Fine-Tuning of Photophysical and Electroluminescence Properties of Benzothiadiazole-Based Emitters by Methyl Substitution

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Supporting Information

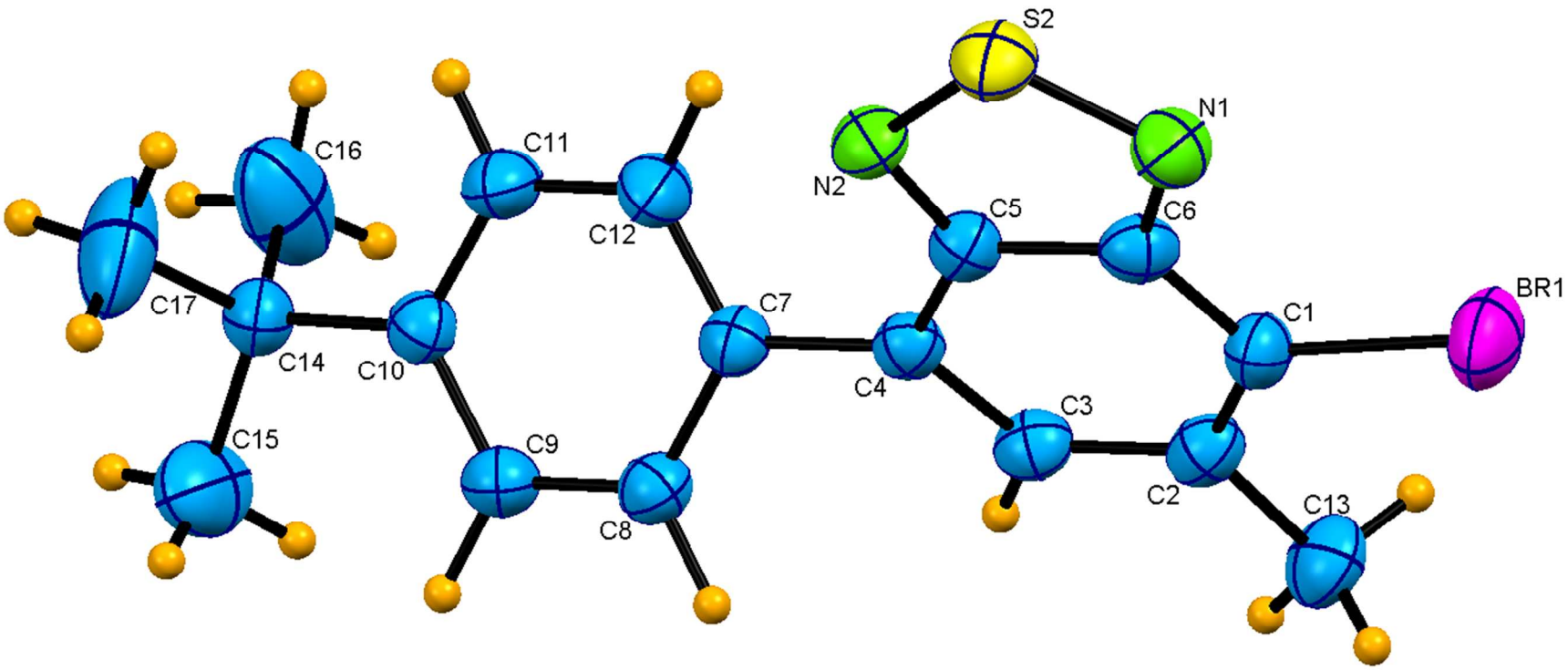

Figure S1. ORTEP plot (50% thermal ellipsoids) of **2a**.

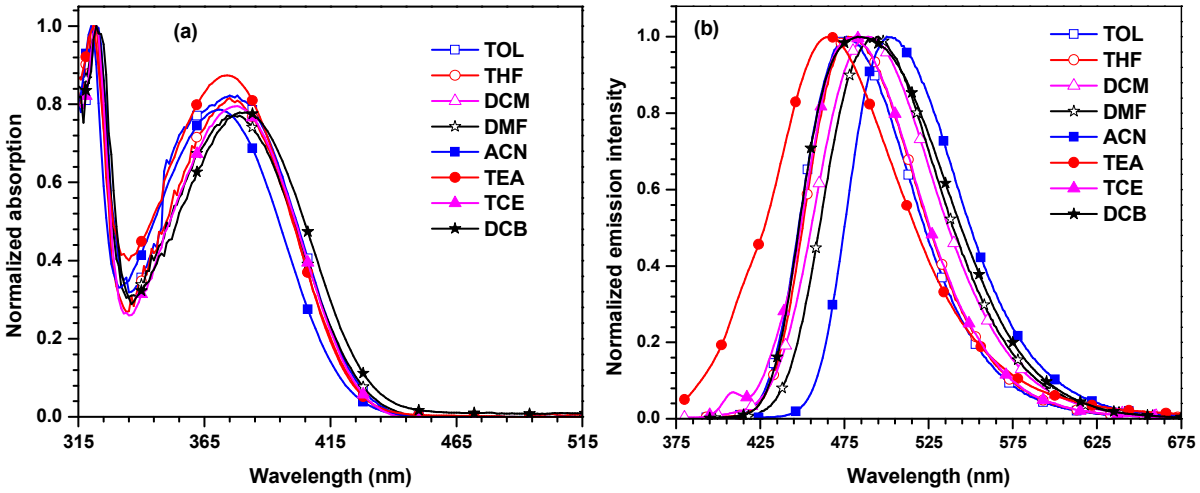

Figure S2 (a) Absorption and (b) emission spectra of **D1** recorded in different solvents.

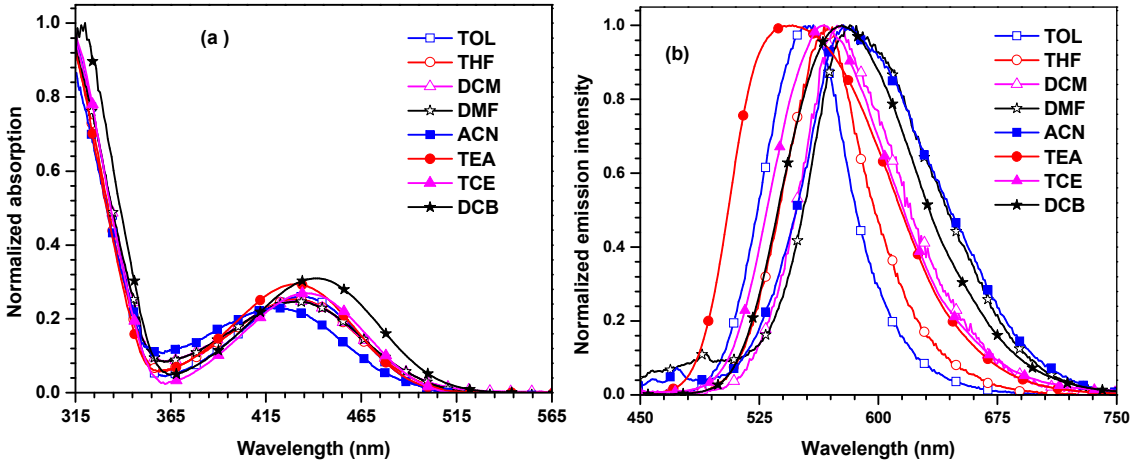

Figure S3 (a) Absorption and (b) emission spectra of **D2** recorded in different solvents.

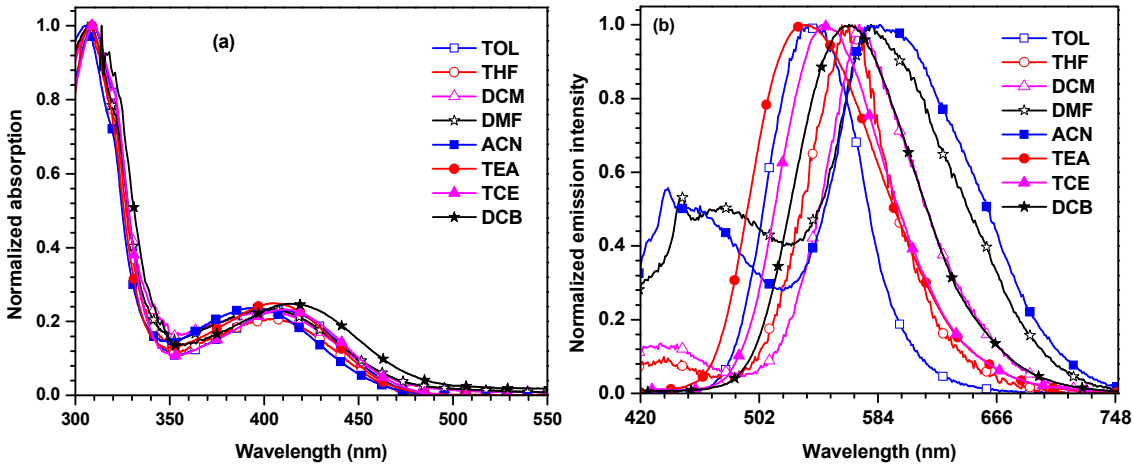

Figure S4 (a) Absorption and (b) emission spectra of **D4** recorded in different solvents.

