

SUPPORTING INFORMATION

The Nucleophilic Intermolecular Chemistry and Reactivity of Dimethylcarbene

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1. Table S-1. Carbene Parameters

carbene	E_{HO}^{a}	E_{LU}^{a}	μ^{b}	η^{c}	ε^{d}	ω^{e}	IRI^{f}	$m_{\text{CXY}}^{\text{g}}$	$\Delta E_{\text{stab}}^{\text{h}}$
Me ₂ C	-9.04	3.39	-2.83	12.43	-0.23	0.32	-0.48	k	28.7
2-Ad:	-8.39	2.96	-2.72	11.35	-0.24	0.33	-0.48	k	25.8
ClCMe	-9.97	2.14	-3.91	12.11	-0.32	0.63	-0.65	0.58	38.8
CBr ₂	-10.42	0.65	-4.89	11.06	-0.44	1.08	-0.88	0.82	42.4
PhCBr	-9.39	0.78	-4.31	10.16	-0.42	0.91	-0.85	0.64	43.2
PhCCl	-9.62	0.94	-4.34	10.56	-0.41	0.89	-0.82	0.72	44.8
PhCF	-9.56	1.46	-4.05	11.02	-0.37	0.74	-0.74	0.96	51.0
ClCSMe	-9.92	2.00	-3.96	11.92	-0.33	0.66	-0.67	0.91 ⁱ	61.5
CCl ₂	-10.91	1.00	-4.96	11.91	-0.42	1.03	-0.83	0.97	45.5
ClCF	-11.71	1.74	-4.99	13.45	-0.37	0.93	-0.74	1.22	56.1
CF ₂	-12.85	2.74	-5.06	15.60	-0.32	0.82	-0.65	1.47	70.9
ClCOMe	-10.49	3.14	-3.67	13.63	-0.27	0.50	-0.54	1.59	72.7
FCOMe	-11.33	4.07	-3.63	15.40	-0.24	0.43	-0.47	1.85	84.1
C(OMe) ₂	-10.20	4.98	-2.61	15.17	-0.17	0.22	-0.34	2.22	92.0
MeOCNMe ₂	-9.43	5.65	-1.89	15.08	-0.13	0.12	-0.25	2.91	95.7
C(NMe ₂) ₂	-8.24	5.94	-1.15	14.17	-0.08	0.05	-0.16	3.60	866
NHC ^j	-8.25	5.34	-1.46	13.59	-0.11	0.08	-0.21	k	109.4
MeCOMe	-9.23	4.04	-2.60	13.27	-0.200	0.25	-0.39	k	59.2

^a E_{HO} and E_{LU} are the HOMO and LUMO energies in eV, computed at the HF/6-31G(d,p)//MP2/6-31G(d,p) level. ^b $\mu = (E_{\text{LU}} + E_{\text{HO}})/2$, in eV. ^c $\eta = E_{\text{LU}} - E_{\text{HO}}$, in eV. ^d $\varepsilon = \mu/\eta$. ^e $\omega = 0.5\mu^2/\eta$, in eV. ^f $(E_{\text{LU}} + E_{\text{HO}})/(E_{\text{LU}} - E_{\text{HO}}) = 2\varepsilon$. ^gCalculated from Eq. (2) of reference 20. ^hCalculated at the B3LYP/6-311++G(2d,p) level, in kcal/mol relative to CH₂, cf. reference 20. ⁱExperimental value. ^jN,N'-dimethyl-1,3-imidazolidene. ^kNot determined.

2. Table S-2. Differential Orbital Energies for Additions of Dimethylcarbene^a

Alkene	$\Delta\epsilon_E = p-\pi$	$\Delta\epsilon_N = \pi^*-\sigma$
2-ethyl-1-butene ^b	12.36	11.19
1-hexene	12.64	10.99
styrene	11.58	9.25
methyl acrylate	13.84	9.80
acrylonitrile	14.04	9.21

^aOrbital energies in eV. Orbital energies for dimethylcarbene (HF/4-31G//3G) are $\epsilon_{HO}(\sigma) = -9.00$ and $\epsilon_{LU}(p) = 3.12$. Orbital energies for the alkenes are given in Table S-3, below. ^bValue calculated is for isobutene.

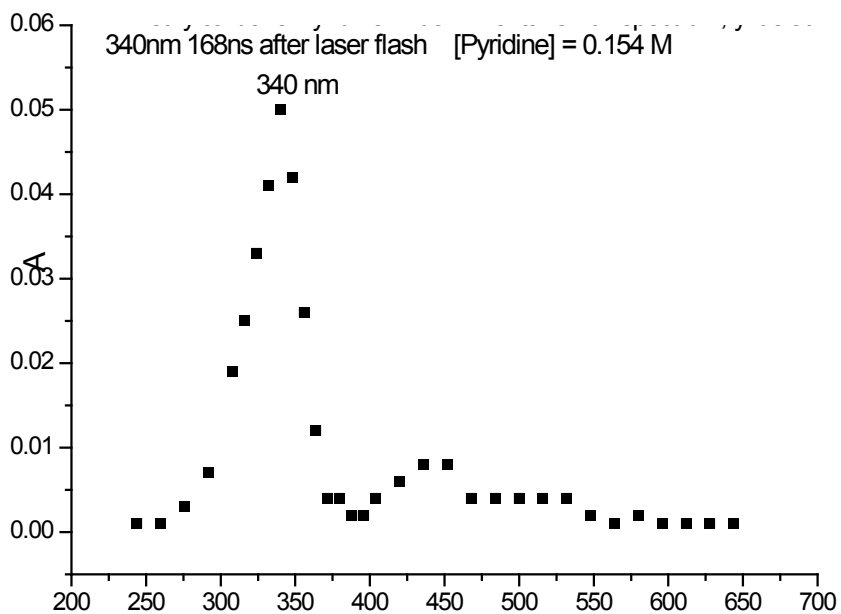
3. Table S-3. Orbital Energies of Alkenes (eV)^a

Alkene	$\epsilon_{HO} (\pi)$	$\epsilon_{LU} (\pi^*)$
2-ethyl-1-hexene ^b	-9.24	2.19
1-hexene	-9.52	1.99
styrene ^c	-8.46	0.25
methyl acrylate	-10.72	0.80
acrylonitrile	-10.92	0.21

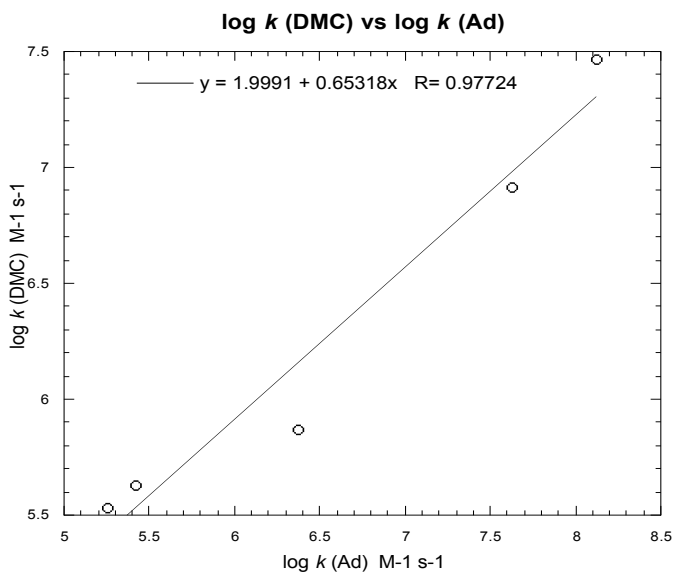
^aSee Reference 21c, Table IV for references to the alkene orbital energy values.

^bValues for isobutene are used for 2-ethyl-1-hexene. ^cSee reference 2, Table 2, note c for orbital energies of styrene.

4. **Figure S-1.** Dimethylcarbene-pyridine ylide **4** in pentane



5. **Figure S-2.** Log $k(\text{DMC})$ versus log $k(\text{Ad})$



Log $k(\text{DMC})$ versus log $k(\text{Ad})$; slope = 0.65; $r = 0.98$.

6. Figures S-3 – S-12. Rate Constants for Alkene Additions at 25 °C

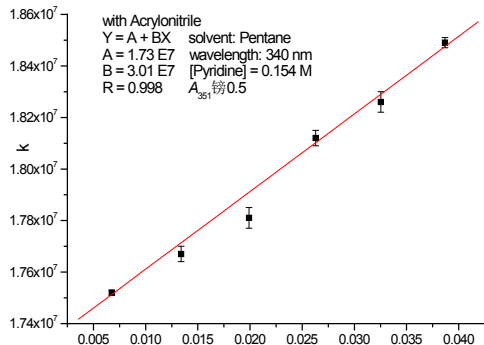


Figure S-3. Rate constant for addition of DMC to AcrCN: $k = 3.01 \exp 7$ $\text{M}^{-1} \text{s}^{-1}$, $r = 0.998$.

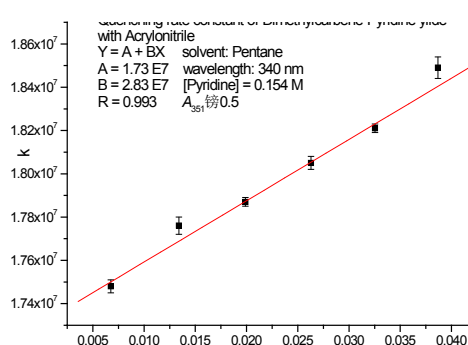


Figure S-4. Rate constant for addition of DMC to AcrCN: $k = 2.83 \exp 7$ $\text{M}^{-1} \text{s}^{-1}$, $r = 0.993$.

