# Supplementary Material

# On the mechanism of the [4+2] cycloaddition of $^1O_2$ with 1,3-dienes: Identifying the putative biradical/dipolar intermediate by employing the *gem*-diphenylcyclopropylcarbinyl radical clock as a mechanistic probe

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**This paper is dedicated to our mentor, Prof. Michael Orfanopoulos, on the occasion of his 67th birthday, and his outstanding contribution to singlet oxygen and fullerene chemistry**

## Table of Contents



# 1. Copies of 1D and 2D NMR Spectra of (*E*)-13 and (*E*,*E*)-14

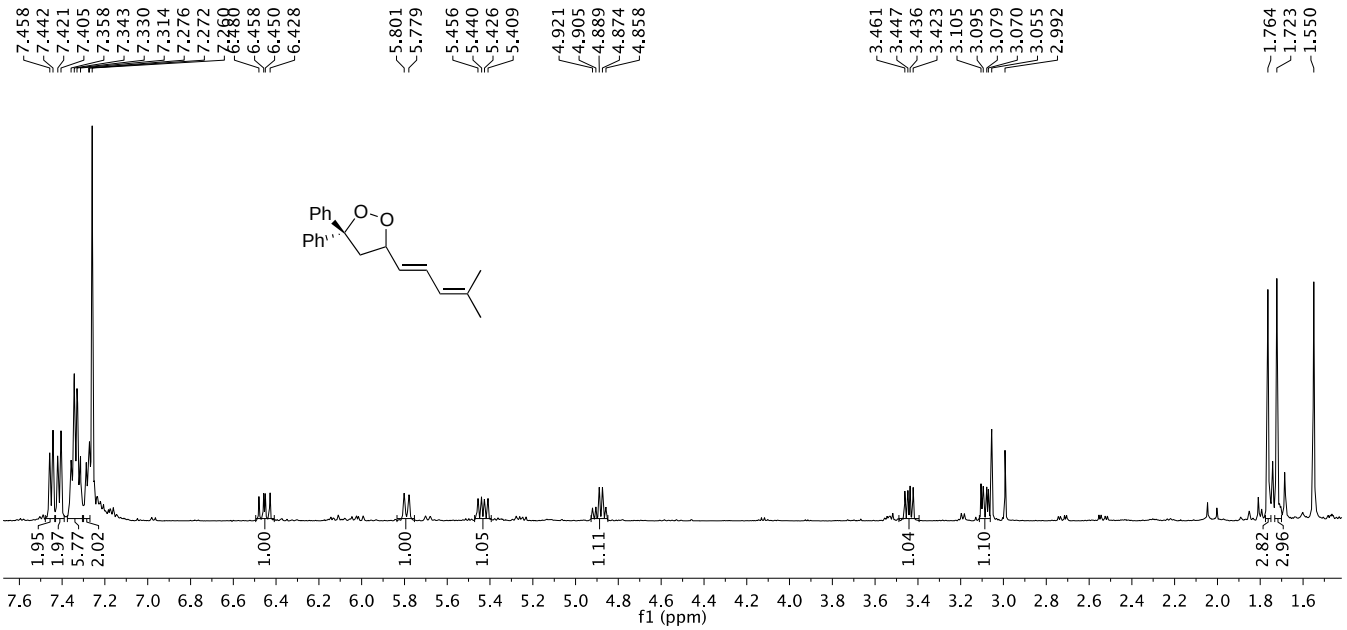



**Figure S1.** $^{1}$H NMR (500 MHz) spectrum of (*E*)-**13** recorded at 25 $^{o}$C in $CDCl_3$.*

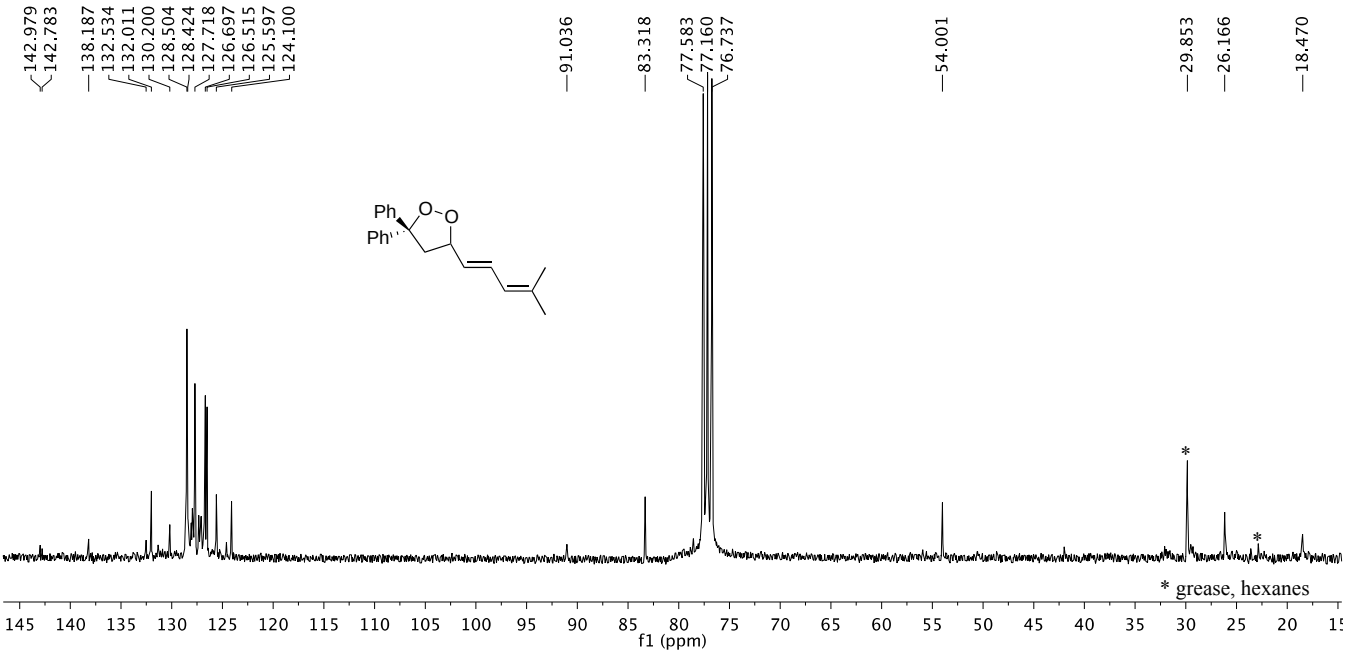



**Figure S2.** $^{13}$C NMR (75 MHz) spectrum of (*E*)-**13** recorded at 25 $^{o}$C in $CDCl_3$.

* The $^{1}$H NMR spectra of this compound showed the presence of minor side-product(s), which could not be separated by flash column chromatography on silica gel (identical $R_f$ values).

