Electronic Supplementary Material (ESI) for ChemComm.

†Supporting information

Revisiting the Racemization Mechanism in Helicenes

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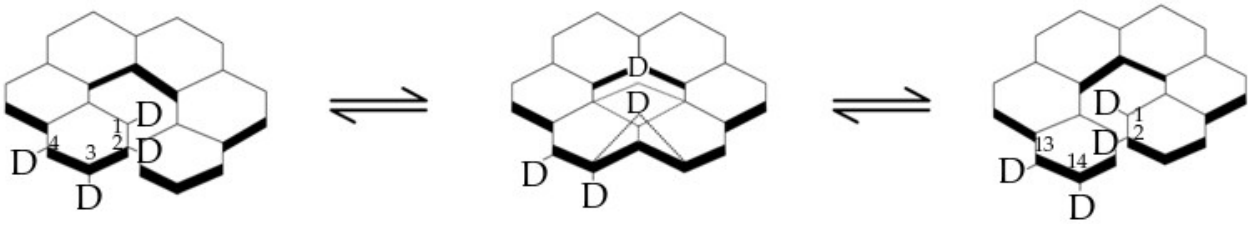

Scheme 1. Hypothetical double Diels-Alder reaction proposed by Martin and Marchant[3] as an alternative to explain the racemization mechanism in helicenes.

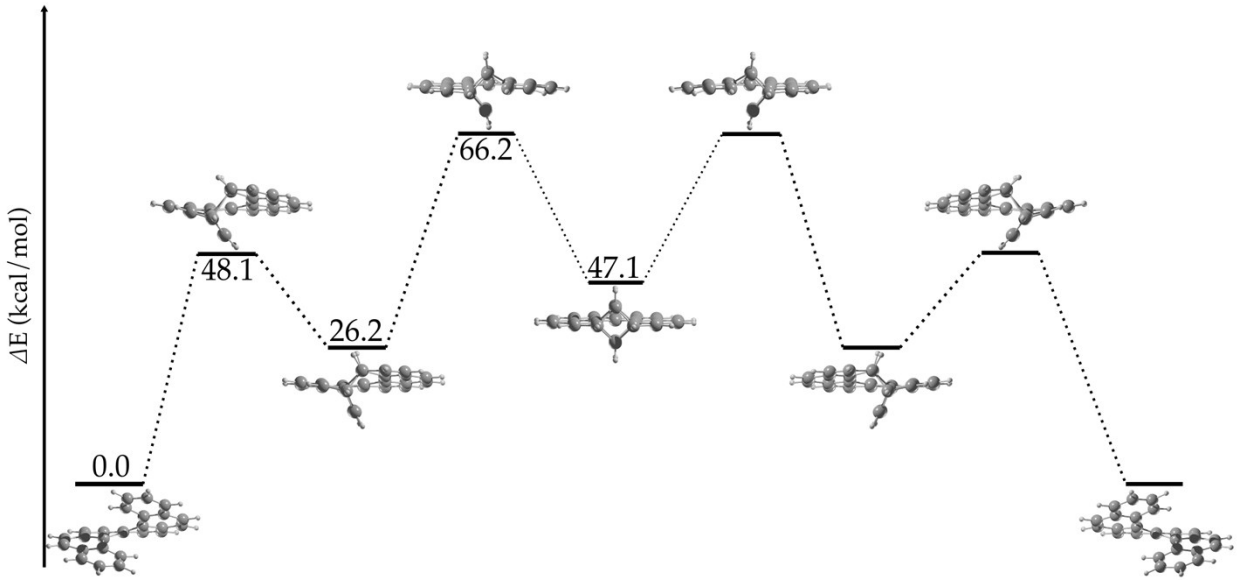

Figure 1-SI. Diels-Alder mechanism for the racemization of [6]helicene.

