Electronic Supplementary Material (ESI) for Chemical Science.

Inhibition of Hydrocarbon Autoxidation by Nitroxide-Catalyzed Cross-Dismutation of Hydroperoxyl and Alkylperoxyl Radicals

Kareem A. Harrison, Evan A. Haidasz, Markus Griesser and Derek A. Pratt*

Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, CANADA K1N 6N5

*dpratt@uottawa.ca

Supplementary Information

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I. General

Reagents were purchased from commercial suppliers and used without further purification unless otherwise indicated. TEMPOH,[1] Ar_2NH,[2] Ar_2NO,[3] Ar_2NOH,[4] Ar_2NOR,[5] TEMPOR,[5] 1-bromocyclooctene,[6] cyclooctyne,[7] STY-BODIPY[8] and PBD-BODIPY[8] were synthesized using literature procedures. Column chromatography was carried out using flash silica gel (40−63 μm, 230−400 mesh). UV−vis spectra and kinetics were measured on a Cary 100 UV−vis spectrophotometer equipped with a temperature controller unit and a thermostated 6 × 6 multicell holder. ^1H and ^{13}C NMR spectra were recorded on Bruker AVANCE spectrometers at 400 and 75 MHz, respectively. ^1H and ^{13}C (with ^1H decoupling) NMR resonances are referenced to $CHCl_3/CDCl_3$ (7.26 and 77 ppm, respectively). High resolution mass spectra were obtained on a Kratos Concept Tandem mass spectrometer. All synthesized compounds were > 95% pure as determined by ^1H NMR.

Cumene and styrene were each extracted three times with NaOH (1M), washed with brine, dried with $MgSO_4$, filtered, distilled under reduced pressure and percolated through a silica column. The purified material could be kept at -20 °C under nitrogen for up to 5 days. Immediately before use, the distilled material was percolated again through a column with silica/basic alumina (1:2). Ethylbenzene and 1-hexadecene were percolated through a column with silica/basic alumina (1:2) immediately before use. Cyclooctene was distilled under reduced pressure (50 mbar/80 °C) and the purified material could be kept at -20 °C under nitrogen for up to 5 days. Norbornene was distilled at atmospheric pressure (120 °C) through a short distillation path and the purified material could be kept at -20 °C under nitrogen for up to 5 days. Dioxane was used directly without prior purification.

II. Co-autoxidations of Cumene and Styrene under Thomas' Conditions

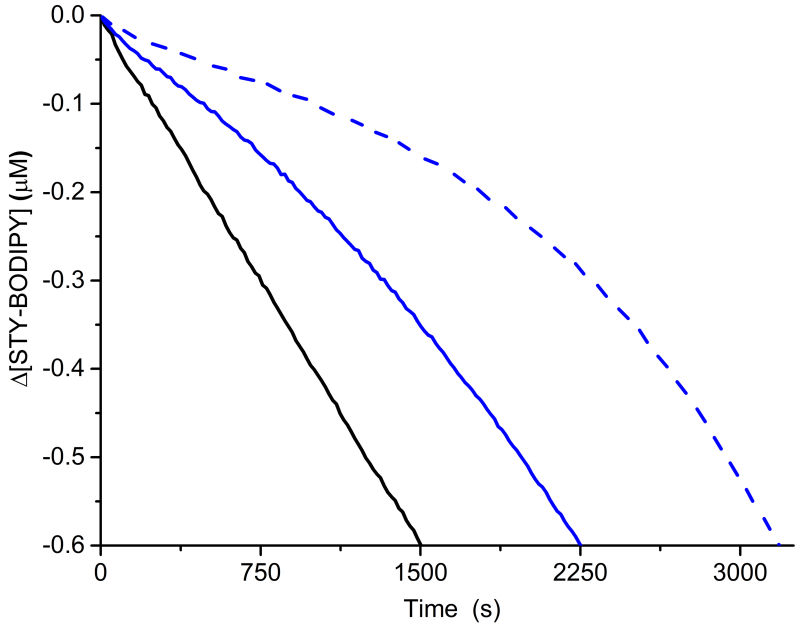


Figure S1. Representative co-autoxidations of cumene (0.29 M) and STY-BODIPY (10 μM) in PhCl initiated with AIBN (1 mM) at 70 °C (black) inhibited by 50 μM of Ar_2NO (blue) and Ar_2NH (blue dash). Reaction progress was monitored at 570 nm (ε = 122 213 M^{-1} cm^{-1}).

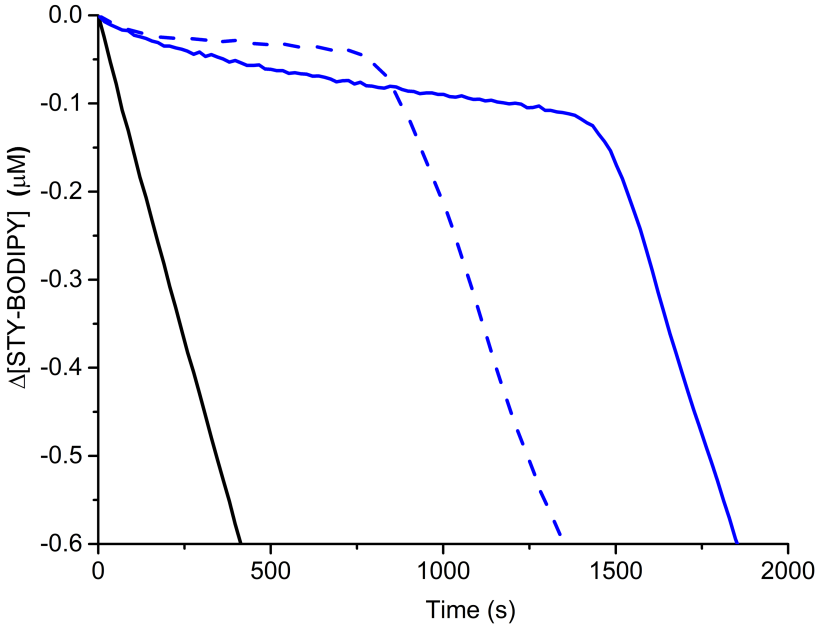


Figure S2. Representative co-autoxidations of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl initiated with AIBN (1 mM) at 70 °C (black) inhibited by 50 μM of Ar_2NO (blue) and Ar_2NH (blue dash). Reaction progress was monitored at 571 nm (ε = 97 235 M^{-1} cm^{-1}).

III. Co-autoxidations of Styrene at 37 °C

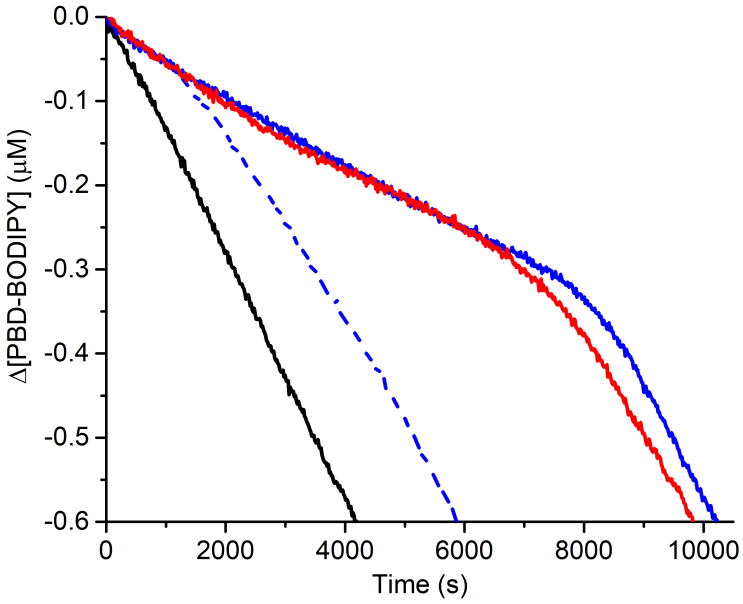


Figure S3. Representative co-autoxidations of styrene (4.3 M) and PBD-BODIPY (10 μM) in PhCl initiated with AIBN (6 mM) at 37 °C (black) inhibited by 2 μM of Ar_2NH (blue dashed line), Ar_2NO (blue line), and TEMPO (red line). Reaction progress was monitored at 591 nm (ε = 139 000 M^{-1} cm^{-1}).

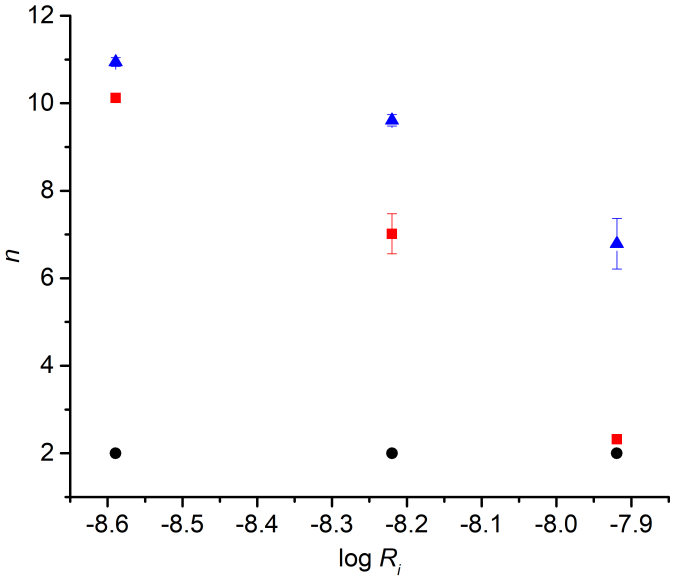


Figure S4. Stoichiometry of peroxyl radical-trapping by Ar_2NO (blue), TEMPO (red) and PMC (black) as a function of rate of initiation of styrene (4.3 M) and PBD-BODIPY (10 μM) co-autoxidations initiated by AIBN (6, 15, and 30 mM) at 37 °C. Reaction progress was monitored at 591 nm (ε = 139 000 M^{-1} cm^{-1}).

IV. UV-vis Spectra and Extinction Coefficients for STY-BODIPY and PBD-BODIPY

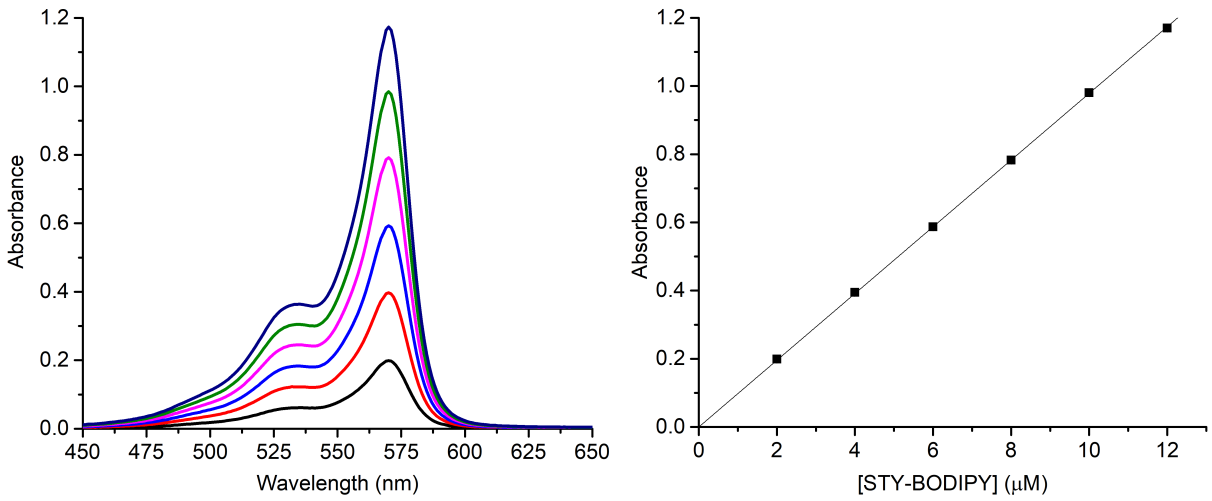


Figure S5. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v styrene/PhCl (left). Extinction coefficient determined for λ_{max} = 571 nm of ε = 97 235 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

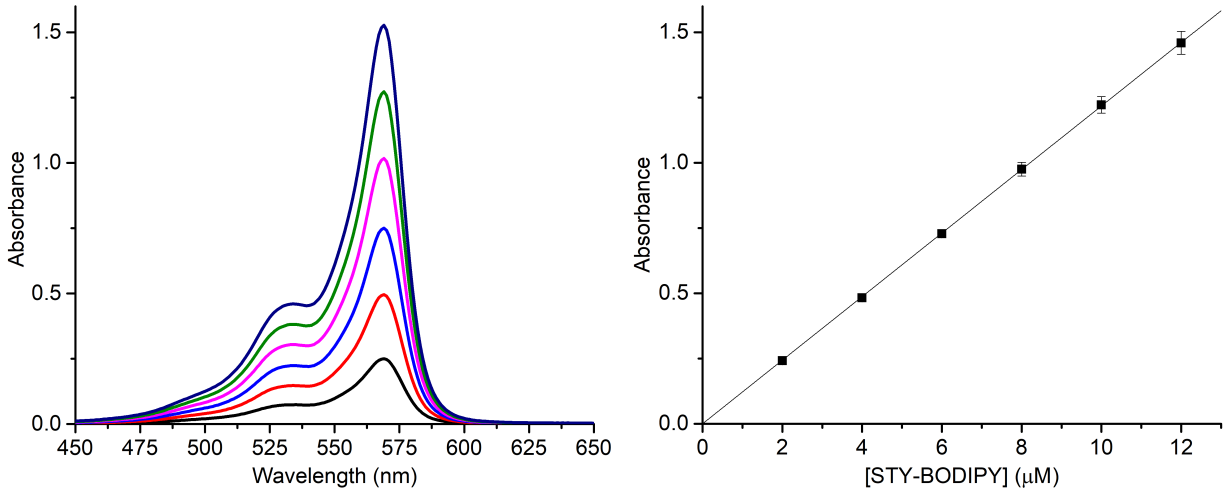


Figure S6. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v cumene/PhCl (left). Extinction coefficient determined for λ_{max} = 570 nm of ε = 112 213 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

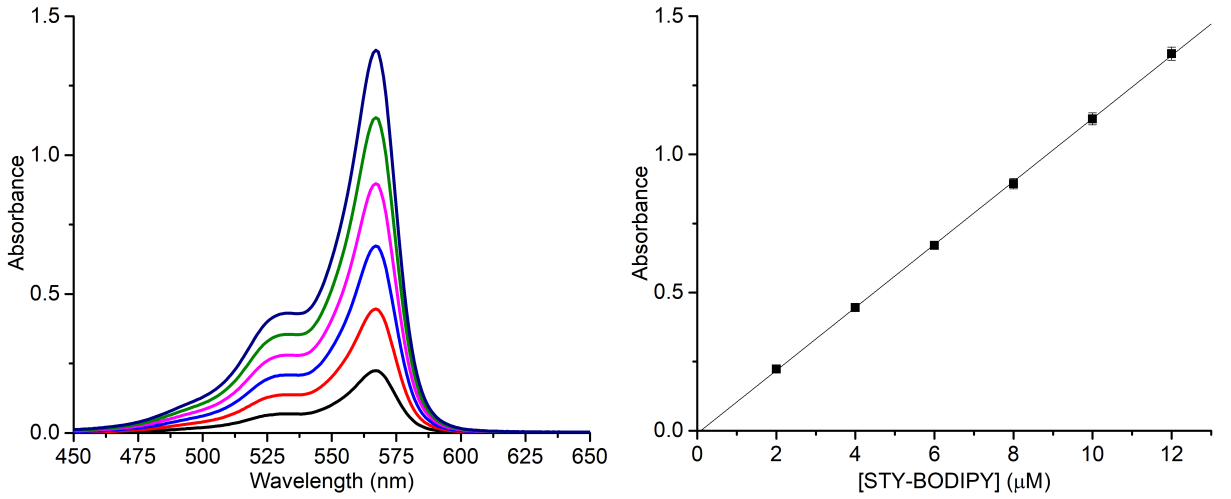


Figure S7. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v dioxane/PhCl (left). Extinction coefficient determined for λ_{max} = 568 nm of ε = 113 982 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

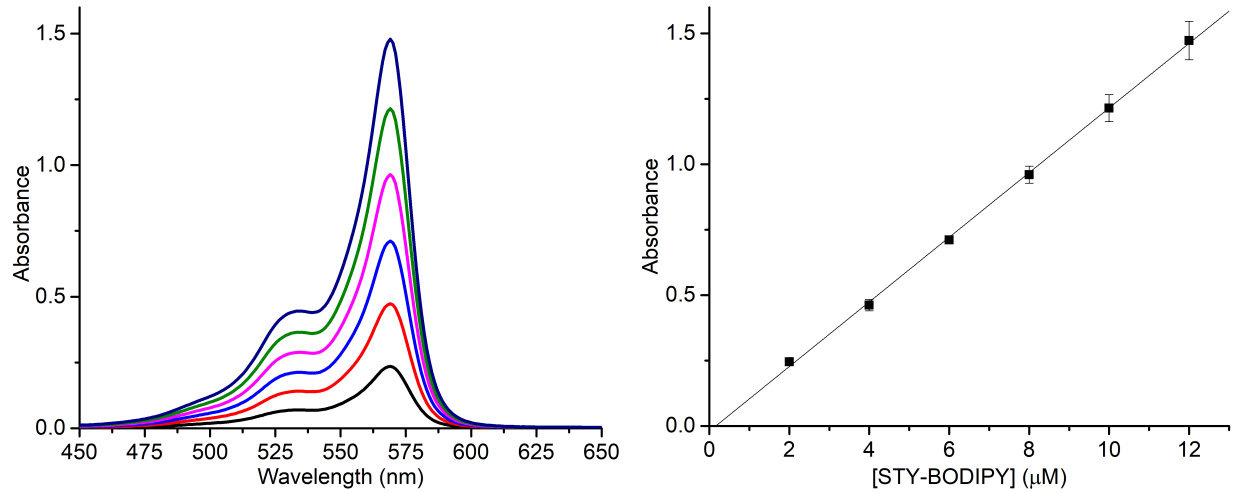


Figure S8. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v ethylbenzene/PhCl (left). Extinction coefficient determined for λ_{max} = 569 nm of ε = 123 481 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

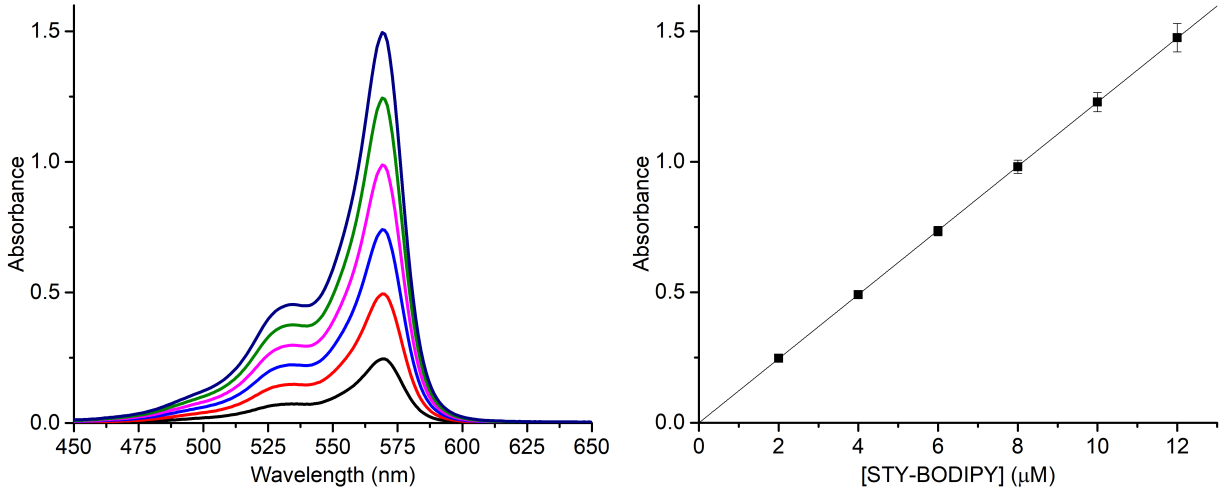


Figure S9. UV-vis spectra for STY-BODIPY (2-12 μM) in 1 M norbornene in PhCl (left). Extinction coefficient determined for λ_{max} = 569 nm of ε = 122 873 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

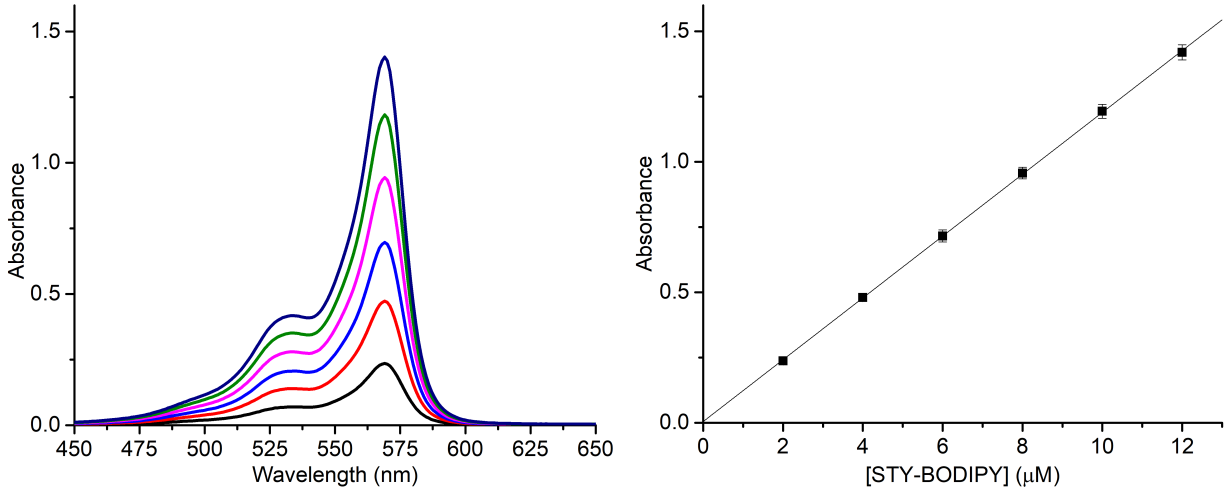


Figure S10. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v cyclooctene/PhCl (left). Extinction coefficient determined for λ_{max} = 568 nm of ε = 118 405 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

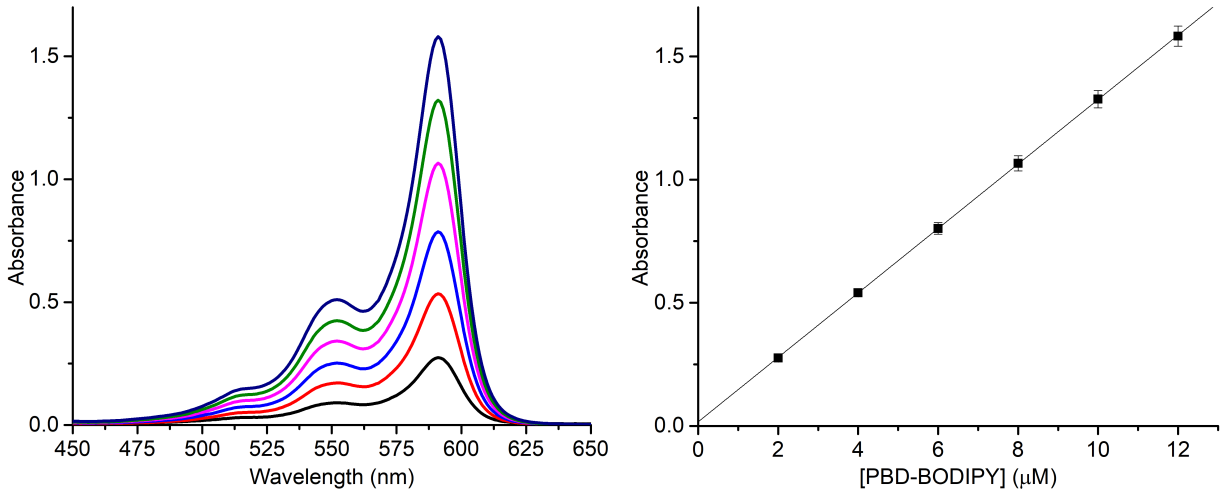


Figure S11. UV-vis spectra for PBD-BODIPY (2-12 μM) in 2.5% v/v 1,4-cyclohexadiene/PhCl (left). Extinction coefficient determined for λ_{max} = 591 nm of ε = 130 797 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

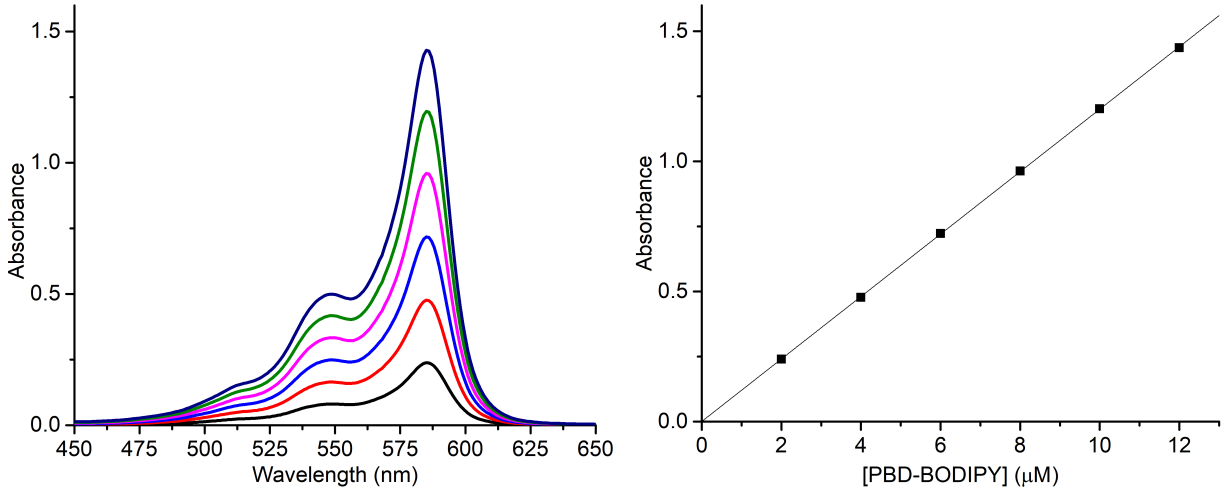


Figure S12. UV-vis spectra for STY-BODIPY (2-12 μM) in 80% v/v 1-hexadecene/PhCl (left). Extinction coefficient determined for λ_{max} = 591 nm of ε = 119 166 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

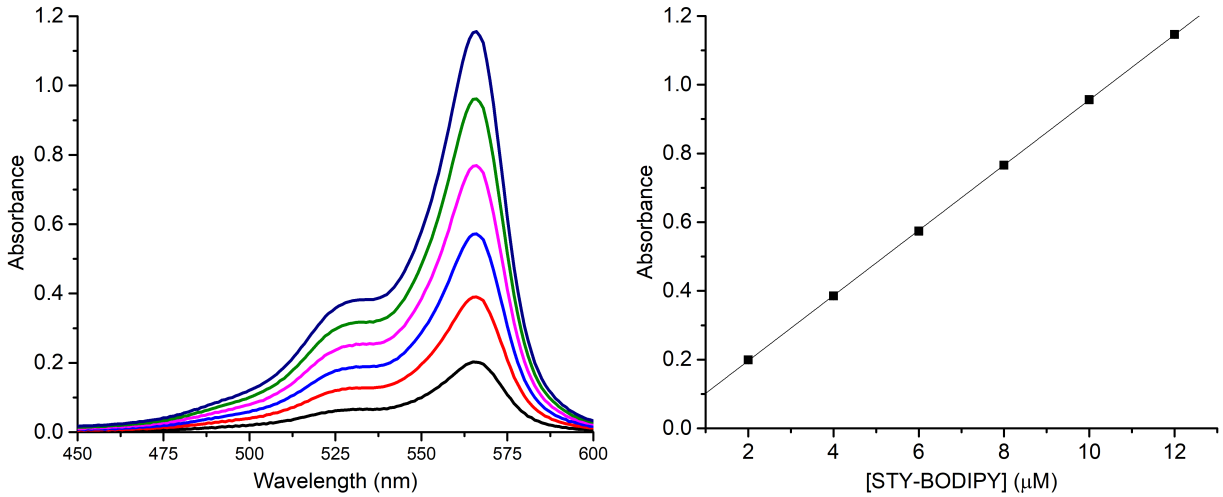


Figure S13. UV-vis spectra for STY-BODIPY (2-12 μM) in 40% v/v styrene/2-octanone (left). Extinction coefficient determined for λ_{max} = 566 nm of ε = 94 876 M^{-1} cm^{-1} (right). Average of three measurements (error bars are too small to be resolved from the data points).

V. Determination of the Rate of Initiation by the Inhibitor Method

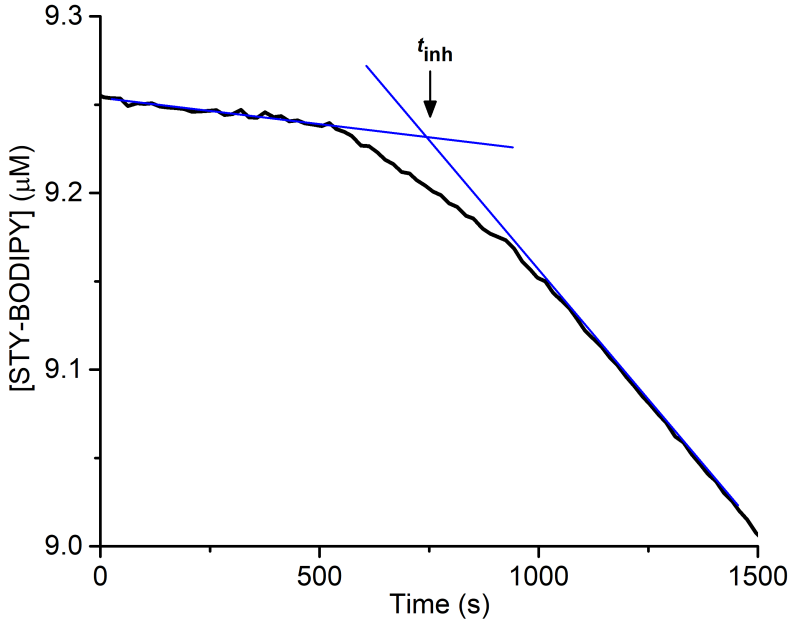


Figure S14. Identification of the inhibited period from a representative co-autoxidation of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C inhibited by PMC (4.0 μM). Reaction progress was monitored by absorbance at 571 nm (ε = 97 235 M^{-1} cm^{-1}). From the average of three measurements t_{inh} = 884 s and R_i = 4.5 ± 0.3 × 10^{-9} M s^{-1} was calculated from 2[PMC]/t_{inh}.

