Supporting Information

Rationalizing the effect of benzo-fusion at [*a*] and [*b*] position of BODIPY on fluorescence yields

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1. Experimental Section

General. All reactions were carried out under argon atmosphere. All reagents were purchased from common suppliers and used as received. All yields given referred to isolated yields. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX400 spectrometer, and referenced to the residual proton signals of deuterated solvents. ^{1}H NMR chemical shifts were referenced to $CDCl_3$ (7.26 ppm). ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.16 ppm). ESI–HRMS spectra were recorded on Bruker Daltonics Apex-III. MALDI–TOF–MS were performed on a microflex MALDI-TOF (Bruker Daltonics, USA) Spectrometer. UV-vis spectra were obtained by a Shimadzu UV-1800 spectrophotometer. Fluorescence spectra and the fluorescence lifetimes of the samples were recorded on a HORIBA JobinYvon Fluorolog-3 spectrofluorimeter.

2. Spectroscopic data

Table S1. Photophysical properties of BODIPY **1-5** in solvents with various polarities.

	Solvent	λ_{abs} [nm]	λ_{em} [nm]	$\Delta\upsilon_{abs-em}$ [cm^{-1}]	τ [ns]	Φ	k_r [10^8]/s	k_{nr} [10^8]/s
1[a]	DCM	631	664	788	5.2	0.93	1.79	0.13
	THF	631	651	487	n.a [e]	0.64	-	-
2[b]	Hexane	599	605	176	5.71	0.91	1.59	0.16
	THF	600	609	217	5.26	0.99	1.89	0.02
	MeCN	597	606	241	5.63	0.87	1.55	0.2
3[c]	DCM	568	n.d [d]	-	-	-		
4	Hexane	556	n.d	-	-	-		
	Toluene	567	n.d	-	-	-		
	DCM	560	n.d	-	-	-		
	THF	558	n.d	-	-	-		
	MeCN	550	n.d	-	-	-		
5	Hexane	557	n.d	-	-	-		
	Toluene	567	n.d	-	-	-		
	DCM	560	n.d	-	-	-		
	THF	559	n.d	-	-	-		
	MeCN	551	n.d	-	-	-		

[a] Y. Tomimori, T. Okujima, T. Yano, S. Mori, N. Ono, H. Yamada, H. Uno, Tetrahedron, 67 (2011) 3187-3193. [b] Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B. Schulz, G. Reck, N. Ono, Chem. Eur. J., 10 (2004) 4853-4871. [c] Y. Ni, W. Zeng, K.-W. Huang, J. Wu, Chem. Commun., 49 (2013) 1217-1219. [d] not detect. [e] not available.

3. DFT and TD-DFT Calculations

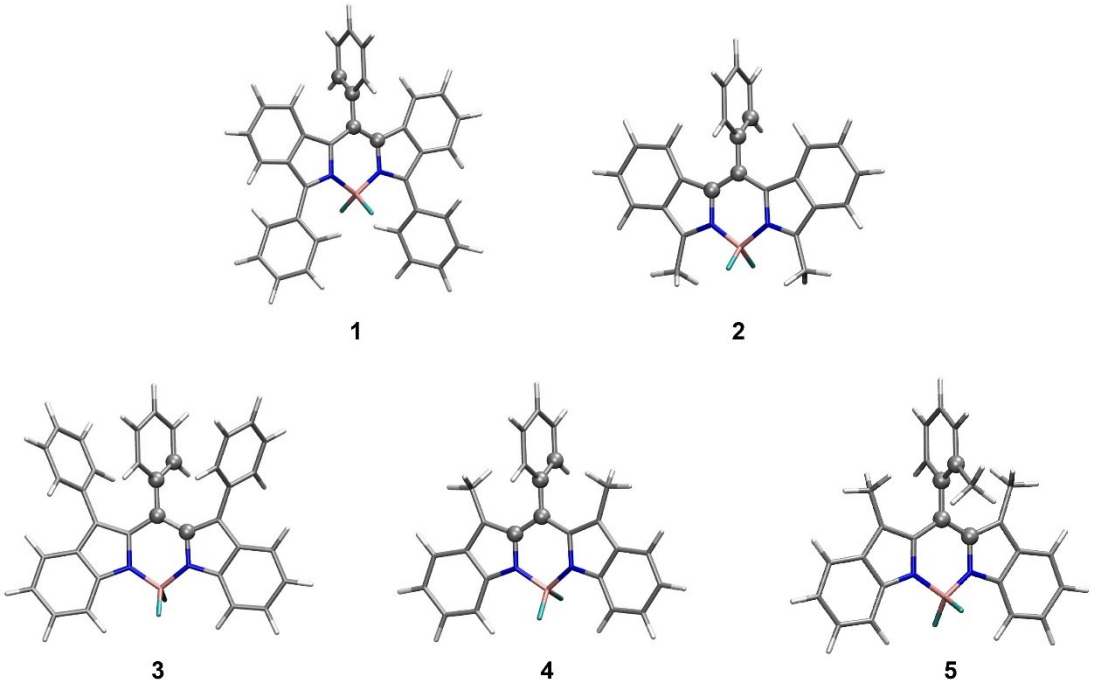


Fig. S1. Optimized geometries of the S_0 state. The atoms for defining the dihedral angle used in the potential energy surface (PES) scan are highlighted in the CPK mode.

Table S2. Dihedral angles, excitation energies, and oscillator strengths of the local minima on the PESs of the S_1 state of **3** and **4**.

Compound	local minimum	optimized dihedral angle (°)	excitation energy (eV)	*f*
3	**A**	57.4	1.43	0.034
	B	122.6	1.46	0.035
	C	171.4	0.89	0.017
4	**D**	−112.7	1.47	0.013
	E	7.3	0.77	0.003

Table S3. Energy levels of S_1 and T_n (n = 1 ~ 4) states and contributions of MO transitions.

Compound	state	n-th	energy (eV)	MO transition
1	S_n	1	2.16	H→L (98.6%)
	T_n	1	0.88	H→L (97.5%)
		2	2.43	H→L+1 (65.7%) H−1→L (20.1%)
		3	2.80	H−1→L (66.5%) H→L+1 (19.5%)
		4	2.89	H→L+2 (35.0%) H−2→L (31.5%)
2	S_n	1	2.41	H→L (98.2%)
	T_n	1	0.99	H→L (97.6%)
		2	2.56	H→L+1 (66.6%) H−1→L (17.1%)
		3	2.87	H→L+2 (50.4%) H−2→L (26.5%) H−1→L+1 (11.3%)
		4	3.06	H−1→L (67.5%) H→L+1 (17.6%)
3	S_n	1	1.43	H→L (95.3%) H−1→L (2.9%)
	T_n	1	0.69	H→L (86.9%) H−1→L (9.3%)
		2	1.23	H−1→L (84.4%) H→L (8.6%)
		3	1.69	H−2→L (94.7%) H−1→L (1.5%)
		4	2.27	H−3→L (86.0%)
4	S_n	1	1.47	H→L (95.4%) H−1→L (3.3%)
	T_n	1	0.69	H→L (82.6%) H−1→L (13.7%)
		2	1.28	H−1→L (76.9%) H→L (12.6%)
		3	1.73	H−2→L (91.1%) H−1→L (5.6%)
		4	2.69	H−3→L (77.3%) H−6→L (10.7%)
5	S_n	1	1.51	H→L (95.1%) H−1→L (3.5%) H−2→L (1.0%)
	T_n	1	0.70	H→L (82.1%) H−1→L (14.2%)
		2	1.28	H−1→L (77.1%) H→L (13.1%) H−2→L (5.0%)
		3	1.75	H−2→L (91.8%) H−1→L (4.9%) H→L (1.0%)
		4	2.74	H−4→L (51.9%) H−6→L (26.0%) H−3→L (13.2%)

4. Singlet Oxygen Efficiency

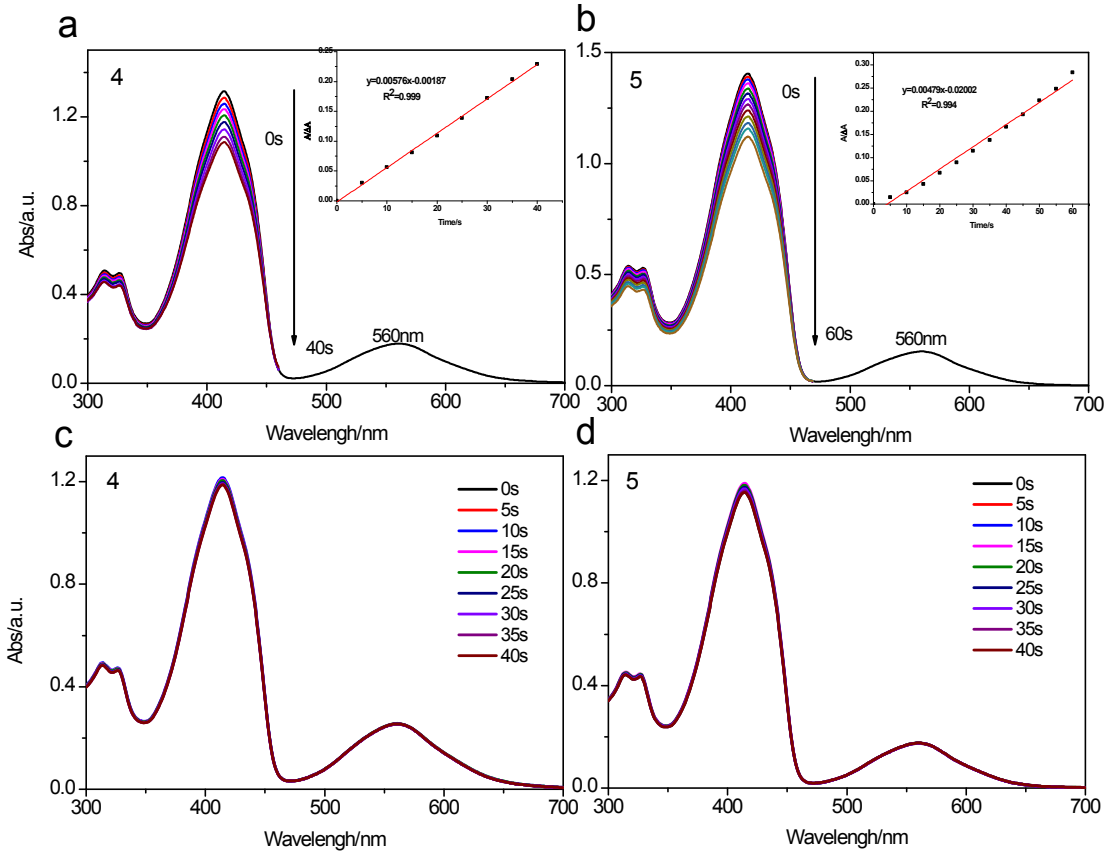


Fig. S2. Changes in the absorption spectra (a, b) of DPBF upon laser illumination (525 nm, 0.23 W) in the presence of **4**(a) , **5**(b) with 5 s interval in DCM, the absorption intensity of DPBF (~417 nm) decrease gradually as the laser irradiation time increase, indicating that $^1O_2$ is continuously produced over time. Changes in the absorption spectra (c, d) of DPBF upon laser illumination (525 nm, 0.23 W) in the presence of **4**(c), **5**(d) after deoxygenation with 5 s interval in DCM.

5. NTO analyses

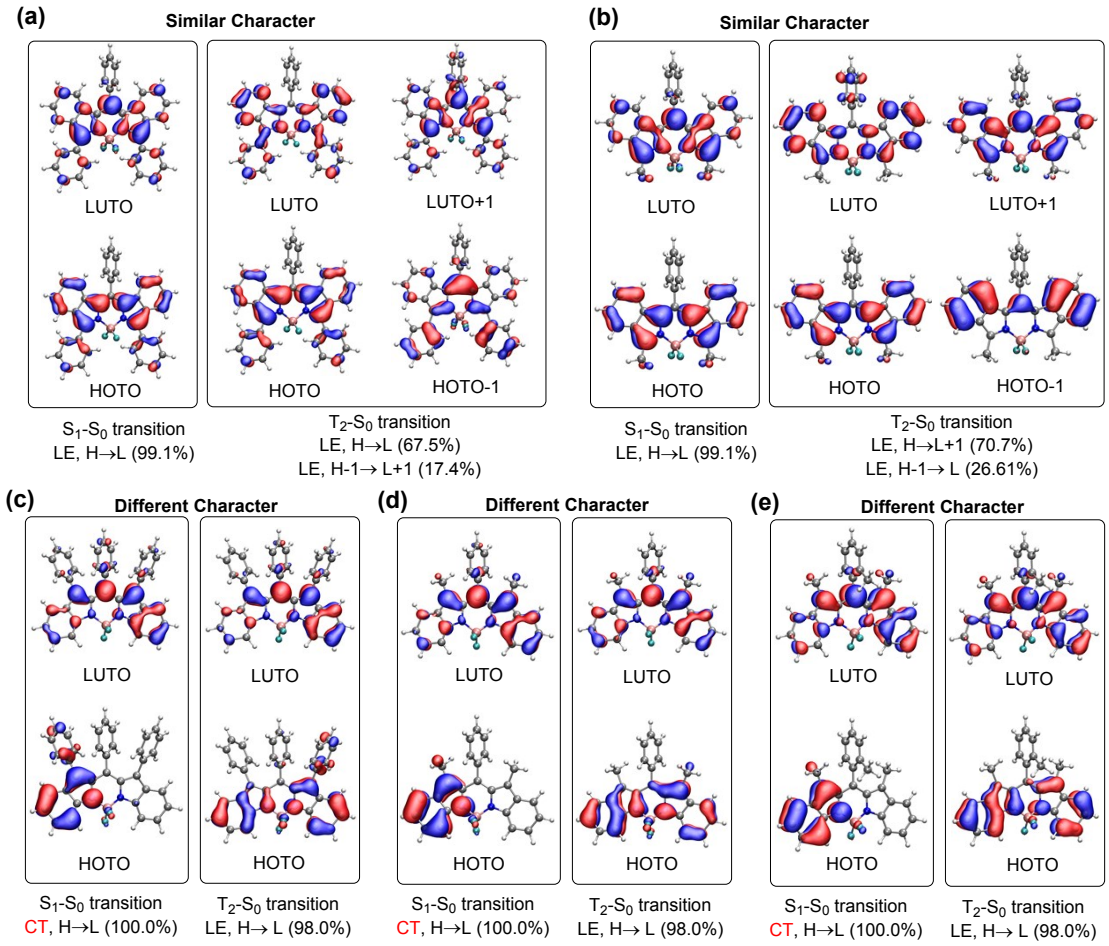
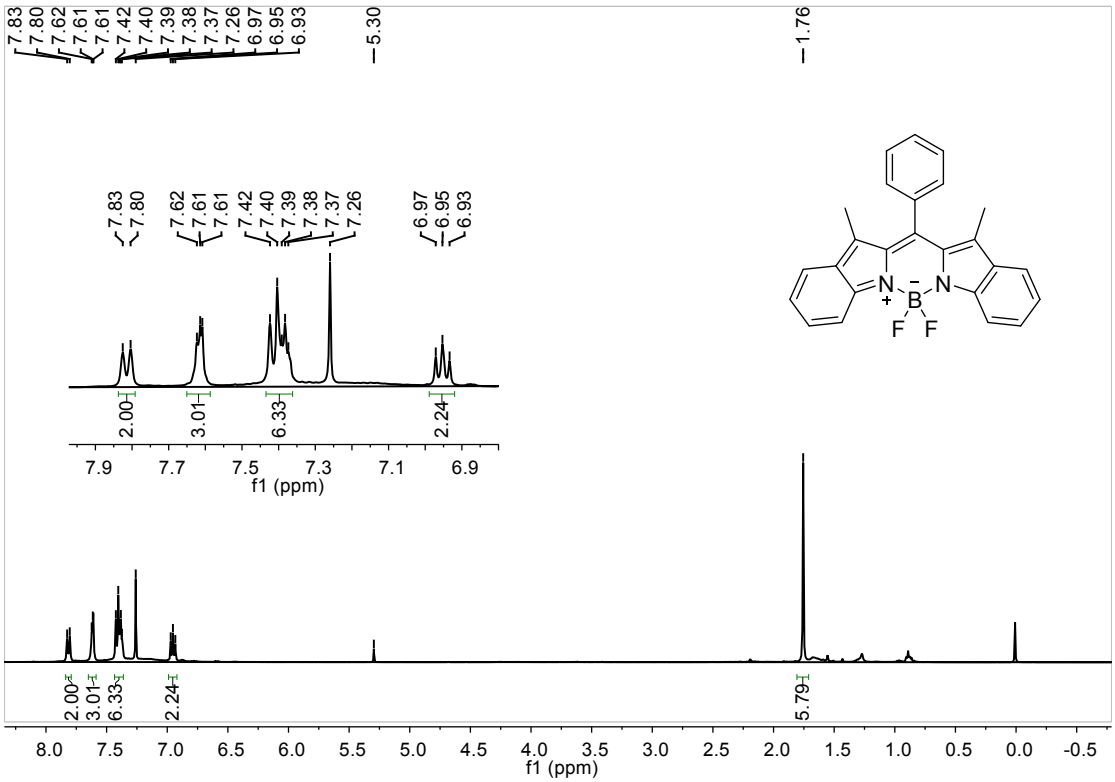


Fig. S3 Natural transition orbital (NTO) analyses for S_1 and T_2 states of the studied compounds. HOTO: highest occupied transition orbital, LUTO: lowest unoccupied transition oribtal.

5. ^{1}H NMR , ^{13}C NMR and HR MS Spectrum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7.80
7.62
7.61
7.61
7.42
7.40
7.39
7.38
7.37
7.26
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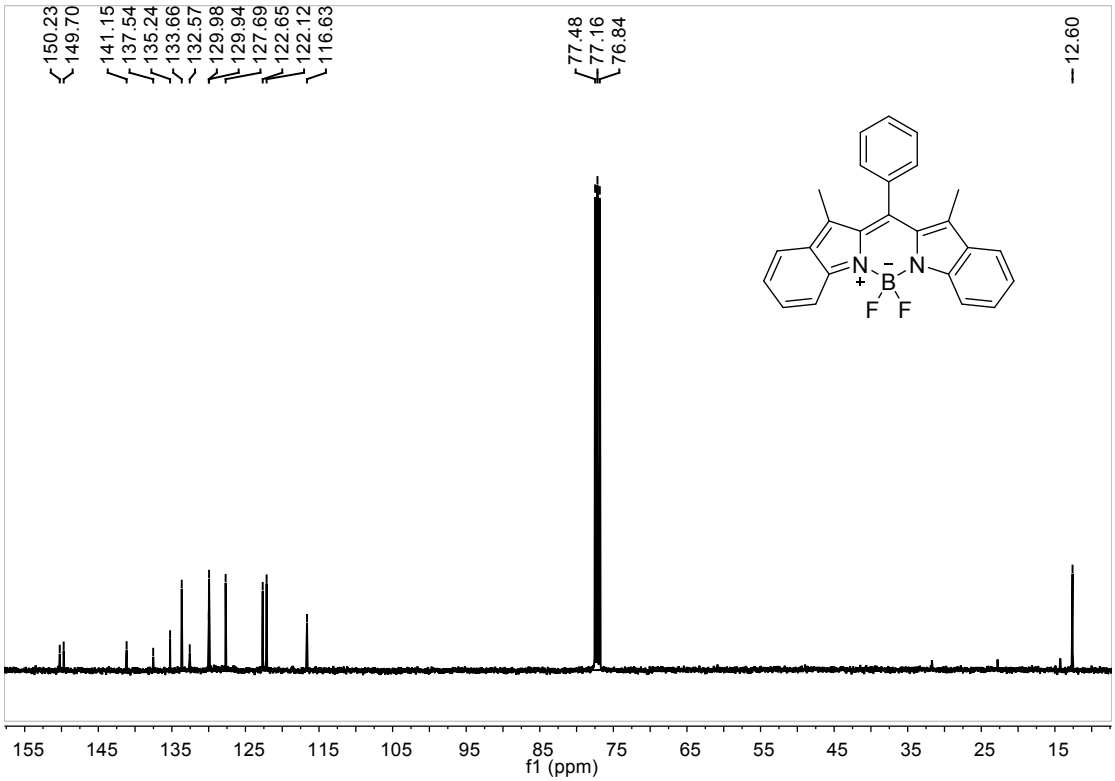
1.76
2.00
3.01
6.33
2.24
5.79
f1 (ppm)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137.54
135.24
133.66
132.57
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122.12
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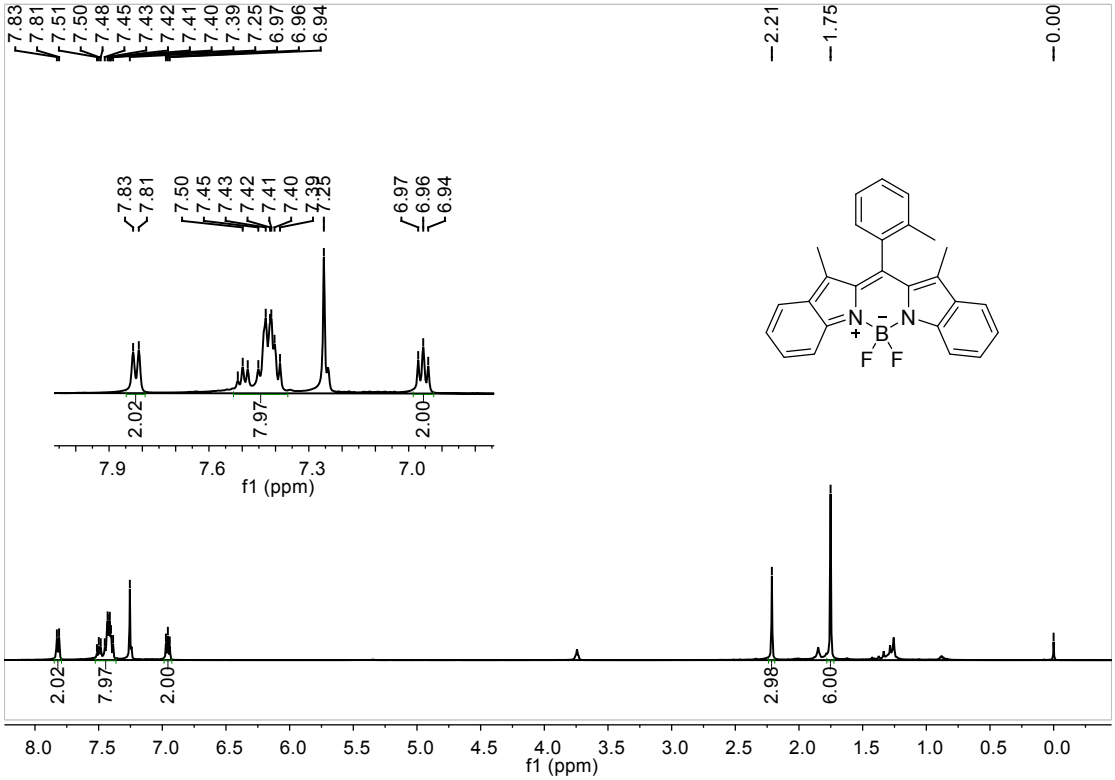
77.16
76.84
12.60
f1 (ppm)


7.83
7.81
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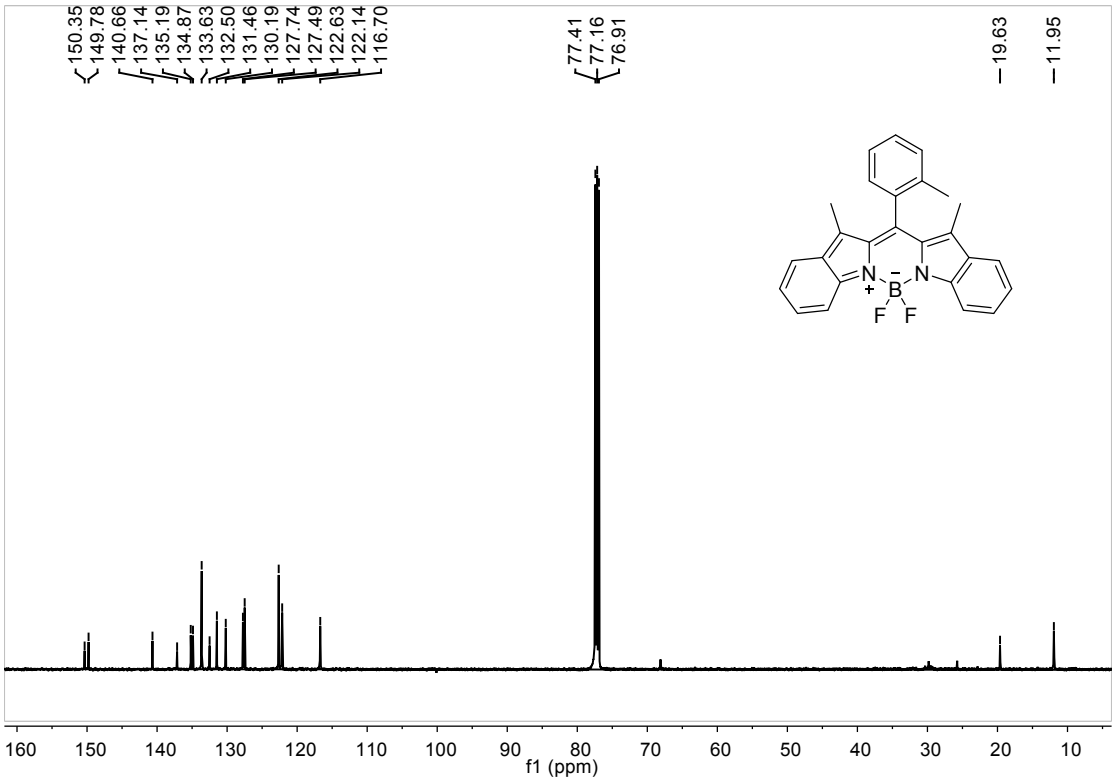
7.50
7.48
7.45
7.43
7.42
7.41
7.40
7.39
7.25
6.97
6.96
6.94
2.21
1.75
0.00
2.02
7.97
2.00
2.98
6.00
f1 (ppm)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135.19
134.87
133.63
132.50
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122.14
116.70
77.41
77.16
76.91
19.63
11.95
f1 (ppm)

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name		Instrument / Ser#	microTOF-Q II 228888.10 324
Comment			

Acquisition Parameter

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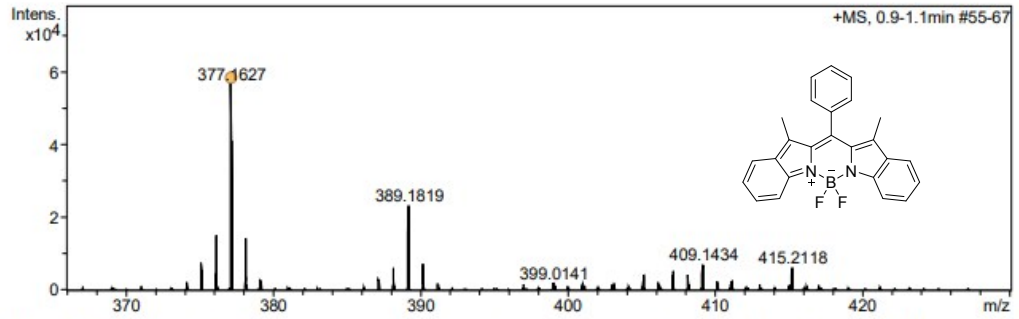

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
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Mass Spectrum SmartFormula Report

Analysis Info

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Comment			

Acquisition Parameter

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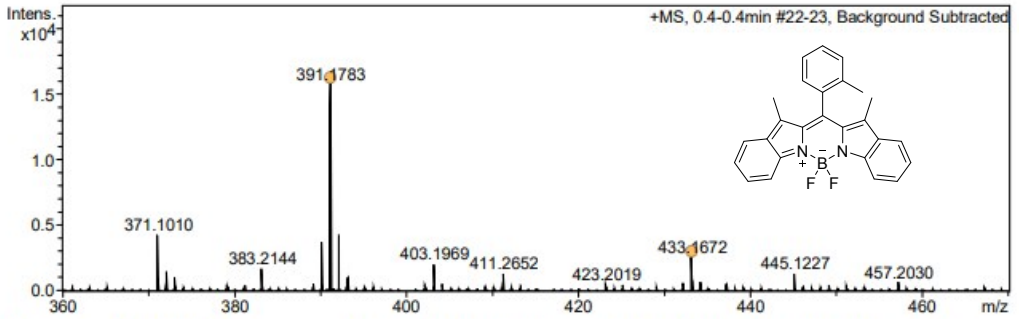

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
391.1783	1	C26H21BFN2	391.1781	-0.5	15.1	1	100.00	17.5	even	ok
433.1672	1	C26H21BF2N2Na	433.1663	2.3	19.9	1	100.00	16.5	even	ok

7. The Cartesian coordinates of the optimized geometries

(1)

C	-1.20640400	1.00281200	0.11865800
N	-1.25415800	-0.38372500	0.12868800
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N	1.25417600	-0.38386900	-0.12829100
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(3)

C	1.202933	-0.623343	-0.008641
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H	-6.349870	-2.950845	0.028260
H	-5.461396	-0.641158	-0.190711
H	4.305873	1.106503	-1.604488
H	5.291720	3.340742	-1.218765
H	4.677556	4.635616	0.804474
H	3.107220	3.658054	2.457853
H	2.143387	1.419908	2.075908
H	1.162086	1.815109	-1.717528
H	1.169953	4.282513	-1.644782
H	0.023423	5.472892	0.205560
H	-1.121393	4.173234	1.979827
H	-1.113529	1.705916	1.905726
H	-4.459407	1.158498	1.305643

H	-5.333974	3.439033	0.938385
H	-4.427666	4.833614	-0.899594
H	-2.672642	3.915816	-2.392502
H	-1.820356	1.629676	-2.037847

(4)

C	1.221734	0.287297	-0.001896
N	1.223368	-1.106885	-0.065464
B	0.051726	-1.981405	0.344830
N	-1.229405	-1.110590	0.079782
C	-1.236902	0.286996	-0.016080
C	0.029190	0.997191	0.031855
C	2.575953	0.750104	0.007431
C	3.382616	-0.396553	-0.093407
C	2.518802	-1.531475	-0.125351
C	-2.492182	-1.578496	-0.022799
C	-3.362803	-0.476632	-0.188685
C	-2.527934	0.720972	-0.203913
C	4.778541	-0.585184	-0.145976
C	5.270145	-1.868673	-0.218714
C	4.399088	-2.978113	-0.240383
C	3.024643	-2.829289	-0.193011
C	-2.950358	-2.899125	0.021180
C	-4.330151	-3.109618	-0.093578
C	-5.189991	-2.039514	-0.253280
C	-4.709971	-0.701105	-0.305177
C	3.091563	2.138027	0.140952
C	-0.008171	2.470079	0.057677
C	-3.069328	2.088086	-0.414987
C	0.378212	3.215746	-1.059107
C	0.306803	4.602098	-1.042091
C	-0.149747	5.264056	0.092239
C	-0.536230	4.531318	1.209494
C	-0.471332	3.145048	1.190872
F	0.061978	-2.297021	1.696876
F	-0.030235	-3.139321	-0.423941
H	5.450545	0.266371	-0.130818
H	6.340811	-2.036328	-0.261574
H	4.820254	-3.976243	-0.298116
H	2.355523	-3.679446	-0.219043
H	-2.247660	-3.715729	0.124930
H	-4.721158	-4.119223	-0.061135
H	-6.256045	-2.215602	-0.343981
H	-5.412714	0.115873	-0.431824

H	2.498344	2.729848	0.840980
H	4.122819	2.114545	0.501405
H	3.088091	2.680048	-0.811798
H	-3.994422	2.041224	-0.995952
H	-3.304832	2.575701	0.538849
H	-2.364942	2.735416	-0.936386
H	0.723281	2.693066	-1.945145
H	0.605459	5.168008	-1.918346
H	-0.203752	6.347312	0.105996
H	-0.886230	5.042761	2.100099
H	-0.768570	2.569368	2.061499

(5)

C	1.207716	0.122072	-0.117166
N	1.146286	-1.268340	-0.051173
B	-0.090687	-2.065568	0.315961
N	-1.309564	-1.134409	-0.034403
C	-1.245142	0.264202	-0.096834
C	0.059047	0.897339	-0.112305
C	2.578648	0.518599	-0.233016
C	3.331003	-0.668132	-0.231530
C	2.416580	-1.759349	-0.117186
C	-2.600269	-1.530566	-0.099621
C	-3.416126	-0.378461	-0.179830
C	-2.520426	0.774372	-0.165447
C	4.713277	-0.930909	-0.322239
C	5.142874	-2.237865	-0.289062
C	4.222963	-3.300941	-0.170767
C	2.860016	-3.081168	-0.084886
C	-3.127387	-2.824921	-0.073996
C	-4.520750	-2.958082	-0.136310
C	-5.327271	-1.839050	-0.216251
C	-4.777866	-0.526593	-0.234593
C	3.135988	1.890471	-0.366367
C	0.124167	2.374696	-0.147456
C	-2.999448	2.179373	-0.230754
C	-0.015357	3.047576	-1.360787
C	0.024977	4.434053	-1.415659
C	0.201266	5.158411	-0.243813
C	0.337831	4.493114	0.968197
C	0.303136	3.101304	1.040175
F	-0.173143	-2.337991	1.675853
F	-0.196258	-3.240422	-0.422743
H	5.424377	-0.116479	-0.411595

H	6.202242	-2.460623	-0.355328
H	4.595981	-4.319440	-0.149738
H	2.153174	-3.897094	-0.008493
H	-2.465638	-3.680147	-0.025853
H	-4.964025	-3.946331	-0.124545
H	-6.404253	-1.954938	-0.264949
H	-5.440427	0.331264	-0.284408
H	2.950021	2.503181	0.521912
H	4.216043	1.842884	-0.518288
H	2.697908	2.431655	-1.209761
H	-4.001572	2.256678	0.199911
H	-2.340844	2.867228	0.298229
H	-3.060968	2.529608	-1.268337
H	-0.150849	2.465469	-2.266945
H	-0.079350	4.944974	-2.366842
H	0.232862	6.242543	-0.271429
H	0.473467	5.063767	1.882259
C	0.455520	2.390700	2.352047
H	-0.354113	1.672076	2.509574
H	1.387391	1.816838	2.385217
H	0.459764	3.098219	3.183380