

Supporting information

Illuminating Weak Bonds: Non-Classical C–H···Br Hydrogen Bonding and Bright Emission in a BODIPY Fluorophore

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Table S-1: The calculated cartesian coordinates of (1) using B3LYP/DEF2-TZVP

Br	2.695900000	1.951090000	5.521220000
C	4.526470000	1.694270000	5.110230000
H	0.100410000	2.144800000	6.547290000
C	5.229940000	2.677710000	4.462940000
C	5.129310000	0.522390000	5.443170000
C	-0.623122975	1.675944741	6.975501551
C	6.542670000	2.479620000	4.126900000
C	6.442130000	0.315540000	5.099390000
C	-0.643690000	0.262070000	6.408080000
C	7.174120000	1.288460000	4.432740000
C	-0.918130000	-0.168290000	5.075540000
C	-0.432320000	-0.874750000	7.169970000
N	-0.891760000	-1.569810000	5.081580000
C	-1.108640000	0.520640000	3.871390000
C	-0.601710000	-1.984400000	6.326160000
B	-1.108640000	-2.504160000	3.871390000
C	-1.299150000	-0.168290000	2.667230000
O	-2.208010000	-3.425980000	4.100880000
O	-0.009270000	-3.425980000	3.641890000
N	-1.325520000	-1.569810000	2.661190000
C	-1.573590000	0.262070000	1.334700000
C	-3.468880000	-3.094040000	4.432740000
C	1.251590000	-3.094040000	3.310040000
C	-1.615570000	-1.984400000	1.416620000
C	-1.784960000	-0.874750000	0.572810000
C	-1.612540000	1.648700000	0.772730000
C	-4.100330000	-1.902880000	4.126900000
C	-4.200870000	-4.066960000	5.099390000
C	1.883050000	-1.902880000	3.615880000
C	1.983590000	-4.066960000	2.643380000
H	-2.317690000	2.144800000	1.195480000
C	-5.413060000	-1.704790000	4.462940000

C	-5.513690000	-3.860110000	5.443170000
C	3.195780000	-1.704790000	3.279840000
C	3.296410000	-3.860110000	2.299600000
C	-6.116530000	-2.688230000	5.110230000
C	3.899240000	-2.688230000	2.632540000
H	4.579448038	-0.240456741	5.974316563
H	6.914498793	-0.622130109	5.352456178
H	8.205756054	1.119961102	4.161197787
H	7.089118163	3.260392319	3.618776993
H	4.746813157	3.611870033	4.217311245
H	3.678912123	-0.770634487	3.525475563
H	3.846275357	-4.622955676	1.768455421
H	1.511222506	-5.004629308	2.390308433
H	-3.728501207	-5.004630109	5.352456178
H	-6.063551962	-4.622956741	5.974316563
H	-5.896186843	-0.770629967	4.217311245
H	-3.553881837	-1.122107681	3.618776993
H	1.336605151	-1.122106610	4.124004926
H	-0.512235007	-3.016360544	6.631858644
H	-0.182947249	-0.902834582	8.220410140
H	-7.156072103	-2.530526114	5.356972172
H	4.938779078	-2.530521597	2.385787970
H	-1.705046247	-3.016360875	1.110922841
H	-2.034332751	-0.902834582	-0.477630140
H	-0.277172736	1.105885599	3.956040542
H	-1.820435943	1.158541649	4.308368004
H	-0.863634102	2.040630149	8.004077997
H	-1.666559973	1.686971030	6.341594982
H	-1.652701950	1.237744920	-0.279292673
H	-0.934451912	2.209038386	0.555731986