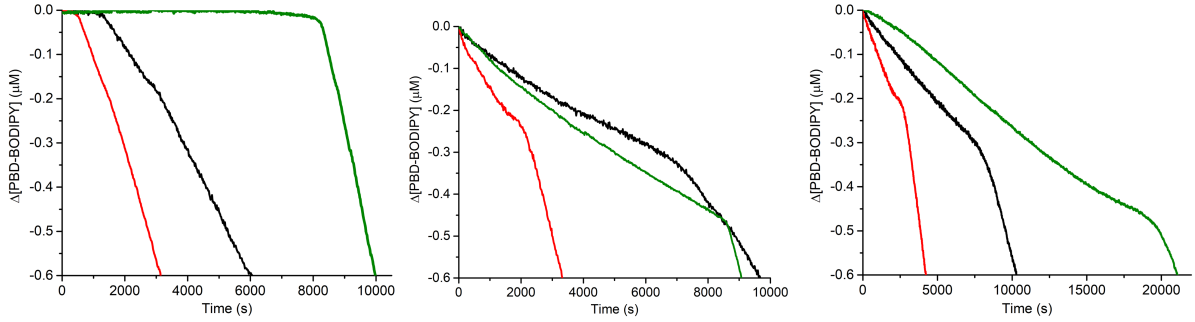


Figure S15. Representative co-autoxidations of styrene (4.3 M) and PBD-BODIPY (10 μM) in PhCl at 37 °C, initiated with AIBN (6 (black), 15 (red) mM) inhibited by 2.0 μM of PMC (left) or 2.0 μM TEMPO (middle) and 2.0 μM of Ar_2NO (right) or initiated with 30 mM AIBN (green) inhibited by 50 μM PMC (left), TEMPO (middle) or Ar_2NO (right). Reaction progress was monitored at 591 nm (ε = 139 000 M^{-1} cm^{-1}).

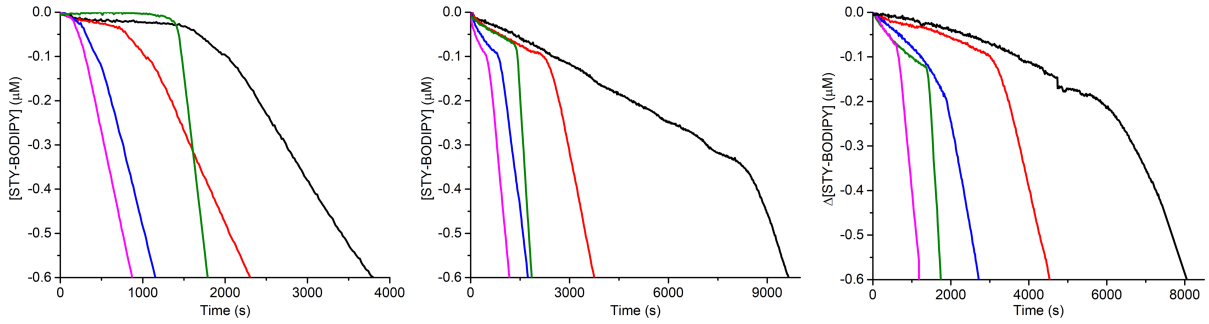


Figure S16. Representative co-autoxidations of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl at 70 °C, initiated with AIBN (62.5 (black), 125 (red), 250 (blue), 375 (magenta) μM) inhibited by 4.0 μM of PMC (left) or 2.0 μM TEMPO (middle) and 2.0 μM of Ar_2NO (right) or initiated with 1 mM AIBN (green) inhibited by 50 μM PMC (left), TEMPO (middle) or Ar_2NO (right). Reaction progress was monitored at 571 nm (ε = 97 235 M^{-1} cm^{-1}).

Table 1. Rates of Initiation Obtained from PMC-Inhibited Autoxidations Under Various Conditions.

substrate	T (°C)	solvent	initiator	[initiator] (mM)	R_i (M s^{-1})
styrene	37	PhCl	AIBN	6	$2.6 \pm 0.2 \times 10^{-9}$
styrene	37	PhCl	AIBN	15	$6.0 \pm 0.2 \times 10^{-9}$
styrene	37	PhCl	AIBN	30	$1.2 \pm 0.4 \times 10^{-8}$
styrene	70	PhCl	^{t}BuOO^{t}Bu	218	$4.5 \pm 0.3 \times 10^{-9}$
styrene	70	2-octanone	^{t}BuOO^{t}Bu	218	$4.2 \pm 0.2 \times 10^{-9}$
styrene	70	PhCl	AIBN	6.25×10^{-3}	$3.7 \pm 0.3 \times 10^{-9}$
styrene	70	PhCl	AIBN	1.25×10^{-2}	$7.2 \pm 0.2 \times 10^{-9}$
styrene	70	PhCl	AIBN	2.50×10^{-2}	$1.4 \pm 0.1 \times 10^{-8}$
styrene	70	PhCl	AIBN	3.75×10^{-2}	$1.9 \pm 0.2 \times 10^{-8}$
styrene	70	PhCl	AIBN	1	$6.1 \pm 0.1 \times 10^{-8}$
cumene	70	PhCl	AIBN	1	$6.1 \pm 0.3 \times 10^{-8}$
1,4-dioxane	70	PhCl	^{t}BuOO^{t}Bu	218	$5.6 \pm 0.1 \times 10^{-9}$
ethylbenzene	70	PhCl	^{t}BuOO^{t}Bu	87	$3.0 \pm 0.1 \times 10^{-9}$
norbornene	70	PhCl	^{t}BuOO^{t}Bu	218	$7.5 \pm 0.4 \times 10^{-9}$
cyclooctene	70	PhCl	^{t}BuOO^{t}Bu	218	$4.5 \pm 0.2 \times 10^{-9}$
1-hexadecene	70	PhCl	^{t}BuOO^{t}Bu	87	$1.1 \pm 0.1 \times 10^{-9}$
1-hexadecene	100	PhCl	dicumyl peroxide	1	$4.6 \pm 0.4 \times 10^{-9}$
1,4-cyclohexadiene	30	PhCl	^{t}BuOO^{t}Bu	218	N/A

VI. Determination of Propagation Rate Constants for STY-BODIPY/PBD-BODIPY

The propagation rate constants for dye autoxidation, i.e. $k_{\mathrm{STY-BODIPY}}$ (or $k_{\mathrm{PBD-BODIPY}}$), are necessary to derive the inhibition rate constants (k_{inh}) of the RTAs in the various co-autoxidation systems reported in the manuscript (as in Figure 2B). These values were derived from the expression which describes the kinetics of an uninhibited autoxidation, e.g. for STY-BODIPY:

$$\frac{-\partial[\mathrm{STY-BODIPY}]}{\partial t} = \frac{k_{\mathrm{STY-BODIPY}}}{\sqrt{2k_t}}\sqrt{Ri}\ [\mathrm{STY\text{-}BODIPY}]$$

Thus, a series of uninhibited co-autoxidations were carried out at different dye concentrations for each dye/substrate combination reported in the manuscript, and the rate of dye consumption plotted as a function of dye concentration (see Figures S17-S23). The $k_{\mathrm{STY-BODIPY}}$ (or $k_{\mathrm{PBD-BODIPY}}$) was derived from the slope of the line of best fit using the rate of initiation, R_i, which was independently determined for each of the various co-autoxidation systems (given in Table 1) and the termination rate constant. Since the dye is present at a very small concentration relative to the substrate, it is assumed that termination occurs via the reaction of two substrate-derived peroxyl radicals (see ref. 8 for further discussion of this assumption). Termination rate constants measured by Howard and Ingold at 30 °C are available for styrene (2.1×10^7 M^{-1} s^{-1}),[9] dioxane (2.5×10^7 M^{-1} s^{-1}),[10] ethylbenzene (1.6×10^7 M^{-1} s^{-1})[11] and 1-octene (1.3×10^8 M^{-1} s^{-1}).[12] Corresponding values at 70°C were estimated by extrapolation based upon the known activation energy for termination of two secondary (butyl)peroxyl radicals (2.7 kcal mol^{-1}).[13] Termination rate constants have not been previously determined for norbornene and cyclooctene, and as such, were assumed to be the same as styrene.

Table S2. Termination rate constants (k_t) used in this work.

substrate	k_t (in M^{-1} s^{-1}) at given T	k_t (in M^{-1} s^{-1}) at 30 °C
styrene	3.4×10^7 (70 °C)	2.1×10^7 M^{-1} s^{-1}
1,4-dioxane	3.9×10^7 (70 °C)	2.5×10^7 M^{-1} s^{-1}
ethylbenzene	2.5×10^7 (70 °C)	1.6×10^7 M^{-1} s^{-1}
norbornene[a]	3.4×10^7 (70 °C)	2.1×10^7 M^{-1} s^{-1}
cyclooctene[a]	3.4×10^7 (70 °C)	2.1×10^7 M^{-1} s^{-1}
1-hexadecene[b]	2.0×10^8 (70 °C)	1.3×10^8 M^{-1} s^{-1}
1-hexadecene[b]	2.7×10^8 (100 °C)	1.3×10^8 M^{-1} s^{-1}

[a] k_t from styrene autoxidation at 30 °C.

[b] k_t from 1-octene autoxidation at 30 °C.

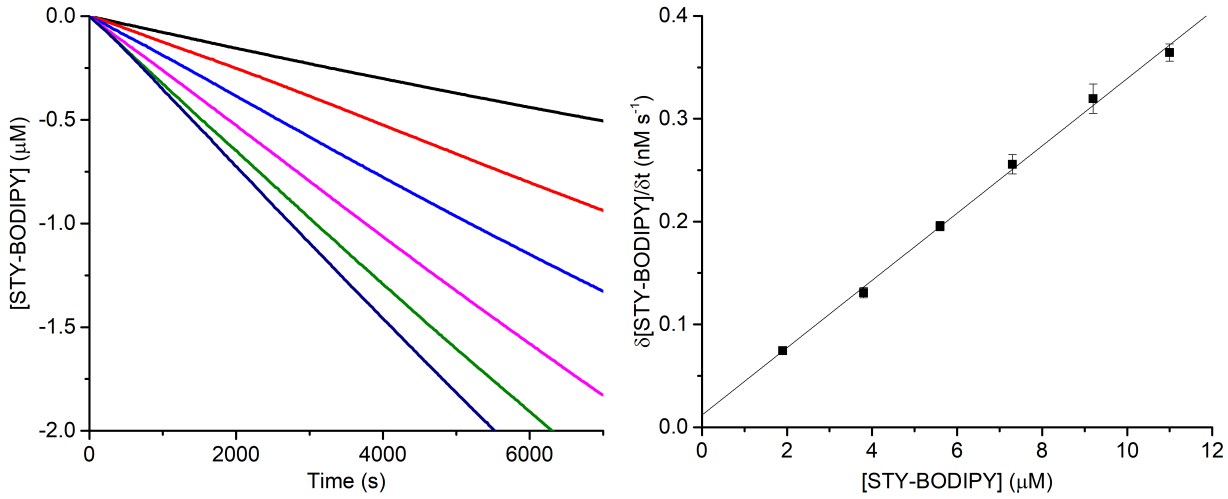


Figure S17. Co-autoxidation of STY-BODIPY and styrene (3.5 M) in PhCl at 70 °C initiated by di-*tert*-butylperoxide (218 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 571 nm (ε = 97 235 M^{-1} cm^{-1}), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 4012 ± 96 M^{-1} s^{-1}.

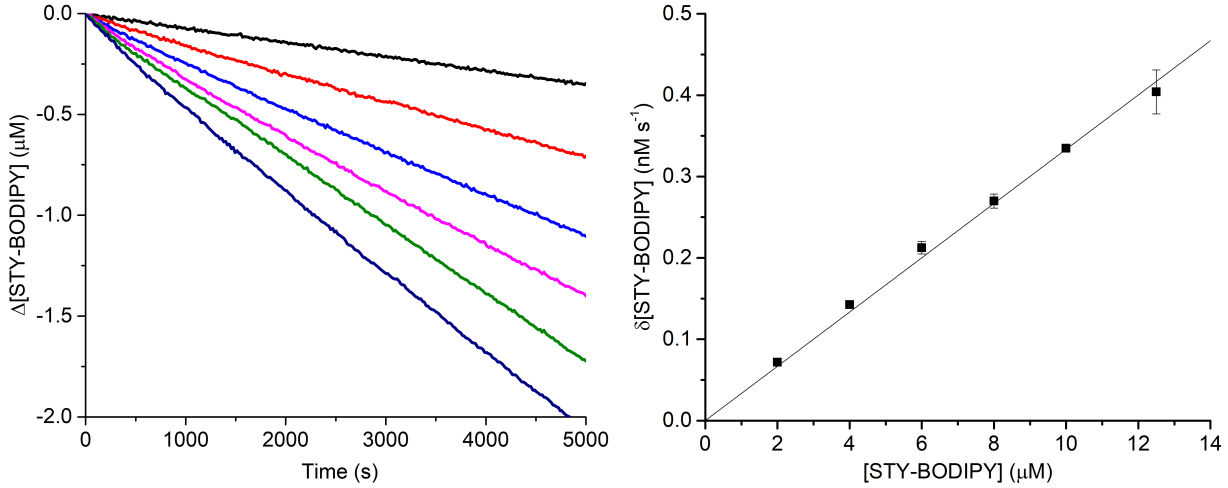


Figure S18. Co-autoxidation of STY-BODIPY and styrene (3.5 M) in 2-octanone at 70 °C initiated by di-*tert*-butylperoxide (218 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 566 nm (ε = 94 876 M^{-1} cm^{-1}), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 4004 ± 264 M^{-1} s^{-1}.

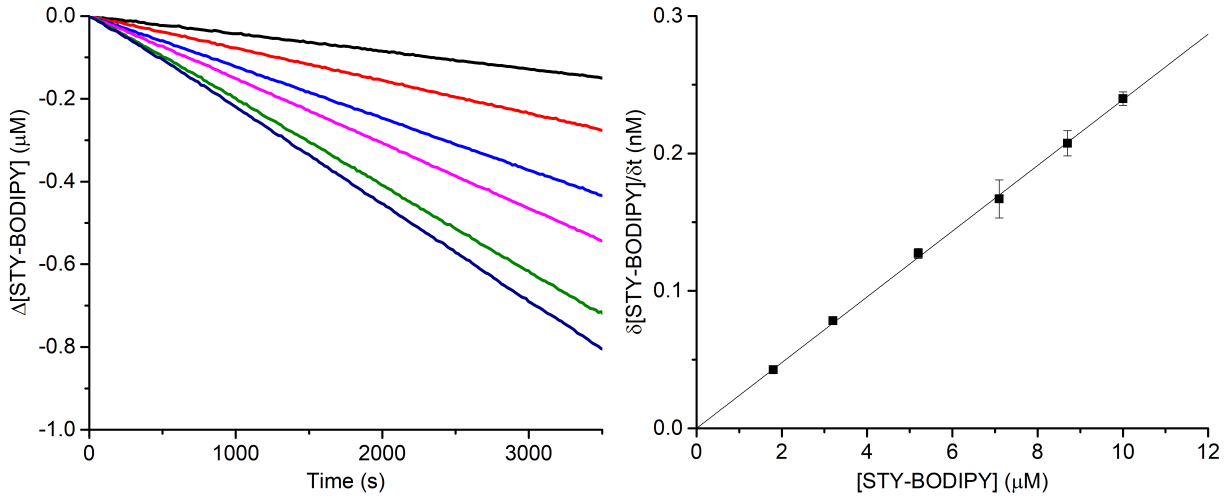


Figure S19. Co-autoxidation of STY-BODIPY and cyclooctene (3.1 M) in PhCl at 70 °C initiated by di-*tert*-butylperoxide (218 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 568 nm (ε = 118 405 $M^{-1}cm^{-1}$), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 2689 ± 134 M^{-1} s^{-1}.

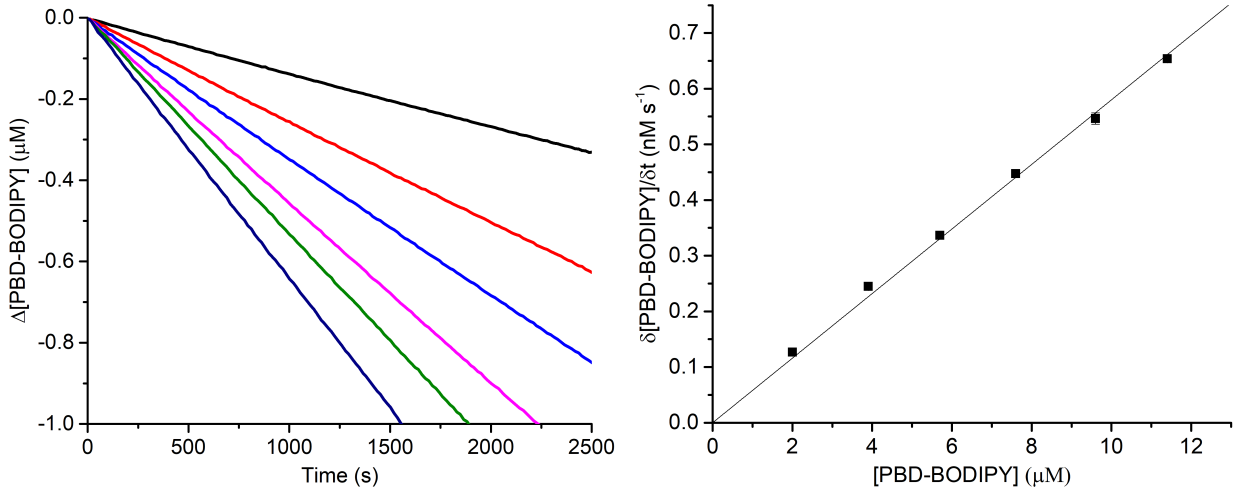


Figure S20. Co-autoxidation of PBD-BODIPY and 1-hexadecene (2.8 M) in PhCl at 100 °C initiated by dicumylperoxide (1 mM) as a function of PBD-BODIPY concentration (left). Reaction progress was monitored by absorbance at 586 nm (ε = 119 166 $M^{-1}cm^{-1}$), and the observed rates were plotted as a function of PBD-BODIPY concentration (right) to yield k_p = 17 802 ± 414 M^{-1} s^{-1}.

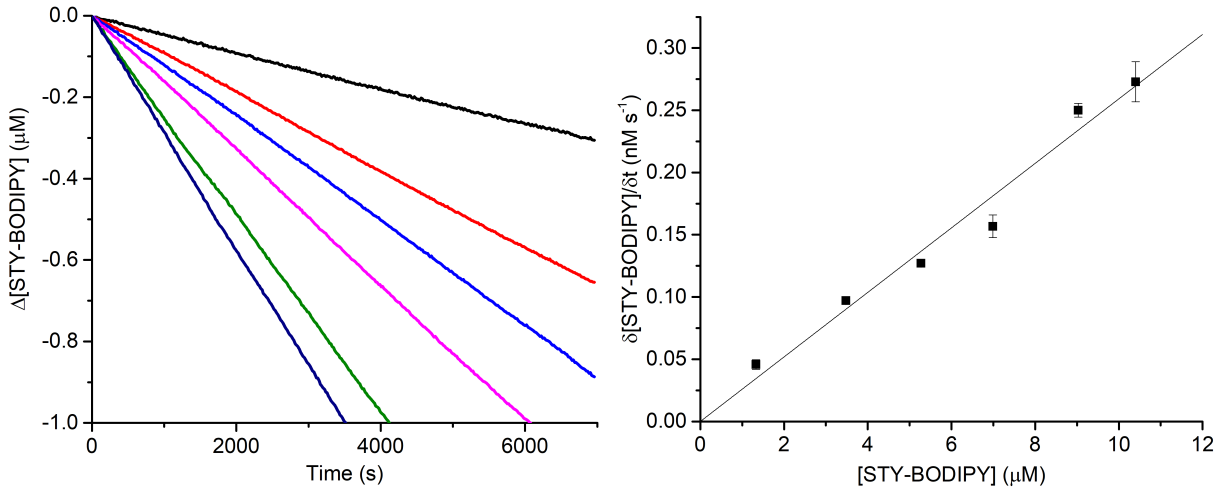


Figure S21. Co-autoxidation of STY-BODIPY and ethylbenzene (3.3 M) in PhCl at 70 °C initiated by di-*tert*-butylperoxide (87 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 569 nm (ε = 123 481 $M^{-1}cm^{-1}$), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 3402 ± 195 M^{-1} s^{-1}.

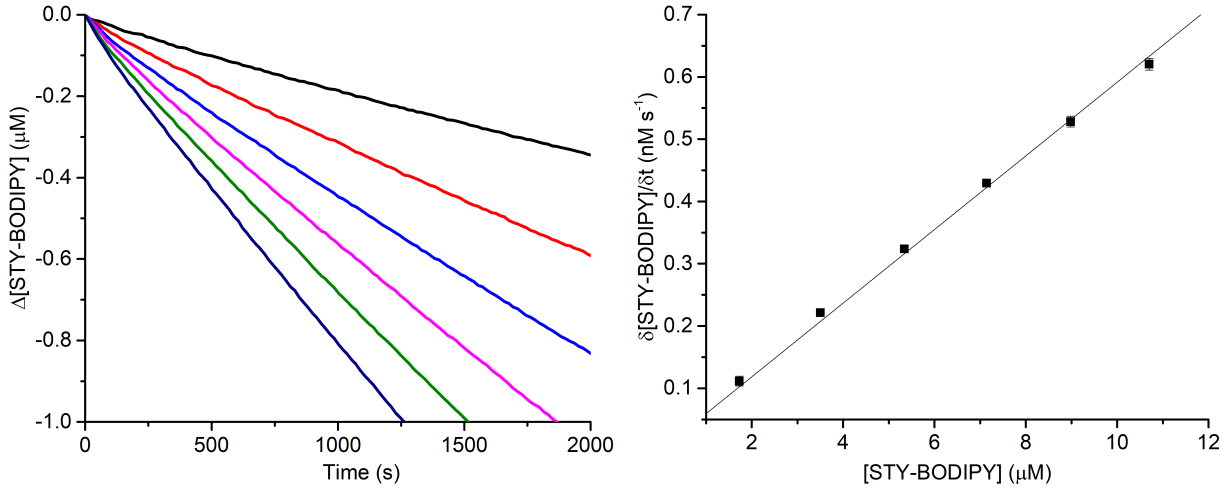


Figure S22. Co-autoxidation of STY-BODIPY and 1,4 dioxane (2.9 M) in PhCl at 70 °C initiated by di-*tert*-butylperoxide (218 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 568 nm (ε = 113 982 $M^{-1}cm^{-1}$), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 6707 ± 44 M^{-1} s^{-1}.

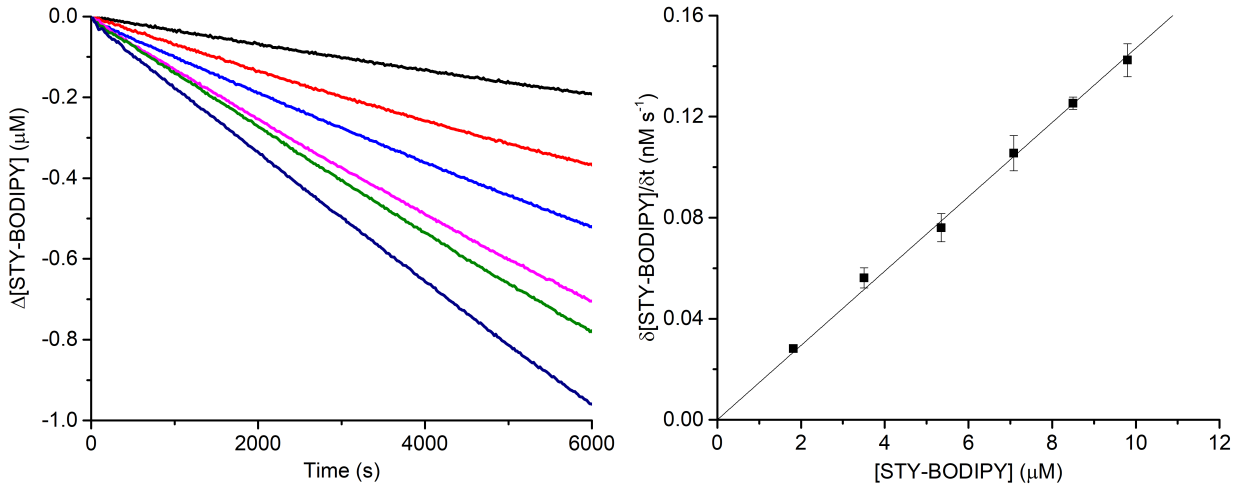


Figure S23. Co-autoxidation of STY-BODIPY and norbornene (1.0 M) in PhCl at 70 °C initiated by di-*tert*-butylperoxide (218 mM) as a function of STY-BODIPY concentration (left). Reaction progress was monitored by absorbance at 569 nm (ε = 122 873 $M^{-1}cm^{-1}$), and the observed rates were plotted as a function of STY-BODIPY concentration (right) to yield k_p = 1358 ± 47 M^{-1} s^{-1}.

VII. Supplemental Data for KIE and KSE Determinations

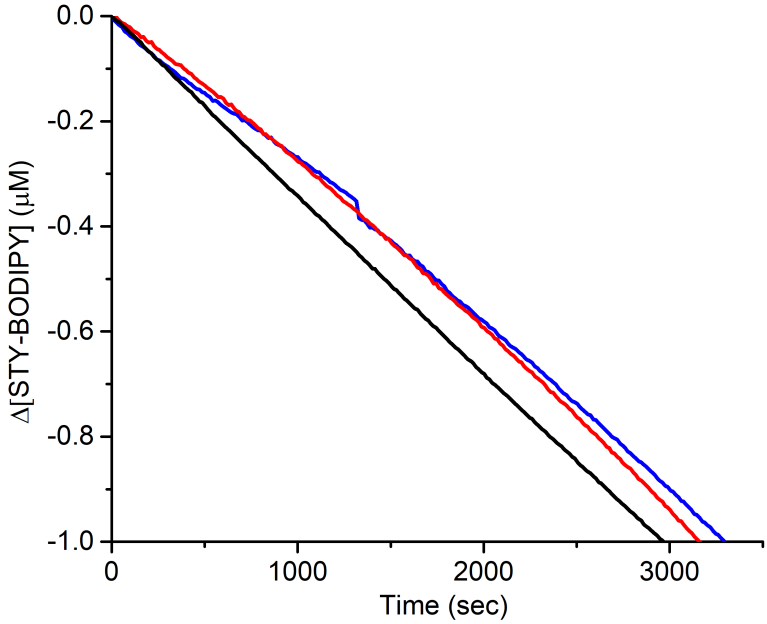


Figure S24. Representative co-autoxidations of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl (black) with 1% MeOH (blue) or 1% MeOD (red) initiated with di-*tert*-butylperoxide (218 mM) at 70 °C. Reaction progress was monitored at 571 nm (ε = 97 235 M^{-1} cm^{-1}).

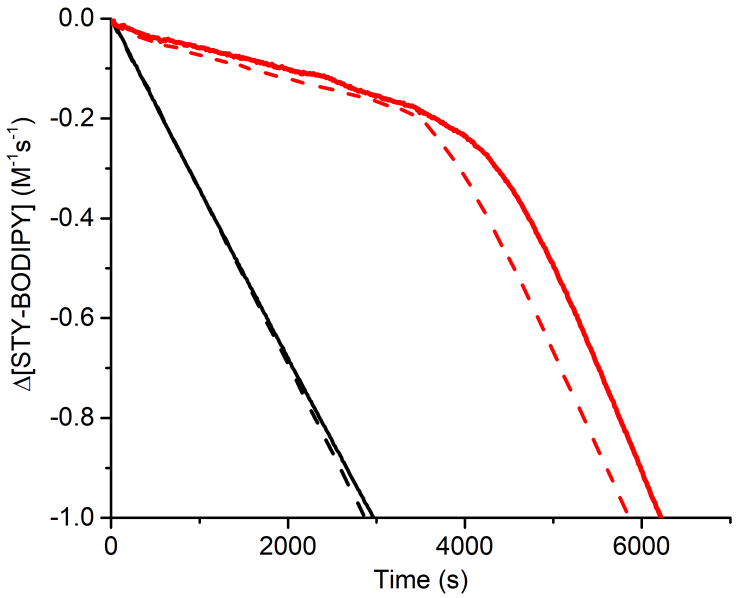


Figure S25. Representative co-autoxidations of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl (solid) or 2-octanone (dashed) initiated with di-*tert*-butylperoxide (218 mM) at 70 °C (black) inhibited by TEMPO (red). Reaction progress was monitored at 571 nm (ε = 97 235 M^{-1} cm^{-1}) for PhCl or 566 nm (ε = 94 876 M^{-1} cm^{-1}) for 2-octanone.

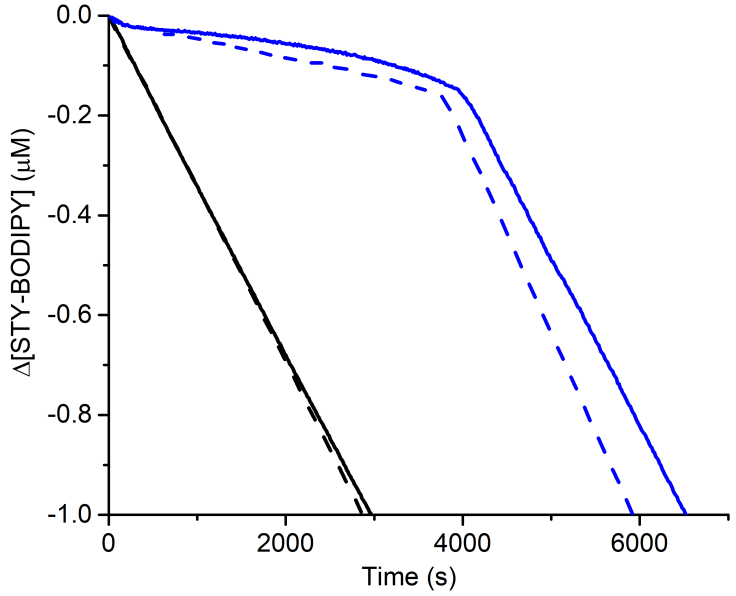


Figure S26. Representative reaction progress curves for the co-autoxidation of styrene (3.5 M) and STY-BODIPY (10 μM) in PhCl (solid) or 2-octanone (dashed) initiated with di-*tert*-butylperoxide (218 mM) at 70 °C (black) inhibited by Ar_2NO (blue). Reaction progress was monitored at 571 nm (ε = 97 235 M^{-1} cm^{-1}) for PhCl or 566 nm (ε = 94 876 M^{-1} cm^{-1}) for 2-octanone.

