Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPORTING INFORMATION

Double Oxidation Localizes Spin in a Ni Bis-Phenoxyl Radical Complex

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Supporting Figures

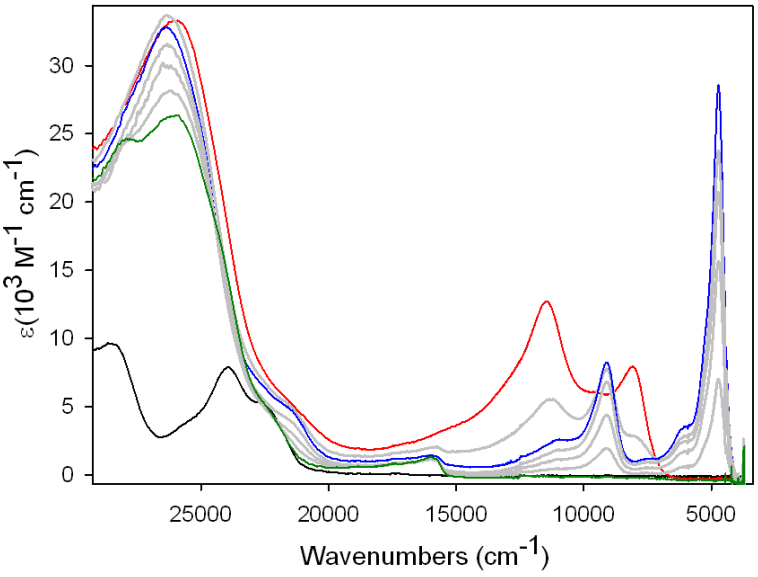

Fig S1. Titration of $[1^{\bullet\bullet}]^{2+}$ (red) to $[1^{\bullet}]^{+}$ (blue) with one equivalent of Ferrocene. $[1^{\bullet}]^{+}$ was recovered in quantitative yield providing evidence for the stability of $[1^{\bullet\bullet}]^{2+}$ under these conditions. Further titration of $[1^{\bullet}]^{+}$ (blue) to 1 (green) also shown. Conditions: 0.25 mM complex in CH_2Cl_2, 198 K.

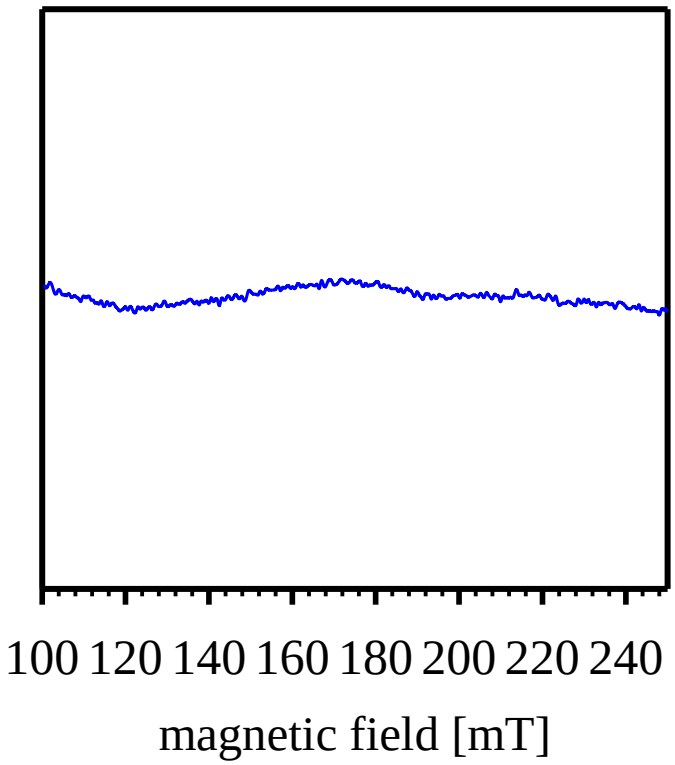

Fig S2. Expansion of the X-Band EPR spectrum for $[1^{\bullet\bullet}]^{2+}$ in the half-field region showing a lack of signal. Conditions: 0.33 mM; frequency, 9.384 GHz; power, 2.0 mW; modulation frequency, 100 kHz; amplitude, 0.6 mT; T = 20 K.

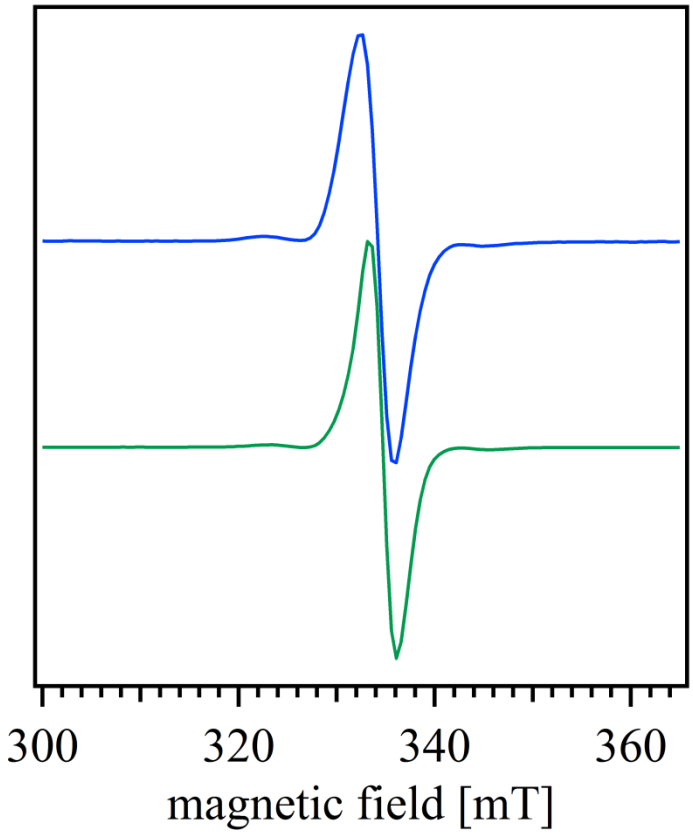

Fig S3. Comparison of $[\mathbf{1}^{\bullet\bullet}]^{2+}$ and chemical oxidant. X-Band EPR spectrum of $[\mathbf{1}^{\bullet\bullet}]^{2+}$ in CH_2Cl_2 solution (blue line) and chemical oxidant spectrum (green). Both spectra were normalized for comparison. Conditions: frequency, 9.384 GHz; power, 2.0 mW; modulation frequency, 100 kHz; amplitude, 0.6 mT; T = 20 K.

