Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Mechanochromism and aggregation induced emission in benzothiazole substituted tetraphenylethylenes: A structure function correlation

Thaksen Jadhav, Bhausaheb Dhokale, Shaikh M. Mobin and Rajneesh Misra*

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

rajneeshmisra@iiti.ac.in

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Crystallographic data

A single crystal X-ray structural study of 3a was performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). 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 F^2. 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 1.2U_{eq} of their parent atoms. The crystal, and refinement data are summarized in Table 1. The CCDC number 1044877 and 1044876 contain the supplementary crystallographic data for **3a** and **3b**. 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 S1. Crystal data and structure refinement for 3a and 3b.

Parameter	**3a**	**3b**
Identification code	rm139	Rm131
Empirical formula	C_{78} H_{56} N_2 S_2	$C_{19.50}$ $H_{13.50}$ $N_{0.50}$ $S_{0.50}$
Formula weight	1085.37	270.84
Temperature	150(2) K	150(2) K
Wavelength(A)	1.5418 A	0.71073
Crystal system, space group	Monoclinic, P 21	Triclinic, P -1
***a*/ (Å)**	8.02640(10)	9.0713(8)

***b*/ (Å)**	25.9353(4)	11.7240(11)
***c*/ (Å)**	14.2385(2)	13.8730(7)
α/(°)	90	91.129(6)
β/ (°)	91.7070(10)	101.715(6)
γ/ (°)	90	97.624(7)
Volume	2962.67(7) $Å^3$	1430.3(2) $Å^3$
Z, Calculated density (mg m^{-3})	2, 1.217	4, 1.258
Absorption coefficient /(mm^{-1})	1.170	0.142
F(000)	1140	568
Crystal size	0.23 x 0.18 x 0.15 mm	0.33 x 0.26 x 0.21 mm
θ range for data collection/(°)	3.11 to 71.34	2.89 to 25.00
Reflections collected / unique	20224 / 10538 [R(int) = 0.0218]	10829 / 5037 [R(int) = 0.0485]
Completeness to theta	θ = 71.34 98.9 %	θ = 25.00; 99.8 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8440 and 0.7746	0.9708 and 0.9546
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10538 / 1 / 740	5037 / 0 / 370
Goodness-of-fit on F^2	1.024	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1283	R1 = 0.0521, wR2 = 0.1326
R indices (all data)	R1 = 0.0486, wR2 = 0.1330	R1 = 0.0822, wR2 = 0.1583
Largest diff. peak and hole ($eÅ^{-3}$)	0.212 and -0.326	0.326 and -0.375

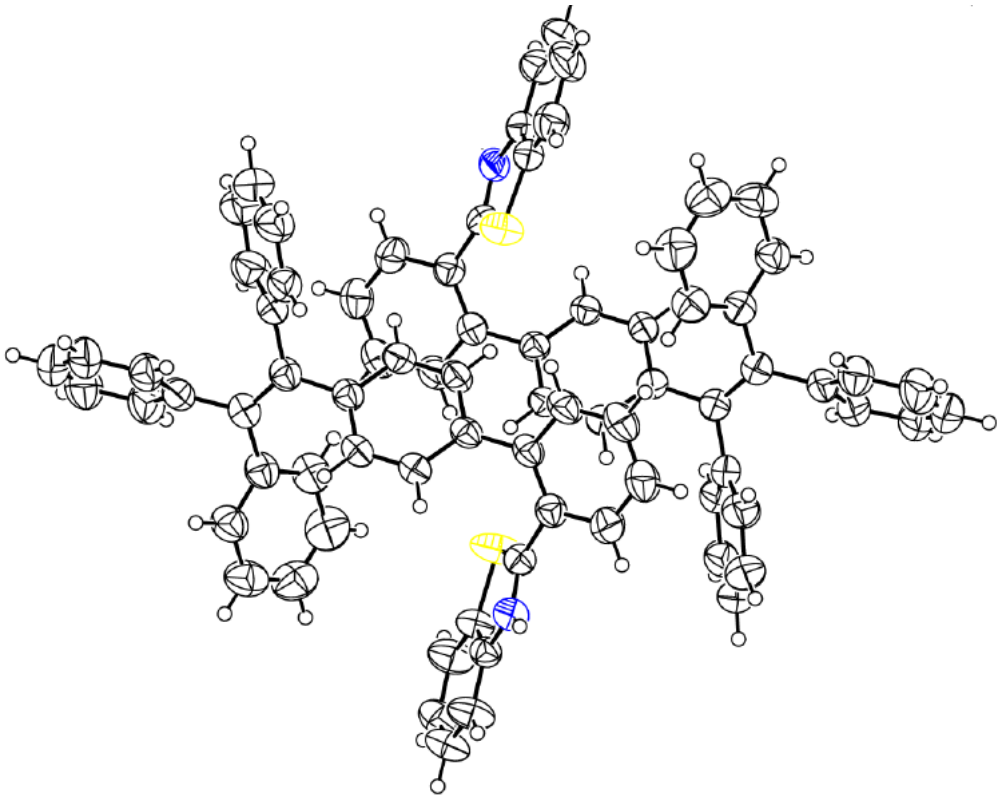


Fig. S1 Crystal structure of **3a.**

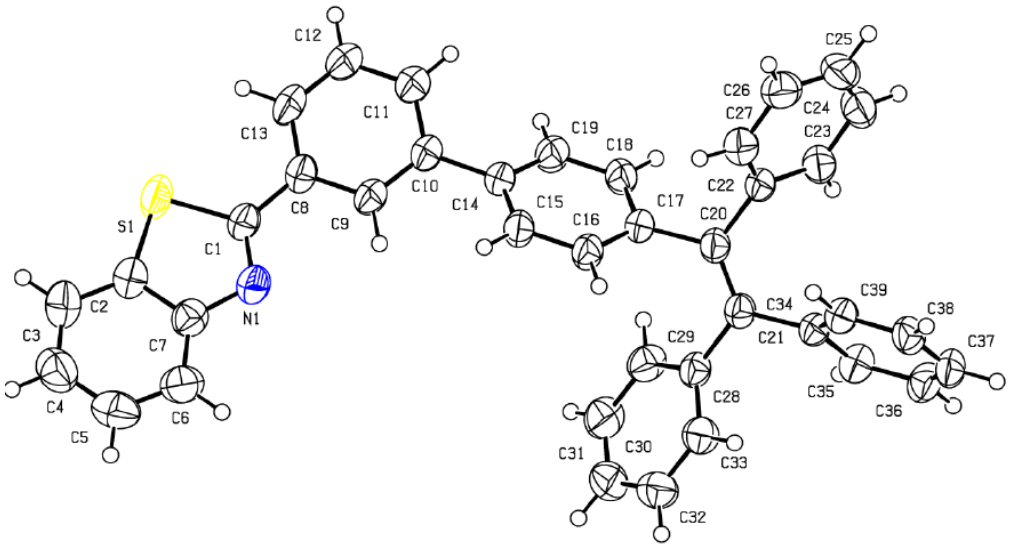


Fig. S2 Crystal structure of **3b.**

Thermogravimetric analysis:

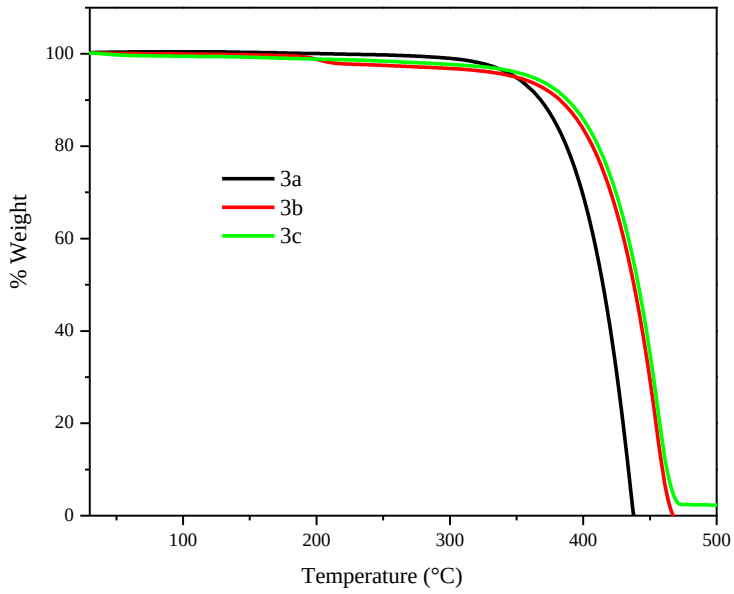


Fig. S3 TGA plots of the BT-TPEs **3a–3c** with the heating rate of 10 °C min^{-1} under N_2 atmosphere.

Photophysical properties:

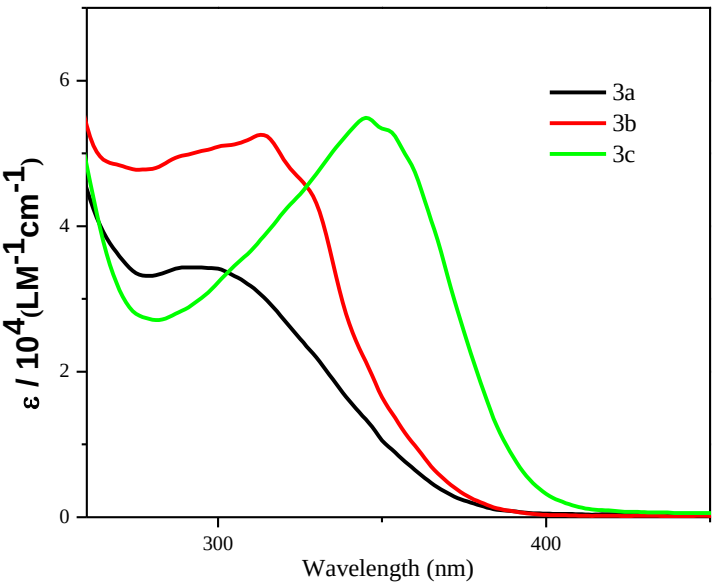


Fig. S4 Electronic absorption spectra of the BT-TPEs **3a–3c** in tetrahydrofuran.

Table S2. Photophysical and thermal properties of the BT-TPEs **3a–3c**.

BT-TPEs	λ_{max}[nm] (ε[Lmol^{-1}cm^{-1}]) [a]	Optical band gap (eV)	HOMO-LUMO gap (eV)[b]	T_d (°C)
3a	298 (34332)	3.35	3.80	349
3b	313 (52540)	3.31	3.55	349
3c	345 (54898)	3.15	3.70	361

[a] Measured in tetrahydrofuran. [b] Theoretical values at B3LYP/6-31G(d) level.

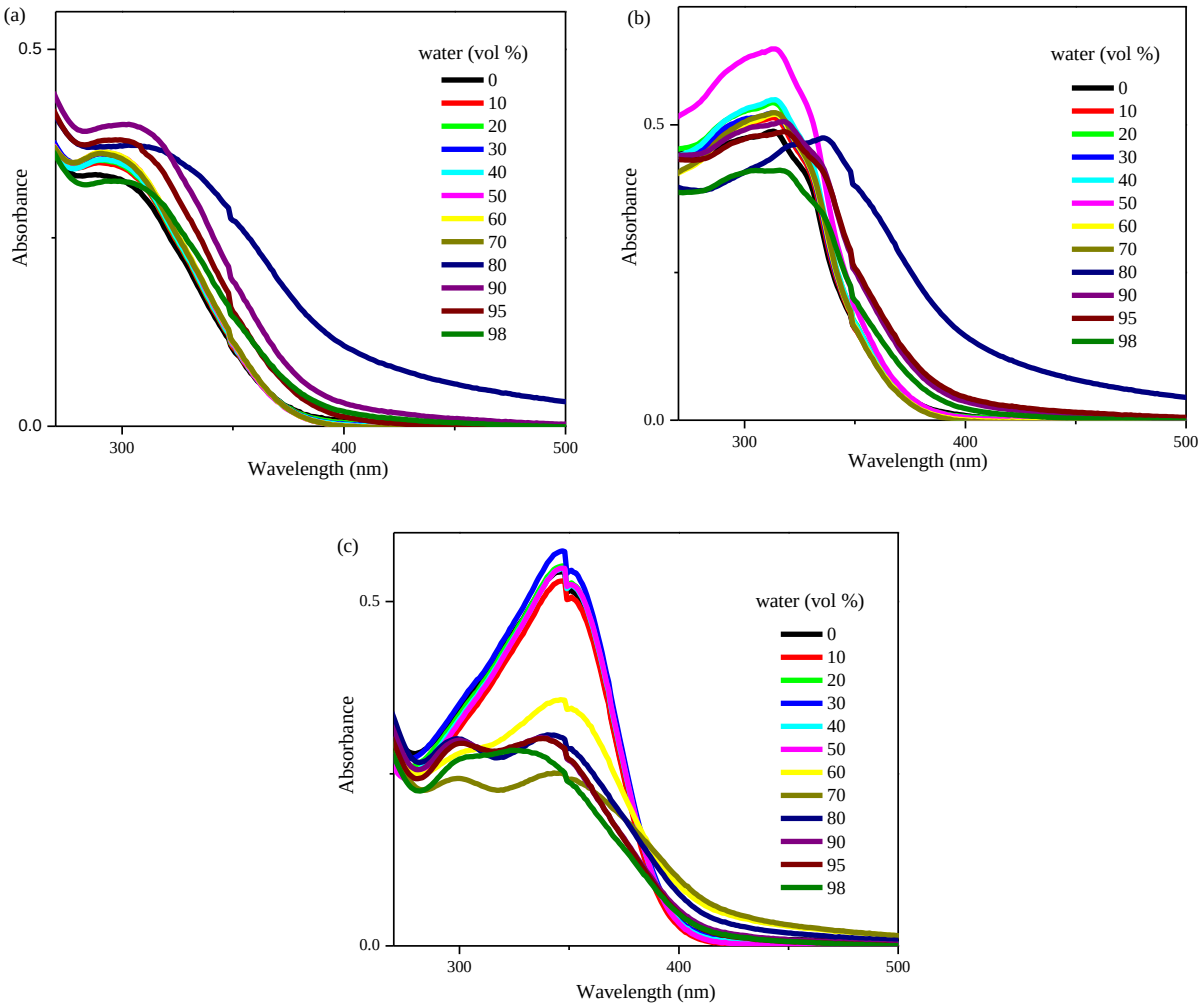


Fig. S5 UV-vis absorption spectra of BT-TPEs **3a–3c** in THF–water mixtures with different water fractions.

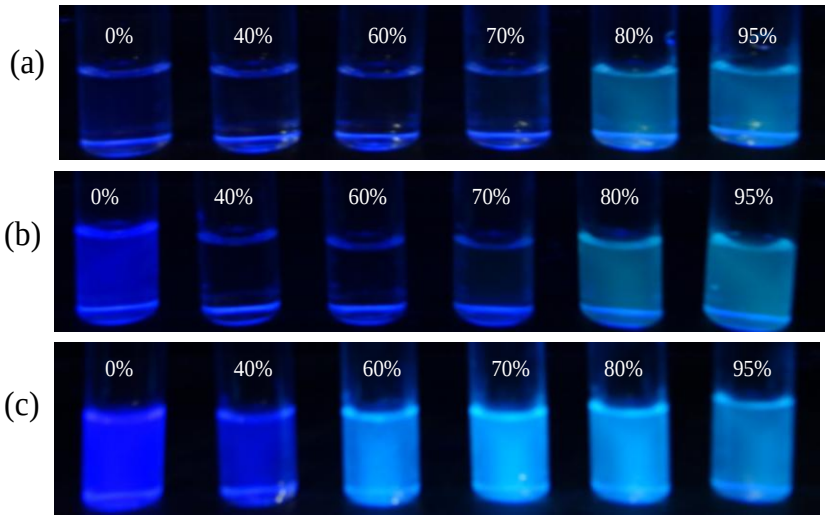


Fig. S6 Photographs of **3a** (a), **3b** (b) and **3c** (c) in THF–water mixtures with different water fractions (10 μM) under 365 nm UV illumination.

Mechanochromic property:

Table S3. Peak absorption wavelengths (λ, in nm) of **3a–3c** under various external stimuli.

BT-TPEs	$\lambda_{Pristine}$ (nm)	$\lambda_{Grinded}$ (nm)
3a	447	443
3b	398,444	455
3c	420	436

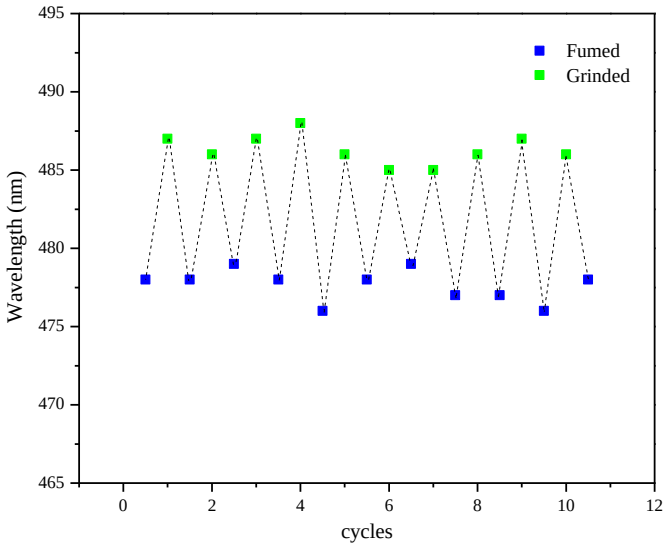


Fig. S7 Repeated switching of the solid-state fluorescence of **3a** by repeated grinding and fuming cycles.

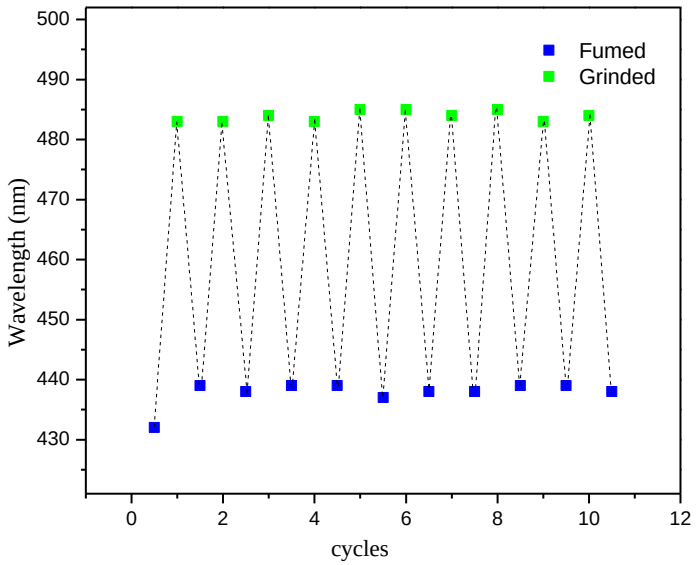


Fig. S8 Repeated switching of the solid-state fluorescence of **3b** by repeated grinding and fuming cycles.

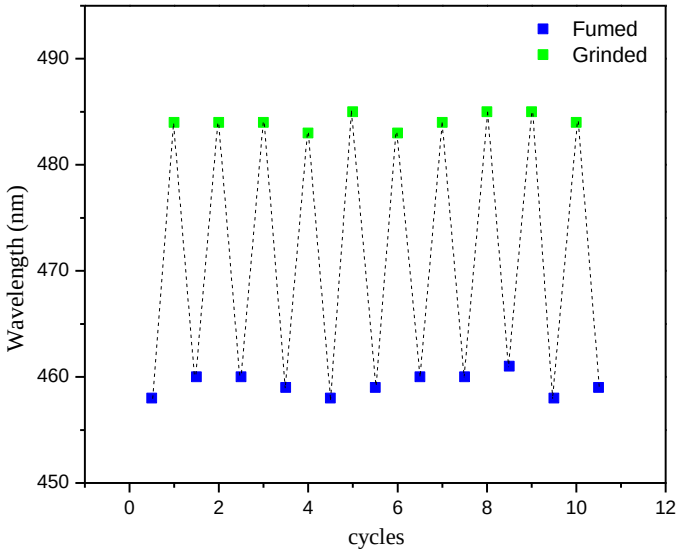


Fig. S9 Repeated switching of the solid-state fluorescence of **3c** by repeated grinding and fuming cycles.

DFT calculation:
DFT calculation data of **3a-3c**:

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	6	0	4.059587	-1.714436	-0.761245
2	6	0	5.073959	-1.949875	0.200625
3	6	0	5.549424	-3.238664	0.455157
4	6	0	4.998777	-4.295909	-0.264709
5	6	0	3.994249	-4.075050	-1.223550
6	6	0	3.521451	-2.793901	-1.478026
7	6	0	4.346778	0.393395	-0.134829
8	1	0	6.326458	-3.414847	1.192807
9	1	0	5.353758	-5.306286	-0.081744
10	1	0	3.585313	-4.918628	-1.772559
11	1	0	2.749329	-2.605070	-2.217175
12	7	0	3.682949	-0.393094	-0.920017
13	16	0	5.543071	-0.426300	0.923949
14	6	0	4.203605	1.862064	-0.076968
15	6	0	5.368889	2.645766	-0.045763
16	6	0	2.936247	2.496799	-0.110549
17	6	0	5.307011	4.036079	-0.077047
18	1	0	6.335783	2.150698	-0.034619
19	6	0	2.900577	3.899048	-0.156891
20	6	0	4.064577	4.665397	-0.144118
21	1	0	6.222807	4.620051	-0.061783
22	1	0	3.998444	5.749624	-0.173352
23	1	0	1.931884	4.390473	-0.171196
24	6	0	1.644250	1.759742	-0.045422
25	6	0	1.370008	0.857698	0.994258
26	6	0	0.639407	1.996081	-0.994386
27	6	0	0.143903	0.207040	1.071075
28	1	0	2.124510	0.667933	1.752826
29	6	0	-0.589826	1.347112	-0.915318
30	1	0	0.835187	2.673307	-1.821478
31	6	0	-0.868032	0.443481	0.122984
32	1	0	-0.038118	-0.493828	1.880810
33	1	0	-1.342981	1.534305	-1.674104
34	6	0	-2.160788	-0.302541	0.184217
35	6	0	-3.374936	0.307088	0.031486
36	6	0	-2.019530	-1.772493	0.419241
37	6	0	-3.542812	1.791974	0.071961
38	6	0	-4.639873	-0.457914	-0.191995
39	6	0	-2.778388	-2.431706	1.401346
40	6	0	-1.072225	-2.522666	-0.300230

41	6	0	-4.306510	2.452034	-0.907136
42	6	0	-2.996363	2.559587	1.114654
43	6	0	-5.799580	-0.153526	0.542758
44	6	0	-4.723351	-1.455687	-1.178128
45	6	0	-2.612278	-3.795005	1.640052
46	1	0	-3.500767	-1.865935	1.981337
47	6	0	-0.912374	-3.887803	-0.068562
48	1	0	-0.457656	-2.027077	-1.046355
49	6	0	-4.488661	3.833343	-0.864066
50	1	0	-4.754714	1.873305	-1.709918
51	6	0	-3.188487	3.939415	1.165100
52	1	0	-2.419606	2.064735	1.889893
53	6	0	-6.990055	-0.844514	0.322623
54	1	0	-5.761201	0.629015	1.295472
55	6	0	-5.916743	-2.138850	-1.406979
56	1	0	-3.843220	-1.692036	-1.768019
57	6	0	-1.682337	-4.530728	0.902737
58	1	0	-3.207393	-4.281900	2.408362
59	1	0	-0.177906	-4.447518	-0.641899
60	6	0	-3.930656	4.583621	0.173142
61	1	0	-5.071990	4.323634	-1.639296
62	1	0	-2.761308	4.511574	1.984722
63	6	0	-7.054131	-1.840609	-0.654047
64	1	0	-7.870494	-0.600865	0.911794
65	1	0	-5.958475	-2.903192	-2.178700
66	1	0	-1.552497	-5.593428	1.089805
67	1	0	-4.079503	5.659506	0.212236
68	1	0	-7.984009	-2.374414	-0.831633

Total Energy (HF) = -1955.3674904 Hartree

3b:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.655634	-0.207407	-1.547265
2	6	0	-7.829563	-0.021051	-0.775864
3	6	0	-9.093208	0.015229	-1.369045
4	6	0	-9.173373	-0.137582	-2.751185
5	6	0	-8.016447	-0.323238	-3.528373
6	6	0	-6.759279	-0.359448	-2.938473
7	6	0	-5.672853	-0.063050	0.440063
8	1	0	-9.989595	0.158120	-0.773269
9	1	0	-10.146332	-0.112528	-3.233838
10	1	0	-8.108873	-0.439685	-4.604455
11	1	0	-5.857122	-0.502135	-3.524870
12	7	0	-5.473523	-0.224914	-0.832836
13	16	0	-7.389920	0.138100	0.911545
14	6	0	-4.597974	-0.036910	1.442199
15	6	0	-4.860770	0.083355	2.815352
16	6	0	-3.266827	-0.128230	1.005388

17	6	0	-3.806009	0.111039	3.724495
18	1	0	-5.883023	0.150488	3.177385
19	6	0	-2.198040	-0.103147	1.909839
20	1	0	-3.082428	-0.195904	-0.060865
21	6	0	-2.488386	0.018242	3.281004
22	1	0	-4.013504	0.194967	4.787625
23	1	0	-1.677061	0.014022	4.002992
24	6	0	-0.796384	-0.200075	1.430011
25	6	0	-0.454499	-1.029333	0.348507
26	6	0	0.235322	0.528079	2.045488
27	6	0	0.860128	-1.124921	-0.096114
28	1	0	-1.223778	-1.627532	-0.131725
29	6	0	1.547718	0.442795	1.591634
30	1	0	0.004007	1.189800	2.875712
31	6	0	1.888862	-0.377100	0.503113
32	1	0	1.097461	-1.790617	-0.921050
33	1	0	2.321868	1.024883	2.081534
34	6	0	3.300274	-0.504012	0.030373
35	6	0	4.094390	0.580385	-0.217088
36	6	0	3.772168	-1.911087	-0.153550
37	6	0	3.555995	1.973237	-0.292191
38	6	0	5.568651	0.468696	-0.437485
39	6	0	4.404078	-2.320386	-1.340079
40	6	0	3.539705	-2.877340	0.841161
41	6	0	4.192080	3.022378	0.394801
42	6	0	2.442070	2.282753	-1.090991
43	6	0	6.181010	1.135600	-1.513456
44	6	0	6.387757	-0.251606	0.448517
45	6	0	4.807225	-3.643025	-1.517353
46	1	0	4.576210	-1.592962	-2.127196
47	6	0	3.953372	-4.197384	0.669523
48	1	0	3.034412	-2.585367	1.757603
49	6	0	3.711129	4.328134	0.312846
50	1	0	5.067677	2.806270	1.000616
51	6	0	1.967961	3.590517	-1.182994
52	1	0	1.948877	1.488855	-1.643259
53	6	0	7.557969	1.057334	-1.715428
54	1	0	5.567228	1.714775	-2.197693
55	6	0	7.766488	-0.319958	0.254036
56	1	0	5.935527	-0.758607	1.295207
57	6	0	4.589076	-4.586373	-0.511402
58	1	0	5.289580	-3.937459	-2.445840
59	1	0	3.774178	-4.924281	1.457611
60	6	0	2.596571	4.618099	-0.477102
61	1	0	4.210918	5.121293	0.863057
62	1	0	1.107458	3.806957	-1.810729
63	6	0	8.357384	0.329382	-0.831655
64	1	0	8.007698	1.570335	-2.561696
65	1	0	8.380646	-0.879015	0.955278
66	1	0	4.904926	-5.617051	-0.649378
67	1	0	2.225539	5.637151	-0.547396
68	1	0	9.432081	0.274483	-0.983757

Total Energy (HF) = -1955.3775369 Hartree

3c:

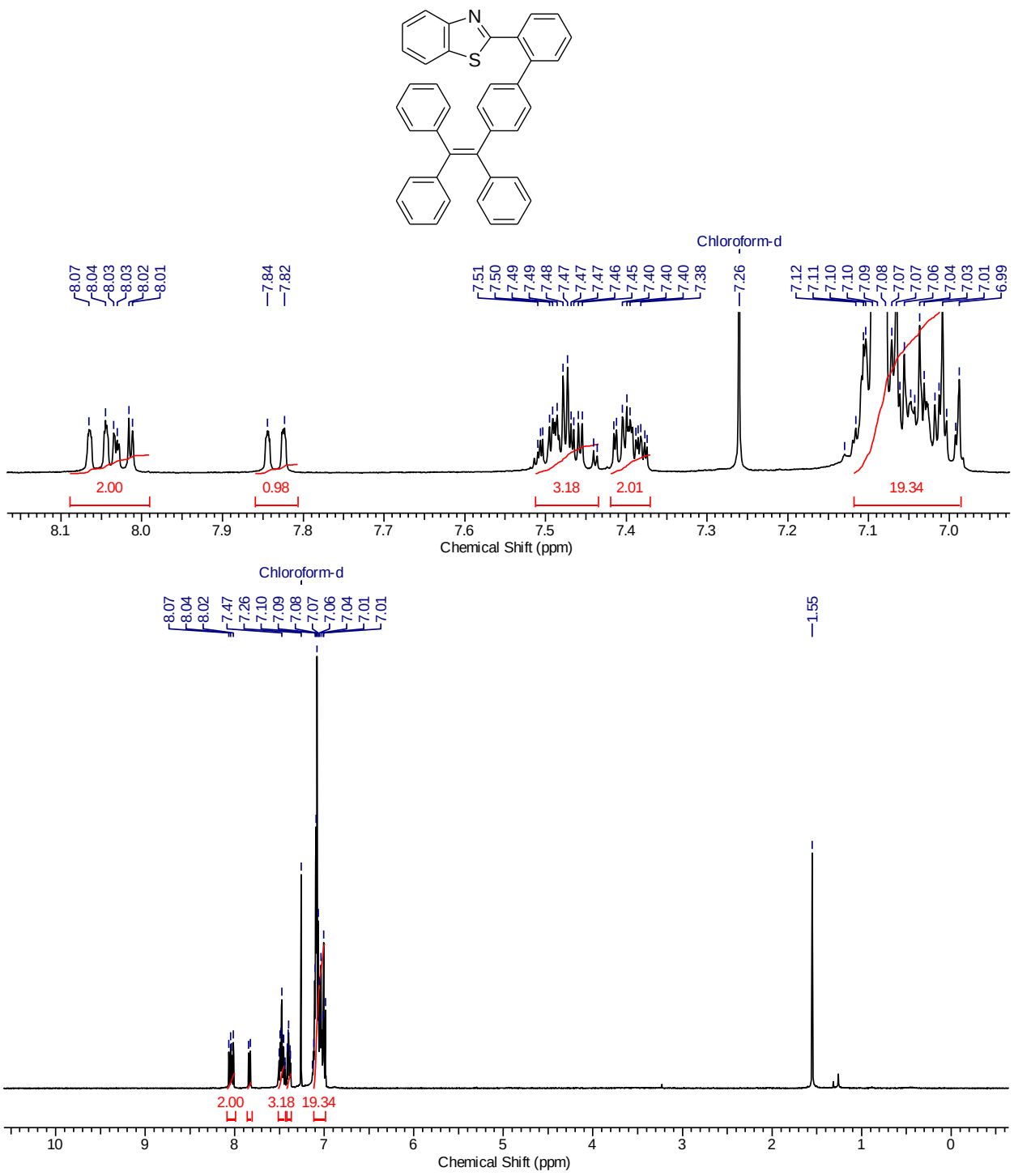
Standard orientation:

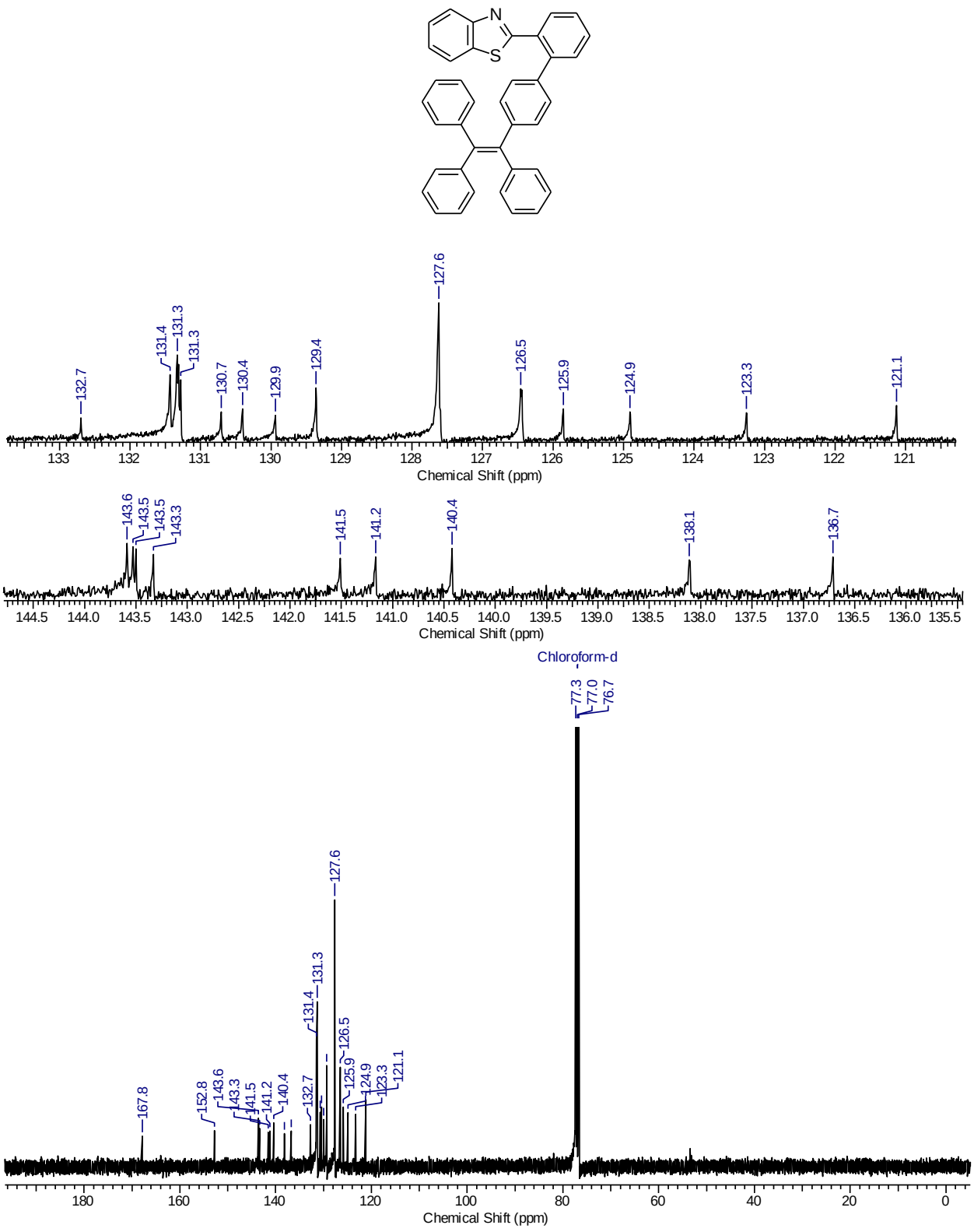
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.413942	-0.046682	-0.708056
2	6	0	-8.749418	0.010613	0.667756
3	6	0	-10.078538	0.066219	1.091951
4	6	0	-11.077673	0.064196	0.121310
5	6	0	-10.758828	0.008259	-1.246898
6	6	0	-9.436604	-0.047084	-1.669261
7	6	0	-6.342210	-0.085966	0.093937
8	1	0	-10.330051	0.109817	2.147307
9	1	0	-12.118688	0.106681	0.429108
10	1	0	-11.558450	0.008226	-1.982202
11	1	0	-9.174685	-0.090906	-2.721698
12	7	0	-7.062578	-0.099624	-0.987331
13	16	0	-7.279945	-0.003237	1.619696
14	6	0	-4.876871	-0.135152	0.101739
15	6	0	-4.128361	-0.112533	1.289115
16	6	0	-4.185924	-0.208719	-1.121272
17	6	0	-2.739703	-0.163299	1.256132
18	1	0	-4.630613	-0.064766	2.251850
19	6	0	-2.799251	-0.259407	-1.148263
20	1	0	-4.758774	-0.216596	-2.042149
21	6	0	-2.041646	-0.238540	0.038092
22	1	0	-2.187498	-0.172631	2.191128
23	1	0	-2.288992	-0.289341	-2.106639
24	6	0	-0.561687	-0.295618	0.004182
25	6	0	0.114067	-1.071192	-0.954085
26	6	0	0.217456	0.415473	0.933209
27	6	0	1.503174	-1.134398	-0.978786
28	1	0	-0.456893	-1.658855	-1.667437
29	6	0	1.606904	0.363804	0.898574
30	1	0	-0.271078	1.037055	1.678406
31	6	0	2.283030	-0.404466	-0.064374
32	1	0	1.996035	-1.761850	-1.715891
33	1	0	2.181239	0.930499	1.624487
34	6	0	3.773159	-0.501943	-0.083929
35	6	0	4.585578	0.595453	-0.021508
36	6	0	4.072965	1.989167	-0.194439
37	6	0	4.445879	3.004016	0.704578
38	6	0	3.256644	2.335819	-1.284522
39	6	0	3.990607	4.311029	0.538818
40	1	0	5.094345	2.759714	1.541320
41	6	0	2.811607	3.645468	-1.457954
42	1	0	2.974127	1.569784	-2.000041

43	6	0	3.171339	4.637742	-0.544019
44	1	0	4.280556	5.076623	1.253897
45	1	0	2.185243	3.891462	-2.311517
46	1	0	2.822350	5.658146	-0.678187
47	6	0	6.056974	0.497570	0.223004
48	6	0	6.962454	1.217592	-0.576370
49	6	0	6.571328	-0.264147	1.286058
50	6	0	8.334903	1.151863	-0.341832
51	1	0	6.582501	1.828417	-1.390543
52	6	0	7.942864	-0.319684	1.529113
53	1	0	5.886575	-0.813429	1.924638
54	6	0	8.831398	0.383117	0.713016
55	1	0	9.017201	1.706437	-0.980951
56	1	0	8.317337	-0.911116	2.360632
57	1	0	9.900743	0.337918	0.901547
58	6	0	4.304746	-1.896446	-0.180965
59	6	0	5.278175	-2.241916	-1.133636
60	6	0	3.795276	-2.913564	0.645637
61	6	0	5.740466	-3.552556	-1.242223
62	1	0	5.670616	-1.473969	-1.792829
63	6	0	4.265476	-4.221997	0.545459
64	1	0	3.027567	-2.670624	1.375050
65	6	0	5.240502	-4.547448	-0.399755
66	1	0	6.490322	-3.797268	-1.990055
67	1	0	3.866090	-4.989311	1.203670
68	1	0	5.602141	-5.568825	-0.483892

Total Energy (HF) = -1955.3784339 Hartree

Copies of NMR and HRMS spectra of the new compounds:




N
S
132.7
131.4
131.3
131.3
130.7
130.4
129.9
129.4
127.6
126.5
125.9
124.9
123.3
121.1
Chemical Shift (ppm)
143.6
143.5
143.5
143.3
141.5
141.2
140.4
138.1
136.7
Chemical Shift (ppm)
Chloroform-d
77.3
77.0
76.7
167.8
152.8
143.6
143.3
141.5
141.2
140.4
132.7
131.4
131.3
127.6
126.5
125.9
124.9
123.3
121.1
Chemical Shift (ppm)

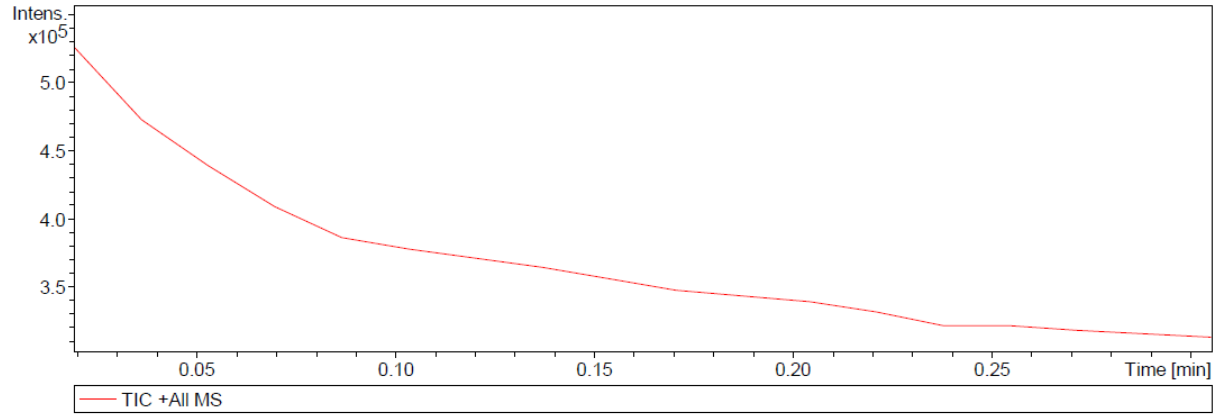
Display Report

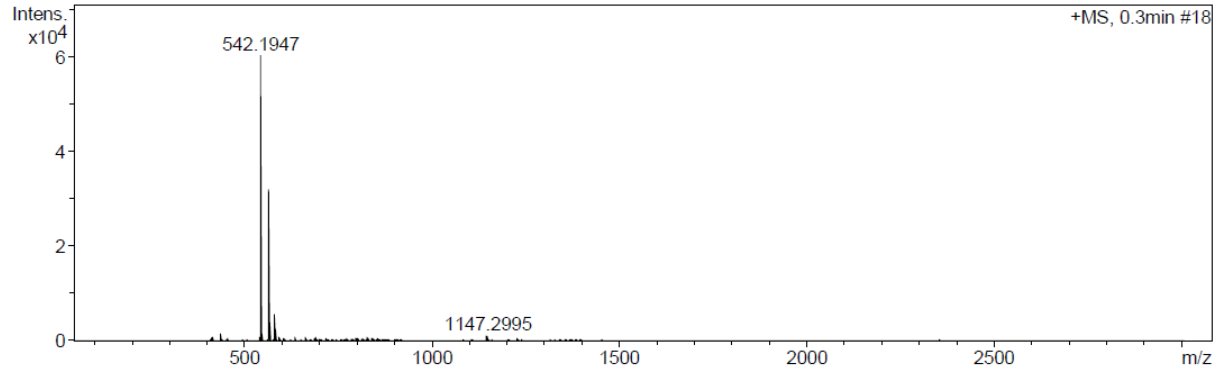
Analysis Info

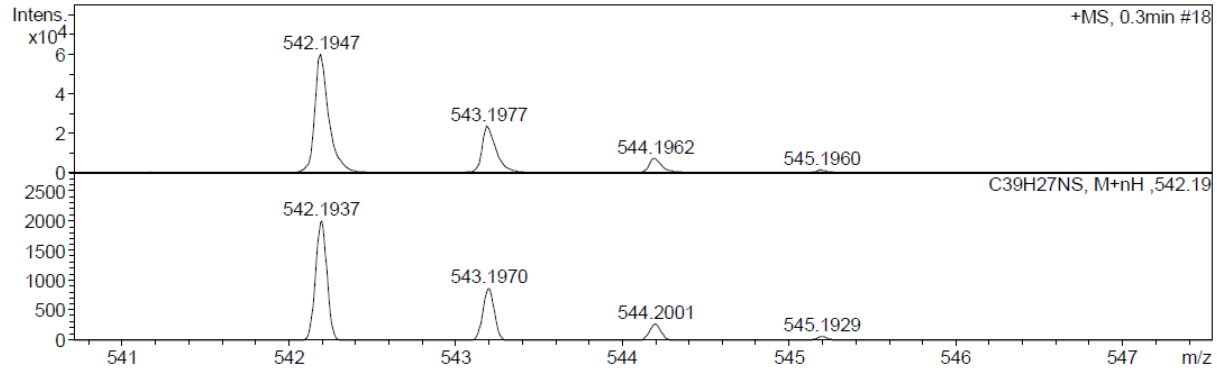
Analysis Name	D:\Data\May 2014\rm-tj-03-126.d	Acquisition Date	5/13/2014 4:06:48 PM
Method	tune_wide.m	Operator	Ghanashyam Bhavsar
Sample Name	rm-tj-03-126	Instrument	micrOTOF-Q II 10348
Comment			

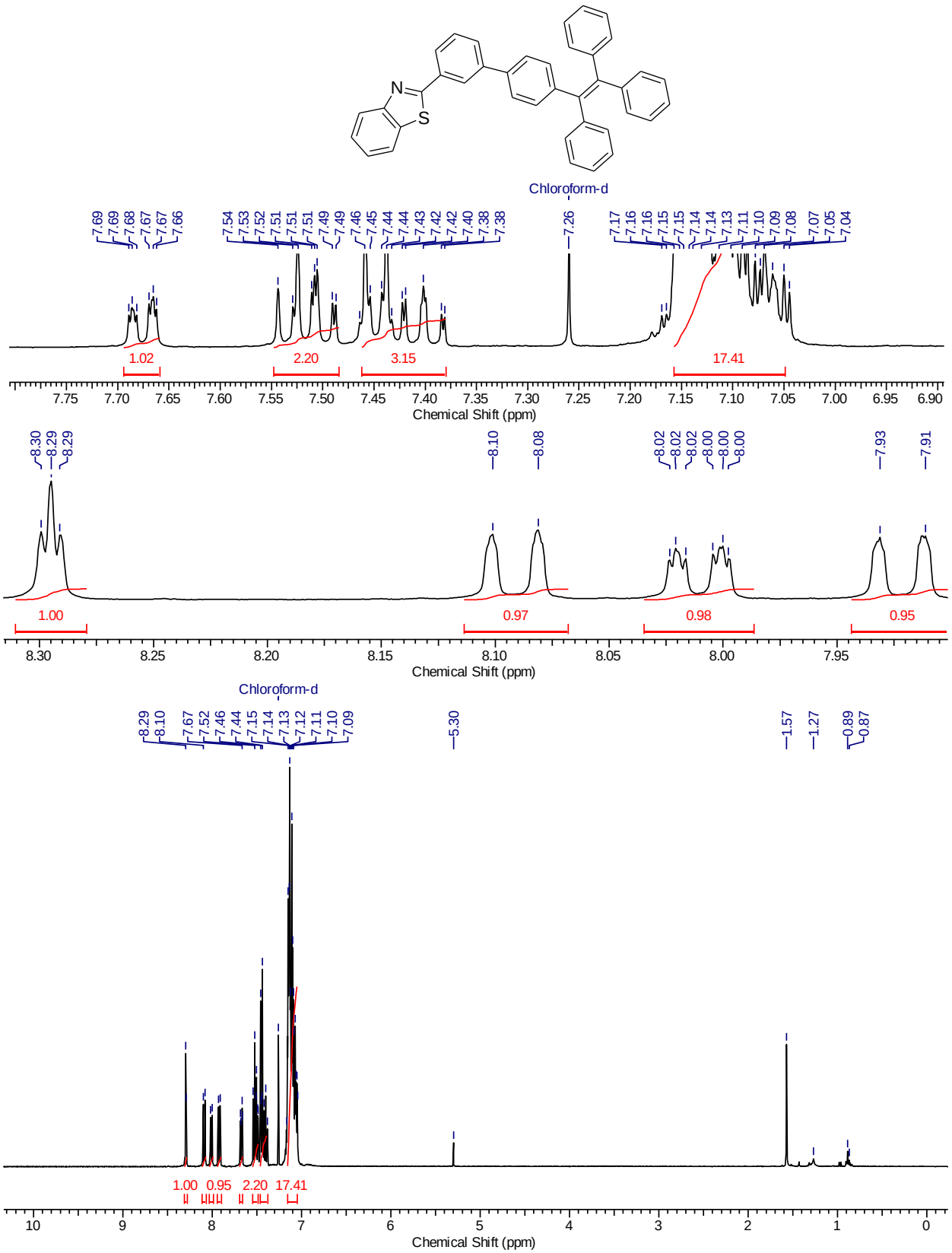
Acquisition Parameter

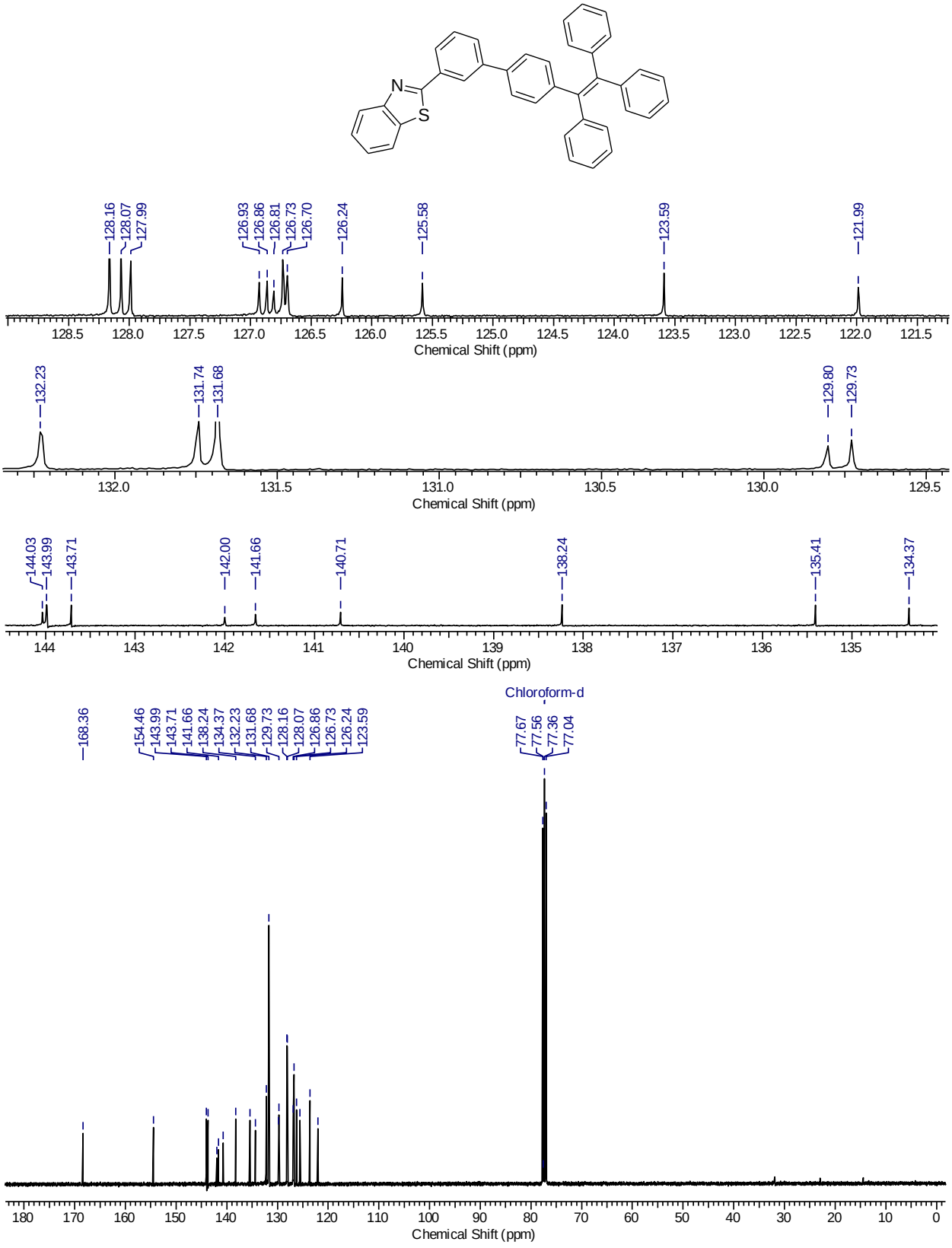
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	650.0 Vpp	Set Divert Valve	Waste

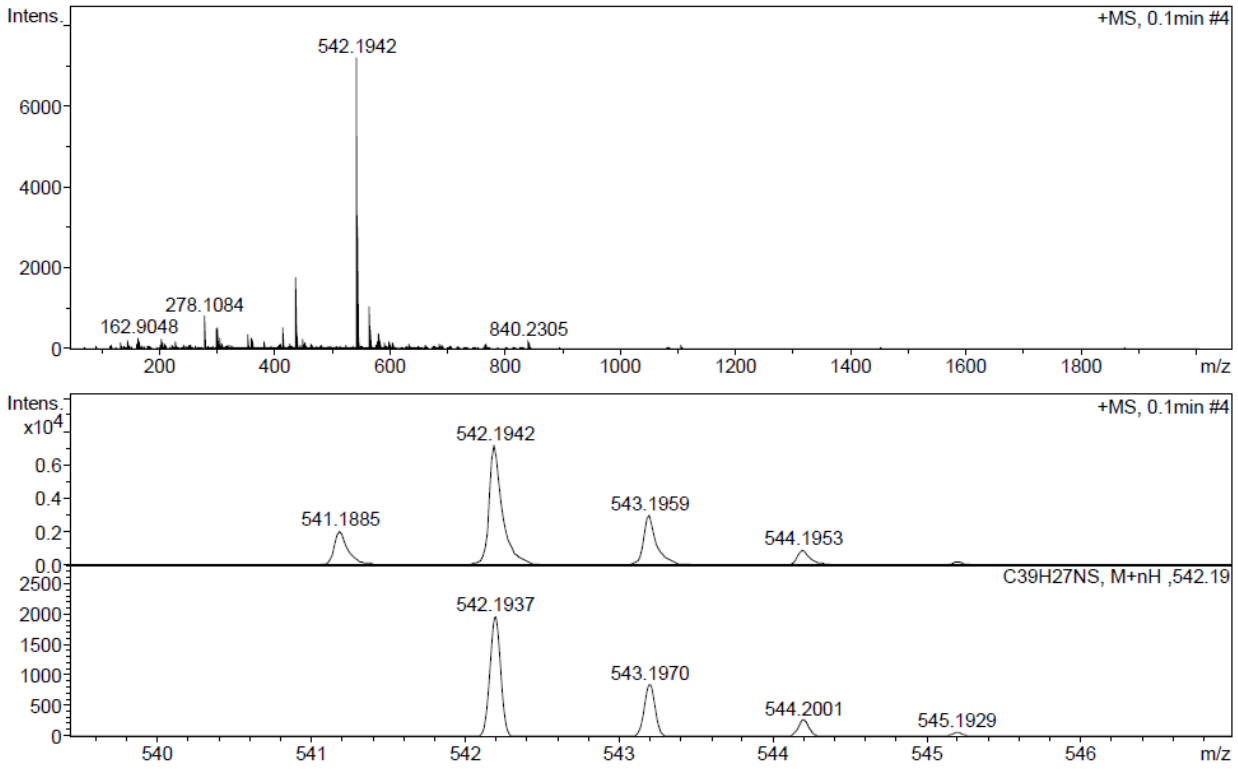


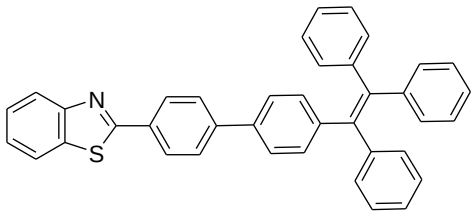


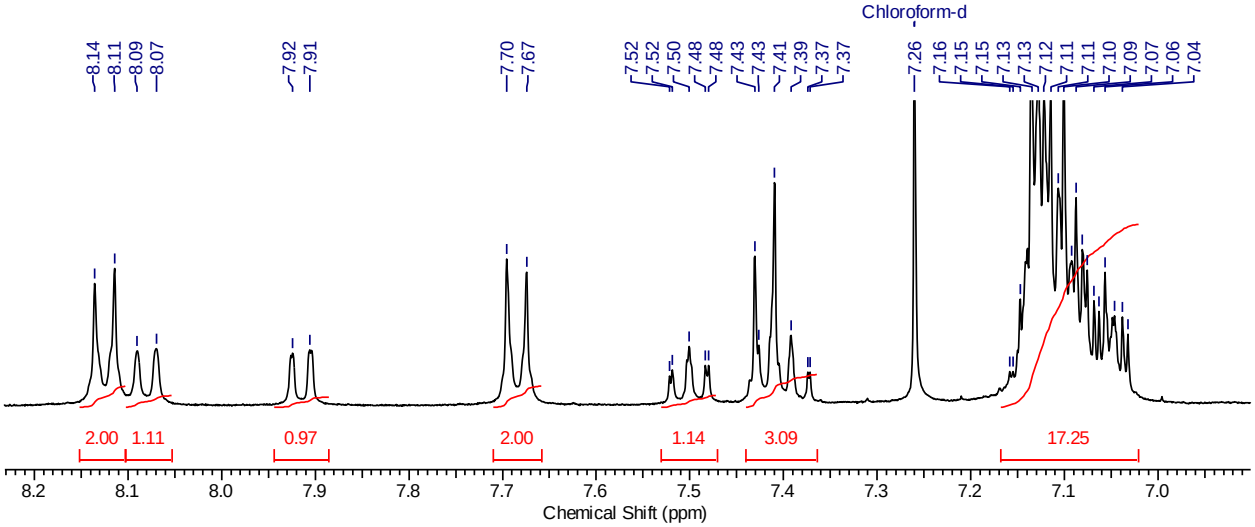


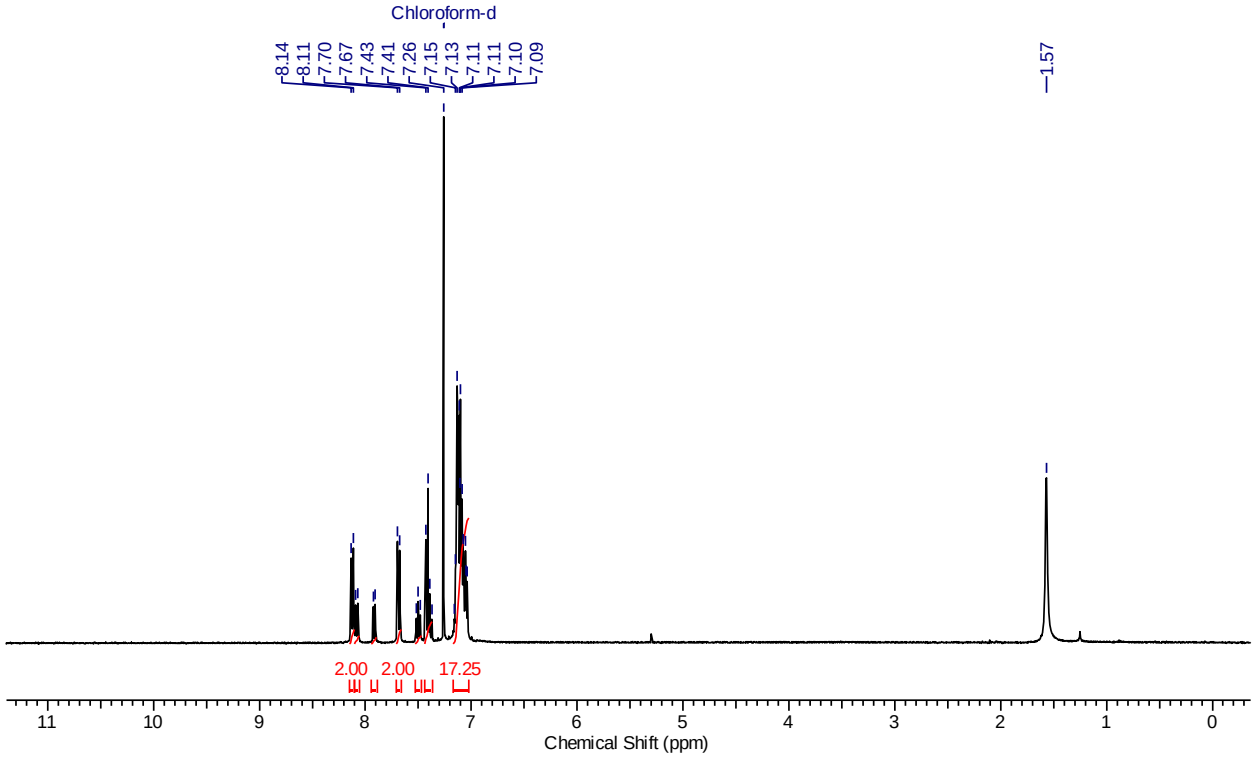

N
S
Chloroform-d
7.69 7.69 7.68 7.67 7.67 7.66 7.54 7.53 7.52 7.51 7.51 7.51 7.49 7.49 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.40 7.38 7.38 7.26 7.17 7.16 7.16 7.15 7.15 7.14 7.14 7.13 7.11 7.10 7.09 7.08 7.07 7.05 7.04
1.02 2.20 3.15 17.41
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90
Chemical Shift (ppm)
8.30 8.29 8.29 8.10 8.08 8.02 8.02 8.02 8.00 8.00 8.00 7.93 7.91
1.00 0.97 0.98 0.95
8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95
Chemical Shift (ppm)
Chloroform-d
8.29 8.10 7.67 7.52 7.46 7.44 7.15 7.14 7.13 7.12 7.11 7.10 7.09 5.30 1.57 1.27 0.89 0.87
1.00 0.95 2.20 17.41
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

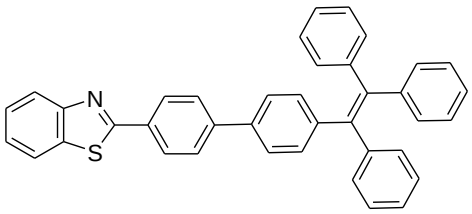

N
S
128.16
128.07
127.99
126.93
126.86
126.81
126.73
126.70
126.24
125.58
123.59
121.99
Chemical Shift (ppm)
132.23
131.74
131.68
129.80
129.73
Chemical Shift (ppm)
144.03
143.99
143.71
142.00
141.66
140.71
138.24
135.41
134.37
Chemical Shift (ppm)
Chloroform-d
168.36
154.46
143.99
143.71
141.66
138.24
134.37
132.23
131.68
129.73
128.16
128.07
126.86
126.73
126.24
123.59
77.67
77.56
77.36
77.04
Chemical Shift (ppm)

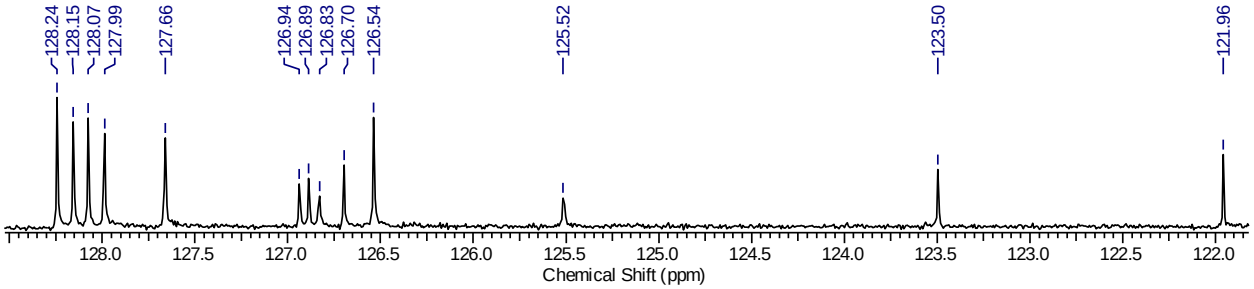

Intens.
+MS, 0.1min #4
542.1942
6000
4000
2000
278.1084
162.9048
840.2305
0
200
400
600
800
1000
1200
1400
1600
1800
m/z
Intens.
x10^4
+MS, 0.1min #4
542.1942
0.6
0.4
541.1885
543.1959
0.2
544.1953
0.0
C39H27NS, M+nH ,542.19
2500
2000
542.1937
1500
1000
543.1970
500
544.2001
545.1929
0
540
541
542
543
544
545
546
m/z

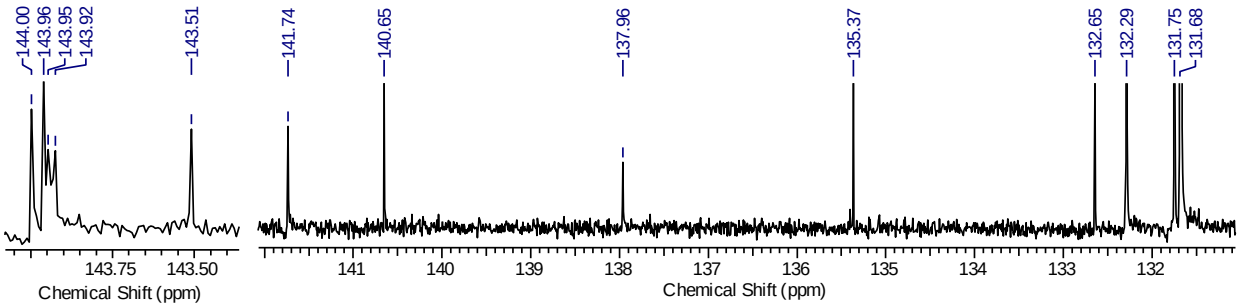

N
S

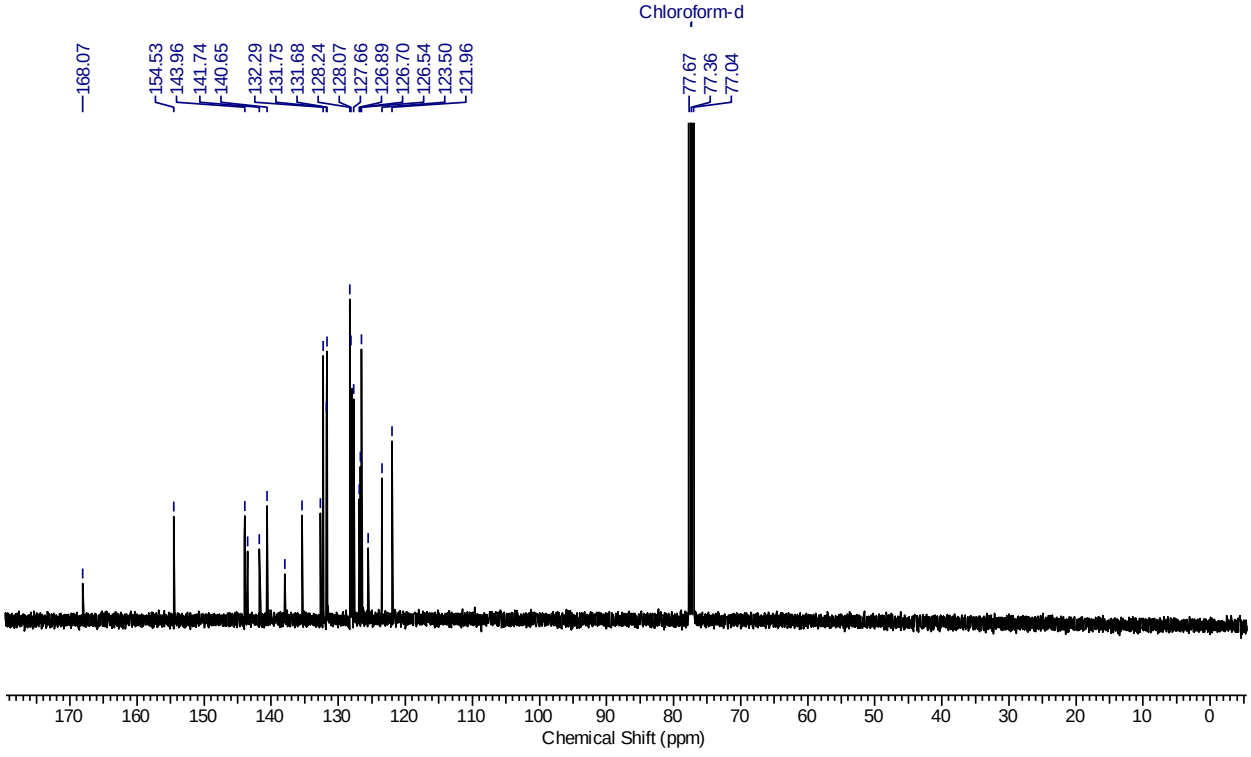

Chloroform-d
8.14
8.11
8.09
8.07
7.92
7.91
7.70
7.67
7.52
7.52
7.50
7.48
7.48
7.43
7.43
7.41
7.39
7.37
7.37
7.26
7.16
7.15
7.15
7.13
7.13
7.12
7.11
7.11
7.10
7.09
7.07
7.06
7.04
2.00
1.11
0.97
2.00
1.14
3.09
17.25
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
Chemical Shift (ppm)

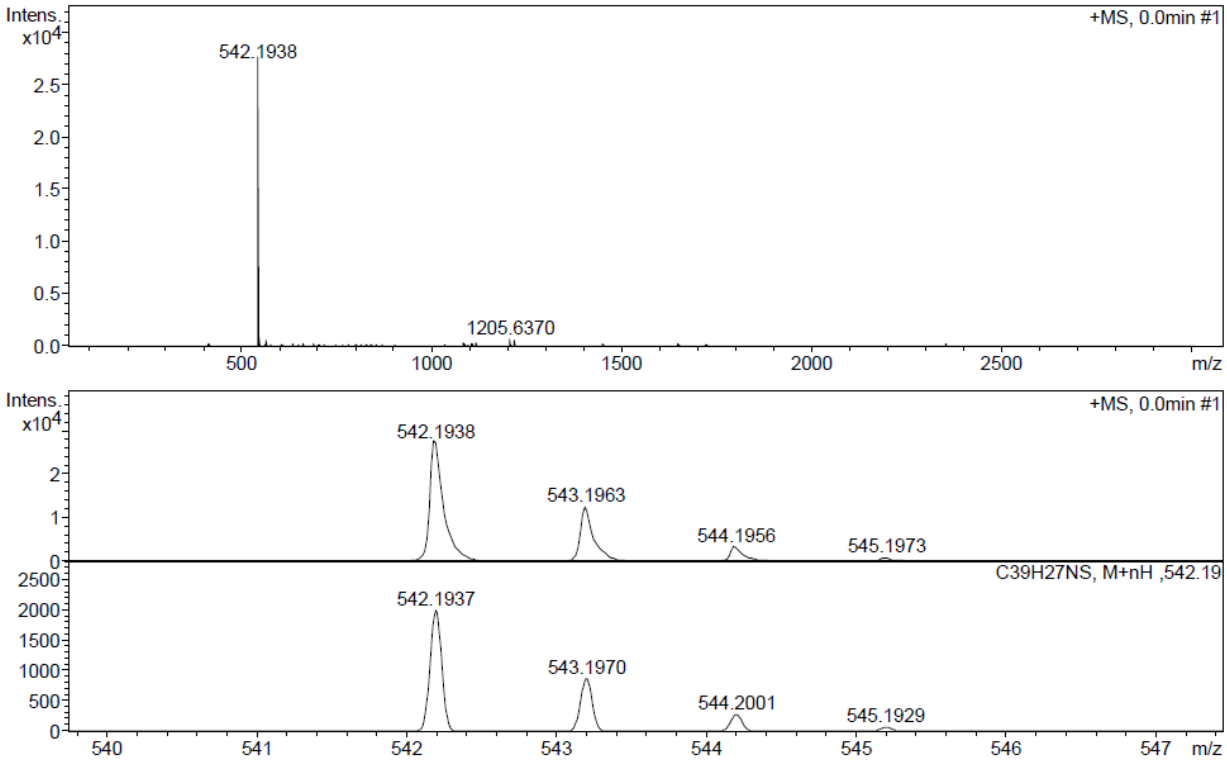

Chloroform-d
8.14
8.11
7.70
7.67
7.43
7.41
7.26
7.15
7.13
7.11
7.11
7.10
7.09
1.57
2.00
2.00
17.25
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


N
S


128.24
128.15
128.07
127.99
127.66
126.94
126.89
126.83
126.70
126.54
125.52
123.50
121.96
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
123.0
122.5
122.0
Chemical Shift (ppm)


144.00
143.96
143.95
143.92
143.51
141.74
140.65
137.96
135.37
132.65
132.29
131.75
131.68
143.75
143.50
141
140
139
138
137
136
135
134
133
132
Chemical Shift (ppm)


Chloroform-d
168.07
154.53
143.96
141.74
140.65
132.29
131.75
131.68
128.24
128.07
127.66
126.89
126.70
126.54
123.50
121.96
77.67
77.36
77.04
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


Intens.
x10^4
+MS, 0.0min #1
542.1938
1205.6370
m/z
Intens.
+MS, 0.0min #1
542.1938
543.1963
544.1956
545.1973
C39H27NS, M+nH ,542.19
542.1937
543.1970
544.2001
545.1929
m/z