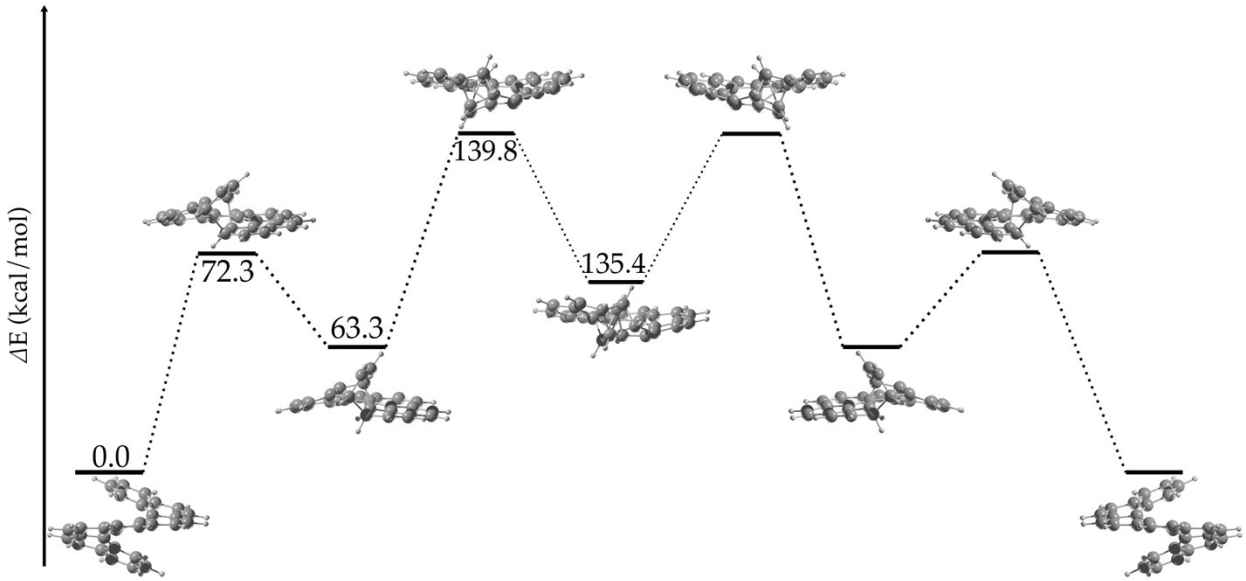

Figure 2-SI. Diels-Alder mechanism for the racemization of [7]helicene.

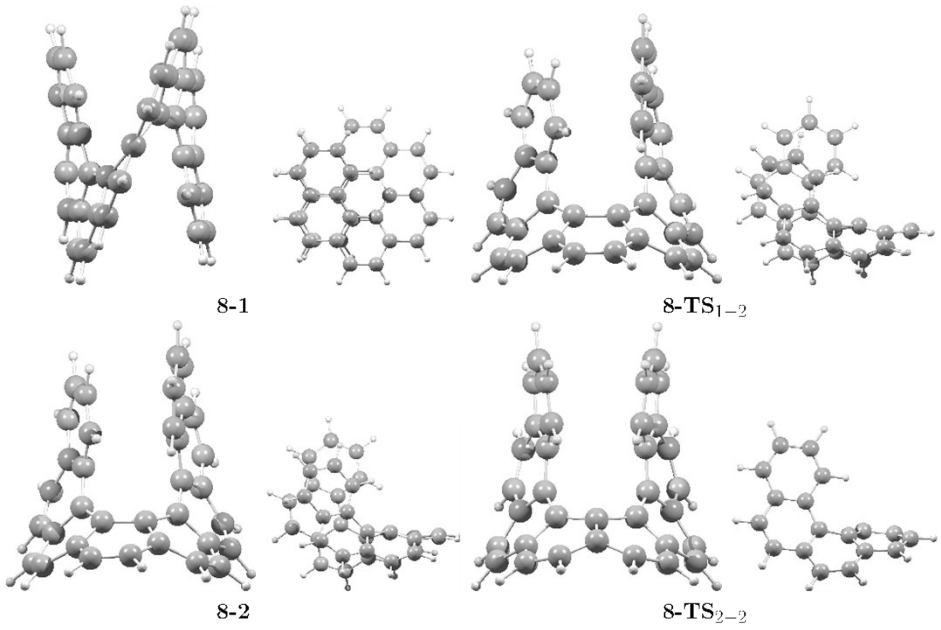

Figure 3-SI. Half of the racemization pathway of [8]helicene. Structures are followed by its side view.