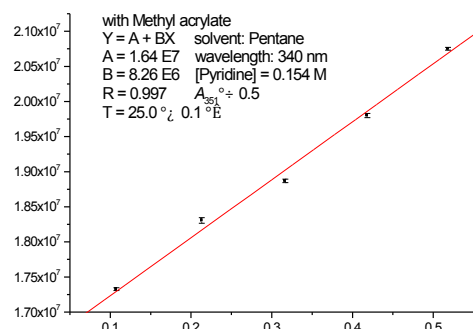


Figure S-5. Rate constant for addition of DMC to MeAcr: $k = 8.26 \text{ Exp } 6$ $\text{M}^{-1} \text{s}^{-1}$, $r = 0.997$.

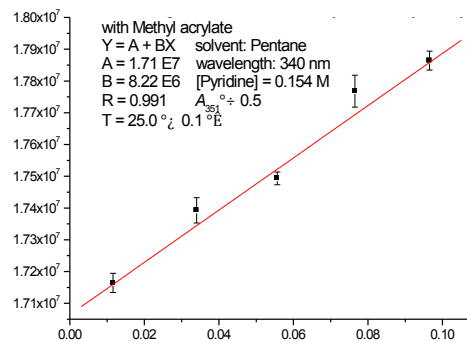


Figure S-6. Rate constant for addition of DMC to MeAcr: $k = 8.22 \text{ Exp } 6$ $\text{M}^{-1} \text{s}^{-1}$, $r = 0.991$.

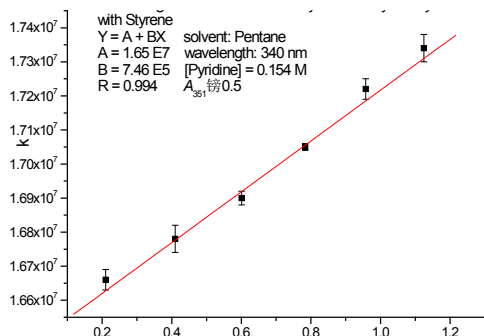


Figure S-7. Rate constant for addition of DMC to styrene: $k = 7.46 \text{ Exp } 5$

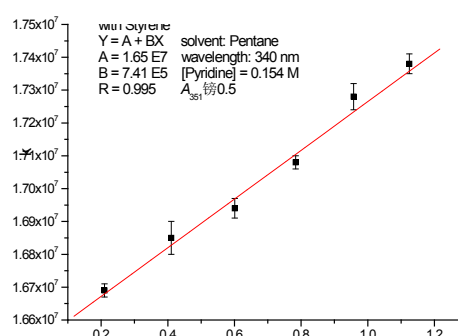


Figure S-8. Rate constant for addition of DMC to styrene: $k = 7.41 \text{ Exp } 5$

$M^{-1} s^{-1}, r = 0.994.$

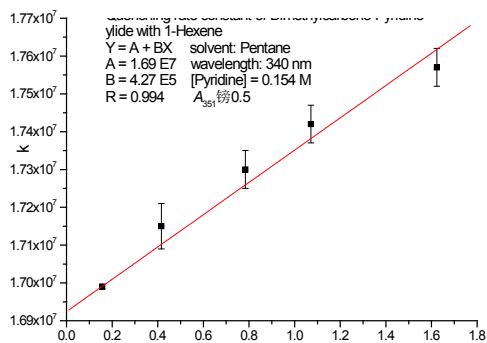


Figure S-9. Rate constant for addition of DMC to 1-hexene: $k = 4.27 \text{ Exp } 5$ $M^{-1} s^{-1}, r = 0.994.$

$M^{-1} s^{-1}, r = 0.995.$

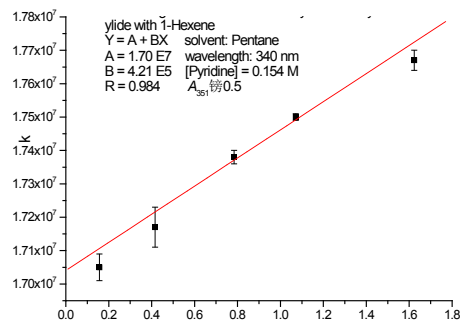


Figure S-10. Rate constant for addition of DMC to 1-hexene: $k = 4.21 \text{ Exp } 5$ $M^{-1} s^{-1}, r = 0.984.$

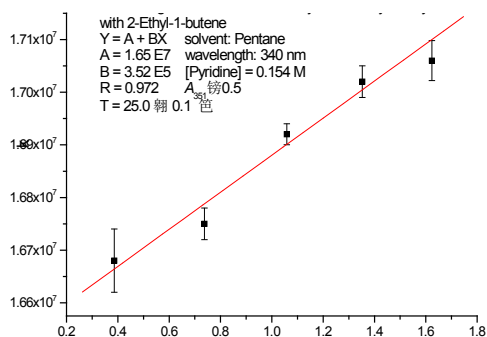


Figure S-11. Rate constant for addition of DMC to 2-ethyl-1-butene: $k = 3.52 \text{ Exp } 5$ $M^{-1} s^{-1}, r = 0.972.$

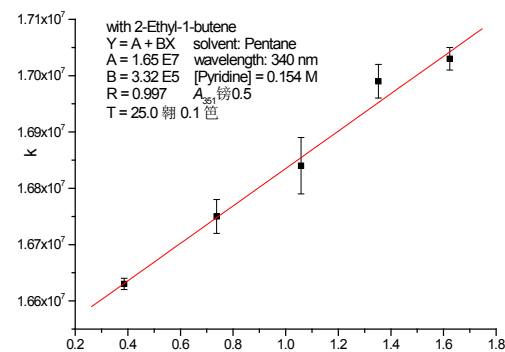


Figure S-12. Rate constant for addition of DMC to 2-ethyl-1-butene: $k = 3.32 \text{ Exp } 5$ $M^{-1} s^{-1}, r = 0.997.$

7. Figures S-13 – S-20. Rate Constants for Alkene Additions at Various Temperatures

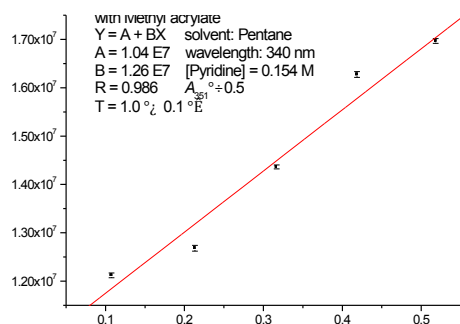


Figure S-13. Rate constant for addition of DMC to MeAcr at 274 K: $k = 1.26 \text{ Exp 7}$
 $\text{M}^{-1} \text{ s}^{-1}$, $r = 0.986$.

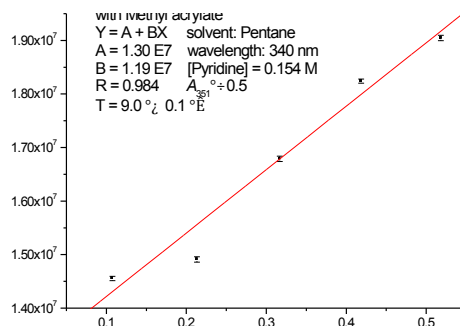


Figure S-14. Rate constant for addition DMC to MeAcr at 282 K: $k = 1.19$
 $\text{M}^{-1} \text{ s}^{-1}$, $r = 0.984$

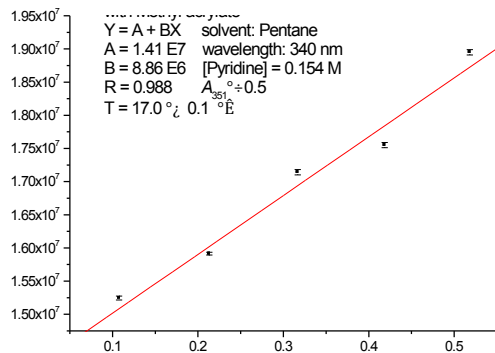


Figure S-15. Rate constant for addition of DMC to MeAcr at 290 K: $k = 8.86 \text{ Exp 6}$
 $\text{M}^{-1} \text{ s}^{-1}$, $r = 0.988$.

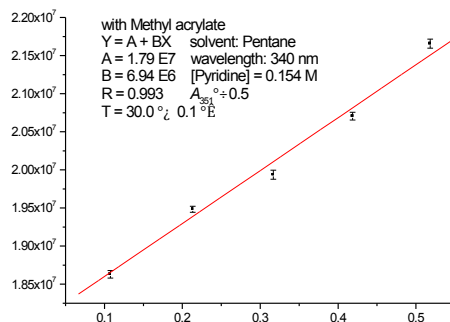


Figure S-16. Rate constant for addition DMC to MeAcr at 303 K: $k = 6.94$
 $\text{M}^{-1} \text{ s}^{-1}$, $r = 0.993$.

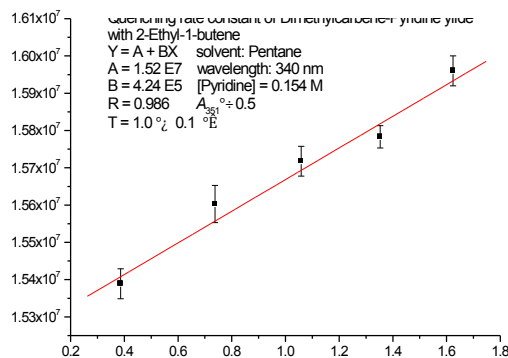


Figure S-17. Rate constant for addition of DMC to 2-ethyl-1-butene at 274 K:
 $k = 4.24 \text{ Exp } 5 \text{ M}^{-1} \text{ s}^{-1}$, $r = 0.986$.

