Suplementary Material

Understanding the selectivity in the formation of δ-lactams *vs* β-lactams in the Staudinger reactions of chloro-cyan-ketene with unsaturated imines. An DFT study.

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*ELF topological analysis of the two competitive channels associated with the stepwise reaction between CCK **17** and UI **18** yielding lactams **β-24** and **δ-20**.*

Recent theoretical works have emphasised that the ELF topological analysis along a reaction path is a valuable tool to understand the bonding changes along the reaction path.[1-3] After an analysis of the electron density, the ELF provides basins, which are the domains in which the probability of finding an electron pair is maximal. The basins are classified as core basins and valence basins. The latter are characterised by the synaptic order, i.e. the number of atomic valence shells in which they participate.[4] Thus, there are monosynaptic, disynaptic, trisynaptic basins and so on. Monosynaptic basins, labelled V(A), correspond to lone pairs or non-bonding regions, while disynaptic basins, labelled V(A,B), connect the core of two nuclei A and B and, thus, correspond to a bonding region between A and B. This description recovers the Lewis bonding model, providing a very suggestive graphical representation of the molecular system.

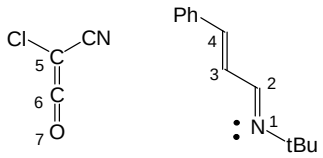
A great deal of work characterising the mechanisms of significant organic reactions involving the formation of new C-C single bonds have shown that it begins in the short C-C distance range of 1.9 - 2.0 Å by merging two monosynaptic basins, V(Cx) and V(Cy), into a new disynaptic basin V(Cx,Cy) associated with the formation of the new Cx-Cy single bond.[5] The Cx and Cy carbons characterised by the presence of the monosynaptic basins, V(Cx) and V(Cy), have been called *pseudoradical* centres.[6,7]

In the present section, an ELF topological analysis of the most relevant points associated with the formation of lactams **β-24** and **δ-20** has been performed in order to characterise the molecular mechanisms. This ELF analysis has been divided into three parts: i) analysis along the nucleophilic attack of UI **18** on CCK **17**; ii) analysis of the ring closure at **ZW-st-18** with formation of β-lactam **β-24**; and iii) analysis of the ring closure at **ZW-sc**-18 with formation of δ-lactam **δ-20**. The *N* populations of the most significant ELF valence basins at specific points along the IRC are displayed in Tables S1, S2 and S3. The attractor positions for the most relevant points associated with the formation of lactams **β-24** and **δ-20** are shown in Figures S1, S2 and S3.

*i) ELF topological analysis along the nucleophilic attack of UI **18** on CCK **17**.*

As commented above, the nucleophilic attack of UI **18** on CCK **17** does not present an activation enthalpy. In order to perform the ELF topological analysis along the N1-C6 bond formation, a relaxed PES calculation was performed taking the N1-C6 distance as the only variable, being modified from 2.6 Å to 1.5 Å (a N1-C6 distance corresponding to intermediate **ZW-st-18**).

Table S1. Valence basin populations *N* calculated from the ELF at some selected points of the relaxed PES scan along the nucleophilic attack of UI **18** on CCK **17**, and at **TS-36**, associated with the nucleophilic attack of UI **18** on DMK **26**. d(N1-C6) distance is given in Angstroms. The GEDT obtained by NBO analysis is given in e.



17 **18**

	P1	**P2**	**P3**	**P4**	**ZW-st-18**	**TS-26**
d(N1-C6)	2.620	2.220	2.020	1.920	1.489	2.056
GEDT	0.08	0.22	0.33	0.39	0.63	0.21
V(N1,C2)	1.51	1.57	1.53	1.73	3.77	1.69
V'(N1,C2)	1.48	1.52	1.53	1.53		1.44
V(C2,C3)	2.24	2.31	2.29	2.32	2.39	2.31
V(C3,C4)	1.72	1.69	1.64	1.64	1.64	1.68
V'(C3,C4)	1.66	1.68	1.66	1.66	1.56	1.65
V(C5,C6)	2.12	2.11	2.10	2.10	3.30	2.14
V'(C5,C6)	2.11	1.55	1.48	1.44		2.12
V(C6,O7)	1.59	2.96	2.78	2.62	2.20	2.50
V'(C6,O7)	1.46					
V(O7)	4.68	4.77	4.94	5.09	2.81	2.70
V'(O7)					2.77	2.52
V(N1)	2.75	2.46	2.39			2.47
V(C6)			0.13			
V(N1,C6)				2.41	1.96	
V(C5)		0.59	0.61	0.64	0.61	

At **P1**, d(N1-C6) = 2.620 Å, the ELF topological analysis is similar to that expected at the separated reagents. In this way, basins to be highlighted are those corresponding to the N-C and C-C double bonds in both UI **18** and CCK **17**. The UI framework presents two pairs of disynaptic basins, V(N1,C2) and V'(N1,C2), and V(C3,C4) and V'(C3,C4), integrating a total of 2.99e and 3.38e, respectively, which are

associated with the N1-C2 and C3-C4 double bonds. On the other hand, one V(N1) monosynaptic basin, integrating 2.75e, associated with the N1 lone pair can be also observed. The CCK framework presents two disynaptic basins, V(C5,C6) and V'(C5,C6), integrating a total of 4.23e, associated with the C5-C6 double bond; two disynaptic basins, V(C6,O7) and V'(C6,O7), integrating a total of 3.05e, associated with the C6-O7 double bond; and one monosynaptic basin, V(O7), integrating 4.68e, associated with the O7 lone pairs.

At **P2**, d(N1-C6) = 2.220 Å, the V(N1) monosynaptic basin has decreased its population to 2.46e, while the two V(C6,O7) and V'(C6,O7) disynaptic basins merge into the V(C6,O7) disynaptic basin, integrating 2.96e. Interestingly, a new V(C5) monosynaptic basin, integrating 0.59e, appears. This monosynaptic basin is kept all along this first step and along the greatest part of the channels associated with the ring closures. The electron density of the new V(C5) monosynaptic basin comes mainly from one of the two disynaptic basins of the C5-C6 bond region.

At **P3,** d(N1-C6) = 2.020 Å, one remarkable change takes place with the appearance of a V(C6) monosynaptic basin at the C6 carbon, integrating 0.13e, together with a slight depopulation of the V(N1) monosynaptic basin to 2.39e. This new V(C6) monosynaptic basin will participate in the subsequent N1-C6 bond formation. At this point the GEDT is 0.33e.

Interestingly, on going from the separated reagents to **P3**, the V(N1) monosynaptic basin experiences a depopulation parallel to the GEDT observed along the nucleophilic attack, while the population of the N1-C2-C3-C4 aza-dienic system remains almost unchanged. Consequently, the GEDT observed along the N1-C6 bond formation comes mainly from the N1 nitrogen lone pair. Note that in polar cycloaddition reactions involving nucleophilic dienes, the GEDT comes mainly from the depopulation of the diene system involved in the cycloaddition.

At **P4**, d(N1-C6) = 1.920 Å, the most relevant changes along the scan take place. Both V(N1) and V(C6) monosynaptic basins merge into a new V(N1,C6) disynaptic basin, which integrates 2.41e. At this point, the formation of the first N1-C6 bond has begun. From this structure to intermediate **ZW-st-18**, no more significant changes take place in the ELF topology; only basin population changes are observed. In this way, the electronic integration at both V(N1,C6) and V(C6,O7) disynaptic basins decreases by

0.49 and 0.35e, respectively, while that of the V(N1,C2) disynaptic basin increases by 0.56e.

At **ZW-st-18**, d(N1-C6) = 1.489 Å, the two pairs of disynaptic basins, V(N1,C2) and V'(N1,C2), and V(C5,C6) and V(C5,C6), merge into two disynaptic basins, V(N1,C2) and V(C5,C6), integrating 3.77 and 3.30e, respectively. On the other hand, while the V(N1,C6) and V(C6,O7) disynaptic basins are depopulated to 1.96 and 2.20e, respectively, the O2 lone pairs appear as two V(O7) and V'(O7) monosynaptic basins, integrating a total of 5.58e.

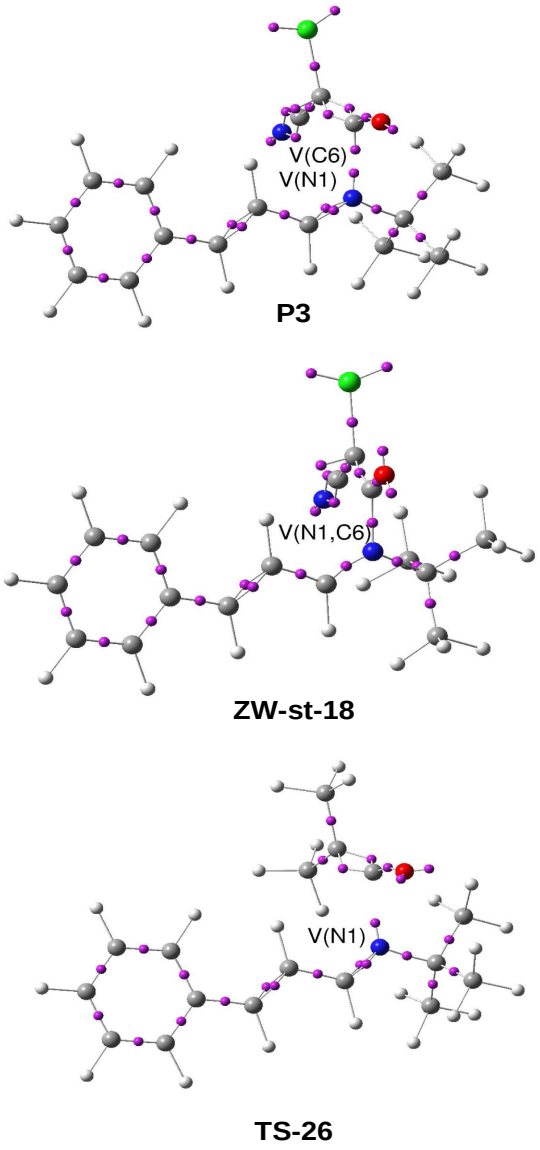


Figure S1. ELF attractor positions for the most relevant points associated with the N1-C7 single bond formation, **P3** and **ZW-st-18**, and those in **TS-26**.

Finally, the ELF valence basin populations of the TS associated with the nucleophilic attack of UI **18** on DMK **26**, **TS-26**, are given in Table S1 (see above). **TS-26** shows two pairs of disynaptic basins, V(N1,C2) and V'(N1,C2), and V(C3,C4) and V'(C3,C4), integrating a total of 3.13 and 3.33e, respectively, associated with the N1-C2 and C3-C4 double bond regions of UI **18**; one pair of disynaptic basins, V(C5,C6) and V'(C5,C6), integrating a total of 4.26e, associated with the C5-C6 double bond; and one V(C6,O7) disynaptic basin, integrating 2.50e, associated with the C6-O7 bonding region of DMK **26**. **TS-26** shows also one V(N1) monosynaptic basin, integrating 2.47e, associated with the N1 lone pair, and two V(O7) and V'(O7) monosynaptic basins, with a total population of 5.22e, associated with the O7 lone pairs. No V(N1,C6) disynaptic basin is found at this TS, indicating that the N1-C6 bond formation has not started yet. At **TS-26** the GEDT, 0.21e, is lower than that at **P3**, 0.33e, as a consequence of the lower electrophilic character of DMK **26** compared with CCK **17**.

