Computational study of the kinetics and mechanism of gas-phase decomposition of N-diacetamides using density functional theory

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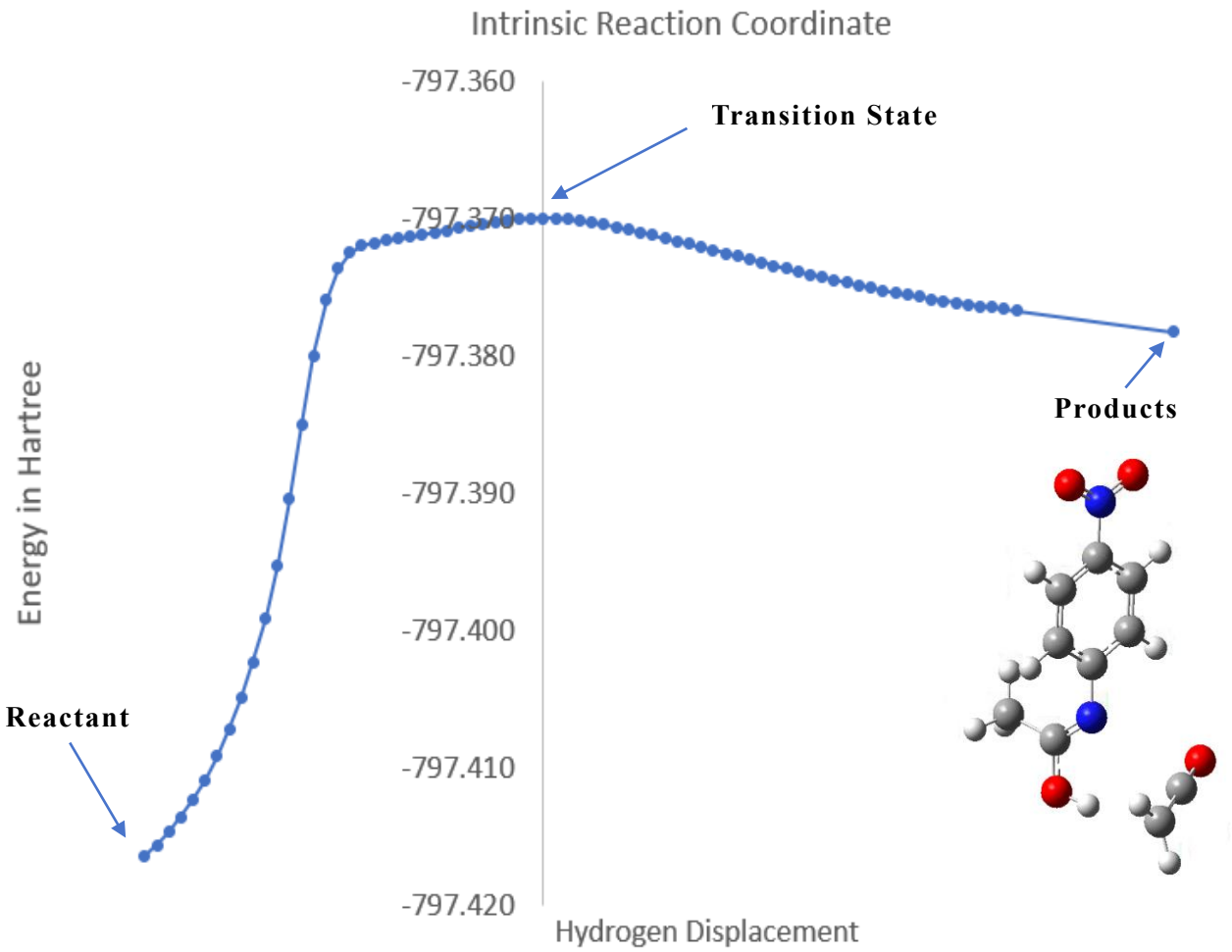
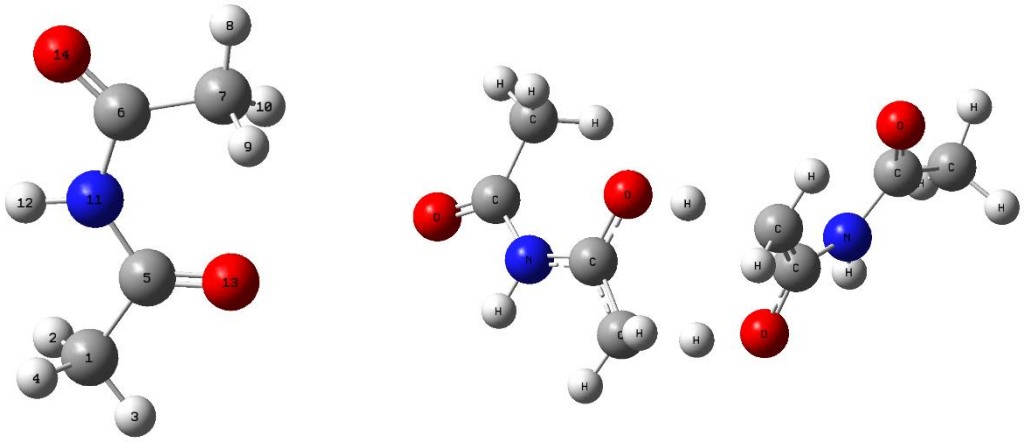
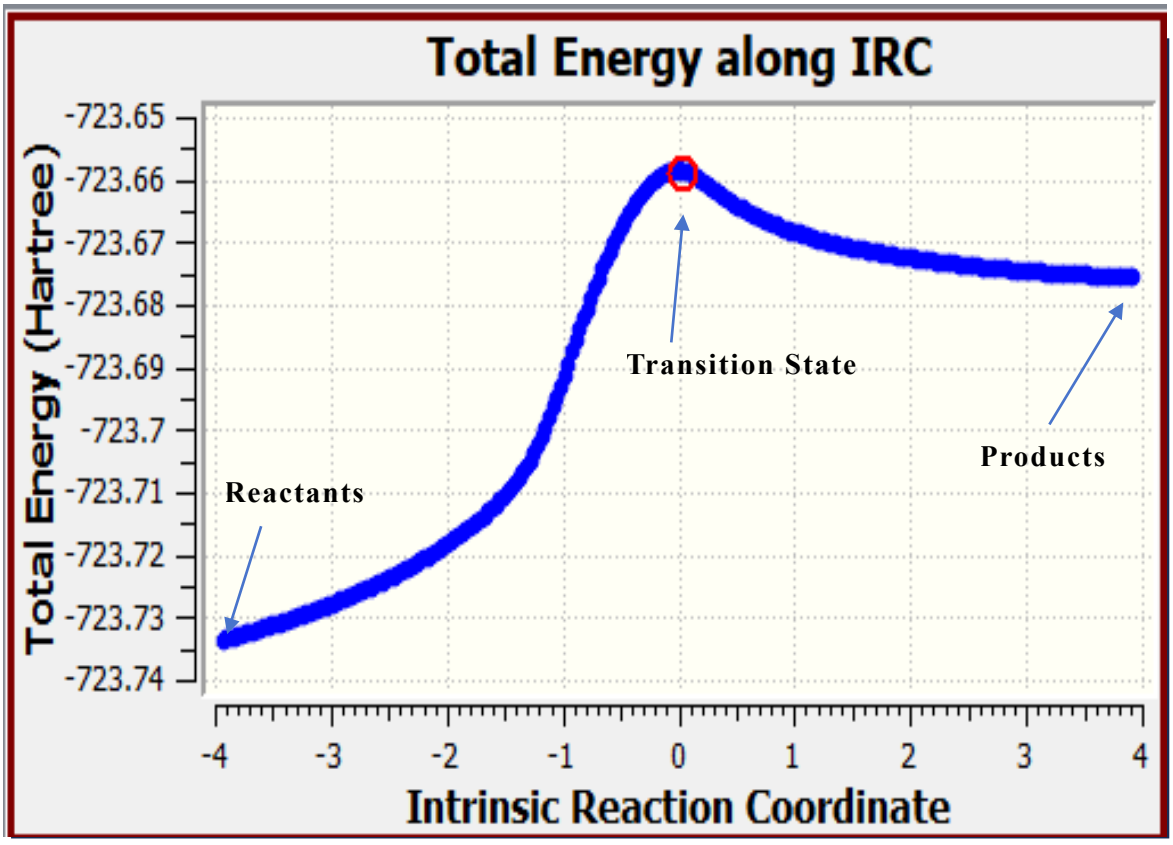