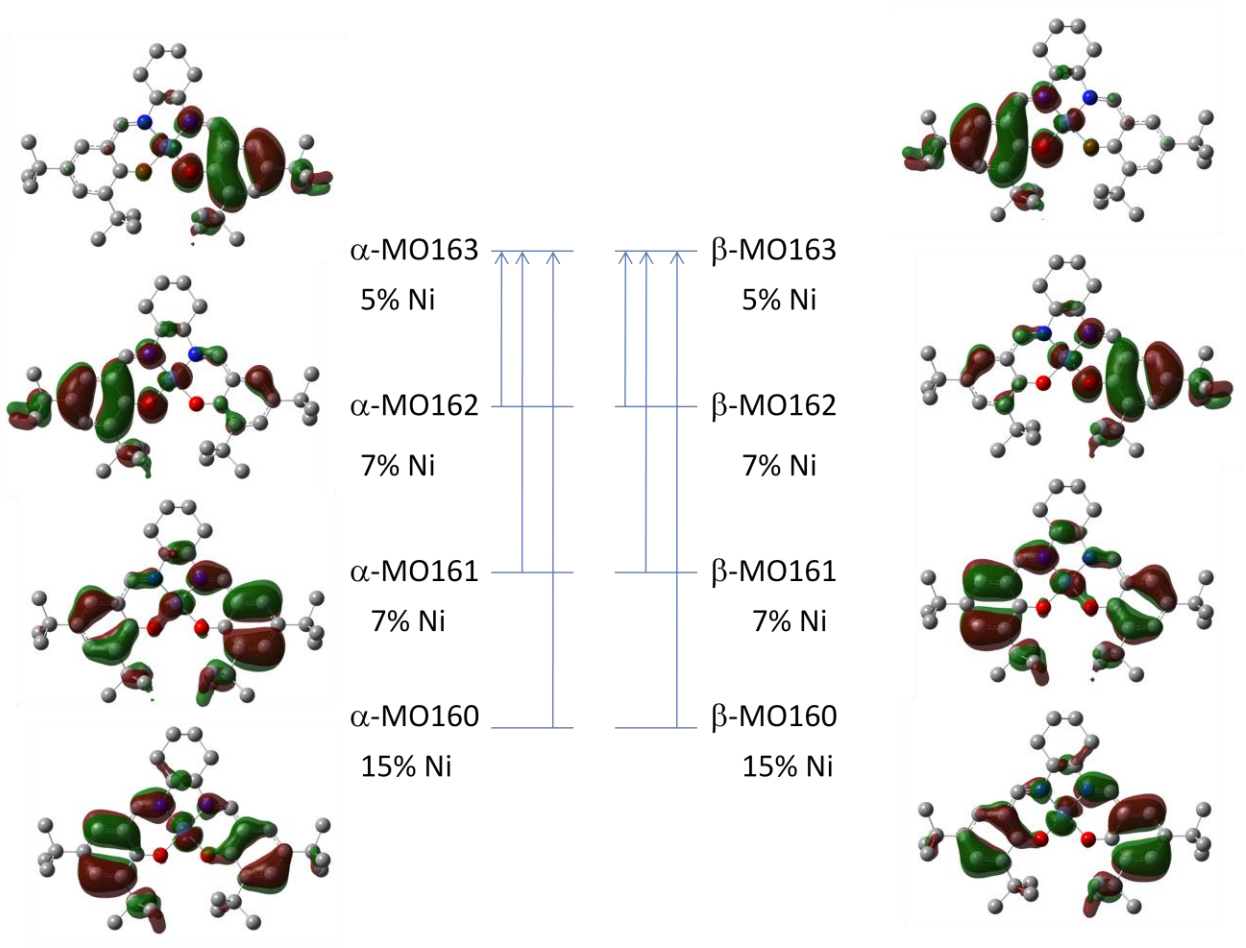

Fig S4. Partial Kohn-Sham molecular orbital diagram for the broken symmetry solution for $[1^{\bullet\bullet}]^{2+}$ and TD-DFT assignment of the low energy transitions at 9780 cm^{-1} (α/β-MO162 → (α/β-MO163), 12400 cm^{-1} (α/β-MO161 → (α/β-MO163), and 14300 cm^{-1} (α/β-MO160 → (α/β-MO163). Molecular orbital compositions calculated using AOMIX.[1]

