Supporting Information

for

Theoretical comparison of ethylene-, disilane- and ethynylene-bonded aromatic compounds from the viewpoint of conjugation formation

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1. HOMO and LUMO energy levels of benzene π, ethane C–C σ, disilane Si–Si σ, and ethylene C=C π bonds

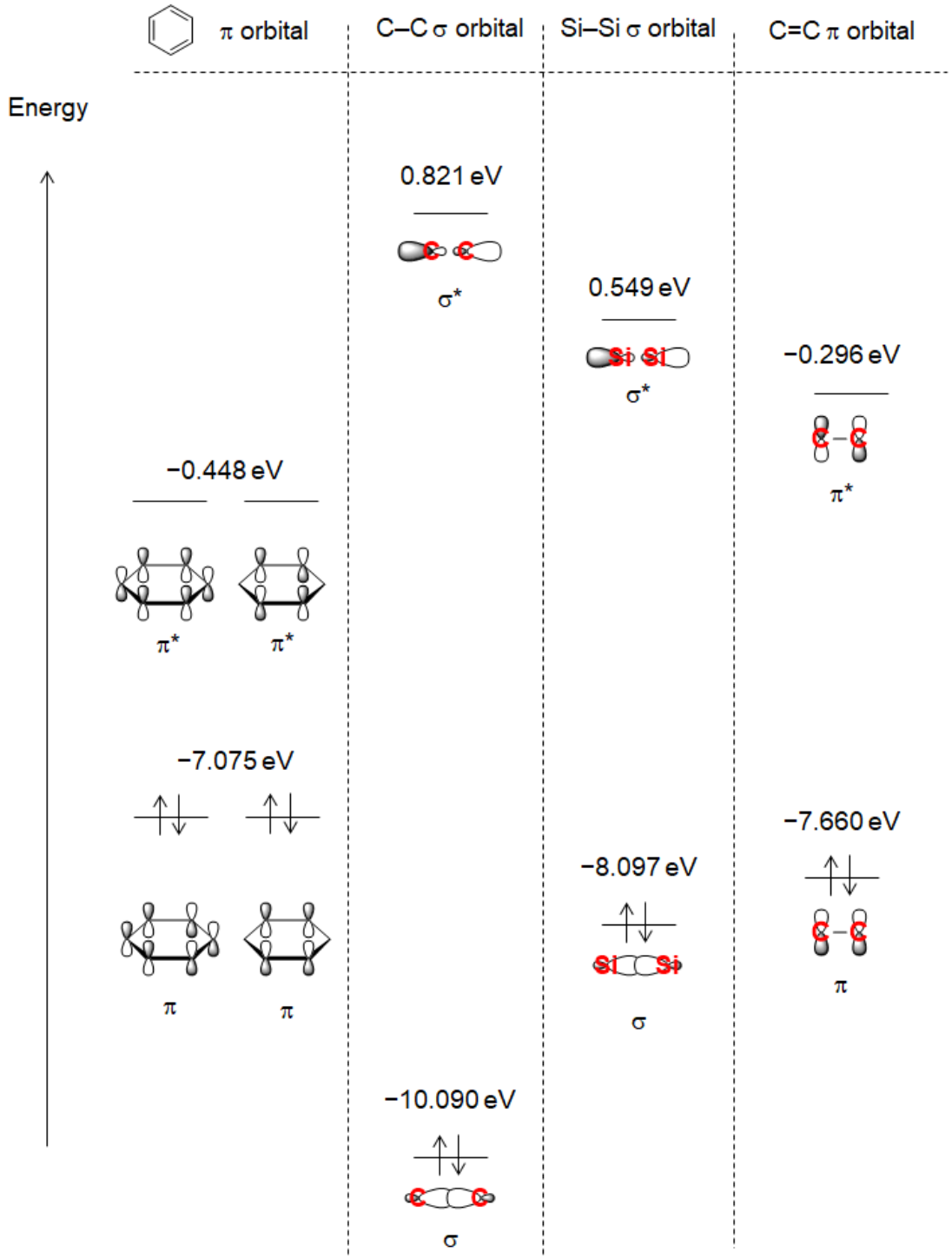

Fig. S1 HOMO and LUMO energy levels of benzene π and π*, ethane C–C σ and σ*, disilane Si–Si σ and σ*, and ethylene C=C π and π* orbitals.

