**Supplementary Materials:**

# A DFT Study of the Copolymerization of Methyl Vinyl Sulfone and Ethylene Catalyzed by Phosphine–Sulfonate and $\alpha$-Diimine Palladium Complexes

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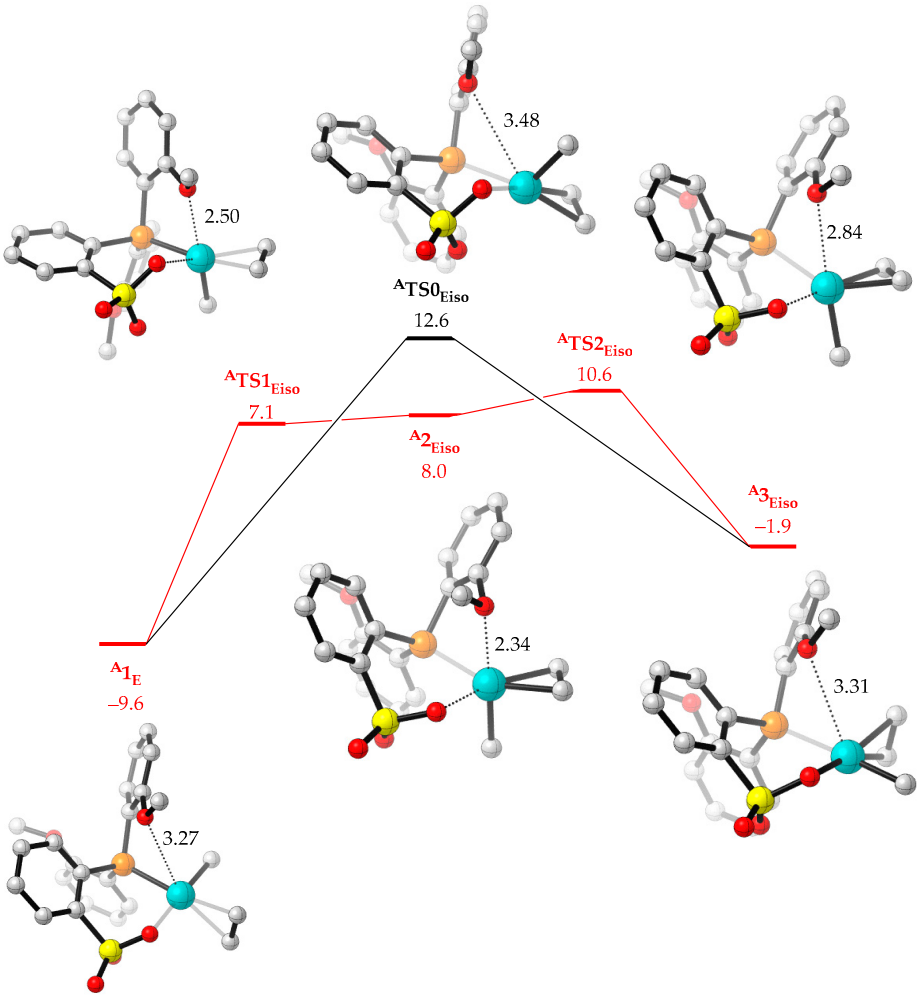


**Figure S1.** Calculated Gibbs free energy profile of *cis*/*trans* isomerization of ethylene mediated by **A** (distances in Å and energy in kcal/mol).