Topologically, **TS-26** resembles **P3** of the attack of UI **18** on CCK **17**, with a similar N1-C6 distance (see Figure S1). The main ELF topologic differences are: i) the absence of the V(C5) monosynaptic basin present in **P3**, and ii) the presence of two V(O7) and V'(O7) monosynaptic basins in **TS-26** with a larger population than that at the V(O7) monosynaptic basin present in **P3**. These behaviours can be related to the presence of the cyano group and the chlorine atom in the C5 carbon of CCK **17**, that not only increases the electrophilicity of CCK **17**, but also polarises the ketene C5-C6-O7 system.

ii) ELF topological analysis of the ring closure at ***ZW-st-18*** *with formation of β-lactam* ***β-24***.

The *N* populations of the most significant ELF valence basins at specific points of the IRC associated with the ring closure at **ZW-st-18** with formation of β-lactam **β-24** are displayed in Table S2. In this cyclisation channel, the first change takes place at **P5**, d(C2-C5)=2.770 Å, consisting of the appearance of one V(N1) monosynaptic basin at the N1 nitrogen, with a population of 0.70e. This electron density comes directly from the V(N1,C2) disynaptic basin, which decreases its integration to 3.02e.

As the cyclisation proceeds, at **P6**, d(C2-C5)=2.582 Å, a second V'(N1) monosynaptic basin appears at N1 nitrogen, whose integration is 0.37e. It also comes from the depopulation of the V(N1,C2) disynaptic basin which still gathers 2.60e. This

new V'(N1) monosynaptic basin is located at the opposite position of the V(N1) monosynaptic basin. The populations of the V(N1) and V'(N1) monosynaptic basins increase along the ring closure at the expense of the populations of the V(N1,C2) and V(C5,C6) disynaptic basins to reach finally 1.07e and 0.87e at β-lactam **β-24**. At **P6**, the population of the V(C5) monosynaptic basin increases to 0.85e.

At **TS-2-18,** no relevant changes with respect to **P6** are observed. While the population of the V'(N1) monosynaptic basin increases to 0.79e, that in the V(C5) monosynaptic basin rises to 0.91e. At this TS, the population of the V(N1,C6) disynaptic basin created along the first step of the reaction remains at 2.09e, a basin population that corresponds to a N1-C6 single bond. ELF topology makes it possible to rule out an electrocyclic mechanism for these ring closure processes such has been proposed.[8,9] Note that the ELF population of the corresponding C-C bond in the TS associated with the ring aperture of cyclobutene, an electrocyclic reaction, is 3.17e.[2]

Table S2. Valence basin populations *N* calculated from the ELF at some selected points of the IRC associated with the ring closure at **ZW-st-18** with formation of β-lactam **β-24**. d(N1-C6) and d(C2-C5) distances are given in Angstroms. The GEDT obtained by NBO analysis is given in e.

	P5	**P6**	**TS-2-18**	**P7**	**P8**	**β-24**
d(N1-C6)	1.478	1.447	1.390	1.371	1.363	1.343
d(C2-C5)	2.770	2.582	2.275	2.103	2.009	1.563
GEDT	0.60	0.55	0.36	0.26	0.21	0.08
V(N1,C2)	3.02	2.60	2.08	1.96	1.88	1.69
V(C2,C3)	2.44	2.44	2.60	2.35	2.28	2.07
V(C3,C4)	1.65	3.24	3.29	1.78	1.75	1.79
V(C3,C4)	1.60			1.59	1.65	1.70
V(C5,C6)	3.18	2.91	2.49	2.33	2.30	2.13
V(C6,O7)	2.24	2.32	2.37	2.42	2.45	2.39
V(O7)	2.85	2.77	2.74	2.75	2.70	2.77
V(O7)	2.66	2.68	2.71	2.66	2.66	2.61
V(N1)	0.70	0.76	0.99	1.02	1.06	1.07
V'(N1)		0.37	0.79	0.93	1.04	0.87
V(N1,C6)	2.04	2.10	2.09	2.14	2.07	2.28
V(C5)	0.70	0.85	0.91	0.99		
V(C2)				0.27		
V(C2,C5)					1.38	1.91

At **P7**, d(C2-C5)=2.103 Å, a new V(C2) monosynaptic basin appears at the C2 carbon, with a population of 0.27e. This electron density comes from the V(C2,C3) disynaptic basin. The V(C2) and V(C5) monosynaptic basins are responsible for the

subsequent C2-C5 single bond formation (see Figure S2). Interestingly, the GEDT at **P7** has decreased to 0.26e as a consequence of a retrodonation process taking place along the ring closure.

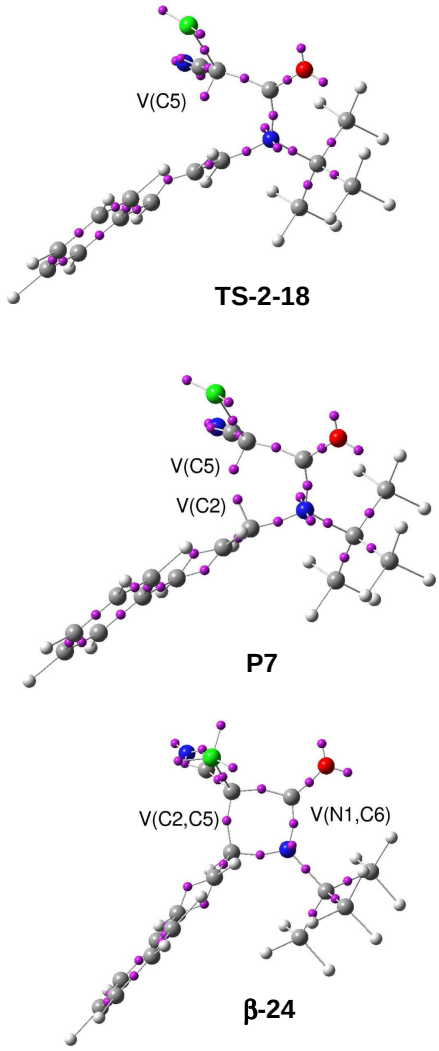


Figure S2. ELF attractor positions for the most relevant points associated with the C2-C5 single bond formation, **TS-2-18**, **P7** and **β-24**.

At **P8**, d(C2-C5)=2.009 Å, the most relevant change along this channel takes place. The V(C2) and V(C5) monosynaptic basins merge into the new V(C2,C5) disynaptic basin, with an initial population of 1.38e, indicating that the formation of the new C2-C5 single bond has already begun. From **P8**, d(C2-C5)=2.009 Å to the complete formation of β-lactam **β-24**, d(C2-C5) = 1.563 Å, scarce but interesting electron density changes take place. Among them, the integration of the V(C2,C5) and V(N1,C6) disynaptic basins increases until reaching 1.91 and 2.28e, at the expenses of the V(C5,C6) and V(N1,C2) disynaptic basins, i.e. the newly formed bonds gain

electron density right after their formation at the expense of the double bond regions yielding β-lactam **β-24**. Along this cyclisation reaction there is a decrease of the GEDT to reach a value of 0.08e at β-lactam **β-24** as a consequence of a retrodonation process.

*iii) ELF Topological analysis of the ring closure at **ZW-sc-18** with formation of δ-lactam **δ-20**.*

The *N* populations of the most significant ELF valence basins at specific points of the IRC associated with the ring closure at **ZW-sc-18** with formation of δ-lactam **δ-20** are displayed in Table S3. Considering the formation of δ-lactam **δ-20** through the C4-C5 single bond formation at **ZW-sc-18**, one can state a clear parallelism between this channel and that associated with the formation of β-lactam **β-24** from **ZW-st-18** with some exceptions. The ELF topology of **ZW-sc-18** is very similar to that of **ZW-st-18** (see Tables S1 and S2). At **P9**, d(C4-C5) = 2.421 Å, two appealing changes take place. Two monosynaptic basins at the N1 nitrogen atom, V(N1) and V'(N1), integrating 0.78 and 0.70e, are formed. Again, these monosynaptic basins are formed at the expense of V(N1,C2) and V(C5,C6) disynaptic basins. At this point, a new V(C3) monosynaptic basin is also created at the C3 carbon, with a initial population of 0.31e, while the population of the V(C5) monosynaptic basin created at the first step of the reaction has increased to 0.72e.

At **TS-4-18**, d(C4-C5) = 2.317 Å, while the V(C3) monosynaptic basin created at **P9** disappears, the population of the V(C2,C3) disynaptic basin increases to 3.28e. **TS-4-18** topologically resembles **TS-2-18**. The population of the V(N1,C6) disynaptic basin at these TSs, 1.88e (**TS-4-18**) and 2.09e (**TS-2-18**), makes it possible to rule out an electrocyclic mechanism for these ring closure processes.

In addition, a recent ELF topological analysis for the electrocyclic ring closure of octa-1,3,5,7-tetraene to cycloocta-1,3,5-triene showed that the C-C bond formation takes place without any rotation of the terminal sp^2 hybridised methylenes of octa-1,3,5,7-tetraene since the spiral geometry of this compound favours the position of a terminal sp^2 carbon above the plain of the other terminal sp^2 carbon.[10] This behaviour, which is similar to that found **ZW-sc-18**, allows establishing that the stereochemistry in δ-lactam **δ-20** is not determined by any rotation.

At **P10**, d(C4-C5) = 2.159 Å, a new V(C4) monosynaptic basin at the C4 carbon, integrating 0.08e, appears, while the V(C5) monosynaptic basin reaches a population of

0.99e. The V(C4) and V(C5) monosynaptic basins are responsible for the subsequent C4-C5 single bond formation (see Figure S3). Interestingly, just as at **P7**, the GEDT at **P10** decreases to 0.24e as a consequence of a retrodonation process that takes place along the ring closure.

At **P11**, d(C4-C5) = 1.941 Å, the most relevant changes along this channel take place. The two V(C4) and V(C5) monosynaptic basins merge into the new V(C4,C5) disynaptic basin, with an initial population of 1.45e, indicating that the formation of C4-C5 single bond has already begun. On the other hand, the V(C2,C3) disynaptic basin splits into two V(C2,C3) and V'(C2,C3) disynaptic basins, integrating 1.89 and 1.73e, respectively, a fact that evidences the formation of the C2-C3 double bond present in δ-lactam **δ-20**.

Table S3. Valence basin populations *N* calculated from the ELF at some selected points of the IRC associated with the ring closure at **ZW-sc-18** with formation of δ-lactam **δ-20**. d(N1-C6) and d(C4-C5) distances are given in Angstroms. The GEDT obtained by NBO analysis is given in e.

