Supplementary Material

Unveiling the High Reactivity of Cyclohexynes in [3+2] Cycloaddition Reactions through the Molecular Electron Density Theory

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1. Topological analysis of the Electron Localisation Function (ELF) and Natural Population Analysis (NPA) of methyl azide (Az) 12 and diazomethane (Da) 14 at the ground state (GS).

ELF localisation domains, basin attractor positions together with the valence basin populations, as well as the proposed Lewis-like structures together with the natural atomic charges of Az 12 and Da 14 are shown in Figure S1.



Figure S1. MPWB1K/6-311G(d) ELF localisation domains of Az **12** and Da **14**, represented at an isosurface value of ELF = 0.75; ELF basin attractor positions, together with the most relevant valence basin populations; and the proposed Lewis-like structures, together with the natural atomic charges. Negative charges are coloured in red, negligible charges are coloured in green, while positive charges are coloured in blue. ELF valence basin populations and natural atomic charges are given in average number of electrons, e.

Topological analysis of the ELF of Az **12** shows the presence of two V(N1) and V(N3) monosynaptic basins, integrating 3.49 and 3.77e, respectively, one V(N1,N2) disynaptic basin integrating 2.62e, and two V(N1,N3) and V'(N2,N3) disynaptic basins integrating a total electron population of 4.04e, in the reactive framework of this TAC. According to Lewis's bonding model, these valence basins can be associated to the presence of two lone pairs at both N1 and N3 nitrogens, an N1–N2 underpopulated double bond and an N2–N3 double bond. Consequently, topological analysis of the ELF indicates that Az **12** has a rather allenic electronic structure, instead of the traditionally assumed propargylic one.

Topological analysis of the ELF of Da 14 shows a similar bonding pattern in the core framework of this TAC; one V(C1,N2) disynaptic basin integrating 2.92e, and two V(N2,N3) and V'(N2,N3) disynaptic basins integrating a total electron population of 3.93e are observed. The most relevant topological difference is the presence of two V(C1) and V'(C1) monosynaptic basins integrating a total population of 0.97e, which can be associated with a C1 *pseudoradical* center. Therefore, topological analysis of the ELF reveals that Da 14 has a *pseudoradical* allenic electronic structure.

Finally, NPA of Az 12 and Da 14 indicates that while the N3 and C1 centers are negatively charged by -0.38e and -0.35e, respectively, and the N2 nitrogen is positively charged by 0.21e (12) and 0.11e (14), the N1 nitrogen of Az 12 and the N3 nitrogen of Da 14 have negligible charges, -0.09e and 0.06e, respectively. Although these charge distributions seem to be qualitatively in quite agreement with the 1,2-zwitterionic Lewis structures proposed by Huisgen for "1,3-dipoles", the values of these charges and the total charges of -0.20e and -0.18e in the core framework of 12 and 14, respectively, suggest that these three-atom-components (TACs) cannot be considered "1,3-dipoles" by means of Lewis structures.

Study of the [3+2] cycloaddition (32CA) reactions of Az 12 and Da 14 with but-2-yne
25.

In order to understand the large acceleration found in the 32CA reactions of Az **12** and Da **14** with strained cyclohexyne (SCH) **9**, the 32CA reactions of these TACs with linear but-2-yne **25** were also analyzed. Due to the symmetry of linear but-2-yne **25**, only one reaction path is feasible for each one of these 32CA reactions. Analysis of the stationary points involved in these reactions indicates that they take place along a one-step mechanism. Consequently, the reagents, one molecular complex (MC), **MC31** and **MC32**, one TS, **TS31** and **TS32**, and the corresponding cycloadduct (CA), **26** and **27**, were localized and characterized along each one 32CA reaction. Relative enthalpies and Gibbs free energies in THF are given in Scheme S1.



Scheme S1. 32CA reactions of but-2-yne 25 with Az 12 and Da 14. MPWB1K/6-311G(d) relative enthalpies, in parentheses, and Gibbs free energies, in brackets, computed at 60°C in THF, are given in kcal·mol⁻¹.

An exploration of the reaction paths between the separated reagents and TSs allowed finding a molecular complex (MC) in which the two reagents are close. These MCs are 1.0 (MC31) and 1.3 (MC32) kcal·mol⁻¹ more stable than separated reagents, being a minimum in their corresponding potential energy surfaces. From these MCs, the activation enthalpies associated to these 32CA reactions are very high, 27.0 (TS31) and 28.9 (TS32) kcal·mol⁻¹. These values account for the low reactivity of these linear

TACs. In spite of this, these 32CA reactions are strongly exothermic: -75.0 (**26**) and - 45.2 (**27**) kcal·mol⁻¹. Inclusion of entropies to enthalpies increases the activation Gibbs free energies by 11-12 kcal·mol⁻¹ and decreases the reaction Gibbs free energies by 15- 17 kcal·mol⁻¹ as a consequence of the unfavourable relative entropies associated to these bimolecular processes (see Table S7).

The gas phase and THF geometries of the TSs involved in the 32CA reactions of Az **12** and Da **14** with but-2-yne **25** are given in Figure S2. The distance between the interacting centers at the two TSs are: 2.168 (N1-C4) and 2.110 (N3-C5) Å at **TS31**, and 2.215 (C1-C4) and 2.180 (N3-C5) Å at **TS32**. These values indicate that from a geometrical point of view, the TSs are very symmetric. Inclusion of solvent effects of THF in the geometry optimizations does not produce any meaningful change.



Figure S2. MPWB1K/6-311G(d) gas phase geometries of the TSs involved in the 32CA reactions of Az **12** and Da **14** with but-2-yne **25**. Distances are given in angstroms, Å. THF ones are given in brackets.

The non-polar nature of the 32CA reactions of Az **12** and Da **14** with but-2-yne **25** was evaluated by computing the global electron density transfer (GEDT) at the corresponding gas phase TSs. Reactions with GEDT values of 0.0e correspond to non-polar processes, while values higher than 0.2e correspond to polar processes. The GEDT at the corresponding TSs are: -0.03 (**TS31**) and 0.04 (**TS32**). These unappreciable values indicate the non-polar character of these 32CA reactions.

3. Bonding Evolution Theory (BET) study of the 32CA reaction between Az 12 and SCH9.

The BET study of the bonding changes along the 32CA reaction between Az **12** and SCH **9** indicates that this reaction is topologically characterized by ten differentiated phases. A simplified representation of the molecular mechanism of the 32CA reaction between Az **12** and SCH **9** by Lewis-like structures is shown in Scheme S2; the populations of the most significant valence basins, among other relevant parameters, of the selected structures of the IRC are included in Table S1; the attractor positions of the ELF basins for the structures involved in the bond formation processes are shown in Figure S3.

Phase I, 3.16 Å \geq d(N1–C5) > 2.79 Å and 3.40 Å \geq d(N3–C4) > 3.14 Å, begins at **S0-1**, which is the first structure of the reaction path between **MC1** and **TS11**. Accordingly, the topological features of the ELF of **S0-1** are very similar to those of the separated reagents (see Table S1); only slight changes in the ELF valence basins populations are noticed. Along *Phase I*, the electron density in the C4–C4' and C5–C5' bonding regions is redistributed in such a manner that while the population of the V(C4,C4') disynaptic basin slightly increases, the V(C5,C5') disynaptic basins is depopulated to 2.54e. These bonding changes demand a very low energy cost (EC) of only 0.9 kcal·mol⁻¹. At **S0-1**, the GEDT is negligible, 0.01e.

Phase II, 2.79 Å \geq d(N1–C5) > 2.51 Å and 3.14 Å \geq d(N3–C4) > 2.91 Å, begins at **S1-1**. At this structure, which is characterized by a fold F^{\dagger} catastrophe, a V(C4) monosynaptic basin, integrating 0.80e, has been created at the C4 carbon of the SCH framework as the consequence of the sudden depopulation of the contiguous V(C4,C4') disynaptic basin to 2.05e. Note that this V(C4) monosynaptic basin is associated to a C4 *pseudoradical* center which, according to formation pattern of other N–C single bonds, will participate in the formation of the corresponding N3–C4 single bond. The bonding changes taking place along *Phase II*, which are mainly associated to the continuous population of the V(C4) monosynaptic basin to 1.12e as the V(C4,C4') and V(C5,C5') disynaptic basins are depopulated to 1.88e and 2.40e, respectively, demand the highest EC along the reaction path towards **TS1**, ca. 1.7 kcal·mol⁻¹, which remains being a low value. At **S1-1**, the GEDT has slightly increased to 0.04e.

Phase III, 2.51 Å \geq d(N1–C5) > 2.35 Å and 2.91 Å \geq d(N3–C4) > 2.76 Å, begins at **S2-1**. At this structure, the two V(N2,N3) and V'(N2,N3) disynaptic basins present at **S1-1** with total population of 4.15e have merged into a new V(N2,N3) disynaptic basin integrating 4.14e. Along *Phase III*, while the V(N1,N2) disynaptic basin is depopulated, the population of the contiguous V(N2,N3) disynaptic basin increases to 4.38e. The bonding changes taking place along *Phase III*, which are mainly associated to the redistribution of the electron density within the N1–N2–N3 azide framework, demand an EC of ca. 1.4 kcal·mol⁻¹. At **S2-1**, the GEDT is 0.08e.

Phase IV, 2.35 Å \geq d(N1–C5) > 1.95 Å and 2.76 Å \geq d(N3–C4) > 2.40 Å, begins at S3-1. At this structure, together with the strong depopulation of the V(N2,N3) disynaptic basin to 3.85e, a new V(N2) monosynaptic basin is created at the N2 nitrogen with an initial population of 0.54e, by means of a cusp C catastrophe. This V(N2) monosynaptic basin is associated to the non-bonding electron density of the N2 nitrogen present at the final triazole 13. Along Phase IV, the changes in electron populations are more pronounced. The two V(N1,N2) and V(N2,N3) disynaptic basins are depopulated to ca. 1.83e and 3.03e, respectively, while the V(N2) monosynaptic basin reaches ca. 2.05e. The population of the V(N3) monosynaptic basin also decreases by ca. 0.11e. On the other hand, the total population of the V(C4,C5) and V'(C4,C5)disynaptic basins decreases from 4.44e to ca. 4.20e, while that of the V(C4)monosynaptic basin increases to ca. 1.31e. Interestingly, the population of the V(C4,C4') disynaptic basin increases to 1.92e. Thus, the bonding changes taking place along Phase IV, which are mainly associated to the depopulation of the N1-N2 and N2–N3 bonding regions, and of the C4–C5 one by a lesser extent, release a molecular relaxation energy (MRE) of ca. 3.6 kcal·mol⁻¹. At **S3-1**, the GEDT slightly increases to 0.11e.

The TS of the reaction, **TS11**, d(N1-C5) = 2.185 Å and d(N3-C4) = 2.601 Å, is found in *Phase IV*. At **TS11**, no V(N1,C5) or V(N3,C4) disynaptic basins associated to the formation of the new N1-C5 or N3-C4 single bonds are observed. The bonding changes taking place from **S3-1** to **TS11**, which follow the same trend as along *Phase IV*, demand an EC of only 1.0 kcal·mol⁻¹. At **TS11**, the GEDT reaches the value of 0.13e.

The very short *Phase V*, 1.95 Å \geq d(N1–C5) > 1.92 Å and 2.40 Å \geq d(N3–C4) > 2.38 Å, begins at **S4-1** (see Figure S3). At this structure, two different topological

changes occur, which are characterized by C^{\dagger} and F^{\dagger} catastrophes. On the one hand, the V(N1) monosynaptic basin present at **S3-1** has been divided into two new V(N1) and V'(N1) monosynaptic basins integrating 2.27e and 1.19e. This topological change can be related to a reorganisation of the N1 non-bonding electron density to a more suitable arrangement for the subsequent formation of the N1–C5 single bond. On the other hand, a V(C5) monosynaptic basin, integrating 0.07e, has been created at the C5 carbon of the SCH framework as the consequence of the depopulation of the V(C5,C5') disynaptic basin to 2.29e. Along short *Phase V*, while the population of the V'(N1) monosynaptic basin increases to 1.24e, that of the V(C5) monosynaptic basin remains unchanged, which makes this C5 *pseudoradical* center chemically meaningless. The bonding changes taking place along *Phase V*, which are mainly associated to the rearrangement of the non-bonding electron density of the N1 nitrogen, release an MRE of ca. 1.3 kcal·mol⁻¹. At **S4-1**, the GEDT slightly decreases to 0.09e as a consequence of a backdonation process.

Phase VI, 1.92 Å \geq d(N1–C5) > 1.50 Å and 2.38 Å \geq d(N3–C4) > 1.98 Å, begins at **S5-1** (see Figure S3). At this structure, the first most relevant topological change along the reaction path takes place by means a cusp C catastrophe. Together with the disappearance of the two V'(N1) and V(C5) monosynaptic basins, a new V(N1,C5) disynaptic basin, associated to the formation of the first N1-C5 single bond, has been created with an initial population of 1.35e. Along *Phase VI*, the population of the recently created V(N1,C5) disynaptic basin increases to 2.07e as the V(N1) monosynaptic and V(C5,C5') disynaptic basins are depopulated to ca. 1.93e and 2.05e. Interestingly, the population of the V(C4) monosynaptic basin, which had been gradually increasing, decreases to ca. 1.05e, while that of the V(C4,C4') disynaptic basin increases to ca. 2.06e. The depopulation of the V(N1,N2) and V(N2,N3) disynaptic basins continues, leading to the increase of the population of the V(N2)monosynaptic basin to ca. 2.73e. In addition, the total population of the two V(C4,C5)and V'(C4,C5) disynaptic basins decreases by 0.37e to 3.78e. The bonding changes taking place along *Phase VI*, which are mainly associated to the formation of the first N1–C5 single bond, release a strong MRE of ca. 44.7 kcal·mol⁻¹. At **S5-1**, the GEDT is 0.08e.