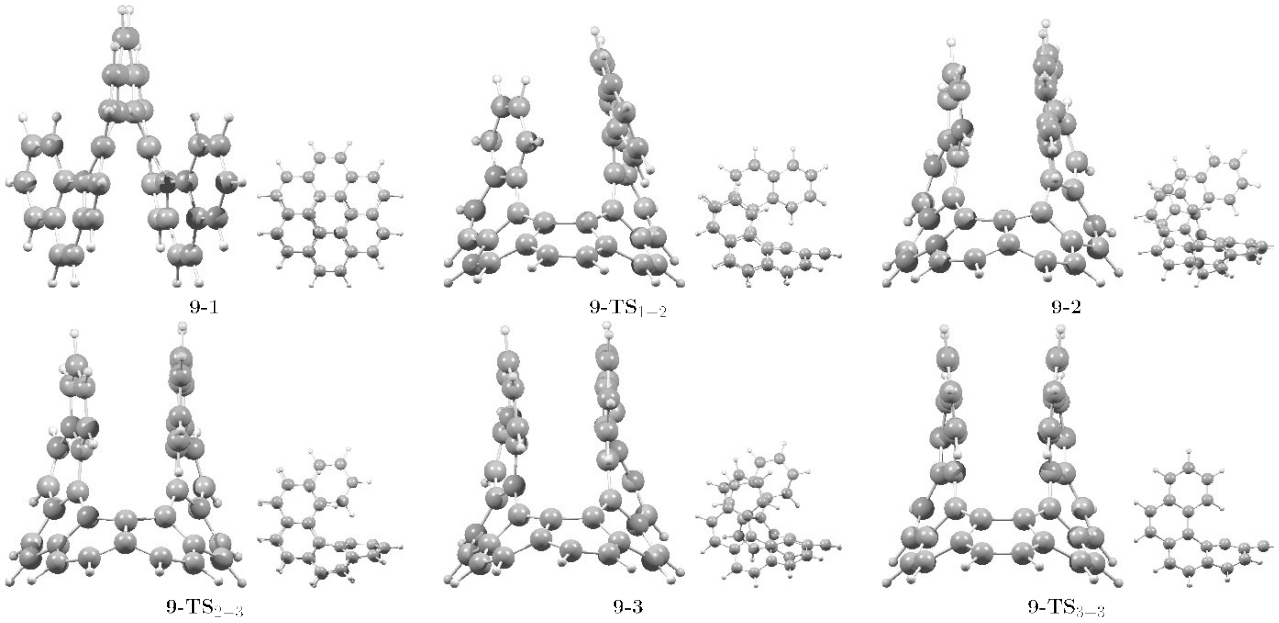

Figure 4-SI. Half of the racemization pathway of [9]helicene. Structures are followed by its side view.

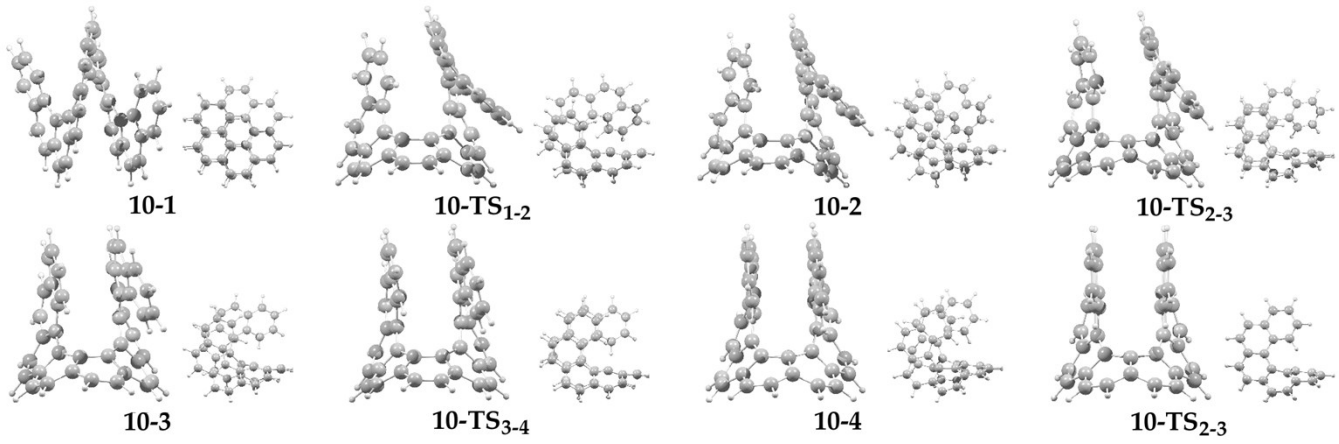

Figure 5-SI. Half of the racemization pathway of [10]helicene. Structures are followed by its side view.

