Exploring the Mechanism of the Intramolecular Diels–Alder Reaction of (2*E*,4*Z*,6*Z*)-2(allyloxy)cycloocta-2,4,6-trien-1-one Using Bonding Evolution Theory

Abel Idrice Adjieufack [1,2,3,*], Jean Moto Ongagna [4], Jean Serge Essomba [2], Monique Bassomo Ewonkem [4], Mónica Oliva [5], Vicent Sixte Safont [5] and Juan Andrés [5,*]

[1] Laboratory of Theoretical Chemistry (LCT), Namur Institute of Structured Matter (NISM), University of Namur, Rue de Bruxelles, 61, B-5000 Namur, Belgium

[2] Physical and Theoretical Chemistry Laboratory, University of Yaoundé 1, Yaoundé P.O. Box 812, Cameroon; jeansergeessomba@gmail.com

[3] Computational Chemistry Laboratory, High Teacher Training College, University of Yaoundé 1, Yaoundé P.O. Box 47, Cameroon

[4] Department of Chemistry, Faculty of Sciences, University of Douala, Douala P.O. Box 2701, Cameroon; jean.monfils@yahoo.fr (J.M.O.); myewon@gmail.com (M.B.E.)

[5] Analytical and Physical Chemistry Department, Jaume I University, Avda. Sos Baynat s/n, 12071 Castelló, Spain; oliva@uji.es (M.O.); safont@uji.es (V.S.S.)

* Correspondence: adjieufack21@gmail.com (A.I.A.); andres@uji.es (J.A.)

Content

Table S1-a. ΔG value (kcal/mol) evaluated in function of different XC DFT functionals as well as MP2 and CCSD(T) for the TSs of path-**a**. The basis set used in all cases was cc-pVTZ.

Species	**B3LYP**	**M05-2X**	**ωB97X-D**	**M06-2X**	**B3LYP(D3)BJ**	**MP2**	**LC-BLYP**	**CCSD(T)**
TS1-a	56.4	56.7	56.8	56.6	55.2	50.3	62.3	52.9
TS2-a	36.9	25.2	27.7	27.7	30.9	13.8	31.5	22.3

Table S1-b. ΔΔG value with respect the reference method (CCSD(T)) evaluated in function of different XC DFT functionals as well as MP2 for the TSs of path-**a**. The basis set used in all cases was cc-pVTZ.

Species	**B3LYP**	**M05-2X**	**ωB97X-D**	**M06-2X**	**B3LYP(D3)BJ**	**MP2**	**LC-BLYP**
TS1-a	3.5	3.8	3.9	3.7	2.3	-2.6	9.4
TS2-a	14.6	2.9	5.4	5.4	8.6	-8.5	9.2

Table S1-c. % deviation with respect the reference method in the ΔG values evaluated in function of different XC DFT functionals as well as MP2 for the TSs of path-**a**.

Species	**B3LYP**	**M05-2X**	**ωB97X-D**	**M06-2X**	**B3LYP(D3)BJ**	**MP2**	**LC-BLYP**
TS1-a	6.7	7.2	7.4	7.0	4.3	-4.9	15.1
TS2-a	65.5	13.0	24.2	24.2	38.6	-38.1	41.3
Average	36.1	10.1	15.8	15.6	21.5	-21.5	28.2

Table S1-d. M05-2X/cc-pVTZ electronic energies (E, Hartree·particle^{-1}), enthalpies (H, Hartree·particle^{-1}), entropies (S, cal·mol^{-1}·K^{-1}), and Gibbs free energies (G, Hartree·particle^{-1}) for the species involved in this intramolecular Diels-Alder reaction.

Species	E	H	S	G
1	-576.89732	-576.66064	135.571	-576.76179
TS1-a	-576.80443	-576.57180	133.679	-576.67153
Int-a	-576.89044	-576.65286	117.541	-576.74055
TS2-a	-576.86511	-576.63113	121.063	-576.72145
2	-576.93942	-576.70372	135.092	-576.80450
TS1-b	-576.85077	-576.61650	127.945	-576.71195
Int-b	-576.90371	-576.66739	138.582	-576.77078
TS2-b1	-576.83862	-576.60460	124.090	-576.69718
TS2-b2	-576.81278	-576.57855	120.915	-576.66876
3-b1	-576.93340	-576.69558	122.214	-576.78676
3-b2	-576.87073	-576.63266	118.334	-576.72095
TS1-c1	-576.80344	-576.56924	121.521	-576.65990
TS1-c2	-576.79208	-576.55790	123.864	-576.65031
4-c1	-576.91232	-576.67382	116.395	-576.76066
4-c2	-576.87645	-576.63857	121.205	-576.72899

Table S2. Topological parameters values of the electron density [$\rho(r)$] and its Laplacian [$\nabla^2\rho(\mathrm{r})$], $|V(r)|/G(r)$ ratio, and ellipticity (ε) at the C…C and O…C critical points in the TSs along the IMDA. In addition, instantly interaction energy(Eint), Lagrangian kinectic energy[G(r)], Energy density[H(r)], QTAIM Charge[Qe] and Eigenvalues of Hessian matrix[λ_{1-3}] at these previous BCPs(Bond critical points)

TS	**BCP**	$\rho(r)$ (a.u)	$\nabla^2\rho(\mathrm{r})$ (a.u)	$V(r)$ (a.u)	**Eint**	$G(r)$ (a.u)	$\lvert V(r)\rvert/G(r)$	$H(r)$ (a.u)	λ_1 (a.u)	λ_2 (a.u)	λ_3 (a.u)	**Qe**	ε (a.u)
TS1-a	**C2 ⋯ C7**	0.061	0.070	-0.044	0.022	0.031	1.433	-0.013	-0.059	-0.051	0.181	0.330	0.172
TS2-a	**C6 ⋯ C13**	0.054	0.043	-0.031	0.016	0.021	1.488	-0.010	-0.052	-0.047	0.142	0.367	0.106
	C3 ⋯ C12	0.053	0.049	-0.032	0.016	0.022	1.444	-0.010	-0.052	-0.043	0.144	0.359	0.208
TS1-b	**O10 ⋯ C11**	0.080	0.115	-0.069	0.035	0.049	1.413	-0.020	-0.092	-0.104	0.310	0.295	0.132
	C3 ⋯ C13	0.065	0.046	-0.039	0.020	0.025	1.542	-0.014	-0.067	-0.061	0.174	0.385	0.104
TS2-b1	**C4 ⋯ C12**	0.061	0.066	-0.041	0.020	0.029	1.421	-0.012	-0.064	-0.039	0.169	0.380	0.638
	C7 ⋯ C11	0.020	0.040	-0.034	0.017	0.022	1.553	-0.011	-0.060	-0.057	0.158	0.383	0.059
TS2-b2	**O10 ⋯ C12**	0.049	0.109	-0.091	0.046	0.059	1.540	-0.032	-0.132	-0.123	0.365	0.362	0.068
	O9 ⋯ C11	0.083	0.102	-0.070	0.035	0.048	1.468	-0.022	-0.113	-0.103	0.317	0.357	0.104
TS1-c1	**C4 ⋯ C12**	0.048	0.041	-0.027	0.014	0.019	1.460	-0.009	-0.045	-0.041	0.126	0.356	0.107
	C7 ⋯ C13	0.051	0.041	-0.029	0.014	0.019	1.474	-0.009	-0.049	-0.043	0.133	0.369	0.369
TS1-c2	**C2 ⋯ C12**	0.046	0.034	-0.024	0.012	0.016	1.482	-0.008	-0.042	-0.040	0.117	0.361	0.047
	C5 ⋯ C13	0.085	0.062	-0.060	0.030	0.038	1.589	-0.022	-0.078	-0.102	0.241	0.322	0.312