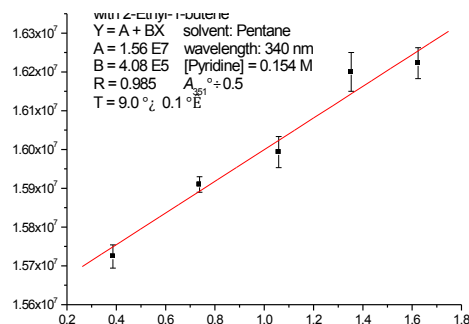


Figure S-18. Rate constant for addition of DMC to 2-ethyl-1-butene at 282 K:
 $k = 4.08 \text{ Exp } 5 \text{ M}^{-1} \text{ s}^{-1}$, $r = 0.986$.

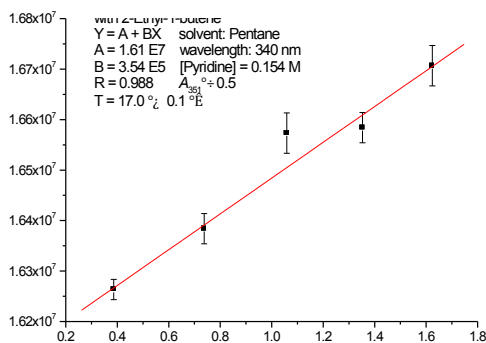


Figure S-19. Rate constant for addition of DMC to 2-ethyl-1-butene at 290 K:
 $k = 3.54 \text{ Exp } 5 \text{ M}^{-1} \text{ s}^{-1}$, $r = 0.988$.

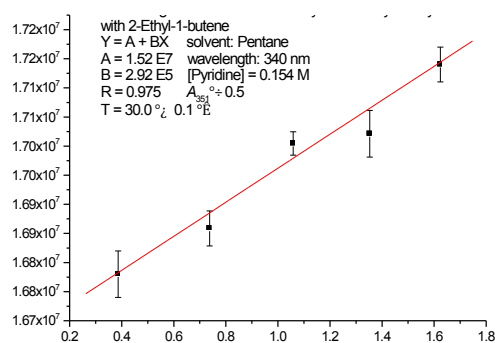


Figure S-20. Rate constant for addition of DMC to 2-ethyl-1-butene at 303 K:
 $k = 2.92 \text{ Exp } 5 \text{ M}^{-1} \text{ s}^{-1}$, $r = 0.975$.

8. Arrhenius Correlations

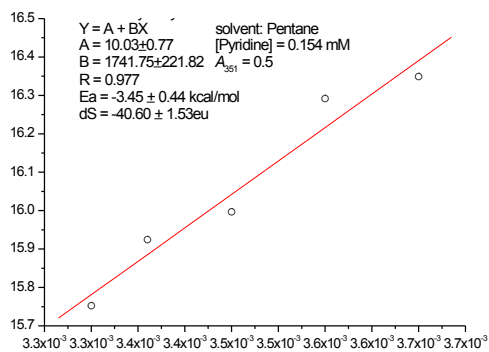


Figure S-21. Activation energy for addition of DMC to MeAc: $E_a = -3.5$ kcal/mol, $\ln A = 10.0 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta S^\ddagger = -40.6$ eu, $r = 0.977$.

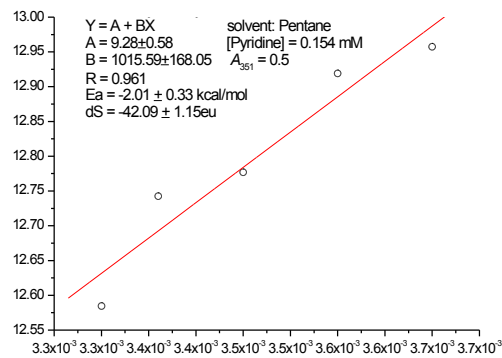


Figure S-22. Activation energy for addition to 2-ethyl-1-butene: $E_a = -2.0$ kcal/mol, $\ln A = 9.28 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta S^\ddagger = -42.1$ eu, $r = 0.961$.

4. Computational details

Electronic structure calculations were carried out using methodologies implemented in the Gaussian 09 suite of programs.¹ Computational methods based on both *ab initio* and density functional theory were applied as discussed in some detail below.

(a) Singlet-Triplet Separation in Ad and DMC

Adamantanylidene (Ad): For reference purposes, a series of calculations were performed for the adiabatic singlet-triplet (S-T) separation in adamantanylidene (^{1,3}Ad): (a) We first optimized the gas-phase geometries of ¹Ad (C_s symmetry) and ³Ad (C_{2v} symmetry) at the MP2 level with the cc-pVTZ basis set.^{2,3} Geometry optimization was followed by normal mode analysis and standard thermodynamic corrections (based on the harmonic oscillator/rigid rotor approximations and ideal gas behavior) were applied to convert from electronic potential energies (*E*) to (standard) enthalpies (*H*; T = 298.15 K) and free energies (*G*; T = 298.15 K, P = 1 atm).⁴ Absolute as well as relative singlet and triplet energies are shown in Table S-4. (b) We then executed single point CCSD(T)⁵/cc-pVTZ calculations on the MP2/cc-pVTZ optimized geometries and obtained a ‘best’ gas-phase S-T potential energy separation of $\Delta E = 2.7$ kcal/mol. Assuming transferability, we applied the thermal energy corrections from the MP2/cc-pVTZ calculations and obtained ‘best’ gas-phase enthalpy and Gibbs free energy values of $\Delta H = 3.2$ kcal/mol and $\Delta G = 3.4$ kcal/mol, respectively, for the S-T separation in Ad (Table S-4). (c) Finally, single point MP2/cc-pVTZ calculations made with three different continuous dielectric solvent models (IPCM,⁶ CPCM,⁷ and SMD⁸) using G09 default parameters for *n*-pentane as model alkane solvent predict differential stabilizations of ¹Ad (relative to ³Ad) of 0.76 kcal/mol (IPCM), 1.50 kcal/mol (CPCM) and 1.75 kcal/mol (SMD), respectively. (d) Assuming transferability and additivity, we combine the CCSD(T) gas phase result for $\Delta G(\text{S-T})$ with the range of differential solvent effects (0.8 to 1.8 kcal/mol) and finally arrive at a ‘best’ computed estimate for the ¹Ad - ³Ad free energy difference (kcal/mol) in alkane solution of $\Delta G(\text{S-T}) \sim 3.4 + (0.8 \text{ to } 1.8) \sim 4.2 \text{ to } 5.2 \sim 4 - 5$ kcal/mol, in favor of ¹Ad.

Table S-4. S-T Separation in Ad. Absolute energies in au; relative energies in kcal/mol.

Species/Calc	E	H	G	ΔE	ΔH	ΔG
$^1\text{Ad}/\text{MP2}$	-388.50523	-388.27837	-388.31757	0.00	0.00	0.00
$^3\text{Ad}/\text{MP2}$	-388.50220	-388.27465	-388.31354	1.90	2.33	2.53
$^1\text{Ad}/\text{CCSD(T)}$	-388.65927			0.00	0.00	0.00
$^3\text{Ad}/\text{CCSD(T)}$	-388.65490			2.74	3.17	3.37
$^1\text{Ad}/\text{MP2}/\text{IPCM}$	-388.50689			0.00		
$^3\text{Ad}/\text{MP2}/\text{IPCM}$	-388.50265			2.66		
$^1\text{Ad}/\text{MP2}/\text{CPCM}$	-388.508157			0.00		
$^3\text{Ad}/\text{MP2}/\text{CPCM}$	-388.502737			3.40		
$^1\text{Ad}/\text{MP2}/\text{SMD}$	-388.517283			0.00		
$^3\text{Ad}/\text{MP2}/\text{SMD}$	-388.517283			3.65		

Dimethyl Carbene (DMC): The adiabatic S-T separation in dimethyl carbene ($^1,^3\text{DMC}$) was estimated from a series of calculations analogous to those described above for adamantanylidene: (a) We first optimized the gas-phase geometries of ^1DMC (C_2 symmetry) and ^3DMC (C_{2v} symmetry) at the MP2 level with the cc-pVTZ basis set, performed normal mode analysis on the optimized geometries and applied standard thermodynamic corrections (based on harmonic oscillator/rigid rotor approximations and ideal gas behavior) to convert from electronic potential energies (E) to (standard) enthalpies (H ; $T = 298.15$ K) and free energies (G ; $T = 298.15$ K, $P = 1$ atm).⁶ The results are shown in Table S-5. (b) Geometries for ^1DMC and ^3DMC were re-optimized at the CCSD/cc-pVTZ level. (c) We then performed single point CCSD(T) calculations on the CCSD/cc-pVTZ optimized geometries with a variety of basis sets, which increased in size from cc-pVTZ (174 bsf) to cc-pV6Z (966 bsf). ΔE for the S-T separation as a function of basis set size is as follows (kcal/mol): (a) cc-pVTZ: 1.09; (b) aug-cc-pVQZ: 2.04; (c) cc-pV5Z: 2.11; (d) jun-cc-pV5Z: 2.16; (e) jul-cc-pV5Z: 2.18; (f) aug-cc-pV5Z:

2.19; and (g) cc-pV6Z: 2.22. Using CCSD(T)/cc-pV6Z//CCSD/cc-pVTZ energies (E and ΔE in Table S-5) and the thermal energy corrections from the MP2/cc-pVTZ calculations we arrive at ‘best’ gas-phase values for the S-T separation in DMC of $\Delta H = 3.1$ kcal/mol and $\Delta G = 1.7$ kcal/mol, respectively. (d) Single point MP2 calculations made with three different continuum dielectric solvent models (IPCM, CPCM, and SMD) using G09 default parameters for *n*-pentane as model alkane solvent predict a differential stabilization of ¹DMC (relative to ³DMC) of 1.41 kcal/mol (IPCM), 1.47 kcal/mol (CPCM) and 1.49 kcal/mol (SMD), respectively. (e) Assuming transferability and additivity, we combine the CCSD(T) gas phase result with the range of differential solvent effects and thus arrive at a ‘best’ computed estimate for the ¹DMC – ³DMC free energy difference in alkane solution of $\Delta G(\text{S-T}) \sim 2.2 + (1.4-1.5) \sim 3.6-3.7 \sim 3.5$ kcal/mol, in favor of ¹DMC.