	ZW-sc-18	**P9**	**TS-4-18**	**P10**	**P11**	**δ-20**
d(N1-C6)	1.489	1.463	1.452	1.433	1.411	1.358
d(C4-C5)	3.045	2.421	2.317	2.159	1.941	1.537
GEDT	0.63	0.47	0.39	0.24	0.09	0.05
V(N1,C2)	3.77	2.48	2.24	2.01	1.91	1.92
V(C2,C3)	2.39	2.79	3.28	3.49	1.89	1.83
V'(C2,C3)					1.73	
V(C3,C4)	1.64	2.63	2.51	2.29	2.12	2.00
V'C3,C4)	1.56					
V(C5,C6)	3.89	2.97	2.80	2.56	2.31	2.09
V(C6,O7)	2.20	2.33	2.37	2.37	1.27	2.39
V'C6,O7)					1.24	
V(O7)	2.81	2.69	2.69	2.69	2.65	2.68
V'O7)	2.77	2.69	2.64	2.64	2.59	2.64
V(N1)		0.78	0.93	1.07	1.16	1.02
V'(N1)		0.70	0.88	1.04	1.12	0.81
V(N1,C6)	1.96	1.90	1.88	1.90	1.90	2.25
V(C3)		0.31				
V(C5)	0.61	0.72	0.82	0.99		
V(C4)				0.08		
V(C4,C5)					1.45	1.92

From **P11** to the complete formation of δ-lactam **δ-20**, d(C4-C5) = 1.537 Å, the same electron population changes than those found from **P8** to β-lactam **β-24** are observed: the V(N1,C6) and V(C4,C5) disynaptic basins associated with the new single

bonds increase their population at the expenses of the C3-C4 and C5-C6 bonding regions. In this particular case, the V'(N1) monosynaptic basin also loses some electron density in favour of these basins associated with the new bonds. Along the cyclisation reaction there is a decrease of the GEDT until reaching a value of 0.05e at δ-lactam **δ-20** as a consequence of a retrodonation process.

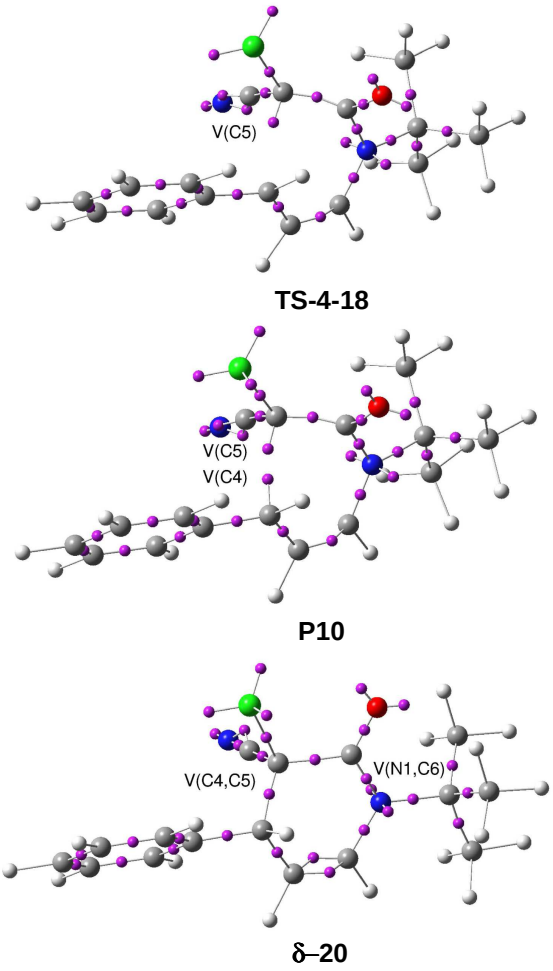


Figure S3. ELF attractor positions for the most relevant points associated with the C4-C5 single bond formation, **TS-4-18**, **P10** and **δ-20**.

From the ELF topological analysis of the two competitive channels associated with the stepwise reactions between UI **18** and CCK **17**, yielding lactams **β-24** and **δ-20**, some interesting conclusions can be drawn: i) along the nucleophilic attack of UI **18** on CCK **17**, the formation of N1-C6 single bond begins at a N1-C6 distance of 1.92 Å, by merging the electron density of two monosynaptic basins located at the N1 and the C6 atoms. The electron density of the new N1-C6 single bond comes mainly from the N1 lone pair present at UI **18**; ii) at this N1-C6 distance, while the formation of the N1-C6 single bond has already begun, the electronic structure of the double bond regions

remain similar to those in the two separated reagents; only the region of the carbonyl C6-O7 double bond is depopulated in order to facilitate the formation of the new N1-C6 single bond; iii) this depopulation of the carbonyl C6-O7 double bond is accompanied by an increase of the electron density of the O7 lone pairs; iv) a large GEDT takes place along the nucleophilic attack of UI **18** on CCK **17**. A significant portion of the electron density transferred to CCK **17** is placed at the V(C5) monosynaptic basin created at the C5 carbon of the ketene framework as a consequence of the polarisation of the disubstituted CCK **17**. The electron density gathered in this V(C5) monosynaptic basin will participate in the subsequent C2-C5 or C4-C5 bond formation in the second step of these competitive reactions; v) at **TS-24,** associated to the nucleophilic attack of UI **18** on DMK **24**, with a N1-C6 distance of 2.056 Å, no significant feature is observed; the N1-C6 bond formation has not started yet; vi) the two competitive cyclisation processes are topologically very similar; vii) both **TS-2-18** and **TS-4-18** present only one V(C5) monosynaptic basin associated with the *pseudoradical* center involved in the subsequent C-C single bond formation; vii) formation of the C2-C5 or C4-C5 single bonds take place at a C-C distance of 2.009 and 1.941 Å, respectively, by merging the electron density of the corresponding two *pseudoradical* centers,[5] with an initial population of 1.38 and 1.45e; ix) the main difference along the two competitive channels is found in the formation of the C3-C4 or C2-C3 double bonds; x) along the cyclisation steps there is a decrease of the GEDT as a consequence of a retrodonation process. Interestingly, a great deal of this retrodonation takes place before formation of the new C-C singe bonds; and xi) the population of the V(N1,C6) disynaptic basin at **TS-4-18** and **TS-2-18**, 2.09 and 1.90e, respectively, which correspond to a single N-C bond, makes it possible to rule out an electrocyclic mechanism along these ring closure processes.[8,9]

Conclusions

An ELF topological analysis along the reaction channels associated with the formation β- and δ-lactams provides interesting conclusions about the molecular mechanisms of these reactions:

i) along the nucleophilic attack of these UIs on the ketene, formation of the N-C single bond begins at a distance of 1.92 Å, by merging the electron density of two

monosynaptic basins located at the N and the C atoms. The electron density of the new N-C single bond comes mainly from the nitrogen lone pair present in UIs;

ii) along this nucleophilic attack, the C-C and C-N double bonds remain unchanged; only the C-O double bond of ketene is depopulated, thus favouring the N-C bond formation;

iii) a large GEDT takes place along the formation of the N-C single bond. A significant portion of the electron density transferred to ketene is placed at the V(C5) monosynaptic basin created at the C5 carbon of the ketene framework as a consequence of the polarisation of the disubstituted electrophilic ketene;

iv) the electron density gathered in this V(C5) monosynaptic basin will participate in the further C2-C5 or C4-C5 bond formation in the second step of these competitive reactions;

v) the two competitive cyclisation processes are topologically very similar;

vi) both TSs present only one V(C5) monosynaptic basin associated with the *pseudoradical* center involved in the subsequent C-C single bond formation. This monosynaptic basin was created in the first step of the reaction;

vii) formation of the C2-C5 or C4-C5 single bonds take place at a C-C distance of 2.009 and 1.941 Å, respectively, with an initial population of 1.38 and 1.45e;

viii) the population of the V(N1,C6) disynaptic basin at the TSs associated with the ring closure processes corresponds to that of a N-C single bond. This behaviour makes it possible to rule out an electrocyclic mechanism along these ring closure processes.

ix) finally, due to the favourable disposition of the double bond in ZW intermediates no specific bond rotation is required along the subsequent C-C single bond formation.

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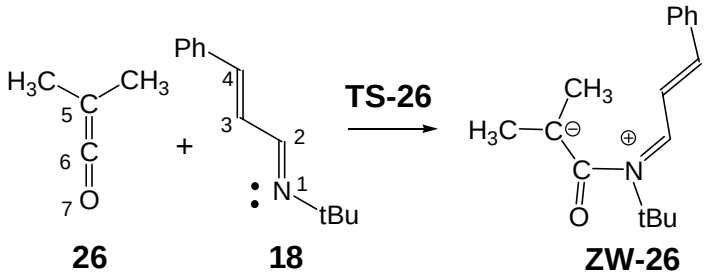
*Study of nucleophilic attack of UI **18** on DMK **26**.*

Given that the nucleophilic attack of UIs **18** and **19** on the C6 carbon of CCK **17** did not present an activation enthalpy as a consequence of the strong electrophilic character of CCK **17**, the nucleophilic attack of UI **18** on dimethylketene (DMK) **26** was studied in order to perform an ELF topological analysis of the TSs involved in the formation of the N1-C6 single bond in Staudinger reactions (see Scheme S1). Analysis of the reaction path associated with this nucleophilic attack allowed the localisation of one TS, **TS-26**, and the corresponding ZW intermediate, **ZW-26**. Relative enthalpies, entropies and free energies are given in Table S4.



Scheme S1. Reaction channel associated with the nucleophilic attack of UI **18** on DMK **26**.

Table S4. MPWB1K/6-311G(d,p) total enthalpies (H, in au), entropies (S, in cal/mol K) and free energies (G, in au), and relative[a] enthalpies (ΔH, in kcal/mol), entropies (ΔS, in cal/mol K) and free energies (ΔG, in kcal/mol), computed at 25.0 ºC and 1 atm in DEE of the stationary structures involved in the nucleophilic attack of UI **18** on the C6 carbon of DMK **26**.

	H	ΔH	S	ΔS	G	ΔG
26	-231.066262		75.7		-231.102209	
TS-26	-790.945480	5.9	152.5	-36.5	-791.017927	16.8
ZW-26	-790.954698	0.1	145.9	-43.1	-791.024017	13.0

(a) Relative to **18** + **26**.

The activation enthalpy associated with the nucleophilic attack of the N1 nitrogen atom of UI **18** on the C6 carbon of DMK **26** is very low, 5.9 kcal/mol, formation of **ZW-26** being slightly endergonic by only 0.1 kcal/mol. When comparing the reaction enthalpy associated with the formation of **ZW-26**, with that associated with formation of **ZW-st-18**, ΔΔH = 25.5 kcal/mol, the barrierless character of the nucleophilic attack of UI **18** on CCK **17** can be easily understood as a consequence of the high electrophilic character of CCK **17**, ω = 2.20 eV, when compared to that of DMK **26**, ω = 0.66 eV.