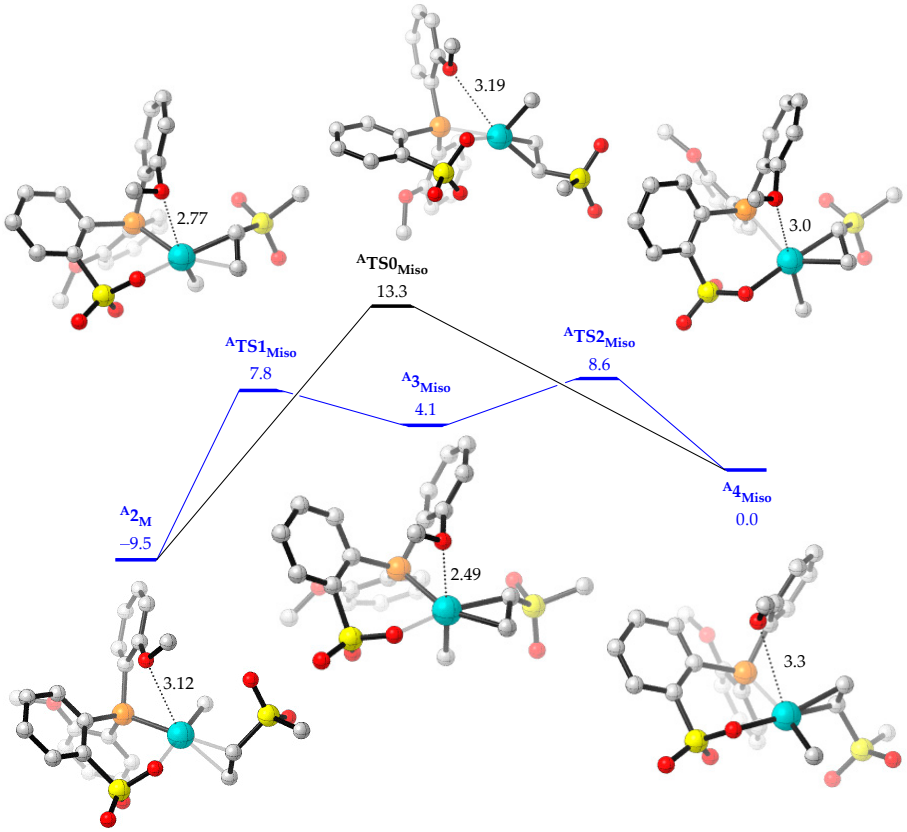


**Figure S2.** Calculated Gibbs free energy profile of *cis*/*trans* isomerization of MVS mediated by **A** (distances in Å and energy in kcal/mol).

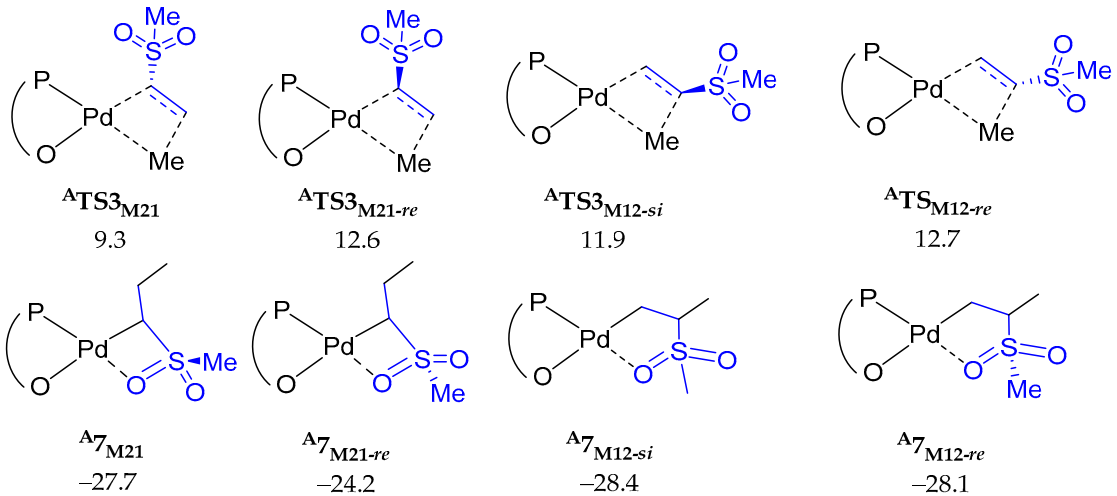


**Figure S3.** Four possible transition states and corresponding intermediate free energies (in kcal/mol) for insertion of MVS into the Pd–Me bond by complex **A.**

