# Rationalizing the diverse reactivity of [1.1.1]propellane through σ-π-delocalization

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## Supporting Information

# 1. Computational Methods

## a. General methods

All calculations were carried out using the ORCA suite of programs (version 4.1.1).[1] Both optimizations and single-point energy calculations were carried out using "Tight" convergence criteria, corresponding to tolerances of $1.0 \times 10^{-8}$ Hartrees for the SCF energy change, and $1.0 \times 10^{-6}$ Hartrees for the optimization step. To speed up the calculations, the resolution-of-identity chain-of-spheres exchange (RIJCOSX) approximation was employed.[2] MP2 calculations were employed with the RI approximation as default for the calculation of correlation integrals. The integration grid "Grid5" was employed for DFT energies, corresponding to a Lebedev-434 angular grid, and a radial integral accuracy (IntAcc) of 5.01. Calculations employing a RI approximation utilized the "GridX6" procedure, corresponding to IntAcc = 4.34 and a Lebedev-194 angular grid. For calculations of triple-ζ basis set quality, calculation of correlation integrals used the def2-TZVP/C auxiliary basis set. All calculations using a quadruple-ζ basis set employed the AutoAux[3] procedure developed by Neese, which generates a large auxiliary basis set for the Coulomb, exchange and correlation integral calculations. Treatment of 28 core electrons with the def2 effective core potential (def2-ECP) was employed for iodine and tellurium.[4] All intermediate structures were verified to be minima by the absence of imaginary frequencies upon calculation of the Hessian. Grimme's quasi-RRHO approach was used to calculate free energies at 298.15 K. A 1 atm to 1 M standard state correction was applied by adding RTln(1/24.5) = 1.89 kcal mol $^{-1}$ to the calculated free energy of each species.[5] Persistent spurious imaginary frequencies for rotations below 35 cm$^{-1}$ in magnitude were ignored, as these correspond to a breakdown of the harmonic approximation.

The Domain-based Local Pair Natural Orbital coupled cluster method with singles, doubles and perturbative triples (DLPNO-CCSD(T)) was used as a benchmark for the potential energy surface.[6] DLPNO-CCSD(T) calculations were run using "NormalPNO" cut-offs,[7] corresponding to $T_{\text{CutPairs}} = 10^{-5}$ Hartrees, $T_{\text{CutPNO}} = 3.33 \times 10^{-7}$ and $T_{\text{CutMKN}} = 10^{-3}$, where $T_{\text{CutPairs}}$ is the correlation threshold for inclusion of a given electron pair in the CCSD calculation, $T_{\text{CutPNO}}$ is the occupation threshold for each PNO (pair natural orbital) formed from an expansion of projected atomic orbitals (PAOs), and $T_{\text{CutMKN}}$ determines the threshold for the inclusion of each localized MO in the PNO expansion based on Mulliken population.

To ensure the validity of this method, energies were also calculated at the CCSD(T)/(ma-)def2-SVP level of theory and compared to those obtained at the DLPNO-CCSD(T)/(ma-)def2-SVP level, and relative energy differences did not exceed 1 kcal mol$^{-1}$. Given the importance of static correlation in the electronic structure of [1.1.1]propellane, which was anticipated to change upon reaction, the $T_1$ diagnostic for each coupled-cluster calculation was monitored, and results for values exceeding 0.02 (for closed shell species) and 0.03 (for radical species) were discarded (see Tables S12–S14).[8] These discarded results only occurred in the dissociation limit of each system.

Dispersion corrections to DFT energies were implemented using Grimme's D3 empirical method with Becke-Johnson damping (D3BJ).[9,10] For ωB97X-D3, Chai's bespoke reparameterization of Grimme's D3 correction was used.[11] The performance of double-hybrid density functionals (*e.g.* B2PLYP, B2GP-PLYP, PWPB95) is known to suffer in instances of significant static correlation, so in this work DSD (Double-hybrid, Spin-component scaled, Dispersion corrected) functionals were also tested for selected properties. These methods use the spin-component scaled (SCS) method for the calculation of MP2-like correlation, which treats same- and opposite-spin correlation energies differently to account for the difference in the origins of short- and long-range correlation. However, we found no uniform improvement between standard and DSD double-hybrid density functionals in the systems tested here.

### b. Static and dynamic correlation

Electron correlation effects are commonly divided into dynamic correlation, which describes the spatial interactions between electrons, and static correlation, that comes from the contribution of near-degenerate electronic states to the overall ground state electronic structure of the molecule.[12] The DFT exchange-correlation functional ($E_{\mathrm{XC}}$) accounts for dynamic correlation effects, but the use of an inexact form of the functional results in the non-physical self-interaction error, where the electron can repel itself. To minimize this error, exact (HF) exchange can be mixed with $E_{\mathrm{XC}}$ (hybrid DFT), and a further perturbative (MP2-like) correction allows a more accurate treatment of non-local correlation (double-hybrid DFT). However, despite significant advances in the development of new density functionals,[13] the treatment of static correlation remains challenging. This is particularly important in systems where substantial mixing of configurations occurs (*e.g.* due to a small HOMO-LUMO gap), and standard methods result in spurious geometries and calculated properties.[12]

An alternative approach for the treatment of correlation effects comes from wavefunction theory (WFT). In contrast with DFT, HF theory does not include correlation between electrons with opposite spins, and as a result electron density is overlocalized. To correct for this error, post-HF methods such as Møller-Plesset perturbation theory and coupled cluster methods include excitations into virtual (unoccupied) orbitals to describe correlation effects. However, these approaches break down if static correlation plays an important role in the description of the system; a single HF wavefunction cannot adequately describe the electronic structure, and post-HF corrections cannot improve upon this. In these cases, a linear combination of electronic configurations can be used as a reference. In the exact limit, all orbitals are optimized to minimize the electronic energy with respect to all possible electronic configurations (full configuration interaction, FCI). However, due to the exponential scaling of FCI, this method can only be applied to small systems (~20 electrons).

Alternatively, static correlation effects can be accounted for using the complete active space self-consistent field (CASSCF) method. In CASSCF, the orbital space is divided into three subspaces: an active space within which all possible occupations are considered, an inactive space where all orbitals are doubly occupied and treated self-consistently (*i.e.* as in HF), and a virtual space where all orbitals are unoccupied. Dynamic correlation is then included by subsequent multi-reference perturbative corrections (*e.g.* CASPT2,[14] NEVPT2[15]) or truncated CI methods (configuration interaction, *e.g.* MRCI)[16].

## 2. Benchmarking the structure and reactivity of [1.1.1]propellane

### Wavefunction-based methods

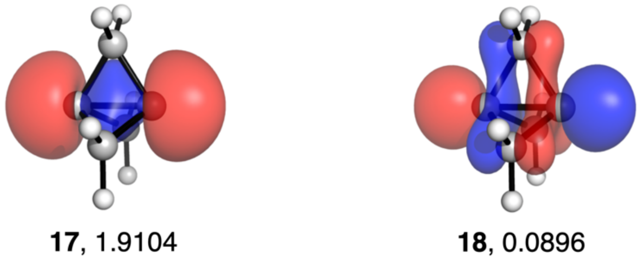
Single-reference methods that do not account for static correlation might ordinarily be expected to be sufficient for the description of [1.1.1]propellane (**1**), given that the calculated HOMO-LUMO gap is 13.0 eV (HF/def2-QZVPP). In 'normal' closed-shell organic molecules (e.g. ethane), only a small correction to the single determinant energy is required to describe the electronic interactions not accounted for by HF theory. However, the significant Pauli repulsion pressure exerted by the wing bonds to the electrons localised along central C–C axis requires an explicit treatment of electron correlation. CASSCF with two electrons in two orbitals (HOMO and LUMO) provides an improved description of the correlation of the electrons in the inter-bridgehead C–C bond with respect to the electrons in the rest of the molecule. These results agree with the work of Shaik and co-workers in the description of the inter-bridgehead C–C bond in [1.1.1]propellane as a 'charge-shift' bond.[17,18]

## Ground-state electronic structure of [1.1.1]propellane

Complete active space (CAS) calculations were carried out using the large def2-QZVPP basis set for cations and radicals, and the minimally-augmented ma-def2-QZVPP basis set for anions. Despite the enhanced performance of the atomic natural orbital (ANO) class of basis sets for the same number of basis functions, we did not consider their use here due to the prohibitively slow optimization procedures.

Each active space was constructed as a pair of bonding and antibonding MOs, where orbitals with an occupancy of $> 1.98$ or $< 0.02$ were not considered to provide important configurations to the active space composition (Fig. S14).

(2,2) active space:



(6,6) active space:

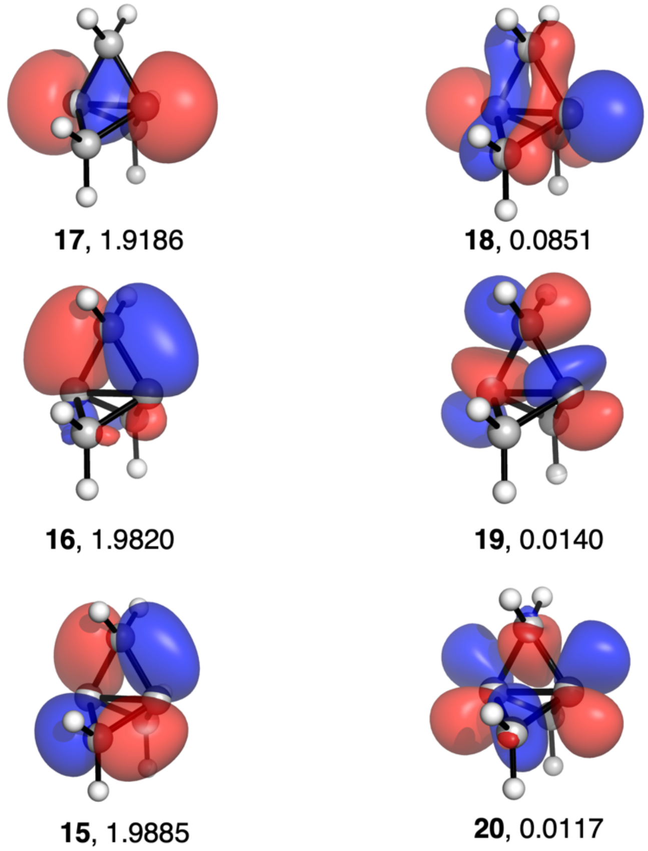


**Figure S1**. Active MOs and occupancies for [1.1.1]propellane, calculated at: **a.** CASSCF(2,2)/def2-QZVPP and **b.** CASSCF(6,6)/def2-QZVPP. Isovalue = 0.05.

## CASSCF active space comparison

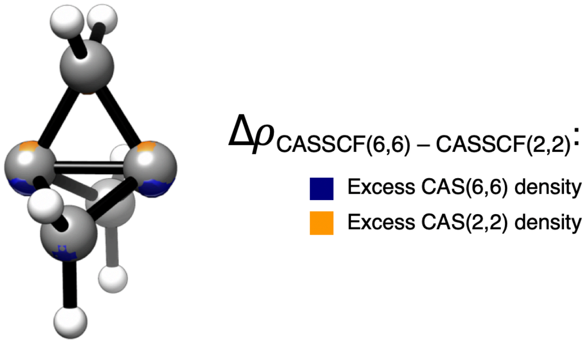


**Figure S2.** Density difference plot for CASSCF(2,2) – CASSCF(6,6) with a def2-QZVPP basis set. Isovalue = 0.01.

## Fractional occupation number weighted density (FOD) analysis

Grimme's implementation of FOD uses Fermi statistics to obtain fractional occupations of Kohn-Sham MOs.[19] This procedure results in a visual representation of areas of enhanced static correlation, and has been calculated in this work for [1.1.1]propellane. Important regions can be seen in yellow, and a comparison between [1.1.1]propellane, (**a**) and BCP (**b**) shows the loss of these correlation effects upon disruption of the $C_1$–$C_3$ bond.

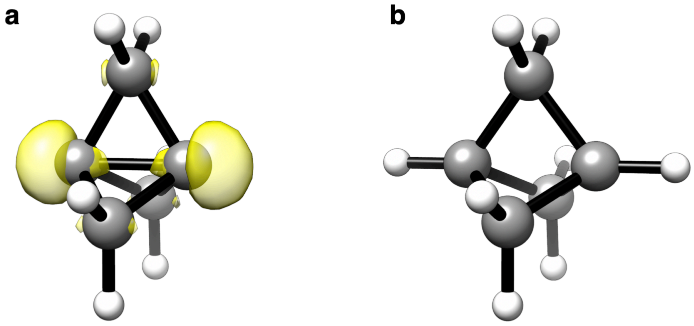


**Figure S3.** FOD plots[19,20] showing regions of localized static correlation for [1.1.1]propellane (**a**) and bicyclo[1.1.1]pentane (**b**), calculated at M06-2X/def2-TZVP ($T_{smear}$ = 15800 K) and plotted at $\sigma = 0.002$ e Bohr$^{-3}$.

## Comparison of Localized and Delocalized MOs for the Description of [1.1.1]Propellane

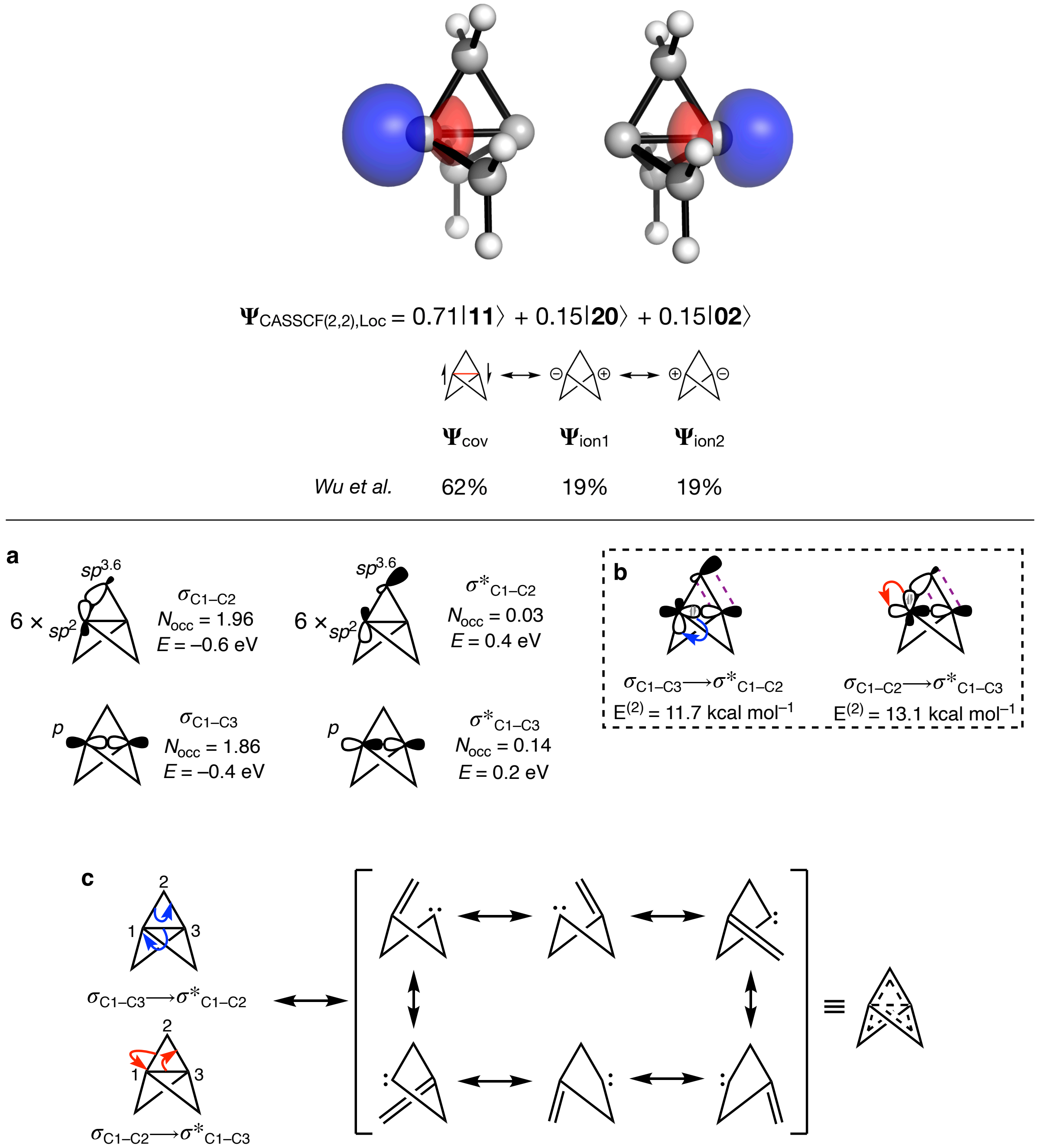


**Figure S4. Top:** Localized MOs (generated with orca_loc) for CASSCF(2,2)/def2-QZVPP (isovalue = 0.05) and the CI coefficients for the $S_0$ state, compared with BOVB/6-31G* calculations by Wu *et al.*[17] |**11**⟩ denotes the covalent contribution to the wavefunction, and |**20**⟩ / |**02**⟩ denote the two ionic contributions. **Bottom: a.** Localized MO representation of [1.1.1]propellane including orbital population ($N_{\mathrm{occ}}$) and energy calculated at the NBO/B2GP-PLYP-D3BJ/def2-TZVP level of theory. **b.** Second-order perturbation theory analysis of the Fock matrix using NBO, calculated at the same level of theory. Dashed purple lines show π-symmetry overlap. **c.** Resonance forms of [1.1.1]propellane showing the delocalization of the C1–C3 bond over the propellane cage.

## Cationic reactivity with [1.1.1]propellane: CASSCF(2,3)/def2-QZVPP

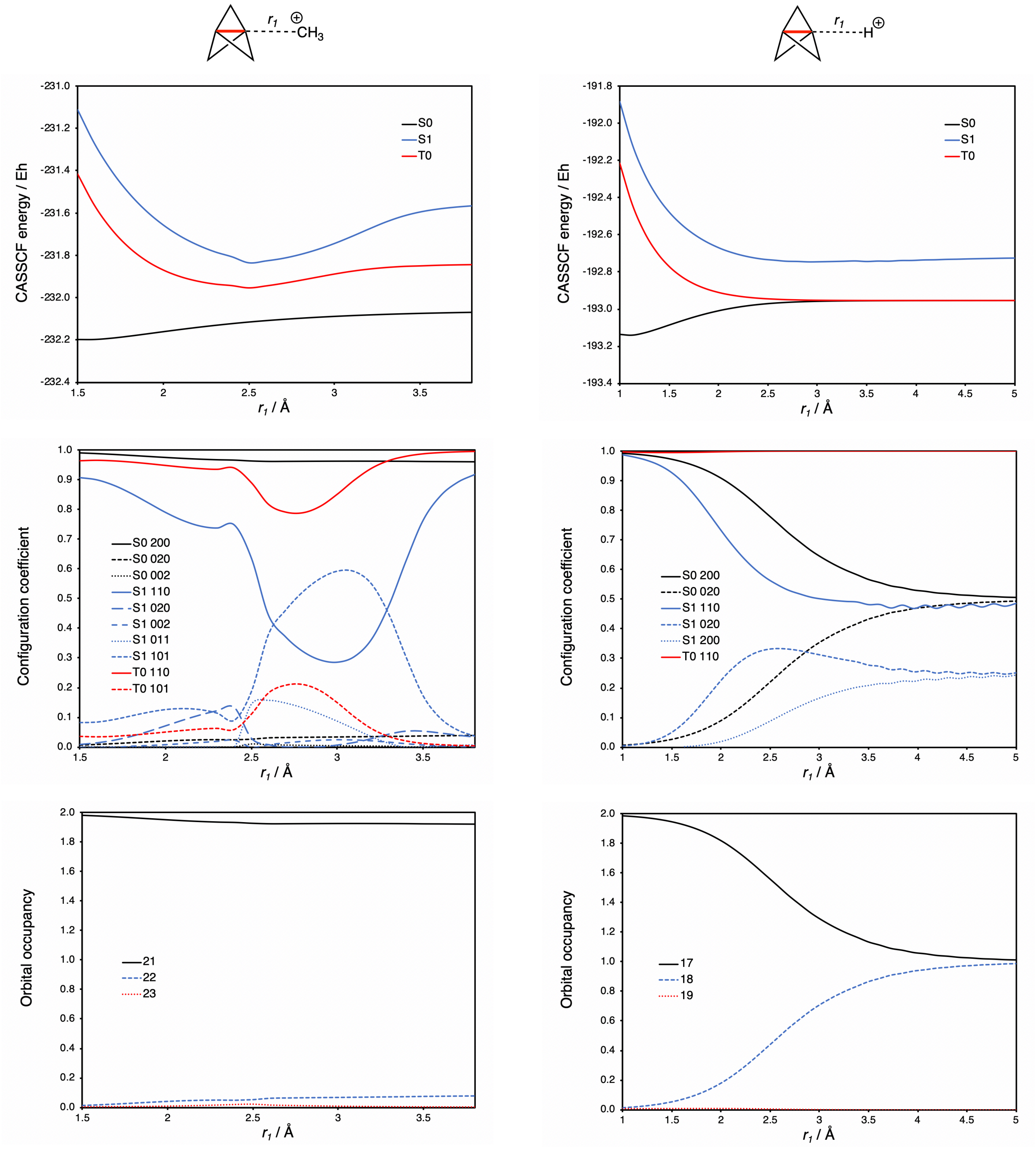


**Figure S5. Left:** Top: CASSCF(2,3)/def2-QZVPP energies for methyl cation addition to [1.1.1]propellane. Middle: Active space composition for each the $S_0$, $S_1$ and $T_0$ states as a function of $r_1$. Bottom: Occupancy of each MO in the active space as a function of $r_1$. **Right:** Top: CASSCF(2,3)/def2-QZVPP energies for proton addition to [1.1.1]propellane. Middle: Active space composition for each the $S_0$, $S_1$ and $T_0$ states as a function of $r_1$. Bottom: Occupancy of each MO in the active space as a function of $r_1$.

## Radical reactivity with [1.1.1]propellane: CASSCF(3,3)/def2-QZVPP

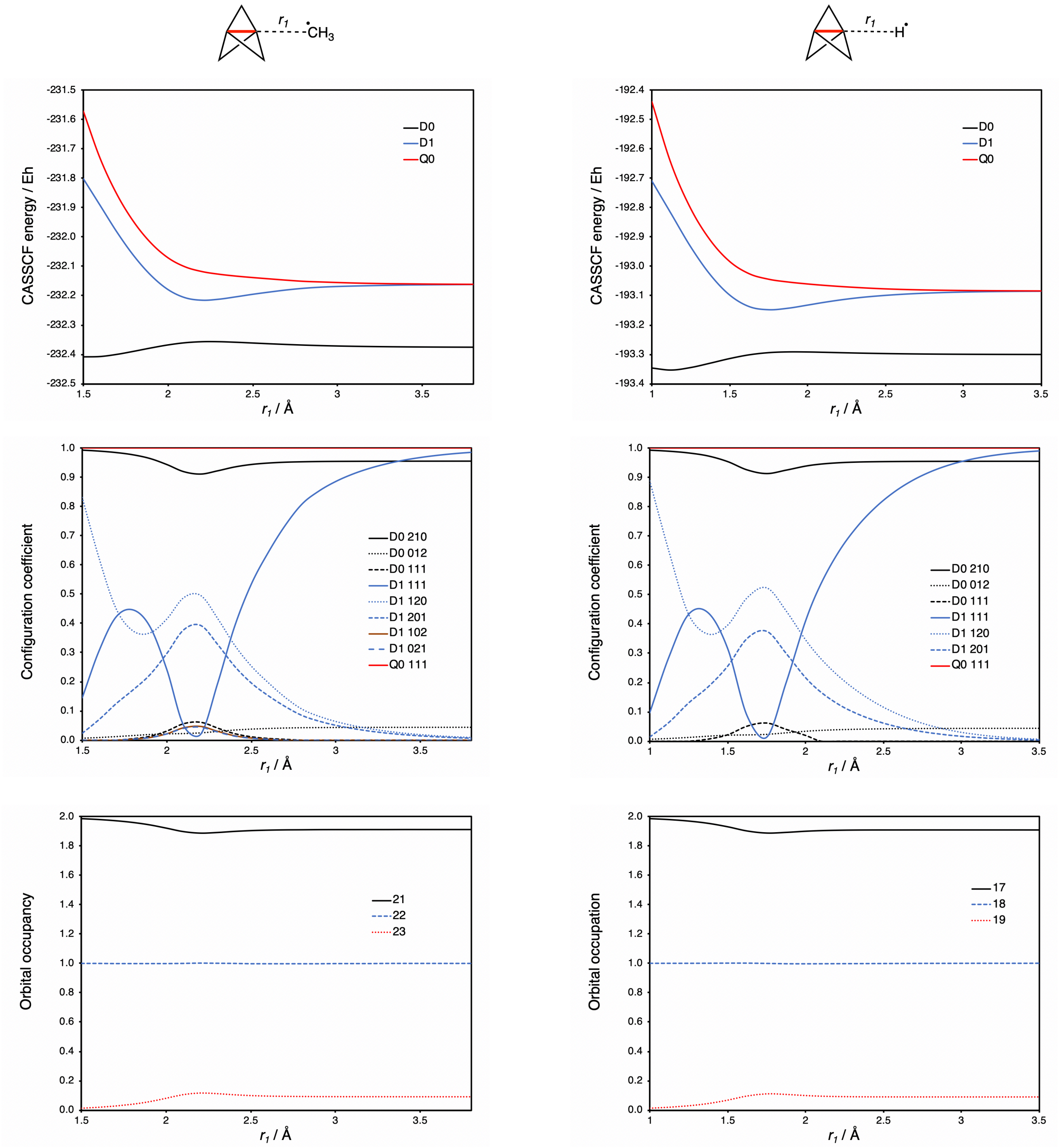


**Figure S6. Left:** Top: CASSCF(3,3)/def2-QZVPP energies for $CH_3^•$ addition to [1.1.1]propellane. Middle: Active space composition for each the $D_0$, $D_1$ and $Q_0$ states as a function of $r_1$. Bottom: Occupancy of each MO in the active space as a function of $r_1$. **Right:** Top: CASSCF(3,3)/def2-QZVPP energies for $H^•$ addition to [1.1.1]propellane. Middle: Active space composition for each the $D_0$, $D_1$ and $Q_0$ states as a function of $r_1$. Bottom: Occupancy of each MO in the active space as a function of $r_1$.

## Anionic addition with [1.1.1]propellane: CASSCF(4,3)/ma-def2-QZVPP

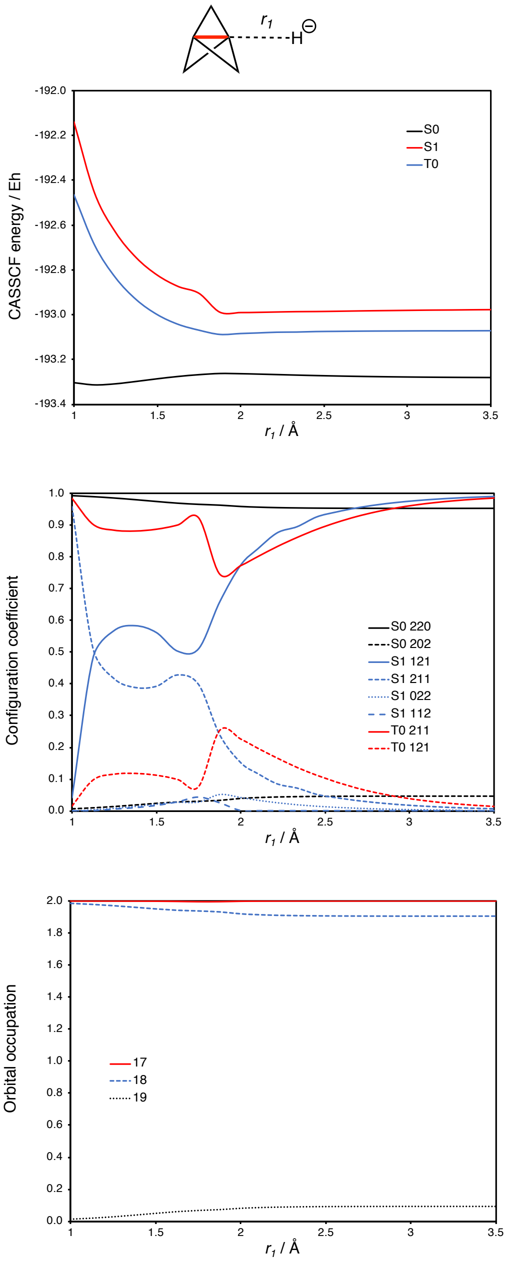


**Figure S7.** Top: CASSCF(4,3)/ma-def2-QZVPP energies for $H^-$ addition to [1.1.1]propellane. Middle: Active space composition for each the $S_0$, $S_1$ and $T_0$ states as a function of $r_1$. Bottom: Occupancy of each MO in the active space as a function of $r_1$.

## Partial atomic charges for anionic, radical and cationic addition reactions

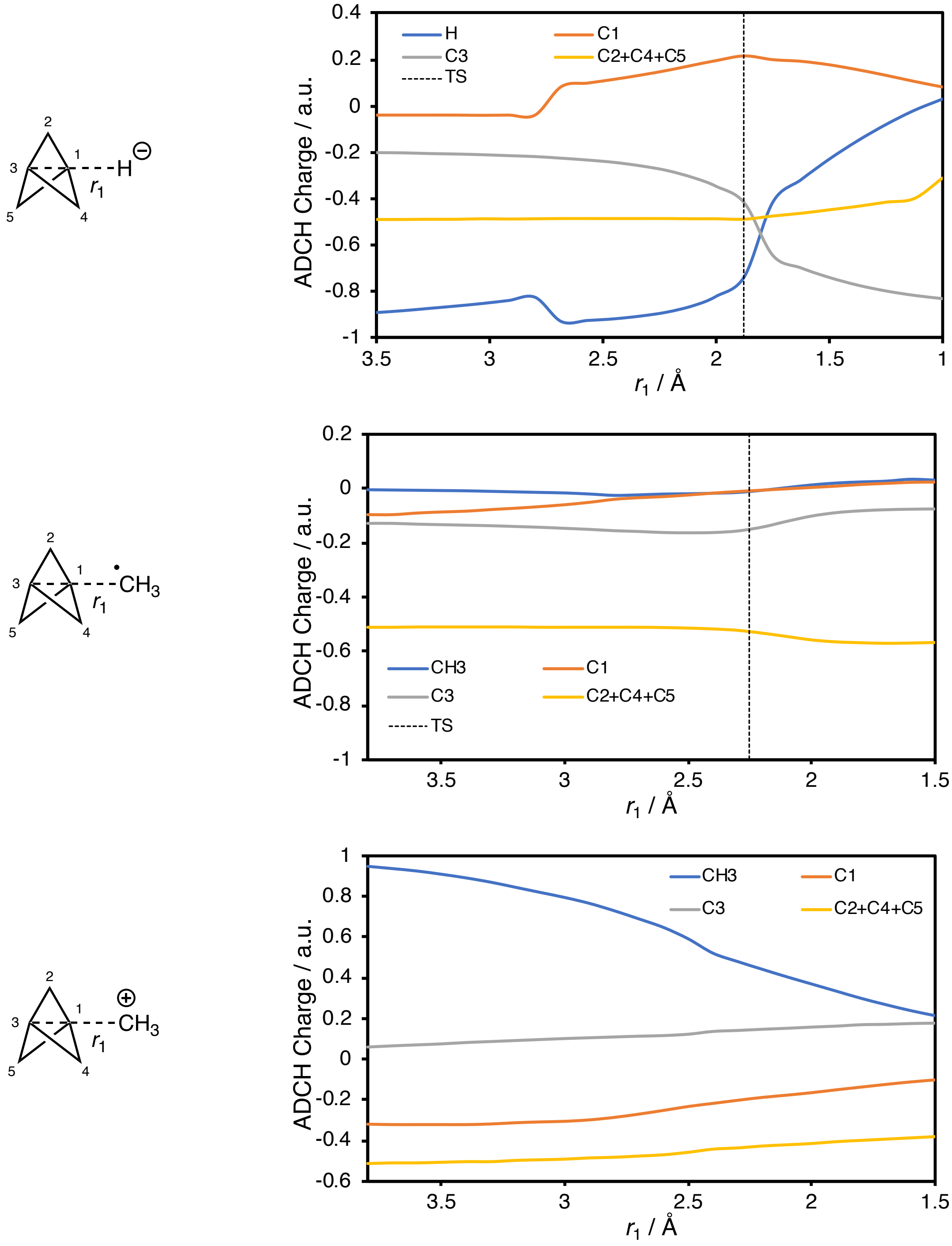


**Figure S8.** Atomic Dipole-moment Corrected Hirshfeld (ADCH) charges for the addition of $H^-$ (top), $CH_3^\bullet$ (middle) and $CH_3^+$ (bottom) to [1.1.1]propellane as a function of the forming bond distance $r_1$ (in Å). Calculations were carried out at the CASSCF($n$,3)/def2-QZVPP ($n$ = 2, 3 and 4 for $CH_3^+$, $CH_3^\bullet$ and $H^-$ respectively, ma-def2-QZVPP for $H^-$) level of theory.