Phase VII, $1.50 \text{ Å} \ge d(N1-C5) > 1.42 \text{ Å}$ and $1.98 \text{ Å} \ge d(N3-C4) > 1.71 \text{ Å}$, begins at **S6-1** (see Figure S3). At this structure, similarly to **S4-1**, the V(N3) monosynaptic

basin present at **S5-1** has been divided into two new V(N3) and V'(N3) monosynaptic basins integrating 3.30e and 0.47e, which is characterized by a cusp C^{\dagger} catastrophe. Again, this topological change can be considered as a reorganisation of the N3 nonbonding electron density to a more suitable arrangement for the subsequent formation of the N3–C4 single bond. The bonding changes taking place along *Phase VII*, which are mainly related to the depopulation of the N2–N3 bonding region and the C4 *pseudoradical* center, as well as to the population of the N1–C5 single bond, release an MRE of ca. 27.5 kcal·mol⁻¹. At **S6-1**, the GEDT strongly increases to 0.15e in the opposite direction, i.e. from the SCH to the azide frameworks.

Phase VIII, 1.42 Å \geq d(N1–C5) > 1.40 Å and 1.71 Å \geq d(N3–C4) > 1.57 Å, begins at **S7-1** (see Figure S3). At this structure, the second most relevant topological change takes place by means a cusp C catastrophe. Similarly to **S5-1**, the two V'(N3) and V(C4) monosynaptic basins present at the previous **S6-1** merge into a V(N3,C4) disynaptic basin integrating an initial population of 1.71e, associated with a new N3–C4 single bond. The bonding changes taking place along *Phase VIII*, which are mainly associated to the increase of the population of the recently formed N3–C4 single bond through the depopulation of the N2–N3 bonding region, release an MRE of ca. 14.8 kcal·mol⁻¹. At **S7-1**, the GEDT reaches 0.23e.

Phase IX, 1.40 Å \geq d(N1–C5) > 1.34 Å and 1.57 Å \geq d(N3–C4) > 1.346 Å, begins at **S8-1**. At this structure, the two V(C4,C5) and V'(C4,C5) disynaptic basins merge into a single V(C4,C5) disynaptic basin after having been progressively depopulated to 3.70e. Along *Phase IX*, the V(N1) monosynaptic basin experiences a strong depopulation. This lost electron density is redistributed into the V(N1,C5) disynaptic basin, whose electron population increases. Thus, the bonding changes taking place along *Phase IX*, which are mainly associated to the redistribution of some N1 nitrogen non-bonding electron density into the N1–C5 single bond, release an MRE of ca. 29.5 kcal·mol⁻¹.

Finally, *Phase X*, 1.342 Å \geq d(N1–C5) \geq 1.342 Å and 1.346 Å \geq d(N3–C4) \geq 1.346 Å, begins at **S9-1** and ends at triazole **13**. At **S9-1**, the V(N1) monosynaptic basin is divided into two new V(N1) and V'(N1) monosynaptic basins integrating 0.69e and 0.60e. This topological change can be associated to the acquirement of a planar arrangement around the N1 nitrogen, whose total electron population has increased to 1.29e. At triazole **13**, the ELF valence basin populations have scarcely varied with

respect those at **S9-1**. The bonding changes taking place along *Phase X*, which are mainly associated final electron density arrangement to form triazole **13**, do not release any amount of MRE. Note that **S9-1** and **13** have similar electronic structures and geometries, and therefore, they are isothermal.

Some appealing conclusions can be drawn from the BET study of the 32CA reaction between Az 12 and SCH 9: i) the molecular mechanism of the reaction is topologically characterized by ten differentiated phases, which emphasizes the nonconcerted nature of the bonding changes; ii) the approach of the N1 nitrogen of Az 12 to the C5 carbon of SCH 9 causes the initial depopulation of the strained C4 and C5 environments leading to the rapid formation of a C4 pseudoradical center with a negligible EC of 1.0 kcal·mol⁻¹. This electron density comes from the contiguous C4-C4' and C5-C5' bonding regions, into which part of the expected alkyne electron density of 6e is already delocalised at the GS of SCH 9. While the C4-C4' bonding region is suddenly depopulated and later is progressively populated, the depopulation of the C5–C5' bonding region is smoother along the reaction path; iii) the highest energy cost to reach **TS11**, i.e. 1.7 kcal·mol⁻¹ (*Phase II*), is mainly associated to the progressive population of the C4 pseudoradical center as both C4-C4' and C5-C5' bonding regions are depopulated; iv) the non-bonding electron density of the N2 nitrogen of triazole 13 is created in Phase IV from the depopulation of both adjacent N1-N2 and N2-N3 bonding regions. First, the N2-N3 bonding region gathers some electron density from the N1-N2 one, and then it is redistributed onto the N2 nitrogen; v) formation of the first N1–C5 single bond begins in *Phase VI*, at an N1–C5 distance of 1.92 Å, through donation of part of the N1 non-bonding electron density to the C5 *pseudoradical* center. However, this C5 pseudoradical center is chemically meaningless; vi) formation of the second N3-C4 single bond begins in *Phase VIII*, at an N-C distance of 1.71 Å, by sharing part of the N3 non-bonding electron density and that of the C4 pseudoradical center; vii) interestingly, formation of the first N1-C5 single bonds involves the most nucleophilic center of Az 12, while formation of the second N3-C4 single bond involves the C4 pseudoradical center created first at a very early stage of the reaction path; viii) formation of the second N3-C4 single bond begins when formation of the first N1-C5 single bond is completed by up to 91.4% and with a quite high 19.6% degree of asynchronicity, measured as the relative difference between the IRC values at

which the formation of both single bonds takes place; ix) the alkyne C4–C5 double bond does not practically participate in the reaction. This bonding region is depopulated by a total of only 1e along the reaction path, but it can be considered a double bond during the entire reaction; and finally, x) the structure of triazole **13** remarkably contrasts with that traditionally expected for a triazole derivative.

Table S1. ELF valence basin populations, distances of the forming bonds, MPWB1K/6-311G(d) relative^a gas phase electronic energies, GEDT and IRC values of the IRC structures, **S0-1** – **S9-1**, defining the ten phases characterizing the molecular mechanism of the 32CA reaction between Az **12** and SCH **9**. **TS11** and triazole **13** are also included. Distances are given in angstroms, Å, GEDT values and electron populations in average number of electrons, e, relative energies in kcal·mol⁻¹ and IRC values in atomic unities, a.u.

Structures	12	9	S0-1	S1-1	S2-1	S3-1	S4-1	S5-1	S6-1	S7- 1	S8-1	S9-1	13	TS11
Catastrophes				F^{\dagger}	С	F^{\dagger}	$C^{\dagger}F^{\dagger}$	С	C^{\dagger}	С	С	C^{\dagger}		
Phases			Ι	II	I	III	V	V	VI	VII	VIII	IX	Χ	
d(N1-C5)			3.164	2.792	2.511	2.353	1.950	1.924	1.503	1.41	9 1.396	1.342	1.342	2.185
d(N3-C4)			3.403	3.141	2.906	2.760	2.401	2.380	1.979	1.71	1 1.567	1.346	1.346	2.601
ΔE^{a}			0.0	0.9	2.6	4.0	0.4	-0.9	-45.6	-73.1	-87.9	-117.4	-117.4	5.0
GEDT			0.01	0.04	0.08	0.11	0.09	0.08	-0.15	-0.23	-0.26	-0.27	-0.27	0.13
IRC			-9.66	-5.50	-2.82	-1.40	1.71	1.89	5.10	6.77	7.66	14.87	15.21	0.00
V(N1,N2)	2.62		2.58	2.58	2.54	2.37	1.83	1.80	1.62	1.65	1.71	1.77	1.78	2.11
V(N2)						0.54	2.05	2.09	2.73	2.86	2.92	3.13	3.14	1.33
V(N2,N3)	2.23		2.27	2.33	4.14	3.85	3.03	3.01	2.61	2.44	2.32	2.11	2.12	3.37
V′(N2,N3)	1.81		1.80	1.82										
V(C4,C5)		2.20	2.27	2.28	2.23	2.20	2.13	2.09	1.88	1.83	3.70	3.46	3.47	2.18
V'(C4,C5)		2.18	2.16	2.19	2.24	2.24	2.07	2.06	1.90	1.94				2.16
V(C4,C4')		2.71	2.71	2.05	1.88	1.85	1.92	1.92	2.06	2.06	2.07	2.10	2.09	1.86
V(C5,C5')		2.71	2.71	2.54	2.40	2.37	2.29	2.24	2.05	2.08	2.09	2.11	2.11	2.37
V(N1)	3.48		3.46	3.45	3.43	3.39	2.27	2.24	1.93	1.77	1.64	0.69	0.69	3.40
V'(N1)							1.19					0.60	0.60	
V(C5)							0.07							
V(N3)	3.77		3.81	3.76	3.73	3.72	3.61	3.62	3.30	3.10	3.03	2.92	2.92	3.64
V'(N3)									0.47					
V(C4)				0.80	1.12	1.23	1.31	1.32	1.05					1.31
V(N1,C5)								1.35	2.07	2.23	2.27	2.40	2.44	
V(N3,C4)										1.71	1.85	2.27	2.28	

^aRelative to the first structure of the IRC, **S0-1**.



Scheme S2. Simplified representation of the molecular mechanism of the 32CA reaction between Az 12 and SCH 9 by Lewis-like structures arising from the topological analysis of the ELF along the reaction path.



Figure S3. ELF localisation domains, together with the electron populations of the ELF valence basins involved in the formation of the new single bonds, for the structures defining the phases associated with the single bond formation processes along the IRC of the 32CA reaction between Az **12** and SCH **9**. The electron populations are given in average number of electrons, e.

The BET study of the bonding changes along the 32CA reaction between DA **14** and SCH **9** indicates that this reaction is topologically characterized by nine differentiated phases. A simplified representation of the molecular mechanism of the 32CA reaction between DA **14** and SCH **9** by Lewis-like structures is shown in Scheme S3; the populations of the most significant valence basins, among other relevant parameters, of the selected structures of the IRC are included in Table S2; the attractor positions of the ELF basins for the structures involved in the bond formation processes are shown in Figure S4.

Phase I, 3.06 Å \geq d(C1–C5) > 2.98 Å and 3.46 Å \geq d(N3–C4) > 3.35 Å, begins at structure **S0-2**, which is the first structure of the reaction path towards **TS12**. The topological features of **S0-2** resemble those of the separated reagents. Of special note is the presence of the two V(C1) and V(C1') monosynaptic basins, integrating 0.57e and 0.28e, associated with the C1 *pseudoradical* center of Da **14**. Along *Phase I*, ELF valence basin populations scarcely vary, thus demanding a negligible EC of only 0.1 kcal·mol⁻¹. At **S0-2**, the GEDT is almost null, 0.02e.

Phase II, 2.98 Å \geq d(C1–C5) > 2.63 Å and 3.35 Å \geq d(N3–C4) > 2.92 Å, begins at structure **S1-2**. At this structure, a V(C4) monosynaptic basin has been created at the C4 carbon of the SCH framework as the consequence of the strong depopulation of the contiguous V(C4,C4') disynaptic basin. This topological change is associated to a fold F^{\dagger} catastrophe. This V(C4) monosynaptic basin, which is related to a C4 *pseudoradical* center, will be involved in the formation of the N3-C4 single bond at the end of the reaction path. Along *Phase II*, the population of the V(C4) monosynaptic basin progressively increases as that of the V(C4,C4') disynaptic basin decreases to 1.88e. On the other hand, part of the total population of the two V(C1) and V(C1') monosynaptic basins is redistributed into the contiguous V(C1,C1') disynaptic basin associated to the carboxylate group, whose population increases to 2.81e. The bonding changes taking place along *Phase II*, which are mainly associated to the formation of a C4 *pseudoradical* center at the SCH framework as well as to the delocalisation of the C1 *pseudoradical* center of the Da moiety, demand a low EC of ca. 1.5 kcal·mol⁻¹. At **S1-2**, the GEDT remains negligible, 0.03e.

Phase III, 2.63 Å \geq d(C1–C5) > 2.22 Å and 2.92 Å \geq d(N3–C4) > 2.58 Å, begins at structure **S2-2**. At this structure, and by means a cusp C catastrophe, the V(C1')

monosynaptic basin present at the previous **S1-2** disappears, thus decreasing the total non-bonding electron density at the C1 carbon by 0.22e. Besides the depopulation of the C1 *pseudoradical* center, this topological change also indicates the loss of the planar arrangement around the C1 carbon. At **S2-2**, the GEDT has slightly increased to 0.08e. The TS of the reaction, **TS2**, d(C1-C5) = 2.307 Å and d(N3-C4) = 2.631 Å, is found in *Phase III*. From **S2-2** to **TS12**, the V(C1) monosynaptic basin recovers part of its initial electron density, increasing its population to 0.65e while the V(C1,C1') disynaptic basin is depopulated to 2.43e. Similarly, while the total population of the V(N2,N3) and V'(N2,N3) disynaptic basins decreases by 0.26e, the population of the V(C1,N2) disynaptic basin increases to 3.33e. The bonding changes taking place from **S2-2** to **TS12**, which are mainly associated to the redistribution of the electron density within the Da framework, demand an EC of ca. 1.9 kcal·mol⁻¹, similar to that demanded along the previous *Phase II*. After **TS12**, the changes in the Da framework follow the same trend but release a low MRE of 0.3 kcal·mol⁻¹.

Phase IV, 2.22 Å \geq d(C1–C5) > 2.13 Å and 2.58 Å \geq d(N3–C4) > 2.52 Å, begins at structure **S3-2**. At this structure, the V(C1,N2) disynaptic basin experiences a strong depopulation to 2.42e, which causes the appearance of a V(N2) monosynaptic basin, which is characterized a fold F^{\dagger} catastrophe and associated with the N2 non-bonding electron density present at pyrazole **15**, integrating an initial population of 1.07e. Along *Phase IV*, the population of the V(N2) monosynaptic basin gradually increases to ca. 1.53e at the expense of the contiguous V(C1,N2) and V(N2,N3) disynaptic basins, which are depopulated by ca. 0.28e and 0.12e, respectively. The bonding changes taking place along *Phase IV*, which are mainly associated to the depopulation of the Da N2–N3 and C1–N2 bonding regions leading to the N2 non-bonding electron density present at pyrazole **15**, release an MRE of 1.5 kcal·mol⁻¹. At **S3-2**, the GEDT has considerably increased to 0.17e.

Phase V, 2.13 Å \geq d(C1–C5) > 2.02 Å and 2.52 Å \geq d(N3–C4) > 2.46 Å, begins at structure **S4-2** (see Figure S4), which is characterized by a fold F^{\dagger} catastrophe. At this structure, a new V(C5) monosynaptic basin, integrating 0.22e, is created at the SCH framework as the consequence of the depopulation of the V(C5,C5') disynaptic basin to 2.30e. This V(C5) monosynaptic basin is associated to a C5 *pseudoradical* center which, together with the V(C1) monosynaptic basin of the Da moiety, is demanded for the formation of the V(C1,C5) disynaptic basin associated to the C1–C5 single bond.