2. Conformational isomers

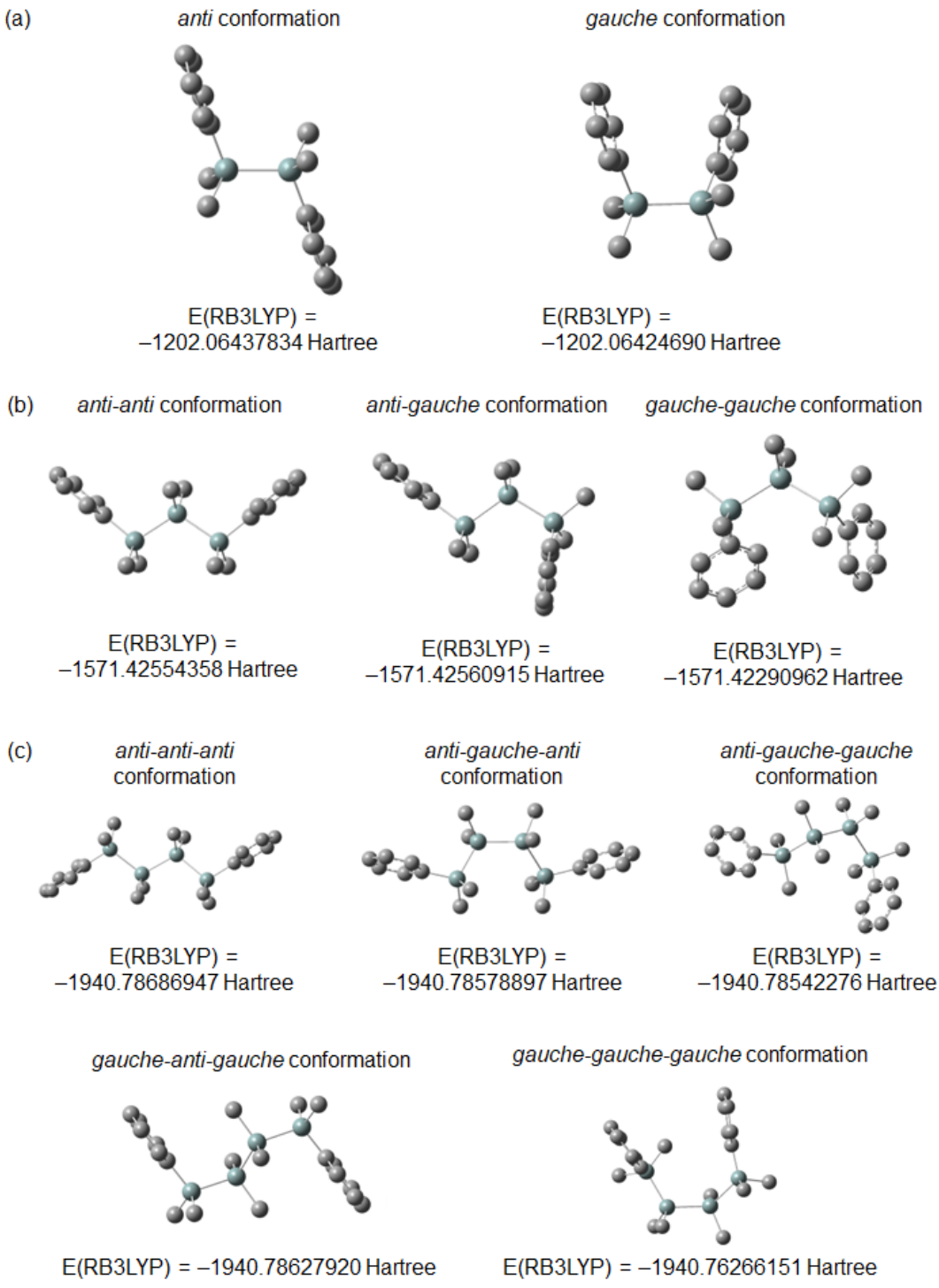

Fig. S2 Representative conformational isomers and energies of (a) **2**, (b) **11**, and (c) **8**. Hydrogens were omitted for clarity.

