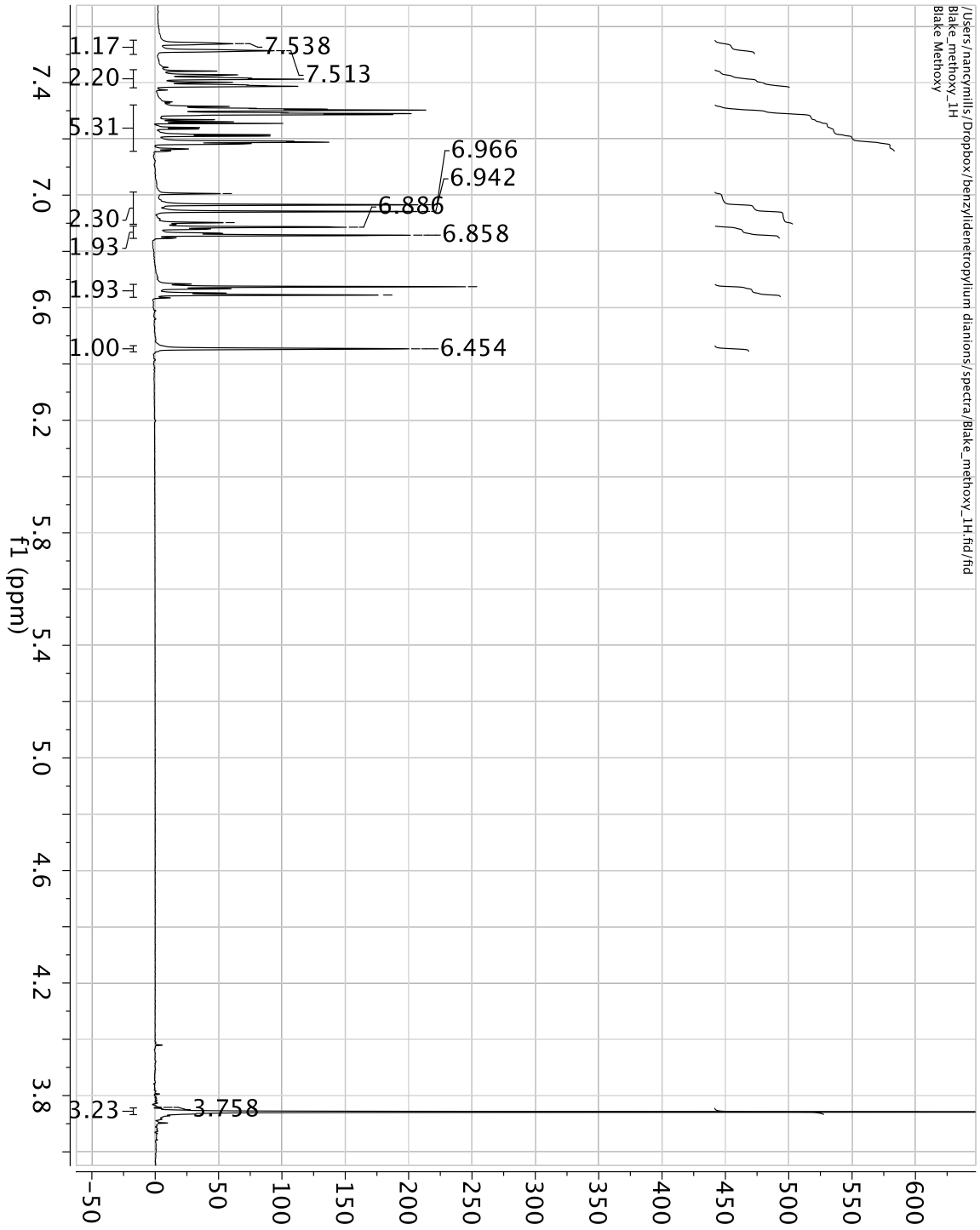
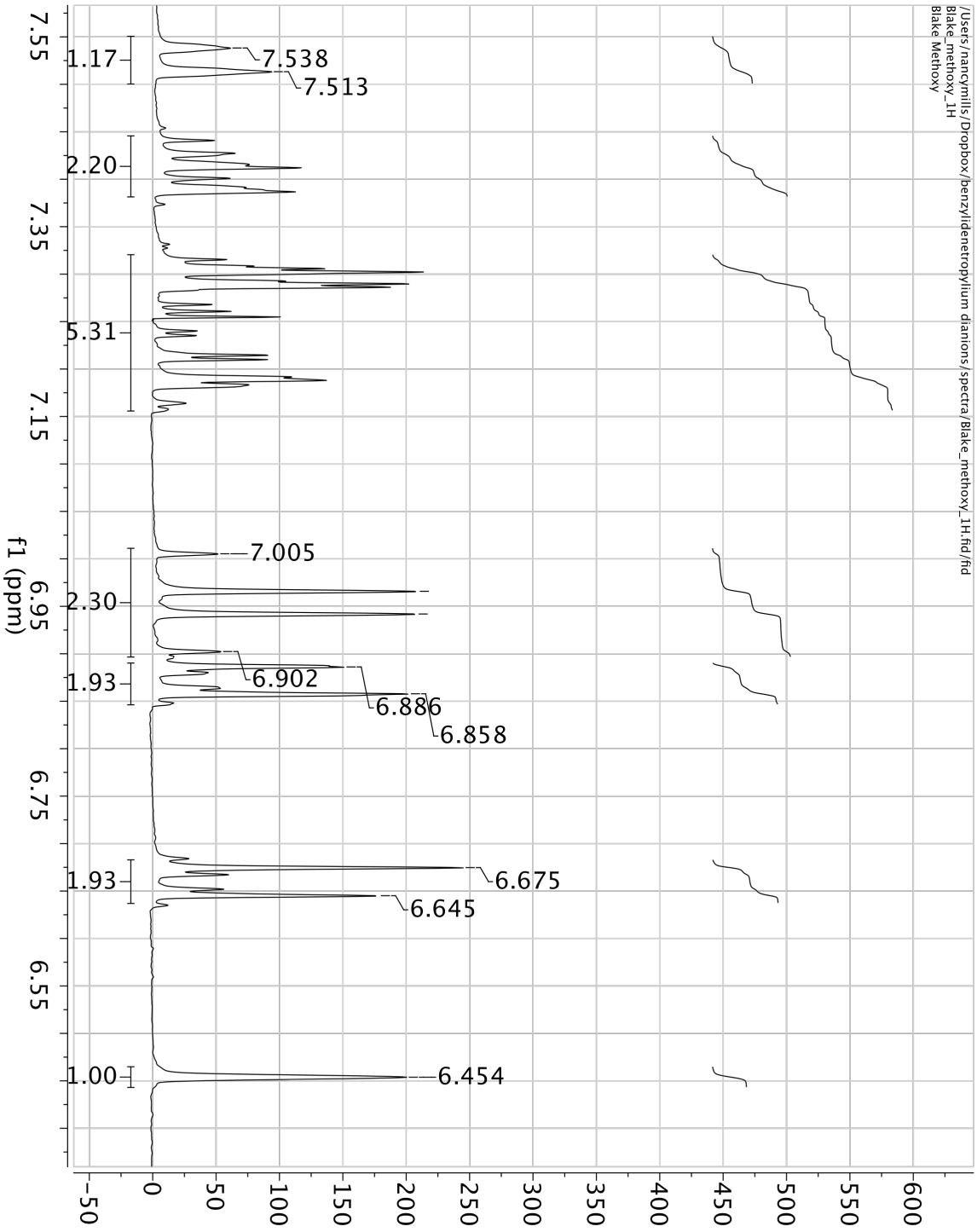
Reduction of benzylidene dibenzocycloheptenes: Over-reduction of antiaromatic dianions to aromatic tetraanions;

Blakely Tresca, MacDonald Higbee, and Nancy S. Mills*

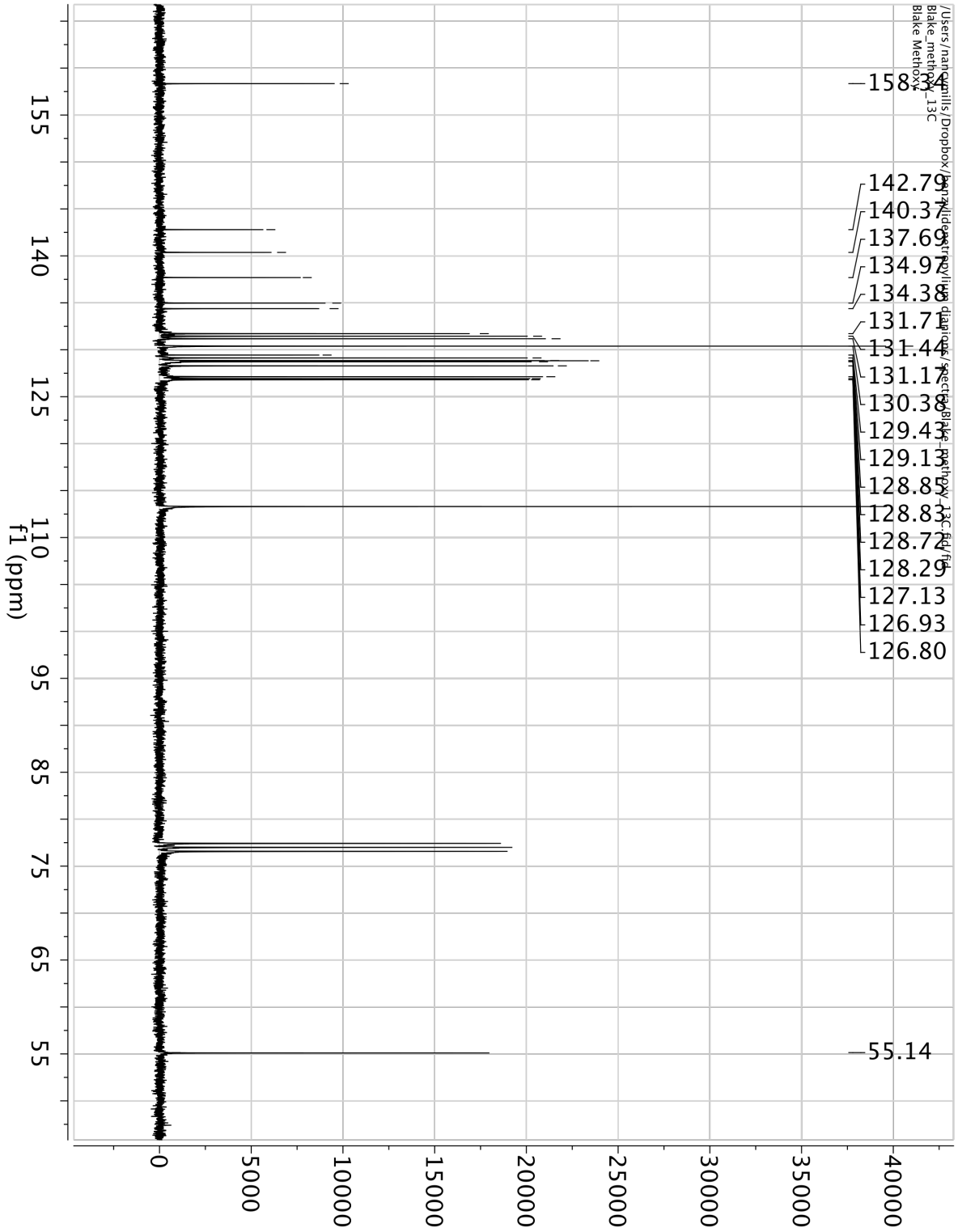
^{1}H NMR spectra of **1c** (entire spectrum)



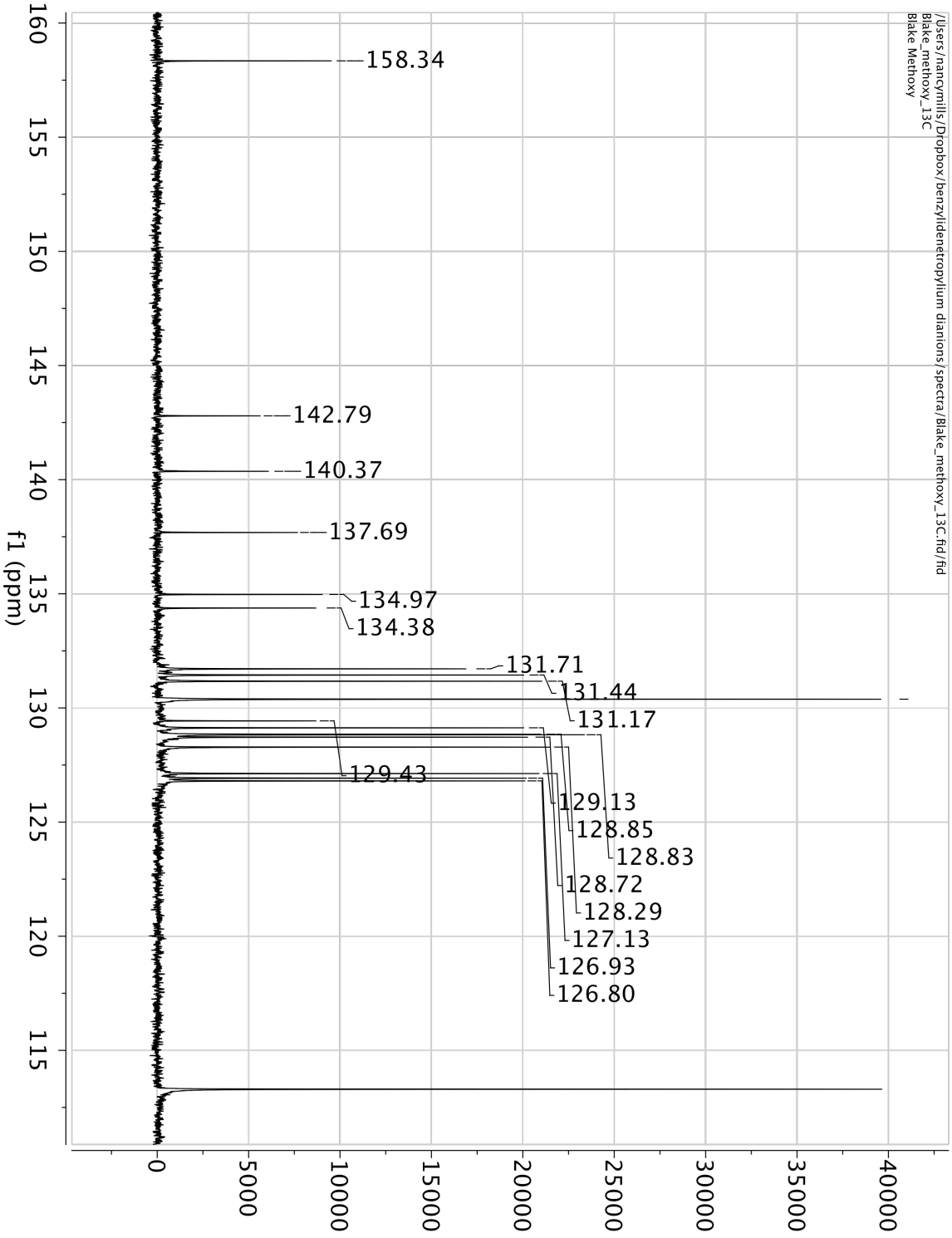
^{1}H NMR spectra of **1c** (aromatic region)



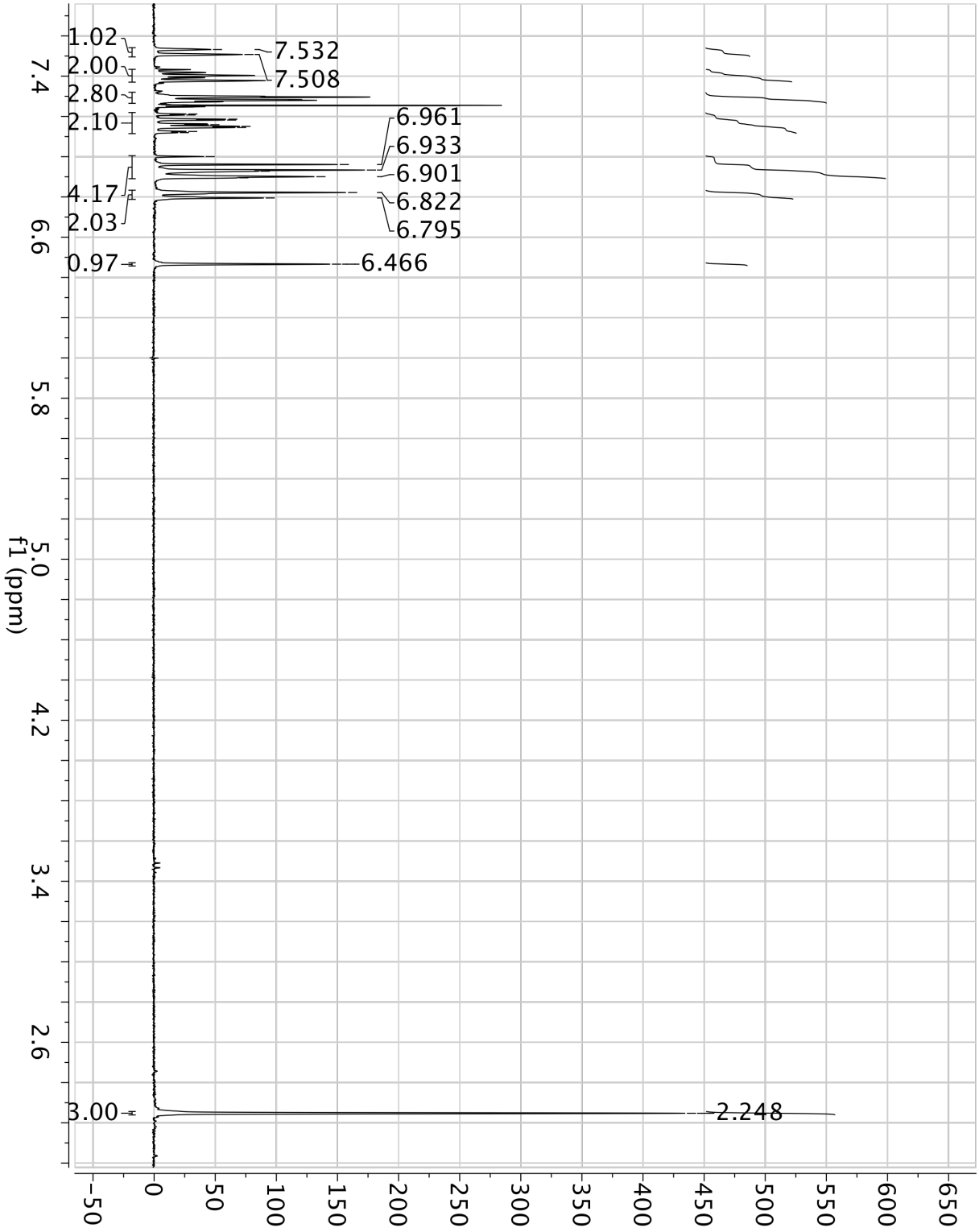
^{13}C NMR spectra of **1c** (entire spectrum)



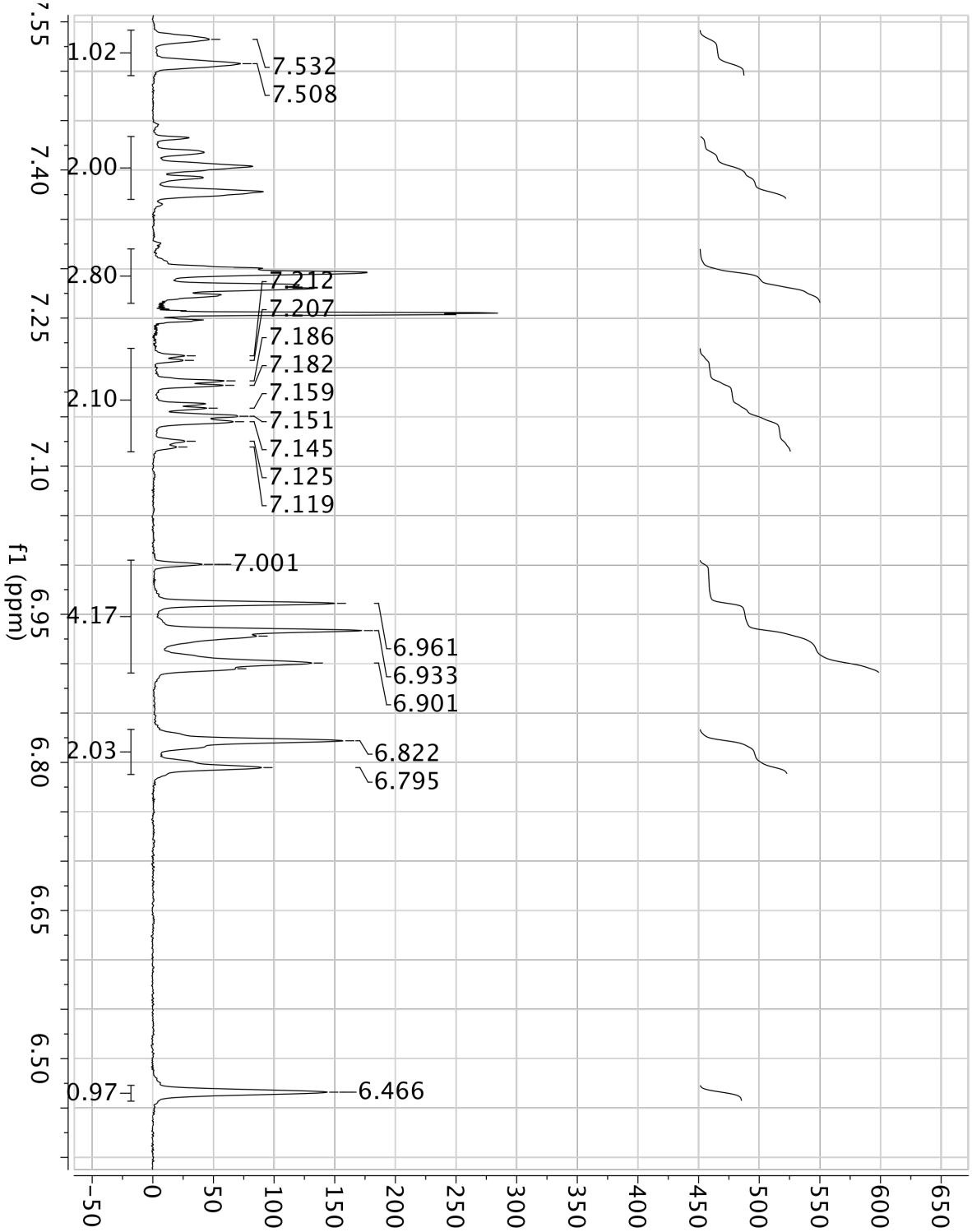
^{13}C NMR spectra of **1c** (aromatic region)