Table S3. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C2–C7 bond lengths (Å**)**, and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS1-a** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**	
V(C2,C3)	3.63	2.96	2.63	2.30	2.27	2.10
V(C3,C4)	2.12	2.99	3.03	3.24	3.26	3.37
V(C4,C5)	3.42	2.85	2.79	2.37	2.35	2.22
V(C5,C6)	2.12	2.75	2.84	3.22	3.24	3.37
V(C6,C7)	3.48	2.88	2.77	2.30	2.27	2.11
V(C2)	-	-	0.31	0.66	-	-
V(C7)	-	-	0.26	0.69	-	-
V(C2,C7)	-	-	-	-	1.44	1.92
Catastrophes	-	-	*F*	*F*	*C*	*C*
***d*(C2-C7)**	2.606	2.094	2.067	1.886	1.859	1.569
E kcal/mol	0.00	13.34	12.78	1.99	-0.36	-40.65
Rx	6.74	-0.32	-0.48	-1.60	-1.76	-15.72

Table S4. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C3–C12/C6–C13 bond lengths (Å**)**, and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS2-a** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**		**SSD-IV**		**SSD-V**	
V(C3,C4)	3.35	3.07	3.02	3.02	2.71	2.45	2.39	2.32	2.28	2.08
V(C4,C5)	2.25	2.72	2.98	2.98	2.91	3.17	3.22	3.26	3.29	3.40
V(C5,C6)	3.35	3.07	2.98	2.98	2.66	2.38	2.31	2.26	2.23	2.06
V(C12,C13)	3.42	3.29	2.84	2.84	2.72	2.38	2.31	2.23	2.16	1.94
V(C3)	-	-	-	-	0.29	0.51	0.56	0.61	-	-
V(C6)	-	-	-	-	0.26	0.51	-	-	-	-
V(C12)	-	-	0.21	0.21	0.27	0.46	0.52	0.57	-	-
V(C13)	-	-	0.25	0.25	0.33	0.56	-	-	-	-
V(C3,C12)	-	-	-	-	-	-	-	-	1.28	1.79
V(C6,C13)	-	-	-	-	-	-	1.20	1.31	1.41	1.83
Catastrophes			*FF*	*FF*	*FFFF*	*FFFF*	*CFF*	*CFF*	*CC*	*CC*
***d*(C3-C12)**	3.235	2.250	2.208	2.208	2.166	2.039	1.997	1.954	1.911	1.555
***d*(C6-C13)**	3.655	2.229	2.184	2.184	2.137	1.999	1.954	1.908	1.863	1.554
E kcal/mol	0.00	14.43	14.22	14.22	13.53	7.70	4.38	0.48	-3.85	-32.17
Rx	-10.47	0.00	0.30	0.30	0.60	1.50	1.79	2.09	2.40	6.86

Table S5. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C3–C13 bond lengths (Å**)**, and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS1-b** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**		**SSD-IV**	
V(C2,C3)	3.43	3.33	3.30	3.20	2.83	2.62	2.45	2.08
V(C2,O10)	1.47	1.57	1.61	1.85	1.93	2.07	2.19	2.43
V(O10,C11)	1.20	0.63	-	-	-	-	-	-
V(C11,C12)	2.05	2.24	2.29	2.88	3.00	3.12	3.18	3.45
V(C12,C13)	3.45	3.29	3.26	2.90	2.58	2.39	2.31	2.03
V(O10)	4.88	5.26	5.85	5.45	5.42	5.32	5.29	5.16
V(C3)	-	-	-	-	0.34	0.52	-	-
V(C13)	-	-	-	-	0.23	0.36	-	-
V(C3,C13)	-	-	-	-	-	-	1.03	1.84
Catastrophes					*FF*	*FF*	*C*	*C*
***d*(O10-C11)**	1.444	1.648	1.696	1.942	1.989	2.079	2.162	4.104
***d*(C3-C13)**	3.826	2.352	2.313	2.116	2.075	1.985	1.889	1.541
E kcal/mol	0.00	19.73	22.14	28.71	28.43	26.18	24.31	-4.48
Rx	-14.15	-1.89	-1.57	0.00	0.31	0.94	1.26	15.41

Table S6. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C4–C12/C7–C11 bond lengths (Å**)**, and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS2-b1** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**		**SSD-IV**		**SSD-V**		**SSD-VI**	
V(C4,C5)	3.46	3.17	3.13	3.13	3.09	3.09	2.67	2.42	2.37	2.37	2.32	2.10
V(C5,C6)	2.17	2.69	2.79	2.79	2.90	2.90	3.01	3.20	3.25	3.25	3.29	3.44
V(C6,C7)	3.47	3.15	2.78	2.78	2.67	2.67	2.56	2.33	2.28	2.28	2.24	2.04
V(C11,C12)	3.44	3.30	3.03	3.03	2.74	2.74	2.63	2.35	2.28	2.28	2.21	1.93
V(C4)	-	-	-	-	-	-	0.38	0.57	0.61	0.61	-	-
V(C7)	-	-	0.37	0.37	0.40	0.40	0.46	0.65	-	-	-	-
V(C11)	-	-	0.28	0.28	0.36	0.36	0.41	0.61	-	-	-	-
V(C12)	-	-	-	-	0.25	0.25	0.31	0.49	0.54	0.54	-	-
V(C4,C12)	-	-	-	-			-	-	-	-	1.24	1.84
V(C7,C11)	-	-	-	-			-	-	1.33	1.33	1.41	1.90
Catastrophes			*FF*	*FF*	*FFF*	*FFF*	*FFFF*	*FFFF*	*CFF*	*CFF*	*CC*	*CC*
***d*(C4-C12)**	3.382	2.203	2.170	2.170	2.137	2.137	2.103	2.002	1.968	1.968	1.933	1.544
***d*(C7-C11)**	4.360	2.216	2.180	2.180	2.144	2.144	2.108	2.002	1.967	1.967	1.932	1.555
E kcal/mol	0.00	43.80	44.04	44.04	43.78	43.78	42.96	36.78	33.55	33.55	29.86	-10.60
Rx	22.18	0.24	0.00	0.00	-0.24	-0.24	-0.48	-1.22	-1.33	-1.33	-1.71	-6.81