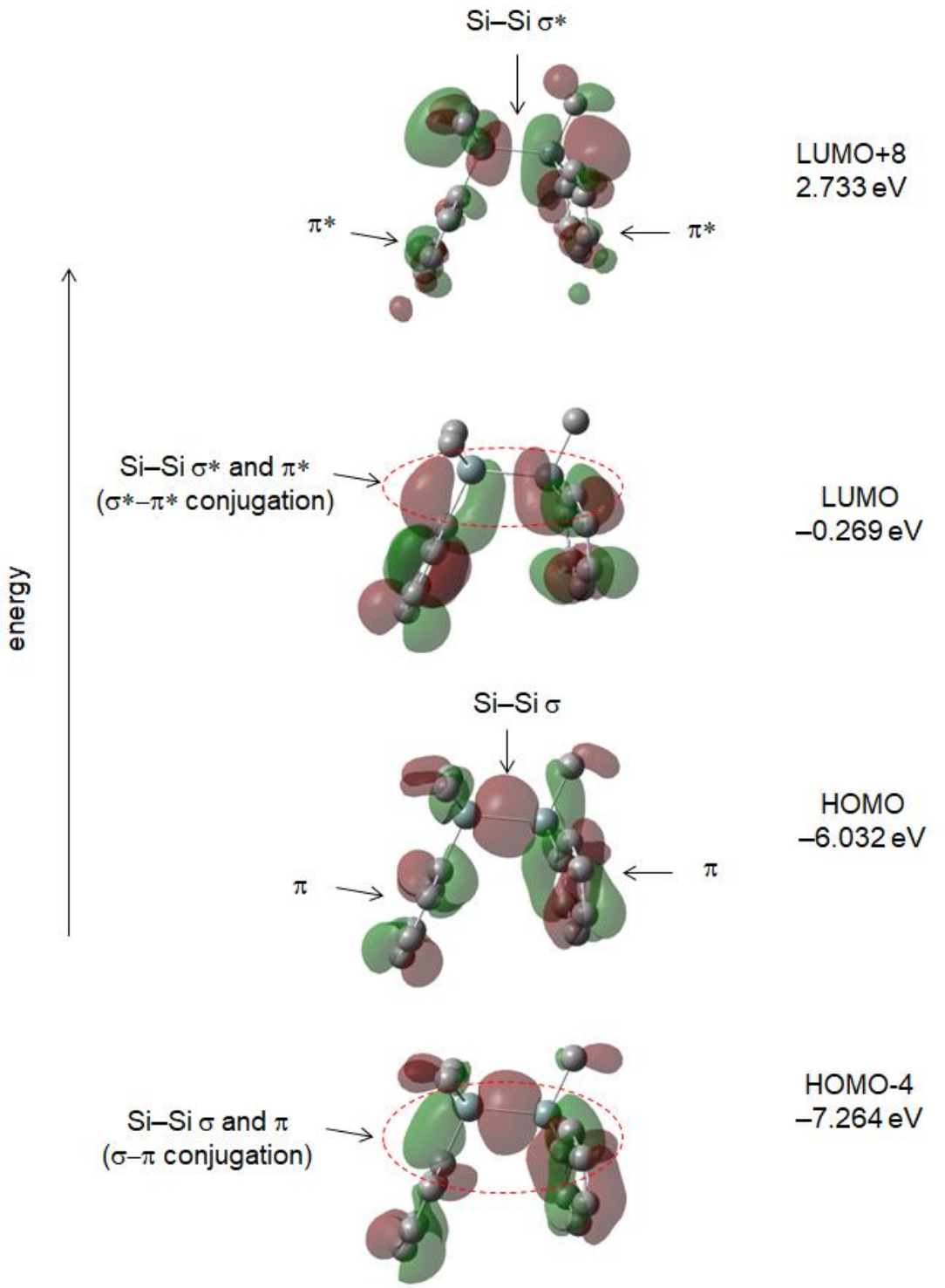

Fig. S3 LUMO+8, LUMO, HOMO, and HOMO-4 and energy levels of *gauche*-**2**. Hydrogen atoms are omitted for clarity. The isovalues are set to 0.03.

3. Comparison of calculation methods

Table S1. DFT calculations of **2** in various basis functions.

B3LYP/	6-31G	6-31G(d)	6-31G(d,p)
LUMO (eV)	–0.336	–0.426	–0.440
HOMO (eV)	–6.076	–6.020	–6.035

4. TD-DFT calculation of 1–11

Table S1. TD-DFT calculations of vertical transitions at the ground state geometry of **1**.

Excited State 1: Singlet-A 5.0746 eV 244.33 nm *f*=0.0006 <S**2>=0.000

HOMO-3 -> LUMO+1 0.18037

HOMO-1 -> LUMO -0.39806

HOMO-1 -> LUMO+3 0.18189

HOMO -> LUMO+1 -0.51040

Excited State 2: Singlet-A 5.3108 eV 233.45 nm *f*=0.0005 <S**2>=0.000

HOMO-3 -> LUMO+1 0.11927

HOMO-3 -> LUMO+2 -0.20650

HOMO-2 -> LUMO -0.35954

HOMO-2 -> LUMO+3 -0.25612

HOMO-1 -> LUMO+3 0.11215

HOMO -> LUMO+2 -0.47606

Excited State 3: Singlet-A 5.4437 eV 227.76 nm *f*=0.3103 <S2>=0.000**

HOMO-1 -> LUMO+1 0.15261

HOMO -> LUMO -0.68202

Excited State 4: Singlet-A 5.8293 eV 212.69 nm *f*=0.0095 <S**2>=0.000

HOMO-3 -> LUMO 0.23397

HOMO-1 -> LUMO+1 -0.12035

HOMO -> LUMO+3 -0.64059

Excited State 5: Singlet-A 5.8624 eV 211.49 nm *f*=0.0072 <S**2>=0.000

HOMO-3 -> LUMO+1 -0.44746

HOMO-3 -> LUMO+2 -0.13960

HOMO-1 -> LUMO 0.31392

HOMO -> LUMO+1 -0.41089

Table S2. TD-DFT calculations of vertical transitions at the ground state geometry of **2**.

Excited State 1: Singlet-A 5.0579 eV 245.13 nm *f*=0.5184 <S2>=0.000**

HOMO -> LUMO 0.69609

Excited State 2: Singlet-A 5.1819 eV 239.26 nm *f*=0.0003 <S**2>=0.000

HOMO-3 -> LUMO+2 0.18651
HOMO-2 -> LUMO 0.36206
HOMO-1 -> LUMO+1 -0.17964
HOMO-1 -> LUMO+3 -0.12907
HOMO -> LUMO+1 0.38119
HOMO -> LUMO+3 -0.36796

Excited State 3: Singlet-A 5.2006 eV 238.40 nm *f*=0.0003 <S**2>=0.000

HOMO-3 -> LUMO+1 0.12900
HOMO-3 -> LUMO+3 -0.15338
HOMO-2 -> LUMO+1 0.18400
HOMO-2 -> LUMO+3 0.13783
HOMO-1 -> LUMO -0.38419
HOMO -> LUMO+2 0.50355

Excited State 4: Singlet-A 5.4897 eV 225.85 nm *f*=0.0000 <S**2>=0.000

HOMO-4 -> LUMO+1 -0.11063
HOMO-3 -> LUMO -0.16402
HOMO-2 -> LUMO -0.10819
HOMO -> LUMO+1 0.53695
HOMO -> LUMO+3 0.37437

Excited State 5: Singlet-A 5.7426 eV 215.90 nm *f*=0.0113 <S**2>=0.000

HOMO-4 -> LUMO+1 0.11385
HOMO-4 -> LUMO+3 -0.17667
HOMO-3 -> LUMO+2 0.30510
HOMO-2 -> LUMO 0.37299
HOMO -> LUMO+1 -0.17285
HOMO -> LUMO+3 0.41592

Table S3. TD-DFT calculations of vertical transitions at the ground state geometry of **3**.

Excited State 1: Singlet-A 4.0044 eV 309.62 nm *f*=0.9830 <S2>=0.000**

HOMO -> LUMO 0.70583

Excited State 2: Singlet-A 4.5976 eV 269.67 nm *f*=0.0068 <S**2>=0.000

HOMO-1 -> LUMO 0.52589

HOMO -> LUMO+1 0.45631

Excited State 3: Singlet-A 4.6073 eV 269.10 nm *f*=0.0000 <S**2>=0.000

HOMO-2 -> LUMO 0.52788

HOMO -> LUMO+2 -0.45303

Excited State 4: Singlet-A 5.1374 eV 241.34 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO 0.54739

HOMO -> LUMO+2 -0.12988

HOMO -> LUMO+3 0.41891

Excited State 5: Singlet-A 5.2321 eV 236.97 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO 0.12390

HOMO-2 -> LUMO 0.44406

HOMO-1 -> LUMO+3 -0.10468

HOMO -> LUMO+2 0.50778

Table S4. TD-DFT calculation of vertical transitions at the ground state geometry of **4**.

Excited State 1: Singlet-A 5.2094 eV 238.00 nm *f*=0.0004 <S**2>=0.000

HOMO-5 ->LUMO+4 -0.12116

HOMO-4 ->LUMO -0.10190

HOMO-4 ->LUMO+5 -0.12798

HOMO-2 ->LUMO -0.35639

HOMO-2 ->LUMO+5 -0.16738

HOMO ->LUMO+1 0.46810

HOMO ->LUMO+4 -0.25992

Excited State 2: Singlet-A 5.3470 eV 231.88 nm *f*=0.0000 <S**2>=0.000

HOMO-5 ->LUMO+3 -0.16865

HOMO-4 ->LUMO+2 -0.25579

HOMO-3 ->LUMO -0.28695

HOMO-3 ->LUMO+5 0.16485

HOMO-2 ->LUMO+2 0.15768

HOMO-1 ->LUMO+1 -0.25477

HOMO-1 ->LUMO+4 -0.18934

HOMO ->LUMO+3 0.41275

Excited State 3: Singlet-A 5.3599 eV 231.32 nm *f*=0.0014 <S**2>=0.000

HOMO-5 ->LUMO+1 -0.17213

HOMO-4 ->LUMO 0.29818

HOMO-4 ->LUMO+5 -0.10480

HOMO-3 ->LUMO+2 0.29306

HOMO-2 ->LUMO+5 0.15036

HOMO-1 ->LUMO+3 -0.30608

HOMO ->LUMO+1 0.18729

HOMO ->LUMO+4 0.35673

Excited State 4: Singlet-A 5.4116 eV 229.11 nm *f*=0.6492 <S2>=0.000**

HOMO ->LUMO 0.69166

Excited State 5: Singlet-A 5.6881 eV 217.97 nm *f*=0.0000 <S**2>=0.000

HOMO ->LUMO+2 0.68861

Table S5. TD-DFT calculation of vertical transitions at the ground state geometry of **5**.