VIII. Monitoring of Nitroxide Formation from Diarylamine during Autoxidations

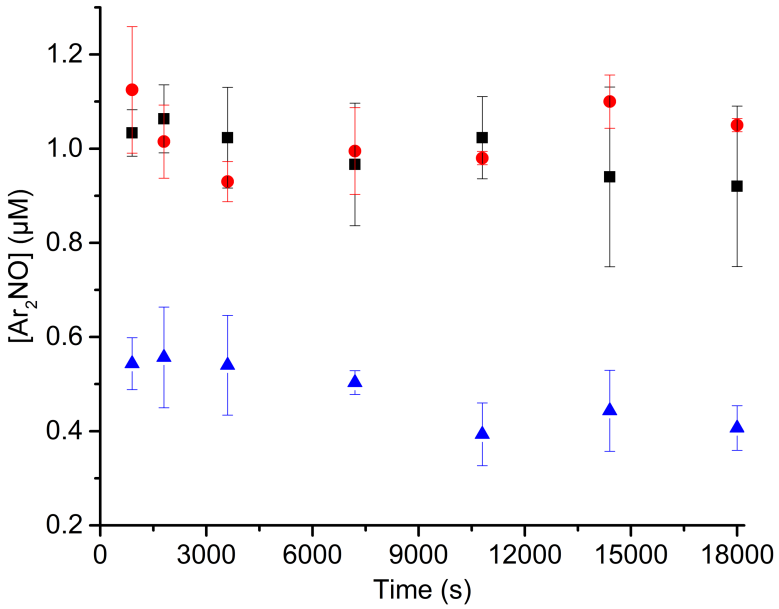


Figure S27. Concentration of Ar_2NO determined by EPR during Ar_2NH-inhibited autoxidations. Cyclooctene (3.1 M, black), norbornene (1.0 M, blue) and 1-hexadecene (2.7 M, red) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C inhibited by 2.0 μM of Ar_2NH.

IX. Autoxidations of Deuterated Cyclooctene

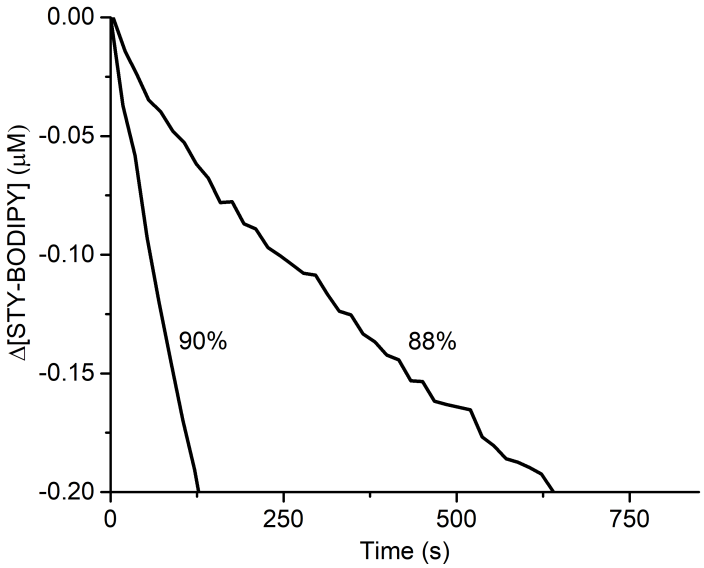


Figure S28 Co-autoxidation of 1,2-d_2-cyclooctene (88 and 90% deuterium incorporation) (3.1 M) and STY-BODIPY (10 μM) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C. Reaction progress was monitored at 568 nm (ε =118 405 M^{-1} cm^{-1}).

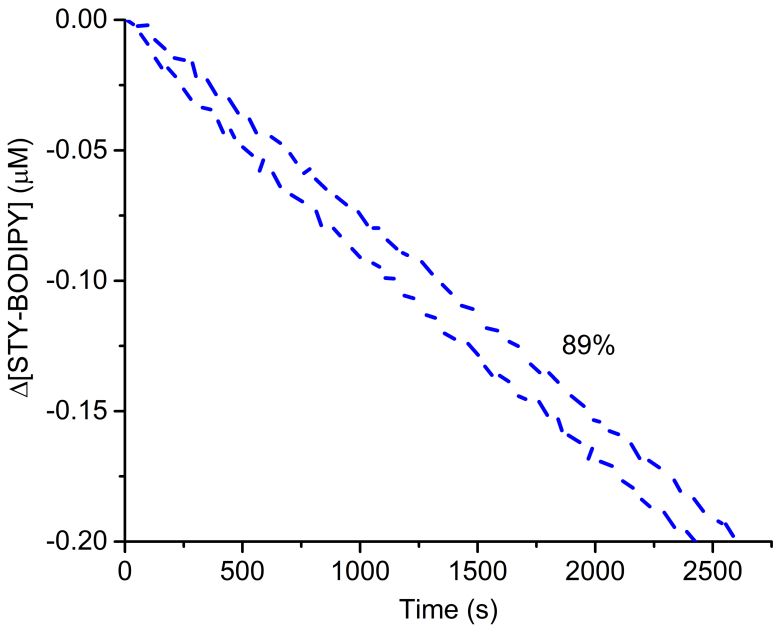


Figure S29. Co-autoxidation of 1,2-d_2-cyclooctene (89% deuterium incorporation) (3.1 M) and STY-BODIPY (10 μM) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C inhibited by DTBNH (blue dash). Reaction progress was monitored at 568 nm (ε =118 405 M^{-1} cm^{-1}).

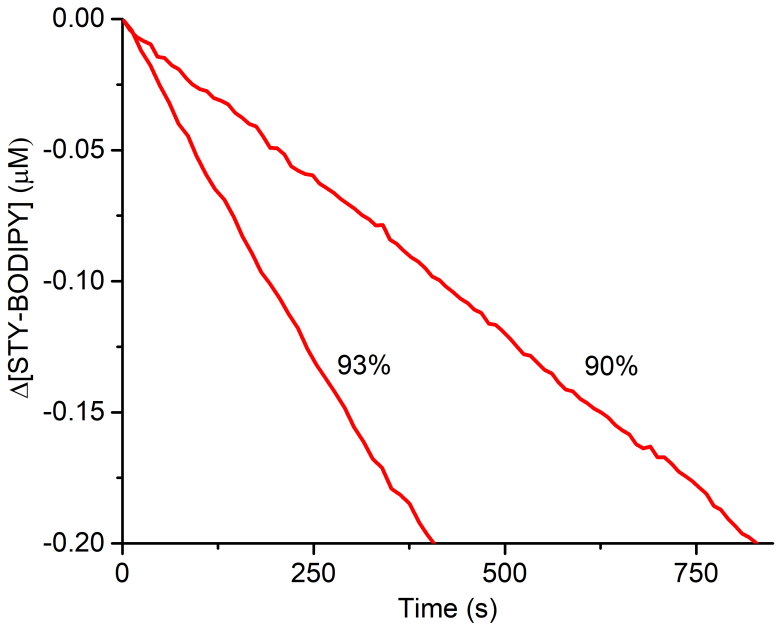


Figure S30. Co-autoxidation of 1,2-d_2-cyclooctene (90 and 93% deuterium incorporation) (3.1 M) and STY-BODIPY (10 μM) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C inhibited by TEMPO (red). Reaction progress was monitored at 568 nm (ε =118 405 M^{-1} cm^{-1}).

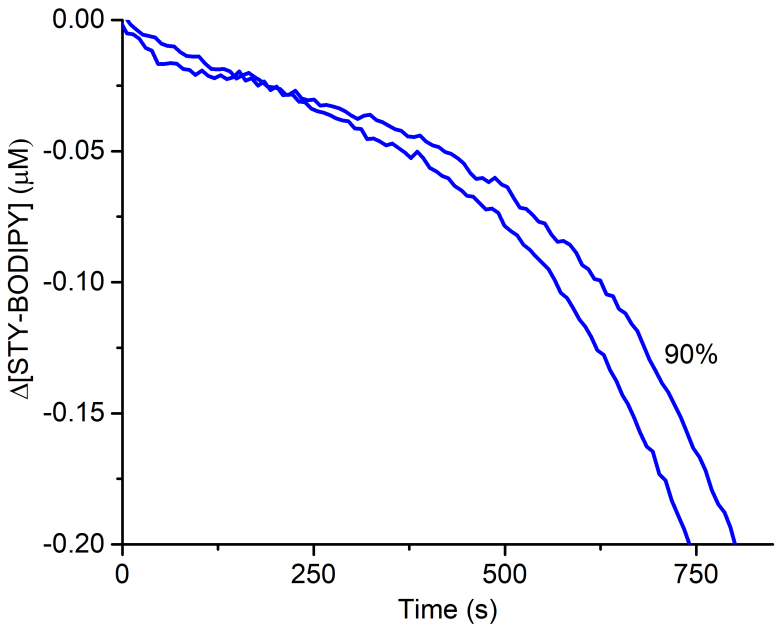


Figure S31. Co-autoxidation of 1,2-d_2-cyclooctene (90% deuterium incorporation) (3.1 M) and STY-BODIPY (10 μM) in PhCl initiated with di-*tert*-butylperoxide (218 mM) at 70 °C inhibited by Ar_2NO (blue) Reaction progress was monitored by absorbance at 568 nm (ε =118 405 M^{-1} cm^{-1}).

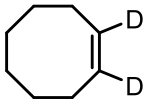
Table S3. Summary of inhibition rate constants (k_{inh}) and stoichiometries (n) derived from co-autoxidations of various substrates inhibited by nitroxides and their precursors.

RTA	k_{inh} (M^{-1} s^{-1})	n
styrene in PhCl, 37 °C, 2 μM RTA, ε = 139 000 M^{-1} cm^{-1} AIBN (6 mM) R_i = 2.8 × 10^{-9} M s^{-1}, k_t = 3.4 × 10^7 M^{-1} s^{-1}, k_p = 2720 M^{-1} s^{-1}		
DTBNH	5.2 ± 0.6 × 10^5	3.1 ± 0.1
DTBNO	7.3 ± 0.7 × 10^5	10.9 ± 0.1
TEMPO	7.1 ± 0.4 × 10^5	10.1 ± 0.1
styrene in PhCl, 37 °C, 2 μM RTA, ε = 139 000 M^{-1} cm^{-1} AIBN (6, 15, and 30 mM) R_i = 2.6 × 10^{-9} M s^{-1}, k_t = 2.3 × 10^7 M^{-1} s^{-1}, k_p = 2720 M^{-1} s^{-1}		
TEMPO, AIBN 6 mM	7.1 ± 0.4 × 10^5	10.1 ± 0.1
TEMPO, AIBN 15 mM	-	7.0 ± 0.4
TEMPO (50 μM), AIBN 30 mM	-	2.3 ± 0.1
DTBNO, AIBN 6 mM	7.3 ± 0.7 × 10^5	10.9 ± 0.1
DTBNO, AIBN 15 mM	-	9.6 ± 0.1

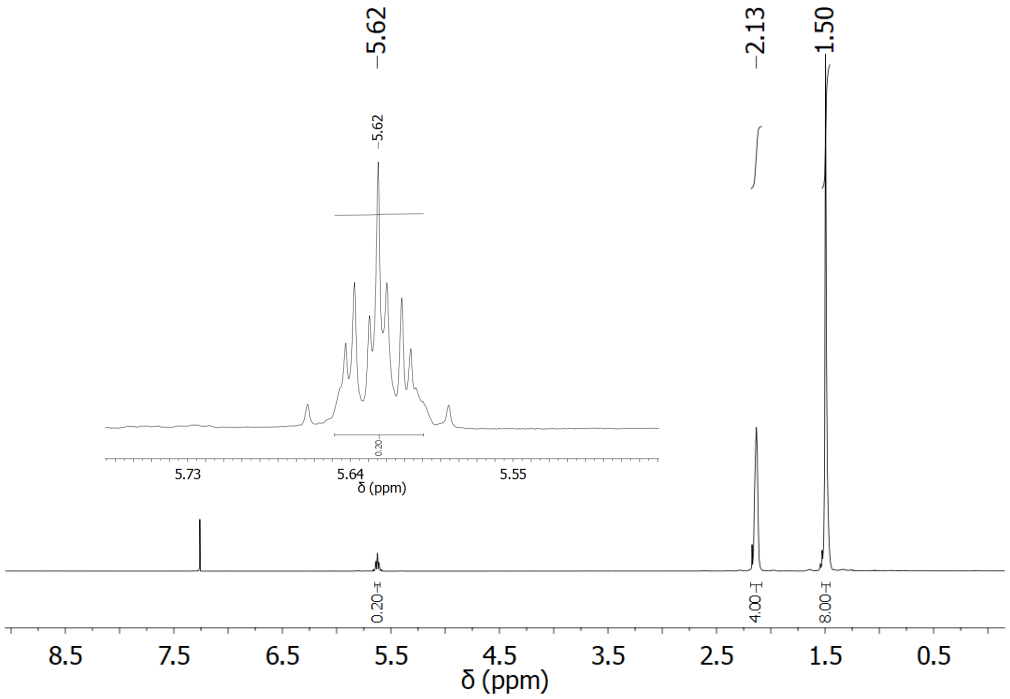
DTBNO (50 μM), AIBN 30 mM	-	6.8 ± 0.6
styrene in PhCl, 70 °C, 2 μM RTA, ε = 97 235 M^{-1} cm^{-1}		
AIBN (0.0625, 0.125, 0.250, 0.375 and 1 mM)		
TEMPO, AIBN 62.5 μM	-	21.9 ± 1.4
TEMPO, AIBN 125 μM	-	10.7 ± 1.1
TEMPO, AIBN 250 μM	-	9.8 ± 0.4
TEMPO, AIBN 375 μM	-	7.6 ± 1.0
TEMPO (50 μM), AIBN 1 mM	-	2.1 ± 0.1
DTBNO, AIBN 62.5 μM	-	18.3 ± 0.5
DTBNO, AIBN 125 μM	-	12.4 ± 0.7
DTBNO, AIBN 250 μM	-	10.1 ± 0.2
DTBNO, AIBN 375 μM	-	5.9 ± 0.6
DTBNO (50 μM), AIBN 1 mM	-	1.9 ± 0.2
styrene in PhCl, 70 °C, 2 μM RTA, ε = 97 235 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (218 mM), R_i = 4.5 × 10^{-9} M s^{-1}, k_t = 3.4 × 10^{7} M^{-1} s^{-1}, k_p = 4012 M^{-1} s^{-1}		
DTBNH	7.9 ± 1.0 × 10^{5}	2.1 ± 0.2
DTBNO	7.9 ± 0.7 × 10^{6}	10.6 ± 0.2
DTBNOH	8.5 ± 1.3 × 10^{6}	11.6 ± 0.1
TEMPH	4.6 ± 0.5 × 10^{5}	1.9 ± 0.1
TEMPO	2.1 ± 0.7 × 10^{6}	9.3 ± 0.9
TEMPOH	3.0 ± 0.7 × 10^{6}	10.0 ± 0.2
DTBNO (MeOD)	3.3 ± 1.3 × 10^{6}	10.4 ± 0.5
TEMPO (MeOD)	1.3 ± 0.4 × 10^{6}	8.9 ± 0.2
DTBNO (MeOH)	1.1 ± 0.3 × 10^{7}	22.0 ± 1.0
TEMPO (MeOH)	5.5 ± 0.6 × 10^{6}	26.3 ± 1.0
styrene in 2-octanone, 70 °C, 2 μM RTA, ε = 94 876 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (218 mM), R_i = 4.2 × 10^{-9} M s^{-1}, k_t = 3.4 × 10^{7} M^{-1} s^{-1}, k_p = 4004 M^{-1} s^{-1}		
DTBNO	2.8 ± 0.3 × 10^{6}	8.6 ± 0.2
TEMPO	1.8 ± 0.5 × 10^{6}	8.5 ± 0.3
styrene in PhCl, 70 °C, 50 μM RTA, ε = 97 235 $M^{-1}$$cm^{-1}$		
1mM AIBN (1 mM), R_i = 6.1 × 10^{-8} M s^{-1}, k_t = 3.4 × 10^{7} M^{-1} s^{-1}, k_p = 4012 M^{-1} s^{-1}		
DTBNH	1.2 ± 0.5 × 10^{6}	0.8 ± 0.2
DTBNO	2.2 ± 0.3 × 10^{5}	1.8 ± 0.2

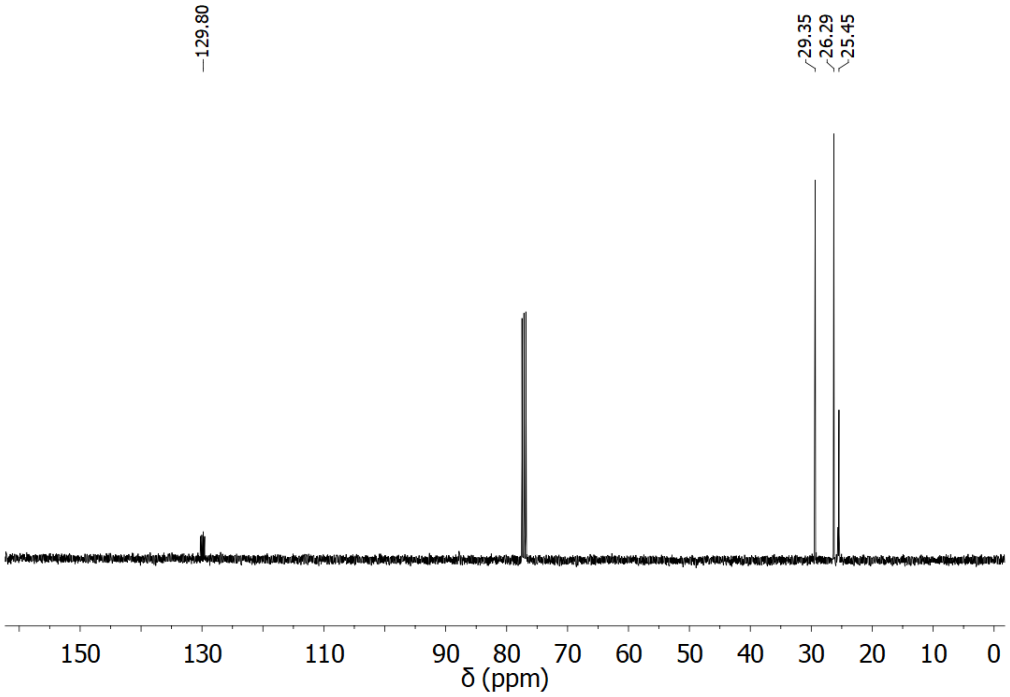
cumene in PhCl, 68.5 °C, 50 μM RTA, ε = 122 213 M^{-1} cm^{-1}		
AIBN (1 mM), R_i = 6.1 × 10^{-8} M s^{-1}, k_t = 1.9 × 10^4 M^{-1} s^{-1}		
DTBNH	-	2.3 ± 0.1
DTBNO	-	1.1 ± 0.1
norbornene in PhCl, 70 °C, 2 μM RTA, ε = 122 873 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (218 mM), R_i = 7.5 × 10^{-9} M s^{-1}, k_t = 3.4 × 10^7 M^{-1} s^{-1}, k_p = 1358 M^{-1} s^{-1}		
DTBNO	2.2 ± 0.3 × 10^6	56.3 ± 1
TEMPO	1.6 ± 0.4 × 10^6	21.8 ± 2
cyclooctene in PhCl, 70 °C, 2 μM RTA, ε = 118 405 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (218 mM), R_i = 4.5 × 10^{-9} M s^{-1}, k_t = 3.4 × 10^7 M^{-1} s^{-1}, k_p = 2689 M^{-1} s^{-1}		
DTBNH	2.5 ± 0.2 × 10^6	15.8 ± 0.2
DTBNO	1.7 ± 0.1 × 10^7	9.9 ± 0.1
TEMPO	2.6 ± 0.2 × 10^7	8.9 ± 0.1
1-hexadecene in PhCl 100 °C, 2 μM RTA, ε = 119 166 M^{-1} cm^{-1}		
dicumyl peroxide (1 mM), R_i = 4.6 × 10^{-9} M s^{-1}, k_t = 2.6 × 10^8 M^{-1} s^{-1}, k_p = 8283 M^{-1} s^{-1}.		
DTBNO	3.4 ± 0.4 × 10^6	117 ± 7
DTBNH	6.2 ± 0.4 × 10^5	23 ± 3
TEMPO	3.2 ± 0.1 × 10^6	-
ethylbenzene in PhCl, 70 °C, 2 μM RTA, ε = 123 481 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (87 mM), R_i = 3.0 × 10^{-9} M s^{-1}, k_t = 2.5 × 10^7 M^{-1} s^{-1}, k_p = 3402 M^{-1} s^{-1}		
DTBNH	4.6 ± 0.7 × 10^5	2.3 ± 0.1
dioxane in PhCl, 70 °C, 2 μM RTA, ε = 113 982 M^{-1} cm^{-1}		
^{t}BuOO^{t}Bu (218 mM), R_i = 5.6 × 10^{-9} M s^{-1}, k_t = 3.9 × 10^7 M^{-1} s^{-1}, k_p = 6707 M^{-1} s^{-1}		
DTBNH	3.3 ± 0.2 × 10^5	1.8 ± 0.1

X. Representative NMR Spectra of Deuterated Cyclooctene



in $CDCl_3$





XI. Computational Data

Calculations were generally performed using the CBS-QB3[15] complete basis set method as implemented in the Gaussian 16 software.[16] Rate constants were calculated via transition state theory at 70 °C. The intramolecular hydrogen abstraction step was also calculated using small curvature tunneling corrections.[17] In addition to this proven methodology we also explored the calculation scheme previously employed by Coote and coworkers[18] to explore the termination reactions of peroxyl radicals to test if it would be appropriate and accurate enough for our calculations. As the transition states in autoxidation are radical reactions (also including dioxygen) they can suffer from spin contamination when employing unrestricted DFT as does the CBS-QB3 methodology.

In short (see complete details in ref 4) this entails optimizing the geometry with the meta-hybrid functional M11 using the 6-31+G(d,p) basis set, then performing a CCSD(T)/cc-pVDZ energy calculation. The results from these calculations were not satisfactory (e.g. ~7 kcal mol^{-1} higher barrier for H-abstraction of 1,4-cyclohexadiene in contrast to CBS-QB3, which matches well to experiment). Therefore, we also employed the spin correction methodology published by Yamaguchi.[19]

$$^{2}E_{AP} = {}^{2}E_{LS} + \frac{\langle \hat{S}^2 \rangle_{LS} - 0.75}{\langle \hat{S}^2 \rangle_{HS} - \langle \hat{S}^2 \rangle_{LS}} ({}^{2}E_{LS} - {}^{4}E_{HS})$$

The results from these calculations are summarized in Table S3 and plotted against the CBS-QB3 results in Figure S7. What can be seen is that the CCSD(T) energies don't accurately reproduce the thermodynamics of the initial H-abstraction reaction of 1,4-CHD. In addition we employed a larger basis set CCSD(T)/cc-pVTZ//M11/cc-pVTZ but also were not satisfied with the results. We therefore employed CBS-QB3 for all results of this study.

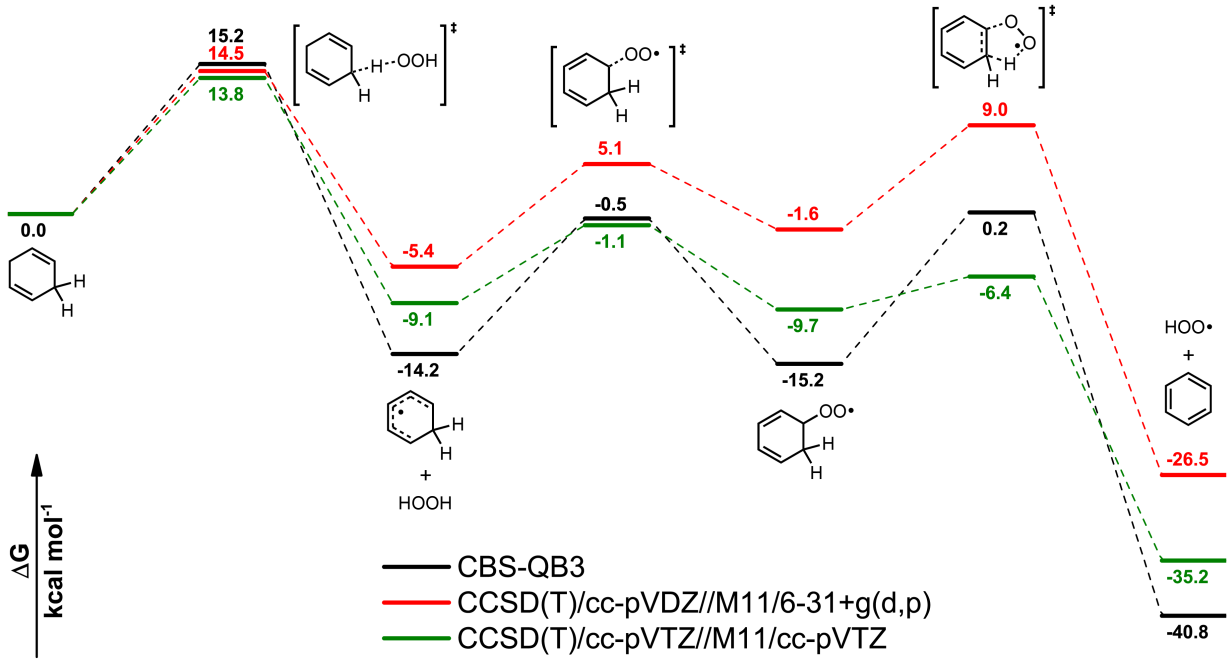


Figure S32. Computed free energy profile for the propagation steps of 1,4-cyclohexadiene autoxidation, compared for three different methodologies.

Table S4. Data for the CCSD(T)/cc-pVDZ//M11/6-31+G(d,p) test calculations. E_{HS}, E_{LS}, E_{AP} … high-spin, low-spin and spin projected CCSD(T) energies, $\langle S^2 \rangle$ … spin squared operator of the corresponding CCSD(T) calculations, G_{corr} … free energy correction at the M11 level of theory.

Molecule	E_{HS}	E_{LS}	E_{AP}	$\langle S^2 \rangle_{HS}$	$\langle S^2 \rangle_{LS}$	G_{corr}	G
O_2s	-149,985293	-149,969766	-149,953128	2,0042	1,0367	-0,014915	**-149,968043**
O_2t			-149,985293		2,0042	-0,015937	**-150,00123**
1,4-cyclohexadiene			-232,746167		-	0,093516	**-232,652651**
HOO*			-150,557989		0,7512	-0,007563	**-150,565552**
HOOH			-151,192886		-	0,004839	**-151,188047**
1,4-cyc-HOO TS	-383,107567	-383,282809	-383,295714	3,8417	0,96206	0,10065	**-383,195064**
cyclohexadiene-rad			-232,118527		1,0638	0,079841	**-232,038686**
cyc + O_2 TS	-382,063422	-382,091564	-382,106324	4,0949	1,9008	0,083019	**-382,023305**
cyc-OO*			-382,120622		0,75176	0,086718	**-382,033904**
cyc-OO*-H TS	-381,998361	-382,097477	-382,099835	3,9862	0,82522	0,082813	**-382,017022**
PhH			-231,581139		-	0,073063	**-231,508076**

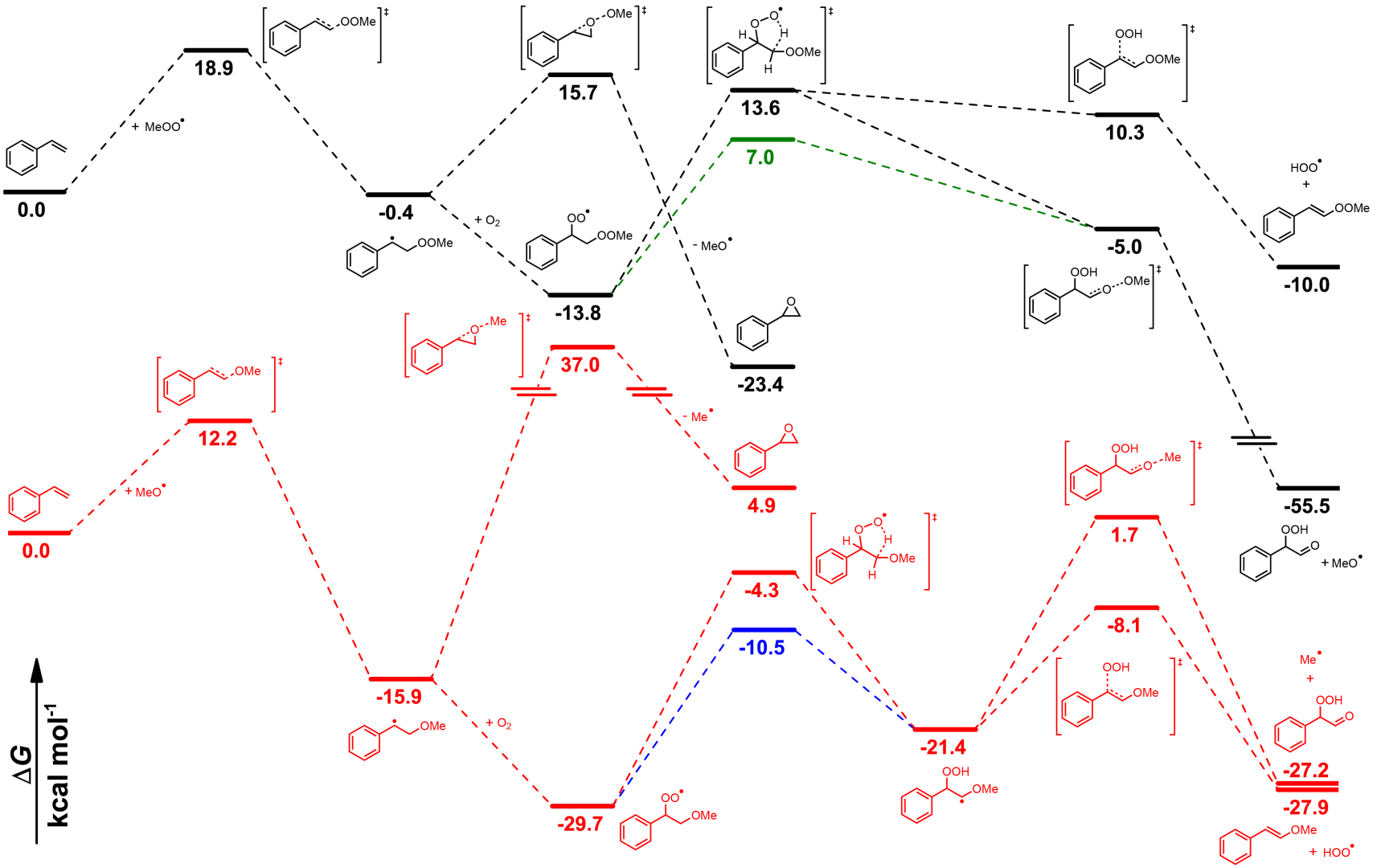


Figure S33. Computed free energy profile for the propagation steps of styrene autoxidation, including pathways to HOO• formation. The differently colored energies were derived employing tunneling corrections.

