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Fluorescent functionalised naphthalimides and their Au(I)-NHC complexes for potential use in cellular bioimaging

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Supplementary Information

Contents

Table S1. Data collection parameters for the X-ray structures.

Sample	[H**L**^{3}]PF_6		[AuCl(**L**^{3})]	
Empirical formula	$C_{20}H_{22}F_6N_3O_2P$		$C_{20}H_{21}AuClN_3O_2$	
Formula weight	481.37		567.81	
Temperature	100(2) K		100(2) K	
Wavelength	0.71075 Å		0.71075 Å	
Crystal system	Monoclinic		Triclinic	
Space group	$P2_1/n$		$P\bar{1}$	
Unit cell dimensions	a = 15.6492(11) Å	α = 90°	a = 9.0951(2) Å	α = 67.576(2)°
	b = 8.2325(6) Å	β = 104.075(7)°	b = 10.0127(2) Å	β = 72.828(2)°
	c = 16.7492(11) Å	γ = 90°	c = 12.2157(3) Å	γ = 76.121(2)°
Volume	2093.1(3) Å^3		972.23(4) Å^3	
Z	4		2	
Density (calculated)	1.528 g / cm^3		1.940 g / cm^3	
Absorption coefficient	0.208 mm^{-1}		7.723 mm^{-1}	
Crystal	Needle; orange		Plate; light yellow	
Crystal size	0.110 × 0.020 × 0.010 mm^3		0.080×0.060×0.010 mm^3	
θ range for data collection	2.507 – 26.023°		1.852 – 27.483°	
Reflections collected	15009		50364	
Independent reflections	4111 [R_{int} = 0.0679]		4450 [R_{int} = 0.0413]	
Absorption correction	Semi–empirical from equivalents		Semi–empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63096		1.00000 and 0.61492	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data / restraints / parameters	4111 / 355 / 355		4450 / 35 / 275	
Goodness-of-fit on F^2	1.103		1.047	
Final R indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.0969, *wR2* = 0.2411		*R1* = 0.0133, *wR2* = 0.0322	
R indices (all data)	*R1* = 0.1438, *wR2* = 0.2652		*R1* = 0.0142, *wR2* = 0.0324	
Largest diff. peak and hole	0.988 and –0.374 e Å^{-3}		0.731 and –0.747 e Å^{-3}	

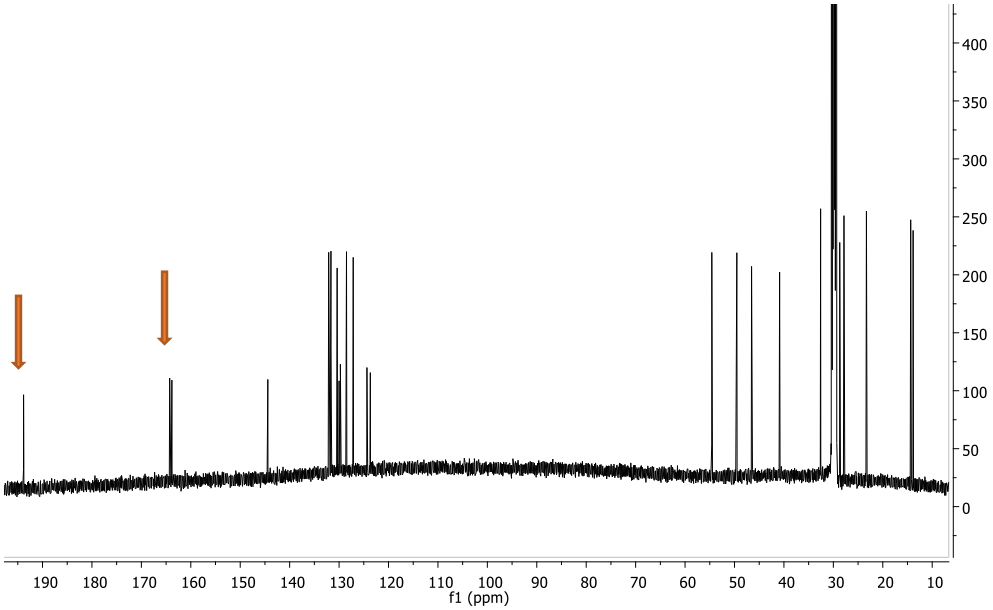

Figure S1. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN) of [AuCl(**L**^{7})]. Arrows highlight the carbene carbon resonance (>190 ppm) and naphthalimide carbonyl resonances (at 160-165 ppm).