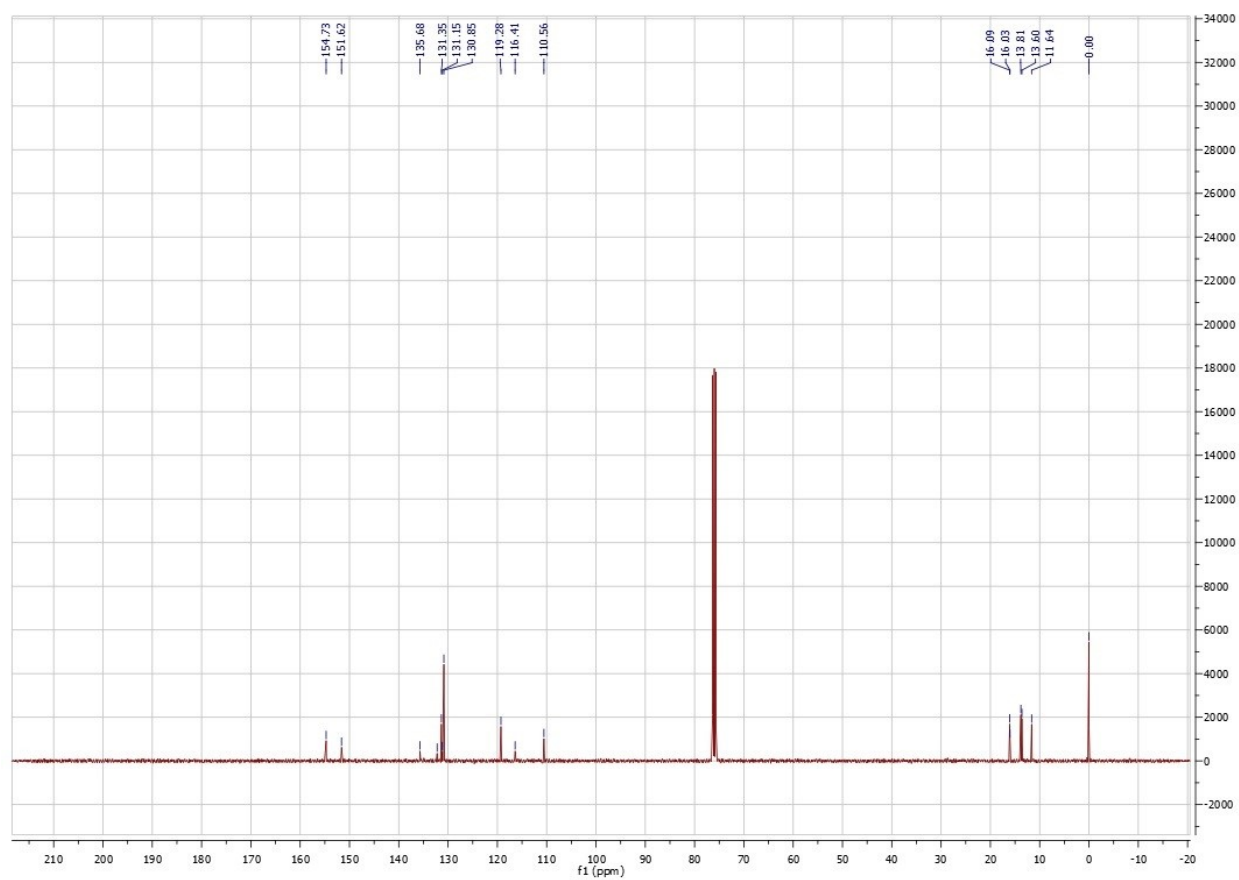


Figure S-1. ^{13}C -NMR of (1) in CDCl_3