Table S7. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), O9–C11/O10–C11 bond lengths (Å), and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS2-b2** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C means " Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**	
V(C1,C2)	2.19	3.79	3.84	3.90	3.93	4.00
V(C1,O9)	2.43	1.71	1.64	1.60	1.55	1.46
V(C2,O10)	2.44	1.56	1.51	1.47	1.42	1.34
V(C11,C12)	3.45	2.23	2.19	2.16	2.12	2.02
V(O9)	5.25	5.76	5.82	5.88	5.13	4.92
V(O10)	5.24	5.85	5.31	5.29	5.23	5.04
V(O9,C11)					0.79	1.21
V(O10,C12)			0.64	0.75	0.85	1.22
Catastrophes	-	-	*C*	*C*	*CC*	*CC*
d*(O10,C12*)	3.722	1.706	1.664	1.623	1.582	1.433
***d*(O9-C11)**	3.351	1.783	1.743	1.703	1.662	1.456
E kcal/mol	0.00	48.25	43.94	39.33	34.74	20.68
Rx	-18.22	1.21	1.52	1.82	2.13	4.22

Table S8. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C4–C12/C7–C13 bond lengths (Å), and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS1-c1** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**		**SSD-IV**		**SSD-V**	
V(C4,C5)	3.34	3.08	3.03	3.03	2.70	2.28	2.23	2.23	2.20	2.01
V(C5,C6)	2.25	2.75	2.82	2.82	2.93	3.29	3.36	3.36	3.37	3.44
V(C6,C7)	3.44	3.12	3.08	3.08	2.71	2.26	2.25	2.25	2.20	2.06
V(C12,C13)	3.42	3.32	3.09	3.09	2.75	2.23	2.18	2.18	2.13	1.90
V(C4)	-	-	-	-	0.30	0.63	0.67	0.67	-	-
V(C7)	-	-	-	-	0.33	0.77	-	-	-	-
V(C12)	-	-	-	-	0.29	0.60	0.64	0.64	-	-
V(C13)	-	-	0.23	0.23	0.31	0.55	-	-	-	-
V(C4,C12)	-	-	-	-	-	-	-	-	1.38	1.91
V(C7,C13)	-	-	-	-	-	-	1.41	1.41	1.47	1.91
Catastrophes	-	-	*F*	*F*	*FFFF*	*FFFF*	*CFF*	*CFF*	*CC*	*CC*
***d*(C4-C12)**	3.567	2.309	2.274	2.274	2.239	2.025	1.989	1.989	1.953	1.544
***d*(C7-C13)**	3.730	2.271	2.233	2.233	2.196	1.970	1.933	1.933	1.896	1.545
E kcal/mol	0.00	28.67	28.46	28.46	27.82	12.34	8.00	8.00	3.39	
Rx	-14.50	0.00	0.25	0.25	0.51	2.04	2.29	2.29	2.54	9.40

Table S9. Basin Populations (e), IRC coordinates (RX, amu$^{1/2}$ Bohr), C2–C12/C5–C13 bond lengths (Å), and energy (kcal/mol) with respect to the beginning of SSD-I along the **TS1-c2** reaction pathway. For each SSD, the first value corresponds to the beginning of the domain while the second to its end. C and F mean "Fold and Cusp" catastrophes.

Basins	**SSD-I**		**SSD-II**		**SSD-III**		**SSD-IV**		**SSD-V**	
V(C2,C3)	3.60	3.14	2.74	2.74	2.64	2.46	2.39	2.25	2.24	2.11
V(C3,C4)	2.19	2.80	2.88	2.88	2.95	3.11	3.15	3.32	3.35	3.45
V(C4,C5)	3.38	3.10	3.07	3.07	2.72	2.53	2.45	2.26	2.22	1.99
V(C12,C13)	3.41	3.38	3.09	3.09	2.78	2.55	2.49	2.22	2.18	1.97
V(C2)	-	-	0.39	0.39	0.42	0.62	-	-	-	-
V(C5)	-	-	-	-	0.30	0.41	0.46	0.63	-	-
V(C12)	-	-	0.29	0.29	0.37	0.48	-	-	-	-
V(C13)	-	-	-	-	0.26	0.38	0.43	0.59	-	-
V(C2,C12)							1.25	1.57	1.63	1.89
V(C5,C13)									1.30	1.85
Catastrophes			*FF*	*FF*	*FFFF*	*FFFF*	*CFF*	*CFF*	*CC*	*CC*
***d*(C2-C12)**	2.975	2.203	1.992	1.992	1.957	1.889	1.854	1.722	1.693	1.518
***d*(C5-C13)**	4.222	2.378	2.345	2.345	2.313	2.248	2.217	2.081	2.044	1.572
E kcal/mol	0.00	52.74	52.95	52.95	52.72	50.75	48.96	37.47	33.98	0.03
Rx	-22.53	-0.24	0.00	0.00	0.24	0.72	0.96	1.92	2.16	7.89