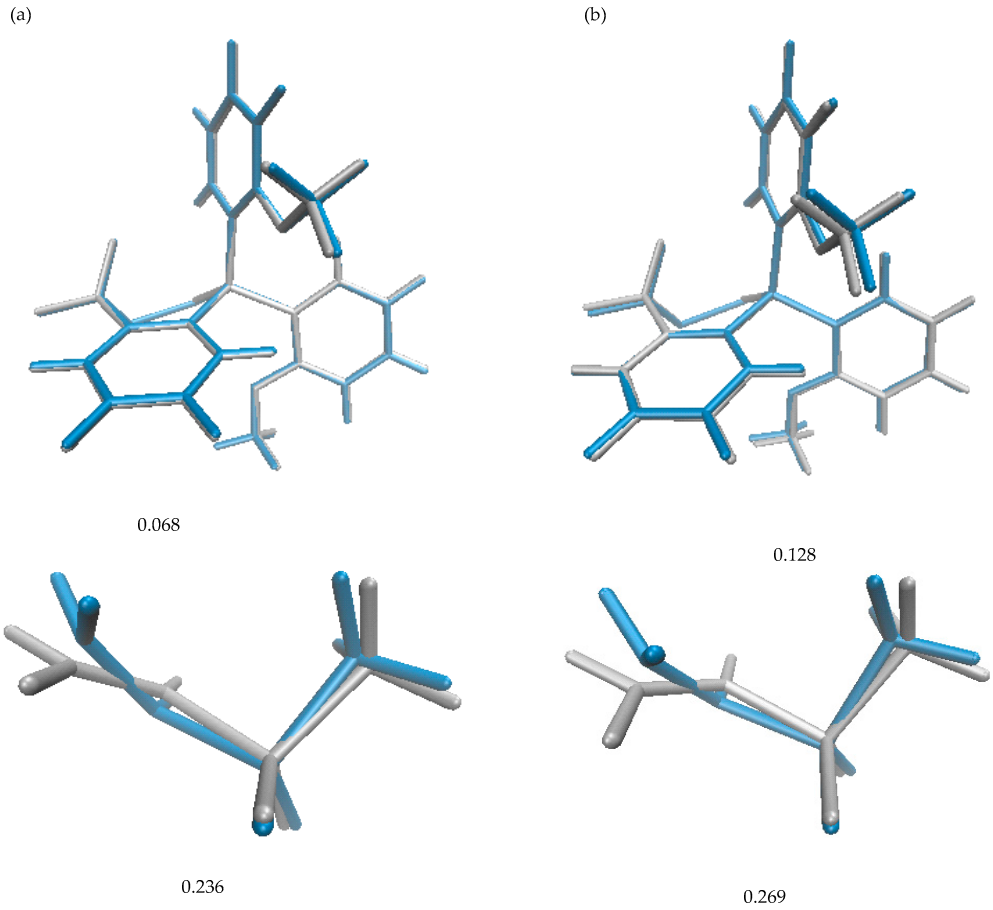


**Figure S4.** Overlay of catalysts and monomers in transition states and stable intermediates (**a**: 2,1-manner **b**: 1,2-manner) (in Å).

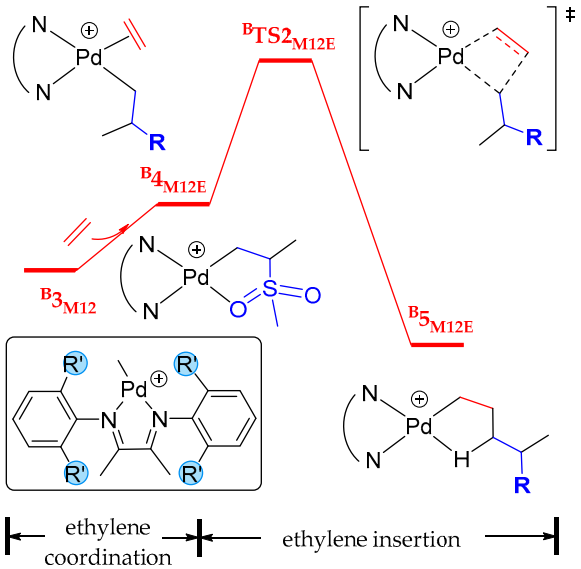


**Figure S5.** The considered chain propagation process based on MVS-inserted product $^{B}3_{M12}$ by catalysts **B1–B7**.

