Electronic Supporting Information

Design and synthesis of benzothiadiazole-based molecular systems: self-assembly, optical and electronic properties

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1. Thermal analysis for BTD-based building blocks

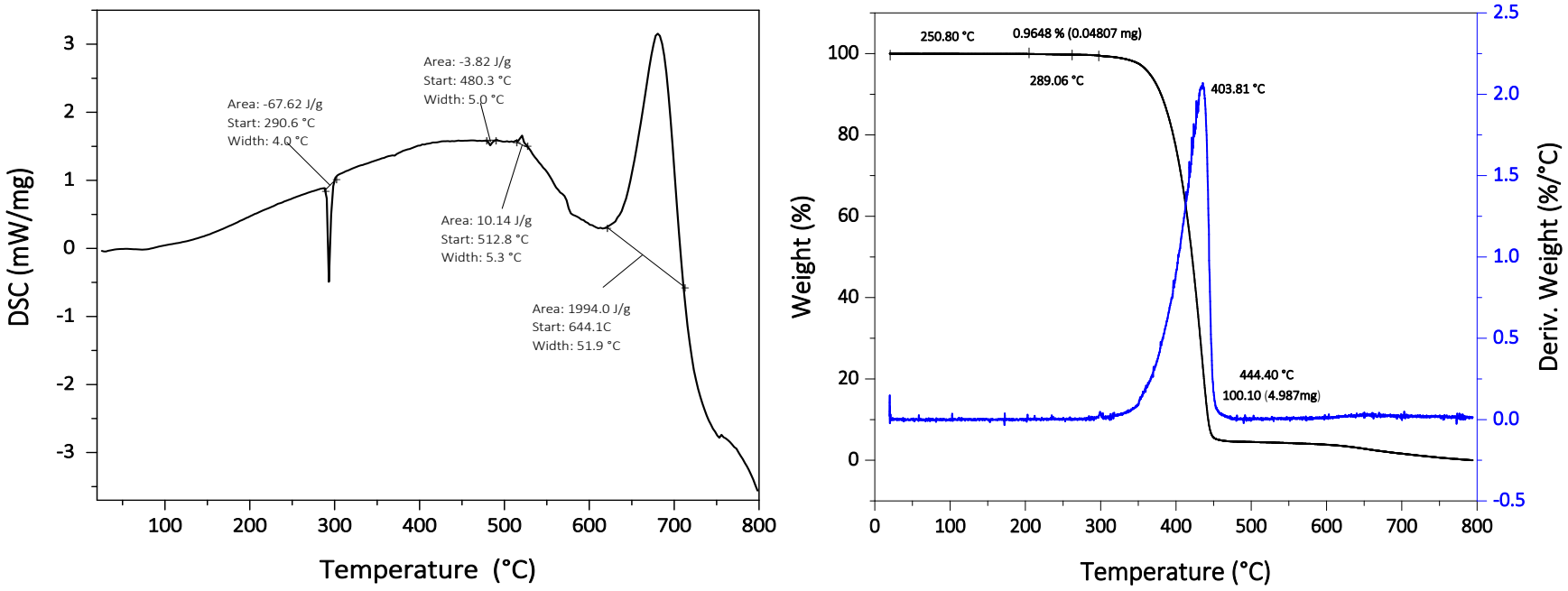

Figure S1. DSC and TGA experiments for **FL-BTD**

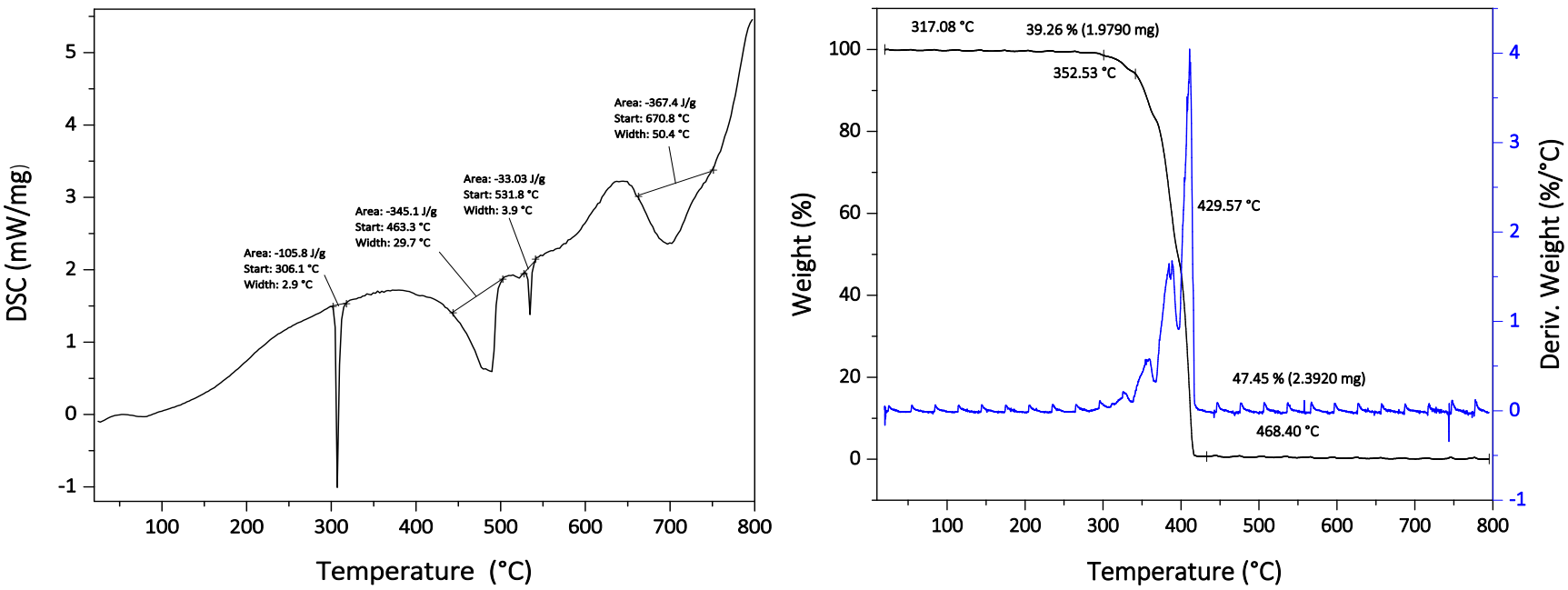

Figure S2. DSC and TGA experiments for **DBF-BTD**

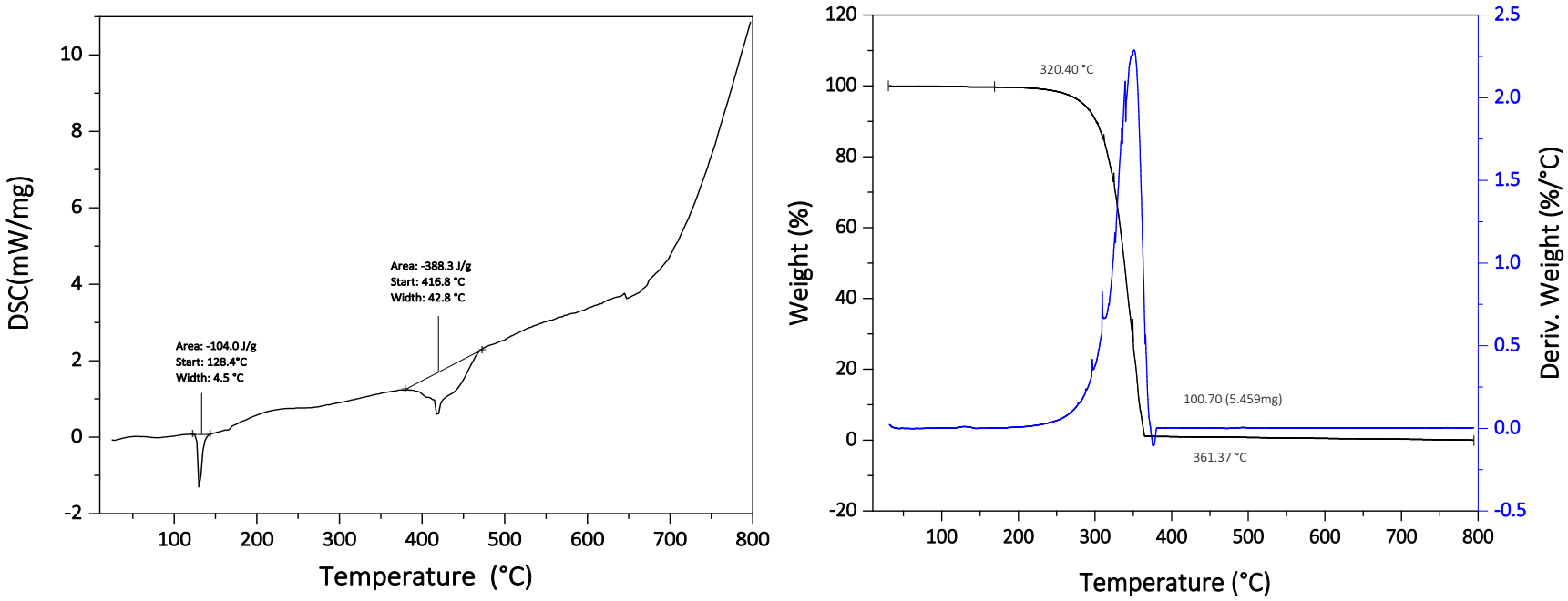

Figure S3. DSC and TGA experiments for **BuO-BTD**

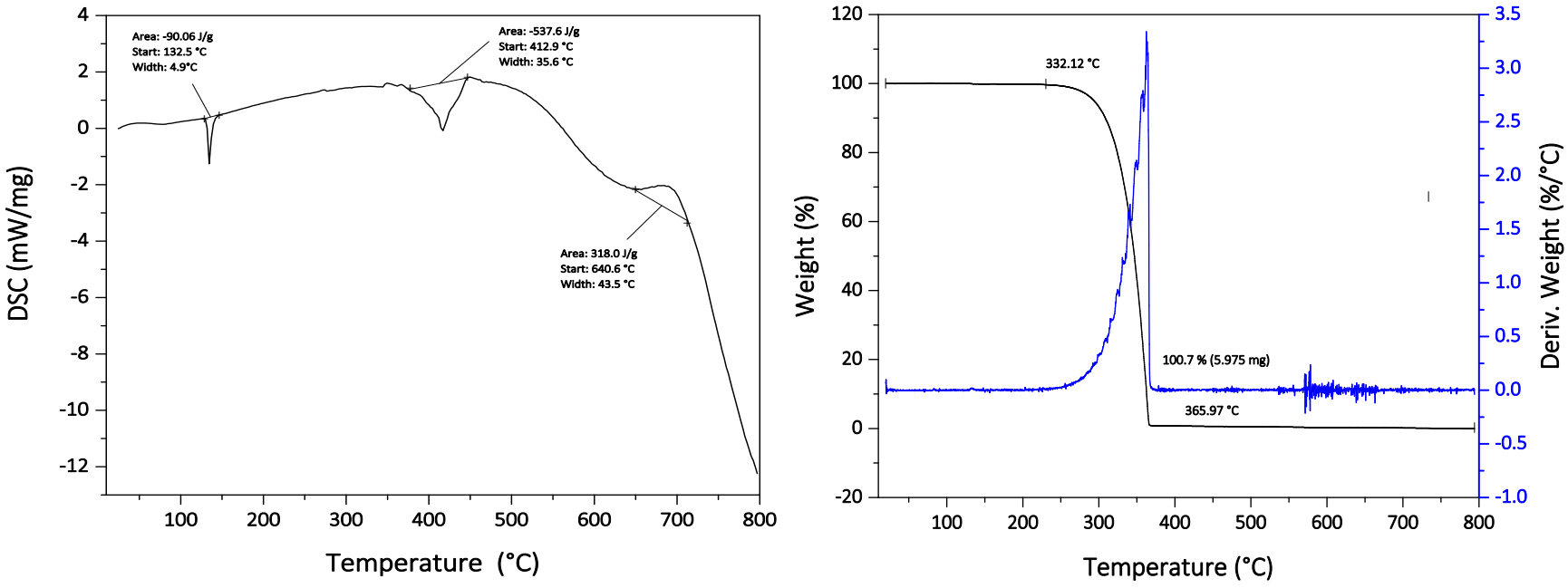

Figure S4. DSC and TGA experiments for **MeO-BTD**

2. Single crystal X-Ray Diffraction experiments of BuO-BTD

	BuO-BTD
Empirical formula	$C_{26}H_{28}N_2O_2S$
Formula weight	432.56
Temperature	173 (2) K
Wavelength	1.54184 Å
Crystal system	Orthorhombic
Space group	Pnca
Unit cell dimensions	a = 7.7834 (2) Å b = 76.7442 (14) Å c = 11.2014 (3) Å $\alpha = \beta = \gamma = 90°$
Volume	6690.9 (3) $Å^3$
Z	12
Density (calculated)	1.288 Mg/m^3
Absorption coefficient	1.49 mm^{-1}
F (000)	2993
Crystal size	0.20 x 0.18 x 0.12 mm^3
q range data collection	4.9 to 71.5°
Index ranges	$-9 \le h \le 9$ $-90 \le k \le 71$ $-13 \le l \le 11$
Reflections collected	8904
Independent reflections	5694 [R(int) = 0.1297]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5694 / 0 / 423
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0809, wR2 = 0.1804
R indices (all data)	R1 = 0.1768, wR2 = 0.2486
Absolute structure parameter	0.5(19)
Extinction coefficient	n/a
Largest diff. peak and hole	0.711 and -0.384 e.$Å^{-3}$

Table S1. Relevant crystal data and structure refinement of **BuO-BTD**

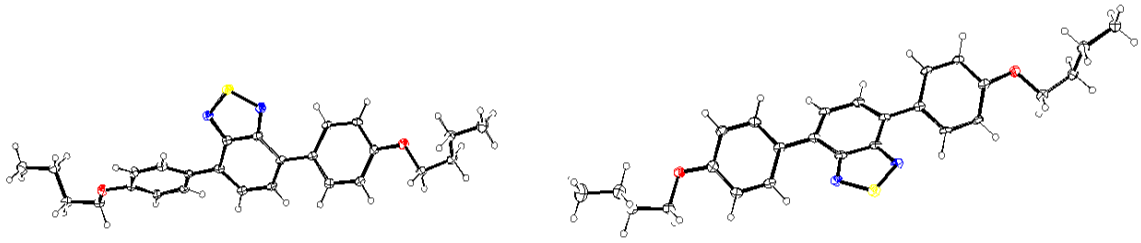

Figure S4. ORTEP diagram of **BuO-BTD** (drawn at 35 % probability level).

