10), 20.69 (C-9), 20.29 (C-10), 20.26 (C-10), 19.64 (C-9), 19.63 (C-9), 11.23 (C-8), 10.79 (C-8), 10.22 (C-8), 10.08 (C-8).

Fenchyl- Δ^3 -1,3,4-oxadiazoline (1-F)

The synthesis was carried out according to the general procedure. The purification was carried out with a gradient ranging from PE/Et₂O 30:1 v/v to 10:1 v/v to yield 0.631 g (2.65 mmol, 11 %) of a colorless oily liquid. The oxadiazoline was isolated as a mixture of four diastereomers with the ratio of 1.0 : 5.8 : 5.4 : 2.2.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 3.47 (s, 0.21H/3H, -OCH₃, A), 3.44 (s, 1.20H/3H, -OCH₃, B), 3.41 (s, 1.10H/3H, -OCH₃, C), 3.39 (s, 0.45H/3H, -OCH₃, D), 2.57 (dq, 0.55H, $^2J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 2.2 Hz, H-7_{syn}), 2.47 (dddd, 0.5H, $^2J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 9.1 Hz, 5.7 Hz, 2.2 Hz, H-7_{syn}), 2.02 (ddt, 0.51H, $^2J_{H,H}$ = 12.4 Hz, $^3J_{H,H}$ = 9.1 Hz, 3.3 Hz, H-4), 1.86-1.94 (m, 1H, H-4), 1.75-1.86 (m, 1.5H, H-5_{aq}+H-6_{aq}), 1.74 (s, 1.34H, -CH₃, H-12), 1.73 (s, 1.10, -CH₃, H-12), 1.51-1.66 (m, 2H, overlay with 1.63 (s, -CH₃), 1.60 (s, -CH₃), H-5_{ax}+H-6_{ax}+H-12), 1.36-1.46 (m, 1.1H, H-7_{anti}), 1.18-1.29 (m, 1.5H, H-5_{ax}+H-6_{ax}), 1.01 (s, 1.47H, -CH₃, H-9), 0.97 (s, 0.48H, -CH₃, H-10), 0.96 (s, 1.16H, -CH₃, H-10), 0.90 (s, 1.51H, -CH₃, H-10), 0.84-0.87 (m (s + s),

1.73H, 2x -CH₃, H-9), 0.81 (s, 0.69H, -CH₃, H-8), 0.74 (s, 1.26H, -CH₃, H-8), 0.71 (s, 1.16H, -CH₃, H-8). **¹³C-NMR** (CDCl₃, 125 MHz): δ [ppm] = 132.10 (C_{quart}, C-2/11), 131.94 (C_{quart}, C-2/11), 131.75 (C_{quart}, C-2/11), 131.43 (C_{quart}, C-2/11), 131.40 (C_{quart}, C-2/11), 131.15 (C_{quart}, C-2/11), 130.5 (C_{quart}, C-2/11), 130.2 (C_{quart}, C-2/11), 53.5 (C_{quart}, C-1), 52.9 (C_{quart}, C-1), 52.6 (C_{quart}, C-1), 51.5 (-OMe, C-13), 51.31 (-OMe, C-13), 51.27 (-OMe, C-13), 51.17 (-OMe, C-13), 49.2 (C-4), 49.0 (C-4), 48.6 (C-4), 48.5 (C-4), 45.1 (C-3), 44.9 (C-3), 43.3 (C-6), 43.0 (C-6), 41.9 (C-7), 41.5 (C-7), 31.5 (C-7, B), 31.4 (C-7, A), 29.8 (C-6, D), 29.6 (C-6, C), 26.4, 26.1 (C-5), 26.02, 25.97 (C-5), 25.95 (C-5), 25.90 (C-5), 25.69 (C-9), 25.67 (C-9), 23.2 (C-10, D), 22.9 (C-10, C), 22.7 (C-10, A), 22.0 (C-9, B), 21.2 (C-12, D), 20.5 (C-12, A), 19.7 (C-12, C), 19.4 (C-12, B), 16.3 (C-8, A), 16.0 (C-8, B), 15.7 (C-8, D), 15.4 (C-8, C).

1.4 Syntheses of reference compounds

Synthesis of *exo*-2-(1,1,1,3,3,3-hexafluoroisopropyl)-oxynorbornane (6-N)

Norbornene (2.0 g, 21 mmol, 1 eq), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 4.4 mL, 42 mmol, 2 eq) and copper(II) triflate (252 mg, 0.7 mmol, 0.03 eq) were dissolved in dioxane (12 mL, 0.55 mL/mmol) and heated to 80 °C in a pressure flask for 4 hours. The reaction was then stirred an additional 19 h at room temperature. The reaction mixture was extracted with diethyl ether and water. The purification via column chromatography (PE/Et₂O 20:1 v/v) yielded 2.54 g (10.1 mmol, 48 %) of a colorless oil.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 4.10 (sept, $^3J_{H,F}$ = 6.0 Hz, 1H, H-8), 3.78 („d“(dd), $^3J_{H,H}$ = 7.3 Hz, 1H, H-2), 2.37 („d“, $^3J_{H,H}$ = 4.9 Hz, 1H, H-1), 2.27-2.33 (m, 1H, H-4), 1.37-1.71 (m, 5H, H-3_{aq}+H-3_{ax}+H-5_{aq}+H-6_{aq}+H-7_{syn}), 1.16 (ddq, $^2J_{H,H}$ = 9.9 Hz, $^3J_{H,H}$ = 2.8 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, H-7_{anti}), 0.90-1.10 (m, 2H, H-5_{ax}+H-6_{ax}).

¹³C-NMR (CDCl₃, 75 MHz): δ [ppm] = 121.6 („q“, C-9+C-10), 87.2 (C-2), 74.3 (sept, C-8), 40.9 (C-1), 39.2 (C-3), 35.4 (C-4), 34.6 (C-7), 28.4 (C-5), 24.1 (C-6). **¹⁹F-NMR** (CDCl₃, 565 MHz): δ [ppm] = -74.13 (qd, $^3J_{H,F}$ = 9.1, 6.2), -74.32 (qd, $^3J_{H,F}$ = 9.2, 6.3).

Synthesis of 2-Isopropyl-2',4',6'-trimethoxy-5-methyl-1,2,3,4-tetrahydro-1,1'-biphenyl (10)

Fenchyl- Δ^3 -1,3,4-oxadiazoline (**1-F**) (106 mg, 0.44 mmol, 1 eq) and 1,3,5-trimethoxybenzene (143 mg, 0.85 mmol, 1.9 eq) were dissolved in 1,1,1,3,3,3-hexafluoro isopropanol (6 mL, 13.6 mL/mmol). The colorless solution was photolyzed in three batches of 2 mL for 2 hours in a photo reactor with UV-B lamps in quartz cuvettes. The solution became a pale pink. The solvent was evaporated and the combined batches purified via column chromatography (PE/Et₂O 9:1 v/v) to yield 33.2 mg (0.11 mmol, 25 %) of a colorless oil.

When using the Bornyl- Δ^3 -1,3,4-oxadiazoline (**1-B**), the same product was isolated with lower conversion.

¹H-NMR (CDCl₃, 400 MHz): δ [ppm] = 6.13 (s, 2H, H-Ar, H-13+H-15), 5.13 (s, 1H, H-2), 3.77-3.84 (m, 1H, H-1, overlay with 3.80 (s, 3H, -OMe, H-18)), 3.73 (s, 6H, -OMe, H-17+H-19), 2.03-2.16 (m, 1H, H-4a), 1.91-2.03 (m, 2H, H-4b+H-6), 1.68-1.77 (m, 1H, H-5a), 1.65 (s, 3H, H-7), 1.23-1.50 (m, 3H, H-8+H-5b), 0.81 (d, 3H, $3J_{H,H}$ = 7.0 Hz, H-10), 0.75 (d, 3H, $3J_{H,H}$ = 6.9 Hz, H-9). **¹³C-NMR** (CDCl₃, 100 MHz): δ [ppm] = 159.8 (C_{quart}, C-14), 159.1 (C_{quart}, C-12+C-16), 131.5 (C_{quart}, C-3), 126.5 (C-2), 114.9 (C_{quart}, C-11), 91.5 (C-13+C-15), 56.0 (-OMe, C-17+C-19), 55.2 (-OMe, C-18), 42.2 (C-6), 35.6 (C-1), 31.0 (C-4), 28.4 (C-8), 23.4 (C-7), 23.1 (C-5), 21.6 (C-10), 16.2 (C-9).

Synthesis of *exo*-2-Norbornyl-(2,2,2-trifluoro) acetate (**5-N**)

Norbornene (2.0 g, 21 mmol, 1 eq), 2,2,2-trifluoro acetic acid (3.1 mL, 4.56 g, 40 mmol, 2.0 eq) and copper(II) triflate (256 mg, 0.70 mmol, 0.03 eq) were dissolved in dioxane (12 mL, 0.55 mL/mmol) and stirred in a pressure flask for 4 h at 80 °C and for 19 h at room temperature. When the reaction was finished, the mixture was extracted with diethyl ether and water. Purification via column chromatography (PE/Et₂O 20:1 v/v) and subsequent distillation yielded 2.26 g (10.9 mmol, 52 %) of a colorless oil.

¹H-NMR (CDCl₃, 300 MHz): δ [ppm] = 4.81 („d“(dd), $3J_{H,H}$ = 7.0 Hz, 1H, H-2), 2.36 („d“, $3J_{H,H}$ = 4.5 Hz, 1H, H-1), 2.31-2.39 (m, 1H, H-4), 1.81 (ddd, $2J_{H,H}$ = 13.8 Hz, $3J_{H,H}$ = 7.0 Hz, $4J_{H,H}$ = 2.5 Hz, 1H, H-3_{aq}), 1.41-1.67 (m, 4H, H-3_{ax}+H-5_{aq}+H-6_{aq}+H-7_{syn}), 1.24 (ddq, $2J_{H,H}$ = 10.2 Hz, $3J_{H,H}$ = 2.8 Hz, $4J_{H,H}$ = 1.4 Hz, 1H, H-7_{anti}), 1.03-1.20 (m, 2H, H-5_{ax}+H-6_{ax}). **¹³C-NMR** (CDCl₃, 75 MHz): δ [ppm] = 157.2 (q, C-8), 114.7 (q, C-9), 82.2 (C-2), 41.5 (C-1), 39.2 (C-3), 35.5 (C-4), 35.3 (C-7), 28.0 (C-5), 24.0 (C-6). **¹⁹F-NMR** (CDCl₃, 565 MHz): δ [ppm] = -75.60 (m).

2. Kinetic studies

2.1 Photolysis of Norcamphor Precursor **1-N** in ACN

Scheme S4 Overview of products observed and characterized in the UV-B photolysis of **1-N** under different conditions.

Figure S4: Kinetic trace of the photolysis of **1-N** in ACN- d_3 . The photolysis was carried out in a quartz NMR tube with UV-B light under exclusion of air and rate constants were determined by four independent runs.

Table S3: Concentrations (c) of the photolysis products determined by ^1H NMR in the UVB irradiation of **1-N** (quartz NMR tube) in ACN-d_3 (kinetic traces see Figure S1).

t [min]	c [mmol/L]							
	1-N	1-N	1-N	1-N	MeOAc	MeOAc	MeOAc	MeOAc
	run 1	run 2	run 3	run 4	run 1	run 2	run 3	run 4
0	33.12103	33.12103	33.12103	33.12103	0	0	0	0
1	28.85504	29.05045	28.52383	28.69937	3.59032	3.80229	4.24612	3.54395
3	20.72051	20.84969	20.42243	19.95542	10.73784	11.38039	11.51949	10.10191
7	7.65758	9.20433	8.37962	7.52179	22.02548	22.44943	23.34039	19.68383
11	-	2.93121	2.3814	1.93427	-	29.42141	29.68969	26.55313
13	0.8479	-	-	-	28.74243	-	-	-
14	0.49019	-	-	-	30.16001	-	-	-
15	-	0.4372	0.42064	0.36102	-	31.55109	31.45504	30.01096
17	0.09936	-	-	-	30.36205	-	-	-
19	-	0.06293	0.09274	0.05962	-	30.47797	31.95517	30.00434
max. conv.	0.3 %	0.2 %	0.3 %	0.2 %	92 %	92 %	96 %	91 %

Table S4: Concentrations (c) of the photolysis products determined by ^1H NMR in the UVB irradiation of **1-N** (quartz NMR tube) in ACN-d_3 (kinetic traces see Figure S1).

t [min]	c [mmol/L]							
	4-N	4-N	4-N	4-N	12	12	12	12
	run 1	run 2	run 3	run 4	run 1	run 2	run 3	run 4
0	0	0	0	0	0	0	0	0
1	0.8479	1.05987	0.9572	0.8214	1.0135	0.83465	1.13274	1.02344
3	2.79541	3.65656	2.50726	1.70905	2.99083	3.25911	3.32866	2.61325
7	8.17758	5.25962	5-39873	3.18955	5.06752	4.69987	5.94191	4.84892
11	-	8.61478	7.89605	5.87898	-	6.19032	7.35287	7.45223
13	11.15185	-	-	-	5.83261	-	-	-
14	12.36408	-	-	-	6.37911	-	-	-
15	-	10.17478	8.99567	7.43567	-	6.68714	7.41249	8.81351
17	12.03618	-	-	-	5.52459	-	-	-

19	-	9.11491	9.13809	7.51847	-	5.8028	7.59134	8.07822
max.	36 %	28 %	28 %	23 %	17 %	18 %	23 %	24 %
conv.								

Table S5: Concentrations (c) of the photolysis products determined by ^1H NMR in the UVB irradiation of **1-N** (quartz NMR tube) in ACN-d_3 (kinetic traces see Figure S1).

t [min]	c [mmol/L]			
	13 run 1	13 run 2	13 run 3	13 run 4
0	0	0	0	0
1	0.03975	0.02981	0.01987	0.02981
3	0.11924	0.04968	0.04968	0.08943
7	0.31796	0.13911	0.18879	0.11924
11	-	0.3279	0.3279	0.36764
13	1.14268	-	-	-
14	1.39108	-	-	-
15	-	1.00357	0.98369	1.3414
17	1.89783	-	-	-
19	-	1.42089	1.73885	2.15618
max.	6 %	4 %	5 %	7 %
conv.				

Table S6: Rate constants (mono exponential fit) of the different diastereomers (**A-D**) of **1-N** in the photolysis experiment with UV-B light in ACN-d_3 (quartz NMR tubes) under exclusion of air.

	k [min^{-1}]				$k_{\phi, \text{isomers}}^a$ [min^{-1}]	$k_{\phi, \text{total}}^a$ [min^{-1}]
	Isomer A <i>endo-1-N</i>	Isomer B <i>endo-1-N</i>	Isomer C <i>endo-1-N</i>	Isomer D <i>endo-1-N</i>		
run 1	0.1679 ± 0.0198	0.1810 ± 0.0176	0.1646 ± 0.0194	0.1561 ± 0.0156	0.167 $\sigma = 0.010$	0.1628 ± 0.0193
	$R^2 = 0.994$	$R^2 = 0.996$	$R^2 = 0.995$	$R^2 = 0.996$		$R^2 = 0.995$
run 2	0.1691 ± 0.0202	0.1750 ± 0.0222	0.1658 ± 0.0217	0.1599 ± 0.0183	0.167 $\sigma = 0.006$	0.1581 ± 0.0148
	$R^2 = 0.993$	$R^2 = 0.992$	$R^2 = 0.992$	$R^2 = 0.994$		$R^2 = 0.996$

run 3	0.1722 ± 0.0152	0.1775 ± 0.0178	0.1689 ± 0.0155	0.1594 ± 0.0172	σ = 0.008	0.1694 ± 0.0162
	R ² = 0.996	R ² = 0.995	R ² = 0.996	R ² = 0.995		R ² = 0.996
run 4	0.1847 ± 0.0153	0.1931 ± 0.0188	0.1792 ± 0.0203	0.1645 ± 0.0191	σ = 0.012	0.1805 ± 0.0189
	R ² = 0.996	R ² = 0.995	R ² = 0.993	R ² = 0.994		R ² = 0.994
k _{∅,runs} ^c [min ⁻¹]	0.174	0.182	0.170	0.160	0.171	0.168
	σ = 0.008	σ = 0.008	σ = 0.007	σ = 0.003	σ = 0.006	σ = 0.010

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S7: Rate constants of the formation of the observed and identified photolysis products of **1-N** (diastereomeric mixture A, B, C, D). Experiment run in quartz NMR tube with UV-B-light in ACN-d₃ under exclusion of air.

	MeOAc	4-N	12	13
	k [min ⁻¹]	k [min ⁻¹]	k [min ⁻¹]	k [min ⁻¹]
run 1	0.1425 ± 0.0157	0.1014 ± 0.0330	0.2053 ± 0.0270	0.1031 ± 0.0186
	R ² = 0.996	R ² = 0.980	R ² = 0.993	R ² = 0.992
run 2	0.1618 ± 0.0252	0.1207 ± 0.0452	0.1718 ± 0.0364	0.1183 ± 0.0355
	R ² = 0.989	R ² = 0.954	R ² = 0.985	R ² = 0.961
run 3	0.1593 ± 0.0183	0.1029 ± 0.0197	0.1867 ± 0.0234	0.1559 ± 0.0209
	R ² = 0.994	R ² = 0.990	R ² = 0.994	R ² = 0.989
run 4	0.1297 ± 0.0157	0.0512 ± 0.0299	0.0568 ± 0.0159	0.1517 ± 0.0357
	R ² = 0.995	R ² = 0.971	R ² = 0.996	R ² = 0.967
k _{∅,runs} ^c [min ⁻¹]	0.148	0.094	0.155	0.132
	σ = 0.015	σ = 0.030	σ = 0.067	σ = 0.026
k _{∅,runs} ^c [min ⁻¹]	0.155	0.108	0.188	0.126
(without run 4)	σ = 0.011	σ = 0.011	σ = 0.017	σ = 0.027

^a average of the rate constants determined in the three runs.

Figure S5: Kinetic trace of the photolysis of *endo-1-N* in ACN- d_3 . The photolysis was carried out in a quartz NMR tube with UV-B light under exclusion of air. Rate constants were determined in three independent runs.

Table S8: Concentrations (*c*) of the observed and identified photolysis products and of *endo-1-N* as determined by ^1H NMR spectroscopy. The photolysis experiments of *endo-1-N* were run in quartz NMR tubes in degassed ACN- d_3 (kinetic traces see Figure S2).

t [min]	c [mmol/L]					
	<i>endo-1-N</i> run 1	<i>endo-1-N</i> run 2	<i>endo-1-N</i> run 3	MeOAc run 1	MeOAc run 2	MeOAc run 3
0	32.61153	32.61153	32.61153	0	0	0
1	28.87425	27.53718	28.00352	3.48291	4.30472	4.15471
3	21.17141	17.66567	19.22776	10.35742	12.50000	11.58035
7	9.59105	4.86890	6.55166	20.94639	23.50639	22.89982
11	2.21432	0.72071	1.22619	26.54905	27.40999	27.44260
15	0.31307	0.05218	0.14675	28.75685	29.63736	28.73076
19	0.06196	0	0.01631	30.13632	30.03196	29.09275
max. conv.	0.2 %	0 %	0 %	92 %	92 %	89 %

Table S9. Concentrations (c) of the observed and identified photolysis products and of *endo-1-N* as determined by ¹H NMR spectroscopy. The photolysis experiments of *endo-1-N* were run in quartz NMR tubes in degassed ACN-d₃ (kinetic traces see Figure S2).

t [min]	c [mmol/L]								
	4-N	4-N	4-N	12	12	12	13	13	13
	run 1	run 2	run 3	run 1	run 2	run 3	run 1	run 2	run 3
0	0	0	0	0	0	0	0	0	0
1	1.31424	1.38599	2.113230	0.42069	0.90986	0.45982	0.04892	0	0
3	4.39277	4.83303	5.53744	2.28933	2.4263	1.04683	0.06848	0.07827	0.09783
7	6.41143	6.17662	9.18015	3.60031	3.63945	2.10344	0.02935	0.04892	0.1174
11	7.92786	7.48761	10.82051	4.68628	4.21667	3.21876	0.1761	0.10762	--
15	9.59431	10.15849	12.86199	5.3222	5.18523	3.51226	0.52831	0.72398	0.42069
19	11.32598	10.47482	13.50444	5.85051	4.61779	3.65901	1.1251	1.32077	0.77289
max. conv.	35 %	32 %	41 %	18 %	14 %	11 %	3 %	4 %	2 %

Table S10. Rate constants (mono-exponential fit) of the depletion of *endo-1-N* (diastereomers **B** and **C**) during UVB photolysis in ACN-d₃(quartz NMR tube) using the data of **Table S6**.

	k _{isomer} [min ⁻¹] of the diastereomers C and B		k _{∅,isomers} ^a [min ⁻¹]	k _{∅,total} ^b [min ⁻¹]
	B-1-N	C-1-N		
run 1	0.1470 ± 0.0147	0.1572 ± 0.0209	0.152	0.1512 ± 0.0203
	R ² = 0.996	R ² = 0.992		R ² = 0.992
run 2	0.2190 ± 0.0247	0.2139 ± 0.0243	0.216	0.2199 ± 0.0248
	R ² = 0.991	R ² = 0.992		R ² = 0.992
run 3	0.1961 ± 0.0229	0.1868 ± 0.0224	0.191	0.1912 ± 0.0223
	R ² = 0.995	R ² = 0.992		R ² = 0.993
k _{∅,runs} ^c	0.187	0.186	0.187	0.187
[min ⁻¹]	σ = 0.037	σ = 0.028	σ = 0.032	σ = 0.035

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S11. Rate constants (mono-exponential fit) of the formation of photoproducts during the UVB photolysis of *endo*-**1-N** (diastereomers **B** and **C**) in degassed ACN- d_3 (quartz NMR tube) using the data of **Tables S6 & S7**.

	k [min^{-1}]			
	MeOAc	4-N	12	13
run 1	0.1446 ± 0.0122	0.0960 ± 0.0299	0.1407 ± 0.0321	0.2088 ± 0.0259
	$R^2 = 0.997$	$R^2 = 0.977$	$R^2 = 0.987$	$R^2 = 0.988$
run 2	0.1862 ± 0.0140	0.1132 ± 0.0441	0.1691 ± 0.0425	0.1927 ± 0.0459
	$R^2 = 0.997$	$R^2 = 0.955$	$R^2 = 0.980$	$R^2 = 0.958$
run 3	0.1844 ± 0.0199	0.1460 ± 0.0163	0.0790 ± 0.0255	0.1326 ± 0.0273
	$R^2 = 0.994$	$R^2 = 0.995$	$R^2 = 0.989$	$R^2 = 0.988$
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.172	0.118	0.130	0.178
	$\sigma = 0.024$	$\sigma = 0.025$	$\sigma = 0.046$	$\sigma = 0.040$

^a average of the rate constants determined in the three runs.

2.2 Photolysis of the Bornyl Precursor **1-B** in ACN

Scheme S5 Overview of products observed and characterized in the UV-B photolysis of **1-B** under different conditions. Highlighted is the diazo **2-B** that shows unexpected stability under the reaction conditions.

Figure S6. Kinetic trace of the photolysis of **1-B** in ACN- d_3 . The photolysis was carried out in quartz NMR tubes with UV-B light (three-fold determination).

Table S12: Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-B** in a quartz NMR tube in ACN- d_3 (kinetic traces see Figure S3) (1 of 3).

t [min]	c [mmol/L]					
	1-B	1-B	1-B	MeOAc	MeOAc	MeOAc
	run 1	run 2	run 3	run 1	run 2	run 3
0	31.32898	31.32898	31.32898	0	0	0
1	28.56890	27.76374	28.36212	2.82274	3.11410	3.01698
3	23.02367	21.20345	21.77991	7.80405	8.46550	8.68439
7	11.82356	10.5516	10.92755	17.28733	18.14574	18.48410
11	5.07216	3.81900	3.93805	23.13958	24.20477	24.70917
15	1.66670	-	1.00566	26.14717	-	27.33140
19	0.22557	0.14725	0.11905	27.87026	27.15656	27.86713
max. conv.	1 %	0.5 %	0.4 %	89 %	87 %	89 %

Table S13. Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-B** in a quartz NMR tube in ACN-d_3 (kinetic traces see Figure S3) (2 of 3).

t [min]	c [mmol/L]					
	8	8	8	15	15	15
	run 1	run 1	run 1	run 1	run 2	run 3
0	0	0	0	-	-	-
1	0.21617	0.22557	0.15038	-	-	-
3	1.04325	0.78009	0.83648	-	-	-
7	2.36847	1.36281	1.46620	-	-	-
11	2.88540	2.12410	1.95493	-	-	-
15	3.30834	-	2.87600	-	-	-
19	3.80647	3.04518	3.29894	5.03770	3.57150	4.04144
max. conv.	12 %	10 %	11 %	16 %	11 %	13 %

Table S14. Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-B** in a quartz NMR tube in ACN-d_3 (kinetic traces see Figure S3) (3 of 3). Last row shows final conversion in %.

t [min]	c [mmol/L]					
	4-B	4-B (b)	4-B (c)	2-B	2-B	2-B
	run 1	run 2	run 3	run 1	run 2	run 3
0	-	-	-	0	0	0
1	-	-	-	1.52259	2.33088	2.25569
3	-	-	-	3.82527	4.60536	5.32906
7	-	-	-	5.93997	11.26903	11.34422
11	-	-	-	9.35170	12.46267	14.75595
15	-	-	-	10.0566	-	12.34048
19	4.16362	3.87226	4.16362	9.99081	11.85175	12.03973
max. conv.	13 %	12 %	13 %	32 %	38 %	38 %

Table S15. Rate constants k (mono-exponential fit) of the different isomers of **1-B** in the photolysis experiment (UVB) in quartz NMR tubes in ACN- d_3 (degassed).

	k_{isomer} [min^{-1}] of the single diastereomers A - D				$k_{\phi, \text{isomers}}^a$ [min^{-1}]	$k_{\phi, \text{total}}^b$ [min^{-1}]
	A-1-B	B-1-B	C-1-B	D-1-B		
run 1	0.1234 ± 0.0166	0.1302 ± 0.0156	0.1122 ± 0.0154	0.1005 ± 0.0140	0.117 $\sigma = 0.013$	0.1100 ± 0.0159 $R^2 = 0.994$
	$R^2 = 0.994$	$R^2 = 0.995$	$R^2 = 0.994$	$R^2 = 0.995$		
run 2	0.1376 ± 0.0200	0.1584 ± 0.0166	0.1310 ± 0.0202	0.1162 ± 0.0100	0.136 $\sigma = 0.018$	0.1333 ± 0.0160 $R^2 = 0.995$
	$R^2 = 0.992$	$R^2 = 0.995$	$R^2 = 0.991$	$R^2 = 0.998$		
run 3	0.1356 ± 0.0141	0.1431 ± 0.0206	0.1275 ± 0.0163	0.1182 ± 0.0170	0.131 $\sigma = 0.011$	0.1254 ± 0.0161 $R^2 = 0.994$
	$R^2 = 0.996$	$R^2 = 0.992$	$R^2 = 0.994$	$R^2 = 0.993$		
$k_{\phi, \text{runs}}^c$ [min^{-1}]	0.132 $\sigma = 0.008$	0.144 $\sigma = 0.014$	0.124 $\sigma = 0.010$	0.160 $\sigma = 0.003$	0.128 $\sigma = 0.010$	0.123 $\sigma = 0.012$

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S16. Rate constants k (mono-exponential fit) of the different reaction products determined from the ^1H NMR monitoring of the photolysis of **1-B** in quartz NMR tubes (ACN- d_3 , degassed, UVB).

	k [min^{-1}]		
	MeOAc	8	2-B
run 1	0.1089 ± 0.0114	0.1041 ± 0.0178	0.1271 ± 0.0317
	$R^2 = 0.997$	$R^2 = 0.992$	$R^2 = 0.978$
run 2	0.1327 ± 0.0194	0.0466 ± 0.0115	0.2203 ± 0.0723
	$R^2 = 0.992$	$R^2 = 0.995$	$R^2 = 0.944$
run 3	0.1288 ± 0.0167	0.0282 ± 0.0192	0.2388 ± 0.0841
	$R^2 = 0.994$	$R^2 = 0.987$	$R^2 = 0.925$
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.123	0.059	0.195
	$\sigma = 0.013$	$\sigma = 0.040$	$\sigma = 0.060$

^a average of the rate constants determined in the three runs.

2.3 Photolysis of Fenchyl Precursor **1-F** in ACN

Scheme 56 Overview of products observed and characterized in the UV-B photolysis of **1-F** under different conditions. The under these reaction conditions unexpectedly stable **2-F** is highlighted.

Figure S7. Kinetic trace of the photolysis of **1-F** in ACN-*d*₃. The photolysis was carried out in a quartz NMR tubes with UV-B light in three independent runs.

Table S17. Concentration (c) changes in dependence of time of **1-F** and MeOAc determined by ^1H NMR of the photolysis of **1-F** in a quartz NMR tubes in ACN-d_3 (plotted kinetic traces see Figure S4). Last row shows final conversion in %.

t [min]	c [mmol/L]					
	1-F	1-F	1-F	MeOAc	MeOAc	MeOAc
	run 1	run 2	run 3	run 1	run 2	run 3
0	31.60870	31.60870	31.60870	0	0	0
1	28.07169	27.32256	27.67342	3.55282	4.02695	3.83414
3	20.96289	19.57527	19.73015	10.21593	11.67941	11.5593
7	9.27083	7.23207	7.66827	21.10829	23.39044	22.96372
11	3.14190	1.96606	2.12094	23.91481	27.84094	27.67658
15	0.85027	0.44884	0.40775	28.72283	28.36249	28.79553
19	0.28764	0.19281	0.01580	29.22224	29.14006	28.89983
max. conv.	1 %	1 %	0 %	92 %	92 %	91 %

Table S18. Concentrations (c) of the reaction products **7** and **4** determined by ^1H NMR of the photolysis (UVB) of **1-F** in a quartz NMR tubes in ACN-d_3 (plotted kinetic traces see Figure S4). Last row shows final conversion in %.

t [min]	c [mmol/L]					
	7	7	7	4-F	4-F	4-F
	run 1	run 2	run 3	run 1	run 2	run 3
0	0	0	0	0	0	0
1	0.27500	0.13276	0.28448	0.30344	0.03793	0.36034
3	1.22326	1.67842	1.01464	1.61204	2.02928	1.97238
7	2.67410	2.63617	2.17152	3.75511	3.55598	3.90684
11	4.19131	4.14390	3.17667	6.03094	5.52836	5.65164
15	5.75594	5.36716	4.17235	8.20246	7.07403	7.34902
19	7.06454	7.12144	5.40509	9.86191	9.30244	8.79986
max. conv.	22 %	23 %	17 %	31 %	29 %	28 %

Table S19. Concentrations (c) of product **2-F** in dependence of time determined by ^1H NMR of the photolysis of **1-F** in a quartz NMR tubes in ACN-d_3 (plotted kinetic traces see Figure S4). Last row shows final conversion in %.

t [min]	c [mmol/L]		
	2-F	2-F	2-F
0	0	0	0
1	2.41332	3.49592	2.81634
3	6.4782	6.77216	7.98752
7	12.36216	14.86557	15.21169
11	12.3511	14.3788	15.77906
15	8.38579	11.01405	12.67983
19	4.51846	4.97837	8.24039
max. conv.	39 %	47 %	50 %

Table S20. Rate constants k (mono-exponential fit) of the different isomers of **1-F** in the photolysis experiment (UVB) in quartz NMR tubes in ACN-d_3 .

	k [min^{-1}] single diastereomers A-D				$k_{\phi, \text{isomers}}^a$	$k_{\phi, \text{total}}^b$
	A-1-F	B-1-F	C-1-F	D-1-F	[min^{-1}]	[min^{-1}]
run 1	0.1456 ± 0.0236	0.1374 ± 0.0169	0.1573 ± 0.0188	0.1496 ± 0.0238	0.147 $\sigma = 0.008$	0.1489 ± 0.0179
	$R^2 = 0.989$	$R^2 = 0.994$	$R^2 = 0.994$	$R^2 = 0.990$		$R^2 = 0.994$
run 2	0.1543 ± 0.0235	0.1641 ± 0.0208	0.1871 ± 0.0220	0.1871 ± 0.0199	0.173 $\sigma = 0.017$	0.1770 ± 0.0210
	$R^2 = 0.990$	$R^2 = 0.992$	$R^2 = 0.993$	$R^2 = 0.994$		$R^2 = 0.993$
run 3	0.434 ± 0.0296	0.1581 ± 0.0203	0.1820 ± 0.0207	0.1898 ± 0.0154	0.168 $\sigma = 0.021$	0.1701 ± 0.0194
	$R^2 = 0.983$	$R^2 = 0.992$	$R^2 = 0.993$	$R^2 = 0.996$		$R^2 = 0.994$
$k_{\phi, \text{runs}}^c$	0.148 $\sigma = 0.006$	0.153 $\sigma = 0.014$	0.175 $\sigma = 0.016$	0.176 $\sigma = 0.022$	0.163 $\sigma = 0.014$	0.165 $\sigma = 0.015$

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S21. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis (UVB) of **1-F** in quartz NMR tubes in ACN- d_3 .

	k [min^{-1}]		
	MeOAc	8	2-B
run 1	0.1543 ± 0.0185 $R^2 = 0.994$	n. d. (linear)	n. d. (linear)
run 2	0.1918 ± 0.0244 $R^2 = 0.991$	n. d. (linear)	n. d. (linear)
run 3	0.1866 ± 0.0230 $R^2 = 0.992$	n. d. (linear)	n. d. (linear)
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.178 $\sigma = 0.020$	n. d.	n. d.

