Supplementary Information

Development of 4,4'-bibenzo[*c*]thiophene fluorophores with substituents on the thiophene rings

Kotaro Obayashi,[a] Saori Miho,[a] Masataka Yasui,[a] Keiichi Imato,[a] Seiji Akiyama,[b] Mio Ishida,[b] and Yousuke Ooyama*[a]

[a]*Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan. E-mail: yooyama@hiroshima-u.ac.jp; Fax: (+81) 82-424-5494*

[b]*Science & Innovation Center, Mitsubishi Chemical Corporation, 1000 Kamoshida-cho, Aoba-ku, Yokohama-shi, Kanagawa 227-8502, Japan*

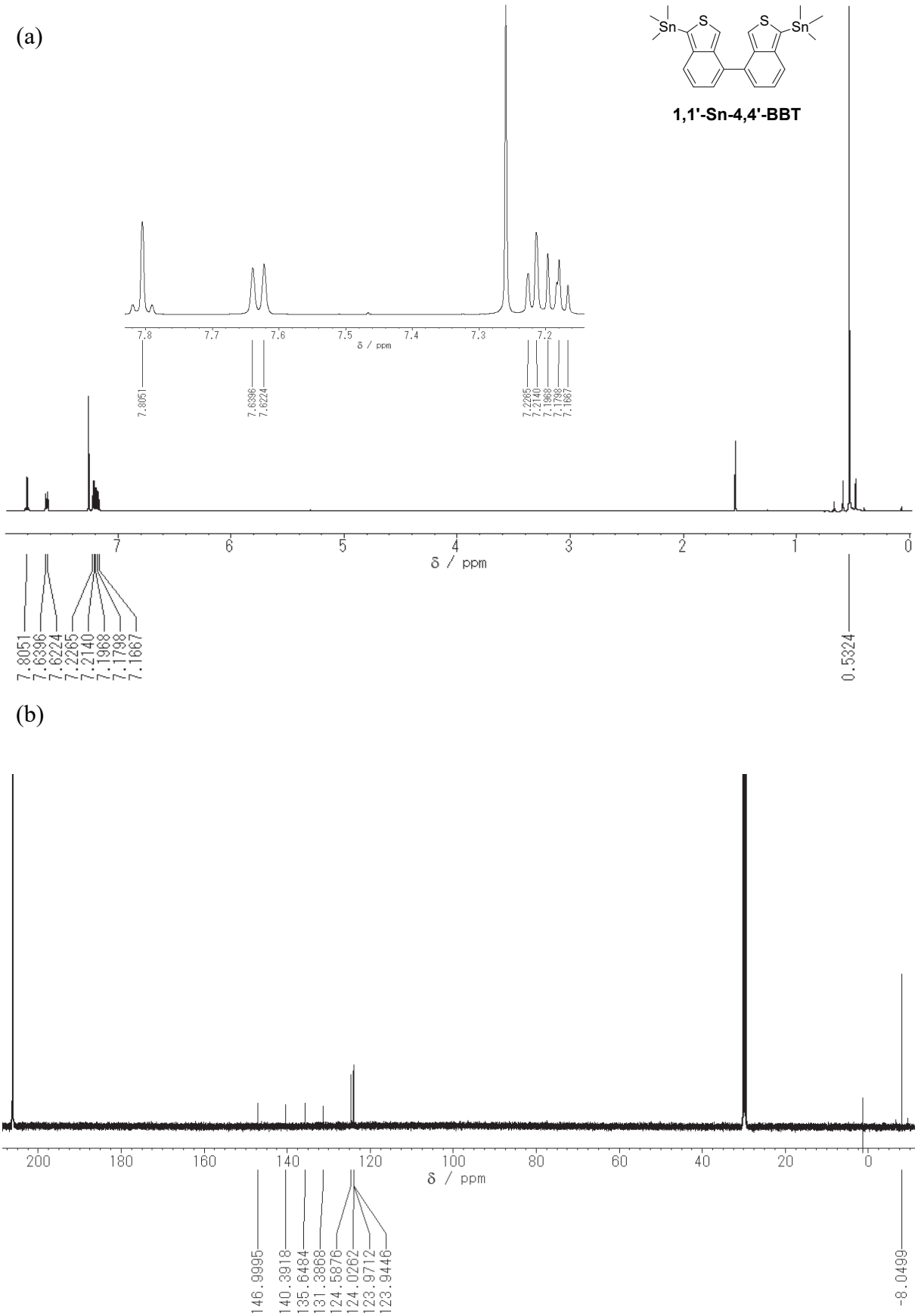

Fig. S1 (a) ^{1}H NMR (500 MHz) spectrum of **1,1′-Sn-4,4′-BBT** in $CDCl_3$. (b) ^{13}C NMR (125 MHz) spectrum of **1,1′-Sn-4,4′-BBT** in acetone-d_6.

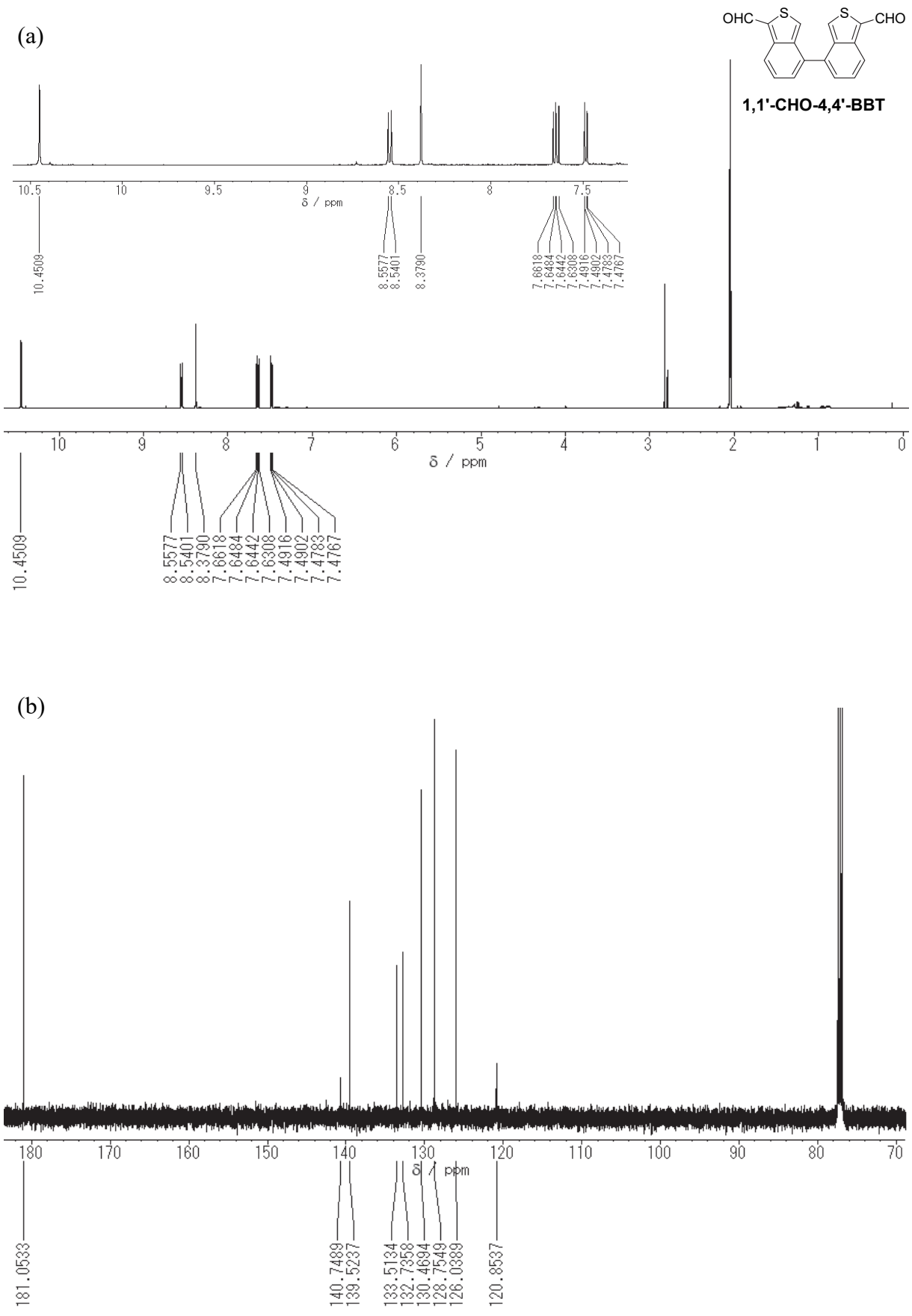

Fig. S2 (a) ^{1}H NMR (500 MHz) spectrum of **1,1′-CHO-4,4′-BBT** in acetone-d_6. (b) ^{13}C NMR (125 MHz) spectrum of **1,1′-CHO-4,4′-BBT** in $CDCl_3$.

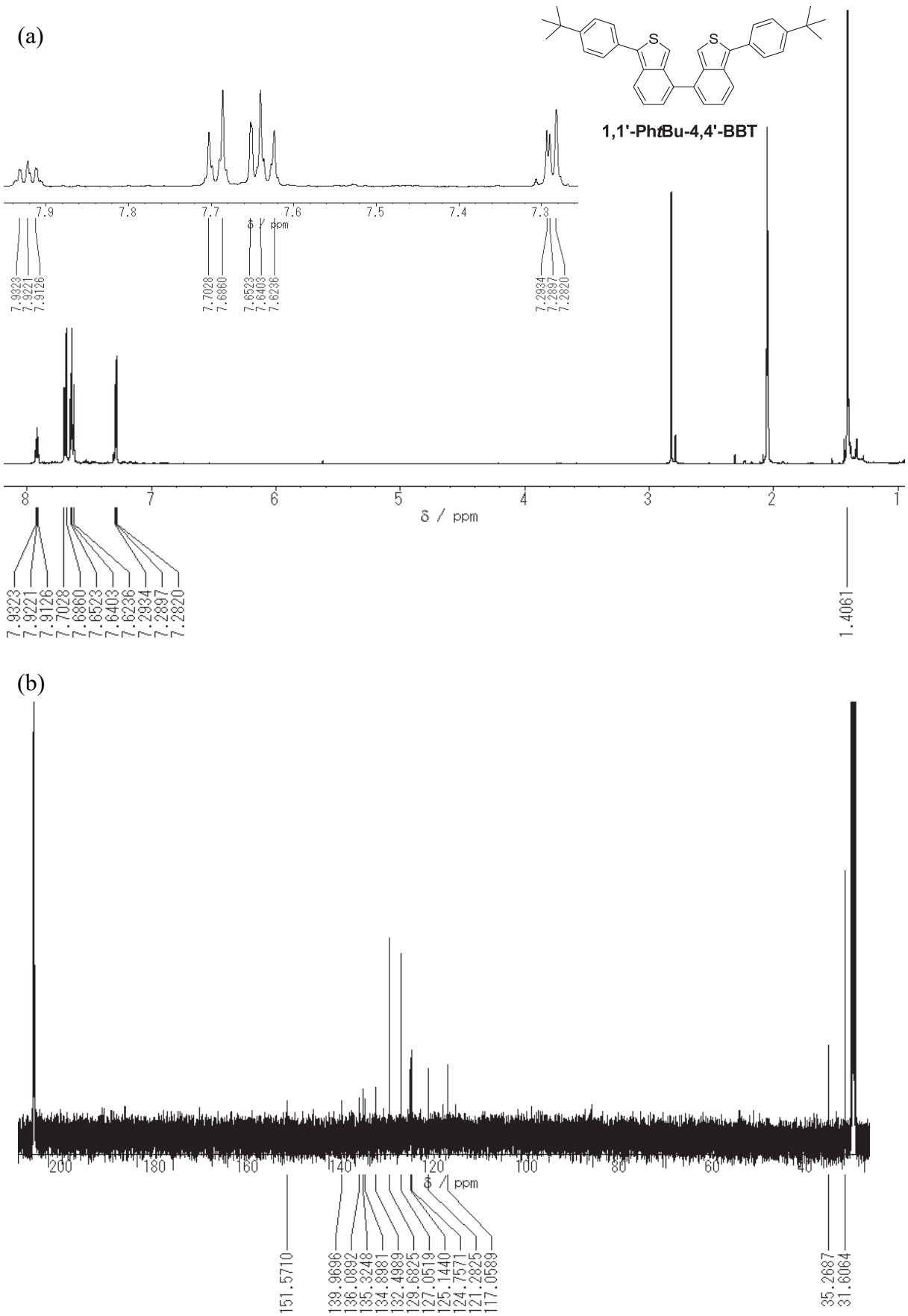

Fig. S3 (a) ^{1}H NMR (500 MHz) and (b) ^{13}C NMR (125 MHz) spectra of **1,1′-PhtBu-4,4′-BBT** in acetone-d_6.

Table S1 Geometrical coordinates of the optimized **BT** by DFT at the B3LYP/LanL2DZ level.

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	0.076458	0.733622	-0.000045
2	C	0	2.514521	0.723431	-0.000267
3	C	0	2.514521	-0.72343	-0.00029
4	C	0	1.335286	-1.439354	-0.000202
5	C	0	0.076457	-0.733623	-0.00007
6	S	0	-2.453815	0	0.000472
7	H	0	3.468721	1.245275	-0.000369
8	H	0	3.468721	-1.245275	-0.00041
9	H	0	1.342006	-2.526545	-0.00025
10	C	0	-1.205674	1.273618	0.000012
11	H	0	-1.50375	2.311902	0.000017
12	C	0	-1.205674	-1.273618	-0.000035
13	H	0	-1.503752	-2.311901	-0.000067
14	C	0	1.335286	1.439354	-0.000154
15	H	0	1.342004	2.526545	-0.000165

Table S2 Geometrical coordinates of the optimized **4,4′-BBT** by DFT at the B3LYP/ LanL2DZ level.

Cartesian coordinates:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	C	0	-3.036781	0.101272	-0.255477
2	C	0	-3.493896	1.212826	-1.050818
3	C	0	-2.601905	2.21064	-1.381215
4	C	0	-1.223742	2.154138	-0.958729
5	C	0	-0.716836	1.103596	-0.209856
6	C	0	-1.633126	0.039572	0.173264
7	S	0	-2.81806	-2.086434	1.192562
8	C	0	1.633126	0.039572	-0.173264
9	C	0	0.716836	1.103596	0.209856
10	C	0	1.223742	2.154138	0.958729
11	C	0	2.601905	2.21064	1.381215
12	C	0	3.493896	1.212826	1.050818
13	C	0	3.036781	0.101272	0.255477
14	S	0	2.81806	-2.086434	-1.192562

15	H	0	-4.530908	1.255347	-1.373901
16	H	0	-2.927571	3.059247	-1.978086
17	H	0	-0.554283	2.955677	-1.260949
18	H	0	0.554284	2.955677	1.26095
19	H	0	2.927571	3.059247	1.978086
20	H	0	4.530908	1.255347	1.373901
21	C	0	-3.794301	-0.970681	0.205218
22	H	0	-4.842953	-1.173851	0.0444
23	C	0	-1.369438	-1.075061	0.964069
24	H	0	-0.439489	-1.371284	1.42387
25	C	0	1.369438	-1.07506	-0.964069
26	H	0	0.439489	-1.371284	-1.42387
27	C	0	3.794302	-0.970681	-0.205219
28	H	0	4.842954	-1.173851	-0.0444

Table S3 Geometrical coordinates of the optimized **1,1′-Si-4,4′-BBT** by DFT at the B3LYP/ LanL2DZ level.

Cartesian coordinates:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	C	0	-3.83307	-0.499042	0.1008
2	C	0	-3.011865	0.570791	0.498118
3	C	0	-3.384166	1.680646	1.341904
4	H	0	-4.38433	1.729674	1.759265
5	C	0	-2.466951	2.674935	1.609445
6	H	0	-2.744526	3.513979	2.243112
7	C	0	-1.13082	2.627915	1.073121
8	H	0	-0.436359	3.425624	1.324801
9	C	0	-0.696051	1.584522	0.272144
10	C	0	-1.644721	0.527569	-0.042311
11	C	0	-1.435932	-0.57304	-0.86682
12	H	0	-0.540557	-0.851575	-1.401113
13	C	0	3.8331	-0.498905	-0.100944
14	C	0	3.011857	0.57094	-0.498136
15	C	0	3.384124	1.680885	-1.341824
16	H	0	4.384296	1.729995	-1.759161
17	C	0	2.466869	2.675164	-1.609266
18	H	0	2.744408	3.51428	-2.242854

19	C	0	1.13074	2.628044	-1.072942
20	H	0	0.436248	3.425745	-1.324552
21	C	0	0.696014	1.584569	-0.272045
22	C	0	1.644731	0.527631	0.042317
23	C	0	1.436008	-0.573029	0.866776
24	H	0	0.540648	-0.851629	1.401066
25	C	0	-5.856969	-2.788992	0.236472
26	H	0	-5.224713	-3.354045	0.933899
27	H	0	-5.59234	-3.1043	-0.78078
28	H	0	-6.898395	-3.086545	0.417332
29	C	0	-6.02059	-0.516728	2.316434
30	H	0	-5.190779	-0.820189	2.967139
31	H	0	-6.915676	-1.065839	2.638516
32	H	0	-6.210028	0.549986	2.487671
33	C	0	-6.841222	0.055952	-0.674295
34	C	0	-6.587849	-0.339572	-2.155101
35	H	0	-7.268509	0.220083	-2.815243
36	H	0	-6.76572	-1.409454	-2.330128
37	H	0	-5.559971	-0.11142	-2.466013
38	C	0	-6.631307	1.587873	-0.525872
39	H	0	-7.316651	2.126108	-1.198783
40	H	0	-5.60739	1.885038	-0.78583
41	H	0	-6.838747	1.934636	0.496422
42	C	0	-8.312529	-0.287653	-0.304529
43	H	0	-8.55138	-0.010262	0.731427
44	H	0	-8.52848	-1.357704	-0.42883
45	H	0	-9.002288	0.264959	-0.960953
46	C	0	5.856995	-2.788823	-0.238176
47	H	0	5.591407	-3.105043	0.778544
48	H	0	6.898634	-3.086099	-0.41827
49	H	0	5.225484	-3.353348	-0.936705
50	C	0	6.02075	-0.514917	-2.316442
51	H	0	6.914625	-1.065449	-2.639476
52	H	0	6.21235	0.551631	-2.48635
53	H	0	5.190159	-0.815861	-2.96731
54	C	0	6.841155	0.055473	0.674731
55	C	0	6.588175	-0.341605	2.155187
56	H	0	7.26878	0.217602	2.815765
57	H	0	6.766412	-1.411608	2.32911

58	H	0	5.560285	-0.114082	2.466522
59	C	0	8.31249 3	-0.287318	0.304333
60	H	0	8.551024	-0.008879	-0.731415
61	H	0	8.528818	-1.357416	0.427578
62	H	0	9.002221	0.264893	0.961126
63	C	0	6.630717	1.587473	0.527865
64	H	0	5.606742	1.884026	0.7883
65	H	0	6.837834	1.935329	-0.49412
66	H	0	7.31601	2.125267	1.201179
67	S	0	-2.883713	-1.589409	-0.985951
68	S	0	2.883841	-1.589341	0.985836
69	Si	0	-5.637667	-0.920273	0.496114
70	Si	0	5.637687	-0.919917	-0.496452

Table S4 Geometrical coordinates of the optimized **1,1′-Sn-4,4′-BBT** by DFT at the B3LYP/LanL2DZ level.

Cartesian coordinates:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	C	0	3.828683	-0.218819	0.279787
2	C	0	3.045749	0.849141	-0.191384
3	C	0	3.503891	1.961205	-0.987729
4	H	0	4.544608	2.011844	-1.299625
5	C	0	2.620003	2.958761	-1.342636
6	H	0	2.959455	3.801557	-1.940224
7	C	0	1.235978	2.907458	-0.945214
8	H	0	0.57076	3.706336	-1.263449
9	C	0	0.720525	1.860257	-0.198089
10	C	0	1.630822	0.800229	0.207407
11	C	0	1.343306	-0.305985	1.00075
12	H	0	0.400222	-0.590309	1.441736
13	C	0	-3.828683	-0.218819	-0.279788
14	C	0	-3.045748	0.849141	0.191383
15	C	0	-3.503889	1.961203	0.987731
16	H	0	-4.544605	2.01184	1.29963
17	C	0	-2.620001	2.958759	1.342638
18	H	0	-2.959451	3.801553	1.940229
19	C	0	-1.235977	2.907457	0.945214

20	H	0	-0.570758	3.706332	1.263451
21	C	0	-0.720525	1.860258	0.198084
22	C	0	-1.630823	0.80023	-0.207412
23	C	0	-1.343307	-0.305984	-1.000754
24	H	0	-0.400223	-0.59031	-1.441739
25	C	0	6.330344	-2.461268	1.028749
26	H	0	5.733378	-3.28737	0.622674
27	H	0	6.107594	-2.370635	2.099208
28	H	0	7.391504	-2.720283	0.920646
29	C	0	6.297137	-0.832803	-2.095681
30	H	0	5.718941	-1.66627	-2.513382
31	H	0	7.363121	-1.02768	-2.271377
32	H	0	6.019708	0.080201	-2.637071
33	C	0	-6.330346	-2.461268	-1.028746
34	H	0	-6.107617	-2.370626	-2.099208
35	H	0	-7.391501	-2.720293	-0.920624
36	H	0	-5.733364	-3.287366	-0.622687
37	C	0	-6.297129	-0.832802	2.095687
38	H	0	-7.363123	-1.027623	2.271391
39	H	0	-6.019646	0.080182	2.637084
40	H	0	-5.718975	-1.666305	2.513378
41	S	0	2.780777	-1.315925	1.262645
42	S	0	-2.780784	-1.315911	-1.262669
43	Sn	0	5.904347	-0.633837	0.002298
44	Sn	0	-5.904347	-0.633838	-0.002293
45	C	0	-7.052068	0.981097	-0.820689
46	H	0	-8.125698	0.802384	-0.677307
47	H	0	-6.793175	1.932155	-0.338967
48	H	0	-6.857267	1.078993	-1.895803
49	C	0	7.052066	0.981098	0.820699
50	H	0	8.125698	0.80236	0.677367
51	H	0	6.793212	1.932149	0.338942
52	H	0	6.857221	1.079025	1.895802

Table S5 Geometrical coordinates of the optimized **1,1′-CHO-4,4′-BBT** by DFT at the B3LYP/LanL2DZ level.

Cartesian coordinates:

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	C	0	-3.020352	0.404723	-0.325363
2	C	0	-3.458925	1.500307	-1.142946
3	C	0	-2.559845	2.501672	-1.45987
4	C	0	-1.197107	2.463889	-1.004027
5	C	0	-0.710354	1.420836	-0.229588
6	C	0	-1.634738	0.364344	0.135899
7	S	0	-2.799259	-1.776787	1.174265
8	C	0	1.634738	0.364344	-0.135899
9	C	0	0.710354	1.420836	0.229588
10	C	0	1.197107	2.463889	1.004027
11	C	0	2.559845	2.501672	1.459869
12	C	0	3.458925	1.500307	1.142946
13	C	0	3.020352	0.404723	0.325363
14	S	0	2.799259	-1.776788	-1.174264
15	H	0	-4.482565	1.546815	-1.501687
16	H	0	-2.878381	3.339717	-2.074773
17	H	0	-0.524766	3.265893	-1.296814
18	H	0	0.524767	3.265893	1.296814
19	H	0	2.878381	3.339717	2.074772
20	H	0	4.482566	1.546815	1.501687
21	C	0	-3.786412	-0.685153	0.136872
22	C	0	-1.385467	-0.742776	0.952558
23	H	0	-0.458779	-1.00568	1.44104
24	C	0	1.385467	-0.742775	-0.952559
25	H	0	0.45878	-1.005679	-1.441041
26	C	0	3.786412	-0.685153	-0.136872
27	C	0	-5.181563	-0.987333	-0.112246
28	O	0	-5.792149	-1.988157	0.340741
29	H	0	-5.706998	-0.25595	-0.753784
30	C	0	5.181563	-0.987333	0.112245
31	O	0	5.79215	-1.988157	-0.340742
32	H	0	5.706999	-0.255949	0.753783

Table S6 Geometrical coordinates of the optimized **1,1′-PhtBu-4,4′-BBT** by DFT at the B3LYP/LanL2DZ level.

Cartesian coordinates:

Center Atomic Atomic Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	C	0	3.050231	1.059743	0.146694
2	C	0	3.504894	2.137496	0.989588
3	C	0	2.61558	3.119076	1.374816
4	C	0	1.234634	3.084019	0.964673
5	C	0	0.721134	2.052422	0.196255
6	C	0	1.633079	1.003457	-0.232911
7	S	0	2.761794	-1.111607	-1.324343
8	C	0	-1.633079	1.00346	0.232899
9	C	0	-0.721134	2.05242	-0.196278
10	C	0	-1.234634	3.084009	-0.964707
11	C	0	-2.61558	3.119062	-1.37485
12	C	0	-3.504894	2.137485	-0.989612
13	C	0	-3.050231	1.059741	-0.146706
14	S	0	-2.761794	-1.111593	1.324354
15	H	0	4.534973	2.160789	1.329921
16	H	0	2.948004	3.933089	2.014657
17	H	0	0.568135	3.87502	1.299497
18	H	0	-0.568135	3.875006	-1.299539
19	H	0	-2.948004	3.933067	-2.0147
20	H	0	-4.534973	2.160774	-1.329945
21	C	0	3.812477	-0.005257	-0.357193
22	C	0	1.332595	-0.100419	-1.023765
23	H	0	0.381995	-0.385209	-1.447304
24	C	0	-1.332595	-0.100408	1.023765
25	H	0	-0.381994	-0.385193	1.447307
26	C	0	-3.812477	-0.005253	0.357192
27	C	0	-5.249909	-0.288695	0.233806
28	C	0	-6.214004	0.74588	0.302447
29	C	0	-5.729318	-1.613427	0.06613
30	C	0	-7.587735	0.469609	0.190705
31	H	0	-5.891456	1.767417	0.483077
32	C	0	-7.100216	-1.880328	-0.035236
33	H	0	-5.018006	-2.433652	-0.002453
34	C	0	-8.068506	-0.84691	0.018099
35	H	0	-8.284142	1.299239	0.25567
36	H	0	-7.417424	-2.912184	-0.16644
37	C	0	5.249909	-0.288698	-0.233804
38	C	0	5.729318	-1.613428	-0.066112

39	C	0	6.214004	0.745877	-0.302455
40	C	0	7.100216	-1.880327	0.035257
41	H	0	5.018006	-2.433652	0.002479
42	C	0	7.587736	0.469607	-0.19071
43	H	0	5.891456	1.767412	-0.483096
44	C	0	8.068506	-0.84691	-0.018089
45	H	0	7.417424	-2.912182	0.166472
46	H	0	8.284142	1.299236	-0.255684
47	C	0	-9.570617	-1.188206	-0.104318
48	C	0	-10.469852	0.070371	-0.020536
49	C	0	-9.832709	-1.882722	-1.473859
50	C	0	-9.977581	-2.154561	1.047566
51	H	0	-10.356191	0.589157	0.940269
52	H	0	-10.249381	0.782639	-0.82633
53	H	0	-11.523063	-0.223073	-0.116172
54	H	0	-9.250219	-2.805903	-1.579573
55	H	0	-10.895601	-2.142867	-1.570305
56	H	0	-9.564371	-1.219185	-2.306061
57	H	0	-11.04148	-2.415689	0.96607
58	H	0	-9.400105	-3.086415	1.019362
59	H	0	-9.812375	-1.686767	2.026674
60	C	0	9.570617	-1.188205	0.104332
61	C	0	9.832708	-1.882707	1.47388
62	C	0	9.977581	-2.154572	-1.047541
63	C	0	10.469852	0.070371	0.020537
64	H	0	9.56437	-1.219161	2.306076
65	H	0	9.250218	-2.805886	1.579604
66	H	0	10.8956	-2.142851	1.57033
67	H	0	9.812376	-1.686788	-2.026655
68	H	0	11.04148	-2.415699	-0.966042
69	H	0	9.400106	-3.086426	-1.019328
70	H	0	11.523063	-0.223072	0.116177
71	H	0	10.356191	0.589147	-0.940273
72	H	0	10.24938	0.782648	0.826323