Table S-5. S-T Separation in DMC. Absolute Energies in au; Relative Energies in kcal/mol.

Species/Calc	E	H	G	ΔE	ΔH	ΔG
¹ DMC/MP2	-117.50893	-117.42705	-117.456953	0.00	0.00	0.00
³ DMC/MP2	-117.51018	-117.42674	-117.458978	-0.79	0.20	-1.27
¹ DMC/CCSD(T)	-117.62058			0.00	0.00	0.00
³ DMC/CCSD(T)	-117.61703			2.22	3.11	1.74
¹ DMC/MP2/IPCM	-117.51122			0.00		
³ DMC/MP2/IPCM	-117.51055			0.42		
¹ DMC/MP2/CPCM	-117.51136			0.00		
³ DMC/MP2/CPCM	-117.51060			0.48		
¹ DMC/MP2/SMD	-117.51492			0.00		
³ DMC/MP2/SMD	-117.51380			0.70		

(b) Potential Energy Surfaces for DMC-Alkene Cycloaddition

We used the dispersion-corrected, long-range separated MN12-SX⁹ exchange-correlation functional and cc-pVTZ basis sets³ (MN12-SX/cc-pVTZ) in DFT calculations to locate stationary points on the DMC-alkene potential energy surfaces. Geometry optimizations were conducted with tight convergence criteria (opt=tight); geometry optimizations and normal mode calculations also employed enhanced integration grid sizes (integral(grid=ultrafine), a pruned (99,590) grid) to improve numerical stability. Normal mode analysis provided the (unscaled) vibrational frequencies used to determine vibrational zero-point energy (ZPE) corrections, and standard thermodynamic corrections (based on statistical mechanical expressions, harmonic oscillator/rigid rotor approximations and ideal gas behavior) were applied to convert from purely electronic energies (E) to (standard) enthalpies (H ; $T = 298.15$ K) and free energies (G ; $T = 298.15$ K, $P = 1$ atm).⁴

Generally speaking, the proper transition states (TS's) for DMC-alkene cycloaddition were difficult to locate. DMC is a highly reactive carbene (viz. the low value of the carbene stabilization energy, 28.7 kcal/mol (Table S-1)) and its reaction with an alkene to form a cyclopropane product is highly exothermic (> 75 kcal/mol, see Table S-11 below); hence, the TS for cycloaddition is 'early', showing almost imperceptible structural distortions in the carbene as well as alkene. Furthermore, the cycloaddition TS is energetically below the separated reactants on the potential energy surface, i.e. the activation energy is negative. DMC also shows considerable (rotational) flexibility in its orientation relative to the alkene and the TS for DMC-alkene cycloaddition is very 'loose'; many 'false' TS's were located during the course of our computational investigations (e.g. geometry searches converged on a TS for methyl group rotation; a TS for complex formation with the $-CN$ group in ACN; or just a TS for DMC rotation from one weakly bound complex orientation to another).

Ultimately, the majority of the transition states for DMC-alkene cycloaddition were located using the 'opt=calcall' option in Gaussian 09, a program option which invokes an analytic calculation of the Hessian at each optimization step. A launch of the standard intrinsic reaction coordinate (IRC) procedure was never successful. The single imaginary frequency required for a proper TS (first-order saddle point on the potential

energy surface) was always found to be very small in magnitude ($\sim 50i \text{ cm}^{-1}$); hence, the curvature of the PES was small and eigenvector-following could not be used to verify the nature of the reactant/product sides of a particular TS.¹⁰ Instead, the nature of the TS's for cycloaddition were validated by displacing ('manually' using GaussView) the TS structures by one vibrational rms displacement along the reaction coordinate (in both a 'forward' and a 'reverse' sense), followed by geometry optimization toward a minimum. This approach successfully located the anticipated shallow DMC:alkene complex on one side of the purported cycloaddition TS and the reaction product cyclopropane structure on the other.

Activation parameters computed at the MN12-SX/cc-pVTZ level (idealized gas phase) are shown in Table S-6.

Table S-6. Computed (MN12-SX/cc-pVTZ, Gas Phase) Activation Parameters for Additions of DMC to Alkenes^a

Alkene	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta H^\ddagger(\text{exp})$	$\Delta S^\ddagger$	$\Delta S^\ddagger(\text{exp})$	$\Delta G^\ddagger$	$\Delta G^\ddagger(\text{exp})^b$	ν_{imag}^c
$\text{CH}_2=\text{CHCN}$	-2.3	-1.6		-31.6		7.9	7.3	-26i
$\text{CH}_2=\text{CHCO}_2\text{Me}$	-3.0	-2.3	-4.1 $\pm$ 0.4	-34.1	-40.6 $\pm$ 1.5	7.9	8.0 $\pm$ 0.9	-23i
$\text{PhCH}=\text{CH}_2$	-3.3	-2.5		-33.5		7.5	9.4	-33i
$\text{CH}_2=\text{CHBu}$	-2.2	-1.4		-33.5		8.6	9.6	-28i
$\text{CH}_2=\text{CEt}_2$	-3.3	-2.5	-2.6 $\pm$ 0.3	-38.6	-42.1 $\pm$ 1.2	9.0	9.9 $\pm$ 0.7	-45i

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants. ^b $\Delta G^\ddagger(\text{exp})$ derived from the Eyring equation, $k_{\text{add}} = (RT/h)\exp(-\Delta G^\ddagger/RT)$, using k_{add} data from Table 2 in Text. ^cReaction coordinate frequency at the TS, in cm^{-1} .

We performed a series of single point CCSD(T)/cc-pVTZ calculations on the MN12-SX/cc-pVTZ optimized geometries to obtain a set of 'best' gas-phase activation

potential energies ($\Delta E^\ddagger$), Table S-7; relative to the MN12-SX/cc-pVTZ values, changes in $\Delta E^\ddagger$ are 0.2 kcal/mol or less. Application of the thermal energy corrections from the MN12-SX/cc-pVTZ calculations to the CCSD(T)/cc-pVTZ activation energies leads to ‘best’ gas-phase $\Delta H^\ddagger$ and $\Delta G^\ddagger$ values for the activation parameters for DMC addition to the five alkenes selected as shown in Table S-7.

Table S-7. Computed (CCSD(T)/cc-pVTZ//MN12-SX/cc-pVTZ, Gas Phase) Activation Parameters for Additions of DMC to Alkenes^a

Alkene	$\Delta E^\ddagger$ ^b	$\Delta E^\ddagger$ ^c	$\Delta H^\ddagger$ ^d	$\Delta G^\ddagger$ ^d	$\Delta G^\ddagger(\text{exp})$ ^e
CH ₂ =CHCN	-2.3	-2.3	-1.6	7.8	7.3
CH ₂ =CHCO ₂ Me	-3.0	-2.9	-2.2	8.0	8.0±0.9
PhCH=CH ₂	-3.3	-3.5	-2.7	7.3	9.4
CH ₂ =CHBu	-2.2	-2.2	-1.4	8.6	9.6
CH ₂ =CEt ₂	-3.3	-3.4	-2.6	8.9	9.9±0.7

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants. ^bMN12-SX/cc-pVTZ values. ^cCCSD(T)/cc-pVTZ//MN12-SX/cc-pVTZ values. ^dZPE and thermal corrections from the MN12-SX/cc-pVTZ calculations applied to the CCSD(T)/cc-pVTZ//MN12-SX/cc-pVTZ $\Delta E^\ddagger$ values.

^e $\Delta G^\ddagger(\text{exp})$ derived from the Eyring equation, $k_{\text{add}} = (RT/h)\exp(-\Delta G^\ddagger/RT)$, using k_{add} data from Table 2 in Text

Finally, general solvent effects were included through reoptimization of reactant and TS structures at the MN12-SX/cc-pVTZ level incorporating the continuum dielectric SMD³ model and default parameters for *n*-pentane provided in Gaussian 09. Computed activation parameters are in Table S-8. Comparison with data in Table S-6 shows that the solvent effects on the activation free energies for DMC-alkene cycloaddition from a short chain alkane (such as *n*-pentane) are very small (0.0-0.2 kcal/mol) when the alkene is

CH₂=CHCN, CH₂=CHBu, or CH₂=CHBu; larger values of approximately 0.9 kcal/mol and 1.7 kcal/mol are computed in the cases of CH₂=CHCO₂Me and PhCH=CH₂, respectively.

Table S-8. Computed (MN12-SX/cc-pVTZ and the SMD Continuum Dielectric Model, *n*-pentane Solvent) Activation Parameters for Additions of DMC to Alkenes^a

Alkene	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$	$\Delta G^\ddagger(\text{exp})^b$	ν_{imag}^c
CH ₂ =CHCN	-2.0	-2.1	-32.7	7.7	7.3	-29i
CH ₂ =CHCO ₂ Me	-1.7	-1.1	-33.1	8.8	8.0±0.9	-39i
PhCH=CH ₂	-1.8	-1.2	-34.1	9.2	9.4	-19i
CH ₂ =CHBu	-1.7	-1.0	-32.3	8.6	9.6	-26i
CH ₂ =CEt ₂	-1.4	-0.7	-31.9	8.8	9.9±0.7	-43i

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants. ^b $\Delta G^\ddagger(\text{exp})$ derived from the Eyring equation, $k_{\text{add}} = (RT/h)\exp(-\Delta G^\ddagger/RT)$, using k_{add} data from Table 2 in Text. ^cReaction coordinate frequency at the TS, in cm⁻¹.

