Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Structure-property relationship in multi-stimuli responsive D-A-A′ benzothiazole functionalized isomers.

Anupama Ekbote, Shaikh M. Mobin and Rajneesh Misra*

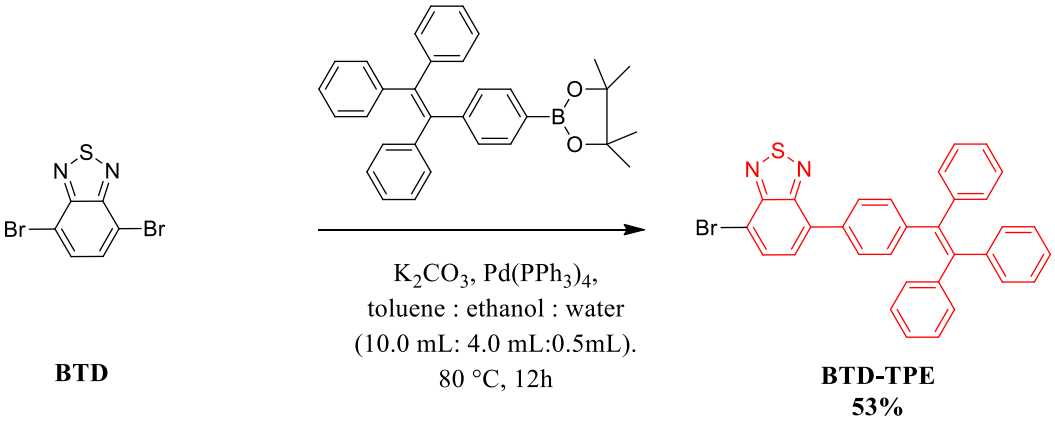
Department of Chemistry, Indian Institute of Technology Indore,

Indore- 453552, India

* Corresponding author - email: rajneeshmisra@iiti.ac.in

Table of contents

Experimental section



Scheme S1. Synthetic route to **BTD-TPE**.

Thermogravimetric analysis:

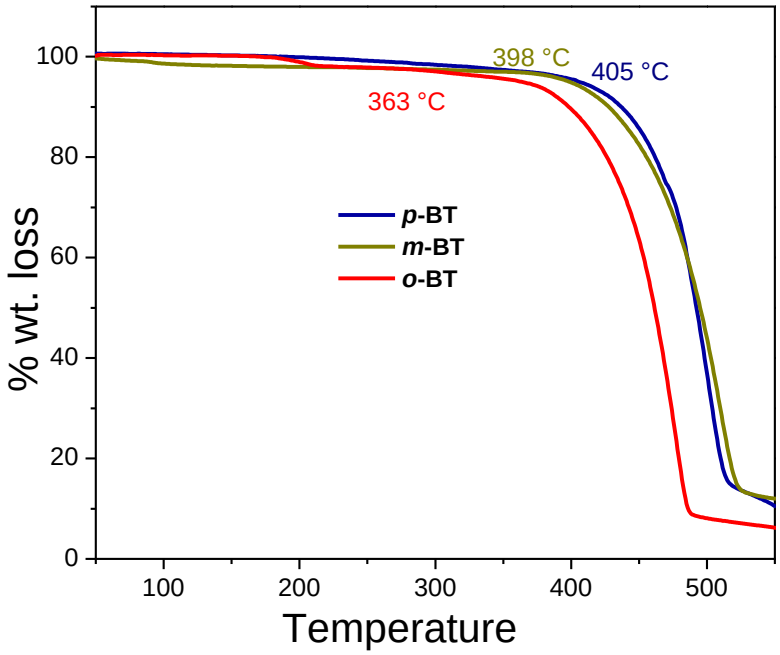


Fig. S1 TGA curves of ***p*-BT, *m*-BT** and ***o*-BT** at a heating rate of 10º C min^{-1} under a nitrogen atmosphere.

TDDFT data

Table S1 Computed vertical transitions, their oscillator strengths and configurations of ***p*-BT**, ***m*-BT** and ***o*-BT**.

Compound	Wavelength(nm)	f[a]	Configuration	Assignment
***p*-BT**	303	0.9296	HOMO-LUMO+2 (0.38378)	π-π*
	394.14	1.0583	HOMO-LUMO (0.56376)	ICT
***m*-BT**	290.83	0.2711	HOMO-LUMO+2 (0.43098)	π-π*
	379.17	0.7519	HOMO-LUMO (0.55230)	ICT
***o*-BT**	311 279	0.2957 0.0349	HOMO-LUMO+2 (0.55045) HOMO-LUMO+2 (0.28821)	π-π*
	369.54	0.5984	HOMO-LUMO(0.55385)	ICT

[a] Oscillator strength.

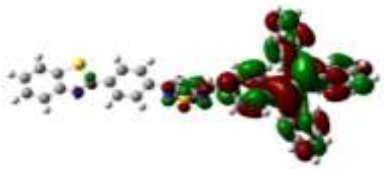
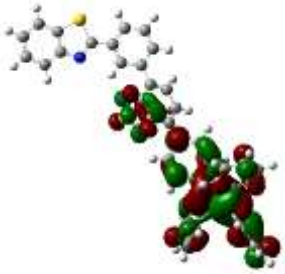
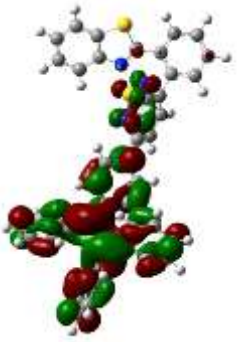
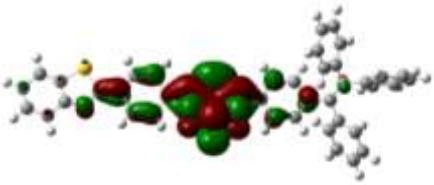
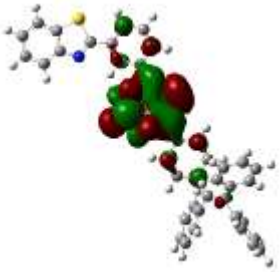
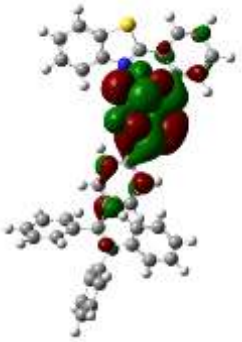
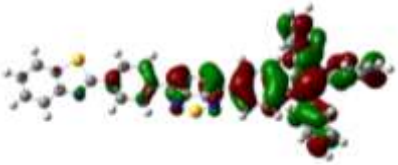
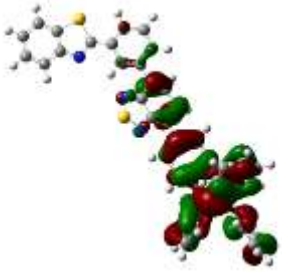
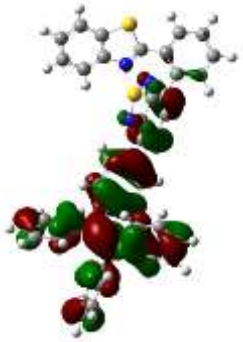
Orbitals	***p*-BT**	***m*-BT**	***o*-BT**
LUMO+2			
LUMO			
HOMO			

Fig. S2 Frontier molecular orbitals of ***p*-BT**, ***m*-BT** and ***o*-BT** at the CAMB3LYP/ 6-31G(d,p) level.

Electrochemical properties

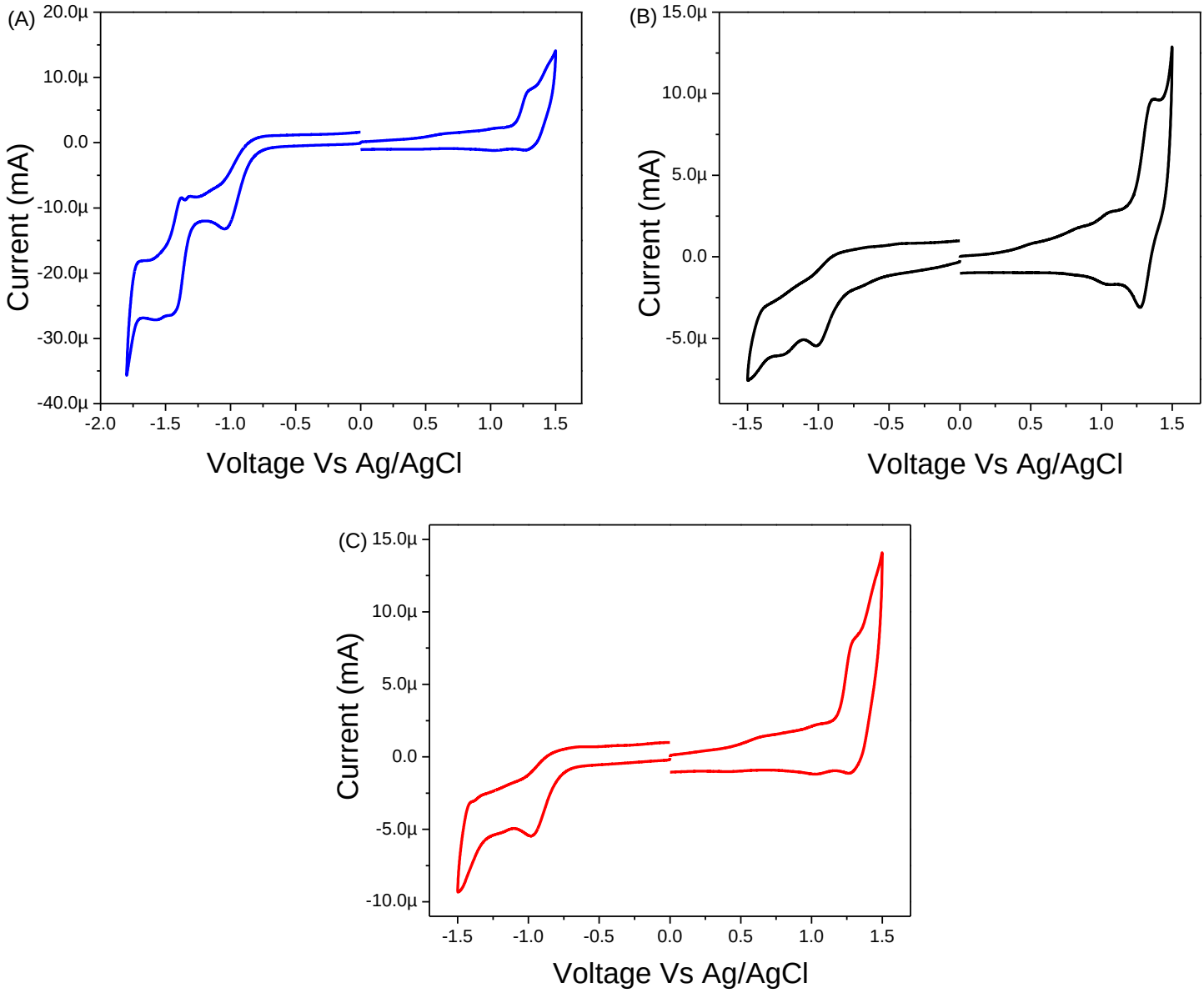


Fig. S3 Cyclic voltammetry (CV) plots of (A) ***p*-BT**, (B) ***m*-BT** and (C) ***o*-BT**.

Solvatochromism

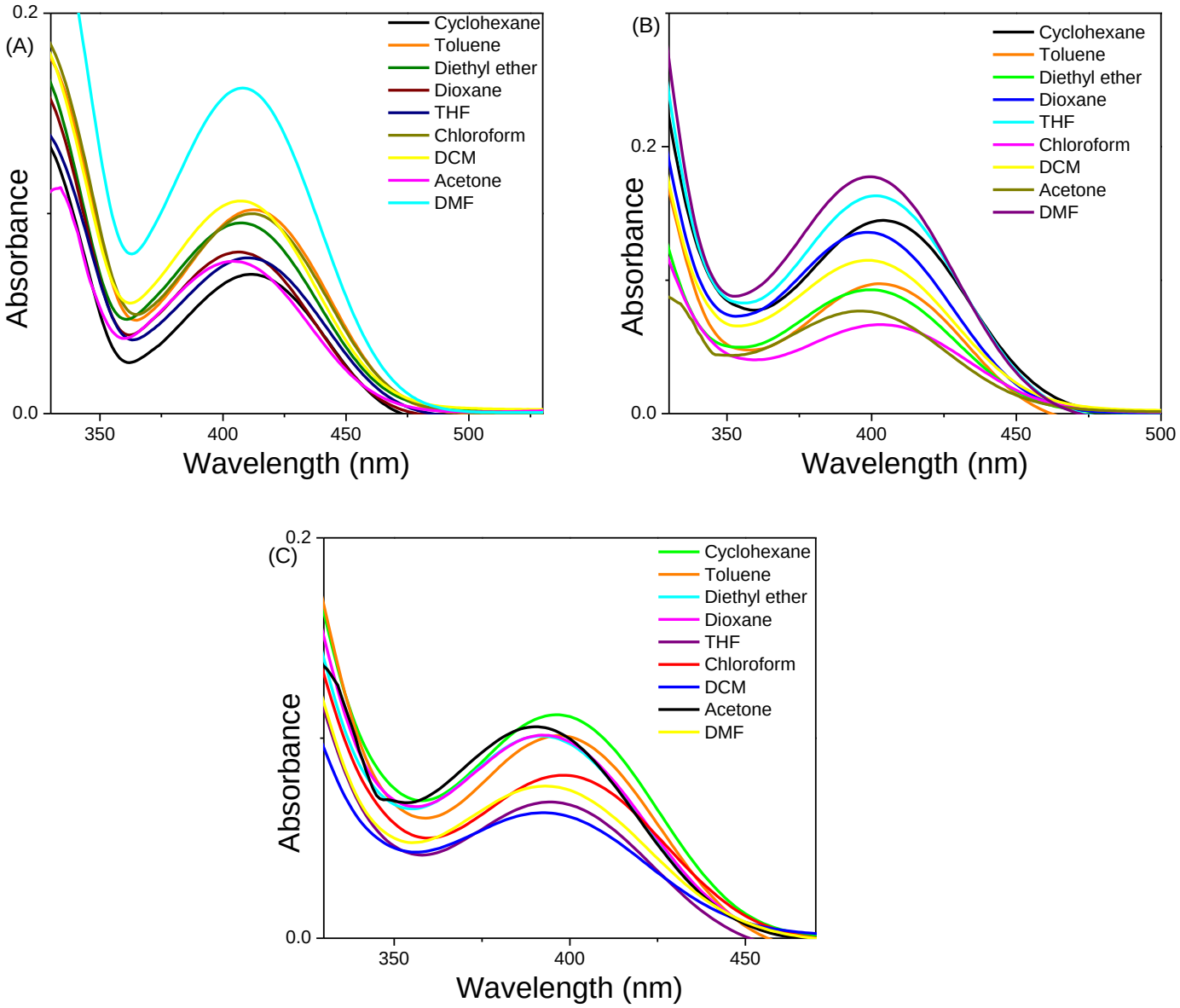


Fig. S4 Electronic absorption spectra of the isomers (A) ***p*-BT**, (B) ***m*-BT** and (C) ***o*-BT** (excitation wavelength or λ_{ex}=370 nm) in solvents of different polarities.

Aggregation induced emission

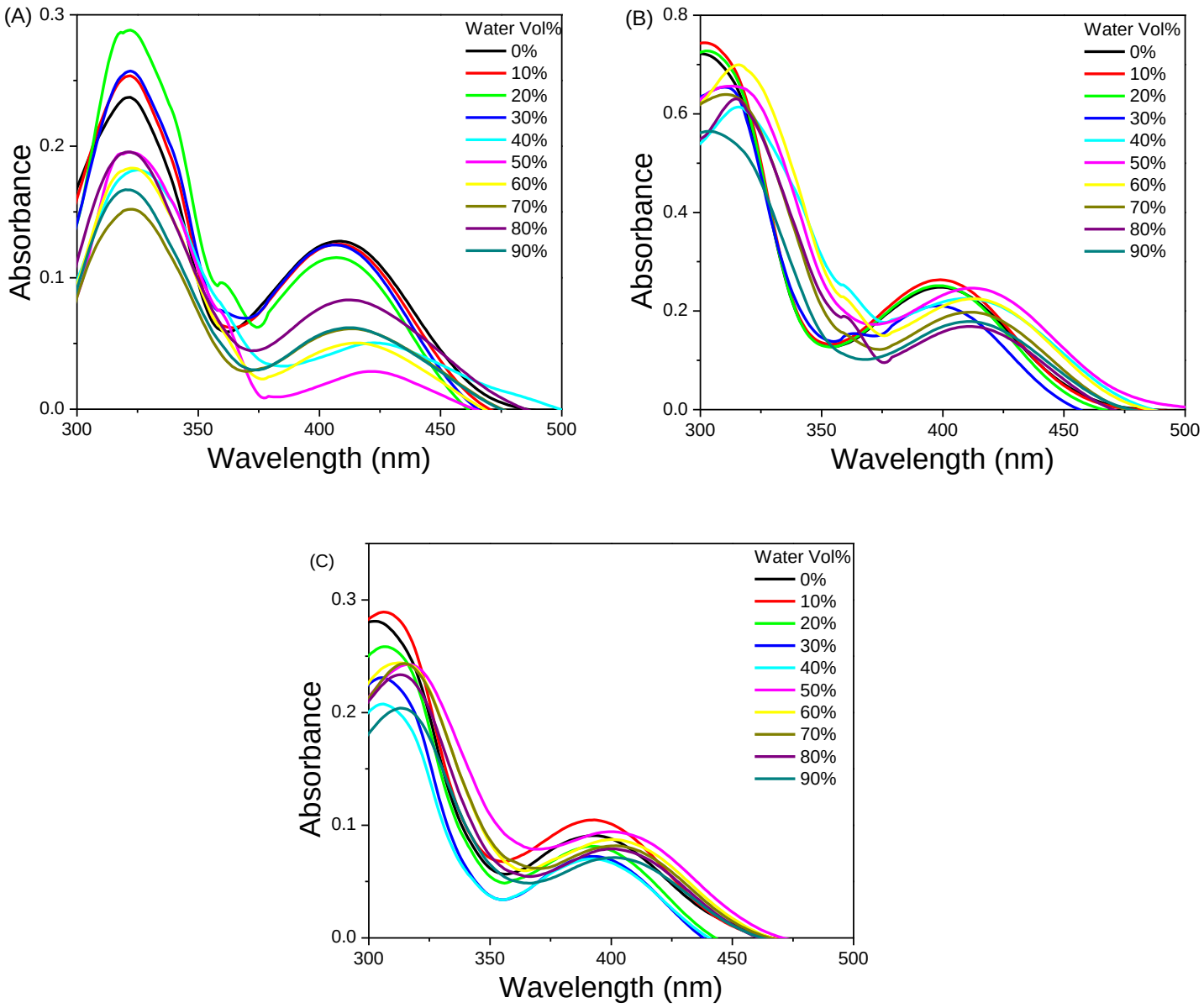


Fig. S5 Electronic absorption spectra of (A) ***p*-BT**, (B) ***m*-BT** and (C) ***o*-BT** in DMF-water mixtures (0% to 90% water), Luminogen concentration: 10 μM; intensity calculated at λmax.