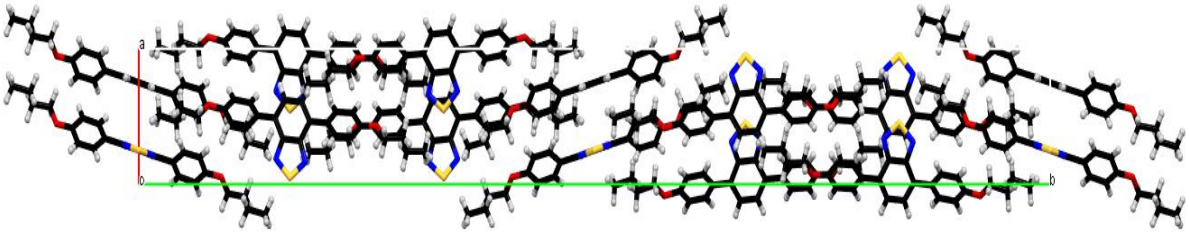

Figure S5. Unit cell of **BuO-BTD**.

3. UV-Vis absorption experiments of BTD-based building blocks

Solvent	FL-BTD			DBF-BTD			MeO-BTD			BuO-BTD		
	λ_{abs} (nm)	E_g^{Opt} [eV]	ε [$M^{-1}\cdot cm^{-1}$]	λ_{abs} (nm)	E_g^{Opt} [eV]	ε [$M^{-1}\cdot cm^{-1}$]	λ_{abs} (nm)	E_g^{Opt} [eV]	ε [$M^{-1}\cdot cm^{-1}$]	λ_{abs} (nm)	E_g^{Opt} [eV]	ε [$M^{-1}\cdot cm^{-1}$]
Heptane	416	**2.86**	17357.25	387	3.08	13174.60	388	**3.20**	10210.81	413	**2.88**	20099.14
Toluene	412	**2.89**	Ind.*	382	3.12	Ind.*	386	**3.22**	12672.62	411	**2.90**	25262.60
Et_2O	413	**2.88**	32494.60	382	3.12	14072.50	384	**3.23**	10329.73	412	**2.89**	15905.17
$CHCl_3$	414	**2.87**	30293.44	382	3.12	10896.61	387	**3.21**	10948.09	415	**2.87**	23586.20
THF	410	**2.90**	14051.04	378	3.15	9119.34	384	**3.23**	11899.29	411	**2.90**	21806.03
Acetone	405	**2.94**	Ind.*	--	--	Ind.*	383	**3.24**	11872.05	409	**2.91**	2767.16
MeOH	406	**2.93**	Ind.*	376	3.17	Ind.*	381	**3.13**	15885.38	406	**2.93**	4526.90
ACN	414	**2.88**	28892.79	380	3.13	10118.74	386	**3.22**	14426.25	414	**2.88**	19099.14
DMF	416	**2.86**	9765.66	373	3.20	8078.10	386	**3.22**	14275.29	413	**2.88**	7408.81

Table S2. Relevant absorption data of BTD-based building blocks. *Indeterminate due to the low solubility of the compound.

4. Chemical computations for BTD-based building blocks

DFT-optimized ground-state geometries

The four BTD derivatives were optimized by applying the density functional theory (DFT) through B3LYP/6-311 + G (d,p) theory level. The local minimum energy structures were confirmed by ascertaining that all the harmonic vibrational frequencies are real. Structures are given in XYZ format.

BuO-BTD

Energy = -1045506.20779942 kcal/mol

Symbol	X	Y	Z
C	-0.708754	-1.036777	0.045626
C	0.708792	-1.036757	-0.04553
C	1.471156	0.111308	-0.086628
C	0.727608	1.340511	-0.046655
C	-0.727628	1.340487	0.04666
C	-1.471144	0.111267	0.086724
H	-1.209514	-1.996901	0.09617
H	1.209581	-1.996866	-0.096075
C	2.947493	0.068421	-0.153565
C	3.686285	0.965802	-0.947068
C	3.661927	-0.901064	0.55965
C	5.064982	0.877368	-1.036153
H	3.16993	1.736555	-1.502836
C	5.05086	-0.996545	0.485965
H	3.129625	-1.585529	1.210534
C	5.76256	-0.104852	-0.321116
H	5.628125	1.563847	-1.657061
H	5.559262	-1.75395	1.066996
C	-2.947491	0.068355	0.153705
C	-3.686282	0.965714	0.947223
C	-3.661923	-0.901142	-0.559496
C	-5.064981	0.877265	1.03633
H	-3.169956	1.736469	1.503015
C	-5.050851	-0.996644	-0.485787
H	-3.129627	-1.585612	-1.210378
C	-5.762555	-0.104963	0.321307
H	-5.628113	1.563733	1.657261
H	-5.559247	-1.754079	-1.066787
S	-0.000062	3.626455	-0.00011
N	-1.25011	2.570085	0.074366
N	1.250071	2.570111	-0.074486
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O	-7.116688	-0.105125	0.47224

C	7.894932	-1.079305	0.226745
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C	-7.894894	-1.079355	-0.226717
H	-7.566862	-2.087684	0.057053
H	-7.746436	-0.963895	-1.308123
C	-9.354278	-0.865715	0.142277
H	-9.45797	-0.955151	1.228964
H	-9.636309	0.160105	-0.118146
C	-10.288808	-1.859733	-0.557011
H	-9.988573	-2.883852	-0.30416
H	-10.174311	-1.766922	-1.643732
C	-11.759745	-1.655926	-0.182612
H	-12.403345	-2.376238	-0.694528
H	-11.913707	-1.7778	0.893865
H	-12.101257	-0.652393	-0.454198
H	7.7466	-0.963984	1.308184
C	9.354291	-0.865685	-0.142357
H	9.457869	-0.954953	-1.22907
H	9.636402	0.160079	0.1182
C	10.28884	-1.859861	0.556679
H	9.988532	-2.883924	0.30369
H	10.174449	-1.767222	1.643426
C	11.759752	-1.656065	0.182178
H	12.40336	-2.376504	0.693906
H	11.913611	-1.777756	-0.894335
H	12.101343	-0.6526	0.453911

FL-BTD

Energy = -1091564.02787043 kcal/mol

Symbol	X	Y	Z
C	-0.828106	-1.239999	-0.362338
C	0.587471	-1.349494	-0.367043
C	1.43712	-0.266944	-0.278646
C	0.789913	1.011689	-0.166618
C	-0.663978	1.124312	-0.165787
C	-1.500816	-0.040533	-0.260316
H	-1.402714	-2.153939	-0.458953
H	1.014192	-2.343751	-0.43068
N	-1.090617	2.385803	-0.055466
N	1.405695	2.19372	-0.068454
S	0.238353	3.338891	0.026905
C	2.907965	-0.42456	-0.306947
C	3.746453	0.35682	0.509412
C	3.491925	-1.393918	-1.14469
C	5.1153	0.146617	0.488738
H	3.315764	1.114259	1.150952
C	4.866733	-1.602633	-1.172633
H	2.856281	-1.973152	-1.804299
C	5.685809	-0.830798	-0.348653

H	5.287164	-2.348712	-1.838019
C	-2.978743	0.025455	-0.24041
C	-3.677137	1.046814	-0.910806
C	-3.715007	-0.966637	0.434922
C	-5.067382	1.080538	-0.930893
H	-3.119457	1.818288	-1.423212
C	-5.099533	-0.93242	0.421673
H	-3.192092	-1.740466	0.986892
C	-5.785381	0.088591	-0.262979
H	-5.5782	1.875942	-1.462449
C	6.201214	0.850136	1.275639
C	7.140728	-0.818956	-0.163378
C	7.462206	0.166127	0.791517
H	6.216525	1.927107	1.07284
H	6.062933	0.733817	2.356731
C	8.783747	0.387342	1.156233
C	8.146545	-1.584572	-0.755115
C	9.789224	-0.380233	0.561966
C	9.471396	-1.357389	-0.385568
H	9.038463	1.144289	1.890987
H	10.824953	-0.216793	0.837841
H	10.263891	-1.94381	-0.83697
H	7.907699	-2.344656	-1.491052
C	-7.227732	-0.123639	-0.101138
C	-6.090054	-1.870227	1.080055
H	-5.980822	-2.899666	0.719772
C	-7.425822	-1.274341	0.687424
H	-5.961219	-1.900472	2.168159
C	-8.7097	-1.703507	0.996624
C	-8.320313	0.599698	-0.581625
H	-8.869013	-2.5887	1.603926
H	-8.177084	1.486698	-1.189054
C	-9.802217	-0.977409	0.514318
C	-9.607014	0.164175	-0.26809
H	-10.465517	0.71594	-0.634437
H	-10.809819	-1.301782	0.748911

DBF – BTD

Energy = -1136648.80230756 kcal/mol

Symbol	X	Y	Z
C	0.684975	-0.276917	0.185939
C	-0.685133	-0.276884	-0.1857
C	-1.417818	0.872002	-0.392032
C	-0.701726	2.102803	-0.197478
C	0.701772	2.10277	0.19745
C	1.417772	0.871933	0.392089
H	1.167211	-1.236527	0.31515

H	-1.167466	-1.236469	-0.314759
N	1.205882	3.332525	0.334202
N	-1.205743	3.332582	-0.334325
S	0.000091	4.388857	-0.000094
C	-2.840504	0.840169	-0.792639
C	-3.738155	-0.121089	-0.313034
C	-3.39158	1.760905	-1.699616
C	-5.091545	-0.184706	-0.687012
C	-4.731382	1.710779	-2.097073
H	-2.753302	2.534988	-2.101131
C	-5.597728	0.743848	-1.598316
H	-5.095375	2.445096	-2.806127
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C	2.840443	0.840038	0.792766
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C	5.091515	-0.1848	0.687118
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H	6.636366	0.714808	1.906342
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O	-3.429961	-1.106929	0.599561
C	-4.591891	-1.810812	0.818992
C	-4.720093	-2.89131	1.676637
C	-6.911046	-1.8979	0.1568
C	5.652471	-1.297787	-0.056656
H	-7.751847	-1.526086	-0.417468
H	-3.878481	-3.257274	2.25114
C	-5.983265	-3.475576	1.760656
C	-7.063767	-2.985985	1.011274
H	-6.131887	-4.32377	2.418749
H	-8.032058	-3.464247	1.101575
O	3.429975	-1.106901	-0.599627
C	4.591923	-1.810731	-0.819104
C	6.911045	-1.89792	-0.156807
C	4.720129	-2.891175	-1.676814
H	3.878514	-3.257069	-2.251351
H	7.751813	-1.526197	0.417566
C	7.063812	-2.985813	-1.011494
C	5.983337	-3.475327	-1.76096
H	8.03217	-3.463895	-1.102044
H	6.132079	-4.32329	-2.419326

Meo – BTD

Energy = -1041209.69131792 kcal/mol

Symbol	X	Y	Z
C	0.710539	-1.423983	0.002312

C	-0.710619	-1.423972	-0.002378
C	-1.46991	-0.275059	-0.005613
C	-0.728924	0.955152	0.001548
C	0.728965	0.95513	-0.001676
C	1.469901	-0.275109	0.005596
H	1.215737	-2.382724	-0.01121
H	-1.215876	-2.38268	0.011013
C	-2.951928	-0.323184	-0.019991
C	-3.70968	0.555442	0.760202
C	-3.600753	-1.285951	-0.802989
C	-5.099904	0.456709	0.76572
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C	-5.758681	-0.50471	-0.009819
H	-6.835247	-0.572217	-0.006179
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C	3.709704	0.555751	-0.759665
C	3.600731	-1.286374	0.802607
C	5.099929	0.457018	-0.765207
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C	4.991386	-1.371717	0.795851
H	3.045893	-1.956886	1.445546
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H	6.835263	-0.572258	0.006251
N	1.252675	2.18449	0.002931
N	-1.252591	2.184524	-0.003167
S	0.000053	3.239347	-0.000177
O	5.750155	1.350741	-1.569126
O	5.528286	-2.33726	1.601713
O	-5.750143	1.350034	1.570054
O	-5.528354	-2.336483	-1.602477
C	7.167992	1.322685	-1.624389
C	6.940245	-2.46675	1.672026
C	-7.167976	1.321872	1.625377
C	-6.940318	-2.46596	-1.672768
H	7.453902	2.115551	-2.313828
H	7.612692	1.521592	-0.642844
H	7.537043	0.363835	-2.005697
H	7.409431	-1.549041	2.043793
H	7.129562	-3.276296	2.375254
H	7.369424	-2.728452	0.69834
H	-7.453888	2.114334	2.315278
H	-7.612731	1.521326	0.643965
H	-7.536959	0.362787	2.006151
H	-7.129661	-3.275207	-2.376333
H	-7.369433	-2.72808	-0.699168
H	-7.409534	-1.548098	-2.044119

TDDFT-optimized excited-state geometries

The four BTD derivatives were optimized by applying time-dependent density functional theory (DFT) through the B3LYP/6-311+G(d,p) protocol. First excited state (root=1) were targeted in all cases, including 10 states in the calculation. The local minimum energy structures were confirmed by ascertaining that all the harmonic vibrational frequencies are real. Structures are given in XYZ format.

