

### Supporting information

**Table S1.** Singlet – triplet gap ( $\Delta E_{ST}$ , kcal/mol) of the molecules. Positive value of  $\Delta E_{ST}$  means singlet is more stable.

Molecules	$\Delta E_{ST}$
<b>I</b>	83.4
<b>2a</b>	98.5
<b>2b</b>	87.8
<b>2c</b>	71.5
<b>2d</b>	34.5
<b>2e</b>	32.0

**Table S2.** AIM properties at the bond critical point of “inverted” C-C bonds in **I**, **2a-2e** calculated at B2PLYP/6-311++G\*\* level. All values are in a. u.

	$\rho(r)$	$\nabla^2\rho$
<b>I</b>	0.181	0.11
<b>2a</b>	0.147	0.23
<b>2b</b>	0.104	0.12
<b>2c</b>	0.091	0.15
<b>2d</b>	-	-
<b>2e</b>	0.093	0.04

Cartesian coordinates of the optimized geometries using B2PLYP/6-311++G\*\* level.

**I**

6	-0.000071000	0.000033000	-0.794780000
6	-0.000053000	0.000012000	0.794883000
6	-0.048938000	1.296262000	-0.000008000
6	-1.098216000	-0.690544000	-0.000025000
6	1.147239000	-0.605747000	-0.000046000
1	2.088347000	-0.066774000	-0.000048000
1	1.232942000	-1.686823000	-0.000046000
1	-0.986220000	1.841795000	0.000009000
1	0.844432000	1.911068000	-0.000015000
1	-2.077408000	-0.224359000	-0.000024000
1	-1.101861000	-1.775002000	-0.000021000

**2a**

6	0.000214000	0.000342000	-0.853114000
6	0.000203000	0.000324000	0.853124000
6	1.199523000	0.424980000	0.000012000
6	-0.967810000	0.825970000	0.000003000
6	-0.231555000	-1.250633000	-0.000015000
9	0.686152000	-2.211883000	-0.000021000
9	-1.432828000	-1.819064000	-0.000030000
9	1.573469000	1.700273000	0.000028000
9	2.292296000	-0.331341000	0.000010000
9	-0.860599000	2.150632000	0.000017000
9	-2.258874000	0.510727000	-0.000009000

**2b**

6	0.000085000	-0.000090000	-0.987975000
6	0.000077000	-0.000096000	0.987962000
14	1.540875000	-0.373289000	-0.000007000
14	-0.447136000	1.521001000	0.000005000
14	-1.093783000	-1.147652000	0.000004000
1	-0.770521000	-2.586270000	-0.000007000
1	-2.546295000	-0.894059000	-0.000045000
1	2.624958000	0.626157000	0.000057000
1	2.047655000	-1.757950000	0.000012000
1	0.498565000	2.652238000	0.000052000
1	-1.854708000	1.960162000	-0.000027000

**2c**

6	-0.000002000	0.000167000	1.041507000
6	-0.000033000	0.000172000	-1.041508000
14	1.335481000	0.749428000	-0.000018000
14	-0.018647000	-1.531087000	-0.000003000

14	-1.316826000	0.781810000	0.000021000
9	-1.484621000	2.366136000	0.000027000
9	-2.787712000	0.169631000	0.000041000
9	2.791063000	0.101643000	-0.000040000
9	1.541966000	2.329188000	-0.000017000
9	1.246662000	-2.499217000	-0.000024000
9	-1.307347000	-2.467843000	0.000013000

**2d**

6	0.000062000	0.000104000	-1.005939000
6	0.000049000	0.000126000	1.005939000
5	-0.193646000	-1.157594000	0.000011000
5	1.099441000	0.411062000	0.000002000
5	-0.905869000	0.746364000	-0.000014000
1	2.200881000	0.822591000	0.000005000
1	-1.813283000	1.494111000	-0.000028000
1	-0.387896000	-2.317246000	0.000023000

**2e**

6	-1.117429000	-0.000039000	-0.000063000
6	1.117442000	0.000036000	-0.000049000
4	0.000053000	-0.877500000	-0.819764000
4	-0.000068000	1.148871000	-0.349830000
4	-0.000003000	-0.271366000	1.169763000

Cartesian coordinates of the optimized geometries calculated MP2(full)/6-311++G\*\* level.

**I**

6	-0.000066000	0.000125000	0.800963000
6	0.000084000	-0.000131000	-0.800873000
6	1.289468000	-0.098369000	0.000096000
6	-0.729932000	-1.067495000	0.000065000
6	-0.559546000	1.165871000	-0.000232000
1	0.019433000	2.085594000	-0.000311000
1	-1.639297000	1.289486000	-0.000329000
1	1.796483000	-1.059652000	0.000259000
1	1.936406000	0.774900000	0.000037000
1	-0.297165000	-2.064400000	0.000277000
1	-1.815916000	-1.025931000	-0.000049000

**2a**

6	0.000029000	0.000119000	-0.864542000
6	0.000020000	0.000099000	0.864543000
6	1.145104000	0.544513000	0.000012000
6	-1.044145000	0.719336000	0.000003000
6	-0.100943000	-1.263766000	-0.000015000
9	0.910325000	-2.124647000	-0.000020000
9	-1.236073000	-1.953165000	-0.000029000
9	1.385202000	1.850702000	0.000028000
9	2.309648000	-0.093949000	0.000011000
9	-1.073895000	2.047079000	0.000018000
9	-2.295250000	0.273780000	-0.000009000

**2b**

6	-0.000017000	-0.000020000	0.996525000
6	0.000011000	-0.000025000	-0.996525000
14	-1.392461000	-0.749906000	-0.000014000
14	0.046767000	1.580818000	-0.000004000
14	1.345691000	-0.830905000	0.000018000
1	1.397031000	-2.301539000	0.000024000
1	2.683533000	-0.218080000	0.000040000
1	-2.691649000	-0.058896000	-0.000039000
1	-1.530798000	-2.214915000	-0.000014000
1	-1.152809000	2.433112000	-0.000025000
1	1.294765000	2.360498000	0.000015000

**2c**

6	0.000043000	-0.000163000	-1.046342000
6	0.000013000	-0.000169000	1.046343000
14	1.377560000	-0.666384000	0.000018000
14	-0.111623000	1.525977000	0.000003000
14	-1.265909000	-0.859747000	-0.000021000
9	-1.337077000	-2.450326000	-0.000027000

9	-2.770387000	-0.338602000	-0.000041000
9	2.790230000	0.068086000	0.000040000
9	1.679488000	-2.229672000	0.000017000
9	1.091590000	2.568701000	0.000024000
9	-1.453922000	2.382274000	-0.000013000

**2d**

6	0.000009000	0.000013000	-1.032679000
6	0.000013000	-0.000012000	1.032679000
5	0.622062000	0.981951000	0.000011000
5	-1.161369000	0.047623000	0.000002000
5	0.539224000	-1.029755000	-0.000014000
1	-2.339164000	0.096974000	0.000005000
1	1.086298000	-2.073427000	-0.000028000
1	1.253146000	1.977350000	0.000023000

**2e**

6	1.139407000	-0.000164000	-0.000090000
6	-1.139427000	0.000095000	0.000081000
4	0.000008000	0.658931000	-1.011608000
4	-0.000243000	-1.205598000	-0.064745000
4	0.000265000	0.546770000	1.076365000