Note that while CCK **17**, is classified as a strong electrophile within the electrophilicity scale, DMK **26** is classified as a moderate electrophile. Inclusion of entropy to enthalpy rises the activation free energy associated with the nucleophilic attack of UI **18** on DMK **26** to 16.8 kcal/mol, the formation of **ZW-26** being endergonic by 13.0 kcal/mol.

The structure of **TS-26** and **ZW-26** associated with the nucleophilic attack of UI **18** on DMK **26** are given in Figure S4. At **TS-26**, the distance between the N1 and C6 carbon atoms is 2.031 Å, while the C2-N1-C6-C5 dihedral angle is -87.0 degrees. At **ZW-26**, the length of the new N1-C6 single bond is 1.491 Å, while the C2-N1-C6-C5 dihedral angle is -66.8 degrees. Note that this dihedral angle in **ZW-26** is lower than those at the other three out of the four ZW intermediates as a consequence of the high steric repulsion between the *endo* methyl group of DMK **26** and the bulky *t*-butyl substituent present at N1 nitrogen of UI **18** in **ZW-26**.

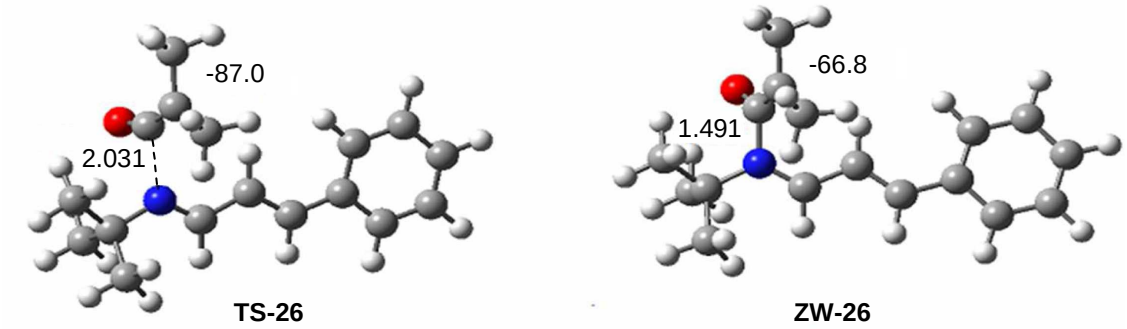
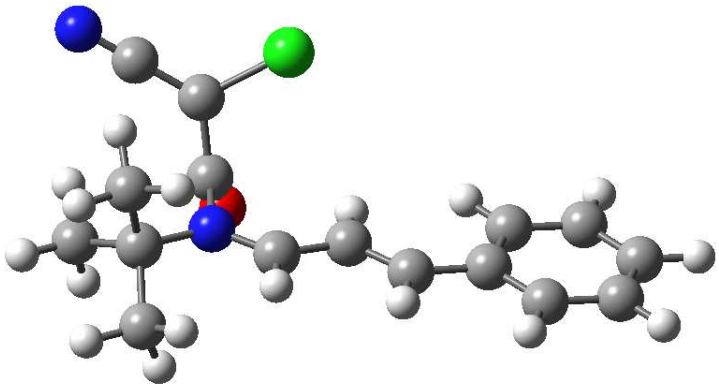


Figure S4. Structures of **TS-26** and the corresponding **ZW-26** associated with the nucleophilic attack of UI **18** on DMK **26**. The distances are given in Angstroms, while the dihedral angles are given in degrees.

Finally, the polar nature of these reactions was analysed by computing the global electron density transfer (GEDT) at **TS-26** and at the ZW intermediate **ZW-26**. The natural atomic charges at these species, obtained through a natural population analysis (NPA), were shared between the ketene and the UI frameworks. The values of the GEDT that fluxes from the UI framework to the ketene are 0.21e (**TS-26**), 0.49e (**ZW-26**). The high GEDT found at **ZW-26** points to the high zwitterionic character of this intermediate. The lower GEDT found at **ZW-26** than at **ZW-st-18**, which is a consequence of the lower electrophilic character of DMK **26** than CCK **17**, accounts for the lower exothermic character associated with the formation of the ZW intermediate **ZW-26**.



TS-rot2-18

Figure S5. TS-rot2-18 involved in the *endo*/*exo* stereoisomeric conversion in the zwitterionic intermediate **ZW-st-18**. The Cl-C5-C6-N1 dihedral angle is 87.9 degrees.

Table S5. MPWB1K/6-311G(d,p) enthalpies (H, in au), entropies (S, in cal/mol K) and free energies (G, in au), computed at 25.0 ºC and 1 atm in DEE, of the stationary structures involved in the reactions of CCK **17** with UIs **18** and **19**.

	H	S	G
CCK **17**	-704.411282	76.8	-704.447795
s-trans **18**	-559.888626	113.4	-559.942490
s-cis **18**	-559.883610	122.1	-559.941612
ZW-st-18	-1264.340644	149.4	-1264.411626
TS-rot-18	-1264.323763	148.3	-1264.394226
ZW-sc-18	-1264.332690	148.2	-1264.403084
TS-2-18	-1264.306914	146.3	-1264.376436
TS-4-18	-1264.318096	141.2	-1264.385190
β-24	-1264.364555	148.8	-1264.435241
δ-20	-1264.379532	139.1	-1264.445627
s-trans **19**	-790.788579	141.9	-790.856007
s-cis **19**	-790.780010	141.0	-790.846987
ZW-st-19	-1495.245502	168.5	-1495.325572
TS-rot-19	-1495.227406	160.5	-1495.305460
ZW-st-19	-1495.232789	161.0	-1495.309271
TS-2-19	-1495.215186	163.1	-1495.292684
TS-4-19	-1495.213664	158.8	-1495.289122
β-21	-1495.267510	169.6	-1495.348072
δ-25	-1495.272130	157.2	-1495.346843

Table S6. MPWB1K/6-31G(d) electronic chemical potential μ, chemical hardness η, global electrophilicity ω, and global nucleophilicity *N* indices, in eV, of ketenes **17** and **26**, and UIs **18** and **19**.

	μ	η	ω	*N*
CCK **17**	-5.25	6.27	2.20	2.01
DMK **26**	-3.13	7.38	0.66	3.58
s-trans **18**	-3.70	6.18	1.11	3.61
s-trans **19**	-3.64	6.05	1.09	3.74

MPWB1K/6-311G(d,p) computed total energies, unique imaginary frequency, and cartesian coordinates of the optimised structures in DEE of the reactions of CCK **17** with UIs **18** and **19**.

CCK **17**
E(RmPW+HF-B95) = -704.442297 au

C	1.31825100	-0.02100000	0.00000000
C	0.00000000	0.06761200	0.00000000
O	2.45008800	-0.11180900	0.00000000
Cl	-0.91961400	-1.39075900	0.00000000
C	-0.62918200	1.31843900	0.00000000
N	-1.15738400	2.33529400	0.00000000

s-trans **18**
E(RmPW+HF-B95) = -560.176215 au

N	2.36388800	-0.52678100	0.00009900
C	1.39891400	0.28543300	-0.00005200
H	1.52827400	1.36767300	-0.00024000
C	3.74103000	-0.06389600	0.00004000
C	0.03240900	-0.19322900	0.00001800
C	-1.01501100	0.62997200	-0.00011000
H	-0.08212400	-1.26609100	0.00018600
H	-0.82411500	1.69552600	-0.00026000
C	4.38721100	-0.66182600	-1.24098300
H	5.45163100	-0.44279400	-1.25822800
H	4.25117200	-1.73880100	-1.25024300
H	3.93609200	-0.25298900	-2.14114000
C	4.38711400	-0.66122700	1.24140300
H	4.25106200	-1.73819500	1.25117900
H	5.45153500	-0.44219800	1.25861700
H	3.93593400	-0.25194300	2.14132600
C	3.92755300	1.44223100	-0.00031500
H	3.48805900	1.90093700	-0.88297100
H	3.48803300	1.90136200	0.88210600
H	4.98845300	1.67412600	-0.00035200
C	-2.42112200	0.25183500	-0.00006100
C	-3.38961700	1.24929600	-0.00009200
C	-2.84190000	-1.07529000	0.00001100
C	-4.73429100	0.93620400	-0.00004700
H	-3.07833300	2.28237900	-0.00015100
C	-4.18243700	-1.38843000	0.00005500
H	-2.11673300	-1.87180900	0.00002500
C	-5.13568200	-0.38450500	0.00002700
H	-5.46806800	1.72548400	-0.00007100
H	-4.48891000	-2.42164400	0.00010700
H	-6.18420200	-0.63296400	0.00006000

s-cis **18**
E(RmPW+HF-B95) = -560.172237 au

N	2.07962200	0.12587200	0.01977500
C	1.47271400	-0.97630100	-0.03691100
H	1.99676600	-1.92848000	-0.09412100
C	3.53019400	0.19546000	0.00764100
C	0.01363500	-1.06814200	-0.03231000
C	-0.77765600	0.00186100	-0.00149600
H	-0.39633200	-2.06597100	-0.06197400
H	-0.28800800	0.96559000	0.01849100
C	3.93330400	0.90012000	1.29447800
H	5.00529500	1.07910500	1.30966600
H	3.41879100	1.85250300	1.37641000
H	3.67260600	0.29520100	2.15879300
C	3.90237100	1.06824200	-1.18186800
H	3.39245600	2.02455000	-1.11814400
H	4.97478300	1.24396500	-1.20315900
H	3.61316100	0.58839100	-2.11301100
C	4.25104300	-1.13671500	-0.09158800
H	4.02331200	-1.78129700	0.75407000
H	3.99546800	-1.66507400	-1.00709700
H	5.32329300	-0.96494000	-0.09669300
C	-2.23144300	0.03346400	0.00299500
C	-2.86199100	1.27266200	-0.01458700
C	-3.02663900	-1.10999200	0.02425900
C	-4.23804100	1.37380400	-0.01493600
H	-2.25687900	2.16558400	-0.02930100
C	-4.39993800	-1.01035400	0.02450700
H	-2.56828400	-2.08513500	0.04397800
C	-5.01274100	0.23124900	0.00424800
H	-4.70510500	2.34485300	-0.02969600
H	-4.99964900	-1.90577300	0.04190900
H	-6.08788700	0.30368800	0.00486000

ZW-st-18
E(RmPW+HF-B95) = -1264.664596 au

C	-1.62211700	1.58463000	0.28157100
C	-1.81099000	0.65153200	-0.71621100
O	-2.09215600	0.78160000	-1.88676800
N	-1.65193300	-0.74056100	-0.21345400
C	-0.47434400	-1.21515000	-0.01463400
H	-0.40885900	-2.23864700	0.32011600
Cl	-1.79150500	3.25979900	-0.12257300
C	-1.37073300	1.26006500	1.61129900
N	-1.16569300	0.98173600	2.71033300