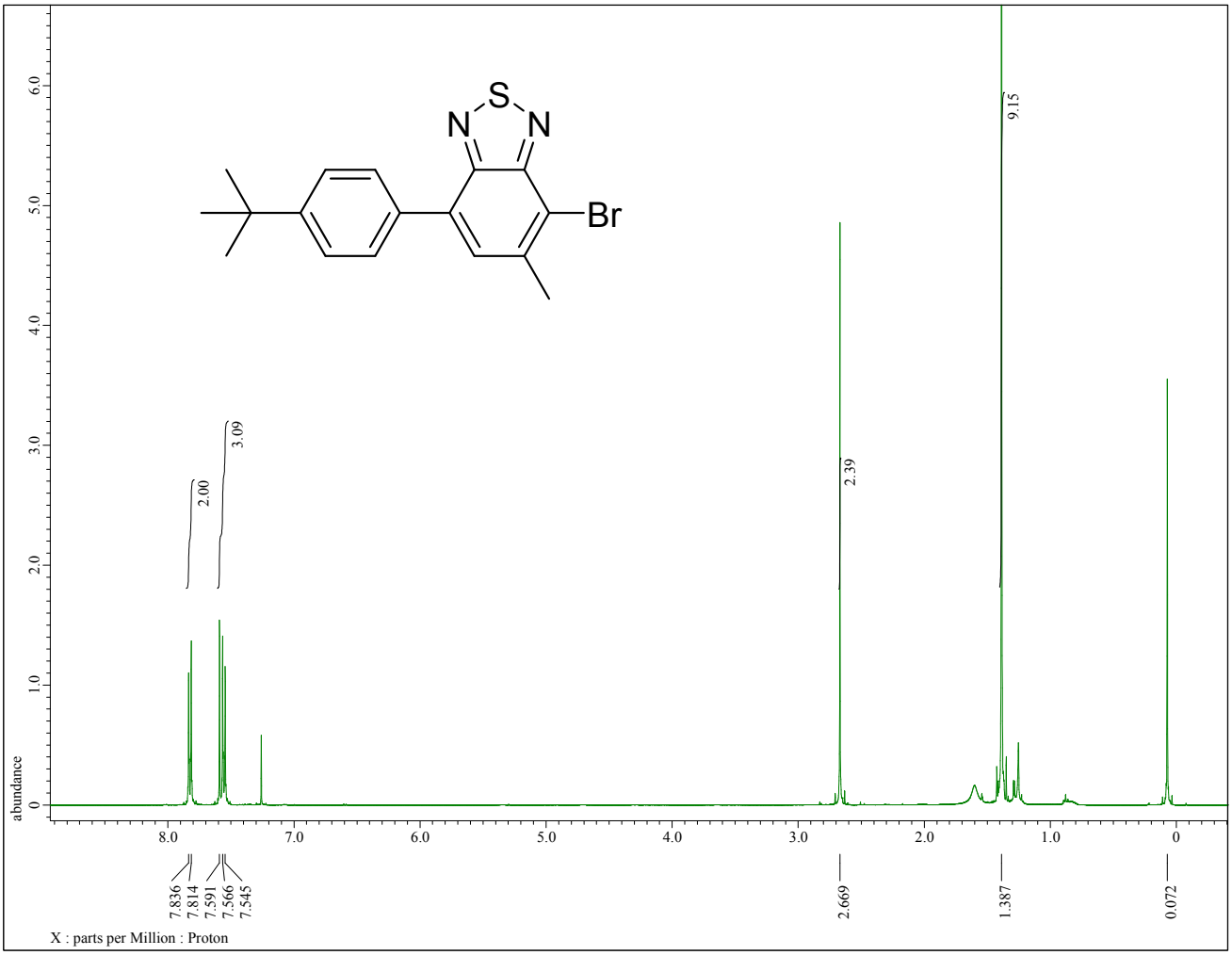

Figure S5 ^{1}H NMR spectrum of **2a** recorded in $CDCl_3$.

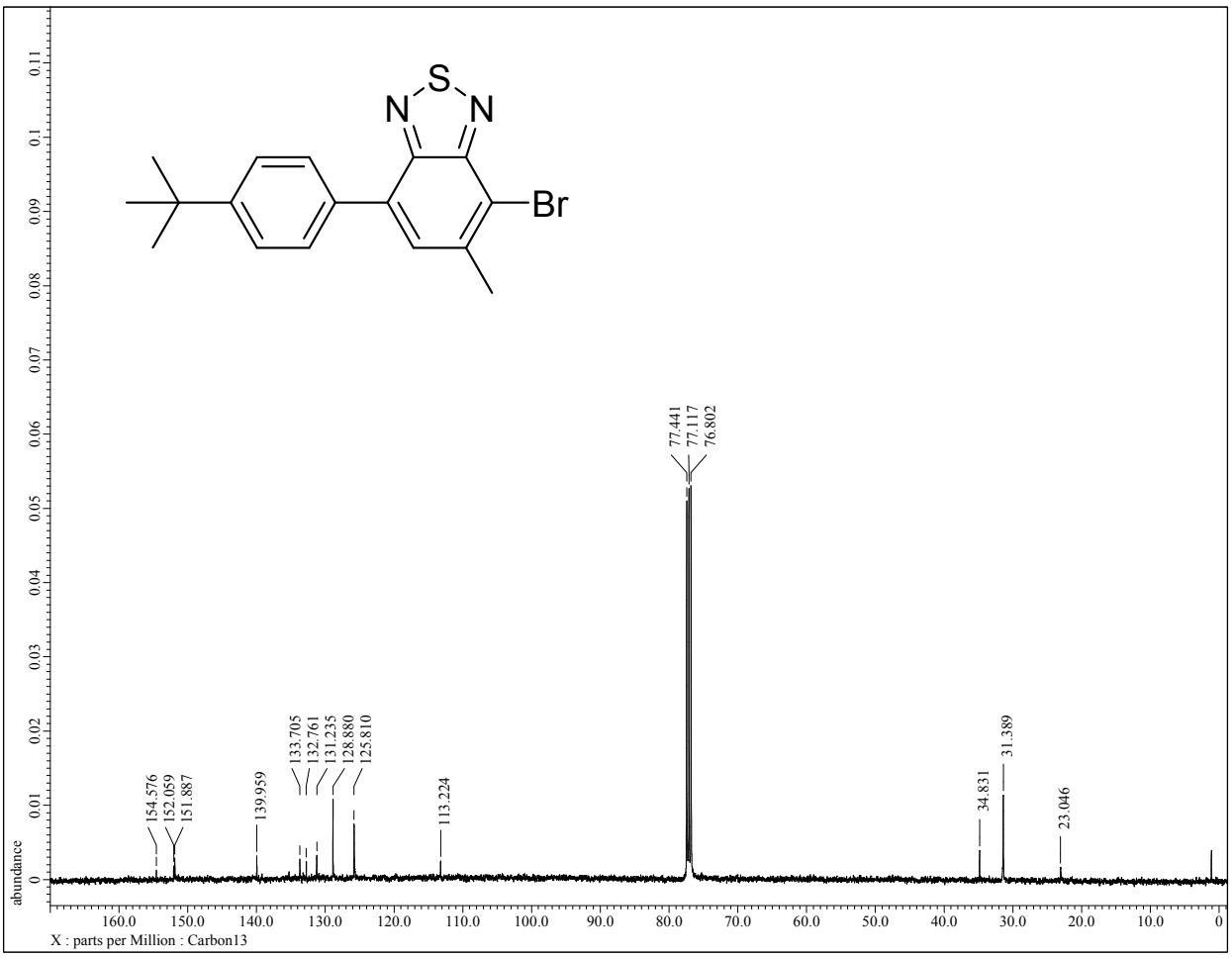

Figure S6 ^{13}C NMR spectrum of **2a** recorded in $CDCl_3$.

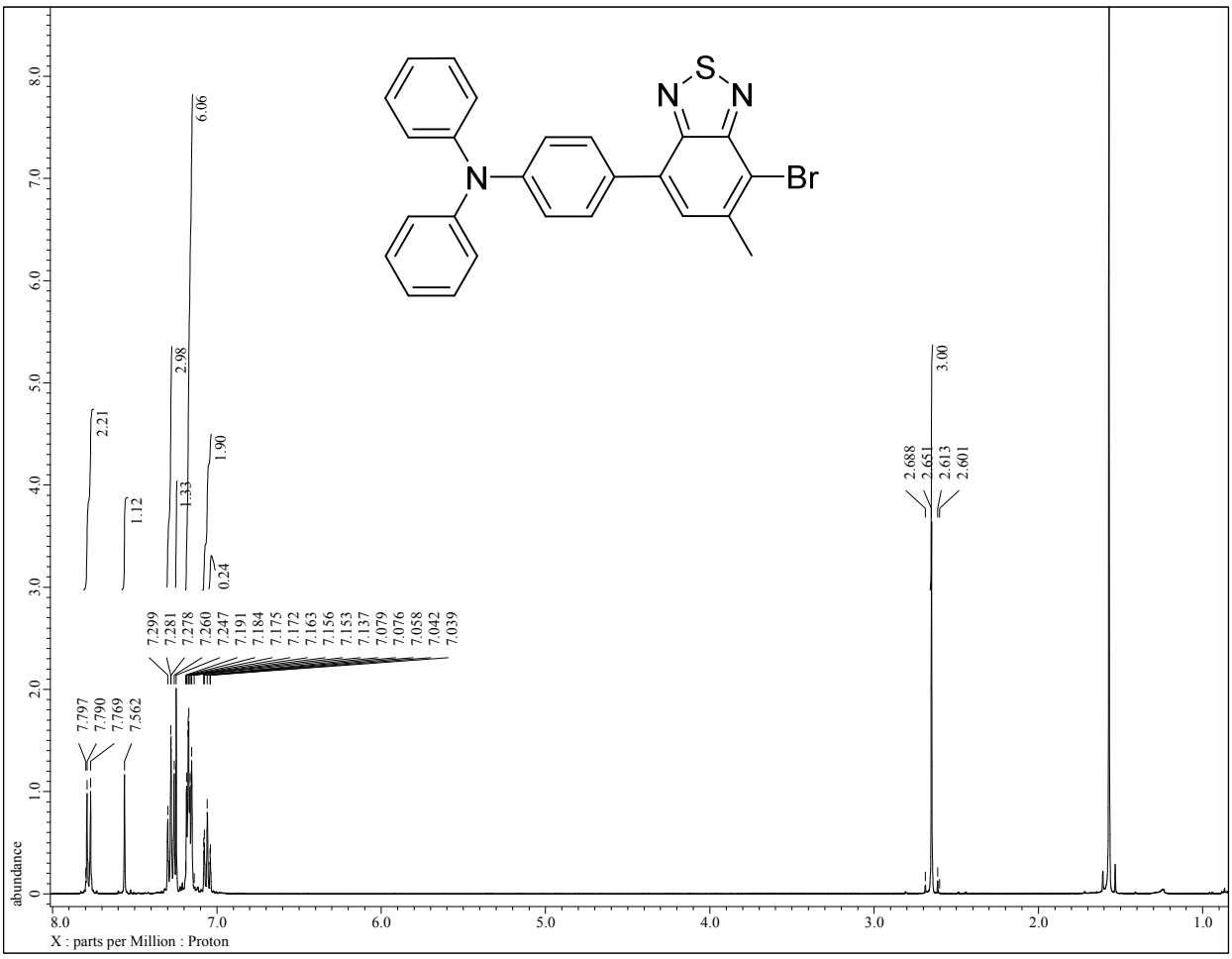

Figure S7 ^{1}H NMR Spectrum of **2b** recorded in $CDCl_3$.

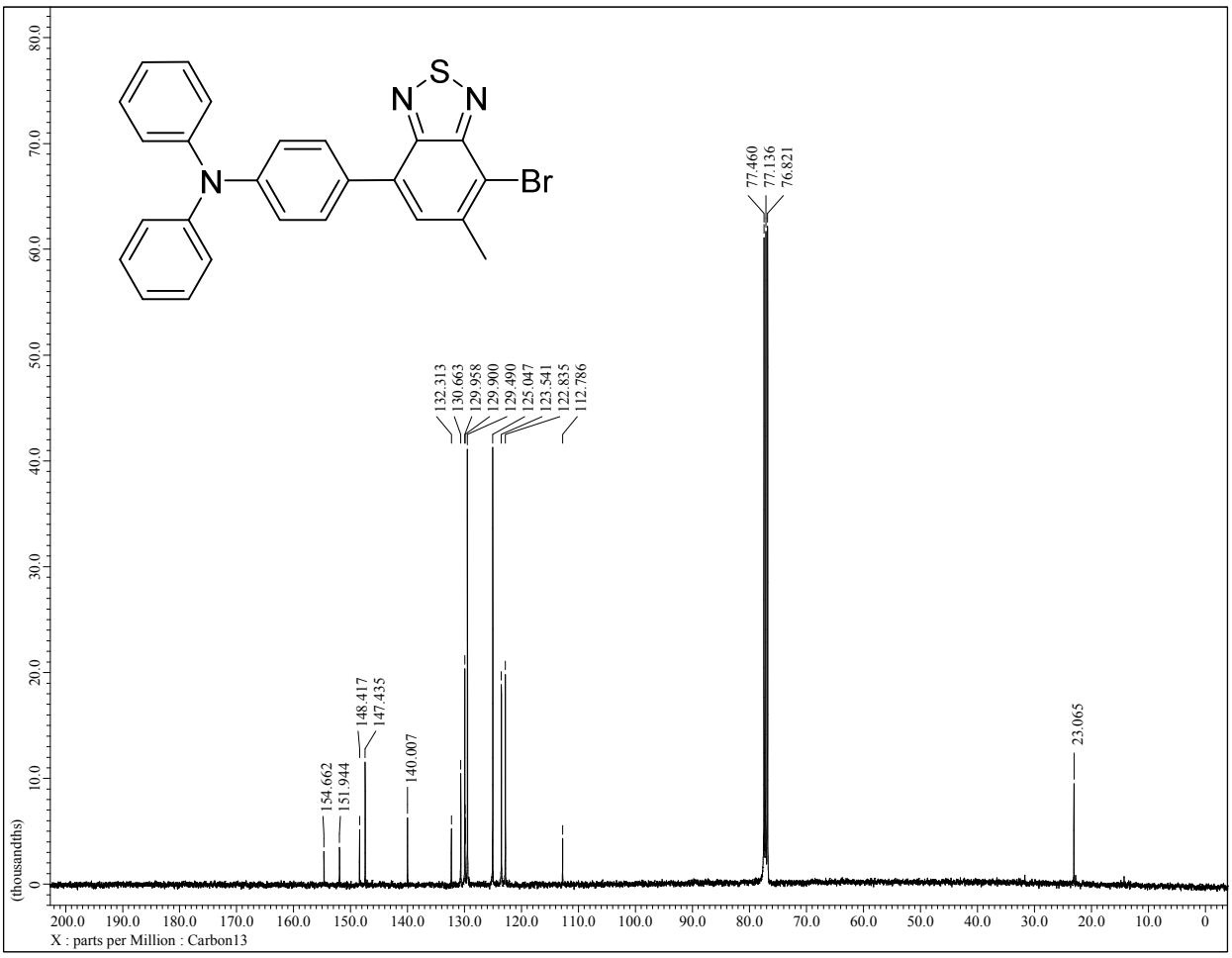

Figure S8 ^{13}C NMR Spectrum of **2b** recorded in $CDCl_3$.