Excited State 1: Singlet-A 4.5573 eV 272.06 nm *f*=1.0884 <S2>=0.000**

HOMO -> LUMO 0.69304

Excited State 2: Singlet-A 4.8411 eV 256.11 nm *f*=0.0010 <S**2>=0.000

HOMO-2 -> LUMO -0.37032

HOMO-2 -> LUMO+2 -0.12589

HOMO -> LUMO+3 0.47651

HOMO -> LUMO+5 -0.29824

Excited State 3: Singlet-A 4.9724 eV 249.34 nm *f*=0.0001 <S**2>=0.000

HOMO-1 -> LUMO -0.24292

HOMO -> LUMO+1 0.63957

Excited State 4: Singlet-A 5.0149 eV 247.23 nm *f*=0.0000 <S**2>=0.000

HOMO-5 -> LUMO+4 -0.11836

HOMO-4 -> LUMO+1 0.23547

HOMO-3 -> LUMO 0.22823

HOMO-3 -> LUMO+2 -0.15873

HOMO-1 -> LUMO+3 0.20060

HOMO-1 -> LUMO+5 0.22603

HOMO -> LUMO+4 0.49842

Excited State 5: Singlet-A 5.0161 eV 247.17 nm *f*=0.0001 <S**2>=0.000

HOMO-4 -> LUMO -0.21851

HOMO-4 -> LUMO+2 0.15911

HOMO-3 -> LUMO+1 -0.23675

HOMO-1 -> LUMO+4 0.29997

HOMO -> LUMO+3 0.28219

HOMO -> LUMO+5 0.40743

Table S6. TD-DFT calculation of vertical transitions at the ground state geometry of **6**.

Excited State 1: Singlet-A 3.2081 eV 386.47 nm *f*=1.8315 <S2>=0.000**

HOMO -> LUMO 0.70752

Excited State 2: Singlet-A 3.8925 eV 318.52 nm *f*=0.0000 <S**2>=0.000

HOMO-1 -> LUMO 0.53361

HOMO -> LUMO+1 0.45816

Excited State 3: Singlet-A 4.2690 eV 290.43 nm *f*=0.0045 <S**2>=0.000

HOMO-4 -> LUMO 0.52000

HOMO -> LUMO+2 -0.42129

HOMO -> LUMO+9 0.20381

Excited State 4: Singlet-A 4.3959 eV 282.04 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO -0.35502

HOMO-1 -> LUMO -0.31987

HOMO -> LUMO+1 0.36557

HOMO -> LUMO+4 -0.33067

Excited State 5: Singlet-A 4.4217 eV 280.40 nm *f*=0.0012 <S**2>=0.000

HOMO-3 -> LUMO+1 0.13784

HOMO-2 -> LUMO 0.55025

HOMO-1 -> LUMO+4 -0.14463

HOMO -> LUMO+2 0.17122

HOMO -> LUMO+3 0.34706

Table S7. TD-DFT calculation of vertical transitions at the ground state geometry of **7**.

Excited State 1: Singlet-A 5.3838 eV 230.29 nm *f*=0.0002 <S**2>=0.000

HOMO-3 -> LUMO+3 0.30535

HOMO-2 -> LUMO -0.37449

HOMO-1 -> LUMO+2 0.32648

89 -> 91 0.38652

Excited State 2: Singlet-A 5.3861 eV 230.19 nm *f*=0.0003 <S**2>=0.000

HOMO-3 -> LUMO 0.36577

HOMO-2 -> LUMO+3 -0.30005

HOMO-1 -> LUMO+1 -0.33239

HOMO -> LUMO+2 -0.36142

HOMO -> LUMO+3 -0.12010

Excited State 3: Singlet-A 5.9405 eV 208.71 nm *f*=0.1684 <S2>=0.000**

HOMO-3 -> LUMO+2 0.17373

HOMO-2 -> LUMO+1 0.19487

HOMO -> LUMO 0.64566

Excited State 4: Singlet-A 6.0567 eV 204.71 nm *f*=0.0011 <S**2>=0.000

HOMO-3 -> LUMO+1 0.27773

HOMO-2 -> LUMO+2 0.27150

HOMO-1 -> LUMO 0.50174

HOMO -> LUMO+3 -0.26454

Excited State 5: Singlet-A 6.1329 eV 202.16 nm *f*=0.0000 <S**2>=0.000

HOMO-1 -> LUMO 0.39514

HOMO -> LUMO+2 -0.23414

HOMO -> LUMO+3 0.52526

Table 8. TD-DFT calculation of vertical transitions at the ground state geometry of **8**.