Fig. S6 Photograph of (A) ***p*-BT** (B) ***m*-BT** and (C) ***o*-BT** in THF–water mixtures with different water fractions (10 μM) (0% water to 90% water from left to right) under 365 nm UV illumination.

Single crystal X-ray analysis

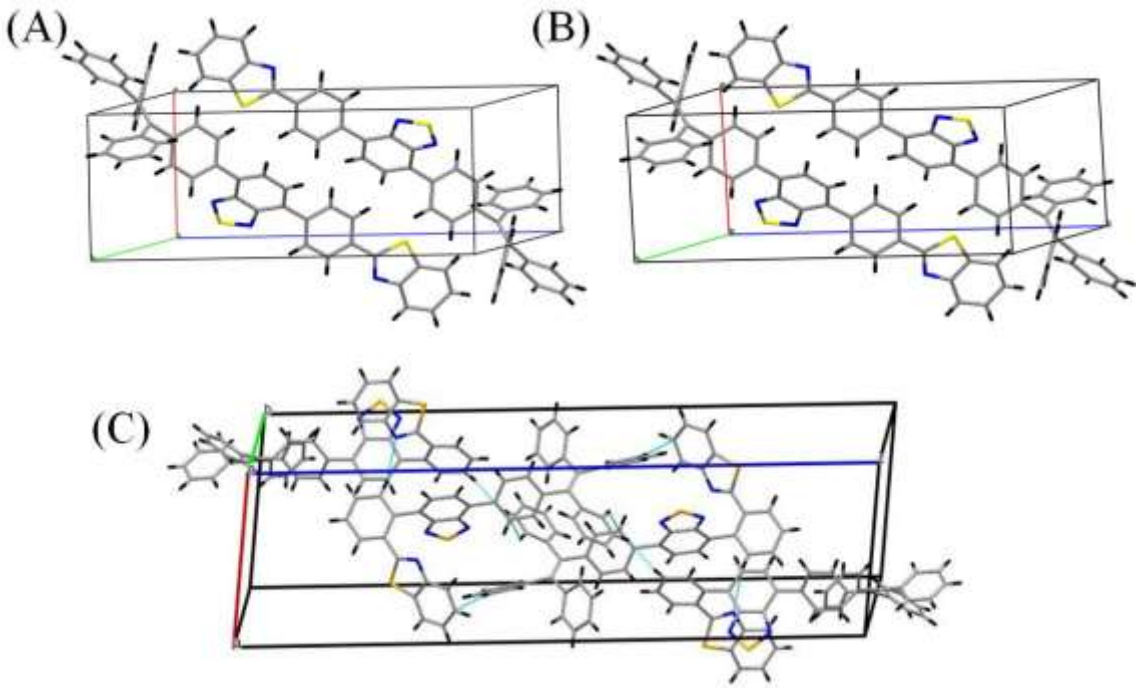


Fig. S7 Unit cell diagrams for the crystal of (A) ***p*-BT 1**, (B) ***p*-BT 2** and (C) ***o*-BT**.

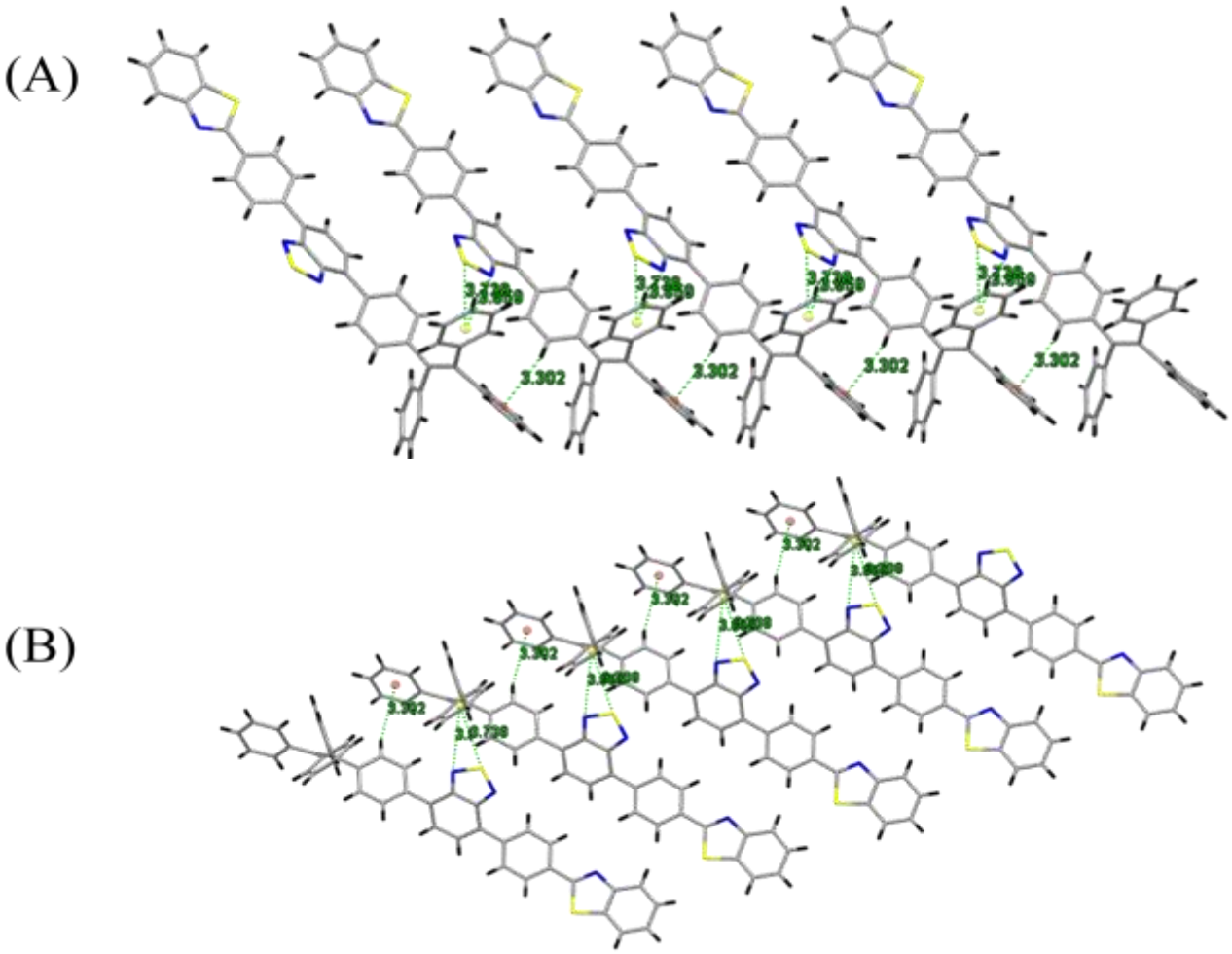


Fig. S8 Crystal packing diagram of ***p*-BT 1** (A) side view and (B) top view.

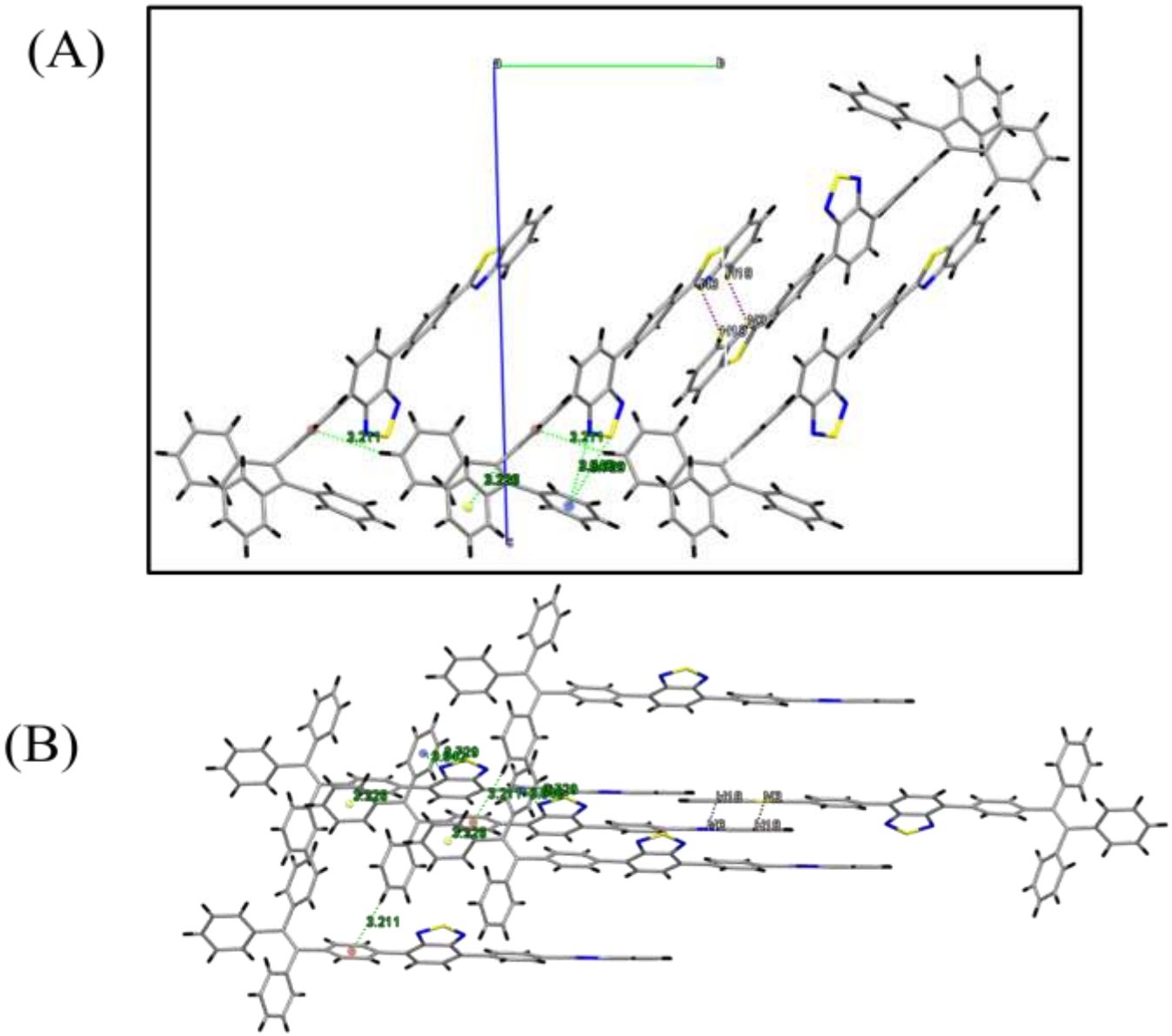


Fig. S9 Crystal packing diagram of ***p*-BT 2** (A) side view and (B) top view.

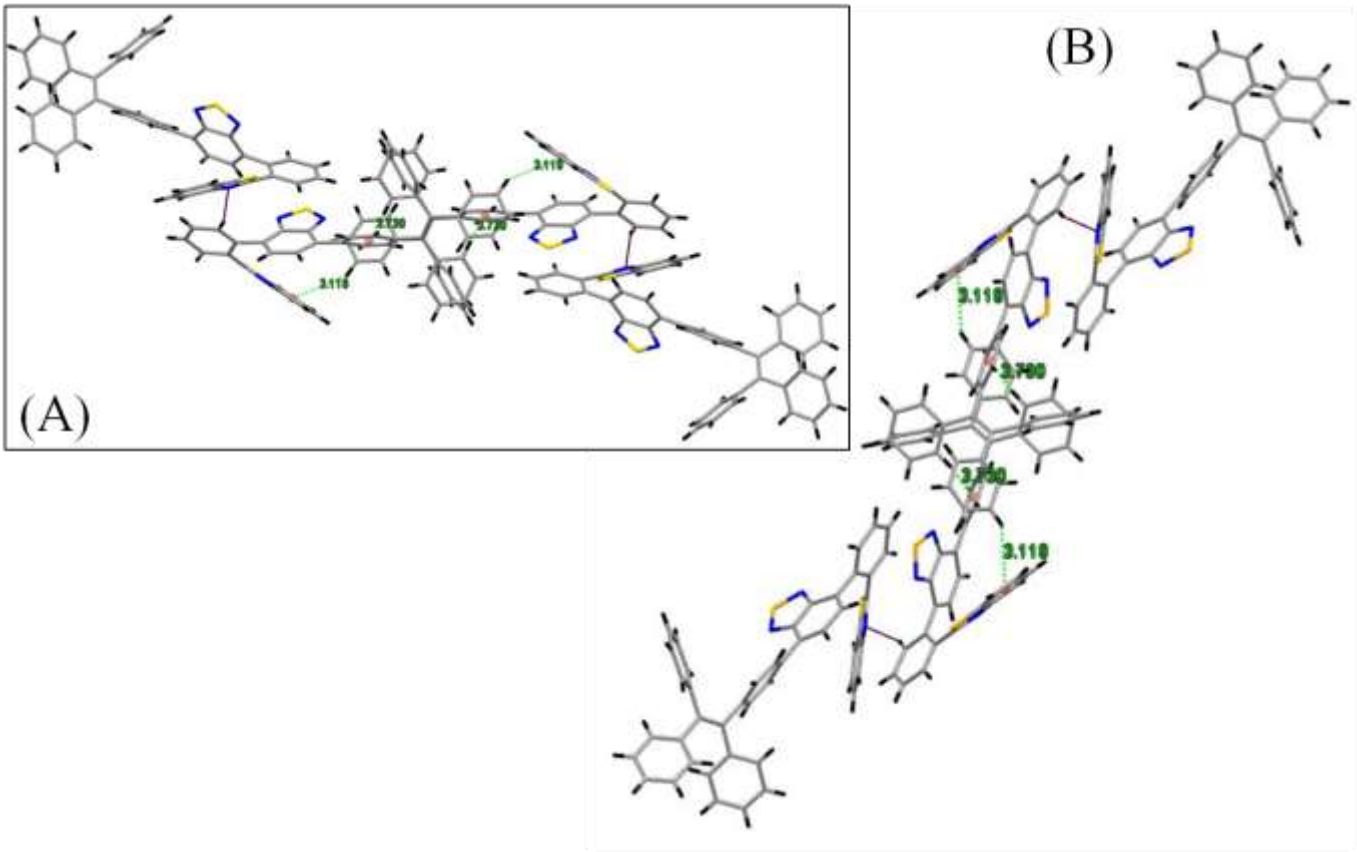


Fig. S10 Crystal packing diagram of ***o*-BT** (A) top view and (B) side view.

Mechanochromism

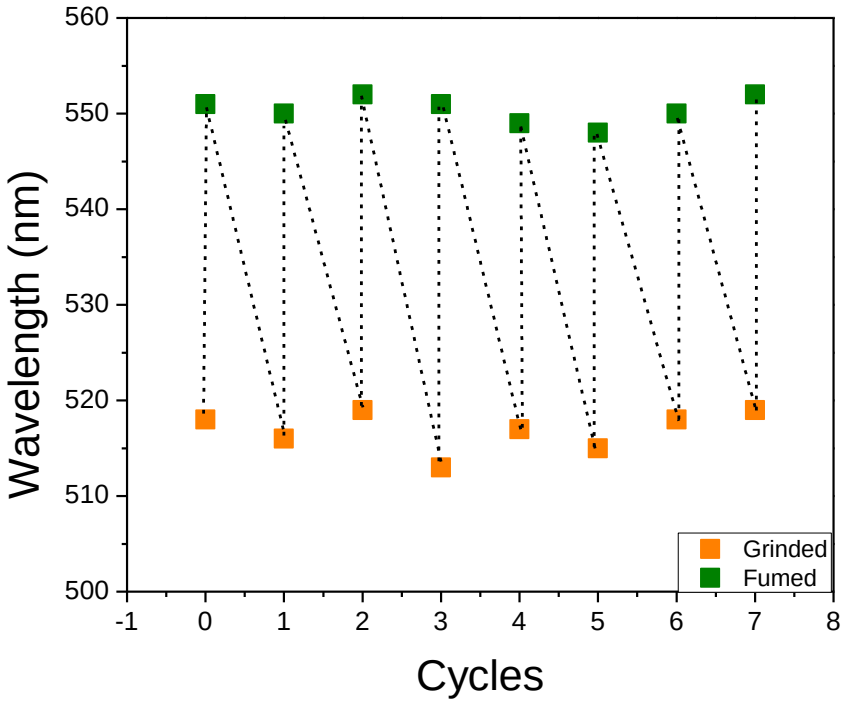


Fig. S11 Repeated switching of the solid-state fluorescence of ***p*-BT** by repeated grinding and fuming cycles.