Along *Phase V*, the changes in the ELF valence basin populations follow the same trend as along the previous phase; the population of the V(C5) monosynaptic basin keeps increasing to 0.41e due to the depopulation of the V(C5,C5') disynaptic basin to 2.14e, while the population of the V(N2) monosynaptic basin also increases to 1.83e as the C1–N2 and N2–C3 bonding regions are depopulated by 0.12e and 0.15e, respectively. The bonding changes taking place along *Phase V*, which are still mainly associated to the redistribution of the C5–C5' bonding region towards the C5 *pseudoradical* center, release an MRE of 3.6 kcal·mol⁻¹. At **S4-2**, the GEDT slightly increases to 0.18e.

Phase VI, 2.02 Å > d(C1–C5) > 1.59 Å and 2.46 Å > d(N3–C4) > 2.16 Å, begins at structure S5-2 (see Figure S4). At this structure, which is characterized by a cusp Ccatastrophe, the first most relevant topological change along the reaction path takes place; the two V(C1) and V(C5) monosynaptic basins present at S4-2 merge into a new V(C1,C5) disynaptic basin, integrating an initial population of 1.35e. Along *Phase VI*, the population of the V(N2) monosynaptic continues increasing to ca. 2.50e as the V(C1,N2), V(N2,N3) and V'(N2,N3) disynaptic basins are depopulated by ca. 0.23e and 0.40e, respectively. In addition, the two V(C4,C5) and V'(C4,C5) disynaptic basins are strongly depopulated to a total of 3.73e which, together with the depopulation of the V(C1,C1') disynaptic basin, contribute to the increase of the population of the recently formed V(C1,C5) disynaptic basin to 1.93e. Interestingly, the population of the V(C4)monosynaptic basin, which had been increasing along the reaction path, decreases to 1.19e. Thus, the bonding changes taking place along *Phase VI*, which are mainly associated to the formation of the C1-C5 single bond and the increase of the N2 nonbonding electron density, release a strong MRE of 33.2 kcal·mol⁻¹. At **S5-2** the GEDT is again 0.18e.

Phase VII, 1.59 Å \geq d(C1–C5) > 1.53 Å and 2.16 Å \geq d(N3–C4) > 1.98 Å, begins at structure **S6-2**, which is characterized by a cusp *C* catastrophe. At this structure, the two V(N2,N3) and V'(N2,N3) disynaptic basins merge into a new single V(N2,N3) disynaptic basin integrating 2.83e. Along *Phase VII*, the populations of the V(N2) monosynaptic and V(C1,C5) disynaptic basins slightly increase by ca. 0.1e mainly due to the depopulation of the V(N2,N3) and V(C4,C5) disynaptic basins, respectively, while, similar to the previous phase, the population of the V(C4) monosynaptic basin again decreases to 1.08e. These bonding changes release an MRE of ca. 12.7 kcal·mol¹. At **S6-2**, the GEDT remarkably decreases to 0.07e as a consequence of a backdonation process from the SCH to the Da frameworks.

Phase VIII, 1.53 Å \geq d(C1–C5) > 1.50 Å and 1.98 Å \geq d(N3–C4) > 1.69 Å, begins at structure **S7-2** characterised by a cusp *C*[†] catastrophe (see Figure S4). At this structure, the V(N3) monosynaptic basin, whose population has not significantly varied along the reaction path, is divided into two V(N3) and V'(N3) monosynaptic basins integrating 3.00e and 0.60e. As the total population of both basins has only varied 0.07e with respect **S6-2**, this topological change can be related just to the reorganisation of the non-bonding electron density of the N3 nitrogen before the formation of the N3-C4 single bond. Along *Phase VIII*, this redistribution continues in such a manner that the V'(N3) monosynaptic basin gathers ca. 0.2e from the V(N3) monosynaptic basin. The V(C4) monosynaptic basin is also depopulated by 0.20e, so that both V'(N3) and V(C4) monosynaptic basins present similar integrations, 0.86e and 0.87e, respectively. The bonding changes taking place along *Phase VIII*, which are mainly associated to the preparation of N3 and C4 centers for the subsequent formation of the N3–C4 single bond, release an MRE of ca. 19.8 kcal·mol⁻¹. At **S7-2**, the GEDT is null, 0.00e.

Finally, *Phase IX*, 1.50 Å \geq d(C1–C5) \geq 1.48 Å and 1.69 Å \geq d(N3–C4) \geq 1.42 Å, begins at structure **S8-2** (see Figure S4) and ends at pyrazole **15**. At **S8-2**, through a cusp *C* catastrophe, the second most relevant topological change along the reaction path takes places; a new V(N3,C4) disynaptic basin, associated with an N3–C4 single bond, is created with an initial population of 1.73e, by the merger of the two V'(N3) and V(C4) monosynaptic basins present at **S7-2**. At pyrazole **15**, the V(N3,C4) disynaptic basin reaches 2.00e. Interestingly, the final population of the V(N2,N3) disynaptic basin suggest that this bonding region may be characterized as an N2–N3 single bond, in contrast to the expected structure of a pyrazole. The bonding changes taking place along *Phase IX*, which are mainly associated to the formation of the N3–C4 single bond, release an MRE of ca. 21.6 kcal·mol⁻¹. At **S8-2** and pyrazole **15**, the GEDT increases to 0.11e and 0.19e, respectively.

Some appealing conclusions can be drawn from the BET study of the 32CA reaction between Da **14** and SCH **9**: i) the molecular mechanism can be topologically divided in nine phases, one less than those associated to the molecular mechanism of the 32CA reaction involving Az **12**; ii) as Da **14** approaches SCH **9**, the strained alkyne

C4'-C4-C5-C5' framework immediately becomes relaxed leading to the formation of a C4 *pseudoradical* center with a negligible energy cost, 0.1 kcal·mol⁻¹; iii) this C4 pseudoradical center is created at the opposite site of the SCH framework facing the most nucleophilic center of Da 14, the C1 carbon; iv) the EC demanded to reach TS12, i.e. 1.9 kcal·mol⁻¹ (*Phase III*), can mainly be associated to the redistribution of the electron density within the Da framework, i.e. depopulation of the N2–N3 and C1–C1' bonding regions towards the C1-N2 double bond and the C1 pseudoradical center, respectively. Further depopulation of the C1-N2 double bond leads to the formation of the N2 non-bonding electron density of pyrazole 15; v) while the C1 and C4 pseudoradical centers are already present at the GS of the reagents or quickly created at the beginning of the reaction, the C5 pseudoradical center is created in Phase V from a smoother depopulation of the C5–C5' bonding region along the reaction path; vi) formation of the first C1–C5 single bond takes place in *Phase VII*, at a C–C distance of ca. 2.02 Å, by the C-to-C coupling of two C1 and C5 pseudoradical centers; vii) while formation of the first single bond follows a sharing model in the 32CA reaction of Da 14, it takes place through a donation model in the 32CA reaction of Az 12; viii) formation of the second N3-C4 single bond takes place in the last *Phase IX*, at an N-C distance of 1.69 Å, by sharing part of the non-bonding electron density of the N3 nitrogen and that of the C4 pseudoradical center; ix) formation of the second N3-C4 single bond begins when formation of the first C1–C5 single bond is completed by up to 97.3% and with a high 27.6% degree of asynchronicity; this 32CA reactions is more asynchronous than that involving Az 12; x) the alkyne C4–C5 multiple bond region is progressively depopulated by a total of only 0.92e; xi) pyrazole 15 does not present any N–N multiple bond, in contrast to the expected traditional Lewis structure; and finally, xii) the C1 pseudoradical center present at the GS of Da 14 favours the formation of the C4 pseudoradical center at the SCH framework compared to the N1 non-bonding electron density of Az 12, i.e. 0.1 (Da 14) vs 0.9 (Az 12) kcal·mol⁻¹ (*Phase I*), which accounts for the earlier character of TS12 and slightly lower activation energy of the 32CA reaction involving Da 14, i.e. 3.5 (Da 14) vs 5.0 (Az 12) kcal·mol⁻¹. Note that at **TS12**, the N2 non-bonding electron density has not yet been created.

Table S2. ELF valence basin populations, distances of the forming bonds, MPWB1K/6-311G(d) relative^a gas phase electronic energies, GEDT and IRC values of the IRC structures, **S0-2** – **S8-2**, defining the ten phases characterizing the molecular mechanism of the *pmr-type* 32CA reaction between Da **14** and SCH **9**. **TS12** and pyrazole **15** are also included. Distances are given in angstroms, Å, GEDT values and electron populations in average number of electrons, e, relative energies in kcal·mol⁻¹ and IRC values in atomic unities, a.u.

Structures	14	9	S0-2	S1-2	S2-2	S3-2	S4-2	S5-2	S6-2	S7-2	S8-2	15	TS12
Catastrophes				F^{\dagger}	С	F^{\dagger}	F^{\dagger}	С	С	C^{\dagger}	С		
Phases			Ι	II	III	IV	V	VI	VII	VIII	IX		
d(C1-C5)			3.059	2.980	2.625	2.221	2.126	2.022	1.593	1.528	1.501	1.483	2.307
d(N3-C4)			3.463	3.353	2.916	2.582	2.524	2.464	2.162	1.976	1.690	1.416	2.631
ΔΕ			0.0	0.1	1.6	3.2	1.7	-1.9	-35.1	-47.8	-67.6	-89.2	3.5
GEDT			0.02	0.03	0.08	0.17	0.18	0.18	0.07	0.00	-0.11	-0.19	0.16
IRC			-8.52	-6.73	-2.53	0.58	1.14	1.74	4.50	5.72	7.55	12.52	0.00
V(C1,C1')	2.40		2.44	2.46	2.81	2.38	2.32	2.30	2.14	2.15	2.11	2.10	2.43
V(C1,N2)	2.94		2.94	2.95	2.97	2.42	2.14	2.01	1.78	1.77	1.83	1.83	3.33
V(N2)						1.07	1.53	1.84	2.50	2.58	2.72	2.82	
V(N2,N3)	2.00		1.91	1.95	1.89	1.69	1.64	1.57	2.83	2.74	2.58	2.42	1.81
V'(N2,N3)	1.87		2.01	1.98	2.03	1.81	1.74	1.66					1.85
V(C4,C5)		2.20	2.26	2.28	2.26	2.14	2.10	2.07	1.85	1.82	1.82	1.77	2.16
V'(C4,C5)		2.18	2.19	2.17	2.18	2.17	2.12	2.04	1.88	1.86	1.86	1.76	2.18
V(C4,C4')		2.71	2.81	2.04	1.88	1.87	1.90	1.93	2.00	2.03	2.08	2.11	1.86
V(C5,C5')		2.71	2.57	2.56	2.45	2.46	2.30	2.13	1.99	1.99	2.05	2.10	2.46
V(C1)	0.46		0.57	0.54	0.33	0.74	0.84						0.65
V'(C1)	0.45		0.28	0.27									
V(N3)	3.64		3.62	3.60	3.57	3.47	3.44	3.43	3.53	3.00	2.78	2.73	3.48
V'(N3)										0.60			
V(C4)				0.85	1.11	1.30	1.32	1.33	1.19	1.07			1.28
V(C5)							0.22						
V(C1,C5)								1.35	1.93	2.03	2.06	2.11	
V(C3,N4)											1.73	2.00	

^aRelative to the first structure of the IRC, **S0-2**



Scheme S3. Simplified representation of the molecular mechanism of the 32CA reaction between Da 14 and SCH 9 by Lewis-like structures arising from the topological analysis of the ELF along the reaction path.



Figure S4. ELF localisation domains, together with the electron populations of the ELF valence basins involved in the formation of the new single bonds, for the structures defining the phases associated with the single bond formation processes along the IRC of the 32CA reaction between Da **14** and SCH **9**. The electron populations are given in average number of electrons, e.

The BET study of the bonding changes along the 32CA reaction between Az **12** and but-2-yne **25** indicates that this reaction is topologically characterized by thirteen differentiated phases. A simplified representation of the molecular mechanism of the 32CA reaction between Az **12** and but-2-yne **25** by Lewis-like structures is shown in Scheme S4; the populations of the most significant valence basins among other relevant parameters, of the selected structures of the IRC are included in Table S3; the attractor positions of the ELF basins for the structures involved in the bond formation processes are shown in Figure S5.

5. BET study of the 32CA reaction of Az 12 with but-2-yne 25

The long *Phase I*, 3.41 Å \geq d(N1–C5) > 2.79 Å and 3.37 Å \geq d(N3–C4) > 2.89 Å, begins at S0-3, which is the discontinue point of the IRC from TS31 towards the separated reagents, i.e. azide 17 with but-2-yne 28. The ELF topology of the initial structure of a reaction path, **S0-3**, usually resembles that of the isolated reagents. Thus, ELF topological analysis of S0-3 shows subtle changes in the valence populations of the ELF basins belonging to the azide and but-2-yne frameworks. It may be observed three disynaptic basins, V(N1,N2), V'(N1,N2) and V(N2,N3) integrating 2.57e, 1.83e and 2.25e, respectively, which can be associated with the N1–N2 and N2–N3 double bonds and two monosynaptic basins, V(N1) and V(N3), integrating 3.49e and 3.81e, all of them belonging to the azide fragment (see Table S3). On the other hand, the two V(C4,C5) and V'(C4,C5) disynaptic basins, integrating a total population of 5.51e, characterize the C4–C5 triple bond of the butyne moiety of **S0-3**, which remains similar in electronic population to that in isolated butyne, 5.54e, with the only difference that in isolated but-2-yne, the electron population is distributed in three V(C4,C5) disynaptic basins (see Table S3). Along *Phase I*, the populations of the ELF valence basins slightly change demanding an EC of 4.5 kcal·mol⁻¹. At **S0-3**, the GEDT is 0.00e.

Phase II, 2.79 Å \geq d(N1–C5) > 2.69 Å and 2.89 Å \geq d(N3–C4) > 2.79 Å, begins at **S1-3** by means a cusp *C* catastrophe, which implies the merger of the two V(C4,C5) and V'(C4,C5) disynaptic basins present at **S0-3** at the but-2-yne framework into one new single V(C4,C5) disynaptic basin integrating 5.49e. This topological change is the consequence of an electron density reorganisation within the C4–C5 bonding region. Then, the bonding changes taking place along *Phase II*, which are mainly related with

the rearrangement around of the C4–C5 bonding region, imply an EC of 2.2 kcal·mol⁻¹. At **S1-3**, the GEDT is 0.02e.

Phase III, 2.69 Å \geq d(N1–C5) > 2.50 Å and 2.79 Å \geq d(N3–C4) > 2.55 Å, begins at **S2-3**. This point is characterized as a cusp *C* catastrophe involving the merger of the two V(N2,N3) and V'(N2,N3) disynaptic basins present at the previous structure, at the azide framework, into one new single V(N2,N3) disynaptic basin integrating 4.13e. The population associated of the other dysinaptic and monosynaptic basins practically remain without changes. The bonding changes taking place along *Phase III*, which are mainly associated to fluctuations on the azide framework, demand an EC of ca. 7.6 kcal·mol⁻¹. At **S2-3**, the GEDT has slightly increased to 0.03e.

Phase IV, 2.50 Å \geq d(N1–C5) > 2.32 Å and 2.55 Å \geq d(N3–C4) > 2.31 Å, begins at **S3-3**. At this structure, which corresponds to a fold F^{\dagger} catastrophe, together with the depopulation of the V(N1,N2) and V(N2,N3) disynaptic basins by 0.13e and 0.46e, respectively, a new V(N2) monosynaptic basin is created at the N2 nitrogen with an initial population of 0.70e (see Table S3). This V(N2) monosynaptic basin, whose population progressively increases along the reaction path, is associated with the nonbonding N2 lone pair present at the final triazole **26**. Along *Phase IV*, the changes in the ELF valence basin populations are mainly associated to reorganization of the azide moiety, displaying a EC of 8.9 kcal·mol⁻¹. At **S3-3**, the GEDT is 0.04e.

Phase V, 2.32 Å \geq d(N1–C5) > 2.16 Å and 2.31 Å \geq d(N3–C4) > 2.10 Å, begins at **S4-3** by means of a cusp *C*[†] catastrophe. At this structure, while the V(N1,N2) disynaptic basin experiences a depopulation by 0.36e to 2.05e, the V(C4,C5) disynaptic basin splits into two new V(C4,C5) and V'(C4,C5) disynaptic basins integrating 2.83e and 2.59e. It is also observed that while the V(N2,N3) disynaptic basin is slightly depopulated, the V(N2) monosynaptic basin is populated. At this phase the TS of the reaction is found, **TS31**, d(N1–C5) = 2.168 Å and d(N3–C4) = 2.111 Å, which only shows a noticeable exchange of electron density from the V(N1,N2) and V(N2,N3) disynaptic basins to the V(N2) monosynaptic basin (see Table S3). Along *Phase V*, the bonding changes, which are mainly related to the reorganisation in the N1-N2 and N2-N3 regions, the formation of the N2 non-bonding electron density, and the depopulation of the C4-C5 bond of the butyne moiety, imply an EC of ca. 4.0 kcal·mol⁻¹. At **S4-3**, the GEDT is slightly reduced to 0.03e.

The short *Phase VI*, 2.16 Å \geq d(N1–C5) > 2.01 Å and 2.10 Å \geq d(N3–C4) > 1.91 Å, begins at **S5-3**, which also corresponds to a fold F^{\dagger} catastrophe. At this structure, the

most notable topological change is the formation of a V(C4) monosynaptic basin at the butyne moiety with an initial population of 0.21e as a consequence of the depopulation of the two V(C4,C5) disynaptic basins by 0.29e. On the other hand, the electron population of both V(N1,N2) and V(N2,N3) disynaptic basins have decreased by 0.21e and 0.26e, respectively. The bonding changes along this phase, which are mainly associated to the formation of a C4 *pseudoradical* center at the butyne framework, involve a MER of 6.1 kcal·mol⁻¹. At **S5-3**, the GEDT inverts its sign, i.e. -0.04e, which means that now the GEDT fluxes from the butyne framework towards the azide one due to a backdonation process.

Phase VII, 2.01 Å \geq d(N1–C5) > 1.99 Å and 1.91 Å \geq d(N3–C4) > 1.89 Å, begins at **S6-3**, which is characterized by means of a fold F^{\dagger} catastrophe implying the creation of a new V(C5) monosynaptic basin at the butyne framework, with an initial population of 0.15e, as a consequence of the depopulation of the two V(C4,C5) disynaptic basins by 0.52e to 4.61e. At the same time, while the population of the V(C4) disynaptic basin increases to 0.56e, the population of the V(N3) monosynaptic basin also increases by 0.12e compared with that observed at **S5-3**. Along this phase, while the V(N1,N2) and V(N2,N3) disynaptic basins continue being slightly depopulated, the V(N2) monosynaptic basin is populated. Note that at this phase, the recently formed V(C5) monosynaptic basin and the V(C4) one, formed in *phase VI*, will be needed for subsequent bond formation events (see later). Along this phase, the changes of the ELF valence basins, which are mostly related to the formation of a C5 pseudoradical center on the butyne moiety by the depopulation of the C4-C5 bonding region, involve a small MER of 1.6 kcal·mol⁻¹. At **S6-3**, the GEDT is -0.15e.

The very short *Phase VIII*, 1.99 Å \geq d(N1–C5) > 1.98 Å and 1.89 Å \geq d(N3–C4) > 1.87 Å, begins at **S7-3**, which is characterized by means of a cusp C^{\dagger} catastrophe implying the split of the V(N1) monosynaptic basin of the azide framework into a second V'(N1) one, integrating 1.36e. At the end of *Phase VIII*, the population of the V(C4) monosynaptic basin remains 0.58e. Along this phase, the V(C4,C5) and V'(C4,C5) disynaptic basins continue being slightly depopulated, while the V(N2) monosynaptic basin is slightly populated. The recently observed changes at the ELF valence basin populations are associated to a low MER of 1.4 kcal·mol⁻¹. At **S7-3**, the GEDT is -0.16e.

Phase IX, 1.98 Å \geq d(N1–C5) > 1.96 Å and 1.87 Å \geq d(N3–C4) > 1.85 Å, begins at **S8-3** by means of a cusp C^{\dagger} catastrophe (see Figure S5). At this structure, the V(N3)

monosynaptic basin of the azide framework splits into a second V'(N3) one integrating 0.37e, while the population of the V'(N1) monosynaptic basin remains 1.36e. At this phase, a slight electron rearrangement on the N1-N2-N3 skeleton occurs compared with that at *phase VIII*, the population of the V(C4,C5) and V'(C4,C5) disynaptic basins slightly decreases, and that of the V(C4) monosynaptic basin slightly increases to 0.60e. Along this phase, the ELF basin population changes, which are mainly associated with rearrangement in the N1-N2-N3 azide moiety, imply a slight MER of 2.0 kcal·mol⁻¹. At **S8-3**, the GEDT is -0.17e.

Phase X, 1.96 Å \geq d(N1–C5) > 1.83 Å and 1.85 Å \geq d(N3–C4) > 1.70 Å, begins at **S9-3** (see Figure S5). At this structure, the most relevant topological change along this reaction takes place: the two V'(N1) and V(C5) monosynaptic basins present in *Phase IX* merge into a new V(N1,C5) disynaptic basin, integrating an initial population of 1.53e, by means of a cusp *C* catastrophe. This significant topological change indicates that the formation of the first N1–C5 single bond take places at an N1–C5 distance of ca. 1.96 Å through the donation of part the N1 non-bonding electron density to the C5 *pseudoradical* center. Along this phase, the population of the V(N1,N2) disynaptic basin remains 1.78e, while that of V(N2) monosynaptic slightly increases and those of the V(N2,N3) and V(C4,C5) disynaptic basins slightly decrease. The bonding changes taking place along *Phase X*, which are mainly associated to the formation of the first N1–C5 single bond, release a strong MRE of ca. 17.2 kcal·mol⁻¹. At **S9-3**, the GEDT is –0.19e.

Phase XI, 1.83 Å \geq d(N1–C5) > 1.46 Å and 1.70 Å \geq d(N3–C4) > 1.39 Å, begins at **S10-3** (see Figure S5), which is characterized by a cusp *C* catastrophe. At this structure, the second most relevant topological change along this reaction takes place; a new V(N3,C4) disynaptic basin, integrating an initial population of 1.45e, is created by the merger of the two V'(N3) and V(C4) monosynaptic basins present in *Phase X*. This merger characterizes the formation of the second N3–C4 single bond at an N3–C4 distance of ca. 1.70 Å by sharing part of the N3 non-bonding electron density and that of the C4 *pseudoradical* center. Along this phase, the electron density rearrangement is mainly related to the further depopulation of the V(N2,N3) and V(C4,C5) disynaptic basins as well as that of the V(N3) monosynaptic basin. At this structure, the V(N1,C5) disynaptic basin reaches a population of 1.81e. The bonding changes taking place along *Phase XI*, which are mainly associated to the formation of the second N3–C4 single

bond and the increase in the population associated to the first N1–C5 single bond, release a strong MRE of ca. 54.1 kcal·mol⁻¹. At **S10-3**, the GEDT is -0.26e.

Phase XII, 1.46 Å \geq d(N1–C5) > 1.35 Å and 1.39 Å \geq d(N3–C4) > 1.35 Å, begins at **S11-3**, which is characterized by a cusp *C* catastrophe involving the merger of the two V(C4,C5) and V'(C4,C5) disynaptic basins of the but-2-yne framework present in previous phases, into one new single V(C4,C5) disynaptic basin integrating a population of 3.71e. This topological change is the consequence of an electron density reorganisation within the C4–C5 bonding region. Also note that, while the population of the V(N2) monosynaptic basin increases to 3.00e, those associated to the V(N1) and V(N3) monosynaptic basins have decreased by 0.54e and 0.32e, respectively, compared with those observed in *Phase XI*. The main bonding changes taking place along *Phase XII*, which are associated to the rearrangement of the C4–C5 bonding region, as well as those associated to N1–N2 and N2–N3 bonding regions, involve a MRE of 18.3 kcal·mol⁻¹. At **S11-3**, the GEDT is –0.30e.

Finally, *Phase XIII*, 1.347 Å \geq d(N1–C5) \geq 1.347 Å and 1.349 Å \geq d(N3–C4) \geq 1.350 Å, begins at S12-3, and ends at triazole 26, d(N1-C5) = 1.347 Å and d(N3-C4) =1.350 Å. At **S12-3**, the V(N1) monosynaptic basin splits into a second V'(N1) one, both integrating a total population of 1.26e. It is worth mentioning that from **S12-3** to **26** only slight electron population changes in basins are observed. The ELF bonding picture of 26 reflects that the V(N1,C5) and V(N3,C4) disynaptic basins have reached an electron population of 2.45e and 2.31e, in agreement with the expected new N-C single bonds at triazole 26. On the other hand, the electron population of the V(C4,C5) disynaptic basin has reached 3.50e, indicative of a C-C double bond character, while the corresponding populations of the V(N1,N2), and V(N2,N3) disynaptic basins are 1.78e and 2.05e, respectively, which are related with N-N single bonds, in contrast to the expected structure of an aromatic triazole. At S12-3, the GEDT is -0.28e. The changes of electron density taking place along Phase XIII, which are mainly associated to the complete rearrangement of the molecular electron density associated with the formation the final triazole 26, do not release any amount of MRE. Note that S12-3 and 26 have similar electronic structures and geometries, and therefore, they are isothermal, in agreement with the reaction between Az 12 and SCH 9.

From this BET study, the molecular mechanism of the 32CA reaction between Az 12 and but-2-yne 25 can be summarised as follows: (i) this 32CA reaction can be

topologically characterized by thirteen differentiated phases, emphasising the nonconcerted nature of the bonding changes; (ii) the reaction begins with the depopulation of the N1-N2, N2-N3 and C4-C5 bonding regions, which leads to the formation of the nitrogen N2 non-bonding electron density present at triazole 26 (*Phases I – V*); (iii) as **TS31** is found at the end of *Phase V* and the bonding changes taking place along *Phases* III and IV demand the highest ECs, i.e. 7.6 and 8.9 kcal·mol⁻¹, the high activation energy of the 32CA reaction between Az 12 and but-2-yne 25, 27.2 kcal·mol⁻¹, can mainly be associated with the depopulation of the N1–N2 and N2–N3 bonding regions; (iv) the depopulation of the C4–C5 bonding region permits the creation of two C4 and C5 pseudoradical centers (Phases VI and VII); (v) in Phases VIII and IX, the N1 and N3 nitrogen non-bonding electron density is redistributed in order to achieve the formation of the corresponding N-C single bonds in later phases; (vi) formation of the N1-C5 single bond takes place in *Phase X*, at an N1–C5 distance of ca. 1.96 Å, through the donation of part of the nitrogen N1 non-bonding electron density to the C5 pseudoradical center; (vii) in Phase XI, the formation of the N3-C4 single bond takes place at an N3-C4 distance of ca. 1.70 Å, by sharing part of the nitrogen N3 nonbonding electron density and that of the C4 pseudoradical center; and finally, (viii) ELF topology shows a very low 4% degree of asynchronicity in the N1-C5 and N3-C4 single bond formation.

Table S3. ELF valence basin populations, distances of the forming bonds, relative^a electronic energies, GEDT and IRC values of the IRC structures, S0-3 – S12-3, defining the thirteen phases characterizing the molecular mechanism of the 32CA reaction between Az 12 and but-2-yne 25. TS31 and triazole 26 are also included. Distances are given in angstroms, Å, GEDT values and electron populations in average number of electrons, e, relative energies in kcal·mol⁻¹ and IRC values in a.u.

Points	12	25	S0-3	S1-3	S2-3	S3-3	S4-3	S5-3	S6-3	S7-3	S8-3	S9-3	S10-3	S11-3	S12-3	26	TS31
Catastrophes				С	С	F^{\dagger}	C^{\dagger}	F^{\dagger}	F^{\dagger}	C^{\dagger}	C^{\dagger}	С	С	С	C^{\dagger}		
Phases				I I	I I	II I	V	V = V	T VI	II VL	II – Ľ	X Z	X X	I X	II XII	Ι	
d(N1-C5)			3.413	2.787	2.694	2.500	2.322	2.161	2.012	1.993	1.978	1.959	1.828	1.457	1.347	1.347	2.168
d(N3-C4)			3.367	2.889	2.786	2.547	2.311	2.101	1.909	1.886	1.868	1.845	1.698	1.392	1.349	1.350	2.110
ΔΕ			0.0	4.5	6.7	14.3	23.2	27.2	21.1	19.5	18.1	16.1	-1.1	-55.2	-73.5	-73.5	27.2
GEDT			0.00	0.02	0.03	0.04	0.03	-0.04	-0.15	-0.16	-0.17	-0.19	-0.26	-0.30	-0.28	-0.28	-0.03
IRC			-14.14	-5.50	-4.69	-2.93	-1.33	0.06	1.30	1.45	1.57	1.72	2.72	5.35	11.22	11.52	0.00
V(N1,N2)	2.62		2.57	2.56	2.54	2.41	2.05	1.84	1.80	1.78	1.77	1.78	1.77	1.78	1.78	1.78	1.85
V(N2)						0.70	1.63	2.13	2.39	2.43	2.44	2.47	2.63	3.00	3.12	3.10	2.12
V(N2,N3)	1.81		1.83	1.65	4.13	3.67	3.09	2.83	2.67	2.65	2.63	2.58	2.47	2.18	2.06	2.05	2.83
V'(N2,N3)	2.23		2.25	2.48													
V(C4,C5)		1.85	3.63	5.49	5.47	5.46	2.83	2.57	2.31	2.29	2.26	2.26	2.11	3.71	3.52	3.50	2.77
V'(C4,C5)		1.85	1.88				2.59	2.56	2.30	2.28	2.25	2.22	2.11				2.57
V"(C4,C5)		1.84															
V(N1)	3.48		3.49	3.44	3.41	3.41	3.42	3.44	3.43	2.08	2.09	2.07	1.93	1.39	0.59	0.61	3.44
V'(N1)										1.36	1.36				0.67	0.60	
V(N3)	3.77		3.81	3.78	3.80	3.74	3.75	3.76	3.88	3.89	3.52	3.46	3.26	2.94	2.91	2.91	3.77
V'(N3)											0.37	0.44					
V(C4)								0.21	0.56	0.58	0.60	0.63					
V(C5)									0.15	0.16	0.17						
V(N1,C5)												1.53	1.81	2.32	2.41	2.45	
V(N3,C4)													1.45	2.14	2.31	2.31	

^a Relative to the first structure of the IRC, **S0-3**.



Scheme S4. Simplified representation of the molecular mechanism of the 32CA reaction between Az 12 and but-2-yne 25 by Lewis-like structures arising from the topological analysis of the ELF along the reaction path.



Figure S5. ELF valence basin attractor positions, together with the electron populations of the ELF valence basins involved in the formation of the new single bonds, for the structures defining the phases associated with the single bond formation processes along the IRC of the 32CA reaction between Az 12 and but-2-yne 25. The electron populations are given in average number of electrons, e.

The BET study of the 32CA reaction between Da **14** with but-2-yne **25** shows that this reaction is topologically characterized by fourteen differentiated phases. A simplified representation of the molecular mechanism by Lewis-like structures is shown in Scheme S5; the populations of the most significant valence basins, among other relevant parameters, of the selected structures of the IRC are included in Table S4; the attractor positions of the ELF basins for the structures involved in the bond formation processes are shown in Figure S6.

The long *Phase I*, 3.41 Å \geq d(C1–C5) > 3.36 Å and 3.43 Å \geq d(N3–C4) > 3.41 Å, begins at, which is the first structure towards TS32. The ELF topology of the initial structure **S0-4** of this reaction path is very similar to that of the separated reagents. Hence, ELF topological analysis of S0-4 shows minor changes in the valence populations of the ELF basins belonging to the Da and butyne frameworks. At the Da moiety, it is observed one V(C1,N2) disynaptic basin, integrating 2.93e and characterizing a partial C1-N2 double bond, two V(N2,N3) and V'(N2,N3) disynaptic basins, with a population of 1.99e and 1.93e, which are associated with an N2-N3 double bond, and one V(N3) monosynaptic basin with a population of 3.66, associated with the N3 nitrogen non-bonding electron density (see Table S4). In addition, two V(C1) and V'(C1) monosynaptic basins, integrating a total population of 0.87e, are observed, being associated with the C1 *pseudoradical* center of Da 14. The population of the two V(C1) monosynaptic basins slightly decrease with respect to that present in isolated Da, ca. 0.04e. On the other hand, three V(C4,C5), V'(C4,C5) and V''(C4,C5) disynaptic basins, integrating a total population of 5.54e, characterize the C4–C5 triple bond of the but-2-yne moiety of **S0-4**, which maintains the same electron population to that in isolated but-2-yne 25, 5.54e (see Table S4). Along Phase I, ELF valence basin populations slightly vary, demanding a negligible EC of ca. 0.1 kcal·mol⁻¹. At **S0-4**, the GEDT is 0.01e.

Phase II, 3.36 Å \geq d(C1–C5) > 3.18 Å and 3.41 Å \geq d(N3–C4) > 3.18 Å, begins at **S1-4** by means of a fold *F* catastrophe associated with the disappearance of one V(C1) monosynaptic basin of the but-2-yne framework, whose electron population is redistributed into the adjacent V(C1,C1') disynaptic basin. This topological change can be attributed to slight electron density reorganisation within the C1–N2–N3 bonding region. The bonding changes taking place along *Phase II*, which are mainly associated

to a reorganisation of the electron density of the C1 *pseudoradical* center of the Da moiety, need a low EC of ca. $0.8 \text{ kcal} \cdot \text{mol}^{-1}$. At **S1-4**, the GEDT is 0.01e.

Phase III, 3.18 Å \geq d(C1–C5) > 3.10 Å and 3.18 Å \geq d(N3–C4) > 3.10 Å, begins at **S2-4** by means a cusp *C* catastrophe involving the merger of the three V(C4,C5), V'(C4,C5) and V''(C4,C5) disynaptic basins present in *Phase II*, in the but-2-yne framework, into two V(C4,C5) and V'(C4,C5) disynaptic basins integrating a total population of 5.54e. Note that along *Phase III*, there is a slight electron density exchange among all bonding regions; while the populations of V(N2,N3) and V'(N2,N3) disynaptic basins increase by ca. 0.02e, and that of the V(C1) monosynaptic basin also increases by 0.03e, the corresponding population of V'(N3) monosynaptic basin decreases in the same extent. The bonding changes taking place along *Phase III*, which are mainly associated to slight electron density rearrangements within the Da framework, demand an EC of ca. 0.6 kcal·mol⁻¹. At **S2-4**, the GEDT remains 0.01e.

Phase IV, 3.10 Å \geq d(C1–C5) > 2.75 Å and 3.10 Å \geq d(N3–C4) > 2.68 Å, begins at **S3-4**. At this structure, which corresponds to a cusp *C* catastrophe, the most significant topological change is the merger of the two V(C4,C5) and V'(C4,C5) disynaptic basins of the butyne moiety into one V(C4,C5) disynaptic basin, which integrates a population of 5.51e. Along this phase, the ELF basin population changes, which are mainly associated to the butyne framework as well as some reorganizations in the Da one, imply an EC of ca. 7.7 kcal·mol⁻¹. At **S3-4**, the GEDT is 0.01e.

Phase V, 2.75Å \geq d(C1–C5) > 2.65 Å and 2.68 Å \geq d(N3–C4) > 2.59 Å, begins at **S4-4** by means a cusp *C*⁺ catastrophe. At this structure, a new V'(C1) monosynaptic basin with a population of 0.28e is created, which, together with the V(C1) monosynaptic basin, integrate a total population of 0.77e. This topological change is the result of the recovery of part of the electron density previously redistributed into the V(C1,C1') disynaptic basin, whose population decreases to 2.47e. In addition, this topological feature points out the planar environment of the C1 *pseudoradical* center. On the other hand, the populations of the other disynaptic and monosynaptic basins experience very slight changes. The bonding changes taking place in *Phase V*, which are primarily associated to the formation of the C1 *pseudoradical* center in the butyne moiety, demand an EC of ca. 3.4 kcal·mol⁻¹. At **S4-4**, the GEDT slightly increases to 0.04e.

Phase VI, 2.65Å \geq d(C1–C5) > 2.38 Å and 2.59 Å \geq d(N3–C4) > 2.32 Å, begins at **S5-4**, characterized as a fold *F* catastrophe associated with the disappearance of the V'(C1) monosynaptic basin, while the population of the contiguous V(C1,C1') disynaptic basin increases to 2.85e. Again, this topological change may suggest the redistribution of the non-bonding electron density of the C1 *pseudoradical* center towards the C1–C1' bonding region in order to acquire the required arrangement for the subsequent C1–N3 single bond formation. At this phase, the electron density rearrangements at the C1 center and around the C1–C1' bonding region imply an EC of ca. 11.9 kcal·mol⁻¹. At **S5-4**, the GEDT is 0.05e.

The short *Phase VII*, 2.38 Å \geq d(C1–C5) > 2.37 Å and 2.32 Å \geq d(N3–C4) > 2.31 Å, begins at **S6-4**, which is characterized by means of a cusp *C*[†] catastrophe implying the split of the V(C4,C5) disynaptic basin of the butyne framework into two V(C4,C5) and V'(C4,C5) disynaptic basins with a total population of 5.42e, which decreases by only 0.03e with respect to that found in *Phase VI*. The population of the V(C1) monosynaptic basin increases to 0.63e. The ELF valence basin population changes taking place along this phase suggest that the electron density in the N3-N2-C1 skeleton suffers a polarization towards the C1 carbon, as the populations of the V(C1) monosynaptic and V(C1,N2) disynaptic basins increase by 0.30e and 0.46e, while those of the V(N2,N3) and V(C1,C1') disynaptic basins decreases by 0.39e and 0.38e. Along this phase, these electron reorganizations entail a low EC of ca. 0.4 kcal·mol⁻¹. At **S6-4**, the GEDT is 0.07e.

Phase VIII, 2.37 Å \geq d(C1–C5) > 2.27 Å and 2.31 Å \geq d(N3–C4) > 2.23 Å, begins at **S7-4**. At this structure, which corresponds to a fold F^{\dagger} catastrophe, a new V(N2) monosynaptic basin is formed at the N2 nitrogen with an initial population of 1.17e, mainly as a consequence of the depopulation of the V(C1,N2) disynaptic basin by 1.13e. The population of the V(N2) monosynaptic basin, which progressively increases along the reaction path, is associated with the N2 non-bonding electron density present at the final pyrazole **27**. The bonding changes taking place along *Phase VIII*, which are mainly associated to the creation of the N2 nitrogen non-bonding electron density from the depopulation of both C1–N2 and N2–N3 bonding regions, demand an EC of ca. 2.6 kcal·mol⁻¹. At **S7-4**, the GEDT remains 0.07e.

The short *Phase IX*, 2.26 Å \geq d(C1–C5) > 2.25 Å and 2.23 Å \geq d(N3–C4) > 2.21 Å, begins at **S8-4** by means of a fold F^{\dagger} catastrophe, which denotes the creation of a

new V(C5) monosynaptic basin at the butyne framework, with an initial population of 0.09e, as a consequence of the slight depopulation of the two V(C4,C5) disynaptic basins by 0.06e to 5.37e. At **S8-4**, the population of the V(C1) monosynaptic basin has increased to 0.73e, while the populations of V(C1,N2) and that of the two V(N2,N3) and V'(N2,N3) disynaptic basins have decreased to 2.10e and 3.20e. The population of the former basin suggests a C1–N2 single bond while that of the latter ones suggests a partial N2–N3 double bond (see Scheme S5). Thus, the bonding changes taking place along *Phase IX*, which are mainly associated to the formation of the C5 *pseudoradical* center and a slight increase of the population at the C4 *pseudoradical* center, practically occur without energy costs $(0.2 \text{ kcal} \cdot \text{mol}^{-1})$. At **S8-4**, the GEDT is 0.05e.

Phase X, 2.25 Å \geq d(C1–C5) > 2.03 Å and 2.21 Å \geq d(N3–C4) > 2.02 Å, begins at **S9-4** by means of a fold F^{\dagger} catastrophe (see Figure S6). At this structure, a new V(C4) monosynaptic basin is formed, with an initial population of 0.14e, mainly from the depopulation of the two V(C4,C5) and V'(C4,C5) disynaptic basins by ca. 0.18e to 5.19e. This depopulation also leads to a slight increase of the population of the V(C5) monosynaptic basin to 0.12e, while the population of the V(C1) monosynaptic basin reaches 0.75e as that of the V(C1,N2) disynaptic basin continues decreasing to 2.07e. It is worth to mention that the TS of this reaction, **TS32**, is found in this phase, at d(C1–C5) = 2.217 Å and d(N3–C4) = 2.117 Å. At **TS32**, the populations of the V(C1), V(C4) and V(C5) monosynaptic basins are 0.77e, 0.23e and 0.25e, while that of the V(N3) monosynaptic basin is 3.56e. The changes of electron density taking place along *Phase X*, which are mainly related to the formation of the C4 *pseudoradical* center as well as to a slight increase of the populations of the C5 and C1 *pseudoradical* centers, release an MRE of ca. 5.8 kcal·mol⁻¹. At **S9-4**, the GEDT is 0.05e.

The short *Phase XI*, 2.03 Å \geq d(C1–C5) > 1.98 Å and 2.02 Å \geq d(N3–C4) > 1.98 Å, begins at **S10-4** (see Figure S6), which is characterized by a cusp *C* catastrophe. At this structure, the most relevant topological change along the reaction path takes place; the two V(C1) and V(C5) monosynaptic basins present in *Phase X* merge into a new V(C1,C5) disynaptic basin, integrating an initial population of 1.36e. This merger characterizes the formation of the first C1–C5 single bond at a C1–C5 distance of 2.030 Å, by the C-to-C coupling of the two C1 and C5 *pseudoradical* centers. The two V(C4,C5) and V'(C4,C5) disynaptic basins have been depopulated by 0.72e reaching a total value of 4.47e, while there is an electron density rearrangement among the

V(C1,N2), V(N2) and V(N2,N3) basins, whose populations reach 1.94e, 2.27e and 1.47e. Along this phase, the V(C4) monosynaptic basin reaches 0.53e. The electron density changes taking place at this phase, which are mostly associated to the formation of the new C1–C5 single bond with the consequent reorganization of the C4–C5 bonding region, release an MRE of ca. $3.7 \text{ kcal} \cdot \text{mol}^{-1}$. At **S10-4**, the GEDT inverts its sign, which means that now the GEDT fluxes from the butyne framework towards the Da one due to a backdonation process, -0.02e.

Phase XII, 1.98 Å \geq d(C1–C5) > 1.85 Å and 1.98 Å \geq d(N3–C4) > 1.87 Å, begins at **S11-4**. At this structure, which is characterized by a cusp C^{\dagger} catastrophe, while the recently formed V(C1,C5) disynaptic basin increases its population reaching 1.45e and the population of the V(C4) monosynaptic basin increases to 0.57e, the V(N3) monosynaptic basin splits into two new V(N3) and V'(N3) monosynaptic basins integrating 2.93e and 0.72e. These bonding changes, which are preferentially related with electron reorganizations around the N3 center, release an MRE of ca. 13.3 kcal·mol⁻¹. At **S11-4**, the GEDT is –0.04e.

Phase XIII, 1.85 Å \geq d(C1–C5) > 1.79 Å and 1.87 Å \geq d(N3–C4) > 1.81 Å, begins at **S12-4** (see Figure S6) by means a cusp *C* catastrophe, involving the merger of the two V(N2,N3) and V'(N2,N3) disynaptic basins into one single V(N2,N3) disynaptic basin integrating 2.72e, attributable to a partial N2–N3 double bond. At **S12-4**, together with an increase of the population of the V(C1,C5) disynaptic basin to 1.62e, the V'(N3) monosynaptic basin increases to 0.87e, while the population of the V(C4) monosynaptic basin also increases to 0.62e. All these bonding changes release an MER of ca. 7.0 kcal·mol⁻¹. At **S12-4**, the GEDT is -0.09e.

The last *Phase XIV*, 1.79 Å \geq d(C1–C5) \geq 1.49 Å and 1.81 Å \geq d(N3–C4) \geq 1.842 Å, begins at **S13-4** (see Figure S6) and ends at the pyrazole **27**, d(C1–C5) = 1.489 Å and d(N3–C4) = 1.422 Å. At **S13-4**, the second most relevant topological change along the reaction path takes place; the two V'(N3) and V(C4) monosynaptic basins present in *Phase XIII* merge into a new V(N3,C4) disynaptic basin, integrating an initial population of 1.54e, by means of a cusp *C* catastrophe. This relevant change indicates that the formation of the second N3–C4 single bond take places at an N3–C4 distance of 1.813 Å by sharing part of the non-bonding electron density of the N3 nitrogen and that of the C4 *pseudoradical* center. The V(C1,C5) formed in *Phase IX* reaches 1.69e. At **S13-4**, the GEDT is –0.11e.

Finally, the ELF bonding picture of pyrazole **27** shows that the V(C1,C5) and V(N3,C4) disynaptic basins integrate an electron population of 2.06e and 1.99e, compatible with the expected C1–C5 and N3–C4 single bonds. The corresponding populations for the V(C1,N2) and V(N2,N3) disynaptic basins are 1.85e and 2.42e, respectively, which are related with two C1–N2 and N2–N3 single bonds, in contrast to the expected classical structure of an aromatic pyrazole, while the V(N2) monosynaptic basin reaches a population of 2.82e. At pyrazole **27**, the GEDT is –0.19e. The changes of electron density taking place along *Phase XIV*, which are mainly related to the formation of the N3–C4 single bond, the population of C1–C5 single bond and the subsequent relaxation of the molecular electron density associated with the formation the final pyrazole **27**, release an MRE of ca. 43.1 kcal·mol⁻¹ (see Table S4).

From this BET study, the molecular mechanism of the 32CA reaction between Da 14 and but-2-yne 25 can be summarised as follows: (i) this 32CA reaction is topologically characterized by fourteen differentiated phases, stressing the nonconcerted nature of the bonding changes; (ii) the reaction begins with the rearrangement and depopulation of the C4-C5 bonding region of the but-2-yne moiety and the C1 pseudoradical center of the Da framework, followed by the depopulation of the N2-N3 bond towards the C1–N2 one (*Phases I – VII*); (iii) then, the bonding changes taking place along Phase VIII are mainly associated to the formation of the N2 nitrogen nonbonding electron density through the depopulation of the contiguous C1-N2 and N2–N3 bonding regions; (iv) next, the stronger depopulation of the C4–C5 bonding region permits the creation of two C4 and C5 *pseudoradical* centers (*Phases IX* and *X*); v) as **TS32** is found in *Phase X*, requiring an EC of 27.9 kcal·mol⁻¹, and the highest ECs demanded to reach it correspond to Phase IV, 7.7 kcal·mol⁻¹, and Phase VI, 11.9 kcal·mol⁻¹, the activation energy of the 32CA reaction between Da 14 and but-2-yne 25 can mainly be related to the rearrangement of the C1 pseudoradical center and the depopulation of the N2–N3 bonding region of Da 14; vi) although TS32 is earlier than TS31, associated with the 32CA reaction of Az 12 with but-2-yne 25, TS32 is found in a later phase compared with TS31 (Phase V); (v) in Phase XI, formation of the first C1–C5 single bond takes place at a C1–C5 distance of ca. 2.03 Å, through the C-to-C coupling of the two C4 and C5 pseudoradical centers; (vi) in Phase XII, the nonbonding electron density of the N3 nitrogen is redistributed in order to prepare itself for

the subsequent N3–C4 bond formation process; (vii) formation of the second N3–C4 single bond takes place in *Phase XIII*, at an N3–C4 distance of ca. 1.81 Å, by sharing part of the non-bonding electron density of the Da N3 nitrogen and that of the C4 *pseudoradical* center; and finally, (vii) ELF topology also shows a very low degree of asynchronicity in the C1–C5 and N3–C4 single bond formation, 7%, which is slightly higher than that found in the 32CA reaction between Az **12** and but-2-yne **25**, 4%.

Table S4. ELF valence basin populations, distances of the forming bonds, relative^a electronic energies, GEDT and IRC values of the IRC structures, **S0-4** – **S13-4**, defining the thirteen phases characterizing the molecular mechanism of the 32CA reaction between Da **14** and but-2-yne **25**. **TS32** and pyrazole **27** are also included. Distances are given in angstroms, Å, GEDT values and electron populations in average number of electrons, e, relative energies in kcal·mol⁻¹ and IRC values in a.u.

Points	14	25	S0-4	S1-4	S2-4	S3-4	S4-4	S5-4	S6-4	S7-4	S8-4	S9-4	S10-4	S11-4	S12-4	S13-4	27	TS32
Catastrophes				F	С	С	C^{\dagger}	F	C^{\dagger}	F^{\dagger}	F^{\dagger}	F^{\dagger}	С	C^{\dagger}	С	С		
Phases				Ι	II I	II .	IV	V V	/I V	VII V.	III I.	X Z	X X	KI X	II XI	II XI	V	
d(C1–C5)			3.410	3.363	3.182	3.102	2.747	2.654	2.375	2.366	2.268	2.249	2.030	1.980	1.848	1.791	1.489	2.217
d(N3-C4)			3.431	3.407	3.182	3.091	2.679	2.585	2.321	2.313	2.225	2.208	2.021	1.980	1.866	1.813	1.422	2.177
ΔΕ			0.0	0.1	0.9	1.5	9.2	12.6	24.5	24.9	27.5	27.7	21.9	18.2	4.9	-2.1	-45.2	27.9
GEDT			0.01	0.01	0.01	0.01	0.04	0.05	0.07	0.07	0.05	0.05	-0.02	-0.04	-0.09	-0.11	-0.19	0.04
IRC			-11.18	-10.07	-7.70	-6.88	-3.74	-3.04	-1.08	-1.01	-0.35	-0.22	1.20	1.52	2.38	2.76	9.66	0.00
V(C1,C1')	2.40		2.42	2.72	2.67	2.68	2.47	2.85	2.47	2.46	2.40	2.39	2.30	2.28	2.22	2.20	2.15	2.38
V(C1,N2)	2.94		2.93	2.93	2.92	2.92	2.98	3.06	3.52	2.39	2.10	2.07	1.94	1.93	1.92	1.90	1.85	2.05
V(N2)										1.17	1.70	1.77	2.27	2.36	2.52	2.60	2.82	1.87
V(N2,N3)	2.00		1.99	1.99	1.99	1.99	1.93	1.95	1.78	1.76	1.62	1.61	1.47	1.42	2.72	2.68	2.42	1.56
V'(N2,N3)	1.87		1.93	1.91	1.93	1.90	1.93	1.89	1.67	1.64	1.58	1.59	1.40	1.40				1.55
V(C4,C5)		1.85	1.30	1.38	1.37	5.51	5.47	5.45	2.62	2.61	2.72	2.61	2.25	2.18	2.08	2.05	1.80	2.54
V'(C4,C5)		1.85	2.05	2.01	4.17				2.80	2.82	2.65	2.58	2.22	2.18	2.05	2.02	1.79	2.50
V"(C4,C5)		1.84	2.19	2.16														
V(C1)	0.46		0.31				0.28	0.33	0.63	0.65	0.73	0.75						0.77
V'(C1)	0.45		0.56	0.57	0.60	0.61	0.49											
V(N3)			3.66	3.66	3.63	3.63	3.59	3.61	3.58	3.58	3.57	3.58	3.61	2.93	2.83	2.81	2.70	3.56
V'(N3)	3.64													0.72	0.87			
V(C4)												0.14	0.53	0.57	0.62			0.23
V(C5)											0.09	0.12						0.20
V(C1,C5)													1.36	1.45	1.62	1.69	2.06	
V(C3,N4)																1.54	1.99	

^a Relative to the first structure of the IRC, **S0-4**.



Scheme S5. Simplified representation of the molecular mechanism of the 32CA reaction between Da 14 and but-2-yne 25 by Lewis-like structures arising from the topological analysis of the ELF along the reaction path.



Figure S6. ELF valence basin attractor positions, together with the electron populations of the ELF valence basins involved in the formation of the new single bonds, for the structures defining the phases associated with the single bond formation processes along the IRC of the 32CA reaction between Da 14 and but-2-yne 25. The electron populations are given in average number of electrons, e.

	Gas phase		THF	
	Е	ΔE	Е	ΔE
9	-233.244174		-233.247340	
12	-204.027643		-204.031099	
MC11	-437.279195	-4.6	-437.283588	-3.2
TS11	-437.267198	2.9	-437.272729	3.6
13	-437.462254	-119.5	-437.471408	-121.1
14	-376.534788		-376.540519	
MC12	-609.783548	-2.9	-609.792268	-2.8
TS12	-609.777086	1.2	-609.784040	2.4
15	-609.924727	-91.5	-609.934088	-91.8

Table S5. MPWB1K/6-311G(d) total (E, in a.u.) and relative^a (Δ E, in kcal·mol⁻¹) energies, in gas phase and in THF, of the stationary points involved in the 32CA reactions of SCH **9** with Az **12** and Da **14**.

(a) relative to the separated reagents

Table S6. MPWB1K/6-311G(d) total (E, in a.u.) and relative^a (Δ E, in kcal·mol⁻¹) energies, in gas phase and in THF, of the stationary points involved in the 32CA reactions of 3-methoxy cyclohexyne **19** with Az **12**.

	Gas phas	se	THF			
	Е	ΔE	Е	ΔE		
19	-347.738079		-347.742776			
12	-204.027643		-204.031099			
MC21	-551.772223	-4.1	-551.778429	-2.9		
MC22	-551.771193	-3.4	-551.778842	-3.1		
TS21	-551.762628	1.9	-551.770171	2.3		
TS22	-551.758070	4.8	-551.763845	6.3		
20	-551.952497	-117.2	-551.962433	-118.3		
21	-551.951995	-116.9	-551.961402	-117.7		

(a) relative to the separated reagents

	Gas phas	se	THF	
	Е	ΔE	Е	ΔE
25	-155.911852		-155.914516	
12	-204.027643		-204.031099	
MC31	-359.945226	-3.6	-359.949660	-2.5
TS31	-359.900558	24.4	-359.904634	25.7
26	-360.061241	-76.4	-360.070524	-78.4
14	-376.534788		-376.540519	
MC32	-532.452274	-3.5	-532.458382	-2.1
TS32	-532.406213	25.4	-532.411989	27.0

Table S7. MPWB1K/6-311G(d,) total (E, in a.u.) and relative^a (Δ E, in kcal·mol⁻¹) energies, in gas phase and in THF, of the stationary points involved in the 32CA reactions of but-2-yne **25** with Az **12** and Da **14**.

27 -532.522722 -47.7 -532.532043 -48.3 (a) relative to the separated reagents

Table S8. MPWB1K/6-311G(d,) enthalpies (H, in a.u.), entropies (S, cal·mol⁻¹·K) and Gibbs free energies (G, in a.u.), computed in THF at 60 °C, of the stationary points involved in the 32CA reactions of SCH **9** with Az **12** and Da **14**.

	Н	ΔH	S	ΔS	G	ΔG
9	-233.114847		76.3		-233.155347	
12	-203.972797		68.6		-204.009240	
MC11	-437.090529	-1.8	111.3	-33.7	-437.150607	8.8
TS11	-437.080992	4.2	104.8	-40.1	-437.136638	17.5
13	-437.273970	-116.9	94.6	-50.3	-437.324186	-100.1
14	-376.451920		86.1		-376.497636	
MC11	-609.568557	-1.1	127.0	-35.4	-609.635960	10.7
TS11	-609.561734	3.2	121.4	-41.0	-609.626164	16.8
15	-609.706871	-87.9	112.9	-49.5	-609.766831	-71.4

(a) relative to the separated reagents

Table S9. MPWB1K/6-311G(d,) enthalpies (H, in a.u.), entropies (S, cal·mol⁻¹·K) and Gibbs free energies (G, in a.u.), computed in THF at 60 °C, of the stationary points involved in the 32CA reaction of 3-methoxy cyclohexyne **19** with Az **12**.