DMC:Alkene Precursor Complexes.

Shallow CMe₂-alkene precursor complexes were located in the entrance channel with geometrical structures very similar to the neighboring TS's for cycloaddition. We tabulate here the energies of these complexes in the gas phase (Table S-9) and in simulated *n*-pentane (Table S-10). The free energies of these complexes are typically 1-2 kcal/mol less than the activation free energies tabulated above for the TS's (Table S-6 or S-8, respectively).

Table S-9. Computed (MN12-SX/cc-pVTZ, Idealized Gas Phase) Parameters for DMC-Alkene Precursor Complexes^a

Alkene	ΔE	ΔH	ΔS	ΔG
CH ₂ =CHCN	-2.4	-1.1	-23.2	5.9
CH ₂ =CHCO ₂ Me	-3.0	-1.7	-28.8	6.9
PhCH=CH ₂	-3.9	-2.5	-29.9	6.4
CH ₂ =CHBu	-2.5	-1.1	-25.7	6.6
CH ₂ =CEt ₂	-3.7	-2.3	-33.3	7.6

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants.

Table S-10. Computed (MN12-SX/cc-pVTZ and the SMD Continuum Dielectric Model, n-pentane Solvent) Parameters for DMC-Alkene Precursor Complexes^a

Alkene	ΔE	ΔH	ΔS	ΔG
CH ₂ =CHCN	-2.8	-1.6	-23.2	5.3
CH ₂ =CHCO ₂ Me	-2.7	-1.6	-28.0	6.8
PhCH=CH ₂	-2.4	-1.1	-31.1	8.0
CH ₂ =CHBu	-2.7	-1.6	-27.7	6.7
CH ₂ =CEt ₂	-2.4	-1.2	-30.0	7.7

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants.

Cycloaddition Reaction Energies

For completeness, we tabulate here the cycloaddition reaction energies for the reaction $^1\text{DMC} + \text{alkene} \rightarrow \text{cyclopropane}$ in the gas phase (Table S-11) and in simulated *n*-pentane (Table S-12); we also show analogous computed gas phase reaction energies for $^1\text{Ad} + \text{alkene} \rightarrow \text{cyclopropane}$ (Table S-13). The cycloaddition reactions of DMC and Ad are highly exothermic; for DMC, the computed exothermicities span the range from 75.6 kcal/mol ($\text{CH}_2=\text{CEt}_2$) to 83.7 kcal/mol ($\text{CH}_2=\text{CHCN}$). Inspection of Tables S-11 and S-13 shows that the exothermicity of a particular $^1\text{DMC} + \text{alkene} \rightarrow \text{cyclopropane}$ reaction is larger than the analogous $^1\text{Ad} + \text{alkene} \rightarrow \text{cyclopropane}$ reaction by approximately 5 kcal/mol, viz. 80.7 kcal/mol ($\text{CH}_2=\text{CEt}_2$) and 88.7 kcal/mol ($\text{CH}_2=\text{CHCN}$).

Table S-11. Computed (MN12-SX/cc-pVTZ, Idealized Gas Phase) Energy Parameters for Cycloaddition of ^1DMC to Alkenes^a

Alkene	ΔE	ΔH	ΔS	ΔG
$\text{CH}_2=\text{CHCN}$	-88.8	-83.7	-45.1	-70.2
$\text{CH}_2=\text{CHCO}_2\text{Me}$	-87.3	-82.2	-45.4	-68.6
$\text{PhCH}=\text{CH}_2$	-84.3	-79.4	-45.2	-65.9
$\text{CH}_2=\text{CHBu}$	-85.8	-80.7	-45.3	-67.2
$\text{CH}_2=\text{CEt}_2$	-80.6	-75.6	-48.1	-61.2

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants.

Table S-12. Computed (MN12-SX/cc-pVTZ and the SMD Continuum Dielectric Model, *n*-pentane Solvent) Energy Parameters for Cycloaddition of ^1DMC to Alkenes^a

Alkene	ΔE	ΔH	ΔS	ΔG
$\text{CH}_2=\text{CHCN}$	-87.1	-82.1	-45.2	-68.6

CH ₂ =CHCO ₂ Me	-87.1	-82.1	-46.2	-68.4
PhCH=CH ₂	-82.2	-77.2	-47.4	-62.8
CH ₂ =CHBu	-83.7	-78.7	-45.0	-65.3
CH ₂ =CEt ₂	-79.8	-75.0	-44.4	-61.7

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants.

Table S-13. Computed (MN12-SX/cc-pVTZ, Idealized Gas Phase) Energy Parameters for Cycloaddition of ¹Ad to Alkenes^a

Alkene	ΔE	ΔH	ΔS	ΔG
CH ₂ =CHCN	-92.6	-88.6	-48.2	-74.3
CH ₂ =CHCO ₂ Me	-91.0	-87.1	-48.0	-72.8
PhCH=CH ₂	-88.2	-84.4	-50.3	-69.4
CH ₂ =CHBu	-89.8	-86.0	-48.6	-71.5
CH ₂ =CEt ₂	-84.7	-80.7	-52.5	-65.1

^aEnergy values in kcal/mol, entropy values in e.u.; computed relative to the lowest energy conformers of the separated reactants.

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(d) MN12-SX/cc-pVTZ Optimized Geometries and Absolute Energies; Gas Phase

REACTANTS

Di-methyl-carbene

Charge = 0 Multiplicity = 1

C,0,-0.0000359585,-0.6706597323,-0.0002692894
C,0,1.2140756779,0.1559250057,0.030281936
H,0,2.0793453453,-0.3215601274,0.4958642327
H,0,1.4389985452,0.1633416349,-1.0549146959
H,0,1.1172576038,1.2119286272,0.3342643607
C,0,-1.2141820775,0.1558844631,-0.0305457937
H,0,-2.0794318277,-0.3214819971,-0.49628677
H,0,-1.4391052465,0.1629310272,1.0546532418
H,0,-1.11740806,1.2119930977,-0.3341772222

SCF Done: E(RMN12SX) = -117.723640972 A.U. after 1 cycles

Zero-point correction=	0.075415 (Hartree/Particle)
Thermal correction to Energy=	0.079926
Thermal correction to Enthalpy=	0.080871
Thermal correction to Gibbs Free Energy=	0.050773
Sum of electronic and zero-point Energies=	-117.648226
Sum of electronic and thermal Energies=	-117.643715
Sum of electronic and thermal Enthalpies=	-117.642770
Sum of electronic and thermal Free Energies=	-117.672868

CCSD/cc-pVTZ = -117.5507281

CCSD(T)/cc-pVTZ = -117.5717864

T1 Diagnostic = 0.01249234

Largest amplitude= 8.29D-02

Acrylonitrile

Charge = 0 Multiplicity = 1

C,0,0.3202586934,0.5135502858,0.0000062753
C,0,0.1874740427,1.8334582521,0.0000443388
H,0,-0.7954649283,2.2913539732,0.0000612725
H,0,1.0492949552,2.4926869836,0.0000596584
C,0,1.5883647865,-0.134450348,-0.000017361
N,0,2.601138113,-0.6782818199,-0.000037175
H,0,-0.5453304926,-0.1438506668,-0.000009009

SCF Done: E(RMN12SX) = -170.744870351 A.U. after 1 cycles

Zero-point correction=	0.050851 (Hartree/Particle)
Thermal correction to Energy=	0.054998
Thermal correction to Enthalpy=	0.055942
Thermal correction to Gibbs Free Energy=	0.024981
Sum of electronic and zero-point Energies=	-170.694019
Sum of electronic and thermal Energies=	-170.689873
Sum of electronic and thermal Enthalpies=	-170.688928
Sum of electronic and thermal Free Energies=	-170.719889

CCSD/cc-pVTZ = -170.4981996

CCSD(T)/cc-pVTZ = -170.5325688

T1 Diagnostic = 0.01339575

Largest amplitude= 1.02D-01

Methyl acrylate

Charge = 0 Multiplicity = 1

C,0,-0.8594654275,0.5773485217,0.5078994044
C,0,-0.4111366045,0.4961627977,1.7509833998
H,0,-0.2297457178,-0.464365585,2.222970988
H,0,-0.210726742,1.3871622795,2.3376039922
C,0,-1.1524810097,-0.5938769066,-0.3454001272
O,0,-1.5594601386,-0.511029062,-1.4735282533
O,0,-0.9194863474,-1.7596571852,0.2631322848
H,0,-1.0466614975,1.5286800442,0.0194737787
C,0,-1.1876911688,-2.9082023812,-0.5204675577
H,0,-0.9511223229,-3.7661670575,0.1082681804
H,0,-2.238745295,-2.9353029657,-0.8214267082
H,0,-0.5690793673,-2.9152523999,-1.4222964588

SCF Done: E(RMN12SX) = -306.326715416 A.U. after 1 cycles

Zero-point correction=	0.095803 (Hartree/Particle)
Thermal correction to Energy=	0.102335
Thermal correction to Enthalpy=	0.103279
Thermal correction to Gibbs Free Energy=	0.065540
Sum of electronic and zero-point Energies=	-306.230912
Sum of electronic and thermal Energies=	-306.224381
Sum of electronic and thermal Enthalpies=	-306.223437
Sum of electronic and thermal Free Energies=	-306.261175

CCSD/cc-pVTZ = -305.9327704
 CCSD(T)/cc-pVTZ = -305.9831602
 T1 Diagnostic = 0.01445614
 Largest amplitude= 9.86D-02

