

Contents

1. Introduction	2
2. Cumulenes N = 3 and N = 4 - Different computation methods	3
2.1. Singlet state - With a rotation of 30°	3
3. Boron and nitrogen linear chain	4
4. Cumulenes N = 3 - DFT Calculations	5
4.1. Singlet state	5
4.2. Triplet state	6
5. Cumulenes N = 4 - DFT Calculations	8
5.1. Singlet state	8
5.2. Triplet state	9
6. Cumulenes N = 3 - CASSCF calculations	11
6.1. Cumulene singlet - $\theta = 0$	11
6.2. Cumulene singlet - $\theta = \pi/2$	12
6.3. Cumulene triplet - $\theta = \pi/2$	13
7. Cumulene N = 4 - CASSCF calculations	14
7.1. Cumulene singlet - $\theta = \pi/2$	14
7.2. Cumulene triplet - $\theta = 0$	15
7.3. Cumulene singlet - $\theta = 0$	16
8. Cumulenes N = 11 - DFT Calculations	17
9. Diphenylbutadiene (DPBD)	20
10. Tolonophane	23
11. Metallacumulenes	28
12. Coordinates	29

1. Introduction

This supporting information describes the results obtained for the different cases studied in the paper associated: cumulenes, diphenylbutadiene and tolanophane.

Computational Details: Ground and excited-states geometries were determined at the DFT level using the B3LYP exchange-correlation functional with the 6-311G(d,p) basis set. Calculations were performed using Gaussian 09 program package^[27]. In order to obtain reliable energies and molecular orbitals CASSCF(8:10)sp/6-311G(d,p) calculations were also carried out. Calculations were performed using Molpro program packages^[28].

2. Cumulenes N = 3 and N = 4 - Different computation methods

2.1. Singlet state - With a rotation of 30°

Table S1. Representation of the molecular orbitals in helices of a [3]-cumulene at 30° of rotation according to different calculation methods in the singlet state

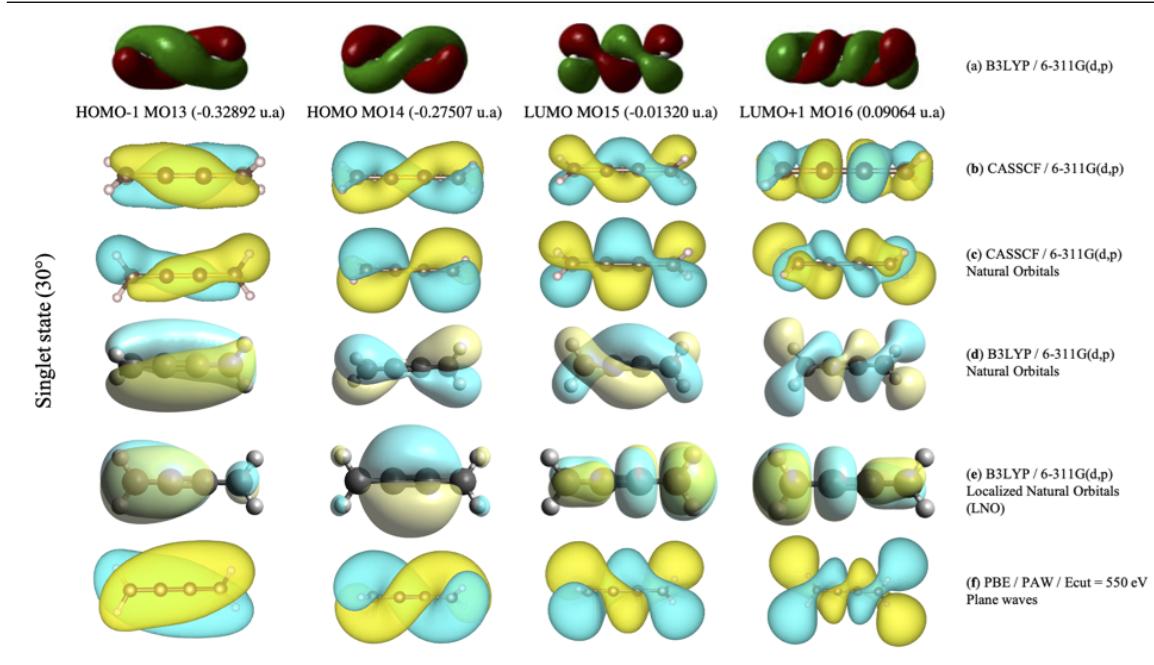
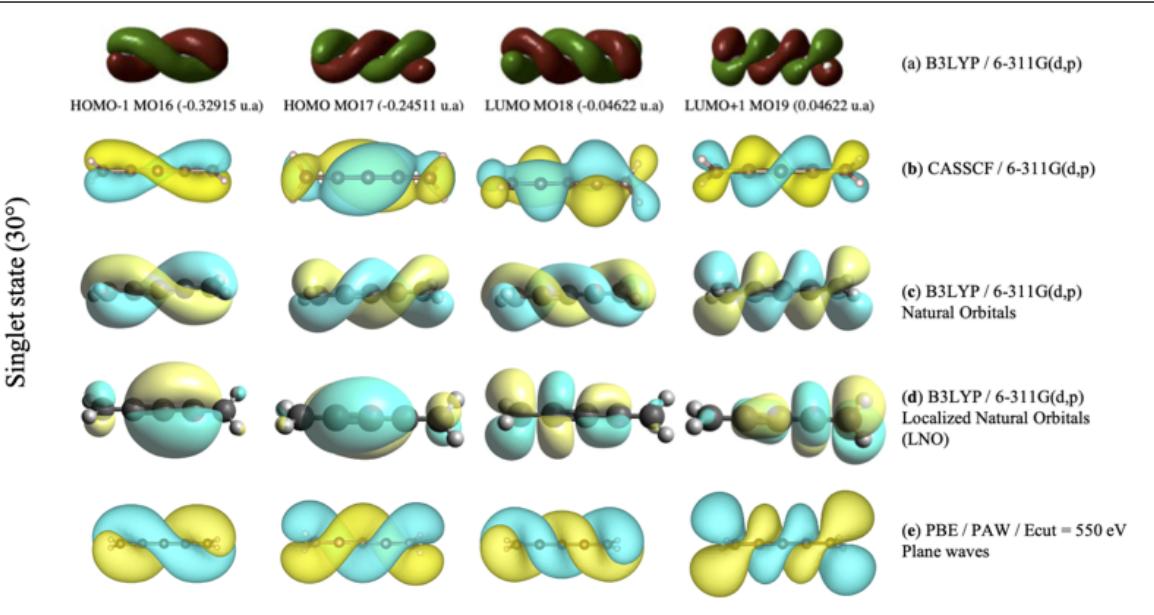


Table S2. Representation of the molecular orbitals in helices of a [4]-cumulene at 30° of rotation according to different calculation methods in the singlet state



3. Boron and nitrogen linear chain

We can also display the presence of helices in linear chains containing boron and nitrogen (by alternations of $B=N$ and $N=B$ pattern with 4 or 5 double bonds, different charges and excited states) as in the 2 following tables by DFT computations:

Table S3. Molecular orbitals of a linear chain $\text{N}=\text{B}=\text{N}=\text{B}=\text{N}$ obtained at the B3LYP/6-311G(d,p) level of theory - c = charge

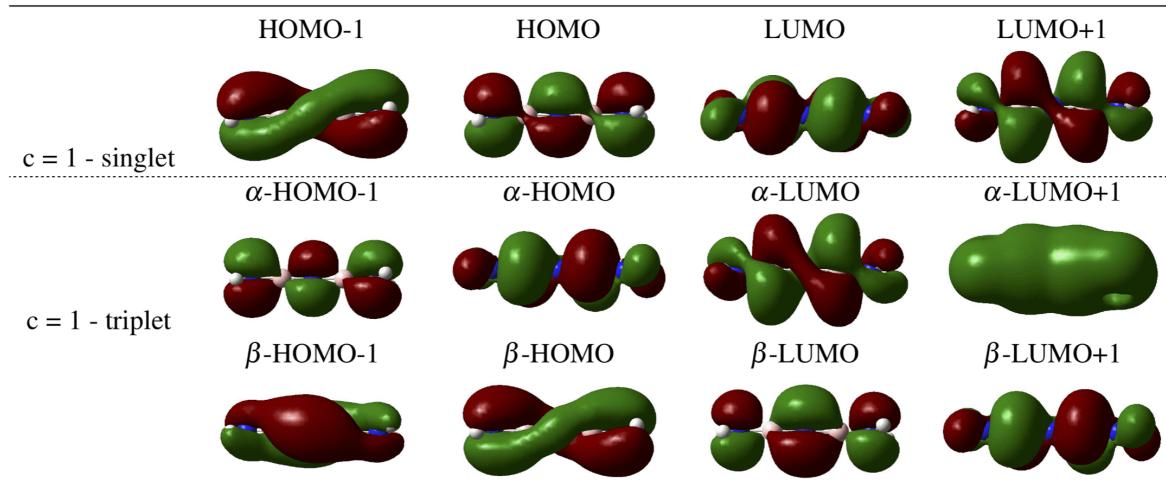
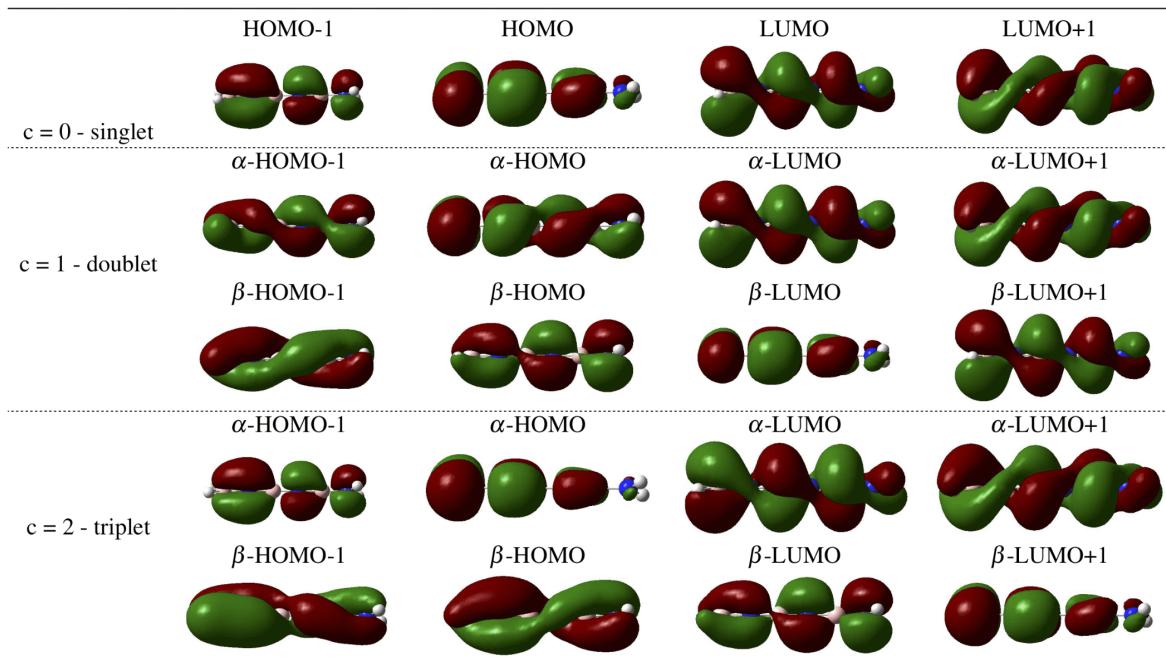


Table S4. Molecular orbitals of a linear chain $\text{B}=\text{N}=\text{B}=\text{N}=\text{B}=\text{N}$ obtained at the B3LYP/6-311G(d,p) level of theory - c = charge



4. Cumulenes N = 3 - DFT Calculations

For molecules containing 3 successive double bonds, one will distinguish cumulenes according to the positions of the ends of chains and their singlet or triplet states.

The DFT calculations were done with a C_2 symmetry. We have observed the shape of the orbitals for rotations from 0° to 90° . We have listed in the following tables the angles of rotation for which we observe changes in the shape of the orbitals.

4.1. Singlet state

Table S5. Molecular orbitals and energies for rotations from 0° to 90° obtained by DFT

0°	HOMO-1 MO13 (-0.31191 u.a)	HOMO MO14 (-0.29364 u.a)	LUMO MO15 (-0.00138 u.a)	LUMO+1 MO16 (0.07999 u.a)
10°	HOMO-1 MO13 (-0.31515 u.a)	HOMO MO14 (-0.29023 u.a)	LUMO MO15 (-0.00285 u.a)	LUMO+1 MO16 (0.08133 u.a)
20°	HOMO-1 MO13 (-0.32166 u.a)	HOMO MO14 (-0.28319 u.a)	LUMO MO15 (-0.00700 u.a)	LUMO+1 MO16 (0.08509 u.a)
30°	HOMO-1 MO13 (-0.32892 u.a)	HOMO MO14 (-0.27507 u.a)	LUMO MO15 (-0.01320 u.a)	LUMO+1 MO16 (0.09064 u.a)
40°	HOMO-1 MO13 (-0.33626 u.a)	HOMO MO14 (-0.26651 u.a)	LUMO MO15 (-0.02084 u.a)	LUMO+1 MO16 (0.09738 u.a)
50°	HOMO-1 MO13 (-0.34348 u.a)	HOMO MO14 (-0.25774 u.a)	LUMO MO15 (-0.02944 u.a)	LUMO+1 MO16 (0.10481 u.a)
60°	HOMO-1 MO13 (-0.35048 u.a)	HOMO MO14 (-0.24884 u.a)	LUMO MO15 (-0.03867 u.a)	LUMO+1 MO16 (0.11261 u.a)
70°	HOMO-1 MO13 (-0.35720 u.a)	HOMO MO14 (-0.23987 u.a)	LUMO MO15 (-0.04831 u.a)	LUMO+1 MO16 (0.12054 u.a)
80°	HOMO-1 MO13 (-0.36359 u.a)	HOMO MO14 (-0.23088 u.a)	LUMO MO15 (-0.05822 u.a)	LUMO+1 MO16 (0.12846 u.a)
90°	HOMO-1 MO13 (-0.37462 u.a)	HOMO MO14 (-0.19304 u.a)	LUMO MO15 (-0.09450 u.a)	LUMO+1 MO16 (0.13688 u.a)

4.2. Triplet state

Table S6. Molecular orbitals and energies for a rotation from 0° to 40° obtained by DFT