C	-2.89590700	-1.56211900	-0.10367800
C	0.74179500	-0.51071200	-0.19875900
C	1.89437000	-1.13115100	0.10467600
H	0.70934800	0.49718000	-0.57341300
H	1.83657300	-2.14221900	0.48523500
C	-3.21161800	-2.11489400	-1.48282300
H	-4.11960800	-2.70807000	-1.42754900
H	-3.35352300	-1.30776200	-2.19084900
H	-2.40472500	-2.75206300	-1.83391300
C	-4.01175400	-0.65346000	0.37664400
H	-4.20047300	0.14796500	-0.32990900
H	-4.91785200	-1.24284900	0.46755100
H	-3.77921300	-0.22375400	1.34621400
C	-2.69230900	-2.68506700	0.89338700
H	-2.01565300	-3.45284600	0.53052200
H	-2.33355100	-2.30687200	1.84662300
H	-3.65177100	-3.16293000	1.05878700
C	3.22793200	-0.59392200	-0.01280500
C	4.30039600	-1.40254500	0.35331800
C	3.48245700	0.69667300	-0.47411000
C	5.59478600	-0.93873100	0.26155300
H	4.10854000	-2.40106800	0.71285300
C	4.77459200	1.15703300	-0.56571300
H	2.66938600	1.34333900	-0.75812700
C	5.83270600	0.34149700	-0.19867700
H	6.41613500	-1.57342900	0.54869100
H	4.96276100	2.15581500	-0.92202300
H	6.84314300	0.70853000	-0.27132600

TS-rot-18

E(RmPW+HF-B95) = -1264.645947 au

1 imaginary frequency: -119.2501 cm^{-1}

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.37745383
O	0.89607969	0.00000000	2.18641913
N	-1.39802167	-0.03070017	1.93696310
C	-2.09446750	1.02949796	1.90980541
H	-3.08921127	0.98068268	2.33024537
Cl	1.52381325	0.02657860	-0.81543051
C	-1.15585322	-0.02502852	-0.77182570
N	-2.12787963	-0.03081975	-1.39107379
C	-1.83744921	-1.30529082	2.59293562
C	-1.65834792	2.27425920	1.28357937
C	-0.98706483	3.20799401	1.94453989
H	-2.02072339	2.40861917	0.27379415
H	-0.68898747	3.00514386	2.96347824
C	-1.22757258	-1.34531580	3.98309169
H	-1.53421094	-2.26741941	4.46723950

H	-0.14698668	-1.31122177	3.93196341
H	-1.57917618	-0.50983045	4.58148151
C	-1.32113234	-2.45110673	1.74360631
H	-0.23712103	-2.45411934	1.70154260
H	-1.64444242	-3.38272340	2.19543897
H	-1.71451026	-2.40143879	0.73283654
C	-3.34854145	-1.35744323	2.67038607
H	-3.75761876	-0.63902033	3.37447205
H	-3.80434535	-1.21138309	1.69506272
H	-3.62681862	-2.34283673	3.02749472
C	-0.57954102	4.50848947	1.42717493
C	0.11507634	5.36592455	2.27004980
C	-0.85290188	4.92623736	0.12894835
C	0.52608970	6.60909258	1.83321824
H	0.33666533	5.04981158	3.27726439
C	-0.44312713	6.16605433	-0.30693430
H	-1.38388102	4.28060403	-0.55100936
C	0.24737264	7.01261674	0.54308993
H	1.06568604	7.26038881	2.50064138
H	-0.65991593	6.47483712	-1.31618217
H	0.56767862	7.98153069	0.19724139

TS-rot2-18

E(RmPW+HF-B95) = -1264.60884852 au

1 imaginary frequency: -129.1732 cm^{-1}

C	-2.15623600	-1.61021200	0.06694000
C	-1.66941600	-0.56264000	0.93876500
O	-1.27088100	-0.62384300	2.05144600
N	-1.50486000	0.77373100	0.27403000
C	-0.32348400	1.15149400	-0.07578700
H	-0.26095000	2.07054300	-0.63769200
Cl	-0.85562700	-2.43302600	-0.76831600
C	-3.44839100	-1.84004100	-0.29482800
N	-4.55459900	-2.02758000	-0.59781500
C	-2.72239000	1.59181700	-0.03618700
C	0.89330400	0.47625700	0.19334300
C	2.03733200	1.00442600	-0.27510800
H	0.88127500	-0.43449700	0.76514800
H	1.97232500	1.92831200	-0.83431000
C	-2.37433800	3.06452700	0.09532400
H	-3.29915300	3.63003800	0.05526400
H	-1.88858500	3.27351200	1.04371600
H	-1.74983800	3.42420000	-0.71637000
C	-3.77606200	1.24345000	0.99764500
H	-3.41973000	1.45112100	2.00220400
H	-4.65533500	1.85091300	0.81291300
H	-4.08693500	0.20560600	0.93426700
C	-3.19604000	1.29187300	-1.44655300
H	-2.39603000	1.46657500	-2.16081300

H	-3.54820200	0.27267000	-1.54748500
H	-4.01593400	1.96200900	-1.68784400
C	3.36900300	0.47225100	-0.12111100
C	4.43147500	1.18363400	-0.67230000
C	3.63326700	-0.72253100	0.54717500
C	5.72383600	0.71923500	-0.55965800
H	4.23336300	2.10702800	-1.19311300
C	4.92345700	-1.18451400	0.65764400
H	2.82863600	-1.29450200	0.97790000
C	5.97125700	-0.46576700	0.10549800
H	6.53671300	1.27903200	-0.99072300
H	5.11774800	-2.10952200	1.17403900
H	6.98012100	-0.83346100	0.19439100

ZW-sc-18
E(RmPW+HF-B95) = -1264.656799 au

C	-1.09579600	1.52875500	0.36770300
C	-1.27302100	0.61386300	-0.64303400
O	-1.12874900	0.70883100	-1.84591200
N	-1.70233400	-0.70925700	-0.12377800
C	-0.84607000	-1.55196400	0.33233000
H	-1.26257700	-2.48116500	0.68931300
Cl	-0.55061600	3.11740200	-0.04544600
C	-1.36486300	1.24986400	1.70458600
N	-1.60251600	0.99722600	2.80297700
C	-3.14479500	-1.07294500	-0.31333900
C	0.56832700	-1.42843900	0.45773700
C	1.36452100	-0.60799300	-0.25115600
H	0.99867900	-2.14098100	1.14091100
H	0.92945700	0.02689600	-1.00837700
C	-3.25549100	-1.76544300	-1.66000200
H	-4.29243700	-2.02920400	-1.84494500
H	-2.90925500	-1.10882500	-2.45033500
H	-2.66128200	-2.67535900	-1.67381500
C	-3.96880600	0.19981700	-0.30212200
H	-3.66995900	0.87705700	-1.09518900
H	-5.00627000	-0.07204400	-0.46507500
H	-3.89403300	0.71125300	0.65212500
C	-3.60579700	-1.97487500	0.81541300
H	-3.19253900	-2.97699900	0.75682700
H	-3.36547400	-1.53893600	1.78116800
H	-4.68362300	-2.07490500	0.74635200
C	2.80286300	-0.52698900	-0.14364100
C	3.47829200	0.30001100	-1.03691900
C	3.53770500	-1.22703200	0.81260200
C	4.85067900	0.41917000	-0.98641500
H	2.91319700	0.85062400	-1.77191600
C	4.90584300	-1.10577200	0.86260400
H	3.04005300	-1.86135900	1.52666800

C	5.56575400	-0.28494400	-0.03762400
H	5.36089400	1.06204500	-1.68373400
H	5.46507900	-1.64782000	1.60667300
H	6.63844400	-0.19303600	0.00651200

TS-2-18

E(RmPW+HF-B95) = -1264.628549 au

1 imaginary frequency: -150.7812 cm^{-1}

C	1.69443200	-0.59640200	0.72262900
C	0.58453400	-0.33797700	0.01224600
C	-0.69773900	-0.53067300	0.59025400
N	-1.86322000	-0.54641100	-0.11088300
C	-2.82920400	-1.65940500	-0.19318200
C	-2.60930200	-2.36289100	-1.52181900
C	-1.98694300	0.67737100	-0.75601200
O	-2.43493500	0.89046800	-1.84971300
C	-1.38212100	1.59419200	0.19506000
C	-1.86903400	1.65963100	1.51322100
N	-2.24899800	1.73698300	2.59561900
Cl	-0.69508500	3.05237800	-0.40595500
C	-4.22985200	-1.08457300	-0.11123500
C	-2.58650100	-2.60799300	0.96101100
H	-0.71649400	-0.97530600	1.57751400
H	0.62457400	0.01237400	-1.00767600
H	1.56609200	-0.94674600	1.73796000
H	-4.41633500	-0.39815500	-0.92992400
H	-4.37493400	-0.56046900	0.82902200
H	-4.95314400	-1.89138900	-0.17123800
H	-1.59595900	-3.05376800	0.91901800
H	-3.31226400	-3.41199900	0.90189400
H	-2.71375900	-2.11116900	1.91893700
H	-3.31988900	-3.17796800	-1.62631200
H	-1.60451300	-2.77238300	-1.57746000
H	-2.75016100	-1.66625500	-2.34111400
C	3.06530300	-0.46872000	0.28201800
C	4.07849200	-0.86734400	1.14967700
C	3.41945500	0.03664900	-0.96815700
C	5.40386200	-0.77102700	0.78300600
H	3.81572400	-1.25547800	2.12116800
C	4.74240100	0.13154000	-1.33285200
H	2.65907800	0.36532900	-1.65676800
C	5.73935600	-0.27165100	-0.46017100
H	6.17464900	-1.08326500	1.46778200
H	5.00195500	0.52650500	-2.30102200
H	6.77400500	-0.19239900	-0.75016500

TS-4-18
E(RmPW+HF-B95) = -1264.639865 au
1 imaginary frequency: -312.0593 cm^{-1}

C	4.97176500	-0.46974400	0.04534600
C	4.48359500	0.45242100	-0.86209300
C	3.14071600	0.46946600	-1.16663500
C	2.27987500	-0.46683600	-0.60017800
C	2.78154500	-1.39029000	0.31581500
C	4.11916200	-1.38606900	0.63808400
C	0.88308900	-0.45126300	-0.95528400
C	0.07349400	-1.59693300	-0.87885700
C	-1.27621400	-1.51563500	-0.68908400
N	-1.94066100	-0.40251800	-0.39543200
C	-3.39703400	-0.34844200	-0.10804700
C	-3.91517300	-1.72263100	0.26227700
C	-1.23077100	0.86142500	-0.35242700
O	-1.48751400	1.72565000	-1.14495300
C	-0.16953400	0.88329500	0.59904000
C	-0.15744000	0.02728600	1.69963300
N	-0.13385500	-0.73599700	2.55934700
Cl	0.79707000	2.30960800	0.67592800
C	-4.12722800	0.17238400	-1.33476600
C	-3.59465000	0.59031300	1.07120600
H	-1.85730000	-2.42053600	-0.67944800
H	0.52552400	-2.57102400	-0.82131200
H	0.59472900	0.35770800	-1.61243800
H	-5.19230900	0.22593600	-1.12655100
H	-3.76919200	1.15867000	-1.60520200
H	-3.97421800	-0.49557800	-2.17770800
H	-3.27245200	1.60049600	0.83588300
H	-4.64997400	0.63097800	1.31964200
H	-3.04793000	0.23868900	1.94173600
H	-3.90998700	-2.40912300	-0.57931200
H	-3.34897800	-2.15520900	1.08246800
H	-4.94624000	-1.61717900	0.58240200
H	2.74846400	1.19374700	-1.86218100
H	2.10991600	-2.08894400	0.78709800
H	5.14849400	1.16695700	-1.31749000
H	4.50174000	-2.09336300	1.35466400
H	6.02007800	-0.47363600	0.29502100