----- Styrene -----

Charge = 0 Multiplicity = 1
 C,0,0.1883052344,-1.9829663815,0.2070270962
 C,0,-1.041697856,-2.0772895462,0.6986182517
 H,0,-1.5711077875,-1.2297598829,1.1232112417
 H,0,-1.5737623084,-3.0219154755,0.6944965329
 H,0,0.6512992244,-2.8814241925,-0.2020146456
 C,0,1.0289092026,-0.7843457225,0.1430784956
 C,0,2.303975139,-0.8842840586,-0.413943411
 C,0,0.6141347732,0.463260492,0.6157009631
 C,0,3.1389999648,0.2173590112,-0.498818412
 H,0,2.6403957873,-1.8492035563,-0.7860105343
 C,0,1.4454655011,1.5635974737,0.5320570235
 H,0,-0.372769535,0.5741610911,1.0548834817
 C,0,2.7125085033,1.4471958216,-0.0255593693
 H,0,4.1273593573,0.1142763064,-0.936734152
 H,0,1.1042131483,2.5247862514,0.9052493674
 H,0,3.3626076514,2.3143403685,-0.0893659296

SCF Done: E(RMN12SX) = -309.480188966 A.U. after 1 cycles

Zero-point correction=	0.133479 (Hartree/Particle)
Thermal correction to Energy=	0.140240
Thermal correction to Enthalpy=	0.141184
Thermal correction to Gibbs Free Energy=	0.101965
Sum of electronic and zero-point Energies=	-309.346710
Sum of electronic and thermal Energies=	-309.339949
Sum of electronic and thermal Enthalpies=	-309.339005
Sum of electronic and thermal Free Energies=	-309.378224

CCSD/cc-pVTZ = -308.9900369
 CCSD(T)/cc-pVTZ = -309.059348
 T1 Diagnostic = 0.01046170
 Largest amplitude= 7.58D-02

1-hexene

Charge = 0 Multiplicity = 1

C,0,-0.6811065974,-0.1616736366,0.6937852946
C,0,0.0112675173,-0.5517359932,1.7519790275
H,0,0.3721276176,-1.5735575248,1.8465485147
H,0,0.2505592391,0.1268399828,2.5643146853
C,0,-1.0563410529,-1.0477384072,-0.4512526074
H,0,-0.6834495279,-0.6086503809,-1.3880703597
H,0,-0.5529336395,-2.0144663068,-0.3351159497
C,0,-2.5643974355,-1.2677612251,-0.5881294416
H,0,-2.9454879699,-1.7345585231,0.3303056322
H,0,-2.7435027639,-1.9898518567,-1.3959151076
H,0,-1.017589159,0.8744796628,0.6389078969
C,0,-3.3574084266,-0.0011017434,-0.876683542
H,0,-3.2439328008,0.7064917153,-0.0463948847
H,0,-2.9330296705,0.4967368404,-1.7594585072
C,0,-4.8327445617,-0.282625722,-1.102684235
H,0,-5.3964943619,0.6313530919,-1.3060135976
H,0,-4.9785636697,-0.9592783554,-1.9508249336
H,0,-5.2795179766,-0.7596098381,-0.2244694751

SCF Done: E(RMN12SX) = -235.686282099 A.U. after 1 cycles

Zero-point correction=	0.165466 (Hartree/Particle)
Thermal correction to Energy=	0.173284
Thermal correction to Enthalpy=	0.174228
Thermal correction to Gibbs Free Energy=	0.133275
Sum of electronic and zero-point Energies=	-235.520816
Sum of electronic and thermal Energies=	-235.512998
Sum of electronic and thermal Enthalpies=	-235.512054
Sum of electronic and thermal Free Energies=	-235.553007

CCSD/cc-pVTZ = -235.3547549

CCSD(T)/cc-pVTZ = -235.4001218

T1 Diagnostic = 0.00928076

Largest amplitude= 4.75D-02

2-ethyl-1-butene

Charge = 0 Multiplicity = 1

C,0,-0.8265628603,0.1296395764,0.3398240163

C,0,-0.0862197931,0.2272520575,1.4376377543
 H,0,0.0274548064,-0.6173454694,2.1110075661
 H,0,0.4351566691,1.1380309792,1.7120563131
 C,0,-1.5341351312,-1.1531537276,-0.0095691958
 H,0,-1.190080568,-1.4924028413,-0.9971932904
 H,0,-1.2397710276,-1.9287017281,0.7055752358
 C,0,-3.0547157541,-1.0306528641,-0.032359824
 H,0,-3.4298747886,-0.6619060397,0.9270065497
 H,0,-3.5213986795,-1.9998056355,-0.2262542082
 H,0,-3.3969068245,-0.3433909088,-0.8106059479
 C,0,-1.0151864586,1.2628978589,-0.631767393
 H,0,-2.0851065023,1.508217268,-0.6804043456
 H,0,-0.7713543779,0.8890836937,-1.6374866586
 C,0,-0.2237488973,2.5239470846,-0.3449056364
 H,0,-0.4053901643,3.2798621746,-1.112502986
 H,0,-0.5018551194,2.9584313462,0.6196045652
 H,0,0.851189471,2.3226531753,-0.3206085146

SCF Done: E(RMN12SX) = -235.691879761 A.U. after 1 cycles

Zero-point correction=	0.165370 (Hartree/Particle)
Thermal correction to Energy=	0.173130
Thermal correction to Enthalpy=	0.174074
Thermal correction to Gibbs Free Energy=	0.133364
Sum of electronic and zero-point Energies=	-235.526510
Sum of electronic and thermal Energies=	-235.518750
Sum of electronic and thermal Enthalpies=	-235.517806
Sum of electronic and thermal Free Energies=	-235.558515

CCSD/cc-pVTZ = -235.3589248
 CCSD(T)/cc-pVTZ = -235.4048086
 T1 Diagnostic = 0.00937162
 Largest amplitude= 2.67D-02

Transition States for DMC/Alkene Cycloaddition

DMC/Acrylonitrile TS

Charge = 0 Multiplicity = 1

C,0,2.0447044281,-1.1433202617,0.1970144214
C,0,1.750887593,-1.1754161119,-1.2483228077
H,0,0.8639022472,-1.760137641,-1.5086930198
C,0,-0.7537154713,0.0701852493,0.3773832749
C,0,-0.2349446602,0.5087523535,1.5185369005
H,0,-0.1141762571,-0.1631206213,2.3612822686
H,0,0.0910720213,1.5375198671,1.637320741
C,0,2.9178985845,-0.0063352174,0.5491101195
H,0,3.9179593132,-0.4602250249,0.419252167
H,0,2.8845876119,0.8864237026,-0.0963569161
H,0,2.8776396056,0.2686980837,1.6066515115
H,0,1.7738094846,-0.2246320422,-1.8048620153
H,0,2.5991006361,-1.7851822064,-1.6129072286
H,0,-1.0689053698,-0.9641331312,0.2638404731
C,0,-0.8932991695,0.8954725411,-0.7738517824
N,0,-0.9892878477,1.5365227806,-1.7238464176

SCF Done: E(RMN12SX) = -288.472139730 A.U. after 1 cycles

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (A⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	-25.5652	39.2287	60.1040
Red. masses --	3.1228	5.5846	2.4213
Frc consts --	0.0012	0.0051	0.0052
IR Inten --	6.5282	4.9293	2.1652

Zero-point correction= 0.127397 (Hartree/Particle)
Thermal correction to Energy= 0.137012
Thermal correction to Enthalpy= 0.137956
Thermal correction to Gibbs Free Energy= 0.091911
Sum of electronic and zero-point Energies= -288.344743
Sum of electronic and thermal Energies= -288.335128
Sum of electronic and thermal Enthalpies= -288.334184
Sum of electronic and thermal Free Energies= -288.380229

CCSD/cc-pVTZ=-288.0514088
 CCSD(T)/cc-pVTZ = -288.1080611
 T1 Diagnostic = 0.01307448
 Largest amplitude= 9.44D-02

DMC/Methyl acrylate TS

Charge = 0 Multiplicity = 1
 C,0,-2.2387469071,0.5540487111,0.1638737294
 C,0,-1.5911983633,1.825961989,0.532818428
 H,0,-1.3895827381,1.9156891744,1.604126399
 C,0,-0.0355618326,-1.771267889,0.5653892484
 C,0,-0.5989469673,-1.3408010161,1.6868158109
 H,0,-0.343311865,-0.3753297461,2.1125597875
 H,0,-1.3297837911,-1.9393719751,2.2199605742
 C,0,-1.9722470288,0.1848086894,-1.2380168912
 H,0,-2.8050586753,0.6994033312,-1.7526736382
 H,0,-1.0394493666,0.554021728,-1.6986103435
 H,0,-2.1177670455,-0.8774119804,-1.4519084888
 H,0,-0.7240975836,2.1586449446,-0.0612934107
 H,0,-2.4155999142,2.5409590419,0.3535720622
 H,0,-0.2797410232,-2.7343382844,0.127859547
 C,0,0.9158886624,-0.9803585101,-0.2359731634
 O,0,1.3661552446,-1.3395995327,-1.2918924836
 O,0,1.2115301266,0.2030770824,0.3149949431
 C,0,2.1007779383,1.0088540125,-0.4362892457
 H,0,2.2341409448,1.9273046304,0.1354792808
 H,0,3.0608093534,0.5034134333,-0.5743650957
 H,0,1.6825022115,1.2325031156,-1.4226573999

SCF Done: E(RMN12SX) = -424.055093284 A.U. after 1 cycles

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (A⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	-23.2996	27.9676	44.1232
Red. masses --	3.3762	3.1089	5.1639
Frc consts --	0.0011	0.0014	0.0059
IR Inten --	0.5428	1.8316	2.8275

Zero-point correction = 0.172344 (Hartree/Particle)
 Thermal correction to Energy= 0.184272
 Thermal correction to Enthalpy= 0.185216
 Thermal correction to Gibbs Free Energy= 0.133587
 Sum of electronic and zero-point Energies= -423.882749
 Sum of electronic and thermal Energies= -423.870821
 Sum of electronic and thermal Enthalpies= -423.869877
 Sum of electronic and thermal Free Energies= -423.921506

CCSD/cc-pVTZ = -423.4861349
 CCSD(T)/cc-pVTZ = -423.5594754
 T1 Diagnostic = 0.01416359
 Largest amplitude= 5.93D-02

----- DMC/Styrene-TS -----

Charge = 0 Multiplicity = 1
 C,0,-3.1485544886,-0.1158627544,-0.8531724476
 C,0,-2.2258167528,0.9594296685,-1.2634135599
 H,0,-1.4220918987,1.1459643909,-0.54575576
 C,0,-0.4520899079,-1.9303862,-1.0948332998
 C,0,-1.4915084636,-2.4999386144,-0.4891933507
 H,0,-1.7707960382,-2.2811835464,0.5359750056
 H,0,-2.1153710257,-3.2158403805,-1.0138309703
 C,0,-3.8578283077,-0.7016261735,-2.0093123921
 H,0,-4.739361027,-0.037590564,-2.0774585633
 H,0,-3.354690014,-0.6662632148,-2.9896738327
 H,0,-4.2707512335,-1.694946197,-1.8161493781
 H,0,-1.8363496542,0.9443278406,-2.2954167931
 H,0,-2.8859487,1.8422413951,-1.1737259316
 H,0,-0.2495559974,-2.190833218,-2.1343814825
 C,0,0.4669826724,-0.9470432313,-0.5210230558
 C,0,0.4162247452,-0.554807973,0.8198473796
 C,0,1.4199461888,-0.3500327003,-1.3468175308
 C,0,1.2838086213,0.4036764203,1.3074139744
 H,0,-0.3154167,-1.0018605204,1.4861269999
 C,0,2.289851084,0.6114953407,-0.8590717255
 H,0,1.4706576875,-0.6476844027,-2.3916344717
 C,0,2.2241626575,0.9930194262,0.4708640989
 H,0,1.2289627666,0.6965798852,2.3517704362
 H,0,3.0218747127,1.0643304785,-1.521109196
 H,0,2.9039293635,1.7454011048,0.8587990967

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (A⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	-33.4872	13.2124	44.0541
Red. masses --	3.1696	4.0945	3.3271
Frc consts --	0.0021	0.0004	0.0038
IR Inten --	1.4996	0.0363	0.5265

Zero-point correction= 0.210141 (Hartree/Particle)
 Thermal correction to Energy= 0.222350
 Thermal correction to Enthalpy= 0.223294
 Thermal correction to Gibbs Free Energy= 0.169911
 Sum of electronic and zero-point Energies= -426.998878
 Sum of electronic and thermal Energies= -426.986670
 Sum of electronic and thermal Enthalpies= -426.985725
 Sum of electronic and thermal Free Energies= -427.039108

CCSD/cc-pVTZ = -426.5444736
 CCSD(T)/cc-pVTZ = -426.6366331
 T1 Diagnostic = 0.01123205
 Largest amplitude= 6.55D-02

DMC/1-Hexene TS

Charge = 0 Multiplicity = 1
 C,0,-3.1945855249,-0.4460806358,0.4790764654
 C,0,-2.5051479046,-1.7470343994,0.3969359621
 H,0,-1.8508292967,-1.839264937,-0.4739987152
 C,0,0.0460510146,0.5496036352,0.92092092
 C,0,-0.9115713293,1.4629444287,0.8402494053
 H,0,-1.4064248885,1.6882119487,-0.1016229298
 H,0,-1.2452758283,2.0173665049,1.7123709363
 C,0,0.5729254146,-0.230089803,-0.2410767397
 H,0,0.5424828628,-1.304024208,-0.0027771204
 H,0,-0.0886446624,-0.0773826959,-1.1024249227
 C,0,2.0088114533,0.138129651,-0.6220601749
 H,0,2.0454958704,1.1999852138,-0.9003911586
 H,0,2.2900601438,-0.42514642,-1.5217550232
 C,0,-3.6343097077,-0.1403955239,1.8539355745
 H,0,-4.6437791148,-0.5924061567,1.8572392635

H,0,-3.0720765326,-0.5939585528,2.6864754732
 H,0,-3.8077856209,0.9241724052,2.0309240152
 H,0,-2.013372039,-2.1325429848,1.3056760316
 H,0,-3.3547483227,-2.4188730059,0.1732440351
 H,0,0.5055108236,0.3519107482,1.8905693285
 C,0,3.0332507421,-0.132985186,0.4703325032
 H,0,2.8035043178,0.4746652167,1.3541944613
 H,0,2.9491982208,-1.1802967585,0.7919880308
 C,0,4.4531501533,0.1543025684,0.0141423248
 H,0,5.1829996749,-0.0391597177,0.8043275394
 H,0,4.7226682342,-0.4656369441,-0.846930124
 H,0,4.5626497762,1.2001578686,-0.2899622216

SCF Done: E(RMN12SX) = -353.413350774 A.U. after 1 cycles

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering
 activities (A⁴/AMU), depolarization ratios for plane and unpolarized
 incident light, reduced masses (AMU), force constants (mDyne/A),
 and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	-27.7608	38.5797	47.7871
Red. masses --	3.0774	3.5586	2.3218
Frc consts --	0.0014	0.0031	0.0031
IR Inten --	1.4521	0.1431	0.2596

Zero-point correction= 0.242051 (Hartree/Particle)
 Thermal correction to Energy= 0.255368
 Thermal correction to Enthalpy= 0.256312
 Thermal correction to Gibbs Free Energy= 0.201194
 Sum of electronic and zero-point Energies= -353.171300
 Sum of electronic and thermal Energies= -353.157983
 Sum of electronic and thermal Enthalpies= -353.157039
 Sum of electronic and thermal Free Energies= -353.212157

CCSD/cc-pVTZ = -352.9077468
 CCSD(T)/cc-pVTZ = -352.9754161
 T1 Diagnostic = 0.01054894
 Largest amplitude= 6.71D-02

----- DMC/2-ethyl-1-butene-TS -----

Charge = 0 Multiplicity = 1

C,0,3.1144877283,-0.2685169813,0.4430397218
C,0,2.5630564386,-1.5031811848,-0.1509692408
H,0,1.7431966083,-1.9415215109,0.4234806334
C,0,0.1573114112,0.6765183654,-0.1847032417
C,0,0.9505163117,1.59848527,0.3552026648
H,0,1.1269109553,1.6285721815,1.4259498589
H,0,1.4481545142,2.3569996589,-0.2405834082
C,0,-0.564179903,-0.3261062758,0.6762549146
H,0,-0.5572526992,-1.3052288016,0.1774281955
H,0,-0.0237380375,-0.4470571541,1.6221840832
C,0,-2.0086779217,0.080450565,0.9559492998
H,0,-2.0436054256,1.027926007,1.5005097717
H,0,-2.5225863831,-0.6755724697,1.5554158115
C,0,3.8624594504,0.524387689,-0.555579591
H,0,4.8730811108,0.0847200107,-0.4688562869
H,0,3.5625340469,0.427844879,-1.6132831966
H,0,3.9875665623,1.57435394,-0.279593898
H,0,2.3316866843,-1.4977966763,-1.2308917923
H,0,3.4087561697,-2.2011519748,-0.0098751757
H,0,-2.5768494569,0.2093666144,0.0300008394
C,0,-0.0990906563,0.5612263437,-1.6599948155
H,0,-1.1852054946,0.5139449593,-1.8232780125
H,0,0.2681750342,-0.4269261405,-1.9817517636
C,0,0.5070154327,1.6435832817,-2.5312977496
H,0,0.2631849594,1.4800717805,-3.5835476619
H,0,0.1357780543,2.6335555028,-2.2504663905
H,0,1.5976396351,1.662910871,-2.4436083699

SCF Done: E(RMN12SX) = -353.420695748 A.U. after 1 cycles

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (A⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

	1	2	3
	A	A	A
Frequencies --	-44.7784	54.0641	71.2745
Red. masses --	2.6894	3.5924	2.9870
Frc consts --	0.0032	0.0062	0.0089
IR Inten --	1.0010	0.1977	0.4695

Zero-point correction= 0.242383 (Hartree/Particle)

Thermal correction to Energy=	0.255239
Thermal correction to Enthalpy=	0.256183
Thermal correction to Gibbs Free Energy=	0.203713
Sum of electronic and zero-point Energies=	-353.178313
Sum of electronic and thermal Energies=	-353.165457
Sum of electronic and thermal Enthalpies=	-353.164513
Sum of electronic and thermal Free Energies=	-353.216982

CCSD/cc-pVTZ = -352.9130154

CCSD(T)/cc-pVTZ = -352.9820007

T1 Diagnostic = 0.01078752

Largest amplitude= 6.29D-02

Precursor Complexes for DMC/Alkene Cycloaddition

----- DMC/Acrylonitrile -----

Charge = 0 Multiplicity = 1

C,0,-1.7469692012,-0.0340942498,-0.5500694656
C,0,-1.3120422886,-1.4181143846,-0.2921686929
H,0,-0.5663285813,-1.792106471,-0.9995881687
C,0,1.1978908885,0.6748358218,-0.6269758466
C,0,0.9385644855,1.7557436637,0.0997359474
H,0,0.3104301876,2.5445413533,-0.3006182627
H,0,1.3390023098,1.8830218856,1.100377775
C,0,-2.3461786259,0.5875540424,0.6454863022
H,0,-3.4143728622,0.3435928821,0.4957195471
H,0,-2.0579795537,0.1942807871,1.6336222587
H,0,-2.3165858077,1.6806000005,0.6309580863
H,0,-1.0461546351,-1.6923895935,0.741226419
H,0,-2.2357884415,-1.9719594973,-0.5467191549
H,0,0.7809243103,0.5562168938,-1.6244914803
C,0,1.9942548392,-0.4047330819,-0.149256722
N,0,2.6169929762,-1.2991570522,0.2176754581