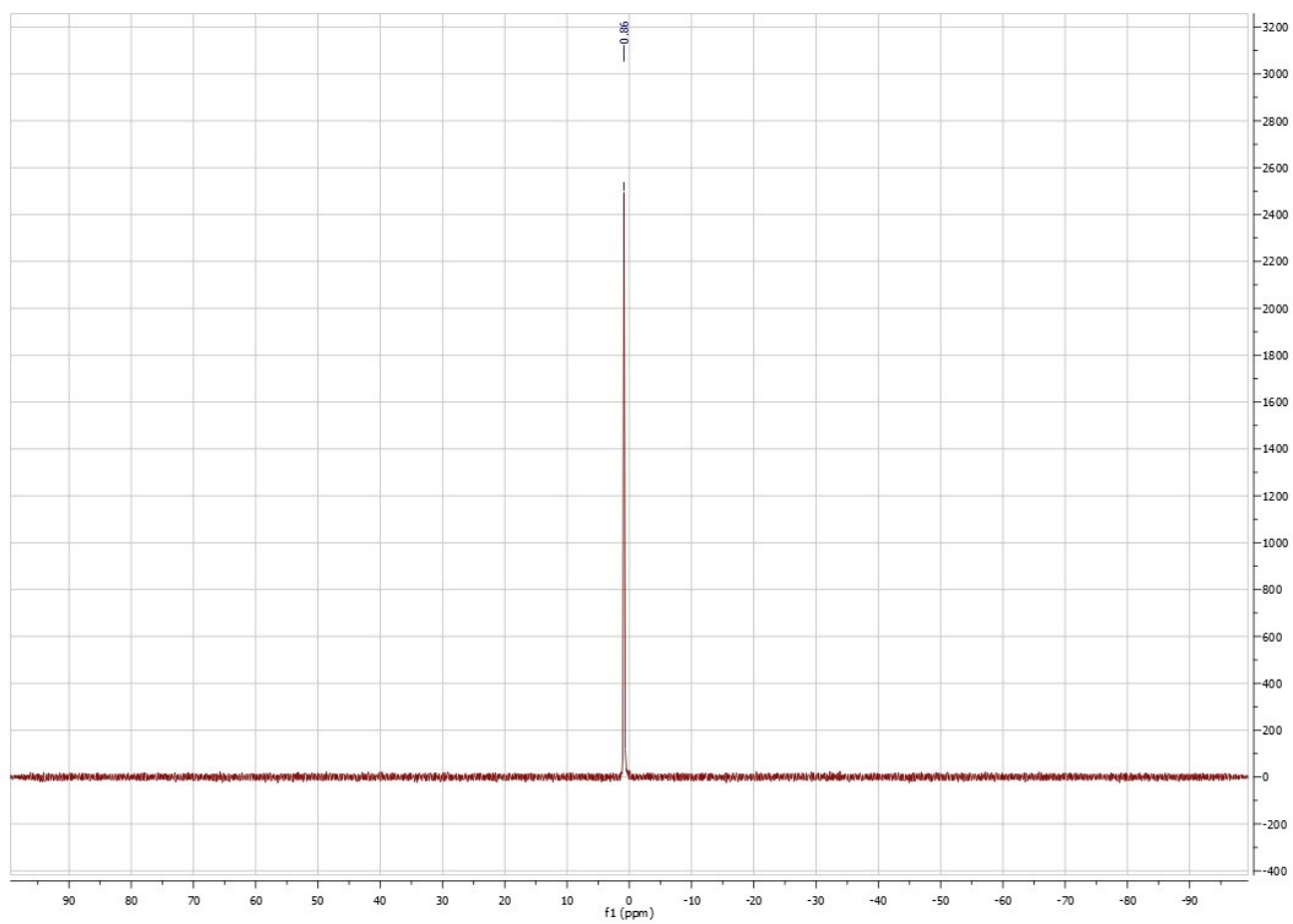


Figure S-2. ^{11}B -NMR of (1) in CDCl_3 .

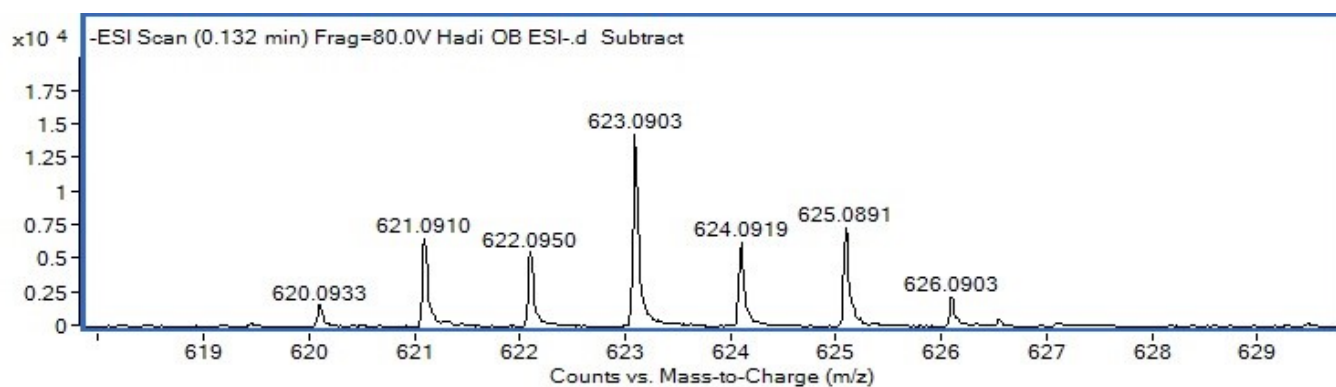


Figure S-3. HRMS Spectrum of (1)

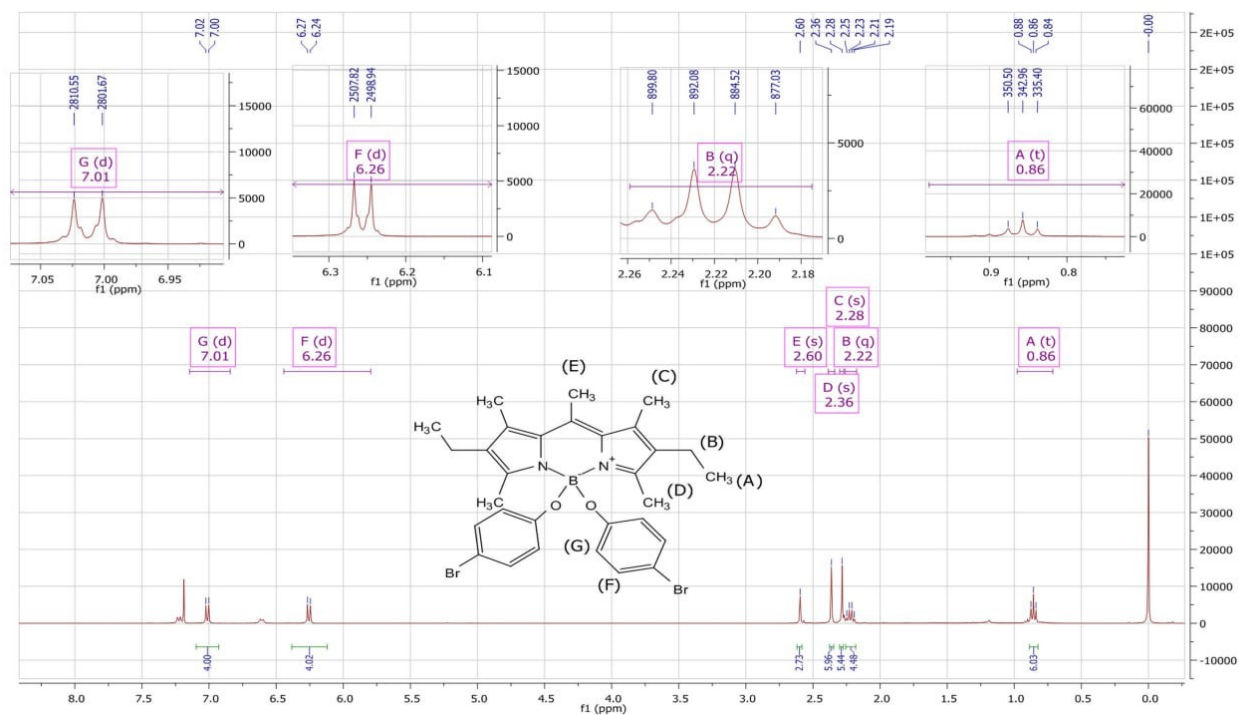


Fig S-4. ¹H-NMR of (1) in CDCl₃

Table S-2. Experimental details

	a
Crystal data	
Chemical formula	C ₃₀ H ₃₃ BBr ₂ N ₂ O ₂
M_r	624.21
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	295
a, b, c (Å)	21.286 (10), 8.765 (4), 16.108 (7)
β (°)	105.98 (2)
V (Å ³)	2889 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.84
Crystal size (mm)	0.20 × 0.15 × 0.13
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan semiempirical (using intensity measurements)
$T_{\min}, T_{\max}$	0.6, 0.7
No. of measured, independent and observed [$I > 2 \sigma(I)$] reflections	19454, 3593, 1942
R_{int}	0.062
$(\sin \theta)_{\max}$ (Å ⁻¹)	0.668
Refinement	
$R[F^2 > 2 \sigma(F^2)], wR(F^2), S$	0.055, 0.170, 1.02
No. of reflections	3593
No. of parameters	171
H-atom treatment	H-atom parameters constrained
$\rho_{\max}, \rho_{\min}$ (e Å ⁻³)	0.34, -0.63

Computer programs: *SHELXL2014/7* (Sheldrick, 2014).

Table S-3. Selected geometric parameters (Å, °)

Br1—C1	1.893 (4)	C8—C13	1.497 (4)
O1—C4	1.345 (3)	C9—C10	1.404 (4)
O1—B1	1.453 (3)	C9—C14	1.492 (4)
N1—C10	1.344 (4)	C10—C16	1.497 (4)
N1—C7	1.401 (3)	C11—C7 ⁱ	1.401 (3)
N1—B1	1.543 (3)	C11—C12	1.508 (5)
B1—O1 ⁱ	1.453 (3)	C12—H12A	0.9600
B1—N1 ⁱ	1.543 (3)	C12—H12B	0.9600
C1—C6	1.359 (6)	C12—H12C	0.9600
C1—C2	1.371 (5)	C13—H13A	0.9600
C2—C3	1.371 (4)	C13—H13B	0.9600
C2—H2A	0.9300	C13—H13C	0.9600
C3—C4	1.383 (4)	C14—C15	1.516 (6)
C3—H3A	0.9300	C14—H14A	0.9700
C4—C5	1.389 (4)	C14—H14B	0.9700
C5—C6	1.372 (5)	C15—H15A	0.9600
C5—H5A	0.9300	C15—H15B	0.9600
C6—H6A	0.9300	C15—H15C	0.9600
C7—C11	1.401 (3)	C16—H16A	0.9600
C7—C8	1.427 (4)	C16—H16B	0.9600
C8—C9	1.384 (4)	C16—H16C	0.9600
C4—O1—B1	126.26 (19)	N1—C10—C9	109.8 (2)
C10—N1—C7	108.4 (2)	N1—C10—C16	122.7 (2)
C10—N1—B1	124.8 (2)	C9—C10—C16	127.4 (3)
C7—N1—B1	126.8 (2)	C7—C11—C7 ⁱ	121.0 (3)
O1—B1—O1 ⁱ	101.2 (3)	C7—C11—C12	119.51 (15)
O1—B1—N1	111.50 (11)	C7 ⁱ —C11—C12	119.51 (15)
O1 ⁱ —B1—N1	113.64 (11)	C11—C12—H12A	109.5
O1—B1—N1 ⁱ	113.64 (11)	C11—C12—H12B	109.5
O1 ⁱ —B1—N1 ⁱ	111.50 (11)	H12A—C12—H12B	109.5

N1—B1—N1 ⁱ	105.6 (3)	C11—C12—H12C	109.5
C6—C1—C2	120.4 (3)	H12A—C12—H12C	109.5
C6—C1—Br1	119.5 (3)	H12B—C12—H12C	109.5
C2—C1—Br1	120.0 (3)	C8—C13—H13A	109.5
C3—C2—C1	120.3 (3)	C8—C13—H13B	109.5
C3—C2—H2A	119.8	H13A—C13—H13B	109.5
C1—C2—H2A	119.8	C8—C13—H13C	109.5
C2—C3—C4	120.4 (3)	H13A—C13—H13C	109.5
C2—C3—H3A	119.8	H13B—C13—H13C	109.5
C4—C3—H3A	119.8	C9—C14—C15	112.2 (3)
O1—C4—C3	125.8 (2)	C9—C14—H14A	109.2
O1—C4—C5	116.2 (3)	C15—C14—H14A	109.2
C3—C4—C5	118.0 (3)	C9—C14—H14B	109.2
C6—C5—C4	121.4 (3)	C15—C14—H14B	109.2
C6—C5—H5A	119.3	H14A—C14—H14B	107.9
C4—C5—H5A	119.3	C14—C15—H15A	109.5
C1—C6—C5	119.5 (3)	C14—C15—H15B	109.5
C1—C6—H6A	120.3	H15A—C15—H15B	109.5
C5—C6—H6A	120.3	C14—C15—H15C	109.5
N1—C7—C11	119.9 (2)	H15A—C15—H15C	109.5
N1—C7—C8	107.1 (2)	H15B—C15—H15C	109.5
C11—C7—C8	132.9 (2)	C10—C16—H16A	109.5
C9—C8—C7	107.2 (2)	C10—C16—H16B	109.5
C9—C8—C13	123.4 (3)	H16A—C16—H16B	109.5
C7—C8—C13	129.4 (3)	C10—C16—H16C	109.5
C8—C9—C10	107.5 (2)	H16A—C16—H16C	109.5
C8—C9—C14	127.9 (3)	H16B—C16—H16C	109.5
C10—C9—C14	124.5 (3)		

Table S-4: Absorption spectrum components of complex 1 computed with TD-DFT-M06L

State	Energy (cm ⁻¹)	Wavelength (nm)	fosc
1	19855.9	503.6	0.000121053
2	21042.6	475.2	0.002445577
3	24424.1	409.4	0.578922710
4	27241.8	367.1	0.067120110
5	27562.3	362.8	0.556324334
6	30073.5	332.5	0.000014621
7	30121.1	332.0	0.005705501
8	30437.4	328.5	0.000113407
9	30765.5	325.0	0.000272367
10	33184.3	301.3	0.000331580
11	34123.9	293.1	0.000367023
12	34286.4	291.7	0.000591104
13	34345.8	291.2	0.001292594
14	34388.4	290.8	0.000024611
15	34550.1	289.4	0.000464274
16	35254.0	283.7	0.000587236
17	35629.0	280.7	0.000464558
18	35943.8	278.2	0.074805535
19	36055.4	277.4	0.000221936
20	36203.4	276.2	0.005181298
21	37270.9	268.3	0.103544379
22	37377.0	267.5	0.007737871
23	37510.3	266.6	0.021716835
24	37566.7	266.2	0.004801011
25	38321.2	261.0	0.015375066
26	38366.8	260.6	0.000031039
27	38525.4	259.6	0.043722074
28	38710.7	258.3	0.006891960
29	39048.4	256.1	0.028793721
30	39201.5	255.1	0.000001852

Table S-5: Type of each transition of the 30 states mentioned in the previous table.

STATE 1: E= 0.090470 au 2.462 eV 19855.9 cm ⁻¹ <S ² > = 0.000000	157a -> 159a : 0.993155 (c= 0.99657178)
STATE 2: E= 0.095877 au 2.609 eV 21042.6 cm ⁻¹ <S ² > = 0.000000	156a -> 159a : 0.988652 (c= 0.99430964) 158a -> 159a : 0.010969 (c= -0.10473421)
STATE 3: E= 0.111284 au 3.028 eV 24424.1 cm ⁻¹ <S ² > = 0.000000	155a -> 159a : 0.273157 (c= -0.52264439) 158a -> 159a : 0.681767 (c= -0.82569160)
STATE 4: E= 0.124123 au 3.378 eV 27241.8 cm ⁻¹ <S ² > = 0.000000	154a -> 159a : 0.960505 (c= -0.98005336) 155a -> 166a : 0.011729 (c= 0.10830047)
STATE 5: E= 0.125583 au 3.417 eV 27562.3 cm ⁻¹ <S ² > = 0.000000	155a -> 159a : 0.683813 (c= 0.82693004) 158a -> 159a : 0.263261 (c= -0.51308926)
STATE 6: E= 0.137025 au 3.729 eV 30073.5 cm ⁻¹ <S ² > = 0.000000	152a -> 159a : 0.443398 (c= -0.66588134) 153a -> 159a : 0.555495 (c= 0.74531511)
STATE 7: E= 0.137242 au 3.735 eV 30121.1 cm ⁻¹ <S ² > = 0.000000	152a -> 159a : 0.553641 (c= -0.74407039) 153a -> 159a : 0.436653 (c= -0.66079749)
STATE 8: E= 0.138683 au 3.774 eV 30437.4 cm ⁻¹ <S ² > = 0.000000	158a -> 160a : 0.998530 (c= 0.99926478)
STATE 9: E= 0.140178 au 3.814 eV 30765.5 cm ⁻¹ <S ² > = 0.000000	158a -> 161a : 0.997886 (c= 0.99894264)
STATE 10: E= 0.151199 au 4.114 eV 33184.3 cm ⁻¹ <S ² > = 0.000000	158a -> 162a : 0.998083 (c= 0.99904106)
STATE 11: E= 0.155480 au 4.231 eV 34123.9 cm ⁻¹ <S ² > = 0.000000	156a -> 160a : 0.063181 (c= 0.25135834) 156a -> 161a : 0.233520 (c= -0.48323946) 157a -> 160a : 0.598292 (c= -0.77349345) 157a -> 161a : 0.100247 (c= 0.31661861)
STATE 12: E= 0.156221 au 4.251 eV 34286.4 cm ⁻¹ <S ² > = 0.000000	156a -> 160a : 0.320031 (c= -0.56571300) 156a -> 161a : 0.079223 (c= -0.28146567) 157a -> 160a : 0.088839 (c= -0.29805818) 157a -> 161a : 0.508992 (c= -0.71343641)

STATE 13: E= 0.156491 au 4.258 eV 34345.8 cm⁻¹ <S²> = 0.0000
 149a -> 159a : 0.770287 (c= -0.87766004)
 150a -> 159a : 0.181452 (c= -0.42597204)
 151a -> 159a : 0.040683 (c= 0.20169971)

STATE 14: E= 0.156685 au 4.264 eV 34388.4 cm⁻¹ <S²> = 0.0000
 149a -> 159a : 0.186991 (c= -0.43242474)
 150a -> 159a : 0.812413 (c= 0.90133948)

STATE 15: E= 0.157422 au 4.284 eV 34550.1 cm⁻¹ <S²> = 0.0000
 158a -> 163a : 0.987853 (c= -0.99390772)

STATE 16: E= 0.160629 au 4.371 eV 35254.0 cm⁻¹ <S²> = 0.0000
 148a -> 159a : 0.999559 (c= -0.99977933)

STATE 17: E= 0.162338 au 4.417 eV 35629.0 cm⁻¹ <S²> = 0.0000
 147a -> 159a : 0.997332 (c= 0.99866514)

STATE 18: E= 0.163772 au 4.456 eV 35943.8 cm⁻¹ <S²> = 0.0000
 144a -> 159a : 0.010806 (c= 0.10395316)
 145a -> 159a : 0.010798 (c= -0.10391194)
 149a -> 159a : 0.035442 (c= 0.18826137)
 151a -> 159a : 0.735457 (c= 0.85758777)
 158a -> 166a : 0.165337 (c= -0.40661648)

STATE 19: E= 0.164281 au 4.470 eV 36055.4 cm⁻¹ <S²> = 0.0000
 158a -> 164a : 0.998202 (c= 0.99910039)

STATE 20: E= 0.164955 au 4.489 eV 36203.4 cm⁻¹ <S²> = 0.0000
 158a -> 165a : 0.997489 (c= -0.99874380)

STATE 21: E= 0.169819 au 4.621 eV 37270.9 cm⁻¹ <S²> = 0.0000
 156a -> 163a : 0.273670 (c= -0.52313462)
 157a -> 162a : 0.676831 (c= -0.82269745)
 157a -> 163a : 0.019675 (c= 0.14026635)

STATE 22: E= 0.170302 au 4.634 eV 37377.0 cm⁻¹ <S²> = 0.0000
 153a -> 162a : 0.024353 (c= -0.15605350)
 153a -> 163a : 0.012406 (c= -0.11138386)
 155a -> 160a : 0.393447 (c= -0.62725353)
 155a -> 161a : 0.076419 (c= -0.27643933)
 156a -> 160a : 0.067842 (c= 0.26046571)
 156a -> 161a : 0.252877 (c= 0.50286838)
 157a -> 160a : 0.088801 (c= -0.29799453)
 157a -> 161a : 0.061169 (c= -0.24732387)

STATE 23: E= 0.170909 au 4.651 eV 37510.3 cm**-1 <S**2> = 0.000
 152a -> 162a : 0.031508 (c= -0.17750462)
 153a -> 163a : 0.012624 (c= 0.11235570)
 155a -> 160a : 0.142116 (c= -0.37698276)
 155a -> 161a : 0.262195 (c= 0.51204948)
 156a -> 160a : 0.290329 (c= -0.53882174)
 156a -> 161a : 0.051143 (c= 0.22614873)
 157a -> 160a : 0.017619 (c= -0.13273705)
 157a -> 161a : 0.145152 (c= 0.38098794)
 157a -> 163a : 0.013572 (c= -0.11649811)

STATE 24: E= 0.171166 au 4.658 eV 37566.7 cm**-1 <S**2> = 0.000
 156a -> 162a : 0.504392 (c= 0.71020534)
 156a -> 163a : 0.015559 (c= 0.12473389)
 157a -> 162a : 0.015505 (c= 0.12451996)
 157a -> 163a : 0.443399 (c= 0.66588227)

STATE 25: E= 0.174604 au 4.751 eV 38321.2 cm**-1 <S**2> = 0.000
 152a -> 162a : 0.011813 (c= -0.10868880)
 152a -> 163a : 0.034464 (c= 0.18564370)
 153a -> 162a : 0.040561 (c= -0.20139885)
 155a -> 160a : 0.442436 (c= 0.66515827)
 156a -> 160a : 0.010925 (c= -0.10452355)
 156a -> 161a : 0.288433 (c= 0.53706002)
 157a -> 160a : 0.130123 (c= -0.36072563)

STATE 26: E= 0.174812 au 4.757 eV 38366.8 cm**-1 <S**2> = 0.000
 154a -> 160a : 0.995704 (c= 0.99784963)

STATE 27: E= 0.175535 au 4.777 eV 38525.4 cm**-1 <S**2> = 0.000
 152a -> 162a : 0.032448 (c= 0.18013415)
 153a -> 163a : 0.026728 (c= -0.16348819)
 155a -> 161a : 0.645738 (c= 0.80357808)
 156a -> 160a : 0.156676 (c= 0.39582354)
 157a -> 161a : 0.103763 (c= -0.32212320)

STATE 28: E= 0.176379 au 4.800 eV 38710.7 cm**-1 <S**2> = 0.000
 154a -> 161a : 0.998401 (c= 0.99920000)

STATE 29: E= 0.177918 au 4.841 eV 39048.4 cm**-1 <S**2> = 0.000
 146a -> 159a : 0.988577 (c= -0.99427193)

STATE 30: E= 0.178615 au 4.860 eV 39201.5 cm**-1 <S**2> = 0.000
 157a -> 164a : 0.992230 (c= 0.99610749)