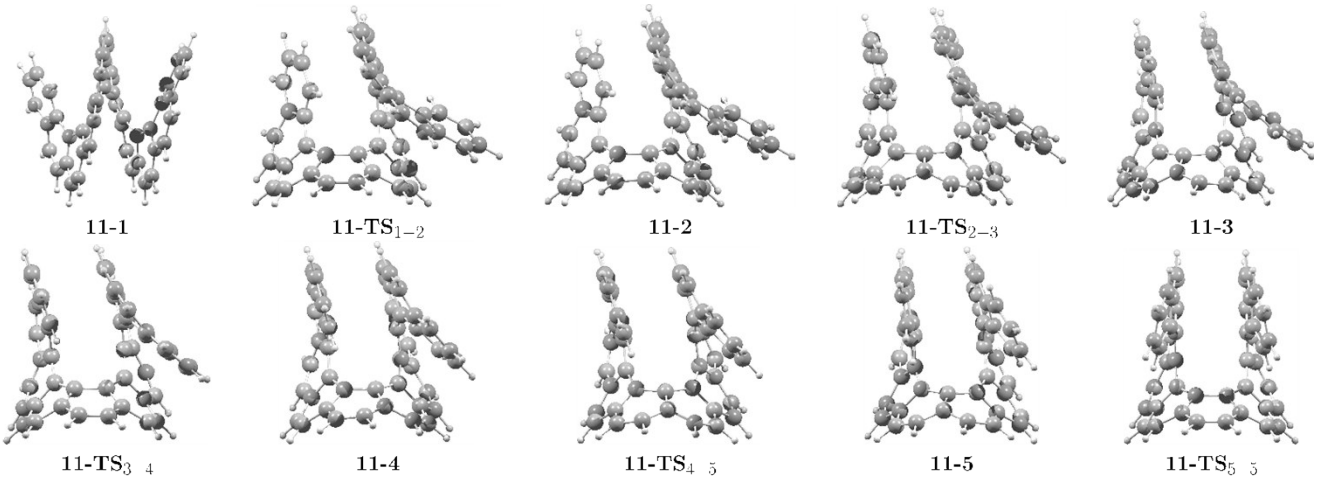

Figure 6-SI. Half of the racemization pathway of [11]helicene. Structures are followed by its side view.

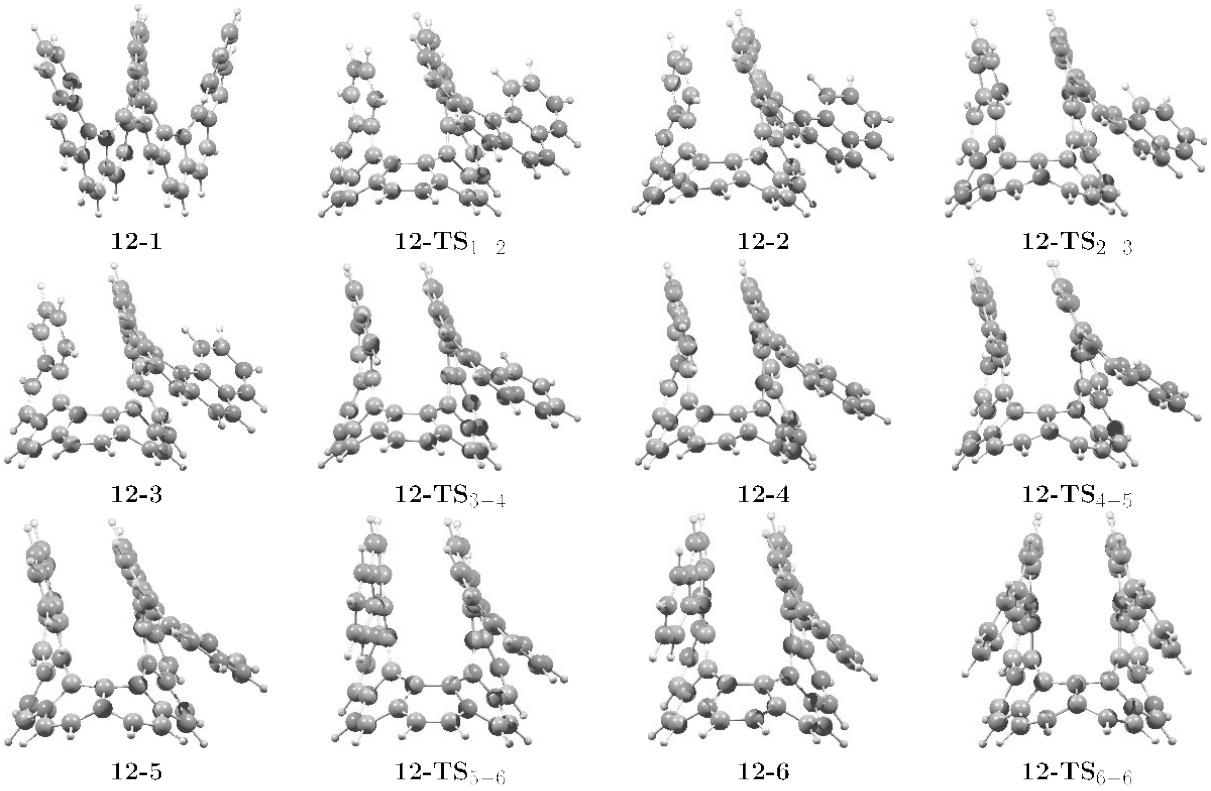

Figure 7-SI. Half of the racemization pathway of [12]helicene. Structures are followed by its side view.

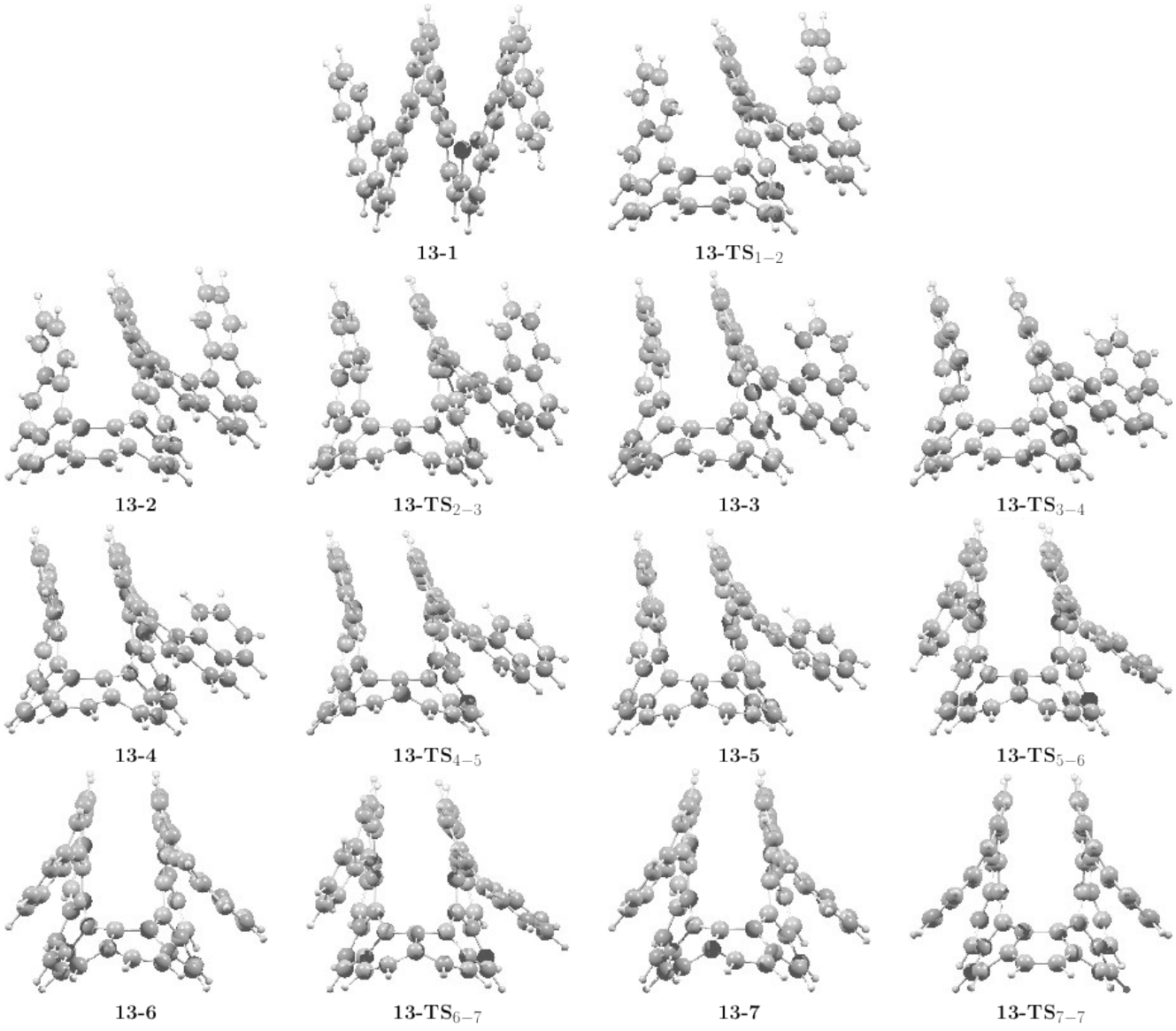

Figure 8-SI. Half of the racemization pathway of [13]helicene. Structures are followed by its side view.