SCF Done: E(RMN12SX) = -288.472256884 A.U. after 1 cycles

Zero-point correction=	0.127282 (Hartree/Particle)
Thermal correction to Energy=	0.137914
Thermal correction to Enthalpy=	0.138858
Thermal correction to Gibbs Free Energy=	0.088841
Sum of electronic and zero-point Energies=	-288.344975
Sum of electronic and thermal Energies=	-288.334343
Sum of electronic and thermal Enthalpies=	-288.333399
Sum of electronic and thermal Free Energies=	-288.383416

----- DMC/Methyl acrylate -----

Charge = 0 Multiplicity = 1

C,0,-2.2487246742,-0.0830843286,-0.1296757511
C,0,-2.1822297911,1.1437987297,0.6848043718
H,0,-2.1569436376,0.9447923878,1.7602834317
C,0,0.5949980445,-1.6905412549,0.1779790868
C,0,-0.2453382536,-1.8178594151,1.1964713709
H,0,-0.4463716719,-0.9906479608,1.8702503492
H,0,-0.757632594,-2.7531949094,1.395342531
C,0,-1.6686439763,0.1095673784,-1.4697211004

H,0,-2.5524286023,0.4702491697,-2.028892714
H,0,-0.886651788,0.8802086804,-1.5843262473
H,0,-1.3766270348,-0.819903982,-1.9658486639
H,0,-1.4406225261,1.9116215586,0.4086774134
H,0,-3.1888295618,1.5688884105,0.5165585751
H,0,0.8087132354,-2.5089268722,-0.5024595786
C,0,1.2736119986,-0.4308628102,-0.1771367227
O,0,1.9859896071,-0.2976050577,-1.1368771636
O,0,0.9944269844,0.5721321491,0.6647760349
C,0,1.6043244974,1.8093894243,0.3465747725
H,0,1.2778132974,2.5139090782,1.1117357175
H,0,2.6942506417,1.718484508,0.3527911046
H,0,1.2914828053,2.1528281163,-0.6445498178

SCF Done: E(RMN12SX) = -424.055102801 A.U. after 1 cycles

Zero-point correction=	0.172471 (Hartree/Particle)
Thermal correction to Energy=	0.185233
Thermal correction to Enthalpy=	0.186178
Thermal correction to Gibbs Free Energy=	0.132024
Sum of electronic and zero-point Energies=	-423.882632
Sum of electronic and thermal Energies=	-423.869869
Sum of electronic and thermal Enthalpies=	-423.868925
Sum of electronic and thermal Free Energies=	-423.923079

----- DMC/Styrene -----

Charge = 0 Multiplicity = 1

C,0,2.4198930466,-0.847756338,0.6827045782
C,0,1.8805775433,-1.7145864695,-0.3803738989
H,0,0.7878990535,-1.6871561735,-0.4388679225
C,0,0.3901713829,1.4093297914,-0.7981326368
C,0,1.3880886632,1.8367212802,-0.0281466789
H,0,1.3950625622,1.6983906941,1.0487556382
H,0,2.2369109141,2.3595473493,-0.4568478247
C,0,3.7967964118,-0.4044747907,0.3955341314
H,0,4.3814881314,-1.2283444675,0.8463626674
H,0,4.1012779347,-0.3383828742,-0.6618261366
H,0,4.098904451,0.488469752,0.9492411245
H,0,2.3336823024,-1.6484016954,-1.3830257863
H,0,2.1036002545,-2.7195015176,0.0224572079
H,0,0.4373319826,1.6106942237,-1.8691215935
C,0,-0.8104743464,0.6957732521,-0.3595398275
C,0,-0.9309296604,0.1411241922,0.9186264931

C,0,-1.874875483,0.5490524736,-1.2501162239
 C,0,-2.0883444529,-0.5178755109,1.289462575
 H,0,-0.0936246943,0.1942535578,1.6093265988
 C,0,-3.0351758877,-0.1073859075,-0.8757540719
 H,0,-1.7860985574,0.9667557366,-2.2504013675
 C,0,-3.1469150786,-0.6408019554,0.3982735039
 H,0,-2.1643737535,-0.9495394498,2.2832322965
 H,0,-3.854146756,-0.2049655901,-1.5821720114
 H,0,-4.0530679643,-1.1598275631,0.6957921653

SCF Done: E(RMN12SX) = -427.210010644 A.U. after 1 cycles

Zero-point correction=	0.210264 (Hartree/Particle)
Thermal correction to Energy=	0.223291
Thermal correction to Enthalpy=	0.224235
Thermal correction to Gibbs Free Energy=	0.169142
Sum of electronic and zero-point Energies=	-426.999747
Sum of electronic and thermal Energies=	-426.986720
Sum of electronic and thermal Enthalpies=	-426.985776
Sum of electronic and thermal Free Energies=	-427.040869

----- DMC/1-Hexene -----

Charge = 0 Multiplicity = 1

C	0	-2.93218	-0.42261	-0.57025
C	0	-2.76298	-1.44552	0.47805
H	0	-1.80268	-1.96582	0.42598
C	0	0.02399	0.61855	0.54799
C	0	-0.8019	1.58694	0.17605
H	0	-1.14295	1.66783	-0.85411
H	0	-1.16418	2.33382	0.8763
C	0	0.58133	-0.41473	-0.37988
H	0	0.5042	-1.40592	0.09027
H	0	-0.03329	-0.44616	-1.28694
C	0	2.04743	-0.16934	-0.74402
H	0	2.13103	0.79724	-1.25904
H	0	2.36432	-0.93196	-1.46791
C	0	-3.93096	0.59447	-0.1905
H	0	-4.85771	0.13739	-0.58465
H	0	-4.09294	0.77852	0.88411
H	0	-3.83061	1.53477	-0.73911
H	0	-3.00707	-1.16678	1.51593
H	0	-3.50352	-2.20153	0.15688
H	0	0.3462	0.57239	1.58958

C	0	2.99626	-0.18954	0.4456
H	0	2.7252	0.60857	1.14801
H	0	2.86707	-1.13285	0.99423
C	0	4.44837	-0.02868	0.03077
H	0	5.12319	-0.0424	0.89044
H	0	4.75531	-0.83252	-0.64606
H	0	4.6022	0.91813	-0.49673

SCF Done: E(RMN12SX) = -353.413881791 A.U. after 14 cycles

Zero-point correction=	0.242161 (Hartree/Particle)
Thermal correction to Energy=	0.256367
Thermal correction to Enthalpy=	0.257311
Thermal correction to Gibbs Free Energy=	0.198479
Sum of electronic and zero-point Energies=	-353.171721
Sum of electronic and thermal Energies=	-353.157515
Sum of electronic and thermal Enthalpies=	-353.156570
Sum of electronic and thermal Free Energies=	-353.215402

DMC/2-ethyl-1-butene

Charge = 0 Multiplicity = 1

C,0,1.9627040932,-1.1735639163,0.1658643688
 C,0,1.8022650298,-0.8497002512,-1.2670360772
 H,0,0.8983161908,-1.2703492736,-1.7165492279
 C,0,-0.8203732184,0.1512496942,0.2625183347
 C,0,-0.1173835423,0.3848114444,1.3680977147
 H,0,-0.0098132151,-0.3817981863,2.1301270248
 H,0,0.3713926087,1.334965487,1.5597708971
 C,0,-1.5128092661,-1.168399382,0.0516741882
 H,0,-1.3467668739,-1.5022116219,-0.9821122951
 H,0,-1.0524156408,-1.9215228088,0.6995780326
 C,0,-3.0142419375,-1.0945261536,0.3156465493
 H,0,-3.210503124,-0.7973238507,1.3496700803
 H,0,-3.4904228464,-2.0636791266,0.1458943368
 C,0,2.9138392804,-0.2519455697,0.8243715234
 H,0,3.8746905154,-0.7701661412,0.6507353575
 H,0,3.0149904561,0.7638838666,0.4058743294
 H,0,2.8059425429,-0.2141212827,1.9112412911
 H,0,1.941521576,0.2015629548,-1.5749588668
 H,0,2.6337878479,-1.4259798947,-1.7125550321
 H,0,-3.506280782,-0.3680106021,-0.3375766675
 C,0,-0.9850367218,1.1596424044,-0.8388971283
 H,0,-2.0586784432,1.3322780208,-0.9992812462

H,0,-0.640063803,0.6894896047,-1.7730072313
 C,0,-0.2731283682,2.4831722132,-0.6408334683
 H,0,-0.4316456161,3.1441504309,-1.4960125303
 H,0,-0.6319677564,3.0016234732,0.2530231136
 H,0,0.8066040139,2.3380724673,-0.5276703712

SCF Done: E(RMN12SX) = -353.421443098 A.U. after 1 cycles

Zero-point correction=	0.242652 (Hartree/Particle)
Thermal correction to Energy=	0.256292
Thermal correction to Enthalpy=	0.257236
Thermal correction to Gibbs Free Energy=	0.202228
Sum of electronic and zero-point Energies=	-353.178791
Sum of electronic and thermal Energies=	-353.165151
Sum of electronic and thermal Enthalpies=	-353.164207
Sum of electronic and thermal Free Energies=	-353.219215