Figure S6. IRC calculation from reactant to products at theory level B3PW91/6-311+G(3df,2p) gd3bj



(A:monomer) (B: dimer)



(C)

Figure S7. Dimer Proposal for the case of Diacetamide $NX(COCH_3)_2$ X = H. (A) monomer; (B) dimer, (C) IRC: intrinsic Reaction for the doble hydrogen migration. Model is discussed in the main manuscript. Theory level: X3LYP/Def2-TZVP.

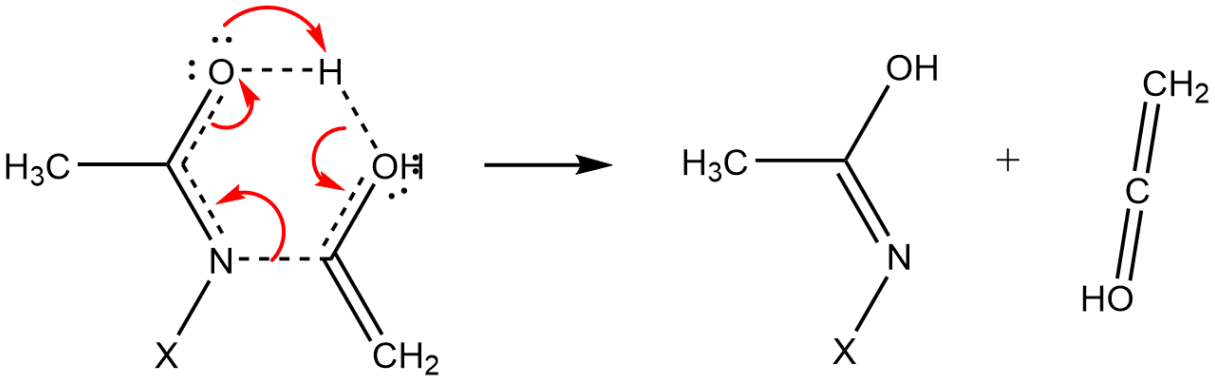
Calculated thermodynamic data at level of theory X3LYP/Def2-TZVP (A) Dimer, (B) monomer

(A): Dimer

Imaginary Freq	1	
Temperature	600.000	Kelvin
Pressure	1.00000	atm
Frequencies scaled by	1.0000	
Electronic Energy (EE)	-723.658572	Hartree
Zero-point Energy Correction	0.218177	Hartree
Thermal Correction to Energy	0.270751	Hartree
Thermal Correction to Enthalpy	0.272651	Hartree
Thermal Correction to Free Energy	0.097094	Hartree
EE + Zero-point Energy	-723.440395	Hartree
EE + Thermal Energy Correction	-723.387821	Hartree
EE + Thermal Enthalpy Correction	-723.385921	Hartree
EE + Thermal Free Energy Correction	-723.561478	Hartree
E (Thermal)	169.899	kcal/mol
Heat Capacity (Cv)	94.097	cal/mol-kelvin
Entropy (S)	183.607	cal/mol-kelvin

(B): monomer

Imaginary Freq	0	
Temperature	600.000	Kelvin
Pressure	1.00000	atm
Frequencies scaled by	1.0000	
Electronic Energy (EE)	-361.860259	Hartree
Zero-point Energy Correction	0.110767	Hartree
Thermal Correction to Energy	0.136759	Hartree
Thermal Correction to Enthalpy	0.138660	Hartree
Thermal Correction to Free Energy	0.025388	Hartree
EE + Zero-point Energy	-361.749492	Hartree
EE + Thermal Energy Correction	-361.723500	Hartree
EE + Thermal Enthalpy Correction	-361.721600	Hartree
EE + Thermal Free Energy Correction	-361.834871	Hartree
E (Thermal)	85.818	kcal/mol
Heat Capacity (Cv)	44.487	cal/mol-kelvin
Entropy (S)	118.464	cal/mol-kelvin



Scheme S6. Final step-path of the dimer formation Scheme 3 (main manuscript)

NBO Analysis

Table S8. Wiberg Indexes for the Phenyl-diacetamide/LC-BLYP– Def2-TZVP

Wiberg Indices for LC-BLYP DEF2TZVP								
BONDS	Reactant	TS	Product	δB	%Ev	δBav	(δB-δBav)/δB	Sincronicity
N11-C5	1.0544	1.63310	1.7404	0.8436	84.36	0.8461	0.0030	0.9585
C5-O12	1.7420	1.13650	1.0322	0.8531	85.31		0.0083	
O12-H9	0.0011	0.63740	0.7020	0.9078	90.78		0.0729	
H9-C7	0.9102	0.05860	0.0165	0.9529	95.29		0.1262	
C7-C6	1.0136	1.61700	1.7289	0.8436	84.36		0.0030	
C6-N11	1.0069	0.33180	0.0072	0.6753	67.53		0.2019	
							0.4153	

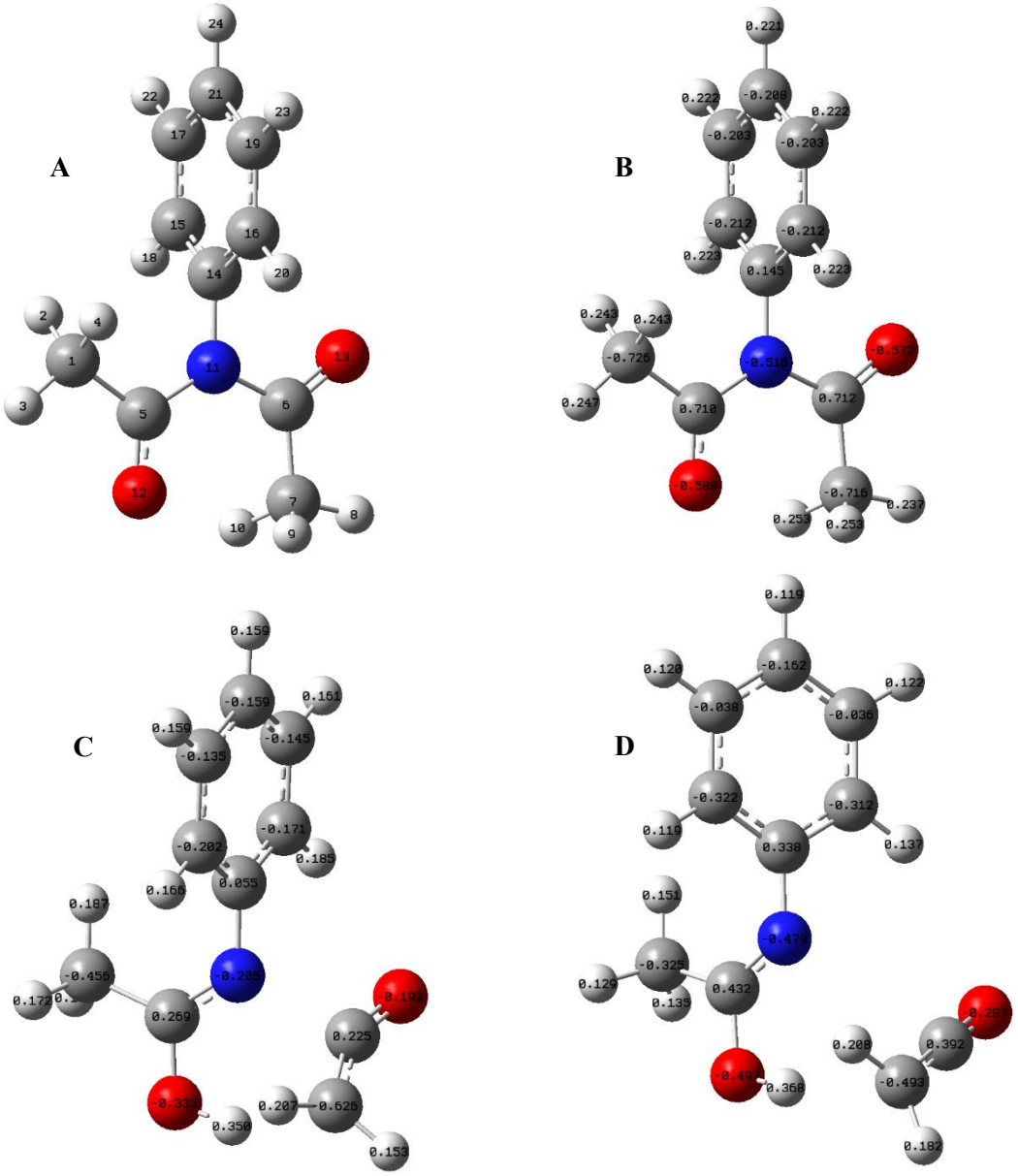


Figure S8. Phenyl-Diacetamide at the level of theory LC-BLYP– Def2-TZVP. (A) Atomic label, (B) NBO charges (reactant), (B) NOB charges for the transition state (TS), y (D) NBO charges for the product.

Geometry input data for the Phenyl-Diacetamide at the level of theory LC-BLYP– Def2-TZVP

Reactant

```
0 1
 C                  0.59440000    2.44957100   -0.00047700
 H                 -0.05219700    2.46602700    0.87423800
 H                  1.24110600    3.32027500   -0.00087600
 H                 -0.05213300    2.46517400   -0.87525900
 C                  1.47366100    1.23885000    0.00016100
 C                  1.46606100   -1.24363500    0.00053200
 C                  2.95232500   -1.32515700    0.00001100
 H                  3.20607100   -2.38054800   -0.00044400
 H                  3.37312400   -0.82552600   -0.86789900
 H                  3.37361900   -0.82613600    0.86802300
 N                  0.82650700    0.00905900    0.00033000
 O                  2.66973200    1.33884600   -0.00002700
 O                  0.78066500   -2.22715100   -0.00026000
 C                 -0.60450900   -0.04318100    0.00016500
 C                 -1.28684200   -0.07333900    1.19209900
 C                 -1.28657600   -0.07377400   -1.19189800
 C                 -2.66144500   -0.11422300    1.19166700
 H                 -0.73327400   -0.07187800    2.12198900
 C                 -2.66118800   -0.11467700   -1.19175400
 H                 -0.73281500   -0.07264900   -2.12167400
 C                 -3.34982300   -0.13180500   -0.00012000
 H                 -3.19905700   -0.13842300    2.12989400
 H                 -3.19858300   -0.13922000   -2.13009700
 H                 -4.43097000   -0.16584000   -0.00022700
```

Transition State

```
0 1
 C                 -0.75181100    2.49386000   -0.63189200
 H                 -0.98634900    3.24598800    0.11970000
 H                  0.32334800    2.41869700   -0.74867900
 H                 -1.20945500    2.81328000   -1.56598400
 C                 -1.35725100    1.20420100   -0.22674100
 C                 -1.70981800   -1.54559300    0.13311500
 C                 -2.61673500   -1.33844400    1.09171700
 H                 -2.47546900   -0.56999000    1.83005400
 H                 -3.00592700    0.35164600    0.09446100
 H                 -3.31698700   -2.13977500    1.27428300
 N                 -0.73505400    0.14384800    0.08116500
 O                 -2.67045700    1.23274600   -0.21113300
 O                 -1.26495900   -2.19951100   -0.72484200
 C                  0.66748700    0.04517300    0.07627500
 C                  1.39664400    0.48216400    1.16250900
 C                  1.30653400   -0.54737400   -0.99153700
 C                  2.76486400    0.34921900    1.16826900
 H                  0.88015200    0.92273800    2.00524100
 C                  2.67610900   -0.68095100   -0.97635500
 H                  0.71868900   -0.91130800   -1.82208900
 C                  3.40848500   -0.23174000    0.09845500
 H                  3.33351700    0.69791100    2.01997900
 H                  3.17549600   -1.14566500   -1.81596900
 H                  4.48464100   -0.33942900    0.10576600
```

Product

0 1

C	-0.12875100	2.56146500	-0.89367000
H	-0.17309700	3.45766800	-0.27680600
H	0.90718100	2.28141700	-1.05061900
H	-0.59825900	2.79943000	-1.84609000
C	-0.89693200	1.47418500	-0.23788900
C	-2.78440800	-1.54100000	0.13632200
C	-3.26477400	-0.95443900	1.19692700
H	-2.56909900	-0.54289300	1.90955500
H	-2.65961700	1.01390000	0.25295100
H	-4.31949300	-1.03399900	1.40390700
N	-0.48226600	0.37402300	0.19932700
O	-2.19492400	1.77024000	-0.14983100
O	-2.39513800	-2.05192500	-0.81079800
C	0.86498900	0.00601100	0.14748000
C	1.80384400	0.59527000	0.97124600
C	1.25558200	-1.01400500	-0.69878500
C	3.11688900	0.18516600	0.93151800
H	1.49210000	1.37599100	1.65300800
C	2.56951300	-1.41583100	-0.73751400
H	0.50974100	-1.48790400	-1.32336900
C	3.50747500	-0.81881600	0.07573200
H	3.84279700	0.65582500	1.58167800
H	2.86412600	-2.21120000	-1.40957600
H	4.53941900	-1.14094300	0.04690700

Table S9. Wiberg indexes for the Diacetamide / B3PW91 – gd3bj – Def2-TZVP – First Stage

Wiberg Indices: B3Pw91 - gd3bj - Def2-TZVP

BONDS	Reactant	TS	Producto	δB	%Ev	δBav	(δB-δBav)/δB	Sincronicity
C6-O13	0.0119	0.4495	0.9206	0.4816	48.16	0.566	0.1491	0.9503
O13-C5	1.7512	1.2962	0.9849	0.5938	59.38		0.0491	
C5-N11	1.0941	1.5438	1.8650	0.5833	58.33		0.0306	
N11-C6	1.0564	0.4229	0.0100	0.6054	60.54		0.0696	
							0.2984	

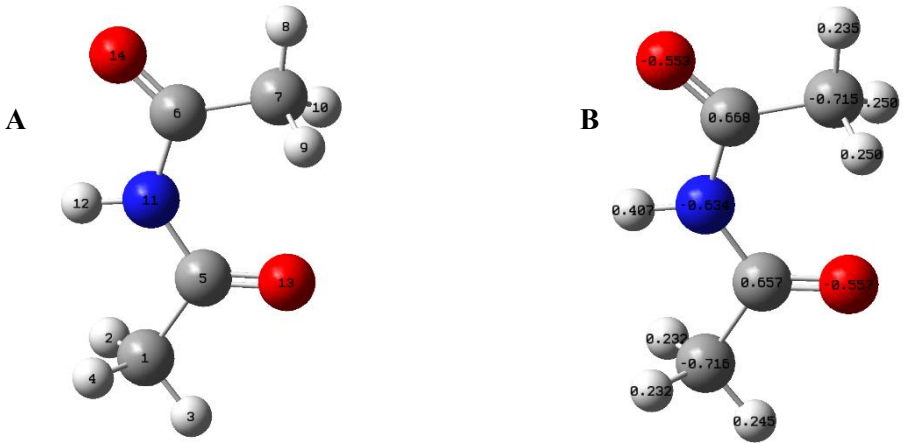


Figure S9. Diacetamide at the level of theory B3PW91-gd3bj-Def2-TZVP. (A) Atomic label, (B) NBO charges (reactant)

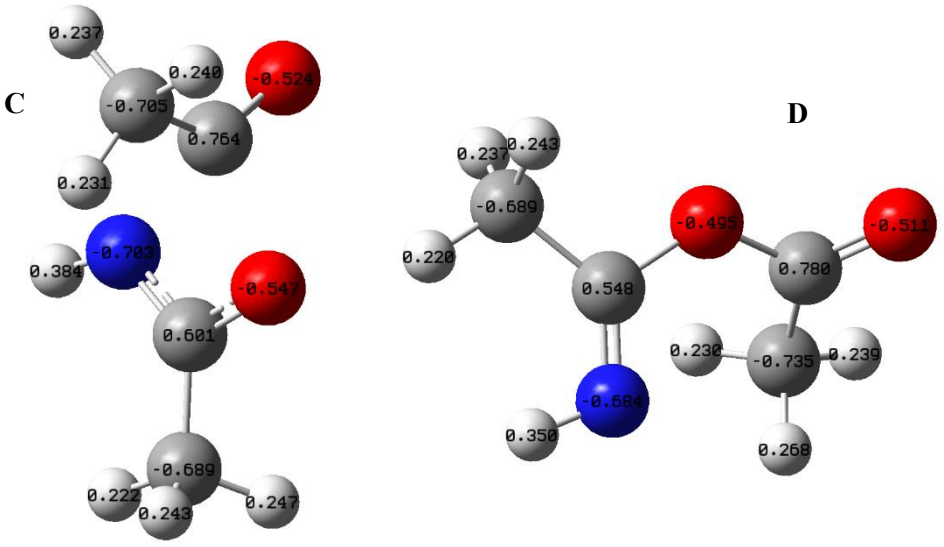


Figure S9 cont. Diacetamide at the level of theory B3PW91-gd3bj-Def2-TZVP. (C) NBO charges (Transition State), (D) NBO charges (product)