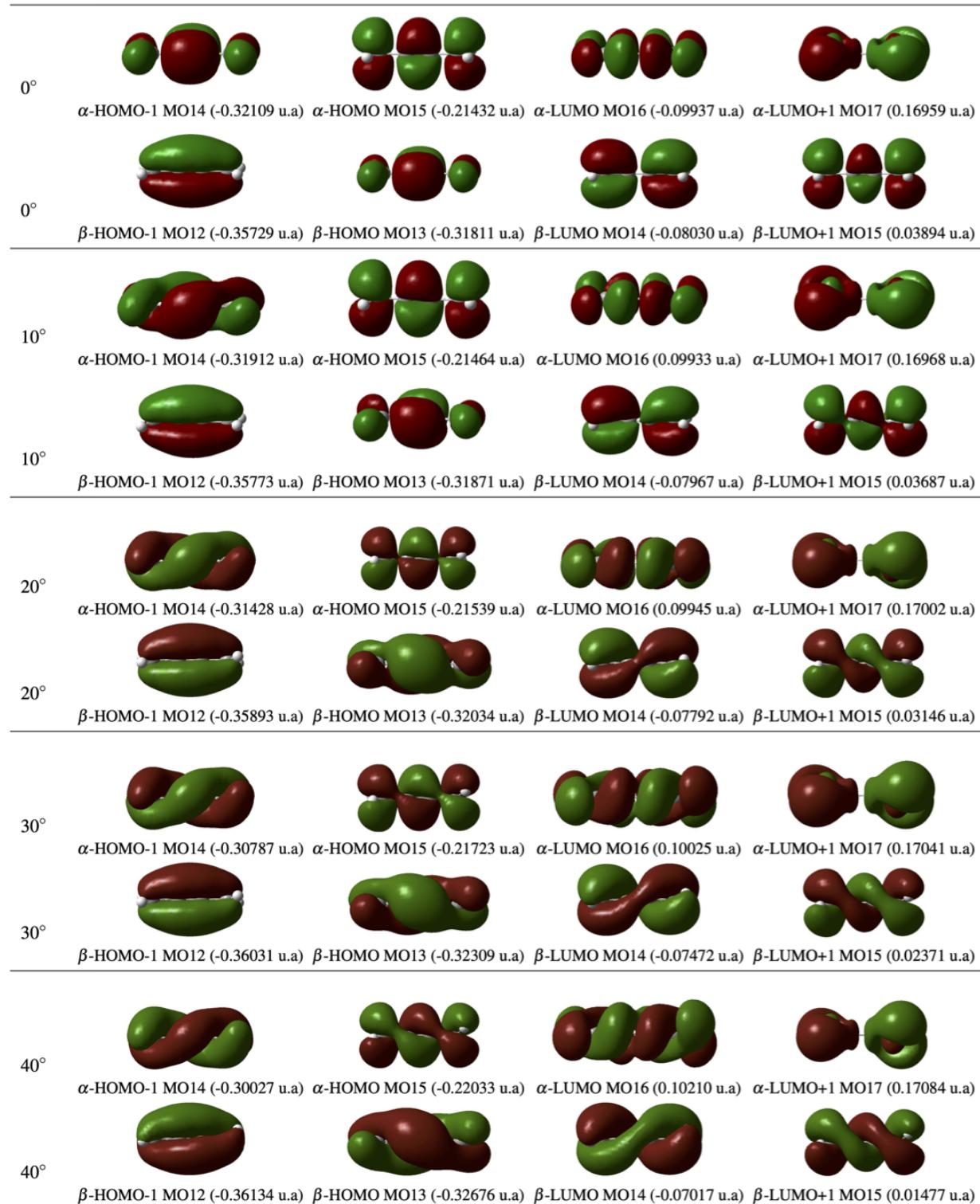


Table S7. Molecular orbitals and energies for a rotation from 50° to 90° obtained by DFT

50°	$\alpha\text{-HOMO-1 MO14 (-0.29177 u.a.)}$	$\alpha\text{-HOMO MO15 (-0.22490 u.a.)}$	$\alpha\text{-LUMO MO16 (0.10559 u.a.)}$	$\alpha\text{-LUMO+1 MO17 (0.16429 u.a.)}$
50°	$\beta\text{-HOMO-1 MO12 (-0.36138 u.a.)}$	$\beta\text{-HOMO MO13 (-0.33112 u.a.)}$	$\beta\text{-LUMO MO14 (-0.06427 u.a.)}$	$\beta\text{-LUMO+1 MO15 (0.00537 u.a.)}$
60°	$\alpha\text{-HOMO-1 MO14 (-0.28273 u.a.)}$	$\alpha\text{-HOMO MO15 (-0.23096 u.a.)}$	$\alpha\text{-LUMO MO16 (-0.11071 u.a.)}$	$\alpha\text{-LUMO+1 MO17 (0.15654 u.a.)}$
60°	$\beta\text{-HOMO-1 MO12 (-0.36020 u.a.)}$	$\beta\text{-HOMO MO13 (-0.33594 u.a.)}$	$\beta\text{-LUMO MO14 (-0.05721 u.a.)}$	$\beta\text{-LUMO+1 MO15 (-0.00414 u.a.)}$
70°	$\alpha\text{-HOMO-1 MO14 (-0.27346 u.a.)}$	$\alpha\text{-HOMO MO15 (-0.23824 u.a.)}$	$\alpha\text{-LUMO MO16 (0.11713 u.a.)}$	$\alpha\text{-LUMO+1 MO17 (0.14853 u.a.)}$
70°	$\beta\text{-HOMO-1 MO12 (-0.35785 u.a.)}$	$\beta\text{-HOMO MO13 (-0.34095 u.a.)}$	$\beta\text{-LUMO MO14 (-0.04931 u.a.)}$	$\beta\text{-LUMO+1 MO15 (-0.01359 u.a.)}$
80°	$\alpha\text{-HOMO-1 MO14 (-0.26420 u.a.)}$	$\alpha\text{-HOMO MO15 (-0.24639 u.a.)}$	$\alpha\text{-LUMO MO16 (0.12446 u.a.)}$	$\alpha\text{-LUMO+1 MO17 (0.14040 u.a.)}$
80°	$\beta\text{-HOMO-1 MO12 (-0.35452 u.a.)}$	$\beta\text{-HOMO MO13 (-0.34586 u.a.)}$	$\beta\text{-LUMO MO14 (-0.04084 u.a.)}$	$\beta\text{-LUMO+1 MO15 (-0.02289 u.a.)}$
90°	$\alpha\text{-HOMO-1 MO14 (-0.25512 u.a.)}$	$\alpha\text{-HOMO MO15 (-0.25512 u.a.)}$	$\alpha\text{-LUMO MO16 (0.13231 u.a.)}$	$\alpha\text{-LUMO+1 MO17 (0.13231 u.a.)}$
90°	$\beta\text{-HOMO-1 MO12 (-0.35045 u.a.)}$	$\beta\text{-HOMO MO13 (-0.35045 u.a.)}$	$\beta\text{-LUMO MO14 (-0.03199 u.a.)}$	$\beta\text{-LUMO+1 MO15 (-0.03199 u.a.)}$

5. Cumulenes N = 4 - DFT Calculations

For molecules containing 4 successive double bonds, one will distinguish cumulenes according to the positions of the ends of chains and their singlet or triplet states.

The DFT calculations were done with a C_2 symmetry. We have observed the shape of the orbitals for rotations from 0° to 90° . We have listed in the following tables the angles of rotation for which we observe changes in the shape of the orbitals.

5.1. Singlet state

Table S8. Molecular orbitals and energies for a rotation from 0° to 90° obtained by DFT

HOMO-1 MO16 (-0.35814 u.a)	HOMO MO17 (-0.21173 u.a)	LUMO MO18 (-0.08421 u.a)	LUMO+1 MO19 (0.04650 u.a)
HOMO-1 MO16 (-0.34128 u.a)	HOMO MO17 (-0.22989 u.a)	LUMO MO18 (-0.06364 u.a)	LUMO+1 MO19 (0.05232 u.a)
HOMO-1 MO16 (-0.33527 u.a)	HOMO MO17 (-0.23756 u.a)	LUMO MO18 (-0.05486 u.a)	LUMO+1 MO19 (0.04986 u.a)
HOMO-1 MO16 (-0.32915 u.a)	HOMO MO17 (-0.24511 u.a)	LUMO MO18 (-0.04622 u.a)	LUMO+1 MO19 (0.04622 u.a)
HOMO-1 MO16 (-0.32287 u.a)	HOMO MO17 (-0.25260 u.a)	LUMO MO18 (-0.03764 u.a)	LUMO+1 MO19 (0.04028 u.a)
HOMO-1 MO16 (-0.31706 u.a)	HOMO MO17 (-0.25996 u.a)	LUMO MO18 (-0.02996 u.a)	LUMO+1 MO19 (0.03468 u.a)
HOMO-1 MO16 (-0.30979 u.a)	HOMO MO17 (-0.26741 u.a)	LUMO MO18 (-0.02064 u.a)	LUMO+1 MO19 (0.02715 u.a)
HOMO-1 MO16 (-0.30301 u.a)	HOMO MO17 (-0.27472 u.a)	LUMO MO18 (-0.01224 u.a)	LUMO+1 MO19 (0.01981 u.a)
HOMO-1 MO16 (-0.29611 u.a)	HOMO MO17 (-0.28195 u.a)	LUMO MO18 (-0.00395 u.a)	LUMO+1 MO19 (0.01213 u.a)
HOMO-1 MO16 (-0.28908 u.a)	HOMO MO17 (-0.28908 u.a)	LUMO MO18 (0.00419 u.a)	LUMO+1 MO19 (0.00419 u.a)

5.2. Triplet state

Table S9. Molecular orbitals and energies for a rotation from 0° to 40° obtained by DFT

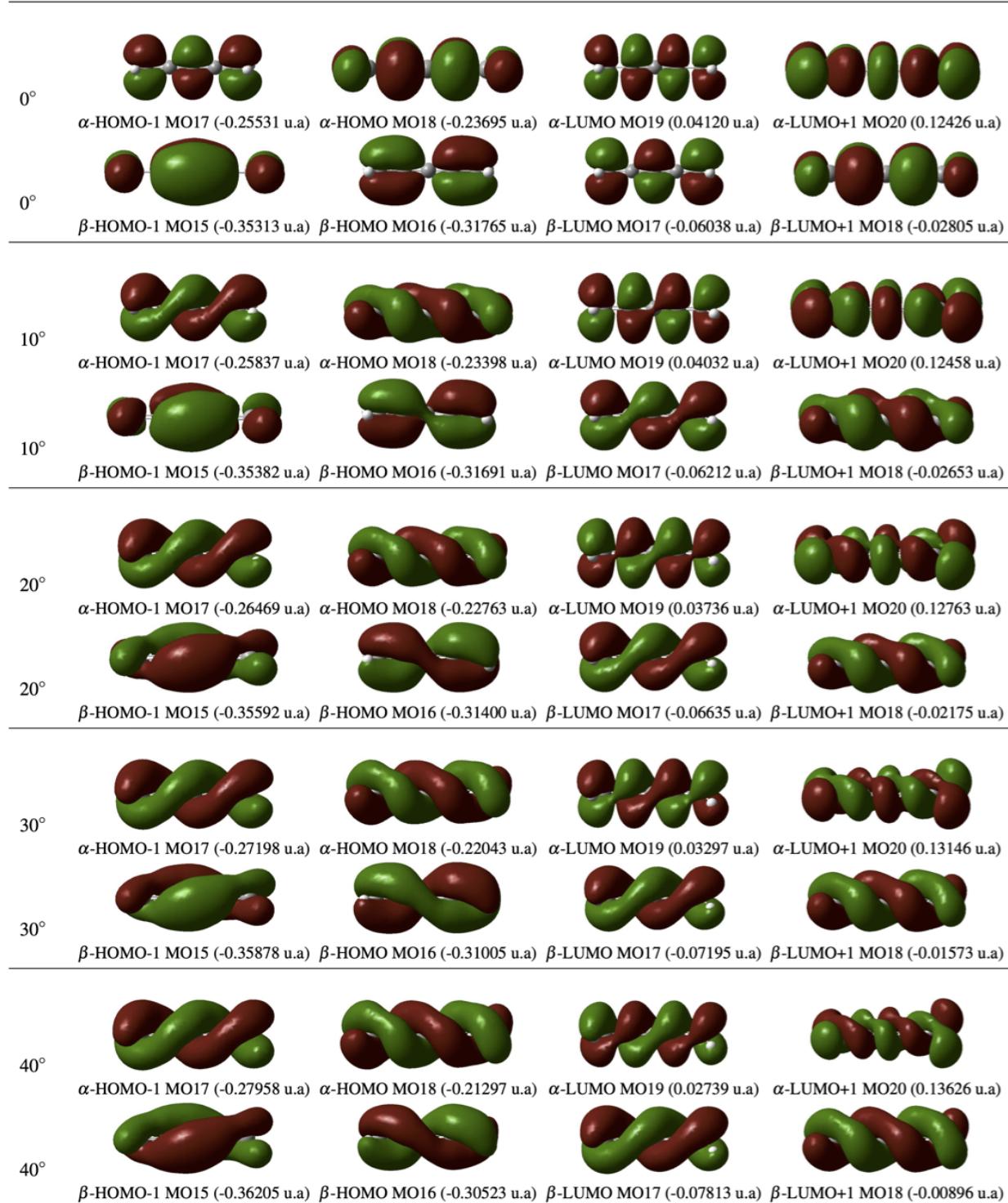


Table S10. Molecular orbitals and energies for a rotation from 50° to 90° obtained by DFT

50°				
	$\alpha\text{-HOMO-1 MO17 (-0.28729 u.a)}$	$\alpha\text{-HOMO MO18 (-0.20550 u.a)}$	$\alpha\text{-LUMO MO19 (0.02096 u.a)}$	$\alpha\text{-LUMO+1 MO20 (0.14171 u.a)}$
50°				
	$\beta\text{-HOMO-1 MO15 (-0.36543 u.a)}$	$\beta\text{-HOMO MO16 (-0.29982 u.a)}$	$\beta\text{-LUMO MO17 (-0.08450 u.a)}$	$\beta\text{-LUMO+1 MO18 (-0.00177 u.a)}$
60°				
	$\alpha\text{-HOMO-1 MO17 (-0.29186 u.a)}$	$\alpha\text{-HOMO MO18 (-0.20329 u.a)}$	$\alpha\text{-LUMO MO19 (0.01913 u.a)}$	$\alpha\text{-LUMO+1 MO20 (0.14954 u.a)}$
60°				
	$\beta\text{-HOMO-1 MO15 (-0.36672 u.a)}$	$\beta\text{-HOMO MO16 (-0.29852 u.a)}$	$\beta\text{-LUMO MO17 (-0.08468 u.a)}$	$\beta\text{-LUMO+1 MO18 (0.00633 u.a)}$
70°				
	$\alpha\text{-HOMO-1 MO17 (-0.29547 u.a)}$	$\alpha\text{-HOMO MO18 (-0.20245 u.a)}$	$\alpha\text{-LUMO MO19 (0.01849 u.a)}$	$\alpha\text{-LUMO+1 MO20 (0.15716 u.a)}$
70°				
	$\beta\text{-HOMO-1 MO15 (-0.36695 u.a)}$	$\beta\text{-HOMO MO16 (-0.29840 u.a)}$	$\beta\text{-LUMO MO17 (-0.08367 u.a)}$	$\beta\text{-LUMO+1 MO18 (0.01343 u.a)}$
80°				
	$\alpha\text{-HOMO-1 MO17 (-0.29823 u.a)}$	$\alpha\text{-HOMO MO18 (-0.20193 u.a)}$	$\alpha\text{-LUMO MO19 (0.01809 u.a)}$	$\alpha\text{-LUMO+1 MO20 (0.16329 u.a)}$
80°				
	$\beta\text{-HOMO-1 MO15 (-0.36694 u.a)}$	$\beta\text{-HOMO MO16 (-0.29846 u.a)}$	$\beta\text{-LUMO MO17 (-0.08298 u.a)}$	$\beta\text{-LUMO+1 MO18 (0.01889 u.a)}$
90°				
	$\alpha\text{-HOMO-1 MO17 (-0.29929 u.a)}$	$\alpha\text{-HOMO MO18 (-0.20174 u.a)}$	$\alpha\text{-LUMO MO19 (0.01794 u.a)}$	$\alpha\text{-LUMO+1 MO20 (0.16506 u.a)}$
90°				
	$\beta\text{-HOMO-1 MO15 (-0.36692 u.a)}$	$\beta\text{-HOMO MO16 (-0.29849 u.a)}$	$\beta\text{-LUMO MO17 (-0.08274 u.a)}$	$\beta\text{-LUMO+1 MO18 (0.02120 u.a)}$

6. Cumulenes N = 3 - CASSCF calculations

For molecules containing 3 successive double bonds, one will distinguish cumulenes according to the positions of the ends of chains and their singlet or triplet states.

