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

Supporting Information

Effect of cyano group on solid state photophysical behavior of tetraphenylethene substituted benzothiadiazoles

Thaksen Jadhav, Bhausaheb Dhokale, Rajneesh Misra*

Department of Chemistry,
Indian Institute of Technology Indore,
Indore- 452 017, India.

rajneeshmisra@iiti.ac.in

Table of Contents

Thermogravimetric analysis

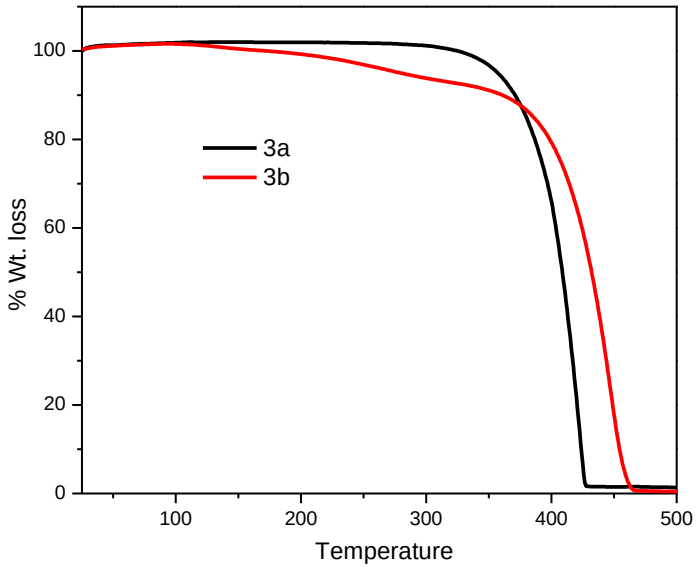


Fig. S1 Thermogravimetric analysis of **3a** and **3b**, measured at a heating rate of 10 $^{\circ}$C/ min under nitrogen atmosphere.

Photophysical properties:

Table S1. Photophysical properties of the 3a and 3b in different solvents.

Compounds	**Solvents**	**$\lambda_{abs.}$(nm)**	**$\lambda_{em.}$(nm)**	**Stokes Shift(cm^{-1})**	**Φ_f[a]**
3a	Cyclohexane	404	509	5106	0.345
	Toluene	403	527	5838	0.289
	Chloroform	403	565	7114	0.238
	Dichloromethane	399	579	7791	0.234
	Acetonitrile	391	614	9289	0.137
3b	Cyclohexane	410	523	5270	0.317
	Toluene	408	545	6161	0.273
	Chloroform	408	590	7560	0.220
	Dichloromethane	401	610	8544	0.233
	Acetonitrile	392	649	10102	0.106

[a] The fluorescence quantum yields using Quinine sulfate as a standard in 0.5 M H_2SO_4 solution.

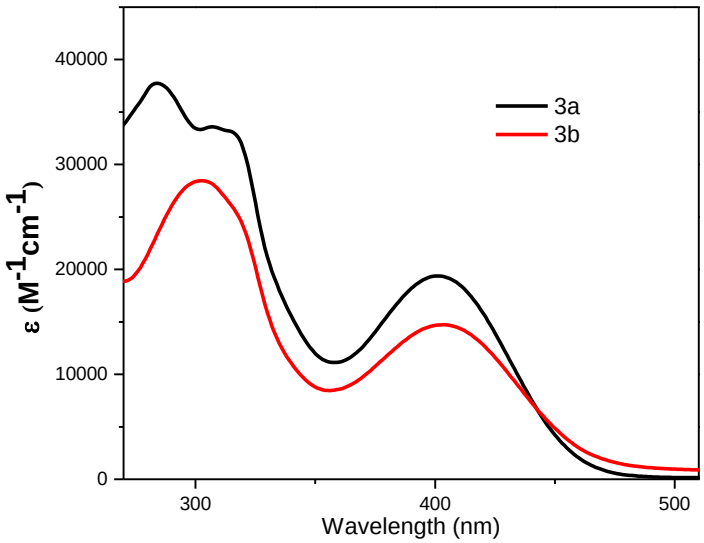


Fig. S2 Absorption spectra of **3a** and **3b** recorded in tetrahydrofuran.

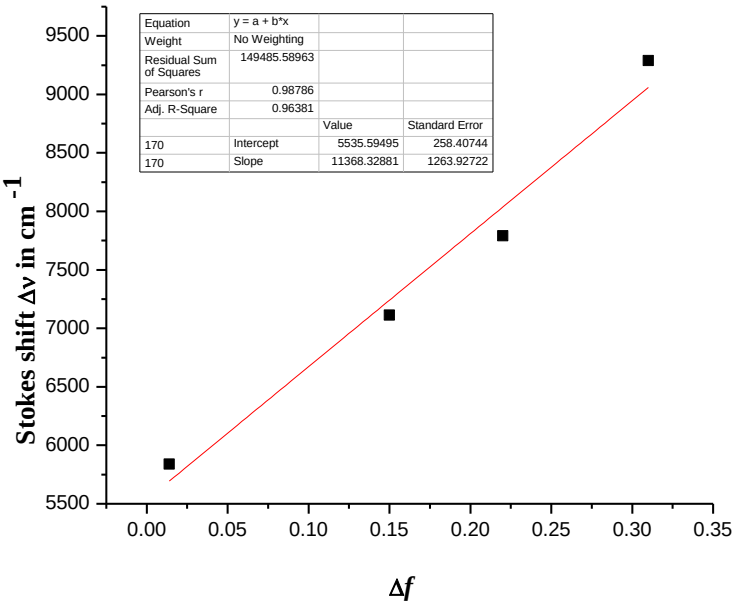


Fig. S3 Stokes Shift ($\Delta\nu$) of **3a** as a function of the solvent polarity parameter (Δf).

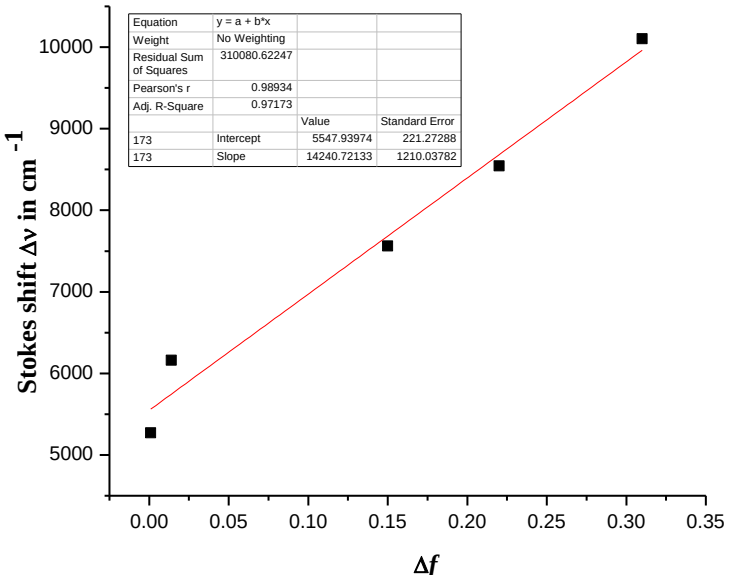


Fig. S4 Stokes Shift ($\Delta\nu$) of **3b** as a function of the solvent polarity parameter (Δf).