Geometry input data for the Diacetamide at the level of theory B3PW91-gd3bj–Def2-TZVP

Reactant

```
0 1
 C                  2.46159600   -0.65021100   -0.00005100
 H                  2.51131500   -1.29214600   -0.88288800
 H                  3.30771700    0.03159000   -0.00031700
 H                  2.51164800   -1.29184800    0.88298600
 C                  1.18522400    0.15445900    0.00009100
 C                 -1.30737300   -0.27568600    0.00012500
 C                 -1.65911700    1.17742400   -0.00004700
 H                 -2.74340800    1.25858200   -0.00020900
 H                 -1.23366200    1.67653500    0.87097400
 H                 -1.23341400    1.67641600   -0.87101600
 N                  0.04534700   -0.63297600    0.00008900
 H                  0.17048600   -1.63534500    0.00005000
 O                  1.16470200    1.36207800    0.00000500
 O                 -2.12596400   -1.16568600   -0.00011900
```

Transition State

```
0 1
 C                  2.54301500    0.09568600   -0.10823400
 H                  2.91591200   -0.73960700   -0.70310600
 H                  2.78793000    1.01439500   -0.64407900
 H                  3.03622000    0.09876700    0.86235100
 C                  1.06376100   -0.02030400    0.02260900
 C                 -1.14180100   -0.20091800   -0.01065600
 C                 -1.72503300    1.17078000   -0.00588700
 H                 -2.38881700    1.25504700    0.85590100
 H                 -0.95839700    1.93786100    0.03926600
 H                 -2.31504600    1.28678100   -0.91681800
 N                  0.36399400   -0.08962700    1.10619100
 H                  0.76791700   -0.08561200    2.03198100
 O                  0.32016100   -0.05418400   -1.02226100
 O                 -1.67432700   -1.24727900   -0.05971800
```

Product

```
0 1
 C                -2.35480000   -0.61988400    0.37301700
 H                -2.45162600   -1.58819500   -0.12139000
 H                -2.25840100   -0.81164800    1.44384000
 H                -3.25000400   -0.02848400    0.19005200
 C                -1.13540900    0.08342700   -0.12905900
 C                 1.26651700   -0.25898100   -0.00345100
 C                 1.54462000    1.09433600    0.57127300
 H                 2.57234700    1.09724200    0.92932700
 H                 1.42596800    1.84432100   -0.20995300
 H                 0.85238900    1.34926300    1.37229500
 N                -1.03869800    1.21617400   -0.67301400
 H                -1.94809600    1.66360400   -0.73032400
 O                -0.04478900   -0.71727200    0.03025200
 O                 2.09513100   -1.01181700   -0.40943000
```

Table S10. Wiberg indexes for the Diacetamide / B3PW91 – gd3bj – Def2-TZVP – Second Stage

Wiberg Indices: B3Pw91 - gd3bj - Def2-TZVP

Bonds	Reactant	TS	Producto	δB	%Ev	δBav	(δB-δBav)/δB	Sincronicity
C5-O13	0.9849	1.2536	1.6721	0.3910	39.10	0.4098	0.0459	0.7829
O13-C6	0.9206	0.5981	0.0028	0.3514	35.14		0.1425	
C6-C7	1.0111	1.3253	1.7761	0.4107	41.07		0.0022	
C7-H9	0.8978	0.3348	0.0120	0.6356	63.56		0.5510	
H9-N11	0.0013	0.4511	0.7992	0.5637	56.37		0.3755	
N11-C5	1.8650	1.5519	1.2206	0.4859	48.59		0.1857	
							1.3028	

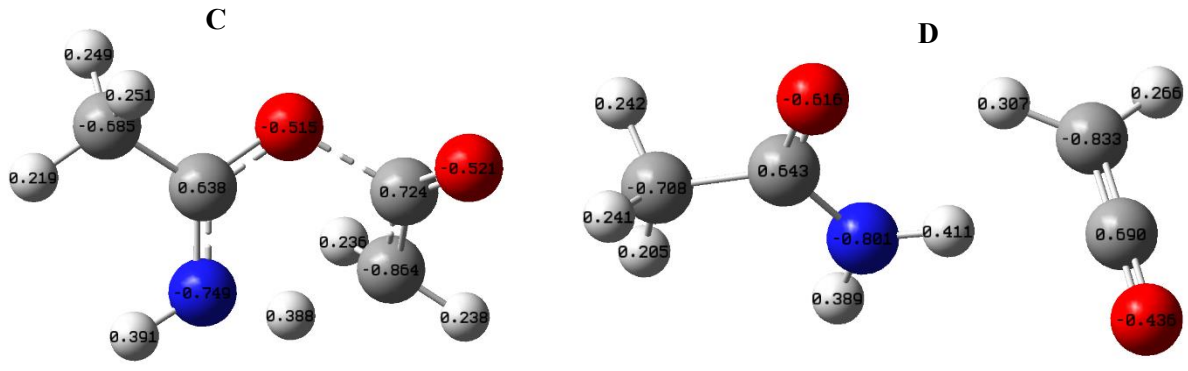
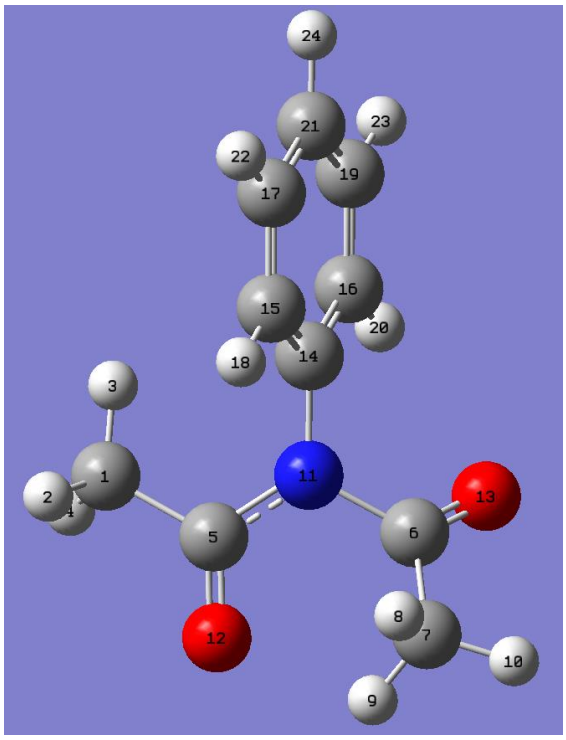


Figure S10. Diacetamide at the level of theory B3PW91-gd3bj-Def2-TZVP. (A) NBO charges (Transition State), (C) NBO charges (product)

Figure S11. Mayer Bond order Analysis for Phenyl-diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation



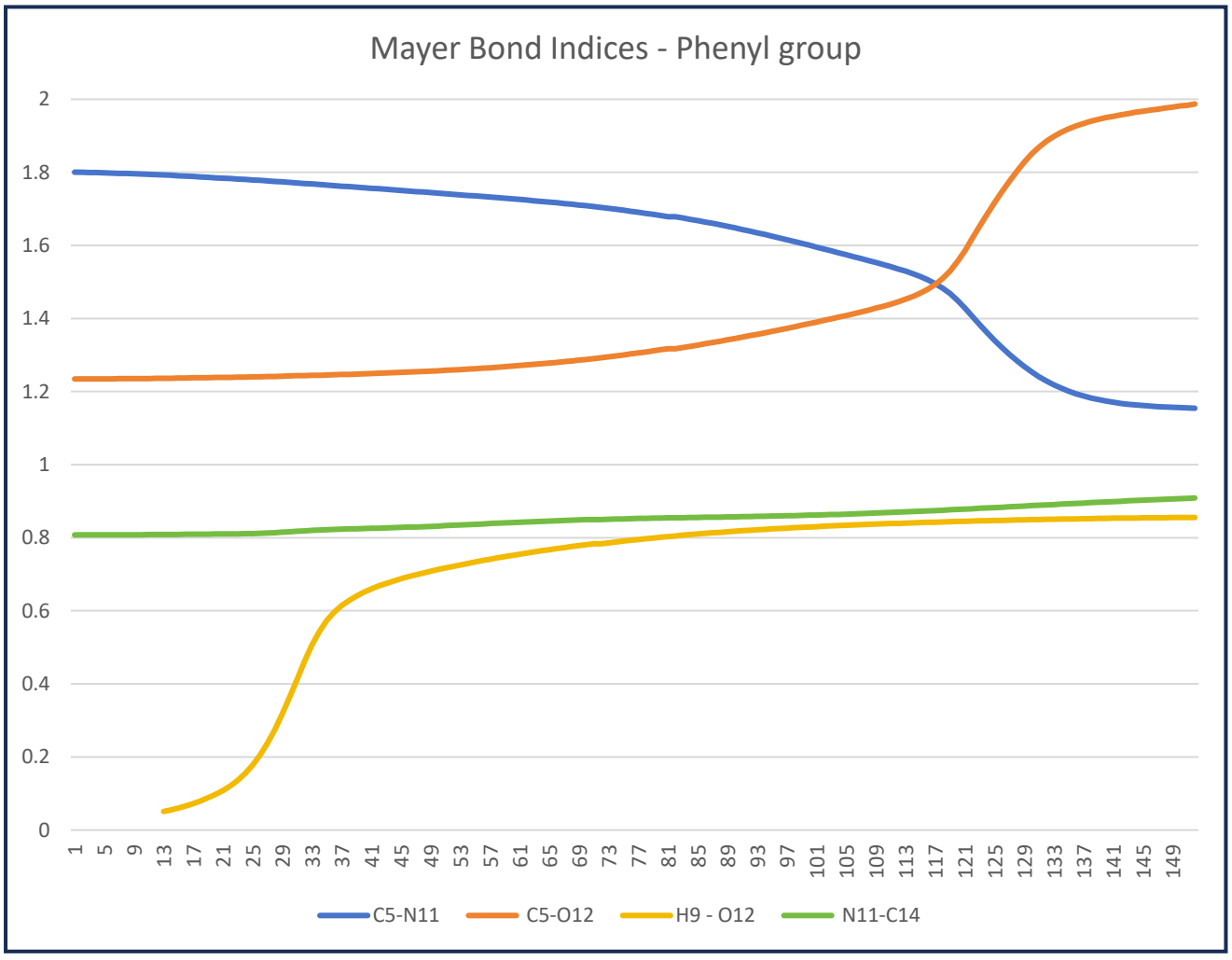
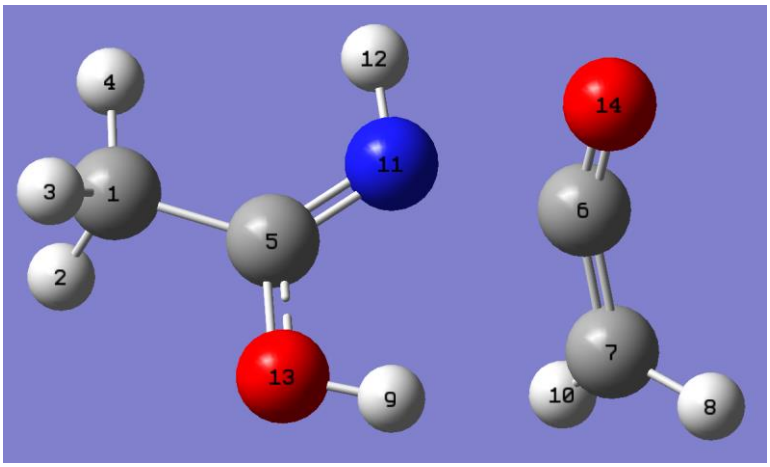


Figure S12. Mayer Bond order Analysis for Diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation



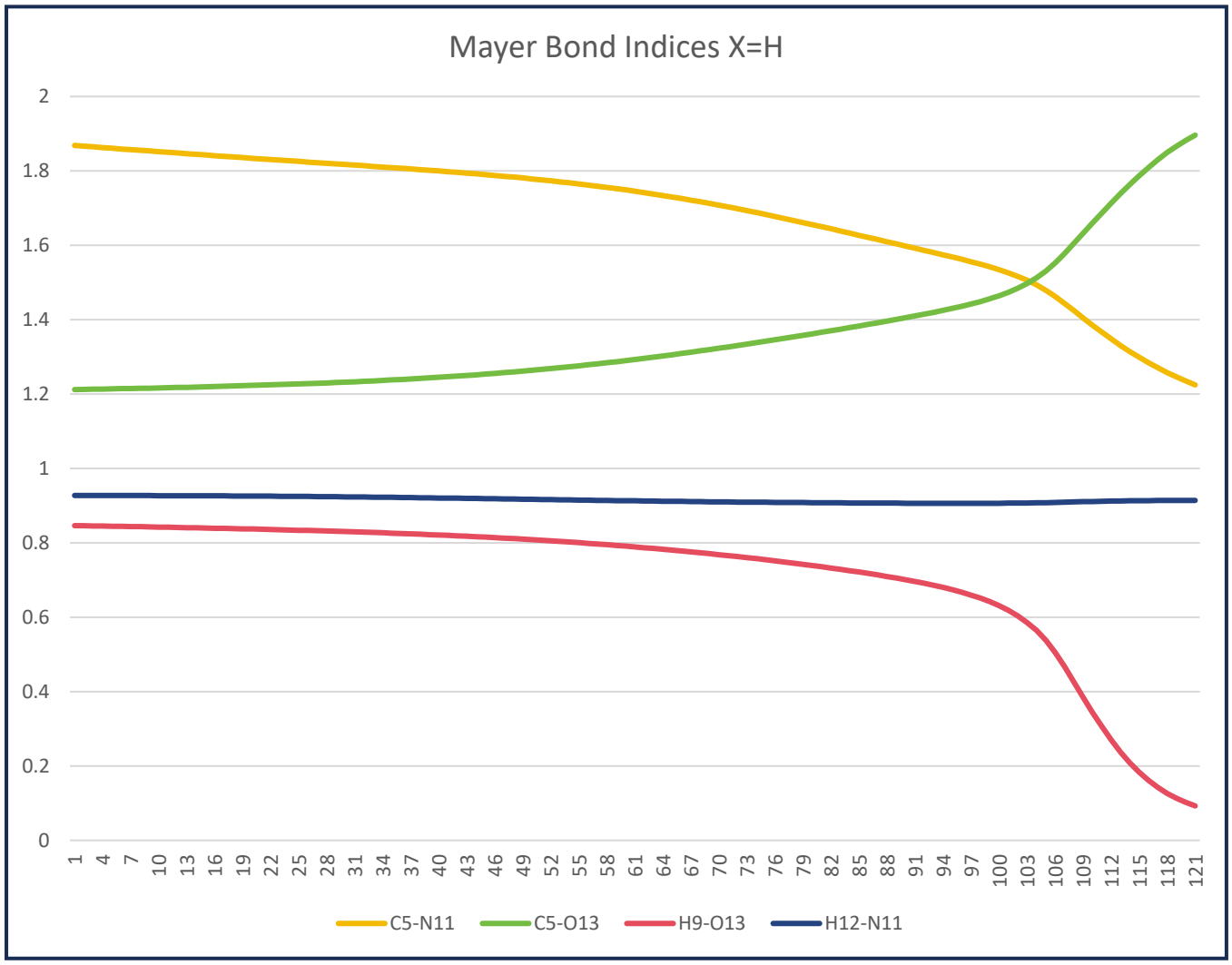
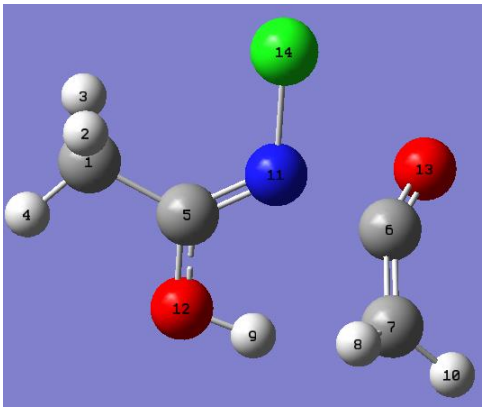


Figure S13. Mayer Bond order Analysis for Chloro-diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation



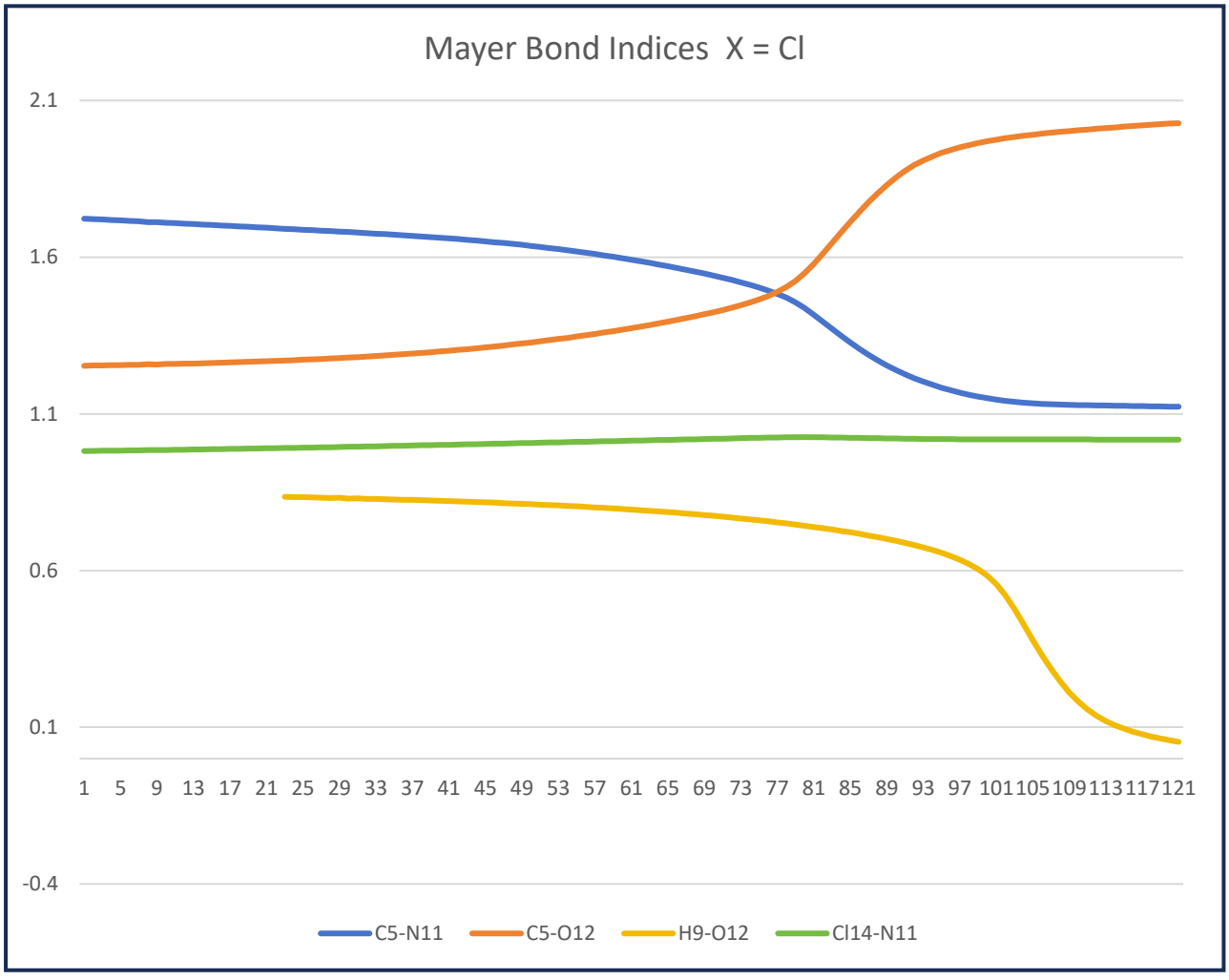


Figure S14. IBSI diagrams for the Phenyl-Diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation

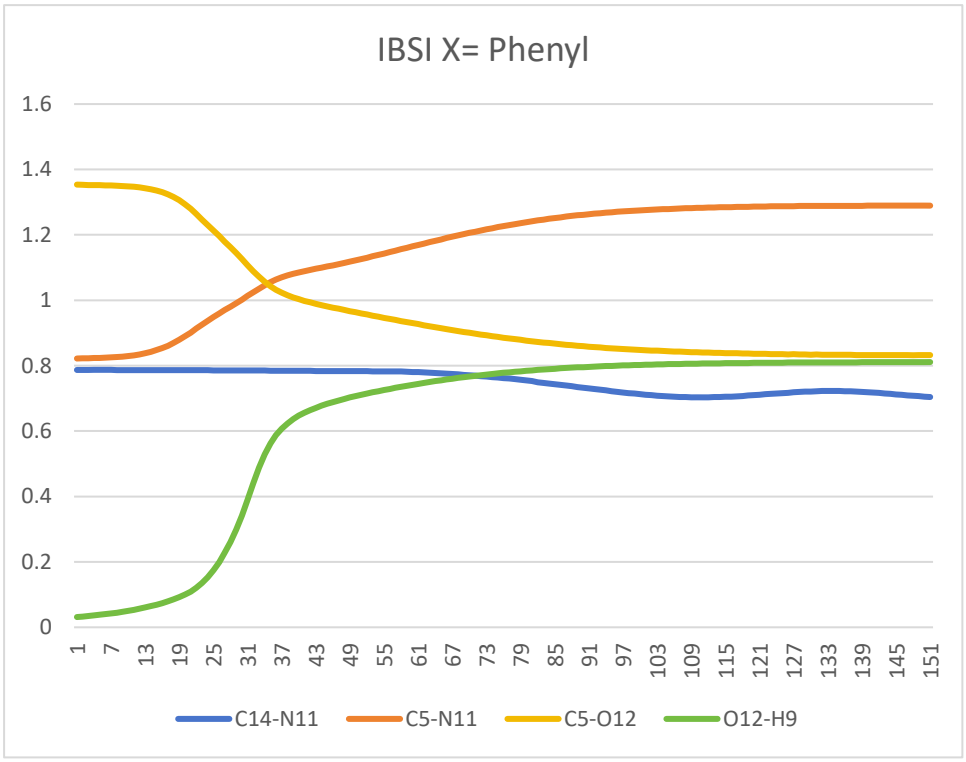


Figure S15. IBSI diagrams for the Diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation

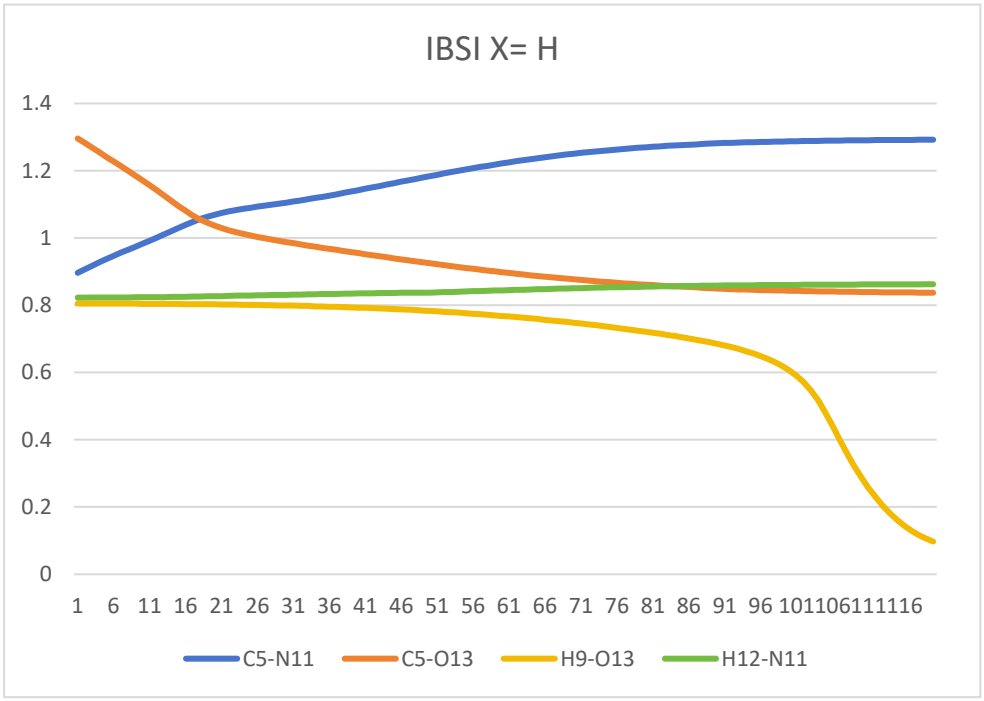


Figure S16. IBSI diagrams for the Chloro-Diacetamide at the level of theory LC-BLYP– Def2-TZVP data from an IRC calculation