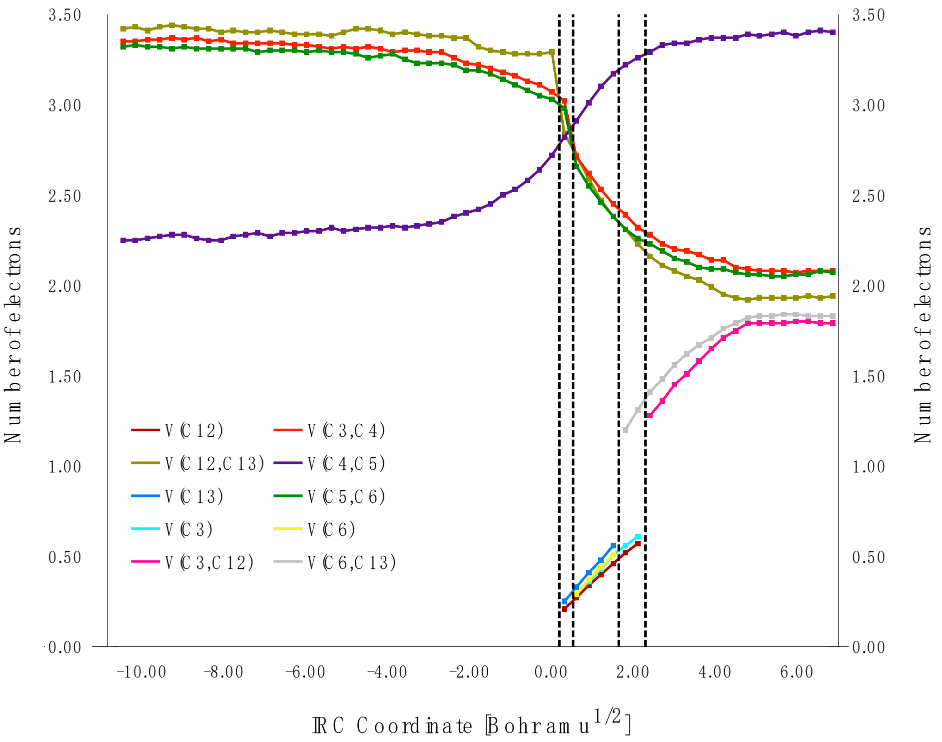

Figure S1. Population evolution (in e) of selected basins along the IRC associated to **TS2-a**

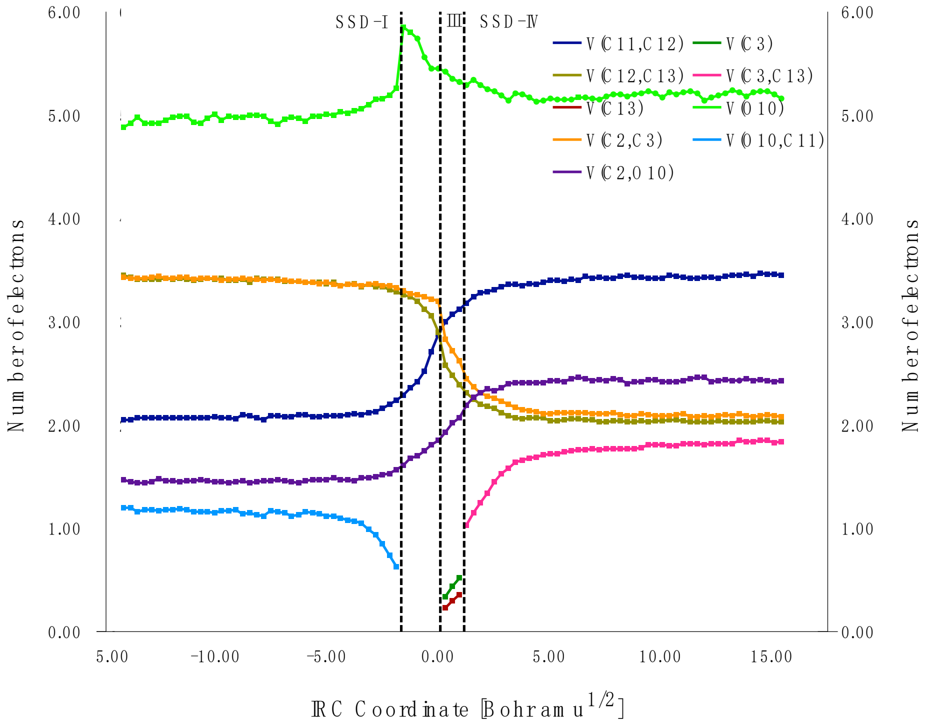

Figure S2. Population evolution (in e) of selected basins along the IRC associated to **TS1-b**

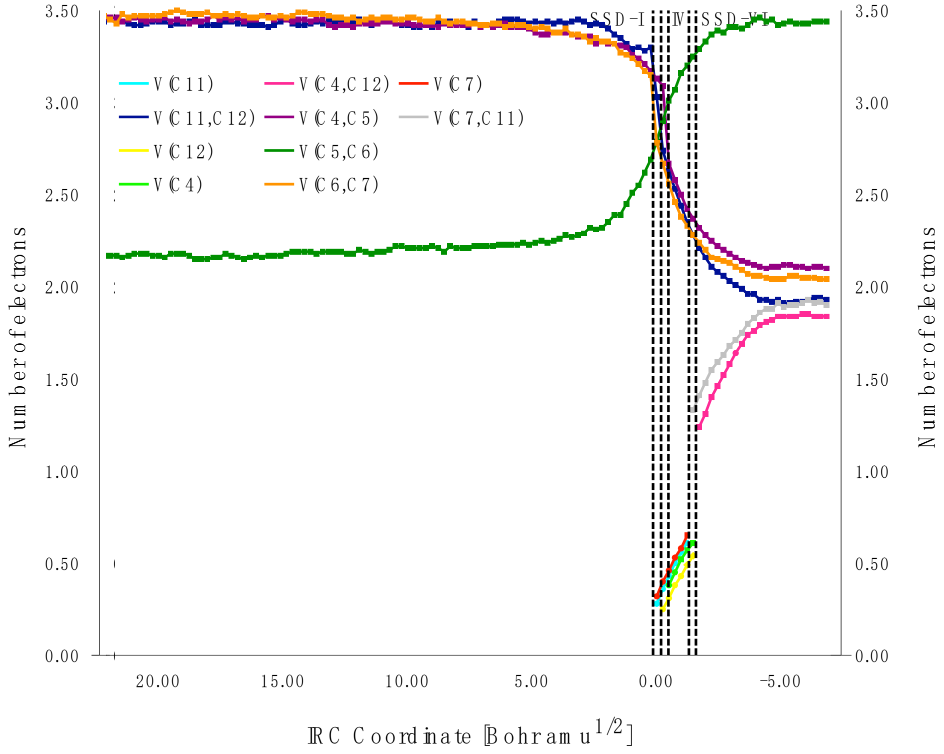

Figure S3. Population evolution (in e) of selected basins along the IRC associated to **TS2-b1**

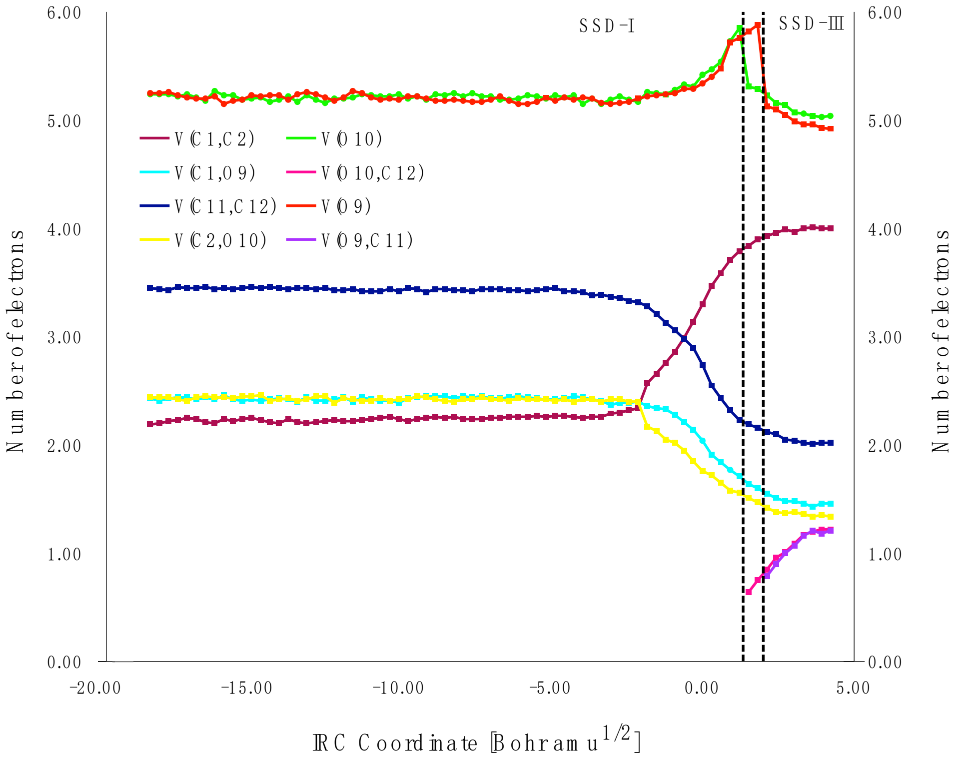

Figure S4. Population evolution (in e) of selected basins along the IRC associated to **TS2-b2**

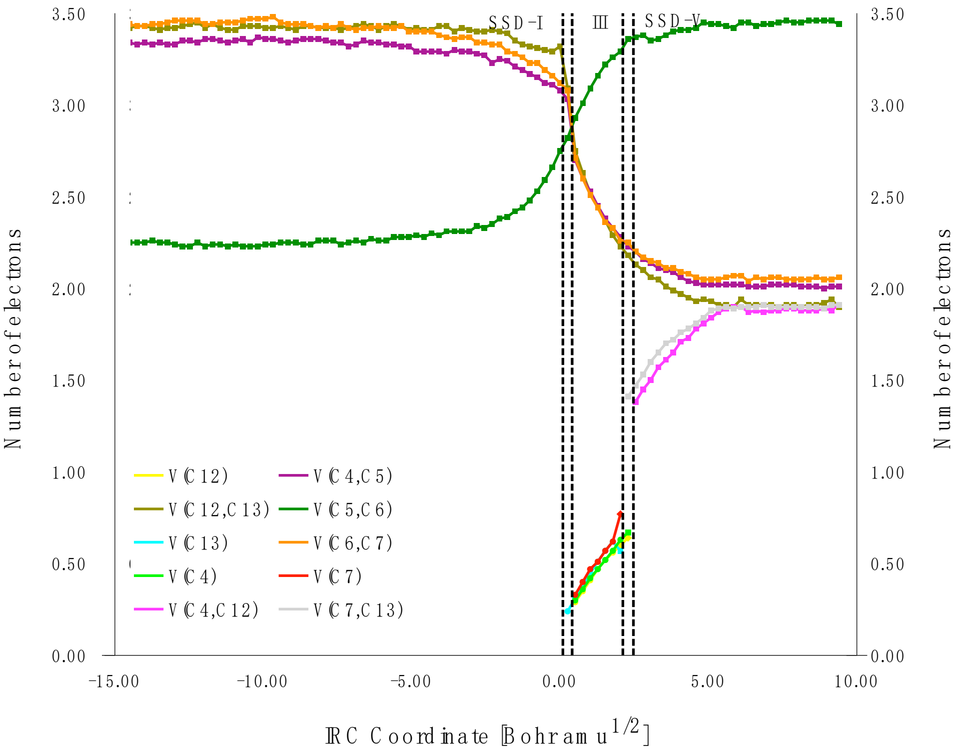

Figure S5. Population evolution (in e) of selected basins along the IRC associated to **TS1-c1**

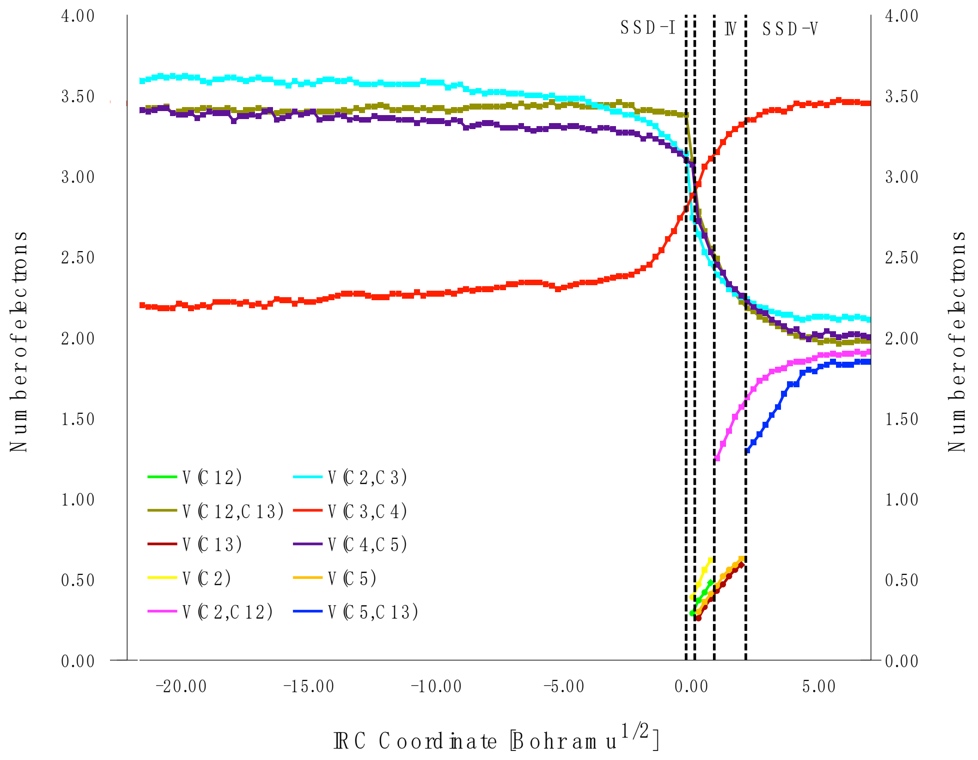

Figure S6. Population evolution (in e) of selected basins along the IRC associated to **TS1-c2**

Cartesian coordinates of the stationary points found

1

C	0.11582100	0.49620300	-1.16173800
C	-1.25976700	1.10392000	-1.20536200
C	-1.58666400	1.56776900	0.17529800
C	-2.32900100	0.85908600	1.02746200
C	-2.82824800	-0.46708300	0.75284100
C	0.25796100	-0.82486200	-0.49945600
C	-0.73000500	-1.63274600	-0.06525600
C	-2.14318800	-1.49203800	0.21098800
O	1.06814400	1.05204300	-1.66096400
O	1.49656500	-1.39759200	-0.55902700
C	2.60609300	-0.65456100	-0.00937800
C	2.27235300	-0.05842700	1.31764400
C	2.35295500	1.23960800	1.55713500
H	-1.98600700	0.36364200	-1.53357800
H	-1.21700600	1.93353600	-1.90290100
H	-1.22032900	2.54102100	0.46775500
H	-2.61971100	1.30806800	1.96756200
H	-3.83300200	-0.68346400	1.09025100
H	-0.36480900	-2.63131500	0.14458000
H	-2.68022400	-2.42864400	0.14296700
H	2.92203200	0.11093600	-0.70716300

H	3.38555900	-1.40426100	0.09321700
H	1.95140100	-0.74298600	2.09202100
H	2.64833900	1.92533900	0.77567600
H	2.12622300	1.65131000	2.52847300

TS1-a

C	-0.99261900	2.38344800	0.14928600
C	-0.62550500	1.88783900	-1.10339900
C	-1.46878500	-1.47180700	-0.09516800
C	-0.40662300	-0.50814300	-0.59964800
H	-0.61659400	2.62166800	-1.89892100
H	-1.20522100	3.44260600	0.18429600
C	-1.54066400	1.53161500	1.13520700
H	-2.51582000	1.79400900	1.53028500
C	-0.99336600	0.28692400	1.30242700
H	0.07660000	0.26754500	1.37842300
C	-1.66331100	-1.06656300	1.38045800
H	-1.17542000	-1.76342100	2.05681500
H	-2.72908500	-1.03801600	1.58982500
O	-2.16819300	-2.18282300	-0.75501600
C	-0.71582800	0.52857100	-1.47541000
H	-1.38932100	0.30463000	-2.29490000
O	0.84084600	-0.85774600	-0.20702200
C	1.89129800	0.07962700	-0.46954600
C	3.17721100	-0.57046700	-0.09542300
H	1.72649300	0.99300700	0.10478100
H	1.85567000	0.33740500	-1.52845600
C	4.06302400	-0.00828400	0.70771600
H	3.36601000	-1.53853500	-0.53829200
H	3.87481800	0.95543000	1.15895500
H	5.00165800	-0.48834200	0.93450000

TS2-a

C	0.88433500	-2.05409200	0.50231300
C	0.52683000	-1.20362000	1.54527900
C	-2.04024000	0.17483800	0.04012300
C	-0.53266400	0.48233100	-0.00327300
H	0.75892400	-1.47518700	2.56356700
H	1.44044100	-2.95562300	0.70840200
C	0.72815200	-1.59616700	-0.79030600
H	1.12968500	-2.16452800	-1.61548200
C	-0.41072800	-0.67522500	-1.05514700
H	-0.39123900	-0.25436500	-2.05511000
C	-1.83817300	-1.15496700	-0.67928200
H	-2.52685600	-1.35174300	-1.49374400
H	-1.83461500	-1.98880100	0.01848000
O	-2.98849300	0.79619200	0.39708300
C	0.13952800	0.09253500	1.26812700
H	0.00821000	0.79411800	2.08060800
O	-0.20735800	1.77315000	-0.40981000
C	1.12986600	2.13694900	-0.03506800

C	1.95580900	0.90768500	0.21877400
H	1.09656400	2.76365000	0.85385100
H	1.52070400	2.72621500	-0.86028100
C	2.25387700	0.02954100	-0.79686700
H	2.54497900	0.88541400	1.12113600
H	1.95340000	0.27254000	-1.80605200
H	3.08706000	-0.64527900	-0.70160100

TS1-b

C	0.18426400	1.51722100	0.26609500
C	1.68295800	1.45211400	0.40421300
C	2.15242200	0.76509300	-0.84077700
C	2.36247600	-0.54702500	-0.93065600
C	2.16448900	-1.49245900	0.15457200
C	-0.63675900	0.38512900	0.82316200
C	-0.21027200	-0.95047600	0.95783500
C	1.10746500	-1.59695300	0.97180800
O	-0.36051600	2.43608400	-0.29644100
O	-1.86867400	0.63404300	0.98072100
C	-2.73501900	0.15398200	-0.68971900
C	-2.39396100	-1.18458400	-0.71391600
C	-1.06298500	-1.53338100	-0.88917300
H	1.97072900	0.88726900	1.28653900
H	2.05923600	2.46862200	0.45168600
H	2.30552400	1.38942400	-1.70876700
H	2.76922100	-0.94360000	-1.85169900
H	2.94881300	-2.22633100	0.28666800
H	-0.93381100	-1.51078900	1.53085900
H	1.16337400	-2.39685300	1.69848700
H	-2.15869400	0.88037600	-1.24120700
H	-3.73354100	0.45751400	-0.42361700
H	-3.06800900	-1.90092100	-0.26781700
H	-0.42032200	-0.91092900	-1.49337200
H	-0.75947000	-2.56677400	-0.82266100

TS2-b1

C	-1.60534300	-0.56318400	0.14117600
C	-1.73291800	0.37816200	-1.01094600
C	-0.76544600	1.54533600	-0.89430000
C	-0.42919300	2.13783500	0.31463400
C	0.25752100	1.54495700	1.36551800
C	-0.36613600	-1.41902100	0.03106700
C	0.84294800	-1.06716600	0.84206200
C	0.97356900	0.35605100	1.38162500
O	-2.37634200	-0.67367800	1.05552900
O	-0.38711700	-2.34495900	-0.74184300
C	1.16980900	0.76182700	-1.52122600
C	2.03299600	0.36040000	-0.51208900
C	2.07943100	-1.08791200	-0.04956800
H	-2.74160100	0.78776600	-1.00587800

H	-1.57798400	-0.17699200	-1.93510600
H	-0.93603200	2.24528000	-1.70258000
H	-0.43271500	3.21966500	0.33958100
H	0.55477900	2.23324900	2.14463600
H	0.85052600	-1.78901700	1.66260500
H	1.72023600	0.34541000	2.16777200
H	1.38331700	1.68361100	-2.03601700
H	0.69896100	-0.00418200	-2.12185100
H	2.84800200	1.01230400	-0.24108000
H	2.97362600	-1.26956200	0.53896600
H	2.02312400	-1.82214600	-0.84824200

TS2-b2

C	0.37008600	1.03559500	-0.80355900
C	-1.02267600	1.58722900	-0.84515900
C	-1.61998300	1.47389300	0.52842700
C	-2.27018400	0.39580000	0.96006500
C	-2.50400500	-0.80304600	0.15519600
C	0.68609500	-0.30883400	-1.12848300
C	-0.10732800	-1.43353600	-0.52557100
C	-1.60570800	-1.51868700	-0.52206500
O	1.29009100	1.67903000	-0.23054800
O	1.92983700	-0.58478100	-1.02680700
C	2.04220800	0.60120500	1.19448000
C	1.91290000	-0.75392300	0.84004300
C	0.56045900	-1.40467300	0.94505700
H	-1.60781800	1.01666400	-1.56151200
H	-0.97958900	2.62727200	-1.15697500
H	-1.50222300	2.31932700	1.19053000
H	-2.72348300	0.42179100	1.94271400
H	-3.53204700	-1.14138800	0.11418100
H	0.27082800	-2.33917300	-0.98730100
H	-1.99733200	-2.35231300	-1.08901900
H	1.30501700	1.05442400	1.83714400
H	3.02544100	1.04022200	1.21651000
H	2.79771300	-1.36679600	0.84967600
H	-0.09123100	-0.83674300	1.60036500
H	0.62411000	-2.42341700	1.31194500

TS1-c1

C	1.44623700	1.44887600	1.12392800
C	1.23956100	0.13835400	1.49428900
C	-1.46505800	0.87224000	-1.01436400
C	-1.97568200	-0.09542000	0.04410300
H	1.96346900	-0.36296400	2.12084200
H	-1.49590900	0.34365600	-1.96881500
H	2.34276000	1.95237900	1.45867500
H	-2.21605300	1.65874900	-1.08451500
C	0.75336100	2.06860100	0.07642600
H	1.22921900	2.98776200	-0.24292200
C	-0.09938900	1.56069000	-0.90986800

H	-0.04260100	2.18987300	-1.79305700
O	-3.09384300	-0.06342000	0.47805500
C	-0.82637100	-0.90670900	0.52777900
O	-0.35576000	-1.79601400	-0.35272300
C	-0.18187200	-0.24212200	1.48653000
H	-0.81717300	0.45481900	2.01851900
C	1.04485400	-2.07831100	-0.22601500
H	1.23282900	-2.86397200	-0.95127100
H	1.24708100	-2.45822700	0.77388600
C	1.80710700	-0.82287100	-0.52727200
H	2.82258200	-0.75465300	-0.17722500
C	1.37471500	-0.03698600	-1.56779800
H	0.58744900	-0.40418500	-2.20686400
H	2.03839700	0.69419200	-1.99633700

TS1-c2

C	1.74791800	-1.17761000	0.38628000
C	0.83967400	-1.37272200	1.43131000
C	0.58774100	1.63946700	-0.87880500
C	-0.32641400	1.37578000	0.28520900
H	1.00611100	-2.26494200	2.01853100
H	0.22279100	1.13571100	-1.76998800
H	2.45210300	-1.99863200	0.32398700
H	0.55412400	2.71068900	-1.04721000
C	2.41145400	0.05309600	-0.08569800
H	3.48846400	-0.03287700	0.00208000
C	1.99182500	1.22000600	-0.56371000
H	2.74901600	1.96367800	-0.76170500
O	-0.67914200	2.27004900	1.00970200
C	-0.93528900	0.01890000	0.59949800
O	-2.30363300	0.06150600	0.27867700
C	-0.42059200	-0.81524300	1.57825100
H	-1.13020900	-1.30789900	2.22775200
C	-2.10994800	-0.37112700	-1.08812700
H	-1.90818100	0.48303800	-1.73190100
H	-3.00287500	-0.88332300	-1.43299700
C	-0.91917800	-1.29642500	-0.89609900
H	-1.25166200	-2.15510000	-0.32673000
C	0.32934200	-1.45897700	-1.46023700
H	0.76113800	-0.74218800	-2.13781200
H	0.74217800	-2.45147500	-1.51826400

Int-a

C	1.64218400	-1.26795600	-0.36695800
C	2.56664900	-0.19346500	0.18922600
C	1.33475600	0.38593700	0.94513400
C	1.16670900	1.86053300	0.89989500
C	0.60181400	2.43798600	-0.16069000
C	0.38749200	-0.46895700	0.02603300
C	-0.10608000	0.31189000	-1.14753400
C	0.02926700	1.63667000	-1.23522700

O	1.80315900	-2.35458400	-0.81969500
O	-0.58929600	-1.26196100	0.63079600
C	-1.75001000	-0.54486400	1.06525100
C	-2.89560100	-0.73963900	0.12518000
C	-3.62844000	0.25015200	-0.35468900
H	2.91427700	0.47373900	-0.59694000
H	3.40452700	-0.54469000	0.78071600
H	1.30102800	-0.00659500	1.95759900
H	1.52027800	2.45301700	1.73065700
H	0.52004800	3.51195000	-0.22407700
H	-0.60400400	-0.25701200	-1.91813000
H	-0.34999500	2.15084200	-2.10569100
H	-1.52417300	0.51577000	1.18049700
H	-2.00024900	-0.95359200	2.04252900
H	-3.11325500	-1.76675200	-0.13530200
H	-3.40181200	1.27851100	-0.10997200
H	-4.47001400	0.06745400	-1.00442200

Int-b

C	0.14756500	1.46159900	0.16414600
C	1.64563300	1.51947100	-0.00995900
C	1.99082900	0.64528700	-1.18830600
C	2.16037700	-0.67089300	-1.13210700
C	2.06926400	-1.48092800	0.08843800
C	-0.37557900	0.42000900	1.15723900
C	-0.37126800	-1.04014400	0.75973600
C	1.02731200	-1.60795800	0.90605700
O	-0.61592700	2.17439500	-0.42991000
O	-0.72943200	0.80978700	2.23800400
C	-3.09678900	0.00995500	-1.14863000
C	-2.48783200	-1.00815400	-0.56477800
C	-1.01144500	-1.25391700	-0.62412600
H	2.13709700	1.16049000	0.89147300
H	1.92144700	2.55033400	-0.20752800
H	2.07565000	1.14414300	-2.14214200
H	2.44559000	-1.19089200	-2.03753600
H	2.95600600	-2.05332700	0.33277300
H	-0.99406100	-1.52375000	1.50902600
H	1.16502000	-2.22767500	1.78064200
H	-2.54343300	0.73967000	-1.72074900
H	-4.16188500	0.15305200	-1.05432000
H	-3.06474500	-1.70811600	0.02732800
H	-0.55487300	-0.60280100	-1.36444900
H	-0.80733500	-2.28055500	-0.92553600

2

C	2.00802500	0.07992700	0.06333000
C	1.72169300	-1.18345500	-0.75274300
C	0.34191700	-0.57583300	-1.11239600
C	-0.97000400	-1.31646400	-0.81831900
C	-0.85280800	-1.99420300	0.51358600

C	0.55753800	0.53291900	-0.04945500
C	-0.38299800	0.25426200	1.14653800
C	-0.53366600	-1.18286200	1.51449500
O	2.99209200	0.57037500	0.52113700
O	0.28162900	1.85417700	-0.42398200
C	-1.10183200	2.11334800	-0.11760400
C	-1.64939200	0.79817800	0.42774900
C	-2.05110200	-0.20969800	-0.67715600
H	1.67122900	-2.06854700	-0.12382700
H	2.41392700	-1.34879300	-1.57193100
H	0.33468900	-0.14129300	-2.10818400
H	-1.23478000	-2.00737900	-1.61214500
H	-1.01118000	-3.05446900	0.63349900
H	-0.09880600	0.88843800	1.98081700
H	-0.40550000	-1.50996400	2.53386200
H	-1.60614300	2.44656800	-1.02079800
H	-1.14678500	2.90251500	0.63032600
H	-2.46483800	0.96535500	1.12340100
H	-2.16091000	0.30627900	-1.63020100
H	-3.00490100	-0.67184900	-0.44021800

3-b1

C	-1.54757800	0.46179400	-0.23054400
C	-0.87396900	1.78456700	-0.04419000
C	0.67004300	1.69616300	-0.07738100
C	1.21950600	1.19896600	1.22836300
C	1.54442300	-0.06875600	1.43754300
C	-1.12044600	-0.70800800	0.65341300
C	-0.09005500	-1.65369100	0.11807700
C	1.36442800	-1.09406800	0.37620100
O	-2.42028500	0.26708100	-1.03969900
O	-1.63851700	-0.82699200	1.73415100
C	1.22316300	0.90327100	-1.27791900
C	1.40171600	-0.61172700	-1.09844900
C	0.19388500	-1.52881800	-1.39354500
H	-1.18955300	2.18581100	0.92014200
H	-1.24007100	2.43562100	-0.83389300
H	1.00147600	2.72570700	-0.19983800
H	1.31560400	1.91956700	2.02842800
H	1.90255700	-0.38369900	2.40657500
H	-0.29072100	-2.63548300	0.53285300
H	2.02827600	-1.93909700	0.52675200
H	2.20580500	1.31897300	-1.48772900
H	0.60737200	1.09630600	-2.15732200
H	2.30266400	-0.90751900	-1.62588700
H	0.51801700	-2.48168900	-1.79955100
H	-0.60170300	-1.13337500	-2.01555100

3-b2

C	0.38854000	0.88375800	-0.82627500
C	-0.94288000	1.53684100	-0.93561500

C	-1.58805000	1.55251500	0.42284300
C	-2.26637000	0.51586900	0.90837700
C	-2.51562600	-0.72930900	0.17600000
C	0.66027000	-0.40435800	-1.06308600
C	-0.14182500	-1.52713300	-0.44093100
C	-1.64534300	-1.53143900	-0.43763800
O	1.34674300	1.60651400	-0.17963700
O	1.98394100	-0.74808900	-0.75734600
C	1.91306000	0.85387100	0.93042000
C	1.87806600	-0.66207500	0.66867800
C	0.54619700	-1.41061200	0.97170600
H	-1.55301500	0.97557100	-1.63761900
H	-0.81186200	2.54938900	-1.31118600
H	-1.48323200	2.44493500	1.02257000
H	-2.74974700	0.61518800	1.87184800
H	-3.55661200	-1.02680900	0.13272400
H	0.18383400	-2.45741700	-0.89587100
H	-2.07661400	-2.37667100	-0.95623900
H	1.36192200	1.12307400	1.83011100
H	2.94075800	1.18873700	1.01153600
H	2.73686000	-1.13709300	1.13226300
H	-0.08898600	-0.84428400	1.64604200
H	0.73498700	-2.38957800	1.40280500

4-c1

C	1.01041200	1.60764000	1.13257100
C	1.32761700	0.12625900	1.19208900
C	-1.45107000	0.57946400	-1.12476400
C	-1.88865300	-0.30778900	0.04499400
H	2.07115100	-0.08828200	1.95479700
H	-1.48819700	-0.02801600	-2.02942600
H	1.26921800	2.22419100	1.98106600
H	-2.21590000	1.34689800	-1.20697800
C	0.27803100	2.09381100	0.13561500
H	-0.04069600	3.12608200	0.15372100
C	-0.04297500	1.26358900	-1.08281200
H	-0.09877900	1.95670300	-1.92180300
O	-2.96744000	-0.22218100	0.56728700
C	-0.70434800	-1.07130200	0.50738800
O	-0.10347300	-1.80844800	-0.45367100
C	-0.05291600	-0.43865300	1.49011200
H	-0.66140300	0.10734500	2.19299800
C	1.31423300	-1.84638100	-0.29586200
H	1.69875100	-2.34187300	-1.18018600
H	1.56404700	-2.42342100	0.59570700
C	1.78188900	-0.40930200	-0.18309200
H	2.86700900	-0.37972500	-0.23188100
C	1.20099500	0.39235500	-1.36897700
H	0.99821000	-0.28380800	-2.19783700
H	1.96459700	1.09080100	-1.70268500

4-c2

C	1.57681400	-1.20133700	0.09614800
C	0.93603800	-1.08332300	1.48067700
C	0.58109500	1.61929600	-0.92427400
C	-0.46308500	1.32541000	0.13447800
H	1.55138900	-1.38959300	2.31367200
H	0.28271900	1.14501800	-1.85887800
H	2.26452400	-2.04146000	0.13415600
H	0.54396200	2.69395300	-1.06769700
C	2.41673700	0.04140100	-0.11311100
H	3.46210800	-0.04347000	0.14973400
C	1.98906700	1.22010500	-0.54392400
H	2.71724600	2.01401500	-0.62022300
O	-0.95031500	2.22146300	0.77252600
C	-0.94145800	-0.10350300	0.44298900
O	-2.37499800	-0.12062000	0.23477000
C	-0.25653800	-0.53199700	1.69298000
H	-0.67073100	-0.35250300	2.67224000
C	-2.14310500	-0.67341300	-1.09755700
H	-2.07804000	0.12719700	-1.83433200
H	-2.90679700	-1.38965500	-1.37722600
C	-0.80092200	-1.20957800	-0.58739000
H	-1.07379400	-2.09968200	-0.02526300
C	0.59366100	-1.43869900	-1.10754000
H	0.87742000	-0.79449400	-1.93171100
H	0.70267200	-2.46224400	-1.45368700