	Н	ΔH	S	ΔS	G	ΔG
19	-347.573585		89.8		-347.621278	
12	-203.972797		68.6		-204.009240	
MC21	-551.548672	-1.4	126.0	-32.5	-551.615580	9.4
MC22	-551.548999	-1.6	127.1	-31.4	-551.616458	8.8
TS21	-551.541669	3.0	117.7	-40.8	-551.604140	16.6
TS22	-551.535084	7.1	117.6	-40.9	-551.597503	20.7
20	-551.728123	-114.0	108.3	-50.2	-551.785610	-97.3
21	-551.726782	-113.2	104.9	-53.5	-551.782490	-95.4

(a) relative to the separated reagents

	Н	ΔH	S	ΔS	G	ΔG
25	-155.820418		76.5		-155.861035	
12	-203.972797		68.6		-204.009240	
MC31	-359.794802	-1.0	111.3	-33.9	-359.853877	10.3
TS31	-359.751812	26.0	100.4	-44.8	-359.805114	40.9
26	-359.912659	-75.0	94.6	-50.6	-359.963368	-58.4
14	-376.451920		86.1		-376.497636	
MC32	-532.274482	-1.3	131.8	-30.8	-532.344467	8.9
TS32	-532.228359	27.6	116.3	-46.3	-532.290104	43.0
27	-532.344380	-45.2	111.6	-51.0	-532.403624	-28.2

Table S10. MPWB1K/6-311G(d,) enthalpies (H, in a.u.), entropies (S, cal·mol⁻¹·K) and Gibbs free energies (G, in a.u.), computed in THF at 60 °C, of the stationary points involved in 32CA reactions of but-2-yne **25** with Az **12** and Da **14**.

(a) relative to the separated reagents

MPWB1K/6-311G(d) computed total energies, single imaginary frequencies and Cartesian coordinates, in THF, of the stationary points involved in the 32CA reactions of of SCH **9** with Az **12** and Da **14**.

9 E = -233.247340421 a.u.

С	0.60213900	-1.27695800	-0.02606900
C –	0.60140100	-1.27688600	0.02626500
C –	1.58019800	-0.18792500	0.11729000
C –	0.70651700	1.02802600	-0.29089900
С	0.70604100	1.02815500	0.29102900
С	1.58018800	-0.18727600	-0.11753300
н –	2.43795900	-0.28178800	-0.54121700
Н –	0.64252500	1.04514400	-1.37752500
Н –	1.21334800	1.94289300	0.00998500
Н	1.21249400	1.94330000	-0.00961400
Н	0.64199600	1.04503800	1.37766700
Н	1.95945500	-0.08796000	-1.13153500
Н	2.43825600	-0.28075200	0.54061700
Н –	1.95988200	-0.08869900	1.13113100

12

E = -204.031099214 a.u.

Ν	1.76004200	0.27743100	0.00009000
Ν	0.70871000	-0.10550900	-0.00016800
Ν	-0.38560700	-0.63031900	0.00007800
С	-1.52019700	0.28419600	0.00000700
Η	-1.52398300	0.91340700	-0.88575000
Η	-2.41295600	-0.32351600	0.00016400
Η	-1.52388900	0.91371600	0.88554300

13

E = -437.471408329a.u.

С	-0.26222000	0.31266200	0.00455500
С	0.23277100	-0.95746600	-0.04784300
Ν	-0.80288300	-1.81585000	-0.06688700
N	-1.89966200	-1.14296800	-0.02802300
N	-1.59109700	0.14370400	0.01676000
С	1.68090200	-1.27228000	-0.06733000
С	2.44879500	-0.03284100	0.37376000
С	1.95968300	1.22134700	-0.33463100
С	0.52293600	1.56440800	0.04100500
Η	1.89951300	-2.11533400	0.58263100
Η	2.33030600	0.09730900	1.44943600
Η	3.51056300	-0.17121800	0.19056600
Η	2.60679900	2.06204800	-0.10222800
Η	2.01783400	1.06730200	-1.41154600
Η	0.48663000	2.00043300	1.03929600
Η	0.11355100	2.30943300	-0.63784600
Н	1.99035400	-1.56468500	-1.07046200

-2.62201600	1.14192400	0.07240400
-3.57242400	0.62933500	0.03751800
-2.55042300	1.71060400	0.99218400
-2.54230900	1.81404300	-0.77402700
	-2.62201600 -3.57242400 -2.55042300 -2.54230900	-2.622016001.14192400-3.572424000.62933500-2.550423001.71060400-2.542309001.81404300

14

E = -376.540519027 a.u.

Ν	-2.97208500	0.30989900	-0.00002600
Ν	-1.99132500	-0.21298400	0.00003800
С	-0.83456600	-0.80283800	-0.00001200
С	0.32446200	0.04915900	-0.00004000
0	0.30682300	1.25131800	0.00002000
0	1.43602200	-0.67655600	0.00004400
С	2.64110400	0.06667800	-0.00002300
Н	3.43702200	-0.66319400	-0.00106500
Н	2.70183400	0.69221900	-0.88255000
Н	2.70283000	0.69072000	0.88350700
Н	-0.82657700	-1.87423000	-0.00003400

15

E = -609.934088035 a.u.

С	0.60548300	-0.12138500	-0.47318500
С	1.23093000	0.92839600	0.05171100
Ν	0.43827400	2.09036300	-0.08494800
Ν	-0.63473900	1.83066600	-0.64888700
С	-0.67907700	0.41583100	-0.98187000
С	2.57471700	0.91291700	0.66864300
С	3.26209100	-0.39640400	0.30832700
С	2.32673200	-1.58409500	0.46446100
С	1.14666400	-1.49768700	-0.49244500
Н	3.15496400	1.76656400	0.32670000
Η	3.60197200	-0.34575800	-0.72574400
Н	4.14768000	-0.53096100	0.92248900
Н	2.86600600	-2.51266600	0.30072100
Н	1.95341900	-1.61360200	1.48762300
Н	1.45678400	-1.75007900	-1.50713700
Н	0.37251500	-2.21614200	-0.23207900
Η	2.48596200	1.01629600	1.75005800
Н	-0.76254300	0.33534500	-2.06511900
С	-1.86032200	-0.31348300	-0.39168400
0	-2.18016800	-1.40632500	-0.75257300
0	-2.44338300	0.35413700	0.57577800
С	-3.52860800	-0.30959800	1.20942500
Η	-3.88842300	0.37333200	1.96356100
Н	-4.30682000	-0.52559800	0.48828000
Н	-3.18951200	-1.23338400	1.66155000

MC11

E = -437.283587560 a.u.

С	0.85912900	-0.83698700	1.15140600
С	0.96153600	0.34882700	1.34168100
Ν	-1.78201500	1.89100000	-0.02709700

Ν	-1.91768500	0.81283200	-0.29360900
Ν	-2.02751200	-0.32483100	-0.70071800
С	1.54751500	1.43120600	0.54362900
С	1.62951500	0.74937600	-0.84878700
С	2.09067700	-0.70603000	-0.82447600
С	1.17363100	-1.66469500	-0.02060100
Η	0.95248100	2.33668500	0.49248200
Η	0.64308800	0.79871400	-1.30681500
Η	2.30134000	1.32515900	-1.48260300
Η	2.16897600	-1.06991700	-1.84726000
Η	3.08938900	-0.75561200	-0.39409100
Η	0.26902300	-1.90609200	-0.57289700
Η	1.68579100	-2.59638300	0.19729900
Η	2.53130900	1.70220100	0.91809200
С	-2.52740500	-1.29379700	0.26630800
Η	-3.54287900	-1.05772200	0.57216400
Н	-2.52738200	-2.25624400	-0.22445000
Н	-1.88824700	-1.34119600	1.14309300

MC12

E = -609.792268278 a.u.

С	-1.20288900	0.34114600	1.23066000
С	-1.81397900	1.15170800	0.58104500
Ν	0.81166200	2.64701400	-0.81334400
Ν	1.37367800	1.96217200	-0.14247700
С	2.01791600	1.14933200	0.63768000
С	-2.74380900	0.99804800	-0.54467600
С	-3.08812400	-0.51125900	-0.44471400
С	-1.90129100	-1.41709000	-0.12285400
С	-1.20762800	-1.12576000	1.23424700
Н	-3.64336800	1.60237800	-0.48509000
Н	-3.84800700	-0.63243300	0.32526800
Н	-3.53536000	-0.83424700	-1.38305600
Н	-2.23064700	-2.45445000	-0.13732500
Н	-1.15489300	-1.30710000	-0.90641100
Н	-1.78360800	-1.51102500	2.07174000
Н	-0.22667700	-1.59031900	1.27896600
Н	-2.25321300	1.23834500	-1.48463500
Н	2.42378500	1.55446800	1.54238100
С	2.10454600	-0.24091800	0.29111000
0	2.64419800	-1.07117700	0.97173100
0	1.51959900	-0.51332200	-0.87504300
С	1.62198300	-1.85875500	-1.30286900
Н	1.13723000	-1.89986500	-2.26719900
Н	2.66141500	-2.15046700	-1.39100800
н	1.12523800	-2.52231100	-0.60415000

TS11

E = -437.272729010 a.u.

1 imaginary frequency -263.2362 cm⁻¹

С	0.16293900	-0.17022800	-0.07493300
С	0.48092100	1.00555000	0.10150500
Ν	-2.05033500	1.91322600	-0.00266500

Ν	-2.22042300	0.81528100	-0.15410500
Ν	-1.92747700	-0.35349400	-0.39017700
С	1.90671200	1.40012500	0.27763200
С	2.75831800	0.23432900	-0.24624300
С	2.26440700	-1.13021900	0.21836100
С	0.82580100	-1.45762100	-0.24393900
Η	2.16430800	2.32247000	-0.23726500
Η	2.74704600	0.26157500	-1.33565600
Η	3.79557900	0.36463700	0.05857100
Η	2.93762600	-1.90760300	-0.13572900
Η	2.28613600	-1.16332600	1.30660500
Η	0.80463700	-1.78403100	-1.28179800
Η	0.41215000	-2.26271100	0.35807400
Η	2.10406500	1.57932300	1.33366000
С	-2.63914500	-1.38813700	0.33949300
Η	-3.67586500	-1.44148700	0.02509400
Η	-2.15864600	-2.32447700	0.09282700
Н	-2.58911700	-1.23225400	1.41299200

TS12

E = -609.784039889 a.u.

1 imaginary frequency -284.9056 cm⁻¹

С	0.91122600	0.05739700	-0.35037800
С	1.42905300	0.97890600	0.27628500
Ν	-0.63421800	2.67398400	-0.03988700
Ν	-1.05156800	1.81274400	-0.60739900
С	-1.14213700	0.61173800	-1.13667500
С	2.78245400	0.88614600	0.88453800
С	3.46401500	-0.32858800	0.23404100
С	2.55151000	-1.54313300	0.11255000
С	1.30122200	-1.29239400	-0.75883800
Н	3.38228500	1.78204000	0.74554100
Н	3.80274800	-0.04119300	-0.76112800
Н	4.35360000	-0.60037000	0.80016900
Н	3.10934900	-2.38260700	-0.29688100
Н	2.21878300	-1.83840300	1.10662300
Н	1.54274700	-1.32857400	-1.81960500
Н	0.54485600	-2.05074300	-0.57761100
Η	2.68735100	0.74904900	1.96065500
Н	-1.00600900	0.55689100	-2.20021300
С	-1.95406600	-0.37939700	-0.44884700
0	-2.15519500	-1.47534300	-0.89057600
0	-2.38572600	0.04665300	0.72610000
С	-3.11400500	-0.89954800	1.49108400
Η	-3.40063000	-0.38623000	2.39641700
Н	-3.99117400	-1.22884600	0.94791500
Н	-2.49167400	-1.75534900	1.72236800

MPWB1K/6-311G(d) computed total energies, single imaginary frequencies and Cartesian coordinates, in THF, of the stationary points involved in the 32CA reaction of 3-methoxy cyclohexyne **19** with Az **12**.

19 E = -347.742776185 a.u.

С	-0.02306500	-1.15540300	0.04336200
С	1.17195100	-1.32653300	-0.02915300
С	2.38574600	-0.54454400	-0.19350100
С	1.85517500	0.84289300	0.27461000
С	0.44023500	1.16764300	-0.18630300
С	-0.63580500	0.18789800	0.30373500
Η	3.22998700	-0.85699900	0.41136200
Η	1.89390100	0.86710000	1.36152100
Η	2.53556800	1.61182900	-0.08341600
Η	0.17164200	2.16782900	0.14686800
Η	0.39150500	1.16816300	-1.27341400
Η	2.70408300	-0.51964700	-1.23189500
0	-1.81392900	0.46676600	-0.36841200
С	-2.88074100	-0.31947000	0.07015600
Η	-3.74921900	-0.04997200	-0.51676600
Η	-2.66168000	-1.37837300	-0.07123900
Н	-3.09180800	-0.14581300	1.12595700
Н	-0.79352100	0.28684900	1.38087600

20

E = -551.962432830 a.u.

С	-1.00791200	0.30277400	0.01228100
С	0.15997000	-0.37888100	-0.17435700
Ν	-0.12534100	-1.69152700	-0.25951400
Ν	-1.39340300	-1.85008800	-0.12374800
Ν	-1.94209800	-0.65550500	0.03841900
С	1.49527000	0.27904000	-0.25958700
С	1.34428200	1.71412100	0.21027100
С	0.12182200	2.40468100	-0.36694800
С	-1.16887800	1.76628300	0.12927200
Η	1.27368000	1.68849600	1.29727400
Η	2.24908300	2.26112900	-0.03647300
Η	0.13396800	3.45868200	-0.10699200
Η	0.15120500	2.34938500	-1.45434600
Η	-1.35238500	2.04237200	1.16728000
Η	-2.02380200	2.11734700	-0.44384200
Η	1.84547200	0.26491700	-1.29678400
С	-3.36226300	-0.52185500	0.20969100
Η	-3.78981600	-1.51241300	0.15388100
Η	-3.58741300	-0.08330600	1.17457300
Η	-3.78021500	0.09726200	-0.57544300
0	2.46769700	-0.32038700	0.55157800
С	3.04159200	-1.47067200	-0.00318500
Η	3.48117400	-1.25372400	-0.97815100
Η	3.82679100	-1.79170500	0.67064100
Η	2.31327900	-2.26846200	-0.11496700

21

E = -551.961402464 a.u.

0.18841800	-0.25146900	-0.22295400
-0.52863600	-1.32633900	0.21278500
0.32900600	-2.33027000	0.46606600
1.52563000	-1.92551300	0.21264400
1.45943900	-0.67639600	-0.21260300
-2.00536100	-1.32831100	0.33485000
-2.54995500	-0.14334500	-0.45300400
-1.78931700	1.13787000	-0.14601400
-0.35395300	1.06702000	-0.64501700
-2.41996400	-2.26289400	-0.03235200
-2.47735400	-0.35856800	-1.51886000
-3.60454800	-0.00434400	-0.23490300
-2.27643600	1.99846800	-0.59519300
-1.78650000	1.29400500	0.93163900
-2.29763300	-1.24653400	1.38127500
2.65881300	0.04452200	-0.54549600
3.45612000	-0.67899500	-0.63740000
2.52524900	0.56949900	-1.48200900
2.90031100	0.75987900	0.23203700
0.45391500	2.14621000	-0.25376300
0.62236100	2.31072600	1.12734100
1.44847000	2.99785800	1.26158000
-0.26133700	2.73355400	1.59901500
0.86426700	1.36871700	1.62013900
-0.35471200	1.12088700	-1.73256200
	0.18841800 -0.52863600 0.32900600 1.52563000 1.45943900 -2.00536100 -2.54995500 -1.78931700 -0.35395300 -2.41996400 -2.47735400 -3.60454800 -2.27643600 -1.78650000 -2.29763300 2.65881300 3.45612000 2.52524900 2.90031100 0.45391500 0.62236100 1.44847000 -0.26133700 0.86426700 -0.35471200	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

MC21

E = -551.778429010 a.u.

С	-0.14359300	1.30392700	1.26479200
С	-0.69467300	0.23518500	1.13350200
Ν	1.33203900	-2.32220400	0.04564000
Ν	1.77066200	-1.34782700	-0.28254600
Ν	2.20199900	-0.29901800	-0.71767700
С	-1.67463100	-0.07814500	0.04561400
С	-1.30303800	0.93302700	-1.05056700
С	-1.06966400	2.35392000	-0.55745300
С	0.10183800	2.49017900	0.45481300
Н	-0.39826300	0.55618700	-1.52228600
Н	-2.09083800	0.93147600	-1.80080700
Н	-0.86554100	3.00003700	-1.40795500
Н	-1.97452900	2.72900900	-0.08425300
Η	1.06223600	2.43019500	-0.05100700
Н	0.05295200	3.43723500	0.98048500
Н	-2.68233500	0.10460600	0.42645000
С	3.16716900	0.36795800	0.15031800
Н	4.04498400	-0.25029700	0.31464200
Н	3.46886400	1.27677400	-0.34940600
Н	2.72353300	0.62044100	1.10978500
0	-1.60237400	-1.34948600	-0.49953000
С	-1.96474000	-2.34310600	0.41261800

Н	-2.99376700	-2.21333000	0.74856600
Н	-1.86836900	-3.29792500	-0.08776700
Н	-1.30483300	-2.32284300	1.28005500

MC22

E = -551.778841678 a.u.

С	-0.46091000	-0.19360900	-0.73447600
С	-0.79868200	-1.34826600	-0.61267300
Ν	2.50142700	-2.23245700	-0.29915600
Ν	2.64945300	-1.13042800	-0.17663800
Ν	2.86369700	0.06336200	-0.14497800
С	-1.82299600	-2.12231900	0.06845100
С	-2.87440200	-0.99778300	0.30387200
С	-2.28307900	0.35091300	0.69453100
С	-1.33266700	0.95910500	-0.34743500
Η	-2.25298300	-2.93624900	-0.50497700
Η	-3.45354600	-0.88478800	-0.61003800
Η	-3.56495200	-1.32542300	1.07734200
Η	-3.08802600	1.05841100	0.88186200
Η	-1.71881400	0.25625400	1.62042100
Η	-1.45479600	-2.52798600	1.00663800
С	2.48821300	0.73132600	1.09605000
Η	2.88592100	1.73486700	1.04489400
Η	1.40842200	0.78860400	1.19530500
Η	2.91009300	0.23052900	1.96317100
0	-0.68811100	2.04378400	0.22810000
С	0.16023900	2.69563700	-0.67125500
Η	0.63719200	3.50919300	-0.13976500
Η	0.92059200	2.00902800	-1.04597300
Η	-0.39776800	3.09694600	-1.51749400
Η	-1.88277900	1.28697200	-1.23317400

TS21

E = -551.770170530 a.u.

1 imaginary frequency -243.6323 cm⁻¹

0 52728400	0 52912000	0 01679600
0.52728400	0.52912000	0.010/9000
-0.33100300	-0.35771900	0.11945100
1.53249300	-2.38351700	-0.13605200
2.13982200	-1.44795200	-0.21704100
2.38909100	-0.25265100	-0.35033300
-1.75659600	0.07477900	0.28830400
-1.89444100	1.46874000	-0.31198000
-0.82536000	2.42686500	0.18809000
0.60921500	1.97524400	-0.15724400
-1.83076800	1.36592400	-1.39413100
-2.88272400	1.86224000	-0.08439300
-0.99509100	3.41947500	-0.22070000
-0.90556300	2.51452900	1.27029900
0.86991000	2.23015800	-1.18237000
1.32567300	2.46760600	0.49487500
-1.97002800	0.11105100	1.36216200
3.53506600	0.28480200	0.36386600
	0.52728400 - 0.33100300 1.53249300 2.13982200 2.38909100 - 1.75659600 - 1.89444100 - 0.82536000 0.60921500 - 1.83076800 - 2.88272400 - 0.99509100 - 0.90556300 0.86991000 1.32567300 - 1.97002800 3.53506600	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

Н	4.45824900	-0.14133800	-0.01234100
Н	3.54619200	1.34833800	0.17264900
Н	3.45825100	0.11277800	1.43309200
0	-2.70315300	-0.74699100	-0.32976200
С	-2.77587200	-2.01342100	0.24817500
Н	-3.08972700	-1.95333000	1.29234800
Н	-3.50775300	-2.58648800	-0.30793400
Н	-1.81099100	-2.51663100	0.20577500

TS22

E = -551.763844588 a.u. 1 imaginary frequency -328.6233 cm⁻¹

С	-0.14364400	-0.20526400	-0.32917700
С	-0.49423400	-1.37801100	-0.26440500
Ν	1.60332200	-2.46701500	-0.18145800
Ν	2.11265000	-1.45747100	-0.17968500
Ν	2.12638400	-0.23806000	-0.32073500
С	-1.79828000	-1.94862600	0.10892500
С	-2.77401000	-0.75595000	0.02224300
С	-2.19190500	0.55994300	0.52343300
С	-0.96175800	1.02115700	-0.26930300
Η	-2.12766800	-2.76083400	-0.53257300
Η	-3.07119900	-0.63293900	-1.01842400
Η	-3.68060600	-0.98488200	0.57850100
Η	-2.94630400	1.34216600	0.47397100
Η	-1.88856300	0.46815200	1.56493900
Η	-1.75311900	-2.34709400	1.12048000
С	2.74920700	0.51673600	0.75765400
Н	3.82597200	0.38279400	0.74790000
Η	2.52997300	1.55869500	0.58168900
Н	2.35358500	0.22901300	1.72683000
0	-0.38933700	2.12467500	0.36234600
С	0.36868700	2.89801200	-0.52206900
Η	0.86857800	3.66520900	0.05640100
Η	1.11380600	2.29360700	-1.03939800
Η	-0.26701300	3.37384600	-1.26901700
Η	-1.26361200	1.30470300	-1.28073900

MPWB1K/6-311G(d) computed total energies, single imaginary frequencies and Cartesian coordinates, in THF, of the stationary points involved in the 32CA reactions of but-2-yne **25** with Az **12** and Da **14**.

25 E = -155.914515582 a.u.

С	-0.59806500	-0.00002800	-0.00000700
С	0.59806600	-0.00004200	-0.00000700
С	2.04831800	0.00001600	0.00000400
Η	2.43992500	0.54956600	0.85085900
Η	2.44001000	-1.01158700	0.05047600
Η	2.43993600	0.46214700	-0.90132000
С	-2.04831700	0.00001400	0.00000400
Η	-2.44000500	-1.01256600	0.02399500
Η	-2.43993500	0.52711400	0.86494200
Н	-2.43994000	0.48556300	-0.88892000

26

E = -360.070523791 a.u.

С	-0.00509800	0.57728900	-0.00000400
С	-1.11523300	-0.22576300	-0.00001000
Ν	-0.70074700	-1.50714700	-0.00000700
Ν	0.58462200	-1.54025900	-0.00001400
Ν	1.01741700	-0.29326000	0.00000500
С	2.42469500	-0.00657600	0.00000800
Н	2.94783700	-0.95172000	0.00003400
Н	2.69679600	0.55785000	-0.88448200
Η	2.69678200	0.55789200	0.88447500
С	-2.54916000	0.14628700	0.00001000
Н	-2.81669500	0.73004000	0.87645100
Н	-2.81644100	0.73109900	-0.87579900
Η	-3.15448900	-0.75265300	-0.00061100
С	0.16528900	2.04405300	0.00000300
Η	-0.80333200	2.52935800	-0.00013900
Η	0.70864600	2.38553300	0.87728400
Н	0.70889700	2.38551500	-0.87713000

27

E = -532.532042506 a.u.

С	-1.02185900	0.67695100	-0.14388100
С	-1.86584100	-0.31043800	0.15619000
Ν	-1.39927300	-1.52847400	-0.40289500
Ν	-0.33307900	-1.36958400	-1.01053200
С	0.04965900	0.02583800	-0.94507700
С	-3.13182500	-0.32665400	0.91550500
С	-1.06861000	2.11658700	0.17918800
Н	-3.95425400	-0.65066500	0.28365100
Η	-1.17577300	2.71051400	-0.72530000

Η	-0.14799200	2.44054500	0.65670800
Н	-3.07050100	-1.02402800	1.74631100
Н	0.08614600	0.40915100	-1.96407300
С	1.41295800	0.25204000	-0.33930800
0	2.00316500	1.28380700	-0.45777900
0	1.83491200	-0.77324700	0.36269100
С	3.08807400	-0.59860700	1.00977400
Н	3.28445700	-1.52810200	1.52169400
Н	3.86082900	-0.39506100	0.27925600
Н	3.03366500	0.22120200	1.71533200
Н	-3.37256400	0.65315400	1.31005200
Н	-1.89749700	2.35090700	0.83671200

MC31

E = -359.949660236 a.u.

С	-1.35075200	0.99544100	-0.14873000
С	-1.82558200	-0.06950600	0.12069700
Ν	0.94336800	-2.00820100	-0.58760800
Ν	1.39869700	-1.00115100	-0.41524600
Ν	1.92108900	0.09175200	-0.34367000
С	1.97630900	0.67151200	0.99229300
Η	2.67366600	0.13040500	1.62607500
Η	2.32538400	1.68793900	0.88080100
Η	0.99671300	0.68176300	1.46141900
С	-2.41039100	-1.35690400	0.44236500
Η	-2.54521300	-1.46934600	1.51411900
Η	-3.38247800	-1.47248600	-0.02776800
Η	-1.77469900	-2.16714000	0.09898700
С	-0.77131500	2.28357100	-0.47808000
Η	-1.43484400	2.85956000	-1.11611200
Η	-0.58258300	2.86919600	0.41727300
Η	0.17236600	2.15862100	-1.00039300

MC32

E = -532.458382247 a.u.

С	2.81698000	-1.05363200	0.00063200
С	3.33310600	0.02640000	-0.00083500
Ν	-1.07617000	2.91950100	0.00287200
Ν	-0.80001000	1.84231500	0.00184700
С	-0.48125800	0.58304400	0.00062900
С	3.96855700	1.33033600	-0.00258800
С	2.18273500	-2.35834600	0.00242300
Н	3.68940500	1.90408900	0.87614600
Н	2.47084800	-2.93172800	-0.87375400
Н	1.10010800	-2.26642000	0.00131400
Н	5.05036800	1.23670900	-0.00624800
Н	0.56562100	0.34327100	0.00067600
С	-1.52337900	-0.40618200	-0.00062700
0	-1.32482500	-1.59198800	-0.00172200
0	-2.73747500	0.13614300	-0.00035300
С	-3.81657400	-0.78075000	-0.00151000
Н	-4.71338500	-0.17924200	-0.00105500

Н	-3.78241400	-1.40601300	-0.88552700
Н	-3.78274800	-1.40785200	0.88121600
Н	3.68352400	1.90460400	-0.87909500
Н	2.46932600	-2.92859500	0.88114000

TS31

E = -359.904634408 a.u.

1 imaginary frequency -521.7804 cm⁻¹

С	-0.44022600	0.99268500	-0.02824400
С	-1.38632400	0.21339100	0.02584900
Ν	-0.50450800	-1.71177200	-0.05226600
Ν	0.59654400	-1.38694300	-0.12050200
Ν	1.24904000	-0.34533000	-0.26164500
С	2.60033700	-0.25911400	0.23517600
Н	3.27349300	-0.89805600	-0.32870600
Н	2.91738500	0.76617600	0.09256900
Н	2.67028500	-0.50341800	1.29186600
С	-2.78377500	-0.20533000	0.12285600
Η	-2.93960000	-0.82152100	1.00292800
Н	-3.44892200	0.65095600	0.18160300
Н	-3.07011100	-0.80266500	-0.73721400
С	0.29821800	2.25078700	-0.06327600
Н	-0.38641500	3.09319900	-0.02246400
Η	0.98063500	2.33354200	0.77775700
Η	0.88634400	2.33558400	-0.97160500

TS32

E = -532.411989388 a.u.

1 imaginary frequency -564.2845 cm⁻¹

С	-1.28392100	0.96811400	0.12453500
С	-2.07676300	0.05697200	0.35702700
Ν	-1.26110100	-1.63935600	-0.74462400
Ν	-0.34713600	-1.12279400	-1.17662100
С	0.26777500	0.06181100	-1.16678100
С	-3.25449700	-0.60684700	0.90817700
С	-0.80457000	2.35138000	0.20563900
Η	-3.88257800	-1.00526900	0.11663300
Η	-0.79600400	2.81968200	-0.77464000
Η	0.20819500	2.40845600	0.59067500
Η	-2.96919400	-1.44504700	1.53732000
Η	0.21788800	0.60931700	-2.09239100
С	1.49728200	0.16984100	-0.38914600
0	2.18769900	1.15134000	-0.39794000
0	1.71737900	-0.88703200	0.37455100
С	2.84874200	-0.80192000	1.22454400
Η	2.89008400	-1.74230000	1.75315300
Η	3.74946900	-0.65563800	0.64103700
Η	2.73576700	0.01935600	1.92175300
Η	-3.85204400	0.07731500	1.50470300
Η	-1.44883400	2.93859900	0.85362400