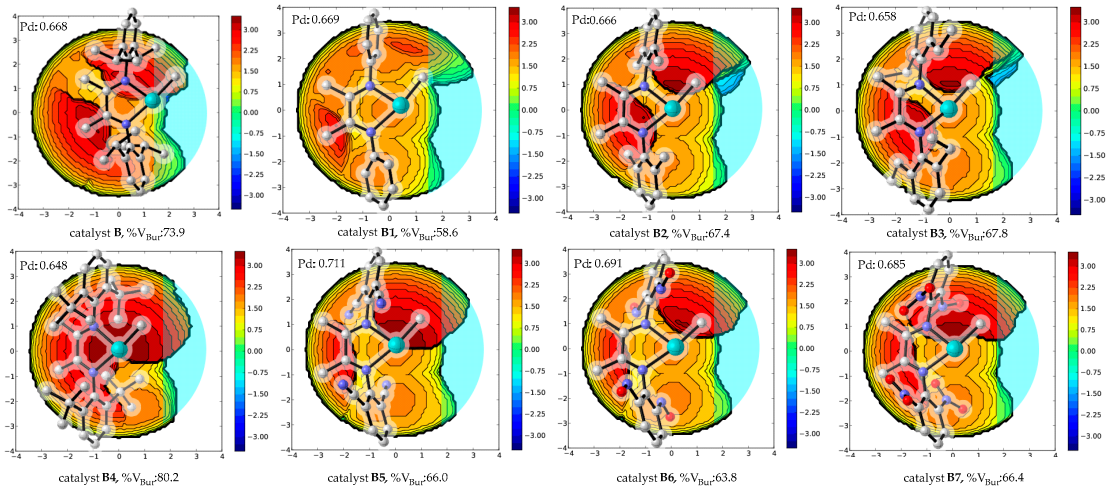


**Figure S6.** Topographical steric maps of catalysts **B** and **B1–B7.** The NBO charges on metal atoms are shown in black.

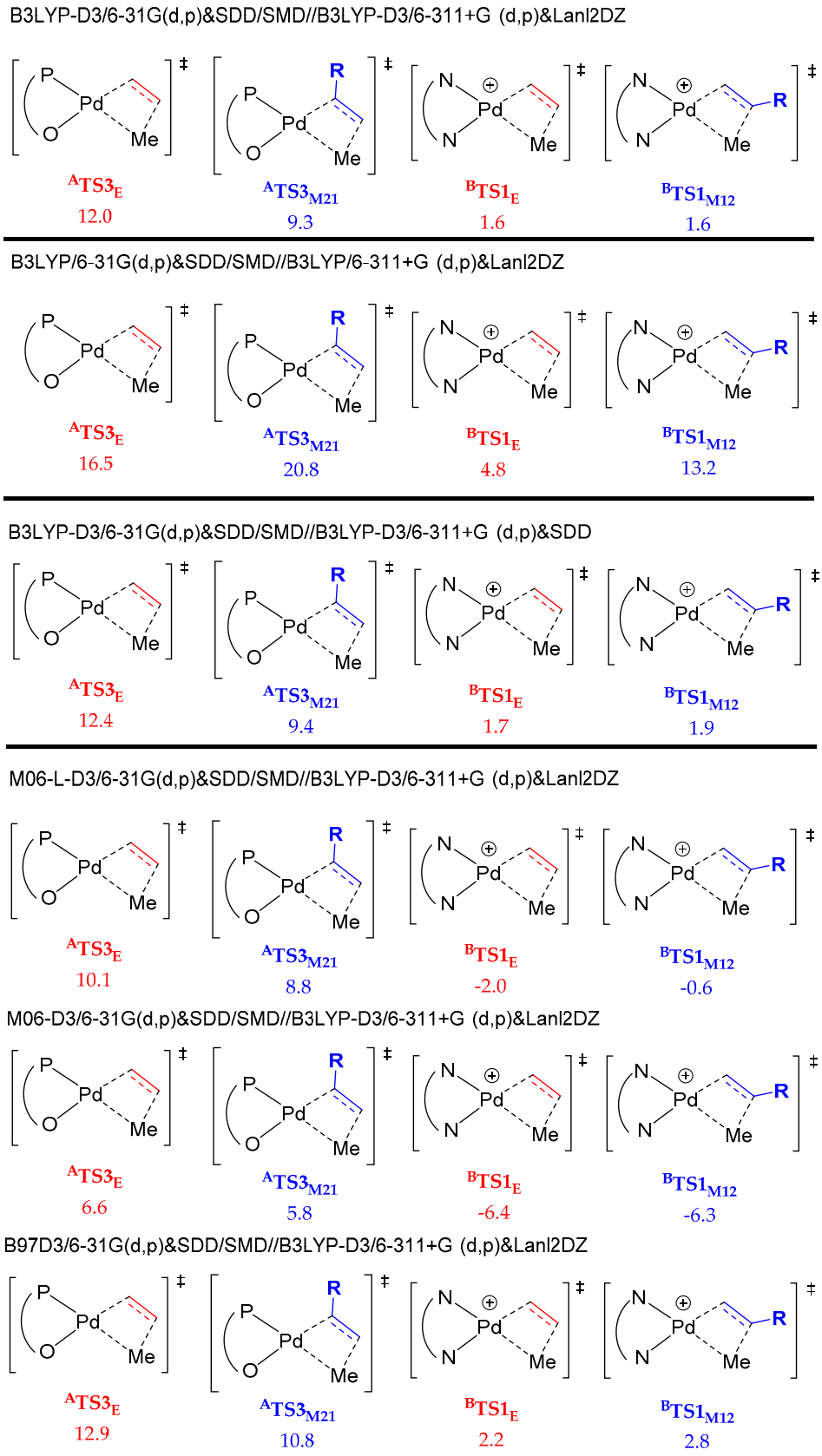


**Figure S7.** Calculated relative Gibbs free energies by different basis sets and methods (in kcal/mol). The relative energies of the corresponding catalysts and monomers were set to be 0.0 kcal/mol.

**Table S1.** Calculated thermodynamic corrections for Gibbs free energies ($\Delta G_{cor}$ in Hartrees), solution-phase single-point energies ($\Delta E_{sol}$ in Hartrees) and solution-phase Gibbs free energies ($\Delta G_{sol}$ in Hartrees).

| **Computational level: B3LYP-D3/6-31G(d,p)&SDD/SMD//B3LYP-D3/6-311+G (d,p)&Lanl2DZ** | | | |
|---|---|---|---|
| species | **$\Delta G_{cor}$** | **$\Delta E_{sol}$** | **$\Delta G_{sol}$** |
| $^{A}$**0** | 0.321177 | −2056.885134 | −2056.560929 |
| $^{B}$**0** | 0.589031 | −1368.712850 | −1368.120791 |
| ethylene | 0.029582 | −78.617676 | −78.585066 |
| MVS | 0.059616 | −666.603201 | −666.540557 |
| $^{A}$**1**$_{E}$ | 0.371631 | −2135.53591 | −2135.161251 |
| $^{A}$**TS0**$_{Eiso}$ | 0.371604 | −2135.500572 | −2135.12594 |
| $^{A}$**TS1**$_{Eiso}$ | 0.374802 | −2135.512441 | −2135.134611 |
| $^{A}$**2**$_{Eiso}$ | 0.373589 | −2135.509851 | −2135.133234 |
| $^{A}$**TS2**$_{Eiso}$ | 0.373151 | −2135.505272 | −2135.129093 |
| $^{A}$**3**$_{Eiso}$ | 0.372247 | −2135.524362 | −2135.149087 |
| $^{A}$**4**$_{E}$ | 0.372194 | −2135.514041 | −2135.138819 |
| $^{A}$**TS3**$_{E}$ | 0.372886 | −2135.502851 | −2135.126937 |
| $^{A}$**5**$_{E}$ | 0.373736 | −2135.543461 | −2135.166697 |
| $^{A}$**6**$_{E}$ | 0.373063 | −2135.547256 | −2135.171165 |
| $^{A}$**1**$_{M}$ | 0.401087 | −2723.528498 | −2723.124383 |
| $^{A}$**2**$_{M}$ | 0.404924 | −2723.524548 | −2723.116596 |
| $^{A}$**TS0**$_{Miso}$ | 0.403249 | −2723.486610 | −2723.080333 |
| $^{A}$**TS1**$_{Miso}$ | 0.406106 | −2723.498255 | −2723.089121 |
| $^{A}$**3**$_{Miso}$ | 0.405848 | −2723.503831 | −2723.094955 |
| $^{A}$**TS2**$_{Miso}$ | 0.404461 | −2723.495330 | −2723.087841 |
| $^{A}$**4**$_{Miso}$ | 0.403832 | −2723.508328 | −2723.101468 |
| $^{A}$**5**$_{M21}$ | 0.405009 | −2723.499433 | −2723.091396 |
| $^{A}$**TS3**$_{M21}$ | 0.406522 | −2723.496237 | −2723.086687 |
| $^{A}$**TS3**$_{M21\text{-}re}$ | 0.406855 | −2723.491354 | −2723.081471 |
| $^{A}$**7**$_{M21\text{-}re}$ | 0.410888 | −2723.553987 | −2723.140071 |
| $^{A}$**TS3**$_{M12\text{-}si}$ | 0.406059 | −2723.491600 | −2723.082513 |
| $^{A}$**7**$_{M12\text{-}si}$ | 0.408956 | −2723.558721 | −2723.146737 |
| $^{A}$**TS3**$_{M12\text{-}re}$ | 0.404891 | −2723.489215 | −2723.081296 |
| $^{A}$**7**$_{M12\text{-}re}$ | 0.409665 | −2723.558967 | −2723.146274 |
| $^{A}$**6**$_{M21}$ | 0.408513 | −2723.544835 | −2723.133294 |
| $^{A}$**7**$_{M21}$ | 0.408999 | −2723.557621 | −2723.145594 |
| $^{A}$**7**$_{EE}$ | 0.426517 | −2214.193457 | −2213.763912 |
| $^{A}$**TS4**$_{EEiso}$ | 0.427766 | −2214.167119 | −2213.736325 |
| $^{A}$**8**$_{EEiso}$ | 0.426254 | −2214.170369 | −2213.741087 |
| $^{A}$**TS**$_{5EEiso}$ | 0.427112 | −2214.166839 | −2213.736699 |
| $^{A}$**9**$_{EE}$ | 0.42674 | −2214.183465 | −2213.753697 |

| | | | |
|---|---|---|---|
| $^{A}$**10**$_{EE}$ | 0.426281 | −2214.173205 | −2213.743896 |
| $^{A}$**TS6**$_{EE}$ | 0.427047 | −2214.161315 | −2213.73124 |
| $^{A}$**11**$_{EE}$ | 0.427778 | −2214.199583 | −2213.768777 |
| $^{A}$**12**$_{EE}$ | 0.425899 | −2214.204582 | −2213.775655 |
| $^{A}$**7**$_{EM}$ | 0.457704 | −2802.187762 | −2801.72703 |
| $^{A}$**8**$_{EM}$ | 0.458502 | −2802.182122 | −2801.720592 |
| $^{A}$**TS4**$_{EMiso}$ | 0.459726 | −2802.152424 | −2801.68967 |
| $^{A}$**9**$_{EMiso}$ | 0.459788 | −2802.156378 | −2801.693562 |
| $^{A}$**TS5**$_{EMiso}$ | 0.461056 | −2802.155475 | −2801.691391 |
| $^{A}$**10**$_{EM}$ | 0.457554 | −2802.169451 | −2801.708869 |
| $^{A}$**11**$_{EM}$ | 0.459054 | −2802.161384 | −2801.699302 |
| $^{A}$**TS6**$_{EM}$ | 0.460555 | −2802.157002 | −2801.693419 |
| $^{A}$**12**$_{EM}$ | 0.462304 | −2802.200931 | −2801.735599 |
| $^{A}$**13**$_{EM}$ | 0.462137 | −2802.215661 | −2801.750496 |
| $^{A}$**8**$_{ME}$ | 0.463404 | −2802.194788 | −2801.728356 |
| $^{A}$**TS4**$_{MEiso}$ | 0.462737 | −2802.162484 | −2801.696719 |
| $^{A}$**9**$_{MEiso}$ | 0.462141 | −2802.165880 | −2801.700711 |
| $^{A}$**TS5**$_{MEiso}$ | 0.461203 | −2802.160567 | −2801.696336 |
| $^{A}$**10**$_{ME}$ | 0.46188 | −2802.186979 | −2801.722071 |
| $^{A}$**11**$_{ME}$ | 0.462456 | −2802.179827 | −2801.714343 |
| $^{A}$**TS6**$_{ME}$ | 0.460552 | −2802.159558 | −2801.695978 |
| $^{A}$**12**$_{ME}$ | 0.465222 | −2802.216627 | −2801.748377 |
| $^{B}$**1**$_{E}$ | 0.643321 | −1447.380075 | −1446.733726 |
| $^{B}$**TS1**$_{E}$ | 0.644326 | −1447.350670 | −1446.703316 |
| $^{B}$**2**$_{E}$ | 0.643846 | −1447.379308 | −1446.732434 |
| $^{B}$**3**$_{E}$ | 0.641615 | −1447.389173 | −1446.744530 |
| $^{B}$**1**$_{M}$ | 0.670899 | −2035.365990 | −2034.692063 |
| $^{B}$**2**$_{M12}$ | 0.674888 | −2035.359010 | −2034.681094 |
| $^{B}$**TS1**$_{M12}$ | 0.676324 | −2035.338145 | −2034.658793 |
| $^{B}$**3**$_{M12}$ | 0.678016 | −2035.406298 | −2034.725254 |
| $^{B}$**2**$_{M21}$ | 0.680377 | −2035.361249 | −2034.677844 |
| $^{B}$**TS1**$_{M21}$ | 0.677834 | −2035.337289 | −2034.656427 |
| $^{B}$**3**$_{M21}$ | 0.677807 | −2035.401918 | −2034.721083 |
| $^{B}$**4**$_{M12E}$ | 0.731374 | −2114.031980 | −2113.297578 |
| $^{B}$**TS2**$_{M12E}$ | 0.730368 | −2113.995897 | −2113.262501 |
| $^{B}$**5M**$_{12E}$ | 0.731723 | −2114.031879 | −2113.297128 |
| $^{B}$**6**$_{M12E}$ | 0.737891 | −2114.060060 | −2113.319141 |
| $^{B}$**4**$_{M21E}$ | 0.735781 | −2114.033821 | −2113.295012 |
| $^{B}$**TS2**$_{M21E}$ | 0.733774 | −2113.995356 | −2113.258554 |
| $^{B}$**5**$_{M21E}$ | 0.731873 | −2114.060217 | −2113.325316 |
| **B1** | - | −896.752514 | - |
| $^{B1}$**3**$_{M12}$ | 0.357831 | −1563.445784 | −1563.084925 |
| $^{B1}$**4**$_{M12E}$ | 0.406441 | −1642.071083 | −1641.661614 |

| | | | |
|---|---|---|---|
| $^{B1}$**TS2**$_{M12E}$ | 0.408263 | −1642.038452 | −1641.627161 |
| **B2** | - | −1054.085972 | - |
| $^{B2}$**3**$_{M12}$ | 0.460186 | −1720.779155 | −1720.315941 |
| $^{B2}$**4**$_{M12E}$ | 0.512109 | −1799.405993 | −1798.890856 |
| $^{B2}$**TS2**$_{M12E}$ | 0.51238 | −1799.374220 | −1798.858812 |
| **B3** | - | −1211.396710 | - |
| $^{B3}$**3**$_{M12}$ | 0.570087 | −1878.090480 | −1877.517365 |
| $^{B3}$**4**$_{M12E}$ | 0.62138 | −1956.716167 | −1956.091759 |
| $^{B3}$**TS2**$_{M12E}$ | 0.622961 | −1956.685609 | −1956.05962 |
| **B4** | - | −1525.979569 | - |
| $^{B4}$**3**$_{M12}$ | 0.794833 | −2192.673584 | −2191.875723 |
| $^{B4}$**4**$_{M12E}$ | 0.845747 | −2271.293873 | −2270.445098 |
| $^{B4}$**TS2**$_{M12E}$ | 0.847142 | −2271.263911 | −2270.413741 |
| **B5** | - | −1265.809304 | - |
| $^{B5}$**3**$_{M12}$ | 0.344306 | −1932.506629 | −1932.159295 |
| $^{B5}$**4**$_{M12E}$ | 0.392661 | −2011.135480 | −2010.739791 |
| $^{B5}$**TS2**$_{M12E}$ | 0.394127 | −2011.103126 | −2010.705971 |
| **B6** | - | −1414.049995 | - |
| $^{B6}$**3**$_{M12}$ | 0.3346 | −2080.746244 | −2080.408616 |
| $^{B6}$**4**$_{M12E}$ | 0.383469 | −2159.375197 | −2158.9887 |
| $^{B6}$**TS2**$_{M12E}$ | 0.383119 | −2159.338828 | −2158.952681 |
| **B7** | - | −1714.983068 | - |
| $^{B7}$**3**$_{M12}$ | 0.35524 | −2381.682892 | −2381.324624 |
| $^{B7}$**4**$_{M12E}$ | 0.40257 | −2460.309932 | −2459.904334 |
| $^{B7}$**TS2**$_{M12E}$ | 0.404218 | −2460.278604 | −2459.871358 |
| **Computational level: B3LYP/6-31G(d,p)&SDD/SMD//B3LYP/6-311+G (d,p)&Lanl2DZ** | | | |
| $^{A}$**0** | 0.320656 | −2056.809506 | −2056.485822 |
| $^{B}$**0** | 0.589947 | −1368.608936 | −1368.015961 |
| ethylene | 0.029574 | −78.616831 | −78.58422916 |
| MVS | 0.059664 | −666.594727 | −666.5320352 |
| $^{A}$**TS3**$_{E}$ | 0.372355 | −2135.419094 | −2135.043711 |
| $^{A}$**TS3**$_{M21}$ | 0.403994 | −2723.391697 | −2722.984675 |
| $^{B}$**TS1**$_{E}$ | 0.638633 | −1447.234195 | −1446.592534 |
| $^{B}$**TS1**$_{M12}$ | 0.671402 | −2035.20143 | −2034.527 |
| **Computational level: B3LYP-D3/6-31G(d,p)&SDD/SMD//B3LYP-D3/6-311+G (d,p)&SDD** | | | |
| $^{A}$**0** | 0.320928 | −2056.885039 | −2056.561083 |
| $^{B}$**0** | 0.588617 | −1368.712846 | −1368.121201 |
| ethylene | 0.029582 | −78.617676 | −78.58506616 |
| MVS | 0.059616 | −666.603201 | −666.5405572 |
| $^{A}$**TS3E** | 0.644196 | −1447.350775 | −1446.703551 |
| $^{A}$**TS3M21** | 0.676202 | −2035.337886 | −2034.658656 |
| $^{B}$**TS1**$_{E}$ | 0.373448 | −2135.502883 | −2135.126407 |
| $^{B}$**TS1**$_{M12}$ | 0.406712 | −2723.496346 | −2723.086606 |

| **Computational level: M06-L-D3/6-31G(d,p)&SDD/SMD//B3LYP-D3/6-311+G (d,p)&Lanl2DZ** | | | |
|---|---|---|---|
| $^{A}$**0** | 0.321177 | −2056.681416 | −2056.357211 |
| $^{B}$**0** | 0.589031 | −1368.50319 | −1367.911131 |
| ethylene | 0.029582 | −78.59476 | −78.56215016 |
| MVS | 0.059616 | −666.537524 | −666.4748802 |
| $^{A}$**TS3E** | 0.372886 | −2135.279196 | −2134.903282 |
| $^{A}$**TS3M21** | 0.406522 | −2723.227678 | −2722.818128 |
| $^{B}$**TS1**$_{E}$ | 0.644326 | −1447.123748 | −1446.476394 |
| $^{B}$**TS1**$_{M12}$ | 0.676324 | −2035.066395 | −2034.387043 |
| **Computational level: M06-D3/6-31G(d,p)&SDD/SMD//B3LYP-D3/6-311+G (d,p)&Lanl2DZ** | | | |
| $^{A}$**0** | 0.321177 | −2055.928937 | −2055.604732 |
| $^{B}$**0** | 0.589031 | −1367.622463 | −1367.030404 |
| ethylene | 0.029582 | −78.539734 | −78.50712416 |
| MVS | 0.059616 | −666.389759 | −666.3271152 |
| $^{A}$**TS3E** | 0.372886 | −2134.477209 | −2134.101295 |
| $^{A}$**TS3M21** | 0.406522 | −2722.332177 | −2721.922627 |
| $^{B}$**TS1**$_{E}$ | 0.644326 | −1446.195119 | −1445.547765 |
| $^{B}$**TS1**$_{M12}$ | 0.676324 | −2034.04691 | −2033.367558 |
| **Computational level: B97D3/6-31G(d,p)&SDD/SMD//B3LYP-D3/6-311+G (d,p)&Lanl2DZ** | | | |
| $^{A}$**0** | 0.321177 | −2056.248052 | −2055.923847 |
| $^{B}$**0** | 0.589031 | −1367.985846 | −1367.393787 |
| ethylene | 0.029582 | −78.557199 | −78.52458916 |
| MVS | 0.059616 | −666.43018 | −666.3675362 |
| $^{A}$**TS3E** | 0.372886 | −2134.803729 | −2134.427815 |
| $^{A}$**TS3M21** | 0.406522 | −2722.683742 | −2722.274192 |
| $^{B}$**TS1**$_{E}$ | 0.644326 | −1446.562199 | −1445.914845 |
| $^{B}$**TS1**$_{M12}$ | 0.676324 | −2034.436238 | −2033.756886 |