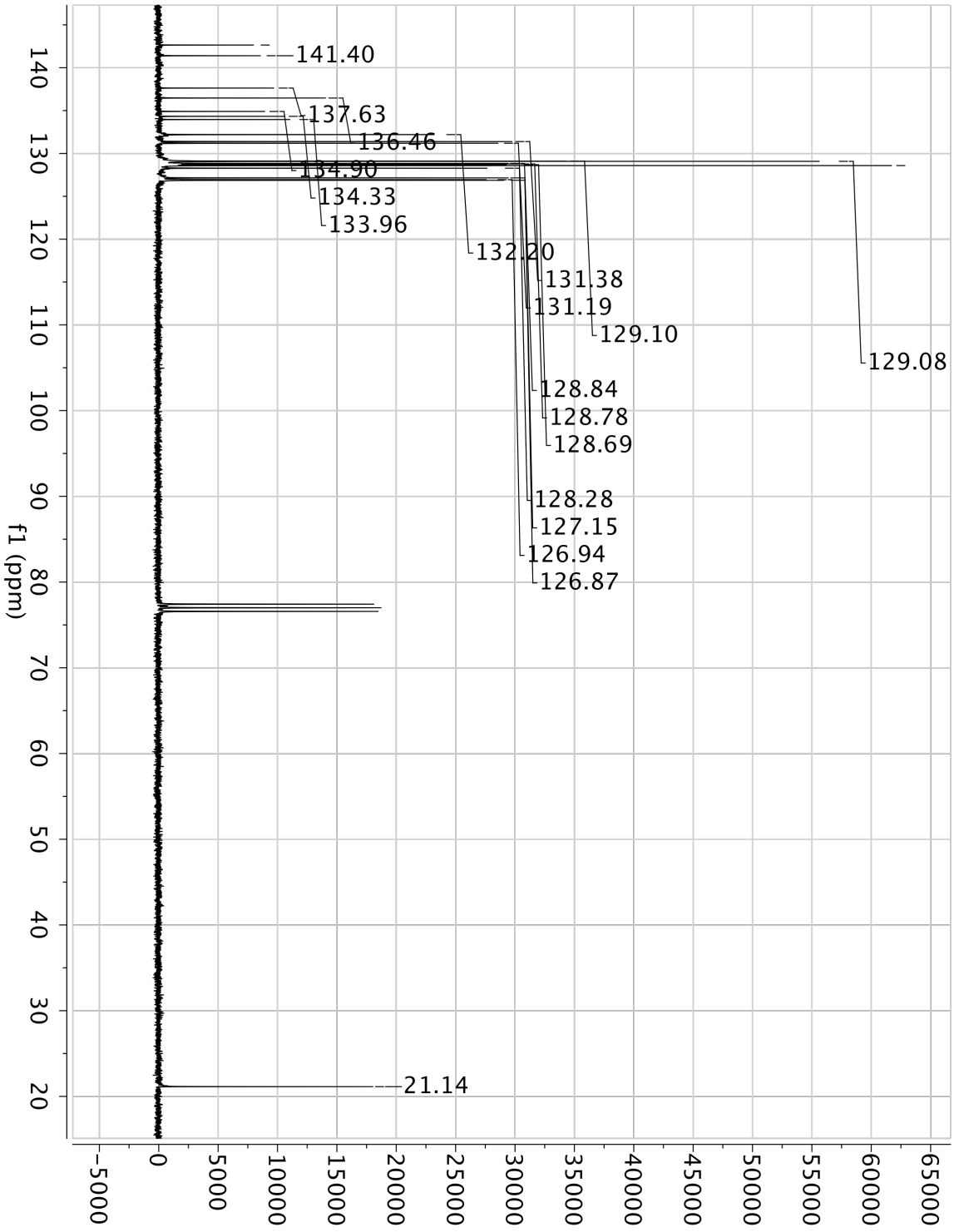
^{1}H NMR spectra of **1f** (entire spectrum)



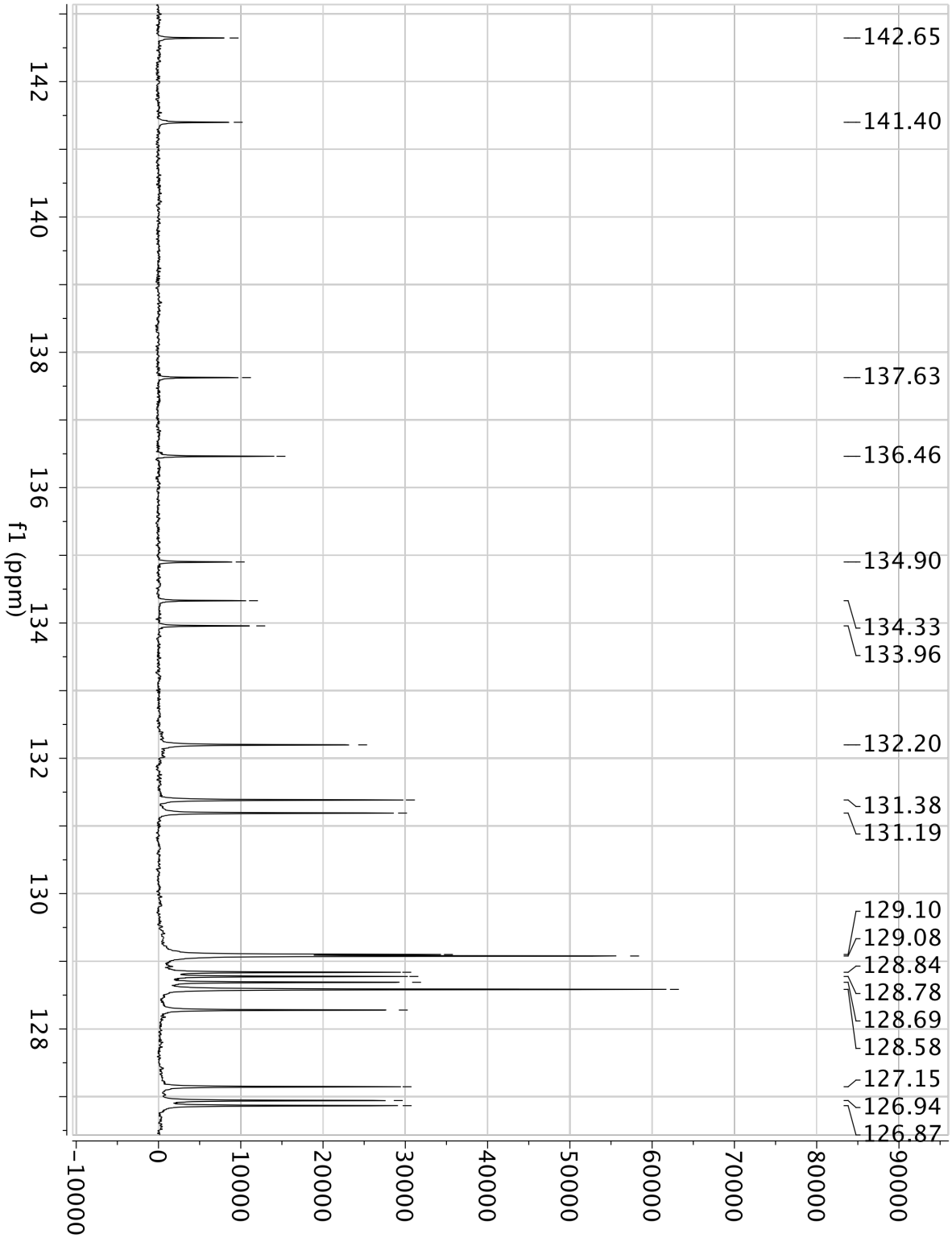
^{1}H NMR spectra of **1f** (aromatic region)



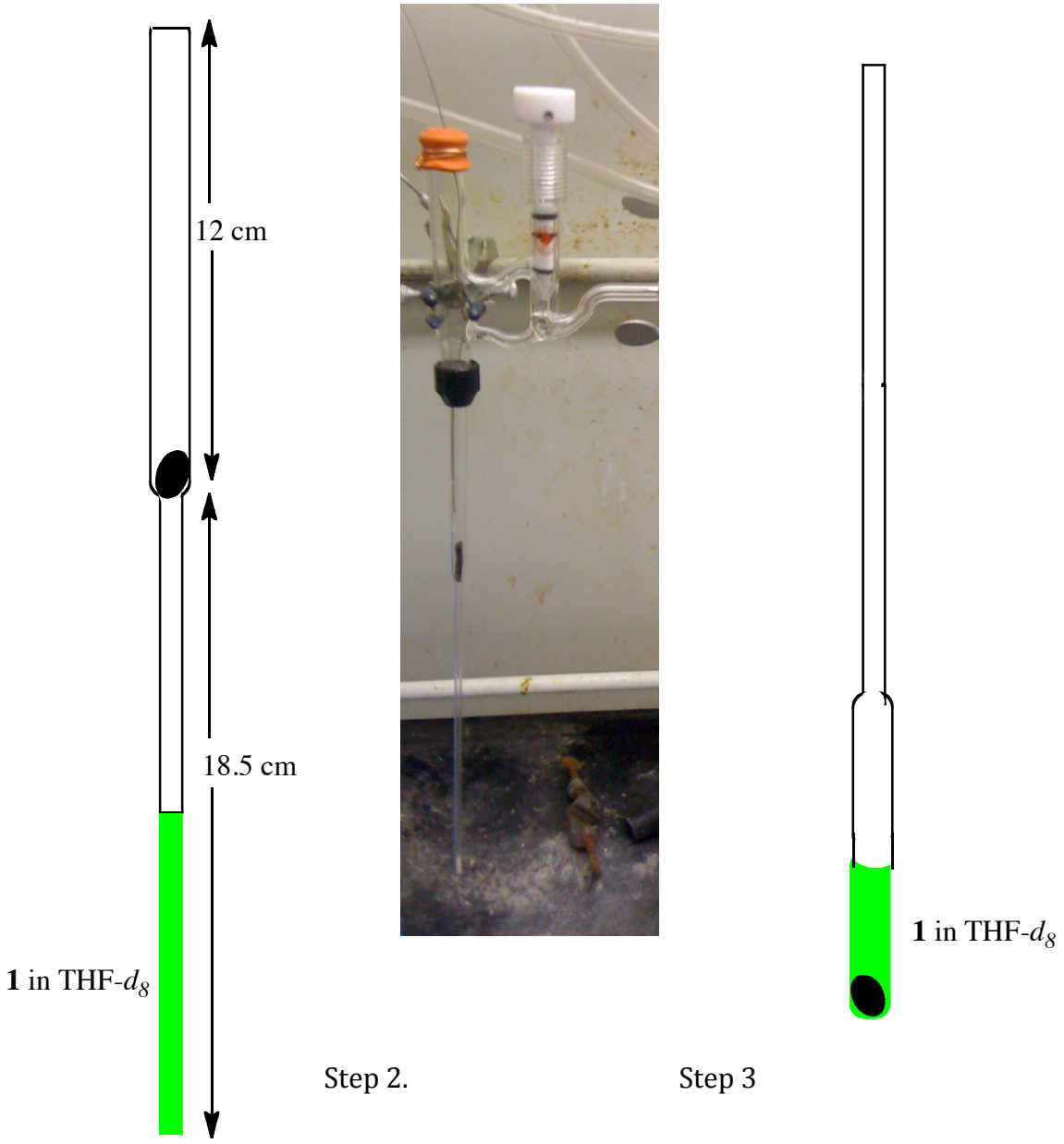
^{13}C NMR spectra of **1f** (entire spectrum)



^{13}C NMR spectra of **1f** (aromatic region)



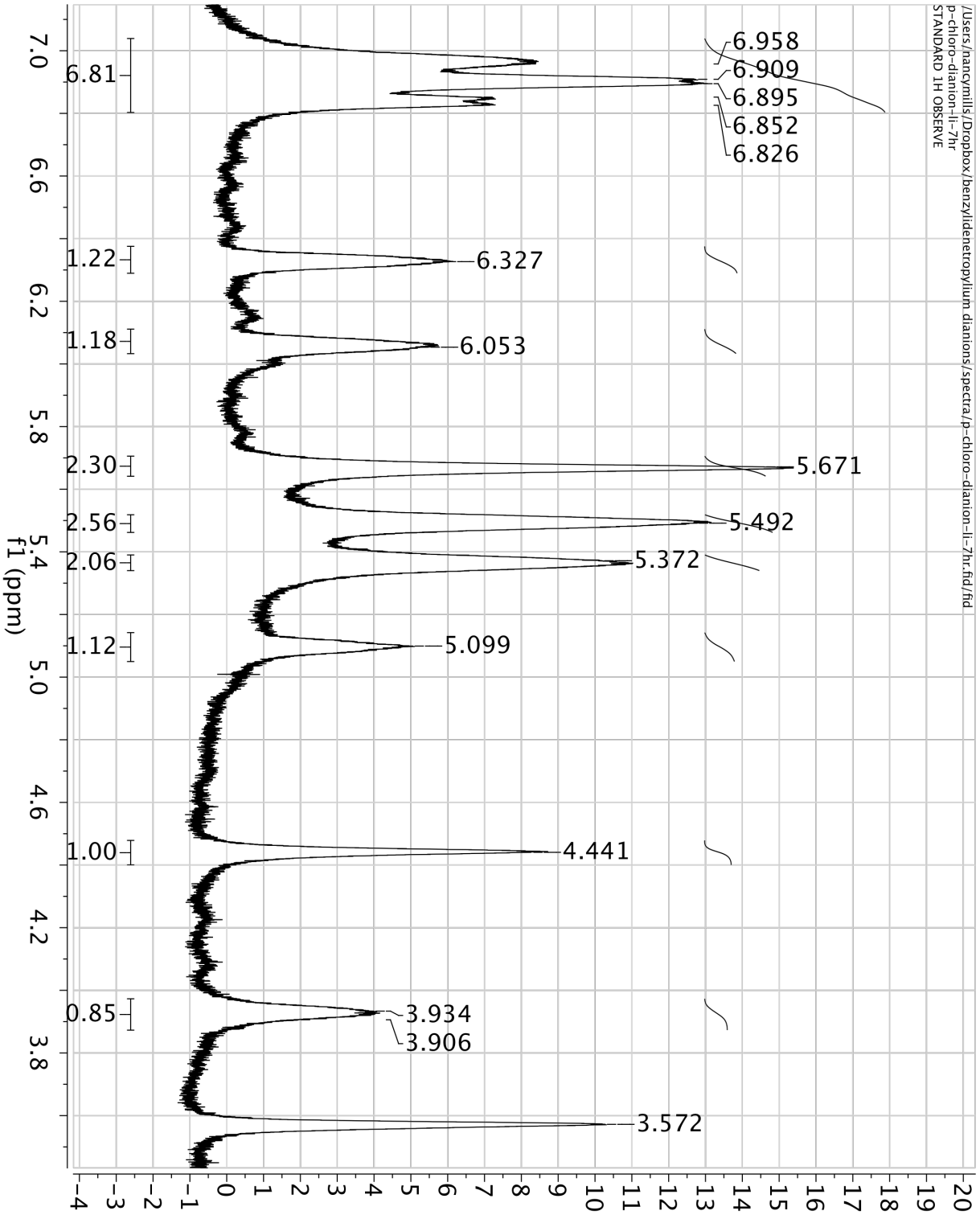
Reduction of **1**
Diagram of insert used:



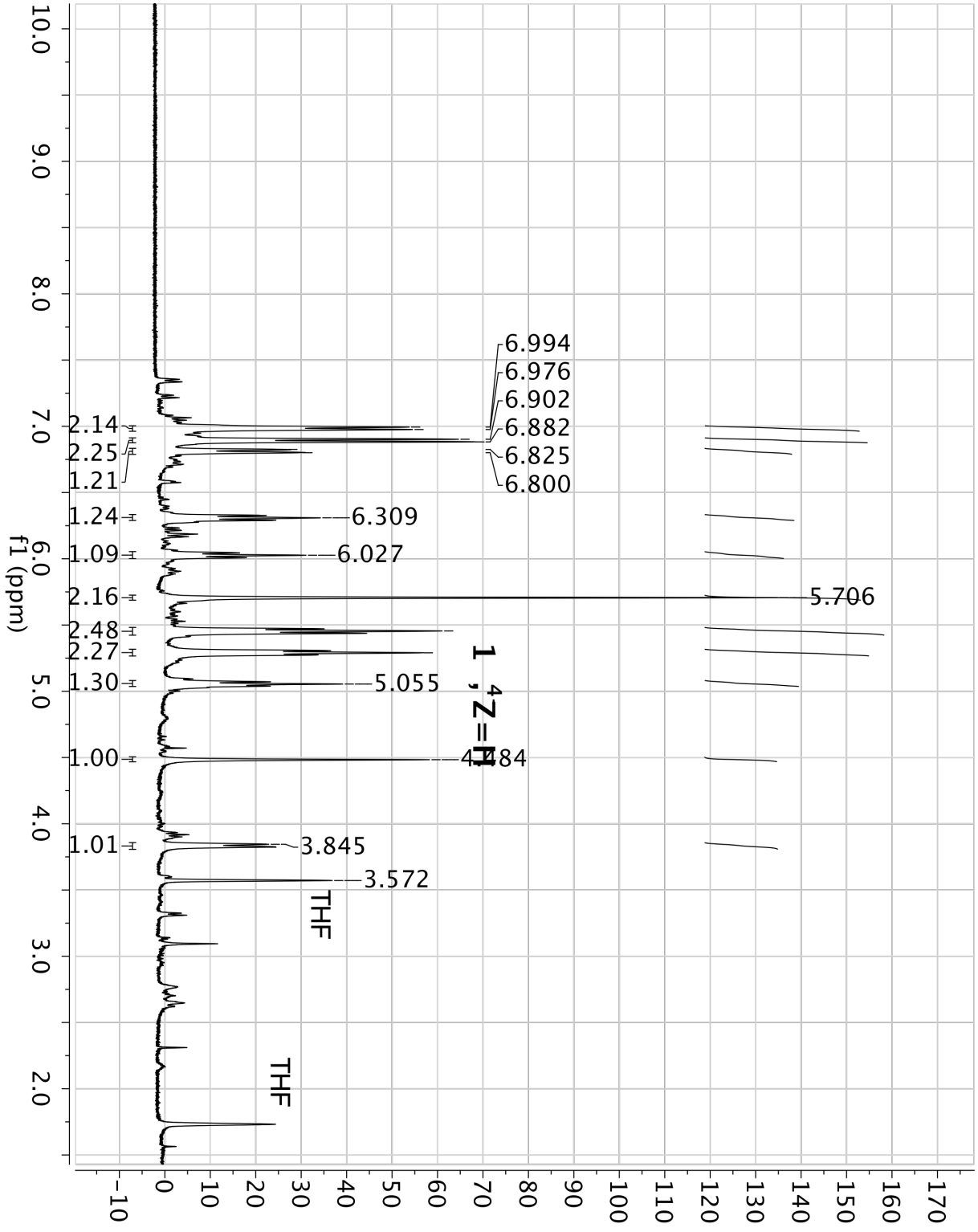
Step 1. Sample in THF-d_8 and small amount of Li or K is added to the insert filled with Ar.
Step 2. The THF solution is degassed by the freeze-pump-thaw method, with the vacuum replaced with Ar. The insert is sealed underneath the manifold.
Step 3. The Li/K is brought into contact with the solution by inverting the insert. Sonication is done at 0 °C. The reaction can be stopped by placing the tube upright for NMR analysis.

Tetra-anions of **1**

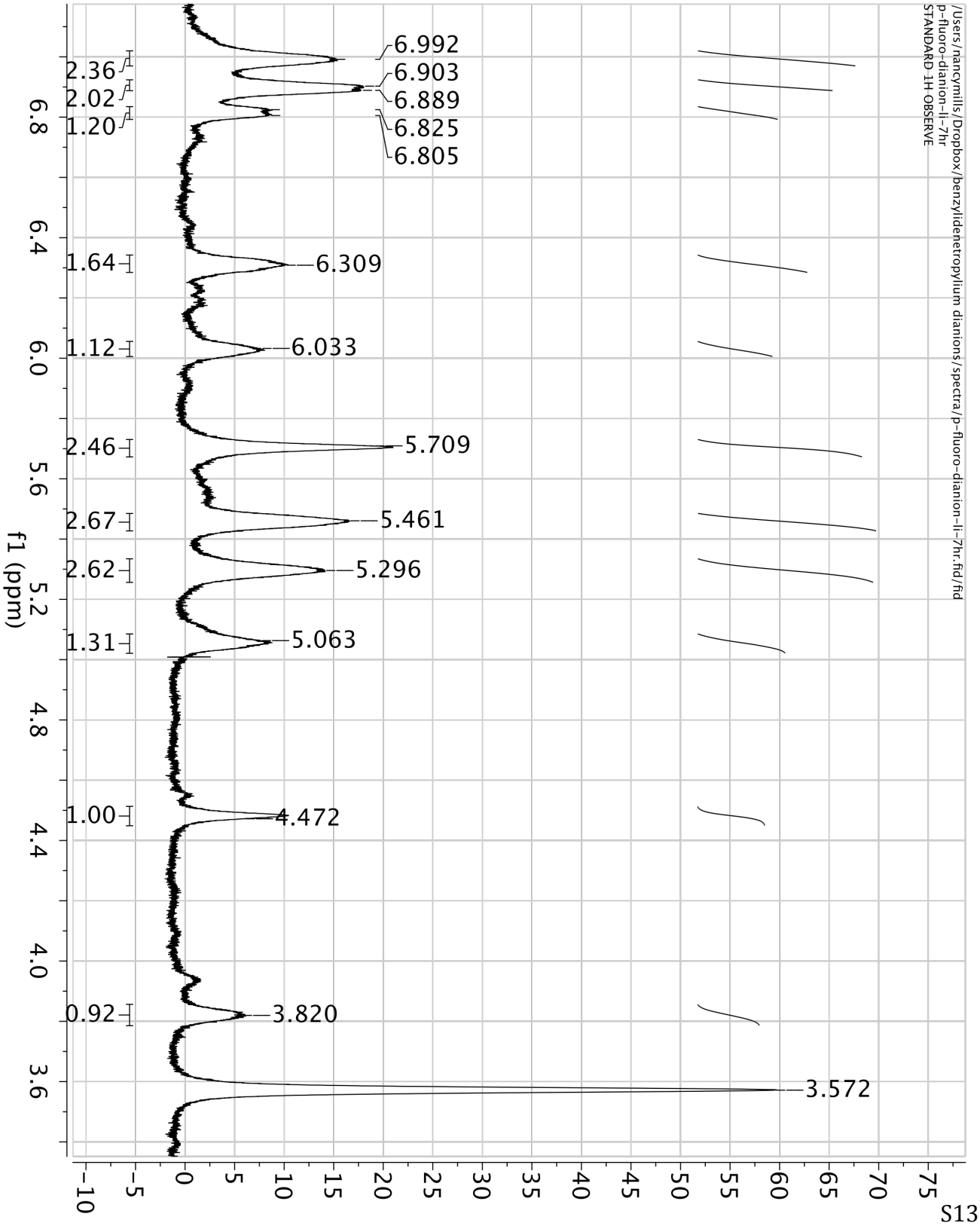
1b^{4-}, p-chloro-substituted phenyl



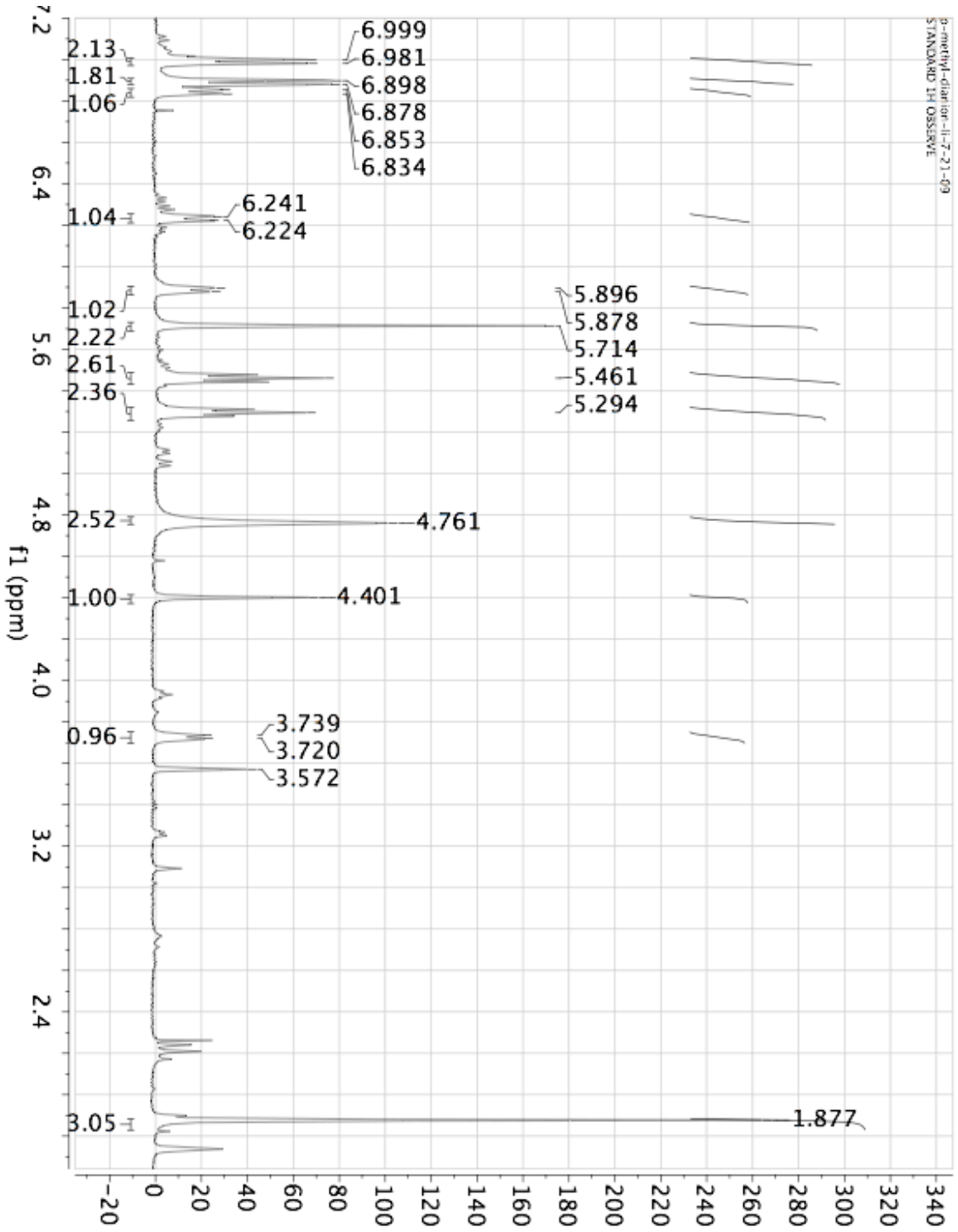
1d^{4-}, full spectrum



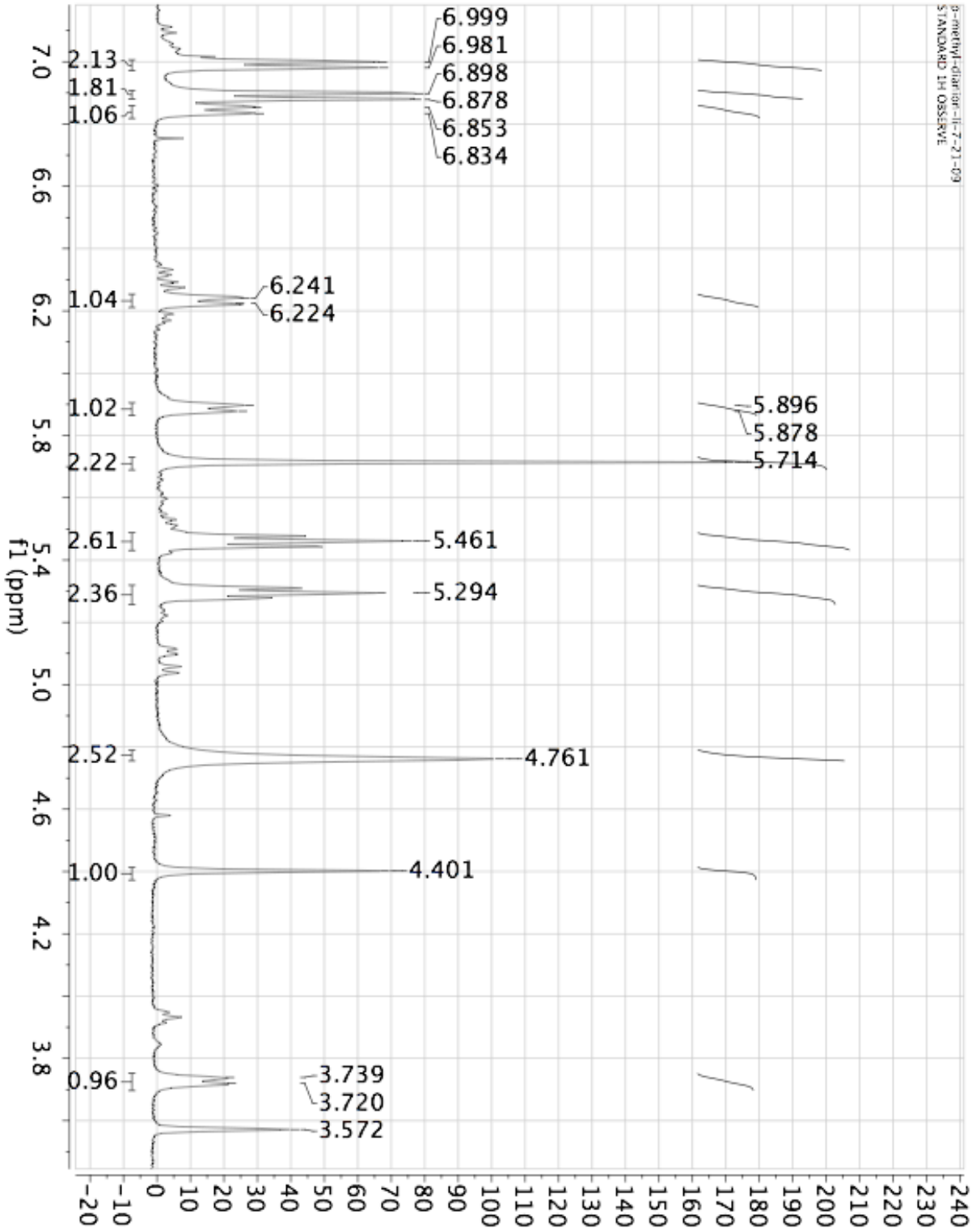
1e^{4-}, p-fluoro-substituted phenyl



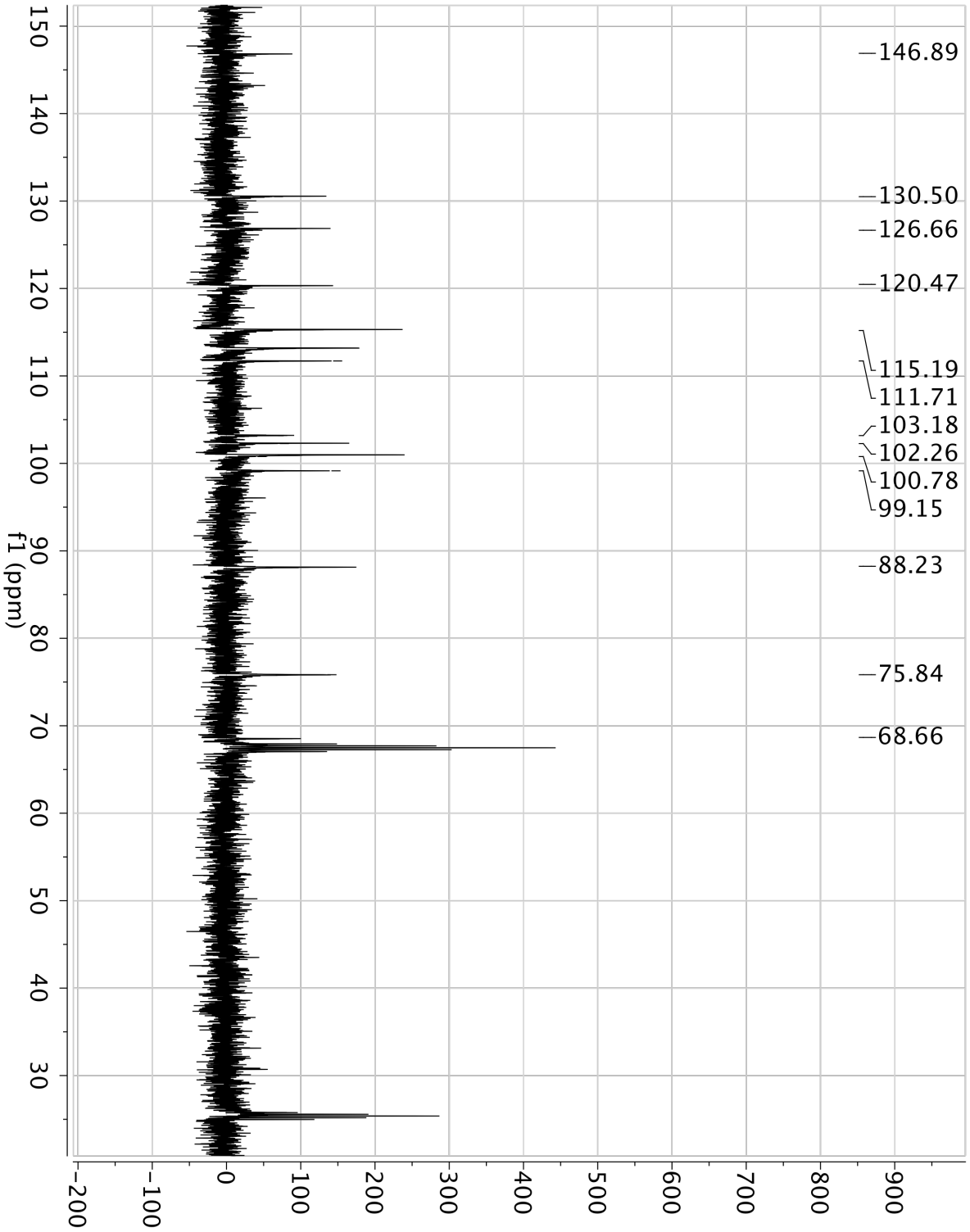
1f^{4-}, ^{1}H NMR spectrum



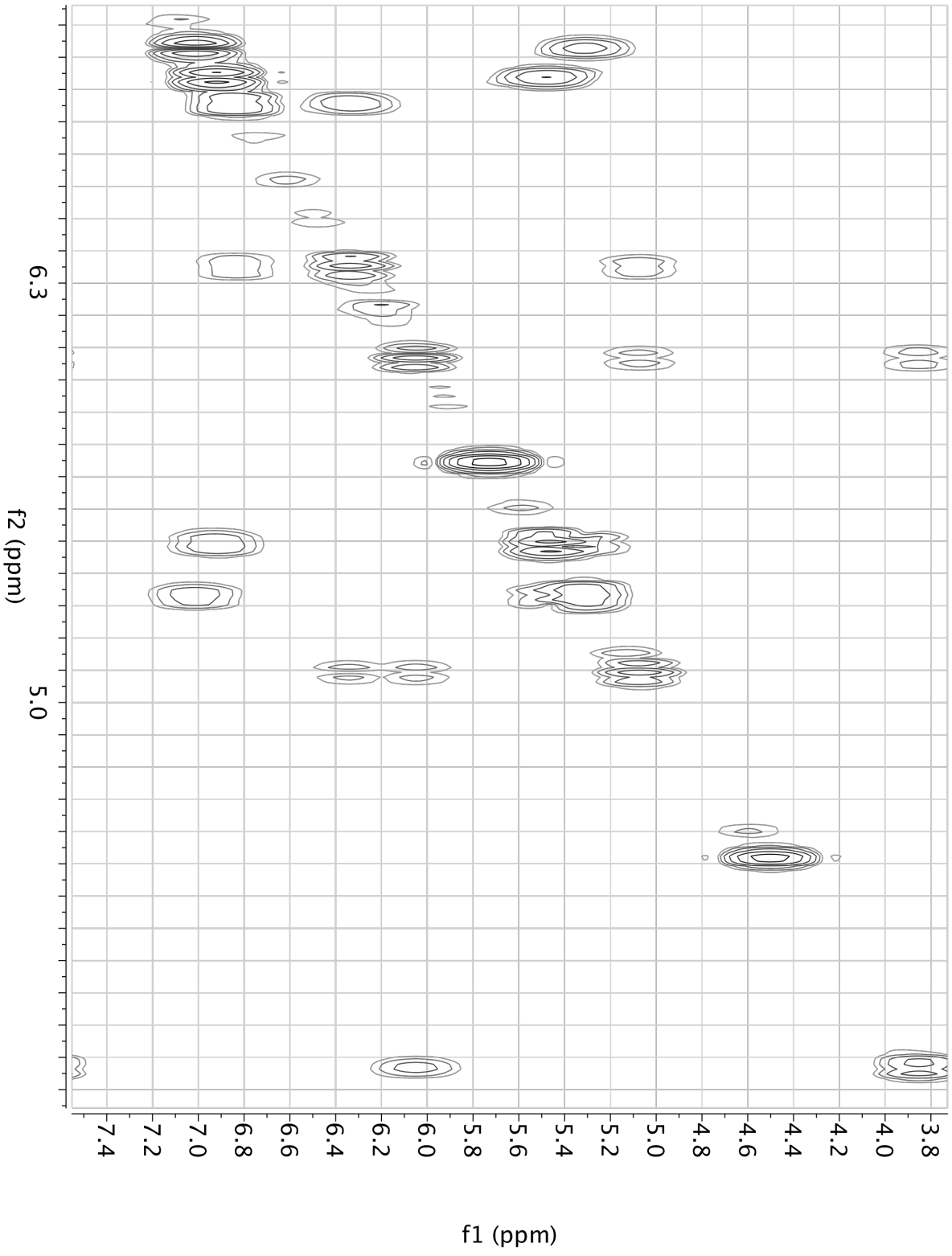
1f^{4-}, ^{1}H NMR spectrum, downfield region



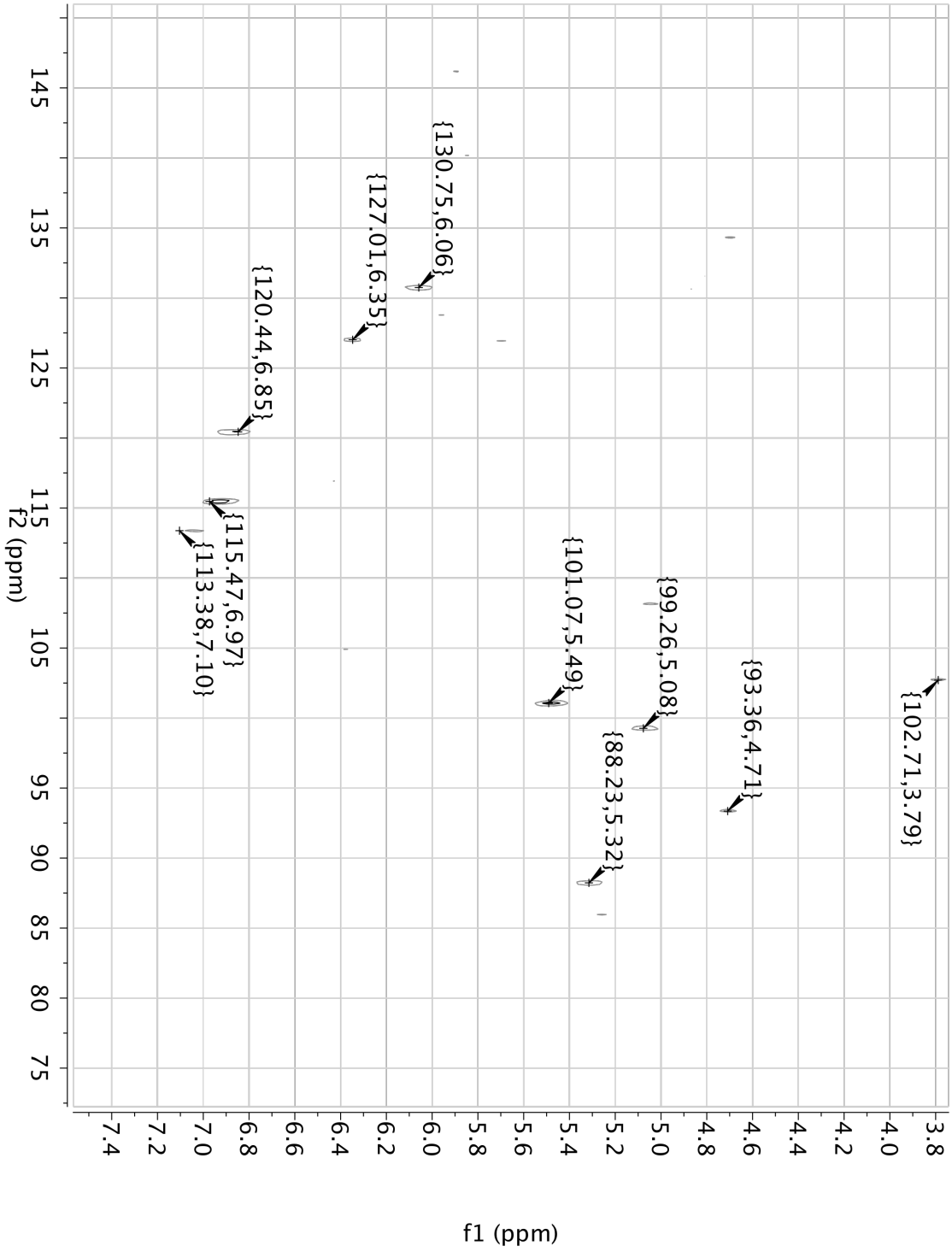
^{13}C NMR spectrum of reduction mixture of **1d**



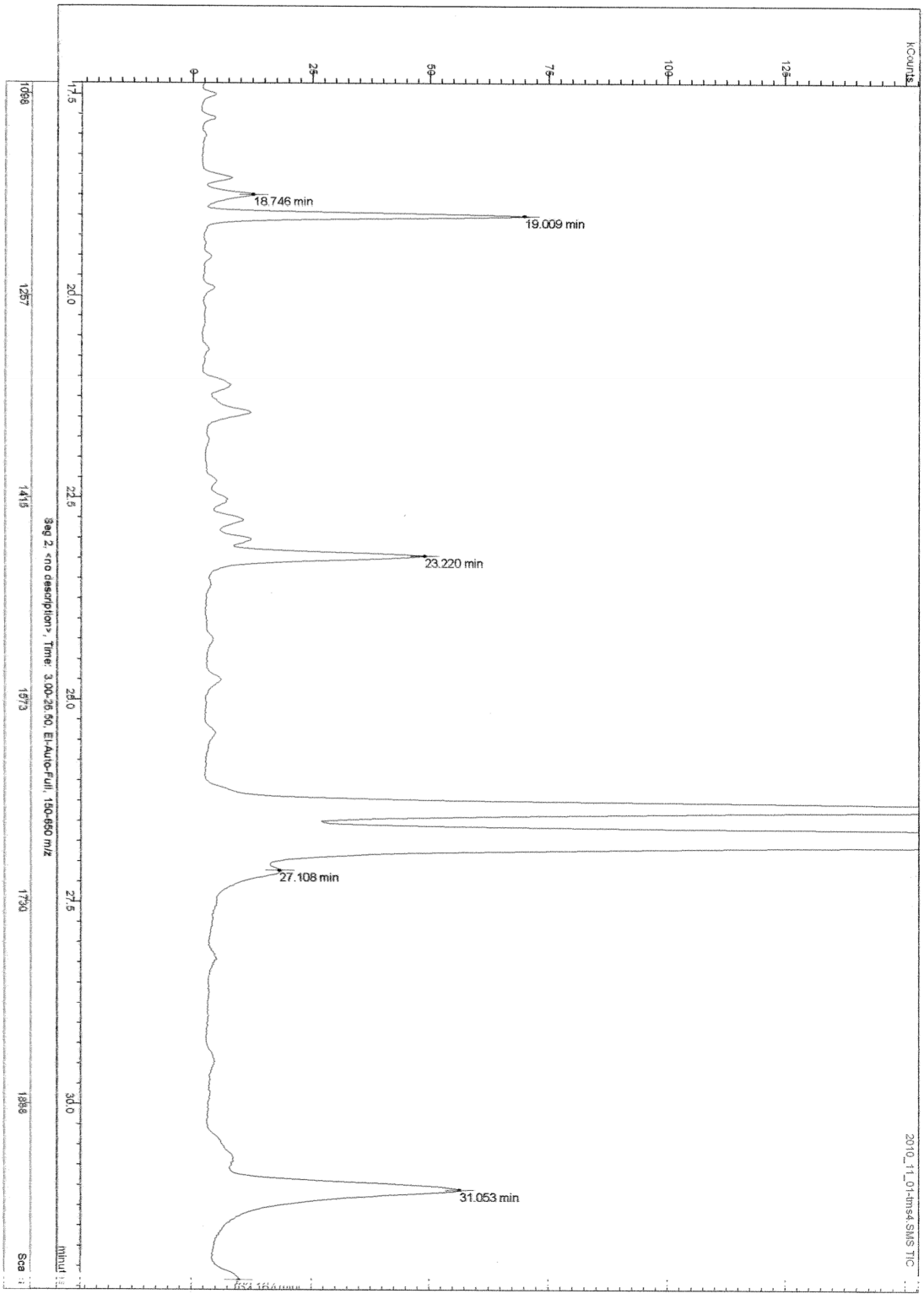
COSY spectrum of reduction mixture of **1d**



HMQC spectrum of reduction mixture of **1d**

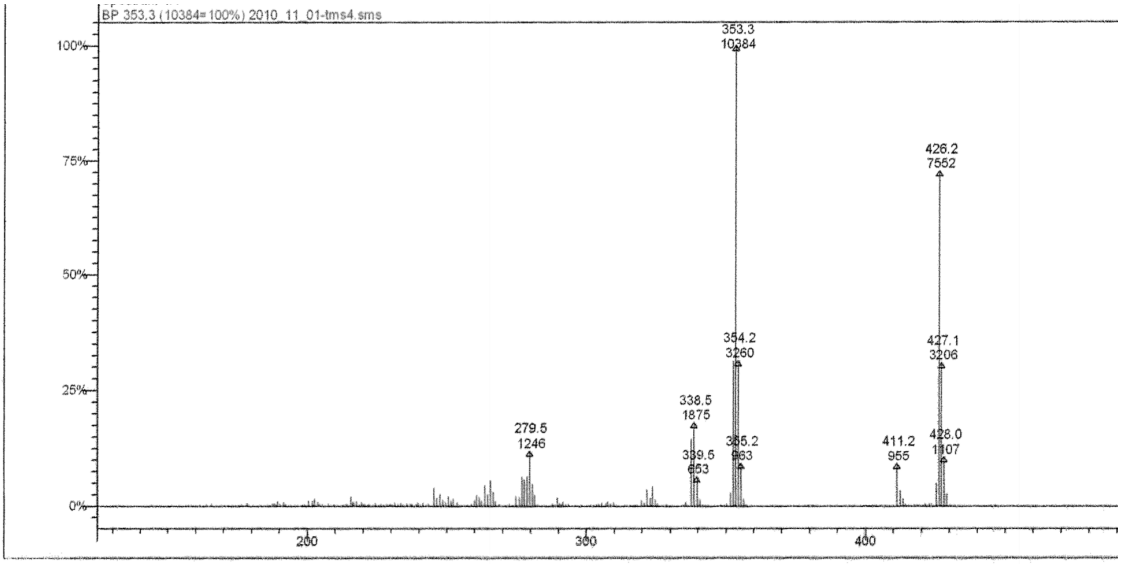


Quench of reaction mixture after 1 hour with $(CH_3)_3SiCl$

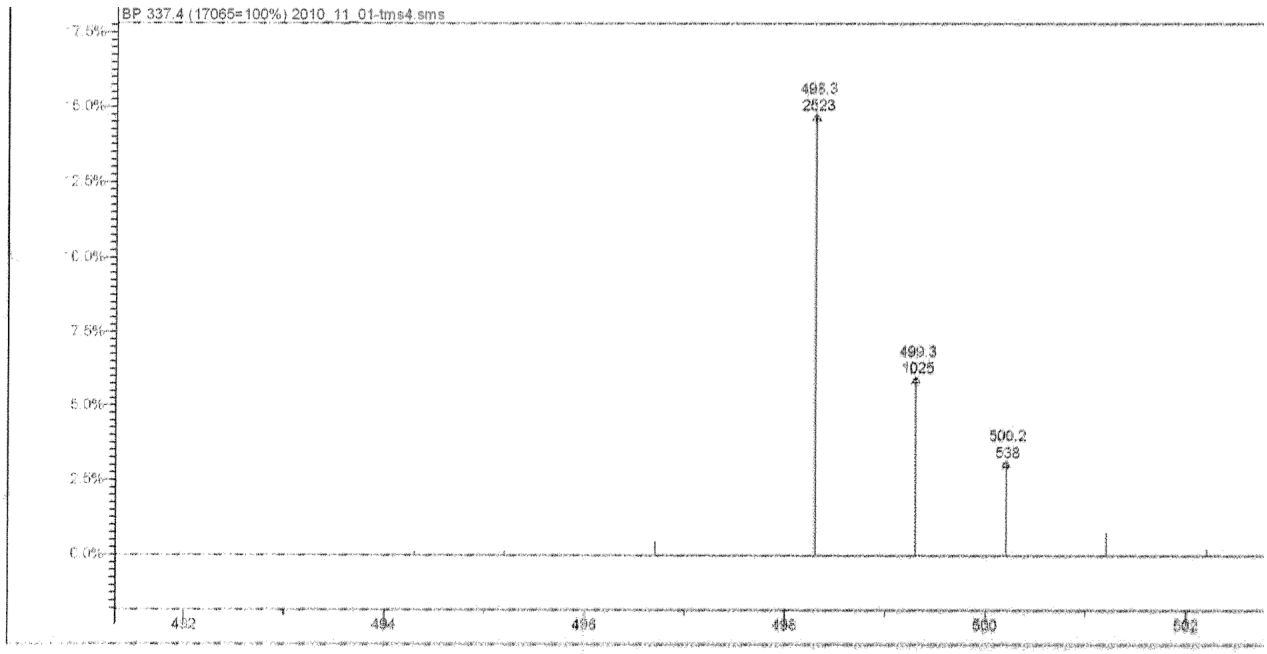


Details on individual products, with a primary focus on peaks near molecular ion

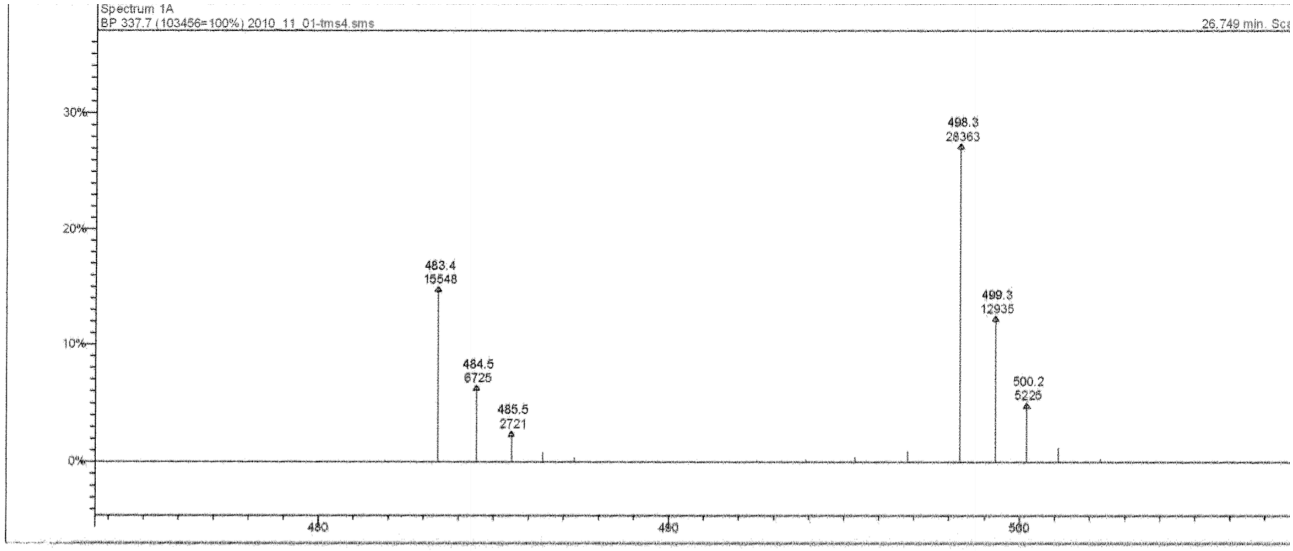
Disubstituted product, retention time 19.0 min, calculated m/z of molecular ion 426.22 (100%), 427.22 (40.4%), 428.22 (10.0%)



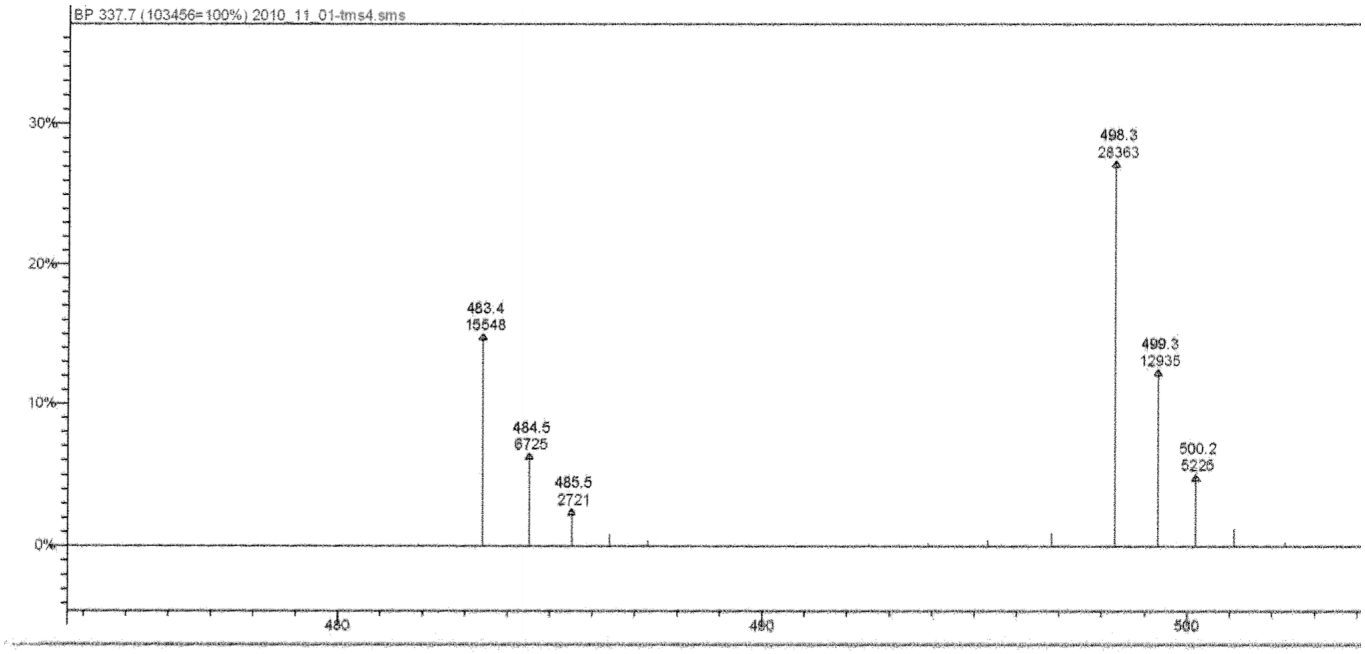
Trisubstituted product A, retention time 23.2 min, calculated m/z of molecular ion 500.28 (100.0%), 501.8 (34.0%), 510.27 (15.2%), 502.27 (10.8%), 502.28 (10.8%) See comments for tetrasubstituted product on fragmentation and loss of 2 mass units



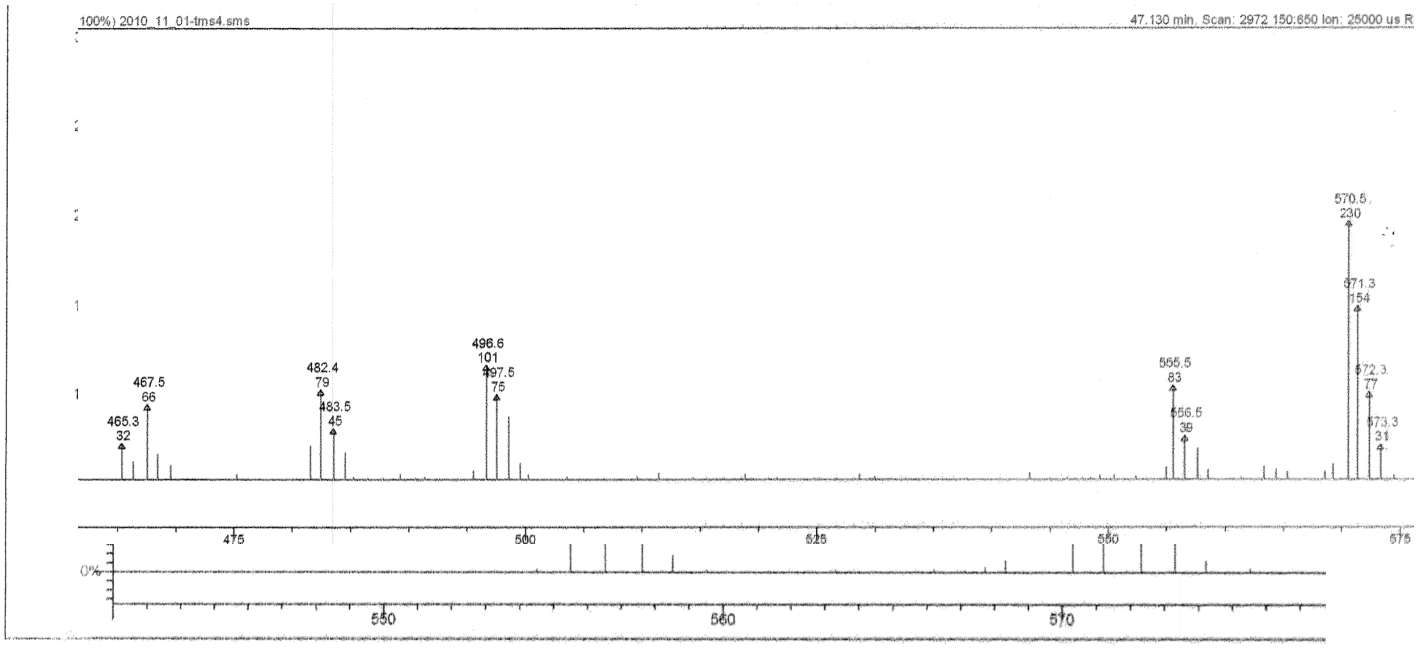
Trisubstituted product b, retention time 26.5 min, see product a for calculated m/z



Trisubstituted product c, retention time 26.8 min, see product a for calculated m/z



Tetrasubstituted product, retention time 27.1 min



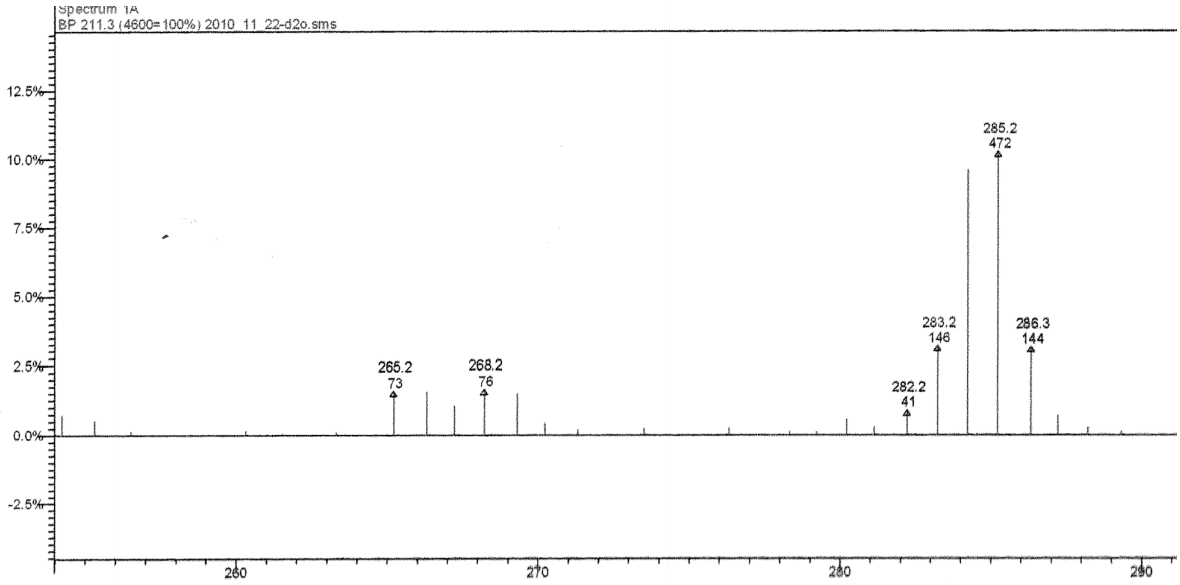
Highest m/z: 570.5, 100%
571.3, 67%
572.3, 33%
573.3, 13%

The calculated mass spectrum for tetrasilylated **1** has the molecular ion as m/z 572.3 (100%) and 571.3 (57.7%). We believe that facile dehydrogenation occurred in the mass spectrometer to give species with two fewer hydrogens. There is no report in the literature of this type of dehydrogenation for suberenes but Boekelheide observed a similar dehydrogenation in conjunction with cyclization in a tetrahydrobenzoperylene system.[1]

Mass spectrum of the tetradeuterated product

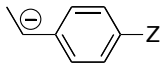
Highest m/z: 285.2, 100%
286.3, 30%

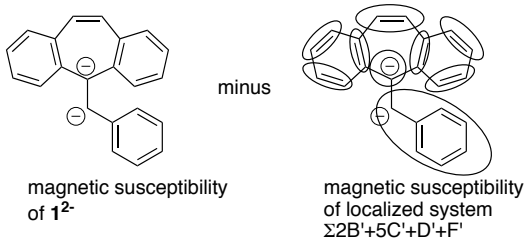
The calculated mass spectrum for D_4**1** has the molecular ion with a mass of 288.2 (100%), 289.2 (23.8%). As discussed above, we believe that dehydration occurred in the mass spectrometer to give species with a loss of 2 (2hydrogens) or a loss of 3 (1 hydrogen and 1 deuterium).



Details on calculations,: Details on the calculation of magnetic susceptibility

Increments for calculation of Λ, magnetic susceptibility exaltation

Compound	**X**	**increment**		X, increment
Ethane (**A**)	-24.39	2 CH_3		
2,3- dimethylbutene (**B**)	-60.22		**B'=B-**2*CH_3CH_3	**-**11.43
cis-2-butene (**C**)	-38.54		**C'=C-** CH_3CH_3	-14.14
t- butyl anion (planar) (**D**)	-35.73		**D'=**(2***D**-3*CH_3CH_3)/2	1.71
Anion of ethyl benzene, Z=H (**F_H**)	-58.11		**F'=**(**F**-(CH_3CH_3/2))	-45.92
Z=CF_3, (**F_{CF3}**)	-82.76			-70.57
Z=CH_3, (**F_{CH3}**)	-69.11			-56.91
Z=OCH_3, (**F_{OCH3}**)	-72.56			-60.37
Z=F, (**F_F**)	-64.42			-52.23
Z=Cl, (**F_{Cl}**)	-78.23			-66.03



Structures from reference 22 as well as cyclooctatetraene-D_{4h}. NICS values shown in regular type; magnetic susceptibility exaltation in *italics*

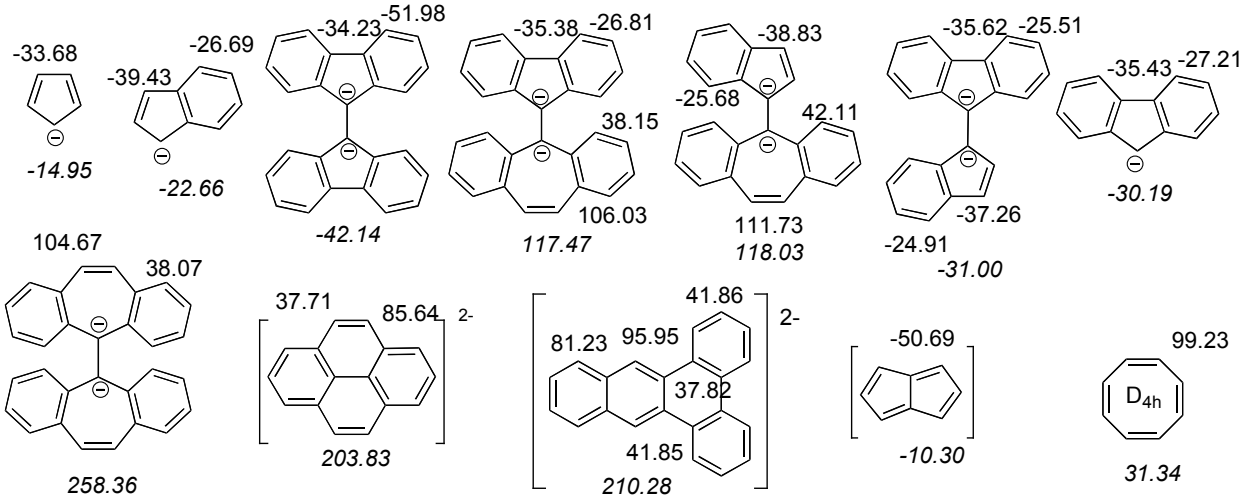


Table of $\Sigma NICS(1)_{zz}/area^2$, and $\Lambda/area^2$ for the reference species used in Figure 1

	$\Lambda/area^2$	$\Sigma NICS(1)_{zz}/area^2$
Cyclopentadienyl anion	-1.2634	-2.8453
Indenyl anion	-0.30021	-0.87598
Tetrabenzo[5.5]fulvalene dianion	-0.054229	-0.22188
Tetrabenzo[5.7]fulvalene dianion	0.10543	0.083753
Tribenzo[5.7]fulvalene dianion	0.19416	0.18590
Tribenzo[5.5]fulvalene dianion	-0.060300	-0.28955
Fluorenyl anion	-0.15616	-0.46472
Tetrabenzo[7.7]fulvalene dianion	0.21322	0.28293
Pyrene dianion	0.45251	0.54777
3,4-Dibenzophenanthrene	0.30000	0.42700
Pentalene dianion	-0.71192	-1.1389
Planar cyclooctatatratene, D_{4h}	0.95178	1.0744

Calculation of ring areas

The optimized geometry is oriented so that the ring of interest is in the xy plane. The Cartesian coordinates then have 0 or very small numbers for Z. The Cartesian coordinates are arranged in the order in which the carbons of the ring system are attached. A new column is created in which the X value for the first atom is added to the X value for the second atom, continuing around the ring, returning to the first atom. A second column is created in which the Y value for the first atom is subtracted from the Y value for the first atom, continuing around the ring. The two new columns are multiplied together; the area is the sum of the multipled values divided by 2. Given below is a table showing the process for the indenyl system of **$1d^{2-}$.** If the sum is negative, ignore the negative sign since an area can't be negative. Also, you will need to repeat the first line in order to have values that can be added to/substracted from the X or Y values for the last atom in the ring.

$1d^{2-}$	**a**	**b**		a1+a2	b2-b1	product
1	-0.05615	2.28787	0.49474	0.30329	1.32744	0.40259
2	0.35944	3.61531	0.50824	2.07312	0.33692	0.69847
3	1.71368	3.95223	0.51929	4.3316	-1.07178	-4.642522
4	2.61792	2.88045	0.51662	4.85046	-1.34777	-6.537304
4a	2.23254	1.53268	0.50374	5.58288	-0.94903	-5.298320
5	3.35034	0.58365	0.54988	6.73785	-1.3432	-9.050280
6	3.38751	-0.75955	0.61856	5.71521	-1.00225	-5.728069
6a	2.3277	-1.7618	0.62126	5.09903	-1.32566	-6.759580
7	2.77133	-3.08746	0.7278	4.69922	-1.11599	-5.244282
8	1.92789	-4.20345	0.68199	2.49428	0.26778	0.667918
9	0.56639	-3.93567	0.47264	0.65747	1.29779	0.853257
10	0.09108	-2.63788	0.37528	0.99811	1.18671	1.184467
10a	0.90703	-1.45117	0.49109	1.14296	1.27722	1.459811
11	0.23593	-0.17395	0.4911	1.06575	1.33133	1.418864

11a	0.82982	1.15738	0.49112	0.77367	1.13049	0.874626
						-17.85016

Calculated ring areas, **1a^{2-}—1f^{2-}**, Å^2

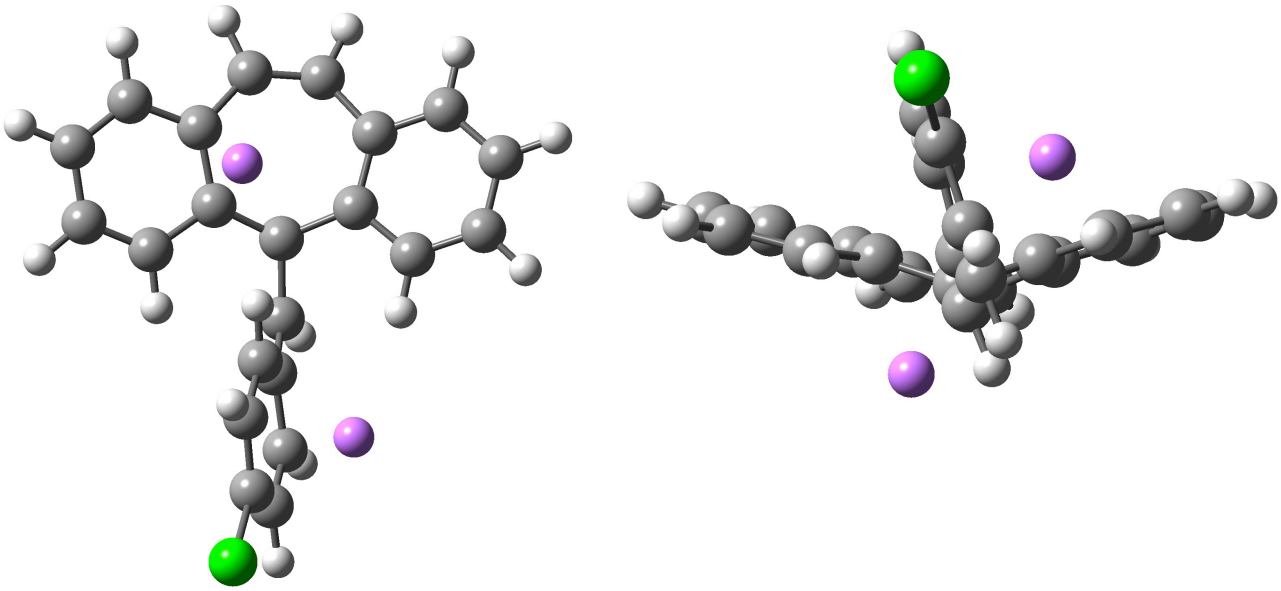
1a^{2-}	**1b^{2-}**	**1c^{2-}**	**1d^{2-}**	**1e^{2-}**	**1f^{2-}**
-17.801	-17.854	-17.856	-17.850	-17.843	-17.851

Calculated chemical shifts of dianions of **$Li_2$1b** and **$Li_2$1d-f**

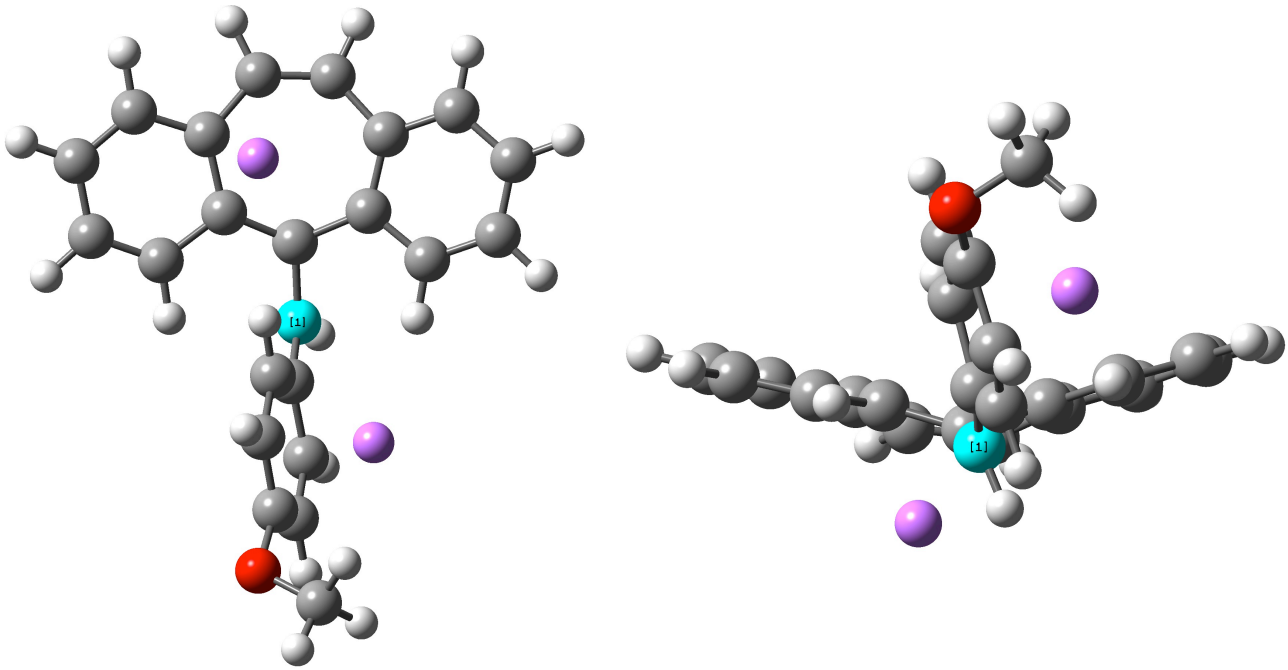
Experimental[a] and calculated[b] ^{1}H NMR chemical shifts for **$Li_2$1b** and **$Li_2$1d-f**.

	$Li_2$1b	**$Li_2$1d**	**$Li_2$1e**	**$Li_2$1f**
1,10	5.147	4.996	2.457	5.109
2,9	5.970	5.128	3.610	5.945
3,8	5.351	5.409	2.509	5.326
4.7	5.126	4.866	1.685	5.123
5,6	4.874	5.380	0.269	4.827
alpha	4.131	4.125	1.016	4.103
o	5.823	5.883	5.247	5.842
o	3.970	4.005	4.165	3.876
m	6.069	6.187	5.688	6.119
m	6.071	6.320	6.183	6.187
p		4.517		
subst				1.650

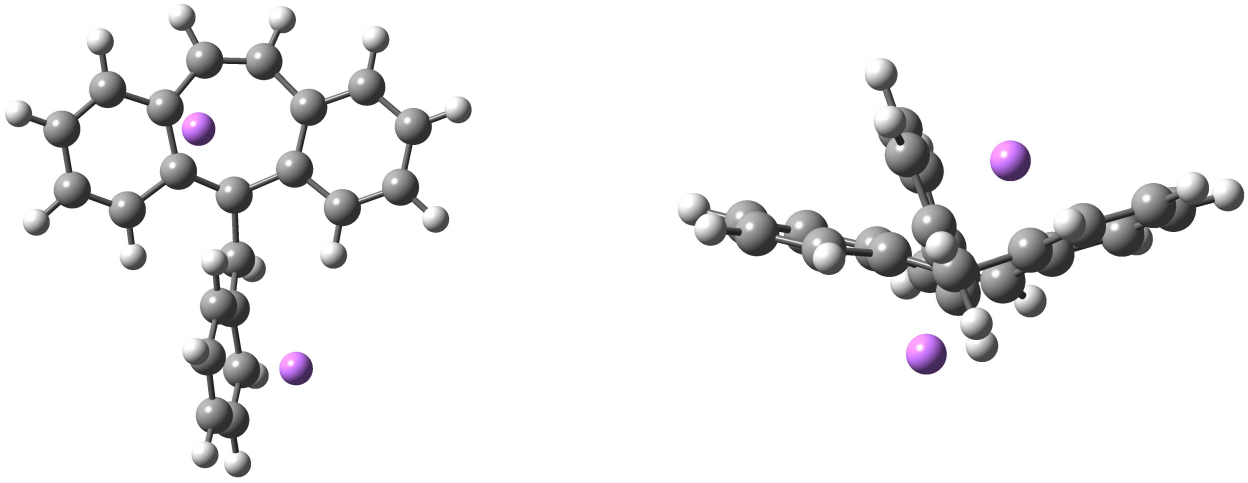
Calculated structure of **$Li_2$1b**



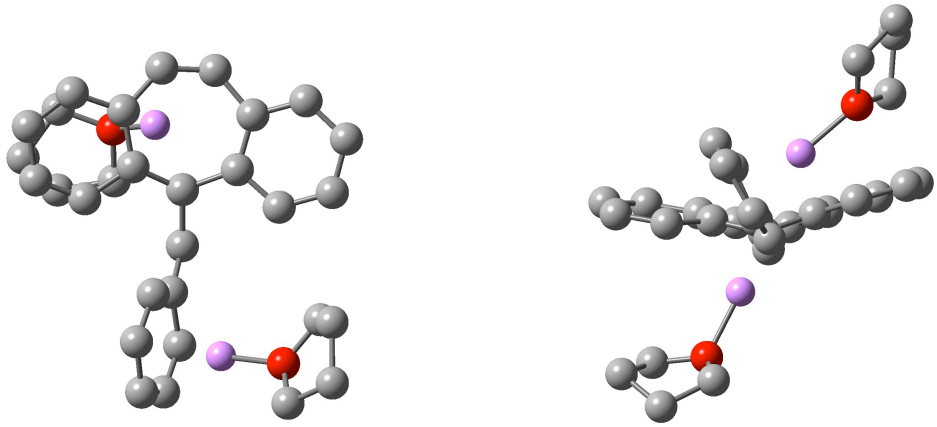
Calculated structure of **$Li_2$1c**



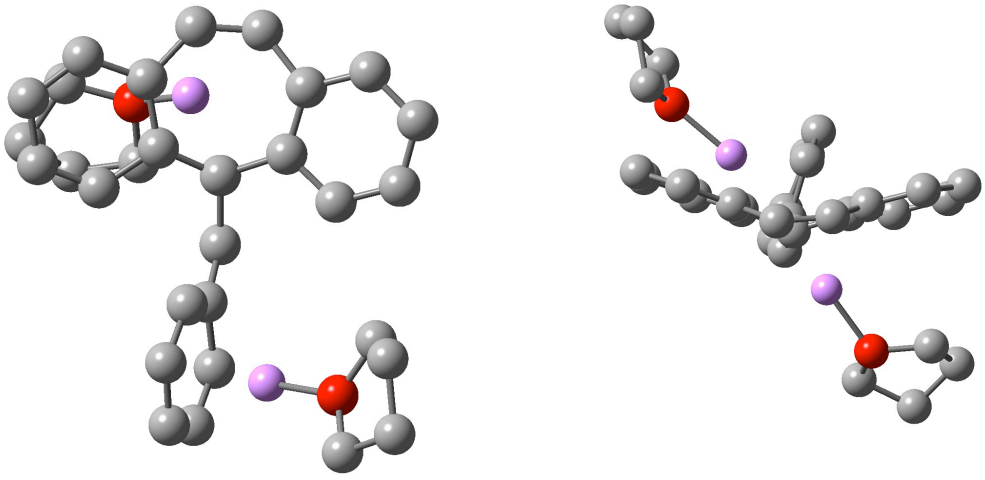
Calculated structure of **$Li_2$1d**



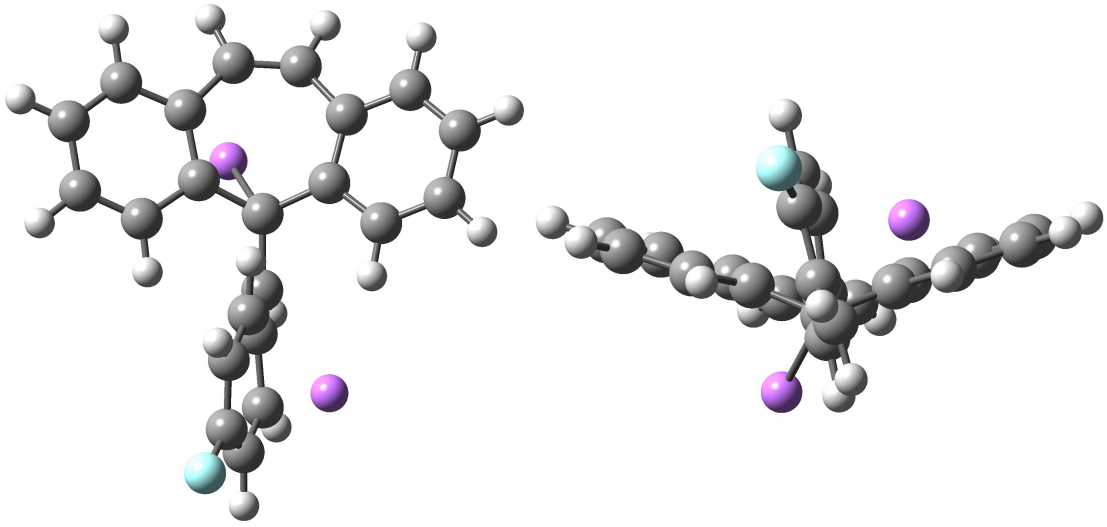
Calculated structure of **$Li_2$1d**, 1THF per Li, no H on structure, optimized at B3LYP/6-31G(d)



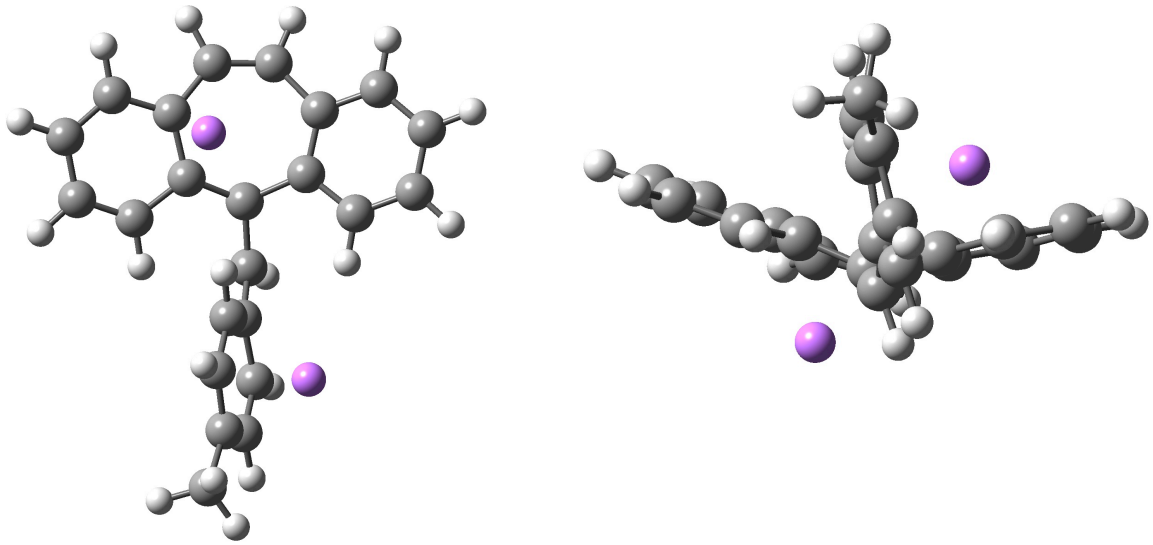
Calculated structure of **$Li_2$1d**, 1THF per Li, no H on structure, optimized at B3LYP/LC-BLYP/6-31+G(d)



Calculated structure of **$Li_2$1e**



Calculated structure of **$Li_2$1f**

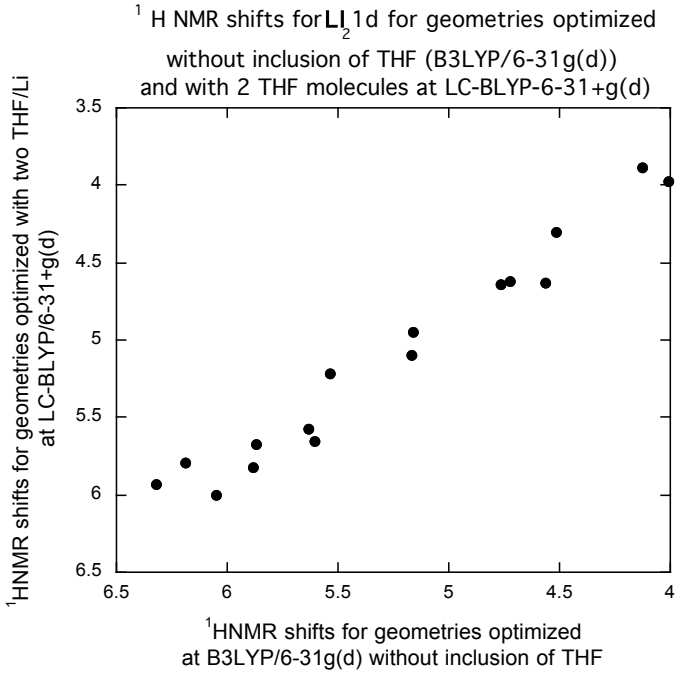


Dihedral angles for **$Li_2$1d**, calculated without THF (B3LYP/6-31G(d)) and with one THF per molecule by two functions and basis sets, B3LYP/6-31G(d) and LC-BLYP/6-31+g(d)

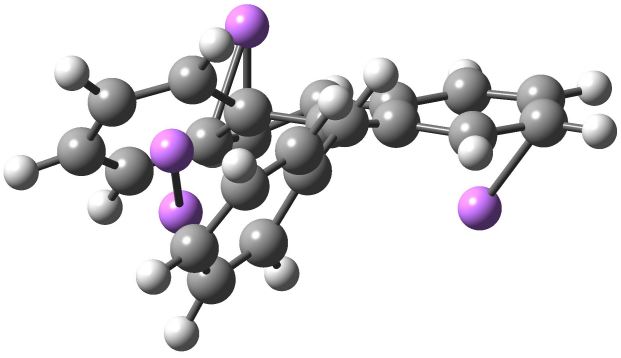
Dihedral angles, dibenzotropylium system	Li_2**1d**, no THF, optimized at B3LYP/6-31g(d) (I)	Li_2**1d**, 2 THF, optimized at B3LYP/6-31g(d) (II)	Li_2**1d**, 2 THF, optimized at LC-BLYP/6-31+g(d) (III)	Difference II-I	Difference III-I
1-2-3-4	3.24625	3.43171	2.67455	0.1855	-0.5717
2-3-4-4a	-3.2721	-3.42952	-2.64971	-0.1574	0.6224
3-4-4a-5	169.1201	168.89189	169.89181	-0.2282	0.7717
4-4a-5-6-	171.05078	171.1651	165.81489	0.1143	-5.2359
4a-5-6-6a	-18.88639	-14.62287	-12.25345	4.2635	6.6329
5-6-6a-7	-144.22531	-150.44624	-147.95532	-6.2209	-3.7300
6-6a-7-8	-178.80569	-177.51427	-176.80807	1.2914	1.9976
6a-7-8-9	0.46068	0.42962	0.78016	-0.0311	0.3195
7-8-9-10	-0.64429	-0.95715	-1.16744	-0.3129	-0.5232
8-9-10-10a	0.27304	0.57983	0.32416	0.3068	0.0511
9-10-10a-11	176.37629	176.29941	177.58138	-0.0769	1.2051
10-10a-11-11a	136.02109	144.04412	138.49292	8.0230	2.4718
10a-11-11a-1	-151.82568	-157.90865	-150.41722	-6.0830	1.4085
11-11a-1-2	-177.21829	-178.6486	-177.55513	-1.4303	-0.3368
11a-1-2-3	1.97838	2.16885	1.97762	0.1905	-0.0008
11-11a-4a-4	-176.45544	1.386	176.8937	177.8414	0.4383
11-10a-6a-6	2.50628	-176.50899	-0.63485	-179.0153	-3.1411
1-11a-4a-4	6.44949	7.02392	6.08971	0.5744	-0.3598
1-11a-4a-5	-163.7277	-163.17473	-165.08915	0.5530	-1.3614
10-10a-6a-7	0.47778	-0.87324	-1.28315	-1.3510	-1.7609
11-11a-4a-5	-176.35089	-176.50899	5.7183	-0.1581	-2.0692
Dihedral angles with benzyl substituent					
i-α-11-11a	90.83182	98.25372	90.49956	7.4219	-0.3323
α-11-10a-10	-19.28291	-17.14151	-16.21394	2.1414	3.0690
o-i-α-11	3.47338	5.39776	2.87802	1.9244	-0.5954

It is apparent that there is little difference but how much difference is too much? To answer this question, we plotted calculated ^{1}H NMR shifts for **1a-f^{2-}** for the geometries optimized with 2 lithiums and no THF (B3LYP/6-31g(d)) vs. the geometries optimized with 2 lithiums, each solvated with a single THF using a functional with long-range correction (LC-BLYP/6-31+g(d)). The linear relationship shown on the next page demonstrates that the geometry optimized for unsolvated lithiums is similar enough to that optimized for two lithiums solvated with one THF each that the magnetic properties are not compromised by the lack of inclusion of at least one solvent molecule.

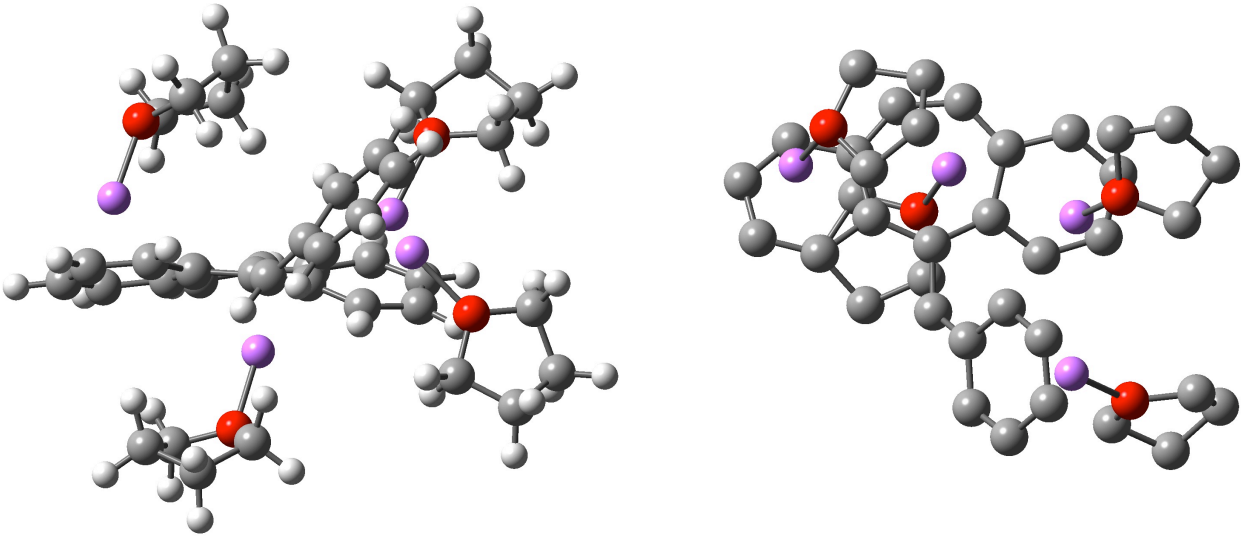
Plot of ^{1}H NMR shifts calculated for **$Li_2$1d** at two different calculated geometries (B3LYP/6-31G(d), no THF) and LC-BLYP/6-31+G(d) with 2THF)



Geometries of **$Li_4$1d**
Calculated geometry of **$Li_4$1d**, no THF



Calculated geometry of **$Li_4$1d**, one THF per lithium, no hydrogens shown

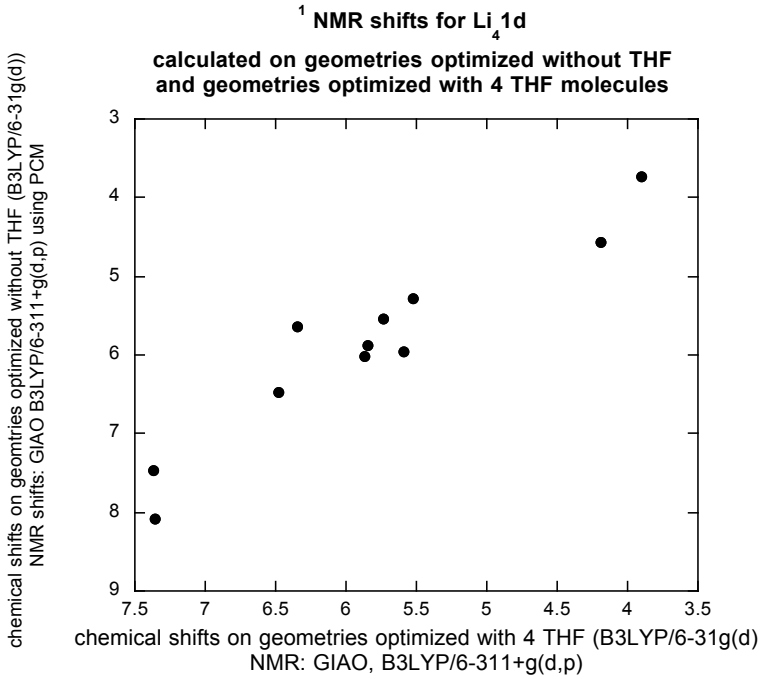


Comparison of dihedral angles for **$Li_4$1d**, calculated without THF and with one THF per lithium

Dihedral angles, dibenzotropylium system	Li_4**1d**, no THF, optimized at B3LYP/6-31g(d) (I)	Li_4**1d**, 4 THF, optimized at B3LYP/6-31g(d) (II)	Difference II-I
1-2-3-4	-4.8761	-4.0777	-0.7985
2-3-4-4a	-2.1722	-7.3085	5.1364
3-4-4a-5	-156.5598	-155.7716	-0.7882
6-5-4a-4	176.6163	178.1767	-1.5604
4a-5-6-6a	34.8936	16.1841	18.7095
5-6-6a-7	160.2736	174.9458	-14.6722
6-6a-7-8	-173.4705	-172.8190	-0.6515
6a-7-8-9	1.2026	1.5207	-0.3182
7-8-9-10	-2.7577	-3.7904	1.0327
8-9-10-10a	-1.6557	-1.3546	-0.3011
9-10-10a-11	-168.6080	-169.1525	0.5445
10-10a-11-11a	-179.3482	-178.4154	-0.9328
10a-11-11a-1	-152.2286	-157.1605	4.9320
11-11a-1-2	-145.4479	-166.8651	21.4172
11a-1-2-3	-8.8383	-0.4132	-8.4251
11-10a-6a-6	-14.9681	-14.4679	-0.5003
1-11a-4a-4	-31.1018	-23.6024	-7.4994
10-10a-6a-7	-8.1556	-9.6862	1.5306
11-11a-4a-5	-42.2884	-24.8786	-17.4098

Dihedral angles with benzyl substituent			
i-α-11-11a	56.0579	58.5952	-2.5373
α-11-10a-10	10.6328	9.4784	1.1545
o-i-α-11	15.9480	3.2292	12.7188
1-2-3-4	-4.8761	-4.0777	-0.7985

Similarly, the chemical shifts calculated with the inclusion of solvent on geometry from optimization with 4 lithiums and no solvent show a linear relationship to chemical shifts calculated without the inclusion of solvent via PCM on geometries optimized with the inclusion of 4 THF molecules to solvate the 4 lithium molecules. It could be argued that two THF molecules per lithium atom is appropriate for more reasonable solvation[2] however this is calculationally too expensive for systems of this size. The final geometry optimization with 4 lithium atoms and 4 THF using B3LYP/6-31g(d) took 85 hours; the calculation of the chemical shifts for the optimized structure at B3LYP/6-311+g(d,p) took 42 hours. The time required for the optimization did not include the time spent on lower level (rhf/3-21g, then rhf/6-31g(d)) optimizations.



Examination of the optimization of **1d^{2-}** by density functional methods with and without long-range correction functionals

Studies of anions without lithium complexation

Choice of basis set

HOMOs for anionic species

A representative set of mono-, di- and trianions was optimized using the four of the functionals shown in the table below (B3LYP/6-31g(d), B3LYP/6-31+g(d), LC-BLYP/6-31+g(d), LC-BLYP/6-311+g(d,p) . While monoanionic molecular species, such as the monoanions of cycloheptatriene, and mono- and dibenzocycloheptatriene had negative HOMOs with LC-BLYP, the polyanions all had positive values for at least one HOMO.

Dianions of benzylidene dibenzocycloheptatriene

The HOMO energies for the dianion of benzylidene dibenzocycloheptatriene (**1d^{2-}**) are listed by method of calculation in the following table. The occupied orbitals with negative energies are shown in bold.

B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- 0.01540 0.02550 0.03747 0.12857 0.15396 Alpha virt. eigenvalues -- 0.20211 0.25359 0.26905 0.28157 0.30324
B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.01003** 0.00018 0.01377 0.10059 0.12623 Alpha virt. eigenvalues -- 0.17416 0.17597 0.18134 0.18904 0.19165
LC-BLYP/6-31+g(d)	Alpha occ. eigenvalues -- **-0.11292 -0.10374 -0.08757** 0.02676 0.05351 Alpha virt. eigenvalues -- 0.22332 0.22722 0.23346 0.24240 0.24354
LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.11408 -0.10545 -0.09009** 0.02331 0.05150 Alpha virt. eigenvalues -- 0.21588 0.21985 0.22775 0.23335 0.23631
wb97xD/6-311+g(d,p)	Alpha occ. eigenvalues **--** **-0.08410 -0.07262 -0.05851** 0.04739 0.06438 Alpha virt. eigenvalues -- 0.22625 0.23091 0.23859 0.23941 0.24163
cam-b3lyp/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.06301 -0.05249 -0.03965** 0.06031 0.08801 Alpha virt. eigenvalues -- 0.19678 0.20123 0.20954 0.21319 0.21644
lc-wpbe-opt/6-311+g(d,p)	Alpha occ. eigenvalues **--** **-0.11040 -0.10046 -0.08588** 0.02640 0.05163 Alpha virt. eigenvalues -- 0.22410 0.22760 0.23524 0.24094 0.24374

While all methods show positive values for at least two HOMOs, the smallest positive value is found for LC-BLYP/6-311+g(d,p) method.

Effects of substituents on the energy of the HOMOs

The next table shows the HOMOs for the geometries optimized with B3LYP/6-31g(d), B3LYP/6-31+g(d), LC-BLYP/6-31+g(d) and LC-BLYP/6-311+g(d,p) for the dianions of

substituted benzylidene dibenzocycloheptatriene. Again, occupied orbitals with negative energies are in bold.

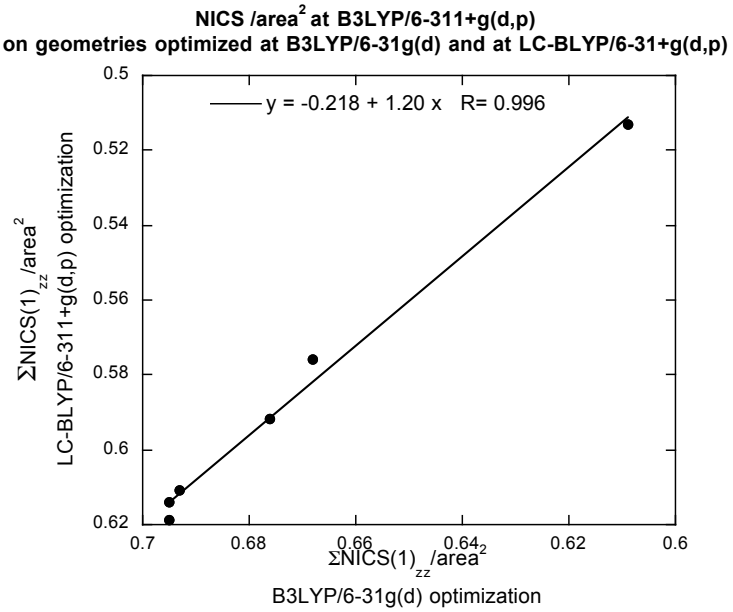
1a^{2+} CF_3	B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- **-0.00231** 0.00305 0.02190 0.10590 0.12899 Alpha virt. eigenvalues -- 0.18720 0.23831 0.25249 0.26345 0.26782
	B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.02179 -0.00141** 0.07773 0.10155 Alpha virt. eigenvalues -- 0.16002 0.16681 0.17292 0.18060
	Lc-blyp/6-31+g(d)	Alpha occ. eigenvalues -- **-0.13346 -0.12496 -0.10105** 0.00091 0.03010 Alpha virt. eigenvalues -- 0.21560 0.22038 0.22668 0.23413 0.23756
	LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.12681 -0.10389 -0.00205** 0.02691 Alpha virt. eigenvalues -- 0.20847 0.21252 0.22060 0.22900
1b^{2+} Cl	B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- 0.00430 0.00861 0.02886 0.11780 0.14204 Alpha virt. eigenvalues -- 0.19392 0.24515 0.25793 0.26042 0.26551
	B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.01344** 0.00743 0.09268 0.11779 Alpha virt. eigenvalues -- 0.16818 0.17202 0.17762 0.17887
	Lc-blyp/6-31+g(d)	Alpha occ. eigenvalues -- **-0.12393 -0.11619 -0.09326** 0.01777 0.04456 Alpha virt. eigenvalues -- 0.22002 0.22413 0.22486 0.23058 0.23867
	LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.12597 -0.11763 -0.09583** 0.01464 0.04227 Alpha virt. eigenvalues -- 0.21264 0.21666 0.22372 0.22517 0.23297
1c^{2+} OCH_3	B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- 0.01596 0.03385 0.12411 0.14996 Alpha virt. eigenvalues -- 0.19861 0.24990 0.26457 0.27110 0.29411
	B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.00974** 0.00940 0.09428 0.12259 Alpha virt. eigenvalues -- 0.16138 0.16987 0.17308 0.17865
	Lc-blyp/6-31+g(d)	Alpha occ. eigenvalues -- **-0.11626 -0.10997 -0.08907** 0.02482 0.05278 Alpha virt. eigenvalues -- 0.21483 0.22221 0.22631 0.23242 0.23987
	LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.11158 -0.09171** 0.02113 0.05074 Alpha virt. eigenvalues -- 0.20698 0.21477 0.21879 0.22654 0.23423
1e^{2+} F	B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- 0.01473 0.03557 0.12625 0.15229 Alpha virt. eigenvalues -- 0.20028 0.25139 0.26480 0.26975 0.30173
	B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.00929** 0.01247 0.09893 0.12549 Alpha virt. eigenvalues -- 0.17292 0.17512 0.18045 0.18805
	Lc-blyp/6-31+g(d)	Alpha occ. eigenvalues -- **-0.11919 -0.11162 -0.08903** 0.02495 0.05246 Alpha virt. eigenvalues -- 0.22228 0.22622 0.23236 0.24120 0.24379
	LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.11296 -0.09167** 0.02119 0.05036 Alpha virt. eigenvalues -- 0.21485 0.21881 0.22664 0.23506
1f^{2+} CH_3	B3lyp/ 6-31g(d)	Alpha occ. eigenvalues -- 0.02158 0.03510 0.12564 0.15139 Alpha virt. eigenvalues -- 0.19975 0.25117 0.26639 0.27601 0.29499
	B3LYP/ 6-31+g(d)	Alpha occ. eigenvalues -- **-0.00201** 0.01299 0.09945 0.12630 Alpha virt. eigenvalues -- 0.16975 0.17325 0.17524 0.18074
	Lc-blyp/6-31+g(d)	Alpha occ. eigenvalues -- **-0.11305 -0.10490 -0.08760** 0.02712 0.05527 Alpha virt. eigenvalues -- 0.21626 0.22305 0.22713 0.23330 0.24192
	LC-BLYP/6-311+g(d,p)	Alpha occ. eigenvalues -- **-0.10677 -0.09018** 0.02353 0.05333 Alpha virt. eigenvalues -- 0.21347 0.21566 0.21962 0.22756 0.23583

As was true for the unsubstituted benzylidene dibenzocycloheptatriene, none of these methods resulted in HOMOs that were all negative. The method with long-range corrections, LC-BLYP, results in the fewest number (2) of HOMOs that were positive; the HOMO's calculated with the 6-31+g(d) basis set were slightly larger than those calculated with the 6-311+g(d,p) basis set. In general, the more electron-withdrawing the substituent

on phenyl, the more stable the dianion, the more negative the HOMO, with both basis sets used.

Comparison of the effect of geometry calculated at the B3LYP/6-31G(d) level and at the LC-BLYP/6-31+G(d) level on NICS calculated at the B3LYP/6-311+G(d.p) level for **1a-f**$^{2-}$

To determine whether it was necessary to optimize geometries with long-range correction functionals, the NICS(1)$_{zz}$ values were calculated at the same basis set, B3LYP/6-311+g(d,p) for the geometries of **1a-f**$^{2-}$ optimized at with B3LYP/6-31g(d) and with LC-BLYP/6-31+g(d,p). The relationship is very linear, showing that the NICS values are responding similarly. Since we are interested in looking at trends in NICS values, this linear relationship shows us that we can use geometries optimized at lower levels.



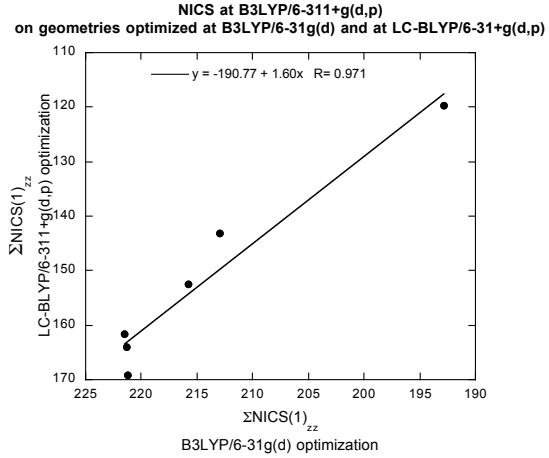
The similarity of geometries that is implied by the agreement of the NICS values is supported by a comparison of dihedral angles for **1d**$^{2-}$ optimized at B3LYP/6-31G(d) and LC-BLYP/6-31+G(d).

	B3LYP/6-31G(d)	LC-BLYP/6-31+G(d)	Difference
1-2-3-4	0.03043	0.29988	0.26945
2-3-4-4a	0.00181	-0.48468	-0.48649
3-4-4a-5	-178.00541	-179.95204	-1.94663
4-4a-5-6-	176.29167	172.88606	-3.40561
4a-5-6-6a	2.67859	2.055687	-0.622903
5-6-6a-7	-179.07497	-175.07414	4.00083
6-6a-7-8	-176.66753	-176.07271	0.59482
6a-7-8-9	2.0842	2.02067	-0.06353

7-8-9-10	-2.61353	-2.09171	0.52182
8-9-10-10a	-0.83562	-1.24136	-0.40574
9-10-10a-11	-174.27647	-175.30165	-1.02518
10-10a-11-11a	-174.80752	178.17301	3.36549
10a-11-11a-1	-179.83738	-174.23045	5.60693
11-11a-1-2	179.34846	179.2762	-0.07226
11a-1-2-3	0.0154	0.4438	0.4284
11-11a-4a-4	-179.282	-179.51012	-0.22812
11-10a-6a-6	-7.8904	-7.52963	0.36077
1-11a-4a-4	-0.05403	0.73117	0.7852
1-11a-4a-5	177.78329	-179.38961	-1.60632
10-10a-6a-7	-4.88591	-4.30557	0.58034
11-11a-4a-5	-1.44469	175.27909	-3.27622 0
i-α-11-11a	75.2523	75.66855	0.41625
α-11-10a-10	11.25999	6.05103	-5.20896
o-i-α-11	-3.37763	-3.19633	0.1813
o'-i-α-11	177.6046	177.6324	0.0278

The $NICS(1)_{zz}$ values calculated for the different optimized geometries are shown in the Table below, along with the calculated areas. The dependence on area is less distinct in systems with very similar areas, as the plot of $NICS(1)_{zz}$ without normalization by square area shows, see below.

$NICS(1)_{zz}$	CF_3, **1a²⁻**	Cl,**1b²⁻**	OCH_3,**1c²⁻**	H, **1d²⁻**	F, **1e²⁻**	CH_3, **1f²⁻**
B3LYP/6-31g(d)	192.85	212.92	215.77	221.21	221.32	221.53
LC-BLYP/6-31+g(d)	119.68	143.13	152.59	169.28	164.14	161.64
Areas						
B3LYP/6-31g(d)	17.80	17.85	17.86	17.85	17.84	17.85
LC-BLYP/6-31+g(d)	15.27	15.77	16.06	16.64	16.28	15.72

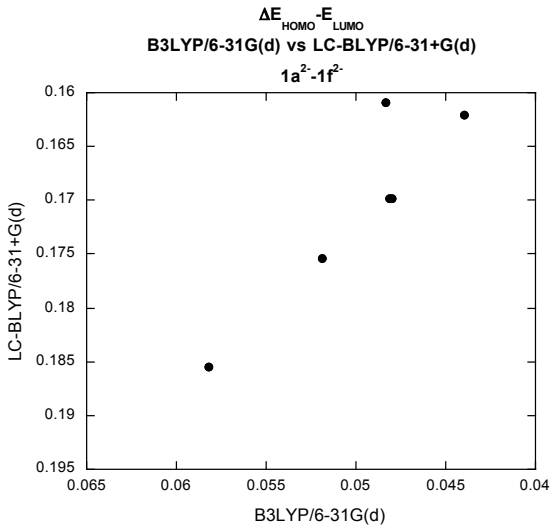


We have therefore chosen to calculate NICS(1)$_{zz}$ on geometries optimized at the lower basis set using a functional without long-range corrections, B3lYP/6-31g(d).

Table of ΔE_{HOMO}-E_{LUMO} for **1a^{2-}—1f^{2-}**, geometries optimized at B3LYP/6-31G(d) and at LC-BLYP/6-31+G(d), in eV

	B3LYP/6-31G(d)	LC-BLYP/6-31+G(d), in eV
1a^{2-}	1.584	5.048
1b^{2-}	1.412	4.774
1c^{2-}	1.196	4.410
1d^{2-}	1.310	4.621
1e^{2-}	1.306	4.621
1f^{-}	1.316	4.381

Plot of ΔE_{HOMO}-E_{LUMO} for **1a^{2-}—1f^{2-}** at two different geometries, the point for **1f^{2-}** is not on the line shown by the other points



Cartesian coordinates and total energies for **1a^{2-} .1f^{2-}** (B3LYP/6-31G(d) and LC-BLYP/6-31+G(d)), **Li$_2$1b, Li$_2$[1d-f], Li$_4$1b**, **Li$_4$1d-f**, **Li$_4$1d-4THF** pp. S29-S38

Optimization at B3LYP/6-31G(d)
1a^{2-}
Total energy, -1184.9113431 Hartrees
Imaginary frequencies: 0

C	3.00226	1.97245	-0.29636
C	1.86228	1.32586	0.33104
C	0.91211	2.2624	0.86674
C	1.03741	3.64313	0.79133
C	2.13527	4.2413	0.1674

C	3.09378	3.3694	-0.36214
H	0.04429	1.84662	1.36103
H	0.25061	4.26073	1.22891
H	2.24273	5.32189	0.0863
H	3.97693	3.78834	-0.85013
C	2.43552	-1.21745	0.15034
C	1.93264	-2.54168	0.41343
C	3.77578	-1.22832	-0.41671
C	2.66144	-3.71155	0.24189
H	0.90694	-2.61308	0.75338
C	4.48314	-2.42584	-0.57454
C	3.974	-3.68753	-0.23678
H	2.18148	-4.66365	0.47942
H	5.48808	-2.35848	-0.9983
H	4.562	-4.5937	-0.3744
C	4.14438	1.26464	-0.87916
H	4.87098	1.93512	-1.34644
C	4.4705	-0.03854	-0.91088
H	5.41954	-0.26787	-1.40374
C	1.58539	-0.09213	0.47655
C	0.32654	-0.46383	1.20119
C	-0.98249	-0.38059	0.77396
C	-2.10037	-0.81084	1.61092
C	-1.40042	0.15129	-0.52057
C	-3.41004	-0.72104	1.22013
H	-1.86363	-1.21943	2.59519
C	-2.71644	0.23584	-0.89547
H	-0.6216	0.48509	-1.20135
C	-3.78506	-0.17661	-0.04448
H	-4.19429	-1.06325	1.8966
H	-2.96114	0.64319	-1.8769
H	0.46314	-0.93624	2.18399
C	-5.1615	-0.18143	-0.49189
F	-6.08193	-0.04098	0.52716
F	-5.61954	-1.34722	-1.14101
F	-5.45661	0.79945	-1.41161

1b^{2-}

Total energy, -1307.4524188 Hartrees

Imaginary frequencies: 0

C	2.4008	2.02358	-0.23262
C	1.2461	1.33654	0.32036
C	0.22771	2.23788	0.78645
C	0.30834	3.62311	0.71672
C	1.42416	4.26042	0.16929
C	2.44793	3.42301	-0.29261

H	-0.65205	1.78693	1.22555
H	-0.52903	4.21221	1.09673
H	1.49918	5.34452	0.09471
H	3.34873	3.87397	-0.71592
C	1.9027	-1.18464	0.14449
C	1.41638	-2.52872	0.33859
C	3.27705	-1.15207	-0.33921
C	2.18058	-3.67602	0.18099
H	0.37395	-2.62567	0.61696
C	4.02167	-2.32977	-0.48085
C	3.52279	-3.61087	-0.21042
H	1.70843	-4.64533	0.35895
H	5.05065	-2.22824	-0.83538
H	4.1402	-4.49998	-0.33116
C	3.60706	1.35733	-0.73198
H	4.34759	2.05598	-1.13166
C	3.97339	0.06426	-0.75574
H	4.96489	-0.12922	-1.1757
C	1.00856	-0.09188	0.45806
C	-0.26329	-0.5039	1.13619
C	-1.56028	-0.46575	0.64821
C	-2.69982	-0.94303	1.42297
C	-1.93435	0.06238	-0.65869
C	-4.0029	-0.90129	0.96793
H	-2.50237	-1.36219	2.41139
C	-3.24126	0.10376	-1.10641
H	-1.1385	0.41989	-1.30682
C	-4.29009	-0.38227	-0.30698
H	-4.81218	-1.27865	1.59361
H	-3.46136	0.50837	-2.09428
H	-0.14764	-0.99423	2.1123
Cl	-6.00175	-0.28063	-0.88045

1c^{2-}

Total energy, -962.3583706 Hartrees

Imaginary frequencies: 0

C	-3.38184	-0.97112	-0.29163
C	-1.98947	-1.10877	0.12215
C	-1.58359	-2.48911	0.24401
C	-2.42819	-3.57734	0.08951
C	-3.78426	-3.41193	-0.22549
C	-4.20979	-2.09356	-0.4284
H	-0.53679	-2.66044	0.46554
H	-2.01215	-4.58127	0.20632
H	-4.46483	-4.25486	-0.33897
H	-5.24745	-1.91284	-0.72176

C	-1.14516	1.35392	0.31161
C	-0.03538	2.16838	0.72342
C	-2.27198	2.13156	-0.17324
C	-0.01282	3.55757	0.66722
H	0.82832	1.64571	1.11125
C	-2.21574	3.53137	-0.21935
C	-1.10548	4.2833	0.1899
H	0.88824	4.07698	1.00098
H	-3.10283	4.05506	-0.58406
H	-1.10248	5.37111	0.12892
C	-4.01336	0.3003	-0.63194
H	-5.0412	0.18957	-0.99073
C	-3.55352	1.56393	-0.60502
H	-4.2656	2.32306	-0.94138
C	-1.01355	-0.09165	0.43634
C	0.23538	-0.60341	1.08815
C	1.52658	-0.66323	0.57665
C	2.63677	-1.23759	1.32562
C	1.91756	-0.15641	-0.73255
C	3.93526	-1.26959	0.85142
H	2.41852	-1.6664	2.30593
C	3.22376	-0.19535	-1.18875
H	1.13632	0.24846	-1.3709
C	4.26019	-0.74777	-0.41487
H	4.72845	-1.72072	1.45303
H	3.46382	0.19243	-2.18164
H	0.0939	-1.10773	2.05358
O	5.59613	-0.77917	-0.89265
C	6.3185	0.38274	-0.55615
H	6.38942	0.52615	0.53586
H	7.33774	0.27857	-0.96464
H	5.86046	1.29307	-0.97783

1d^{2-}

Total energy, -847.837286Hartrees

Imaginary frequencies: 0

C	-1.66518	2.117	0.11137
C	-0.48828	1.35402	-0.2648
C	0.64626	2.18086	-0.5685
C	0.64561	3.5709	-0.51541
C	-0.49762	4.28316	-0.15019
C	-1.63213	3.51778	0.15554
H	1.55068	1.66868	-0.86715
H	1.56857	4.10111	-0.76073
H	-0.51525	5.37132	-0.09553
H	-2.55698	4.0308	0.43096

C	-1.31126	-1.11925	-0.13749
C	-0.87497	-2.49454	-0.21345
C	-2.7361	-1.00187	0.15894
C	-1.71146	-3.59485	-0.11769
H	0.18901	-2.6489	-0.34955
C	-3.55431	-2.13757	0.23795
C	-3.09247	-3.44984	0.08423
H	-1.27122	-4.59281	-0.18953
H	-4.61601	-1.97143	0.44048
H	-3.76632	-4.30339	0.14901
C	-2.97331	1.53271	0.42681
H	-3.72471	2.28355	0.68814
C	-3.41441	0.26162	0.42589
H	-4.46932	0.13829	0.69024
C	-0.32973	-0.09043	-0.38186
C	0.96884	-0.58491	-0.94517
C	2.21985	-0.64893	-0.3413
C	3.38286	-1.20902	-1.01624
C	2.5166	-0.15747	0.99687
C	4.63955	-1.25358	-0.44336
H	3.23792	-1.61053	-2.02215
C	3.7864	-0.21142	1.54351
H	1.6934	0.25242	1.57773
C	4.89197	-0.75411	0.85375
H	5.46176	-1.69444	-1.01784
H	3.93143	0.17841	2.55644
H	5.88653	-0.78716	1.29779
H	0.90038	-1.07759	-1.92467

1e^{2-}

Total energy, -947.074245Hartrees

Imaginary frequencies: 0

C	2.09256	2.0359	-0.16487
C	0.89755	1.34564	0.28639
C	-0.16851	2.23881	0.64457
C	-0.09253	3.62627	0.57309
C	1.06593	4.26771	0.13353
C	2.13641	3.43577	-0.22524
H	-1.07995	1.78191	1.00531
H	-0.96797	4.21104	0.86422
H	1.14191	5.35243	0.06348
H	3.07173	3.89234	-0.5583
C	1.56768	-1.17259	0.13736
C	1.05672	-2.51955	0.24556
C	2.97903	-1.13976	-0.23527

C	1.82164	-3.66735	0.1149
H	-0.00589	-2.6109	0.43826
C	3.72493	-2.32172	-0.34661
C	3.19663	-3.60378	-0.15819
H	1.3286	-4.63762	0.2164
H	4.78223	-2.21904	-0.60592
H	3.8157	-4.49539	-0.25035
C	3.34617	1.37452	-0.54366
H	4.12382	2.07865	-0.85344
C	3.71334	0.08004	-0.55174
H	4.74355	-0.10629	-0.87076
C	0.66306	-0.08672	0.42808
C	-0.62762	-0.50007	1.067
C	-1.91059	-0.49258	0.52581
C	-3.06926	-0.98379	1.25819
C	-2.23976	0.01568	-0.79898
C	-4.35871	-0.95883	0.75042
H	-2.90286	-1.39399	2.25593
C	-3.53603	0.03874	-1.29329
H	-1.42352	0.3742	-1.42042
C	-4.60021	-0.44212	-0.52643
H	-5.19601	-1.34243	1.3363
H	-3.73827	0.42742	-2.29264
H	-0.53629	-1.00175	2.03962
F	-5.90081	-0.41466	-1.03239

1f^{2-}

Total energy, -887.1557954 Hartrees

Imaginary frequencies: 0

C	-3.00769	-1.12305	-0.24917
C	-1.59968	-1.16823	0.13186
C	-1.10188	-2.51905	0.24685
C	-1.87716	-3.66036	0.11447
C	-3.24856	-3.5847	-0.1685
C	-3.76372	-2.29764	-0.36365
H	-0.04126	-2.62118	0.44434
H	-1.39394	-4.63473	0.22301
H	-3.87531	-4.47058	-0.26353
H	-4.81787	-2.18581	-0.63154
C	-0.90963	1.34424	0.28733
C	0.15833	2.22976	0.66036
C	-2.0961	2.04492	-0.17152
C	0.09204	3.6172	0.59279
H	1.06479	1.7667	1.02557
C	-2.12944	3.44513	-0.22901
C	-1.05744	4.26865	0.14264

H	0.96817	4.19492	0.89551
H	-3.05791	3.90882	-0.57131
H	-1.12464	5.35397	0.07416
C	-3.72916	0.1034	-0.57416
H	-4.75756	-0.07482	-0.9032
C	-3.351	1.39423	-0.56317
H	-4.1196	2.10476	-0.88084
C	-0.68587	-0.08909	0.42227
C	0.60164	-0.51694	1.0593
C	1.88712	-0.50921	0.53103
C	3.03656	-1.01498	1.26758
C	2.23923	-0.00062	-0.78638
C	4.32381	-0.98928	0.76964
H	2.85534	-1.44388	2.25599
C	3.54018	0.01393	-1.25379
H	1.43269	0.35622	-1.42278
C	4.64148	-0.46982	-0.50909
H	5.1334	-1.39484	1.38759
H	3.72648	0.41154	-2.2577
H	0.50227	-1.02058	2.03045
C	6.05693	-0.37988	-1.01153
H	6.67472	-1.22861	-0.66928
H	6.0966	-0.38587	-2.11322
H	6.6137	0.53211	-0.7002

Optimization at LC-BLYP/6-31+G(d)

1^{2-}

Total energy, -1182.0809071 Hartrees

C	2.88058	1.955	-0.34788
C	1.81268	1.30226	0.3381
C	0.92402	2.20306	0.97874
C	1.08074	3.5661	0.99175
C	2.14073	4.17198	0.34535
C	3.01073	3.33029	-0.3229
H	0.07232	1.77441	1.48435
H	0.3426	4.16735	1.51504
H	2.27363	5.24752	0.3364
H	3.84318	3.76203	-0.87322
C	2.41691	-1.19192	0.1503
C	2.0157	-2.50462	0.54034
C	3.69159	-1.17498	-0.50738
C	2.8048	-3.61951	0.42526
H	1.01989	-2.6167	0.94078
C	4.45932	-2.31639	-0.60999
C	4.07084	-3.55599	-0.12946
H	2.40708	-4.57171	0.76705

H	5.41391	-2.22769	-1.12372
H	4.70393	-4.42944	-0.23069
C	3.88937	1.26568	-1.15401
H	4.46479	1.93449	-1.79088
C	4.23113	-0.00924	-1.20464
H	5.05029	-0.25039	-1.87957
C	1.54238	-0.10737	0.44154
C	0.3097	-0.48989	1.18244
C	-0.97078	-0.40248	0.76725
C	-2.08968	-0.82096	1.59958
C	-1.37313	0.13166	-0.52387
C	-3.37516	-0.7242	1.20025
H	-1.86104	-1.22499	2.58173
C	-2.66844	0.21803	-0.89686
H	-0.58878	0.46665	-1.19181
C	-3.73217	-0.18722	-0.05758
H	-4.16397	-1.05842	1.86857
H	-2.90627	0.62641	-1.87501
H	0.45565	-0.9258	2.17557
C	-5.08955	-0.19369	-0.51065
F	-6.01413	-0.04947	0.48285
F	-5.54084	-1.35378	-1.14884
F	-5.38072	0.76465	-1.43167

1b^{2-}

Total energy, -1304.79802 Hartrees

C	2.26725	2.01297	-0.2889
C	1.19584	1.31011	0.34183
C	0.23396	2.17028	0.9322
C	0.32778	3.53895	0.95218
C	1.39166	4.19414	0.36176
C	2.33337	3.3928	-0.2584
H	-0.61945	1.69677	1.39339
H	-0.46385	4.10531	1.43519
H	1.47629	5.27478	0.35891
H	3.17507	3.86246	-0.76197
C	1.90102	-1.15586	0.15627
C	1.52514	-2.49241	0.49391
C	3.20693	-1.08512	-0.43789
C	2.35298	-3.57867	0.39015
H	0.51477	-2.6381	0.8444
C	4.01447	-2.20011	-0.52938
C	3.64362	-3.46365	-0.09964
H	1.9689	-4.55121	0.68849
H	4.99044	-2.0685	-0.9917
H	4.30874	-4.31436	-0.18987

C	3.35387	1.37315	-1.03244
H	3.94578	2.0725	-1.61973
C	3.7469	0.11259	-1.07687
H	4.61891	-0.08535	-1.69782
C	0.977	-0.11062	0.43668
C	-0.27145	-0.54521	1.12133
C	-1.54164	-0.49225	0.64111
C	-2.68486	-0.96594	1.39509
C	-1.89622	0.05741	-0.65024
C	-3.96029	-0.92401	0.91662
H	-2.50444	-1.37971	2.38323
C	-3.18103	0.08955	-1.10637
H	-1.09663	0.4445	-1.2702
C	-4.2339	-0.40258	-0.34297
H	-4.77595	-1.30262	1.52621
H	-3.38775	0.5101	-2.08626
H	-0.15376	-1.00805	2.10512
Cl	-5.8948	-0.33127	-0.94198

1c^{2-}

Total energy, -959.7148927 Hartrees

C	-1.25572	0.00157	-1.2453
C	0.16314	0.12778	-1.43825
C	0.52677	0.13669	-2.82136
C	-0.34615	-0.08313	-3.85268
C	-1.69687	-0.3005	-3.6285
C	-2.10789	-0.21743	-2.30842
C	1.09514	0.10256	0.95646
C	2.29713	-0.01504	1.7015
C	-0.07679	0.07881	1.77271
C	2.35206	-0.18559	3.06188
C	0.00812	-0.08802	3.14172
C	1.20171	-0.23584	3.82603
C	-1.92247	0.19308	0.03984
C	-1.44149	0.24627	1.26932
C	1.20331	0.23878	-0.47494
C	2.58159	0.28157	-1.0359
C	3.47258	1.31218	-0.96801
C	4.78411	1.25639	-1.57549
C	3.21771	2.55499	-0.27649
C	5.68491	2.281	-1.49377
C	4.141	3.56203	-0.21418
C	5.38987	3.45477	-0.81182
O	6.33381	4.48945	-0.71408
C	7.13363	4.38715	0.42256
H	1.56303	0.33938	-3.04553

H	0.04086	-0.06826	-4.8689
H	-2.39958	-0.47395	-4.43503
H	-3.16881	-0.30363	-2.08293
H	3.21713	0.03096	1.13865
H	3.32708	-0.26947	3.53455
H	-0.92411	-0.09443	3.70176
H	1.22657	-0.35931	4.90277
H	-3.00016	0.32094	-0.04786
H	-2.17527	0.41039	2.05617
H	2.89883	-0.58545	-1.62142
H	5.04899	0.35763	-2.12612
H	2.24884	2.68084	0.19214
H	6.65485	2.18907	-1.97914
H	3.89503	4.48176	0.31318
H	7.70337	3.44928	0.4273
H	7.83196	5.23037	0.42357
H	6.53211	4.41836	1.33913

1d^{2-}

Total energy, -845.4186203Hartrees

C	-1.46453	2.13897	0.17528
C	-0.40126	1.32003	-0.31357
C	0.70572	2.068	-0.79154
C	0.75281	3.43849	-0.83744
C	-0.30298	4.20858	-0.38772
C	-1.38807	3.51764	0.12186
C	-1.35864	-1.06125	-0.17058
C	-1.07472	-2.43953	-0.42772
C	-2.71331	-0.85239	0.26339
C	-2.00729	-3.44094	-0.396
C	-3.62739	-1.88602	0.28532
C	-3.33091	-3.19258	-0.06609
C	-2.69356	1.62689	0.78464
C	-3.21011	0.41082	0.80189
C	-0.31381	-0.11811	-0.36891
C	0.9535	-0.68678	-0.90685
C	2.16601	-0.75089	-0.29023
C	3.32745	-1.35542	-0.90827
C	2.43683	-0.21229	1.0237
C	4.5419	-1.42268	-0.29264
C	3.66738	-0.29748	1.60726
C	4.76703	-0.90147	0.9871
H	1.55561	1.50057	-1.1393
H	1.64984	3.91295	-1.2263
H	-0.27893	5.29224	-0.40709
H	-2.23335	4.07914	0.51303

H	-0.0481	-2.68604	-0.65242
H	-1.6842	-4.45451	-0.62187
H	-4.6339	-1.64962	0.62439
H	-4.07932	-3.97572	-0.03497
H	-3.28423	2.3968	1.27747
H	-4.169	0.3164	1.30893
H	0.89331	-1.16359	-1.88925
H	3.20702	-1.77427	-1.90456
H	1.61722	0.26337	1.55023
H	5.36482	-1.90131	-0.82297
H	3.79276	0.12846	2.602
H	5.73817	-0.95439	1.46522

1e^{2-}

Total energy, -944.5564711 Hartrees

C	-1.90158	2.05524	0.23385
C	-0.82181	1.31619	-0.33934
C	0.19838	2.14367	-0.87612
C	0.15243	3.51496	-0.8985
C	-0.91827	4.206	-0.3641
C	-1.91927	3.43647	0.20226
H	1.05587	1.63795	-1.29378
H	0.98742	4.05414	-1.33791
H	-0.96668	5.28899	-0.36387
H	-2.77183	3.93448	0.6582
C	-1.60383	-1.12702	-0.17053
C	-1.2441	-2.47979	-0.46382
C	-2.93798	-1.01608	0.3533
C	-2.10137	-3.54402	-0.38392
H	-0.22028	-2.65148	-0.75968
C	-3.77566	-2.11071	0.42136
C	-3.414	-3.39067	0.03494
H	-1.72527	-4.53081	-0.64373
H	-4.77159	-1.94746	0.82795
H	-4.10339	-4.22389	0.10456
C	-3.05272	1.4534	0.90942
H	-3.66237	2.17552	1.44918
C	-3.48414	0.20482	0.93954
H	-4.40115	0.0399	1.50282
C	-0.64065	-0.11175	-0.42493
C	0.6251	-0.58483	-1.04955
C	1.87603	-0.56438	-0.50264
C	3.03883	-1.08355	-1.18695
C	2.1783	-0.00716	0.7953
C	4.29411	-1.0728	-0.64012
H	2.89754	-1.50715	-2.17725

C	3.44372	-0.00675	1.32118
H	1.35952	0.41173	1.36756
C	4.50131	-0.54012	0.61546
H	5.13745	-1.48255	-1.18938
H	3.6256	0.41928	2.30394
H	0.53938	-1.0664	-2.0271
F	5.78476	-0.52212	1.15799

1f^{2-}

Total energy, -1337.6753927 Hartrees

C	2.97033	-0.99302	0.36637
C	1.63761	-1.12003	-0.15857
C	1.29414	-2.47803	-0.4502
C	2.16545	-3.53068	-0.37255
C	3.47713	-3.36073	0.04402
C	3.8221	-2.07674	0.43257
H	0.27182	-2.66401	-0.74252
H	1.80151	-4.52226	-0.63158
H	4.17719	-4.18515	0.11217
H	4.81557	-1.90123	0.84022
C	0.8305	1.31352	-0.33562
C	-0.1937	2.12855	-0.88287
C	1.9011	2.06462	0.23809
C	-0.15838	3.49996	-0.91478
H	-1.0465	1.61402	-1.29912
C	1.90826	3.44581	0.19704
C	0.9043	4.20313	-0.38012
H	-0.99571	4.02933	-1.36157
H	2.75415	3.9537	0.65453
H	0.94407	5.2865	-0.38721
C	3.49804	0.23294	0.95854
H	4.41184	0.07773	1.52985
C	3.05254	1.47646	0.92552
H	3.64849	2.20556	1.4712
C	0.66346	-0.1172	-0.41377
C	-0.59589	-0.60635	-1.03933
C	-1.85112	-0.58864	-0.50703
C	-3.00371	-1.12387	-1.19627
C	-2.17881	-0.03201	0.78396
C	-4.25947	-1.10872	-0.66153
H	-2.84581	-1.56694	-2.17659
C	-3.45238	-0.03718	1.27961
H	-1.37019	0.38496	1.37323
C	-4.54834	-0.57124	0.59677
H	-5.07441	-1.54016	-1.24516
H	-3.61874	0.40006	2.2651

H	-0.49833	-1.09501	-2.01253
C	-5.94602	-0.47358	1.12219
H	-6.55859	-1.32257	0.79671
H	-5.9594	-0.47274	2.21763
H	-6.47987	0.43634	0.80343

Optimized at B3LYP/6-31G(d)

$Li_2$1b

Total energy, -1322.594973 Hartrees

C	2.4497231084	-1.4551182198	0.0115927945
C	1.0506163602	-1.2836660961	0.2009530872
C	0.2565101361	-2.4185299082	-0.0545455346
C	0.7871023506	-3.6411612667	-0.4837326807
C	2.1537751573	-3.7810400309	-0.6828275145
C	-2.972038174	-2.676814267	-0.4216534095
C	-0.7437141277	1.3026716025	0.2384772794
C	0,0.2403719104	2.353087485	0.2644047528
C	-2.0868337362	1.7596194115	-0.1028736313
C	-0.020553932	3.6519527351	-0.1197216621
C	-2.3124312453	3.1073984169	-0.4882272426
C	-1.3063526065	4.0491216028	-0.5358849472
C	-3.4250649625	-0.3837756932	0.29344848
C	-3.2863966241	0.9570504348	0.1066857521
C	-0.4084965674	-0.0261021402	0.7299081855
C	0.9604219961	-0.2475425526	1.3005210539
C	2.1533979867	-0.2040110594	0.6232611908
C	3.429249569	-0.5998032609	1.2345740769
C	2.2901972625	0.1471546399	-0.8011018619
C	4.6545586378	-0.4451399053	0.6025129873
C	3.5243795478	0.3133215052	-1.4187578873
C	4.7294227828	-0.0014902934	-0.7445358951
H	0.8080391286	-2.344465519	0.1410115039
H	-0.120768654	-4.487005905	-0.6419870047
H	-2.5851126602	-4.7249720211	-1.0034704404
H	-4.0504173454	-2.7691056389	-0.5369244556
H	1.2362499168	2.0961669045	0.5978092574
H	0.7894665992	4.3779046967	-0.097383544
H	-3.3308591159	3.392525094	-0.7462654034
H	-1.5068777417	5.0686843195	-0.8503099248
H	-4.4384759555	-0.7321055627	0.4913984145
H	-4.2053021789	1.5424651672	0.1741691803
H	1.011256337	-0.6524768761	2.3150473165
H	3.4135809568	-0.9713870879	2.2564609308
H	1.3900148504	0.3489385005	-1.3706644522
H	5.5691439478	-0.7208456063	1.1212462101
H	3.5659291194	0.622784195	-2.4600337125

Li	-1.9821335424	0.8092532909	1.90920696
Li	3.4630054052	-1.7380498553	-0.7105853323
Cl	6.293593388	0.2167488141	-1.5335243568

$Li_2$1c

Total energy, -971.1224128 Hartrees

C	2.872481	1.660399	-0.157058
C	1.540414	1.348813	0.238159
C	0.622425	2.416697	0.164913
C	0.966538	3.694173	-0.293375
C	2.263104	3.965268	-0.708207
C	3.206420	2.935520	-0.620877
C	1.501618	-1.258046	0.234510
C	0.633343	-2.399744	0.356380
C	2.825700	-1.576581	-0.287608
C	0.968416	-3.663530	-0.083876
C	3.132232	-2.892525	-0.722568
C	2.225048	-3.929563	-0.661597
C	3.980821	0.691915	-0.047550
C	3.955296	-0.655313	-0.230460
C	1.098511	0.023286	0.801025
C	-0.209287	0.087868	1.532179
C	-1.460905	-0.033683	0.973437
C	-2.694851	0.238014	1.722032
C	-1.710241	-0.357646	-0.441419
C	-3.963079	0.064176	1.183840
C	-2.991245	-0.541280	-0.955505
C	-4.150984	-0.304800	-0.176675
H	-0.379932	2.240833	0.541218
H	0.213099	4.479887	-0.301834
H	2.552036	4.952531	-1.056974
H	4.240735	3.131904	-0.897515
H	-0.333179	-2.242491	0.814961
H	0.240622	-4.465335	0.021791
H	4.132652	-3.072832	-1.112272
H	2.483200	-4.922283	-1.017413
H	4.971300	1.142514	0.013027
H	4.929672	-1.142610	-0.299742
H	-0.184573	0.452415	2.562508
H	-2.602524	0.542716	2.762040
H	-0.856845	-0.508892	-1.092503
H	-4.842067	0.243888	1.799556
H	-3.118451	-0.830351	-1.996734
Li	2.893020	-0.654990	1.738100
Li	-2.876447	1.466348	-0.132742
O	-5.414942	-0.606844	-0.669738

C -6.136526 0.498464 -1.187632
H -6.314269 1.266121 -0.418182
H -5.610948 0.962314 -2.037742
H -7.102205 0.119067 -1.534775

$Li_2$1d

Total energy, -863.001948 Hartrees

C,0,2.2465076204,1.6382529999,0.9280037512
C,0,0.8820754379,1.3597152659,0.6473476037
C,0,0.1030114658,2.4562709534,0.2340847357
C,0,0.6218154334,3.7496364331,0.0952232617
C,0,1.9609081693,3.9991556558,0.3628402158
C,0,2.7595304225,2.9299454494,0.7838526214
C,0,0.8097508485,-1.2263681981,0.378428072
C,0,-0.0386544279,-2.341973728,0.0398096207
C,0,2.2338903873,-1.5545365627,0.4069003993
C,0,0.4426038607,-3.5692072196,-0.3619347493
C,0,2.6850488348,-2.8345099784,-0.0147843307
C,0,1.8270932398,-3.8294703393,-0.4300182185
C,0,3.1826135687,0.6003268775,1.4052578006
C,0,3.2373400579,-0.7120476319,1.0422089012
C,0,0.2274348877,0.0152647392,0.8507539669
C,0,-1.2589291949,0.0961170656,1.0261715326
C,0,-2.2192067077,0.026834767,0.0474228505
C,0,-3.6418819047,0.2784374162,0.3168211653
C,0,-1.9433643932,-0.2173250668,-1.3794005621
C,0,-4.6338326674,0.0876179306,-0.6333303105
C,0,-2.9552959655,-0.4172929486,-2.3102975504
C,0,-4.3282026115,-0.2425433779,-1.9857097883
H,0,-0.9551543779,2.2883294599,0.0639662086
H,0,-0.0377842311,4.5612064241,-0.2059541188
H,0,2.3779795715,4.9984714127,0.2755315449
H,0,3.8060511022,3.1044558217,1.0270566046
H,0,-1.1077568309,-2.1904025437,0.0962490408
H,0,-0.267669068,-4.3483813462,-0.6307915656
H,0,3.7573626558,-3.0212865099,0.0080926101
H,0,2.2031073665,-4.7924454486,-0.7617334032
H,0,4.0531487144,0.9814278301,1.9385581178
H,0,4.1482726589,-1.2438299469,1.3243534401
H,0,-1.6136734894,0.4237778526,2.0075712082
H,0,-3.9245132441,0.5588321464,1.329288203
H,0,-0.9092208777,-0.3127760166,-1.6919264016
H,0,-5.6716023954,0.2546563413,-0.3499640234
H,0,-2.6798136306,-0.6444669941,-3.3387689342
H,0,-5.1099789747,-0.4120754917,-2.7167001535
Li,0,1.4623572121,-0.8537957605,2.373576603

Li,0,-3.2944213736,1.5483037271,-1.5110039995

$Li_2$1e

Total energy, -956.0944381 Hartrees

C,0,-2.4349082469,-1.4163725639,-0.0317984686
C,0,-1.0516796313,-1.2632095337,0.2107442119
C,0,-0.2731335116,-2.3973072051,-0.0592039883
C,0,-0.8000925148,-3.5746221962,-0.565985444
C,0,-2.1496526822,-3.6882983895,-0.8318462709
C,0,-2.9527769251,-2.59942137,-0.5421452963
C,0,-0.7517283364,1.3008779831,0.260076336
C,0,0.2493405664,2.3095276425,0.1487149551
C,0,-2.0785832753,1.7613250989,0.0032942725
C,0,-0.014966078,3.5906315923,-0.2568587633
C,0,-2.3188903476,3.0865029873,-0.407800655
C,0,-1.314595171,4.0010517175,-0.564076221
C,0,-3.4214969906,-0.3731138329,0.3054456016
C,0,-3.2841075449,0.954067348,0.2594855708
C,0,-0.4290508088,-0.032352136,0.8111927011
C,0,0.9703472461,-0.2323083816,1.3431516051
C,0,2.1319002852,-0.2586483709,0.6516651543
C,0,3.4261448648,-0.574803658,1.2733603703
C,0,2.2573039158,-0.0665416556,-0.801356453
C,0,4.6289330669,-0.3344409629,0.6444544607
C,0,3.4736544285,0.1793597999,-1.4076867097
C,0,4.670570409,0.0385828393,-0.7031457251
H,0,0.7722341392,-2.3602314556,0.1676392099
H,0,-0.1437506892,-4.4105764624,-0.7424334924
H,0,-2.5709502816,-4.5968801087,-1.2225187346
H,0,-4.0161680848,-2.6718672632,-0.6985245191
H,0,1.2561765369,2.0499977736,0.3921413976
H,0,0.8005855713,4.2889881259,-0.3354407198
H,0,-3.3377755435,3.3793089244,-0.5978281196
H,0,-1.5214175004,5.004622834,-0.8882817394
H,0,-4.4138532481,-0.7399509497,0.5136628746
H,0,-4.180096491,1.5327187666,0.4239142184
H,0,1.0597769855,-0.4741017943,2.3946156845
H,0,3.4364157678,-0.8775663362,2.3053037146
H,0,1.3633248048,0.0212371283,-1.3878035372
H,0,5.555783059,-0.4850595889,1.1707537918
H,0,3.5136385504,0.4235125855,-2.4553194045
Li,0,-1.8698598289,0.8045551308,2.0882768039
Li,0,3.5897836074,-1.8710984434,-0.5927292045
F,0,5.8502316067,0.3261419909,-1.2922219984

$Li_2$1f

Total energy, -902.3168567 Hartrees

C,0,-2.4742614989,-1.4572693845,0.0445081632
C,0,-1.070715765,-1.292797301,0.1909648809
C,0,-0.2859871629,-2.4250223413,-0.0970810391
C,0,-0.8331177651,-3.6451895371,-0.5128847987
C,0,-2.2063825196,-3.7814722597,-0.6639641265
C,0,-3.0141826137,-2.6759662255,-0.3748216177
C,0,-0.7414265235,1.2863957776,0.2218392385
C,0,0.2466301785,2.3360006399,0.247657115
C,0,-2.0867858136,1.7498299336,-0.1124634517
C,0,-0.0102208486,3.6326921184,-0.1419176344
C,0,-2.3056811123,3.0974410665,-0.506826512
C,0,-1.295564669,4.0329699805,-0.5623817233
C,0,-3.4324372324,-0.3750787812,0.3481990193
C,0,-3.2877051457,0.9615122755,0.1261903583
C,0,-0.4080510163,-0.0394678611,0.7078321486
C,0,0.9572843431,-0.2753701619,1.2795554008
C,0,2.1577314563,-0.225298019,0.6124407235
C,0,3.4252860144,-0.638930684,1.2258397508
C,0,2.3173231475,0.1483963436,-0.8019767203
C,0,4.6558576013,-0.4676336578,0.6061554002
C,0,3.5652396859,0.3242600558,-1.391906921
C,0,4.7872382397,0.0088080112,-0.7334550225
H,0,0.7847969636,-2.3494767903,0.0597442239
H,0,-0.1743925781,-4.4915062712,-0.6982465313
H,0,-2.6503912359,-4.7241477097,-0.971268592
H,0,-4.0959227921,-2.7651488116,-0.4568479097
H,0,1.2413032139,2.0747912641,0.5813739913
H,0,0.8017225681,4.3567837893,-0.1219148864
H,0,-3.323643853,3.3865856324,-0.7626549594
H,0,-1.4911324338,5.0516576242,-0.8830164122
H,0,-4.4439000768,-0.7114866381,0.574686814
H,0,-4.2010377414,1.5554703786,0.1986133294
H,0,0.99603379,-0.7137243906,2.2808315096
H,0,3.3954751179,-1.0390591318,2.2371438095
H,0,1.4251753493,0.3551656703,-1.3831469668
H,0,5.5564294798,-0.7607070267,1.1453467705
H,0,3.6046876103,0.6557967147,-2.4293215526
Li,0,-1.9611173596,0.8229776073,1.9063972919
Li,0,3.501269032,-1.7160527169,-0.7328459012
C,0,6.1345459152,0.2871433907,-1.3561100134
H,0,6.5045797449,1.2956497418,-1.1174288657
H,0,6.8973820534,-0.4197490458,-1.0060103119
H,0,6.0953534427,0.215308021,-2.4499706392

Optimized at B3LYP/6-31G(d)

$Li_2$1d-2THF

Total energy, -1327.9777066 Hartrees

C	-0.684064	3.111167	-0.188840
C	-0.106098	1.831065	-0.437232
C	1.164149	1.850734	-1.054251
C	1.831528	3.032742	-1.399958
C	1.259207	4.268193	-1.131360
C	-0.004197	4.283770	-0.527938
C	-1.581014	0.192526	0.965182
C	-1.767204	-1.185965	1.352956
C	-2.429021	1.122595	1.705442
C	-2.547910	-1.582969	2.420659
C	-3.215610	0.672679	2.793709
C	-3.266251	-0.650521	3.193278
C	-2.029785	3.281655	0.388463
C	-2.689607	2.489641	1.270797
C	-0.767780	0.509452	-0.185954
C	-0.173383	-0.606602	-0.986581
C	0.760367	-1.537964	-0.582028
C	1.391650	-2.473601	-1.515654
C	1.272353	-1.667754	0.788583
C	2.219144	-3.506316	-1.104451
C	2.087791	-2.721561	1.181031
C	2.604482	-3.663884	0.256011
H	1.613679	0.896504	-1.305156
H	2.796197	2.972022	-1.901396
H	1.754408	5.196031	-1.404107
H	-0.492268	5.237452	-0.333851
H	-1.250900	-1.940360	0.776239
H	-2.599418	-2.642895	2.664309
H	-3.813621	1.415621	3.319862
H	-3.864065	-0.959831	4.045306
H	-2.478740	4.256826	0.200618
H	-3.599807	2.918958	1.694303
H	-0.308538	-0.532685	-2.071151
H	1.144053	-2.381243	-2.571715
H	0.947637	-0.944219	1.528508
H	2.623993	-4.185061	-1.853809
H	2.388665	-2.785214	2.226065
H	3.226725	-4.492341	0.575565
Li	-2.880882	1.044721	-0.552805
Li	3.248788	-1.681163	-0.372660
C	4.794629	0.821586	-0.263937
C	5.795968	1.193677	0.823417

C	6.880383	0.119895	0.634656
C	6.063307	-1.124593	0.265508
O	4.820351	-0.631519	-0.306377
H	5.099898	1.205216	-1.246063
H	6.174758	2.213267	0.709900
H	7.550431	0.396810	-0.187045
H	5.810228	-1.729137	1.143697
C	-5.319504	-0.485967	-0.533544
C	-5.206611	-2.003325	-0.645632
C	-4.737360	-2.184224	-2.098012
C	-3.784683	-1.001160	-2.290460
O	-4.250235	0.035461	-1.369359
H	-5.165078	-0.108946	0.481333
H	-4.447440	-2.367997	0.053854
H	-4.237051	-3.141455	-2.269983
H	-2.752242	-1.249670	-2.018196
H	5.331053	1.108051	1.812151
H	3.767890	1.134567	-0.062506
H	7.490448	-0.039921	1.528110
H	6.555129	-1.763893	-0.473852
H	-6.275894	-0.112374	-0.921429
H	-6.153213	-2.508236	-0.431011
H	-5.586437	-2.114484	-2.788077
H	-3.804386	-0.583398	-3.301349

Optimized at LC-BLYP/6-31+G(d)

Li_2**1d-2THF**

Total energy, -1323.9598801Hartrees

C	-0.60571	3.09484	-0.29671
C	-0.08702	1.80517	-0.51794
C	1.20582	1.7627	-1.04693
C	1.94821	2.90036	-1.32278
C	1.43025	4.15213	-1.07393
C	0.1429	4.22612	-0.56625
C	-1.6267	0.28236	0.86541
C	-1.79225	-1.05412	1.34556
C	-2.4635	1.2383	1.52733
C	-2.57046	-1.38032	2.41997
C	-3.25118	0.86975	2.62821
C	-3.30342	-0.41019	3.11031
C	-1.98135	3.32288	0.17009
C	-2.70541	2.58246	1.01275
C	-0.83202	0.53555	-0.30326
C	-0.25078	-0.62948	-1.03423
C	0.68805	-1.49426	-0.57224
C	1.2992	-2.52385	-1.40121

C	1.24693	-1.44949	0.77295
C	2.1284	-3.48845	-0.89174
C	2.06472	-2.43936	1.26151
C	2.55447	-3.47768	0.45242
H	1.62239	0.7903	-1.27817
H	2.94049	2.7972	-1.75494
H	1.99396	5.0531	-1.2928
H	-0.30991	5.19962	-0.39375
H	-1.25246	-1.83934	0.8361
H	-2.61365	-2.41928	2.73739
H	-3.85602	1.64378	3.09559
H	-3.91028	-0.66486	3.97235
H	-2.39949	4.28891	-0.1065
H	-3.64605	3.01992	1.34601
H	-0.47583	-0.70699	-2.10143
H	1.02382	-2.55756	-2.45217
H	0.93722	-0.64039	1.42542
H	2.51253	-4.25353	-1.56252
H	2.39743	-2.37253	2.29495
H	3.19304	-4.25665	0.85033
Li	-2.85799	1.05679	-0.69467
Li	3.12582	-1.62385	-0.41759
C	4.70439	0.76631	-0.06911
C	5.83247	0.98625	0.91245
C	6.83291	-0.07152	0.47473
C	5.93123	-1.23865	0.12226
O	4.69359	-0.65023	-0.29704
H	4.89396	1.269	-1.02351
H	6.22729	2.00296	0.86973
H	7.38304	0.26824	-0.40792
H	5.72743	-1.87682	0.9877
C	-5.10311	-0.63817	-0.3275
C	-5.05369	-2.13719	-0.53266
C	-4.74566	-2.24803	-2.01679
C	-3.76382	-1.11381	-2.21278
O	-4.18391	-0.09502	-1.2895
H	-4.78469	-0.32875	0.67027
H	-4.24074	-2.56509	0.05997
H	-4.31941	-3.21249	-2.29947
H	-2.74128	-1.40946	-1.95585
H	5.48919	0.79492	1.93352
H	3.72016	1.06305	0.29639
H	7.55927	-0.33122	1.24708
H	6.31285	-1.85861	-0.69152
H	-6.09532	-0.22699	-0.5406
H	-5.98721	-2.62417	-0.24341

H	-5.64926	-2.0835	-2.61235
H	-3.77666	-0.68316	-3.21602

Optimized at B3LYP/6-31G(d)
Li_4**1b**
Total energy, -1337.6753927 Hartrees
Imaginary frequencies: 0

C	-0.4026	1.41974	1.37562
C	-1.28243	2.51008	1.12102
C	-0.95794	3.41166	0.05684
C	0.25279	3.25835	-0.62586
C	1.23307	2.25392	-0.27539
C	2.5886	2.35934	-0.57802
C	3.63527	1.44185	-0.20596
C	3.61523	0.02012	-0.08146
C	4.86778	-0.67162	-0.12384
C	5.00555	-2.06804	-0.15121
C	3.83439	-2.86516	-0.16225
C	2.58187	-2.23489	-0.08407
C	2.38892	-0.81812	0.04234
C	1.08239	-0.33037	0.35844
C	0.69869	1.06068	0.52403
C	0.06041	-1.31568	0.78374
C	-1.22634	-1.36344	0.30135
C	-2.3218	-1.99692	1.03508
C	-1.68078	-0.64634	-0.9142
C	-3.64618	-1.73401	0.77406
C	-3.03842	-0.44606	-1.19847
C	-4.02914	-0.85196	-0.29445
H	-0.67032	0.70514	2.15596
H	-2.06508	2.77121	1.83323
H	-1.63466	4.21924	-0.20788
H	0.50467	3.96594	-1.41442
H	2.9182	3.29965	-1.02413
H	4.63646	1.85231	-0.33899
H	5.7667	-0.05973	-0.17385
H	5.99239	-2.51901	-0.19764
H	3.89441	-3.94791	-0.2225
H	1.68959	-2.853	-0.08479
H	0.29651	-1.9863	1.61653
H	-2.06646	-2.64667	1.86974
H	-0.94479	-0.47233	-1.70209
H	-4.42367	-2.17944	1.38831
H	-3.33256	0.05228	-2.12077
Li	2.37984	2.07896	1.46495
Li	-1.00632	1.46236	-0.80003

Li	-2.61556	0.39635	0.92006
Li	3.73635	-1.50472	-1.7854
Cl	-5.74119	-0.57994	-0.63761

Li_4**1d**

Total energy, -878.082428 Hartrees

Imaginary frequencies: 0

C	1.17925	1.21136	-1.28553
C	2.15156	2.21023	-0.99967
C	1.86246	3.16976	0.02404
C	0.60491	3.16147	0.63485
C	-0.45103	2.25059	0.25087
C	-1.80398	2.49788	0.47391
C	-2.91542	1.67798	0.06373
C	-3.03154	0.25867	-0.03274
C	-4.34785	-0.30369	-0.05038
C	-4.6276	-1.67876	-0.00937
C	-3.5451	-2.58882	0.0802
C	-2.23294	-2.08877	0.06568
C	-1.89052	-0.70116	-0.06888
C	-0.5258	-0.35444	-0.31535
C	0.0014	0.98851	-0.49169
C	0.41943	-1.44446	-0.65684
C	1.66783	-1.59183	-0.09999
C	2.75329	-2.315	-0.76387
C	2.10444	-0.90415	1.13732
C	4.07431	-2.15663	-0.41081
C	3.45108	-0.80754	1.50008
C	4.47994	-1.30709	0.67766
H	1.42055	0.44872	-2.02693
H	2.99573	2.37227	-1.67022
H	2.60232	3.91201	0.3103
H	0.38257	3.91292	1.39114
H	-2.06191	3.47779	0.88031
H	-3.87635	2.18864	0.13007
H	-5.18198	0.3958	-0.06164
H	-5.65603	-2.02766	-0.0133
H	-3.71759	-3.65875	0.15166
H	-1.40773	-2.79156	0.12419
H	0.17818	-2.09845	-1.5015
H	2.49634	-2.94639	-1.6124
H	1.33123	-0.64024	1.86269
H	4.84087	-2.67301	-0.98526
H	3.713	-0.31104	2.43516
H	5.52163	-1.22281	0.96321
Li	-1.50918	2.13482	-1.54643

Li	1.64579	1.24513	0.92564
Li	3.31355	0.01838	-0.63424
Li	-3.40005	-1.21255	1.68281

Li_4**1e**
Total energy, -977.3064473 Hartrees
Imaginary frequencies: 0

C	-0.75172	1.40107	1.31972
C	-1.63264	2.48554	1.04343
C	-1.28488	3.39268	-0.00724
C	-0.04981	3.25572	-0.65064
C	0.9297	2.2625	-0.26944
C	2.29409	2.38739	-0.5208
C	3.33709	1.47708	-0.12139
C	3.32653	0.05393	-0.01661
C	4.5863	-0.62584	-0.02818
C	4.73829	-2.02013	-0.07629
C	3.57528	-2.82746	-0.13913
C	2.31521	-2.20992	-0.08789
C	2.10428	-0.79731	0.05473
C	0.78289	-0.32768	0.34042
C	0.38194	1.05755	0.50414
C	-0.23695	-1.32949	0.72776
C	-1.51435	-1.39463	0.21346
C	-2.59623	-2.07974	0.91747
C	-1.96893	-0.65359	-0.99032
C	-3.92605	-1.87365	0.63119
C	-3.3419	-0.52526	-1.30717
C	-4.31168	-1.01521	-0.44631
H	-1.03346	0.68012	2.08995
H	-2.44155	2.7341	1.73037
H	-1.96128	4.19409	-0.29112
H	0.22103	3.97126	-1.42562
H	2.62835	3.33597	-0.94554
H	4.33807	1.8991	-0.21383
H	5.48052	-0.00507	-0.03874
H	5.73037	-2.46136	-0.09871
H	3.64749	-3.90837	-0.21675
H	1.42893	-2.83536	-0.12594
H	-0.00666	-2.01539	1.54921
H	-2.32749	-2.72601	1.75056
H	-1.23272	-0.47069	-1.77604
H	-4.7058	-2.35733	1.21344
H	-3.65384	-0.02127	-2.22046

Li	2.01444	2.08147	1.50995
Li	-1.28119	1.44247	-0.87433
Li	-2.87865	0.34211	0.79106
Li	3.51395	-1.43639	-1.73756
F	-5.63958	-0.87378	-0.73262

Li_4**1f**
Total energy, -917.3971632 Hartrees
Imaginary frequencies: 0

C	-0.74528	1.35975	1.33848
C	-1.65106	2.4241	1.06803
C	-1.3303	3.34072	0.01588
C	-0.09827	3.22942	-0.63733
C	0.9031	2.25355	-0.26816
C	2.26224	2.40199	-0.53647
C	3.32605	1.51172	-0.14643
C	3.34409	0.08883	-0.0357
C	4.61638	-0.56662	-0.05749
C	4.79515	-1.95842	-0.09607
C	3.64728	-2.78868	-0.13789
C	2.37597	-2.19534	-0.07955
C	2.13889	-0.78562	0.05219
C	0.81167	-0.34002	0.34379
C	0.38703	1.03911	0.51172
C	-0.19195	-1.35636	0.73988
C	-1.47066	-1.42608	0.23426
C	-2.56946	-2.06453	0.95508
C	-1.92297	-0.72055	-0.9848
C	-3.89283	-1.83519	0.65291
C	-3.28313	-0.56234	-1.29464
C	-4.31544	-0.9949	-0.4428
H	-1.01308	0.62867	2.10261
H	-2.45995	2.65532	1.76118
H	-2.02451	4.12936	-0.26074
H	0.1512	3.94998	-1.41494
H	2.57477	3.35545	-0.96686
H	4.31791	1.95192	-0.25225
H	5.49828	0.07119	-0.08297
H	5.79537	-2.38048	-0.12554
H	3.73984	-3.86872	-0.2062
H	1.50082	-2.83718	-0.10147
H	0.03969	-2.01846	1.58068
H	-2.31801	-2.68581	1.81284
H	-1.17414	-0.51219	-1.75269
H	-4.66035	-2.29554	1.27379
H	-3.55163	-0.0599	-2.22568

Li	2.00909	2.09293	1.49752
Li	-1.29248	1.39135	-0.84871
Li	-2.94177	0.28261	0.79284
Li	3.5419	-1.41556	-1.74695
C	-5.77766	-0.84321	-0.78974
H	-6.20543	-1.76909	-1.20424
H	-6.38746	-0.58056	0.08487
H	-5.9267	-0.05598	-1.53729

Optimized at B3LYP/6-31G(d)

$Li_4$1d-4THF

Total energy, -1808.0017982 Hartrees

C	0.96555	-0.96413	-0.93692
C	1.96456	-0.64944	-1.891
C	1.71164	0.39873	-2.81472
C	0.45962	1.01679	-2.80176
C	-0.65544	0.55529	-2.00506
C	-1.96426	0.86179	-2.3848
C	-3.21815	0.49226	-1.78496
C	-3.53238	-0.01897	-0.50778
C	-4.9246	-0.18495	-0.17493
C	-5.40727	-0.54084	1.08898
C	-4.4762	-0.72658	2.14026
C	-3.09965	-0.62475	1.85019
C	-2.53678	-0.37193	0.55923
C	-1.10881	-0.53302	0.38687
C	-0.29903	-0.30872	-0.80482
C	-0.40708	-1.16129	1.5324
C	0.70481	-0.66734	2.17464
C	1.43306	-1.4151	3.20144
C	1.33134	0.6262	1.84599
C	2.60085	-0.96046	3.78134
C	2.49778	1.06983	2.46427
C	3.21184	0.27258	3.38674
H	1.18862	-1.72584	-0.19377
H	2.88813	-1.22139	-1.92273
H	2.47988	0.73435	-3.50902
H	0.25464	1.80011	-3.53195
H	-2.05868	1.39102	-3.33471
H	-4.08464	0.71006	-2.41125
H	-5.64318	0.02223	-0.9678
H	-6.47702	-0.63289	1.2595
H	-4.80208	-0.96394	3.14894
H	-2.40289	-0.75999	2.67025
H	-0.82675	-2.08467	1.94687
H	1.01444	-2.36817	3.52142

H	0.75535	1.3083	1.22367
H	3.0897	-1.57484	4.53572
H	2.88459	2.05227	2.19653
H	4.12458	0.62382	3.85474
Li	-1.88521	-1.25078	-2.12101
Li	1.63189	1.14292	-0.77108
Li	2.99057	-0.92363	1.56054
Li	-4.20525	1.24648	1.35649
C	-2.33447	3.24404	2.00449
C	-1.63538	4.32932	1.18653
C	-2.20629	4.09354	-0.22138
C	-3.65895	3.72377	0.07491
O	-3.63306	3.05576	1.36917
H	-1.79197	2.29233	1.96317
H	-1.90703	5.32647	1.55387
H	-1.70956	3.2504	-0.71418
H	-4.07486	3.02607	-0.65715
C	3.75767	-3.53783	0.43973
C	5.02291	-4.20737	-0.09093
C	5.65673	-3.07703	-0.91797
C	5.34107	-1.835	-0.07873
O	4.1287	-2.15049	0.65063
H	5.68012	-4.49644	0.73744
H	5.17357	-3.00752	-1.89893
H	5.15379	-0.94151	-0.68226
C	2.0162	4.04778	-1.14971
C	3.19409	4.99354	-1.37911
C	4.33617	4.01058	-1.68014
C	4.02846	2.85446	-0.72548
O	2.58902	2.85451	-0.55339
H	1.26357	4.43704	-0.45887
H	3.00689	5.69944	-2.19353
H	5.33039	4.43478	-1.51165
H	4.49174	2.99834	0.25826
C	-3.76818	-3.40681	-1.94078
C	-3.90586	-4.02207	-0.55174
C	-2.59323	-4.81172	-0.42235
C	-1.58148	-3.9064	-1.13509
O	-2.35338	-3.10827	-2.08245
H	-4.05779	-4.10783	-2.73516
H	-3.96115	-3.23012	0.2018
H	-2.6744	-5.77916	-0.93283
H	-0.82471	-4.46124	-1.69866
H	4.80329	-5.10112	-0.68192
H	6.73119	-3.20657	-1.07628
H	6.12945	-1.61779	0.6517

H	3.40559	-3.93436	1.39531
H	2.93938	-3.57475	-0.28923
H	-4.3145	-2.46802	-2.06011
H	-4.79629	-4.65208	-0.46245
H	-2.30908	-4.99927	0.61714
H	-1.08906	-3.21267	-0.44597
H	-2.51058	3.51935	3.04813
H	-0.54627	4.23271	1.23648
H	-2.13046	4.97176	-0.87045
H	-4.30628	4.60522	0.16316
H	1.52576	3.76141	-2.08745
H	3.41021	5.56865	-0.47103
H	4.28051	3.67076	-2.7205
H	4.32254	1.87559	-1.11764

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