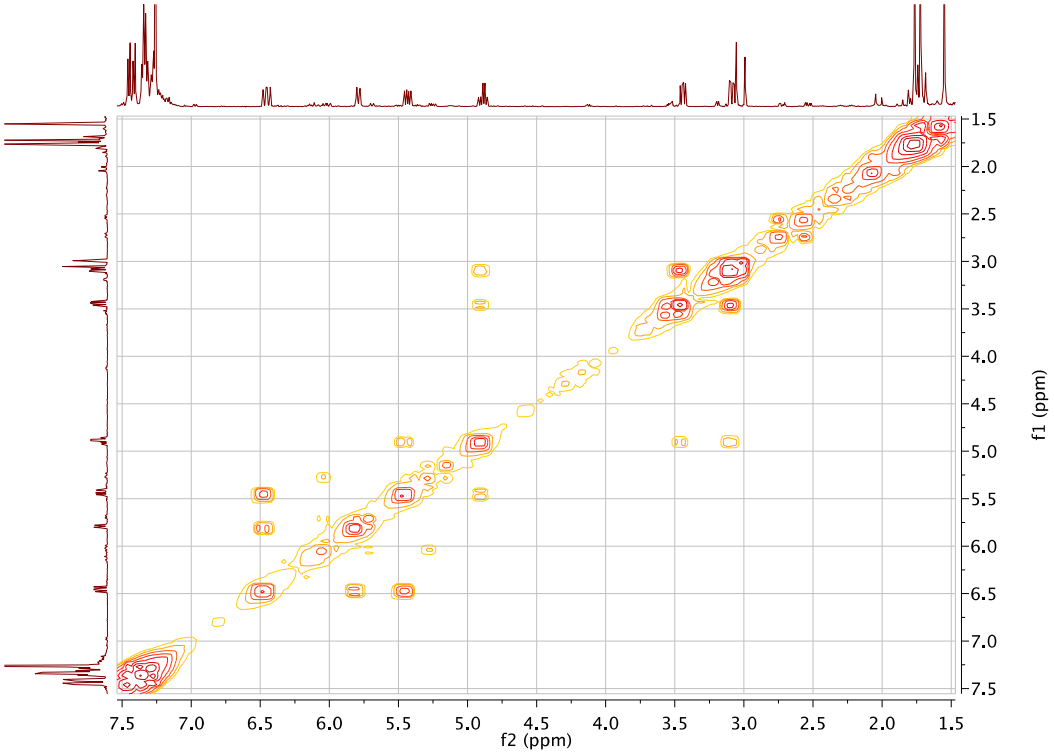



**Figure S3.** COSY (500 MHz) spectrum of (*E*)-**13** recorded at 25 °C in $CDCl_3$.

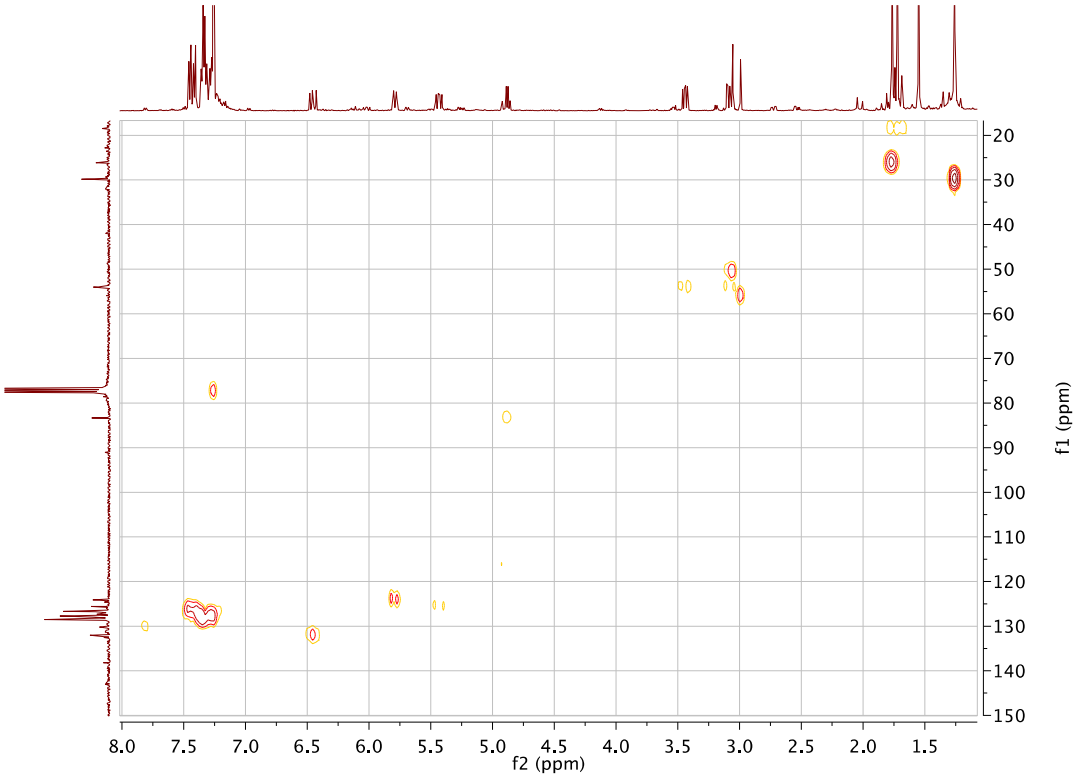



**Figure S4.** HMQC (500 MHz) spectrum of (*E*)-**13** recorded at 25 °C in $CDCl_3$.

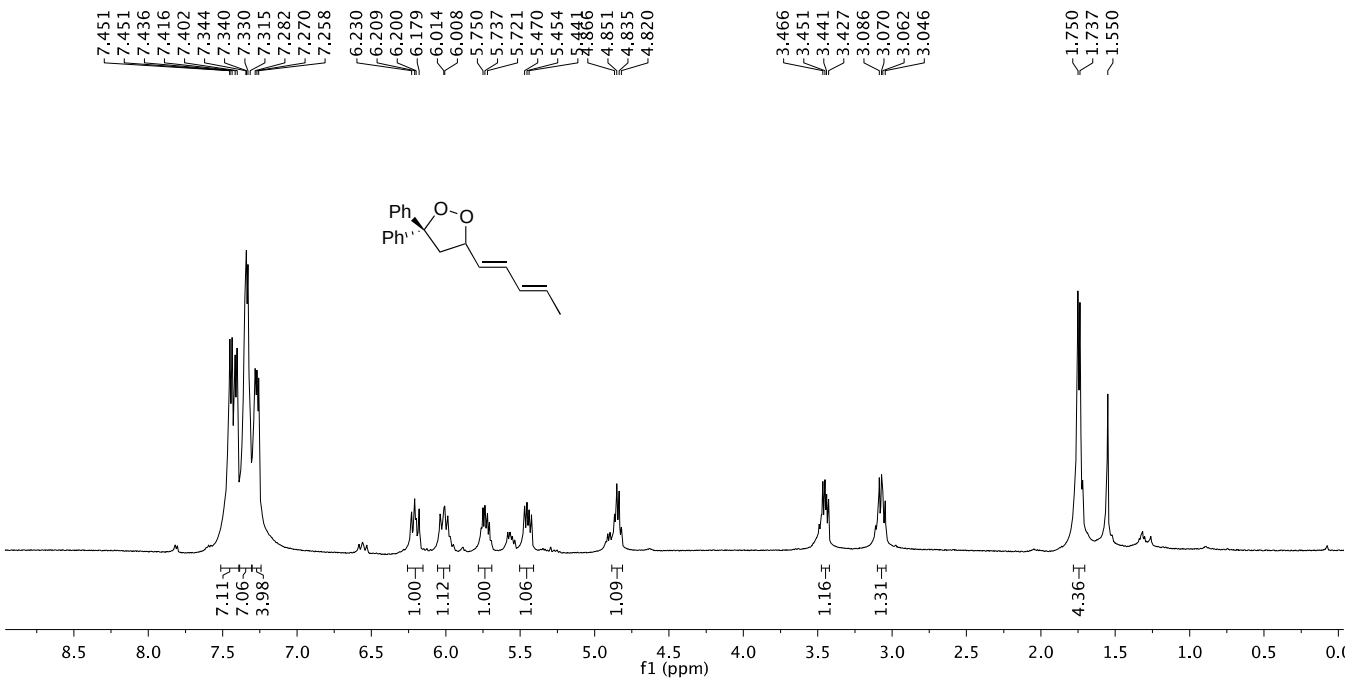



**Figure S5.** $^{1}$H NMR (500 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$. †

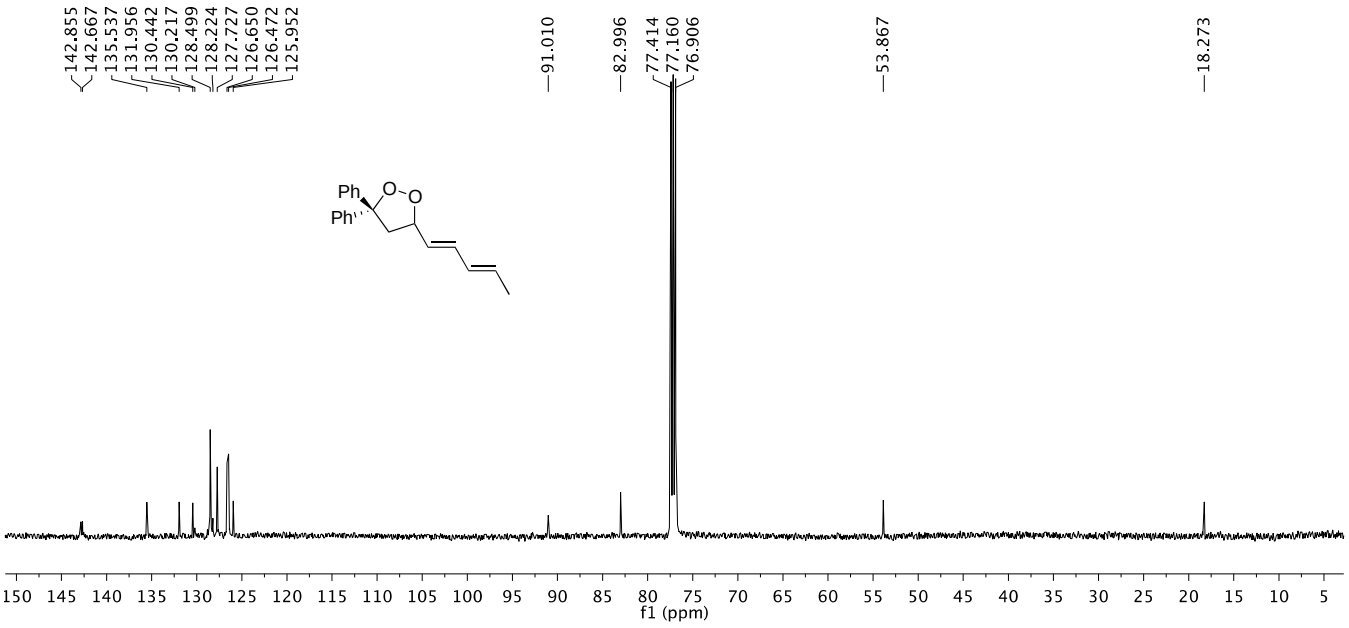



**Figure S6.** $^{13}$C NMR (125 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$.

† The $^{1}$H NMR spectra of this compound showed the presence of minor side-product(s), which could not be separated by flash column chromatography on silica gel (identical $R_f$ values).

