**Table S3.** ELF valence basin populations, distances of the C2[C1]–C3[N1] forming bonds, IRC values, and relativea electronic energies of **TS4** and the selected structures of the IRC involved in the formation of the new C2[C1]–C3[N1]single bonds along the 32CA reaction of hydroxyparthenolide**1** and nitrileimine **2**.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | V(N1,N2) | V(N1) | V(N2) | V(C1,N1) | V(C2,C3) | V(C1) | V(C3) | V(C2) | V(C1,C2) | V(C1,C2) | V(N2,C3) | V(N2,C3) |
| 1 | 1.95 | 3.55 | - | - | - | - | 0.67 | - | 1.72 | 1.76 | 3.26 | 2.01 |
| 2 | 1.94 | 3.54 | - | - | - | - | 0.69 | - | 1.72 | 1.76 | 3.25 | 2.02 |
| 3 | 1.95 | 3.54 | - | - | - | - | 0.70 | - | 1.72 | 1.76 | 3.23 | 2.02 |
| 4 | 1.95 | 3.55 | - | - | - | - | 0.72 | - | 1.72 | 1.76 | 3.22 | 2.02 |
| 5 | 1.95 | 3.54 | - | - | - | - | 0.73 | - | 1.72 | 1.76 | 3.21 | 2.02 |
| 6 | 1.95 | 3.54 | - | - | - | - | 0.75 | - | 1.72 | 1.76 | 3.18 | 2.04 |
| 7 | 1.95 | 3.54 | - | - | - | - | 0.77 | - | 1.72 | 1.76 | 3.16 | 2.05 |
| 8 | 1.95 | 3.53 | - | - | - | - | 0.78 | - | 1.71 | 1.76 | 3.15 | 2.05 |
| 9 | 1.95 | 3.53 | - | - | - | - | 0.80 | - | 1.71 | 1.76 | 3.12 | 2.07 |
| 10 | 1.95 | 3.52 | - | - | - | - | 0.81 | - | 1.71 | 1.76 | 3.10 | 2.08 |
| 11 | 1.95 | 3.52 | - | - | - | - | 0.83 | - | 1.71 | 1.76 | 3.07 | 2.10 |
| 12 | 1.95 | 3.52 | - | - | - | - | 0.85 | - | 1.71 | 1.76 | 3.04 | 2.11 |
| 13 | 1.95 | 3.51 | - | - | - | - | 0.87 | - | 1.71 | 1.76 | 3.01 | 2.13 |
| 14 | 1.95 | 3.51 | - | - | - | - | 0.88 | - | 1.70 | 1.77 | 3.00 | 2.14 |
| 15 | 1.95 | 3.51 | - | - | - | - | 0.90 | - | 1.70 | 1.76 | 2.96 | 2.17 |
| 16 | 1.95 | 3.49 | - | - | - | - | 0.92 | - | 1.70 | 1.76 | 2.93 | 2.19 |
| 17 | 1.95 | 3.49 | - | - | - | - | 0.93 | - | 1.70 | 1.77 | 2.90 | 2.21 |
| 18 | 1.94 | 3.48 | - | - | - | - | 0.95 | - | 1.69 | 1.77 | 2.87 | 2.23 |
| 19 | 1.94 | 3.48 | - | - | - | - | 0.96 | - | 1.68 | 1.77 | 2.84 | 2.26 |
| 20 | 1.94 | 3.48 | - | - | - | - | 0.97 | - | 1.68 | 1.77 | 2.81 | 2.29 |
| 21 | 1.93 | 3.47 | - | - | - | - | 0.99 | - | 1.67 | 1.77 | 2.77 | 2.33 |
| 22 | 1.93 | 3.46 | - | - | - | - | 1.01 | - | 1.66 | 1.77 | 2.73 | 2.36 |
| 23 | 1.91 | 3.46 | 0.81 | - | - | - | 1.03 | - | 1.65 | 1.77 | 2.69 | 1.60 |
| 24 | 1.90 | 3.45 | 0.94 | - | - | - | 1.04 | - | 1.64 | 1.77 | 2.63 | 1.53 |
| 25 | 1.89 | 3.44 | 1.11 | - | - | - | 1.06 | - | 1.63 | 1.78 | 2.57 | 1.42 |
| 26 | 1.88 | 3.42 | 1.27 | - | - | - | 1.09 | - | 1.61 | 1.78 | 2.50 | 1.34 |
| 27 | 1.87 | 3.41 | 1.41 | - | - | - | 1.12 | - | 1.59 | 1.79 | 2.44 | 1.27 |
| 28 | 1.85 | 3.40 | 1.54 | - | - | - | 1.14 | - | 1.56 | 1.80 | 2.37 | 1.21 |
| 29 | 1.84 | 3.39 | 1.67 | - | - | - | 1.16 | - | 1.55 | 1.79 | 2.30 | 1.18 |
| 30 | 1.83 | 3.37 | 1.79 | - | - | - | 1.19 | - | - | 3.30 | 2.24 | 1.14 |
| 31 | 1.81 | 3.35 | 1.89 | - | - | - | 1.22 | - | - | 3.29 | 2.17 | 1.11 |
| 32 | 1.79 | 3.34 | 1.99 | - | - | - | 1.23 | - | - | 3.28 | 2.14 | 1.09 |
| 33 | 1.78 | 3.32 | 2.08 | - | - | - | 1.26 | 0.28 | - | 2.98 | 2.09 | 1.07 |
| 34 | 1.77 | 3.30 | 2.15 | - | - | - | 1.27 | 0.36 | - | 2.88 | 2.02 | 1.10 |
| 35 | 1.75 | 3.29 | 2.24 | - | 1.72 | - | - | - | - | 2.79 | - | 3.07 |
| 36 | 1.74 | 3.27 | 2.29 | - | 1.78 | 0.13 | - | - | - | 2.59 | - | 3.07 |
| 37 | 1.73 | 3.26 | 2.34 | - | 1.83 | 0.16 | - | - | - | 2.50 | - | 3.06 |
| 38 | 1.72 | 3.25 | 2.39 | - | 1.85 | 0.18 | - | - | - | 2.42 | - | 3.08 |
| 39 | 1.71 | 3.24 | 2.44 | - | 1.69 | 0.20 | - | - | - | 2.36 | - | 3.26 |
| 40 | 1.69 | 3.23 | 2.47 | - | 1.72 | 0.22 | - | - | - | 2.31 | - | 3.25 |
| 41 | 1.68 | 3.23 | 2.50 | - | 1.77 | 0.25 | - | - | - | 2.27 | - | 3.23 |
| 42 | 1.67 | 3.23 | 2.53 | - | 1.80 | 0.27 | - | - | - | 2.23 | - | 3.22 |
| 43 | 1.65 | 3.23 | 2.56 | - | 1.82 | 0.29 | - | - | - | 2.20 | - | 3.21 |
| 44 | 1.63 | 3.23 | 2.59 | - | 1.85 | 0.32 | - | - | - | 2.18 | - | 3.19 |
| 45 | 1.62 | 3.23 | 2.61 | - | 1.87 | 0.34 | - | - | - | 2.16 | - | 3.19 |
| 46 | 1.60 | 3.22 | 2.63 | - | 1.88 | 0.36 | - | - | - | 2.14 | - | 3.18 |
| 47 | 1.58 | 3.15 | 2.66 | - | 1.89 | 0.38 | - | - | - | 2.12 | - | 3.18 |
| 48 | 1.56 | 3.08 | 2.68 | - | 1.90 | 0.40 | - | - | - | 2.10 | - | 3.17 |
| 49 | 1.55 | 3.02 | 2.70 | - | 1.92 | 0.41 | - | - | - | 2.08 | - | 3.16 |
| 50 | 1.52 | 2.33 | 2.72 | 1.10 | 1.93 | - | - | - | - | 2.06 | - | 3.14 |
| 51 | 1.51 | 2.26 | 2.75 | 1.16 | 1.94 | - | - | - | - | 2.04 | - | 3.13 |
| 52 | 1.49 | 2.22 | 2.77 | 1.22 | 1.95 | - | - | - | - | 2.02 | - | 3.13 |
| 53 | 1.47 | 2.18 | 2.79 | 1.27 | 1.96 | - | - | - | - | 2.00 | - | 3.11 |
| 54 | 1.45 | 2.15 | 2.81 | 1.33 | 1.97 | - | - | - | - | 1.99 | - | 3.11 |
| 55 | 1.44 | 2.11 | 2.82 | 1.38 | 1.98 | - | - | - | - | 1.97 | - | 3.10 |
| 56 | 1.42 | 2.08 | 2.83 | 1.44 | 1.98 | - | - | - | - | 1.96 | - | 3.09 |
| 57 | 1.41 | 2.06 | 2.84 | 1.47 | 1.99 | - | - | - | - | 1.95 | - | 3.09 |
| 58 | 1.41 | 2.04 | 2.85 | 1.50 | 1.99 | - | - | - | - | 1.94 | - | 3.09 |
| 59 | 1.40 | 2.02 | 2.85 | 1.53 | 1.99 | - | - | - | - | 1.94 | - | 3.08 |
| 60 | 1.40 | 2.02 | 2.85 | 1.54 | 1.99 | - | - | - | - | 1.94 | - | 3.08 |
| 61 | 1.40 | 2.01 | 2.86 | 1.55 | 1.99 | - | - | - | - | 1.94 | - | 3.07 |