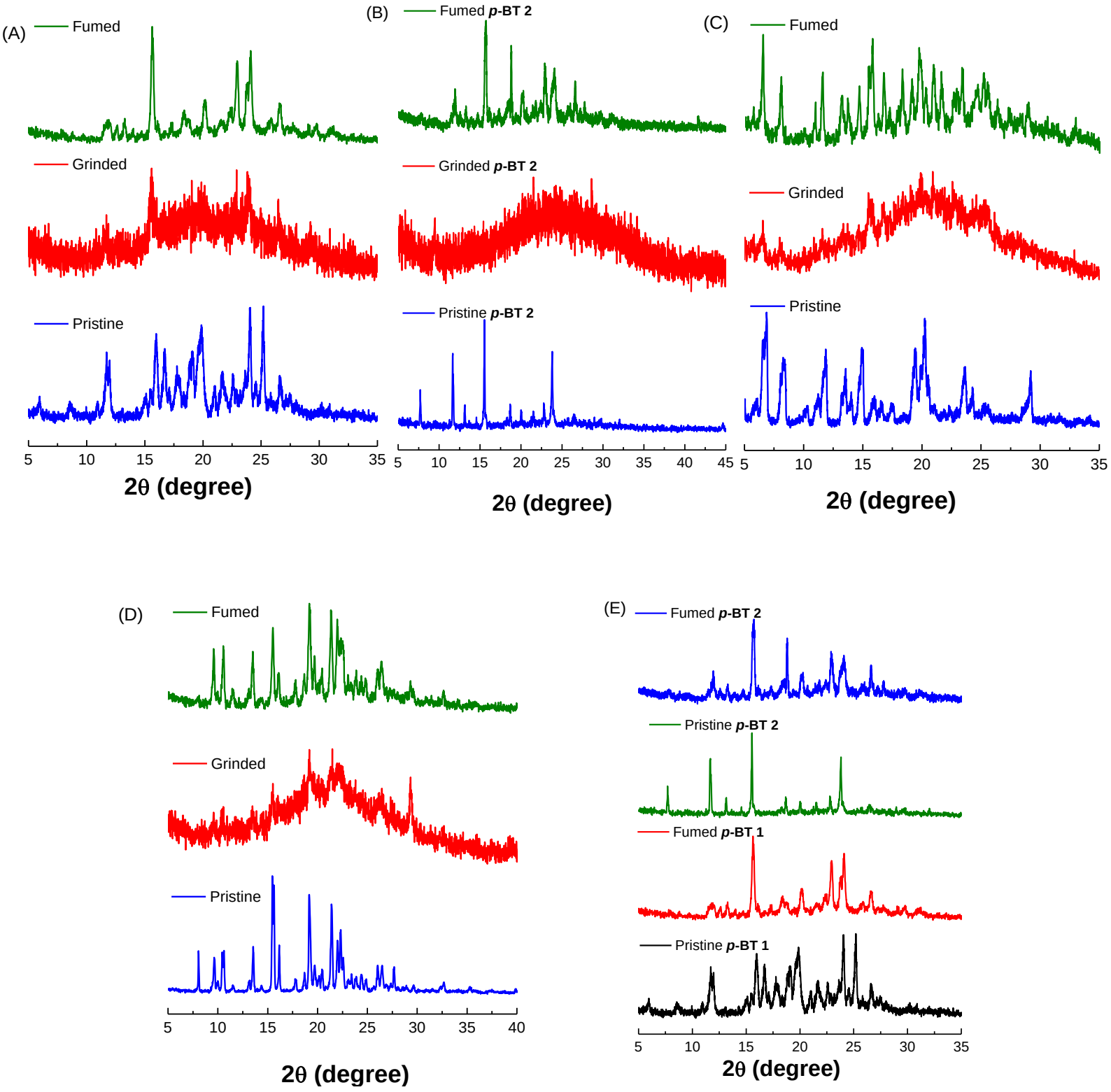


Fig. S12 PXRD patterns of pristine, grinded and fumed solids of (A) ***p*-BT 1** (B) ***p*-BT 2** (C) ***m*-BT** and (D) ***o*-BT**, (E) Fumed patterns of ***p*-BT 1** and ***p*-BT 2**.

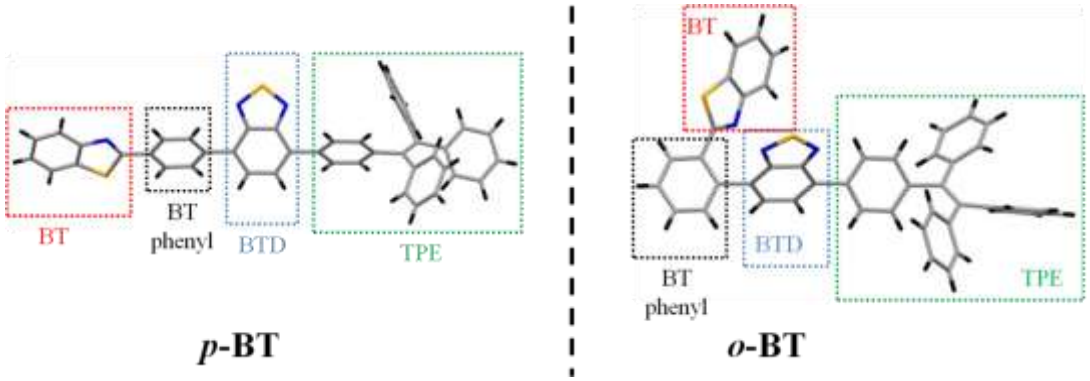


Fig. S13 Schematic diagram for measurement of dihedral angles.

Crystallographic data

Single crystal X-ray structures of ***p*-BT** and ***o*-BT** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F2. The positions of all the atoms were obtained by direct methods. All non hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. The crystal and refinement data are summarized in Table S1. The CCDC number 1847593, 1863992 and 1847594 contains the supplementary crystallographic data for ***p*-BT 1**, ***p*-BT 2** and ***o*-BT**. These data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S2. Crystal data and structure refinement for ***p*-BT** and ***o*-BT**

Identification code	rm211	rm262	rm241
Empirical formula	C45 H29 N3 S2	C45 H29 N3 S2	C45 H29 N3 S2
Formula weight	675.83	675.83	675.83
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	1.54184 A	0.71073 A	0.71073 A
Crystal system, space group	Triclinic, P -1	Triclinic, P -1	Monoclinic, P 21/n
a/(Å)	7.6932(3)	7.6440(8)	11.0588(10)
b/(Å)	9.9070(2)	9.8294(8)	8.5477(7)
c/(Å)	22.3507(6)	22.3403(19)	36.929(3)
Alpha/(º)	88.016(2)	87.824(7)	90
Beta/(º)	83.522(3)	83.835(8)	98.260(7)
Gamma/(º)	83.631(2)	83.258(7)	90
Volume	1681.75(9) $Å^3$	1656.8(3) $Å^3$	3454.6(5) $Å^3$
Z, Calculated density	2, 1.335 mg/m^{-3}	2, 1.355 mg/m^{-3}	4, 1.299 mg/m^{-3}
Absorption coefficient	1.727 mm^{-1}	0.200 mm^{-1}	0.192 mm^{-1}
F(000)	704	704	1408
Crystal size	0.230 x 0.180 x 0.140 mm	0.230 x 0.180 x 0.130 mm	0.230 x 0.180 x 0.130 mm
Θ range for data collection/(º)	3.982 to 71.221	2.938 to 29.320	3.026 to 29.143
Reflections collected / unique	10875 / 6398 [R(int) = 0.0207]	20784 / 7817 [R(int) = 0.1927]	29511 / 8224 [R(int) = 0.1475]
Completeness to theta	Θ = 67.684 99.8 %	Θ = 25.242 99.8 %	Θ = 25.242 99.8 %
Absorption	Semi-empirical from	Semi-empirical from	Semi-empirical from

correction	equivalents	equivalents	equivalents
Max. and min. transmission	1.00000 and 0.42833	-	1.00000 and 0.52239
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6398 / 0 / 451	7817 / 0 / 451	8224 / 0 / 451
Goodness-of-fit on F^2	1.043	0.944	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0467, wR2 = 0.1336	R1 = 0.0985, wR2 = 0.2157	R1 = 0.0897, wR2 = 0.2097
R indices (all data)	R1 = 0.0483, wR2 = 0.1378	R1 = 0.2544, wR2 = 0.3547	R1 = 0.1470, wR2 = 0.2435
Extinction coefficient	n/a	n/a	n/a
Largest diff. peak and hole ($e.Å^{-3}$)	0.229 and -0.393	0.607 and -0.737	0.332 and -0.407

DFT calculations:

DFT calculation data of *p*-BT, ***m*-BT** and ***o*-BT**

Calculation method: B3LYP/6-31G(d,p) with Gaussian 09.

***p*-BT:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.554216	-1.095097	3.391089
2	16	0	-9.529337	1.375048	-1.422271
3	7	0	-2.783111	-0.780096	2.348953
4	7	0	-0.271917	-0.873219	2.390806
5	7	0	-9.486801	-0.697680	0.176165
6	6	0	-11.058751	0.667637	-0.946848
7	6	0	-12.356094	1.046222	-1.297525
8	1	0	-12.536326	1.890150	-1.955349
9	6	0	-13.417104	0.308624	-0.778264
10	1	0	-14.434466	0.585251	-1.037663
11	6	0	-13.190584	-0.785884	0.074434

12	1	0	-14.037099	-1.342688	0.464337
13	6	0	-11.900383	-1.162857	0.423763
14	1	0	-11.709291	-2.004764	1.080616
15	6	0	-10.816064	-0.433408	-0.087926
16	6	0	-8.696214	0.136068	-0.430335
17	6	0	-7.233667	0.095583	-0.332704
18	6	0	-6.625216	-0.878557	0.478731
19	1	0	-7.258530	-1.580403	1.009171
20	6	0	-5.244205	-0.944790	0.597412
21	1	0	-4.799963	-1.700765	1.232577
22	6	0	-4.412053	-0.046248	-0.097798
23	6	0	-5.027805	0.930729	-0.901664
24	1	0	-4.415354	1.661960	-1.419392
25	6	0	-6.409912	1.001596	-1.018535
26	1	0	-6.846978	1.775878	-1.642430
27	6	0	-2.937028	-0.124948	-0.028090
28	6	0	-2.142993	0.158334	-1.122879
29	1	0	-2.622076	0.403637	-2.065387
30	6	0	-0.724362	0.101181	-1.101075
31	1	0	-0.198917	0.304808	-2.028390
32	6	0	0.011246	-0.239390	0.018481
33	6	0	-0.766760	-0.545888	1.191263
34	6	0	-2.224721	-0.491327	1.167698
35	6	0	1.489429	-0.276034	-0.004176
36	6	0	2.226630	-1.226212	0.725371
37	1	0	1.707719	-1.937047	1.356213
38	6	0	3.613555	-1.272104	0.639726
39	1	0	4.154776	-2.030811	1.196476
40	6	0	4.331691	-0.356168	-0.148853
41	6	0	3.593916	0.593637	-0.875782
42	1	0	4.117812	1.312707	-1.496328
43	6	0	2.206850	0.632106	-0.804701
44	1	0	1.671358	1.395446	-1.360915
45	6	0	5.818836	-0.436944	-0.249629
46	6	0	6.628679	0.659475	-0.147514
47	6	0	6.354383	-1.816010	-0.469685
48	6	0	5.798639	-2.649363	-1.456040
49	1	0	4.989392	-2.272448	-2.074241
50	6	0	6.275988	-3.944034	-1.652125
51	1	0	5.840516	-4.566386	-2.428755
52	6	0	7.304921	-4.441954	-0.850342
53	1	0	7.672236	-5.453411	-0.997502
54	6	0	7.851721	-3.633551	0.147694
55	1	0	8.643854	-4.015681	0.785238
56	6	0	7.382186	-2.334746	0.335549
57	1	0	7.811172	-1.711656	1.113312
58	6	0	8.079106	0.626556	-0.507535
59	6	0	8.515195	0.093981	-1.732525
60	1	0	7.785518	-0.324431	-2.417706
61	6	0	9.866134	0.099840	-2.075078
62	1	0	10.179757	-0.312651	-3.029800
63	6	0	10.811739	0.636312	-1.199491
64	1	0	11.864714	0.638520	-1.465758
65	6	0	10.392913	1.178538	0.017061
66	1	0	11.120043	1.602578	0.703787
67	6	0	9.040536	1.184338	0.353619
68	1	0	8.720259	1.619507	1.295436
69	6	0	6.135530	1.984304	0.338318

70	6	0	6.452245	3.163361	-0.359399
71	1	0	7.041626	3.099152	-1.269060
72	6	0	6.015467	4.405275	0.097802
73	1	0	6.260361	5.302134	-0.464167
74	6	0	5.272099	4.498246	1.276130
75	1	0	4.938022	5.466599	1.637133
76	6	0	4.969551	3.338616	1.991900
77	1	0	4.402911	3.401098	2.916508
78	6	0	5.396010	2.095375	1.528058
79	1	0	5.158926	1.198364	2.090515

Total Energy (HF) = -2692.9483231Hartree

***m*-BT:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	9.706253	-0.654784	-0.573462
2	7	0	7.733018	0.908731	0.140583
3	6	0	10.097571	0.866554	0.200088
4	6	0	11.347134	1.405621	0.512604
5	1	0	12.263087	0.873786	0.276737
6	6	0	11.386413	2.649397	1.137870
7	1	0	12.347189	3.087582	1.390399
8	6	0	10.203602	3.343860	1.445817
9	1	0	10.264826	4.312011	1.933265
10	6	0	8.960474	2.808052	1.135156
11	1	0	8.038714	3.331214	1.366283
12	6	0	8.897600	1.555535	0.505646
13	6	0	7.970133	-0.234804	-0.425770
14	6	0	6.922508	-1.142485	-0.915858
15	6	0	5.580146	-0.819129	-0.663923
16	1	0	5.364315	0.083503	-0.108197
17	6	0	4.541407	-1.640456	-1.121160
18	6	0	4.872336	-2.810753	-1.829027
19	6	0	6.202361	-3.138802	-2.079630
20	1	0	6.441442	-4.048451	-2.621920
21	6	0	7.227467	-2.310928	-1.630466
22	1	0	8.260159	-2.575240	-1.837636
23	1	0	4.082526	-3.477567	-2.160369
24	6	0	3.119105	-1.286381	-0.902574
25	6	0	2.158471	-1.509927	-1.868299
26	6	0	2.640055	-0.697007	0.318500
27	1	0	2.464857	-1.921077	-2.825223
28	6	0	0.784858	-1.186906	-1.697846
29	7	0	3.386365	-0.424425	1.395037
30	6	0	1.230749	-0.365772	0.494336
31	1	0	0.117551	-1.368098	-2.534275
32	6	0	0.270227	-0.618158	-0.548644
33	16	0	2.375580	0.203746	2.525050
34	7	0	0.957157	0.147732	1.699586
35	6	0	-1.168718	-0.303611	-0.412321
36	6	0	-1.621966	0.841151	0.267393

37	6	0	-2.134559	-1.137830	-1.004155
38	1	0	-0.905514	1.502547	0.738634
39	6	0	-2.977957	1.140717	0.333907
40	6	0	-3.490560	-0.845280	-0.920341
41	1	0	-1.819720	-2.042345	-1.515573
42	1	0	-3.298144	2.042780	0.846125
43	6	0	-3.944973	0.298543	-0.242400
44	1	0	-4.211921	-1.513894	-1.377811
45	6	0	-5.395307	0.646645	-0.177271
46	6	0	-6.358941	-0.258071	0.170429
47	6	0	-5.709750	2.068531	-0.518254
48	6	0	-7.818656	0.009122	-0.009841
49	6	0	-6.037082	-1.590891	0.765968
50	6	0	-5.169737	2.662104	-1.672624
51	6	0	-6.499690	2.863286	0.329062
52	6	0	-8.330070	0.477512	-1.231959
53	6	0	-8.726339	-0.260381	1.029593
54	6	0	-6.652476	-2.757438	0.278597
55	6	0	-5.161325	-1.709463	1.858519
56	1	0	-4.540177	2.069307	-2.329535
57	6	0	-5.436956	3.993693	-1.985358
58	6	0	-6.757194	4.198490	0.022899
59	1	0	-6.909769	2.426846	1.233788
60	1	0	-7.646904	0.673465	-2.051651
61	6	0	-9.697173	0.688899	-1.401863
62	6	0	-10.092001	-0.037211	0.864084
63	1	0	-8.352049	-0.643343	1.974144
64	1	0	-7.348680	-2.682766	-0.551364
65	6	0	-6.375763	-4.001888	0.841640
66	6	0	-4.894168	-2.952386	2.429806
67	1	0	-4.691590	-0.817875	2.260452
68	1	0	-5.019710	4.428346	-2.889311
69	6	0	-6.231904	4.768154	-1.138235
70	1	0	-7.366360	4.795719	0.695381
71	1	0	-10.070487	1.046299	-2.357338
72	6	0	-10.583683	0.438319	-0.353074
73	1	0	-10.773604	-0.239835	1.685354
74	1	0	-6.852628	-4.891841	0.440701
75	6	0	-5.495110	-4.104758	1.920295
76	1	0	-4.217748	-3.019328	3.277069
77	1	0	-6.434155	5.808143	-1.377288
78	1	0	-11.648774	0.604970	-0.485256
79	1	0	-5.285209	-5.073329	2.364654

Total Energy = -2692.9468749Hartree

***o*-BT:**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.780349	-1.738778	-0.895963
2	6	0	6.485531	-1.218627	-0.742728
3	6	0	5.370049	-2.057324	-0.994365

4	6	0	5.607383	-3.372677	-1.419515
5	6	0	6.899036	-3.871512	-1.578027
6	1	0	7.046733	-4.897380	-1.901716
7	6	0	7.992450	-3.052025	-1.305688
8	1	0	9.005084	-3.425703	-1.421339
9	1	0	4.754074	-4.019651	-1.597489
10	6	0	3.957071	-1.635102	-0.810755
11	6	0	3.029783	-1.747600	-1.821439
12	6	0	3.454604	-1.173547	0.451290
13	1	0	3.359884	-2.085799	-2.799080
14	6	0	1.659576	-1.396072	-1.660790
15	7	0	4.175525	-1.052908	1.570062
16	6	0	2.053660	-0.815068	0.618430
17	1	0	1.014670	-1.474651	-2.530095
18	6	0	1.124082	-0.927045	-0.477301
19	16	0	3.148660	-0.512460	2.732439
20	7	0	1.756371	-0.426486	1.864149
21	6	0	-0.309545	-0.581793	-0.354265
22	6	0	-0.753883	0.491884	0.438070
23	6	0	-1.278092	-1.309320	-1.069640
24	1	0	-0.036027	1.069843	1.006806
25	6	0	-2.102237	0.826813	0.495003
26	6	0	-2.626796	-0.982032	-0.998238
27	1	0	-0.972441	-2.159351	-1.672084
28	1	0	-2.413571	1.673551	1.098949
29	6	0	-3.072276	0.090316	-0.207099
30	1	0	-3.349648	-1.568275	-1.555476
31	6	0	-4.513509	0.476053	-0.151258
32	6	0	-5.514456	-0.432210	0.053357
33	6	0	-4.775709	1.937110	-0.333178
34	6	0	-6.957687	-0.102024	-0.153359
35	6	0	-5.252889	-1.833013	0.504963
36	6	0	-4.161924	2.648258	-1.379241
37	6	0	-5.590827	2.648387	0.563402
38	6	0	-7.403153	0.514375	-1.334906
39	6	0	-7.916240	-0.456020	0.812439
40	6	0	-5.879537	-2.917853	-0.133522
41	6	0	-4.425926	-2.100648	1.609057
42	1	0	-3.512086	2.119740	-2.070238
43	6	0	-4.381563	4.014863	-1.542257
44	6	0	-5.801658	4.017221	0.407394
45	1	0	-6.058260	2.119523	1.387376
46	1	0	-6.679933	0.778665	-2.099219
47	6	0	-8.755508	0.785915	-1.534644
48	6	0	-9.267053	-0.173349	0.618470
49	1	0	-7.593340	-0.952412	1.722553
50	1	0	-6.539731	-2.728889	-0.974644
51	6	0	-5.659175	-4.225641	0.294795
52	6	0	-4.214905	-3.407495	2.045016
53	1	0	-3.949489	-1.274675	2.126571
54	1	0	-3.907059	4.541788	-2.365279
55	6	0	-5.202749	4.705609	-0.649030
56	1	0	-6.431787	4.547610	1.115661
57	1	0	-9.077605	1.258367	-2.458278
58	6	0	-9.692906	0.448855	-0.556709
59	1	0	-9.988636	-0.443935	1.384143
60	1	0	-6.143250	-5.049703	-0.221735
61	6	0	-4.825586	-4.476229	1.386561

62	1	0	-3.574860	-3.590011	2.903459
63	1	0	-5.368433	5.772088	-0.770971
64	1	0	-10.746469	0.662396	-0.711909
65	1	0	-4.659568	-5.494609	1.725695
66	1	0	8.632450	-1.088889	-0.722387
67	6	0	6.328577	0.200751	-0.379871
68	16	0	7.495776	0.973144	0.738176
69	7	0	5.393189	0.982189	-0.820127
70	6	0	6.614618	2.473139	0.555038
71	6	0	5.516967	2.264360	-0.317195
72	6	0	6.859299	3.722875	1.129225
73	6	0	4.656964	3.332037	-0.615810
74	1	0	7.700784	3.878453	1.796479
75	6	0	5.991626	4.767532	0.822086
76	6	0	4.900508	4.573560	-0.043012
77	1	0	3.820325	3.166362	-1.286208
78	1	0	6.162914	5.746979	1.258312
79	1	0	4.240640	5.406601	-0.265040

Total Energy = -2692.9392163Hartree

TDDFT calculation data of *p*-BT, ***m*-BT** and ***o*-BT**

***p*-BT:**

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.1457 eV  394.14 nm  f=1.0583
<S**2>=0.000
     174 ->177         0.17522
     175 ->177        -0.34492
     176 ->177         0.56376
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2691.73601105
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:      Singlet-A      3.8873 eV  318.95 nm  f=0.1114
<S**2>=0.000
     164 ->177         0.12356
     175 ->177         0.48699
     175 ->179         0.10139
     176 ->177         0.26238
     176 ->179         0.37320

 Excited State   3:      Singlet-A      4.0919 eV  303.00 nm  f=0.9296
<S**2>=0.000
     174 ->177        -0.20780
     175 ->177        -0.20397
     175 ->178        -0.32420
     175 ->179         0.11324
     176 ->177        -0.12937
     176 ->178         0.28750
     176 ->179         0.38378
```

```
 Excited State   4:      Singlet-A      4.2764 eV  289.92 nm  f=0.2161
<S**2>=0.000
     174 ->177         0.13774
     175 ->177        -0.19450
     175 ->178         0.37111
     176 ->177        -0.22012
     176 ->178        -0.17703
     176 ->179         0.36886
     176 ->180         0.12687

 Excited State   5:      Singlet-A      4.5538 eV  272.27 nm  f=0.0958
<S**2>=0.000
     159 ->177        -0.10350
     164 ->177         0.34192
     165 ->177         0.40546
     166 ->177        -0.10285
     168 ->177        -0.10977
     170 ->177         0.12067
     171 ->177        -0.13789
     172 ->177        -0.14165

 Excited State   6:      Singlet-A      4.5719 eV  271.19 nm  f=0.0795
<S**2>=0.000
     159 ->177         0.25419
     159 ->178        -0.10794
     164 ->177         0.12751
     165 ->177         0.26175
     167 ->177         0.22292
     168 ->177         0.16433
     170 ->177        -0.16671
     171 ->177         0.16987
     172 ->177         0.17325
     173 ->177         0.15252
     173 ->178         0.15318

 Excited State   7:      Singlet-A      4.6098 eV  268.96 nm  f=0.0302
<S**2>=0.000
     165 ->177        -0.11395
     166 ->177        -0.14597
     168 ->177        -0.11221
     170 ->177         0.14739
     171 ->177        -0.12627
     172 ->177        -0.12040
     173 ->177         0.32693
     173 ->178         0.38442
     175 ->182        -0.10626

 Excited State   8:      Singlet-A      4.6304 eV  267.76 nm  f=0.0735
<S**2>=0.000
     162 ->177         0.15777
     174 ->177         0.53635
     175 ->178        -0.14497
     176 ->177        -0.13226
     176 ->178         0.20823

 Excited State   9:      Singlet-A      4.7135 eV  263.04 nm  f=0.0698
<S**2>=0.000
     159 ->177        -0.24400
```

```
     159 ->178         0.10409
     166 ->177         0.28328
     167 ->177        -0.26785
     167 ->178        -0.13488
     173 ->177         0.11673
     173 ->178         0.22115
     175 ->184        -0.11085
     176 ->181         0.10729

 Excited State  10:      Singlet-A      4.7900 eV  258.84 nm  f=0.0010
<S**2>=0.000
     159 ->177         0.40056
     159 ->178        -0.14463
     166 ->178         0.13885
     167 ->177        -0.20471
     167 ->178        -0.17802
     174 ->177        -0.13967
     175 ->182         0.13162
     176 ->180        -0.12365
     176 ->181        -0.12290

 Excited State  11:      Singlet-A      4.8917 eV  253.46 nm  f=0.0808
<S**2>=0.000
     159 ->177         0.13011
     162 ->177         0.10098
     172 ->179         0.11624
     174 ->178        -0.21564
     174 ->179        -0.16594
     175 ->178        -0.15380
     175 ->179         0.20947
     176 ->180         0.38576

 Excited State  12:      Singlet-A      4.9887 eV  248.53 nm  f=0.0026
<S**2>=0.000
     162 ->177        -0.12436
     162 ->178        -0.20992
     163 ->177         0.28871
     163 ->178         0.51971

 Excited State  13:      Singlet-A      5.0113 eV  247.41 nm  f=0.0523
<S**2>=0.000
     163 ->178        -0.12145
     166 ->177        -0.10861
     170 ->177         0.14999
     170 ->179         0.12946
     172 ->179         0.18275
     174 ->178         0.21569
     175 ->181         0.12683
     176 ->178         0.15368
     176 ->180        -0.12129
     176 ->181         0.32807
     176 ->183         0.12127

 Excited State  14:      Singlet-A      5.0945 eV  243.37 nm  f=0.0559
<S**2>=0.000
     168 ->179         0.12512
     169 ->179        -0.14491
     171 ->177        -0.13436
```

```
     171 ->179        -0.12343
     174 ->178        -0.18732
     175 ->180        -0.11391
     176 ->178        -0.12215
     176 ->180        -0.16325
     176 ->181         0.26908
     176 ->183        -0.23597
     176 ->185        -0.11178
     176 ->187         0.11938

 Excited State  15:      Singlet-A      5.1062 eV  242.81 nm  f=0.0139
<S**2>=0.000
     161 ->177         0.10107
     162 ->177         0.10191
     164 ->177        -0.17061
     165 ->177         0.14876
     166 ->177        -0.13516
     167 ->177        -0.10605
     170 ->177         0.14320
     171 ->177         0.17559
     171 ->179         0.12154
     174 ->179        -0.18873
     175 ->179         0.21778
     176 ->178         0.16295
     176 ->183        -0.16176

 Excited State  16:      Singlet-A      5.1434 eV  241.05 nm  f=0.0264
<S**2>=0.000
     169 ->183         0.11617
     171 ->179         0.33351
     172 ->177        -0.22594
     172 ->179        -0.16318
     172 ->181        -0.11115
     176 ->181         0.19338
     176 ->187        -0.19972
     176 ->189         0.13447

 Excited State  17:      Singlet-A      5.2309 eV  237.02 nm  f=0.0476
<S**2>=0.000
     170 ->179         0.26082
     171 ->177         0.19185
     172 ->177         0.16831
     174 ->178        -0.17194
     176 ->178        -0.16786
     176 ->180        -0.18397
     176 ->181        -0.12790
     176 ->186         0.16762
     176 ->188         0.10290
     176 ->189         0.14491

 Excited State  18:      Singlet-A      5.2709 eV  235.22 nm  f=0.0595
<S**2>=0.000
     162 ->177        -0.10073
     169 ->177        -0.12436
     170 ->179         0.23792
     172 ->179        -0.12476
     174 ->178         0.16069
     176 ->180         0.25323
```

```
     176 ->187         0.19921
     176 ->188        -0.11808
     176 ->189         0.13847

 Excited State  19:      Singlet-A      5.3383 eV  232.25 nm  f=0.0606
<S**2>=0.000
     164 ->177         0.19500
     165 ->177        -0.11418
     167 ->177         0.13162
     167 ->178        -0.10048
     168 ->179        -0.14226
     169 ->177        -0.12560
     170 ->177        -0.13890
     172 ->179         0.13097
     173 ->177         0.13356
     174 ->179        -0.14022
     175 ->179         0.14015
     175 ->182         0.10547
     176 ->183        -0.18225
     176 ->184         0.12308
     176 ->185         0.25180

 Excited State  20:      Singlet-A      5.3440 eV  232.01 nm  f=0.0256
<S**2>=0.000
     157 ->177        -0.12899
     158 ->177         0.17490
     159 ->177        -0.10207
     166 ->177        -0.15822
     166 ->178         0.16326
     167 ->177         0.16127
     167 ->178        -0.16775
     173 ->177         0.30715
     173 ->178        -0.13390
     175 ->182         0.19803
     176 ->182        -0.14120
     176 ->185        -0.16232
 SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 NState=   20
LETran=     370.
```

***m*-BT:**

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.2699 eV  379.17 nm  f=0.7519
<S**2>=0.000
     174 ->177         0.18695
     175 ->177         0.36501
     176 ->177         0.55230
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2691.73044038
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:      Singlet-A      3.9681 eV  312.45 nm  f=0.2472
<S**2>=0.000
```

```
     174 ->177         0.13469
     175 ->177         0.36824
     176 ->177        -0.20755
     176 ->179         0.50719

 Excited State   3:      Singlet-A      4.2631 eV  290.83 nm  f=0.2711
<S**2>=0.000
     175 ->177        -0.35225
     176 ->177         0.33665
     176 ->179         0.43098

 Excited State   4:      Singlet-A      4.3522 eV  284.87 nm  f=0.2409
<S**2>=0.000
     164 ->177         0.12617
     174 ->177         0.48158
     174 ->178         0.35858
     175 ->177        -0.20870

 Excited State   5:      Singlet-A      4.4543 eV  278.35 nm  f=0.2707
<S**2>=0.000
     173 ->178        -0.19392
     174 ->177         0.21482
     174 ->178        -0.32836
     175 ->178         0.42763
     176 ->178         0.17210

 Excited State   6:      Singlet-A      4.5693 eV  271.34 nm  f=0.1237
<S**2>=0.000
     159 ->177        -0.10384
     165 ->177         0.55122
     166 ->177        -0.13479
     167 ->177        -0.13054
     170 ->177         0.10599
     175 ->178         0.11484

 Excited State   7:      Singlet-A      4.6160 eV  268.60 nm  f=0.0951
<S**2>=0.000
     159 ->177         0.31730
     165 ->177         0.22690
     166 ->177        -0.15170
     168 ->177         0.16288
     169 ->177        -0.11192
     170 ->177        -0.25898
     172 ->177         0.19887
     174 ->178        -0.11900
     176 ->178        -0.10140
     176 ->182         0.12219

 Excited State   8:      Singlet-A      4.6805 eV  264.90 nm  f=0.1826
<S**2>=0.000
     170 ->177        -0.16585
     172 ->177         0.15437
     172 ->179        -0.10240
     174 ->177        -0.20956
     174 ->178         0.29675
     175 ->177         0.11333
     175 ->178         0.15745
     175 ->179        -0.13393
```

```
     176 ->178         0.23648
     176 ->180         0.17491
     176 ->181         0.11450
     176 ->182         0.11908

 Excited State   9:      Singlet-A      4.7619 eV  260.37 nm  f=0.1218
<S**2>=0.000
     173 ->177         0.13981
     173 ->178         0.54749
     173 ->186        -0.10242
     174 ->178        -0.14514
     174 ->183        -0.18179
     175 ->178         0.15096
     176 ->178         0.10715

 Excited State  10:      Singlet-A      4.7819 eV  259.28 nm  f=0.0251
<S**2>=0.000
     159 ->177         0.41747
     159 ->180        -0.10968
     161 ->177        -0.11197
     163 ->177         0.10674
     164 ->177         0.11153
     166 ->177         0.10547
     174 ->177        -0.22232
     174 ->178         0.15165
     176 ->178         0.14201
     176 ->182        -0.15254

 Excited State  11:      Singlet-A      4.8663 eV  254.78 nm  f=0.3055
<S**2>=0.000
     159 ->177         0.12275
     170 ->177         0.11490
     172 ->179        -0.11467
     174 ->177         0.13463
     174 ->178        -0.14032
     174 ->179        -0.12956
     175 ->179        -0.28649
     175 ->180         0.15549
     175 ->181        -0.10478
     176 ->180         0.36835
     176 ->181         0.18781

 Excited State  12:      Singlet-A      5.0210 eV  246.93 nm  f=0.0834
<S**2>=0.000
     166 ->177         0.17072
     167 ->177         0.15791
     168 ->177        -0.17895
     171 ->177         0.12152
     172 ->177        -0.11407
     172 ->179        -0.17872
     175 ->179         0.11312
     175 ->180        -0.14807
     176 ->181         0.22993
     176 ->182         0.26139
     176 ->184        -0.13464

 Excited State  13:      Singlet-A      5.0371 eV  246.14 nm  f=0.0875
<S**2>=0.000
```

```
     162 ->178        -0.10269
     165 ->177         0.10117
     166 ->177         0.14145
     167 ->177         0.26588
     168 ->177        -0.11556
     169 ->177        -0.19395
     170 ->177        -0.18994
     170 ->179         0.13205
     172 ->177        -0.11818
     172 ->179         0.12298
     173 ->177        -0.14470
     176 ->180         0.20785
     176 ->182        -0.23721

 Excited State  14:      Singlet-A      5.0501 eV  245.51 nm  f=0.0020
<S**2>=0.000
     162 ->178         0.60220
     162 ->194         0.12695
     163 ->178         0.26904

 Excited State  15:      Singlet-A      5.1126 eV  242.51 nm  f=0.0119
<S**2>=0.000
     168 ->179        -0.15682
     169 ->179         0.13727
     171 ->177         0.10885
     172 ->177        -0.11201
     173 ->177        -0.11013
     175 ->179        -0.14568
     175 ->180         0.14184
     176 ->181        -0.19191
     176 ->182         0.27045
     176 ->183        -0.12626
     176 ->184         0.17120
     176 ->185         0.14776
     176 ->187        -0.10924

 Excited State  16:      Singlet-A      5.1493 eV  240.78 nm  f=0.0120
<S**2>=0.000
     169 ->184         0.11747
     171 ->177        -0.14816
     171 ->179         0.38722
     172 ->177        -0.11815
     172 ->182         0.12473
     172 ->185        -0.10780
     176 ->182         0.14324
     176 ->187         0.20251
     176 ->188         0.10097
     176 ->189        -0.15977

 Excited State  17:      Singlet-A      5.2400 eV  236.61 nm  f=0.0065
<S**2>=0.000
     159 ->177         0.14439
     163 ->177        -0.13415
     164 ->177        -0.13769
     170 ->179         0.18536
     171 ->177         0.12740
     172 ->177        -0.24733
     172 ->179         0.10443
```

```
     173 ->177         0.29046
     175 ->179         0.10457
     176 ->178         0.11384
     176 ->180         0.12473
     176 ->181         0.10560
     176 ->182         0.18211
     176 ->185         0.11475
     176 ->189         0.12124

 Excited State  18:      Singlet-A      5.2749 eV  235.05 nm  f=0.0162
<S**2>=0.000
     167 ->177         0.12032
     169 ->177        -0.12645
     170 ->177        -0.10296
     170 ->179        -0.24348
     173 ->177         0.40265
     176 ->180         0.10980
     176 ->182        -0.12026
     176 ->187        -0.15078
     176 ->189        -0.14633

 Excited State  19:      Singlet-A      5.2894 eV  234.40 nm  f=0.0130
<S**2>=0.000
     164 ->177         0.16216
     166 ->177         0.11162
     170 ->179         0.12594
     172 ->179        -0.12964
     173 ->177         0.36441
     174 ->179        -0.11272
     175 ->179        -0.14940
     175 ->181         0.10497
     176 ->178        -0.24606
     176 ->180        -0.10515
     176 ->184         0.10358

 Excited State  20:      Singlet-A      5.3483 eV  231.82 nm  f=0.0542
<S**2>=0.000
     164 ->177        -0.11157
     164 ->178        -0.13415
     168 ->179         0.11719
     170 ->177        -0.11424
     173 ->177         0.14748
     175 ->180         0.18683
     176 ->178         0.24778
     176 ->180        -0.10068
     176 ->181        -0.22202
     176 ->185        -0.24300
 SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 NState=   20
LETran=     370.
```

_o_-BT:

```
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.3551 eV  369.54 nm  f=0.5984
<S**2>=0.000
     174 ->177         0.11463
     175 ->177        -0.39084
```

```
     176 ->177         0.55385
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2691.72082955
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:      Singlet-A      3.9867 eV  311.00 nm  f=0.2957
<S**2>=0.000
     175 ->177        -0.35143
     176 ->177        -0.14938
     176 ->178        -0.10097
     176 ->179         0.55045

 Excited State   3:      Singlet-A      4.2860 eV  289.28 nm  f=0.1865
<S**2>=0.000
     166 ->177        -0.14566
     174 ->177         0.32980
     175 ->177         0.36563
     175 ->178         0.12602
     176 ->177         0.25222
     176 ->178        -0.13228
     176 ->179         0.28821

 Excited State   4:      Singlet-A      4.4219 eV  280.39 nm  f=0.0349
<S**2>=0.000
     174 ->177         0.13090
     174 ->178         0.15159
     175 ->177        -0.15601
     175 ->178         0.44293
     176 ->177        -0.17021
     176 ->178        -0.27360
     176 ->179        -0.20584
     176 ->180        -0.11937

 Excited State   5:      Singlet-A      4.4454 eV  278.91 nm  f=0.0796
<S**2>=0.000
     167 ->177        -0.10819
     174 ->177         0.52029
     175 ->178        -0.22572
     176 ->177        -0.21464
     176 ->178         0.19003

 Excited State   6:      Singlet-A      4.6027 eV  269.38 nm  f=0.1513
<S**2>=0.000
     166 ->177         0.45238
     167 ->177         0.32960
     173 ->177        -0.14732
     174 ->177         0.19428
     174 ->178         0.10834

 Excited State   7:      Singlet-A      4.6569 eV  266.24 nm  f=0.0134
<S**2>=0.000
     159 ->177         0.32531
     160 ->177        -0.15259
     163 ->177        -0.13269
     166 ->177         0.13411
     168 ->177         0.18219
     169 ->177        -0.12636
```

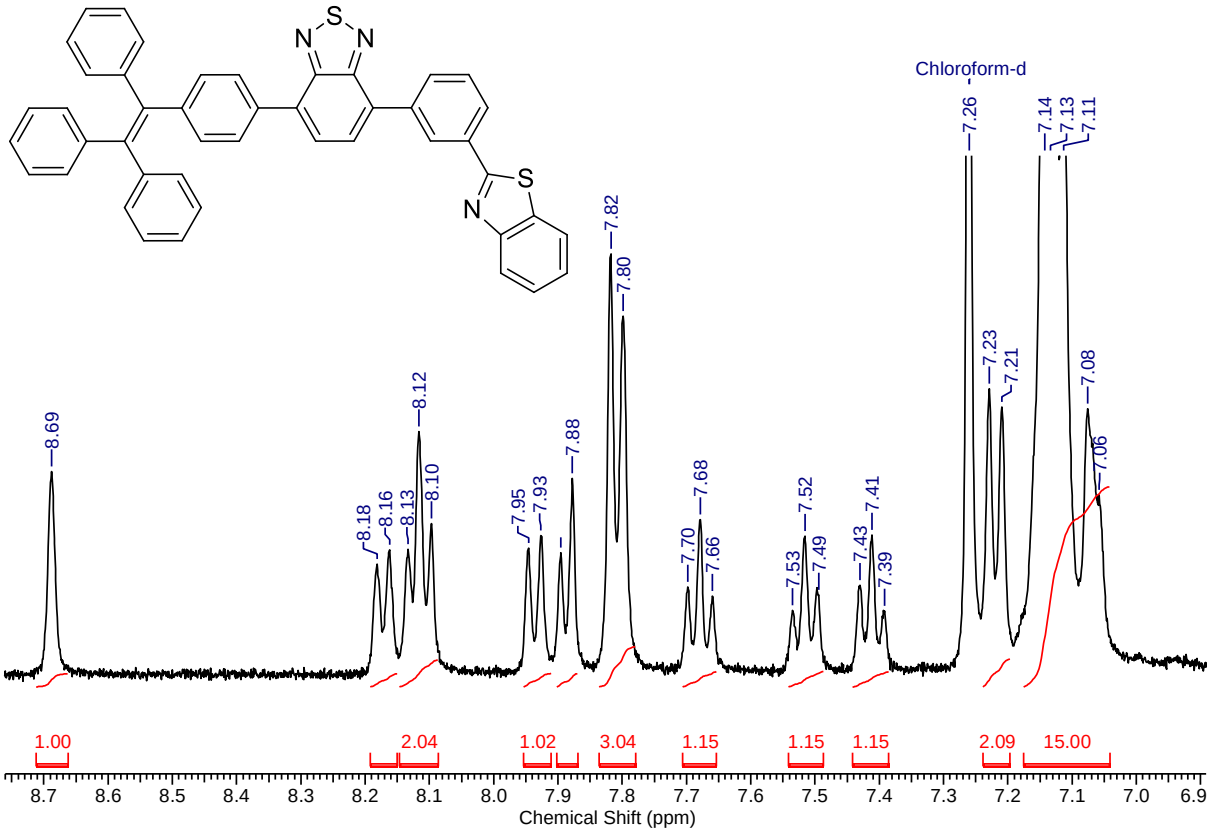
```
     170 ->177        -0.19526
     171 ->177        -0.20247
     172 ->177         0.25653
     176 ->182         0.15440

 Excited State   8:      Singlet-A      4.6913 eV  264.29 nm  f=0.0918
<S**2>=0.000
     173 ->177         0.19538
     173 ->178         0.39940
     173 ->185        -0.13190
     174 ->178        -0.38046
     174 ->183         0.13858
     176 ->178        -0.16420

 Excited State   9:      Singlet-A      4.7780 eV  259.49 nm  f=0.0343
<S**2>=0.000
     159 ->177         0.34952
     160 ->177        -0.17669
     161 ->177        -0.10159
     163 ->177        -0.14591
     170 ->177         0.10061
     171 ->177         0.10331
     172 ->177        -0.14781
     172 ->179         0.15425
     173 ->177        -0.16218
     176 ->182        -0.22976

 Excited State  10:      Singlet-A      4.8439 eV  255.96 nm  f=0.0959
<S**2>=0.000
     159 ->177         0.14514
     173 ->177         0.50295
     173 ->178         0.10872
     174 ->178         0.33997
     176 ->178         0.11700

 Excited State  11:      Singlet-A      4.8930 eV  253.39 nm  f=0.2812
<S**2>=0.000
     173 ->177        -0.31562
     173 ->178         0.41074
     174 ->178         0.27478
     174 ->183         0.14366
     175 ->179         0.12494
     176 ->180         0.13815
     176 ->181        -0.11300

 Excited State  12:      Singlet-A      4.9132 eV  252.35 nm  f=0.1679
<S**2>=0.000
     159 ->177         0.12807
     167 ->177         0.10649
     170 ->177         0.10758
     172 ->179        -0.11811
     173 ->177         0.19131
     173 ->178        -0.14417
     174 ->179        -0.11078
     175 ->179         0.25696
     176 ->180         0.30126
     176 ->181        -0.21430
```

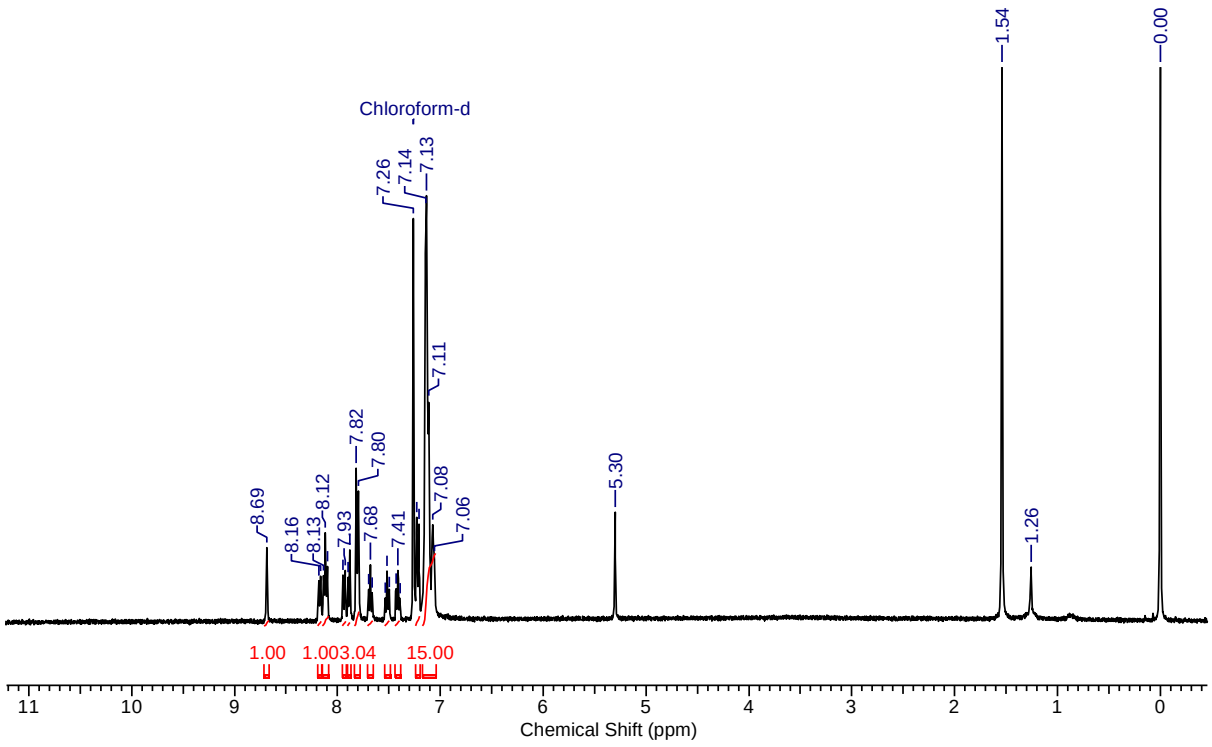
```
 Excited State  13:      Singlet-A      5.0360 eV  246.19 nm  f=0.0214
<S**2>=0.000
     162 ->178         0.20031
     164 ->177         0.15603
     164 ->178         0.27467
     165 ->177        -0.19714
     165 ->178        -0.17921
     167 ->177        -0.16370
     167 ->178        -0.11739
     174 ->181         0.11835
     175 ->180         0.18288
     176 ->181        -0.10567
     176 ->182         0.12889

 Excited State  14:      Singlet-A      5.0520 eV  245.42 nm  f=0.2489
<S**2>=0.000
     162 ->178        -0.17284
     164 ->178        -0.14095
     170 ->177         0.10513
     170 ->179        -0.13722
     171 ->177         0.11236
     171 ->179        -0.12876
     172 ->179        -0.12567
     175 ->182         0.13612
     176 ->180        -0.17209
     176 ->181         0.12772
     176 ->182         0.35346
     176 ->184        -0.10846
     176 ->187         0.13612

 Excited State  15:      Singlet-A      5.0991 eV  243.15 nm  f=0.0101
<S**2>=0.000
     162 ->178         0.17387
     164 ->177         0.12868
     164 ->178         0.12640
     167 ->177         0.11769
     167 ->179        -0.11235
     168 ->179        -0.10509
     175 ->179         0.22923
     175 ->181         0.11121
     176 ->180        -0.10379
     176 ->181         0.21934
     176 ->182         0.10294
     176 ->184         0.25482
     176 ->186         0.11331

 Excited State  16:      Singlet-A      5.1554 eV  240.49 nm  f=0.0369
<S**2>=0.000
     169 ->184         0.13160
     170 ->177         0.16070
     170 ->179        -0.16051
     171 ->177        -0.10930
     171 ->179         0.35858
     172 ->182         0.13273
     172 ->186        -0.11103
     176 ->187        -0.22087
     176 ->188         0.19459
```

```
 Excited State  17:      Singlet-A      5.1989 eV  238.48 nm  f=0.0128
<S**2>=0.000
     165 ->177         0.22700
     166 ->177        -0.12609
     167 ->177         0.18385
     168 ->177         0.10382
     169 ->177         0.13384
     169 ->179        -0.12596
     172 ->177         0.27026
     172 ->179        -0.11520
     175 ->177        -0.10034
     176 ->180        -0.18738
     176 ->182        -0.19716
     176 ->184        -0.14461
     176 ->186        -0.15853

 Excited State  18:      Singlet-A      5.2463 eV  236.33 nm  f=0.0084
<S**2>=0.000
     162 ->177         0.10782
     162 ->178         0.36636
     164 ->177        -0.18091
     164 ->178         0.10062
     165 ->177         0.15331
     175 ->179        -0.16717
     176 ->178         0.28443
     176 ->182         0.11560

 Excited State  19:      Singlet-A      5.2847 eV  234.61 nm  f=0.0383
<S**2>=0.000
     169 ->177         0.11005
     170 ->179         0.29642
     171 ->177         0.13731
     172 ->177        -0.12298
     175 ->186        -0.11014
     176 ->182         0.21474
     176 ->186        -0.11742
     176 ->187        -0.19321
     176 ->188        -0.19349

 Excited State  20:      Singlet-A      5.3408 eV  232.14 nm  f=0.0421
<S**2>=0.000
     158 ->177         0.14332
     162 ->178        -0.14085
     165 ->177         0.18181
     167 ->177         0.15651
     168 ->179        -0.11806
     172 ->179         0.10351
     175 ->180         0.12343
     176 ->178        -0.13243
     176 ->180         0.10160
     176 ->181        -0.20885
     176 ->186         0.25490
 SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 NState=   20
LETran=     370.
```

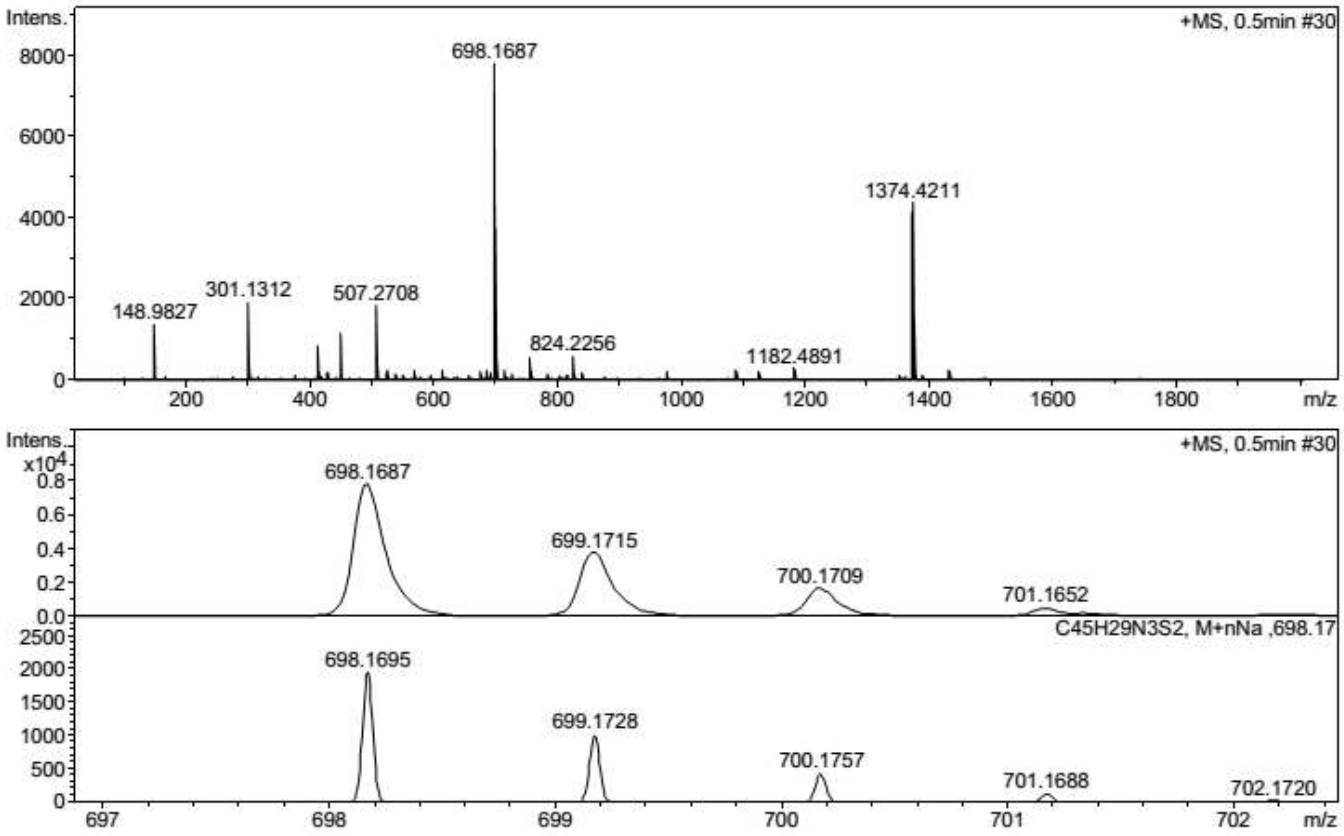
Copies of NMR and HRMS of new compounds:

^{1}H NMR of ***m*-BT**:

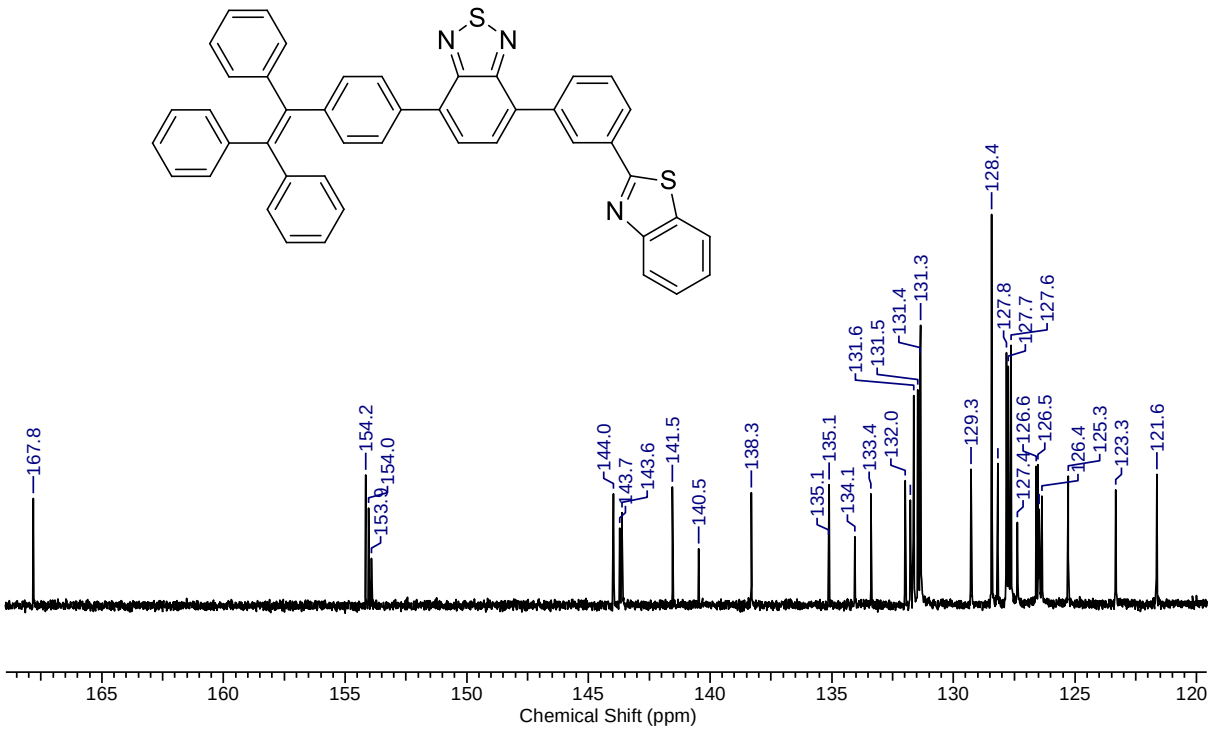


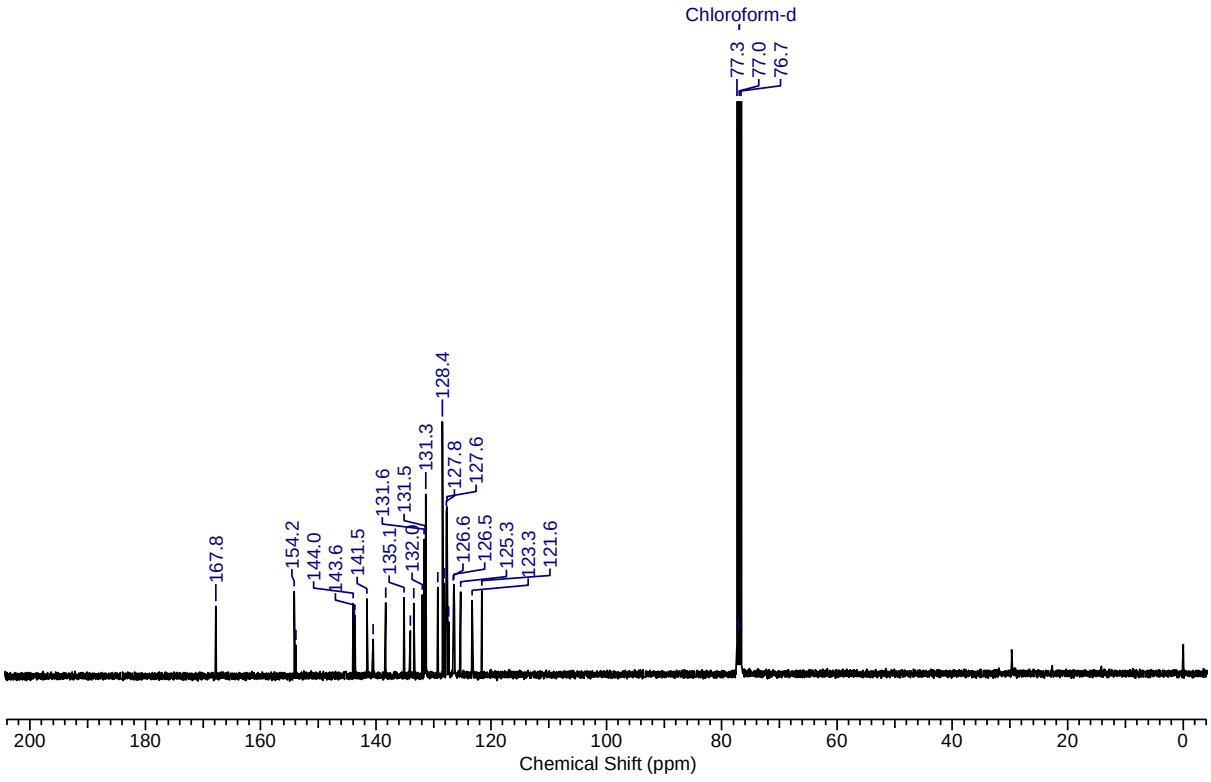


HRMS of ***m*-BT**:

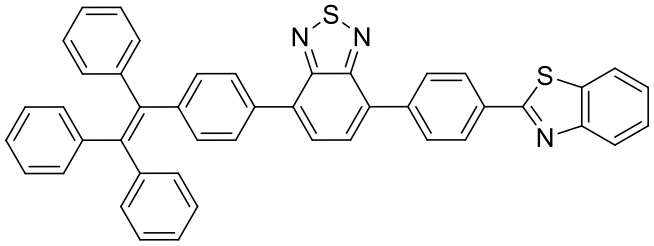

Intens.
+MS, 0.5min #30
698.1687
1374.4211
301.1312
507.2708
148.9827
824.2256
1182.4891
m/z
Intens.
x10^4
+MS, 0.5min #30
698.1687
699.1715
700.1709
701.1652
C45H29N3S2, M+nNa ,698.17
698.1695
699.1728
700.1757
701.1688
702.1720
m/z

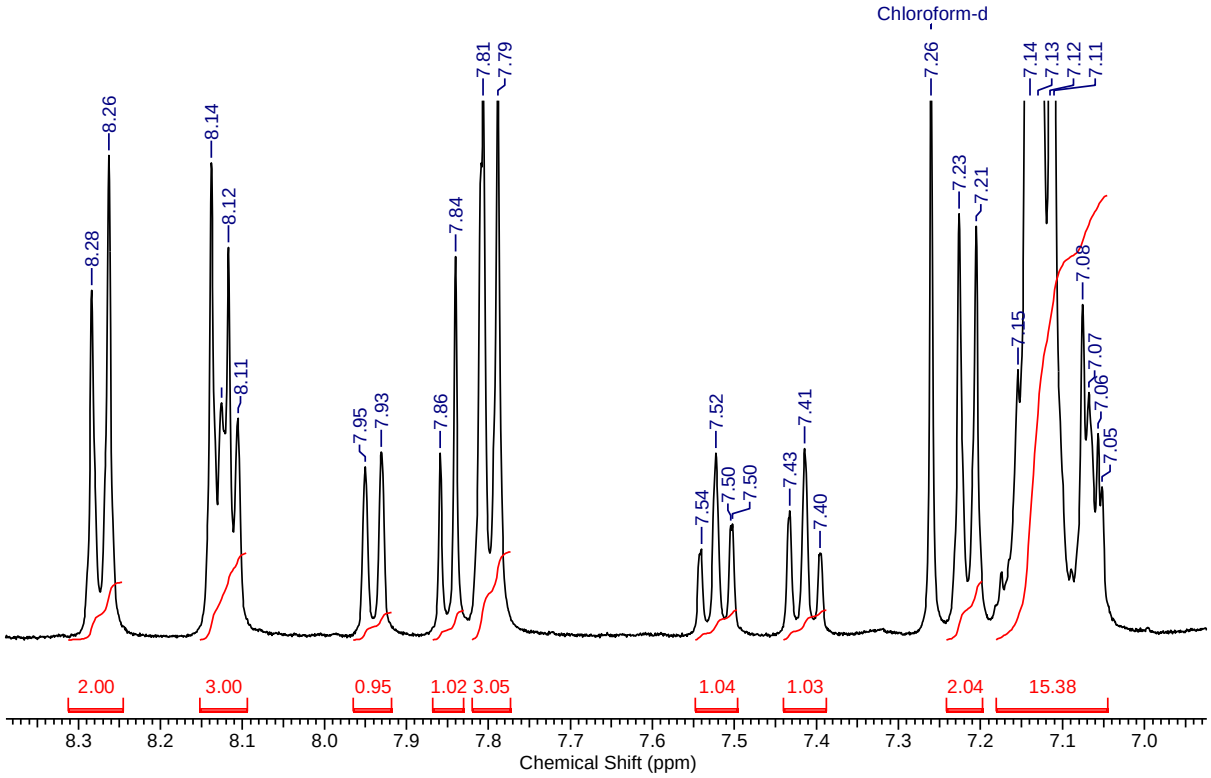
^{13}C NMR of ***m*-BT**:

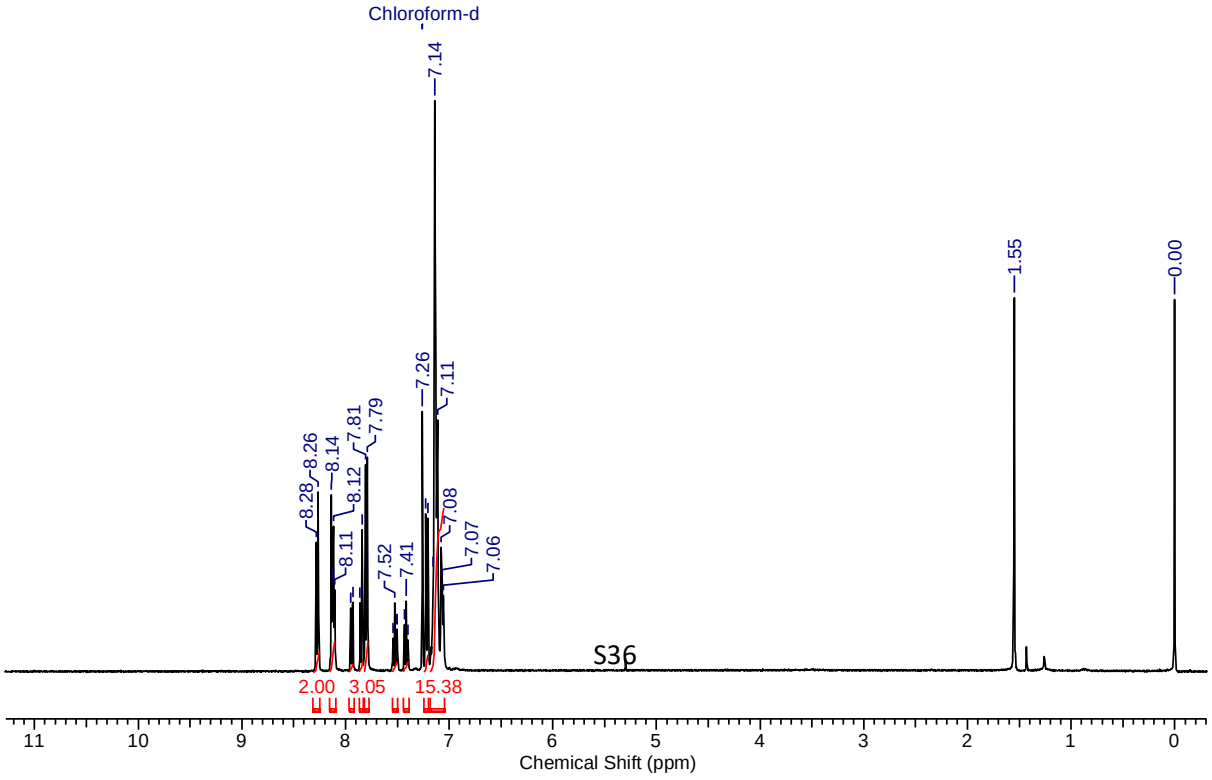




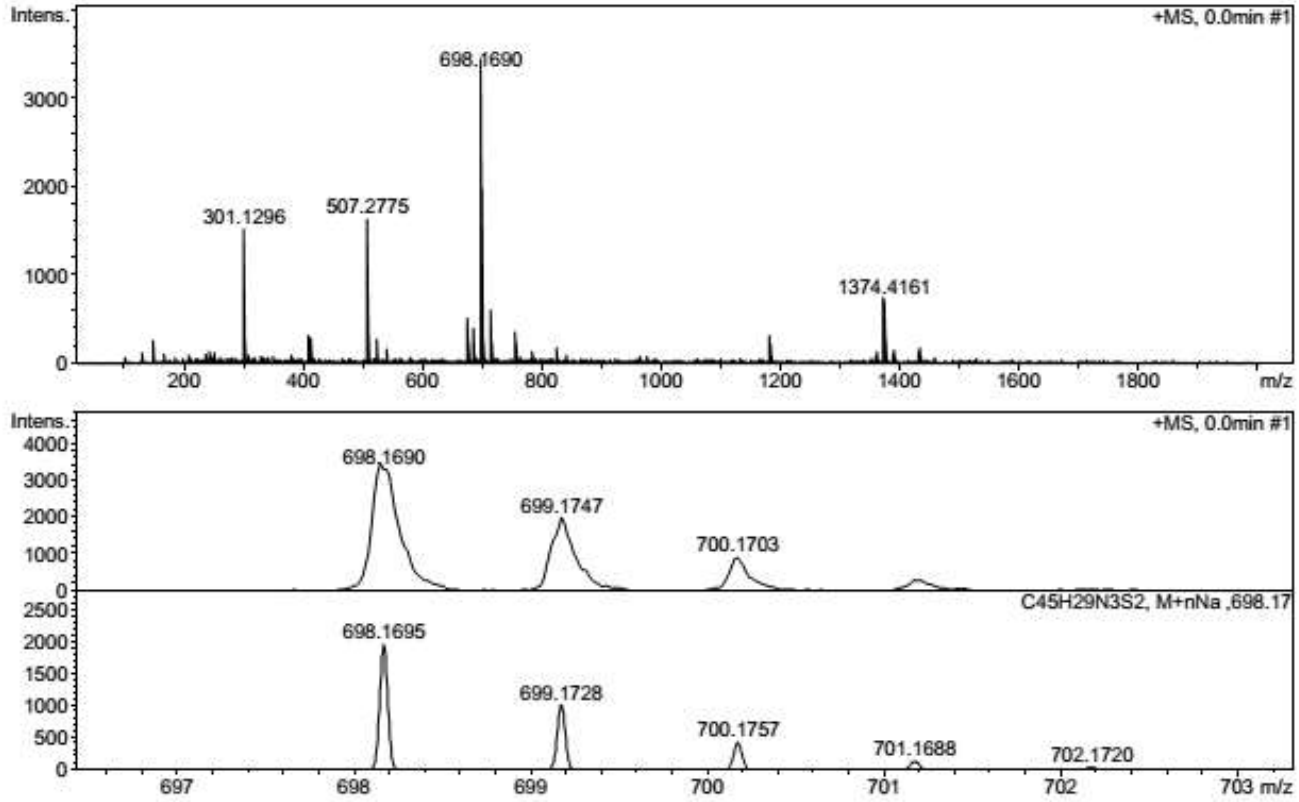
^{1}H NMR of ***p*-BT**:


S
N
N
S
N

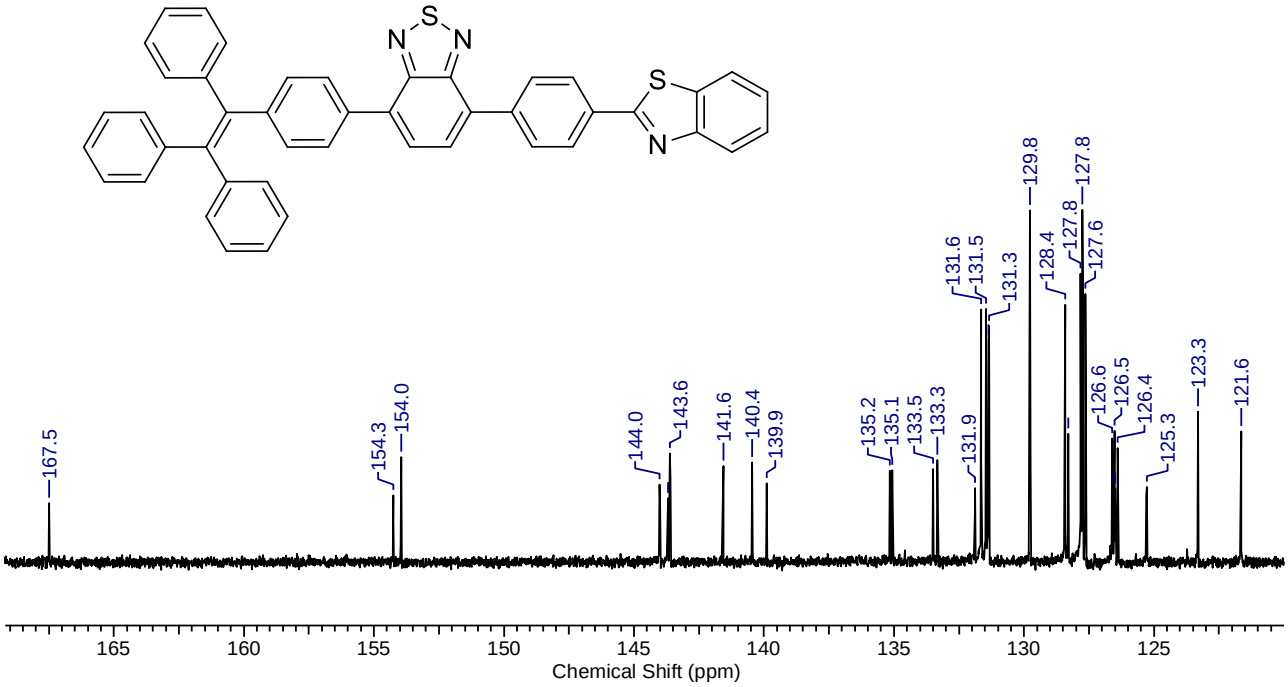

Chloroform-d
8.28
8.26
8.14
8.12
8.11
7.95
7.93
7.86
7.84
7.81
7.79
7.54
7.52
7.50
7.50
7.43
7.41
7.40
7.26
7.23
7.21
7.15
7.14
7.13
7.12
7.11
7.08
7.07
7.06
7.05
2.00
3.00
0.95
1.02
3.05
1.04
1.03
2.04
15.38
Chemical Shift (ppm)

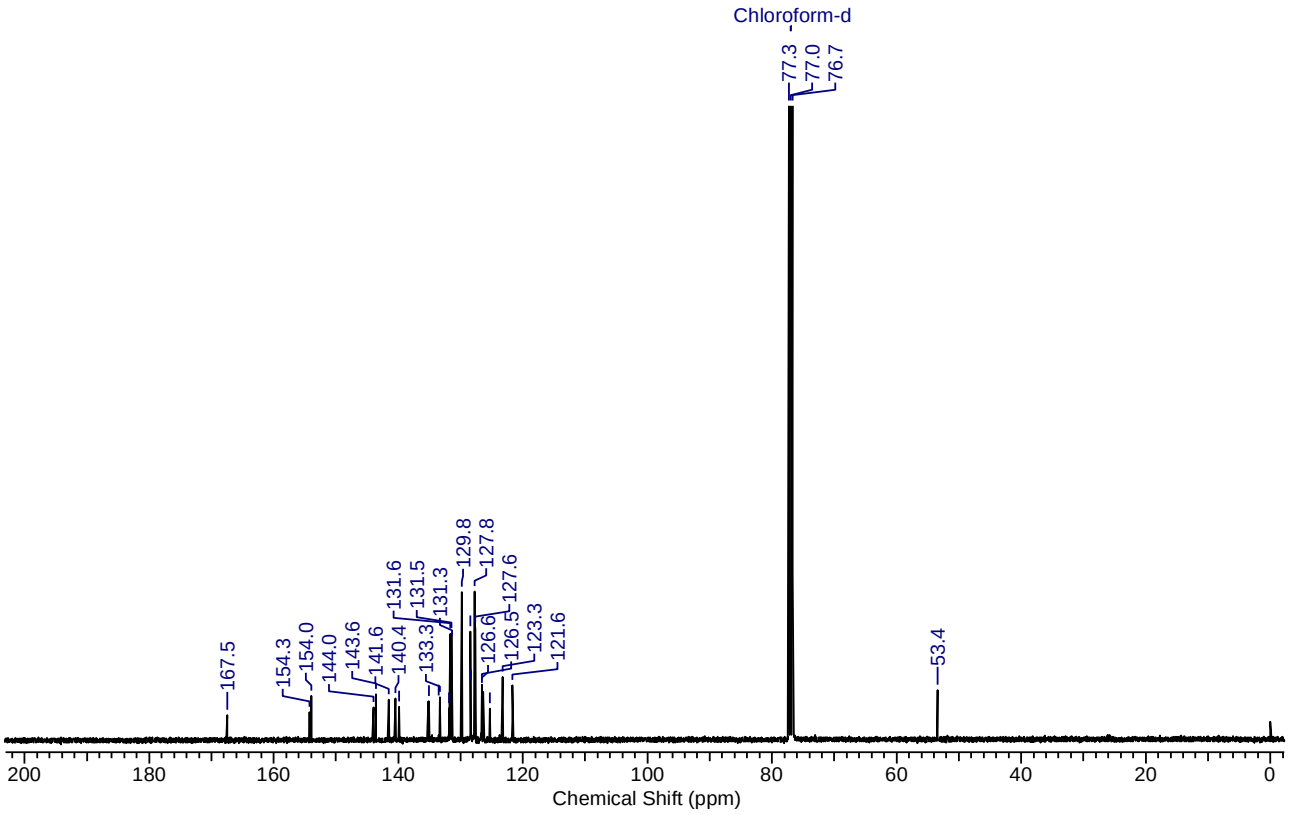

Chloroform-d
7.14
8.28
8.26
8.14
8.12
8.11
7.81
7.79
7.52
7.41
7.26
7.11
7.08
7.07
7.06
1.55
0.00
2.00
3.05
15.38
Chemical Shift (ppm)

HRMS of ***p*-BT**:

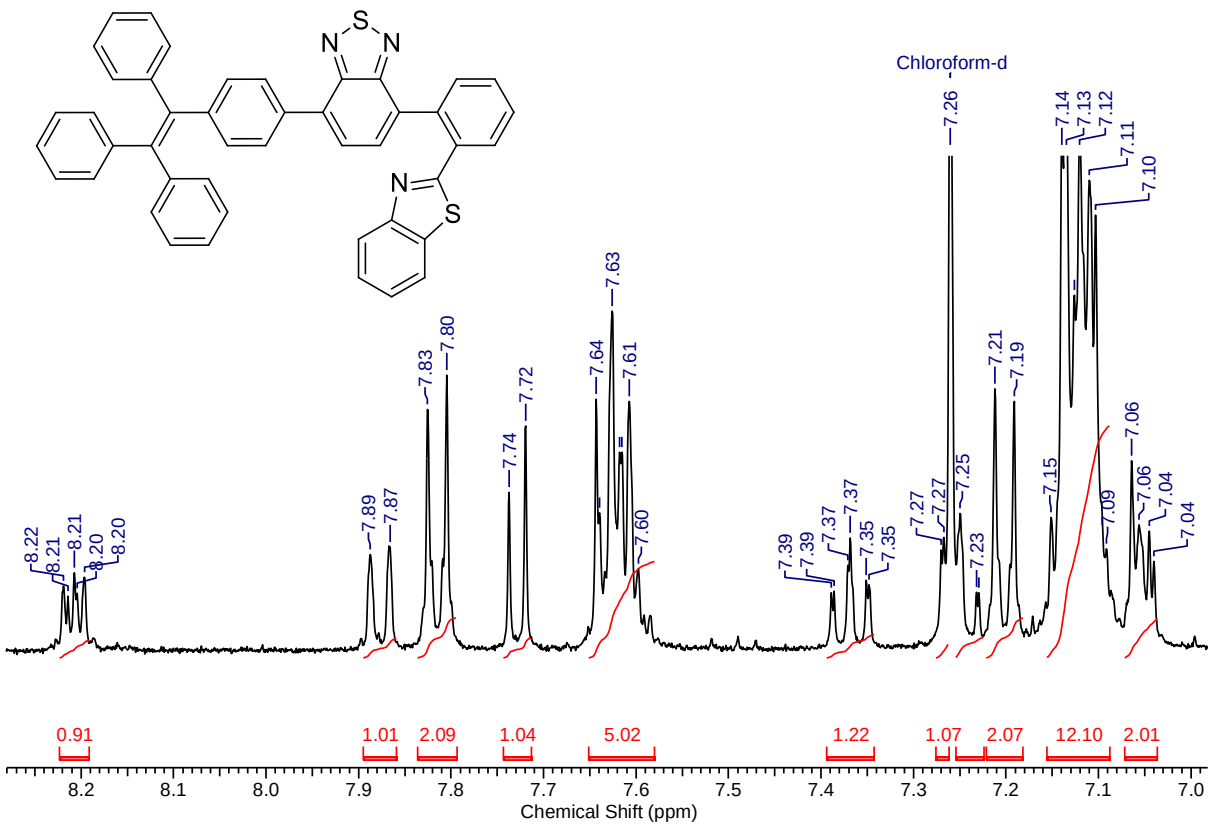

Intens.
+MS, 0.0min #1
698.1690
507.2775
301.1296
1374.4161
m/z
Intens.
+MS, 0.0min #1
698.1690
699.1747
700.1703
C45H29N3S2, M+nNa ,698.17
698.1695
699.1728
700.1757
701.1688
702.1720
m/z

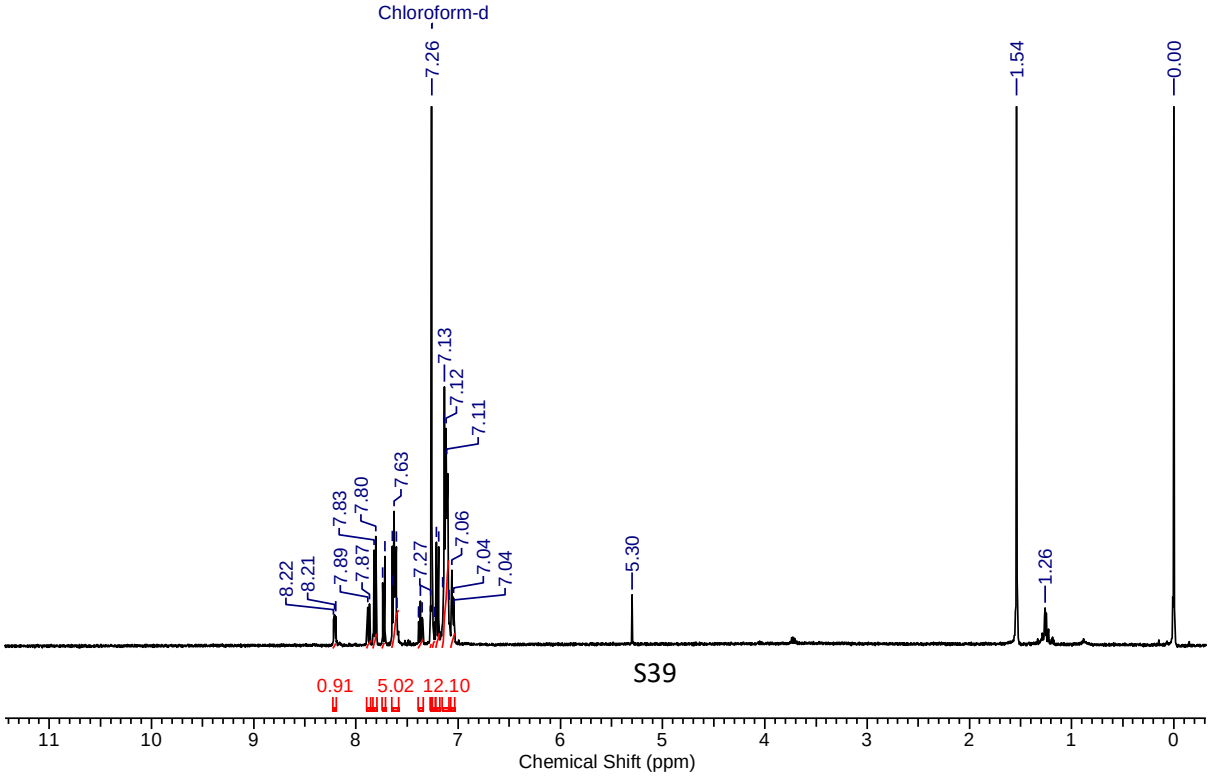
^{13}C NMR of ***p*-BT**:



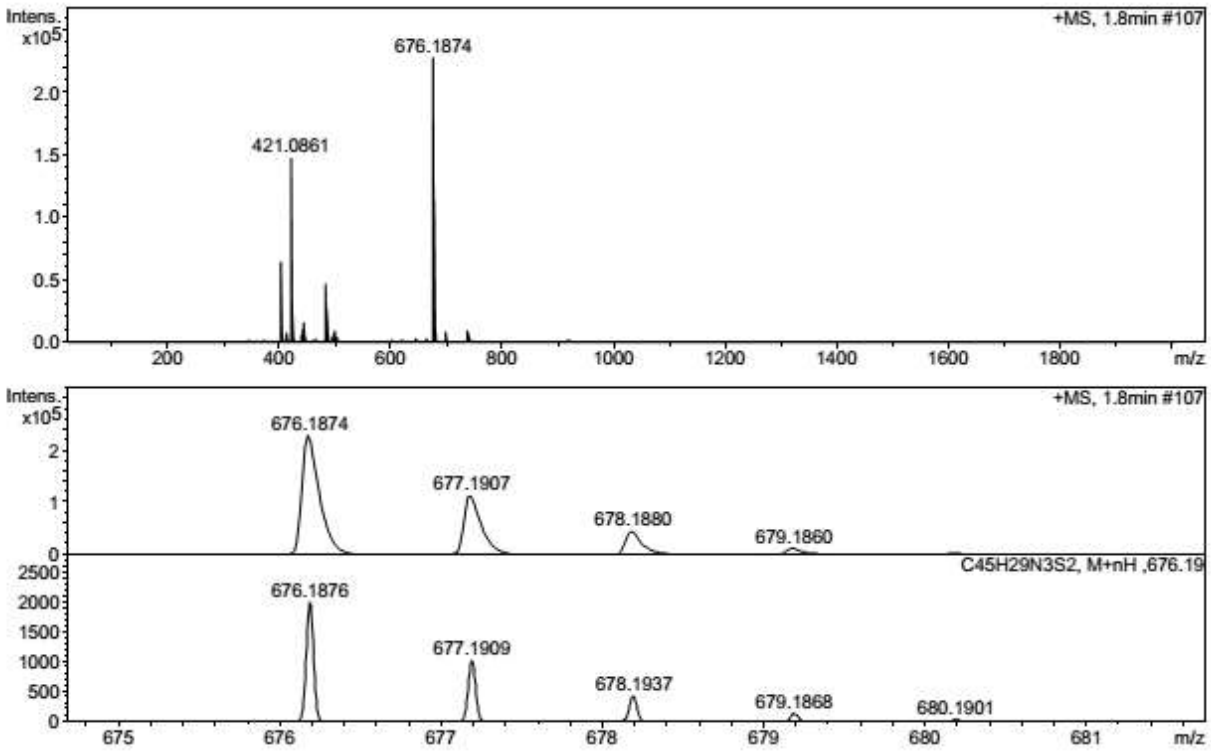


^{1}H NMR of ***o*-BT**:

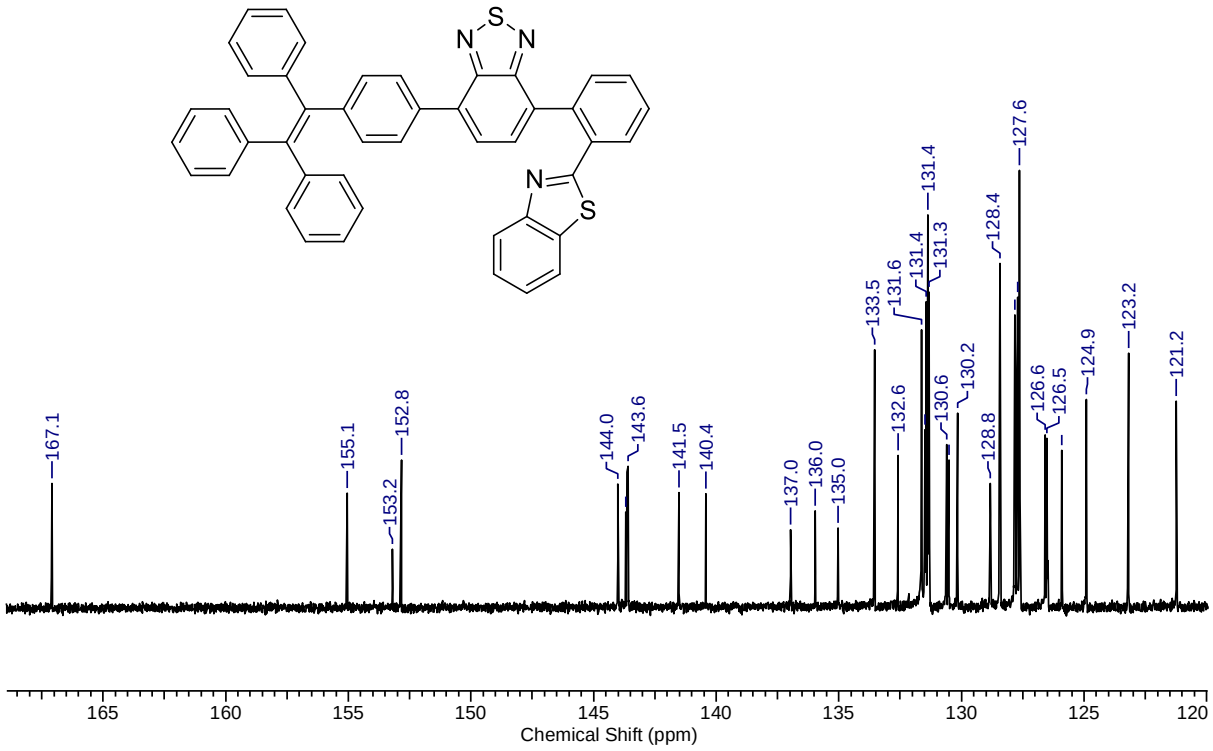

Chloroform-d
Chemical Shift (ppm)

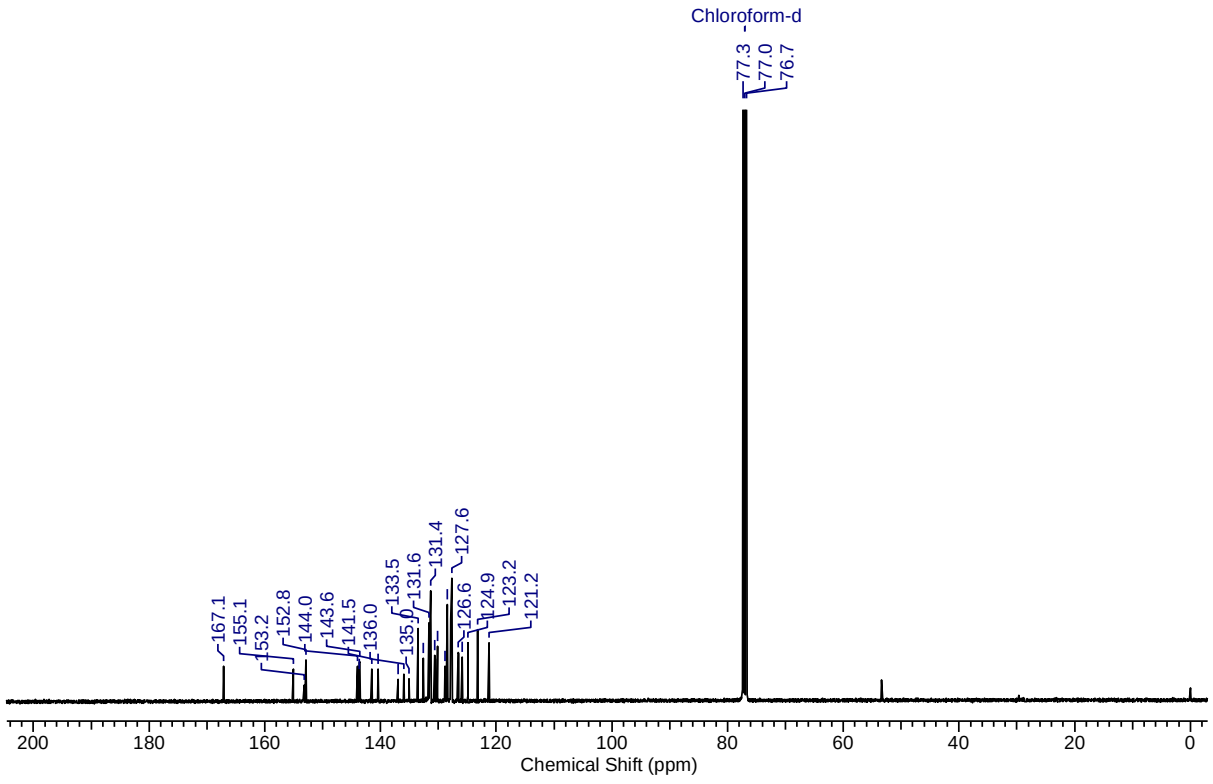

Chloroform-d
Chemical Shift (ppm)

HRMS of ***o*-BT**:

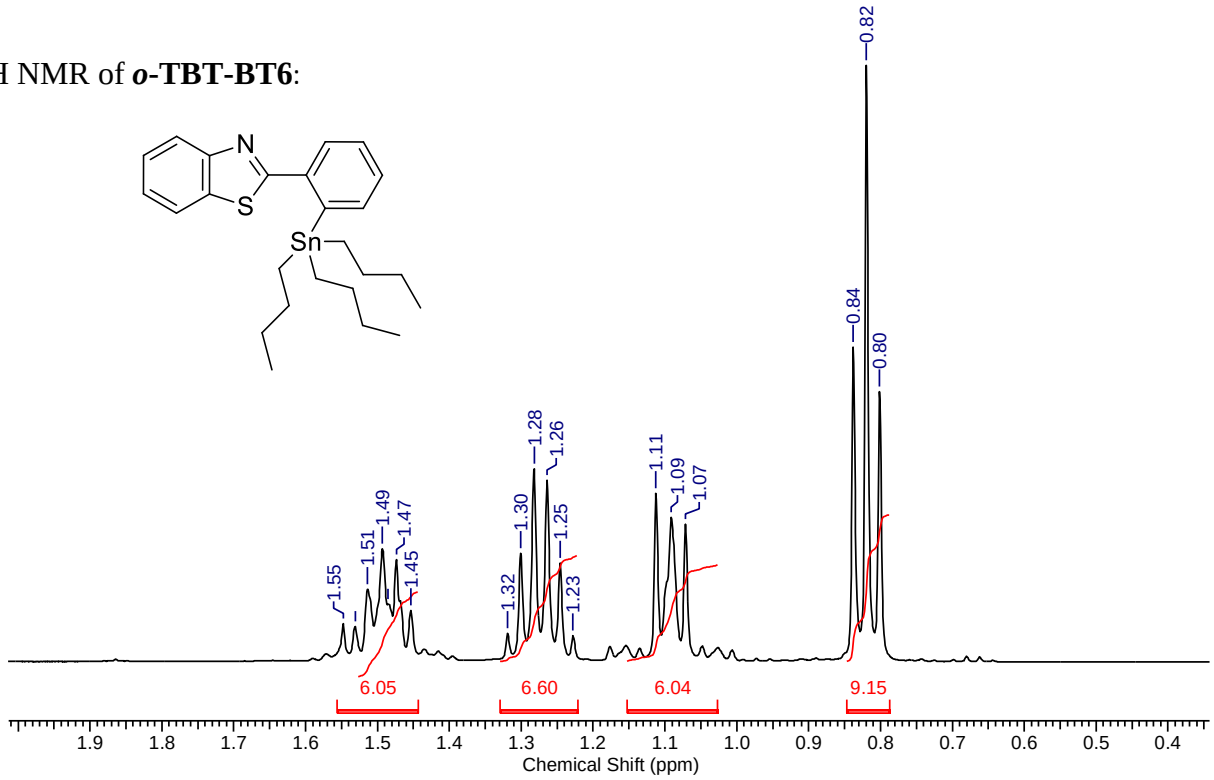

Intens.
x10^5
+MS, 1.8min #107
676.1874
421.0861
m/z
676.1874
677.1907
678.1880
679.1860
C45H29N3S2, M+nH ,676.19
676.1876
677.1909
678.1937
679.1868
680.1901

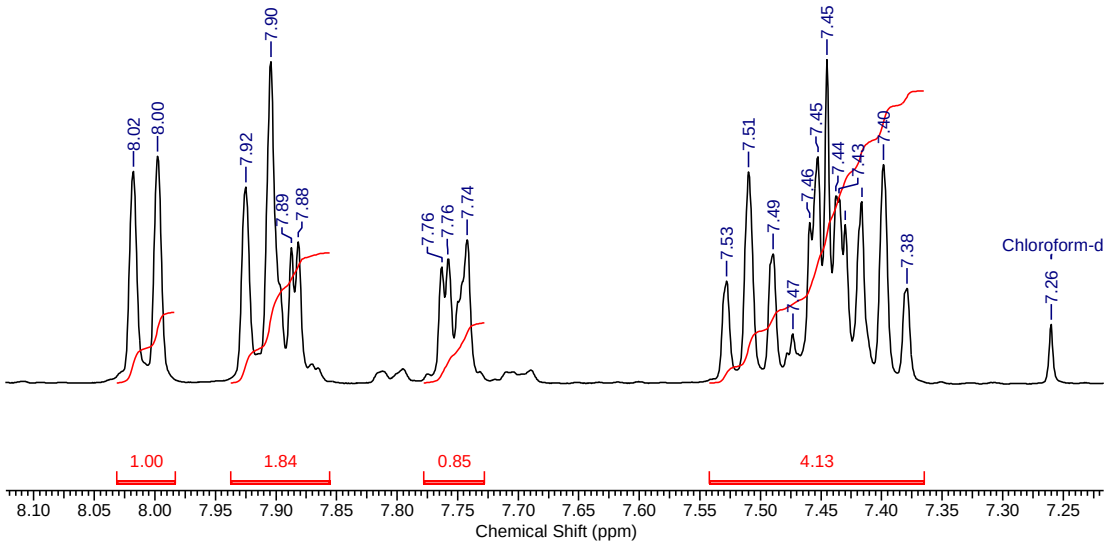
^{13}C NMR of ***o*-BT**:

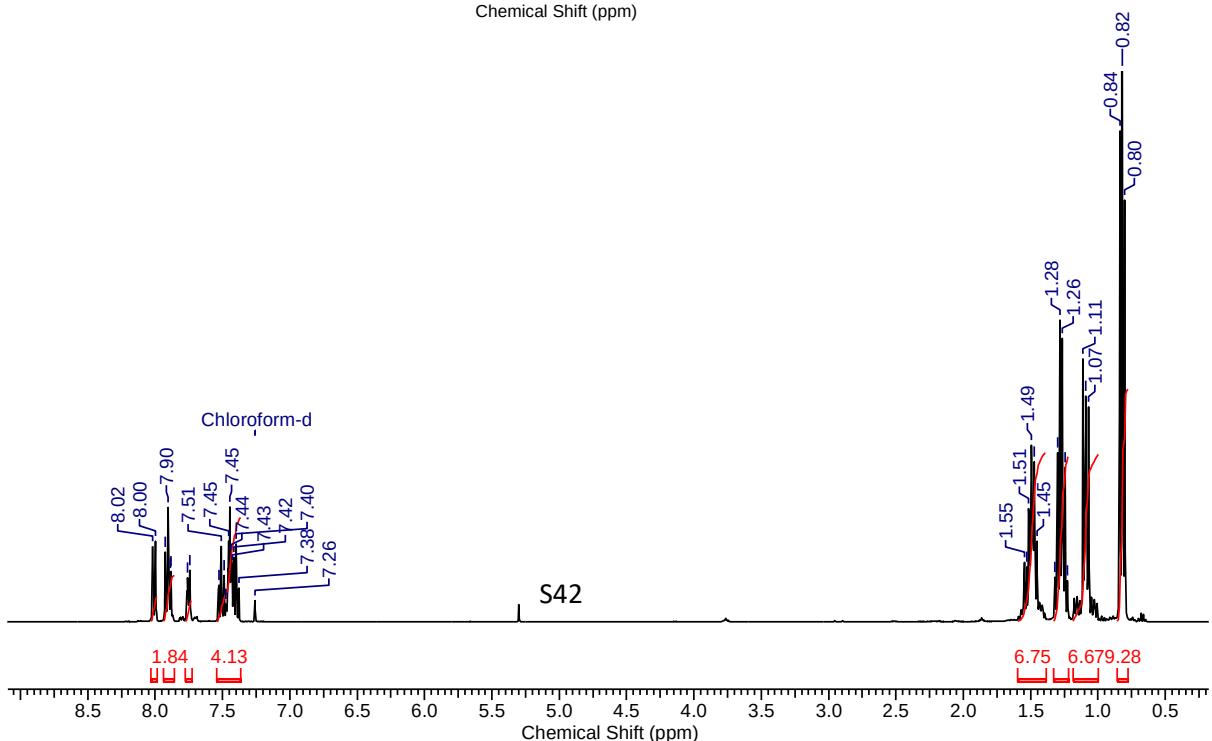




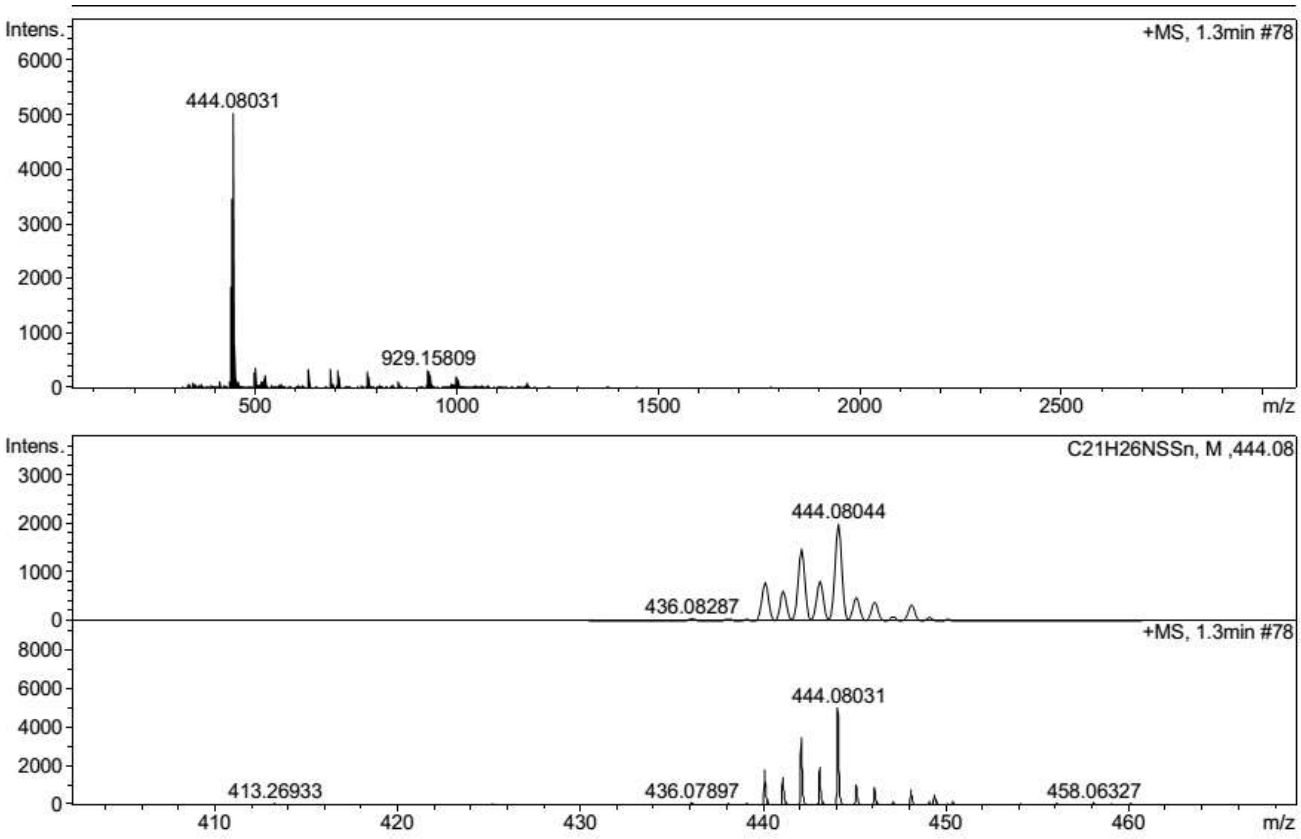
^{1}H NMR of ***o*-TBT-BT6**:







HRMS of ***o*-TBT-BT6**:



^{13}C NMR of ***o*-TBT-BT6**: