Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Through-space communication in a TTF-C_{60}-TTF triad

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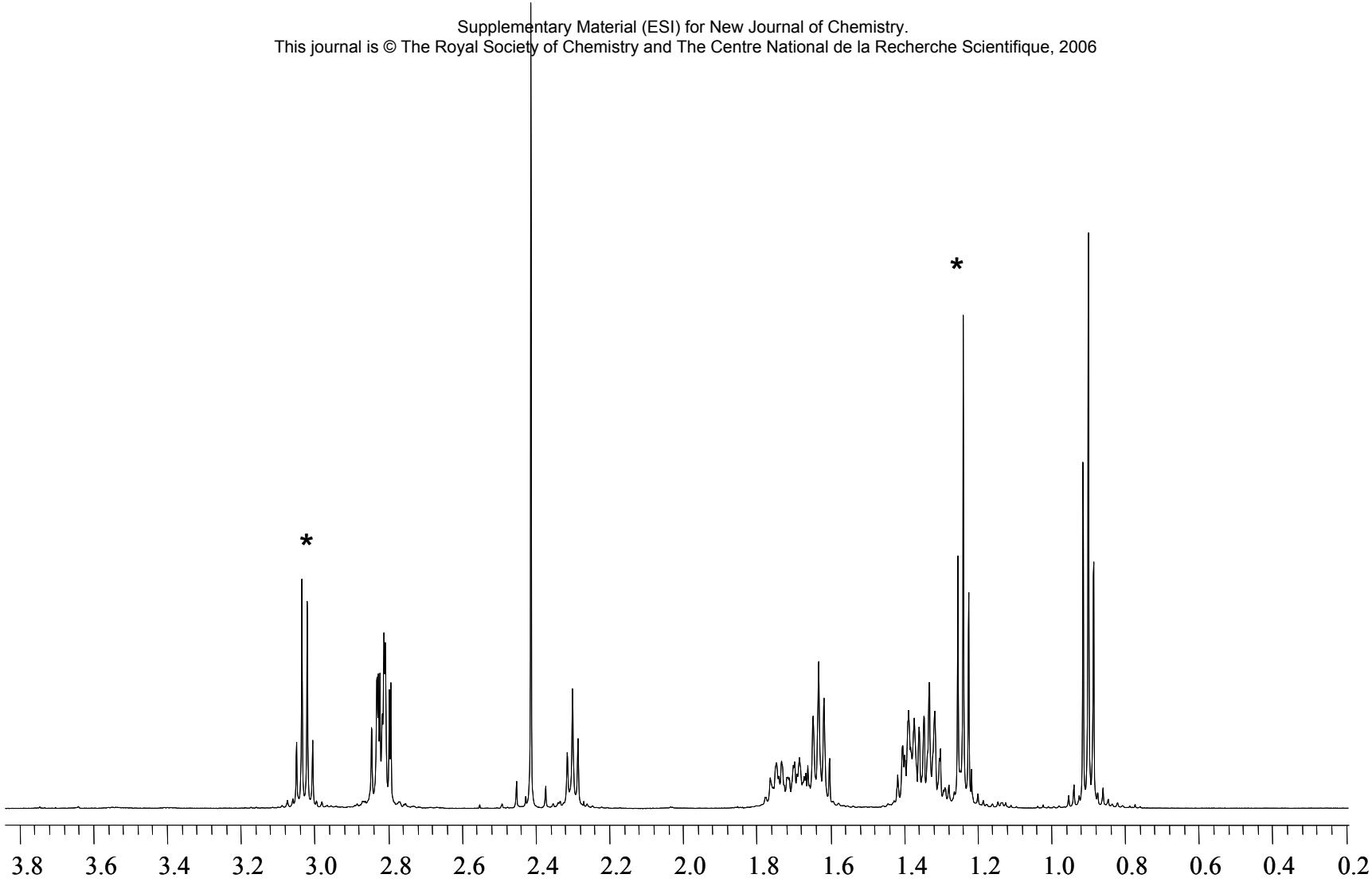
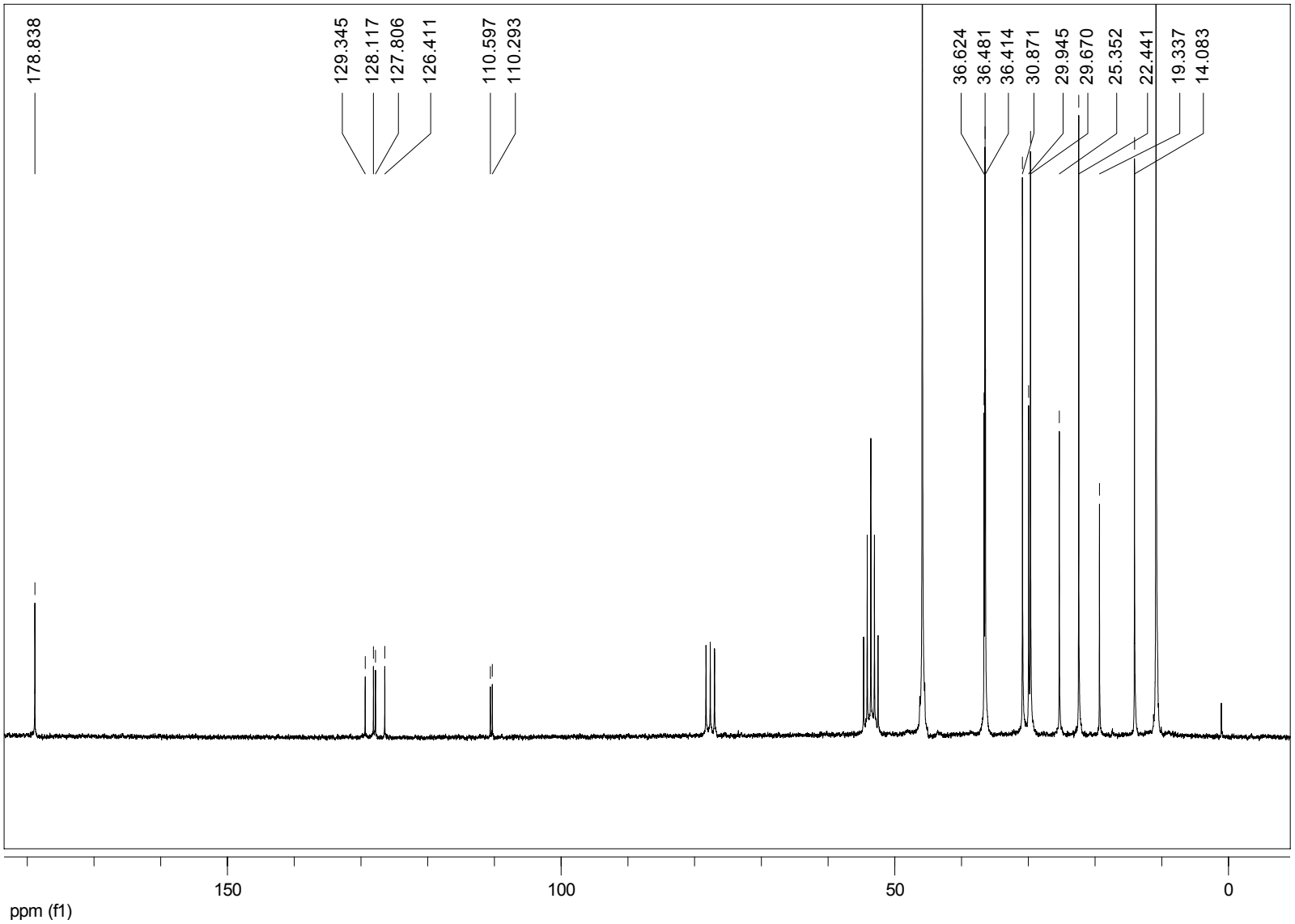
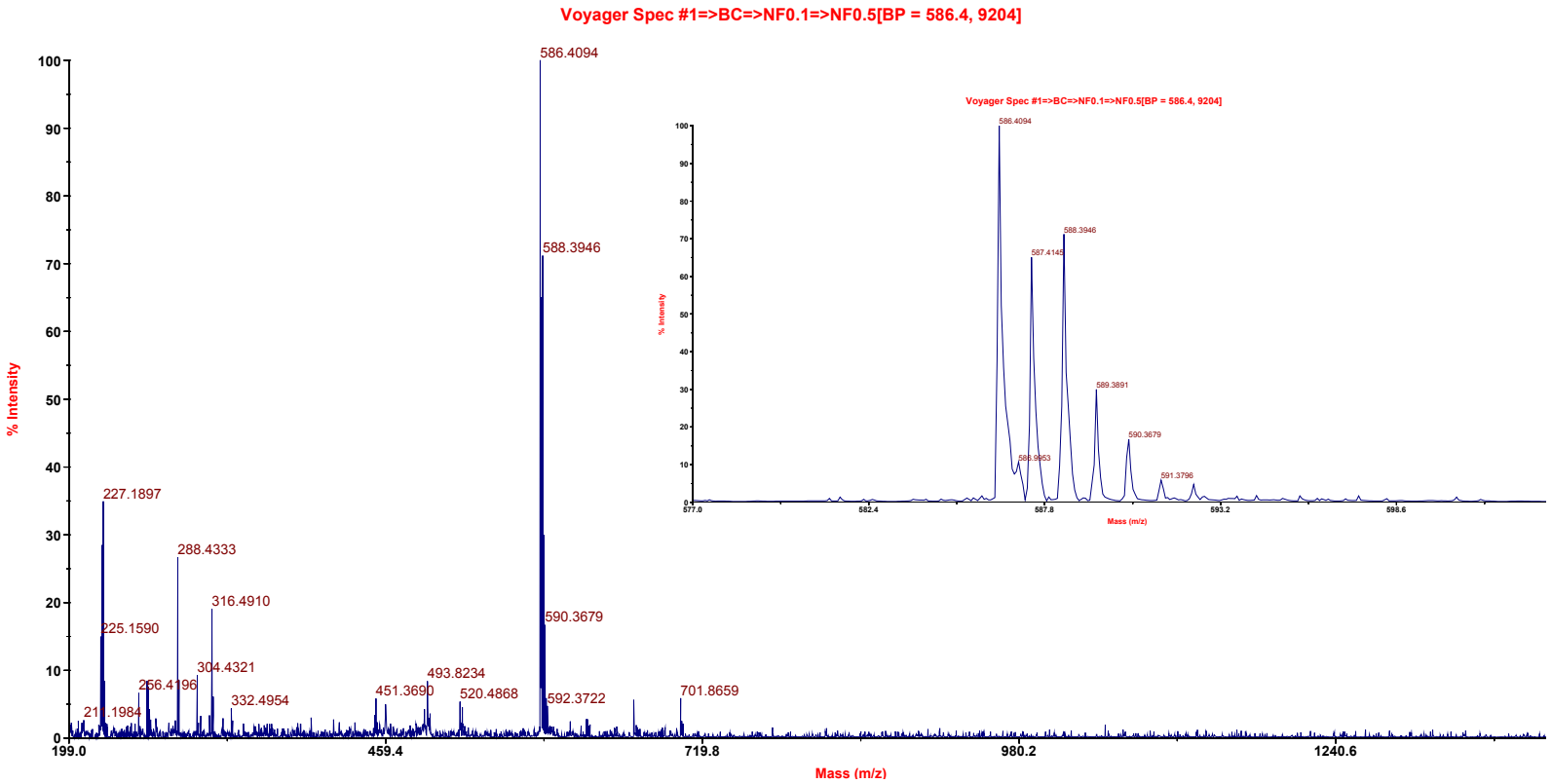


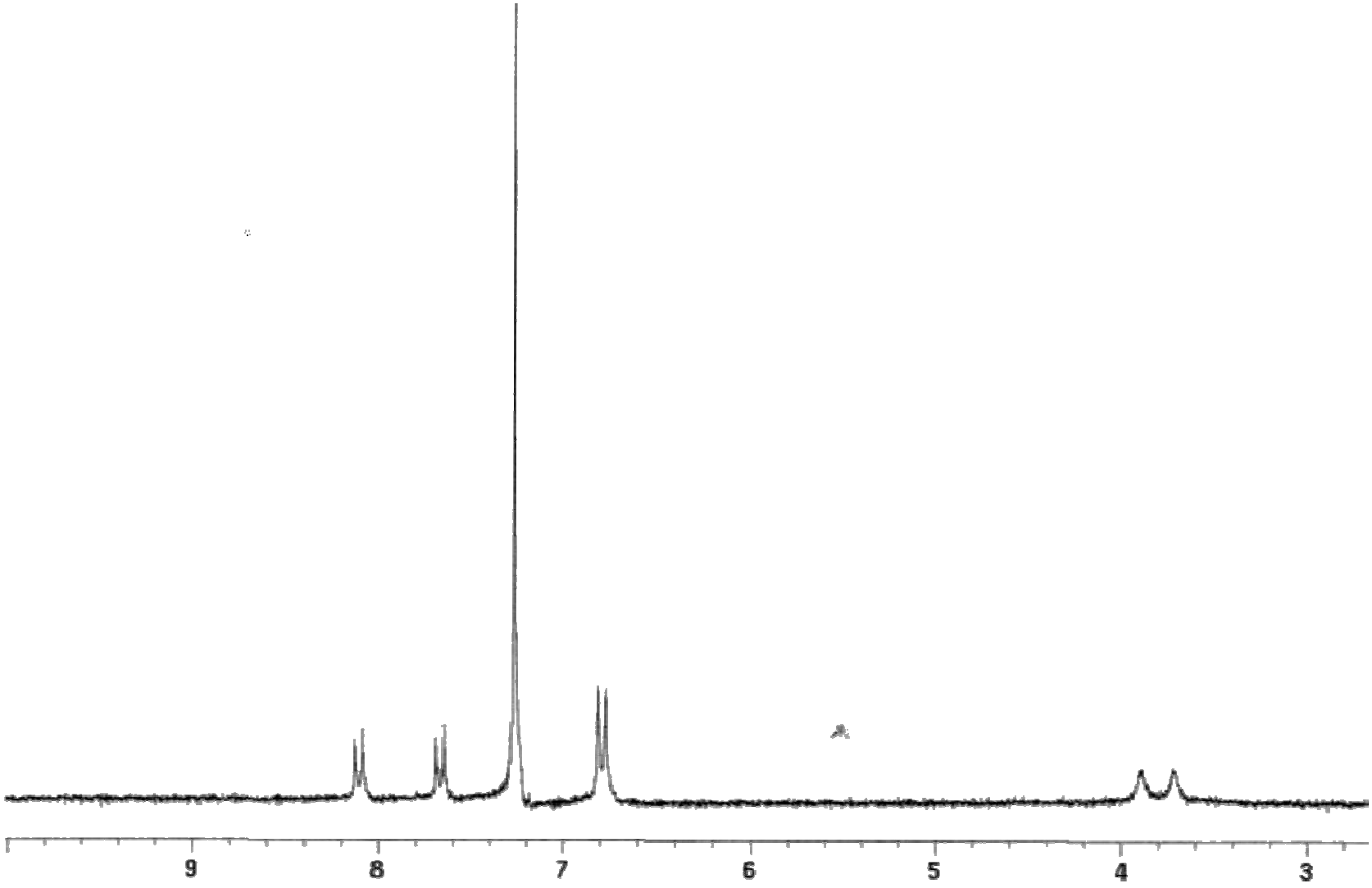
^{1}H NMR of compound **3** (the asterisks * indicate the signals due to CH_2 and CH_3 groups from triethylamine used to improve the resolution of this spectrum)



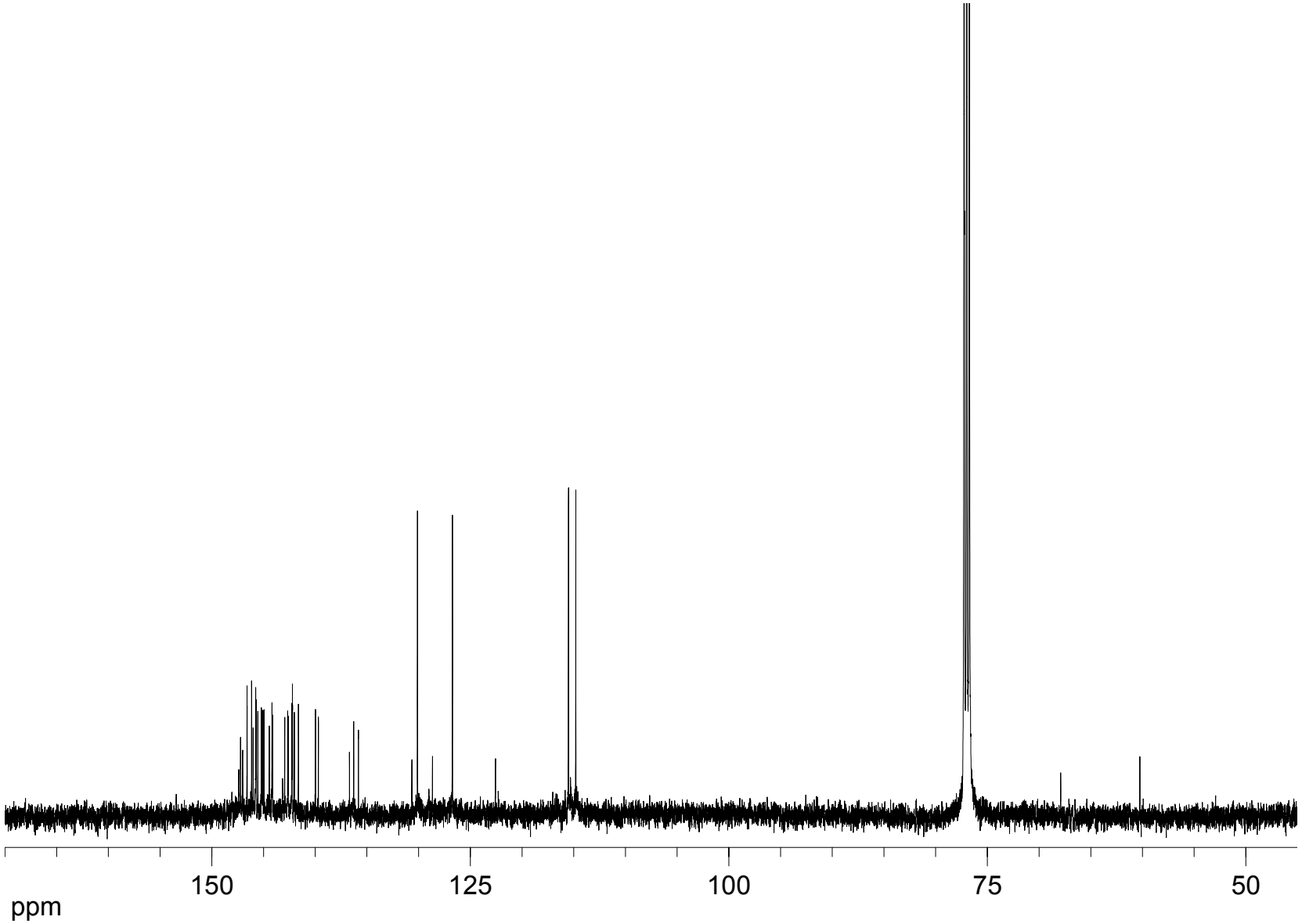
^{13}C NMR of compound **3**



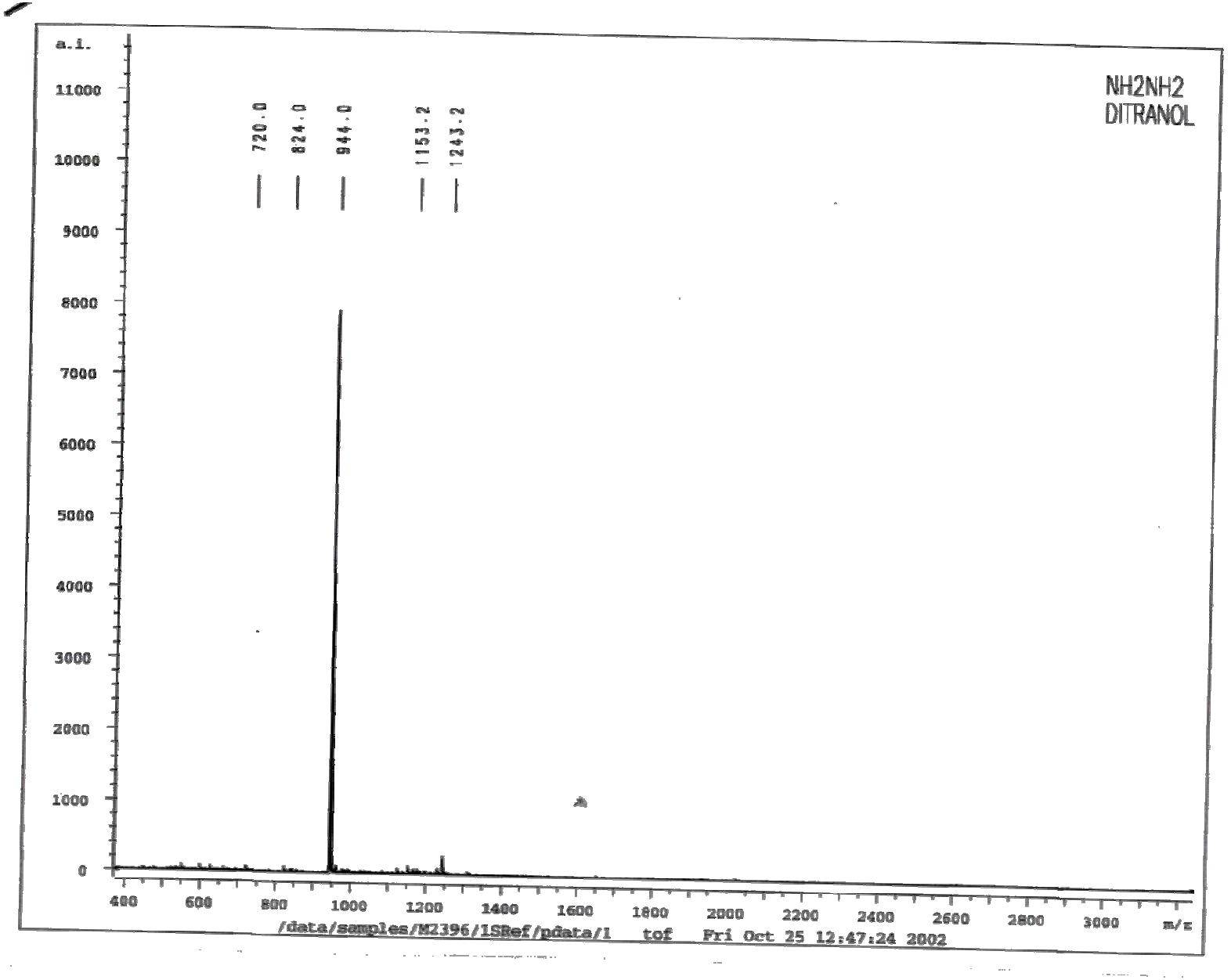
Mass Spectrum of compound **3**



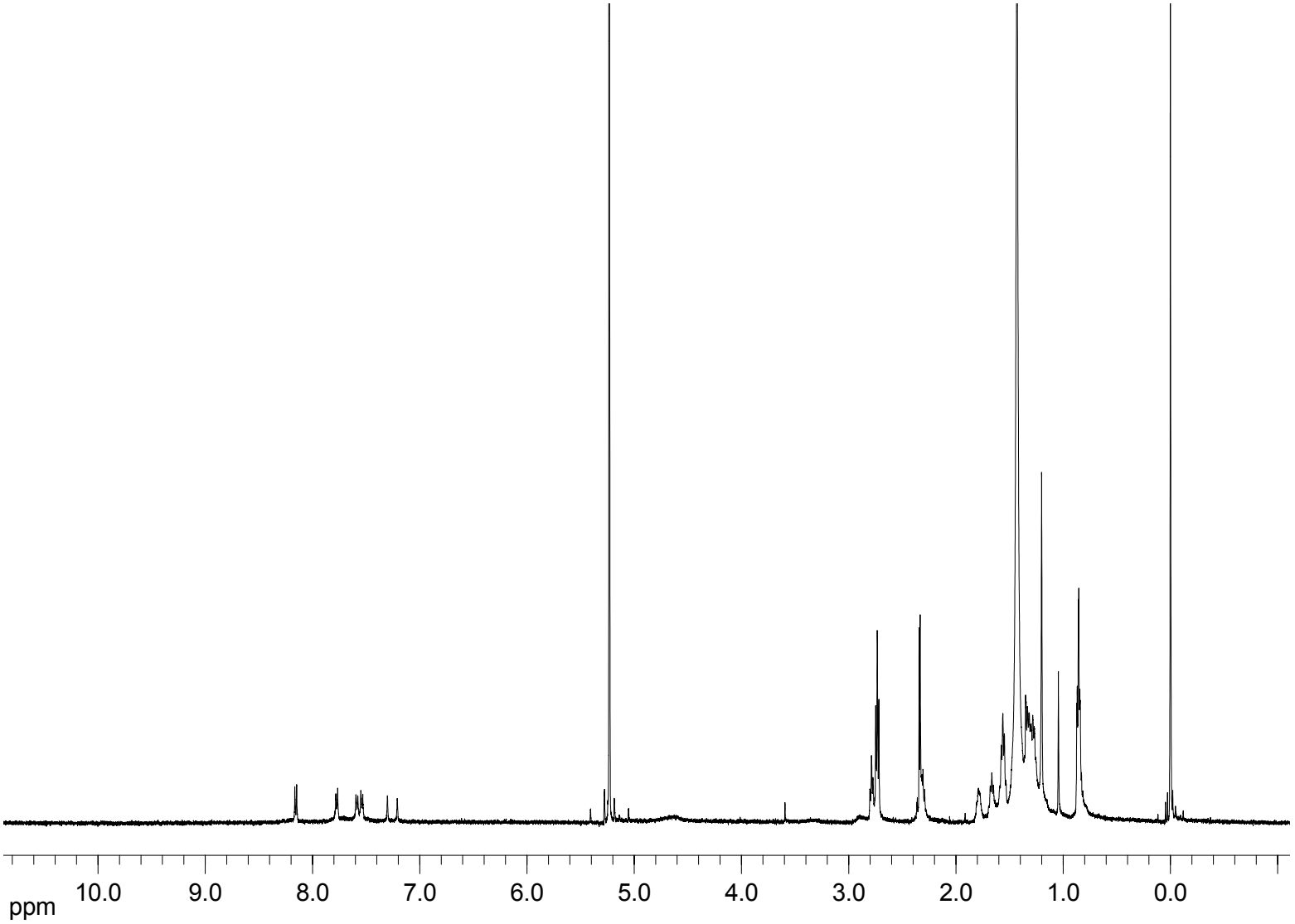
^{1}H NMR of compound **6**



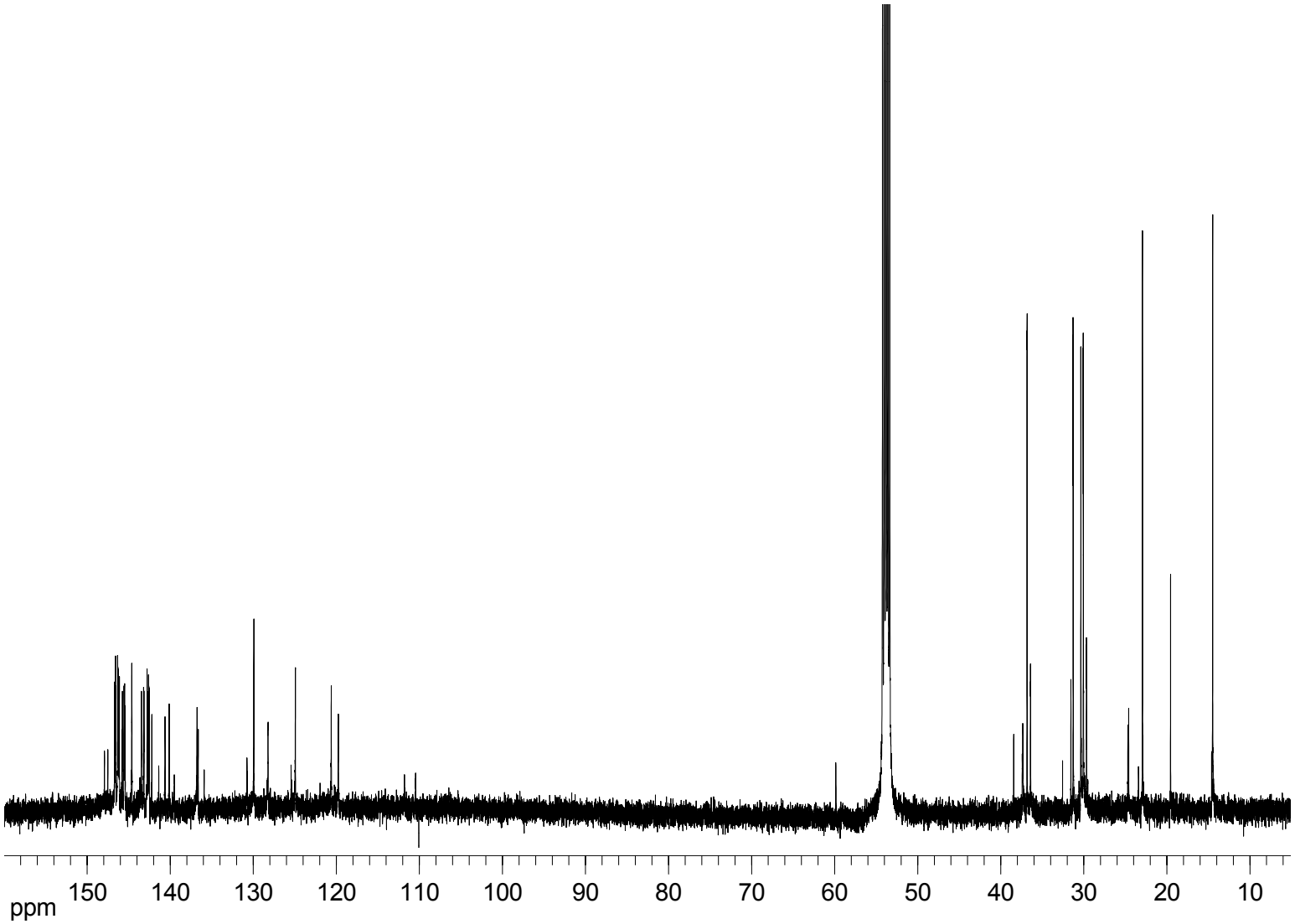
^{13}C NMR of compound **6**.



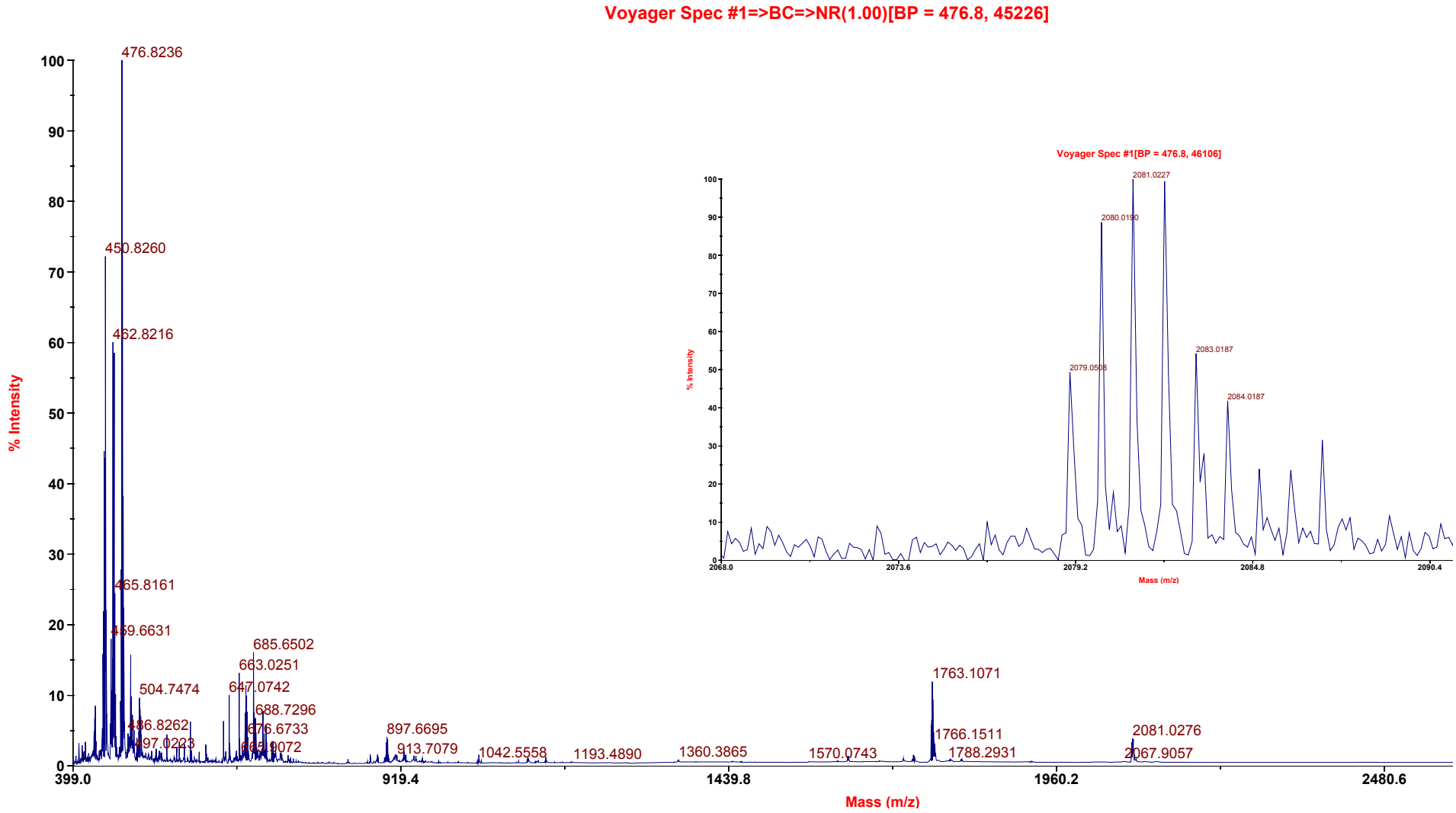
Mass spectra of compound **6**



^{1}H NMR of compound **7**.



^{13}C NMR of compound **7**.



Mass spectra of compound **7.**

Data File D:\DATOS\BISTTF\TEST0001.D Sample Name: BisTTF

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                                               Inj Volume : 5 µl
Acq. Method     : C:\DOCUME~1\FREDER~1.OSW\MISDOC~1\RETROCYC.M
Last changed    : 06/11/2006 16:15:57  by Fred
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Last changed    : 08/11/2006 10:37:22  by Fred
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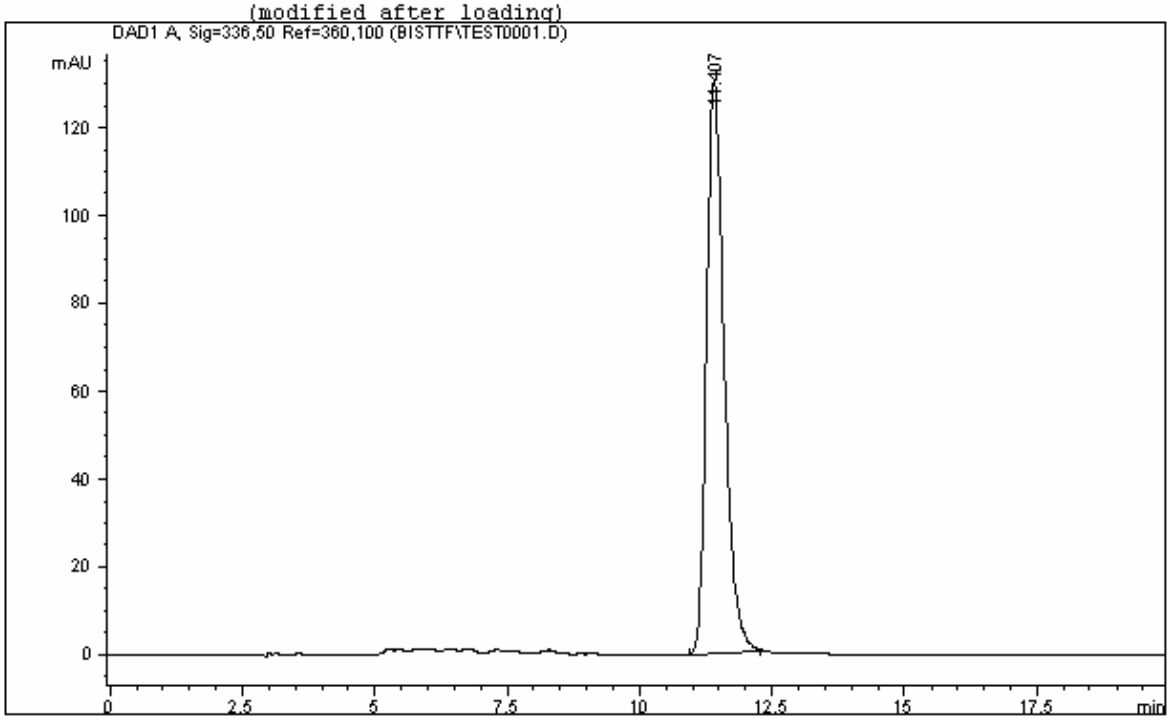


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                        Area Percent Report
==========================================================================

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Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=336,50 Ref=360,100

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  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  11.407 BB    0.3564 3044.25757  130.38162 100.0000

Totals :                  3044.25757  130.38162

 Results obtained with enhanced integrator!
==========================================================================
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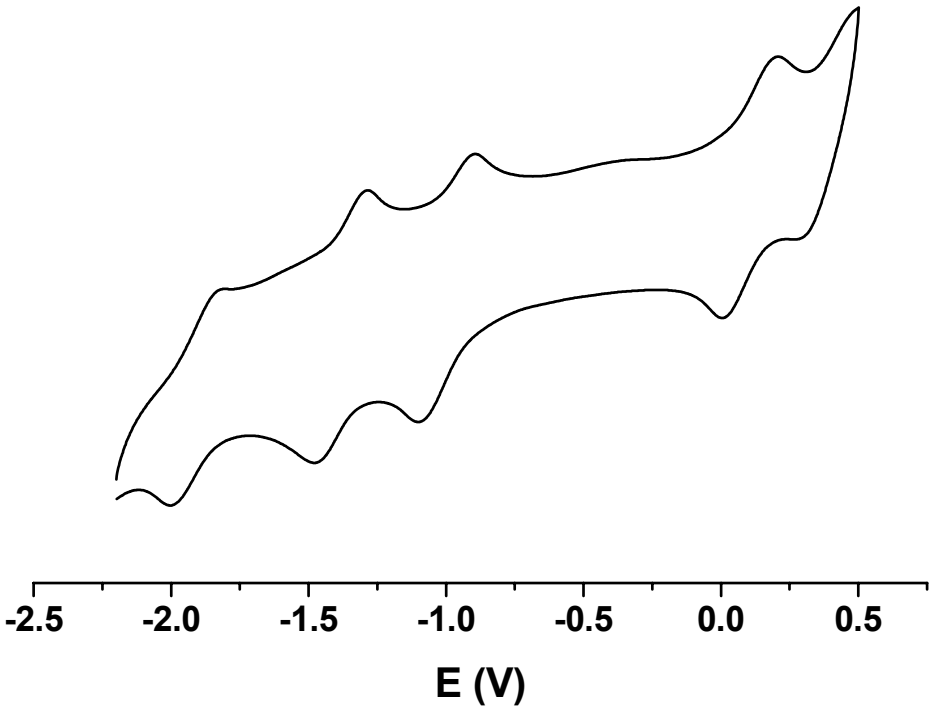
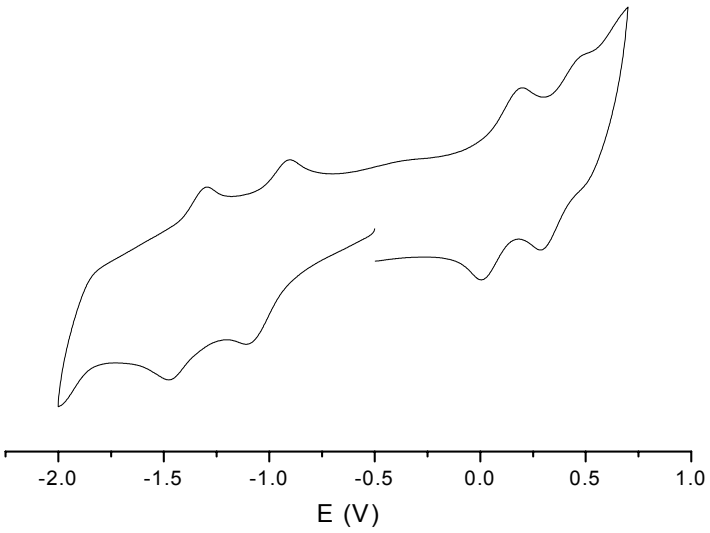
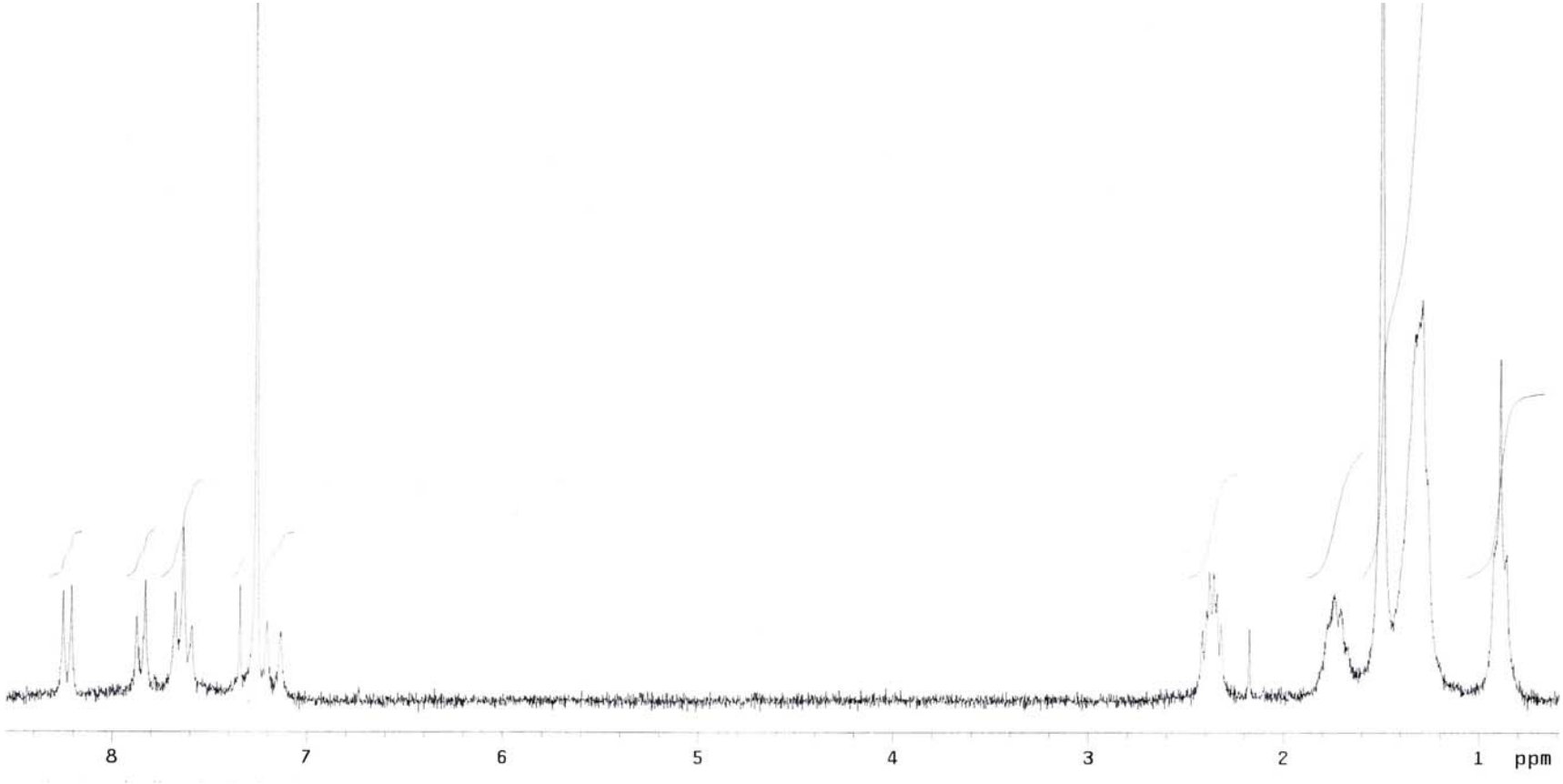
LC1100 08/11/2006 10:39:14 Fred Page 1 of 1

HPLC plot of compound **7**

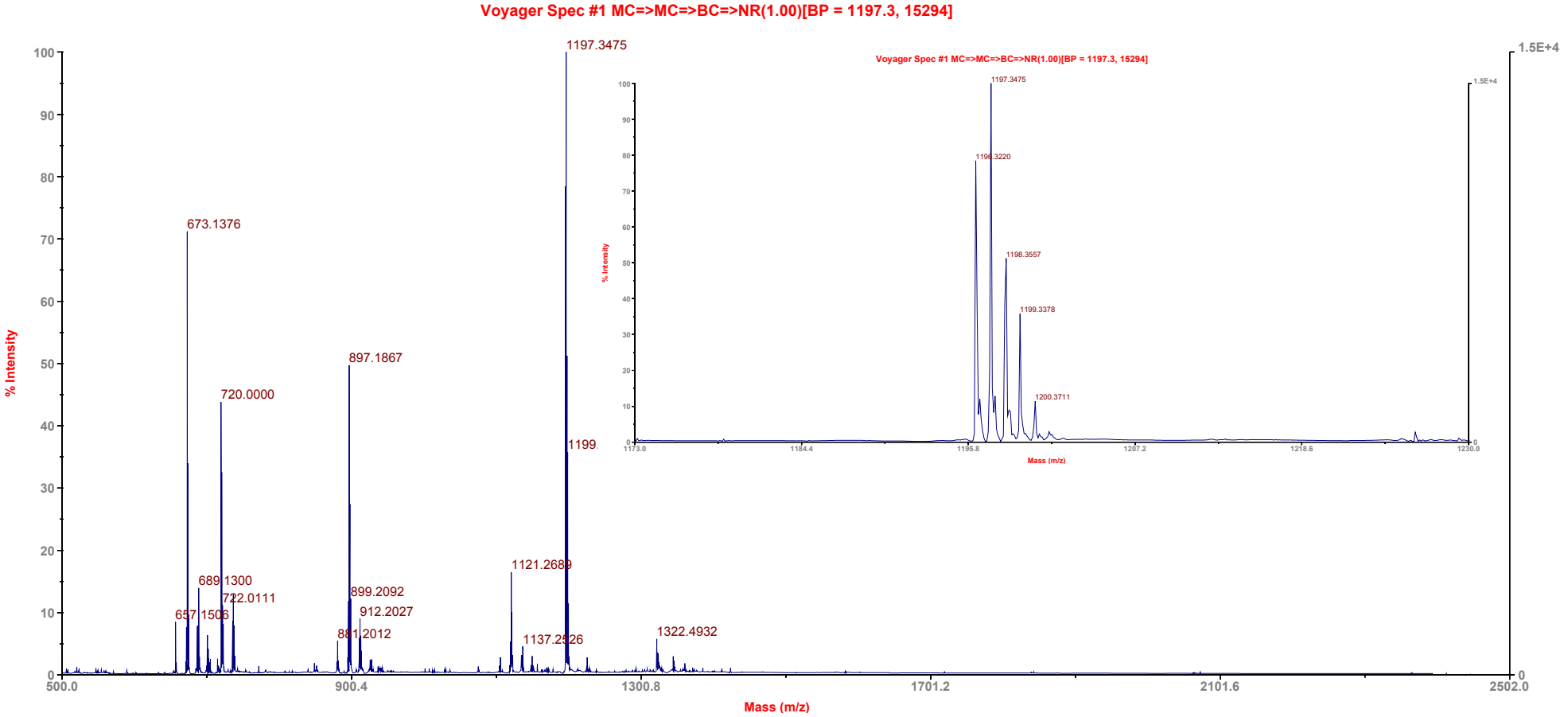




Cyclic voltammograms of triad **7** in *o*-DCB/acetonitrile 4:1 containing 0.1 M $(n\text{-Bu})_4NClO_4$. Scan rate 100 mV s^{-1}



^{1}H NMR of compound **8**.



Mass spectra of compound **8.**

Data File D:\DATOS\BISTTF\TEST0002.D Sample Name: Bis C8

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Acq. Operator   : Fred                             Inj :   1
                                                Inj Volume : 5 µl
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Last changed    : 06/11/2006 16:15:57  by Fred
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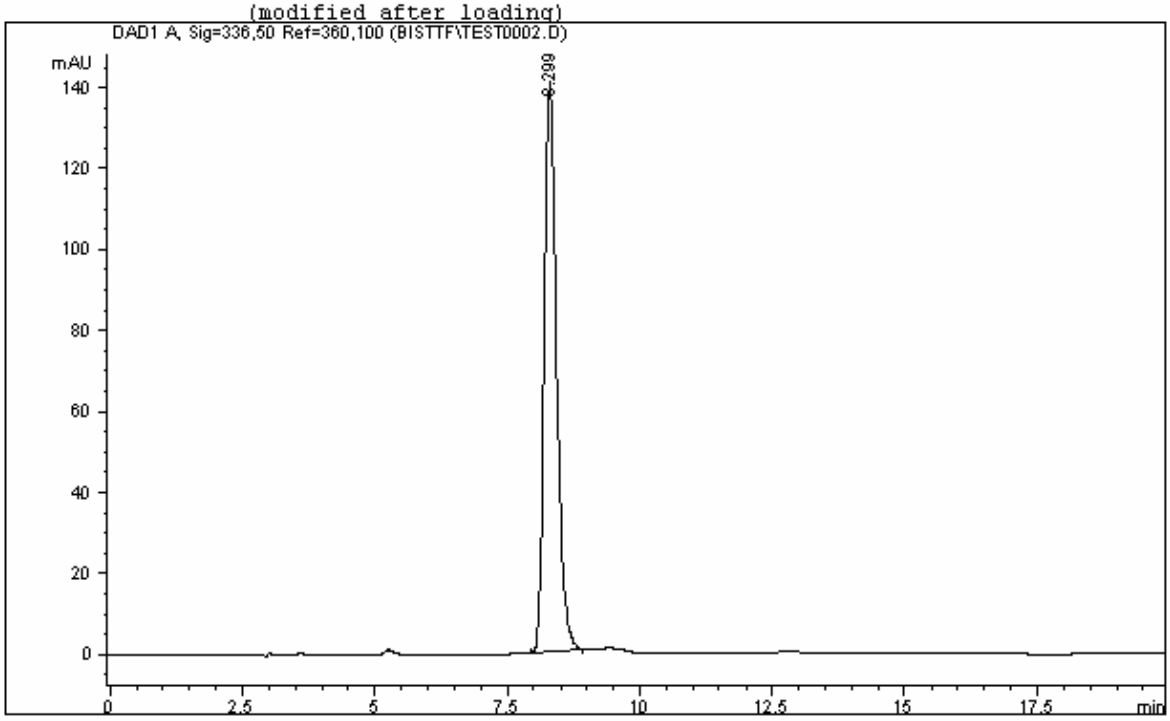


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==========================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: DAD1 A, Sig=336,50 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
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Totals :                  2277.69141  141.19724

 Results obtained with enhanced integrator!
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HPLC plot of compound **8**

COMPUTATIONAL STUDIES:

Level of theory: MM+
Specific program: Hyperchem 7.5
Default Input Parameters.

Level of theory: DFT-B3PW91
Specific program: Gaussian 03
Basis set: 6-31G*
Default Input Parameters.

Cartesian coordinates of compound 7:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	5.422189	-1.826023	2.810881
2	6	0	6.051360	-3.534682	2.609231
3	6	0	6.747452	-0.787620	2.127413
4	6	0	7.283999	-3.606659	2.061098
5	16	0	8.021453	-1.983679	1.630723
6	16	0	5.064510	-4.972338	3.092721
7	6	0	6.769207	0.541806	2.002580
8	16	0	8.163864	-5.152010	1.716835
9	6	0	3.288651	-4.829330	3.467476
10	16	0	8.079480	1.577689	1.288980
11	16	0	5.488938	1.737636	2.479940
12	6	0	9.785056	-5.107360	0.886443
13	6	0	3.040035	-4.857440	4.983735
14	6	0	6.176679	3.357052	1.960762
15	6	0	7.406146	3.280407	1.401090
16	1	0	2.761250	-5.687098	2.989642
17	1	0	2.859217	-3.910302	3.015492
18	6	0	9.568901	-4.917238	-0.624021
19	6	0	3.432971	-3.573598	5.736328
20	16	0	5.182178	4.847376	2.220398
21	16	0	8.367566	4.674860	0.766402
22	1	0	10.339876	-6.054273	1.079429
23	1	0	10.397805	-4.269647	1.291472
24	1	0	3.573017	-5.730840	5.431866
25	1	0	1.957074	-5.054369	5.165679
26	6	0	10.904171	-4.842155	-1.382755
27	6	0	2.648250	-2.307067	5.350523
28	6	0	5.804722	6.545730	2.028921
29	6	0	9.999105	4.432043	0.013508
30	1	0	8.995688	-3.977330	-0.812149
31	1	0	8.966575	-5.765405	-1.030805
32	1	0	4.523710	-3.385265	5.595936
33	1	0	3.289648	-3.748312	6.830485
34	6	0	10.695186	-4.644653	-2.892890
35	6	0	1.133703	-2.422522	5.560944
36	6	0	5.550628	7.038088	0.595358
37	1	0	11.483194	-5.780336	-1.208015
38	1	0	11.510338	-3.995588	-0.981232
39	1	0	2.847765	-2.032224	4.289932
40	1	0	3.027823	-1.454946	5.964096
41	1	0	5.272245	7.209116	2.748489
42	1	0	6.886882	6.608128	2.283382
43	1	0	9.982743	4.808563	-1.033384
44	1	0	10.269014	3.352835	0.010228
45	1	0	10.762670	4.996641	0.595735

46	6	0	12.029418	-4.566898	-3.646353
47	6	0	6.039089	8.484966	0.402435
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49	1	0	10.090817	-5.490267	-3.300232
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51	1	0	0.894807	-2.744472	6.600461
52	1	0	0.673526	-3.150600	4.854604
53	1	0	6.068321	6.379931	-0.141154
54	1	0	4.458721	6.985016	0.374468
55	6	0	5.898971	8.983608	-1.045242
56	1	0	12.647061	-3.713580	-3.284688
57	1	0	11.862433	-4.424297	-4.740233
58	1	0	12.621591	-5.501757	-3.513578
59	1	0	5.470674	9.161506	1.084354
60	1	0	7.112652	8.550790	0.700511
61	6	0	4.471003	8.928959	-1.523150
62	1	0	6.275697	10.030710	-1.123269
63	1	0	6.541469	8.364282	-1.713476
64	8	0	3.681945	9.817384	-1.198835
65	7	0	4.086378	7.928456	-2.442322
66	6	0	2.861502	7.220376	-2.368929
67	1	0	4.796127	7.578446	-3.089204
68	6	0	2.528548	6.368042	-3.434185
69	6	0	2.005356	7.292704	-1.256600
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71	6	0	0.839741	6.514719	-1.207439
72	1	0	3.194572	6.297108	-4.309614
73	1	0	2.253115	7.934644	-0.395572
74	6	0	0.519287	5.652030	-2.267262
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76	1	0	0.192286	6.559318	-0.316146
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79	7	0	-1.809335	5.246427	-1.644169
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86	6	0	-1.022344	1.729534	-3.627620
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88	6	0	-1.704486	2.466795	0.296251
89	6	0	-2.624880	1.893912	-1.781354
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91	6	0	-3.222181	1.003759	-0.770048
92	6	0	-2.651724	1.365831	0.527419
93	6	0	1.728519	1.170058	-3.751774
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97	6	0	-2.292614	1.378803	-2.977070
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99	6	0	-4.953261	3.880723	-0.743466
100	6	0	-3.823518	5.569536	0.579316
101	6	0	-3.488535	-0.283222	-1.050309
102	6	0	-2.587521	-0.029236	-3.296093
103	6	0	-2.396480	0.416543	1.445290
104	6	0	3.320736	0.679141	-1.968013
105	6	0	2.796185	0.342591	-3.160856
106	6	0	2.792681	1.566365	0.179778
107	6	0	0.774565	0.272370	-4.420151
108	6	0	1.177006	1.173450	1.969659
109	6	0	-0.266379	1.458089	2.000118

110	6	0	-1.509248	-0.548072	-4.150948
111	6	0	-6.148380	4.140908	-0.056034
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116	6	0	-3.160470	-0.825365	-2.377708
117	6	0	-1.079446	-1.814611	-4.005046
118	6	0	-2.687976	-0.996857	1.144831
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120	6	0	3.268878	0.184589	0.361717
121	6	0	3.596799	-0.366525	-0.964959
122	6	0	2.497881	-1.068850	-3.463269
123	6	0	1.618333	-0.084287	2.144105
124	6	0	1.249250	-1.112847	-4.246630
125	6	0	-6.188173	5.122333	0.948527
126	1	0	-7.049233	3.555245	-0.301416
127	1	0	-5.035845	6.591381	2.064991
128	6	0	-2.700643	-2.512680	-0.766736
129	6	0	-2.683214	-2.207945	-2.206914
130	6	0	-1.691906	-2.681069	-2.982173
131	6	0	-1.616968	-1.820001	1.736114
132	6	0	-0.666813	-0.914256	2.406870
133	6	0	0.652826	-1.175607	2.362614
134	6	0	0.364588	-2.107386	-4.046430
135	6	0	3.329386	-1.655423	-1.242940
136	6	0	2.754212	-2.022815	-2.549264
137	6	0	2.703701	-0.602129	1.294698
138	7	0	-7.367652	5.400049	1.676824
139	6	0	-0.623446	-3.502262	-2.385172
140	6	0	-1.732627	-3.272204	-0.224186
141	6	0	0.646072	-3.151350	-3.044689
142	6	0	1.785150	-3.112304	-2.330866
143	6	0	-1.163933	-2.908432	1.085731
144	6	0	1.145605	-2.367515	1.650701
145	6	0	2.413668	-2.012803	0.992387
146	6	0	2.714629	-2.519630	-0.217487
147	1	0	-7.278232	5.712904	2.644932
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149	6	0	-0.644709	-3.789277	-1.070446
150	6	0	1.761679	-3.419921	-0.888901
151	6	0	0.280238	-3.198763	1.044273
152	8	0	-8.808555	5.437068	-0.118803
153	6	0	-9.863244	5.342673	2.005598
154	6	0	0.602364	-3.743994	-0.288044
155	6	0	-9.976851	4.008776	2.764138
156	1	0	-10.792722	5.512322	1.412488
157	1	0	-9.789827	6.186280	2.731995
158	6	0	-10.021352	2.795370	1.819148
159	1	0	-10.904226	4.031062	3.384697
160	1	0	-9.116907	3.911785	3.467602
161	6	0	-10.402031	1.481141	2.516617
162	1	0	-9.044628	2.675748	1.291396
163	1	0	-10.785140	2.997316	1.030235
164	16	0	-9.104918	0.961294	3.685505
165	1	0	-10.550063	0.684699	1.750483
166	1	0	-11.374517	1.596167	3.049050
167	6	0	-7.961586	-0.371453	3.242944
168	6	0	-7.191313	-1.044254	4.125248
169	16	0	-7.794484	-0.934054	1.506064
170	16	0	-6.190872	-2.390665	3.383352
171	6	0	-6.612554	-2.311249	1.617207
172	16	0	-7.144707	-0.710800	5.904240
173	6	0	-6.074963	-1.673552	7.007254

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175	16	0	-6.515599	-2.943311	-1.147355
176	16	0	-5.006297	-4.482733	0.725231
177	1	0	-5.475876	-2.406983	6.422425
178	1	0	-6.701330	-2.221723	7.746231
179	1	0	-5.384756	-0.987516	7.546128
180	6	0	-5.465074	-4.237550	-1.911128
181	6	0	-4.759356	-4.978646	-1.025912
182	16	0	-3.604631	-6.327149	-1.372499
183	16	0	-5.418682	-4.392025	-3.713912
184	6	0	-3.166388	-6.982081	-3.008415
185	6	0	-6.269506	-3.169611	-4.766109
186	6	0	-1.635866	-7.031269	-3.168314
187	6	0	-5.565505	-1.808881	-4.633131
188	1	0	-3.584680	-6.360672	-3.828713
189	1	0	-3.591082	-8.003570	-3.134172
190	1	0	-7.336422	-3.079009	-4.460342
191	1	0	-6.249137	-3.506537	-5.827109
192	6	0	-0.933296	-8.007655	-2.209657
193	6	0	-6.224090	-0.728907	-5.506609
194	1	0	-1.219551	-6.004599	-3.049110
195	1	0	-1.403868	-7.343188	-4.214322
196	1	0	-4.492527	-1.904282	-4.923891
197	1	0	-5.599654	-1.478875	-3.569444
198	6	0	0.570669	-8.170237	-2.489965
199	6	0	-5.563025	0.653575	-5.369589
200	1	0	-1.422122	-9.007306	-2.299927
201	1	0	-1.064565	-7.676495	-1.152411
202	1	0	-7.308559	-0.645098	-5.255493
203	1	0	-6.162074	-1.055240	-6.573116
204	6	0	1.379453	-6.889632	-2.241491
205	6	0	-5.850609	1.342760	-4.028659
206	1	0	0.724889	-8.511093	-3.541191
207	1	0	0.973812	-8.974724	-1.828024
208	1	0	-5.940378	1.315364	-6.185586
209	1	0	-4.460900	0.559981	-5.518556
210	1	0	2.471940	-7.076851	-2.365788
211	1	0	1.218640	-6.508011	-1.207286
212	1	0	1.103694	-6.083700	-2.958359
213	1	0	-6.944986	1.482335	-3.873387
214	1	0	-5.373300	2.349681	-3.990249
215	1	0	-5.458991	0.761813	-3.163927

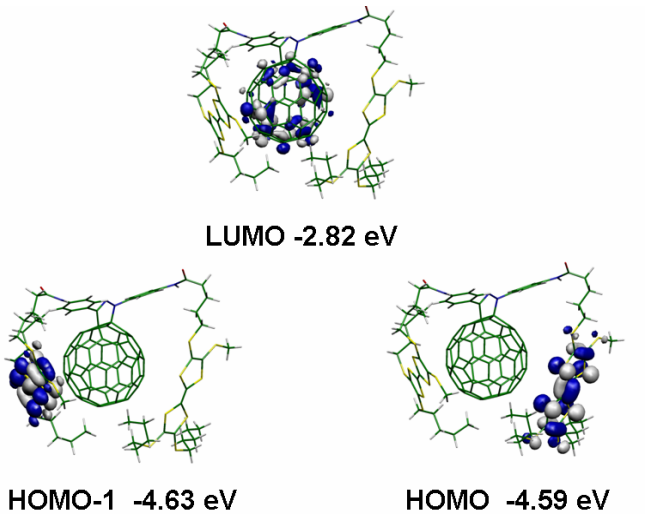
Computed total energies of target or optimized structures

SCF Done: E(RB+HF-PW91) = -11241.5068365 A.U. after 42 cycles

Molecular Orbital Calculations

Molecular Orbital calculations were carried out at the B3PW91/6-31G* level of theory using the GAUSSIAN 03 software.

The flexibility of the spacers in **7** leads to a high number of conformations displaying similar energies. A conformational search was conducted by using simulated annealing with the MM+ force field as implemented in Hyperchem leading to a minimum in energy that corresponds to a bent conformation with the center of the TTF moieties placed at 7.0 and 7.2 Å respectively from the center of the C_{60} core (Figure). Conformations with the two TTF moieties separated away from the C_{60} are c.a. 22-24 kcal/mol less stable than the geometry shown in Figure 1 while those conformations with one TTF close to the fullerene spheroid and the other one separated from it are ca 12 kcal/mol above the more stable conformation.
Molecular orbitals calculated at the B3PW91/6-31G* level on the basis of the optimized structure are also shown in Figure 1. It can be seen that the HOMO is placed on one of two TTF groups, whereas the LUMO spreads over the C_{60} spheroid, which predicts the charge-separated states as $(TTF)^{\bullet+}$–(spacer)–$Pz(C_{60})^{\bullet-}$–(spacer)–TTF.



Optimized structure and the HOMOs and LUMO of **7** calculated by B3PW91/6-31G* level.