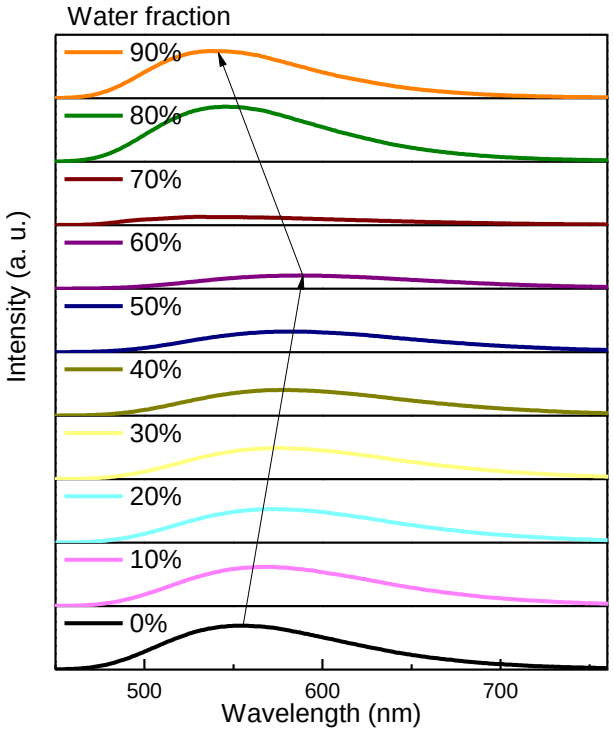


Fig. S5 Fluorescence spectra of **3a** in THF-Water mixtures with different water fractions.

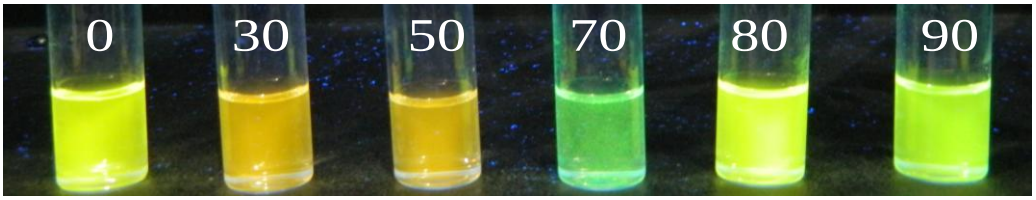


Fig. S6 Fluorescence pictures of **3a** solutions with different water fractions under UV (365 nm) light.

Mechanochromism

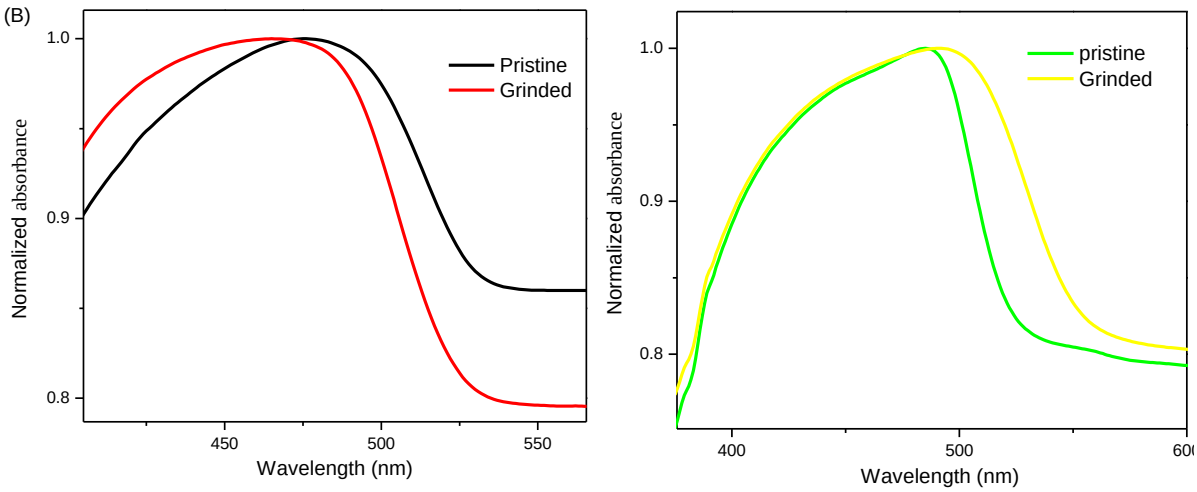


Fig. S7 Absorption spectra of **3a** (A) and **3b** (B) as Original and Grinded solids.

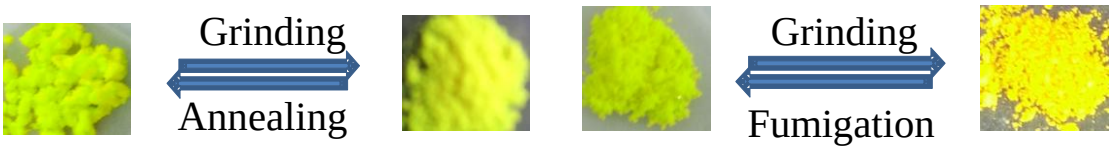


Fig. S8 The photographs taken under day light of **3a** (left) and **3b** (right).

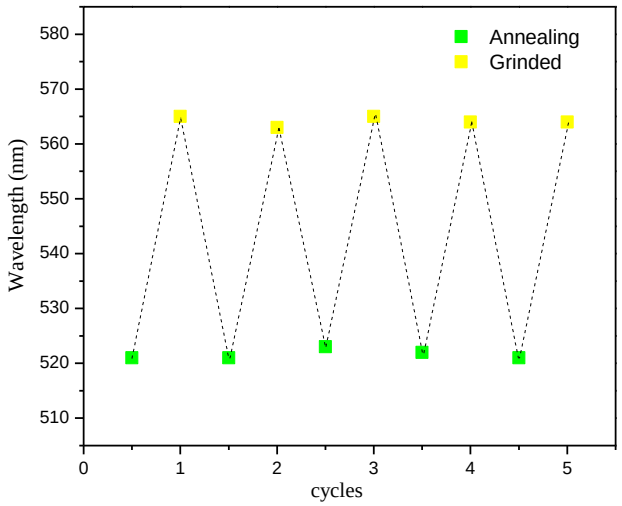


Fig. S9 Repeated switching of the solid-state fluorescence of **3b** by repeated grinding and fuming cycles.

DFT calculation data of 3a, and 3b:

Calculation method: B3LYP/6-31+G(d) with Gaussian 09

3a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-3.168325	2.274532	-0.475447
2	6	0	-3.523474	1.018927	-0.178912
3	6	0	-2.617260	-0.071245	0.074865
4	6	0	-3.220234	-1.280745	0.362079
5	1	0	-2.591848	-2.148365	0.539630
6	6	0	-4.628410	-1.463948	0.421865
7	1	0	-4.996974	-2.452646	0.678905
8	6	0	-5.541608	-0.454105	0.190775
9	6	0	-4.969419	0.830886	-0.114323
10	16	0	-4.556898	3.129871	-0.664688
11	7	0	-5.658956	1.948057	-0.374307
12	6	0	-1.145428	0.076517	0.050758
13	6	0	-0.489686	0.924103	-0.860447
14	6	0	-0.347640	-0.660567	0.945605
15	6	0	0.897920	1.015821	-0.879001
16	1	0	-1.072173	1.514874	-1.557069
17	6	0	1.039171	-0.574301	0.917659
18	1	0	-0.822878	-1.284516	1.697197
19	6	0	1.696333	0.256814	-0.005336
20	1	0	1.375869	1.683197	-1.590417
21	1	0	1.625049	-1.146669	1.629763
22	6	0	3.183308	0.390449	-0.016498
23	6	0	4.019793	-0.690874	-0.004736
24	6	0	3.683497	1.799345	-0.043907
25	6	0	3.144162	2.764755	0.824635
26	6	0	4.656951	2.211044	-0.970011
27	6	0	3.585736	4.086495	0.790700
28	1	0	2.375089	2.471469	1.533787
29	6	0	5.090508	3.535170	-1.012262
30	1	0	5.072452	1.484280	-1.661072
31	6	0	4.561289	4.477813	-0.128567
32	1	0	3.162795	4.812732	1.480045
33	1	0	5.840742	3.831486	-1.740829
34	1	0	4.900432	5.509816	-0.161132
35	6	0	5.487822	-0.573470	0.250932
36	6	0	6.411652	-1.235446	-0.577174
37	6	0	5.981969	0.148041	1.351000
38	6	0	7.781521	-1.151821	-0.333397
39	1	0	6.048149	-1.814810	-1.421272
40	6	0	7.351113	0.221766	1.602398
41	1	0	5.283192	0.651356	2.011845

42	6	0	8.257587	-0.422825	0.758356
43	1	0	8.477854	-1.661051	-0.994755
44	1	0	7.709753	0.781486	2.462369
45	1	0	9.325042	-0.363484	0.953633
46	6	0	3.538651	-2.084832	-0.250846
47	6	0	3.935598	-3.137469	0.592865
48	6	0	2.731152	-2.392479	-1.359190
49	6	0	3.512686	-4.444452	0.356215
50	1	0	4.577688	-2.923211	1.442676
51	6	0	2.318570	-3.701416	-1.603728
52	1	0	2.429980	-1.596208	-2.032814
53	6	0	2.702326	-4.732581	-0.744132
54	1	0	3.821558	-5.240079	1.029405
55	1	0	1.699485	-3.916102	-2.471020
56	1	0	2.379624	-5.752809	-0.934270
57	6	0	-7.001974	-0.697153	0.244386
58	6	0	-7.527488	-1.918928	-0.214362
59	6	0	-7.893910	0.252401	0.774263
60	6	0	-8.892067	-2.188579	-0.136036
61	1	0	-6.862001	-2.651663	-0.662018
62	6	0	-9.258210	-0.020654	0.853909
63	1	0	-7.513924	1.203798	1.126814
64	6	0	-9.764283	-1.240641	0.401895
65	1	0	-9.274957	-3.136375	-0.505257
66	1	0	-9.928706	0.724672	1.273584
67	1	0	-10.829310	-1.448136	0.461801

Total Energy (HF) = - 1971.3872002 Hartree

Data for **3b**:

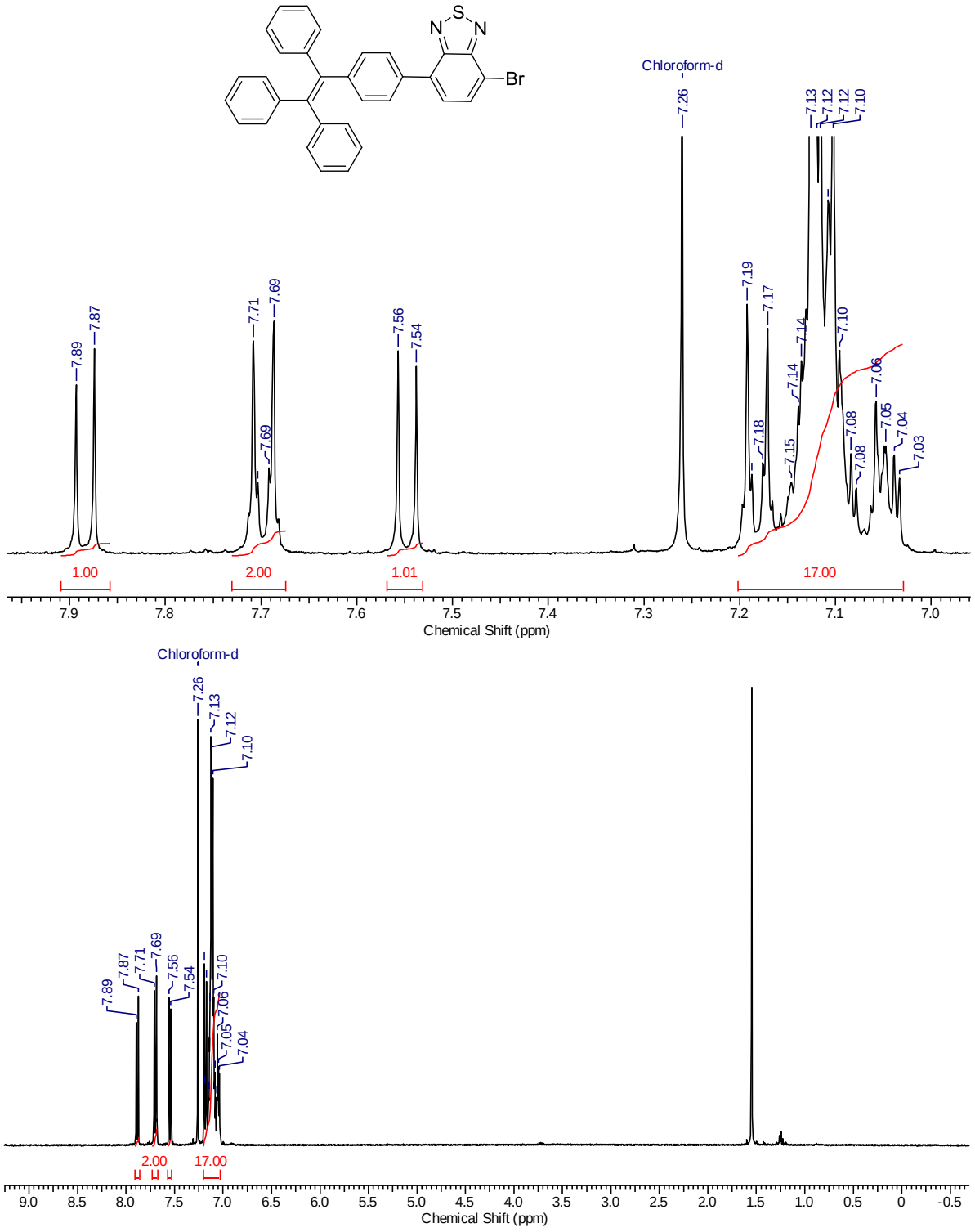
Standard orientation:

