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SUPPLEMENTARY MATERIAL

Cartesian Coordinates for the Lithium-Complexed Oxyallyl Cation **1**

O	1	-2.0420998	-.3239442	-.3774184
C	2	-1.6236220	.1737525	.7401727
C	3	-.2281527	.4099107	1.0251050
C	4	-2.5019945	.5153893	1.7461651
N	5	.8501855	.1744784	.2404870
H	6	.0140373	.8430975	2.0171079
H	7	-2.2598286	.9397098	2.7220635
Br	8	-4.2936402	.2045759	1.3628404
C	9	2.2629692	.4927383	.7182529
C	10	3.1649561	.1080973	-.3804001
C	11	2.4162668	-.4075988	-1.4644076
C	12	.9742266	-.3932515	-1.1445476
C	13	4.5404694	.1976507	-.4391000
O	14	.0404984	-.7553374	-1.8279040
O	15	2.4479662	.9638505	1.8058104
C	16	3.0454621	-.8379047	-2.6168701
C	17	4.4456971	-.7469495	-2.6767034
H	18	2.4745734	-1.2393875	-3.4630396
C	19	5.1770220	-.2409447	-1.6129222
H	20	5.1225302	.5976367	.4008878
H	21	4.9638507	-1.0839671	-3.5840741
H	22	6.2711271	-.1791092	-1.6817509
Li	23	-1.9569665	-.9871251	-1.9887967

Cartesian Coordinates for the Transition Structures Listed in Table 4

Endo/Bond Formation near Br

32 endo transition state bond forming near Br

C	1	-1.7153389	.4479279	-1.8082426
O	2	-3.3708380	-1.4303070	-.4826249
C	3	-3.0898605	-1.6192344	.8341719
C	4	-3.0932886	-.4090821	1.5135010
C	5	-3.3788475	.5946650	.5512467
C	6	-3.4919037	-.0529177	-.6935968
H	7	-4.1161508	.2053874	-1.5563770
C	8	.1019537	-.5437164	-.6108218
H	9	-2.9260087	-2.6514890	1.1408663
H	10	-2.9301840	-.2552787	2.5787075
Li	11	.8600011	2.9859652	.0946061
O	12	-.3185610	1.8265243	-.5462070
H	13	-3.4741549	1.6644830	.7352814
N	14	1.2594127	-.6838244	.1491844
C	15	-.5946318	.6324000	-.9545136
H	16	-.2899489	-1.5070093	-.9862696
H	17	-1.8596790	-.4358593	-2.4416820
Br	18	-2.4061458	2.0747328	-2.4583405
C	19	1.8145320	-2.0425100	.4527528
C	20	3.0753555	-1.8213406	1.1934862
C	21	3.2900135	-.4320963	1.3476760
C	22	2.1796670	.3141906	.7082049

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C	23	5.3152895	-.8954196	2.5212551
O	24	2.0386355	1.5253608	.6406797
O	25	1.2439535	-3.0496970	.1201575
H	26	5.8287851	-2.9719279	2.7765494
C	27	3.9689342	-2.7430695	1.6960821
C	28	4.4049441	.0430671	2.0089127
H	29	3.8038124	-3.8207572	1.5758222
H	30	6.2083685	-.5386640	3.0497972
C	31	5.1029832	-2.2569665	2.3685570
H	32	4.5797851	1.1183774	2.1323540

Endo/Bond Formation near N

32 endo ts bond forming near N

C	1	-1.4097773	.8056741	-2.1859942
O	2	-2.6139257	-1.7859997	-.4547961
C	3	-1.6784475	-1.3952088	.5212599
C	4	-2.2950997	-.3956798	1.3240543
C	5	-3.5516515	-.1196049	.7516358
C	6	-3.6892920	-.9818892	-.3400662
H	7	-4.4756418	-1.1210679	-1.0834427
C	8	-.1281802	-.4926829	-.6019808
H	9	-1.0855359	-2.2470681	.8746472
H	10	-1.8617252	.0836077	2.2022395
Li	11	.1349063	2.9407531	.8787229
O	12	-.5798003	1.8663328	-.2882033
H	13	-4.2747430	.6243289	1.0859111
N	14	.9880391	-.6450997	.2223422
C	15	-.7101199	.8029591	-1.0134045
H	16	-.2111722	-1.3045006	-1.3582968
H	17	-1.5723850	-.0238635	-2.8728283
Br	18	-2.0903015	2.4686813	-2.6943151
C	19	1.7845221	-1.9235595	.2128469
C	20	2.9546459	-1.6938356	1.0829006
C	21	2.8910646	-.3896478	1.6251117
C	22	1.6739544	.2986763	1.1356851
C	23	4.9396989	-.7928555	2.7815579
O	24	1.2688519	1.4063461	1.4364724
O	25	1.4180037	-2.8827315	-.4142542
H	26	5.8412576	-2.7295383	2.5007611
C	27	3.9984534	-2.5438279	1.3832552
C	28	3.8767544	.0720850	2.4751487
H	29	4.0491839	-3.5553653	.9616115
H	30	5.7337829	-.4446537	3.4544753
C	31	4.9999676	-2.0713271	2.2481300
H	32	3.8369719	1.0824257	2.8995163

Exo/Bond Formation near Br

32 exo transition state bond forming near Br

C	1	-1.7532204	.7131595	-1.7329497
H	2	4.1894848	-3.4030772	1.0858794
C	3	-2.8363589	-1.6581819	.7659131

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C	4	5.1454929	-1.9138012	2.3624603
H	5	4.0466155	1.2818729	2.9126960
C	6	-3.3832551	-.5060846	-1.0516046
H	7	5.8899695	-.2787954	3.5502921
C	8	.1004702	-.2898844	-.5925407
H	9	-4.1345967	.1553786	-1.4965312
C	10	-2.9427755	-1.7787767	-1.4762697
Li	11	.1555990	2.9950648	1.0691685
O	12	-.7459181	1.8745246	.0253960
O	13	-3.3742176	-.4857802	.3420898
N	14	1.2129813	-.4448081	.2313734
C	15	-.7650319	.8169504	-.7112743
H	16	-.0997339	-1.1725527	-1.2286123
H	17	-1.6332026	.0978092	-2.6324756
Br	18	-2.7080687	2.3237356	-1.9605536
C	19	1.9822961	-1.7290429	.2425299
C	20	3.1408650	-1.5131292	1.1366423
C	21	3.0973097	-.1953549	1.6479934
C	22	1.9090325	.5064479	1.1048290
C	23	5.1046532	-.6223797	2.8651549
O	24	1.5582873	1.6556600	1.3248560
O	25	1.6214440	-2.6918185	-.3854333
H	26	5.9627871	-2.5866927	2.6516188
C	27	4.1543084	-2.3812152	1.4828873
C	28	4.0721233	.2615572	2.5121868
C	29	-2.5619974	-2.4913206	-.3140972
H	30	-2.7272135	-1.7698349	1.8435661
H	31	-2.8999304	-2.1401063	-2.5033563
H	32	-2.1556521	-3.5011925	-.2765346

Exo/Bond Formation near N

32 exo ts bond forming near N

C	1	-1.6119421	.6835011	-2.0615783
H	2	4.1091094	-3.3887857	1.1320608
C	3	-1.6127885	-1.4367365	.6241832
C	4	4.9926379	-1.8584475	2.4119466
H	5	3.7494700	1.2846410	2.9586928
C	6	-3.6463979	-.6008349	.2928042
H	7	5.6583024	-.1917120	3.6029856
C	8	-.1387448	-.4865050	-.5456446
H	9	-4.4285605	.1446901	.4456283
C	10	-3.5450832	-1.7177462	-.5493442
Li	11	.1249548	3.0487488	.7260070
O	12	-.6172149	1.8816027	-.3349614
O	13	-2.5386202	-.4640823	1.0417964
N	14	1.0024276	-.5674538	.2581681
C	15	-.7958645	.7714224	-.9681946
H	16	-.1744110	-1.3044891	-1.2971497
H	17	-1.8248350	-.1932321	-2.6711779
Br	18	-2.3756245	2.2967720	-2.6087853
C	19	1.8323007	-1.8203107	.2869657
C	20	2.9746749	-1.5480337	1.1811499
C	21	2.8703674	-.2337060	1.6910798

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C	22	1.6568428	.4217362	1.1473539
C	23	4.8915476	-.5702802	2.9150003
O	24	1.2490927	1.5443142	1.3776856
O	25	1.5086184	-2.7994752	-.3349546
H	26	5.8390450	-2.4936766	2.7031200
C	27	4.0262183	-2.3697677	1.5296406
C	28	3.8215287	.2662860	2.5583889
C	29	-2.2801014	-2.2785568	-.3160673
H	30	-.9781015	-1.7762215	1.4496397
H	31	-4.3056789	-2.0765207	-1.2432092
H	32	-1.8613037	-3.1721245	-.7815821

Cartesian Coordinates for the Stationary Points on the reaction potential fo the addition of oxyallyl cation Li^+-**1** with furan

Transition Structure A (formation of first bond)

C	1	-1.7153389	.4479279	-1.8082426
O	2	-3.3708380	-1.4303070	-.4826249
C	3	-3.0898605	-1.6192344	.8341719
C	4	-3.0932886	-.4090821	1.5135010
C	5	-3.3788475	.5946650	.5512467
C	6	-3.4919037	-.0529177	-.6935968
H	7	-4.1161508	.2053874	-1.5563770
C	8	.1019537	-.5437164	-.6108218
H	9	-2.9260087	-2.6514890	1.1408663
H	10	-2.9301840	-.2552787	2.5787075
Li	11	.8600011	2.9859652	.0946061
O	12	-.3185610	1.8265243	-.5462070
H	13	-3.4741549	1.6644830	.7352814
N	14	1.2594127	-.6838244	.1491844
C	15	-.5946318	.6324000	-.9545136
H	16	-.2899489	-1.5070093	-.9862696
H	17	-1.8596790	-.4358593	-2.4416820
Br	18	-2.4061458	2.0747328	-2.4583405
C	19	1.8145320	-2.0425100	.4527528
C	20	3.0753555	-1.8213406	1.1934862
C	21	3.2900135	-.4320963	1.3476760
C	22	2.1796670	.3141906	.7082049
C	23	5.3152895	-.8954196	2.5212551
O	24	2.0386355	1.5253608	.6406797
O	25	1.2439535	-3.0496970	.1201575
H	26	5.8287851	-2.9719279	2.7765494
C	27	3.9689342	-2.7430695	1.6960821
C	28	4.4049441	.0430671	2.0089127
H	29	3.8038124	-3.8207572	1.5758222
H	30	6.2083685	-.5386640	3.0497972
C	31	5.1029832	-2.2569665	2.3685570
H	32	4.5797851	1.1183774	2.1323540

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Intermediate B (intermediate prior to second bond formation)

C	1	-1.8878390	.5909551	-1.7145158
O	2	-2.8372790	-1.5093748	-.8387246
C	3	-2.8176758	-1.8224055	.4271572
C	4	-3.0746476	-.6865684	1.2714895
C	5	-3.2195338	.4034105	.4603201
C	6	-3.0558640	-.0387578	-.9688853
H	7	-4.0009119	.0588107	-1.5603149
C	8	.0428426	-.4029909	-.5945643
H	9	-2.6264929	-2.8741077	.6763038
H	10	-3.1181268	-.7224114	2.3637832
Li	11	1.2490707	2.8210038	-.4507484
O	12	-.3698653	1.9528609	-.4823926
H	13	-3.3979640	1.4476237	.7371006
N	14	1.1163632	-.5300802	.3504376
C	15	-.6301560	.7603680	-.8819143
H	16	-.1974893	-1.3390072	-1.1139815
H	17	-1.6804649	.0491798	-2.6648291
Br	18	-2.5574868	2.3578881	-2.1488300
C	19	1.3296367	-1.8051184	1.0349099
C	20	2.7240359	-1.7799255	1.5527178
C	21	3.3217917	-.5511902	1.1796981
C	22	2.3231552	.2458177	.4132998
C	23	5.3365351	-1.2233599	2.2632585
O	24	2.4560610	1.3860604	-.0398519
O	25	.4552617	-2.6404001	1.1427609
H	26	5.3268918	-3.1606178	3.2020453
C	27	3.4226323	-2.7206715	2.2760874
C	28	4.6232641	-.2612763	1.5287047
H	29	2.9619804	-3.6718970	2.5662384
H	30	6.3748476	-1.0144119	2.5481955
C	31	4.7502865	-2.4243583	2.6289930
H	32	5.0920621	.6872223	1.2426851

Transition Structure C (transition structure leading to second bond formation)

C	1	-1.9556106	.6258980	-1.6684652
O	2	-2.7194949	-1.4550921	-.6984596
C	3	-2.3328790	-1.5648602	.5559396
C	4	-2.7514831	-.4247725	1.3415979
C	5	-3.2678282	.4943106	.4784940
C	6	-3.1127013	-.0441741	-.9225041
H	7	-4.0490224	-.0572951	-1.5255460
C	8	-.0960086	-.4334646	-.4429113
H	9	-1.8847277	-2.5201263	.8601154
H	10	-2.6473631	-.3497389	2.4264268
Li	11	1.1720460	2.9113190	-.3397179
O	12	-.3949812	1.9427833	-.4622966
H	13	-3.6866474	1.4814332	.6889069
N	14	1.0055843	-.5407535	.4791774
C	15	-.7012511	.7665403	-.8257530
H	16	-.2407590	-1.3370417	-1.0517873
H	17	-1.7468423	.1134785	-2.6339856

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Br	18	-2.6376490	2.3973099	-2.0406074
C	19	1.3189249	-1.8483068	1.0722182
C	20	2.7219744	-1.7785902	1.5561769
C	21	3.2487407	-.5065522	1.2296236
C	22	2.1956960	.2735327	.5248300
C	23	5.3203137	-1.1270400	2.2340569
O	24	2.2864767	1.4262052	.0973557
O	25	.5061878	-2.7453177	1.1443855
H	26	5.4287165	-3.1050035	3.0778710
C	27	3.4827101	-2.7175204	2.2172472
C	28	4.5432717	-.1682994	1.5629344
H	29	3.0758048	-3.7033049	2.4710611
H	30	6.3539832	-.8802029	2.5058066
C	31	4.8026355	-2.3721230	2.5541847
H	32	4.9582343	.8148075	1.3127605

Product D-Li^+

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H	1	1.4781768	2.0034966	-3.5562954
C	2	1.1544614	1.5060193	-2.6208076
C	3	2.1855581	1.4479658	-1.5021460
C	4	1.5329932	1.6507411	-.3467478
C	5	.0641375	1.8667561	-.6755005
O	6	.0868147	2.2878354	-2.0521360
C	7	.6088352	.0904493	-2.8338917
N	8	-1.0973745	.0970761	.7175080
H	9	3.2450465	1.2734142	-1.6838530
H	10	1.9322316	1.7013519	.6643056
H	11	-.0747143	-2.1281577	4.1890107
H	12	-.4371168	2.6741186	-.1041261
C	13	-.7364717	.5134580	-.6616615
H	14	-3.3968339	1.6450863	3.9798457
Li	15	.6576160	-3.0464737	-.1042497
Br	16	2.1721199	-.9877570	-3.1889327
H	17	-.0917059	.0258348	-3.6956165
C	18	-.0070562	-.4841402	-1.5726683
O	19	.0987215	-1.6853399	-1.3559114
H	20	-1.7256015	.7029719	-1.1646882
C	21	-2.0647847	.9185987	1.5045049
C	22	-.5052948	-.8723738	1.5917097
O	23	-2.7328859	1.7807561	.9959736
C	24	-1.9927760	.4099539	2.8956109
O	25	.2861810	-1.7487140	1.2306300
C	26	-1.0597073	-.6526487	2.9497957
H	27	-2.9256960	.4728901	6.1406987
H	28	-1.2872247	-1.3823066	6.2414166
C	29	-2.6704807	.8241367	4.0213181
C	30	-.7964834	-1.3048102	4.1372276
C	31	-1.4833072	-.8793853	5.2860869
C	32	-2.3996711	.1592180	5.2300232

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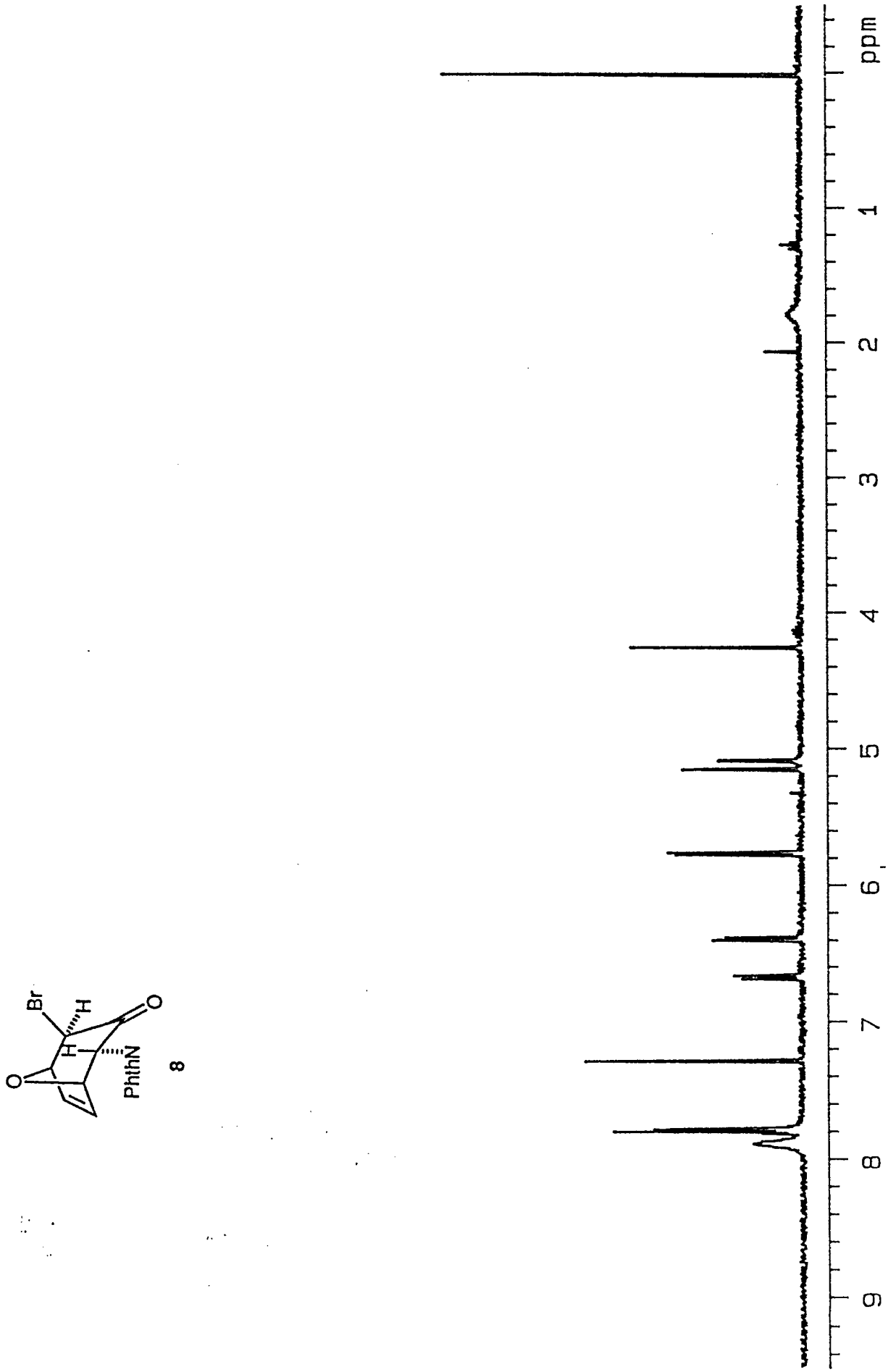

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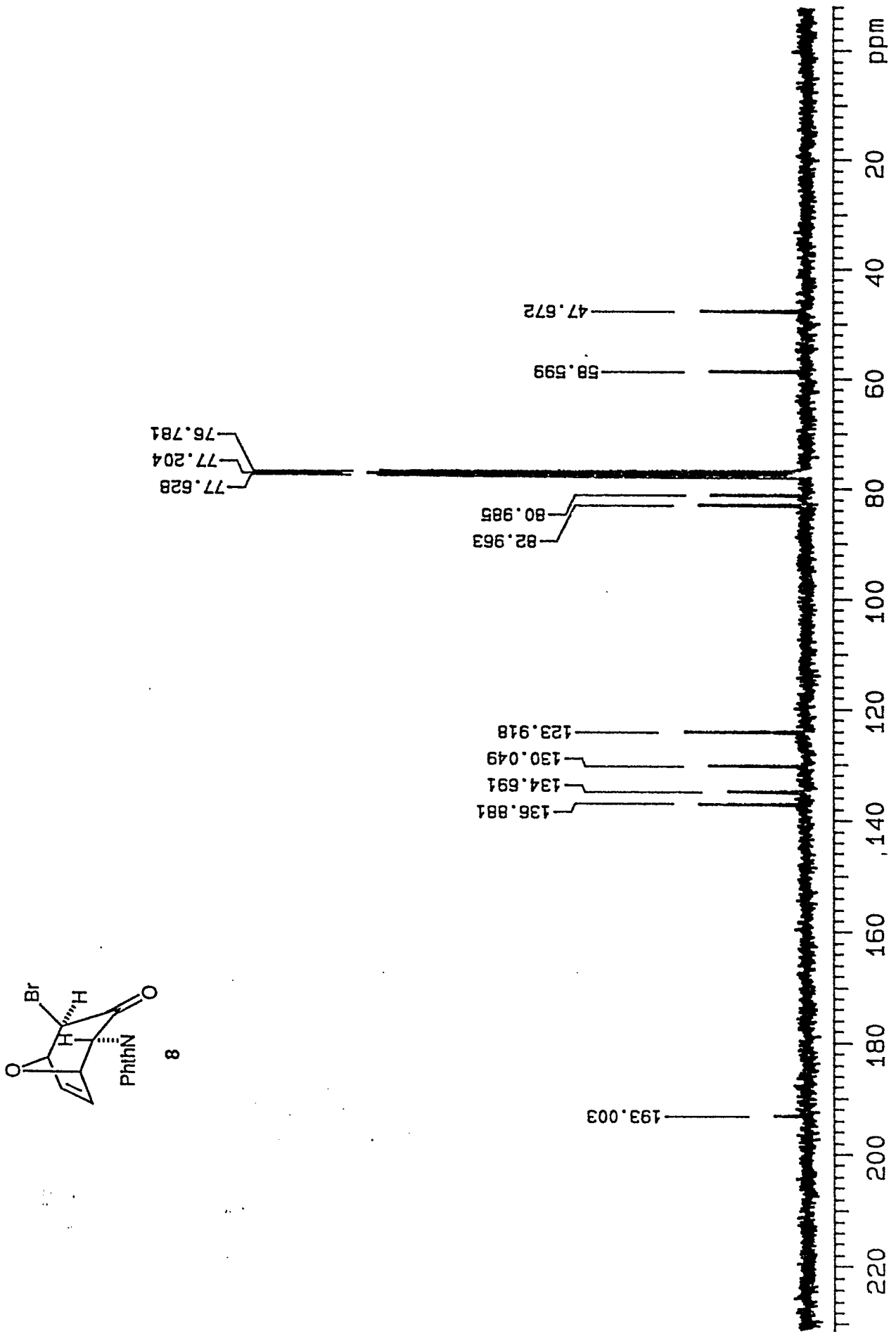
Gs1486-8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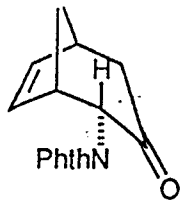

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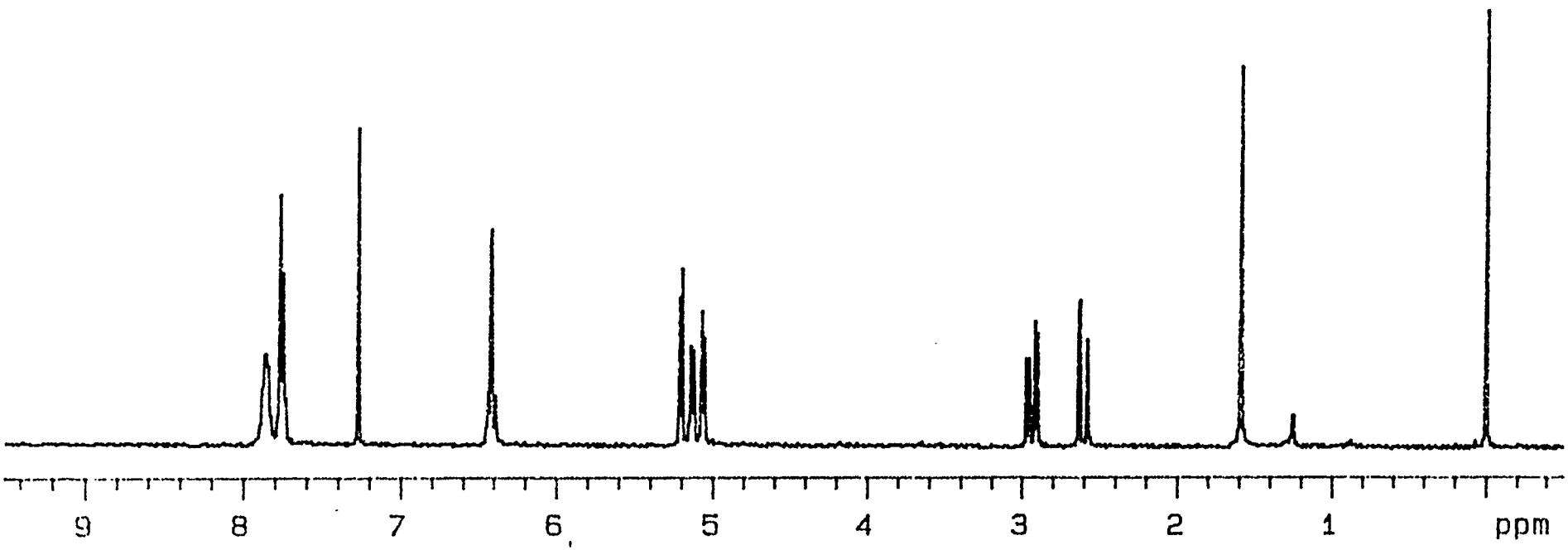

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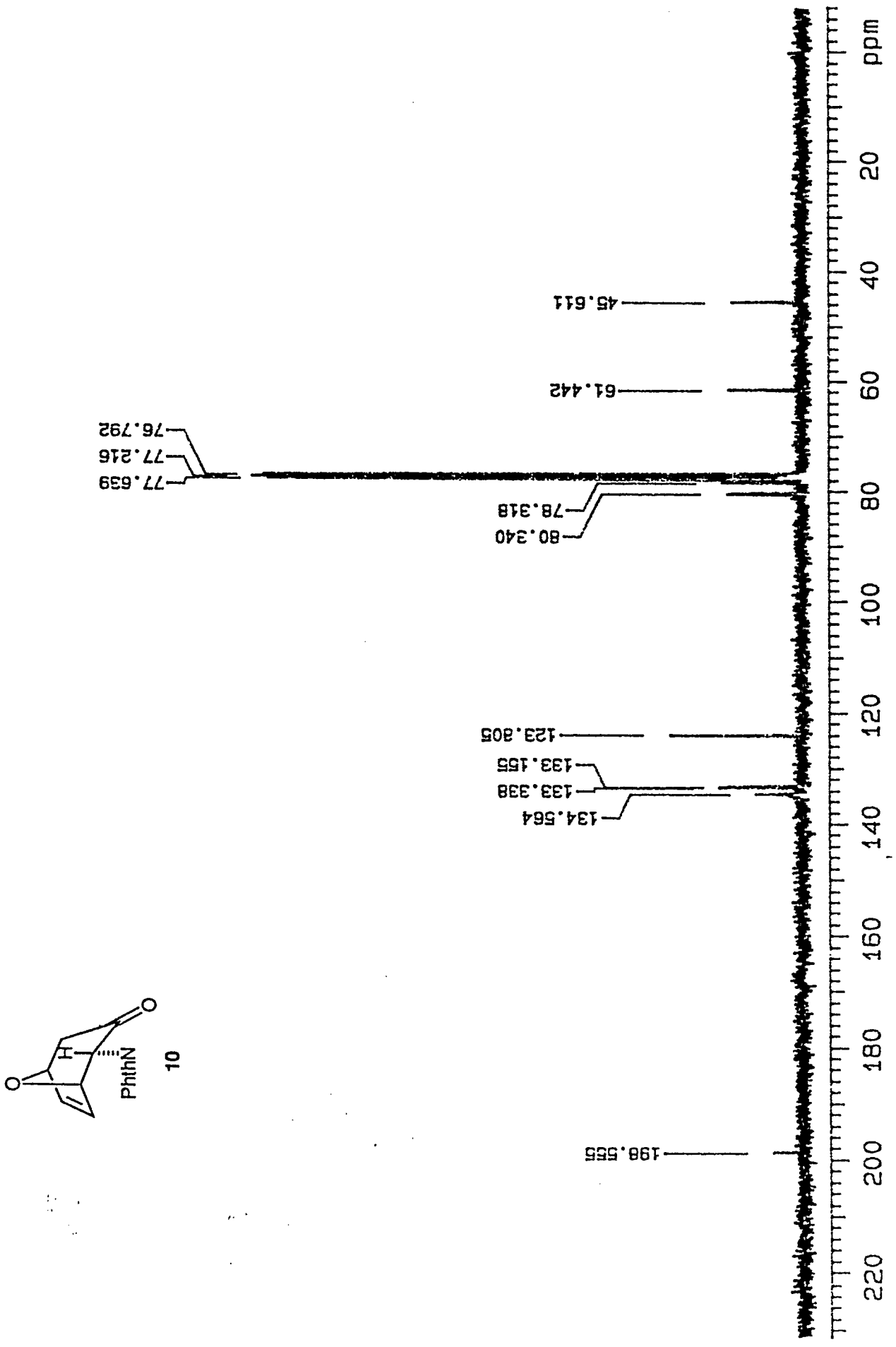
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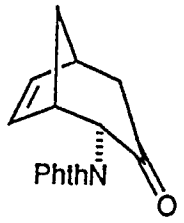

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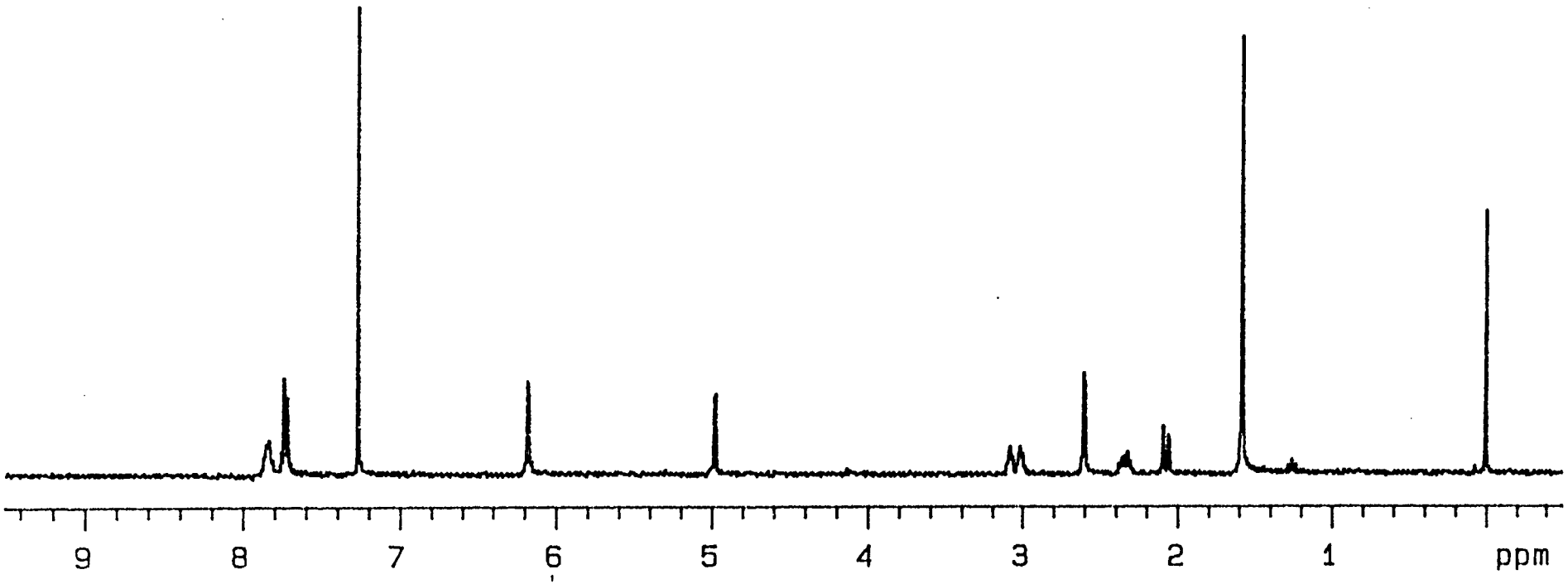

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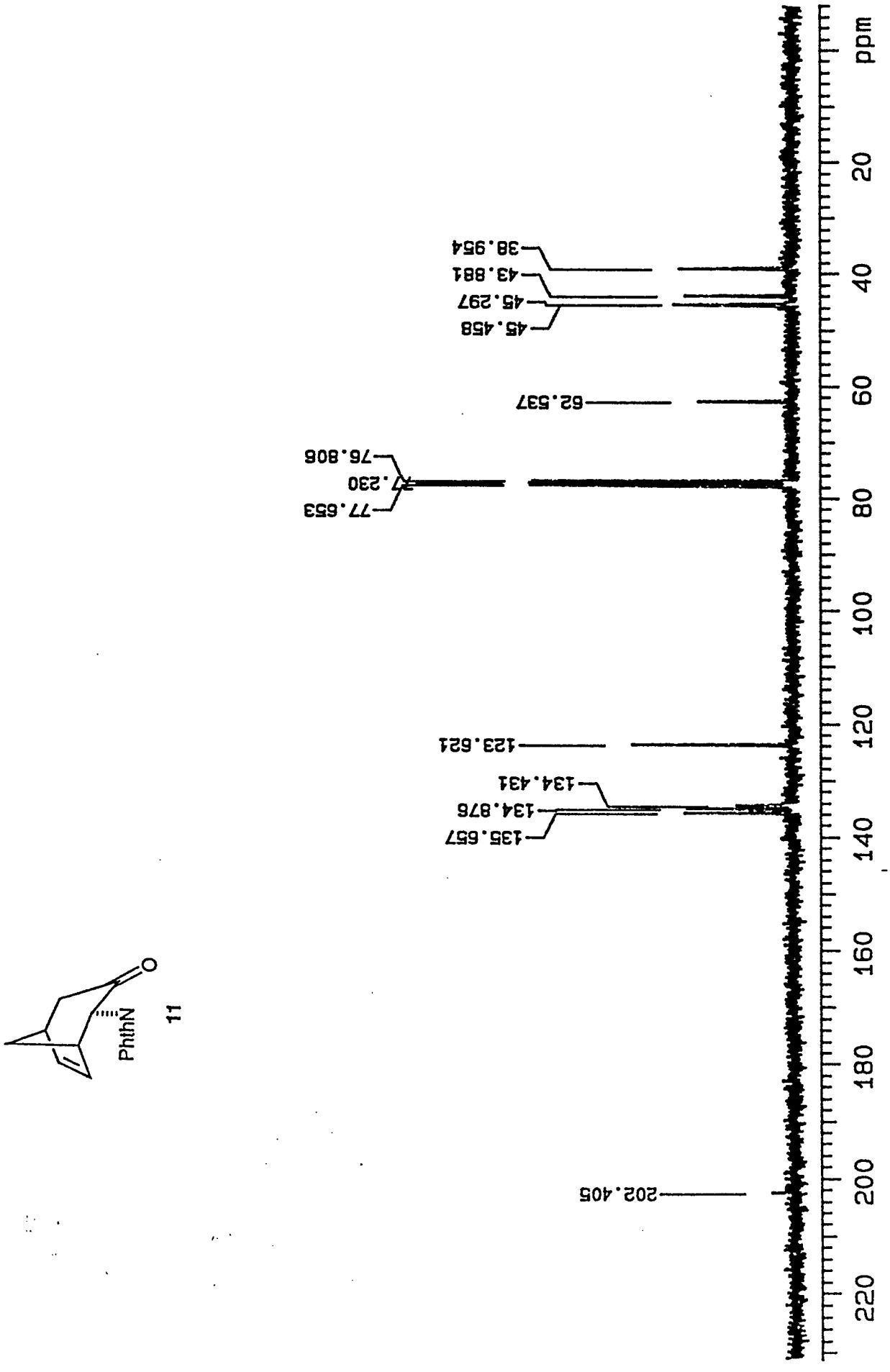
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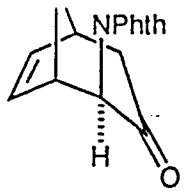
PhthN
11



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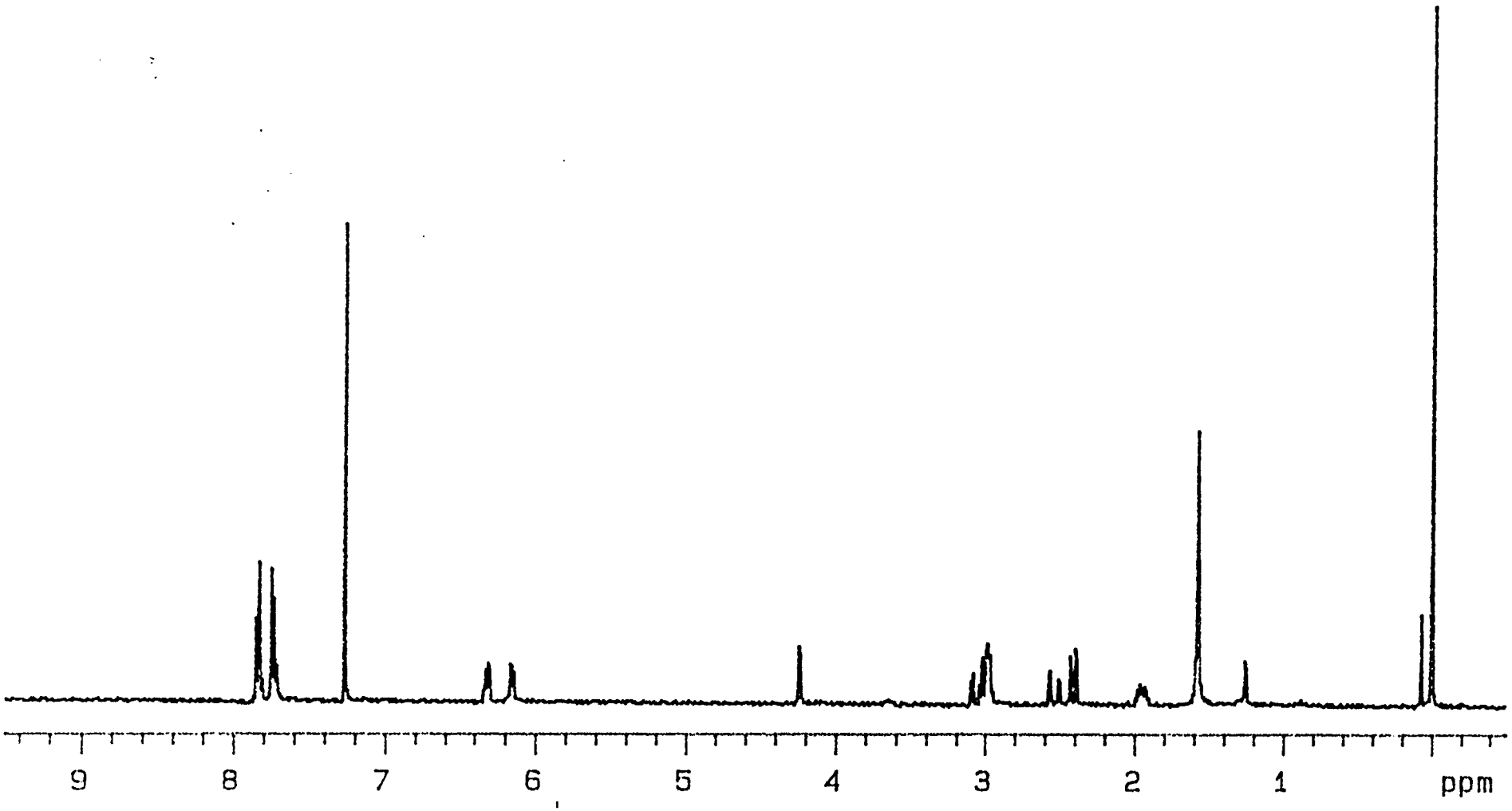
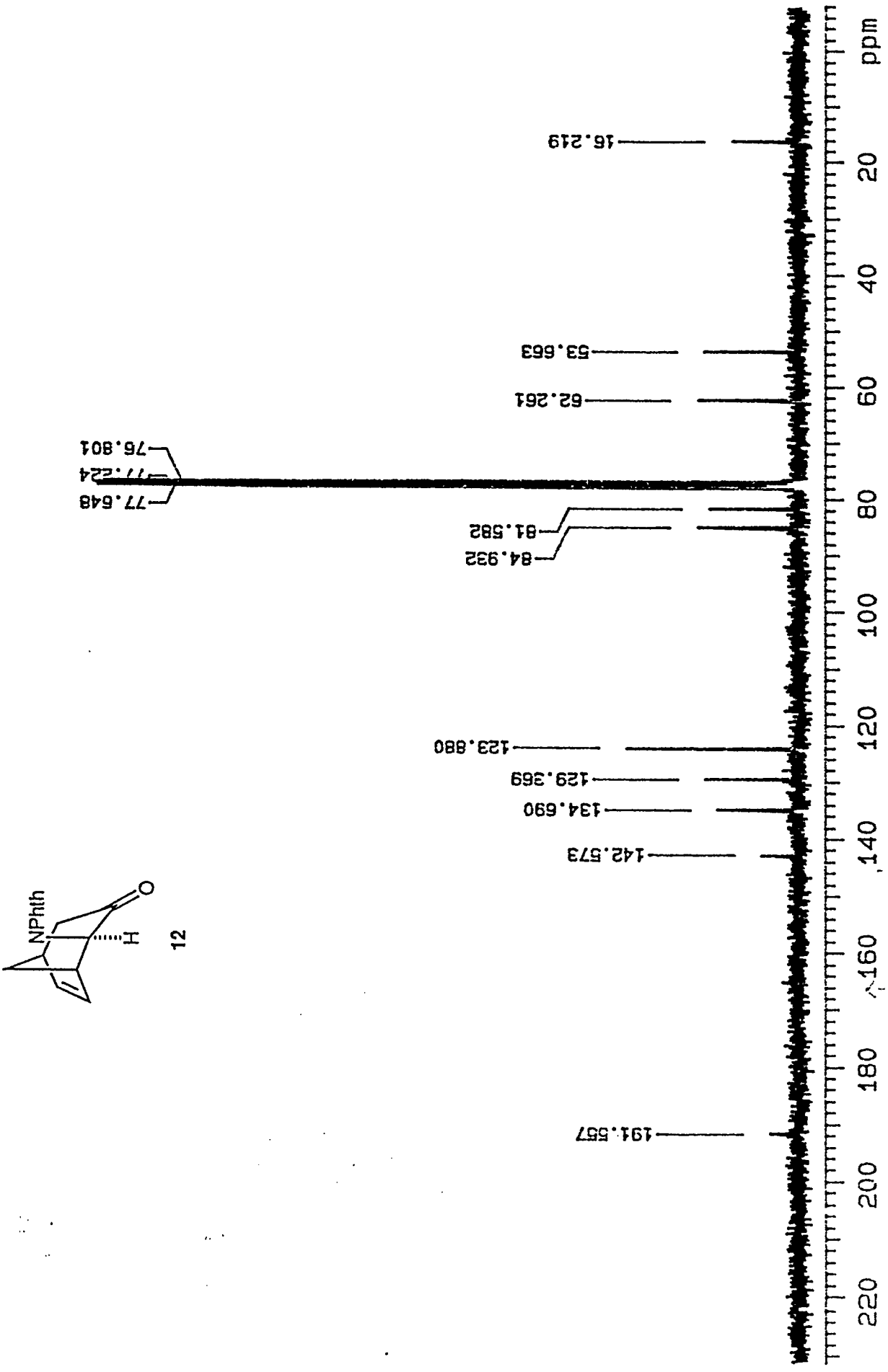


Gr 1486-13

G14486-14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40
60
80
100
120
140
160
180
200
220
16.219
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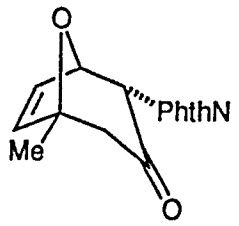
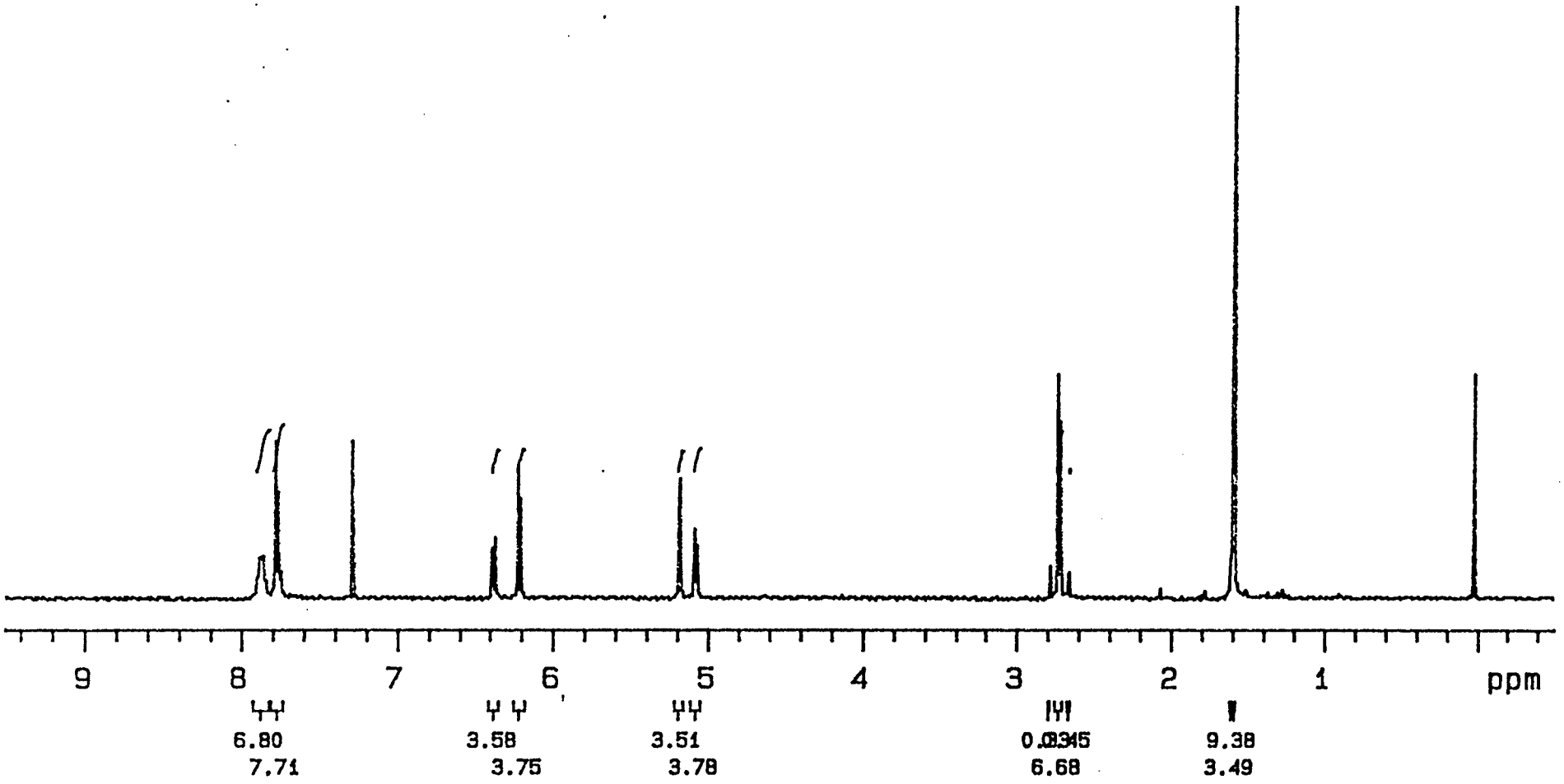
62.261
76.801
77.224
77.648
81.582
84.932
123.880
129.369
134.690
142.573
191.557
NPhth
H
O

12

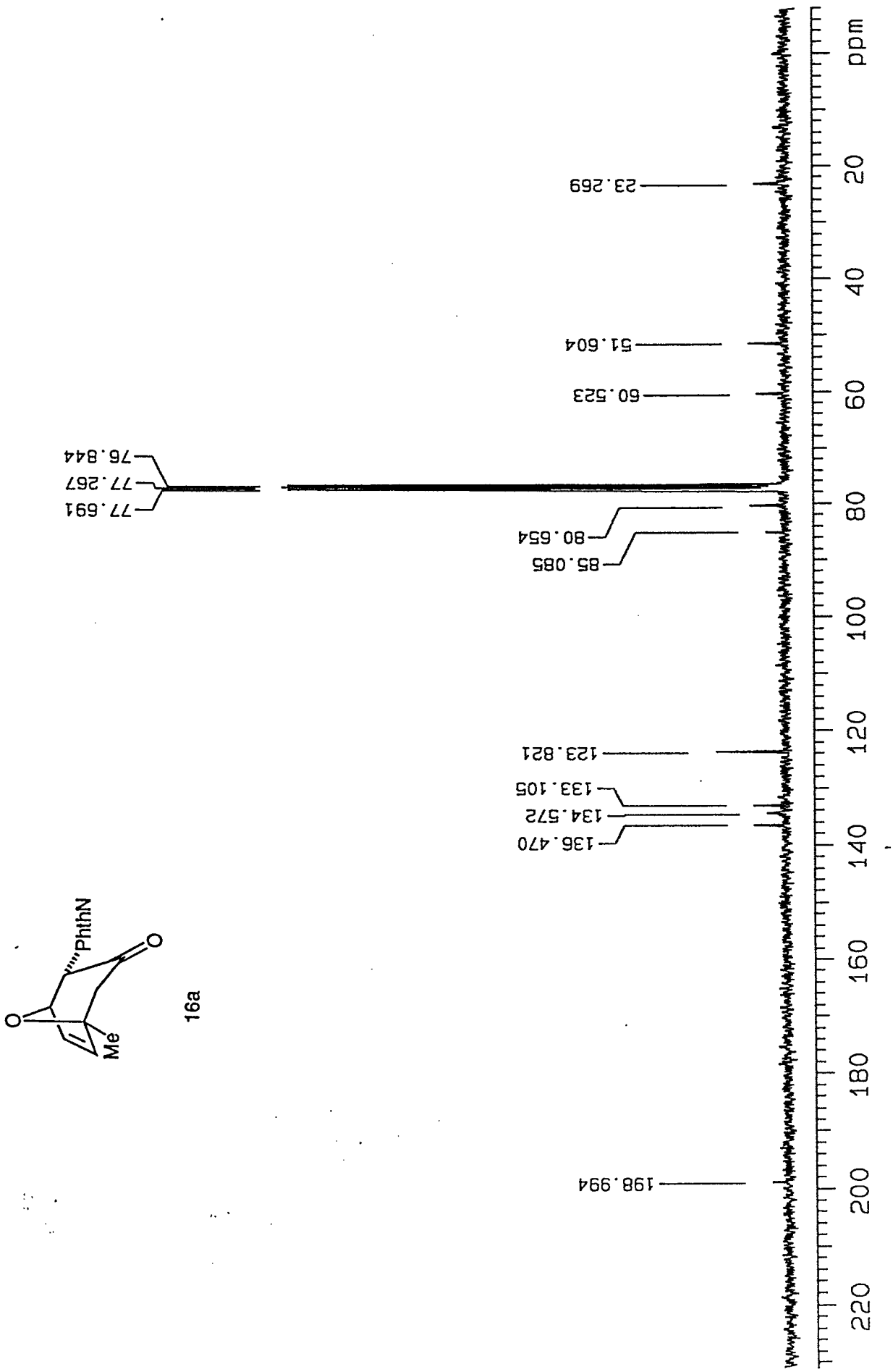


16a



G1486-15

Gr 1486-16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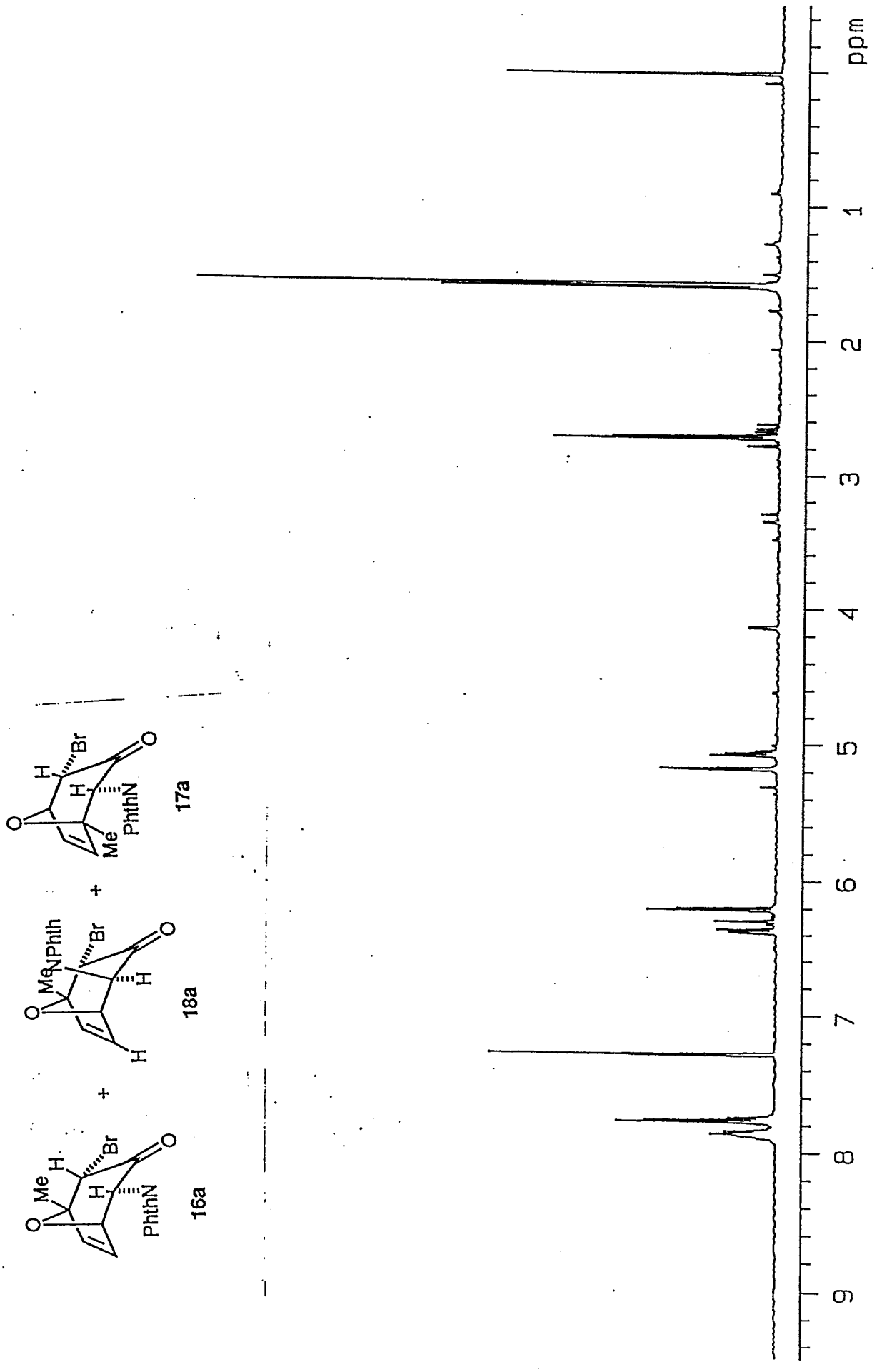
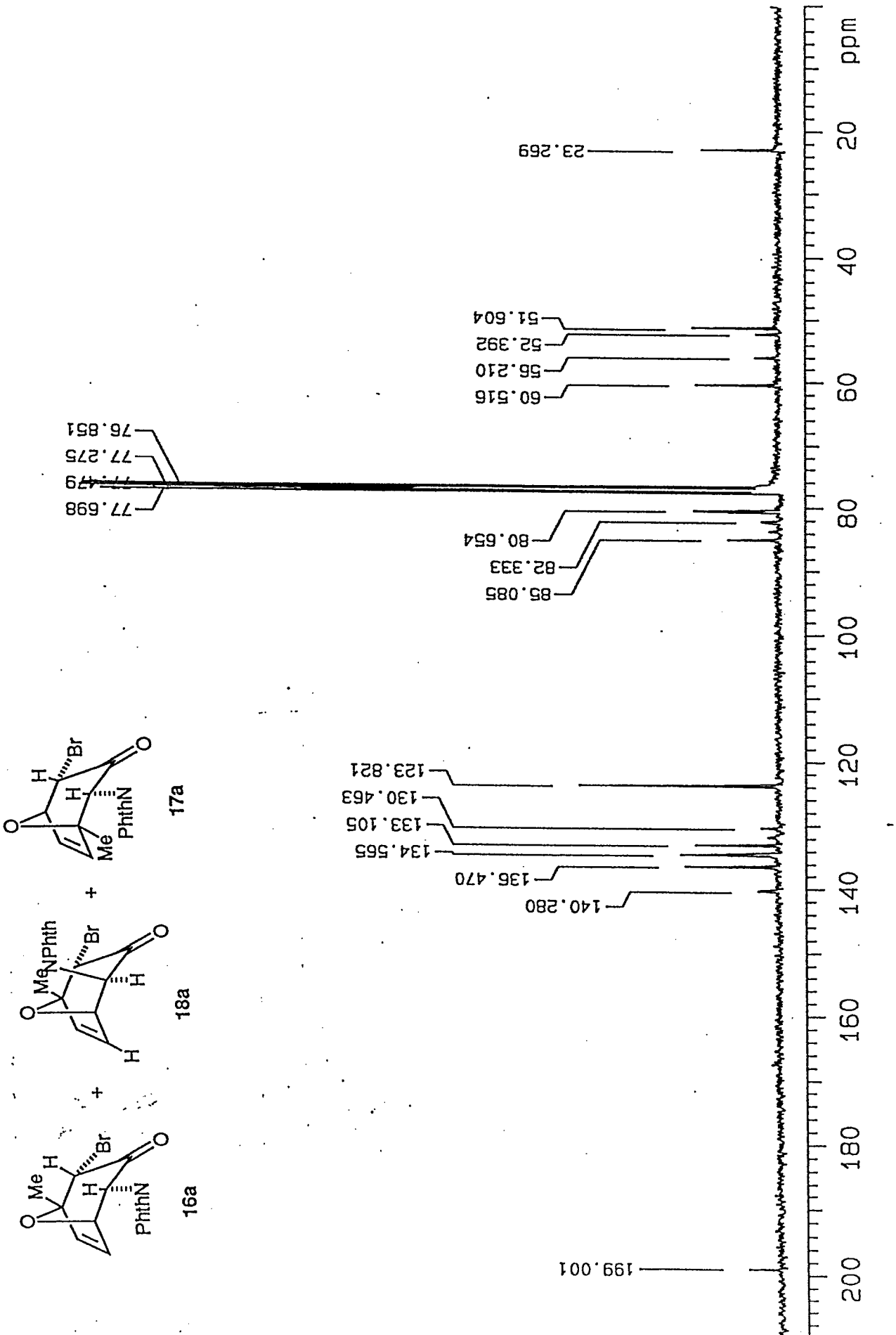
60.523
76.844
77.267
77.691
80.654
85.085
123.821
133.105
134.572
136.470
198.994
ppm
20
40
60
80
100
120
140
160
180
200
220
PhthN
Me
16a

Gr 1488e-17



Gr1486-18


23.269
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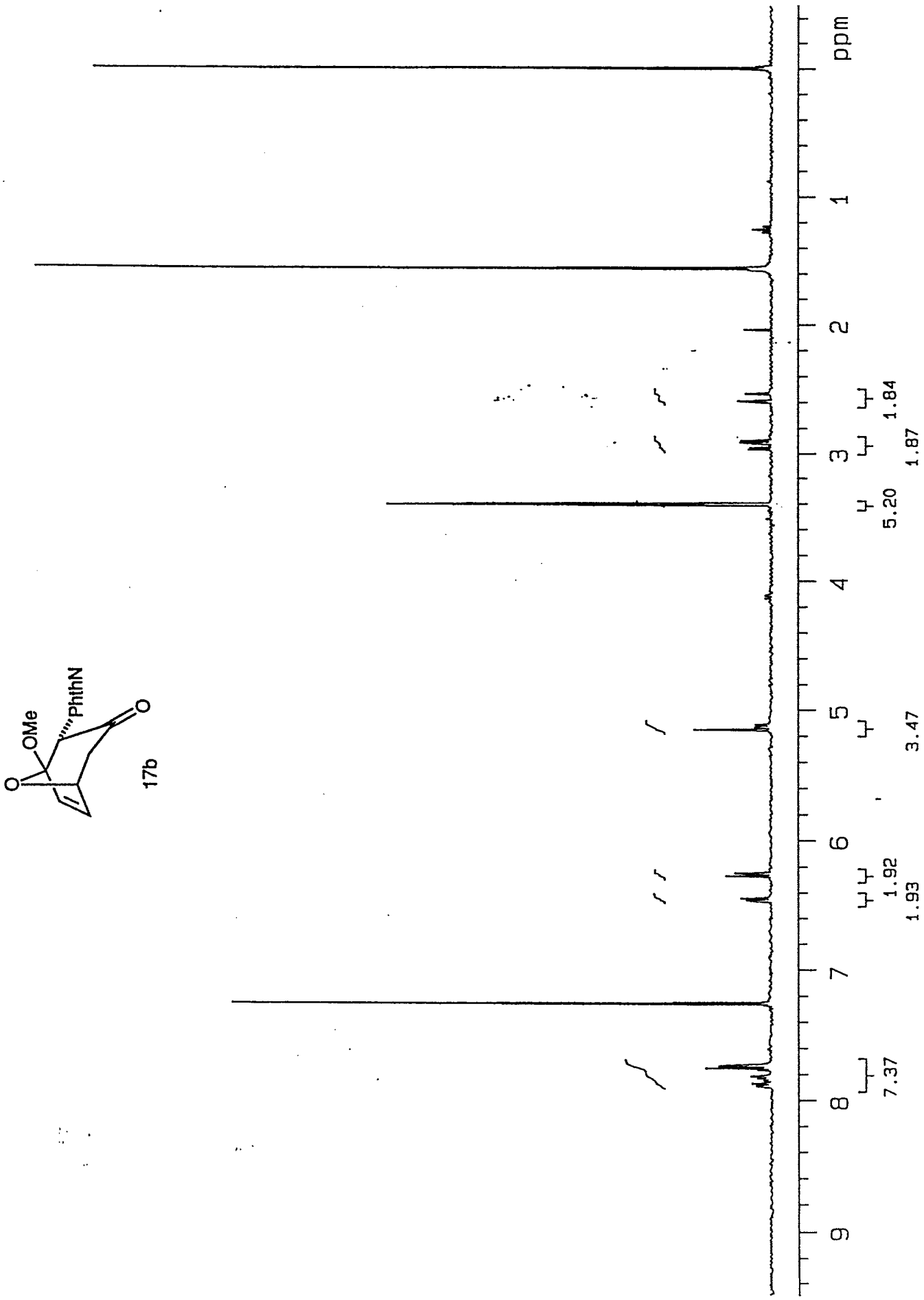
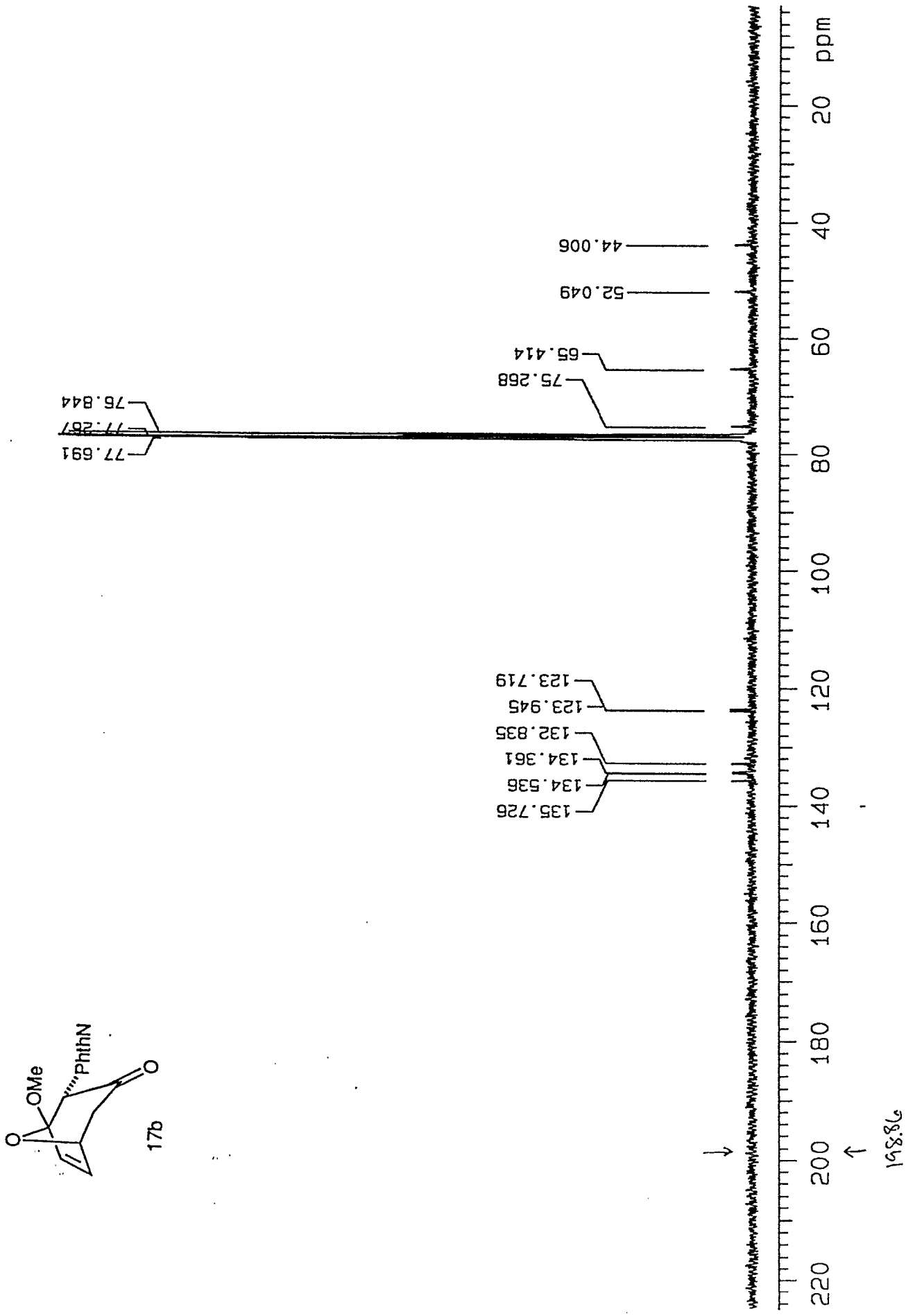
52.392
56.210
60.516
76.851
77.275
77.479
77.698
80.654
82.333
85.085
123.821
130.463
133.105
134.565
136.470
140.280
199.001
20
40
60
80
100
120
140
160
180
200
ppm
17a
18a
16a
Br
PhthN
Me
O
H

Gr1486-19



G71486-20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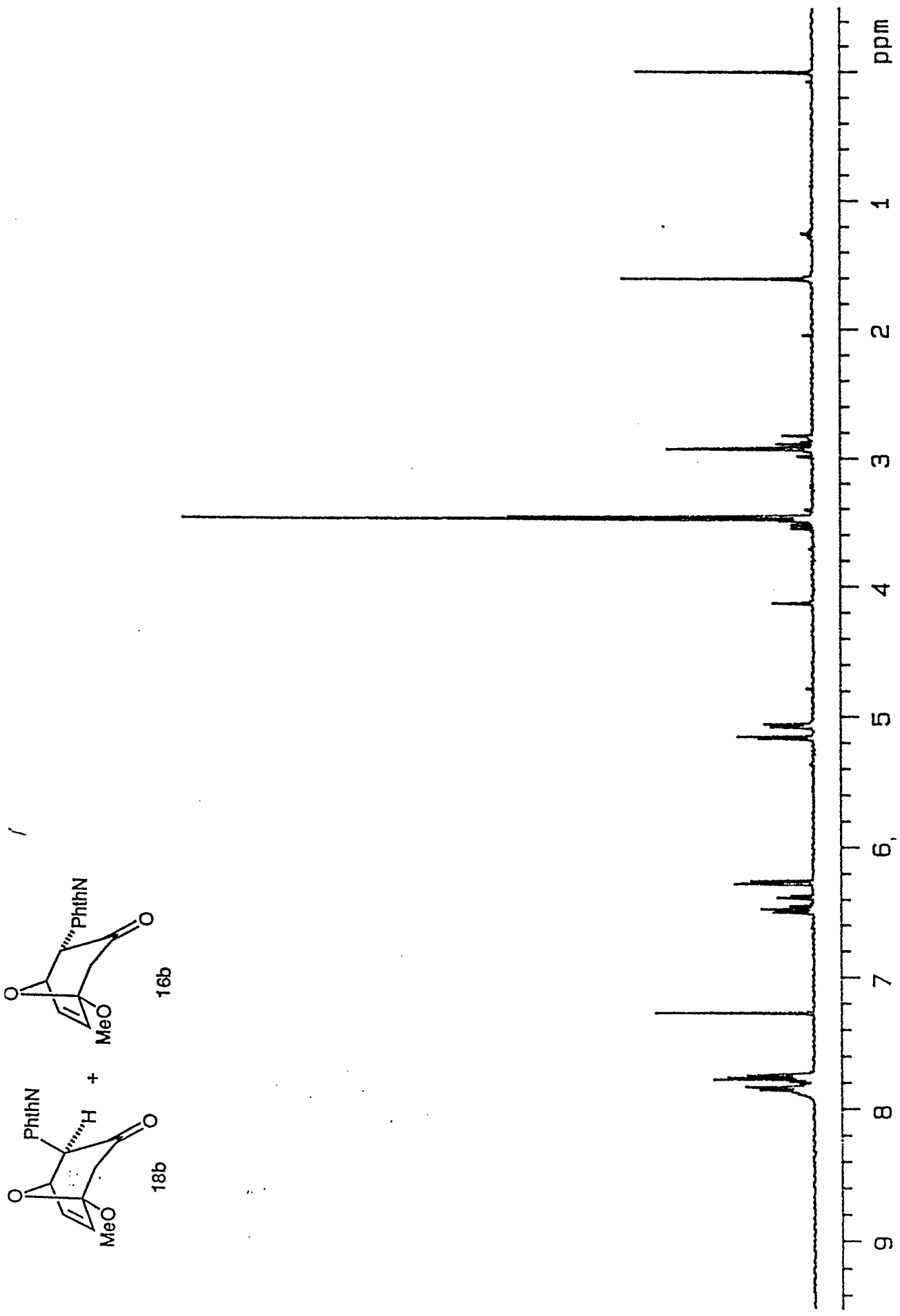
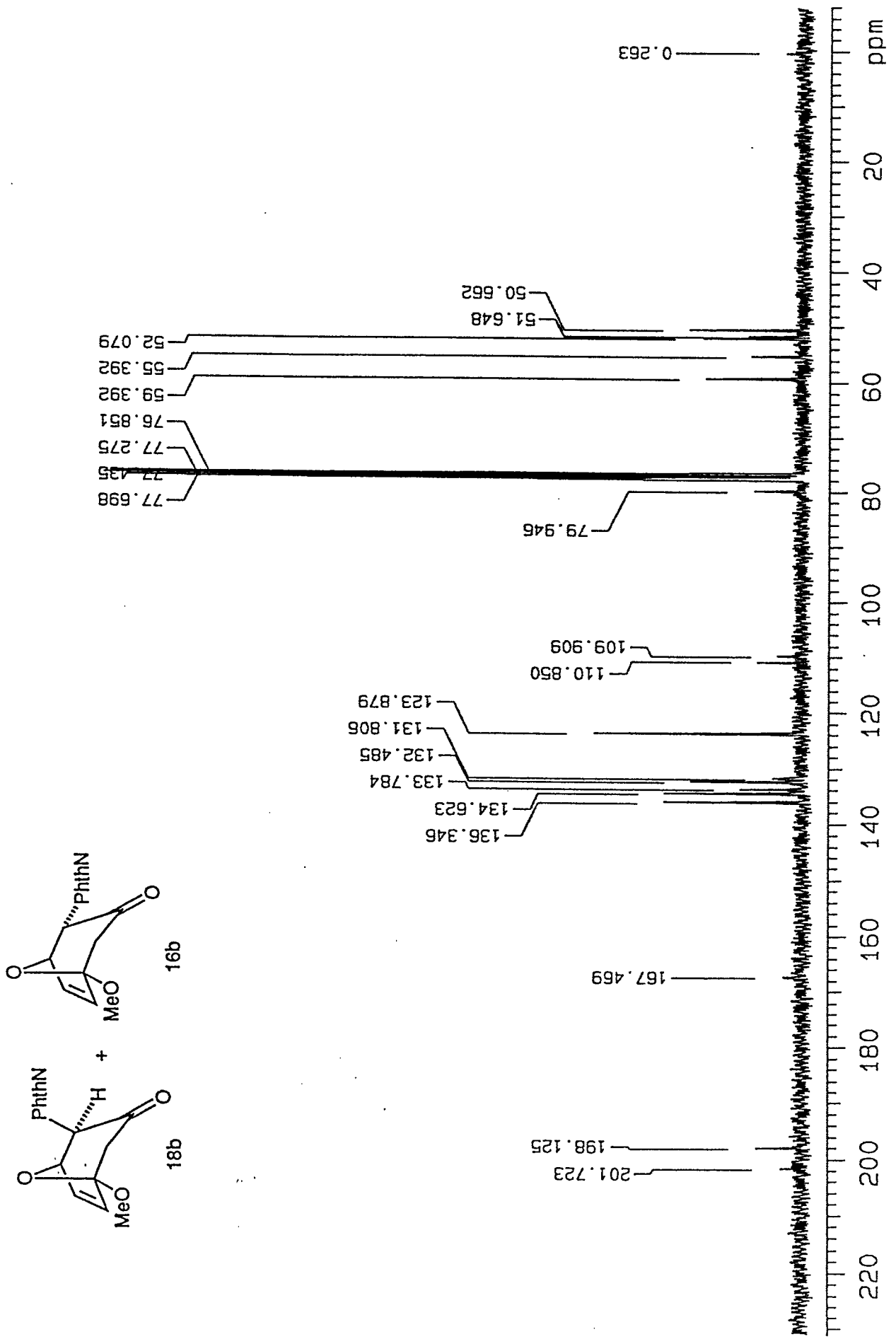
65.414
75.268
76.844
77.287
77.691
123.719
123.945
132.835
134.361
134.536
135.726
20
40
60
80
100
120
140
160
180
200
220
ppm
198.86
OMe
PhthN
O
O
17b

G1486-21



Gr1486-22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55.392
59.392
76.851
77.275
77.435
77.698
79.946
109.909
110.850
123.879
131.806
132.485
133.784
134.623
136.346
167.469
198.125
201.723
ppm
20
40
60
80
100
120
140
160
180
200
220
PhthN
O
O
MeO
16b
+
PhthN
H
O
O
MeO
18b