

Supporting information for:

Iterative double cyclization reaction by $S_{RN}1$

mechanism. A theoretical interpretation of the

regiochemical outcome of diazaheterocycles

Lucas E. Peisino, Gloria P. Camargo Solorzano, María E. Budén,* and Adriana
B. Pierini*

*INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad
Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina.*

E-mail: eugebuden@yahoo.com.ar; adriana@fcq.unc.edu.ar

Phone: +54-0351-5353867

Contents

HPLC PROFILE	S3
OPTIMIZATION OF PHOTOLYSIS REACTION	S3
REACTION COORDINATE OF RADICAL DIANION $[26^-]^{•-}$	S4
CHARACTERIZATION DATA – NMR SPECTRUMS OF COMPOUNDS:	S5
7	S5

*To whom correspondence should be addressed

8	S10
13	S14
14	S18
10	S21
9	S26
18	S31
12	S34
11	S38
19	S43
20	S47
21	S51
XYZ COORDINATES OF THE SOLUTION PHASE STRUCTURES	S56

HPLC PROFILE

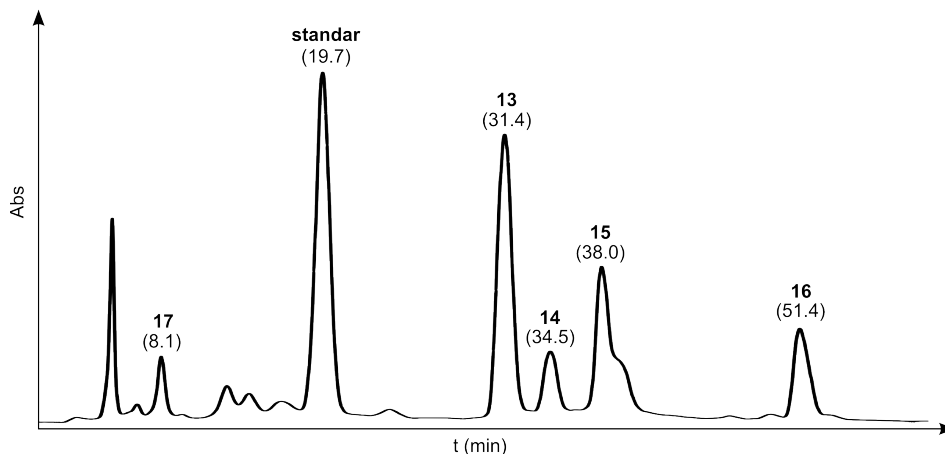


Figure S1: Chromatographic profile of **8** reaction crude (Table 1, entry 7). %I⁻ = 73%.

OPTIMIZATION OF PHOTOLYSIS REACTION

Initially, the reaction mixture was degassed by nitrogen bubble just 20 min before irradiation, and nitrogen bubbles were used as means of shake during all time of reaction (S1, entry 1), in this case yield of compound **13** was 24%. When irradiation time is 120 minutes, the products yield increases slightly (S1, entry 2). In argon atmosphere results of reaction are essentially the same as observed for the reactions in nitrogen atmosphere (S1, entries 3 and 5). In entry 3 of S1 is presented reaction with previous degassing by bubble of nitrogen and sonication, the yield of product **13** increase about 10%. When 16 lamps were employed instead of 9 yield of products decrease, a possible explanation could be that the newly formed products could be sensitive toward ultraviolet light, facilitating their decomposition (S1, entries 6 and 7).

Considering the above presented, we conclude that major conditions for this reaction are (S1, entry 5): previous degassing by nitrogen bubble and sonication; nitrogen bubble during all reaction time and 9 lamps to irradiation by 120 minutes.

Table S1: Photolysis reaction of compound **8**, conditions optimization.^a

Entry	Atmosphere	Time (min), Lamps	Yield (%)	
1	N ₂	60, 9	13 (24)	14 (7)
2	Ar	120, 9	13 (28)	14 (5)
3 ^b	Ar	120, 9	13 (37)	14 (5)
4 ^b	N ₂	60, 9	13 (28)	14 (5)
5 ^b	N ₂	120, 9	13 (36)	14 (5)
6 ^b	N ₂	60, 16	13 (11)	14 (7)
7 ^b	N ₂	120, 16	13 (11)	14 (7)

^a Photostimulated reactions were performed with [substrate] = 1 mg/mL with acetonitrile as solvent (7 mL) in a quartz tube. Irradiation was conducted in a photochemical reactor equipped with Hg high pressure lamps 254 nm. During all reaction time inert gas was constant bubble. Oxidation reactions were carried out by stirring of reaction crude with MnO₂ in CHCl₃. Products yield were determined by ¹H-NMR.

^b Degassing by sonication.

REACTION COORDINATE OF RADICAL DIANION

[**26**⁻]^{•-}

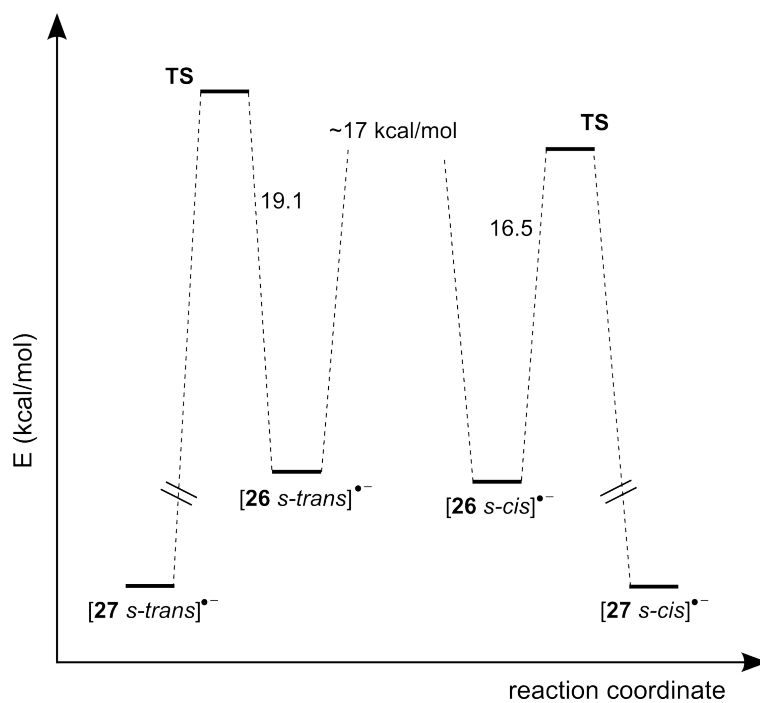
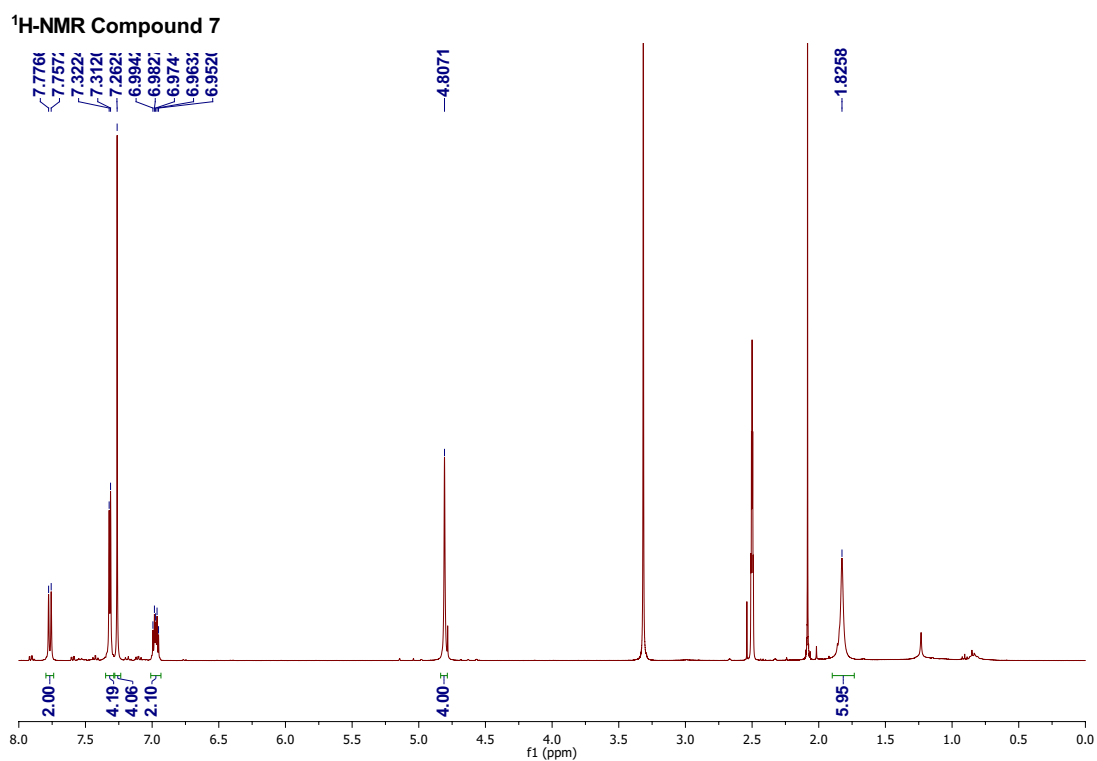


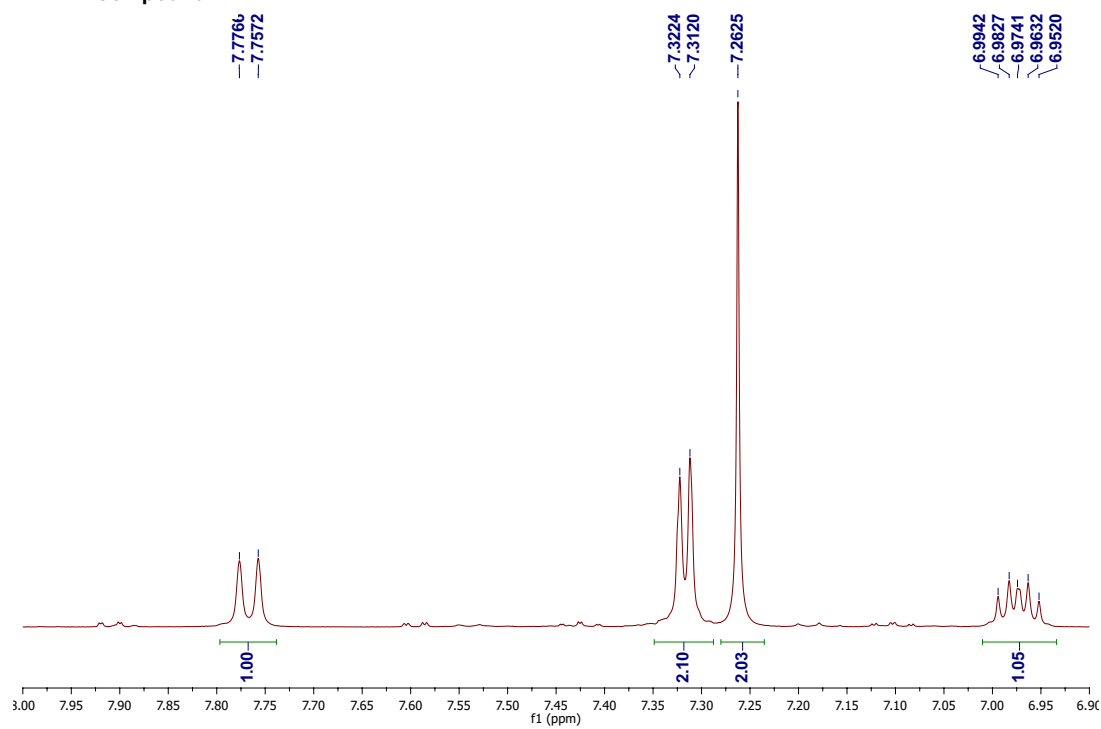
Figure S2: PES to cyclization of [**26**⁻]^{•-} radical dianion.

CHARACTERIZATION DATA – NMR SPECTRUMS OF COMPOUNDS:

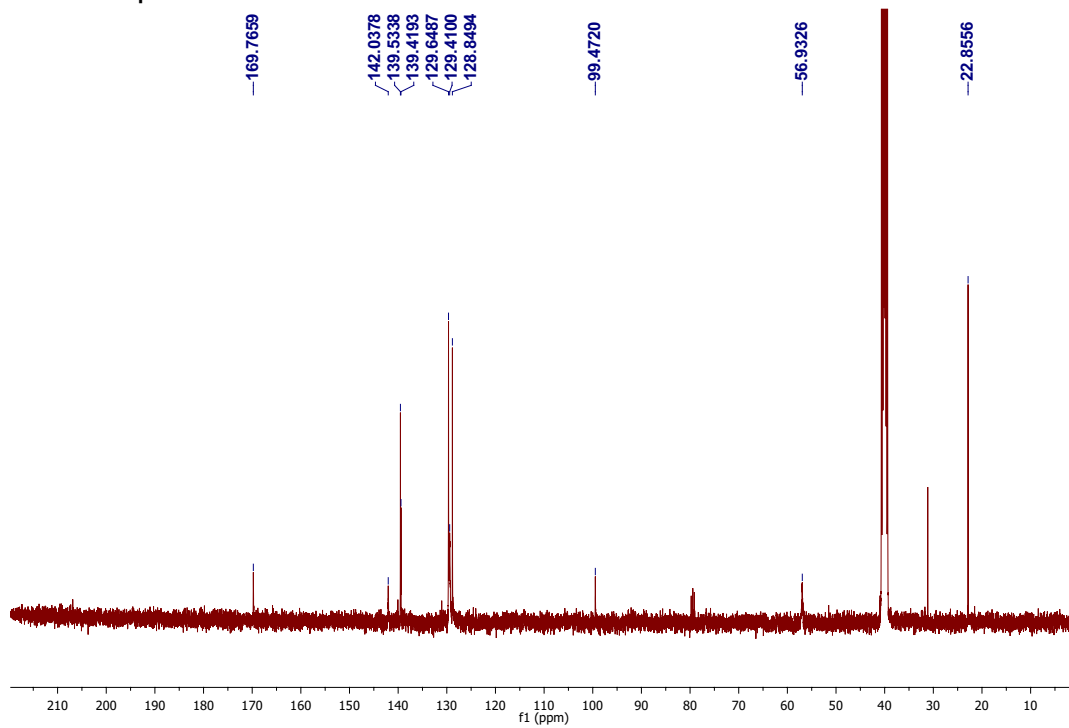
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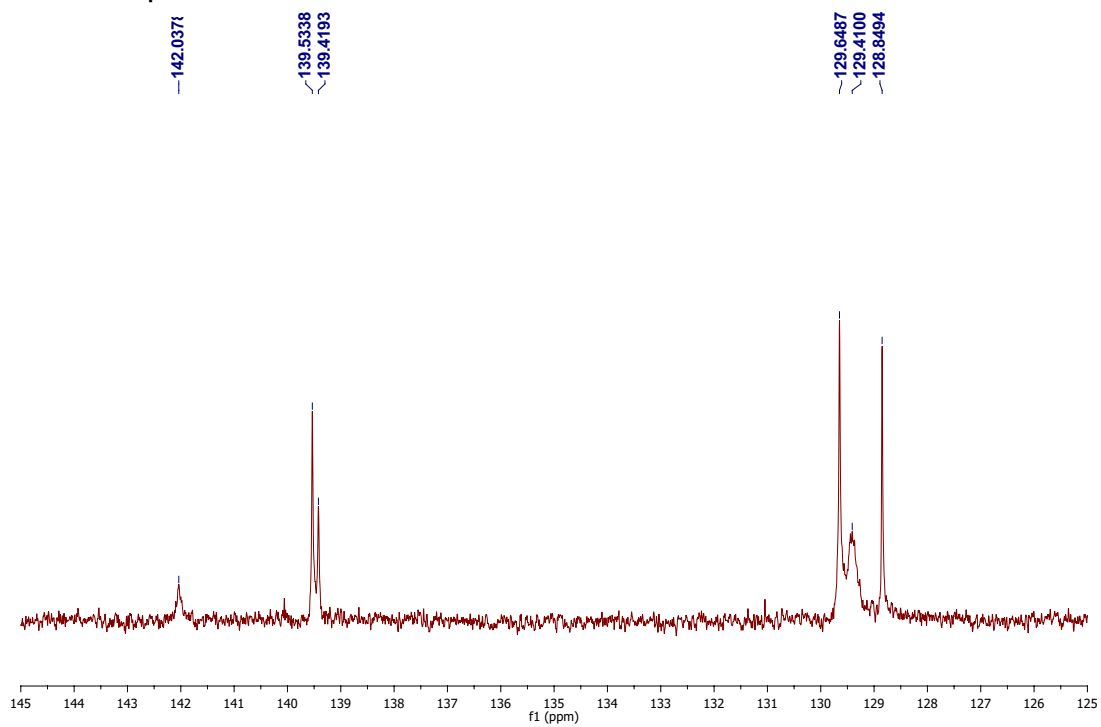
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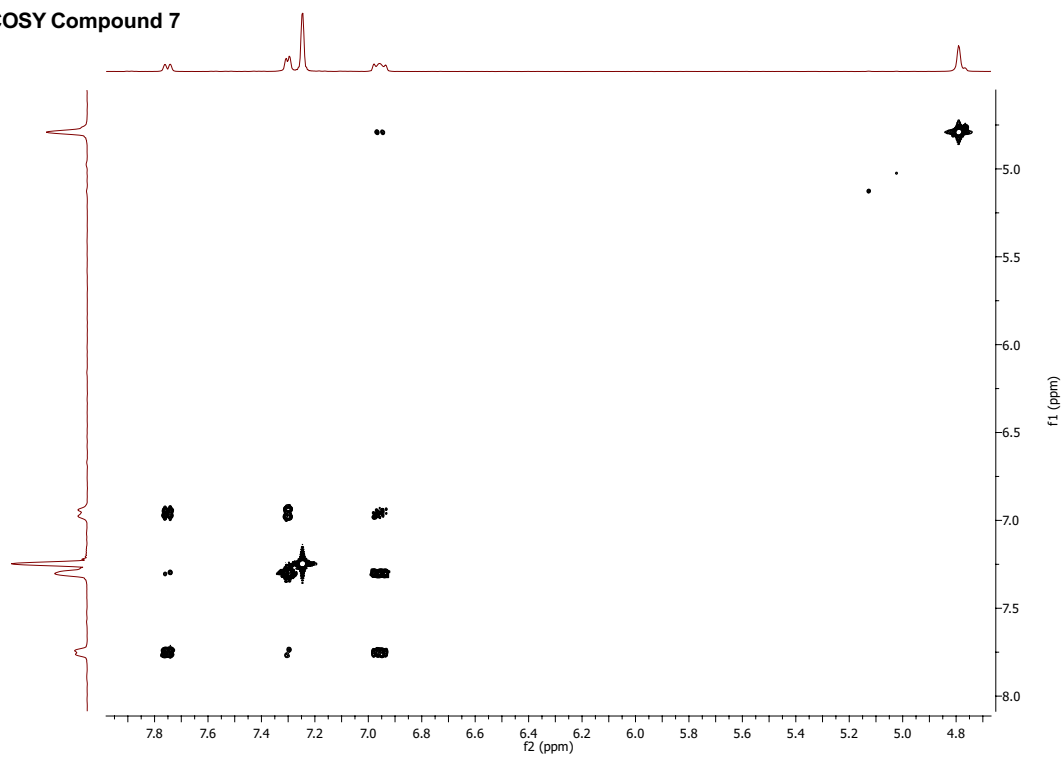
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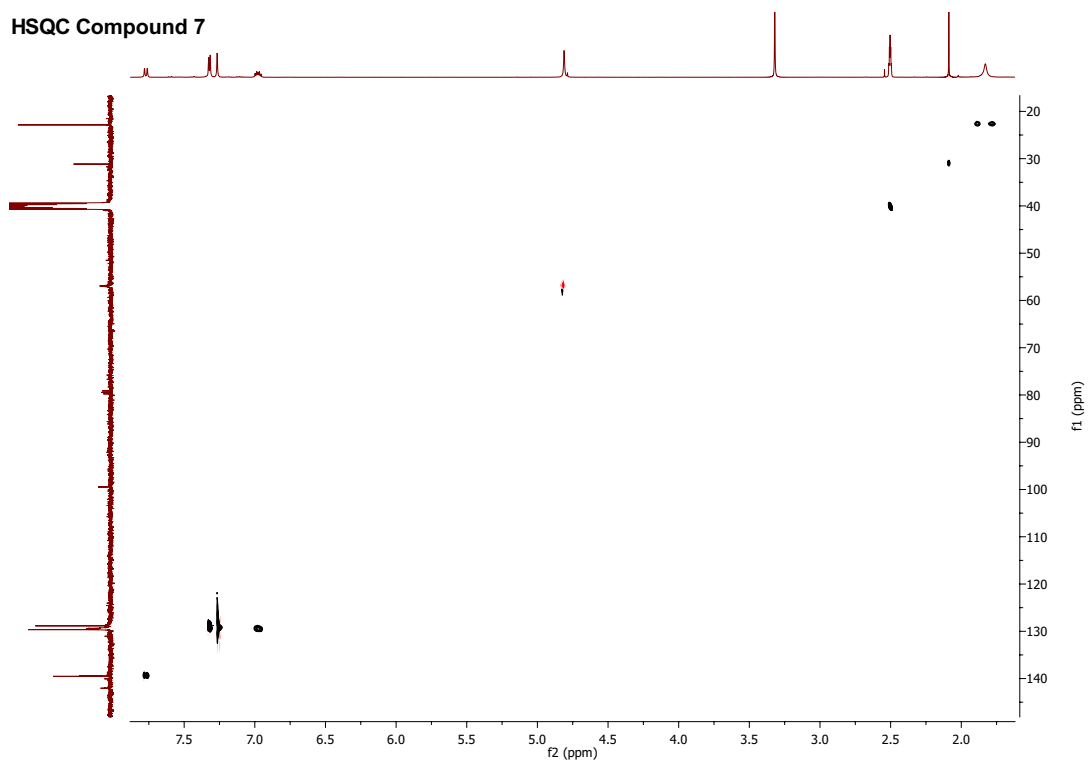
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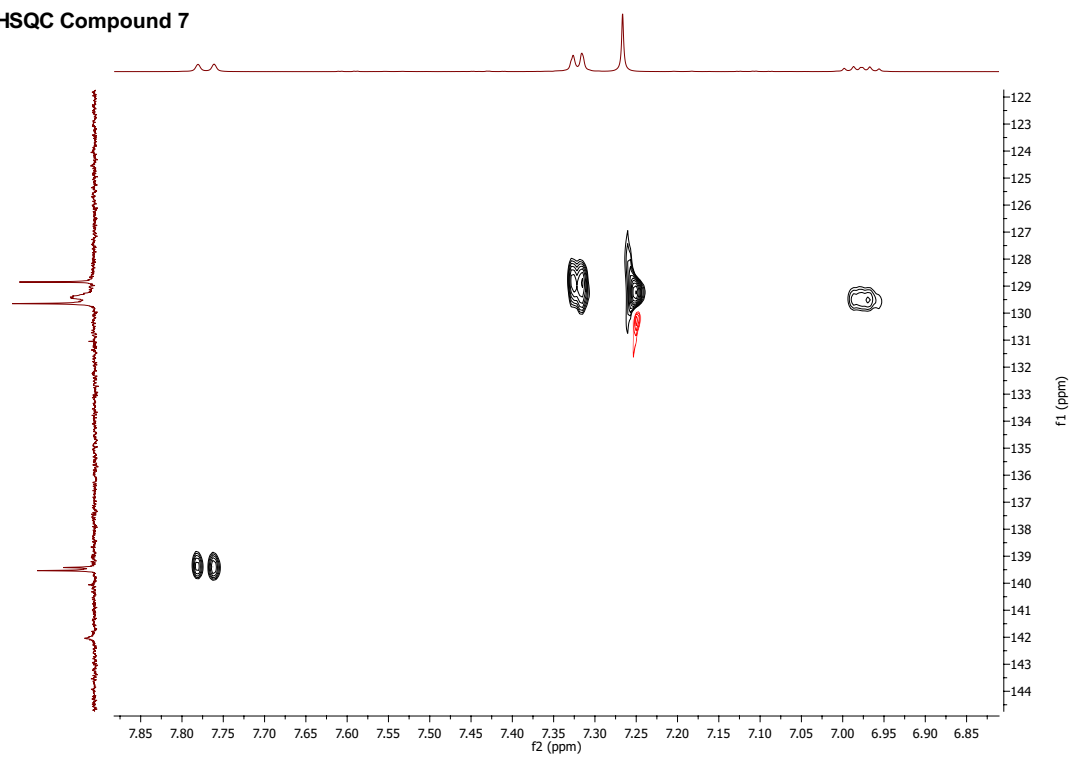
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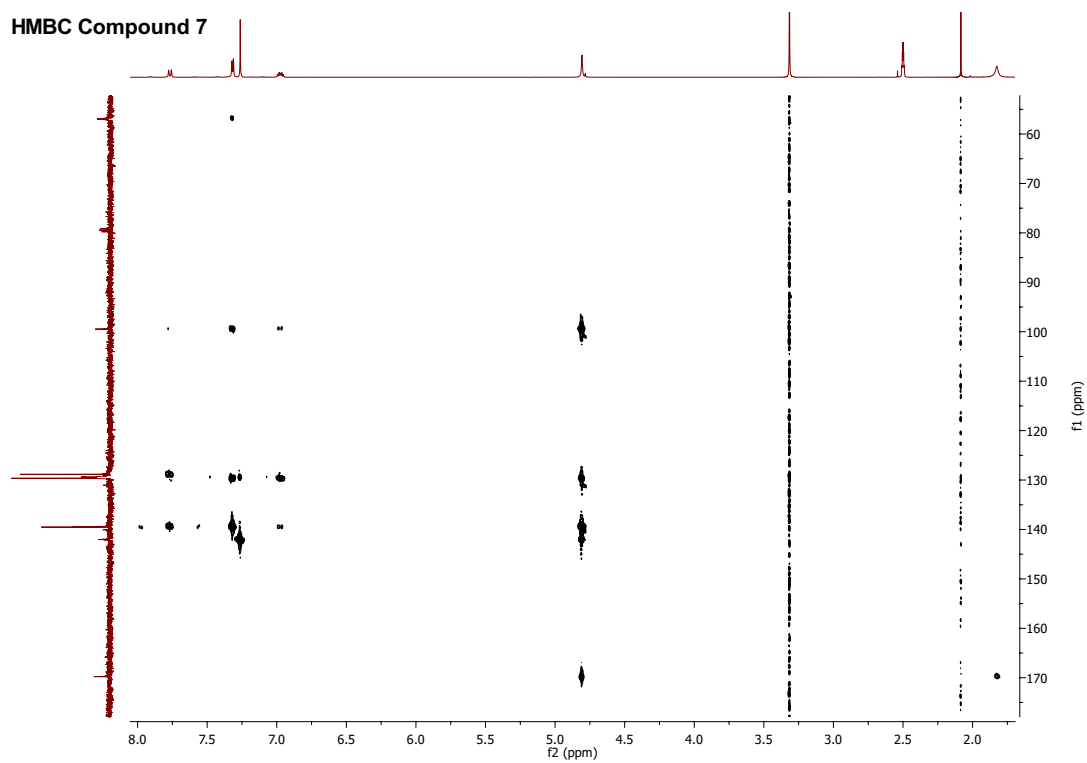
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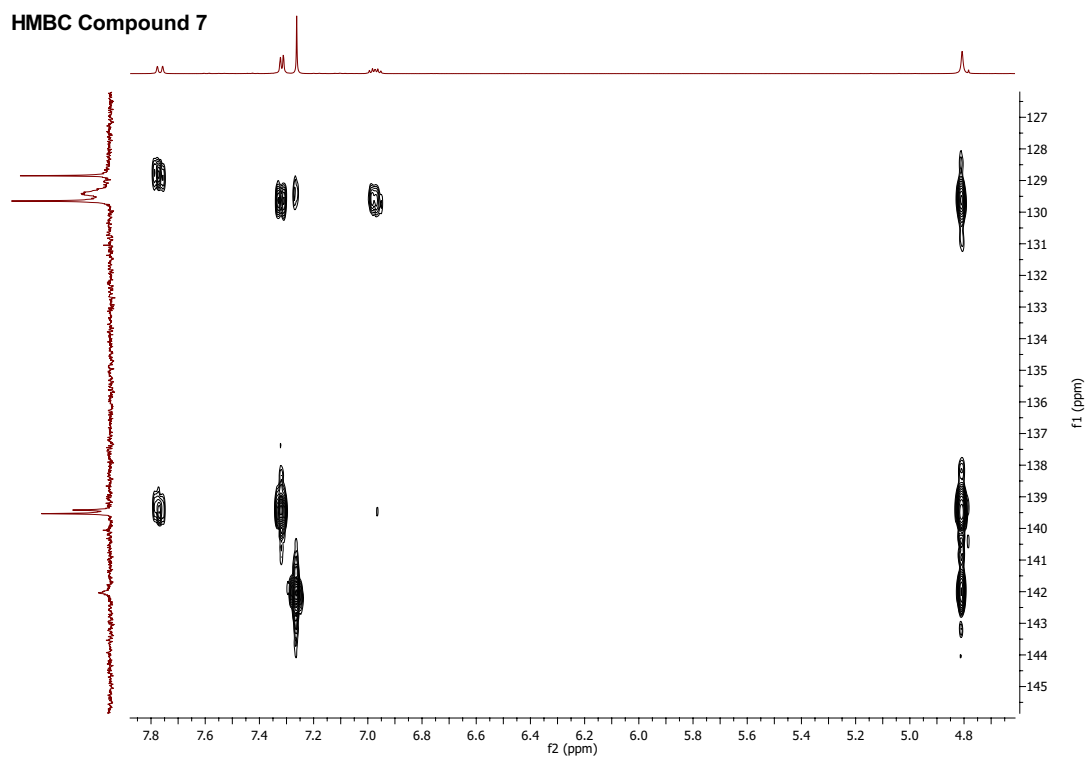
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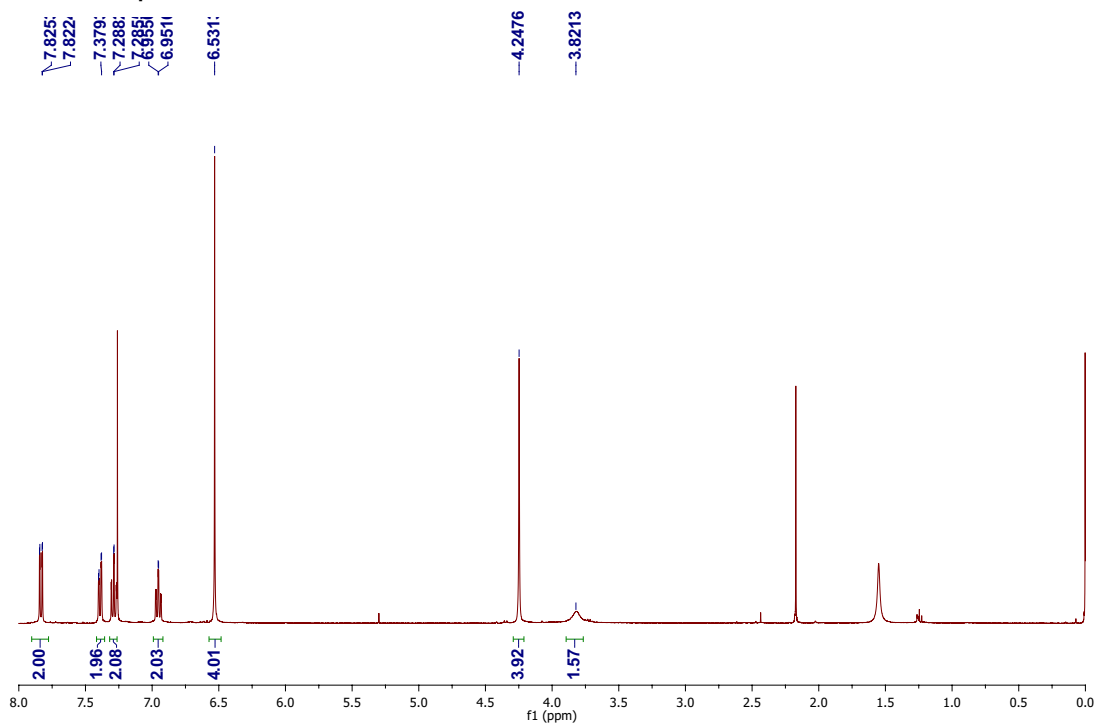
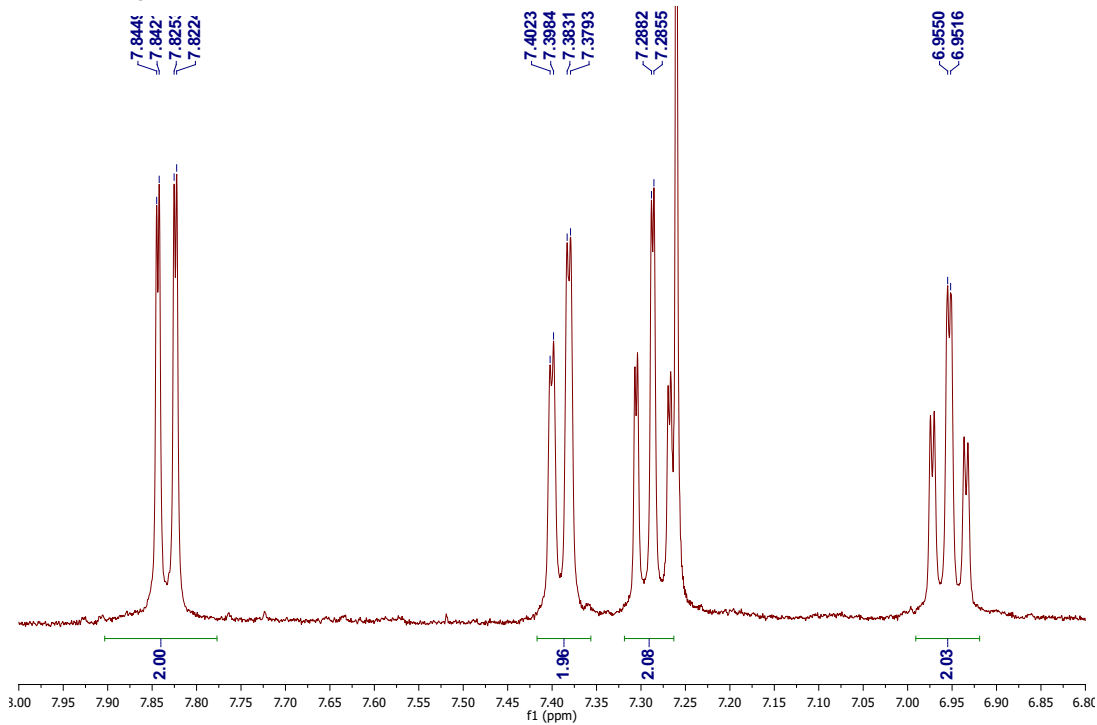


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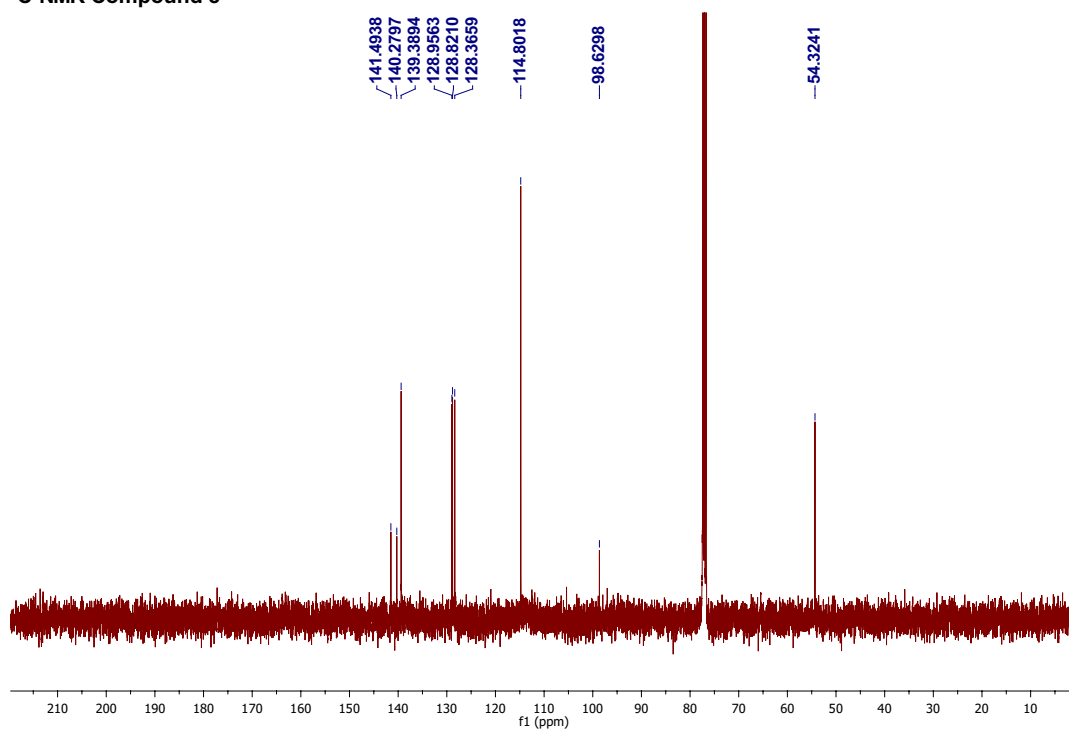


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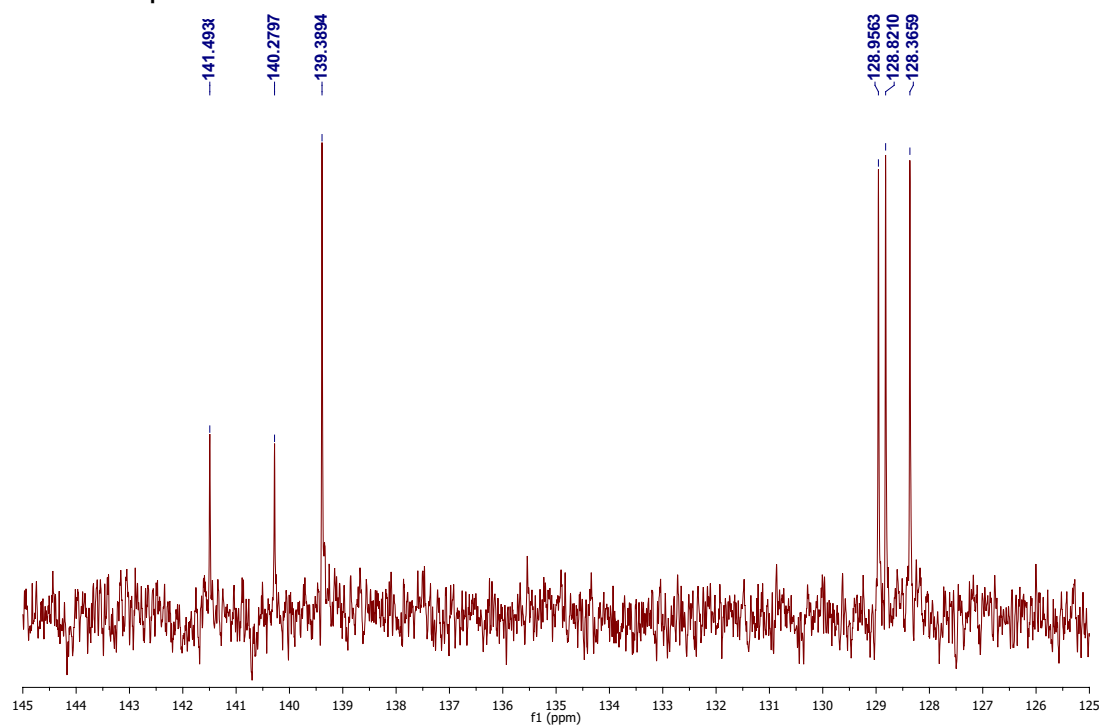


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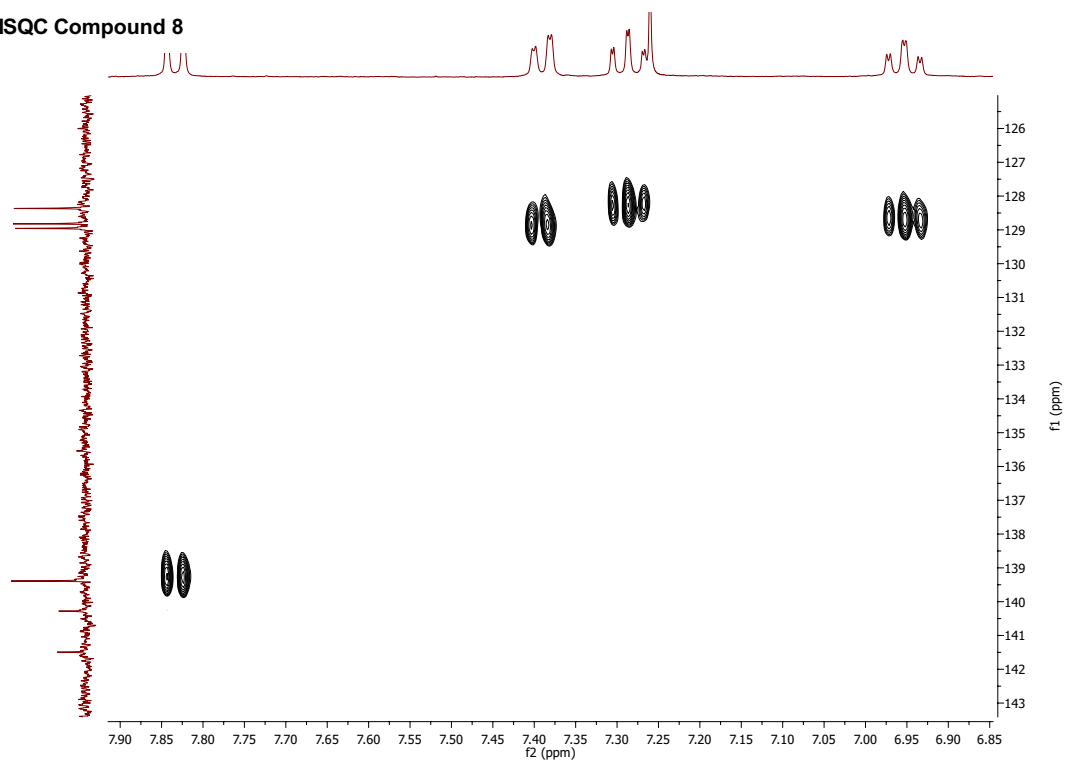
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¹³C-NMR Compound 8

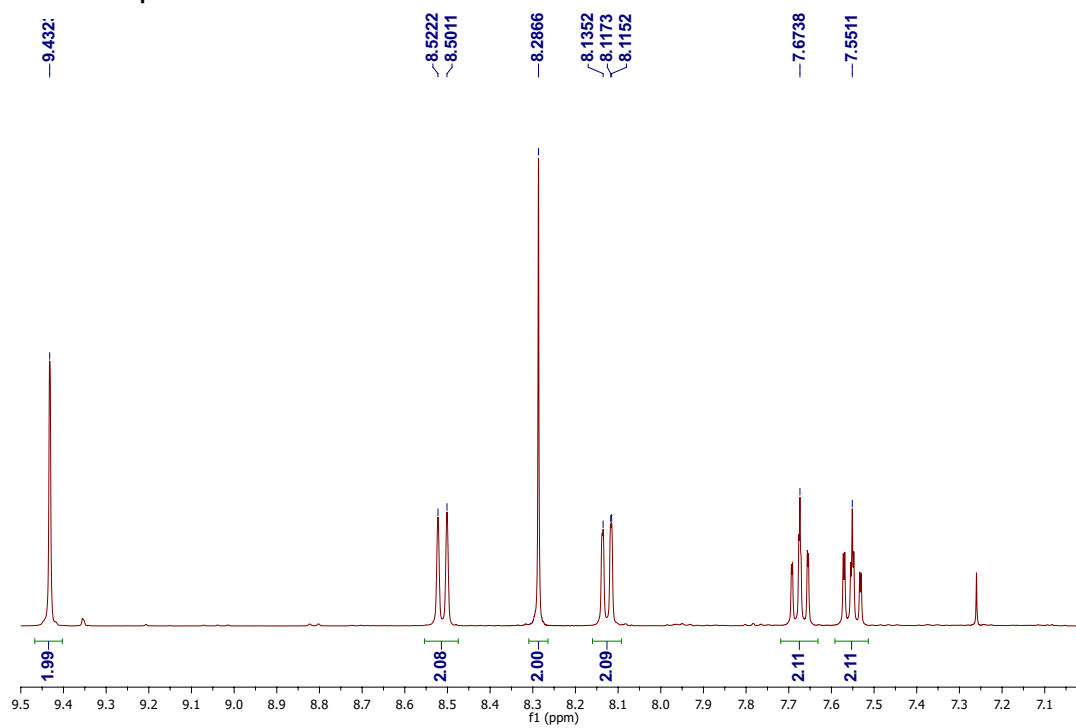


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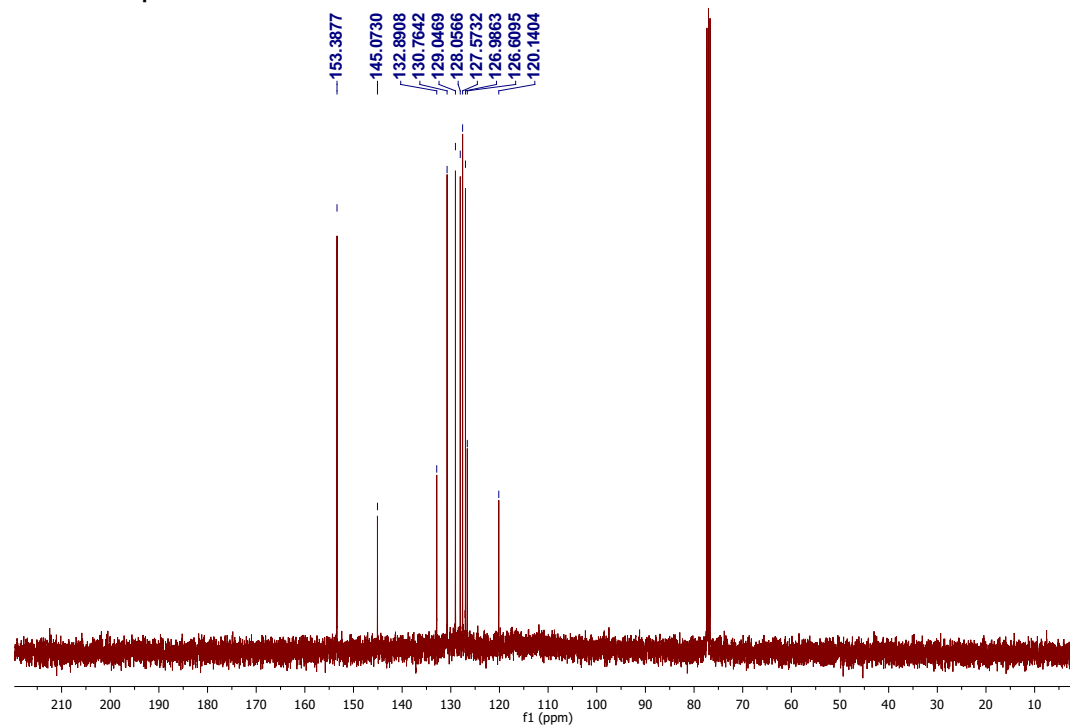


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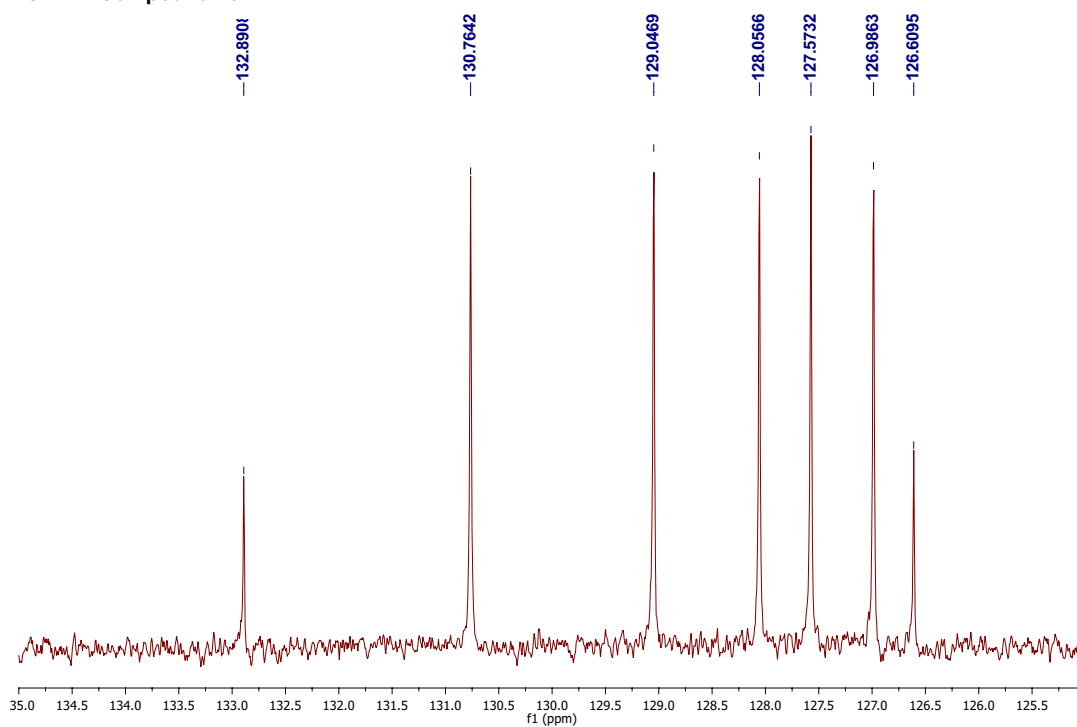
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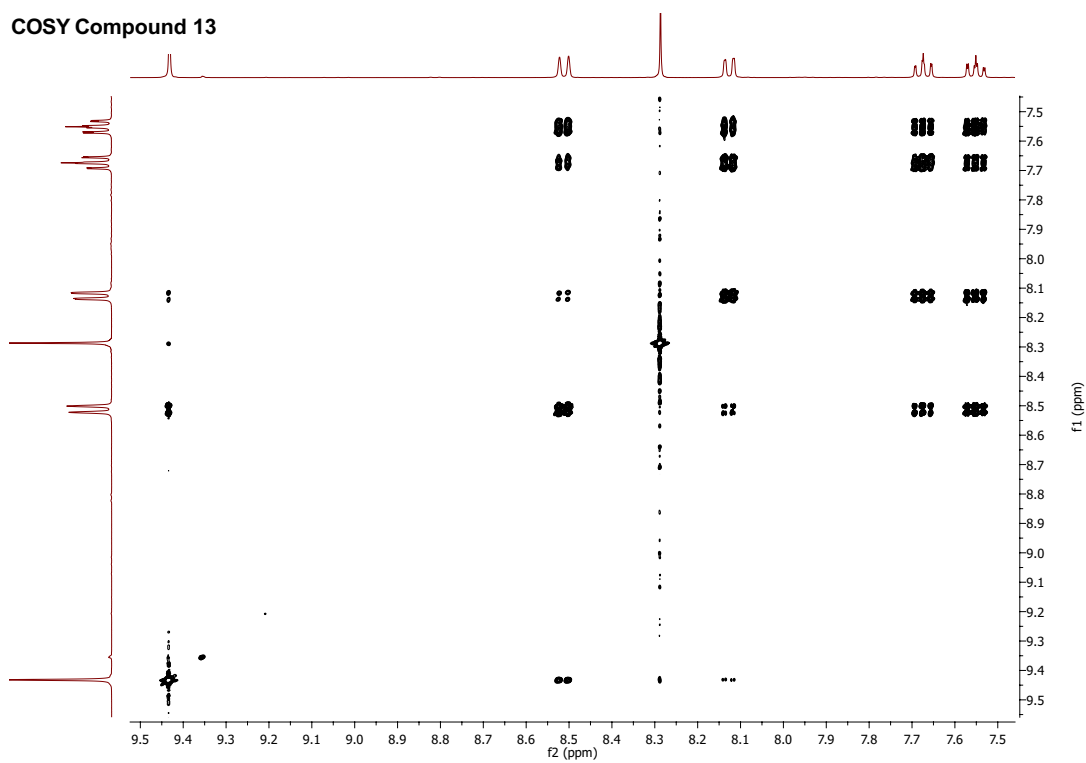
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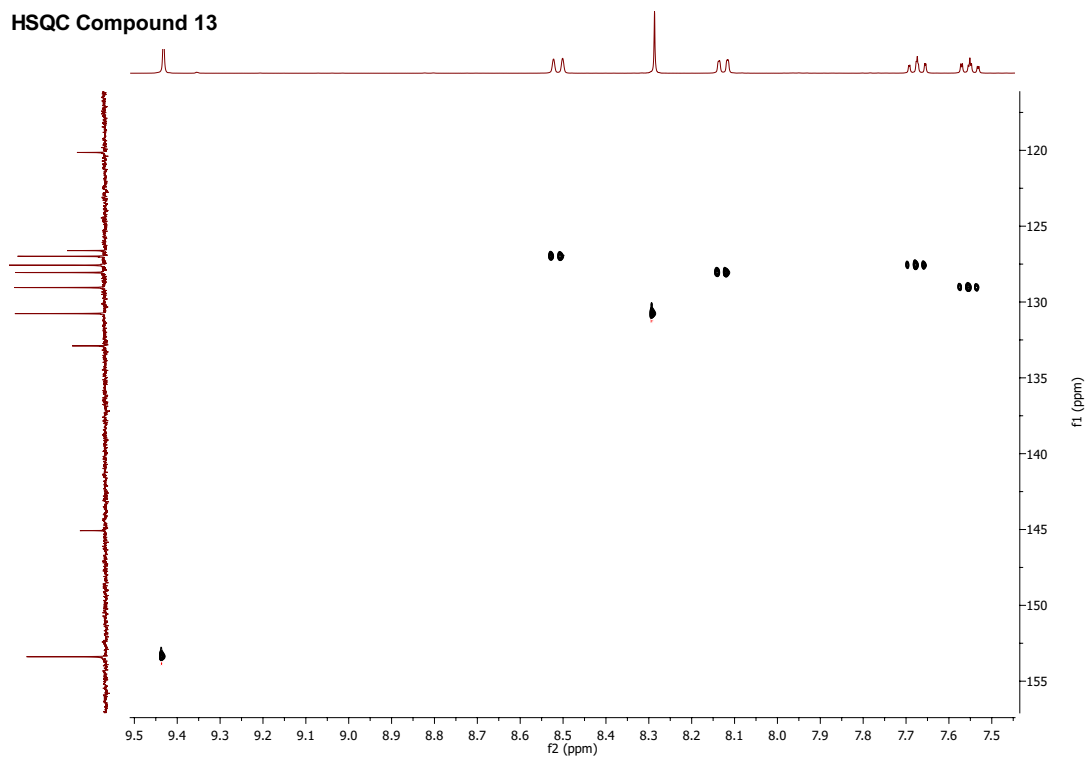
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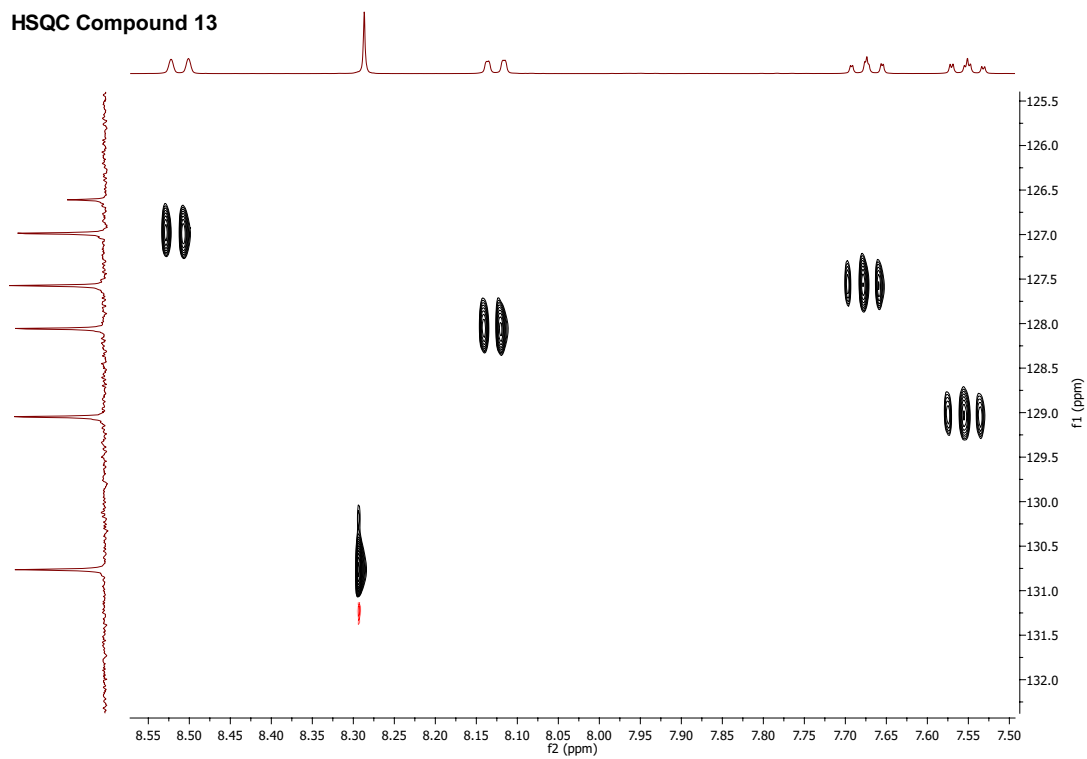
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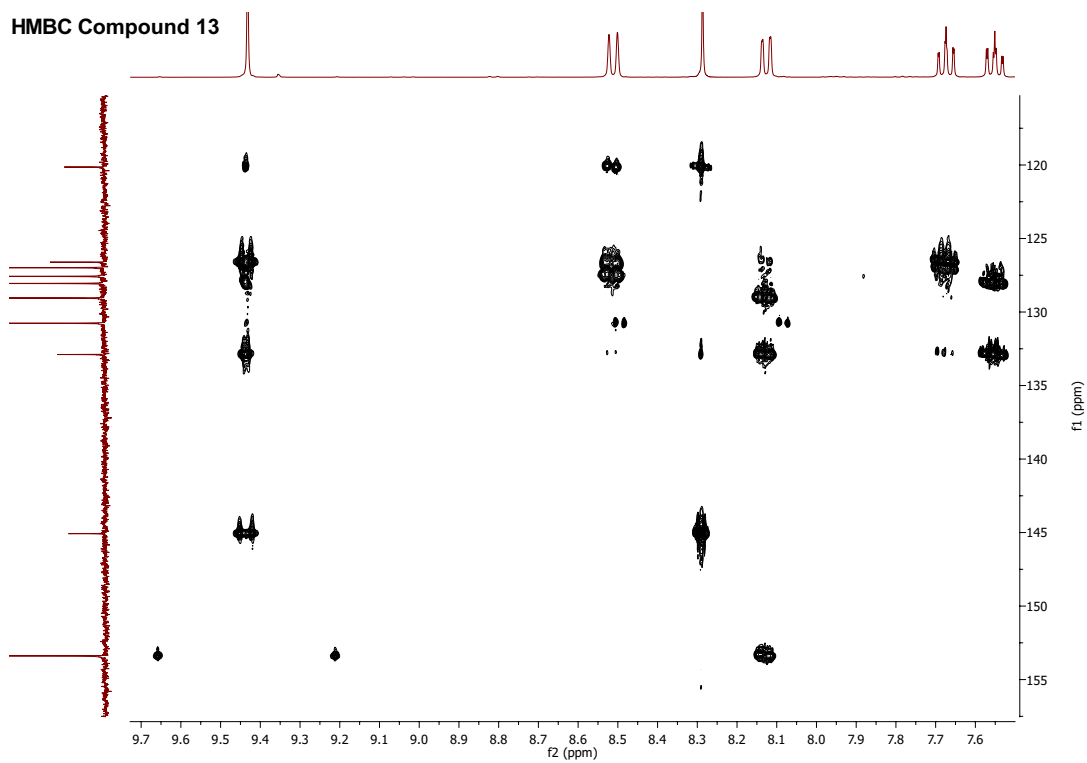
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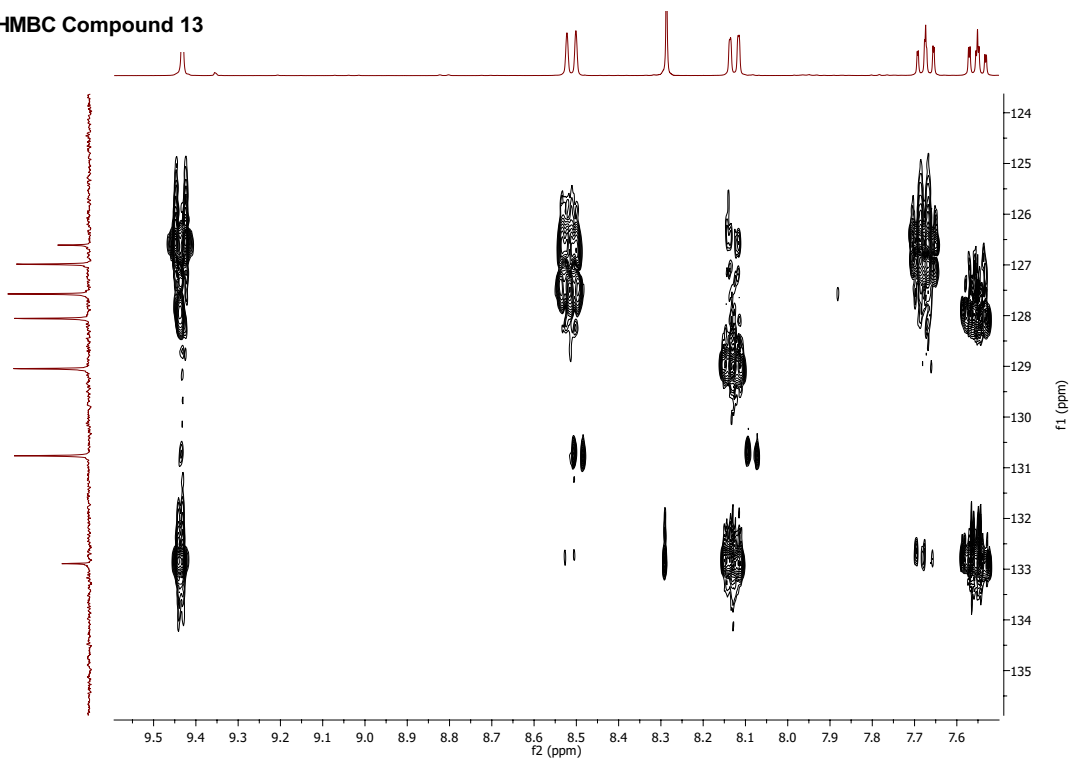
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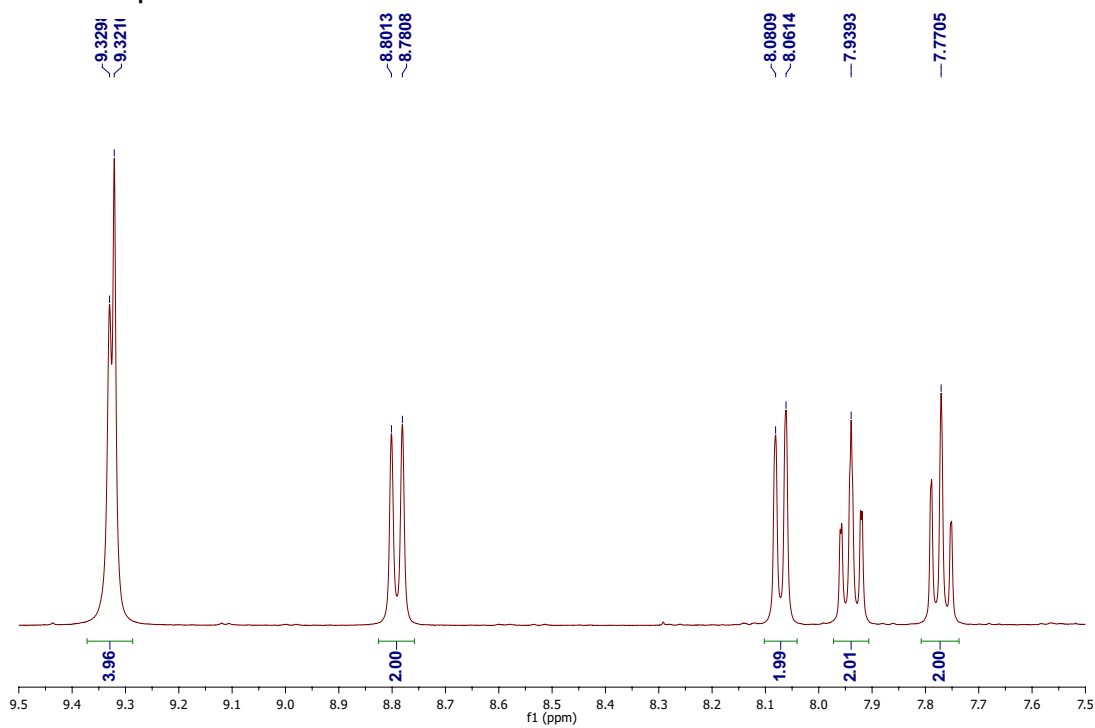


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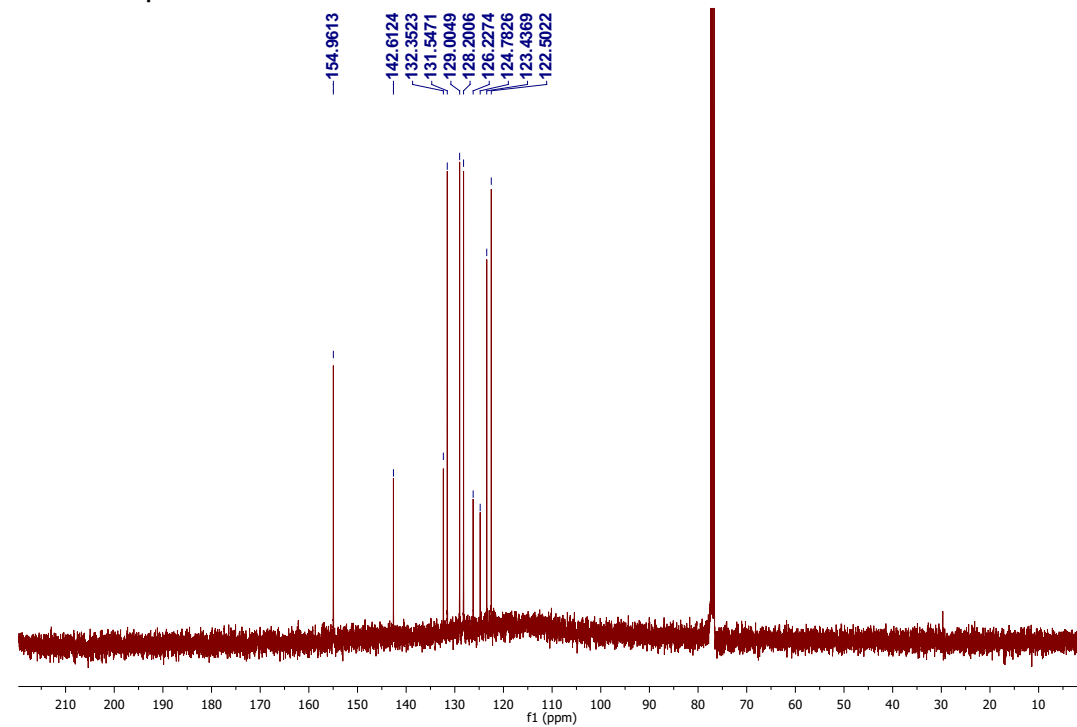


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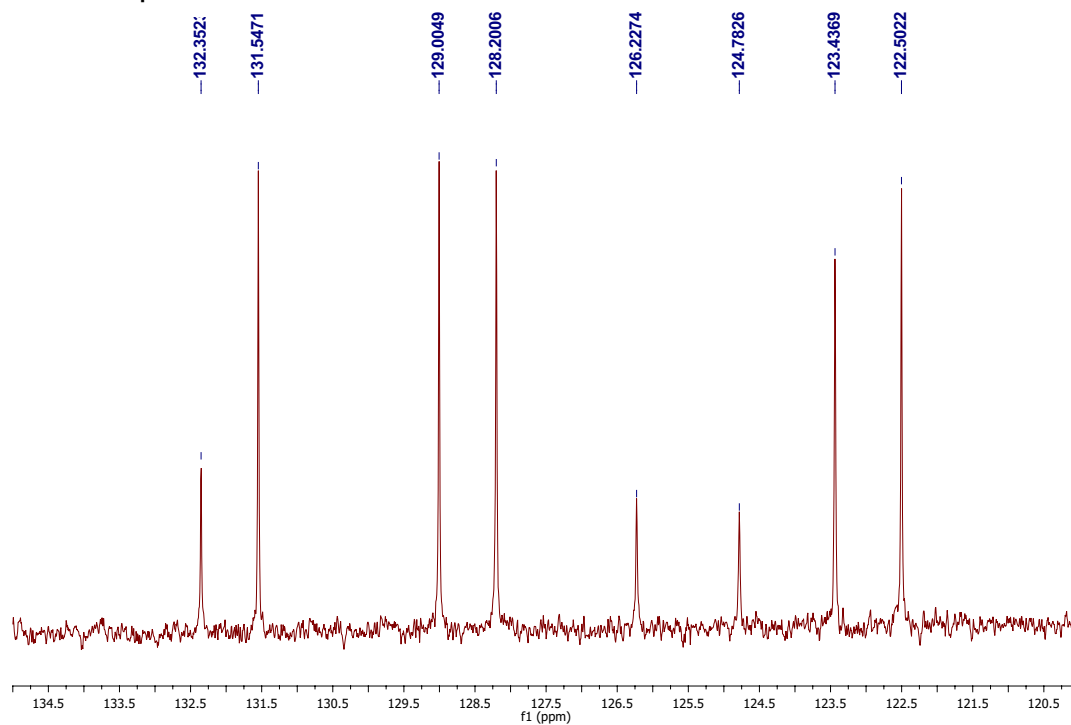
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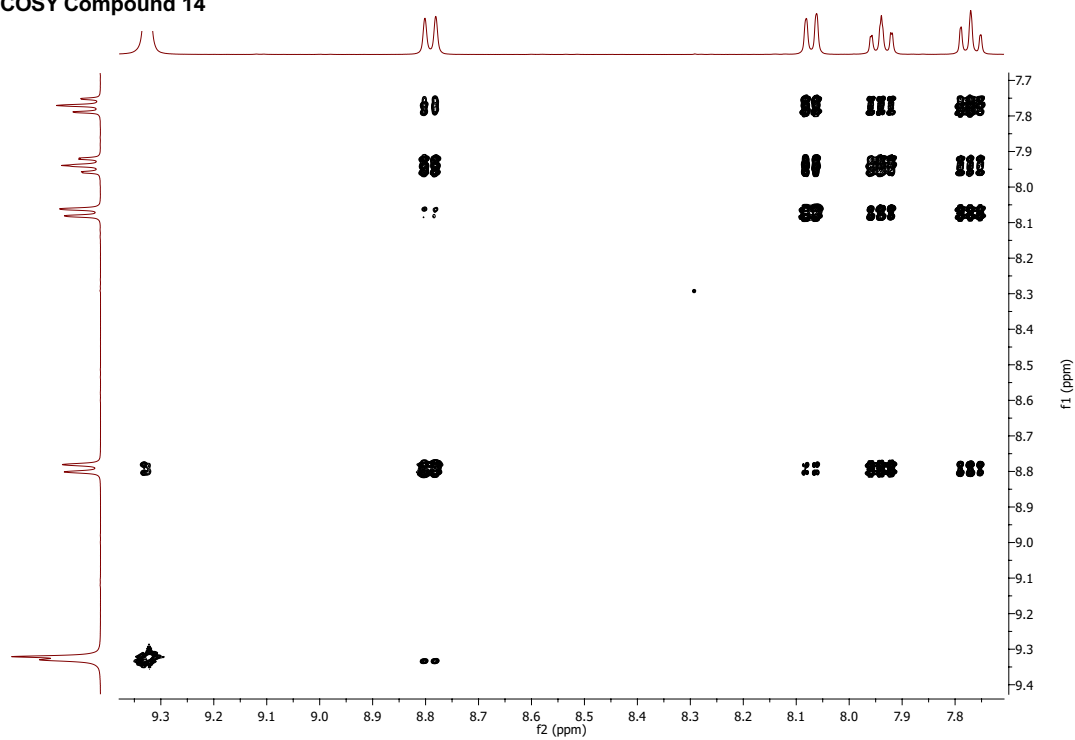
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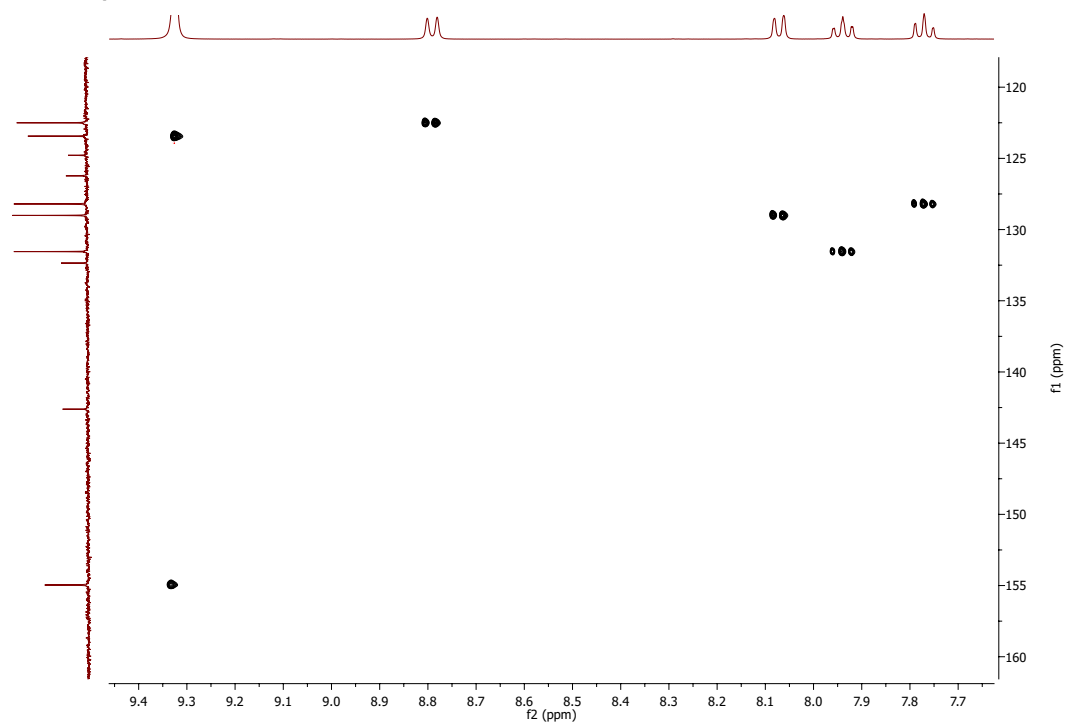
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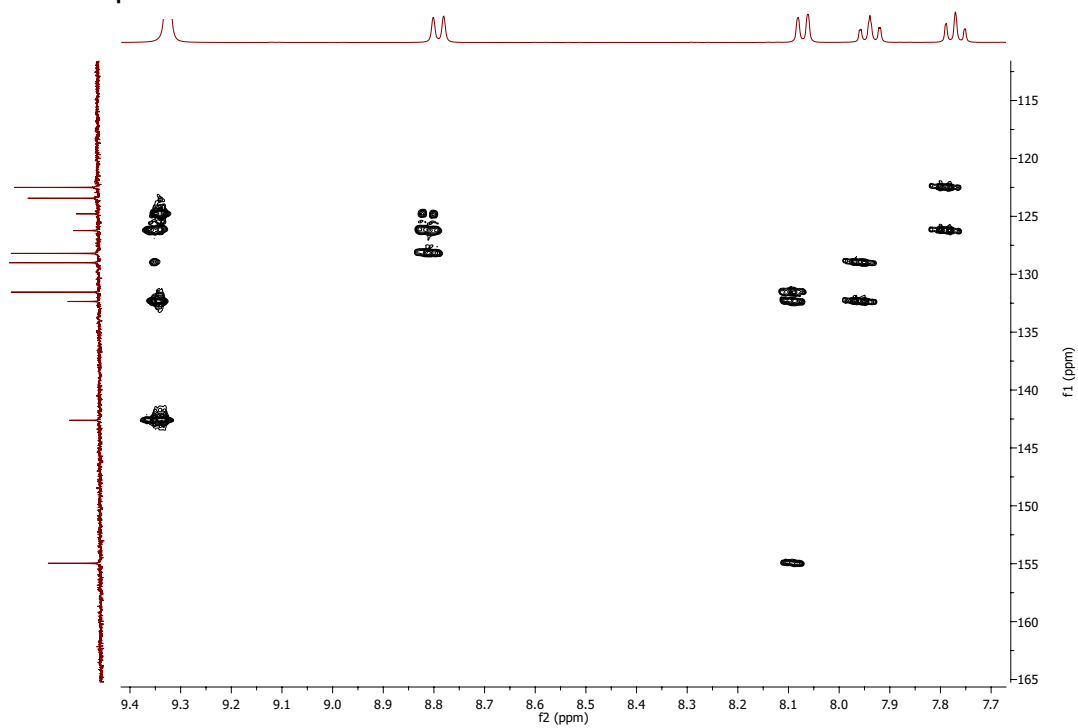
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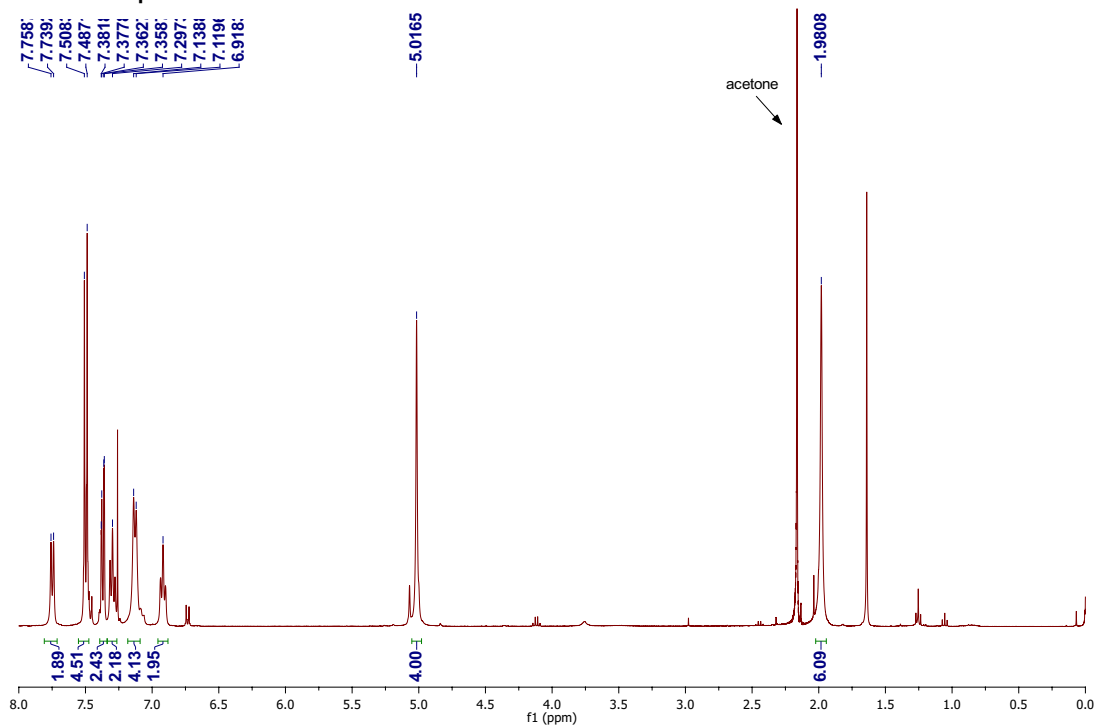


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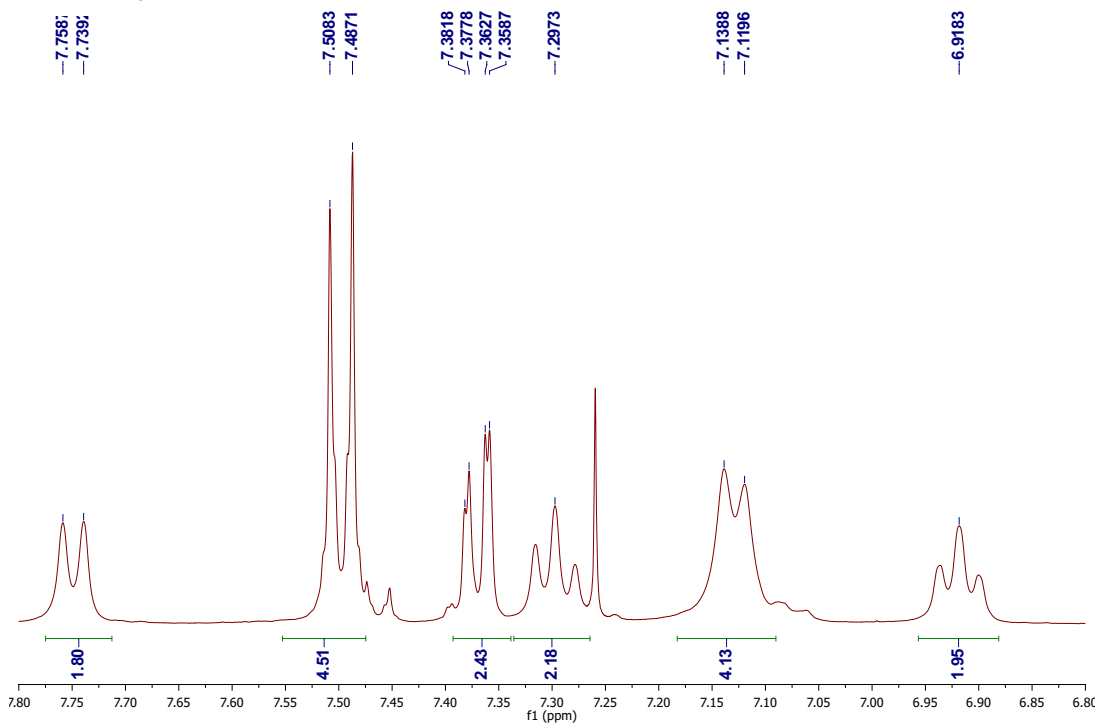


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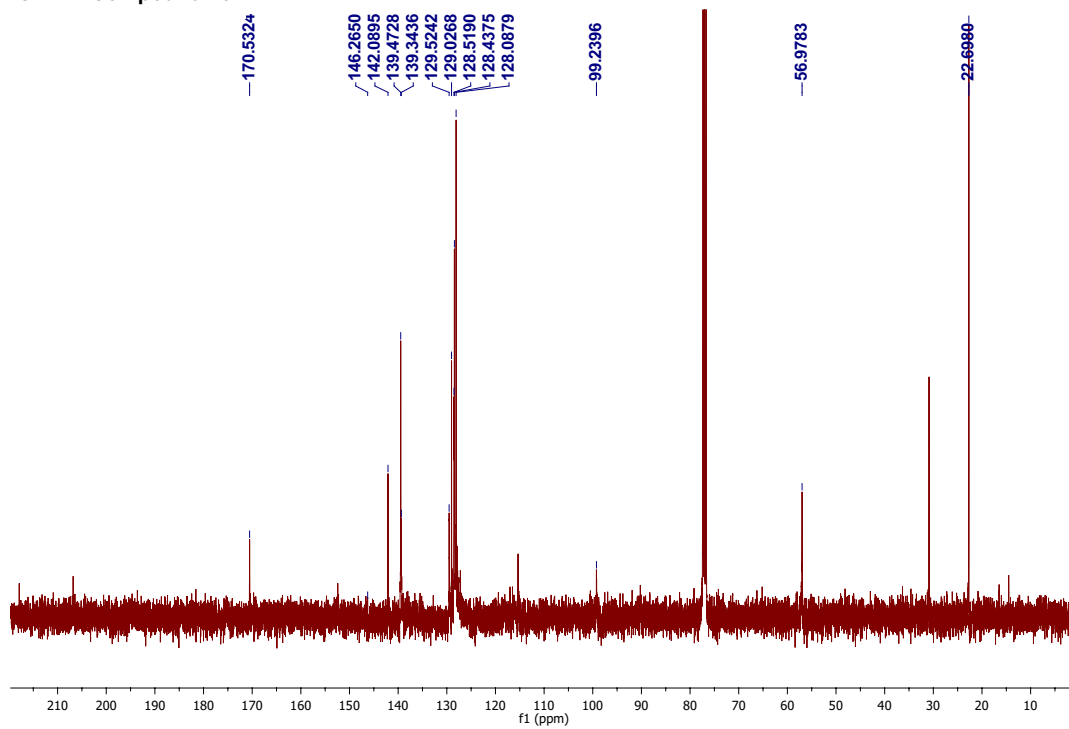
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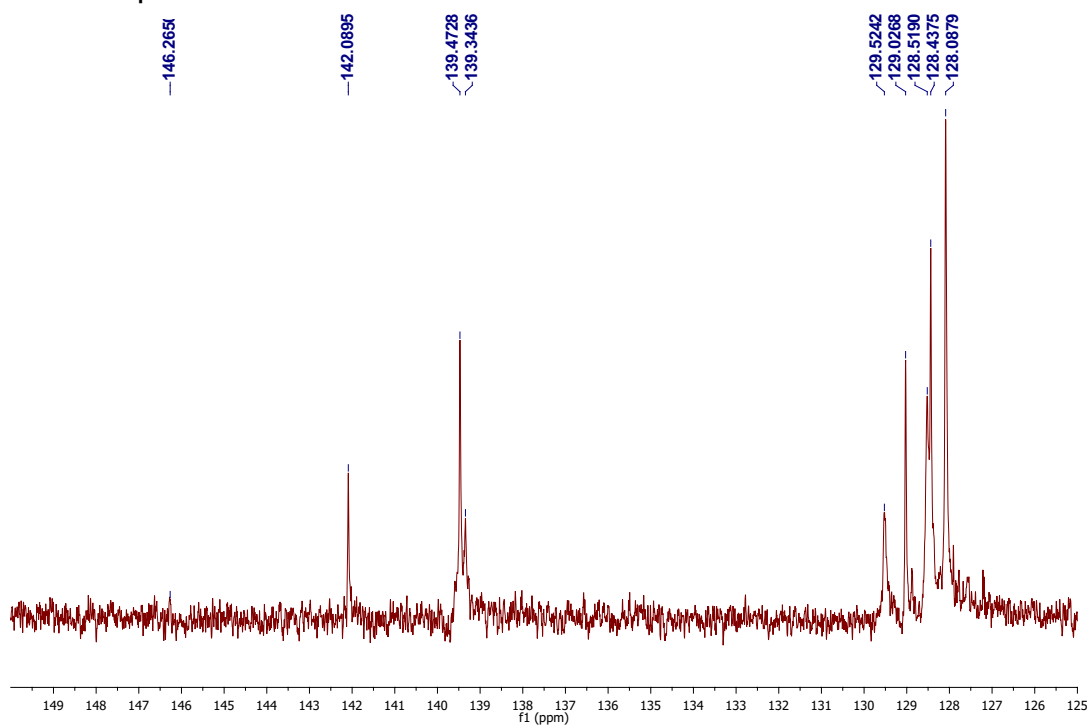
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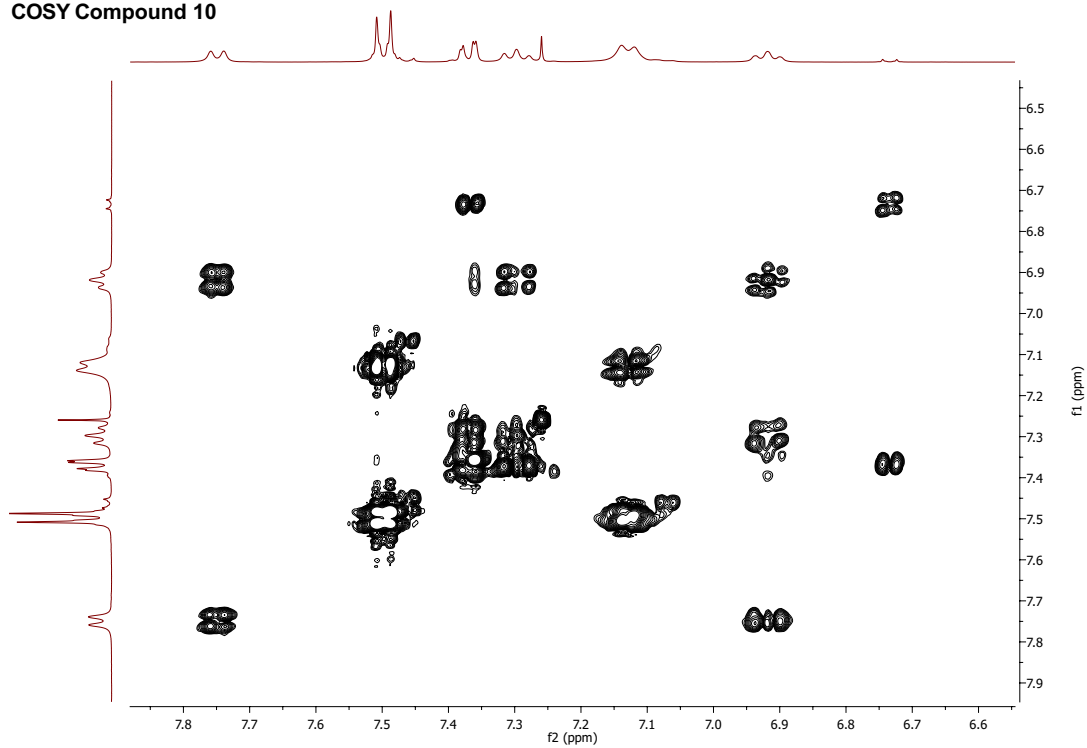
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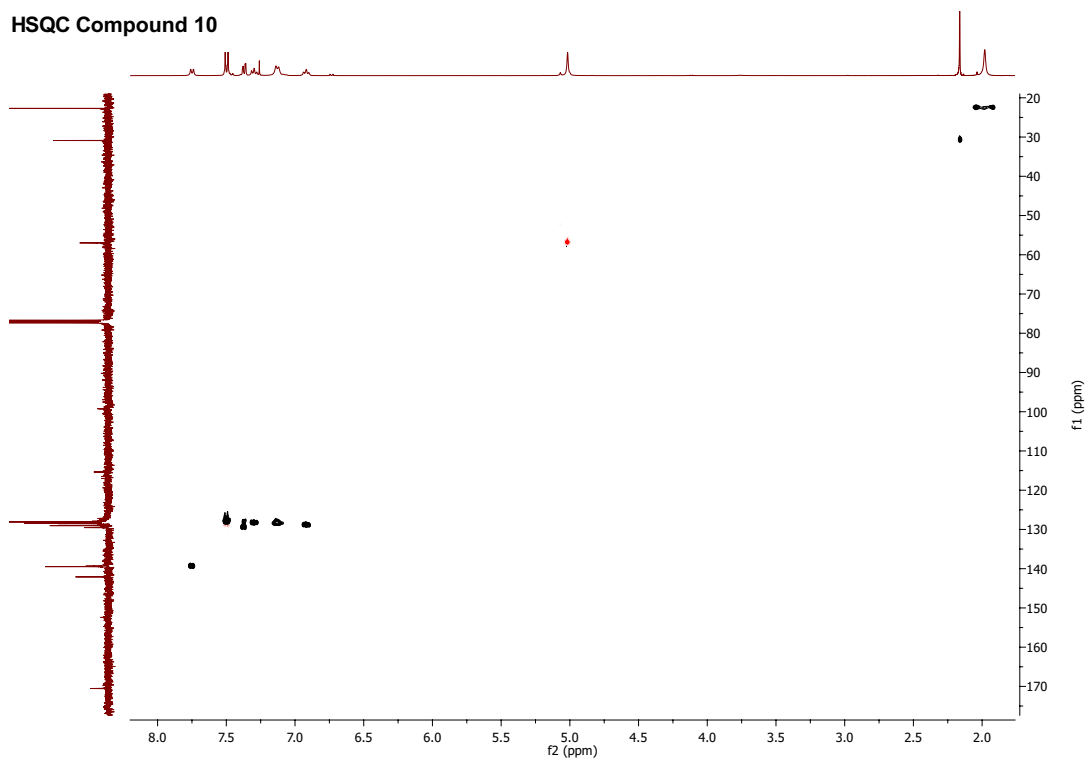
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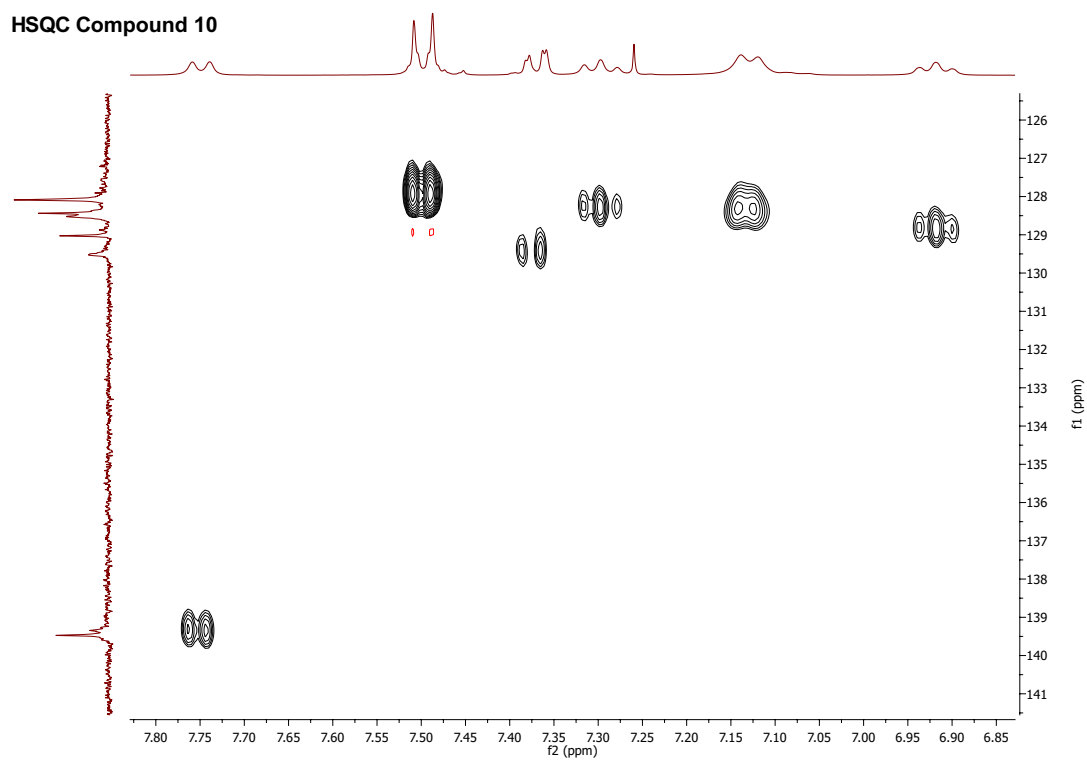
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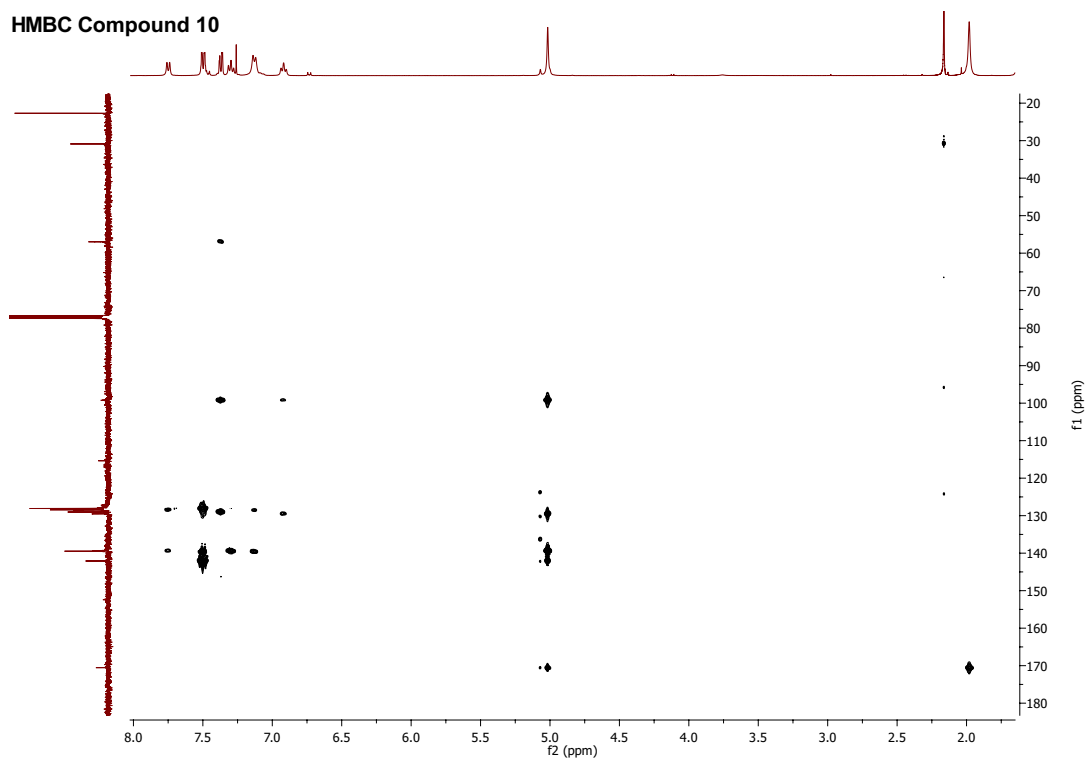
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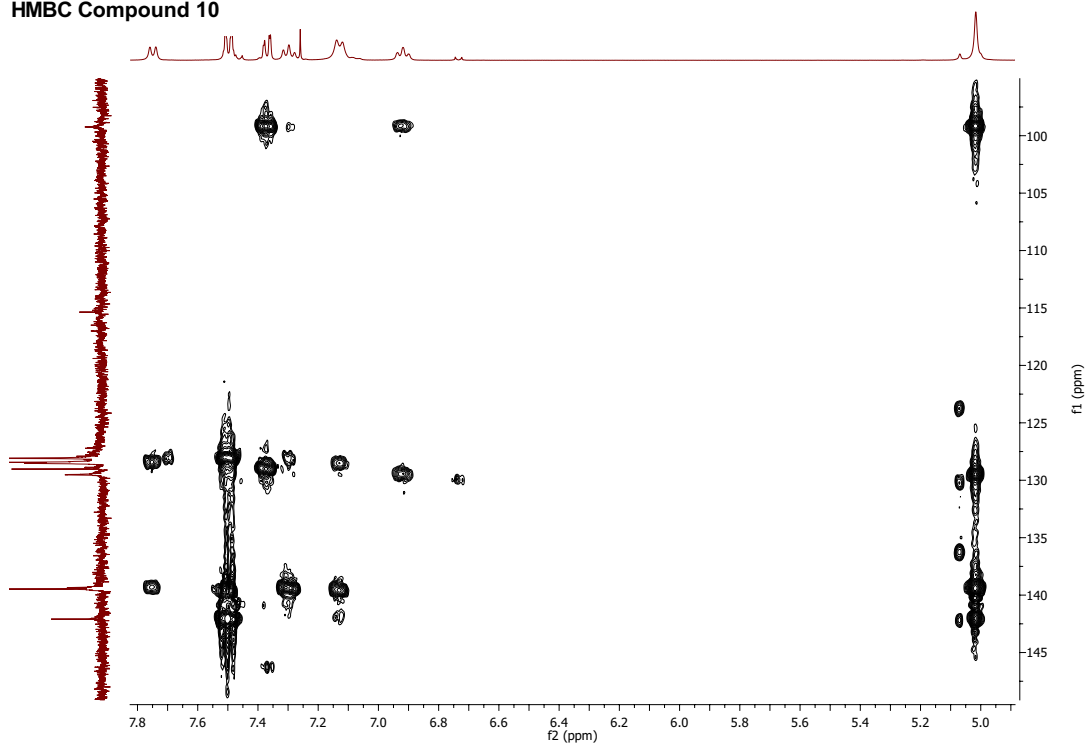
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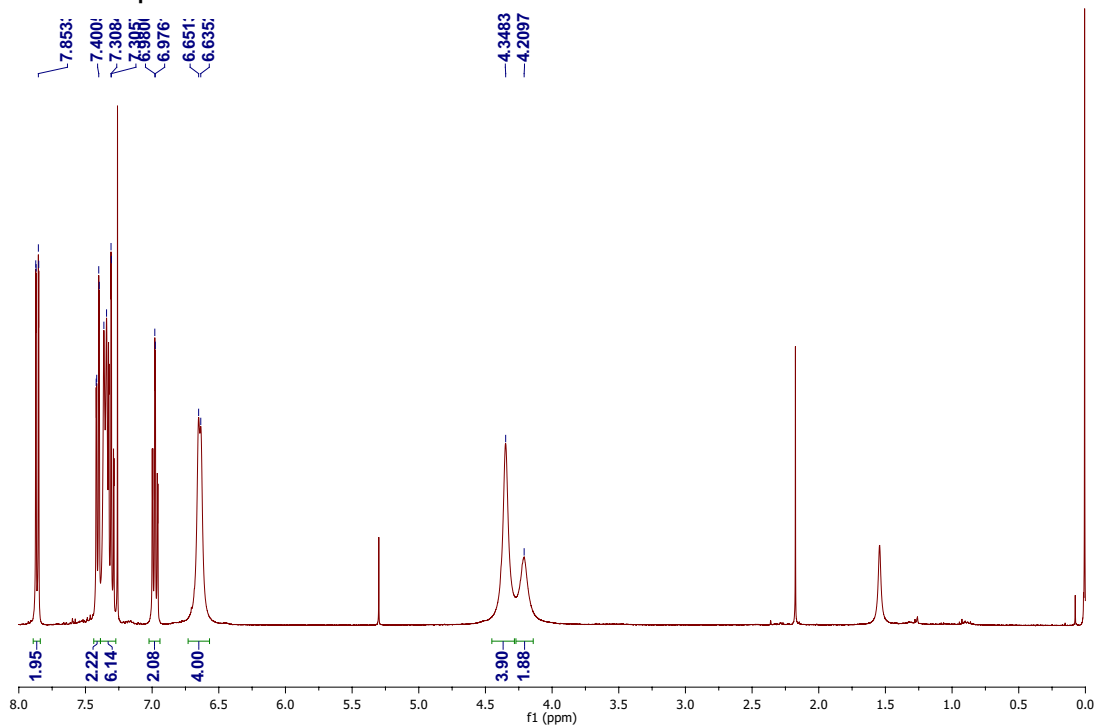
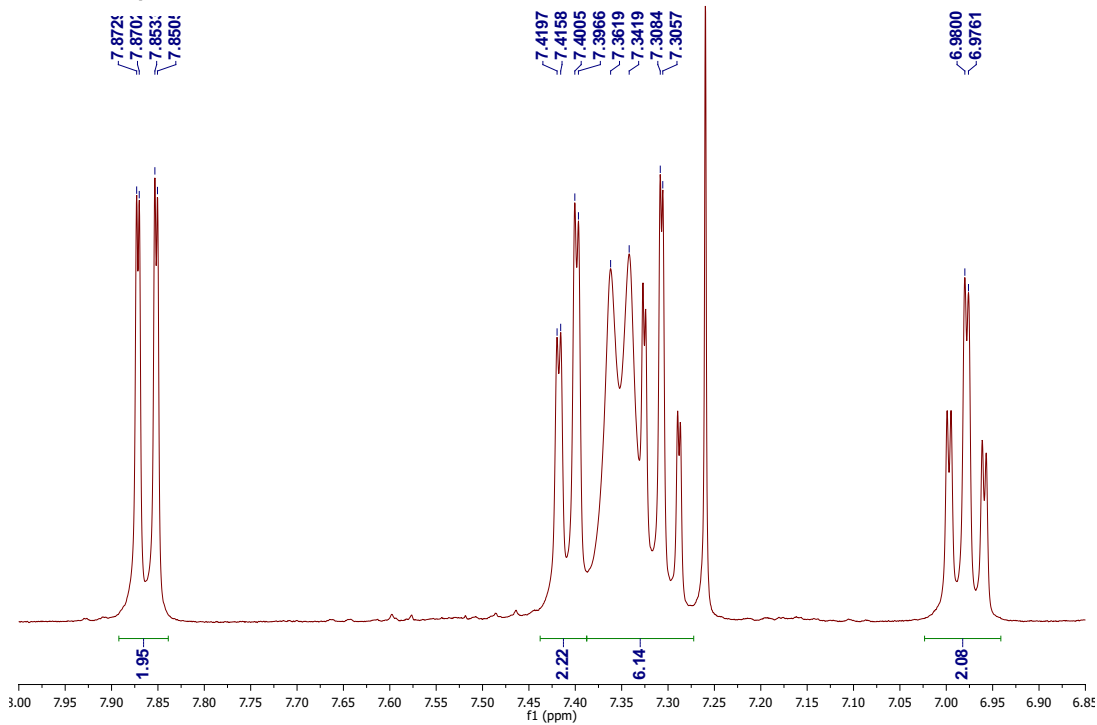
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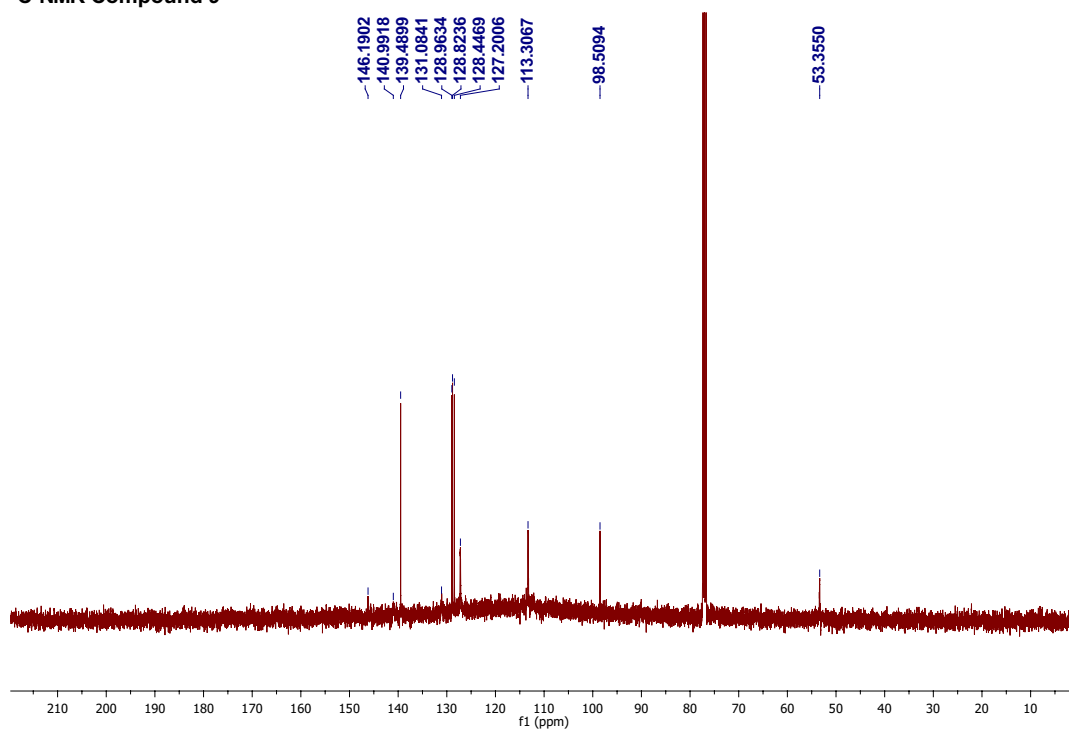
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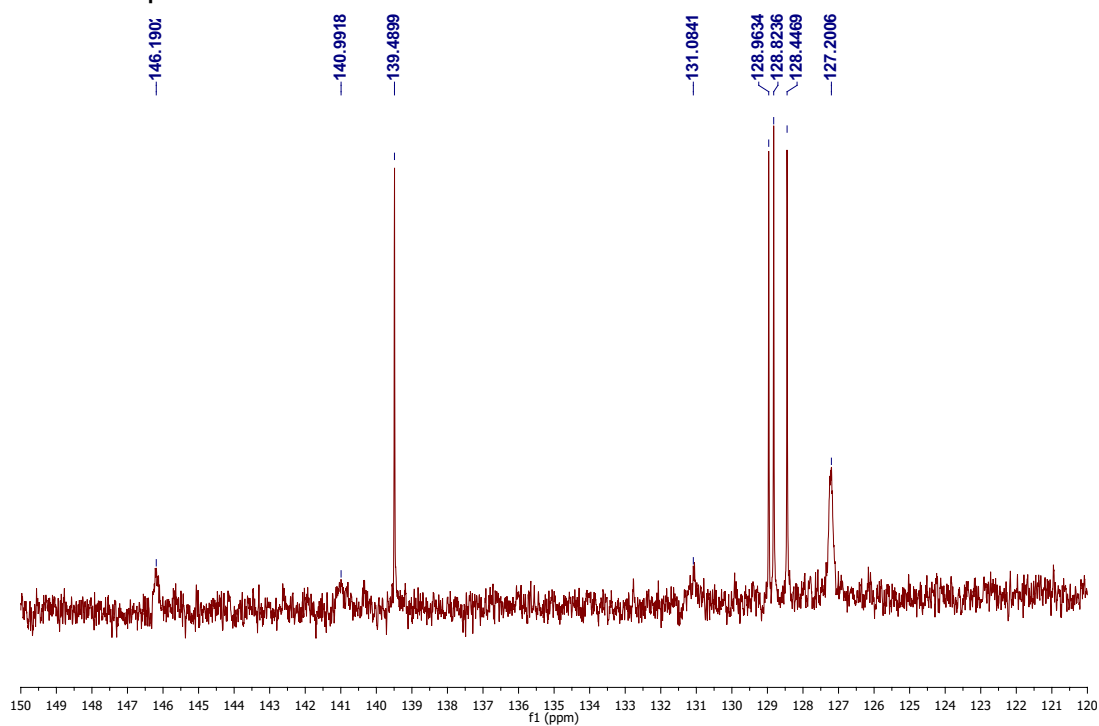
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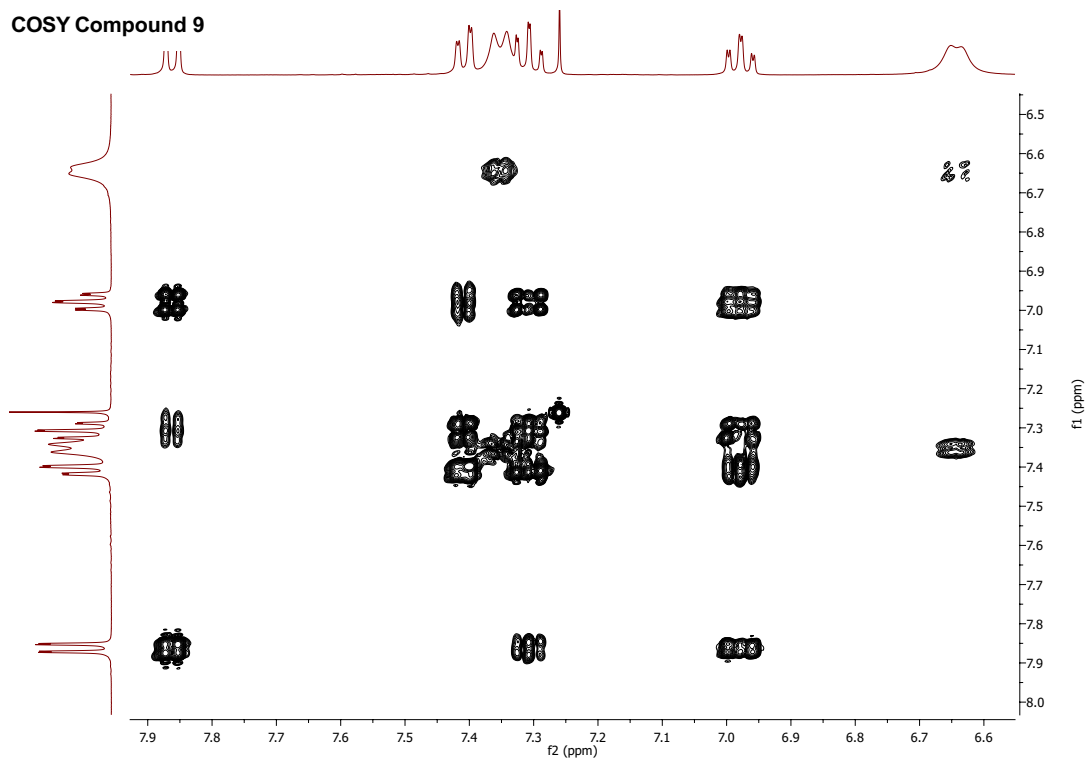
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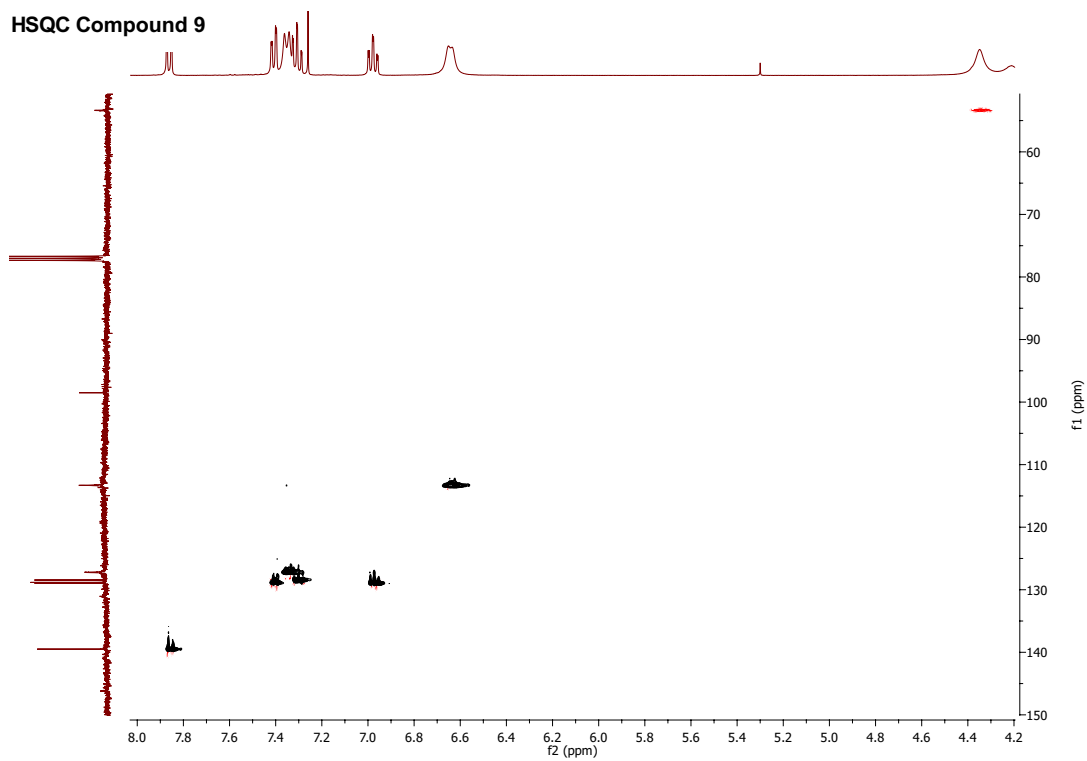
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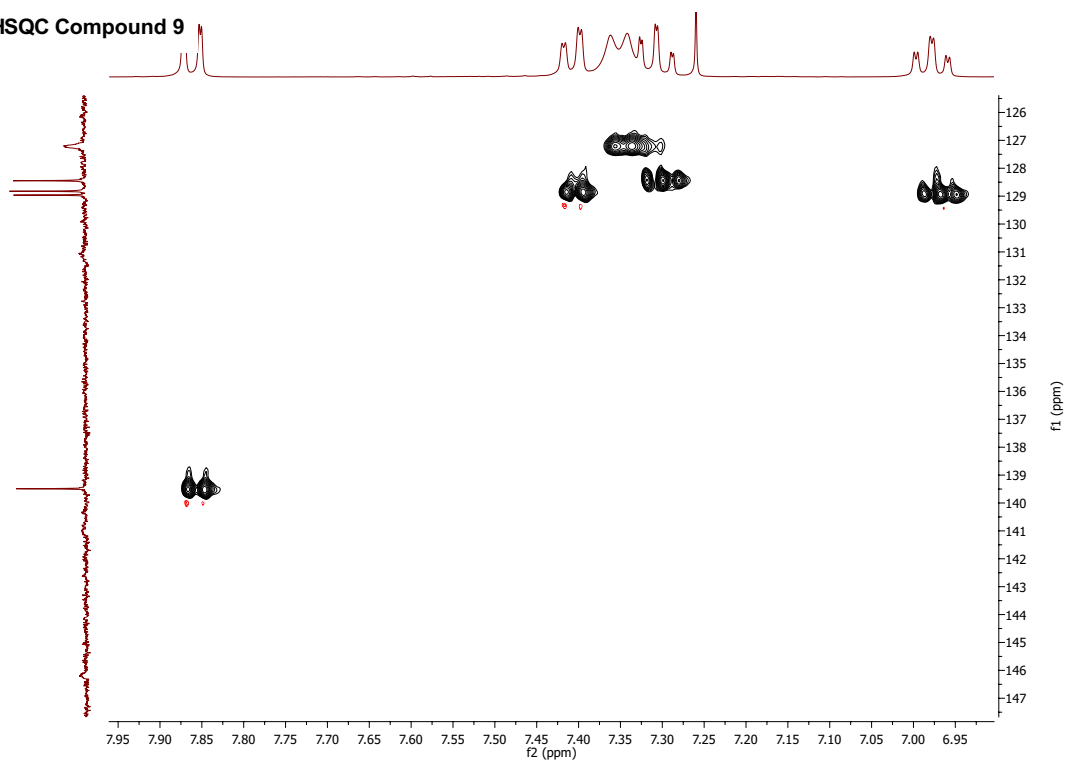
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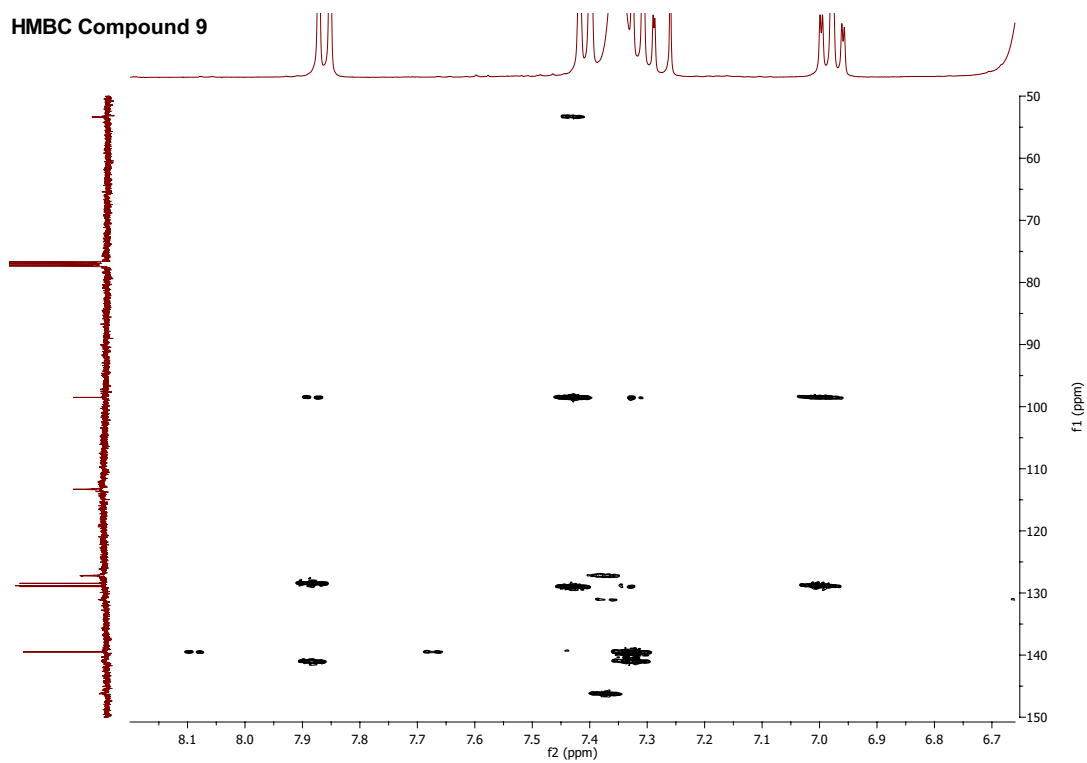
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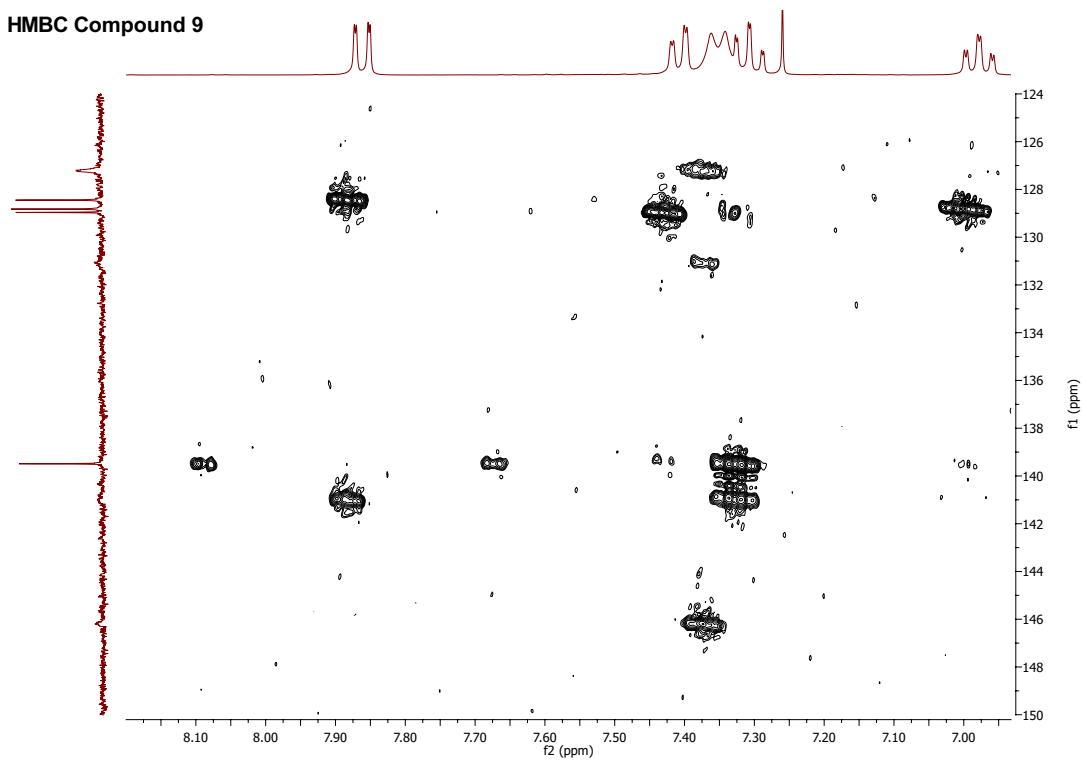
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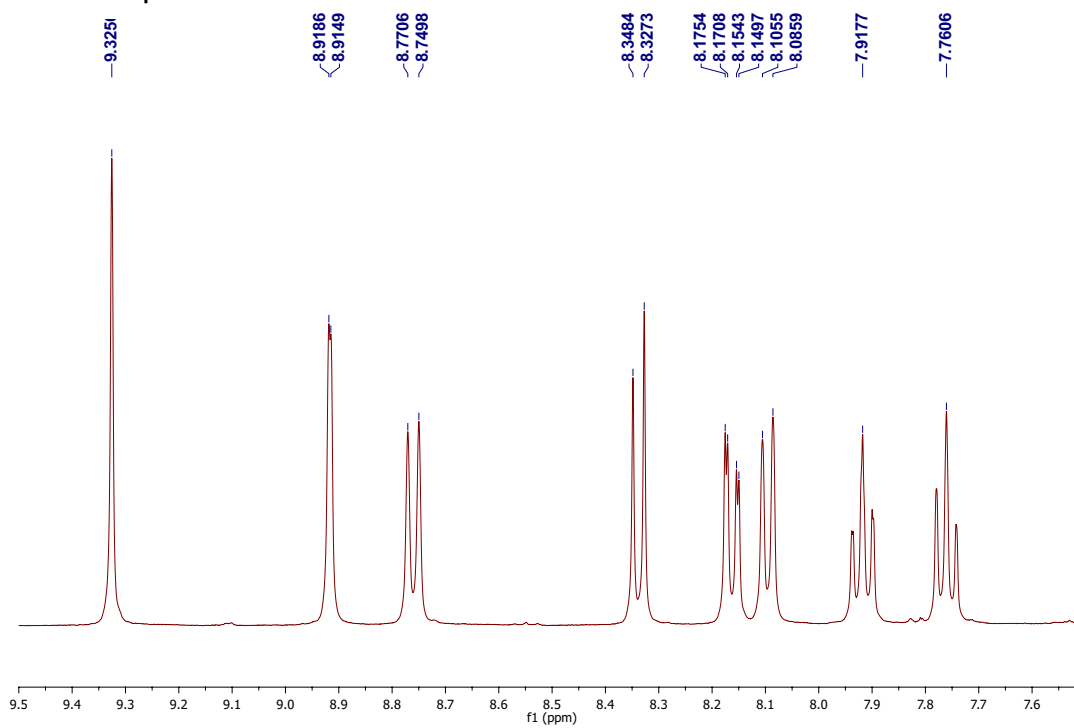
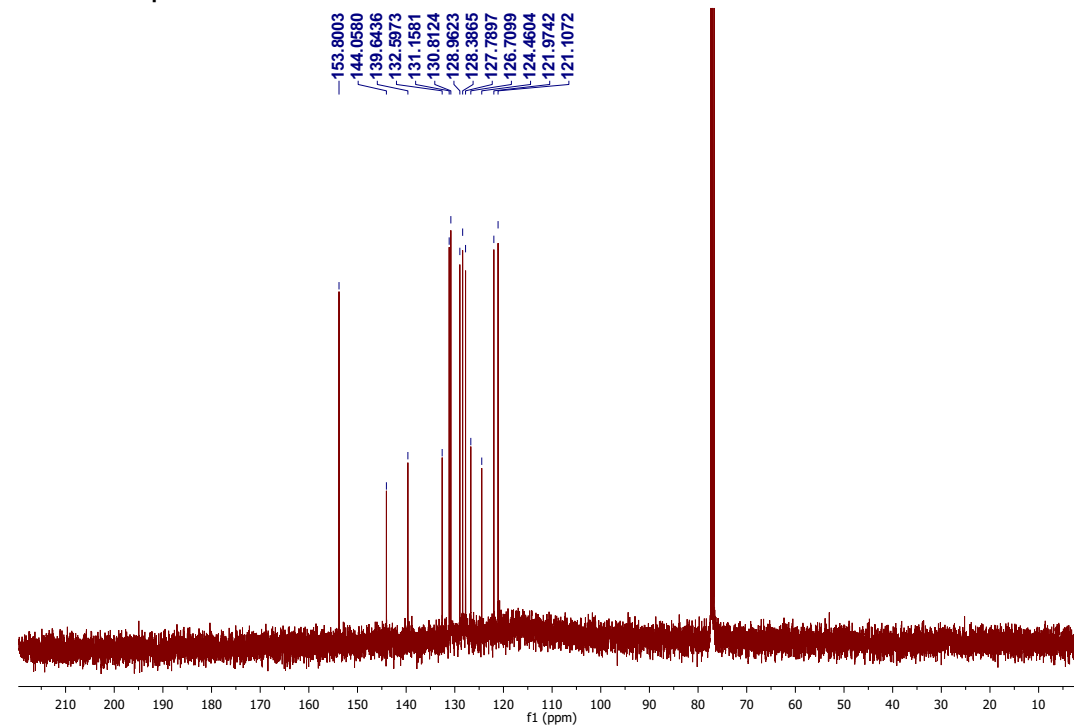
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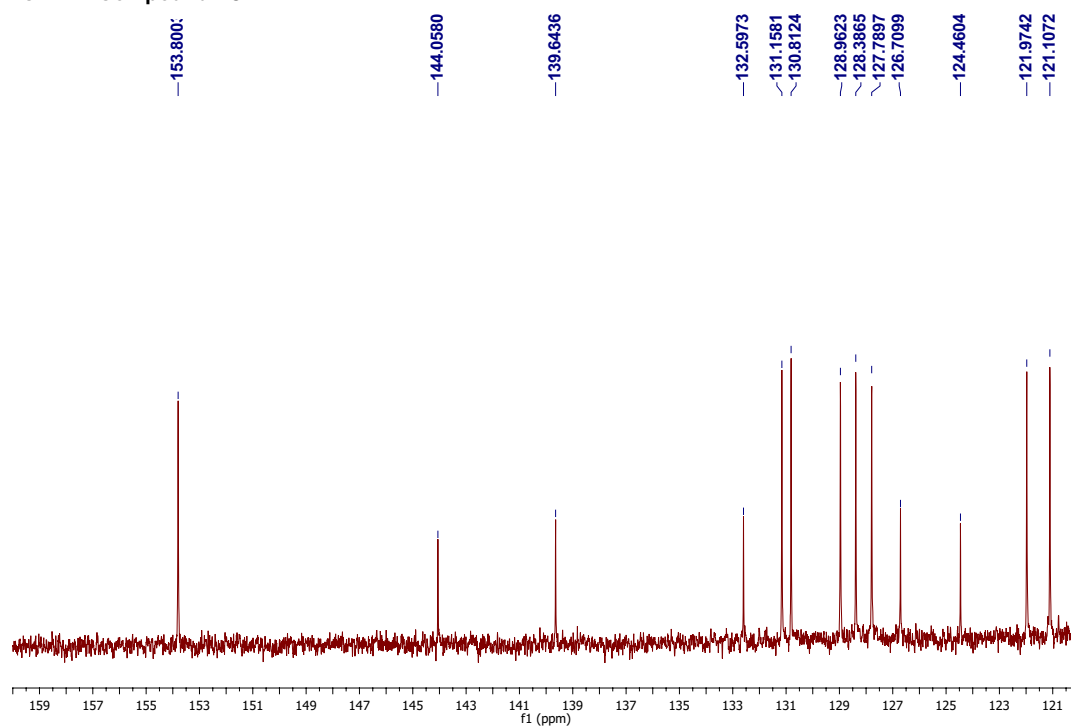
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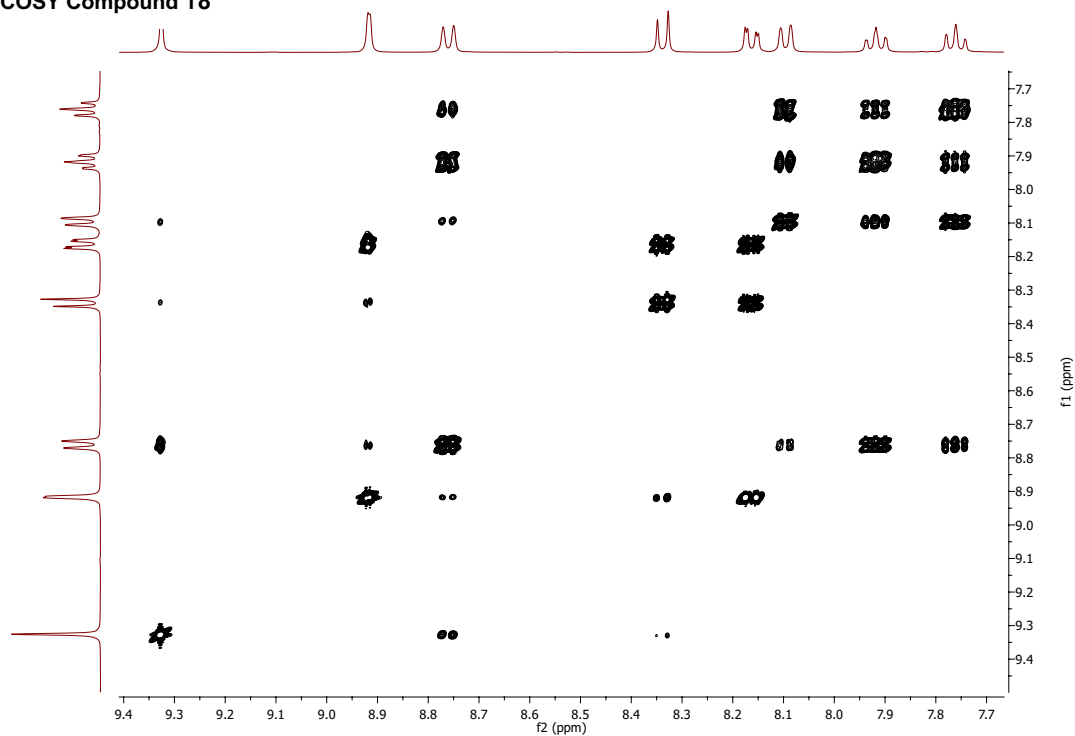
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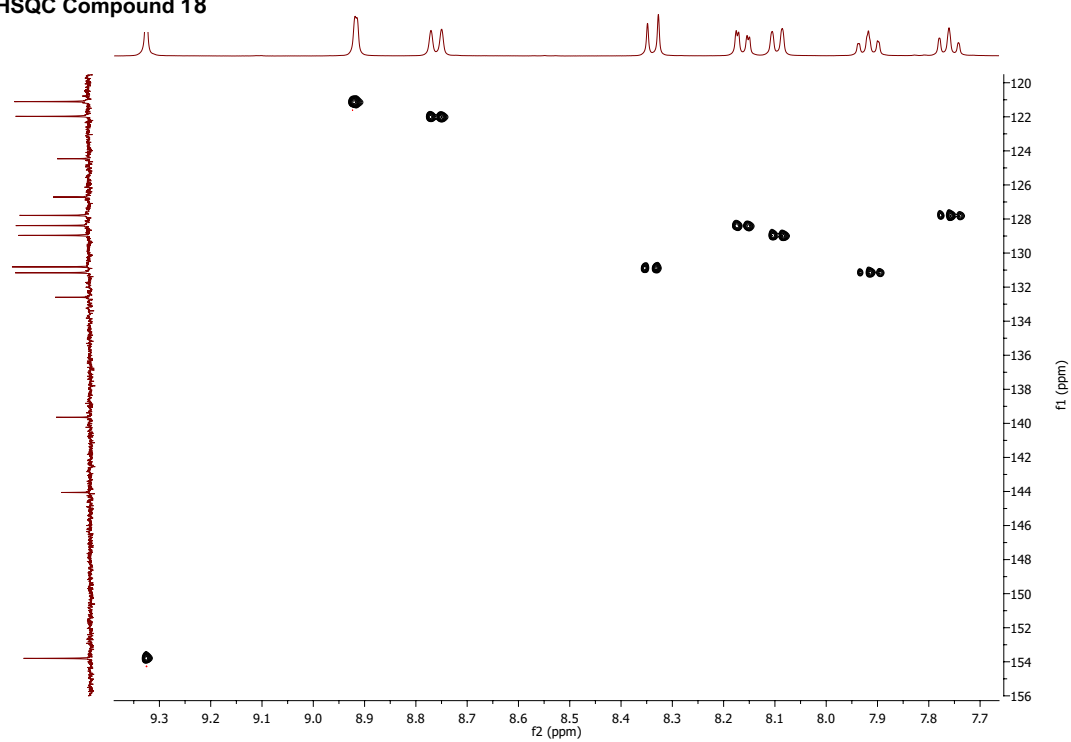
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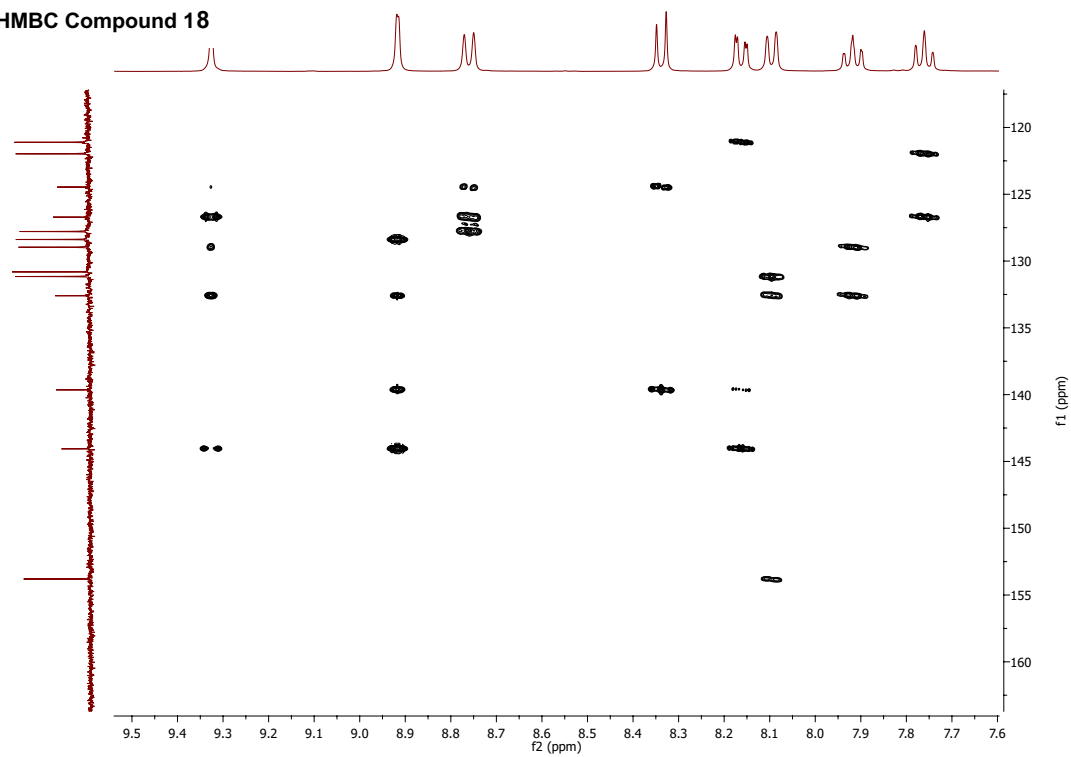
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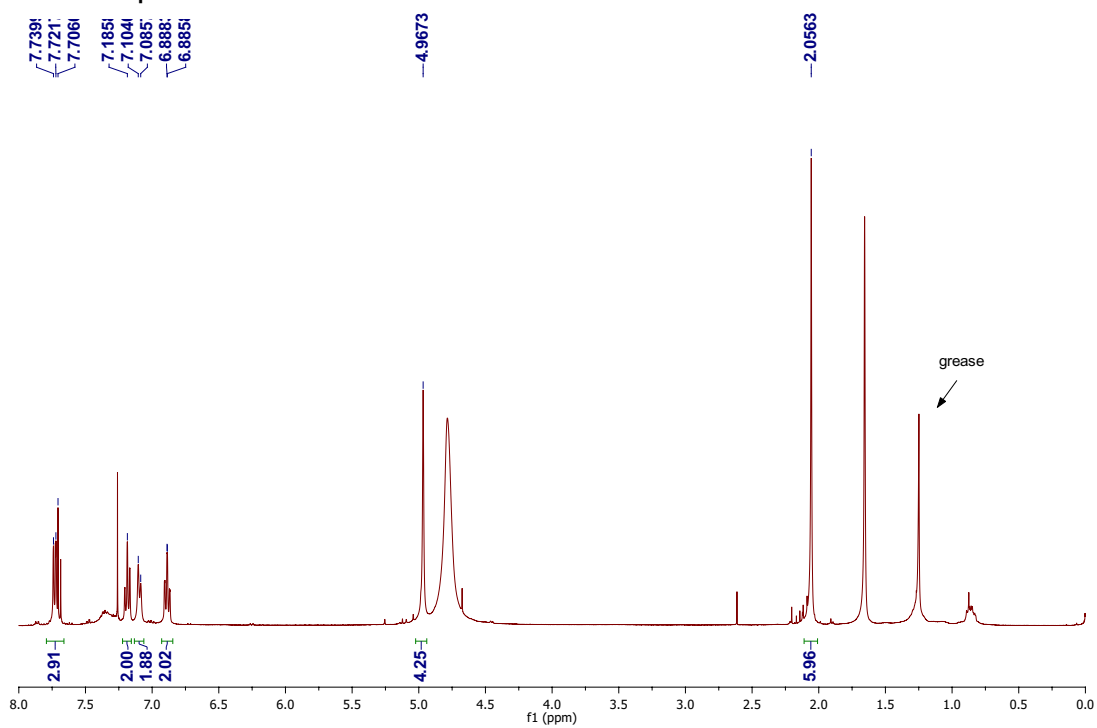
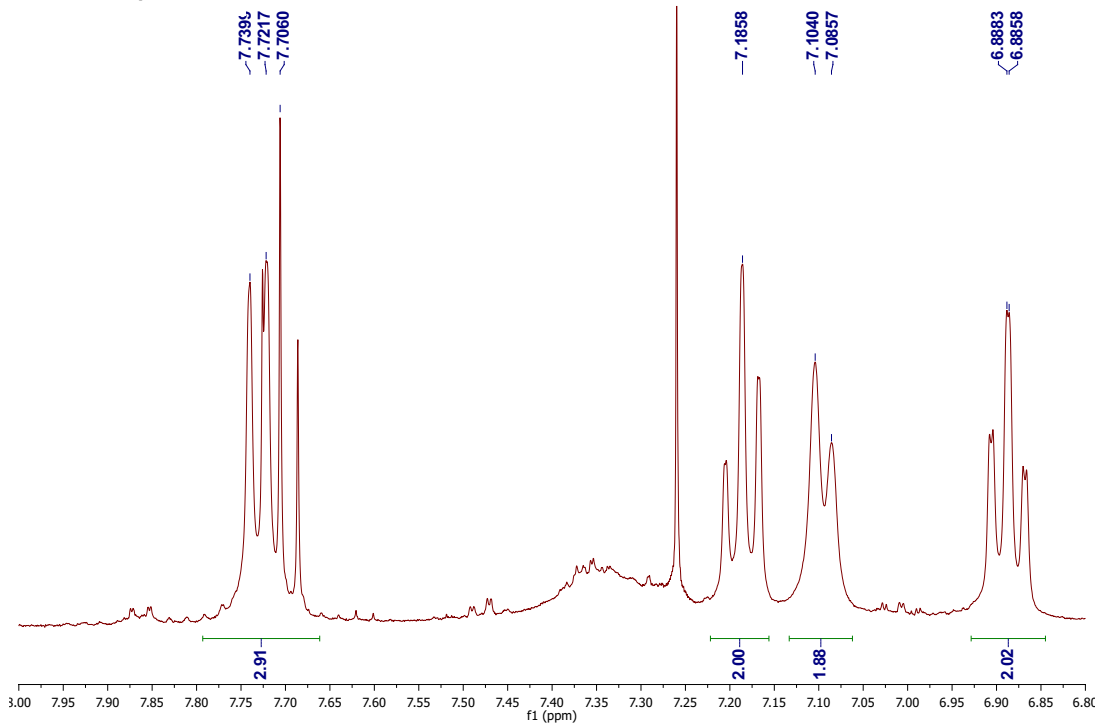
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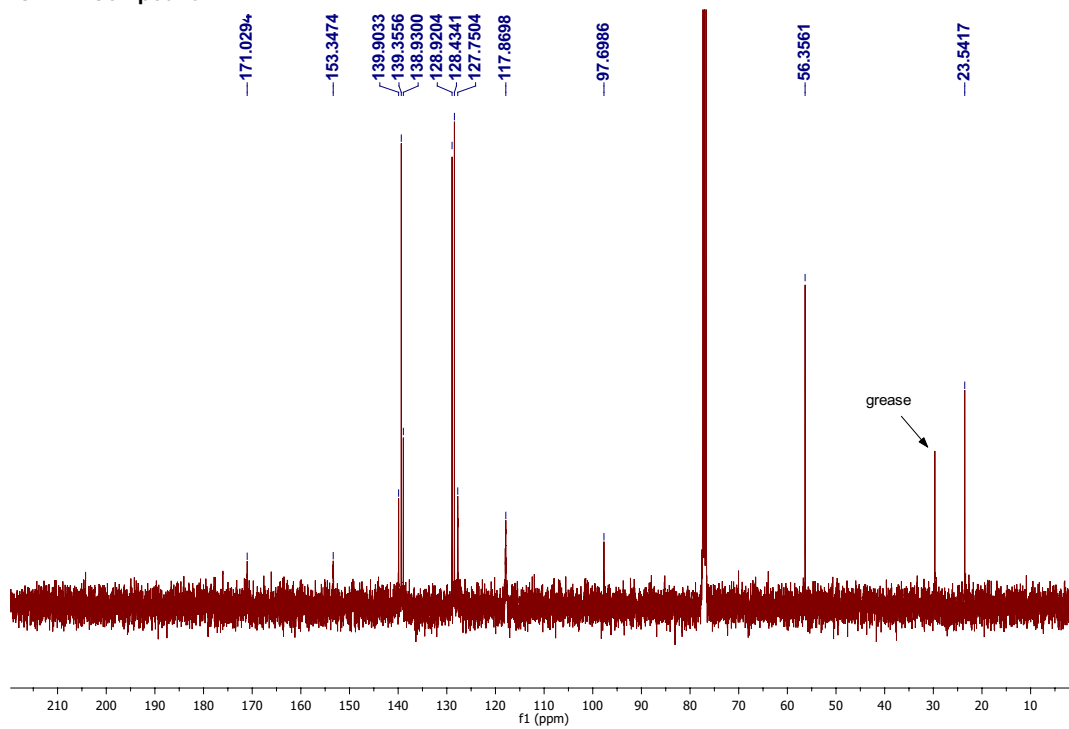
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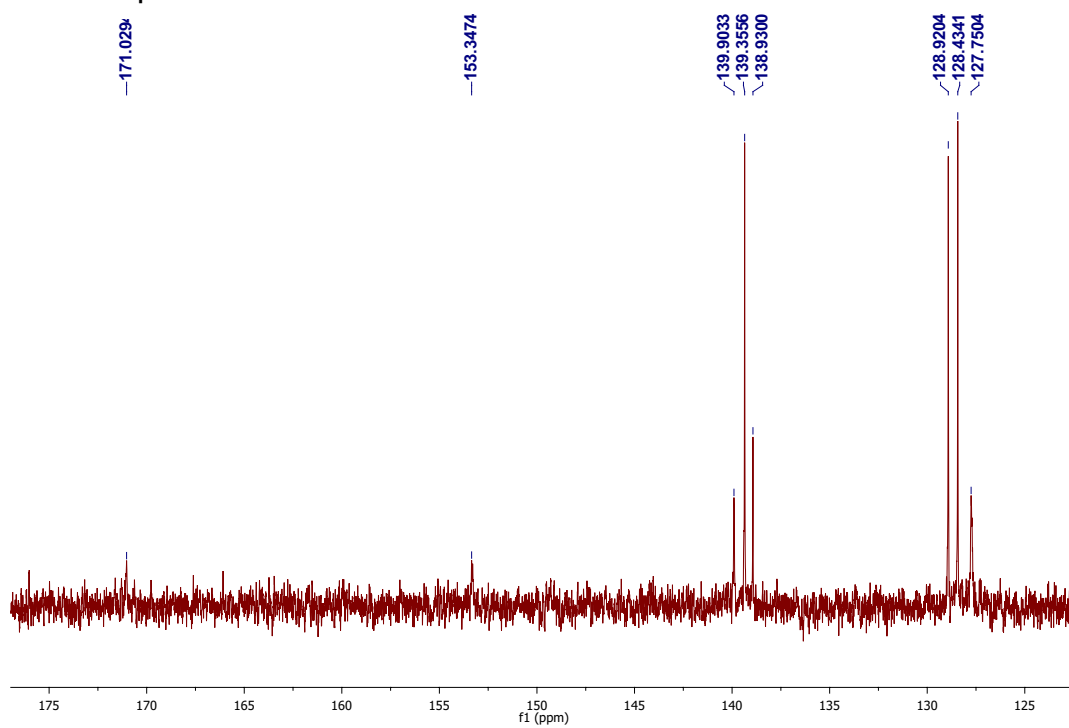
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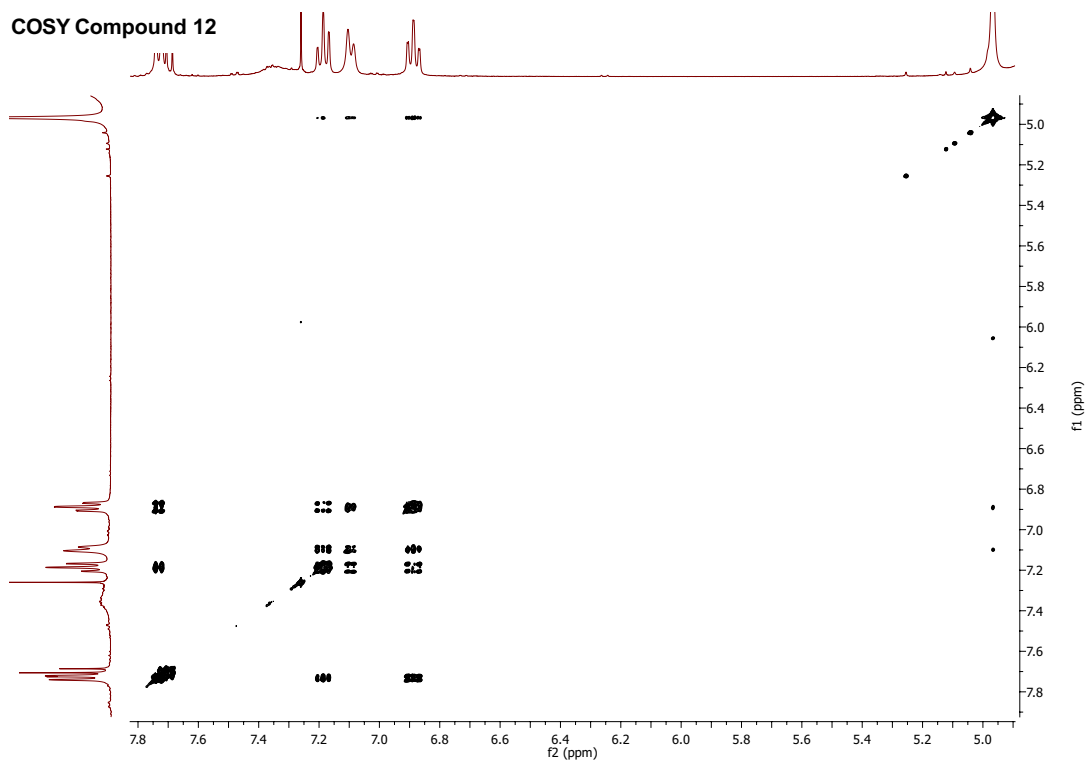
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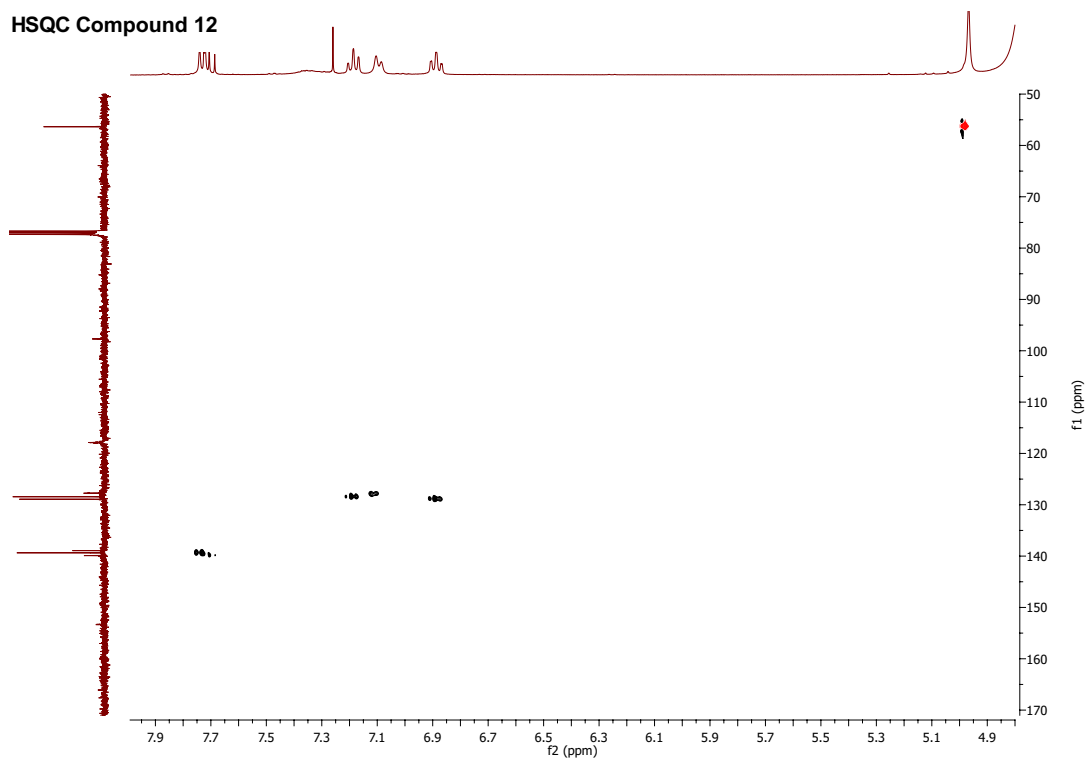
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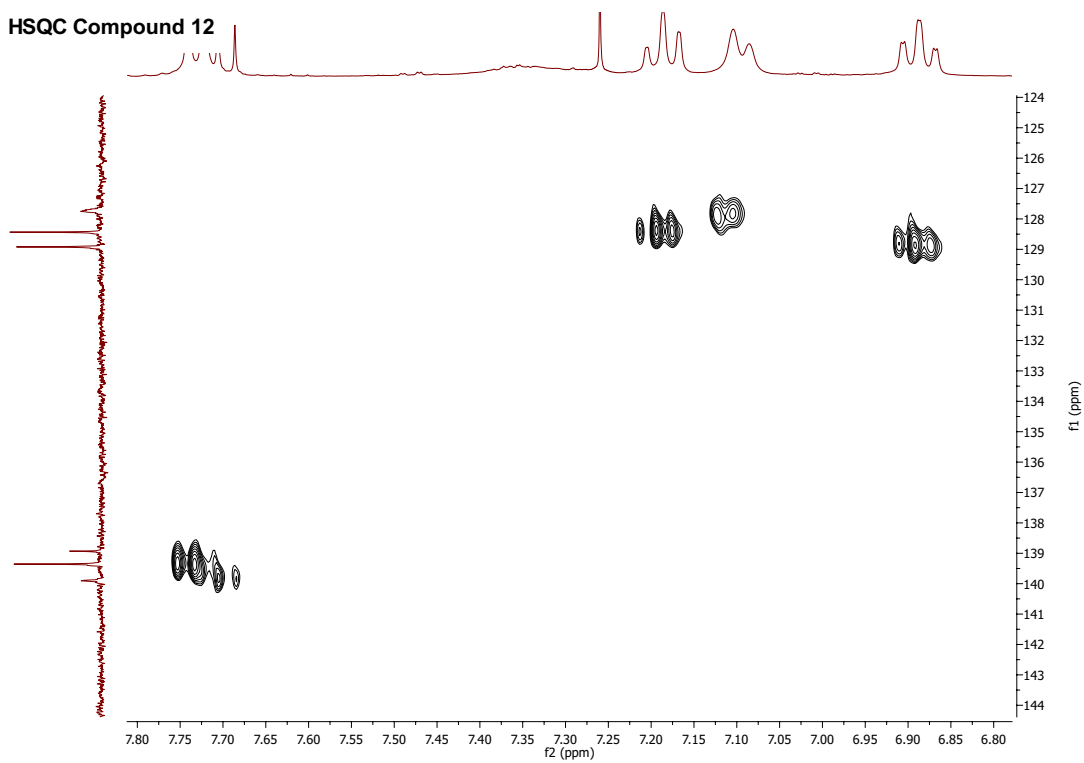
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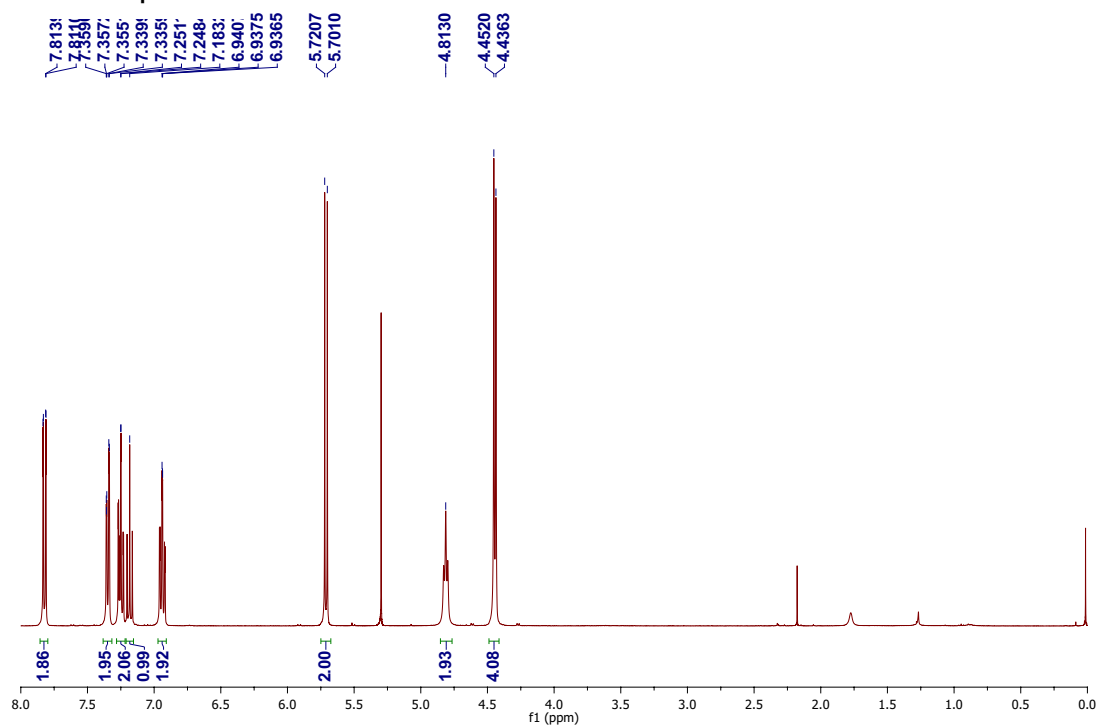


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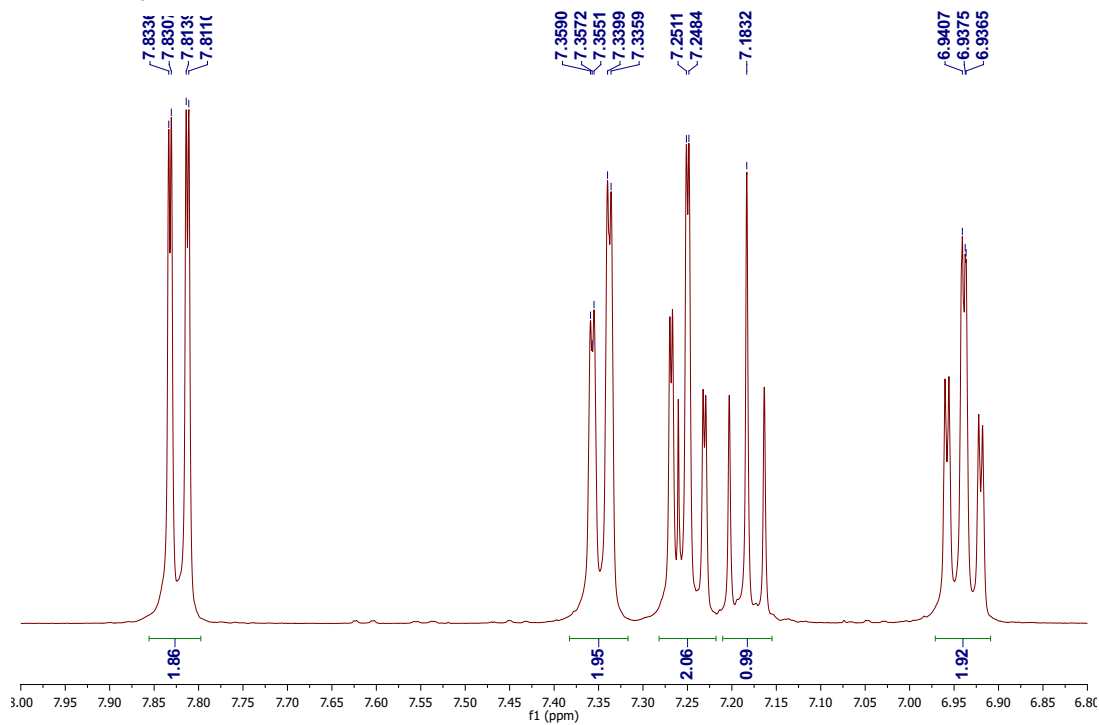


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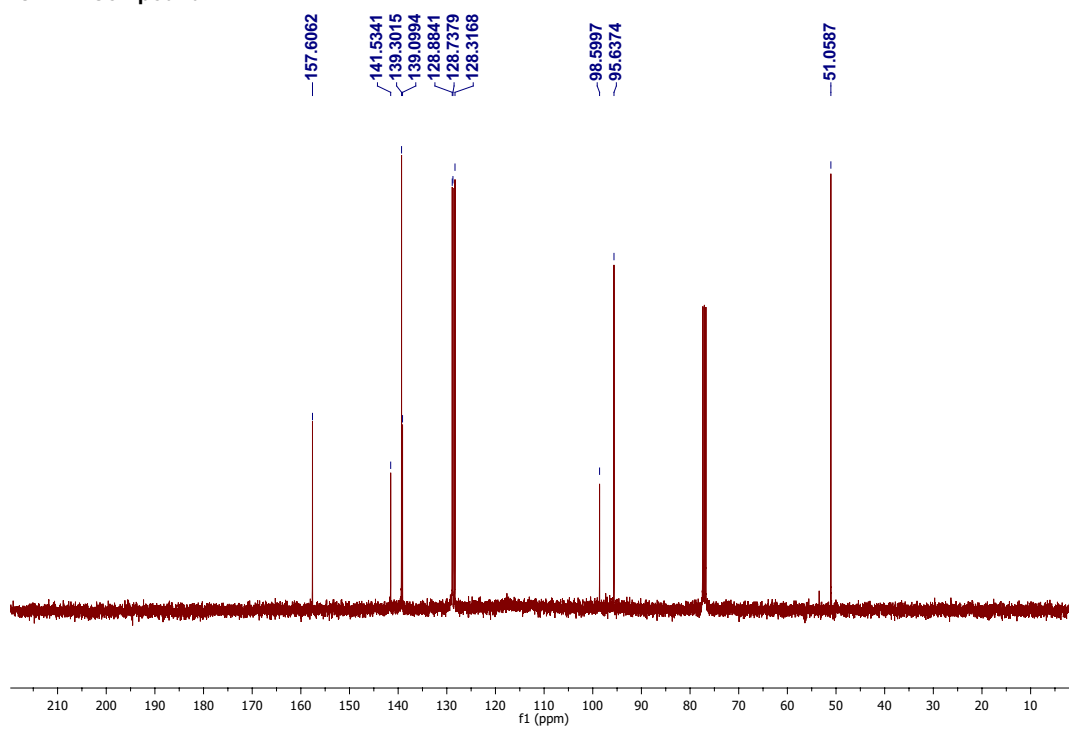
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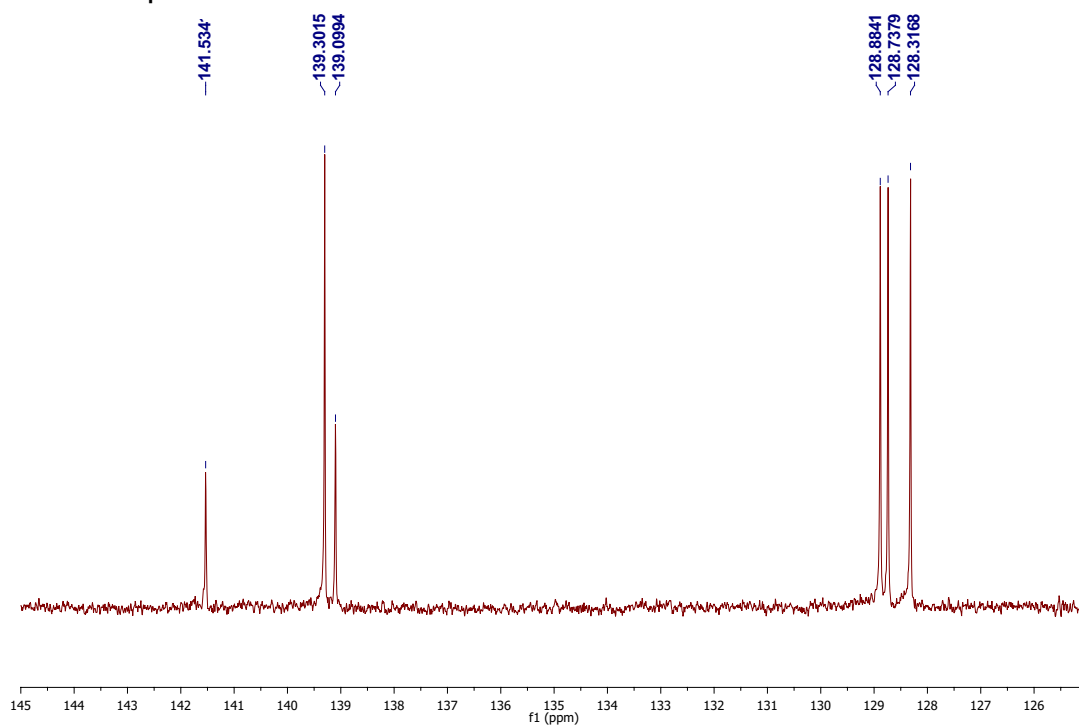
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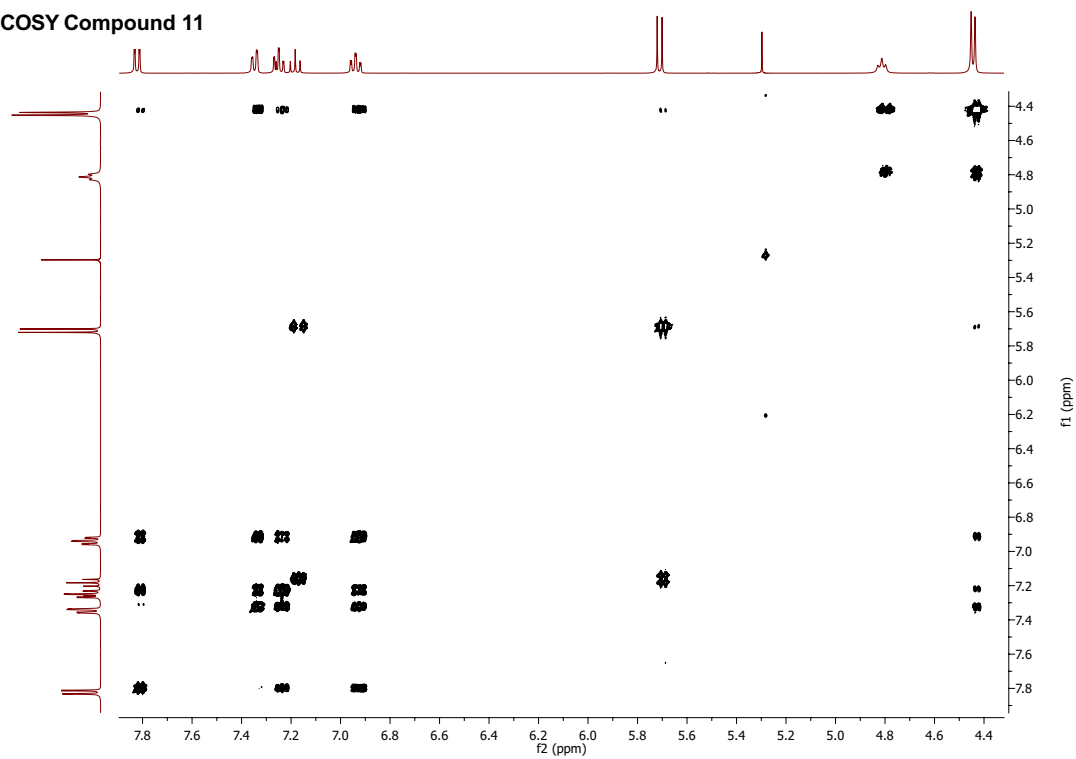
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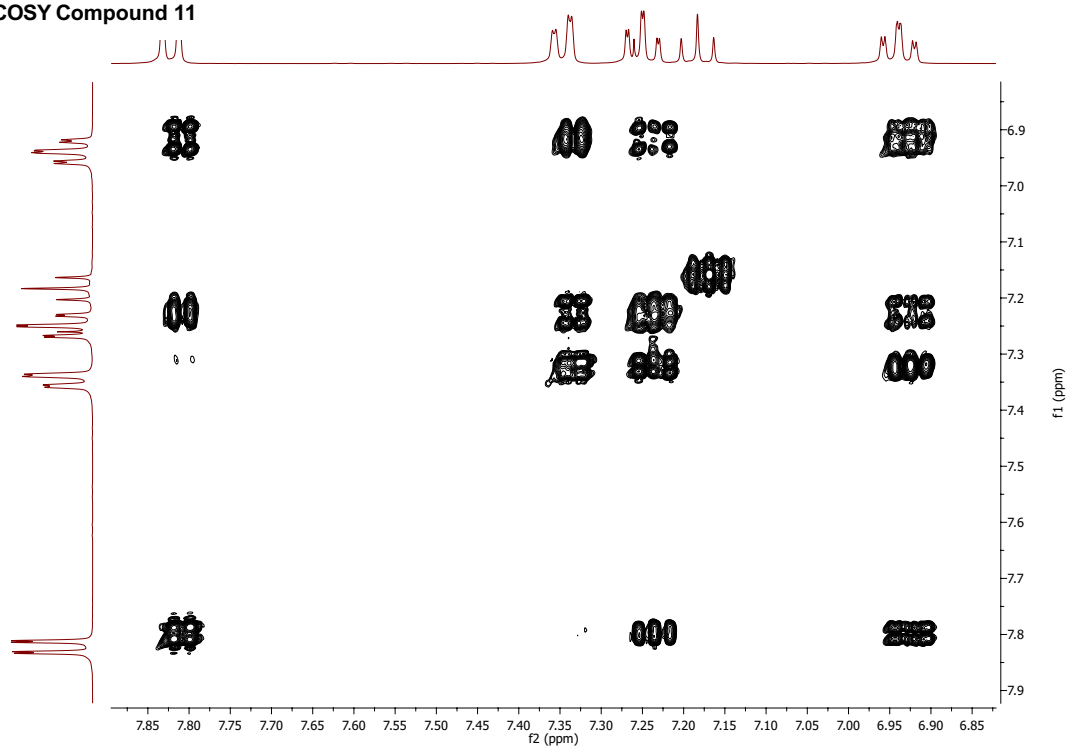
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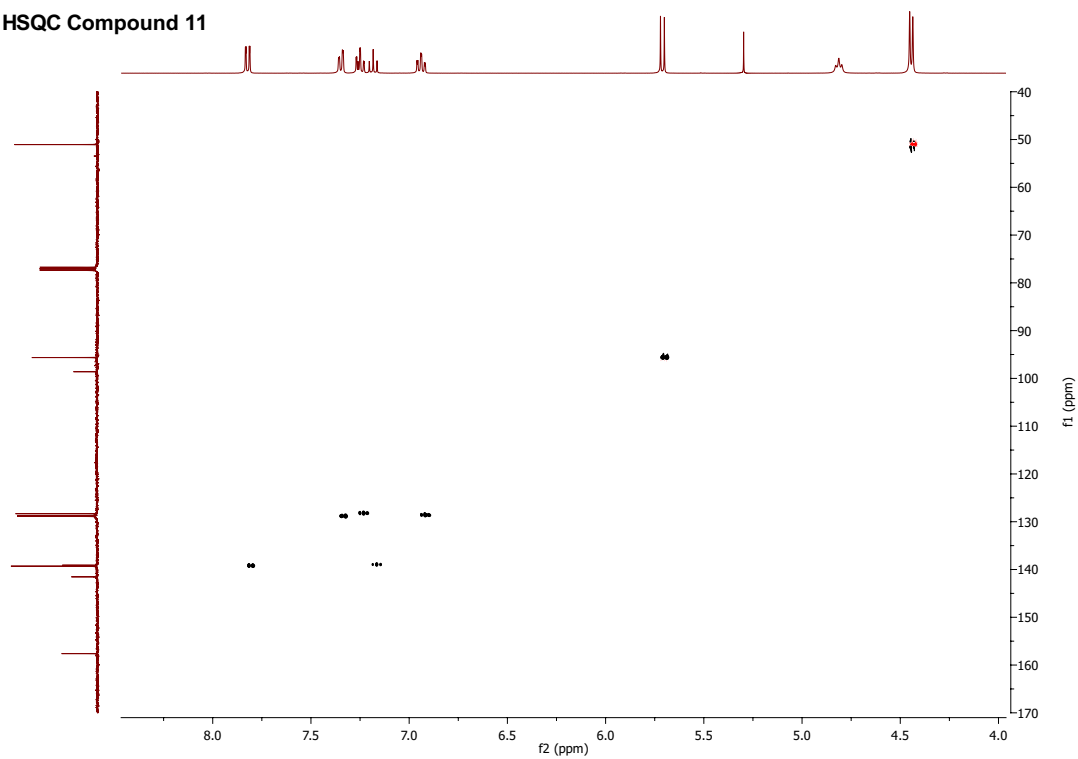
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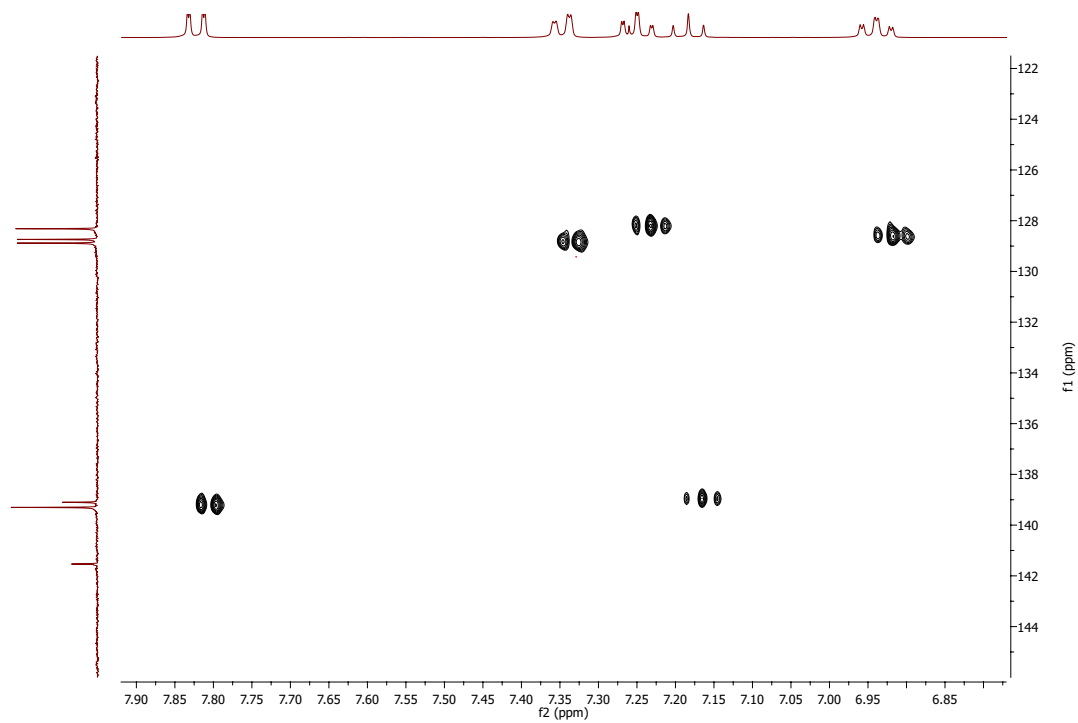
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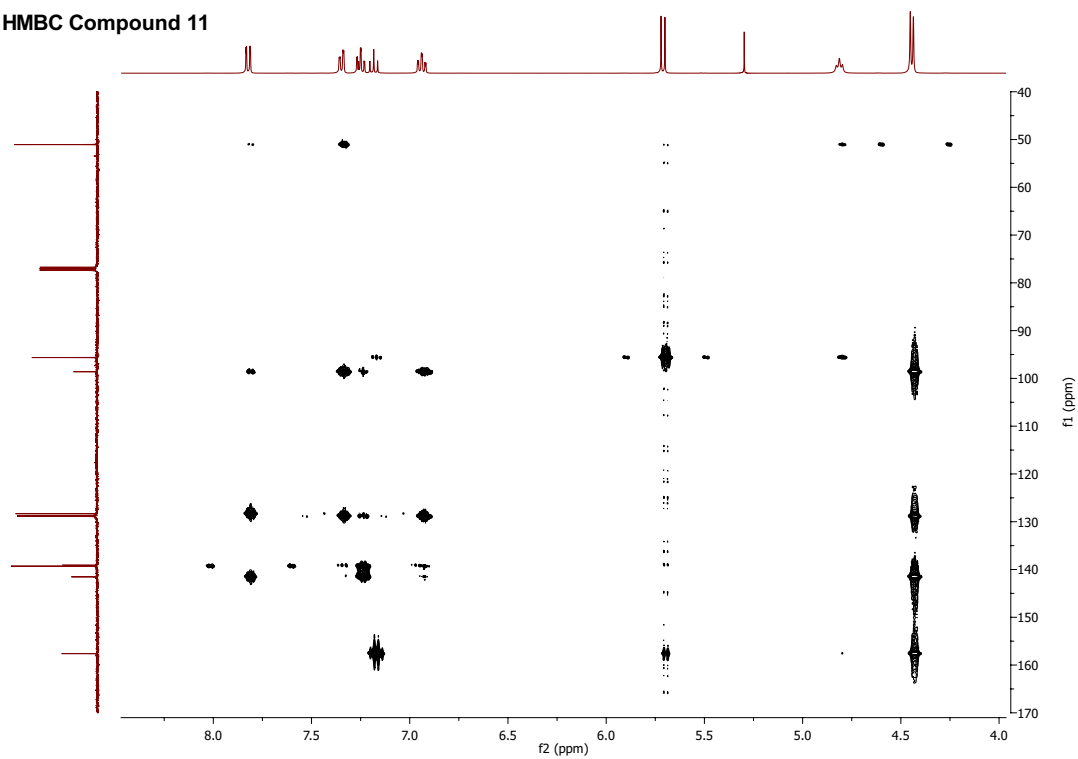
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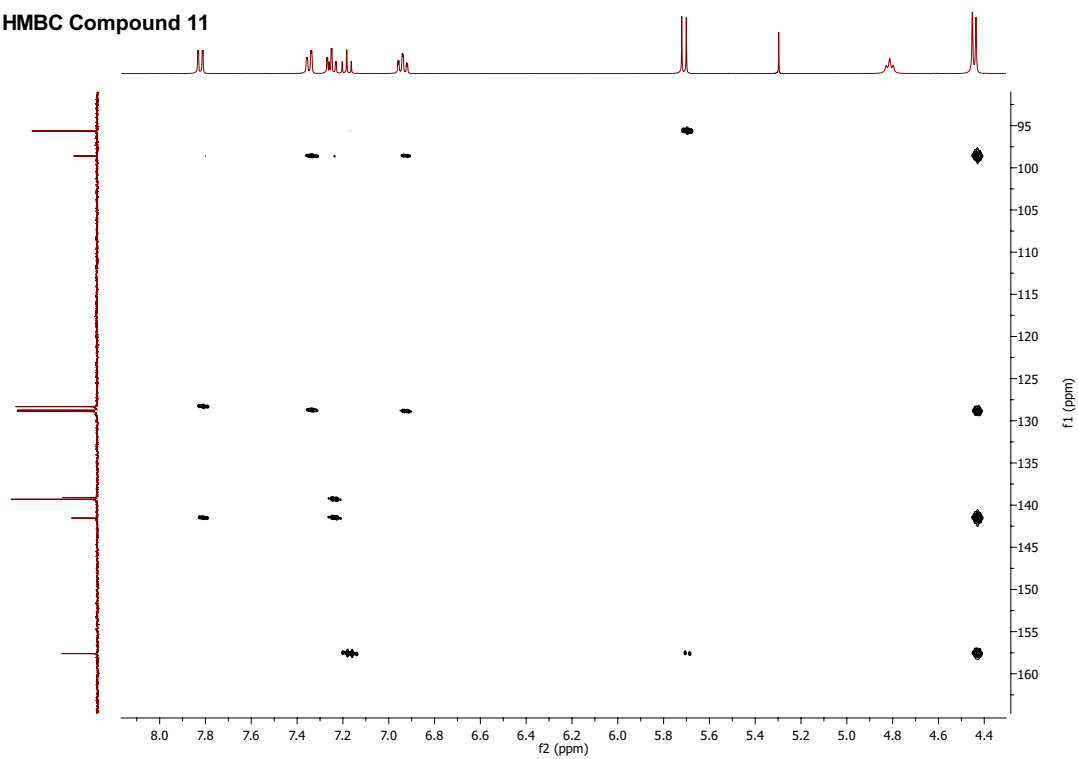
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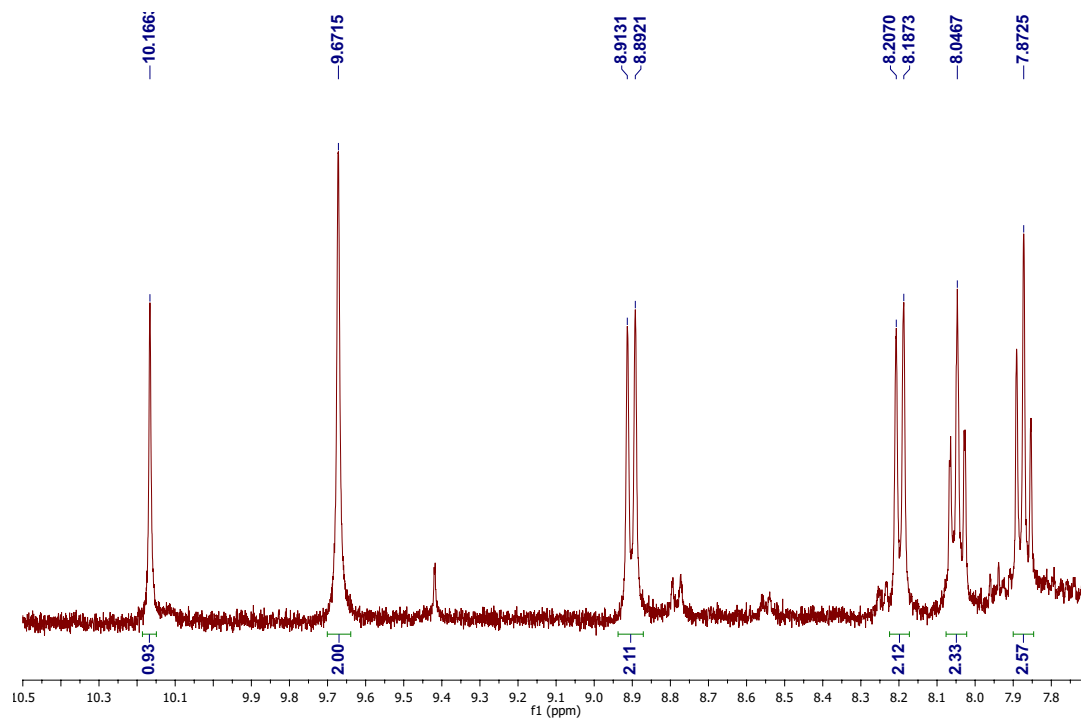
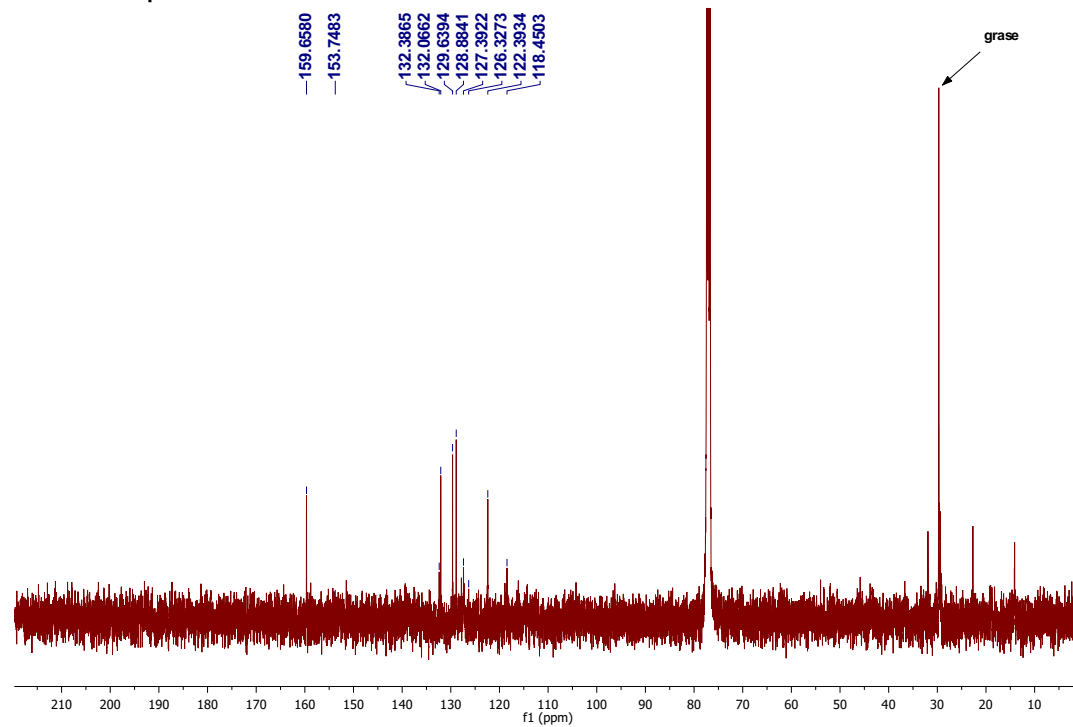
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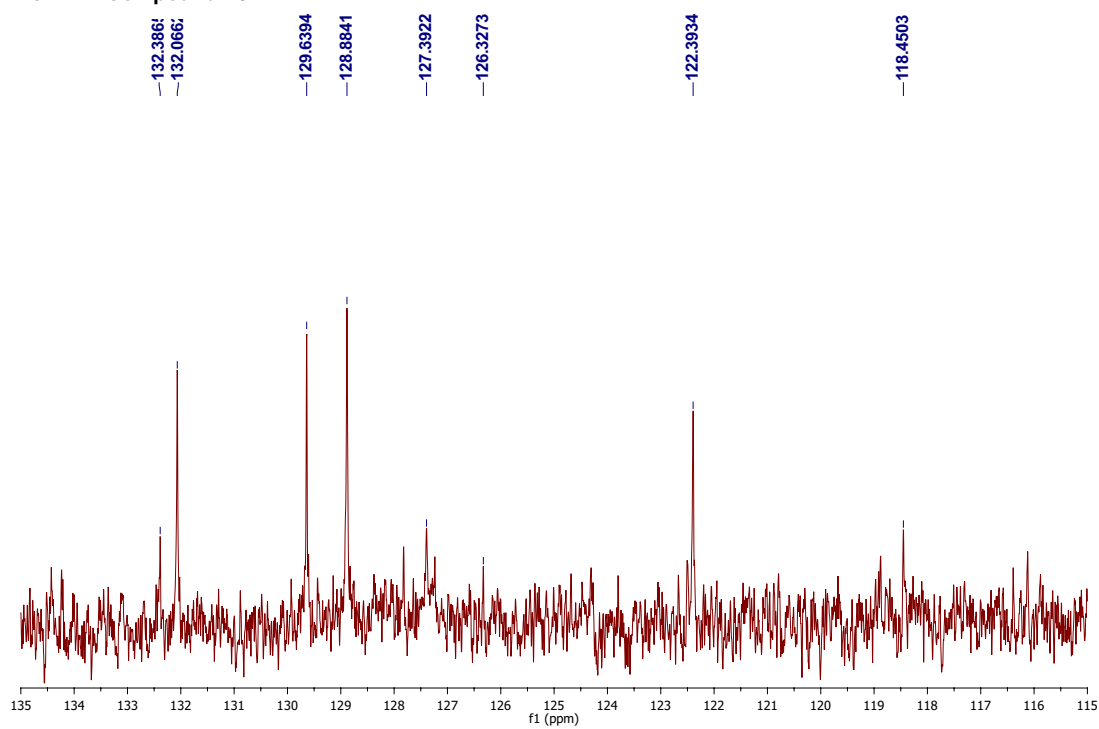
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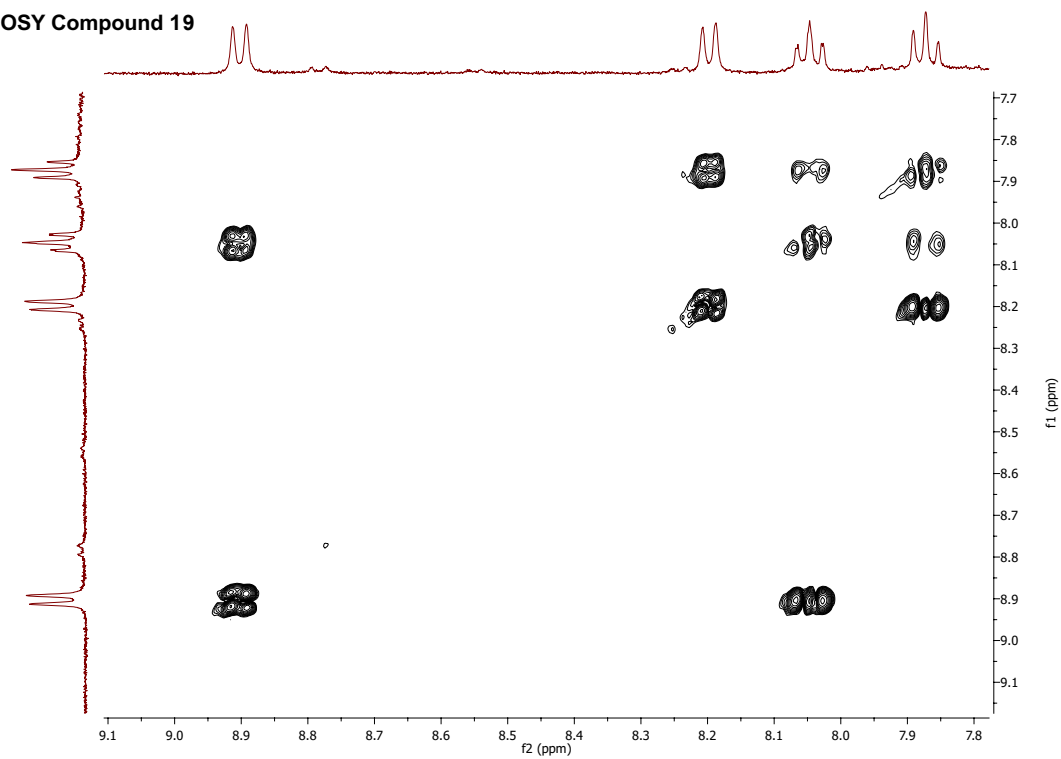
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¹H-NMR Compound 19¹³C-NMR Compound 19

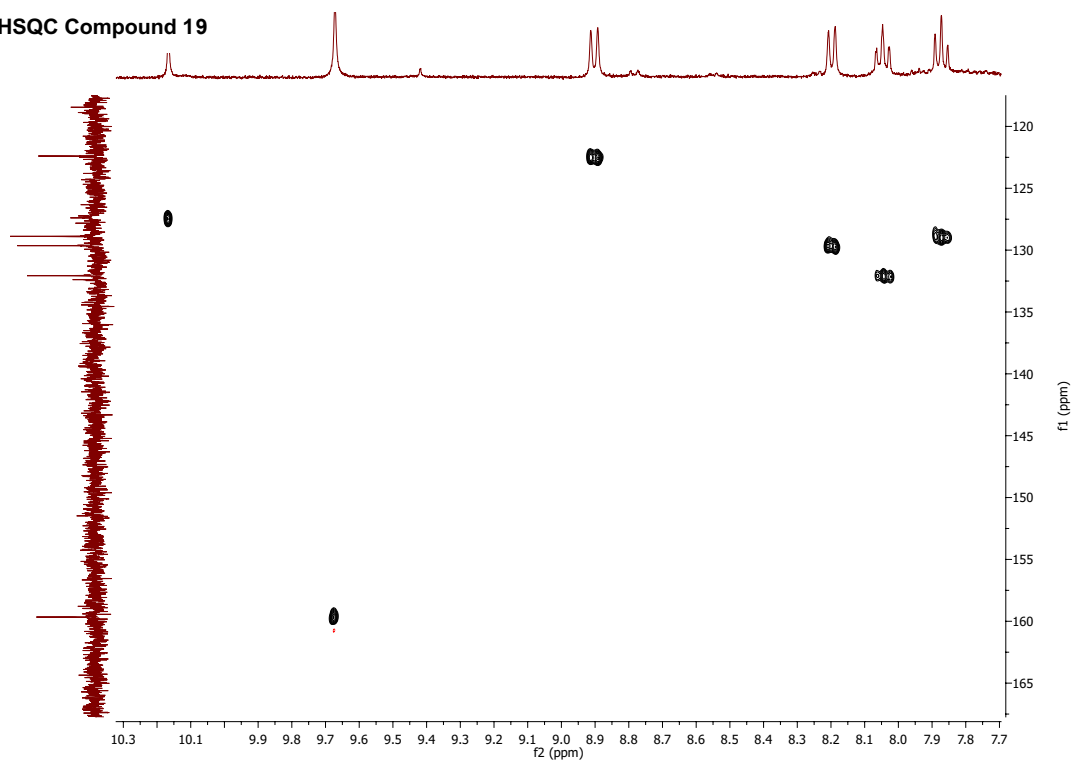
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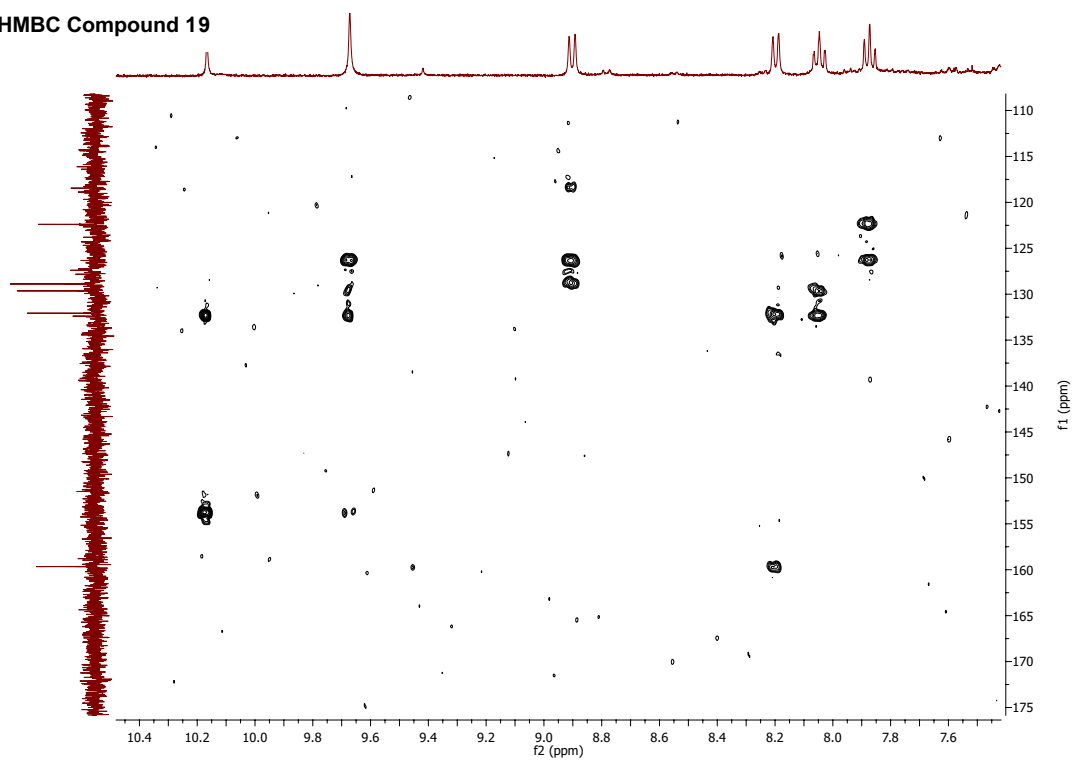
COSY Compound 19



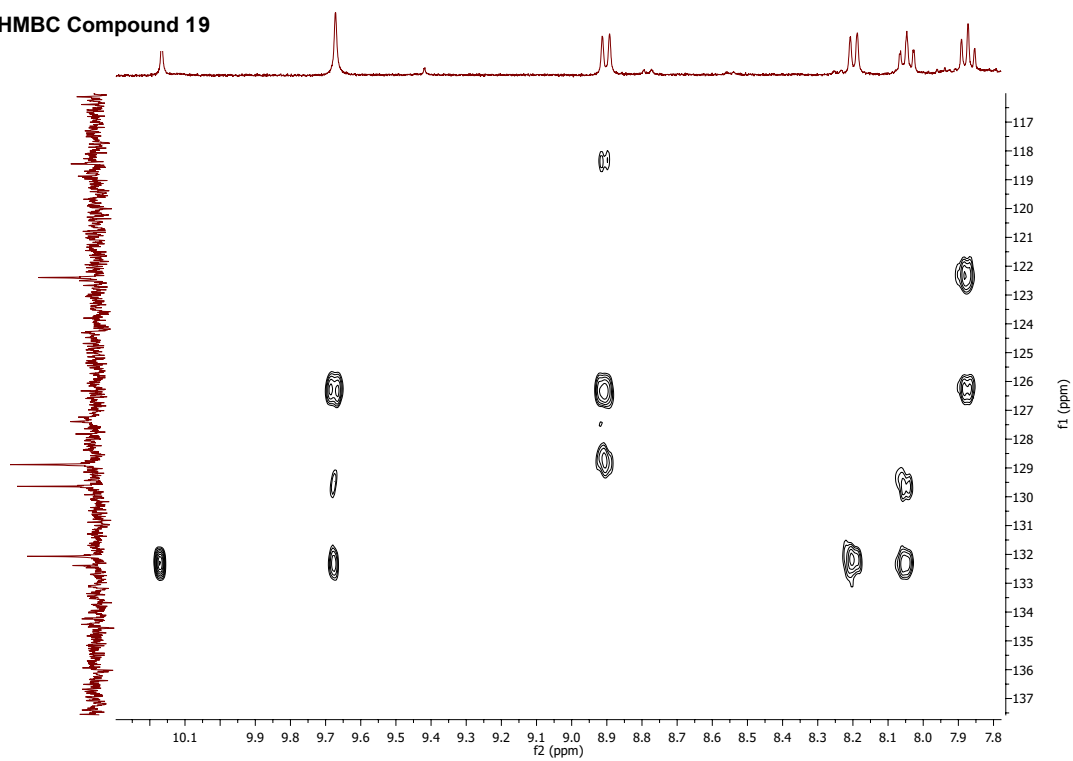
HSQC Compound 19

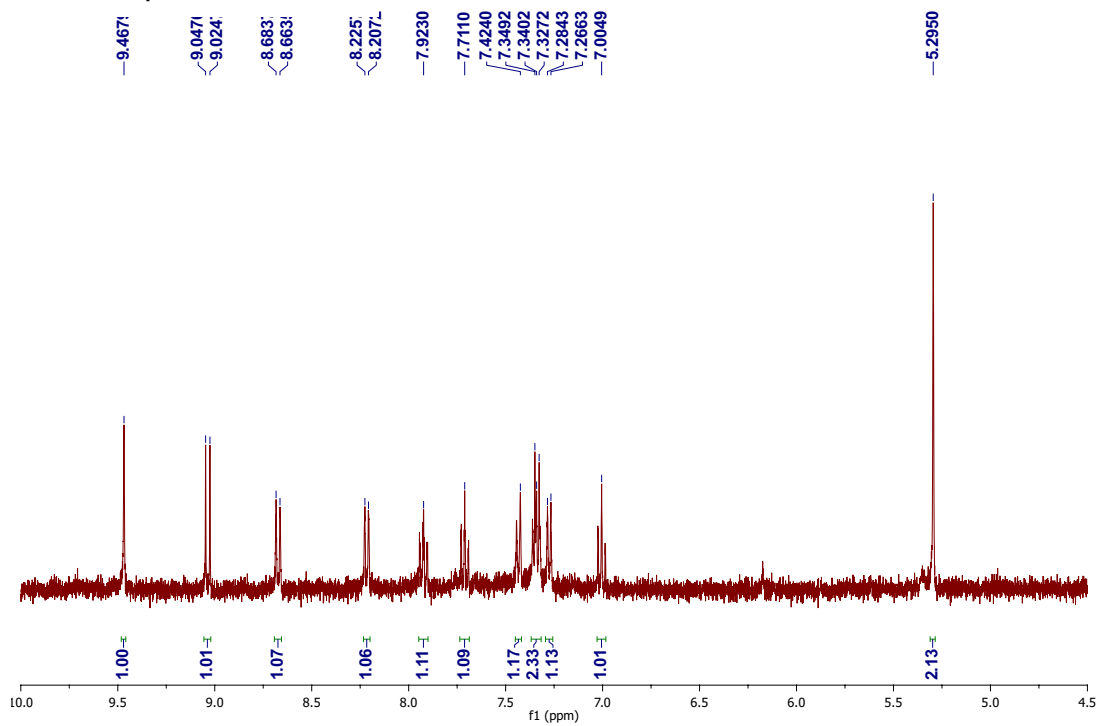
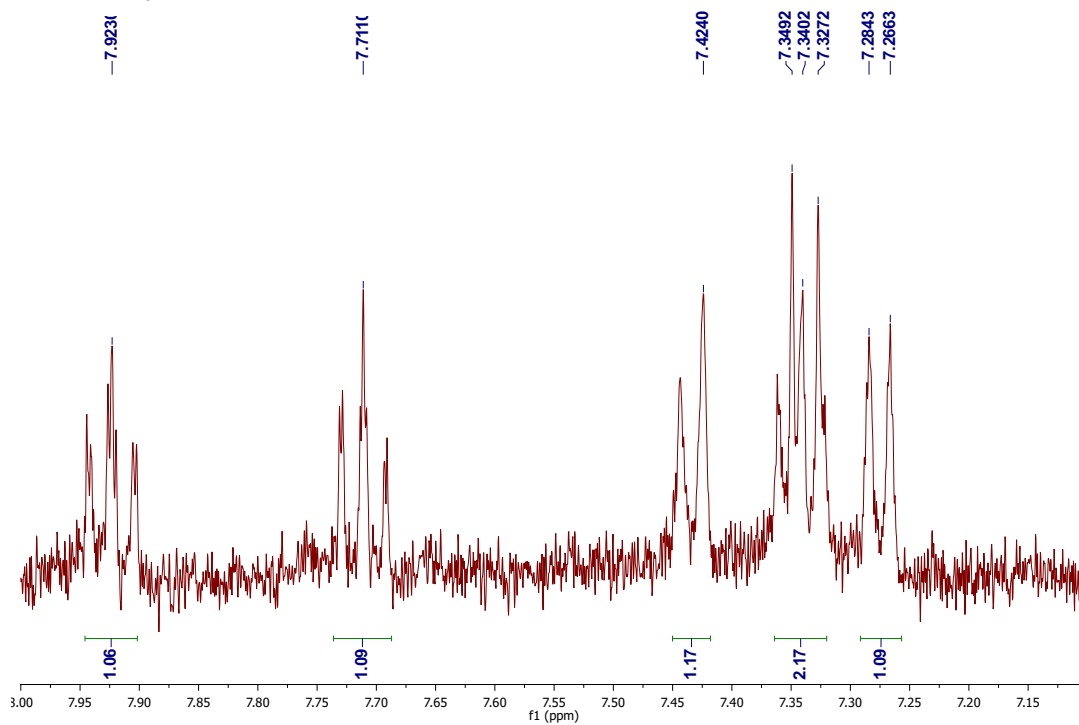


HMBC Compound 19

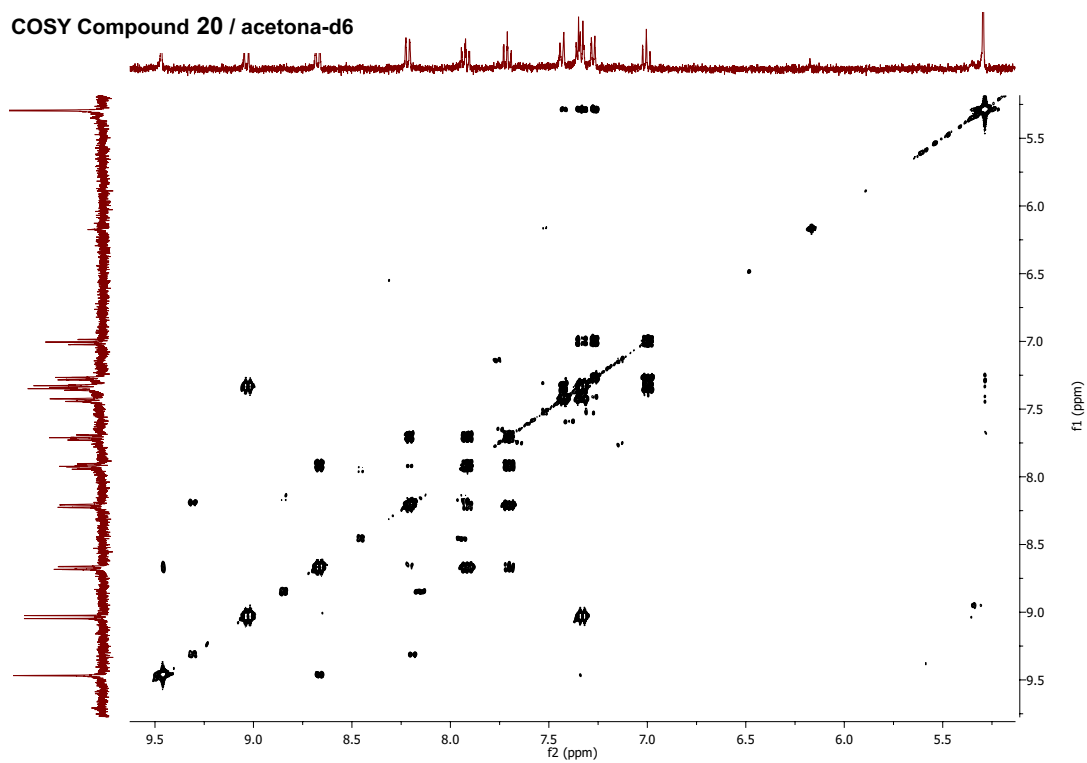


HMBC Compound 19

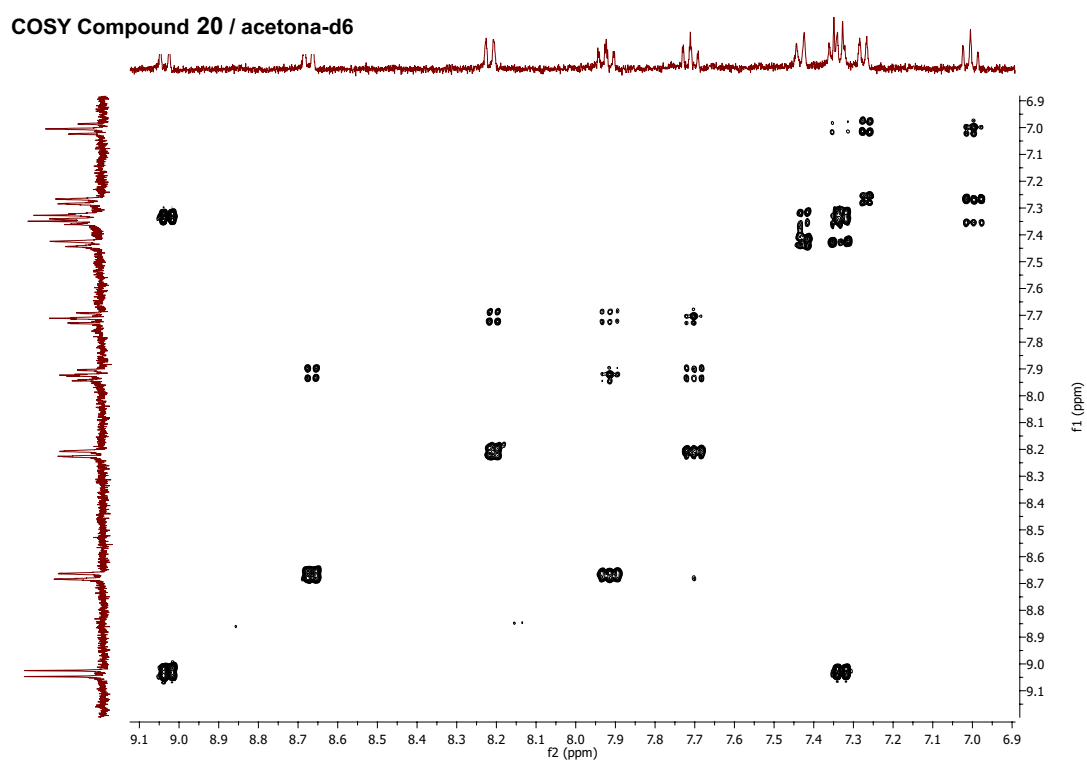


¹H-NMR Compound 20 / acetona-d₆¹H-NMR Compound 20 / acetona-d₆

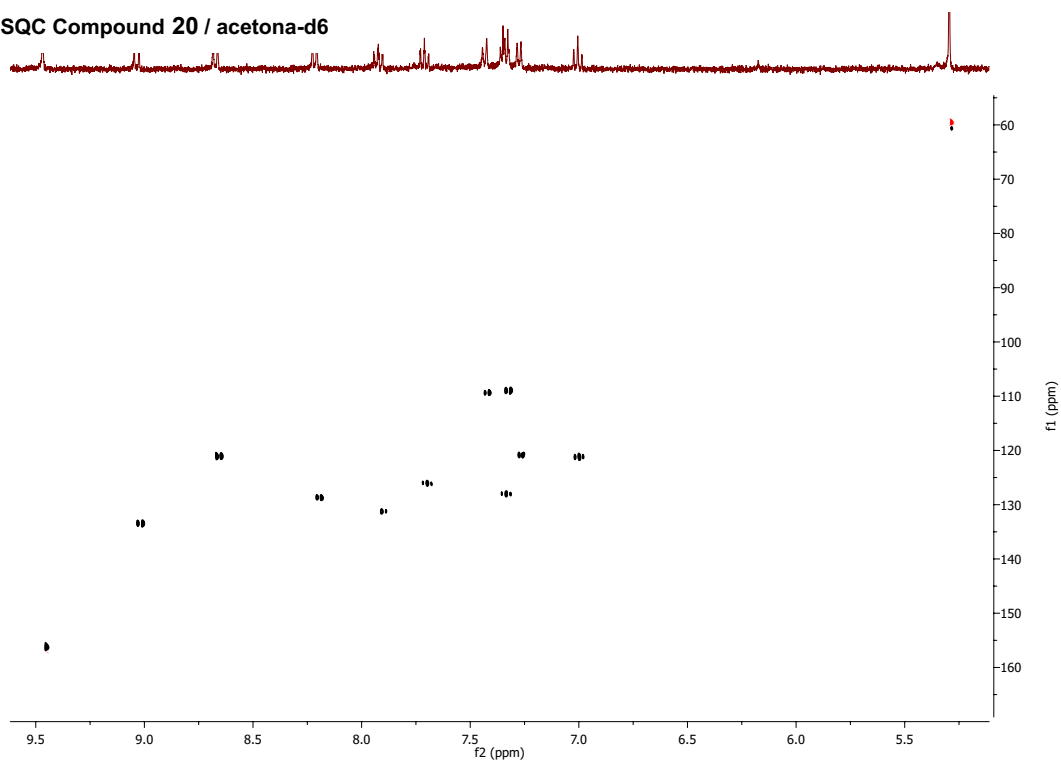
COSY Compound 20 / acetona-d6



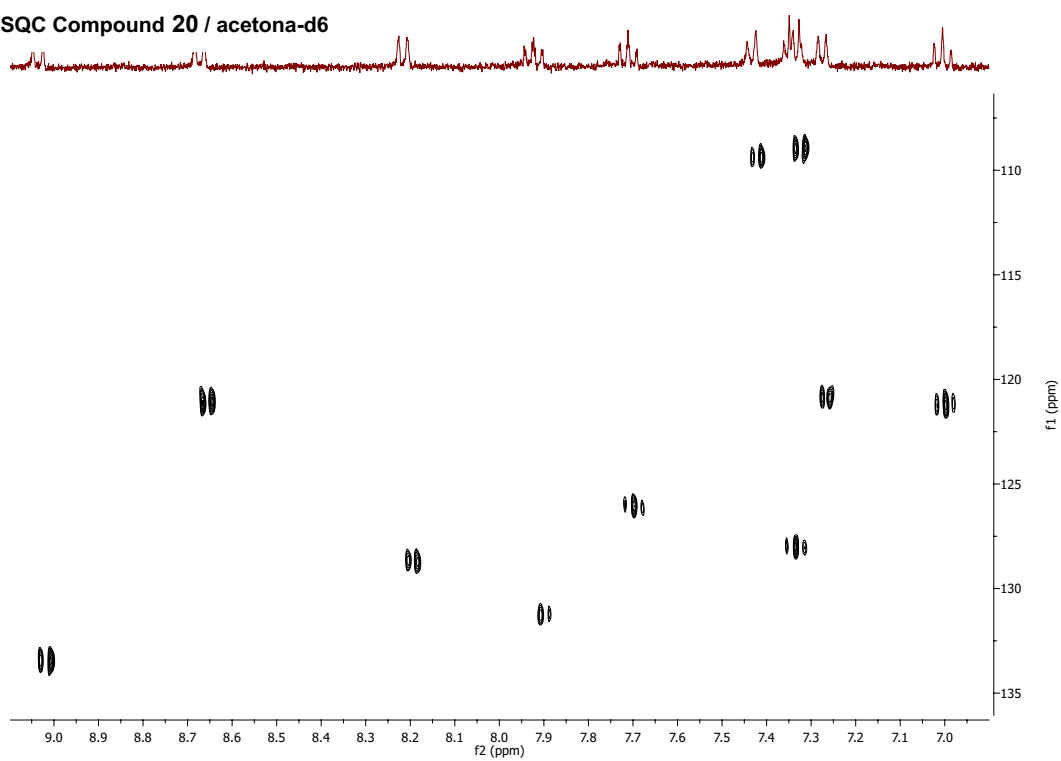
COSY Compound 20 / acetona-d6



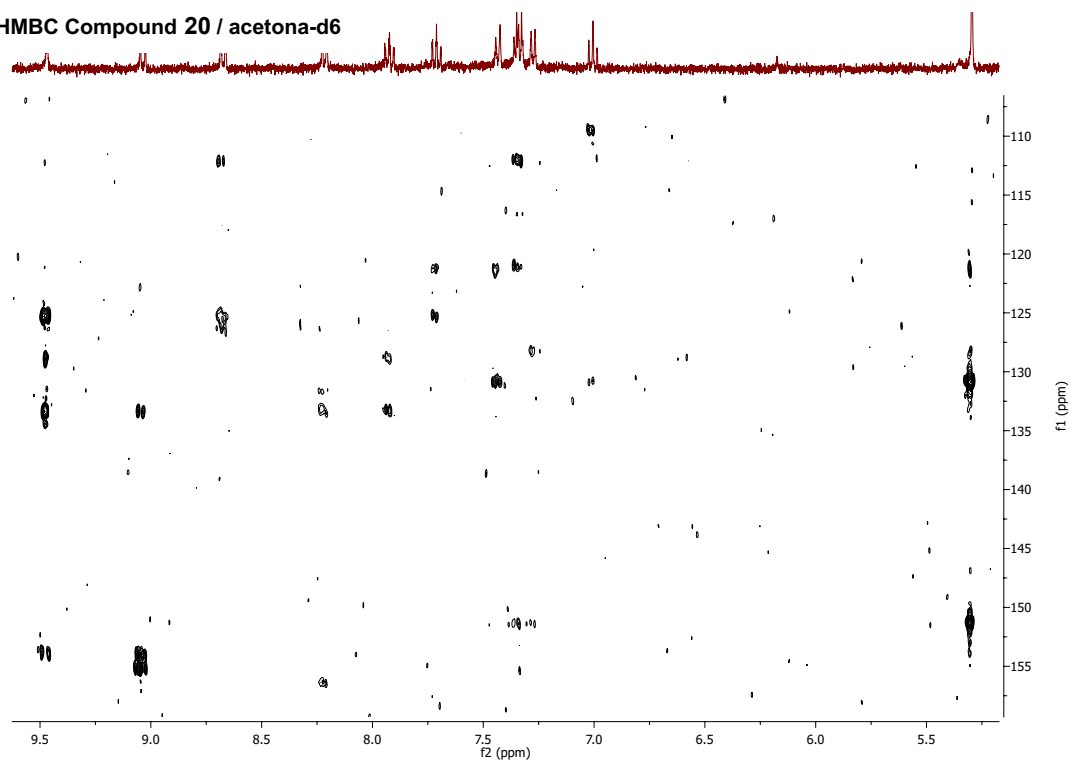
HSQC Compound 20 / acetona-d6



HSQC Compound 20 / acetona-d6

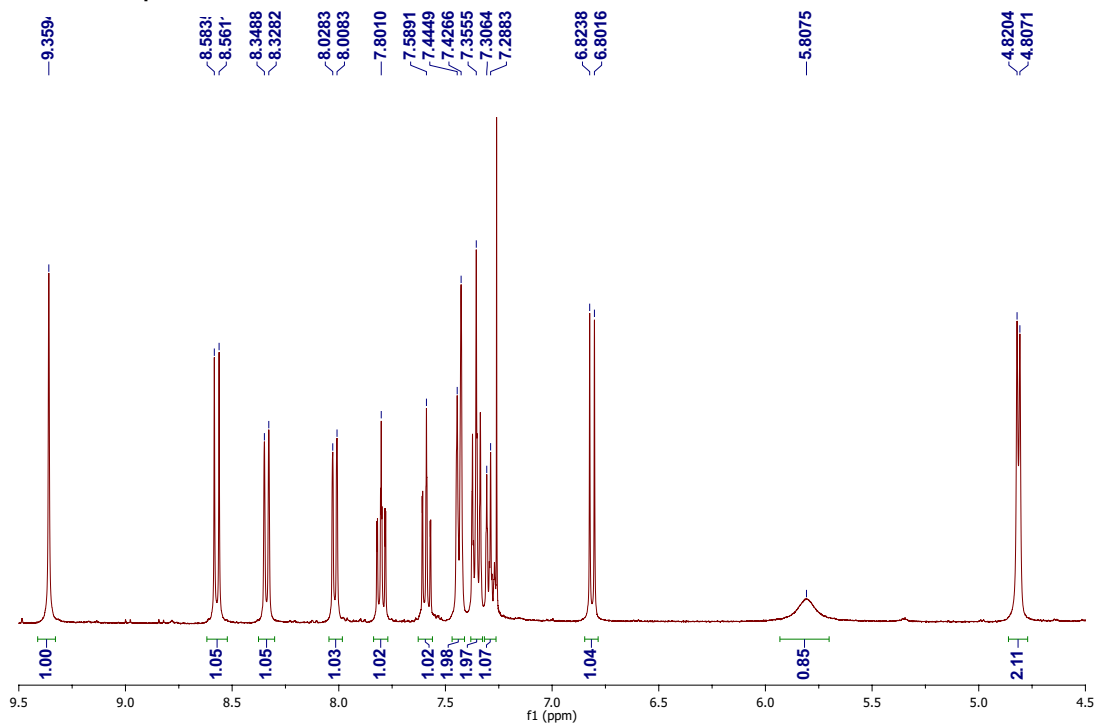


HMBC Compound 20 / acetona-d6

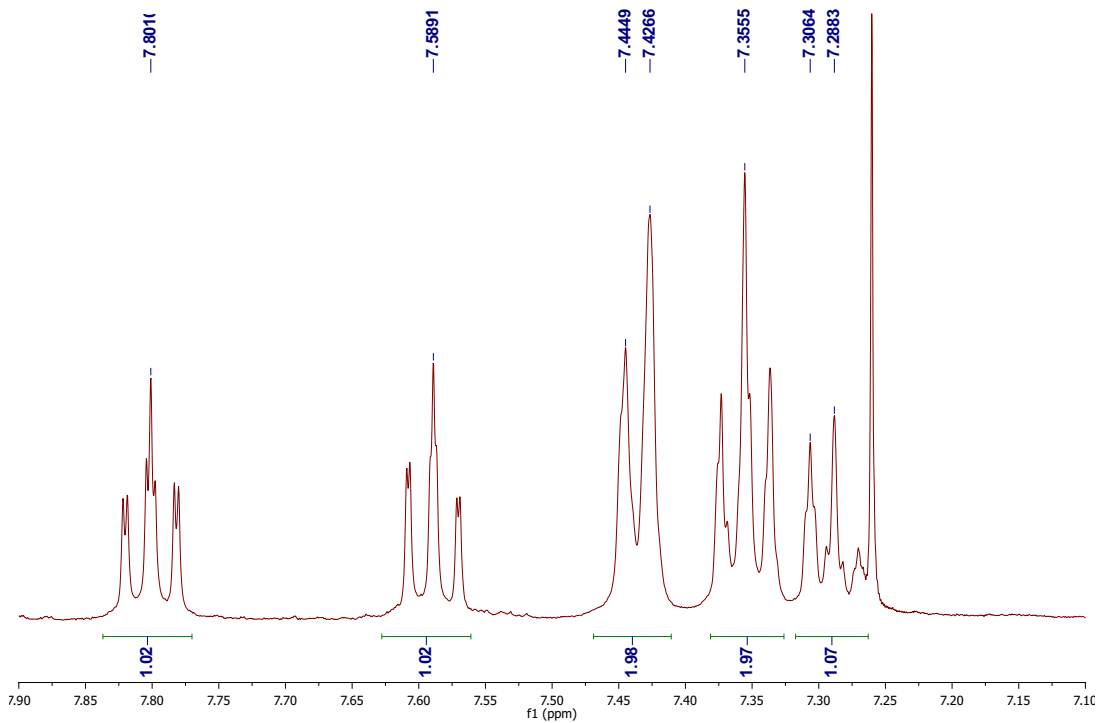


21

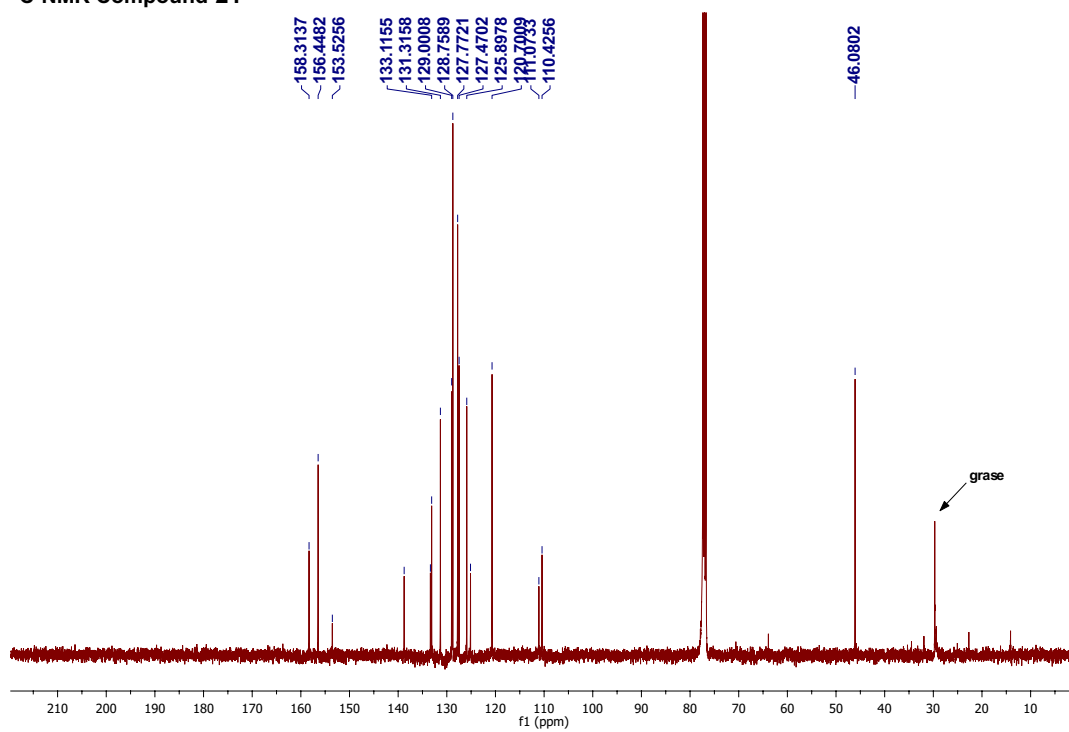
¹H-NMR Compound 21



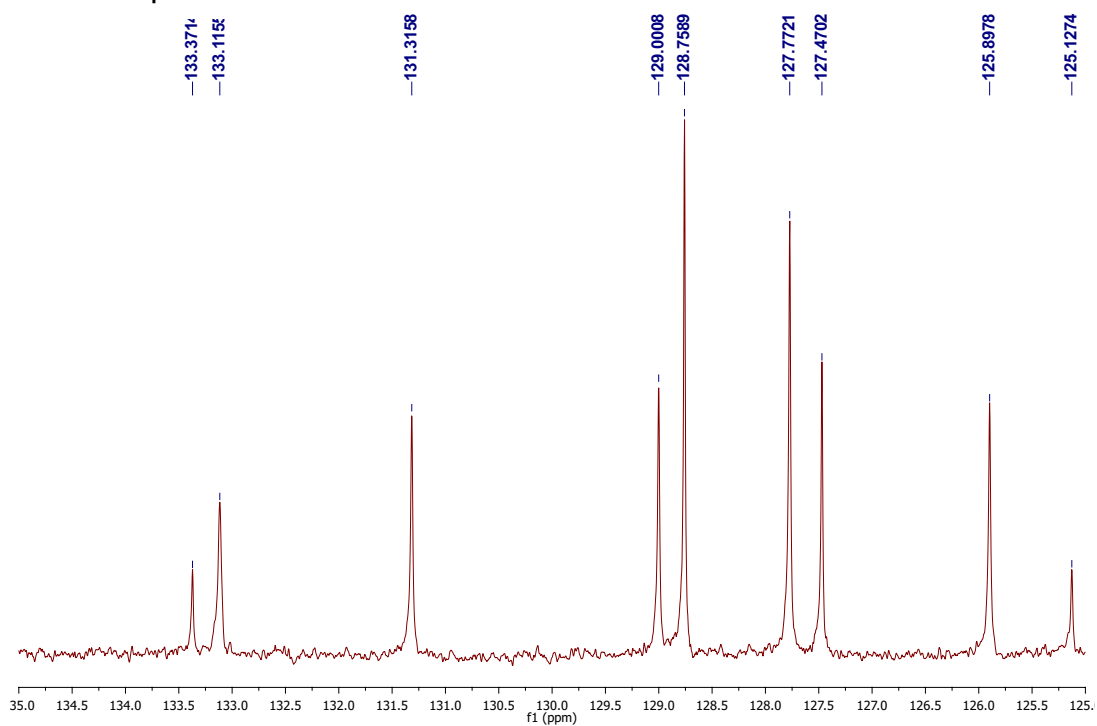
¹H-NMR Compound 21



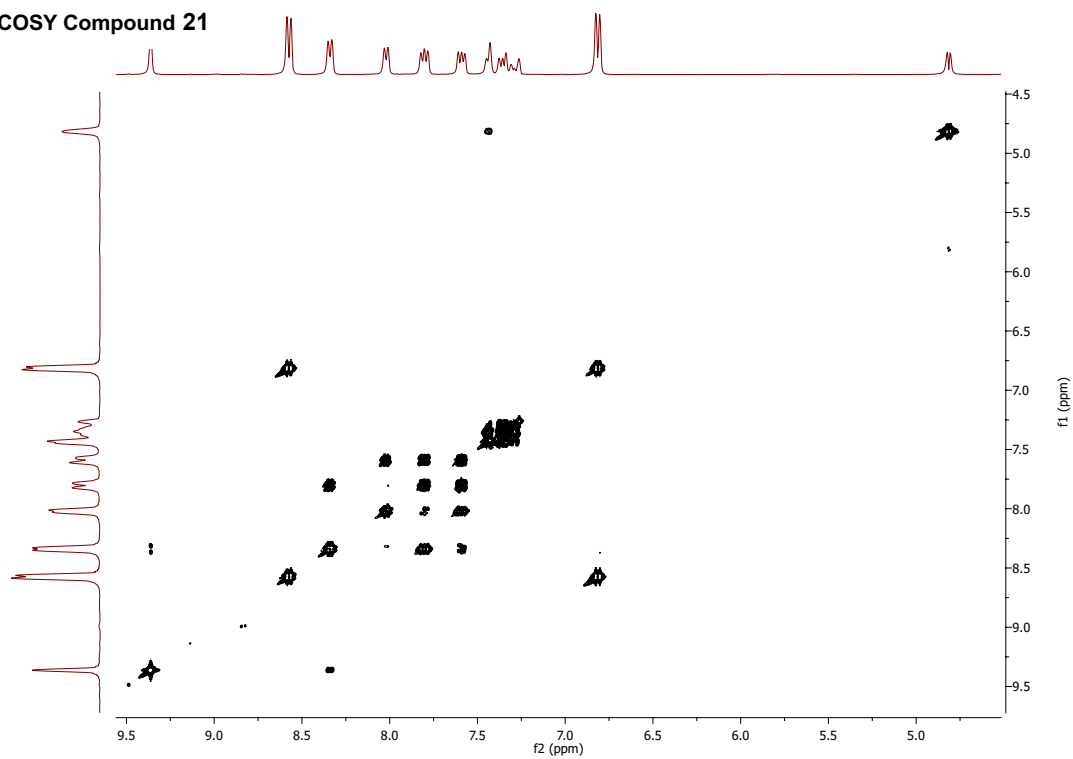
¹³C-NMR Compound 21



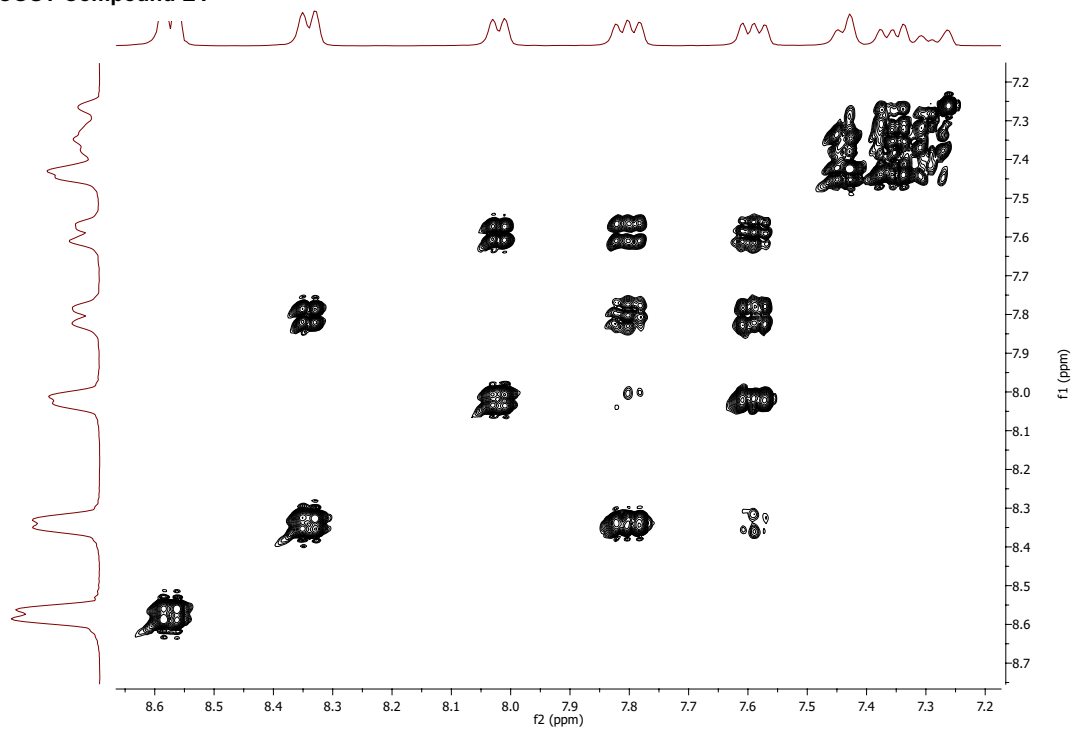
¹³C-NMR Compound 21



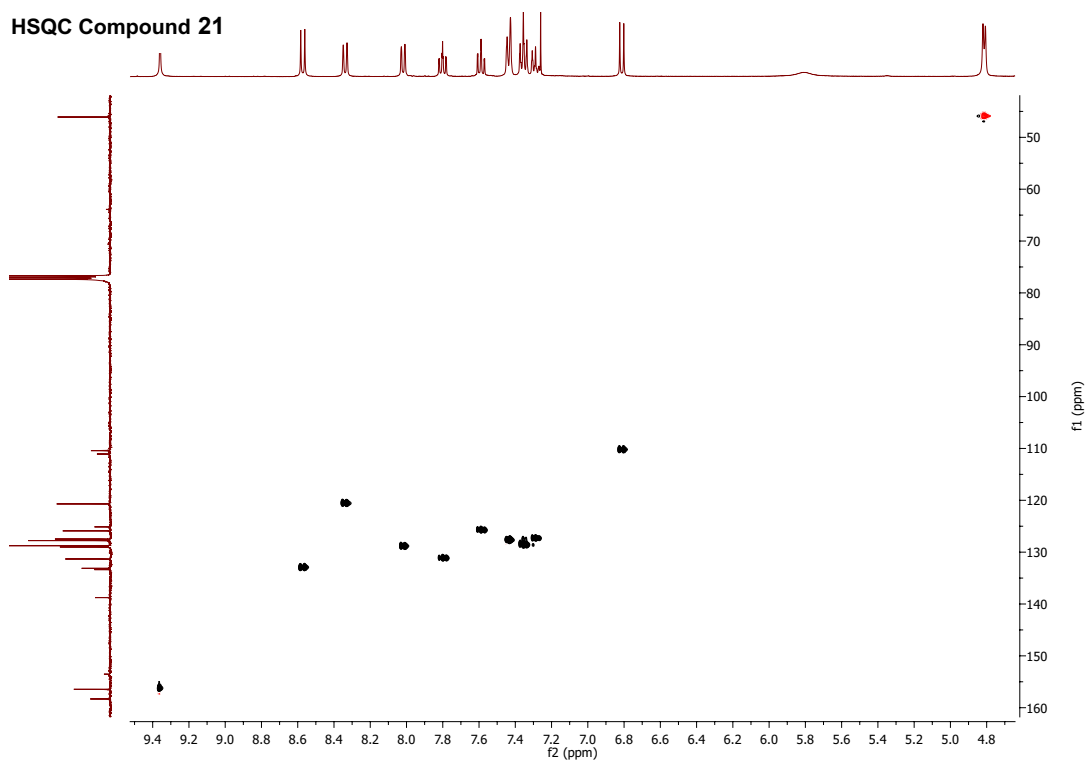
COSY Compound 21



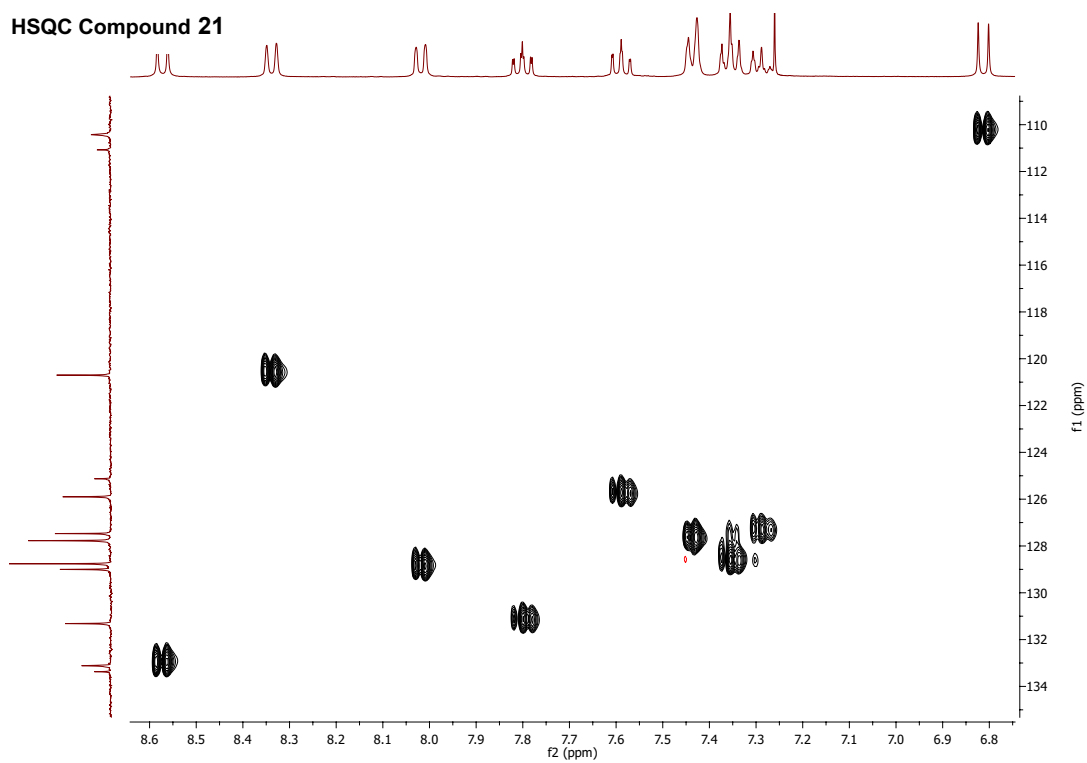
COSY Compound 21



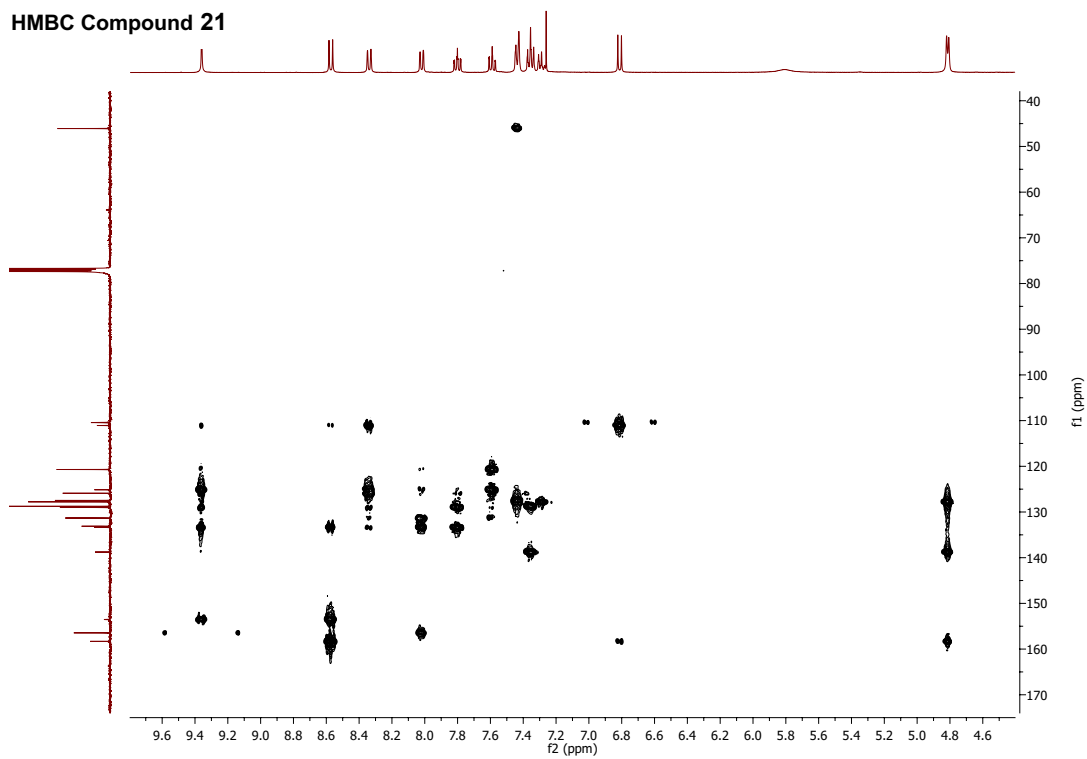
HSQC Compound 21



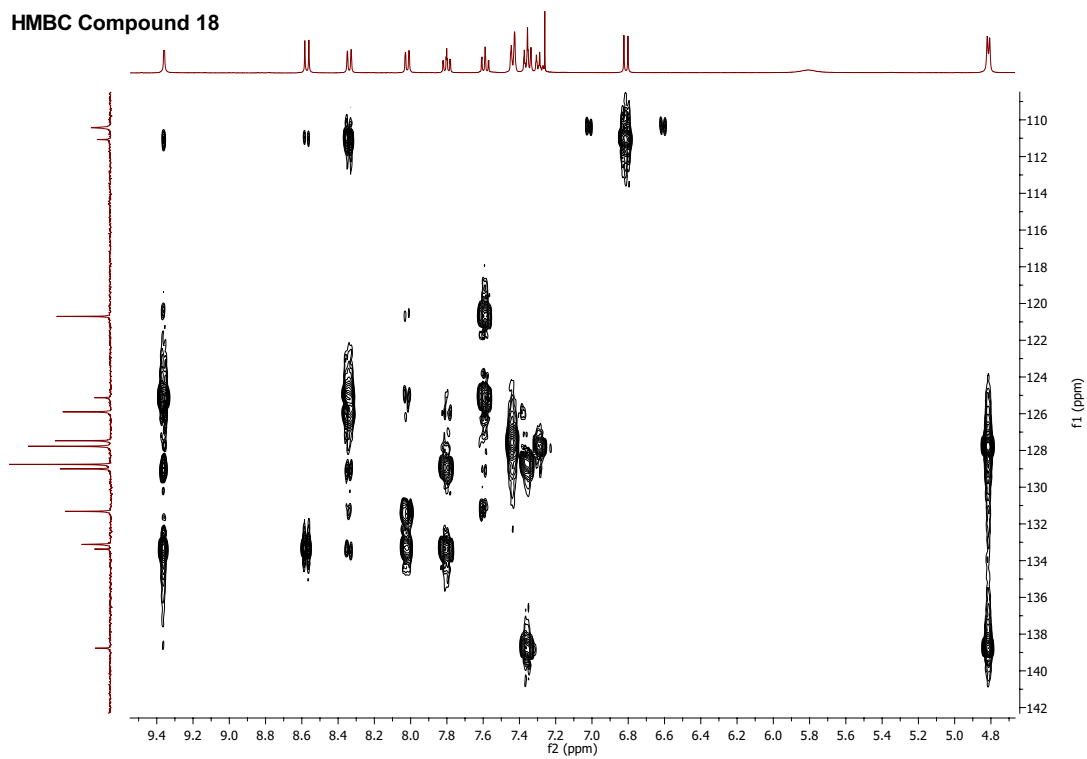
HSQC Compound 21



HMBC Compound 21



HMBC Compound 18



XYZ COORDINATES OF THE SOLUTION PHASE STRUCTURES

Coordinates in Angstrom, energies in kcal/mol

26 *s-cis*^{•-}

minima

B3LYP/6-31++G**, -552865.87

xyz coordinates:

C	0.358870	-0.394526	6.213356
N	0.292780	-1.470631	5.224886
C	-0.850529	-1.613904	4.470403
C	-1.644024	-0.464504	4.170739
C	-1.148005	0.855273	4.628333
C	-0.133737	0.899790	5.608823
C	0.371464	2.128526	6.044525
C	-1.618222	2.070006	4.095264
C	-1.118239	3.293009	4.542630
C	-0.120552	3.327381	5.522940
C	-1.216868	-2.873819	3.935373
C	-2.354902	-3.010093	3.173941
C	-3.221116	-1.895326	2.901041
C	-2.806910	-0.625077	3.424716
N	-4.325942	-2.136380	2.175659
C	-5.266798	-1.056287	1.934498
C	-5.018353	-0.193411	0.678033
C	-3.877871	-0.420649	-0.109957
C	-3.640243	0.355861	-1.254732

C	-4.552590	1.357253	-1.593667
C	-5.687842	1.559867	-0.783157
C	-5.985091	0.804873	0.375838
H	-0.249162	-0.650211	7.100165
H	0.734338	-2.336623	5.513170
H	1.154863	2.145865	6.799253
H	-2.370787	2.065020	3.312904
H	-1.498917	4.217566	4.116551
H	0.278260	4.277121	5.869139
H	-0.591038	-3.738453	4.145711
H	-2.639721	-3.980570	2.776591
H	-3.416047	0.245365	3.213119
H	-6.255974	-1.518753	1.815616
H	-5.356309	-0.379603	2.799783
H	-3.167777	-1.200700	0.161161
H	-2.755551	0.176706	-1.864159
H	-4.385040	1.973555	-2.478664
H	-6.372668	2.356591	-1.093853
H	1.395277	-0.295539	6.547073

TS

B3LYP/6-31++G**, -552862.03, 1 imaginary freq

xyz coordinates:

C	0.069901	-0.012992	-0.055239
C	0.030696	-0.015861	1.335796
C	1.199919	-0.007573	2.094777
C	2.438510	-0.013463	1.428497

C	2.494004	-0.018312	0.026992
C	1.311376	-0.019188	-0.720416
C	-1.615511	0.001853	3.090369
C	-0.969709	-1.088370	3.798510
N	0.325261	-1.115356	4.143328
C	1.134446	-0.026327	3.630297
C	-2.991110	-0.051059	2.733958
C	-3.716045	-1.240288	2.945804
C	-3.106688	-2.308004	3.640803
C	-1.796348	-2.229171	4.080357
N	-5.079041	-1.373080	2.521269
C	-5.426427	-0.502551	1.394642
C	-4.964715	0.926536	1.577343
C	-3.709129	1.126113	2.201731
C	-5.707011	2.014475	1.111476
C	-5.216470	3.319803	1.228926
C	-3.970569	3.528761	1.830378
C	-3.230138	2.447112	2.313303
H	-1.148604	0.975186	3.143619
H	-3.692965	-3.207031	3.823793
H	-1.343812	-3.063471	4.613012
H	-4.949251	-0.924225	0.495611
H	-6.508809	-0.550051	1.235834
H	-5.729262	-1.239798	3.296467
H	-2.276836	2.641027	2.795847
H	-3.575932	4.537044	1.932408
H	-5.797261	4.160012	0.856614

H	-6.672961	1.838174	0.640769
H	0.776435	0.966947	3.973678
H	2.152827	-0.131317	4.024603
H	3.365314	-0.013823	2.003838
H	3.458453	-0.024967	-0.476733
H	1.351588	-0.026804	-1.809129
H	-0.848321	-0.011175	-0.645121

26 *s-trans*^{•-}

minima

B3LYP/6-31++G**, -552866.68

xyz coordinates:

C	0.418631	-0.668223	6.600989
N	-0.942959	-1.185013	6.458690
C	-1.624609	-0.942499	5.285097
C	-1.345379	0.249430	4.546182
C	-0.371402	1.208527	5.118640
C	0.477348	0.776165	6.159767
C	1.390504	1.663294	6.737906
C	-0.284503	2.547539	4.694947
C	0.636958	3.424488	5.267615
C	1.481355	2.984339	6.292707
C	-2.633353	-1.823329	4.831322
C	-3.324619	-1.580477	3.660971
C	-3.036616	-0.422972	2.858349
C	-2.032963	0.467977	3.361367
N	-3.619548	-0.098379	1.689478

C	-4.641810	-0.991260	1.157925
C	-5.096010	-0.620309	-0.249373
C	-5.678762	0.649136	-0.438659
C	-6.132331	1.046046	-1.701276
C	-6.003132	0.155956	-2.774994
C	-5.425830	-1.107087	-2.559175
C	-4.944959	-1.561905	-1.302916
H	0.716369	-0.764982	7.648510
H	-1.086256	-2.105399	6.859294
H	2.036429	1.315668	7.541361
H	-0.950590	2.915782	3.920633
H	0.686283	4.453825	4.922166
H	2.195100	3.665459	6.748287
H	-2.853032	-2.714540	5.415940
H	-4.082292	-2.287750	3.342229
H	-1.824668	1.346859	2.758830
H	-4.283580	-2.033046	1.125983
H	-5.509520	-0.985292	1.845890
H	-5.778471	1.336686	0.403344
H	-6.581195	2.028183	-1.842851
H	-6.351929	0.445801	-3.767710
H	-5.350612	-1.766299	-3.430658
H	1.123700	-1.272639	6.001765

TS

B3LYP/6-31++G**, -552862.87, 1 imaginary freq

xyz coordinates:

C	-0.016186	0.019976	-0.002694
C	0.019514	-0.017293	1.402691
C	1.255910	-0.021927	2.047060
C	2.443678	-0.013093	1.320343
C	2.408610	0.025383	-0.087266
C	1.173943	0.041675	-0.745125
C	-1.283762	-0.022167	2.220583
N	-1.324306	1.030536	3.214758
C	-0.385163	0.957107	4.173811
C	0.535584	-0.153018	4.354841
C	1.504940	-0.114110	5.379698
C	1.676831	1.007596	6.184393
C	0.782419	2.115747	6.046081
C	-0.211213	2.061602	5.067366
C	0.931073	3.245784	6.987037
C	2.137160	3.368227	7.717112
C	3.233159	2.361724	7.453983
N	2.637389	1.042662	7.222976
C	-0.080391	4.201136	7.212297
C	0.105646	5.252888	8.111010
C	1.305927	5.369057	8.821198
C	2.312233	4.417736	8.622753
H	-2.130519	0.109378	1.535087
H	3.246249	4.493040	9.176589
H	1.452951	6.182373	9.527189
H	-0.691987	5.975913	8.264663
H	-1.028586	4.115862	6.689484

H	3.832880	2.688945	6.581112
H	3.910888	2.296194	8.310596
H	-0.883799	2.904546	4.930010
H	2.148885	-0.980243	5.532232
H	0.283351	-1.119132	3.936969
H	1.134166	0.073367	-1.832116
H	-0.974920	0.031548	-0.523467
H	-1.406635	-1.032624	2.664762
H	3.412402	-0.029199	1.824340
H	3.334995	0.045766	-0.660689
H	3.348488	0.327085	7.103428

27 *s-cis*^{•-}

minima

B3LYP/6-31++G**, -552896.55

xyz coordinates:

C	-0.714335	0.396792	0.516496
C	-0.623300	-0.971616	0.825170
C	0.616111	-1.652291	0.852520
C	1.907916	-0.844409	0.586613
C	1.729808	0.648573	0.363700
C	0.433084	1.185912	0.294991
C	2.862842	1.540491	0.492920
C	2.698765	2.920403	0.158831
C	1.394249	3.282003	-0.504950
N	0.239792	2.587511	0.074794
C	4.141046	1.146344	0.976086

C	5.165798	2.075972	1.163304
C	4.969397	3.433072	0.874524
C	3.723190	3.838982	0.366766
N	0.702562	-2.958201	1.070499
C	2.051741	-3.519913	0.965740
C	2.782909	-3.003509	-0.254872
C	2.690068	-1.617741	-0.480046
C	3.459591	-3.817862	-1.168670
C	4.055149	-3.257273	-2.305738
C	3.955270	-1.880627	-2.534142
C	3.269961	-1.064056	-1.624790
H	2.504216	-0.975667	1.514030
H	-1.689571	0.874402	0.443093
H	-1.526867	-1.553101	1.001083
H	1.441033	2.993501	-1.568484
H	1.207500	4.360696	-0.471971
H	-0.097774	3.055448	0.914810
H	4.333160	0.104044	1.213092
H	6.128285	1.736064	1.541790
H	5.768742	4.155024	1.021942
H	3.558501	4.884691	0.107409
H	2.644493	-3.270020	1.870026
H	1.983506	-4.613727	0.940254
H	3.515781	-4.891696	-0.997103
H	4.583894	-3.892248	-3.012939
H	4.407553	-1.441282	-3.420489
H	3.187936	0.004314	-1.804293

27 *s-trans*^{•-}

minima

B3LYP/6-31++G**, -552898.64

xyz coordinates:

C	0.062167	0.365699	-0.034258
C	0.041780	0.080555	1.334665
C	1.246317	0.005495	2.056804
C	2.459950	0.220474	1.395837
C	2.478542	0.491930	0.020866
C	1.280324	0.563211	-0.696870
C	-1.224844	-0.110755	2.140279
N	-1.201596	0.620768	3.407268
C	-0.070231	0.525635	4.099988
C	1.095300	-0.317059	3.543718
C	2.353084	-0.237217	4.365120
C	2.420325	0.410268	5.563841
C	1.289465	1.151217	6.104794
C	0.097834	1.179065	5.341146
C	1.420839	1.771745	7.407546
C	2.717622	1.932804	7.983151
C	3.901093	1.518618	7.145054
N	3.568402	0.307346	6.387523
C	0.316018	2.243814	8.171465
C	0.493826	2.834401	9.421647
C	1.774832	2.973699	9.975429
C	2.878932	2.510643	9.239175
H	-2.098545	0.206693	1.558528

H	3.883341	2.614517	9.648515
H	1.913170	3.425845	10.954151
H	-0.377365	3.178855	9.976176
H	-0.692557	2.127210	7.784965
H	4.180526	2.347921	6.464007
H	4.771423	1.308285	7.775293
H	-0.750624	1.761797	5.692785
H	3.213350	-0.813604	4.025237
H	0.725791	-1.366786	3.557706
H	1.292315	0.780379	-1.762483
H	-0.874916	0.437305	-0.584317
H	-1.362393	-1.196464	2.328992
H	3.393604	0.183322	1.950495
H	3.427793	0.654088	-0.484857
H	4.369597	-0.042757	5.869462

32 *s-cis*^{•-}

minima

B3LYP/6-31++G**, -562953.22

xyz coordinates:

C	4.002719	-0.255723	0.252803
C	5.278413	0.269490	0.462882
C	5.555791	1.616617	0.197245
C	4.527335	2.440586	-0.274966
C	3.243489	1.928413	-0.471366
C	2.950353	0.569661	-0.220056
N	2.342709	-1.900661	0.948008

C	3.708252	-1.726279	0.447012
C	1.622304	-0.019685	-0.390866
C	1.324888	-1.269111	0.223520
N	0.137990	-1.864840	0.222359
C	0.529419	0.590064	-1.044171
C	-0.720062	0.005562	-1.065424
C	-0.943231	-1.267064	-0.408322
N	-2.094679	-1.932448	-0.360601
C	-3.230735	-1.365801	-1.050768
C	-4.011310	-0.273721	-0.298994
C	-4.488383	1.059223	1.698297
C	-3.732372	0.083250	1.034824
C	-5.069542	0.409323	-0.869040
C	-5.852302	1.378803	-0.280308
C	-5.545789	1.710488	1.054579
H	6.068235	-0.383623	0.830753
H	6.553616	2.014933	0.361791
H	4.721112	3.491560	-0.478226
H	2.456855	2.596420	-0.811927
H	2.101986	-2.863258	1.165122
H	4.402959	-2.170145	1.166532
H	3.847190	-2.259769	-0.514172
H	0.668033	1.547260	-1.544190
H	-1.536532	0.512253	-1.568274
H	-2.981904	-0.962162	-2.050089
H	-3.947374	-2.178671	-1.240787
H	-4.246136	1.313797	2.727412

H	-2.908573	-0.416529	1.538493
H	-6.667831	1.870953	-0.805470
H	-6.129194	2.468045	1.573370

TS

B3LYP/6-31++G**, -562951.26, 1 imaginary freq

xyz coordinates:

C	-0.013740	0.005505	-0.005505
C	0.004206	-0.008918	1.399808
C	1.239159	-0.011931	2.040169
C	2.440278	-0.031163	1.345153
C	2.414937	-0.018106	-0.062863
C	1.186304	0.001272	-0.732119
C	0.588682	-0.273475	4.269937
C	-0.335222	0.862809	4.194157
N	-1.283261	0.986666	3.283956
C	-1.287782	-0.008959	2.224699
C	1.572173	-0.285089	5.263399
C	1.773232	0.819361	6.108836
C	0.818223	1.877025	5.968211
N	-0.182777	1.900305	5.096620
C	2.757605	0.885992	7.191890
C	2.951929	2.118939	7.864890
C	2.208808	3.330392	7.351625
N	0.883010	2.940073	6.869053
C	3.514287	-0.225537	7.626126
C	4.426749	-0.115125	8.676209

C	4.603804	1.106486	9.336830
C	3.856429	2.216176	8.923638
H	-0.965912	0.020482	-0.536726
H	1.159194	0.015999	-1.819498
H	3.346064	-0.019249	-0.627721
H	3.397928	-0.048173	1.866887
H	-1.450224	-1.035140	2.611671
H	2.199233	-1.168094	5.362127
H	2.796059	3.807217	6.542708
H	3.382607	-1.190809	7.145470
H	4.993803	-0.989965	8.986532
H	5.307069	1.193879	10.160869
H	3.985005	3.173134	9.426764
H	0.287903	-1.220030	3.836780
H	2.085280	4.075174	8.143516
H	-2.134333	0.195845	1.558467
H	0.301349	3.718180	6.573333

32 *s-trans*^{•-}

minima

B3LYP/6-31++G**, -562954.59

xyz coordinates:

C	-3.375454	-1.196637	-0.096603
C	-4.664386	-1.730054	-0.089029
C	-5.774220	-0.929817	0.213477
C	-5.574166	0.425700	0.499987
C	-4.289723	0.973039	0.477105

C	-3.158993	0.177779	0.184976
N	-1.136049	-1.308455	-1.051454
C	-2.157442	-2.063799	-0.322330
C	-1.793963	0.696673	0.125885
C	-0.786900	-0.060497	-0.524017
N	0.470470	0.338095	-0.731939
C	-1.378057	1.974564	0.587532
C	-0.094168	2.419454	0.392053
C	0.869856	1.590777	-0.305087
N	2.098054	2.060616	-0.502155
C	3.022146	1.223710	-1.235500
C	3.850019	0.243432	-0.391525
C	4.444173	-0.822419	1.732435
C	3.659822	0.074400	0.993703
C	4.857510	-0.535462	-0.931527
C	5.663876	-1.436067	-0.270062
C	5.444520	-1.580005	1.114739
H	-4.803662	-2.786709	-0.312499
H	-6.773949	-1.356298	0.219961
H	-6.423883	1.065179	0.729406
H	-4.166400	2.034227	0.676853
H	-0.313403	-1.852028	-1.295196
H	-2.414782	-2.954911	-0.902979
H	-1.766788	-2.410338	0.655191
H	-2.086177	2.612793	1.112820
H	0.226851	3.393451	0.752143
H	2.523431	0.630849	-2.019885

H	3.743319	1.877038	-1.749013
H	4.269684	-0.929774	2.800523
H	2.884950	0.662526	1.479127
H	6.435564	-2.011654	-0.776419
H	6.051226	-2.274776	1.691520

TS coupling

B3LYP/6-31++G**, -562944.24, 1 imaginary freq

xyz coordinates:

C	-0.020555	0.027968	0.021074
C	-0.016236	0.027925	1.416397
C	1.207582	0.040425	2.134679
C	2.407183	0.044846	1.389417
C	2.392475	0.027560	-0.006570
C	1.178338	0.022881	-0.703626
C	1.162955	0.077525	3.597301
C	-0.049452	0.427203	4.232841
N	-1.177811	0.700031	3.454003
C	-1.298488	-0.069387	2.212844
N	-0.181813	0.626033	5.571973
C	0.898046	0.321901	6.426040
C	2.126131	-0.124787	5.826667
C	2.257549	-0.203314	4.455452
N	0.784472	0.478755	7.731760
C	-0.533194	0.878674	8.210362
C	-1.112885	2.108619	7.534461
C	-0.788934	2.304908	6.188467

C	-1.406684	3.301740	5.426632
C	-2.324626	4.164447	6.053439
C	-2.604811	4.028713	7.418145
C	-1.990114	3.000015	8.158878
H	-0.972462	0.021717	-0.507738
H	1.163246	0.020683	-1.790417
H	3.333854	0.032169	-0.551719
H	3.362691	0.077414	1.906190
H	-2.029902	0.715560	4.004901
H	-1.514014	-1.134204	2.431270
H	-2.144043	0.323276	1.639932
H	3.206296	-0.523265	4.030734
H	2.947653	-0.384212	6.488887
H	-0.485987	1.032576	9.295922
H	-1.257297	0.053354	8.045360
H	-3.296710	4.711693	7.905735
H	-2.799835	4.958237	5.477654
H	-1.158250	3.442777	4.376742
H	-2.207140	2.893407	9.222231

32 *s-trans*^{•-} + NH_{3(l)}

minima

B3LYP/6-31++G**, -598434.10

xyz coordinates:

C	0.088352	-3.582878	1.134039
C	0.002210	-2.622814	2.141559
C	0.963311	-1.583572	2.236872

C	2.007517	-1.562613	1.286421
C	2.097297	-2.539314	0.291409
C	1.137078	-3.555667	0.203279
C	0.806387	-0.580891	3.285833
C	-0.435835	-0.459399	3.958253
N	-1.463404	-1.342225	3.612461
C	-1.056457	-2.694390	3.218240
N	-0.737256	0.478729	4.862438
C	0.214196	1.423232	5.198613
C	1.515546	1.364768	4.562071
C	1.783973	0.389053	3.634944
N	-0.018686	2.376525	6.091935
C	-1.350515	2.393678	6.671887
C	-1.487572	3.533301	7.663912
C	-2.410017	4.553883	7.539727
C	-2.579015	5.630870	8.389134
C	-1.725236	5.690488	9.506540
C	-0.768899	4.684027	9.702704
C	-0.650510	3.624305	8.797270
N	0.280577	5.341280	5.427367
H	-0.665838	-4.365660	1.083760
H	1.199589	-4.309674	-0.576032
H	2.913331	-2.498640	-0.425728
H	2.747897	-0.768820	1.319315
H	-2.222336	-1.319527	4.284493
H	-0.649289	-3.246993	4.087567
H	-1.935922	-3.238125	2.861320

H	2.763449	0.352441	3.164021
H	2.261849	2.101808	4.843442
H	-1.574841	1.447081	7.197907
H	-2.139682	2.492543	5.906695
H	-0.110618	4.728740	10.565961
H	-1.812534	6.513724	10.211062
H	-3.327677	6.400024	8.217464
H	0.103213	2.854950	8.946976
H	-0.556147	5.699952	5.883627
H	0.281549	4.323195	5.598001
H	0.154660	5.486882	4.427307

TS reduction

B3LYP/6-31++G**, -598427.62, 1 imaginary freq

xyz coordinates:

C	-1.167681	4.888193	7.300100
C	-1.205570	3.573796	7.767653
C	-1.428529	3.404426	9.145228
C	-1.605450	4.506202	9.994026
C	-1.561510	5.807333	9.482476
C	-1.336849	6.004083	8.108124
C	-1.040394	2.385149	6.841248
N	0.270514	2.376123	6.208812
C	0.461423	1.426553	5.299691
C	1.729448	1.372430	4.598303
C	1.941103	0.420951	3.632032
C	0.938742	-0.532516	3.308386

C	-0.262791	-0.425517	4.052941
N	-0.507818	0.488496	4.998098
N	-1.312569	-1.294805	3.742020
C	-0.936010	-2.634807	3.281865
C	0.055037	-2.530380	2.145314
C	1.026858	-1.499319	2.218426
C	2.009792	-1.447357	1.205851
C	2.029863	-2.385883	0.171012
C	1.058845	-3.393681	0.105299
C	0.071089	-3.452070	1.099190
N	-0.656824	4.950019	4.790522
H	-0.690447	-4.228689	1.067073
H	1.066572	-4.117243	-0.704737
H	2.798953	-2.321353	-0.594625
H	2.755597	-0.658161	1.221774
H	-2.031733	-1.290254	4.456744
H	-0.478741	-3.215200	4.107031
H	-1.837771	-3.165228	2.962485
H	2.893545	0.392022	3.108028
H	2.493923	2.099175	4.856632
H	-1.228204	1.462352	7.417497
H	-1.847681	2.422390	6.085788
H	-1.775599	4.346346	11.055307
H	-1.698553	6.662765	10.138893
H	-1.298432	7.009018	7.694489
H	-1.462950	2.394929	9.550108
H	-0.893490	5.089879	5.982910

H	-0.149080	4.055455	4.874919
H	-1.580201	4.690683	4.424864

33 *s-cis*^{•-}

minima

B3LYP/6-31++G**, -562981.36

xyz coordinates:

C	0.079751	0.079994	-0.020442
C	0.076770	-0.097108	1.362666
C	1.242312	0.160354	2.130839
C	2.398776	0.591163	1.438719
C	2.396982	0.750114	0.050856
C	1.238294	0.498470	-0.692309
C	-1.132467	-0.639318	2.086961
N	-1.227487	-0.032021	3.414290
C	-0.076668	-0.097319	4.211426
C	1.197164	-0.007073	3.587112
N	-0.303258	-0.166814	5.537359
C	0.743841	-0.143787	6.407192
C	2.201773	0.009610	5.909209
C	2.332543	-0.005199	4.415908
N	0.508434	-0.243369	7.691905
C	1.680715	-0.217129	8.569613
C	2.818795	-1.070518	8.056009
C	3.075507	-0.983412	6.677609
C	4.082226	-1.771954	6.111791
C	4.839035	-2.634499	6.916535

C	4.583440	-2.719768	8.288872
C	3.565550	-1.941634	8.855034
H	3.349902	-2.016890	9.919684
H	5.165119	-3.393839	8.913322
H	5.621500	-3.242960	6.468746
H	4.273547	-1.722708	5.043393
H	2.039488	0.824487	8.689783
H	3.328454	0.083229	3.993884
H	-1.047382	-1.742084	2.166080
H	3.304263	0.818682	1.994027
H	3.303720	1.082707	-0.450418
H	1.231864	0.627624	-1.771597
H	-0.830208	-0.121501	-0.583798
H	2.516797	1.004847	6.298827
H	-2.050754	-0.421692	1.532703
H	1.378435	-0.548062	9.570033
H	-2.048219	-0.320971	3.938628

33 *s-trans*^{•-}

minima

B3LYP/6-31++G**, -562966.16

xyz coordinates:

C	0.118524	0.124479	-0.011652
C	0.065608	-0.101527	1.360744
C	1.229981	0.054082	2.148538
C	2.443861	0.432411	1.526875
C	2.478438	0.628301	0.142678

C	1.326841	0.481504	-0.639320
N	1.081889	-0.140014	3.533931
C	-0.183444	0.278266	4.113266
N	-1.289332	0.211225	3.391324
C	-1.170610	-0.503968	2.123277
C	-0.119661	0.801198	5.426828
C	1.068164	0.806306	6.182444
C	2.223194	0.152536	5.686746
C	2.181191	-0.380845	4.392795
N	3.251630	-1.152831	3.886192
C	3.925496	-1.957363	4.915236
C	4.353218	-1.066892	6.059112
C	3.455255	-0.047442	6.463115
C	3.804442	0.738062	7.580403
C	4.997364	0.518127	8.273279
C	5.881728	-0.485807	7.859586
C	5.550445	-1.270756	6.748339
H	6.227507	-2.057470	6.419370
H	6.815808	-0.652602	8.389980
H	5.242352	1.140987	9.130754
H	3.143891	1.539455	7.900743
H	2.965406	-1.723945	3.095279
H	3.250315	-2.746405	5.301104
H	4.789346	-2.451700	4.459665
H	1.062623	1.216920	7.187773
H	-1.049368	1.172985	5.848679
H	-2.068561	-0.323073	1.520185

H	-1.135951	-1.599022	2.304503
H	1.362632	0.644162	-1.713451
H	3.418215	0.916534	-0.324174
H	3.340730	0.569058	2.119641
H	-0.789793	0.009995	-0.601548

[**26** *s-cis*⁻]^{•-}

minima

B3LYP/6-31+G*, -552545.37

xyz coordinates:

C	0.202092	0.267178	0.223605
C	0.133591	-0.050262	1.597425
C	1.343059	-0.302598	2.284402
C	2.564026	-0.244866	1.604469
C	2.619046	0.089601	0.247459
C	1.426974	0.349981	-0.439697
C	-1.132559	-0.215084	2.334132
C	-1.056600	-0.907144	3.610959
N	0.068916	-1.213922	4.258579
C	1.284256	-0.575199	3.772717
C	-2.320817	-1.292645	4.197340
C	-3.521729	-0.931361	3.654120
C	-3.623344	-0.159732	2.430452
C	-2.369337	0.154541	1.804535
N	-4.849926	0.163885	1.997258
C	-4.982161	0.882909	0.741590
C	-4.902872	2.422706	0.780164

C	-5.161683	3.128970	-0.430996
C	-4.598898	3.073619	1.987289
C	-4.537078	4.475117	2.048907
C	-4.779645	5.214723	0.889483
C	-5.079148	4.536146	-0.309940
H	-2.390128	0.711983	0.873969
H	-2.282596	-1.858740	5.126771
H	-4.453607	-1.213010	4.142336
H	1.405142	0.393210	4.304492
H	2.152142	-1.177205	4.073883
H	-0.710911	0.437298	-0.339366
H	1.449566	0.602559	-1.497374
H	3.575375	0.140491	-0.267412
H	3.484549	-0.453357	2.148143
H	-4.258794	0.533494	-0.018761
H	-5.970433	0.633219	0.326723
H	-4.409125	2.488484	2.886066
H	-4.302138	4.973006	2.989106
H	-4.736559	6.305224	0.915492
H	-5.259789	5.161996	-1.191403

TS

B3LYP/6-31+G*, -552529.93, 1 imaginary freq

xyz coordinates:

C	-0.017265	0.052556	0.011938
C	-0.004379	0.017338	1.429706
C	1.270199	-0.011539	2.066154

C	2.442767	-0.081042	1.314517
C	2.409863	-0.063461	-0.089250
C	1.166752	0.019329	-0.729730
C	-1.189162	-0.056657	2.275129
C	-0.988615	-0.499927	3.641381
N	0.210947	-0.599634	4.247975
C	1.268014	0.139960	3.571371
C	-2.164987	-0.945815	4.342517
C	-3.431571	-0.869049	3.789937
C	-3.679543	-0.318816	2.491536
C	-2.504612	0.113602	1.750722
N	-4.952383	-0.183499	2.057870
C	-5.120027	0.571243	0.827166
C	-4.633738	2.021358	0.946075
C	-3.325965	2.265130	1.395409
C	-5.495011	3.090606	0.644615
C	-5.055783	4.416978	0.778750
C	-3.753656	4.671892	1.223068
C	-2.901652	3.591520	1.527179
H	-2.604629	0.127401	0.673538
H	-2.029697	-1.342298	5.348574
H	-4.296617	-1.201668	4.364834
H	1.160261	1.230723	3.794708
H	2.244759	-0.150917	3.982909
H	-0.963069	0.092121	-0.522168
H	1.115869	0.048398	-1.816986
H	3.331571	-0.098043	-0.665688

H	3.401651	-0.116630	1.832411
H	-4.594581	0.095725	-0.030092
H	-6.185767	0.569194	0.560422
H	-6.514053	2.894735	0.304341
H	-5.727447	5.240628	0.542679
H	-3.405739	5.699876	1.332893
H	-1.887972	3.815198	1.874724

[**26** *s-trans*⁻]^{•-}

minima

B3LYP/6-31+G*, -552546.05

xyz coordinates:

C	-0.271135	0.340743	0.450269
C	0.825014	-0.236147	1.122924
C	2.161470	-0.118888	0.645878
C	2.284719	0.633236	-0.551764
C	1.205397	1.220633	-1.236407
C	-0.090910	1.072305	-0.730076
C	0.528631	-1.004828	2.406016
N	0.358723	-0.125073	3.560007
C	0.098126	-0.701493	4.743239
C	-0.025681	-2.121655	4.999737
C	-0.258877	-2.610289	6.264038
C	-0.372258	-1.764244	7.423239
C	-0.364250	-0.328826	7.165614
C	-0.110043	0.143674	5.887620
C	-0.762612	0.545958	8.285456

C	-0.813689	-0.016093	9.580254
C	-0.318838	-1.435012	9.769256
N	-0.488725	-2.326770	8.629791
C	-1.172532	1.885545	8.121607
C	-1.597222	2.649207	9.209633
C	-1.650090	2.082366	10.489155
C	-1.266508	0.748728	10.660932
H	-0.382444	-1.620115	2.260349
H	-1.309135	0.296386	11.650760
H	-1.992062	2.668953	11.338388
H	-1.902995	3.681550	9.055859
H	-1.175155	2.333741	7.132133
H	0.762539	-1.390855	10.021983
H	-0.801063	-1.880784	10.649476
H	-0.075674	1.214831	5.699081
H	-0.322551	-3.685103	6.430382
H	0.084169	-2.824580	4.179287
H	-0.944821	1.511542	-1.244310
H	-1.280567	0.217431	0.849559
H	1.357080	-1.716754	2.571190
H	3.277221	0.776842	-0.993190
H	1.370774	1.783635	-2.156923

TS

B3LYP/6-31+G*, -552527.56, 1 imaginary freq

xyz coordinates:

C	0.007157	0.030192	0.013235
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C	-0.018797	-0.014050	1.416920
C	1.171007	-0.035349	2.158903
C	2.384908	-0.047100	1.463264
C	2.429289	-0.008270	0.055455
C	1.233454	0.034364	-0.670541
C	-1.353182	-0.039000	2.178437
N	-1.389495	0.893538	3.288943
C	-0.460420	0.706169	4.242055
C	0.457553	-0.446772	4.287498
C	1.359887	-0.579506	5.355504
C	1.640464	0.478086	6.277641
C	0.699850	1.607417	6.265112
C	-0.295433	1.672091	5.273139
C	0.713155	2.493911	7.423757
C	1.830234	2.438473	8.300782
C	3.003024	1.593479	7.857555
N	2.656182	0.369183	7.149134
C	-0.356575	3.355307	7.781637
C	-0.310776	4.127028	8.943782
C	0.790004	4.049376	9.808406
C	1.849858	3.190496	9.475811
H	-2.172357	0.203350	1.487996
H	2.715762	3.120315	10.134458
H	0.822805	4.641271	10.720224
H	-1.147196	4.780832	9.184944
H	-1.240524	3.409130	7.151930
H	3.643541	2.232287	7.202577

H	3.632486	1.348025	8.724806
H	-0.983199	2.516467	5.251522
H	1.994080	-1.465643	5.408409
H	0.127210	-1.356133	3.796356
H	1.251670	0.071866	-1.758439
H	-0.925107	0.062003	-0.555122
H	-1.538011	-1.084931	2.506884
H	3.334534	-0.079988	2.008144
H	3.385823	-0.004815	-0.469168

[27*s-cis*⁻]^{•-}

minima

B3LYP/6-31+G*, -552560.84

xyz coordinates:

C	0.032361	-0.015783	1.374937
C	1.245346	-0.008759	2.090904
C	2.465703	-0.004290	1.406101
C	2.490895	0.007519	0.005328
C	1.286773	-0.002032	-0.707610
C	-1.238909	-0.044037	2.233202
C	-1.002842	-1.101523	3.332850
N	0.155964	-1.104390	4.013337
C	1.116686	-0.083586	3.596622
C	-2.562152	-0.126733	1.486846
C	-3.527716	-1.160264	1.787876
C	-3.229234	-2.080572	2.853502
C	-2.024321	-2.037324	3.578924

N	-4.729267	-1.264093	1.175672
C	-4.825041	-0.464569	-0.038851
C	-4.316982	0.943634	0.132838
C	-3.062347	1.042145	0.827547
C	-4.937002	2.065258	-0.404317
C	-4.333351	3.338991	-0.343691
C	-3.077975	3.446697	0.272500
C	-2.450885	2.335275	0.843119
H	-1.210235	0.927697	2.779340
H	-3.971143	-2.845590	3.079219
H	-1.848140	-2.773177	4.365995
H	-4.213972	-0.942595	-0.848975
H	-5.862928	-0.462536	-0.402527
H	-1.476416	2.467784	1.305933
H	-2.576644	4.413885	0.311188
H	-4.815608	4.206846	-0.788332
H	-5.894200	1.944883	-0.914772
H	0.819155	0.919515	3.975289
H	2.092163	-0.297357	4.052358
H	3.399383	-0.016696	1.967487
H	3.441661	0.016006	-0.523565
H	1.298242	0.001360	-1.795771
H	-0.874711	-0.035918	-0.570834

[**27***s-trans*⁻]^{•-}

minima

B3LYP/6-31+G*, -552555.80

xyz coordinates:

C	0.053107	-0.203738	-0.049848
C	0.007122	-0.027669	1.329832
C	1.209186	0.070931	2.097152
C	2.441258	0.008091	1.377204
C	2.468529	-0.144971	-0.009468
C	1.278587	-0.260403	-0.744846
C	-1.286073	0.143670	2.094008
N	-1.297268	-0.444192	3.421320
C	-0.193303	-0.152124	4.175324
C	1.105885	0.189599	3.532409
C	2.229428	0.470274	4.346685
C	2.254690	0.370516	5.753403
C	0.983057	-0.127882	6.462954
C	-0.222059	-0.221323	5.567143
C	0.797281	0.689839	7.744540
C	1.964227	0.939252	8.489892
C	3.252828	0.417603	7.894556
N	3.352776	0.658628	6.457274
C	-0.427328	1.180731	8.212018
C	-0.495974	1.896676	9.415562
C	0.666301	2.142686	10.153679
C	1.897483	1.669915	9.681085
H	4.115256	0.872257	8.398533
H	-0.884303	-0.279040	-0.603087
H	1.300268	-0.389453	-1.824750
H	3.429248	-0.189909	-0.521325

H	3.384001	0.059706	1.915813
H	-1.488448	1.247738	2.140468
H	-2.117253	-0.270365	1.503068
H	3.166653	0.771338	3.878767
H	-1.159746	-0.528985	6.032182
H	1.267425	-1.139508	6.849281
H	0.617382	2.704730	11.083848
H	2.809787	1.873390	10.240656
H	3.317534	-0.672706	8.106091
H	-1.329539	1.009573	7.632007
H	-1.455749	2.266873	9.770237