β-24
E(RmPW+HF-B95) = -1264.688782 au

C	1.80384800	-1.39739100	0.09302700
C	2.67491200	-0.26524700	-0.50169400
O	3.66170500	-0.26484500	-1.16597400
N	1.86864600	0.66921600	0.02489900

C	0.87795200	-0.24458800	0.59303200
H	0.83634800	-0.20043200	1.67781700
Cl	1.13932900	-2.49926400	-1.10798200
C	2.44129700	-2.13993800	1.15030100
N	2.95194200	-2.69946500	2.00507700
C	1.89717600	2.13074600	0.01474100
C	-0.48041600	-0.17478500	0.01256100
C	-1.56491500	-0.12312200	0.77567300
H	-0.54132100	-0.16290000	-1.06484600
H	-1.42736500	-0.12504800	1.84943400
C	1.12314800	2.64137100	-1.18910000
H	1.15802600	3.72685900	-1.21643700
H	1.55536700	2.26148600	-2.11010600
H	0.08167100	2.33727200	-1.13847600
C	3.34191000	2.59018100	-0.04546200
H	3.82145500	2.27617600	-0.96473400
H	3.36744900	3.67435900	0.00672900
H	3.90715000	2.19213100	0.79212800
C	1.25562800	2.61109200	1.30301700
H	0.21710000	2.29808200	1.37012000
H	1.79439500	2.23356300	2.16768000
H	1.28015300	3.69565700	1.33229500
C	-2.95303500	-0.05451800	0.33486900
C	-3.94771200	0.07359700	1.29615300
C	-3.32812100	-0.11272000	-1.00377400
C	-5.27828200	0.14742100	0.93692200
H	-3.66990600	0.11545200	2.33775800
C	-4.65533300	-0.03896300	-1.36313500
H	-2.58044200	-0.22299700	-1.77184000
C	-5.63614600	0.09213500	-0.39493100
H	-6.03471500	0.24654500	1.69784800
H	-4.92962300	-0.08742500	-2.40412500
H	-6.67356200	0.14757200	-0.68078800

δ-20

E(RmPW+HF-B95) = -1264.704256 au

C	0.13179000	0.71683600	0.25513300
C	-1.39812800	0.79535700	-0.02546500
O	-1.94758100	1.85725900	-0.08144700
N	-2.01114200	-0.40978500	-0.13058100
C	-1.24128400	-1.56848700	-0.24996800
H	-1.76997500	-2.49012900	-0.11562800
Cl	0.83018300	2.33027200	0.05657800
C	0.28509300	0.32595400	1.64984800
N	0.37442000	0.02368400	2.74736000
C	-3.50516400	-0.44997700	-0.21275700
C	0.05377700	-1.56957500	-0.51564500
C	0.80265800	-0.29086700	-0.68692700

H	0.57764800	-2.50514600	-0.59428700
H	0.63660600	0.10306200	-1.69154300
C	-3.95523400	0.22218700	-1.49993100
H	-5.03531700	0.14209100	-1.58438200
H	-3.68573900	1.26959700	-1.51508500
H	-3.51137600	-0.27301100	-2.35940600
C	-4.09316900	0.23398900	1.01123800
H	-3.82605400	1.28142300	1.05612700
H	-5.17566000	0.15761800	0.96981000
H	-3.75251100	-0.25932900	1.91728300
C	-3.99507700	-1.88574700	-0.22821000
H	-3.64983700	-2.43213000	-1.10101700
H	-3.71369400	-2.42697200	0.67071200
H	-5.07867000	-1.85759400	-0.26738900
C	2.28377200	-0.41818500	-0.47006900
C	3.16355100	0.27185400	-1.28695500
C	2.79162000	-1.21930500	0.54084600
C	4.52691900	0.16946700	-1.09614600
H	2.77495100	0.89465100	-2.07737000
C	4.15501800	-1.31887200	0.73581100
H	2.11843600	-1.76922000	1.17942700
C	5.02542800	-0.62535300	-0.08213800
H	5.20002700	0.70999200	-1.74105500
H	4.53689700	-1.94329500	1.52659400
H	6.08945300	-0.70725400	0.06750600

s-trans **19**
E(RmPW+HF-B95) = -791.164681 au

N	2.62639100	-1.28869000	0.14363600
C	1.65006500	-0.51226100	-0.05399500
H	1.77012900	0.52630400	-0.35000400
C	3.99466300	-0.82396900	-0.00939700
C	0.29430400	-1.00789000	0.08129000
C	-0.82272300	-0.26850400	0.02136000
H	0.21771800	-2.07543100	0.21931800
C	4.64328600	-1.74561700	-1.03133200
H	5.70226100	-1.52032100	-1.12817800
H	4.53208700	-2.78103200	-0.72458300
H	4.17527800	-1.62537500	-2.00474400
C	4.66196700	-1.02369300	1.34344200
H	4.54101900	-2.05148700	1.67129200
H	5.72325000	-0.79759700	1.28049000
H	4.21460200	-0.37237800	2.08964200
C	4.15558300	0.62013300	-0.44942400
H	3.69683300	0.79849500	-1.41914000
H	3.72110700	1.31129600	0.26902000
H	5.21269900	0.85377600	-0.53506000
C	-2.14801400	-0.91271200	0.04669300

C	-3.22409000	-0.28273900	0.66204400
C	-2.35262700	-2.16449700	-0.52374400
C	-4.45787600	-0.89602700	0.72885700
H	-3.08503900	0.69100500	1.10265900
C	-3.58750900	-2.77522700	-0.46145500
H	-1.54000600	-2.65084200	-1.03841200
C	-4.64446200	-2.14518600	0.16849800
H	-5.27654300	-0.39670100	1.22081500
H	-3.72809900	-3.74237900	-0.91586200
H	-5.60973700	-2.62208500	0.21462800
C	-0.79108100	1.20653700	-0.03963800
C	-1.54240900	1.88654700	-0.99052600
C	-0.03486300	1.94236400	0.86272700
C	-1.50932300	3.26357200	-1.05866500
H	-2.14933300	1.32524100	-1.68296700
C	-0.00908300	3.32193300	0.80118000
H	0.52067000	1.42420100	1.62802900
C	-0.74132500	3.98555500	-0.16330200
H	-2.08715800	3.77598800	-1.81036200
H	0.57851200	3.87832500	1.51296100
H	-0.72188100	5.06190300	-0.21267100

s-cis **19**
E(RmPW+HF-B95) = -791.155830 au

N	-2.09923500	-0.85716300	0.24220500
C	-1.36341000	-1.56052100	-0.49727700
H	-1.76630900	-2.29420000	-1.19555600
C	-3.54730700	-0.93093600	0.15413000
C	0.09638900	-1.50191400	-0.45467800
C	0.87314100	-0.44112900	-0.20281500
H	0.58795300	-2.44047600	-0.66809400
C	-4.00373000	0.45900700	-0.26580900
H	-5.08817300	0.52773300	-0.23529000
H	-3.57939900	1.20753600	0.39591300
H	-3.67052700	0.67773300	-1.27725400
C	-4.04459500	-1.22453600	1.56082900
H	-3.65216200	-0.48902500	2.25603700
H	-5.13062400	-1.19554200	1.59454200
H	-3.71675000	-2.20918300	1.88384700
C	-4.10025700	-1.96348800	-0.81119700
H	-3.78968800	-1.76601900	-1.83453300
H	-3.78808800	-2.97062200	-0.54451900
H	-5.18558700	-1.93434800	-0.78460600
C	2.33434800	-0.61724900	-0.09143000
C	3.20239900	0.36264900	-0.55994700
C	2.87669100	-1.76526600	0.47456200
C	4.56903700	0.18636700	-0.49165800
H	2.79698500	1.26459500	-0.98892700

C	4.24327400	-1.93866300	0.54904500
H	2.21784000	-2.51519600	0.88155800
C	5.09505100	-0.96517600	0.06208700
H	5.22586700	0.95223800	-0.87070200
H	4.64454500	-2.83151000	1.00022400
H	6.16261300	-1.09911800	0.12352700
C	0.35908900	0.93818600	-0.07446400
C	0.74455800	1.72793800	0.99836000
C	-0.47984100	1.48199100	-1.03602700
C	0.27440200	3.01995700	1.12641200
H	1.41076000	1.32038100	1.74207400
C	-0.93810900	2.77703200	-0.91807100
H	-0.77678900	0.87498300	-1.87630300
C	-0.56826700	3.54880400	0.16818000
H	0.57123400	3.61570900	1.97423500
H	-1.58685300	3.18624500	-1.67557700
H	-0.92939700	4.55991000	0.26257900

ZW-st-19
E(RmPW+HF-B95) = -1495.657056 au

C	2.36809400	-1.38837300	0.99358100
C	2.47761100	-1.08830300	-0.35062400
O	2.88929300	-1.74983000	-1.27797100
N	2.02363300	0.29367100	-0.64010200
C	0.76558400	0.56894200	-0.59824700
H	0.48168800	1.59489100	-0.76695800
Cl	2.86309400	-2.95805100	1.52667600
C	1.92610000	-0.48423400	1.95343800
N	1.55576600	0.27789100	2.73508700
C	3.06968600	1.27361200	-1.05413300
C	-0.26078700	-0.38852000	-0.41233000
C	-1.55542800	-0.03640100	-0.21373700
H	0.00090300	-1.42867300	-0.50506800
C	3.36416800	1.04802400	-2.52758500
H	4.13140200	1.74729700	-2.84682800
H	3.70990700	0.03565900	-2.69502700
H	2.47318700	1.21749700	-3.12565900
C	4.30546100	1.01208700	-0.21332500
H	4.69677900	0.01513800	-0.38775600
H	5.07135400	1.72830800	-0.49108900
H	4.08914200	1.12620800	0.84469700
C	2.58294900	2.68879700	-0.81869100
H	1.78862300	2.97750200	-1.50078000
H	2.24813700	2.82891200	0.20553000
H	3.41452600	3.36166600	-0.99741800
C	-2.60784800	-1.04663500	-0.33508800
C	-3.75741700	-0.98115400	0.44635000
C	-2.46545100	-2.09835600	-1.23547000

C	-4.72708100	-1.95635200	0.34284900
H	-3.87561200	-0.17515000	1.15149000
C	-3.44127900	-3.06336200	-1.34572300
H	-1.59784000	-2.14200800	-1.87274800
C	-4.57236100	-2.99695700	-0.55304600
H	-5.60496300	-1.90419600	0.96501400
H	-3.32354500	-3.86561400	-2.05476800
H	-5.33480500	-3.75381000	-0.63613400
C	-1.93136800	1.33381600	0.14184400
C	-3.00643500	1.95515500	-0.48738700
C	-1.21956400	2.02725900	1.11608700
C	-3.33302700	3.25668900	-0.17749900
H	-3.56835200	1.41691000	-1.23335100
C	-1.56356100	3.32586200	1.43550200
H	-0.42619000	1.52811300	1.65181000
C	-2.61279600	3.94361200	0.78478500
H	-4.15354500	3.73759000	-0.68350200
H	-1.01590900	3.84935500	2.20128800
H	-2.87910200	4.95773300	1.03332900

TS-rot-19

E(RmPW+HF-B95) = -1495.637548 au

1 imaginary frequency: -18.9291 cm^{-1}

C	1.82105400	-2.10244800	-0.21323100
C	1.62657100	-0.84841300	-0.74691800
O	1.29985500	-0.46610700	-1.84433900
N	1.85673200	0.22655800	0.28508200
C	0.92579600	0.46677900	1.11393700
H	1.06150100	1.29949100	1.78779700
Cl	1.53359100	-3.47545700	-1.22610100
C	2.26051400	-2.32744000	1.08691300
N	2.61246500	-2.49570300	2.17103000
C	3.06029100	1.10124000	0.12790800
C	-0.30860800	-0.31736300	1.13395800
C	-1.40864100	0.19074400	0.58187400
H	-0.25701900	-1.32187800	1.52191500
C	2.65924200	2.20656200	-0.83446700
H	3.49856400	2.88094800	-0.97356700
H	2.37041400	1.78839300	-1.79170600
H	1.81705600	2.76814600	-0.43509300
C	4.18028300	0.25139300	-0.43709600
H	3.92079800	-0.14933000	-1.41142100
H	5.05942300	0.87613100	-0.55266100
H	4.42508600	-0.56917100	0.23106600
C	3.46828300	1.66605100	1.47345700
H	2.76699100	2.40422400	1.85017900
H	3.59436100	0.87786300	2.21016500
H	4.42075500	2.17004800	1.34987400

C	-2.61641500	-0.61822100	0.37973100
C	-3.87079600	-0.02246700	0.38096600
C	-2.52051700	-1.98964500	0.17357300
C	-5.00726900	-0.78841900	0.22002900
H	-3.95245400	1.04376700	0.51799300
C	-3.65705500	-2.75148100	0.00693400
H	-1.54889300	-2.45324100	0.10693600
C	-4.90352700	-2.15395700	0.03627200
H	-5.97607000	-0.31697900	0.23386300
H	-3.56900300	-3.81197700	-0.16155600
H	-5.79124000	-2.74979100	-0.09822200
C	-1.38958000	1.60066600	0.12093100
C	-1.39363200	1.90602900	-1.23209800
C	-1.31589800	2.62694800	1.05149500
C	-1.31597500	3.22146000	-1.64317300
H	-1.43210600	1.10810800	-1.95535400
C	-1.24347700	3.94285600	0.63698900
H	-1.32629900	2.38858000	2.10383600
C	-1.24187200	4.24101900	-0.71166200
H	-1.30959600	3.45126000	-2.69586800
H	-1.19434600	4.73336400	1.36764800
H	-1.18482400	5.26633400	-1.03813100

ZW-st-19
E(RmPW+HF-B95) = -1495.642545 au

C	-0.88209600	-1.16953000	1.41685900
C	-1.52697300	-0.13930900	0.75919800
O	-1.89437200	0.93675700	1.16951400
N	-1.88142200	-0.48710400	-0.65099900
C	-1.00976000	-0.74783800	-1.55789400
H	-1.41578600	-1.08343100	-2.49961500
Cl	-0.43996900	-0.90798500	3.07166200
C	-0.56973900	-2.40229700	0.86165900
N	-0.29938500	-3.41845100	0.38782100
C	-3.35376600	-0.47902900	-0.94520100
C	0.41874800	-0.76618200	-1.47062600
C	1.24514400	0.10038100	-0.85037300
H	0.85143300	-1.58732400	-2.02108200
C	-3.77587200	0.96434100	-1.16645400
H	-4.84165900	0.98831800	-1.37513100
H	-3.56339200	1.56364600	-0.29018000
H	-3.25136200	1.38744300	-2.01930900
C	-4.06967300	-1.08224500	0.25018000
H	-3.91667400	-0.48845400	1.14367200
H	-5.13288200	-1.10724800	0.03599200
H	-3.73176400	-2.09782500	0.43461200
C	-3.66138100	-1.30712500	-2.17658300
H	-3.29903900	-0.85237200	-3.09391800

H	-3.26839800	-2.31657900	-2.09216000
H	-4.74016300	-1.37451700	-2.26362200
C	2.66376500	-0.23712100	-0.70884800
C	3.64068500	0.75144700	-0.75269700
C	3.04678900	-1.56060900	-0.51632000
C	4.97349700	0.41856400	-0.63572600
H	3.34741700	1.77925100	-0.89118500
C	4.37917600	-1.88838000	-0.38857700
H	2.28891100	-2.32358700	-0.43190100
C	5.34484300	-0.90064200	-0.45430800
H	5.72431200	1.18974900	-0.68317400
H	4.66463400	-2.91417100	-0.22482900
H	6.38647100	-1.15779300	-0.35333800
C	0.77573000	1.39461800	-0.35166800
C	1.15765900	1.83941800	0.90793500
C	-0.08056700	2.17401900	-1.11841900
C	0.64006800	3.01201000	1.41153800
H	1.82412400	1.23794400	1.50449500
C	-0.57963200	3.35695500	-0.61948300
H	-0.33525900	1.85475400	-2.11700500
C	-0.23154800	3.76911600	0.65183700
H	0.91142600	3.33408600	2.40295100
H	-1.24025600	3.95809200	-1.22221800
H	-0.63256800	4.68721600	1.04865800

TS-2-19
E(RmPW+HF-B95) = -1495.625046 au
1 imaginary frequency: -150.7812 cm^{-1}

C	-2.24098300	0.01473800	1.65161500
C	-3.05940000	0.05825600	0.46088600
N	-2.20845700	-0.37311900	-0.55177700
C	-0.96510700	0.12924400	-0.26236000
O	-4.19157300	0.45204800	0.34054500
H	-0.89668400	1.17532200	-0.01922000
Cl	-2.70757100	1.00888000	2.98348900
C	-2.69527400	-0.89731800	-1.84983600
C	-1.51602600	-1.13639100	1.98552400
N	-0.89032600	-2.06348800	2.25745900
C	0.22050700	-0.61315500	-0.38543500
C	1.46197500	-0.06733600	-0.25603200
H	0.12622600	-1.68360200	-0.44589800
C	-3.79881200	-1.90134400	-1.57406000
H	-4.63656200	-1.43779400	-1.06740200
H	-3.42397800	-2.71885200	-0.96495600
H	-4.14885900	-2.30912900	-2.51744500
C	-1.57956700	-1.57929700	-2.61306500
H	-0.75352400	-0.90696500	-2.82312600
H	-1.98401700	-1.91511200	-3.56283400

H	-1.20366500	-2.44950400	-2.08453900
C	-3.22177100	0.28262600	-2.65263800
H	-3.63067800	-0.06840500	-3.59600700
H	-2.41922800	0.98421000	-2.86785700
H	-4.00042000	0.79613200	-2.10019000
C	2.61816500	-0.93662400	-0.05033000
C	3.85953000	-0.58958700	-0.57706800
C	2.49398900	-2.12773000	0.66216500
C	4.94269800	-1.42693800	-0.42149900
H	3.96277800	0.33045700	-1.12853300
C	3.58332300	-2.95475400	0.82591800
H	1.54995600	-2.37575300	1.12172000
C	4.80670500	-2.61051700	0.27971200
H	5.89450700	-1.15655100	-0.84746700
H	3.48140900	-3.86557600	1.39203600
H	5.65630300	-3.26066700	0.40893000
C	1.68423300	1.37725600	-0.32633000
C	2.52556700	1.99652200	0.59421500
C	1.07400700	2.15050200	-1.30940400
C	2.71749500	3.35971800	0.55444000
H	3.00623300	1.40247600	1.35406400
C	1.28571100	3.51271300	-1.35916800
H	0.45996000	1.67080600	-2.05480100
C	2.09990600	4.11966700	-0.42290700
H	3.35218900	3.83222000	1.28535600
H	0.81877000	4.09924700	-2.13261800
H	2.26084300	5.18443200	-0.45870900

TS-4-19

E(RmPW+HF-B95) = -1495.622912 au

1 imaginary frequency: -370.5810 cm^{-1}

C	-0.10927300	-0.90632300	1.17293200
C	-1.31123700	-0.21557800	0.79504700
O	-1.77190300	0.72111500	1.38735200
N	-1.92876300	-0.69896300	-0.40482900
C	-1.19080000	-0.98944700	-1.49500700
H	-1.70397100	-1.54225500	-2.26103400
Cl	0.68144600	-0.37543600	2.61682100
C	-0.00798200	-2.27141200	0.90296600
N	0.07575500	-3.38760200	0.63410300
C	-3.41683500	-0.77194500	-0.41903500
C	0.12132500	-0.72097500	-1.67692100
C	0.90308500	0.08962300	-0.79087300
H	0.62652500	-1.22498700	-2.48210500
C	-3.98103200	0.61771300	-0.66850800
H	-5.06631900	0.57033100	-0.70823400
H	-3.68119200	1.29871700	0.11842200
H	-3.62154900	1.00390800	-1.61944700

C	-3.89465500	-1.32545700	0.91381800
H	-3.64796000	-0.66504100	1.73569400
H	-4.97372700	-1.43709600	0.88276100
H	-3.45557500	-2.30240700	1.09923800
C	-3.88751800	-1.71222000	-1.51308000
H	-3.70784400	-1.31839400	-2.50917800
H	-3.42744200	-2.69275900	-1.42517000
H	-4.96010100	-1.83421100	-1.40633100
C	2.31974000	-0.25944400	-0.66413000
C	3.32136100	0.71035000	-0.64573900
C	2.69324100	-1.60320500	-0.66341300
C	4.64984100	0.34501000	-0.60222600
H	3.06256200	1.75228600	-0.71074200
C	4.01950700	-1.96348900	-0.59936200
H	1.93068100	-2.36280300	-0.69295600
C	5.00226300	-0.98984300	-0.56680800
H	5.41167800	1.10650700	-0.60471200
H	4.28920200	-3.00615000	-0.57953000
H	6.04132200	-1.27281600	-0.52660600
C	0.46948000	1.45023300	-0.47391500
C	1.01667000	2.14765200	0.60465700
C	-0.51419700	2.07604600	-1.23765200
C	0.59426400	3.42224500	0.90421800
H	1.76056700	1.67494000	1.21960800
C	-0.92613200	3.35648600	-0.94064700
H	-0.92945500	1.56005000	-2.08650000
C	-0.37578600	4.03197900	0.13162800
H	1.02043300	3.94080600	1.74663700
H	-1.67688700	3.83013700	-1.55107000
H	-0.70122500	5.03267700	0.36389100

β-21

E(RmPW+HF-B95) = -1495.679101 au

C	-2.02763600	0.75617800	-1.10807000
C	-3.08122900	-0.27824700	-0.65038700
O	-4.14516000	-0.60820400	-1.07123500
N	-2.31609700	-0.64523500	0.38509300
C	-1.16529200	0.20337800	0.07499600
H	-0.98077600	0.96498500	0.82614600
Cl	-1.40592900	0.48984300	-2.73244200
C	-2.42942700	2.13060300	-0.94893300
N	-2.74280700	3.21799400	-0.79287800
C	-2.56143900	-1.62523400	1.44353800
C	0.07176500	-0.53048400	-0.27974400
C	1.31549100	-0.11072000	-0.03604200
H	-0.07834800	-1.49260600	-0.74650800
C	-2.52397200	-3.01523100	0.83172700
H	-2.73945500	-3.76253200	1.58987400

H	-3.26693800	-3.09920300	0.04387800
H	-1.54440900	-3.22498800	0.41090300
C	-3.92817800	-1.34585200	2.04410600
H	-4.70386000	-1.42118400	1.28971400
H	-4.13450100	-2.06934100	2.82705600
H	-3.95794000	-0.35022500	2.47701700
C	-1.48583600	-1.46867900	2.49857700
H	-0.49743000	-1.66703800	2.09443500
H	-1.49474500	-0.46845600	2.92298300
H	-1.67262900	-2.17605400	3.30014400
C	2.46722300	-0.99311500	-0.30001500
C	3.67100200	-0.46179800	-0.74630500
C	2.37460700	-2.36734400	-0.11590600
C	4.74269400	-1.28455200	-1.02664300
H	3.76010300	0.60340000	-0.88501900
C	3.44778100	-3.18918400	-0.39109700
H	1.46093200	-2.79143100	0.26892200
C	4.63453900	-2.65075800	-0.85118800
H	5.66524500	-0.85670400	-1.38321600
H	3.36104900	-4.25194800	-0.23496800
H	5.47371600	-3.29251400	-1.06359200
C	1.59659000	1.23857200	0.48995900
C	2.43228300	1.40707500	1.58729700
C	1.04276800	2.36133800	-0.10844000
C	2.67646000	2.66665700	2.09237400
H	2.88419600	0.54173200	2.04539900
C	1.29405700	3.62430300	0.39176600
H	0.43722200	2.24324700	-0.99361700
C	2.10676000	3.77797900	1.49694800
H	3.31594900	2.78373400	2.95180900
H	0.85721500	4.48508500	-0.08669700
H	2.30374100	4.76171600	1.89010200

δ-25

E(RmPW+HF-B95) = -1495.684172 au

C	0.03110200	-0.89164700	0.73606700
C	-1.50759200	-0.64668700	0.78079500
O	-2.07588000	-0.55765600	1.83227400
N	-2.09728500	-0.61397300	-0.43643400
C	-1.30630200	-0.62205500	-1.58609300
H	-1.82057300	-0.84703400	-2.49835500
Cl	0.71103400	-0.66871100	2.35735000
C	0.18755600	-2.30568500	0.41157100
N	0.26620300	-3.42348700	0.19204100
C	-3.58577300	-0.47715500	-0.51277600
C	-0.00802500	-0.37270500	-1.59494400
C	0.73008300	-0.02143400	-0.33251900
H	0.52627400	-0.38511700	-2.52807600

C	-3.98837900	0.85837600	0.09274800
H	-5.06010000	0.99260200	-0.02331300
H	-3.74910700	0.90452400	1.14680900
H	-3.48487500	1.67252100	-0.42175600
C	-4.23859000	-1.64269800	0.21171600
H	-3.99445200	-1.64796100	1.26561700
H	-5.31659800	-1.56137300	0.10777100
H	-3.92514700	-2.58413200	-0.23076300
C	-4.04341500	-0.50084400	-1.95875000
H	-3.62622600	0.31808100	-2.53742900
H	-3.81393000	-1.44269500	-2.44893000
H	-5.12215900	-0.38766200	-1.95910200
C	2.20260000	-0.38601200	-0.40867600
C	3.13369000	0.29896500	0.35795600
C	2.63634100	-1.43310300	-1.20565300
C	4.46659600	-0.05380500	0.32611600
H	2.81107600	1.12051600	0.97600000
C	3.97202000	-1.78628600	-1.23899800
H	1.92965600	-1.98847000	-1.80025400
C	4.89076600	-1.09754200	-0.47439100
H	5.17621600	0.49029800	0.92741700
H	4.29079700	-2.60275200	-1.86572100
H	5.93286000	-1.37064200	-0.50216300
C	0.54032000	1.47678200	-0.12234500
C	1.13760700	2.31333500	-1.05995100
C	-0.22131700	2.04879700	0.88072600
C	0.97636900	3.67823800	-0.99831000
H	1.74002600	1.88145700	-1.84390900
C	-0.38512500	3.42372500	0.94082500
H	-0.68818800	1.45020600	1.64259300
C	0.20911700	4.24200900	0.00700500
H	1.45094900	4.30565900	-1.73483200
H	-0.97984100	3.84741600	1.73333400
H	0.08247900	5.31072200	0.05993600

DMK **26**
E(RmPW+HF-B95) = -231.164760951 au

C	0.33242000	-0.00001200	-0.00001000
C	-0.96766500	-0.00008900	-0.00004700
O	-2.12514400	-0.00006400	-0.00009300
C	1.08773700	-1.29373300	0.00004600
C	1.08752000	1.29384500	0.00006600
H	1.72600000	-1.35988900	0.87893700
H	0.42855000	-2.15452000	-0.00020600
H	1.72640100	-1.35969000	-0.87856800
H	1.72586200	1.36003600	0.87889700
H	1.72608100	1.35998800	-0.87860900
H	0.42818600	2.15451900	-0.00003900

TS-26
E(RmPW+HF-B95) = -791.333351031 au
1 imaginary frequency: -200.0542 cm^{-1}

C	-1.67314600	2.15334600	0.29974200
C	-1.94314600	1.33179200	-0.70455600
O	-2.23461600	1.14669100	-1.83564200
N	-1.80567100	-0.55537000	0.03228700
C	-0.68917100	-1.15069600	0.05039000
H	-0.63611500	-2.23642500	0.10926600
C	-1.69050800	3.61327800	-0.05571300
C	-1.37263100	1.81700700	1.71568600
C	-3.05822000	-1.32601000	0.06463200
C	0.57260100	-0.45870600	0.00358000
C	1.71835200	-1.14248500	0.03118800
H	0.53682500	0.61737300	-0.05480900
H	1.65898200	-2.22158400	0.09287200
C	-3.24677900	-2.00158100	-1.28465800
H	-4.19837400	-2.52569500	-1.30967000
H	-3.23159900	-1.25815800	-2.07433200
H	-2.45474200	-2.72343900	-1.46899400
C	-4.19417800	-0.35213600	0.31873400
H	-4.28490400	0.35517500	-0.49895500
H	-5.12987700	-0.89634700	0.40871200
H	-4.02628900	0.20179900	1.23848100
C	-3.03153800	-2.35936600	1.18039000
H	-2.28858400	-3.13315000	1.01168000
H	-2.82841700	-1.88595200	2.13721300
H	-3.99974800	-2.84761700	1.24046700
H	-0.72874500	4.07969500	0.16002800
H	-1.90900600	3.77072900	-1.10630100
H	-2.44181000	4.14707300	0.52705600
H	-0.35677600	2.10985000	1.98905300
H	-2.04113800	2.36099900	2.38366400

H	-1.48423600	0.76093700	1.92141100
C	3.06621000	-0.60300900	-0.01027700
C	4.13805900	-1.48510400	0.06558900
C	3.33278500	0.75922100	-0.12460300
C	5.43870000	-1.02629800	0.03178900
H	3.94320000	-2.54261600	0.15210600
C	4.63044100	1.21683900	-0.15882000
H	2.52084800	1.46431100	-0.19166300
C	5.68829100	0.32699100	-0.08025300
H	6.25655700	-1.72516700	0.09195100
H	4.82149600	2.27345500	-0.24912000
H	6.70235000	0.69033000	-0.10803100

ZW-26

E(RmPW+HF-B95) = -791.345297259 au

C	-1.47349200	1.88770700	0.49907100
C	-1.93726400	1.04169100	-0.45768200
O	-2.46163900	1.25503900	-1.56639000
N	-1.86086400	-0.40340100	-0.09791600
C	-0.72362900	-0.98076400	0.04019200
H	-0.72202900	-2.02244400	0.32392500
C	-1.55705900	3.34747600	0.20832100
C	-0.90626100	1.52000600	1.82809500
C	-3.14432900	-1.16027700	-0.05545100
C	0.54177900	-0.36024000	-0.16322800
C	1.65913600	-1.02160200	0.16965200
H	0.54836700	0.63315300	-0.57904300
H	1.55289700	-2.00381600	0.61095400
C	-3.47368900	-1.60561000	-1.47089200
H	-4.41667300	-2.14552900	-1.46746400
H	-3.54496100	-0.73812500	-2.11513900
H	-2.70027800	-2.26837000	-1.85105200
C	-4.21721700	-0.22733300	0.47266400
H	-4.32953700	0.62526000	-0.18660300
H	-5.15791400	-0.76709900	0.51559000
H	-3.97075800	0.12405500	1.47029300
C	-3.02464300	-2.36311100	0.86176000
H	-2.39257200	-3.14558800	0.45248200
H	-2.65482900	-2.08210400	1.84431200
H	-4.01450800	-2.78971100	0.98489000
H	-0.57093200	3.81780200	0.20816100
H	-2.01092000	3.51244500	-0.76197800
H	-2.14796500	3.87249900	0.96142000
H	0.17943600	1.64835900	1.87100400
H	-1.32032800	2.17044800	2.59915800
H	-1.11867100	0.49783900	2.12705300
C	3.02383400	-0.56543200	0.01183500
C	4.05409900	-1.40215600	0.42920500

C	3.35007000	0.66935900	-0.54565000
C	5.37283500	-1.02250000	0.29458600
H	3.81112600	-2.35973600	0.86245100
C	4.66629900	1.04661600	-0.68040500
H	2.57221800	1.33694900	-0.87684400
C	5.68172100	0.20323200	-0.26140400
H	6.15853000	-1.68251100	0.62260500
H	4.90562200	2.00320700	-1.11438000
H	6.71070500	0.50413300	-0.36927400