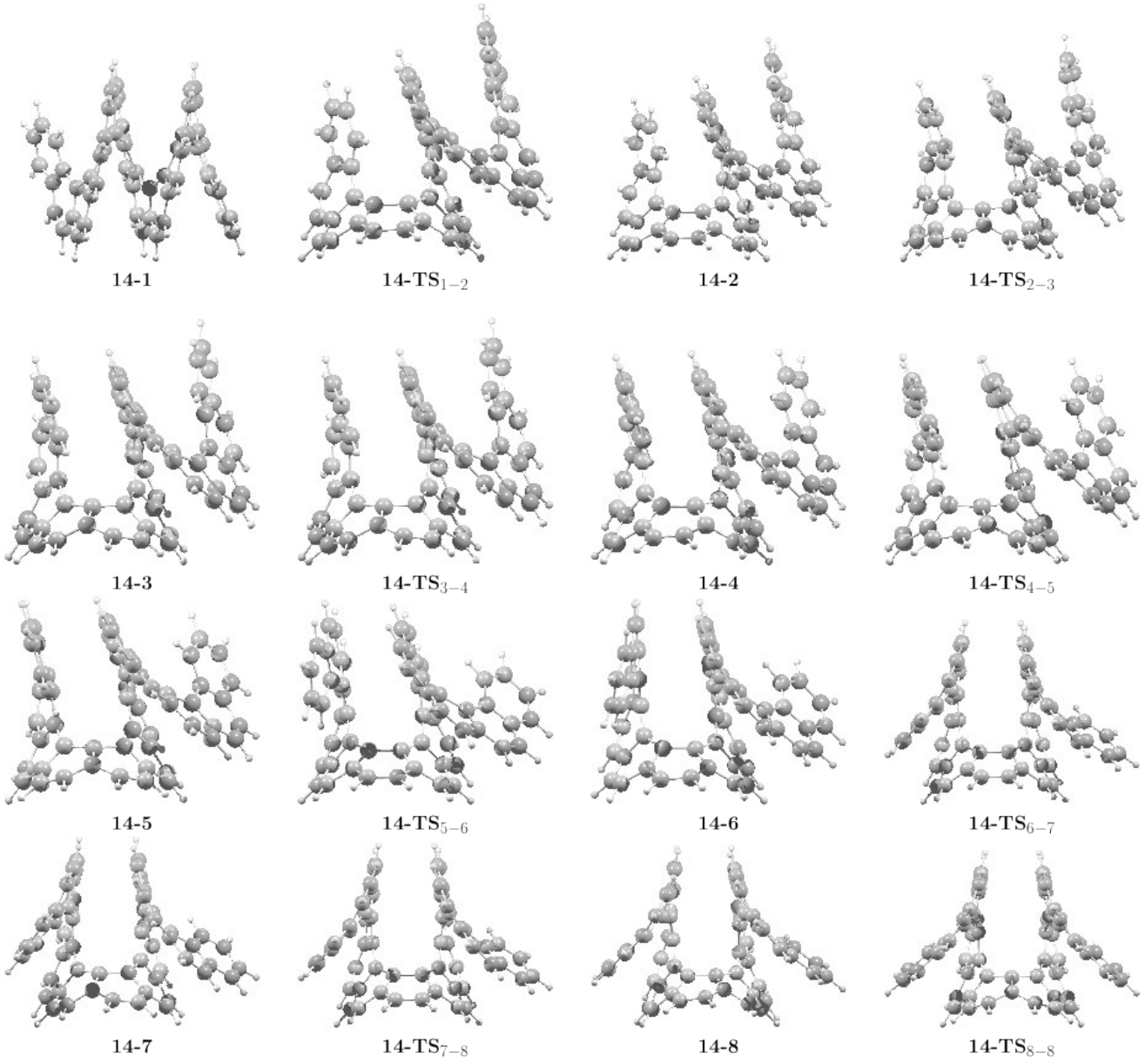

Figure 9-SI. Half of the racemization pathway of [14]helicene. Structures are followed by its side view.