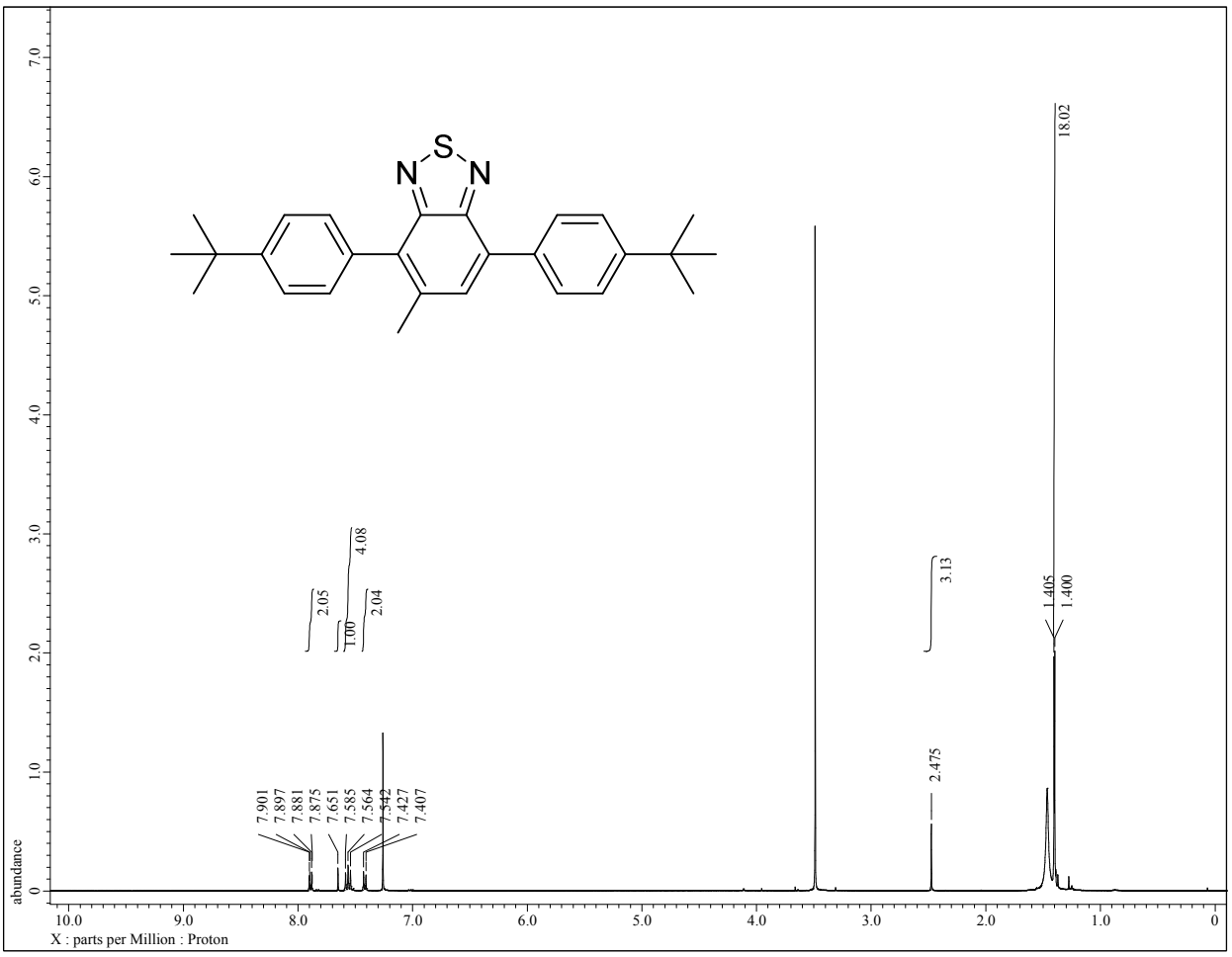

Figure S9 ^{1}H NMR Spectrum of **D1** recorded in $CDCl_3$.

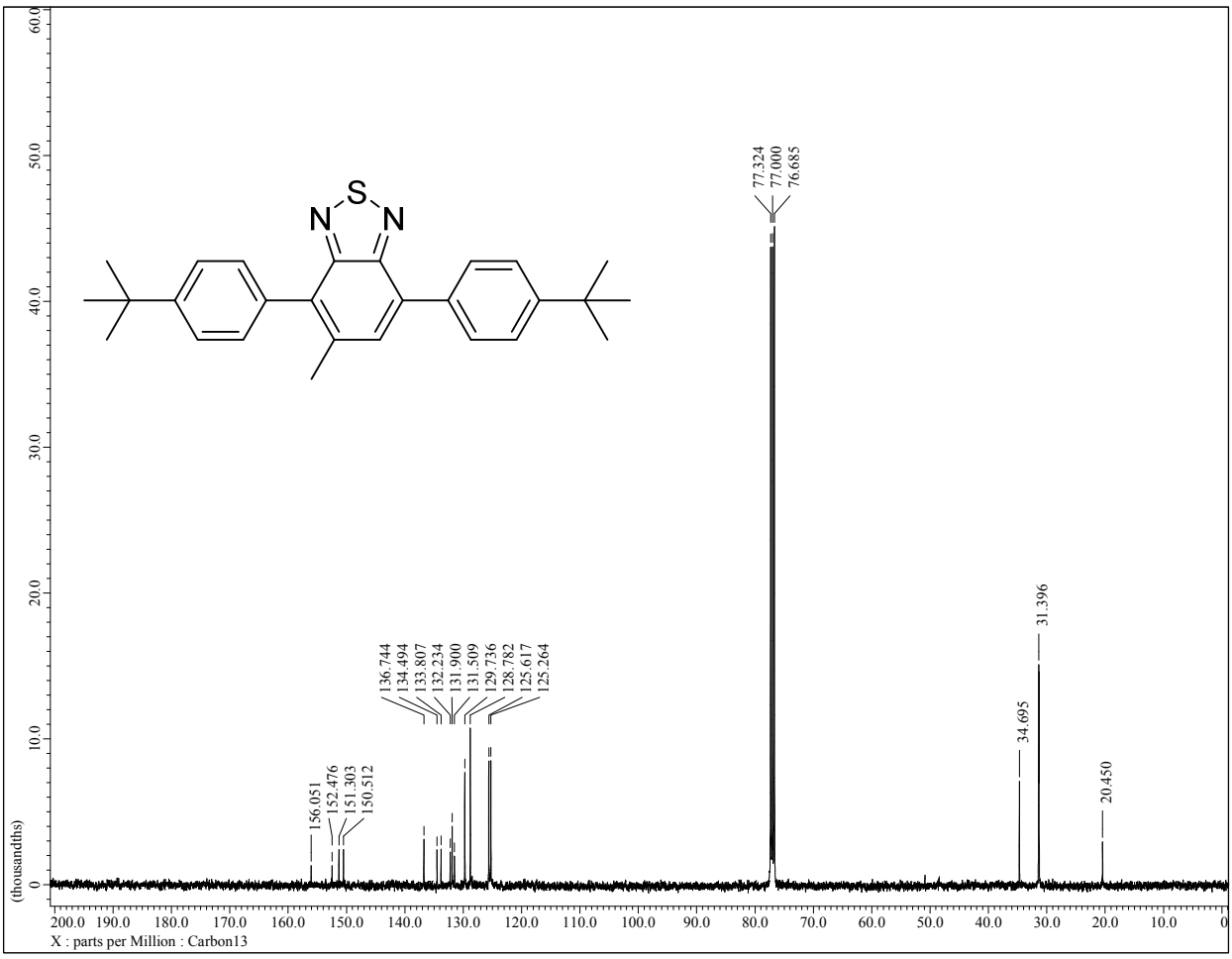

Figure S10 ^{13}C NMR Spectrum of **2a** recorded in $CDCl_3$.