Excited State 1: Singlet-A 4.7277 eV 262.25 nm *f*=0.8925 <S2>=0.000**

HOMO ->LUMO 0.69857

Excited State 2: Singlet-A 5.0910 eV 243.54 nm *f*=0.0001 <S**2>=0.000

HOMO-3 ->LUMO 0.26959
HOMO-2 ->LUMO+1 0.18745
HOMO-1 ->LUMO+3 0.19223
HOMO ->LUMO+1 0.16850
HOMO ->LUMO+2 0.55613

Excited State 3: Singlet-A 5.1132 eV 242.48 nm *f*=0.0009 <S**2>=0.000

HOMO-3 ->LUMO+1 0.20530
HOMO-2 ->LUMO 0.29861
HOMO-1 ->LUMO+2 0.20877
HOMO ->LUMO+3 0.54815

Excited State 4: Singlet-A 5.1958 eV 238.63 nm *f*=0.0007 <S**2>=0.000

HOMO ->LUMO+1 0.66837
HOMO ->LUMO+2 -0.13613

Excited State 5: Singlet-A 5.4673 eV 226.78 nm *f*=0.0036 <S**2>=0.000

HOMO-6 ->LUMO+3 -0.10193
HOMO-5 ->LUMO+2 0.10861
HOMO-4 ->LUMO+2 0.20219
HOMO-3 ->LUMO 0.34268
HOMO-2 ->LUMO+1 0.18464
HOMO-1 ->LUMO+3 0.23854
HOMO ->LUMO+2 -0.32515
HOMO ->LUMO+4 -0.33101

Table 9. TD-DFT calculation of vertical transitions at the ground state geometry of **9**.

Excited State 1: Singlet-A 3.1436 eV 394.40 nm *f*=1.5734 <S2>=0.000**

HOMO -> LUMO 0.71417

Excited State 2: Singlet-A 4.0675 eV 304.81 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO -0.13886
HOMO-1 -> LUMO -0.47984

HOMO -> LUMO+1 0.49469

Excited State 3: Singlet-A 4.1884 eV 296.02 nm *f*=0.0018 <S**2>=0.000

HOMO-2 -> LUMO -0.54500

HOMO -> LUMO+2 -0.43595

Excited State 4: Singlet-A 4.2133 eV 294.27 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO -0.52587

HOMO-1 -> LUMO 0.17560

HOMO -> LUMO+3 -0.42566

Excited State 5: Singlet-A 4.6289 eV 267.85 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO 0.38635

HOMO-1 -> LUMO 0.27545

HOMO -> LUMO+1 0.36084

HOMO -> LUMO+3 -0.36468

Table 9. TD-DFT calculation of vertical transitions at the ground state geometry of **10**.

Excited State 1: Singlet-A 5.3358 eV 232.36 nm *f*=0.0008 <S**2>=0.000

HOMO-3 -> LUMO -0.18713

HOMO-3 -> LUMO+3 -0.19415

HOMO-2 -> LUMO 0.28214

HOMO-2 -> LUMO+3 -0.14434

HOMO-1 -> LUMO+1 0.38174

HOMO -> LUMO+2 0.41017

Excited State 2: Singlet-A 5.3504 eV 231.73 nm *f*=0.0018 <S**2>=0.000

HOMO-3 -> LUMO+2 0.27811

HOMO-2 -> LUMO -0.13005

HOMO-2 -> LUMO+1 0.32077

HOMO-2 -> LUMO+2 0.14063

HOMO-1 -> LUMO 0.34658

HOMO -> LUMO -0.21219

HOMO -> LUMO+3 -0.29730

Excited State 3: Singlet-A 5.7076 eV 217.23 nm *f*=0.0265 <S**2>=0.000

HOMO-3 -> LUMO -0.28129

HOMO -> LUMO -0.21321

HOMO -> LUMO+1 0.59002

Excited State 4: Singlet-A 5.7374 eV 216.10 nm *f*=0.0156 <S2>=0.000**

HOMO-3 -> LUMO+1 -0.30413

HOMO-3 -> LUMO+2 0.11825

HOMO-1 -> LUMO 0.16564

HOMO -> LUMO 0.54813

HOMO -> LUMO+1 0.20797

Excited State 5: Singlet-A 5.8663 eV 211.35 nm *f*=0.0007 <S**2>=0.000

HOMO-3 -> LUMO+1 0.12122

HOMO-2 -> LUMO 0.43663

HOMO-2 -> LUMO+1 -0.11995

HOMO-1 -> LUMO 0.38654

HOMO-1 -> LUMO+1 -0.34574

Table 10. TD-DFT calculation of vertical transitions at the ground state geometry of **11**.