6.1. Cumulene singlet - $\theta = 0$

3 para (singlet)	CASPT2(10:8)/6-311G(d,p)	E= -154.27970935 u.a.
------------------	--------------------------	-----------------------

CASPT2(opt)	CASSCF
-154.27970935	-153.81735106

	X	Y	Z
C	-0.018577187	0.000000000	1.967299627
C	0.024930148	0.000000000	0.637004866
C	0.024930148	0.000000000	-0.637004866
C	-0.018577187	0.000000000	-1.967299627
H	0.891120536	0.000000000	-2.558663305
H	-0.966827862	0.000000000	-2.494615568
H	-0.966827862	0.000000000	2.494615568
H	0.891120536	0.000000000	2.558663305

CI VECTOR		
=====		
2222222222000	0.9280734	
2222222220200	-0.2383700	
2222222 /2 \ /0 \	0.1559824	
2222222202020	-0.1403941	
22222222022200	-0.0725624	
2222222022002	-0.0633713	
2222222 / \20 / \	-0.0630348	
2222222 /2 / \0 \	0.0610232	
2222222 / / \ \0	-0.0529612	
22222 /22 \ 2020	0.0504234	

6.2. Cumulene singlet - $\theta = \pi/2$

3 perp (singlet) CASPT2(10:8)/6-311G(d,p) E= -154.23604622 u.a.

CASPT2(opt)	CASSCF
-154.23604622	-153.72490992

	X	Y	Z
C	-0.000784434	-0.001130506	2.006222202
C	0.000364032	-0.000869284	0.627920998
C	0.000364032	0.000869284	-0.627920998
C	-0.000784434	0.001130506	-2.006222202
H	0.617485404	0.698150473	-2.562463476
H	-0.612475534	-0.710758778	-2.564186100
H	0.617485404	-0.698150473	2.562463476
H	-0.612475534	0.710758778	2.564186100

CI VECTOR
=====
2222222222000 0.8362013
2222222220200 -0.5072976
2222222 / \ 200 -0.1148478
2222222 / 22 \ 00 -0.0756171
22222 / \ 220 / \ 0.0717389

Imaginary Vibration	Wavenumber
Nr	[1/cm]
1	1416.76

6.3. Cumulene triplet - $\theta = \pi/2$

3 perp (triplet) CASPT2(10:8)/6-311G(d,p) E= -154.22875921 u.a.

CASPT2(opt)	CASSCF
-154.22875921	-153.74233909

	X	Y	Z
C	0.0000000000	-0.000598834	2.001930659
C	0.0000000000	-0.001658742	0.627458606
C	0.0000000000	-0.002423220	-0.646296792
C	0.0000000000	-0.003655430	-1.988573394
H	0.0000000000	0.926570483	-2.550684098
H	0.0000000000	-0.934900649	-2.549049170
H	0.930491299	-0.000183423	2.560177291
H	-0.930491299	-0.000183423	2.560177291

CI VECTOR
=====
2222222 /00 22 / 0.9617912
222222 / \ /0 22 / 0.1639530
2222220 /20 22 / -0.1088867
222222 / / \0 22 / -0.1008935
2222222 /00 2 /2 0.0756974
2222202 /02 22 / -0.0625570
22222 / \ / \ 22 / -0.0519467

7. Cumulene N = 4 - CASSCF calculations

In this part, the cumulenes contain 4 successive double bonds with once again 2 orientations of the ends of chains.

7.1. Cumulene singlet - $\theta = \pi/2$

4 perp (singlet)	CASPT2(10:8)/6-311G(d,p)	E= -192.24875717 u.a.
------------------	--------------------------	-----------------------

CASPT2(opt)	CASSCF
-192.24875717	-191.64268131

	X	Y	Z
C	2.609236041	0.000000000	-0.000050945
C	1.280974128	0.000000000	-0.000875554
C	-0.000995055	0.000000000	-0.000011912
C	-1.280261536	0.000000000	0.000181849
C	-2.609252722	0.000000000	0.000154551
H	3.169828032	0.000000000	0.937319075
H	3.168071735	0.000000000	-0.930436185
H	-3.167167451	-0.931312624	0.000145595
H	-3.167167451	0.931312624	0.000145595

CI VECTOR		
=====		
222222222222000	0.9483487	
222222222220200	-0.1548496	
22222222202020	-0.1509444	
22222222 /2 \ 200	0.1063755	
22222222 /2 \ 2020	-0.1013521	
222222202222002	-0.0806617	
22222222022200	-0.0749715	
222222220222020	-0.0703742	

7.2. Cumulene triplet - $\theta = 0$

4 para (triplet) CASPT2(10:8)/6-311G(d,p) E=-192.2035070 u.a.

CASPT2(opt)	CASSCF
-192.20350703	-191.59105149

	X	Y	Z
C	0.001200780	0.004291193	-2.636770614
C	-0.000856940	-0.004987765	-1.292275544
C	-0.001829169	-0.001370694	0.000000000
C	-0.000856940	-0.004987765	1.292275544
C	0.001200780	0.004291193	2.636770614
H	0.003297900	0.938065457	-3.194491445
H	0.003503577	-0.921597322	-3.207292320
H	0.003503577	-0.921597322	3.207292320
H	0.003297900	0.938065457	3.194491445

CI VECTOR
=====
22222222222 / /00 0.9307024
2222222222 / \ /0 0.1851188
222222222 /2 / \0 / -0.1461723
22222222220 / /20 -0.1173034
22222222202 / /02 -0.0989781
2222222222 / / / \0 -0.0787450
2222222222 / / \ /0 -0.0786449
222222222 /2 / 0 \ 0.0719179
22222222 /2 \ 2 / 0 0.0592773

7.3. Cumulene singlet - $\theta = 0$

4 para (singlet) CASPT2(10:8)/6-311G(d,p) E= -192.19892090 u.a.

CASPT2	CASSCF(opt)
-192.19892090	-191.59968762

	X	Y	Z
C	2.6340851398	-0.0000094084	0.00000000000
C	1.2639443292	0.0000129768	0.00000000000
C	0.0067212673	0.0000142676	0.00000000000
C	-1.3108999926	0.0000366644	0.00000000000
C	-2.6119572700	-0.0000104112	0.00000000000
H	3.1846373274	-0.9227067538	0.00000000000
H	3.1846671299	0.9226700788	0.00000000000
H	-3.1756293915	0.9196363181	0.00000000000
H	-3.1755655395	-0.9196967322	0.00000000000

CI VECTOR
=====
2222222222 / \00 0.9371978
22222222 /2 \0 \ 0.1489065
222222222 / \ / \0 0.1284763
22222222 /22 \ / \0 0.0997084
2222222202 / \02 -0.0958522
22222222 /2 \0 \ 0.0913815
222222222 / \ \0 0.0764149
222222222 /2 \00 0.0717417

Imaginary	Vibration	Wavenumber
Nr		[1/cm]
1		874.35

8. Cumulenes N = 11 - DFT Calculations

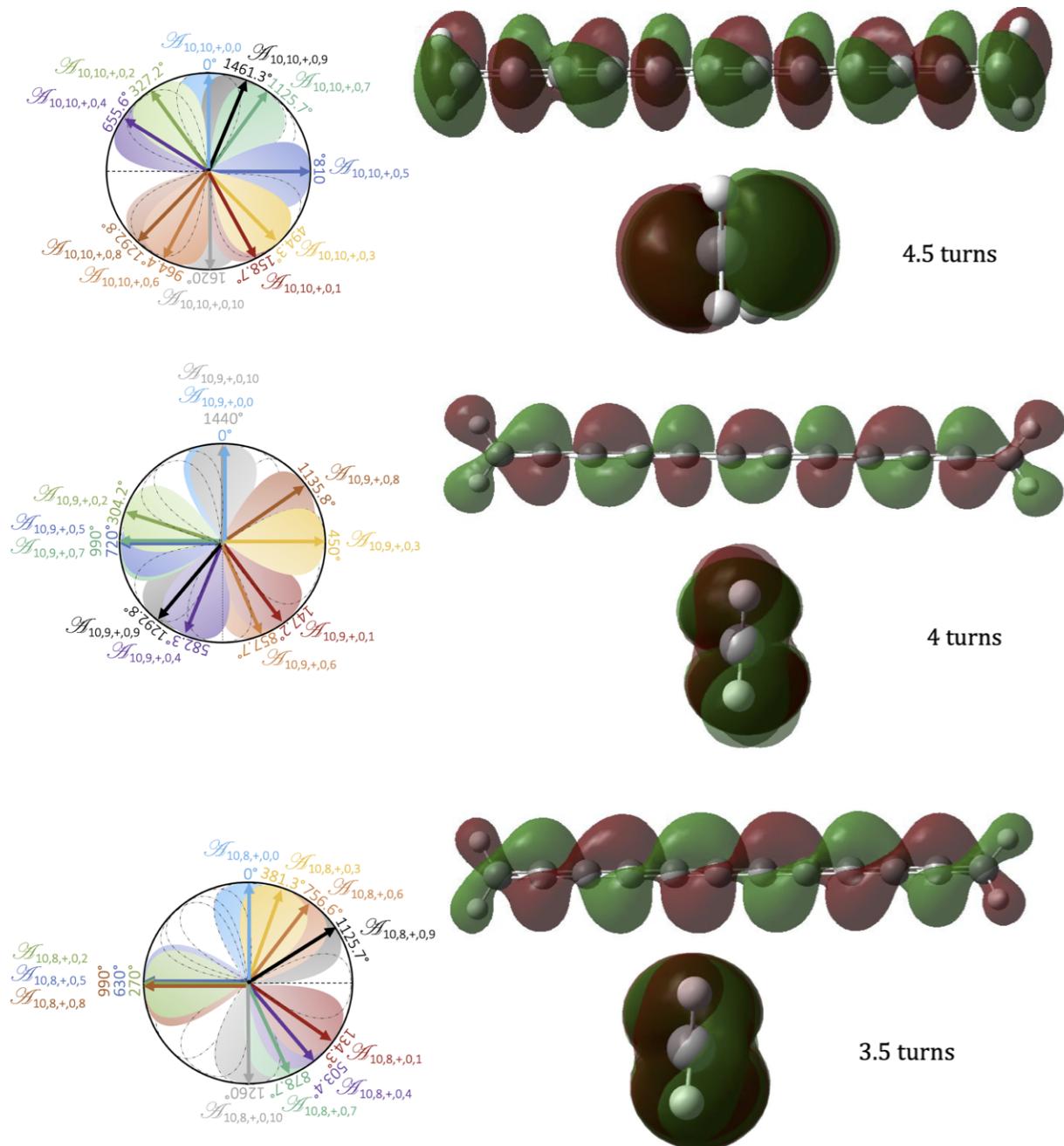


Figure S1. Distribution for $\theta = 10$, $N = 11, n = 10, n = 9, n = 8$ - Corresponding MOs obtained by B3LYP/6-311G(d,p) level of theory for the [11]-cumulene in its ground singlet state.

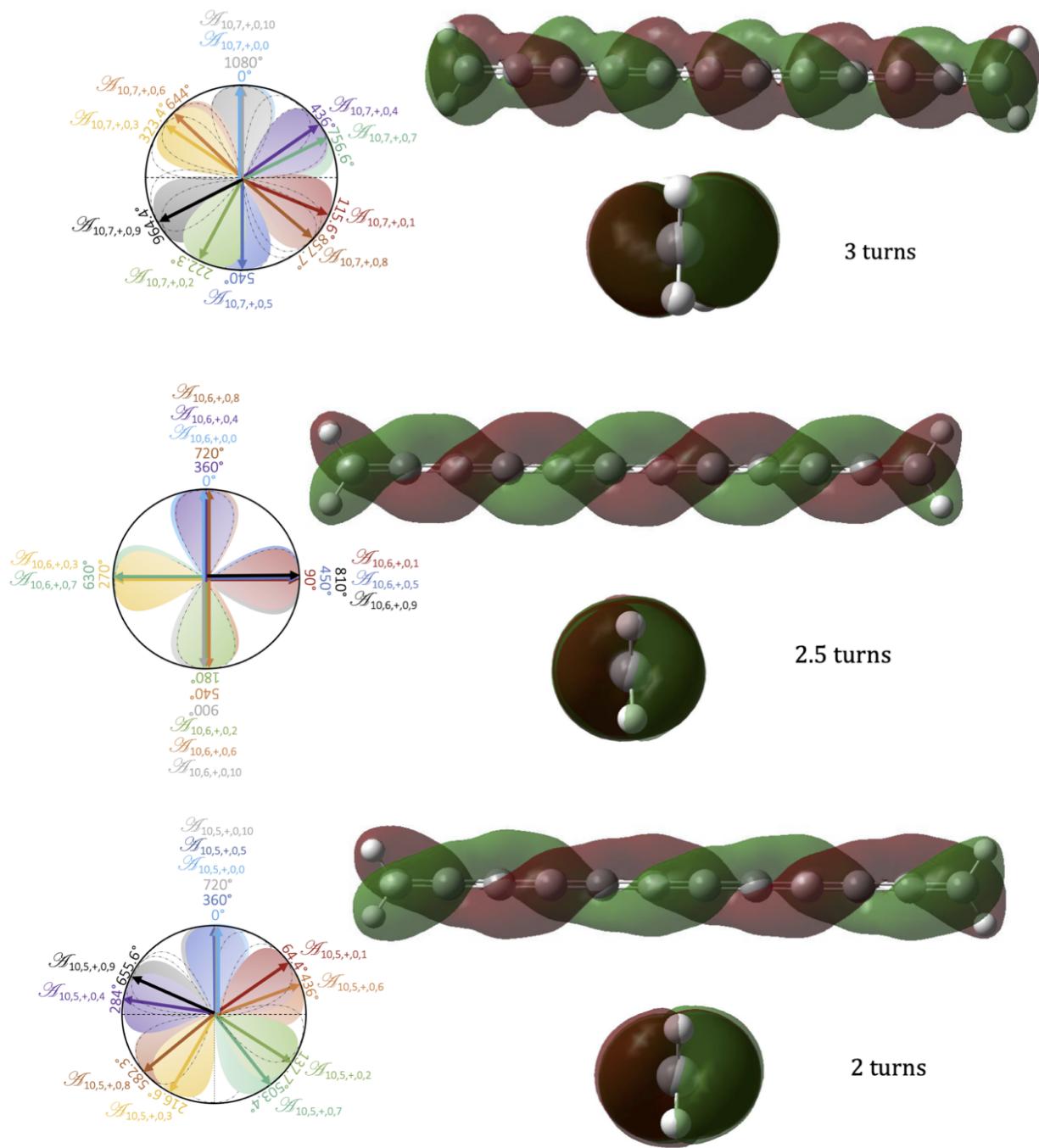


Figure S2. Distribution for $\theta = 10$, $N = 11$, $n = 7$ (LUMO), $n = 6$ (HOMO), $n = 5$ and $n = 9$ - Corresponding MOs obtained by B3LYP/6-311G(d,p) level of theory for the [11]-cumulene in its ground singlet state.

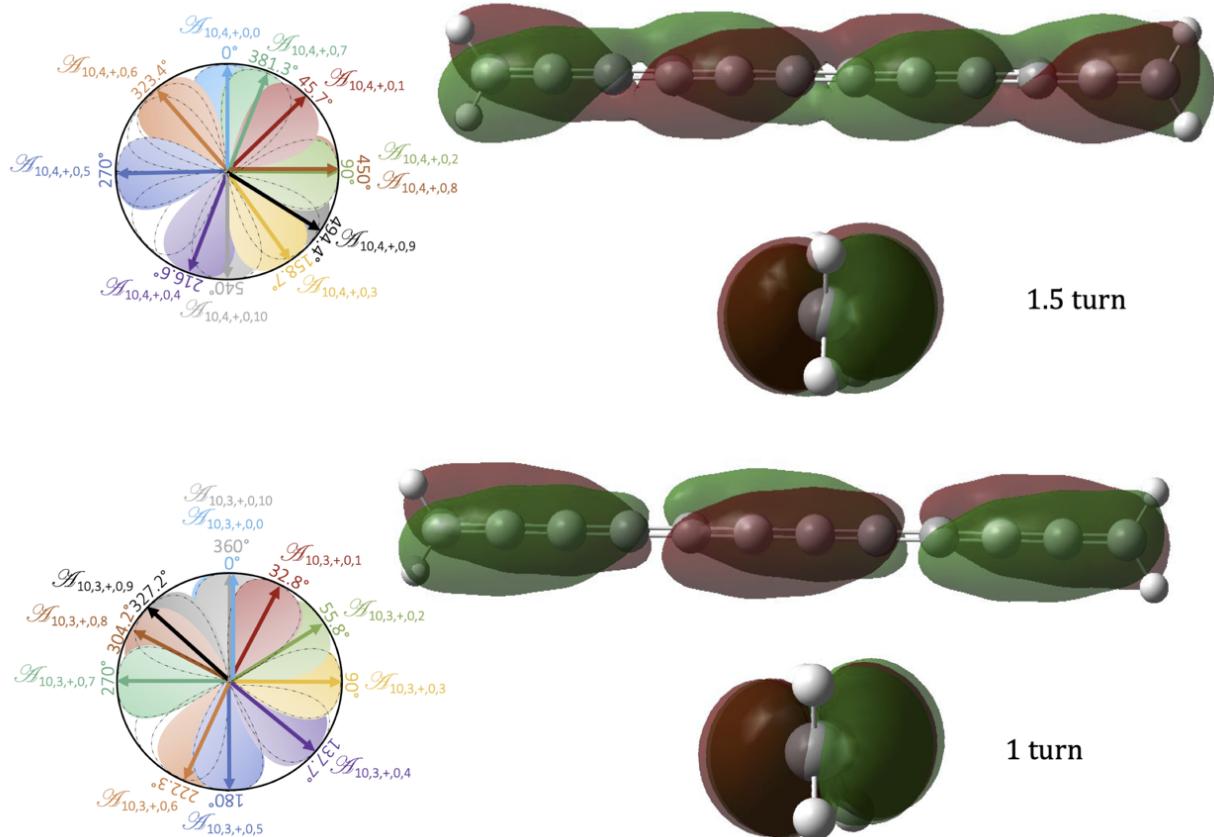


Figure S3. Distribution for $\theta = 10$, $N = 11, n = 4, n = 3$ - Corresponding MOs obtained by B3LYP/6-311G(d,p) level of theory for the [11]-cumulene in its ground singlet state.

9. Diphenylbutadiene (DPBD)

Our interest was focused on the DPBD molecule for its particularity to have a linear chain containing an alternation of triple and simple bonds like carbyne systems^[36].

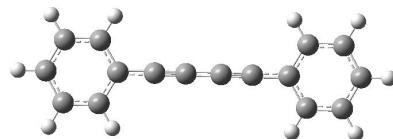


Figure S4. Representation of the molecule of Diphenylbutadiyne

The B3LYP/6-311G(d,p) calculations were done with a C_2 symmetry. We have observed the shape of the orbitals for rotations from 0° to 90°. We have listed in the following tables the angles of rotation for which we observed changes in the shape of the orbitals.

Table S11. Molecular orbitals and energies for a rotation from 0° to 13° obtained by DFT

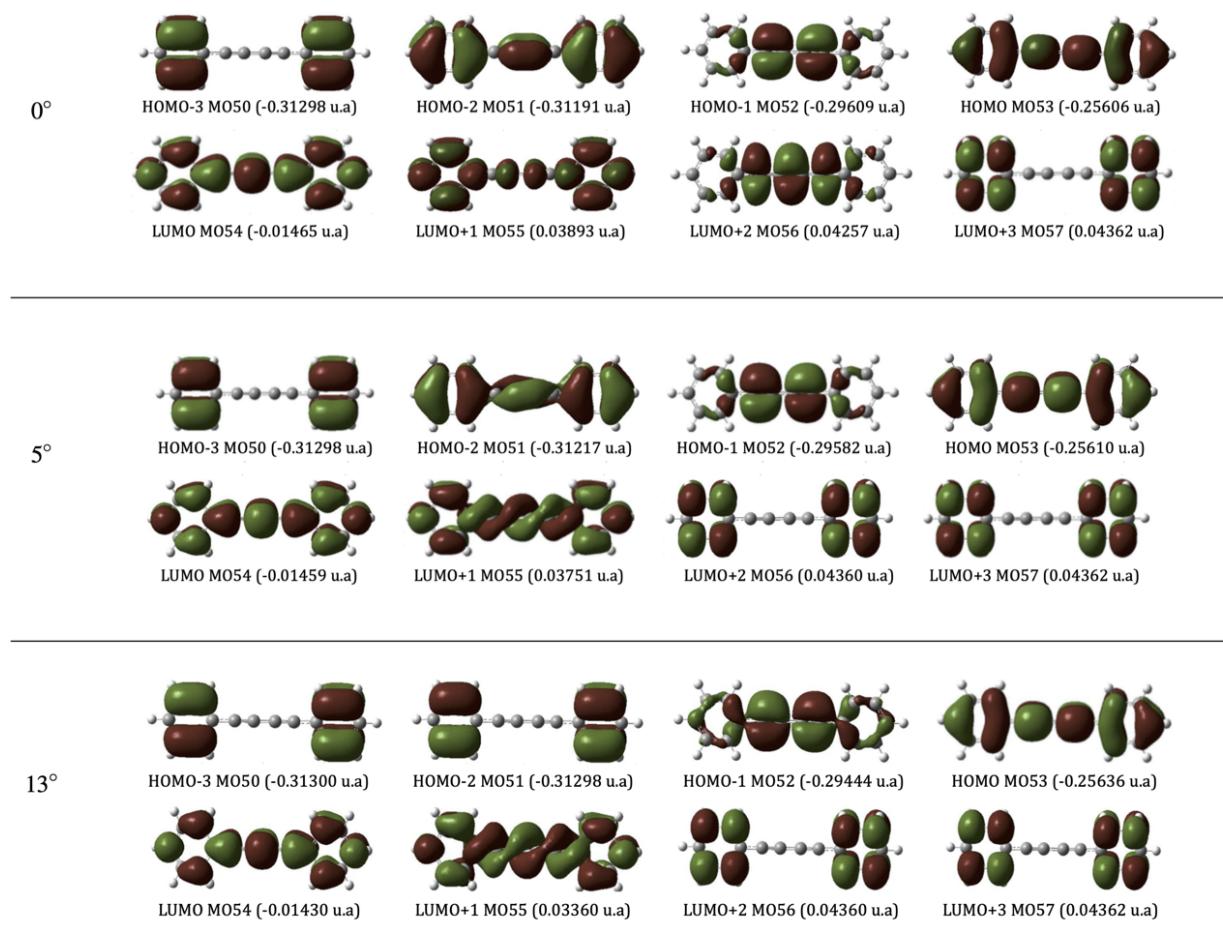
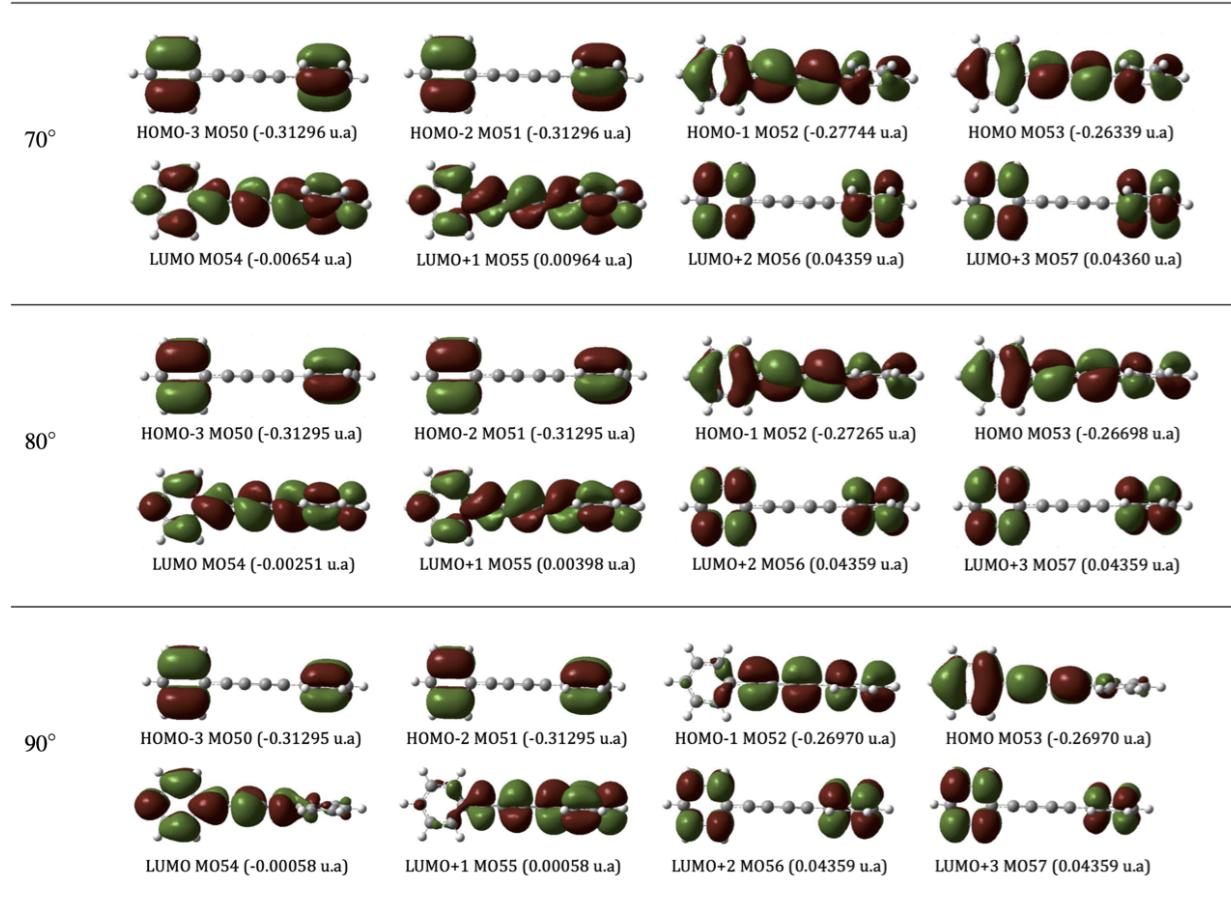


Table S12. Molecular orbitals and energies for a rotation from 20° to 60° obtained by DFT

20°	HOMO-3 M050 (-0.31300 u.a)	HOMO-2 M051 (-0.31298 u.a)	HOMO-1 M052 (-0.29259 u.a)	HOMO M053 (-0.25677 u.a)
	LUMO M054 (-0.01385 u.a)	LUMO+1 M055 (0.03008 u.a)	LUMO+2 M056 (0.04360 u.a)	LUMO+3 M057 (0.04362 u.a)
30°	HOMO-3 M050 (-0.31299 u.a)	HOMO-2 M051 (-0.31297 u.a)	HOMO-1 M052 (-0.28943 u.a)	HOMO M053 (-0.25766 u.a)
	LUMO M054 (-0.01288 u.a)	LUMO+1 M055 (0.02515 u.a)	LUMO+2 M056 (0.04360 u.a)	LUMO+3 M057 (0.04362 u.a)
40°	HOMO-3 M050 (-0.31298 u.a)	HOMO-2 M051 (-0.31297 u.a)	HOMO-1 M052 (-0.28601 u.a)	HOMO M053 (-0.25889 u.a)
	LUMO M054 (-0.01152 u.a)	LUMO+1 M055 (0.02042 u.a)	LUMO+2 M056 (0.04360 u.a)	LUMO+3 M057 (0.04361 u.a)
50°	HOMO-3 M050 (-0.31298 u.a)	HOMO-2 M051 (-0.31297 u.a)	HOMO-1 M052 (-0.28428 u.a)	HOMO M053 (-0.25963 u.a)
	LUMO M054 (-0.01071 u.a)	LUMO+1 M055 (0.01814 u.a)	LUMO+2 M056 (0.04360 u.a)	LUMO+3 M057 (0.04361 u.a)
60°	HOMO-3 M050 (-0.31296 u.a)	HOMO-2 M051 (-0.31296 u.a)	HOMO-1 M052 (-0.27911 u.a)	HOMO M053 (-0.26234 u.a)
	LUMO M054 (-0.00771 u.a)	LUMO+1 M055 (0.01166 u.a)	LUMO+2 M056 (0.04359 u.a)	LUMO+3 M057 (0.04360 u.a)

Table S13. Molecular orbitals and energies for a rotation from 70° to 90° obtained by DFT

10. Tolonophane

Carbyne molecules are very promising for electronic and mechanical applications. They would offer, in their chain version, a "specific resistance surpassing that of all known materials to date"^[35]. Flexible and very resistant, these materials also have singular electrical properties. Carbyne-carbyne cross-linking are equally promising. The tolonophane molecule is a representative example of these systems^[34]. It consists of two tolane (diphenylethyne) units (see fig.S5). X-ray analysis revealed that this molecule has a twisted structure with D_2 symmetry in agreement with the modelling. Our study shows that these systems generate helical states. These helical states appear for a twist of the molecule in the form of a braid.

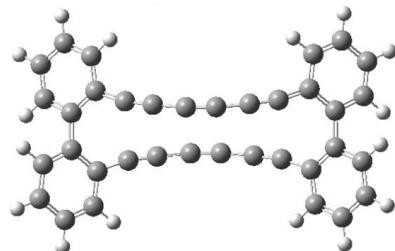


Figure S5. Representation of the molecule of Tolanophane

Table S14. Molecular orbitals and energies for a rotation from 0° to 5° obtained by DFT

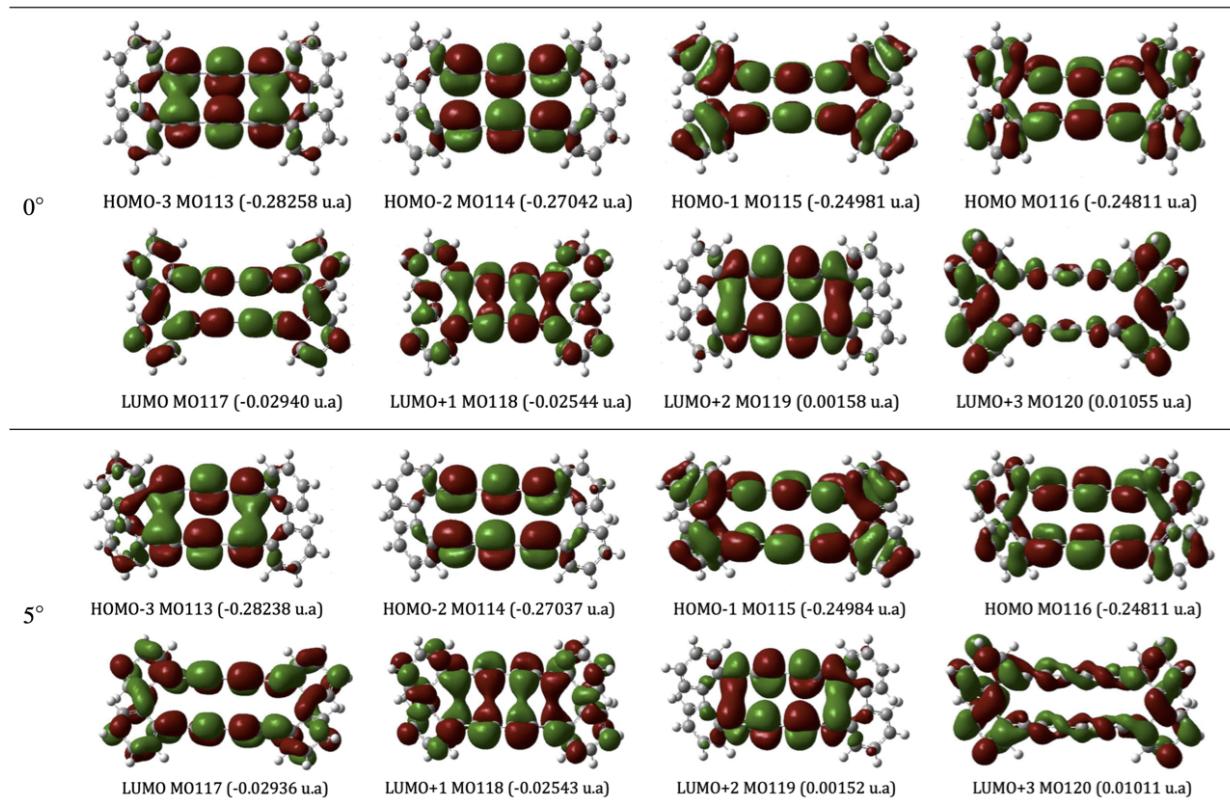


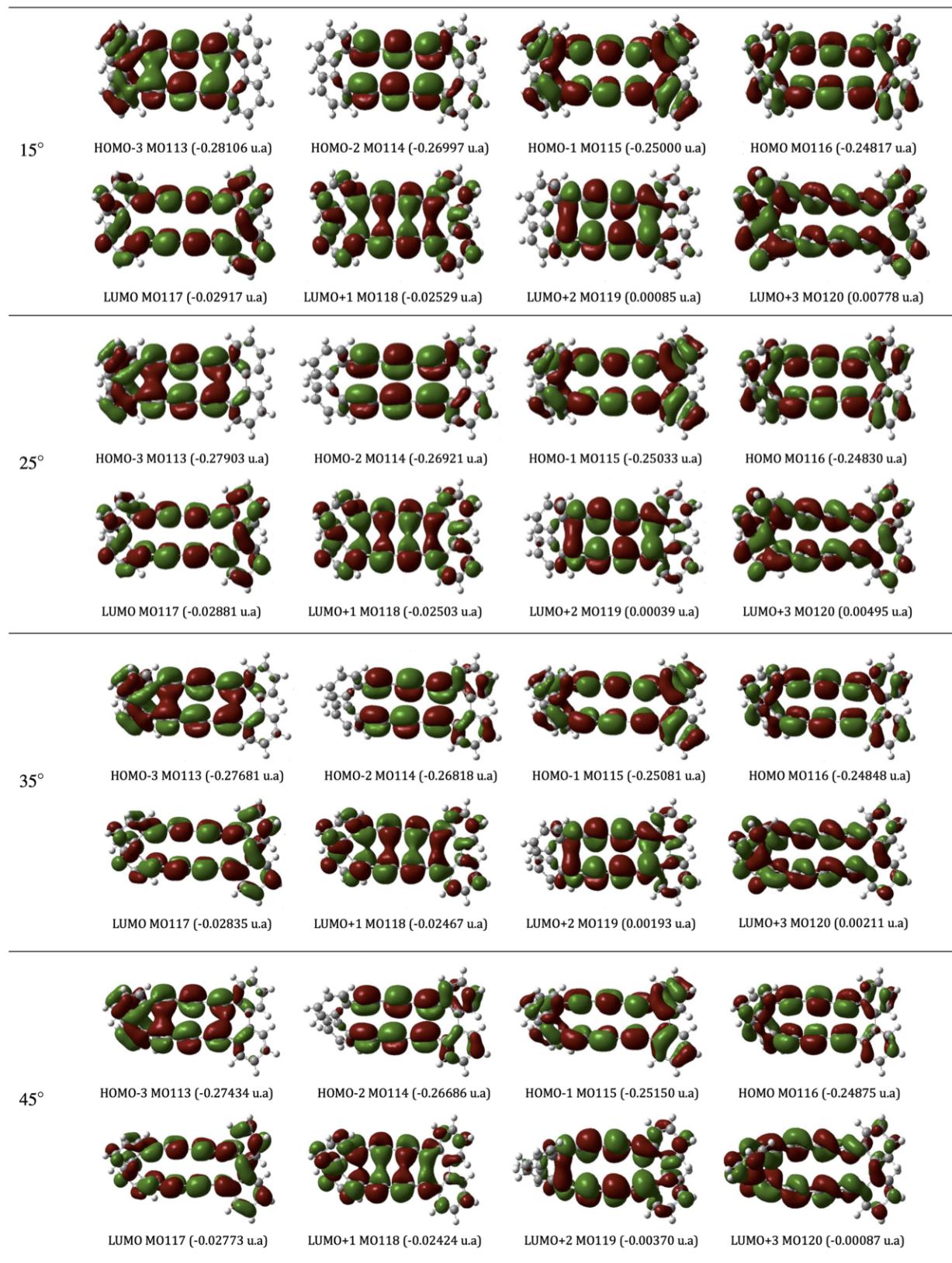
Table S15. Molecular orbitals and energies for a rotation from 15° to 45° obtained by DFT

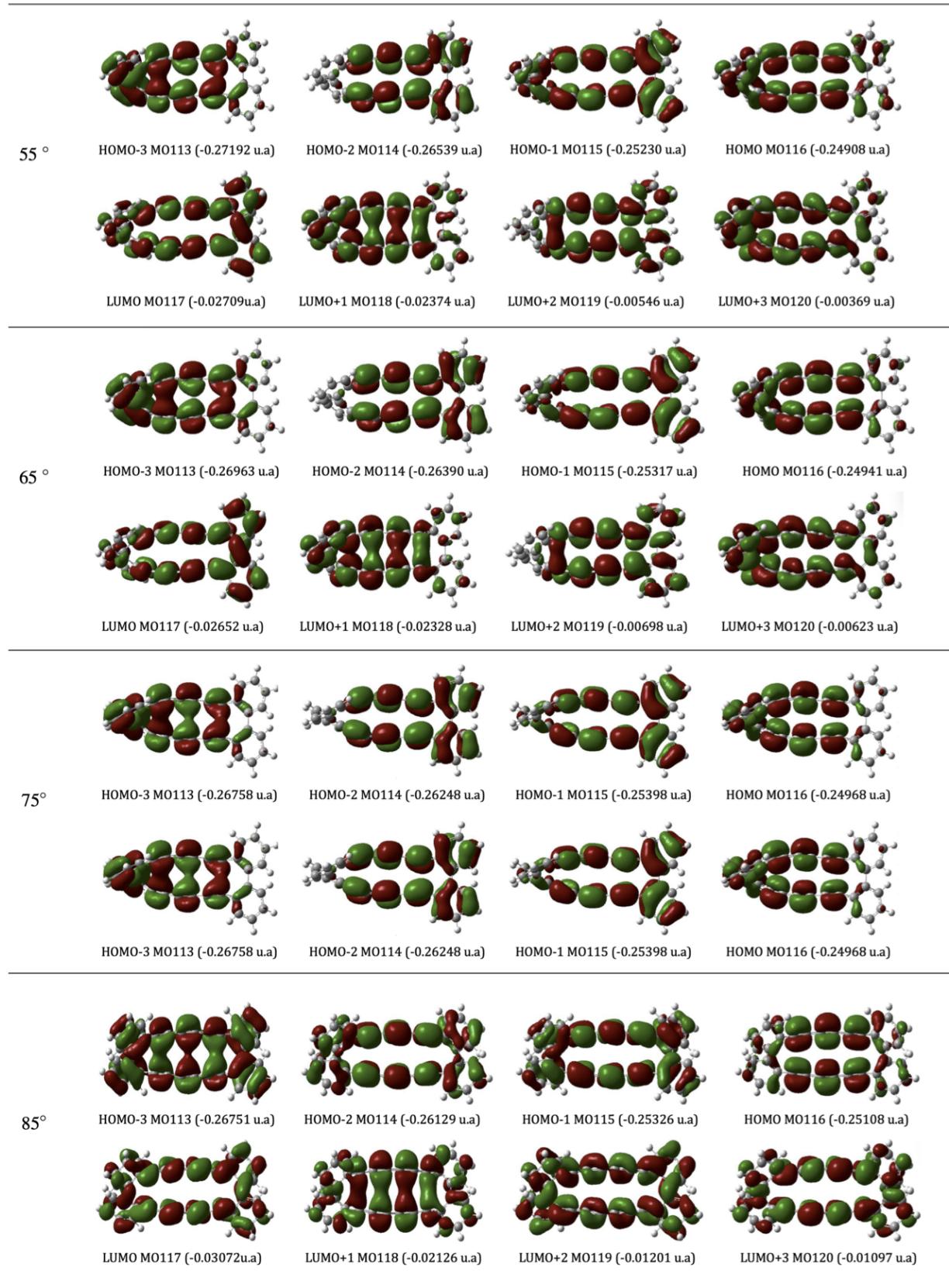
Table S16. Molecular orbitals and energies for a rotation from 55° to 85° obtained by DFT

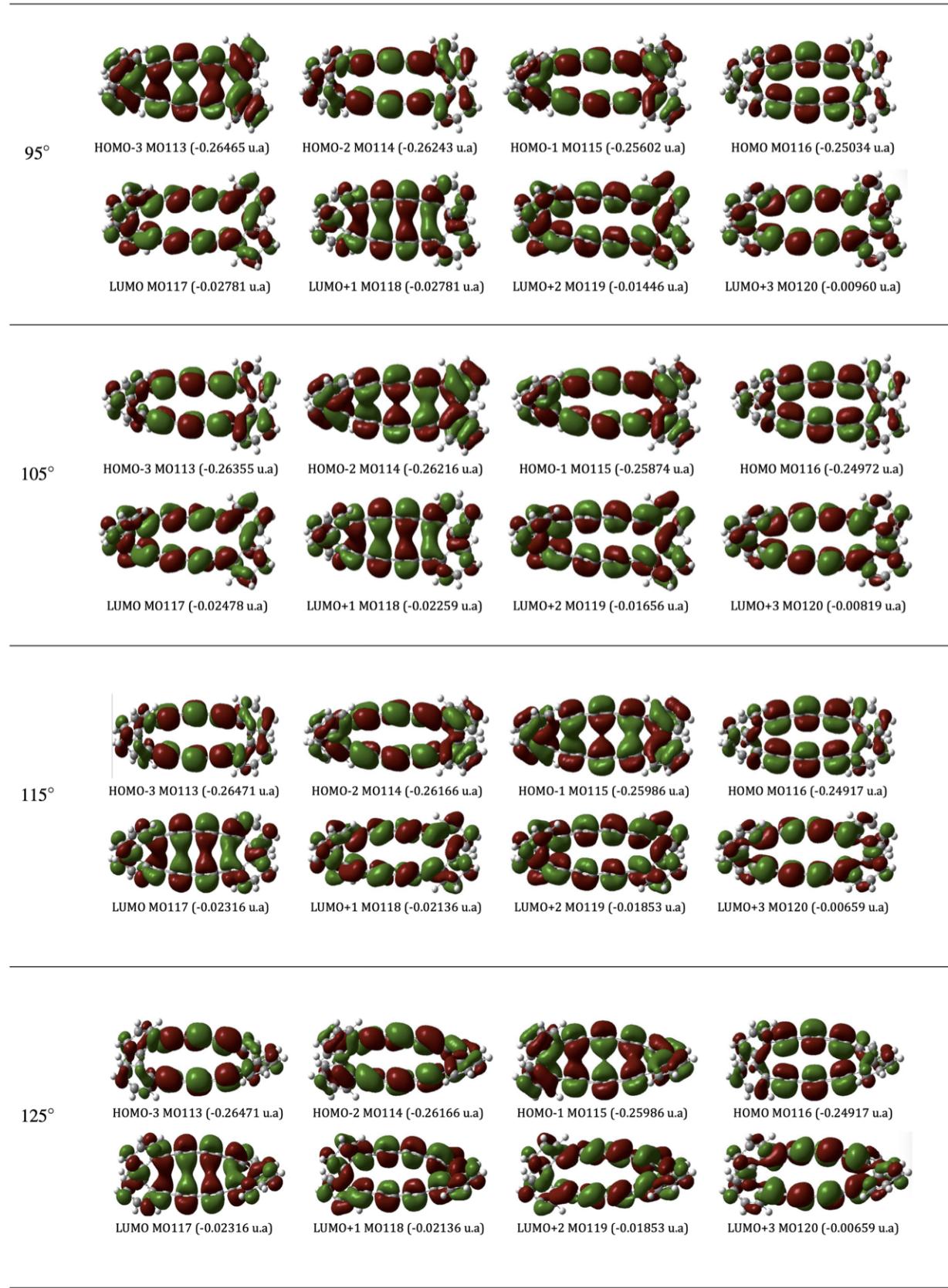
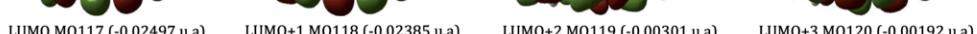
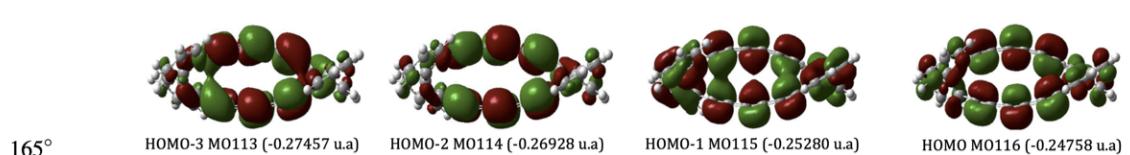
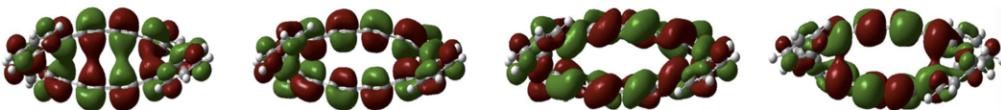
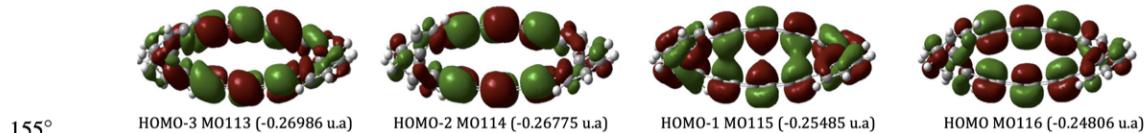
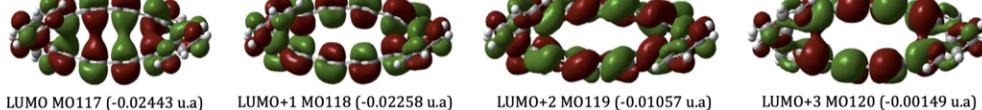
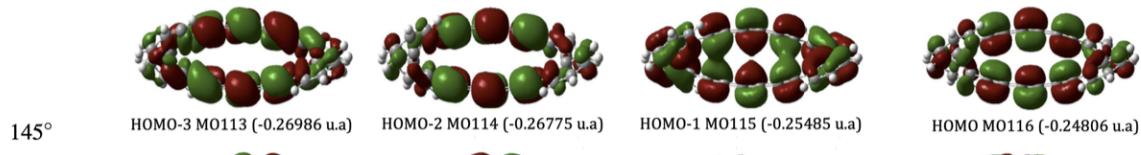
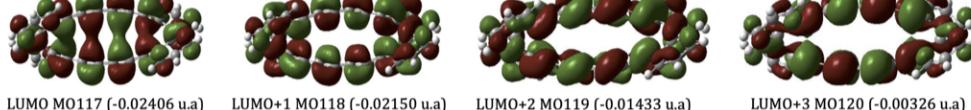
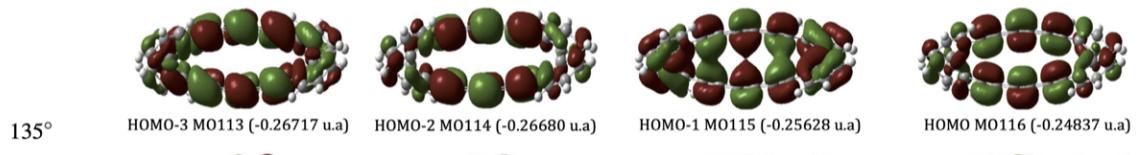
Table S17. Molecular orbitals and energies for a rotation from 95° to 125° obtained by DFT

Table S18. Molecular orbitals and energies for a rotation from 135° to 165° obtained by DFT

11. Metallacumulenes

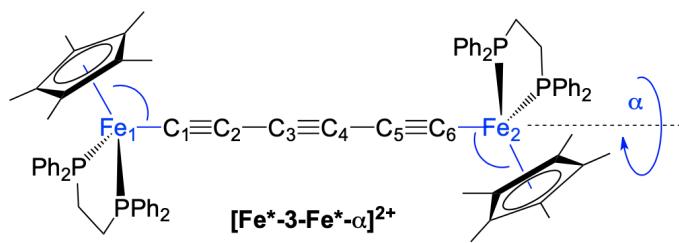


Figure S6. Representation of the $[\text{Cp}^*(\text{dppe})\text{M}-(\text{C}_2)_3-\text{M}(\text{dppe})\text{Cp}^*]^{2+}$ (Cp^* = pentamethylcyclopentadienyl; dppe = (diphenylphosphino)ethane); M = Fe), two-electron oxidized unsaturated system - see Gendron et al. [23,25]

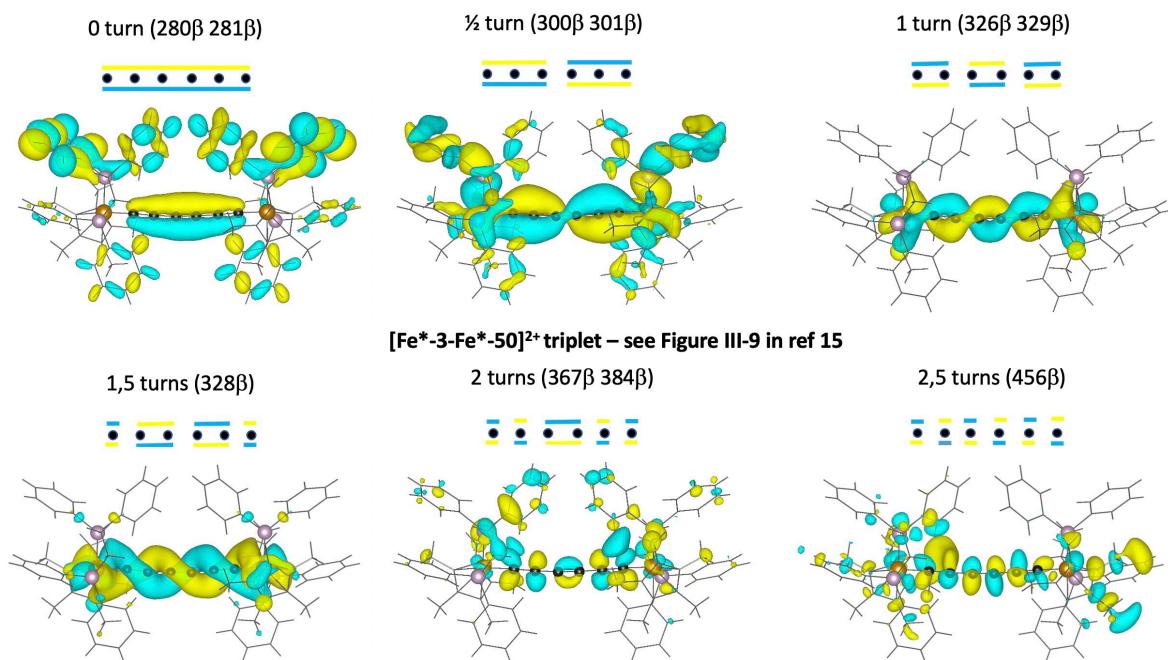


Figure S7. spinorbitals of the $[\text{Cp}^*(\text{dppe})\text{M}-(\text{C}_2)_3-\text{M}(\text{dppe})\text{Cp}^*]^{2+}$ (Cp^* = pentamethylcyclopentadienyl; dppe = (diphenylphosphino)ethane); M = Fe), two-electron oxidized unsaturated system in his triplet state. See figure III-9 in Gendron et al. [25]

12. Coordinates

Table S19. Figure 8 - B=N=B=N=B (doublet – ground state) - B3LYP/6-311G(d,p) - E= -186.5632313 u.a.

	X	Y	Z
B	-4.370347	1.748977	0.580094
B	-1.712079	1.602983	0.328505
B	0.946481	1.459266	0.077966
N	-3.010407	1.672638	0.450578
N	-0.414073	1.532583	0.206082
H	-5.037437	2.176373	-0.319453
H	-4.899374	1.388590	1.593549
H	1.475621	1.820679	-0.935093
H	1.613366	1.033340	0.978402

Table S20. Figure 8 - B=N=B=N=B (doublet – 25°) - B3LYP/6-311G(d,p) - E= -186.4314572 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
B	0.000000	0.000000	1.080047
B	4.197719	0.000000	3.645766
H	4.242730	0.389467	4.652151
H	5.113886	-0.389467	3.226870
H	-0.961197	0.000000	1.572594
N	1.127850	0.000000	1.769409
N	3.069874	0.000000	2.956408
B	2.080018	0.000086	2.351605

Table S21. Figure 8 - B=N=B=N=B (quadruplet – ground state 45°) - B3LYP/6-311G(d,p) - E= -186.2492410 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
B	0.000000	0.000000	1.080047
B	4.197719	0.000000	3.645766
H	4.338467	0.651640	4.495517
H	5.018149	-0.651640	3.383504
H	-0.961197	0.000000	1.572594
N	1.127850	0.000000	1.769409
N	3.069874	0.000000	2.956408
B	2.080039	0.000143	2.351571

Table S22. Figure 8 - B=N=B=N=B (quadruplet – 70°) - B3LYP/6-311G(d,p) - E= -186.2462315 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
B	0.000000	0.000000	1.080047
B	4.197719	0.000000	3.645766
H	4.513931	0.865982	4.208445
H	4.842685	-0.865982	3.670576
H	-0.961197	0.000000	1.572594
N	1.127850	0.000000	1.769409
N	3.069874	0.000000	2.956408
B	2.080078	0.000190	2.351508

Table S23. Figure 8 - B=N=B=N=B (quadruplet – 20°) - B3LYP/6-311G(d,p) - E= -186.2450474 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
B	0.000000	0.000000	1.080047
B	4.197719	0.000000	3.645766
H	4.226685	0.315192	4.678402
H	5.129931	-0.315192	3.200619
H	-0.961197	0.000000	1.572594
N	1.127850	0.000000	1.769409
N	3.069874	0.000000	2.956408
B	2.080015	0.000069	2.351611

Table S24. Figure 14 - N=3 Cumulene (ground state – singlet 0°) - cam-B3LYP/6-31G(d,p) - E= -154.6318801 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.080047
C	3.344478	0.000000	3.124250
H	3.344459	0.000000	4.204306
H	4.305674	0.000000	2.631682
H	-0.961197	0.000000	1.572594
C	1.127850	0.000000	1.769409
C	2.216633	0.000000	2.434891

Table S25. Figure 14 - N=3 Cumulene (singlet - 50°) - cam-B3LYP/6-31G(d,p) - E= -154.6048614 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.080047
C	3.344478	0.000000	3.124250
H	3.516138	0.705955	3.923426
H	4.133995	-0.705955	2.912563
H	-0.961197	0.000000	1.572594
C	1.127850	0.000000	1.769409
C	2.216633	0.000000	2.434891

Table S26. Figure 14 - N=3 Cumulene (singlet - 90°) - cam-B3LYP/6-31G(d,p) - E= -154.5166171 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.080047
C	3.344478	0.000000	3.124250
H	3.825067	0.921558	3.417994
H	3.825067	-0.921558	3.417994
H	-0.961197	0.000000	1.572594
C	1.127850	0.000000	1.769409
C	2.216633	0.000000	2.434891

Table S27. Figure 15 - N=4 Cumulene (singlet - 0°) - cam-B3LYP/6-31G(d,p) - E= -192.6098812 u.a.

	X	Y	Z
H	0.000000	0.933723	3.143505
C	0.000000	0.000000	2.593591
C	0.000000	0.000000	-2.593591
H	-0.000000	-0.933723	-3.143505
H	0.000000	0.933723	-3.143505
H	-0.000000	-0.933723	3.143505
C	0.000000	0.000000	1.281388
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.281388

Table S28. Figure 15 - N=4 Cumulene (singlet - 50°) - cam-B3LYP/6-31G(d,p) - E= -192.6684340 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.099937
C	4.352022	0.000000	3.829850
H	4.528892	-0.713793	4.647821
H	5.165454	0.713781	3.633081
H	-0.990298	0.000000	1.578666
C	1.101661	0.000173	1.791008
C	2.176018	0.000198	2.464884
C	3.250287	0.000129	3.138898

Table S29. Figure 15 - N=4 Cumulene (ground state singlet - 90°) - cam-B3LYP/6-31G(d,p) - E= -192.6832059 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.086016
C	4.417163	0.000000	3.768843
H	4.899029	-0.928208	4.061511
H	4.899045	0.928202	4.061521
H	-0.963733	0.000000	1.586657
C	1.117539	0.000039	1.764823
C	2.208549	0.000038	2.427490
C	3.299571	0.000000	3.090126

Table S30. Figure 16 - N=3 Cumulene (triplet - 0°) – cam-B3LYP/6-31G(d,p) - E= -154.5547707 u.a.

	X	Y	Z
H	-0.000000	2.575445	-0.932041
C	-0.000000	2.024440	-0.000052
C	-0.000000	-2.024440	-0.000052
H	0.000000	-2.575040	0.932194
H	-0.000000	-2.575445	-0.932041
H	0.000000	2.575040	0.932194
C	-0.000000	0.606188	0.000027
C	-0.000000	-0.606188	0.000027

Table S31. Figure 16 - N=3 Cumulene (triplet - 50°) – cam-B3LYP/6-31G(d,p) - E= -154.5705293 u.a.

	X	Y	Z
H	-2.555843	0.392934	-0.842664
C	-1.998140	0.000001	-0.000017
C	1.998140	-0.000001	-0.000017
H	2.555773	0.392950	0.842670
H	2.555843	-0.392934	-0.842664
H	-2.555773	-0.392950	0.842670
C	-0.617631	0.000000	0.000016
C	0.617631	-0.000000	0.000016

Table S32. Figure 16 - N=3 Cumulene (ground state triplet - 90°) – cam-B3LYP/6-31G(d,p) - E= -154.5808779 u.a.

	X	Y	Z
H	0.928768	-0.000000	-2.547378
C	0.000000	0.000000	-1.986231
C	-0.000000	-0.000000	1.986231
H	0.000000	0.928768	2.547378
H	-0.000000	-0.928768	2.547378
H	-0.928768	-0.000000	-2.547378
C	0.000000	0.000000	-0.623812
C	-0.000000	-0.000000	0.623812

Table S33. Figure 17 - N=4 Cumulene (ground state triplet - 0°) – cam-B3LYP/6-31G(d,p) - E= -192.6351638 u.a.

	X	Y	Z
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.099937
C	4.352022	0.000000	3.829850
H	4.352022	0.000000	4.929787
H	5.342321	0.000000	3.351121
H	-0.990298	0.000000	1.578666
C	1.101661	0.000000	1.791008
C	2.175992	0.000000	2.464925
C	3.250361	0.000000	3.138779

Table S34. Figure 17 - N=4 Cumulene (50°) – cam-B3LYP/6-31G(d,p) - E= -192.6147359 u.a.

	X	Y	Z
1	-3.153189	-0.393788	-0.844482
6	-2.568682	0.000000	0.000000
6	2.568682	0.000000	0.000000
1	3.153189	-0.393788	0.844482
1	3.153189	0.393788	-0.844482
1	-3.153189	0.393788	0.844482
6	-1.268207	0.000000	0.000000
6	0.000000	0.000000	0.000000
6	1.268207	0.000000	0.000000

Table S35. Figure 17 - N=4 Cumulene (90°) – cam-B3LYP/6-31G(d,p) - E= -192.5973200 u.a.

	X	Y	Z
H	-3.1531887	0.0000000	-0.9317827
C	-2.5686826	0.0000000	0.0000000
C	2.5686824	0.0000000	0.0000000
H	3.1531887	-0.9317830	0.0000000
H	3.1531887	0.9317830	0.0000000
H	-3.1531887	0.0000000	0.9317827
C	-1.2682073	0.0000000	0.0000000
C	0.0000000	0.0000000	0.0000000
C	1.2682070	0.0000000	0.0000000

Table S36. Figure 18 - 1-phosphaallene (ground state) - B3LYP/6-311G(d,p) - E= -419.3455757 u.a.

	X	Y	Z
C	0.000000	-0.011419	-1.877712
C	0.000000	0.047326	-0.575047
H	0.927530	-0.028925	-2.444242
H	-0.927530	-0.028925	-2.444242
P	0.000000	-0.056168	1.067721
H	0.000000	1.356050	1.305560

Table S37. Figure 18 - 1-phosphaallene (25°) - B3LYP/6-311G(d,p) - E= -419.3388514 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.303989
P	0.177398	0.000000	2.940427
H	-0.392006	-0.840659	-0.566744
H	0.392006	0.840659	-0.566744
H	-1.222670	0.000000	3.241649

Table S38. Figure 18 - 2-diphosphoallene - (ground state) - B3LYP/6-311G(d,p) - E= -721.9987958 u.a.

	X	Y	Z
P	-0.036202	0.047476	-1.640611
C	0.000000	-0.085642	0.000000
P	0.036202	0.047476	1.640611
H	0.961485	-0.948684	-1.898339
H	-0.961485	-0.948684	1.898339

Table S39. Figure 18 - 2-diphosphoallene - (25°) - B3LYP/6-311G(d,p) - E= -721.9932616 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.646401
P	0.265356	0.000000	-1.624876
H	-0.196523	-1.336812	-1.856689
H	-1.011955	1.003127	1.800741

Table S40. Figure 18 - Phosphaazaallenes - (ground state) - B3LYP/6-311G(d,p) - E= -435.4130891 u.a.

	X	Y	Z
P	0.068359	0.297005	-0.095087
C	-0.085272	0.019299	1.551910
N	-0.086552	-0.070701	2.758473
H	0.000966	-1.100681	-0.374399
H	-0.952978	-0.073247	3.292946

Table S41. Figure 18 - Phosphaazaallenes - (25°) - B3LYP/6-311G(d,p) - E= -435.4095288 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.209916
P	0.216580	0.000000	-1.663254
H	-0.839374	-0.943715	-1.837745
H	-0.798129	0.337783	1.744009

Table S42. Figure 18 - Arsaallene - (ground state) - B3LYP/6-311G(d,p) - E=-2313.843111 u.a.

	X	Y	Z
C	0.018099	0.000000	-2.426533
C	-0.059250	0.000000	-1.125637
As	0.025585	0.000000	0.639022
H	0.043024	0.927119	-2.995655
H	0.043024	-0.927119	-2.995655
H	-1.497501	0.000000	0.820692

Table S43. Figure 18 - Arsaallene - (25°) - B3LYP/6-311G(d,p) - E=-2313.836815 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.303193
As	0.189423	0.000000	3.059706
H	0.391837	0.840297	-0.569593
H	-0.391837	-0.840297	-0.569593
H	-1.320194	0.000000	3.331465

Table S44. Figure 18 - Arsaphosphaallene - (ground state) - B3LYP/6-311G(d,p) - E=-2616.496319 u.a.

	X	Y	Z
P	0.045080	0.246883	-0.231187
C	0.017451	0.005117	1.394805
As	0.199949	-0.036729	3.153681
H	-0.007382	-1.136276	-0.609909
H	-1.310574	-0.007320	3.42645

Table S45. Figure 18 - Arsaphosphaallene - (25°) - B3LYP/6-311G(d,p) E=-2616.491034 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
As	0.000000	0.000000	1.768813
P	0.282047	0.000000	-1.619727
H	-0.731238	-0.954232	-1.969021
H	-1.415614	0.582954	1.883496

Table S46. Figure 18 - Diarsaallene - (ground state) - B3LYP/6-311G(d,p) - E=-4510.994032 u.a.

	X	Y	Z
As	0.063564	0.298768	-0.304508
C	0.010966	0.019457	1.438906
As	0.190255	-0.045562	3.194989
H	-0.000544	-1.191461	-0.675724
H	-1.319718	-0.009527	3.480179

Table S47. Figure 18 - Diarsaallene - (25°) - B3LYP/6-311G(d,p) - E=-4510.988940 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
As	0.000000	0.000000	1.766409
As	0.314719	0.000000	-1.738168
H	-0.733341	-1.077692	-2.058864
H	-1.441719	0.517175	1.895350

Table S48. Figure 18 - Silaallene – (ground state) - B3LYP/6-311G(d,p) - E= -368.0610706 u.a.

	X	Y	Z
C	0.000000	0.000000	-1.894020
C	0.000000	0.000000	-0.585768
Si	0.000000	0.000000	1.103947
H	0.000000	0.923441	-2.473611
H	0.000000	-0.923441	-2.473611
H	-1.257891	0.000000	1.868301
H	1.257891	0.000000	1.868301

Table S49. Figure 18 - Silaallene – (25°) - B3LYP/6-311G(d,p) - E= -368.0570393 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.308252
Si	0.000000	-0.000000	2.997967
H	0.239004	0.891977	-0.579589
H	-0.390264	-0.836923	-0.579589
H	-1.257889	-0.000000	3.762325
H	1.257889	-0.000000	3.762325

Table S50. Figure 18 - Phosphasilaallene - (ground state) - B3LYP/6-311G(d,p) - E= -670.7155311 u.a.

	X	Y	Z
C	0.100214	0.000000	-0.011829
P	0.005703	0.000000	1.623679
Si	0.463676	0.000000	-1.669461
H	0.581954	1.252213	-2.437596
H	0.581954	-1.252213	-2.437596
H	-1.427234	0.000000	1.779157

Table S51. Figure 18 - Phosphasilaallene - (25°) - B3LYP/6-311G(d,p) - E= -670.7104108 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
Si	0.000000	0.000000	1.697012
P	0.257971	0.000000	-1.617798
H	0.484817	-1.155593	2.472650
H	-0.573601	1.114192	2.472650
H	-1.108413	0.000000	-2.076576

Table S52. Figure 18 - Silaketene - (ground state) - B3LYP/6-311G(d,p) - E= -404.0295178 u.a.

	X	Y	Z
O	0.115688	-0.013552	-0.645947
C	0.045441	0.008518	0.490281
Si	-0.468461	0.137199	2.301554
H	0.718023	1.041811	2.544381
H	0.189309	-1.200583	2.552255

Table S53. Figure 18 - Silaketene - (25°) - B3LYP/6-311G(d,p) - E= -404.0169148 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
Si	0.000000	0.000000	1.887158
O	0.248458	0.000000	-1.111172
H	-0.982175	-1.148720	1.858798
H	-1.371493	0.635056	1.857425

Table S54. Figure 18 - Silaketene - (25°) - B3LYP/6-311G(d,p) - E= -404.0185416 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
Si	0.000000	0.000000	1.887158
O	0.248458	0.000000	-1.111172
H	-0.982175	-1.148720	1.858798
H	-0.395098	1.458831	1.857425

Table S55. Figure 18 - Germaallene - (ground state) - B3LYP/6-311G(d,p) - E=-2155.54766 u.a.

	X	Y	Z
C	0.000000	0.063224	-2.425513
C	0.000000	-0.175149	-1.141748
Ge	0.000000	0.024511	0.635809
H	0.000000	1.069081	-2.844133
H	0.000000	-0.754304	-3.147142
H	-1.287955	-0.373154	1.355095
H	1.287955	-0.373154	1.355095

Table S56. Figure 18 - Germaallene - (25°) - B3LYP/6-311G(d,p) - E=-2155.541842 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.305708
Ge	0.520826	0.000000	3.016940
H	0.912531	0.000000	-0.595212
H	-0.935528	0.000000	-0.560257
H	-0.216938	0.966345	3.942261
H	0.824518	-1.368219	3.625287

Table S57. Figure 18 - Germaphosphaallene - (ground state) - B3LYP/6-311G(d,p) - E=-2458.2022231 u.a.

	X	Y	Z
Ge	0.021293	0.000000	-1.078017
C	-0.231277	0.000000	0.684195
P	0.091520	0.000000	2.291837
H	-0.162676	1.294942	-1.860629
H	-0.162676	-1.294942	-1.860629
H	-1.264624	0.000000	2.777310

Table S58. Figure 18 - Germaphosphaallene - (conformer) - B3LYP/6-311G(d,p) E= -2458.18923418 u.a.

	X	Y	Z
P	0.437540	-0.007406	-0.119182
C	0.007622	-0.004246	1.505794
Ge	0.191588	-0.009903	3.305041
H	-0.129250	1.100302	-0.796248
H	-0.163609	-1.093905	-0.801094
H	-1.386772	0.014698	3.472083

Table S59. Figure 18 - Germaphosphaallene - (25°) - B3LYP/6-311G(d,p) - E=-2458.1971654 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
P	0.000000	0.000000	1.639729
Ge	0.594543	0.000000	-1.678005
H	1.109978	1.297507	-2.289564
H	0.078285	-1.049738	-2.655108
H	-1.425176	0.000000	1.848732

Table S60. Figure 19 - Phosphabutatriene - (ground state) - B3LYP/6-311G(d,p) - E= -457.4324610 u.a.

	X	Y	Z
C	0.000000	-0.020106	-2.588873
C	0.000000	0.010152	-1.272144
C	0.000000	0.066818	-0.008111
H	0.000000	0.894326	-3.174105
H	0.000000	-0.960000	-3.132146
P	0.000000	-0.063575	1.642964
H	0.000000	1.341764	1.924186

Table S61. Figure 19 - Phosphabutatriene - (25°) - B3LYP/6-311G(d,p) - E= -457.4270831 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.317077
C	0.027602	0.000000	2.582079
P	-0.140689	0.000000	4.229723
H	0.840720	0.392034	-0.564075
H	-0.840297	-0.391837	-0.564723
H	1.257820	0.000000	4.543147

Table S62. Figure 19 - Diphosphabutatriene - (ground state) - B3LYP/6-311G(d,p) - E= -760.0905143 u.a.

	X	Y	Z
P	0.000000	0.054616	-2.288556
C	0.000000	-0.052992	-0.629569
C	0.000000	0.052992	0.629569
P	0.000000	-0.054616	2.288556
H	0.000000	-1.355091	-2.541186
H	0.000000	1.355091	2.541186

Table S63. Figure 19 - Diphosphabutatriene - (25°) - B3LYP/6-311G(d,p) - E= -760.0725249 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.263590
P	0.246389	0.000000	2.907704
P	-0.246389	0.000000	-1.644114
H	0.094029	1.374612	-1.857785
H	-1.005296	-0.601429	3.257939

Table S64. Figure 19 - Arsabutatriene - (ground state) - B3LYP/6-311G(d,p) - E=-2351.932895 u.a.

	X	Y	Z
C	0.000000	-0.022698	-2.621162
C	0.000000	-0.000130	-1.301076
C	0.000000	0.046173	-0.039327
H	0.000000	0.895185	-3.200333
H	0.000000	-0.959654	-3.168899
As	0.000000	-0.101490	1.732519
H	0.000000	1.411992	1.990048

Table S65. Figure 19 - Arsabutatriene - (25°) - B3LYP/6-311G(d,p) - E= -2351.92786894 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.320279
C	0.024723	0.000000	2.582635
As	-0.153225	0.000000	4.351696
H	0.840734	0.392041	-0.563398
H	-0.840558	-0.391958	-0.563678
H	1.355630	0.000000	4.635079

Table S66. Figure 19 - Silabutatriene - (ground state) - B3LYP/6-311G(d,p) - E= -406.1578684 u.a.

	X	Y	Z
C	0.000000	0.009004	-2.145764
C	0.000000	0.003578	-0.826980
C	0.000000	-0.001655	0.439312
Si	0.000000	-0.008951	2.132007
H	0.000000	-0.916607	-2.710226
H	0.000000	1.239383	2.912512
H	0.000000	0.939397	-2.702152
H	0.000000	-1.264150	2.901290

Table S67. Figure 19 - Silabutatriene - (25°) - B3LYP/6-311G(d,p) - E= -406.1531776 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.319835
C	0.005549	0.000000	2.586541
Si	0.016922	0.000000	4.279090
H	0.839858	0.391632	-0.561196
H	-1.229778	0.000000	5.062417
H	-0.839679	-0.391549	-0.559464
H	1.273304	0.000000	5.044905

Table S68. Figure 20 - [Re2H8]2- - B3LYP/Def2SV - E= -161.2745560 u.a.

	X	Y	Z
Re	-0.491963	0.021196	1.323299
H	0.748254	1.103723	1.880919
H	-1.428653	1.445578	1.743391
H	-1.284734	-1.474405	1.791522
H	0.848575	-0.914020	1.914440
Re	-0.340551	-0.007649	-0.909812
H	0.452195	1.487514	-1.377951
H	-1.680160	0.929120	-1.500866
H	-1.581311	-1.089451	-1.467857
H	0.597578	-1.431615	-1.330425

Table S69. Supplementary Information (Table S9) - Diphenylbutadiyne – (ground state – 0°) – cam- B3LYP/6-31G(d,p) - E= -615.26293291 u.a.

	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.405452
C	5.669550	0.000000	4.713029
C	5.669550	0.000000	6.118481
C	6.893010	0.000000	4.021336
C	-1.223461	0.000000	2.097145
C	-2.423336	0.000000	1.390026
C	-2.417663	0.000000	-0.004971
C	-1.206074	0.000000	-0.696495
C	8.092886	0.000000	4.728455
C	8.087213	0.000000	6.123454
C	6.875623	0.000000	6.814977
C	4.455911	0.000000	4.005001
H	6.898214	0.000000	2.921211
H	9.047971	0.000000	4.182491
C	3.417862	0.000000	3.399410
H	4.714441	0.000000	6.664438
H	6.870401	0.000000	7.915084
C	2.251688	0.000000	2.719071
H	9.037271	0.000000	6.677692
H	-3.367722	0.000000	-0.559209
C	1.213639	0.000000	2.113481
H	-1.200851	0.000000	-1.796603
H	-3.378421	0.000000	1.935990
H	0.955109	0.000000	-0.545956
H	-1.228664	0.000000	3.197270

Table S70. Supplementary Information (Table S9) - Diphenylbutadiyne – (25°) – cam- B3LYP/6-31G(d,p) – E= -615.2628907 u.a.

	X	Y	Z
C	-4.031453	-0.261633	-1.180150
C	-3.322910	0.000000	0.000000
C	3.322910	0.000000	0.000000
C	4.031453	-0.261633	1.180150
C	4.031453	0.261633	-1.180150
C	-4.031453	0.261633	1.180150
C	-5.418215	0.260474	1.175595
C	-6.114730	0.000000	0.000000
C	-5.418215	-0.260474	-1.175595
C	5.418215	0.260474	-1.175595
C	6.114730	0.000000	0.000000
C	5.418215	-0.260474	1.175595
C	1.895959	0.000000	0.000000
H	3.482597	0.464265	-2.092923
H	5.958521	0.464122	-2.094165
C	0.684542	0.000000	0.000000
H	3.482597	-0.464265	2.092923
H	5.958521	-0.464122	2.094165
C	-0.684542	0.000000	0.000000
H	7.199732	0.000000	0.000000
H	-7.199732	0.000000	0.000000
C	-1.895959	0.000000	0.000000
H	-5.958521	-0.464122	-2.094165
H	-5.958521	0.464122	2.094165
H	-3.482597	-0.464265	-2.092923
H	-3.482597	0.464265	2.092923

Table S71. Supplementary Information (Table S9) - Diphenylbutadiyne – (90°) – cam- B3LYP/6-31G(d,p) - E= -615.2626881 u.a.

	X	Y	Z
C	-4.032071	0.000000	-1.208695
C	-3.323703	0.000000	0.000000
C	3.323702	0.000000	0.000000
C	4.032071	-1.208695	0.000000
C	4.032071	1.208695	0.000000
C	-4.032071	0.000000	1.208695
C	-5.418923	0.000000	1.204108
C	-6.115339	0.000000	0.000000
C	-5.418923	0.000000	-1.204108
C	5.418923	1.204109	0.000000
C	6.115339	0.000000	0.000000
C	5.418923	-1.204109	0.000000
C	1.896063	0.000000	0.000000
H	3.483103	2.143643	0.000000
H	5.959233	2.144986	0.000000
C	0.684783	0.000000	0.000000
H	3.483103	-2.143643	0.000000
H	5.959233	-2.144986	0.000000
C	-0.684783	0.000000	0.000000
H	7.200363	0.000000	0.000000
H	-7.200364	0.000000	0.000000
C	-1.896063	0.000000	0.000000
H	-5.959233	0.000000	-2.144986
H	-5.959233	0.000000	2.144986
H	-3.483103	0.000000	-2.143643
H	-3.483103	0.000000	2.143643

Table S72. Supplementary Information (Table S10) - Tolanophane – (0°) – cam- B3LYP/6-31G(d,p) - E=-1380.3367984 u.a.

	X	Y	Z
C	1.644148	-4.313521	-0.395376
C	3.031536	-4.473708	-0.237925
C	0.774098	-5.316210	0.077878
C	1.337547	-6.435616	0.699489
C	2.707383	-6.579013	0.856114
C	3.561791	-5.591982	0.378806
H	3.682753	-3.692013	-0.611768
H	4.636240	-5.690017	0.490695
H	3.105159	-7.458476	1.351351
H	0.671711	-7.203436	1.078508
C	-0.705536	-5.315470	-0.095330
C	-2.962262	-4.471604	0.221387
C	-3.493347	-5.588611	-0.396924
C	-2.639721	-6.575694	-0.875526
C	-1.269799	-6.433587	-0.718554
H	-3.612899	-3.689905	0.596229
H	-4.567868	-5.685605	-0.509055
H	-0.604523	-7.201394	-1.098587
H	-3.038161	-7.454156	-1.372001
C	-1.574776	-4.312710	0.379238
C	1.072739	-1.948697	-1.380082
C	1.221020	-3.092994	-1.004262
C	0.963057	-0.608490	-1.612938
C	0.961052	0.608714	-1.616888
C	1.071178	1.948847	-1.382997
C	1.218947	3.093184	-1.007223
C	-1.576958	4.313144	0.376725
C	-2.964328	4.473319	0.219026
C	-0.706833	5.315949	-0.096187
C	-1.270231	6.435367	-0.717838
C	-2.640039	6.578702	-0.874773
C	-3.494516	5.591618	-0.397710
H	-3.615590	3.691567	0.592673
C	0.772767	5.315481	0.077419
H	-0.604373	7.203265	-1.096650
H	-3.037738	7.458184	-1.370038
H	-4.568945	5.689630	-0.509789
C	1.336621	6.433828	0.700606
C	1.642399	4.312890	-0.396795
C	3.029815	4.472216	-0.238736
C	2.706473	6.576343	0.857826
C	3.560480	5.589462	0.379502
H	0.671076	7.201504	1.080430
H	3.680732	3.690639	-0.613338
H	3.104550	7.454977	1.354287
H	4.634953	5.686780	0.491801
C	-1.154013	3.092518	0.985425
C	-1.005521	1.948332	1.361613
C	-0.895914	0.608040	1.593591
C	-0.892338	-0.609143	1.600981
C	-1.002823	-1.949116	1.365998
C	-1.150792	-3.093333	0.989968

Table S73. Supplementary Information (Table S10) - Tolanophane – (165°) – cam- B3LYP/6-31G(d,p) - E= -1380.34605184 u.a.

	X	Y	Z
C	-1.465109	-4.199278	-0.779788
C	-2.848410	-4.352592	-0.967903
C	-0.741237	-5.201036	-0.099581
C	-1.444690	-6.315067	0.368815
C	-2.812061	-6.452433	0.183707
C	-3.518739	-5.465539	-0.493403
H	-3.384063	-3.571774	-1.495607
H	-4.588187	-5.560106	-0.647986
H	-3.323600	-7.327703	0.569950
H	-0.896333	-7.083155	0.903639
C	0.736379	-5.201062	0.098309
C	2.843548	-4.352850	0.966873
C	3.513878	-5.465674	0.492086
C	2.807203	-6.452388	-0.185289
C	1.439833	-6.314971	-0.370373
H	3.379198	-3.572172	1.494789
H	4.583324	-5.560285	0.646657
H	0.891478	-7.082919	-0.905400
H	3.318744	-7.327558	-0.571756
C	1.460249	-4.199484	0.778783
C	0.875245	-2.996382	1.273622
C	0.537023	-1.881802	1.612532
C	-0.541966	-1.881360	-1.612969
C	-0.880108	-2.996037	-1.274297
C	0.156732	-0.587314	1.812091
C	-0.161879	0.586748	1.812303
C	-0.541966	1.881360	1.612969
C	-0.161879	-0.586748	-1.812303
C	0.537023	1.881802	-1.612532
C	0.875245	2.996382	-1.273622
C	-1.465109	4.199278	0.779788
C	-2.848410	4.352592	0.967903
C	-0.741237	5.201036	0.099581
C	-1.444690	6.315067	-0.368815
C	-2.812061	6.452433	-0.183707
C	-3.518739	5.465539	0.493403
H	-3.384063	3.571774	1.495607
C	0.736379	5.201062	-0.098309
H	-0.896333	7.083155	-0.903639
H	-3.323600	7.327703	-0.569950
H	-4.588187	5.560106	0.647986
C	1.439833	6.314971	0.370373
C	1.460249	4.199484	-0.778783
C	2.843548	4.352850	-0.966873
C	2.807203	6.452388	0.185289
C	3.513878	5.465674	-0.492086
H	0.891478	7.082919	0.905400
H	3.379198	3.572172	-1.494789
H	3.318744	7.327558	0.571756
H	4.583324	5.560285	-0.646657
C	-0.880108	2.996037	1.274297

Table S74. Supplementary Information - Metallacumulene – B3LYP/def2svp - E=-6907.7447252 u.a.

	X	Y	Z		X	Y	Z
H	9.496348	17.258600	24.740008	C	6.980347	17.012598	17.321916
H	-2.001465	17.258600	26.715915	C	0.514536	17.012598	34.134006
H	8.283415	16.962394	23.737646	H	6.571543	16.356594	16.770514
H	-0.788532	16.962394	27.718276	H	0.923340	16.356594	34.685408
H	8.014193	17.732194	25.116665	C	6.588990	17.150325	18.655036
H	-0.519310	17.732194	26.339257	C	0.905893	17.150325	32.800886
C	8.144286	20.498457	25.625255	H	5.911213	16.589208	19.011934
C	-0.649403	20.498457	25.830667	H	1.583670	16.589208	32.443988
H	7.430998	19.864208	25.847339	C	5.384840	22.683854	22.228547
H	0.063886	19.864208	25.608583	C	2.110043	22.683854	29.227375
H	7.792436	21.412177	25.660039	C	5.623617	22.913623	23.587189
H	-0.297552	21.412177	25.795883	C	1.871267	22.913623	27.868733
Fe	7.537720	19.968801	22.459584	H	6.271721	22.394510	24.048440
Fe	-0.042837	19.968801	28.996338	H	1.223162	22.394510	27.407482
P	6.581342	18.450787	21.166702	C	4.911275	23.905662	24.267436
P	0.913541	18.450787	30.289220	C	2.583609	23.905662	27.188486
P	6.350227	21.436108	21.281552	H	5.083864	24.062970	25.188703
P	1.144656	21.436108	30.174370	H	2.411019	24.062970	26.267219
C	9.091680	21.192449	23.300065	C	3.958095	24.660402	23.610653
C	-1.596797	21.192449	28.155857	C	3.536788	24.660402	27.845269
C	9.624507	20.491930	22.161242	H	3.475357	25.329794	24.081372
C	-2.129623	20.491930	29.294680	H	4.019526	25.329794	27.374551
C	9.521530	19.099093	22.421609	C	3.704400	24.437996	22.265389
C	-2.026646	19.099093	29.034313	C	3.790484	24.437996	29.190533
C	8.897605	18.918022	23.696275	H	3.042635	24.949914	21.817311
C	-1.402721	18.918022	27.759647	H	4.452249	24.949914	29.638611
C	8.657065	20.212292	24.241503	C	4.421758	23.463361	21.571558
C	-1.162181	20.212292	27.214420	C	3.073125	23.463361	29.884365
C	9.239211	22.660593	23.560844	H	4.255763	23.326638	20.646174
C	-1.744328	22.660593	27.895079	H	3.239120	23.326638	30.809748
H	8.451570	22.988595	24.042265	C	7.193088	22.538429	20.071720
H	-0.956687	22.988595	27.413657	C	0.301795	22.538429	31.384202
H	9.322994	23.137535	22.708528	C	7.753149	23.737645	20.532765
H	-1.828111	23.137535	28.747395	C	-0.258266	23.737645	30.923157
H	10.042181	22.816227	24.101954	H	7.595784	24.012765	21.428304
H	-2.547298	22.816227	27.353968	H	-0.100900	24.012765	30.027618
C	10.376714	21.134379	21.024067	C	8.537369	24.534891	19.697121
C	-2.881831	21.134379	30.431856	C	-1.042486	24.534891	31.758801
H	11.238652	21.467402	21.350091	H	8.932216	25.331467	20.030761
H	9.852650	21.880752	20.666757	H	-1.437333	25.331467	31.425161
H	-2.357766	21.880752	30.789166	C	8.735553	24.158358	18.373675
H	10.528518	20.471681	20.316856	C	-1.240670	24.158358	33.082247
C	10.139516	17.988237	21.625278	H	9.276324	24.690524	17.801691
C	-2.644633	17.988237	29.830645	H	-1.781441	24.690524	33.654232
H	10.286952	18.289463	20.703805	C	8.146270	23.007003	17.893900
H	-2.792069	18.289463	30.752117	C	-0.651386	23.007003	33.562022
H	9.538094	17.215089	21.623837	H	8.261932	22.769369	16.980454
H	-2.043210	17.215089	29.832086	H	-0.767048	22.769369	34.475468
H	10.995449	17.735541	22.027251	C	7.383489	22.183651	18.725839
C	8.651057	17.603336	24.382492	C	0.111394	22.183651	32.730083
C	-1.156174	17.603336	27.073430	C	6.993325	21.388749	18.382114
				H	0.501559	21.388749	33.073809
				C	6.074510	19.782542	23.528323
				C	1.420373	19.782542	27.927599
				C	5.150289	19.656697	24.362321
				C	2.344594	19.656697	27.093601
				C	4.188215	19.574863	25.294085
				C	3.306668	19.574863	26.161838
				H	-3.033635	20.471681	31.139066
				H	-3.743768	21.467402	30.105831
				H	-3.500566	17.735541	29.428671