Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information for

The synthesis of enantiopure cyclopropyl esters from (-)-levoglucosenone.

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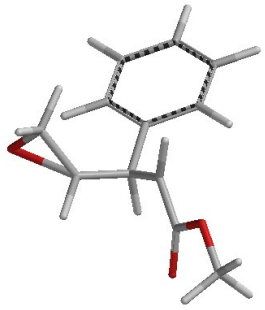
Transition state 33



Method : B3LYP
Basis set : 6-311+G**

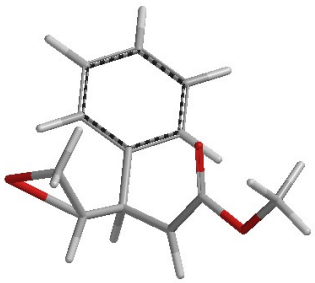
Charge : -1

Energy : -690.937377 hartrees
Solvation : -239.64 kJ/mol (SM54/AM1)

XYZ file

H	1.039197	0.320213	1.418312
C	1.182906	0.161781	0.358418
C	0.025671	-0.316282	-0.478470
H	0.276076	-0.173896	-1.534576
C	0.309182	-1.714011	-0.074670
H	1.120948	-2.197006	-0.597819
O	-1.004569	-3.091597	-0.142846
C	-0.380283	-2.500124	0.949458
H	-1.036774	-1.923883	1.624596
H	0.256018	-3.166920	1.556613
C	2.452382	0.354149	-0.207990
O	2.815296	0.197522	-1.381198
O	3.397704	0.789563	0.747490
C	4.712077	0.970349	0.250585
H	5.132274	0.035620	-0.136643
H	5.308013	1.318148	1.098219
H	4.746025	1.711782	-0.554653
C	-1.332567	0.307182	-0.212863
C	-3.837938	1.550445	0.120515
C	-2.519212	-0.421516	-0.379127
C	-1.423020	1.661789	0.129487
C	-2.661630	2.281470	0.288810
C	-3.757934	0.196903	-0.208712
H	-2.443679	-1.480364	-0.611970
H	-0.503509	2.220533	0.270019
H	-2.708669	3.335201	0.548675
H	-4.666991	-0.385028	-0.331631
H	-4.804179	2.028879	0.250648

Transition state 34



Method : B3LYP
Basis set : 6-311+G**

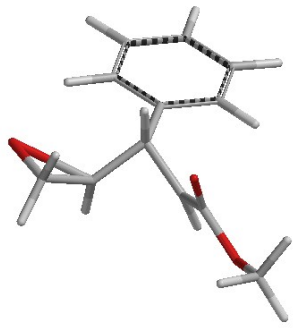
Charge : -1

Energy : -690.928501 hartrees
Solvation : -248.87 kJ/mol (SM54/AM1

XYZ file

H	1.926552	0.384465	2.039731
C	1.334706	0.226783	1.148589
C	-0.102637	0.700473	1.158976
H	-0.398511	0.871841	2.200791
C	0.350760	1.966126	0.545174
H	0.807535	2.683138	1.211316
O	-0.881063	3.189872	-0.350521
C	0.157290	2.407175	-0.844316
H	-0.130112	1.604467	-1.537428
H	1.006574	2.963109	-1.280340
C	1.964681	-0.385275	0.045929
O	1.522896	-0.666332	-1.068037
O	3.308266	-0.715531	0.352171
C	4.028207	-1.314316	-0.711911
H	3.569942	-2.254784	-1.035525
H	5.032198	-1.506183	-0.325090
H	4.088068	-0.653976	-1.583713
C	-1.189776	-0.148060	0.525060
C	-3.301503	-1.740530	-0.433497
C	-2.309080	0.442183	-0.075990
C	-1.139024	-1.541867	0.627343
C	-2.185696	-2.332944	0.159138
C	-3.352646	-0.351824	-0.553086
H	-2.328127	1.524415	-0.182066
H	-0.258235	-1.999294	1.064665
H	-2.123844	-3.414085	0.243588
H	-4.209456	0.120299	-1.025637
H	-4.115069	-2.355024	-0.807644

Transition State 36



Method : B3LYP
Basis set : 6-311+G**

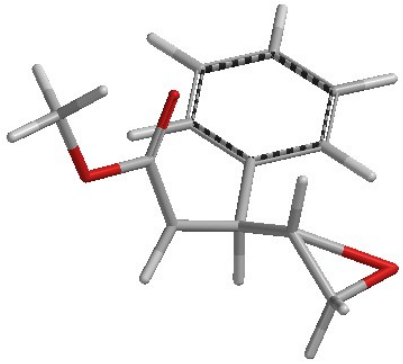
Charge : -1

Energy : -690.937828 hartrees
Solvation : -244.00 kJ/mol (SM54/AM1)

XYZ file

H	0.932506	-0.787629	1.444885
C	1.082999	-0.352041	0.466532
C	-0.060811	0.347716	-0.214006
H	0.191421	0.519183	-1.264572
C	0.236144	1.544584	0.585638
H	-0.059000	1.540652	1.626668
O	-0.562929	3.247570	0.030985
C	0.751831	2.813116	0.044742
H	1.239442	2.711957	-0.938442
H	1.429916	3.367436	0.720263
C	2.338130	-0.494740	-0.157906
O	2.704078	-0.121193	-1.275548
O	3.252512	-1.183103	0.667279
C	4.545379	-1.355915	0.111726
H	4.513751	-1.929010	-0.820796
H	5.123709	-1.901128	0.861587
H	5.026954	-0.395688	-0.100768
C	-1.448605	-0.256590	-0.108337
C	-4.041120	-1.340220	0.003899
C	-2.571809	0.581886	-0.113169
C	-1.641689	-1.639301	-0.039287
C	-2.927263	-2.179787	0.013035
C	-3.855804	0.042600	-0.058385
H	-2.404708	1.654779	-0.152631
H	-0.769505	-2.284848	-0.020300
H	-3.058684	-3.256647	0.067068
H	-4.716884	0.704565	-0.061232
H	-5.042499	-1.757664	0.049655

Transition state 37



Method : B3LYP
Basis set : 6-311+G**

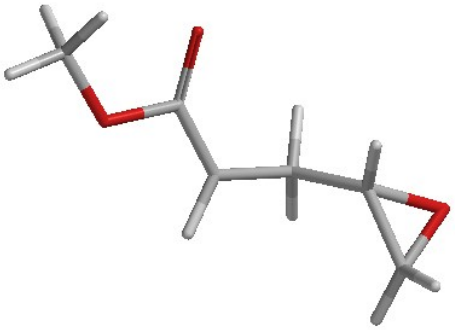
Charge : -1

Energy : -690.934581 hartrees
Solvation : -244.68 kJ/mol (SM54/AM1)

XYZ file

H	1.911574	-0.726179	1.728861
C	1.324970	-0.337519	0.908828
C	-0.104638	-0.810042	0.778215
H	-0.403355	-1.287122	1.718024
C	0.323499	-1.839032	-0.181130
H	0.540923	-1.517342	-1.189967
O	-0.857086	-3.341776	-0.479262
C	0.387105	-3.273649	0.120033
H	0.420567	-3.511894	1.201238
H	1.195818	-3.831847	-0.386352
C	1.961092	0.507245	-0.019675
O	1.520770	1.021700	-1.051535
O	3.301182	0.767698	0.356615
C	4.018455	1.602341	-0.535924
H	4.047924	1.185027	-1.547687
H	5.032287	1.671239	-0.133803
H	3.578096	2.603429	-0.599612
C	-1.209463	0.152294	0.379263
C	-3.356897	1.856676	-0.238536
C	-2.342285	-0.340543	-0.279824
C	-1.162586	1.506649	0.716872
C	-2.228392	2.353206	0.414162
C	-3.406882	0.505757	-0.585961
H	-2.361755	-1.393112	-0.546132
H	-0.272712	1.893695	1.200294
H	-2.170803	3.406293	0.673592
H	-4.277651	0.109482	-1.100384
H	-4.183701	2.517060	-0.482552

Enolate generated from methyl ester of 9



Job type : Geometry optimization.
Method : B3LYP
Basis set : 6-311+G**

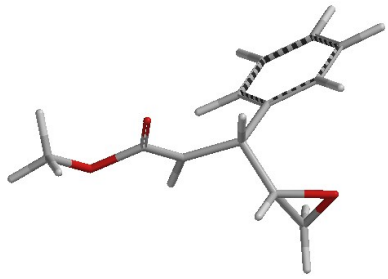
Charge : -1

Energy : -459.842561 hartrees
Solvation : -267.94 kJ/mol (SM54/AM1)

XYZ file

H	-0.166013	1.495869	0.915223
C	-0.167976	0.447004	0.643656
C	1.088680	-0.363311	0.785643
H	1.634532	-0.137108	1.715578
C	2.048504	-0.151022	-0.368646
H	1.643333	-0.402637	-1.347350
O	3.451296	-0.554360	-0.218110
C	3.126075	0.839002	-0.329546
H	3.272480	1.421973	0.580150
H	3.469298	1.324003	-1.243601
C	-1.330118	-0.123206	0.158538
O	-1.565747	-1.291386	-0.219079
O	-2.421507	0.818523	0.109815
C	-3.633614	0.294241	-0.382391
H	-3.543221	-0.067859	-1.414767
H	-4.357469	1.115779	-0.349283
H	-4.003630	-0.541358	0.224817
H	0.828208	-1.428109	0.814282

Enolate generated from methyl ester analogue of 23



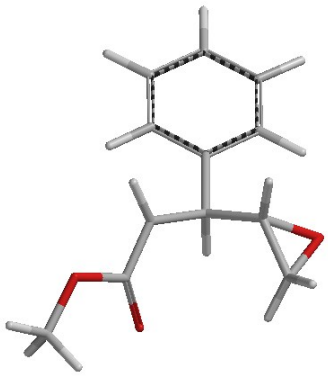
Job type : Geometry optimization.
Method : B3LYP
Basis set : 6-311+G**

Charge : -1

Energy : -690.951420 hartrees
Solvation : -248.02 kJ/mol (SM54/AM1)
XYZ file

H	1.288594	0.031857	1.517512
C	1.293288	-0.033835	0.435506
C	0.084094	-0.549495	-0.290548
H	0.348064	-0.557592	-1.355470
C	-0.110338	-2.015874	0.112039
H	0.777400	-2.611098	-0.088864
O	-1.347153	-2.747227	-0.162767
C	-0.981929	-2.466874	1.197944
H	-1.619819	-1.742896	1.701679
H	-0.711147	-3.338513	1.792934
C	2.474263	0.208132	-0.247621
O	2.734584	0.130333	-1.466005
O	3.533435	0.612505	0.632150
C	4.755345	0.912066	-0.007350
H	5.132232	0.068300	-0.596663
H	5.465985	1.148014	0.791324
H	4.670620	1.772874	-0.682698
C	-1.201270	0.275763	-0.157491
C	-3.558325	1.823466	0.036589
C	-2.320082	-0.002183	-0.957481
C	-1.291164	1.347894	0.736104
C	-2.454810	2.111834	0.838043
C	-3.482863	0.761653	-0.865926
H	-2.275446	-0.831080	-1.654154
H	-0.414588	1.590046	1.326115
H	-2.494230	2.942017	1.537685
H	-4.331099	0.530616	-1.504060
H	-4.461979	2.421527	0.106941

Enolate generated from methyl ester analogue of 31



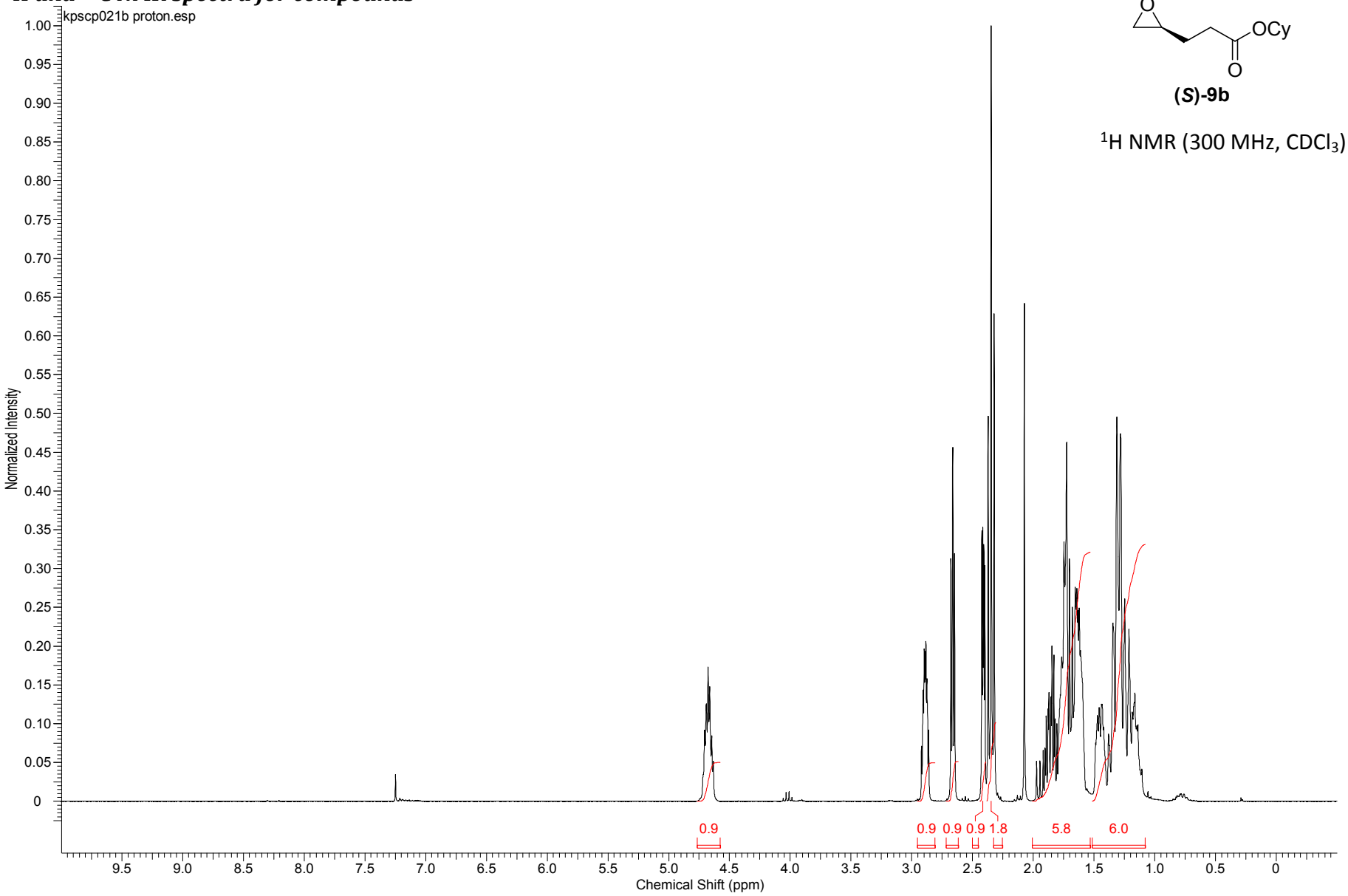
Job type : Geometry optimization.
Method : B3LYP
Basis set : 6-311+G**

Charge : -1

Energy : -690.953802 hartrees
Solvation : -242.50 kJ/mol (SM54/AM1)
XYZ file

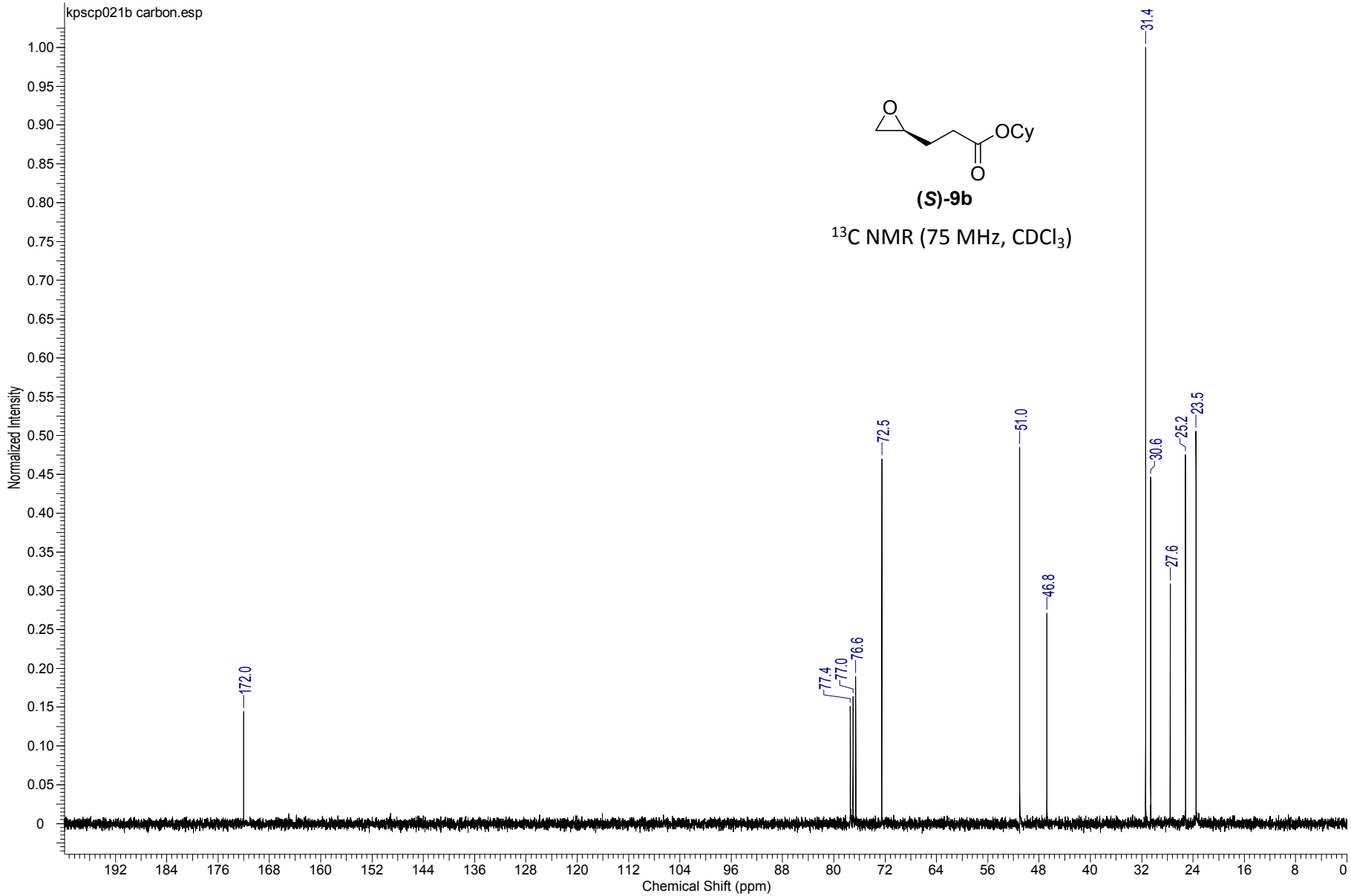
H	0.889441	-0.988954	1.414783
C	1.055246	-0.455252	0.486746
C	-0.025162	0.426478	-0.078551
H	0.225082	0.608764	-1.133264
C	0.019207	1.788077	0.603741
H	-0.235616	1.781712	1.663921
O	-0.493958	2.975318	-0.090234
C	0.923874	2.832513	0.135423
H	1.524895	2.632460	-0.747398
H	1.345909	3.544464	0.843757
C	2.299780	-0.502465	-0.116338
O	2.716577	0.069379	-1.147399
O	3.213597	-1.359516	0.581349
C	4.496469	-1.457950	0.001700
H	4.462310	-1.866487	-1.015603
H	5.069302	-2.133127	0.645639
H	5.003481	-0.486787	-0.051321
C	-1.433282	-0.179471	-0.049474
C	-4.019256	-1.328981	-0.062302
C	-2.585100	0.622352	-0.097339
C	-1.611401	-1.568463	-0.009238
C	-2.884000	-2.138250	-0.019179
C	-3.859868	0.056188	-0.102017
H	-2.478253	1.699574	-0.142946
H	-0.721976	-2.187732	0.030593
H	-2.988759	-3.219175	0.012186
H	-4.732748	0.701863	-0.139769
H	-5.011905	-1.769158	-0.064380

^{1}H and ^{13}C NMR spectra for compounds



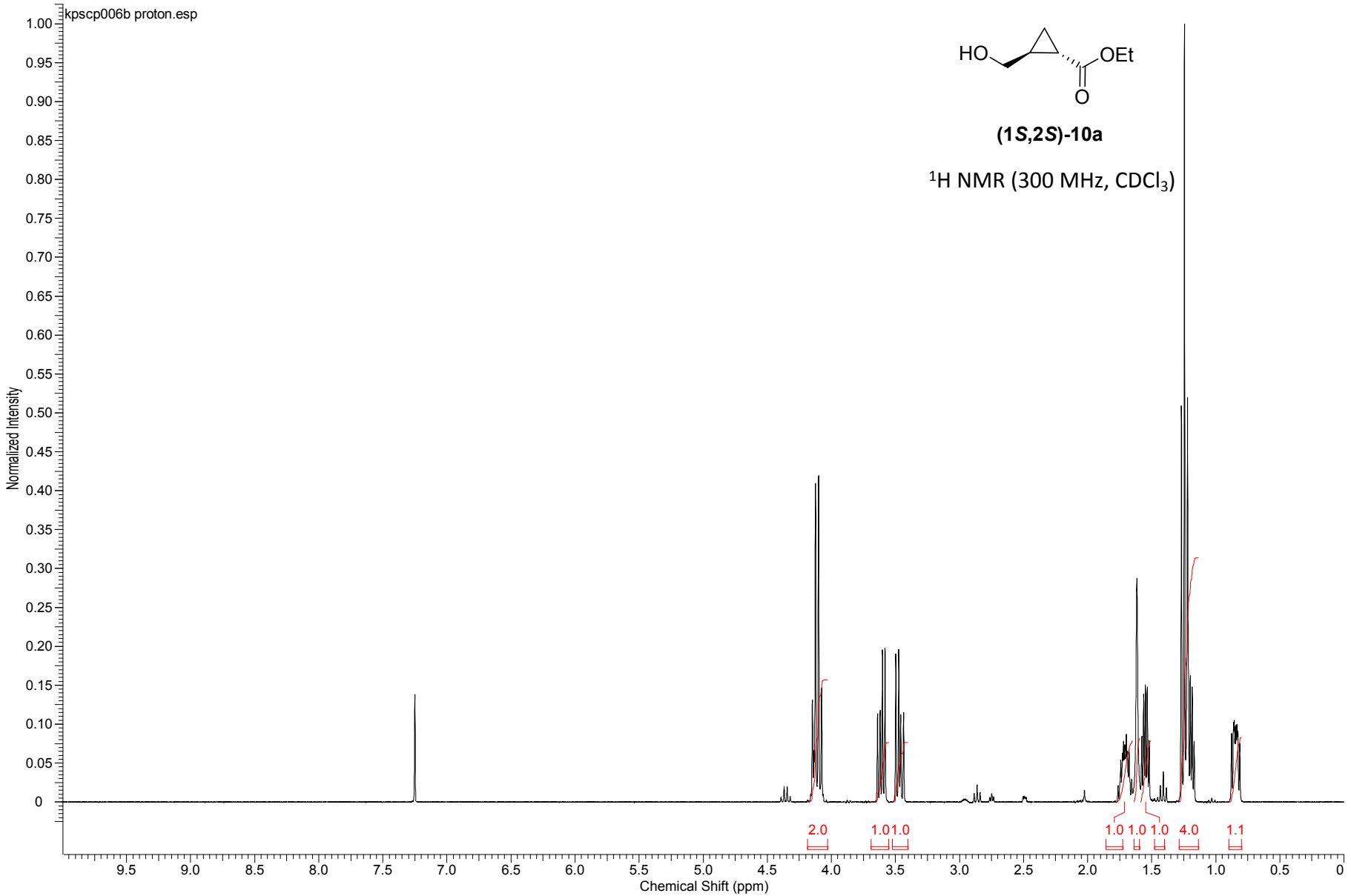
(*S*)-9b

^{1}H NMR (300 MHz, $CDCl_3$)



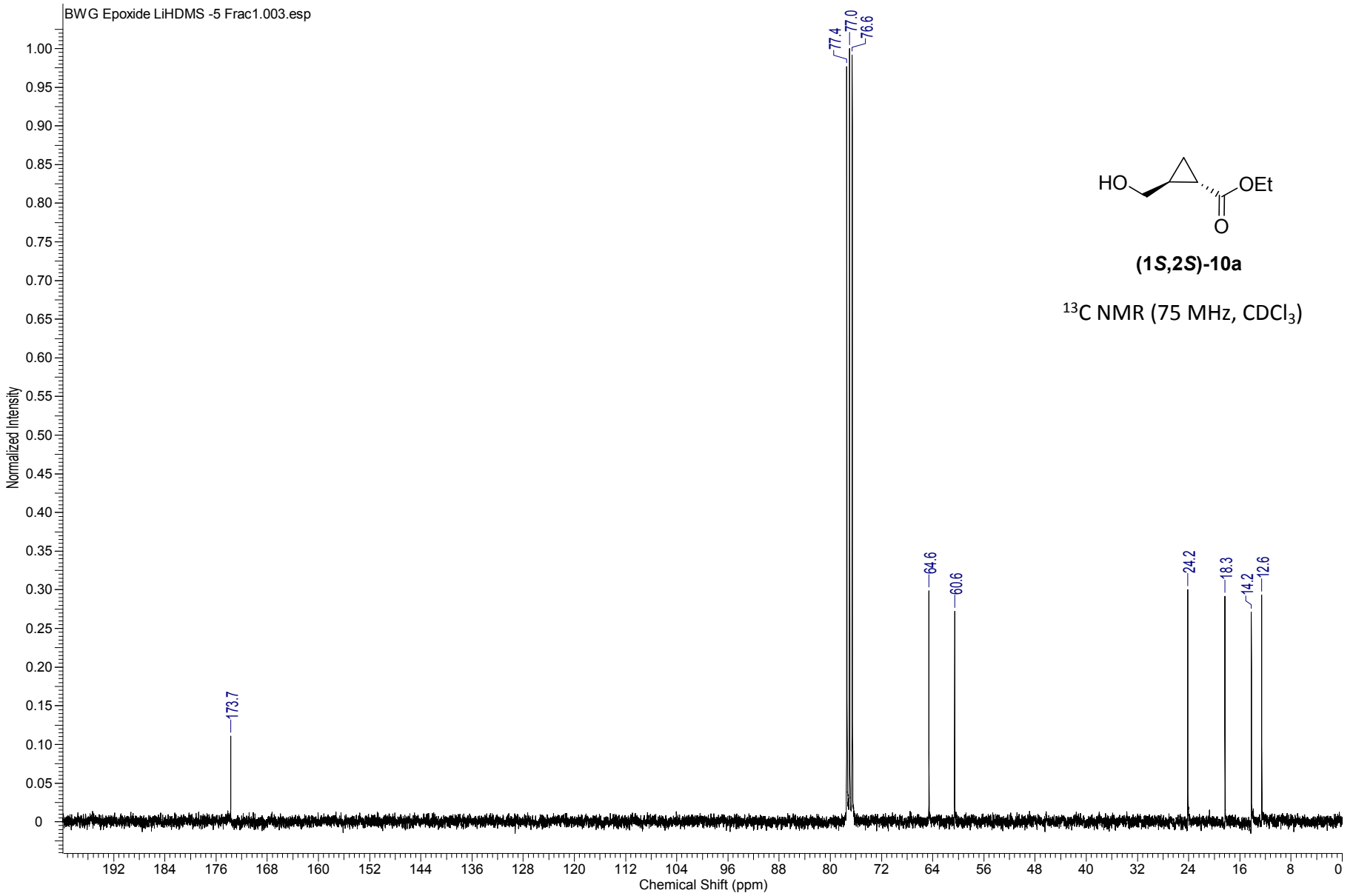
(*S*)-9b

^{13}C NMR (75 MHz, $CDCl_3$)



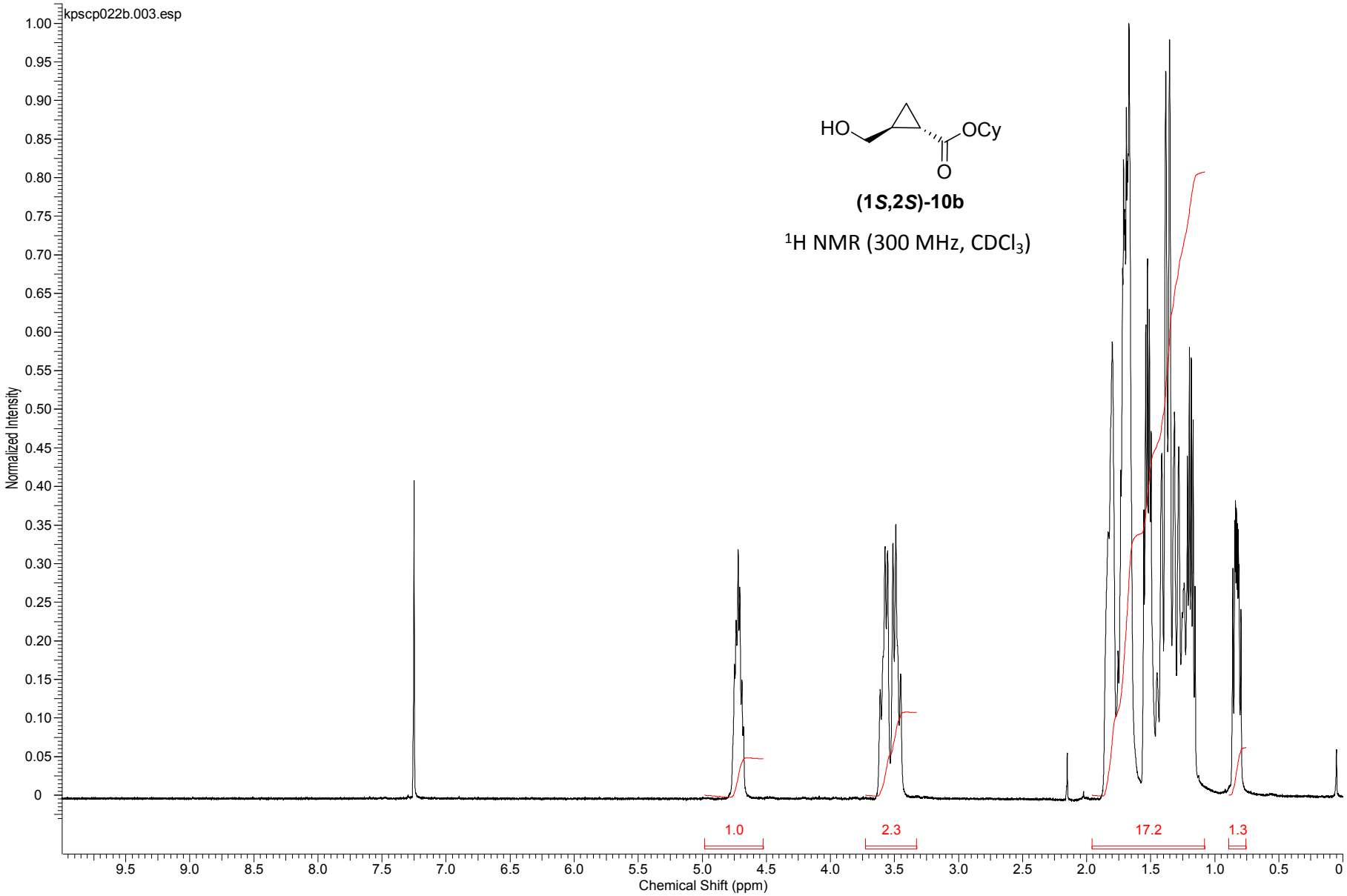
(1*S*,2*S*)-10a

^{1}H NMR (300 MHz, $CDCl_3$)



(1*S*,2*S*)-10a

^{13}C NMR (75 MHz, $CDCl_3$)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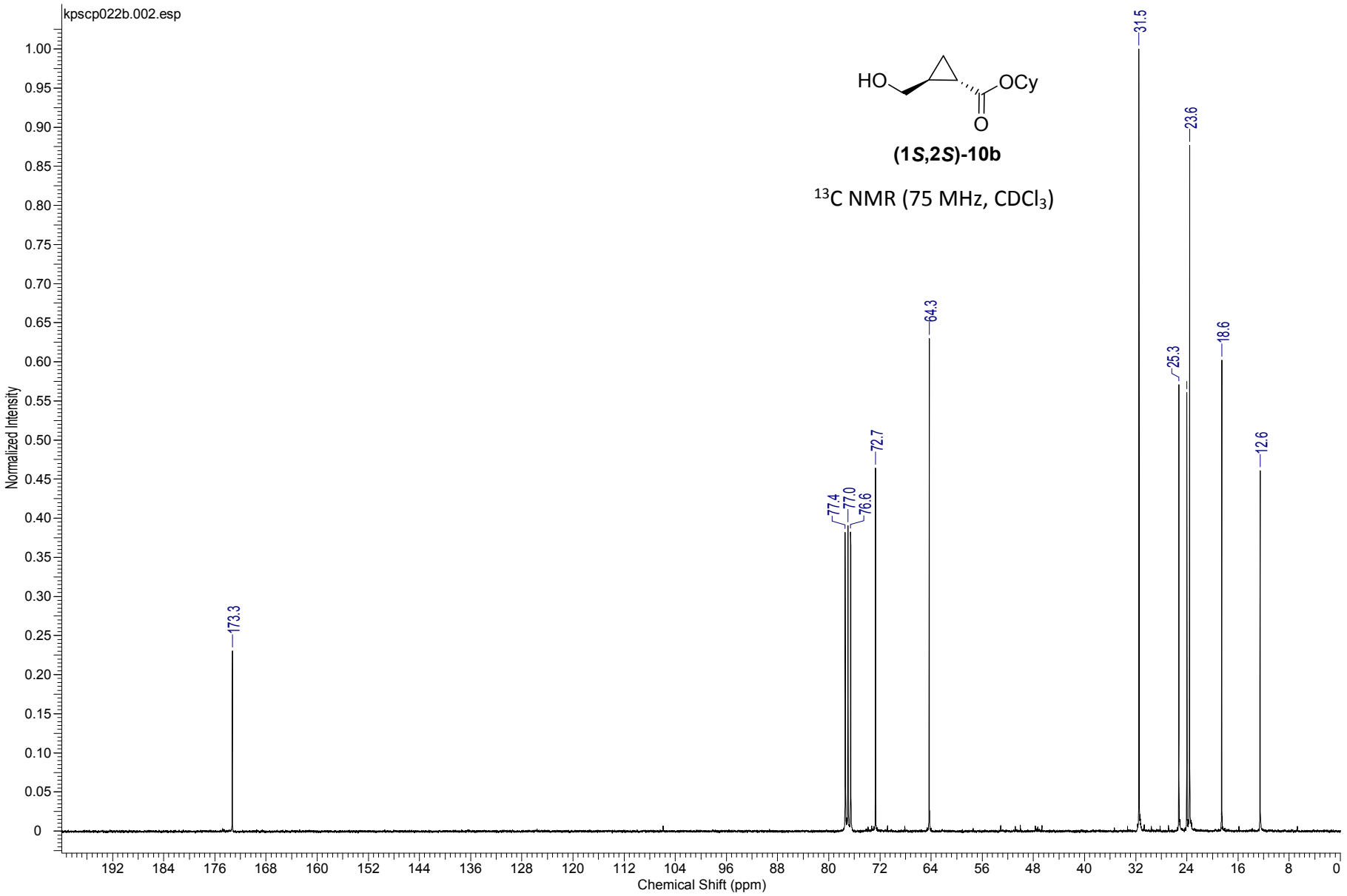
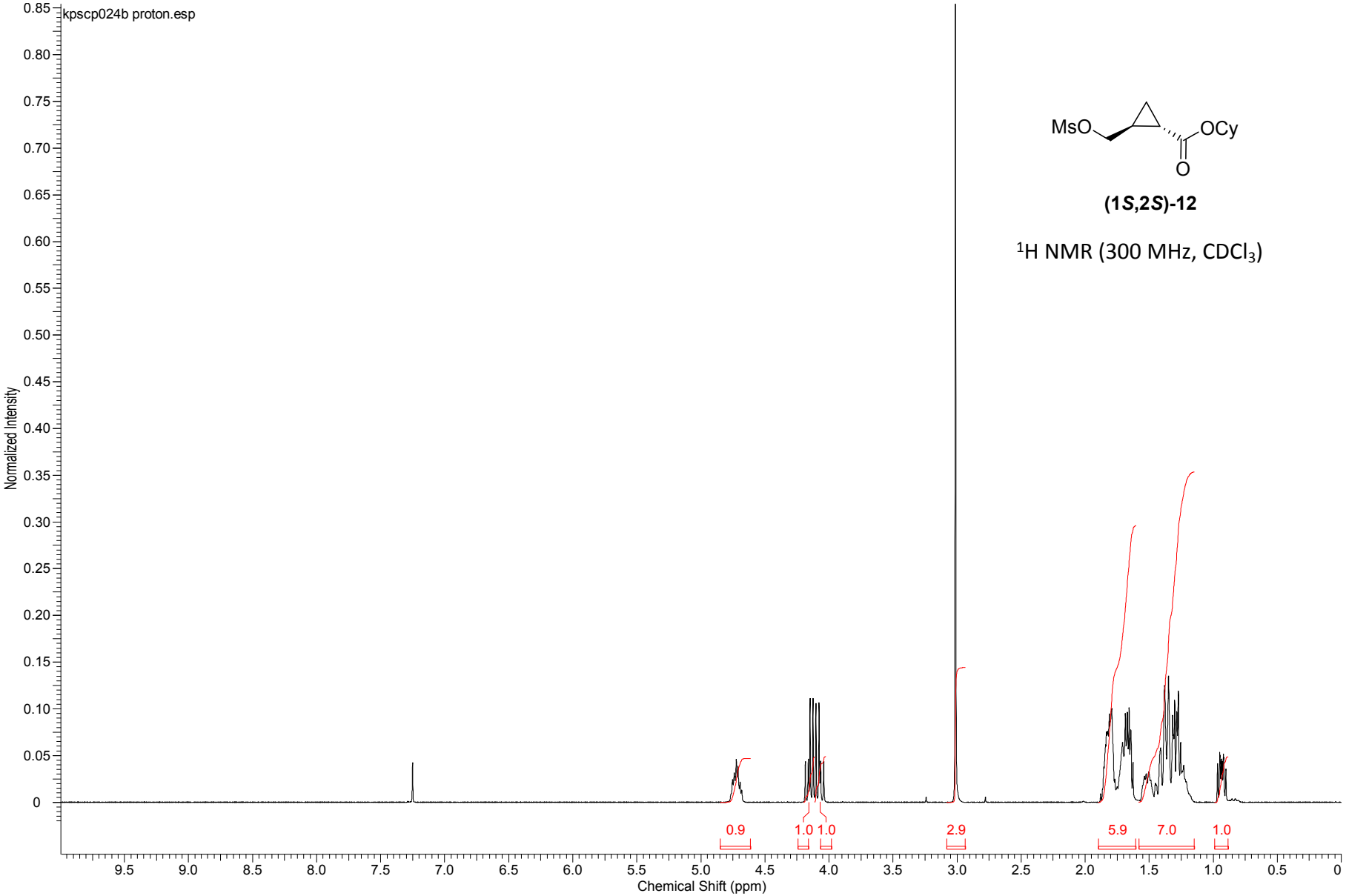
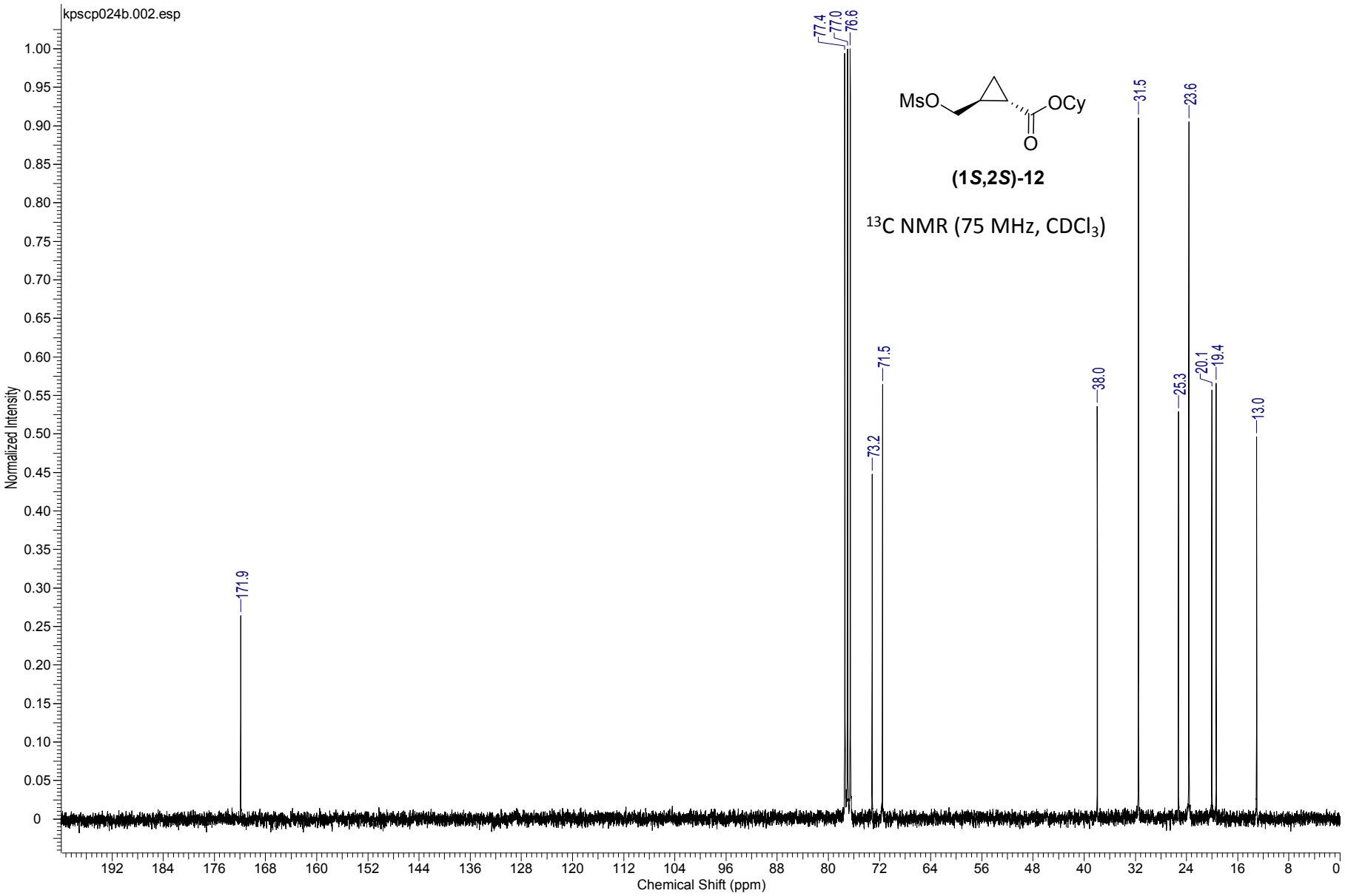
HO
OCy
O
(1S,2S)-10b
1H NMR (300 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
1.0
2.3
17.2
1.3


kpscp022b.002.esp
HO
OCy
O
(1S,2S)-10b
13C NMR (75 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
173.3
77.4
77.0
76.6
72.7
64.3
31.5
25.3
23.6
18.6
12.6



(1*S*,2*S*)-12

^{1}H NMR (300 MHz, $CDCl_3$)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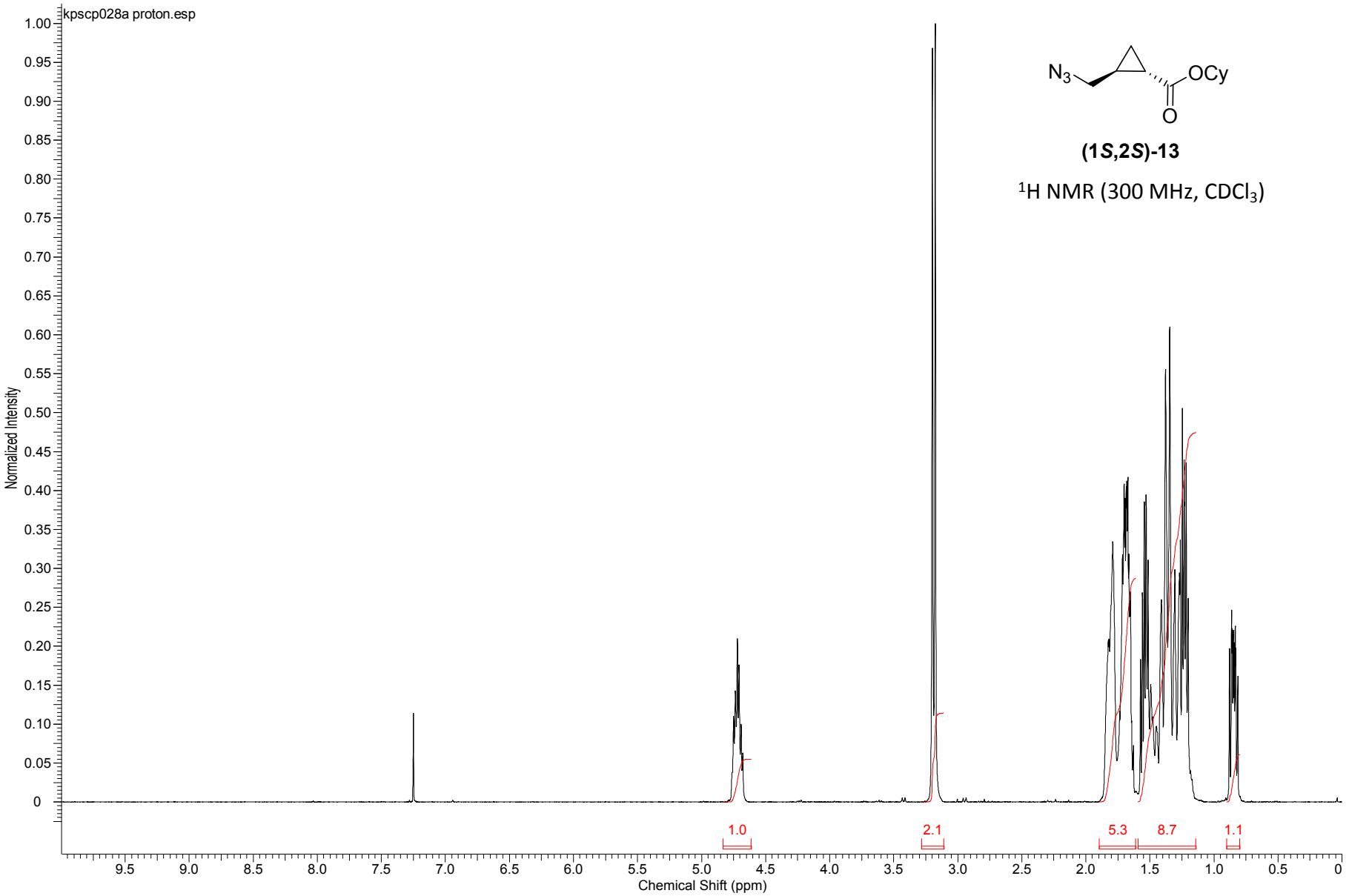
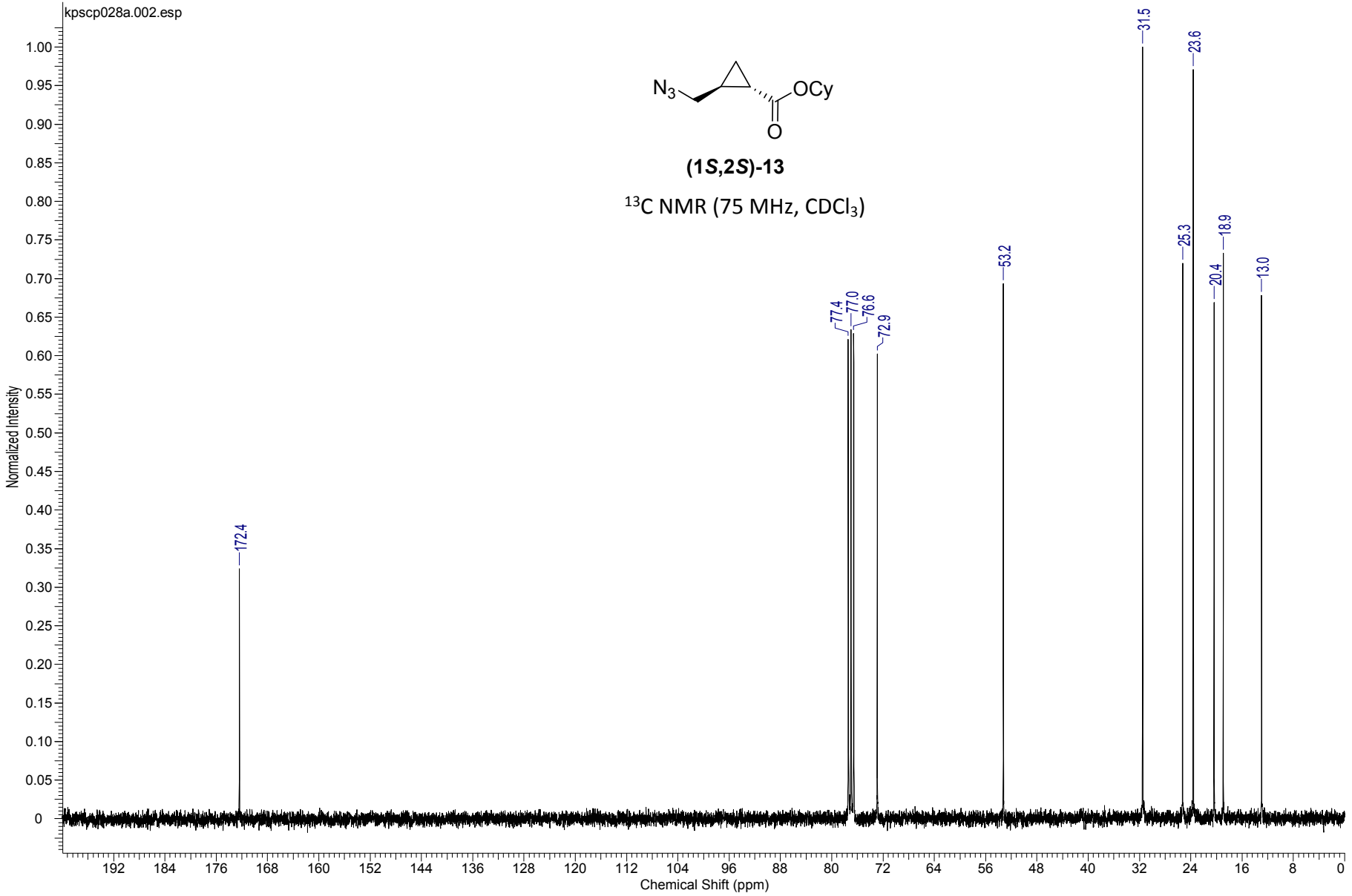
77.4
77.0
76.6
71.5
73.2
171.9
38.0
31.5
25.3
23.6
20.1
19.4
13.0
MsO
OCy
O
(1S,2S)-12
13C NMR (75 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)



(1*S*,2*S*)-13

^{1}H NMR (300 MHz, $CDCl_3$)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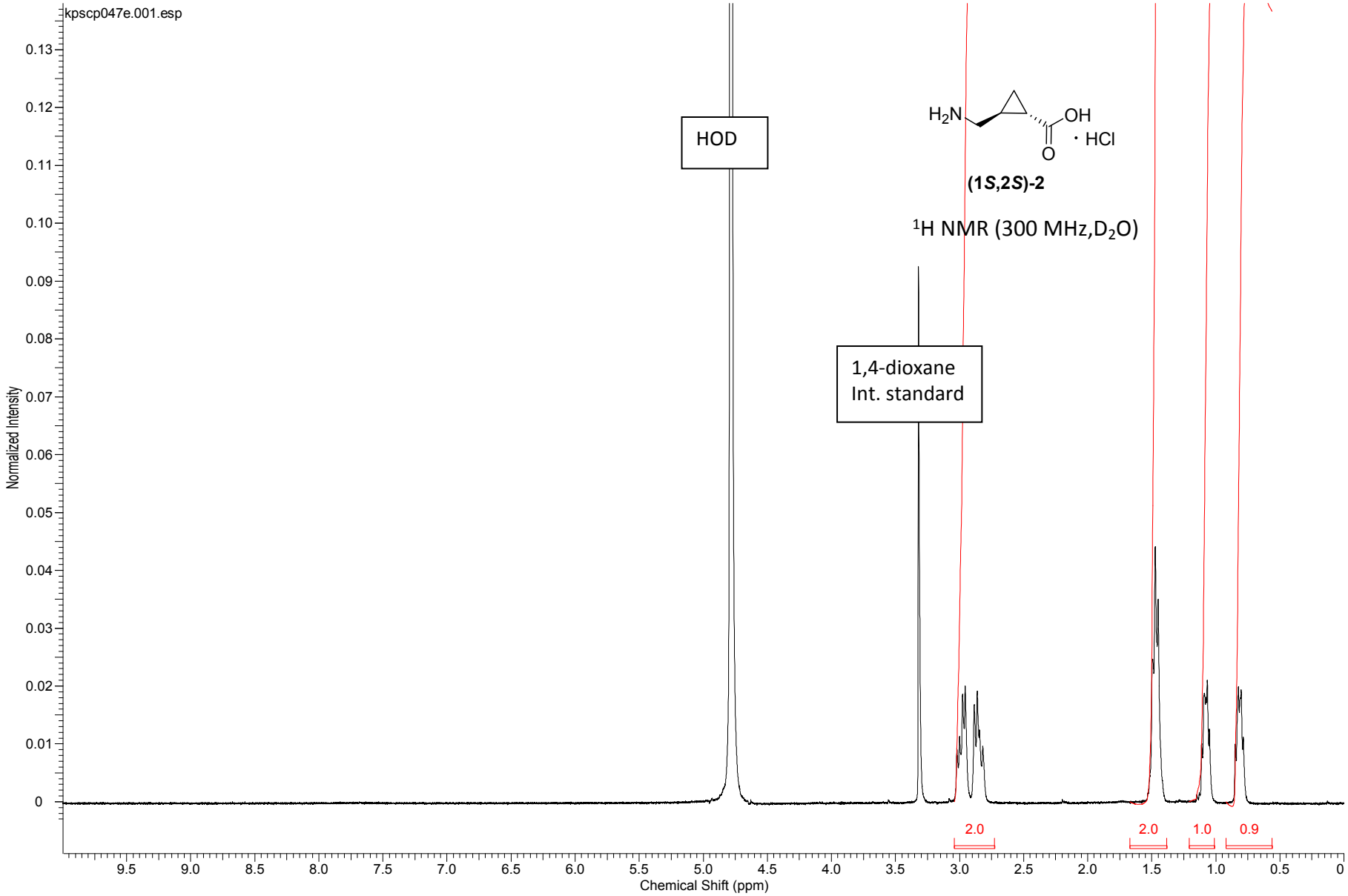
N3
OCy
O
(1S,2S)-13
13C NMR (75 MHz, CDCl3)
Normalized Intensity
Chemical Shift (ppm)
172.4
77.4
77.0
76.6
72.9
53.2
31.5
25.3
23.6
20.4
18.9
13.0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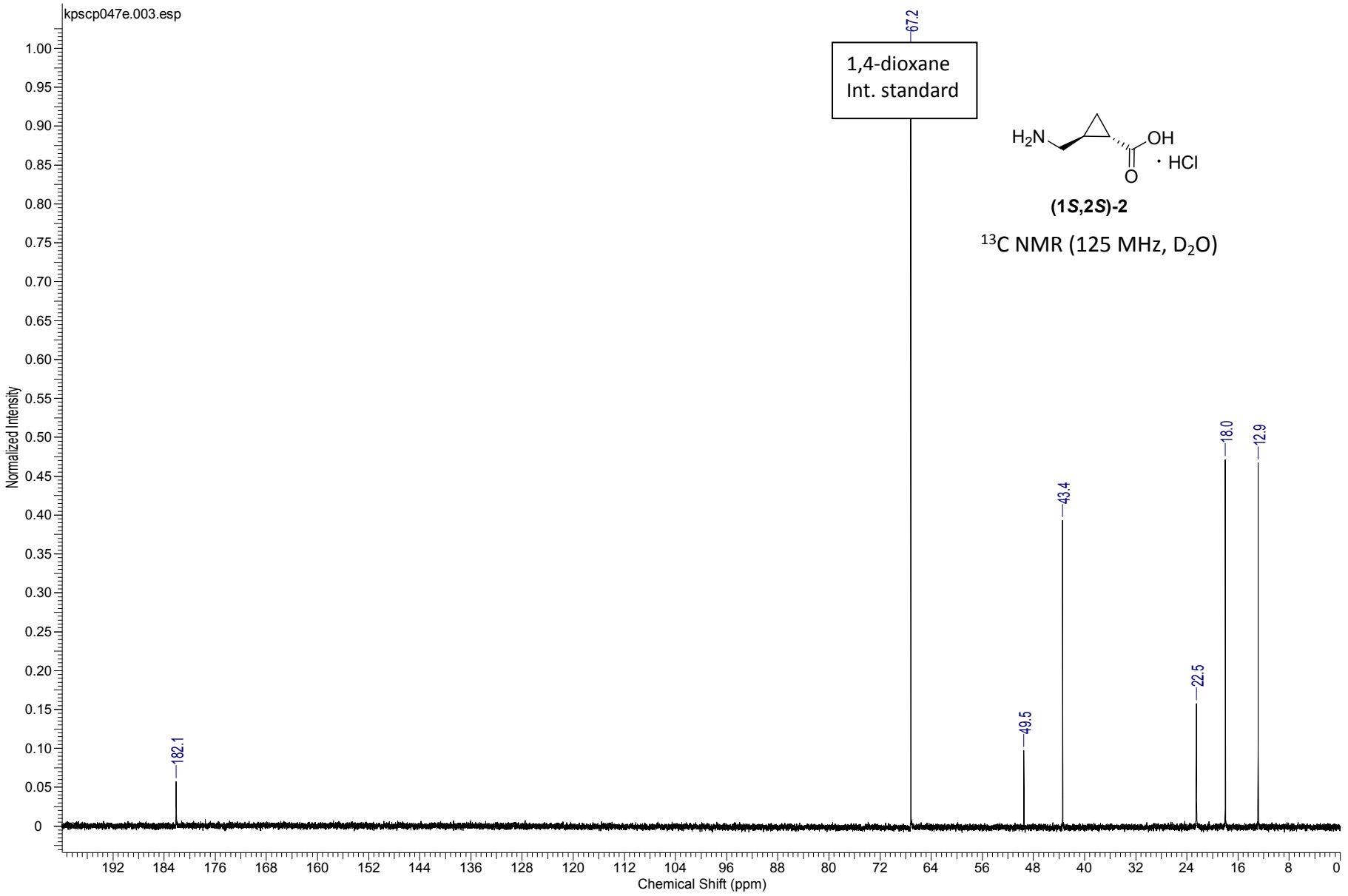
HOD
1,4-dioxane
Int. standard
H_2N
OH
O
· HCl
(1S,2S)-2
^{1}H NMR (300 MHz,D_2O)
Normalized Intensity
Chemical Shift (ppm)
2.0
2.0
1.0
0.9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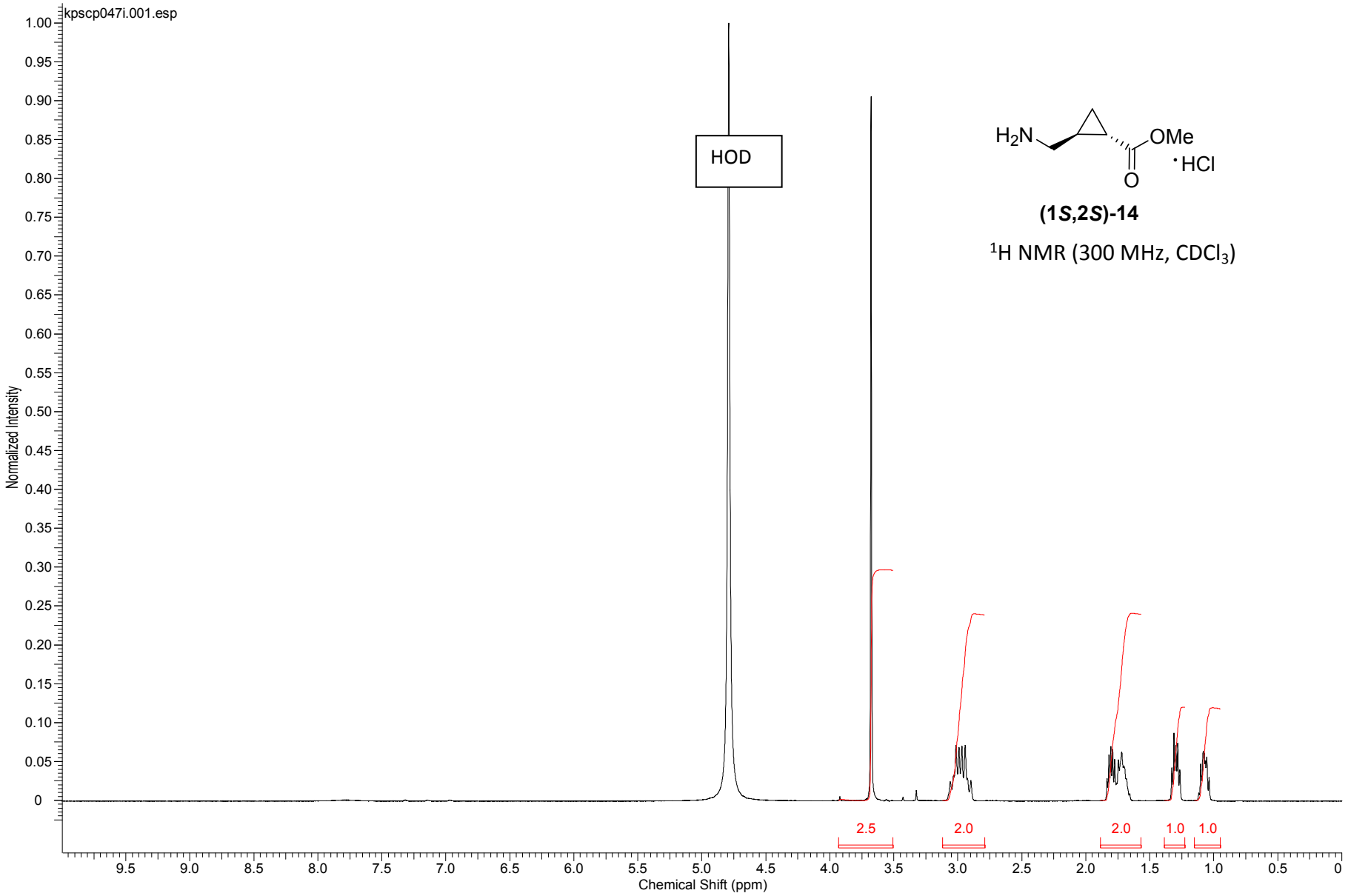
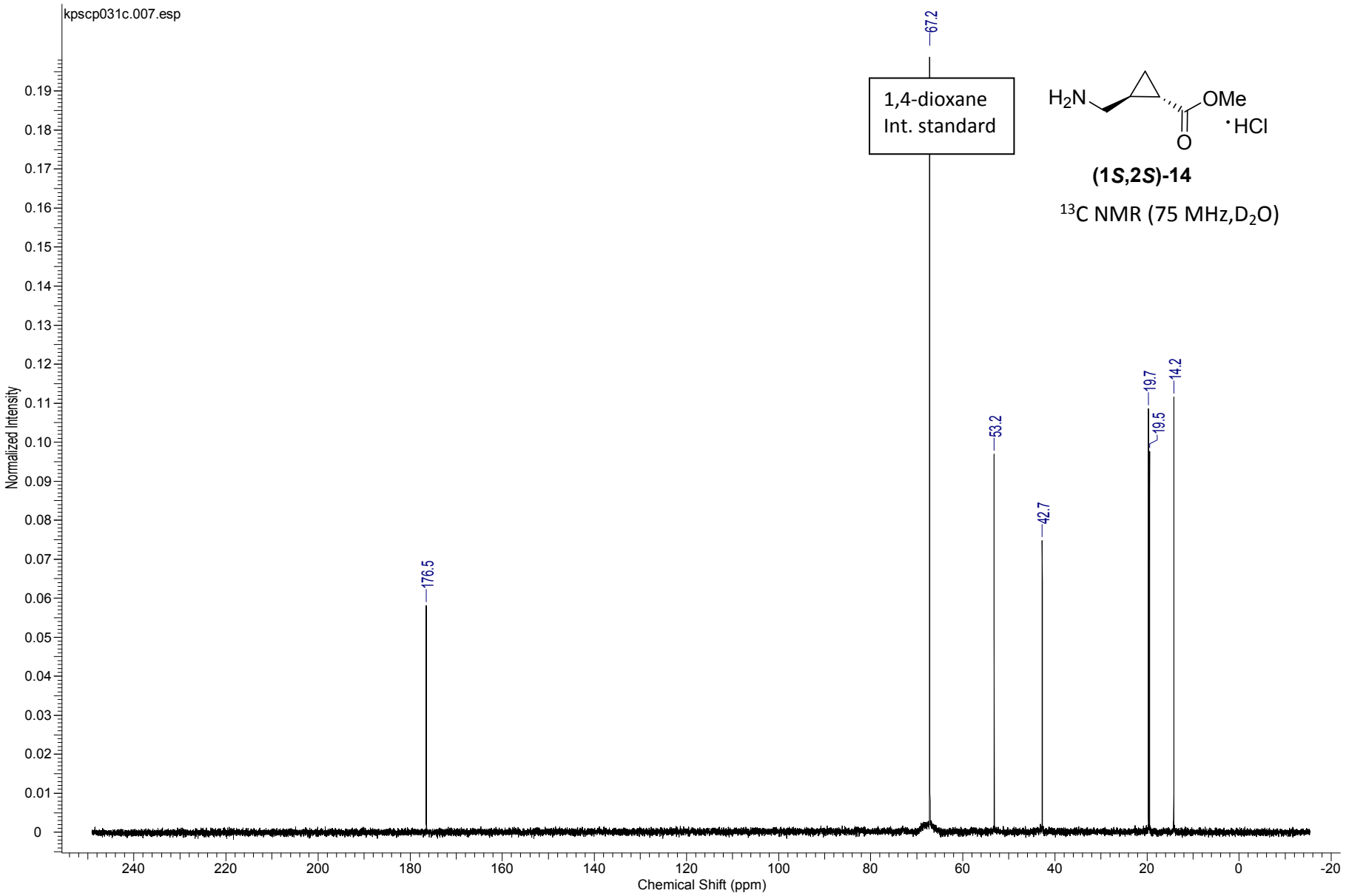
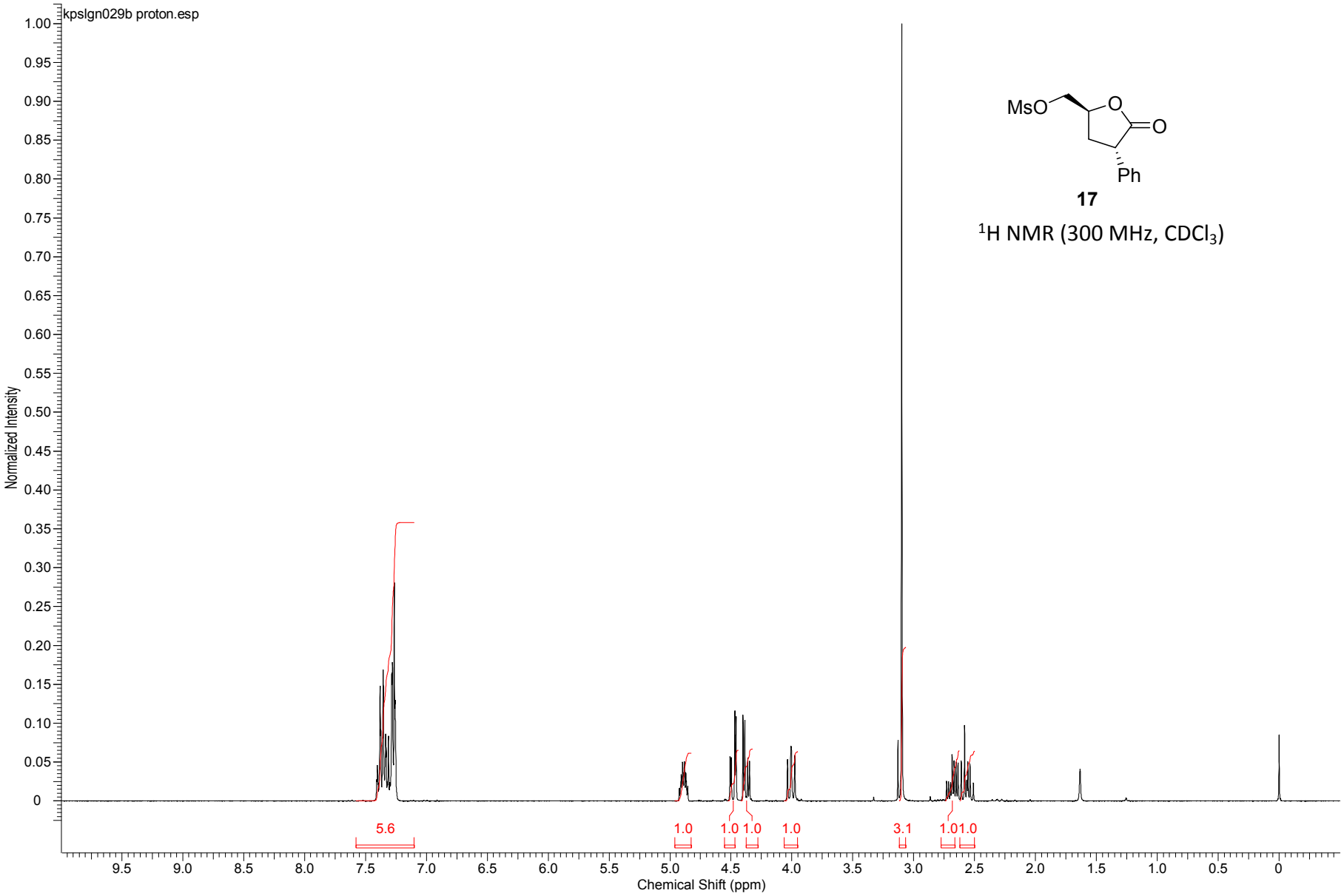
67.2
1,4-dioxane
Int. standard
H_2N
OH
O
· HCl
(1S,2S)-2
^{13}C NMR (125 MHz, D_2O)
182.1
49.5
43.4
22.5
18.0
12.9
Normalized Intensity
Chemical Shift (ppm)



(1*S*,2*S*)-14

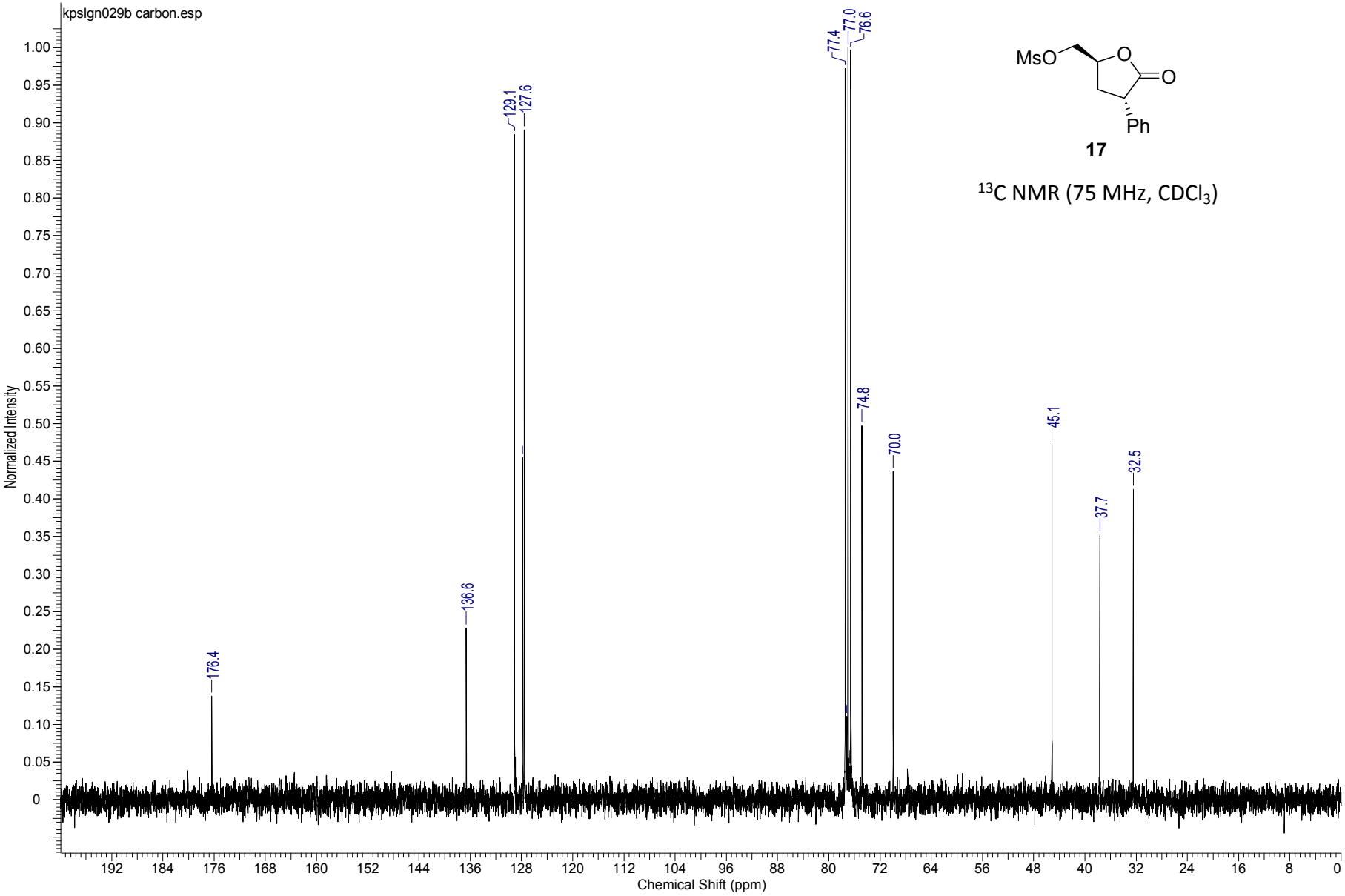
^{1}H NMR (300 MHz, $CDCl_3$)


kpscp031c.007.esp
67.2
1,4-dioxane
Int. standard
H2N
OMe
O
·HCl
(1S,2S)-14
13C NMR (75 MHz,D2O)
176.5
53.2
42.7
19.7
19.5
14.2
Normalized Intensity
Chemical Shift (ppm)



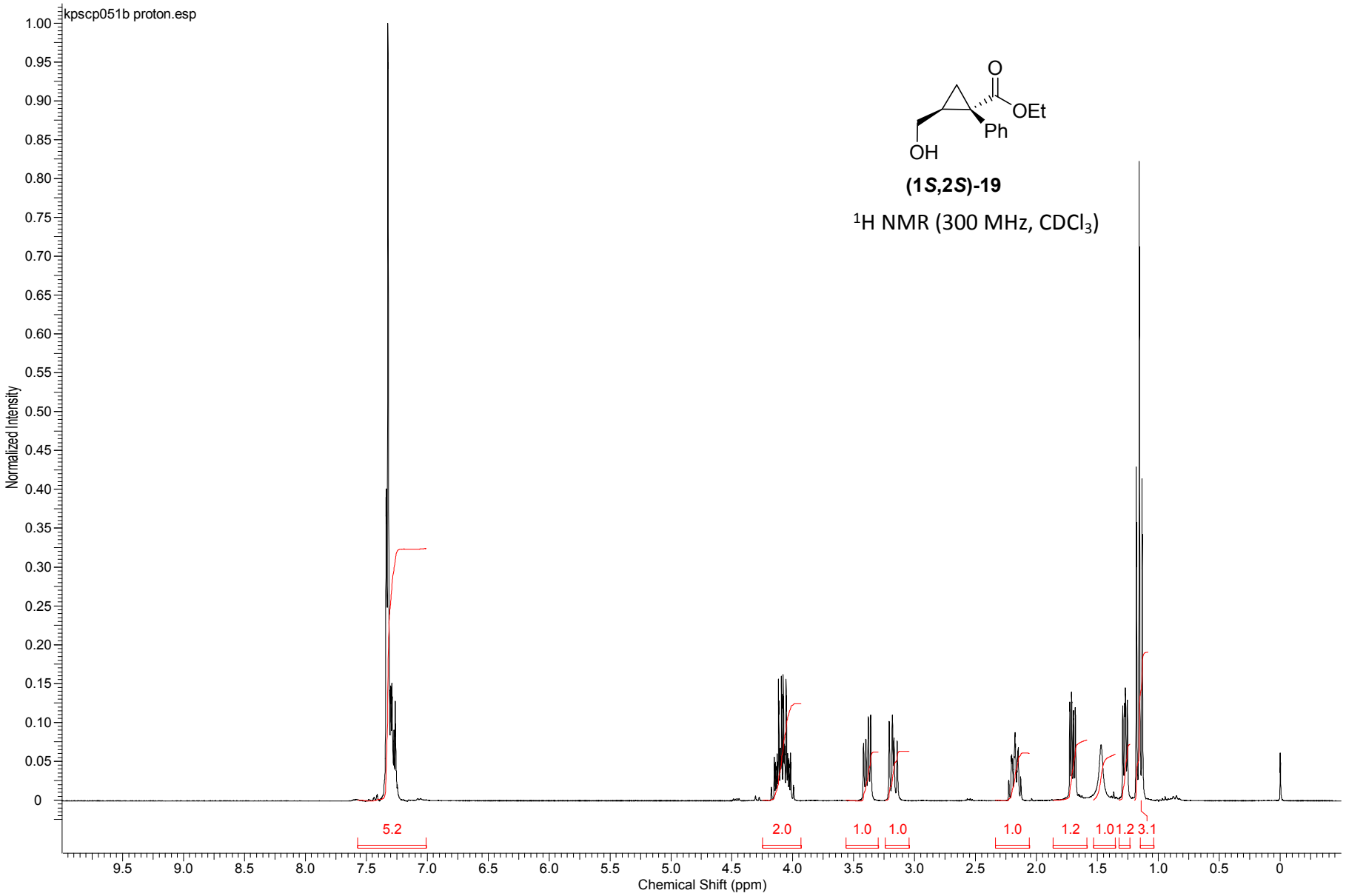
17

^{1}H NMR (300 MHz, $CDCl_3$)



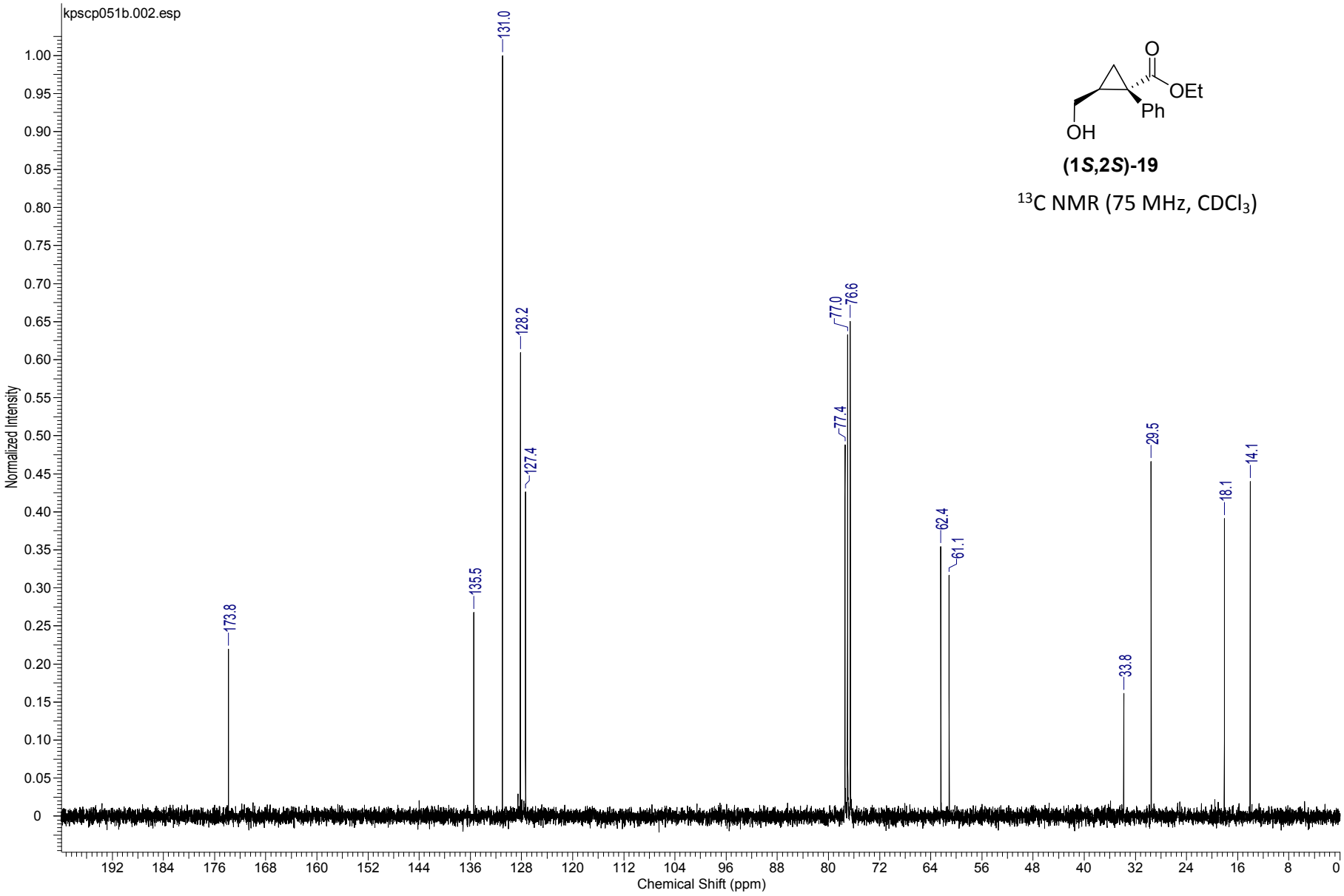
17

^{13}C NMR (75 MHz, $CDCl_3$)



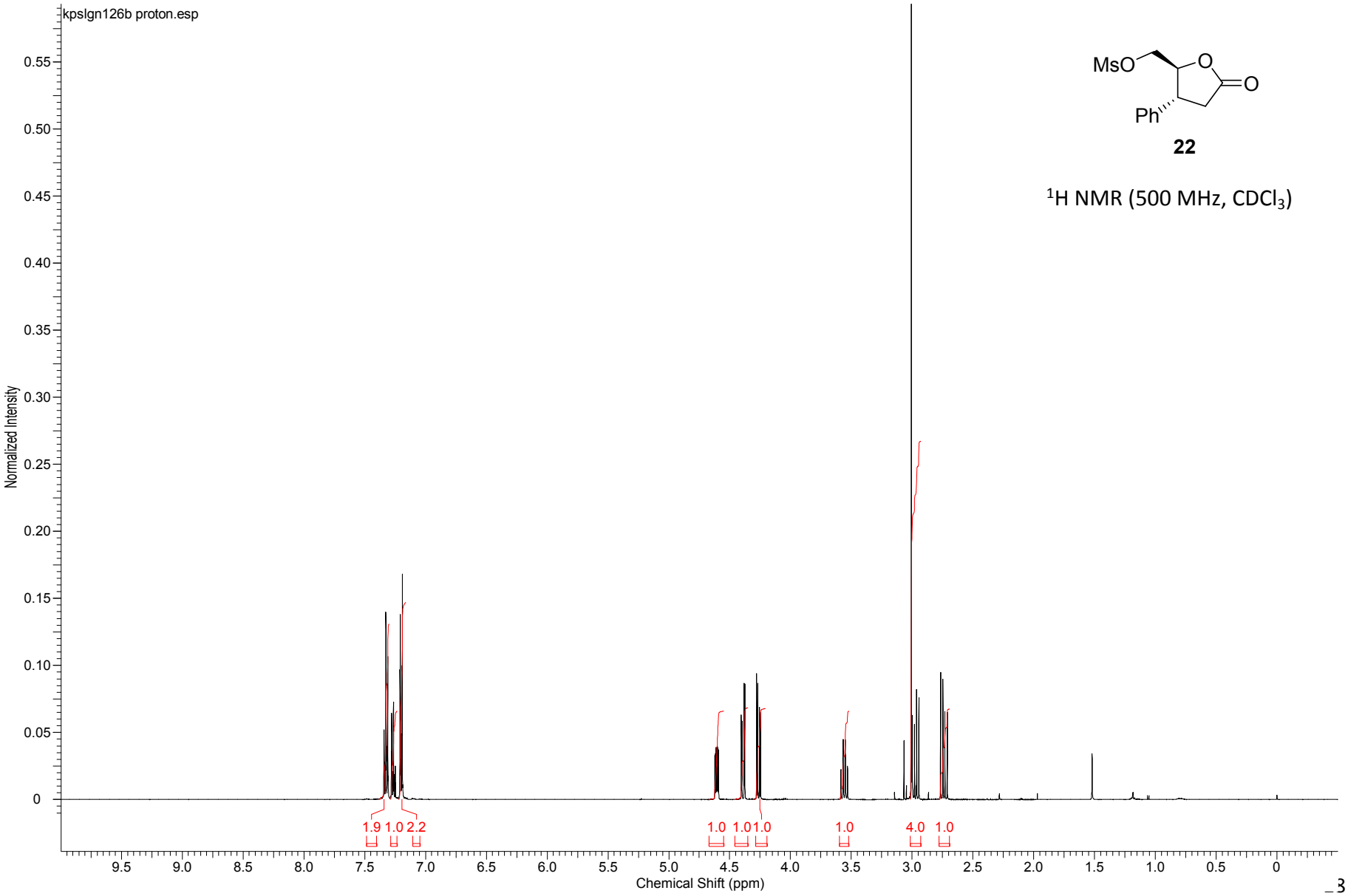
(1*S*,2*S*)-19

^{1}H NMR (300 MHz, $CDCl_3$)



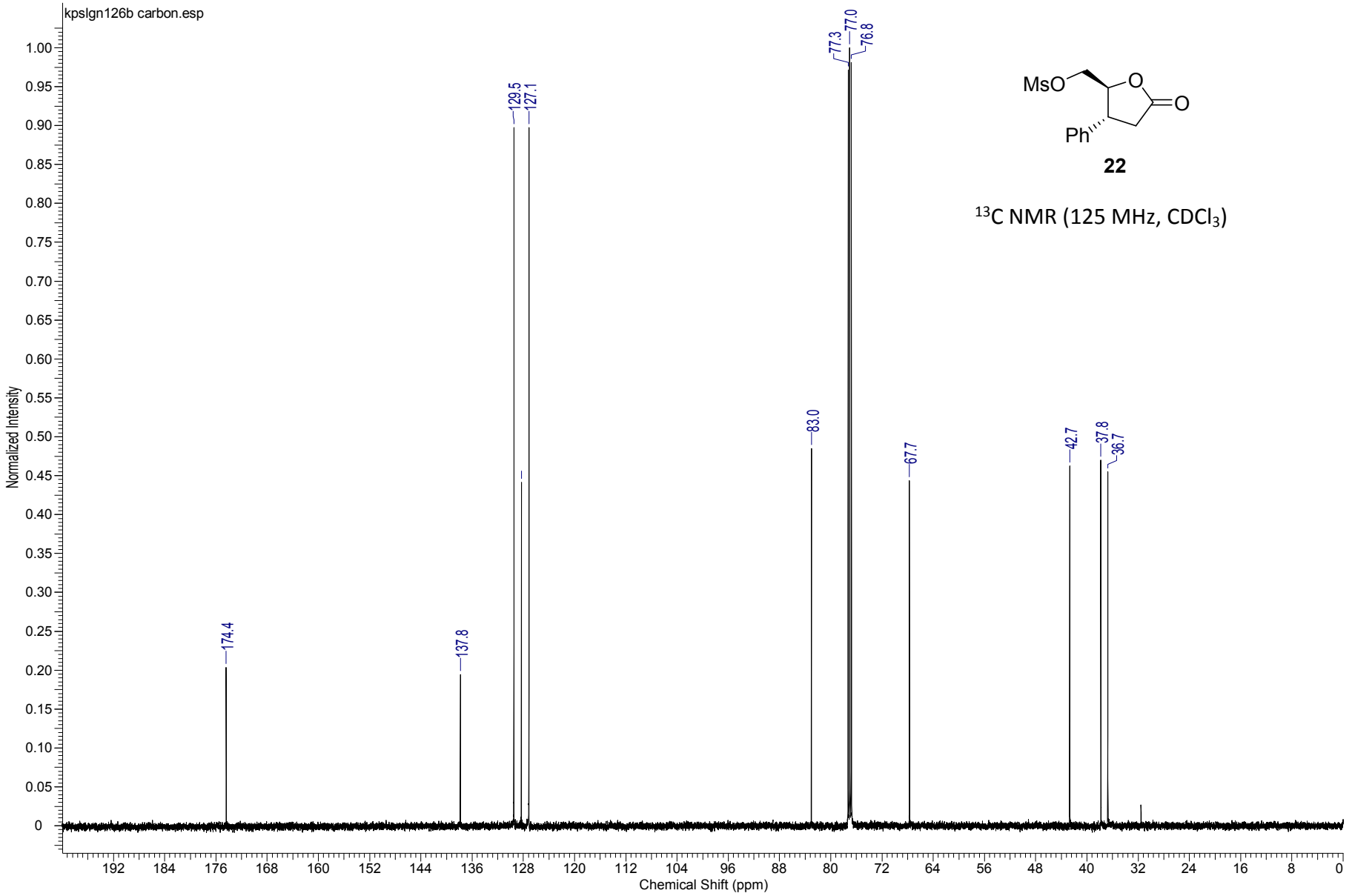
(1*S*,2*S*)-19

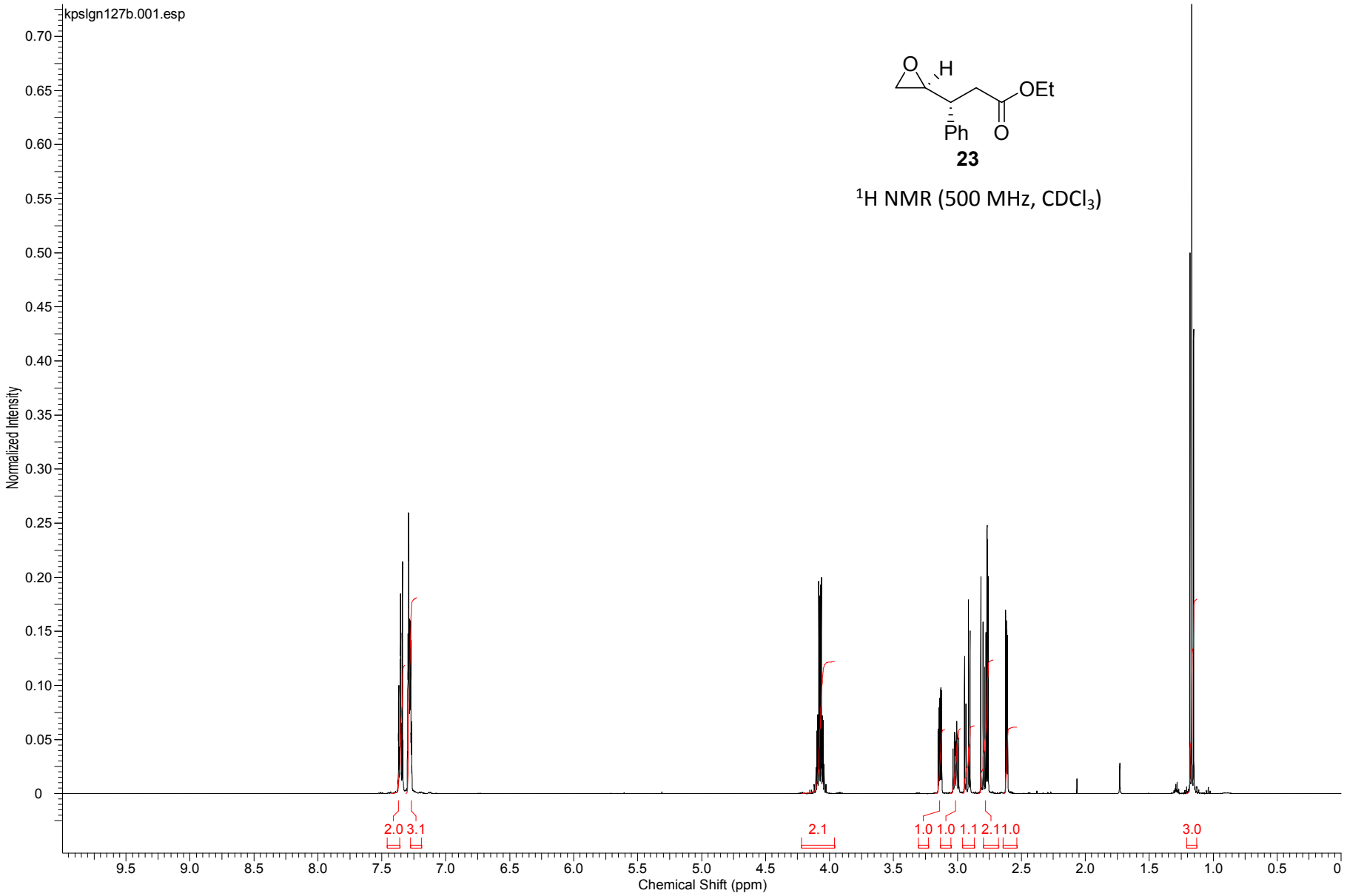
^{13}C NMR (75 MHz, $CDCl_3$)



22

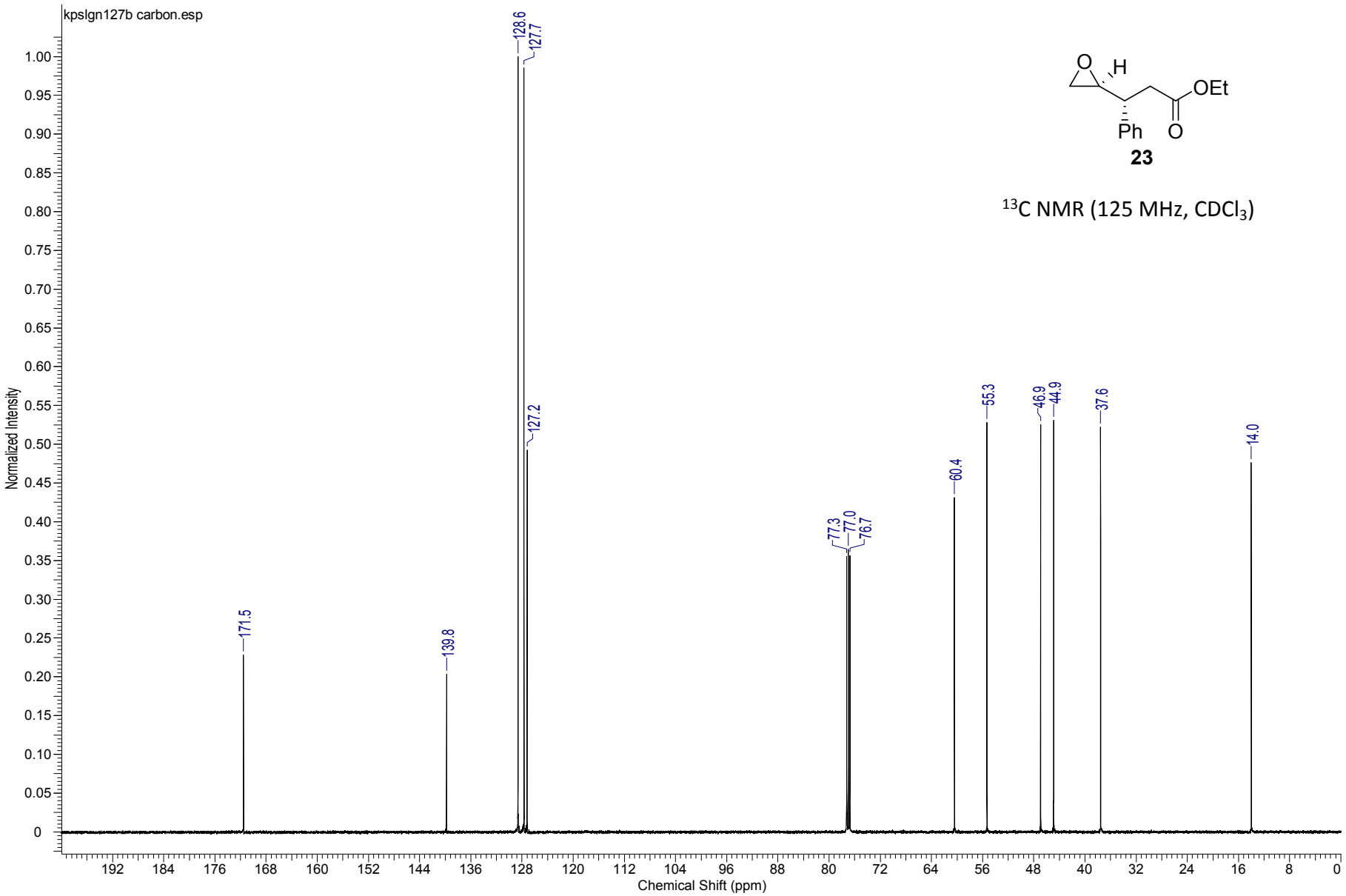
^{1}H NMR (500 MHz, $CDCl_3$)


kpslgn126b carbon.esp
Normalized Intensity
Chemical Shift (ppm)
174.4
137.8
129.5
127.1
77.3
77.0
76.8
83.0
67.7
42.7
37.8
36.7
MsO
O
O
Ph
22
^{13}C NMR (125 MHz, $CDCl_3$)



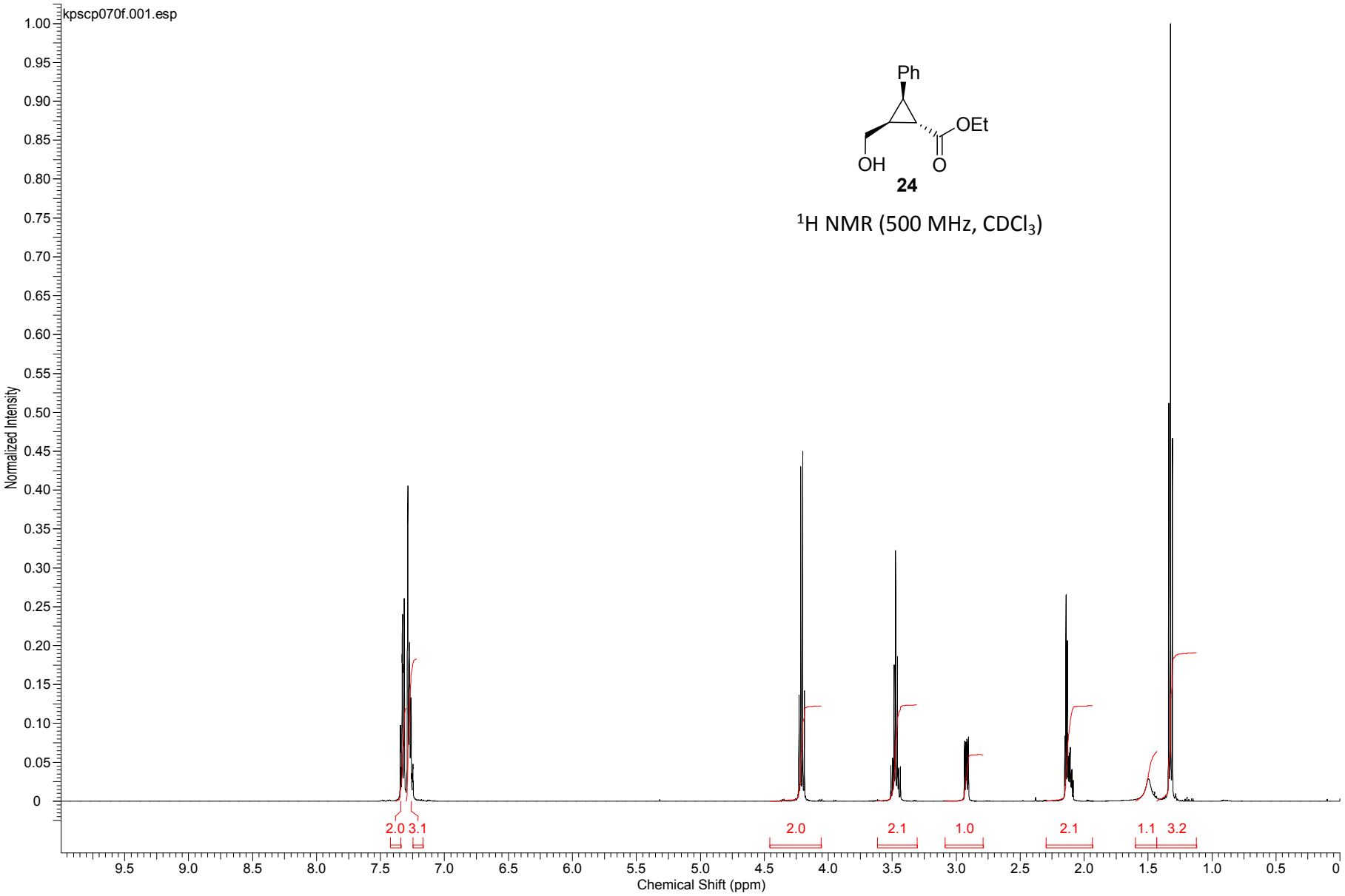
23

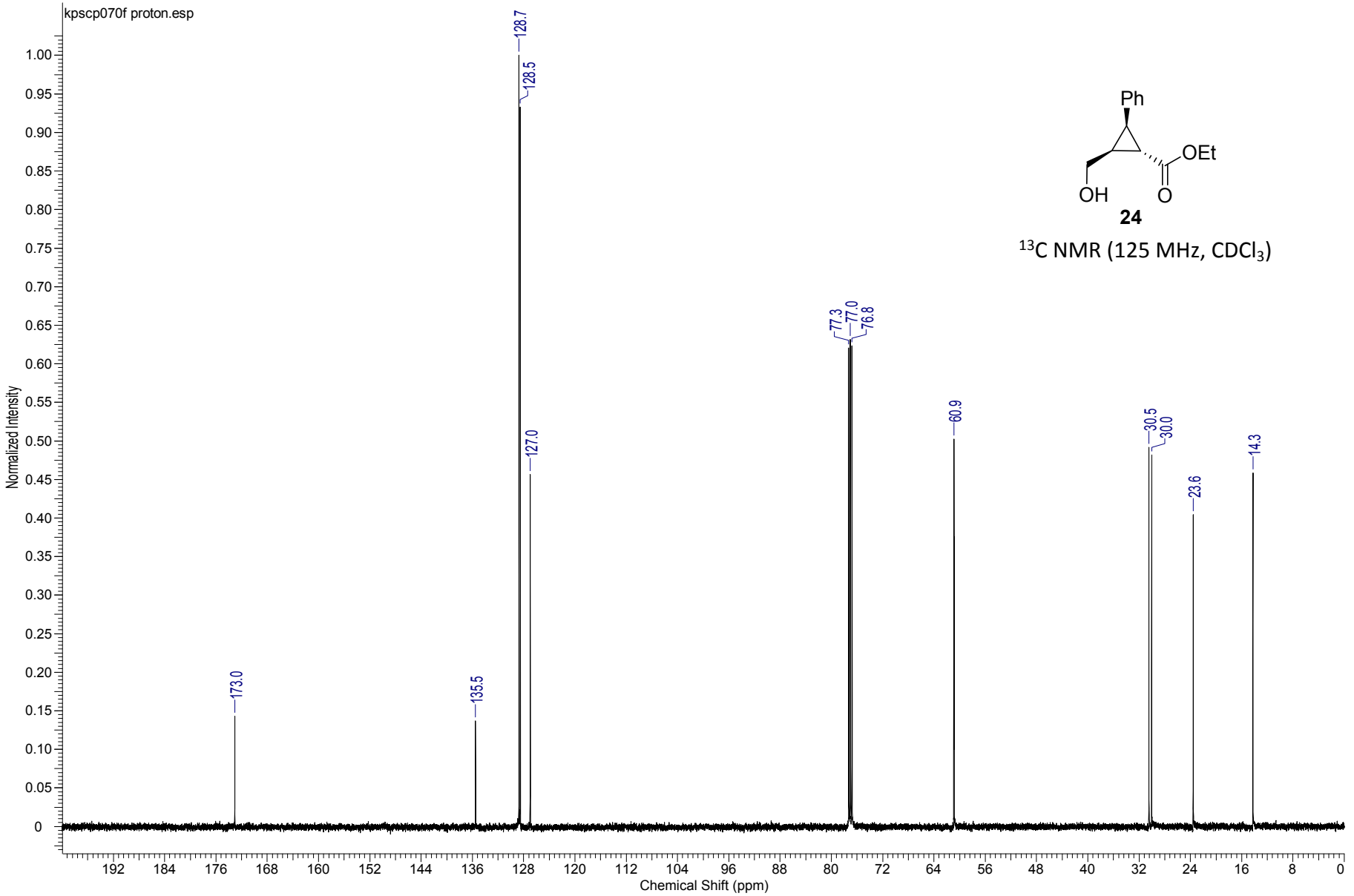
^{1}H NMR (500 MHz, $CDCl_3$)

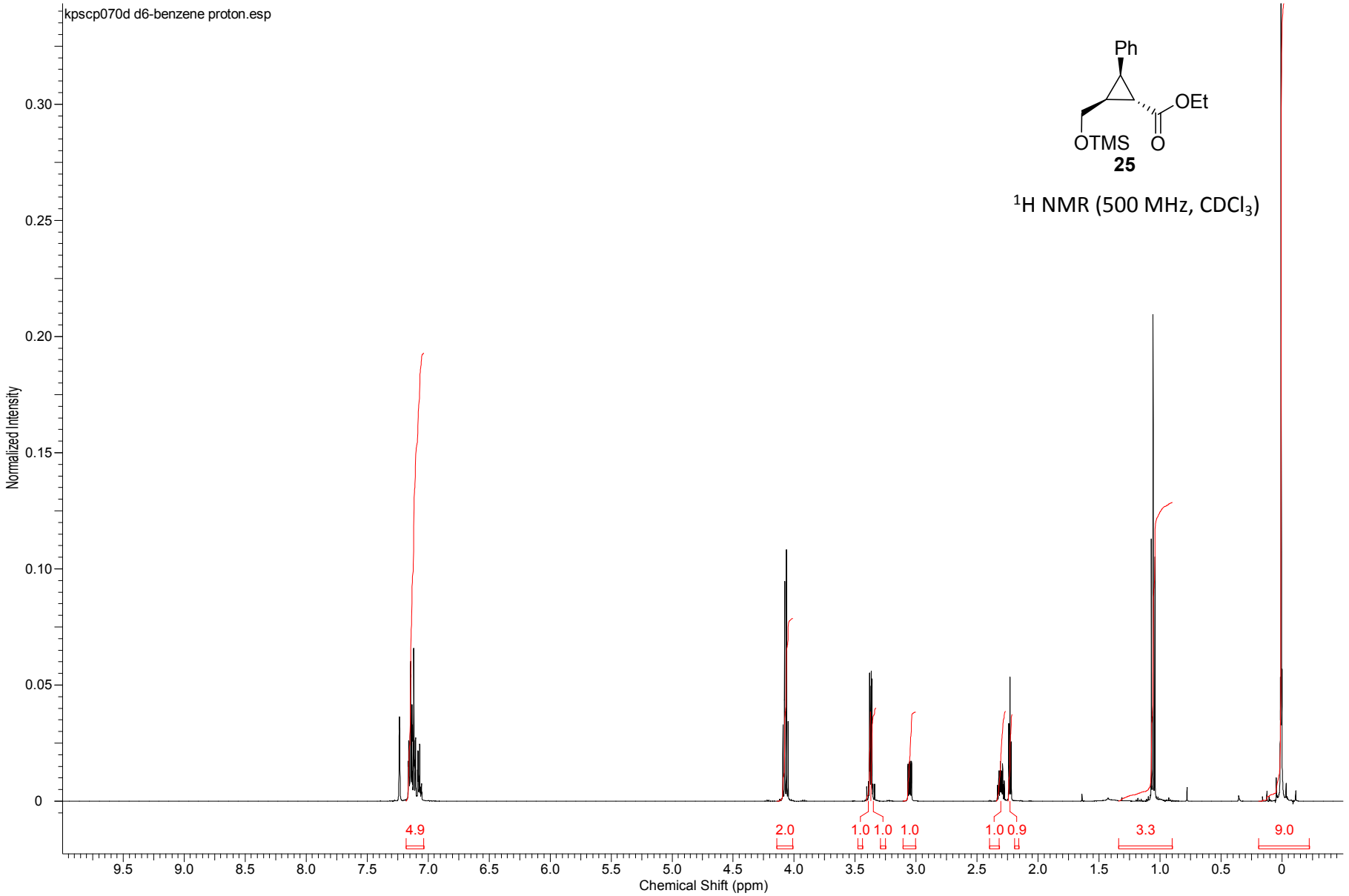


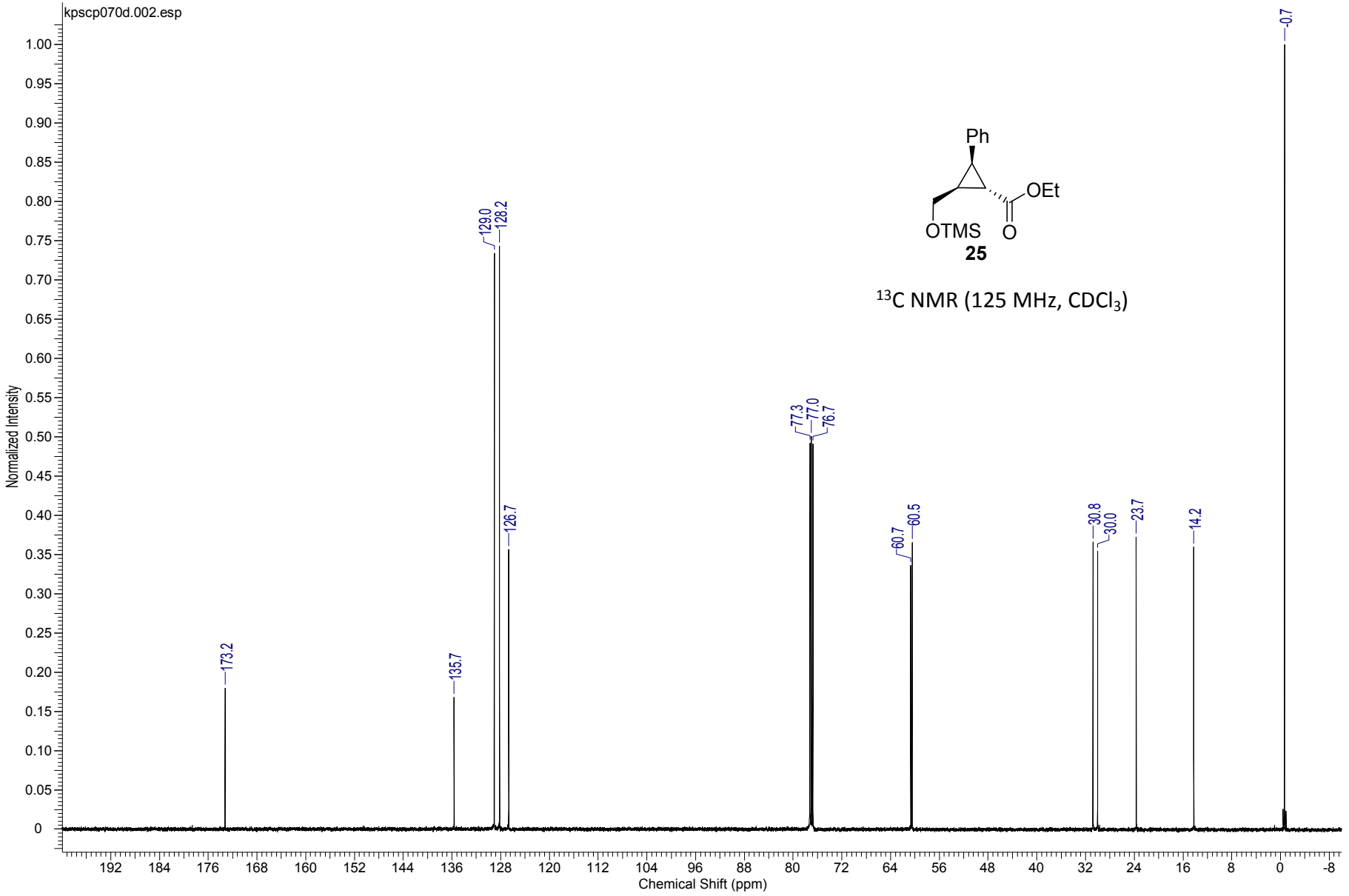
23

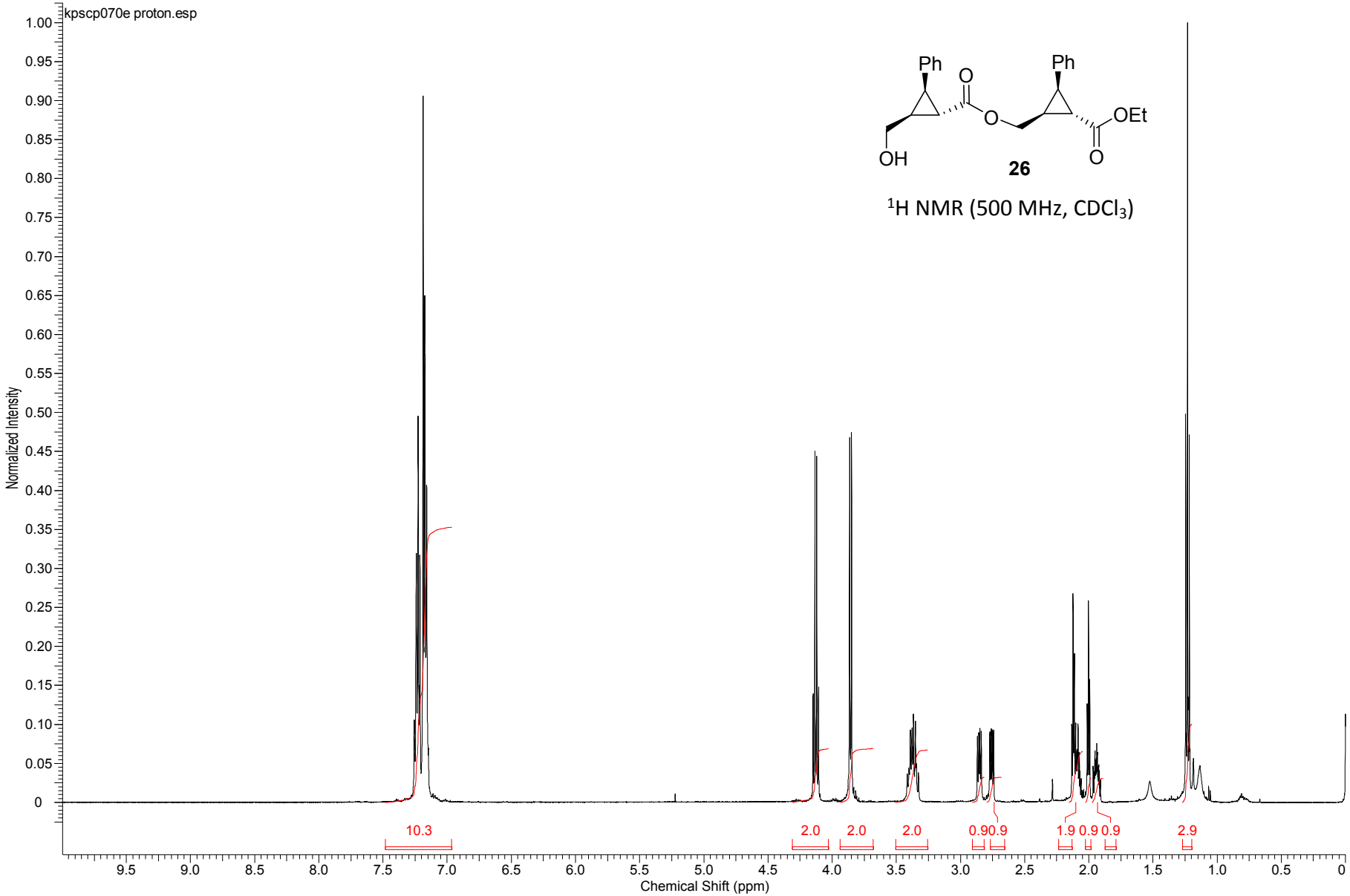
^{13}C NMR (125 MHz, $CDCl_3$)

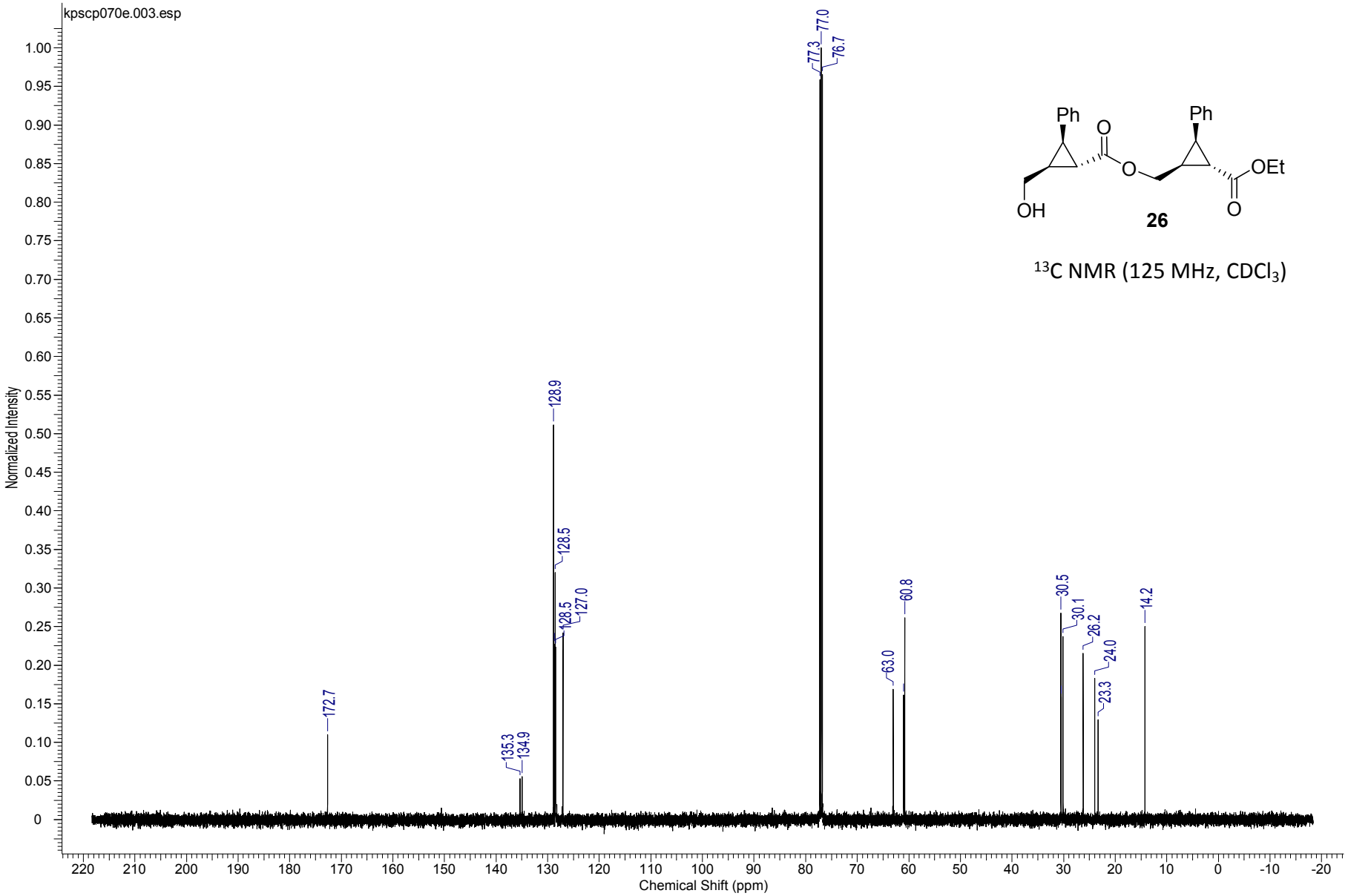

kpscp070f.001.esp
Normalized Intensity
Chemical Shift (ppm)
2.0 3.1
2.0
2.1
1.0
2.1
1.1 3.2
Ph
OEt
OH
O
24
^{1}H NMR (500 MHz, $CDCl_3$)


kpscp070f proton.esp
Normalized Intensity
Chemical Shift (ppm)
128.7
128.5
127.0
77.3
77.0
76.8
60.9
30.5
30.0
23.6
14.3
173.0
135.5
Ph
OEt
OH
O
24
^{13}C NMR (125 MHz, $CDCl_3$)


kpscp070d d6-benzene proton.esp
Ph
OEt
OTMS
O
25
^{1}H NMR (500 MHz, $CDCl_3$)
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
4.9
2.0
1.0
1.0
1.0
1.0
0.9
3.3
9.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

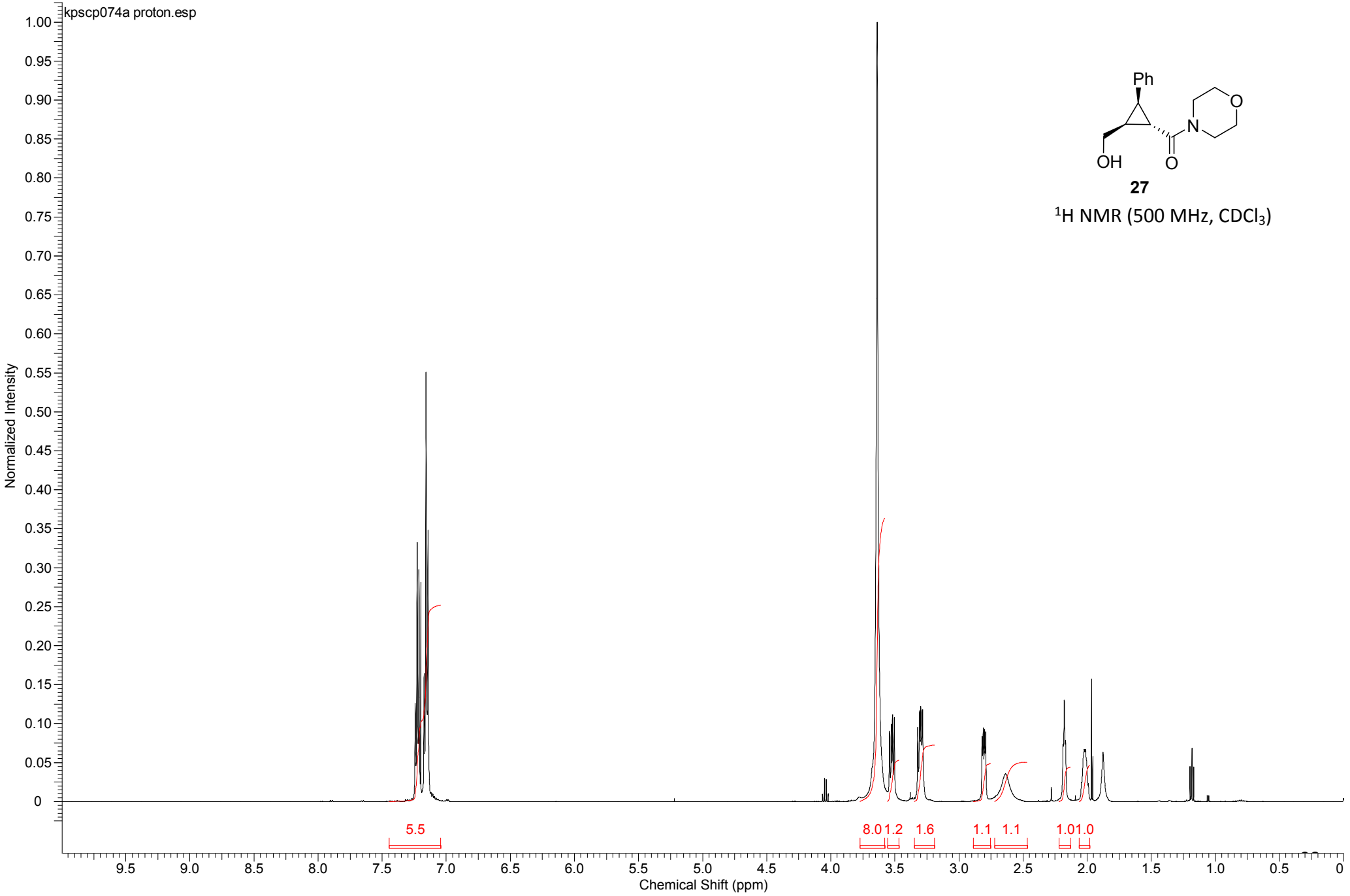

kpscp070d.002.esp
Normalized Intensity
Chemical Shift (ppm)
Ph
OEt
OTMS
O
25
^{13}C NMR (125 MHz, $CDCl_3$)
173.2
135.7
129.0
128.2
126.7
77.3
77.0
76.7
60.7
60.5
30.8
30.0
23.7
14.2
0.7


kpscp070e proton.esp
Normalized Intensity
Chemical Shift (ppm)
10.3
2.0
2.0
2.0
0.9
0.9
1.9
0.9
0.9
2.9
Ph
O
Ph
O
OEt
OH
O
26
^{1}H NMR (500 MHz, $CDCl_3$)



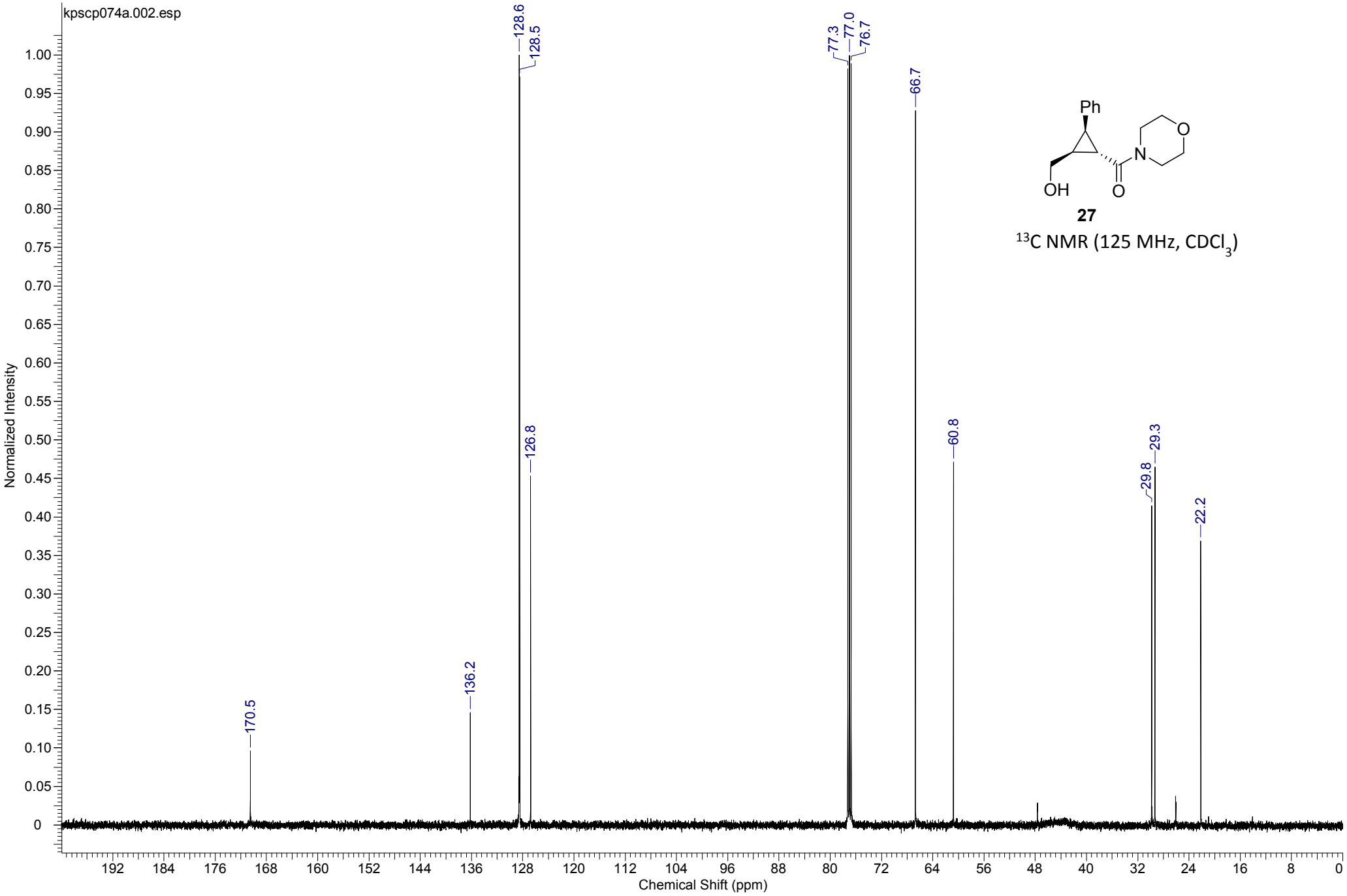
26

^{13}C NMR (125 MHz, $CDCl_3$)



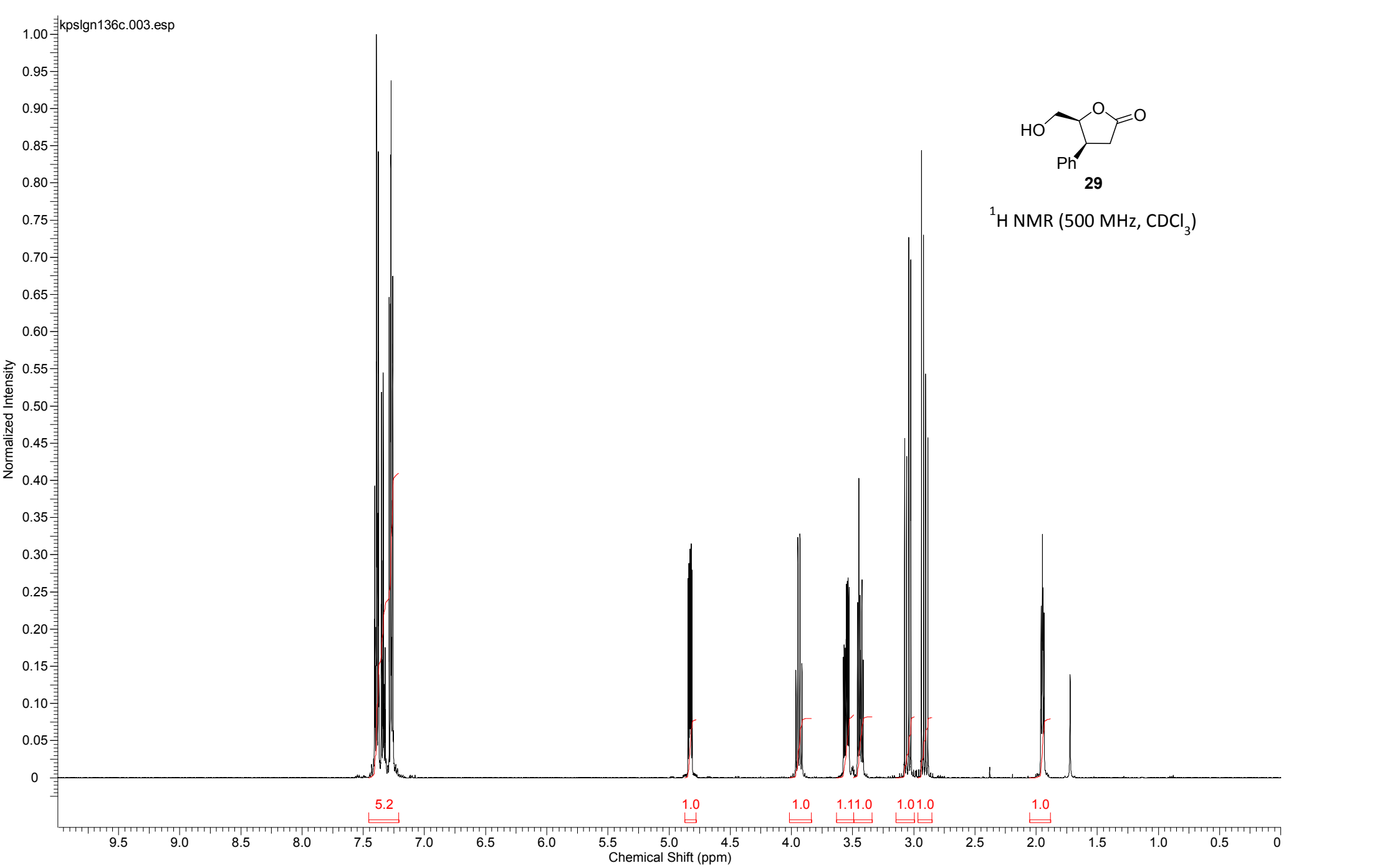
27

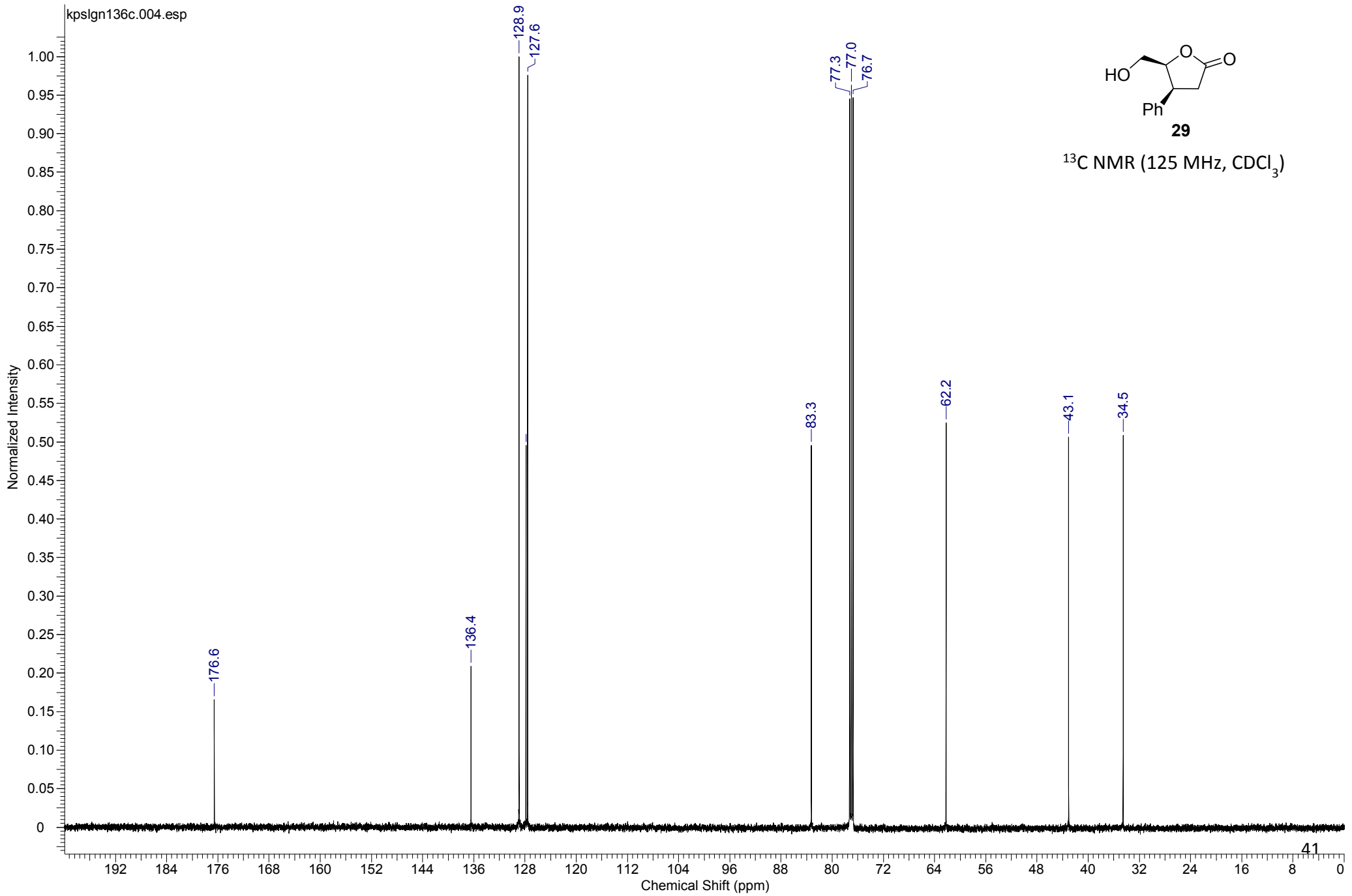
^{1}H NMR (500 MHz, $CDCl_3$)

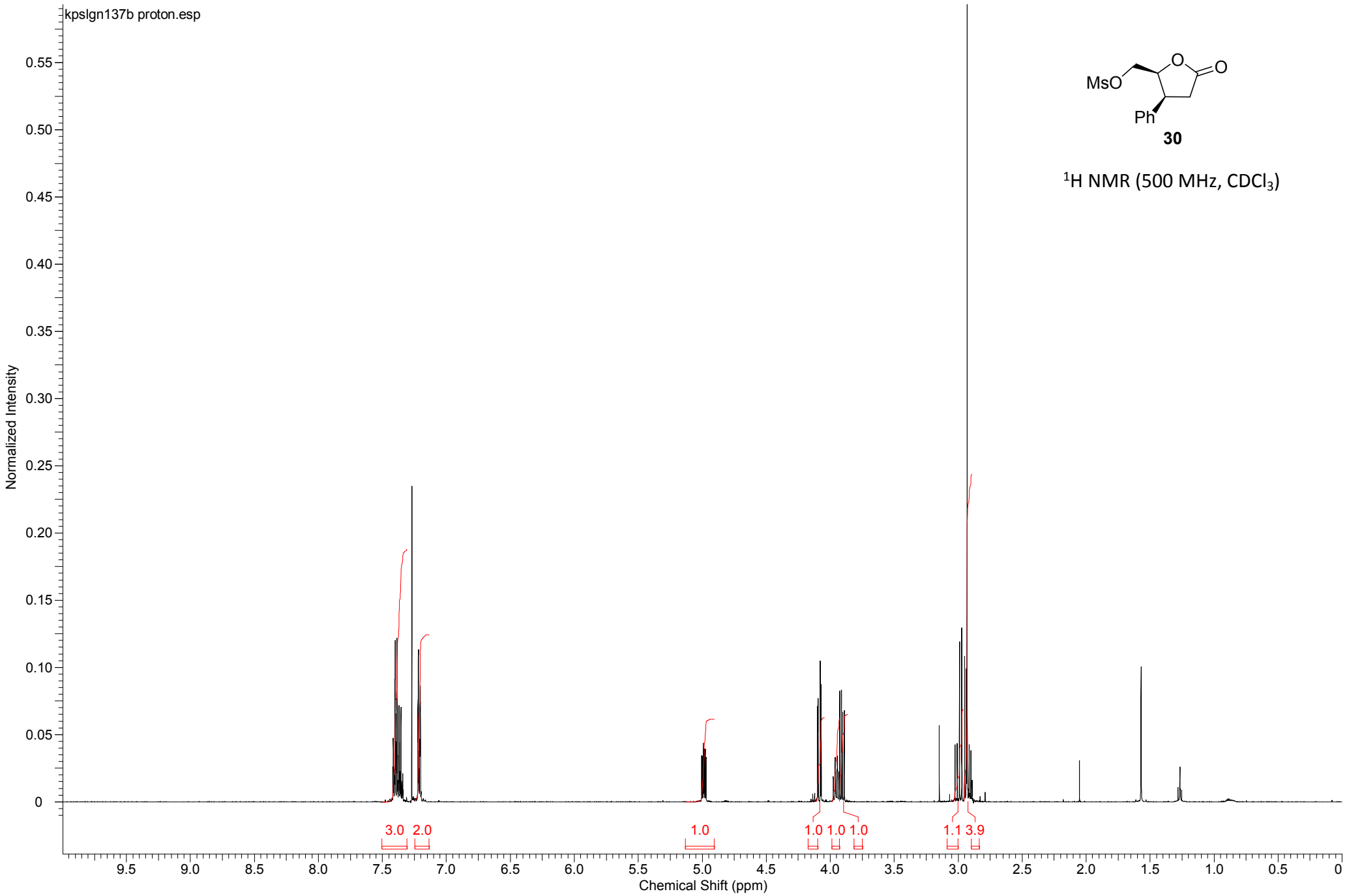


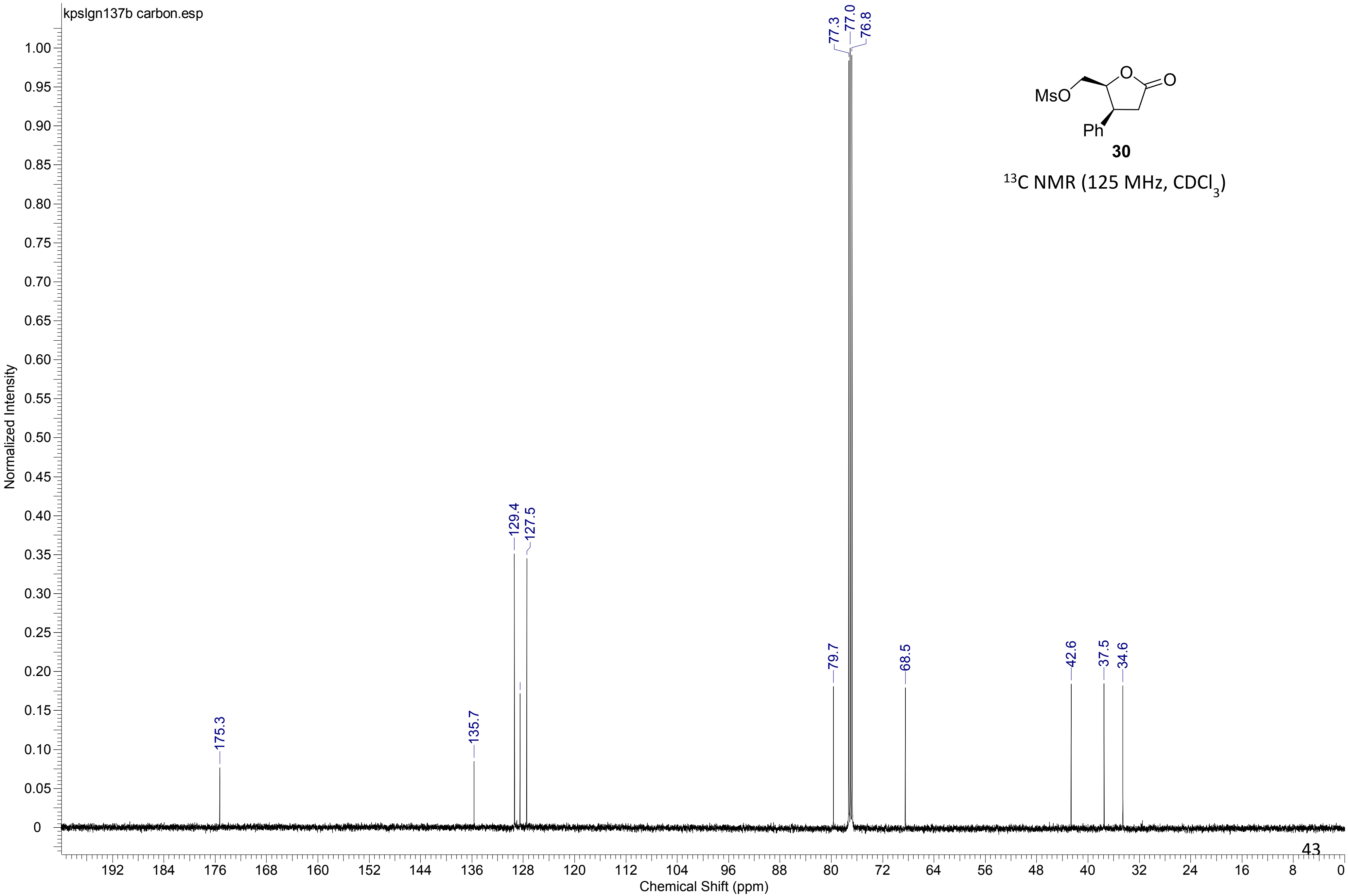
27

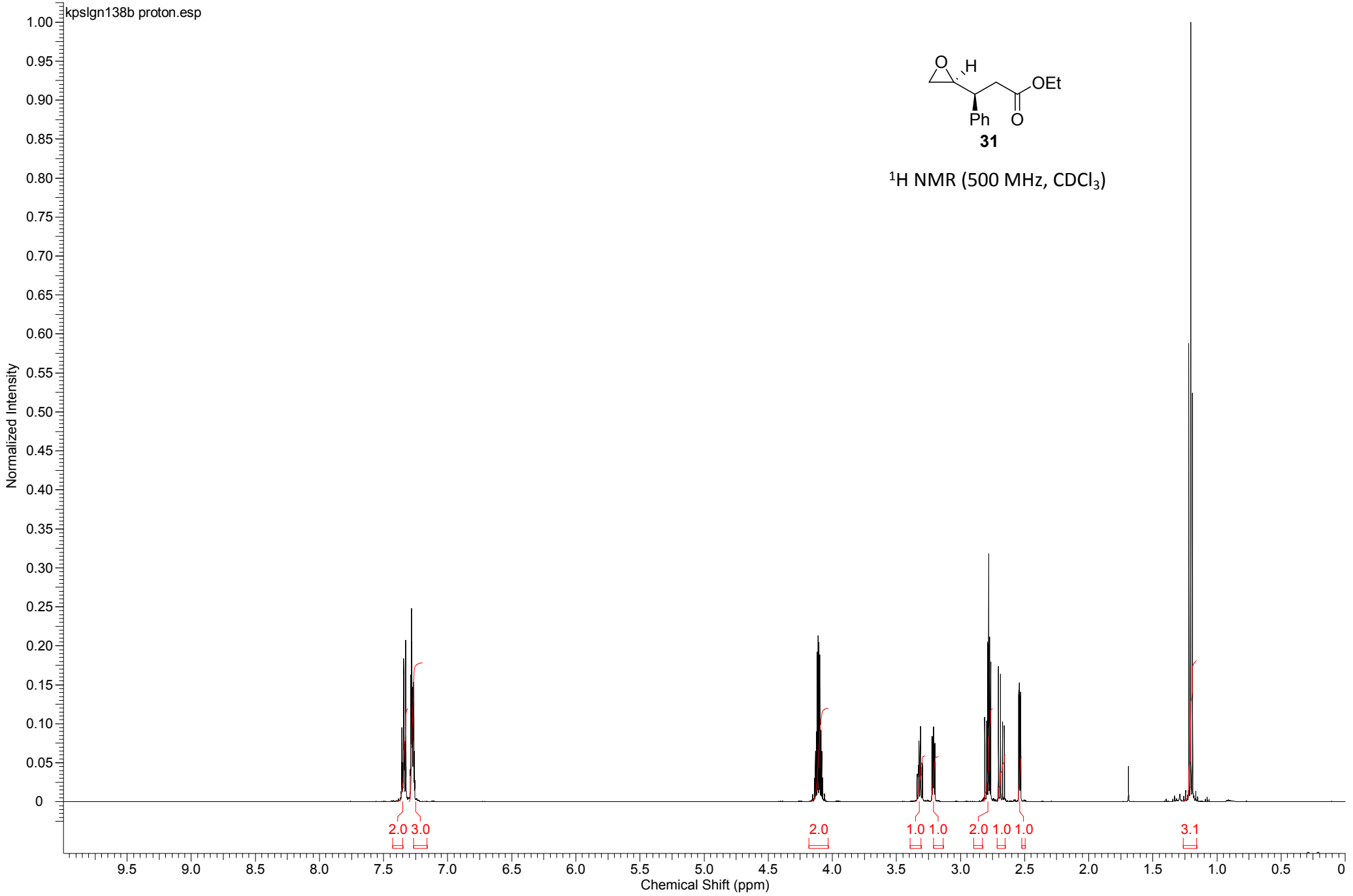
^{13}C NMR (125 MHz, $CDCl_3$)


kpslgn136c.003.esp
Normalized Intensity
Chemical Shift (ppm)
5.2
1.0
1.0
1.1
1.0
1.0
1.0
1.0
HO
O
O
Ph
29
1H NMR (500 MHz, CDCl3)


kpslgn136c.004.esp
128.9
127.6
77.3
77.0
76.7
83.3
62.2
43.1
34.5
136.4
176.6
Normalized Intensity
Chemical Shift (ppm)
HO
O
O
Ph
29
^{13}C NMR (125 MHz, $CDCl_3$)

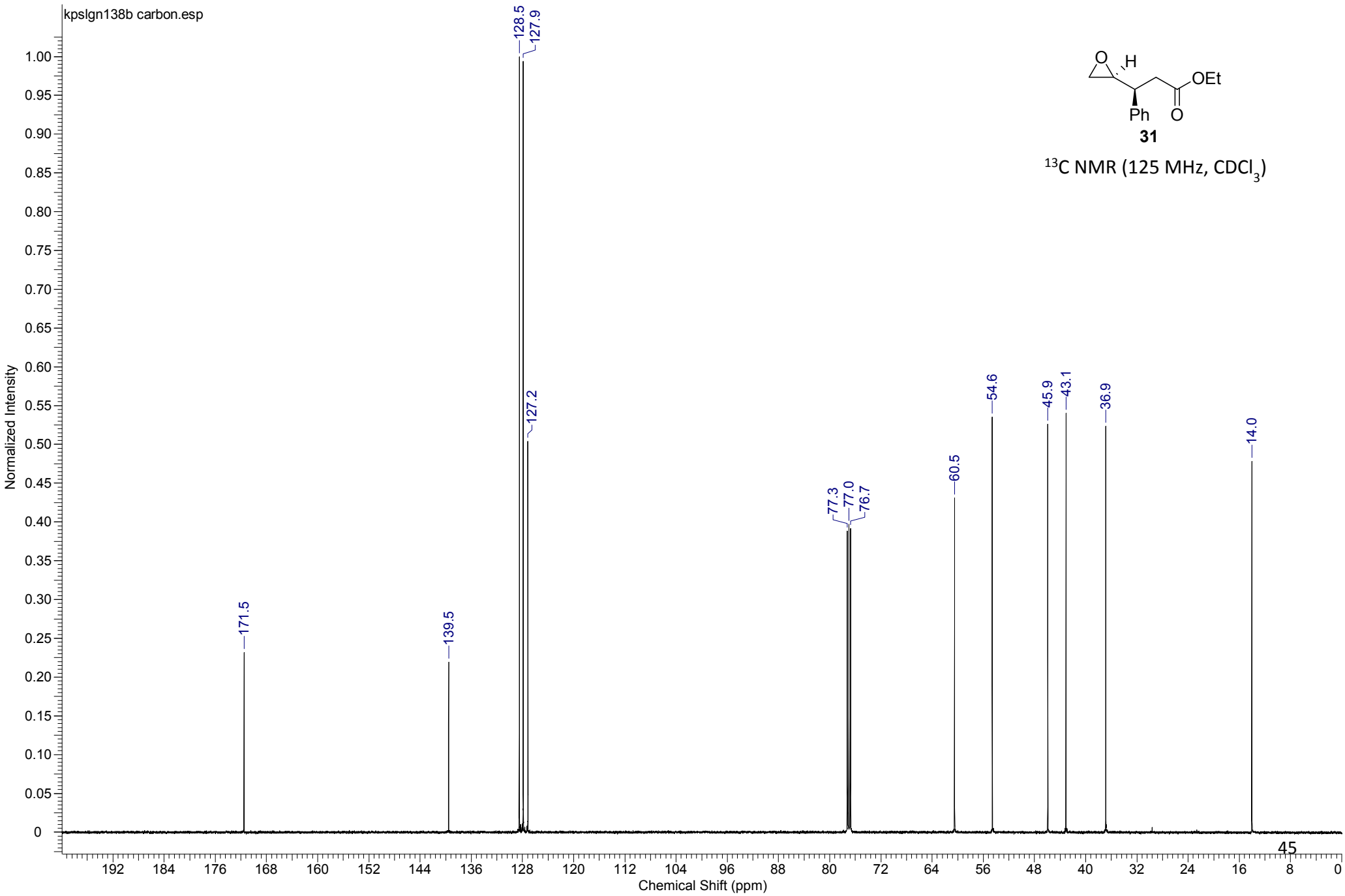

kpslgn137b proton.esp
Normalized Intensity
Chemical Shift (ppm)
3.0 2.0
1.0
1.0 1.0 1.0
1.1 3.9
MsO
O
O
Ph
30
^{1}H NMR (500 MHz, $CDCl_3$)

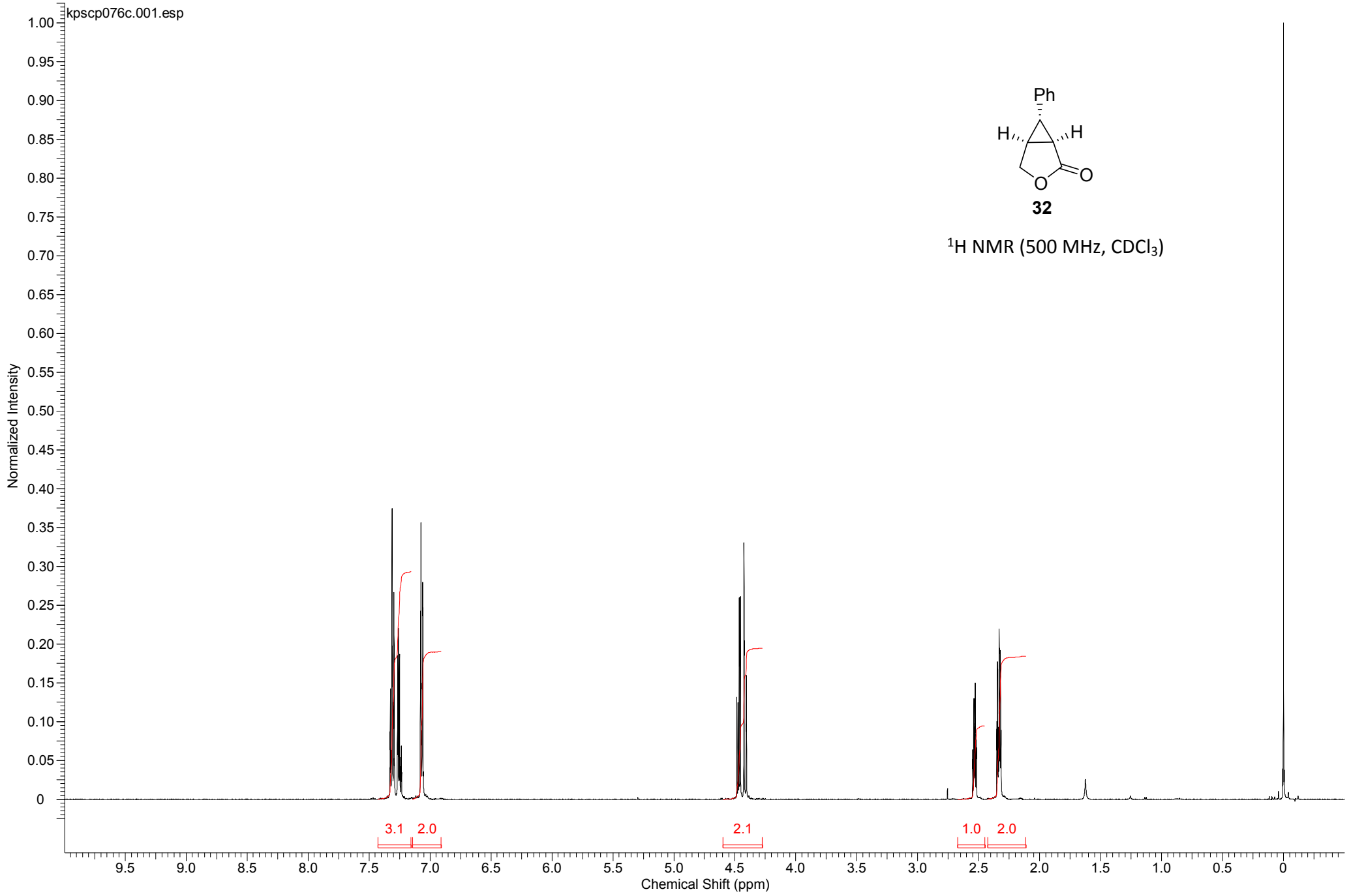

kpslgn137b carbon.esp
MsO
O
O
Ph
30
^{13}C NMR (125 MHz, CDCl$_3$)
77.3
77.0
76.8
175.3
135.7
129.4
127.5
79.7
68.5
42.6
37.5
34.6
Normalized Intensity
Chemical Shift (ppm)

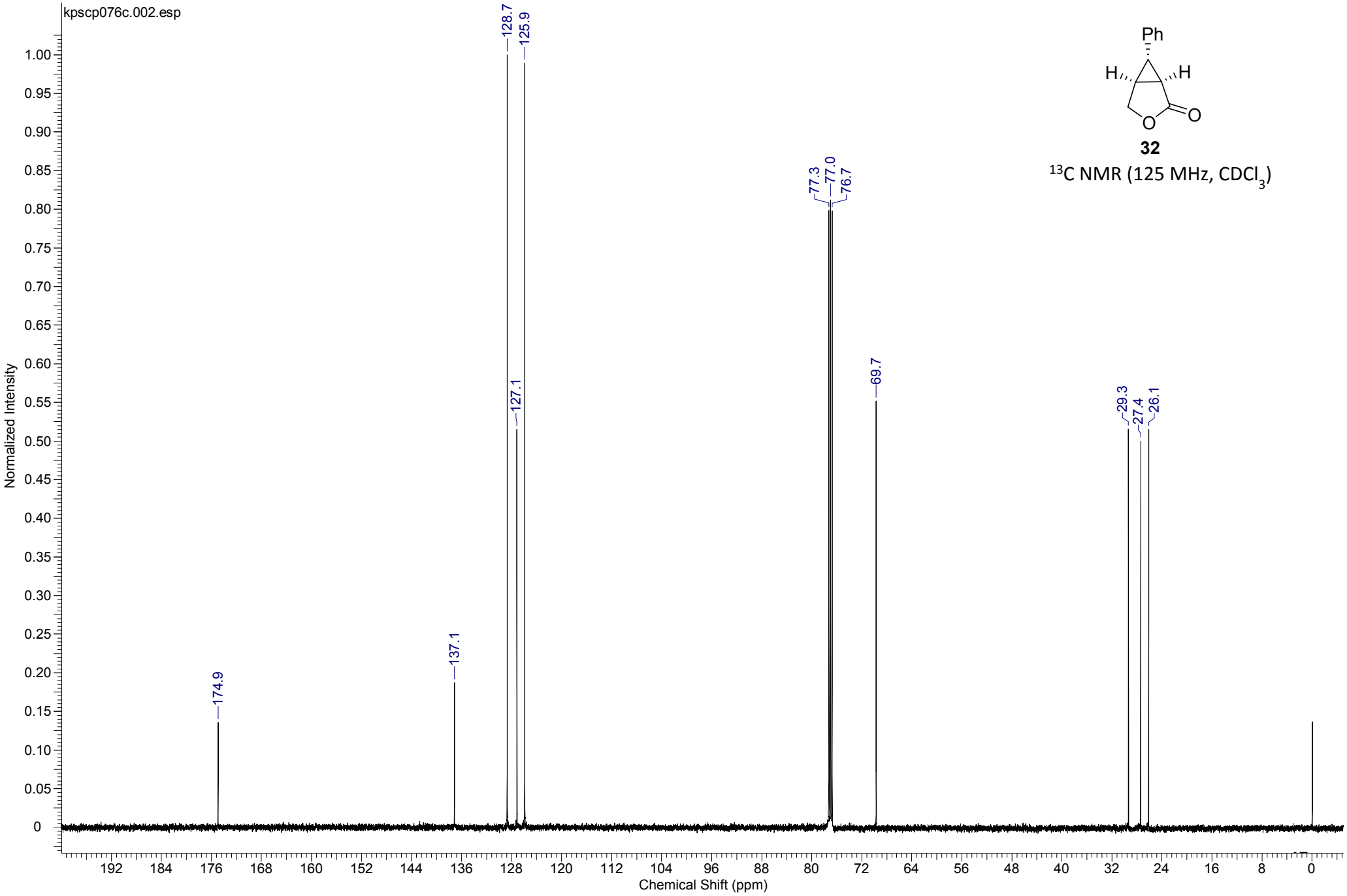


31

^{1}H NMR (500 MHz, $CDCl_3$)


kpsIgn138b carbon.esp
128.5
127.9
127.2
171.5
139.5
77.3
77.0
76.7
60.5
54.6
45.9
43.1
36.9
14.0
Normalized Intensity
Chemical Shift (ppm)
O
H
OEt
Ph
O
31
^{13}C NMR (125 MHz, $CDCl_3$)


kpscp076c.001.esp
Normalized Intensity
Chemical Shift (ppm)
3.1
2.0
2.1
1.0
2.0
Ph
H
H
O
O
32
^{1}H NMR (500 MHz, $CDCl_3$)


kpscp076c.002.esp
128.7
125.9
77.3
77.0
76.7
127.1
69.7
29.3
27.4
26.1
174.9
137.1
Normalized Intensity
Chemical Shift (ppm)
Ph
H
H
O
O
32
13C NMR (125 MHz, CDCl3)