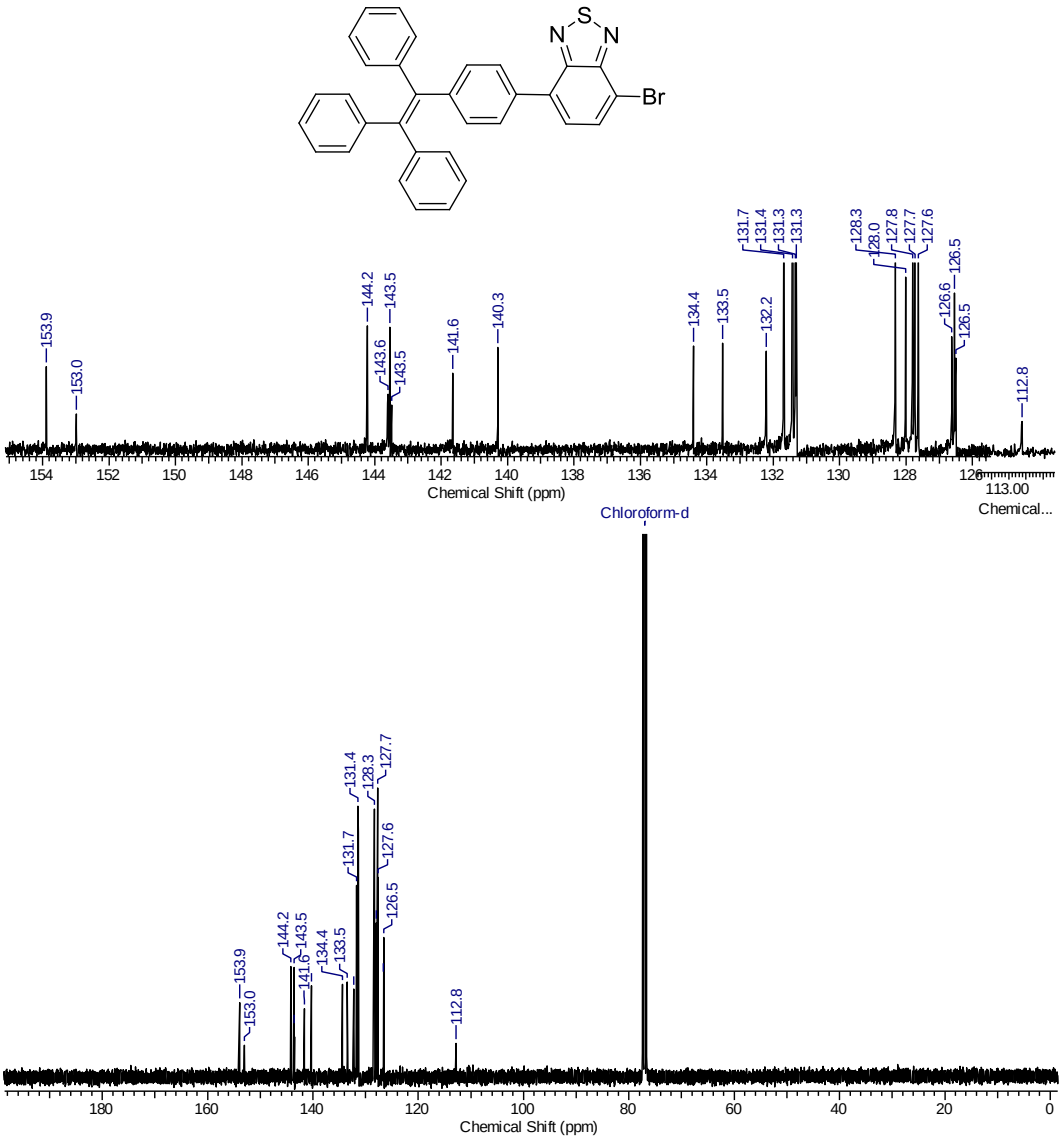
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.616365	2.423859	-0.493964
2	6	0	-3.009429	1.175707	-0.214645
3	6	0	-2.136323	0.057395	0.035182
4	6	0	-2.775626	-1.137815	0.306423
5	1	0	-2.174179	-2.024576	0.480856
6	6	0	-4.188038	-1.280893	0.350861
7	1	0	-4.585457	-2.261467	0.595693
8	6	0	-5.069246	-0.241646	0.122252
9	6	0	-4.459965	1.030214	-0.162816
10	16	0	-3.975851	3.322291	-0.682566
11	7	0	-5.114485	2.170032	-0.414024
12	6	0	-0.661656	0.162854	0.024222
13	6	0	0.025369	1.003769	-0.870041

14	6	0	0.106854	-0.610541	0.914420
15	6	0	1.415024	1.053908	-0.877503
16	1	0	-0.533398	1.620562	-1.563474
17	6	0	1.495415	-0.564077	0.898296
18	1	0	-0.391738	-1.230473	1.654139
19	6	0	2.184091	0.259713	-0.008602
20	1	0	1.917758	1.716095	-1.576416
21	1	0	2.058289	-1.162833	1.607056
22	6	0	3.674107	0.350416	-0.007369
23	6	0	4.479610	-0.754211	0.004000
24	6	0	4.214865	1.744558	-0.022024
25	6	0	3.703214	2.717677	0.854605
26	6	0	5.201773	2.134857	-0.943007
27	6	0	4.184245	4.025852	0.833146
28	1	0	2.925257	2.441128	1.560870
29	6	0	5.675112	3.445669	-0.972519
30	1	0	5.596767	1.401832	-1.639446
31	6	0	5.172732	4.395745	-0.081164
32	1	0	3.782599	4.758267	1.528618
33	1	0	6.435474	3.725790	-1.696909
34	1	0	5.542974	5.417232	-0.103716
35	6	0	5.948397	-0.679150	0.270535
36	6	0	6.859141	-1.361577	-0.555400
37	6	0	6.454091	0.021032	1.379045
38	6	0	8.228949	-1.318063	-0.301113
39	1	0	6.485841	-1.925035	-1.405969
40	6	0	7.822809	0.054181	1.641059
41	1	0	5.764909	0.539582	2.038170
42	6	0	8.716979	-0.610050	0.799146
43	1	0	8.915649	-1.842252	-0.960772
44	1	0	8.190671	0.597694	2.507457
45	1	0	9.784149	-0.582104	1.002622
46	6	0	3.961616	-2.132650	-0.253519
47	6	0	4.322083	-3.199851	0.588337
48	6	0	3.154300	-2.412033	-1.369410
49	6	0	3.863911	-4.493099	0.342417
50	1	0	4.963476	-3.007930	1.443974
51	6	0	2.706649	-3.707676	-1.623232
52	1	0	2.881973	-1.604688	-2.042198
53	6	0	3.054289	-4.753097	-0.765494
54	1	0	4.144953	-5.300225	1.014041
55	1	0	2.089145	-3.901038	-2.496626
56	1	0	2.704643	-5.762941	-0.963084
57	6	0	-6.534737	-0.443589	0.164169
58	6	0	-7.090907	-1.658149	-0.281427
59	6	0	-7.407291	0.540155	0.666760
60	6	0	-8.457868	-1.893850	-0.216409
61	1	0	-6.444798	-2.417592	-0.710562
62	6	0	-8.776231	0.313450	0.737107
63	1	0	-7.007188	1.487614	1.005094
64	6	0	-9.315086	-0.907355	0.298469
65	1	0	-8.870484	-2.832646	-0.571626

66	1	0	-9.435850	1.078113	1.134566
67	6	0	-10.726839	-1.142847	0.368923
68	7	0	-11.872885	-1.335940	0.427508

Total Energy (HF) = - 2063.6309771 Hartree


N
S
N
Br
Chloroform-d
7.26
7.89
7.87
7.71
7.69
7.56
7.54
7.19
7.17
7.14
7.13
7.12
7.12
7.10
7.18
7.15
7.10
7.08
7.08
7.06
7.05
7.04
7.03
1.00
2.00
1.01
17.00
Chemical Shift (ppm)
Chloroform-d
7.26
7.13
7.12
7.10
7.89
7.87
7.71
7.69
7.56
7.54
7.10
7.06
7.05
7.04
2.00
17.00
Chemical Shift (ppm)


N
S
N
Br
153.9
153.0
144.2
143.5
143.6
143.5
141.6
140.3
134.4
133.5
132.2
131.7
131.4
131.3
131.3
128.3
128.0
127.8
127.7
127.6
126.6
126.5
126.5
112.8
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
Chemical Shift (ppm)
113.00
Chemical...
Chloroform-d
153.9
153.0
144.2
143.5
141.6
134.4
133.5
131.7
131.4
128.3
127.7
127.6
126.5
112.8
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

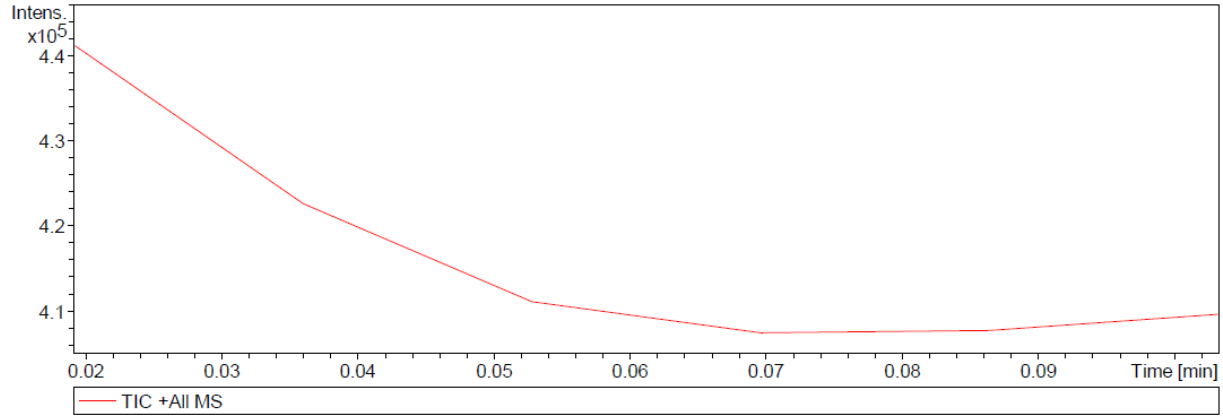
Display Report

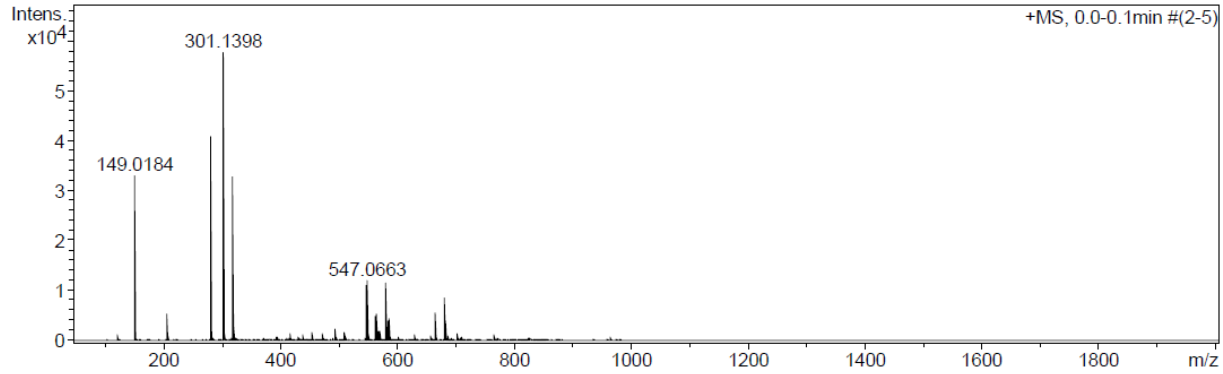
Analysis Info

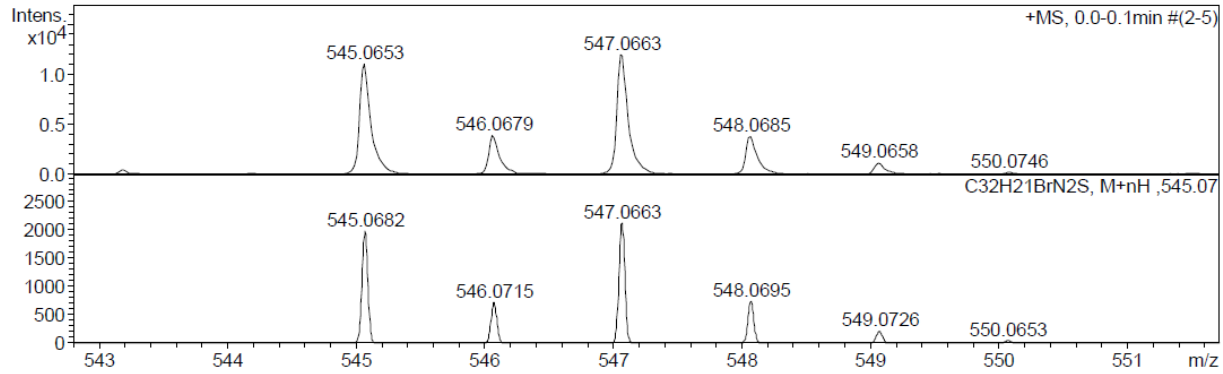
Analysis Name	D:\Data\May 2014\rm-tj-03-122_.d	Acquisition Date	5/7/2014 3:56:11 PM
Method	tune_low.m	Operator	Ghanashyam Bhavsar
Sample Name	rm-tj-03-122_	Instrument	micrOTOF-Q II 10348
Comment			