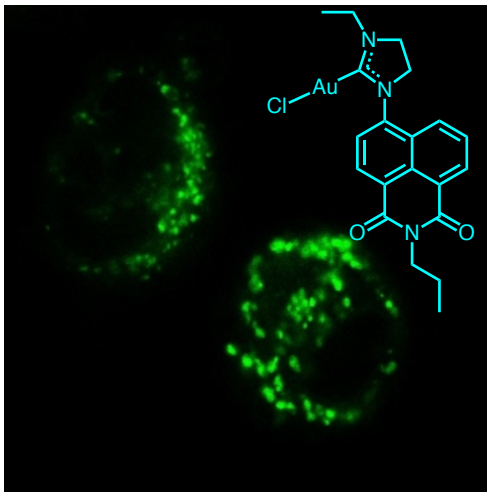

Figure S2. Confocal fluorescence microscopy images of MCF-7 cells incubated with [AuCl(**L**^{3})] showing localized signals (λ_{ex} = 405 nm and λ_{em} = 525 nm). Cells incubated with 100 μg/ml of the fluorophore.

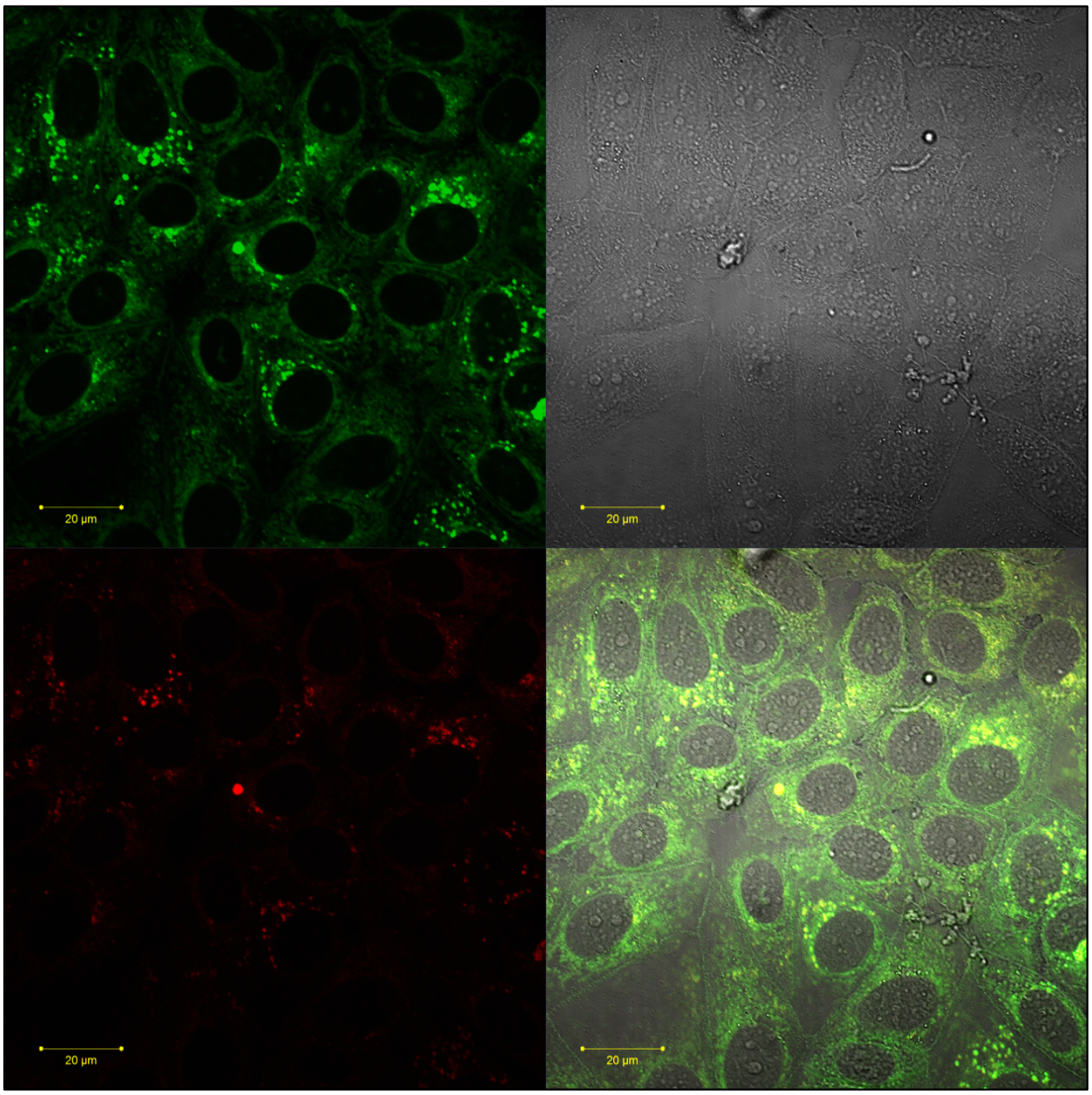

Figure S3. Confocal fluorescence microscopy images of MCF-7 cells incubated with [H**L**^{3}]PF_6 (clockwise from top right) DIC image; superimposed image; incubated with LysoTrackerRed. Note strong fluorescence co-localisation manifesting as yellow signal in overlay.