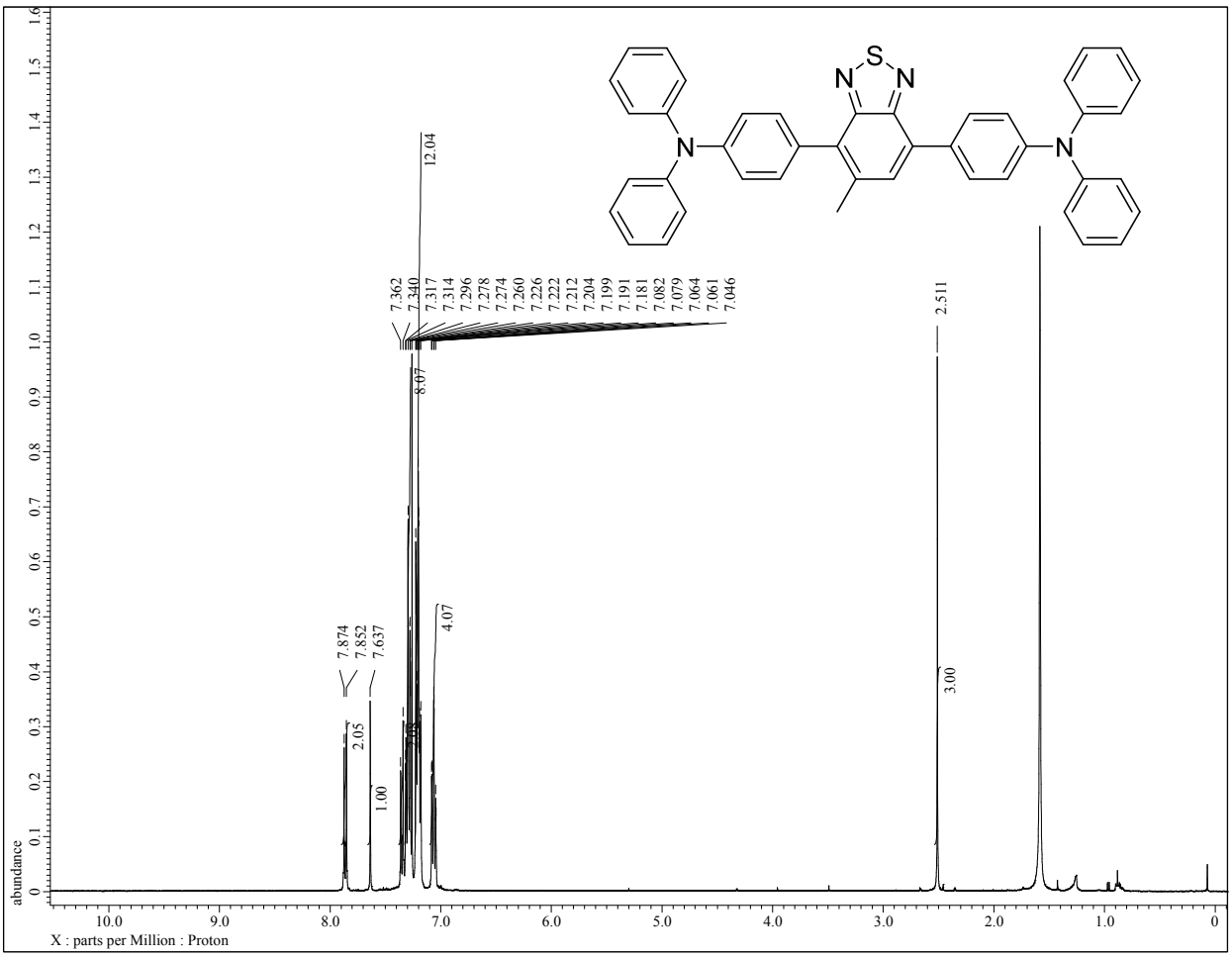

Figure S11 ^{1}H NMR Spectrum of **D2** recorded in $CDCl_3$.

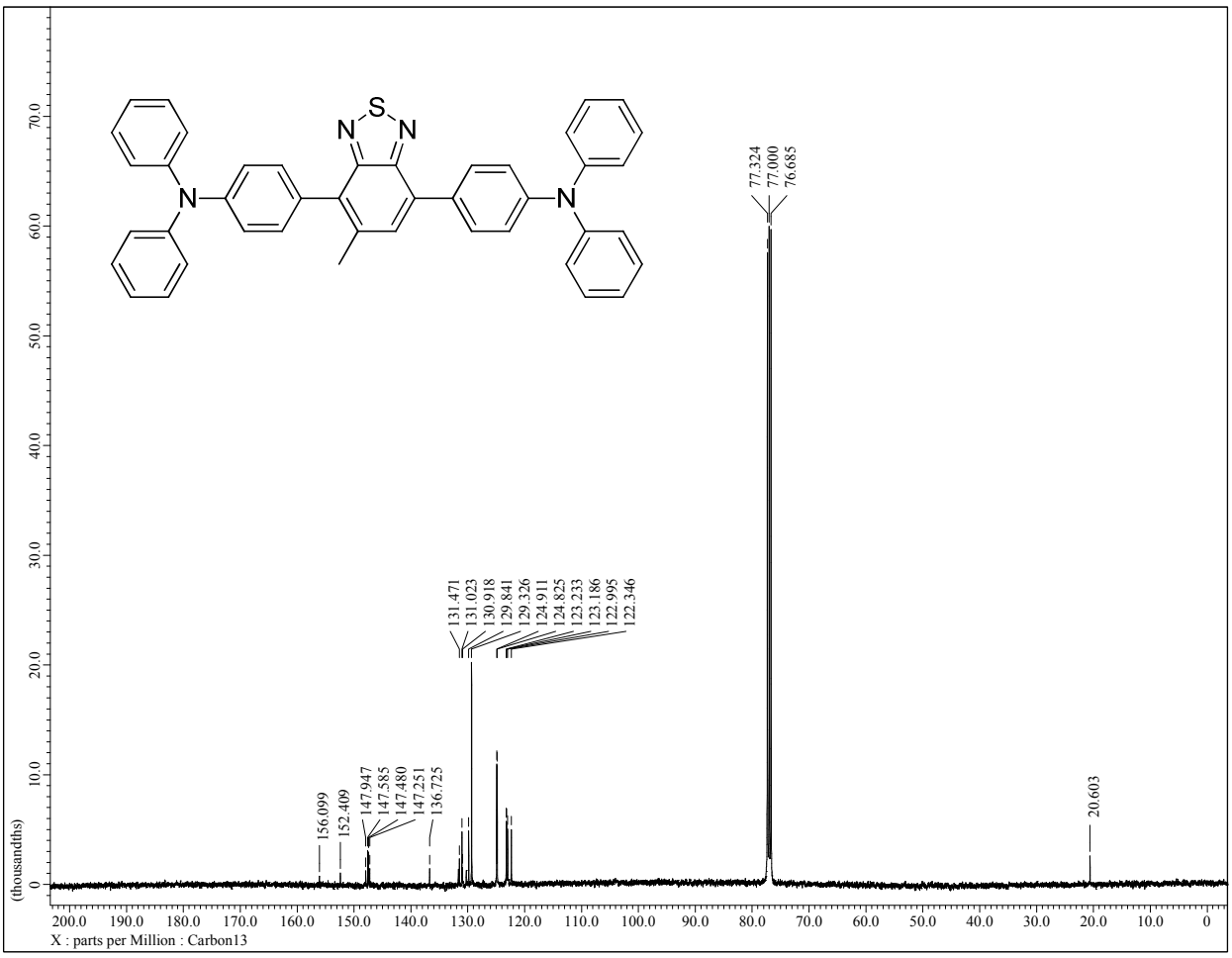

Figure S12 ^{13}C NMR Spectrum of **D2** recorded in $CDCl_3$.

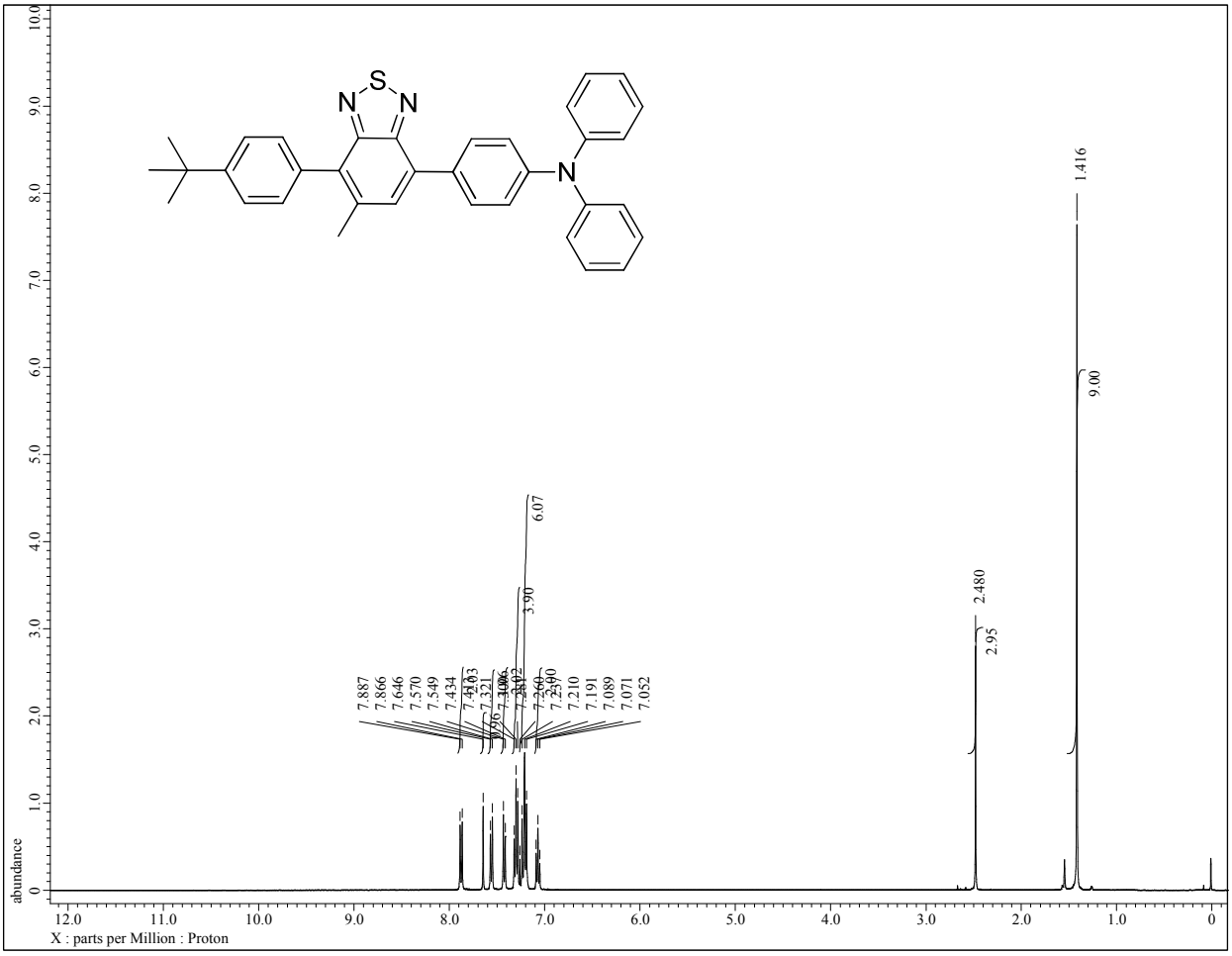

Figure S13 ^{1}H NMR Spectrum of **D3** recorded in $CDCl_3$.

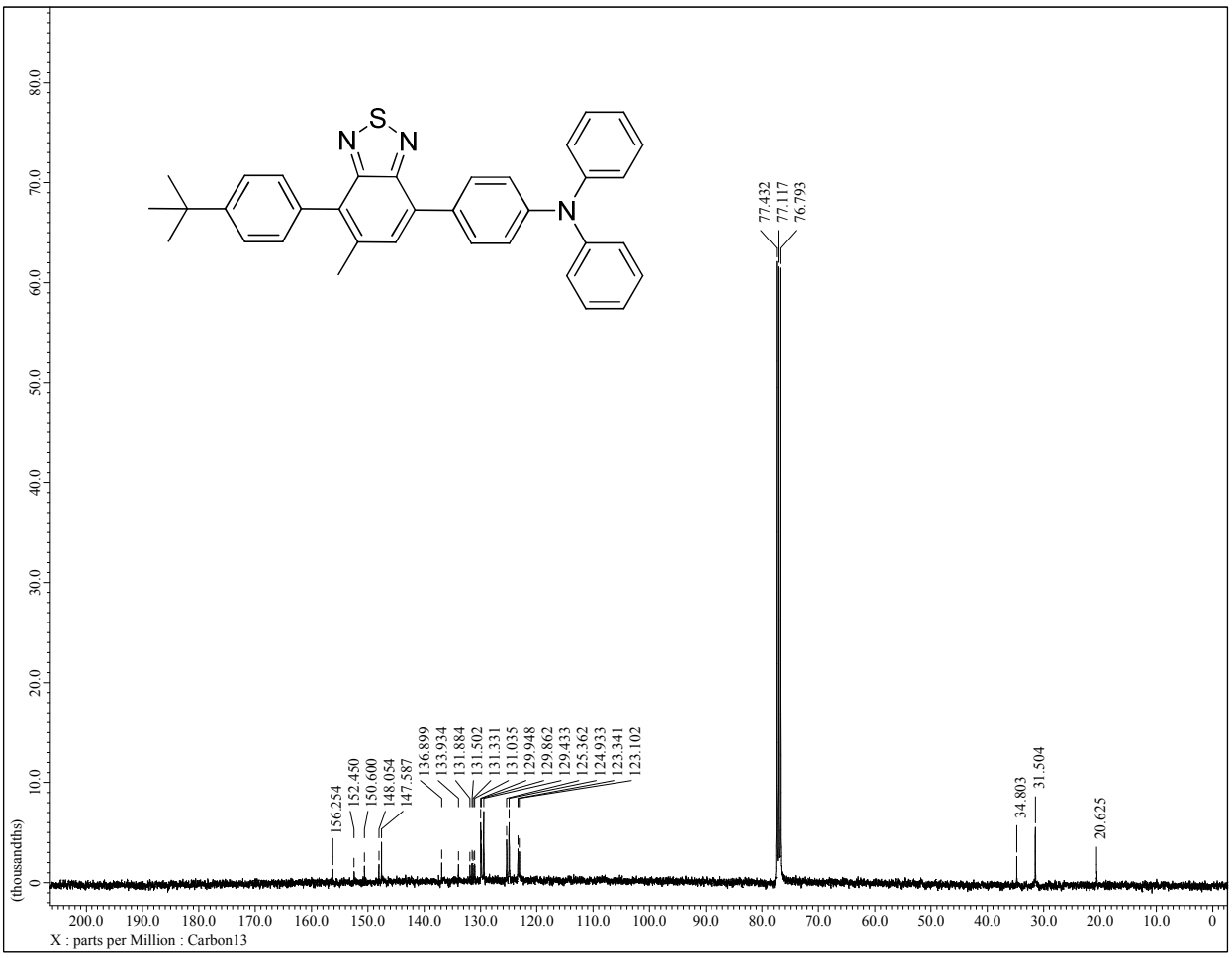

Figure S14 ^{13}C NMR Spectrum of **D3** recorded in $CDCl_3$.

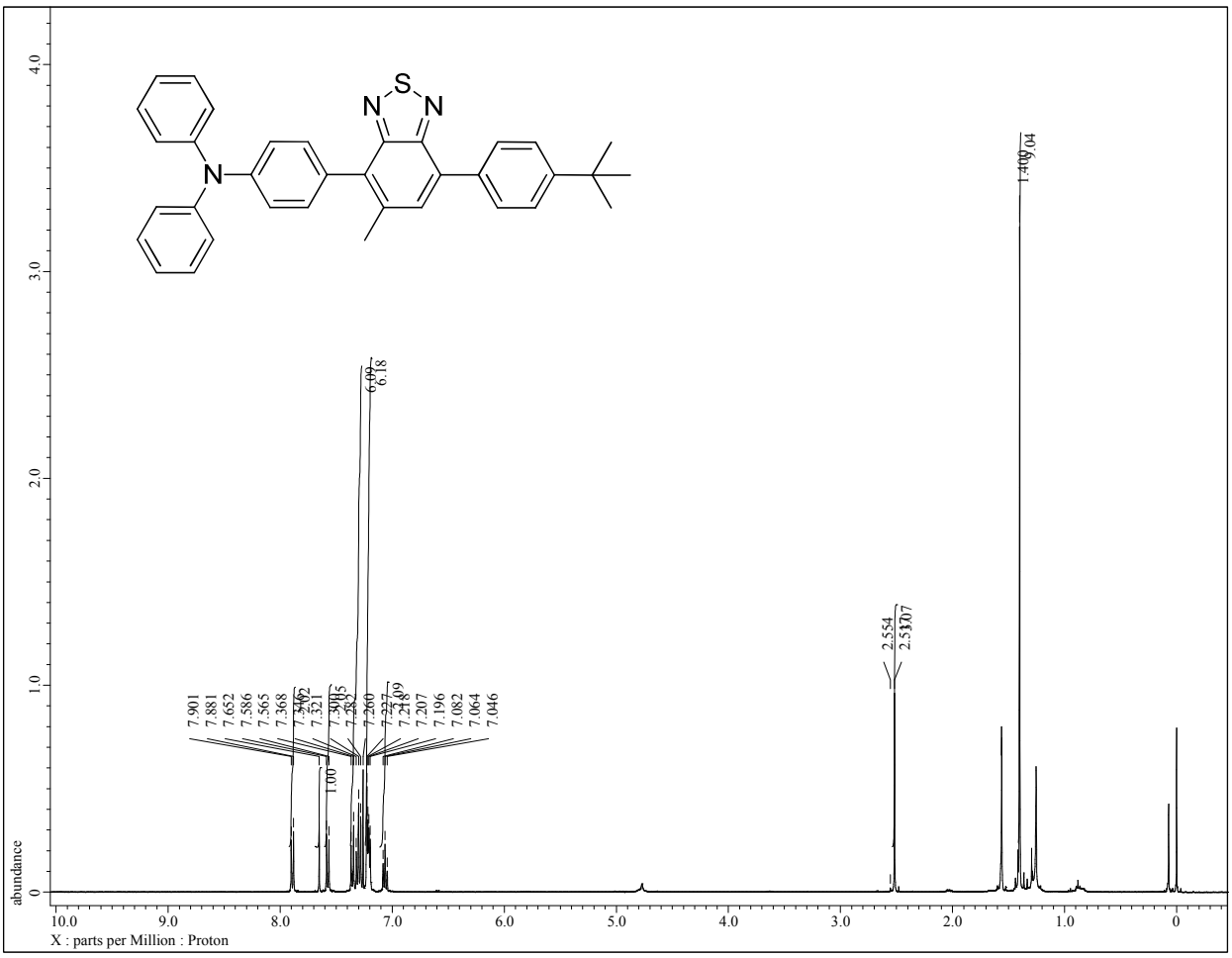

Figure S15 ^{1}H NMR Spectrum of **D4** recorded in $CDCl_3$.

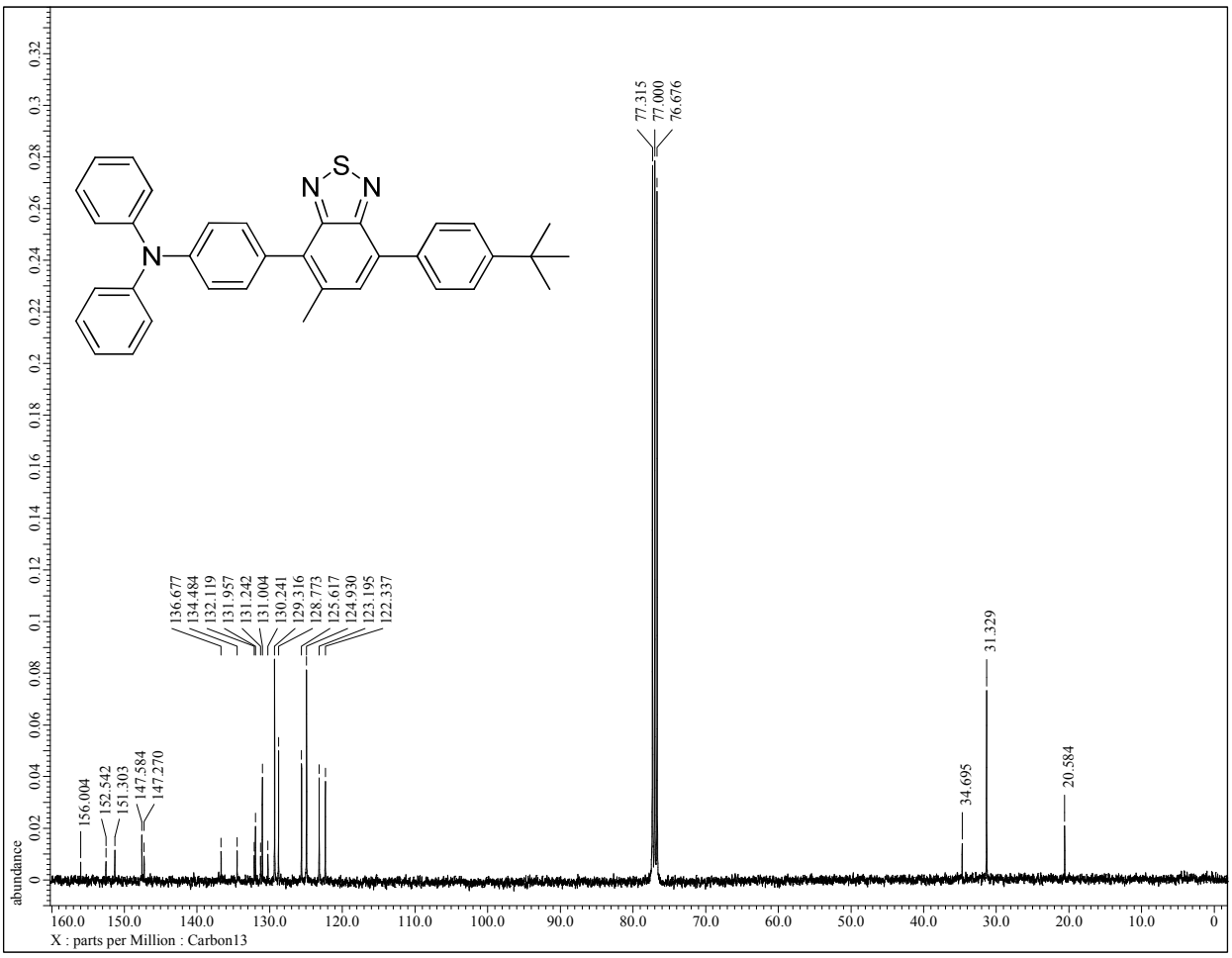

Figure S16 ^{13}C NMR Spectrum of **D4** recorded in $CDCl_3$.

Table S1 Emission data of the dyes recorded in various solvents

Dye	λ_{em}(nm)								$\Delta\lambda$,	Stokes shift (cm^{-1})							
	TOL	DCM	THF	ACN	TEA	TCE	DCB	DMF	(λ_{TOL}–λ_{DMF}) (nm)	TOL	DCM	THF	ACN	TEA	TCE	DCB	DMF
D1	476	489	477	504	466	481	485	495	19	5801	6146	5845	7186	5350	5665	5767	6253
D2	559	577	566	578	546	566	577	582	23	5152	5817	5534	6508	4833	5268	5345	6128
D3	546	575	563	469(sh), 586	544	551	566	463(sh), 580	34	5270	6532	6048	7325	5258	5436	5697	6739
D4	537	427(sh), 571	439(sh), 564	439(sh), 461(sh), 585	534	545	564	448, 477(sh), 579	42	5768	7301	7022	8287	5965	6042	6483	7666

Table S2 Crystal data and structure refinement for **2a**

Empirical formula	C17 H17 Br N2 S
Formula weight	361.29
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic,
Space group	C 2/c
Unit cell dimensions	a = 18.6401(12) Å a = 90°
	b = 14.9843(10) Å b = 112.356(3)°
	c = 12.6094(9) Å g = 90°
Volume	3257.2(4) $Å^3$
z	8
Density (calculated)	1.474 Mg/m^3
Absorption coefficient	2.647 mm^{-1}
F(000)	1472
Crystal size	None

Theta range for data collection	1.801 to 28.326°
Index ranges	-24<=h<=21, -19<=k<=19, -16<=l<=16
Reflections collected	24989
Independent reflections	4057 [R(int) = 0.0546]
Completeness to theta = 25.242°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4057 / 0 / 201
Goodness-of-fit on F^2	0.987
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.1067
R indices (all data)	R1 = 0.1207, wR2 = 0.1435
Extinction coefficient	n/a
Largest diff. peak and hole	0.450 and -0.385 e. $Å^{-3}$

Table S3.Cartesian coordinates of the optimized structure **D2**

Atomic No.	X	Y	Z
16	-0.092016000	-3.353049000	-0.321160000
7	-1.302559000	-2.249806000	-0.187458000
7	1.210992000	-2.353631000	-0.231615000
6	-1.427621000	0.195646000	0.080247000
6	-0.721001000	-1.050675000	-0.063104000
6	0.733029000	-1.112381000	-0.095780000
6	1.516025000	0.088813000	0.028873000
6	0.786248000	1.250078000	0.170571000
6	-0.644169000	1.334175000	0.207733000
1	1.329583000	2.187520000	0.248775000
6	-2.912550000	0.202098000	0.068866000
6	-3.632632000	1.035074000	-0.803346000
6	-3.652111000	-0.640577000	0.916705000
6	-5.023207000	1.033045000	-0.831363000
1	-3.094781000	1.670696000	-1.499985000
6	-5.041491000	-0.633374000	0.913033000
1	-3.129525000	-1.299608000	1.600985000
6	-5.751885000	0.201526000	0.034028000
1	-5.551136000	1.670580000	-1.532195000
1	-5.586171000	-1.278530000	1.593785000
7	-7.169643000	0.199966000	0.017304000
6	-7.883099000	1.418097000	-0.156428000
6	-7.884490000	-1.022174000	0.160104000
6	-8.998834000	1.475847000	-1.006863000
6	-7.485196000	2.580411000	0.523702000
6	-9.029905000	-1.085470000	0.969606000
6	-7.457507000	-2.180858000	-0.508097000
6	-9.701261000	2.668841000	-1.164207000
1	-9.309287000	0.583010000	-1.538985000
6	-8.183038000	3.772978000	0.345391000
1	-6.629457000	2.540631000	1.189235000

6	-9.733950000	-2.280966000	1.097795000
1	-9.362127000	-0.195351000	1.493168000
6	-8.157661000	-3.376069000	-0.358154000
1	-6.576733000	-2.138026000	-1.139819000
6	-9.296968000	3.825515000	-0.494857000
1	-10.562086000	2.695469000	-1.826249000
1	-7.861365000	4.662477000	0.879630000
6	-9.301543000	-3.434274000	0.440320000
1	-10.618178000	-2.312336000	1.728041000
1	-7.812616000	-4.263212000	-0.881430000
1	-9.842760000	4.754755000	-0.625696000
1	-9.848408000	-4.365748000	0.549001000
6	2.994152000	0.091070000	0.029072000
6	3.706056000	1.015353000	0.816098000
6	3.746677000	-0.796284000	-0.762164000
6	5.094045000	1.059591000	0.814746000
1	3.163249000	1.684359000	1.476968000
6	5.134985000	-0.746497000	-0.783501000
1	3.236182000	-1.523585000	-1.381054000
6	5.835055000	0.180391000	0.006791000
1	5.613447000	1.766621000	1.452411000
1	5.687342000	-1.429239000	-1.419962000
7	7.250821000	0.221257000	-0.001805000
6	7.930772000	1.468803000	0.071412000
6	8.001606000	-0.986157000	-0.070438000
6	9.057010000	1.618534000	0.896201000
6	7.489197000	2.566856000	-0.684189000
6	9.131063000	-1.074170000	-0.899483000
6	7.627441000	-2.103448000	0.692845000
6	9.727176000	2.838683000	0.955038000
1	9.401127000	0.775589000	1.485915000
6	8.155317000	3.787980000	-0.604445000
1	6.625012000	2.455001000	-1.330290000