Excited State 1: Singlet-A 4.8927 eV 253.40 nm *f*=0.6601 <S2>=0.000**

HOMO -> LUMO 0.69813

Excited State 2: Singlet-A 5.1305 eV 241.66 nm *f*=0.0000 <S**2>=0.000

HOMO-3 -> LUMO+2 -0.20898

HOMO-2 -> LUMO 0.32900

HOMO-1 -> LUMO+3 -0.18664

HOMO -> LUMO+3 0.55198

Excited State 3: Singlet-A 5.1738 eV 239.64 nm *f*=0.0001 <S**2>=0.000

HOMO-3 -> LUMO+1 0.36720

HOMO-2 -> LUMO+2 -0.23153

HOMO-1 -> LUMO+3 -0.22257

HOMO -> LUMO+4 0.49905

Excited State 4: Singlet-A 5.3878 eV 230.12 nm *f*=0.0147 <S**2>=0.000

HOMO-4 -> LUMO+2	0.10314
HOMO-1 -> LUMO	-0.15067
HOMO -> LUMO+2	0.67656

Excited State 5: Singlet-A 5.5761 eV 222.35 nm *f*=0.0000 <S**2>=0.000

HOMO-5 -> LUMO+4	0.10180
HOMO-4 -> LUMO+3	0.23954
HOMO-3 -> LUMO+2	0.14188
HOMO-2 -> LUMO	-0.38144
HOMO-1 -> LUMO+4	0.26734
HOMO -> LUMO+3	0.39758
HOMO -> LUMO+5	-0.18701

5. Considerations on conformational isomers of 1 and 2

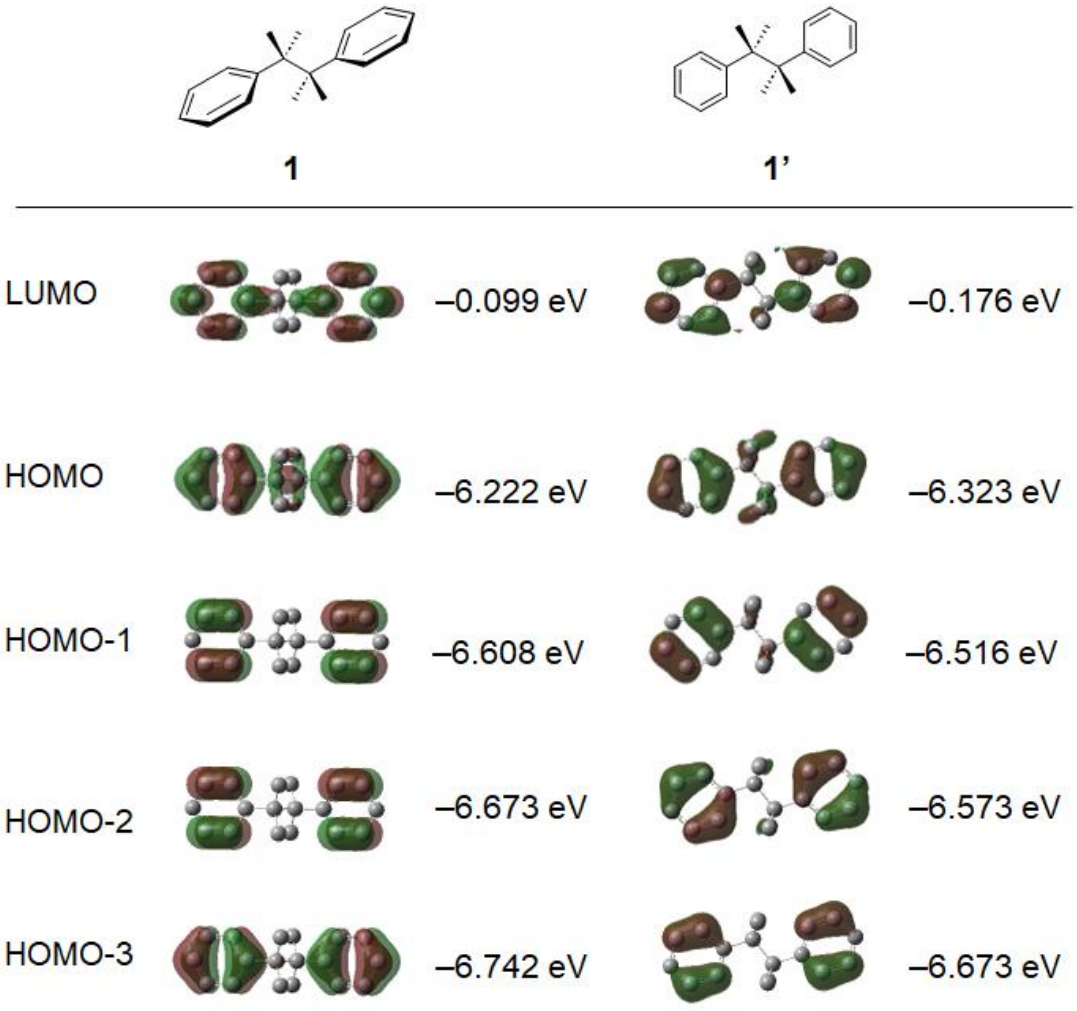

Fig. S4 Comparison of molecular orbitals of **1** and **1'**. Hydrogen atoms are omitted for clarity. The isovalues are set to 0.03.