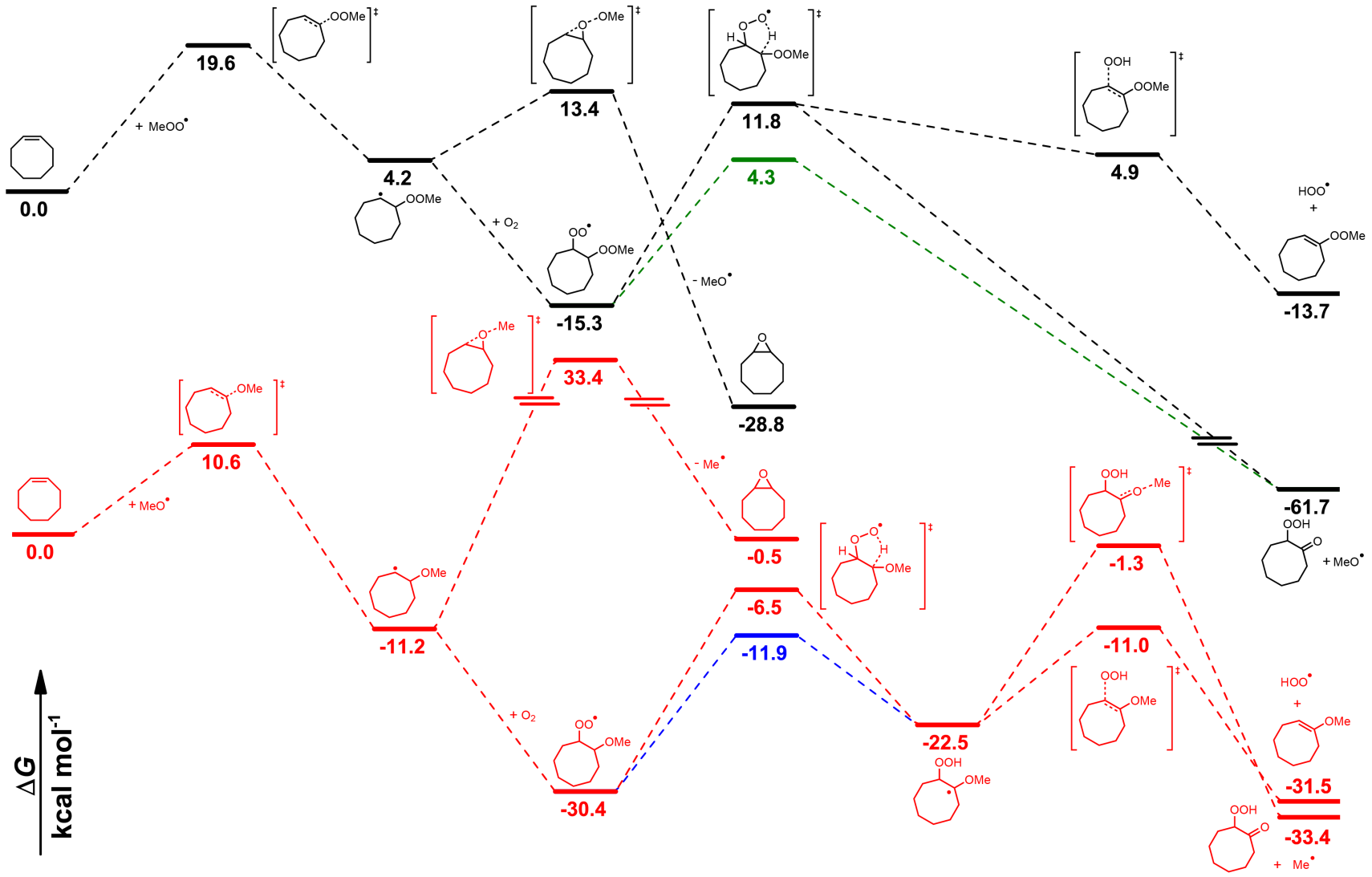


Figure S34. Computed free energy profile for the propagation steps of cyclooctene autoxidation, including pathways to HOO• formation. The differently colored energies were derived employing tunneling corrections.

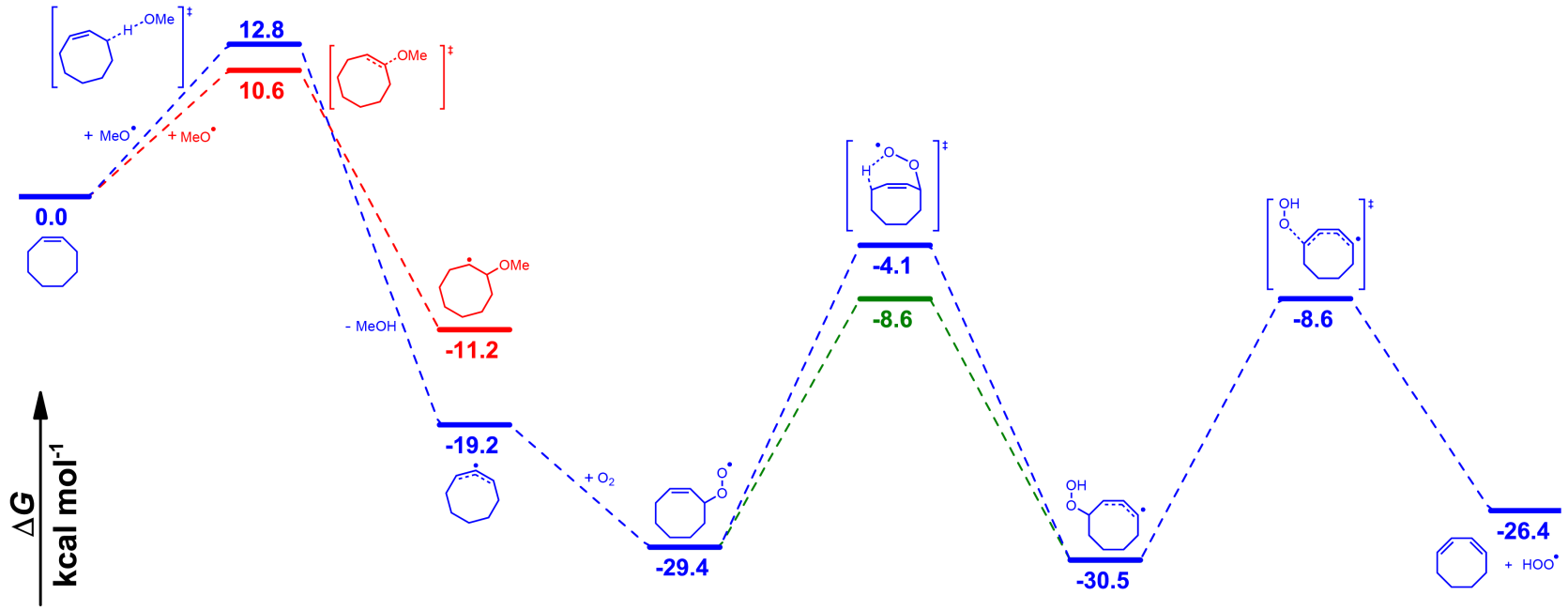


Figure S35. Computed free energy profile for the reactions of an alkoxyl radical (MeO•) with cyclooctene, comparing addition vs. hydrogen abstraction and the possible follow-up reactions leading to the formation of HOO•. The differently colored energies were derived employing tunneling corrections.

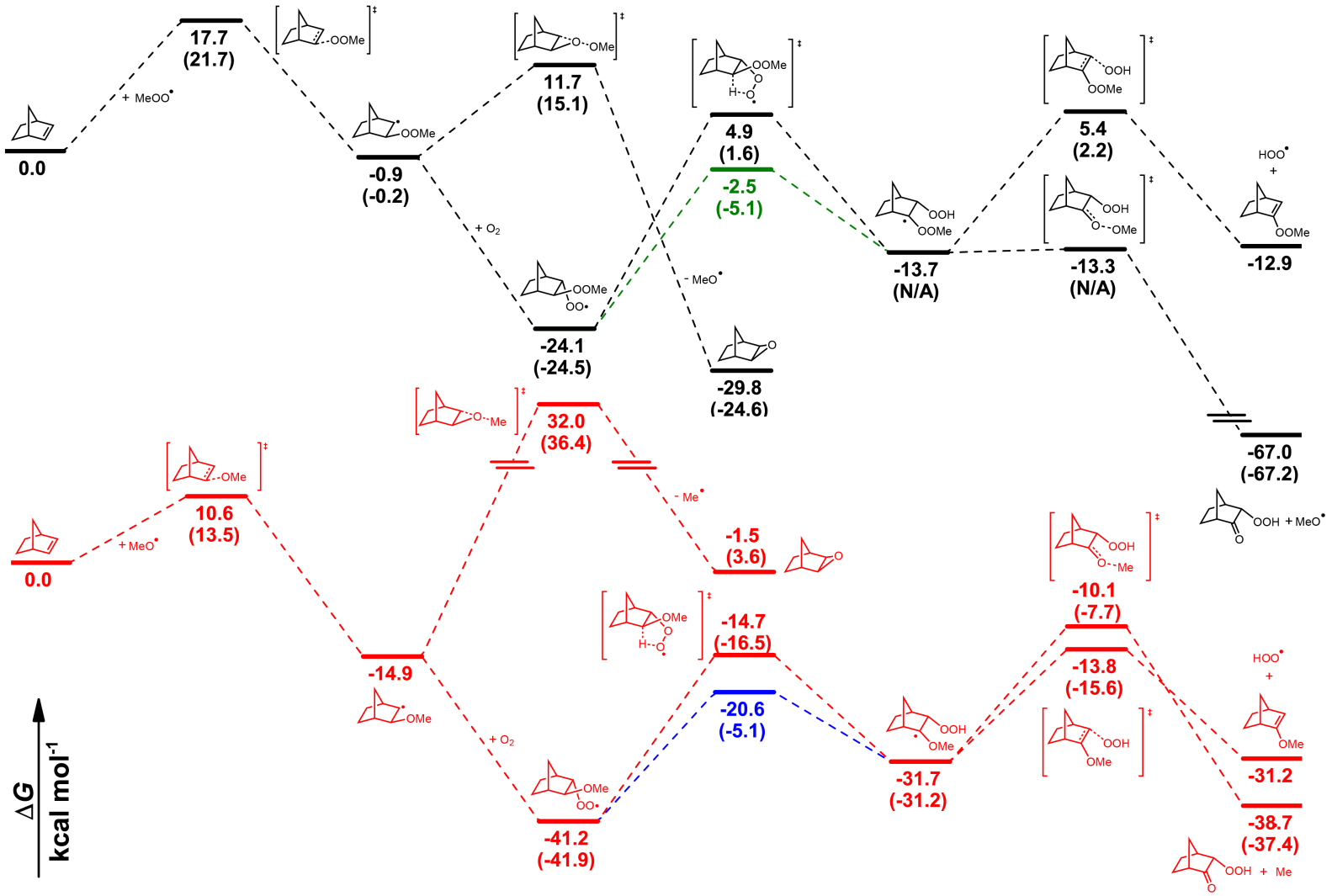


Figure S36. Computed free energy profile for the propagation steps of norbornene autoxidation, including pathways to HOO• formation (values in parentheses denote the endo-pathway). The differently colored energies were derived employing tunneling corrections.7

Optimized Gaussian Structures and CBS-QB3 Energies

hydroperoxyl radical

HOO•

CBS-QB3 Enthalpy= -150.737287 CBS-QB3 Free Energy= -150.763268

```
0 2
 O                  0.05528600    0.71849700    0.00000000
 O                  0.05528600   -0.60965600    0.00000000
 H                 -0.88456800   -0.87073000    0.00000000
```

hydrogen peroxide

HOOH

CBS-QB3 Enthalpy= -151.374582 CBS-QB3 Free Energy= -151.401132

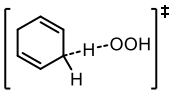
```
0 1
 O                 -0.71709500   -0.11848600   -0.05265700
 O                  0.71709500    0.11848500   -0.05266200
 H                  1.01852700   -0.66735700    0.42128100
 H                 -1.01852600    0.66736400    0.42127400
```

1,4-Cyclohexadiene

CBS-QB3 Enthalpy= -232.933952 CBS-QB3 Free Energy= -232.968094

```
0 1
 C                  0.00000000    1.49719200    0.00000000
 C                 -1.25442600    0.66544900    0.00000000
 C                 -1.25442600   -0.66544900    0.00000000
 C                  0.00000000   -1.49719200    0.00000000
 C                  1.25442600   -0.66544900    0.00000000
 C                  1.25442600    0.66544900    0.00000000
 H                  0.00000000    2.17161600   -0.86941800
 H                 -2.19913400    1.20251500    0.00000000
 H                 -2.19913400   -1.20251500    0.00000000
 H                  0.00000000   -2.17161500    0.86941900
 H                  2.19913400   -1.20251500    0.00000000
 H                  2.19913400    1.20251500    0.00000000
 H                  0.00000000   -2.17161600   -0.86941800
 H                  0.00000000    2.17161500    0.86941900
```

1,4-Cyclohexadiene H-abstraction by HOO• TS



TS freq.: -1459.46 cm^{-1}
CBS-QB3 Enthalpy= -383.662631 CBS-QB3 Free Energy= -383.707083

```
0 2
 C                 -0.14490000    0.66577200    1.10091600
 C                  0.32028000   -0.72323300    1.24567100
 C                  1.17507300   -1.28624100    0.37784800
 C                  1.78599900   -0.52827600   -0.76609300
 C                  1.45957800    0.93751900   -0.74793300
 C                  0.59553100    1.47818800    0.12321900
 H                 -1.30123800    0.54752100    0.61474900
 H                 -0.08442800   -1.31002500    2.06485200
 H                  1.47052900   -2.32395100    0.50198200
 H                  2.87713400   -0.67118100   -0.76682900
 H                  1.96107400    1.56650200   -1.47688400
 H                  0.38988000    2.54323500    0.09146300
```

H	1.45598700	-0.96685900	-1.72134300
H	-0.38421300	1.17206400	2.03914800
O	-2.42522100	0.23203200	0.00525100
O	-2.01230300	-0.52987100	-1.08142100
H	-2.03390100	-1.43696800	-0.73955200

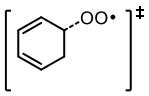
Cyclohexadienyl radical

CBS-QB3 Enthalpy= -232.318036 CBS-QB3 Free Energy= -232.352889

0 2

C	-1.45347900	0.00000200	-0.00000200
C	-0.73966900	-1.22463600	-0.00000200
C	0.62292600	-1.25504200	0.00000000
C	1.44668200	-0.00000300	0.00000300
C	0.62293000	1.25504100	0.00000200
C	-0.73966500	1.22463800	0.00000000
H	-2.53628600	0.00000400	-0.00000400
H	-1.29425200	-2.15779000	-0.00000400
H	1.14925500	-2.20375500	-0.00000100
H	2.13395200	-0.00000500	0.86546100
H	1.14926300	2.20375100	0.00000300
H	-1.29424400	2.15779400	0.00000000
H	2.13395700	-0.00000300	-0.86545200

Cyclohexadienyl radical oxygen addition TS

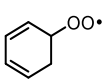


TS freq.: -319.26 cm^{-1}
CBS-QB3 Enthalpy= -382.474649 CBS-QB3 Free Energy= -382.515477

0 2

C	1.48130800	-0.72915500	-0.63494300
C	0.71504100	-1.39893300	0.39098100
C	-0.06576200	-0.69225500	1.26866600
C	-0.29076600	0.67462000	1.03843300
C	0.64925900	1.46425000	0.17747000
C	1.47391800	0.61263100	-0.73947800
H	-0.64458700	-1.21023500	2.02413400
H	0.79471900	-2.47612400	0.48108800
H	2.07892100	-1.32860500	-1.31247600
H	-0.91553600	1.23551300	1.72324600
H	0.08199200	2.20956200	-0.39596000
H	1.32055200	2.06270600	0.81989200
H	2.08358100	1.11389700	-1.48363200
O	-1.78753700	0.48005900	-0.39464600
O	-1.78466600	-0.62926800	-0.96323600

2,4-cyclohexadiene peroxyl radical



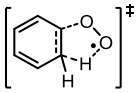
CBS-QB3 Enthalpy= -382.498575 CBS-QB3 Free Energy= -382.539013

0 2

C	-1.65124700	-1.01957700	-0.15799300
C	-0.48646200	-1.36953100	0.40844500
C	0.58147600	-0.34441800	0.61945600
C	0.06160700	1.08574400	0.72531300
C	-1.14505500	1.35987700	-0.12666800
C	-1.94634200	0.36368600	-0.52585700
H	-2.40373900	-1.77552800	-0.35805200
H	-0.26419400	-2.40129600	0.65281200
H	1.23403300	-0.58009600	1.46042800

H	-0.19942300	1.27890900	1.77633900
H	-1.37483300	2.39174900	-0.36951400
H	-2.83738700	0.56657700	-1.10911700
H	0.88892600	1.76318000	0.49547700
O	1.48520200	-0.46609800	-0.58238800
O	2.57389100	0.25382600	-0.44318100

Cyclohexadiene peroxyl radical internal H-abstraction TS



TS freq.: -306.78 cm^{-1}
CBS-QB3 Enthalpy= -382.473236 CBS-QB3 Free Energy= -382.514510

0 2

C	0.69500500	1.40801600	0.29667400
C	-0.19828500	0.55816400	0.95347000
C	-0.08337100	-0.89520800	0.81214100
C	1.09556600	-1.37809800	0.07534600
C	1.92136900	-0.51627100	-0.57579700
C	1.71812300	0.89029900	-0.47631600
H	0.58796800	2.48110100	0.40572200
H	1.26274800	-2.44838700	0.02234600
H	2.75891700	-0.89118700	-1.15320500
H	2.39953100	1.56107400	-0.98723800
H	-1.02506700	-1.16696400	0.16714200
H	-0.89859400	0.96208700	1.67091400
O	-2.12725300	0.64299100	-0.42000000
O	-2.33256000	-0.57345700	-0.62590700
H	-0.29744300	-1.45541100	1.72847600

benzene

CBS-QB3 Enthalpy= -231.784315 CBS-QB3 Free Energy= -231.816512

0 1

C	1.20717800	0.69696300	0.00000000
C	0.00000000	1.39392600	0.00000000
C	-1.20717800	0.69696400	0.00000000
C	-1.20717800	-0.69696300	0.00000000
C	0.00000000	-1.39392600	0.00000000
C	1.20717800	-0.69696400	0.00000000
H	2.14631300	1.23917900	0.00000000
H	0.00000200	2.47834800	0.00000000
H	-2.14631400	1.23917700	0.00000000
H	-2.14631300	-1.23917900	0.00000000
H	-0.00000200	-2.47834800	0.00000000
H	2.14631400	-1.23917700	0.00000000

methylperoxyl radical

MeOO•

CBS-QB3 Enthalpy= -189.954731 CBS-QB3 Free Energy= -189.985244

0 2

C	1.09605800	-0.18318200	0.00000000
H	1.87467600	0.57860400	0.00000800
H	1.14883700	-0.80072600	0.89698200
H	1.14884100	-0.80070700	-0.89699400
O	-0.15733600	0.54388500	0.00000000
O	-1.18625200	-0.27864500	0.00000000

methylperoxyl radical

MeO•

CBS-QB3 Enthalpy= -114.870535 CBS-QB3 Free Energy= -114.897461

```
0 2
 C                  0.57342800    0.00000000   -0.01405500
 H                  0.87136300   -0.00000900    1.05454200
 H                  1.01145200   -0.90926600   -0.45439500
 H                  1.01145300    0.90927300   -0.45438000
 O                 -0.79185400    0.00000000   -0.00768000
```

methanol

MeOH

CBS-QB3 Enthalpy= -115.535676 CBS-QB3 Free Energy= -115.562684

```
0 1
 C                  0.66364400   -0.01953800    0.00000300
 H                  1.03509400   -0.54226400   -0.89204900
 H                  1.08287900    0.98757500   -0.00006000
 H                  1.03506100   -0.54218200    0.89210600
 O                 -0.75012600    0.12170000    0.00000100
 H                 -1.13388600   -0.75949700   -0.00002200
```

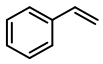
methyl radical

Me•

CBS-QB3 Enthalpy= -39.740781 CBS-QB3 Free Energy= -39.764594

```
0 2
 C                  0.00000000    0.00000000    0.00000100
 H                  1.06406300   -0.18749600   -0.00000200
 H                 -0.69441000   -0.82775500   -0.00000200
 H                 -0.36965500    1.01525200   -0.00000200
```

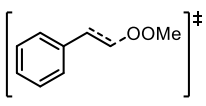
styrene



CBS-QB3 Enthalpy= -309.031150 CBS-QB3 Free Energy= -309.070748

```
0 1
 C                 -2.26145200    0.26094500    0.00000300
 C                 -1.77806700   -1.04426700    0.00000400
 C                 -0.40595000   -1.27907500    0.00000000
 C                  0.51410300   -0.22010400   -0.00000400
 C                  0.00842700    1.09057500   -0.00000600
 C                 -1.35997100    1.32683700   -0.00000200
 H                 -3.32903500    0.44930000    0.00000600
 H                 -2.46812300   -1.88067600    0.00000800
 H                 -0.03554400   -2.29920300    0.00000100
 H                  0.69062700    1.93261800   -0.00001100
 H                 -1.72838500    2.34679900   -0.00000400
 C                  1.95326600   -0.52815100   -0.00000700
 C                  2.97226800    0.33471600    0.00000900
 H                  2.18562200   -1.59100200   -0.00002200
 H                  3.99695400   -0.01657700    0.00000500
 H                  2.83214100    1.40988200    0.00002700
```

styrene – methylperoxyl radical addition TS

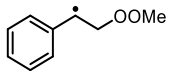


TS freq.: -487.83 cm^{-1}
CBS-QB3 Enthalpy= -498.975261 CBS-QB3 Free Energy= -499.025836

```
0 2
```

C	1.61053100	1.53084300	-0.74650800
H	1.55286600	1.05284700	-1.71506800
H	2.35729600	2.30937300	-0.66046500
C	0.51691800	1.56033400	0.09494000
H	0.55758100	2.22590000	0.95255800
C	-0.66908900	0.73696200	-0.01219000
C	-1.74301400	0.95606700	0.87697300
C	-0.80962200	-0.28936300	-0.97212100
C	-2.90499200	0.20057300	0.80321600
H	-1.65296400	1.73597700	1.62610800
C	-1.97171100	-1.04495100	-1.03910600
H	0.00756900	-0.50841000	-1.64734600
C	-3.02714100	-0.80419300	-0.15715100
H	-3.71770400	0.39230600	1.49494000
H	-2.05683800	-1.83077300	-1.78150300
H	-3.93306500	-1.39651600	-0.21571200
O	2.89375200	0.23096900	-0.05911700
O	2.39838300	-1.04814600	-0.19182700
C	2.08624400	-1.56582700	1.10447200
H	1.75992900	-2.59357800	0.93540500
H	2.97551100	-1.54849400	1.73914400
H	1.28398700	-0.98388400	1.56433700

styrene – methylperoxyl adduct

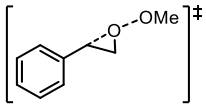


CBS-QB3 Enthalpy= -499.006444 CBS-QB3 Free Energy= -499.056571

0 2

C	1.73037100	1.16456700	-0.85080900
H	1.49781200	0.67112000	-1.79821000
H	2.22265200	2.11594700	-1.07535100
C	0.52729400	1.38766900	0.00125200
H	0.60406300	2.17635400	0.74403200
C	-0.67837700	0.65000100	-0.03815000
C	-1.76231700	1.02918900	0.80603600
C	-0.88388200	-0.47103500	-0.89245000
C	-2.96500200	0.34740500	0.78568300
H	-1.63115200	1.87715600	1.47017800
C	-2.09279200	-1.14539200	-0.90284000
H	-0.07294300	-0.81801400	-1.51871800
C	-3.14379700	-0.74445600	-0.07131300
H	-3.77312800	0.66140100	1.43719200
H	-2.22232600	-1.99849500	-1.55990200
H	-4.08688800	-1.27822400	-0.08679800
O	2.78634600	0.43245800	-0.19618700
O	2.35878100	-0.95942300	-0.13687800
C	2.43031200	-1.34699500	1.22476300
H	2.16865100	-2.40793900	1.22273400
H	3.44426100	-1.22002000	1.61662900
H	1.71711800	-0.78927900	1.83970500

styrene – methylperoxyl fragmentation TS



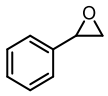
TS freq.: -638.56 cm^{-1}
CBS-QB3 Enthalpy= -498.978994 CBS-QB3 Free Energy= -499.031039

0 2

C	-1.40639500	-0.73648200	-1.14715000
H	-1.20812900	0.03391600	-1.89986400
H	-2.04533200	-1.52223100	-1.56368200
C	-0.23043600	-1.23641800	-0.40284500
H	-0.33650000	-2.20604900	0.06823500
C	0.97770500	-0.50869700	-0.16350600
C	2.02967900	-1.13294600	0.54555800
C	1.18130100	0.81031800	-0.63187400
C	3.23501100	-0.48070200	0.75538800
H	1.88486500	-2.14019800	0.92125000

C	2.38450100	1.45953900	-0.40876800
H	0.37648600	1.32677300	-1.13896200
C	3.41929500	0.81826000	0.27839000
H	4.03197700	-0.97895900	1.29543900
H	2.52154900	2.47364100	-0.76656500
H	4.35902200	1.33139600	0.44705600
O	-1.84157300	-0.24656900	0.07872500
O	-3.52306000	0.41458300	-0.20827300
C	-3.97024100	0.67961400	1.07826000
H	-4.97843900	1.10649000	0.95631300
H	-4.05977300	-0.22562500	1.69503800
H	-3.35118500	1.42180900	1.60140400

styrene oxide

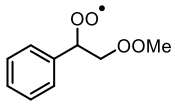


CBS-QB3 Enthalpy= -384.155298 CBS-QB3 Free Energy= -384.195750

0 1

C	-2.58859700	-0.28549200	0.11501200
C	-2.13830700	1.03206200	0.05672800
C	-0.77802500	1.29959000	-0.07255800
C	0.14712200	0.25346500	-0.13501800
C	-0.31065500	-1.06615200	-0.08612400
C	-1.67126700	-1.33229600	0.03973300
H	-3.64800600	-0.49487200	0.21077800
H	-2.84676000	1.85145500	0.10593000
H	-0.43241500	2.32736800	-0.12611400
H	0.40826800	-1.87277300	-0.16649400
H	-2.01713400	-2.35957800	0.07168000
C	1.60344100	0.55583000	-0.24770200
C	2.58294800	0.07767900	0.74779500
H	1.84538400	1.47561000	-0.77788800
H	3.49225600	0.64658600	0.92837400
H	2.22887000	-0.52910100	1.57769900
O	2.48619700	-0.53160200	-0.54139600

styrene – methylperoxyl + oxygen adduct

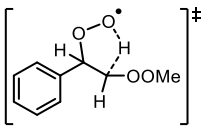


CBS-QB3 Enthalpy= -649.205976 CBS-QB3 Free Energy= -649.262498

0 2

C	1.37498000	0.82052500	0.62628200
H	0.89938400	1.06904400	1.57531400
H	2.18699100	1.52690000	0.42563900
C	0.35104400	0.86310600	-0.52498600
H	0.83922500	0.50807900	-1.43312600
C	-0.90667600	0.06036100	-0.27417500
C	-0.89448500	-1.30323800	-0.58573600
C	-2.05889200	0.62364700	0.28031200
C	-2.01393500	-2.09277400	-0.33956800
H	-0.00072500	-1.74488700	-1.01163400
C	-3.18027700	-0.16798900	0.51806400
H	-2.08559500	1.67926500	0.51928900
C	-3.16133600	-1.52647700	0.21150700
H	-1.99088700	-3.14893800	-0.58348500
H	-4.07139300	0.28118800	0.94186400
H	-4.03636400	-2.13908100	0.39711000
O	1.88096400	-0.48482000	0.82026200
O	2.67476700	-0.81013000	-0.36953400
C	3.84611900	-1.44397000	0.11622100
H	4.40333400	-1.71492200	-0.78332700
H	3.59930900	-2.34681200	0.68262400
H	4.44080500	-0.76410100	0.73417100
O	0.05313700	2.25743400	-0.86055700
O	-0.14928300	3.01190600	0.20583400

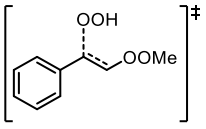
styrene – methylperoxyl 1,4-HAT TS



TS freq.: -1880.11 cm^{-1}
CBS-QB3 Enthalpy= -649.163028 CBS-QB3 Free Energy= -649.218834

```
0 2
 C                  1.34574300    0.51001400    0.32504300
 H                  1.14093000    0.32248000    1.38003100
 H                  1.83208600    1.74484000    0.18977900
 C                  0.14595700    0.94257700   -0.55017700
 H                  0.44672600    0.82898600   -1.59845300
 C                 -1.14163600    0.21742100   -0.26993400
 C                 -1.52950600   -0.84960500   -1.08472900
 C                 -1.94384700    0.57472000    0.81948900
 C                 -2.69839800   -1.55546500   -0.81307500
 H                 -0.91491400   -1.12604100   -1.93496300
 C                 -3.11821500   -0.12426100    1.08175900
 H                 -1.65237000    1.41160500    1.44210000
 C                 -3.49617300   -1.19293900    0.27015500
 H                 -2.99021900   -2.38174500   -1.45140100
 H                 -3.74010300    0.16593500    1.92110700
 H                 -4.41006100   -1.73764000    0.47865100
 O                  2.07248300   -0.48585500   -0.26331700
 O                  2.80378100   -1.19623100    0.77964600
 C                  3.79989800   -1.94529800    0.10060400
 H                  4.31468800   -2.48004500    0.90089500
 H                  4.50039900   -1.28948400   -0.42342100
 H                  3.35033600   -2.66044800   -0.59405500
 O                  0.01656800    2.32734700   -0.21771600
 O                  1.34961400    2.82206100   -0.24674900
```

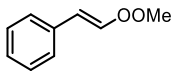
styrene – methylperoxyl – hydroperoxyl radical elimination TS



TS freq.: -482.17 cm^{-1}
CBS-QB3 Enthalpy= -649.168326 CBS-QB3 Free Energy= -649.224573

```
0 2
 C                  1.27650400   -0.82150200    0.36485000
 H                 -0.56729000    2.34656900   -0.19907400
 H                  1.20708200   -0.67198500    1.43482100
 C                  0.29588000   -0.45733500   -0.55994000
 H                  0.48833900   -0.78155100   -1.57763500
 C                 -1.12863900   -0.35737700   -0.18808700
 C                 -1.54294400    0.07199500    1.08306000
 C                 -2.10946200   -0.64994800   -1.14689100
 C                 -2.89702300    0.18519800    1.38504400
 H                 -0.80695600    0.32713200    1.83492800
 C                 -3.46185200   -0.54052800   -0.84200100
 H                 -1.80299900   -0.96857200   -2.13729400
 C                 -3.86086300   -0.12367400    0.42680900
 H                 -3.19979300    0.51593100    2.37217400
 H                 -4.20454700   -0.77941200   -1.59473800
 H                 -4.91451400   -0.03813900    0.66660100
 O                  2.44688500   -1.28958500   -0.09592700
 O                  3.55130200   -0.72035600    0.72572500
 C                  4.08535200    0.36416100   -0.02915800
 H                  4.84525400    0.79120900    0.63074900
 H                  3.31577800    1.10791700   -0.25210700
 H                  4.55428800    0.00771100   -0.95085800
 O                  0.76999700    1.31322700   -1.01474800
 O                  0.37477000    2.21136900   -0.01376000
```

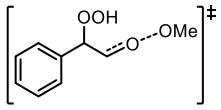
styrene – 2-methylperoxyl



CBS-QB3 Enthalpy= -498.442849 CBS-QB3 Free Energy= -498.493255

```
0 1
 C                -1.32068400   -0.87106500    0.08305600
 H                -0.99767700   -1.86609300    0.37018900
 C                -0.49684000    0.15261900   -0.15803800
 H                -0.93404600    1.10992300   -0.41054300
 C                 0.96733600    0.08810900   -0.07781000
 C                 1.69262600   -1.11642000   -0.07030100
 C                 1.69570800    1.28728400   -0.01339400
 C                 3.07880300   -1.11745000    0.02564000
 H                 1.17178600   -2.06308600   -0.16125100
 C                 3.08407400    1.28639700    0.07724700
 H                 1.15908500    2.23029600   -0.02860800
 C                 3.78478900    0.08324700    0.10222500
 H                 3.61364400   -2.06104400    0.02804800
 H                 3.61902700    2.22848200    0.12777600
 H                 4.86657000    0.07905200    0.17060200
 O                -2.68204800   -0.89358300    0.02720200
 O                -3.19775600    0.38752000   -0.43241000
 C                -4.38540700    0.60001300    0.31441000
 H                -4.78393500    1.53575400   -0.08298500
 H                -4.17339300    0.70563200    1.38232900
 H                -5.10506700   -0.20680900    0.14789400
```

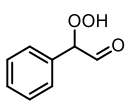
styrene – 2-methylperoxyl 1-hydroperoxyl peroxide fragmentation TS



TS freq.: -64.32 cm^{-1}
CBS-QB3 Enthalpy= -649.192468 CBS-QB3 Free Energy= -649.248404

```
0 2
 C                 1.26902400   -0.55205100    0.03787600
 H                -0.98091000    2.75275100    0.05258100
 H                 1.21121300   -1.06368500    0.98695300
 C                 0.28454700    0.43496700   -0.45594700
 H                 0.42807900    0.60153000   -1.52858000
 C                -1.13801100   -0.01983500   -0.18087500
 C                -1.89926100   -0.62403100   -1.18363400
 C                -1.69705700    0.14825500    1.08984900
 C                -3.19453900   -1.06214400   -0.92088000
 H                -1.47508300   -0.75079600   -2.17427500
 C                -2.99444800   -0.28711100    1.35249900
 H                -1.11161900    0.62718200    1.86704100
 C                -3.74542800   -0.89501100    0.34864000
 H                -3.77605500   -1.52853100   -1.70822500
 H                -3.41824600   -0.15162300    2.34141800
 H                -4.75523400   -1.23265300    0.55253200
 O                 2.48183100   -0.50044500   -0.57434500
 O                 3.43507500   -1.28838500    0.19267800
 C                 4.54497200   -0.42955500    0.42334300
 H                 5.25152000   -1.05474700    0.97354800
 H                 4.25792800    0.43659000    1.02619600
 H                 4.99395000   -0.10543800   -0.51944300
 O                 0.58714400    1.68742500    0.21782300
 O                -0.15459200    2.74997000   -0.45302800
```

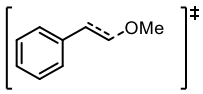
styrene – 1-hydroperoxyl aldehyde product



CBS-QB3 Enthalpy= -534.384427 CBS-QB3 Free Energy= -534.431522

```
0 1
 C                  1.62175300    0.45082500    1.21647600
 H                  3.34984600    0.09783800   -0.68358900
 H                  1.20085700    0.40225000    2.24263700
 C                  1.00404300   -0.53766600    0.22839500
 H                  1.16043500   -1.54895500    0.62981100
 C                 -0.47736800   -0.25824700    0.08472300
 C                 -1.42697200   -1.17795500    0.53358300
 C                 -0.90187500    0.94067700   -0.49895700
 C                 -2.78654900   -0.90142400    0.40887100
 H                 -1.10344300   -2.11538600    0.97305700
 C                 -2.26015900    1.21045800   -0.63200900
 H                 -0.16546100    1.64987500   -0.85814500
 C                 -3.20443100    0.29197400   -0.17529900
 H                 -3.51737000   -1.62143800    0.75883200
 H                 -2.58204900    2.13813200   -1.09106400
 H                 -4.26246300    0.50476100   -0.27759800
 O                  2.48997400    1.23605300    0.92738500
 O                  1.58385600   -0.42431900   -1.06201800
 O                  2.98979500   -0.76410100   -0.95144600
```

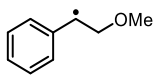
styrene – methoxy radical addition TS



TS freq.: -235.13 cm^{-1}
CBS-QB3 Enthalpy= -423.899386 CBS-QB3 Free Energy= -423.948723

```
0 2
 C                  1.35723500   -1.13402100   -0.65661500
 C                  0.39062600   -0.59626100    0.21442500
 C                  0.71739300    0.58584800    0.90875600
 C                  1.95034300    1.19795600    0.73301000
 C                  2.89430300    0.65002300   -0.13792700
 C                  2.59149800   -0.52004300   -0.83186900
 C                 -0.88523800   -1.28278000    0.36233700
 C                 -1.97233500   -0.85750500    1.05762000
 C                 -2.49213100    1.31348000   -0.91414000
 H                  1.12590700   -2.04452800   -1.19943000
 H                  0.00253000    1.02282700    1.59551200
 H                  2.18137400    2.10588200    1.27893700
 H                  3.85666100    1.13077000   -0.27105600
 H                  3.31821500   -0.95380500   -1.50952100
 H                 -2.83528300   -1.49737100    1.16429100
 H                 -1.94873700    0.01860100    1.69282200
 H                 -0.98026800   -2.20890600   -0.19780100
 H                 -1.56640700    1.11457000   -1.47547000
 H                 -3.18958600    1.79036900   -1.62451400
 H                 -2.28257100    2.04892600   -0.11978900
 O                 -3.12399900    0.16656000   -0.46844500
```

styrene – methoxy adduct

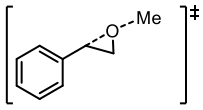


CBS-QB3 Enthalpy= -423.946747 CBS-QB3 Free Energy= -423.993510

```
0 2
 C                  1.51172500    1.28380300    0.25779600
 C                  0.38385300    0.52716000   -0.17047200
 C                  0.58518900   -0.86119500   -0.41846700
 C                  1.83546600   -1.43490900   -0.25936500
 C                  2.92874600   -0.66706500    0.15473800
 C                  2.75423000    0.69703800    0.41426900
 C                 -0.86795400    1.16310800   -0.34301300
 C                 -2.11105600    0.50164900   -0.86565600
 C                 -2.93916900   -0.45378600    1.15005200
 H                  1.38357000    2.34283400    0.45690700
 H                 -0.26081700   -1.46985900   -0.70920800
 H                  1.96538800   -2.49395900   -0.45436100
```

H	3.90313200	-1.12560900	0.27762000
H	3.59705500	1.29800600	0.73787700
H	-2.93808900	1.22588900	-0.86278800
H	-1.96567600	0.17720800	-1.90326900
H	-0.91988200	2.22767800	-0.13567400
H	-3.79134600	0.24130500	1.17696800
H	-3.25589300	-1.41634700	1.55254600
H	-2.13602000	-0.04988100	1.77890300
O	-2.50845000	-0.68651100	-0.17935200

styrene – methoxy fragmentation TS

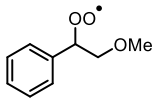


TS freq.: -767.94 cm^{-1}
CBS-QB3 Enthalpy= -423.860107 CBS-QB3 Free Energy= -423.909242

0 2

C	1.55464700	-1.22838100	-0.30188000
C	0.48891900	-0.43976500	0.16996000
C	0.73459500	0.92267800	0.42831100
C	1.99822900	1.46276900	0.23625900
C	3.04992500	0.66258500	-0.21536500
C	2.82068300	-0.68564700	-0.48525200
C	-0.80697500	-1.05619900	0.37778300
C	-1.95710200	-0.43042700	1.03212300
C	-3.93133600	0.78782900	-0.81369000
H	1.38055600	-2.27745500	-0.51748800
H	-0.07853000	1.56157200	0.74998100
H	2.16680400	2.51548900	0.43445700
H	4.03555800	1.08915700	-0.36198900
H	3.62885100	-1.31348100	-0.84353400
H	-2.68661400	-1.10182300	1.49632700
H	-1.76937400	0.44856500	1.65646500
H	-0.91768700	-2.09099700	0.08093500
H	-4.64567000	0.05758100	-0.45821100
H	-3.81360500	1.70065100	-0.24536800
H	-3.74484700	0.83179100	-1.87643800
O	-2.15811900	-0.17421100	-0.33557900

styrene – methoxy + oxygen adduct

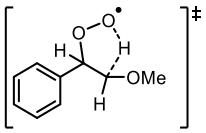


CBS-QB3 Enthalpy= -574.146964 CBS-QB3 Free Energy= -574.200056

0 2

C	1.46214200	0.92406100	-0.47744900
C	0.62320700	0.16112500	0.33878900
C	1.07516100	-1.07219700	0.81922600
C	2.34192300	-1.53944900	0.48118700
C	3.17528800	-0.77512400	-0.33278800
C	2.73205400	0.45628900	-0.80870500
C	-0.77805100	0.60960900	0.70074800
C	-1.87904900	0.04907000	-0.20716600
C	-2.91112200	-2.01117600	-0.71011700
H	1.12984900	1.88470100	-0.84996900
H	0.42521500	-1.67059900	1.44651100
H	2.67953700	-2.49801800	0.85901100
H	4.16497000	-1.13494000	-0.59059700
H	3.37640200	1.05985700	-1.43798100
H	-2.80960900	0.60885000	-0.03548800
H	-1.60020600	0.15642700	-1.26130200
H	-1.00561000	0.31329200	1.72685700
H	-2.54697400	-2.00816900	-1.74628400
H	-2.95729500	-3.03916800	-0.35094800
H	-3.92113100	-1.57887200	-0.68992900
O	-2.03044400	-1.31018100	0.14890300
O	-0.86907700	2.06914700	0.76989100
O	-1.09853800	2.62770800	-0.40532300

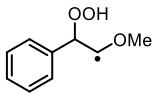
styrene – methoxy 1,4-HAT TS



TS freq.: -1896.36 cm^{-1}
CBS-QB3 Enthalpy= -574.108249 CBS-QB3 Free Energy= -574.159572

```
0 2
 C                  1.47781200   -0.87357000    0.75287600
 C                  0.76339000   -0.24872800   -0.27516800
 C                  1.38312100    0.75352700   -1.02742700
 C                  2.69517300    1.13066600   -0.75471800
 C                  3.40448600    0.50123900    0.26642600
 C                  2.79394500   -0.50353400    1.01517800
 C                 -0.67203600   -0.60545000   -0.55209900
 C                 -1.70493200    0.12679300    0.32779000
 C                 -2.80117000    2.18896200    0.68622900
 H                  1.00344300   -1.65974800    1.32705400
 H                  0.83498800    1.23737700   -1.82887800
 H                  3.16629100    1.90868900   -1.34485100
 H                  4.42890300    0.78888500    0.47442500
 H                  3.34448500   -1.00167600    1.80538600
 H                 -2.50681300   -0.92771700    0.16696000
 H                 -1.45558400    0.17879200    1.39455300
 H                 -0.94028100   -0.40103900   -1.59539100
 H                 -2.15111300    2.44583800    1.52941800
 H                 -3.03770400    3.08674500    0.11823700
 H                 -3.72580600    1.73795700    1.06020300
 O                 -2.13450800    1.30167900   -0.21113100
 O                 -0.91267500   -1.97945200   -0.23506800
 O                 -2.32776100   -2.09891800   -0.27150600
```

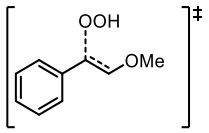
styrene – methoxy – hydroperoxyl



CBS-QB3 Enthalpy= -574.133646 CBS-QB3 Free Energy= -574.186777

```
0 2
 C                 -1.77746100    1.06303000    0.25295700
 C                 -0.90760000    0.05372600   -0.16765000
 C                 -1.42235600   -1.22101400   -0.42800800
 C                 -2.78086300   -1.48215700   -0.27036500
 C                 -3.64250500   -0.47332300    0.15497200
 C                 -3.13559600    0.79712200    0.41565600
 C                  0.56886000    0.33184700   -0.38898500
 C                  1.44402200   -0.75509400    0.13025900
 C                  3.64698000   -1.54600900    0.44051000
 H                 -1.38403100    2.05040100    0.45297100
 H                 -0.75651700   -2.00967500   -0.76101500
 H                 -3.16507100   -2.47428100   -0.48005700
 H                 -4.70014900   -0.67620700    0.28066200
 H                 -3.79886900    1.58876700    0.74625100
 H                  1.20563400   -1.25862600    1.06538500
 H                  2.74680300    1.60569800   -0.12827100
 H                  0.77234400    0.50271800   -1.45234900
 H                  3.41092100   -2.55552800    0.09141000
 H                  4.65678800   -1.27941600    0.13339400
 H                  3.57145100   -1.50855500    1.53267500
 O                  2.76836200   -0.59366900   -0.15966400
 O                  0.89831600    1.58700800    0.28000900
 O                  2.01829900    2.18240200   -0.40998700
```

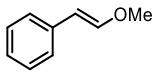
styrene – methoxy – hydroperoxyl radical elimination TS



TS freq.: -494.87 cm^{-1}
CBS-QB3 Enthalpy= -574.112146 CBS-QB3 Free Energy= -574.165652

```
0 2
 C                -1.85632900    0.64302100   -1.03292000
 C                -0.67398800    0.14634000   -0.46095000
 C                -0.77787200   -0.86042800    0.51353900
 C                -2.02633800   -1.35580400    0.88560200
 C                -3.18898100   -0.86216500    0.29937100
 C                -3.09869300    0.14189100   -0.66421200
 C                 0.61179400    0.75165000   -0.86762100
 C                 1.84107200    0.08872600   -0.91847800
 C                 3.46199900   -1.41487900   -0.12035600
 H                -1.79365400    1.43266700   -1.77410300
 H                 0.11935800   -1.25679200    0.96482700
 H                -2.08770500   -2.13539100    1.63710300
 H                -4.15695200   -1.25464400    0.58992200
 H                -3.99727100    0.53647200   -1.12530100
 H                 2.68554600    0.54687900   -1.42311600
 H                 0.05103500    1.30986800    1.92929900
 H                 0.51718600    1.50478100   -1.64318600
 H                 4.04340900   -0.67092500    0.43155400
 H                 3.48091500   -2.36373500    0.41213400
 H                 3.88336100   -1.55007300   -1.12187400
 O                 2.09161100   -1.01980400   -0.19751200
 O                 0.86974700    2.07085100    0.42103700
 O                 0.97599100    1.47780000    1.69133500
```

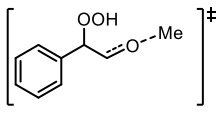
styrene – 2-methoxy



CBS-QB3 Enthalpy= -423.388745 CBS-QB3 Free Energy= -423.433951

```
0 1
 C                 1.29218600    1.27374200   -0.05056100
 C                 0.48286100    0.12957700    0.04451100
 C                 1.12655400   -1.11802700    0.12518900
 C                 2.51231700   -1.21347300    0.08318300
 C                 3.29938200   -0.06693800   -0.02426600
 C                 2.67974500    1.17868800   -0.08583700
 C                -0.97735400    0.28863500    0.06595200
 C                -1.86116100   -0.69036900   -0.18223100
 C                -3.80417500    0.63600900    0.15396000
 H                 0.82072500    2.24982900   -0.10533500
 H                 0.54044700   -2.02240100    0.24217200
 H                 2.98253500   -2.18876300    0.14785900
 H                 4.38022500   -0.14465400   -0.05010300
 H                 3.27757000    2.08041600   -0.16209600
 H                -1.55604100   -1.69812000   -0.43863300
 H                -1.33501400    1.29110000    0.27261800
 H                -3.52590400    1.40727400   -0.57271700
 H                -4.88053900    0.47719900    0.12274800
 H                -3.50773000    0.96080400    1.15741300
 O                -3.21230100   -0.61497000   -0.17416500
```

styrene – 2-methoxy 1-hydroperoxyl ether fragmentation TS



TS freq.: -592.90 cm^{-1}
CBS-QB3 Enthalpy= -574.095947 CBS-QB3 Free Energy= -574.149980

```
0 2
 C                  1.46583000   -0.35274200   -1.03020900
 C                  0.94349000    0.09745000    0.18699300
 C                  1.80983400    0.33378600    1.25539200
 C                  3.17861100    0.11276700    1.11687700
 C                  3.69231700   -0.33495400   -0.09767200
 C                  2.83376500   -0.56376500   -1.17224800
 C                 -0.54447700    0.33300500    0.32742400
 C                 -1.34044000   -0.94066200    0.10165800
 C                 -4.05002100   -0.96430700    0.64082200
 H                  0.79725300   -0.52554700   -1.86570000
 H                  1.41294800    0.69621400    2.19776500
 H                  3.84245900    0.29705100    1.95394200
 H                  4.75771900   -0.50286600   -0.20813700
 H                  3.23056500   -0.90745100   -2.12081500
 H                 -0.94885900   -1.85874300    0.56124000
 H                 -2.73894900    1.07393100   -0.76680900
 H                 -0.76189800    0.71670200    1.33667900
 H                 -3.99621000    0.00052700    1.12916200
 H                 -4.79133200   -1.07449700   -0.13879600
 H                 -3.87417600   -1.83613300    1.25792000
 O                 -2.47658800   -0.94580700   -0.45427500
 O                 -0.88807300    1.35244100   -0.61890400
 O                 -2.24321100    1.79303400   -0.34065600
```

cyclooctene

CBS-QB3 Enthalpy= -312.578164 CBS-QB3 Free Energy= -312.618354

```
0 1
 C                 -1.71895300    0.79825400   -0.04838400
 C                 -1.66162600   -0.68373900    0.38836700
 C                  1.86966500    0.49312400    0.05720500
 C                 -0.76130100   -1.56655300   -0.44498700
 C                  1.37834800   -0.84738000    0.65116500
 C                  0.56381000   -1.65777700   -0.31857800
 H                 -1.94967100    0.84775300   -1.11953200
 H                 -1.36244000   -0.72429700    1.44231900
 H                  2.65456500    0.29486100   -0.68226400
 H                  2.24976600   -1.42068500    0.98400900
 H                 -2.56895800    1.26128900    0.46659800
 H                 -2.67839800   -1.08689600    0.34835500
 H                  2.34681100    1.06480600    0.86235500
 H                 -1.24867600   -2.15694100   -1.21766100
 H                  0.78669400   -0.63925900    1.54798500
 C                 -0.47307500    1.66176300    0.23365100
 H                 -0.76643300    2.70100600    0.05093800
 H                 -0.22955800    1.61265300    1.30277300
 C                  0.78822200    1.36099300   -0.61071800
 H                  1.26378900    2.30889900   -0.88423400
 H                  0.48242700    0.89803100   -1.55408800
 H                  1.10955000   -2.31332500   -0.99388300
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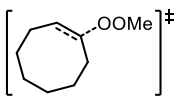
cyclooctene – methylperoxyl radical addition TS

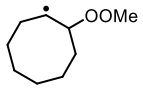


TS freq.: -468.28 cm^{-1}
CBS-QB3 Enthalpy= -502.519883 CBS-QB3 Free Energy= -502.572395

```
0 2
 C                  2.38115200   -1.52475600    0.05700900
 C                  0.87734200   -1.72578200   -0.25769600
 C                  1.37977300    1.93480400   -0.03001000
 C                 -0.06435600   -0.95813600    0.62090500
 C                  0.14699600    1.23028600   -0.63287800
 C                 -0.55201800    0.31150600    0.33563800
 H                  2.55894500   -1.75834200    1.11375500
```

H	0.69842500	-1.47229800	-1.30803500
H	1.04648200	2.66323100	0.71894100
H	-0.56325900	1.98580800	-0.97732100
H	2.94001400	-2.27118100	-0.51887500
H	0.65528400	-2.79303000	-0.15704200
H	1.84868500	2.51889700	-0.83057900
H	-0.47126700	-1.47497000	1.48486900
H	0.44100300	0.66242200	-1.51932000
C	2.96901700	-0.13625500	-0.25232600
H	4.05273500	-0.21232500	-0.11555100
H	2.82379900	0.09344700	-1.31529100
C	2.44363100	1.03013200	0.61768300
H	3.28427600	1.67416100	0.89621100
H	2.05741600	0.62612800	1.55975300
H	-1.10129600	0.80735400	1.13141900
O	-2.06262200	-0.03441100	-0.78975300
O	-3.10465400	-0.66560500	-0.11850400
C	-3.96994700	0.32042600	0.43491700
H	-4.79693700	-0.23683100	0.88021800
H	-3.46181600	0.90575500	1.20932600
H	-4.34382400	0.98854600	-0.34588100

cyclooctene – methylperoxyl adduct

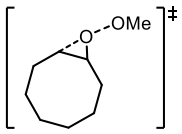


CBS-QB3 Enthalpy= -502.543768 CBS-QB3 Free Energy= -502.596945

0 2

C	2.29745000	-1.58660400	-0.09183400
C	0.76193000	-1.70111000	-0.27983900
C	1.39580600	1.90654500	0.08184200
C	-0.03924700	-0.87457800	0.67065600
C	0.15153400	1.32307800	-0.60511100
C	-0.70568700	0.39879200	0.27148000
H	2.55074000	-1.90443000	0.92701700
H	0.50606500	-1.44449600	-1.31342400
H	1.07918200	2.56584700	0.89907700
H	-0.48651800	2.14701200	-0.93823100
H	2.77601000	-2.30623200	-0.76613100
H	0.49351200	-2.75736400	-0.15238000
H	1.89140400	2.55523100	-0.64990500
H	-0.19678300	-1.24375100	1.67831000
H	0.43919200	0.77843500	-1.50861100
C	2.90438800	-0.19494500	-0.33962100
H	3.99172000	-0.29667500	-0.26196600
H	2.71213600	0.11005600	-1.37559000
C	2.43602500	0.91263800	0.63494700
H	3.30266700	1.50292900	0.95114000
H	2.05101500	0.44529400	1.54746700
H	-1.05140000	0.94029000	1.16001700
O	-1.86863200	0.15141600	-0.56943200
O	-2.83921100	-0.58366600	0.23775600
C	-4.06985100	0.08998200	0.05525300
H	-4.79359900	-0.49396400	0.62950900
H	-4.03218000	1.11541700	0.43981200
H	-4.36451500	0.10162300	-0.99935300

cyclooctene – methylperoxyl fragmentation TS



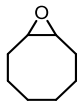
TS freq.: -657.43 cm^{-1}
CBS-QB3 Enthalpy= -502.529287 CBS-QB3 Free Energy= -502.582202

0 2

C	2.43383400	-1.45170700	-0.18375000
C	0.91002800	-1.74999000	-0.24985600
C	1.20887800	1.95104000	-0.02747700

C	0.11873500	-1.05255900	0.80125800
C	-0.05626500	1.19510800	-0.45963000
C	-0.58747800	0.23783000	0.59857600
H	2.80414600	-1.70153700	0.81774500
H	0.53759900	-1.48041800	-1.24175800
H	0.95271500	2.64986200	0.77785000
H	-0.85536300	1.90579800	-0.68298600
H	2.92781100	-2.14458100	-0.87374500
H	0.77403900	-2.83100900	-0.14289300
H	1.53986100	2.57175900	-0.86792800
H	-0.02409300	-1.54089700	1.75867100
H	0.12007100	0.63983700	-1.38502800
C	2.86238100	-0.01685300	-0.53469600
H	3.95650500	-0.01255100	-0.57191600
H	2.53286600	0.22289300	-1.55283500
C	2.39415500	1.08617200	0.44542700
H	3.23035300	1.76389100	0.64503500
H	2.15625500	0.62870000	1.41319300
H	-0.77970200	0.76520200	1.54283800
O	-1.70044700	-0.52227700	0.20392900
O	-3.03890200	0.57915600	-0.01164000
C	-4.08222000	-0.27530100	-0.35822900
H	-4.95620600	0.37571000	-0.50527900
H	-3.89424800	-0.81552700	-1.29608700
H	-4.32009900	-0.99460400	0.43707700

cyclooctene oxide

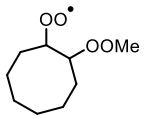


CBS-QB3 Enthalpy= -387.710400 CBS-QB3 Free Energy= -387.752089

0 1

C	-0.92281500	1.81369300	0.03200200
C	0.54429100	1.61124900	-0.38745000
C	-0.98836000	-1.80670600	-0.07975200
C	1.32520800	0.67039500	0.50534400
C	0.41273900	-1.49220500	-0.63371000
C	1.28308600	-0.79439200	0.38141400
H	-0.96762900	2.05343100	1.10254700
H	0.59538700	1.25488800	-1.41940500
H	-0.91275200	-2.62049100	0.65126200
H	0.89770800	-2.42284600	-0.94822200
H	-1.29777600	2.70290800	-0.48615000
H	1.05515200	2.58075000	-0.37790800
H	-1.60353500	-2.19590500	-0.89889400
H	0.34000800	-0.87094200	-1.52862600
C	-1.89550200	0.65312700	-0.26001200
H	-2.90603500	1.03995300	-0.09352000
H	-1.85083300	0.40319100	-1.32755600
C	-1.72472900	-0.63004500	0.58961500
H	-2.71610500	-0.99636700	0.87515200
H	-1.22730900	-0.37252400	1.53117200
H	1.49304500	-1.37315700	1.28263000
H	1.56206800	1.07404600	1.49087300
O	2.41688700	-0.05095500	-0.09225800

cyclooctene – methylperoxyl + oxygen adduct



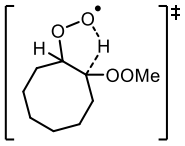
CBS-QB3 Enthalpy= -652.755274 CBS-QB3 Free Energy= -652.812472

0 2

C	2.35410400	1.06736100	0.51416900
C	1.01506000	1.17526900	1.26820100
C	1.28828100	-2.20424700	-0.37484700
C	-0.30746200	0.93881000	0.52660200
C	0.08436100	-1.60663900	0.37236600

C	-0.49138000	-0.34160800	-0.29325800
H	2.26598900	1.55118100	-0.46321300
H	1.03025300	0.51151800	2.13933500
H	0.92712900	-2.69442700	-1.28638400
H	-0.71702800	-2.34608100	0.41138300
H	3.06958700	1.67148900	1.08218000
H	0.93264800	2.18762600	1.67696000
H	1.71492000	-2.99927400	0.24744500
H	-1.12048300	0.99211100	1.25215800
H	0.35248400	-1.40625200	1.41238100
C	2.98384600	-0.33119200	0.34196800
H	4.04248300	-0.16526900	0.11777100
H	2.96801500	-0.86535800	1.30108400
C	2.40840100	-1.22739700	-0.77440200
H	3.22107700	-1.83060900	-1.19204300
H	2.07402700	-0.58804200	-1.59931400
H	-0.02972200	-0.18030100	-1.27042100
O	-1.85939200	-0.49090000	-0.67564700
O	-0.60555300	2.11764700	-0.32023800
O	0.09175500	2.15157800	-1.43703000
O	-2.63576100	-0.73268900	0.54986600
C	-3.96073600	-0.36383900	0.21478600
H	-4.33838300	-0.96731900	-0.61665000
H	-4.54190400	-0.57433900	1.11535900
H	-4.02633900	0.69914700	-0.03715700

cyclooctene – methylperoxyl 1,4-HAT TS

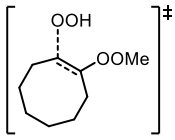


TS freq.: -2002.36 cm^{-1}
CBS-QB3 Enthalpy= -652.714164 CBS-QB3 Free Energy= -652.769371

0 2

C	2.37158900	-1.24918400	-0.37970800
C	1.07798400	-1.36358800	-1.20618000
C	1.36392100	2.09357700	0.27309900
C	-0.27812600	-1.05721200	-0.54695200
C	0.29365400	1.55605900	-0.69402400
C	-0.57540700	0.42507000	-0.16668000
H	2.20199600	-1.70190600	0.60115600
H	1.16049100	-0.78406300	-2.13401700
H	0.86283700	2.59133500	1.11047200
H	-0.37256800	2.38128800	-0.96013200
H	3.10709800	-1.88591600	-0.88391700
H	0.99281100	-2.40806800	-1.52370300
H	1.90933700	2.87726100	-0.26599500
H	-1.07037200	-1.40896300	-1.21476900
H	0.76969600	1.23900300	-1.62709100
C	3.02949600	0.13355600	-0.19444900
H	4.05483800	-0.05798700	0.13798100
H	3.12861300	0.63448100	-1.16700900
C	2.37204600	1.07722700	0.83353200
H	3.15547200	1.65425300	1.33584000
H	1.89923400	0.46965400	1.60828700
H	-0.35027000	0.09510100	1.10939600
O	-1.88194500	0.82537500	-0.37495400
O	-0.48105300	-1.79717300	0.66730500
O	-0.02324500	-0.95873800	1.71614300
O	-2.80300900	-0.17433600	0.15983400
C	-4.09591800	0.34840700	-0.09325100
H	-4.76893500	-0.40586700	0.31807700
H	-4.24473800	1.30138200	0.42268500
H	-4.27696100	0.46452300	-1.16620400

cyclooctene – methylperoxyl – hydroperoxyl radical elimination TS



TS freq.: -454.13 cm^{-1}
CBS-QB3 Enthalpy= -652.723262 CBS-QB3 Free Energy= -652.780235

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0 2
 C                  2.45860400   -1.18349100   -0.52827600
 C                  1.19576900   -1.23294400   -1.41461900
 C                  1.19195200    2.00504100    0.52517700
 C                 -0.14998800   -0.87168000   -0.79946000
 C                  0.36640700    1.66467100   -0.73412300
 C                 -0.51459400    0.45915900   -0.63280700
 H                  2.28868400   -1.82444500    0.33886100
 H                  1.35466000   -0.61365100   -2.30773800
 H                  0.51066000    2.30357800    1.32772800
 H                 -0.26171100    2.52373500   -0.98954000
 H                  3.26013700   -1.64796000   -1.11525800
 H                  1.10896600   -2.25911500   -1.78208100
 H                  1.79423400    2.88810200    0.27861300
 H                 -0.96642200   -1.53473200   -1.05005800
 H                  1.04382500    1.51322200   -1.58001200
 C                  2.97352100    0.18169100   -0.03493800
 H                  3.96518600   -0.00175200    0.39163100
 H                  3.14804500    0.85162300   -0.88787800
 C                  2.10721600    0.88195700    1.03756900
 H                  2.76310100    1.32439300    1.79460100
 H                  1.50332700    0.13603600    1.55579700
 H                 -1.56030300   -0.96789200    1.78199300
 O                 -1.77630900    0.85218800   -0.26559200
 O                 -0.08351300   -1.71897200    0.90608400
 O                 -0.60400400   -0.89221300    1.92098000
 O                 -2.65991500   -0.28792900   -0.04063300
 C                 -3.97017200    0.21815700   -0.25544000
 H                 -4.62098900   -0.63254700   -0.04459200
 H                 -4.19307200    1.03763900    0.43331500
 H                 -4.10068600    0.54380200   -1.29058900
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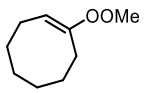
cyclooctene – 1-methylperoxyl



CBS-QB3 Enthalpy= -501.996150 CBS-QB3 Free Energy= -502.046656

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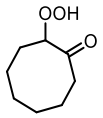
0 1
 C                  2.24810700    1.48010500   -0.30513300
 C                  1.03769700    1.77338400    0.60916200
 C                  1.13088500   -1.91863400    0.11502400
 C                 -0.27532300    1.16678300    0.17010600
 C                  0.23348900   -1.12743400    1.09154500
 C                 -0.62204400   -0.09855600    0.40849900
 H                  1.98225100    1.73004900   -1.33931000
 H                  1.28928400    1.46264900    1.63053500
 H                  0.50803900   -2.61651600   -0.45367100
 H                 -0.40671600   -1.82492000    1.64007700
 H                  3.05409000    2.16833200   -0.02246600
 H                  0.90879900    2.85938000    0.65625800
 H                  1.81517800   -2.53131400    0.71372000
 H                 -0.95131200    1.78557100   -0.40537900
 H                  0.85307800   -0.61808400    1.83298400
 C                  2.82163700    0.04917700   -0.27011100
 H                  3.76780400    0.07748800   -0.82082100
 H                  3.09486200   -0.20885700    0.76165000
 C                  1.94309100   -1.07018300   -0.87862400
 H                  2.58606000   -1.76145100   -1.43363300
 H                  1.26660500   -0.63247500   -1.61911700
 O                 -1.79303500   -0.71188500   -0.00173800
 O                 -2.61813100    0.17951600   -0.79583200
 C                 -3.84739400    0.30024900   -0.09526000
 H                 -4.46344000    0.93175600   -0.73960100
 H                 -4.32718900   -0.67476200    0.03096500
```

```
 H                -3.70892000    0.78275400    0.87712200
```