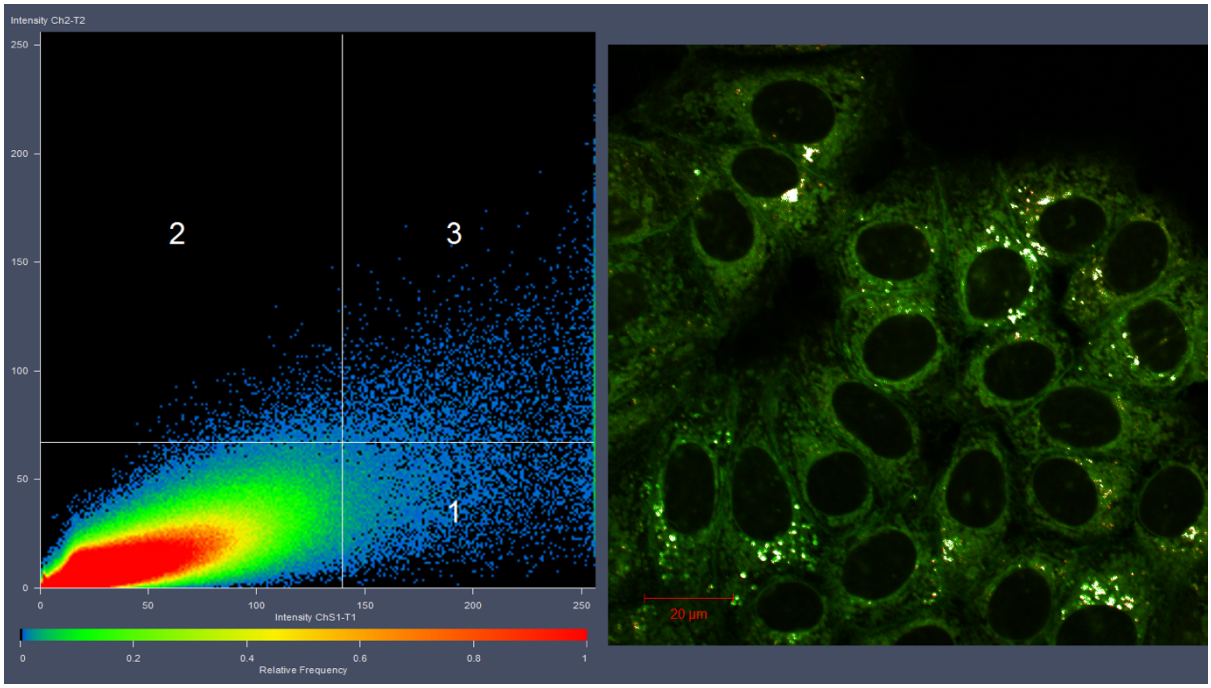

Figure S4. Left: Scatter plot of pixel intensity values (8 bit; 0-255) showing [H**L**^{3}]PF_6 fluorescence (vertical axis) versus lysosomal fluorescence (horizontal axis). Co-localised pixels in region 3 are displayed as a white binary overlay mask in adjacent image. Right: [H**L**^{3}]PF_6 fluorescence (green) superimposed upon Lysotracker fluorescence (red). White binary overlay mask shows co-localised signal (i.e. region 3 of plot) corresponding to lysosomal compartment.

TD-DFT data: details of excited states

[H**L**]PF_6
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.6205 eV 342.45 nm f=0.3948 <S**2>=0.000
89 -> 90 0.69742
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1088.87922432
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9138 eV 316.79 nm f=0.0017 <S**2>=0.000
86 -> 90 0.68080
86 -> 94 0.11515

Excited State 3: Singlet-A 4.0427 eV 306.68 nm f=0.0205 <S**2>=0.000
88 -> 90 0.65854
89 -> 91 -0.11325
89 -> 92 -0.17756

Excited State 4: Singlet-A 4.1639 eV 297.76 nm f=0.0214 <S**2>=0.000
87 -> 90 0.67618
88 -> 90 0.12242

Excited State 5: Singlet-A 4.2975 eV 288.50 nm f=0.0229 <S**2>=0.000
84 -> 90 0.50394
85 -> 90 -0.43564
86 -> 93 0.11385
89 -> 92 -0.13191

Excited State 6: Singlet-A 4.4781 eV 276.87 nm f=0.0298 <S**2>=0.000
84 -> 90 0.44186
85 -> 90 0.47602
87 -> 90 -0.10028
89 -> 92 0.19606

Excited State 7: Singlet-A 4.9400 eV 250.98 nm f=0.1016 <S**2>=0.000
83 -> 90 -0.11315
89 -> 91 0.66433
89 -> 92 -0.17067

Excited State 8: Singlet-A 5.1707 eV 239.78 nm f=0.0932 <S**2>=0.000
83 -> 90 -0.37300
89 -> 91 -0.14254
89 -> 92 -0.19878
89 -> 93 0.53124

Excited State 9: Singlet-A 5.3734 eV 230.74 nm f=0.4140 <S**2>=0.000
83 -> 90 -0.32352

85 -> 90 -0.23543
88 -> 90 0.10332
88 -> 94 0.11031
89 -> 92 0.52856

Excited State 10: Singlet-A 5.4703 eV 226.65 nm f=0.0865 <S**2>=0.000
83 -> 90 0.46040
87 -> 91 -0.19244
88 -> 90 0.12893
89 -> 92 0.15627
89 -> 93 0.43104

Excited State 11: Singlet-A 5.6123 eV 220.92 nm f=0.0638 <S**2>=0.000
83 -> 92 -0.10766
85 -> 91 -0.13929
87 -> 92 0.25943
88 -> 91 0.57107
88 -> 93 0.17429

Excited State 12: Singlet-A 5.6951 eV 217.70 nm f=0.2754 <S**2>=0.000
86 -> 93 -0.14149
87 -> 91 0.61508
87 -> 92 -0.15513
89 -> 92 0.10449

Excited State 13: Singlet-A 5.7014 eV 217.46 nm f=0.0030 <S**2>=0.000
82 -> 90 0.69408

Excited State 14: Singlet-A 5.7209 eV 216.72 nm f=0.0305 <S**2>=0.000
84 -> 90 -0.16898
86 -> 91 0.36919
86 -> 92 -0.25132
86 -> 93 0.43284
87 -> 91 0.19345

Excited State 15: Singlet-A 5.8388 eV 212.35 nm f=0.1976 <S**2>=0.000
85 -> 93 -0.10593
87 -> 91 0.11049
87 -> 92 0.51476
88 -> 91 -0.31273
88 -> 92 0.14849
88 -> 93 0.22817

Excited State 16: Singlet-A 5.9563 eV 208.16 nm f=0.0010 <S**2>=0.000
86 -> 91 0.37416
86 -> 92 0.55521
88 -> 93 0.16899

Excited State 17: Singlet-A 5.9813 eV 207.29 nm f=0.0019 <S**2>=0.000
83 -> 92 -0.10329

85 -> 91 0.17137
86 -> 92 -0.15331
87 -> 92 -0.18932
88 -> 92 -0.38225
88 -> 93 0.46348

Excited State 18: Singlet-A 5.9934 eV 206.87 nm f=0.0962 <S**2>=0.000
85 -> 91 0.25591
85 -> 92 0.23260
87 -> 92 -0.20375
87 -> 93 -0.32053
88 -> 92 0.41848
89 -> 94 -0.14935

Excited State 19: Singlet-A 6.0374 eV 205.36 nm f=0.0132 <S**2>=0.000
85 -> 91 0.38655
85 -> 92 0.20919
85 -> 93 0.15638
87 -> 93 0.14949
88 -> 91 0.15266
89 -> 94 0.44084

Excited State 20: Singlet-A 6.0640 eV 204.46 nm f=0.0365 <S**2>=0.000
84 -> 91 0.17694
84 -> 92 -0.15930
84 -> 93 0.25563
85 -> 91 -0.16576
85 -> 92 0.38452
85 -> 93 -0.28185
86 -> 94 0.16465
87 -> 93 0.11664
89 -> 94 0.18598

Excited State 21: Singlet-A 6.0899 eV 203.59 nm f=0.0631 <S**2>=0.000
80 -> 90 0.11231
85 -> 91 0.18183
87 -> 93 0.53821
88 -> 92 0.13840
89 -> 94 -0.34401

Excited State 22: Singlet-A 6.1458 eV 201.74 nm f=0.0019 <S**2>=0.000
77 -> 90 0.20517
78 -> 90 -0.15542
79 -> 90 0.62979

Excited State 23: Singlet-A 6.2033 eV 199.87 nm f=0.0132 <S**2>=0.000
84 -> 91 0.26372
84 -> 92 -0.12193
84 -> 93 0.31882
85 -> 91 0.28641

85 -> 92 -0.27180
86 -> 93 0.13845
86 -> 94 0.23529
87 -> 93 -0.12964

Excited State 24: Singlet-A 6.2365 eV 198.80 nm f=0.1424 <S**2>=0.000
80 -> 90 0.37403
83 -> 91 -0.10063
85 -> 91 0.12593
85 -> 92 0.24315
87 -> 93 -0.14194
88 -> 92 -0.29081
88 -> 93 -0.31124
89 -> 94 -0.18649

[AuCl(L)]
Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.4849 eV 355.78 nm f=0.2882 <S**2>=0.000
106 ->108 -0.14507
107 ->108 0.68228
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1684.31084698
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.8695 eV 320.42 nm f=0.0416 <S**2>=0.000
106 ->108 0.67161
107 ->108 0.14552

Excited State 3: Singlet-A 3.9518 eV 313.74 nm f=0.0005 <S**2>=0.000
101 ->108 0.67869
101 ->113 -0.11082

Excited State 4: Singlet-A 4.0130 eV 308.96 nm f=0.0471 <S**2>=0.000
102 ->108 -0.25888
104 ->108 -0.15777
105 ->108 0.59915
107 ->109 0.13774

Excited State 5: Singlet-A 4.1998 eV 295.21 nm f=0.0190 <S**2>=0.000
102 ->108 0.53207
104 ->108 0.23292
105 ->108 0.33555
107 ->109 -0.14830

Excited State 6: Singlet-A 4.3258 eV 286.62 nm f=0.0040 <S**2>=0.000
99 ->108 0.24736
100 ->108 -0.14291

102 ->108 -0.18054
103 ->108 -0.32831
104 ->108 0.50491

Excited State 7: Singlet-A 4.3429 eV 285.49 nm f=0.0120 <S**2>=0.000
99 ->108 0.33712
100 ->108 -0.31562
103 ->108 0.49729

Excited State 8: Singlet-A 4.3623 eV 284.22 nm f=0.0088 <S**2>=0.000
99 ->108 -0.27095
100 ->108 0.27703
102 ->108 -0.19225
103 ->108 0.35964
104 ->108 0.39353
107 ->109 0.10322

Excited State 9: Singlet-A 4.5175 eV 274.45 nm f=0.0218 <S**2>=0.000
99 ->108 0.44602
100 ->108 0.45507
102 ->108 0.14113
107 ->109 0.17235
107 ->110 -0.12035

Excited State 10: Singlet-A 4.9957 eV 248.18 nm f=0.0941 <S**2>=0.000
96 ->108 -0.19810
98 ->108 0.12047
107 ->109 0.41446
107 ->110 0.49317

Excited State 11: Singlet-A 5.1000 eV 243.10 nm f=0.1911 <S**2>=0.000
96 ->108 0.17754
98 ->108 -0.14929
100 ->108 -0.16689
102 ->108 0.10049
105 ->109 0.17649
107 ->109 0.39287
107 ->110 -0.30639
107 ->111 -0.29062

Excited State 12: Singlet-A 5.1964 eV 238.60 nm f=0.0107 <S**2>=0.000
97 ->108 -0.11756
98 ->108 0.65959
107 ->110 -0.18063

Excited State 13: Singlet-A 5.2289 eV 237.12 nm f=0.0012 <S**2>=0.000
97 ->108 0.67513
98 ->108 0.11320
107 ->111 -0.11929

Excited State 14: Singlet-A 5.2708 eV 235.23 nm f=0.1001 <S**2>=0.000

97 ->108	-0.12002
105 ->111	-0.22200
106 ->109	0.45737
106 ->111	-0.16587
107 ->109	-0.19219
107 ->110	0.10230
107 ->111	-0.30161

Excited State 15: Singlet-A 5.3510 eV 231.70 nm f=0.0648 <S**2>=0.000

96 ->108	0.39668
100 ->108	0.10763
105 ->109	-0.19849
106 ->109	-0.18303
106 ->110	-0.18094
106 ->111	0.16092
107 ->110	0.23595
107 ->111	-0.31661

Excited State 16: Singlet-A 5.4584 eV 227.14 nm f=0.0037 <S**2>=0.000

96 ->108	0.45080
105 ->109	0.20914
106 ->111	-0.13162
107 ->110	0.12993
107 ->111	0.40014

Excited State 17: Singlet-A 5.5355 eV 223.98 nm f=0.3625 <S**2>=0.000

100 ->108	0.15578
102 ->108	-0.11327
105 ->109	0.16238
105 ->111	-0.12449
106 ->109	-0.38758
106 ->110	0.40347
106 ->111	-0.11117
107 ->109	-0.14891
107 ->111	-0.12633

Excited State 18: Singlet-A 5.6022 eV 221.31 nm f=0.0264 <S**2>=0.000

95 ->108	0.19149
96 ->108	0.14936
103 ->109	-0.24735
103 ->110	-0.11721
103 ->111	0.21941
104 ->109	-0.24990
104 ->111	0.22102
105 ->110	-0.14241
105 ->111	0.11769
106 ->109	0.16247
106 ->110	0.33658

Excited State 19: Singlet-A 5.6200 eV 220.61 nm f=0.0207 <S**2>=0.000
95 ->108 0.33160
96 ->108 0.12723
103 ->109 0.25348
103 ->111 -0.24124
104 ->109 0.22623
104 ->110 0.10545
104 ->111 -0.18789
105 ->109 -0.14260
105 ->110 -0.13870
106 ->109 0.10050
106 ->110 0.23685

Excited State 20: Singlet-A 5.6436 eV 219.69 nm f=0.0450 <S**2>=0.000
95 ->108 0.56728
105 ->109 0.12796
105 ->110 0.11107
105 ->111 -0.13473
106 ->109 -0.17061
106 ->110 -0.23788

Excited State 21: Singlet-A 5.7039 eV 217.37 nm f=0.1735 <S**2>=0.000
102 ->110 -0.12501
103 ->109 -0.13345
104 ->109 0.13542
104 ->111 -0.12040
105 ->109 0.39771
106 ->111 0.48136

Excited State 22: Singlet-A 5.7561 eV 215.40 nm f=0.0677 <S**2>=0.000
100 ->110 0.11702
102 ->109 -0.12361
102 ->110 -0.23735
103 ->109 0.31878
103 ->111 -0.14538
104 ->109 -0.29448
104 ->110 -0.14678
104 ->111 0.11976
105 ->109 0.13868
105 ->110 0.17137
105 ->111 0.24389

Excited State 23: Singlet-A 5.7694 eV 214.90 nm f=0.0031 <S**2>=0.000
99 ->108 -0.17805
101 ->109 0.12171
101 ->110 0.60808
101 ->111 0.17006
105 ->110 -0.10568

Excited State 24: Singlet-A 5.8073 eV 213.50 nm f=0.0563 <S**2>=0.000

103 ->109	-0.16037
104 ->109	0.11452
104 ->111	-0.11826
105 ->109	-0.20955
105 ->110	0.55252
106 ->110	0.13076
106 ->111	0.11160