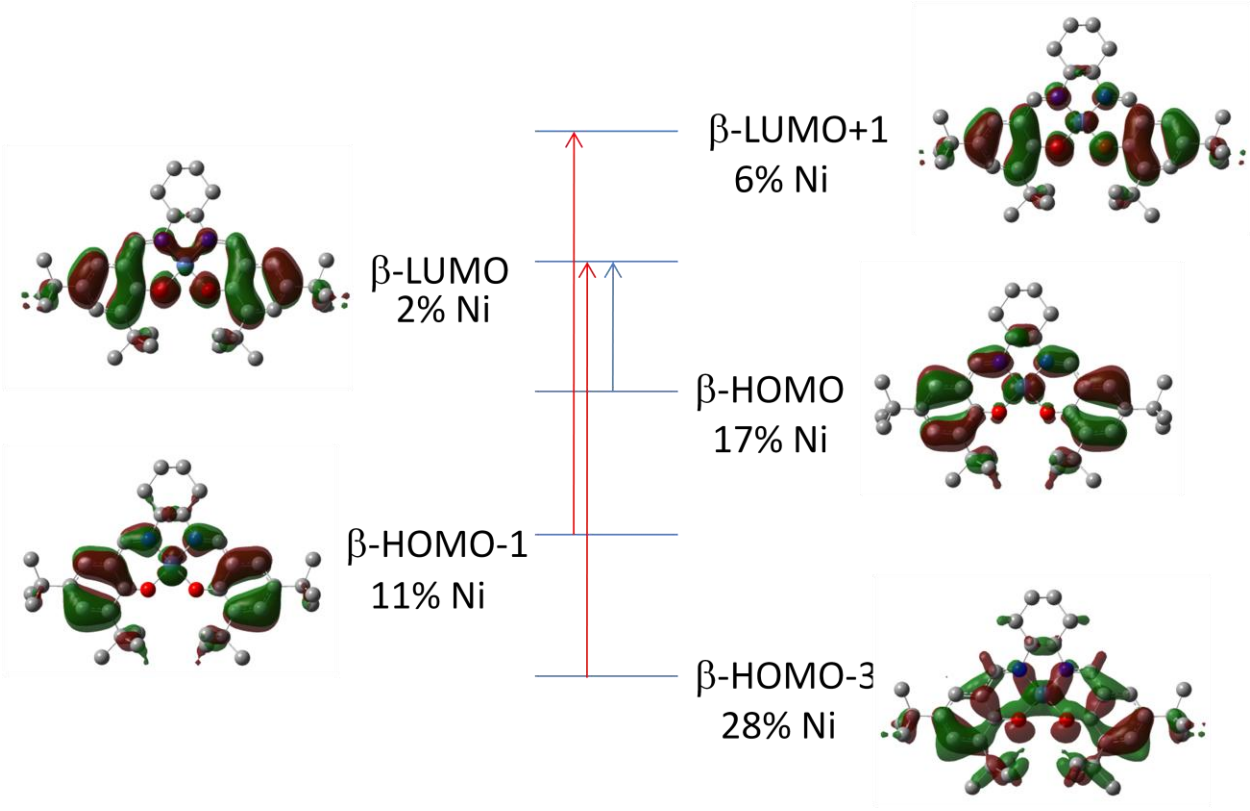

Fig S5. Selected Kohn-Sham molecular orbitals of the triplet solution for $[1^{\bullet\bullet}]^{2+}$ and TD-DFT assignment of the low energy transitions at 10250 cm^{-1} (β-HOMO → (β-LUMO), and 13900 cm^{-1} (β-HOMO-1 → β-LUMO+1 / β-HOMO-3 → β-LUMO). Molecular orbital compositions calculated using AOMIX.[1]

3. Calculation Details

A) Optimized XYZ coordinates (Å) for $[1^{\bullet\bullet}]^{2+}$(broken symmetry).

Ni	-0.00001400	0.76215100	-0.00000700
O	1.28034800	-0.57126100	0.04528900
O	-1.28037000	-0.57126700	-0.04530900
N	1.23880100	2.09809500	-0.29492900
N	-1.23883600	2.09808800	0.29492300
C	2.56021900	-0.52019400	0.04115600
C	3.25050500	0.73440700	-0.20071800
C	4.63495300	0.77789000	-0.26530700
C	5.42186100	-0.38324300	-0.07955700
C	4.73415700	-1.59464300	0.19156600
C	3.35810000	-1.72991900	0.27167100
C	2.52293100	1.96486900	-0.37276200
C	-2.56024100	-0.52020400	-0.04116200

C	-3.25053300	0.73439100	0.20072100
C	-4.63498100	0.77786200	0.26532000
C	-5.42187800	-0.38327800	0.07957200
C	-4.73416600	-1.59467100	-0.19157000
C	-3.35810600	-1.72993300	-0.27169700
C	-2.52296500	1.96485500	0.37276800
C	0.58573000	3.42037800	-0.49572600
C	-0.58577200	3.42037500	0.49571800
C	6.94399300	-0.36538500	-0.14655400
C	-6.94401000	-0.36543800	0.14658300
C	2.70349600	-3.07700700	0.59148500
C	-2.70343700	-3.07699900	-0.59150300
C	1.85175800	-2.94422200	1.88316200
C	3.74813700	-4.18451400	0.83859800
C	1.82347200	-3.51771700	-0.60789900
C	-1.85167900	-2.94415300	-1.88315700
C	-1.82338900	-3.51763100	0.60788800
C	-3.74797200	-4.18460800	-0.83863200
H	5.12053900	1.72810500	-0.45787900
H	5.33804000	-2.47694100	0.35086900
H	3.12438900	2.84796200	-0.58113300
H	-5.12057200	1.72807100	0.45790600
H	-5.33804900	-2.47696800	-0.35086200
H	-3.12442500	2.84794400	0.58114700
H	0.16337000	3.39444700	-1.51082500
H	-0.16341200	3.39444900	1.51081700
H	1.39344300	-3.91205000	2.11112600
H	1.05432700	-2.20623200	1.78154000
H	2.47897900	-2.66617400	2.73742200
H	4.36711800	-4.38058900	-0.04390300
H	3.22450400	-5.11502900	1.07596000
H	4.40301400	-3.95755400	1.68714300
H	2.42938300	-3.64022300	-1.51241100
H	1.02587300	-2.80395600	-0.81497100
H	1.36811500	-4.48704000	-0.37972800
H	-1.05431900	-2.20608800	-1.78151700
H	-2.47890200	-2.66617000	-2.73743600
H	-1.39326900	-3.91194200	-2.11109800
H	-1.02586400	-2.80379100	0.81497300
H	-1.36793300	-4.48690900	0.37972000
H	-2.42930100	-3.64019900	1.51239200
H	-3.22424500	-5.11508100	-1.07595200
H	-4.40283400	-3.95773200	-1.68721000
H	-4.36696800	-4.38072200	0.04384900
C	1.45918600	4.66936200	-0.35198100
H	2.24097800	4.68615000	-1.11942100
H	1.95421500	4.66292700	0.62901500
C	0.58621900	5.93177900	-0.49390200
H	1.21129400	6.81636300	-0.33767800
H	0.20649400	5.99700100	-1.52227000
C	-1.45923600	4.66935300	0.35197000
H	-1.95426500	4.66291200	-0.62902600
H	-2.24102800	4.68613900	1.11941000
C	-0.58627700	5.93177600	0.49388700
H	-1.21135800	6.81635600	0.33766100
H	-0.20655200	5.99700400	1.52225500

C	-7.50855800	1.03322900	0.46022700
H	-7.16787600	1.40993300	1.43173300
H	-7.25359600	1.76638800	-0.31379100
H	-8.60000400	0.97995000	0.50274800
C	-7.40817700	-1.34923200	1.25732500
H	-8.50195400	-1.34534000	1.29999200
H	-7.08960400	-2.37825000	1.06511400
H	-7.02975200	-1.04909500	2.24009300
C	-7.50981400	-0.83471700	-1.22361900
H	-7.19320400	-1.85005000	-1.48120000
H	-8.60335800	-0.83181600	-1.17538700
H	-7.20458800	-0.16272000	-2.03257000
C	7.50979400	-0.83465800	1.22365100
H	7.19320400	-1.84999900	1.48122500
H	8.60333900	-0.83173300	1.17543000
H	7.20454600	-0.16267200	2.03260200
C	7.50852400	1.03329100	-0.46018900
H	7.16785000	1.40999000	-1.43170100
H	7.25353700	1.76644500	0.31382400
H	8.59997100	0.98002900	-0.50269400
C	7.40818400	-1.34916800	-1.25729700
H	8.50196100	-1.34525500	-1.29996000
H	7.08963000	-2.37819300	-1.06508900
H	7.02975800	-1.04903600	-2.24006500

B) TD-DFT excitation energies and oscillator strengths for $[\mathbf{1}^{\bullet\bullet}]^{2+}$(broken symmetry).

Excited State 1: 3.578-A 0.5587 eV 2219.15 nm f=0.0000 <S**2>=2.951
157A -> 164A 0.10344
159A -> 164A -0.74416
159A -> 165A 0.18711
161A -> 164A -0.12789
157B -> 164B -0.10344
159B -> 164B 0.74416
159B -> 165B -0.18710
161B -> 164B -0.12789
159A <- 164A -0.35118
159B <- 164B 0.35118
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3171.74545874
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.435-A 1.0199 eV 1215.65 nm f=0.0000 <S**2>=2.700
140A -> 164A 0.12969
147A -> 164A 0.13807
156A -> 164A 0.18713
157A -> 164A 0.24492
158A -> 164A 0.33894
160A -> 164A 0.18113
161A -> 164A -0.27134
162A -> 164A 0.32420
140B -> 164B -0.12969
147B -> 164B -0.13805
156B -> 164B 0.18712
157B -> 164B -0.24493

158B -> 164B -0.33894
160B -> 164B -0.18113
161B -> 164B -0.27134
162B -> 164B 0.32420
158A <- 164A 0.10073
158B <- 164B -0.10072

Excited State 3: 3.550-A 1.1069 eV 1120.07 nm f=0.0000 <S**2>=2.901
156A -> 164A -0.49975
156A -> 165A 0.12596
157A -> 164A 0.22172
160A -> 164A 0.39041
162A -> 164A -0.13139
156B -> 164B 0.49976
156B -> 165B -0.12596
157B -> 164B 0.22170
160B -> 164B 0.39041
162B -> 164B 0.13139
156A <- 164A -0.13797
160A <- 164A 0.10115
156B <- 164B 0.13797
160B <- 164B 0.10115

Excited State 4: 1.586-A 1.2087 eV 1025.74 nm f=0.0058 <S**2>=0.379
160A -> 163A -0.13376
161A -> 163A -0.21713
162A -> 163A 0.65452
160B -> 163B 0.13403
161B -> 163B -0.21803
162B -> 163B 0.65590

Excited State 5: 1.827-A 1.2124 eV 1022.64 nm f=0.1460 <S**2>=0.585
160A -> 163A -0.11581
161A -> 163A -0.37868
162A -> 163A 0.57561
160B -> 163B -0.11548
161B -> 163B 0.37816
162B -> 163B -0.57405

Excited State 6: 2.154-A 1.4933 eV 830.27 nm f=0.0116 <S**2>=0.910
159A -> 163A 0.11024
160A -> 163A 0.35563
161A -> 163A 0.53419
162A -> 163A 0.25253
159B -> 163B -0.11030
160B -> 163B -0.35565
161B -> 163B 0.53428
162B -> 163B 0.25259

Excited State 7: 2.078-A 1.5369 eV 806.73 nm f=0.0488 <S**2>=0.829
159A -> 163A 0.33232
160A -> 163A 0.17620
161A -> 163A 0.48818
162A -> 163A 0.32797
159B -> 163B 0.33232
160B -> 163B 0.17612

161B -> 163B -0.48809
162B -> 163B -0.32792

Excited State 8: 2.317-A 1.6347 eV 758.47 nm f=0.0146 <S**2>=1.092
158A -> 163A -0.15980
159A -> 163A 0.58897
160A -> 163A -0.21808
161A -> 163A -0.18041
162A -> 163A -0.19042
158B -> 163B -0.15984
159B -> 163B 0.58914
160B -> 163B -0.21811
161B -> 163B 0.18041
162B -> 163B 0.19042

Excited State 9: 2.068-A 1.6623 eV 745.87 nm f=0.0009 <S**2>=0.819
158A -> 163A -0.14007
159A -> 163A 0.65147
160A -> 163A -0.20719
158B -> 163B 0.14004
159B -> 163B -0.65132
160B -> 163B 0.20713

Excited State 10: 2.246-A 1.7707 eV 700.19 nm f=0.0896 <S**2>=1.011
156A -> 163A -0.11530
157A -> 163A 0.13823
158A -> 163A 0.28086
159A -> 163A 0.16735
159A -> 164A 0.18872
160A -> 163A 0.48768
161A -> 163A -0.24953
162A -> 163A -0.10272
156B -> 163B 0.11532
157B -> 163B 0.13822
158B -> 163B 0.28088
159B -> 163B 0.16735
159B -> 164B 0.18872
160B -> 163B 0.48771
161B -> 163B 0.24953
162B -> 163B 0.10272

Excited State 11: 3.571-A 1.9221 eV 645.05 nm f=0.0002 <S**2>=2.938
117A -> 164A 0.15154
137A -> 164A 0.13117
141A -> 164A 0.20717
142A -> 164A 0.20893
143A -> 164A -0.36358
150A -> 164A 0.16755
157A -> 164A 0.23850
158A -> 164A -0.27475
117B -> 164B -0.15154
137B -> 164B -0.13118
141B -> 164B -0.20717
142B -> 164B -0.20893
143B -> 164B 0.36358
150B -> 164B -0.16754

157B -> 164B -0.23850
158B -> 164B 0.27475

Excited State 12: 2.245-A 1.9650 eV 630.96 nm f=0.0206 <S**2>=1.010
156A -> 163A 0.24781
159A -> 163A -0.19505
160A -> 163A -0.49553
161A -> 163A 0.36080
156B -> 163B 0.24782
159B -> 163B 0.19503
160B -> 163B 0.49553
161B -> 163B 0.36078

Excited State 13: 2.387-A 1.9926 eV 622.24 nm f=0.0070 <S**2>=1.175
154A -> 163A -0.10528
155A -> 163A 0.13780
157A -> 163A -0.35757
158A -> 163A 0.50704
159A -> 164A -0.11764
160A -> 163A -0.15878
154B -> 163B -0.10537
155B -> 163B 0.13789
157B -> 163B -0.35785
158B -> 163B 0.50746
159B -> 164B -0.11764
160B -> 163B -0.15881

