

## Supporting Information

### ***O*-Ylide and $\pi$ -Complex Formation in Reactions of a Carbene with Dibenzo and Monobenzo Crown Ethers**

Pablo Højjemberg, Robert A. Moss,\* David V. Feinblum, and Karsten Krogh-Jespersen\*

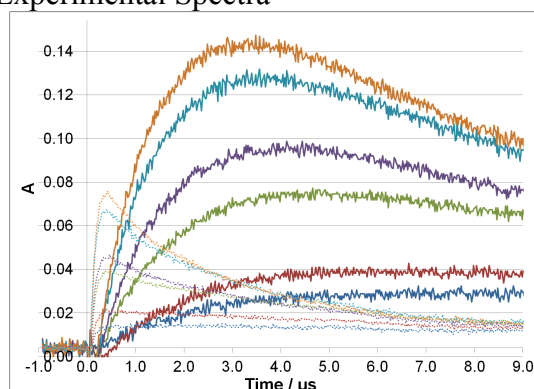
*Department of Chemistry and Chemical Biology, Rutgers, The State University of New  
Jersey, New Brunswick, New Jersey 08903*

E-mail: moss@rutchem.rutgers.edu, krogh@rutchem.rutgers.edu

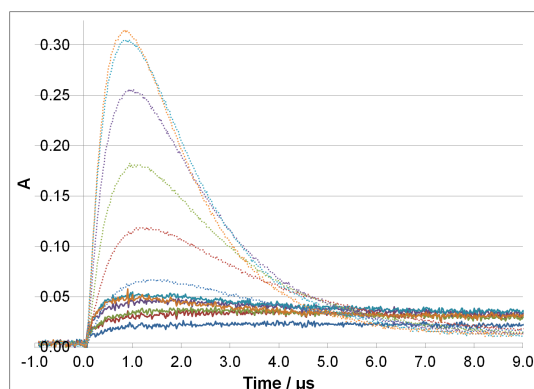
### Contents

|                                                                                             | Page  |
|---------------------------------------------------------------------------------------------|-------|
| 1. Figures S-1 – S-12. Experimental Spectra                                                 | S-2   |
| 2. Tables S-1 – S-3. Computed Relative Energies of Conformers                               | S-6   |
| 3. Figures S-13 – S-16. Pictures of Conformers and Relative Energies                        | S-9   |
| 4. Geometries, Energies, Orbitals, and Excitations for <b>1</b> , <b>3a</b> , and <b>3b</b> | S-24  |
| 5. Geometries, Energies, Orbitals and Excitations for <i>O</i> -Ylides <b>10a-10d</b>       | S-33  |
| 6. Geometries, Energies, Orbitals, and Excitations for Half-Sandwiches <b>11a-11d</b>       | S-48  |
| 7. Geometries, Energies, Orbitals, and Excitations for Full-Sandwiches <b>12a-12d</b>       | S-74  |
| 8. Geometry and Energy of TS for <b>10a</b> $\leftrightarrow$ <b>12a</b> Interconversion    | S-104 |

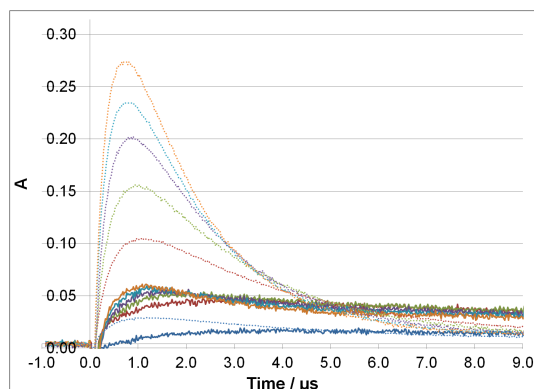
## 1. Figures S-1 – S-12. Experimental Spectra



**Figure S-1.** Overlap of spectra of *O*-Ylide of PNPCC with DB-18-C-6 at 492 nm (dotted lines), and spectra of the corrected  $\pi$ -complex of PNPCC with DB-18-C-6 monitored at 388 nm (solid lines). The ylide maxima are at shorter times. Concentrations of DB-18-C-6 are 2.41, 4.82, 9.64, 14.5, 19.3, and 24.1 mM in DCE.

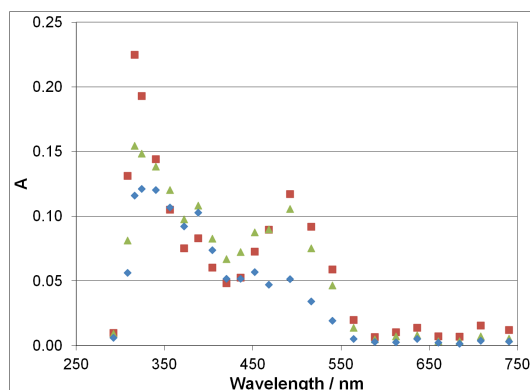


**Figure S-2.** Control experiment. Overlap of spectra of *O*-ylide of PNPCC with 18-C-6 at 492 nm (dotted lines), and the corrected absorption at 388 nm (solid lines) for various concentrations of 18-C-6 (2.08, 4.16, 8.32, 12.5, 16.6, and 20.8 mM) in DCE.

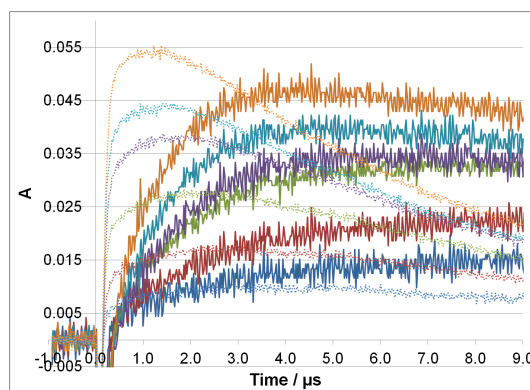


**Figure S-3.** Overlap of spectra of *O*-ylide of PNPCC with B-18-C-6 at 492 nm (dotted lines), and spectra of the corrected (product) absorption at 388 nm (“noisy” lines) for various concentrations of B-18-C-6 (2.55, 5.10, 10.2, 15.3, 20.4, and 25.5 mM) in DCE.

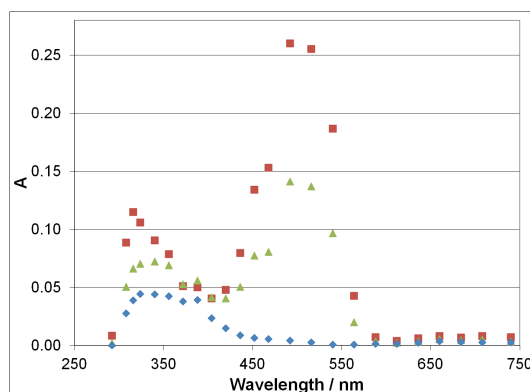




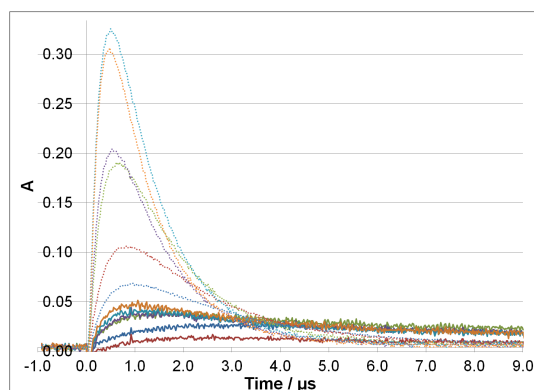
**Figure S-4.** Calibrated UV-vis spectra of PNPCC and 0.021 M DB-15-C-5 in DCE. The ylide absorption at 492 nm is maximized after 808 ns (■); the  $\pi$ -complex at  $\sim 360$  nm is maximized at  $\sim 3$   $\mu$ s (▲). At 9  $\mu$ s (◆), only persistent products remain.



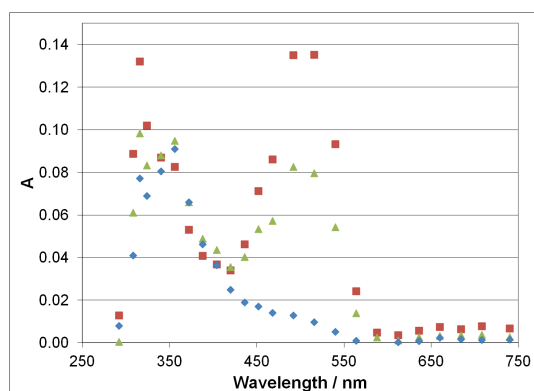
**Figure S-5.** Overlap of spectra of *O*-ylide of PNPCC with DB-15-C-5 at 492 nm (dotted lines), and spectra of the corrected  $\pi$ -complex absorption monitored at 388 nm ("noisy" lines) for various concentrations of DB-15-C-5 (2.45, 4.90, 9.8, 14.7, 19.6, and 24.5 mM) in DCE.



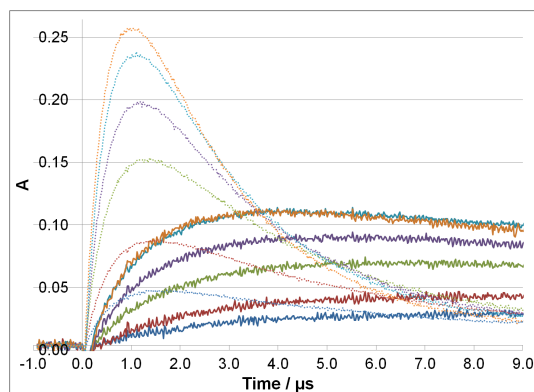
**Figure S-6.** Calibrated UV-vis spectra of PNPCC and 0.020 M B-15-C-5 in DCE. The ylide absorption at  $\sim 500$  nm is maximized after 628 ns (■); residual carbene absorption is at 316 nm. Other spectra obtained at 1.7  $\mu$ s (▲). At 9  $\mu$ s (◆), absorption of persistent products is almost constant over time at  $\sim 388$  nm.



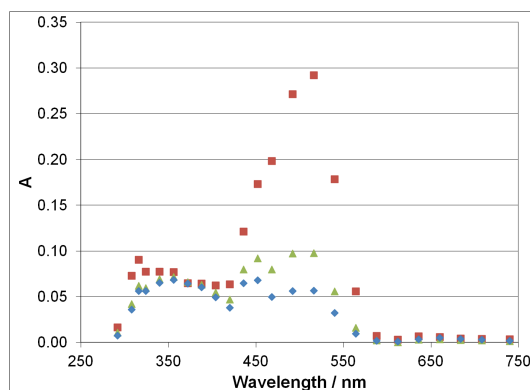
**Figure S-7.** Overlap of spectra of *O*-ylide of PNPCC with B-15-C-5 at ~500 nm (dotted lines), and spectra of the corrected (product) absorption at 388 nm (“noisy” lines) for various concentrations of B-15-C-5 (3.21, 6.42, 12.8, 19.3, 25.7, and 32.1 mM) in DCE.



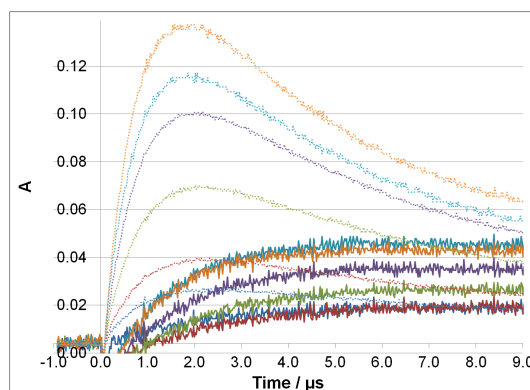
**Figure S-8.** Calibrated UV-vis spectra of PNPCC and 0.020 M DB-21-C-7 in DCE. The ylide absorption at 492 nm is maximized after 1000 ns (■); the  $\pi$ -complex at ~390 nm is maximized at ~3-4  $\mu$ s (▲). At 9  $\mu$ s (◆), only persistent products remain.



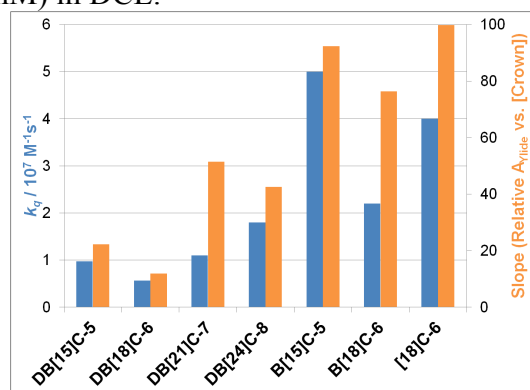
**Figure S-9.** Overlap of spectra of *O*-ylide of PNPCC with DB-21-C-7 at 492 nm (dotted lines), and spectra of the corrected  $\pi$ -complex absorption at 388 nm (“noisy” lines) for various concentrations of DB-21-C-7 (2.68, 5.36, 10.7, 16.1, 21.4, and 26.8 mM) in DCE.



**Figure S-10.** Calibrated UV-vis spectra of PNPCC and 0.023 M DB-24-C-8 in DCE. The ylide absorption at 492 nm is maximized after 2  $\mu$ s (■); the  $\pi$ -complex at  $\sim$ 390 nm is maximized at  $\sim$ 6  $\mu$ s (▲). At 9  $\mu$ s (◆), only persistent products remain.



**Figure S-11.** Overlap of spectra of *O*-ylide of PNPCC with DB-24-C-8 at 492 nm (dotted lines), and spectra of the corrected  $\pi$ -complex absorption at 388 nm ("noisy" lines) for various concentrations of DB-21-C-7 (1.04, 2.07, 4.14, 6.21, 8.28, and 10.4 mM) in DCE.



**Figure S-12.** Comparison of the quenching rate constant for carbene decay and the slope of the relative *O*-ylide absorbance maxima vs the concentration of crown compounds for reactions of PNPCC with crown ethers in DCE.

## 2. Tables S-1 – S-3. Computed Relative Energies of Conformers

**Table S-1.** Computed Relative Energies of Conformers Relative potential energies ( $E$ ), enthalpies ( $H$ ), entropies ( $S$ ) and free energies ( $G$ ) of DB-18-C-6 conformers **3a-k** (B97D/6-311+G(d)).<sup>a</sup>

| Conformer | $\Delta E$ | $\Delta H$ | $\Delta S$ | $\Delta G$ |
|-----------|------------|------------|------------|------------|
| <b>3a</b> | 0.00       | 0.00       | 0.00       | 0.00       |
| <b>3b</b> | 1.54       | 1.88       | 3.44       | 0.86       |
| <b>3c</b> | 1.68       | 2.13       | 0.43       | 2.00       |
| <b>3d</b> | 3.15       | 3.53       | 2.02       | 3.52       |
| <b>3e</b> | 3.39       | 3.95       | 1.26       | 3.58       |
| <b>3f</b> | 4.44       | 4.53       | 2.79       | 3.69       |
| <b>3g</b> | 4.26       | 4.15       | 1.22       | 3.79       |
| <b>3h</b> | 3.34       | 3.54       | -1.73      | 4.05       |
| <b>3i</b> | 6.07       | 6.20       | 4.68       | 4.81       |
| <b>3j</b> | 5.58       | 6.28       | 1.78       | 5.75       |
| <b>3k</b> | 5.94       | 6.57       | -3.43      | 7.59       |

<sup>a</sup> Units are kcal/mol for  $\Delta E$ ,  $\Delta H$ , and  $\Delta G$ ; units are cal/(deg•mol) for  $\Delta S$ . The standard state for concentrations is P = 1 atm, T = 298.15 K.

**Table S-2.** Relative potential energies ( $E$ ), enthalpies ( $H$ ), entropies ( $S$ ) and free energies ( $G$ ) of DB18-C-6/PNPCC  $O$ -ylides **10a-k** from (B97D/6-311+G(d)). All values are relative to the sum of free species.<sup>a</sup>

| $O$ -Ylide | $\Delta E$ | $\Delta H$ | $\Delta S$ | $\Delta G$ |
|------------|------------|------------|------------|------------|
| <b>10a</b> | -16.19     | -13.82     | -50.40     | 1.21       |
| <b>10b</b> | -15.35     | -12.79     | -47.26     | 1.30       |
| <b>10c</b> | -12.44     | -9.52      | -42.82     | 3.25       |
| <b>10d</b> | -10.31     | -7.64      | -42.24     | 4.95       |
| <b>10e</b> | -11.33     | -9.09      | -48.29     | 5.31       |
| <b>10f</b> | -9.60      | -7.22      | -45.45     | 6.33       |
| <b>10g</b> | -8.14      | -5.94      | -44.90     | 7.45       |
| <b>10h</b> | -6.92      | -4.46      | -41.59     | 7.94       |
| <b>10i</b> | -3.81      | -1.66      | -38.53     | 9.83       |
| <b>10j</b> | -4.57      | -2.45      | -43.74     | 10.59      |
| <b>10k</b> | -1.90      | 0.61       | -40.97     | 12.83      |

<sup>a</sup> Units are kcal/mol for  $\Delta E$ ,  $\Delta H$ , and  $\Delta G$ ; units are cal/(deg•mol) for  $\Delta S$ . The standard state is a concentration of 1.0 M for all species and T = 298.15 K.

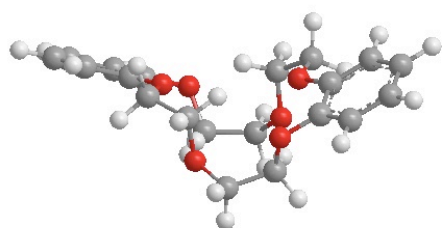
**Table S-3.** Relative potential energies ( $E$ ), enthalpies ( $H$ ), entropies ( $S$ ) and free energies ( $G$ ) of DB-18-C-6/PNPCC  $\pi$ -complexes **11a-i** and **12a-h** (B97D/6-311+G(d)). All values are relative to the sum of free species.<sup>a</sup>

| Complex    | $\Delta E$ | $\Delta H$ | $\Delta S$ | $\Delta G$ |
|------------|------------|------------|------------|------------|
| <b>12a</b> | -18.37     | -16.61     | -40.67     | -4.48      |
| <b>12b</b> | -17.29     | -15.45     | -36.91     | -4.44      |
| <b>12c</b> | -18.36     | -16.23     | -41.62     | -3.82      |
| <b>12d</b> | -18.36     | -15.85     | -41.20     | -3.57      |
| <b>11a</b> | -15.61     | -13.98     | -35.18     | -3.49      |
| <b>12e</b> | -16.60     | -14.44     | -39.23     | -2.74      |
| <b>11b</b> | -14.66     | -12.94     | -35.00     | -2.50      |
| <b>11c</b> | -14.56     | -12.95     | -35.96     | -2.23      |
| <b>11d</b> | -13.86     | -11.91     | -33.15     | -2.03      |
| <b>11e</b> | -13.23     | -11.41     | -35.68     | -0.77      |
| <b>11f</b> | -12.00     | -10.47     | -34.73     | -0.12      |
| <b>12f</b> | -10.20     | -8.22      | -34.40     | 2.04       |
| <b>12g</b> | -11.41     | -9.23      | -39.49     | 2.54       |
| <b>11g</b> | -9.86      | -7.92      | -35.44     | 2.64       |
| <b>11h</b> | -9.87      | -7.85      | -36.32     | 2.98       |
| <b>11i</b> | -9.05      | -6.99      | -33.91     | 3.12       |
| <b>12h</b> | -8.53      | -6.60      | -42.01     | 5.93       |

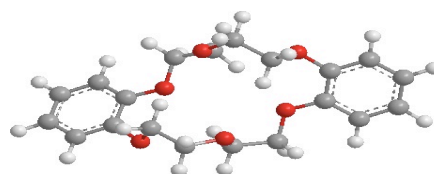
<sup>a</sup> Units are kcal/mol for  $\Delta E$ ,  $\Delta H$ , and  $\Delta G$ ; units are cal/(deg•mol) for  $\Delta S$ . The standard state is a concentration of 1.0 M for all species and T = 298.15 K.

### 3. Figures S-13 – S-16. Pictures of Conformers and Relative Energies

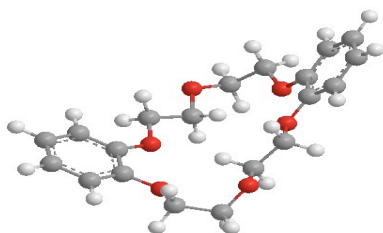
**Figure S-13.** DB18-C-6 (**3**) conformers located by B97D/6-311+G(d) calculations. Two views (left, right) are offered for each conformer. Enthalpies and Gibbs free energies are shown in parenthesis, relative to **3a** (kcal/mol; T = 298.15 K; P = 1 atm).



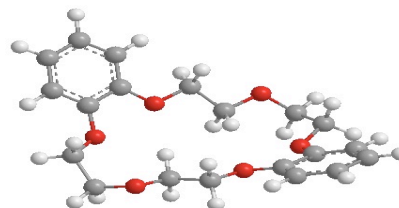
**3a** (0.0; 0.0)



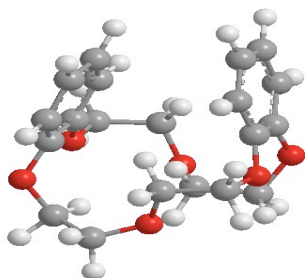
**3a** (0.0; 0.0)



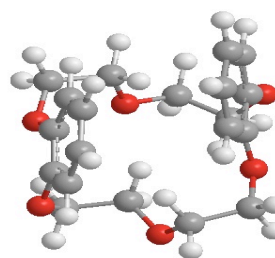
**3b** (1.9; 0.9)



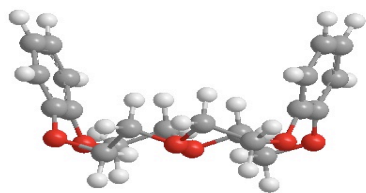
**3b** (1.9; 0.9)



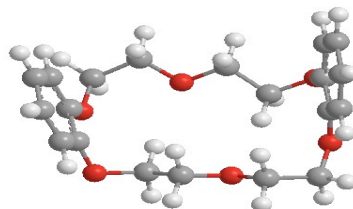
**3c** (2.1; 2.0)



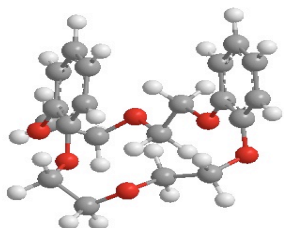
**3c** (2.1; 2.0)



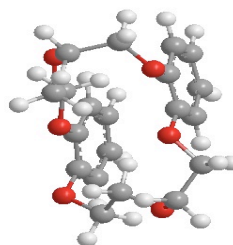
**3d** (3.5; 3.5)



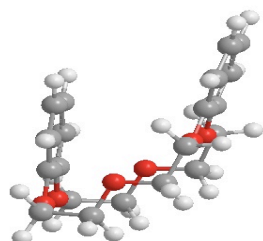
**3d** (3.5; 3.5)



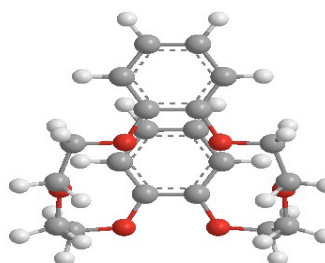
**3e** (4.0; 3.6)



**3e** (4.0; 3.6)

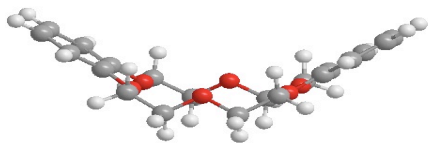


**3f** (4.5; 3.7)

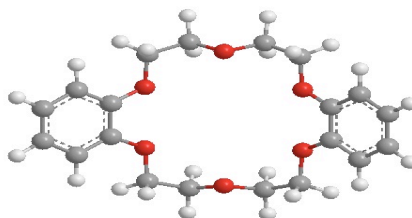


**3f** (4.5; 3.7)

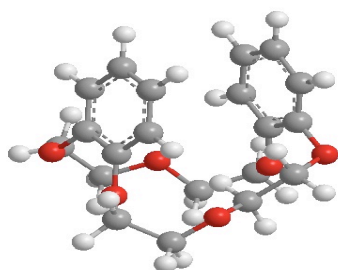




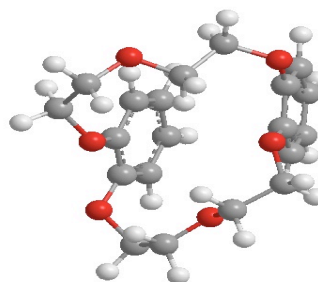
**3g** (4.2; 3.8)



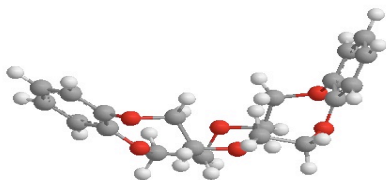
**3g** (4.2; 3.8)



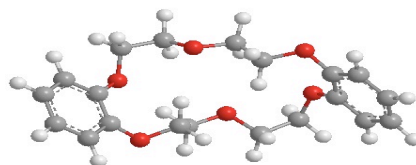
**3h** (3.5; 4.1)



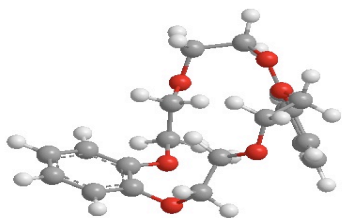
**3h** (3.5; 4.1)



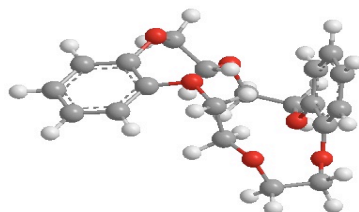
**3i** (6.2; 4.8)



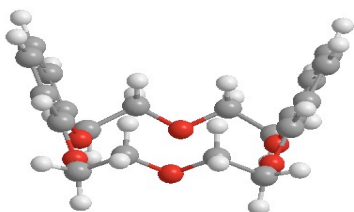
**3i** (6.2; 4.8)



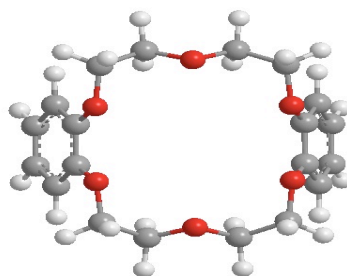
**3j** (6.3; 5.8)



**3j** (6.3; 5.8)

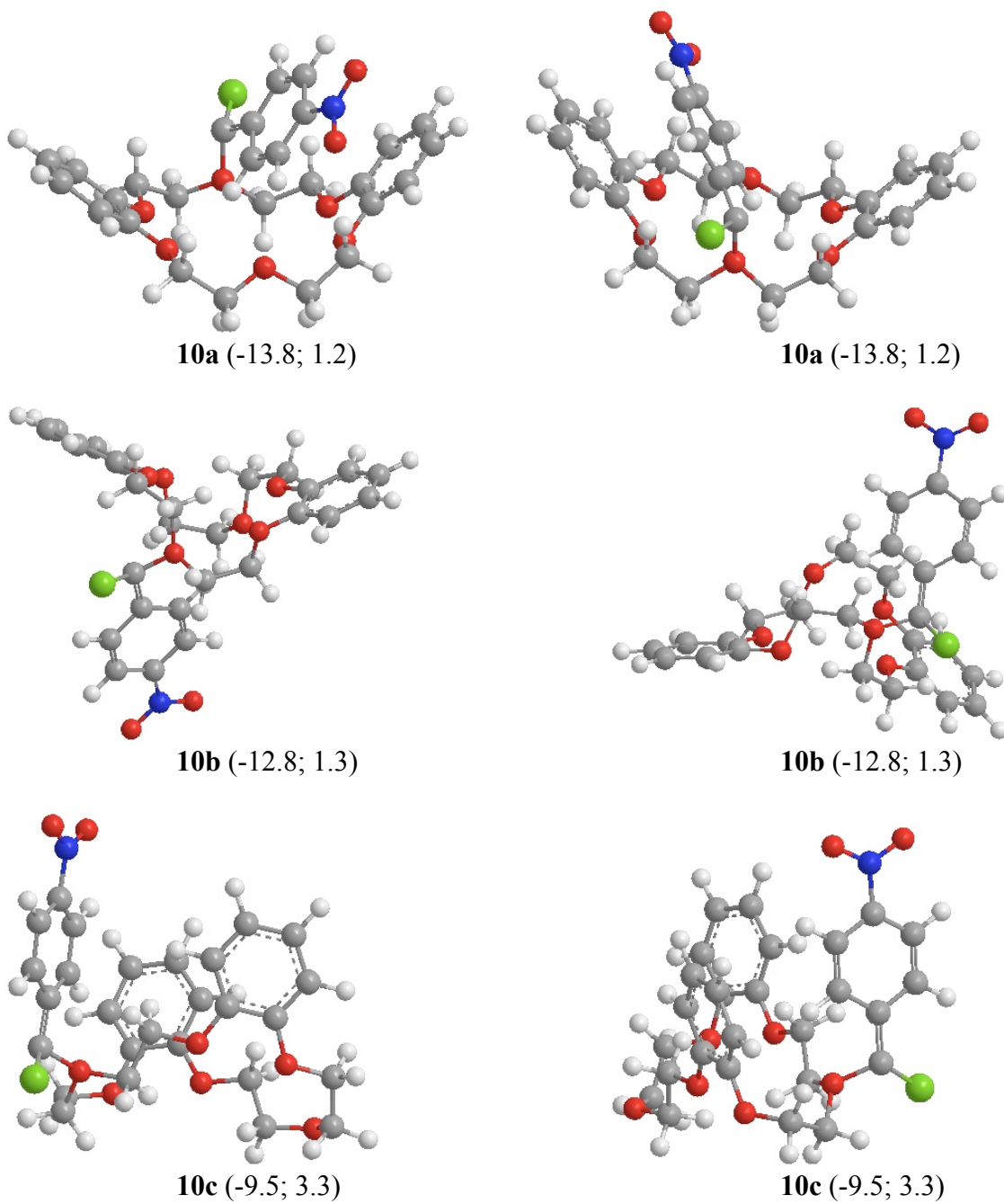


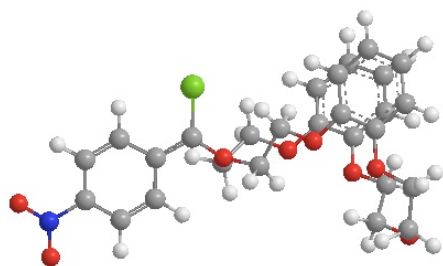
**3k** (6.6; 7.6)



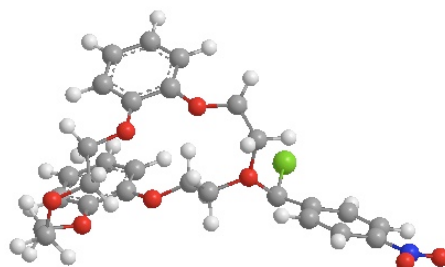
**3k** (6.6; 7.6)

**Figure S-14.** DB-18-C-6/PNPCC *O*-ylide (**10**) conformers located by B97D/6-311+G(d) calculations. Two views (left, right) are offered for each conformer. Enthalpies and Gibbs free energies are shown in parenthesis, relative to free **1** and conformer **3a** (kcal/mol; T = 298.15 K;  $[\text{I}] = 1.0 \text{ M}$ ).

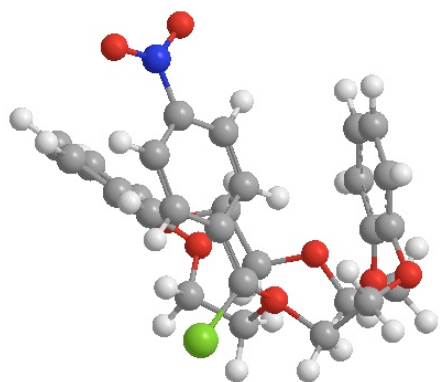




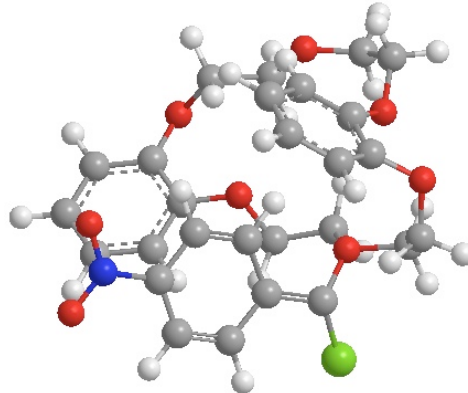
**10d** (-7.6; 5.0)



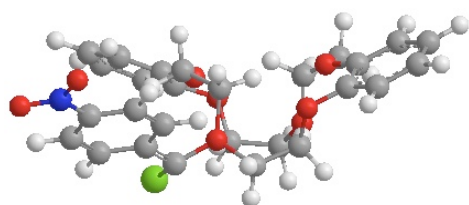
**10d** (-7.6; 5.0)



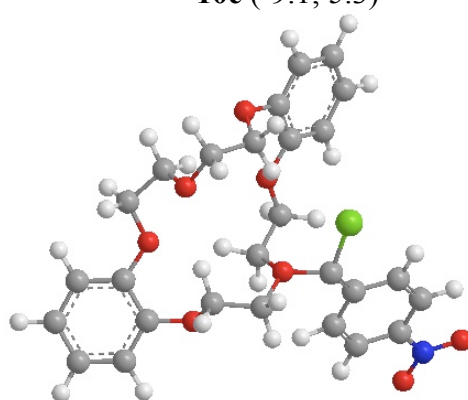
**10e** (-9.1; 5.3)



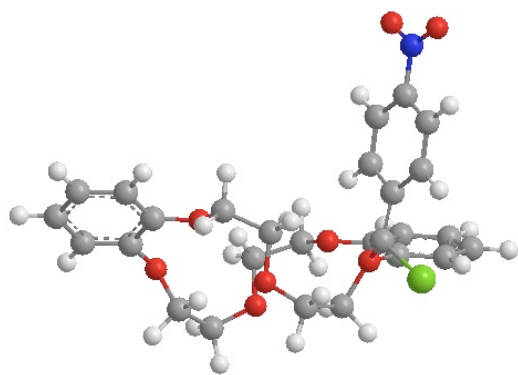
**10e** (-9.1; 5.3)



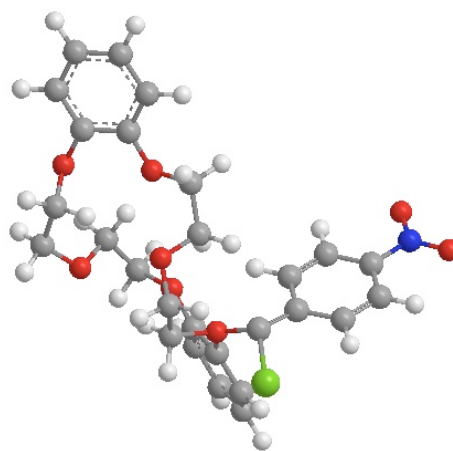
**10f** (-7.2; 6.3)



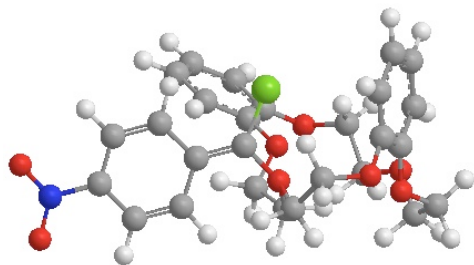
**10f** (-7.2; 6.3)



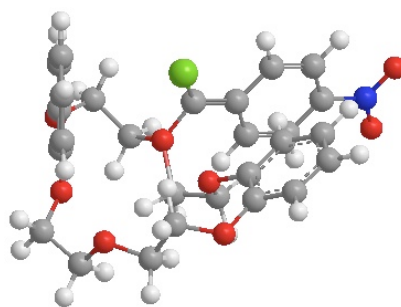
**10g** (-5.9; 7.4)



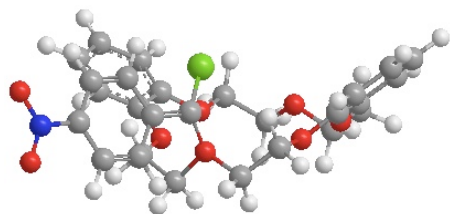
**10g** (-5.9; 7.4)



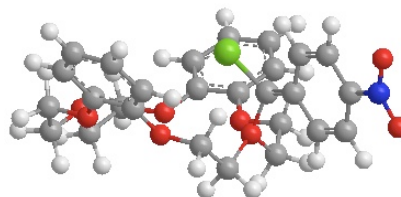
**10h** (-4.5; 7.9)



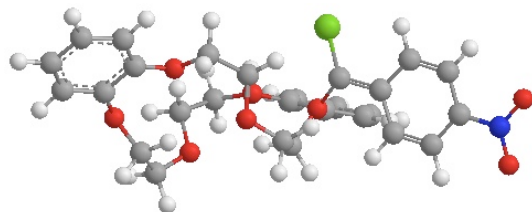
**10h** (-4.5; 7.9)



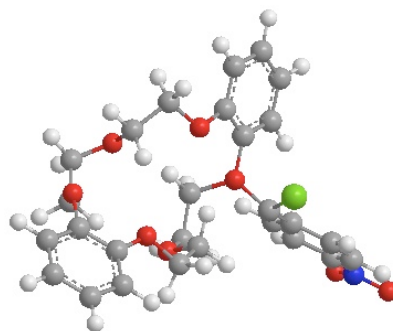
**10i** (-1.7; 9.8)



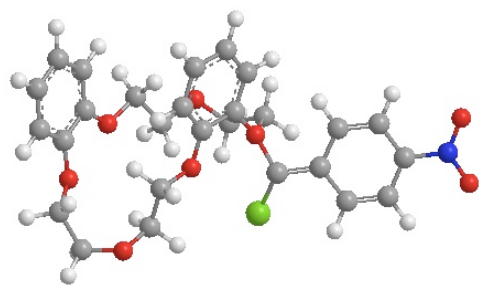
**10i** (-1.7; 9.8)



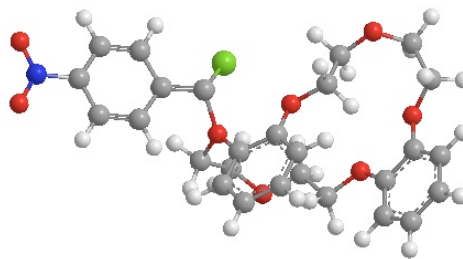
**10j** (-2.5; 10.6)



**10j** (-2.5; 10.6)

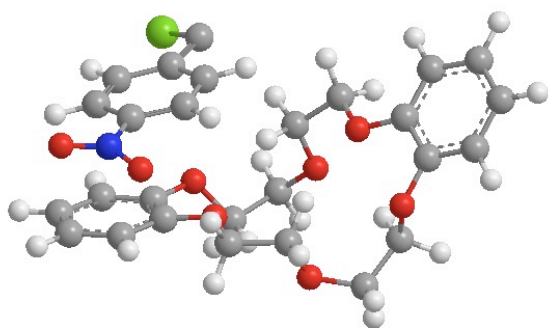


**10k** (0.6; 12.8)

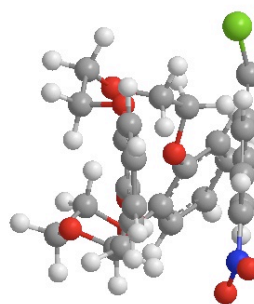


**10k** (0.6; 12.8)

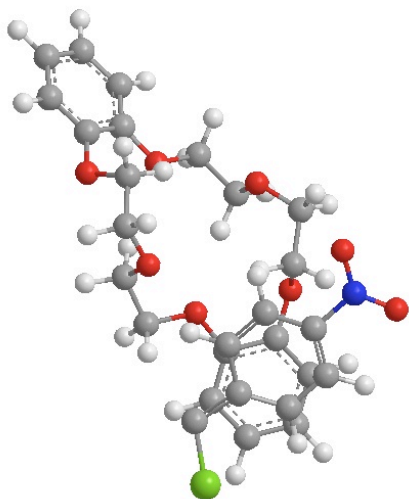
**Figure S-15.** DB-18-C-6/PNPCC half-sandwich  $\pi$ -complexes (**11**) located by B97D/6-311+G(d) calculations. Two views (left, right) are offered for each complex. Enthalpies and Gibbs free energies are shown in parenthesis, relative to free **1** and conformer **3a** (kcal/mol; T = 298.15 K; [] = 1.0 M).