^a average of the rate constants determined in the three runs.

Figure S8. Kinetic trace of the photolysis of **1-N** in ACN- d_3 in the presence of 2 equiv. of TFA. The photolysis was carried out in quartz fluorescence cuvettes (1 cm path length) with UV-B light (two independent runs).

Table S22. Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-N** in a quartz cuvette in presence of 2 equiv. of TFA in ACN-d_3 (kinetic traces see Figure S5).

t [min]	c [mmol/L]							
	1-N	1-N	MeOAc	MeOAc	4-N	4-N	5-N	5-N
	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
0	30.74274	31.08293	0	0	0	0	0	0
1	28.06813	29.72461	1.74926	1.68159	1.11596	0.78951	1.36498	0.73667
3	25.85772	26.57901	4.78665	4.88313	2.22577	2.04215	2.20425	2.00485
7	19.60157	19.17817	11.50394	11.48203	5.18323	5.23437	4.4454	4.55054
13	10.34801	9.62327	20.88662	21.45655	9.02914	9.38394	8.23598	8.16859
21	1.99213	1.97687	28.64302	28.49994	12.49693	12.23735	11.28874	10.91011
30	0.03997	0.16163	30.1863	30.24058	13.27164	12.5171	11.93433	11.57217
max. conv.	0.1 %	0.5 %	98 %	97 %	43 %	40 %	39 %	37 %

2.4 Photolysis of 1-N in ACN + Acid

Table S23. Rate constants k (mono-exponential fit) of the different diastereomers A-D of **1-N** in the photolysis experiments (UVB) in quartz cuvettes (fluorescence cell, path length 1 cm) in presence of 2 equiv. of TFA in ACN-d_3 (kinetic traces see Figure S5).

	k [min^{-1}] of the single diastereomers A-D				$k_{\phi, \text{isomers}}^a$	$k_{\phi, \text{total}}^b$
	A-1-N	B-1-N	C-1-N	D-1-N	[min^{-1}]	[min^{-1}]
run 1	0.0589 ± 0.0119	0.0596 ± 0.0134	0.0552 ± 0.0130	0.0482 ± 0.0142	0.056	0.0554 ± 0.0131
	$R^2 = 0.990$	$R^2 = 0.988$	$R^2 = 0.988$	$R^2 = 0.985$	$\sigma = 0.005$	$R^2 = 0.988$
run 2	0.0701 ± 0.0106	0.0678 ± 0.0130	0.0631 ± 0.0129	0.0510 ± 0.0187	0.063	0.0635 ± 0.0128
	$R^2 = 0.993$	$R^2 = 0.989$	$R^2 = 0.989$	$R^2 = 0.975$	$\sigma = 0.009$	$R^2 = 0.989$
$k_{\phi, \text{runs}}^c$	0.065	0.064	0.059	0.050	0.060	0.060

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S24. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis of **1-N** in the photolysis experiment in the cuvette with UV-B-light in the presence of 2 equiv. TFA in ACN- d_3 (kinetic traces see Figure S5).

	k [min^{-1}]		
	MeOAc	4-N	5-N
run 1	0.0626 ± 0.0130 $R^2 = 0.988$	0.0613 ± 0.0118 $R^2 = 0.990$	0.0595 ± 0.0146 $R^2 = 0.985$
run 2	0.0648 ± 0.0132 $R^2 = 0.988$	0.0744 ± 0.0158 $R^2 = 0.985$	0.0661 ± 0.0118 $R^2 = 0.991$
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.064	0.068	0.063

^a average of the rate constants determined in the two runs.

Figure S9. Kinetic trace derived of the ^1H -NMR monitoring of the photolysis (UVB) of **1-N** in ACN- d_3 in the presence of 2 equiv. of TFA and 3 equiv. of TMB. The photolysis was carried out in quartz cuvettes (fluorescence cell, path length 1 cm) in two independent runs.

Table S25. Concentrations (c) of the starting materials (summation over all diastereomers) and reaction products determined by ^1H NMR of the photolysis of **1-N** in quartz cuvettes (fluorescence cell, 1 cm path length) in presence of 2 equiv. of TFA and 3 equiv. of TMB in ACN-d_3 (kinetic traces see Figure S6).

t [min]	c [mmol/L]							
	1-N	1-N	MeOAc	MeOAc	4-N	4-N	5-N	5-N
	run 1	run 2	run 1	run 2	run 1	run 2	run 1	run 2
0	30.74274	31.25266	0	0	0	0	0	0
1	28.98119	29.48376	1.63859	1.72202	0.60256	0.70943	0.47036	0.72194
3	25.47959	26.41475	5.27853	5.19106	2.08128	2.12518	1.84456	1.89391
7	18.78689	19.28289	11.60539	11.27283	4.84813	4.94729	4.43618	4.63164
13	9.96065	9.61644	20.50848	21.29867	8.62334	9.05076	7.86707	8.19444
21	2.29956	1.55326	27.72073	29.39623	12.06345	12.41042	10.94749	11.3072
30	0.18446	0.10313	30.55521	31.08700	12.93962	13.09173	11.86055	12.02914
max. conv.	0.6 %	0.3 %	99 %	99 %	42 %	42 %	39 %	38 %11

Table S26. Rate constants k (mono-exponential fit) of the different diastereomers of **1-N** in the photolysis experiment in the quartz cuvette with UV-B light in presence of 2 equiv. of TFA and 3 equiv. of TMB in ACN-d_3 (kinetic traces see Figure S6).

	k [min^{-1}] of the single diastereomers A-D				$k_{\phi, \text{isomers}}^a$ [min^{-1}]	$k_{\phi, \text{total}}^b$ [min^{-1}]
	A-1-N	B-1-N	C-1-N	D-1-N		
run 1	$0.0628 \pm$	$0.0650 \pm$	$0.0625 \pm$	$0.0592 \pm$	0.062 $\sigma = 0.002$	$0.0626 \pm$
	0.0099	0.0103	0.0097	0.0099		0.0099
	$R^2 = 0.993$	$R^2 = 0.993$	$R^2 = 0.994$	$R^2 = 0.993$		$R^2 = 0.993$
run 2	$0.0667 \pm$	$0.0658 \pm$	$0.0615 \pm$	$0.0603 \pm$	0.064 $\sigma = 0.003$	$0.0634 \pm$
	0.0121	0.0135	0.0156	0.0129		0.0135
	$R^2 = 0.990$	$R^2 = 0.988$	$R^2 = 0.983$	$R^2 = 0.988$		$R^2 = 0.988$
$k_{\phi, \text{isomers}}^a$ [min^{-1}]	0.065	0.065	0.062	0.060	0.063	0.063

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S27. Rate constants k (mono-exponential fit) of the different reaction products of the UVB-photolysis of **1-N** in a quartz cuvette (fluorescence cell, path length 1 cm) in the presence of 2 equiv. TFA and 3 equiv. TMB in ACN- d_3 (kinetic traces see Figure S6).

	k [min^{-1}]		
	MeOAc	4-N	5-N
run 1	0.0626 ± 0.0130	0.0613 ± 0.0118	0.0595 ± 0.0146
	$R^2 = 0.988$	$R^2 = 0.990$	$R^2 = 0.985$
run 2	0.0648 ± 0.0132	0.0744 ± 0.0158	0.0661 ± 0.0118
	$R^2 = 0.988$	$R^2 = 0.985$	$R^2 = 0.991$
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.064	0.068	0.063

^a average of two runs.

2.5 Photolysis of **1-B** in ACN + Acid

Figure S10. Kinetic traces obtained from ^1H -monitoring of the photolysis of **1-B** in ACN- d_3 in the presence of 2 equiv. of TFA. The photolysis was carried out in a quartz cuvette with UV-B light in two independent runs

Table S28. Concentrations (c) of the reaction products determined by ^1H NMR monitoring of the photolysis of **1-B** in quartz cuvettes (fluorescence cell, 1 cm path length) in presence of 2 equiv. of TFA in ACN-d_3 (degassed, kinetic traces see Figure S7).

t [min]	c [mmol/L]					
	1-B run 1	1-B run 2	MeOAc run 1	MeOAc run 2	8 run 1	8 run 2
0	30.76951	31.88847	0	0	0	0
1	29.02488	31.07531	2.30771	1.82721	1.633860	1.32975
3	25.14177	27.06055	5.96313	5.39553	4.22773	3.77878
7	17.49555	20.43413	13.60936	12.33446	9.49855	9.04995
13	7.87392	10.89310	23.30791	21.9010	16.65246	15.76566
21	1.22463	2.41077	29.16950	30.45667	21.51712	22.51964
30	0.08615	0.10842	30.57874	32.84193	23.04944	24.20335
max. conv.	0.3 %	0.3 %	99 %	103 %	75 %	76 %

Table S29. Rate constants k (mono-exponential fit) of the different isomers of the bornyl oxadiazoline **1-B** in the photolysis experiment in the quartz cuvette with UV-B light in presence of 2 equiv. of TFA in ACN-d_3 .

	k [min^{-1}] of the different diastereomers A-D				$k_{\phi, \text{isomers}}^a$ [min^{-1}]	$k_{\phi, \text{total}}^b$ [min^{-1}]
	A-1-B	B-1-B	C-1-B	D-1-B		
run 1	0.1006 $\pm$ 0.0050 $R^2 = 0.999$	0.0808 $\pm$ 0.0149 $R^2 = 0.987$	0.0843 $\pm$ 0.0105 $R^2 = 0.994$	0.0646 $\pm$ 0.0162 $R^2 = 0.982$	0.083 $\sigma = 0.015$	0.0771 $\pm$ 0.0126 $R^2 = 0.991$
run 2	0.0583 $\pm$ 0.0124 $R^2 = 0.989$	0.0708 $\pm$ 0.0124 $R^2 = 0.990$	0.0539 $\pm$ 0.0127 $R^2 = 0.988$	0.0523 $\pm$ 0.0134 $R^2 = 0.987$	0.059 $\sigma = 0.008$	0.0572 $\pm$ 0.0117 $R^2 = 0.991$
$k_{\phi, \text{runs}}^c$ [min^{-1}]	0.079	0.076	0.069	0.058	0.071	0.067

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S30. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis (UVB) of **1-B** in a quartz cuvette (fluorescence cell, 1 cm path length) in the presence of 2 equiv. TFA in ACN- d_3 .

	k [min^{-1}]	
	MeOAc	8
run 1	0.0807 ± 0.0119 $R^2 = 0.992$	0.0707 ± 0.0104 $R^2 = 0.993$
run 2	0.0588 ± 0.0104 $R^2 = 0.992$	0.0567 ± 0.0109 $R^2 = 0.991$
$k_{\phi, \text{runs}}^a$ [min^{-1}]	0.070	0.064

^a average of two runs.

2.6 Photolysis of **1-F** in ACN + Acid

Figure S11. Kinetic trace of the photolysis of **1-F** in ACN- d_3 in the presence of 2 equiv. of TFA. The photolysis was carried out in a quartz cuvette (fluorescence cell, 1 cm pathlength) with UV-B light in two independent runs. X was a structurally unassigned compound.

Table S31. Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-F** in quartz cuvettes (fluorescence cell, 1 cm path length) in presence of 2 equiv. of TFA in ACN-d_3 (plotted kinetic traces see Figure S8).

t [min]	c [mmol/L]					
	1-F	1-F	MeOAc	MeOAc	7	7
	run 1	run 2	run 1	run 2	run 1	run 2
0	31.60866	31.32898	0	0	0	0
1	29.93972	27.322	1.94709	2.67549	1.19481	2.46246
3	26.16565	24.97233	4.94043	5.38545	2.67409	3.75948
7	20.01144	19.70906	10.95872	10.77404	5.53784	6.34412
13	11.52452	12.17757	17.66924	18.85378	9.16967	10.34796
21	4.39993	4.44245	25.03722	26.6265	12.96271	14.52098
30	0.5089	0.54512	27.91045	29.99436	14.42303	16.10936
35	0.1454	-	29.09893	-	15.39026	-
max. conv.	0.5 %	2 %	92 %	96 %	49 %	51 %

Table S32. Rate constants k (mono-exponential fit) of the different diastereomers A-D of **1-F** in the photolysis experiment in a quartz cuvette (fluorescence cell, 1 cm pathlength) with UV-B light in presence of 2 equiv. of TFA in ACN-d_3 (degassed).

	k [min ⁻¹] of the diastereomers A-D				$k_{\phi, \text{isomers}}^a$	$k_{\phi, \text{total}}^b$
	A-1-F	B-1-F	C-1-F	D-1-F	[min ⁻¹]	[min ⁻¹]
run 1	0.0552 ± 0.0067 R ² = 0.996	0.0605 ± 0.0068 R ² = 0.996	0.0684 ± 0.0071 R ² = 0.996	0.0635 ± 0.0069 R ² = 0.996	0.062 σ = 0.006	0.0615 ± 0.0057 R ² = 0.997
run 2	0.0511 ± 0.0150 R ² = 0.983	0.0449 ± 0.0094 R ² = 0.993	0.0544 ± 0.0114 R ² = 0.991	0.0440 ± 0.0117 R ² = 0.989	0.049 σ = 0.005	0.0488 ± 0.0091 R ² = 0.994
$k_{\phi, \text{runs}}^c$ [min ⁻¹]	0.053	0.053	0.061	0.054	0.056	0.055

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function. ^c average of the independently determined rate constants of each run per isomer.

Table S33. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis of **1-F** in the photolysis experiment (UVB, quartz fluorescence cuvette, 1 cm pathlength) in the presence of 2 equiv. TFA in ACN- d_3 .

	k [min^{-1}]	
	MeOAc	7
run 1	0.0591 ± 0.0051 $R^2 = 0.997$	0.0556 ± 0.0051 $R^2 = 0.997$
run 2	0.0495 ± 0.0079 $R^2 = 0.995$	0.0543 ± 0.0125 $R^2 = 0.989$
$k_{\phi, \text{runs}}^a$		
[min^{-1}]	0.054	0.055

^a average of the independently determined rate constants of each run per isomer.

2.7 Photolysis of **1-N** in HFIP

Figure S12. Kinetic trace of photolysis (UVB, quartz NMR tubes) of **1-N** in HFIP- d_2 (degassed) in presence of 3 equiv. TMB.

Table S34. Concentrations (c) of the reaction products determined by ^1H NMR of the photolysis of **1-N** in a quartz NMR tube in presence of 3 equiv. of TMB in HFIP- d_2 (kinetic traces see Figure S9).

t [min]	c [mmol/L]					
	1-N	MeOAc	4-N	12	6-N	10
0	58.08921	0	0	0	0	0
1	53.15163	6.3143	0.97067	0.19169	1.95180	1.81238
2	48.29537	11.73983	2.01831	0.45310	3.38079	2.69244
4	38.80359	18.61759	3.07786	0.83648	10.49091	5.71598
7	26.62810	30.4097	5.74473	1.48127	15.23099	7.51094
11	13.47670	41.59769	7.95909	1.95180	20.87726	8.89636
15	6.64541	46.71535	9.52547	2.05636	22.23655	10.68261
17	3.72933	50.02643	9.32361	2.23063	26.5934	11.24898
max. conv.	6 %	86 %	16 %	4 %	46 %	19 %

Table S35. Rate constants k (mono-exponential fit) of the different diastereomers of **1-N** in the photolysis experiment (UVB) in quartz NMR tubes in presence of 3 equiv. of TMB in HFIP- d_2 .

k [min^{-1}] of the diastereomeres A-D					$\emptyset$ k [min^{-1}] ^a	total k [min^{-1}] ^b
	A-1-N	B-1-N	C-1-N	D-1-N		
run 1	0.1014 $\pm$	0.0921 $\pm$	0.1156 $\pm$	0.1156 $\pm$	0.087	0.817 $\pm$
	0.0091	0.0087	0.0185	0.0253	$\sigma =$	0.0076
	R ² = 0.998	R ² = 0.991	R ² = 0.992	R ² = 0.983	0.015	R ² = 0.998

^a average of the independently determined rate constants of each run per isomer.

^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function.

Table S36. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis of **1-N** in the photolysis experiment in the quartz NMR tube with UV-B light in presence of 3 equiv. of TMB in HFIP- d_2 (degassed).

run 1	k [min^{-1}]				
	MeOAc	4-N	12	6-N	10
	0.0952 $\pm$ 0.0091 R ² = 0.998	0.0837 $\pm$ 0.0183 R ² = 0.991	0.1156 $\pm$ 0.0185 R ² = 0.992	0.931 $\pm$ 0.0253 R ² = 0.983	0.1361 $\pm$ 0.0203 R ² = 0.991

2.8 Photolysis of **1-B** in HFIP

Figure S13. Kinetic traces of the photolysis (UVB) of **1-B** in HFIP- d_2 (degassed) in the presence of 3 equiv. of TMB in a quartz NMR tube.

Table S37: Concentrations (c) in dependence of time determined by ^1H NMR of the photolysis (UVB) of **1-B** in quartz NMR tubes in presence of 3 equiv. of TMB in HFIP- d_2 (degassed, plotted kinetic traces see Figure S10).

t [min]	c [mmol/L]			
	1-B	MeOAc	8	10
0	57.90267	0	0	0
1	52.79566	4.65537	3.75209	0.13028
2	49.39098	8.57539	5.76711	0.4169
4	41.14564	16.3575	10.70041	0.52981
7	28.92238	26.13727	17.02339	1.23333
11	15.75532	37.56725	25.15292	2.2582
15	6.7225	46.20633	31.42378	2.86618
17	3.9258	49.06672	32.98715	2.93567
max. conv.	7 %	85 %	57 %	5 %

Table S38. Rate constants k (mono-exponential fit) of the different isomers of **1-B** in the photolysis experiment (UVB) in quartz NMR tubes in presence of 3 equiv. of TMB in HFIP- d_2 (degassed).

	k [min^{-1}] of each diastereomer A-D				$k_{\phi, \text{isomers}}^a$	$k_{\phi, \text{total}}^b$
	A-1-B	B-1-B	C-1-B	D-1-B	[min^{-1}]	[min^{-1}] ^b
run 1	0.0626 ± 0.0111	0.0803 ± 0.0077	0.0538 ± 0.0080	0.0459 ± 0.0082	0.061	0.576 ± 0.0078
	$R^2 = 0.996$	$R^2 = 0.998$	$R^2 = 0.998$	$R^2 = 0.998$	$\sigma = 0.015$	$R^2 = 0.998$

^a average of the independently determined rate constants of each isomer per run. ^b fitting all data points of all runs and all isomers of the starting material together with a mono-exponential function.

Table S39. Rate constants k (mono-exponential fit) of the different reaction products of the photolysis (UVB) of **1-B** in in quartz NMR tubes in presence of 3 equiv. of TMB in HFIP- d_2 (degassed).

	k [min^{-1}]	
	MeOAc	8
run 1	0.0591 ± 0.0030	0.0507 ± 0.0073
	$R^2 = 1.000$	$R^2 = 0.998$

2.9 Photolysis of **1-F** in HFIP

Figure S14. Kinetic traces of the photolysis (UVB) of **1-F** in HFIP- d_2 in the presence of 3 equiv. of TMB in a quartz NMR tubes. The sample was degassed prior to irradiation.

Table S40: Concentrations (c) of substrate **1-F** and reaction products determined by ^1H NMR of the photolysis of **1-F** in a quartz NMR tube in presence of 3 equiv. of TMB in HFIP- d_2 (plotted kinetic traces see Figure S11).

t [min]	c [mmol/L]			
	1-F	MeOAc	7	10
0	57.90388	0	0	0
1	51.96291	4.71338	3.31789	0.90330
2	46.10307	8.88825	6.18413	4.96815
4	36.47944	21.12334	12.19456	3.63057
7	22.40880	33.74638	18.30921	8.45976
11	8.69716	45.19977	25.01448	10.54430
15	3.09207	50.44007	27.13376	11.89925
max. conv.	5 %	88 %	47 %	21 %

Table S41. Rate constants k (mono-exponential fit) of the different isomers of **1-F** in the photolysis experiment in the quartz NMR tubes (UV-B light, 3 equiv. TMB in HFIP- d_2)

	k [min^{-1}]			
	1-F	MeOAc	8	10
run 1	0.1036 ± 0.0151	0.1015 ± 0.0174	0.1144 ± 0.0131	0.1068 ± 0.0691
	$R^2 = 0.996$	$R^2 = 0.994$	$R^2 = 0.997$	$R^2 = 0.913$

3. TRIR studies & TRUV

3.1 ns-TRUV

The time-resolved UV-vis spectroscopy was run on a an Applied Photophysics LKS80 instrument with a SureliteTM SL I-10 Nd:YAG pump laser (355 nm third harmonic, 10 Hz repetition rate, 4 – 6 ns pulse width, 6 mm FWHM diameter, 26 mJ pulse energy, 266 nm fourth harmonic, 10 Hz repetition rate, 4- 6- ns pulse width, 6 mm FWHM diameter, 19 mJ pulse energy). The beam paths of pump and probe were set in an orthogonal alignment. The pump wavelength of the reported experiments was 266 nm and had been chosen based on the maximum absorption of the precursors **1N**, **1B**, **1F** (Figure S-12)

Figure S15 Absorption spectra of **1-N**, **1-B**, **1-F** in HFIP (1.5mM). With the Nd:YAG and its 1st to 4th harmonics being available as a pump source the 266 nm wavelength was chosen.

In a set of experiments with 1,3,5-trimethoxybenzene (TMB) as trapping agent in HFIP as solvent a transient spectrum was recorded after pumping at 266 nm that matched reported data of the according cyclohexadienyl cation.^{23,24}

²³ S. Steenken, M. Ashokkumar, P. Maruthamuthu, and R. A. McClelland *J. Am. Chem. Soc.* **1998**, *120*, 11925-11931.

²⁴ Pezacki, J. P.; Shukla, D.; Luszyk, J.; Warkentin, J. Lifetimes of Dialkylcarbocations Derived from Alkanediazonium Ions in Solution: Cyclohexadienyl Cations as Kinetic Probes for Cation Reactivity. *J. Am. Chem. Soc.* **1999**, *121*, 6589–6598.

To countercheck if the UV signature might arise also from a photoprotonation of the TMB by HFIP during excitation (TMB has an absorption at 266 nm) the experiment was re-run without the precursors **1** and the transient spectrum was recorded as well as the kinetic trace at its maximum absorption (details see Figure S13).

Figure S16 A) Comparison of the UV-vis data (back) of TMB in HFIP (0.25 mM) and the transient absorption spectrum (red) of the 266 nm pump-probe experiment with a solution of TMB in HFIP (10 mM, RLE 16, averaged of 8 individual measurements). In comparison to published data²³ this can be assigned to the photo protonation product **TMBH⁺**. B) Kinetic trace recorded at 345 nm of the same reaction solution as used in (A), i.e. 10 mM TMB in HFIP, 266 nm pump with RLE = 16 and 16 shots begin averaged using a resolution of 400ns/div and 10mV/div. C) left: 3D representation of the spectral evolution (280 nm – 420 nm) over time (up to 7 μ s) measured of a HFIP solution of **1-B** and 0.3 eq TMB under the same conditions used in (A). Right: comparison to the transient spectra recorded of the HFIP solutions of **1-B** only (red), and TMB only (blue) and the mixture **1-B** + 0.3 eq TMB. D) Kinetic trace recorded of the experiment described in C (**1-B**, 0.3 eq TMB, HFIP).

One clearly sees that the transient spectra overlap of the different experiments (**1-B**, **1-B** + TMB, TMB) in HFIP (Figure S13 Part C) but still imply the formation of a cyclohexadienyl cation by trapping one of the **1-B** derived cations. This conclusion is drawn less on the only slightly differing absorption maxima (350 nm vs. 345 nm) but mostly on the life-times of the species that differ quite significantly under otherwise same experimental conditions: **TMBH⁺** ($\lambda_{\text{max}} = 350$ nm) with $\tau > 3.5$ μ s (no decline over the period of measurements) and the potential cyclohexadienyl cation ($\lambda_{\text{max}} = 345$ nm) with a τ of 0.5 μ s.

Puzzling was the transient spectrum arising from pumping a **1-B** HFIP solution without TMB at 266 nm. To elucidate what gave rise to the transient absorption at 325 nm that grows in with a rate constant of $k_{\text{growth}} = 5.8 \times 10^6$ 1/s and has an average lifetime of 5.3 μ s a couple of additional experiments were run, i.e. TRUV in ACN, TRIR studies in HFIP and ACN (vide infra, section 3.2) and TDDFT calculations. The experiment ($\lambda_{\text{pump}} = 266$ nm) in HFIP without TMB indicated that the transient either comes from the precursor **1-B** itself, i.e. an excited state or from intermediates of its follow-up chemistry. Based on the TRIR data (see below section 3.2) the determined life-time (5.3 μ s) of the transient is too long for a triplet excited state of the **1-B**, since the fragmentation to the next intermediate **2-B** is already

happening on ps-scales. The similarity of the UV spectrum to the TMBH^+ and potential TMB-trapping product indicate however, that this transient may be a stabilized carbocation (Fig. S14). The TDDFT calculations of the carbocations evolving in the rearrangement process suggest that most likely the Phe^+ is the here observed cation. Repetition of this experiment in ACN was done to check on this hypothesis. ACN should avoid the protonation of the diazo **2-B** and hence shut down the cationic pathway altogether. And indeed, no transient at the indicative 345 nm is arising, only a bleach of the parent was visible (see UV-spectra Fig. S12). Therefore, both transients at 325 nm and 345 nm produced under pumping the HFIP solutions with 266 nm most likely represent stabilized carbocations and hence are in line with the trapping studies of the stationary photolysis.

Figure S-17 The pump-probe experiments were done with a 42 mM solution of **1-B** in HFIP and ACN using as $\lambda_{\text{pump}} = 266$ nm with 0.3 W/pulse. The spectra were recorded from 280-450nm with 4 nm resolution. The kinetic trace in HFIP was recorded at 330 nm. a) shows the growing in and decline of a transient with a maximum at 325 nm whereas in ACN (b) this species is not evolving but only showing the bleach of the parent (**1-B**, compare Figure S12 for its UV-vis absorption spectrum).

Figure S-18 TDDFT data on the postulated stabilized Cation Phe^+ . Also show the most likely pathway from B^+ to Phe^+ via T^+ .

Since the UV-spectra are helpful in the identification if the desired fragmentation and formation of cations occurs or not, they do not reveal enough structural information to tell apart the different carbo

cationic structures with high enough certainty. To obtain an unambiguous interpretation of the intermediates and products, we chose the product analysis of the stationary photolysis by NMR to complement the ns-TRUV by TMB trapping.

3.2 fs-TRIR

Femtosecond transient infrared absorption spectroscopy (fs-TRIR) was performed by exciting the sample with 267-nm pulses derived from a two-step co-linear third-harmonic generation (400-nm pulses from second harmonic generation of 800-nm pulses, 267-nm pulses from sum-frequency generation of 800-nm and 400-nm pulses). The excitation pulses had a pulse duration of 100 fs, a pulse energy of 4.5 μ J and a focal size of 170 μ m in the sample plane.

Probe pulses were generated in a three-step process in a home-built optical parametric amplifier, pumped by 200- μ J pulses from a commercial Ti:sapphire laser amplifier (Spectra Physics Spitfire Ace, 90 fs, 800 nm, 11 nm bandwidth 3 kHz repetition rate). Dual-stage signal and idler amplification from a sapphire-generated white-light continuum in BBO and subsequent difference frequency generation in AgGaS₂ yielded pulses at 4.93 μ m (2030 cm^{-1}) and 5.78 μ m (1730 cm^{-1}) wavelength of $\sim$ 100 fs duration with a FWHM bandwidth of 275 cm^{-1} and 260 cm^{-1} , respectively. Absorbance changes were measured by imaging the transmitted probe pulses in a Triax180 spectrometer onto a 32x2 MCT detector array (Infrared Systems).

The sample (NORCOX in ACN and HFIP solution of 180mM) was measured between 1-mm thick CaF₂ windows in a commercial flow cell (Harrick Scientific Products) and continuously cycled in a closed-loop liquid circuit by a peristaltic pump (Ismatec Reglo Digital). Sample consumption by the irreversible excitation process was monitored by pump-probe signal strength and the sample replaced after $\sim$ 1/3 sample consumption.

Product formation was monitored by the induced absorption of the stretching vibration of the diazo group of the diazonium ion and the keto group of the split-off ester. The absorbance changes were analyzed by subtracting a polynomial fit to the background which varying slowly with frequency. The resulting absorption lineshapes were analyzed by a sum of two Gaussians (diazo stretching) and a Lorentzian (CO stretching).

The resulting induced absorption lineshapes, indicative of the diazonium ion and the ester, respectively, are displayed in Fig. 1 (panel A) for a time delay of 60 ps after 267-nm excitation. The instrument response function was $\sim$ 180 fs as measured in 0.5-mm thick ZnSe. The amplitude of the fit lineshapes is displayed in panels B (keto stretching) and C (diazo stretching) of the same figure. It is evident that the absorption of both products in either ACN or HFIP solution grows in on two timescales describes by time constants in Fig. 1. We attribute the picosecond time constant to the formation of the products and the longer time constant to product thermalization. We note that the lineshape formation is complex and is governed by anharmonic coupling to other modes that are transiently populated during the intramolecular vibrational energy redistribution process and subsequent thermalization with the solvent. A more detailed analysis of the product formation and thermalization process, including a differentiated lineshape analysis will be published in a subsequent manuscript.

4. Computational Chemistry

4.1 General Information

Geometry optimizations of stationary points were performed using different levels of DFT such as B3LYP²⁵ and M062X in conjunction with the 6-31G*, 6-31+G(d,p) or 6-311+G** basis sets²⁶. Stationary points were identified as TSs or minima by frequency calculations (one or no imaginary frequency respectively). In order to verify that the transition states correspond to the expected reaction pathways, intrinsic reaction coordinate (IRC) calculations were conducted for all TS structures. B3LYP is most widely used in predicting geometries and chemical behaviour of monoterpenes, terpenoid carbocations and other small biologically active molecules.²⁷ In addition, the functional was also previously applied successfully in the investigation of Δ^3 -1,3,4-oxadiazoline reaction mechanisms.^{2,28}

In order to evaluate possible shortcomings in the results from B3LYP calculations arising from the neglect of dispersion effects the Truhlar functional M06-2X²⁹ was employed.

BOMD trajectory calculations for the dissociation of diazonium ions **3** and the corresponding potential energy surface (PES) scans were executed at the M062X level of theory. The BOMD algorithm was used as implemented in used version of Gaussian09.

TDDFT calculations were used to compare experimental with computed data of potential transients.

All calculations presented herein were performed with the Gaussian09 program package.³⁰

Stationary points were identified as TSs or minima by harmonic frequency calculations. In order to verify that the transition states correspond to the expected reaction pathways, intrinsic reaction coordinate (IRC) calculations were conducted for all TS structures. To identify the structural area of reaction path bifurcations BOMD simulations were used in combination with projected frequency analysis on along the IRC of the diazonium TS structures at the B3LYP/6-311+G** level of theory³¹.

²⁵ B3: Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; LYP: Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

²⁶ 6-31G: [a] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724; 6-311: [b] Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-54. [c] McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639-48.

²⁷ [a] Hong, Y., Tantillo, D. Biosynthetic consequences of multiple sequential post-transition-state bifurcations. *Nature Chem* **6**, 104–111 (2014). [b] Y. J. Hong, D. J. Tantillo, 'Quantum chemical dissection of the classic terpinyl/pinyl/bornyl/camphyl cation conundrum—the role of pyrophosphate in manipulating pathways to monoterpenes', *Org. Biomol. Chem.* **2010**, *8*, 4589 – 4600.

²⁸ Mieusset, Jean-Luc; Billing, Peter; Abraham, Michael; Arion, Vladimir B.; Brecker, Lothar; Brinker, Udo H. '2-Methoxy- Δ^3 -1,3,4-oxadiazoline, a Multipurpose Precursor for the Generation of a Carbene, an Ylide, or a Diazo Compound', *Eur. J. Org. Chem.* **2008**, *31*, 5336–5345.

²⁹ Zhao, Y., Truhlar, D.G *Theor Chem Account* **2008**, *120*, 215–241

³⁰ Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

³¹ S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, K. Morokuma, 'Intrinsic Reaction Coordinate: Calculation, Bifurcation, and Automated Search', *Int. J. Qua. Chem.* **2015**, *115*, 258 – 269.

BOMD trajectory calculations for the dissociation of diazonium ions $\mathbf{F-N_2^+}$ and $\mathbf{B-N_2^+}$ and the corresponding potential energy surface (PES) scans were executed at the M06-2X/6-31G* level of theory.

4.2 Optimized structures

4.2.1 Structures optimized at the M06-2X/6-311+G** level of theory

Bornyl cation ($\mathbf{B^+}$), TS M06-2X/6-311+G**
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optimized xyz-matrix

```

C      1.38653400 -0.52266200 -1.26348700
H      2.34380900 -0.03073800 -1.49055000
H      1.32974500 -1.37964300 -1.94006900
C      0.25277800  0.39474000 -1.51658800
H     -0.15723700  0.55253900 -2.51592600
C     -0.36725400  0.87243300 -0.34705300
C     -1.67870000  1.61207100 -0.44743600
H     -2.36118900  1.13841200 -1.15548600
H     -2.16380600  1.65289600  0.52929900
H     -1.50926400  2.64203800 -0.76988700
C      0.69857200  1.46910800  0.63842500
H      1.20988200  2.29455200  0.14254900
H      0.14838200  1.89177800  1.47913700
C      1.65237600  0.32726400  1.05005100
H      2.69410700  0.56067900  0.83145800
H      1.58525600  0.11690500  2.11694800
C      1.15477300 -0.85807000  0.21872700
H      1.55329700 -1.82519100  0.52362500
C     -0.39159800 -0.75105200  0.28626800
C     -1.17547500 -1.76060000 -0.55010600
H     -0.76647800 -1.95165600 -1.54261300
H     -1.19575400 -2.71169200 -0.01283500
H     -2.21128100 -1.43433500 -0.66549800
C     -1.02209500 -0.68263500  1.66650200
H     -0.63729300  0.10594200  2.30842500
H     -2.10616300 -0.58401700  1.59456600
H     -0.81548000 -1.64205400  2.15503300

```

Thermodynamic Data

```

Zero-point correction=      0.247060 (Hartree/Particle)
Thermal correction to Energy=      0.256896
Thermal correction to Enthalpy=      0.257840
Thermal correction to Gibbs Free Energy=      0.213497
Sum of electronic and zero-point Energies=     -390.656779
Sum of electronic and thermal Energies=     -390.646943
Sum of electronic and thermal Enthalpies=     -390.645999

```

Sum of electronic and thermal Free Energies= -390.690341

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	161.204	40.438	93.327

$\nu_{\text{imag}} = -313 \text{ cm}^{-1}$

fenchyl cation, TS
M06-2X/6-311+G**

optimized xyz-matrix

C	0.62580600	-0.30084900	1.33754900
H	1.46223700	0.09750300	1.91839600
H	0.32505900	-1.25981800	1.76183100
C	0.00294300	-0.92679100	-0.59038900
H	-0.06955800	-1.91059900	-1.06463700
C	1.24546600	-0.35776500	-0.20450500
C	2.51535100	-1.14269800	-0.43908700
H	2.37771000	-2.20774000	-0.24578700
H	2.85226300	-1.01581800	-1.47007400
H	3.30714000	-0.77380900	0.21498500
C	1.32841500	1.18208300	-0.45974500
H	2.32643300	1.49338000	-0.14804700
H	1.24474300	1.37383100	-1.53008000
C	0.21861100	1.85066500	0.37931500
H	0.64948200	2.46236500	1.17222600
H	-0.42988000	2.49580900	-0.21132600
C	-0.52336700	0.65943200	0.98750600
H	-1.19391700	0.91181300	1.80753200
C	-1.20338500	-0.20593900	-0.11125500
C	-2.21315200	-1.20072700	0.49468100
H	-3.08676800	-0.63845700	0.82992000
H	-2.54064300	-1.92800400	-0.25095100
H	-1.80886000	-1.73894500	1.35314800
C	-1.87141200	0.52761500	-1.29522600
H	-1.17991100	1.16871000	-1.84185100
H	-2.31007300	-0.18819600	-1.99259000
H	-2.67711600	1.14781400	-0.89576500

thermodynamic data

Zero-point correction=	0.247405 (Hartree/Particle)
Thermal correction to Energy=	0.257216
Thermal correction to Enthalpy=	0.258160
Thermal correction to Gibbs Free Energy=	0.213780
Sum of electronic and zero-point Energies=	-390.655825
Sum of electronic and thermal Energies=	-390.646014
Sum of electronic and thermal Enthalpies=	-390.645069
Sum of electronic and thermal Free Energies=	-390.689450

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.406	40.233	93.406

$\nu_{\text{imag}} = -356 \text{ cm}^{-1}$

optimized xyz-matrix

C	1.86046300	0.24565200	-0.89103800
H	2.87655300	0.04713900	-0.54469000
H	1.86526200	0.88637800	-1.77199500
C	-0.25974800	0.01170100	-0.86885700
H	-0.29488500	0.76923600	-1.65323700
C	0.89390200	0.73437700	0.20928900
C	0.71610400	2.16799800	0.59622100
H	0.55442600	2.80995200	-0.27143300
H	-0.10041700	2.30177000	1.30964000
H	1.63778800	2.49991400	1.08675000
C	1.04975900	-0.34591400	1.27208200
H	1.97697100	-0.15942000	1.82029900
H	0.24452800	-0.35264000	2.00903300
C	1.13028100	-1.61593500	0.38102800
H	2.11650300	-2.07872800	0.42182000
H	0.40735200	-2.38326700	0.64636600
C	0.91709900	-0.97605600	-1.00505300
H	0.95098700	-1.62409600	-1.87761100
C	-1.52057700	-0.13807300	-0.25311300
C	-1.97942100	-1.35918100	0.43738300
H	-3.06420100	-1.36563300	0.54394700
H	-1.62792000	-2.26465500	-0.05673900
H	-1.55835200	-1.35771800	1.45405600
C	-2.44495200	1.01415500	-0.26121800
H	-1.98802300	1.93496600	-0.61862000
H	-3.28116500	0.75169700	-0.92636200
H	-2.89286600	1.15276000	0.72842800

thermodynamic data

Zero-point correction=	0.246680 (Hartree/Particle)
Thermal correction to Energy=	0.257274
Thermal correction to Enthalpy=	0.258218
Thermal correction to Gibbs Free Energy=	0.211858
Sum of electronic and zero-point Energies=	-390.650061
Sum of electronic and thermal Energies=	-390.639467
Sum of electronic and thermal Enthalpies=	-390.638523
Sum of electronic and thermal Free Energies=	-390.684883

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.442	42.300	97.573

phenandryl cation
M06-2X/6-311+G**

optimized xyz-matrix

C	1.35752400	-1.14726300	-0.19203400
C	0.18752000	-1.14675800	-1.17575400
C	-0.81783600	-0.01428200	-0.93329700
C	-0.15593500	1.23808500	-0.52877500
C	1.14198700	1.34714100	-0.09072600
C	1.90387500	0.19427800	0.11635700
C	3.26176400	0.28177600	0.68526800
C	-1.99441200	-0.36488500	0.04891800
C	-2.96292400	0.80508900	0.22256200
C	-1.50552800	-0.88154500	1.40204500
H	2.17150900	-1.79414800	-0.53475900
H	1.07899300	-1.55515500	0.79313000
H	-0.32165500	-2.11169700	-1.14556700
H	0.59591000	-1.03760800	-2.18375800
H	-1.32602800	0.22304900	-1.87816500
H	-0.75832900	2.14380300	-0.55731400
H	1.55116200	2.31432500	0.17661600
H	3.44612600	1.21605200	1.21262000
H	3.95605000	0.23197300	-0.16864100
H	3.49222100	-0.58116500	1.31340000
H	-2.52403100	-1.17641900	-0.45915800
H	-3.88360400	0.45395000	0.69030300
H	-3.23295300	1.26087400	-0.73375100
H	-2.54873700	1.58034600	0.87405900
H	-2.35783900	-1.02042500	2.06947900
H	-0.82911300	-0.16929700	1.88760500
H	-1.00589400	-1.84828000	1.31653100

thermodynamic data

Zero-point correction=	0.247556 (Hartree/Particle)
Thermal correction to Energy=	0.258563
Thermal correction to Enthalpy=	0.259507
Thermal correction to Gibbs Free Energy=	0.211607
Sum of electronic and zero-point Energies=	-390.684162
Sum of electronic and thermal Energies=	-390.673155
Sum of electronic and thermal Enthalpies=	-390.672211
Sum of electronic and thermal Free Energies=	-390.720110

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total	162.250	42.456	100.814
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optimized xyz-matrix

C	1.08396300	-0.97523700	0.65732000
C	-0.18495200	-1.10078000	-0.19213700
C	-0.70121600	0.40490100	-0.63866500
C	0.18913900	1.51850900	-0.09051100
C	1.64235500	1.17958700	-0.30938600
C	2.08860000	-0.02218500	0.04980900
C	3.50734800	-0.48296600	-0.07916300
C	-1.95059900	0.05063100	-0.05440700
C	-2.26756600	0.35411700	1.36132800
C	-2.99650400	-0.59007200	-0.88409600
H	1.50034700	-1.98111500	0.75712900
H	0.82063800	-0.64919500	1.67069600
H	-0.91711400	-1.71413000	0.35087800
H	-0.01914500	-1.60575400	-1.14339300
H	-0.71877400	0.40045600	-1.72636700
H	-0.00324700	1.68260900	0.97440900
H	-0.08346500	2.44066000	-0.60643000
H	2.29997600	1.92652800	-0.73778700
H	4.13723700	0.29035300	-0.51756800
H	3.56748400	-1.37912000	-0.70373700
H	3.91450300	-0.74674400	0.90126300
H	-3.04539500	-0.29442000	1.76081300
H	-2.64714800	1.38681600	1.36630300
H	-1.38763500	0.34632700	2.00388100
H	-3.74296200	0.19787200	-1.06685400
H	-3.51382800	-1.39100700	-0.35392000
H	-2.62488100	-0.92916400	-1.84986700

thermodynamic data

Zero-point correction=	0.246181 (Hartree/Particle)
Thermal correction to Energy=	0.257579
Thermal correction to Enthalpy=	0.258523
Thermal correction to Gibbs Free Energy=	0.209923
Sum of electronic and zero-point Energies=	-390.664171
Sum of electronic and thermal Energies=	-390.652773
Sum of electronic and thermal Enthalpies=	-390.651829
Sum of electronic and thermal Free Energies=	-390.700429

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.633	43.742	102.288

TS-Phenandryl-Terpinyl
M06-2X/6-311+G**

optimized xyz-matrix

C	-1.39266500	1.17815800	0.18325700
C	-0.16361000	1.62148300	-0.61917100
C	0.89061800	0.55200200	-0.86110300
C	0.40515800	-0.87100800	-0.93075900
C	-0.96252600	-1.18776400	-0.49923400
C	-1.80142900	-0.25504800	-0.01733000
C	-3.20239500	-0.59891200	0.37881300
C	1.64258300	-0.13572100	0.24491300
C	1.20729500	0.05114400	1.67916700
C	3.10475200	-0.41124100	-0.02150800
H	-2.23937400	1.81984000	-0.07435500
H	-1.24108300	1.33239200	1.25760600
H	0.30165800	2.49254100	-0.15278000
H	-0.49351700	1.94489200	-1.60875600
H	1.54797800	0.81084800	-1.68638200
H	0.86963300	-1.49015700	-1.69644800
H	-1.27826900	-2.21989700	-0.59542800
H	-3.39940500	-1.66777600	0.31256500
H	-3.90683200	-0.06935100	-0.26930400
H	-3.39959500	-0.26176700	1.40046500
H	1.13369000	-1.33888100	0.02719700
H	1.85359900	-0.51367500	2.34994800
H	0.17516900	-0.26404700	1.83731200
H	1.28239000	1.11424300	1.92462500
H	3.49945200	-1.18642900	0.63475700
H	3.64360000	0.51972900	0.17996000
H	3.28422700	-0.68105600	-1.06325300

thermodynamic data

Zero-point correction=	0.245407 (Hartree/Particle)
Thermal correction to Energy=	0.255840
Thermal correction to Enthalpy=	0.256785
Thermal correction to Gibbs Free Energy=	0.210567
Sum of electronic and zero-point Energies=	-390.661446
Sum of electronic and thermal Energies=	-390.651012
Sum of electronic and thermal Enthalpies=	-390.650068
Sum of electronic and thermal Free Energies=	-390.696286

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.542	41.011	97.274

$\nu_{\text{imag}} = -389 \text{ cm}^{-1}$

TS-Pinyl-Terpinyl
M06-2X/6-311+G**

optimized xyz-matrix

C	-0.28933700	-0.64984400	-1.66437400
H	0.18986100	-1.52368800	-2.11367900
H	-1.02408300	-0.29280400	-2.38318700
C	0.70359300	0.43320000	-1.29960200
H	0.81973900	1.29217600	-1.95366700
C	1.45732000	0.32552300	-0.18878900
C	2.42440600	1.38588800	0.24042700
H	2.44048000	2.22819900	-0.45016400
H	2.17109300	1.75367300	1.24040200
H	3.43421900	0.97074100	0.30774200
C	1.43427900	-0.93444600	0.64240700
H	2.28413400	-1.54584200	0.32153000
H	1.65200400	-0.68343700	1.68517000
C	0.12964100	-1.76867300	0.52097300
H	0.32901800	-2.71554000	0.01911400
H	-0.25505900	-2.02413700	1.51029500
C	-0.91649900	-1.02742800	-0.31165200
H	-1.82788000	-1.63882300	-0.42587100
C	-1.36880100	0.25494700	0.31233900
C	-2.21576600	1.20649600	-0.42294800
H	-3.20634800	1.14499000	0.05728800
H	-1.87917900	2.23121700	-0.24081800
H	-2.32083700	1.01031400	-1.48432800
C	-1.22055200	0.49165100	1.75400900
H	-0.21940300	0.26045400	2.11993300
H	-1.53830200	1.48515100	2.06260300
H	-1.87915600	-0.25653000	2.23089500

thermodynamic data

Zero-point correction=	0.245849 (Hartree/Particle)
Thermal correction to Energy=	0.256295
Thermal correction to Enthalpy=	0.257239
Thermal correction to Gibbs Free Energy=	0.210625
Sum of electronic and zero-point Energies=	-390.662467
Sum of electronic and thermal Energies=	-390.652022
Sum of electronic and thermal Enthalpies=	-390.651078
Sum of electronic and thermal Free Energies=	-390.697692

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.828	41.095	98.108

$\nu_{\text{imag}} = -85 \text{ cm}^{-1}$

TS-TerpinyI-Bornyl
M06-2X/6-311+G**

optimized xyz-matrix

C	-1.81145400	0.23313000	1.30261600
H	-2.61607100	0.66294100	0.71917700
H	-2.05008500	0.01685100	2.33674100
C	-0.44771900	0.62921100	1.08135300
H	0.16878100	0.65060800	1.96503400
C	0.22992600	0.87708800	-0.25011400
C	1.13341200	2.07623200	-0.41496400
H	1.84340300	2.16091100	0.40997100
H	1.69701700	1.99381200	-1.34645400
H	0.54453500	2.99435700	-0.45611100
C	-0.84708600	0.63206200	-1.31809500
H	-1.56009600	1.45822800	-1.31634200
H	-0.40978700	0.58712200	-2.31582700
C	-1.52006100	-0.71494000	-0.91118200
H	-2.60657200	-0.65446400	-0.95028000
H	-1.22720600	-1.54542600	-1.54348900
C	-1.06013200	-0.90882500	0.53691200
H	-0.99362100	-1.85349800	1.06145300
C	0.81340000	-0.49804000	0.07351800
C	1.90230300	-0.64430700	1.12882000
H	1.89993100	-1.65861400	1.53430300
H	2.85849600	-0.50970300	0.61703900
H	1.88660600	0.06222800	1.95344900
C	1.09580000	-1.51902900	-1.02743000
H	0.68334000	-1.26360000	-1.99728600
H	2.18083800	-1.55584800	-1.13798600
H	0.77015100	-2.52141000	-0.74200200

thermodynamic data

Zero-point correction=	0.248487 (Hartree/Particle)
Thermal correction to Energy=	0.258284
Thermal correction to Enthalpy=	0.259228
Thermal correction to Gibbs Free Energy=	0.214772
Sum of electronic and zero-point Energies=	-390.614451
Sum of electronic and thermal Energies=	-390.604655
Sum of electronic and thermal Enthalpies=	-390.603711
Sum of electronic and thermal Free Energies=	-390.648166

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	162.076	40.232	93.565

$\nu_{\text{imag}} = -295 \text{ cm}^{-1}$

Diazo norbornane (**2-N**)

M06-2X/6-311+G**

O 1

C -1.3607140000 0.9468050000 -0.0431210000
 C 0.0804760000 1.4014680000 -0.3607860000
 C 0.8356950000 0.1752450000 0.1206570000
 C -0.1476150000 -0.8003570000 0.7351350000
 C -0.9515640000 -1.4352050000 -0.4205010000
 C -1.7346960000 -0.2136480000 -0.9934850000
 H -1.4595270000 0.0090560000 -2.0264540000
 H -2.8110080000 -0.3941170000 -0.9721130000
 H -1.6352700000 -2.1966360000 -0.0356020000
 H -0.3009070000 -1.9058890000 -1.1580600000
 C -1.1759740000 0.2044790000 1.2939530000
 H -2.0915600000 -0.2823690000 1.6381640000
 H -0.7701770000 0.8358750000 2.0864460000
 H 0.2909110000 -1.5052090000 1.4398140000
 H 0.3486020000 2.2991210000 0.2068960000
 H 0.2243520000 1.6094600000 -1.4245780000
 H -2.0782390000 1.7664110000 -0.0406960000
 N 2.0850850000 -0.0435680000 -0.0507090000
 N 3.2019400000 -0.2290650000 -0.1928520000

Thermodynamic Data

Zero-point correction= 0.163989 (Hartree/Particle)

Thermal correction to Energy= 0.171228

Thermal correction to Enthalpy= 0.172172

Thermal correction to Gibbs Free Energy= 0.131846

Sum of electronic and zero-point Energies= -381.965868

Sum of electronic and thermal Energies= -381.958630

Sum of electronic and thermal Enthalpies= -381.957686

Sum of electronic and thermal Free Energies= -381.998011

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	107.447	28.713	84.872

Norbornyl *endo* diazonium (***endo*-N-N₂⁺**)

M06-2X/6-311+G**

1 1

C -1.4292980000 0.5777130000 -0.5908520000
 C -0.0900830000 1.3259140000 -0.7066930000
 C 0.7025990000 0.7177790000 0.4959180000
 C -0.2381380000 -0.3457000000 1.1124370000

C -0.4196380000 -1.5118230000 0.1248940000
 C -1.2254530000 -0.8772970000 -1.0481390000
 H -0.7029410000 -0.9383800000 -2.0043380000
 H -2.1856420000 -1.3773960000 -1.1721990000
 H -0.9912400000 -2.2966290000 0.6202570000
 H 0.5191010000 -1.9739550000 -0.1905010000
 C -1.5630060000 0.4265250000 0.9338720000
 H -2.4123710000 -0.1867960000 1.2366400000
 H -1.5992000000 1.3764600000 1.4716270000
 H 0.0470470000 -0.6227360000 2.1254050000
 H -0.1941010000 2.3977370000 -0.5370230000
 H 0.4102480000 1.1781890000 -1.6650160000
 H -2.2399670000 1.1014900000 -1.0927440000
 N 1.9570530000 0.0949940000 0.0299520000
 N 2.8802020000 -0.3795110000 -0.3065370000
 H 1.0663930000 1.4549610000 1.2153670000

Thermodynamic Data

Zero-point correction= 0.176660 (Hartree/Particle)
 Thermal correction to Energy= 0.184094
 Thermal correction to Enthalpy= 0.185038
 Thermal correction to Gibbs Free Energy= 0.144770
 Sum of electronic and zero-point Energies= -382.325838
 Sum of electronic and thermal Energies= -382.318404
 Sum of electronic and thermal Enthalpies= -382.317460
 Sum of electronic and thermal Free Energies= -382.357728

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	115.521	29.985	84.752

Norbornyl *exo* diazonium (***exo*-N-N₂⁺**)
 M06-2X/6-311+G**

1 1

C -1.0783130000 1.0336790000 0.4231310000
 C 0.0843310000 1.2860380000 -0.5601470000
 C 0.7034920000 -0.1394530000 -0.6929550000
 C -0.1302620000 -1.0180710000 0.2650650000
 C -1.4855900000 -1.1814520000 -0.4637180000
 C -2.1566050000 0.2140020000 -0.3046960000
 H -2.4385490000 0.6582510000 -1.2598650000
 H -3.0576960000 0.1458240000 0.3045820000
 H -2.0547600000 -1.9625570000 0.0400550000
 H -1.3674880000 -1.4916540000 -1.5036500000
 C -0.4700170000 -0.0097370000 1.3740030000
 H -1.1939290000 -0.4168040000 2.0804490000
 H 0.3966020000 0.3536660000 1.9343900000
 H 0.3525640000 -1.9547150000 0.5396780000
 H 0.8069850000 1.9959570000 -0.1537340000

H -0.2319040000 1.6462790000 -1.5387560000
H -1.4364680000 1.9523290000 0.8826240000
N 2.1085870000 -0.1109450000 -0.1950250000
N 3.1197920000 -0.1044240000 0.2143990000
H 0.8237760000 -0.5290340000 -1.7054810000

Thermodynamic Data

Zero-point correction= 0.176244 (Hartree/Particle)

Thermal correction to Energy= 0.183759

Thermal correction to Enthalpy= 0.184703

Thermal correction to Gibbs Free Energy= 0.144284

Sum of electronic and zero-point Energies= -382.326918

Sum of electronic and thermal Energies= -382.319403

Sum of electronic and thermal Enthalpies= -382.318459

Sum of electronic and thermal Free Energies= -382.358879

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	115.311	30.173	85.071

Norbornyl *endo* diazonium dissociation (***endo*-N-N₂⁺-TS**)

M06-2X/6-311+G**

1 1

C 1.4569840000 -0.4418560000 -0.7214490000
C 0.1881980000 -1.3125850000 -0.7240960000
C -0.4798170000 -0.8486290000 0.5573050000
C 0.3370410000 0.2314710000 1.1656020000
C 0.3572550000 1.4846010000 0.2568780000
C 1.0650830000 1.0107940000 -1.0429540000
H 0.4216790000 1.0742380000 -1.9220890000
H 1.9492920000 1.6142520000 -1.2457400000
H 0.9367250000 2.2526920000 0.7687220000
H -0.6393800000 1.8968200000 0.0931270000
C 1.7315520000 -0.3911620000 0.7923270000
H 0.4236000000 -2.3736880000 -0.5919960000
H -0.4387490000 -1.2297090000 -1.6132020000
H 2.2536200000 -0.8475620000 -1.3397880000
N -2.1119700000 -0.0836640000 0.0349460000
N -3.0920570000 0.2887670000 -0.2615160000
H -0.9983460000 -1.5682630000 1.1877270000
H 2.5199100000 0.3013240000 1.0898150000
H 1.9255510000 -1.3677570000 1.2402330000
H 0.1365120000 0.4161360000 2.2174990000

Thermodynamic Data

Zero-point correction= 0.173603 (Hartree/Particle)

Thermal correction to Energy= 0.181426

Thermal correction to Enthalpy= 0.182370

Thermal correction to Gibbs Free Energy= 0.140467

Sum of electronic and zero-point Energies= -382.322411
 Sum of electronic and thermal Energies= -382.314587
 Sum of electronic and thermal Enthalpies= -382.313643
 Sum of electronic and thermal Free Energies= -382.355547

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	113.847	30.002	88.193

$V_{\text{imag}} = -XXX \text{ cm}^{-1}$

Norbornyl exo diazonium dissociation (**exo-N-N₂⁺-TS**)

1 1

C -1.0862160000 1.0344560000 0.4387990000
 C 0.0089960000 1.2320350000 -0.6387450000
 C 0.5812150000 -0.1743560000 -0.7570810000
 C -0.1372170000 -1.0185330000 0.2430620000
 C -1.5401760000 -1.1521180000 -0.4544090000
 C -2.2190700000 0.2201990000 -0.2007330000
 H -2.5980200000 0.6762040000 -1.1156110000
 H -3.0544010000 0.1189940000 0.4919660000
 H -2.0628810000 -1.9736200000 0.0355510000
 H -1.4640700000 -1.4114500000 -1.5127850000
 C -0.4340540000 -0.0067020000 1.3634930000
 H 0.7628200000 1.9515580000 -0.3142110000
 H -0.3640610000 1.5670970000 -1.6086080000
 H -1.3924030000 1.9682930000 0.9039720000
 N 2.2537230000 -0.0838840000 -0.1741330000
 N 3.2639030000 -0.0718910000 0.2340020000
 H 0.8476950000 -0.5880130000 -1.7275950000
 H -1.1253590000 -0.4086400000 2.1041240000
 H 0.4614130000 0.3538490000 1.8771320000
 H 0.3250110000 -1.9737280000 0.4806770000

Thermodynamic Data

Zero-point correction= 0.174060 (Hartree/Particle)
 Thermal correction to Energy= 0.181721
 Thermal correction to Enthalpy= 0.182666
 Thermal correction to Gibbs Free Energy= 0.141636
 Sum of electronic and zero-point Energies= -382.326091
 Sum of electronic and thermal Energies= -382.318430
 Sum of electronic and thermal Enthalpies= -382.317486
 Sum of electronic and thermal Free Energies= -382.358516

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	114.032	29.742	86.354

$V_{\text{imag}} = -XXX \text{ cm}^{-1}$

Diazo bornane (2-B)

O 1

C -0.9694170000 1.2129660000 0.5815200000
 C 0.4874190000 1.3716330000 1.0686860000
 C 1.1308130000 0.2760790000 0.2417140000
 C 0.0637760000 -0.4598350000 -0.5589430000
 C -0.3552350000 0.5225680000 -1.6779790000
 C -1.0159980000 1.6906770000 -0.8886340000
 H -0.4742430000 2.6300810000 -1.0124090000
 H -2.0410560000 1.8662250000 -1.2177700000
 H -1.0599190000 0.0483970000 -2.3668710000
 H 0.5108160000 0.8405410000 -2.2606760000
 C -1.1289160000 -0.3260300000 0.4461840000
 C -2.4831620000 -0.7481600000 -0.1280910000
 C -0.9122940000 -1.0960480000 1.7498480000
 C 0.4463950000 -1.8503910000 -1.0174920000
 H 0.5835110000 1.1934590000 2.1444190000
 H 0.8829940000 2.3674250000 0.8519660000
 H -1.6991830000 1.6963440000 1.2336550000
 N 2.3849300000 0.0372310000 0.1578210000
 N 3.5011040000 -0.1910020000 0.0812400000
 H 1.3048480000 -1.8150340000 -1.6944510000
 H -0.3808080000 -2.3185100000 -1.5569510000
 H 0.7136570000 -2.4847780000 -0.1682560000
 H -1.0893570000 -2.1633950000 1.5911930000
 H -1.6197330000 -0.7557280000 2.5117950000
 H 0.0985750000 -0.9849660000 2.1445000000
 H -3.2651880000 -0.5805340000 0.6181460000
 H -2.4813780000 -1.8166260000 -0.3621860000
 H -2.7660550000 -0.2072460000 -1.0304120000

Thermodynamic Data

Zero-point correction= 0.248111 (Hartree/Particle)
 Thermal correction to Energy= 0.259505
 Thermal correction to Enthalpy= 0.260449
 Thermal correction to Gibbs Free Energy= 0.211959
 Sum of electronic and zero-point Energies= -499.801682
 Sum of electronic and thermal Energies= -499.790287
 Sum of electronic and thermal Enthalpies= -499.789343
 Sum of electronic and thermal Free Energies= -499.837834

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.842	46.174	102.058

Diazo bornane *endo* dissociation (**endoTS-2-B**)

O 1

C 0.8125340000 -1.4093170000 0.2390230000
 C -0.4258640000 -1.2644320000 1.1346200000
 C -0.9098190000 0.1727950000 0.8874730000
 C -0.0156430000 0.6620910000 -0.2480150000
 C -0.2294510000 -0.1598560000 -1.5459800000
 C 0.3016190000 -1.5771140000 -1.2038550000
 H -0.4795420000 -2.3381610000 -1.2581140000
 H 1.0958040000 -1.8831060000 -1.8865190000
 H 0.3448530000 0.2973830000 -2.3559580000
 H -1.2736080000 -0.1537500000 -1.8587570000
 C 1.3494090000 0.0471480000 0.2569230000
 C 2.5246160000 0.2933170000 -0.6898360000
 C 1.7707390000 0.5494810000 1.6451850000
 C -0.0616020000 2.1645930000 -0.4554390000
 H -0.1815380000 -1.3535200000 2.1971230000
 H -1.1989860000 -2.0093700000 0.9372200000
 H 1.5256320000 -2.1718910000 0.5596020000
 N -2.6495800000 -0.0077040000 0.1062620000
 N -3.7063540000 0.2864940000 0.1559090000
 H -1.0540850000 2.4691920000 -0.8000030000
 H 0.6658960000 2.4889500000 -1.2050950000
 H 0.1344520000 2.6901000000 0.4816390000
 H 0.9682350000 0.5252920000 2.3832490000
 H 2.1138490000 1.5852940000 1.5760480000
 H 2.6053440000 -0.0496700000 2.0211610000
 H 2.7491250000 1.3615170000 -0.7535010000
 H 2.3617500000 -0.0785840000 -1.7005720000
 H 3.4151300000 -0.2034470000 -0.2933060000

Thermodynamic Data

Zero-point correction= 0.243352 (Hartree/Particle)
 Thermal correction to Energy= 0.255307
 Thermal correction to Enthalpy= 0.256251
 Thermal correction to Gibbs Free Energy= 0.206404
 Sum of electronic and zero-point Energies= -499.753011
 Sum of electronic and thermal Energies= -499.741056
 Sum of electronic and thermal Enthalpies= -499.740111
 Sum of electronic and thermal Free Energies= -499.789958

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.207	47.228	104.911

$$V_{\text{imag}} = -\text{XXX cm}^{-1}$$

Exo-bornyldiazonium dissociation TS (**exo-TS-2-B**)