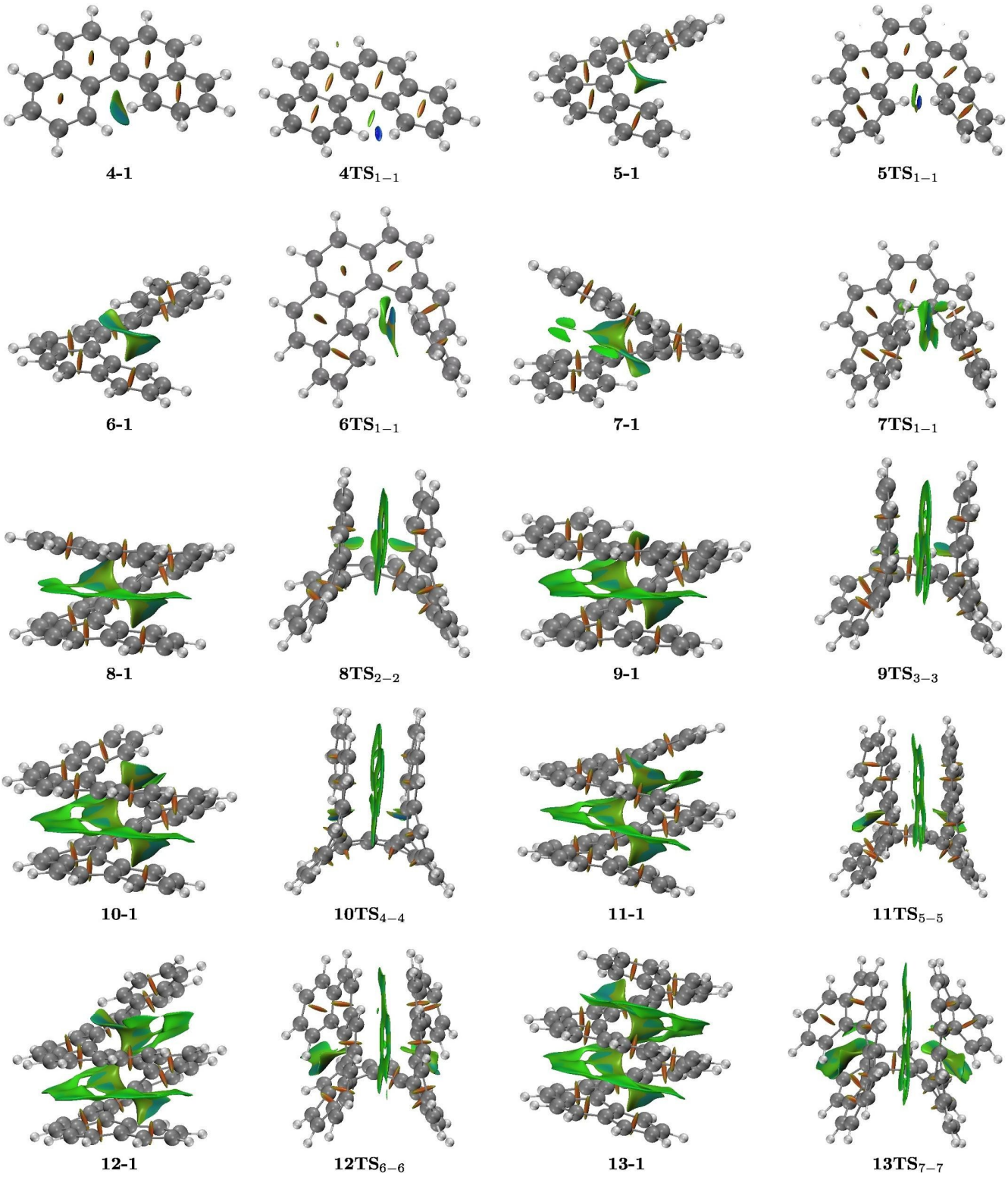

Figure 10-SI. NCI plots of [*n*]helicenes (*n* = 4-12) and its corresponding achiral transition state. Attractive interactions in green and repulsion contacts in red.

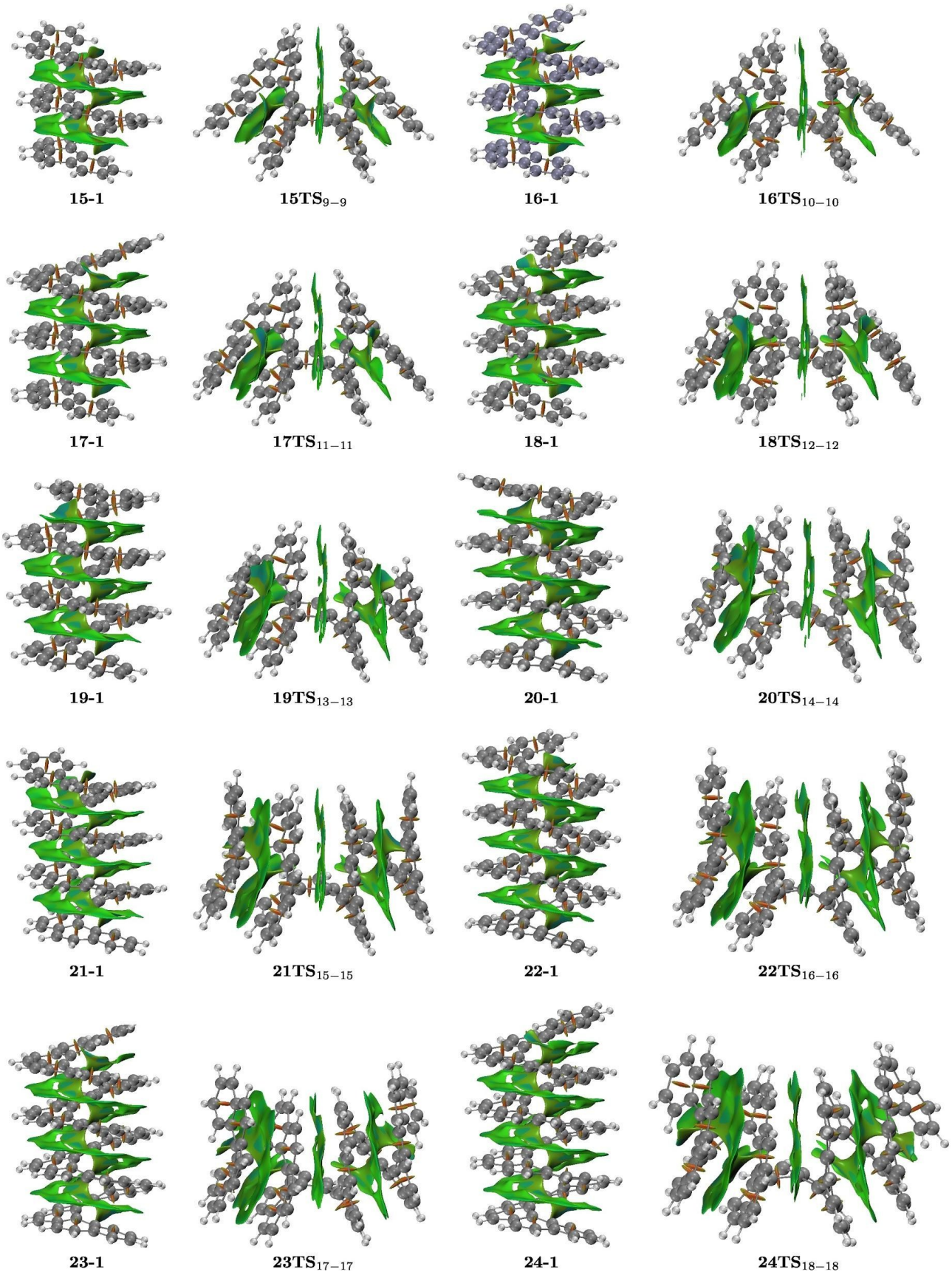

Figure 11-SI. NCI plots of [*n*]helicenes (*n* = 13-24) and its corresponding achiral transition state. Attractive interactions in green and repulsion contacts in red.

Table 1-SI. Relative energies (kcal/mol) of [*n*]helicenes (*n* = 4-14) calculated at the TPSS-D3(BJ)/6-311G(d,p) level. Values at the PBE0-D3/def2-TZVP//PBE0-D3/6-31G(d) level are given within parentheses.

[*n*]	**TS_{1-2}**	**2**	**TS_{2-3}**	**3**	**TS_{3-4}**	**4**	**TS_{4-5}**	**5**	**TS_{5-6}**	**6**	**TS_{6-7}**	**7**	**TS_{7-8}**	**8**	**TS_{8-8}**
4	4.0 (4.0)														
5	23.3 (24.4)														
6	35.7 (36.9)														
7	41.5 (42.0)														
8	39.6 (39.2)	38.3 (38.6)	42.9 (42.7)												
9	45.5 (44.2)	40.6 (40.0)	42.1 (41.2)	37.6 (37.8)	42.9 (42.3)										
10	48.8 (47.5)	48.1 (47.2)	50.7 (49.4)	45.1 (44.5)	46.2 (45.3)	38.7 (38.6)	43.6 (42.5)								
11	47.8 (46.3)	47.2 (46.0)	50.9 (49.5)	48.1 (47.4)	51.0 (49.6)	47.4 (46.6)	50.2 (48.8)	48.2 (47.3)	55.0 (52.6)						
12	50.4 (48.5)	48.9 (47.5)	51.4 (49.8)	48.9 (47.5)	50.3 (49.0)	47.3 (46.5)	50.6 (49.2)	49.5 (48.6)	58.7 (57.0)	58.6 (56.7)	66.4 (63.3)				
13	51.9 (50.2)	51.5 (50.1)	53.9 (52.1)	50.2 (49.1)	52.0 (50.4)	48.3 (47.2)	50.9 (49.3)	49.2 (47.9)	57.5 (55.7)	57.4 (55.7)	66.7 (63.9)	62.9 (60.9)	67.9 (65.0)		
14	51.5 (49.5)	51.0 (49.3)	53.9 (52.1)	51.5 (50.3)	53.6 (51.7)	50.9 (49.4)	53.1 (51.1)	51.7 (50.1)	59.8 (57.4)	59.4 (56.9)	67.1 (63.7)	62.2 (59.8)	67.0 (63.7)	62.7 (60.3)	68.7 (65.0)