6	9.871136000	-2.253417000	-0.954571000
1	9.422666000	-0.216059000	-1.495650000
6	8.363315000	-3.284095000	0.616649000
1	6.759390000	-2.040080000	1.340235000
6	9.279754000	3.931947000	0.210734000
1	10.596921000	2.937124000	1.598340000
1	7.800451000	4.626971000	-1.196217000
6	9.491121000	-3.366558000	-0.202335000
1	10.742383000	-2.304790000	-1.601324000
1	8.059226000	-4.139345000	1.213266000
1	9.800705000	4.882849000	0.264492000
1	10.066055000	-4.285965000	-0.253769000
6	-1.228126000	2.715159000	0.409344000
1	-1.249662000	3.283079000	-0.529139000
1	-2.248110000	2.677459000	0.793714000
1	-0.613967000	3.287565000	1.111890000

Table S4 Cartesian coordinates of the optimized structure **D3**

Atomic No.	X	Y	Z
16	1.956363000	-2.152784000	2.502374000
7	0.634612000	-1.522611000	1.753473000
7	3.146050000	-1.427916000	1.631663000
6	0.284880000	0.060526000	-0.118654000
6	1.089018000	-0.720095000	0.785131000
6	2.541778000	-0.664192000	0.713255000
6	3.225369000	0.161554000	-0.246062000
6	2.424270000	0.889287000	-1.113190000
6	0.995082000	0.817282000	-1.026896000
1	0.436051000	1.387520000	-1.763278000
6	4.711706000	0.199535000	-0.254833000
6	5.409699000	1.409205000	-0.151568000
6	5.469216000	-0.979594000	-0.350215000
6	6.805188000	1.443946000	-0.152045000
1	4.856350000	2.337910000	-0.048404000
6	6.858465000	-0.937917000	-0.357613000
1	4.961584000	-1.935645000	-0.419992000
6	7.565836000	0.273034000	-0.257649000
1	7.293983000	2.407034000	-0.060661000
1	7.401772000	-1.874610000	-0.440793000
6	9.104985000	0.268674000	-0.260370000
6	9.618436000	-0.568375000	0.935355000
6	9.615888000	-0.357599000	-1.579853000
6	9.694689000	1.686606000	-0.142647000
1	9.279733000	-0.142436000	1.885284000
1	9.265380000	-1.602668000	0.889706000
1	10.714077000	-0.590141000	0.943246000
1	9.273429000	0.218693000	-2.445588000
1	10.711522000	-0.374123000	-1.594518000
1	9.266136000	-1.386424000	-1.704765000

1	10.788032000	1.632695000	-0.149702000
1	9.390639000	2.325311000	-0.978387000
1	9.394687000	2.176163000	0.789523000
6	-1.193696000	0.065638000	-0.087472000
6	-1.909715000	1.229744000	-0.421977000
6	-1.943764000	-1.077514000	0.244850000
6	-3.298217000	1.252796000	-0.447533000
1	-1.369510000	2.142496000	-0.653622000
6	-3.332966000	-1.059872000	0.234525000
1	-1.431344000	-1.987874000	0.529479000
6	-4.037391000	0.103995000	-0.117743000
1	-3.817762000	2.166885000	-0.712979000
1	-3.882272000	-1.955899000	0.501765000
7	-5.453131000	0.122890000	-0.131739000
6	-6.159740000	1.287194000	0.283553000
6	-6.185445000	-1.021567000	-0.555578000
6	-7.254439000	1.753905000	-0.460670000
6	-5.778530000	1.979367000	1.443820000
6	-7.321821000	-1.438107000	0.155482000
6	-5.790017000	-1.744307000	-1.692421000
6	-7.954990000	2.884574000	-0.045780000
1	-7.550225000	1.224873000	-1.360421000
6	-6.474284000	3.119585000	1.840843000
1	-4.938361000	1.618190000	2.027431000
6	-8.048472000	-2.548409000	-0.269162000
1	-7.629120000	-0.887033000	1.037874000
6	-6.512815000	-2.864209000	-2.098570000
1	-4.916910000	-1.423432000	-2.250562000
6	-7.568003000	3.577208000	1.103128000
1	-8.800052000	3.232557000	-0.632923000
1	-6.167022000	3.643398000	2.741483000
6	-7.647825000	-3.271245000	-1.394440000
1	-8.925277000	-2.857154000	0.292835000

1	-6.193162000	-3.412173000	-2.980351000
1	-8.111958000	4.461609000	1.420136000
1	-8.212250000	-4.140083000	-1.718545000
6	2.988056000	1.762466000	-2.212268000
1	2.986437000	2.820802000	-1.922671000
1	4.014084000	1.493417000	-2.465826000
1	2.374214000	1.679422000	-3.114909000

Table S5 Cartesian coordinates of the optimized structure **D4**

Atomic No.	X	Y	Z
16	1.788085000	-0.386180000	3.259841000
7	0.556201000	-0.285246000	2.176953000
7	3.072071000	-0.272577000	2.238816000
6	0.385025000	-0.026631000	-0.266877000
6	1.114965000	-0.163497000	0.966702000
6	2.569816000	-0.155534000	1.004977000
6	3.327916000	-0.006395000	-0.207863000
6	2.578316000	0.104635000	-1.358652000
6	1.145773000	0.096137000	-1.421014000
6	4.807816000	0.031680000	-0.236504000
6	5.479467000	0.861528000	-1.146297000
6	5.594914000	-0.767947000	0.610966000
6	6.871616000	0.885612000	-1.217315000
1	4.907149000	1.521419000	-1.791606000
6	6.982461000	-0.740681000	0.530816000
1	5.114349000	-1.414993000	1.334650000
6	7.661327000	0.083816000	-0.382968000
1	7.336329000	1.553907000	-1.932925000
1	7.547790000	-1.382289000	1.200451000
6	9.199300000	0.083635000	-0.429186000
6	9.756251000	0.501306000	0.952515000
6	9.701941000	-1.338477000	-0.774729000
6	9.754033000	1.058641000	-1.484643000
1	9.421377000	1.508476000	1.220833000
1	9.432691000	-0.179717000	1.744844000
1	10.851996000	0.499461000	0.937938000
1	9.330454000	-1.658054000	-1.753855000
1	10.797226000	-1.359438000	-0.803397000

1	9.374248000	-2.076257000	-0.036620000
1	10.848117000	1.022042000	-1.480639000
1	9.419404000	0.800650000	-2.494775000
1	9.458508000	2.092849000	-1.279740000
6	-1.100217000	-0.015032000	-0.243858000
6	-1.831296000	1.017839000	-0.853084000
6	-1.827352000	-1.027690000	0.405284000
6	-3.222083000	1.034541000	-0.835834000
1	-1.302416000	1.828617000	-1.344491000
6	-3.216350000	-1.015845000	0.436227000
1	-1.294743000	-1.828940000	0.905372000
6	-3.938555000	0.015327000	-0.188300000
1	-3.759482000	1.842862000	-1.319469000
1	-3.751549000	-1.807105000	0.949575000
7	-5.356022000	0.030045000	-0.160039000
6	-6.053814000	1.260201000	-0.000655000
6	-6.088141000	-1.182791000	-0.288375000
6	-7.186756000	1.541302000	-0.780547000
6	-5.621272000	2.208663000	0.939842000
6	-7.208861000	-1.426411000	0.521544000
6	-5.704017000	-2.152723000	-1.228214000
6	-7.873199000	2.742475000	-0.614697000
1	-7.522931000	0.814174000	-1.512084000
6	-6.303614000	3.414727000	1.085138000
1	-4.751291000	1.994433000	1.551535000
6	-7.929722000	-2.610969000	0.385901000
1	-7.507982000	-0.683815000	1.253492000
6	-6.420449000	-3.342101000	-1.343308000
1	-4.843778000	-1.968108000	-1.862743000
6	-7.434850000	3.688606000	0.313795000
1	-8.747934000	2.944076000	-1.226431000
1	-5.955479000	4.137660000	1.817353000
6	-7.539151000	-3.578372000	-0.541997000

1	-8.793826000	-2.783059000	1.021273000
1	-6.108803000	-4.081820000	-2.075251000
1	-7.968016000	4.626441000	0.435158000
1	-8.098943000	-4.503345000	-0.639569000
1	3.106923000	0.173407000	-2.305256000
6	0.534234000	0.186435000	-2.801529000
1	-0.481040000	-0.211236000	-2.827234000
1	0.491041000	1.224163000	-3.155385000
1	1.142677000	-0.369201000	-3.522117000