## Second-order perturbation theory analysis for anionic, radical and cationic additions

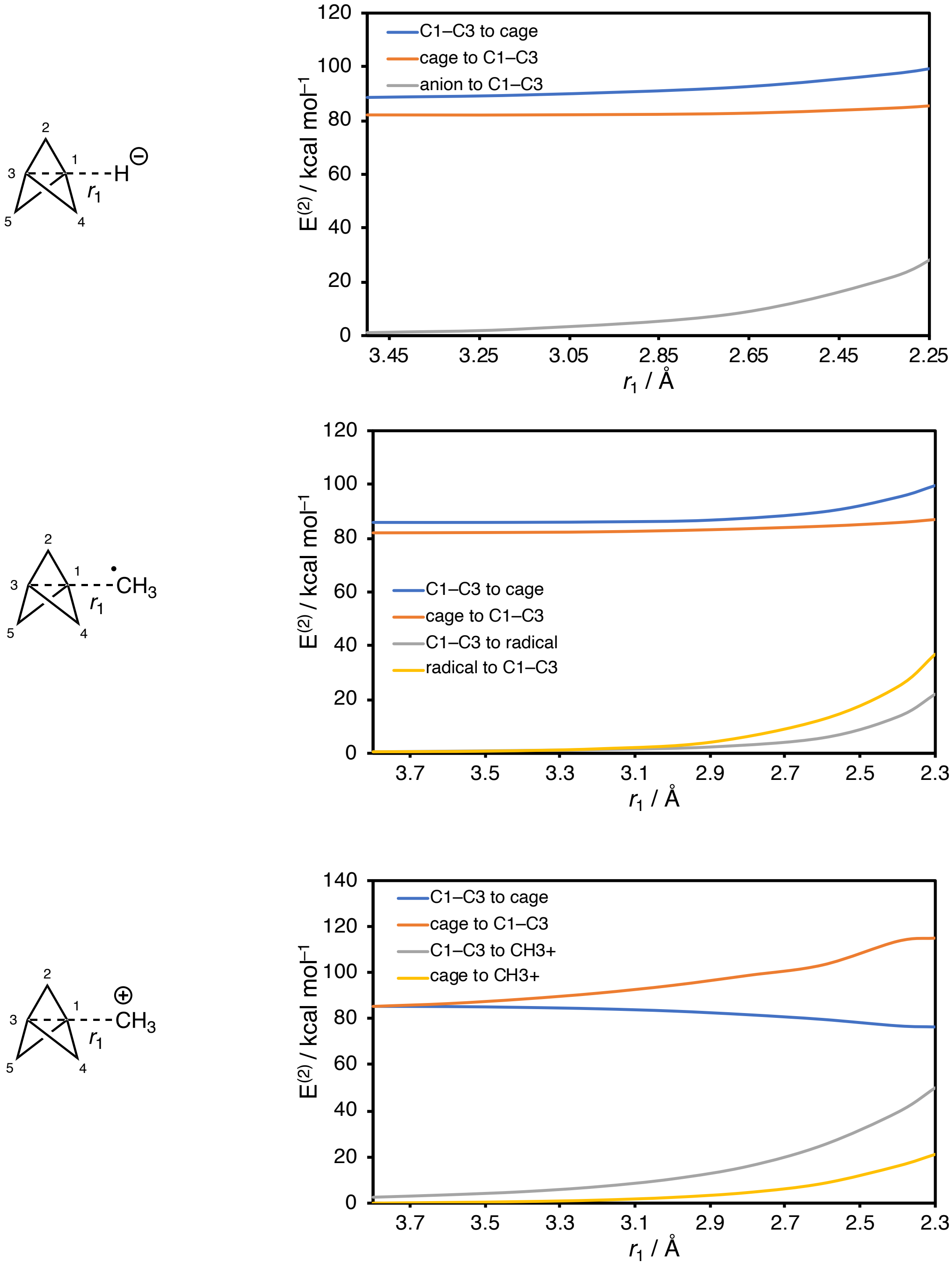


**Figure S9.** Second-order perturbation theory analysis of the Fock matrix generated using natural bonding orbitals (NBOs) for the addition of $H^-$ (top), $CH_3^{\bullet}$ (middle) and $CH_3^+$ (bottom) to [1.1.1]propellane as a function of the forming bond distance $r_1$ (in Å). Calculations were carried out at the [NBO/SMD(*solvent*)-B2GP-PLYP-D3BJ/def2-TZVP//CASSCF($n$,3)/def2-QZVPP (*solvent* = THF (anionic), $Et_2O$ (radical / cation); $n$ = 2, 3 and 4 for $CH_3^+$, $CH_3^{\bullet}$ and $H^-$ respectively, ma-def2-QZVPP for $H^-$)] level of theory.

## DLPNO-CCSD(T) benchmark vs CCSD(T)

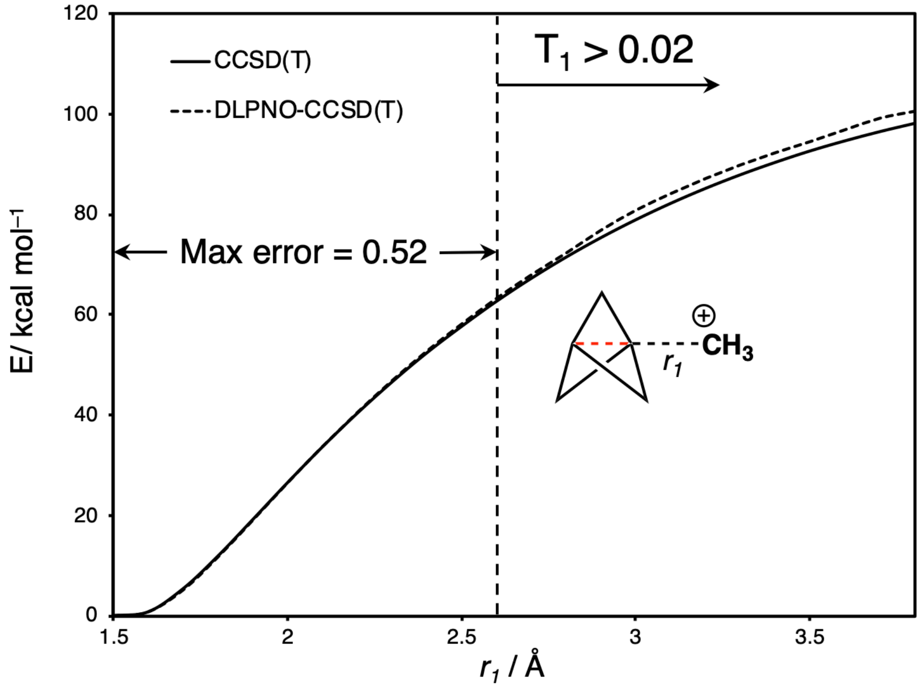


**Figure S10.** Comparison of DLPNO-CCSD(T)/def2-SVP and CCSD(T)/def2-SVP energies for the methyl cation addition to [1.1.1]propellane, using a def2-SVP basis set and CASSCF(2,3)/def2-QZVPP geometries. Max error represents maximum absolute deviation of DLPNO-CCSD(T) from CCSD(T). Error (in kcal mol$^{-1}$) increases after $r_1$ ~ 2.6 Å, as $T_1$ diagnostic exceeds 0.02.

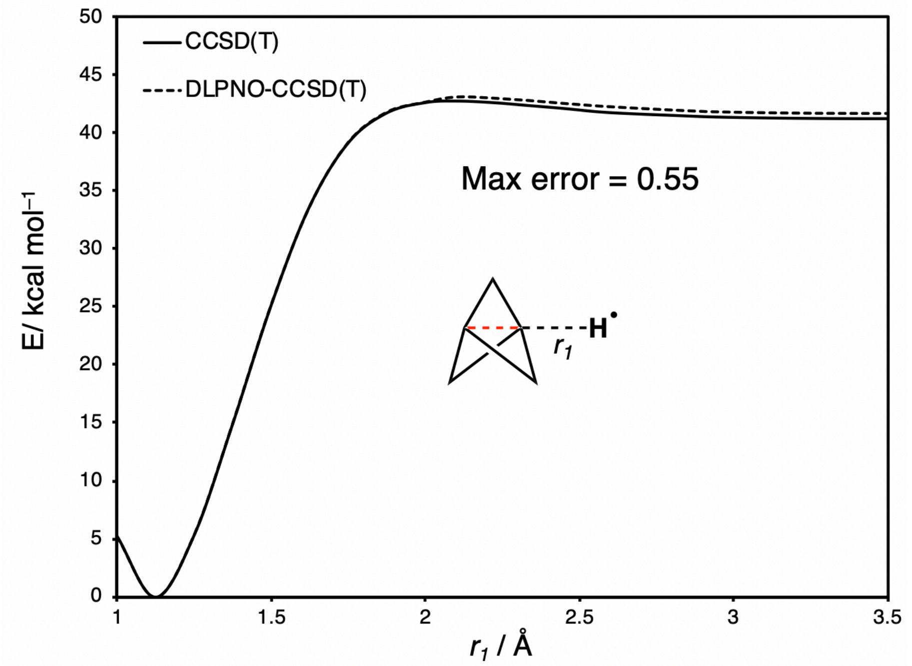


**Figure S11.** Comparison of DLPNO-CCSD(T)/def2-SVP and CCSD(T)/def2-SVP energies for the hydrogen atom addition to [1.1.1]propellane, using a def2-SVP basis set and CASSCF(3,3)/def2-QZVPP geometries. Error in kcal mol$^{-1}$. Max error represents maximum absolute deviation of DLPNO-CCSD(T) from CCSD(T). $T_1$ diagnostic does not exceed 0.03.

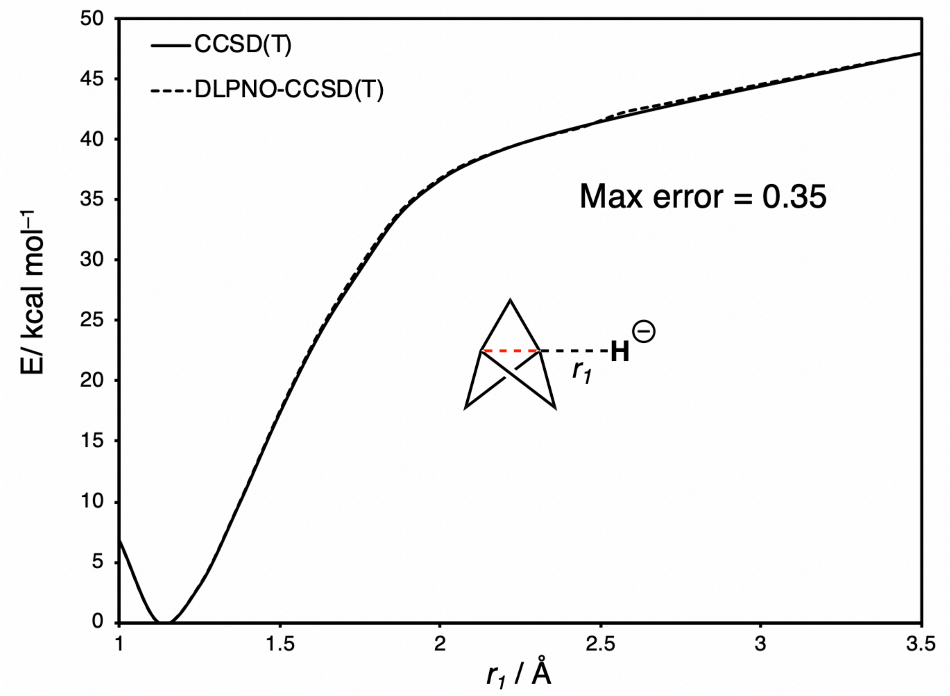


**Figure S12.** Comparison of DLPNO-CCSD(T)/ma-def2-SVP and CCSD(T)/ma-def2-SVP energies for the hydride addition to [1.1.1]propellane. Error in kcal mol$^{-1}$. Max error represents maximum absolute deviation of DLPNO-CCSD(T) from CCSD(T). $T_1$ diagnostic does not exceed 0.02.

### a. Suitability of DFT for the description of the ground state of [1.1.1]propellane

Given the inherent complexity and computational cost associated with CAS calculations, we investigated whether DFT could accurately reproduce investigations on the reactivity of [1.1.1]propellane, which have up to now have solely employed DFT approaches. Geometry optimization using three classes of density functionals (GGA, hybrid GGA and double-hybrid GGA) revealed that BLYP[21,22] (GGA) provided an excellent agreement with the experimental $C_1$–$C_3$ distance[23] (**Fig. S1a**, left), while the inclusion of (20%) HF exchange with B3LYP[24] significantly underestimated this bond length. Moving to the double-hybrid density functional B2PLYP[25] appeared to compensate for this error by including virtual orbitals that allowed electron delocalization to occur, resulting in a decrease in error despite a high proportion of HF exchange in the functional (53%). These findings explained the excellent geometry from MP2 itself, which was also noted by Schreiner.[26]

To test whether these results translated into the electronic properties of [1.1.1]propellane, the singlet triplet gap ($S_0 \rightarrow T_0$) and the ionization potential were calculated employing the aforementioned functionals. The $S_0 \rightarrow T_0$ gap was calculated at a range of $C_1$–$C_3$ distances (1.54 Å – 2.00 Å), to capture long- and short-range electronic effects (**Fig. S1a**, middle). As before, pure DFT (BLYP) performed favorably compared with hybrid DFT (B3LYP); however, inclusion of MP2-like correlation in the functional (B2PLYP) markedly reduced the calculated error. Vertical ionization potentials also yielded similar results (**Fig. S1a**, right). From these three tests, it became clear that electron delocalization through population of virtual orbitals (*i.e.* correlation) had a significant impact on the electronic structure of [1.1.1]propellane.

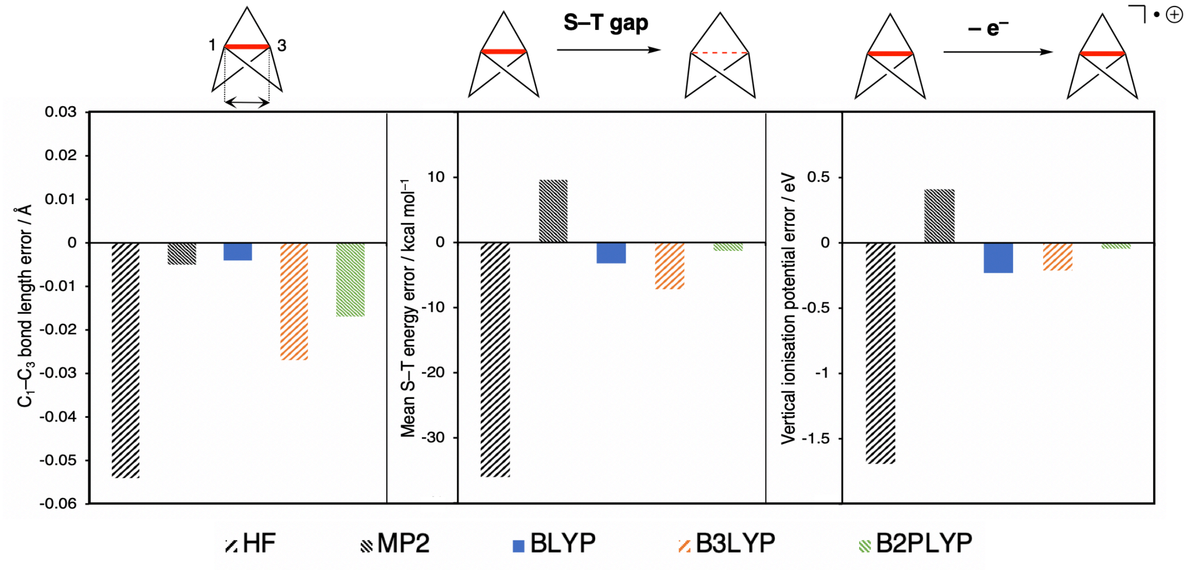


**Figure S13.** Left: Deviation of $C_1$–$C_3$ bond length of [1.1.1]propellane at each level of theory (def2-QZVPP basis set) from the experimental value[23] of 1.594 Å; middle: Average deviation of vertical $S_0 \rightarrow T_0$ transitions of [1.1.1]propellane at $C_1$–$C_3$ distances ranging from 1.54 to 2.00 Å (0.05 Å intervals) at each level of theory, geometries optimized at the CASSCF(2,2)/def2-QZVPP level of theory; right: Vertical ionization potentials (eV) at each level of theory.

Expanding the range of functionals under study shows that the results obtained in the analysis of BLYP, B3LYP and B2PLYP are generally true. The best-performing functionals were double-hybrids, with B2GP-PLYP and DSD-PBEB95 achieving near-chemical accuracy. We suggest that B2GP-PLYP should be used to describe geometries over DSD-PBEB95 as the latter showed instability for optimisation. Despite the very poor geometry calculated with M06-2X the singlet-triplet and ionization potential errors were surprisingly small.

### $C_1$–$C_3$ bond length error for [1.1.1]propellane

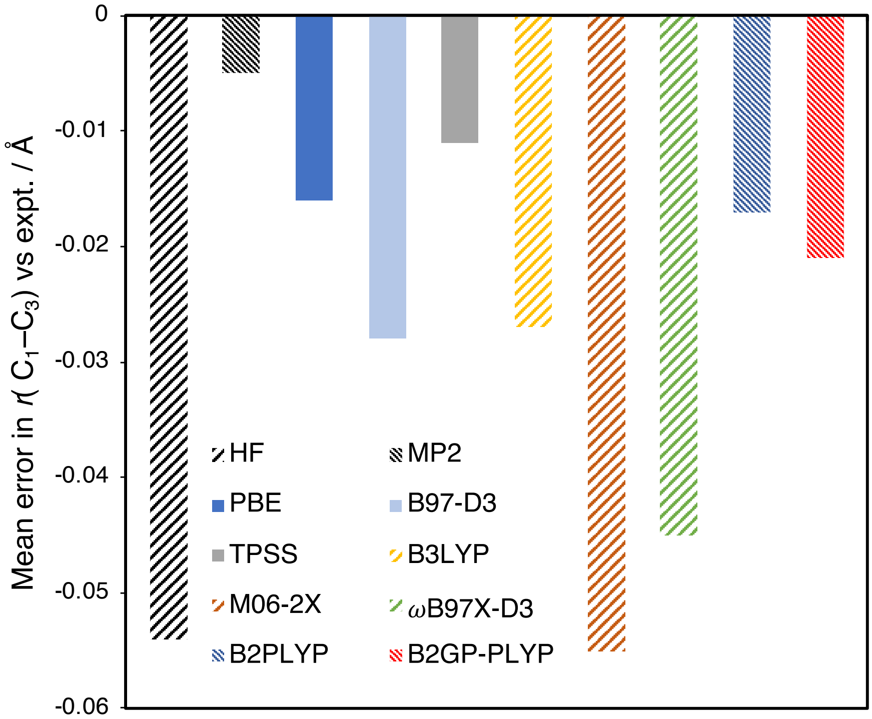


**Figure S14.** Comparison of $C_1$–$C_3$ bond lengths for [1.1.1]propellane vs value obtained via gas-phase electron diffraction (1.594 Å). All values in Å, using a def2-QZVPP basis set.

**Table S1.** Error in $C_1$–$C_3$ bond lengths vs value obtained via gas-phase electron diffraction (1.594 Å).

| Method | DFT Class | Error / Å |
|---|---|---|
| MP2 | - | -0.005 |
| HF | - | -0.054 |
| PBE | GGA | -0.016 |
| B97-D3 | GGA | -0.028 |
| TPSS | Meta-GGA | -0.011 |
| B3LYP | Single-hybrid GGA | -0.027 |
| M06-2X | Meta-single-hybrid GGA | -0.055 |
| ωB97X-D3 | Range-separated hybrid | -0.045 |
| B2PLYP | Double-hybrid | -0.017 |
| B2GP-PLYP | Double-hybrid | -0.021 |
| Expt. (gas-phase electron diffraction) |  | 1.594 |

## Error in singlet-triplet transition energies for [1.1.1]propellane

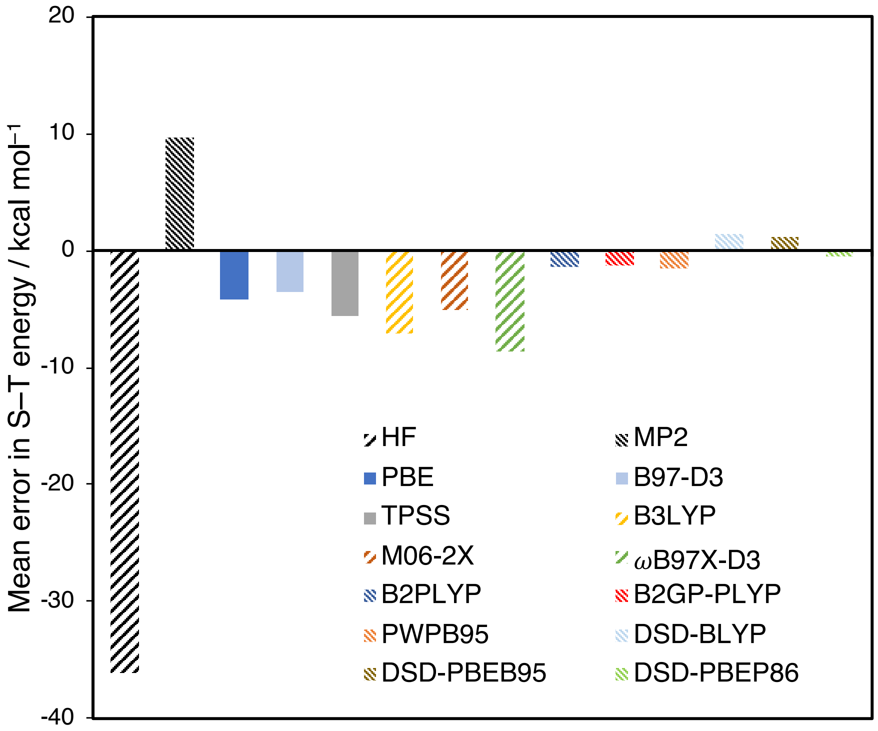


**Figure S15.** Comparison of vertical singlet-triplet energy gaps in the range r($C_1$–$C_3$) = 1.54 – 2.00 Å (0.05 Å intervals), vs DLPNO-CCSD(T). All calculations used a def2-QZVPP basis set.

**Table S2.** Error in vertical singlet-triplet energy gaps vs DLPNO-CCSD(T).

| **Method** | **DFT Class** | **Mean error / kcal mol$^{-1}$** |
|---|---|---|
| HF | - | -36.1 |
| MP2 | - | 9.7 |
| PBE | GGA | -4.1 |
| B97-D3 | GGA | -3.6 |
| TPSS | Meta-GGA | -5.5 |
| B3LYP | Single-hybrid GGA | -7.1 |
| M06-2X | Meta-single-hybrid GGA | -5.0 |
| ωB97X-D3 | Range-separated hybrid | -8.7 |
| B2PLYP | Double-hybrid | -1.3 |
| B2GP-PLYP | Double-hybrid | -1.2 |
| PWPB95 | Double-hybrid | -1.5 |
| DSD-BLYP | SCS-corrected double-hybrid | 1.4 |
| DSD-PBEB95 | SCS-corrected double-hybrid | 1.2 |
| DSD-PBEP86 | SCS-corrected double-hybrid | -0.5 |
| Reference value (DLPNO-CCSD(T)) | | 111.4 (at 1.59 Å) |

**First ionization potential error for [1.1.1]propellane**

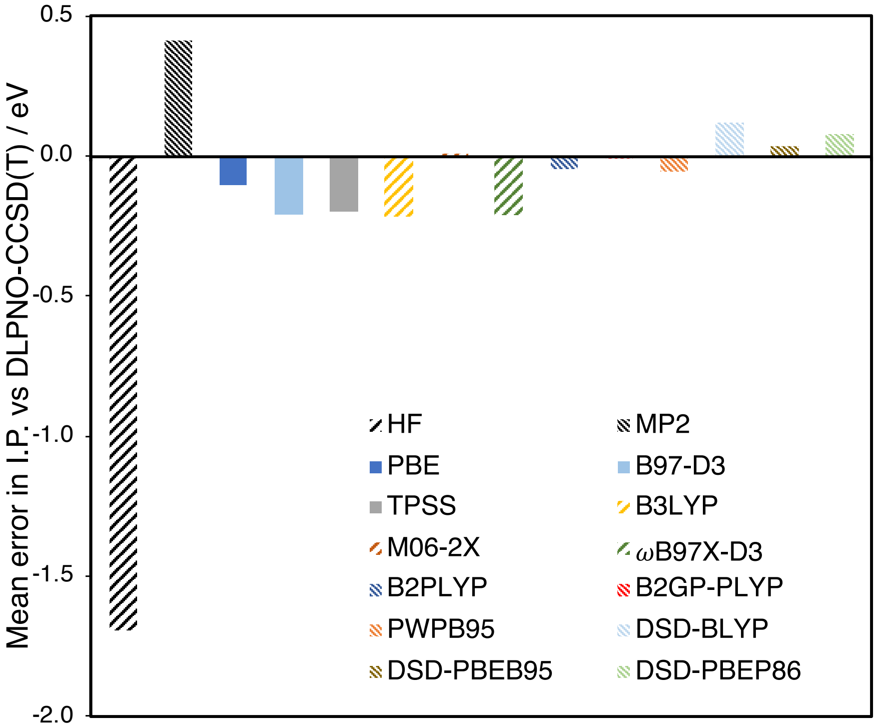


**Figure S16.** Comparison of calculated first vertical ionization potentials for [1.1.1]propellane vs DLPNO-CCSD(T). All calculations used a def2-QZVPP basis set at the CASSCF(2,2)/def2-QZVPP geometry.

**Table S3.** Error in first vertical ionization potentials vs DLPNO-CCSD(T).

| **Method** | **DFT Class** | **Error / eV** |
|---|---|---|
| HF | - | -1.69 |
| MP2 | - | 0.41 |
| PBE | GGA | -0.10 |
| B97-D3 | GGA | -0.21 |
| TPSS | Meta-GGA | -0.20 |
| B3LYP | Single-hybrid GGA | -0.21 |
| M06-2X | Meta-single-hybrid GGA | 0.01 |
| ωB97X-D3 | Range-separated hybrid | -0.21 |
| B2PLYP | Double-hybrid | -0.04 |
| B2GP-PLYP | Double-hybrid | -0.01 |
| PWPB95 | Double-hybrid | -0.06 |
| DSD-BLYP | SCS-corrected double-hybrid | 0.12 |
| DSD-PBEB95 | SCS-corrected double-hybrid | 0.03 |
| DSD-PBEP86 | SCS-corrected double-hybrid | 0.08 |
| Reference value (DLPNO-CCSD(T)) | | 9.85 |

## b. Suitability of DFT for the description of the reactivity of [1.1.1]propellane

The suitability of DFT to describe the reactivity of [1.1.1]propellane was next tested to ensure that good performance for the ground state was also seen for the entire potential energy surface (PES). To obtain accurate transition states for the description of the kinetics of addition, we suggest that the difference between the PESs calculated at a given method and DLPNO-CCSD(T) should be minimized, such that the mean absolute error (MAE) does not exceed 1 kcal mol$^{-1}$ (i.e. chemical accuracy). In addition, the maximum energy difference between the two PESs should be minimized. Geometries were obtained from a relaxed scan of the addition of H$^{\bullet}$ [CASSCF(3,3)/def2-QZVPP], H$^{-}$ [CASSCF(4,3)/ma-def2-QZVPP] and $CH_3^+$ [CASSCF(2,3)/def2-QZVPP] to [1.1.1]propellane. The zero-point of each potential energy surface was taken as the energy of the global minimum energy point on the PES calculated at DLPNO-CCSD(T)/(ma-)def2-QZVPP//CASSCF($n$,3)/(ma-)def2-QZVPP.

- Radical reactivity was found to be highly dependent on the level of theory employed. B2PLYP, B2GP-PLYP (with and without D3BJ) and PWPB95 were the only functionals to achieve 1 kcal mol$^{-1}$ accuracy with a reasonable maximum error.
- Anionic reactivity was much less sensitive to the level of theory employed; $\omega$B97X-D3 provided chemical accuracy and is therefore a cheaper alternative to double-hybrid DFT. All double-hybrid DFT methods tested (except PWPB95) achieved near-chemical accuracy.
- Cationic reactivity was well-described by M06-2X, B2GP-PLYP-D3BJ, and the DSD-corrected double-hybrid funcionals.

## Radical PES

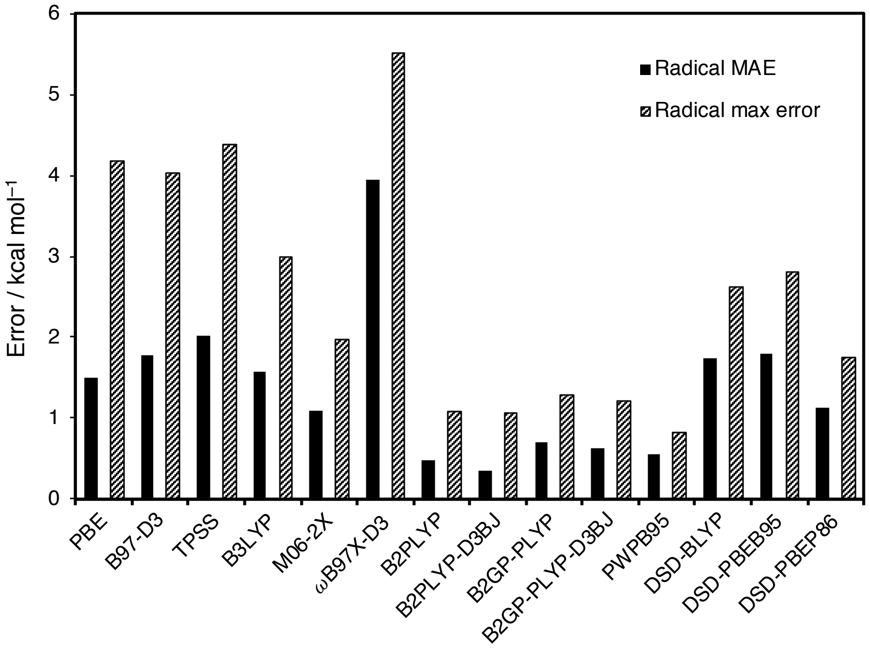


**Figure S17.** Mean absolute error (black) and maximum error (shaded) for the addition of a hydrogen atom to [1.1.1]propellane, relative to DLPNO-CCSD(T) energies. All calculations using a def2-QZVPP basis set, at CASSCF(3,3)/def2-QZVPP geometries.

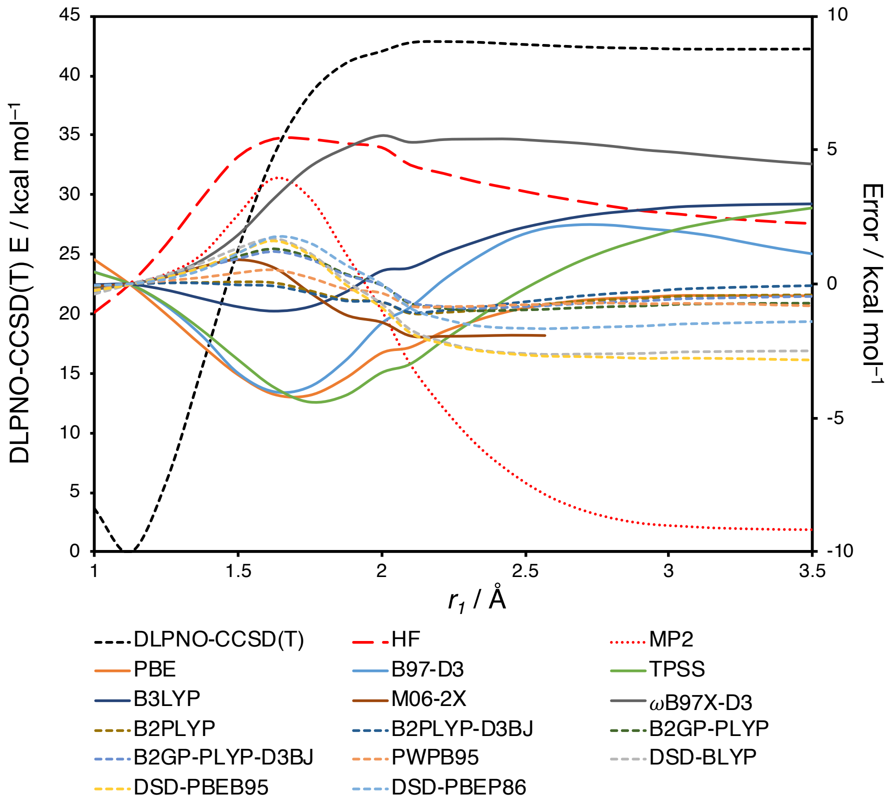


**Figure S18.** DLPNO-CCSD(T) energies for the addition of a hydrogen atom to [1.1.1]propellane (black dashes), and the error in each method vs DLPNO-CCSD(T) as a function of $r_1$. Convergence failures for M06-2X result in incomplete data.

## Anionic PES

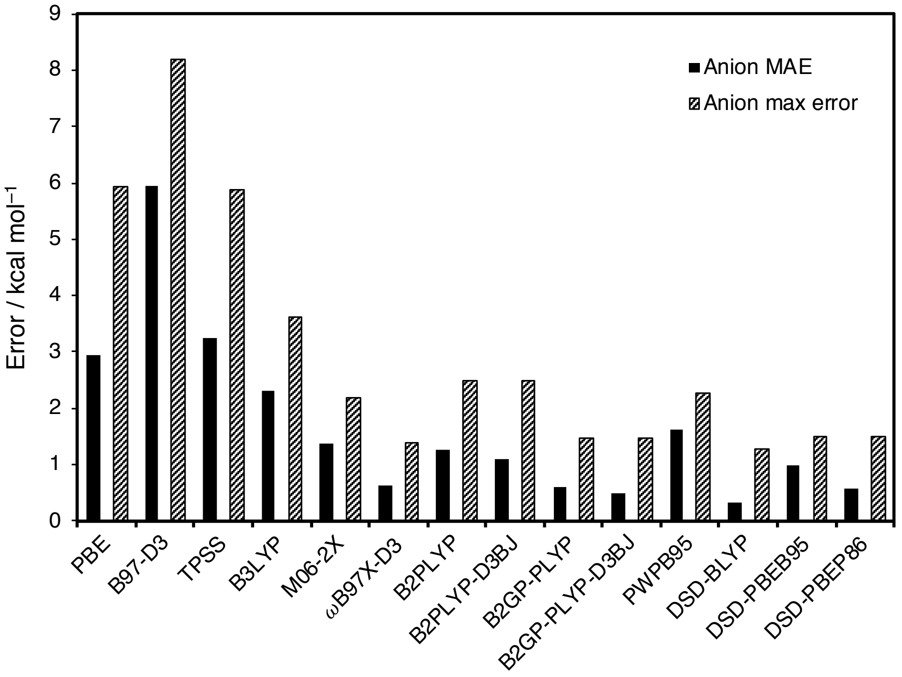


**Figure S19.** Mean absolute error (black) and maximum error (shaded) for the addition of a hydride to [1.1.1]propellane, relative to DLPNO-CCSD(T) energies. All calculations using a ma-def2-QZVPP basis set, at CASSCF(4,3)/ma-def2-QZVPP geometries.

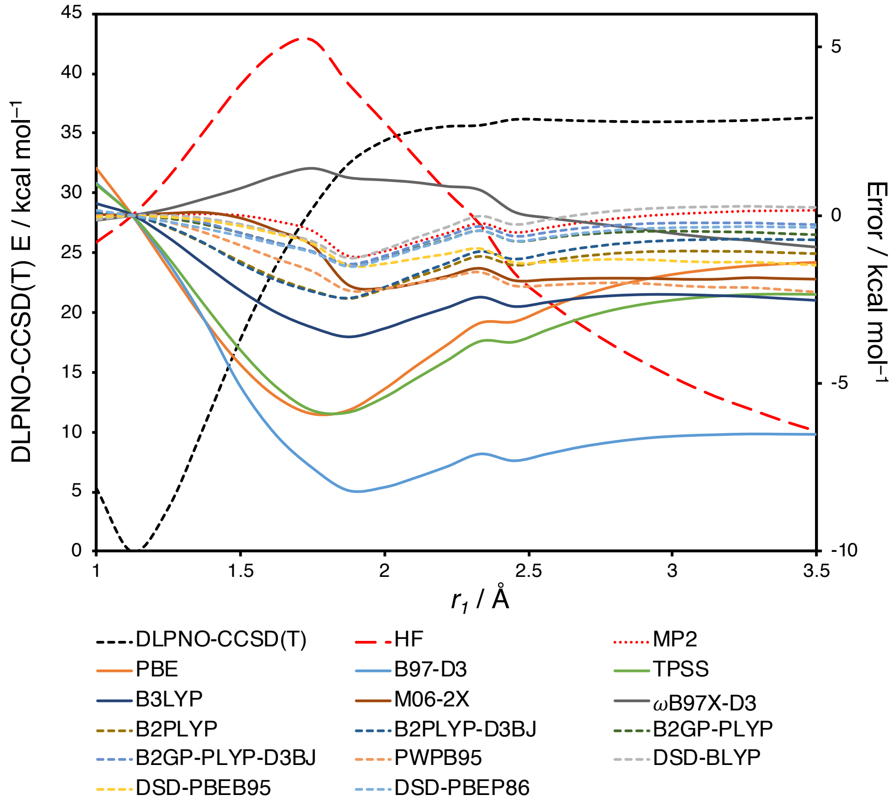


**Figure S20.** DLPNO-CCSD(T) energies for the addition of hydride to [1.1.1]propellane (long dashes black line), and the error in each method vs DLPNO-CCSD(T) as a function of $r_1$.

## Cationic PES

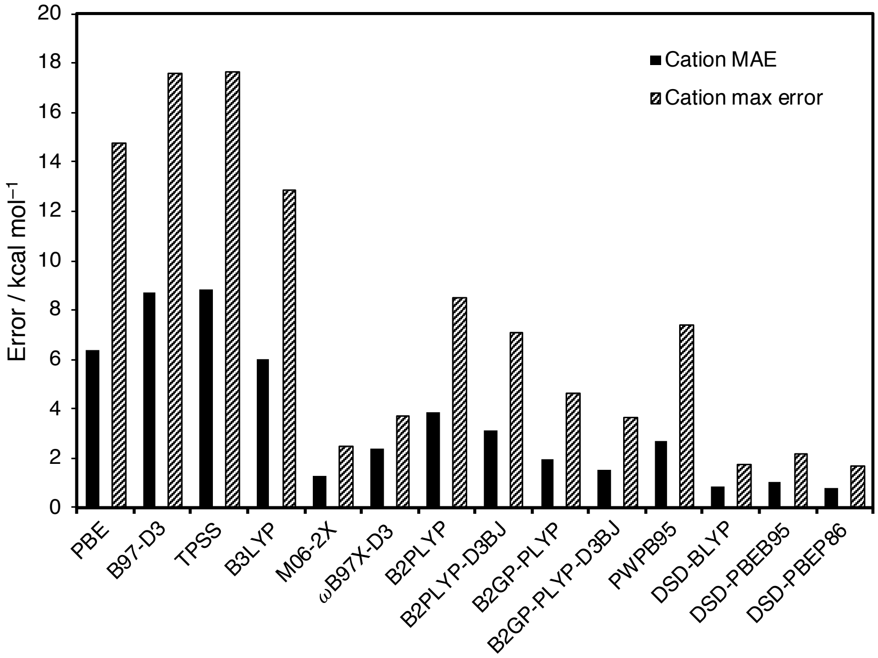


**Figure S21.** Mean absolute error (black) and maximum error (shaded) for the addition of a methyl cation to [1.1.1]propellane, relative to DLPNO-CCSD(T) energies. All calculations using a def2-QZVPP basis set, at CASSCF(2,3)/def2-QZVPP geometries.

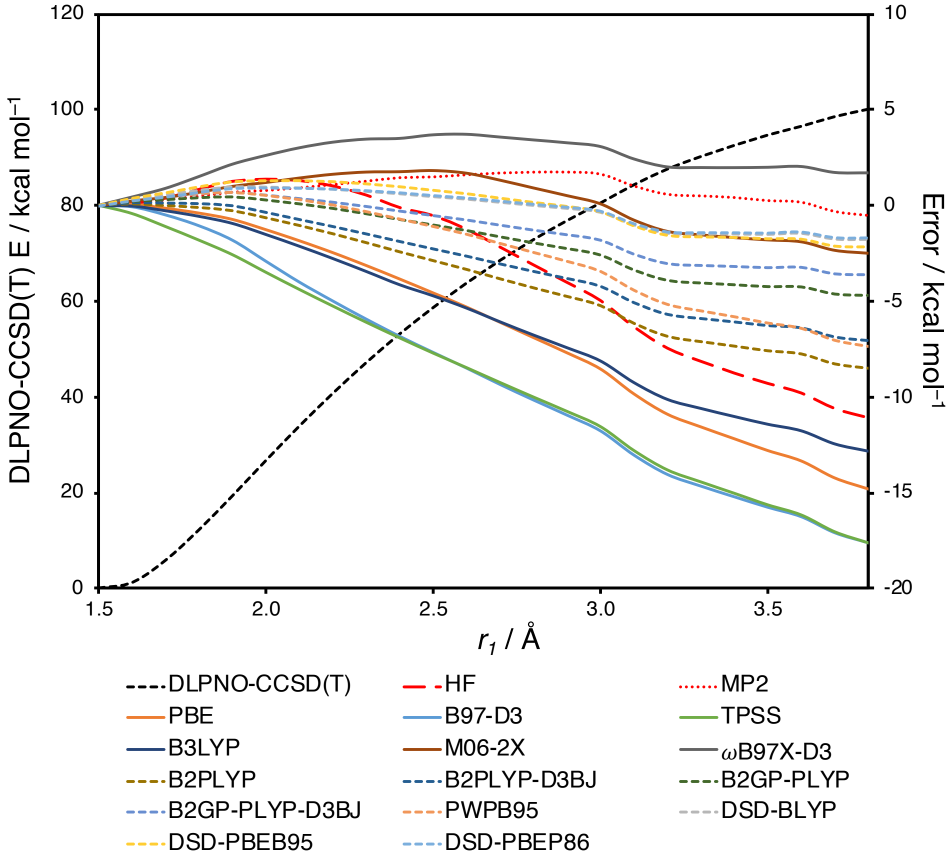


**Figure S22.** DLPNO-CCSD(T) energies for the addition of a methyl cation to [1.1.1]propellane (black dashes), and the error in each method vs DLPNO-CCSD(T) as a function of $r_1$.

### c. Solvation effects

To best describe the properties of charged species (or those with significant changes in localization of charge), gas-phase optimisation and energy calculation is not sufficient to model reactions in solution. We therefore examined the effect of the inclusion of solvation on each PES. We employed the SMD implicit solvation model for diethyl ether to represent a typical polar solvent that is present in most reactions of [1.1.1]propellane (given that it is commonly synthesized in diethyl ether).

For both anionic and cationic reactivity, inclusion of implicit solvation alters the PES significantly, therefore solvation should be accounted for when describing the kinetics of these systems. This was not found to be the case for radical reactivity, however for consistency we employed implicit solvation when examining experimental radical reactivity.

**d.**

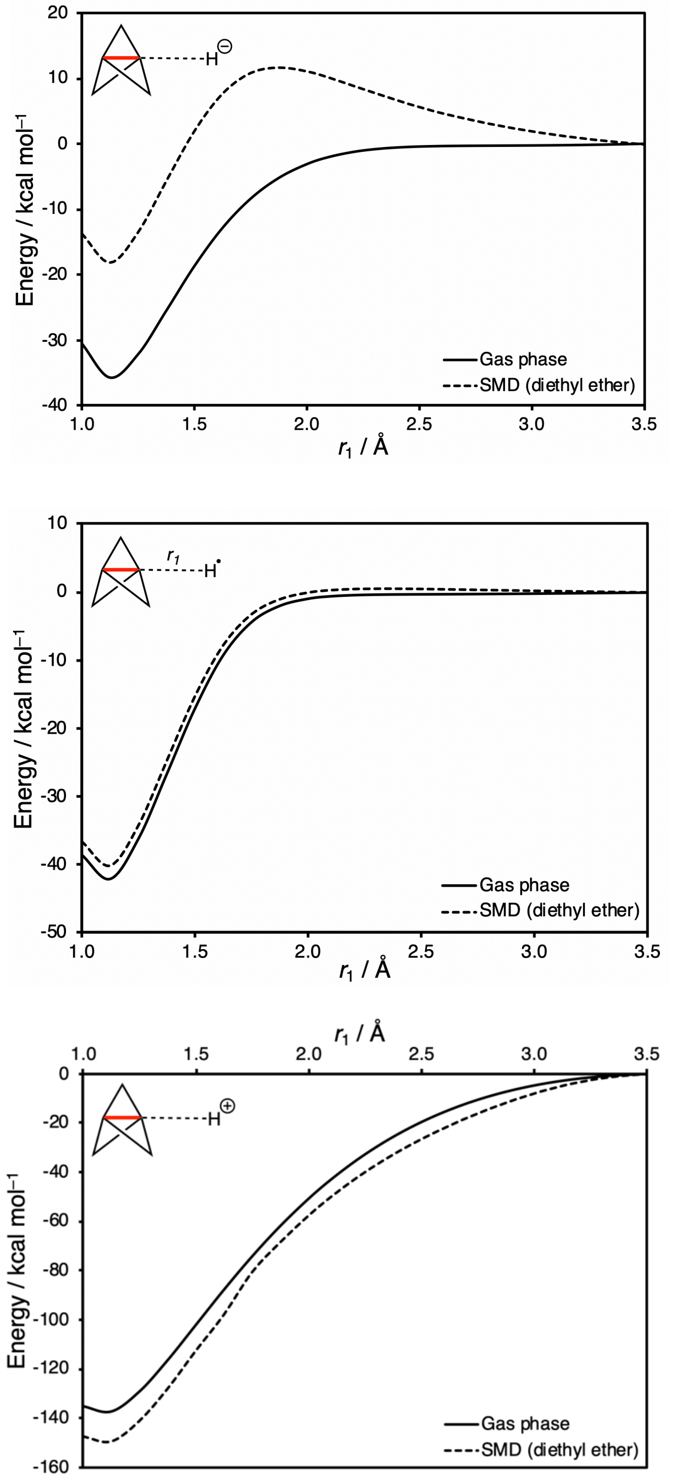


**Figure S23.** Effects of implicit solvation (SMD for diethyl ether) on PES for anionic, radical and cationic additions to [1.1.1]propellane. Top: addition of hydride at the (SMD-)B2GP-PLYP-D3BJ/def2-QZVPP level of theory. Middle: addition of a hydrogen atom at the (SMD-)B2PLYP-D3BJ/def2-QZVPP level of theory. Bottom: addition of a proton at the (SMD)DSD-BLYP/def2-QZVPP level of theory.

### e. Distortion/Interaction Analysis (DIA)

Decomposition of activation barriers can give insight into the origins of reactivity. In this study, we employed Distortion/Interaction Analysis (DIA),[27,28] which partitions the difference in electronic energy between an adduct and a reference state into energy coming from the distortion of the fragments ($\Delta$E(distortion)) and from the interaction of the fragments ($\Delta$E(int)). $\Delta$E(int) accounts for electrostatics, sterics and charge-transfer effects.

Employing this analysis to the additions of $H^-$, $CH_3^{\bullet}$, and $CH_3^+$ to [1.1.1]propellane reveals that unlike 'traditional' addition reactions, geometric distortion ($\Delta$E(distortion) is not the cause of the barrier to addition. Instead, for radicals and anions, the barrier originates primarily from destabilizing electronic interactions ($\Delta$E(int)). For cationic additions, this is not the case as charge transfer relieves repulsion inside the cage, resulting in barrierless addition.

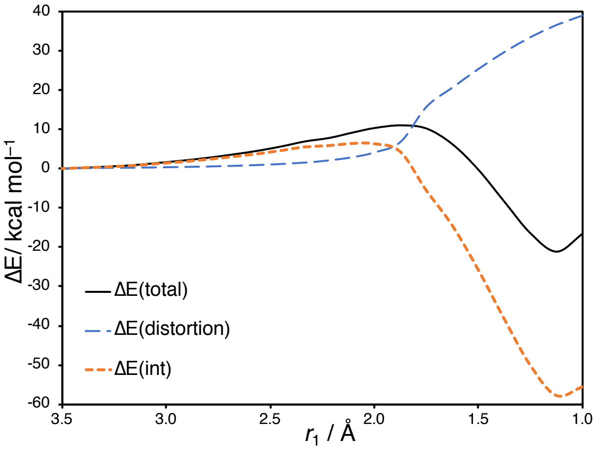


**Figure S24.** DIA for [1.1.1]propellane + $H^-$ at SMD($Et_2O$)-DLPNO-CCSD(T)/ma-def2-QZVPP//CASSCF(4,3)/ma-def2-QZVPP. $r_1$ is the length of the forming C–C bond.

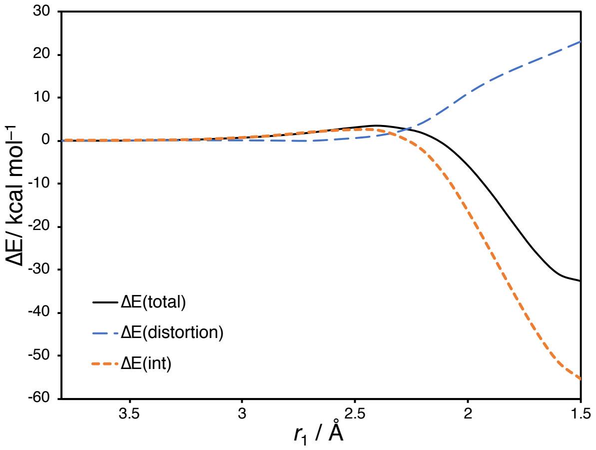


**Figure S25.** DIA for [1.1.1]propellane + $^{\bullet}CH_3$ at SMD($Et_2O$)-DLPNO-CCSD(T)/def2-QZVPP//CASSCF(2,3)/def2-QZVPP. $r_1$ is the length of the forming C–C bond.

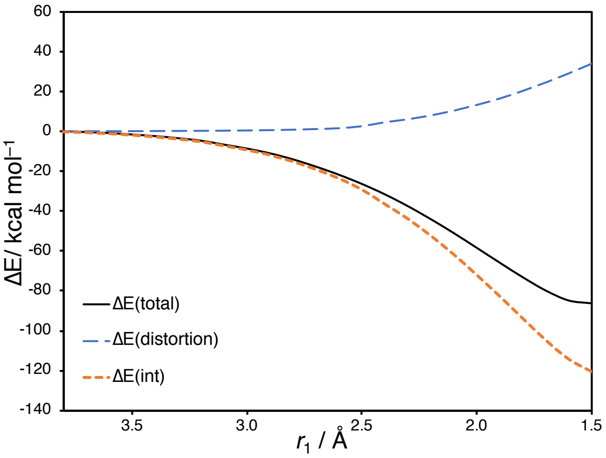


**Figure S26.** DIA for [1.1.1]propellane + $^{+}CH_3$ at SMD($Et_2O$)-DLPNO-CCSD(T)/def2-QZVPP//CASSCF(2,3)/def2-QZVPP. $r_1$ is the length of the forming C–C bond.

# 3. Analysis of experimental systems

## a. Turboamide addition to [1.1.1]propellane

Baran's turboamide addition[29] was modelled using geometries calculated at B2GP-PLYP-D3BJ/ma-def2-TZVP. Single point energies were calculated using DLPNO-CCSD(T)/ma-def2-QZVPP.

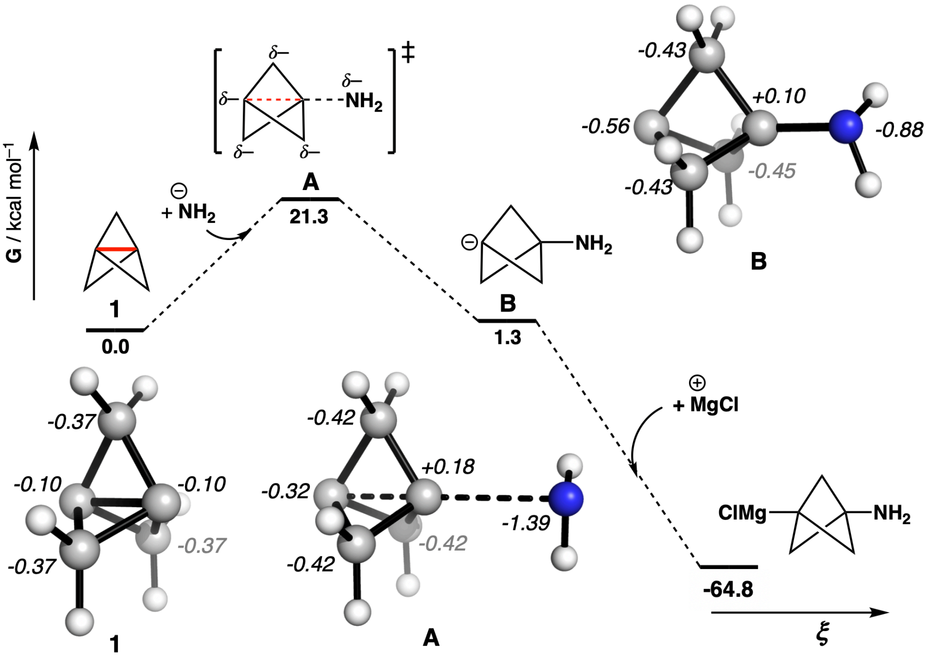


**Figure S27.** Free energy profile for the addition of $NH_2^-$ to [1.1.1]propellane, calculated at SMD(THF)-DLPNO-CCSD(T)/ma-def2-QZVPP//SMD(THF)-B2GP-PLYP-D3BJ/ma-def2-TZVP. NPA charges for each species are shown in italics, generated with NBO7.

**Table S4.** Thermodynamic quantities for the addition of $NH_2^-$ to [1.1.1]propellane. Geometries and thermodynamic corrections calculated at B2GP-PLYP-D3BJ/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-QZVPP. All energies report in kcal $mol^{-1}$.

| | **B2GP-PLYP-D3BJ** | | | | **DLPNO-CCSD(T)** | |
|---|---|---|---|---|---|---|
| **Species** | **ΔE** | **ΔH** | **ΔTqh-S** | **ΔG** | **ΔE** | **$\Delta G^a$** |
| [1.1.1]propellane + $NH_2^-$ + $MgCl^+$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $[NH_2\text{-BCP}]^-$ + $MgCl^+$ | -16.7 | -14.1 | -11.7 | -2.4 | -13.1 | 1.2 |
| TS $[[1.1.1]\text{propellane--}NH_2]^-$ + $MgCl^+$ | 25.8 | 23.6 | 1.9 | 21.7 | 25.5 | 21.4 |
| $NH_2$-BCP-MgCl | -97.4 | -93.2 | -22.4 | -70.8 | -91.4 | -64.8 |

[a] ΔG(DLPNO-CCSD(T)) = [ΔG(B2GP-PLYP-D3BJ) – ΔE(B2GP-PLYP-D3BJ)] + ΔE(DLPNO-CCSD(T))

### b. Iodination of [1.1.1]propellane

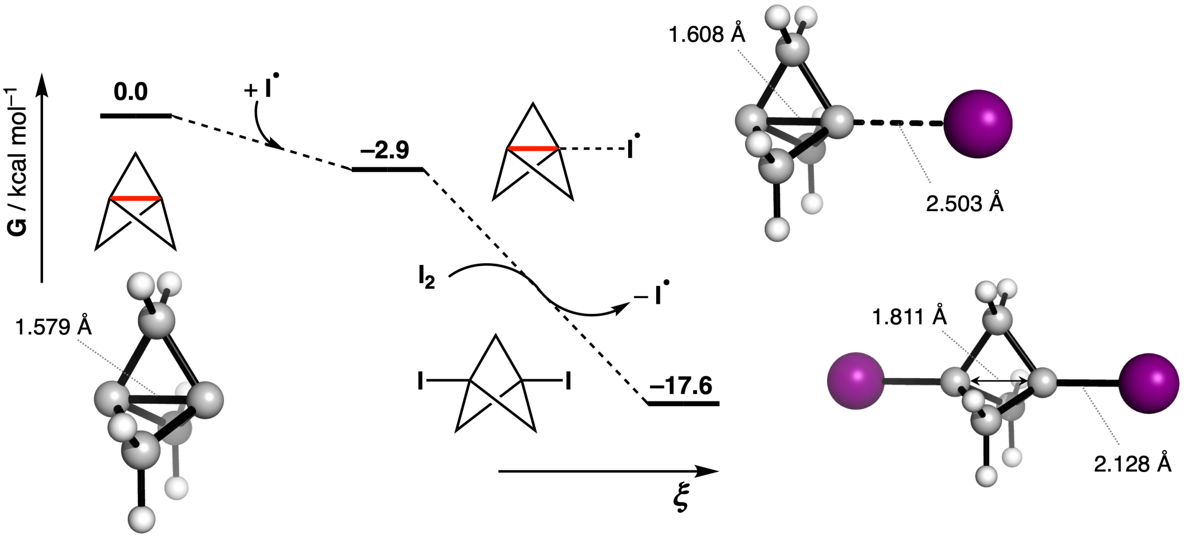


**Figure S28.** Free energy profile for the radical iodination of [1.1.1]propellane, calculated at SMD($Et_2O$)-DLPNO-CCSD(T)/def2-QZVPP//B2GP-PLYP-D3BJ/def2-TZVP.

**Table S5.** Thermodynamic quantities for the radical iodination of [1.1.1]propellane. Geometries and thermodynamic corrections calculated at B2GP-PLYP-D3BJ/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-QZVPP. All energies report in kcal mol$^{-1}$.

| | **B2GP-PLYP-D3BJ** | | | | **DLPNO-CCSD(T)** | |
|---|---|---|---|---|---|---|
| **Species** | **ΔE** | **ΔH** | **ΔTqh-S** | **ΔG** | **ΔE** | **ΔG** |
| [1.1.1]propellane + I• + $I_2$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| IBCP• + $I_2$ | -7.9 | -8.2 | -6.7 | -1.5 | -8.5 | -2.1 |
| IBCPI + I• | -24.5 | -23.3 | -11.3 | -12.0 | -27.1 | -14.6 |

[a] ΔG(DLPNO-CCSD(T)) = [ΔG(B2GP-PLYP-D3BJ) – ΔE(B2GP-PLYP-D3BJ)] + ΔE(DLPNO-CCSD(T))

### c. Halogen and chalcogen radical addition to [1.1.1]propellane

Geometries and energies were calculated at the B2PLYP-D3BJ/def2-TZVP level of theory. Relaxed scans of the forming C–X bond ($r_1$) were carried out, and normalized by subtracting the C–X bond length ($r_e$) in the parent saturated bicyclo[1.1.1]pentyl adduct.

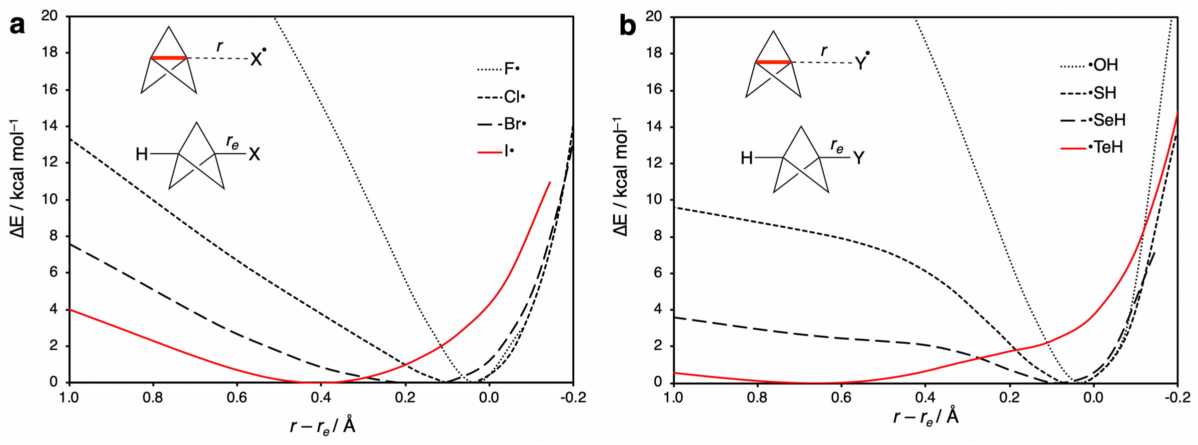


**Figure S29.** Potential energy surfaces of the formation of a C–X bond between [1.1.1]propellane and a halide radical (**a**) and chalcogen hydride radical (**b**).

# 4. Energetics and Thermodynamic Quantities

**Table S6.** Calculated $C_1$–$C_3$ bond lengths at each level of theory using a def2-QZVPP basis set. Values are reported in in Ångstroms.

| **Method** | **$r(C_1–C_3)$ / Å** | **Error in $r(C_1–C_3)$ / Å** |
|---|---|---|
| HF | 1.54 | -0.056 |
| MP2 | 1.589 | -0.007 |
| PBE | 1.578 | -0.018 |
| PBE0 | 1.556 | -0.04 |
| B97-D3 | 1.566 | -0.03 |
| TPSS | 1.583 | -0.013 |
| TPSSh | 1.573 | -0.023 |
| B3LYP | 1.567 | -0.029 |
| M06-2X | 1.539 | -0.057 |
| ωB97X-D3 | 1.549 | -0.047 |
| B2PLYP | 1.577 | -0.019 |
| B2PLYP-D3BJ | 1.577 | -0.019 |
| B2GP-PLYP | 1.573 | -0.023 |
| B2GP-PLYP-D3BJ | 1.573 | -0.023 |
| CASSCF(2,2) | 1.589 | -0.007 |
| CASSCF(6,6) | 1.591 | -0.005 |
| Expt (gas-phase electron diffraction)[23] | 1.594 | |

**Table S7.** Singlet energies of [1.1.1]propellane as a function of $C_1$–$C_3$ (Å) in Hartrees, using CASSCF(2,2)/def2-QZVPP geometries.

| | Singlet energy / Ha | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$C_1 - C_3$ / Å** | **DLPNO-CCSD(T)** | **HF** | **MP2** | **PBE** | **B97-D3** | **TPSS** | **B3LYP** | **M06-2X** |
| 1.54 | -193.70136 | -192.77039 | -193.64846 | -193.83671 | -193.96183 | -194.13888 | -193.96086 | -194.02298 |
| 1.59 | -193.70234 | -192.76896 | -193.64963 | -193.83735 | -193.96187 | -194.13971 | -193.96094 | -194.02179 |
| 1.64 | -193.70094 | -192.76494 | -193.64842 | -193.83567 | -193.95963 | -194.13818 | -193.95870 | -194.01818 |
| 1.69 | -193.69741 | -192.75858 | -193.64507 | -193.83191 | -193.95538 | -194.13453 | -193.95438 | -194.01241 |
| 1.74 | -193.69190 | -192.75009 | -193.63976 | -193.82625 | -193.94933 | -194.12894 | -193.94814 | -194.00468 |
| 1.80 | -193.68457 | -192.73963 | -193.63263 | -193.81884 | -193.94166 | -194.12158 | -193.94012 | -193.99515 |
| 1.85 | -193.67559 | -192.72735 | -193.62379 | -193.80979 | -193.93250 | -194.11257 | -193.93045 | -193.98396 |
| 1.90 | -193.66498 | -192.71338 | -193.61334 | -193.79923 | -193.92203 | -194.10202 | -193.91923 | -193.97125 |
| 1.95 | -193.65289 | -192.69786 | -193.60139 | -193.78725 | -193.91039 | -194.09005 | -193.90656 | -193.95713 |
| 2.00 | -193.63941 | -192.68090 | -193.58801 | -193.77393 | -193.89764 | -194.07675 | -193.89256 | -193.94170 |

| $C_1 - C_3$ / Å | ωB97X-D3 | B2PLYP | B2GP-PLYP | PWPB95 | DSD-BLYP | DSD-PBEB95 | DSD-PBEP86 |
|---|---|---|---|---|---|---|---|
| 1.54 | -194.03960 | -193.92617 | -193.89247 | -193.95583 | -193.87536 | -193.77165 | -193.76185 |
| 1.59 | -194.03878 | -193.92675 | -193.89287 | -193.95586 | -193.87583 | -193.77188 | -193.76239 |
| 1.64 | -194.03568 | -193.92499 | -193.89090 | -193.95352 | -193.87393 | -193.76971 | -193.76054 |
| 1.69 | -194.03053 | -193.92114 | -193.88681 | -193.94904 | -193.86989 | -193.76537 | -193.75654 |
| 1.74 | -194.02347 | -193.91535 | -193.88076 | -193.94262 | -193.86388 | -193.75906 | -193.75057 |
| 1.80 | -194.01457 | -193.90778 | -193.87291 | -193.93440 | -193.85606 | -193.75092 | -193.74279 |
| 1.85 | -194.00391 | -193.89854 | -193.86336 | -193.92451 | -193.84654 | -193.74109 | -193.73331 |
| 1.90 | -193.99161 | -193.88773 | -193.85224 | -193.91307 | -193.83543 | -193.72967 | -193.72225 |
| 1.95 | -193.97782 | -193.87546 | -193.83963 | -193.90017 | -193.82283 | -193.71677 | -193.70969 |
| 2.00 | -193.96264 | -193.86183 | -193.82564 | -193.88591 | -193.80884 | -193.70247 | -193.69574 |

**Table S8.** Triplet energies of [1.1.1]propellane as a function of $C_1$–$C_3$ (Å) in Hartrees, using CASSCF(2,2)/def2-QZVPP geometries.

| | **Triplet energy / Ha** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$C_1 - C_3$ / Å** | **DLPNO-CCSD(T)** | **HF** | **MP2** | **PBE** | **B97-D3** | **TPSS** | **B3LYP** | **M06-2X** |
| 1.54 | -193.51322 | -192.62381 | -193.44921 | -193.65936 | -193.78365 | -193.96284 | -193.78423 | -193.83832 |
| 1.59 | -193.52479 | -192.63699 | -193.45993 | -193.66927 | -193.79271 | -193.97322 | -193.79467 | -193.84868 |
| 1.64 | -193.53403 | -192.64754 | -193.46835 | -193.67703 | -193.7998 | -193.98139 | -193.80293 | -193.85669 |
| 1.69 | -193.54091 | -192.65538 | -193.47444 | -193.68263 | -193.80494 | -193.98734 | -193.80897 | -193.86234 |
| 1.74 | -193.54541 | -192.66045 | -193.47816 | -193.68607 | -193.8081 | -193.99106 | -193.81273 | -193.86562 |
| 1.80 | -193.54748 | -192.66271 | -193.4795 | -193.68731 | -193.80922 | -193.99253 | -193.81418 | -193.86653 |
| 1.85 | -193.54711 | -192.66214 | -193.47845 | -193.68636 | -193.80828 | -193.99175 | -193.81332 | -193.86507 |
| 1.90 | -193.54444 | -192.65882 | -193.47507 | -193.68326 | -193.80538 | -193.98877 | -193.81018 | -193.86131 |
| 1.95 | -193.53944 | -192.65281 | -193.46942 | -193.67806 | -193.80063 | -193.98365 | -193.80482 | -193.85532 |
| 2.00 | -193.53224 | -192.64425 | -193.46161 | -193.67084 | -193.79408 | -193.97649 | -193.79734 | -193.8472 |

| **$C_1 - C_3$ / Å** | **ωB97X-D3** | **B2PLYP** | **B2GP-PLYP** | **PWPB95** | **DSD-BLYP** | **DSD-PBEB95** | **DSD-PBEP86** |
|---|---|---|---|---|---|---|---|
| 1.54 | -193.86116 | -193.74202 | -193.70729 | -193.77054 | -193.6869 | -193.58263 | -193.5758 |
| 1.59 | -193.87198 | -193.75264 | -193.71796 | -193.78094 | -193.69742 | -193.59316 | -193.58658 |
| 1.64 | -193.88051 | -193.76105 | -193.72637 | -193.78906 | -193.70566 | -193.60138 | -193.59505 |
| 1.69 | -193.88674 | -193.76718 | -193.73246 | -193.79488 | -193.7116 | -193.60724 | -193.60118 |
| 1.74 | -193.89055 | -193.771 | -193.73621 | -193.79836 | -193.71518 | -193.61071 | -193.60494 |
| 1.80 | -193.89183 | -193.77247 | -193.73756 | -193.79947 | -193.71637 | -193.61179 | -193.6063 |
| 1.85 | -193.89058 | -193.77159 | -193.73651 | -193.79822 | -193.71518 | -193.61047 | -193.60526 |
| 1.90 | -193.88696 | -193.76839 | -193.73312 | -193.79465 | -193.71163 | -193.60681 | -193.60187 |
| 1.95 | -193.88109 | -193.76296 | -193.72745 | -193.78884 | -193.70581 | -193.60087 | -193.59619 |
| 2.00 | -193.87302 | -193.75537 | -193.71959 | -193.78089 | -193.6978 | -193.59276 | -193.58833 |

**Table S9.** Singlet-triplet energy gaps of [1.1.1]propellane as a function of C$_1$–C$_3$ (Å) in Hartrees, using CASSCF(2,2)/def2-QZVPP geometries.

| | **S → T energy / kcal mol$^{-1}$** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **C$_1$ – C$_3$ / Å** | **DLPNO-CCSD(T)** | **HF** | **MP2** | **PBE** | **B97-D3** | **TPSS** | **B3LYP** | **M06-2X** |
| 1.54 | 118.1 | 92.0 | 125.0 | 111.3 | 111.8 | 110.5 | 110.8 | 115.9 |
| 1.59 | 111.4 | 82.8 | 119.0 | 105.5 | 106.2 | 104.5 | 104.3 | 108.6 |
| 1.64 | 104.7 | 73.7 | 113.0 | 99.5 | 100.3 | 98.4 | 97.7 | 101.3 |
| 1.69 | 98.2 | 64.8 | 107.1 | 93.7 | 94.4 | 92.4 | 91.2 | 94.2 |
| 1.74 | 91.9 | 56.2 | 101.4 | 88.0 | 88.6 | 86.5 | 85.0 | 87.3 |
| 1.80 | 86.0 | 48.3 | 96.1 | 82.5 | 83.1 | 81.0 | 79.0 | 80.7 |
| 1.85 | 80.6 | 40.9 | 91.2 | 77.5 | 77.9 | 75.8 | 73.5 | 74.6 |
| 1.90 | 75.6 | 34.2 | 86.8 | 72.8 | 73.2 | 71.1 | 68.4 | 69.0 |
| 1.95 | 71.2 | 28.3 | 82.8 | 68.5 | 68.9 | 66.8 | 63.8 | 63.9 |
| 2.00 | 67.2 | 23.0 | 79.3 | 64.7 | 65.0 | 62.9 | 59.8 | 59.3 |

| **C$_1$ – C$_3$ / Å** | **ωB97X-D3** | **B2PLYP** | **B2GP-PLYP** | **PWPB95** | **DSD-BLYP** | **DSD-PBEB95** | **DSD-PBEP86** |
|---|---|---|---|---|---|---|---|
| 1.54 | 118.1 | 92.0 | 125.0 | 111.3 | 111.8 | 110.5 | 110.8 |
| 1.59 | 111.4 | 82.8 | 119.0 | 105.5 | 106.2 | 104.5 | 104.3 |
| 1.64 | 104.7 | 73.7 | 113.0 | 99.5 | 100.3 | 98.4 | 97.7 |
| 1.69 | 98.2 | 64.8 | 107.1 | 93.7 | 94.4 | 92.4 | 91.2 |
| 1.74 | 91.9 | 56.2 | 101.4 | 88.0 | 88.6 | 86.5 | 85.0 |
| 1.80 | 86.0 | 48.3 | 96.1 | 82.5 | 83.1 | 81.0 | 79.0 |
| 1.85 | 80.6 | 40.9 | 91.2 | 77.5 | 77.9 | 75.8 | 73.5 |
| 1.90 | 75.6 | 34.2 | 86.8 | 72.8 | 73.2 | 71.1 | 68.4 |
| 1.95 | 71.2 | 28.3 | 82.8 | 68.5 | 68.9 | 66.8 | 63.8 |
| 2.00 | 67.2 | 23.0 | 79.3 | 64.7 | 65.0 | 62.9 | 59.8 |

**Table S10.** Error in singlet-triplet energy gaps of [1.1.1]propellane as a function of $C_1$–$C_3$ (Å) in Hartrees, compared *c.f.* DLPNO-CCSD(T) reference, using CASSCF(2,2)/def2-QZVPP geometries.

| | Error in S → T energy / kcal mol$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| **$C_1$ – $C_3$ / Å** | **HF** | **MP2** | **PBE** | **B97-D3** | **TPSS** | **B3LYP** | **M06-2X** |
| 1.54 | -26.1 | 7.0 | -6.8 | -6.2 | -7.6 | -7.2 | -2.2 |
| 1.59 | -28.6 | 7.6 | -5.9 | -5.3 | -6.9 | -7.1 | -2.8 |
| 1.64 | -31.1 | 8.3 | -5.2 | -4.4 | -6.4 | -7.0 | -3.4 |
| 1.69 | -33.4 | 8.9 | -4.5 | -3.8 | -5.8 | -7.0 | -4.0 |
| 1.74 | -35.7 | 9.5 | -4.0 | -3.3 | -5.4 | -7.0 | -4.7 |
| 1.80 | -37.8 | 10.1 | -3.5 | -2.9 | -5.0 | -7.0 | -5.3 |
| 1.85 | -39.7 | 10.6 | -3.2 | -2.7 | -4.8 | -7.1 | -6.0 |
| 1.90 | -41.4 | 11.1 | -2.9 | -2.4 | -4.6 | -7.2 | -6.7 |
| 1.95 | -42.9 | 11.6 | -2.7 | -2.3 | -4.4 | -7.4 | -7.3 |
| 2.00 | -44.3 | 12.1 | -2.6 | -2.3 | -4.3 | -7.5 | -7.9 |
| **Mean error** | -36.1 | 9.7 | -4.1 | -3.6 | -5.5 | -7.1 | -5.0 |

| **$C_1$ – $C_3$ / Å** | **ωB97X-D3** | **B2PLYP** | **B2GP-PLYP** | **PWPB95** | **DSD-BLYP** | **DSD-PBEB95** | **DSD-PBEP86** |
|---|---|---|---|---|---|---|---|
| 1.54 | -6.1 | -2.5 | -1.9 | -1.8 | 0.2 | 0.6 | -1.3 |
| 1.59 | -6.7 | -2.2 | -1.7 | -1.7 | 0.5 | 0.7 | -1.1 |
| 1.64 | -7.4 | -1.9 | -1.5 | -1.5 | 0.9 | 0.9 | -0.9 |
| 1.69 | -8.0 | -1.6 | -1.4 | -1.5 | 1.1 | 1.0 | -0.7 |
| 1.74 | -8.5 | -1.3 | -1.2 | -1.4 | 1.4 | 1.2 | -0.5 |
| 1.80 | -9.0 | -1.1 | -1.1 | -1.4 | 1.6 | 1.3 | -0.4 |
| 1.85 | -9.5 | -1.0 | -1.0 | -1.4 | 1.8 | 1.3 | -0.3 |
| 1.90 | -10.0 | -0.8 | -0.9 | -1.3 | 2.0 | 1.5 | -0.1 |
| 1.95 | -10.5 | -0.6 | -0.8 | -1.3 | 2.2 | 1.5 | 0.0 |
| 2.00 | -11.0 | -0.4 | -0.7 | -1.4 | 2.4 | 1.6 | 0.2 |
| **Mean** | -8.7 | -1.3 | -1.2 | -1.5 | 1.4 | 1.2 | -0.5 |

**Table S11.** Error in first ionization potential of [1.1.1]propellane *c.f.* DLPNO-CCSD(T) reference, using CASSCF(2,2)/def2-QZVPP equilibrium geometry.

| Method | Neutral state / Ha | +1 state / Ha | Ionization potential / eV | Error v expt. / eV | Error vs DLPNO-CCSD(T) / eV |
|---|---|---|---|---|---|
| HF | -192.76909 | -192.46921 | 8.16 | -1.58 | -1.69 |
| MP2 | -193.64963 | -193.27246 | 10.26 | 0.52 | 0.41 |
| PBE | -193.83737 | -193.47910 | 9.75 | 0.01 | -0.10 |
| PBE0 | -193.86022 | -193.50501 | 9.67 | -0.07 | -0.19 |
| B97-D3 | -193.96193 | -193.60748 | 9.64 | -0.10 | -0.21 |
| TPSS | -194.13973 | -193.78500 | 9.65 | -0.09 | -0.20 |
| TPSSh | -194.11951 | -193.76563 | 9.63 | -0.11 | -0.22 |
| B3LYP | -193.96099 | -193.60676 | 9.64 | -0.10 | -0.21 |
| M06-2X | -194.02190 | -193.65957 | 9.86 | 0.12 | 0.01 |
| ωB97X-D3 | -194.03887 | -193.68448 | 9.64 | -0.10 | -0.21 |
| B2PLYP | -193.92678 | -193.56630 | 9.81 | 0.07 | -0.04 |
| B2GP-PLYP | -193.89290 | -193.53112 | 9.84 | 0.10 | -0.01 |
| PWPB95 | -193.95591 | -193.59590 | 9.80 | 0.06 | -0.06 |
| DSD-BLYP | -193.87586 | -193.50936 | 9.97 | 0.23 | 0.12 |
| DSD-PBEB95 | -193.77191 | -193.40866 | 9.88 | 0.14 | 0.03 |
| DSD-PBEP86 | -193.76241 | -193.39757 | 9.93 | 0.19 | 0.08 |
| DLPNO-CCSD(T) | -193.70236 | -193.34030 | 9.85 | | |
| Expt. | | | 9.74 | | |

**Table S12.** CCSD(T) and DLPNO-CCSD(T) energies (Hartrees) and $T_1$ diagnostics for the addition of methyl cation to [1.1.1]propellane as a function of $r_1$ (Å), using CASSCF(2,3)/def2-QZVPP geometries. Energies calculated with a ma-def2-SVP basis set. Shaded rows indicate $T_1 > 0.02$, where a single determinant is no longer appropriate to describe the system.

| | **CCSD(T)** | | **DLPNO-CCSD(T)** | | |
|---|---|---|---|---|---|
| **$r_1$ / Å** | **E / Ha** | **$T_1$ diagnostic** | **E / Ha** | **$T_1$ diagnostic** | **Relative error / kcal mol$^{-1}$** |
| 1.00 | -193.62329 | 0.010 | -193.62132 | 0.009 | 0.00 |
| 1.13 | -193.63033 | 0.010 | -193.62833 | 0.009 | 0.02 |
| 1.25 | -193.61959 | 0.010 | -193.61757 | 0.009 | 0.03 |
| 1.38 | -193.60078 | 0.010 | -193.59872 | 0.010 | 0.06 |
| 1.50 | -193.57913 | 0.010 | -193.57698 | 0.010 | 0.11 |
| 1.63 | -193.55743 | 0.011 | -193.55517 | 0.010 | 0.18 |
| 1.75 | -193.53718 | 0.011 | -193.53477 | 0.010 | 0.27 |
| 1.88 | -193.51911 | 0.012 | -193.51653 | 0.011 | 0.38 |
| 2.00 | -193.50354 | 0.013 | -193.50076 | 0.013 | 0.51 |
| 2.10 | -193.49296 | 0.015 | -193.49001 | 0.015 | 0.61 |
| 2.22 | -193.48268 | 0.018 | -193.47951 | 0.018 | 0.75 |
| 2.33 | -193.4746 | 0.022 | -193.47112 | 0.022 | 0.94 |
| 2.45 | -193.4686 | 0.027 | -193.46477 | 0.026 | 1.17 |
| 2.57 | -193.46438 | 0.033 | -193.4602 | 0.031 | 1.39 |
| 2.68 | -193.46249 | 0.039 | -193.4578 | 0.037 | 1.70 |
| 2.80 | -193.46192 | 0.045 | -193.45656 | 0.043 | 2.13 |
| 2.92 | -193.46344 | 0.051 | -193.45713 | 0.050 | 2.72 |
| 3.03 | -193.46592 | 0.058 | -193.45862 | 0.056 | 3.35 |
| 3.15 | -193.46971 | 0.064 | -193.46127 | 0.062 | 4.06 |
| 3.27 | -193.47457 | 0.070 | -193.46492 | 0.068 | 4.82 |
| 3.38 | -193.48029 | 0.076 | -193.46924 | 0.074 | 5.69 |
| 3.50 | -193.48762 | 0.082 | -193.47463 | 0.079 | 6.92 |

**Table S13.** CCSD(T) and DLPNO-CCSD(T) energies (Hartrees) and $T_1$ diagnostics for the addition of a hydrogen atom to [1.1.1]propellane as a function of $r_1$ (Å), using CASSCF(3,3)/def2-QZVPP geometries. Energies calculated with a ma-def2-SVP basis set.

| | **CCSD(T)** | | **DLPNO-CCSD(T)** | | |
|---|---|---|---|---|---|
| **$r_1$ / Å** | **E / Ha** | **$T_1$ diagnostic** | **E / Ha** | **$T_1$ diagnostic** | **Relative error / kcal mol$^{-1}$** |
| 1.00 | -193.85478 | 0.010 | -193.85286 | 0.011 | 0.00 |
| 1.13 | -193.86322 | 0.011 | -193.86127 | 0.012 | 0.01 |
| 1.25 | -193.8548 | 0.011 | -193.85282 | 0.012 | 0.04 |
| 1.38 | -193.83954 | 0.013 | -193.83752 | 0.014 | 0.06 |
| 1.50 | -193.82323 | 0.017 | -193.82118 | 0.015 | 0.08 |
| 1.63 | -193.80962 | 0.022 | -193.80763 | 0.019 | 0.05 |
| 1.75 | -193.80093 | 0.025 | -193.79883 | 0.021 | 0.11 |
| 1.88 | -193.79682 | 0.026 | -193.79468 | 0.020 | 0.14 |
| 2.00 | -193.79539 | 0.025 | -193.7933 | 0.017 | 0.11 |
| 2.10 | -193.79518 | 0.024 | -193.79259 | 0.014 | 0.42 |
| 2.22 | -193.79539 | 0.023 | -193.79274 | 0.012 | 0.46 |
| 2.33 | -193.79579 | 0.021 | -193.79306 | 0.011 | 0.50 |
| 2.45 | -193.7962 | 0.019 | -193.79348 | 0.010 | 0.51 |
| 2.57 | -193.79667 | 0.012 | -193.79385 | 0.009 | 0.57 |
| 2.68 | -193.79694 | 0.012 | -193.79413 | 0.009 | 0.56 |
| 2.80 | -193.79714 | 0.013 | -193.79439 | 0.009 | 0.52 |
| 2.92 | -193.79734 | 0.010 | -193.7946 | 0.009 | 0.51 |
| 3.03 | -193.79745 | 0.010 | -193.79471 | 0.009 | 0.51 |
| 3.15 | -193.79752 | 0.010 | -193.79478 | 0.009 | 0.51 |
| 3.27 | -193.79756 | 0.010 | -193.79482 | 0.009 | 0.51 |
| 3.38 | -193.79759 | 0.010 | -193.79484 | 0.009 | 0.52 |
| 3.50 | -193.79759 | 0.010 | -193.79485 | 0.009 | 0.52 |

**Table S14.** CCSD(T) and DLPNO-CCSD(T) energies (Hartrees) and $T_1$ diagnostics for the addition of hydride atom to [1.1.1]propellane as a function of $r_1$ (Å), using CASSCF(4,3)/ma-def2-QZVPP geometries. Energies calculated with a ma-def2-SVP basis set.

| | **CCSD(T)** | | **DLPNO-CCSD(T)** | | |
|---|---|---|---|---|---|
| **$r_1$ / Å** | **E / Ha** | **$T_1$ diagnostic** | **E / Ha** | **$T_1$ diagnostic** | **Relative error / kcal mol$^{-1}$** |
| 1.00 | -193.86145 | 0.015 | -193.85888 | 0.009 | 0.00 |
| 1.13 | -193.87239 | 0.015 | -193.86977 | 0.011 | 0.03 |
| 1.25 | -193.86756 | 0.015 | -193.86485 | 0.012 | 0.09 |
| 1.38 | -193.85669 | 0.016 | -193.85394 | 0.013 | 0.11 |
| 1.50 | -193.84482 | 0.016 | -193.84193 | 0.014 | 0.20 |
| 1.63 | -193.83431 | 0.016 | -193.83131 | 0.014 | 0.27 |
| 1.75 | -193.82594 | 0.017 | -193.82277 | 0.014 | 0.38 |
| 1.88 | -193.81849 | 0.016 | -193.81552 | 0.017 | 0.25 |
| 2.00 | -193.81403 | 0.016 | -193.81117 | 0.019 | 0.19 |
| 2.10 | -193.81166 | 0.016 | -193.80887 | 0.020 | 0.14 |
| 2.22 | -193.80968 | 0.016 | -193.80703 | 0.020 | 0.05 |
| 2.33 | -193.80814 | 0.016 | -193.80555 | 0.020 | 0.01 |
| 2.45 | -193.80683 | 0.017 | -193.80432 | 0.020 | -0.03 |
| 2.57 | -193.80564 | 0.017 | -193.80251 | 0.020 | 0.35 |
| 2.68 | -193.80451 | 0.017 | -193.80149 | 0.020 | 0.28 |
| 2.80 | -193.80342 | 0.017 | -193.80046 | 0.020 | 0.25 |
| 2.92 | -193.80237 | 0.017 | -193.79945 | 0.020 | 0.22 |
| 3.03 | -193.80133 | 0.018 | -193.79847 | 0.020 | 0.18 |
| 3.15 | -193.8003 | 0.018 | -193.7975 | 0.020 | 0.15 |
| 3.27 | -193.7993 | 0.018 | -193.79652 | 0.020 | 0.13 |
| 3.38 | -193.79827 | 0.018 | -193.79558 | 0.019 | 0.08 |
| 3.50 | -193.79728 | 0.018 | -193.79466 | 0.019 | 0.03 |

**Table S15.** Methyl cation addition to [1.1.1]propellane: Part I, WFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| $r_1$ / Å | CASSCF(2,3) $S_0$ | CASSCF(2,3) $S_1$ | CASSCF(2,3) $T_0$ | DLPNO-CCSD(T) | SMD($Et_2O$)-DLPNO-CCSD(T) | HF | MP2 |
|---|---|---|---|---|---|---|---|
| 1.5 | -232.19923 | -231.11284 | -231.41505 | -233.29562 | -233.36849 | -232.18017 | -233.21873 |
| 1.6 | -232.19893 | -231.27512 | -231.56495 | -233.29385 | -233.36625 | -232.17828 | -233.21665 |
| 1.7 | -232.19259 | -231.40400 | -231.67779 | -233.28641 | -233.35834 | -232.17037 | -233.20901 |
| 1.8 | -232.18315 | -231.50752 | -231.76210 | -233.27625 | -233.34776 | -232.15949 | -233.19856 |
| 1.9 | -232.17238 | -231.59092 | -231.82415 | -233.26492 | -233.33620 | -232.14749 | -233.18690 |
| 2.0 | -232.16134 | -231.65768 | -231.86869 | -233.25315 | -233.32437 | -232.13554 | -233.17498 |
| 2.1 | -232.15059 | -231.71069 | -231.90010 | -233.24167 | -233.31263 | -232.12418 | -233.16330 |
| 2.2 | -232.14043 | -231.75194 | -231.92126 | -233.23077 | -233.30156 | -232.11371 | -233.15212 |
| 2.3 | -232.13099 | -231.78406 | -231.93495 | -233.22051 | -233.29116 | -232.10422 | -233.14159 |
| 2.4 | -232.12233 | -231.80768 | -231.94236 | -233.21095 | -233.28175 | -232.09570 | -233.13175 |
| 2.5 | -232.11452 | -231.83628 | -231.95300 | -233.20218 | -233.27346 | -232.08760 | -233.12292 |
| 2.6 | -232.10774 | -231.82719 | -231.94369 | -233.19398 | -233.26613 | -232.08054 | -233.11454 |
| 2.7 | -232.10168 | -231.81496 | -231.93145 | -233.18644 | -233.25965 | -232.07448 | -233.10685 |
| 2.8 | -232.09627 | -231.79675 | -231.91727 | -233.17951 | -233.25385 | -232.06904 | -233.09986 |
| 2.9 | -232.09147 | -231.77322 | -231.90222 | -233.17319 | -233.24903 | -232.06417 | -233.09353 |
| 3.0 | -232.08723 | -231.74455 | -231.88748 | -233.16733 | -233.24524 | -232.05981 | -233.08783 |
| 3.1 | -232.08350 | -231.71159 | -231.87448 | -233.16125 | -233.24211 | -232.05593 | -233.08273 |
| 3.2 | -232.08023 | -231.67656 | -231.86424 | -233.15602 | -233.23897 | -232.05247 | -233.07817 |
| 3.3 | -232.07736 | -231.64304 | -231.85681 | -233.15184 | -233.23693 | -232.04938 | -233.07411 |
| 3.4 | -232.07486 | -231.61561 | -231.85168 | -233.14811 | -233.23528 | -232.04664 | -233.07052 |
| 3.5 | -232.07267 | -231.59587 | -231.84915 | -233.14468 | -233.23400 | -232.04406 | -233.06734 |
| 3.6 | -232.07076 | -231.58261 | -231.84632 | -233.14176 | -233.23283 | -232.04194 | -233.06455 |
| 3.7 | -232.06909 | -231.57359 | -231.84453 | -233.13855 | -233.23204 | -232.04002 | -233.06209 |
| 3.8 | -232.06761 | -231.56709 | -231.84322 | -233.13607 | -233.23141 | -232.03831 | -233.05993 |

**Table S16.** Methyl cation addition to [1.1.1]propellane: Part II, single-hybrid DFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| **$r_1$ / Å** | **PBE** | **B97-D3** | **TPSS** | **B3LYP** | **M06-2X** | **ωB97X-D3** |
|---|---|---|---|---|---|---|
| 1.5 | -233.45369 | -233.62046 | -233.82503 | -233.61141 | -233.67458 | -233.71115 |
| 1.6 | -233.45184 | -233.61880 | -233.82395 | -233.60966 | -233.67239 | -233.70869 |
| 1.7 | -233.44473 | -233.61203 | -233.81759 | -233.60261 | -233.66466 | -233.70052 |
| 1.8 | -233.43498 | -233.60278 | -233.80857 | -233.59292 | -233.65407 | -233.68938 |
| 1.9 | -233.42418 | -233.59265 | -233.79845 | -233.58219 | -233.64225 | -233.67702 |
| 2.0 | -233.41325 | -233.58262 | -233.78814 | -233.57133 | -233.63014 | -233.66452 |
| 2.1 | -233.40270 | -233.57288 | -233.77809 | -233.56084 | -233.61829 | -233.65241 |
| 2.2 | -233.39277 | -233.56354 | -233.76857 | -233.55096 | -233.60707 | -233.64103 |
| 2.3 | -233.38359 | -233.55479 | -233.75966 | -233.54178 | -233.59663 | -233.63052 |
| 2.4 | -233.37515 | -233.54666 | -233.75140 | -233.53333 | -233.58704 | -233.62090 |
| 2.5 | -233.36753 | -233.53923 | -233.74390 | -233.52549 | -233.57818 | -233.61184 |
| 2.6 | -233.36050 | -233.53234 | -233.73691 | -233.51831 | -233.57020 | -233.60359 |
| 2.7 | -233.35422 | -233.52615 | -233.73060 | -233.51191 | -233.56324 | -233.59628 |
| 2.8 | -233.34856 | -233.52051 | -233.72489 | -233.50609 | -233.55697 | -233.58959 |
| 2.9 | -233.34350 | -233.51544 | -233.71975 | -233.50082 | -233.55129 | -233.58351 |
| 3.0 | -233.33898 | -233.51089 | -233.71516 | -233.49607 | -233.54612 | -233.57796 |
| 3.1 | -233.33497 | -233.50683 | -233.71108 | -233.49180 | -233.54141 | -233.57292 |
| 3.2 | -233.33142 | -233.50320 | -233.70746 | -233.48797 | -233.53713 | -233.56835 |
| 3.3 | -233.32829 | -233.49999 | -233.70427 | -233.48454 | -233.53324 | -233.56422 |
| 3.4 | -233.32555 | -233.49715 | -233.70150 | -233.48149 | -233.52974 | -233.56050 |
| 3.5 | -233.32309 | -233.49459 | -233.69903 | -233.47870 | -233.52651 | -233.55704 |
| 3.6 | -233.32104 | -233.49246 | -233.69695 | -233.47633 | -233.52375 | -233.55406 |
| 3.7 | -233.31923 | -233.49057 | -233.69513 | -233.47421 | -233.52125 | -233.55134 |
| 3.8 | -233.31767 | -233.48894 | -233.69358 | -233.47234 | -233.51902 | -233.54890 |

**Table S17.** Methyl cation addition to [1.1.1]propellane: Part III, double-hybrid DFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| $r_1$ / Å | B2PLYP | B2PLYP-D3BJ | B2GP-PLYP | B2GP-PLYP-D3BJ | PWPB95 | DSD-BLYP | DSD-PBEB95 | DSD-PBEP86 |
|---|---|---|---|---|---|---|---|---|
| 1.5 | -233.56443 | -233.57375 | -233.52374 | -233.53045 | -233.59852 | -233.50005 | -233.37400 | -233.36417 |
| 1.6 | -233.56253 | -233.57174 | -233.52160 | -233.52822 | -233.59625 | -233.49772 | -233.37161 | -233.36196 |
| 1.7 | -233.55523 | -233.56432 | -233.51400 | -233.52054 | -233.58856 | -233.48992 | -233.36371 | -233.35420 |
| 1.8 | -233.54524 | -233.55422 | -233.50369 | -233.51014 | -233.57817 | -233.47939 | -233.35305 | -233.34365 |
| 1.9 | -233.53418 | -233.54306 | -233.49229 | -233.49868 | -233.56673 | -233.46777 | -233.34129 | -233.33199 |
| 2.0 | -233.52299 | -233.53184 | -233.48077 | -233.48714 | -233.55521 | -233.45602 | -233.32943 | -233.32018 |
| 2.1 | -233.51216 | -233.52097 | -233.46962 | -233.47595 | -233.54408 | -233.44461 | -233.31795 | -233.30872 |
| 2.2 | -233.50194 | -233.51064 | -233.45909 | -233.46535 | -233.53362 | -233.43381 | -233.30713 | -233.29788 |
| 2.3 | -233.49243 | -233.50101 | -233.44928 | -233.45545 | -233.52392 | -233.42373 | -233.29705 | -233.28776 |
| 2.4 | -233.48363 | -233.49208 | -233.44019 | -233.44627 | -233.51498 | -233.41437 | -233.28774 | -233.27838 |
| 2.5 | -233.47560 | -233.48393 | -233.43188 | -233.43788 | -233.50683 | -233.40585 | -233.27927 | -233.26985 |
| 2.6 | -233.46813 | -233.47633 | -233.42414 | -233.43004 | -233.49928 | -233.39785 | -233.27136 | -233.26185 |
| 2.7 | -233.46137 | -233.46944 | -233.41712 | -233.42293 | -233.49250 | -233.39057 | -233.26419 | -233.25457 |
| 2.8 | -233.45519 | -233.46313 | -233.41069 | -233.41642 | -233.48633 | -233.38390 | -233.25762 | -233.24791 |
| 2.9 | -233.44958 | -233.45740 | -233.40484 | -233.41048 | -233.48075 | -233.37782 | -233.25164 | -233.24183 |
| 3.0 | -233.44449 | -233.45219 | -233.39952 | -233.40507 | -233.47573 | -233.37229 | -233.24622 | -233.23631 |
| 3.1 | -233.43989 | -233.44748 | -233.39468 | -233.40016 | -233.47122 | -233.36727 | -233.24134 | -233.23129 |
| 3.2 | -233.43574 | -233.44322 | -233.39030 | -233.39571 | -233.46717 | -233.36271 | -233.23690 | -233.22674 |
| 3.3 | -233.43200 | -233.43939 | -233.38634 | -233.39168 | -233.46353 | -233.35859 | -233.23285 | -233.22262 |
| 3.4 | -233.42865 | -233.43595 | -233.38276 | -233.38804 | -233.46029 | -233.35487 | -233.22918 | -233.21890 |
| 3.5 | -233.42560 | -233.43283 | -233.37949 | -233.38471 | -233.45739 | -233.35148 | -233.22585 | -233.21550 |
| 3.6 | -233.42295 | -233.43009 | -233.37659 | -233.38176 | -233.45491 | -233.34846 | -233.22297 | -233.21249 |
| 3.7 | -233.42056 | -233.42764 | -233.37397 | -233.37909 | -233.45269 | -233.34574 | -233.22034 | -233.20975 |
| 3.8 | -233.41845 | -233.42547 | -233.37160 | -233.37669 | -233.45072 | -233.34328 | -233.21793 | -233.20729 |

**Table S18.** Hydrogen atom addition to [1.1.1]propellane: Part I, WFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| $r_1$ / Å | CASSCF(3,3) $D_0$ | CASSCF(3,3) $D_1$ | CASSCF(3,3) $Q_0$ | DLPNO-CCSD(T) | HF | MP2 |
|---|---|---|---|---|---|---|
| 1.0 | -193.34610 | -192.70859 | -192.44060 | -194.26396 | -193.33557 | -194.19691 |
| 1.1 | -193.35303 | -192.82153 | -192.65308 | -194.26986 | -193.33975 | -194.20253 |
| 1.3 | -193.34432 | -192.93435 | -192.80471 | -194.26049 | -193.32805 | -194.19258 |
| 1.4 | -193.32927 | -193.02919 | -192.91188 | -194.24520 | -193.30998 | -194.17613 |
| 1.5 | -193.31335 | -193.09888 | -192.98451 | -194.22948 | -193.29179 | -194.15806 |
| 1.6 | -193.30044 | -193.13821 | -193.02600 | -194.21680 | -193.27804 | -194.14320 |
| 1.8 | -193.29294 | -193.14890 | -193.04472 | -194.20867 | -193.26992 | -194.13622 |
| 1.9 | -193.29041 | -193.14371 | -193.05414 | -194.20449 | -193.26600 | -194.13535 |
| 2.0 | -193.29067 | -193.13305 | -193.06083 | -194.20288 | -193.26463 | -194.13712 |
| 2.1 | -193.29171 | -193.12412 | -193.06525 | -194.20171 | -193.26450 | -194.13917 |
| 2.2 | -193.29316 | -193.11493 | -193.06964 | -194.20157 | -193.26487 | -194.14165 |
| 2.3 | -193.29453 | -193.10746 | -193.07329 | -194.20166 | -193.26547 | -194.14393 |
| 2.5 | -193.29570 | -193.10183 | -193.07644 | -194.20188 | -193.26608 | -194.14579 |
| 2.6 | -193.29664 | -193.09738 | -193.07873 | -194.20208 | -193.26668 | -194.14725 |
| 2.7 | -193.29737 | -193.09395 | -193.08040 | -194.20227 | -193.26722 | -194.14831 |
| 2.8 | -193.29792 | -193.09140 | -193.08163 | -194.20240 | -193.26766 | -194.14900 |
| 2.9 | -193.29834 | -193.08951 | -193.08252 | -194.20247 | -193.26802 | -194.14941 |
| 3.0 | -193.29865 | -193.08814 | -193.08317 | -194.20257 | -193.26830 | -194.14965 |
| 3.2 | -193.29887 | -193.08716 | -193.08365 | -194.20259 | -193.26851 | -194.14978 |
| 3.3 | -193.29904 | -193.08645 | -193.08398 | -194.20259 | -193.26867 | -194.14983 |
| 3.4 | -193.29916 | -193.08596 | -193.08423 | -194.20258 | -193.26878 | -194.14986 |
| 3.5 | -193.29924 | -193.08569 | -193.08448 | -194.20256 | -193.26886 | -194.14985 |

**Table S19.** Hydrogen atom addition to [1.1.1]propellane: Part II, single-hybrid DFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| $r_1$ / Å | PBE | B97-D3 | TPSS | B3LYP | M06-2X[a] | ωB97X-D3 |
|---|---|---|---|---|---|---|
| 1.0 | -194.39668 | -194.52570 | -194.70513 | -194.52626 | -194.57789 | -194.60958 |
| 1.1 | -194.40408 | -194.53235 | -194.71173 | -194.53213 | -194.58362 | -194.61518 |
| 1.3 | -194.39648 | -194.52426 | -194.70355 | -194.52310 | -194.57385 | -194.60531 |
| 1.4 | -194.38309 | -194.51077 | -194.68981 | -194.50832 | -194.55794 | -194.58909 |
| 1.5 | -194.36911 | -194.49727 | -194.67582 | -194.49309 | -194.54181 | -194.57188 |
| 1.6 | -194.35761 | -194.48571 | -194.66478 | -194.48067 | -194.52961 | -194.55706 |
| 1.8 | -194.34954 | -194.47728 | -194.65753 | -194.47228 | -194.52297 | -194.54704 |
| 1.9 | -194.34433 | -194.47154 | -194.65296 | -194.46723 | -194.52011 | -194.54176 |
| 2.0 | -194.34122 | -194.46771 | -194.65001 | -194.46437 | -194.51895 | -194.53941 |
| 2.1 | -194.33970 | -194.46558 | -194.64832 | -194.46300 | -194.51859 | -194.53863 |
| 2.2 | -194.33861 | -194.46378 | -194.64677 | -194.46200 | -194.51847 | -194.53833 |
| 2.3 | -194.33802 | -194.46253 | -194.64554 | -194.46139 | -194.51853 | -194.53839 |
| 2.5 | -194.33768 | -194.46166 | -194.64450 | -194.46097 | -194.51871 | -194.53861 |
| 2.6 | -194.33752 | -194.46123 | -194.64361 | -194.46071 | -194.51893 | -194.53892 |
| 2.7 | -194.33746 | -194.46120 | -194.64285 | -194.46054 | - | -194.53924 |
| 2.8 | -194.33745 | -194.46135 | -194.64221 | -194.46042 | - | -194.53955 |
| 2.9 | -194.33745 | -194.46162 | -194.64166 | -194.46032 | - | -194.53984 |
| 3.0 | -194.33745 | -194.46190 | -194.64119 | -194.46025 | - | -194.54010 |
| 3.2 | -194.33747 | -194.46219 | -194.64081 | -194.46019 | - | -194.54030 |
| 3.3 | -194.33748 | -194.46257 | -194.64049 | -194.46014 | - | -194.54048 |
| 3.4 | -194.33748 | -194.46293 | -194.64022 | -194.46010 | - | -194.54064 |
| 3.5 | -194.33746 | -194.46323 | -194.63993 | -194.46006 | - | -194.54076 |

[a] Serious convergence failures were observed at separations past 2.6 Å.

**Table S20.** Hydrogen atom addition to [1.1.1]propellane: Part III, double-hybrid DFT methods. Energies in Hartrees. All calculations used a def2-QZVPP basis set.

| $r_1$ / Å | B2PLYP | B2PLYP-D3BJ | B2GP-PLYP | B2GP-PLYP-D3BJ | PWPB95 | DSD-BLYP | DSD-PBEB95 | DSD-PBEP86 |
|---|---|---|---|---|---|---|---|---|
| 1.0 | -194.48674 | -194.49347 | -194.45296 | -194.45782 | -194.51512 | -194.43342 | -194.32745 | -194.32124 |
| 1.1 | -194.49237 | -194.49907 | -194.45832 | -194.46317 | -194.52068 | -194.43874 | -194.33298 | -194.32704 |
| 1.3 | -194.48292 | -194.48959 | -194.44848 | -194.45331 | -194.51110 | -194.42878 | -194.32318 | -194.31740 |
| 1.4 | -194.46762 | -194.47432 | -194.43268 | -194.43753 | -194.49562 | -194.41280 | -194.30730 | -194.30156 |
| 1.5 | -194.45186 | -194.45871 | -194.41633 | -194.42128 | -194.47963 | -194.39621 | -194.29071 | -194.28485 |
| 1.6 | -194.43923 | -194.44609 | -194.40321 | -194.40817 | -194.46677 | -194.38296 | -194.27733 | -194.27120 |
| 1.8 | -194.43157 | -194.43839 | -194.39556 | -194.40050 | -194.45909 | -194.37568 | -194.27002 | -194.26342 |
| 1.9 | -194.42792 | -194.43469 | -194.39237 | -194.39726 | -194.45559 | -194.37316 | -194.26761 | -194.26055 |
| 2.0 | -194.42643 | -194.43314 | -194.39141 | -194.39627 | -194.45421 | -194.37290 | -194.26736 | -194.26006 |
| 2.1 | -194.42596 | -194.43261 | -194.39131 | -194.39614 | -194.45381 | -194.37328 | -194.26771 | -194.26034 |
| 2.2 | -194.42576 | -194.43235 | -194.39146 | -194.39625 | -194.45370 | -194.37388 | -194.26822 | -194.26085 |
| 2.3 | -194.42573 | -194.43227 | -194.39169 | -194.39645 | -194.45377 | -194.37444 | -194.26870 | -194.26134 |
| 2.5 | -194.42574 | -194.43223 | -194.39187 | -194.39660 | -194.45392 | -194.37484 | -194.26912 | -194.26168 |
| 2.6 | -194.42578 | -194.43221 | -194.39202 | -194.39671 | -194.45408 | -194.37513 | -194.26945 | -194.26192 |
| 2.7 | -194.42581 | -194.43219 | -194.39213 | -194.39678 | -194.45420 | -194.37531 | -194.26967 | -194.26206 |
| 2.8 | -194.42582 | -194.43215 | -194.39219 | -194.39681 | -194.45432 | -194.37541 | -194.26984 | -194.26214 |
| 2.9 | -194.42582 | -194.43211 | -194.39221 | -194.39681 | -194.45445 | -194.37546 | -194.26998 | -194.26215 |
| 3.0 | -194.42581 | -194.43206 | -194.39222 | -194.39679 | -194.45452 | -194.37548 | -194.27006 | -194.26214 |
| 3.2 | -194.42579 | -194.43200 | -194.39222 | -194.39676 | -194.45454 | -194.37548 | -194.27009 | -194.26212 |
| 3.3 | -194.42577 | -194.43195 | -194.39220 | -194.39672 | -194.45457 | -194.37546 | -194.27012 | -194.26208 |
| 3.4 | -194.42574 | -194.43189 | -194.39218 | -194.39668 | -194.45462 | -194.37543 | -194.27015 | -194.26203 |
| 3.5 | -194.42571 | -194.43183 | -194.39215 | -194.39663 | -194.45465 | -194.37540 | -194.27016 | -194.26198 |

**Table S21.** Hydride addition to [1.1.1]propellane: Part I, WFT methods. Energies in Hartrees. All calculations used a ma-def2-QZVPP basis set.

| $r_1$ / Å | CASSCF(4,3) $S_0$ | CASSCF(4,3) $S_1$ | CASSCF(4,3) $T_0$ | DLPNO-CCSD(T) | SMD($Et_2O$)-DLPNO-CCSD(T) | HF | MP2 |
|---|---|---|---|---|---|---|---|
| 1.0 | -193.30422 | -192.13982 | -192.46557 | -194.27328 | -194.35300 | -193.29064 | -194.21062 |
| 1.1 | -193.31403 | -192.45880 | -192.69123 | -194.28176 | -194.36031 | -193.29784 | -194.21914 |
| 1.3 | -193.30912 | -192.63191 | -192.83557 | -194.27597 | -194.35288 | -193.29025 | -194.21331 |
| 1.4 | -193.29848 | -192.74571 | -192.93366 | -194.26501 | -194.34006 | -193.27709 | -194.2023 |
| 1.5 | -193.28682 | -192.82235 | -192.99972 | -194.25352 | -194.32699 | -193.26342 | -194.19087 |
| 1.6 | -193.27649 | -192.87286 | -193.04290 | -194.24366 | -194.31655 | -193.25192 | -194.1813 |
| 1.8 | -193.26852 | -192.90346 | -193.06902 | -194.23612 | -194.31011 | -193.24388 | -194.17422 |
| 1.9 | -193.26330 | -192.98748 | -193.08779 | -194.23016 | -194.30880 | -193.23999 | -194.16948 |
| 2.0 | -193.26424 | -192.98910 | -193.08382 | -194.22707 | -194.30990 | -193.23873 | -194.16617 |
| 2.1 | -193.26589 | -192.98827 | -193.08127 | -194.22585 | -194.31165 | -193.23904 | -194.16453 |
| 2.2 | -193.26814 | -192.98662 | -193.07800 | -194.22517 | -194.31392 | -193.24011 | -194.16339 |
| 2.3 | -193.27039 | -192.98513 | -193.07728 | -194.22502 | -194.31536 | -193.24154 | -194.16276 |
| 2.5 | -193.27246 | -192.98456 | -193.07505 | -194.22424 | -194.31745 | -193.24303 | -194.16242 |
| 2.6 | -193.27427 | -192.98345 | -193.07419 | -194.22428 | -194.31925 | -193.24443 | -194.16224 |
| 2.7 | -193.27583 | -192.98216 | -193.07340 | -194.22441 | -194.32071 | -193.2457 | -194.16212 |
| 2.8 | -193.27713 | -192.98098 | -193.07282 | -194.22451 | -194.32203 | -193.2468 | -194.16202 |
| 2.9 | -193.27822 | -192.98005 | -193.07252 | -194.22455 | -194.32313 | -193.24772 | -194.16193 |
| 3.0 | -193.27911 | -192.97904 | -193.07215 | -194.22453 | -194.32406 | -193.2485 | -194.16181 |
| 3.2 | -193.27983 | -192.97814 | -193.07186 | -194.22446 | -194.32497 | -193.24914 | -194.16167 |
| 3.3 | -193.28040 | -192.97766 | -193.07187 | -194.22437 | -194.32557 | -193.24962 | -194.16151 |
| 3.4 | -193.28084 | -192.97678 | -193.07156 | -194.22419 | -194.32606 | -193.25002 | -194.16132 |
| 3.5 | -193.28117 | -192.97619 | -193.07135 | -194.224 | -194.32648 | -193.25031 | -194.16112 |

**Table S22.** Hydride addition to [1.1.1]propellane: Part II, single-hybrid DFT methods. Energies in Hartrees. All calculations used a ma-def2-QZVPP basis set.

| $r_1$ / Å | PBE | B97-D3 | TPSS | B3LYP | M06-2X | ωB97X-D3 |
|---|---|---|---|---|---|---|
| 1.0 | -194.40682 | -194.53471 | -194.71081 | -194.53162 | -194.58573 | -194.6136 |
| 1.1 | -194.41754 | -194.54475 | -194.72075 | -194.54064 | -194.59424 | -194.62184 |
| 1.3 | -194.41427 | -194.54118 | -194.71697 | -194.53591 | -194.58837 | -194.61574 |
| 1.4 | -194.40576 | -194.53294 | -194.70824 | -194.52622 | -194.57736 | -194.60431 |
| 1.5 | -194.39639 | -194.52462 | -194.69889 | -194.51596 | -194.56614 | -194.59233 |
| 1.6 | -194.38807 | -194.51708 | -194.69078 | -194.50713 | -194.55686 | -194.58188 |
| 1.8 | -194.38134 | -194.51109 | -194.68436 | -194.5003 | -194.55003 | -194.57397 |
| 1.9 | -194.37521 | -194.50621 | -194.6785 | -194.49479 | -194.54596 | -194.56846 |
| 2.0 | -194.37112 | -194.50297 | -194.6747 | -194.4913 | -194.54302 | -194.56548 |
| 2.1 | -194.36889 | -194.50133 | -194.67266 | -194.4896 | -194.54159 | -194.56435 |
| 2.2 | -194.36712 | -194.50009 | -194.67106 | -194.48842 | -194.54056 | -194.56387 |
| 2.3 | -194.36591 | -194.49933 | -194.66998 | -194.48777 | -194.54002 | -194.5639 |
| 2.5 | -194.36508 | -194.49888 | -194.66924 | -194.48743 | -194.53982 | -194.56415 |
| 2.6 | -194.36448 | -194.49859 | -194.6687 | -194.48727 | -194.53982 | -194.56447 |
| 2.7 | -194.36402 | -194.49839 | -194.66829 | -194.48721 | -194.5399 | -194.5648 |
| 2.8 | -194.36365 | -194.49824 | -194.66797 | -194.48718 | -194.53998 | -194.56508 |
| 2.9 | -194.36334 | -194.49811 | -194.66772 | -194.48718 | -194.54004 | -194.56533 |
| 3.0 | -194.36306 | -194.49798 | -194.6675 | -194.48717 | -194.54006 | -194.56552 |
| 3.2 | -194.3628 | -194.49786 | -194.66729 | -194.48714 | -194.53999 | -194.56562 |
| 3.3 | -194.36255 | -194.49773 | -194.66712 | -194.48709 | -194.53981 | -194.56563 |
| 3.4 | -194.36228 | -194.49756 | -194.66692 | -194.48701 | -194.53968 | -194.56563 |
| 3.5 | -194.36202 | -194.49738 | -194.66675 | -194.4869 | -194.53952 | -194.56558 |

**Table S23.** Hydride addition to [1.1.1]propellane: Part III, double-hybrid DFT methods. Energies in Hartrees. All calculations used a ma-def2-QZVPP basis set.

| $r_1$ / Å | **B2PLYP** | **B2PLYP-D3BJ** | **B2GP-PLYP** | **B2GP-PLYP-D3BJ** | **PWPB95** | **DSD-BLYP** | **DSD-PBEB95** | **DSD-PBEP86** |
|---|---|---|---|---|---|---|---|---|
| 1.0 | -194.49426 | -194.5011 | -194.45987 | -194.46482 | -194.52107 | -194.44252 | -194.33381 | -194.32977 |
| 1.1 | -194.50291 | -194.50972 | -194.46821 | -194.47313 | -194.52955 | -194.45081 | -194.34224 | -194.3385 |
| 1.3 | -194.49769 | -194.50445 | -194.46253 | -194.46743 | -194.52406 | -194.44501 | -194.33652 | -194.333 |
| 1.4 | -194.48751 | -194.49427 | -194.45186 | -194.45675 | -194.5136 | -194.43418 | -194.32571 | -194.32235 |
| 1.5 | -194.47687 | -194.48377 | -194.44077 | -194.44575 | -194.50273 | -194.42298 | -194.31449 | -194.31122 |
| 1.6 | -194.4678 | -194.47471 | -194.43137 | -194.43636 | -194.4935 | -194.41351 | -194.30501 | -194.30176 |
| 1.8 | -194.46085 | -194.4677 | -194.42427 | -194.42922 | -194.48655 | -194.40639 | -194.29793 | -194.29459 |
| 1.9 | -194.45528 | -194.46207 | -194.41895 | -194.42386 | -194.48152 | -194.40124 | -194.29303 | -194.28931 |
| 2.0 | -194.45173 | -194.45846 | -194.41551 | -194.42039 | -194.47832 | -194.39773 | -194.28985 | -194.28586 |
| 2.1 | -194.45 | -194.45667 | -194.41387 | -194.41871 | -194.47686 | -194.396 | -194.2884 | -194.2842 |
| 2.2 | -194.44879 | -194.45541 | -194.41275 | -194.41755 | -194.47592 | -194.39477 | -194.28748 | -194.28307 |
| 2.3 | -194.44812 | -194.45468 | -194.41217 | -194.41694 | -194.4755 | -194.39408 | -194.28707 | -194.28247 |
| 2.5 | -194.44777 | -194.45427 | -194.41189 | -194.41663 | -194.47537 | -194.39371 | -194.28696 | -194.28218 |
| 2.6 | -194.4476 | -194.45405 | -194.41178 | -194.41648 | -194.47538 | -194.39352 | -194.28698 | -194.28204 |
| 2.7 | -194.44751 | -194.45391 | -194.41174 | -194.41641 | -194.47543 | -194.3934 | -194.28702 | -194.28198 |
| 2.8 | -194.44747 | -194.45382 | -194.41174 | -194.41637 | -194.47549 | -194.39333 | -194.28707 | -194.28194 |
| 2.9 | -194.44743 | -194.45374 | -194.41173 | -194.41634 | -194.47558 | -194.39326 | -194.28714 | -194.2819 |
| 3.0 | -194.44739 | -194.45365 | -194.41171 | -194.41629 | -194.47567 | -194.39318 | -194.2872 | -194.28183 |
| 3.2 | -194.44733 | -194.45355 | -194.41166 | -194.41622 | -194.47566 | -194.39308 | -194.28717 | -194.28175 |
| 3.3 | -194.44724 | -194.45343 | -194.41159 | -194.41612 | -194.47557 | -194.39296 | -194.28705 | -194.28162 |
| 3.4 | -194.44712 | -194.45328 | -194.41148 | -194.41599 | -194.4755 | -194.39282 | -194.28695 | -194.28147 |
| 3.5 | -194.44698 | -194.45311 | -194.41134 | -194.41584 | -194.47543 | -194.39265 | -194.28684 | -194.28129 |

**Table S24.** Methyl radical addition to [1.1.1]propellane, calculated at CAS(3,3)/def2-QZVPP. All energies in Hartrees.

| CAS(3,3) | CASSCF(3,3) $D_0$ | CASSCF(3,3) $D_1$ | CASSCF(3,3) $Q_0$ | DLPNO-CCSD(T) |
|---|---|---|---|---|
| 1.5 | -232.40793 | -231.80266 | -231.57177 | -233.52673 |
| 1.6 | -232.40671 | -231.89407 | -231.73336 | -233.52402 |
| 1.7 | -232.39921 | -231.98545 | -231.85635 | -233.51598 |
| 1.8 | -232.38867 | -232.06611 | -231.95007 | -233.50519 |
| 1.9 | -232.37737 | -232.13153 | -232.02046 | -233.49391 |
| 2.0 | -232.36714 | -232.17937 | -232.07029 | -233.48400 |
| 2.1 | -232.35970 | -232.20671 | -232.10069 | -233.47649 |
| 2.2 | -232.35618 | -232.21518 | -232.11682 | -233.47206 |
| 2.3 | -232.35616 | -232.21173 | -232.12582 | -233.47017 |
| 2.4 | -232.35809 | -232.20366 | -232.13218 | -233.46928 |
| 2.5 | -232.36069 | -232.19495 | -232.13723 | -233.46991 |
| 2.6 | -232.36330 | -232.18727 | -232.14177 | -233.47085 |
| 2.7 | -232.36567 | -232.18017 | -232.14617 | -233.47188 |
| 2.8 | -232.36777 | -232.17465 | -232.15000 | -233.47262 |
| 2.9 | -232.36948 | -232.17091 | -232.15210 | -233.47326 |
| 3.0 | -232.37084 | -232.16854 | -232.15407 | -233.47371 |
| 3.1 | -232.37189 | -232.16696 | -232.15580 | -233.47408 |
| 3.2 | -232.37271 | -232.16564 | -232.15703 | -233.47440 |
| 3.3 | -232.37335 | -232.16462 | -232.15800 | -233.47456 |
| 3.4 | -232.37385 | -232.16355 | -232.15848 | -233.47465 |
| 3.5 | -232.37423 | -232.16300 | -232.15910 | -233.47478 |
| 3.6 | -232.37453 | -232.16254 | -232.15956 | -233.47482 |
| 3.7 | -232.37477 | -232.16218 | -232.15991 | -233.47482 |
| 3.8 | -232.37495 | -232.16191 | -232.16018 | -233.47481 |

**Table S25.** Solvation effects on radical PES – addition of $H^{\bullet}$ to [1.1.1]propellane, calculated at B2PLYP-D3BJ/def2-QZVPP with and without SMD for $Et_2O$.

| | **Gas phase** | | **SMD implicit solvation** | |
|---|---|---|---|---|
| ***r*₁ / Å** | **E / Ha** | **ΔE / kcal mol$^{-1}$** | **E / Ha** | **ΔE / kcal mol$^{-1}$** |
| 1.0 | -194.49401 | -38.6 | -194.50392 | -36.6 |
| 1.1 | -194.49965 | -42.2 | -194.50956 | -40.1 |
| 1.3 | -194.49025 | -36.3 | -194.50017 | -34.2 |
| 1.4 | -194.47511 | -26.8 | -194.48511 | -24.8 |
| 1.5 | -194.45967 | -17.1 | -194.46994 | -15.2 |
| 1.6 | -194.44715 | -9.2 | -194.45799 | -7.7 |
| 1.8 | -194.43938 | -4.4 | -194.45075 | -3.2 |
| 1.9 | -194.43555 | -2.0 | -194.44725 | -1.0 |
| 2.0 | -194.43389 | -0.9 | -194.44568 | 0.0 |
| 2.1 | -194.43331 | -0.5 | -194.44511 | 0.3 |
| 2.2 | -194.43301 | -0.4 | -194.44483 | 0.5 |
| 2.3 | -194.43290 | -0.3 | -194.44476 | 0.6 |
| 2.5 | -194.43286 | -0.3 | -194.44480 | 0.5 |
| 2.6 | -194.43283 | -0.2 | -194.44489 | 0.5 |
| 2.7 | -194.43280 | -0.2 | -194.44499 | 0.4 |
| 2.8 | -194.43276 | -0.2 | -194.44509 | 0.3 |
| 2.9 | -194.43272 | -0.2 | -194.44520 | 0.3 |
| 3.0 | -194.43266 | -0.1 | -194.44530 | 0.2 |
| 3.2 | -194.43260 | -0.1 | -194.44539 | 0.2 |
| 3.3 | -194.43255 | -0.1 | -194.44548 | 0.1 |
| 3.4 | -194.43249 | 0.0 | -194.44557 | 0.0 |
| 3.5 | -194.43244 | 0.0 | -194.44565 | 0.0 |

**Table S26.** Solvation effects on anionic PES – addition of H to [1.1.1]propellane, calculated at B2GP-PLYP-D3BJ/def2-QZVPP with and without SMD for $Et_2O$.

| | **Gas phase** | | **SMD implicit solvation** | |
|---|---|---|---|---|
| ***r*₁ / Å** | **E / Ha** | **ΔE / kcal mol$^{-1}$** | **E / Ha** | **ΔE / kcal mol$^{-1}$** |
| 1.0 | -194.46498 | -30.6 | -194.54956 | -13.6 |
| 1.1 | -194.47327 | -35.8 | -194.55660 | -18.1 |
| 1.3 | -194.46759 | -32.2 | -194.54921 | -13.4 |
| 1.4 | -194.45697 | -25.6 | -194.53677 | -5.6 |
| 1.5 | -194.44608 | -18.7 | -194.52459 | 2.0 |
| 1.6 | -194.43676 | -12.9 | -194.51546 | 7.8 |
| 1.8 | -194.42963 | -8.4 | -194.51044 | 10.9 |
| 1.9 | -194.42457 | -5.2 | -194.50914 | 11.7 |
| 2.0 | -194.42120 | -3.1 | -194.51006 | 11.2 |
| 2.1 | -194.41943 | -2.0 | -194.51161 | 10.2 |
| 2.2 | -194.41814 | -1.2 | -194.51377 | 8.8 |
| 2.3 | -194.41740 | -0.7 | -194.51589 | 7.5 |
| 2.5 | -194.41702 | -0.5 | -194.51796 | 6.2 |
| 2.6 | -194.41683 | -0.4 | -194.51979 | 5.0 |
| 2.7 | -194.41675 | -0.3 | -194.52131 | 4.1 |
| 2.8 | -194.41671 | -0.3 | -194.52271 | 3.2 |
| 2.9 | -194.41668 | -0.3 | -194.52391 | 2.5 |
| 3.0 | -194.41664 | -0.3 | -194.52495 | 1.8 |
| 3.2 | -194.41658 | -0.2 | -194.52586 | 1.2 |
| 3.3 | -194.41649 | -0.2 | -194.52663 | 0.8 |
| 3.4 | -194.41638 | -0.1 | -194.52729 | 0.3 |
| 3.5 | -194.41624 | 0.0 | -194.52784 | 0.0 |

**Table S27.** Solvation effects on cationic PES – addition of $H^+$ to [1.1.1]propellane, calculated at DSD-BLYP/def2-QZVPP with and without SMD for $Et_2O$.

| | **Gas phase** | | **SMD implicit solvation** | |
|---|---|---|---|---|
| $r_1$ **/ Å** | **E / Ha** | **ΔE / kcal mol$^{-1}$** | **E / Ha** | **ΔE / kcal mol$^{-1}$** |
| 1.0 | -194.20064 | -134.8 | -194.29514 | -147.1 |
| 1.1 | -194.20413 | -137.0 | -194.29851 | -149.2 |
| 1.3 | -194.19131 | -129.0 | -194.28531 | -140.9 |
| 1.4 | -194.17111 | -116.3 | -194.26451 | -127.9 |
| 1.5 | -194.14832 | -102.0 | -194.23995 | -112.5 |
| 1.6 | -194.12547 | -87.6 | -194.21656 | -97.8 |
| 1.8 | -194.10388 | -74.1 | -194.18903 | -80.5 |
| 1.9 | -194.08416 | -61.7 | -194.16965 | -68.3 |
| 2.0 | -194.06658 | -50.7 | -194.15246 | -57.6 |
| 2.1 | -194.05409 | -42.8 | -194.14025 | -49.9 |
| 2.2 | -194.04122 | -34.8 | -194.12762 | -42.0 |
| 2.3 | -194.03008 | -27.8 | -194.11654 | -35.0 |
| 2.5 | -194.02056 | -21.8 | -194.10678 | -28.9 |
| 2.6 | -194.01251 | -16.8 | -194.09813 | -23.5 |
| 2.7 | -194.00579 | -12.5 | -194.09031 | -18.6 |
| 2.8 | -194.00027 | -9.1 | -194.08340 | -14.2 |
| 2.9 | -193.99582 | -6.3 | -194.07724 | -10.4 |
| 3.0 | -193.99232 | -4.1 | -194.07189 | -7.0 |
| 3.2 | -193.98967 | -2.4 | -194.06750 | -4.2 |
| 3.3 | -193.98776 | -1.2 | -194.06421 | -2.2 |
| 3.4 | -193.98650 | -0.4 | -194.06203 | -0.8 |
| 3.5 | -193.98581 | 0.0 | -194.06074 | 0.0 |

**Table S28.** Distortion/interaction analysis for methyl cation addition to [1.1.1]propellane, calculated at SMD($Et_2O$)-DLPNO-CCSD(T)/def2-QZVPP//CASSCF(2,3)/def2-QZVPP.

| ***r*₁ / Å** | **E([1.1.1]propellane) / Ha** | **E(CH3) / Ha** | **E(PES) / Ha** | **ΔE(distortion) total/ kcal mol$^{-1}$** | **ΔE(interaction) / kcal mol$^{-1}$** | **ΔE(total) / kcal mol$^{-1}$** |
|---|---|---|---|---|---|---|
| 1.5 | -193.69992 | -39.47345 | -233.36849 | 34.2 | -120.2 | -86.0 |
| 1.6 | -193.70077 | -39.48043 | -233.36625 | 29.3 | -113.9 | -84.6 |
| 1.7 | -193.70153 | -39.48701 | -233.35834 | 24.7 | -104.3 | -79.6 |
| 1.8 | -193.70222 | -39.49309 | -233.34776 | 20.5 | -93.5 | -73.0 |
| 1.9 | -193.70285 | -39.49861 | -233.33620 | 16.6 | -82.4 | -65.8 |
| 2.0 | -193.70286 | -39.50376 | -233.32437 | 13.4 | -71.7 | -58.3 |
| 2.1 | -193.70347 | -39.50778 | -233.31263 | 10.5 | -61.4 | -51.0 |
| 2.2 | -193.70405 | -39.51108 | -233.30156 | 8.0 | -52.0 | -44.0 |
| 2.3 | -193.70462 | -39.51359 | -233.29116 | 6.1 | -43.6 | -37.5 |
| 2.4 | -193.70509 | -39.51548 | -233.28175 | 4.6 | -36.2 | -31.6 |
| 2.5 | -193.70656 | -39.51724 | -233.27346 | 2.6 | -29.0 | -26.4 |
| 2.6 | -193.70707 | -39.51836 | -233.26613 | 1.6 | -23.3 | -21.8 |
| 2.7 | -193.70717 | -39.51892 | -233.25965 | 1.1 | -18.9 | -17.7 |
| 2.8 | -193.70728 | -39.51934 | -233.25385 | 0.8 | -14.9 | -14.1 |
| 2.9 | -193.70738 | -39.51961 | -233.24903 | 0.6 | -11.6 | -11.1 |
| 3.0 | -193.70745 | -39.51978 | -233.24524 | 0.4 | -9.1 | -8.7 |
| 3.1 | -193.70752 | -39.51990 | -233.24211 | 0.3 | -7.0 | -6.7 |
| 3.2 | -193.70757 | -39.51997 | -233.23897 | 0.2 | -5.0 | -4.7 |
| 3.3 | -193.70762 | -39.52002 | -233.23693 | 0.2 | -3.6 | -3.5 |
| 3.4 | -193.70766 | -39.52005 | -233.23528 | 0.1 | -2.6 | -2.4 |
| 3.5 | -193.70775 | -39.52007 | -233.23400 | 0.1 | -1.7 | -1.6 |
| 3.6 | -193.70777 | -39.52009 | -233.23283 | 0.0 | -0.9 | -0.9 |
| 3.7 | -193.70779 | -39.52010 | -233.23204 | 0.0 | -0.4 | -0.4 |
| 3.8 | -193.70781 | -39.52011 | -233.23141 | 0.0 | 0.0 | 0.0 |

**Table S29.** Distortion/interaction analysis for methyl radical addition to [1.1.1]propellane, calculated at DLPNO-CCSD(T)/def2-QZVPP//CASSCF(3,3)/def2-QZVPP.

| **$r_1$ / Å** | **E([1.1.1]propellane) / Ha** | **E(CH3) / Ha** | **E(PES) / Ha** | **ΔE(distortion) total / kcal mol$^{-1}$** | **ΔE(interaction) / kcal mol$^{-1}$** | **ΔE(total) / kcal mol$^{-1}$** |
|---|---|---|---|---|---|---|
| 1.5 | -193.67864 | -39.75913 | -233.52673 | 23.0 | -55.6 | -32.6 |
| 1.6 | -193.68038 | -39.76093 | -233.52402 | 20.8 | -51.6 | -30.9 |
| 1.7 | -193.68220 | -39.76252 | -233.51598 | 18.6 | -44.5 | -25.8 |
| 1.8 | -193.68426 | -39.76396 | -233.50519 | 16.4 | -35.5 | -19.1 |
| 1.9 | -193.68688 | -39.76525 | -233.49391 | 14.0 | -26.0 | -12.0 |
| 2.0 | -193.69038 | -39.76657 | -233.48400 | 11.0 | -16.7 | -5.8 |
| 2.1 | -193.69478 | -39.76787 | -233.47649 | 7.4 | -8.4 | -1.0 |
| 2.2 | -193.69861 | -39.76914 | -233.47206 | 4.2 | -2.4 | 1.7 |
| 2.3 | -193.70069 | -39.77019 | -233.47017 | 2.2 | 0.7 | 2.9 |
| 2.4 | -193.70156 | -39.77098 | -233.46928 | 1.2 | 2.3 | 3.5 |
| 2.5 | -193.70193 | -39.77151 | -233.46991 | 0.6 | 2.5 | 3.1 |
| 2.6 | -193.70210 | -39.77191 | -233.47085 | 0.2 | 2.2 | 2.5 |
| 2.7 | -193.70219 | -39.77227 | -233.47188 | 0.0 | 1.9 | 1.8 |
| 2.8 | -193.70224 | -39.77216 | -233.47262 | 0.0 | 1.4 | 1.4 |
| 2.9 | -193.70228 | -39.77204 | -233.47326 | 0.0 | 0.9 | 1.0 |
| 3.0 | -193.70230 | -39.77198 | -233.47371 | 0.1 | 0.6 | 0.7 |
| 3.1 | -193.70231 | -39.77195 | -233.47408 | 0.1 | 0.4 | 0.5 |
| 3.2 | -193.70232 | -39.77194 | -233.47440 | 0.1 | 0.2 | 0.3 |
| 3.3 | -193.70232 | -39.77194 | -233.47456 | 0.1 | 0.1 | 0.2 |
| 3.4 | -193.70233 | -39.77195 | -233.47465 | 0.1 | 0.0 | 0.1 |
| 3.5 | -193.70234 | -39.77198 | -233.47478 | 0.0 | 0.0 | 0.0 |
| 3.6 | -193.70235 | -39.77201 | -233.47482 | 0.0 | 0.0 | 0.0 |
| 3.7 | -193.70235 | -39.77203 | -233.47482 | 0.0 | 0.0 | 0.0 |
| 3.8 | -193.70235 | -39.77205 | -233.47481 | 0.0 | 0.0 | 0.0 |

**Table S30.** Distortion/interaction analysis for hydride addition to [1.1.1]propellane, calculated at SMD($Et_2O$)-DLPNO-CCSD(T)/def2-QZVPP//CASSCF(4,3)/def2-QZVPP.

| $r_1$ / Å | E([1.1.1]propellane) | E(H) | E(PES) | ΔE(distortion) total / kcal mol$^{-1}$ | ΔE(interaction) / kcal mol$^{-1}$ | ΔE tot |
|---|---|---|---|---|---|---|
| 1.0 | -193.64472 | -0.61706 | -194.35300 | 39.1 | -55.7 | -16.6 |
| 1.1 | -193.64857 | -0.61706 | -194.36031 | 36.7 | -57.9 | -21.2 |
| 1.3 | -193.65354 | -0.61706 | -194.35288 | 33.5 | -50.1 | -16.6 |
| 1.4 | -193.65955 | -0.61706 | -194.34006 | 29.8 | -38.3 | -8.5 |
| 1.5 | -193.66647 | -0.61706 | -194.32699 | 25.4 | -25.8 | -0.3 |
| 1.6 | -193.67406 | -0.61706 | -194.31655 | 20.7 | -14.4 | 6.2 |
| 1.8 | -193.68188 | -0.61706 | -194.31011 | 15.8 | -5.5 | 10.3 |
| 1.9 | -193.69624 | -0.61706 | -194.30880 | 6.8 | 4.3 | 11.1 |
| 2.0 | -193.70048 | -0.61706 | -194.30990 | 4.1 | 6.3 | 10.4 |
| 2.1 | -193.70237 | -0.61706 | -194.31165 | 2.9 | 6.4 | 9.3 |
| 2.2 | -193.70374 | -0.61706 | -194.31392 | 2.0 | 5.8 | 7.9 |
| 2.3 | -193.70464 | -0.61706 | -194.31536 | 1.5 | 5.5 | 7.0 |
| 2.5 | -193.70523 | -0.61706 | -194.31745 | 1.1 | 4.6 | 5.7 |
| 2.6 | -193.70566 | -0.61706 | -194.31925 | 0.8 | 3.7 | 4.5 |
| 2.7 | -193.70598 | -0.61706 | -194.32071 | 0.6 | 3.0 | 3.6 |
| 2.8 | -193.70624 | -0.61706 | -194.32203 | 0.5 | 2.3 | 2.8 |
| 2.9 | -193.70642 | -0.61706 | -194.32313 | 0.4 | 1.7 | 2.1 |
| 3.0 | -193.70659 | -0.61706 | -194.32406 | 0.3 | 1.3 | 1.5 |
| 3.2 | -193.70672 | -0.61706 | -194.32497 | 0.2 | 0.8 | 0.9 |
| 3.3 | -193.70678 | -0.61706 | -194.32557 | 0.1 | 0.4 | 0.6 |
| 3.4 | -193.70692 | -0.61706 | -194.32606 | 0.1 | 0.2 | 0.3 |
| 3.5 | -193.70700 | -0.61706 | -194.32648 | 0.0 | 0.0 | 0.0 |

**Table S31.** Thermodynamic quantities for turboamide addition [1.1.1]propellane. Geometries and thermodynamic corrections calculated at SMD(THF)-B2GP-PLYP-D3BJ/ma-def2-TZVP, single point energies at SMD(THF)-DLPNO-CCSD(T)/ma-def2-QZVPP. All energies are reported in Ha.

| | | | **B2GP-PLYP-D3BJ** | | | | **DLPNO-CCSD(T)** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Eel** | **ZPE** | **H** | **Tqh-S** | **Total corr** | **qh-G** | **CC E** | **CC G** | **Imag. freq.** |
| $MgCl^+$ | -659.980305 | 0.0010803 | -659.975676 | 0.02580335 | -0.02117447 | -660.00148 | -659.58006 | -659.60124 | - |
| $NH_2$-BCP-MgCl | -909.96952 | 0.12367043 | -909.83659 | 0.04334866 | 0.08958631 | -909.87993 | -909.38112 | -909.29153 | -28.2* |
| $NH_2$-BCP$^-$ | -249.860643 | 0.11950798 | -249.734796 | 0.03457954 | 0.09126717 | -249.769376 | -249.67618 | -249.58492 | - |
| $NH_2^-$ | -55.9591635 | 0.01899001 | -55.9363922 | 0.02208584 | 0.00068539 | -55.9584781 | -55.945311 | -55.94463 | - |
| [1.1.1]Propellane | -193.87488 | 0.09399087 | -193.775978 | 0.0312099 | 0.06769256 | -193.807187 | -193.71005 | -193.64235 | - |
| TS [[1.1.1]Propellane--$NH_2$]$^-$ | -249.81956 | 0.1147128 | -249.697228 | 0.03765615 | 0.08467572 | -249.734884 | -249.63559 | -249.55092 | -254.8 |

*Spurious persistent imaginary frequency

**Table S32.** Thermodynamic quantities for the radical iodination of [1.1.1]propellane. Geometries and thermodynamic corrections calculated at B2GP-PLYP-D3BJ/def2-TZVP, single point energies at DLPNO-CCSD(T)/def2-QZVPP. All energies are reported in Ha.

| | | | **B2PLYP-D3BJ** | | | | **DLPNO-CCSD(T)** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Species** | **$E_{el}$** | **ZPE** | **H** | **Tqh-S** | **Total corr** | **qh-G** | **E CC** | **G CC** | **Imag. freq.** |
| I• | -297.47175 | 0.00000 | -297.46845 | 0.01921 | -0.01590 | -297.48766 | -297.26755 | -297.28346 | - |
| [1.1.1]Propellane | -193.87506 | 0.09402 | -193.77613 | 0.03120 | 0.06773 | -193.80733 | -193.70903 | -193.64130 | - |
| IBCP• | -491.35948 | 0.09475 | -491.25772 | 0.03971 | 0.06204 | -491.29743 | -490.99011 | -490.92806 | - |
| IBCPI | -788.92955 | 0.09714 | -788.82433 | 0.04283 | 0.06239 | -788.86716 | -788.35806 | -788.29567 | - |
| $I_2$ | -595.01537 | 0.00048 | -595.01104 | 0.02960 | -0.02527 | -595.04064 | -594.60587 | -594.63115 | - |

**Table S33.** PES for the gas-phase addition of F• to [1.1.1]propellane. $r_1$ is the forming C–F bond distance, $r_e$ is the equilibrium C–F bond length in the parent 1-fluorobicyclo[1.1.1]pentane. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.30 | 1.36 | -0.06 | -293.70148 | 2.0 |
| 1.41 | 1.36 | 0.05 | -293.70471 | 0.0 |
| 1.52 | 1.36 | 0.16 | -293.69774 | 4.4 |
| 1.63 | 1.36 | 0.27 | -293.68705 | 11.1 |
| 1.74 | 1.36 | 0.38 | -293.67582 | 18.1 |
| 1.86 | 1.36 | 0.49 | -293.66565 | 24.5 |
| 1.97 | 1.36 | 0.60 | -293.65724 | 29.8 |
| 2.08 | 1.36 | 0.71 | -293.65045 | 34.0 |
| 2.19 | 1.36 | 0.83 | -293.64490 | 37.5 |
| 2.30 | 1.36 | 0.94 | -293.64033 | 40.4 |
| 2.41 | 1.36 | 1.05 | -293.63655 | 42.8 |
| 2.52 | 1.36 | 1.16 | -293.63352 | 44.7 |
| 2.63 | 1.36 | 1.27 | -293.63098 | 46.3 |
| 2.74 | 1.36 | 1.38 | -293.62882 | 47.6 |
| 2.86 | 1.36 | 1.49 | -293.62753 | 48.4 |
| 2.97 | 1.36 | 1.60 | -293.62645 | 49.1 |
| 3.08 | 1.36 | 1.71 | -293.62560 | 49.6 |
| 3.19 | 1.36 | 1.83 | -293.62492 | 50.1 |
| 3.30 | 1.36 | 1.94 | -293.62439 | 50.4 |

**Table S34.** PES for the solvent-phase addition of F• to [1.1.1]propellane. $r_1$ is the forming C–F bond distance, $r_e$ is the equilibrium C–F bond length in the parent 1-fluorobicyclo[1.1.1]pentane. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.30 | 1.38 | -0.08 | -293.71052 | 2.9 |
| 1.41 | 1.38 | 0.03 | -293.71522 | 0.0 |
| 1.52 | 1.38 | 0.15 | -293.7102 | 3.2 |
| 1.63 | 1.38 | 0.26 | -293.70189 | 8.4 |
| 1.74 | 1.38 | 0.37 | -293.69333 | 13.7 |
| 1.86 | 1.38 | 0.48 | -293.6856 | 18.6 |
| 1.97 | 1.38 | 0.59 | -293.67871 | 22.9 |
| 2.08 | 1.38 | 0.70 | -293.6723 | 26.9 |
| 2.19 | 1.38 | 0.81 | -293.66604 | 30.9 |
| 2.30 | 1.38 | 0.92 | -293.65985 | 34.7 |
| 2.41 | 1.38 | 1.03 | -293.65411 | 38.3 |
| 2.52 | 1.38 | 1.15 | -293.6494 | 41.3 |
| 2.63 | 1.38 | 1.26 | -293.64575 | 43.6 |
| 2.74 | 1.38 | 1.37 | -293.64304 | 45.3 |
| 2.86 | 1.38 | 1.48 | -293.64106 | 46.5 |
| 2.97 | 1.38 | 1.59 | -293.63962 | 47.4 |
| 3.08 | 1.38 | 1.70 | -293.63856 | 48.1 |
| 3.19 | 1.38 | 1.81 | -293.63779 | 48.6 |
| 3.30 | 1.38 | 1.92 | -293.63724 | 48.9 |

**Table S35.** PES for the gas-phase addition of Cl• to [1.1.1]propellane. $r_1$ is the forming C–Cl bond distance, $r_e$ is the equilibrium C–Cl bond length in the parent 1-chlorobicyclo[1.1.1]pentane. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.50 | 1.77 | -0.27 | -653.92064 | 28.0 |
| 1.61 | 1.77 | -0.16 | -653.95028 | 9.4 |
| 1.71 | 1.77 | -0.05 | -653.96259 | 1.7 |
| 1.82 | 1.77 | 0.05 | -653.96534 | 0.0 |
| 1.93 | 1.77 | 0.16 | -653.96344 | 1.2 |
| 2.04 | 1.77 | 0.27 | -653.95978 | 3.5 |
| 2.14 | 1.77 | 0.37 | -653.95598 | 5.9 |
| 2.25 | 1.77 | 0.48 | -653.95261 | 8.0 |
| 2.36 | 1.77 | 0.59 | -653.94961 | 9.9 |
| 2.46 | 1.77 | 0.70 | -653.94682 | 11.6 |
| 2.57 | 1.77 | 0.80 | -653.94414 | 13.3 |
| 2.68 | 1.77 | 0.91 | -653.94158 | 14.9 |
| 2.79 | 1.77 | 1.02 | -653.93918 | 16.4 |
| 2.89 | 1.77 | 1.12 | -653.93700 | 17.8 |
| 3.00 | 1.77 | 1.23 | -653.93507 | 19.0 |
| 3.11 | 1.77 | 1.34 | -653.93339 | 20.0 |
| 3.21 | 1.77 | 1.45 | -653.93196 | 20.9 |
| 3.32 | 1.77 | 1.55 | -653.93077 | 21.7 |
| 3.43 | 1.77 | 1.66 | -653.92978 | 22.3 |
| 3.54 | 1.77 | 1.77 | -653.92898 | 22.8 |
| 3.64 | 1.77 | 1.87 | -653.92831 | 23.2 |
| 3.75 | 1.77 | 1.98 | -653.92776 | 23.6 |
| 3.86 | 1.77 | 2.09 | -653.92731 | 23.9 |
| 3.96 | 1.77 | 2.20 | -653.92694 | 24.1 |
| 4.07 | 1.77 | 2.30 | -653.92663 | 24.3 |
| 4.18 | 1.77 | 2.41 | -653.92638 | 24.4 |
| 4.29 | 1.77 | 2.52 | -653.92616 | 24.6 |
| 4.39 | 1.77 | 2.62 | -653.92598 | 24.7 |
| 4.50 | 1.77 | 2.73 | -653.92583 | 24.8 |

**Table S36.** PES for the solvent-phase addition of Cl• to [1.1.1]propellane. $r_1$ is the forming C–Cl bond distance, $r_e$ is the equilibrium C–Cl bond length in the parent 1-chlorobicyclo[1.1.1]pentane. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.50 | 1.78 | -0.28 | -653.93048 | 29.4 |
| 1.61 | 1.78 | -0.17 | -653.96061 | 10.5 |
| 1.71 | 1.78 | -0.07 | -653.97359 | 2.3 |
| 1.82 | 1.78 | 0.04 | -653.97728 | 0.0 |
| 1.93 | 1.78 | 0.15 | -653.97665 | 0.4 |
| 2.04 | 1.78 | 0.25 | -653.9745 | 1.7 |
| 2.14 | 1.78 | 0.36 | -653.97213 | 3.2 |
| 2.25 | 1.78 | 0.47 | -653.96971 | 4.8 |
| 2.36 | 1.78 | 0.58 | -653.96722 | 6.3 |
| 2.46 | 1.78 | 0.68 | -653.9645 | 8.0 |
| 2.57 | 1.78 | 0.79 | -653.96163 | 9.8 |
| 2.68 | 1.78 | 0.90 | -653.95872 | 11.6 |
| 2.79 | 1.78 | 1.00 | -653.95589 | 13.4 |
| 2.89 | 1.78 | 1.11 | -653.95323 | 15.1 |
| 3.00 | 1.78 | 1.22 | -653.95108 | 16.4 |
| 3.11 | 1.78 | 1.33 | -653.94906 | 17.7 |
| 3.21 | 1.78 | 1.43 | -653.94739 | 18.8 |
| 3.32 | 1.78 | 1.54 | -653.94606 | 19.6 |
| 3.43 | 1.78 | 1.65 | -653.94503 | 20.2 |
| 3.54 | 1.78 | 1.75 | -653.94424 | 20.7 |
| 3.64 | 1.78 | 1.86 | -653.94363 | 21.1 |
| 3.75 | 1.78 | 1.97 | -653.94318 | 21.4 |
| 3.86 | 1.78 | 2.08 | -653.94285 | 21.6 |
| 3.96 | 1.78 | 2.18 | -653.94261 | 21.8 |
| 4.07 | 1.78 | 2.29 | -653.94245 | 21.9 |
| 4.18 | 1.78 | 2.40 | -653.94235 | 21.9 |
| 4.29 | 1.78 | 2.50 | -653.94225 | 22.0 |
| 4.39 | 1.78 | 2.61 | -653.94208 | 22.1 |
| 4.50 | 1.78 | 2.72 | -653.94197 | 22.2 |

**Table S37.** PES for the gas-phase addition of Br• to [1.1.1]propellane. $r_1$ is the forming C–Br bond distance, $r_e$ is the equilibrium C–Br bond length in the parent 1-bromobicyclo[1.1.1]pentane. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.60 | 1.93 | -0.33 | -2767.59589 | 40.1 |
| 1.71 | 1.93 | -0.23 | -2767.63247 | 17.1 |
| 1.81 | 1.93 | -0.12 | -2767.65063 | 5.8 |
| 1.92 | 1.93 | -0.01 | -2767.65803 | 1.1 |
| 2.03 | 1.93 | 0.10 | -2767.65979 | 0.0 |
| 2.14 | 1.93 | 0.20 | -2767.65901 | 0.5 |
| 2.24 | 1.93 | 0.31 | -2767.65745 | 1.5 |
| 2.35 | 1.93 | 0.42 | -2767.65579 | 2.5 |
| 2.46 | 1.93 | 0.52 | -2767.65409 | 3.6 |
| 2.56 | 1.93 | 0.63 | -2767.65224 | 4.7 |
| 2.67 | 1.93 | 0.74 | -2767.65025 | 6.0 |
| 2.78 | 1.93 | 0.85 | -2767.64821 | 7.3 |
| 2.89 | 1.93 | 0.95 | -2767.64623 | 8.5 |
| 2.99 | 1.93 | 1.06 | -2767.64435 | 9.7 |
| 3.10 | 1.93 | 1.17 | -2767.64265 | 10.8 |
| 3.21 | 1.93 | 1.27 | -2767.64118 | 11.7 |
| 3.31 | 1.93 | 1.38 | -2767.63991 | 12.5 |
| 3.42 | 1.93 | 1.49 | -2767.63878 | 13.2 |
| 3.53 | 1.93 | 1.60 | -2767.63778 | 13.8 |
| 3.64 | 1.93 | 1.70 | -2767.63694 | 14.3 |
| 3.74 | 1.93 | 1.81 | -2767.63625 | 14.8 |
| 3.85 | 1.93 | 1.92 | -2767.63567 | 15.1 |
| 3.96 | 1.93 | 2.02 | -2767.63517 | 15.4 |
| 4.06 | 1.93 | 2.13 | -2767.63474 | 15.7 |
| 4.17 | 1.93 | 2.24 | -2767.63437 | 15.9 |
| 4.28 | 1.93 | 2.35 | -2767.63407 | 16.1 |
| 4.39 | 1.93 | 2.45 | -2767.63383 | 16.3 |
| 4.49 | 1.93 | 2.56 | -2767.63363 | 16.4 |
| 4.60 | 1.93 | 2.67 | -2767.63345 | 16.5 |

**Table S38.** PES for the solvent-phase addition of Br• to [1.1.1]propellane. $r_1$ is the forming C–Br bond distance, $r_e$ is the equilibrium C–Br bond length in the parent 1-bromobicyclo[1.1.1]pentane. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.60 | 1.95 | -0.35 | -2767.60705 | 41.8 |
| 1.71 | 1.95 | -0.24 | -2767.64390 | 18.6 |
| 1.81 | 1.95 | -0.13 | -2767.66254 | 6.9 |
| 1.92 | 1.95 | -0.02 | -2767.67062 | 1.9 |
| 2.03 | 1.95 | 0.08 | -2767.67328 | 0.2 |
| 2.14 | 1.95 | 0.19 | -2767.67360 | 0.0 |
| 2.24 | 1.95 | 0.30 | -2767.67308 | 0.3 |
| 2.35 | 1.95 | 0.40 | -2767.67215 | 0.9 |
| 2.46 | 1.95 | 0.51 | -2767.67067 | 1.8 |
| 2.56 | 1.95 | 0.62 | -2767.66901 | 2.9 |
| 2.67 | 1.95 | 0.73 | -2767.66698 | 4.2 |
| 2.78 | 1.95 | 0.83 | -2767.66479 | 5.5 |
| 2.89 | 1.95 | 0.94 | -2767.66265 | 6.9 |
| 2.99 | 1.95 | 1.05 | -2767.66060 | 8.2 |
| 3.10 | 1.95 | 1.15 | -2767.65875 | 9.3 |
| 3.21 | 1.95 | 1.26 | -2767.65719 | 10.3 |
| 3.31 | 1.95 | 1.37 | -2767.65591 | 11.1 |
| 3.42 | 1.95 | 1.48 | -2767.65482 | 11.8 |
| 3.53 | 1.95 | 1.58 | -2767.65389 | 12.4 |
| 3.64 | 1.95 | 1.69 | -2767.65314 | 12.8 |
| 3.74 | 1.95 | 1.80 | -2767.65257 | 13.2 |
| 3.85 | 1.95 | 1.90 | -2767.65227 | 13.4 |
| 3.96 | 1.95 | 2.01 | -2767.65193 | 13.6 |
| 4.06 | 1.95 | 2.12 | -2767.65166 | 13.8 |
| 4.17 | 1.95 | 2.23 | -2767.65146 | 13.9 |
| 4.28 | 1.95 | 2.33 | -2767.65135 | 14.0 |
| 4.39 | 1.95 | 2.44 | -2767.65123 | 14.0 |
| 4.49 | 1.95 | 2.55 | -2767.65105 | 14.2 |
| 4.60 | 1.95 | 2.65 | -2767.65088 | 14.3 |

**Table S39.** PES for the gas-phase addition of I• to [1.1.1]propellane. $r_1$ is the forming C–I bond distance, $r_e$ is the equilibrium C–I bond length in the parent 1-iodobicyclo[1.1.1]pentane. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 2.00 | 2.14 | -0.14 | -491.42760 | 8.8 |
| 2.11 | 2.14 | -0.03 | -491.43585 | 3.6 |
| 2.21 | 2.14 | 0.08 | -491.43943 | 1.4 |
| 2.32 | 2.14 | 0.18 | -491.44089 | 0.4 |
| 2.43 | 2.14 | 0.29 | -491.44150 | 0.1 |
| 2.54 | 2.14 | 0.40 | -491.44161 | 0.0 |
| 2.64 | 2.14 | 0.51 | -491.44121 | 0.2 |
| 2.75 | 2.14 | 0.61 | -491.44036 | 0.8 |
| 2.86 | 2.14 | 0.72 | -491.43919 | 1.5 |
| 2.96 | 2.14 | 0.83 | -491.43786 | 2.4 |
| 3.07 | 2.14 | 0.93 | -491.43645 | 3.2 |
| 3.18 | 2.14 | 1.04 | -491.43504 | 4.1 |
| 3.29 | 2.14 | 1.15 | -491.43371 | 5.0 |
| 3.39 | 2.14 | 1.26 | -491.43250 | 5.7 |
| 3.50 | 2.14 | 1.36 | -491.43143 | 6.4 |
| 3.61 | 2.14 | 1.47 | -491.43049 | 7.0 |
| 3.71 | 2.14 | 1.58 | -491.42966 | 7.5 |
| 3.82 | 2.14 | 1.68 | -491.42893 | 8.0 |
| 3.93 | 2.14 | 1.79 | -491.42831 | 8.3 |
| 4.04 | 2.14 | 1.90 | -491.42777 | 8.7 |
| 4.14 | 2.14 | 2.01 | -491.42730 | 9.0 |
| 4.25 | 2.14 | 2.11 | -491.42690 | 9.2 |
| 4.36 | 2.14 | 2.22 | -491.42654 | 9.5 |
| 4.46 | 2.14 | 2.33 | -491.42624 | 9.6 |
| 4.57 | 2.14 | 2.43 | -491.42599 | 9.8 |
| 4.68 | 2.14 | 2.54 | -491.42577 | 9.9 |
| 4.79 | 2.14 | 2.65 | -491.42558 | 10.1 |
| 4.89 | 2.14 | 2.76 | -491.42542 | 10.2 |
| 5.00 | 2.14 | 2.86 | -491.42527 | 10.2 |

**Table S40.** PES for the solvent-phase addition of I• to [1.1.1]propellane. $r_1$ is the forming C–I bond distance, $r_e$ is the equilibrium C–I bond length in the parent 1-iodobicyclo[1.1.1]pentane. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 2.00 | 2.14 | -0.14 | -491.43648 | 10.9 |
| 2.11 | 2.14 | -0.04 | -491.44518 | 5.5 |
| 2.21 | 2.14 | 0.07 | -491.44951 | 2.8 |
| 2.32 | 2.14 | 0.18 | -491.45195 | 1.2 |
| 2.43 | 2.14 | 0.28 | -491.45337 | 0.3 |
| 2.54 | 2.14 | 0.39 | -491.45392 | 0.0 |
| 2.64 | 2.14 | 0.50 | -491.45364 | 0.2 |
| 2.75 | 2.14 | 0.61 | -491.45273 | 0.7 |
| 2.86 | 2.14 | 0.71 | -491.45144 | 1.6 |
| 2.96 | 2.14 | 0.82 | -491.44998 | 2.5 |
| 3.07 | 2.14 | 0.93 | -491.44851 | 3.4 |
| 3.18 | 2.14 | 1.03 | -491.44708 | 4.3 |
| 3.29 | 2.14 | 1.14 | -491.44580 | 5.1 |
| 3.39 | 2.14 | 1.25 | -491.44470 | 5.8 |
| 3.50 | 2.14 | 1.36 | -491.44379 | 6.4 |
| 3.61 | 2.14 | 1.46 | -491.44303 | 6.8 |
| 3.71 | 2.14 | 1.57 | -491.44241 | 7.2 |
| 3.82 | 2.14 | 1.68 | -491.44190 | 7.5 |
| 3.93 | 2.14 | 1.78 | -491.44151 | 7.8 |
| 4.04 | 2.14 | 1.89 | -491.44120 | 8.0 |
| 4.14 | 2.14 | 2.00 | -491.44098 | 8.1 |
| 4.25 | 2.14 | 2.11 | -491.44082 | 8.2 |
| 4.36 | 2.14 | 2.21 | -491.44072 | 8.3 |
| 4.46 | 2.14 | 2.32 | -491.44059 | 8.4 |
| 4.57 | 2.14 | 2.43 | -491.44072 | 8.3 |
| 4.68 | 2.14 | 2.53 | -491.44066 | 8.3 |
| 4.79 | 2.14 | 2.64 | -491.44059 | 8.4 |
| 4.89 | 2.14 | 2.75 | -491.44055 | 8.4 |
| 5.00 | 2.14 | 2.86 | -491.44049 | 8.4 |

**Table S41.** PES for the gas-phase addition of •OH to [1.1.1]propellane. $r_1$ is the forming C–O bond distance, $r_e$ is the equilibrium C–O bond length in the parent bicyclo[1.1.1]pentan-1-ol. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.20 | 1.39 | -0.19 | -269.64443 | 20.7 |
| 1.31 | 1.39 | -0.07 | -269.67286 | 2.9 |
| 1.43 | 1.39 | 0.04 | -269.67749 | 0.0 |
| 1.54 | 1.39 | 0.15 | -269.67074 | 4.2 |
| 1.65 | 1.39 | 0.26 | -269.65960 | 11.2 |
| 1.76 | 1.39 | 0.38 | -269.64787 | 18.6 |
| 1.88 | 1.39 | 0.49 | -269.63797 | 24.8 |
| 1.99 | 1.39 | 0.60 | -269.63159 | 28.8 |
| 2.10 | 1.39 | 0.71 | -269.62826 | 30.9 |
| 2.21 | 1.39 | 0.83 | -269.62660 | 31.9 |
| 2.33 | 1.39 | 0.94 | -269.62573 | 32.5 |
| 2.44 | 1.39 | 1.05 | -269.62519 | 32.8 |
| 2.55 | 1.39 | 1.16 | -269.62517 | 32.8 |
| 2.66 | 1.39 | 1.28 | -269.62537 | 32.7 |
| 2.78 | 1.39 | 1.39 | -269.62571 | 32.5 |
| 2.89 | 1.39 | 1.50 | -269.62663 | 31.9 |
| 3.00 | 1.39 | 1.61 | -269.62711 | 31.6 |

**Table S42.** PES for the solvent-phase addition of •OH to [1.1.1]propellane. $r_1$ is the forming C–O bond distance, $r_e$ is the equilibrium C–O bond length in the parent bicyclo[1.1.1]pentan-1-ol. Calculated at the SMD(Et$_2$O)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | ΔE$_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.20 | 1.39 | -0.19 | -269.65647 | 20.8 |
| 1.31 | 1.39 | -0.08 | -269.68490 | 3.0 |
| 1.43 | 1.39 | 0.04 | -269.68964 | 0.0 |
| 1.54 | 1.39 | 0.15 | -269.68347 | 3.9 |
| 1.65 | 1.39 | 0.26 | -269.67309 | 10.4 |
| 1.76 | 1.39 | 0.37 | -269.66234 | 17.1 |
| 1.88 | 1.39 | 0.49 | -269.65340 | 22.7 |
| 1.99 | 1.39 | 0.60 | -269.64753 | 26.4 |
| 2.10 | 1.39 | 0.71 | -269.64428 | 28.5 |
| 2.21 | 1.39 | 0.82 | -269.64259 | 29.5 |
| 2.33 | 1.39 | 0.94 | -269.64174 | 30.1 |
| 2.44 | 1.39 | 1.05 | -269.64120 | 30.4 |
| 2.55 | 1.39 | 1.16 | -269.64084 | 30.6 |
| 2.66 | 1.39 | 1.27 | -269.64072 | 30.7 |
| 2.78 | 1.39 | 1.39 | -269.64202 | 29.9 |
| 2.89 | 1.39 | 1.50 | -269.64328 | 29.1 |
| 3.00 | 1.39 | 1.61 | -269.64387 | 28.7 |

**Table S43.** PES for the gas-phase addition of •SH to [1.1.1]propellane. $r_1$ is the forming C–S bond distance, $r_e$ is the equilibrium C–S bond length in the parent bicyclo[1.1.1]pentane-1-thiol. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.60 | 1.79 | -0.19 | -592.53339 | 13.1 |
| 1.71 | 1.79 | -0.08 | -592.54975 | 2.8 |
| 1.82 | 1.79 | 0.02 | -592.55423 | 0.0 |
| 1.93 | 1.79 | 0.13 | -592.55249 | 1.1 |
| 2.04 | 1.79 | 0.24 | -592.54814 | 3.8 |
| 2.15 | 1.79 | 0.35 | -592.54360 | 6.7 |
| 2.25 | 1.79 | 0.46 | -592.54030 | 8.7 |
| 2.36 | 1.79 | 0.57 | -592.53841 | 9.9 |
| 2.47 | 1.79 | 0.68 | -592.53736 | 10.6 |
| 2.58 | 1.79 | 0.79 | -592.53660 | 11.1 |
| 2.69 | 1.79 | 0.90 | -592.53592 | 11.5 |
| 2.80 | 1.79 | 1.01 | -592.53524 | 11.9 |
| 2.91 | 1.79 | 1.12 | -592.53459 | 12.3 |
| 3.02 | 1.79 | 1.22 | -592.53396 | 12.7 |
| 3.13 | 1.79 | 1.33 | -592.53345 | 13.0 |
| 3.24 | 1.79 | 1.44 | -592.53296 | 13.3 |
| 3.35 | 1.79 | 1.55 | -592.53256 | 13.6 |
| 3.45 | 1.79 | 1.66 | -592.53235 | 13.7 |

**Table S44.** PES for the solvent-phase addition of •SH to [1.1.1]propellane. $r_1$ is the forming C–S bond distance, $r_e$ is the equilibrium C–S bond length in the parent bicyclo[1.1.1]pentane-1-thiol. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.60 | 1.80 | -0.20 | -592.54494 | 13.5 |
| 1.71 | 1.80 | -0.09 | -592.56158 | 3.0 |
| 1.82 | 1.80 | 0.02 | -592.56643 | 0.0 |
| 1.93 | 1.80 | 0.13 | -592.56519 | 0.8 |
| 2.04 | 1.80 | 0.24 | -592.56151 | 3.1 |
| 2.15 | 1.80 | 0.35 | -592.55792 | 5.3 |
| 2.25 | 1.80 | 0.46 | -592.55551 | 6.8 |
| 2.36 | 1.80 | 0.57 | -592.55411 | 7.7 |
| 2.47 | 1.80 | 0.68 | -592.55323 | 8.3 |
| 2.58 | 1.80 | 0.79 | -592.55250 | 8.7 |
| 2.69 | 1.80 | 0.90 | -592.55177 | 9.2 |
| 2.80 | 1.80 | 1.01 | -592.55108 | 9.6 |
| 2.91 | 1.80 | 1.11 | -592.55043 | 10.0 |
| 3.02 | 1.80 | 1.22 | -592.54983 | 10.4 |
| 3.13 | 1.80 | 1.33 | -592.54931 | 10.7 |
| 3.24 | 1.80 | 1.44 | -592.54893 | 11.0 |
| 3.35 | 1.80 | 1.55 | -592.54864 | 11.2 |
| 3.45 | 1.80 | 1.66 | -592.54829 | 11.4 |

**Table S45.** PES for the gas-phase addition of •SeH to [1.1.1]propellane. $r_1$ is the forming C–Se bond distance, $r_e$ is the equilibrium C–Se bond length in the parent bicyclo[1.1.1]pentane-1-selenol. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.80 | 1.94 | -0.14 | -2595.64262 | 6.7 |
| 1.91 | 1.94 | -0.04 | -2595.65143 | 1.2 |
| 2.01 | 1.94 | 0.07 | -2595.65336 | 0.0 |
| 2.12 | 1.94 | 0.18 | -2595.65202 | 0.8 |
| 2.23 | 1.94 | 0.29 | -2595.64979 | 2.2 |
| 2.34 | 1.94 | 0.39 | -2595.64808 | 3.3 |
| 2.44 | 1.94 | 0.50 | -2595.64723 | 3.8 |
| 2.55 | 1.94 | 0.61 | -2595.64681 | 4.1 |
| 2.66 | 1.94 | 0.71 | -2595.64642 | 4.4 |
| 2.76 | 1.94 | 0.82 | -2595.64594 | 4.7 |
| 2.87 | 1.94 | 0.93 | -2595.64539 | 5.0 |
| 2.98 | 1.94 | 1.04 | -2595.64476 | 5.4 |
| 3.09 | 1.94 | 1.14 | -2595.64413 | 5.8 |
| 3.19 | 1.94 | 1.25 | -2595.64350 | 6.2 |
| 3.30 | 1.94 | 1.36 | -2595.64290 | 6.6 |
| 3.41 | 1.94 | 1.46 | -2595.64229 | 6.9 |
| 3.51 | 1.94 | 1.57 | -2595.64177 | 7.3 |

**Table S46.** PES for the solvent-phase addition of •SeH to [1.1.1]propellane. $r_1$ is the forming C–Se bond distance, $r_e$ is the equilibrium C–Se bond length in the parent bicyclo[1.1.1]pentane-1-selenol. Calculated at the SMD(Et$_2$O)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | ΔE$_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.80 | 1.94 | -0.14 | -2595.65254 | 7.1 |
| 1.91 | 1.94 | -0.04 | -2595.66164 | 1.4 |
| 2.01 | 1.94 | 0.07 | -2595.66390 | 0.0 |
| 2.12 | 1.94 | 0.18 | -2595.66308 | 0.5 |
| 2.23 | 1.94 | 0.28 | -2595.66160 | 1.4 |
| 2.34 | 1.94 | 0.39 | -2595.66066 | 2.0 |
| 2.44 | 1.94 | 0.50 | -2595.66028 | 2.3 |
| 2.55 | 1.94 | 0.61 | -2595.66001 | 2.4 |
| 2.66 | 1.94 | 0.71 | -2595.65962 | 2.7 |
| 2.76 | 1.94 | 0.82 | -2595.65912 | 3.0 |
| 2.87 | 1.94 | 0.93 | -2595.65855 | 3.4 |
| 2.98 | 1.94 | 1.03 | -2595.65801 | 3.7 |
| 3.09 | 1.94 | 1.14 | -2595.65747 | 4.0 |
| 3.19 | 1.94 | 1.25 | -2595.65686 | 4.4 |
| 3.30 | 1.94 | 1.36 | -2595.65636 | 4.7 |
| 3.41 | 1.94 | 1.46 | -2595.65594 | 5.0 |
| 3.51 | 1.94 | 1.57 | -2595.65551 | 5.3 |

**Table S47.** PES for the gas-phase addition of •TeH to [1.1.1]propellane. $r_1$ is the forming C–Te bond distance, $r_e$ is the equilibrium C–Te bond length in the parent bicyclo[1.1.1]pentane-1-tellurol. Calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.80 | 2.14 | -0.34 | -462.27509 | 36.1 |
| 1.91 | 2.14 | -0.23 | -462.30568 | 16.9 |
| 2.02 | 2.14 | -0.12 | -462.32142 | 7.0 |
| 2.13 | 2.14 | -0.01 | -462.32835 | 2.7 |
| 2.24 | 2.14 | 0.10 | -462.33064 | 1.2 |
| 2.35 | 2.14 | 0.21 | -462.33106 | 1.0 |
| 2.46 | 2.14 | 0.32 | -462.33140 | 0.8 |
| 2.57 | 2.14 | 0.43 | -462.33198 | 0.4 |
| 2.68 | 2.14 | 0.54 | -462.33244 | 0.1 |
| 2.79 | 2.14 | 0.65 | -462.33260 | 0.0 |
| 2.90 | 2.14 | 0.76 | -462.33246 | 0.1 |
| 3.01 | 2.14 | 0.87 | -462.33208 | 0.3 |
| 3.12 | 2.14 | 0.98 | -462.33154 | 0.7 |
| 3.23 | 2.14 | 1.09 | -462.33092 | 1.1 |
| 3.34 | 2.14 | 1.20 | -462.33023 | 1.5 |
| 3.45 | 2.14 | 1.31 | -462.32959 | 1.9 |
| 3.56 | 2.14 | 1.42 | -462.32899 | 2.3 |
| 3.67 | 2.14 | 1.53 | -462.32840 | 2.6 |
| 3.78 | 2.14 | 1.64 | -462.32789 | 3.0 |
| 3.89 | 2.14 | 1.75 | -462.32733 | 3.3 |
| 4.00 | 2.14 | 1.86 | -462.32720 | 3.4 |

**Table S48.** PES for the solvent-phase addition of •TeH to [1.1.1]propellane. $r_1$ is the forming C–Te bond distance, $r_e$ is the equilibrium C–Te bond length in the parent bicyclo[1.1.1]pentane-1-tellurol. Calculated at the SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP level of theory.

| $r_1$ / Å | $r_e$ / Å | $r_1 - r_e$ / Å | E / Ha | $\Delta E_{rel}$ / kcal mol$^{-1}$ |
|---|---|---|---|---|
| 1.80 | 2.14 | -0.34 | -462.28443 | 37.8 |
| 1.91 | 2.14 | -0.23 | -462.31517 | 18.5 |
| 2.02 | 2.14 | -0.12 | -462.33107 | 8.5 |
| 2.13 | 2.14 | -0.01 | -462.33820 | 4.0 |
| 2.24 | 2.14 | 0.10 | -462.34091 | 2.3 |
| 2.35 | 2.14 | 0.21 | -462.34192 | 1.7 |
| 2.46 | 2.14 | 0.32 | -462.34284 | 1.1 |
| 2.57 | 2.14 | 0.43 | -462.34381 | 0.5 |
| 2.68 | 2.14 | 0.54 | -462.34442 | 0.1 |
| 2.79 | 2.14 | 0.65 | -462.34463 | 0.0 |
| 2.90 | 2.14 | 0.76 | -462.34452 | 0.1 |
| 3.01 | 2.14 | 0.87 | -462.34421 | 0.3 |
| 3.12 | 2.14 | 0.98 | -462.34380 | 0.5 |
| 3.23 | 2.14 | 1.09 | -462.34334 | 0.8 |
| 3.34 | 2.14 | 1.20 | -462.34289 | 1.1 |
| 3.45 | 2.14 | 1.31 | -462.34246 | 1.4 |
| 3.56 | 2.14 | 1.42 | -462.34206 | 1.6 |
| 3.67 | 2.14 | 1.53 | -462.34171 | 1.8 |
| 3.78 | 2.14 | 1.64 | -462.34135 | 2.1 |
| 3.89 | 2.14 | 1.75 | -462.34109 | 2.2 |
| 4.00 | 2.14 | 1.86 | -462.34090 | 2.3 |

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# 6. Cartesian Coordinates

## a. Optimized geometries of [1.1.1]propellane

Method: **B2GP-PLYP/def2-QZVPP**
Electronic energy: -193.893163840377

| | | | |
|---|---|---|---|
| H | -0.63838721378956 | -1.97724178876231 | 0.00015418049634 |
| H | -1.95245998682131 | -0.71065733341697 | 0.00015438758636 |
| H | -1.39324597435256 | 1.54149363757171 | 0.00015453650393 |
| H | 0.36061981639131 | 2.04619943427858 | 0.00015385747527 |
| H | 1.59181660432488 | -1.33527226711980 | 0.00015467551063 |
| H | 2.03140069793870 | 0.43601045764156 | 0.00015387742990 |
| C | -0.89592042284597 | -0.92947027226381 | 0.00011058685024 |
| C | -0.35712684279462 | 1.24054067151907 | 0.00011078900485 |
| C | -0.00009391654920 | 0.00000986500632 | -0.78629506310911 |
| C | -0.00009318602110 | 0.00001068919479 | 0.78708825313472 |
| C | 1.25278042451942 | -0.31098309364914 | 0.00011091911688 |

Method: **B2GP-PLYP-D3BJ/def2-QZVPP**
Electronic energy: -193.897504960224

| | | | |
|---|---|---|---|
| H | -0.63811940411159 | -1.97700567817602 | 0.00015424795119 |
| H | -1.95223397599385 | -0.71038053407095 | 0.00015446099237 |
| H | -1.39317573031758 | 1.54114322321004 | 0.00015460156818 |
| H | 0.36074564931322 | 2.04586593729136 | 0.00015391697530 |
| H | 1.59146420583990 | -1.33521490120167 | 0.00015474527530 |
| H | 2.03106280448518 | 0.43612408212293 | 0.00015393791391 |
| C | -0.89579471326890 | -0.92933973256295 | 0.00011055319437 |
| C | -0.35707683831782 | 1.24036669787900 | 0.00011078465267 |
| C | -0.00009382550572 | 0.00000983305008 | -0.78631798049255 |
| C | -0.00009311033907 | 0.00001066058232 | 0.78711082900637 |
| C | 1.25260493821622 | -0.31093958812415 | 0.00011090296289 |

Method: **B2PLYP/def2-QZVPP**
Electronic energy: -193.927212274426

| | | | |
|---|---|---|---|
| H | -0.64065747893612 | -1.98078464255152 | 0.00016021112215 |
| H | -1.95591662707981 | -0.71304763453495 | 0.00016033681454 |
| H | -1.39518786782156 | 1.54521624359652 | 0.00016017212611 |
| H | 0.36028625019535 | 2.05037914086674 | 0.00015981753892 |
| H | 1.59561410506612 | -1.33707653926369 | 0.00016008546948 |
| H | 2.03558533618765 | 0.43583746091091 | 0.00015990420084 |
| C | -0.89777655444065 | -0.93139533323165 | 0.00012891206901 |
| C | -0.35786356316674 | 1.24311795656503 | 0.00012882943983 |
| C | -0.00008993838018 | 0.00000959951268 | -0.78823244457970 |
| C | -0.00008954107774 | 0.00001013789554 | 0.78893597552498 |
| C | 1.25538587945368 | -0.31162638976561 | 0.00012920027384 |

Method: **B2PLYP-D3BJ/def2-QZVPP**
Electronic energy: -193.933120777034

| | | | |
|---|---|---|---|
| H | -0.64024538572965 | -1.98043855352008 | 0.00016032696880 |
| H | -1.95558416950881 | -0.71262996540017 | 0.00016029578138 |
| H | -1.39509532373058 | 1.54469241245423 | 0.00016020650985 |
| H | 0.36048093476889 | 2.04988765593374 | 0.00015988194118 |
| H | 1.59508148282843 | -1.33700477065162 | 0.00016016916221 |
| H | 2.03508647491594 | 0.43601059449448 | 0.00015987516353 |
| C | -0.89760253678832 | -0.93121681747541 | 0.00012900241730 |
| C | -0.35779819123057 | 1.24288421626929 | 0.00012906914927 |
| C | -0.00008981218871 | 0.00001179902184 | -0.78826919289869 |
| C | -0.00008940780472 | 0.00001239601038 | 0.78897207014018 |
| C | 1.25514593446810 | -0.31156896713668 | 0.00012929566500 |

Method: **B3LYP/def2-QZVPP**
Electronic energy: -193.962108508333

| | | | |
|---|---|---|---|
| H | -0.64542219022892 | -1.98499819367769 | 0.00015577247597 |
| H | -1.96009460572551 | -0.71826310070543 | 0.00015609378286 |
| H | -1.39677834405877 | 1.55183237078879 | 0.00015374628060 |
| H | 0.35736422744348 | 2.05704474714091 | 0.00015600322355 |
| H | 1.60230393957025 | -1.33856993446644 | 0.00015423468183 |
| H | 2.04205841510286 | 0.43314714358118 | 0.00015517851153 |
| C | -0.90018866622147 | -0.93382260126466 | 0.00012181101057 |
| C | -0.35905867762361 | 1.24679957500051 | 0.00012223184945 |
| C | 0.00007253327124 | 0.00017875199065 | -0.78294908403086 |
| C | 0.00007223894385 | 0.00017911025110 | 0.78370275631216 |
| C | 1.25896112952660 | -0.31288786863892 | 0.00012225590233 |

Method: **B97-D3/def2-QZVPP**
Electronic energy: -193.963604787004

| | | | |
|---|---|---|---|
| H | -0.64452375589021 | -1.99039602432322 | 0.00016106043083 |
| H | -1.96540532629597 | -0.71735953678029 | 0.00016092962345 |
| H | -1.40171063738072 | 1.55330360005585 | 0.00016076991356 |
| H | 0.36130594395336 | 2.06084522176699 | 0.00016069142006 |
| H | 1.60392699457159 | -1.34330651084447 | 0.00016090802246 |
| H | 2.04600159573776 | 0.43719172639277 | 0.00016062906405 |
| C | -0.90173838923684 | -0.93550177248780 | 0.00012079936634 |
| C | -0.35947498127938 | 1.24875774042814 | 0.00012054316424 |
| C | -0.00006253454473 | 0.00007325106347 | -0.78274145125943 |
| C | -0.00006252222700 | 0.00007343042084 | 0.78346579829158 |
| C | 1.26103361259214 | -0.31304112569227 | 0.00012032196288 |

Method: **BLYP/def2-QZVPP**
Electronic energy: -193.995952437034

| | | | |
|---|---|---|---|
| H | -0.651443 | -1.997915 | 0.000161 |
| H | -1.972659 | -0.724539 | 0.000161 |
| H | -1.404763 | 1.563054 | 0.000161 |
| H | 0.358698 | 2.070728 | 0.000160 |
| H | 1.613796 | -1.345998 | 0.000161 |
| H | 2.055963 | 0.434956 | 0.000160 |
| C | -0.906620 | -0.940567 | 0.000135 |
| C | -0.361420 | 1.255517 | 0.000135 |
| C | -0.000061 | 0.000072 | -0.794823 |
| C | -0.000061 | 0.000072 | 0.795507 |
| C | 1.267861 | -0.314742 | 0.000135 |

Method: **CASSCF(2,2)/def2-QZVPP**
Electronic energy: -192.799449432723

| | | | |
|---|---|---|---|
| H | -0.642105 | -1.967659 | 0.000169 |
| H | -1.942754 | -0.714148 | 0.000169 |
| H | -1.383138 | 1.539944 | 0.000169 |
| H | 0.352752 | 2.039588 | 0.000168 |
| H | 1.589791 | -1.325262 | 0.000169 |
| H | 2.025064 | 0.427878 | 0.000168 |
| C | -0.889067 | -0.922372 | 0.000159 |
| C | -0.354412 | 1.231174 | 0.000159 |
| C | -0.000063 | 0.000061 | -0.794111 |
| C | -0.000063 | 0.000061 | 0.794672 |
| C | 1.243285 | -0.308625 | 0.000159 |

Method: **CASSCF(6,6)/def2-QZVPP**
Electronic energy: -192.824428212209

| | | | |
|---|---|---|---|
| H | -0.643494 | -1.970261 | 0.000367 |
| H | -1.945306 | -0.715603 | 0.000376 |
| H | -1.385223 | 1.537918 | 0.000186 |
| H | 0.348622 | 2.044886 | 0.000185 |
| H | 1.587869 | -1.327416 | 0.000185 |
| H | 2.030514 | 0.423958 | 0.000190 |
| C | -0.892008 | -0.925415 | -0.000283 |
| C | -0.355255 | 1.233119 | 0.000201 |
| C | 0.004177 | 0.004460 | -0.795522 |
| C | 0.004121 | 0.004391 | 0.795955 |
| C | 1.245274 | -0.309396 | 0.000210 |

Method: **HF/def2-QZVPP**
Electronic energy: -192.770275059488

| | | | |
|---|---|---|---|
| H | -0.64398603691774 | -1.97158980566900 | 0.00014298651641 |
| H | -1.94661314462494 | -0.71617390613066 | 0.00014284226696 |
| H | -1.38559904513789 | 1.54354420562450 | 0.00014281261598 |
| H | 0.35292467325566 | 2.04394325140641 | 0.00014251701834 |
| H | 1.59347822177781 | -1.32758794909483 | 0.00014291296245 |
| H | 2.02941057384621 | 0.42821102472082 | 0.00014244657988 |
| C | -0.89499090867674 | -0.92851910666188 | 0.00011731605620 |
| C | -0.35677297653489 | 1.23937499995618 | 0.00011747645598 |
| C | -0.00006486857624 | 0.00005894308564 | -0.76950116910584 |
| C | -0.00006472632476 | 0.00005922675257 | 0.77034356797639 |
| C | 1.25156823791352 | -0.31068088398975 | 0.00011729065724 |

Method: **M06-2X/def2-QZVPP**
Electronic energy: -194.021399910986

| | | | |
|---|---|---|---|
| H | -0.63805989400885 | -1.98063236906032 | 0.00016728334931 |
| H | -1.95605146155625 | -0.71060818637849 | 0.00016752967545 |
| H | -1.39717362739629 | 1.54341540218246 | 0.00016504118280 |
| H | 0.36136622959469 | 2.05013555983533 | 0.00016803107862 |
| H | 1.59411354995728 | -1.33933149359211 | 0.00016585254503 |
| H | 2.03468578813888 | 0.43702107379331 | 0.00016518503253 |
| C | -0.89918798940752 | -0.93271133185242 | 0.00009399190531 |
| C | -0.35900032410392 | 1.24574190486122 | 0.00009562827892 |
| C | 0.00036429126971 | 0.00032488584242 | -0.76920415403184 |
| C | 0.00036313063712 | 0.00032577134860 | 0.76997002962730 |
| C | 1.25787030687516 | -0.31304121698000 | 0.00009658135658 |

Method: **MP2/def2-QZVPP**
Electronic energy: -193.650015048206

| | | | |
|---|---|---|---|
| H | -0.63238400540068 | -1.97710428734467 | 0.00017028555712 |
| H | -1.95254378739654 | -0.70460898667510 | 0.00017034632717 |
| H | -1.39609940950178 | 1.53624669834006 | 0.00017053815869 |
| H | 0.36589999250362 | 2.04322204960784 | 0.00016988762126 |
| H | 1.58672124509094 | -1.33830641711551 | 0.00017052485280 |
| H | 2.02823019763909 | 0.44118559056083 | 0.00016975826357 |
| C | -0.89450968428148 | -0.92799925406862 | 0.00013805752781 |
| C | -0.35655678176820 | 1.23853527094695 | 0.00013813501468 |
| C | -0.00011695956752 | -0.00002084246735 | -0.79442411591268 |
| C | -0.00011630554935 | -0.00002002322166 | 0.79503894425241 |
| C | 1.25076549823190 | -0.31048979856277 | 0.00013863833719 |

Method: **PBE/def2-QZVPP**
Electronic energy: -193.839407226097

| | | | |
|---|---|---|---|
| H | -0.64297372949852 | -1.99507526681065 | 0.00016791144602 |
| H | -1.97014672106154 | -0.71608597165889 | 0.00016782048242 |
| H | -1.40648734418772 | 1.55441269539375 | 0.00016772241221 |
| H | 0.36485800907762 | 2.06425220477221 | 0.00016737812647 |
| H | 1.60514603798796 | -1.34805997274488 | 0.00016782507063 |
| H | 2.04926941755766 | 0.44083748218726 | 0.00016736918431 |
| C | -0.90192289129065 | -0.93569887169795 | 0.00013676867408 |
| C | -0.35953831800285 | 1.24900965227229 | 0.00013689017647 |
| C | -0.00008835617726 | 0.00007716077523 | -0.78861303897752 |
| C | -0.00008821169262 | 0.00007739259415 | 0.78924759061872 |
| C | 1.26126210728793 | -0.31310650508252 | 0.00013676278618 |

Method: **PBE0/def2-QZVPP**
Electronic energy: -193.861238191777

| | | | |
|---|---|---|---|
| H | -0.63792351987593 | -1.98129505837175 | 0.00015881645811 |
| H | -1.95669774257581 | -0.71077988192798 | 0.00015889777289 |
| H | -1.39731013087569 | 1.54370153766249 | 0.00015638847264 |
| H | 0.36212814640444 | 2.05035636451567 | 0.00015865417607 |
| H | 1.59411376921304 | -1.33944597951333 | 0.00015654897509 |
| H | 2.03515816720469 | 0.43763520188468 | 0.00015809968812 |
| C | -0.89585867537024 | -0.92932890994157 | 0.00011025604824 |
| C | -0.35737675722971 | 1.24084128796502 | 0.00011103842055 |
| C | 0.00007566855505 | 0.00020725977781 | -0.77751309301354 |
| C | 0.00007523630027 | 0.00020756446101 | 0.77828419792496 |
| C | 1.25290583824990 | -0.31145938651207 | 0.00011119507689 |

Method: **TPSS/def2-QZVPP**
Electronic energy: -194.140827851247

| | | | |
|---|---|---|---|
| H | -0.64271711638259 | -1.98884460495078 | 0.00015991466796 |
| H | -1.96390676809258 | -0.71552777688760 | 0.00015963596943 |
| H | -1.40115229641229 | 1.55108627864947 | 0.00015918152223 |
| H | 0.36215761705956 | 2.05854804126497 | 0.00015937927623 |
| H | 1.60159711360770 | -1.34285232888981 | 0.00015940145959 |
| H | 2.04367151795053 | 0.43798714523271 | 0.00015941837853 |
| C | -0.90061033064164 | -0.93434433248878 | 0.00012359115946 |
| C | -0.35899913798928 | 1.24711961462215 | 0.00012351127974 |
| C | -0.00007659587488 | 0.00004312494282 | -0.79113395187402 |
| C | -0.00007650115027 | 0.00004317303030 | 0.79185781829770 |
| C | 1.25940249792575 | -0.31261833452544 | 0.00012309986314 |

Method: **TPSSh/def2-QZVPP**
Electronic energy: -194.120194004811

| | | | |
|---|---|---|---|
| H | -0.64066259104255 | -1.98385297013177 | 0.00016096414756 |
| H | -1.95905538081662 | -0.71338293631024 | 0.00016080652613 |
| H | -1.39798016734300 | 1.54699346195397 | 0.00015954486760 |
| H | 0.36133101644478 | 2.05346891043372 | 0.00016045380260 |
| H | 1.59741920338236 | -1.33989724559028 | 0.00015955248385 |
| H | 2.03848765996615 | 0.43698810233360 | 0.00016051571360 |
| C | -0.89823314599161 | -0.93183983686694 | 0.00012851369087 |
| C | -0.35815943544563 | 1.24393917328720 | 0.00012872769608 |
| C | -0.00000078875027 | 0.00010617742466 | -0.78631199985712 |
| C | -0.00000092890033 | 0.00010627762363 | 0.78701527227246 |
| C | 1.25614455849673 | -0.31198911415755 | 0.00012864865637 |

Method: **ωB97X-D3/def2-QZVPP**
Electronic energy: -194.041195193729

| | | | |
|---|---|---|---|
| H | -0.64127984506030 | -1.98272385743102 | 0.00015434044029 |
| H | -1.95803355111233 | -0.71393865753253 | 0.00015491806825 |
| H | -1.39726537668176 | 1.54702263915563 | 0.00014774635003 |
| H | 0.35920393236224 | 2.05376590492278 | 0.00015636454045 |
| H | 1.59762954126420 | -1.33930906465500 | 0.00014909392865 |
| H | 2.03852821825773 | 0.43501139853253 | 0.00015403958136 |
| C | -0.89817018107793 | -0.93165700527494 | 0.00010614926110 |
| C | -0.35846051716032 | 1.24425196159074 | 0.00010531918393 |
| C | 0.00034801048019 | 0.00035139327412 | -0.77407436550932 |
| C | 0.00034742115217 | 0.00035157897763 | 0.77489174564300 |
| C | 1.25644234757609 | -0.31248629155994 | 0.00010564851226 |

## b. Optimized geometries for turboamide addition to [1.1.1]propellane

All optimizations at **SMD(THF)-B2GP-PLYP-D3BJ/ma-def2-TZVP**

### [1.1.1]Propellane

Electronic energy: -193.874880178143

| | | | |
|---|---|---|---|
| C | 1.25842661291874 | -0.31228521937359 | 0.00004039410191 |
| C | -0.00008329699269 | -0.00002490684503 | 0.78268766087644 |
| C | -0.00011707548640 | 0.00008403763782 | -0.78266169205783 |
| C | -0.35868864776948 | 1.24613418861113 | -0.00004335071722 |
| C | -0.89996915868771 | -0.93358544651637 | 0.00005960283086 |
| H | 2.03513382870813 | 0.43967752108122 | 0.00042521838818 |
| H | 1.59327619468041 | -1.34029818032623 | -0.00025065404248 |
| H | 0.36421706278493 | 2.04996026113443 | -0.00020654814435 |
| H | -1.39836245683899 | 1.54261546263746 | -0.00019804963099 |
| H | -1.95750018222266 | -0.70948026407144 | 0.00042629253542 |
| H | -0.63704288109430 | -1.98215745396940 | -0.00027887413993 |

### $NH_2^-$

Electronic energy: -55.959163470345

| | | | |
|---|---|---|---|
| N | 0.05218000321783 | -0.19959354240781 | 2.36709097757783 |
| H | 0.78345155637911 | 0.39330196972943 | 2.76582723227992 |
| H | 0.40876856200306 | -1.13744837902162 | 2.56343778454224 |

### $MgCl^+$

Electronic energy: -659.980305298611

| | | | |
|---|---|---|---|
| Mg | -0.06044964496947 | 0.18976204469847 | -0.26519037584768 |
| Cl | -0.31695567413053 | 0.56901267190153 | -2.41010599635232 |

### TS [[1.1.1]Propellane--$NH_2$]$^-$

Electronic energy: -249.819560144799

Imaginary frequency: -254.8 $cm^{-1}$

| | | | |
|---|---|---|---|
| C | 1.22783597618075 | -0.30764731826634 | 0.18854052694911 |
| C | -0.04902124709223 | 0.01586542323502 | 0.88331420965335 |
| C | 0.04012201236485 | -0.00983738842526 | -0.78384844880664 |
| C | -0.35599213892461 | 1.23111549208776 | 0.08110373949203 |
| C | -0.89690016636861 | -0.91110926844434 | 0.08468359654974 |
| H | 2.01899528650408 | 0.43310773235627 | 0.22255885580503 |
| H | 1.57278619503335 | -1.33505086079405 | 0.22581300385726 |
| H | 0.35959331372325 | 2.04544114483878 | 0.10958001705251 |
| H | -1.39227726703438 | 1.54502022487378 | 0.02410879356601 |
| H | -1.95795199655422 | -0.69578706183577 | 0.02840803212150 |
| H | -0.65335507547102 | -1.96730011759924 | 0.11633190342508 |
| N | -0.09138136114370 | 0.05209558083425 | 3.24065712222891 |
| H | 0.66568205300018 | 0.73210284625452 | 3.15830483250738 |
| H | 0.41207051478231 | -0.83497343631537 | 3.19304242849873 |

### $NH_2$–BCP$^-$

Electronic energy: -249.860643182755

| | | | |
|---|---|---|---|
| C | 1.20606907531917 | -0.29620106420628 | 0.03886055366177 |
| C | 0.01823268704826 | 0.00441473780666 | 0.96737402635847 |
| C | 0.00436020879679 | -0.00363405821307 | -0.97092986759808 |
| C | -0.32716308942193 | 1.17935847122496 | 0.05812466373171 |
| C | -0.83936042871952 | -0.88262094745610 | 0.07039404395170 |
| H | 2.02541568239499 | 0.42942276802214 | 0.04399888749152 |
| H | 1.59025206232515 | -1.32096981748906 | 0.05424801142554 |
| H | 0.36790048168644 | 2.02463753375444 | 0.06394596639869 |
| H | -1.36471693797350 | 1.52543712460310 | 0.08405298151410 |
| H | -1.91808941947497 | -0.70287050146491 | 0.09750820753477 |
| H | -0.62045964846305 | -1.95463426714174 | 0.08736734881939 |
| N | -0.04277992177278 | 0.02911805353210 | 2.42734085524826 |
| H | 0.63253839447018 | 0.70315301680897 | 2.77486586488320 |
| H | 0.25199768428474 | -0.87385746508121 | 2.78658101867896 |

### $NH_2$–BCP–MgCl

Electronic energy: -909.969521023790

Spurious imaginary frequency: -28.2 cm$^{-1}$

| | | | |
|---|---|---|---|
| C | 1.13531642812298 | -0.43023572255626 | 0.12000446167143 |
| C | 0.01970701209239 | 0.02430682460096 | 1.09468161708528 |
| C | -0.06826588848078 | -0.02762487956670 | -0.81120337516297 |
| C | -0.23006964900351 | 1.21081691143992 | 0.15329281189557 |
| C | -0.96625375958432 | -0.78575695403325 | 0.24195801201649 |
| H | 2.02275154226992 | 0.20347186421963 | 0.06755163970594 |
| H | 1.39863992628321 | -1.48951281217292 | 0.14292223401246 |
| H | 0.55468977626294 | 1.96796521945786 | 0.10387347165146 |
| H | -1.22180377889889 | 1.66402317268282 | 0.19943898111551 |
| H | -2.01319817963720 | -0.48214975510290 | 0.29456930522148 |
| H | -0.86164517834598 | -1.87186529581437 | 0.27395604196769 |
| N | 0.01144564142376 | 0.09118144732087 | 2.53359772517375 |
| H | 0.75464968509446 | 0.70248181299272 | 2.85391997629383 |
| H | 0.20144112376847 | -0.82645477331560 | 2.92175973523219 |
| Mg | -0.14748229599881 | -0.09622916164021 | -2.89512541434978 |
| Cl | -0.07113540536864 | -0.18025789851257 | -5.14218322353032 |

### NH2–BCP–H

Electronic energy: -250.438945683428

| | | | |
|---|---|---|---|
| C | 1.22411255552164 | -0.30869130259694 | -0.00457134598583 |
| C | 0.02532679975068 | -0.00061891618189 | 0.94890384385985 |
| C | 0.01176581253692 | -0.01706363141320 | -0.91720954197043 |
| C | -0.32227332912699 | 1.17759598608422 | 0.01117572268851 |
| C | -0.83816699478994 | -0.89759349771649 | 0.03309808954316 |
| H | 2.03140317338134 | 0.42308512502898 | -0.01700527749061 |
| H | 1.59440462397138 | -1.33354097723706 | 0.00148311214962 |
| H | 0.37850427598304 | 2.01198439242242 | 0.00100547128703 |
| H | -1.35969490348742 | 1.51009481367264 | 0.02354765895765 |
| H | -1.91036149715496 | -0.70545448641746 | 0.04714036244836 |
| H | -0.60960553233066 | -1.96289847966028 | 0.04283691849830 |
| N | -0.04218810738682 | 0.03150436626478 | 2.37533414650243 |
| H | 0.60978116110331 | 0.71642656726350 | 2.73989402111346 |
| H | 0.22742773919855 | -0.86762337540049 | 2.75753135200712 |
| H | -0.00382518867007 | -0.02460924471273 | -2.00187845960861 |

## c. Optimized geometries for iodination of [1.1.1]propellane

All optimization at **B2GP-PLYP-D3BJ/def2-TZVP**

### [1.1.1]Propellane

Electronic energy: -193.875061199134

| | | | |
|---|---|---|---|
| C | 1.25765457495549 | -0.31164573482424 | 0.00003553461739 |
| C | -0.00020018238749 | 0.00011522698375 | 0.78342071295777 |
| C | -0.00023110908384 | 0.00020823141575 | -0.78339978957591 |
| C | -0.35820241208490 | 1.24569750557138 | -0.00003908164816 |
| C | -0.89965603710381 | -0.93334728024205 | 0.00005354994989 |
| H | 2.03515370971246 | 0.43957300409740 | 0.00036492789051 |
| H | 1.59203216045346 | -1.33987077658761 | -0.00020972472375 |
| H | 0.36456213556998 | 2.04971249578073 | -0.00017728295804 |
| H | -1.39778044155789 | 1.54253376749376 | -0.00017247378842 |
| H | -1.95756821578226 | -0.71029287003702 | 0.00037476510738 |
| H | -0.63647418269121 | -1.98204356965185 | -0.00025113782866 |

### $I_2$

Electronic energy: -595.101235585257

| | | | |
|---|---|---|---|
| I | 1.71781863033837 | 0.21441831457651 | 0.06879588256422 |
| I | -0.08713922583837 | 2.20131309902349 | 0.06559184473578 |

### I–BCP•

Electronic energy: -491.359476994709

| | | | |
|---|---|---|---|
| C | 1.25935717895490 | -0.33174166285792 | 0.04873080321657 |
| C | -0.01363821471284 | 0.00079899292021 | 0.81870054005581 |
| C | -0.29578580282361 | 1.28182015937070 | 0.04183648840914 |
| C | -0.91452011954376 | -0.87068748929918 | -0.04906588298113 |
| I | -0.10431022932527 | -0.07586515668477 | 3.35359159035519 |
| C | 0.04543186319821 | 0.05114702615512 | -0.76280053847147 |
| H | 0.45593112932937 | 2.05640291236160 | 0.10305726021555 |
| H | -1.32473940058161 | 1.61321344758696 | 0.02194426936557 |
| H | 1.55345077637548 | -1.37209766320106 | 0.03451905683801 |
| H | 2.06042034503748 | 0.39165941833893 | 0.11085456664186 |
| H | -1.96231384073373 | -0.60494931681820 | -0.07173279213371 |
| H | -0.68820168517462 | -1.92772566787240 | -0.06680036151139 |

### I–BCP–I

Electronic energy: -788.929545029417

| | | | |
|---|---|---|---|
| C | 1.21723736261303 | -0.32274071249550 | 0.17440830884559 |
| C | -0.02017935037673 | -0.00495447912406 | 1.03734480315635 |
| C | -0.28709775882458 | 1.23814571292257 | 0.16550671365855 |
| C | -0.88496101957970 | -0.84346158895727 | 0.07493854236759 |
| I | -0.10638824217613 | -0.07456426893177 | 3.15638236295896 |
| C | 0.05079002954009 | 0.05330721159847 | -0.76070493528499 |
| H | 0.45055535903260 | 2.03304937983265 | 0.22020339289676 |
| H | -1.31334957334608 | 1.59196657972182 | 0.13591562552039 |
| H | 1.53377952890594 | -1.36128215453789 | 0.15271828873796 |
| H | 2.03799453174314 | 0.38597655588499 | 0.23005881799493 |
| H | -1.94244403256656 | -0.59863254287952 | 0.04136344396070 |
| H | -0.68037793086858 | -1.90959767000247 | 0.04830402934883 |
| I | 0.13469614870356 | 0.12378790956799 | -2.87973771176159 |

i. Solvent phase calculations:
All optimization at **SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP**

### [1.1.1]Propellane

Electronic energy: -193.915920793779

| | | | |
|---|---|---|---|
| C | 1.26013851011898 | -0.31215703458730 | 0.00003581566501 |
| C | -0.00024312568038 | 0.00015763708745 | 0.78503141991262 |
| C | -0.00027272369514 | 0.00025596763110 | -0.78500588379346 |
| C | -0.35886140911346 | 1.24825878301896 | -0.00003616722269 |
| C | -0.90142416011176 | -0.93520989559196 | 0.00005235871298 |
| H | 2.03906146598905 | 0.43933166567560 | 0.00038136886851 |
| H | 1.59503208495095 | -1.34153216825554 | -0.00022710230124 |
| H | 0.36432068834557 | 2.05352703204056 | -0.00018424658384 |
| H | -1.39951532433328 | 1.54581328102777 | -0.00018215194540 |
| H | -1.96073470614135 | -0.71257001018031 | 0.00038300589892 |
| H | -0.63821130032920 | -1.98523525786632 | -0.00024841721141 |

### I–BCP•

Electronic energy: -491.446566511246

| | | | |
|---|---|---|---|
| C | 1.26141909751730 | -0.33218947945308 | 0.04810162754699 |
| C | -0.01359809083616 | 0.00082469016291 | 0.82068115853203 |
| C | -0.29611229713259 | 1.28381000553411 | 0.04117603416482 |
| C | -0.91588065886818 | -0.87196738442448 | -0.04950437025694 |
| I | -0.10503447956215 | -0.07662702320136 | 3.36256349693164 |
| C | 0.04570332316963 | 0.05127567504556 | -0.76789233785440 |
| H | 0.45570516848717 | 2.06002583568020 | 0.10229288746793 |
| H | -1.32618908082877 | 1.61585028514814 | 0.02119045942402 |
| H | 1.55636764255664 | -1.37360181532736 | 0.03383385293872 |
| H | 2.06394699228167 | 0.39143803119277 | 0.11012245789039 |
| H | -1.96507073801520 | -0.60639863739411 | -0.07236753503869 |
| H | -0.69017487876937 | -1.93046518296331 | -0.06736273174651 |

### $I_2$

Electronic energy: -595.103675518515

| | | | |
|---|---|---|---|
| I | 1.71958189183626 | 0.21247731907803 | 0.06879901258552 |
| I | -0.08890248733626 | 2.20325409452197 | 0.06558871471448 |

### I–BCP–I

Electronic energy: -789.058900234573

| | | | |
|---|---|---|---|
| C | 1.22056792232142 | -0.32375223988707 | 0.17455009583224 |
| C | -0.02013623949325 | -0.00499258193019 | 1.03803083326125 |
| C | -0.28797453809074 | 1.24137647673513 | 0.16559561255905 |
| C | -0.88743005558157 | -0.84579618386199 | 0.07482391635802 |
| I | -0.10644773190252 | -0.07463527899697 | 3.16857469099907 |
| C | 0.05096520142598 | 0.05335666399041 | -0.76129907261526 |
| H | 0.45013881237816 | 2.03727911359808 | 0.22021832728701 |
| H | -1.31546584447994 | 1.59490814703801 | 0.13582251018920 |
| H | 1.53698401185466 | -1.36344197480151 | 0.15272873404225 |
| H | 2.04218680584847 | 0.38555281024116 | 0.23021962957660 |
| H | -1.94595085661210 | -0.60040081955157 | 0.04114781714879 |
| H | -0.68273798130314 | -1.91306400086682 | 0.04809603343598 |
| I | 0.13555554643457 | 0.12460980089334 | -2.89180744567419 |

## d. Optimized geometries for halogen and chalcogen radical addition to [1.1.1]propellane

### i. Gas-phase calculations:

All optimizations at **B2PLYP-D3BJ/def2-TZVP**

**H–BCP–F**

Electronic energy: -294.385993623382

| | | | |
|---|---|---|---|
| C | 1.21404095882843 | -0.32095632371962 | 0.15636538480641 |
| C | -0.01941603244193 | -0.00429584061846 | 1.01657654356473 |
| C | -0.28553203017300 | 1.23486900465708 | 0.14740908030789 |
| C | -0.88152249670268 | -0.84001521685011 | 0.05672418702691 |
| F | -0.07339806316932 | -0.04847190189692 | 2.37754722253409 |
| C | 0.05283977867799 | 0.05493528066164 | -0.80891689118975 |
| H | 0.44545948831193 | 2.03930008376063 | 0.20605355793779 |
| H | -1.31131187528260 | 1.59872154593917 | 0.12190730405692 |
| H | 1.54100629549269 | -1.35916095490193 | 0.13893899432274 |
| H | 2.04368821469004 | 0.38121249694014 | 0.21584186309671 |
| H | -1.94410725548507 | -0.60448423592655 | 0.02563826896186 |
| H | -0.68753342474680 | -1.91109430687045 | 0.03302828672897 |
| H | 0.09604149490034 | 0.09044030152539 | -1.89041211985527 |

**H–BCP–Cl**

Electronic energy: -654.640209070809

| | | | |
|---|---|---|---|
| C | 1.21283611089551 | -0.31901660284022 | 0.11985679333003 |
| C | -0.01850851045202 | -0.00359071897705 | 0.99168617431971 |
| C | -0.28343107063724 | 1.23333840119763 | 0.11096422219978 |
| C | -0.87804697034899 | -0.83687214541768 | 0.02024959842970 |
| Cl | -0.08847290791746 | -0.06084921792025 | 2.75655743739317 |
| C | 0.05439192956656 | 0.05620822802446 | -0.84559824390012 |
| H | 0.44672099209124 | 2.03775342366267 | 0.17797840132035 |
| H | -1.30921547383742 | 1.59737668572119 | 0.09397856788136 |
| H | 1.53997118945010 | -1.35716715099419 | 0.11095142092257 |
| H | 2.04239265170279 | 0.38235786037672 | 0.18762656885751 |
| H | -1.94086809103322 | -0.60207472286889 | -0.00274352744317 |
| H | -0.68488854352107 | -1.90812175575596 | 0.00461975043104 |
| H | 0.09737374694119 | 0.09165764849161 | -1.92942548144194 |

**H–BCP–Br**

Electronic energy: -2768.331200997683

| | | | |
|---|---|---|---|
| C | 1.21466224333573 | -0.31877498946588 | 0.10713937087055 |
| C | -0.01772602830380 | -0.00298629967198 | 0.97704553061992 |
| C | -0.28300050290129 | 1.23502265199729 | 0.09837302433119 |
| C | -0.87823161584076 | -0.83718855639557 | 0.00800091059345 |
| Br | -0.09627608801313 | -0.06695344063388 | 2.90770563409899 |
| C | 0.05482530479316 | 0.05660023874460 | -0.85647506837569 |
| H | 0.44747874222251 | 2.03889532040974 | 0.16508808710725 |
| H | -1.30866861502134 | 1.59871672037139 | 0.08109120957221 |
| H | 1.54141630291182 | -1.35681747126947 | 0.09773895094556 |
| H | 2.04374106524443 | 0.38289435427595 | 0.17452447365998 |
| H | -1.94079961120988 | -0.60207424889472 | -0.01473487821408 |
| H | -0.68463973291828 | -1.90817670147591 | -0.00749443897827 |

| | | | |
|---|---|---|---|
| H | 0.09747358860082 | 0.09184235470845 | -1.94130112393104 |

**H–BCP–I**

Electronic energy: -492.098321896974

| | | | |
|---|---|---|---|
| C | 1.21536705832429 | -0.31831565051947 | 0.09091278212056 |
| C | -0.01718100125580 | -0.00254958258658 | 0.96481787757616 |
| C | -0.28243719376493 | 1.23563290742118 | 0.08217084927792 |
| C | -0.87766499940296 | -0.83671373737641 | -0.00831184957038 |
| I | -0.10333316530555 | -0.07290484751303 | 3.09407957462001 |
| C | 0.05541324689428 | 0.05709971763632 | -0.87112327196610 |
| H | 0.44754652903085 | 2.03995591359498 | 0.14943103811548 |
| H | -1.30800622978269 | 1.59974761036248 | 0.06530813116510 |
| H | 1.54256103982191 | -1.35626662655816 | 0.08196460350054 |
| H | 2.04486013729491 | 0.38286023170688 | 0.15886411122850 |
| H | -1.94040212492194 | -0.60214788656074 | -0.03072061369743 |
| H | -0.68464888788657 | -1.90785223604473 | -0.02346957468043 |
| H | 0.09818064385420 | 0.09245411913728 | -1.95722197538993 |

**H–BCP–OH**

Electronic energy: -270.357312890293

| | | | |
|---|---|---|---|
| C | 1.17202731631616 | -0.31044248501109 | 0.20706961709208 |
| C | -0.07629354347690 | 0.01157219701930 | 1.04593371811093 |
| C | -0.31371994971408 | 1.24278004414152 | 0.12830465916882 |
| C | -0.90877119561993 | -0.82883161636488 | 0.03814481311152 |
| O | -0.09364059817500 | -0.04570377502195 | 2.43111353965092 |
| C | 0.04900925905839 | 0.05622076766698 | -0.80235244475966 |
| H | 0.41484675956249 | 2.04950183432662 | 0.20082580402261 |
| H | -1.33757089161803 | 1.61273143164567 | 0.06135344732901 |
| H | 1.50111532418772 | -1.34894984327854 | 0.21162544187415 |
| H | 2.00324732530313 | 0.38900237766242 | 0.28798004620551 |
| H | -1.97204444433430 | -0.59588408505308 | -0.03375054313417 |
| H | -0.71840533338209 | -1.90166362499806 | 0.02905435752746 |
| H | -0.97654069559106 | 0.19137301673525 | 2.73645952624112 |
| H | 0.12695138268348 | 0.08135511132985 | -1.88351992704030 |

**H–BCP–SH**

Electronic energy: -593.227946362585

| | | | |
|---|---|---|---|
| C | 1.19709286295139 | -0.31434945290603 | 0.12621678903830 |
| C | -0.04182886231740 | 0.00332110353478 | 1.00235581843927 |
| C | -0.28828346877598 | 1.23470182918495 | 0.08829196179642 |
| C | -0.88219733347762 | -0.83248606791003 | -0.00222648173755 |
| S | -0.02627828090882 | -0.08034244759691 | 2.79169342620305 |
| C | 0.05634831094629 | 0.05669018783566 | -0.85858914520745 |
| H | 0.44097669634849 | 2.04015214136131 | 0.16186633492117 |
| H | -1.31252757248471 | 1.60587110626665 | 0.05291154786552 |
| H | 1.52710213780540 | -1.35255558754429 | 0.12358692619841 |
| H | 2.02920828942526 | 0.38475144138814 | 0.20007542730154 |
| H | -1.94709992741600 | -0.60299148360996 | -0.04364654538809 |
| H | -0.69059425906990 | -1.90469544559533 | -0.01131088535283 |
| H | -1.30592324589952 | 0.27713184517087 | 2.97048096870283 |
| H | 0.11421536807313 | 0.08786218122017 | -1.94346408738060 |

**H–BCP–SeH**
Electronic energy: -2596.323966679141

| | | | |
|---|---|---|---|
| C | 1.20723999233440 | -0.31603207928206 | 0.09925914354315 |
| C | -0.02795726017227 | 0.00064420342832 | 0.98040425553677 |
| C | -0.28054816558250 | 1.23386195425853 | 0.07372101741687 |
| C | -0.87490885599210 | -0.83424192755794 | -0.01633663494391 |
| Se | -0.00823725588583 | -0.09130596078564 | 2.91803307739398 |
| C | 0.05935857518913 | 0.05664107199262 | -0.87642565376902 |
| H | 0.44895973347014 | 2.03915169502436 | 0.14386860747025 |
| H | -1.30496212724985 | 1.60421100451473 | 0.04441080862588 |
| H | 1.53703070777836 | -1.35419829764023 | 0.09138546144775 |
| H | 2.03947650497326 | 0.38332508178447 | 0.16792583670668 |
| H | -1.93964426001021 | -0.60437839545206 | -0.05163036532829 |
| H | -0.68312310010828 | -1.90623543082969 | -0.02855699984825 |
| H | -1.41286441882503 | 0.30214589240287 | 3.07461186264048 |
| H | 0.11039064528078 | 0.08947253894173 | -1.96242836149235 |

**H–BCP–TeH**
Electronic energy: -462.989845597269

| | | | |
|---|---|---|---|
| C | 1.22137434866250 | -0.31818599544293 | 0.05944913467155 |
| C | -0.00578140460891 | -0.00043297500962 | 0.95685401436242 |
| C | -0.26597792831746 | 1.23325923591446 | 0.05034489183113 |
| C | -0.86312445596677 | -0.83414614863251 | -0.03411583265471 |
| Te | 0.01678974483967 | -0.09802247236576 | 3.09234323241453 |
| C | 0.06346571437634 | 0.05593097417193 | -0.90235612172441 |
| H | 0.46469521222840 | 2.03818199079733 | 0.11310371937145 |
| H | -1.28993366489985 | 1.60510907861698 | 0.03179746913546 |
| H | 1.55070416509779 | -1.35657573912014 | 0.04683723254554 |
| H | 2.05542829932701 | 0.38012073715739 | 0.11847946013588 |
| H | -1.92788314237985 | -0.60366922150214 | -0.05829688407295 |
| H | -0.67308889306072 | -1.90646078311619 | -0.04858768788808 |
| H | -1.57954585045381 | 0.31898132358662 | 3.22248351598124 |
| H | 0.10308857035568 | 0.08897134574458 | -1.99009408870908 |

**F–BCP•**
Electronic energy: -293.703618363626

| | | | |
|---|---|---|---|
| C | 1.22888275433815 | -0.32668813709853 | 0.14187658136157 |
| C | -0.01869421175930 | -0.00358301701888 | 0.98651840050953 |
| C | -0.29219594057213 | 1.25128935837710 | 0.13518531407346 |
| C | -0.89703533611735 | -0.85351095777328 | 0.04777670282424 |
| F | -0.06884329118899 | -0.04605234160894 | 2.36217107618699 |
| C | 0.04585176535333 | 0.05118849978135 | -0.77198577638872 |
| H | 0.44473014920544 | 2.04716122294225 | 0.19267786823139 |
| H | -1.31893560986615 | 1.60554956395817 | 0.11389657166363 |
| H | 1.54630107194901 | -1.36542385834180 | 0.12650557998661 |
| H | 2.05021723873765 | 0.38169952896290 | 0.19997592733468 |
| H | -1.95529371436394 | -0.60913577535897 | 0.02138224889229 |
| H | -0.69390256391569 | -1.92051917462136 | 0.02685510162431 |

**Cl–BCP•**

Electronic energy: -653.963727232452

| | | | |
|---|---|---|---|
| C | 1.23216090111041 | -0.32590872256117 | 0.10129761057898 |
| C | -0.01718165837457 | -0.00234116367894 | 0.94194370760716 |
| C | -0.29110628175356 | 1.25432024533282 | 0.09462022604235 |
| C | -0.89676544900018 | -0.85342158241990 | 0.00679013110130 |
| Cl | -0.08405351103058 | -0.05883524464239 | 2.75628945144712 |
| C | 0.04707526509946 | 0.05223601642358 | -0.80281661394325 |
| H | 0.44683832327525 | 2.04779208282599 | 0.15998678078665 |
| H | -1.31820990956781 | 1.60598575231336 | 0.08140472512002 |
| H | 1.54697450395229 | -1.36486247595687 | 0.09394028296534 |
| H | 2.05110052916602 | 0.38362072370136 | 0.16714319592862 |
| H | -1.95406404606229 | -0.60709520649078 | -0.01159451977288 |
| H | -0.69168635501445 | -1.91951551264707 | -0.00616938156141 |

**Br–BCP•**

Electronic energy: -2767.658999374391

| | | | |
|---|---|---|---|
| C | 1.23873147845720 | -0.32670002108997 | 0.08502806107722 |
| C | -0.01550863846936 | -0.00092423886937 | 0.90784636243108 |
| C | -0.29154338531975 | 1.26082748734819 | 0.07844467622712 |
| C | -0.90023391992557 | -0.85689468656649 | -0.00883839171401 |
| Br | -0.09447256714235 | -0.06750292345137 | 2.93717093710379 |
| C | 0.04689191876763 | 0.05211291943595 | -0.80302279456163 |
| H | 0.44902755371474 | 2.05081372025322 | 0.14262633731426 |
| H | -1.31890015136856 | 1.60904942539819 | 0.06472315527815 |
| H | 1.55003319156343 | -1.36581016353261 | 0.07693090123673 |
| H | 2.05435626047618 | 0.38550315256621 | 0.14958366392631 |
| H | -1.95586821866955 | -0.60707507749795 | -0.02648857560361 |
| H | -0.69143121028405 | -1.92142468179401 | -0.02116873641541 |

**I–BCP•**

Electronic energy: -491.434273608436

| | | | |
|---|---|---|---|
| C | 1.25633897870466 | -0.33054064417966 | 0.05006399135495 |
| C | -0.01316094878475 | 0.00105835698512 | 0.82789040052566 |
| C | -0.29460301238839 | 1.27848340186040 | 0.04340741928635 |
| C | -0.91170186153670 | -0.86809329863407 | -0.04608233779473 |
| I | -0.10637609662550 | -0.07742913916387 | 3.32749514423457 |
| C | 0.04601694374456 | 0.05139493412498 | -0.77841745843294 |
| H | 0.45238841848136 | 2.05946811297289 | 0.10633513328888 |
| H | -1.32297524348232 | 1.61655172055433 | 0.02685282949256 |
| H | 1.55741611784058 | -1.37033708764371 | 0.03913012199471 |
| H | 2.06325976796273 | 0.38831725305100 | 0.11341136556790 |
| H | -1.96267268950612 | -0.60858201012283 | -0.06633995044936 |
| H | -0.69284837441011 | -1.92831659980458 | -0.06091165906855 |

## HO–BCP•

Electronic energy: -269.676498334952

| | | | |
|---|---|---|---|
| C | 1.19096079750633 | -0.31810911382660 | 0.20497692950541 |
| C | -0.07292967251997 | 0.01139985661118 | 1.02213640025574 |
| C | -0.31859370905045 | 1.25892774903635 | 0.12311777976912 |
| C | -0.92319175825707 | -0.84400804876802 | 0.03697522511946 |
| O | -0.08958025558134 | -0.04364383463840 | 2.42169390960672 |
| C | 0.04371975207272 | 0.05099457187656 | -0.75704996376992 |
| H | 0.41590792947845 | 2.05677101035817 | 0.19533877592759 |
| H | -1.34355883871540 | 1.61825115473798 | 0.05910212947816 |
| H | 1.50971870312994 | -1.35715919255162 | 0.21220881931270 |
| H | 2.01343325786233 | 0.38787668605371 | 0.28407445699037 |
| H | -1.98167930714952 | -0.60104156885986 | -0.03100612483858 |
| H | -0.72388853098056 | -1.91260268880387 | 0.03273428227019 |
| H | -0.97782536779545 | 0.19182441877444 | 2.71586438037304 |

## HS–BCP•

Electronic energy: -592.553240447216

| | | | |
|---|---|---|---|
| C | 1.21844203822789 | -0.32245671531978 | 0.11560184953836 |
| C | -0.03789435609362 | 0.00389279793603 | 0.96009440737782 |
| C | -0.29545099487624 | 1.25489447597318 | 0.08010062893964 |
| C | -0.90058192773790 | -0.84940380018412 | -0.00627121493797 |
| S | -0.02284478942681 | -0.07705445448047 | 2.78804368044513 |
| C | 0.04856212612833 | 0.05207144473650 | -0.81258637026824 |
| H | 0.44112946446184 | 2.04984892380906 | 0.15222722187334 |
| H | -1.32106551927596 | 1.61377259153221 | 0.04910508985375 |
| H | 1.53615627271965 | -1.36149832803547 | 0.11421980095729 |
| H | 2.04034730907465 | 0.38456362611631 | 0.18610161975092 |
| H | -1.96003111776624 | -0.60829362221140 | -0.04229587059267 |
| H | -0.69803631249183 | -1.91665363799901 | -0.01142683997825 |
| H | -1.30623919294377 | 0.27579669812697 | 2.94725299704087 |

## HSe–BCP•

Electronic energy: -2595.652606850470

| | | | |
|---|---|---|---|
| C | 1.23129165440793 | -0.32482080355053 | 0.08371785573227 |
| C | -0.02175960379508 | 0.00078758146073 | 0.92455137190515 |
| C | -0.28822720635196 | 1.25655780641972 | 0.06435396975097 |
| C | -0.89507525644205 | -0.85326516768364 | -0.02204770353553 |
| Se | -0.00772965897584 | -0.08768700357244 | 2.93005362277711 |
| C | 0.04996512803487 | 0.05225671422248 | -0.82596122970526 |
| H | 0.44991363895539 | 2.04971121506901 | 0.13194034522670 |
| H | -1.31430906624601 | 1.61266379785298 | 0.04144107658745 |
| H | 1.54708414269303 | -1.36393253204045 | 0.07553048724342 |
| H | 2.05171796236220 | 0.38381926114777 | 0.14791112954289 |
| H | -1.95360855415434 | -0.61013378164914 | -0.04988991624645 |
| H | -0.69025457383427 | -1.91951134854221 | -0.03171426841351 |
| H | -1.41651560665387 | 0.30303426086571 | 3.05028025913479 |

### HTe–BCP•

Electronic energy: -462.325972764910

| | | | |
|---|---|---|---|
| C | 1.28024129473001 | -0.33469323478283 | -0.02044133231998 |
| C | 0.02455484720748 | -0.00093392495218 | 0.76916066218766 |
| C | -0.27090823349357 | 1.27983249652298 | 0.00354124489379 |
| C | -0.89391336756561 | -0.87160672755218 | -0.07524173773161 |
| Te | -0.05093786076372 | -0.09260405006038 | 3.54741158738885 |
| C | 0.05080367808630 | 0.04960709394685 | -0.81622505192856 |
| H | 0.47860412703523 | 2.05911964003056 | 0.04917567885429 |
| H | -1.29857064481848 | 1.62007210096377 | 0.00297718980429 |
| H | 1.57966285921163 | -1.37462304433442 | -0.04382840957928 |
| H | 2.08863100221054 | 0.38396132426734 | 0.02092734910284 |
| H | -1.94476368397431 | -0.61127589565656 | -0.07925240407502 |
| H | -0.67597048036746 | -1.93150676737213 | -0.09723438495213 |
| H | -1.62494053749804 | 0.32413198897917 | 3.25919560835486 |

ii. Solvent-phase calculations:
All optimizations at **SMD($Et_2O$)-B2PLYP-D3BJ/def2-TZVP**

### H–BCP–F

Electronic energy: -294.394543000766

| | | | |
|---|---|---|---|
| C | 1.21624514750904 | -0.32161094808689 | 0.15670260293921 |
| C | -0.01916874242758 | -0.00405292093348 | 1.00851143579752 |
| C | -0.28613425944179 | 1.23714979821136 | 0.14770225145748 |
| C | -0.88324769683960 | -0.84166162012853 | 0.05688775393371 |
| F | -0.07337639467089 | -0.04841974815986 | 2.38397324247146 |
| C | 0.05286903772113 | 0.05502329711547 | -0.80874132148482 |
| H | 0.44790095623836 | 2.03867570603045 | 0.20637548307634 |
| H | -1.31315461116254 | 1.59719701316156 | 0.12172577842864 |
| H | 1.53925337370875 | -1.36100595003887 | 0.13883236913188 |
| H | 2.04325406590762 | 0.38352696649303 | 0.21644473084759 |
| H | -1.94487448608239 | -0.60228317102870 | 0.02577275094452 |
| H | -0.68499983584930 | -1.91184980168238 | 0.03295519154713 |
| H | 0.09568849828921 | 0.09031131174686 | -1.89044058679067 |

### H–BCP–Cl

Electronic energy: -654.650112909522

| | | | |
|---|---|---|---|
| C | 1.21531603353850 | -0.31975299948272 | 0.12031769879060 |
| C | -0.01829031586585 | -0.00336799976706 | 0.98445409586647 |
| C | -0.28408550396057 | 1.23592457439376 | 0.11139935990626 |
| C | -0.87997230848341 | -0.83874479295024 | 0.02051702222662 |
| Cl | -0.08881052106713 | -0.06090041364722 | 2.76385547264033 |
| C | 0.05432271166730 | 0.05622730504061 | -0.84455404259895 |
| H | 0.44878458673865 | 2.03785554282707 | 0.17757168849560 |
| H | -1.31091817421395 | 1.59680335519756 | 0.09336063958894 |
| H | 1.53907802090621 | -1.35890630049951 | 0.11014530532846 |
| H | 2.04267748204207 | 0.38421982742320 | 0.18732197171668 |
| H | -1.94199166713659 | -0.60068868758685 | -0.00326748584730 |
| H | -0.68306486611932 | -1.90925161385020 | 0.00403767414061 |
| H | 0.09720957485409 | 0.09158213560164 | -1.92845771795432 |

### H–BCP–Br

Electronic energy: -2768.342169614749

| | | | |
|---|---|---|---|
| C | 1.21701595649028 | -0.31942249914393 | 0.10779776639599 |
| C | -0.01752731244088 | -0.00276079426609 | 0.97070618992177 |
| C | -0.28361730587577 | 1.23749729548741 | 0.09896658250264 |
| C | -0.88006340871225 | -0.83893717090890 | 0.00852109714632 |
| Br | -0.09669910759830 | -0.06746394969465 | 2.91420480354422 |
| C | 0.05473682148393 | 0.05657980735770 | -0.85507145584770 |
| H | 0.44940616278804 | 2.03914540138912 | 0.16428763126062 |
| H | -1.31023804719096 | 1.59837652981750 | 0.08012048731162 |
| H | 1.54076996250342 | -1.35838816037243 | 0.09678451907759 |
| H | 2.04410517825870 | 0.38471350008664 | 0.17388465450378 |
| H | -1.94191015874708 | -0.60075016399071 | -0.01537073928656 |
| H | -0.68305584767530 | -1.90927606268474 | -0.00815476201020 |
| H | 0.09733215961618 | 0.09168619962310 | -1.93997509222010 |

### H–BCP–I

Electronic energy: -492.105548462677

| | | | |
|---|---|---|---|
| C | 1.21787833759774 | -0.31905758326307 | 0.09135222170275 |
| C | -0.01695046095897 | -0.00235614826995 | 0.95845803928404 |
| C | -0.28306959627032 | 1.23818151040838 | 0.08260651448909 |
| C | -0.87957131620442 | -0.83855348564339 | -0.00802799119195 |
| I | -0.10373613155618 | -0.07293578759833 | 3.09952906751060 |
| C | 0.05530359350656 | 0.05709921643591 | -0.86944467399811 |
| H | 0.44986915315839 | 2.03975498625615 | 0.14893750456518 |
| H | -1.30981247211529 | 1.59864247469575 | 0.06451892776176 |
| H | 1.54128846822575 | -1.35813643960159 | 0.08106324591082 |
| H | 2.04487656819868 | 0.38501807615087 | 0.15854826621060 |
| H | -1.94136907513716 | -0.60029807653556 | -0.03102099125299 |
| H | -0.68242792509036 | -1.90881103756359 | -0.02413838753482 |
| H | 0.09797590954559 | 0.09245222722843 | -1.95568006115697 |

### H–BCP–OH

Electronic energy: -270.367518943607

| | | | |
|---|---|---|---|
| C | 1.17428701094351 | -0.31130923878008 | 0.20610198305626 |
| C | -0.07555067531217 | 0.01048119930980 | 1.04370634406791 |
| C | -0.31381208757953 | 1.24287160628626 | 0.13015507371037 |
| C | -0.90888316618596 | -0.83008980007719 | 0.03871042736008 |
| O | -0.09754975555181 | -0.04606958777606 | 2.43247863780260 |
| C | 0.04921069552229 | 0.05632304921944 | -0.80249791824072 |
| H | 0.41689794461218 | 2.04822830908593 | 0.20250711733820 |
| H | -1.33857801492329 | 1.61032151469456 | 0.06766206325340 |
| H | 1.50219452766905 | -1.35070570720567 | 0.20743299760463 |
| H | 2.00482149186572 | 0.38990380690236 | 0.28526274462070 |
| H | -1.97177396728296 | -0.59533880576284 | -0.02873724732585 |
| H | -0.71537810221739 | -1.90278496737251 | 0.02816937118021 |
| H | -0.98306284007103 | 0.19934404147278 | 2.73138025742856 |
| H | 0.12738765371139 | 0.08188593080322 | -1.88408979645636 |

**H–BCP–SH**
Electronic energy: -593.237912944533

| | | | |
|---|---|---|---|
| C | 1.19946379357755 | -0.31585959221611 | 0.12505518835161 |
| C | -0.04204253894879 | -0.00270825905521 | 0.99818005624897 |
| C | -0.29077372029635 | 1.23283409889570 | 0.09267968569691 |
| C | -0.88223208309768 | -0.83722693591956 | -0.00605809441824 |
| S | -0.03396921262716 | -0.08943117960788 | 2.79147167427051 |
| C | 0.05671559218292 | 0.05739011821347 | -0.85861574927765 |
| H | 0.43968774705518 | 2.03735742329758 | 0.16834488966698 |
| H | -1.31645531619133 | 1.59996509849121 | 0.05993995865283 |
| H | 1.52925127570185 | -1.35424022962190 | 0.11789251450926 |
| H | 2.02898355023435 | 0.38619289997879 | 0.20191194494150 |
| H | -1.94692928773799 | -0.60713981269884 | -0.04551441299637 |
| H | -0.68539575266030 | -1.90872529544927 | -0.02012389982833 |
| H | -1.30097256615703 | 0.31195830103477 | 2.97662507812676 |
| H | 0.11487923416479 | 0.09269471545724 | -1.94354677854473 |

**H–BCP–SeH**
Electronic energy: -2596.331949814691

| | | | |
|---|---|---|---|
| C | 1.21018377905514 | -0.31667590684315 | 0.09797183741529 |
| C | -0.02496260770703 | 0.00107021768235 | 0.97669816934351 |
| C | -0.27985897947411 | 1.23557801409746 | 0.07375409501742 |
| C | -0.87546092608750 | -0.83466724278723 | -0.01484536207036 |
| Se | -0.01337319358704 | -0.08805852522210 | 2.91887789756574 |
| C | 0.05939475481551 | 0.05650615553644 | -0.87643543959819 |
| H | 0.45270283258445 | 2.03864026409892 | 0.14101618162975 |
| H | -1.30533475378674 | 1.60294739288120 | 0.04647470134867 |
| H | 1.53686537959882 | -1.35583529023798 | 0.08980795503962 |
| H | 2.04088592931657 | 0.38459007270779 | 0.16548699855941 |
| H | -1.93945701814144 | -0.60135854795778 | -0.04746959869670 |
| H | -0.68039394620289 | -1.90626692811072 | -0.02856084716654 |
| H | -1.41940103029090 | 0.29752111531756 | 3.07824590642700 |
| H | 0.10842049510716 | 0.08907055963724 | -1.96278043941465 |

**H–BCP–TeH**
Electronic energy: -462.997049619735

| | | | |
|---|---|---|---|
| C | 1.22366050466089 | -0.31865431542094 | 0.05866429240820 |
| C | -0.00293595202436 | 0.00068954603232 | 0.95442047003976 |
| C | -0.26514201774012 | 1.23518410427579 | 0.05013983486276 |
| C | -0.86399818763597 | -0.83393694955001 | -0.03189983660855 |
| Te | 0.01454977243180 | -0.09420033226000 | 3.09347333311355 |
| C | 0.06314609870993 | 0.05570506639591 | -0.90212010838612 |
| H | 0.46822379638883 | 2.03825876478758 | 0.10977042554328 |
| H | -1.28992560725294 | 1.60513119412695 | 0.03307316586571 |
| H | 1.55028843459488 | -1.35791697255072 | 0.04680786942704 |
| H | 2.05675126767691 | 0.38085966093983 | 0.11673803162871 |
| H | -1.92824193129324 | -0.60044242556425 | -0.05402334481297 |
| H | -0.67178225481995 | -1.90613714801729 | -0.04728826188473 |
| H | -1.58500521251745 | 0.31040537227019 | 3.22071261443688 |
| H | 0.10062200402081 | 0.08811578533465 | -1.99022643023353 |

**F–BCP•**

Electronic energy: -293.713736699727

| | | | |
|---|---|---|---|
| C | 1.23230361395108 | -0.32769280030161 | 0.14176546333589 |
| C | -0.01844191320017 | -0.00334135214645 | 0.97704964866367 |
| C | -0.29312452028335 | 1.25482391789319 | 0.13501985791534 |
| C | -0.89969434609463 | -0.85603780562299 | 0.04746452547283 |
| F | -0.06877605946616 | -0.04595257208216 | 2.36751696264464 |
| C | 0.04566748214928 | 0.05116527911389 | -0.76880977352518 |
| H | 0.44778581061923 | 2.04667001282142 | 0.19306143230807 |
| H | -1.32142053422633 | 1.60392308685998 | 0.11385464024432 |
| H | 1.54436615101379 | -1.36791136462990 | 0.12644333185755 |
| H | 2.04992728725719 | 0.38462257461157 | 0.20070949938073 |
| H | -1.95656697100704 | -0.60656030867349 | 0.02183942299523 |
| H | -0.69094368891286 | -1.92173375564345 | 0.02692058500692 |

**Cl–BCP•**

Electronic energy: -653.975751300721

| | | | |
|---|---|---|---|
| C | 1.23689828496095 | -0.32724748005623 | 0.10087597769405 |
| C | -0.01680406409267 | -0.00200278005781 | 0.92988159042552 |
| C | -0.29226818200721 | 1.25919641780231 | 0.09418544718791 |
| C | -0.90034348198487 | -0.85691758283185 | 0.00605000274504 |
| Cl | -0.08492373346299 | -0.05907234761750 | 2.77028572825275 |
| C | 0.04670330773874 | 0.05205907342489 | -0.79587559980366 |
| H | 0.44977009463154 | 2.04847053255957 | 0.15883975130300 |
| H | -1.32077289323840 | 1.60577898302009 | 0.08021211018457 |
| H | 1.54633017437106 | -1.36750107590345 | 0.09229034567442 |
| H | 2.05205929152307 | 0.38624445570240 | 0.16613358112753 |
| H | -1.95610801754689 | -0.60546543168475 | -0.01264722725608 |
| H | -0.68945846909233 | -1.92156785215766 | -0.00739611123505 |

**Br–BCP•**

Electronic energy: -2767.672814636528

| | | | |
|---|---|---|---|
| C | 1.24588095914315 | -0.32865036795638 | 0.08311688919655 |
| C | -0.01490790420193 | -0.00032023098638 | 0.88779166527760 |
| C | -0.29329036793958 | 1.26819246297412 | 0.07641558423731 |
| C | -0.90564830330455 | -0.86211082831324 | -0.01135840052293 |
| Br | -0.09572337968773 | -0.06873892067551 | 2.97637096422328 |
| C | 0.04625064026858 | 0.05167815261292 | -0.78908367286107 |
| H | 0.45216999283065 | 2.05294666761888 | 0.13835783868697 |
| H | -1.32205571345983 | 1.61028361606214 | 0.06007528435739 |
| H | 1.55073472392472 | -1.36906469394133 | 0.07235294218723 |
| H | 2.05669967978129 | 0.38837602667311 | 0.14555539921790 |
| H | -1.95913901401996 | -0.60597983764902 | -0.03101616858346 |
| H | -0.68988900153481 | -1.92463713421933 | -0.02574272911676 |

**I–BCP•**

Electronic energy: -491.446566511246

| | | | |
|---|---|---|---|
| C | 1.26141909751730 | -0.33218947945308 | 0.04810162754699 |
| C | -0.01359809083616 | 0.00082469016291 | 0.82068115853203 |
| C | -0.29611229713259 | 1.28381000553411 | 0.04117603416482 |
| C | -0.91588065886818 | -0.87196738442448 | -0.04950437025694 |
| I | -0.10503447956215 | -0.07662702320136 | 3.36256349693164 |
| C | 0.04570332316963 | 0.05127567504556 | -0.76789233785440 |
| H | 0.45570516848717 | 2.06002583568020 | 0.10229288746793 |
| H | -1.32618908082877 | 1.61585028514814 | 0.02119045942402 |
| H | 1.55636764255664 | -1.37360181532736 | 0.03383385293872 |
| H | 2.06394699228167 | 0.39143803119277 | 0.11012245789039 |
| H | -1.96507073801520 | -0.60639863739411 | -0.07236753503869 |
| H | -0.69017487876937 | -1.93046518296331 | -0.06736273174651 |

**HO–BCP•**

Electronic energy: -269.688568666720

| | | | |
|---|---|---|---|
| C | 1.19484096115610 | -0.31939876278356 | 0.20374504905191 |
| C | -0.07146985065222 | 0.01000453029024 | 1.01844375698364 |
| C | -0.31872003850248 | 1.26051740492144 | 0.12497325847632 |
| C | -0.92405060067812 | -0.84653799783179 | 0.03704868101981 |
| O | -0.09442244529157 | -0.04392597842475 | 2.42081202712786 |
| C | 0.04335561749478 | 0.05125342633105 | -0.75430840611462 |
| H | 0.41871089479846 | 2.05583977133070 | 0.19780897394720 |
| H | -1.34495025004205 | 1.61615869986403 | 0.06753792068423 |
| H | 1.51114396579113 | -1.35948048044850 | 0.20770625962706 |
| H | 2.01557011366356 | 0.38915736896442 | 0.28150621526556 |
| H | -1.98188201620986 | -0.60082521741497 | -0.02428842531339 |
| H | -0.72025404003739 | -1.91448053458374 | 0.03194201252813 |
| H | -0.98537931149034 | 0.20119876978543 | 2.70723967671629 |

**HSe–BCP•**

Electronic energy: -2595.663142311681

| | | | |
|---|---|---|---|
| C | 1.23634211118624 | -0.32614513136593 | 0.08144432436390 |
| C | -0.01806588448422 | 0.00095222768223 | 0.91600459887547 |
| C | -0.28832830253800 | 1.26041737072077 | 0.06458558814738 |
| C | -0.89750970168696 | -0.85550215548020 | -0.02057882480805 |
| Se | -0.01278868515305 | -0.08464115829182 | 2.93255322649287 |
| C | 0.04910782951048 | 0.05209010412959 | -0.82159650204200 |
| H | 0.45402731979696 | 2.04975793986566 | 0.12960479407815 |
| H | -1.31586983459272 | 1.61151610513357 | 0.04564584100256 |
| H | 1.54725809376550 | -1.36648830066099 | 0.07336563480849 |
| H | 2.05367820071802 | 0.38568080875613 | 0.14514415707514 |
| H | -1.95459840358044 | -0.60717619318520 | -0.04356872987644 |
| H | -0.68748063180797 | -1.92062802591617 | -0.03144711217755 |
| H | -1.42327911113383 | 0.29964640861236 | 3.04901000406007 |

**HTe–BCP•**

Electronic energy: -462.337988422332

| | | | |
|---|---|---|---|
| C | 1.28443351653653 | -0.33607319551987 | -0.02055524528989 |
| C | 0.02772656228889 | 0.00034556585053 | 0.76759766931109 |
| C | -0.27034366922636 | 1.28407350550197 | 0.00538378626871 |
| C | -0.89674107493754 | -0.87280576123964 | -0.06966358266983 |
| Te | -0.05259731629289 | -0.08621918415751 | 3.53666892576653 |
| C | 0.04951319553875 | 0.04928710508789 | -0.81132210390603 |
| H | 0.48363082641749 | 2.05954048264679 | 0.04584537005849 |
| H | -1.29941615292095 | 1.62016924575827 | 0.00649177311670 |
| H | 1.57867903112294 | -1.37758008208310 | -0.04481308152706 |
| H | 2.09032563263903 | 0.38560019525292 | 0.01780168853874 |
| H | -1.94623305822001 | -0.60690082633559 | -0.07077318545459 |
| H | -0.67432219277461 | -1.93183860996874 | -0.09376797246742 |
| H | -1.63216230017127 | 0.31188255920609 | 3.25127195825456 |