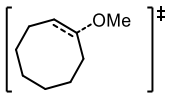
cyclooctene – hydroperoxyl ketone product



CBS-QB3 Enthalpy= -537.940934 CBS-QB3 Free Energy= -537.988988

```
0 1
 C                 0.26339400    1.94374900   -0.08373600
 C                -0.57363700    1.31836200    1.04967900
 C                 2.19627300   -1.06853000   -0.03175500
 C                -1.22205100   -0.07195300    0.84485000
 C                 1.04942500   -1.32447000    0.97101500
 C                -0.30351200   -1.16874800    0.30493200
 H                -0.25338100    1.80075100   -1.03569500
 H                 0.02645400    1.29079600    1.96638000
 H                 2.29169500   -1.94541000   -0.67748000
 H                 1.11835200   -2.35073500    1.34488500
 H                 0.26233500    3.02334400    0.10115200
 H                -1.41821500    1.97859400    1.26522600
 H                 3.12910800   -0.99119300    0.53660100
 H                -1.54275000   -0.42266000    1.83739900
 H                 1.13200600   -0.65718300    1.83117800
 C                 1.74185100    1.51623500   -0.22090900
 H                 2.23356500    2.30123300   -0.80397700
 H                 2.22837400    1.53808700    0.76358300
 C                 2.02958300    0.17168800   -0.92675000
 H                 2.95412300    0.26991000   -1.50431800
 H                 1.24260400   -0.01843200   -1.66430100
 H                -1.97734300   -0.61714200   -1.56733400
 O                -0.63820300   -1.87339600   -0.62548600
 O                -2.45964400   -0.03559400    0.14774500
 O                -2.21651300    0.27174600   -1.25191600
```

cyclooctene – methoxy radical addition TS



TS freq.: -255.16 cm^{-1}
CBS-QB3 Enthalpy= -427.448783 CBS-QB3 Free Energy= -427.498902

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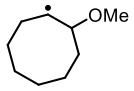
0 2
 C                -1.81540200    1.66016600   -0.05320300
 C                -0.28264500    1.69597200   -0.27135000
 C                -1.21398400   -1.89092100   -0.00196600
 C                 0.51848600    0.86454700    0.68938500
 C                 0.13639200   -1.33026100   -0.49681000
 C                 0.81806600   -0.45727900    0.51656200
 H                -2.03600200    1.92965500    0.98687400
 H                -0.06185800    1.38763600   -1.29846600
 H                -1.03125600   -2.63360800    0.78389200
 H                 0.80111600   -2.15706600   -0.75522800
 H                -2.25166900    2.45289800   -0.67169400
 H                 0.04318000    2.73751100   -0.18621700
 H                -1.66946400   -2.43901100   -0.83512500
 H                 0.93076700    1.37412900    1.55653600
 H                -0.01400500   -0.76254300   -1.41812300
 C                -2.53405400    0.34028200   -0.38984800
 H                -3.60854900    0.54614200   -0.34307700
 H                -2.33306500    0.07146700   -1.43437900
 C                -2.22519400   -0.86131200    0.53454000
 H                -3.15583500   -1.40140900    0.73770100
 H                -1.88485600   -0.48512900    1.50531500
 H                 1.33447000   -0.96876500    1.32412900
 O                 2.56481700   -0.21752000   -0.61090700
 C                 3.66437100    0.18311000    0.13653600
 H                 3.82254500   -0.41568300    1.04869200
 H                 4.54731000    0.02843400   -0.50492000
```

H	3.65240800	1.24967500	0.40826500

cyclooctene – methoxy adduct

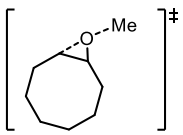


CBS-QB3 Enthalpy= -427.485208 CBS-QB3 Free Energy= -427.533611

0 2

C	-1.80324300	1.64742100	-0.10487100
C	-0.25923200	1.69532000	-0.24811200
C	-1.06529600	-1.88486200	0.07657700
C	0.47420400	0.81342600	0.70738700
C	0.21439100	-1.35859700	-0.58735700
C	1.11504000	-0.47249200	0.28318800
H	-2.07083000	1.96998200	0.90901600
H	0.01850300	1.44558800	-1.27722600
H	-0.79528200	-2.55240000	0.90423900
H	0.82323100	-2.20737900	-0.91271900
H	-2.22961500	2.39266600	-0.78635500
H	0.04822500	2.73815500	-0.09205100
H	-1.57430700	-2.51737500	-0.66026800
H	0.50527400	1.10030600	1.75450700
H	-0.03037400	-0.80176800	-1.49664400
C	-2.46470800	0.28573300	-0.37900600
H	-3.54807300	0.43722700	-0.33281600
H	-2.25550300	-0.02302200	-1.41030600
C	-2.07586800	-0.84577800	0.60328700
H	-2.97807900	-1.39535600	0.89228900
H	-1.69764000	-0.39893400	1.52886500
H	1.42360900	-1.03617600	1.17757400
O	2.28708200	-0.24434300	-0.53317500
C	3.37173000	0.34074400	0.16059300
H	3.68449700	-0.27770000	1.01540700
H	4.19992800	0.40714400	-0.54630100
H	3.13766700	1.34829500	0.52806600

cyclooctene – methoxy fragmentation TS



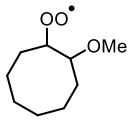
TS freq.: -809.50 cm^{-1}
CBS-QB3 Enthalpy= -427.412785 CBS-QB3 Free Energy= -427.462522

0 2

C	2.01451400	-1.44163600	-0.14189700
C	0.50151600	-1.73083000	-0.29980300
C	0.82137400	1.97424800	-0.00651500
C	-0.36013800	-1.06315700	0.72422600
C	-0.43640800	1.22623200	-0.47888500
C	-0.98101000	0.25542800	0.55472600
H	2.32679900	-1.69768300	0.87819700
H	0.17962000	-1.43736500	-1.30252600
H	0.54545700	2.67408600	0.79156100
H	-1.21811700	1.95533900	-0.71682800
H	2.55075600	-2.13113600	-0.80399900
H	0.35090800	-2.81342000	-0.23402700
H	1.18347600	2.59315900	-0.83549900
H	-0.49862500	-1.55308300	1.68024200
H	-0.23700100	0.68332500	-1.40619800
C	2.47629700	-0.00801300	-0.46069300
H	3.57101900	-0.01606100	-0.44861400
H	2.19676100	0.24302500	-1.49140500
C	1.98187500	1.09761300	0.50386700
H	2.81565200	1.76992300	0.73072700
H	1.70649900	0.64141000	1.46121300
H	-1.23485700	0.76879200	1.49211600
O	-1.99159100	-0.63927700	0.12378100
C	-3.76400900	0.15363800	-0.33614900

H	-4.28956300	-0.78423300	-0.44639900
H	-3.98321000	0.73259200	0.55235000
H	-3.55690700	0.70440100	-1.24442100

cyclooctene – methoxy + oxygen adduct

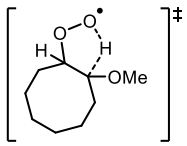


CBS-QB3 Enthalpy= -577.695681 CBS-QB3 Free Energy= -577.748727

0 2

C	1.85644800	-1.43644100	-0.16121100
C	0.70278700	-1.33673400	-1.17557400
C	1.35568900	2.05078600	0.26912600
C	-0.65889400	-0.76141200	-0.75573100
C	0.25255700	1.64627500	-0.72180900
C	-0.77340100	0.65235700	-0.14961100
H	1.47527300	-1.81543300	0.79156900
H	1.03655000	-0.78387000	-2.06001000
H	0.91534100	2.70312300	1.03236400
H	-0.31115200	2.53641900	-1.00731200
H	2.52760200	-2.21253300	-0.54503500
H	0.47897000	-2.34720900	-1.53340400
H	2.08715000	2.66526800	-0.26854400
H	-1.31184300	-0.78111500	-1.63273000
H	0.69737900	1.26318100	-1.64347100
C	2.71488000	-0.18177800	0.09400900
H	3.63273400	-0.53037000	0.57843600
H	3.03462000	0.25029900	-0.86342500
C	2.09623200	0.91106400	0.98904000
H	2.89328600	1.37332800	1.58055500
H	1.43303800	0.43397000	1.71902700
H	-0.64147800	0.55970500	0.93515100
O	-2.06660600	1.19659700	-0.41284500
C	-3.12805700	0.68923000	0.38324000
H	-2.87225500	0.71463900	1.45087400
H	-3.98556600	1.33893600	0.20466200
H	-3.39641400	-0.33940000	0.11765900
O	-1.33426200	-1.74893600	0.12043400
O	-0.87446700	-1.75129000	1.35675600

cyclooctene – methoxy 1,4-HAT TS



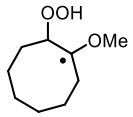
TS freq.: -1844.66 cm^{-1}
CBS-QB3 Enthalpy= -577.660040 CBS-QB3 Free Energy= -577.710742

0 2

C	1.90360000	-1.42214300	-0.21081700
C	0.69066300	-1.43501900	-1.15961100
C	1.22117000	2.04055500	0.21241600
C	-0.68039100	-0.95297900	-0.66015700
C	0.16583500	1.56194700	-0.80252700
C	-0.83620600	0.55077300	-0.27865300
H	1.59315800	-1.80476400	0.76514900
H	0.92896200	-0.90880800	-2.09193800
H	0.72229900	2.64083000	0.98135800
H	-0.40775700	2.42600000	-1.14547300
H	2.60741400	-2.15781000	-0.61575100
H	0.51964900	-2.47706400	-1.44967000
H	1.89383900	2.72364400	-0.31932400
H	-1.41856800	-1.20104100	-1.43302600
H	0.67403100	1.15812800	-1.68367300
C	2.69227700	-0.11045100	-0.01717300
H	3.65555500	-0.39526200	0.41819500
H	2.93351400	0.32826800	-0.99474800

C	2.05800200	0.95184800	0.90472200
H	2.85564100	1.46524500	1.45170000
H	1.45873900	0.44074500	1.66283100
H	-0.66470700	0.18508300	0.98383200
O	-2.10913800	1.06179300	-0.42634900
C	-3.20527100	0.35316700	0.16334400
H	-3.02960000	0.20793700	1.23254700
H	-4.08044000	0.98018600	0.00141700
H	-3.35441200	-0.62451500	-0.30073800
O	-1.12858700	-1.66263700	0.50810200
O	-0.63044800	-0.92578000	1.62175200

cyclooctene – methoxy – hydroperoxyl

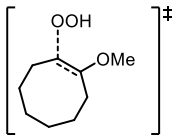


CBS-QB3 Enthalpy= -577.684961 CBS-QB3 Free Energy= -577.738078

0 2

C	1.93339300	-1.36703000	-0.20129500
C	0.75108500	-1.43123000	-1.18834400
C	1.10685700	2.09294500	0.22090800
C	-0.64040600	-0.93978000	-0.74622000
C	0.18014600	1.59038900	-0.91278300
C	-0.79690200	0.53439900	-0.52794600
H	1.61843600	-1.79556500	0.75336200
H	1.01294800	-0.92395900	-2.12506300
H	0.50576300	2.65179800	0.94537900
H	-0.37827800	2.45062800	-1.30214600
H	2.69238300	-2.04782300	-0.60389000
H	0.60775400	-2.48366600	-1.45204500
H	1.81016100	2.81046700	-0.21928400
H	-1.34437300	-1.28330200	-1.52466600
H	0.79653900	1.22302500	-1.73736100
C	2.63564000	-0.01834700	0.06086900
H	3.58509100	-0.26090600	0.54928900
H	2.91308700	0.45080400	-0.89257600
C	1.88462200	0.99209900	0.95725000
H	2.60437800	1.48707300	1.61758000
H	1.20603800	0.43738500	1.60984500
H	-1.17562200	-0.43834800	1.77386900
O	-1.84568300	0.96640900	0.25603500
C	-3.17051100	0.55637700	-0.12660000
H	-3.28861000	-0.52636500	-0.04502800
H	-3.85042800	1.05356800	0.56435700
H	-3.38879600	0.88354800	-1.14806900
O	-1.17546500	-1.70307100	0.36690700
O	-0.63260300	-1.23174900	1.62973500

cyclooctene – methoxy – hydroperoxyl radical elimination TS



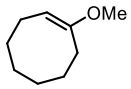
TS freq.: -390.98 cm^{-1}
CBS-QB3 Enthalpy= -577.664259 CBS-QB3 Free Energy= -577.717892

0 2

C	1.92052000	-1.29176200	-0.57299800
C	0.68131500	-1.17714700	-1.48597400
C	1.05778700	1.97124600	0.57102100
C	-0.63540800	-0.71490800	-0.88569200
C	0.15975300	1.72283100	-0.65881200
C	-0.85822300	0.62788500	-0.56816800
H	1.64343400	-1.89668800	0.29392500
H	0.92227100	-0.54064600	-2.34931000
H	0.43479800	2.30480700	1.40762500
H	-0.38898100	2.64340200	-0.87772500

H	2.65475300	-1.87761700	-1.13833600
H	0.50203400	-2.17432000	-1.89582100
H	1.70823500	2.81647600	0.31545800
H	-1.49707600	-1.26123000	-1.25378000
H	0.80069000	1.52545000	-1.52325400
C	2.63246000	-0.01215300	-0.08959300
H	3.60475700	-0.33463300	0.29742900
H	2.86443400	0.63828200	-0.94383100
C	1.91964900	0.78187900	1.02679900
H	2.67255600	1.17795700	1.71675600
H	1.30531500	0.09042800	1.60535500
H	-1.31943600	-0.79864500	2.21269200
O	-2.05847600	1.09110800	-0.13422000
C	-3.19881200	0.22617900	-0.14605800
H	-2.98404800	-0.71773600	0.35944600
H	-3.98688400	0.77205900	0.36976000
H	-3.51540500	0.02378000	-1.17473100
O	-0.88182500	-1.79500400	0.67006700
O	-0.49666000	-1.19553200	1.89355300

cyclooctene – 2-methoxy

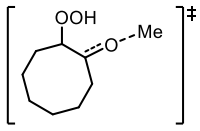


CBS-QB3 Enthalpy= -426.941273 CBS-QB3 Free Energy= -426.987321

0 1

C	-1.97306600	-1.33928400	-0.32091100
C	-0.79778100	-1.74675600	0.59582600
C	-0.56080800	1.93631900	0.13418500
C	0.56922800	-1.25674000	0.17205100
C	0.24648600	1.05128700	1.10816300
C	1.03352900	-0.02293500	0.41399600
H	-1.72489300	-1.60337600	-1.35626700
H	-1.02566800	-1.42472500	1.61893700
H	0.13247500	2.57408300	-0.42408600
H	0.93933200	1.67945000	1.67502300
H	-2.83764200	-1.95695200	-0.04818200
H	-0.76857400	-2.84051600	0.63341500
H	-1.18699000	2.60923800	0.73182500
H	1.17684300	-1.95978200	-0.38567600
H	-0.43246600	0.59103100	1.82913800
C	-2.42146300	0.13546700	-0.27791400
H	-3.36289200	0.19247000	-0.83470700
H	-2.67794800	0.40867000	0.75404900
C	-1.44583100	1.17932500	-0.87171600
H	-2.02355900	1.93218700	-1.41849400
H	-0.81184300	0.69040800	-1.61817800
O	2.25027800	0.46356000	0.01326100
C	3.11051700	-0.39897500	-0.71328200
H	2.65356500	-0.71732500	-1.65749900
H	4.01097100	0.17742900	-0.92140800
H	3.37221000	-1.28701300	-0.12635600

cyclooctene – 2-methoxy 1-hydroperoxyl ether fragmentation TS



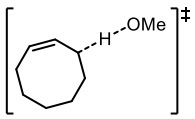
TS freq.: -663.07 cm^{-1}
CBS-QB3 Enthalpy= -577.647776 CBS-QB3 Free Energy= -577.702465

0 2

C	-1.16078900	-1.77303500	-0.67793400
C	-0.34942300	-1.93611300	0.61985100
C	-1.73567900	1.56748500	0.42758200
C	0.83693800	-0.98840200	0.90998700
C	-0.71250800	1.03028100	1.46119400
C	0.57917600	0.51413800	0.88497600
H	-0.48211200	-1.56421000	-1.50910000

H	-1.03290500	-1.90782700	1.47686400
H	-1.44323600	2.58007900	0.13330500
H	-0.47566200	1.83991800	2.16105100
H	-1.60479800	-2.75202400	-0.88905100
H	0.09585000	-2.93548400	0.63033400
H	-2.69886300	1.67303700	0.93969000
H	1.15115300	-1.22006200	1.94198300
H	-1.18190200	0.23559200	2.04692300
C	-2.31434800	-0.74908100	-0.67711200
H	-2.97009800	-1.01679000	-1.51207700
H	-2.92498900	-0.87836800	0.22657600
C	-1.93078000	0.73568100	-0.84965500
H	-2.71473500	1.23349300	-1.43044500
H	-1.02877400	0.79059700	-1.46741300
H	2.33458000	-0.04983700	-1.08857000
O	1.49152000	1.30624700	0.47251200
C	1.35128500	2.32777600	-1.08199500
H	1.08191700	1.63598800	-1.87160900
H	0.60024500	3.06266600	-0.82608600
H	2.36792300	2.69782600	-1.10465300
O	2.02253200	-1.35540300	0.20965500
O	1.92884500	-0.92546600	-1.17705300

cyclooctene –methoxy H-abstraction TS



TS freq.: -1163.57 cm^{-1}
CBS-QB3 Enthalpy= -427.444131 CBS-QB3 Free Energy= -427.495404

0 2

C	1.76488500	-1.32787100	-0.65505500
C	0.49161600	-1.75610100	0.10909300
C	0.46771200	1.92913900	0.12371400
C	0.32414400	-1.15901900	1.48408900
C	-0.61872600	1.07753400	0.79969500
C	-0.19657300	0.04166600	1.77464100
H	2.64269800	-1.43895300	-0.00650800
H	-0.37467500	-1.50562500	-0.50938800
H	0.69137500	2.76598100	0.80076800
H	-1.38411800	1.73457200	1.22340800
H	1.90373900	-2.03550300	-1.48025400
H	0.50766400	-2.84549400	0.21314900
H	0.03018600	2.38430700	-0.77254600
H	0.63082100	-1.78446700	2.31981300
H	-1.23505400	0.55174100	-0.13270000
C	1.74436700	0.09015000	-1.24972800
H	2.61325700	0.17105900	-1.91165000
H	0.86416800	0.19820100	-1.89391600
C	1.79988300	1.25727800	-0.23835700
H	2.43536200	2.04702200	-0.65308400
H	2.30070200	0.92212300	0.67614800
H	-0.32672000	0.29513100	2.82632900
O	-2.00542600	0.11847000	-1.11627600
C	-3.20821600	-0.32442600	-0.55753200
H	-3.81448800	-0.70485900	-1.39193100
H	-3.07433900	-1.15281500	0.15328700
H	-3.78172700	0.47972100	-0.07409000

cyclooctenyl radical

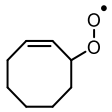
CBS-QB3 Enthalpy= -311.941985 CBS-QB3 Free Energy= -311.983669

0 2

C	-1.17404000	-1.31626400	-0.33611500
C	0.07041500	-1.61915200	0.54879100
C	0.07043100	1.61915500	0.54878700
C	1.39888900	-1.26071500	-0.05852600

C	1.39890000	1.26070000	-0.05852400
C	1.92128600	-0.00000900	-0.31112200
H	-0.88284000	-1.35199600	-1.39160800
H	-0.05907900	-1.12958900	1.52136900
H	0.08545700	2.69145500	0.76047200
H	2.01570800	2.09998000	-0.36640000
H	-1.89596200	-2.12714600	-0.19199700
H	0.08542800	-2.69145100	0.76048600
H	-0.05906400	1.12960200	1.52137100
H	2.01569300	-2.10000200	-0.36638700
C	-1.90747200	0.00000700	-0.04126400
H	-2.83630800	0.00001500	-0.62388400
H	-2.21625700	0.00000700	1.01284400
C	-1.17402700	1.31627200	-0.33611200
H	-1.89594400	2.12715800	-0.19198800
H	-0.88283500	1.35200600	-1.39160800
H	2.89972100	-0.00000900	-0.78816200

cyclooctene peroxyl radical

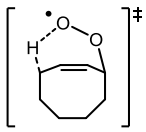


CBS-QB3 Enthalpy= -462.138008 CBS-QB3 Free Energy= -462.184543

0 2

C	2.45726200	-0.36758900	-0.29088800
C	-1.08875100	0.37117600	0.59308200
C	1.33889500	-1.33564500	-0.75338300
C	-0.61332500	-1.02517100	0.88521300
C	0.37471300	-1.73657500	0.33678600
H	0.79678600	-0.89752000	-1.59148300
H	3.19104400	-0.93132700	0.29593100
H	-1.14094200	0.93083700	1.53405600
H	1.81261300	-2.23851600	-1.14842200
H	-1.19459600	-1.50142900	1.67155800
H	0.52499700	-2.73202200	0.74899000
C	-0.40546200	1.22423100	-0.47499100
H	-1.06922100	2.07445800	-0.66058400
O	-2.54624000	0.29436100	0.26131000
O	-2.76851300	-0.36303400	-0.85652400
C	0.97965900	1.78529000	-0.08858700
H	1.41836500	2.23226200	-0.98826400
H	0.82594400	2.61519200	0.61099900
C	1.99886300	0.82862300	0.55314900
H	2.88621100	1.41695500	0.81161300
H	1.60212400	0.46132000	1.50475300
H	-0.37392100	0.66424900	-1.40796800
H	2.98750000	-0.01111400	-1.18176400

cyclooctene peroxyl radical 1,6-HAT TS



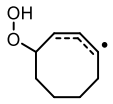
TS freq.: -1775.98 cm^{-1}
CBS-QB3 Enthalpy= -462.099973 CBS-QB3 Free Energy= -462.144159

0 2

C	1.47823500	-0.98785300	-0.78668500
C	-1.08261000	0.92173200	0.49569200
C	0.27901900	-1.70269900	-0.12816000
C	-0.67840600	-0.11506700	1.52031200
C	-0.15639100	-1.32030900	1.21441400
H	-0.77195200	-1.23968500	-0.84427800
H	2.23816400	-1.75603400	-0.96851000
H	-1.68152100	1.67630100	1.00882000
H	0.30035400	-2.78065400	-0.28621800
H	-1.00890200	0.06401200	2.53849700
H	-0.13511300	-2.07881800	1.99502000

C	-0.01212300	1.61631500	-0.37086000
H	-0.27903600	2.67399500	-0.44724600
O	-2.11180800	0.26363200	-0.32780100
O	-1.54657500	-0.47589100	-1.37072900
C	1.44682000	1.52108400	0.09917200
H	2.01265500	2.21678200	-0.52859600
H	1.53160100	1.91283000	1.11853500
C	2.14471000	0.13056500	0.03734700
H	3.14605000	0.28062800	-0.37809300
H	2.29847900	-0.24487400	1.05186500
H	-0.09938800	1.20999900	-1.37864500
H	1.20014700	-0.61902300	-1.78030300

cyclooctenyl radical - hydroperoxyl

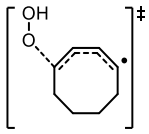


CBS-QB3 Enthalpy= -462.138230 CBS-QB3 Free Energy= -462.186271

0 2

C	-1.01556700	-1.38960900	-0.74676100
C	-2.28475700	-0.81413800	-0.09505000
C	0.98815700	0.71196300	0.45124700
C	-2.38618000	0.67922500	0.02740400
C	-0.03427300	1.70708700	-0.01895800
C	-1.42494200	1.67809000	-0.05327200
H	-0.64673100	-0.69453400	-1.50602800
H	-2.43888900	-1.28226000	0.89105500
H	3.10026900	-0.92589700	-0.71681600
H	-1.28290400	-2.30973500	-1.27618100
H	-3.15725200	-1.12966500	-0.68010000
H	1.63438400	1.26191000	1.14984200
H	-3.40880300	1.04208500	0.09725400
H	0.41787900	2.65991800	-0.27749600
H	-1.85771600	2.67037500	-0.17853200
C	0.10241600	-1.71838700	0.24572200
H	0.97578400	-2.07366600	-0.31046500
H	-0.21408400	-2.55631800	0.87850300
C	0.52413200	-0.56570300	1.16200900
H	-0.28828000	-0.29591400	1.84484300
H	1.34873700	-0.91233000	1.79023900
O	1.80068400	0.44365300	-0.71277800
O	3.07477600	-0.09179500	-0.22974200

cyclooctenyl radical - hydroperoxyl elimination TS



TS freq.: -450.11 cm^{-1}
CBS-QB3 Enthalpy= -462.103541 CBS-QB3 Free Energy= -462.151293

0 2

C	1.24284800	0.57098400	1.25190200
C	-0.86212600	-0.48335000	-0.98808100
C	1.26729500	1.65459500	0.21702500
C	-0.62656000	0.86405500	-1.24950900
C	0.43742600	1.74535700	-0.84980000
H	-3.63995200	-0.30586400	0.47951300
H	1.65385100	0.95297300	2.19129900
H	-1.74674600	-0.86760100	-1.48640300
H	2.00076300	2.44755200	0.34193200
H	-1.40878700	1.35753000	-1.82122500
H	0.52163700	2.64392400	-1.45785200
C	0.13086000	-1.58857200	-0.67615800
H	0.03127500	-2.30623900	-1.49942900
O	-1.81297100	-0.55002900	0.78026400
O	-2.94511700	0.24873800	0.86591100
C	1.62417100	-1.25398400	-0.52868800

H	2.18795700	-2.17813500	-0.69497900
H	1.92353300	-0.57097900	-1.32899000
C	2.04250300	-0.68091500	0.83111500
H	3.11255600	-0.44557700	0.80020100
H	1.91420800	-1.44589500	1.60552100
H	-0.22956700	-2.12290800	0.21199100
H	0.20547000	0.28252800	1.44219500

cyclooctadiene

CBS-QB3 Enthalpy= -311.376902 CBS-QB3 Free Energy= -311.416403

0 1

C	-0.96326200	-1.09393600	0.76546700
C	1.33480000	1.16072000	0.35026400
C	0.01896800	-1.75460500	-0.15902800
C	1.84948800	-0.04884600	0.07919100
C	1.22656700	-1.26236400	-0.46507000
H	-1.60145300	-1.84838500	1.23618100
H	2.02862800	1.87157200	0.79769500
H	-0.28807000	-2.68751900	-0.62590100
H	2.91202600	-0.16400400	0.29080200
H	1.86359600	-1.84983600	-1.12353000
C	-0.02028400	1.77698800	0.08858500
H	0.17946200	2.72724400	-0.42418500
C	-1.06615700	1.00484900	-0.73270500
H	-1.78388200	1.72959800	-1.13170900
H	-0.57908800	0.55124300	-1.59998600
C	-1.85345300	-0.06061000	0.04368400
H	-2.52473900	-0.57859400	-0.65085300
H	-2.49549800	0.42813000	0.78609600
H	-0.45492700	2.07766400	1.05362200
H	-0.41605700	-0.59028600	1.56944500

norbornene

CBS-QB3 Enthalpy= -272.162362 CBS-QB3 Free Energy= -272.197150

0 1

C	-0.22194600	-1.27849300	0.78022100
C	-0.22194600	0.25070500	1.12789200
C	-0.22194600	0.25070500	-1.12789200
C	-0.22194600	-1.27849300	-0.78022100
H	0.64271200	-1.79130500	1.20497700
H	-1.12069600	-1.75888200	1.17650900
H	0.64271200	-1.79130500	-1.20497700
H	-1.12069600	-1.75888200	-1.17650900
C	-1.13162800	0.79242000	0.00000000
H	-1.20463800	1.88166300	0.00000000
H	-2.13395500	0.35274400	0.00000000
C	1.12576500	0.78896400	0.66854000
C	1.12576500	0.78896400	-0.66854000
H	-0.50825600	0.47852100	2.15451400
H	-0.50825600	0.47852100	-2.15451400
H	1.95918500	1.01014400	1.32406100
H	1.95918500	1.01014400	-1.32406100

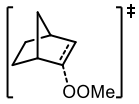
norbornene – methylperoxyl radical addition TS – exo path

TS freq.: -435.89 cm^{-1}
CBS-QB3 Enthalpy= -462.107436 CBS-QB3 Free Energy= -462.154210

0 2

C	-2.34942300	-0.86969600	-0.51464100
C	-0.97821500	-1.06085900	0.20846300
C	-1.34080600	1.16632400	0.38566200
C	-2.62161600	0.66121100	-0.36703500
H	-2.31302100	-1.19327800	-1.55709800
H	-3.12200200	-1.45999300	-0.01586100
H	-2.75960000	1.16309000	-1.32653500
H	-3.51184200	0.85276700	0.23886000
C	-1.09817200	-0.02179700	1.34730900
H	-0.18068600	0.07362600	1.92655800
H	-1.94523300	-0.21104200	2.01248200
C	0.06999200	-0.38485100	-0.66106300
C	-0.20409700	0.97598900	-0.59043800
H	-0.74197900	-2.08558400	0.48916400
H	-1.44181600	2.15809300	0.82578900
H	0.52096700	-0.86788000	-1.51758000
H	0.21071400	1.74612500	-1.22801300
O	1.64100900	-0.72941800	0.42218800
O	2.77259100	-0.52736500	-0.35014100
C	3.40041700	0.68734400	0.05148400
H	3.63963500	0.66159500	1.11783600
H	4.31625000	0.75144700	-0.53997600
H	2.75133000	1.54329900	-0.16044400

norbornene – methylperoxyl radical addition TS - endo path

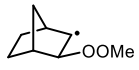


TS freq.: -465.71 cm^{-1}
CBS-QB3 Enthalpy= -462.101139 CBS-QB3 Free Energy= -462.147775

0 2

C	1.25688500	-1.39336900	0.39082900
C	1.19067600	-0.61940600	-0.96118300
C	1.64717600	1.01604200	0.53487400
C	1.51061400	-0.26246500	1.43344400
H	0.34941600	-1.95808200	0.58922500
H	2.09445800	-2.09485500	0.35834900
H	0.69165200	-0.16533900	2.14676800
H	2.43236800	-0.42766800	1.99786600
C	2.32484900	0.41343300	-0.72676500
H	2.43369500	1.13711700	-1.53727700
H	3.29254300	-0.05612500	-0.52240300
C	-0.03179400	0.30253500	-0.93624400
C	0.29283400	1.32853600	-0.05425900
H	1.26643300	-1.25366200	-1.84316200
H	2.14789100	1.85251100	1.02189900
H	-0.71632900	0.39736100	-1.76655300
H	-0.32518500	2.18064200	0.19557100
O	-1.40642400	-0.73567200	-0.02981000
O	-2.64633600	-0.32315400	-0.49875500
C	-3.31610800	0.40026700	0.53000300
H	-2.78111200	1.32570500	0.76647900
H	-4.30430400	0.63095300	0.12638900
H	-3.41023900	-0.21138400	1.43116900

norbornene – methylperoxyl adduct - exo path



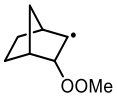
CBS-QB3 Enthalpy= -462.135565 CBS-QB3 Free Energy= -462.183750

0 2

C	1.77858900	1.33980800	-0.41760600
C	0.52094500	0.86021900	0.35058700
C	1.83402900	-0.99084000	0.30187300
C	2.71545500	0.08855300	-0.40781600
H	1.53627400	1.66995500	-1.43153600
H	2.24244200	2.18601100	0.09405200
H	3.02132000	-0.22240000	-1.40863900

H	3.62350200	0.27149500	0.17470800
C	1.12806700	-0.12075700	1.37552600
H	0.36966400	-0.66699600	1.93800600
H	1.82746800	0.35464400	2.06871200
C	-0.24671900	-0.11034500	-0.57987100
C	0.68279500	-1.28922200	-0.61068500
H	-0.10997000	1.65735100	0.74009900
H	2.39272700	-1.86007000	0.64972900
H	-0.46375100	0.32583100	-1.56357300
H	0.57630100	-2.14353100	-1.26541400
O	-1.48671600	-0.57078700	-0.02485200
O	-2.41731400	0.57081400	-0.11878700
C	-3.69486200	0.01277100	0.10193300
H	-3.94582300	-0.72742300	-0.66555100
H	-3.76467000	-0.44542200	1.09464200
H	-4.38304100	0.85922000	0.04023700

norbornene – methylperoxyl adduct - endo path

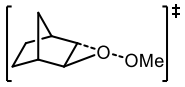


CBS-QB3 Enthalpy= -462.135161 CBS-QB3 Free Energy= -462.182782

0 2

C	1.01302900	1.45634500	-0.26138000
C	0.61312100	0.53216900	0.91253500
C	2.07274300	-0.74574300	-0.27035200
C	2.04560100	0.60295900	-1.06429000
H	0.14493700	1.73342300	-0.85903900
H	1.46719100	2.37478900	0.11794700
H	1.75349500	0.45625000	-2.10569100
H	3.04038500	1.05963600	-1.05809500
C	1.92998800	-0.22518600	1.18483200
H	1.83126800	-1.02967100	1.91828700
H	2.74658900	0.43572700	1.48849300
C	-0.26307500	-0.62571300	0.35239100
C	0.73761000	-1.39649000	-0.45934500
H	0.15682900	1.04657000	1.75723500
H	2.93689200	-1.37242900	-0.49291200
H	-0.69532500	-1.21454700	1.17632500
H	0.47187500	-2.12194800	-1.21655600
O	-1.33312400	-0.23119500	-0.50462200
O	-2.34527400	0.40143600	0.35492000
C	-3.59225500	-0.00679200	-0.17184500
H	-3.72470000	-1.09173500	-0.10005100
H	-4.33474200	0.50019300	0.44936300
H	-3.70808100	0.31251900	-1.21296300

norbornene – methylperoxyl fragmentation TS - exo path



TS freq.: -628.93 cm^{-1}
CBS-QB3 Enthalpy= -462.116492 CBS-QB3 Free Energy= -462.163800

0 2

C	2.02121600	1.20185400	-0.42059800
C	0.60975400	1.00237100	0.18744700
C	1.57865500	-1.03684000	0.47501300
C	2.71736800	-0.17964200	-0.18487100
H	1.97685400	1.46517600	-1.48117600
H	2.55550400	2.00622300	0.08901400
H	3.09887700	-0.62749900	-1.10476000
H	3.55534300	-0.09810900	0.51315000
C	0.90056500	0.04086600	1.35803800
H	-0.00390400	-0.31487800	1.84685600
H	1.58644400	0.46056500	2.09782100
C	-0.15465800	0.07067300	-0.77948800
C	0.58284300	-1.21143700	-0.62553200
H	0.06871900	1.91565700	0.42772100
H	1.92610600	-1.94627800	0.96335400

H	-0.33359300	0.48007400	-1.77894600
H	0.44887500	-2.07339700	-1.26261600
O	-1.26335900	-0.57030900	-0.22936800
O	-2.54010100	0.66443600	-0.09195600
C	-3.66597300	-0.09176800	0.21598300
H	-3.58286900	-0.60542200	1.18385900
H	-4.49314400	0.63061500	0.28637600
H	-3.91414600	-0.82221300	-0.56601500

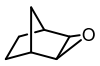
norbornene – methylperoxyl fragmentation TS - endo path

TS freq.: -597.57 cm^{-1}
CBS-QB3 Enthalpy= -462.111495 CBS-QB3 Free Energy= -462.158393

0 2

C	0.74870800	1.50218600	0.06012400
C	0.81527500	0.36935500	1.10473000
C	1.93220900	-0.52159600	-0.66234300
C	1.47972200	0.88818600	-1.17384300
H	-0.28039700	1.77825500	-0.15914300
H	1.27619200	2.38395100	0.43296400
H	0.82854100	0.80674400	-2.04389800
H	2.36233700	1.46689600	-1.45929500
C	2.22137500	-0.21417700	0.83914700
H	2.44692700	-1.11112500	1.42249100
H	3.02686300	0.51207200	0.97961300
C	-0.08966800	-0.80938700	0.60834100
C	0.73368900	-1.39496100	-0.48161000
H	0.59831500	0.67864700	2.12645500
H	2.73100800	-0.96939600	-1.25386900
H	-0.46373200	-1.45719900	1.40920100
H	0.47509800	-2.28998400	-1.02824400
O	-1.04390300	-0.49861200	-0.35019000
O	-2.41239300	0.32143000	0.51888000
C	-3.49273400	0.09154100	-0.32465400
H	-3.72412700	-0.97590100	-0.44144200
H	-4.35275700	0.57777000	0.16152200
H	-3.36535700	0.54984900	-1.31522100

norbornene oxide - exo path



CBS-QB3 Enthalpy= -347.296262 CBS-QB3 Free Energy= -347.332367

0 1

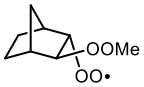
C	-1.29112700	0.87780500	0.78400600
C	0.13846400	0.37723100	1.13740000
C	0.13846400	0.37723100	-1.13740000
C	-1.29112700	0.87780500	-0.78400600
H	-2.06862400	0.23150300	1.20014300
H	-1.45715300	1.88153000	1.18220400
H	-2.06862400	0.23150300	-1.20014300
H	-1.45715300	1.88153000	-1.18220400
C	0.96759600	1.01040000	0.00000000
H	2.00876900	0.69548200	0.00000000
H	0.91058100	2.10120600	0.00000000
C	0.13846400	-1.09963500	0.73423600
C	0.13846400	-1.09963500	-0.73423600
H	0.46093200	0.59234700	2.15654500
H	0.46093200	0.59234700	-2.15654500
H	-0.36545400	-1.84996900	1.33533600
H	-0.36545400	-1.84996900	-1.33533600
O	1.28825700	-1.55434000	0.00000000

norbornene oxide - endo path

CBS-QB3 Enthalpy= -347.288241 CBS-QB3 Free Energy= -347.324203

```
0 1
 C                -1.07080600   -0.88905000    0.78187800
 C                -0.31965700    0.41864200    1.13324400
 C                -0.31965600    0.41866500   -1.13323500
 C                -1.07080500   -0.88903400   -0.78189700
 H                -0.57311400   -1.76876700    1.18922000
 H                -2.08662700   -0.85293700    1.18382000
 H                -0.57311300   -1.76874400   -1.18925600
 H                -2.08662700   -0.85291300   -1.18383800
 C                -0.80592000    1.36207000    0.00001300
 H                -0.29285400    2.32798800    0.00002300
 H                -1.88705300    1.53315400    0.00001500
 C                 1.16629000    0.27432200    0.73505600
 C                 1.16629000    0.27433600   -0.73505100
 H                -0.46760100    0.76699400    2.15593400
 H                -0.46759900    0.76703700   -2.15591900
 H                 1.96094000    0.67977100    1.35314100
 H                 1.96094000    0.67979700   -1.35312500
 O                 1.50478700   -0.91638500   -0.00000900
```

norbornene – methylperoxyl + oxygen adduct - exo path



CBS-QB3 Enthalpy= -612.354261 CBS-QB3 Free Energy= -612.405322

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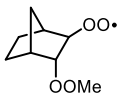
0 2
 C                 2.03840300   -0.53378400    1.29510000
 C                 0.96897500   -1.33238600    0.51124800
 C                 1.65337300    0.23786000   -0.98060100
 C                 2.54221000    0.51680000    0.25458400
 H                 1.62720100   -0.06810800    2.19401300
 H                 2.84509800   -1.19700400    1.61457300
 H                 2.45305900    1.54253300    0.61026500
 H                 3.59005400    0.34595900   -0.00277200
 C                 1.52915500   -1.30216400   -0.92920300
 H                 0.83291100   -1.71582200   -1.66025700
 H                 2.49539900   -1.80227100   -1.02845100
 C                -0.27295500   -0.43456400    0.36225700
 C                 0.20273900    0.63771700   -0.65783100
 H                 0.73353000   -2.31063100    0.92936100
 H                 2.02639600    0.66752800   -1.91017700
 H                -0.60059200    0.02816500    1.29805000
 H                -0.45283400    0.64650800   -1.52748100
 O                -1.30047200   -1.27319500   -0.16658200
 O                 0.18702000    1.99350600   -0.10964300
 O                -1.00680200    2.36109900    0.31167400
 O                -2.42105500   -0.45246300   -0.59417400
 C                -3.37863900   -0.44124500    0.45410500
 H                -4.20761000    0.14693100    0.05433900
 H                -3.71826600   -1.45455600    0.68716700
 H                -2.99344500    0.04978000    1.35321100
```

norbornene – methylperoxyl + oxygen adduct - endo path

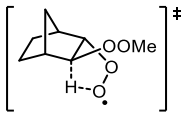


CBS-QB3 Enthalpy= -612.354714 CBS-QB3 Free Energy= -612.405882

```
0 2
 C                -1.77155600   -1.66390600   -0.04362500
 C                -1.09630800   -0.81157700    1.05569900
 C                -1.75468300    0.74315500   -0.46260100
```

C	-2.17659500	-0.59899400	-1.11170700
H	-1.10689900	-2.42844400	-0.44186100
H	-2.65176400	-2.16333900	0.36834800
H	-1.68106000	-0.76281200	-2.07145500
H	-3.25297700	-0.60578700	-1.29603100
C	-1.97286400	0.46034500	1.04188700
H	-1.60309100	1.26177200	1.68515300
H	-3.01504900	0.25398900	1.29597800
C	0.23635900	-0.24348000	0.51011200
C	-0.22765800	0.82011400	-0.52239900
H	-0.98301000	-1.31778000	2.01407400
H	-2.24568200	1.62290500	-0.87857700
H	0.81604500	0.24876500	1.29709900
H	0.21782600	0.66692000	-1.50467600
O	0.98770700	-1.31100100	-0.05360300
O	0.13851000	2.18044200	-0.09803900
O	1.42978300	2.32732800	0.11462200
C	3.26133500	-0.93359500	0.21161000
H	3.12261800	-0.35895600	1.13300700
H	3.41872600	-1.99132600	0.44198000
H	4.12332800	-0.53787300	-0.32999000
O	2.17560100	-0.76181900	-0.68634200

norbornene – methylperoxyl 1,4-HAT TS - exo path

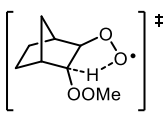


TS freq.: -1937.96 cm^{-1}
CBS-QB3 Enthalpy= -612.309650 CBS-QB3 Free Energy= -612.359044

0 2

C	2.01948600	-0.20006400	1.30852700
C	0.94354100	-1.16239000	0.74132500
C	1.65401400	0.01070200	-1.08982000
C	2.55211800	0.55023800	0.04561100
H	1.60345100	0.48282200	2.05100000
H	2.80966300	-0.77511900	1.79612600
H	2.48557800	1.63145600	0.14466200
H	3.59339700	0.28803200	-0.15723500
C	1.50459400	-1.47378800	-0.67547200
H	0.80349500	-2.04292900	-1.28935100
H	2.46396800	-1.99713300	-0.64578800
C	-0.27709300	-0.34810100	0.33505100
C	0.20461800	0.51269500	-0.87332100
H	0.70659800	-2.01594000	1.37512800
H	2.03655000	0.19367000	-2.09385500
H	-0.65173600	0.76882700	0.95769900
H	-0.45091700	0.36817800	-1.73423700
O	-1.36283400	-1.18728600	0.17860800
O	0.17453400	1.87385500	-0.42652300
O	-0.81473300	1.95708200	0.59559900
O	-2.40422500	-0.55640100	-0.61839500
C	-3.43670000	-0.14112300	0.27186000
H	-3.09964200	0.67617700	0.91346200
H	-4.22273700	0.21892000	-0.39548700
H	-3.80706900	-0.98397800	0.86099300

norbornene – methylperoxyl 1,4-HAT TS - endo path



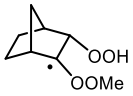
TS freq.: -1934.39 cm^{-1}
CBS-QB3 Enthalpy= -612.315004 CBS-QB3 Free Energy= -612.364304

0 2

C	-1.82655400	-1.60975800	0.13165700
C	-1.05230100	-0.66533900	1.09568000
C	-1.71478600	0.72850800	-0.57117000
C	-2.28573000	-0.64475700	-1.00869400

H	-1.20036100	-2.42676000	-0.22781200
H	-2.68064900	-2.04874100	0.65271500
H	-1.91771800	-0.95236900	-1.99062300
H	-3.37495300	-0.59659000	-1.07078500
C	-1.86405400	0.64508400	0.96343500
H	-1.42526000	1.49158600	1.48791300
H	-2.90249200	0.51601000	1.27881000
C	0.23995100	-0.25279100	0.40224700
C	-0.18432900	0.65327900	-0.79826500
H	-0.90715100	-1.06308400	2.09999600
H	-2.16452800	1.58951500	-1.06581700
H	0.75146700	0.84481400	0.97603100
H	0.07704400	0.25732200	-1.78110400
O	1.10733700	-1.29722900	0.22374500
O	0.56498400	1.85914400	-0.67854200
O	0.79159700	2.07171000	0.71045600
C	3.30777400	-0.54100400	0.13233800
H	3.09943700	0.35192000	0.72727500
H	3.61929100	-1.37497000	0.76671400
H	4.08789600	-0.31734000	-0.59827300
O	2.18835100	-0.90245400	-0.67296000

norbornene – methylperoxyl – hydroperoxyl - exo path

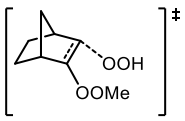


CBS-QB3 Enthalpy= -612.336427 CBS-QB3 Free Energy= -612.388819

0 2

C	1.84472500	-1.06360300	1.22564000
C	0.96673500	-1.58442000	0.05686800
C	1.61186800	0.47407200	-0.66029500
C	2.24959200	0.36816200	0.74621700
H	1.30046300	-1.05228700	2.17082100
H	2.72239700	-1.70403600	1.34968600
H	1.87680600	1.14320500	1.41735100
H	3.33495900	0.47519600	0.68271700
C	1.71139000	-0.98203400	-1.16838900
H	1.18518100	-1.15317000	-2.11070500
H	2.74249400	-1.33457400	-1.26577000
C	-0.29186300	-0.74854000	0.03373300
C	0.07062600	0.60915300	-0.51239100
H	0.78724000	-2.65865300	0.05722400
H	2.04757600	1.24335800	-1.29709200
H	0.53973400	3.25856800	0.35668200
H	-0.41214800	0.80482200	-1.47602800
O	-1.43002000	-1.41373000	-0.33122300
O	-0.37595000	1.60507500	0.41666700
O	-0.15392100	2.90318300	-0.21536200
O	-2.52276000	-0.47486000	-0.54465100
C	-3.18755400	-0.29089100	0.70179000
H	-2.52534300	0.18012800	1.43259300
H	-4.00903700	0.38713000	0.46084700
H	-3.58221800	-1.23841700	1.07919300

norbornene – methylperoxyl – hydroperoxyl radical elimination TS - exo path



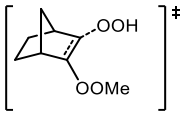
TS freq.: -365.21 cm^{-1}
CBS-QB3 Enthalpy= -612.306444 CBS-QB3 Free Energy= -612.358378

0 2

C	1.90047300	-0.33626300	1.37000000
C	1.45966600	-1.28965600	0.21069400
C	1.63427600	0.71927600	-0.81421400
C	2.07814300	1.03527200	0.64630900
H	1.15400900	-0.29689800	2.16432500
H	2.83710800	-0.69042600	1.80800300

H	1.47315500	1.82307500	1.08778400
H	3.12441100	1.35174100	0.65239200
C	2.25114500	-0.69468900	-0.98426600
H	2.00631700	-1.16857200	-1.93653300
H	3.33520900	-0.71216000	-0.83201900
C	0.07721000	-0.86842400	-0.22626000
C	0.13411500	0.39230800	-0.80656700
H	1.56509700	-2.35322500	0.41882800
H	1.92652000	1.47349300	-1.54410000
H	-0.57598900	0.75573800	-1.53261300
O	-0.96140500	-1.66437100	0.05976300
O	-0.73545700	1.60433200	0.48237300
O	-1.73924600	2.33131900	-0.19946700
O	-2.18308400	-1.14327800	-0.54582000
C	-3.01788400	-0.71206000	0.53045100
H	-3.91529300	-0.35087400	0.02350600
H	-3.27123200	-1.55177400	1.18364100
H	-2.54427600	0.10352100	1.07802700
H	-1.26435700	3.11776200	-0.50290400

norbornene – methylperoxyl – hydroperoxyl radical elimination TS - endo path

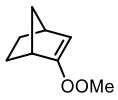


TS freq.: -330.75 cm^{-1}
CBS-QB3 Enthalpy= -612.311214 CBS-QB3 Free Energy= -612.363450

0 2

C	2.33417200	-1.32365600	0.05506300
C	1.36127000	-0.70052600	-1.00063300
C	1.60471400	0.96886100	0.50630200
C	2.48665900	-0.17383700	1.10250500
H	1.93474000	-2.24417300	0.48394900
H	3.29025000	-1.56446200	-0.41760800
H	2.15536300	-0.46856700	2.10025900
H	3.52673600	0.15245100	1.18445900
C	1.84084600	0.76889600	-1.00995500
H	1.21767300	1.42240300	-1.61799100
H	2.89104900	0.86366700	-1.29868300
C	0.04899900	-0.52592700	-0.27195600
C	0.14884700	0.53467200	0.61408000
H	1.30600700	-1.23065400	-1.95021900
H	1.80250700	1.96099100	0.90842500
H	-0.43047400	0.60311700	1.52270300
O	-0.92322000	-1.42524100	-0.47733500
O	-0.69607100	2.10717700	-0.20910900
O	-2.09612000	2.03989600	-0.09682000
O	-1.90410500	-1.38837400	0.61470200
C	-3.16260200	-1.11679700	0.00322900
H	-3.86807800	-1.17166900	0.83622700
H	-3.17250900	-0.11747800	-0.43625300
H	-3.41019900	-1.88332100	-0.73626900
H	-2.26436000	2.41991500	0.77768800

norbornene – methylperoxyl



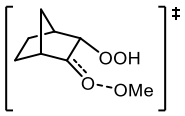
CBS-QB3 Enthalpy= -461.578531 CBS-QB3 Free Energy= -461.624191

0 1

C	-1.72588300	-1.15487100	-0.71882100
C	-0.90901100	-0.94453100	0.60066500
C	-1.66351100	1.12957000	0.14239000
C	-2.26591700	0.27774000	-1.02693500
H	-1.10185800	-1.55874900	-1.51755500
H	-2.54284800	-1.86029000	-0.54557700
H	-1.94462300	0.64823100	-2.00147200
H	-3.35948000	0.30164100	-1.00394900

C	-1.77553800	0.12044800	1.30944700
H	-1.32922500	0.48867200	2.23454900
H	-2.79784300	-0.22186300	1.49761000
C	0.27598900	-0.07361000	0.21731600
C	-0.15152500	1.16433900	-0.05855400
H	-0.66672000	-1.85632400	1.14527900
H	-2.14162100	2.09885800	0.28366200
H	0.41344600	1.96565400	-0.50849200
O	1.47483900	-0.69132300	0.08591200
O	2.41540100	0.20634100	-0.58872900
C	3.63150700	0.08817400	0.13017000
H	4.32770300	0.72678700	-0.41829600
H	3.52701600	0.44675700	1.15863300
H	3.99746900	-0.94308000	0.12406600

norbornene – 2-methylperoxyl 1-hydroperoxyl peroxide fragmentation TS - exo path

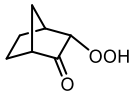


TS freq.: -199.97 cm^{-1}
CBS-QB3 Enthalpy= -612.336713 CBS-QB3 Free Energy= -612.388139

0 2

C	1.49380700	-1.24593800	1.28725400
C	0.79666200	-1.63576000	-0.04653900
C	1.72929800	0.38489400	-0.52069200
C	2.10271600	0.15716500	0.96504200
H	0.79314500	-1.21985700	2.12298000
H	2.27433400	-1.97350900	1.52795300
H	1.69475700	0.93624900	1.60996200
H	3.18823500	0.15674000	1.08774400
C	1.79680800	-1.05235600	-1.08436300
H	1.44027500	-1.13777800	-2.11364400
H	2.79599400	-1.49189300	-1.01404000
C	-0.35824700	-0.68856600	-0.26325700
C	0.20238600	0.66581500	-0.62193100
H	0.53109200	-2.68763500	-0.13970400
H	2.33519400	1.13497900	-1.02747400
H	0.76622900	3.17880800	0.55534400
H	-0.09288300	0.97697600	-1.63160700
O	-1.51715000	-1.18088700	-0.70283400
O	-0.29766000	1.63585000	0.30518300
O	0.16367800	2.94006800	-0.16207000
O	-2.65046300	-0.19546100	-0.46640300
C	-3.05756300	-0.33027500	0.88133600
H	-2.24254600	-0.08796600	1.57194800
H	-3.84784600	0.41712000	0.99282200
H	-3.45842700	-1.32866900	1.08561400

norbornene – hydroperoxyl ketone product - exo path



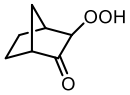
CBS-QB3 Enthalpy= -497.532047 CBS-QB3 Free Energy= -497.576242

0 1

C	1.67385500	-0.44814100	-1.10179500
C	1.67341700	0.46513500	0.16272200
C	0.07194600	-1.10035900	0.61473300
C	0.56820500	-1.50628300	-0.79032100
H	1.47822900	0.11704800	-2.01478100
H	2.65732600	-0.91231700	-1.20692500
H	-0.24396400	-1.48684100	-1.51720300
H	0.97934300	-2.51778700	-0.77423000
C	1.35938500	-0.55866200	1.27740100
H	1.18927300	-0.09927200	2.25534900
H	2.13594500	-1.31985000	1.37962700
C	0.36640600	1.23810800	0.08825700
C	-0.73601500	0.20990800	0.49275000

H	2.54754900	1.10482600	0.26802200
H	-0.45763000	-1.88410800	1.15429400
H	-1.14406600	0.50404900	1.46902800
O	0.18220100	2.38223000	-0.22649400
O	-1.75312400	0.25313900	-0.47988500
O	-2.85941400	-0.56121500	0.02115100
H	-3.56250500	0.10278600	0.00615900

norbornene – hydroperoxyl ketone product - endo path

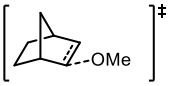


CBS-QB3 Enthalpy= -497.533685 CBS-QB3 Free Energy= -497.576510

0 1

C	2.11963500	0.60112500	-0.57153000
C	1.11572500	0.97513500	0.55706500
C	0.66761600	-1.22886100	0.13923100
C	1.82133400	-0.90947700	-0.84188600
H	1.99619000	1.22478400	-1.45938500
H	3.13974700	0.74928600	-0.21131300
H	1.54702200	-1.10315600	-1.88122900
H	2.69103700	-1.52927900	-0.61493800
C	1.04208400	-0.35116000	1.35920800
H	0.27604500	-0.34806900	2.13637700
H	2.00304500	-0.62318000	1.80196900
C	-0.26957900	0.96493300	-0.06317100
C	-0.58372800	-0.51905200	-0.39898400
H	1.33868300	1.89468600	1.09450500
H	0.50650200	-2.28909800	0.32947200
H	-0.78000100	-0.68992900	-1.46146000
O	-1.06015400	1.87506400	-0.16066900
O	-1.72535200	-0.91221500	0.36088700
O	-2.89261400	-0.34838300	-0.28780500
H	-2.77183700	0.60236400	-0.11290400

norbornene – methoxy radical addition TS – exo path

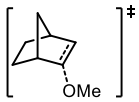


TS freq.: -185.24 cm^{-1}
CBS-QB3 Enthalpy= -387.033103 CBS-QB3 Free Energy= -387.077738

0 2

C	-1.96247300	-0.91790900	-0.56382700
C	-0.53289400	-1.07961400	0.05230000
C	-1.04049500	1.07375200	0.51751200
C	-2.32371600	0.56421300	-0.23078200
H	-1.97572900	-1.12522400	-1.63590200
H	-2.65838500	-1.61239800	-0.08650900
H	-2.54494900	1.15841700	-1.11944800
H	-3.19062300	0.62487100	0.43280300
C	-0.65937900	-0.19706400	1.31470200
H	0.28773900	-0.10422800	1.84262100
H	-1.45077400	-0.52651200	1.99416400
C	0.38812900	-0.21384900	-0.78720400
C	0.05414400	1.08327700	-0.52641400
H	-0.20140100	-2.10659800	0.19219400
H	-1.18387800	1.99778500	1.07678900
H	0.93251900	-0.56901400	-1.65099000
H	0.41293800	1.96192300	-1.04789700
O	2.20108000	-0.51461100	0.35853400
C	3.26815800	0.22079100	-0.13051800
H	4.17112400	-0.18857200	0.35357400
H	3.41740300	0.11403400	-1.21775900
H	3.22653900	1.29082500	0.12346900

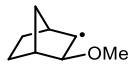
norbornene – methoxy radical addition TS - endo path



TS freq.: -292.36 cm^{-1}
CBS-QB3 Enthalpy= -387.029077 CBS-QB3 Free Energy= -387.073020

```
0 2
 C                -0.82020400    1.42814400   -0.34336700
 C                -0.77997900    0.10998900   -1.17695900
 C                -1.33876900   -0.62373300    0.88651900
 C                -1.13771300    0.92067100    1.09461000
 H                 0.11878400    1.97091500   -0.39685100
 H                -1.62184200    2.06650300   -0.72435600
 H                -0.32334400    1.12723500    1.78852000
 H                -2.05241200    1.36702400    1.49395700
 C                -1.97143000   -0.64614600   -0.53020300
 H                -2.11005200   -1.65742700   -0.91869500
 H                -2.91404600   -0.09391800   -0.59672600
 C                 0.38136600   -0.74488300   -0.67469700
 C                 0.00979000   -1.22066700    0.55737700
 H                -0.81010100    0.25966100   -2.25559600
 H                -1.88542600   -1.11634400    1.69026800
 H                 1.16177100   -1.13567500   -1.31009900
 H                 0.60373400   -1.83964100    1.21688500
 O                 1.86496900    0.59116700   -0.01061800
 C                 3.08251000   -0.06222800    0.11996200
 H                 3.83948600    0.71542200    0.30993300
 H                 3.12253700   -0.75488100    0.97569200
 H                 3.39772500   -0.60508900   -0.78744800
```

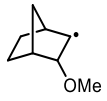
norbornene – methoxy adduct - exo path



CBS-QB3 Enthalpy= -387.075371 CBS-QB3 Free Energy= -387.118424

```
0 2
 C                -1.66665100   -1.01781000   -0.67127500
 C                -0.42579400   -1.04667200    0.25693800
 C                -1.12983500    1.10396200    0.40030300
 C                -2.19672900    0.44616500   -0.53448100
 H                -1.41234500   -1.27452000   -1.70320900
 H                -2.41202300   -1.74142200   -0.33368100
 H                -2.27817100    0.96093800   -1.49395200
 H                -3.18211600    0.47374200   -0.05901400
 C                -0.84428700   -0.06726000    1.37506400
 H                -0.03466600    0.14113600    2.07489600
 H                -1.73259900   -0.39273300    1.92347500
 C                 0.70863400   -0.25712500   -0.42744500
 C                 0.15511000    1.14777200   -0.37339800
 H                -0.10779100   -2.04178700    0.56675400
 H                -1.44955500    2.05083700    0.83732100
 H                 0.90294700   -0.60550800   -1.45456800
 H                 0.49360100    1.98265900   -0.97414300
 O                 1.90690200   -0.44471300    0.34358600
 C                 3.04511700    0.18584500   -0.20851900
 H                 3.89466800   -0.08344000    0.42041600
 H                 3.24031000   -0.16090100   -1.23463000
 H                 2.94913600    1.27944800   -0.22148200
```

norbornene – methoxy adduct - endo path

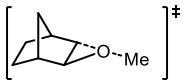


CBS-QB3 Enthalpy= -387.075364 CBS-QB3 Free Energy= -387.118367

```
0 2
 C                 0.61780700    1.46363800   -0.20537100
```

C	0.14351800	0.49735000	0.90690800
C	1.67460800	-0.73872900	-0.22746400
C	1.70769400	0.64120300	-0.96398000
H	-0.20764700	1.75209800	-0.85677400
H	1.03793900	2.37329700	0.23059700
H	1.49310600	0.53942200	-2.02925300
H	2.69836700	1.09658700	-0.86461000
C	1.43743100	-0.27634500	1.23385400
H	1.28702400	-1.10814900	1.92696200
H	2.23341900	0.36805700	1.61779500
C	-0.70376300	-0.63429600	0.24241300
C	0.35139500	-1.36929000	-0.53401200
H	-0.34935700	0.98556100	1.74878400
H	2.55174200	-1.35908600	-0.41538600
H	-1.14375100	-1.26969100	1.03430700
H	0.12507300	-2.00485900	-1.38022700
O	-1.75560900	-0.20313200	-0.61401100
C	-2.90068500	0.26437200	0.07532100
H	-3.66282500	0.47138400	-0.67677800
H	-3.28549500	-0.49328800	0.77305500
H	-2.70075000	1.18630200	0.63759900

norbornene – methoxy fragmentation TS - exo path

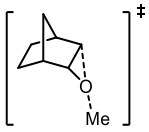


TS freq.: -788.40 cm^{-1}
CBS-QB3 Enthalpy= -386.999275 CBS-QB3 Free Energy= -387.043619

0 2

C	1.66960500	1.13967100	-0.51618500
C	0.26041400	1.06432100	0.13183600
C	1.11159200	-1.00819000	0.51710500
C	2.28154000	-0.27063400	-0.21567300
H	1.61596700	1.34720700	-1.58870900
H	2.26506000	1.93526300	-0.06299300
H	2.60278900	-0.79318100	-1.11940900
H	3.14890600	-0.19838300	0.44689300
C	0.52736400	0.15543800	1.35074600
H	-0.37861800	-0.11907500	1.88620600
H	1.25924400	0.57913900	2.04278300
C	-0.56219800	0.11973100	-0.76886200
C	0.06948300	-1.18660700	-0.55491900
H	-0.20255100	2.03081800	0.33322800
H	1.40915600	-1.90599400	1.05778100
H	-0.81278000	0.49161600	-1.76600700
H	-0.02594600	-2.02679200	-1.22540500
O	-1.57934100	-0.61713800	-0.12374400
C	-3.32110900	0.36380000	0.13832400
H	-3.85849300	-0.45914600	0.58732600
H	-3.04040900	1.18062900	0.79048700
H	-3.56774400	0.60982700	-0.88645600

norbornene – methoxy fragmentation TS - endo path



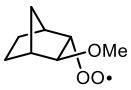
TS freq.: -783.70 cm^{-1}
CBS-QB3 Enthalpy= -386.992468 CBS-QB3 Free Energy= -387.036629

0 2

C	0.45901300	1.51200300	0.16230000
C	0.46072600	0.32650300	1.15364600
C	1.47727900	-0.54372300	-0.67872700
C	1.12966000	0.91052700	-1.11317600
H	-0.54580600	1.87671500	-0.04226300
H	1.04843600	2.33719400	0.57103500
H	0.45959800	0.92055700	-1.97199700
H	2.04473600	1.44578900	-1.38117000

C	1.82384600	-0.33183000	0.82584700
H	1.99594300	-1.27031700	1.35984500
H	2.67870500	0.33207900	0.98819400
C	-0.51569100	-0.77602400	0.62473900
C	0.21483900	-1.35457800	-0.50598400
H	0.29429300	0.60424000	2.19519600
H	2.23147100	-1.02464500	-1.30253500
H	-1.00668800	-1.38778800	1.38706000
H	-0.01259100	-2.30289000	-0.96730000
O	-1.33003900	-0.42873200	-0.47266900
C	-3.14979000	0.36023800	0.00423000
H	-3.45867000	0.57207900	-1.00927100
H	-3.59823300	-0.49702900	0.48844900
H	-2.89016900	1.20517400	0.62885400

norbornene – methoxy + oxygen adduct - exo path

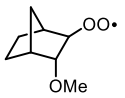


CBS-QB3 Enthalpy= -537.297066 CBS-QB3 Free Energy= -537.344774

0 2

C	-1.87418100	-0.41250700	-1.21081400
C	-0.86950800	-1.29639500	-0.43527500
C	-1.27185900	0.42111100	0.99345700
C	-2.17711000	0.75308000	-0.21604500
H	-1.46195900	-0.05608600	-2.15821300
H	-2.77774700	-0.97977600	-1.44473000
H	-1.96769700	1.73639600	-0.63618700
H	-3.22377800	0.74495200	0.09692500
C	-1.34467800	-1.12293400	1.02486900
H	-0.66544000	-1.58359900	1.74447100
H	-2.35869500	-1.48972700	1.20118200
C	0.48624400	-0.57207300	-0.39795300
C	0.19913300	0.61128400	0.58994200
H	-0.77579600	-2.31681200	-0.80483000
H	-1.53908800	0.94311400	1.91248500
H	0.79409100	-0.18853400	-1.37952200
H	0.87793500	0.55908400	1.44219600
O	1.46167300	-1.46066500	0.11250000
C	2.80157100	-1.02498600	-0.07247000
H	3.44158100	-1.78524300	0.37529300
H	3.04123800	-0.93366300	-1.14050100
H	2.99086000	-0.05690000	0.40474100
O	0.38100500	1.92957800	-0.00728400
O	1.64817500	2.18950200	-0.26366200

norbornene – methoxy + oxygen adduct - endo path



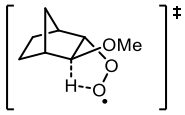
CBS-QB3 Enthalpy= -537.298238 CBS-QB3 Free Energy= -537.345893

0 2

C	1.94998100	1.17020100	-0.16503100
C	1.09080800	0.63481500	1.00142200
C	1.16885500	-1.12938600	-0.42077600
C	1.98454200	-0.03660600	-1.15589700
H	1.51479200	2.06627900	-0.60487800
H	2.95288400	1.41986700	0.18936600
H	1.55737300	0.20949400	-2.13110200
H	3.00534300	-0.38522000	-1.32749800
C	1.51506900	-0.84692200	1.05962800
H	0.92843800	-1.44835900	1.75816200
H	2.57601400	-0.97886800	1.28395600
C	-0.37197500	0.50646300	0.52130000
C	-0.30042000	-0.70469500	-0.46817700
H	1.17963000	1.20769000	1.92458300
H	1.33491400	-2.14276800	-0.78673700
H	-1.02870200	0.23223000	1.35767900
H	-0.67208700	-0.44959200	-1.46157200

O	-0.81488700	1.70584000	-0.07208700
C	-2.22694000	1.81444000	-0.19068300
H	-2.42676800	2.77083300	-0.67392600
H	-2.65225800	1.00187900	-0.78982700
H	-2.70683100	1.80076500	0.79703000
O	-1.09811200	-1.84303800	-0.00096800
O	-2.38978400	-1.58206300	-0.00518900

norbornene – methoxy 1,4-HAT TS - exo path

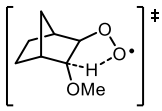


TS freq.: -1837.03 cm^{-1}
CBS-QB3 Enthalpy= -537.256506 CBS-QB3 Free Energy= -537.302571

0 2

C	-1.72340300	-0.35832400	-1.24580100
C	-0.67413100	-1.27081100	-0.56102500
C	-1.29163700	0.16039900	1.09605900
C	-2.12248000	0.64189100	-0.11392200
H	-1.32310800	0.14885100	-2.12441100
H	-2.57805500	-0.95824600	-1.56805500
H	-1.89968700	1.67451600	-0.37598100
H	-3.18780900	0.57166300	0.12025400
C	-1.25675800	-1.37112500	0.87521100
H	-0.59796700	-1.90332000	1.56650900
H	-2.24791400	-1.83142800	0.90501500
C	0.58360200	-0.45249900	-0.29489400
C	0.21153500	0.48306700	0.90703200
H	-0.46425400	-2.20561600	-1.07922400
H	-1.66968000	0.50342200	2.05988600
H	0.68618300	0.64158700	-1.04351700
H	0.76154000	0.24815300	1.82418900
O	1.72689800	-1.19920200	-0.25317100
C	2.93621800	-0.47972800	0.01285000
H	3.73999100	-1.21251600	-0.02287600
H	3.09148100	0.29035300	-0.74832200
H	2.91145200	-0.00425900	0.99724800
O	0.61581800	1.80024700	0.55250400
O	0.50730300	1.88890700	-0.86980500

norbornene – methoxy 1,4-HAT TS - endo path



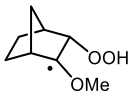
TS freq.: -1893.79 cm^{-1}
CBS-QB3 Enthalpy= -537.259220 CBS-QB3 Free Energy= -537.305367

0 2

C	1.78972500	-1.37627100	-0.07677300
C	0.88166800	-0.59702300	-1.07103000
C	1.27545900	0.92463100	0.56476300
C	2.07399100	-0.31752900	1.03739100
H	1.29510500	-2.27198100	0.30147800
H	2.70987600	-1.69015400	-0.57539800
H	1.76530000	-0.65758800	2.02946700
H	3.13839000	-0.07960400	1.09406500
C	1.45707400	0.83343500	-0.96616500
H	0.88455200	1.57970800	-1.51398900
H	2.50664600	0.88376300	-1.26672000
C	-0.47132100	-0.40356000	-0.41014500
C	-0.21848200	0.58189900	0.78353400
H	0.81899700	-1.04003900	-2.06510200
H	1.56079900	1.86170800	1.04344200
H	-1.14624800	0.60078300	-0.99657200
H	-0.39114500	0.15899100	1.77769300
O	-1.19693800	-1.54473500	-0.23526600
C	-2.50070600	-1.37766700	0.33243400
H	-2.94269500	-2.37110300	0.37950800

H	-2.44675900	-0.94733300	1.33628800
H	-3.10695900	-0.72389400	-0.30124600
O	-1.17762400	1.62876600	0.66310300
O	-1.42172600	1.80212500	-0.72870900

norbornene – methoxy – hydroperoxyl - exo path

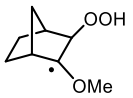


CBS-QB3 Enthalpy= -537.280055 CBS-QB3 Free Energy= -537.329652

0 2

C	-1.85033000	-0.80927800	-1.09533200
C	-0.97006600	-1.45900400	0.00727700
C	-1.17009900	0.68831500	0.71383500
C	-1.92633800	0.68367500	-0.63763900
H	-1.41097600	-0.92265700	-2.08725900
H	-2.84221900	-1.27067400	-1.10997000
H	-1.45998900	1.35611100	-1.35938600
H	-2.96042200	1.00797100	-0.49899100
C	-1.49203400	-0.71720300	1.26917300
H	-0.93141100	-0.96765900	2.17362200
H	-2.55897500	-0.86985100	1.45788200
C	0.41112200	-0.86637400	-0.11118800
C	0.35170300	0.53280700	0.44532300
H	-0.97766000	-2.54807400	0.02227100
H	-1.40328100	1.53468600	1.35951600
H	0.34995500	3.24071200	-0.38340400
H	0.91940000	0.64718300	1.38037700
O	1.48154700	-1.69301000	0.00403600
C	2.77366900	-1.09933300	-0.15275900
H	3.48991600	-1.91752800	-0.09346900
H	2.85046200	-0.59600300	-1.11983100
H	2.98047600	-0.37610400	0.64147600
O	0.91423900	1.43843500	-0.51420800
O	1.00283500	2.74960700	0.13330100

norbornene – methoxy – hydroperoxyl - endo path

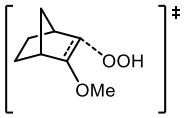


CBS-QB3 Enthalpy= -537.279911 CBS-QB3 Free Energy= -537.328816

0 2

C	1.95375500	-1.26323300	0.01250000
C	0.97916300	-0.65147300	-1.04237900
C	1.13370600	0.98894900	0.51412300
C	2.06054500	-0.12274100	1.07731100
H	1.56368200	-2.19615300	0.42339400
H	2.92421900	-1.48106100	-0.44192100
H	1.75756500	-0.44920500	2.07579300
H	3.08494500	0.24817700	1.15647700
C	1.38764300	0.83763900	-1.00370900
H	0.75382000	1.48270300	-1.60868300
H	2.43616000	0.99397700	-1.27099200
C	-0.38436300	-0.56857400	-0.40865200
C	-0.31798500	0.48115300	0.68297900
H	0.99300700	-1.15368400	-2.01020300
H	1.28789400	1.97648700	0.94861700
H	-1.87648300	1.57804900	-1.14082500
H	-0.47229300	0.05901200	1.68562600
O	-1.09233800	-1.72502500	-0.30516200
C	-2.39953700	-1.64395300	0.26408900
H	-2.79079800	-2.66011200	0.27226200
H	-2.37474800	-1.25424900	1.28525900
H	-3.04763600	-1.00482600	-0.34431200
O	-1.36627400	1.47224500	0.68157200
O	-1.38099900	2.19206500	-0.57741800

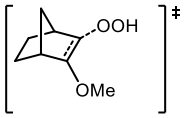
norbornene – methoxy – hydroperoxyl radical elimination TS - exo path



TS freq.: -360.51 cm^{-1}
CBS-QB3 Enthalpy= -537.251868 CBS-QB3 Free Energy= -537.301105

```
0 2
 C                  1.76992500    0.03899900   -1.28707600
 C                  1.44012000    1.09177800   -0.17680300
 C                  1.12637600   -0.88095200    0.87896700
 C                  1.60486600   -1.32043900   -0.53803600
 H                  1.09636400    0.13159000   -2.14017700
 H                  2.79114000    0.18249600   -1.64953400
 H                  0.88263900   -1.97620100   -1.01792400
 H                  2.55993500   -1.84633600   -0.45817600
 C                  2.00290300    0.38389600    1.08132700
 H                  1.78763500    0.92165000    2.00687800
 H                  3.07575800    0.17540800    1.01881100
 C                 -0.03029500    0.97595500    0.13722200
 C                 -0.26888400   -0.25811100    0.74456800
 H                  1.77156400    2.10687100   -0.39058200
 H                  1.20225300   -1.65834400    1.63887600
 H                 -2.00263100   -2.76913600    0.34395900
 H                 -1.07963100   -0.47221700    1.42583500
 O                 -0.87638400    1.92461100   -0.25934200
 C                 -2.27606300    1.69936700   -0.01036000
 H                 -2.79655300    2.53209300   -0.47869200
 H                 -2.57867100    0.74724600   -0.44636900
 H                 -2.47355900    1.70067800    1.06578800
 O                 -1.30236400   -1.28341500   -0.57946800
 O                 -2.37749200   -1.91103800    0.10161700
```

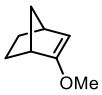
norbornene – methoxy – hydroperoxyl radical elimination TS - endo path



TS freq.: -345.98 cm^{-1}
CBS-QB3 Enthalpy= -537.255183 CBS-QB3 Free Energy= -537.303998

```
0 2
 C                 -2.27813900    0.86550000   -0.22392200
 C                 -1.05400900    0.39392700   -1.07972300
 C                 -1.01962100   -1.03256100    0.67484500
 C                 -2.23810700   -0.10892200    0.99801600
 H                 -2.19698800    1.91580900    0.06244900
 H                 -3.20127800    0.74921000   -0.79803600
 H                 -2.11583300    0.41405500    1.94918600
 H                 -3.15562700   -0.69940500    1.06522400
 C                 -1.12763600   -1.13565800   -0.86503700
 H                 -0.29248500   -1.67832400   -1.30335400
 H                 -2.07684700   -1.56284300   -1.20014300
 C                  0.16271100    0.71120300   -0.24993200
 C                  0.23795400   -0.18495900    0.81492800
 H                 -1.03112600    0.77310500   -2.10077600
 H                 -0.98880600   -1.96720800    1.23178700
 H                  2.50653200   -1.42617300   -1.10211800
 H                  0.64759200    0.06259000    1.78621200
 O                  0.92454700    1.77439500   -0.53968200
 C                  1.99391800    2.06442000    0.37245200
 H                  2.60457900    2.82488100   -0.11019200
 H                  1.59620800    2.45651700    1.31361500
 H                  2.57880500    1.16264300    0.56795000
 O                  1.79510300   -1.33040400    0.63768400
 O                  1.91320700   -2.00181100   -0.59944900
```

norbornene – methoxy



CBS-QB3 Enthalpy= -386.524663 CBS-QB3 Free Energy= -386.565594

```
0 1
 C                -1.26932800   -1.17472800   -0.72992800
 C                -0.48214900   -0.94047900    0.60390700
 C                -1.25190800    1.11694000    0.10949700
 C                -1.81674400    0.24926900   -1.06587500
 H                -0.62532400   -1.58157900   -1.51155200
 H                -2.08346700   -1.88591500   -0.56763900
 H                -1.47635900    0.61447600   -2.03622200
 H                -2.91078100    0.26202600   -1.06991600
 C                -1.38223600    0.11590400    1.28260000
 H                -0.96326400    0.49829000    2.21493500
 H                -2.40596200   -0.23387800    1.44920300
 C                 0.70557000   -0.07050000    0.24138500
 C                 0.26521800    1.16560600   -0.05152200
 H                -0.23642600   -1.84459700    1.15972400
 H                -1.74290200    2.08273200    0.23069500
 H                 0.81765800    1.99695100   -0.46523800
 O                 1.92596500   -0.64238100    0.15919300
 C                 2.97555800    0.20455300   -0.29719200
 H                 3.88359600   -0.39602800   -0.28728400
 H                 2.77634700    0.55953300   -1.31446200
 H                 3.09527900    1.06765000    0.36697700
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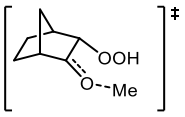
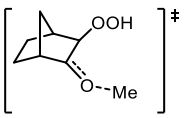
norbornene – 2-methoxy 1-hydroperoxyl ether fragmentation TS - exo path



TS freq.: -592.92 cm^{-1}
CBS-QB3 Enthalpy= -537.244678 CBS-QB3 Free Energy= -537.295307

```
0 2
 C                 1.10987100   -1.26420700    1.20420200
 C                 0.78718000   -1.53327800   -0.29702000
 C                 1.47533500    0.63878600   -0.28347000
 C                 1.56538100    0.23044000    1.20636200
 H                 0.24773700   -1.44327700    1.84941700
 H                 1.91231800   -1.92775400    1.53895900
 H                 0.92872400    0.85177700    1.83786600
 H                 2.59148800    0.33241400    1.56702200
 C                 1.87126400   -0.67616700   -0.99370800
 H                 1.75752400   -0.63853900   -2.08015700
 H                 2.88940200   -0.99422200   -0.75470700
 C                -0.45019600   -0.73296000   -0.64898900
 C                -0.01671100    0.74008400   -0.68711000
 H                 0.71725000   -2.58606200   -0.56775300
 H                 2.05717600    1.52227000   -0.54570900
 H                -0.16319500    3.13383100    0.79841900
 H                -0.13180200    1.16141400   -1.69410100
 O                -1.62245000   -1.15589800   -0.79887600
 C                -2.87899900   -1.06595200    0.63595300
 H                -2.77724600   -0.03077700    0.93188900
 H                -3.76731500   -1.32589000    0.07705400
 H                -2.51226300   -1.81803800    1.32335800
 O                -0.85348600    1.47803600    0.19756400
 O                -0.59013100    2.89565800   -0.03604700
```

norbornene – 2-methoxy 1-hydroperoxyl ether fragmentation TS - endo path

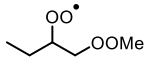


TS freq.: -585.22 cm^{-1}
CBS-QB3 Enthalpy= -537.241195 CBS-QB3 Free Energy= -537.291445

0 2

C	-2.12080000	-1.26346400	-0.08784900
C	-0.79678300	-1.06772500	0.71030600
C	-1.29205900	1.03807700	0.01233100
C	-2.44663100	0.18574700	-0.58002000
H	-2.00550700	-1.97452300	-0.90782200
H	-2.90496700	-1.64371800	0.57261100
H	-2.49511800	0.25644800	-1.66966200
H	-3.40813600	0.52808100	-0.19079200
C	-1.05021300	0.31262200	1.36050600
H	-0.19067200	0.69382000	1.90871200
H	-1.93335400	0.32225000	2.00615800
C	0.28133800	-0.72270100	-0.30522900
C	-0.02036300	0.69734400	-0.79874300
H	-0.53051500	-1.90001000	1.36106900
H	-1.49949700	2.10828600	0.05385000
H	1.43825200	2.60214300	0.83534000
H	-0.20407000	0.70922900	-1.88049200
O	1.25211500	-1.43202300	-0.66644000
C	2.93686000	-1.30649600	0.23016800
H	2.75756400	-1.89912100	1.11829500
H	3.54322600	-1.76886100	-0.53623900
H	3.04487800	-0.23901600	0.36528000
O	1.06853600	1.62674500	-0.73844300
O	1.60932800	1.67584900	0.61924100

1-butene – methylperoxyl + oxygen adduct

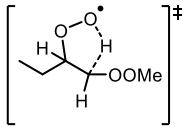


CBS-QB3 Enthalpy= -497.044358 CBS-QB3 Free Energy= -497.095908

0 2

C	-0.12927700	-0.45699400	0.86353800
H	0.19959800	-0.26873400	1.89054600
H	-0.34947100	-1.52147600	0.74082100
C	0.96868500	-0.05759200	-0.12996100
H	0.59816500	-0.17563200	-1.14972400
O	-1.31278600	0.31523200	0.73695000
O	-1.91614800	-0.03786100	-0.54624000
C	-3.22487700	-0.50013900	-0.25232300
H	-3.66125100	-0.72085300	-1.22915800
H	-3.81337000	0.27443900	0.24810500
H	-3.20324300	-1.40918900	0.35753100
O	2.05824300	-1.03705500	0.03294000
O	1.73142700	-2.23088000	-0.42080900
C	1.61623900	1.30551400	0.08465700
H	1.90778200	1.40169000	1.13647300
H	2.54291900	1.31948700	-0.49773500
C	0.72993900	2.48599300	-0.33139100
H	-0.18400700	2.53209900	0.26054300
H	1.27322400	3.42542700	-0.20456300
H	0.43951400	2.40656200	-1.38268400

1-butene – methylperoxyl 1,4-HAT TS



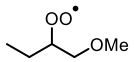
TS freq.: -1930.56 cm^{-1}
CBS-QB3 Enthalpy= -497.001351 CBS-QB3 Free Energy= -497.051660

0 2

C	-0.10747700	-0.45339000	0.38259900
H	-0.19274700	-0.29884000	1.46010500
H	0.18903800	-1.73764800	0.16756600
C	1.23333400	-0.07937300	-0.27382200
H	1.07794800	-0.05641400	-1.36082200
O	-1.18097200	0.02951700	-0.31549400
O	-2.33198900	0.06575800	0.58010800

C	-3.47352200	0.00356700	-0.26220500
H	-4.31380100	0.06256300	0.43214200
H	-3.50788400	-0.93951200	-0.81414200
H	-3.50224100	0.85233700	-0.95123300
O	2.05704800	-1.19301700	0.07952900
O	1.24178400	-2.32941300	-0.18489900
C	1.90665700	1.19522600	0.21928600
H	2.03120200	1.12611400	1.30428600
H	2.91223100	1.22391500	-0.21266700
C	1.13847500	2.46662300	-0.15591800
H	0.14121300	2.48367100	0.29007500
H	1.67496400	3.35270700	0.19066000
H	1.01831400	2.55242300	-1.23956200

1-butene – methoxy + oxygen adduct

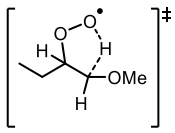


CBS-QB3 Enthalpy= -421.988758 CBS-QB3 Free Energy= -422.036230

0 2

C	-0.44890600	0.08855300	-0.16826400
C	0.97088700	0.43793200	0.26693800
C	3.20152000	-0.27441200	-0.01394200
H	1.19920500	1.46195900	-0.05790900
H	1.04711700	0.39754800	1.36491100
H	-0.52317200	0.15516000	-1.25611600
H	3.37646900	-0.36364700	1.06730100
H	3.78279200	-1.03648100	-0.53292000
H	3.53640400	0.71876300	-0.34323200
O	1.84140500	-0.49538500	-0.33854200
O	-1.34619900	1.11921000	0.37483100
O	-1.24783100	2.26060500	-0.27763800
C	-0.95311900	-1.24771600	0.35169400
H	-0.18803100	-1.98931900	0.10765500
H	-1.00436600	-1.19448300	1.44518500
C	-2.30968800	-1.65869500	-0.22637400
H	-2.63168200	-2.61863800	0.18403800
H	-3.07863400	-0.91860700	0.00592800
H	-2.25925500	-1.76166800	-1.31435500

1-butene – methoxy 1,4-HAT TS



TS freq.: -1942.47 cm^{-1}
CBS-QB3 Enthalpy= -421.946700 CBS-QB3 Free Energy= -421.992605

0 2

C	-0.54514000	0.05371100	-0.20538900
C	0.90514200	0.13925600	0.28377500
C	3.08263900	-0.75300200	0.08099100
H	0.84693300	1.45880500	0.05760300
H	1.04580500	0.02829900	1.36700700
H	-0.51805500	0.02813600	-1.30289000
H	3.02255200	-1.24411200	1.05859800
H	3.63721100	-1.38265100	-0.61234000
H	3.59107200	0.21051100	0.18790600
O	1.78166200	-0.57619600	-0.47683400
O	-1.08718200	1.30128800	0.24099600
O	-0.10909000	2.25500400	-0.15215200
C	-1.38536600	-1.08419200	0.35580400
H	-0.86594700	-2.02040300	0.12444500
H	-1.41139900	-0.99098200	1.44657700
C	-2.80983100	-1.11530200	-0.20887900
H	-3.37758500	-1.94797800	0.21356000
H	-3.33946200	-0.18915700	0.02186800
H	-2.79890700	-1.23405500	-1.29622400

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