Excited State 14: 2.134-A 2.0270 eV 611.65 nm f=0.0002 <S**2>=0.888
154A -> 163A -0.12205
155A -> 163A 0.17200
157A -> 163A -0.35608
158A -> 163A 0.51516
159A -> 163A 0.10635
154B -> 163B 0.12196
155B -> 163B -0.17184
157B -> 163B 0.35582
158B -> 163B -0.51477
159B -> 163B -0.10629

Excited State 15: 2.227-A 2.2200 eV 558.49 nm f=0.0237 <S**2>=0.989
156A -> 163A -0.25735
157A -> 163A -0.13195
159A -> 164A 0.56111
159A -> 165A -0.13608
160A -> 163A -0.20443
156B -> 163B 0.25736
157B -> 163B -0.13196
159B -> 164B 0.56111
159B -> 165B -0.13607
160B -> 163B -0.20443

Excited State 16: 2.282-A 2.3008 eV 538.87 nm f=0.0001 <S**2>=1.051
147A -> 164A -0.10080
156A -> 163A -0.10958
156A -> 164A -0.12829
157A -> 164A -0.21966

158A -> 164A -0.27573
160A -> 164A -0.19826
161A -> 164A 0.25557
162A -> 164A -0.40811
147B -> 164B -0.10079
156B -> 163B 0.10958
156B -> 164B 0.12829
157B -> 164B -0.21967
158B -> 164B -0.27573
160B -> 164B -0.19826
161B -> 164B -0.25557
162B -> 164B 0.40811

Excited State 17: 2.321-A 2.3611 eV 525.12 nm f=0.0078 <S**2>=1.097
156A -> 163A -0.43409
157A -> 163A -0.33722
158A -> 163A -0.22741
159A -> 164A -0.22174
160A -> 163A 0.22705
156B -> 163B 0.43414
157B -> 163B -0.33725
158B -> 163B -0.22742
159B -> 164B -0.22174
160B -> 163B 0.22703

Excited State 18: 2.302-A 2.4410 eV 507.92 nm f=0.0000 <S**2>=1.075
156A -> 163A 0.52451
156A -> 164A -0.24566
157A -> 164A 0.12742
160A -> 163A 0.16287
160A -> 164A 0.24207
161A -> 163A -0.12231
156B -> 163B 0.52448
156B -> 164B -0.24566
157B -> 164B -0.12741
160B -> 163B -0.16289
160B -> 164B -0.24208
161B -> 163B -0.12231

Excited State 19: 2.262-A 2.4648 eV 503.02 nm f=0.0001 <S**2>=1.029
155A -> 163A -0.12465
156A -> 163A 0.36971
156A -> 164A 0.34816
157A -> 164A -0.17895
160A -> 163A 0.10121
160A -> 164A -0.32846
160A -> 165A 0.10912
162A -> 164A 0.12097
155B -> 163B 0.12461
156B -> 163B 0.36968
156B -> 164B 0.34817
157B -> 164B 0.17894
160B -> 163B -0.10121
160B -> 164B 0.32846
160B -> 165B -0.10912
162B -> 164B 0.12097

Excited State 20: 2.132-A 2.6028 eV 476.35 nm f=0.0058 <S**2>=0.886
156A -> 163A -0.44058
157A -> 163A 0.39588
158A -> 163A 0.21626
159A -> 164A -0.17334
160A -> 163A -0.21192
156B -> 163B 0.44059
157B -> 163B 0.39588
158B -> 163B 0.21626
159B -> 164B -0.17334
160B -> 163B -0.21192

Excited State 21: 2.185-A 2.6561 eV 466.79 nm f=0.0028 <S**2>=0.943
155A -> 163A -0.14428
157A -> 163A 0.50945
158A -> 163A 0.40360
160A -> 163A -0.14160
155B -> 163B 0.14425
157B -> 163B -0.50945
158B -> 163B -0.40357
160B -> 163B 0.14159

Excited State 22: 2.200-A 2.7960 eV 443.44 nm f=0.0366 <S**2>=0.960
117A -> 164A 0.13472
137A -> 164A 0.13028
141A -> 164A 0.20306
142A -> 164A 0.20176
143A -> 164A -0.34693
150A -> 164A 0.16311
157A -> 164A 0.24101
158A -> 164A -0.29395
117B -> 164B 0.13472
137B -> 164B 0.13029
141B -> 164B 0.20306
142B -> 164B 0.20176
143B -> 164B -0.34693
150B -> 164B 0.16310
157B -> 164B 0.24100
158B -> 164B -0.29396

Excited State 23: 2.138-A 2.8492 eV 435.15 nm f=0.0069 <S**2>=0.893
150A -> 163A 0.12105
155A -> 163A 0.63660
157A -> 163A 0.13888
150B -> 163B 0.12082
155B -> 163B 0.63497
157B -> 163B 0.13819

Excited State 24: 2.382-A 2.8542 eV 434.39 nm f=0.0001 <S**2>=1.169
155A -> 163A -0.61186
157A -> 163A -0.22372
155B -> 163B 0.61361
157B -> 163B 0.22403

Excited State 25: 2.347-A 2.9747 eV 416.80 nm f=0.0003 <S**2>=1.127

143A -> 163A -0.10020
150A -> 163A -0.19242
152A -> 163A 0.28609
153A -> 163A -0.15785
154A -> 163A -0.54962
157A -> 163A 0.10895
143B -> 163B 0.10085
150B -> 163B 0.19326
152B -> 163B -0.28762
153B -> 163B -0.15855
154B -> 163B 0.55254
157B -> 163B -0.10937

Excited State 26: 2.202-A 2.9798 eV 416.09 nm f=0.0054 <S**2>=0.963
143A -> 163A 0.12371
150A -> 163A 0.17593
152A -> 163A -0.30848
153A -> 163A 0.14529
154A -> 163A 0.55460
143B -> 163B 0.12320
150B -> 163B 0.17487
152B -> 163B -0.30694
153B -> 163B -0.14443
154B -> 163B 0.55181

Excited State 27: 2.462-A 3.0556 eV 405.77 nm f=0.1044 <S**2>=1.265
140A -> 163A -0.16303
147A -> 163A -0.20953
150A -> 163A -0.10375
151A -> 163A -0.41141
153A -> 163A 0.28455
155A -> 163A -0.10100
160A -> 165A -0.14962
161A -> 166A 0.11143
162A -> 165A 0.20802
140B -> 163B -0.16304
147B -> 163B -0.20952
150B -> 163B -0.10375
151B -> 163B 0.41149
153B -> 163B -0.28458
155B -> 163B -0.10102
160B -> 165B -0.14961
161B -> 166B -0.11145
162B -> 165B -0.20802

Excited State 28: 2.505-A 3.0967 eV 400.37 nm f=0.0000 <S**2>=1.318
140A -> 163A 0.14849
147A -> 163A 0.18250
151A -> 163A 0.45956
153A -> 163A -0.27547
155A -> 163A 0.10064
160A -> 165A -0.14442
161A -> 165A 0.11788
161A -> 166A -0.11824
162A -> 165A 0.10414
140B -> 163B -0.14846

147B -> 163B -0.18244
151B -> 163B 0.45951
153B -> 163B -0.27541
155B -> 163B -0.10063
160B -> 165B 0.14443
161B -> 165B 0.11789
161B -> 166B -0.11822
162B -> 165B 0.10418

Excited State 29: 2.305-A 3.1564 eV 392.80 nm f=0.0029 <S**2>=1.079
142A -> 163A 0.10076
148A -> 163A -0.10335
149A -> 163A -0.21178
150A -> 163A 0.54284
152A -> 163A 0.20023
153A -> 163A 0.19173
154A -> 163A -0.16077
155A -> 163A -0.11248
142B -> 163B 0.10089
148B -> 163B -0.10349
149B -> 163B -0.21209
150B -> 163B 0.54360
152B -> 163B 0.20054
153B -> 163B -0.19199
154B -> 163B -0.16099
155B -> 163B -0.11260

Excited State 30: 2.254-A 3.1581 eV 392.59 nm f=0.0005 <S**2>=1.020
149A -> 163A -0.23642
150A -> 163A 0.53805
152A -> 163A 0.21744
153A -> 163A 0.16862
154A -> 163A -0.18851
149B -> 163B 0.23611
150B -> 163B -0.53731
152B -> 163B -0.21714
153B -> 163B 0.16837
154B -> 163B 0.18825

C) Optimized XYZ coordinates (Å) for $[1^{\bullet\bullet}]^{2+}$(triplet).

Ni	0.00007045	0.75964170	0.00003801
O	-1.28234476	-0.57684337	-0.04930790
O	1.28222339	-0.57701264	0.04842518
N	-1.23915917	2.09729642	0.29934317
N	1.23916972	2.09726804	-0.29908212
C	-2.56178410	-0.52157436	-0.04365316
C	-3.24987774	0.73154087	0.20391892
C	-4.63357553	0.77555039	0.26989512
C	-5.42443691	-0.38527591	0.08143795
C	-4.73945143	-1.59449578	-0.19702582
C	-3.36258979	-1.72960846	-0.28011511
C	-2.52214251	1.96359081	0.37813931
C	2.56171150	-0.52179491	0.04346007
C	3.24977582	0.73136210	-0.20396301
C	4.63346853	0.77547923	-0.26976453

C	5.42437970	-0.38527536	-0.08122664
C	4.73946522	-1.59454398	0.19719864
C	3.36257558	-1.72978128	0.28029565
C	2.52210947	1.96343968	-0.37830601
C	-0.58390218	3.41884926	0.49807518
C	0.58387648	3.41876207	-0.49805480
C	-6.94636142	-0.36378957	0.15356294
C	6.94632930	-0.36356444	-0.15294129
C	-2.70907309	-3.07446011	-0.60935869
C	2.70915384	-3.07494689	0.60902061
C	-1.85335390	-2.93371120	-1.89786776
C	-3.75426394	-4.17904973	-0.86741464
C	-1.83149212	-3.52529569	0.58844879
C	1.85346259	-2.93494426	1.89764536
C	1.83154173	-3.52494870	-0.58912107
C	3.75429331	-4.17967541	0.86667519
H	-5.11855330	1.72544962	0.46588920
H	-5.34363467	-2.47592119	-0.36021641
H	-3.12446122	2.84591159	0.58789914
H	5.11839121	1.72538800	-0.46583607
H	5.34373537	-2.47589080	0.36042761
H	3.12442089	2.84563893	-0.58858287
H	-0.15790235	3.39221643	1.51176710
H	0.15785919	3.39197325	-1.51173189
H	-1.40162368	-3.90251129	-2.13456089
H	-1.05101332	-2.20258517	-1.78621640
H	-2.47637682	-2.64271398	-2.75091121
H	-4.37527828	-4.38186572	0.01212496
H	-3.23109287	-5.10813918	-1.11123831
H	-4.40728493	-3.94465339	-1.71539782
H	-2.43909075	-3.65481982	1.49082955
H	-1.03384837	-2.81358485	0.80239605
H	-1.37662607	-4.49306155	0.35273160
H	1.05153366	-2.20335485	1.78667516
H	2.47677436	-2.64495312	2.75082551
H	1.40135555	-3.90375035	2.13360217
H	1.03416157	-2.81276297	-0.80244534
H	1.37636581	-4.49273193	-0.35403951
H	2.43913881	-3.65397759	-1.49155816
H	3.23112861	-5.10884877	1.11010760
H	4.40699347	-3.94523334	1.71486622
H	4.37547507	-4.38208143	-0.01283125
C	-1.45737217	4.66821879	0.35806487
H	-2.23630387	4.68466830	1.12845764
H	-1.95620295	4.66186612	-0.62103479
C	-0.58407305	5.93066438	0.49632871
H	-1.20978698	6.81528601	0.34278228
H	-0.19979770	5.99600459	1.52300340
C	1.45736136	4.66817776	-0.35826881
H	1.95625096	4.66192152	0.62080125
H	2.23624980	4.68453464	-1.12870618
C	0.58406426	5.93060124	-0.49665707
H	1.20977413	6.81524828	-0.34323054
H	0.19976889	5.99582493	-1.52333304
C	7.50645331	1.03464211	-0.47659299
H	7.16150679	1.40522268	-1.44897129

H	7.25303297	1.77166492	0.29427641
H	8.59784149	0.98339387	-0.52283371
C	7.41047818	-1.35285817	-1.25873849
H	8.50412663	-1.34674376	-1.30394652
H	7.09462149	-2.38134716	-1.05938246
H	7.02915295	-1.05968879	-2.24251043
C	7.51722323	-0.82270109	1.21867786
H	7.20354294	-1.83711107	1.48340851
H	8.61062254	-0.81752483	1.16749719
H	7.21261203	-0.14630414	2.02420578
C	-7.51754201	-0.82265527	-1.21804631
H	-7.20381726	-1.83696088	-1.48312111
H	-8.61093227	-0.81761516	-1.16662309
H	-7.21320487	-0.14601856	-2.02347696
C	-7.50661122	1.03424963	0.47772264
H	-7.16100841	1.40488000	1.44984866
H	-7.25398993	1.77137575	-0.29330928
H	-8.59794811	0.98269357	0.52478121
C	-7.41005907	-1.35345012	1.25919801
H	-8.50369418	-1.34749120	1.30471888
H	-7.09411787	-2.38183903	1.05945019
H	-7.02848878	-1.06051392	2.24294492

D) TD-DFT excitation energies and oscillator strengths for $[1^{\bullet\bullet}]^{2+}$(triplet).

Excited State 1: 4.134-A 0.4952 eV 2503.76 nm f=0.0001 <S**2>=4.023
159A -> 164A -0.64205
159A -> 165A -0.21109
161A -> 164A -0.42262
161A -> 165A -0.13716
157B -> 164B -0.13807
159B -> 164B 0.77785
159B -> 165B 0.12719
159A <- 164A -0.32318
159A <- 165A -0.10715
161A <- 164A -0.21187
159B <- 164B 0.40004
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3171.74663748
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 3.976-A 0.9301 eV 1333.04 nm f=0.0000 <S**2>=3.702
140A -> 164A -0.11242
144A -> 164A 0.11033
147A -> 164A -0.17305
156A -> 164A -0.41016
156A -> 165A -0.13335
158A -> 164A -0.24657
161A -> 164A 0.22463
163A -> 164A -0.43211
163A -> 165A -0.13828
139B -> 164B 0.11919
148B -> 164B 0.14760
157B -> 164B 0.19499
158B -> 164B 0.38297
161B -> 164B 0.46531

156A <- 164A -0.12395
163A <- 164A -0.10123
158B <- 164B 0.12990
161B <- 164B 0.14873

Excited State 3: 4.113-A 1.0845 eV 1143.21 nm f=0.0000 <S**2>=3.979
157A -> 164A -0.53919
157A -> 165A -0.17837
160A -> 164A 0.38151
160A -> 165A 0.12499
162A -> 164A -0.19427
156B -> 164B 0.56976
160B -> 164B 0.39881
157A <- 164A -0.14974
156B <- 164B 0.16513
160B <- 164B 0.10645

Excited State 4: 3.037-A 1.2704 eV 975.94 nm f=0.0637 <S**2>=2.056
159B -> 162B -0.10361
160B -> 163B -0.39332
161B -> 162B 0.89939

Excited State 5: 3.033-A 1.3569 eV 913.74 nm f=0.0151 <S**2>=2.050
158B -> 163B 0.11685
159B -> 163B 0.11319
160B -> 162B 0.86126
161B -> 163B -0.46054

Excited State 6: 3.030-A 1.5534 eV 798.13 nm f=0.0127 <S**2>=2.045
158B -> 162B -0.17875
159B -> 162B 0.96795

Excited State 7: 3.029-A 1.6370 eV 757.39 nm f=0.0002 <S**2>=2.043
158B -> 163B -0.22145
159B -> 163B 0.94581
160B -> 162B -0.15004
161B -> 163B -0.10053

Excited State 8: 3.025-A 1.7222 eV 719.94 nm f=0.1241 <S**2>=2.038
159A -> 164A 0.13137
156B -> 163B 0.16542
158B -> 162B 0.68079
159B -> 162B 0.13375
159B -> 164B 0.15309
160B -> 163B 0.55510
161B -> 162B 0.30140

Excited State 9: 3.026-A 1.8514 eV 669.69 nm f=0.0102 <S**2>=2.039
158B -> 163B 0.29035
159B -> 163B 0.22585
160B -> 162B 0.38202
161B -> 163B 0.81874

Excited State 10: 3.029-A 1.8896 eV 656.14 nm f=0.0165 <S**2>=2.044
159A -> 164A -0.16125
161A -> 164A -0.11818

155B -> 163B 0.16169
156B -> 163B -0.33647
157B -> 162B -0.48980
158B -> 162B 0.49285
159B -> 162B 0.15774
159B -> 164B -0.17731
160B -> 163B -0.45407
161B -> 162B -0.16814

Excited State 11: 4.131-A 1.8968 eV 653.64 nm f=0.0000 <S**2>=4.016
117A -> 164A -0.14566
136A -> 164A 0.12750
142A -> 164A 0.27015
143A -> 164A 0.38502
143A -> 165A 0.12654
148A -> 164A 0.12412
150A -> 164A 0.18365
156A -> 164A -0.16861
158A -> 164A 0.32585
158A -> 165A 0.10621
117B -> 164B 0.14853
137B -> 164B -0.11924
141B -> 164B -0.25881
143B -> 164B -0.39493
150B -> 164B -0.19226
157B -> 164B 0.32699
158B -> 164B -0.22118

Excited State 12: 3.030-A 2.0433 eV 606.77 nm f=0.0063 <S**2>=2.046
154B -> 162B -0.16869
155B -> 162B 0.33789
156B -> 162B -0.42925
157B -> 163B -0.41242
158B -> 163B 0.58475
159B -> 163B 0.11981
160B -> 162B -0.17636
161B -> 163B -0.20591

Excited State 13: 3.029-A 2.1037 eV 589.37 nm f=0.0477 <S**2>=2.044
159A -> 164A -0.19740
161A -> 164A -0.11935
155B -> 163B -0.15004
156B -> 163B -0.38057
157B -> 162B 0.73935
158B -> 162B 0.34498
159B -> 164B -0.24098

Excited State 14: 3.030-A 2.1719 eV 570.85 nm f=0.0061 <S**2>=2.046
154B -> 162B -0.11367
155B -> 162B 0.27253
156B -> 162B 0.77086
157B -> 163B -0.49269
161B -> 163B -0.11471

Excited State 15: 3.052-A 2.2104 eV 560.92 nm f=0.0017 <S**2>=2.079
156A -> 164A 0.14025

158A -> 164A 0.14139
159A -> 164A 0.39715
159A -> 165A 0.12489
161A -> 164A 0.14836
163A -> 164A 0.32500
163A -> 165A 0.14543
157B -> 162B 0.19241
158B -> 162B 0.13699
158B -> 164B 0.17608
159B -> 164B 0.51784
160B -> 163B -0.33367
161B -> 162B -0.11020
161B -> 164B 0.31793

Excited State 16: 3.053-A 2.2435 eV 552.64 nm f=0.0001 <S**2>=2.081
156A -> 164A 0.22692
158A -> 164A 0.11409
159A -> 164A -0.20333
161A -> 164A -0.32386
163A -> 164A 0.38331
148B -> 164B 0.10387
157B -> 162B -0.11221
157B -> 164B 0.21007
158B -> 162B -0.14135
158B -> 164B 0.34273
159B -> 164B -0.27695
160B -> 163B 0.30513
161B -> 162B 0.11142
161B -> 164B 0.43181

Excited State 17: 3.024-A 2.4372 eV 508.72 nm f=0.0000 <S**2>=2.036
157A -> 164A 0.44064
157A -> 165A 0.13957
160A -> 164A -0.34983
160A -> 165A -0.11091
162A -> 164A 0.23576
155B -> 162B 0.28647
156B -> 164B 0.51343
160B -> 164B 0.41207

Excited State 18: 3.028-A 2.5346 eV 489.17 nm f=0.0015 <S**2>=2.042
155B -> 162B -0.29224
156B -> 162B 0.43819
157B -> 163B 0.35200
158B -> 163B 0.67207
160B -> 162B -0.21724
161B -> 163B -0.16080

Excited State 19: 3.027-A 2.5561 eV 485.05 nm f=0.0113 <S**2>=2.040
159A -> 164A -0.12900
161A -> 164A -0.10443
156B -> 163B 0.82613
157B -> 162B 0.16944
158B -> 162B 0.24724
159B -> 164B -0.18365
160B -> 163B -0.32936

161B -> 162B -0.15629

Excited State 20: 3.029-A 2.7225 eV 455.41 nm f=0.0001 <S**2>=2.044
150B -> 163B -0.13805
154B -> 162B 0.15545
155B -> 162B 0.75923
156B -> 164B -0.10997
157B -> 163B 0.53797

Excited State 21: 3.025-A 2.7759 eV 446.65 nm f=0.0352 <S**2>=2.037
117A -> 164A 0.12618
136A -> 164A -0.12672
142A -> 164A -0.25910
143A -> 164A -0.35802
143A -> 165A -0.11730
148A -> 164A -0.11864
150A -> 164A -0.17428
156A -> 164A 0.13836
158A -> 164A -0.34559
158A -> 165A -0.11262
117B -> 164B 0.13421
137B -> 164B -0.12146
141B -> 164B -0.25863
143B -> 164B -0.38570
150B -> 164B -0.19377
157B -> 164B 0.34592
158B -> 164B -0.22406

Excited State 22: 3.026-A 2.8606 eV 433.41 nm f=0.0002 <S**2>=2.039
143B -> 163B 0.14079
149B -> 162B 0.17871
151B -> 163B -0.26609
154B -> 162B 0.86876
157B -> 163B -0.27440

Excited State 23: 3.053-A 2.9051 eV 426.78 nm f=0.0311 <S**2>=2.080
143B -> 162B -0.12734
148B -> 162B -0.27999
150B -> 162B -0.15492
152B -> 163B -0.18223
153B -> 162B -0.51961
154B -> 163B -0.10681
155B -> 163B 0.66199
157B -> 162B 0.21744

Excited State 24: 3.131-A 2.9537 eV 419.76 nm f=0.0004 <S**2>=2.201
160A -> 165A -0.13949
161A -> 166A -0.15452
162A -> 165A 0.16873
163A -> 166A -0.12244
140B -> 162B -0.16348
148B -> 163B 0.23719
150B -> 163B -0.13465
152B -> 162B 0.80351
153B -> 163B 0.16930

Excited State 25: 3.028-A 2.9727 eV 417.08 nm f=0.0064 <S**2>=2.042
143B -> 162B -0.14870
147B -> 162B 0.12163
149B -> 163B -0.13679
150B -> 162B 0.42377
151B -> 162B 0.68439
152B -> 163B -0.10544
154B -> 163B -0.48195
155B -> 163B -0.10274

Excited State 26: 3.113-A 3.0137 eV 411.40 nm f=0.0624 <S**2>=2.173
160A -> 166A 0.12024
161A -> 165A 0.12364
162A -> 166A -0.13872
139B -> 162B 0.13860
143B -> 162B -0.14826
148B -> 162B 0.35653
150B -> 162B -0.33208
151B -> 162B 0.16673
152B -> 163B 0.27362
153B -> 162B 0.41971
154B -> 163B -0.21862
155B -> 163B 0.46057
157B -> 162B 0.11130
161B -> 165B 0.11643

Excited State 27: 3.031-A 3.0795 eV 402.62 nm f=0.0056 <S**2>=2.046
147B -> 162B 0.17136
149B -> 163B -0.37417
150B -> 162B 0.58837
151B -> 162B -0.42923
153B -> 162B 0.31360
155B -> 163B 0.34369
157B -> 162B 0.12971

Excited State 28: 3.028-A 3.1062 eV 399.15 nm f=0.0004 <S**2>=2.043
146B -> 162B -0.12911
147B -> 163B -0.10931
149B -> 162B 0.83749
150B -> 163B -0.32470
151B -> 163B 0.19687
152B -> 162B -0.10459
153B -> 163B -0.15393
154B -> 162B -0.18499

Excited State 29: 3.219-A 3.1309 eV 396.00 nm f=0.0096 <S**2>=2.341
160A -> 166A -0.16009
161A -> 165A -0.14736
162A -> 166A -0.26662
163A -> 164A -0.29139
163A -> 165A 0.75986
138B -> 162B 0.11084
145B -> 162B -0.17476
150B -> 162B 0.12461
153B -> 162B -0.10278
160B -> 166B -0.16804

161B -> 165B -0.14918

Excited State 30: 3.328-A 3.1850 eV 389.28 nm f=0.0441 <S**2>=2.519
160A -> 164A 0.10136
160A -> 165A -0.21154
161A -> 166A -0.16581
162A -> 164A 0.13012
162A -> 165A -0.23886
163A -> 166A 0.78144
144B -> 162B -0.13914
160B -> 165B -0.22869
161B -> 166B -0.19341

4. References

1. (a) S. I. Gorelsky, *AOMix: Program for Molecular Orbital Analysis*, http://www.sg-chem.net/ 2007, **University of Ottawa, Canada**; (b) S. I. Gorelsky and A. B. P. Lever, *J. Organomet. Chem.*, 2001, **635**, 187; (c) S. I. Gorelsky and E. I. Solomon, *Theoretical Chem. Acc.*, 2008, **119**, 57.