BuO-BTD

```
Energy: -1045498.9086881
C          -0.68996       -0.94462        0.00560
C           0.68995       -0.94463       -0.00559
C           1.45380        0.24880       -0.03064
C           0.71773        1.48442       -0.03234
C          -0.71772        1.48443        0.03240
C          -1.45380        0.24882        0.03067
H          -1.19514       -1.90047        0.03256
H           1.19511       -1.90048       -0.03257
C           2.90892        0.17608       -0.06164
C           3.71759        1.25444       -0.51436
C           3.59020       -0.99549        0.35490
C           5.09004        1.14909       -0.57105
H           3.23228        2.17180       -0.81141
C           4.96929       -1.10450        0.31720
H           3.02980       -1.83166        0.75128
C           5.73806       -0.02840       -0.15762
H           5.69691        1.97202       -0.92914
H           5.43899       -2.01500        0.66346
C          -2.90892        0.17610        0.06167
C          -3.71760        1.25445        0.51442
C          -3.59020       -0.99546       -0.35490
C          -5.09005        1.14908        0.57110
H          -3.23229        2.17180        0.81149
C          -4.96929       -1.10448       -0.31720
H          -3.02980       -1.83162       -0.75129
C          -5.73806       -0.02840        0.15765
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H          -5.43898       -2.01497       -0.66348
S           0.00002        3.80974        0.00004
N          -1.27527        2.71522        0.06453
N           1.27529        2.71521       -0.06446
O           7.08503       -0.02732       -0.24612
O          -7.08503       -0.02732        0.24614
C           7.82975       -1.18581        0.16016
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H	7.51158	-2.04912	-0.43628
C	-7.82975	-1.18580	-0.16017
H	-7.51158	-2.04913	0.43624
H	-7.62245	-1.39851	-1.21563
C	-9.30489	-0.89093	0.05438
H	-9.46490	-0.64416	1.10925
H	-9.57337	-0.00020	-0.52329
C	-10.19970	-2.06848	-0.35069
H	-9.91578	-2.95828	0.22406
H	-10.02412	-2.31555	-1.40460
C	-11.68876	-1.78099	-0.13818
H	-12.30312	-2.63515	-0.43433
H	-11.90350	-1.56465	0.91266
H	-12.01256	-0.91769	-0.72725
H	7.62246	-1.39855	1.21561
C	9.30489	-0.89093	-0.05439
H	9.46490	-0.64413	-1.10926
H	9.57337	-0.00022	0.52330
C	10.19970	-2.06849	0.35064
H	9.91578	-2.95828	-0.22412
H	10.02413	-2.31559	1.40455
C	11.68876	-1.78100	0.13814
H	12.30313	-2.63517	0.43427
H	11.90350	-1.56463	-0.91270
H	12.01256	-0.91771	0.72723

DBF-BTD

Energy: -1136633.4027704

C	-0.67497	-0.10656	-0.13553
C	0.67496	-0.10656	0.13553
C	1.41920	1.09262	0.30944
C	0.69870	2.33085	0.17439
C	-0.69871	2.33086	-0.17431
C	-1.41921	1.09263	-0.30940
H	-1.17639	-1.05574	-0.24007
H	1.17638	-1.05575	0.24005
N	-1.23442	3.55932	-0.31573
N	1.23441	3.55931	0.31587
S	-0.00001	4.65505	0.00009
C	2.83469	1.03582	0.63878
C	3.67815	-0.06051	0.33224
C	3.49158	2.09041	1.33403
C	5.03418	-0.13168	0.69093
C	4.82696	2.02556	1.71145
H	2.90965	2.96851	1.56767
C	5.62034	0.91944	1.39801

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H          6.66475        0.88391        1.68542
C         -2.83470        1.03583       -0.63874
C         -3.49159        2.09045       -1.33395
C         -3.67815       -0.06051       -0.33223
C         -4.82698        2.02560       -1.71137
H         -2.90967        2.96856       -1.56757
C         -5.03419       -0.13168       -0.69092
C         -5.62035        0.91946       -1.39796
H         -5.25847        2.85758       -2.25511
H         -6.66476        0.88394       -1.68537
C          5.52547       -1.38639        0.15513
O          3.31167       -1.16869       -0.39076
C          4.42605       -1.96696       -0.49457
C          4.47790       -3.18543       -1.15273
C          6.74961       -2.06091        0.14776
C         -5.52547       -1.38641       -0.15516
H          7.62081       -1.64189        0.63770
H          3.60697       -3.59796       -1.64592
C          5.70690       -3.84189       -1.14622
C          6.82639       -3.28768       -0.50502
H          5.79969       -4.79811       -1.64752
H          7.76632       -3.82669       -0.52119
O         -3.31167       -1.16871        0.39073
C         -4.42604       -1.96699        0.49452
C         -6.74960       -2.06093       -0.14781
C         -4.47788       -3.18548        1.15264
H         -3.60695       -3.59803        1.64581
H         -7.62080       -1.64190       -0.63773
C         -6.82637       -3.28772        0.50493
C         -5.70688       -3.84195        1.14610
H         -7.76630       -3.82674        0.52108
H         -5.79967       -4.79819        1.64737
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FL-BTD

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55
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C          0.79632        1.05466       -0.04483
C         -0.64168        1.18620       -0.05872
C         -1.48525        0.02415       -0.12862
H         -1.41690       -2.13122       -0.30852
H          0.96087       -2.34605       -0.32776
N         -1.08000        2.45781        0.02859
N          1.45506        2.22573        0.06634
S          0.28508        3.42714        0.13422
C          2.86160       -0.43984       -0.19032
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C          3.76553        0.52956        0.32305
C          3.41428       -1.64100       -0.72694
C          5.12048        0.27918        0.31711
H          3.36698        1.45730        0.70645
C          4.77355       -1.88293       -0.74679
H          2.75656       -2.37734       -1.16812
C          5.64538       -0.92196       -0.21384
H          5.15384       -2.80156       -1.17952
C         -2.94240        0.07721       -0.11386
C         -3.65470        1.25344       -0.48370
C         -3.70343       -1.06605        0.26181
C         -5.03714        1.28981       -0.50756
H         -3.08491        2.13237       -0.74335
C         -5.07858       -1.02319        0.25276
H         -3.20057       -1.96582        0.59301
C         -5.76512        0.15178       -0.13803
H         -5.54418        2.20071       -0.80589
C          6.25056        1.15262        0.81937
C          7.09335       -0.89905       -0.09362
C          7.47573        0.31909        0.51597
H          6.27479        2.11959        0.30490
H          6.15620        1.36706        1.88970
C          8.81484        0.59543        0.74851
C          8.06074       -1.83961       -0.46911
C          9.77671       -0.34697        0.37179
C          9.40078       -1.55367       -0.23170
H          9.11804        1.52688        1.21471
H         10.82660       -0.14212        0.54831
H         10.16357       -2.26962       -0.51577
H          7.77439       -2.77497       -0.93678
C         -7.19631       -0.09023       -0.05193
C         -6.07605       -2.09941        0.62898
H         -5.96653       -2.99584        0.00839
C         -7.40567       -1.41430        0.39819
H         -5.95870       -2.41802        1.67096
C         -8.69260       -1.90282        0.56672
C         -8.28543        0.74397       -0.33213
H         -8.86280       -2.91718        0.91195
H         -8.13194        1.76029       -0.67683
C         -9.77693       -1.06586        0.28510
C         -9.57266        0.24589       -0.16028
H        -10.42767        0.87759       -0.37239
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MeO-BTD

```
49
MeOBTD.out      Energy: -1041201.0514052
C          0.67550       -1.48118       -0.02523
C         -0.71512       -1.46853       -0.02067
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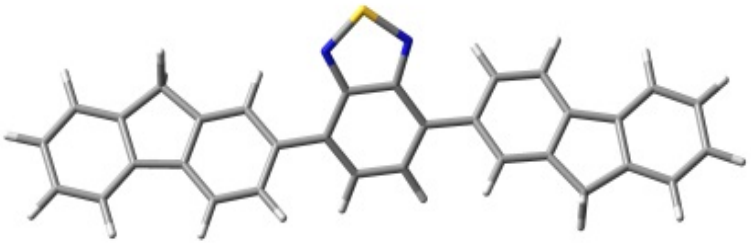
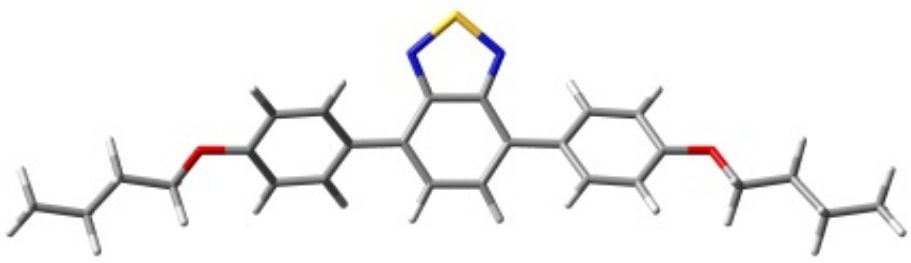
C	-0.72015	0.94614	0.09111
C	0.73570	0.92998	0.12906
C	1.43323	-0.30084	0.04182
H	1.17083	-2.44468	-0.06081
H	-1.23995	-2.41253	-0.08985
C	-2.93611	-0.32630	0.02831
C	-3.70318	0.68734	-0.56264
C	-3.59919	-1.42222	0.60746
C	-5.09144	0.59000	-0.58922
H	-3.23104	1.55875	-0.98987
C	-4.98674	-1.50294	0.58309
H	-3.05295	-2.20684	1.11338
C	-5.75724	-0.50169	-0.01884
H	-6.83380	-0.56544	-0.03545
C	2.91312	-0.35858	0.01696
C	3.60157	-1.42380	-0.56293
C	3.71566	0.66002	0.54973
C	5.03207	-1.49922	-0.57260
H	3.07882	-2.23633	-1.04716
C	5.14662	0.58570	0.52692
H	3.25771	1.54841	0.96049
C	5.83007	-0.49583	-0.02889
H	6.90598	-0.54883	-0.04355
N	1.29854	2.15254	0.23670
N	-1.24902	2.18106	0.14491
S	0.02581	3.25895	0.25645
O	5.49894	-2.60384	-1.15795
O	5.73622	1.63950	1.08813
O	-5.74440	1.62638	-1.20712
O	-5.52887	-2.61137	1.18839
C	6.91244	-2.82017	-1.26104
C	7.16575	1.72252	1.14600
C	-7.15938	1.61327	-1.25239
C	-6.93856	-2.74253	1.23136
H	7.02291	-3.77354	-1.77051
H	7.37836	-2.02678	-1.84999
H	7.36447	-2.87388	-0.26793
H	7.58866	1.72770	0.13867
H	7.38031	2.66465	1.64276
H	7.57407	0.89262	1.72766
H	-7.44995	2.52344	-1.77595
H	-7.53972	0.74519	-1.80422
H	-7.59663	1.62279	-0.24689
H	-7.13640	-3.67425	1.76038
H	-7.40542	-1.91379	1.77648
H	-7.37077	-2.80274	0.22548



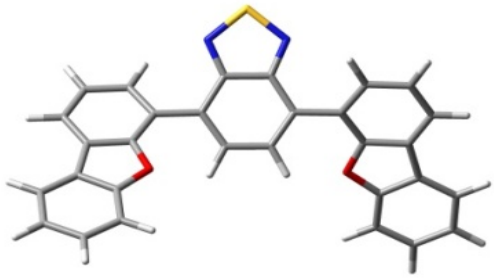
Solvent	E_{HOMO} (Hartrees)	E_{LUMO} (Hartrees)	ΔE (Hartrees)	$E_g^{Calc.}$ (eV)	λ (nm)
Gas phase	-0.20872	-0.09941	0.10931	**2.97443**	417.12
Heptane	-0.20708	-0.09832	0.10876	**2.95947**	419.23
Toluene	-0.20710	-0.09829	0.10881	**2.96083**	419.04
Et_2O	-0.20770	-0.09857	0.10913	**2.96954**	417.81
$CHCl_3$	-0.20780	-0.09863	0.10917	**2.97062**	417.66
THF	-0.20818	-0.09906	0.10912	**2.96926**	417.85
DCM	-0.20842	-0.099260	0.10916	**2.97310**	417.02
Acetone	-0.20892	-0.09964	0.10928	**2.97362**	417.24
MeOH	-0.20934	-0.99630	0.10971	**2.98532**	415.60
ACN	-0.20907	-0.09983	0.10924	**2.97253**	417.39
DMF	-0.20905	-0.09985	0.10920	**2.97144**	417.54
DMSO	-0.20907	-0.09999	0.10917	**2.97062**	417.66

Table S3. Computed data for **FL-BTD**.



Solvent	E_{HOMO} (Hartrees)	E_{LUMO} (Hartrees)	ΔE (Hartrees)	$E_g^{Calc.}$ (eV)	λ (nm)
Gas phase	-0.20463	-0.09244	0.11219	**3.05280**	406.41
Heptane	-0.20363	-0.09320	0.11043	**3.00491**	412.89
Toluene	-0.20388	-0.09366	0.11022	**2.99920**	413.68
Et_2O	-0.20486	-0.09494	0.10992	**2.99103**	414.81
$CHCl_3$	-0.20530	-0.09519	0.11011	**2.99620**	414.09
THF	-0.20557	-0.09597	0.10960	**2.98233**	416.02
DCM	-0.20620	-0.09624	0.10996	**2.99216**	414.36
Acetone	-0.20661	-0.09709	0.10952	**2.98015**	416.32
MeOH	-0.20928	-0.09748	0.11180	**3.04219**	407.83
ACN	-0.20734	-0.09733	0.11001	**2.99348**	414.47
DMF	-0.20725	-0.09733	0.10992	**2.99103**	414.81
DMSO	-0.20735	-0.09741	0.10994	**2.99158**	414.73

Table S4. Computed data for **BuO-BTD**.



Solvent	E_{HOMO} (Hartrees)	E_{LUMO} (Hartrees)	ΔE (Hartrees)	$E_g^{Calc.}$ (eV)	λ (nm)
Gas phase	-0.21901	-0.10026	0.11875	**3.23131**	383.96
Heptane	-0.21871	-0.09926	0.11945	**3.08500**	402.17
Toluene	-0.21908	-0.09930	0.11978	**3.25933**	380.66
Et_2O	-0.22001	-0.10000	0.12001	**3.26559**	379.93
$CHCl_3$	-0.22005	-0.10013	0.11992	**3.26314**	380.22
THF	-0.22077	-0.10075	0.12002	**3.26586**	379.90
DCM	-0.21286	-0.10103	0.11963	**3.25529**	380.87
Acetone	-0.22178	-0.10164	0.12014	**3.26913**	379.52
MeOH	-0.22289	-0.10181	0.12108	**3.29471**	376.57
ACN	-0.22201	-0.10192	0.12009	**3.26777**	379.68
DMF	-0.22217	-0.10189	0.12028	**3.27294**	379.08
DMSO	-0.22231	-0.10194	0.12037	**3.27539**	378.79

Table S5. Computed data for **DBF-BTD**.

Solvent	E_{HOMO} (Hartrees)	E_{LUMO} (Hartrees)	ΔE (Hartrees)	$E_g^{Calc.}$ (eV)	λ (nm)
Gas phase	-0.21492	-0.09235	0.12257	**3.33535**	371.99
Heptane	-0.21420	-0.09288	0.12132	**3.30124**	375.83
Toluene	-0.21444	-0.09348	0.12096	**3.29144**	376.95
Et_2O	-0.21549	-0.09530	0.12019	**3.27049**	379.36
$CHCl_3$	-0.21630	-0.09580	0.12050	**3.27893**	378.39
THF	-0.21650	-0.09689	0.11961	**3.25471**	381.20
DCM	-0.21045	-0.09761	0.11990	**3.26264**	380.01
Acetone	-0.21787	-0.09869	0.11918	**3.24301**	382.58
MeOH	-0.22153	-0.09955	0.12198	**3.31920**	373.79
ACN	-0.21839	-0.09924	0.11915	**3.24219**	382.67
DMF	-0.21809	-0.09920	0.11889	**3.23512**	383.51
DMSO	-0.21819	-0.09934	0.11885	**3.23403**	383.64

Table S6. Computed data for **MeO-BTD**.

BTD derivative	Solvent	λ_{max} (nm)	Ω_A (Ev)	Electronic transitions (major contribution)	f
BuO-BTD	Gas phase	482	2.57	HOMO ✂ LUMO (98.95 %)	0.2829
	Toluene	489	2.53	HOMO ✂ LUMO (99.33 %)	0.3391
	Chloroform	487	2.54	HOMO ✂ LUMO (99.31 %)	0.3268
	DMSO	486	2.55	HOMO ✂ LUMO (99.30 %)	0.3152
FL-BTD	Gas phase	489	2.53	HOMO ✂ LUMO (99.00 %)	0.4648
	Toluene	494	2.51	HOMO ✂ LUMO (99.26 %)	0.5587
	Chloroform	491	2.52	HOMO ✂ LUMO (99.24 %)	0.5421
	DMSO	487	2.55	HOMO ✂ LUMO (99.22 %)	0.5239
MeO-BTD	Gas phase	420	2.95	HOMO ✂ LUMO (97.51 %)	0.2485
	Toluene	424	2.92	HOMO ✂ LUMO (98.82 %)	0.2996
	Chloroform	423	2.93	HOMO ✂ LUMO (98.81 %)	0.2884
	DMSO	423	2.93	HOMO ✂ LUMO (98.82 %)	0.2756
DBF-BTD	Gas phase	431	2.87	HOMO ✂ LUMO (98.34 %)	0.2187
	Toluene	450	2.75	HOMO ✂ LUMO (98.71 %)	0.3273
	Chloroform	446	2.78	HOMO ✂ LUMO (98.68 %)	0.3075
	DMSO	442	2.80	HOMO ✂ LUMO (98.65 %)	0.2844

Table S7. Electronic absorption properties of the BTD derivatives in different solvents: maximum absorption wavelengths (λ_{max}), vertical absorption energies (Ω_A), the most important electronic transitions and the oscillator strengths (f) calculated using TD-DFT B3LYP/6-311+g(d,p).

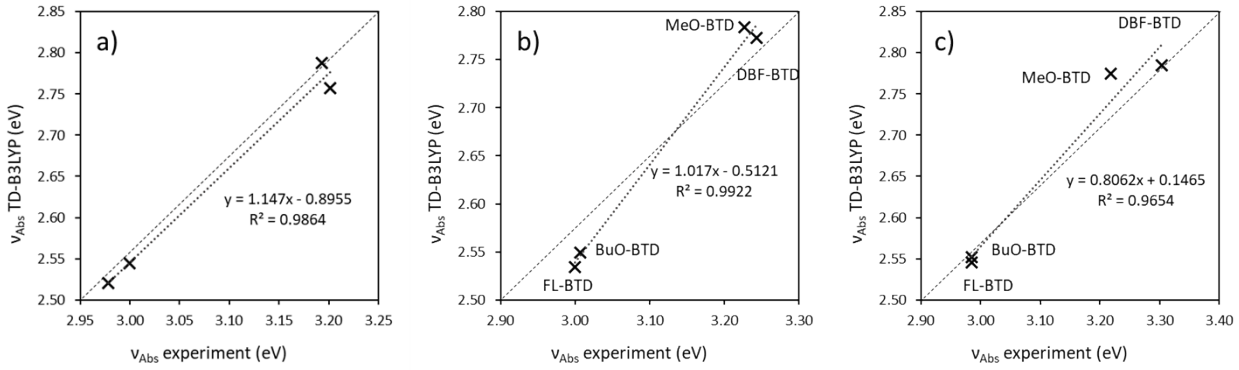


Figure S6. Comparison between UV-Vis absorption maxima calculated at the TD-B3LYP/6-311G+(d,p) level in (a) PhMe, (b) $CHCl_3$ and (C) DMSO, vs experimental values.

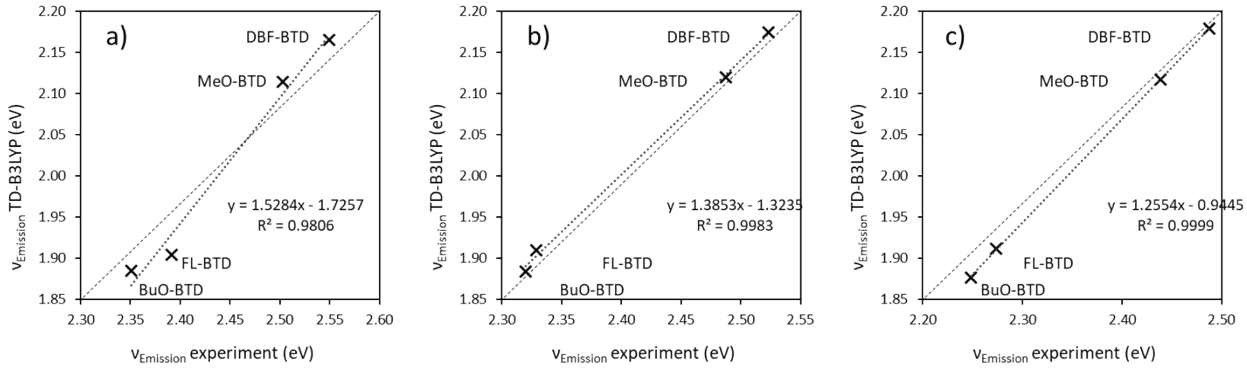


Figure S7. Comparison between fluorescence emission maxima calculated at the TD-B3LYP/6-311G+(d,p) level in (a) PhMe, (b) $CHCl_3$ and (C) DMSO, vs experimental values.

5. FTIR-ATR experiments of BTD-based building blocks

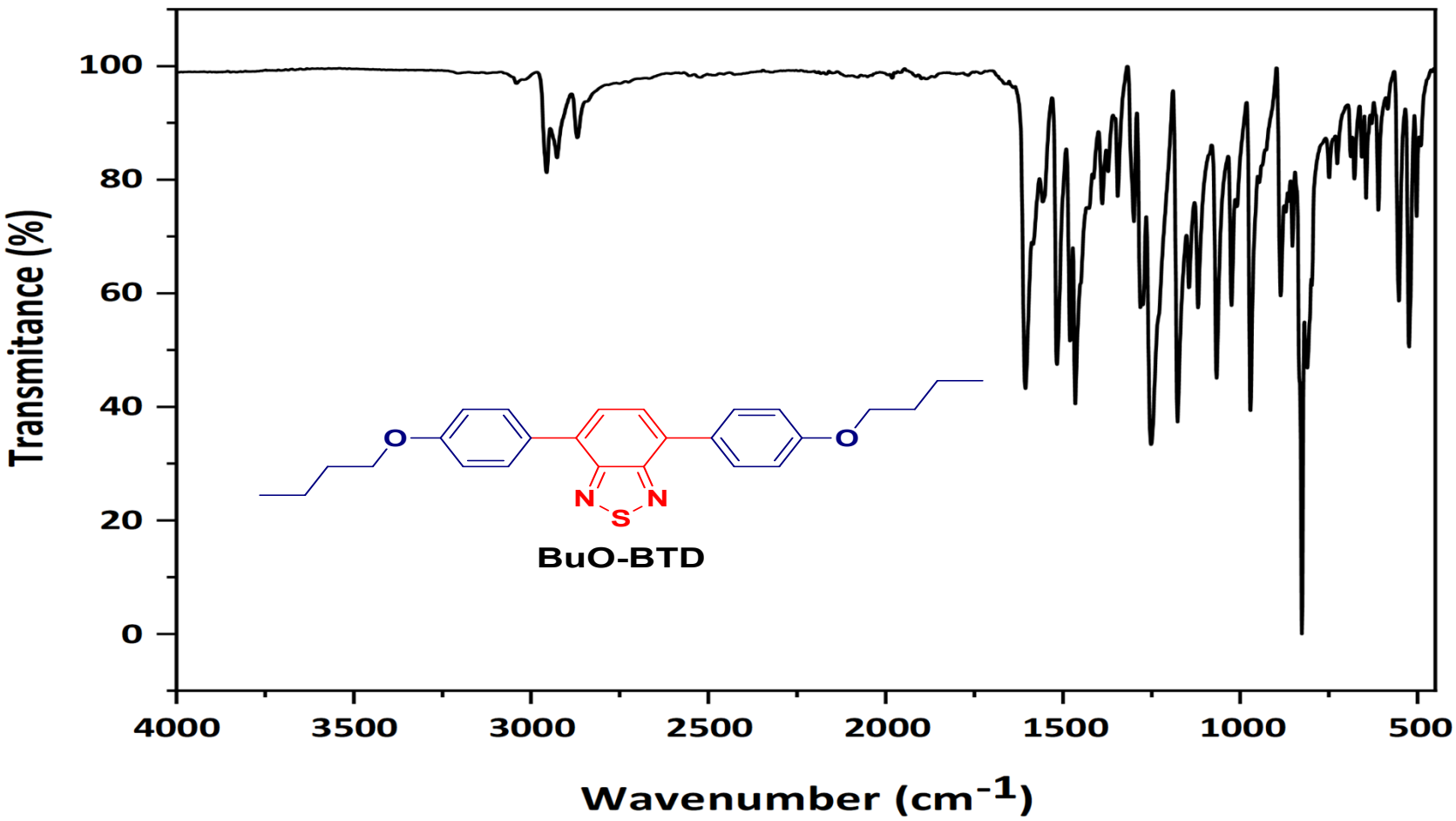


Figure S8. Infrared spectrum of **BuO-BTD**

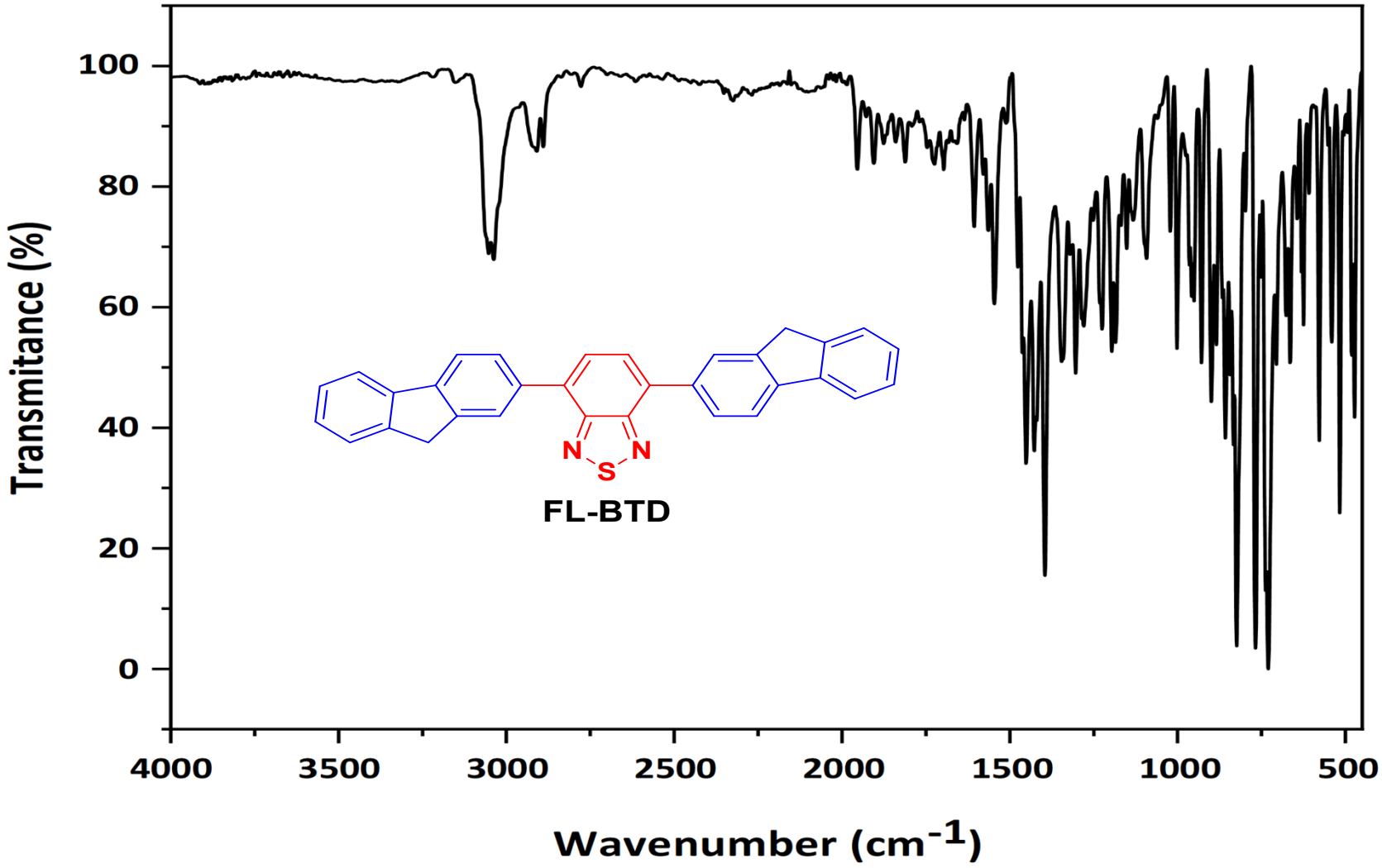


Figure S9. Infrared spectrum of **FL-BTD**

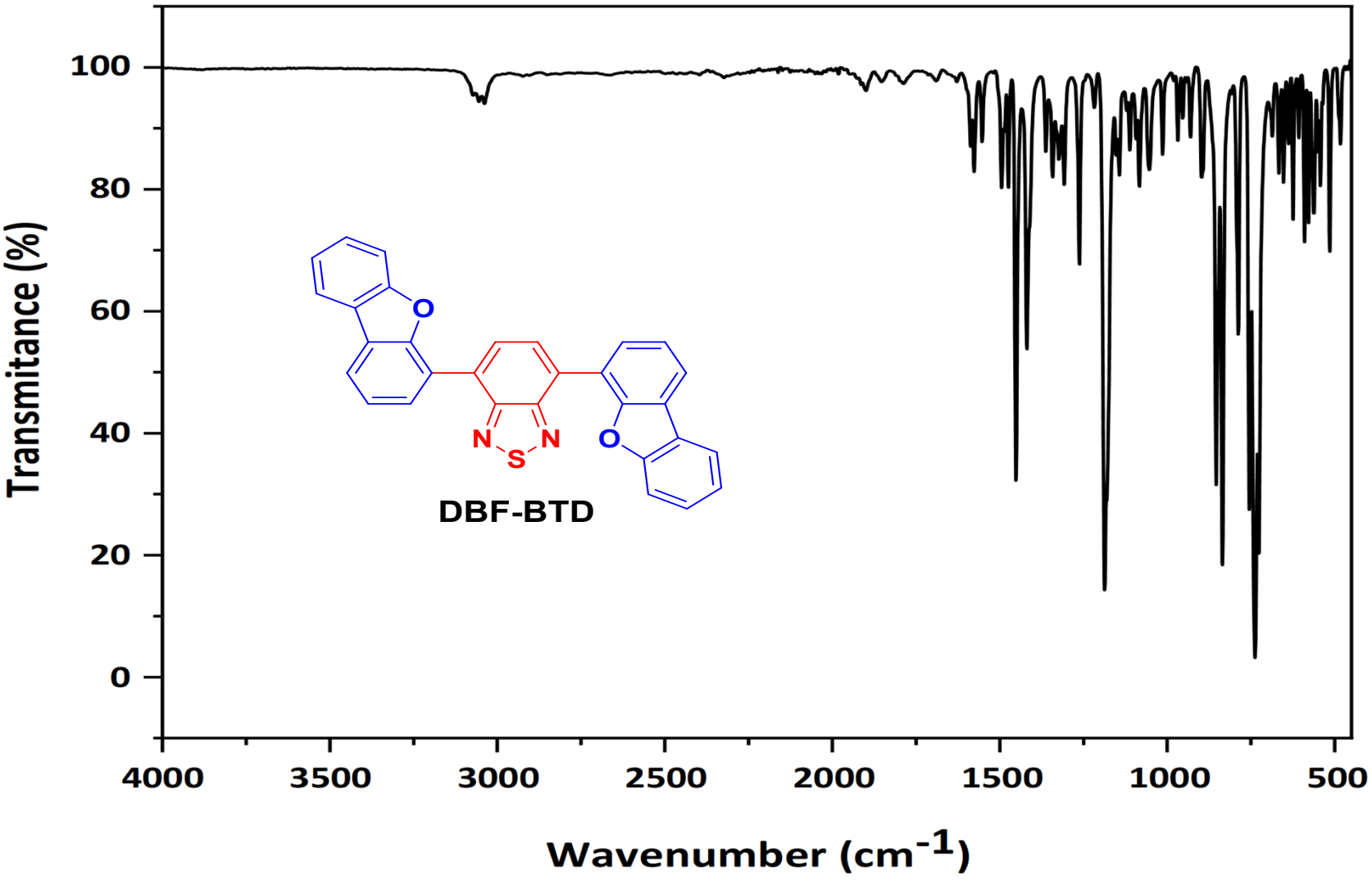


Figure S10. Infrared spectrum of **DBF-BTD**

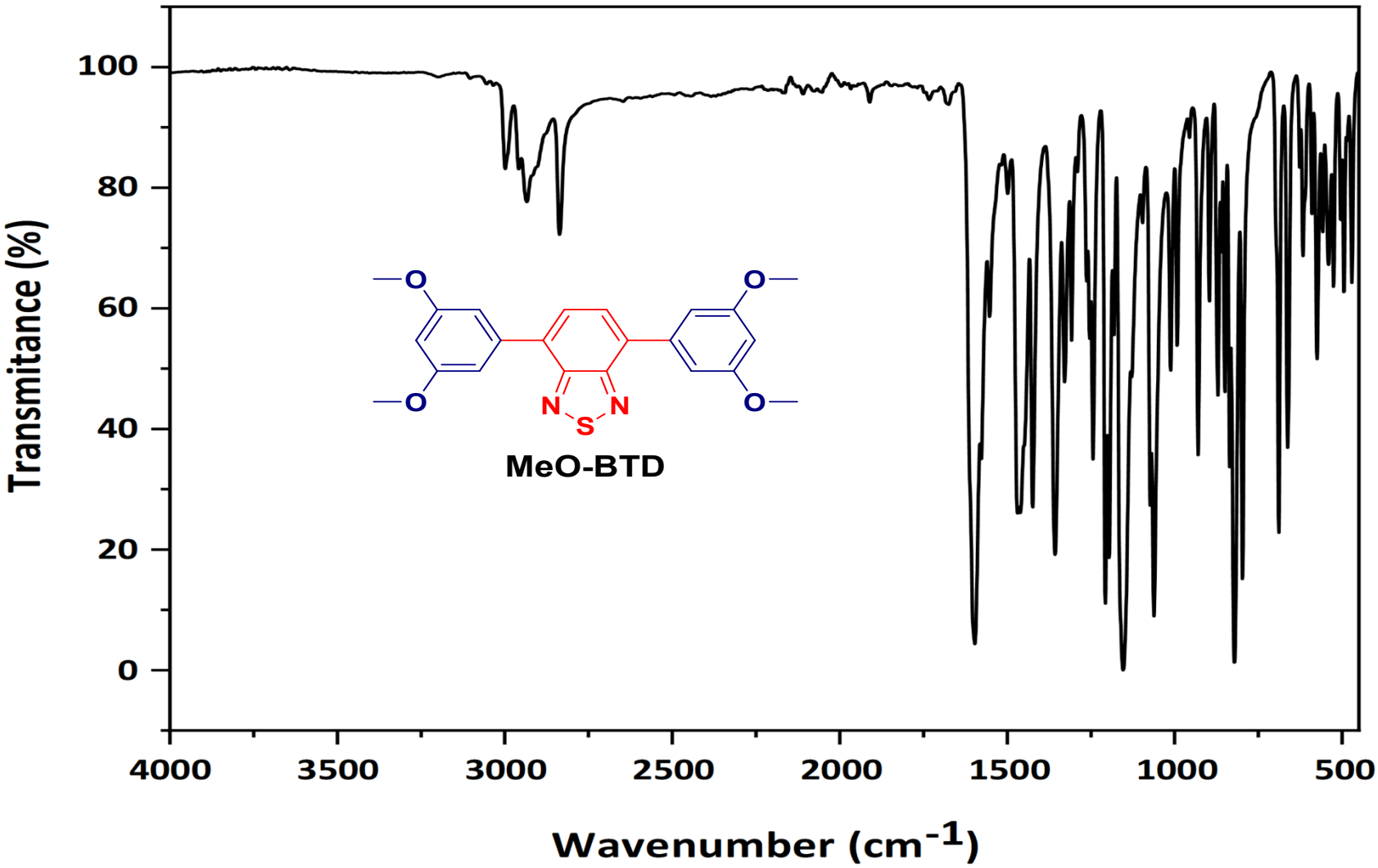
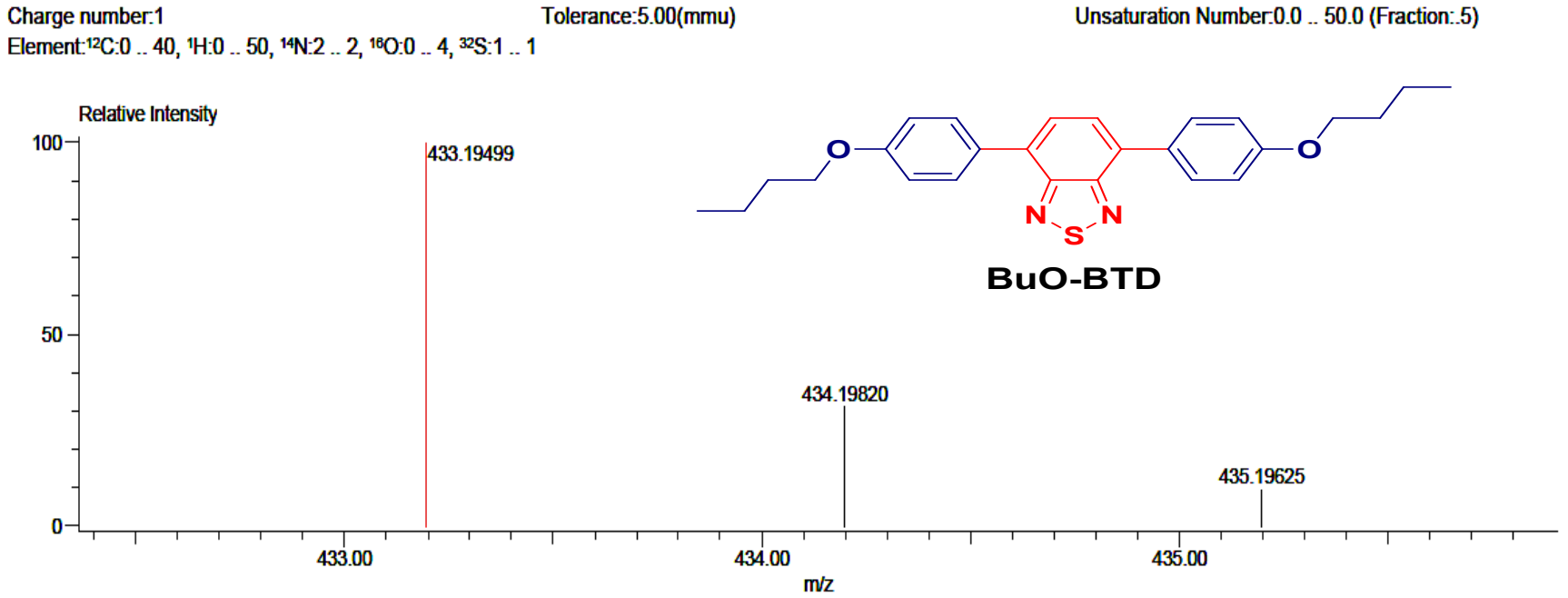


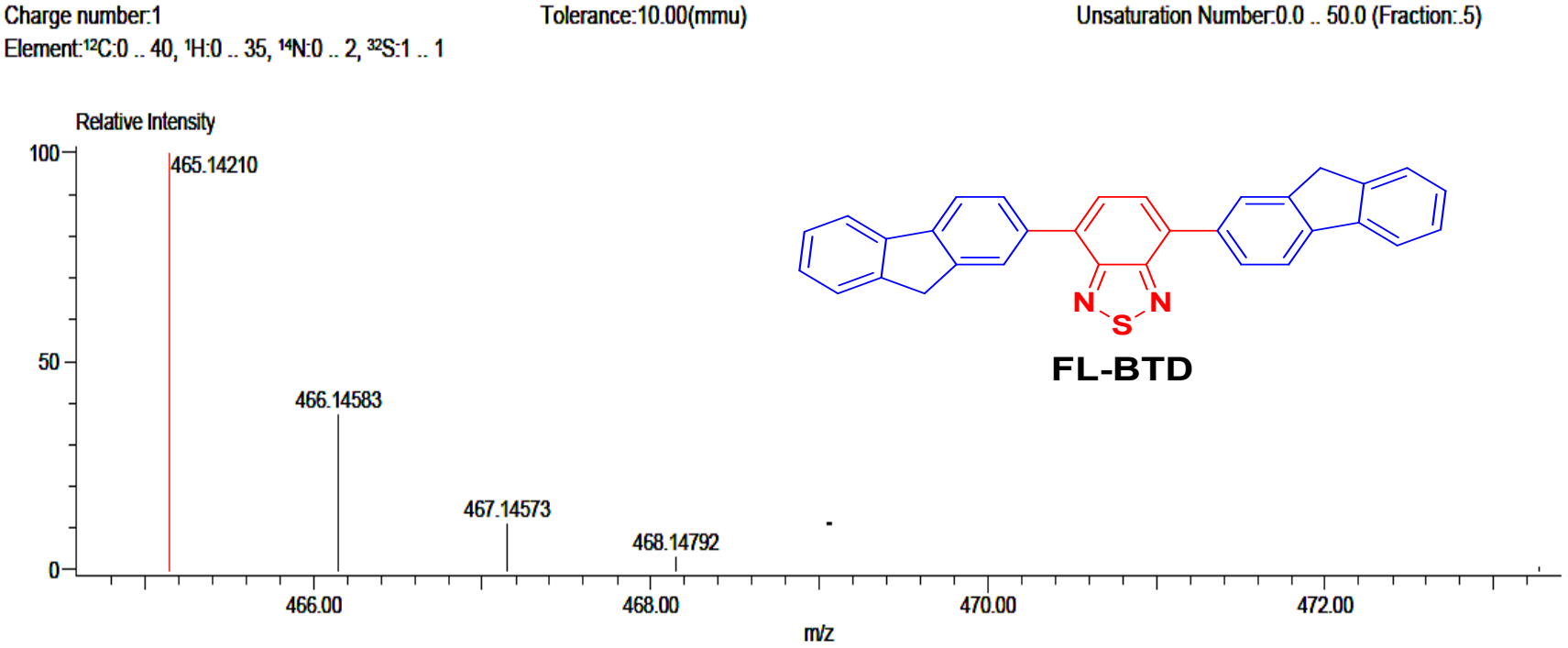
Figure S11. Infrared spectrum of **MeO-BTD**

6. High-resolution mass spectrometry (ESI-TOF) experiments of BTD-based building blocks



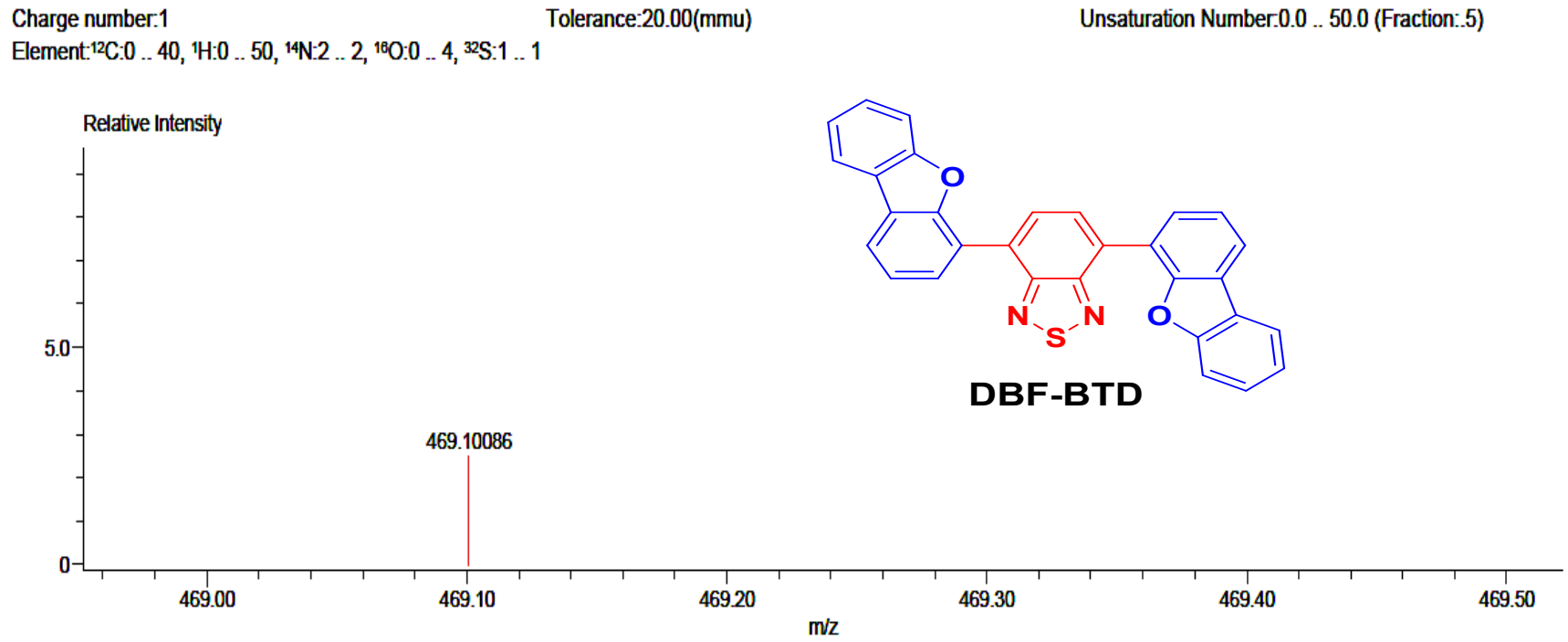
Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
433.19499	771951.46	433.19497	0.01	0.03	$^{12}C_{26}{}^{1}H_{29}{}^{14}N_{2}{}^{16}O_{2}{}^{32}S_{1}$	14.5

Figure S12. HRMS spectrum of **BuO-BTD**



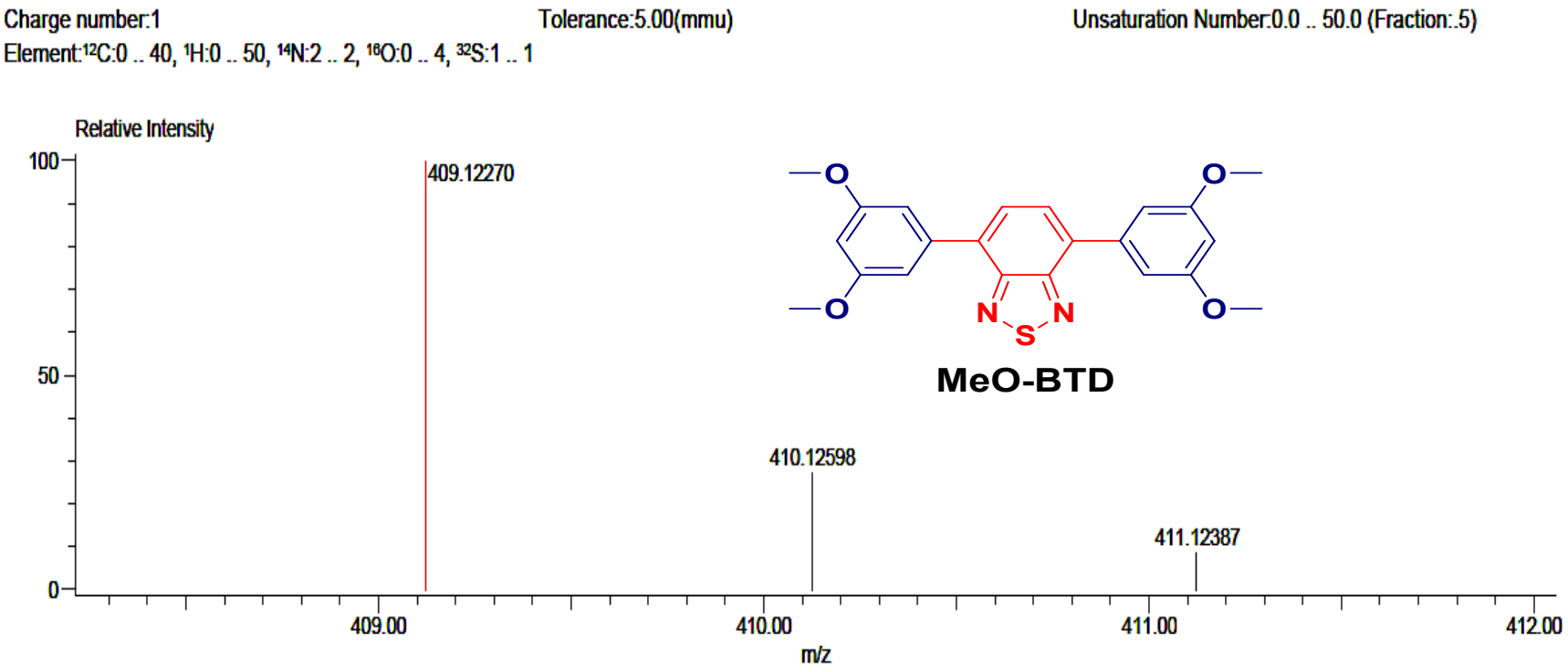
Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
465.14210	351103.08	465.14254	-0.44	-0.94	$^{12}C_{32}{}^{1}H_{21}{}^{14}N_{2}{}^{32}S_{1}$	24.5

Figure S13. HRMS spectrum of **FL-BTD**.



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
469.10086	5375.58	469.10107	-0.21	-0.46	$^{12}C_{30}{}^{1}H_{17}{}^{14}N_{2}{}^{16}O_{2}{}^{32}S_{1}$	24.5

Figure S14. HRMS spectrum of **DBF-BTD**.



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
409.12270	481329.26	409.12220	0.50	1.22	$^{12}C_{22}{}^{1}H_{21}{}^{14}N_{2}{}^{16}O_{4}{}^{32}S_{1}$	14.5

Figure S15. HRMS spectrum of **MeO-BTD**.

7. Solution NMR (^{1}H, ^{13}C) experiments of BTD-based building blocks

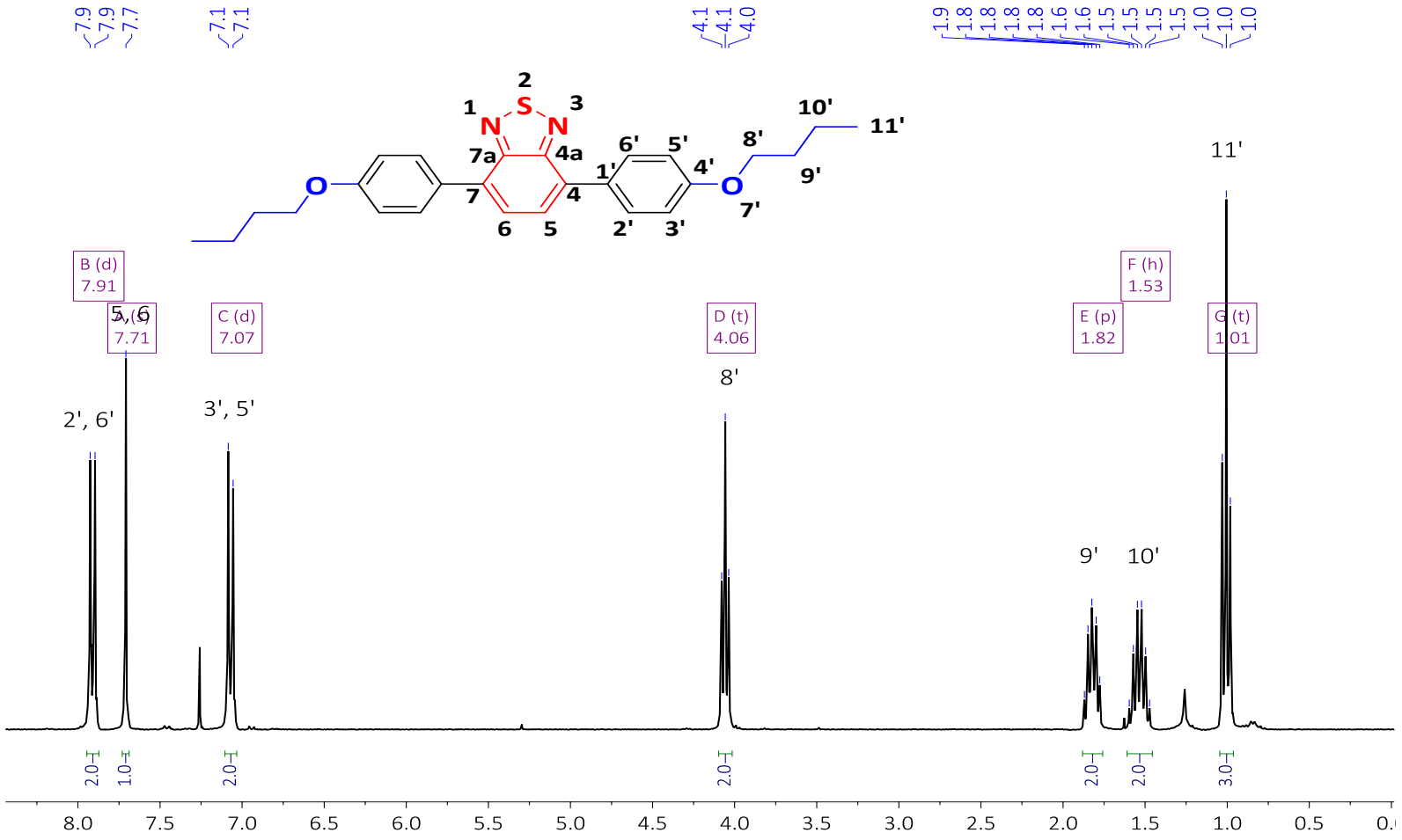


Figure S16. ^{1}H-NMR spectrum of **BuO-BTD** in $CDCl_3$ [400 MHz, $CDCl_3$].

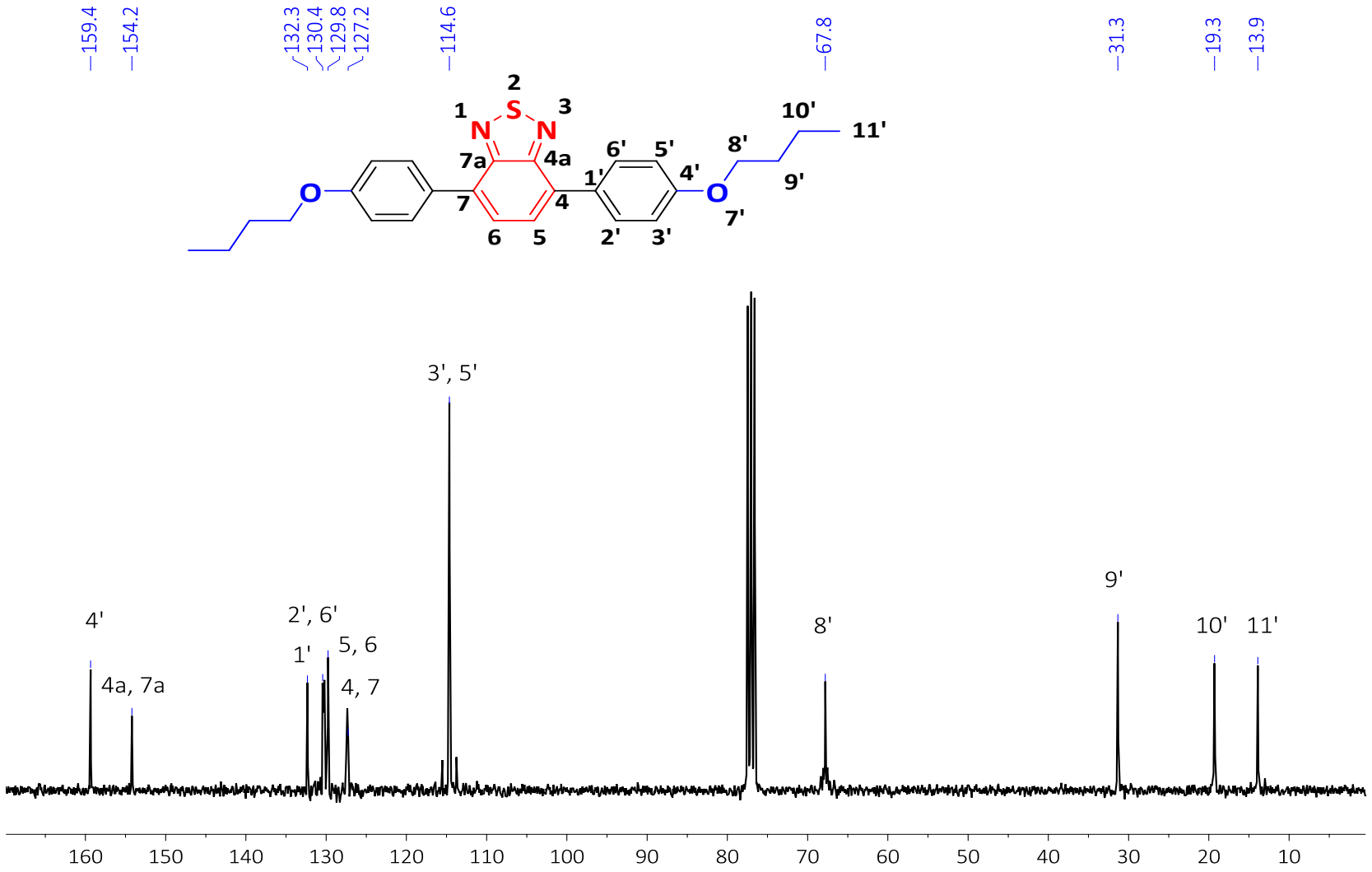


Figure S17. ^{13}C-NMR spectrum of **BuO-BTD** in $CDCl_3$ [100 MHz, $CDCl_3$].

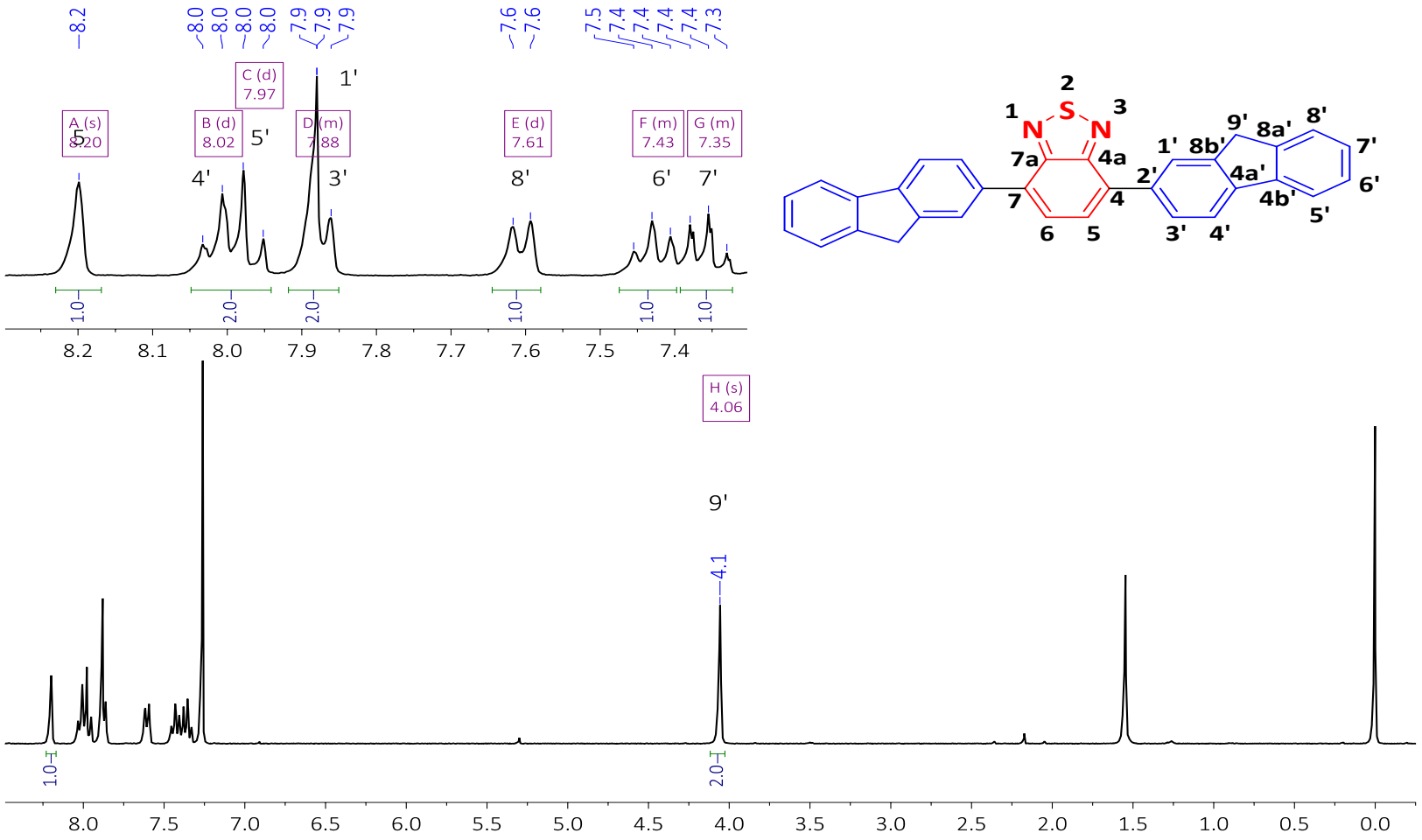


Figure S18. ^{1}H-NMR spectrum of **FL-BTD** in $CDCl_3$ [400 MHz, $CDCl_3$].

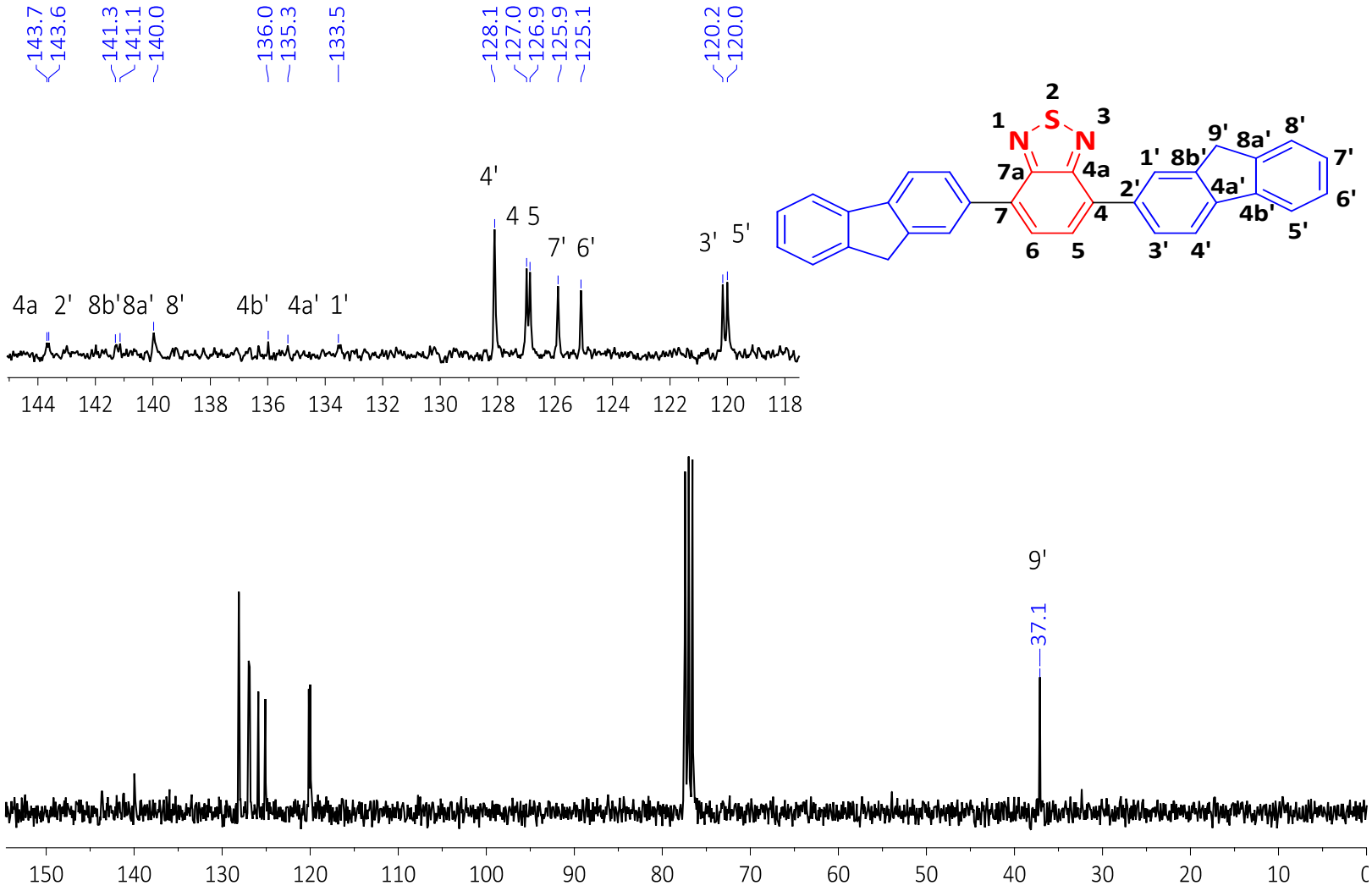


Figure S19. ^{13}C-NMR spectrum of **FL-BTD** in $CDCl_3$ [100 MHz, $CDCl_3$].

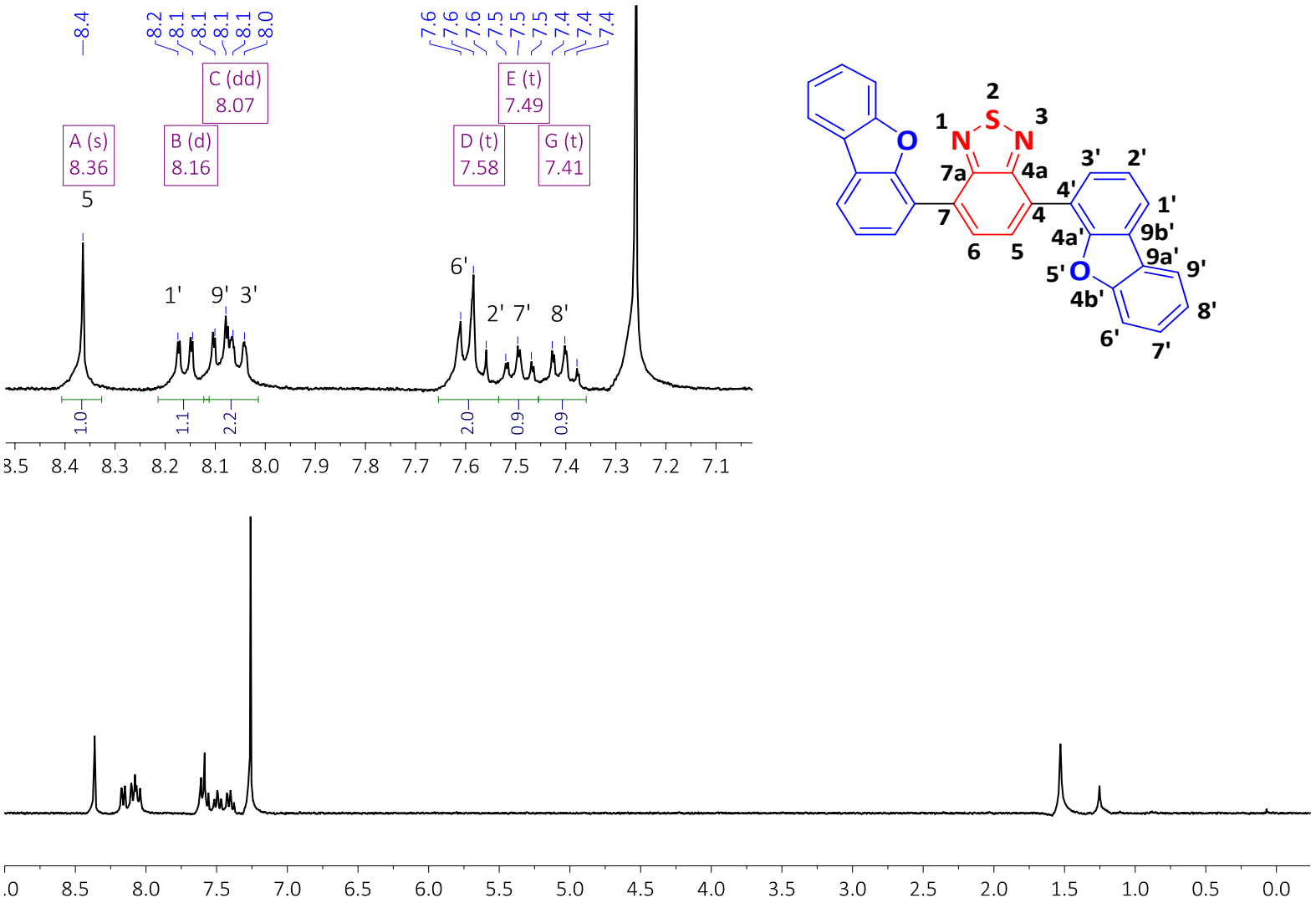


Figure S20. ^{1}H-NMR spectrum of **DBF-BTD** in $CDCl_3$ [400 MHz, $CDCl_3$].

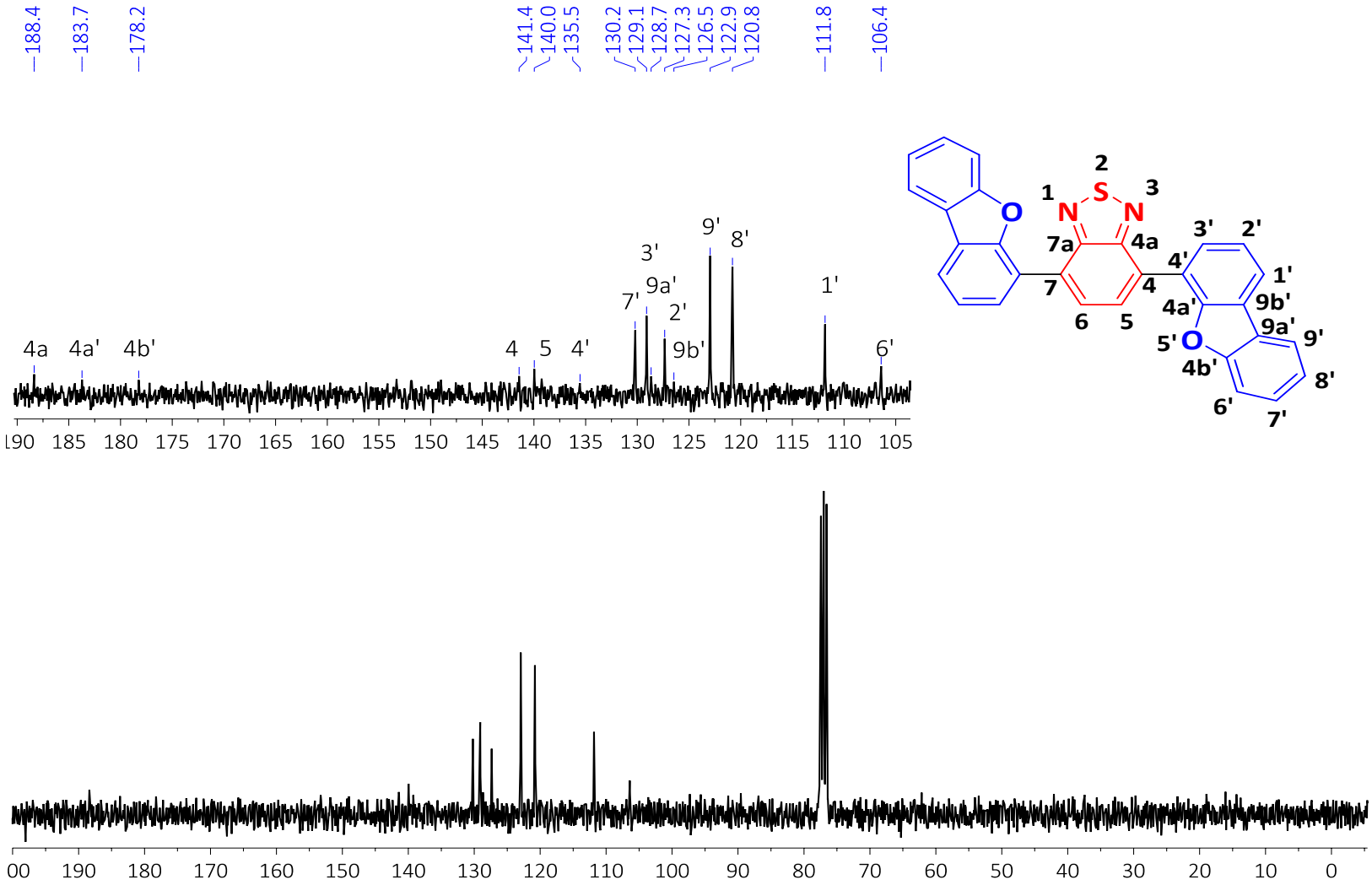


Figure S21. ^{13}C-NMR spectrum of **DBF-BTD** in $CDCl_3$ [100 MHz, $CDCl_3$].

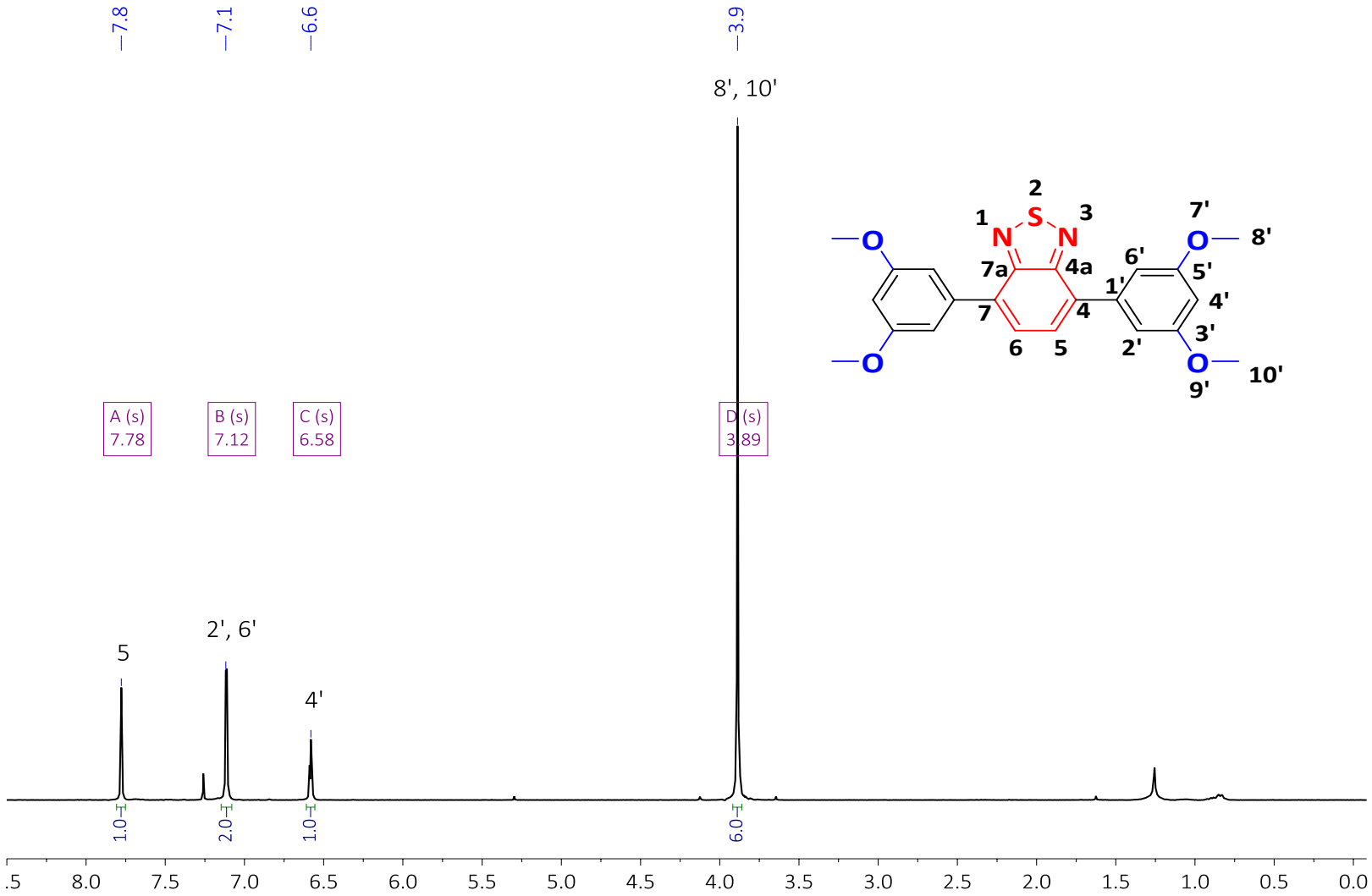


Figure S22. ^{1}H-NMR spectrum of **MeO-BTD** in $CDCl_3$ [400 MHz, $CDCl_3$].

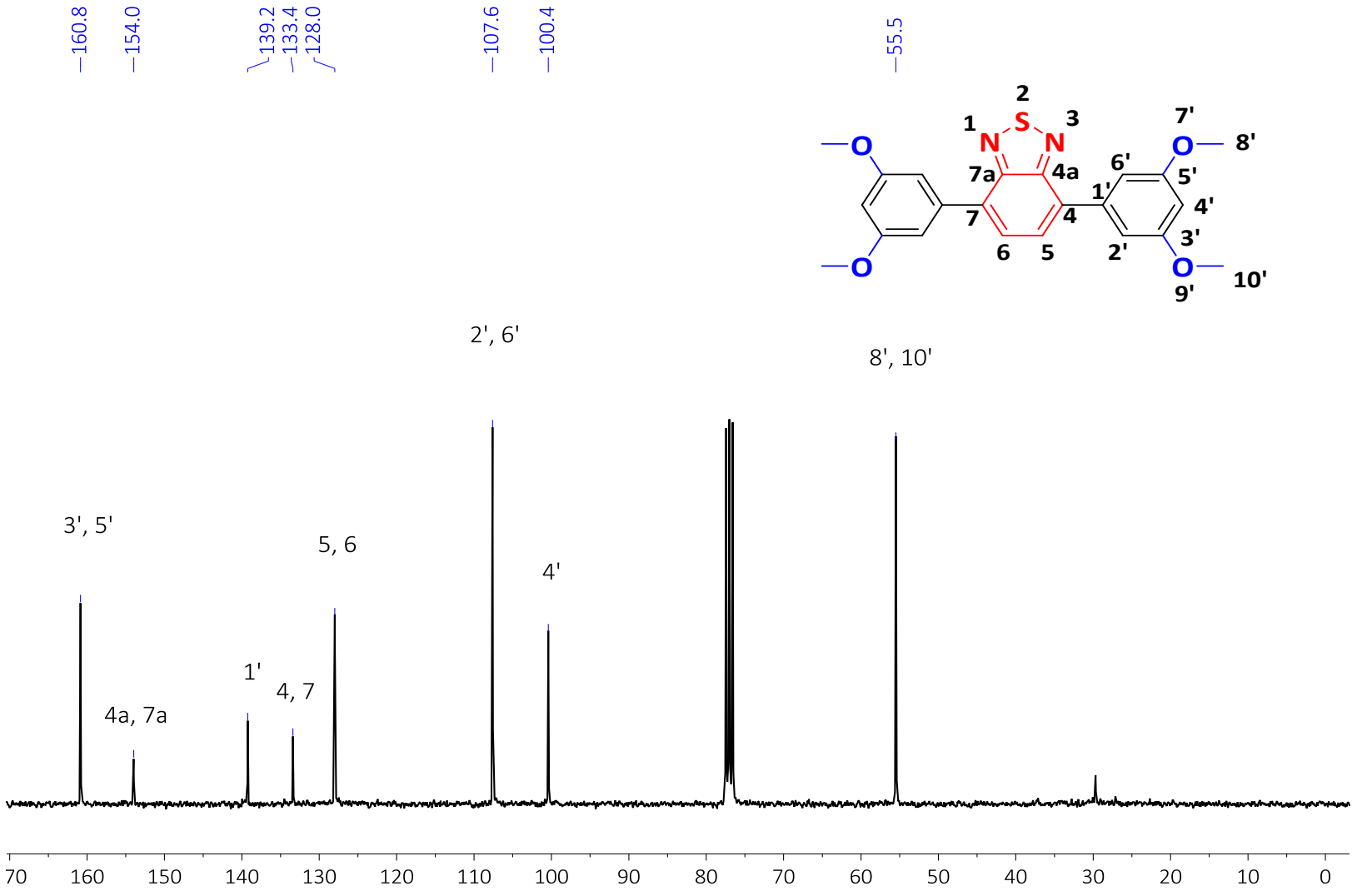


Figure S23. ^{13}C-NMR spectrum of **MeO-BTD** in $CDCl_3$ [100 MHz, $CDCl_3$].