Electronic Supplementary Information

Can the high reactivity of azomethine betaines in [3+2] cycloaddition reactions be explained using singlet-diradical character descriptors? What molecular mechanism is actually involved in these cycloadditions?

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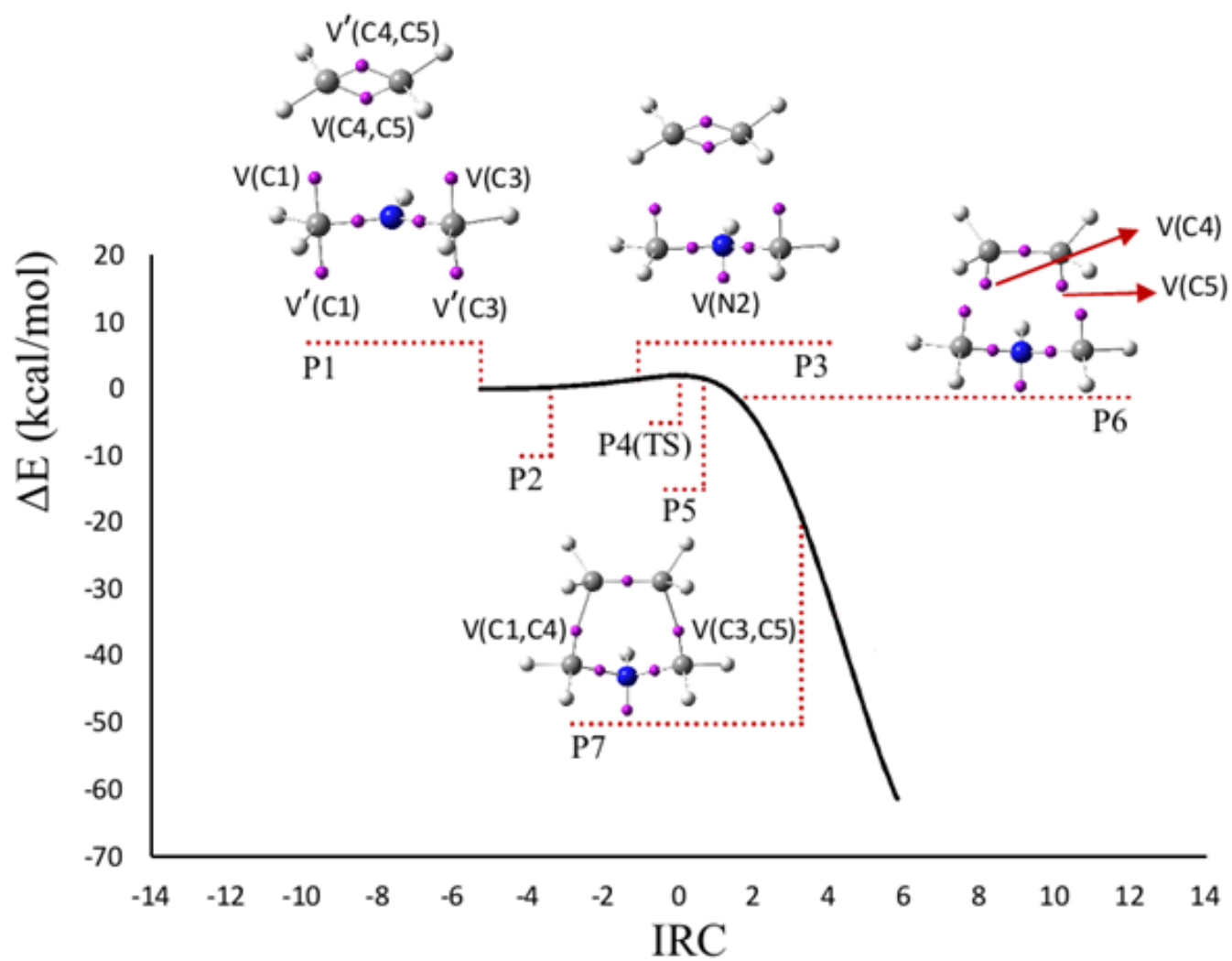
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Fig. S1

The ELF topological study of [3+2] cycloaddition reaction of AZB2 toward ethylene.

At point **P1** the two interacting fragments are very far apart, d(C1−C4) and d(C3−C5) are 3.250Å, and the ELF valence basin shapes are very similar to those in the isolated AZB1 and ethylene. Indeed, the ELF picture associated with **P1** shows four monosynaptic basins, a pair on each terminal carbon atoms of AZB1 specified as V(C1) and V′(C1); and V(C3) and V′(C3). The population of the electronic density for V(C1), V′(C1), V(C3), and V′(C3) is 0.59, 0.40, 0.59, and 0.40e, respectively, providing a bonding structure picture where 0.99e is located on each terminal carbon. This picture is in complete agreement with the electronic density displayed by the HOMO shape of AZB1 presented in Fig. 4 of main text, which is responsible for the pseudo-diradical character of AZB1 in its ground electronic state. It is interesting to note that there is not monosynaptic basin associated with the N2 nitrogen lone pair in AZB1 fragment. This behavior implies that the delocalization of the nitrogen lone pair into P_z atomic orbitals of two neighboring unsaturated carbon atoms (see the shape of HOMO-n of AZB1 in Fig. 4 in the main text). On the other hand, the ELF picture for ethylene fragment reveals two disynaptic basins, V(C4,C5) and V′(C4,C5), corresponded to C-C double bond in ethylene. The sum of population of these two disynaptic basins is 3.47e. At **P2**, d(C1−C4) = d(C3−C5) = 3.018Å, no significant changes happen in the ELF valence basin shapes except some minor changes in their populations. At **P3**, d(C1−C4) = d(C3−C5) = 2.696Å, the two monosynaptic basins on the AZB1 terminal carbon atoms merge into only one, whereas a new V(N2) monosynaptic basin emerges over the N2 nitrogen atom of AZB1, integrating 0.38e. In fact, two monosynaptic basins on terminal carbons are sacrificed to form a monosynaptic basin on central nitrogen. Interestingly, the shape of V(N2) remains unchanged along the IRC profile indicating that the lone pair of N2 nitrogen atom does not involve in the cycloaddition reaction. Passing through points **P4**, d(C1−C4) = d(C3−C5) = 2.534Å, which is corresponded with the TS of reaction, and **P5**, d(C1−C4) = d(C3−C5) = 2.439Å, any noticeable changes do not take place in the ELF valence basin shapes except a slight change in the corresponding populations. At **P6**, d(C1−C4) = d(C3−C5) = 2.309Å, two V(C4) and V(C5) monosynaptic basins each one with an initial population of 0.33e appear over C4 and C5 carbon atoms of ethylene. The electronic density of these basins mainly comes from the disappeared V′(C4,C5) disynaptic basin. Note that the population of V(C4,C5) is 2.78e. Therefore, at P6, the four *pseudoradical* centers required for the C1−C4 and C3-C5 single bonds formation are present. At **p7**, d(C1−C4) = d(C3−C5) = 2.052Å, two C1-C4 and C3-C5 single bonds start to form by merging of V(C1) and V(C4); and V(C3) and

V(C5) monosynaptic basins into two new V(C1,C4) and V(C3,C5) disynaptic basins, respectively. Initial population of V(C1,C4) and V(C3,C5) disynaptic basins is 1.51e. From **P7** to the end of IRC profile where the final cycloadduct is reached, while the shapes of attractor remains unchanged, their populations slightly change.
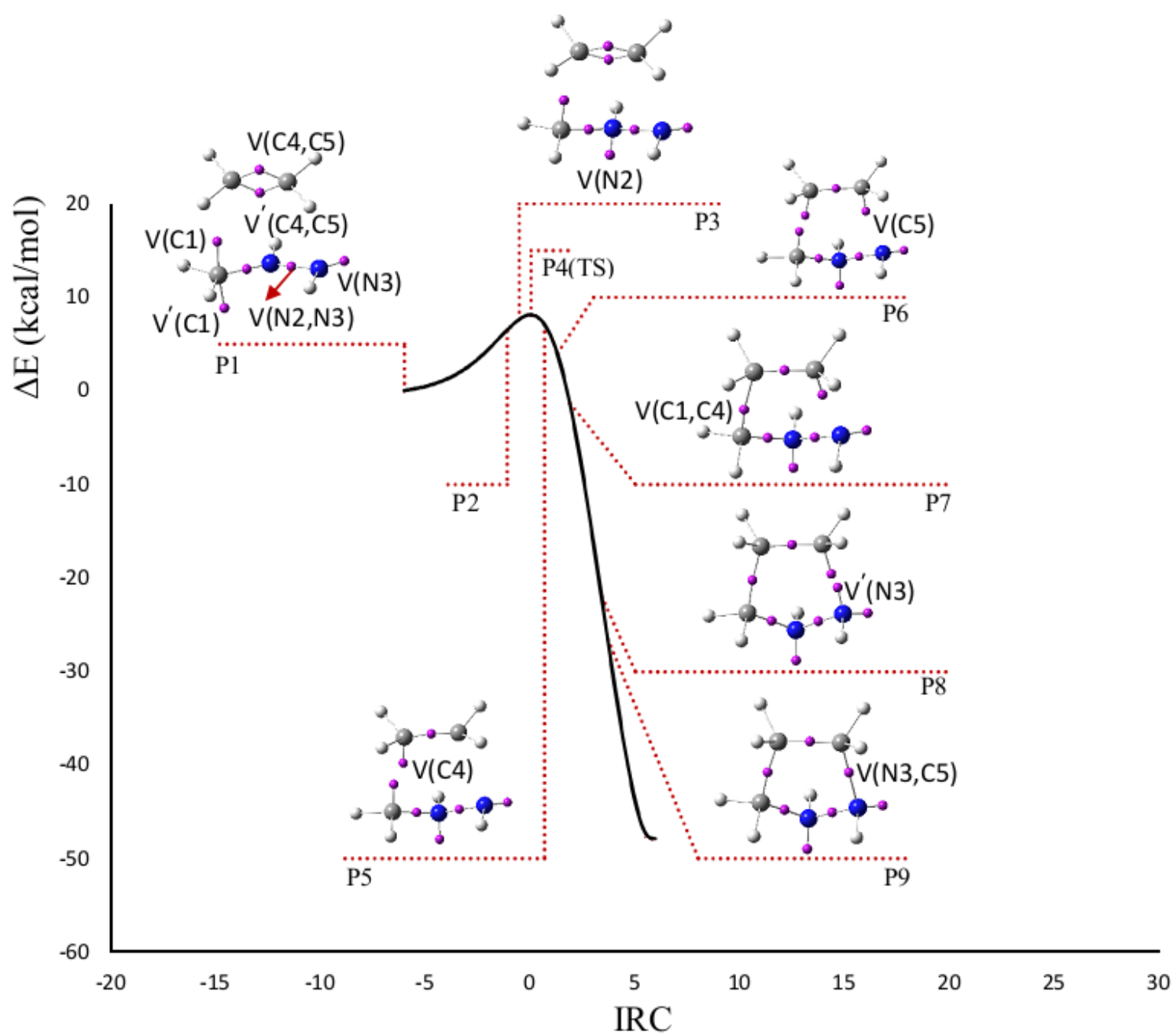
Fig. S2

The ELF topological study of [3+2] cycloaddition reaction of AZB2 toward ethylene.

At **P1**, d(C1-C4) = 3.213Å and d(N3-C5) = 3.039Å, where the interacting fragments due to the large separation have no noticeable interaction, the ELF valence basin shapes show a very similar pattern to those in the separate AZB2 and ethylene; *i.e.*, there are two V(C1), integrating 0.41e, and V′(C1), integrating 0.37e, monosynaptic basins over C1 carbon atom and a V(N3) monosynaptic basin with an initial integration of 3.53e over N3 nitrogen atom of AZB2. However, while a V(C1,N2) disynaptic basin can be observed in the AZB2 fragment, the V(N2,N3) disynaptic basin with an initial integration of 1.89e is more important to be followed along the IRC profile. Indeed, the formation of V′(N3) monosynaptic basin over the N3 nitrogen atom at **P8** is a direct consequence of successive depopulation of V(N2,N3) disynaptic basin along cycloaddition reaction. On the other hand, the C-C double bond of ethylene fragment, as can be seen, is characterized by the presence of the two V(C4,C5), integrating 1.73e, and V′(C4,C5), integrating 1.72e, disynaptic basins. At **P2**, d(C1-C4) = 2.473Å and d(N3-C5) = 2.496Å, the ELF valence basin shapes are very similar to those found at **P1** except some slight changes in their populations. At **P3**, d(C1-C4) = 2.372Å and d(N3-C5) = 2.420Å, one of monosynaptic basins of C1 carbon atom disappears and, instead, a V(N2) monosynaptic basin integrating 0.9e emerges over N2 nitrogen atom. At this point, the V(N2,N3) disynaptic basin depopulates to 1.75e. At **P4**, d(C1-C4) = 2.282Å and d(N3-C5) = 2.352Å, which is also corresponded to the TS of reaction, while some minor changes is found in the population of ELF valence basins, corresponding ELF valence shapes remain unchanged when they are compared with those at the previous point **P3**. At **P5**, d(C1-C4) = 2.172Å and d(N3-C5) = 2.268Å, a new V(C4) monosynaptic basin integrating 0.35e appears over C4 carbon atom. The electronic density of this basin mainly comes from the V′(C4,C5) disynaptic basin which disappears at **P5**. In fact, some of electron density of C-C double bond of ethylene fragment which is breaking at **P5** concentrates over C4 carbon atom to form V(C4) monosynaptic basin. At **P5**, the two *pseudoradical* centers required for the subsequent C1−C4 single bond formation are present. At **P6**, d(C1-C4) = 2.074Å and d(N3-C5) = 2.190Å, a new V(C5) monosynaptic basin emerges over C5 atom with an initial population of 0.32e. At **P7**, d(C1-C4) = 1.977Å and d(N3-C5) = 2.111Å, the first C1-C4 single bond begins to form which is characterized by the presence of a new V(C1,C4) disynaptic basin, integrating 1.41e, as a result of merging the two V(C1) and V(C4) monosynaptic basins. At **P8**, d(C1-C4) = 1.752Å and d(N3-C5) = 1.896Å, a new V′(N3) monosynaptic basin with an

initial integration of 0.58e, appears over N3 atom. The electron density of this basin, as mentioned earlier, comes mainly from the depopulation of V(N2,N3) disynaptic basin. At **P8**, the population of V(N2,N3) is 1.42e. When this value is compared with corresponding initial population at **P1**, 1.89e, it is clear that the population of V(N2,N3) disynaptic basin reduces by about 25% to form a V′(N3) monosynaptic basin over N3 atom. It is also much clear that two *pseudoradical* centers required for the subsequent N3−C5 single bond formation are present at **P8**. Finally, at **P9**, d(C1-C4) = 1.713Å and d(N3-C5) = 1.848Å, the two V′(N3) and V(C5) monosynaptic basins merge into a new V (N3,C5) disynaptic basin integrating 1.23e allowing the second N3-C5 single bond starts to form. It is interesting to note that the population of V(C1,C4) disynaptic basin is 1.69e at **P9**. If this value is compared with corresponding value in the cycloadduct, 1.86e, one can easily be concluded that the formation of C1-C4 single bond, started at **P7**, has completed by more than of 89% when the formation of second N3-C5 single bond starts.
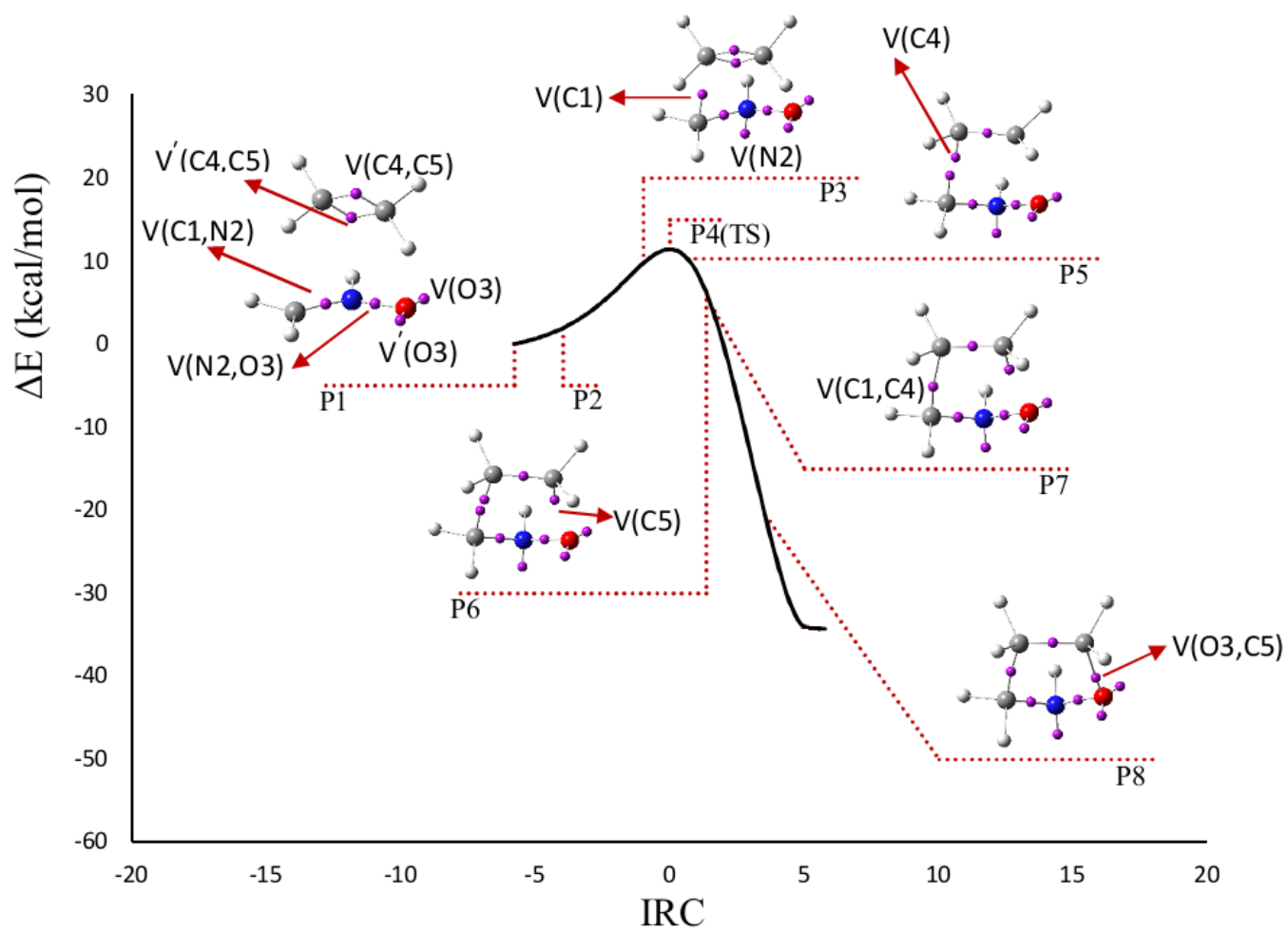
Fig. S3

The ELF topological study of [3+2] cycloaddition reaction of AZB3 toward ethylene.

Starting from **P1**, d(C1-C4) = 3.134Å and d(O3-C5) = 2.824Å, the ELF valence basins shape in two interacting fragment is very similar to those found in isolated reagents. As shown, while there are two V(C1,N2) and V(N2,O3) disynaptic basins corresponded to the C1-N2 and N2-O3 single bonds, respectively, two V(O3) and V'(O3) monosynaptic basins associated with the O3 lone pairs look like over the oxygen atom. Population of V(C1,N2), V(N2,O3), V(O3), and V'(O3) basins is 3.86, 1.38, 2.87, and 3.02e, respectively. On the other hand, two V(C4,C5) and V'(C4,C5) disynaptic basins with population of 1.72 and 1.73e, respectively, distinguish the C-C double bond in ethylene fragment. As two fragments approach, at **P2** where d(C1-C4) = 2.860Å and d(O3-C5) = 2.640Å, a very similar ELF pattern to that presented at **P1** is observed; the unique difference corresponds to the slight change in populations. At **P3**, d(C1-C4) = 2.368Å and d(O3-C5) = 2.299Å, two new V(C1) monosynaptic basin integrating 0.37e and V(N2) monosynaptic basin integrating 0.87e emerge over C1 and N2 atoms of AZB3 fragment, respectively. At **P4**, the TS position, values of d(C1-C4) and d(O3-C5) are 2.200 and 2.185Å, respectively. The TS position does not include a distinctive feature in its ELF basins shape. At **P5**, d(C1-C4) = 2.093Å and d(O3-C5) = 2.111Å, the V'(C4,C5) disynaptic basin disappears and some of corresponding electron density accumulates over C4 to form a new V(C4) monosynaptic basin with an initial integration of 0.44e. Therefore, At **P5**, two *pseudoradical* centers required for the subsequent C1-C4 single bond formation are present. At **P6**, d(C1-C4) = 1.977Å and d(O3-C5) = 2.028Å, a new V(C5) monosynaptic basin integrating 0.17e appears over C5 atom. At **P7**, d(C1-C4) = 1.949Å and d(O3-C5) = 2.007Å, the first C1-C4 single bond starts to form by the merging of two V(C1) and V(C4) monosynaptic basins into a new V(C1,C4) disynaptic basin with an initial population of 1.32e. At **P8** where d(C1-C4) = 1.659Å and d(O3-C5) = 1.718Å, the second O3-C5 single bond starts to form. This single bond formation is characterized by the presence of a new V(O3,C5) disynaptic basin integrating 0.70e. When O3-C5 single bond formation begins, the population of V(C1,C4) disynaptic basin 1.71e. In other word, formation of O3-C5 single bond is accompanied with the completion of C1-C4 single bond by more than of 92%. Note that the population of V(C1,C4) disynaptic basin is 1.85e in the corresponding cycloadduct. It is worth noting that the C5-X3 carbon-heteroatom single bond formation in the reaction of AZB3 toward ethylene provides a quite different pattern in comparison with what provides in the reaction of AZB2 toward ethylene. Indeed, in

the case of AZB2 and ethylene, formation of C5-N3 single bond takes place via coupling of two C5 and N3 pseudoradical centers exhibiting a direct participation of both carbon and nitrogen heteroatom in the formation of corresponding single bond. Besides, in the case of AZB3 and ethylene, formation of C5-O3 single bond carries out through the nucleophilic attack of C5 carbon atom of ethylene on the O3 oxygen atom of AZB3; that is, oxygen heteroatom does not directly participate in the formation of corresponding single bond via forming of a monosynaptic basin. Such behavior may be explained considering the very higher electronegativity of oxygen than carbon.

Cartesian Coordinates of B3LYP/6-31G(d) optimized structures of species involved in the studied [3+2] cycloaddition reactions.

AZB1

0 1

C	-1.22900900	0.18374500	-0.00037500
H	-1.34303500	1.25808600	0.00142400
H	-2.07227400	-0.48793500	0.00058700
N	-0.00000600	-0.34101300	-0.00010200
H	0.00010000	-1.35811900	0.00032100
C	1.22897200	0.18371300	0.00035000
H	2.07237300	-0.48774700	-0.00032500
H	1.34310100	1.25806100	-0.00114700

AZB2

0 1

H	-1.17696500	1.12701000	0.00027000
N	-0.03389500	-0.35605000	-0.00002600
H	-0.03096300	-1.37638300	0.00015800
C	1.16524000	0.20032500	0.00004200
H	2.03100400	-0.44478100	-0.00006600
H	1.24335600	1.27938200	-0.00015800
N	-1.26008700	0.10073900	-0.00004000

AZB3

0 1

N	-0.06032400	0.34379300	-0.00009000
H	-0.07974600	1.37843500	-0.00010400
C	1.13062500	-0.19199300	0.00002200

H	1.98913900	0.46515000	0.00002200
H	1.20641200	-1.27056500	0.00016400
O	-1.18466100	-0.22845200	0.00005200

Ethylene

0 1

C	0.00000000	0.66542900	0.00000000
H	0.92369100	1.23953300	0.00000000
H	-0.92365300	1.23957600	0.00000000
C	0.00000000	-0.66542900	0.00000000
H	-0.92369100	-1.23953300	0.00000000
H	0.92365300	-1.23957600	0.00000000

TS1

0 1

C	0.90843100	1.20612800	0.19814400
H	0.73962300	1.29033200	1.26271500
H	1.26359900	2.07223200	-0.34501600
N	1.26711900	0.00000100	-0.27759400
H	1.56905300	0.00000200	-1.24674500
C	0.90843600	-1.20612700	0.19814300
H	1.26360500	-2.07222900	-0.34501900
H	0.73962800	-1.29033300	1.26271400
C	-1.55708300	-0.67992800	-0.06112800
H	-1.76448500	-1.24763300	0.84113700
H	-1.56629000	-1.24827500	-0.98596900
C	-1.55708300	0.67992500	-0.06112900
H	-1.56629100	1.24827100	-0.98597200
H	-1.76448700	1.24763200	0.84113400

TS2

0 1

H	-0.60550500	-1.14519500	1.12981400
N	-1.23681700	-0.06523800	-0.27472000
H	-1.51684200	-0.07911200	-1.25179100
C	-0.83532400	1.12231400	0.21061200
H	-1.20525800	2.00355800	-0.30532600
H	-0.72195500	1.19123700	1.28629400
C	1.39319800	0.71887300	-0.07123000
H	1.68012800	1.29172000	0.80672300
H	1.44541300	1.26380300	-1.00968000
C	1.45316300	-0.65547800	-0.05955600
H	1.48963400	-1.22947000	-0.97794900
H	1.72944200	-1.19824100	0.84014500
N	-0.81479500	-1.25084000	0.13226400

TS3

0 1

N	1.22976900	-0.07689000	0.24911700
H	1.52201900	-0.09191500	1.23296000
C	0.79216900	1.08906900	-0.23171100
H	1.13836500	1.98676400	0.27341700
H	0.63597600	1.13088400	-1.30129900
C	-1.34760200	0.71278300	0.11828900
H	-1.67348900	1.33081900	-0.71417800
H	-1.42285100	1.18498700	1.09474200
C	-1.38204300	-0.66264000	0.01138400
H	-1.42126100	-1.29737000	0.88937000
H	-1.61388500	-1.14810700	-0.92973600
O	0.73145000	-1.17413800	-0.20960900