**Supplementary Material**

**Unveiling the Different Reactivity of Bent and Linear Three-Atom-Components Participating in [3+2] Cycloaddition Reactions**

Mar Ríos-Gutiérrez,\*a Luis R. Domingo,a Fatemeh Ghodsib

a Department of Organic Chemistry, University of Valencia, Dr Moliner 50, 46100 Burjassot, Valencia, Spain

b Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran

email: rios@utopia.uv.es

**Index**

**S2** Table with the MPWB1K/6-311G(d,p) gas phase total electronic energies of the stationary points involved in the 32CA reactions of TACs **1-8** with ethylene **9**.

**S3** Table with the MPWB1K/6-311G(d,p) gas phase total electronic energies of the stationary points involved in the 32CA reactions of TACs **1-8** with DCE **10**.

**Table S1.** MPWB1K/6-311G(d,p) gas phase total electronic energies, in a.u., of the stationary points involved in the 32CA reactions of TACs **1-8** with ethylene **9**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **TAC** | **MC-n** | **TS-n** | **CA-n** |
| ethylene | -78.552848 |  |  |  |
| **1** | -133.837059 | -212.392758 | -212.389771 | -212.513907 |
| **2** | -149.876570 | -228.433098 | -228.419234 | -228.524020 |
| **3** | -165.916866 | -244.474252 | -244.444998 | -244.538593 |
| **4** | -169.750050 | -248.308204 | -248.284052 | -248.368246 |
| **5** | -132.620870 | -211.175604 | -211.162310 | -211.303513 |
| **61** | -148.694350 | -227.248800 | -227.221300 | -227.315090 |
| **62** | -148.651349 | -227.205475 | -227.191473 | -227.313995 |
| **7** | -164.740775 | -243.298496 | -243.259959 | -243.341410 |
| **8** | -168.532259 | -247.087461 | -247.060254 | -247.166050 |

**Table S2.** MPWB1K/6-311G(d,p) gas phase total electronic energies, in a.u., of the stationary points involved in the 32CA reactions of TACs **1-8** with DCE **10**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **TAC** | **MCo-n** | **TSo-n** | **CAo-n** |
| DCE | -262.988892 |  |  |  |
| **1** | -133.837059 |  |  | -396.947875 |
| **2** | -149.876570 | -412.878639 | -412.877304 | -412.944505 |
| **3** | -165.916866 | -428.912199 | -428.896290 | -428.964587 |
| **4** | -169.750050 | -432.751300 | -432.739455 | -432.797076 |
| **5** | -132.620870 | -395.620740 | -395.619747 | -395.731022 |
| **61** | -148.694350 | -411.689624 | -411.665255 | -411.737771 |
| **62** | -148.651349 | -411.648530 | -411.638635 | -411.737356 |
| **7** | -164.740775 | -427.733598 | -427.694784 | -427.759921 |
| **8** | -168.532259 | -431.527581 | -431.496811 | -431.582214 |
|  |  | **MCm-n** | **TSm-n** | **CAm-n** |
| **2** |  | -412.874814 | -412.872861 | -412.950873 |
| **4** |  | -432.753337 | -432.730784 | -432.789673 |
| **5** |  | -395.616378 | -395.612628 | -395.727411 |
| **61** |  | -411.687397 | -411.675887 | -411.732903 |
| **62** |  | -411.647858 | -411.639973 | -411.7376652 |
| **7** |  | -427.738564 | -427.703604 | -427.759330 |
| **8** |  | -431.523606 | -431.499454 | -431.582168 |