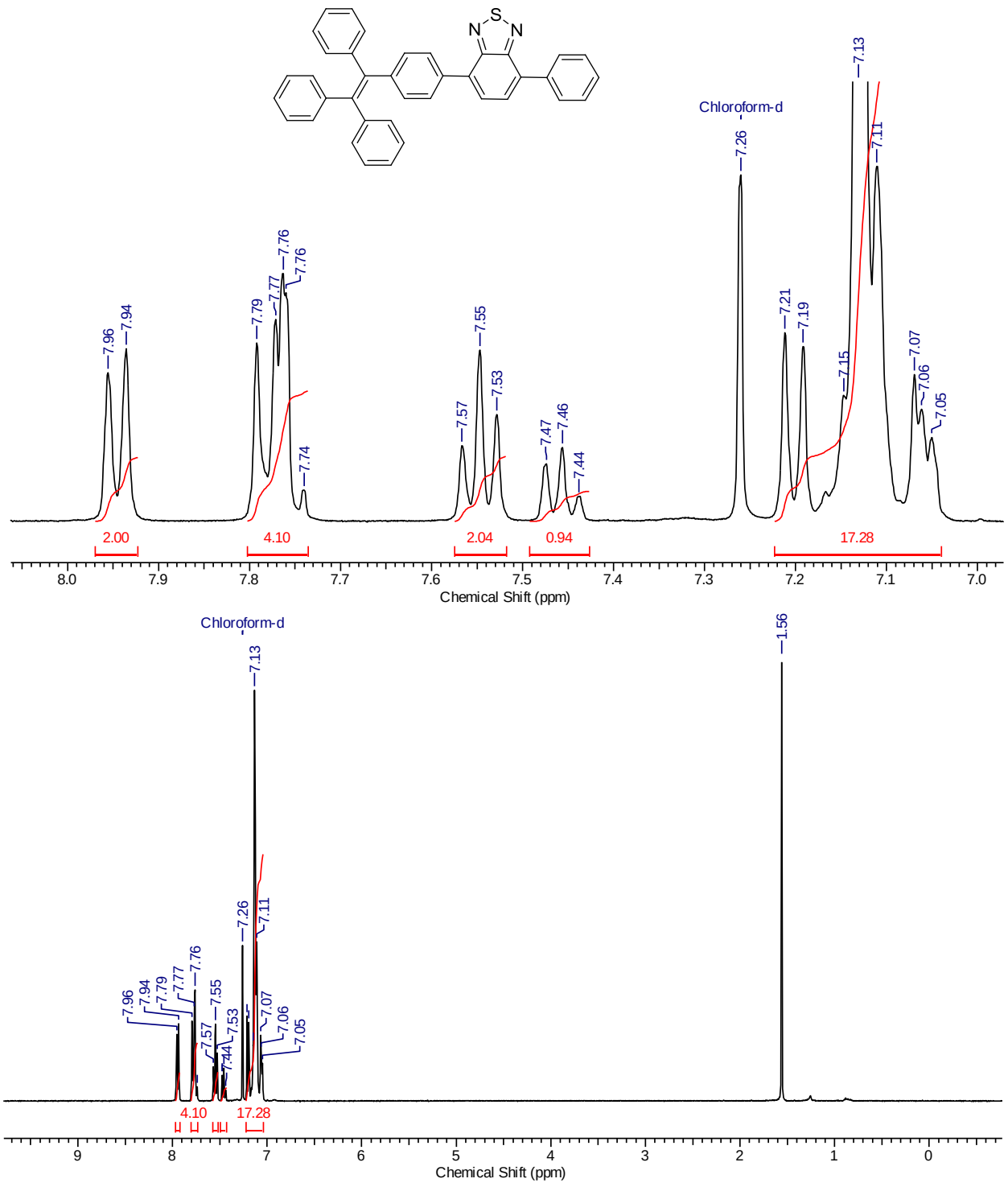
Acquisition Parameter

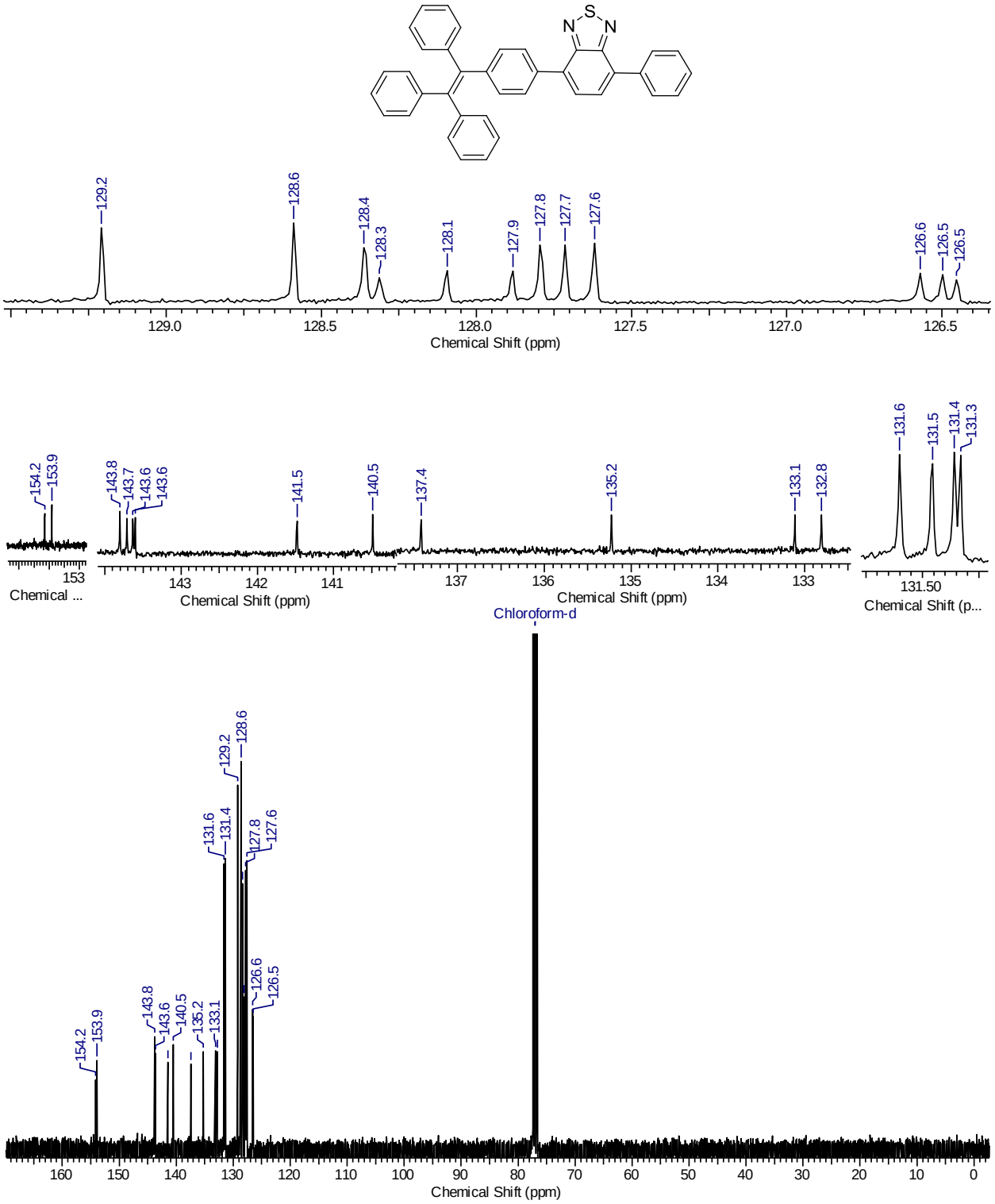
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste








Chloroform-d
7.96
7.94
7.79
7.77
7.76
7.76
7.74
7.57
7.55
7.53
7.47
7.46
7.44
7.26
7.21
7.19
7.15
7.13
7.11
7.07
7.06
7.05
2.00
4.10
2.04
0.94
17.28
Chemical Shift (ppm)
Chloroform-d
1.56
4.10
17.28
Chemical Shift (ppm)


N
S
N
129.2
128.6
128.4
128.3
128.1
127.9
127.8
127.7
127.6
126.6
126.5
126.5
129.0
128.5
128.0
127.5
127.0
126.5
Chemical Shift (ppm)
154.2
153.9
143.8
143.7
143.6
143.6
141.5
140.5
137.4
135.2
133.1
132.8
131.6
131.5
131.4
131.3
153
Chemical ...
143
142
141
137
136
135
134
133
Chemical Shift (ppm)
131.50
Chemical Shift (p...
Chloroform-d
129.2
128.6
131.6
131.4
127.8
127.6
126.6
126.5
143.8
143.6
140.5
135.2
133.1
154.2
153.9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

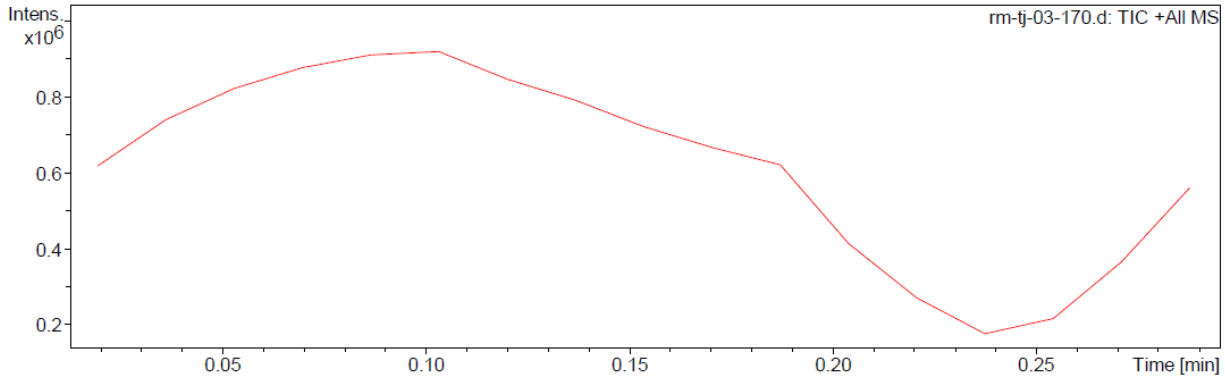
Display Report

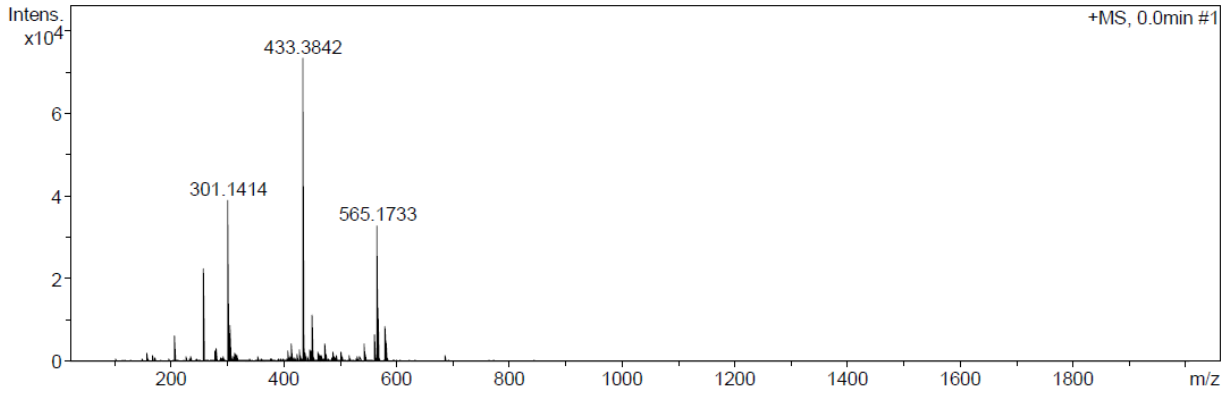
Analysis Info

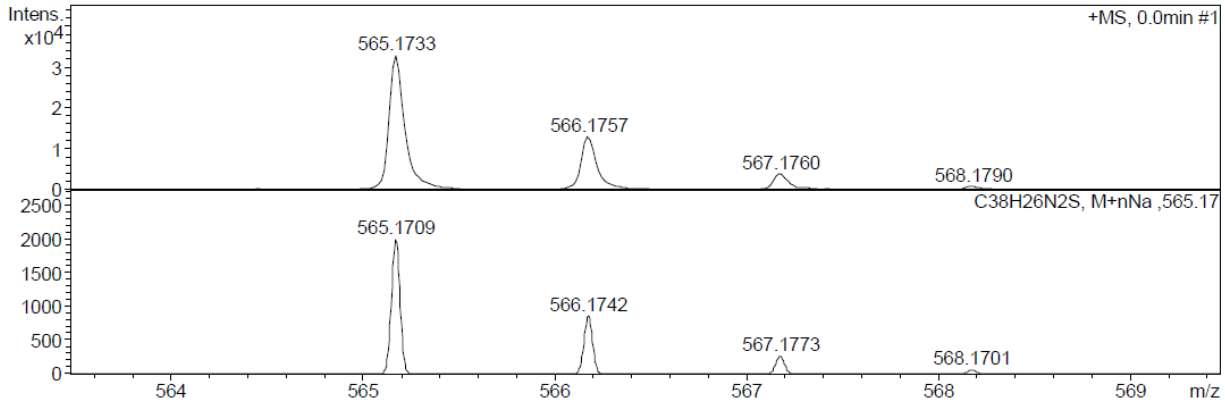
Analysis Name	D:\Data\February 2015\rm-tj-03-170.d	Acquisition Date	2/17/2015 3:50:22 PM
Method	tune_low.m	Operator	Ghanashyam Bhavsar
Sample Name	1	Instrument	micrOTOF-Q II 10348
Comment			

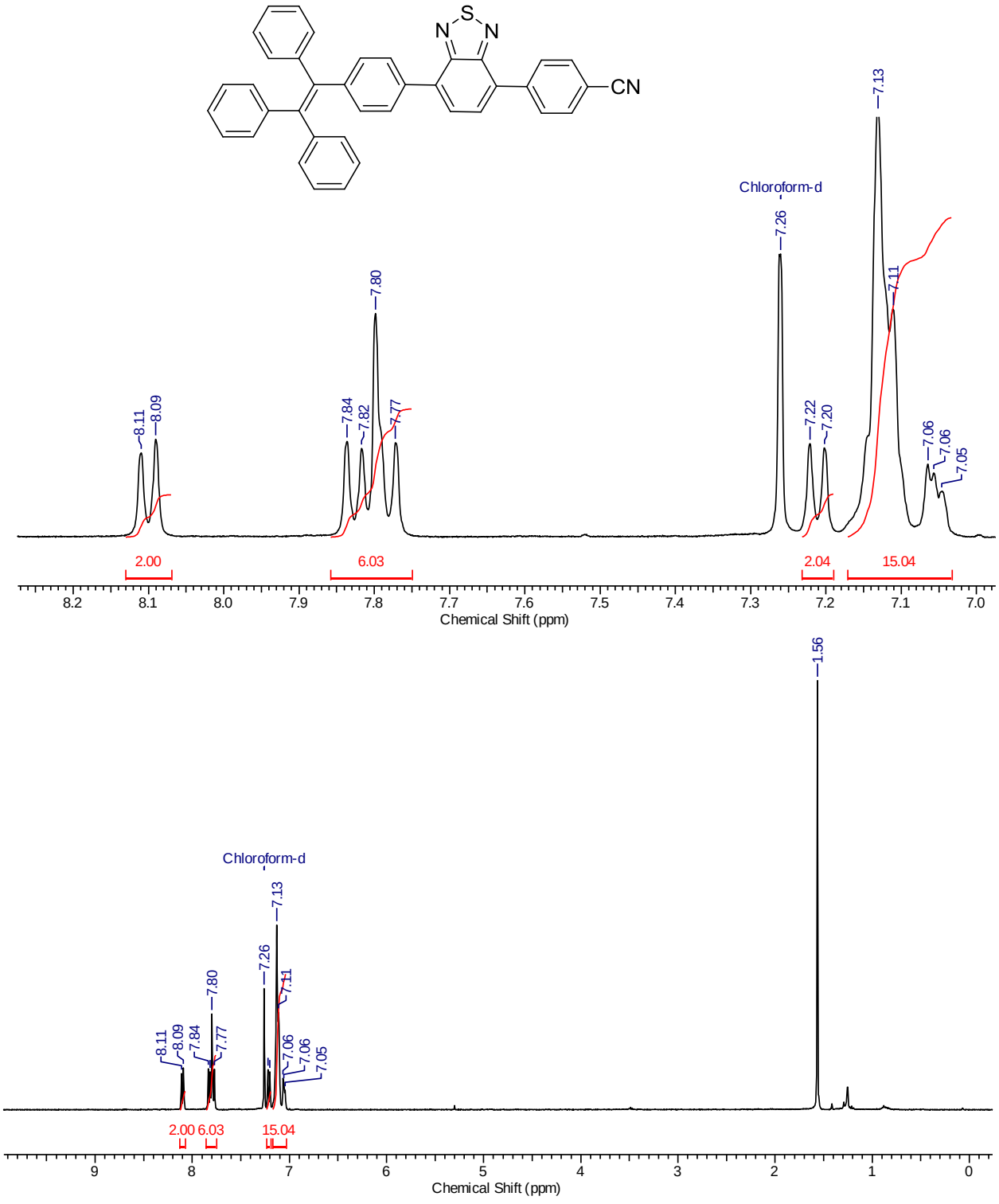
Acquisition Parameter

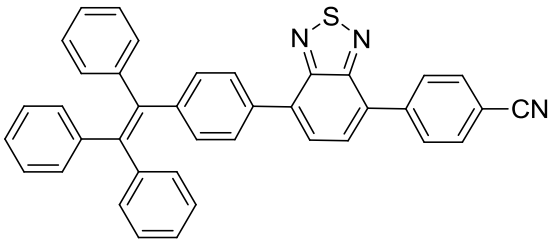
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	21 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Waste

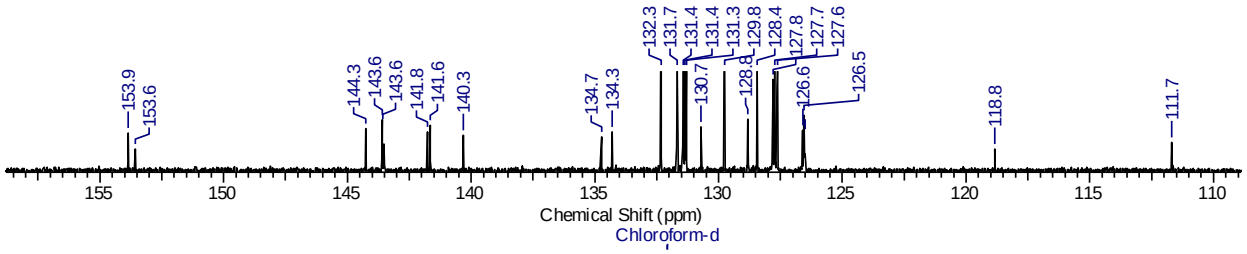


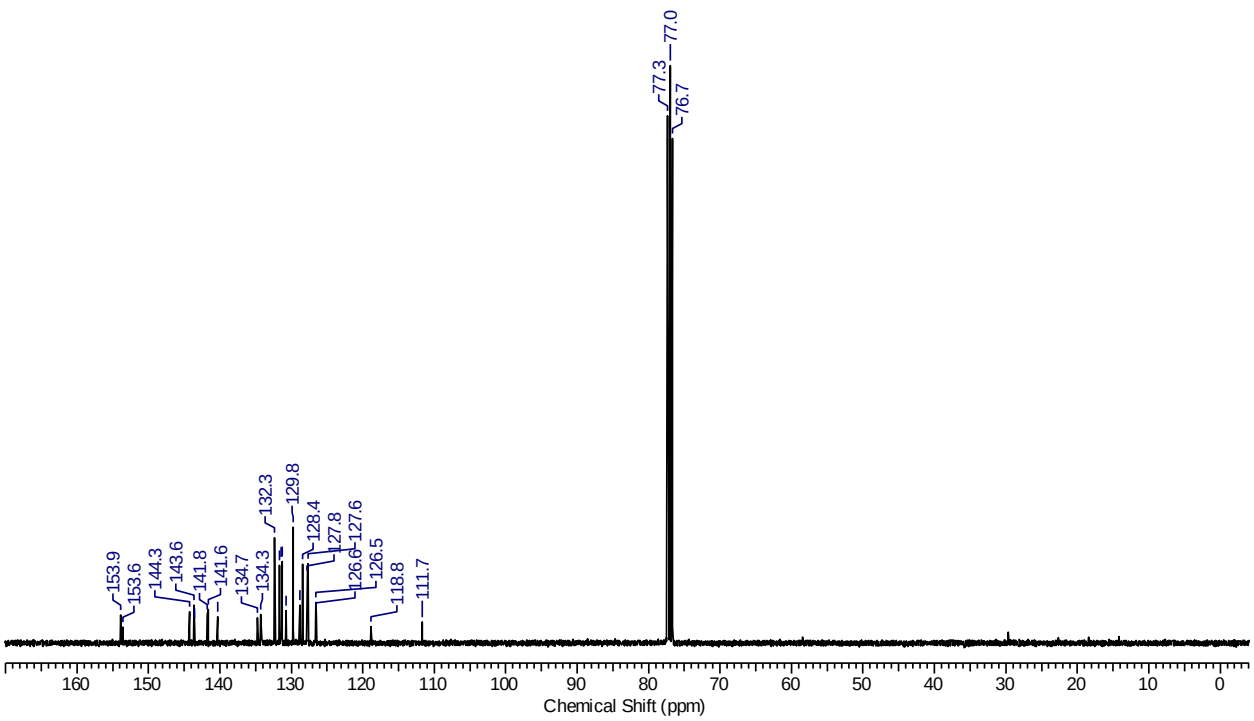





N
S
N
CN
Chloroform-d
8.11
8.09
7.84
7.82
7.80
7.77
7.26
7.22
7.20
7.13
7.11
7.06
7.06
7.05
2.00
6.03
2.04
15.04
Chemical Shift (ppm)
1.56
Chloroform-d
7.13
7.26
7.11
7.80
8.11
8.09
7.84
7.77
7.06
7.06
7.05
2.00
6.03
15.04
Chemical Shift (ppm)


S
N
N
CN


153.9
153.6
144.3
143.6
143.6
141.8
141.6
140.3
134.7
134.3
132.3
131.7
131.4
131.4
131.3
129.8
128.4
127.8
127.7
127.6
126.6
126.5
118.8
111.7
155
150
145
140
135
130
125
120
115
110
Chemical Shift (ppm)


Chloroform-d
77.3
77.0
76.7
153.9
153.6
144.3
143.6
141.8
141.6
134.7
134.3
132.3
129.8
128.4
127.8
127.6
126.6
126.5
118.8
111.7
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

Display Report

Analysis Info

Analysis Name	D:\Data\February 2015\rm-tj-03-173.d	Acquisition Date	2/18/2015 1:35:14 PM
Method	tune_wide.m	Operator	Ghanashyam Bhavsar
Sample Name	1	Instrument	micrOTOF-Q II 10348
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	21 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste