Synthesis and electronic communication in diphenothiazine dumbbells bridged by heterocycles

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[§] *X-ray structure analysis.*

Electronic Supplementary Information (ESI)

a) General considerations

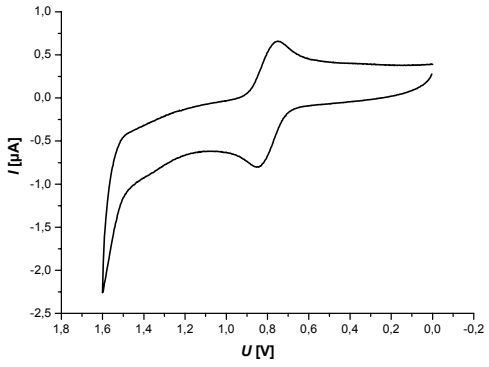
Reagents, catalysts and ligands were purchased reagent grade and used without further purification. The used solvents were dried and distilled according to standard procedures. 2,5-Dibromofurane (**6**) and 9,9'-dihexyl-2,7-dibromofluorene (**2**) were prepared according to literature. Column chromatography: silica gel 60, mesh 70-230. TLC: silica gel plates. ^{1}H and ^{13}C NMR spectra: CD_2Cl_2, (locked to Me_4Si). The assignments of quaternary C, CH, CH_2 and CH_3 have been made by using DEPT spectra. Elemental analyses were carried out in the Microanalytical Laboratories, Institut für Pharmazeutische Chemie, Heinrich-Heine University, Düsseldorf, Germany.

Fluorescence measurements (Perkin-Elmer LS-55) were performed in dry and degassed CH_2Cl_2 at room temperature. To avoid re-absorption and re-emission effects the concentrations were strictly kept below 1 μM. The solutions were irradiated at approximately 10 nm less in energy than the longest wave length absorption maximum.

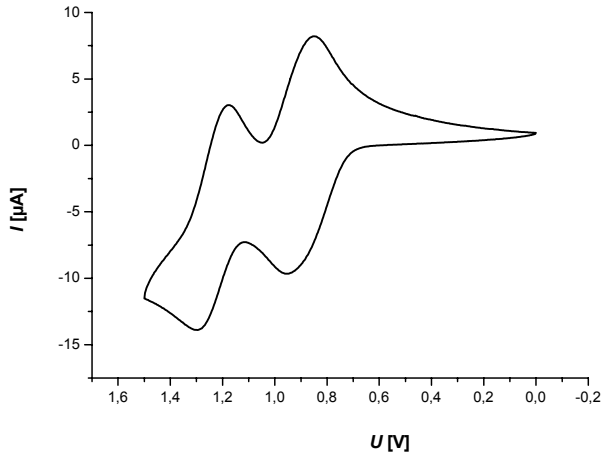
Electrochemistry: Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 100, 250, 500, and 1000 mVs^{-1}. The electrolyte was Bu_4NPF_6 (0.025 M). The working electrode was a 1 mm platinum disk, the counter-electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc^{+} in CH_2Cl_2 ($E_0^{0/+1}$= 450 mV).[25]

b) Cyclovoltammograms of 8-13

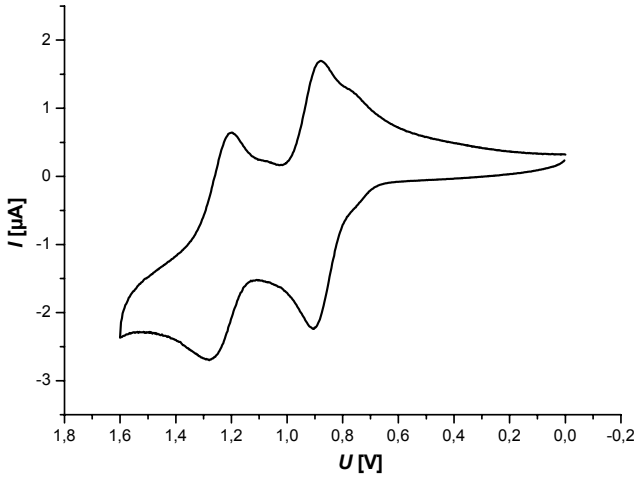
Cyclovoltammogram of **8** in CH_2Cl_2



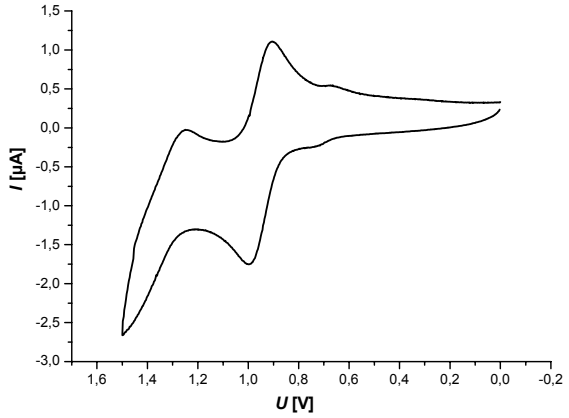
Cyclovoltammogram of **9** in CH_2Cl_2



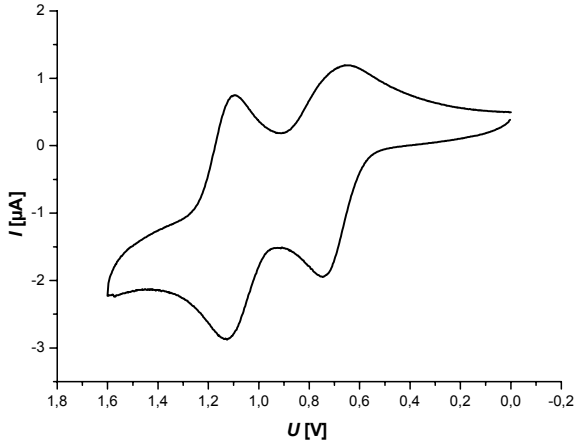
Cyclovoltammogram of **10** in CH_2Cl_2



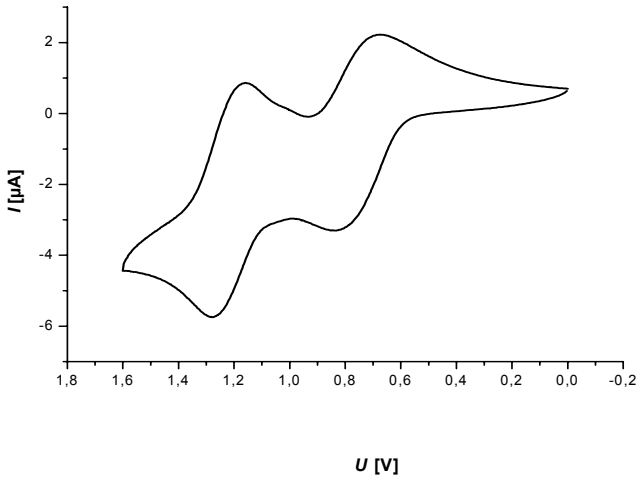
Cyclovoltammogram of **11** in CH_2Cl_2



Cyclovoltammogram of **12** in CH_2Cl_2

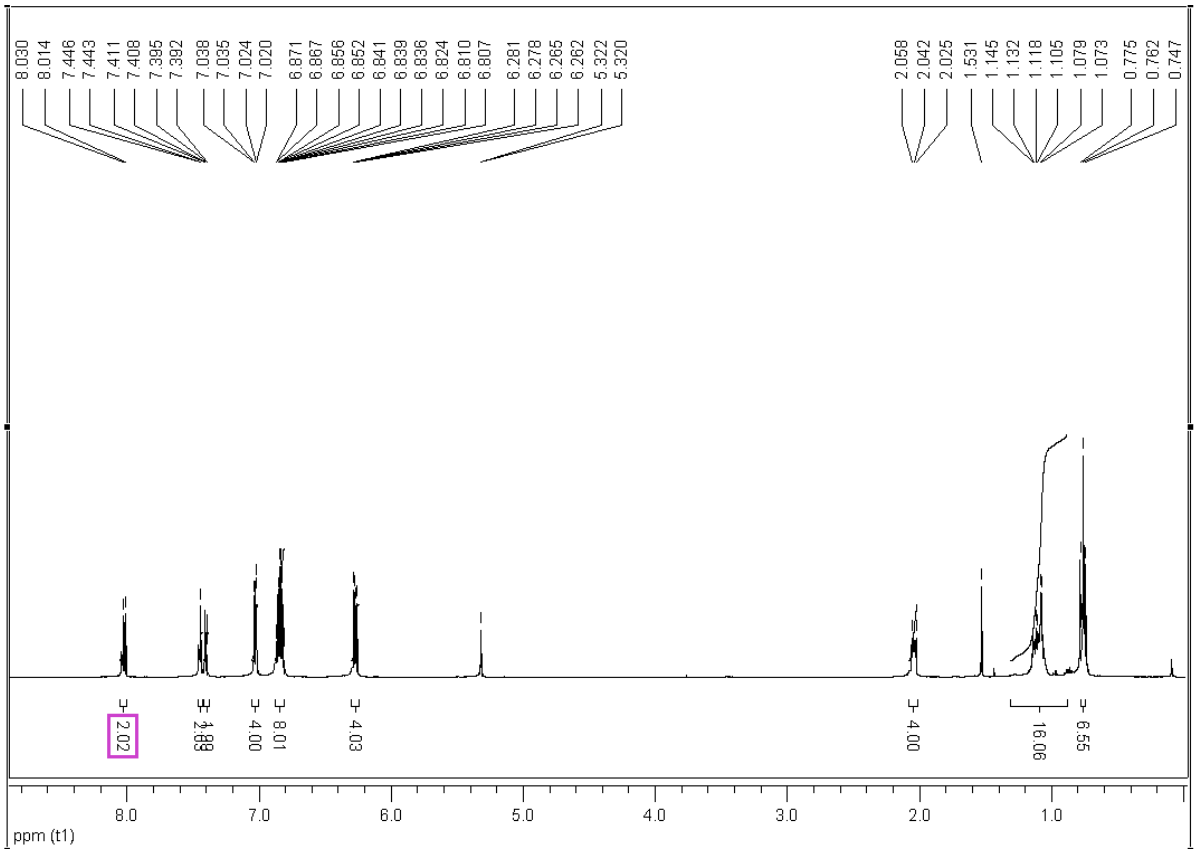


Cyclovoltammogram of **13** in CH_2Cl_2

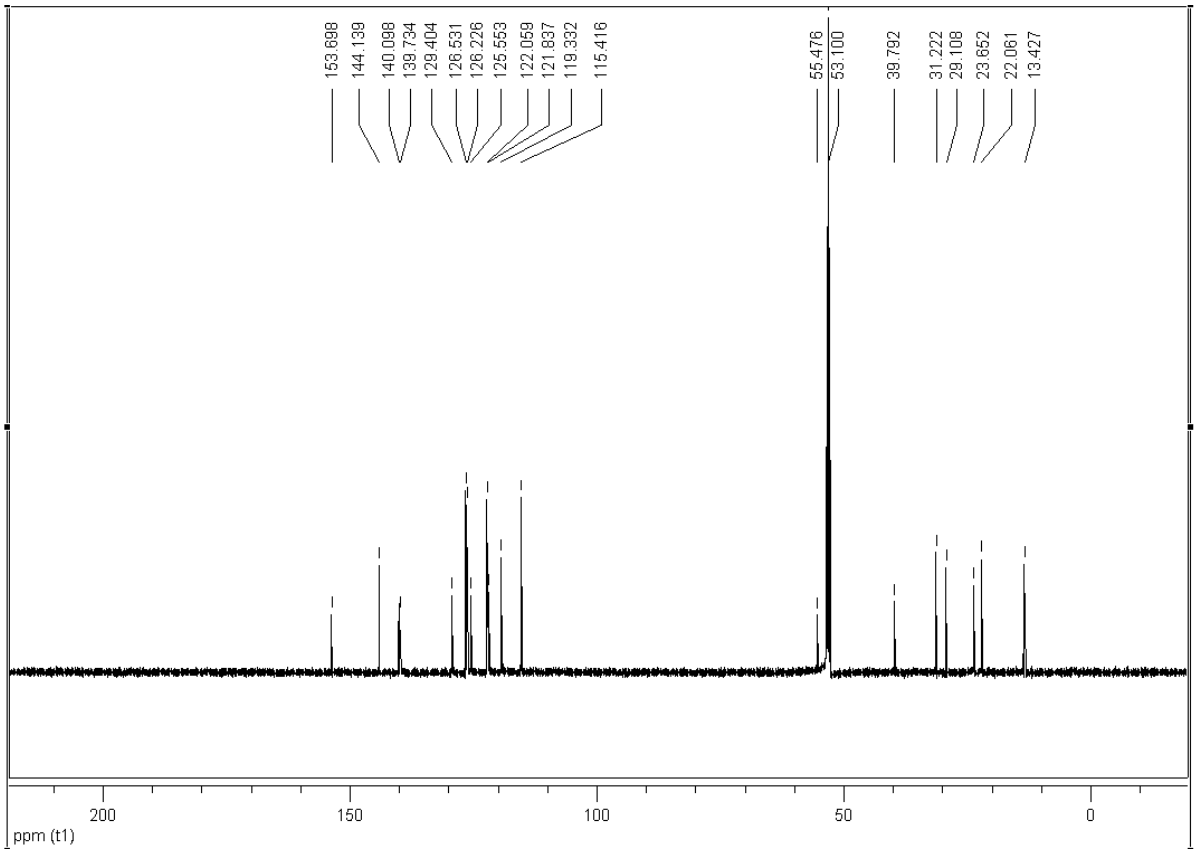


c) ^{1}H and ^{13}C NMR spectra of 8-13

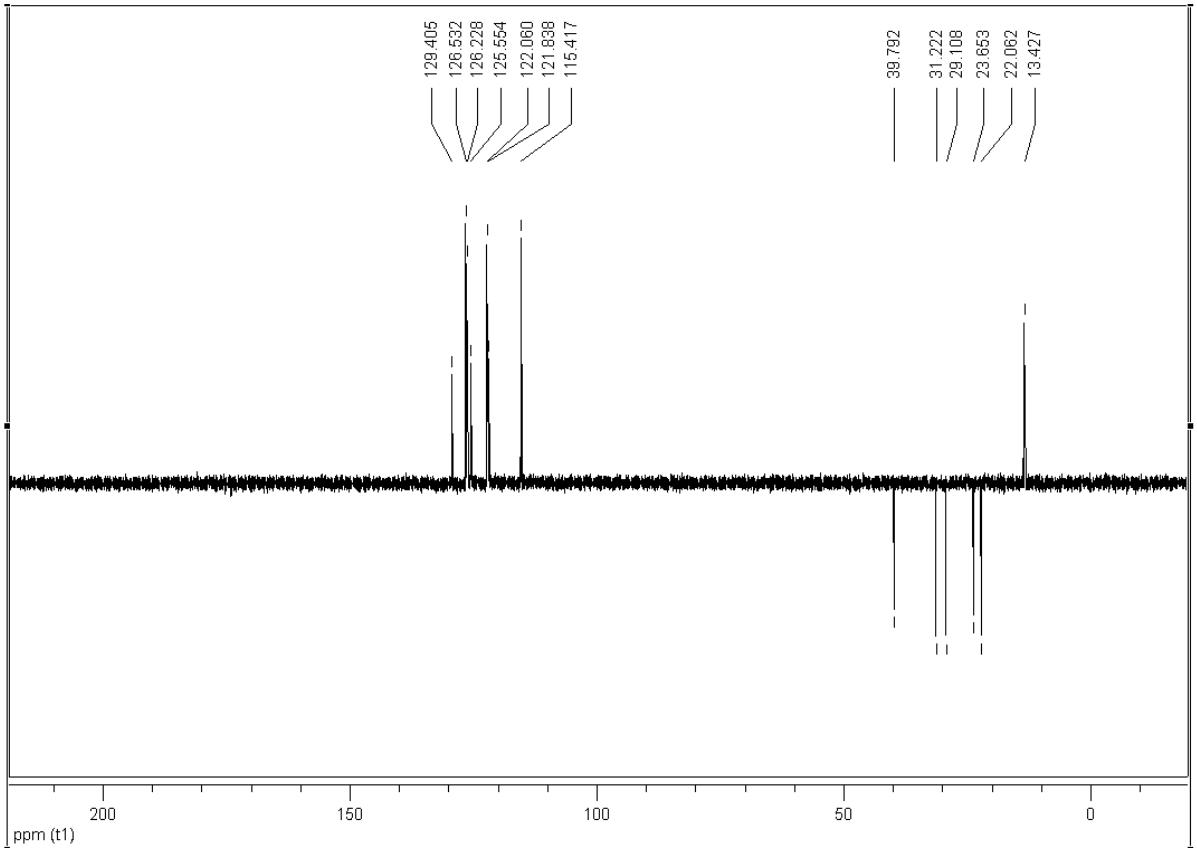
^{1}H NMR spectra of **8** recorded in CD_2Cl_2 (298K, 500 MHz)



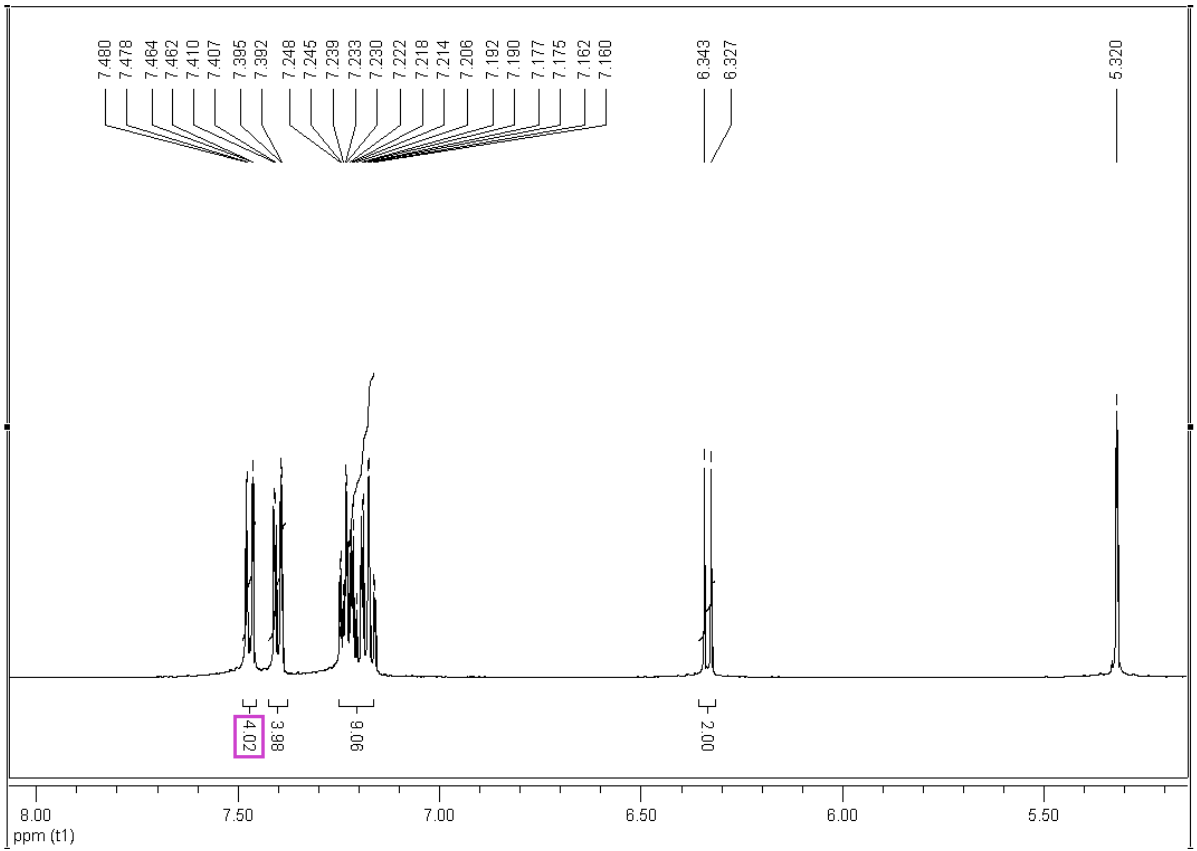
^{13}C NMR spectra of **8** recorded in CD_2Cl_2 (298K, 125 MHz)



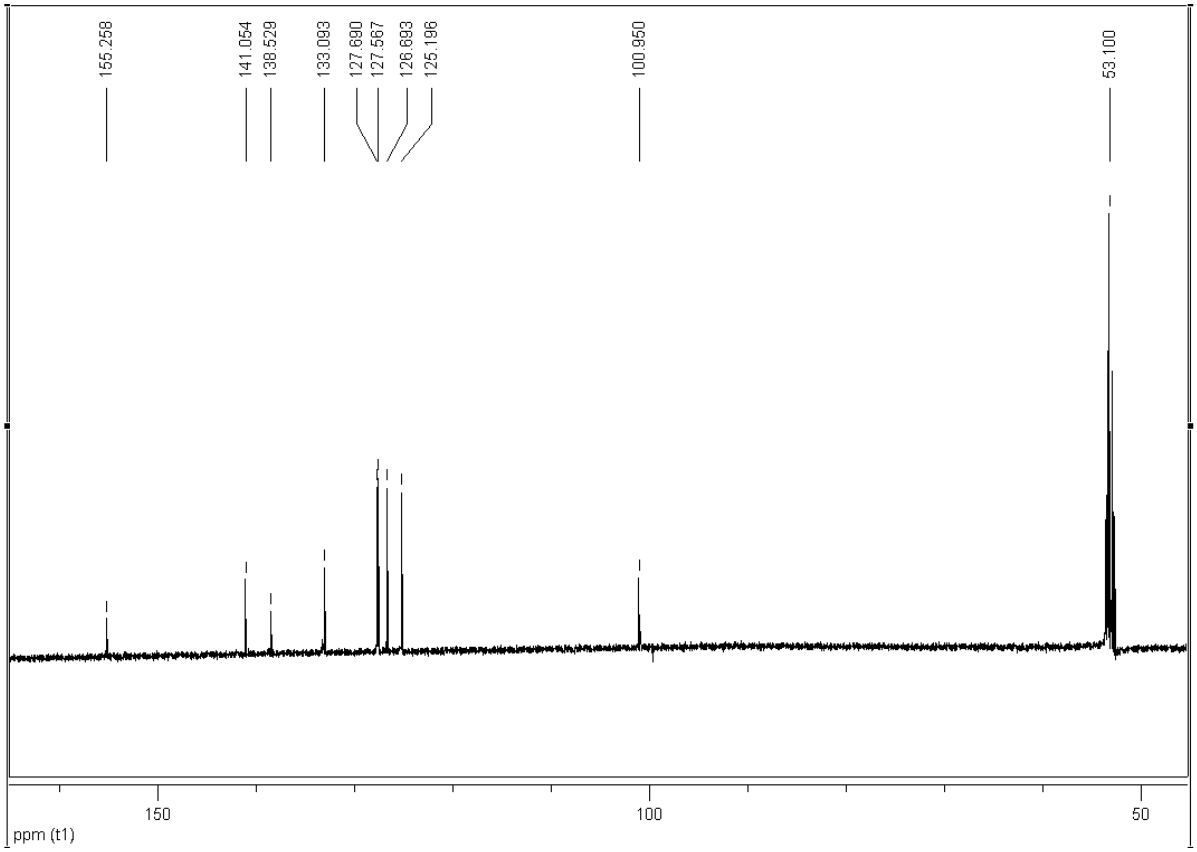
DEPT NMR spectra of **8** recorded in CD_2Cl_2 (298K, 125 MHz)



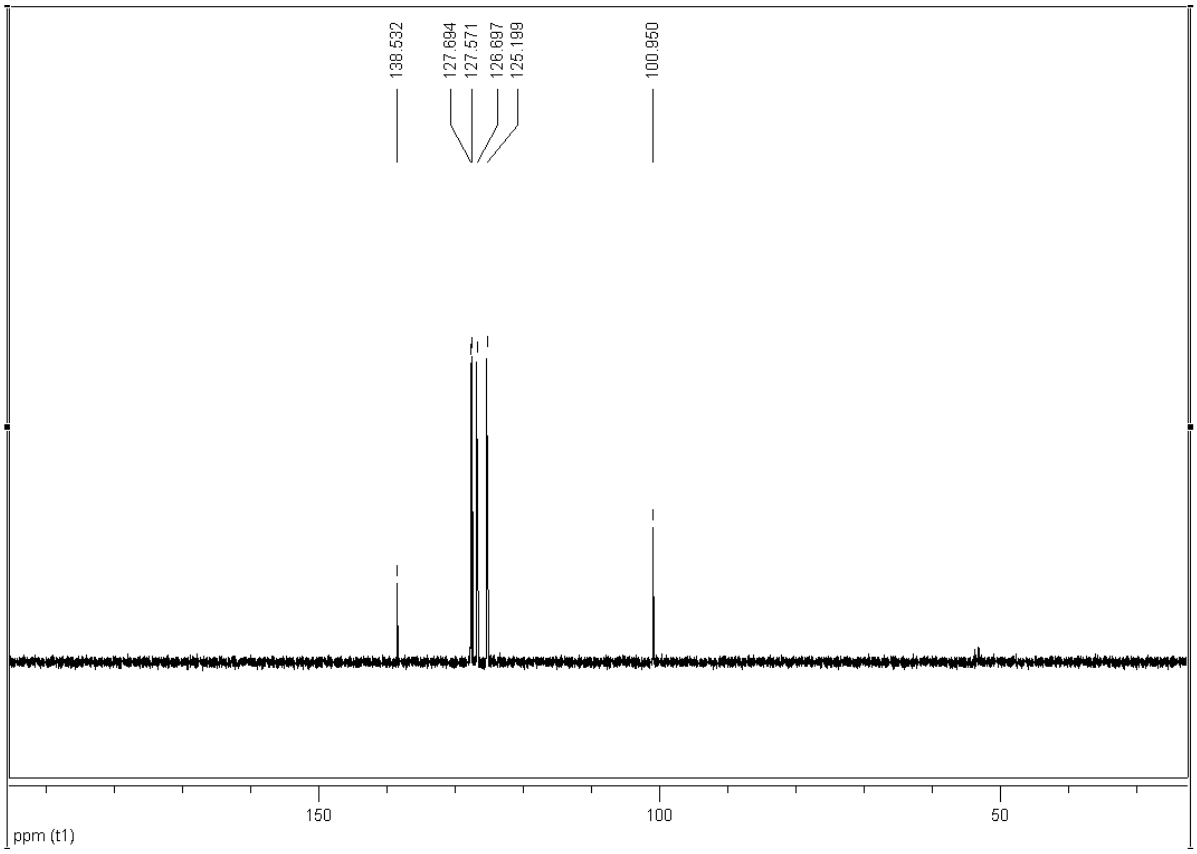
^1H NMR spectra of **9** recorded in CD_2Cl_2 (298K, 500 MHz)



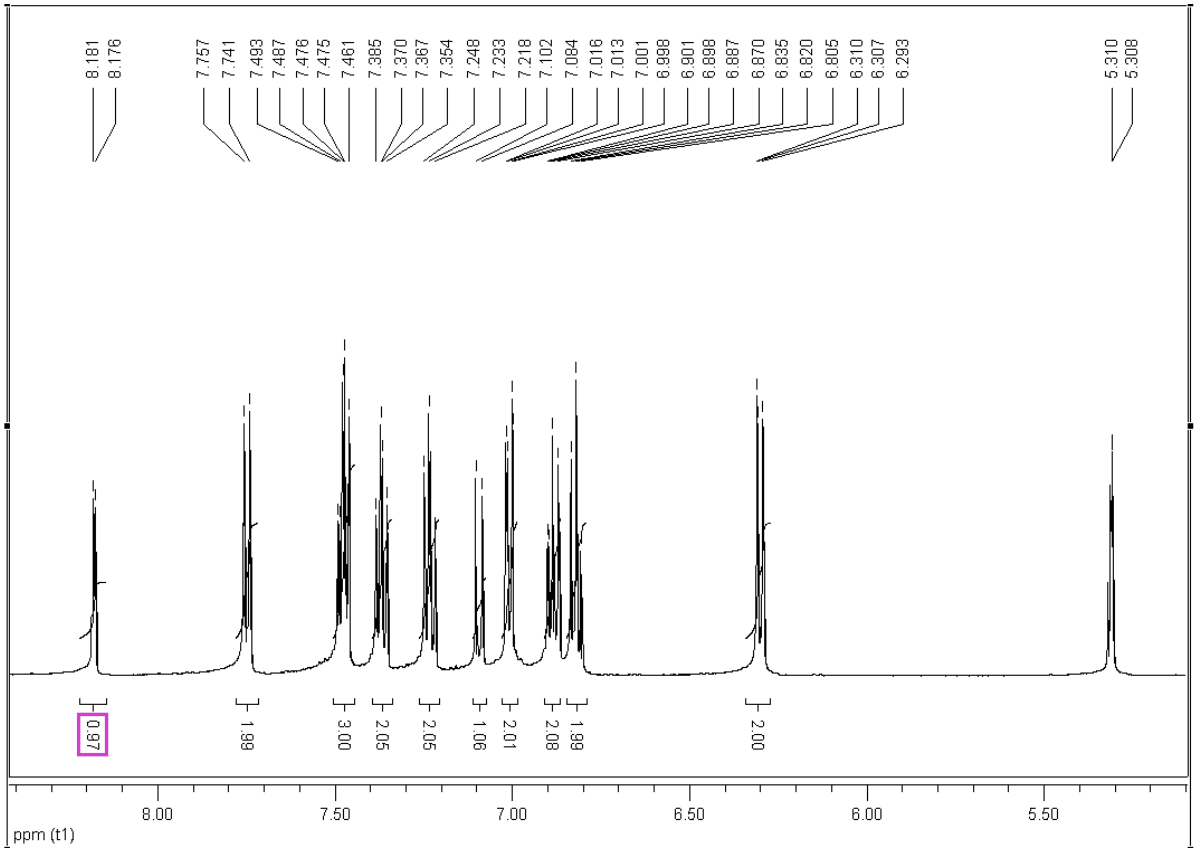
^{13}C NMR spectra of **9** recorded in CD_2Cl_2 (298K, 125 MHz)



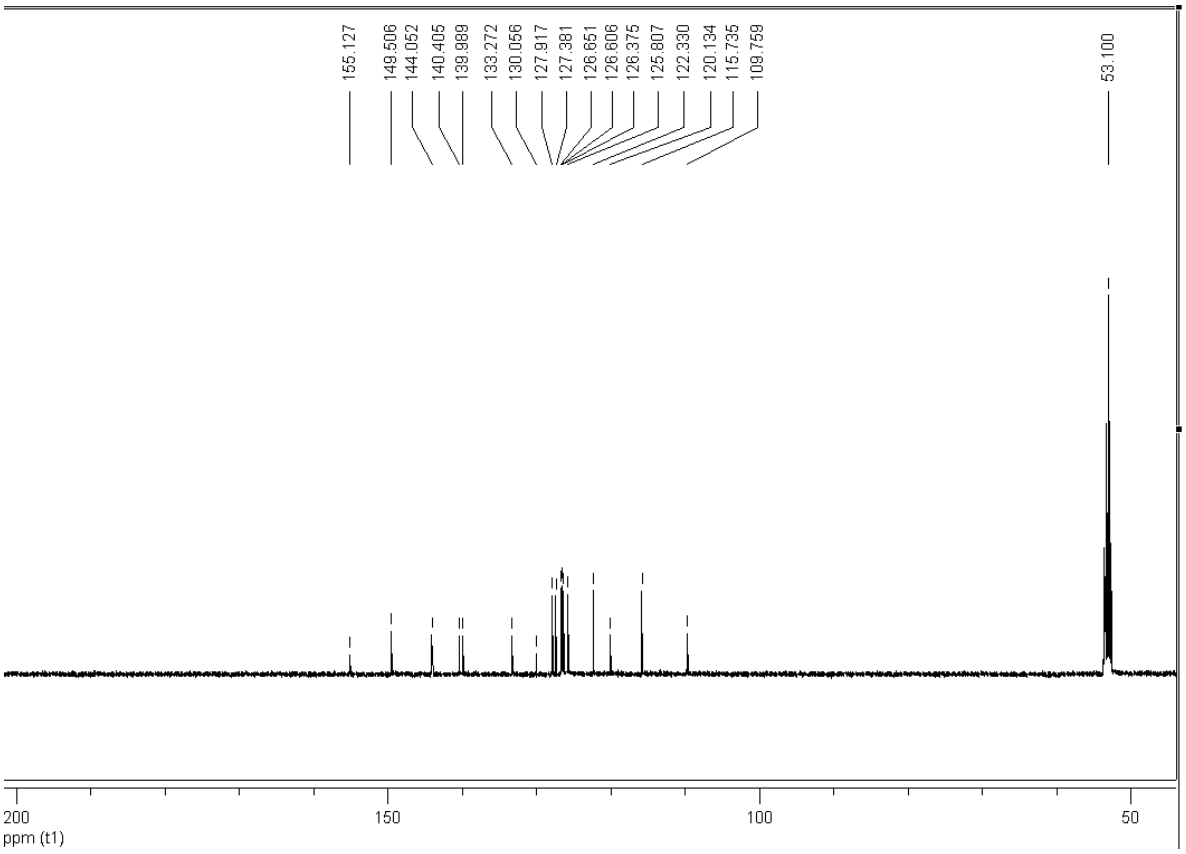
DEPT NMR spectra of **9** recorded in CD_2Cl_2 (298K, 125 MHz)



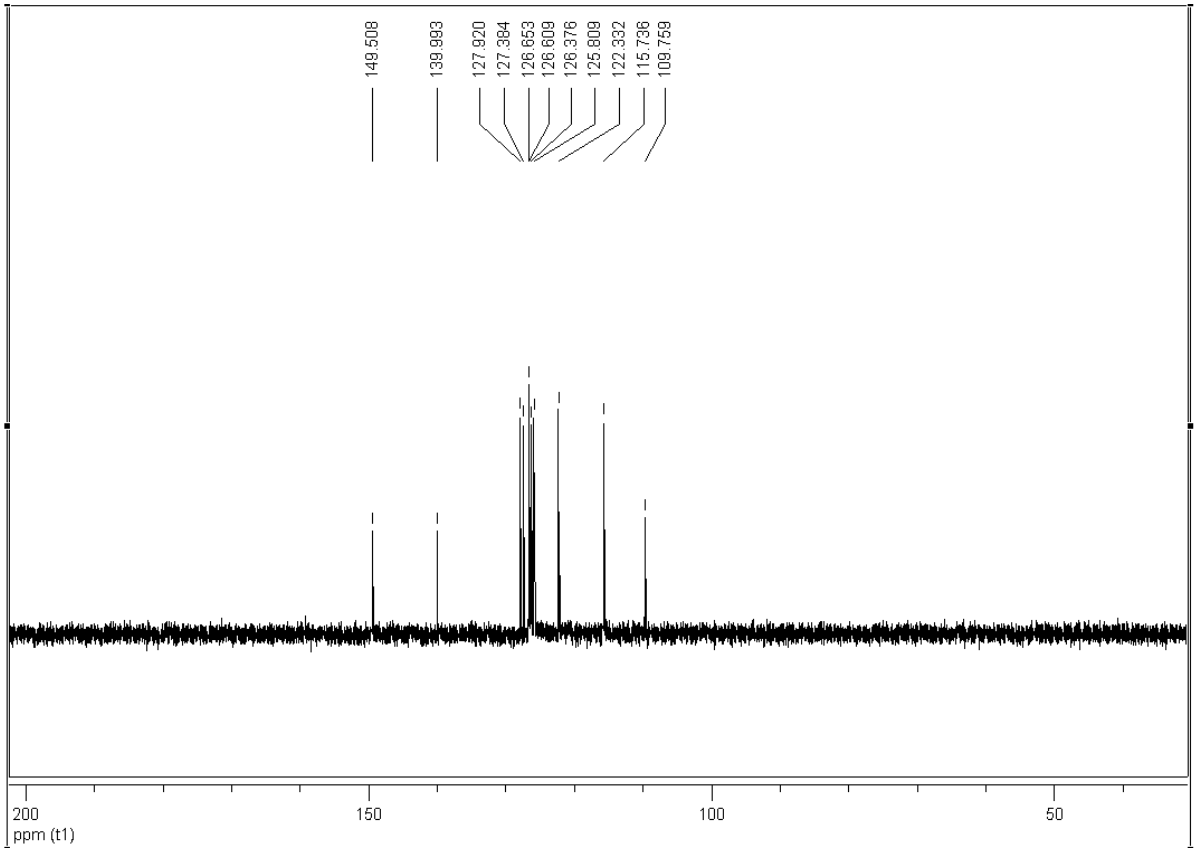
^{1}H NMR spectra of **10** recorded in CD_2Cl_2 (298K, 500 MHz)



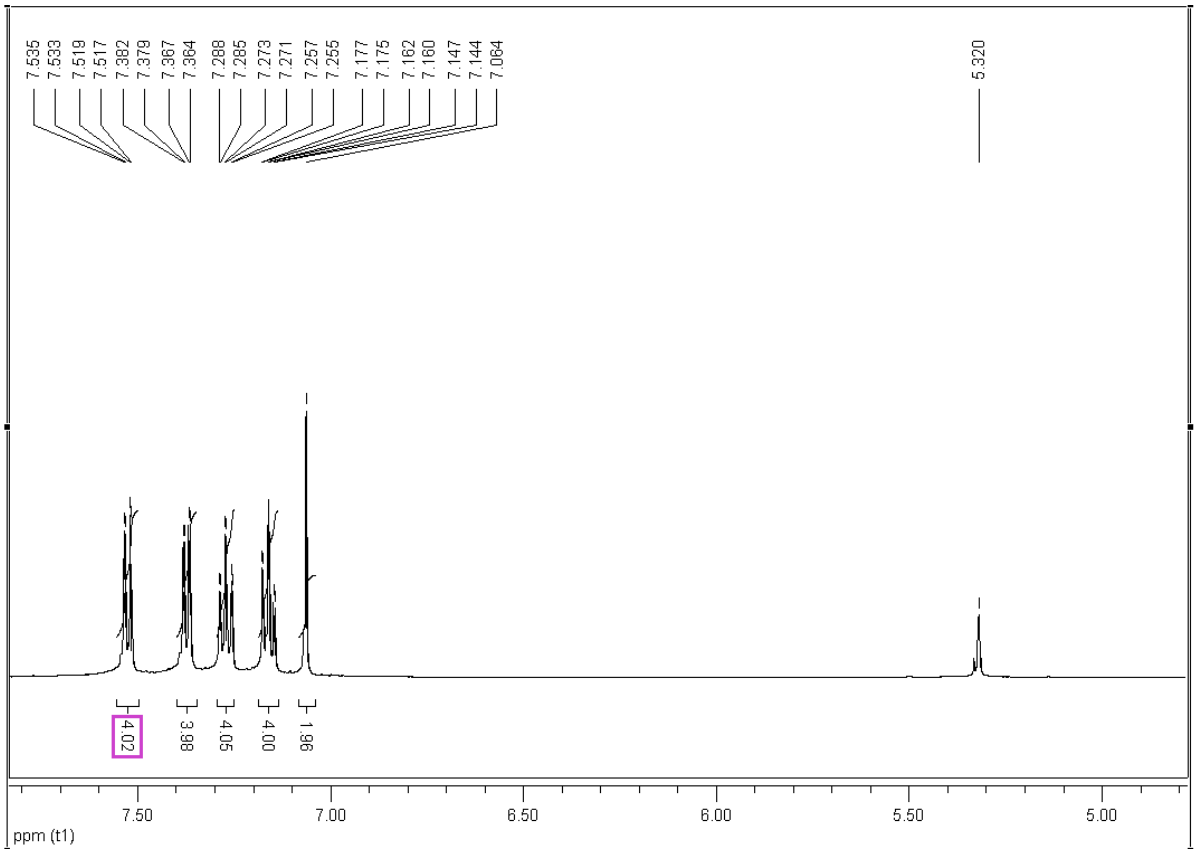
^{13}C NMR spectra of **10** recorded in CD_2Cl_2 (298K, 125 MHz)



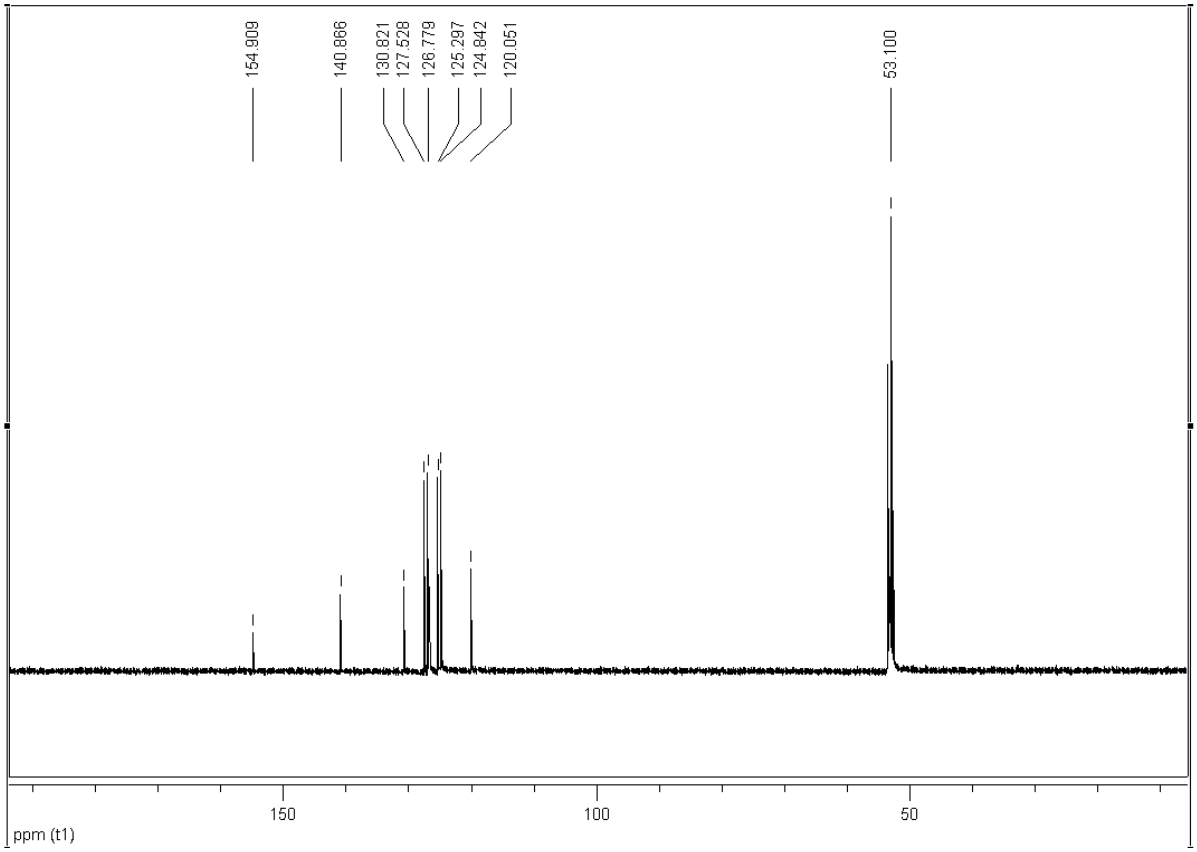
DEPT NMR spectra of **10** recorded in CD_2Cl_2 (298K, 125 MHz)



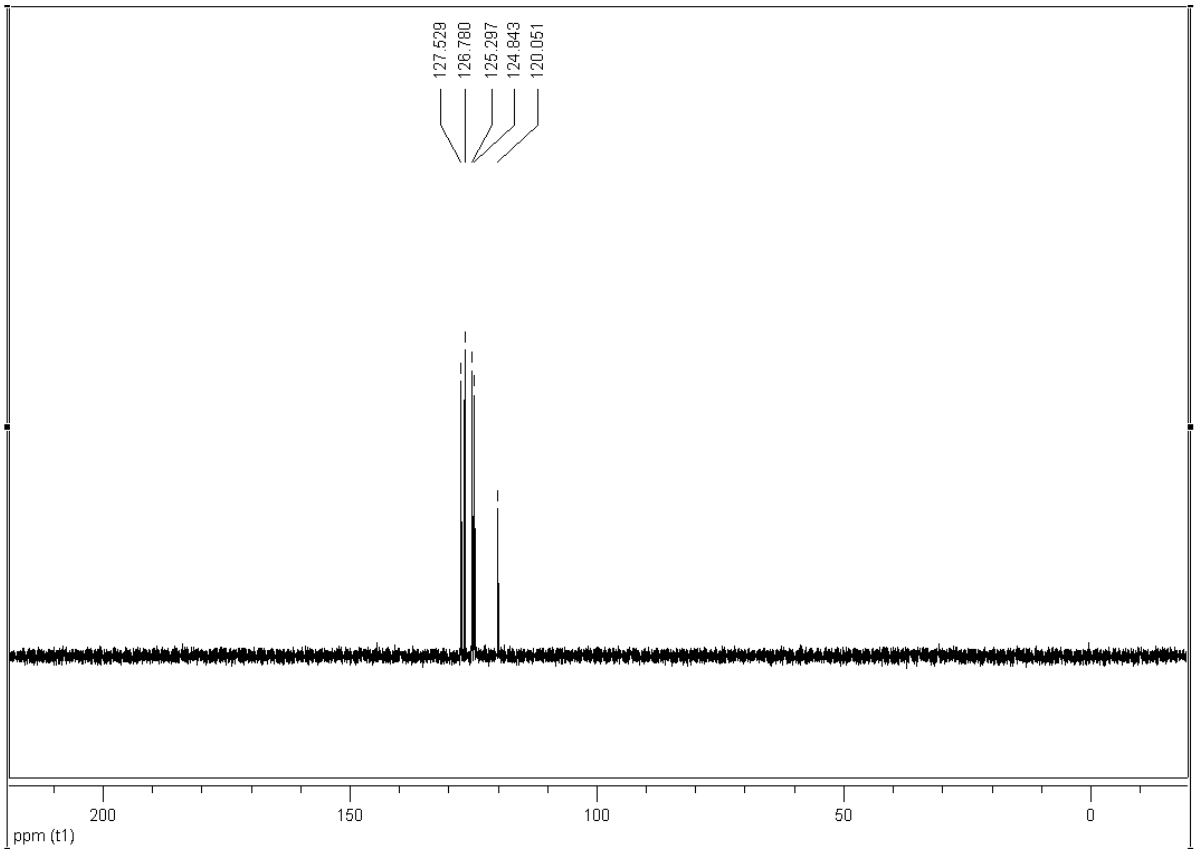
^1H NMR spectra of **11** recorded in CD_2Cl_2 (298K, 500 MHz)



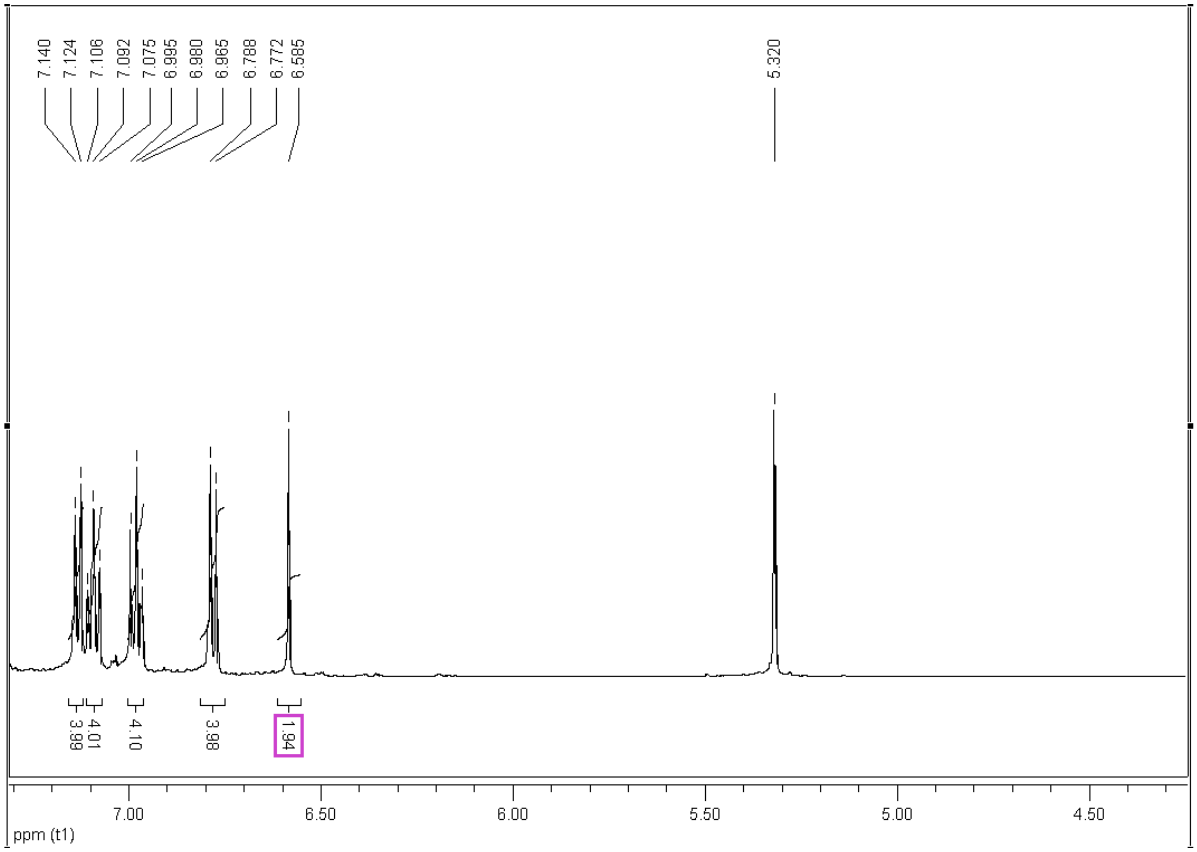
^{13}C NMR spectra of **11** recorded in CD_2Cl_2 (298K, 125 MHz)



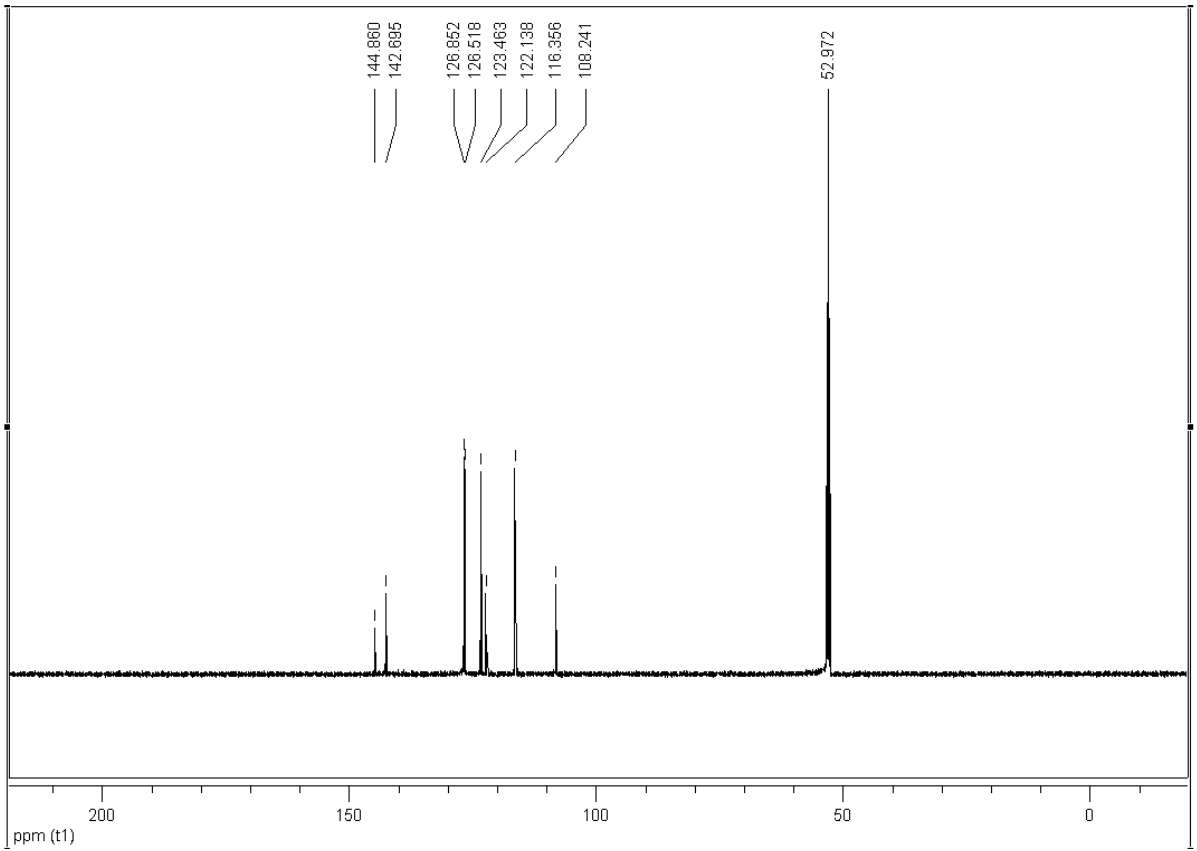
DEPT NMR spectra of **11** recorded in CD_2Cl_2 (298K, 125 MHz)



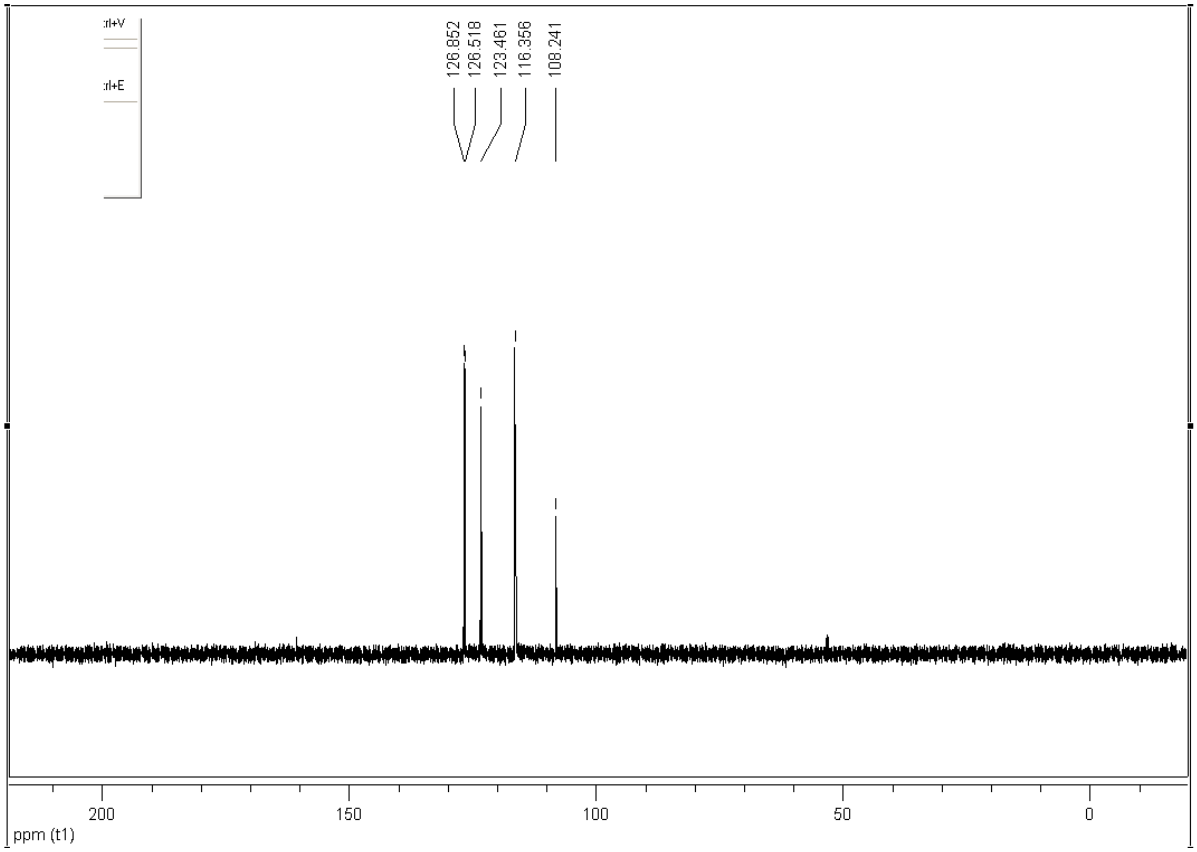
^{1}H NMR spectra of **12** recorded in CD_2Cl_2 (298K, 500 MHz)



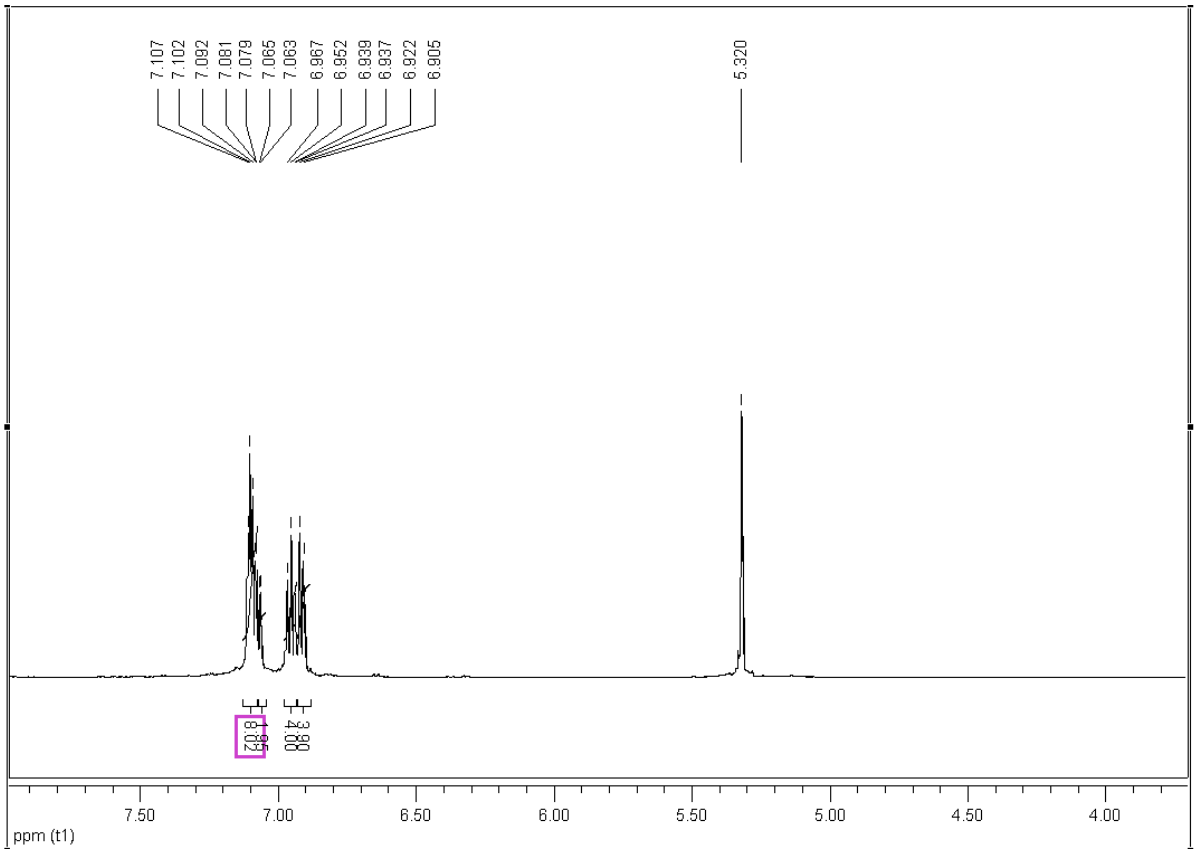
^{13}C NMR spectra of **12** recorded in CD_2Cl_2 (298K, 125 MHz)



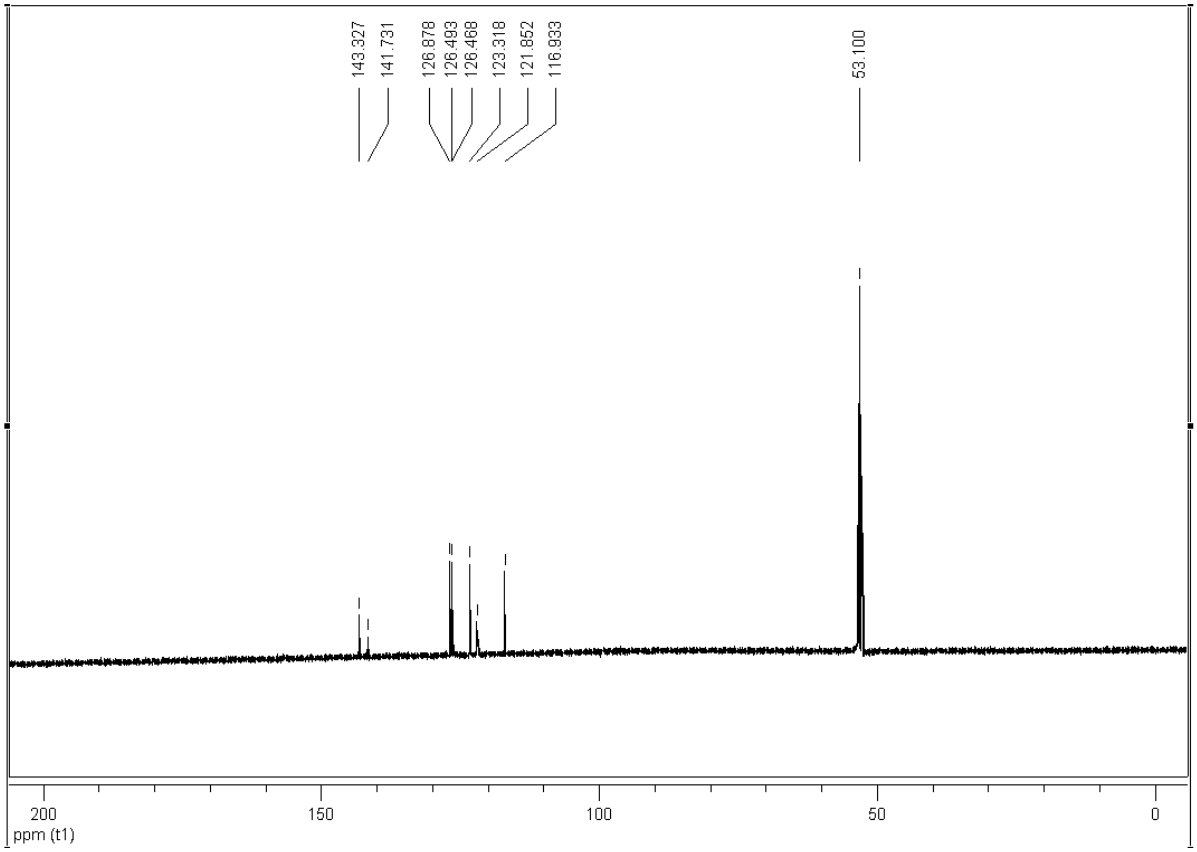
DEPT NMR spectra of **12** recorded in CD_2Cl_2 (298K, 125 MHz)



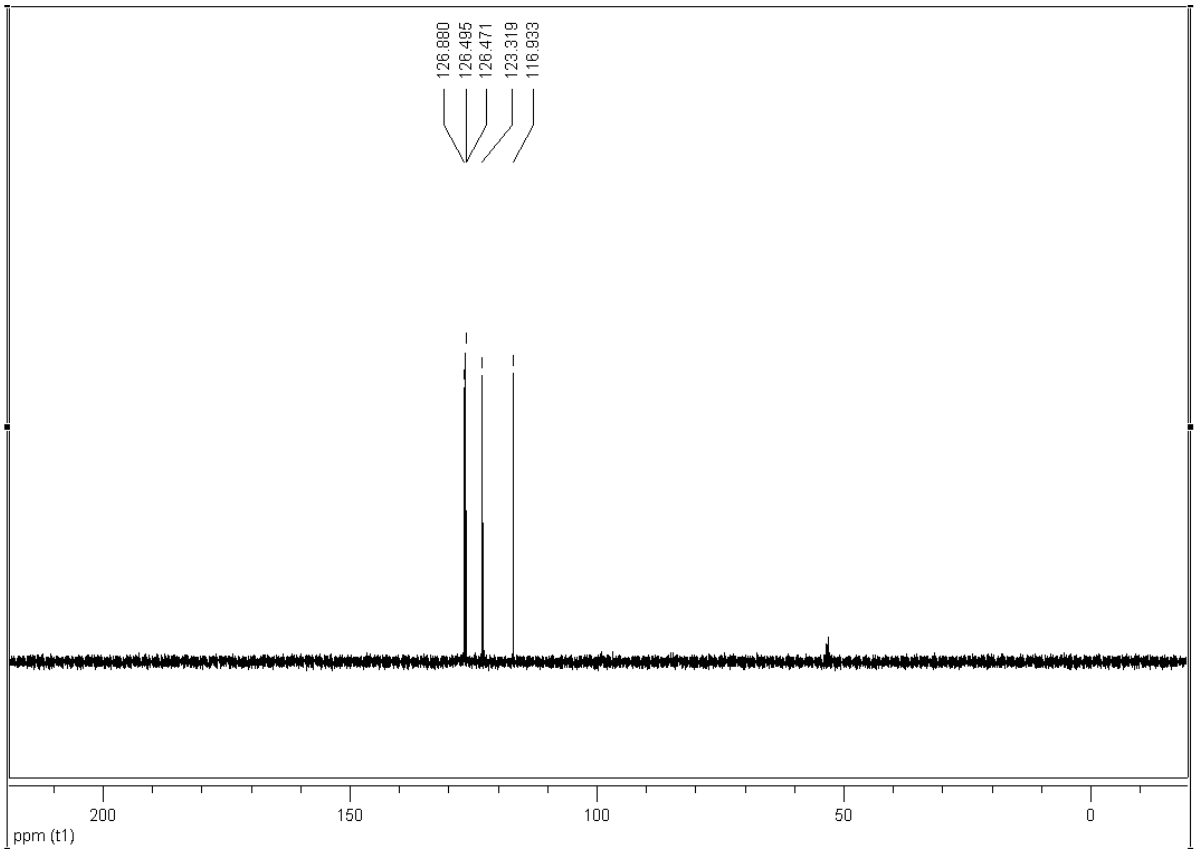
^{1}H NMR spectra of **13** recorded in CD_2Cl_2 (298K, 500 MHz)



^{13}C NMR spectra of **13** recorded in CD_2Cl_2 (298K, 125 MHz)



DEPT NMR spectra of **13** recorded in CD_2Cl_2 (298K, 125 MHz)



d) Molecular modelling coordinates of **11** and **13**

Molecular modelling coordinates (B3LYP/6-31+G(d,p)) of **11**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.231496	-2.222135	-1.198757
2	6	0	3.509430	-1.188972	-0.292436
3	6	0	4.568311	-1.340471	0.617500
4	6	0	5.320101	-2.520731	0.633397
5	6	0	5.003648	-3.563556	-0.238399
6	6	0	3.960901	-3.410480	-1.158099
7	1	0	2.436920	-2.088913	-1.926328
8	1	0	6.146735	-2.617256	1.330772
9	1	0	5.581713	-4.482157	-0.212998
10	1	0	3.726554	-4.207943	-1.856660
11	6	0	3.490660	1.251034	-0.259260
12	6	0	3.221076	2.332489	-1.109333
13	6	0	4.552564	1.352832	0.659449
14	6	0	3.965242	3.509700	-1.001644
15	1	0	2.411661	2.253378	-1.820668
16	6	0	5.314560	2.521953	0.738558
17	1	0	3.730008	4.345730	-1.653327
18	1	0	6.139864	2.574235	1.442185
19	7	0	2.756465	0.021385	-0.301849
20	16	0	4.911031	-0.013130	1.755253
21	6	0	1.349382	-0.042203	-0.306586
22	6	0	0.684709	-1.107889	0.354611
23	1	0	1.245430	-1.870345	0.882607
24	6	0	5.008457	3.610585	-0.079455
25	1	0	5.592713	4.522786	-0.005364
26	6	0	-0.684743	-1.107900	0.354571
27	1	0	-1.245482	-1.870363	0.882536

28	6	0	-1.349407	-0.042234	-0.306671
29	7	0	0.670194	0.934206	-0.901229
30	7	0	-0.670212	0.934189	-0.901268
31	7	0	-2.756498	0.021326	-0.302005
32	6	0	-3.490710	1.250960	-0.259531
33	6	0	-3.509445	-1.189047	-0.292334
34	6	0	-4.568216	-1.340422	0.617749
35	6	0	-3.231633	-2.222322	-1.198570
36	1	0	-2.437145	-2.089183	-1.926252
37	6	0	-3.961034	-3.410656	-1.157663
38	1	0	-3.726785	-4.208214	-1.856147
39	6	0	-5.003665	-3.563613	-0.237807
40	1	0	-5.581729	-4.482210	-0.212225
41	6	0	-3.221277	2.332277	-1.109825
42	1	0	-2.412043	2.253076	-1.821360
43	6	0	-3.965418	3.509507	-1.002183
44	1	0	-3.730292	4.345439	-1.654031
45	6	0	-4.552474	1.352890	0.659318
46	16	0	-4.910797	-0.012918	1.755352
47	6	0	-5.320010	-2.520680	0.633896
48	1	0	-6.146560	-2.617110	1.331383
49	6	0	-5.008477	3.610541	-0.079828
50	1	0	-5.592707	4.522763	-0.005774
51	6	0	-5.314460	2.522027	0.738382
52	1	0	-6.139655	2.574404	1.442130

Energy (HF) = - 2093.2382134 Hartrees

Molecular modelling coordinates (B3LYP/6-31+G(d,p)) of **13**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.892591	-2.366803	0.923209
2	6	0	-3.310071	-1.240221	0.199425
3	6	0	-4.443967	-1.354301	-0.626224
4	6	0	-5.153455	-2.556872	-0.692416
5	6	0	-4.718996	-3.676881	0.018492
6	6	0	-3.581552	-3.576835	0.820366
7	1	0	-2.016588	-2.299601	1.556728
8	1	0	-6.037143	-2.613654	-1.321122
9	1	0	-5.264845	-4.612167	-0.054946
10	1	0	-3.228003	-4.437268	1.380444
11	6	0	-3.310068	1.240023	0.199705
12	6	0	-2.892600	2.366431	0.923765
13	6	0	-4.443960	1.354300	-0.625924
14	6	0	-3.581557	3.576490	0.821197
15	1	0	-2.016611	2.299075	1.557287
16	6	0	-5.153441	2.556887	-0.691846
17	1	0	-3.228015	4.436786	1.381492
18	1	0	-6.037123	2.613819	-1.320547
19	7	0	-2.610208	-0.000107	0.284612
20	16	0	-4.921056	0.000116	-1.679574
21	6	0	-4.718987	3.676730	0.019329
22	1	0	-5.264832	4.612034	-0.053898
23	6	0	-1.254267	-0.000146	0.671234
24	6	0	-0.712850	-0.000267	1.933793
25	16	0	0.000073	-0.000024	-0.555262
26	6	0	0.712777	-0.000231	1.933855
27	1	0	-1.320944	-0.000350	2.831742
28	6	0	1.254307	-0.000106	0.671354

29	1	0	1.320751	-0.000274	2.831890
30	7	0	2.610270	-0.000016	0.284807
31	6	0	3.309971	1.240168	0.199576
32	6	0	3.310254	-1.240061	0.199788
33	6	0	2.892507	2.366644	0.923538
34	6	0	4.443703	1.354432	-0.626261
35	6	0	2.893047	-2.366532	0.923911
36	6	0	4.444020	-1.354190	-0.626025
37	6	0	3.581272	3.576774	0.820623
38	1	0	2.016653	2.299256	1.557249
39	6	0	5.153004	2.557113	-0.692550
40	16	0	4.920895	0.000086	-1.679659
41	6	0	3.582098	-3.576515	0.821186
42	1	0	2.017167	-2.299266	1.557594
43	6	0	5.153606	-2.556713	-0.692119
44	6	0	4.718527	3.677024	0.018495
45	1	0	3.227736	4.437121	1.380843
46	1	0	6.036566	2.614050	-1.321420
47	1	0	3.228757	-4.436862	1.381529
48	6	0	4.719390	-3.676618	0.019092
49	1	0	6.037186	-2.613539	-1.320974
50	1	0	5.264219	4.612395	-0.055027
51	1	0	5.265305	-4.611870	-0.054279

Energy (HF) = - 2381.937506 Hartree

e) UV/Vis-NIR spectra of **9** and **9-H**$^+$