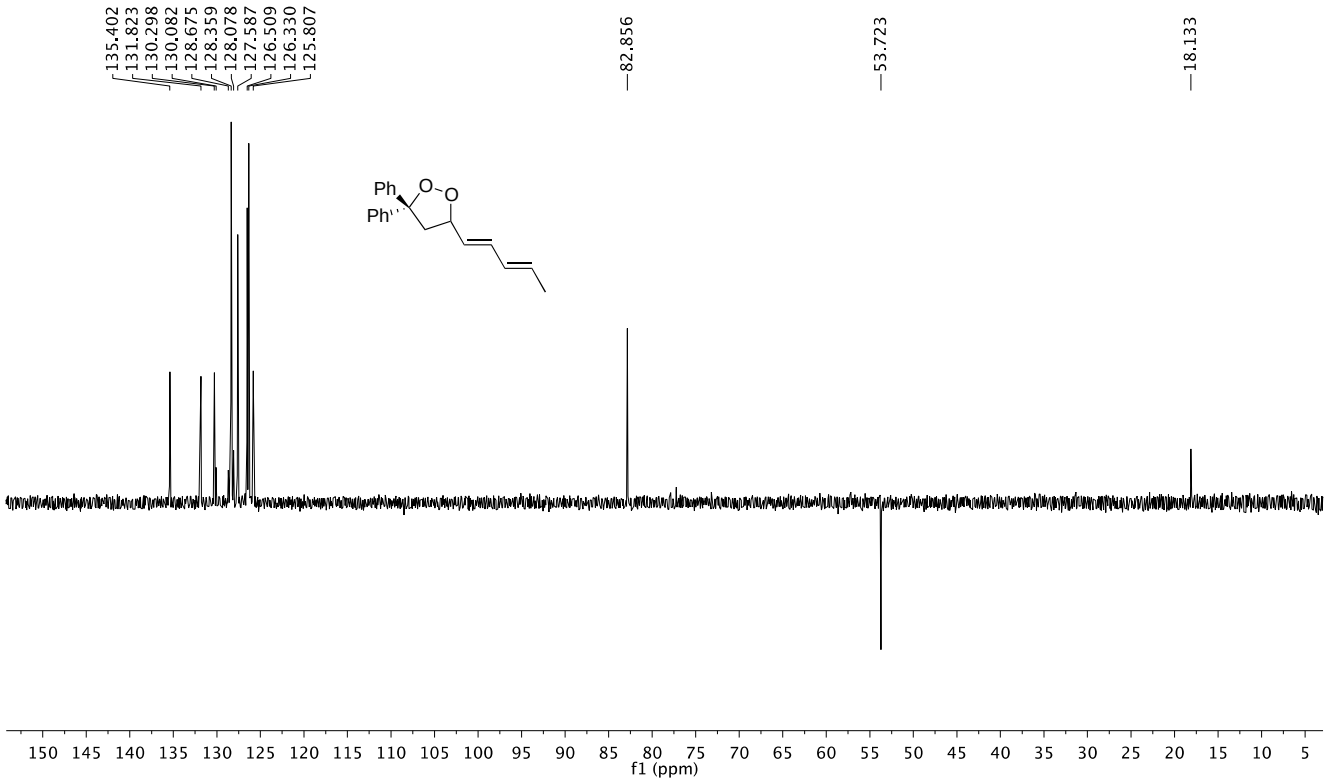



**Figure S7.** DEPT 135 (125 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$.

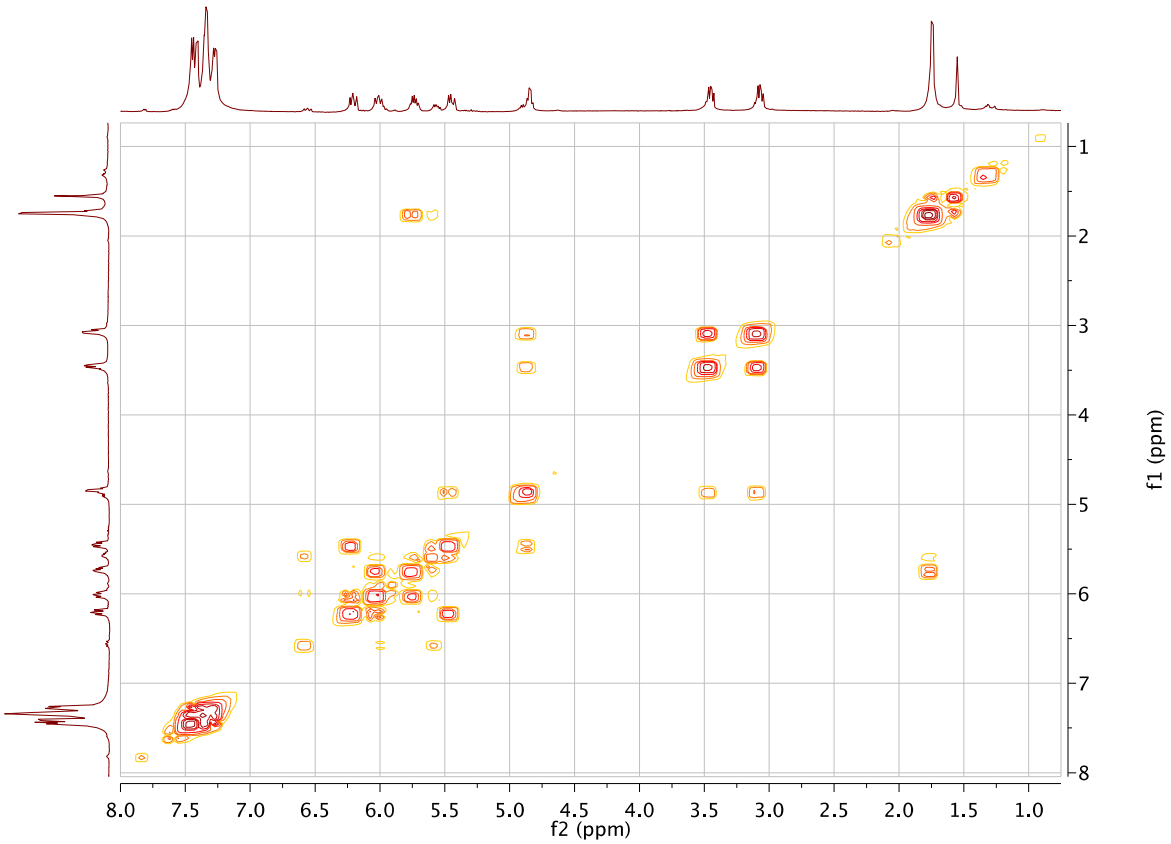



**Figure S8.** COSY (500 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$.

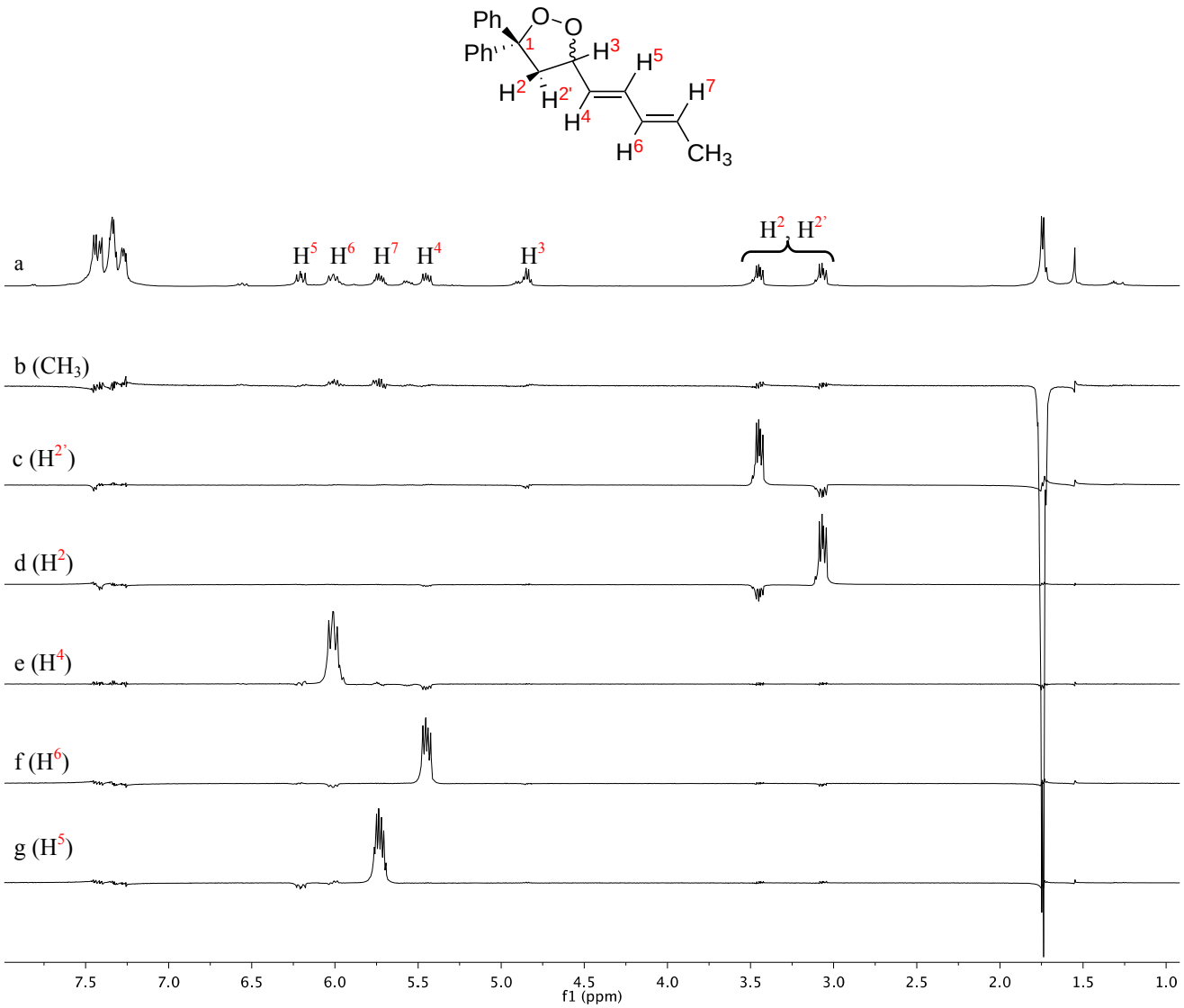



**Figure S9. (**a) $^{1}$H NMR (500 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 $^{o}$C in $CDCl_3$. (b–g) Difference Nuclear Overhauser Effect (NOE; 500 MHz) spectra of (*E*,*E*)-**14** recorded at 25 $^{o}$C in $CDCl_3$; the protons which were irradiated are depicted in parenthesis.

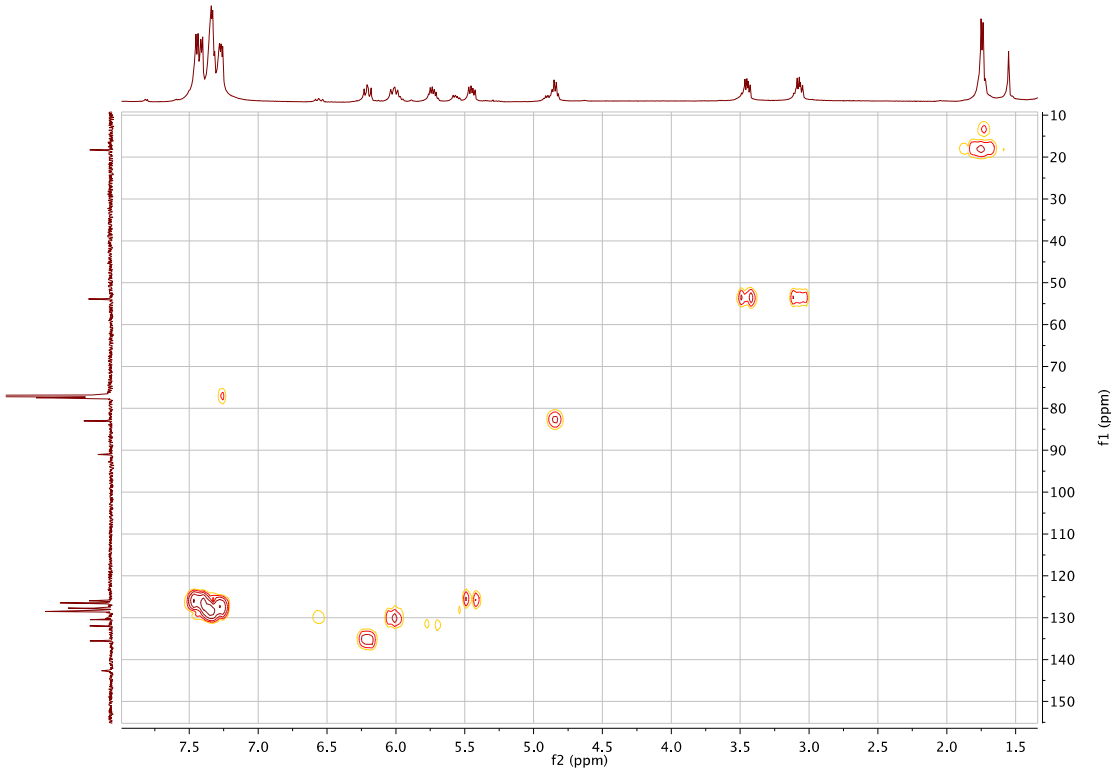



**Figure S10.** HMQC (500 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$.

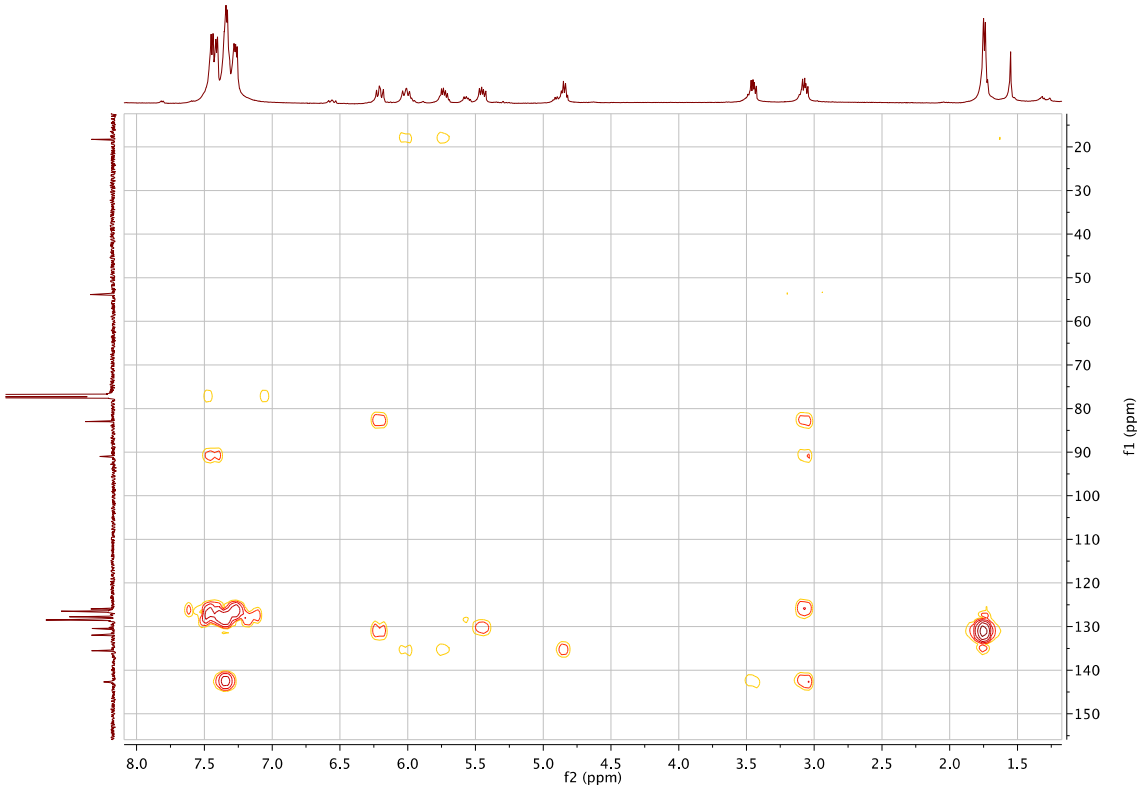



**Figure S11.** HMBC (500 MHz) spectrum of (*E*,*E*)-**14** recorded at 25 °C in $CDCl_3$.

Optimized Geometries, Relative Free Energies (kcal mol$^{-1}$), and Boltzmann Populations (%) of the Four Low-Energy Conformers of (*E*)-13 and (*E*,*E*)-14

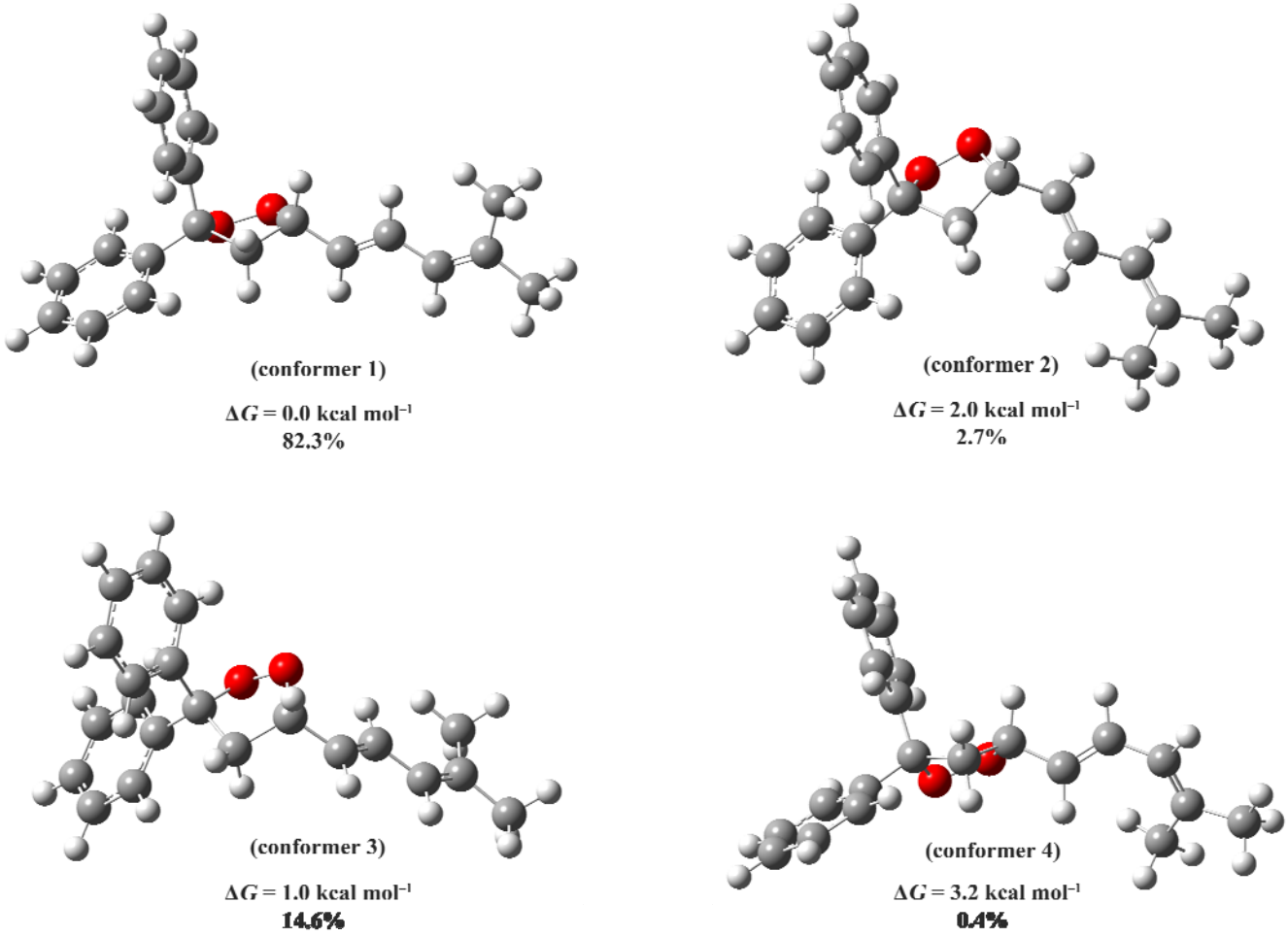



**Figure S12**. Optimized geometries, relative Gibbs free energies ($\Delta G$ in kcal mol$^{-1}$) and calculated Boltzmann populations (%) calculated thereof, for the four low-energy conformers of (*E*)-**13** that are within 5 kcal mol$^{-1}$ of the global minimum. Geometry optimizations and energy calculations were carried out at the M06-2X/6-31+G(d,p) level of theory using the IEFPCM solvation model for chloroform.

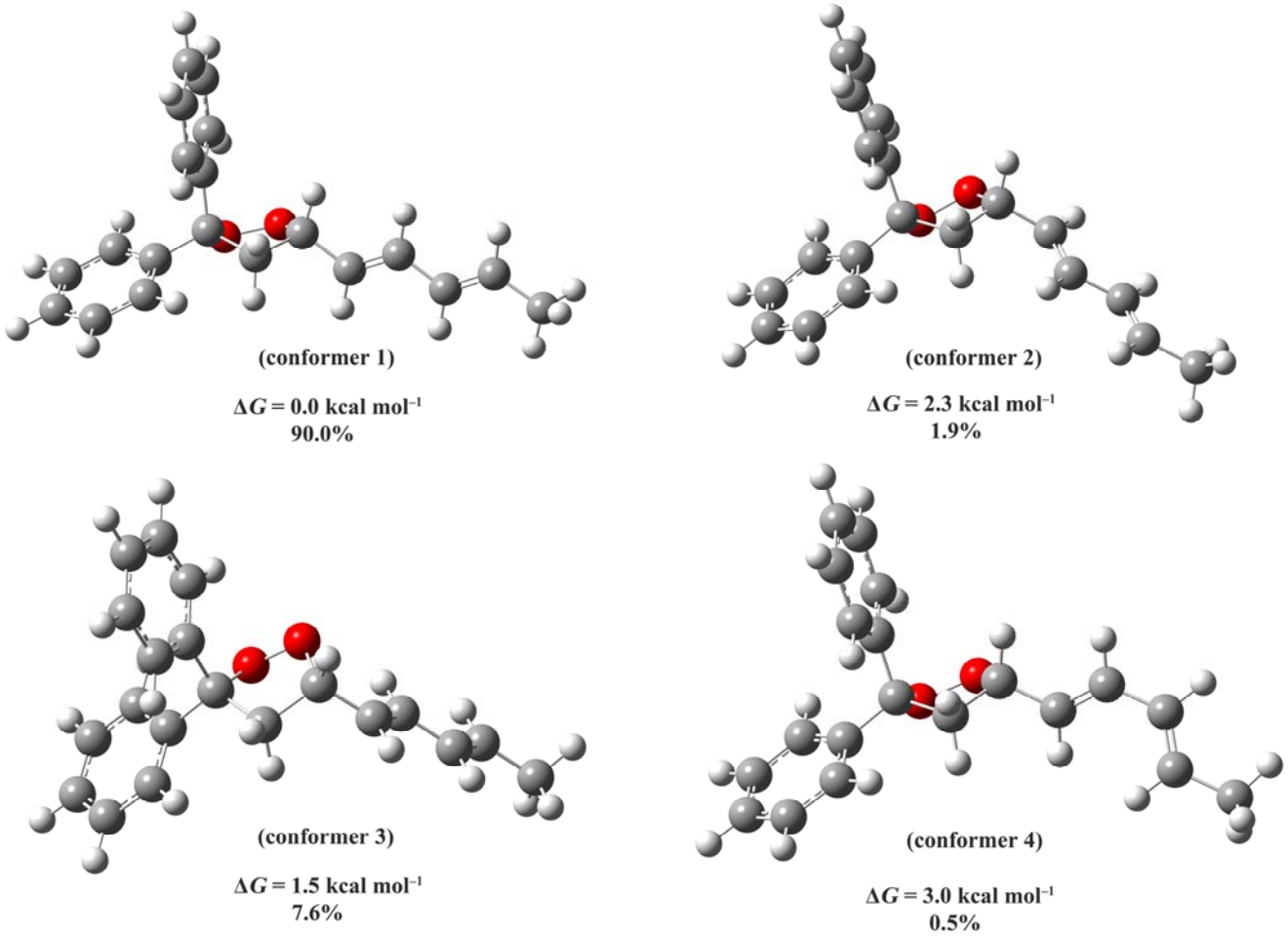
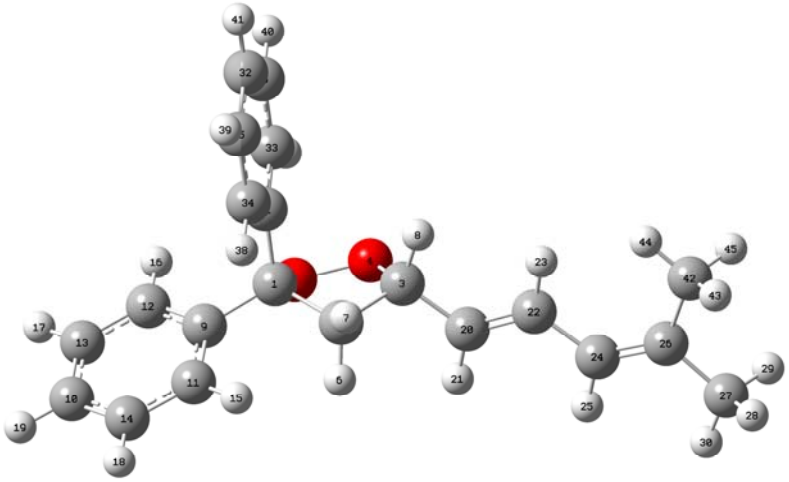



**Figure S13**. Optimized geometries, relative Gibbs free energies ($\Delta G$, in kcal mol$^{-1}$) and Boltzmann populations (%) calculated thereof, for the four low-energy conformers of (*E*,*E*)-**14** that are within 5 kcal mol$^{-1}$ of the global minimum. Geometry optimizations and energy calculations were carried out at the M06-2X/6-31+G(d,p) level of theory using the IEFPCM solvation model for chloroform.

## 2. Cartesian Coordinates (Å), Zero-Point Corrected Total Energies (a.u.), and Gibbs Free Energies (a.u.) of the Four Low-Energy Conformers of (*E*)-13 and (*E*,*E*)-14



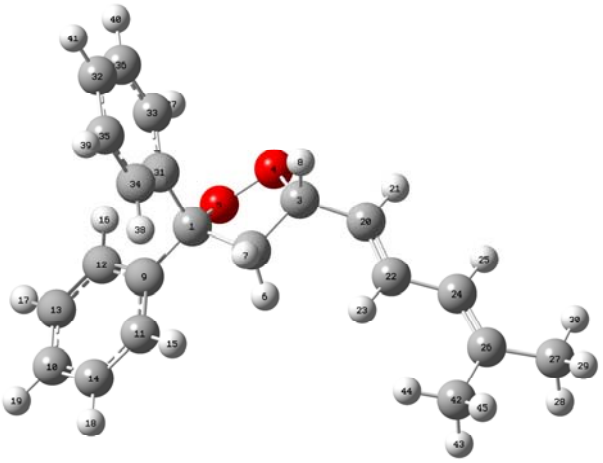
(*E*)-**13** (Conformer 1)

Total energy after ZPVE correction: –963.071892 a.u.

Free Gibbs energy: –963.124618 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) x | y | z |
|---|---|---|---|---|
| 1 | C | -1.264958 | -0.23929 | -0.222824 |
| 2 | C | 0.005702 | -0.638548 | 0.529316 |
| 3 | C | 1.077212 | 0.010421 | -0.345438 |
| 4 | O | 0.488182 | 0.045399 | -1.671416 |
| 5 | O | -0.857984 | -0.461374 | -1.577169 |
| 6 | H | 0.110939 | -1.72798 | 0.518625 |
| 7 | H | 0.048868 | -0.273591 | 1.557171 |
| 8 | H | 1.238657 | 1.053041 | -0.040388 |
| 9 | C | -2.472033 | -1.13125 | 0.002948 |
| 10 | C | -4.757519 | -2.698064 | 0.396822 |
| 11 | C | -2.589568 | -1.930522 | 1.140319 |
| 12 | C | -3.511154 | -1.113002 | -0.934135 |
| 13 | C | -4.643327 | -1.899236 | -0.742788 |
| 14 | C | -3.731897 | -2.708247 | 1.338763 |
| 15 | H | -1.795456 | -1.950083 | 1.88208 |
| 16 | H | -3.427175 | -0.479206 | -1.813514 |
| 17 | H | -5.440648 | -1.884881 | -1.480315 |
| 18 | H | -3.814838 | -3.323868 | 2.229811 |

| | | | | |
|---|---|---|---|---|
| 19 | H | -5.643994 | -3.306903 | 0.54918 |
| 20 | C | 2.373855 | -0.72749 | -0.399338 |
| 21 | H | 2.320299 | -1.768891 | -0.720544 |
| 22 | C | 3.548821 | -0.170095 | -0.071886 |
| 23 | H | 3.552955 | 0.876286 | 0.231322 |
| 24 | C | 4.813915 | -0.89544 | -0.096382 |
| 25 | H | 4.748336 | -1.935509 | -0.417805 |
| 26 | C | 6.027061 | -0.412775 | 0.231378 |
| 27 | C | 7.249531 | -1.286532 | 0.151824 |
| 28 | H | 7.73694 | -1.357133 | 1.131567 |
| 29 | H | 7.986241 | -0.855221 | -0.536383 |
| 30 | H | 7.007048 | -2.295729 | -0.188408 |
| 31 | C | -1.625569 | 1.228349 | 0.011719 |
| 32 | C | -2.311597 | 3.902335 | 0.482342 |
| 33 | C | -1.597659 | 2.154112 | -1.031229 |
| 34 | C | -2.001421 | 1.64817 | 1.291866 |
| 35 | C | -2.34209 | 2.977408 | 1.527659 |
| 36 | C | -1.940732 | 3.486819 | -0.79459 |
| 37 | H | -1.300668 | 1.82939 | -2.023351 |
| 38 | H | -2.042461 | 0.928455 | 2.107696 |
| 39 | H | -2.635814 | 3.290631 | 2.525489 |
| 40 | H | -1.914528 | 4.200655 | -1.613168 |
| 41 | H | -2.577853 | 4.939542 | 0.664213 |
| 42 | C | 6.297206 | 0.992654 | 0.695075 |
| 43 | H | 6.762754 | 0.976307 | 1.68746 |
| 44 | H | 5.404329 | 1.615457 | 0.748979 |
| 45 | H | 7.011809 | 1.478363 | 0.020429 |



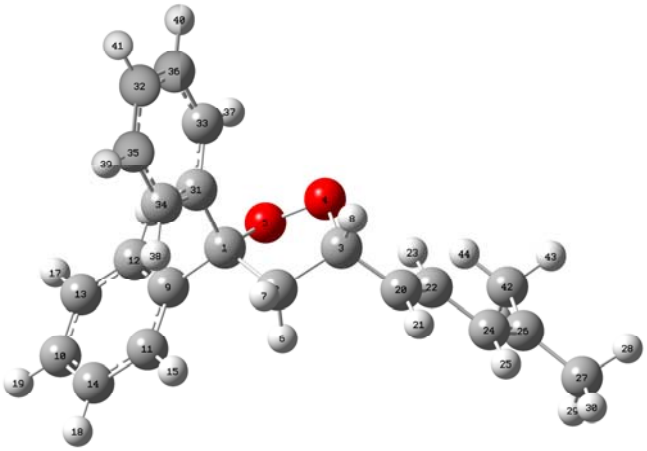
(*E*)-**13** (Conformer 2)

Total energy after ZPVE correction: –963.068399 a.u.

Free Gibbs energy: –963.121400 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | 1.051492 | 0.010845 | -0.281007 |
| 2 | C | -0.308114 | -0.166007 | 0.401772 |
| 3 | C | -0.892367 | -1.335734 | -0.390893 |
| 4 | O | -0.140089 | -1.363604 | -1.63443 |
| 5 | O | 0.690036 | -0.193524 | -1.651205 |
| 6 | H | -0.901923 | 0.738413 | 0.244507 |
| 7 | H | -0.240165 | -0.38241 | 1.469617 |
| 8 | H | -0.648718 | -2.287742 | 0.101665 |
| 9 | C | 1.642446 | 1.406666 | -0.205695 |
| 10 | C | 2.829901 | 3.937894 | -0.073537 |
| 11 | C | 1.30391 | 2.290145 | 0.819776 |
| 12 | C | 2.588312 | 1.793933 | -1.161302 |
| 13 | C | 3.171841 | 3.056047 | -1.100399 |
| 14 | C | 1.899435 | 3.550745 | 0.88791 |
| 15 | H | 0.57749 | 2.00156 | 1.575118 |
| 16 | H | 2.86382 | 1.101504 | -1.952711 |
| 17 | H | 3.898116 | 3.350796 | -1.852421 |
| 18 | H | 1.630637 | 4.229508 | 1.692185 |
| 19 | H | 3.289329 | 4.920784 | -0.023202 |
| 20 | C | -2.360789 | -1.279278 | -0.692624 |
| 21 | H | -2.687566 | -1.939999 | -1.496243 |
| 22 | C | -3.266526 | -0.547009 | -0.029001 |
| 23 | H | -2.936323 | 0.096802 | 0.784087 |

| | | | | |
|---|---|---|---|---|
| 24 | C | -4.692195 | -0.581065 | -0.34187 |
| 25 | H | -4.97127 | -1.238939 | -1.16576 |
| 26 | C | -5.671591 | 0.106989 | 0.273216 |
| 27 | C | -7.103559 | -0.031692 | -0.168544 |
| 28 | H | -7.507733 | 0.940423 | -0.475342 |
| 29 | H | -7.729678 | -0.386703 | 0.658795 |
| 30 | H | -7.205831 | -0.728131 | -1.003781 |
| 31 | C | 2.074651 | -1.026994 | 0.182701 |
| 32 | C | 3.991003 | -2.869827 | 1.064122 |
| 33 | C | 2.661675 | -1.915367 | -0.718676 |
| 34 | C | 2.456048 | -1.063883 | 1.527442 |
| 35 | C | 3.408115 | -1.980005 | 1.967674 |
| 36 | C | 3.616501 | -2.832979 | -0.277556 |
| 37 | H | 2.362092 | -1.890733 | -1.761471 |
| 38 | H | 2.018964 | -0.361583 | 2.235154 |
| 39 | H | 3.697645 | -1.996544 | 3.014522 |
| 40 | H | 4.065651 | -3.522357 | -0.987033 |
| 41 | H | 4.733849 | -3.58514 | 1.405093 |
| 42 | C | -5.466374 | 1.054983 | 1.423527 |
| 43 | H | -5.832744 | 2.053072 | 1.156396 |
| 44 | H | -4.42557 | 1.147994 | 1.734111 |
| 45 | H | -6.052543 | 0.725996 | 2.289571 |



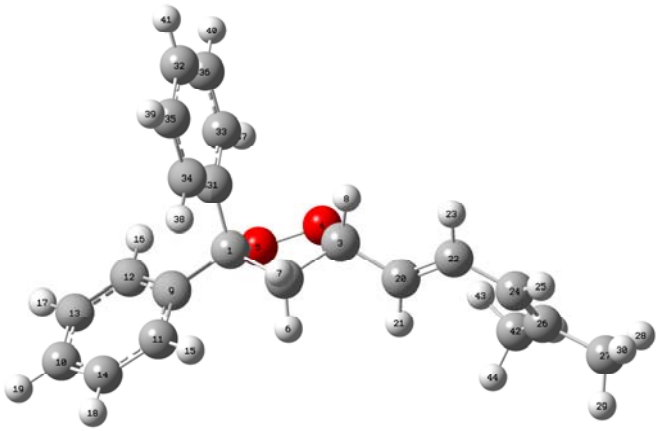
(*E*)-**13** (Conformer 3)

Total energy after ZPVE correction: –963.069762 a.u.

Free Gibbs energy: –963.122989 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | -1.013492 | 0.012349 | -0.142973 |
| 2 | C | -0.119163 | -0.232856 | -1.364053 |
| 3 | C | 0.879526 | -1.275822 | -0.818907 |
| 4 | O | 0.660099 | -1.300963 | 0.602624 |
| 5 | O | -0.060661 | -0.105687 | 0.921541 |
| 6 | H | 0.410335 | 0.688101 | -1.621302 |
| 7 | H | -0.663725 | -0.595814 | -2.237444 |
| 8 | H | 0.612326 | -2.281996 | -1.167008 |
| 9 | C | -1.598106 | 1.409059 | -0.032739 |
| 10 | C | -2.764288 | 3.941055 | 0.222634 |
| 11 | C | -1.809056 | 2.203937 | -1.160039 |
| 12 | C | -1.985237 | 1.885024 | 1.224791 |
| 13 | C | -2.556447 | 3.147918 | 1.352468 |
| 14 | C | -2.394553 | 3.464518 | -1.032857 |
| 15 | H | -1.522988 | 1.845663 | -2.145574 |
| 16 | H | -1.835949 | 1.2612 | 2.102358 |
| 17 | H | -2.844551 | 3.512046 | 2.334447 |
| 18 | H | -2.556444 | 4.073645 | -1.917495 |
| 19 | H | -3.214894 | 4.924302 | 0.321871 |
| 20 | C | 2.307418 | -0.962202 | -1.163487 |
| 21 | H | 2.552174 | -1.027538 | -2.225173 |
| 22 | C | 3.245025 | -0.609138 | -0.274947 |
| 23 | H | 2.959507 | -0.559352 | 0.773086 |

| | | | | |
|---|---|---|---|---|
| 24 | C | 4.61926 | -0.29553 | -0.655343 |
| 25 | H | 4.836744 | -0.363348 | -1.722321 |
| 26 | C | 5.623389 | 0.058824 | 0.167566 |
| 27 | C | 6.997209 | 0.350827 | -0.373499 |
| 28 | H | 7.739726 | -0.318746 | 0.077137 |
| 29 | H | 7.301822 | 1.373838 | -0.121718 |
| 30 | H | 7.040211 | 0.234442 | -1.458907 |
| 31 | C | -2.119855 | -1.035571 | -0.006658 |
| 32 | C | -4.208291 | -2.886846 | 0.239451 |
| 33 | C | -2.229307 | -1.824016 | 1.139186 |
| 34 | C | -3.066039 | -1.176324 | -1.026302 |
| 35 | C | -4.104498 | -2.096786 | -0.906088 |
| 36 | C | -3.269925 | -2.745823 | 1.26011 |
| 37 | H | -1.492767 | -1.720146 | 1.929374 |
| 38 | H | -3.002664 | -0.552444 | -1.916098 |
| 39 | H | -4.834088 | -2.194273 | -1.70498 |
| 40 | H | -3.343235 | -3.357321 | 2.15509 |
| 41 | H | -5.016819 | -3.605797 | 0.335031 |
| 42 | C | 5.50043 | 0.199093 | 1.660571 |
| 43 | H | 6.202495 | -0.478888 | 2.160204 |
| 44 | H | 4.499205 | -0.010459 | 2.036941 |
| 45 | H | 5.774073 | 1.215937 | 1.965841 |



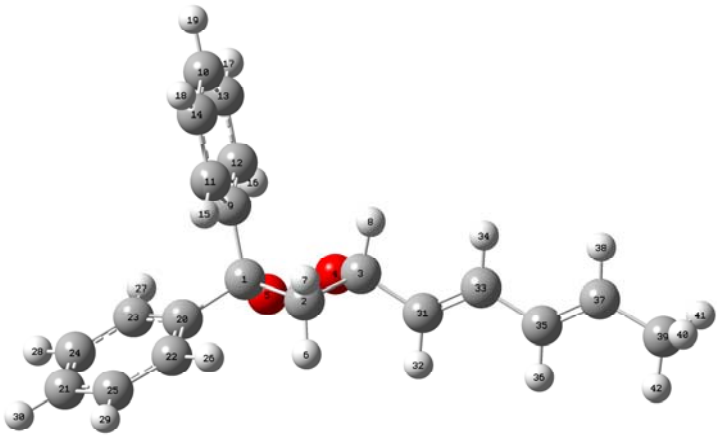
(*E*)-**13** (Conformer 4)

Total energy after ZPVE correction: –963.067142 a.u.

Free Gibbs energy: –963.119528 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | 1.09923 | -0.182463 | 0.11359 |
| 2 | C | -0.109401 | -0.311248 | -0.814947 |
| 3 | C | -1.147688 | 0.511264 | -0.05482 |
| 4 | O | -0.751424 | 0.396931 | 1.336411 |
| 5 | O | 0.477648 | -0.354853 | 1.391662 |
| 6 | H | -0.418328 | -1.359809 | -0.871351 |
| 7 | H | 0.057304 | 0.079117 | -1.820607 |
| 8 | H | -1.067729 | 1.572909 | -0.323913 |
| 9 | C | 2.136915 | -1.284509 | 0.002524 |
| 10 | C | 4.116072 | -3.256455 | -0.164462 |
| 11 | C | 2.248704 | -2.07366 | -1.142322 |
| 12 | C | 3.029685 | -1.481048 | 1.062145 |
| 13 | C | 4.007631 | -2.467849 | 0.982807 |
| 14 | C | 3.239157 | -3.054037 | -1.227162 |
| 15 | H | 1.569474 | -1.928268 | -1.978131 |
| 16 | H | 2.953053 | -0.856504 | 1.948814 |
| 17 | H | 4.689966 | -2.618876 | 1.814358 |
| 18 | H | 3.319769 | -3.660288 | -2.12482 |
| 19 | H | 4.883309 | -4.022579 | -0.228856 |
| 20 | C | -2.556385 | 0.035657 | -0.204981 |
| 21 | H | -2.732379 | -1.011937 | 0.037916 |
| 22 | C | -3.546363 | 0.826904 | -0.639287 |
| 23 | H | -3.290655 | 1.852562 | -0.913784 |

| | | | | |
|---|---|---|---|---|
| 24 | C | -4.9495 | 0.444973 | -0.842761 |
| 25 | H | -5.430984 | 0.90461 | -1.706177 |
| 26 | C | -5.701378 | -0.360897 | -0.070989 |
| 27 | C | -7.129578 | -0.660633 | -0.440742 |
| 28 | H | -7.811765 | -0.308297 | 0.341836 |
| 29 | H | -7.281857 | -1.743175 | -0.527515 |
| 30 | H | -7.413193 | -0.194652 | -1.387182 |
| 31 | C | 1.756992 | 1.193427 | 0.000496 |
| 32 | C | 2.990483 | 3.695352 | -0.245396 |
| 33 | C | 1.767804 | 2.079386 | 1.077744 |
| 34 | C | 2.369517 | 1.565838 | -1.200494 |
| 35 | C | 2.982524 | 2.809726 | -1.324666 |
| 36 | C | 2.383946 | 3.326262 | 0.953212 |
| 37 | H | 1.287536 | 1.792412 | 2.007806 |
| 38 | H | 2.380682 | 0.87329 | -2.040485 |
| 39 | H | 3.458022 | 3.086263 | -2.261407 |
| 40 | H | 2.385829 | 4.010115 | 1.797415 |
| 41 | H | 3.469196 | 4.665739 | -0.339994 |
| 42 | C | -5.230953 | -1.007077 | 1.204588 |
| 43 | H | -4.363583 | -0.49968 | 1.631524 |
| 44 | H | -4.958209 | -2.055787 | 1.032666 |
| 45 | H | -6.039737 | -1.007269 | 1.942841 |



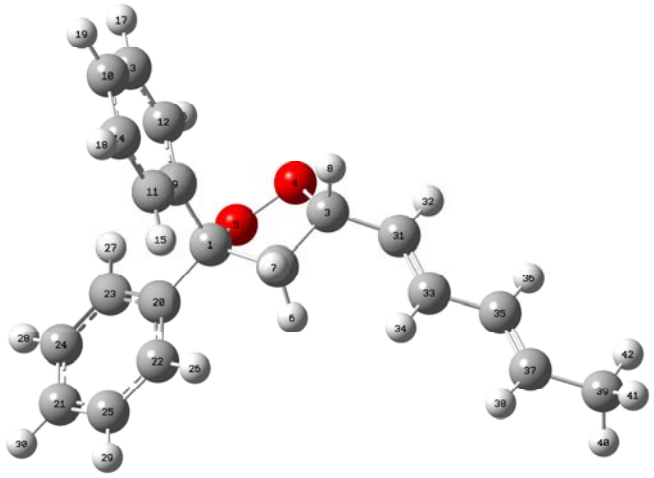
(*E*,*E*)-**14** (Conformer 1)

Total energy after ZPVE correction: –923.801146 a.u.

Free Gibbs energy: –923.851989 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | -0.933244 | -0.227447 | -0.214853 |
| 2 | C | 0.333795 | -0.611022 | 0.551267 |
| 3 | C | 1.401726 | 0.08536 | -0.290395 |
| 4 | O | 0.838377 | 0.125869 | -1.626739 |
| 5 | O | -0.498064 | -0.41179 | -1.56617 |
| 6 | H | 0.468042 | -1.696807 | 0.518166 |
| 7 | H | 0.349755 | -0.268143 | 1.587442 |
| 8 | H | 1.526407 | 1.126341 | 0.036598 |
| 9 | C | -1.332353 | 1.226052 | 0.043232 |
| 10 | C | -2.088213 | 3.872726 | 0.557498 |
| 11 | C | -1.736955 | 1.610181 | 1.32578 |
| 12 | C | -1.310574 | 2.173461 | -0.980174 |
| 13 | C | -1.688572 | 3.492599 | -0.721784 |
| 14 | C | -2.112497 | 2.925912 | 1.583224 |
| 15 | H | -1.773418 | 0.872754 | 2.125867 |
| 16 | H | -0.991154 | 1.87622 | -1.973977 |
| 17 | H | -1.666974 | 4.223665 | -1.525142 |
| 18 | H | -2.428362 | 3.21161 | 2.582547 |
| 19 | H | -2.381684 | 4.899429 | 0.756262 |
| 20 | C | -2.122634 | -1.15201 | -0.02926 |
| 21 | C | -4.376802 | -2.780193 | 0.289319 |
| 22 | C | -2.23571 | -1.987179 | 1.082338 |
| 23 | C | -3.150843 | -1.128847 | -0.978323 |

| | | | | |
|---|---|---|---|---|
| 24 | C | -4.267125 | -1.945323 | -0.824643 |
| 25 | C | -3.362563 | -2.795601 | 1.243369 |
| 26 | H | -1.450609 | -2.010958 | 1.833471 |
| 27 | H | -3.070879 | -0.467193 | -1.837353 |
| 28 | H | -5.05575 | -1.926624 | -1.571358 |
| 29 | H | -3.442234 | -3.439014 | 2.114863 |
| 30 | H | -5.25115 | -3.412683 | 0.412598 |
| 31 | C | 2.720983 | -0.612688 | -0.331484 |
| 32 | H | 2.706546 | -1.648647 | -0.673363 |
| 33 | C | 3.87027 | -0.027209 | 0.030998 |
| 34 | H | 3.855003 | 1.014509 | 0.357823 |
| 35 | C | 5.167598 | -0.695118 | 0.028169 |
| 36 | H | 5.188417 | -1.734447 | -0.303603 |
| 37 | C | 6.305342 | -0.096435 | 0.406609 |
| 38 | H | 6.261418 | 0.943507 | 0.735081 |
| 39 | C | 7.652584 | -0.749901 | 0.414116 |
| 40 | H | 8.084507 | -0.743532 | 1.420791 |
| 41 | H | 8.351783 | -0.2107 | -0.234184 |
| 42 | H | 7.592544 | -1.785822 | 0.070718 |



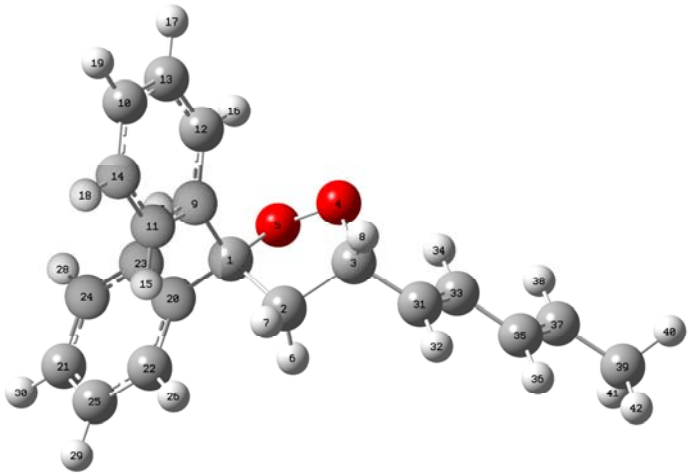
(*E*,*E*)-**14** (Conformer 2)

Total energy after ZPVE correction: –923.797575 a.u.

Free Gibbs energy: –923.848337 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | 0.756402 | 0.032656 | -0.238178 |
| 2 | C | -0.576956 | -0.134228 | 0.497726 |
| 3 | C | -1.232728 | -1.251937 | -0.315833 |
| 4 | O | -0.5207 | -1.267073 | -1.582227 |
| 5 | O | 0.330405 | -0.112999 | -1.597373 |
| 6 | H | -1.148956 | 0.792806 | 0.405715 |
| 7 | H | -0.468885 | -0.397799 | 1.551496 |
| 8 | H | -1.014793 | -2.230383 | 0.134809 |
| 9 | C | 1.771805 | -1.046288 | 0.141527 |
| 10 | C | 3.678601 | -2.965501 | 0.867285 |
| 11 | C | 2.206727 | -1.146957 | 1.466568 |
| 12 | C | 2.301302 | -1.908766 | -0.818737 |
| 13 | C | 3.251228 | -2.864592 | -0.455226 |
| 14 | C | 3.15403 | -2.101352 | 1.829414 |
| 15 | H | 1.815748 | -0.465203 | 2.219862 |
| 16 | H | 1.960563 | -1.834369 | -1.846416 |
| 17 | H | 3.65492 | -3.533441 | -1.21019 |
| 18 | H | 3.485333 | -2.167573 | 2.861817 |
| 19 | H | 4.417351 | -3.710609 | 1.148048 |
| 20 | C | 1.387167 | 1.409391 | -0.139498 |
| 21 | C | 2.647848 | 3.902478 | 0.032661 |
| 22 | C | 1.121936 | 2.259492 | 0.934617 |
| 23 | C | 2.296631 | 1.810369 | -1.124208 |

| | | | | |
|---|---|---|---|---|
| 24 | C | 2.916432 | 3.053967 | -1.04299 |
| 25 | C | 1.754005 | 3.500879 | 1.022458 |
| 26 | H | 0.424559 | 1.959653 | 1.712633 |
| 27 | H | 2.515314 | 1.143386 | -1.954262 |
| 28 | H | 3.613888 | 3.360005 | -1.817431 |
| 29 | H | 1.542299 | 4.153511 | 1.864549 |
| 30 | H | 3.135749 | 4.870611 | 0.098618 |
| 31 | C | -2.70653 | -1.125085 | -0.56763 |
| 32 | H | -3.084077 | -1.735458 | -1.388568 |
| 33 | C | -3.561496 | -0.390165 | 0.155191 |
| 34 | H | -3.19913 | 0.210586 | 0.990732 |
| 35 | C | -4.999188 | -0.3425 | -0.097129 |
| 36 | H | -5.372828 | -0.937113 | -0.932485 |
| 37 | C | -5.855554 | 0.382712 | 0.634987 |
| 38 | H | -5.46199 | 0.970449 | 1.466293 |
| 39 | C | -7.333062 | 0.452498 | 0.399827 |
| 40 | H | -7.649759 | 1.482648 | 0.203805 |
| 41 | H | -7.886477 | 0.112987 | 1.282129 |
| 42 | H | -7.628056 | -0.166544 | -0.45136 |



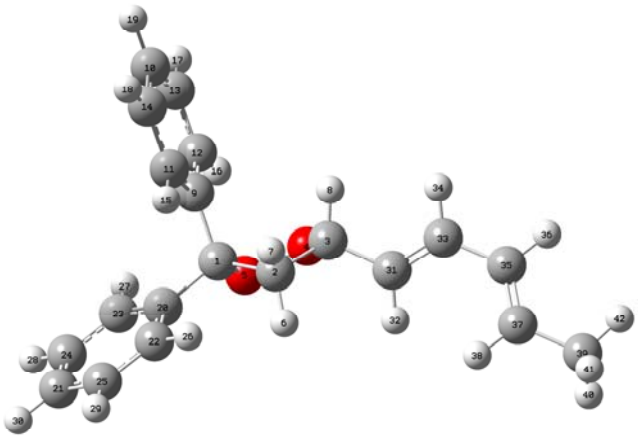
(*E*,*E*)-**14** (Conformer 3)

Total energy after ZPVE correction: –923.798972 a.u.

Free Gibbs energy: –923.849666 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | 0.720883 | 0.007158 | 0.107874 |
| 2 | C | -0.213153 | -0.238654 | 1.299639 |
| 3 | C | -1.19647 | -1.279695 | 0.721878 |
| 4 | O | -0.910524 | -1.32735 | -0.686359 |
| 5 | O | -0.191995 | -0.127109 | -0.989242 |
| 6 | H | -0.749094 | 0.682548 | 1.542014 |
| 7 | H | 0.30371 | -0.603198 | 2.189014 |
| 8 | H | -0.95885 | -2.284172 | 1.094813 |
| 9 | C | 1.842184 | -1.03 | 0.016898 |
| 10 | C | 3.95897 | -2.858317 | -0.145811 |
| 11 | C | 2.752644 | -1.155931 | 1.070382 |
| 12 | C | 2.001514 | -1.821965 | -1.120658 |
| 13 | C | 3.056173 | -2.732294 | -1.19994 |
| 14 | C | 3.805071 | -2.064928 | 0.991731 |
| 15 | H | 2.650299 | -0.529553 | 1.95479 |
| 16 | H | 1.292681 | -1.729751 | -1.937227 |
| 17 | H | 3.168437 | -3.346596 | -2.08895 |
| 18 | H | 4.506488 | -2.150774 | 1.816753 |
| 19 | H | 4.778513 | -3.568293 | -0.209174 |
| 20 | C | 1.295887 | 1.408789 | 0.009916 |
| 21 | C | 2.448691 | 3.949487 | -0.2187 |
| 22 | C | 1.473716 | 2.205689 | 1.141579 |
| 23 | C | 1.709522 | 1.887186 | -1.238128 |

| | | | | |
|---|---|---|---|---|
| 24 | C | 2.274024 | 3.154414 | -1.352676 |
| 25 | C | 2.05253 | 3.470552 | 1.027865 |
| 26 | H | 1.166737 | 1.845533 | 2.120176 |
| 27 | H | 1.586216 | 1.262097 | -2.118766 |
| 28 | H | 2.582805 | 3.520331 | -2.327689 |
| 29 | H | 2.188469 | 4.081172 | 1.915832 |
| 30 | H | 2.893998 | 4.93613 | -0.30757 |
| 31 | C | -2.634872 | -0.944033 | 0.995093 |
| 32 | H | -2.927966 | -0.98206 | 2.045739 |
| 33 | C | -3.527811 | -0.601334 | 0.059428 |
| 34 | H | -3.213891 | -0.571877 | -0.98368 |
| 35 | C | -4.917161 | -0.260166 | 0.352492 |
| 36 | H | -5.224769 | -0.291813 | 1.399494 |
| 37 | C | -5.809943 | 0.08089 | -0.586717 |
| 38 | H | -5.48447 | 0.107038 | -1.62805 |
| 39 | C | -7.240327 | 0.435024 | -0.317011 |
| 40 | H | -7.918693 | -0.241246 | -0.848633 |
| 41 | H | -7.465787 | 1.4487 | -0.665914 |
| 42 | H | -7.467111 | 0.380237 | 0.751028 |



(*E*,*E*)-**14** (Conformer 4)

Total energy after ZPVE correction: –923.796518 a.u.

Free Gibbs energy: –923.847114 a.u.

| Atom label | Atom type | Cartesian coordinates (Å) | | |
|---|---|---|---|---|
| | | x | y | z |
| 1 | C | -0.815863 | -0.17248 | -0.217611 |
| 2 | C | 0.495274 | -0.347816 | 0.550576 |
| 3 | C | 1.426055 | 0.553953 | -0.25917 |
| 4 | O | 0.868718 | 0.540255 | -1.597885 |
| 5 | O | -0.34673 | -0.23394 | -1.568723 |
| 6 | H | 0.820382 | -1.391054 | 0.486635 |
| 7 | H | 0.445051 | -0.039818 | 1.596542 |
| 8 | H | 1.364397 | 1.588827 | 0.103248 |
| 9 | C | -1.470736 | 1.177391 | 0.078236 |
| 10 | C | -2.695922 | 3.627413 | 0.658628 |
| 11 | C | -1.937227 | 1.447264 | 1.368821 |
| 12 | C | -1.623284 | 2.139597 | -0.920057 |
| 13 | C | -2.234987 | 3.360468 | -0.628629 |
| 14 | C | -2.546143 | 2.665263 | 1.659167 |
| 15 | H | -1.838031 | 0.694747 | 2.14932 |
| 16 | H | -1.255621 | 1.931959 | -1.919924 |
| 17 | H | -2.347769 | 4.104295 | -1.412426 |
| 18 | H | -2.907815 | 2.862067 | 2.664402 |
| 19 | H | -3.171355 | 4.577863 | 0.883068 |
| 20 | C | -1.822268 | -1.299488 | -0.074655 |
| 21 | C | -3.750566 | -3.314344 | 0.160963 |
| 22 | C | -1.795942 | -2.174586 | 1.011323 |
| 23 | C | -2.827595 | -1.431655 | -1.039189 |

| | | | | |
|---|---|---|---|---|
| 24 | C | -3.780681 | -2.439295 | -0.926864 |
| 25 | C | -2.7608 | -3.176722 | 1.130917 |
| 26 | H | -1.027777 | -2.079944 | 1.774369 |
| 27 | H | -2.858094 | -0.740643 | -1.878009 |
| 28 | H | -4.551553 | -2.539474 | -1.685546 |
| 29 | H | -2.733265 | -3.850361 | 1.982569 |
| 30 | H | -4.49801 | -4.097159 | 0.251925 |
| 31 | C | 2.848035 | 0.100223 | -0.312408 |
| 32 | H | 3.018008 | -0.898395 | -0.717072 |
| 33 | C | 3.869836 | 0.861314 | 0.098763 |
| 34 | H | 3.655883 | 1.878456 | 0.430966 |
| 35 | C | 5.279267 | 0.445382 | 0.125408 |
| 36 | H | 6.018968 | 1.230014 | -0.03774 |
| 37 | C | 5.702349 | -0.803892 | 0.356919 |
| 38 | H | 4.963399 | -1.575493 | 0.577993 |
| 39 | C | 7.139255 | -1.228218 | 0.351195 |
| 40 | H | 7.313365 | -1.998477 | -0.408139 |
| 41 | H | 7.42455 | -1.662651 | 1.315228 |
| 42 | H | 7.801039 | -0.383913 | 0.141461 |

## 3. Full Citation for Gaussian 09 (Ref. 56 of Main Manuscript)

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