Supplementary Information

Enhancement of fluorescence and photostability of luminescent radicals by quadruple addition of phenyl groups

Sara Mattiello [*a] Yohei Hattori [*b] Ryota Kitajima [b] Ryota Matsuoka [c,d] Tetsuro, Kusamoto [c,d,e] Kingo Uchida [b] and Luca Beverina [a]

[a]Department of Materials Science, University of Milano-Bicocca,
Via R. Cozzi 55, 20126 Milano, Italy.
[b]Materials Chemistry Course, Faculty of Advanced Science and Technology, Ryukoku University,
Seta, Otsu, Shiga 520-2194, Japan.
[c]Department of Life and Coordination-Complex Molecular Science, Institute for Molecular Science,
5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787, Japan.
[d]SOKENDAI (The Graduate University for Advanced Studies),
Shonan Village, Hayama, Kanagawa 240-0193, Japan.
[e]JST-PRESTO,
4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan.

Contents

Table S1. Torsion angles of the aryl rings of the radicals in the ground state optimized using UB3LYP/6-31G(d).

	F_2PyBTM	*m*Ph_2-F_2PyBTM	**1**	**2**	**3**
φ_1	31°	32°	32°	31°	32°
φ_2	53°	53°	52°	52°	52°
φ_3	53°	53°	52°	52°	53°
ϕ_4	-	86°	67°	65°	65°
ϕ_5	-	86°	67°	65°	80°
ϕ_6	-	-	50°	48°	48°
ϕ_7	-	-	50°	48°	-

φ_1: Torsion angle of pyridyl ring. φ_2 and φ_3: Torsion angles of dirhlorophenyl rings. ϕ_4 and ϕ_5: Dihedral angles between *m*-phenyl groups and dichlorophenyl groups. ϕ_6 and ϕ_7: Dihedral angles between *p*-phenyl groups and dichlorophenyl groups.

Table S2. Experimental and TD-DFT calculated absorption data using UB3LYP/6-31G(d).

	Observed absorption maxima in cyclohexane	Calculated largest transition	Calculated second largest transition
1	382 nm ($\varepsilon = 1.6 \times 10^4$ $M^{-1}cm^{-1}$), 362 nm ($\varepsilon = 1.6 \times 10^4$ $M^{-1}cm^{-1}$)	398 nm (D_8, $f = 0.0940$)	382 nm (D_{11}, $f = 0.0808$)
2	364 nm ($\varepsilon = 1.1 \times 10^4$ $M^{-1}cm^{-1}$)	385 nm (D_{11}, $f = 0.1131$)	368 nm (D_{15}, $f = 0.0715$)
3	358 nm ($\varepsilon = 1.5 \times 10^4$ $M^{-1}cm^{-1}$)	363 nm (D_{15}, $f = 0.0985$)	386 nm (D_{10}, $f = 0.0804$)

Table S3. Torsion angles of the aryl rings of the radicals in the D_1 excited state optimized using UM06-2X/6-31G(d).

	F_2PyBTM	*m*Ph_2-F_2PyBTM	**1**	**2**	**3**
φ_1	13°	24°	25°	25°	24°
φ_2	55°	44°	42°	42°	42°
φ_3	55°	47°	47°	48°	49°
ϕ_4	-	65°	63°	51°	50°
ϕ_5	-	77°	66°	65°	71°
ϕ_6	-	-	38°	36°	36°
ϕ_7	-	-	49°	48°	-

Table S4. Torsion angles of of the aryl rings of the radicals in the D_1 excited state optimized using UB3LYP/6-31G(d).

	F_2PyBTM	*m*Ph_2-F_2PyBTM	**1**	**2**	**3**
φ_1	20°	24°	24°	24°	23°
φ_2	52°	47°	50°	51°	51°
φ_3	52°	52°	49°	50°	50°
ϕ_4	-	50°	47°	47°	48°
ϕ_5	-	86°	67°	66°	90°
ϕ_6	-	-	48°	48°	49°
ϕ_7	-	-	49°	48°	-

Table S5. TD-DFT calculated emission wavelength

	UB3LYP/6-31G(d)// UB3LYP/6-31G(d)	UM06-2X/6-31G(d)// UM06-2X/6-31G(d)	UBMK/6-31G(d)// UM06-2X/6-31G(d)	UPBE0/6-31G(d)// UM06-2X/6-31G(d)
1	669 nm (f = 0.0318)	584 nm (f = 0.0680)	592 nm (f = 0.0718)	628 nm (f = 0.0612)
2	790 nm (f = 0.0375)	615 nm (f = 0.1053)	635 nm (f = 0.1130)	695 nm (f = 0.0991)
3	829 nm (f = 0.0323)	625 nm (f = 0.0997)	649 nm (f = 0.1020)	715 nm (f = 0.0850)

Table S6. Emission properties.

	Solvent	Φ_f / %	τ / ns	k_f / 10^7 s^{-1}	k_{nr} / 10^7 s^{-1}
1	Cyclohexane	6	9	0.7	10
2	Cyclohexane	17	13	1.3	6.4
3	Cyclohexane	15	13	1.2	6.5
1	Toluene	9	11	0.8	8.3
2	Toluene	19	12	1.6	6.7
3	Toluene	11	9	1.2	10
1	Chloroform	13	14	0.9	6.2
2	Chloroform	2	1.9	1.1	52
3	Chloroform	1	1.2	0.8	82
1	Dichloromethane	11	15	0.7	6.0
2	Dichloromethane	0.3	0.8	0.4	1.3×10^2
3	Dichloromethane	0.3	0.6	0.5	1.7×10^2
1	Acetone	11	13	0.8	6.9
2	Acetone	0			
3	Acetone	0			

Table S7. Stability of **1**, **2**, **3**, and PyBTM in dichloromethane or cyclohexane under 370 nm UV irradiation.

Exp. no.	$t_{1/2}$ [s] PyBTM in dichloromethane	$t_{1/2}$ [s] **1** in dichloromethane	$t_{1/2}$ [s] PyBTM in cyclohexane	$t_{1/2}$ [s] **2** in cyclohexane	$t_{1/2}$ [s] **3** in cyclohexane
1	234	3084	238	1594	2550
2	342	3064	198	1510	1998
3	234	2794	184	1642	2276
4	318		178		
5	292		234		
Ave	284	2981	206	1582	2275
σ	49	162	28	67	276

Cartesian coordinates of the optimized geometries by DFT calculation

Ph_4-F_2PyBTM (**1**, Ground state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.701912	2.494084	-2.533769
2	17	0	-0.809142	-0.200674	-2.174564
3	17	0	0.809142	-0.200664	2.174559
4	17	0	-1.701913	2.494107	2.533748
5	7	0	0.000025	6.121606	0.000007
6	6	0	3.312643	0.635074	-1.480428
7	1	0	3.912333	0.850231	-2.357189
8	6	0	1.719752	0.062198	0.692401
9	6	0	-2.129079	1.329344	1.288406
10	6	0	1.049454	5.426187	0.451854
11	1	0	1.905583	5.979728	0.829227
12	6	0	0.000010	3.255382	-0.000002
13	6	0	-3.312647	0.635099	1.480413
14	6	0	-3.717890	-0.374339	0.599291
15	6	0	2.129078	1.329324	-1.288424
16	6	0	1.080285	4.039292	0.462209
17	6	0	-1.719753	0.062200	-0.692408
18	6	0	-2.905730	-0.673416	-0.519718
19	6	0	2.905726	-0.673424	0.519714
20	6	0	-1.269516	1.068499	0.198198
21	6	0	1.269516	1.068490	-0.198213
22	6	0	-1.080256	4.039307	-0.462208
23	6	0	-1.049410	5.426201	-0.451844
24	6	0	0.000002	1.802861	-0.000008
25	1	0	-1.905534	5.979753	-0.829213
26	9	0	-2.174540	3.433669	-0.956386
27	9	0	2.174562	3.433641	0.956385
28	6	0	3.717886	-0.374359	-0.599300
29	6	0	3.330175	-1.696872	1.525245
30	6	0	2.625302	-2.900790	1.668821
31	6	0	4.451351	-1.469833	2.334535
32	6	0	3.036100	-3.857649	2.596043
33	1	0	1.751611	-3.084832	1.049454
34	6	0	4.858579	-2.424227	3.266897
35	1	0	5.004563	-0.540767	2.231770
36	6	0	4.153889	-3.621427	3.398917
37	1	0	2.481272	-4.787143	2.692672
38	1	0	5.728042	-2.231040	3.889446
39	1	0	4.472693	-4.365896	4.123502
40	1	0	-3.912339	0.850263	2.357171
41	6	0	-3.330182	-1.696878	-1.525233
42	6	0	-2.625291	-2.900785	-1.668816
43	6	0	-4.451384	-1.469869	-2.334495
44	6	0	-3.036095	-3.857659	-2.596019
45	1	0	-1.751583	-3.084807	-1.049467
46	6	0	-4.858617	-2.424277	-3.266840
47	1	0	-5.004612	-0.540813	-2.231724
48	6	0	-4.153907	-3.621465	-3.398869
49	1	0	-2.481252	-4.787144	-2.692654
50	1	0	-5.728100	-2.231111	-3.889368
51	1	0	-4.472714	-4.365945	-4.123440
52	6	0	-4.996940	-1.079454	0.901837
53	6	0	-5.070903	-2.478920	0.987593
54	6	0	-6.153912	-0.330031	1.171393
55	6	0	-6.266871	-3.107215	1.329827
56	1	0	-4.185954	-3.075712	0.793938
57	6	0	-7.352421	-0.960007	1.506187
58	1	0	-6.114984	0.753760	1.100160
59	6	0	-7.412575	-2.351640	1.587764
60	1	0	-6.302216	-4.191191	1.398030
61	1	0	-8.238541	-0.361894	1.701190
62	1	0	-8.344694	-2.844395	1.850665
63	6	0	4.996933	-1.079478	-0.901847
64	6	0	5.070914	-2.478948	-0.987533
65	6	0	6.153889	-0.330055	-1.171474

66	6	0	6.266880	-3.107244	-1.329769
67	1	0	4.185979	-3.075742	-0.793824
68	6	0	7.352397	-0.960033	-1.506270
69	1	0	6.114952	0.753739	-1.100293
70	6	0	7.412567	-2.351669	-1.587778
71	1	0	6.302236	-4.191224	-1.397919
72	1	0	8.238504	-0.361918	-1.701329
73	1	0	8.344684	-2.844425	-1.850681

$(MeOPh)_4$-F_2PyBTM (**2**, Ground state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.651978	3.037434	-2.566699
2	17	0	-0.853793	0.336801	-2.155169
3	17	0	0.853794	0.336819	2.155170
4	17	0	-1.651986	3.037453	2.566678
5	7	0	0.000008	6.661197	-0.000017
6	6	0	3.279296	1.171832	-1.550917
7	1	0	3.856256	1.384245	-2.443363
8	6	0	1.733104	0.597859	0.653015
9	6	0	-2.103145	1.869434	1.331127
10	6	0	1.057571	5.965024	0.431536
11	1	0	1.921016	6.518149	0.792650
12	6	0	0.000002	3.793665	-0.000009
13	6	0	-3.279302	1.171846	1.550906
14	6	0	-3.703600	0.158794	0.681544
15	6	0	2.103140	1.869423	-1.331141
16	6	0	1.088533	4.578157	0.441411
17	6	0	-1.733105	0.597853	-0.653017
18	6	0	-2.914409	-0.139928	-0.455997
19	6	0	2.914408	-0.139924	0.455999
20	6	0	-1.264562	1.607202	0.225116
21	6	0	1.264560	1.607199	-0.225126
22	6	0	-1.088527	4.578159	-0.441432
23	6	0	-1.057558	5.965027	-0.431566
24	6	0	-0.000001	2.341008	-0.000006
25	1	0	-1.921001	6.518154	-0.792683
26	9	0	-2.192531	3.973472	-0.915196
27	9	0	2.192535	3.973468	0.915178
28	6	0	3.703595	0.158787	-0.681547
29	6	0	3.356492	-1.163880	1.450518
30	6	0	2.641067	-2.360105	1.633151
31	6	0	4.506389	-0.962786	2.218937
32	6	0	3.065013	-3.318252	2.542801
33	1	0	1.741386	-2.539356	1.050953
34	6	0	4.942164	-1.913353	3.144879
35	1	0	5.077207	-0.046873	2.096189
36	6	0	4.220569	-3.100734	3.308494
37	1	0	2.516656	-4.244664	2.682091
38	1	0	5.836879	-1.717207	3.724433
39	1	0	-3.856264	1.384267	2.443348
40	6	0	-3.356490	-1.163894	-1.450508
41	6	0	-2.641065	-2.360122	-1.633122
42	6	0	-4.506382	-0.962807	-2.218935
43	6	0	-3.065008	-3.318280	-2.542763
44	1	0	-1.741388	-2.539368	-1.050917
45	6	0	-4.942153	-1.913384	-3.144869
46	1	0	-5.077200	-0.046892	-2.096201
47	6	0	-4.220559	-3.100768	-3.308465
48	1	0	-2.516652	-4.244694	-2.682040
49	1	0	-5.836865	-1.717244	-3.724430
50	6	0	-4.971900	-0.547107	1.014316
51	6	0	-5.063247	-1.951470	1.062310
52	6	0	-6.112401	0.190182	1.358434
53	6	0	-6.239902	-2.581984	1.436262
54	1	0	-4.197269	-2.555091	0.813399
55	6	0	-7.307806	-0.430390	1.727983
56	1	0	-6.076675	1.275768	1.320311

57	6	0	-7.375147	-1.827024	1.769924
58	1	0	-6.305482	-3.664507	1.482411
59	1	0	-8.168507	0.180664	1.974537
60	6	0	4.971894	-0.547117	-1.014317
61	6	0	5.063241	-1.951480	-1.062298
62	6	0	6.112395	0.190169	-1.358447
63	6	0	6.239894	-2.581999	-1.436248
64	1	0	4.197264	-2.555099	-0.813377
65	6	0	7.307797	-0.430407	-1.727994
66	1	0	6.076669	1.275755	-1.320334
67	6	0	7.375139	-1.827042	-1.769921
68	1	0	6.305475	-3.664522	-1.482386
69	1	0	8.168498	0.180644	-1.974557
70	8	0	-8.482381	-2.543212	2.117657
71	8	0	-4.552947	-4.100437	-4.175626
72	8	0	4.552961	-4.100393	4.175664
73	8	0	8.482371	-2.543233	-2.117651
74	6	0	9.656651	-1.832668	-2.477679
75	1	0	10.025243	-1.214857	-1.648063
76	1	0	10.402685	-2.591343	-2.720877
77	1	0	9.489046	-1.194366	-3.355218
78	6	0	5.709591	-3.934022	4.980202
79	1	0	5.621380	-3.059457	5.638278
80	1	0	5.782951	-4.837025	5.589032
81	1	0	6.616178	-3.834529	4.368617
82	6	0	-9.656665	-1.832642	2.477664
83	1	0	-10.025244	-1.214836	1.648039
84	1	0	-10.402703	-2.591315	2.720855
85	1	0	-9.489071	-1.194336	3.355201
86	6	0	-5.709576	-3.934075	-4.980169
87	1	0	-5.621360	-3.059520	-5.638259
88	1	0	-5.782936	-4.837087	-5.588985
89	1	0	-6.616163	-3.834569	-4.368588

(MeOPh)$_3$-F$_2$PyBTM (**3**, Ground state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.027504	2.376270	-2.973723
2	17	0	-1.905910	-0.536824	-1.608467
3	17	0	0.362356	0.657599	2.234348
4	17	0	-2.481496	2.988783	2.579514
5	7	0	-1.923677	6.181620	-0.886057
6	6	0	2.038065	1.030283	-1.933378
7	1	0	2.431902	1.128254	-2.938222
8	6	0	0.955471	0.719719	0.578388
9	6	0	-2.898702	1.536704	1.686050
10	6	0	-0.705641	5.761162	-0.527348
11	1	0	0.084983	6.501839	-0.437337
12	6	0	-1.400595	3.415623	-0.346276
13	6	0	-3.897376	0.749795	2.240681
14	6	0	-4.241006	-0.449755	1.626194
15	6	0	0.801338	1.580853	-1.641627
16	6	0	-0.420704	4.429562	-0.262100
17	6	0	-2.614156	-0.053493	-0.077583
18	6	0	-3.615093	-0.890437	0.450604
19	6	0	2.207755	0.136187	0.315165
20	6	0	-2.205023	1.169135	0.509796
21	6	0	0.192911	1.441582	-0.374106
22	6	0	-2.666225	3.914850	-0.725567
23	6	0	-2.888098	5.259858	-0.982721
24	6	0	-1.135509	2.014395	-0.069860
25	1	0	-3.880804	5.587513	-1.280944
26	9	0	-3.697321	3.063335	-0.871374
27	9	0	0.830934	4.112202	0.112516
28	6	0	2.757646	0.297684	-0.980359
29	6	0	2.964016	-0.578155	1.387734
30	6	0	2.506301	-1.798949	1.913493
31	6	0	4.158938	-0.053950	1.888356
32	6	0	3.221101	-2.470301	2.895030

33	1	0	1.578367	-2.226464	1.543778
34	6	0	4.886064	-0.712853	2.882215
35	1	0	4.534175	0.887698	1.498070
36	6	0	4.418352	-1.930218	3.389101
37	1	0	2.872253	-3.415482	3.299038
38	1	0	5.806083	-0.270769	3.246836
39	1	0	-4.388533	1.057671	3.155132
40	6	0	-4.005445	-2.172496	-0.207172
41	6	0	-3.246243	-3.337405	-0.012286
42	6	0	-5.139664	-2.245124	-1.019022
43	6	0	-3.611726	-4.534384	-0.611513
44	1	0	-2.361477	-3.301912	0.617199
45	6	0	-5.517808	-3.441861	-1.631450
46	1	0	-5.740590	-1.354812	-1.182210
47	6	0	-4.751371	-4.595035	-1.427566
48	1	0	-3.030607	-5.439044	-0.463266
49	1	0	-6.402379	-3.460498	-2.257445
50	6	0	4.068659	-0.271915	-1.396955
51	6	0	4.400759	-1.625600	-1.196013
52	6	0	4.996208	0.531427	-2.073178
53	6	0	5.602837	-2.144725	-1.651094
54	1	0	3.702452	-2.280583	-0.686572
55	6	0	6.215609	0.025571	-2.528713
56	1	0	4.773720	1.583103	-2.233562
57	6	0	6.523862	-1.322927	-2.319490
58	1	0	5.852741	-3.190824	-1.504611
59	1	0	6.908037	0.687272	-3.036291
60	8	0	-5.024740	-5.815586	-1.971033
61	8	0	5.045024	-2.663943	4.353183
62	8	0	7.677211	-1.929185	-2.720379
63	6	0	8.640412	-1.150961	-3.413747
64	1	0	9.011651	-0.323119	-2.795229
65	1	0	9.465063	-1.828831	-3.640983
66	1	0	8.234113	-0.747065	-4.350373
67	6	0	6.258622	-2.165836	4.893993
68	1	0	6.113445	-1.193905	5.383782
69	1	0	6.578360	-2.899245	5.636445
70	1	0	7.034348	-2.068553	4.122939
71	6	0	-6.165074	-5.939706	-2.806536
72	1	0	-6.090333	-5.292426	-3.690293
73	1	0	-6.189783	-6.983295	-3.125277
74	1	0	-7.090363	-5.704310	-2.264283
75	17	0	-5.492173	-1.415445	2.384492

Ph_4-F_2PyBTM (**1**, First doublet excited state, UM06-2X/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.942433	2.754745	-2.336188
2	17	0	-0.472028	-0.438610	-1.966270
3	17	0	0.494254	-0.337828	1.921836
4	17	0	-1.880963	2.712777	2.295712
5	7	0	-0.143921	6.209014	-0.006229
6	6	0	3.437915	0.826939	-1.264149
7	1	0	4.137801	1.110215	-2.043159
8	6	0	1.600719	0.077754	0.629217
9	6	0	-2.233852	1.510878	1.114724
10	6	0	0.956286	5.544357	0.360669
11	1	0	1.818778	6.122531	0.680556
12	6	0	-0.030520	3.336662	-0.021787
13	6	0	-3.434927	0.870670	1.197858
14	6	0	-3.720135	-0.276060	0.425309
15	6	0	2.246687	1.516728	-1.150337
16	6	0	1.041949	4.165718	0.365917
17	6	0	-1.544323	-0.025383	-0.662370
18	6	0	-2.721145	-0.725191	-0.531343
19	6	0	2.777715	-0.669235	0.514919
20	6	0	-1.201067	1.152989	0.123477
21	6	0	1.267337	1.184036	-0.189659
22	6	0	-1.156226	4.090810	-0.406512

23	6	0	-1.189763	5.473234	-0.379370
24	6	0	-0.002302	1.895497	-0.042424
25	1	0	-2.096739	5.986153	-0.687812
26	9	0	-2.256337	3.431196	-0.811130
27	9	0	2.189082	3.604671	0.772185
28	6	0	3.724810	-0.271231	-0.448319
29	6	0	3.055155	-1.819362	1.422631
30	6	0	2.265137	-2.971155	1.371425
31	6	0	4.135358	-1.774284	2.305936
32	6	0	2.554151	-4.061565	2.184687
33	1	0	1.425986	-3.006573	0.681096
34	6	0	4.421275	-2.862608	3.124658
35	1	0	4.757066	-0.884076	2.338996
36	6	0	3.633605	-4.008989	3.064085
37	1	0	1.937349	-4.953530	2.131995
38	1	0	5.263363	-2.815544	3.808041
39	1	0	3.859674	-4.859530	3.699740
40	1	0	-4.131403	1.172924	1.972022
41	6	0	-3.035955	-1.867474	-1.426603
42	6	0	-2.227023	-3.009525	-1.430827
43	6	0	-4.169706	-1.828065	-2.244098
44	6	0	-2.557643	-4.099285	-2.226693
45	1	0	-1.347334	-3.039435	-0.794010
46	6	0	-4.487002	-2.912074	-3.056024
47	1	0	-4.800852	-0.944039	-2.239468
48	6	0	-3.687007	-4.051458	-3.043140
49	1	0	-1.931628	-4.985814	-2.213867
50	1	0	-5.363793	-2.868101	-3.694024
51	1	0	-3.940508	-4.900979	-3.669446
52	6	0	-4.974808	-0.977341	0.680022
53	6	0	-5.072448	-2.385997	0.703339
54	6	0	-6.135131	-0.228155	0.972820
55	6	0	-6.274823	-3.006539	1.004666
56	1	0	-4.191904	-2.989068	0.514477
57	6	0	-7.338149	-0.855175	1.256617
58	1	0	-6.090608	0.855947	0.932617
59	6	0	-7.414004	-2.248325	1.276426
60	1	0	-6.323287	-4.090235	1.033793
61	1	0	-8.221582	-0.257921	1.457910
62	1	0	-8.354452	-2.739659	1.504416
63	6	0	5.021150	-0.970936	-0.655462
64	6	0	5.096784	-2.361345	-0.803966
65	6	0	6.198578	-0.220618	-0.751546
66	6	0	6.318336	-2.980906	-1.039056
67	1	0	4.191245	-2.956358	-0.738938
68	6	0	7.422296	-0.842135	-0.982338
69	1	0	6.151591	0.857815	-0.625801
70	6	0	7.485658	-2.224799	-1.126985
71	1	0	6.358261	-4.059349	-1.157219
72	1	0	8.326305	-0.244256	-1.045263
73	1	0	8.438945	-2.711783	-1.307441

(MeOPh)$_4$-F$_2$PyBTM (**2**, First doublet excited state, UM06-2X/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.822639	3.271310	-2.368548
2	17	0	-0.556664	0.228973	-1.939713
3	17	0	0.532696	0.228980	2.008347
4	17	0	-1.900394	3.327446	2.351814
5	7	0	0.037843	6.795793	-0.096872
6	6	0	3.395405	1.443407	-1.280234
7	1	0	4.059120	1.725826	-2.089693
8	6	0	1.557632	0.597179	0.647983
9	6	0	-2.223041	2.071869	1.187414
10	6	0	1.108266	6.084894	0.257036
11	1	0	2.012770	6.620252	0.533549
12	6	0	-0.010735	3.916278	-0.038708
13	6	0	-3.400404	1.366943	1.346219

14	6	0	-3.699782	0.259898	0.547569
15	6	0	2.199195	2.086515	-1.170778
16	6	0	1.107156	4.703306	0.303304
17	6	0	-1.615435	0.633239	-0.601828
18	6	0	-2.779447	-0.128252	-0.446593
19	6	0	2.739722	-0.102749	0.513450
20	6	0	-1.268894	1.746993	0.200063
21	6	0	1.193361	1.744007	-0.156556
22	6	0	-1.109801	4.719749	-0.407985
23	6	0	-1.055820	6.099844	-0.422554
24	6	0	-0.013817	2.477635	0.011824
25	1	0	-1.941260	6.652702	-0.724553
26	9	0	-2.257745	4.130864	-0.774768
27	9	0	2.235282	4.078518	0.689726
28	6	0	3.702672	0.308138	-0.496308
29	6	0	3.108196	-1.186318	1.449502
30	6	0	2.287340	-2.314375	1.623968
31	6	0	4.316041	-1.129984	2.150497
32	6	0	2.676246	-3.350947	2.448069
33	1	0	1.348089	-2.377857	1.083215
34	6	0	4.706966	-2.153378	3.008180
35	1	0	4.959740	-0.263616	2.030266
36	6	0	3.888166	-3.275381	3.152536
37	1	0	2.061610	-4.235228	2.576406
38	1	0	5.641924	-2.067492	3.548268
39	1	0	-4.076307	1.645728	2.147644
40	6	0	-3.070955	-1.286192	-1.337222
41	6	0	-2.256347	-2.426320	-1.324572
42	6	0	-4.189810	-1.283150	-2.164965
43	6	0	-2.557528	-3.526550	-2.107598
44	1	0	-1.379960	-2.443985	-0.681663
45	6	0	-4.504728	-2.380012	-2.965794
46	1	0	-4.838111	-0.411562	-2.177232
47	6	0	-3.686386	-3.508993	-2.935199
48	1	0	-1.937730	-4.416900	-2.100864
49	1	0	-5.383989	-2.341119	-3.597599
50	6	0	-4.978608	-0.454740	0.799459
51	6	0	-5.045605	-1.851437	0.935265
52	6	0	-6.158981	0.272028	0.954380
53	6	0	-6.242979	-2.484394	1.211415
54	1	0	-4.142867	-2.444223	0.826623
55	6	0	-7.376184	-0.351588	1.228669
56	1	0	-6.134491	1.352610	0.841059
57	6	0	-7.419231	-1.738770	1.358127
58	1	0	-6.299191	-3.561852	1.324487
59	1	0	-8.270664	0.251152	1.332167
60	6	0	4.910584	-0.431246	-0.804349
61	6	0	4.991959	-1.850031	-0.751132
62	6	0	6.064356	0.260930	-1.240737
63	6	0	6.143837	-2.513139	-1.102240
64	1	0	4.119165	-2.425496	-0.466535
65	6	0	7.233916	-0.396065	-1.579884
66	1	0	6.050779	1.345887	-1.265381
67	6	0	7.282122	-1.796566	-1.514181
68	1	0	6.198441	-3.596119	-1.086184
69	1	0	8.100236	0.179641	-1.882462
70	8	0	-8.544165	-2.453918	1.623391
71	8	0	-3.900261	-4.635275	-3.665571
72	8	0	4.173962	-4.335857	3.940064
73	8	0	8.360166	-2.537217	-1.826488
74	6	0	9.523185	-1.868176	-2.278501
75	1	0	9.914607	-1.195531	-1.507369
76	1	0	10.254062	-2.647729	-2.487928
77	1	0	9.318932	-1.300019	-3.192522
78	6	0	5.374954	-4.299173	4.683180
79	1	0	5.385060	-3.450420	5.376634
80	1	0	5.408353	-5.230451	5.247286
81	1	0	6.247811	-4.239882	4.022514
82	6	0	-9.744546	-1.734508	1.792089
83	1	0	-10.009406	-1.180728	0.883002
84	1	0	-10.515814	-2.475429	2.002004
85	1	0	-9.674552	-1.032998	2.632350
86	6	0	-5.030182	-4.656594	-4.508434
87	1	0	-4.976606	-3.866779	-5.267602
88	1	0	-5.024986	-5.630327	-4.998101
89	1	0	-5.957988	-4.541896	-3.934842

$(MeOPh)_3$-F_2PyBTM (**3**, First doublet excited state, UM06-2X/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.046529	2.393843	-2.964511
2	17	0	-1.787148	-0.614292	-1.569459
3	17	0	0.222951	0.667323	2.225848
4	17	0	-2.743900	2.985748	2.502307
5	7	0	-1.980163	6.249214	-0.919430
6	6	0	2.039216	1.154269	-1.881316
7	1	0	2.452976	1.279994	-2.875453
8	6	0	0.840143	0.752545	0.580883
9	6	0	-3.058125	1.510839	1.597382
10	6	0	-0.747240	5.766523	-0.704048
11	1	0	0.085141	6.467113	-0.732639
12	6	0	-1.487304	3.428893	-0.359707
13	6	0	-4.049460	0.693201	2.120639
14	6	0	-4.297857	-0.542277	1.535248
15	6	0	0.757954	1.626903	-1.625315
16	6	0	-0.487507	4.438552	-0.429660
17	6	0	-2.607947	-0.099426	-0.092010
18	6	0	-3.578796	-0.981229	0.415081
19	6	0	2.137584	0.213938	0.343522
20	6	0	-2.283903	1.175288	0.452924
21	6	0	0.089312	1.476248	-0.367504
22	6	0	-2.767832	4.000906	-0.606909
23	6	0	-2.969915	5.343296	-0.862146
24	6	0	-1.240394	2.049223	-0.094469
25	1	0	-3.985234	5.689973	-1.043622
26	9	0	-3.855360	3.190394	-0.614814
27	9	0	0.810452	4.084238	-0.203357
28	6	0	2.747783	0.427080	-0.929146
29	6	0	2.894030	-0.473496	1.396560
30	6	0	2.339093	-1.541882	2.155541
31	6	0	4.231616	-0.083432	1.687321
32	6	0	3.078348	-2.187950	3.117342
33	1	0	1.332081	-1.875573	1.940109
34	6	0	4.970229	-0.692513	2.683397
35	1	0	4.660525	0.749282	1.143659
36	6	0	4.401601	-1.762717	3.405608
37	1	0	2.676521	-3.026276	3.675819
38	1	0	5.969603	-0.338826	2.905025
39	1	0	-4.603472	1.004325	2.997511
40	6	0	-3.866734	-2.303289	-0.219479
41	6	0	-3.205799	-3.465183	0.207534
42	6	0	-4.813645	-2.419227	-1.239606
43	6	0	-3.479150	-4.698542	-0.369022
44	1	0	-2.470652	-3.397830	1.004933
45	6	0	-5.100129	-3.652176	-1.830609
46	1	0	-5.337658	-1.532179	-1.583950
47	6	0	-4.429630	-4.799934	-1.394635
48	1	0	-2.971983	-5.600555	-0.040528
49	1	0	-5.840812	-3.701860	-2.620556
50	6	0	4.050389	-0.165337	-1.315170
51	6	0	4.340375	-1.536711	-1.127464
52	6	0	5.019740	0.619397	-1.965933
53	6	0	5.540825	-2.083771	-1.547322
54	1	0	3.593906	-2.182817	-0.676438
55	6	0	6.233001	0.083899	-2.390233
56	1	0	4.825754	1.676589	-2.122980
57	6	0	6.502964	-1.278249	-2.180556
58	1	0	5.753591	-3.140346	-1.419461
59	1	0	6.957607	0.728076	-2.874597
60	8	0	-4.627397	-6.055864	-1.897923
61	8	0	5.019744	-2.440338	4.378567
62	8	0	7.647101	-1.905530	-2.550946
63	6	0	8.638468	-1.163651	-3.253357
64	1	0	9.031393	-0.341621	-2.641944
65	1	0	9.440739	-1.870891	-3.467625
66	1	0	8.243945	-0.762453	-4.194796

67	6	0	6.357728	-2.090451	4.753190
68	1	0	6.399155	-1.060913	5.123076
69	1	0	6.624352	-2.781540	5.551870
70	1	0	7.042183	-2.215788	3.907957
71	6	0	-5.584982	-6.218151	-2.930636
72	1	0	-5.317873	-5.640079	-3.825495
73	1	0	-5.584249	-7.282013	-3.176174
74	1	0	-6.590238	-5.923634	-2.600721
75	17	0	-5.549013	-1.553266	2.252489

Ph_4-F_2PyBTM (**1**, First doublet excited state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-1.838116	2.580950	2.468278
2	17	0	0.693384	-0.253466	2.142596
3	17	0	-0.696078	-0.318580	-2.071168
4	17	0	1.743523	2.476006	-2.479591
5	7	0	0.119686	6.173120	-0.049318
6	6	0	-3.406696	0.708199	1.382426
7	1	0	-4.052317	0.965304	2.214566
8	6	0	-1.698237	0.037723	-0.654683
9	6	0	2.149412	1.345017	-1.237442
10	6	0	-1.000444	5.491822	-0.341148
11	1	0	-1.884996	6.064330	-0.612048
12	6	0	0.011228	3.264115	-0.007705
13	6	0	3.384809	0.712792	-1.367963
14	6	0	3.766866	-0.312622	-0.515808
15	6	0	-2.209555	1.387698	1.229211
16	6	0	-1.082631	4.112391	-0.336234
17	6	0	1.636912	0.041401	0.693373
18	6	0	2.865706	-0.670639	0.557450
19	6	0	-2.884319	-0.701702	-0.511724
20	6	0	1.213110	1.073867	-0.166184
21	6	0	-1.285725	1.104540	0.191043
22	6	0	1.159964	4.045042	0.294496
23	6	0	1.188552	5.426182	0.258820
24	6	0	-0.025375	1.835131	0.010033
25	1	0	2.114549	5.939708	0.509621
26	9	0	2.305930	3.395789	0.646447
27	9	0	-2.264061	3.552258	-0.688205
28	6	0	-3.768376	-0.345244	0.533611
29	6	0	-3.247084	-1.777199	-1.487663
30	6	0	-2.547359	-2.992314	-1.519606
31	6	0	-4.308472	-1.590535	-2.383447
32	6	0	-2.902582	-3.996768	-2.419006
33	1	0	-1.719832	-3.146261	-0.832072
34	6	0	-4.661527	-2.592335	-3.288070
35	1	0	-4.857846	-0.653774	-2.368325
36	6	0	-3.961531	-3.799305	-3.307681
37	1	0	-2.351729	-4.933992	-2.426872
38	1	0	-5.485684	-2.428376	-3.977327
39	1	0	-4.238269	-4.580796	-4.010484
40	1	0	4.006490	0.961795	-2.220163
41	6	0	3.276135	-1.690782	1.526519
42	6	0	2.422090	-2.764239	1.885586
43	6	0	4.562144	-1.625537	2.124215
44	6	0	2.845529	-3.731890	2.782541
45	1	0	1.447392	-2.845517	1.420018
46	6	0	4.958716	-2.570287	3.060457
47	1	0	5.216853	-0.797520	1.879272
48	6	0	4.108451	-3.631980	3.385665
49	1	0	2.193294	-4.565580	3.023652
50	1	0	5.930884	-2.483862	3.535665
51	1	0	4.424808	-4.380373	4.106366
52	6	0	5.020465	-1.040752	-0.809920
53	6	0	5.073289	-2.450467	-0.868257
54	6	0	6.189620	-0.316802	-1.123019
55	6	0	6.251575	-3.105378	-1.215827
56	1	0	4.175999	-3.028178	-0.673187

57	6	0	7.367469	-0.975449	-1.461498
58	1	0	6.171509	0.767991	-1.070611
59	6	0	7.404051	-2.373253	-1.509704
60	1	0	6.266667	-4.190306	-1.268757
61	1	0	8.261233	-0.399257	-1.683444
62	1	0	8.323226	-2.885724	-1.778712
63	6	0	-5.066896	-1.029927	0.794467
64	6	0	-5.164996	-2.424975	0.927332
65	6	0	-6.230440	-0.263105	0.976698
66	6	0	-6.384251	-3.029984	1.227149
67	1	0	-4.278441	-3.037557	0.801944
68	6	0	-7.451341	-0.868584	1.273977
69	1	0	-6.175797	0.816684	0.866976
70	6	0	-7.533420	-2.255747	1.400598
71	1	0	-6.435196	-4.110922	1.330071
72	1	0	-8.338947	-0.254455	1.402396
73	1	0	-8.483584	-2.729805	1.632093

(MeOPh)$_4$-F$_2$PyBTM (**2**, First doublet excited state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	1.662214	2.968224	-2.635656
2	17	0	-0.768658	0.181564	-2.084607
3	17	0	0.759790	0.417557	2.128031
4	17	0	-1.796816	3.192980	2.414643
5	7	0	0.035235	6.739654	-0.233778
6	6	0	3.307481	1.207225	-1.519426
7	1	0	3.898363	1.409628	-2.405519
8	6	0	1.654602	0.646010	0.630707
9	6	0	-2.186627	1.957709	1.220104
10	6	0	1.121594	6.011703	0.065272
11	1	0	2.046063	6.543484	0.282459
12	6	0	-0.024053	3.824567	-0.125258
13	6	0	-3.367631	1.266748	1.434693
14	6	0	-3.743548	0.183383	0.631114
15	6	0	2.093083	1.863137	-1.362759
16	6	0	1.118433	4.632533	0.130694
17	6	0	-1.719416	0.562402	-0.638992
18	6	0	-2.889822	-0.189100	-0.434630
19	6	0	2.872605	-0.076811	0.483894
20	6	0	-1.290505	1.659028	0.161002
21	6	0	1.201214	1.640550	-0.260989
22	6	0	-1.137434	4.652544	-0.445664
23	6	0	-1.079147	6.032203	-0.482081
24	6	0	-0.045110	2.398564	-0.075325
25	1	0	-1.981050	6.582716	-0.742152
26	9	0	-2.321046	4.067567	-0.755179
27	9	0	2.286472	4.015738	0.472632
28	6	0	3.718830	0.218313	-0.630333
29	6	0	3.324341	-1.043231	1.490770
30	6	0	2.490552	-2.095166	1.963350
31	6	0	4.638438	-0.953055	2.028700
32	6	0	2.948627	-3.003992	2.887494
33	1	0	1.493768	-2.203159	1.555269
34	6	0	5.095441	-1.830893	2.993376
35	1	0	5.277734	-0.140023	1.707245
36	6	0	4.254305	-2.876221	3.427298
37	1	0	2.332414	-3.829619	3.226372
38	1	0	6.086823	-1.703028	3.410320
39	1	0	-3.986292	1.538853	2.282456
40	6	0	-3.269323	-1.297876	-1.363866
41	6	0	-2.543530	-2.500592	-1.405285
42	6	0	-4.374444	-1.174655	-2.210324
43	6	0	-2.911895	-3.537475	-2.251436
44	1	0	-1.676789	-2.620183	-0.760860
45	6	0	-4.756142	-2.205115	-3.073542
46	1	0	-4.952658	-0.255405	-2.198325
47	6	0	-4.023613	-3.395945	-3.094691
48	1	0	-2.353933	-4.468497	-2.280652

49	1	0	-5.618274	-2.066036	-3.715833
50	6	0	-5.020597	-0.511609	0.956787
51	6	0	-5.106482	-1.908274	1.115108
52	6	0	-6.185140	0.234227	1.182924
53	6	0	-6.296290	-2.522531	1.477771
54	1	0	-4.224388	-2.519760	0.957852
55	6	0	-7.392372	-0.368920	1.545973
56	1	0	-6.155597	1.313305	1.057759
57	6	0	-7.451734	-1.757629	1.695443
58	1	0	-6.355864	-3.599208	1.604773
59	1	0	-8.268503	0.250523	1.701450
60	6	0	4.954805	-0.538019	-0.935338
61	6	0	4.991808	-1.952122	-0.949370
62	6	0	6.128097	0.144112	-1.307555
63	6	0	6.142187	-2.640229	-1.294873
64	1	0	4.090642	-2.511288	-0.719003
65	6	0	7.293385	-0.534485	-1.653543
66	1	0	6.131703	1.230306	-1.303468
67	6	0	7.308014	-1.938829	-1.647641
68	1	0	6.162314	-3.725013	-1.323656
69	1	0	8.178671	0.031494	-1.919265
70	8	0	-8.572607	-2.458498	2.046195
71	8	0	-4.305011	-4.471470	-3.891364
72	8	0	4.588223	-3.795958	4.340391
73	8	0	8.383022	-2.702136	-1.966652
74	6	0	9.578526	-2.057271	-2.392234
75	1	0	9.992790	-1.419444	-1.601330
76	1	0	10.283269	-2.858887	-2.617029
77	1	0	9.408467	-1.456713	-3.294111
78	6	0	5.882539	-3.754400	4.951788
79	1	0	6.022105	-2.817464	5.500845
80	1	0	5.902711	-4.595024	5.644435
81	1	0	6.670790	-3.871945	4.200921
82	6	0	-9.765030	-1.731549	2.287389
83	1	0	-10.094874	-1.185325	1.393292
84	1	0	-10.520518	-2.473178	2.554542
85	1	0	-9.646005	-1.021153	3.116628
86	6	0	-5.418160	-4.381386	-4.764324
87	1	0	-5.299263	-3.565193	-5.489555
88	1	0	-5.459441	-5.333248	-5.297675
89	1	0	-6.355855	-4.235337	-4.211401

$(MeOPh)_3$-F_2PyBTM (**3**, First doublet excited state, UB3LYP/6-31G(d))

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.046529	2.393843	-2.964511
2	17	0	-1.787148	-0.614292	-1.569459
3	17	0	0.222951	0.667323	2.225848
4	17	0	-2.743900	2.985748	2.502307
5	7	0	-1.980163	6.249214	-0.919430
6	6	0	2.039216	1.154269	-1.881316
7	1	0	2.452976	1.279994	-2.875453
8	6	0	0.840143	0.752545	0.580883
9	6	0	-3.058125	1.510839	1.597382
10	6	0	-0.747240	5.766523	-0.704048
11	1	0	0.085141	6.467113	-0.732639
12	6	0	-1.487304	3.428893	-0.359707
13	6	0	-4.049460	0.693201	2.120639
14	6	0	-4.297857	-0.542277	1.535248
15	6	0	0.757954	1.626903	-1.625315
16	6	0	-0.487507	4.438552	-0.429660
17	6	0	-2.607947	-0.099426	-0.092010
18	6	0	-3.578796	-0.981229	0.415081
19	6	0	2.137584	0.213938	0.343522
20	6	0	-2.283903	1.175288	0.452924
21	6	0	0.089312	1.476248	-0.367504
22	6	0	-2.767832	4.000906	-0.606909
23	6	0	-2.969915	5.343296	-0.862146

24	6	0	-1.240394	2.049223	-0.094469
25	1	0	-3.985234	5.689973	-1.043622
26	9	0	-3.855360	3.190394	-0.614814
27	9	0	0.810452	4.084238	-0.203357
28	6	0	2.747783	0.427080	-0.929146
29	6	0	2.894030	-0.473496	1.396560
30	6	0	2.339093	-1.541882	2.155541
31	6	0	4.231616	-0.083432	1.687321
32	6	0	3.078348	-2.187950	3.117342
33	1	0	1.332081	-1.875573	1.940109
34	6	0	4.970229	-0.692513	2.683397
35	1	0	4.660525	0.749282	1.143659
36	6	0	4.401601	-1.762717	3.405608
37	1	0	2.676521	-3.026276	3.675819
38	1	0	5.969603	-0.338826	2.905025
39	1	0	-4.603472	1.004325	2.997511
40	6	0	-3.866734	-2.303289	-0.219479
41	6	0	-3.205799	-3.465183	0.207534
42	6	0	-4.813645	-2.419227	-1.239606
43	6	0	-3.479150	-4.698542	-0.369022
44	1	0	-2.470652	-3.397830	1.004933
45	6	0	-5.100129	-3.652176	-1.830609
46	1	0	-5.337658	-1.532179	-1.583950
47	6	0	-4.429630	-4.799934	-1.394635
48	1	0	-2.971983	-5.600555	-0.040528
49	1	0	-5.840812	-3.701860	-2.620556
50	6	0	4.050389	-0.165337	-1.315170
51	6	0	4.340375	-1.536711	-1.127464
52	6	0	5.019740	0.619397	-1.965933
53	6	0	5.540825	-2.083771	-1.547322
54	1	0	3.593906	-2.182817	-0.676438
55	6	0	6.233001	0.083899	-2.390233
56	1	0	4.825754	1.676589	-2.122980
57	6	0	6.502964	-1.278249	-2.180556
58	1	0	5.753591	-3.140346	-1.419461
59	1	0	6.957607	0.728076	-2.874597
60	8	0	-4.627397	-6.055864	-1.897923
61	8	0	5.019744	-2.440338	4.378567
62	8	0	7.647101	-1.905530	-2.550946
63	6	0	8.638468	-1.163651	-3.253357
64	1	0	9.031393	-0.341621	-2.641944
65	1	0	9.440739	-1.870891	-3.467625
66	1	0	8.243945	-0.762453	-4.194796
67	6	0	6.357728	-2.090451	4.753190
68	1	0	6.399155	-1.060913	5.123076
69	1	0	6.624352	-2.781540	5.551870
70	1	0	7.042183	-2.215788	3.907957
71	6	0	-5.584982	-6.218151	-2.930636
72	1	0	-5.317873	-5.640079	-3.825495
73	1	0	-5.584249	-7.282013	-3.176174
74	1	0	-6.590238	-5.923634	-2.600721
75	17	0	-5.549013	-1.553266	2.252489

Results of TD-DFT calculations

Ph_4-F_2PyBTM (**1**, Optimized ground state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.146-A     2.4164 eV  513.09 nm  f=0.0652  <S**2>=0.901
    185A ->186A      -0.17024
    172B ->185B      -0.14043
    173B ->185B       0.12848
    174B ->185B       0.14890
    180B ->185B      -0.16243
    182B ->185B       0.15531
    184B ->185B       0.90219
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -3709.99947978
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  2.112-A     2.4677 eV  502.42 nm  f=0.0108  <S**2>=0.865
    185A ->187A      -0.13478
    171B ->185B      -0.12240
    175B ->185B      -0.16544
    178B ->185B      -0.19404
    183B ->185B       0.92740

 Excited State   3:  2.098-A     2.6331 eV  470.86 nm  f=0.0090  <S**2>=0.850
    173B ->185B       0.14232
    179B ->185B       0.12991
    180B ->185B       0.17086
    182B ->185B       0.92206
    184B ->185B      -0.19511

 Excited State   4:  2.170-A     2.6910 eV  460.73 nm  f=0.0139  <S**2>=0.927
    185A ->187A      -0.22285
    171B ->185B      -0.25968
    177B ->185B      -0.18561
    181B ->185B       0.88623

 Excited State   5:  2.126-A     2.7489 eV  451.03 nm  f=0.0074  <S**2>=0.880
    176B ->185B      -0.36841
    180B ->185B       0.87601
    184B ->185B       0.15517

 Excited State   6:  2.240-A     2.9937 eV  414.15 nm  f=0.0002  <S**2>=1.004
    172B ->185B       0.42784
    172B ->187B       0.11356
    173B ->185B       0.67191
    173B ->187B       0.14351
    174B ->185B       0.47673
    176B ->185B      -0.12532
    179B ->185B       0.12698

 Excited State   7:  2.172-A     3.0676 eV  404.17 nm  f=0.0132  <S**2>=0.929
    185A ->187A       0.34188
    185A ->190A       0.11018
    170B ->185B       0.17509
    171B ->185B       0.30561
    175B ->185B       0.37437
    178B ->185B       0.59693
    181B ->185B       0.25289
    183B ->185B       0.34057

 Excited State   8:  2.527-A     3.1146 eV  398.08 nm  f=0.0940  <S**2>=1.346
    183A ->188A      -0.10760
    184A ->187A      -0.12276
    185A ->186A       0.63015
    172B ->185B       0.24163
    174B ->185B      -0.23908
    176B ->185B       0.25841
    179B ->185B      -0.23011
    180B ->185B       0.13640
    182B ->185B       0.14742
    183B ->186B       0.14490
    184B ->185B       0.30851
    184B ->187B       0.11744
```

```
Excited State   9:  2.124-A     3.1902 eV  388.64 nm  f=0.0056  <S**2>=0.878
   185A ->187A       0.38423
   185A ->190A       0.10326
   170B ->185B       0.27614
   171B ->185B       0.21400
   175B ->185B      -0.10385
   177B ->185B       0.59695
   178B ->185B      -0.47229
   181B ->185B       0.27248

Excited State  10:  2.066-A     3.2166 eV  385.46 nm  f=0.0020  <S**2>=0.818
   174B ->185B      -0.17299
   176B ->185B       0.44477
   179B ->185B       0.82575
   180B ->185B       0.20208
   182B ->185B      -0.19643

Excited State  11:  2.232-A     3.2462 eV  381.93 nm  f=0.0808  <S**2>=0.995
   185A ->186A      -0.43120
   172B ->185B       0.27763
   173B ->185B       0.17756
   174B ->185B      -0.15846
   176B ->185B       0.58006
   179B ->185B      -0.42423
   180B ->185B       0.25526
   182B ->185B      -0.10673

Excited State  12:  2.131-A     3.2560 eV  380.79 nm  f=0.0101  <S**2>=0.885
   185A ->187A      -0.24440
   185A ->190A      -0.12636
   170B ->185B      -0.28008
   171B ->185B      -0.18217
   177B ->185B       0.74064
   178B ->185B       0.44061

Excited State  13:  3.086-A     3.3324 eV  372.05 nm  f=0.0420  <S**2>=2.130
   181A ->187A       0.11872
   182A ->188A      -0.16906
   183A ->187A       0.11403
   183A ->189A       0.17162
   184A ->186A       0.32764
   185A ->187A      -0.27273
   185A ->189A      -0.12987
   185A ->190A       0.13634
   170B ->185B       0.29468
   171B ->185B       0.20828
   177B ->185B       0.15606
   178B ->185B       0.22529
   181B ->185B      -0.13343
   181B ->187B      -0.12142
   182B ->188B       0.16519
   183B ->187B      -0.17191
   183B ->189B      -0.14912
   184B ->186B      -0.32197

Excited State  14:  2.213-A     3.3810 eV  366.71 nm  f=0.0080  <S**2>=0.974
   185A ->186A       0.15896
   172B ->185B      -0.54991
   174B ->185B       0.58587
   176B ->185B       0.44660
   179B ->185B      -0.16508
   180B ->185B       0.10290

Excited State  15:  2.134-A     3.3898 eV  365.76 nm  f=0.0200  <S**2>=0.888
   185A ->187A      -0.26000
   170B ->185B      -0.16404
   175B ->185B       0.84654
   177B ->185B       0.12604
   178B ->185B      -0.34821
```

$(MeOPh)_4$-F_2PyBTM (**2**, Optimized ground state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:
```

```
Excited State   1:  2.086-A     2.0895 eV  593.37 nm  f=0.0837  <S**2>=0.838
   207B ->217B       0.10827
   216B ->217B       0.97058
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -4168.10412119
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:  2.077-A     2.1521 eV  576.12 nm  f=0.0182  <S**2>=0.829
   212B ->217B       0.16664
   215B ->217B       0.97020

Excited State   3:  2.089-A     2.4215 eV  512.02 nm  f=0.0252  <S**2>=0.841
   205B ->217B      -0.11295
   209B ->217B      -0.11752
   210B ->217B       0.14679
   211B ->217B       0.25023
   213B ->217B       0.92048

Excited State   4:  2.098-A     2.4433 eV  507.45 nm  f=0.0117  <S**2>=0.851
   217A ->219A      -0.10951
   204B ->217B       0.20709
   212B ->217B      -0.15886
   214B ->217B       0.94595

Excited State   5:  2.126-A     2.7554 eV  449.96 nm  f=0.0078  <S**2>=0.880
   210B ->217B       0.79134
   211B ->217B      -0.55291

Excited State   6:  2.102-A     2.7980 eV  443.12 nm  f=0.0017  <S**2>=0.854
   217A ->219A      -0.12206
   204B ->217B       0.16510
   208B ->217B       0.14257
   212B ->217B       0.92234
   215B ->217B      -0.20257

Excited State   7:  2.093-A     2.8997 eV  427.58 nm  f=0.0092  <S**2>=0.845
   209B ->217B      -0.19851
   210B ->217B       0.50469
   211B ->217B       0.73965
   213B ->217B      -0.33139

Excited State   8:  2.293-A     2.9366 eV  422.20 nm  f=0.0120  <S**2>=1.064
   217A ->218A       0.34787
   203B ->217B      -0.16270
   203B ->219B      -0.10597
   205B ->217B       0.46207
   207B ->217B       0.60266
   209B ->217B       0.27090
   211B ->217B       0.16845
   213B ->217B       0.15682
   216B ->217B      -0.17417

Excited State   9:  2.339-A     2.9870 eV  415.07 nm  f=0.0042  <S**2>=1.118
   215A ->219A      -0.11166
   216A ->218A      -0.10781
   217A ->219A      -0.51085
   202B ->217B      -0.18770
   204B ->217B       0.60435
   206B ->217B       0.15894
   212B ->217B      -0.24701
   214B ->217B      -0.28037
   216B ->218B       0.10732

Excited State  10:  2.526-A     3.0488 eV  406.66 nm  f=0.0452  <S**2>=1.345
   216A ->219A       0.10846
   217A ->218A       0.47762
   203B ->217B       0.70287
   203B ->219B       0.12992
   205B ->217B      -0.18142
   207B ->217B      -0.11794
   215B ->218B       0.12515
   216B ->219B      -0.10995

Excited State  11:  2.491-A     3.2205 eV  384.98 nm  f=0.1131  <S**2>=1.301
   216A ->219A      -0.12145
   217A ->218A      -0.47121
   203B ->217B       0.58187
```

```
   203B ->219B       0.10198
   205B ->217B       0.13814
   207B ->217B       0.33502
   209B ->217B       0.30297
   214B ->218B      -0.10056
   215B ->218B      -0.15687
   216B ->219B       0.12279

 Excited State  12:  3.156-A     3.2539 eV  381.03 nm  f=0.0189  <S**2>=2.240
   204A ->219A      -0.12164
   211A ->220A       0.11563
   212A ->221A       0.11599
   213A ->219A      -0.15960
   214A ->218A       0.14357
   215A ->219A      -0.11374
   215A ->221A      -0.10889
   216A ->218A       0.35346
   217A ->219A       0.14139
   217A ->221A       0.15307
   217A ->222A       0.12613
   217A ->225A       0.12875
   202B ->217B      -0.31601
   204B ->217B       0.27837
   204B ->219B       0.10256
   208B ->217B       0.17867
   211B ->220B      -0.10692
   212B ->221B      -0.10547
   213B ->218B       0.14328
   214B ->219B       0.13238
   215B ->219B       0.18981
   215B ->221B      -0.12601
   216B ->218B      -0.34080

 Excited State  13:  2.109-A     3.2976 eV  375.98 nm  f=0.0037  <S**2>=0.862
   217A ->219A       0.21210
   202B ->217B       0.25938
   204B ->217B       0.10020
   208B ->217B       0.89722
   212B ->217B      -0.12082

 Excited State  14:  2.069-A     3.3094 eV  374.64 nm  f=0.0005  <S**2>=0.820
   203B ->217B      -0.11839
   205B ->217B      -0.18726
   207B ->217B      -0.36111
   209B ->217B       0.87405
   210B ->217B       0.14167
   211B ->217B       0.15639

 Excited State  15:  2.188-A     3.3680 eV  368.13 nm  f=0.0715  <S**2>=0.947
   217A ->219A       0.46555
   202B ->217B       0.40148
   204B ->217B       0.51481
   206B ->217B       0.32381
   208B ->217B      -0.34799
```

$(MeOPh)_3$-F_2PyBTM (**3**, Optimized ground state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.077-A     2.0443 eV  606.49 nm  f=0.0511  <S**2>=0.828
   196B ->197B       0.97585
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -4282.12122900
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  2.069-A     2.3345 eV  531.10 nm  f=0.0166  <S**2>=0.821
   186B ->197B      -0.10218
   193B ->197B      -0.17205
   194B ->197B      -0.49327
   195B ->197B       0.83272

 Excited State   3:  2.075-A     2.3728 eV  522.52 nm  f=0.0134  <S**2>=0.826
   186B ->197B       0.11802
   191B ->197B       0.11081
```

```
   193B ->197B       0.13314
   194B ->197B       0.79971
   195B ->197B       0.53524

Excited State   4:  2.175-A     2.6773 eV  463.09 nm  f=0.0089  <S**2>=0.933
   197A ->199A       0.19479
   186B ->197B       0.13502
   187B ->197B       0.15806
   188B ->197B       0.13779
   189B ->197B      -0.14032
   190B ->197B      -0.18119
   191B ->197B      -0.39260
   192B ->197B       0.58320
   193B ->197B      -0.48798
   194B ->197B       0.15917

Excited State   5:  2.117-A     2.7241 eV  455.14 nm  f=0.0084  <S**2>=0.871
   188B ->197B      -0.34425
   190B ->197B      -0.45375
   192B ->197B       0.50867
   193B ->197B       0.58217

Excited State   6:  2.128-A     2.8004 eV  442.73 nm  f=0.0068  <S**2>=0.882
   197A ->199A      -0.10601
   187B ->197B      -0.11544
   188B ->197B      -0.35698
   189B ->197B       0.33068
   191B ->197B       0.60736
   192B ->197B       0.28190
   193B ->197B      -0.45503
   196B ->197B      -0.12541

Excited State   7:  2.116-A     2.8902 eV  428.98 nm  f=0.0063  <S**2>=0.869
   197A ->199A       0.12935
   186B ->197B       0.14787
   188B ->197B       0.66006
   189B ->197B       0.27850
   190B ->197B       0.22452
   191B ->197B       0.29045
   192B ->197B       0.35426
   193B ->197B       0.30724
   194B ->197B      -0.19157

Excited State   8:  2.281-A     2.9488 eV  420.46 nm  f=0.0051  <S**2>=1.051
   197A ->198A       0.36340
   197A ->199A       0.13932
   184B ->197B      -0.12703
   185B ->197B      -0.13698
   186B ->197B       0.70312
   187B ->197B       0.15961
   188B ->197B      -0.23316
   191B ->197B      -0.14750
   192B ->197B      -0.17665
   193B ->197B       0.13822
   194B ->197B      -0.18280
   196B ->197B      -0.10012

Excited State   9:  2.403-A     3.0283 eV  409.42 nm  f=0.0072  <S**2>=1.193
   197A ->198A       0.32542
   197A ->199A      -0.10878
   185B ->197B       0.83748
   185B ->199B       0.15367
   196B ->198B       0.11116

Excited State  10:  2.718-A     3.2084 eV  386.43 nm  f=0.0804  <S**2>=1.597
   193A ->201A       0.10136
   194A ->198A       0.14872
   196A ->198A       0.15655
   197A ->198A      -0.35257
   197A ->199A       0.38290
   184B ->197B      -0.25689
   185B ->197B       0.30902
   186B ->197B       0.19454
   187B ->197B       0.11675
   190B ->197B      -0.21410
   191B ->197B       0.27752
   192B ->197B      -0.19859
```

```
   194B ->198B      -0.13606
   196B ->198B      -0.26401

 Excited State  11:  2.176-A     3.2171 eV  385.39 nm  f=0.0080  <S**2>=0.933
   197A ->198A      -0.17368
   185B ->197B       0.18139
   186B ->197B       0.10824
   188B ->197B      -0.38713
   189B ->197B       0.11591
   190B ->197B       0.74164
   191B ->197B      -0.25729
   192B ->197B       0.25547
   193B ->197B       0.14415
   196B ->198B      -0.10659

 Excited State  12:  2.094-A     3.2573 eV  380.64 nm  f=0.0068  <S**2>=0.846
   197A ->198A      -0.15883
   197A ->199A      -0.11133
   184B ->197B       0.13121
   189B ->197B       0.81696
   190B ->197B      -0.28665
   191B ->197B      -0.38327

 Excited State  13:  2.204-A     3.3174 eV  373.74 nm  f=0.0477  <S**2>=0.964
   197A ->198A      -0.34178
   197A ->199A      -0.29678
   184B ->197B       0.52195
   185B ->197B       0.11767
   186B ->197B       0.35770
   187B ->197B       0.39509
   189B ->197B      -0.14279
   191B ->197B       0.17342

 Excited State  14:  2.089-A     3.3723 eV  367.66 nm  f=0.0031  <S**2>=0.841
   197A ->198A       0.10840
   184B ->197B      -0.11652
   185B ->197B      -0.12770
   186B ->197B      -0.37260
   187B ->197B       0.84930
   188B ->197B      -0.11985
   189B ->197B       0.21289

 Excited State  15:  2.840-A     3.4135 eV  363.22 nm  f=0.0985  <S**2>=1.766
   189A ->200A      -0.11674
   190A ->200A       0.10030
   191A ->200A      -0.16628
   192A ->199A       0.10397
   194A ->198A      -0.11715
   196A ->198A      -0.21381
   196A ->199A       0.20017
   197A ->198A      -0.11200
   197A ->199A       0.48559
   197A ->201A      -0.12549
   197A ->207A       0.10743
   184B ->197B       0.21859
   186B ->197B      -0.16482
   187B ->197B      -0.15034
   188B ->197B      -0.17100
   189B ->197B       0.10716
   191B ->197B       0.10572
   191B ->199B       0.13202
   191B ->200B       0.11893
   192B ->197B      -0.10320
   192B ->200B       0.13380
   196B ->198B       0.20377
```

Ph_4-F_2PyBTM (**1**, Optimized first doublet excited state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.092-A     1.8528 eV  669.16 nm  f=0.0318  <S**2>=0.844
   185A ->186A       0.11112
   174B ->185B       0.10441
   184B ->185B       0.96744
```

```
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -3710.00985630
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   2:  2.104-A     2.2579 eV  549.11 nm  f=0.0482  <S**2>=0.857
   185A ->187A      -0.11332
   173B ->185B       0.13255
   179B ->185B      -0.18154
   182B ->185B       0.10109
   183B ->185B       0.92507

Excited State   3:  2.110-A     2.3915 eV  518.44 nm  f=0.0240  <S**2>=0.863
   185A ->186A       0.11031
   173B ->185B       0.10449
   175B ->185B       0.10988
   180B ->185B       0.18618
   181B ->185B       0.36602
   182B ->185B       0.84580
   183B ->185B      -0.10173

Excited State   4:  2.130-A     2.5072 eV  494.51 nm  f=0.0205  <S**2>=0.885
   185A ->187A      -0.18284
   172B ->185B      -0.19784
   178B ->185B       0.19931
   180B ->185B      -0.13025
   181B ->185B       0.84044
   182B ->185B      -0.29935

Excited State   5:  2.099-A     2.5789 eV  480.76 nm  f=0.0067  <S**2>=0.851
   176B ->185B       0.22659
   177B ->185B       0.60609
   178B ->185B       0.63434
   179B ->185B       0.27824
   180B ->185B      -0.10283
   181B ->185B      -0.11976
   183B ->185B       0.10751

Excited State   6:  2.671-A     2.7889 eV  444.56 nm  f=0.0289  <S**2>=1.534
   184A ->186A      -0.26714
   184A ->188A       0.17622
   185A ->186A       0.40284
   185A ->187A       0.12360
   174B ->185B       0.28245
   175B ->185B       0.15314
   176B ->185B       0.19177
   179B ->185B       0.19248
   180B ->185B       0.36443
   181B ->185B       0.11045
   182B ->185B      -0.34470
   184B ->185B      -0.20837
   184B ->186B      -0.30386
   184B ->188B       0.13945

Excited State   7:  2.356-A     2.8697 eV  432.05 nm  f=0.0065  <S**2>=1.138
   184A ->186A       0.13986
   185A ->186A      -0.21083
   171B ->185B       0.54716
   171B ->187B       0.11739
   172B ->185B      -0.16279
   173B ->185B       0.38907
   174B ->185B       0.48787
   180B ->185B       0.26520
   184B ->186B       0.18044

Excited State   8:  2.383-A     2.8831 eV  430.03 nm  f=0.0226  <S**2>=1.169
   184A ->186A       0.16453
   185A ->186A      -0.29119
   185A ->187A       0.13496
   172B ->185B       0.18551
   173B ->185B      -0.18398
   174B ->185B      -0.10611
   175B ->185B       0.30213
   176B ->185B       0.15945
   177B ->185B      -0.30996
   179B ->185B       0.55637
   180B ->185B       0.17780
   183B ->185B       0.27397
```

```
   184B ->186B       0.22058

Excited State   9:  2.178-A     2.9603 eV  418.82 nm  f=0.0095  <S**2>=0.936
   184A ->186A       0.12026
   171B ->185B      -0.29717
   172B ->185B       0.13270
   174B ->185B      -0.14293
   176B ->185B      -0.19835
   177B ->185B       0.29511
   179B ->185B      -0.25886
   180B ->185B       0.75399
   182B ->185B      -0.11847
   184B ->186B       0.12823

Excited State  10:  2.072-A     3.0148 eV  411.25 nm  f=0.0019  <S**2>=0.823
   185A ->187A      -0.15582
   177B ->185B      -0.59957
   178B ->185B       0.65014
   179B ->185B      -0.24199
   180B ->185B       0.15128
   181B ->185B      -0.25646

Excited State  11:  2.221-A     3.0697 eV  403.90 nm  f=0.0028  <S**2>=0.983
   184A ->186A       0.12898
   171B ->185B      -0.29348
   172B ->185B       0.16679
   173B ->185B      -0.14594
   174B ->185B       0.32452
   176B ->185B       0.68965
   178B ->185B      -0.13851
   179B ->185B      -0.35971
   180B ->185B      -0.10716
   184B ->186B       0.14904

Excited State  12:  2.162-A     3.1180 eV  397.64 nm  f=0.0213  <S**2>=0.919
   185A ->187A      -0.40756
   185A ->190A      -0.10110
   170B ->185B       0.23185
   171B ->185B      -0.17043
   172B ->185B      -0.27178
   173B ->185B       0.11273
   175B ->185B      -0.40749
   176B ->185B       0.23045
   178B ->185B      -0.25401
   179B ->185B       0.45728
   180B ->185B       0.20806
   181B ->185B      -0.11484

Excited State  13:  2.483-A     3.1649 eV  391.75 nm  f=0.0545  <S**2>=1.291
   183A ->187A      -0.10969
   184A ->186A      -0.24449
   185A ->186A      -0.31978
   185A ->187A       0.14265
   185A ->188A      -0.15967
   170B ->185B       0.16280
   171B ->185B       0.21317
   172B ->185B      -0.20972
   174B ->185B      -0.37724
   176B ->185B       0.45343
   179B ->185B      -0.21422
   180B ->185B       0.17266
   183B ->185B       0.11337
   183B ->187B       0.12314
   184B ->186B      -0.18352

Excited State  14:  2.466-A     3.2163 eV  385.49 nm  f=0.0828  <S**2>=1.270
   183A ->187A       0.10949
   184A ->186A       0.18645
   185A ->186A       0.44946
   185A ->187A      -0.16829
   185A ->188A       0.16113
   171B ->185B       0.43690
   173B ->185B      -0.11015
   174B ->185B      -0.42158
   175B ->185B       0.21417
   176B ->185B       0.21347
   183B ->187B      -0.13494
```

```
   184B ->188B      -0.11909

 Excited State  15:  2.127-A     3.2385 eV  382.85 nm  f=0.0267  <S**2>=0.881
   185A ->186A      -0.10365
   185A ->187A      -0.32746
   170B ->185B       0.25952
   171B ->185B      -0.18995
   172B ->185B      -0.10412
   173B ->185B       0.23110
   175B ->185B       0.76727
   177B ->185B       0.17449
```

$(MeOPh)_4$-F_2PyBTM (**2**, Optimized first doublet excited state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.062-A     1.5703 eV  789.57 nm  f=0.0375  <S**2>=0.813
   216B ->217B       0.98390
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -4168.11366658
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  2.069-A     1.9662 eV  630.57 nm  f=0.0540  <S**2>=0.820
   212B ->217B       0.12372
   215B ->217B       0.97040

 Excited State   3:  2.080-A     2.1879 eV  566.68 nm  f=0.0430  <S**2>=0.832
   209B ->217B      -0.15581
   211B ->217B       0.15048
   213B ->217B      -0.15713
   214B ->217B       0.93302

 Excited State   4:  2.079-A     2.2829 eV  543.11 nm  f=0.0258  <S**2>=0.830
   204B ->217B       0.18064
   209B ->217B       0.11137
   211B ->217B      -0.11651
   212B ->217B      -0.13340
   213B ->217B       0.92580
   214B ->217B       0.17996

 Excited State   5:  2.108-A     2.5680 eV  482.80 nm  f=0.0070  <S**2>=0.861
   207B ->217B      -0.15487
   208B ->217B       0.27929
   209B ->217B       0.56970
   210B ->217B      -0.26776
   211B ->217B       0.66077

 Excited State   6:  2.161-A     2.6002 eV  476.83 nm  f=0.0021  <S**2>=0.917
   217A ->218A       0.11410
   217A ->219A      -0.13409
   204B ->217B       0.15145
   208B ->217B       0.11036
   210B ->217B       0.13367
   212B ->217B       0.88341
   215B ->217B      -0.13579
   216B ->217B      -0.11070

 Excited State   7:  2.551-A     2.7442 eV  451.80 nm  f=0.0030  <S**2>=1.377
   216A ->218A       0.10764
   216A ->220A       0.13191
   217A ->218A      -0.36648
   217A ->219A       0.14006
   205B ->217B      -0.17829
   206B ->217B       0.22980
   207B ->217B       0.51568
   208B ->217B      -0.23936
   209B ->217B      -0.18767
   210B ->217B       0.11049
   211B ->217B       0.30986
   212B ->217B       0.21332
   216B ->218B      -0.23158
   216B ->219B       0.10971
   216B ->220B      -0.12557
```

```
Excited State   8:  2.161-A     2.7686 eV  447.82 nm  f=0.0119  <S**2>=0.918
   217A ->218A      -0.16737
   203B ->217B       0.10393
   204B ->217B       0.18778
   206B ->217B       0.11597
   207B ->217B       0.16366
   209B ->217B       0.63309
   210B ->217B       0.16822
   211B ->217B      -0.51400
   212B ->217B       0.10653
   213B ->217B      -0.23893
   214B ->217B       0.19103

Excited State   9:  2.460-A     2.8526 eV  434.64 nm  f=0.0062  <S**2>=1.263
   216A ->218A      -0.16035
   216A ->220A      -0.11843
   217A ->218A       0.15290
   217A ->219A      -0.28344
   203B ->217B       0.24075
   204B ->217B       0.48358
   207B ->217B       0.37195
   210B ->217B       0.19746
   211B ->217B       0.29783
   212B ->217B      -0.26401
   213B ->217B      -0.14290
   214B ->217B      -0.12945
   216B ->218B       0.21896
   216B ->220B       0.12460

Excited State  10:  2.511-A     2.8991 eV  427.67 nm  f=0.0207  <S**2>=1.327
   216A ->219A      -0.19174
   217A ->218A      -0.32234
   217A ->219A      -0.16582
   202B ->217B      -0.12412
   203B ->217B      -0.38112
   204B ->217B       0.38623
   205B ->217B       0.27939
   206B ->217B      -0.27591
   207B ->217B      -0.21881
   208B ->217B       0.14153
   209B ->217B      -0.14507
   210B ->217B       0.13125
   212B ->217B      -0.13259
   213B ->217B      -0.11136
   214B ->217B      -0.10288
   216B ->218B      -0.21464
   216B ->219B       0.13228
   216B ->220B      -0.11615

Excited State  11:  2.418-A     3.0077 eV  412.23 nm  f=0.0043  <S**2>=1.211
   216A ->218A       0.19193
   217A ->220A      -0.11190
   203B ->217B       0.77889
   203B ->219B       0.13992
   204B ->217B       0.17702
   206B ->217B      -0.10306
   207B ->217B      -0.16511
   208B ->217B       0.17069
   209B ->217B      -0.19565
   210B ->217B      -0.12976
   216B ->218B      -0.18998
   216B ->220B      -0.10703

Excited State  12:  2.112-A     3.0701 eV  403.85 nm  f=0.0066  <S**2>=0.866
   217A ->219A       0.17681
   204B ->217B      -0.17921
   207B ->217B      -0.17809
   208B ->217B       0.16870
   210B ->217B       0.87351
   211B ->217B       0.18006

Excited State  13:  2.073-A     3.1241 eV  396.87 nm  f=0.0013  <S**2>=0.825
   206B ->217B       0.17124
   207B ->217B       0.31378
   208B ->217B       0.86200
   209B ->217B      -0.24739
```

```
 Excited State  14:  2.806-A     3.1736 eV  390.67 nm  f=0.1385  <S**2>=1.718
   213A ->219A      -0.10819
   215A ->219A      -0.13481
   216A ->218A       0.34397
   217A ->218A       0.47473
   217A ->220A      -0.23095
   202B ->217B      -0.15463
   203B ->217B      -0.25163
   204B ->217B       0.19458
   207B ->217B       0.27052
   209B ->217B       0.11157
   213B ->219B       0.10673
   215B ->218B       0.17196
   215B ->219B       0.16484
   216B ->218B      -0.10686
   216B ->220B      -0.12263

 Excited State  15:  2.777-A     3.2635 eV  379.91 nm  f=0.0650  <S**2>=1.678
   214A ->218A       0.14193
   215A ->218A      -0.13628
   216A ->219A       0.11748
   216A ->220A      -0.18917
   217A ->218A      -0.14483
   217A ->219A       0.43763
   217A ->220A       0.23016
   202B ->217B       0.16153
   204B ->217B       0.15722
   205B ->217B       0.22958
   206B ->217B      -0.40899
   207B ->217B       0.22730
   214B ->218B      -0.16659
   215B ->218B       0.10078
   216B ->220B       0.27422
```

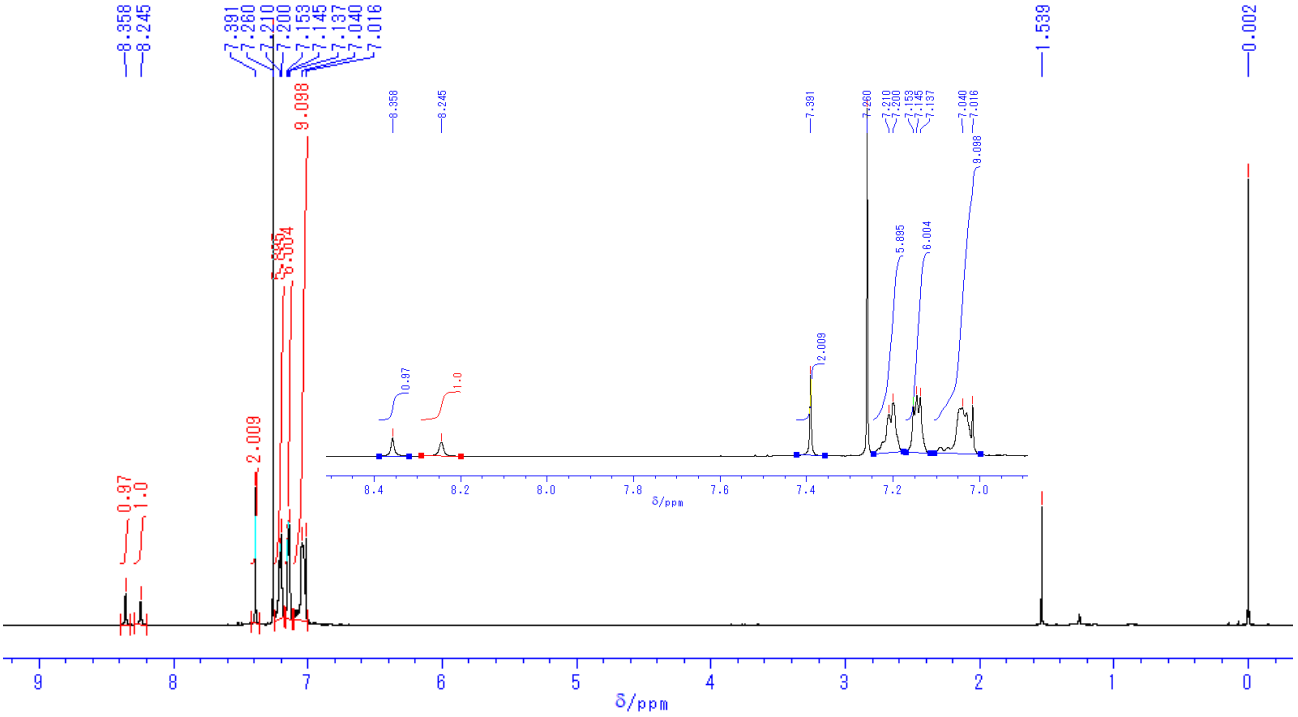
$(MeOPh)_3$-F_2PyBTM (**3**, Optimized first doublet excited state structure, UB3LYP/6-31G(d))

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.058-A     1.4964 eV  828.55 nm  f=0.0323  <S**2>=0.809
   193B ->197B      -0.10654
   196B ->197B       0.98564
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -4282.13178412
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  2.071-A     2.1077 eV  588.24 nm  f=0.0444  <S**2>=0.822
   186B ->197B      -0.15027
   189B ->197B       0.10220
   193B ->197B       0.10854
   194B ->197B       0.63702
   195B ->197B       0.71799

 Excited State   3:  2.052-A     2.1927 eV  565.44 nm  f=0.0054  <S**2>=0.803
   194B ->197B       0.72778
   195B ->197B      -0.67638

 Excited State   4:  2.124-A     2.5044 eV  495.06 nm  f=0.0082  <S**2>=0.877
   196A ->199A      -0.10971
   197A ->199A      -0.11466
   186B ->197B      -0.13426
   187B ->197B      -0.10601
   189B ->197B      -0.21419
   190B ->197B      -0.49541
   191B ->197B       0.29323
   192B ->197B       0.70152

 Excited State   5:  2.129-A     2.5406 eV  488.00 nm  f=0.0138  <S**2>=0.883
   196A ->199A       0.10375
   197A ->198A      -0.10151
   186B ->197B       0.17409
   187B ->197B       0.10234
   188B ->197B      -0.37024
   190B ->197B      -0.23691
   191B ->197B       0.29973
```

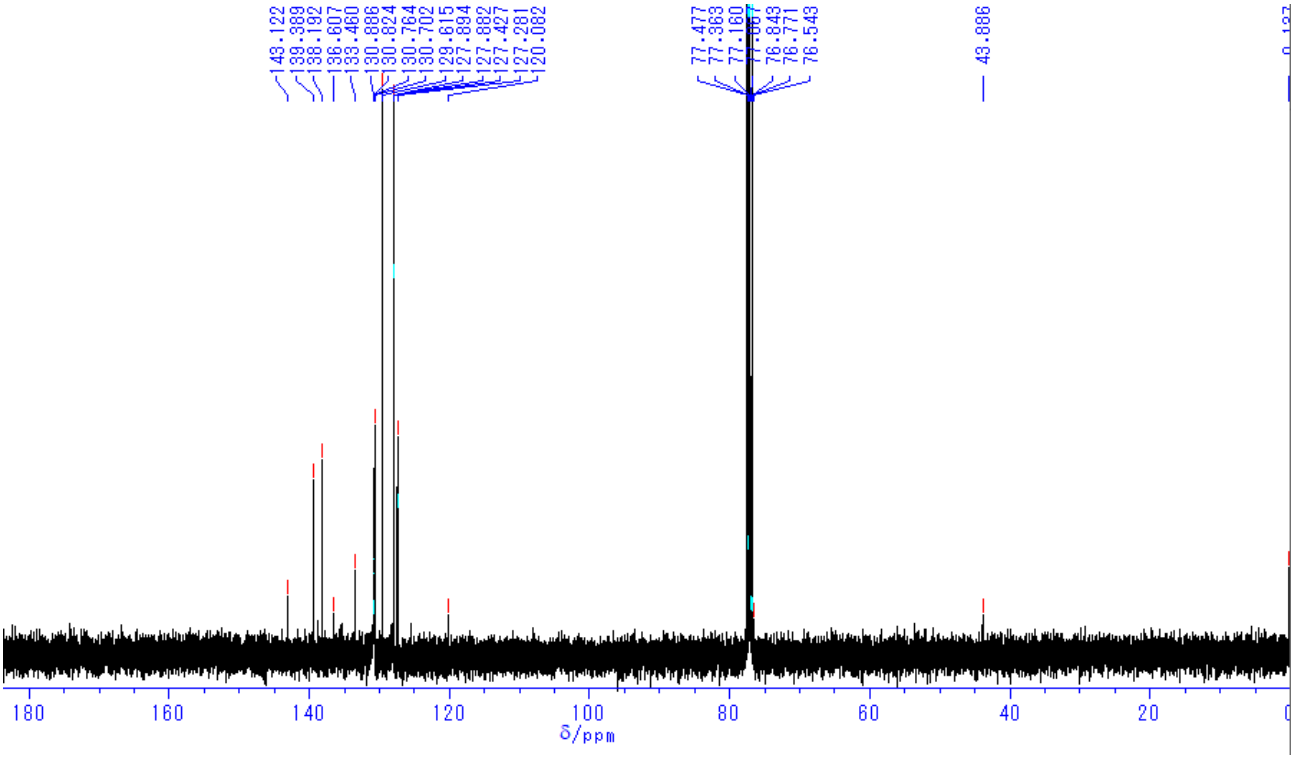
```
   192B ->197B      -0.18123
   193B ->197B       0.73746
   196B ->197B       0.10478

Excited State   6:  2.184-A     2.6149 eV  474.14 nm  f=0.0105  <S**2>=0.943
   197A ->198A       0.17517
   187B ->197B       0.15726
   188B ->197B      -0.26526
   189B ->197B       0.40865
   190B ->197B       0.33336
   191B ->197B       0.65972
   192B ->197B       0.10064
   193B ->197B      -0.20706
   194B ->197B      -0.10956

Excited State   7:  2.232-A     2.7303 eV  454.10 nm  f=0.0012  <S**2>=0.995
   197A ->198A      -0.22647
   186B ->197B       0.27009
   188B ->197B       0.70010
   189B ->197B       0.20016
   190B ->197B       0.20541
   191B ->197B       0.27813
   192B ->197B       0.24700
   193B ->197B       0.27853
   196B ->198B      -0.13665

Excited State   8:  2.437-A     2.7755 eV  446.71 nm  f=0.0109  <S**2>=1.235
   196A ->199A       0.14248
   196A ->201A       0.10725
   197A ->198A      -0.31212
   197A ->199A       0.12191
   186B ->197B       0.57491
   187B ->197B       0.13937
   188B ->197B      -0.19469
   189B ->197B      -0.10211
   193B ->197B      -0.48237
   194B ->197B       0.17601
   195B ->197B       0.12212
   196B ->198B      -0.21965
   196B ->201B      -0.11333

Excited State   9:  2.725-A     2.8724 eV  431.64 nm  f=0.0133  <S**2>=1.606
   196A ->198A      -0.11272
   196A ->201A      -0.10159
   197A ->198A       0.35958
   197A ->199A       0.11634
   197A ->201A       0.12309
   185B ->197B       0.55071
   185B ->199B       0.11751
   186B ->197B       0.42398
   188B ->197B       0.15467
   189B ->197B      -0.11899
   190B ->197B      -0.10984
   196B ->198B       0.31851
   196B ->200B      -0.10380
   196B ->201B       0.14702

Excited State  10:  2.447-A     2.9670 eV  417.87 nm  f=0.0138  <S**2>=1.247
   196A ->198A       0.14781
   197A ->198A      -0.17102
   197A ->201A      -0.11415
   185B ->197B       0.71641
   185B ->199B       0.13169
   186B ->197B      -0.35238
   187B ->197B      -0.11861
   191B ->197B       0.16489
   192B ->197B      -0.23328
   196B ->198B      -0.23261
   196B ->201B      -0.11285

Excited State  11:  2.093-A     2.9876 eV  415.00 nm  f=0.0006  <S**2>=0.845
   185B ->197B       0.26909
   187B ->197B       0.15250
   188B ->197B      -0.32236
   190B ->197B       0.47755
   191B ->197B      -0.40985
   192B ->197B       0.55813
```

```
   193B ->197B       0.20905

Excited State  12:  2.057-A     3.0678 eV  404.15 nm  f=0.0002  <S**2>=0.808
   189B ->197B       0.80743
   190B ->197B      -0.49471
   191B ->197B      -0.27612

Excited State  13:  2.070-A     3.2226 eV  384.73 nm  f=0.0019  <S**2>=0.821
   197A ->199A       0.11520
   184B ->197B       0.13104
   186B ->197B      -0.27406
   187B ->197B       0.86956
   188B ->197B       0.26289
   189B ->197B      -0.14535
   190B ->197B      -0.13021

Excited State  14:  2.937-A     3.2505 eV  381.43 nm  f=0.0718  <S**2>=1.906
   194A ->198A      -0.13661
   196A ->198A       0.28578
   196A ->201A       0.10021
   197A ->198A       0.42600
   197A ->199A      -0.18249
   197A ->200A       0.28243
   197A ->201A      -0.24851
   184B ->197B      -0.27470
   186B ->197B       0.14964
   187B ->197B       0.16299
   194B ->198B       0.17831
   195B ->198B       0.11928
   196B ->200B       0.23768
   196B ->201B      -0.22378
   196B ->209B      -0.11761

Excited State  15:  2.446-A     3.2885 eV  377.02 nm  f=0.0607  <S**2>=1.246
   194A ->198A      -0.13121
   196A ->199A       0.34625
   196A ->201A       0.10173
   197A ->199A       0.40021
   197A ->200A       0.13796
   197A ->201A      -0.11829
   197A ->206A      -0.10518
   172B ->197B      -0.10555
   184B ->197B       0.49841
   186B ->197B      -0.23193
   187B ->197B      -0.28159
   196B ->200B       0.14022
   196B ->201B      -0.13299
```

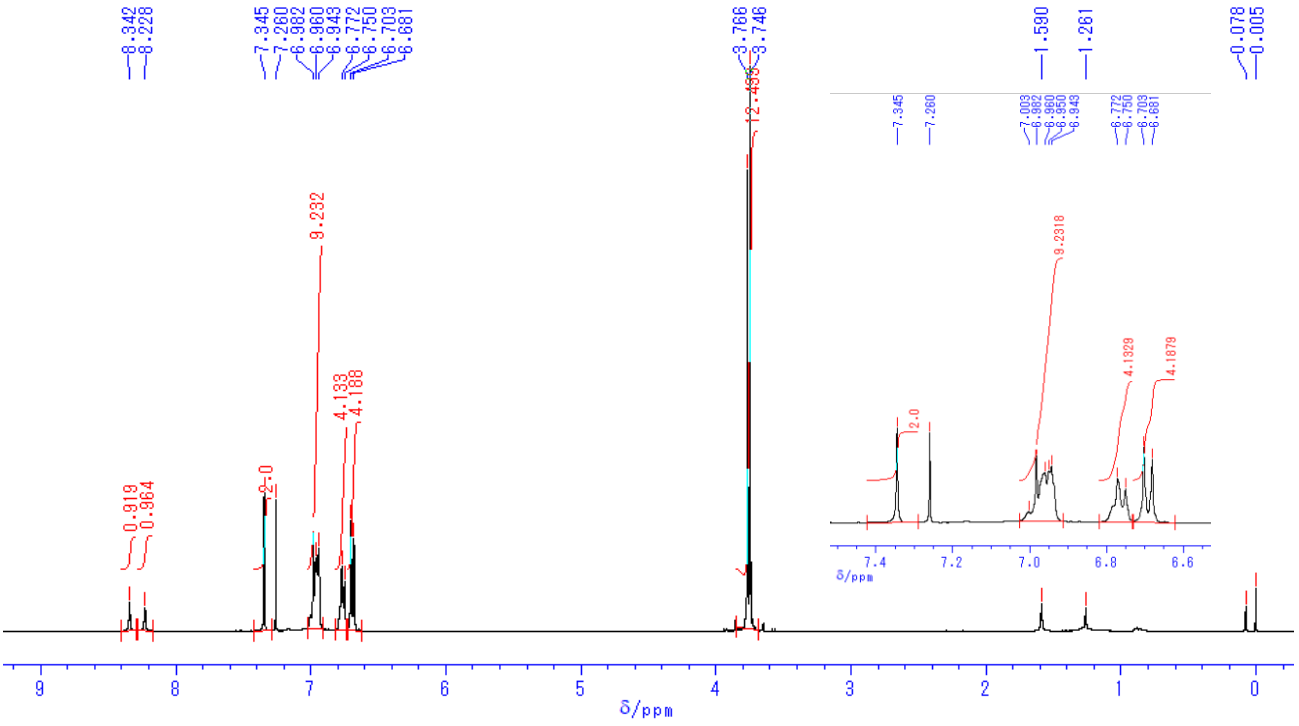
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of αH-Ph$_4$-F$_2$PyBTM (**1H**)



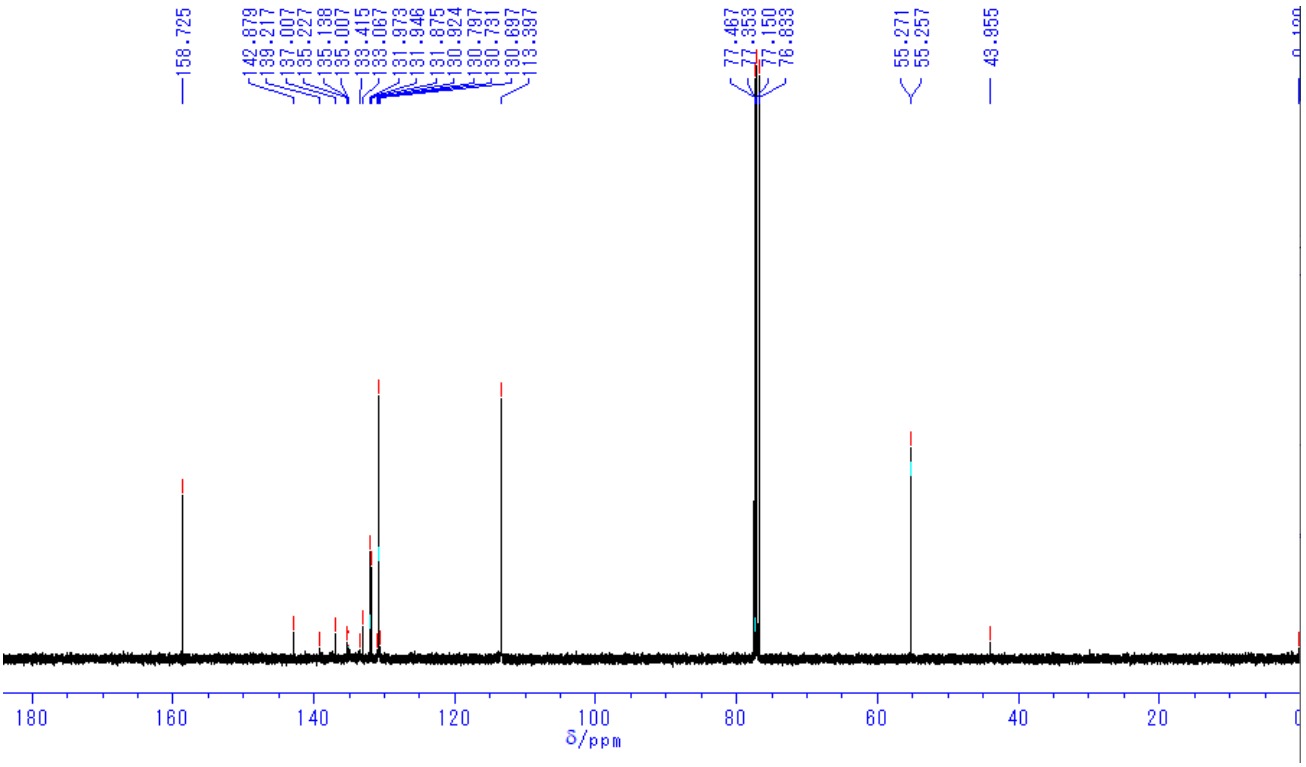
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of αH-Ph$_4$-F$_2$PyBTM (**1H**)



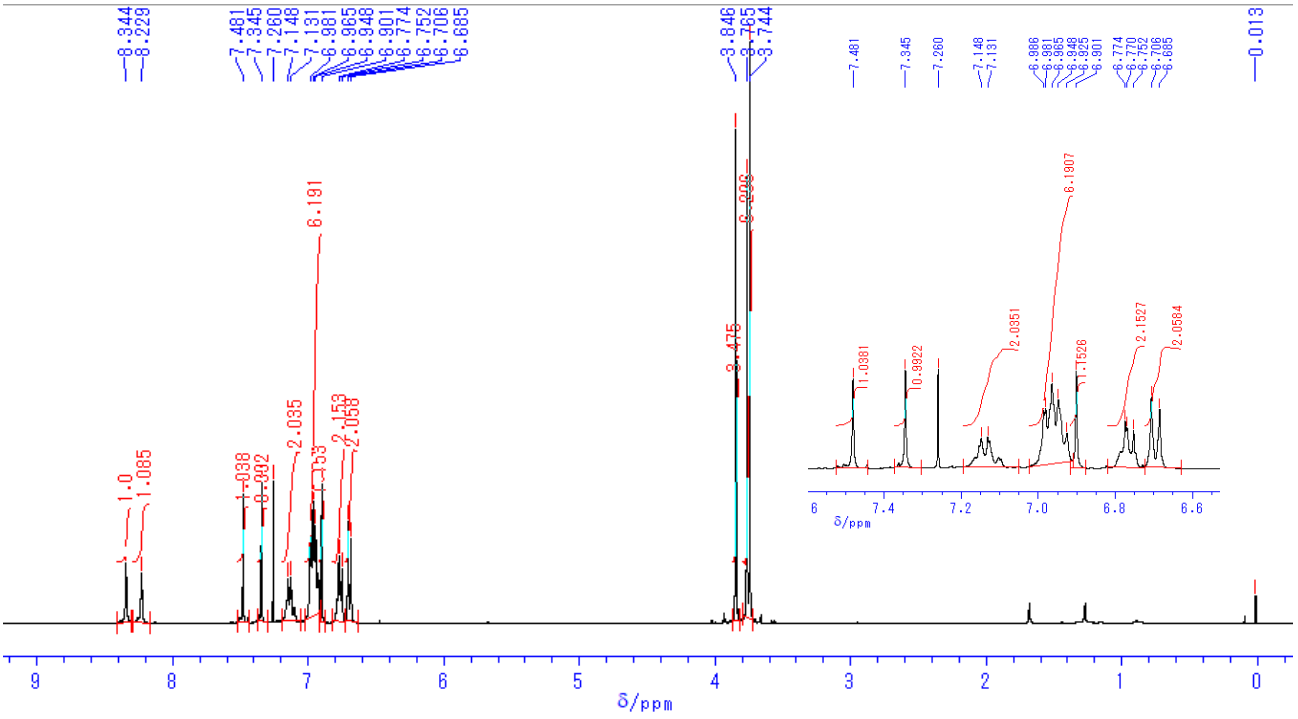
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of αH-$(MeOPh)_4$-F_2PyBTM (**2H**)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of αH-$(MeOPh)_4$-F_2PyBTM (**2H**)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of αH-$(MeOPh)_3$-F_2PyBTM (**3H**)



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of αH-$(MeOPh)_3$-F_2PyBTM (**3H**)