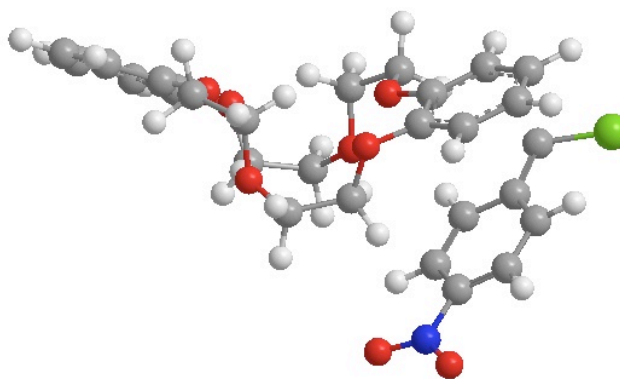
**11a** (-14.0, -3.5)



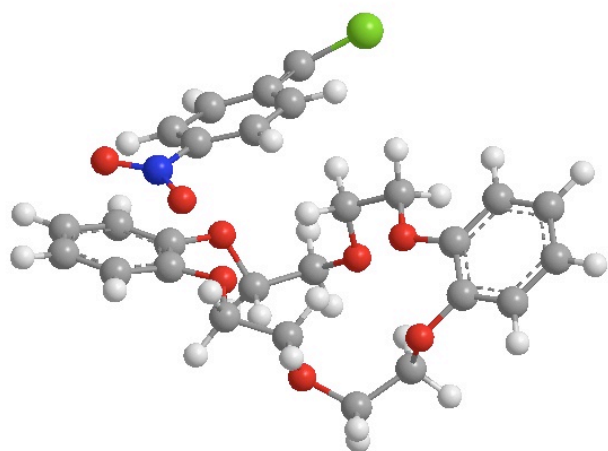
**11a** (-14.0, -3.5)



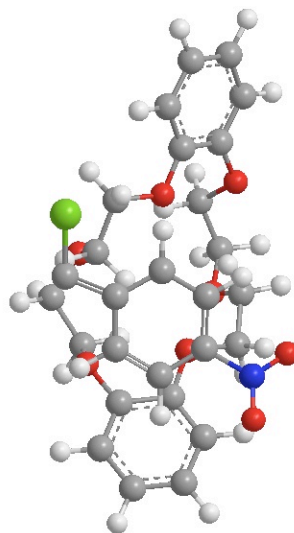
**11b** (-12.9, -2.5)



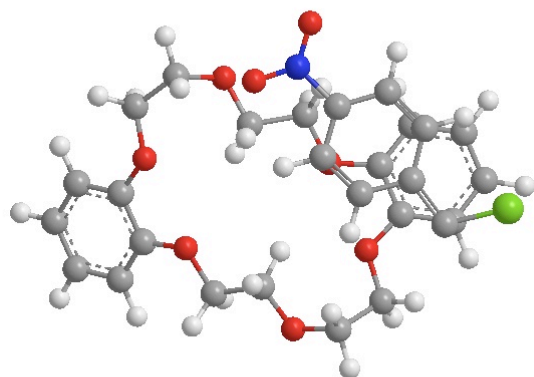
**11b** (-12.9, -2.5)



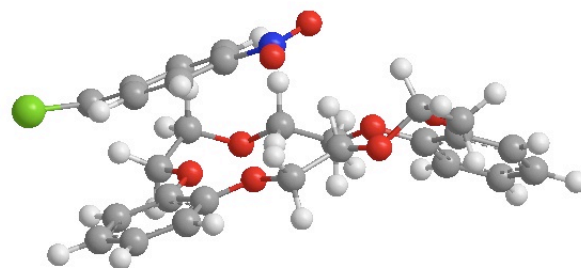
**11c** (-13.0, -2.2)



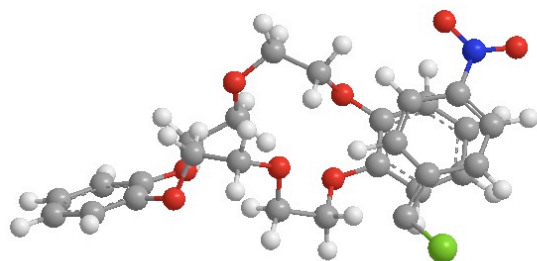
**11c** (-13.0, -2.2)



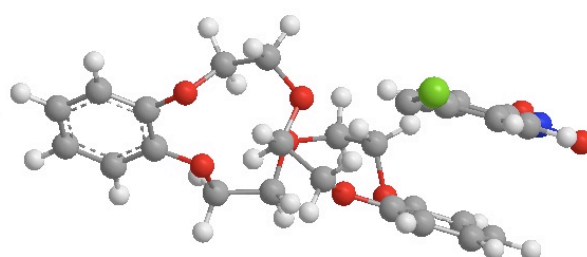
**11d** (-11.9, -2.0)



**11d** (-11.9, -2.0)

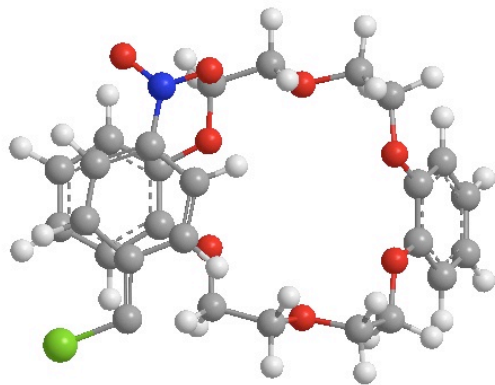


**11e** (-11.4, -0.8)

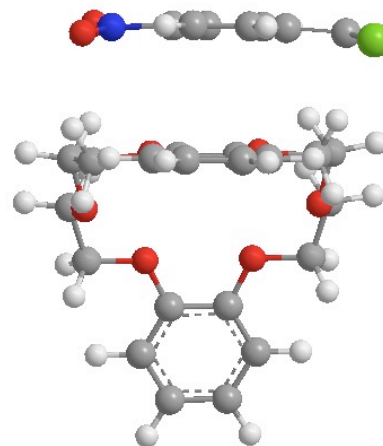


**11e** (-11.4, -0.8)

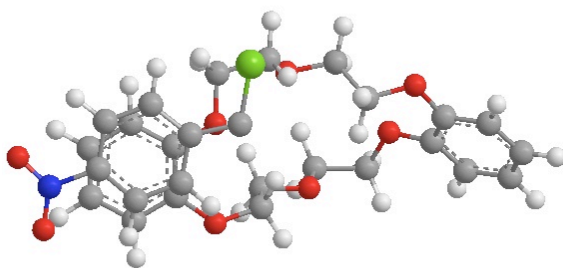




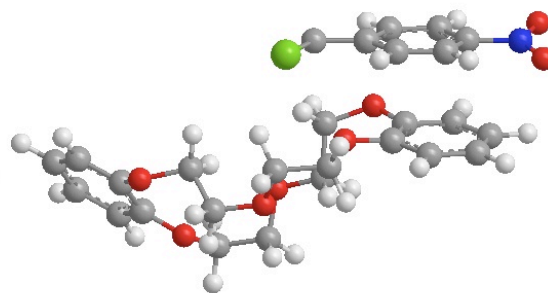
**11f** (-10.5, -0.1)



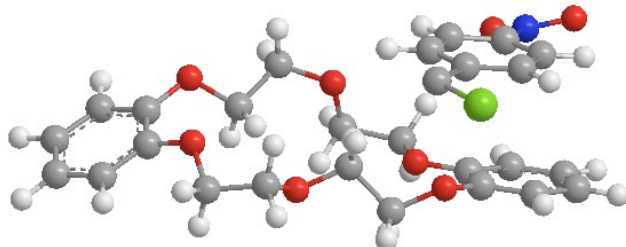
**11f** (-10.5, -0.1)



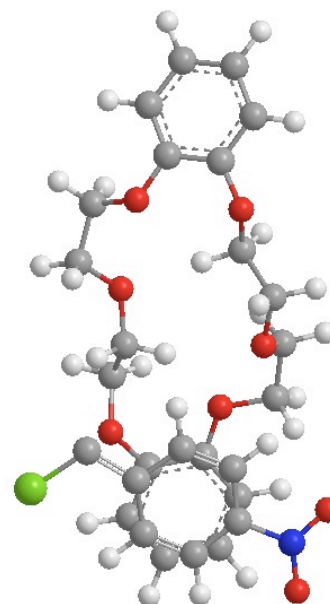
**11g** (-7.9, 2.6)



**11g** (-7.9, 2.6)

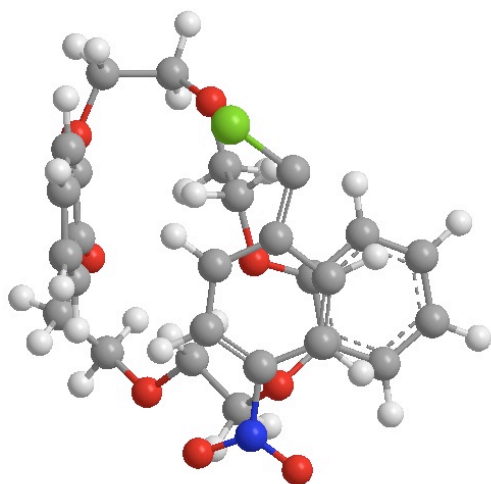


**11h** (-7.9, 3.0)

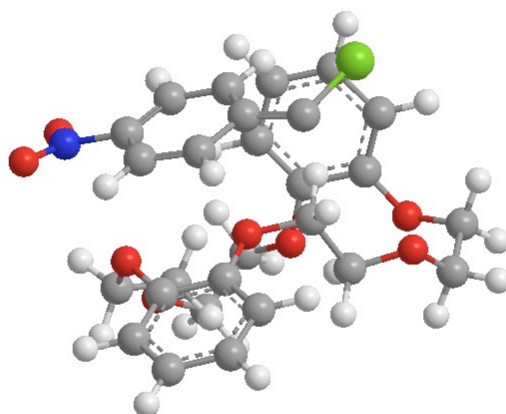


**11h** (-7.9, 3.0)



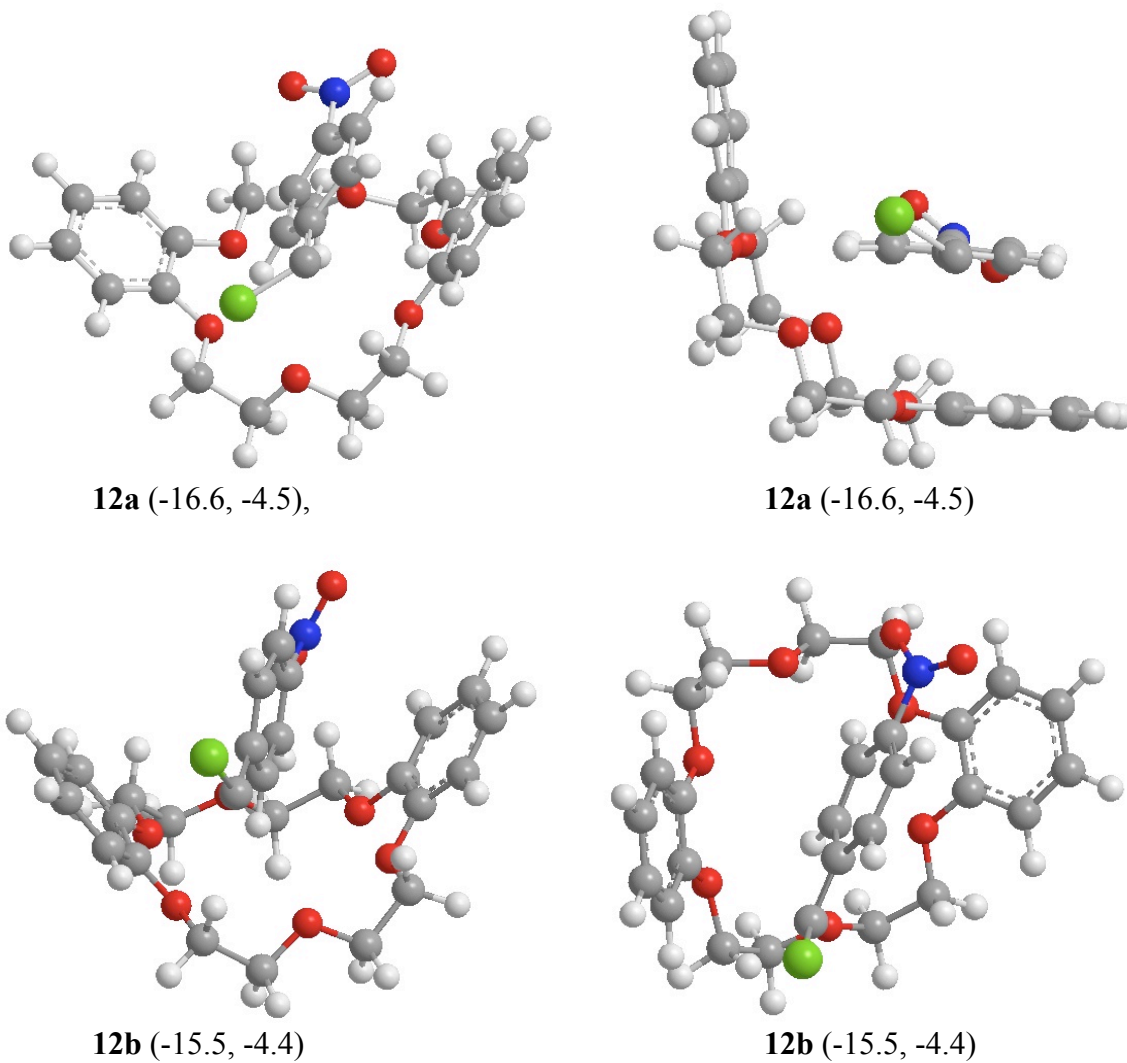


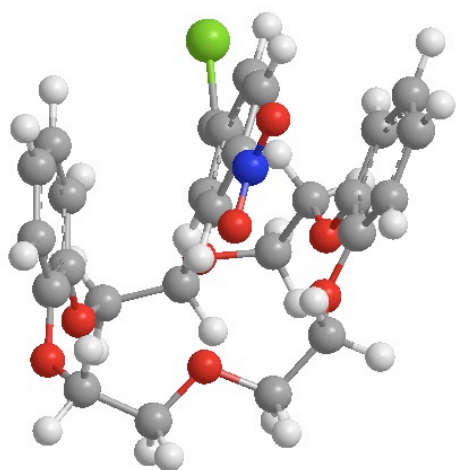
**11i** (-7.0, 3.1)



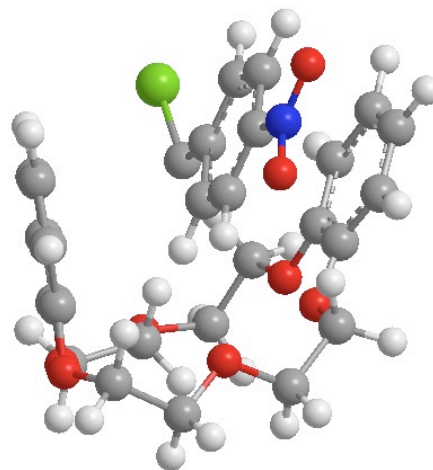
**11i** (-7.0, 3.1)

**Figure S-16.** Examples of full-sandwich  $\pi$ -complexes (**12**) formed between PNPCC and DB-18-C-6 (B97D/6-311+G(d)). Enthalpies and Gibbs energies of formation are shown in parenthesis, relative to free **1** and conformer **3a** (kcal/mol; T = 298.15 K; [] = 1.0 M).

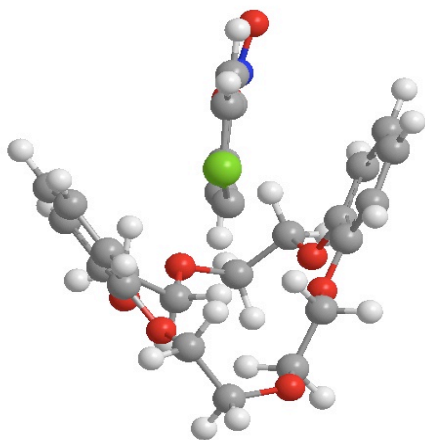




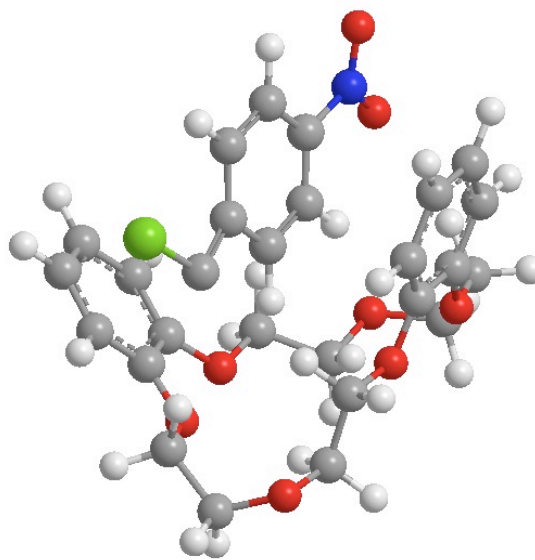
**12c** (-16.2, -3.8)



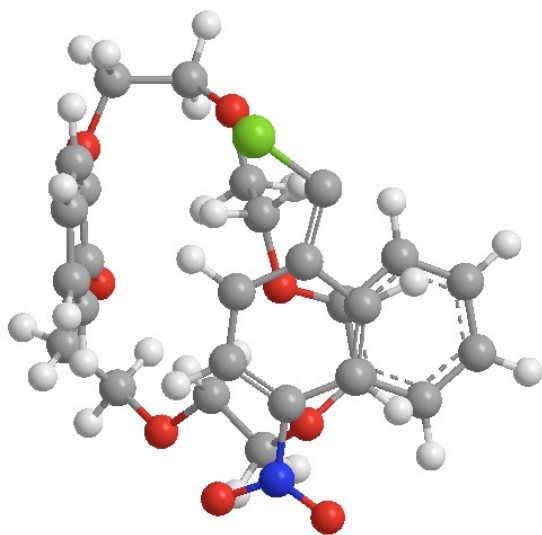
**12c** (-16.2, -3.8)



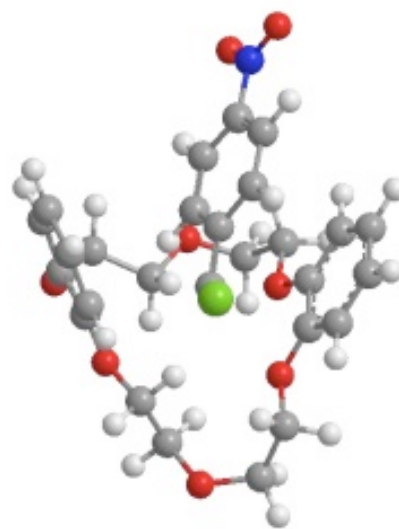
**12d** (-15.9, -3.6)



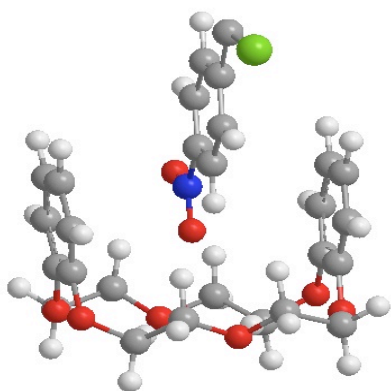
**12d** (-15.9, -3.6)



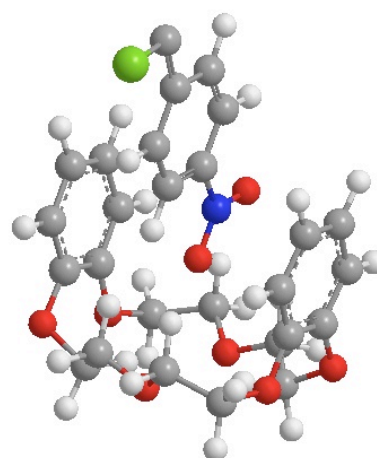
**12e** (-14.4, -2.7)



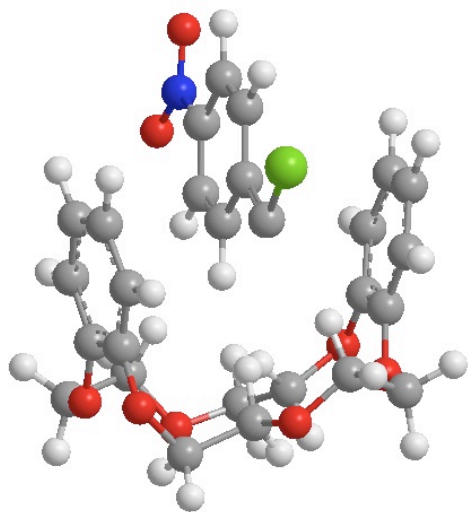
**12e** (-14.4, -2.7)



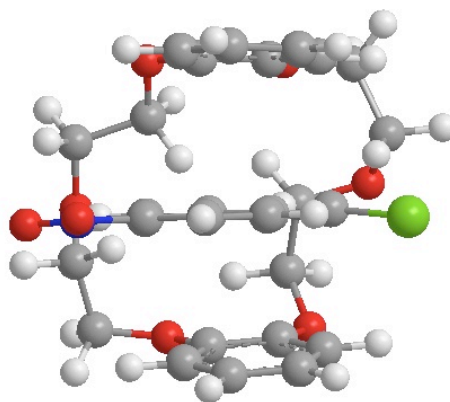
**12f** (-8.2, 2.0)



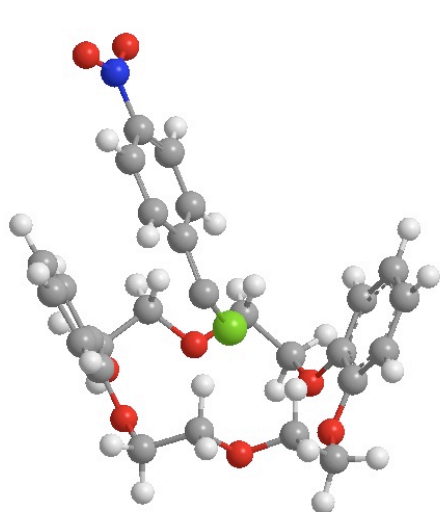
**12f** (-8.2, 2.0)



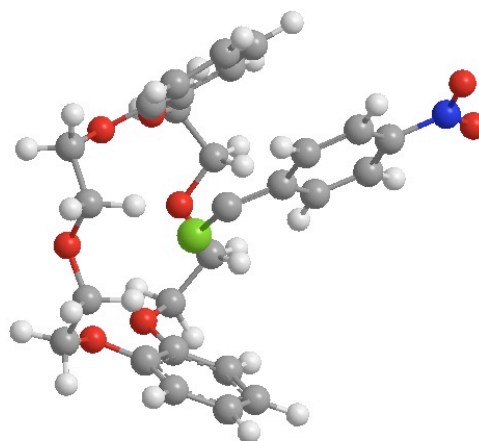
**12g** (-9.2, 2.5)



**12g** (-9.2, 2.5)



**12h** (-8.5, 5.9)



**12h** (-8.5, 5.9)

#### 4. Geometries, Energies, Orbitals, and Excitations for 1, 3a, and 3b.

##### PNPCC (1):

-----  
Para-Nitro-Phenyl-Chloro-Carbene, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,-2.2577905346,-2.6218084324,-1.0258493388  
C,0,-3.3113401717,-2.3730703058,-0.1527485395  
C,0,-3.0669629594,-1.6093556528,0.9999900678  
C,0,-1.7988152665,-1.1106641001,1.316410588  
C,0,-0.739690336,-1.4050329138,0.4567556202  
C,0,-0.9480489338,-2.1394518184,-0.7427727417  
C,0,0.2878905342,-2.358880499,-1.4991561574  
Cl,0,-0.0202779559,-2.8610844794,-3.1464913502  
N,0,-4.2101951211,-1.3269320155,1.9344868309  
O,0,-3.9825309497,-0.6085451918,2.9052479652  
O,0,-5.2984766266,-1.8308079786,1.6646413883  
H,0,-2.4356933636,-3.2035938118,-1.9284251679  
H,0,-4.3134787506,-2.7456836875,-0.3491442919  
H,0,-1.6533897237,-0.5306026846,2.2237199727  
H,0,0.2694665391,-1.0665852787,0.6882540144

SCF Done: E(RB97D) = -934.188385835 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -934.094758  
Sum of electronic and thermal Energies= -934.085188  
Sum of electronic and thermal Enthalpies= -934.084244  
Sum of electronic and thermal Free Energies= -934.132247

-----  
# 6-311+g(d) td=(nstates=10) scrf=(cpcm,solvent=dichloroethane) b3lyp  
-----

##### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 1.5100 eV 821.10 nm f=0.0062 <S\*\*2>=0.000**

43 -> 44 0.69298  
43 -> 45 0.15816

**Excited State 2: Singlet-A 3.2760 eV 378.47 nm f=0.0108 <S\*\*2>=0.000**

43 -> 44 -0.15440  
43 -> 45 0.68326

**Excited State 3: Singlet-A 3.4014 eV 364.51 nm f=0.0341 <S\*\*2>=0.000**

42 -> 44 0.69801

Excited State 4: Singlet-A 3.5943 eV 344.94 nm  $f=0.0055$   $\langle S^2 \rangle=0.000$   
 40 -> 44 0.62279  
 40 -> 45 -0.29460  
 41 -> 44 0.13394

**Excited State 5: Singlet-A 3.9015 eV 317.79 nm  $f=0.5261$   $\langle S^2 \rangle=0.000$**   
 40 -> 44 -0.11888  
 41 -> 44 0.68006

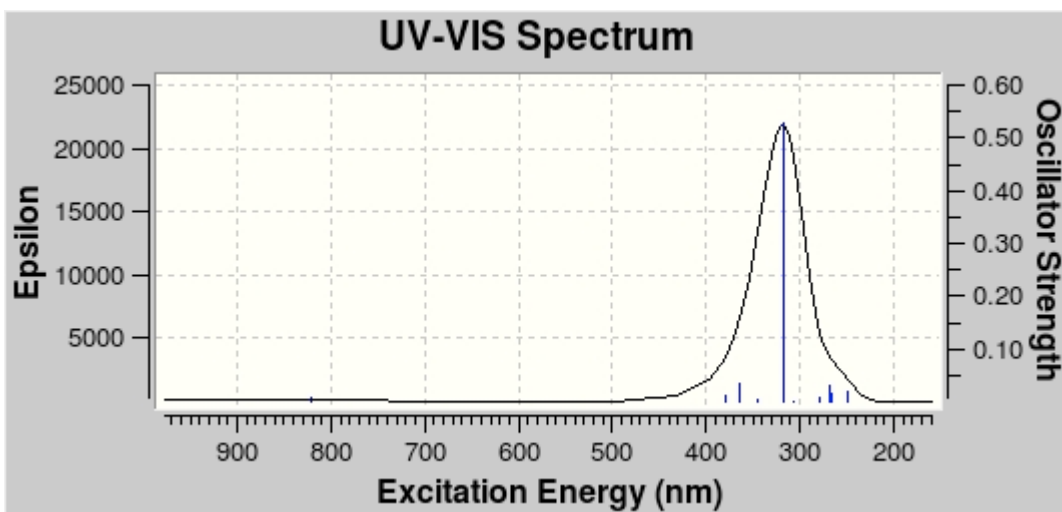
Excited State 6: Singlet-A 4.0415 eV 306.78 nm  $f=0.0003$   $\langle S^2 \rangle=0.000$   
 39 -> 44 0.64706  
 39 -> 45 -0.27862

Excited State 7: Singlet-A 4.4381 eV 279.36 nm  $f=0.0089$   $\langle S^2 \rangle=0.000$   
 43 -> 46 0.70300

Excited State 8: Singlet-A 4.6388 eV 267.28 nm  $f=0.0319$   $\langle S^2 \rangle=0.000$   
 37 -> 44 -0.37040  
 42 -> 45 0.58279

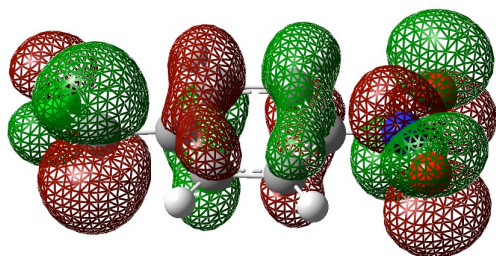
Excited State 9: Singlet-A 4.6482 eV 266.73 nm  $f=0.0155$   $\langle S^2 \rangle=0.000$   
 37 -> 44 0.55096  
 37 -> 45 0.10722  
 41 -> 45 0.10294  
 42 -> 45 0.39346

Excited State 10: Singlet-A 4.9632 eV 249.81 nm  $f=0.0198$   $\langle S^2 \rangle=0.000$   
 38 -> 44 0.68794  
 38 -> 45 0.14116

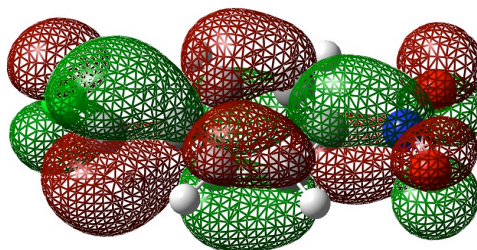


Computed electronic spectrum of PNPCC (TD-B3LYP/6-311+G(d)). Note that the computed intensity of the  $\sigma \rightarrow p$  transition at  $\lambda = 821$  nm is so low ( $f = 0.0062$ ) that it barely registers on this plot as an individual feature.

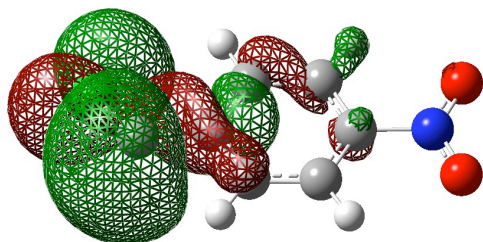




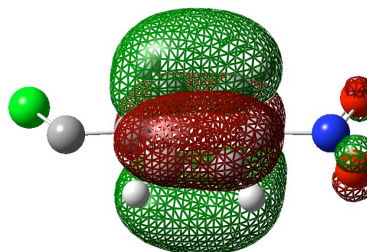
**MO 45.  $\pi^*$ (phenyl)**



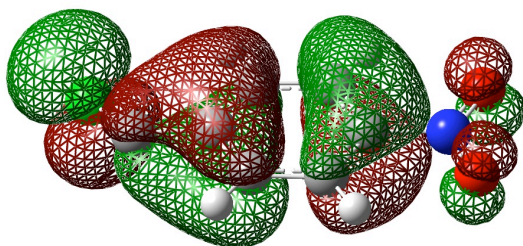
**MO 44 --- LUMO, p**



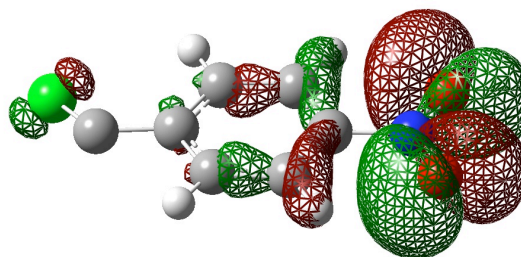
**MO 43 – HOMO,  $\sigma$**



**MO 42,  $\pi_1$ (phenyl)**



**MO 41,  $\pi_2$ (phenyl)**



**MO 40, O(NO<sub>2</sub>) lone-pairs**



**3a:**

-----  
DB18C-6-1, **3a**, C2 symmetry, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,-2.2022439431,-1.2596480785,1.6025370169  
O,0,-2.8540655989,-1.6331903092,0.3605853688  
C,0,-1.093619891,-2.2667595502,1.892175457  
O,0,0.1419402854,-2.0165646955,1.2257632028  
C,0,0.0864609706,-2.1806052911,-0.1940556524  
C,0,-3.7528557837,-0.7117486975,-0.1353093503  
C,0,-3.3162482735,0.5362601026,-0.6516355465  
C,0,1.5013114432,-2.1214113056,-0.7341136487  
C,0,-0.0864609706,2.1806052911,-0.1940556524  
O,0,-0.1419402854,2.0165646955,1.2257632028  
C,0,-1.5013114432,2.1214113056,-0.7341136487  
O,0,-1.9701110594,0.7688197969,-0.6029793972  
C,0,5.6183828364,-1.0770598115,-1.2328133212  
C,0,6.0460656759,0.1604199756,-0.7416184878  
C,0,5.1082045039,1.0478288319,-0.1912900614  
C,0,3.7528557837,0.7117486975,-0.1353093503  
C,0,3.3162482735,-0.5362601026,-0.6516355465  
C,0,4.2595439276,-1.4263713423,-1.190255909  
O,0,1.9701110594,-0.7688197969,-0.6029793972  
O,0,2.8540655989,1.6331903092,0.3605853688  
C,0,1.093619891,2.2667595502,1.892175457  
C,0,2.2022439431,1.2596480785,1.6025370169  
C,0,-5.1082045039,-1.0478288319,-0.1912900614  
C,0,-6.0460656759,-0.1604199756,-0.7416184878  
C,0,-5.6183828364,1.0770598115,-1.2328133212  
C,0,-4.2595439276,1.4263713423,-1.190255909  
H,0,-1.7831670708,-0.2477938853,1.5329487719  
H,0,-2.9532575776,-1.2922794048,2.4115400834  
H,0,-1.4550724473,-3.2860087156,1.6573513999  
H,0,-0.8525503507,-2.2208800964,2.9630135487  
H,0,-0.5366620722,-1.4010254424,-0.6522716155  
H,0,-0.3506830164,-3.164727568,-0.4471313697  
H,0,2.1572425476,-2.7976554977,-0.1644867146  
H,0,1.5120019277,-2.4191043624,-1.7961906705  
H,0,0.3506830164,3.164727568,-0.4471313697  
H,0,0.5366620722,1.4010254424,-0.6522716155  
H,0,-1.5120019277,2.4191043624,-1.7961906705  
H,0,-2.1572425476,2.7976554977,-0.1644867146  
H,0,6.3358911258,-1.7781399721,-1.6601257056  
H,0,7.1000979592,0.4357310956,-0.7783111915  
H,0,5.4113715612,2.017201023,0.2046781943

H,0,3.9336989276,-2.3831699987,-1.5945695518  
 H,0,1.4550724473,3.2860087156,1.6573513999  
 H,0,0.8525503507,2.2208800964,2.9630135487  
 H,0,1.7831670708,0.2477938853,1.5329487719  
 H,0,2.9532575776,1.2922794048,2.4115400834  
 H,0,-5.4113715612,-2.017201023,0.2046781943  
 H,0,-7.1000979592,-0.4357310956,-0.7783111915  
 H,0,-6.3358911258,1.7781399721,-1.6601257056  
 H,0,-3.9336989276,2.3831699987,-1.5945695518

SCF Done: E(RB97D) = -1227.31503276 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -1226.910712  
 Sum of electronic and thermal Energies= -1226.886952  
 Sum of electronic and thermal Enthalpies= -1226.886008  
 Sum of electronic and thermal Free Energies= -1226.964021

---

# 6-311+g(d) td=(nstates=10) scrf=(cpcm,solvent=dichloroethane) b3lyp

---

#### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-B 4.9188 eV 252.06 nm f=0.1115 <S\*\*2>=0.000**

93 -> 100 0.21318  
 94 -> 99 -0.21068  
 95 -> 97 0.43055  
 96 -> 98 0.45501

**Excited State 2: Singlet-A 4.9222 eV 251.89 nm f=0.0194 <S\*\*2>=0.000**

93 -> 99 -0.21712  
 94 -> 100 0.21323  
 95 -> 98 0.43065  
 96 -> 97 0.45340

**Excited State 3: Singlet-A 5.3849 eV 230.24 nm f=0.0002 <S\*\*2>=0.000**

95 -> 98 0.49810  
 96 -> 97 -0.49721

**Excited State 4: Singlet-B 5.3855 eV 230.22 nm f=0.0000 <S\*\*2>=0.000**

95 -> 97 0.50362  
 96 -> 98 -0.49414

**Excited State 5: Singlet-A 5.4682 eV 226.74 nm f=0.0243 <S\*\*2>=0.000**

93 -> 97 0.20096  
 94 -> 98 0.20801  
 95 -> 98 -0.11762

95 ->100     -0.34665  
 96 -> 99     0.51793

**Excited State 6: Singlet-B 5.4820 eV 226.17 nm f=0.1778 <S\*\*2>=0.000**

93 -> 98     -0.20531  
 94 -> 97     -0.21555  
 95 -> 99     -0.42113  
 96 ->100     0.45509

**Excited State 7: Singlet-B 5.6149 eV 220.81 nm f=0.0000 <S\*\*2>=0.000**

95 -> 99     0.51229  
 96 ->100     0.48603

**Excited State 8: Singlet-A 5.6184 eV 220.68 nm f=0.0007 <S\*\*2>=0.000**

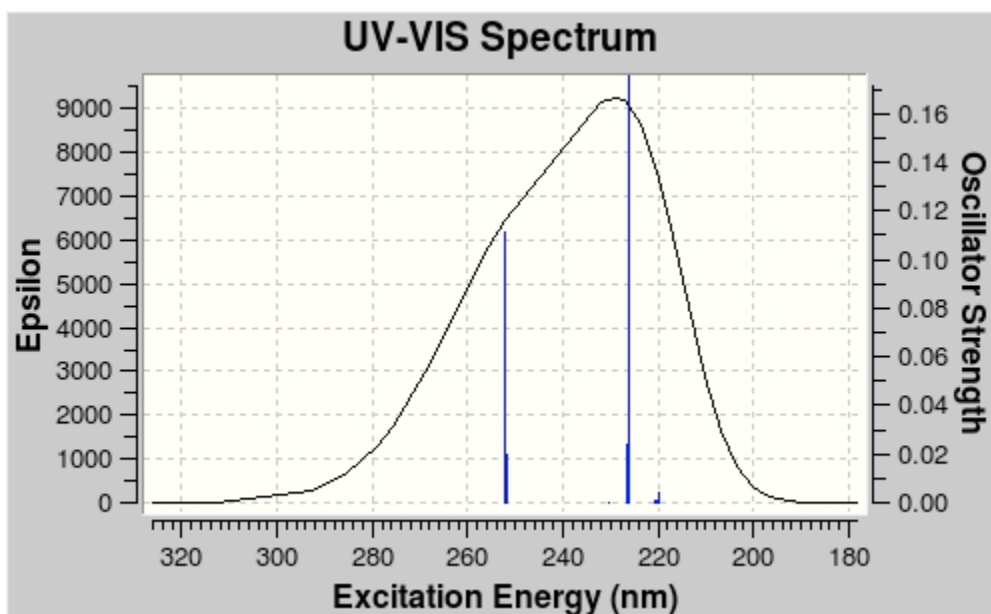
95 ->100     0.53827  
 95 ->102     0.10039  
 96 -> 99     0.41594  
 96 ->101     -0.14285

**Excited State 9: Singlet-A 5.6279 eV 220.30 nm f=0.0005 <S\*\*2>=0.000**

95 ->100     0.16657  
 95 ->102     -0.37159  
 96 ->101     0.54459

**Excited State 10: Singlet-B 5.6349 eV 220.03 nm f=0.0038 <S\*\*2>=0.000**

95 ->101     0.53908  
 96 ->102     -0.41452



Computed electronic spectrum of **3a** (TD-B3LYP/6-311+G(d)).

### 3b:

DB18-C-6 monomer, from X-ray; **3b** C2 symmetry; B97D/6-311+G(d)

Charge = 0 Multiplicity = 1

C,0,3.453477717,2.3986479811,-0.5803666114  
H,0,4.4418934223,2.5930894277,-1.0354220459  
H,0,3.4980857671,2.6605673478,0.4889178494  
C,0,2.3937004842,3.2412606841,-1.2851394374  
H,0,2.7503146321,4.2815408198,-1.3082430472  
H,0,2.2704106635,2.8920495594,-2.3259619014  
C,0,0.2823100471,2.1612803222,-0.9184474559  
H,0,0.7311890456,1.2100101212,-0.6089038971  
H,0,0.0936650412,2.1184747609,-2.0062007092  
C,0,-1.0223807645,2.3966479379,-0.1656566881  
H,0,-0.8288122982,2.4955954243,0.9143818515  
H,0,-1.5269731922,3.3099495655,-0.5191484331  
C,0,-3.0300800187,1.1401758054,0.2391646357  
C,0,-3.5962847519,2.140408639,1.0399538298  
H,0,-3.0802082579,3.0896544065,1.1682754481  
C,0,-4.823679384,1.9224333093,1.691048168  
H,0,-5.2458247826,2.7116022505,2.3133007744  
C,0,-5.4886373066,0.7049050462,1.5440194926  
H,0,-6.4384964638,0.5276233535,2.048425444  
C,0,-4.9324993425,-0.3045812293,0.7383731243  
H,0,-5.4530202679,-1.2535390524,0.6204417762  
C,0,-3.7137215263,-0.0979973696,0.0830422932  
C,0,-3.453477717,-2.3986479811,-0.5803666114  
H,0,-4.4418934223,-2.5930894277,-1.0354220459  
H,0,-3.4980857671,-2.6605673478,0.4889178494  
C,0,-2.3937004842,-3.2412606841,-1.2851394374  
H,0,-2.7503146321,-4.2815408198,-1.3082430472  
H,0,-2.2704106635,-2.8920495594,-2.3259619014  
C,0,-0.2823100471,-2.1612803222,-0.9184474559  
H,0,-0.7311890456,-1.2100101212,-0.6089038971  
H,0,-0.0936650412,-2.1184747609,-2.0062007092  
C,0,1.0223807645,-2.3966479379,-0.1656566881  
H,0,0.8288122982,-2.4955954243,0.9143818515  
H,0,1.5269731922,-3.3099495655,-0.5191484331  
C,0,3.0300800187,-1.1401758054,0.2391646357  
C,0,3.5962847519,-2.140408639,1.0399538298  
H,0,3.0802082579,-3.0896544065,1.1682754481  
C,0,4.823679384,-1.9224333093,1.691048168  
H,0,5.2458247826,-2.7116022505,2.3133007744  
C,0,5.4886373066,-0.7049050462,1.5440194926  
H,0,6.4384964638,-0.5276233535,2.048425444

C,0,4.9324993425,0.3045812293,0.7383731243  
 H,0,5.4530202679,1.2535390524,0.6204417762  
 C,0,3.7137215263,0.0979973696,0.0830422932  
 O,0,3.1014135319,1.0176507989,-0.7268050804  
 O,0,1.138200864,3.2702560525,-0.6131860975  
 O,0,-1.8353957527,1.2436249256,-0.4180581228  
 O,0,-3.1014135319,-1.0176507989,-0.7268050804  
 O,0,-1.138200864,-3.2702560525,-0.6131860975  
 O,0,1.8353957527,-1.2436249256,-0.4180581228

SCF Done: E(RB97D) = -1227.31258614 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -1226.908193  
 Sum of electronic and thermal Energies= -1226.883952  
 Sum of electronic and thermal Enthalpies= -1226.883008  
 Sum of electronic and thermal Free Energies= -1226.962658

-----  
 # 6-311+g(d) td=(nstates=10) scrf=(cpcm,solvent=dichloroethane) b3lyp  
 -----

#### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-B 4.8530 eV 255.48 nm f=0.1251 <S\*\*2>=0.000**

93 -> 100 0.20551  
 94 -> 99 0.20512  
 95 -> 97 0.44719  
 96 -> 98 0.45769

**Excited State 2: Singlet-A 4.8604 eV 255.09 nm f=0.0471 <S\*\*2>=0.000**

93 -> 99 0.21262  
 94 -> 100 0.21021  
 95 -> 98 0.43825  
 96 -> 97 0.46137

**Excited State 3: Singlet-B 5.2571 eV 235.84 nm f=0.0000 <S\*\*2>=0.000**

95 -> 97 0.50354  
 96 -> 98 -0.49541

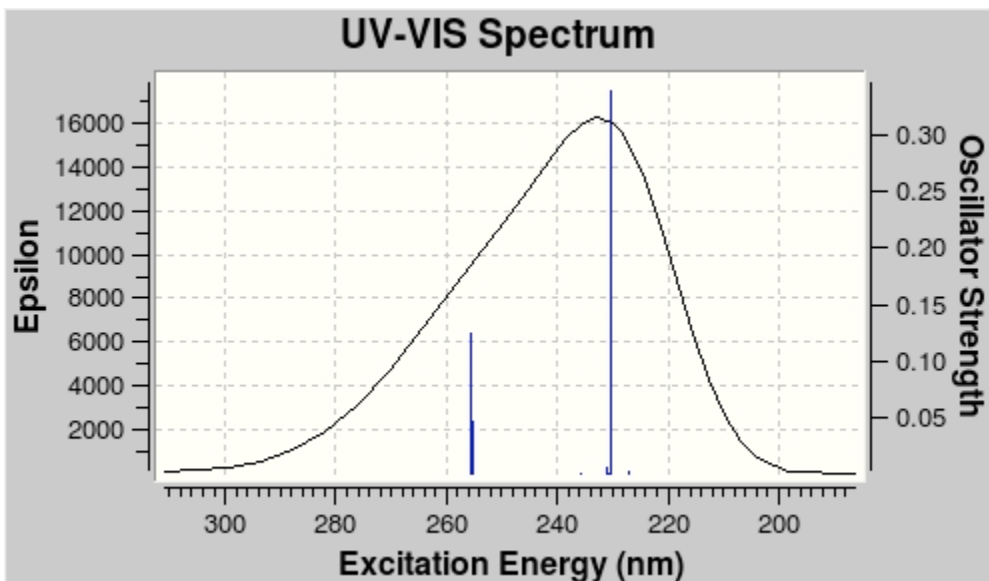
**Excited State 4: Singlet-A 5.2572 eV 235.84 nm f=0.0001 <S\*\*2>=0.000**

95 -> 98 0.50768  
 96 -> 97 -0.49090

**Excited State 5: Singlet-A 5.3627 eV 231.20 nm f=0.0046 <S\*\*2>=0.000**

93 -> 97 -0.14908  
 94 -> 98 -0.15199  
 95 -> 100 0.39774

|                         |                  |                  |                  |                 |                           |  |
|-------------------------|------------------|------------------|------------------|-----------------|---------------------------|--|
| 96 -> 99                | 0.52003          |                  |                  |                 |                           |  |
| Excited State 6:        | Singlet-A        | 5.3748 eV        | 230.68 nm        | f=0.0009        | <S**2>=0.000              |  |
| 95 ->100                | -0.11608         |                  |                  |                 |                           |  |
| 95 ->102                | 0.32511          |                  |                  |                 |                           |  |
| 95 ->106                | 0.10515          |                  |                  |                 |                           |  |
| 96 ->101                | 0.58243          |                  |                  |                 |                           |  |
|                         |                  |                  |                  |                 |                           |  |
| Excited State 7:        | Singlet-B        | 5.3799 eV        | 230.46 nm        | f=0.0191        | <S**2>=0.000              |  |
| 95 -> 99                | 0.13203          |                  |                  |                 |                           |  |
| 95 ->101                | 0.56823          |                  |                  |                 |                           |  |
| 96 ->102                | 0.34638          |                  |                  |                 |                           |  |
| 96 ->106                | 0.10276          |                  |                  |                 |                           |  |
|                         |                  |                  |                  |                 |                           |  |
| <b>Excited State 8:</b> | <b>Singlet-B</b> | <b>5.3856 eV</b> | <b>230.22 nm</b> | <b>f=0.3391</b> | <b>&lt;S**2&gt;=0.000</b> |  |
| 93 -> 98                | -0.15850         |                  |                  |                 |                           |  |
| 94 -> 97                | -0.16202         |                  |                  |                 |                           |  |
| 95 -> 99                | 0.39960          |                  |                  |                 |                           |  |
| 95 ->101                | -0.11913         |                  |                  |                 |                           |  |
| 96 ->100                | 0.50853          |                  |                  |                 |                           |  |
|                         |                  |                  |                  |                 |                           |  |
| Excited State 9:        | Singlet-B        | 5.4583 eV        | 227.15 nm        | f=0.0022        | <S**2>=0.000              |  |
| 95 -> 99                | 0.53785          |                  |                  |                 |                           |  |
| 96 ->100                | -0.45329         |                  |                  |                 |                           |  |
|                         |                  |                  |                  |                 |                           |  |
| Excited State 10:       | Singlet-A        | 5.4589 eV        | 227.12 nm        | f=0.0001        | <S**2>=0.000              |  |
| 95 ->100                | 0.54575          |                  |                  |                 |                           |  |
| 96 -> 99                | -0.44434         |                  |                  |                 |                           |  |



Computed electronic spectrum of **3b** (TD-B3LYP/6-311+G(d)).

## 5. Geometries, Energies, Orbitals, and Excitations for *O*-Ylides 10a-10d.

### 10a:

-----  
O-Ylide 10a, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,2.0923696529,-2.91573459,-1.5190408815  
O,0,2.1270476692,-1.4978752361,-1.7313345041  
C,0,0.8102398594,-3.4429503387,-2.1315049401  
O,0,-0.2847703472,-3.0882597066,-1.2939168273  
C,0,-1.5333837076,-3.4811525006,-1.8380976973  
C,0,3.0913173841,-0.7837715566,-1.0791056377  
C,0,2.9753159718,0.6291246505,-1.1530739999  
C,0,-2.6332477477,-3.1820257667,-0.8389498426  
C,0,0.1843435305,2.7480066691,-2.1827386743  
O,0,-0.8596225737,2.4163557832,-1.0556169963  
C,0,1.5976064056,2.486055885,-1.73948848  
O,0,1.8802025846,1.103059788,-1.8489760572  
C,0,-5.4926717115,-1.5703934395,1.8274210658  
C,0,-5.7033251401,-0.1930863653,1.8437037074  
C,0,-4.9699188887,0.6350607712,0.9768547046  
C,0,-4.0257743899,0.0904850403,0.0993519829  
C,0,-3.8071597419,-1.3145277552,0.0798946285  
C,0,-4.5500486221,-2.1285279713,0.947539079  
O,0,-2.8679134574,-1.7681208529,-0.8050150706  
O,0,-3.2714830828,0.832132381,-0.7836984863  
C,0,-2.2197002421,2.8408821328,-1.494158288  
C,0,-3.2848976873,2.2432168395,-0.6089144247  
C,0,4.1491952331,-1.3445634012,-0.3519240766  
C,0,5.0849054467,-0.5240710922,0.2969843784  
C,0,4.9828827959,0.8627034281,0.2021901436  
C,0,3.9308210517,1.4380288243,-0.5297232026  
C,0,0.0114940159,0.2570596435,0.4912507653  
C,0,0.7196319832,-0.7948700804,1.0388857533  
C,0,1.676868714,-0.5538609673,2.0439826924  
C,0,1.8883393602,0.7526021435,2.5177178624  
C,0,1.1740274549,1.8118745121,1.9729969424  
C,0,0.2315876558,1.6027378348,0.9242408127  
C,0,-0.579879733,2.6534396067,0.37220269  
Cl,0,-0.1015705613,4.3881693989,0.5836553164  
N,0,2.4740079205,-1.6533365077,2.5598544588  
O,0,3.287227454,-1.4254791736,3.469749092  
O,0,2.3193561532,-2.7822488956,2.0526612362  
H,0,2.9606680682,-3.3890944338,-2.0087807426  
H,0,2.1224682268,-3.1390072418,-0.4429856937

H,0,0.6735859828,-3.0239202093,-3.1454011497  
 H,0,0.8787370256,-4.5448883967,-2.2187412321  
 H,0,-1.5405862445,-4.5713400001,-2.0383415854  
 H,0,-1.7265835836,-2.9568628447,-2.7924562967  
 H,0,-2.3338795135,-3.5386584776,0.1589684901  
 H,0,-3.5576749375,-3.7030591157,-1.1408398632  
 H,0,-0.1309925491,2.1048616482,-3.0083500481  
 H,0,0.0259029163,3.8099308942,-2.3953922773  
 H,0,2.258151272,3.0747862145,-2.404420518  
 H,0,1.7514316494,2.8499450592,-0.7168455756  
 H,0,-6.051198415,-2.2248602079,2.4963422723  
 H,0,-6.429560517,0.2516359774,2.5235192611  
 H,0,-5.1436876361,1.7088791073,0.9958833236  
 H,0,-4.3950433782,-3.2045498004,0.9523091079  
 H,0,-2.3035264949,2.4858800362,-2.5264082553  
 H,0,-2.2442240956,3.9366860746,-1.4488669128  
 H,0,-4.2532317204,2.6749312488,-0.9241967063  
 H,0,-3.0893768047,2.5099470441,0.4383550265  
 H,0,4.2301489261,-2.4236096335,-0.2539026443  
 H,0,5.8798507314,-0.983301978,0.8833045222  
 H,0,5.7049664183,1.5090835748,0.7003807189  
 H,0,3.8612856007,2.5221133892,-0.5900284596  
 H,0,-0.7210116798,0.0452303917,-0.2820997948  
 H,0,0.5418938978,-1.8025143731,0.6802411403  
 H,0,2.635293017,0.9265927431,3.2879812345  
 H,0,1.3609431748,2.8206421745,2.3363074331

SCF Done: E(RB97D) = -2161.52923464 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.026925  
 Sum of electronic and thermal Energies= -2160.993202  
 Sum of electronic and thermal Enthalpies= -2160.992258  
 Sum of electronic and thermal Free Energies= -2161.091552

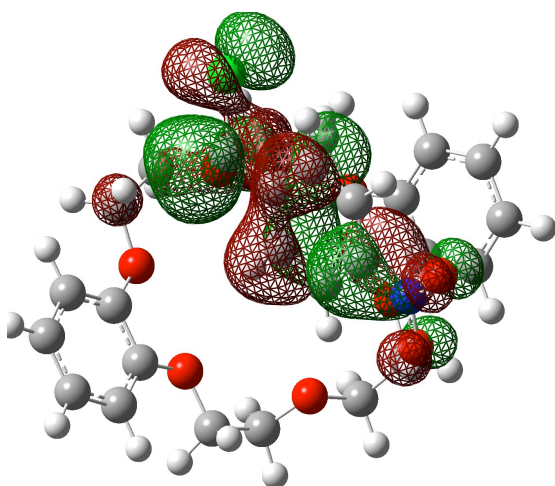
-----  
 # 6-311+g(d) b3lyp td=(nstates=10) scrf=(cpcm,solvent=dichloroethane)  
 -----

### Excitation energies and oscillator strengths:

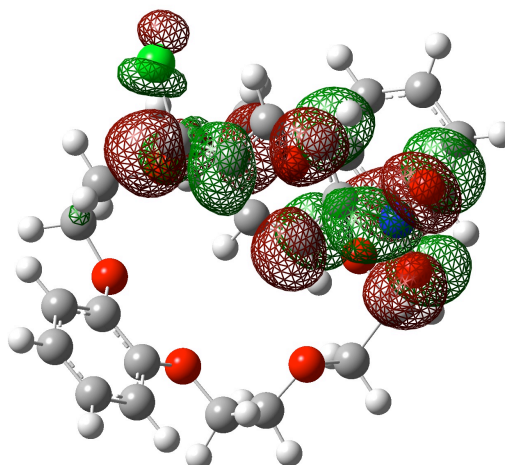
**Excited State 1: Singlet-A 2.6162 eV 473.90 nm f=0.4821 <S\*\*2>=0.000**  
 139 ->140 0.70788  
  
**Excited State 2: Singlet-A 2.8422 eV 436.23 nm f=0.0003 <S\*\*2>=0.000**  
 138 ->140 0.70578



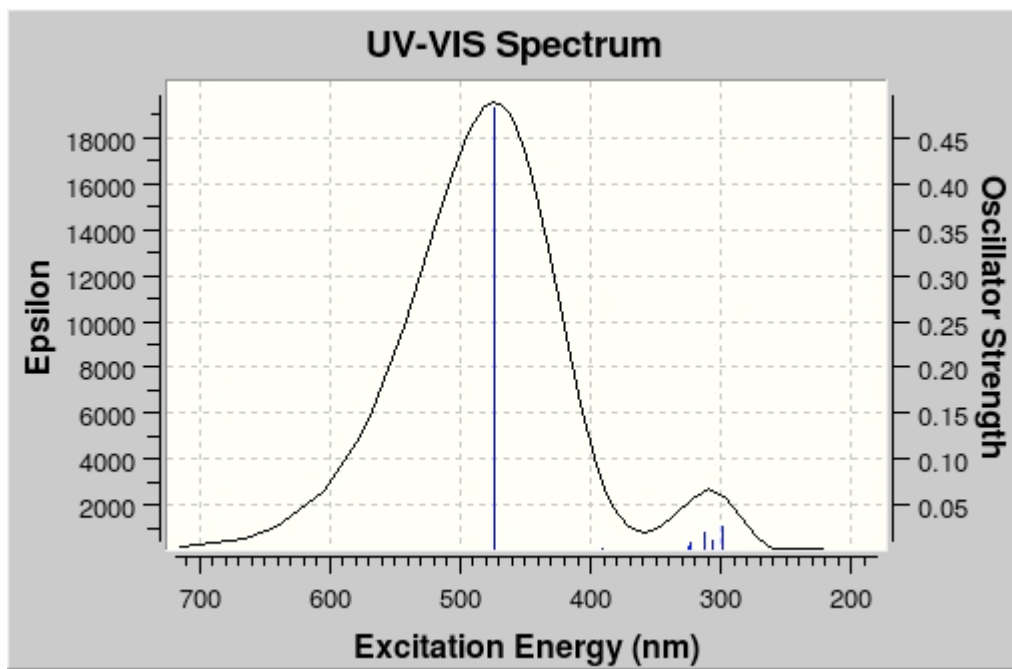
|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 3:  | Singlet-A | 3.1755 eV | 390.44 nm | f=0.0019 | <S**2>=0.000 |
| 137 ->140         | 0.70581   |           |           |          |              |
| Excited State 4:  | Singlet-A | 3.5821 eV | 346.12 nm | f=0.0014 | <S**2>=0.000 |
| 136 ->140         | 0.69965   |           |           |          |              |
| Excited State 5:  | Singlet-A | 3.8170 eV | 324.82 nm | f=0.0042 | <S**2>=0.000 |
| 131 ->140         | 0.48608   |           |           |          |              |
| 132 ->140         | 0.13603   |           |           |          |              |
| 134 ->140         | 0.23744   |           |           |          |              |
| 139 ->141         | -0.38825  |           |           |          |              |
| 139 ->142         | 0.13305   |           |           |          |              |
| Excited State 6:  | Singlet-A | 3.8389 eV | 322.97 nm | f=0.0083 | <S**2>=0.000 |
| 131 ->140         | 0.42224   |           |           |          |              |
| 132 ->140         | 0.15614   |           |           |          |              |
| 139 ->141         | 0.49619   |           |           |          |              |
| 139 ->142         | -0.14403  |           |           |          |              |
| Excited State 7:  | Singlet-A | 3.9710 eV | 312.23 nm | f=0.0208 | <S**2>=0.000 |
| 134 ->140         | 0.27143   |           |           |          |              |
| 139 ->141         | 0.28276   |           |           |          |              |
| 139 ->142         | 0.47724   |           |           |          |              |
| 139 ->143         | -0.29309  |           |           |          |              |
| Excited State 8:  | Singlet-A | 4.0174 eV | 308.62 nm | f=0.0001 | <S**2>=0.000 |
| 135 ->140         | 0.70520   |           |           |          |              |
| Excited State 9:  | Singlet-A | 4.0482 eV | 306.27 nm | f=0.0115 | <S**2>=0.000 |
| 131 ->140         | -0.11630  |           |           |          |              |
| 134 ->140         | 0.59330   |           |           |          |              |
| 139 ->142         | -0.27930  |           |           |          |              |
| 139 ->143         | 0.14424   |           |           |          |              |
| Excited State 10: | Singlet-A | 4.1490 eV | 298.83 nm | f=0.0265 | <S**2>=0.000 |
| 139 ->142         | 0.14774   |           |           |          |              |
| 139 ->144         | 0.18925   |           |           |          |              |
| 139 ->145         | 0.48459   |           |           |          |              |
| 139 ->146         | -0.34546  |           |           |          |              |
| 139 ->147         | -0.16845  |           |           |          |              |
| 139 ->148         | 0.14661   |           |           |          |              |



**10a-HOMO-MO139**



**10a-LUMO-MO140**



Computed electronic spectrum of **10a** (TD-B3LYP/6-311+G(d)).

## 10b:

-----  
O-Ylide 10b, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,0.2655909331,-1.72565731,-1.2402029336  
O,0,1.5160488078,-1.0593027642,-0.9818032532  
C,0,-0.3912723541,-2.0679922882,0.0716446583  
O,0,-1.1904371151,-0.8845534165,0.6319797001  
C,0,-0.307364272,0.2619636975,1.0540429688  
C,0,2.1518839852,-0.576191656,-2.1176575146  
C,0,1.6121431739,0.520301187,-2.8347138549  
C,0,-1.0647777374,1.326788794,1.8054985264  
C,0,-1.6511999592,2.1965335367,-2.5570337126  
O,0,-2.437947244,1.003075342,-2.6149272727  
C,0,-0.3029163549,1.9370090565,-3.1956262735  
O,0,0.4450691105,1.0432935467,-2.3462684897  
C,0,-3.857856416,4.1586303781,3.2675174406  
C,0,-4.8533993761,4.6252161678,2.4046528278  
C,0,-4.8712649796,4.1908794923,1.0709449531  
C,0,-3.902918966,3.3033182452,0.5945443866  
C,0,-2.8854030978,2.8415550453,1.4674230422  
C,0,-2.8746829242,3.270769969,2.8032058459  
O,0,-1.944239383,2.0030915441,0.9116993409  
O,0,-3.9153675235,2.9463888521,-0.7364288329  
C,0,-3.8412062415,1.2194538569,-2.4233477934  
C,0,-4.247941225,1.557903219,-0.9966533143  
C,0,3.3618895707,-1.1487133915,-2.5116404748  
C,0,4.0510387734,-0.6534450763,-3.6290588313  
C,0,3.5108143988,0.413896305,-4.3532060427  
C,0,2.2974946031,1.0009233468,-3.9623847369  
H,0,-0.3977693546,-1.1023275414,-1.8539410896  
H,0,0.4586727076,-2.671583943,-1.7766042758  
H,0,0.3181935629,-2.3512482678,0.8551818421  
H,0,-1.1606835531,-2.8305827321,-0.0593727003  
H,0,0.1180288591,0.6218737873,0.1165624572  
H,0,0.4679913719,-0.1711303309,1.6955773041  
H,0,-1.6215736179,0.8966770263,2.6462924452  
H,0,-0.303556467,2.0267144909,2.1978407634  
H,0,-2.1469144145,3.005988016,-3.1226760399  
H,0,-1.5325684938,2.5335867619,-1.5192051137  
H,0,-0.4218478716,1.4785465828,-4.1892114293  
H,0,-3.8327905999,4.4824208318,4.3080394461  
H,0,-5.616227479,5.3162374919,2.7626876806  
H,0,-5.6367243958,4.5325591687,0.3744321008  
H,0,-2.0987614049,2.9300748989,3.4859206732

H,0,-4.1944731928,2.012169879,-3.10753308  
 H,0,-4.3234738267,0.2763166423,-2.704619119  
 H,0,-3.7384898357,0.9013055821,-0.2832983289  
 H,0,-5.3378235035,1.4272047057,-0.8842984427  
 H,0,3.7511834611,-1.9843048817,-1.9301123733  
 H,0,4.9953158455,-1.1054401107,-3.9308500658  
 H,0,4.031694016,0.8038602456,-5.2277139276  
 H,0,1.8972268998,1.8393471916,-4.5283787693  
 H,0,0.2432625795,2.8889407331,-3.2991824224  
 C,0,-2.3524093639,-1.1867121728,1.5021347112  
 Cl,0,-1.7298355733,-1.9834417418,3.0111302987  
 C,0,-3.3881733239,-1.8441450736,0.7636319063  
 C,0,-4.4168838227,-2.585792997,1.424960097  
 C,0,-3.508020534,-1.6880141523,-0.6558743885  
 C,0,-5.4950614893,-3.1059201321,0.7267948478  
 H,0,-4.3577656963,-2.7374619622,2.5006507398  
 C,0,-4.5846787226,-2.2174256992,-1.3514728112  
 H,0,-2.7631814432,-1.1175532776,-1.2040413298  
 C,0,-5.5895979413,-2.9233743824,-0.6672198322  
 H,0,-6.2711255401,-3.6650946695,1.2436690359  
 H,0,-4.6585079894,-2.0997644247,-2.4301097605  
 N,0,-6.7214887864,-3.4737605716,-1.4045065055  
 O,0,-7.5781223334,-4.1124467896,-0.7734129026  
 O,0,-6.77612394,-3.2739292713,-2.6299144811

SCF Done: E(RB97D) = -2161.52790200 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -2161.025267  
 Sum of electronic and thermal Energies= -2160.991570  
 Sum of electronic and thermal Enthalpies= -2160.990626  
 Sum of electronic and thermal Free Energies= -2161.091412

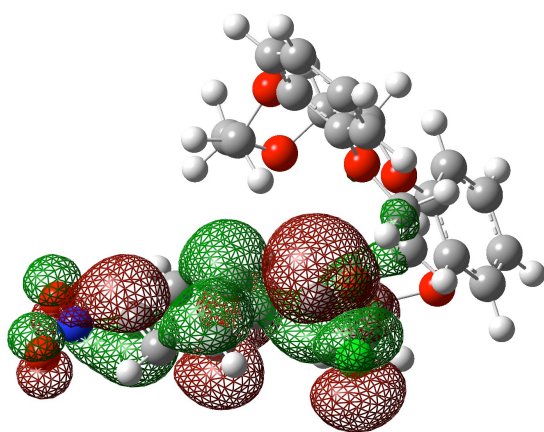
-----  
 # 6-311+g(d) b3lyp pop=none td=(nstates=10) scrf=(cpcm,solvent=dichloroethane)  
 -----

**Excited State 1: Singlet-A 2.6502 eV 467.84 nm f=0.5822 <S\*\*2>=0.000**  
 139 ->140 0.70907  
 139 <-140 -0.10047

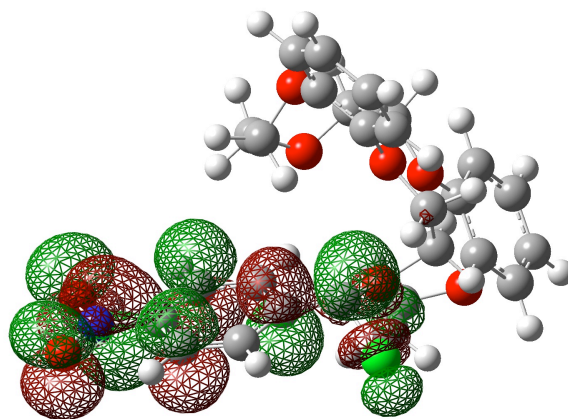
Excited State 2: Singlet-A 3.3412 eV 371.07 nm f=0.0011 <S\*\*2>=0.000  
 138 ->140 0.70563

Excited State 3: Singlet-A 3.4848 eV 355.78 nm f=0.0002 <S\*\*2>=0.000  
 137 ->140 0.70575

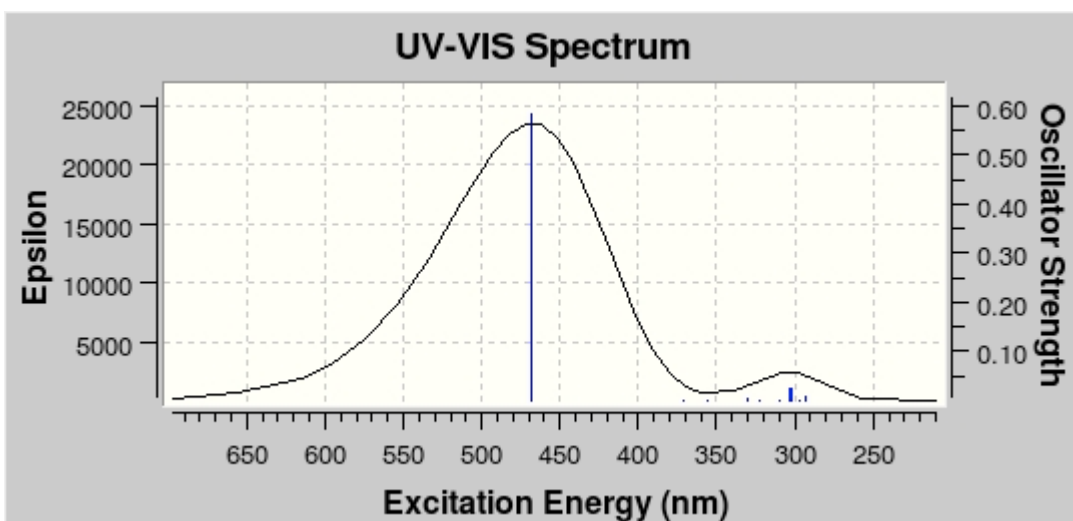
|                   |           |           |           |          |                               |
|-------------------|-----------|-----------|-----------|----------|-------------------------------|
| Excited State 4:  | Singlet-A | 3.7564 eV | 330.06 nm | f=0.0044 | $\langle S^2 \rangle = 0.000$ |
| 133 ->140         | 0.14697   |           |           |          |                               |
| 139 ->141         | 0.68674   |           |           |          |                               |
| Excited State 5:  | Singlet-A | 3.8456 eV | 322.40 nm | f=0.0001 | $\langle S^2 \rangle = 0.000$ |
| 131 ->140         | 0.69029   |           |           |          |                               |
| Excited State 6:  | Singlet-A | 3.9988 eV | 310.06 nm | f=0.0000 | $\langle S^2 \rangle = 0.000$ |
| 136 ->140         | 0.70523   |           |           |          |                               |
| Excited State 7:  | Singlet-A | 4.0899 eV | 303.15 nm | f=0.0253 | $\langle S^2 \rangle = 0.000$ |
| 133 ->140         | 0.46933   |           |           |          |                               |
| 134 ->140         | 0.10405   |           |           |          |                               |
| 139 ->143         | 0.26482   |           |           |          |                               |
| 139 ->144         | 0.40230   |           |           |          |                               |
| Excited State 8:  | Singlet-A | 4.1077 eV | 301.84 nm | f=0.0245 | $\langle S^2 \rangle = 0.000$ |
| 133 ->140         | 0.47534   |           |           |          |                               |
| 134 ->140         | 0.10643   |           |           |          |                               |
| 139 ->141         | -0.10603  |           |           |          |                               |
| 139 ->143         | -0.30209  |           |           |          |                               |
| 139 ->144         | -0.37607  |           |           |          |                               |
| Excited State 9:  | Singlet-A | 4.1714 eV | 297.23 nm | f=0.0000 | $\langle S^2 \rangle = 0.000$ |
| 134 ->140         | 0.15831   |           |           |          |                               |
| 135 ->140         | 0.68718   |           |           |          |                               |
| Excited State 10: | Singlet-A | 4.2336 eV | 292.86 nm | f=0.0090 | $\langle S^2 \rangle = 0.000$ |
| 139 ->143         | 0.55640   |           |           |          |                               |
| 139 ->144         | -0.36629  |           |           |          |                               |
| 139 ->147         | -0.17205  |           |           |          |                               |



**10b-HOMO-MO139**



**10b-LUMO-MO140**



Computed electronic spectrum of **10b** (TD-B3LYP/6-311+G(d)).

## 10c:

-----  
O-Ylide 10c, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,0.8388596838,4.0485870387,-0.6566050924  
H,0,0.79320282,5.1402875047,-0.7807342901  
H,0,1.7813905571,3.6885342256,-1.0875052539  
C,0,0.8137273577,3.7385780649,0.8269916192  
H,0,1.6247750503,4.2388013237,1.3627698438  
H,0,-0.1551282411,3.9664461719,1.2832615988  
C,0,-0.1984947902,1.5093121454,1.3949764101  
H,0,-0.9860115028,1.9473126085,0.7813010513  
H,0,-0.3625720186,1.6875646171,2.4621026972  
C,0,-0.0156956907,0.0371931031,1.0609171602  
H,0,0.2663816808,-0.0892361609,0.0094622364  
H,0,0.7428665389,-0.4366564793,1.6972996949  
C,0,-1.4812715328,-1.8306248924,0.8815661225  
C,0,-0.4483326616,-2.6761950438,0.4596853397  
H,0,0.5810975114,-2.3237311491,0.4457963094  
C,0,-0.7345012541,-3.9863711372,0.0400829251  
H,0,0.0809926717,-4.6301773416,-0.2875353699  
C,0,-2.0504400811,-4.4511670221,0.0445022862  
H,0,-2.2788211085,-5.4675576526,-0.2753686211  
C,0,-3.0935485963,-3.6073036009,0.4628387632  
H,0,-4.1187875334,-3.9731193952,0.4678820081  
C,0,-2.8219600851,-2.2974571134,0.8763157891  
C,0,-5.1338418383,-1.6171478047,0.8919075472  
H,0,-5.6031415257,-2.3443314633,1.5775478321  
H,0,-5.1768759558,-2.0171234759,-0.1334142829  
C,0,-5.8680903161,-0.2821498357,0.9586796187  
H,0,-6.9474872266,-0.4771816284,0.8925805652  
H,0,-5.6600145964,0.2064767605,1.9263267355  
C,0,-4.3409297786,1.3226834234,-0.0500616324  
H,0,-3.9080564739,1.2704008816,0.9589240884  
H,0,-4.5590415625,2.372276945,-0.2963635102  
C,0,-3.3508904917,0.7578852072,-1.0704261815  
H,0,-3.0141301192,-0.2401261867,-0.77007837  
H,0,-3.8161232001,0.7047638413,-2.0666150276  
C,0,-1.1890843692,1.3622754065,-1.9426568348  
C,0,-1.0725794052,0.1642919613,-2.6666680942  
H,0,-1.8372918483,-0.6028569668,-2.5744861614  
C,0,0.0323478369,-0.0627020903,-3.5004751576  
H,0,0.1082732803,-1.0060952479,-4.040051007  
C,0,1.0193601956,0.915139633,-3.6413451441  
H,0,1.8693666218,0.7565131611,-4.3038461935

C,0,0.9112376914,2.1161560381,-2.924935031  
 H,0,1.6713081724,2.887097888,-3.0457818324  
 C,0,-0.1591817942,2.3341076903,-2.0508414726  
 O,0,-0.3095491089,3.4987261991,-1.3155885083  
 O,0,1.0555384671,2.2769065625,1.0115869214  
 O,0,-1.3064614767,-0.5306209089,1.2975107864  
 O,0,-3.7701527578,-1.3907935457,1.2766334112  
 O,0,-5.5763456328,0.6004425703,-0.1230515545  
 O,0,-2.2326879377,1.6673001581,-1.1120189883  
 C,0,2.4228889235,1.9635694006,1.6099348968  
 C,0,2.9567100565,0.7538597252,1.0377181301  
 C,0,3.8183602031,-0.1238094747,1.76195466  
 C,0,2.7433125662,0.4578820589,-0.345171579  
 C,0,4.3912911404,-1.235244341,1.1557046418  
 H,0,4.0224116302,0.0679808973,2.812846429  
 C,0,3.2977123842,-0.6590070971,-0.9449770695  
 H,0,2.1129670488,1.1072202169,-0.9445493941  
 C,0,4.1223437004,-1.5200264159,-0.1946909682  
 H,0,5.0294612265,-1.9068885211,1.7248864394  
 H,0,3.0964031302,-0.8786976421,-1.9902979073  
 Cl,0,2.2361648698,2.0423550486,3.4055994579  
 N,0,4.6846173147,-2.7148577343,-0.8184481021  
 O,0,4.3818544192,-2.9548161296,-1.9991482614  
 O,0,5.430319761,-3.43691598,-0.1389251228

SCF Done: E(RB97D) = -2161.52327205 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.020439  
 Sum of electronic and thermal Energies= -2160.986352  
 Sum of electronic and thermal Enthalpies= -2160.985408  
 Sum of electronic and thermal Free Energies= -2161.088307

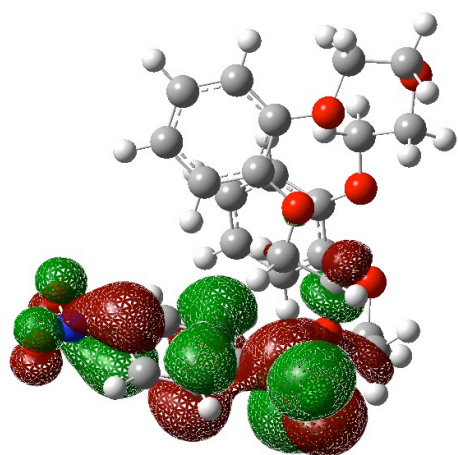
-----  
 # 6-311+g(d) pop=none b3lyp td=(nstates=10) scrf=(cpcm,solvent=dichloroethane)  
 -----

### Excitation energies and oscillator strengths:

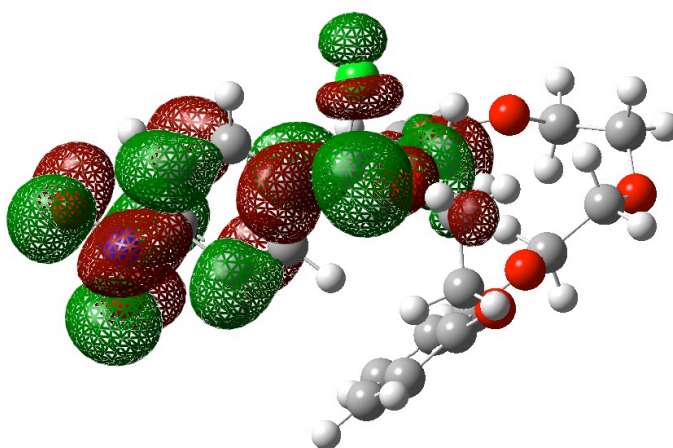
|                  |           |           |           |          |              |
|------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 1: | Singlet-A | 2.6093 eV | 475.17 nm | f=0.4708 | <S**2>=0.000 |
| 139 ->140        | 0.70761   |           |           |          |              |
| Excited State 2: | Singlet-A | 3.0336 eV | 408.71 nm | f=0.0036 | <S**2>=0.000 |
| 138 ->140        | 0.70478   |           |           |          |              |
| Excited State 3: | Singlet-A | 3.1842 eV | 389.38 nm | f=0.0003 | <S**2>=0.000 |
| 137 ->140        | 0.70511   |           |           |          |              |



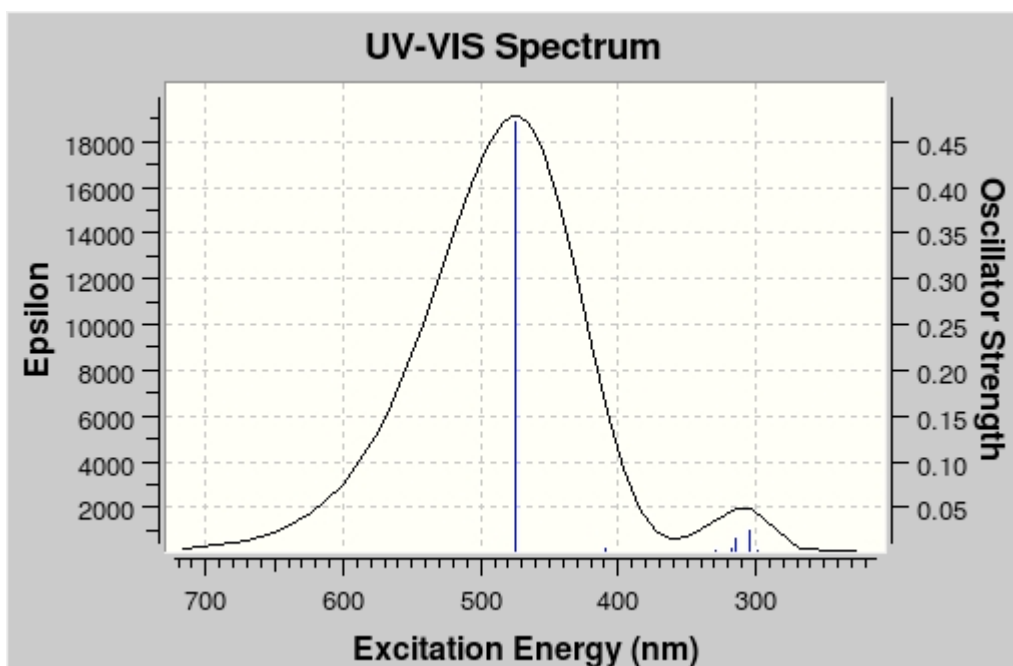
|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 4:  | Singlet-A | 3.7701 eV | 328.86 nm | f=0.0021 | <S**2>=0.000 |
| 134 ->140         | -0.19326  |           |           |          |              |
| 136 ->140         | -0.29464  |           |           |          |              |
| 139 ->141         | 0.57105   |           |           |          |              |
| 139 ->142         | 0.12028   |           |           |          |              |
| 139 ->143         | 0.15267   |           |           |          |              |
| Excited State 5:  | Singlet-A | 3.7884 eV | 327.27 nm | f=0.0014 | <S**2>=0.000 |
| 136 ->140         | 0.63110   |           |           |          |              |
| 139 ->141         | 0.27000   |           |           |          |              |
| Excited State 6:  | Singlet-A | 3.8233 eV | 324.29 nm | f=0.0002 | <S**2>=0.000 |
| 131 ->140         | 0.68093   |           |           |          |              |
| 131 ->142         | -0.10878  |           |           |          |              |
| Excited State 7:  | Singlet-A | 3.9124 eV | 316.90 nm | f=0.0038 | <S**2>=0.000 |
| 135 ->140         | 0.68941   |           |           |          |              |
| Excited State 8:  | Singlet-A | 3.9469 eV | 314.13 nm | f=0.0164 | <S**2>=0.000 |
| 139 ->142         | 0.66449   |           |           |          |              |
| 139 ->143         | -0.15659  |           |           |          |              |
| Excited State 9:  | Singlet-A | 4.0717 eV | 304.51 nm | f=0.0250 | <S**2>=0.000 |
| 134 ->140         | 0.65474   |           |           |          |              |
| 139 ->141         | 0.21526   |           |           |          |              |
| Excited State 10: | Singlet-A | 4.1492 eV | 298.81 nm | f=0.0034 | <S**2>=0.000 |
| 134 ->140         | 0.12207   |           |           |          |              |
| 139 ->141         | -0.17171  |           |           |          |              |
| 139 ->142         | 0.12495   |           |           |          |              |
| 139 ->143         | 0.65614   |           |           |          |              |



**10c-HOMO-MO139**



**10c-LUMO-MO140**



Computed electronic spectrum of **10c** (TD-B3LYP/6-311+G(d)).

## 10d:

-----  
O-Ylide 10d, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,0.8294935621,-2.0853779107,-1.6412422374  
H,0,1.1595252975,-2.8035906246,-2.4130533161  
H,0,0.7104317541,-2.6248702912,-0.6929522405  
C,0,1.8819329644,-1.0085318952,-1.5077921543  
H,0,2.8895141393,-1.4192713815,-1.4139002079  
H,0,1.8330846529,-0.2760102406,-2.319448788  
C,0,0.504491621,0.5969571589,-0.0112094504  
H,0,0.053599077,0.7318137066,-0.9969634295  
H,0,0.8580383331,1.5409033472,0.4108665705  
C,0,-0.4544759093,-0.1151859764,0.9367759537  
H,0,-0.7830668732,-1.0757687243,0.5187991575  
H,0,0.0172580037,-0.2826212699,1.9140968055  
C,0,-2.6768714479,0.3489177395,1.7013482161  
C,0,-2.7910768792,-0.8822376711,2.3553601535  
H,0,-1.9487218877,-1.570444849,2.376408822  
C,0,-3.997098952,-1.2435454788,2.9798123633  
H,0,-4.0702753694,-2.2086721157,3.4802006986  
C,0,-5.0867907143,-0.3727906258,2.9565871384  
H,0,-6.0230052714,-0.6441755356,3.4439056707  
C,0,-4.9798146601,0.8691996506,2.3066771384  
H,0,-5.8265052097,1.5534054506,2.2999348181  
C,0,-3.7860409996,1.2370176995,1.6756351283  
C,0,-4.7336222694,3.1553295749,0.5523003967  
H,0,-5.1073969921,3.7925487926,1.3723423894  
H,0,-5.5375016631,2.4693425041,0.2423856402  
C,0,-4.2997226477,4.0167727501,-0.6320007323  
H,0,-5.0650917713,4.7854449932,-0.8043203924  
H,0,-3.3473315588,4.5183631229,-0.3861616808  
C,0,-3.1019529141,2.3910197979,-1.980065459  
H,0,-2.3340566132,2.5820316393,-1.2185362478  
H,0,-2.6636286497,2.5208566746,-2.9800141591  
C,0,-3.6335616028,0.9648084049,-1.8273513533  
H,0,-4.0970076401,0.8298414651,-0.8428980244  
H,0,-4.3811034013,0.7471025125,-2.6064155439  
C,0,-2.7250944296,-1.2492228116,-1.6952677016  
C,0,-3.9657741998,-1.8182839876,-1.3766604337  
H,0,-4.8547612684,-1.1941744063,-1.3321603066  
C,0,-4.0709832216,-3.1899558361,-1.0946546769  
H,0,-5.0446801251,-3.607397951,-0.8397393531  
C,0,-2.9409937414,-4.0067559495,-1.1369013048

H,0,-3.0164339655,-5.0725829835,-0.9239907242  
 C,0,-1.6912850668,-3.4512613022,-1.4605294207  
 H,0,-0.810578401,-4.0899707169,-1.5051974841  
 C,0,-1.5767873663,-2.0846614521,-1.7322939556  
 O,0,-0.3886991223,-1.4514929896,-2.0332208557  
 O,0,1.7282149837,-0.206846444,-0.2266466078  
 O,0,-1.5549234118,0.7877045776,1.0454632961  
 O,0,-3.5888806561,2.4120453898,0.9986012402  
 O,0,-4.1906047404,3.3182544472,-1.8713763539  
 O,0,-2.513307221,0.074148222,-1.9619344945  
 C,0,2.6189163637,-0.3851410828,0.9659442494  
 C,0,3.9819683734,-0.063530231,0.6151128292  
 C,0,5.0912355969,-0.5913265041,1.3417387342  
 C,0,4.2686634638,0.9204510462,-0.3825627876  
 C,0,6.3881850632,-0.1627017204,1.0945128259  
 H,0,4.9197969678,-1.3441448112,2.1077385808  
 C,0,5.5654481415,1.3433642413,-0.6361648032  
 H,0,3.4549064347,1.3674584091,-0.9516806906  
 C,0,6.6331496614,0.8035392587,0.102566991  
 H,0,7.2240768513,-0.5780104845,1.6520326337  
 H,0,5.7682669678,2.0885082417,-1.4015374413  
 Cl,0,2.3237187926,-2.0699957895,1.5989394923  
 N,0,8.0027610948,1.242527732,-0.1703789752  
 O,0,8.1783656471,2.0861965608,-1.0626865636  
 O,0,8.9193220258,0.7489219326,0.5024724181

SCF Done: E(RB97D) = -2161.51987557 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -2161.017484  
 Sum of electronic and thermal Energies= -2160.983364  
 Sum of electronic and thermal Enthalpies= -2160.982419  
 Sum of electronic and thermal Free Energies= -2161.085590

---

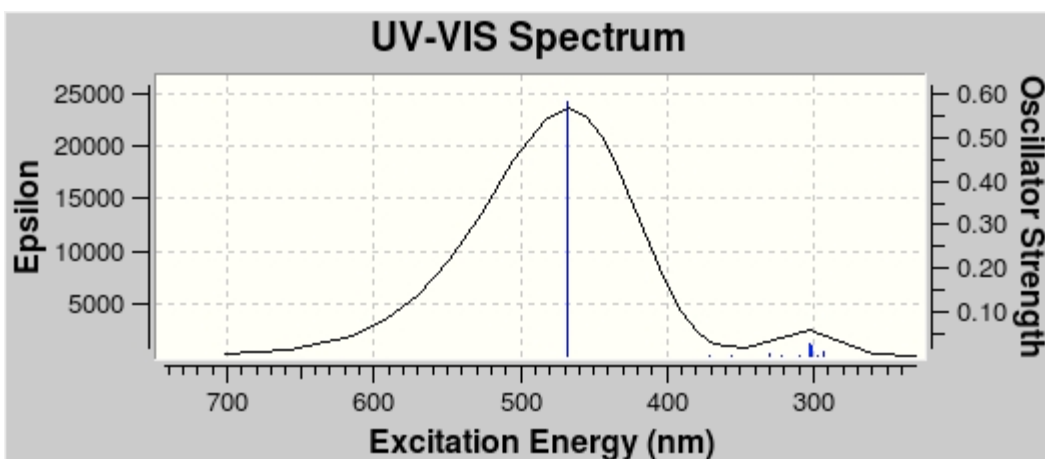
# 6-311+g(d) pop=none rb3lyp scrf=(cpcm,solvent=dichloroethane) td=(nstates=10)

---

### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 2.6373 eV 470.11 nm f=0.6316 <S\*\*2>=0.000**  
 139 ->140 0.70784  
  
 Excited State 2: Singlet-A 3.0522 eV 406.22 nm f=0.0018 <S\*\*2>=0.000  
 138 ->140 0.70548  
  
 Excited State 3: Singlet-A 3.2375 eV 382.96 nm f=0.0003 <S\*\*2>=0.000

|                   |           |           |           |          |              |  |  |
|-------------------|-----------|-----------|-----------|----------|--------------|--|--|
| 137 ->140         | 0.70544   |           |           |          |              |  |  |
| Excited State 4:  | Singlet-A | 3.8209 eV | 324.49 nm | f=0.0006 | <S**2>=0.000 |  |  |
| 134 ->140         | -0.23768  |           |           |          |              |  |  |
| 139 ->141         | 0.65393   |           |           |          |              |  |  |
| Excited State 5:  | Singlet-A | 3.8396 eV | 322.91 nm | f=0.0000 | <S**2>=0.000 |  |  |
| 131 ->140         | 0.68951   |           |           |          |              |  |  |
| 131 ->142         | -0.11121  |           |           |          |              |  |  |
| Excited State 6:  | Singlet-A | 3.9050 eV | 317.50 nm | f=0.0002 | <S**2>=0.000 |  |  |
| 136 ->140         | 0.70479   |           |           |          |              |  |  |
| Excited State 7:  | Singlet-A | 4.0042 eV | 309.63 nm | f=0.0447 | <S**2>=0.000 |  |  |
| 139 ->142         | 0.67612   |           |           |          |              |  |  |
| Excited State 8:  | Singlet-A | 4.0219 eV | 308.27 nm | f=0.0003 | <S**2>=0.000 |  |  |
| 135 ->140         | 0.69999   |           |           |          |              |  |  |
| Excited State 9:  | Singlet-A | 4.0838 eV | 303.60 nm | f=0.0244 | <S**2>=0.000 |  |  |
| 134 ->140         | 0.65254   |           |           |          |              |  |  |
| 139 ->141         | 0.21906   |           |           |          |              |  |  |
| 139 ->142         | 0.11061   |           |           |          |              |  |  |
| Excited State 10: | Singlet-A | 4.4159 eV | 280.77 nm | f=0.0005 | <S**2>=0.000 |  |  |
| 127 ->140         | -0.22252  |           |           |          |              |  |  |
| 128 ->140         | -0.17670  |           |           |          |              |  |  |
| 130 ->140         | 0.63186   |           |           |          |              |  |  |



Computed electronic spectrum of **10d** (TD-B3LYP/6-311+G(d)).

## 6. Geometries, Energies, Orbitals and Excitations for Half-Sandwiches 11a-11d

### 11a:

-----  
Half-sandwich 11a, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,3.8479703555,1.6440236943,0.1458601601  
O,0,3.8726236256,1.0589408179,-1.1817271856  
C,0,3.1108086207,2.9774913067,0.079637255  
O,0,1.6881716638,2.8852547229,0.1285864947  
C,0,1.1009546523,2.2985978641,-1.0345352855  
C,0,4.3692948185,-0.2272092878,-1.2463684195  
C,0,3.6510818418,-1.3204009494,-0.6956234446  
C,0,-0.4008947827,2.4716158166,-0.9545939717  
C,0,0.790037257,-1.3098286279,1.5894592424  
O,0,1.3867028135,-0.4730047277,2.5834871434  
C,0,1.8771545592,-1.993025128,0.790837186  
O,0,2.4609393362,-1.0172775111,-0.093264663  
C,0,-4.5084194595,2.4205142969,0.1982195221  
C,0,-4.8779170816,1.6872984336,1.3286253077  
C,0,-3.8959461719,0.9912861232,2.0527542649  
C,0,-2.5590358382,1.0070922189,1.6468934739  
C,0,-2.190863636,1.7178389216,0.4731527227  
C,0,-3.1710527724,2.43888003,-0.2288877171  
O,0,-0.888769075,1.605194025,0.0894685439  
O,0,-1.6448481432,0.260263082,2.3541102557  
C,0,0.4534048841,0.0218175014,3.5408341958  
C,0,-0.5731208417,1.008300651,2.9930866963  
C,0,5.569364245,-0.457771824,-1.9242083613  
C,0,6.0804830797,-1.7581602026,-2.0564256402  
C,0,5.3840037432,-2.8328151666,-1.4945974755  
C,0,4.1738058041,-2.6184142871,-0.8166816535  
H,0,3.3480746626,0.9721203371,0.8554071078  
H,0,4.8896561041,1.8128878526,0.4711360879  
H,0,3.4270177432,3.5271239583,-0.8271117436  
H,0,3.3874566337,3.5711062887,0.961543245  
H,0,1.3635403593,1.2341461582,-1.1089139735  
H,0,1.4677759416,2.8076492889,-1.9454077379  
H,0,-0.6594883093,3.5143298645,-0.7142687112  
H,0,-0.866778909,2.1957377089,-1.912580445  
H,0,0.1637023874,-2.0873426651,2.0624618243  
H,0,0.1458357305,-0.7188566698,0.9262183491  
H,0,1.4392279574,-2.81857429,0.2069429703  
H,0,2.6522622944,-2.4004354501,1.457677633  
H,0,-5.2551151792,2.973667248,-0.3711380294

H,0,-5.9165468761,1.6640121075,1.6584822967  
 H,0,-4.1497447318,0.4217177798,2.9467265869  
 H,0,-2.9009264806,2.9922702482,-1.1251444198  
 H,0,-0.07176287,-0.8195551621,4.0308054264  
 H,0,1.0613050626,0.5404683104,4.2945817887  
 H,0,-0.0970534615,1.6885207221,2.2765647499  
 H,0,-1.0086817871,1.5907270451,3.8231839596  
 H,0,6.092777276,0.401237283,-2.3443251621  
 H,0,7.0178851073,-1.9235245777,-2.5874237715  
 H,0,5.7718338959,-3.8479000959,-1.5839484993  
 H,0,3.6314621919,-3.4641602928,-0.3980185784  
 C,0,-3.7611545062,-1.62667126,-0.0607122573  
 C,0,-2.4298333369,-2.1330754432,-0.0315686261  
 C,0,-1.5102720812,-1.6746053235,-1.0148423773  
 C,0,-1.87843132,-0.7170805056,-1.9562765042  
 C,0,-3.2007083883,-0.2606137289,-1.9511042933  
 C,0,-4.1568628243,-0.7176720217,-1.0324789779  
 H,0,-4.4818578405,-1.96176732,0.6816507897  
 H,0,-0.4993036215,-2.076226608,-1.0121062312  
 H,0,-1.1714313723,-0.3373621727,-2.688332651  
 H,0,-5.1678068717,-0.3240601778,-1.0657780395  
 N,0,-3.6129929049,0.7544797395,-2.9664625274  
 O,0,-4.8155842519,0.9127777222,-3.1604041443  
 O,0,-2.7174951523,1.3787154542,-3.5395783554  
 C,0,-1.8574101554,-3.1428231212,0.8560945488  
 Cl,0,-2.8784619439,-3.4693178051,2.2480343655

SCF Done: E(RB97D) = -2161.52832168 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.028551  
 Sum of electronic and thermal Energies= -2160.993466  
 Sum of electronic and thermal Enthalpies= -2160.992522  
 Sum of electronic and thermal Free Energies= -2161.099050

-----  
 # 6-311+g(d) pop=none b3lyp td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 1.4955 eV 829.02 nm f=0.0052 <S\*\*2>=0.000**  
 137 ->140 0.67593  
 137 ->141 -0.15692  
 138 ->140 -0.10089

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 2:  | Singlet-A | 1.5961 eV | 776.81 nm | f=0.0007 | <S**2>=0.000 |
| 138 ->140         | 0.65073   |           |           |          |              |
| 139 ->140         | -0.26966  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 3:  | Singlet-A | 1.8310 eV | 677.13 nm | f=0.0009 | <S**2>=0.000 |
| 137 ->140         | 0.12607   |           |           |          |              |
| 138 ->140         | 0.25638   |           |           |          |              |
| 139 ->140         | 0.64569   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 4:  | Singlet-A | 2.3495 eV | 527.70 nm | f=0.0381 | <S**2>=0.000 |
| 135 ->140         | 0.66113   |           |           |          |              |
| 136 ->140         | 0.23630   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 5:  | Singlet-A | 2.5346 eV | 489.16 nm | f=0.0003 | <S**2>=0.000 |
| 135 ->140         | -0.23123  |           |           |          |              |
| 136 ->140         | 0.66145   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 6:  | Singlet-A | 2.7158 eV | 456.52 nm | f=0.0091 | <S**2>=0.000 |
| 133 ->140         | -0.39309  |           |           |          |              |
| 134 ->140         | 0.57385   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 7:  | Singlet-A | 2.8532 eV | 434.54 nm | f=0.0020 | <S**2>=0.000 |
| 133 ->140         | 0.58229   |           |           |          |              |
| 134 ->140         | 0.39852   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 8:  | Singlet-A | 2.9664 eV | 417.96 nm | f=0.0004 | <S**2>=0.000 |
| 138 ->141         | 0.65770   |           |           |          |              |
| 139 ->141         | -0.25357  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 9:  | Singlet-A | 3.1785 eV | 390.07 nm | f=0.0057 | <S**2>=0.000 |
| 137 ->140         | 0.12100   |           |           |          |              |
| 137 ->141         | 0.49056   |           |           |          |              |
| 138 ->141         | -0.17421  |           |           |          |              |
| 139 ->141         | -0.45298  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 10: | Singlet-A | 3.2396 eV | 382.71 nm | f=0.0030 | <S**2>=0.000 |
| 137 ->141         | 0.46620   |           |           |          |              |
| 138 ->141         | 0.18402   |           |           |          |              |
| 139 ->141         | 0.47814   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 11: | Singlet-A | 3.2971 eV | 376.05 nm | f=0.0190 | <S**2>=0.000 |
| 131 ->140         | 0.11738   |           |           |          |              |
| 132 ->140         | -0.68180  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 12: | Singlet-A | 3.3887 eV | 365.87 nm | f=0.0322 | <S**2>=0.000 |
| 130 ->140         | 0.62927   |           |           |          |              |



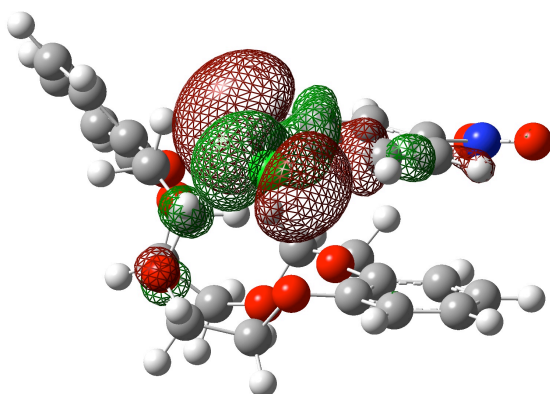
|                   |           |           |                  |                 |              |
|-------------------|-----------|-----------|------------------|-----------------|--------------|
| 131 ->140         | -0.26068  |           |                  |                 |              |
| Excited State 13: | Singlet-A | 3.5610 eV | 348.17 nm        | f=0.0122        | <S**2>=0.000 |
| 126 ->140         | 0.18970   |           |                  |                 |              |
| 129 ->140         | 0.16425   |           |                  |                 |              |
| 130 ->140         | 0.22715   |           |                  |                 |              |
| 131 ->140         | 0.59086   |           |                  |                 |              |
| 132 ->140         | 0.10122   |           |                  |                 |              |
| Excited State 14: | Singlet-A | 3.5740 eV | 346.90 nm        | f=0.0297        | <S**2>=0.000 |
| 124 ->140         | -0.15629  |           |                  |                 |              |
| 126 ->140         | 0.39362   |           |                  |                 |              |
| 126 ->141         | 0.19785   |           |                  |                 |              |
| 127 ->140         | 0.10101   |           |                  |                 |              |
| 129 ->140         | 0.38129   |           |                  |                 |              |
| 130 ->140         | -0.15599  |           |                  |                 |              |
| 131 ->140         | -0.25741  |           |                  |                 |              |
| Excited State 15: | Singlet-A | 3.6688 eV | 337.95 nm        | f=0.0120        | <S**2>=0.000 |
| 135 ->141         | 0.65629   |           |                  |                 |              |
| 136 ->141         | 0.21461   |           |                  |                 |              |
| Excited State 16: | Singlet-A | 3.9166 eV | 316.56 nm        | f=0.0000        | <S**2>=0.000 |
| 135 ->141         | -0.21063  |           |                  |                 |              |
| 136 ->141         | 0.67085   |           |                  |                 |              |
| Excited State 17: | Singlet-A | 3.9472 eV | <b>314.11 nm</b> | <b>f=0.3303</b> | <S**2>=0.000 |
| 124 ->140         | 0.10696   |           |                  |                 |              |
| 126 ->140         | -0.35455  |           |                  |                 |              |
| 126 ->141         | -0.10279  |           |                  |                 |              |
| 129 ->140         | 0.54518   |           |                  |                 |              |
| 130 ->140         | 0.11592   |           |                  |                 |              |
| Excited State 18: | Singlet-A | 4.0769 eV | 304.12 nm        | f=0.0005        | <S**2>=0.000 |
| 121 ->140         | 0.18132   |           |                  |                 |              |
| 122 ->140         | 0.60050   |           |                  |                 |              |
| 122 ->141         | 0.26014   |           |                  |                 |              |
| Excited State 19: | Singlet-A | 4.1330 eV | 299.98 nm        | f=0.0031        | <S**2>=0.000 |
| 133 ->141         | -0.30773  |           |                  |                 |              |
| 134 ->141         | 0.61356   |           |                  |                 |              |
| Excited State 20: | Singlet-A | 4.2221 eV | 293.66 nm        | f=0.0026        | <S**2>=0.000 |
| 133 ->141         | 0.58013   |           |                  |                 |              |
| 134 ->141         | 0.28867   |           |                  |                 |              |
| 138 ->142         | -0.25598  |           |                  |                 |              |

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 21: | Singlet-A | 4.2243 eV | 293.50 nm | f=0.0079 | <S**2>=0.000 |
| 133 ->141         | 0.23889   |           |           |          |              |
| 134 ->141         | 0.13750   |           |           |          |              |
| 138 ->142         | 0.60013   |           |           |          |              |
| 139 ->142         | -0.23014  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 22: | Singlet-A | 4.2683 eV | 290.48 nm | f=0.0084 | <S**2>=0.000 |
| 124 ->140         | 0.10043   |           |           |          |              |
| 127 ->140         | 0.52672   |           |           |          |              |
| 128 ->140         | -0.41345  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 23: | Singlet-A | 4.3662 eV | 283.96 nm | f=0.0039 | <S**2>=0.000 |
| 127 ->140         | 0.41365   |           |           |          |              |
| 128 ->140         | 0.55310   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 24: | Singlet-A | 4.4163 eV | 280.74 nm | f=0.0069 | <S**2>=0.000 |
| 137 ->142         | 0.64310   |           |           |          |              |
| 139 ->142         | -0.24752  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 25: | Singlet-A | 4.4850 eV | 276.44 nm | f=0.0072 | <S**2>=0.000 |
| 123 ->140         | -0.10077  |           |           |          |              |
| 124 ->140         | 0.46311   |           |           |          |              |
| 125 ->140         | -0.40645  |           |           |          |              |
| 126 ->140         | 0.28906   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 26: | Singlet-A | 4.4903 eV | 276.12 nm | f=0.0156 | <S**2>=0.000 |
| 124 ->140         | 0.43337   |           |           |          |              |
| 125 ->140         | 0.53507   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 27: | Singlet-A | 4.5197 eV | 274.32 nm | f=0.0024 | <S**2>=0.000 |
| 130 ->141         | 0.12664   |           |           |          |              |
| 131 ->141         | -0.14031  |           |           |          |              |
| 132 ->141         | 0.59596   |           |           |          |              |
| 139 ->142         | 0.27852   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 28: | Singlet-A | 4.5261 eV | 273.93 nm | f=0.0004 | <S**2>=0.000 |
| 132 ->141         | -0.27558  |           |           |          |              |
| 137 ->142         | 0.26285   |           |           |          |              |
| 138 ->142         | 0.22241   |           |           |          |              |
| 139 ->142         | 0.53957   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 29: | Singlet-A | 4.6134 eV | 268.75 nm | f=0.0052 | <S**2>=0.000 |
| 118 ->140         | -0.16205  |           |           |          |              |
| 119 ->140         | -0.59912  |           |           |          |              |
| 119 ->141         | 0.12040   |           |           |          |              |

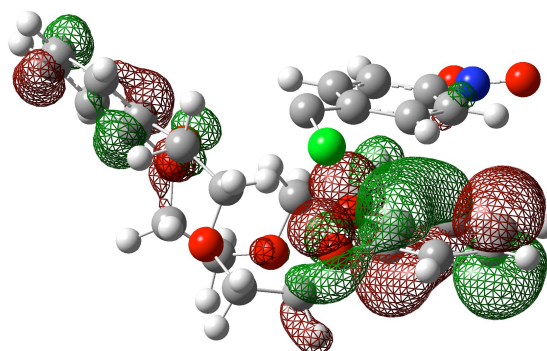
|           |          |
|-----------|----------|
| 123 ->140 | 0.15450  |
| 126 ->140 | 0.10514  |
| 129 ->141 | -0.10732 |
| 130 ->141 | -0.11610 |

Excited State 30: Singlet-A 4.7287 eV 262.20 nm f=0.0015 <S\*\*2>=0.000

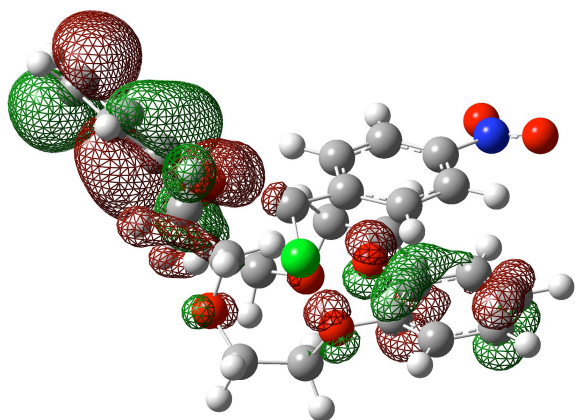
|           |          |
|-----------|----------|
| 120 ->140 | 0.16452  |
| 123 ->140 | 0.59648  |
| 125 ->140 | -0.11916 |
| 130 ->141 | 0.25765  |



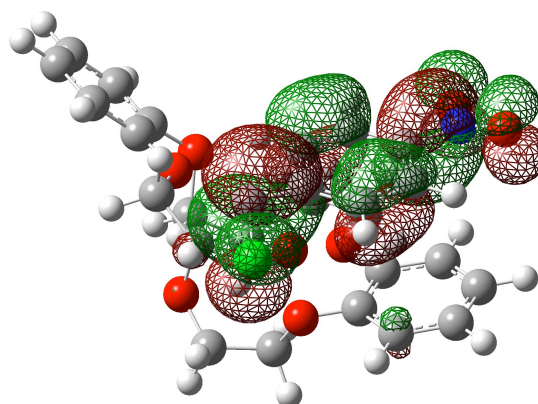
11a-σ-MO137



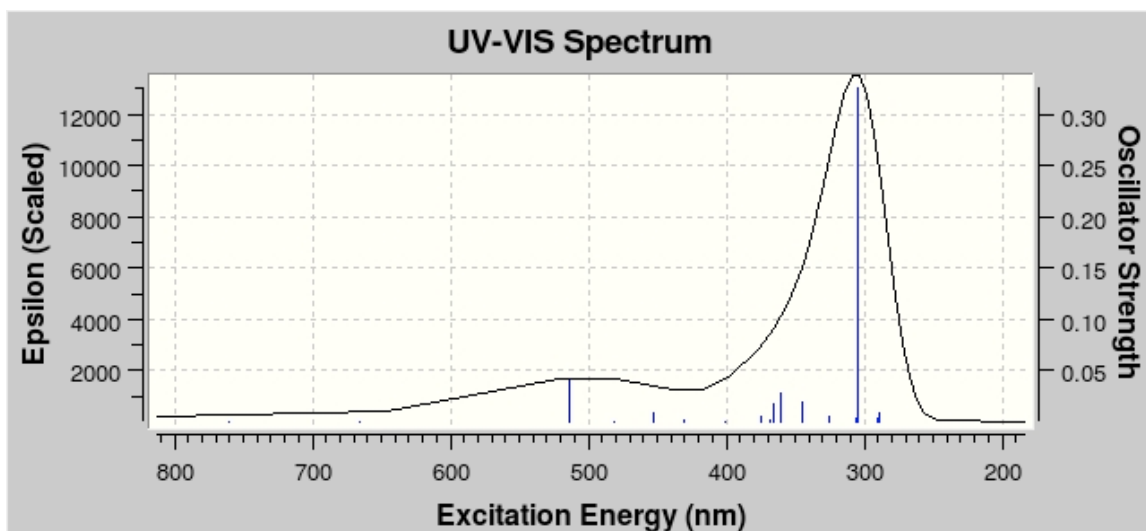
11a-MO138



11a-HOMO-MO139



11a-LUMO-p-MO140



Computed electronic spectrum of **11a** (TD-B3LYP/6-311+G(d)).

## 11b:

-----  
Half-sandwich 11b, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,-2.7954942385,1.8131920047,-1.5529390431  
O,0,-3.7267217021,2.1344569999,-0.4898248133  
C,0,-1.5387889326,2.6577306102,-1.3635303577  
O,0,-0.5820792381,2.12439807,-0.4479138449  
C,0,-1.0371672295,2.0681363745,0.9100225727  
C,0,-4.8526816581,1.3383975545,-0.4271664655  
C,0,-4.7704643961,-0.0191805698,-0.020870376  
C,0,0.1319672464,1.7075975762,1.8025733215  
C,0,-1.8525246741,-2.2044446565,0.3794730424  
O,0,-1.3974303311,-2.0285605843,-0.9645226755  
C,0,-3.3370660178,-1.9030369318,0.4261847426  
O,0,-3.5163391377,-0.4871017821,0.2599557042  
C,0,3.7153651,-0.0286063719,3.3278419572  
C,0,4.0912493839,-1.2940785894,2.8756590644  
C,0,3.2368179148,-2.0017492827,2.0101537043  
C,0,2.025722988,-1.450751246,1.5912042322  
C,0,1.6586696463,-0.1474528566,2.022799215  
C,0,2.506988689,0.5486178365,2.9058926546  
O,0,0.4791195473,0.3282945712,1.5438761793  
O,0,1.1679832564,-2.2117287937,0.8250413663  
C,0,-0.0978642196,-2.5570043205,-1.2159074585  
C,0,1.0448899327,-1.7953669919,-0.5567225149  
C,0,-6.0993944292,1.9077788106,-0.6976827117  
C,0,-7.2754932125,1.1510059223,-0.5800276618  
C,0,-7.1942595897,-0.1899014496,-0.1931033794  
C,0,-5.949418945,-0.775418675,0.0866501992  
H,0,-2.5416939635,0.745081132,-1.5371950835  
H,0,-3.2678850671,2.0630414103,-2.5190898682  
H,0,-1.8294366801,3.6803351737,-1.0584751397  
H,0,-1.0093718937,2.7180953697,-2.3245677581  
H,0,-1.8479066822,1.3352572177,1.0134193335  
H,0,-1.4237619829,3.056238471,1.2199598243  
H,0,1.0017456188,2.3500753305,1.6046550568  
H,0,-0.1632429463,1.8137115301,2.8595285793  
H,0,-1.6965793197,-3.2518049892,0.6990485885  
H,0,-1.2990230466,-1.5510152328,1.0678115848  
H,0,-3.7550438614,-2.2180883802,1.3972488902  
H,0,-3.8584543878,-2.4407117578,-0.380661356  
H,0,4.360696122,0.5307176424,4.0044667988  
H,0,5.0318854941,-1.7412184976,3.1971501309  
H,0,3.493163254,-3.0006753634,1.6570014488

H,0,2.2224331579,1.5312541596,3.271337504  
 H,0,-0.0515962833,-3.620855806,-0.9152568472  
 H,0,0.0341020069,-2.4950947931,-2.3042697129  
 H,0,0.8640814015,-0.7152521,-0.6155876092  
 H,0,1.9892509452,-2.0347496853,-1.0728109443  
 H,0,-6.1283638778,2.9553609723,-0.9977650224  
 H,0,-8.2415928183,1.6082294312,-0.7933581812  
 H,0,-8.0983693006,-0.7919849368,-0.0988518536  
 H,0,-5.9037389337,-1.8150354211,0.4048562034  
 C,0,3.6809756864,1.6739829537,0.0509369676  
 C,0,4.6829798788,0.6768838629,-0.1089061133  
 C,0,4.6328165789,-0.2114487776,-1.1763270029  
 C,0,3.5869259436,-0.0924735111,-2.1056586848  
 C,0,2.5821707134,0.8731782385,-1.984570544  
 C,0,2.6201956082,1.7369071608,-0.8920333988  
 H,0,5.4780366059,0.5901059106,0.6276446505  
 H,0,5.3792852853,-0.9916476652,-1.3009140003  
 H,0,1.7723277234,0.9128234328,-2.7073604892  
 H,0,1.8164632488,2.453679151,-0.7433934072  
 N,0,3.5157961361,-1.0678373064,-3.2366932733  
 O,0,4.482850728,-1.8079986916,-3.4149862259  
 O,0,2.4868200552,-1.0793378453,-3.9140209861  
 C,0,3.544703442,2.6567649011,1.1265531972  
 Cl,0,5.0789534874,2.9812054697,1.9261578696

SCF Done: E(RB97D) = -2161.52679718 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.026888  
 Sum of electronic and thermal Energies= -2160.991805  
 Sum of electronic and thermal Enthalpies= -2160.990861  
 Sum of electronic and thermal Free Energies= -2161.097472

-----  
 # b3lyp/6-311+g(d) pop=none td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

# Excitation energies and oscillator strengths:

|                         |                  |                  |                  |                 |                           |
|-------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| <b>Excited State 1:</b> | <b>Singlet-A</b> | <b>1.5125 eV</b> | <b>819.72 nm</b> | <b>f=0.0160</b> | <b>&lt;S**2&gt;=0.000</b> |
| 135 ->140               | -0.11170         |                  |                  |                 |                           |
| 137 ->140               | 0.46544          |                  |                  |                 |                           |
| 137 ->141               | -0.12442         |                  |                  |                 |                           |
| 138 ->140               | 0.39969          |                  |                  |                 |                           |
| 139 ->140               | 0.30164          |                  |                  |                 |                           |

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 2:  | Singlet-A | 1.7885 eV | 693.23 nm | f=0.0124 | <S**2>=0.000 |
| 137 ->140         | 0.49652   |           |           |          |              |
| 138 ->140         | -0.34435  |           |           |          |              |
| 139 ->140         | -0.35579  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 3:  | Singlet-A | 1.9768 eV | 627.21 nm | f=0.0001 | <S**2>=0.000 |
| 138 ->140         | -0.46591  |           |           |          |              |
| 139 ->140         | 0.52878   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 4:  | Singlet-A | 2.4662 eV | 502.74 nm | f=0.0584 | <S**2>=0.000 |
| 135 ->140         | 0.67566   |           |           |          |              |
| 136 ->140         | 0.13728   |           |           |          |              |
| 137 ->140         | 0.11559   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 5:  | Singlet-A | 2.6784 eV | 462.91 nm | f=0.0011 | <S**2>=0.000 |
| 134 ->140         | 0.16075   |           |           |          |              |
| 135 ->140         | -0.12037  |           |           |          |              |
| 136 ->140         | 0.67613   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 6:  | Singlet-A | 2.8193 eV | 439.77 nm | f=0.0027 | <S**2>=0.000 |
| 133 ->140         | -0.16194  |           |           |          |              |
| 134 ->140         | 0.66065   |           |           |          |              |
| 136 ->140         | -0.15396  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 7:  | Singlet-A | 2.8787 eV | 430.69 nm | f=0.0025 | <S**2>=0.000 |
| 133 ->140         | 0.68206   |           |           |          |              |
| 134 ->140         | 0.16099   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 8:  | Singlet-A | 2.9784 eV | 416.28 nm | f=0.0103 | <S**2>=0.000 |
| 137 ->141         | 0.14632   |           |           |          |              |
| 138 ->141         | 0.52173   |           |           |          |              |
| 139 ->141         | 0.42930   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 9:  | Singlet-A | 3.2328 eV | 383.52 nm | f=0.0095 | <S**2>=0.000 |
| 137 ->140         | 0.11701   |           |           |          |              |
| 137 ->141         | 0.63835   |           |           |          |              |
| 139 ->141         | -0.26079  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 10: | Singlet-A | 3.2789 eV | 378.13 nm | f=0.0008 | <S**2>=0.000 |
| 137 ->141         | 0.19524   |           |           |          |              |
| 138 ->141         | -0.46628  |           |           |          |              |
| 139 ->141         | 0.49114   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 11: | Singlet-A | 3.3005 eV | 375.65 nm | f=0.0272 | <S**2>=0.000 |
| 132 ->140         | -0.69401  |           |           |          |              |

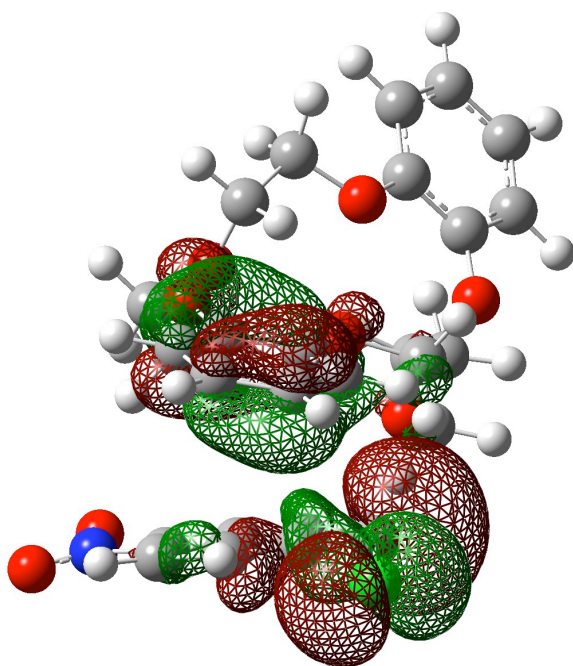
|                          |                  |                  |                  |                 |                           |
|--------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 12:        | Singlet-A        | 3.5274 eV        | 351.49 nm        | f=0.0123        | <S**2>=0.000              |
| 130 ->140                | 0.65609          |                  |                  |                 |                           |
| 131 ->140                | -0.23157         |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 13:        | Singlet-A        | 3.6043 eV        | 343.99 nm        | f=0.0225        | <S**2>=0.000              |
| 126 ->140                | -0.28489         |                  |                  |                 |                           |
| 126 ->141                | -0.14611         |                  |                  |                 |                           |
| 127 ->140                | 0.51585          |                  |                  |                 |                           |
| 127 ->141                | 0.25351          |                  |                  |                 |                           |
| 129 ->140                | 0.22394          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 14:        | Singlet-A        | 3.6564 eV        | 339.09 nm        | f=0.0005        | <S**2>=0.000              |
| 130 ->140                | 0.23443          |                  |                  |                 |                           |
| 131 ->140                | 0.66415          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 15:        | Singlet-A        | 3.7650 eV        | 329.30 nm        | f=0.0073        | <S**2>=0.000              |
| 129 ->140                | 0.17736          |                  |                  |                 |                           |
| 135 ->141                | 0.65759          |                  |                  |                 |                           |
| 136 ->141                | 0.13221          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| <b>Excited State 16:</b> | <b>Singlet-A</b> | <b>3.8783 eV</b> | <b>319.69 nm</b> | <b>f=0.3514</b> | <b>&lt;S**2&gt;=0.000</b> |
| 126 ->140                | 0.10874          |                  |                  |                 |                           |
| 127 ->140                | -0.18482         |                  |                  |                 |                           |
| 129 ->140                | 0.62487          |                  |                  |                 |                           |
| 135 ->141                | -0.17938         |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 17:        | Singlet-A        | 3.9794 eV        | 311.57 nm        | f=0.0017        | <S**2>=0.000              |
| 134 ->141                | 0.14089          |                  |                  |                 |                           |
| 135 ->141                | -0.13071         |                  |                  |                 |                           |
| 136 ->141                | 0.67932          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 18:        | Singlet-A        | 4.0887 eV        | 303.24 nm        | f=0.0003        | <S**2>=0.000              |
| 122 ->140                | 0.61927          |                  |                  |                 |                           |
| 122 ->141                | 0.27768          |                  |                  |                 |                           |
| 128 ->140                | 0.10064          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 19:        | Singlet-A        | 4.1299 eV        | 300.21 nm        | f=0.0030        | <S**2>=0.000              |
| 134 ->141                | 0.68239          |                  |                  |                 |                           |
| 136 ->141                | -0.12966         |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 20:        | Singlet-A        | 4.1909 eV        | 295.84 nm        | f=0.0005        | <S**2>=0.000              |
| 133 ->141                | 0.69274          |                  |                  |                 |                           |
|                          |                  |                  |                  |                 |                           |
| Excited State 21:        | Singlet-A        | 4.2376 eV        | 292.58 nm        | f=0.0031        | <S**2>=0.000              |
| 137 ->142                | 0.16667          |                  |                  |                 |                           |
| 138 ->142                | 0.52767          |                  |                  |                 |                           |



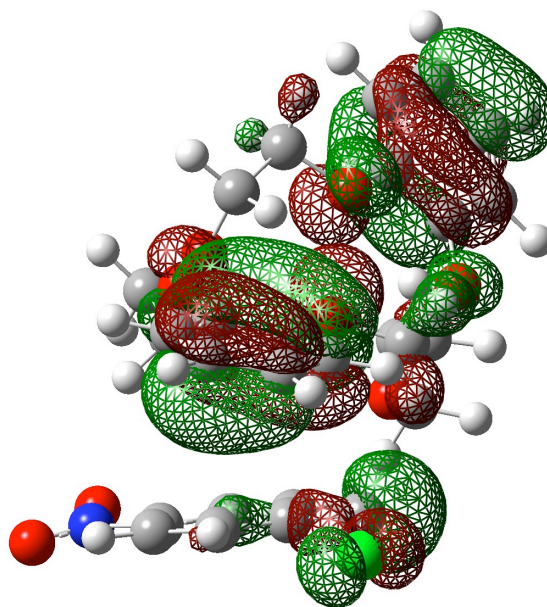
|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| 139 ->142         | 0.43188   |           |           |          |              |
| Excited State 22: | Singlet-A | 4.3452 eV | 285.33 nm | f=0.0003 | <S**2>=0.000 |
| 122 ->140         | -0.11792  |           |           |          |              |
| 125 ->140         | -0.25613  |           |           |          |              |
| 128 ->140         | 0.63374   |           |           |          |              |
| Excited State 23: | Singlet-A | 4.4213 eV | 280.42 nm | f=0.0013 | <S**2>=0.000 |
| 124 ->140         | -0.30205  |           |           |          |              |
| 126 ->140         | 0.53518   |           |           |          |              |
| 127 ->140         | 0.31454   |           |           |          |              |
| Excited State 24: | Singlet-A | 4.4696 eV | 277.39 nm | f=0.0145 | <S**2>=0.000 |
| 130 ->141         | 0.18231   |           |           |          |              |
| 132 ->141         | 0.62385   |           |           |          |              |
| 137 ->142         | 0.23716   |           |           |          |              |
| Excited State 25: | Singlet-A | 4.5162 eV | 274.53 nm | f=0.0029 | <S**2>=0.000 |
| 124 ->140         | -0.15482  |           |           |          |              |
| 132 ->141         | -0.20740  |           |           |          |              |
| 137 ->142         | 0.60686   |           |           |          |              |
| 139 ->142         | -0.16772  |           |           |          |              |
| Excited State 26: | Singlet-A | 4.5484 eV | 272.59 nm | f=0.0012 | <S**2>=0.000 |
| 123 ->140         | 0.12454   |           |           |          |              |
| 124 ->140         | 0.56489   |           |           |          |              |
| 125 ->140         | 0.17728   |           |           |          |              |
| 126 ->140         | 0.19095   |           |           |          |              |
| 127 ->140         | 0.12850   |           |           |          |              |
| 128 ->140         | 0.15396   |           |           |          |              |
| 132 ->141         | -0.10962  |           |           |          |              |
| 137 ->142         | 0.17628   |           |           |          |              |
| Excited State 27: | Singlet-A | 4.6347 eV | 267.51 nm | f=0.0001 | <S**2>=0.000 |
| 138 ->142         | -0.46104  |           |           |          |              |
| 139 ->142         | 0.52708   |           |           |          |              |
| Excited State 28: | Singlet-A | 4.6474 eV | 266.78 nm | f=0.0067 | <S**2>=0.000 |
| 119 ->140         | -0.24188  |           |           |          |              |
| 120 ->140         | 0.12703   |           |           |          |              |
| 123 ->140         | 0.29279   |           |           |          |              |
| 124 ->140         | -0.22091  |           |           |          |              |
| 125 ->140         | 0.44048   |           |           |          |              |
| 126 ->140         | -0.17298  |           |           |          |              |
| 128 ->140         | 0.20236   |           |           |          |              |

Excited State 29: Singlet-A 4.7040 eV 263.57 nm f=0.0140 <S\*\*2>=0.000  
 119 ->140 0.39102  
 120 ->140 -0.14670  
 123 ->140 -0.28642  
 125 ->140 0.42582  
 128 ->140 0.11044

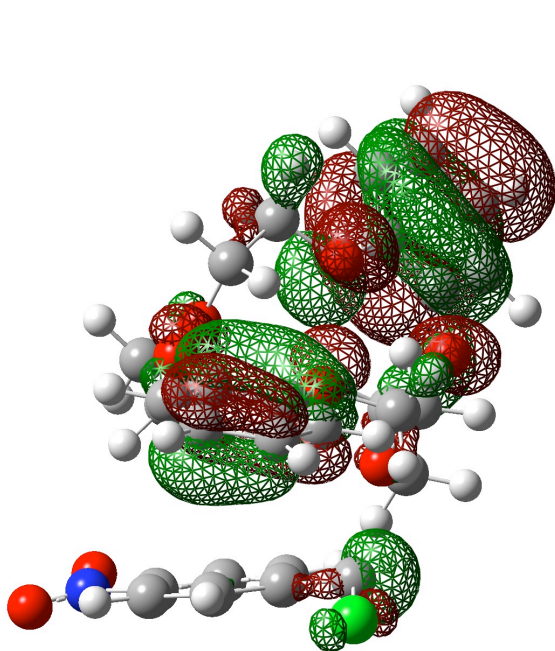
Excited State 30: Singlet-A 4.7586 eV 260.55 nm f=0.0159 <S\*\*2>=0.000  
 119 ->140 0.43232  
 120 ->140 0.16815  
 123 ->140 0.46687



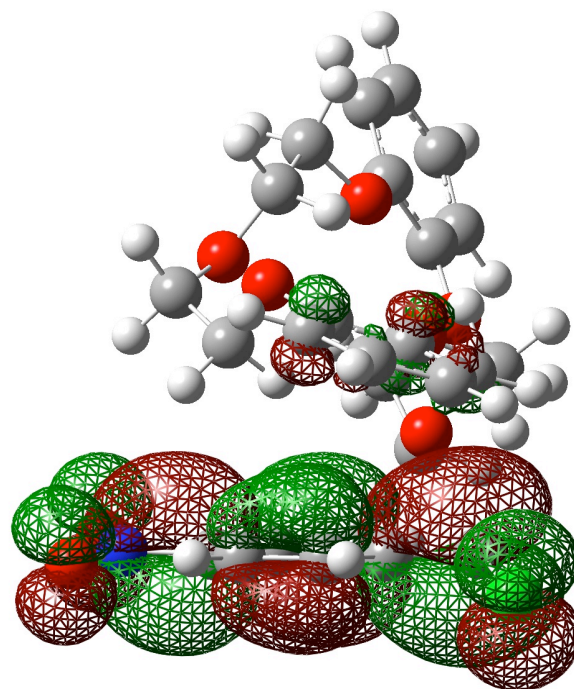
11b-σ-MO137



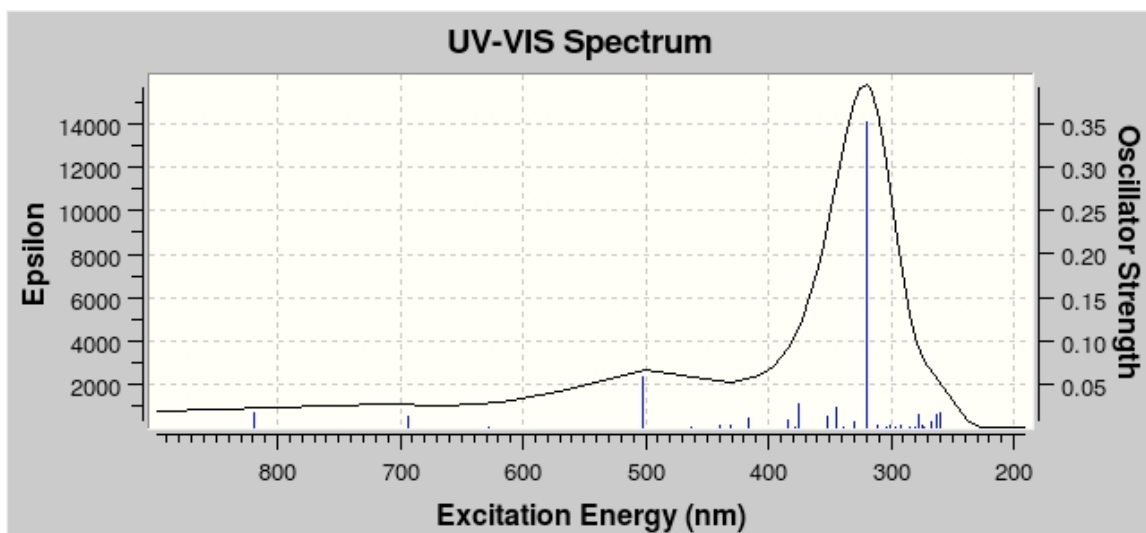
11b-MO138



**11b-HOMO-MO139**



**11b-LUMO-p-MO140**



Computed electronic spectrum of **11b** (TD-B3LYP/6-311+G(d)).

## 11c:

-----  
Half-sandwich 11c, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,3.7519474099,1.6397828189,0.2621355737  
O,0,3.8016247919,1.1393032086,-1.0992698703  
C,0,3.0348650596,2.9856667144,0.2620272062  
O,0,1.6105422591,2.9119006793,0.2586660614  
C,0,1.0549446522,2.4129334106,-0.9609837294  
C,0,4.2482710492,-0.1585963121,-1.2361611137  
C,0,3.476934843,-1.2551387767,-0.7701499704  
C,0,-0.4430456605,2.6275616991,-0.932708469  
C,0,0.5734190149,-1.2718637045,1.4586622008  
O,0,1.1979218424,-0.4941740883,2.4804505797  
C,0,1.6547015937,-1.945238927,0.6417696798  
O,0,2.2868978456,-0.9429492299,-0.1720779679  
C,0,-4.5658347715,2.7317529134,0.2011617957  
C,0,-4.9569796919,2.0291021111,1.3455468416  
C,0,-4.0040935014,1.286352088,2.0603997494  
C,0,-2.6757157439,1.224458824,1.6306159553  
C,0,-2.2867952006,1.9115809632,0.4494617036  
C,0,-3.2366500682,2.6788485772,-0.2441755144  
O,0,-1.00165882,1.717004949,0.0375926991  
O,0,-1.7983449909,0.4113779273,2.3103018513  
C,0,0.2926520048,0.0169010426,3.4572381763  
C,0,-0.673890949,1.0791402601,2.9450260941  
C,0,5.4508841174,-0.3948173438,-1.9077544918  
C,0,5.9124445096,-1.7039510464,-2.1149472083  
C,0,5.1642956119,-2.783149654,-1.6342827615  
C,0,3.9506672233,-2.5630031259,-0.9641098569  
H,0,3.2248385665,0.9336592759,0.9160567834  
H,0,4.7876615422,1.7718570366,0.6217369696  
H,0,3.3878195968,3.589710006,-0.5952273204  
H,0,3.2910006372,3.514773973,1.1901276999  
H,0,1.2892270633,1.3474932032,-1.089034984  
H,0,1.4739751939,2.9630525311,-1.8238945298  
H,0,-0.68286934,3.6617289381,-0.6422484078  
H,0,-0.8680352493,2.4189040763,-1.9257698103  
H,0,-0.0737314295,-2.0473642765,1.9123465857  
H,0,-0.0588604706,-0.6428950707,0.8174693032  
H,0,1.2136413781,-2.7231187644,0.0006178214  
H,0,2.4008698665,-2.4131559936,1.3020432795  
H,0,-5.2930462409,3.3121738453,-0.3659628679  
H,0,-5.9905302127,2.0639604012,1.6894949061  
H,0,-4.2754528796,0.7361002837,2.9614796578

H,0,-2.9521845366,3.2033323346,-1.1538619012  
 H,0,-0.2795867948,-0.8108307228,3.9157694557  
 H,0,0.9308480304,0.470207466,4.2276720365  
 H,0,-0.1654560137,1.7418094947,2.2339370202  
 H,0,-1.0597426954,1.6714373792,3.7925652974  
 H,0,6.0160692729,0.4669757456,-2.2629512078  
 H,0,6.8526713047,-1.8730105995,-2.6397321383  
 H,0,5.5143758411,-3.8052810174,-1.7807890589  
 H,0,3.3691002548,-3.4110000911,-0.6067513554  
 C,0,-3.0662980234,-1.757322826,0.1155743669  
 C,0,-1.9906815141,-2.6304588023,-0.2034147152  
 C,0,-1.258143728,-2.3990368611,-1.4043890099  
 C,0,-1.5906264298,-1.3457568765,-2.2449868387  
 C,0,-2.7049212654,-0.5550050191,-1.9194232464  
 C,0,-3.4580079882,-0.7421674776,-0.7581092683  
 H,0,-3.5861510659,-1.8977329517,1.061196026  
 H,0,-0.4205112228,-3.0436853398,-1.6616383648  
 H,0,-1.023389671,-1.134406175,-3.148334563  
 H,0,-4.2916920849,-0.0830345877,-0.5330158252  
 N,0,-3.0869310503,0.549311924,-2.8434811109  
 O,0,-4.2652408063,0.8924300927,-2.8613411129  
 O,0,-2.1892590953,1.0515230922,-3.5245571381  
 C,0,-1.7640450844,-3.6413698621,0.8286816962  
 Cl,0,-0.6957660558,-4.9306396729,0.2709710454

SCF Done: E(RB97D) = -2161.52663923 A.U. after 3 cycles

Sum of electronic and zero-point Energies= -2161.026898  
 Sum of electronic and thermal Energies= -2160.991815  
 Sum of electronic and thermal Enthalpies= -2160.990870  
 Sum of electronic and thermal Free Energies= -2161.097023

-----  
 # 6-311+g(d) pop=none b3lyp td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 1.5476 eV 801.14 nm f=0.0065 <S\*\*2>=0.000**  
 137 ->140 0.67754  
 137 ->141 -0.14813  
 138 ->140 0.13931

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 2:  | Singlet-A | 1.6334 eV | 759.08 nm | f=0.0055 | <S**2>=0.000 |
| 137 ->140         | -0.11913  |           |           |          |              |
| 138 ->140         | 0.66145   |           |           |          |              |
| 139 ->140         | -0.21571  |           |           |          |              |
| Excited State 3:  | Singlet-A | 1.7549 eV | 706.51 nm | f=0.0000 | <S**2>=0.000 |
| 138 ->140         | 0.20446   |           |           |          |              |
| 139 ->140         | 0.67141   |           |           |          |              |
| Excited State 4:  | Singlet-A | 2.3370 eV | 530.52 nm | f=0.0009 | <S**2>=0.000 |
| 135 ->140         | 0.66917   |           |           |          |              |
| 136 ->140         | -0.21971  |           |           |          |              |
| Excited State 5:  | Singlet-A | 2.4606 eV | 503.88 nm | f=0.0003 | <S**2>=0.000 |
| 135 ->140         | 0.21845   |           |           |          |              |
| 136 ->140         | 0.66978   |           |           |          |              |
| Excited State 6:  | Singlet-A | 2.7005 eV | 459.12 nm | f=0.0098 | <S**2>=0.000 |
| 133 ->140         | 0.50299   |           |           |          |              |
| 134 ->140         | 0.48890   |           |           |          |              |
| Excited State 7:  | Singlet-A | 2.7980 eV | 443.12 nm | f=0.0025 | <S**2>=0.000 |
| 133 ->140         | -0.49018  |           |           |          |              |
| 134 ->140         | 0.50662   |           |           |          |              |
| Excited State 8:  | Singlet-A | 2.9429 eV | 421.30 nm | f=0.0006 | <S**2>=0.000 |
| 138 ->141         | 0.68015   |           |           |          |              |
| 139 ->141         | -0.18143  |           |           |          |              |
| Excited State 9:  | Singlet-A | 3.1190 eV | 397.51 nm | f=0.0001 | <S**2>=0.000 |
| 138 ->141         | 0.18100   |           |           |          |              |
| 139 ->141         | 0.68175   |           |           |          |              |
| Excited State 10: | Singlet-A | 3.2963 eV | 376.13 nm | f=0.0107 | <S**2>=0.000 |
| 137 ->140         | 0.14670   |           |           |          |              |
| 137 ->141         | 0.67601   |           |           |          |              |
| Excited State 11: | Singlet-A | 3.3776 eV | 367.07 nm | f=0.0219 | <S**2>=0.000 |
| 130 ->140         | 0.40479   |           |           |          |              |
| 131 ->140         | 0.42446   |           |           |          |              |
| 132 ->140         | -0.37264  |           |           |          |              |
| Excited State 12: | Singlet-A | 3.4112 eV | 363.46 nm | f=0.0196 | <S**2>=0.000 |
| 130 ->140         | 0.54393   |           |           |          |              |
| 131 ->140         | -0.39607  |           |           |          |              |
| 132 ->140         | 0.15554   |           |           |          |              |

Excited State 13: Singlet-A 3.5162 eV 352.61 nm f=0.0072 <S\*\*2>=0.000  
130 ->140 -0.13586  
131 ->140 -0.37834  
132 ->140 -0.56735

Excited State 14: Singlet-A 3.5308 eV 351.16 nm f=0.1121 <S\*\*2>=0.000  
124 ->140 0.30575  
124 ->141 0.18956  
125 ->140 -0.15985  
129 ->140 0.52313  
129 ->141 0.12731  
132 ->140 -0.10811

Excited State 15: Singlet-A 3.6545 eV 339.26 nm f=0.0027 <S\*\*2>=0.000  
135 ->141 0.67246  
136 ->141 -0.18975

Excited State 16: Singlet-A 3.8200 eV 324.56 nm f=0.0007 <S\*\*2>=0.000  
135 ->141 0.18608  
136 ->141 0.67926

**Excited State 17: Singlet-A 3.9736 eV 312.02 nm f=0.2497 <S\*\*2>=0.000**  
124 ->140 -0.39433  
124 ->141 -0.16216  
125 ->140 0.21375  
127 ->140 0.18465  
129 ->140 0.42867

Excited State 18: Singlet-A 4.0741 eV 304.32 nm f=0.0023 <S\*\*2>=0.000  
121 ->140 0.17916  
122 ->140 0.35623  
122 ->141 0.16599  
133 ->141 0.25332  
134 ->141 0.47441

Excited State 19: Singlet-A 4.0926 eV 302.95 nm f=0.0115 <S\*\*2>=0.000  
121 ->140 -0.21154  
122 ->140 -0.42438  
122 ->141 -0.19438  
133 ->141 0.10751  
134 ->141 0.43686

Excited State 20: Singlet-A 4.1399 eV 299.48 nm f=0.0023 <S\*\*2>=0.000  
133 ->141 0.64183  
134 ->141 -0.27094

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 21: | Singlet-A | 4.2396 eV | 292.44 nm | f=0.0160 | <S**2>=0.000 |
| 127 ->140         | -0.16369  |           |           |          |              |
| 128 ->140         | 0.11926   |           |           |          |              |
| 138 ->142         | 0.64991   |           |           |          |              |
| 139 ->142         | -0.17023  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 22: | Singlet-A | 4.2486 eV | 291.82 nm | f=0.0497 | <S**2>=0.000 |
| 124 ->140         | 0.11676   |           |           |          |              |
| 125 ->140         | -0.14143  |           |           |          |              |
| 127 ->140         | 0.48990   |           |           |          |              |
| 128 ->140         | -0.40097  |           |           |          |              |
| 138 ->142         | 0.20215   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 23: | Singlet-A | 4.2921 eV | 288.86 nm | f=0.0057 | <S**2>=0.000 |
| 126 ->140         | -0.10762  |           |           |          |              |
| 127 ->140         | 0.42666   |           |           |          |              |
| 128 ->140         | 0.54139   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 24: | Singlet-A | 4.3565 eV | 284.60 nm | f=0.0128 | <S**2>=0.000 |
| 119 ->140         | -0.10506  |           |           |          |              |
| 124 ->140         | 0.29749   |           |           |          |              |
| 125 ->140         | 0.55562   |           |           |          |              |
| 126 ->140         | 0.27349   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 25: | Singlet-A | 4.4159 eV | 280.77 nm | f=0.0017 | <S**2>=0.000 |
| 137 ->142         | 0.10663   |           |           |          |              |
| 138 ->142         | 0.17758   |           |           |          |              |
| 139 ->142         | 0.67475   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 26: | Singlet-A | 4.4297 eV | 279.89 nm | f=0.0023 | <S**2>=0.000 |
| 125 ->140         | -0.26667  |           |           |          |              |
| 126 ->140         | 0.62626   |           |           |          |              |
| 128 ->140         | 0.11881   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 27: | Singlet-A | 4.4868 eV | 276.33 nm | f=0.0057 | <S**2>=0.000 |
| 137 ->142         | 0.69037   |           |           |          |              |
| 139 ->142         | -0.10271  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 28: | Singlet-A | 4.5798 eV | 270.72 nm | f=0.0126 | <S**2>=0.000 |
| 119 ->140         | -0.10925  |           |           |          |              |
| 124 ->140         | -0.10795  |           |           |          |              |
| 130 ->141         | -0.64108  |           |           |          |              |
| 131 ->141         | -0.12890  |           |           |          |              |
| 132 ->141         | 0.16720   |           |           |          |              |

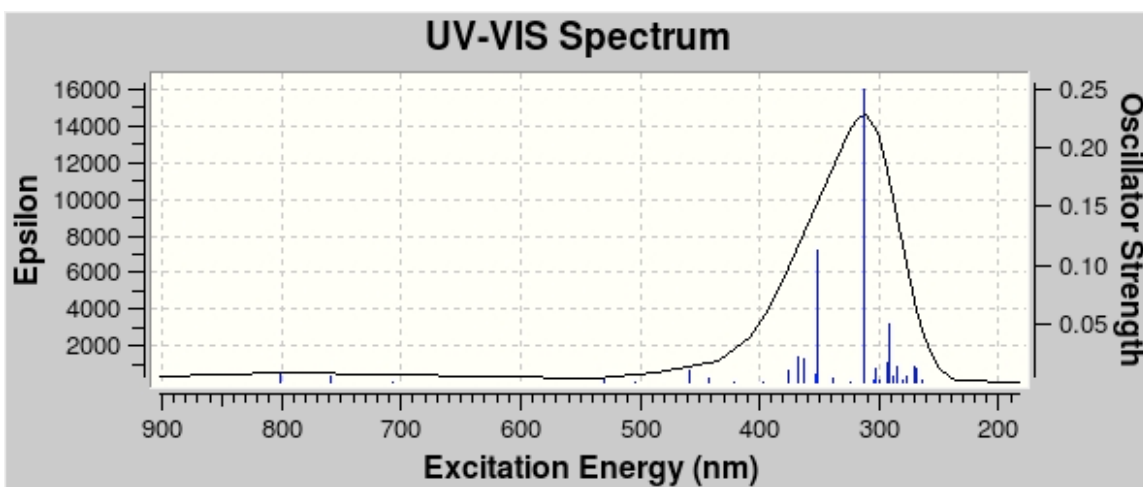


Excited State 29: Singlet-A 4.6207 eV 268.32 nm f=0.0116 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 118 ->140 | -0.24011 |
| 119 ->140 | -0.56642 |
| 119 ->141 | 0.10304  |
| 124 ->140 | -0.13529 |
| 129 ->141 | 0.18588  |
| 130 ->141 | 0.12170  |
| 131 ->141 | 0.11121  |

Excited State 30: Singlet-A 4.7027 eV 263.64 nm f=0.0024 <S\*\*2>=0.000

|           |         |
|-----------|---------|
| 123 ->140 | 0.68291 |
|-----------|---------|



Computed electronic spectrum of **11c** (TD-B3LYP/6-311+G(d)).

## 11d:

-----  
Half-sandwich 11e, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,3.9739584473,2.3007945726,0.1563460735  
H,0,5.0078734741,2.2206355331,-0.2144728007  
H,0,3.937943616,2.9293949796,1.0601517425  
C,0,3.0942631429,2.8731900854,-0.954695906  
H,0,3.4460444729,3.894316419,-1.1634555583  
H,0,3.2269606725,2.2735426488,-1.8729732677  
C,0,0.9606459821,1.7893669653,-0.9168317898  
H,0,1.3045645181,0.9427625073,-0.3121747165  
H,0,1.0695532722,1.5288279095,-1.985976518  
C,0,-0.501143017,2.0832410283,-0.5990652589  
H,0,-0.605812055,2.4255928026,0.4427467414  
H,0,-0.9102920481,2.8563405281,-1.2687079447  
C,0,-2.5116423046,0.7744422482,-0.4371365773  
C,0,-3.3015982806,1.8776554452,-0.0891514176  
H,0,-2.8675336638,2.8754551457,-0.0858637557  
C,0,-4.6510433481,1.7058664409,0.2668529238  
H,0,-5.2476116335,2.5769273671,0.5379338948  
C,0,-5.2150672682,0.4300665668,0.2753799593  
H,0,-6.2598020994,0.2875860261,0.5516197454  
C,0,-4.4330045559,-0.6845978227,-0.0745771962  
H,0,-4.8752698593,-1.6792845034,-0.0699097471  
C,0,-3.0885545509,-0.5270866939,-0.4314791323  
C,0,-2.6109128497,-2.8882284636,-0.3917318053  
H,0,-3.4223163824,-3.2718560416,-1.0357335656  
H,0,-2.9589968502,-2.8871358587,0.6537639648  
C,0,-1.3783651308,-3.7755694525,-0.5402518457  
H,0,-1.6902220548,-4.8224979038,-0.4245707911  
H,0,-0.9422082457,-3.6500668356,-1.5453788278  
C,0,0.3631451277,-2.3551519227,0.2928911498  
H,0,-0.2037489215,-1.4810737027,0.6393591292  
H,0,0.6027991632,-2.1932777444,-0.7697678292  
C,0,1.6482365273,-2.5014024006,1.0992521775  
H,0,1.4322733112,-2.6991089452,2.1610055095  
H,0,2.2722575089,-3.3204736523,0.7098935053  
C,0,3.5695788568,-1.1078145248,1.4993301435  
C,0,4.2502951465,-2.083252145,2.2284078778  
H,0,3.7819075959,-3.046831684,2.4171114557  
C,0,5.5498097462,-1.8289832985,2.7117427583  
H,0,6.0683371048,-2.6024198633,3.2782094635  
C,0,6.1593729397,-0.5967481958,2.4787204895  
H,0,7.163525598,-0.3964571112,2.850173153

C,0,5.4862583167,0.3940013722,1.7434362382  
 H,0,5.9644006396,1.3509768257,1.5531844301  
 C,0,4.1976687419,0.1472650203,1.2444467223  
 O,0,3.4712603164,0.99382185,0.4779687833  
 O,0,1.7116077298,2.9768941334,-0.6283004642  
 O,0,-1.1889857862,0.8388905341,-0.7824978605  
 O,0,-2.2556399073,-1.5544750394,-0.786918624  
 O,0,-0.3802274345,-3.563313712,0.4580737388  
 O,0,2.3286957851,-1.2478963707,0.9558977666  
 C,0,3.5259497575,-3.3198926291,-1.6938929846  
 C,0,3.2069144759,-2.0142820577,-2.0822446159  
 C,0,4.136540381,-1.0060598326,-1.8386994893  
 C,0,5.3961680475,-1.289216143,-1.2454266452  
 C,0,5.6820144155,-2.6334544488,-0.8740213064  
 C,0,4.7506422707,-3.6428074563,-1.0852527327  
 H,0,2.2470905413,-1.8006367366,-2.5432562539  
 H,0,3.9038394896,0.0239294996,-2.0963819054  
 H,0,6.6312383674,-2.8698301864,-0.398810078  
 H,0,4.9497080485,-4.6697648012,-0.7895801461  
 N,0,2.5245048711,-4.4053202844,-1.925010606  
 O,0,2.7701489179,-5.5186806606,-1.4612827343  
 O,0,1.5107221266,-4.1176595795,-2.5637018109  
 C,0,6.2274453088,-0.0928665235,-1.0686472731  
 Cl,0,7.9141132442,-0.5006071962,-0.7510600056

SCF Done: E(RB97D) = -2161.52553271 A.U. after 3 cycles

Sum of electronic and zero-point Energies= -2161.025565  
 Sum of electronic and thermal Energies= -2160.990168  
 Sum of electronic and thermal Enthalpies= -2160.989223  
 Sum of electronic and thermal Free Energies= -2161.096717

-----  
 # 6-311+g(d) pop=none rb3lyp td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

# Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 1.4639 eV 846.97 nm f=0.0293 <S\*\*2>=0.000**  
 135 ->140 -0.13089  
 137 ->140 0.34997  
 138 ->140 0.58097  
 139 ->140 -0.11011

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 2:  | Singlet-A | 1.5975 eV | 776.11 nm | f=0.0103 | <S**2>=0.000 |
| 137 ->140         | 0.57938   |           |           |          |              |
| 137 ->141         | -0.12370  |           |           |          |              |
| 138 ->140         | -0.37003  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 3:  | Singlet-A | 1.7133 eV | 723.64 nm | f=0.0002 | <S**2>=0.000 |
| 138 ->140         | 0.13689   |           |           |          |              |
| 139 ->140         | 0.69321   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 4:  | Singlet-A | 2.4332 eV | 509.56 nm | f=0.0575 | <S**2>=0.000 |
| 135 ->140         | 0.68014   |           |           |          |              |
| 137 ->140         | 0.15114   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 5:  | Singlet-A | 2.5750 eV | 481.50 nm | f=0.0002 | <S**2>=0.000 |
| 136 ->140         | 0.70383   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 6:  | Singlet-A | 2.7868 eV | 444.90 nm | f=0.0118 | <S**2>=0.000 |
| 138 ->141         | 0.68634   |           |           |          |              |
| 139 ->141         | -0.12987  |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 7:  | Singlet-A | 2.9671 eV | 417.86 nm | f=0.0010 | <S**2>=0.000 |
| 133 ->140         | 0.32144   |           |           |          |              |
| 134 ->140         | 0.59387   |           |           |          |              |
| 139 ->141         | 0.16643   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 8:  | Singlet-A | 2.9857 eV | 415.26 nm | f=0.0013 | <S**2>=0.000 |
| 133 ->140         | 0.57481   |           |           |          |              |
| 134 ->140         | -0.35826  |           |           |          |              |
| 139 ->141         | 0.16908   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 9:  | Singlet-A | 3.0077 eV | 412.22 nm | f=0.0004 | <S**2>=0.000 |
| 133 ->140         | -0.23835  |           |           |          |              |
| 138 ->141         | 0.11607   |           |           |          |              |
| 139 ->141         | 0.65228   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 10: | Singlet-A | 3.1215 eV | 397.19 nm | f=0.0156 | <S**2>=0.000 |
| 134 ->140         | -0.10374  |           |           |          |              |
| 137 ->140         | 0.13238   |           |           |          |              |
| 137 ->141         | 0.67119   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 11: | Singlet-A | 3.3899 eV | 365.74 nm | f=0.0291 | <S**2>=0.000 |
| 132 ->140         | 0.69412   |           |           |          |              |
|                   |           |           |           |          |              |
| Excited State 12: | Singlet-A | 3.6087 eV | 343.57 nm | f=0.0209 | <S**2>=0.000 |
| 127 ->140         | -0.10908  |           |           |          |              |
| 128 ->140         | 0.57417   |           |           |          |              |

|                          |                  |                                                        |
|--------------------------|------------------|--------------------------------------------------------|
| 128 ->141                | 0.26887          |                                                        |
| 130 ->140                | 0.10486          |                                                        |
| 131 ->140                | -0.22958         |                                                        |
| Excited State 13:        | Singlet-A        | 3.7289 eV 332.49 nm f=0.0154 <S**2>=0.000              |
| 131 ->140                | -0.16472         |                                                        |
| 135 ->141                | 0.67225          |                                                        |
| Excited State 14:        | Singlet-A        | 3.8660 eV 320.71 nm f=0.0097 <S**2>=0.000              |
| 136 ->141                | 0.69465          |                                                        |
| <b>Excited State 15:</b> | <b>Singlet-A</b> | <b>3.8824 eV 319.35 nm f=0.3686 &lt;S**2&gt;=0.000</b> |
| 128 ->140                | 0.19693          |                                                        |
| 131 ->140                | 0.62445          |                                                        |
| 135 ->141                | 0.16074          |                                                        |
| 136 ->141                | -0.11250         |                                                        |
| Excited State 16:        | Singlet-A        | 4.0391 eV 306.96 nm f=0.0021 <S**2>=0.000              |
| 138 ->142                | 0.68853          |                                                        |
| 139 ->142                | -0.12092         |                                                        |
| Excited State 17:        | Singlet-A        | 4.0998 eV 302.42 nm f=0.0007 <S**2>=0.000              |
| 120 ->140                | 0.13923          |                                                        |
| 122 ->140                | -0.11236         |                                                        |
| 123 ->140                | 0.59528          |                                                        |
| 123 ->141                | 0.25361          |                                                        |
| 124 ->140                | 0.11598          |                                                        |
| Excited State 18:        | Singlet-A        | 4.2525 eV 291.56 nm f=0.0014 <S**2>=0.000              |
| 133 ->141                | 0.64394          |                                                        |
| 134 ->141                | 0.25387          |                                                        |
| Excited State 19:        | Singlet-A        | 4.3091 eV 287.73 nm f=0.0004 <S**2>=0.000              |
| 133 ->141                | -0.23974         |                                                        |
| 134 ->141                | 0.65075          |                                                        |
| Excited State 20:        | Singlet-A        | 4.3519 eV 284.90 nm f=0.0030 <S**2>=0.000              |
| 126 ->140                | -0.11592         |                                                        |
| 127 ->140                | 0.10491          |                                                        |
| 130 ->140                | 0.65011          |                                                        |
| 133 ->141                | 0.11156          |                                                        |
| Excited State 21:        | Singlet-A        | 4.3685 eV 283.82 nm f=0.0002 <S**2>=0.000              |
| 138 ->142                | 0.11983          |                                                        |
| 139 ->142                | 0.69493          |                                                        |

|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| Excited State 22: | Singlet-A | 4.3890 eV | 282.49 nm | f=0.0033 | <S**2>=0.000 |
| 137 ->142         | 0.68862   |           |           |          |              |
| Excited State 23: | Singlet-A | 4.4267 eV | 280.09 nm | f=0.0037 | <S**2>=0.000 |
| 125 ->140         | -0.12615  |           |           |          |              |
| 126 ->140         | 0.12075   |           |           |          |              |
| 127 ->140         | 0.34211   |           |           |          |              |
| 129 ->140         | 0.55926   |           |           |          |              |
| 132 ->141         | -0.11071  |           |           |          |              |
| Excited State 24: | Singlet-A | 4.4841 eV | 276.50 nm | f=0.0127 | <S**2>=0.000 |
| 124 ->140         | 0.10385   |           |           |          |              |
| 126 ->140         | 0.61240   |           |           |          |              |
| 127 ->140         | -0.14080  |           |           |          |              |
| 128 ->140         | -0.11659  |           |           |          |              |
| 132 ->141         | -0.19798  |           |           |          |              |
| Excited State 25: | Singlet-A | 4.5674 eV | 271.45 nm | f=0.0119 | <S**2>=0.000 |
| 126 ->140         | 0.18447   |           |           |          |              |
| 129 ->140         | 0.13051   |           |           |          |              |
| 132 ->141         | 0.64117   |           |           |          |              |
| Excited State 26: | Singlet-A | 4.6150 eV | 268.65 nm | f=0.0070 | <S**2>=0.000 |
| 117 ->140         | -0.16435  |           |           |          |              |
| 122 ->140         | -0.10920  |           |           |          |              |
| 124 ->140         | -0.11073  |           |           |          |              |
| 126 ->140         | 0.10950   |           |           |          |              |
| 127 ->140         | 0.50592   |           |           |          |              |
| 128 ->140         | 0.12576   |           |           |          |              |
| 129 ->140         | -0.36062  |           |           |          |              |
| Excited State 27: | Singlet-A | 4.6327 eV | 267.63 nm | f=0.0022 | <S**2>=0.000 |
| 117 ->140         | -0.46614  |           |           |          |              |
| 117 ->141         | 0.10602   |           |           |          |              |
| 122 ->140         | -0.21588  |           |           |          |              |
| 123 ->140         | -0.11514  |           |           |          |              |
| 125 ->140         | 0.35672   |           |           |          |              |
| 129 ->140         | 0.12469   |           |           |          |              |
| 132 ->141         | -0.12720  |           |           |          |              |
| Excited State 28: | Singlet-A | 4.6694 eV | 265.53 nm | f=0.0595 | <S**2>=0.000 |
| 117 ->140         | -0.19789  |           |           |          |              |
| 125 ->140         | -0.19883  |           |           |          |              |
| 126 ->140         | -0.10622  |           |           |          |              |
| 127 ->140         | -0.16557  |           |           |          |              |
| 131 ->141         | 0.11724   |           |           |          |              |

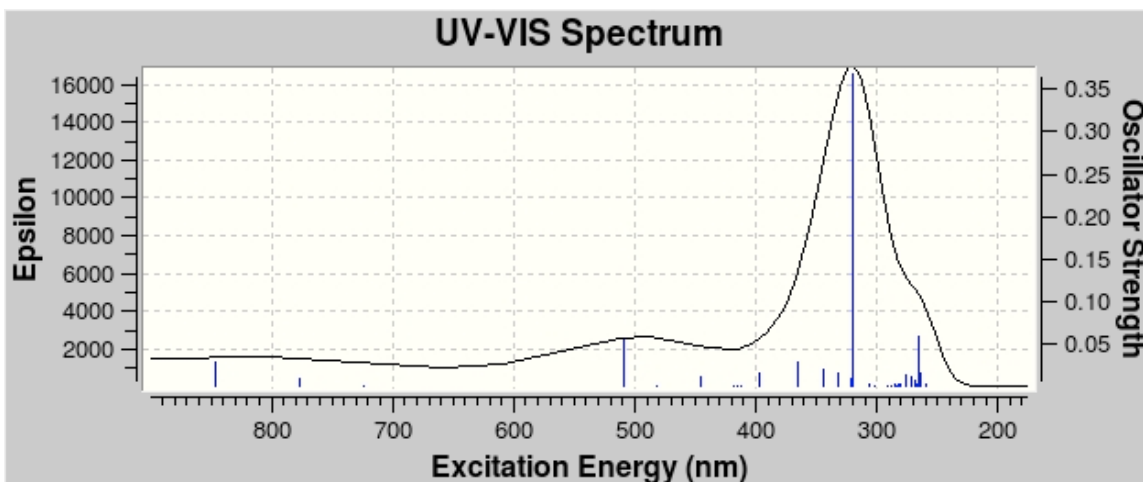
|           |         |
|-----------|---------|
| 135 ->145 | 0.12896 |
| 137 ->145 | 0.11766 |
| 138 ->143 | 0.54573 |

Excited State 29: Singlet-A 4.7040 eV 263.57 nm f=0.0150 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 117 ->140 | 0.33832  |
| 122 ->140 | -0.13688 |
| 125 ->140 | 0.42453  |
| 138 ->143 | 0.33101  |

Excited State 30: Singlet-A 4.7761 eV 259.59 nm f=0.0026 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 117 ->140 | -0.13066 |
| 118 ->140 | -0.15889 |
| 120 ->140 | -0.12227 |
| 121 ->140 | -0.22155 |
| 122 ->140 | 0.35614  |
| 124 ->140 | 0.46477  |
| 127 ->140 | 0.15953  |
| 130 ->140 | -0.11445 |



Computed electronic spectrum of **11d** (TD-B3LYP/6-311+G(d)).

## 7. Geometries, Energies, Orbitals, and Excitations for Full-Sandwiches 12a-12d

### 12a:

-----  
Full-sandwich 12a, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,1.860591933,2.7505087202,1.6341153217  
O,0,1.9812773495,1.3283799333,1.5475734719  
C,0,0.5895514173,3.0634705362,2.4023690963  
O,0,-0.5272886195,2.7825605114,1.5704278233  
C,0,-1.7744328033,2.8920721211,2.2384070671  
C,0,3.0279714403,0.8140905202,0.8338129188  
C,0,3.123753091,-0.6070518872,0.8232430435  
C,0,-2.872520006,2.4712913183,1.2782612104  
C,0,0.927506868,-3.1832592045,2.2292169343  
O,0,-0.1530321207,-2.9737541601,1.3298840462  
C,0,2.2073201927,-2.6967963774,1.5768464713  
O,0,2.1587445171,-1.2667612802,1.5304604246  
C,0,-5.3619698272,0.4446917711,-1.5150749184  
C,0,-5.2720482906,-0.9433422062,-1.6048794235  
C,0,-4.371964545,-1.6445029229,-0.7830606035  
C,0,-3.5585118387,-0.9598829832,0.1278336343  
C,0,-3.6427062961,0.4599674121,0.2128014884  
C,0,-4.548621184,1.1450377926,-0.606370236  
O,0,-2.7969184012,1.0509334856,1.1141595488  
O,0,-2.6550276253,-1.550921336,0.9699213291  
C,0,-1.4039476614,-3.3696679065,1.8745825299  
C,0,-2.5113669067,-2.9776581573,0.9145786201  
C,0,3.9643617234,1.5737979995,0.1238268956  
C,0,4.9878422304,0.9447538428,-0.6061977671  
C,0,5.0826857729,-0.4461038297,-0.6172520847  
C,0,4.1552214627,-1.2205317725,0.1021038434  
C,0,1.9884922996,0.7803106809,-2.3759595076  
C,0,1.9382422916,-0.6096161247,-2.4063478569  
C,0,0.8776304667,-1.2455684036,-1.7471835691  
C,0,-0.099584542,-0.5497124335,-1.0260917118  
C,0,-0.064312805,0.8391317492,-1.0330984222  
C,0,0.957948113,1.5323697546,-1.7406737918  
C,0,1.1513745546,2.9680350536,-1.824178824  
Cl,0,-0.3682987991,3.8455359489,-1.7255297257  
N,0,0.7871205186,-2.7265007916,-1.8137862707  
O,0,-0.3359655936,-3.2261066096,-1.8149555797  
O,0,1.8431826878,-3.3619696699,-1.8799629334  
H,0,2.7341903631,3.1698595046,2.1622392028



H,0,1.8165414933,3.1955269291,0.6267085642  
 H,0,0.5482908846,2.4554449409,3.324215248  
 H,0,0.5960833364,4.1329697635,2.6901114362  
 H,0,-1.9565688436,3.9385931607,2.5532793758  
 H,0,-1.7909250092,2.25070887,3.138167929  
 H,0,-2.7314331837,2.9769526681,0.3099545885  
 H,0,-3.8599057102,2.7501778164,1.683745846  
 H,0,0.7514822201,-2.6404235225,3.1756410726  
 H,0,1.0343978057,-4.2613380985,2.4603561294  
 H,0,3.0807890894,-3.0228824433,2.1673973476  
 H,0,2.2910821308,-3.1160176412,0.5646426631  
 H,0,-6.0574091405,0.9978115805,-2.1462114959  
 H,0,-5.8943118446,-1.4952874054,-2.3091393732  
 H,0,-4.3083074059,-2.7274791794,-0.8611936995  
 H,0,-4.6274937175,2.2282182896,-0.5456744217  
 H,0,-1.5693314538,-2.8863819832,2.8548396283  
 H,0,-1.4303358609,-4.4674487672,2.0199822635  
 H,0,-3.456159641,-3.4597918888,1.2175673472  
 H,0,-2.2562385906,-3.2947095025,-0.1066222096  
 H,0,3.8858169538,2.6577100629,0.105503918  
 H,0,5.7010230011,1.5550145641,-1.1604396561  
 H,0,5.8742856819,-0.9445761987,-1.177018237  
 H,0,4.2377373633,-2.3043265417,0.0820124416  
 H,0,2.8103236804,1.3120480546,-2.8505271683  
 H,0,2.7032608278,-1.1985694372,-2.9042130641  
 H,0,-0.8464067949,-1.0884733091,-0.4550501495  
 H,0,-0.7899887002,1.391274618,-0.4466650194

SCF Done: E(RB97D) = -2161.53271745 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.032665  
 Sum of electronic and thermal Energies= -2160.997654  
 Sum of electronic and thermal Enthalpies= -2160.996710  
 Sum of electronic and thermal Free Energies= -2161.100630

-----  
 # 6-311+g(d) rb3lyp pop=none td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

# **Excitation energies and oscillator strengths:**

**Excited State 1: Singlet-A 1.4708 eV 842.95 nm f=0.0044 <S\*\*2>=0.000**  
 137 ->140 -0.10720  
 139 ->140 0.69621

|                   |           |           |                  |                 |              |
|-------------------|-----------|-----------|------------------|-----------------|--------------|
| Excited State 2:  | Singlet-A | 1.6422 eV | 754.97 nm        | f=0.0096        | <S**2>=0.000 |
| 137 ->140         | 0.65789   |           |                  |                 |              |
| 137 ->141         | 0.14986   |           |                  |                 |              |
| 138 ->140         | 0.16805   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 3:  | Singlet-A | 1.7096 eV | 725.21 nm        | f=0.0012        | <S**2>=0.000 |
| 137 ->140         | -0.15459  |           |                  |                 |              |
| 138 ->140         | 0.68512   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 4:  | Singlet-A | 2.3383 eV | 530.22 nm        | f=0.0081        | <S**2>=0.000 |
| 136 ->140         | 0.69896   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 5:  | Singlet-A | 2.5678 eV | 482.85 nm        | f=0.0001        | <S**2>=0.000 |
| 135 ->140         | 0.70426   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 6:  | Singlet-A | 2.7458 eV | 451.53 nm        | f=0.0030        | <S**2>=0.000 |
| 139 ->141         | 0.70335   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 7:  | Singlet-A | 2.9436 eV | 421.20 nm        | f=0.0001        | <S**2>=0.000 |
| 138 ->141         | 0.70306   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 8:  | Singlet-A | 3.0743 eV | 403.30 nm        | f=0.0012        | <S**2>=0.000 |
| 133 ->140         | -0.41601  |           |                  |                 |              |
| 134 ->140         | 0.56496   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 9:  | Singlet-A | 3.1180 eV | 397.65 nm        | f=0.0013        | <S**2>=0.000 |
| 133 ->140         | 0.56250   |           |                  |                 |              |
| 134 ->140         | 0.41376   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 10: | Singlet-A | 3.2640 eV | 379.86 nm        | f=0.0238        | <S**2>=0.000 |
| 132 ->140         | -0.43188  |           |                  |                 |              |
| 137 ->140         | -0.12482  |           |                  |                 |              |
| 137 ->141         | 0.53097   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 11: | Singlet-A | 3.2824 eV | 377.73 nm        | f=0.0222        | <S**2>=0.000 |
| 132 ->140         | 0.54550   |           |                  |                 |              |
| 137 ->141         | 0.42469   |           |                  |                 |              |
|                   |           |           |                  |                 |              |
| Excited State 12: | Singlet-A | 3.5213 eV | <b>352.10 nm</b> | <b>f=0.1439</b> | <S**2>=0.000 |
| 130 ->140         | -0.25289  |           |                  |                 |              |
| 130 ->141         | 0.19494   |           |                  |                 |              |
| 131 ->140         | 0.57203   |           |                  |                 |              |
| 131 ->141         | -0.13871  |           |                  |                 |              |
| 136 ->141         | 0.10314   |           |                  |                 |              |

|                          |                  |                  |                  |                 |                           |
|--------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 13:        | Singlet-A        | 3.6077 eV        | 343.67 nm        | f=0.0129        | <S**2>=0.000              |
| 136 ->141                | 0.69436          |                  |                  |                 |                           |
| Excited State 14:        | Singlet-A        | 3.8051 eV        | 325.84 nm        | f=0.0017        | <S**2>=0.000              |
| 135 ->141                | 0.70285          |                  |                  |                 |                           |
| <b>Excited State 15:</b> | <b>Singlet-A</b> | <b>3.9353 eV</b> | <b>315.05 nm</b> | <b>f=0.1556</b> | <b>&lt;S**2&gt;=0.000</b> |
| 125 ->140                | 0.10028          |                  |                  |                 |                           |
| 127 ->140                | 0.13983          |                  |                  |                 |                           |
| 129 ->140                | 0.12298          |                  |                  |                 |                           |
| 130 ->140                | 0.48040          |                  |                  |                 |                           |
| 130 ->141                | -0.17334         |                  |                  |                 |                           |
| 131 ->140                | 0.36236          |                  |                  |                 |                           |
| 131 ->141                | 0.16508          |                  |                  |                 |                           |
| Excited State 16:        | Singlet-A        | 4.1359 eV        | 299.78 nm        | f=0.0008        | <S**2>=0.000              |
| 123 ->140                | 0.52687          |                  |                  |                 |                           |
| 123 ->141                | -0.27326         |                  |                  |                 |                           |
| 129 ->140                | -0.12549         |                  |                  |                 |                           |
| 132 ->141                | 0.16128          |                  |                  |                 |                           |
| 134 ->141                | 0.11351          |                  |                  |                 |                           |
| 139 ->142                | 0.22613          |                  |                  |                 |                           |
| Excited State 17:        | Singlet-A        | 4.1457 eV        | 299.07 nm        | f=0.0005        | <S**2>=0.000              |
| 123 ->140                | -0.18391         |                  |                  |                 |                           |
| 139 ->142                | 0.66565          |                  |                  |                 |                           |
| Excited State 18:        | Singlet-A        | 4.2737 eV        | 290.11 nm        | f=0.0020        | <S**2>=0.000              |
| 123 ->140                | -0.11517         |                  |                  |                 |                           |
| 132 ->141                | 0.10610          |                  |                  |                 |                           |
| 133 ->141                | 0.40236          |                  |                  |                 |                           |
| 134 ->141                | 0.54710          |                  |                  |                 |                           |
| Excited State 19:        | Singlet-A        | 4.3605 eV        | 284.33 nm        | f=0.0020        | <S**2>=0.000              |
| 123 ->140                | -0.12403         |                  |                  |                 |                           |
| 132 ->141                | 0.53986          |                  |                  |                 |                           |
| 133 ->141                | -0.39351         |                  |                  |                 |                           |
| 134 ->141                | 0.15048          |                  |                  |                 |                           |
| Excited State 20:        | Singlet-A        | 4.4092 eV        | 281.19 nm        | f=0.0020        | <S**2>=0.000              |
| 138 ->142                | 0.70133          |                  |                  |                 |                           |
| Excited State 21:        | Singlet-A        | 4.4493 eV        | 278.66 nm        | f=0.0021        | <S**2>=0.000              |
| 129 ->140                | 0.21259          |                  |                  |                 |                           |
| 132 ->141                | 0.37447          |                  |                  |                 |                           |
| 133 ->141                | 0.39890          |                  |                  |                 |                           |

134 ->141 -0.37712

Excited State 22: Singlet-A 4.4745 eV 277.09 nm f=0.0052 <S\*\*2>=0.000

123 ->140 0.15300

126 ->140 0.14771

129 ->140 0.58488

130 ->140 -0.18106

132 ->141 -0.15769

133 ->141 -0.11716

134 ->141 0.11363

Excited State 23: Singlet-A 4.5329 eV 273.52 nm f=0.0011 <S\*\*2>=0.000

123 ->140 0.11359

127 ->140 -0.31487

128 ->140 0.58381

Excited State 24: Singlet-A 4.6127 eV 268.79 nm f=0.0002 <S\*\*2>=0.000

117 ->140 0.10327

122 ->140 0.13345

125 ->140 0.51411

126 ->140 0.15668

127 ->140 -0.37849

128 ->140 -0.11516

Excited State 25: Singlet-A 4.6366 eV 267.40 nm f=0.0055 <S\*\*2>=0.000

125 ->140 0.15942

127 ->140 0.29183

128 ->140 0.16211

129 ->140 -0.10895

130 ->140 -0.28955

131 ->141 0.32591

137 ->142 0.36430

Excited State 26: Singlet-A 4.6451 eV 266.91 nm f=0.0065 <S\*\*2>=0.000

124 ->140 -0.14682

125 ->140 -0.20972

126 ->140 0.42054

128 ->140 -0.15864

130 ->140 0.10282

131 ->141 -0.10190

137 ->142 0.42191

Excited State 27: Singlet-A 4.6560 eV 266.29 nm f=0.0125 <S\*\*2>=0.000

124 ->140 -0.13792

126 ->140 0.43708

127 ->140 0.16545

|           |          |
|-----------|----------|
| 128 ->140 | 0.12057  |
| 129 ->140 | -0.16802 |
| 130 ->140 | -0.13762 |
| 131 ->141 | 0.11058  |
| 137 ->142 | -0.39483 |

Excited State 28: Singlet-A 4.6916 eV 264.27 nm f=0.0022 <S\*\*2>=0.000

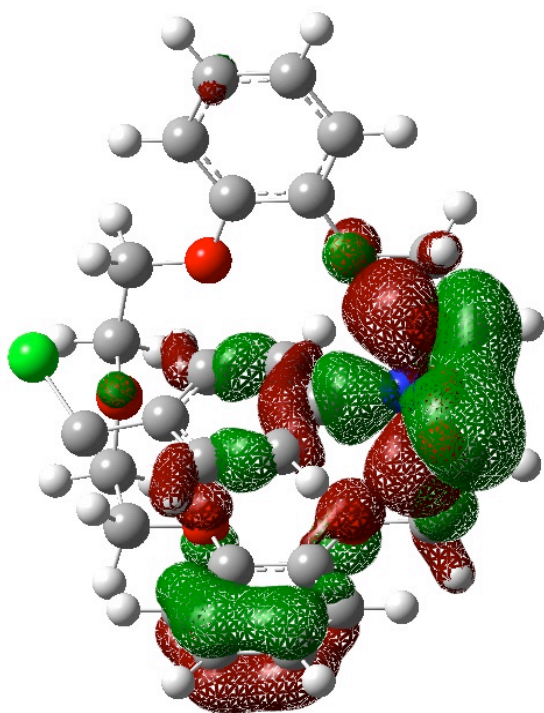
|           |          |
|-----------|----------|
| 125 ->140 | -0.28166 |
| 127 ->140 | -0.30620 |
| 128 ->140 | -0.15899 |
| 131 ->141 | 0.50436  |

Excited State 29: Singlet-A 4.7717 eV 259.83 nm f=0.0091 <S\*\*2>=0.000

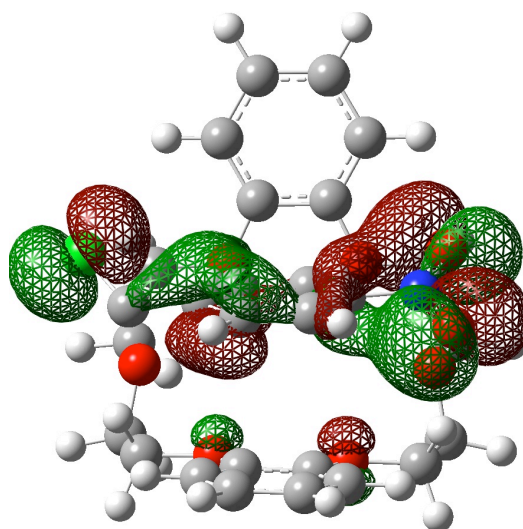
|           |          |
|-----------|----------|
| 117 ->140 | 0.11164  |
| 122 ->140 | -0.23096 |
| 124 ->140 | 0.55750  |
| 126 ->140 | 0.22291  |
| 128 ->140 | 0.12517  |

Excited State 30: Singlet-A 4.8117 eV 257.67 nm f=0.0165 <S\*\*2>=0.000

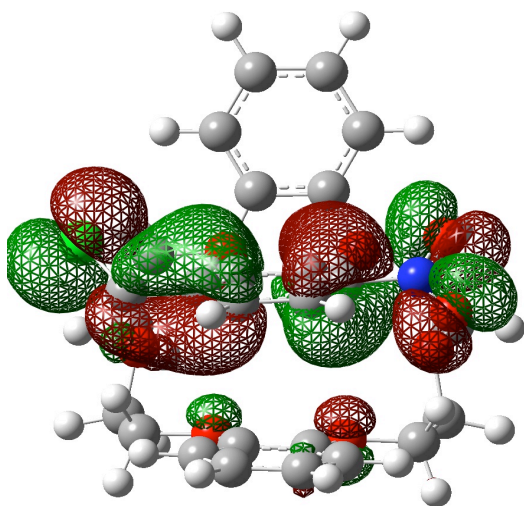
|           |          |
|-----------|----------|
| 117 ->140 | 0.40882  |
| 118 ->140 | -0.10687 |
| 119 ->140 | -0.11231 |
| 120 ->140 | -0.10228 |
| 122 ->140 | 0.39082  |
| 125 ->140 | -0.21360 |
| 130 ->141 | 0.12389  |
| 139 ->143 | 0.12607  |
| 139 ->144 | -0.11032 |



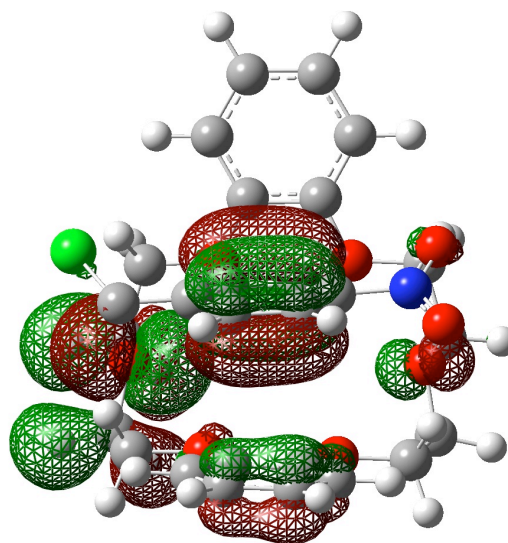
12a-MO129



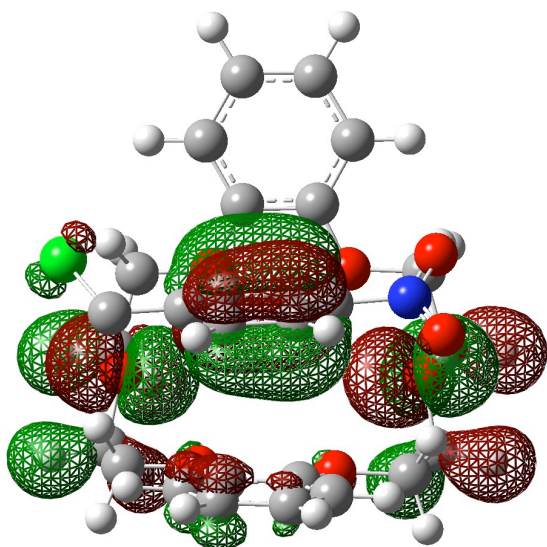
12a-MO130



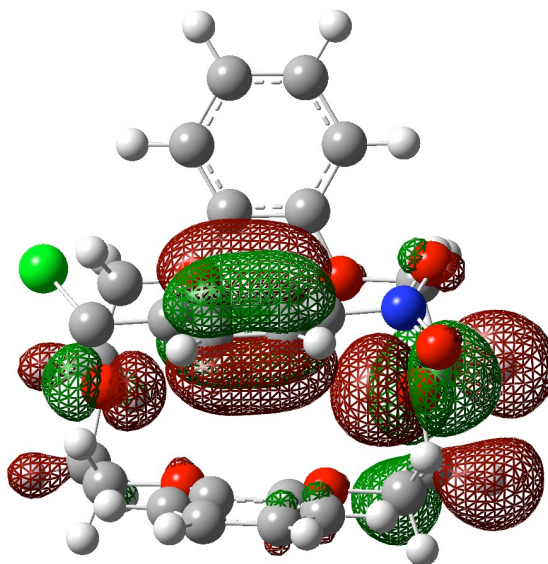
12a-MO131



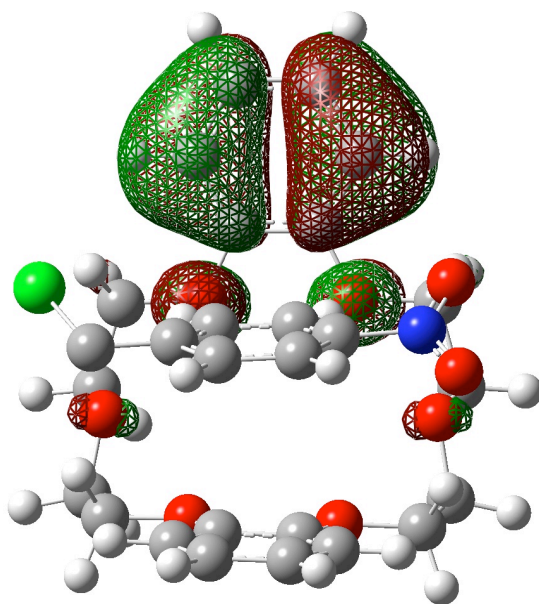
12a-MO132



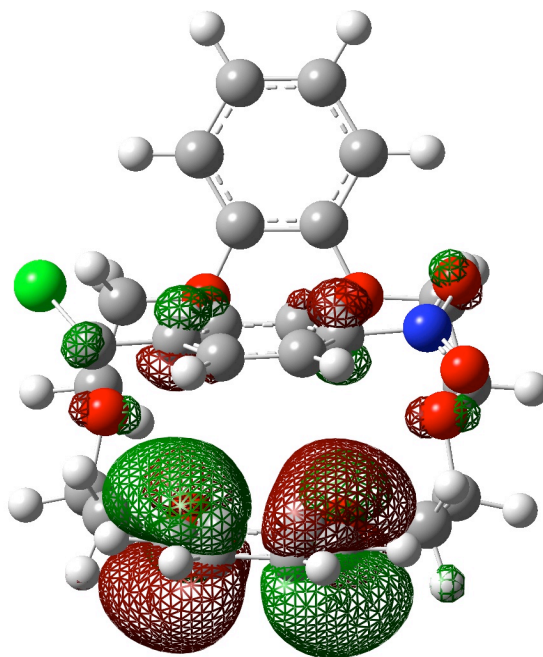
12a-MO133



12a-MO134

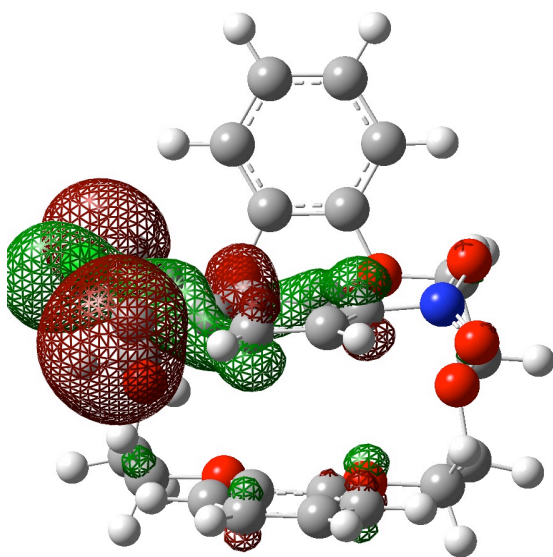


12a-MO135

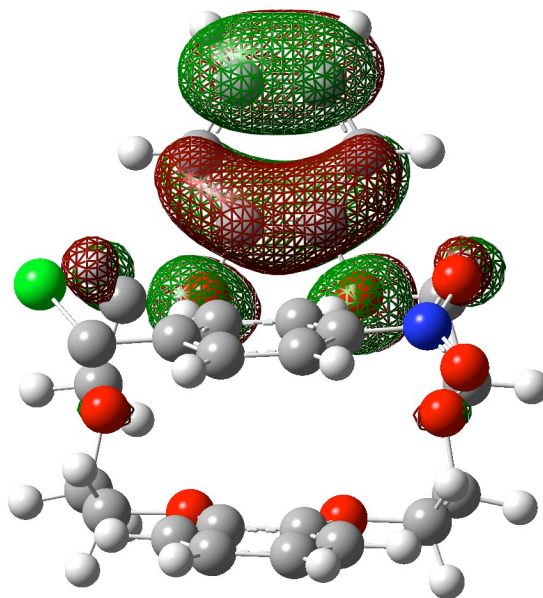


12a-MO136

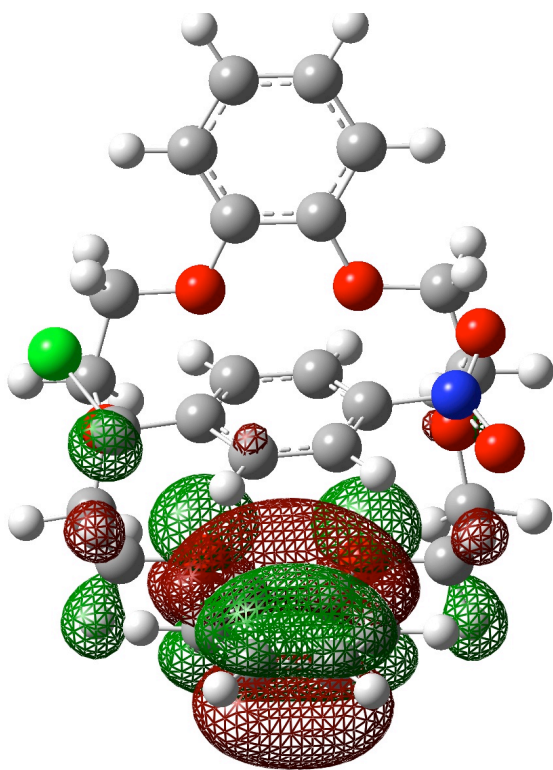




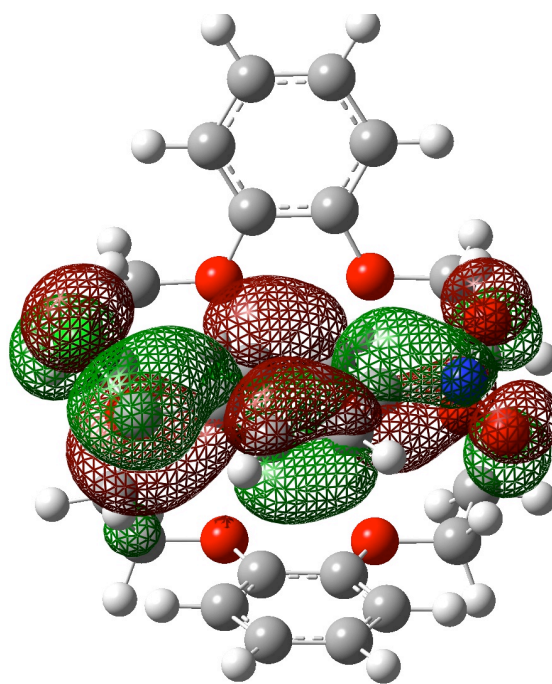
12a- $\sigma$ -MO137



12a-MO138

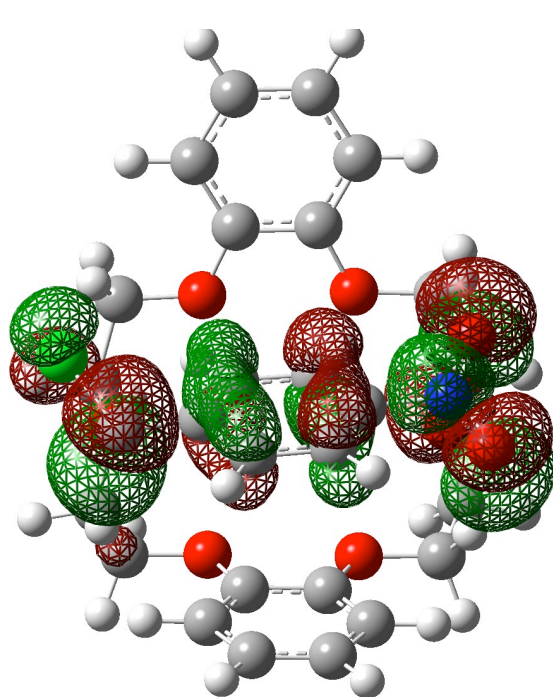


12a-HOMO-MO139

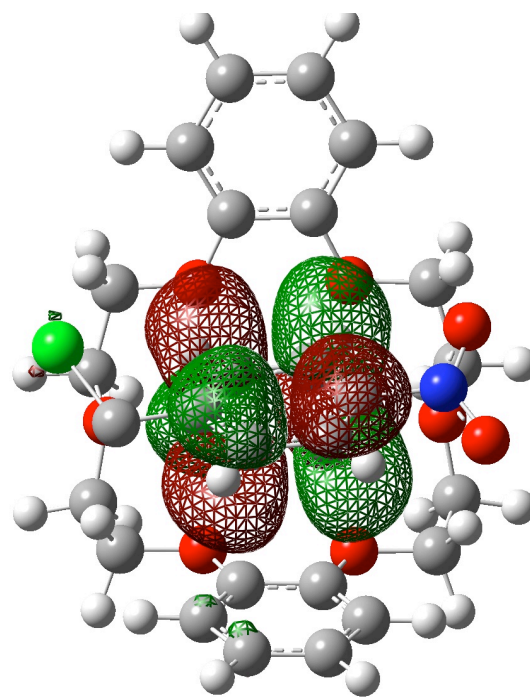


12a-LUMO-p-MO140

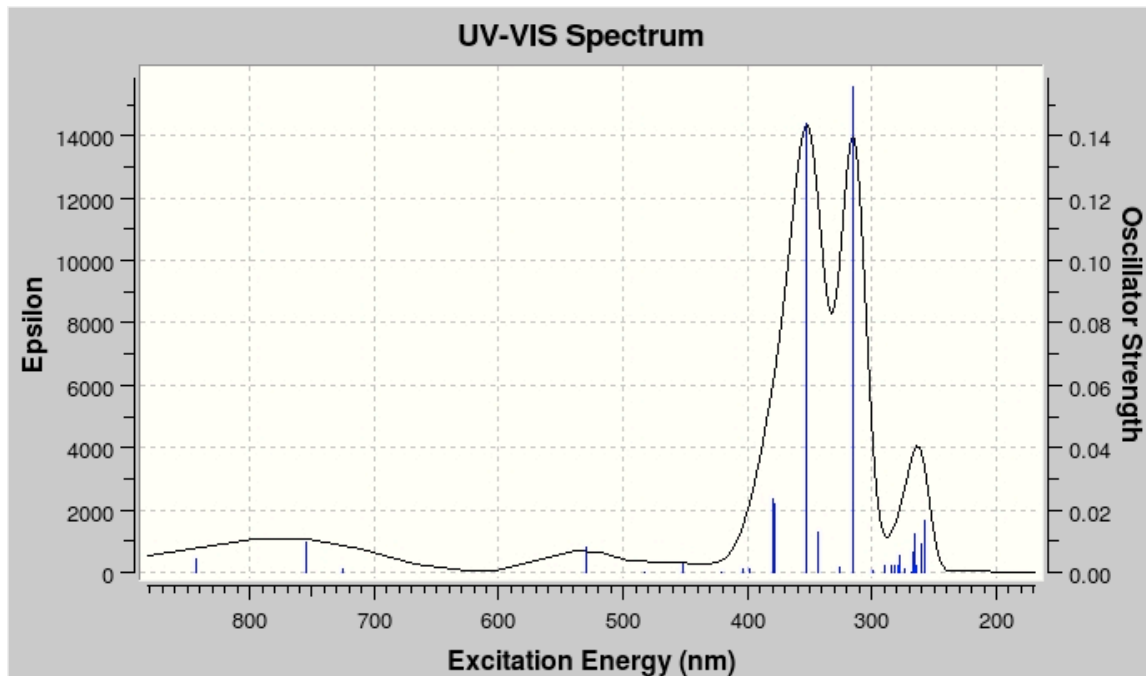




12a-MO141



12a-MO142



Computed electronic spectrum of **12a** (TD-B3LYP/6-311+G(d)).

## 12b:

-----  
Full-sandwich 12b, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,2.0320555872,2.9116399223,2.71842538  
O,0,2.2104934844,3.0744684491,1.3051004011  
C,0,1.4812758034,1.5450232033,3.108951457  
O,0,2.346931474,0.5280814777,2.6313349333  
C,0,1.7676188013,-0.7654927,2.7849209732  
C,0,1.1225490311,3.0502337402,0.4792349414  
C,0,1.4062120582,2.879632292,-0.9041620995  
C,0,2.6361442188,-1.7910964478,2.058210668  
C,0,2.977304579,0.4928522892,-2.1097911054  
O,0,3.4253181626,-0.7995448092,-1.6959175654  
C,0,3.3522833835,1.5084494874,-1.031630753  
O,0,2.7042938836,2.7704962381,-1.3447755632  
C,0,-1.362869209,-3.438978507,0.4640664967  
C,0,-0.9942013211,-3.5803377937,-0.8777487723  
C,0,0.356029196,-3.5406551813,-1.2526880413  
C,0,1.3578446848,-3.3530576999,-0.2853504098  
C,0,0.9808998493,-3.2004299458,1.0789090096  
C,0,-0.3683152504,-3.254607205,1.436298948  
O,0,1.9359928437,-3.0617687284,2.0610368852  
O,0,2.6980266588,-3.3377352991,-0.5303067069  
C,0,2.8477344809,-1.8277878454,-2.4889162652  
C,0,3.176592301,-3.1834374082,-1.8775617222  
C,0,-0.2109033806,3.2150386538,0.8902560698  
C,0,-1.2495803724,3.2125503655,-0.0524889797  
C,0,-0.9691909075,3.0543532351,-1.4132546871  
C,0,0.3602623762,2.8924254496,-1.8306705762  
H,0,3.0381840432,3.046426894,3.13030209  
H,0,1.377016286,3.7008573967,3.1237985328  
H,0,0.4717432015,1.4033708848,2.6860208355  
H,0,1.3933658426,1.5071338361,4.2132813196  
H,0,0.7629019611,-0.7797530369,2.3298949858  
H,0,1.6684230576,-1.0238402427,3.855551483  
H,0,3.5802548267,-1.9701002457,2.5848334381  
H,0,2.8496764111,-1.4591308288,1.0356250904  
H,0,3.4313955895,0.7658898702,-3.0804952384  
H,0,1.8833240042,0.4885241164,-2.2263491892  
H,0,4.4275653475,1.7203856539,-1.0218639627  
H,0,3.0481666518,1.1466620061,-0.0424705819  
H,0,-2.4126085729,-3.4688586543,0.7555941001  
H,0,-1.7548963917,-3.7206230959,-1.6459671904  
H,0,0.6221677962,-3.6562977082,-2.300498247

H,0,-0.6218061603,-3.1457574368,2.4907800638  
 H,0,1.7591004331,-1.6791563583,-2.5534938132  
 H,0,3.2567213468,-1.8099799942,-3.519599879  
 H,0,4.2610116283,-3.3087937794,-1.7858277672  
 H,0,2.7814445084,-3.9861381089,-2.5217440184  
 H,0,-0.445016319,3.3614319028,1.9427056623  
 H,0,-2.2779553217,3.3365130032,0.2874054292  
 H,0,-1.7749261899,3.0518821824,-2.1471551284  
 H,0,0.6095450975,2.76369181,-2.883275665  
 C,0,-3.2648077326,0.1860250556,1.6314832943  
 C,0,-2.0211432404,0.0200375778,1.0418029297  
 C,0,-1.945020193,-0.1419539198,-0.350986591  
 C,0,-3.0807297276,-0.1531078507,-1.1655026361  
 C,0,-4.3284658835,-0.0016239346,-0.5615391643  
 C,0,-4.4534831804,0.1851251667,0.8436141115  
 C,0,-5.8483875911,0.3207680791,1.2684362365  
 Cl,0,-5.9883177264,0.739025491,2.9735445  
 N,0,-0.6030267437,-0.301528243,-0.9803070241  
 O,0,-0.5562173035,-0.4554096187,-2.202871884  
 O,0,0.3796159051,-0.2656745044,-0.2421476819  
 H,0,-3.3337989608,0.3146980237,2.7102615186  
 H,0,-1.1087997413,0.0175958373,1.628983657  
 H,0,-2.9767633134,-0.2840014242,-2.2389078535  
 H,0,-5.2380878221,-0.017887725,-1.1609347099

SCF Done: E(RB97D) = -2161.51969948 A.U. after 3 cycles

Sum of electronic and zero-point Energies= -2161.019340  
 Sum of electronic and thermal Energies= -2160.984286  
 Sum of electronic and thermal Enthalpies= -2160.983342  
 Sum of electronic and thermal Free Energies= -2161.090239

-----  
 # 6-311+g(d) rb3lyp pop=none td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

### Excitation energies and oscillator strengths:

**Excited State 1: Singlet-A 1.3222 eV 937.71 nm f=0.0204 <S\*\*2>=0.000**  
 137 ->140 -0.34892  
 139 ->140 0.59711

|                          |                  |                  |                  |                 |                           |
|--------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 2:         | Singlet-A        | 1.5437 eV        | 803.15 nm        | f=0.0010        | <S**2>=0.000              |
| 138 ->140                | 0.70534          |                  |                  |                 |                           |
| Excited State 3:         | Singlet-A        | 1.6129 eV        | 768.71 nm        | f=0.0014        | <S**2>=0.000              |
| 137 ->140                | 0.58458          |                  |                  |                 |                           |
| 137 ->141                | -0.10625         |                  |                  |                 |                           |
| 139 ->140                | 0.37131          |                  |                  |                 |                           |
| Excited State 4:         | Singlet-A        | 2.3921 eV        | 518.31 nm        | f=0.0113        | <S**2>=0.000              |
| 135 ->140                | -0.25405         |                  |                  |                 |                           |
| 136 ->140                | 0.65154          |                  |                  |                 |                           |
| Excited State 5:         | Singlet-A        | 2.4233 eV        | 511.63 nm        | f=0.0242        | <S**2>=0.000              |
| 135 ->140                | 0.63519          |                  |                  |                 |                           |
| 136 ->140                | 0.26710          |                  |                  |                 |                           |
| 137 ->140                | -0.12691         |                  |                  |                 |                           |
| Excited State 6:         | Singlet-A        | 2.8239 eV        | 439.05 nm        | f=0.0091        | <S**2>=0.000              |
| 139 ->141                | 0.69353          |                  |                  |                 |                           |
| Excited State 7:         | Singlet-A        | 2.8426 eV        | 436.17 nm        | f=0.0005        | <S**2>=0.000              |
| 138 ->141                | 0.70336          |                  |                  |                 |                           |
| Excited State 8:         | Singlet-A        | 3.0563 eV        | 405.67 nm        | f=0.0008        | <S**2>=0.000              |
| 134 ->140                | 0.69714          |                  |                  |                 |                           |
| Excited State 9:         | Singlet-A        | 3.1254 eV        | 396.70 nm        | f=0.0011        | <S**2>=0.000              |
| 133 ->140                | 0.69583          |                  |                  |                 |                           |
| Excited State 10:        | Singlet-A        | 3.1856 eV        | 389.20 nm        | f=0.0069        | <S**2>=0.000              |
| 133 ->140                | 0.10351          |                  |                  |                 |                           |
| 137 ->140                | 0.11537          |                  |                  |                 |                           |
| 137 ->141                | 0.66815          |                  |                  |                 |                           |
| Excited State 11:        | Singlet-A        | 3.3477 eV        | 370.35 nm        | f=0.0316        | <S**2>=0.000              |
| 132 ->140                | 0.69714          |                  |                  |                 |                           |
| <b>Excited State 12:</b> | <b>Singlet-A</b> | <b>3.5558 eV</b> | <b>348.68 nm</b> | <b>f=0.0953</b> | <b>&lt;S**2&gt;=0.000</b> |
| 126 ->140                | -0.10297         |                  |                  |                 |                           |
| 129 ->140                | 0.24556          |                  |                  |                 |                           |
| 129 ->141                | 0.14129          |                  |                  |                 |                           |
| 130 ->140                | 0.31530          |                  |                  |                 |                           |
| 130 ->141                | 0.17278          |                  |                  |                 |                           |
| 131 ->140                | 0.48051          |                  |                  |                 |                           |
| 131 ->141                | 0.12241          |                  |                  |                 |                           |

|                          |                  |                  |                  |                 |                           |
|--------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 13:        | Singlet-A        | 3.6875 eV        | 336.23 nm        | f=0.0010        | <S**2>=0.000              |
| 136 ->141                | 0.70150          |                  |                  |                 |                           |
| Excited State 14:        | Singlet-A        | 3.8199 eV        | 324.58 nm        | f=0.0120        | <S**2>=0.000              |
| 135 ->141                | 0.68165          |                  |                  |                 |                           |
| <b>Excited State 15:</b> | <b>Singlet-A</b> | <b>3.9847 eV</b> | <b>311.15 nm</b> | <b>f=0.2773</b> | <b>&lt;S**2&gt;=0.000</b> |
| 129 ->140                | -0.22656         |                  |                  |                 |                           |
| 130 ->140                | -0.34620         |                  |                  |                 |                           |
| 130 ->141                | -0.10122         |                  |                  |                 |                           |
| 131 ->140                | 0.48255          |                  |                  |                 |                           |
| 135 ->141                | -0.12593         |                  |                  |                 |                           |
| 139 ->142                | 0.11025          |                  |                  |                 |                           |
| Excited State 16:        | Singlet-A        | 4.1049 eV        | 302.04 nm        | f=0.0294        | <S**2>=0.000              |
| 121 ->140                | 0.15034          |                  |                  |                 |                           |
| 122 ->140                | 0.37043          |                  |                  |                 |                           |
| 122 ->141                | 0.17449          |                  |                  |                 |                           |
| 123 ->140                | 0.19385          |                  |                  |                 |                           |
| 124 ->140                | 0.11405          |                  |                  |                 |                           |
| 125 ->140                | 0.15813          |                  |                  |                 |                           |
| 139 ->142                | 0.40953          |                  |                  |                 |                           |
| Excited State 17:        | Singlet-A        | 4.1087 eV        | 301.76 nm        | f=0.0218        | <S**2>=0.000              |
| 121 ->140                | -0.12059         |                  |                  |                 |                           |
| 122 ->140                | -0.28618         |                  |                  |                 |                           |
| 122 ->141                | -0.13625         |                  |                  |                 |                           |
| 123 ->140                | -0.13957         |                  |                  |                 |                           |
| 125 ->140                | -0.12437         |                  |                  |                 |                           |
| 139 ->142                | 0.54720          |                  |                  |                 |                           |
| Excited State 18:        | Singlet-A        | 4.2080 eV        | 294.64 nm        | f=0.0176        | <S**2>=0.000              |
| 138 ->142                | 0.70519          |                  |                  |                 |                           |
| Excited State 19:        | Singlet-A        | 4.3917 eV        | 282.31 nm        | f=0.0043        | <S**2>=0.000              |
| 128 ->140                | 0.14566          |                  |                  |                 |                           |
| 129 ->140                | 0.50600          |                  |                  |                 |                           |
| 130 ->140                | -0.42772         |                  |                  |                 |                           |
| 133 ->141                | 0.10989          |                  |                  |                 |                           |
| Excited State 20:        | Singlet-A        | 4.4315 eV        | 279.78 nm        | f=0.0002        | <S**2>=0.000              |
| 133 ->141                | 0.67296          |                  |                  |                 |                           |
| 134 ->141                | -0.14439         |                  |                  |                 |                           |
| Excited State 21:        | Singlet-A        | 4.4431 eV        | 279.05 nm        | f=0.0036        | <S**2>=0.000              |
| 128 ->140                | 0.19385          |                  |                  |                 |                           |

|           |          |
|-----------|----------|
| 134 ->141 | -0.19443 |
| 137 ->142 | 0.60167  |
| 139 ->142 | 0.10754  |

Excited State 22: Singlet-A 4.4534 eV 278.40 nm f=0.0009 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 117 ->140 | 0.13627  |
| 124 ->140 | 0.10834  |
| 126 ->140 | 0.18295  |
| 127 ->140 | -0.17832 |
| 128 ->140 | 0.37049  |
| 133 ->141 | -0.13891 |
| 134 ->141 | -0.33173 |
| 137 ->142 | -0.32095 |

Excited State 23: Singlet-A 4.4701 eV 277.37 nm f=0.0013 <S\*\*2>=0.000

|           |         |
|-----------|---------|
| 117 ->140 | 0.11714 |
| 126 ->140 | 0.20035 |
| 128 ->140 | 0.28167 |
| 134 ->141 | 0.56682 |

Excited State 24: Singlet-A 4.5082 eV 275.02 nm f=0.0085 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 127 ->140 | -0.16092 |
| 128 ->140 | -0.22797 |
| 132 ->141 | 0.63125  |

Excited State 25: Singlet-A 4.5239 eV 274.07 nm f=0.0024 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 117 ->140 | -0.12772 |
| 122 ->140 | 0.10675  |
| 124 ->140 | -0.13056 |
| 125 ->140 | 0.15375  |
| 126 ->140 | -0.13260 |
| 127 ->140 | 0.42502  |
| 128 ->140 | 0.33668  |
| 132 ->141 | 0.28964  |

Excited State 26: Singlet-A 4.5474 eV 272.65 nm f=0.0053 <S\*\*2>=0.000

|           |          |
|-----------|----------|
| 125 ->140 | -0.10399 |
| 126 ->140 | 0.51052  |
| 127 ->140 | 0.38022  |
| 128 ->140 | -0.14133 |
| 129 ->140 | 0.21066  |

Excited State 27: Singlet-A 4.6161 eV 268.59 nm f=0.0041 <S\*\*2>=0.000

|           |         |
|-----------|---------|
| 117 ->140 | 0.25885 |
| 118 ->140 | 0.14762 |
| 124 ->140 | 0.42487 |

|           |          |
|-----------|----------|
| 125 ->140 | -0.16280 |
| 126 ->140 | -0.27502 |
| 127 ->140 | 0.28147  |
| 130 ->140 | -0.13046 |
| 131 ->141 | 0.10692  |

Excited State 28: Singlet-A 4.6684 eV 265.58 nm f=0.0015 <S\*\*2>=0.000

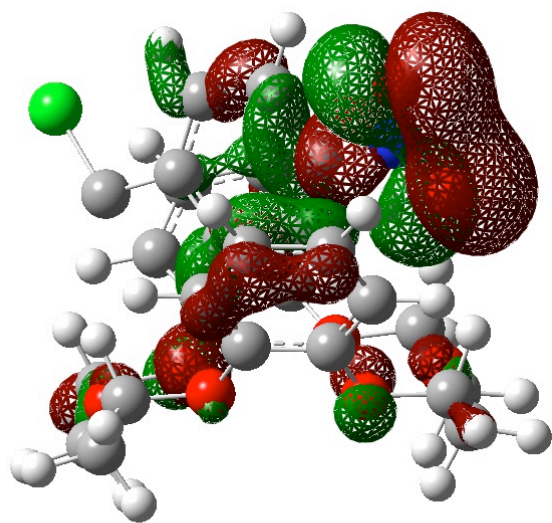
|           |          |
|-----------|----------|
| 122 ->140 | -0.16970 |
| 123 ->140 | -0.28535 |
| 124 ->140 | 0.25431  |
| 125 ->140 | 0.54448  |

Excited State 29: Singlet-A 4.7198 eV 262.69 nm f=0.0022 <S\*\*2>=0.000

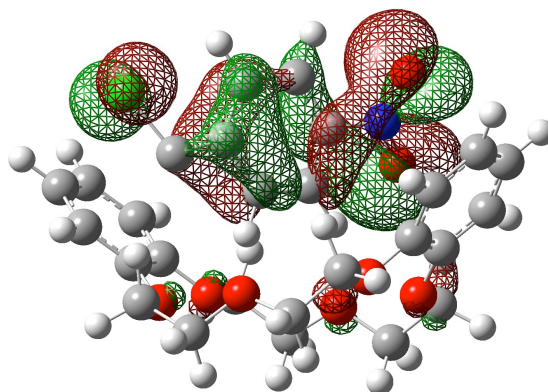
|           |          |
|-----------|----------|
| 117 ->140 | 0.12984  |
| 122 ->140 | -0.28463 |
| 123 ->140 | 0.52833  |
| 125 ->140 | 0.23689  |
| 131 ->141 | 0.10353  |

Excited State 30: Singlet-A 4.7397 eV 261.59 nm f=0.0057 <S\*\*2>=0.000

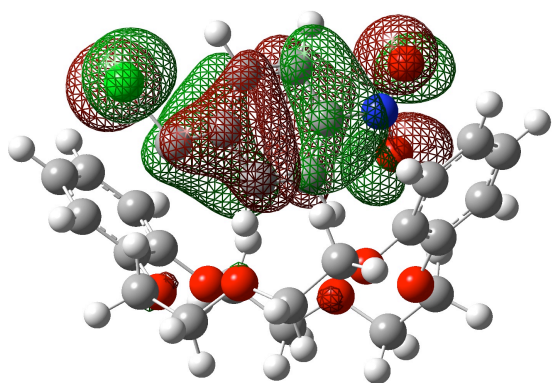
|           |          |
|-----------|----------|
| 117 ->140 | -0.41276 |
| 118 ->140 | -0.23181 |
| 121 ->140 | -0.10505 |
| 122 ->140 | -0.14252 |
| 123 ->140 | 0.18077  |
| 124 ->140 | 0.40761  |
| 131 ->141 | -0.12235 |



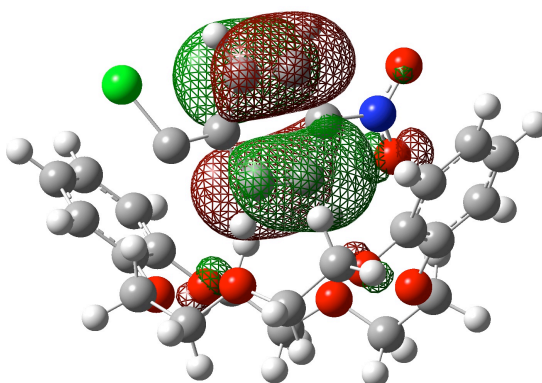
12b-MO129



12b-MO130

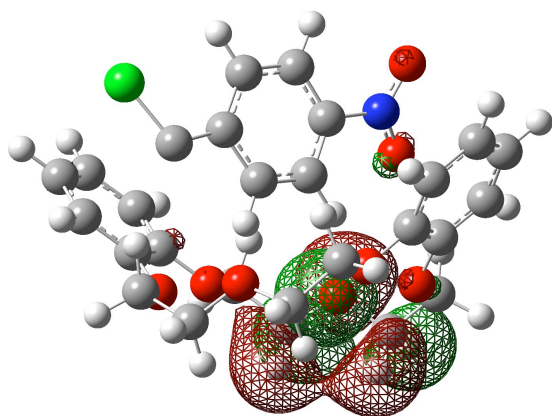


12b-MO131

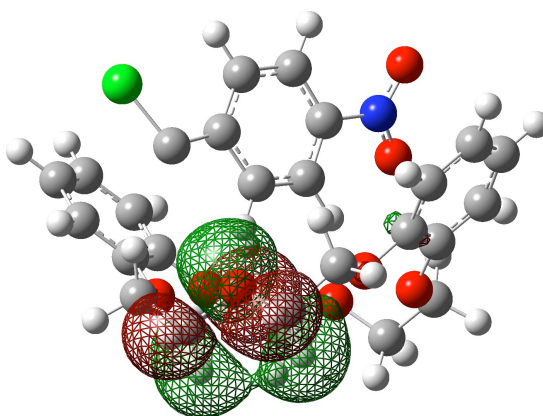


12b-MO132

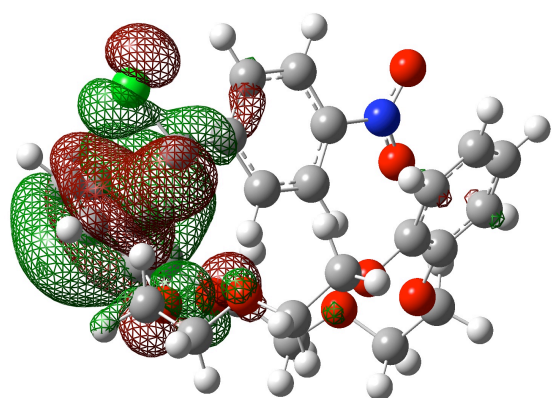




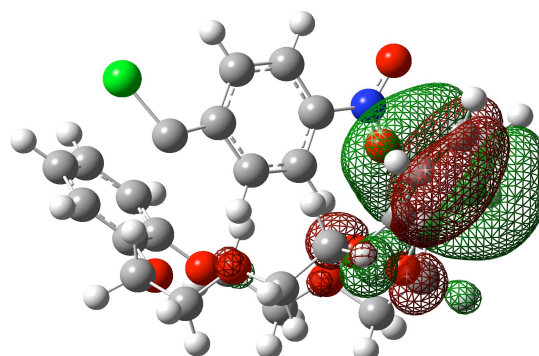
12b-MO133



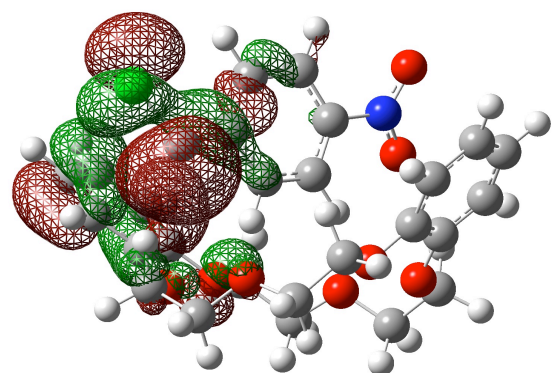
12b-MO134



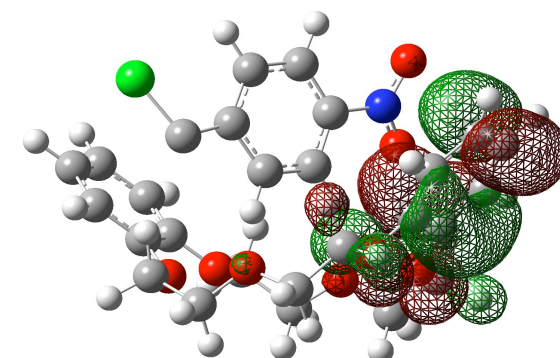
12b-MO135



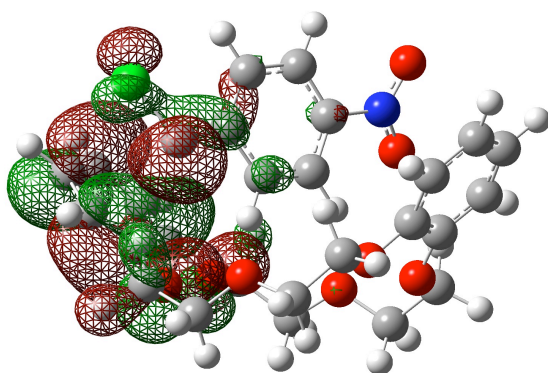
12b-MO136



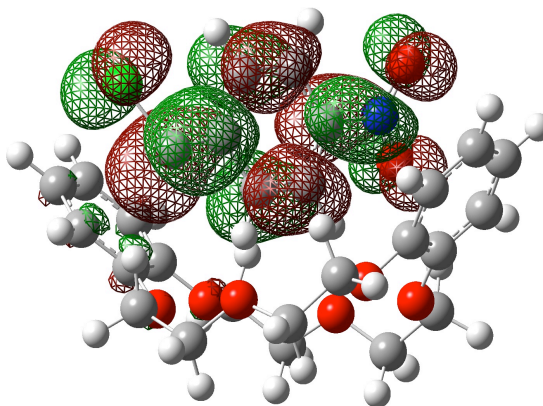
12b-σ-MO137



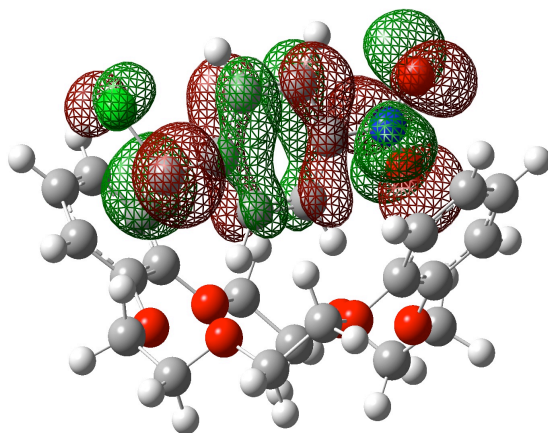
12b-MO138



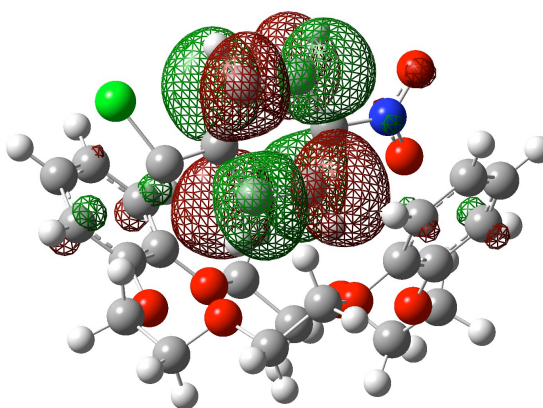
12b-HOMO-MO139



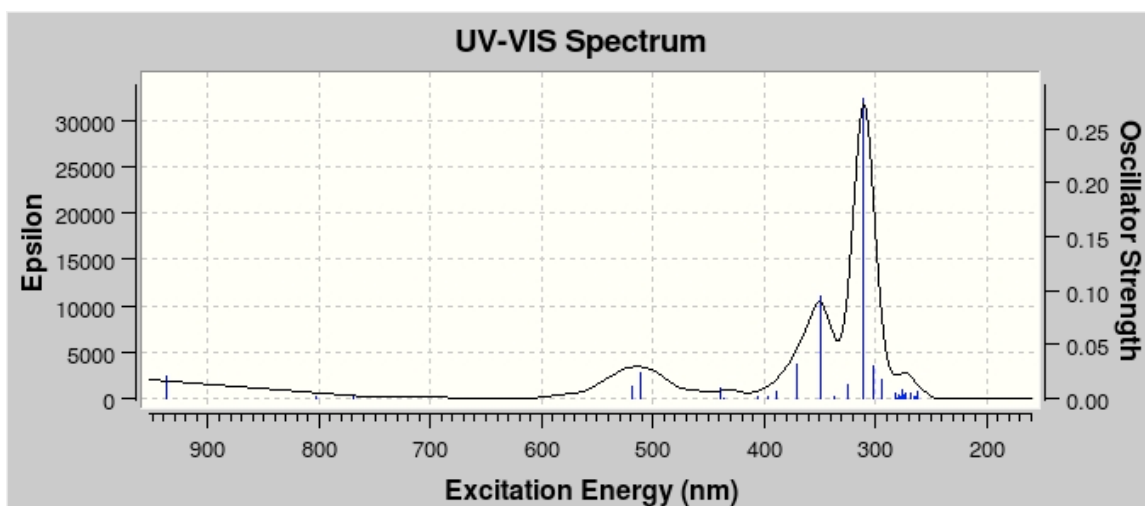
12b-LUMO-p-MO140



12b-MO141



12b-MO142



Computed electronic spectrum of **12b** (TD-B3LYP/6-311+G(d)).

## 12c:

-----  
Full-sandwich 12c, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,0.744869494,-2.4095870394,1.1148990838  
O,0,1.0278638905,-1.0177498772,1.3243494883  
C,0,-0.678322378,-2.5219678471,0.6040496542  
O,0,-0.7524104655,-1.9759163669,-0.7119289006  
C,0,-2.033518954,-2.1495036014,-1.328714737  
C,0,2.3058309604,-0.6453314077,1.6396972477  
C,0,2.5845684633,0.7502189922,1.6641053865  
C,0,-3.1459487385,-1.3876293714,-0.5970414601  
C,0,-0.5840479009,1.4771558154,0.5164306625  
O,0,-1.9618853735,1.5756139412,0.9085844782  
C,0,0.308583538,1.7047703781,1.7391396026  
O,0,1.6986950641,1.7378127731,1.3251863168  
C,0,-7.7762015081,-1.1084683864,-0.4532557853  
C,0,-7.8407077866,0.184924073,0.0766718582  
C,0,-6.7054496346,1.0083192469,0.0663782265  
C,0,-5.4947472085,0.5437949171,-0.472657168  
C,0,-5.4190719014,-0.7806770781,-0.9766659033  
C,0,-6.5632263859,-1.5856048214,-0.9710389953  
O,0,-4.2574747675,-1.2953077575,-1.5167706829  
O,0,-4.3655474949,1.3102704863,-0.5785563382  
C,0,-2.6744841547,2.6885476288,0.3732354651  
C,0,-4.1571127197,2.3593057274,0.3795762622  
C,0,3.3412763778,-1.5545663769,1.9084650464  
C,0,4.6434828599,-1.1071033271,2.1789052746  
C,0,4.9215940859,0.2615568033,2.1964756212  
C,0,3.8916749524,1.1769729084,1.9448966264  
H,0,1.453865531,-2.8353188899,0.3919851212  
H,0,0.8367924081,-2.9569757074,2.0679273631  
H,0,-1.3595473038,-1.9900044717,1.2887953037  
H,0,-0.9643478636,-3.5910315038,0.5905629968  
H,0,-2.2754762742,-3.2253121093,-1.4010223061  
H,0,-1.9313409105,-1.7455713198,-2.3434272524  
H,0,-3.4792890439,-1.9254018537,0.3058236598  
H,0,-2.792662745,-0.3919806091,-0.3064647983  
H,0,-0.3266377585,2.2088453306,-0.2638600272  
H,0,-0.4212185625,0.4724160405,0.1131410486  
H,0,0.1070108427,2.6915882328,2.1790575527  
H,0,0.1455806854,0.9341674797,2.5001945297  
H,0,-8.6574352444,-1.7499756331,-0.4542844547  
H,0,-8.7744061038,0.5652352477,0.491755949  
H,0,-6.7652833777,2.0236125902,0.4561608756

H,0,-6.4786278357,-2.5953336083,-1.3729420603  
 H,0,-2.5043069241,3.5999815579,0.9770624255  
 H,0,-2.3517284428,2.8946940981,-0.6606398915  
 H,0,-4.4760179567,2.0209673308,1.3777451652  
 H,0,-4.7389010934,3.2546772907,0.1026287647  
 H,0,3.1396460049,-2.6230203978,1.8881031377  
 H,0,5.4288402248,-1.837717702,2.3712544883  
 H,0,5.9287192787,0.6216915225,2.4057220688  
 H,0,4.0776673599,2.2504883424,1.9455542173  
 C,0,2.2799610271,-1.205540554,-1.6970292417  
 C,0,3.6328459504,-1.3755144697,-1.384953356  
 C,0,4.5043026167,-0.296868685,-1.1803243609  
 C,0,3.990977048,0.9924934096,-1.2499547266  
 C,0,2.619613011,1.2193161874,-1.5561101828  
 C,0,1.7860830741,0.0930572832,-1.7907388342  
 H,0,1.6261265223,-2.0606188183,-1.8327826782  
 H,0,5.5444022511,-0.4827223311,-0.9297271462  
 H,0,4.6478097166,1.8378215004,-1.0588488417  
 H,0,0.7345777985,0.256731232,-2.0141536635  
 N,0,4.1658879365,-2.7608086437,-1.2290289312  
 O,0,3.3469103121,-3.6660232487,-1.0507305383  
 O,0,5.3842415318,-2.9159575147,-1.273183339  
 C,0,1.8900336449,2.4865774772,-1.6429740601  
 Cl,0,2.9067023503,3.8751234848,-1.265346307

SCF Done: E(RB97D) = -2161.51917742 A.U. after 3 cycles

Sum of electronic and zero-point Energies= -2161.018901  
 Sum of electronic and thermal Energies= -2160.983698  
 Sum of electronic and thermal Enthalpies= -2160.982754  
 Sum of electronic and thermal Free Energies= -2161.088737

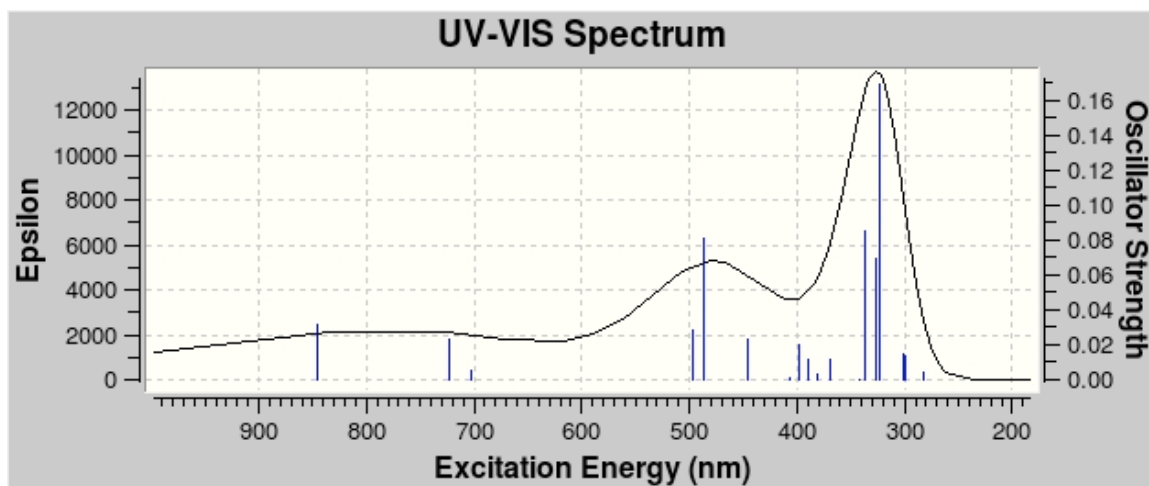
-----  
 # 6-311+g(d) rb3lyp td=(add=10) scrf=(cpcm,solvent=dichloroethane)  
 -----

# **Excitation energies and oscillator strengths:**

**Excited State 1: Singlet-A 1.4671 eV 845.11 nm f=0.0317 <S\*\*2>=0.000**  
 137 ->140 -0.36297  
 137 ->141 -0.11159  
 139 ->140 0.57974

|                         |                  |                  |                  |                 |                           |
|-------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 2:        | Singlet-A        | 1.7151 eV        | 722.88 nm        | f=0.0228        | <S**2>=0.000              |
| 137 ->140               | 0.47116          |                  |                  |                 |                           |
| 138 ->140               | -0.35208         |                  |                  |                 |                           |
| 139 ->140               | 0.37182          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 3:        | Singlet-A        | 1.7655 eV        | 702.25 nm        | f=0.0052        | <S**2>=0.000              |
| 137 ->140               | 0.32516          |                  |                  |                 |                           |
| 138 ->140               | 0.60519          |                  |                  |                 |                           |
| 139 ->140               | 0.13754          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 4:        | Singlet-A        | 2.4997 eV        | 496.01 nm        | f=0.0285        | <S**2>=0.000              |
| 135 ->140               | -0.45873         |                  |                  |                 |                           |
| 136 ->140               | 0.52963          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| <b>Excited State 5:</b> | <b>Singlet-A</b> | <b>2.5455 eV</b> | <b>487.07 nm</b> | <b>f=0.0804</b> | <b>&lt;S**2&gt;=0.000</b> |
| 135 ->140               | 0.50747          |                  |                  |                 |                           |
| 136 ->140               | 0.45608          |                  |                  |                 |                           |
| 137 ->140               | 0.13577          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 6:        | Singlet-A        | 2.7803 eV        | 445.94 nm        | f=0.0236        | <S**2>=0.000              |
| 139 ->141               | 0.68545          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 7:        | Singlet-A        | 3.0451 eV        | 407.16 nm        | f=0.0014        | <S**2>=0.000              |
| 138 ->141               | 0.69503          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 8:        | Singlet-A        | 3.1148 eV        | 398.05 nm        | f=0.0197        | <S**2>=0.000              |
| 134 ->140               | -0.22994         |                  |                  |                 |                           |
| 137 ->140               | -0.13122         |                  |                  |                 |                           |
| 137 ->141               | 0.62123          |                  |                  |                 |                           |
| 138 ->141               | 0.10772          |                  |                  |                 |                           |
| 139 ->141               | 0.11045          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 9:        | Singlet-A        | 3.1886 eV        | 388.83 nm        | f=0.0111        | <S**2>=0.000              |
| 133 ->140               | 0.10270          |                  |                  |                 |                           |
| 134 ->140               | 0.65423          |                  |                  |                 |                           |
| 137 ->141               | 0.21722          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 10:       | Singlet-A        | 3.2526 eV        | 381.19 nm        | f=0.0028        | <S**2>=0.000              |
| 132 ->140               | 0.12796          |                  |                  |                 |                           |
| 133 ->140               | 0.68209          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 11:       | Singlet-A        | 3.3648 eV        | 368.48 nm        | f=0.0120        | <S**2>=0.000              |
| 132 ->140               | 0.68034          |                  |                  |                 |                           |
| 133 ->140               | -0.14562         |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 12:       | Singlet-A        | 3.6286 eV        | 341.69 nm        | f=0.0002        | <S**2>=0.000              |

|                          |                  |                                                        |
|--------------------------|------------------|--------------------------------------------------------|
| 128 ->140                | 0.63378          |                                                        |
| 128 ->141                | -0.29415         |                                                        |
| <b>Excited State 13:</b> | <b>Singlet-A</b> | <b>3.6830 eV 336.64 nm f=0.0854 &lt;S**2&gt;=0.000</b> |
| 131 ->140                | 0.49429          |                                                        |
| 136 ->141                | 0.48335          |                                                        |
| <b>Excited State 14:</b> | <b>Singlet-A</b> | <b>3.7941 eV 326.78 nm f=0.0692 &lt;S**2&gt;=0.000</b> |
| 131 ->140                | 0.22986          |                                                        |
| 135 ->141                | 0.62591          |                                                        |
| 136 ->141                | -0.19339         |                                                        |
| <b>Excited State 15:</b> | <b>Singlet-A</b> | <b>3.8316 eV 323.59 nm f=0.1691 &lt;S**2&gt;=0.000</b> |
| 131 ->140                | -0.41922         |                                                        |
| 135 ->141                | 0.30064          |                                                        |
| 136 ->141                | 0.46391          |                                                        |
| Excited State 16:        | Singlet-A        | 4.1186 eV 301.04 nm f=0.0059 <S**2>=0.000              |
| 130 ->140                | 0.18931          |                                                        |
| 137 ->142                | -0.10306         |                                                        |
| 139 ->142                | 0.66114          |                                                        |
| Excited State 17:        | Singlet-A        | 4.1267 eV 300.44 nm f=0.0142 <S**2>=0.000              |
| 124 ->140                | 0.43931          |                                                        |
| 124 ->141                | -0.19242         |                                                        |
| 130 ->140                | 0.45937          |                                                        |
| 139 ->142                | -0.20837         |                                                        |
| Excited State 18:        | Singlet-A        | 4.1394 eV 299.52 nm f=0.0134 <S**2>=0.000              |
| 124 ->140                | -0.44658         |                                                        |
| 124 ->141                | 0.19242          |                                                        |
| 130 ->140                | 0.49504          |                                                        |
| Excited State 19:        | Singlet-A        | 4.3818 eV 282.95 nm f=0.0039 <S**2>=0.000              |
| 138 ->142                | 0.69316          |                                                        |
| Excited State 20:        | Singlet-A        | 4.3988 eV 281.86 nm f=0.0036 <S**2>=0.000              |
| 129 ->140                | 0.69013          |                                                        |



Computed electronic spectrum of **12c** (TD-B3LYP/6-311+G(d)).

## 12d:

-----  
Full-sandwich 12d, B97D/6-311+G(d)  
-----

Charge = 0 Multiplicity = 1

C,0,4.1692861232,2.7331212,0.6051003395  
H,0,5.259471731,2.85970789,0.7234716179  
H,0,3.6476737758,3.220817579,1.4416108704  
C,0,3.7409208134,3.314663192,-0.7410280567  
H,0,4.2621422144,4.2722282513,-0.8758185791  
H,0,4.0562550199,2.6306220579,-1.5490234447  
C,0,1.458238533,2.5145467411,-0.9315592869  
H,0,1.9954010073,1.5582710693,-0.9181767011  
H,0,0.885662773,2.589233196,-1.8687348534  
C,0,0.5182149937,2.5987244059,0.2698338725  
H,0,1.0930193282,2.6044548129,1.2078477049  
H,0,-0.0871090251,3.5171371875,0.2191241094  
C,0,-1.2811106244,1.2893854731,1.1866665144  
C,0,-1.5041555484,2.1944908899,2.2330724628  
H,0,-0.9109015815,3.1033162666,2.297425653  
C,0,-2.4548253384,1.9130182172,3.2268037946  
H,0,-2.5998158772,2.6208510646,4.0426900372  
C,0,-3.1992589657,0.7328658332,3.1728994018  
H,0,-3.9391157153,0.5079534914,3.9405775522  
C,0,-2.9950620502,-0.1769189869,2.1223668709  
H,0,-3.5720008016,-1.0982884774,2.0861304816  
C,0,-2.0338217916,0.0810400423,1.1390406866  
C,0,-2.1170833294,-2.1536655129,0.2144763275  
H,0,-3.1573371812,-2.2580724018,-0.140530354  
H,0,-2.0578548106,-2.4993438165,1.2565996369  
C,0,-1.1744015623,-2.9857125961,-0.6511179917  
H,0,-1.6070739721,-3.9907193044,-0.7579222755  
H,0,-1.0801722213,-2.5375269629,-1.6552777861  
C,0,1.0501980409,-2.1232271197,-0.3088607505  
H,0,0.598900251,-1.1334735866,-0.1669046591  
H,0,1.425355759,-2.1917134265,-1.3454111543  
C,0,2.1781611367,-2.3105949697,0.7035195615  
H,0,1.7402484736,-2.3925288682,1.7072095036  
H,0,2.7690444928,-3.2175333366,0.5039501172  
C,0,3.6901055483,-0.7438751526,1.7331771258  
C,0,3.9041132967,-1.5409426044,2.8633008355  
H,0,3.574657428,-2.5779909548,2.8617203759  
C,0,4.529567533,-1.0131962167,4.0096110802  
H,0,4.6764399166,-1.6512821993,4.8805564321  
C,0,4.9492846049,0.312904938,4.0210124063  
H,0,5.4190027271,0.7414188066,4.9055304654



C,0,4.750100116,1.1242125087,2.8863614195  
 H,0,5.077141495,2.159211989,2.9037436979  
 C,0,4.132376378,0.6075452697,1.7367961994  
 O,0,3.8544574523,1.3250023219,0.6142503794  
 O,0,2.3574729807,3.6318696593,-0.8610513137  
 O,0,-0.3378459079,1.4409172478,0.2109789  
 O,0,-1.7098454027,-0.7759538522,0.1227392466  
 O,0,0.1080526481,-3.1720914874,-0.0515852083  
 O,0,3.0137804356,-1.1441919569,0.6129977876  
 C,0,-0.337296186,-0.840777038,4.5035673304  
 C,0,0.1989637084,-0.6878424892,3.2241847458  
 C,0,1.0861640494,0.3620794136,2.9994508673  
 C,0,1.4971794196,1.2238163604,4.0511125733  
 C,0,0.9712269076,0.98848974,5.3566363946  
 C,0,0.0393359785,-0.0156051678,5.578872905  
 H,0,-0.1134471929,-1.3431268398,2.4196120373  
 H,0,1.4474552242,0.5460582404,1.9933794651  
 H,0,1.2728394441,1.6303270533,6.1819105476  
 H,0,-0.4034989069,-0.1745422256,6.5587930247  
 N,0,-1.3566698226,-1.9027271967,4.7272886499  
 O,0,-1.9725248762,-1.8904341843,5.7937914381  
 O,0,-1.5279634933,-2.7289808429,3.8277429334  
 C,0,2.285593913,2.3599756625,3.5903573708  
 Cl,0,2.9304713928,3.3414456427,4.9186358535

SCF Done: E(RB97D) = -2161.53269527 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.031222  
 Sum of electronic and thermal Energies= -2160.996451  
 Sum of electronic and thermal Enthalpies= -2160.995507  
 Sum of electronic and thermal Free Energies= -2161.099173

-----  
 # 6-311+g(d) pop=none rb3lyp td=(add=20) scrf=(cpcm,solvent=dichloroethane)  
 -----

# **Excitation energies and oscillator strengths:**

**Excited State 1: Singlet-A 1.2996 eV 954.00 nm f=0.0134 <S\*\*2>=0.000**  
 137 ->140 0.26357  
 138 ->140 0.36917  
 139 ->140 0.52294

|                         |                  |                  |                  |                 |                           |
|-------------------------|------------------|------------------|------------------|-----------------|---------------------------|
| Excited State 2:        | Singlet-A        | 1.4960 eV        | 828.76 nm        | f=0.0192        | <S**2>=0.000              |
| 138 ->140               | 0.55037          |                  |                  |                 |                           |
| 139 ->140               | -0.43507         |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 3:        | Singlet-A        | 1.6858 eV        | 735.48 nm        | f=0.0119        | <S**2>=0.000              |
| 137 ->140               | 0.62289          |                  |                  |                 |                           |
| 137 ->141               | 0.10397          |                  |                  |                 |                           |
| 138 ->140               | -0.23891         |                  |                  |                 |                           |
| 139 ->140               | -0.17996         |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 4:        | Singlet-A        | 2.3215 eV        | 534.06 nm        | f=0.0086        | <S**2>=0.000              |
| 136 ->140               | 0.70505          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| <b>Excited State 5:</b> | <b>Singlet-A</b> | <b>2.5560 eV</b> | <b>485.07 nm</b> | <b>f=0.0913</b> | <b>&lt;S**2&gt;=0.000</b> |
| 135 ->140               | 0.66988          |                  |                  |                 |                           |
| 137 ->140               | -0.15531         |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 6:        | Singlet-A        | 2.8051 eV        | 441.99 nm        | f=0.0058        | <S**2>=0.000              |
| 138 ->141               | -0.26552         |                  |                  |                 |                           |
| 139 ->141               | 0.64618          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 7:        | Singlet-A        | 2.8395 eV        | 436.64 nm        | f=0.0129        | <S**2>=0.000              |
| 135 ->140               | -0.11189         |                  |                  |                 |                           |
| 138 ->141               | 0.64239          |                  |                  |                 |                           |
| 139 ->141               | 0.23979          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 8:        | Singlet-A        | 3.0331 eV        | 408.78 nm        | f=0.0014        | <S**2>=0.000              |
| 134 ->140               | 0.68911          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 9:        | Singlet-A        | 3.0497 eV        | 406.55 nm        | f=0.0037        | <S**2>=0.000              |
| 133 ->140               | 0.70004          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 10:       | Singlet-A        | 3.2005 eV        | 387.39 nm        | f=0.0126        | <S**2>=0.000              |
| 134 ->140               | 0.10080          |                  |                  |                 |                           |
| 137 ->141               | 0.67049          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 11:       | Singlet-A        | 3.4367 eV        | 360.76 nm        | f=0.0143        | <S**2>=0.000              |
| 132 ->140               | 0.69447          |                  |                  |                 |                           |
|                         |                  |                  |                  |                 |                           |
| Excited State 12:       | Singlet-A        | 3.5696 eV        | 347.34 nm        | f=0.0275        | <S**2>=0.000              |
| 128 ->140               | 0.48366          |                  |                  |                 |                           |
| 128 ->141               | -0.23103         |                  |                  |                 |                           |
| 129 ->140               | 0.22390          |                  |                  |                 |                           |
| 129 ->141               | -0.10235         |                  |                  |                 |                           |
| 130 ->140               | -0.12293         |                  |                  |                 |                           |
| 131 ->140               | -0.30472         |                  |                  |                 |                           |

136 ->141      -0.13141

Excited State 13:    Singlet-A    3.6642 eV 338.37 nm f=0.0085 <S\*\*2>=0.000  
136 ->141      0.68970

**Excited State 14:    Singlet-A    3.8326 eV 323.50 nm f=0.1370 <S\*\*2>=0.000**  
128 ->140      0.19643  
129 ->140      0.12717  
131 ->140      0.44634  
135 ->141      0.44069

**Excited State 15:    Singlet-A    3.9566 eV 313.36 nm f=0.1717 <S\*\*2>=0.000**  
128 ->140      -0.13712  
131 ->140      -0.39621  
135 ->141      0.53080  
139 ->142      -0.10723

Excited State 16:    Singlet-A    4.0460 eV 306.44 nm f=0.0148 <S\*\*2>=0.000  
138 ->142      0.69413

Excited State 17:    Singlet-A    4.0537 eV 305.86 nm f=0.0676 <S\*\*2>=0.000  
131 ->140      -0.13134  
139 ->142      0.67957

Excited State 18:    Singlet-A    4.0936 eV 302.87 nm f=0.0005 <S\*\*2>=0.000  
122 ->140      0.38878  
122 ->141      -0.16398  
123 ->140      0.45701  
123 ->141      -0.19290  
124 ->140      -0.21684

Excited State 19:    Singlet-A    4.2930 eV 288.81 nm f=0.0049 <S\*\*2>=0.000  
128 ->140      0.30507  
129 ->140      -0.34716  
130 ->140      0.51436

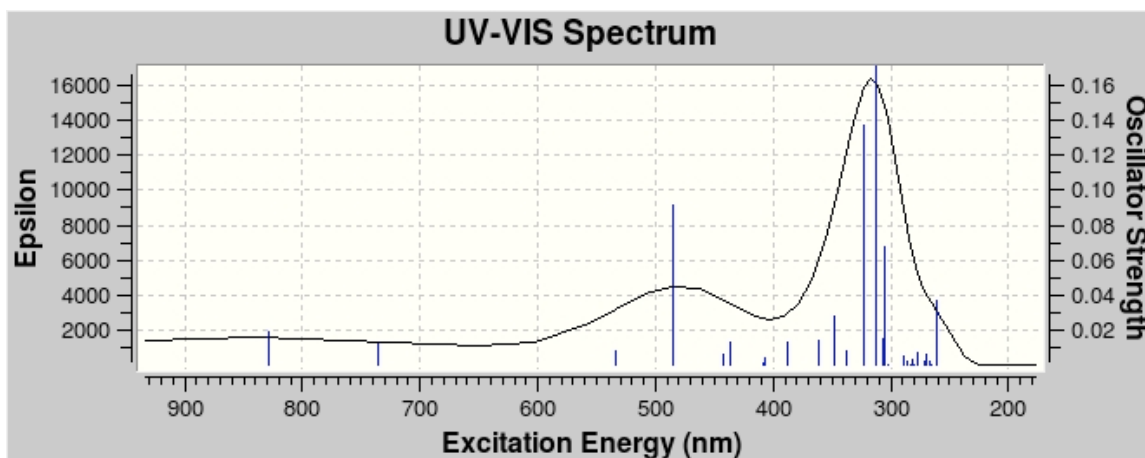
Excited State 20:    Singlet-A    4.3275 eV 286.50 nm f=0.0023 <S\*\*2>=0.000  
128 ->140      -0.13690  
129 ->140      0.53163  
130 ->140      0.43002

Excited State 21:    Singlet-A    4.3857 eV 282.70 nm f=0.0006 <S\*\*2>=0.000  
133 ->141      0.68957  
134 ->141      -0.11498

Excited State 22:    Singlet-A    4.4040 eV 281.53 nm f=0.0034 <S\*\*2>=0.000

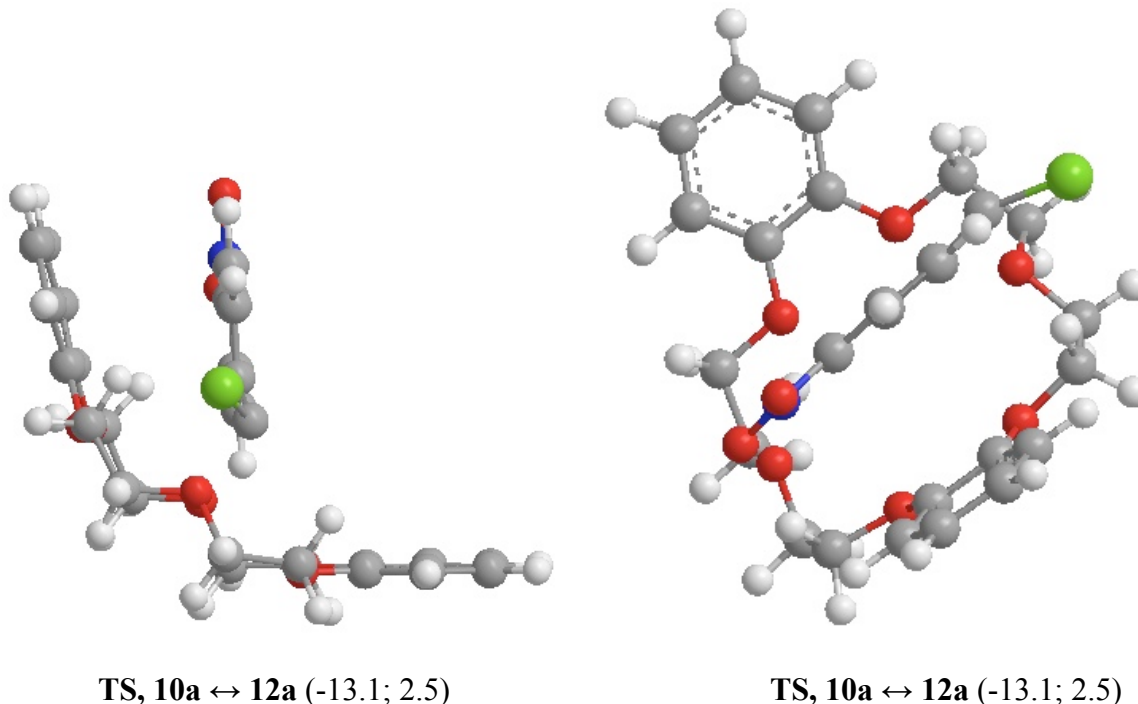
|                   |           |           |           |          |              |
|-------------------|-----------|-----------|-----------|----------|--------------|
| 137 ->142         | 0.68001   |           |           |          |              |
| Excited State 23: | Singlet-A | 4.4322 eV | 279.74 nm | f=0.0004 | <S**2>=0.000 |
| 133 ->141         | 0.12590   |           |           |          |              |
| 134 ->141         | 0.68681   |           |           |          |              |
| Excited State 24: | Singlet-A | 4.4709 eV | 277.31 nm | f=0.0074 | <S**2>=0.000 |
| 126 ->140         | 0.24541   |           |           |          |              |
| 127 ->140         | 0.62881   |           |           |          |              |
| Excited State 25: | Singlet-A | 4.5640 eV | 271.66 nm | f=0.0023 | <S**2>=0.000 |
| 126 ->140         | 0.61933   |           |           |          |              |
| 127 ->140         | -0.25816  |           |           |          |              |
| 130 ->140         | 0.11216   |           |           |          |              |
| Excited State 26: | Singlet-A | 4.5972 eV | 269.70 nm | f=0.0060 | <S**2>=0.000 |
| 117 ->140         | 0.38576   |           |           |          |              |
| 118 ->140         | -0.19408  |           |           |          |              |
| 119 ->140         | 0.33840   |           |           |          |              |
| 120 ->140         | -0.10184  |           |           |          |              |
| 125 ->140         | 0.30797   |           |           |          |              |
| 126 ->140         | 0.16121   |           |           |          |              |
| Excited State 27: | Singlet-A | 4.6401 eV | 267.20 nm | f=0.0021 | <S**2>=0.000 |
| 125 ->140         | 0.12320   |           |           |          |              |
| 132 ->141         | 0.67227   |           |           |          |              |
| Excited State 28: | Singlet-A | 4.6590 eV | 266.12 nm | f=0.0005 | <S**2>=0.000 |
| 117 ->140         | -0.18804  |           |           |          |              |
| 118 ->140         | 0.12263   |           |           |          |              |
| 119 ->140         | -0.13175  |           |           |          |              |
| 124 ->140         | 0.12745   |           |           |          |              |
| 125 ->140         | 0.59880   |           |           |          |              |
| 132 ->141         | -0.15926  |           |           |          |              |
| Excited State 29: | Singlet-A | 4.7402 eV | 261.56 nm | f=0.0369 | <S**2>=0.000 |
| 135 ->145         | 0.15034   |           |           |          |              |
| 136 ->142         | -0.10982  |           |           |          |              |
| 137 ->145         | -0.15306  |           |           |          |              |
| 138 ->143         | 0.21124   |           |           |          |              |
| 138 ->144         | -0.19795  |           |           |          |              |
| 139 ->143         | 0.57102   |           |           |          |              |
| Excited State 30: | Singlet-A | 4.7536 eV | 260.82 nm | f=0.0108 | <S**2>=0.000 |
| 121 ->140         | -0.15186  |           |           |          |              |
| 123 ->140         | 0.17126   |           |           |          |              |

|           |          |
|-----------|----------|
| 124 ->140 | 0.46982  |
| 136 ->142 | 0.17420  |
| 136 ->146 | 0.11841  |
| 138 ->143 | 0.22564  |
| 138 ->144 | 0.22157  |
| 139 ->144 | -0.17899 |



Computed electronic spectrum of **12d** (TD-B3LYP/6-311+G(d)).

## 8. Geometry and Energy of TS for 10a $\leftrightarrow$ 12a Interconversion.



Two views (left, right) are offered for the TS. Enthalpy and Gibbs free energy is shown in parenthesis, relative to free **1** and conformer **3a** (kcal/mol; T = 298.15 K; [] = 1.0 M).

-----  
TS for 10a  $\leftrightarrow$  12a interconversion  
-----

Charge = 0 Multiplicity = 1  
C,0,2.870842609,-2.3682566387,-1.5943844946  
O,0,2.7601204883,-0.9393568774,-1.6435235941  
C,0,1.7076663729,-2.9523295108,-2.3696765208  
O,0,0.5195972466,-2.814450542,-1.5985730773  
C,0,-0.6289549612,-3.2747231618,-2.2919074244  
C,0,3.6091969688,-0.2132912678,-0.8579332247  
C,0,3.3740179411,1.1873295945,-0.8151504827  
C,0,-1.8464852053,-3.1279681846,-1.4016917271  
C,0,0.5403471615,3.2302678254,-1.9309863503  
O,0,-0.5467495101,2.6098274299,-1.1362677188  
C,0,1.9132874057,2.9913809604,-1.3456240205  
O,0,2.2980019933,1.6394842722,-1.5482981754  
C,0,-5.1621444706,-1.8904611642,0.9216744485  
C,0,-5.4902851477,-0.5366717472,0.9598473378  
C,0,-4.7154532141,0.3917475663,0.2432030512  
C,0,-3.6119802043,-0.0292239533,-0.5080392039

C,0,-3.2770552285,-1.4110241825,-0.5514732362  
C,0,-4.0596454316,-2.3260674611,0.1665636649  
O,0,-2.1884746018,-1.740306555,-1.3122126744  
O,0,-2.8014905239,0.808797411,-1.2373121481  
C,0,-1.8498564579,2.9430755747,-1.7236080597  
C,0,-2.9812459875,2.2088422658,-1.0404850934  
C,0,4.6597039478,-0.7536353191,-0.1043099196  
C,0,5.4736202563,0.0727494625,0.686511906  
C,0,5.2559982733,1.4490423839,0.7098799498  
C,0,4.2110495248,2.0048098872,-0.0470263144  
C,0,0.2550938435,0.4555403854,0.5117771599  
C,0,1.0212125006,-0.5892933821,0.9994151614  
C,0,1.8992687124,-0.362940729,2.074963831  
C,0,2.0000251783,0.9038600026,2.6663459282  
C,0,1.2395990646,1.9568388776,2.1648972855  
C,0,0.3562883696,1.7647260362,1.0680888252  
C,0,-0.6030402816,2.7764085903,0.6337184961  
Cl,0,-0.1435473114,4.5093608977,0.9255533862  
N,0,2.7419585062,-1.4592030598,2.5651026174  
O,0,3.4643882611,-1.2534910352,3.5480628044  
O,0,2.6982946469,-2.5428405727,1.9603261365  
H,0,3.8223872101,-2.6856530502,-2.0543238451  
H,0,2.8437590564,-2.7148234113,-0.5515471669  
H,0,1.6000130055,-2.4352343691,-3.3407218361  
H,0,1.9098402352,-4.0230999773,-2.5681160481  
H,0,-0.5169469157,-4.3458607215,-2.553809647  
H,0,-0.772226195,-2.7055796146,-3.2289383606  
H,0,-1.6299274229,-3.5305490139,-0.3994210417  
H,0,-2.6895261718,-3.6918494813,-1.8360257402  
H,0,0.454360261,2.7919477873,-2.933273929  
H,0,0.3481379783,4.3112725399,-1.9682700907  
H,0,2.6084129063,3.672554169,-1.8704514479  
H,0,1.9300903179,3.2512502978,-0.2823733474  
H,0,-5.7518970845,-2.6203221339,1.4760670358  
H,0,-6.3420740445,-0.1867888427,1.5426229824  
H,0,-4.9816977712,1.4458047886,0.2791354709  
H,0,-3.813193955,-3.3850256382,0.1504459092  
H,0,-1.7802644412,2.6643438092,-2.7828999876  
H,0,-2.0033880454,4.0278339979,-1.6264092174  
H,0,-3.9251950671,2.5499204387,-1.5047041966  
H,0,-2.9865956516,2.4504763654,0.0290885788  
H,0,4.8328266772,-1.82633883,-0.1029245173  
H,0,6.2660151749,-0.3749809473,1.2852357947  
H,0,5.8835791137,2.1014068951,1.3166639883  
H,0,4.0525208682,3.0803986975,-0.0153498985  
H,0,-0.4211023774,0.2690175429,-0.3169283512

H,0,0.9473556439,-1.5703001255,0.5425399668  
H,0,2.6959641434,1.0605532955,3.4861950318  
H,0,1.3359374962,2.942257903,2.6161483214

SCF Done: E(RB97D) = -2161.52717613 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -2161.025270  
Sum of electronic and thermal Energies= -2160.992004  
Sum of electronic and thermal Enthalpies= -2160.991060  
Sum of electronic and thermal Free Energies= -2161.089443

\*\*\*\*\* 1 imaginary frequencies (negative Signs) \*\*\*\*\*

Diagonal vibrational polarizability:

148.1569562 110.3584966 169.8296024

Harmonic frequencies (cm<sup>-1</sup>), IR intensities (KM/Mole), Raman scattering activities (A<sup>4</sup>/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

|                | 1         | 2       | 3       |
|----------------|-----------|---------|---------|
|                | A         | A       | A       |
| Frequencies -- | -184.6699 | 20.2140 | 31.8026 |
| Red. masses -- | 8.5025    | 6.2836  | 6.1610  |
| Frc consts --  | 0.1708    | 0.0015  | 0.0037  |
| IR Inten --    | 190.8162  | 0.1820  | 0.0552  |