O 1

C -1.1087170000 -0.7661330000 -1.0145470000
 C 0.2260840000 -1.5396480000 -0.8987360000
 C 0.8911980000 -1.0074730000 0.3830310000
 C -0.0337800000 0.1176950000 0.7792710000
 C -1.1835240000 -0.7752790000 1.3767630000
 C -1.9763100000 -1.2821280000 0.1439330000
 H -2.0688030000 -2.3693130000 0.1273370000
 H -2.9844220000 -0.8664930000 0.1118840000
 H -1.7912810000 -0.1601520000 2.0425810000
 H -0.7701630000 -1.5889140000 1.9769760000
 C -0.7103840000 0.6471650000 -0.5319910000
 C -1.8895550000 1.5886060000 -0.2607820000
 C 0.2298410000 1.3754930000 -1.4964740000
 C 0.5075630000 1.1364800000 1.7595640000
 H 0.8718190000 -1.3923110000 -1.7651480000
 H 0.0760400000 -2.6195050000 -0.8108110000
 H -1.5791730000 -0.8129730000 -1.9988840000
 N 2.4392010000 -0.1674200000 -0.1506500000
 N 3.5283270000 -0.0647110000 -0.0353790000
 H 0.7163700000 2.2210520000 -1.0005060000
 H -0.3484610000 1.7782270000 -2.3327550000
 H 1.0082550000 0.7412890000 -1.9178430000
 H -2.5529550000 1.2454700000 0.5332080000
 H -2.4889140000 1.7154910000 -1.1671410000
 H -1.5182720000 2.5767060000 0.0262280000
 H -0.2849720000 1.8084270000 2.1002380000
 H 1.2946610000 1.7456800000 1.3056950000
 H 0.9330700000 0.6335700000 2.6309610000

Thermodynamic Data

Zero-point correction= 0.243523 (Hartree/Particle)
 Thermal correction to Energy= 0.255278
 Thermal correction to Enthalpy= 0.256222
 Thermal correction to Gibbs Free Energy= 0.207248
 Sum of electronic and zero-point Energies= -499.758761
 Sum of electronic and thermal Energies= -499.747006
 Sum of electronic and thermal Enthalpies= -499.746062
 Sum of electronic and thermal Free Energies= -499.795036

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.189	47.086	103.076

$V_{\text{imag}} = -\text{XXX cm}^{-1}$

endo bornane diazonium (*endo*-B-N₂⁺)

1 1

C -0.7521710000 1.4061590000 0.2685740000
 C 0.5095130000 1.2876920000 1.1454090000
 C 0.9754500000 -0.1598310000 0.8001210000
 C 0.0215980000 -0.6601560000 -0.3249360000
 C 0.2727410000 0.2176170000 -1.5706780000
 C -0.2827690000 1.6169530000 -1.1810360000
 H 0.4679350000 2.4050350000 -1.2553790000
 H -1.1113450000 1.9060030000 -1.8258440000
 H -0.2614550000 -0.2116840000 -2.4180970000
 H 1.3238650000 0.2395690000 -1.8726470000
 C -1.3030380000 -0.0436930000 0.2543080000
 C -2.4931100000 -0.2491490000 -0.6865250000
 C -1.7120030000 -0.5770130000 1.6321420000
 C 0.0786920000 -2.1565070000 -0.5491710000
 H 0.3078580000 1.3493510000 2.2132910000
 H 1.2612430000 2.0392310000 0.8998610000
 H -1.4451270000 2.1614560000 0.6386650000
 N 2.3663010000 -0.1687080000 0.3290490000
 N 3.3851910000 -0.1815790000 -0.0627660000
 H 1.0479300000 -2.4707840000 -0.9487930000
 H -0.6767620000 -2.4473490000 -1.2815750000
 H -0.1092230000 -2.7115790000 0.3732340000
 H -1.9705500000 -1.6366310000 1.5717640000
 H -2.6040990000 -0.0466500000 1.9721030000
 H -0.9607500000 -0.4614240000 2.4163800000
 H -3.3370150000 0.3489460000 -0.3351910000
 H -2.8086770000 -1.2949120000 -0.6750520000
 H -2.2952360000 0.0317150000 -1.7195370000
 H 1.0215450000 -0.8407160000 1.6535760000

Thermodynamic Data

Zero-point correction= 0.260071 (Hartree/Particle)
 Thermal correction to Energy= 0.271795
 Thermal correction to Enthalpy= 0.272739
 Thermal correction to Gibbs Free Energy= 0.223948
 Sum of electronic and zero-point Energies= -500.165645
 Sum of electronic and thermal Energies= -500.153921
 Sum of electronic and thermal Enthalpies= -500.152977
 Sum of electronic and thermal Free Energies= -500.201767

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 170.554 47.746 102.689

1 1

C -1.0594940000 0.7588620000 1.0274750000
 C 0.2772510000 1.5312110000 0.9758750000
 C 0.9257340000 0.9446820000 -0.3104090000
 C -0.0588930000 -0.1520880000 -0.8034620000
 C -1.2069770000 0.7263500000 -1.3792670000
 C -1.9280440000 1.2920810000 -0.1244440000
 H -1.9809130000 2.3811330000 -0.1256740000
 H -2.9490870000 0.9202070000 -0.0521820000
 H -1.8612440000 0.0959970000 -1.9814500000
 H -0.8290980000 1.5035990000 -2.0479730000
 C -0.6675190000 -0.6597030000 0.5418560000
 C -1.8580550000 -1.5973310000 0.3165720000
 C 0.3090920000 -1.3900000000 1.4720310000
 C 0.5116630000 -1.1623290000 -1.7770560000
 H 0.8970440000 1.3590220000 1.8551240000
 H 0.1485300000 2.6076360000 0.8658140000
 H -1.5253530000 0.8044520000 2.0117000000
 N 2.2526840000 0.3431670000 -0.0123680000
 N 3.2257080000 -0.1212340000 0.1565180000
 H 0.9106410000 -0.6771470000 -2.6720980000
 H -0.2827720000 -1.8379370000 -2.0985040000
 H 1.2995590000 -1.7772860000 -1.3323610000
 H 0.7612260000 -2.2508190000 0.9713630000
 H -0.2387570000 -1.7777600000 2.3331460000
 H 1.1079690000 -0.7707500000 1.8843790000
 H -2.3919270000 -1.7428950000 1.2581500000
 H -1.5069790000 -2.5779030000 -0.0141550000
 H -2.5743660000 -1.2339130000 -0.4185970000
 H 1.1982410000 1.6704240000 -1.0807650000

Thermodynamic Data

Zero-point correction= 0.260281 (Hartree/Particle)
 Thermal correction to Energy= 0.271880
 Thermal correction to Enthalpy= 0.272824
 Thermal correction to Gibbs Free Energy= 0.224484
 Sum of electronic and zero-point Energies= -500.165191
 Sum of electronic and thermal Energies= -500.153593
 Sum of electronic and thermal Enthalpies= -500.152648
 Sum of electronic and thermal Free Energies= -500.200988

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	170.607	47.664	101.740

endo bornane diazonium dissociation (*endo*-B-N₂⁺-TS)

1 1

C 0.8055770000 -1.4147930000 0.2510030000
 C -0.4648530000 -1.2912030000 1.1304090000
 C -0.8780910000 0.1481750000 0.8105780000
 C -0.0233560000 0.6711230000 -0.3140900000
 C -0.2512820000 -0.2177850000 -1.5713200000
 C 0.3363190000 -1.6128980000 -1.2032330000
 H -0.3983730000 -2.4156440000 -1.2879400000
 H 1.1669930000 -1.8785470000 -1.8562150000
 H 0.2634740000 0.2324890000 -2.4195880000
 H -1.3072580000 -0.2593690000 -1.8517250000
 C 1.3558150000 0.0468010000 0.2616460000
 C 2.5322770000 0.2967590000 -0.6932050000
 C 1.7795150000 0.5645740000 1.6499640000
 C -0.0971350000 2.1716430000 -0.5445720000
 H -0.2729730000 -1.3809330000 2.1999170000
 H -1.2248090000 -2.0315590000 0.8768340000
 H 1.4938500000 -2.1777140000 0.6139260000
 N -2.5572660000 0.1312790000 0.2928140000
 N -3.6105300000 0.1614870000 -0.0071220000
 H -1.0704080000 2.4665100000 -0.9496220000
 H 0.6546990000 2.4814020000 -1.2721390000
 H 0.0702840000 2.7373160000 0.3755390000
 H 2.0105830000 1.6315630000 1.6096720000
 H 2.6911790000 0.0508400000 1.9636340000
 H 1.0466040000 0.4174940000 2.4464720000
 H 3.3910470000 -0.2891460000 -0.3539630000
 H 2.8304400000 1.3472510000 -0.6728590000
 H 2.3356880000 0.0231880000 -1.7280440000
 H -1.0751730000 0.8211160000 1.6431760000

Thermodynamic Data

Zero-point correction= 0.257120 (Hartree/Particle)
 Thermal correction to Energy= 0.269025
 Thermal correction to Enthalpy= 0.269970
 Thermal correction to Gibbs Free Energy= 0.220749
 Sum of electronic and zero-point Energies= -500.162342
 Sum of electronic and thermal Energies= -500.150436
 Sum of electronic and thermal Enthalpies= -500.149492
 Sum of electronic and thermal Free Energies= -500.198712

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.816	47.748	103.593

$$V_{\text{imag}} = -XXX \text{ cm}^{-1}$$

exo bornane diazonium dissociation (**exo-B-N₂⁺-TS**)

1 1

C -1.0822610000 -0.7178870000 -1.0640020000
 C 0.2774450000 -1.4707640000 -1.0348450000
 C 0.8822620000 -0.9485580000 0.2754310000
 C -0.0640970000 0.1174670000 0.8090330000
 C -1.2116340000 -0.8351920000 1.3388820000
 C -1.9434120000 -1.3287230000 0.0587610000
 H -1.9879700000 -2.4172260000 -0.0049950000
 H -2.9697440000 -0.9659130000 0.0189760000
 H -1.8552500000 -0.2409420000 1.9877840000
 H -0.8241160000 -1.6487960000 1.9578730000
 C -0.7125940000 0.6925730000 -0.5093790000
 C -1.9258050000 1.5978910000 -0.2342040000
 C 0.2435500000 1.4908040000 -1.4138410000
 C 0.4876510000 1.0664020000 1.8602990000
 H 0.8947160000 -1.2311780000 -1.9001260000
 H 0.1799000000 -2.5570830000 -1.0005930000
 H -1.5392270000 -0.7301200000 -2.0531850000
 N 2.3887110000 -0.2794600000 -0.0422090000
 N 3.4052130000 0.1134190000 -0.1589640000
 H 0.9034530000 0.5256390000 2.7154830000
 H -0.3106750000 1.7063320000 2.2389500000
 H 1.2656200000 1.7222520000 1.4584230000
 H 0.6234580000 2.3772480000 -0.8993840000
 H -0.2978750000 1.8432390000 -2.2947800000
 H 1.0986000000 0.9277870000 -1.7932910000
 H -2.4558430000 1.7962100000 -1.1688520000
 H -1.6007170000 2.5628990000 0.1624420000
 H -2.6458850000 1.1792950000 0.4674000000
 H 1.2574560000 -1.6714250000 0.9992660000

Thermodynamic Data

Zero-point correction= 0.257881 (Hartree/Particle)
 Thermal correction to Energy= 0.269431
 Thermal correction to Enthalpy= 0.270375
 Thermal correction to Gibbs Free Energy= 0.222130
 Sum of electronic and zero-point Energies= -500.164373
 Sum of electronic and thermal Energies= -500.152823
 Sum of electronic and thermal Enthalpies= -500.151878
 Sum of electronic and thermal Free Energies= -500.200124

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 169.071 47.209 101.541

O 1

```

C -0.1927260000 -1.5920950000 0.3684100000
C -1.1700410000 -0.3949330000 0.1554310000
C -0.1265090000 0.7098880000 0.0201830000
C 1.2721350000 0.1398900000 0.1817510000
C 1.5539430000 -0.7130670000 -1.0834000000
C 0.5789860000 -1.9168490000 -0.9284510000
H -0.0695090000 -2.0614840000 -1.7916370000
H 1.1363960000 -2.8454910000 -0.7888470000
H 2.5965470000 -1.0452090000 -1.0865460000
H 1.3828080000 -0.1369710000 -1.9949320000
C 0.9421400000 -0.9680620000 1.2049490000
H 1.7789290000 -1.6574330000 1.3499000000
H 0.6311290000 -0.5680440000 2.1707780000
C 2.3455540000 1.1443320000 0.5411430000
C -2.0706740000 -0.1965020000 1.3826110000
C -2.0592320000 -0.5190390000 -1.0856540000
H -0.6982110000 -2.4544250000 0.8073710000
N -0.3938820000 1.9212480000 -0.2931330000
N -0.6437200000 3.0032490000 -0.5604410000
H 2.0866830000 1.6814030000 1.4568420000
H 2.4777220000 1.8802770000 -0.2574600000
H 3.3029220000 0.6399060000 0.6926550000
H -2.7630840000 0.3169850000 -1.1254110000
H -2.6423180000 -1.4445180000 -1.0518440000
H -1.4790150000 -0.5040610000 -2.0088950000
H -2.8009860000 -1.0086380000 1.4498550000
H -2.6203190000 0.7451400000 1.3008890000
H -1.4979520000 -0.1703000000 2.3104510000
  
```

Thermodynamic Data

Zero-point correction= 0.247347 (Hartree/Particle)
 Thermal correction to Energy= 0.258960
 Thermal correction to Enthalpy= 0.259905
 Thermal correction to Gibbs Free Energy= 0.210603
 Sum of electronic and zero-point Energies= -499.802400
 Sum of electronic and thermal Energies= -499.790786
 Sum of electronic and thermal Enthalpies= -499.789842
 Sum of electronic and thermal Free Energies= -499.839143

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.500	46.464	103.763

fenchane *endo*-diazonium (*endo*-F-N₂⁺)

1 1

C -0.5818570000 -1.5172250000 -0.1933790000
 C -1.2558700000 -0.1740170000 0.2186810000
 C 0.0363120000 0.6259340000 0.6634080000
 C 1.2609780000 -0.2503970000 0.2809990000
 C 1.2857690000 -0.4203170000 -1.2563980000
 C 0.1118560000 -1.3920970000 -1.5578280000
 H -0.5426240000 -1.0515210000 -2.3578880000
 H 0.4947180000 -2.3689030000 -1.8552090000
 H 2.2470160000 -0.8478240000 -1.5449430000
 H 1.2056760000 0.5315710000 -1.7919050000
 C 0.6421030000 -1.5907660000 0.7362650000
 H 1.3071150000 -2.4223850000 0.4968250000
 H 0.4143720000 -1.6222370000 1.8038850000
 C 2.5593140000 0.1966370000 0.9209060000
 C -2.1598590000 -0.3549860000 1.4404720000
 C -2.0445870000 0.5058610000 -0.9002260000
 H -1.2878490000 -2.3448020000 -0.1233590000
 N 0.1218380000 1.9337400000 0.0178030000
 N 0.2062810000 2.8908830000 -0.5012000000
 H 2.4639190000 0.2843770000 2.0060440000
 H 2.9006570000 1.1573290000 0.5226560000
 H 3.3414740000 -0.5350140000 0.7107230000
 H -2.5680910000 1.3922190000 -0.5311220000
 H -2.8024750000 -0.1872210000 -1.2705010000
 H -1.4264500000 0.7940900000 -1.7534830000
 H -3.0358070000 -0.9416050000 1.1568400000
 H -2.5124760000 0.6086550000 1.8177220000
 H -1.6549460000 -0.8797730000 2.2537690000
 H 0.0339810000 0.8889130000 1.7263280000

Thermodynamic Data

Zero-point correction= 0.260086 (Hartree/Particle)
 Thermal correction to Energy= 0.271672
 Thermal correction to Enthalpy= 0.272616
 Thermal correction to Gibbs Free Energy= 0.224215
 Sum of electronic and zero-point Energies= -500.168473
 Sum of electronic and thermal Energies= -500.156888
 Sum of electronic and thermal Enthalpies= -500.155943
 Sum of electronic and thermal Free Energies= -500.204344

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.476	47.609	101.868

fenchane *exo*-diazonium (*exo*-F-N₂⁺)

1 1

C -1.2585120000 -0.2373570000 0.9113520000
 C -0.8313810000 0.9265800000 -0.0354100000
 C 0.4659620000 0.2903210000 -0.6796400000
 C 0.6221730000 -1.1134580000 -0.0300650000
 C -0.5505410000 -1.9186470000 -0.6573030000
 C -1.8081660000 -1.4194670000 0.1008220000
 H -2.6343380000 -1.1540950000 -0.5559600000
 H -2.1747560000 -2.1868270000 0.7834060000
 H -0.3669790000 -2.9800760000 -0.4851230000
 H -0.6108410000 -1.7791500000 -1.7402540000
 C 0.0867920000 -0.8131900000 1.3809250000
 H -0.0261200000 -1.7268800000 1.9669790000
 H 0.7126190000 -0.1195580000 1.9499900000
 C 1.9847120000 -1.7610800000 -0.1778060000
 C -0.5543840000 2.1953250000 0.7782370000
 C -1.8271040000 1.2552460000 -1.1493050000
 H -1.9274900000 0.1215970000 1.6934330000
 N 1.6566370000 1.0947860000 -0.3329640000
 N 2.5377030000 1.6647750000 -0.0319970000
 H 2.7756550000 -1.1959960000 0.3237040000
 H 2.2558540000 -1.8911200000 -1.2289590000
 H 1.9608390000 -2.7504090000 0.2818140000
 H -1.5130580000 2.1464690000 -1.6979060000
 H -2.8072930000 1.4591020000 -0.7123490000
 H -1.9418710000 0.4396030000 -1.8653170000
 H -1.5042060000 2.5688590000 1.1635620000
 H -0.1254880000 2.9903850000 0.1614880000
 H 0.0959860000 2.0189930000 1.6382960000
 H 0.4938020000 0.2965460000 -1.7729150000

Thermodynamic Data

Zero-point correction= 0.259815 (Hartree/Particle)

Thermal correction to Energy= 0.271405

Thermal correction to Enthalpy= 0.272349

Thermal correction to Gibbs Free Energy= 0.223989

Sum of electronic and zero-point Energies= -500.169052

Sum of electronic and thermal Energies= -500.157462

Sum of electronic and thermal Enthalpies= -500.156517

Sum of electronic and thermal Free Energies= -500.204877

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	170.309	47.704	101.782

fenchane *endo*-diazonium dissociation (***endo*-F-N₂⁺-TS**)

1 1

C 0.7451050000 -1.4771280000 0.3028780000
 C 1.2771370000 -0.0925110000 -0.2125160000
 C -0.0747150000 0.4892340000 -0.7007940000
 C -1.2164600000 -0.4063920000 -0.2963980000
 C -1.2734160000 -0.5306090000 1.2553710000
 C 0.0043480000 -1.3310390000 1.6449860000
 H 0.5940140000 -0.8496650000 2.4238060000
 H -0.2621150000 -2.3203670000 2.0209050000
 H -2.1847960000 -1.0654350000 1.5260130000
 H -1.3334540000 0.4468590000 1.7420290000
 C -0.4369560000 -1.7306710000 -0.6564030000
 H -1.0532120000 -2.5910660000 -0.3877160000
 H -0.1709390000 -1.8210320000 -1.7108980000
 C -2.5420970000 -0.1461300000 -0.9944730000
 C 2.1977150000 -0.2663850000 -1.4411050000
 C 2.0202850000 0.7488370000 0.8379500000
 H 1.5304440000 -2.2323420000 0.3062310000
 N -0.3512690000 2.0891080000 0.0256350000
 N -0.5876590000 3.1007970000 0.3725510000
 H -2.4269150000 -0.0918460000 -2.0803490000
 H -3.0015020000 0.7862600000 -0.6520100000
 H -3.2463000000 -0.9505150000 -0.7734860000
 H 2.4029480000 1.6749500000 0.4011510000
 H 2.8810860000 0.1839760000 1.2010290000
 H 1.4051730000 0.9998440000 1.7033740000
 H 3.1227670000 -0.7555860000 -1.1292630000
 H 2.4626470000 0.7023040000 -1.8737390000
 H 1.7502210000 -0.8786190000 -2.2260020000
 H -0.1032490000 0.8897140000 -1.7153470000

Thermodynamic Data

Zero-point correction= 0.257047 (Hartree/Particle)
 Thermal correction to Energy= 0.268817
 Thermal correction to Enthalpy= 0.269761
 Thermal correction to Gibbs Free Energy= 0.220862
 Sum of electronic and zero-point Energies= -500.164495
 Sum of electronic and thermal Energies= -500.152725
 Sum of electronic and thermal Enthalpies= -500.151781
 Sum of electronic and thermal Free Energies= -500.200680

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.685	47.567	102.916

V_{imag} = -XXX cm⁻¹

fenchane *exo*-diazonium dissociation (*exo*-F-
N₂⁺-TS)

1 1

C 1.2898070000 -0.3718580000 0.8968380000
 C 0.3259740000 -1.2035190000 -0.0346500000
 C -0.4819010000 -0.0322650000 -0.6622050000
 C -0.0187670000 1.2669300000 -0.0187010000
 C 1.4025210000 1.4367410000 -0.6907740000
 C 2.3069690000 0.4147730000 0.0489730000
 H 2.8939140000 -0.2076940000 -0.6249000000
 H 3.0131480000 0.9260810000 0.7052530000
 H 1.7153010000 2.4684090000 -0.5211940000
 H 1.3750900000 1.2941040000 -1.7745700000
 C 0.3778490000 0.7683320000 1.3918020000
 H 0.9185720000 1.5308100000 1.9545910000
 H -0.4735410000 0.4458560000 1.9959170000
 C -0.9177230000 2.4851750000 -0.1638290000
 C -0.5150270000 -2.1753700000 0.8186350000
 C 1.0165280000 -2.0086660000 -1.1505710000
 H 1.7342940000 -1.0022790000 1.6664700000
 N -2.1287600000 -0.2163500000 -0.2927800000
 N -3.1997910000 -0.2599570000 -0.0658540000
 H -1.8707530000 2.3623730000 0.3588200000
 H -1.1248520000 2.7152300000 -1.2128960000
 H -0.4256260000 3.3564970000 0.2719660000
 H 0.2930560000 -2.6312690000 -1.6833910000
 H 1.7655630000 -2.6724520000 -0.7132500000
 H 1.5206210000 -1.3789900000 -1.8851380000
 H 0.1468770000 -2.9419660000 1.2245090000
 H -1.2687410000 -2.6886790000 0.2150850000
 H -1.0076670000 -1.6903320000 1.6634260000
 H -0.6227780000 -0.0331890000 -1.7433810000

Thermodynamic Data

Zero-point correction= 0.257722 (Hartree/Particle)
 Thermal correction to Energy= 0.269217
 Thermal correction to Enthalpy= 0.270161
 Thermal correction to Gibbs Free Energy= 0.221992
 Sum of electronic and zero-point Energies= -500.167404
 Sum of electronic and thermal Energies= -500.155910
 Sum of electronic and thermal Enthalpies= -500.154965
 Sum of electronic and thermal Free Energies= -500.203134

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	168.936	47.106	101.379

$$V_{\text{imag}} = -\text{XXX cm}^{-1}$$

4.2.2. Structures optimized at the M06-2X/6-31G* level of theory

Norbornyl cation (**N⁺**)

optimized xyz-matrix

```
C 0.9802780000 -0.6709780000 0.0000040000
C 0.0267990000 -0.8495390000 -1.1958650000
C -1.1246610000 -0.0077670000 -0.6968410000
C -1.1245310000 -0.0075550000 0.6969780000
C -0.1728760000 1.3918360000 -0.0001160000
C 1.2522840000 0.8421410000 -0.0001490000
H 1.7997470000 1.1642030000 -0.8880100000
H 1.7998520000 1.1643580000 0.8875920000
H -0.4806950000 1.9832260000 0.8680720000
H -0.4807380000 1.9829840000 -0.8684600000
C 0.0269580000 -0.8493080000 1.1960150000
H 0.4303010000 -0.5145670000 2.1537810000
H -0.3263790000 -1.8829640000 1.3008360000
H -1.9459120000 0.3595020000 1.3046270000
H -1.9461190000 0.3592030000 -1.3044420000
H -0.3265270000 -1.8832330000 -1.3003860000
H 0.4299920000 -0.5149940000 -2.1537600000
H 1.8609720000 -1.3107000000 -0.0000020000
```

Thermodynamic Data

Zero-point correction= 0.166365 (Hartree/Particle)
 Thermal correction to Energy= 0.172020
 Thermal correction to Enthalpy= 0.172964
 Thermal correction to Gibbs Free Energy= 0.137533
 Sum of electronic and zero-point Energies= -272.764734
 Sum of electronic and thermal Energies= -272.759080
 Sum of electronic and thermal Enthalpies= -272.758135
 Sum of electronic and thermal Free Energies= -272.793566

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	107.944	23.720	74.57

Bornyl cation (**B⁺**)

optimized xyz-matrix

```
C 1.3938390000 -0.5211030000 -1.2607020000
```

H 2.3535650000 -0.0298920000 -1.4878380000
 H 1.3383930000 -1.3829120000 -1.9350100000
 C 0.2575400000 0.3955340000 -1.5194560000
 H -0.1476470000 0.5541540000 -2.5221550000
 C -0.3717410000 0.8686360000 -0.3491110000
 C -1.6872550000 1.6031280000 -0.4549360000
 H -2.3689720000 1.1225950000 -1.1622250000
 H -2.1752580000 1.6462230000 0.5225560000
 H -1.5228440000 2.6341150000 -0.7829700000
 C 0.6875090000 1.4743900000 0.6403890000
 H 1.1925420000 2.3085600000 0.1485500000
 H 0.1291490000 1.8899720000 1.4824880000
 C 1.6499940000 0.3391690000 1.0522820000
 H 2.6920600000 0.5800780000 0.8321000000
 H 1.5860880000 0.1294770000 2.1219440000
 C 1.1594670000 -0.8517450000 0.2229040000
 H 1.5632270000 -1.8180020000 0.5325100000
 C -0.3885830000 -0.7514290000 0.2870340000
 C -1.1665170000 -1.7666100000 -0.5502250000
 H -0.7544640000 -1.9547130000 -1.5444820000
 H -1.1808460000 -2.7206060000 -0.0140580000
 H -2.2065900000 -1.4478060000 -0.6680170000
 C -1.0230520000 -0.6866920000 1.6674430000
 H -0.6361840000 0.1008560000 2.3135100000
 H -2.1086150000 -0.5826390000 1.5938180000
 H -0.8208090000 -1.6491200000 2.1555470000

Thermodynamic data

Zero-point correction= 0.249360 (Hartree/Particle)
 Thermal correction to Energy= 0.259150
 Thermal correction to Enthalpy= 0.260094
 Thermal correction to Gibbs Free Energy= 0.215850
 Sum of electronic and zero-point Energies= -390.552743
 Sum of electronic and thermal Energies= -390.542953
 Sum of electronic and thermal Enthalpies= -390.542009
 Sum of electronic and thermal Free Energies= -390.586253

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.619	40.180	93.119

Fenchyl cation (F^+)

optimized xyz-matrix

C 0.6244800000 -0.3052340000 1.3351750000
 H 1.4625250000 0.0874500000 1.9220900000

H 0.3200390000 -1.2668490000 1.7569690000
 C 0.0027450000 -0.9259910000 -0.5931180000
 H -0.0688550000 -1.9128970000 -1.0638460000
 C 1.2478840000 -0.3568990000 -0.2067210000
 C 2.5187680000 -1.1426960000 -0.4406160000
 H 2.3808350000 -2.2104820000 -0.2515910000
 H 2.8602930000 -1.0126130000 -1.4716410000
 H 3.3100660000 -0.7764040000 0.2187360000
 C 1.3338610000 1.1838470000 -0.4558290000
 H 2.3326720000 1.4938890000 -0.1373500000
 H 1.2575620000 1.3805640000 -1.5280680000
 C 0.2200970000 1.8511530000 0.3804410000
 H 0.6484110000 2.4656650000 1.1756000000
 H -0.4287140000 2.4969580000 -0.2134330000
 C -0.5233180000 0.6589390000 0.9871580000
 H -1.1935600000 0.9125820000 1.8105780000
 C -1.2058760000 -0.2050200000 -0.1119130000
 C -2.2143020000 -1.2022230000 0.4939670000
 H -3.0914970000 -0.6418100000 0.8291930000
 H -2.5405000000 -1.9326520000 -0.2520900000
 H -1.8094620000 -1.7406080000 1.3549100000
 C -1.8787460000 0.5303570000 -1.2928930000
 H -1.1892790000 1.1768540000 -1.8401380000
 H -2.3167950000 -0.1850970000 -1.9938020000
 H -2.6873030000 1.1480590000 -0.8900300000

Thermodynamic data

Zero-point correction= 0.249697 (Hartree/Particle)

Thermal correction to Energy= 0.259497

Thermal correction to Enthalpy= 0.260441

Thermal correction to Gibbs Free Energy= 0.216043

Sum of electronic and zero-point Energies= -390.551925

Sum of electronic and thermal Energies= -390.542126

Sum of electronic and thermal Enthalpies= -390.541182

Sum of electronic and thermal Free Energies= -390.585580

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.837	40.003	93.443

Camphyl cation (C⁺)

optimized xyz matrix

C 0.9222520000 0.9390860000 -0.8040540000
 C -0.3775170000 0.8776430000 -0.2196500000
 C -0.7279330000 -0.5493920000 0.0591320000
 C 0.6665260000 -1.2191430000 -0.1229310000
 C 1.5655470000 -0.6878760000 1.0077330000
 C 1.5350030000 0.8249700000 0.7433340000

H 0.9952630000 1.4018060000 1.5017990000
 H 2.5086730000 1.3066160000 0.6195930000
 H 2.5791100000 -1.0795810000 0.8998180000
 H 1.2131600000 -0.9419320000 2.0079910000
 C 1.2506890000 -0.4623880000 -1.3262000000
 H 2.3259030000 -0.6143980000 -1.4432110000
 H 0.7658900000 -0.6652940000 -2.2828680000
 H 0.6155830000 -2.3055200000 -0.2094630000
 C -1.7067260000 -0.9741640000 -1.0749510000
 C -1.4067480000 -0.7833870000 1.4117500000
 C -1.2418360000 2.0311930000 0.0879530000
 H 1.2471860000 1.8481720000 -1.3052330000
 H -2.0537660000 2.0056190000 -0.6567360000
 H -0.7255920000 2.9868730000 -0.0145640000
 H -1.7161550000 1.9430190000 1.0693680000
 H -2.6722120000 -0.4771550000 -0.9516670000
 H -1.8646000000 -2.0525530000 -0.9848500000
 H -1.3348390000 -0.7660560000 -2.0800640000
 H -1.4705930000 -1.8586760000 1.6023780000
 H -2.4256140000 -0.3864570000 1.4133140000
 H -0.8629330000 -0.3237450000 2.2416990000

Thermodynamic data

Zero-point correction= 0.251006 (Hartree/Particle)
 Thermal correction to Energy= 0.261158
 Thermal correction to Enthalpy= 0.262102
 Thermal correction to Gibbs Free Energy= 0.216823
 Sum of electronic and zero-point Energies= -390.582068
 Sum of electronic and thermal Energies= -390.571917
 Sum of electronic and thermal Enthalpies= -390.570973
 Sum of electronic and thermal Free Energies= -390.616252

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	163.879	40.995	95.298

Pinyll cation (P ⁺)
---------------------------------	---

1 1

C 0.8618150000 1.1824880000 0.2563330000
 C 0.6250180000 1.2220240000 -1.2685320000
 C -0.0342610000 -0.1518480000 -1.2553770000
 C -1.1774330000 -0.3004560000 -0.4713200000
 C -1.6220660000 0.8708200000 0.3446920000
 C -0.4105780000 1.6451240000 0.9526240000
 H -0.5449150000 2.7201260000 0.8151800000
 H -0.3567440000 1.4584990000 2.0282160000
 H -2.3487000000 0.5678020000 1.1025250000
 H -2.1545570000 1.5276340000 -0.3592500000

C 0.9381810000 -0.3553960000 0.2884950000
 C 0.4809410000 -1.1157130000 1.5196900000
 C 2.2152670000 -0.9775320000 -0.2554150000
 C -1.9449580000 -1.5691720000 -0.4353440000
 H 0.1991400000 -0.9256280000 -1.9847660000
 H 1.5423800000 1.2197360000 -1.8547490000
 H -0.0177520000 2.0327730000 -1.6228990000
 H 1.7546660000 1.6850300000 0.6393380000
 H 2.9684080000 -0.9082040000 0.5389860000
 H 2.6104350000 -0.4744920000 -1.1381300000
 H 2.0713470000 -2.0372870000 -0.4813340000
 H -0.4517160000 -0.7625490000 1.9621050000
 H 1.2676870000 -0.9878620000 2.2733740000
 H 0.3971920000 -2.1875890000 1.3179430000
 H -1.4499790000 -2.3789450000 -0.9745180000
 H -2.9174300000 -1.3804840000 -0.9120680000
 H -2.1610110000 -1.8705870000 0.5949690000

Thermodynamic data

Zero-point correction= 0.250874 (Hartree/Particle)
 Thermal correction to Energy= 0.261059
 Thermal correction to Enthalpy= 0.262004
 Thermal correction to Gibbs Free Energy= 0.216890
 Sum of electronic and zero-point Energies= -390.565963
 Sum of electronic and thermal Energies= -390.555778
 Sum of electronic and thermal Enthalpies= -390.554834
 Sum of electronic and thermal Free Energies= -390.599948

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	163.817	41.465	94.950

α -Fenchyl cation (α -F⁺)

optimized xyz-matrix

C 0.5163530000 0.3933240000 1.1412620000
 C 1.0801480000 -0.3787030000 -0.0846170000
 C -0.1952740000 -0.2229840000 -0.9376340000
 C -1.3217420000 -0.3882580000 -0.0957690000
 C -0.5107310000 1.4268170000 -0.7372060000
 C 0.1968230000 1.7881900000 0.5762560000
 H 1.0960370000 2.3784940000 0.3972960000
 H -0.4536610000 2.3603610000 1.2407760000
 H -1.5594020000 1.7315360000 -0.7973280000
 H -0.0328890000 1.7886330000 -1.6524500000
 C -0.8779850000 -0.2369280000 1.3240160000

H -1.5811290000 0.3360750000 1.9360770000
 H -0.8266010000 -1.2490410000 1.7502130000
 C -2.7081450000 -0.6709560000 -0.5203570000
 C 1.3818090000 -1.8570650000 0.1928720000
 C 2.3160690000 0.2552910000 -0.7261900000
 H 1.1443490000 0.3777550000 2.0327330000
 H -2.8803890000 -1.7357900000 -0.3015070000
 H -2.8602490000 -0.5213090000 -1.5906200000
 H -3.4402300000 -0.1075170000 0.0640560000
 H 2.6500150000 -0.3491720000 -1.5743190000
 H 3.1344550000 0.2854850000 -0.0004610000
 H 2.1541180000 1.2723010000 -1.0900280000
 H 2.2194890000 -1.9361920000 0.8917940000
 H 1.6742880000 -2.3635740000 -0.7311770000
 H 0.5375820000 -2.4085820000 0.6154790000
 H -0.2397400000 -0.5118300000 -1.9863390000

Thermodynamic data

Zero-point correction= 0.249954 (Hartree/Particle)
 Thermal correction to Energy= 0.260320
 Thermal correction to Enthalpy= 0.261265
 Thermal correction to Gibbs Free Energy= 0.215454
 Sum of electronic and zero-point Energies= -390.580465
 Sum of electronic and thermal Energies= -390.570098
 Sum of electronic and thermal Enthalpies= -390.569154
 Sum of electronic and thermal Free Energies= -390.614964

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	163.354	41.578	96.416

Phellandryl cation (Ph⁺)

optimized xyz-matrix

C 1.4844250000 -1.1960680000 -0.3078700000
 C 0.1594130000 -1.1358290000 -0.6787860000
 C -0.6934610000 0.0712830000 -0.5994550000
 C -0.0682780000 1.1329250000 0.3082680000
 C 1.4279640000 1.2816960000 0.0389470000
 C 2.1561030000 -0.0143970000 0.0234400000
 C 3.6050470000 -0.0145820000 0.3098630000
 H 1.9114520000 1.9722580000 0.7382810000
 H 1.6008020000 1.7154020000 -0.9640700000
 H -0.2156430000 0.8468270000 1.3560140000
 H -0.5618440000 2.0958980000 0.1626130000
 C -2.1578080000 -0.3138320000 -0.2461050000
 H -0.7165600000 0.4534860000 -1.6413470000
 H -0.2996880000 -2.0368020000 -1.0900120000
 H 2.0343920000 -2.1296070000 -0.3717210000

H 4.1043540000 -0.9374730000 0.0137000000
 H 3.7174880000 0.1094920000 1.3993530000
 H 4.0952760000 0.8551360000 -0.1409400000
 C -3.0634370000 0.9160750000 -0.2683100000
 C -2.2504220000 -1.0460180000 1.0948170000
 H -2.4903080000 -1.0001800000 -1.0364740000
 H -2.8265500000 1.5996330000 0.5536920000
 H -4.1060450000 0.6111200000 -0.1464790000
 H -2.9813640000 1.4653670000 -1.2116440000
 H -1.6107340000 -1.9364660000 1.1297260000
 H -3.2779420000 -1.3755070000 1.2690390000
 H -1.9743690000 -0.3961110000 1.9314170000

Thermodynamic data

Zero-point correction= 0.249033 (Hartree/Particle)
 Thermal correction to Energy= 0.260243
 Thermal correction to Enthalpy= 0.261187
 Thermal correction to Gibbs Free Energy= 0.212494
 Sum of electronic and zero-point Energies= -390.582219
 Sum of electronic and thermal Energies= -390.571009
 Sum of electronic and thermal Enthalpies= -390.570065
 Sum of electronic and thermal Free Energies= -390.618758

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	163.305	42.475	102.484

Terpinyl cation (T^+)

optimized xyz-matrix

C 0.9614820000 0.2640980000 0.9217740000
 C -0.0593080000 1.4007670000 1.0429200000
 C -1.3637250000 1.1256790000 0.3439210000
 C -1.7758890000 -0.0722230000 -0.0832150000
 C -0.9488080000 -1.3184200000 0.1192570000
 C 0.2106910000 -1.1366520000 1.0867130000
 H -0.1619350000 -1.0813520000 2.1142900000
 H 0.9211150000 -1.9663100000 1.0386050000
 H -0.6136510000 -1.7101100000 -0.8528260000
 H -1.5936910000 -2.1097750000 0.5231280000
 C 1.6909420000 0.1493090000 -0.3305620000
 C 3.0149880000 -0.4915630000 -0.3245410000
 C 1.1548330000 0.6037600000 -1.6173020000
 C -3.0891680000 -0.2713490000 -0.7851450000
 H 0.3797290000 2.3350500000 0.6712180000
 H -0.2329460000 1.5674370000 2.1136420000
 H 1.6928830000 0.2822110000 1.7387890000
 H -3.7454500000 -0.9227780000 -0.1974730000

H -2.9443870000 -0.7585300000 -1.7567080000
H -3.6047810000 0.6769140000 -0.9493620000
H 1.9489420000 0.8171700000 -2.3379110000
H 0.4314040000 1.4153510000 -1.5314750000
H 0.6006110000 -0.2660630000 -2.0199580000
H 3.7323670000 0.3502380000 -0.3130910000
H 3.2183610000 -1.0463580000 -1.2450660000
H 3.2043420000 -1.0922530000 0.5669090000
H -2.0091380000 1.9887250000 0.1943670000

Thermodynamic data

Zero-point correction= 0.248012 (Hartree/Particle)
Thermal correction to Energy= 0.259243
Thermal correction to Enthalpy= 0.260187
Thermal correction to Gibbs Free Energy= 0.211832
Sum of electronic and zero-point Energies= -390.563997
Sum of electronic and thermal Energies= -390.552766
Sum of electronic and thermal Enthalpies= -390.551822
Sum of electronic and thermal Free Energies= -390.600177

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.677	43.135	101.773

Norbornyl *endo* diazonium (***endo*-N-N₂⁺**)

optimized xyz-matrix

C 1.4275220000 -0.5724850000 -0.5970320000
C 0.0883630000 -1.3224590000 -0.7154570000
C -0.7031830000 -0.7245600000 0.4971710000
C 0.2404340000 0.3399720000 1.1164160000
C 0.4149800000 1.5117140000 0.1332310000
C 1.2209630000 0.8859030000 -1.0444250000
H 0.6967290000 0.9534520000 -2.0018610000
H 2.1821970000 1.3893780000 -1.1665150000
H 0.9835090000 2.2992440000 0.6326100000
H -0.5298860000 1.9698300000 -0.1778570000
C 1.5650520000 -0.4311750000 0.9285960000
H 2.4171130000 0.1805140000 1.2354610000
H 1.6022820000 -1.3861630000 1.4618520000
H -0.0433920000 0.6100510000 2.1339920000
H 0.1917230000 -2.3977460000 -0.5551020000
H -0.4174290000 -1.1666850000 -1.6721480000
H 2.2388680000 -1.0937940000 -1.1058090000
N -1.9549390000 -0.1040800000 0.0390310000
N -2.8719420000 0.3884410000 -0.3119780000
H -1.0583380000 -1.4700690000 1.2150000000

Thermodynamic Data

Zero-point correction= 0.178008 (Hartree/Particle)
 Thermal correction to Energy= 0.185415
 Thermal correction to Enthalpy= 0.186359
 Thermal correction to Gibbs Free Energy= 0.146131
 Sum of electronic and zero-point Energies= -382.224675
 Sum of electronic and thermal Energies= -382.217268
 Sum of electronic and thermal Enthalpies= -382.216324
 Sum of electronic and thermal Free Energies= -382.256553

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	116.350	29.801	84.669

Norbornyl *exo* diazonium (***exo*-N-N₂⁺**)

optimized xyz-matrix

C -1.0779200000 1.0353870000 0.4215640000
 C 0.0883140000 1.2866050000 -0.5584610000
 C 0.7053380000 -0.1426760000 -0.6916350000
 C -0.1334290000 -1.0195710000 0.2695100000
 C -1.4870290000 -1.1813890000 -0.4635450000
 C -2.1556040000 0.2158740000 -0.3090530000
 H -2.4344040000 0.6595900000 -1.2680490000
 H -3.0611470000 0.1508700000 0.2979830000
 H -2.0598570000 -1.9629350000 0.0401510000
 H -1.3657430000 -1.4943440000 -1.5046860000
 C -0.4733000000 -0.0078490000 1.3756840000
 H -1.1996260000 -0.4132900000 2.0840420000
 H 0.3961370000 0.3536110000 1.9373710000
 H 0.3496460000 -1.9579650000 0.5472650000
 H 0.8139920000 1.9946810000 -0.1487600000
 H -0.2227290000 1.6496320000 -1.5400370000
 H -1.4366860000 1.9574450000 0.8798500000
 N 2.1055290000 -0.1138200000 -0.1980970000
 N 3.1232190000 -0.1036000000 0.2147820000
 H 0.8209610000 -0.5336470000 -1.7063040000

Thermodynamic Data

Zero-point correction= 0.177614 (Hartree/Particle)
 Thermal correction to Energy= 0.185112
 Thermal correction to Enthalpy= 0.186056
 Thermal correction to Gibbs Free Energy= 0.145632
 Sum of electronic and zero-point Energies= -382.225583
 Sum of electronic and thermal Energies= -382.218085
 Sum of electronic and thermal Enthalpies= -382.217141
 Sum of electronic and thermal Free Energies= -382.257565

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	116.159	29.992	85.079

endo bornane diazonium (*endo*-B-N₂⁺)

optimized xyz-matrix

```

C -0.7458070000 1.4096960000 0.2600520000
C 0.5111190000 1.2911750000 1.1441590000
C 0.9766370000 -0.1605190000 0.8041460000
C 0.0177330000 -0.6645240000 -0.3215510000
C 0.2760040000 0.2049030000 -1.5724600000
C -0.2683600000 1.6104510000 -1.1893130000
H 0.4916390000 2.3928880000 -1.2638420000
H -1.0927560000 1.9062020000 -1.8405170000
H -0.2635640000 -0.2264920000 -2.4186860000
H 1.3296120000 0.2147030000 -1.8745210000
C -1.3041730000 -0.0380770000 0.2527190000
C -2.4951170000 -0.2415320000 -0.6889670000
C -1.7180740000 -0.5642240000 1.6324610000
C 0.0702670000 -2.1634880000 -0.5373450000
H 0.3048160000 1.3537190000 2.2134390000
H 1.2686240000 2.0415170000 0.9027600000
H -1.4371400000 2.1733590000 0.6234200000
N 2.3614660000 -0.1701820000 0.3341120000
N 3.3853110000 -0.1833230000 -0.0652300000
H 1.0389970000 -2.4828940000 -0.9384890000
H -0.6896730000 -2.4568660000 -1.2671300000
H -0.1171450000 -2.7151550000 0.3896390000
H -1.9951690000 -1.6214390000 1.5741820000
H -2.5999000000 -0.0170760000 1.9788160000
H -0.9582970000 -0.4629720000 2.4137820000
H -3.3440410000 0.3485620000 -0.3302310000
H -2.8051990000 -1.2911180000 -0.6896400000
H -2.2997210000 0.0528680000 -1.7211730000
H 1.0201010000 -0.8384310000 1.6626040000

```

Thermodynamic Data

Zero-point correction= 0.262349 (Hartree/Particle)
 Thermal correction to Energy= 0.274059
 Thermal correction to Enthalpy= 0.275003
 Thermal correction to Gibbs Free Energy= 0.226198
 Sum of electronic and zero-point Energies= -500.030324
 Sum of electronic and thermal Energies= -500.018614
 Sum of electronic and thermal Enthalpies= -500.017670

Sum of electronic and thermal Free Energies= -500.066475

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	171.975	47.508	102.719

Exo-bornane diazonium (**exo-B-N₂⁺**)

optimized xyz-matrix

```

C -1.0582650000 0.7641300000 1.0250230000
C 0.2839100000 1.5277470000 0.9814800000
C 0.9319250000 0.9415500000 -0.3085500000
C -0.0595070000 -0.1556590000 -0.8035660000
C -1.2013030000 0.7278290000 -1.3838040000
C -1.9186080000 1.3036280000 -0.1312180000
H -1.9607010000 2.3955470000 -0.1354130000
H -2.9461420000 0.9424560000 -0.0600070000
H -1.8604890000 0.0971500000 -1.9847960000
H -0.8177540000 1.5005400000 -2.0580990000
C -0.6733770000 -0.6579730000 0.5418830000
C -1.8701270000 -1.5892460000 0.3168050000
C 0.2973280000 -1.3952420000 1.4733040000
C 0.5126050000 -1.1700040000 -1.7738230000
H 0.9023970000 1.3458550000 1.8626350000
H 0.1649880000 2.6077880000 0.8761700000
H -1.5296160000 0.8143000000 2.0092050000
N 2.2517820000 0.3432490000 -0.0132730000
N 3.2294480000 -0.1274350000 0.1584210000
H 0.9149970000 -0.6885590000 -2.6715480000
H -0.2828140000 -1.8478640000 -2.0951330000
H 1.3009140000 -1.7847920000 -1.3245380000
H 0.7304770000 -2.2718600000 0.9788250000
H -0.2493910000 -1.7619860000 2.3468300000
H 1.1145600000 -0.7848920000 1.8691560000
H -2.4011870000 -1.7386510000 1.2616460000
H -1.5262020000 -2.5713170000 -0.0235630000
H -2.5902410000 -1.2163180000 -0.4132290000
H 1.2001140000 1.6713440000 -1.0793830000

```

Thermodynamic Data

Zero-point correction= 0.262577 (Hartree/Particle)
 Thermal correction to Energy= 0.274165
 Thermal correction to Enthalpy= 0.275109
 Thermal correction to Gibbs Free Energy= 0.226700
 Sum of electronic and zero-point Energies= -500.029968
 Sum of electronic and thermal Energies= -500.018380

Sum of electronic and thermal Enthalpies= -500.017436
 Sum of electronic and thermal Free Energies= -500.065845

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	172.041	47.413	101.885

fenchane *endo*-diazonium (***endo*-F-N₂⁺**)

optimized xyz-matrix

```
C -0.5711440000 -1.5150110000 -0.2183280000
C -1.2572270000 -0.1859600000 0.2183630000
C 0.0322520000 0.6229440000 0.6701050000
C 1.2654730000 -0.2468150000 0.2825710000
C 1.2983480000 -0.3933580000 -1.2573310000
C 0.1248130000 -1.3590070000 -1.5798060000
H -0.5311120000 -1.0001170000 -2.3741970000
H 0.5087160000 -2.3304110000 -1.9006050000
H 2.2628580000 -0.8192100000 -1.5463980000
H 1.2252850000 0.5695160000 -1.7785150000
C 0.6501460000 -1.5966480000 0.7144150000
H 1.3221140000 -2.4234560000 0.4668340000
H 0.4178760000 -1.6456770000 1.7828310000
C 2.5598940000 0.1973560000 0.9348310000
C -2.1511330000 -0.3934190000 1.4443800000
C -2.0626240000 0.5046790000 -0.8832590000
H -1.2722530000 -2.3514650000 -0.1659990000
N 0.1081350000 1.9287290000 0.0316520000
N 0.1830720000 2.8927650000 -0.4914620000
H 2.4592670000 0.2751040000 2.0220830000
H 2.9015900000 1.1638310000 0.5468430000
H 3.3454260000 -0.5327240000 0.7216880000
H -2.5904090000 1.3831250000 -0.4961400000
H -2.8199500000 -0.1902530000 -1.2569140000
H -1.4556380000 0.8118800000 -1.7406480000
H -3.0237680000 -0.9874140000 1.1586580000
H -2.5129710000 0.5624100000 1.8374970000
H -1.6349310000 -0.9238280000 2.2496290000
H 0.0266660000 0.8796730000 1.7363820000
```

Thermodynamic Data

Zero-point correction= 0.262115 (Hartree/Particle)
 Thermal correction to Energy= 0.273728
 Thermal correction to Enthalpy= 0.274672
 Thermal correction to Gibbs Free Energy= 0.226109
 Sum of electronic and zero-point Energies= -500.033458
 Sum of electronic and thermal Energies= -500.021845
 Sum of electronic and thermal Enthalpies= -500.020901

Sum of electronic and thermal Free Energies= -500.069464

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	171.767	47.454	102.210

fenchane *exo*-diazonium (***exo*-F-N₂⁺**)

1 1

C -1.2203090000 -0.3992700000 0.9091130000
 C -0.9458920000 0.8145140000 -0.0331330000
 C 0.4239290000 0.3480990000 -0.6806440000
 C 0.7606310000 -1.0269000000 -0.0280380000
 C -0.2956780000 -1.9773210000 -0.6582510000
 C -1.6101970000 -1.6420290000 0.0943620000
 H -2.4622650000 -1.4841440000 -0.5682140000
 H -1.8802780000 -2.4518960000 0.7763950000
 H 0.0226080000 -3.0086110000 -0.4838530000
 H -0.3689360000 -1.8481190000 -1.7438550000
 C 0.1872840000 -0.7972250000 1.3820670000
 H 0.1937800000 -1.7176980000 1.9723010000
 H 0.7191600000 -0.0252040000 1.9505710000
 C 2.1986140000 -1.4876710000 -0.1731550000
 C -0.8286780000 2.1065220000 0.7837410000
 C -1.9748970000 1.0172010000 -1.1473280000
 H -1.9341110000 -0.1328830000 1.6922020000
 N 1.4974880000 1.2948890000 -0.3403270000
 N 2.3032410000 1.9762430000 -0.0335360000
 H 2.9062190000 -0.8179020000 0.3284260000
 H 2.4884750000 -1.5806820000 -1.2251940000
 H 2.3092830000 -2.4722020000 0.2885950000
 H -1.7697570000 1.9390120000 -1.7007190000
 H -2.9742740000 1.1036580000 -0.7103240000
 H -1.9898390000 0.1892820000 -1.8615500000
 H -1.8169670000 2.3533020000 1.1799310000
 H -0.5108030000 2.9544420000 0.1666930000
 H -0.1520650000 2.0132350000 1.6392710000
 H 0.4458200000 0.3529680000 -1.7760410000

Thermodynamic Data

Zero-point correction= 0.261982 (Hartree/Particle)
 Thermal correction to Energy= 0.273575
 Thermal correction to Enthalpy= 0.274519
 Thermal correction to Gibbs Free Energy= 0.226108
 Sum of electronic and zero-point Energies= -500.034071
 Sum of electronic and thermal Energies= -500.022477
 Sum of electronic and thermal Enthalpies= -500.021533
 Sum of electronic and thermal Free Energies= -500.069945

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	171.671	47.507	101.890

Norbornyl *endo* diazonium dissociation TS
(*endo*-N-N₂⁺-TS)

optimized xyz-matrix

```

C 1.4509260000 -0.4139800000 -0.7470500000
C 0.2033520000 -1.3152320000 -0.7258120000
C -0.4501510000 -0.8729750000 0.5685400000
C 0.3593130000 0.2109840000 1.1756510000
C 0.3380920000 1.4787890000 0.2828380000
C 1.0169870000 1.0335410000 -1.0418760000
H 0.3440780000 1.0918060000 -1.9018750000
H 1.8821440000 1.6604360000 -1.2661020000
H 0.9208920000 2.2480630000 0.7939150000
H -0.6712360000 1.8774680000 0.1533790000
C 1.7608290000 -0.3752820000 0.7606020000
H 2.5404270000 0.3335110000 1.0517990000
H 1.9888530000 -1.3535430000 1.1932380000
H 0.4687530000 -2.3724910000 -0.5966680000
H -0.4467540000 -1.2537820000 -1.6030180000
H 2.2429470000 -0.7953560000 -1.3908690000
N -2.1179330000 -0.0954210000 0.0449150000
N -3.1026010000 0.2817160000 -0.2588590000
H -0.9790020000 -1.5944810000 1.1905580000
H 0.1765490000 0.3792270000 2.2358840000

```

Thermodynamic Data

Zero-point correction= 0.174913 (Hartree/Particle)
 Thermal correction to Energy= 0.182727
 Thermal correction to Enthalpy= 0.183671
 Thermal correction to Gibbs Free Energy= 0.141894
 Sum of electronic and zero-point Energies= -382.219833
 Sum of electronic and thermal Energies= -382.212019
 Sum of electronic and thermal Enthalpies= -382.211075
 Sum of electronic and thermal Free Energies= -382.252852

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	114.663	29.896	87.928

Norbornyl *exo* diazonium dissociation (*exo*-N-N₂⁺-TS)

optimized xyz-matrix

```
C 1.0836790000 -1.0379390000 0.4382440000
C -0.0044860000 -1.2239730000 -0.6497650000
C -0.5643660000 0.1861910000 -0.7667160000
C 0.1420500000 1.0206380000 0.2450140000
C 1.5522570000 1.1477270000 -0.4486940000
C 2.2253700000 -0.2258940000 -0.1898060000
H 2.6132210000 -0.6822280000 -1.1035200000
H 3.0561850000 -0.1270550000 0.5121620000
H 2.0721790000 1.9716590000 0.0450500000
H 1.4835160000 1.4081320000 -1.5095560000
C 0.4291690000 0.0025750000 1.3630700000
H 1.1167180000 0.3999580000 2.1129430000
H -0.4747790000 -0.3554430000 1.8685350000
H -0.3159270000 1.9806310000 0.4818650000
H -0.7686170000 -1.9396430000 -0.3328870000
H 0.3718270000 -1.5609330000 -1.6202460000
H 1.3817440000 -1.9780120000 0.9021300000
N -2.2703930000 0.0875230000 -0.1795420000
N -3.2834970000 0.0641240000 0.2408310000
H -0.8408650000 0.6054560000 -1.7335860000
```

Thermodynamic Data

Zero-point correction= 0.175335 (Hartree/Particle)
 Thermal correction to Energy= 0.183039
 Thermal correction to Enthalpy= 0.183983
 Thermal correction to Gibbs Free Energy= 0.142790
 Sum of electronic and zero-point Energies= -382.223880
 Sum of electronic and thermal Energies= -382.216176
 Sum of electronic and thermal Enthalpies= -382.215232
 Sum of electronic and thermal Free Energies= -382.256425

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	114.859	29.678	86.698

endo bornane diazonium dissociation (*endo*-B-N₂⁺-TS)

optimized xyz-matrix

```
C 0.8224760000 -1.4174290000 0.2390330000
```

C -0.4345060000 -1.2921310000 1.1310350000
 C -0.8118730000 0.1505850000 0.8409630000
 C -0.0200070000 0.6693430000 -0.2975260000
 C -0.2743380000 -0.2176570000 -1.5438810000
 C 0.3372060000 -1.6039780000 -1.2053510000
 H -0.3889660000 -2.4160940000 -1.2899780000
 H 1.1664180000 -1.8457290000 -1.8726630000
 H 0.2087450000 0.2479420000 -2.4057830000
 H -1.3419140000 -0.2659610000 -1.7824310000
 C 1.3633850000 0.0400120000 0.2514950000
 C 2.5065100000 0.3129260000 -0.7263610000
 C 1.8059670000 0.5494790000 1.6303290000
 C -0.0799540000 2.1654660000 -0.5236560000
 H -0.2381970000 -1.4072460000 2.1995500000
 H -1.2184420000 -2.0067200000 0.8650930000
 H 1.5215360000 -2.1787630000 0.5908550000
 N -2.6130610000 0.1336290000 0.2930510000
 N -3.6661900000 0.1609630000 -0.0136840000
 H -1.0619580000 2.4670230000 -0.9044980000
 H 0.6614690000 2.4618030000 -1.2704660000
 H 0.1176360000 2.7249300000 0.3961880000
 H 2.0025880000 1.6255360000 1.5960260000
 H 2.7421170000 0.0575610000 1.9101290000
 H 1.0951170000 0.3670050000 2.4420650000
 H 3.3713350000 -0.2889960000 -0.4274610000
 H 2.8077940000 1.3636890000 -0.6810870000
 H 2.2732940000 0.0701840000 -1.7637420000
 H -1.0530080000 0.8220080000 1.6661470000

Thermodynamic Data

Zero-point correction= 0.259645 (Hartree/Particle)
 Thermal correction to Energy= 0.271748
 Thermal correction to Enthalpy= 0.272692
 Thermal correction to Gibbs Free Energy= 0.222656
 Sum of electronic and zero-point Energies= -500.025690
 Sum of electronic and thermal Energies= -500.013587
 Sum of electronic and thermal Enthalpies= -500.012643
 Sum of electronic and thermal Free Energies= -500.062679

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.524	47.622	105.310

exo bornane diazonium dissociation (**exo-B-N₂⁺-TS**)

optimized xyz-matrix

C -1.1037620000 -0.6652540000 -1.0797640000

C 0.1876860000 -1.5201650000 -0.9930440000
 C 0.7848510000 -1.0224890000 0.3158980000
 C -0.0739440000 0.1002430000 0.8068460000
 C -1.2877480000 -0.7872670000 1.3053800000
 C -2.0395320000 -1.1986340000 0.0148490000
 H -2.1852910000 -2.2789630000 -0.0579290000
 H -3.0250560000 -0.7332570000 -0.0408840000
 H -1.8872980000 -0.1555150000 1.9654360000
 H -0.9632610000 -1.6400410000 1.9112580000
 C -0.6476850000 0.7061620000 -0.5157360000
 C -1.7882070000 1.6946310000 -0.2520880000
 C 0.3804140000 1.4259650000 -1.3977610000
 C 0.5033010000 1.0137720000 1.8676670000
 H 0.8552400000 -1.3502670000 -1.8405820000
 H 0.0050650000 -2.5969600000 -0.9388730000
 H -1.5265640000 -0.6435110000 -2.0861850000
 N 2.3869700000 -0.3479500000 -0.0339210000
 N 3.3923070000 0.0748430000 -0.1520160000
 H 0.8614080000 0.4491340000 2.7348380000
 H -0.2665630000 1.7063670000 2.2176550000
 H 1.3341590000 1.6125090000 1.4776680000
 H 0.8873390000 2.2246010000 -0.8446720000
 H -0.1350550000 1.9001710000 -2.2378640000
 H 1.1412960000 0.7755380000 -1.8389350000
 H -2.3267830000 1.8935790000 -1.1836120000
 H -1.3843420000 2.6485890000 0.1017880000
 H -2.5147810000 1.3481570000 0.4852520000
 H 1.1833100000 -1.7301770000 1.0437170000

Thermodynamic Data

Zero-point correction= 0.260782 (Hartree/Particle)
 Thermal correction to Energy= 0.272351
 Thermal correction to Enthalpy= 0.273295
 Thermal correction to Gibbs Free Energy= 0.224866
 Sum of electronic and zero-point Energies= -500.028262
 Sum of electronic and thermal Energies= -500.016692
 Sum of electronic and thermal Enthalpies= -500.015748
 Sum of electronic and thermal Free Energies= -500.064177

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.903	46.835	101.928

fenchane *endo*-diazonium dissociation (***endo*-F-N₂⁺-TS**)

optimized xyz-matrix

C 1.0182900000 -1.3176890000 0.3289160000
 C 1.2693580000 0.1249970000 -0.2141350000

C -0.1390830000 0.3934550000 -0.7500790000
 C -1.1030330000 -0.6349190000 -0.2969160000
 C -1.1237460000 -0.7104470000 1.2530640000
 C 0.2595560000 -1.2827730000 1.6599390000
 H 0.7591190000 -0.7003810000 2.4356240000
 H 0.1545280000 -2.3008050000 2.0431360000
 H -1.9418770000 -1.3707110000 1.5517340000
 H -1.3330710000 0.2705400000 1.6941050000
 C -0.0882390000 -1.8036580000 -0.6271760000
 H -0.5553760000 -2.7510390000 -0.3402300000
 H 0.1988550000 -1.8652680000 -1.6810570000
 C -2.4516660000 -0.6438700000 -0.9867870000
 C 2.2436410000 0.1113640000 -1.4044080000
 C 1.7726460000 1.1288900000 0.8294350000
 H 1.9352590000 -1.9102960000 0.3457290000
 N -0.7632150000 2.0389040000 -0.0152160000
 N -1.2042460000 2.9802850000 0.3357260000
 H -2.3498680000 -0.6133980000 -2.0758750000
 H -3.0600830000 0.2108970000 -0.6715370000
 H -3.0001220000 -1.5515600000 -0.7225920000
 H 1.9859680000 2.0979730000 0.3676800000
 H 2.7056040000 0.7517200000 1.2572680000
 H 1.0641750000 1.2794520000 1.6482910000
 H 3.2422600000 -0.1480270000 -1.0421430000
 H 2.3009680000 1.0980670000 -1.8749390000
 H 1.9672760000 -0.6200700000 -2.1692010000
 H -0.2477310000 0.7964800000 -1.7606840000

Thermodynamic Data

Zero-point correction= 0.259860 (Hartree/Particle)
 Thermal correction to Energy= 0.271831
 Thermal correction to Enthalpy= 0.272775
 Thermal correction to Gibbs Free Energy= 0.223082
 Sum of electronic and zero-point Energies= -500.027831
 Sum of electronic and thermal Energies= -500.015859
 Sum of electronic and thermal Enthalpies= -500.014915
 Sum of electronic and thermal Free Energies= -500.064608

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.577	47.353	104.587

fenchane *exo*-diazonium dissociation (***exo*-F-N₂⁺-TS**)

optimized xyz-matrix

C 1.2614410000 -0.3093950000 0.9436790000
 C 0.4067710000 -1.1682230000 -0.0522110000
 C -0.4307650000 -0.0536610000 -0.6927990000
 C -0.0849080000 1.2488720000 -0.0388890000

C 1.3532220000 1.4738620000 -0.6536710000
 C 2.2750680000 0.5323430000 0.1567110000
 H 2.9458680000 -0.0588620000 -0.4681150000
 H 2.8967100000 1.1036470000 0.8501870000
 H 1.5935370000 2.5301600000 -0.5054950000
 H 1.3826740000 1.2936800000 -1.7343470000
 C 0.2661680000 0.7757320000 1.3862680000
 H 0.7335610000 1.5701360000 1.9742140000
 H -0.6045550000 0.4056370000 1.9392350000
 C -1.0321250000 2.4149520000 -0.2402360000
 C -0.4110040000 -2.2124860000 0.7240450000
 C 1.2055560000 -1.8859140000 -1.1501930000
 H 1.6921130000 -0.9261820000 1.7353290000
 N -2.1472470000 -0.3335440000 -0.2696160000
 N -3.2105610000 -0.4095260000 -0.0110530000
 H -2.0002700000 2.2397100000 0.2404900000
 H -1.2008220000 2.6181320000 -1.3027260000
 H -0.6041440000 3.3144570000 0.2092450000
 H 0.5557720000 -2.5525660000 -1.7249970000
 H 1.9900080000 -2.4927780000 -0.6884000000
 H 1.6847390000 -1.1943780000 -1.8488400000
 H 0.2770680000 -2.9661340000 1.1147090000
 H -1.1257200000 -2.7254320000 0.0719920000
 H -0.9458270000 -1.7797560000 1.5743630000
 H -0.6226080000 -0.0744690000 -1.7683780000

Thermodynamic Data

Zero-point correction= 0.260224 (Hartree/Particle)
 Thermal correction to Energy= 0.272002
 Thermal correction to Enthalpy= 0.272946
 Thermal correction to Gibbs Free Energy= 0.223764
 Sum of electronic and zero-point Energies= -500.031791
 Sum of electronic and thermal Energies= -500.020013
 Sum of electronic and thermal Enthalpies= -500.019069
 Sum of electronic and thermal Free Energies= -500.068250

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	170.684	46.988	103.511

Diazo norbornane (**2-N**)

optimized xyz-matrix

C -1.3624520000 0.9455860000 -0.0442860000
 C 0.0785960000 1.4017480000 -0.3614960000
 C 0.8361230000 0.1782840000 0.1241770000

C -0.1478470000 -0.7993160000 0.7360360000
 C -0.9496660000 -1.4356930000 -0.4206720000
 C -1.7356570000 -0.2162580000 -0.9933910000
 H -1.4637690000 0.0067860000 -2.0296180000
 H -2.8140800000 -0.3985860000 -0.9700730000
 H -1.6329560000 -2.2018690000 -0.0379970000
 H -0.2957430000 -1.9053030000 -1.1594330000
 C -1.1780040000 0.2041380000 1.2932200000
 H -2.0955960000 -0.2836530000 1.6386970000
 H -0.7739010000 0.8371760000 2.0886850000
 H 0.2895980000 -1.5062030000 1.4431580000
 H 0.3426130000 2.3057610000 0.2025300000
 H 0.2218760000 1.6112150000 -1.4276840000
 H -2.0824150000 1.7667260000 -0.0431390000
 N 2.0861370000 -0.0420990000 -0.0504180000
 N 3.2078380000 -0.2297570000 -0.1933900000

Thermodynamic Data

Zero-point correction= 0.165485 (Hartree/Particle)
 Thermal correction to Energy= 0.172687
 Thermal correction to Enthalpy= 0.173631
 Thermal correction to Gibbs Free Energy= 0.133389
 Sum of electronic and zero-point Energies= -381.863098
 Sum of electronic and thermal Energies= -381.855897
 Sum of electronic and thermal Enthalpies= -381.854953
 Sum of electronic and thermal Free Energies= -381.895195

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	108.363	28.481	84.696

Diazo bornane (2-B)

optimized xyz-matrix

C -0.9700780000 1.2143460000 0.5781620000
 C 0.4864470000 1.3748560000 1.0662410000
 C 1.1310810000 0.2755370000 0.2443210000
 C 0.0639800000 -0.4610270000 -0.5567310000
 C -0.3539420000 0.5197300000 -1.6787760000
 C -1.0171860000 1.6885780000 -0.8930730000
 H -0.4778710000 2.6318170000 -1.0201390000
 H -2.0451580000 1.8613910000 -1.2230330000
 H -1.0578680000 0.0439630000 -2.3713330000
 H 0.5144210000 0.8377390000 -2.2621200000
 C -1.1299260000 -0.3252520000 0.4462490000
 C -2.4844890000 -0.7491680000 -0.1274860000
 C -0.9153090000 -1.0924060000 1.7523460000

C 0.4464380000 -1.8531350000 -1.0146000000
 H 0.5792100000 1.2045720000 2.1460180000
 H 0.8814940000 2.3733780000 0.8481890000
 H -1.7014380000 1.7014270000 1.2302060000
 N 2.3869840000 0.0379740000 0.1592480000
 N 3.5079280000 -0.1912080000 0.0807920000
 H 1.3118880000 -1.8202260000 -1.6860320000
 H -0.3792140000 -2.3203220000 -1.5614280000
 H 0.7064610000 -2.4915540000 -0.1635430000
 H -1.0862480000 -2.1632900000 1.5955970000
 H -1.6272870000 -0.7546560000 2.5140640000
 H 0.0959870000 -0.9755080000 2.1500540000
 H -3.2704080000 -0.5756110000 0.6162210000
 H -2.4846860000 -1.8206840000 -0.3573970000
 H -2.7657800000 -0.2121500000 -1.0355130000

Thermodynamic Data

Zero-point correction= 0.250364 (Hartree/Particle)
 Thermal correction to Energy= 0.261764
 Thermal correction to Enthalpy= 0.262708
 Thermal correction to Gibbs Free Energy= 0.214231
 Sum of electronic and zero-point Energies= -499.665323
 Sum of electronic and thermal Energies= -499.653922
 Sum of electronic and thermal Enthalpies= -499.652978
 Sum of electronic and thermal Free Energies= -499.701455

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	164.259	45.946	102.029

diazo fenchane (2-F)

optimized xyz-matrix

C -0.1878820000 -1.5908670000 0.3768060000
 C -1.1695580000 -0.3993540000 0.1526280000
 C -0.1293210000 0.7075700000 0.0066950000
 C 1.2715670000 0.1443660000 0.1783270000
 C 1.5622970000 -0.7203130000 -1.0770240000
 C 0.5878060000 -1.9235560000 -0.9160890000
 H -0.0600860000 -2.0746500000 -1.7819680000
 H 1.1460760000 -2.8534380000 -0.7698290000
 H 2.6076650000 -1.0515730000 -1.0729350000
 H 1.3960610000 -0.1519610000 -1.9969610000
 C 0.9425910000 -0.9553230000 1.2105950000
 H 1.7826930000 -1.6418840000 1.3683780000
 H 0.6264730000 -0.5468020000 2.1742980000
 C 2.3417370000 1.1557400000 0.5324390000

C -2.0714310000 -0.1919060000 1.3781210000
 C -2.0608120000 -0.5393760000 -1.0859660000
 H -0.6911290000 -2.4546410000 0.8220590000
 N -0.4005050000 1.9216940000 -0.2986270000
 N -0.6521820000 3.0102230000 -0.5594980000
 H 2.0815550000 1.6976880000 1.4473120000
 H 2.4708620000 1.8904780000 -0.2704150000
 H 3.3032460000 0.6557960000 0.6867150000
 H -2.7639490000 0.2993490000 -1.1381360000
 H -2.6473930000 -1.4645000000 -1.0406410000
 H -1.4807980000 -0.5380800000 -2.0120420000
 H -2.8005850000 -1.0066980000 1.4568190000
 H -2.6255160000 0.7486900000 1.2869550000
 H -1.4983280000 -0.1530820000 2.3080640000

Thermodynamic Data

Zero-point correction= 0.249714 (Hartree/Particle)
 Thermal correction to Energy= 0.261324
 Thermal correction to Enthalpy= 0.262268
 Thermal correction to Gibbs Free Energy= 0.213025
 Sum of electronic and zero-point Energies= -499.666384
 Sum of electronic and thermal Energies= -499.654773
 Sum of electronic and thermal Enthalpies= -499.653829
 Sum of electronic and thermal Free Energies= -499.703072

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	163.983	46.201	103.642

Diazo norbornane *endo* dissociation (**endoTS-2-N**)

optimized xyz-matrix

C 1.4537950000 -0.5501730000 -0.6543630000
 C 0.1853970000 -1.4002690000 -0.4991810000
 C -0.5691070000 -0.8056050000 0.6971020000
 C 0.3518260000 0.3268250000 1.1308890000
 C 0.3937120000 1.4891730000 0.1070980000
 C 1.0325040000 0.8464730000 -1.1539640000
 H 0.3255760000 0.7739900000 -1.9871100000
 H 1.8916300000 1.4267630000 -1.5019380000
 H 1.0395090000 2.2780140000 0.5088100000
 H -0.5883860000 1.9297870000 -0.0743890000
 C 1.7433380000 -0.3000870000 0.8359080000
 H 2.5497040000 0.4159660000 1.0266700000
 H 1.9433160000 -1.2211150000 1.3925990000
 H 0.1825340000 0.6654300000 2.1559490000

H 0.4506700000 -2.4239790000 -0.1965840000
H -0.4343120000 -1.4953830000 -1.3961880000
H 2.2554280000 -1.0173280000 -1.2310040000
N -2.1023240000 0.0440500000 -0.1130390000
N -3.2068840000 0.1030690000 -0.0980690000

Thermodynamic Data

Zero-point correction= 0.161089 (Hartree/Particle)
Thermal correction to Energy= 0.168685
Thermal correction to Enthalpy= 0.169629
Thermal correction to Gibbs Free Energy= 0.128510
Sum of electronic and zero-point Energies= -381.812149
Sum of electronic and thermal Energies= -381.804553
Sum of electronic and thermal Enthalpies= -381.803609
Sum of electronic and thermal Free Energies= -381.844728

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.852	29.297	86.543

Diazo norbornane *exo* dissociation (*exoTS-2-N*)

optimized xyz-matrix C -1.1677100000 1.0120150000 0.4130600000

C -0.0185730000 1.2180730000 -0.5999670000
C 0.6475320000 -0.1621450000 -0.7686840000
C -0.1204440000 -0.9846630000 0.2384850000
C -1.4658780000 -1.1752390000 -0.5358890000
C -2.2282080000 0.1578880000 -0.2982890000
H -2.5755370000 0.6151650000 -1.2295500000
H -3.1005300000 0.0031580000 0.3444300000
H -1.9994340000 -2.0340260000 -0.1207970000
H -1.2892040000 -1.3794280000 -1.5964870000
C -0.5453180000 -0.0197790000 1.3636450000
H -1.2728100000 -0.4506370000 2.0608870000
H 0.3118790000 0.3648010000 1.9274130000
H 0.3473680000 -1.9282220000 0.5267900000
H 0.7111350000 1.9517470000 -0.2437510000
H -0.3671150000 1.5765480000 -1.5759670000
H -1.5481300000 1.9291340000 0.8682910000
N 2.3234180000 0.0100890000 0.0570410000
N 3.4157200000 -0.1422500000 -0.0335310000

Thermodynamic Data

Zero-point correction= 0.160972 (Hartree/Particle)
Thermal correction to Energy= 0.168590
Thermal correction to Enthalpy= 0.169534
Thermal correction to Gibbs Free Energy= 0.128598
Sum of electronic and zero-point Energies= -381.817506

Sum of electronic and thermal Energies= -381.809888
 Sum of electronic and thermal Enthalpies= -381.808944
 Sum of electronic and thermal Free Energies= -381.849880

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	105.792	29.411	86.157

optimized xyz-matrix

```

C 0.8302840000 -1.4037340000 0.2580890000
C -0.4153390000 -1.2547160000 1.1433660000
C -0.9121200000 0.1753690000 0.8808740000
C -0.0138900000 0.6541350000 -0.2558420000
C -0.2192310000 -0.1877970000 -1.5439770000
C 0.3281680000 -1.5944340000 -1.1849340000
H -0.4444950000 -2.3677220000 -1.2351580000
H 1.1308470000 -1.8984330000 -1.8626340000
H 0.3512680000 0.2671760000 -2.3614390000
H -1.2655980000 -0.1960220000 -1.8571470000
C 1.3549340000 0.0581230000 0.2596500000
C 2.5332690000 0.3027620000 -0.6841900000
C 1.7633250000 0.5826700000 1.6442360000
C -0.0752850000 2.1540130000 -0.4860960000
H -0.1771430000 -1.3345730000 2.2109680000
H -1.1867990000 -2.0068420000 0.9508520000
H 1.5487410000 -2.1587320000 0.5930420000
N -2.6802990000 -0.0293900000 0.0871480000
N -3.7343200000 0.2965600000 0.1646050000
H -1.0693580000 2.4419410000 -0.8462990000
H 0.6576020000 2.4782040000 -1.2336730000
H 0.1053020000 2.6983990000 0.4458480000
H 0.9501220000 0.5704590000 2.3745650000
H 2.1071770000 1.6197840000 1.5637600000
H 2.5946550000 -0.0099770000 2.0431380000
H 2.7502980000 1.3738160000 -0.7619030000
H 2.3762280000 -0.0827990000 -1.6934700000
H 3.4287970000 -0.1832120000 -0.2797850000
  
```

Thermodynamic Data

Zero-point correction= 0.245496 (Hartree/Particle)
 Thermal correction to Energy= 0.257492
 Thermal correction to Enthalpy= 0.258436
 Thermal correction to Gibbs Free Energy= 0.208446
 Sum of electronic and zero-point Energies= -499.611808

Sum of electronic and thermal Energies= -499.599812
 Sum of electronic and thermal Enthalpies= -499.598868
 Sum of electronic and thermal Free Energies= -499.648858

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.579	47.063	105.214

exo-diazo bornane dissociation TS (**exoTS-2-B**)

optimized xyz-matrix

```

C -1.1309840000 -0.7536020000 -1.0139320000
C 0.2076370000 -1.5233320000 -0.9277250000
C 0.8908880000 -1.0145660000 0.3536950000
C -0.0254670000 0.1088410000 0.7715340000
C -1.1606530000 -0.8009320000 1.3769960000
C -1.9768470000 -1.2885610000 0.1519590000
H -2.0704090000 -2.3778660000 0.1202020000
H -2.9880380000 -0.8728560000 0.1465350000
H -1.7567170000 -0.1995370000 2.0697860000
H -0.7303180000 -1.6251630000 1.9550260000
C -0.7278670000 0.6548610000 -0.5186610000
C -1.9047600000 1.5897250000 -0.2153880000
C 0.1946800000 1.3987840000 -1.4882780000
C 0.5323300000 1.1143770000 1.7582250000
H 0.8459380000 -1.3535890000 -1.7992020000
H 0.0637530000 -2.6086660000 -0.8656550000
H -1.6197390000 -0.7891260000 -1.9926150000
N 2.4662280000 -0.1560690000 -0.1871200000
N 3.5583660000 -0.0667510000 -0.0257250000
H 0.6624470000 2.2604180000 -0.9973330000
H -0.3912280000 1.7822470000 -2.3311530000
H 0.9916630000 0.7785560000 -1.9018430000
H -2.5609270000 1.2273940000 0.5796320000
H -2.5164820000 1.7369340000 -1.1129380000
H -1.5324310000 2.5739910000 0.0909540000
H -0.2562210000 1.7733590000 2.1381720000
H 1.3012200000 1.7418530000 1.2928570000
H 0.9915810000 0.5982300000 2.6069370000
  
```

Thermodynamic Data

Zero-point correction= 0.245578 (Hartree/Particle)
 Thermal correction to Energy= 0.257407
 Thermal correction to Enthalpy= 0.258352
 Thermal correction to Gibbs Free Energy= 0.209086
 Sum of electronic and zero-point Energies= -499.617929
 Sum of electronic and thermal Energies= -499.606100
 Sum of electronic and thermal Enthalpies= -499.605156

Sum of electronic and thermal Free Energies= -499.654421

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.526	46.960	103.688

endo diazo fenchane dissociation (***endo*-TS-2-F**)

optimized xyz-matrix

```

C 1.4041820000 -0.9332820000 0.2547260000
C 1.1350140000 0.5210370000 -0.2212540000
C -0.3099330000 0.4437840000 -0.7651550000
C -0.8088540000 -0.9167810000 -0.3233600000
C -0.7924470000 -1.1133920000 1.2201520000
C 0.7092580000 -1.2002640000 1.5965040000
H 1.0025830000 -0.5007570000 2.3825190000
H 0.9617880000 -2.2046770000 1.9508090000
H -1.3146410000 -2.0461330000 1.4639220000
H -1.3215480000 -0.3042680000 1.7315450000
C 0.4801730000 -1.7069070000 -0.7041530000
H 0.3680520000 -2.7694430000 -0.4593740000
H 0.7469860000 -1.6196920000 -1.7617580000
C -2.1064490000 -1.3497350000 -0.9826410000
C 2.0394440000 0.8604770000 -1.4224500000
C 1.3590460000 1.6078510000 0.8343550000
H 2.4633520000 -1.2095360000 0.2386610000
N -1.4261940000 1.6901500000 0.2543290000
N -2.1898210000 2.4832670000 0.1548000000
H -2.3307350000 -2.4004490000 -0.7667850000
H -2.0503340000 -1.2149120000 -2.0663600000
H -2.9441700000 -0.7456260000 -0.6150430000
H 1.7523440000 1.8287900000 -1.8416730000
H 1.9618010000 0.1189660000 -2.2221530000
H 3.0870320000 0.9054330000 -1.1018130000
H 1.1578940000 2.5951520000 0.4053830000
H 2.4022040000 1.5916340000 1.1703850000
H 0.7128870000 1.4848640000 1.7074750000

```

Thermodynamic Data

Zero-point correction= 0.245865 (Hartree/Particle)
 Thermal correction to Energy= 0.257704
 Thermal correction to Enthalpy= 0.258648
 Thermal correction to Gibbs Free Energy= 0.209115
 Sum of electronic and zero-point Energies= -499.612478
 Sum of electronic and thermal Energies= -499.600639
 Sum of electronic and thermal Enthalpies= -499.599694
 Sum of electronic and thermal Free Energies= -499.649227

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.712	46.872	104.251

exo-diazo fenchane dissociation TS (**exo-TS-2-F**)

optimized xyz-matrix

```

C 1.3318020000 -0.3330060000 0.8871470000
C 0.3758150000 -1.1447740000 -0.0441080000
C -0.5011370000 -0.0614910000 -0.7175310000
C -0.0472000000 1.2131700000 -0.0398230000
C 1.3374920000 1.4042640000 -0.7564440000
C 2.3055740000 0.4759340000 0.0170650000
H 2.9289820000 -0.1403510000 -0.6348820000
H 2.9766620000 1.0603970000 0.6542630000
H 1.6230130000 2.4583720000 -0.6838320000
H 1.2668580000 1.1594100000 -1.8225120000
C 0.4060310000 0.7886330000 1.3748180000
H 0.9402830000 1.5787840000 1.9162930000
H -0.4358500000 0.4486360000 1.9879540000
C -0.9611610000 2.4160640000 -0.1652100000
C -0.4195410000 -2.1653850000 0.7807800000
C 1.0990270000 -1.9217500000 -1.1562670000
H 1.8123060000 -0.9453270000 1.6569260000
N -2.2532020000 -0.2576790000 -0.0337200000
N -3.3286540000 -0.3348090000 -0.2818620000
H -1.8900070000 2.2684130000 0.3966720000
H -1.2235220000 2.5910210000 -1.2133330000
H -0.4743780000 3.3157250000 0.2267630000
H -0.8825530000 -1.7151750000 1.6635210000
H 0.2528610000 -2.9623010000 1.1173860000
H -1.2075950000 -2.6235330000 0.1741450000
H 0.3884420000 -2.5700140000 -1.6771410000
H 1.8945780000 -2.5446820000 -0.7294070000
H 1.5426930000 -1.2619080000 -1.9063180000

```

Thermodynamic Data

Zero-point correction= 0.246093 (Hartree/Particle)
 Thermal correction to Energy= 0.257742
 Thermal correction to Enthalpy= 0.258686
 Thermal correction to Gibbs Free Energy= 0.209851
 Sum of electronic and zero-point Energies= -499.618245
 Sum of electronic and thermal Energies= -499.606596
 Sum of electronic and thermal Enthalpies= -499.605652
 Sum of electronic and thermal Free Energies= -499.654487

E (Thermal) CV S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.735	46.592	102.782

4.2.3 Structures optimized at the B3LYP/6-31G* level of theory

optimized xyz-matrix

```

C -1.3649370000 0.9528440000 -0.0347440000
C 0.0824960000 1.3999400000 -0.3691070000
C 0.8454860000 0.1731190000 0.1169290000
C -0.1466130000 -0.8054180000 0.7294720000
C -0.9679090000 -1.4358440000 -0.4279610000
C -1.7656840000 -0.2083570000 -0.9840440000
H -1.5176860000 0.0151690000 -2.0273500000
H -2.8456310000 -0.3863750000 -0.9391710000
H -1.6447200000 -2.2083510000 -0.0420340000
H -0.3258290000 -1.9037490000 -1.1799230000
C -1.1696670000 0.2047660000 1.3042240000
H -2.0860670000 -0.2778900000 1.6633140000
H -0.7560900000 0.8323720000 2.1007010000
H 0.2910790000 -1.5224580000 1.4280020000
H 0.3568450000 2.3101950000 0.1837770000
H 0.2182630000 1.6080210000 -1.4383350000
H -2.0768700000 1.7827230000 -0.0235680000
N 2.0988580000 -0.0455200000 -0.0543280000
N 3.2308100000 -0.2310470000 -0.1933900000

```

Thermodynamic Data

Zero-point correction= 0.163652 (Hartree/Particle)
 Thermal correction to Energy= 0.170926
 Thermal correction to Enthalpy= 0.171870 40
 Thermal correction to Gibbs Free Energy= 0.131588
 Sum of electronic and zero-point Energies= -382.035064
 Sum of electronic and thermal Energies= -382.027790
 Sum of electronic and thermal Enthalpies= -382.026846
 Sum of electronic and thermal Free Energies= -382.067128

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	107.258 28.	900	84.782

Endo-diaz norbornane dissociation TS (*endo*-TS-2-N)

optimized xyz-matrix

```
C 1.4971720000 -0.5898470000 -0.6113170000
C 0.1738980000 -1.3784400000 -0.5238740000
C -0.5993730000 -0.7641390000 0.6475140000
C 0.3324110000 0.3352280000 1.1200800000
C 0.4561800000 1.4926260000 0.0788090000
C 1.1811620000 0.8319750000 -1.1326530000
H 0.5553720000 0.8047000000 -2.0314500000
H 2.0964790000 1.3748280000 -1.3919180000
H 1.0705000000 2.2877210000 0.5189070000
H -0.5127780000 1.9271680000 -0.1750100000
C 1.7212890000 -0.3469580000 0.8971880000
H 2.5449800000 0.3372410000 1.1318210000
H 1.8588820000 -1.2718020000 1.4684670000
H 0.1238400000 0.6956320000 2.1319100000
H 0.3706520000 -2.4234120000 -0.2335990000
H -0.4139670000 -1.4303950000 -1.4467390000
H 2.3037100000 -1.1005440000 -1.1456380000
N -2.1983690000 0.0965190000 -0.1586070000
N -3.3122170000 0.0915080000 -0.0815710000
```

Thermodynamic Data

Zero-point correction= 0.158994 (Hartree/Particle)
 Thermal correction to Energy= 0.166793
 Thermal correction to Enthalpy= 0.167737
 Thermal correction to Gibbs Free Energy= 0.126186
 Sum of electronic and zero-point Energies= -381.982831
 Sum of electronic and thermal Energies= -381.975032
 Sum of electronic and thermal Enthalpies= -381.974087 41
 Sum of electronic and thermal Free Energies= -382.015639

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	104.664	29.880	87.452

exo-diaz norbornane dissociation TS (*exo*-TS-2-N)

optimized xyz-matrix

C -1.2256870000 1.0163740000 0.3736820000
 C -0.0267370000 1.2238550000 -0.5897630000
 C 0.6521320000 -0.1513240000 -0.7110170000
 C -0.1246670000 -0.9666930000 0.2889820000
 C -1.4485980000 -1.2086940000 -0.5326490000
 C -2.2423810000 0.1226300000 -0.3674170000
 H -2.5524210000 0.5490560000 -1.3275710000
 H -3.1458820000 -0.0270280000 0.2341540000
 H -1.9761320000 -2.0644370000 -0.1001990000
 H -1.2362730000 -1.4527400000 -1.5789190000
 C -0.6202650000 0.0177590000 1.3790610000
 H -1.3638250000 -0.4159190000 2.0592850000
 H 0.2030870000 0.4337840000 1.9710450000
 H 0.3502440000 -1.8948760000 0.6155720000
 H 0.6857550000 1.9555500000 -0.1926680000
 H -0.3174730000 1.5896320000 -1.5836740000
 H -1.6440510000 1.9372010000 0.7901010000
 N 2.4002900000 0.0257320000 0.0927160000
 N 3.4874520000 -0.1591130000 -0.0830590000

Thermodynamic Data

Zero-point correction= 0.159142 (Hartree/Particle)
 Thermal correction to Energy= 0.166904
 Thermal correction to Enthalpy= 0.167848
 Thermal correction to Gibbs Free Energy= 0.126516
 Sum of electronic and zero-point Energies= -381.988010
 Sum of electronic and thermal Energies= -381.980248
 Sum of electronic and thermal Enthalpies= -381.979304
 Sum of electronic and thermal Free Energies= -382.020636

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	104.734	29.839	86.990

Norbornyl *endo*-diazonium ion (***endo*-N-N₂⁺**)

optimized xyz-matrix

C 1.4336630000 -0.6082370000 -0.5717140000
 C 0.0703570000 -1.3233260000 -0.7170160000
 C -0.7346430000 -0.6960900000 0.4876480000
 C 0.2329830000 0.3682840000 1.1060860000
 C 0.4598600000 1.5223570000 0.1035140000
 C 1.2906530000 0.8565420000 -1.0432940000
 H 0.8055120000 0.9341100000 -2.0213460000
 H 2.2733740000 1.3264360000 -1.1351050000
 H 1.0271250000 2.3107920000 0.6055080000

H -0.4676070000 1.9916120000 -0.2437440000
 C 1.5411260000 -0.4497910000 0.9602820000
 H 2.4052070000 0.1388800000 1.2819310000
 H 1.5398640000 -1.3966340000 1.5109230000
 H -0.0684230000 0.6637970000 2.1123960000
 H 0.1346420000 -2.4021930000 -0.5545380000
 H -0.4132790000 -1.1542300000 -1.6832100000
 H 2.2390010000 -1.1651980000 -1.0549260000
 N -1.9778270000 -0.0935800000 0.0340890000
 N -2.9026530000 0.4035760000 -0.3184670000
 H -1.0760490000 -1.4357760000 1.2197140000

Thermodynamic Data

Zero-point correction= 0.175907 (Hartree/Particle)
 Thermal correction to Energy= 0.183422
 Thermal correction to Enthalpy= 0.184366
 Thermal correction to Gibbs Free Energy= 0.143943
 Sum of electronic and zero-point Energies= -382.393977
 Sum of electronic and thermal Energies= -382.386462
 Sum of electronic and thermal Enthalpies= -382.385518
 Sum of electronic and thermal Free Energies= -382.425941

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	115.099	30.291	85.077

Norbornyl *exo*-diazonium ion (*exo*-N-N₂⁺)

optimized xyz-matrix C -1.1034960000 1.0386770000 0.4063090000

C 0.0965060000 1.3048390000 -0.5375120000
 C 0.7248900000 -0.1326100000 -0.6672270000
 C -0.1357150000 -1.0160810000 0.2950570000
 C -1.4767820000 -1.2011250000 -0.4675870000
 C -2.1573900000 0.2010740000 -0.3530680000
 H -2.4082060000 0.6307530000 -1.3273430000
 H -3.0847730000 0.1410490000 0.2227470000
 H -2.0546750000 -1.9777380000 0.0410640000
 H -1.3349720000 -1.5368620000 -1.4999070000
 C -0.5116790000 0.0048560000 1.3878840000
 H -1.2497950000 -0.4029050000 2.0841380000
 H 0.3391580000 0.3777230000 1.9709570000
 H 0.3534080000 -1.9460700000 0.5917300000
 H 0.8076810000 2.0083940000 -0.0946090000
 H -0.1772720000 1.6790910000 -1.5268120000
 H -1.4848640000 1.9606560000 0.8492630000
 N 2.1172230000 -0.1143210000 -0.2022510000
 N 3.1484640000 -0.1158400000 0.2011030000
 H 0.8165080000 -0.5207430000 -1.6863310000

Thermodynamic Data

Zero-point correction= 0.175775 (Hartree/Particle)
 Thermal correction to Energy= 0.183328
 Thermal correction to Enthalpy= 0.184272
 Thermal correction to Gibbs Free Energy= 0.143792
 Sum of electronic and zero-point Energies= -382.394814
 Sum of electronic and thermal Energies= -382.387261
 Sum of electronic and thermal Enthalpies= -382.386316
 Sum of electronic and thermal Free Energies= -382.426797

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	115.040	30.386	85.198

endo-Norbornyl diazonium ion dissociation TS
 (*endo*-N-N₂⁺-TS)

optimized xyz-matrix

```

C 1.4880970000 -0.5122530000 -0.6558800000
C 0.1544230000 -1.2975320000 -0.7421980000
C -0.5501500000 -0.7967890000 0.5227110000
C 0.2856130000 0.2793980000 1.1404260000
C 0.4203950000 1.5031850000 0.1939510000
C 1.2337430000 0.9645300000 -1.0260870000
H 0.6964280000 1.0691440000 -1.9735220000
H 2.1796420000 1.5021350000 -1.1320530000
H 0.9605730000 2.2897150000 0.7269110000
H -0.5530090000 1.9221070000 -0.0814080000
C 1.6634090000 -0.4446460000 0.8786260000
H 0.2981060000 -2.3793120000 -0.6398220000
H -0.4107760000 -1.1337890000 -1.6644730000
H 2.2947630000 -0.9903370000 -1.2134290000
N -2.1365450000 -0.0693370000 0.0070570000
N -3.1308510000 0.3237300000 -0.2675940000
H -1.0446500000 -1.5202100000 1.1715980000
H 2.4797220000 0.1983550000 1.2209180000
H 1.7629700000 -1.4212070000 1.3635040000
H 0.0348250000 0.5072840000 2.1762390000
  
```

Thermodynamic Data

Zero-point correction= 0.173778 (Hartree/Particle)
 Thermal correction to Energy= 0.181559
 Thermal correction to Enthalpy= 0.182503
 Thermal correction to Gibbs Free Energy= 0.141108
 Sum of electronic and zero-point Energies= -382.390595
 Sum of electronic and thermal Energies= -382.382815
 Sum of electronic and thermal Enthalpies= -382.381871

Sum of electronic and thermal Free Energies= -382.423266

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	113.930	30.007	87.123

exo-Norbornyl diazonium ion dissociation TS
(*exo*-N-N₂⁺-TS)

optimized xyz-matrix

```

C -1.1122630000 1.0363480000 0.4288450000
C 0.0292650000 1.2566010000 -0.6076540000
C 0.6120760000 -0.1583850000 -0.7287840000
C -0.1368970000 -1.0144570000 0.2626110000
C -1.5288010000 -1.1738320000 -0.4623520000
C -2.2197780000 0.2079440000 -0.2541370000
H -2.5601200000 0.6544580000 -1.1927600000
H -3.0907870000 0.1168790000 0.4003060000
H -2.0595430000 -1.9877900000 0.0393270000
H -1.4322470000 -1.4625550000 -1.5142190000
C -0.4744150000 -0.0009970000 1.3785930000
H 0.7665000000 1.9743820000 -0.2354220000
H -0.3025330000 1.6130740000 -1.5876410000
H -1.4457200000 1.9699890000 0.8843360000
N 2.2521380000 -0.0876470000 -0.1860600000
N 3.2771930000 -0.0873790000 0.2245220000
H 0.8460720000 -0.5664980000 -1.7120950000
H -1.1791140000 -0.4104870000 2.1069190000
H 0.4043290000 0.3692610000 1.9201050000
H 0.3327200000 -1.9648590000 0.5191810000

```

Thermodynamic Data

Zero-point correction= 0.173923 (Hartree/Particle)
 Thermal correction to Energy= 0.181602
 Thermal correction to Enthalpy= 0.182546
 Thermal correction to Gibbs Free Energy= 0.141462
 Sum of electronic and zero-point Energies= -382.393900
 Sum of electronic and thermal Energies= -382.386221
 Sum of electronic and thermal Enthalpies= -382.385277
 Sum of electronic and thermal Free Energies= -382.426362

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	113.957	29.817	86.470

Diazo bornane (**2-B**) **optimized xyz-matrix**

```

C 0.9586990000 1.2287860000 -0.5726040000
C -0.5060570000 1.3733870000 -1.0590530000
C -1.1432430000 0.2485150000 -0.2562220000
C -0.0632280000 -0.4729930000 0.5578890000
C 0.3339860000 0.5277710000 1.6853000000
C 1.0034050000 1.7023840000 0.9039640000
H 0.4672540000 2.6483960000 1.0338390000
H 2.0314390000 1.8735080000 1.2378840000
H 1.0292470000 0.0639070000 2.3955650000
H -0.5442960000 0.8438870000 2.2564200000
C 1.1449110000 -0.3180040000 -0.4487150000
C 2.5127310000 -0.7299480000 0.1253680000
C 0.9533060000 -1.0839520000 -1.7687230000
C -0.4253490000 -1.8714010000 1.0354350000
H -0.5990020000 1.2273260000 -2.1436300000
H -0.9169120000 2.3642580000 -0.8268080000
H 1.6789330000 1.7333080000 -1.2247990000
N -2.4033690000 0.0195140000 -0.1695700000
N -3.5359480000 -0.2010430000 -0.0997960000
H -1.2956530000 -1.8484790000 1.7024680000
H 0.4038140000 -2.3174910000 1.5959980000
H -0.6679640000 -2.5341920000 0.1973340000
H 1.1090440000 -2.1583940000 -1.6153600000
H 1.6868440000 -0.7534240000 -2.5144770000
H -0.0453370000 -0.9579410000 -2.1949020000
H 3.3041340000 -0.5034430000 -0.5998390000
H 2.5449280000 -1.8102360000 0.3104860000
H 2.7737880000 -0.2275570000 1.0595470000

```

Thermodynamic Data

Zero-point correction= 0.247669 (Hartree/Particle)
 Thermal correction to Energy= 0.259276
 Thermal correction to Enthalpy= 0.260221
 Thermal correction to Gibbs Free Energy= 0.211400
 Sum of electronic and zero-point Energies= -499.891304
 Sum of electronic and thermal Energies= -499.879697
 Sum of electronic and thermal Enthalpies= -499.878752
 Sum of electronic and thermal Free Energies= -499.927572

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.698	46.648	102.751

endo-diazobornane dissociation TS
(*endo*-TS-2-B)

optimized xyz-matrix

```

C 0.8562360000 -1.3966250000 0.2941790000
C -0.4318920000 -1.2490970000 1.1297850000
C -0.9398650000 0.1607130000 0.8144610000
C -0.0098860000 0.6488250000 -0.2857770000
C -0.1693120000 -0.2374080000 -1.5676620000
C 0.4117200000 -1.6245130000 -1.1677260000
H -0.3315690000 -2.4258770000 -1.2378910000
H 1.2494050000 -1.9121800000 -1.8108360000
H 0.3982030000 0.2155330000 -2.3887700000
H -1.2119470000 -0.2825920000 -1.8899570000
C 1.3689230000 0.0793070000 0.2882420000
C 2.5794240000 0.3322050000 -0.6257190000
C 1.7373530000 0.6292510000 1.6823060000
C -0.1010830000 2.1475210000 -0.5596970000
H -0.2421150000 -1.3099060000 2.2100810000
H -1.1856430000 -2.0165930000 0.9215790000
H 1.5669500000 -2.1402170000 0.6711580000
N -2.7560260000 -0.0459620000 0.0415010000
N -3.8033280000 0.3005940000 0.2199150000
H -1.0858010000 2.4026690000 -0.9691010000
H 0.6535080000 2.4752900000 -1.2848420000
H 0.0262500000 2.7265700000 0.3609050000
H 0.9188550000 0.5841690000 2.4056270000
H 2.0398940000 1.6802830000 1.6079870000
H 2.5883340000 0.0744710000 2.0970610000
H 2.8093630000 1.4027510000 -0.6789600000
H 2.4487150000 -0.0297120000 -1.6479830000
H 3.4633730000 -0.1681490000 -0.2103250000

```

Thermodynamic Data

Zero-point correction= 0.242764 (Hartree/Particle)
 Thermal correction to Energy= 0.254998
 Thermal correction to Enthalpy= 0.255942
 Thermal correction to Gibbs Free Energy= 0.205520
 Sum of electronic and zero-point Energies= -499.837183
 Sum of electronic and thermal Energies= -499.824949
 Sum of electronic and thermal Enthalpies= -499.824005
 Sum of electronic and thermal Free Energies= -499.874426

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.013	47.805	106.121

exo-diazo bornane dissociation TS
(*exo*TS-2-B)

optimized xyz-matrix

```
C -1.1254940000 -0.7840140000 -1.0145670000
C 0.2765440000 -1.4478470000 -0.9916200000
C 0.9420800000 -0.9316690000 0.2920080000
C -0.0226420000 0.1223720000 0.7672040000
C -1.0819120000 -0.8937470000 1.3840320000
C -1.8890600000 -1.4215710000 0.1651330000
H -1.8869780000 -2.5151300000 0.1063530000
H -2.9351030000 -1.1028650000 0.1997720000
H -1.7012750000 -0.3428450000 2.0989070000
H -0.5835310000 -1.6921540000 1.9440310000
C -0.8161830000 0.6509490000 -0.4973840000
C -2.0640460000 1.4880250000 -0.1519350000
C 0.0266610000 1.4904260000 -1.4719000000
C 0.4992900000 1.1342440000 1.7763770000
H 0.8764300000 -1.1791120000 -1.8663660000
H 0.2313680000 -2.5450010000 -0.9848120000
H -1.6420850000 -0.8405120000 -1.9785590000
N 2.5708820000 -0.0501100000 -0.2207660000
N 3.6732830000 -0.0546520000 -0.0328310000
H 0.3131350000 2.4451410000 -1.0146190000
H -0.5587660000 1.7240350000 -2.3698010000
H 0.9452590000 0.9967230000 -1.7947270000
H -2.7126040000 1.0289800000 0.5982210000
H -2.6696380000 1.6579980000 -1.0509000000
H -1.7711080000 2.4732800000 0.2299300000
H -0.3148120000 1.7362630000 2.1966580000
H 1.2198550000 1.8198350000 1.3153990000
H 1.0092730000 0.6256900000 2.6016040000
```

Thermodynamic Data

Zero-point correction= 0.243119 (Hartree/Particle)
 Thermal correction to Energy= 0.255179
 Thermal correction to Enthalpy= 0.256123
 Thermal correction to Gibbs Free Energy= 0.206379
 Sum of electronic and zero-point Energies= -499.842376
 Sum of electronic and thermal Energies= -499.830316
 Sum of electronic and thermal Enthalpies= -499.829371
 Sum of electronic and thermal Free Energies= -499.879115

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	160.127	47.633	104.695

Endo-bornane diazonium ion
(*endo*-B-N₂⁺)

optimized xyz-matrix

```
C -0.7487640000 1.4138750000 0.2513290000
C 0.5188670000 1.3101710000 1.1303800000
C 0.9987260000 -0.1491410000 0.7956160000
C 0.0184010000 -0.6722180000 -0.3327010000
C 0.2604710000 0.1986190000 -1.5944480000
C -0.2841190000 1.6093510000 -1.2092170000
H 0.4743870000 2.3936120000 -1.2950490000
H -1.1138860000 1.9049740000 -1.8547140000
H -0.2864180000 -0.2355550000 -2.4347340000
H 1.3111240000 0.2102720000 -1.9078640000
C -1.3112500000 -0.0418390000 0.2628150000
C -2.5232210000 -0.2546480000 -0.6654580000
C -1.7183650000 -0.5605520000 1.6562680000
C 0.0893190000 -2.1772090000 -0.5424070000
H 0.3226430000 1.3760010000 2.2019900000
H 1.2696440000 2.0649900000 0.8813930000
H -1.4349870000 2.1826390000 0.6157330000
N 2.3721430000 -0.1642280000 0.3488270000
N 3.4043500000 -0.1802480000 -0.0557520000
H 1.0554630000 -2.4878250000 -0.9584640000
H -0.6769900000 -2.4881810000 -1.2588190000
H -0.0753500000 -2.7325590000 0.3873970000
H -2.0040360000 -1.6165430000 1.6096590000
H -2.5935840000 -0.0058360000 2.0098510000
H -0.9532060000 -0.4620760000 2.4336980000
H -3.3712800000 0.3279650000 -0.2901970000
H -2.8283390000 -1.3061340000 -0.6660010000
H -2.3520720000 0.0444890000 -1.7007870000
H 1.0210450000 -0.8173530000 1.6623070000
```

Thermodynamic Data

Zero-point correction= 0.259798 (Hartree/Particle)
 Thermal correction to Energy= 0.271643
 Thermal correction to Enthalpy= 0.272587
 Thermal correction to Gibbs Free Energy= 0.223656
 Sum of electronic and zero-point Energies= -500.254073
 Sum of electronic and thermal Energies= -500.242228
 Sum of electronic and thermal Enthalpies= -500.241283
 Sum of electronic and thermal Free Energies= -500.290214

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.459	48.136	102.984

exo-bornane diazonium ion (**exo-B-N₂⁺**)

optimized xyz-matrix

```

C -1.0518580000 0.7896430000 1.0196210000
C 0.3323450000 1.4841000000 1.0339890000
C 0.9838300000 0.9037750000 -0.2697320000
C -0.0545770000 -0.1652230000 -0.8072910000
C -1.1488520000 0.7785130000 -1.4040270000
C -1.8522390000 1.3947660000 -0.1562350000
H -1.8200340000 2.4883530000 -0.1527710000
H -2.9052830000 1.1093790000 -0.1091140000
H -1.8324820000 0.1784150000 -2.0097820000
H -0.7234100000 1.5292460000 -2.0790050000
C -0.7262330000 -0.6557590000 0.5306120000
C -1.9734620000 -1.5277630000 0.2823200000
C 0.1898220000 -1.4567430000 1.4758470000
C 0.5038810000 -1.1887690000 -1.7844010000
H 0.9189770000 1.2366800000 1.9210660000
H 0.2777780000 2.5728830000 0.9649800000
H -1.5491170000 0.8565370000 1.9905410000
N 2.2863530000 0.3077330000 0.0045050000
N 3.2730820000 -0.1694140000 0.1665140000
H 0.9347270000 -0.7120990000 -2.6725830000
H -0.3050410000 -1.8397020000 -2.1286270000
H 1.2668530000 -1.8346560000 -1.3346080000
H 0.5257720000 -2.3866720000 1.0040930000
H -0.3675020000 -1.7390100000 2.3748130000
H 1.0763980000 -0.9202690000 1.8280960000
H -2.4996680000 -1.6918160000 1.2284220000
H -1.6844220000 -2.5118620000 -0.1019360000
H -2.6889540000 -1.0953870000 -0.4192580000
H 1.2434340000 1.6525120000 -1.0256910000

```

Thermodynamic Data

Zero-point correction= 0.259949 (Hartree/Particle)
 Thermal correction to Energy= 0.271719
 Thermal correction to Enthalpy= 0.272663
 Thermal correction to Gibbs Free Energy= 0.224007
 Sum of electronic and zero-point Energies= -500.252758
 Sum of electronic and thermal Energies= -500.240988
 Sum of electronic and thermal Enthalpies= -500.240044
 Sum of electronic and thermal Free Energies= -500.288700

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.506	48.111	102.405

endo-bornane diazonium ion dissociation TS
(*endo*-B-N₂⁺-TS)

optimized xyz-matrix

```
C 0.8064010000 -1.4192660000 0.2412380000
C -0.4614860000 -1.2971680000 1.1275970000
C -0.8658600000 0.1477270000 0.8192370000
C -0.0230640000 0.6745270000 -0.3095720000
C -0.2603190000 -0.2107480000 -1.5701820000
C 0.3308050000 -1.6082130000 -1.2132530000
H -0.4054420000 -2.4127310000 -1.3011170000
H 1.1615830000 -1.8690750000 -1.8724540000
H 0.2467350000 0.2460050000 -2.4230680000
H -1.3220960000 -0.2505640000 -1.8384980000
C 1.3602220000 0.0421840000 0.2596320000
C 2.5336930000 0.3006890000 -0.6998010000
C 1.7925170000 0.5521870000 1.6501660000
C -0.0927640000 2.1778540000 -0.5347700000
H -0.2675270000 -1.3962320000 2.1985430000
H -1.2292480000 -2.0321820000 0.8705290000
H 1.4955220000 -2.1880060000 0.5983150000
N -2.5681620000 0.1309520000 0.3045680000
N -3.6257470000 0.1639650000 -0.0103830000
H -1.0682430000 2.4770060000 -0.9368510000
H 0.6607800000 2.4877890000 -1.2641330000
H 0.0790360000 2.7412860000 0.3887990000
H 2.0169960000 1.6233770000 1.6171300000
H 2.7114690000 0.0399680000 1.9530810000
H 1.0648230000 0.3938140000 2.4527340000
H 3.3951870000 -0.2903790000 -0.3687330000
H 2.8331030000 1.3531720000 -0.6720210000
H 2.3317650000 0.0356900000 -1.7385680000
H -1.0679440000 0.8180060000 1.6552600000
```

Thermodynamic Data

Zero-point correction= 0.257701 (Hartree/Particle)
 Thermal correction to Energy= 0.269873
 Thermal correction to Enthalpy= 0.270817
 Thermal correction to Gibbs Free Energy= 0.220691
 Sum of electronic and zero-point Energies= -500.250895
 Sum of electronic and thermal Energies= -500.238723
 Sum of electronic and thermal Enthalpies= -500.237779
 Sum of electronic and thermal Free Energies= -500.287905

E (Thermal)

CV

S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	169.348	47.901	105.500

exo-bornane diazonium ion dissociation TS
(*exo-B-N₂⁺*-TS)

optimized xyz-matrix

```

C -1.0862610000 -0.7067700000 -1.0712280000
C 0.2689040000 -1.4712500000 -1.0400020000
C 0.8686400000 -0.9602840000 0.2768280000
C -0.0666010000 0.1117700000 0.8107290000
C -1.2222240000 -0.8437750000 1.3305740000
C -1.9566290000 -1.3196290000 0.0446890000
H -2.0114940000 -2.4097020000 -0.0275760000
H -2.9816560000 -0.9453710000 0.0055130000
H -1.8614810000 -0.2480740000 1.9872030000
H -0.8402420000 -1.6673470000 1.9441540000
C -0.7086290000 0.6990330000 -0.5063230000
C -1.9169580000 1.6135150000 -0.2296890000
C 0.2564360000 1.4984640000 -1.4030120000
C 0.4871410000 1.0492110000 1.8737850000
H 0.8944540000 -1.2307310000 -1.9023810000
H 0.1650790000 -2.5597270000 -1.0121430000
H -1.5390820000 -0.7104470000 -2.0652680000
N 2.3970270000 -0.2881270000 -0.0455500000
N 3.4196190000 0.1130510000 -0.1592500000
H 0.8913070000 0.4982510000 2.7308330000
H -0.3087710000 1.6981220000 2.2492730000
H 1.2782800000 1.6979780000 1.4798530000
H 0.6364210000 2.3841100000 -0.8820580000
H -0.2782050000 1.8553250000 -2.2892520000
H 1.1159840000 0.9329290000 -1.7765450000
H -2.4443500000 1.8208510000 -1.1666500000
H -1.5847540000 2.5759840000 0.1738520000
H -2.6439110000 1.1965200000 0.4698900000
H 1.2529840000 -1.6848580000 0.9967870000

```

Thermodynamic Data

Zero-point correction= 0.258207 (Hartree/Particle)
 Thermal correction to Energy= 0.270075
 Thermal correction to Enthalpy= 0.271019
 Thermal correction to Gibbs Free Energy= 0.221848
 Sum of electronic and zero-point Energies= -500.251934
 Sum of electronic and thermal Energies= -500.240067
 Sum of electronic and thermal Enthalpies= -500.239123
 Sum of electronic and thermal Free Energies= -500.288294

E (Thermal)

CV

S

	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	169.475	47.479	103.490

Bornyl cation (B ⁺)
---	---

optimized xyz-matrix

```

C 1.3740030000 -0.4676500000 -1.3028610000
H 2.3714880000 -0.0425230000 -1.5019290000
H 1.2548740000 -1.2648960000 -2.0478510000
C 0.3054530000 0.5453210000 -1.4832900000
H -0.0501170000 0.8382510000 -2.4738800000
C -0.3317280000 0.9387220000 -0.2880570000
C -1.6068420000 1.7540510000 -0.3501780000
H -2.2806030000 1.4085450000 -1.1402190000
H -2.1414300000 1.7076250000 0.6030650000
H -1.3767240000 2.8089090000 -0.5384610000
C 0.7290390000 1.3877930000 0.7921120000
H 1.2646140000 2.2604310000 0.4093890000
H 0.1692790000 1.7178950000 1.6704180000
C 1.6596550000 0.1843080000 1.0814370000
H 2.7074320000 0.4116080000 0.8678120000
H 1.6088720000 -0.1184600000 2.1299800000
C 1.1250220000 -0.9177540000 0.1504030000
H 1.5074300000 -1.9169170000 0.3740650000
C -0.4276070000 -0.7965850000 0.2331710000
C -1.2425580000 -1.6984020000 -0.6978600000
H -0.8462930000 -1.7961900000 -1.7111090000
H -1.2783900000 -2.7038010000 -0.2626760000
H -2.2767280000 -1.3472960000 -0.7717910000
C -1.0696310000 -0.8212100000 1.6138090000
H -0.6308540000 -0.1413310000 2.3430160000
H -2.1449760000 -0.6308910000 1.5560600000
H -0.9467030000 -1.8425260000 2.0019980000

```

Thermodynamic Data

Zero-point correction= 0.247449 (Hartree/Particle)
 Thermal correction to Energy= 0.257371
 Thermal correction to Enthalpy= 0.258315
 Thermal correction to Gibbs Free Energy= 0.213820
 Sum of electronic and zero-point Energies= -390.750682
 Sum of electronic and thermal Energies= -390.740760
 Sum of electronic and thermal Enthalpies= -390.739816
 Sum of electronic and thermal Free Energies= -390.784312

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.503	40.596	93.649

diazo fenchane (2-F)

optimized xyz-matrix

```

C 0.2080680000 1.5992110000 0.3476730000
C 1.1842410000 0.3853780000 0.1566680000
C 0.1218640000 -0.7156380000 0.0134940000
C -1.2808600000 -0.1283220000 0.1860340000
C -1.5698640000 0.7251440000 -1.0888130000
C -0.5679000000 1.9163900000 -0.9576140000
H 0.0785960000 2.0322990000 -1.8308130000
H -1.1057450000 2.8633070000 -0.8361870000
H -2.6097800000 1.0763550000 -1.0822320000
H -1.4267730000 0.1416380000 -2.0038060000
C -0.9314970000 0.9939380000 1.1985560000
H -1.7627930000 1.6940800000 1.3480060000
H -0.6201700000 0.6073660000 2.1731920000
C -2.3724360000 -1.1161830000 0.5681910000
C 2.0697680000 0.1843360000 1.4068070000
C 2.1109800000 0.4966030000 -1.0689610000
H 0.7176890000 2.4692880000 0.7741600000
N 0.3738260000 -1.9339540000 -0.3035860000
N 0.6089930000 -3.0334060000 -0.5736350000
H -2.1263090000 -1.6421760000 1.4976000000
H -2.5220440000 -1.8713710000 -0.2132550000
H -3.3266480000 -0.5963770000 0.7120250000
H 2.7825350000 -0.3688720000 -1.1165740000
H 2.7371700000 1.3952040000 -1.0026780000
H 1.5579570000 0.5314360000 -2.0112900000
H 2.7930470000 1.0044490000 1.5005830000
H 2.6353350000 -0.7516140000 1.3301360000
H 1.4840160000 0.1413570000 2.3294690000

```

Thermodynamic Data

Zero-point correction= 0.247385 (Hartree/Particle)
 Thermal correction to Energy= 0.259102
 Thermal correction to Enthalpy= 0.260046
 Thermal correction to Gibbs Free Energy= 0.210805
 Sum of electronic and zero-point Energies= -499.894554
 Sum of electronic and thermal Energies= -499.882838
 Sum of electronic and thermal Enthalpies= -499.881894
 Sum of electronic and thermal Free Energies= -499.931135

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	162.589	46.763	103.637

Endo-diazo fenchane dissociation TS
(*endo*-TS-2-F)

optimized xyz-matrix

```
C 1.5215160000 -0.7274200000 0.3113810000
C 1.0578460000 0.6677270000 -0.2182320000
C -0.3732530000 0.3932720000 -0.7252580000
C -0.6607580000 -1.0434680000 -0.3328430000
C -0.6623300000 -1.2373120000 1.2242950000
C 0.8238060000 -1.0563490000 1.6486660000
H 0.9625230000 -0.2838730000 2.4096660000
H 1.2282830000 -1.9861860000 2.0639800000
H -1.0182700000 -2.2509590000 1.4475930000
H -1.3444990000 -0.5389100000 1.7151060000
C 0.7486910000 -1.6530740000 -0.6516820000
H 0.7830290000 -2.7145650000 -0.3776720000
H 1.0401270000 -1.5649000000 -1.7023280000
C -1.8647140000 -1.6651310000 -1.0331210000
C 1.8817300000 1.0707730000 -1.4744520000
C 1.1775840000 1.8350810000 0.7779910000
H 2.6094340000 -0.8529270000 0.3366590000
N -1.6904010000 1.5147680000 0.2952400000
N -2.5307720000 2.2268180000 0.1148340000
H -1.9375020000 -2.7399240000 -0.8246770000
H -1.8006520000 -1.5254480000 -2.1173160000
H -2.7971420000 -1.1960530000 -0.6965870000
H 1.4829060000 1.9955080000 -1.9020610000
H 1.8600330000 0.3112170000 -2.2606720000
H 2.9299200000 1.2331990000 -1.1923100000
H 0.8281250000 2.7651990000 0.3176210000
H 2.2272270000 1.9762490000 1.0637850000
H 0.5939530000 1.6766930000 1.6882210000
```

Thermodynamic Data

Zero-point correction= 0.243421 (Hartree/Particle)
 Thermal correction to Energy= 0.255531
 Thermal correction to Enthalpy= 0.256475
 Thermal correction to Gibbs Free Energy= 0.206124
 Sum of electronic and zero-point Energies= -499.838809
 Sum of electronic and thermal Energies= -499.826699
 Sum of electronic and thermal Enthalpies= -499.825754
 Sum of electronic and thermal Free Energies= -499.876106

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 160.348 47.438 105.973

Exo-diazo fenchane dissociation TS
(*exo*-TS-2-F)

optimized xyz-matrix

```
C 1.3866970000 -0.4142030000 0.8344570000
C 0.3035700000 -1.1695540000 -0.0206660000
C -0.5147280000 -0.0191000000 -0.6571600000
C 0.0447110000 1.2254550000 -0.0100590000
C 1.4045090000 1.3255440000 -0.8215180000
C 2.3550680000 0.3240760000 -0.1119360000
H 2.8801550000 -0.3369900000 -0.8058910000
H 3.1176090000 0.8532760000 0.4703860000
H 1.7597360000 2.3598760000 -0.7617140000
H 1.2545610000 1.0976300000 -1.8830210000
C 0.5737380000 0.7737450000 1.3794090000
H 1.1980180000 1.5282570000 1.8751950000
H -0.2370220000 0.4970170000 2.0617000000
C -0.7966580000 2.4920800000 -0.0874090000
C -0.5310100000 -2.0983120000 0.8885600000
C 0.8782150000 -2.0456580000 -1.1576870000
H 1.8797990000 -1.0524650000 1.5752790000
N -2.3470010000 -0.1136080000 -0.0139850000
N -3.4072290000 -0.1588620000 -0.3620110000
H -1.7024630000 2.4048280000 0.5236470000
H -1.1076980000 2.6913350000 -1.1188620000
H -0.2326950000 3.3598870000 0.2756220000
H -0.9279140000 -1.5806200000 1.7657310000
H 0.0987490000 -2.9257290000 1.2374650000
H -1.3740970000 -2.5278320000 0.3377420000
H 0.0690590000 -2.5955430000 -1.6491520000
H 1.5975890000 -2.7726330000 -0.7584430000
H 1.3815550000 -1.4574490000 -1.9296660000
```

Thermodynamic Data

Zero-point correction= 0.243682 (Hartree/Particle)
 Thermal correction to Energy= 0.255583
 Thermal correction to Enthalpy= 0.256527
 Thermal correction to Gibbs Free Energy= 0.207053
 Sum of electronic and zero-point Energies= -499.843409
 Sum of electronic and thermal Energies= -499.831508
 Sum of electronic and thermal Enthalpies= -499.830564
 Sum of electronic and thermal Free Energies= -499.880038

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	160.381	47.240	104.127

endo-fenchane diazonium ion
(*endo*-F-N₂⁺)

optimized xyz-matrix

```

C -0.5366880000 -1.5174630000 -0.2513720000
C -1.2715240000 -0.2155450000 0.2147830000
C 0.0196840000 0.6421750000 0.6579900000
C 1.2880210000 -0.2252790000 0.2843890000
C 1.3529700000 -0.3663640000 -1.2603900000
C 0.1694850000 -1.3197800000 -1.6113290000
H -0.4817220000 -0.9326760000 -2.3971950000
H 0.5460220000 -2.2840850000 -1.9643080000
H 2.3180070000 -0.8062100000 -1.5282610000
H 1.3083170000 0.5969080000 -1.7830570000
C 0.6798350000 -1.5928230000 0.6936910000
H 1.3663380000 -2.4073600000 0.4423690000
H 0.4408520000 -1.6670240000 1.7588710000
C 2.5657530000 0.2338070000 0.9715480000
C -2.1323800000 -0.4595470000 1.4678990000
C -2.1384990000 0.4586940000 -0.8586390000
H -1.2153640000 -2.3740670000 -0.2248790000
N 0.0654080000 1.9332710000 0.0349340000
N 0.1151020000 2.9040610000 -0.4996460000
H 2.4458530000 0.2976140000 2.0588960000
H 2.9053230000 1.2101220000 0.6049200000
H 3.3683650000 -0.4819020000 0.7674260000
H -2.6761770000 1.3231880000 -0.4528130000
H -2.8941560000 -0.2545800000 -1.2020690000
H -1.5806470000 0.7827660000 -1.7421390000
H -2.9863370000 -1.0907740000 1.2019340000
H -2.5296580000 0.4805360000 1.8670760000
H -1.5835400000 -0.9652590000 2.2677700000
H 0.0050090000 0.8842270000 1.7270060000

```

Thermodynamic Data

Zero-point correction= 0.259529 (Hartree/Particle)
 Thermal correction to Energy= 0.271338
 Thermal correction to Enthalpy= 0.272282
 Thermal correction to Gibbs Free Energy= 0.223348
 Sum of electronic and zero-point Energies= -500.258763
 Sum of electronic and thermal Energies= -500.246955
 Sum of electronic and thermal Enthalpies= -500.246011
 Sum of electronic and thermal Free Energies= -500.294945

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 170.267 48.097 102.991

exo-fenchane diazonium ion
(*exo*-F-N₂⁺)

optimized xyz-matrix

```
C -0.3128220000 -1.2952410000 0.8645690000
C -1.2145210000 -0.3566080000 -0.0109560000
C -0.0665350000 0.5629810000 -0.6632620000
C 1.2938240000 0.0861750000 -0.0065230000
C 1.5441940000 -1.2929520000 -0.6940370000
C 0.5229110000 -2.2516320000 -0.0138050000
H -0.0697420000 -2.8283440000 -0.7265860000
H 1.0374940000 -2.9739630000 0.6263080000
H 2.5778040000 -1.5904060000 -0.4933230000
H 1.4398460000 -1.2410240000 -1.7834600000
C 0.7832270000 -0.3449330000 1.3865460000
H 1.5618370000 -0.8645720000 1.9533080000
H 0.4208300000 0.4852150000 2.0025470000
C 2.4533410000 1.0680780000 -0.0985680000
C -2.2001670000 0.4265580000 0.8764980000
C -2.0022690000 -1.0502010000 -1.1327790000
H -0.9100780000 -1.8002700000 1.6278670000
N -0.2870980000 1.9618710000 -0.3723500000
N -0.4338720000 3.0239660000 -0.0899620000
H 2.2574700000 2.0061010000 0.4342480000
H 2.7094310000 1.3045820000 -1.1377870000
H 3.3395440000 0.6210390000 0.3620190000
H -2.6677060000 -0.3432440000 -1.6402080000
H -2.6271200000 -1.8411980000 -0.7050660000
H -1.3586040000 -1.5079400000 -1.8889770000
H -2.9271680000 -0.2785390000 1.2898390000
H -2.7694760000 1.1676580000 0.3034060000
H -1.7230040000 0.9285380000 1.7242100000
H -0.0516730000 0.5421580000 -1.7582560000
```

Thermodynamic Data

Zero-point correction= 0.259716 (Hartree/Particle)
 Thermal correction to Energy= 0.271439
 Thermal correction to Enthalpy= 0.272383
 Thermal correction to Gibbs Free Energy= 0.223691
 Sum of electronic and zero-point Energies= -500.258447
 Sum of electronic and thermal Energies= -500.246724
 Sum of electronic and thermal Enthalpies= -500.245780
 Sum of electronic and thermal Free Energies= -500.294472

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	170.331	48.018	102.481

endo-fenchane diazonium ion dissociation TS
(*endo*-F-N₂⁺-TS)

optimized xyz-matrix

```

C 0.7698030000 -1.4618000000 0.3279790000
C 1.2814830000 -0.0778180000 -0.2113850000
C -0.0773640000 0.4719180000 -0.7130970000
C -1.2085100000 -0.4314880000 -0.2997490000
C -1.2710800000 -0.5328580000 1.2552150000
C 0.0193480000 -1.3041880000 1.6650020000
H 0.5983380000 -0.7966550000 2.4390530000
H -0.2322030000 -2.2932540000 2.0588010000
H -2.1770030000 -1.0806630000 1.5287160000
H -1.3521410000 0.4544780000 1.7241940000
C -0.4042450000 -1.7506070000 -0.6338220000
H -1.0121590000 -2.6169680000 -0.3539860000
H -0.1313890000 -1.8555210000 -1.6879650000
C -2.5364490000 -0.2038340000 -1.0085410000
C 2.2084880000 -0.2581430000 -1.4368390000
C 2.0110940000 0.7984490000 0.8230230000
H 1.5686320000 -2.2064680000 0.3481130000
N -0.3858030000 2.0903970000 0.0101530000
N -0.6531140000 3.1027910000 0.3592590000
H -2.4171330000 -0.1622210000 -2.0969080000
H -3.0133190000 0.7274390000 -0.6805740000
H -3.2287180000 -1.0192470000 -0.7787880000
H 2.3787580000 1.7235530000 0.3660630000
H 2.8822290000 0.2537930000 1.1991440000
H 1.3894400000 1.0587290000 1.6842410000
H 3.1448870000 -0.7222830000 -1.1122540000
H 2.4542150000 0.7086820000 -1.8901360000
H 1.7751730000 -0.8974930000 -2.2114260000
H -0.1105910000 0.8739990000 -1.7288970000

```

Thermodynamic Data

Zero-point correction= 0.257595 (Hartree/Particle)
 Thermal correction to Energy= 0.269710
 Thermal correction to Enthalpy= 0.270654
 Thermal correction to Gibbs Free Energy= 0.220569
 Sum of electronic and zero-point Energies= -500.254527
 Sum of electronic and thermal Energies= -500.242412
 Sum of electronic and thermal Enthalpies= -500.241468
 Sum of electronic and thermal Free Energies= -500.291553

E (Thermal)	CV	S
KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin

Total 169.245 47.769 105.412

exo-fenchane diazonium ion dissociation TS
(*exo*-F-N₂⁺-TS)

optimized xyz-matrix

```
C 1.2960000000 -0.3454570000 0.9022040000
C 0.3550190000 -1.1973660000 -0.0358970000
C -0.4702010000 -0.0429490000 -0.6679450000
C -0.0452150000 1.2658200000 -0.0207390000
C 1.3777890000 1.4639230000 -0.6887210000
C 2.3013360000 0.4633870000 0.0587470000
H 2.9079230000 -0.1473730000 -0.6127470000
H 2.9927940000 0.9930590000 0.7202990000
H 1.6654790000 2.5058360000 -0.5196060000
H 1.3587400000 1.3183230000 -1.7747780000
C 0.3573570000 0.7765040000 1.3926880000
H 0.8797390000 1.5529890000 1.9587760000
H -0.4926390000 0.4367140000 1.9941500000
C -0.9701070000 2.4658140000 -0.1722570000
C -0.4747370000 -2.1866970000 0.8117520000
C 1.0684020000 -1.9912730000 -1.1480800000
H 1.7504880000 -0.9678630000 1.6762990000
N -2.1312180000 -0.2640020000 -0.2975350000
N -3.2075070000 -0.3139580000 -0.0565080000
H -1.9276800000 2.3175210000 0.3400750000
H -1.1723920000 2.6953490000 -1.2246560000
H -0.5009850000 3.3477450000 0.2733980000
H 0.3603720000 -2.6354350000 -1.6805410000
H 1.8345300000 -2.6349430000 -0.7044730000
H 1.5592070000 -1.3515920000 -1.8868380000
H 0.1988190000 -2.9467380000 1.2173580000
H -1.2211580000 -2.7085920000 0.2023520000
H -0.9782730000 -1.7111830000 1.6587470000
H -0.6177430000 -0.0483250000 -1.7500310000
```

Thermodynamic Data

Zero-point correction= 0.257991 (Hartree/Particle)
 Thermal correction to Energy= 0.269896
 Thermal correction to Enthalpy= 0.270840
 Thermal correction to Gibbs Free Energy= 0.221378
 Sum of electronic and zero-point Energies= -500.256723
 Sum of electronic and thermal Energies= -500.244817
 Sum of electronic and thermal Enthalpies= -500.243873
 Sum of electronic and thermal Free Energies= -500.293335

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	169.362	47.458	104.101

Fenchyl cation (F⁺)

optimized xyz-matrix

```

C 0.6026110000 -0.3087590000 1.3527620000
H 1.4561170000 0.0615950000 1.9316400000
H 0.2833220000 -1.2645030000 1.7752770000
C 0.0061980000 -0.9373760000 -0.5705410000
H -0.0587220000 -1.9512520000 -0.9786510000
C 1.2594390000 -0.3592610000 -0.2217420000
C 2.5275630000 -1.1613350000 -0.4431400000
H 2.3800570000 -2.2300660000 -0.2598890000
H 2.8785720000 -1.0356520000 -1.4732310000
H 3.3240970000 -0.8064200000 0.2178140000
C 1.3643450000 1.1844280000 -0.4491680000
H 2.3614870000 1.4928530000 -0.1232770000
H 1.2971220000 1.3898140000 -1.5212300000
C 0.2412660000 1.8603440000 0.3796140000
H 0.6654190000 2.4734760000 1.1799200000
H -0.3933040000 2.5154000000 -0.2207730000
C -0.5268710000 0.6755780000 0.9826560000
H -1.1991390000 0.9470330000 1.7993420000
C -1.2159230000 -0.2014680000 -0.1193420000
C -2.2430160000 -1.1871710000 0.4943040000
H -3.1160560000 -0.6186230000 0.8296000000
H -2.5786760000 -1.9178430000 -0.2487100000
H -1.8483190000 -1.7319460000 1.3568990000
C -1.8873480000 0.5274480000 -1.3147720000
H -1.2040630000 1.1884360000 -1.8523070000
H -2.2992400000 -0.1946620000 -2.0263880000
H -2.7182630000 1.1277860000 -0.9298190000

```

Thermodynamic Data

Zero-point correction= 0.247837 (Hartree/Particle)
 Thermal correction to Energy= 0.257731
 Thermal correction to Enthalpy= 0.258675
 Thermal correction to Gibbs Free Energy= 0.214134
 Sum of electronic and zero-point Energies= -390.750380
 Sum of electronic and thermal Energies= -390.740486
 Sum of electronic and thermal Enthalpies= -390.739542
 Sum of electronic and thermal Free Energies= -390.784083

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.729	40.442	93.744

4.2.4 Structures optimized at the B3LYP/6-311+G** level of theory

Diazo norbornane (**2-N**)

optimized xyz-matrix

```

C -1.3628260000 0.9538530000 -0.0330050000
C 0.0842380000 1.3976030000 -0.3699400000
C 0.8456780000 0.1698590000 0.1127530000
C -0.1457070000 -0.8058860000 0.7277840000
C -0.9692830000 -1.4343400000 -0.4280470000
C -1.7666460000 -0.2059310000 -0.9816190000
H -1.5193890000 0.0173510000 -2.0223450000
H -2.8440470000 -0.3826090000 -0.9354480000
H -1.6440690000 -2.2045730000 -0.0414710000
H -0.3304160000 -1.9005130000 -1.1800370000
C -1.1658300000 0.2054780000 1.3050080000
H -2.0796510000 -0.2753720000 1.6646710000
H -0.7498190000 0.8311170000 2.0979450000
H 0.2927850000 -1.5208780000 1.4237000000
H 0.3633600000 2.3028090000 0.1834770000
H 0.2188290000 1.6020790000 -1.4371980000
H -2.0719680000 1.7822980000 -0.0200250000
N 2.0975130000 -0.0464040000 -0.0542910000
N 3.2234350000 -0.2300990000 -0.1929760000

```

Thermodynamic Data

Zero-point correction= 0.162107 (Hartree/Particle)
 Thermal correction to Energy= 0.169419
 Thermal correction to Enthalpy= 0.170363
 Thermal correction to Gibbs Free Energy= 0.130018
 Sum of electronic and zero-point Energies= -382.136500
 Sum of electronic and thermal Energies= -382.129188
 Sum of electronic and thermal Enthalpies= -382.128244
 Sum of electronic and thermal Free Energies= -382.168589

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	106.312	29.183	84.913

endo-Norbornyl diazonium ion (*endo*-N-N₂⁺)

optimized xyz-matrix

```

C 1.4839820000 -0.5285950000 -0.6421790000

```

C 0.1445310000 -1.3005520000 -0.7334210000
 C -0.5687760000 -0.7795370000 0.5189140000
 C 0.2783710000 0.2934490000 1.1329840000
 C 0.4319810000 1.5054160000 0.1781230000
 C 1.2461080000 0.9451800000 -1.0310440000
 H 0.7157220000 1.0422750000 -1.9802080000
 H 2.1948550000 1.4718620000 -1.1391380000
 H 0.9787290000 2.2886220000 0.7039450000
 H -0.5301180000 1.9364750000 -0.1079500000
 C 1.6480820000 -0.4447610000 0.8916740000
 H 0.2768820000 -2.3800700000 -0.6211480000
 H -0.4065570000 -1.1381070000 -1.6611870000
 H 2.2889840000 -1.0183370000 -1.1862590000
 N -2.1255420000 -0.0613700000 0.0042860000
 N -3.1135210000 0.3244950000 -0.2690720000
 H -1.0550840000 -1.4976620000 1.1766720000
 H 2.4684090000 0.1906470000 1.2292950000
 H 1.7335110000 -1.4149850000 1.3864760000
 H 0.0224360000 0.5338080000 2.1626980000

Thermodynamic Data

Zero-point correction= 0.172463 (Hartree/Particle)
 Thermal correction to Energy= 0.180221
 Thermal correction to Enthalpy= 0.181165
 Thermal correction to Gibbs Free Energy= 0.139882
 Sum of electronic and zero-point Energies= -382.489557
 Sum of electronic and thermal Energies= -382.481798
 Sum of electronic and thermal Enthalpies= -382.480854
 Sum of electronic and thermal Free Energies= -382.522138

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	113.091	30.149	86.889

exo-Norbornyl diazonium (**exo-N-N₂⁺**)

optimized xyz-matrix

C -1.1131540000 1.0338540000 0.4279310000
 C 0.0326120000 1.2610240000 -0.6000520000
 C 0.6254100000 -0.1504560000 -0.7201550000
 C -0.1345810000 -1.0125400000 0.2614750000
 C -1.5202310000 -1.1765220000 -0.4653810000
 C -2.2138910000 0.2044430000 -0.2624130000
 H -2.5466140000 0.6501380000 -1.2011410000
 H -3.0879520000 0.1132260000 0.3834960000
 H -2.0539400000 -1.9874940000 0.0320720000
 H -1.4188140000 -1.4644990000 -1.5143650000
 C -0.4782200000 -0.0033160000 1.3778070000

H 0.7611800000 1.9822160000 -0.2250670000
H -0.2974810000 1.6146720000 -1.5787330000
H -1.4524450000 1.9622480000 0.8831330000
N 2.2399320000 -0.0865010000 -0.1788260000
N 3.2617990000 -0.0920440000 0.2167890000
H 0.8514150000 -0.5545250000 -1.7050410000
H -1.1846320000 -0.4145080000 2.0994880000
H 0.3930580000 0.3683120000 1.9249790000
H 0.3364390000 -1.9589000000 0.5201570000

Thermodynamic Data

Zero-point correction= 0.172570 (Hartree/Particle)
Thermal correction to Energy= 0.180235
Thermal correction to Enthalpy= 0.181179
Thermal correction to Gibbs Free Energy= 0.140188
Sum of electronic and zero-point Energies= -382.492619
Sum of electronic and thermal Energies= -382.484954
Sum of electronic and thermal Enthalpies= -382.484009
Sum of electronic and thermal Free Energies= -382.525000

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	113.099	29.984	86.272

Diazo bornane (**2-B**)

optimized xyz-matrix

C -0.9589110000 1.2263890000 0.5754690000
C 0.5067730000 1.3725400000 1.0556080000
C 1.1436660000 0.2513390000 0.2502470000
C 0.0633620000 -0.4717080000 -0.5599850000
C -0.3399740000 0.5284350000 -1.6839450000
C -1.0097670000 1.7000470000 -0.8998800000
H -0.4770800000 2.6448870000 -1.0301130000
H -2.0366760000 1.8680590000 -1.2300380000
H -1.0350700000 0.0632700000 -2.3893530000
H 0.5338290000 0.8468290000 -2.2558350000
C -1.1418100000 -0.3199080000 0.4510450000
C -2.5084290000 -0.7332690000 -0.1206260000
C -0.9431080000 -1.0846120000 1.7690440000
C 0.4264570000 -1.8673900000 -1.0389630000
H 0.6064390000 1.2229010000 2.1364650000
H 0.9150620000 2.3608610000 0.8207080000
H -1.6764660000 1.7268900000 1.2291720000
N 2.4008590000 0.0206260000 0.1669160000
N 3.5277360000 -0.1980700000 0.1000460000
H 1.2873590000 -1.8403400000 -1.7140500000

H -0.4045130000 -2.3158480000 -1.5901020000
H 0.6799970000 -2.5266440000 -0.2045250000
H -1.0921820000 -2.1573100000 1.6150040000
H -1.6773980000 -0.7592200000 2.5128070000
H 0.0524030000 -0.9521180000 2.1944020000
H -3.2968840000 -0.5047650000 0.6035450000
H -2.5401780000 -1.8118810000 -0.3008310000
H -2.7683630000 -0.2346550000 -1.0540620000

Thermodynamic Data

Zero-point correction= 0.245124 (Hartree/Particle)
Thermal correction to Energy= 0.256808
Thermal correction to Enthalpy= 0.257752
Thermal correction to Gibbs Free Energy= 0.208756
Sum of electronic and zero-point Energies= -500.025524
Sum of electronic and thermal Energies= -500.013841
Sum of electronic and thermal Enthalpies= -500.012897
Sum of electronic and thermal Free Energies= -500.061892

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	161.149	47.068	103.120

endo-bornane diazonium ion dissociation TS
(*endo*-B-N₂⁺-TS)

optimized xyz-matrix

C 0.8055770000 -1.4147930000 0.2510040000
C -0.4648530000 -1.2912020000 1.1304090000
C -0.8780910000 0.1481750000 0.8105770000
C -0.0233560000 0.6711230000 -0.3140900000
C -0.2512810000 -0.2177850000 -1.5713200000
C 0.3363190000 -1.6128980000 -1.2032330000
H -0.3983730000 -2.4156440000 -1.2879400000
H 1.1669930000 -1.8785470000 -1.8562150000
H 0.2634740000 0.2324890000 -2.4195880000
H -1.3072580000 -0.2593690000 -1.8517260000
C 1.3558150000 0.0468010000 0.2616460000
C 2.5322780000 0.2967590000 -0.6932050000
C 1.7795150000 0.5645740000 1.6499640000
C -0.0971350000 2.1716430000 -0.5445720000
H -0.2729740000 -1.3809330000 2.1999170000
H -1.2248090000 -2.0315590000 0.8768330000
H 1.4938500000 -2.1777140000 0.6139260000
N -2.5572660000 0.1312790000 0.2928140000
N -3.6105310000 0.1614870000 -0.0071220000
H -1.0704080000 2.4665090000 -0.9496220000
H 0.6546990000 2.4814020000 -1.2721400000

H 0.0702840000 2.7373160000 0.3755380000
H 2.0105830000 1.6315630000 1.6096720000
H 2.6911790000 0.0508400000 1.9636350000
H 1.0466030000 0.4174940000 2.4464720000
H 3.3910470000 -0.2891460000 -0.3539630000
H 2.8304400000 1.3472510000 -0.6728580000
H 2.3356880000 0.0231880000 -1.7280430000
H -1.0751740000 0.8211160000 1.6431760000

Thermodynamic Data

Zero-point correction= 0.255437 (Hartree/Particle)
Thermal correction to Energy= 0.267606
Thermal correction to Enthalpy= 0.268550
Thermal correction to Gibbs Free Energy= 0.218529
Sum of electronic and zero-point Energies= -500.382546
Sum of electronic and thermal Energies= -500.370377
Sum of electronic and thermal Enthalpies= -500.369433
Sum of electronic and thermal Free Energies= -500.419454

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	167.925	48.176	105.277

exo-bornane diazonium ion dissociation TS
(*exo*-B-N₂⁺-TS)

optimized xyz-matrix

C -1.0822610000 -0.7178870000 -1.0640020000
C 0.2774450000 -1.4707640000 -1.0348440000
C 0.8822620000 -0.9485580000 0.2754310000
C -0.0640970000 0.1174670000 0.8090330000
C -1.2116340000 -0.8351920000 1.3388820000
C -1.9434120000 -1.3287230000 0.0587610000
H -1.9879710000 -2.4172260000 -0.0049950000
H -2.9697440000 -0.9659130000 0.0189750000
H -1.8552500000 -0.2409420000 1.9877840000
H -0.8241160000 -1.6487960000 1.9578730000
C -0.7125940000 0.6925730000 -0.5093790000
C -1.9258050000 1.5978900000 -0.2342040000
C 0.2435500000 1.4908040000 -1.4138410000
C 0.4876510000 1.0664020000 1.8602990000
H 0.8947160000 -1.2311780000 -1.9001260000
H 0.1799000000 -2.5570830000 -1.0005930000
H -1.5392270000 -0.7301200000 -2.0531850000
N 2.3887110000 -0.2794600000 -0.0422090000
N 3.4052130000 0.1134180000 -0.1589640000
H 0.9034520000 0.5256400000 2.7154830000
H -0.3106760000 1.7063320000 2.2389500000
H 1.2656200000 1.7222520000 1.4584230000
H 0.6234580000 2.3772480000 -0.8993840000

H -0.2978750000 1.8432380000 -2.2947800000
H 1.0986000000 0.9277870000 -1.7932910000
H -2.4558430000 1.7962090000 -1.1688520000
H -1.6007170000 2.5628990000 0.1624420000
H -2.6458850000 1.1792950000 0.4673990000
H 1.2574560000 -1.6714250000 0.9992660000

Thermodynamic Data

Zero-point correction= 0.255939 (Hartree/Particle)
Thermal correction to Energy= 0.267803
Thermal correction to Enthalpy= 0.268748
Thermal correction to Gibbs Free Energy= 0.219664
Sum of electronic and zero-point Energies= -500.383290
Sum of electronic and thermal Energies= -500.371426
Sum of electronic and thermal Enthalpies= -500.370481
Sum of electronic and thermal Free Energies= -500.419565

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	168.049	47.760	103.306

diazo fenchane (2-F)

optimized xyz-matrix

C -0.2141420000 -1.5988100000 0.3415000000
C -1.1849690000 -0.3797930000 0.1582430000
C -0.1188950000 0.7174620000 0.0201350000
C 1.2804980000 0.1232790000 0.1883040000
C 1.5637860000 -0.7226720000 -1.0916470000
C 0.5580660000 -1.9103090000 -0.9663710000
H -0.0891170000 -2.0171050000 -1.8368310000
H 1.0912310000 -2.8578480000 -0.8524850000
H 2.5999530000 -1.0768220000 -1.0873590000
H 1.4214210000 -0.1341190000 -2.0005160000
C 0.9275020000 -1.0029250000 1.1945510000
H 1.7550260000 -1.7047560000 1.3369990000
H 0.6185310000 -0.6214640000 2.1686860000
C 2.3749910000 1.1037260000 0.5747310000
C -2.0666410000 -0.1823030000 1.4106030000
C -2.1101040000 -0.4804930000 -1.0669710000
H -0.7266860000 -2.4664330000 0.7624660000
N -0.3660760000 1.9327960000 -0.3008140000
N -0.5972020000 3.0254600000 -0.5755870000
H 2.1281080000 1.6297680000 1.5010820000
H 2.5324800000 1.8552770000 -0.2053450000
H 3.3231260000 0.5787290000 0.7222160000
H -2.7787970000 0.3844080000 -1.1088150000

H -2.7366810000 -1.3763580000 -1.0057870000
H -1.5576820000 -0.5112760000 -2.0068860000
H -2.7873130000 -1.0018490000 1.5020620000
H -2.6321490000 0.7511470000 1.3377770000
H -1.4790550000 -0.1420700000 2.3290760000

Thermodynamic Data

Zero-point correction= 0.244830 (Hartree/Particle)
Thermal correction to Energy= 0.256613
Thermal correction to Enthalpy= 0.257557
Thermal correction to Gibbs Free Energy= 0.208174
Sum of electronic and zero-point Energies= -500.028260
Sum of electronic and thermal Energies= -500.016477
Sum of electronic and thermal Enthalpies= -500.015533
Sum of electronic and thermal Free Energies= -500.064916

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	161.027	47.181	103.935

endo-fenchane diazonium dissociation TS
(*endo*-F-N₂⁺-TS)

optimized xyz-matrix

C 0.7451050000 -1.4771280000 0.3028780000
C 1.2771370000 -0.0925110000 -0.2125160000
C -0.0747150000 0.4892340000 -0.7007940000
C -1.2164600000 -0.4063920000 -0.2963980000
C -1.2734160000 -0.5306090000 1.2553710000
C 0.0043480000 -1.3310390000 1.6449860000
H 0.5940140000 -0.8496650000 2.4238060000
H -0.2621150000 -2.3203670000 2.0209050000
H -2.1847960000 -1.0654350000 1.5260130000
H -1.3334540000 0.4468590000 1.7420290000
C -0.4369560000 -1.7306710000 -0.6564030000
H -1.0532120000 -2.5910660000 -0.3877160000
H -0.1709390000 -1.8210320000 -1.7108980000
C -2.5420970000 -0.1461300000 -0.9944730000
C 2.1977150000 -0.2663850000 -1.4411050000
C 2.0202850000 0.7488370000 0.8379500000
H 1.5304440000 -2.2323420000 0.3062310000
N -0.3512690000 2.0891080000 0.0256350000
N -0.5876590000 3.1007970000 0.3725510000
H -2.4269150000 -0.0918460000 -2.0803490000
H -3.0015020000 0.7862600000 -0.6520100000
H -3.2463000000 -0.9505150000 -0.7734860000
H 2.4029480000 1.6749500000 0.4011510000
H 2.8810860000 0.1839760000 1.2010290000
H 1.4051730000 0.9998440000 1.7033740000

H 3.1227670000 -0.7555860000 -1.1292630000
H 2.4626470000 0.7023040000 -1.8737390000
H 1.7502210000 -0.8786190000 -2.2260020000
H -0.1032490000 0.8897140000 -1.7153470000

Thermodynamic Data

Zero-point correction= 0.255390 (Hartree/Particle)
Thermal correction to Energy= 0.267479
Thermal correction to Enthalpy= 0.268423
Thermal correction to Gibbs Free Energy= 0.218508
Sum of electronic and zero-point Energies= -500.385893
Sum of electronic and thermal Energies= -500.373804
Sum of electronic and thermal Enthalpies= -500.372860
Sum of electronic and thermal Free Energies= -500.422775

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	167.846	48.014	105.056

exo-fenchane diazonium ion dissociation TS
(*exo*-F-N₂⁺-TS)

optimized xyz-matrix

C 1.2898070000 -0.3718580000 0.8968380000
C 0.3259740000 -1.2035190000 -0.0346500000
C -0.4819010000 -0.0322650000 -0.6622050000
C -0.0187670000 1.2669300000 -0.0187010000
C 1.4025210000 1.4367410000 -0.6907740000
C 2.3069690000 0.4147730000 0.0489730000
H 2.8939140000 -0.2076940000 -0.6249000000
H 3.0131480000 0.9260810000 0.7052530000
H 1.7153010000 2.4684090000 -0.5211940000
H 1.3750900000 1.2941040000 -1.7745700000
C 0.3778490000 0.7683320000 1.3918020000
H 0.9185720000 1.5308100000 1.9545910000
H -0.4735410000 0.4458560000 1.9959170000
C -0.9177230000 2.4851750000 -0.1638290000
C -0.5150270000 -2.1753700000 0.8186350000
C 1.0165280000 -2.0086660000 -1.1505710000
H 1.7342940000 -1.0022790000 1.6664700000
N -2.1287600000 -0.2163500000 -0.2927800000
N -3.1997910000 -0.2599570000 -0.0658540000
H -1.8707530000 2.3623730000 0.3588200000
H -1.1248520000 2.7152300000 -1.2128960000
H -0.4256260000 3.3564970000 0.2719660000
H 0.2930560000 -2.6312690000 -1.6833910000
H 1.7655630000 -2.6724520000 -0.7132500000
H 1.5206210000 -1.3789900000 -1.8851380000
H 0.1468770000 -2.9419660000 1.2245090000

H -1.2687410000 -2.6886790000 0.2150850000
H -1.0076670000 -1.6903320000 1.6634260000
H -0.6227780000 -0.0331890000 -1.7433810000

Thermodynamic Data

Zero-point correction= 0.255690 (Hartree/Particle)
Thermal correction to Energy= 0.267595
Thermal correction to Enthalpy= 0.268539
Thermal correction to Gibbs Free Energy= 0.219156
Sum of electronic and zero-point Energies= -500.387758
Sum of electronic and thermal Energies= -500.375853
Sum of electronic and thermal Enthalpies= -500.374908
Sum of electronic and thermal Free Energies= -500.424291

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	167.919	47.747	103.935

4.3 Studies on the topology of the underlying PES

4.3.1 IRC-Profiles, PES Scans and Activation Barriers based on Stationary Points

In the following section one finds the summarized results of:

- the activation barriers for the thermal dissociation of the diazoniumions **N-N₂⁺**, **B-N₂⁺**, **F-N₂⁺**, in dependence of their configuration at C2 (*endo*, *exo*) as calculated at various levels of theory with and without implicit solvent modelling.
- The relaxed PES scans in the region of the N₂-dissociation and potential skeletal rearrangements of the resulting carbocations.
- IRC calculations starting at the respective transition states that indicate the dinitrogen release.

4.3.1.1 Norbornyl system

Table S42 Activation barriers and driving forces for the thermal dissociation to the indicated product structures **N⁺** and nor-**P⁺** (see below, exemplified for the *endo*-configuration).

Level of theory	<i>endo</i> [kcal/mol]		<i>exo</i> [kcal/mol]	
	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)	$\Delta_R G$ ($\Delta_R H$)	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)	$\Delta_R G$ ($\Delta_R H$)
B3LYP/6-31G*, Gasphase	1.7 (2.3)	25.8 (14.8)	0.3 (0.7)	25.3 (14.3)
M062X/6-311+G**, Gasphase	1.4 (2.4)	26.0 (15.4)	0.2 (0.6)	25.2 (14.7)
M062X/6-311+G**, PCM=ACN	3.0 (3.9)	25.9 (15.2)	1.4 (2.0)	25.0 (14.4)
BB1K/6-31+G(d,p), Gasphase	34.8 (37.4)	28.5 (16.2)	32.8 (35.1)	28.1 (15.8)

Figure S19. Relaxed PES scan driving the bond lengths C2-N₂ (coordinate for the N₂-release) and C2-C7 (norbornyl vs nor-pinyl cation rearrangement) to learn more about the topology in this region and dimension of the PES.

Figure S20. Relaxed PES scan driving the bond lengths C2-N₂ (coordinate for the N₂-release) and C2-C7 (norbornyl vs norpinyl cation rearrangement) to learn more about the topology in this region and dimension of the PES.

4.3.3.2 Bornyl system

Table S43. Activation barriers and driving forces for the thermal dissociation to the indicated product structures C⁺, P⁺ and T⁺ (see below, exemplified for the *endo*-configuration).

Level of theory	<i>endo</i> [kcal/mol]	<i>exo</i> [kcal/mol]
	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)
B3LYP/6-31G*, Gasphase	1.4 (2.2)	0.3 (0.6)
M062X/6-311+G**, Gasphase	1.9 (2.2)	0.5 (0.5)
M062X/6-311+G**, PCM=ACN	3.1 (3.9)	1.4 (1.3)
BB1K/6-31+G(d,p), Gasphase	33.4 (36.7)	31.7 (34.2)

Figure S21 Relaxed PES scan driving the bond lengths C2-N₂ (coordinate for the N₂-release) and C2-C7 (pinyI vs camphyl cation rearrangement) to learn more about the topology in this region and dimension of the PES.

4.3.3.3 Fenchyl system

Table S44. Activation barriers and driving forces for the thermal dissociation to the indicated product structures **P⁺** and **α-F⁺** (see below, exemplified for the *endo*-configuration).

Level of theory	<i>endo</i> [kcal/mol]	<i>exo</i> [kcal/mol]
	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)	$\Delta^\ddagger G$ ($\Delta^\ddagger H$)
B3LYP/6-31G*, Gasphase	2.1 (2.9)	0.7 (1.2)
M062X/6-311+G**, Gasphase	2.3 (2.6)	1.1 (1.0)
M062X/6-311+G**, PCM=ACN	2.9 (4.0)	1.2 (1.8)
BB1K/6-31+G(d,p), Gasphase	34.1 (38.2)	33.4 (35.2)

Figure S22. Relaxed PES scan driving the bond lengths C2-N₂ (coordinate for the N₂-release) and C2-C7 (pinyl vs α-fenchyl cation rearrangement) to learn more about the topology in this region and dimension of the PES. In case of the endo-isomer the PES features in this representation a VRI.

Figure 23. Relaxed PES scan driving the bond lengths C2-N₂ (coordinate for the N₂-release) and C2-C7 (pinyl vs α -fenchyl cation rearrangement) to learn more about the topology in this region and dimension of the PES. However, in case of the *exo*-isomer there is only one direct valley available resembling the α -fenchyl cation α -F⁺.

4.3.2 Identification of the VRI points using the projected frequencies along the IRC

4.3.3.2.1 Procedure of the projected frequency analysis along the IRC

Since scanning the potential energy surfaces by driving a specific set of coordinates is introducing a bias by the choice of the geometric parameters and visualization of the hypersurface in 3D, i.e. the reduction in dimensionality, alternative evidence not only for the identification of reaction path bifurcations and but especially for the characterization of the associated VRIs are needed. Therefore, a mass weighted frequency analysis of the IRC was done. The calculations were conducted with B3LYP/6-311+G** starting at the dissociation TS structures of the diazonium ions. According to Satoshi Maeda *et al.*³², bifurcations are implied by the occurrence of negative projected frequencies along the IRC therefore frequency analysis of every point along the IRC were conducted by using the “projected”-option in Gaussian.^[2]

4.3.3.2.2 Results of the identification of the VRI points

Mass-weighted frequency analysis of IRCs – endo isomers

In Figure S-13 and S14, the graphs show the lowest projected frequency of the IRC of the *endo*-Fenchyl diazonium ion respectively the *endo*-Bornyl diazonium ion on each point.

In Figure S-13, the frequencies become imaginary in two points, so there are two VRT points on this IRC. The first one however seems to be the essential one for the observed reaction path bifurcations happening in the carbocation rearrangements because this imaginary frequency indicates two atomic motions: the bond breaking process between carbon and the dinitrogen and a suitable movement for the formation of the pinyl cation P⁺. The second valley however mostly describes a deformative vibration of the dinitrogen with some interaction with the fenchyl moiety.

In Figure 2 which shows the IRC of the dissociation of the *endo*-bornyl diazonium ion. In the projected frequency analysis only one inversion of sign is observed, indicating one VRI. The vibration corresponds mostly to the formation of the P⁺ which is also the product of this IRC. To a lesser extend this imaginary

³² S. Maeda, Y. Harabuchi, Y. Ono, T. Taketsugu, K. Morokuma, Intrinsic Reaction Coordinate: Calculation, Bifurcation, and Automated Search, *Int. J. Qua. Chem.* **2015**, *115*, 258 – 269.

frequency also has contributions of the camphyl $\mathbf{C}^+$ and bornyl cation $\mathbf{B}^+$ formation. This is in accordance to the molecular dynamics simulations that showed formation of $\mathbf{C}^+$ and $\mathbf{B}^+$.

Figure S24. The *endo*-fenchyl diazonium ion's IRC with the frequency analysis. Only the reverse path is displayed with the reaction coordinate put in as absolute value. Underneath the corresponding structures to the crucial points on the IRC.

Figure S25. The *endo*-bornyl diazonium ion's IRC with the frequency analysis. Only the forward path is displayed. Underneath the corresponding structures to crucial points on the IRC.

Mass-weighted frequency analysis of IRCs – *exo* isomers

For the *exo*-bornyl diazonium ion there is a negative frequency visible along the IRC but not in the same manner as for the *endo*-diazonium ions. Here, this is purely the displacement movements of the dissociating nitrogen. The same is visible for the Fenchyl system (See both GIFs). Since the

displacement in the imaginary frequencies show no reformation of the bonds in the bornyl or fenchyl framework, it can be assumed that no bifurcation is present on the framework.

Figure S26: The N_2 -release of the *exo*-bornyl diazonium ion: IRC along the product forming way. It shows one negative frequency in the mass-weighted frequency analysis.

Figure S27: The N_2 -release of the *exo*-fenchyl diazonium ion: IRCs along the product forming way. Both show a negative frequency in the mass-weighted frequency analysis.

4.4 BOMDs Simulations

4.4.1 BOMD simulations: Initial conditions

The trajectories were either calculated with M062X/6-31G* level of theory. The seed numbers were randomly generated, the temperature was set to 298 K.

4.4.2 BOMD simulations: Results

Table S45. Gasphase, M06-2X/6-31G*: BOMD results starting at the N₂-release TS of the norbornyl system **N**. Relative numbers are given in %, numbers in parenthesis are absolute numbers of BOMD simulations. Decision on the MD results: N⁺ trajectories are the ones that do not feature the nor-pinyll cation at any time during the simulation. Likewise, nor-pinyll cation trajectories are the ones that show the formation of the nor-pinyll-cation at least once.

#	final cationic structure	<i>endo-N-N₂⁺</i>		<i>exo-N-N₂⁺</i>	
		dissociation [%]	no dissociation [%]	dissociation [%]	no dissociation [%]
1		50 (25)	50 (25)	100 (50)	0 (0)
2	N⁺	32-40 (8-10)	-	100 (50)	-
3	nor-P⁺	60-68 (15-17)	-	0 (0)	-

Table S46. Gasphase, M06-2X/6-31G*: BOMD results starting at the N₂-release TS of the bornyl system **B**. Relative numbers are given in %, numbers in parenthesis are absolute numbers of BOMD simulations.

#	final cationic structure	<i>endo-B-N₂⁺</i>		<i>exo-B-N₂⁺</i>	
		dissociation [%]	no dissociation [%]	dissociation [%]	no dissociation [%]
1		30 (22)	70 (51)	88 (44)	12 (6)
2	B⁺	9 (2)	-	0 (0)	-
3	P⁺	82 (18)	-	0 (0)	-
4	C⁺	9 (2)	-	100 (44)	-

Table S47. Gasphase, M06-2X/6-31G*: BOMD results starting at the N₂-release TS of the fenchyl system **F**. Relative numbers are given in %, numbers in parenthesis are absolute numbers of BOMD simulations.

#	final cationic structure	<i>endo-F-N₂⁺</i>		<i>exo-F-N₂⁺</i>	
		dissociation [%]	no dissociation [%]	dissociation [%]	no dissociation [%]
1		88 (44)	12 (6)	68 (34)	32 (16)
2	F⁺	0	-	0	
3	P⁺	89 (39)	-	0	
4	C⁺	11 (5)	-	100 (34)	

5. NMR spectra of synthesized compounds

Figure S28 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of 11-N.

Figure S29 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of **11-B**.

Figure S30 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of 11-F.

Figure S32 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of *endo*-1-N.

Figure S34: ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of 1-F.

Figure S36 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of 5-N.

Figure S37 ¹H-NMR (upper) and ¹³C-NMR spectrum (lower) of **10**.