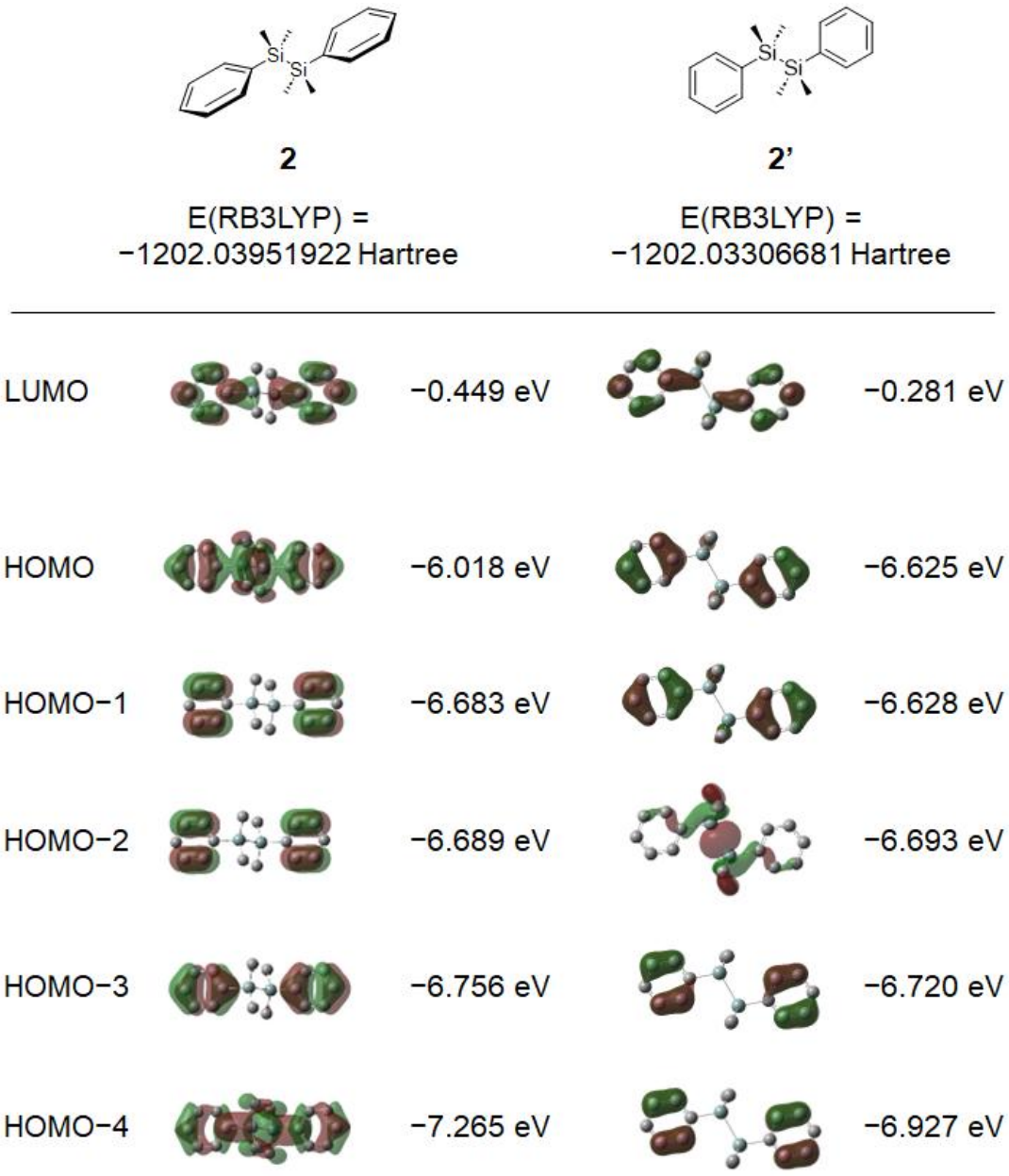

Fig. S5 Comparison of molecular orbitals of **2** and **2'**. Hydrogen atoms are omitted for clarity. The isovalues are set to 0.03.