Supporting Information for

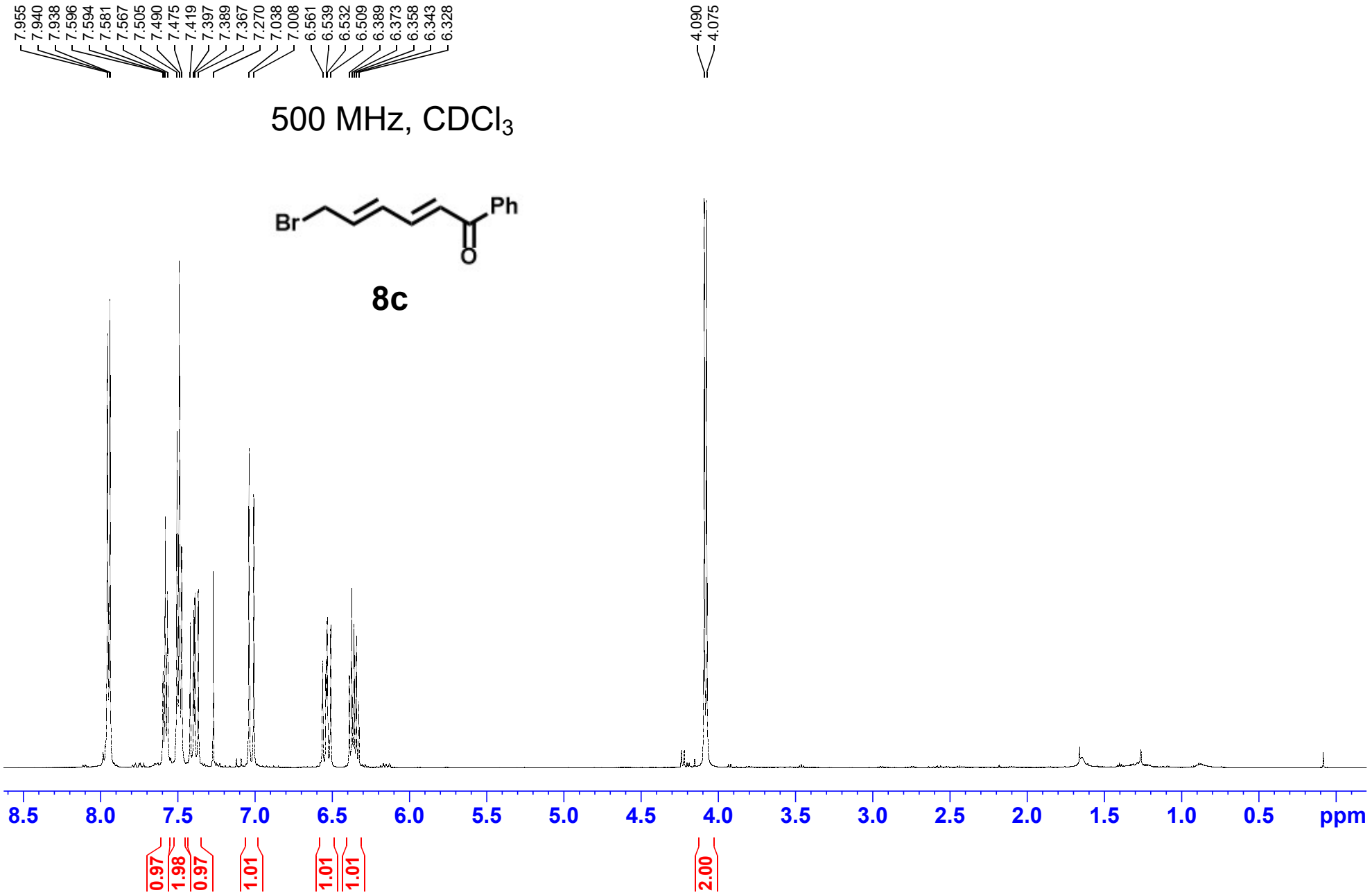
Generation and Reactions of ε-Carbonyl Cations via Group 13 Catalysis

Page M. Penner and James R. Green*

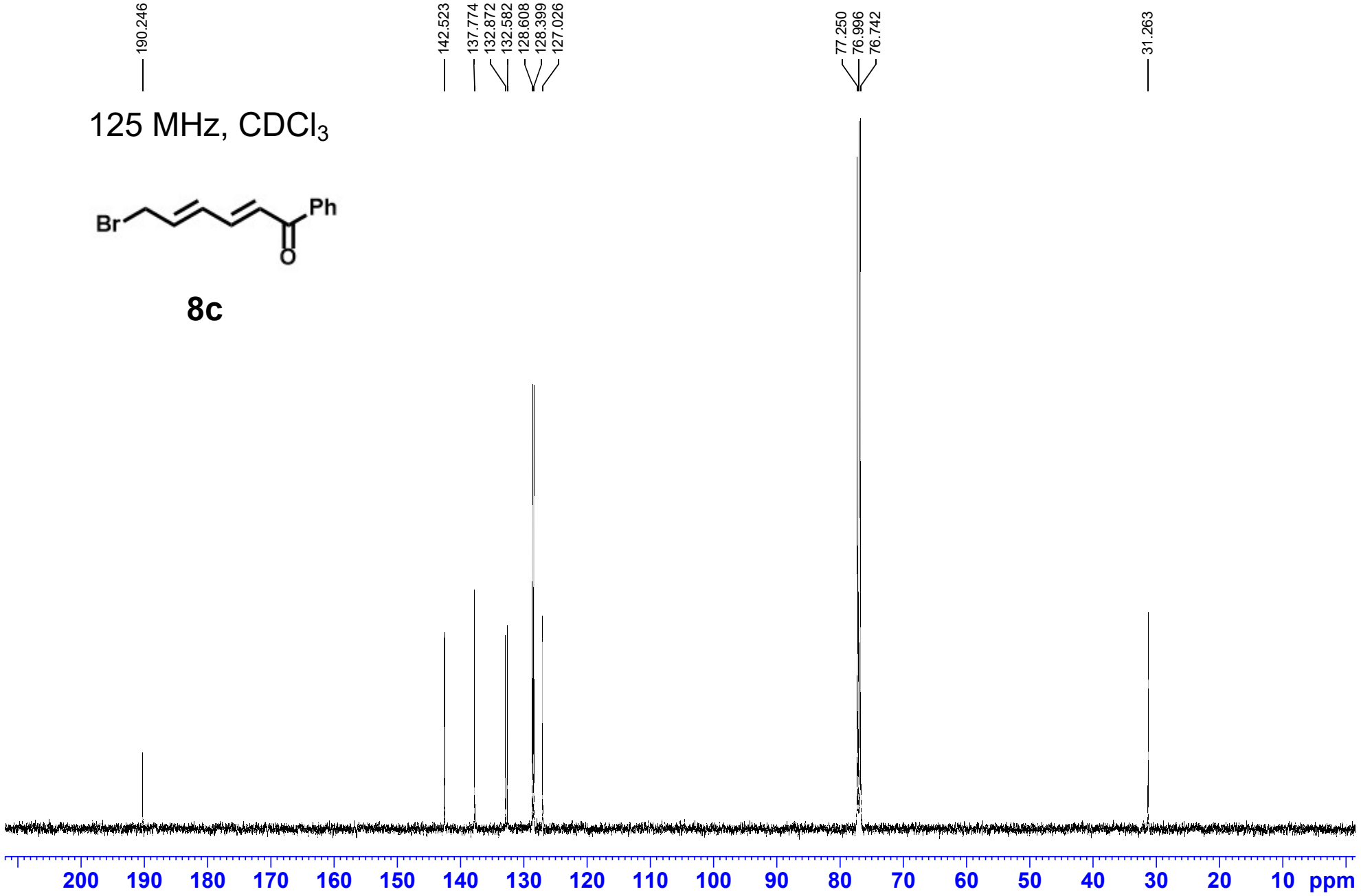
Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Canada

*Correspondence: jgreen@uwindsor.ca

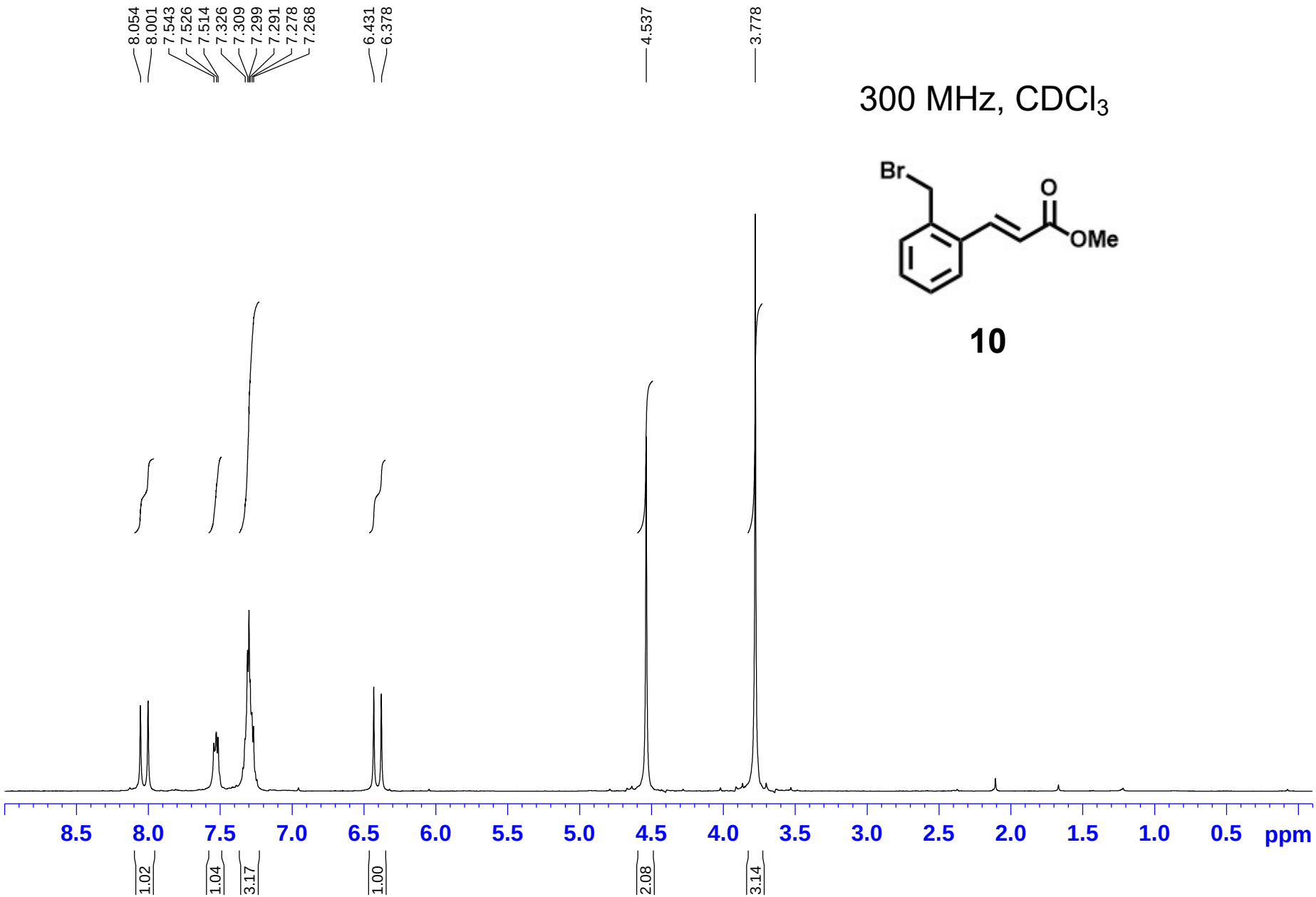
pmp.098 30, 1H, Br-CH2-C=C-C=C-C(O)Ph, 500 MHz, 3/17/22



pmp.098 31, 13C, Br-CH2-C=C-C=C-C(O)Ph, 500/125 MHz, 3/17/22



pmp.143b SM C
1D 1H 300 MHz B82



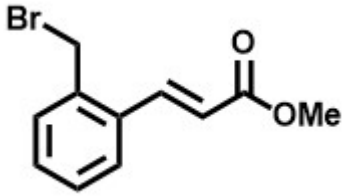
300 MHz, $CDCl_3$

10

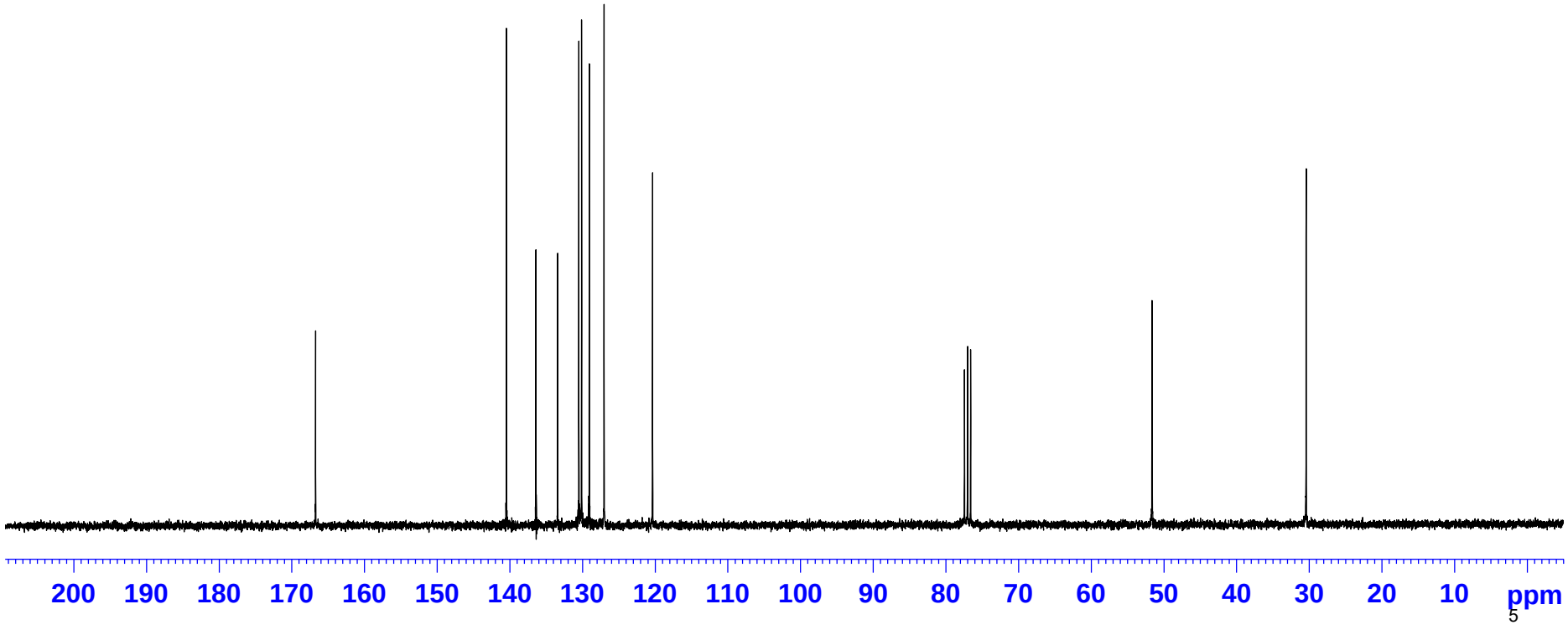
pmp.143bc 20 SM C
13C 1D 300 MHz B82

166.725
140.458
136.409
133.426
130.497
130.120
129.059
127.028
120.352
51.614
30.404

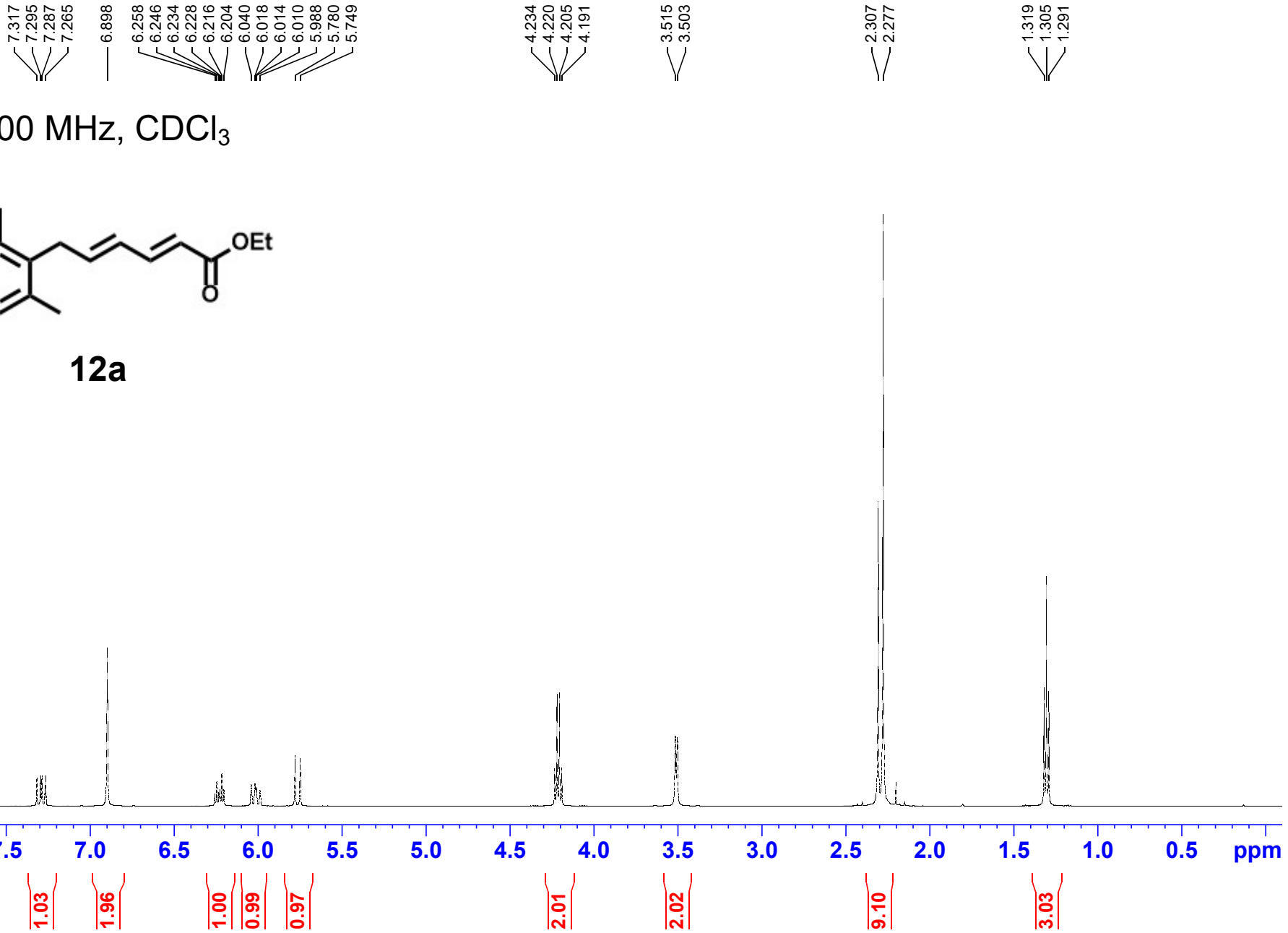
75 MHz, $CDCl_3$



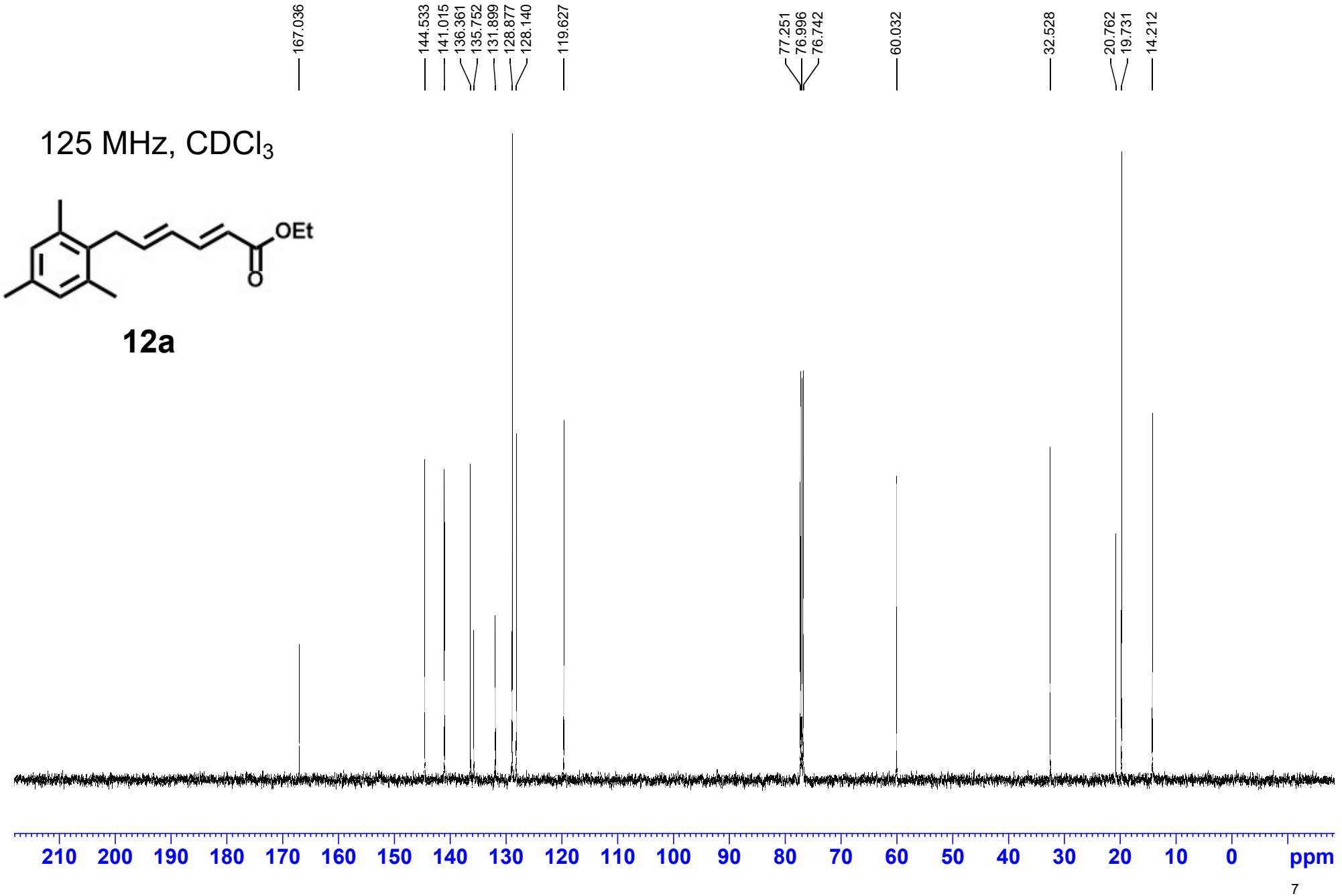
10



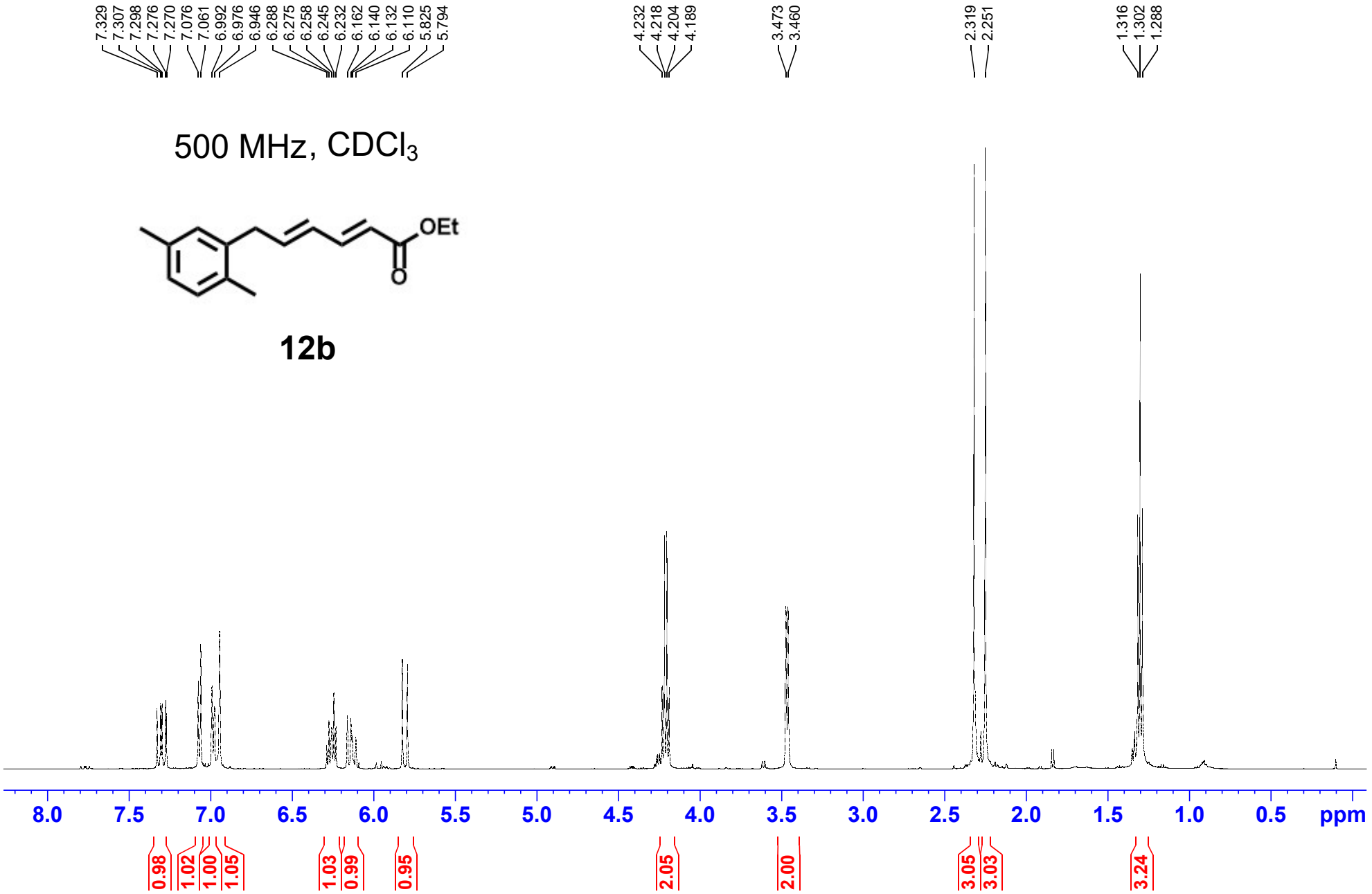
pmp.031 20, 1H, sorbate + mesitylene, 1H, 500, 1/15/22



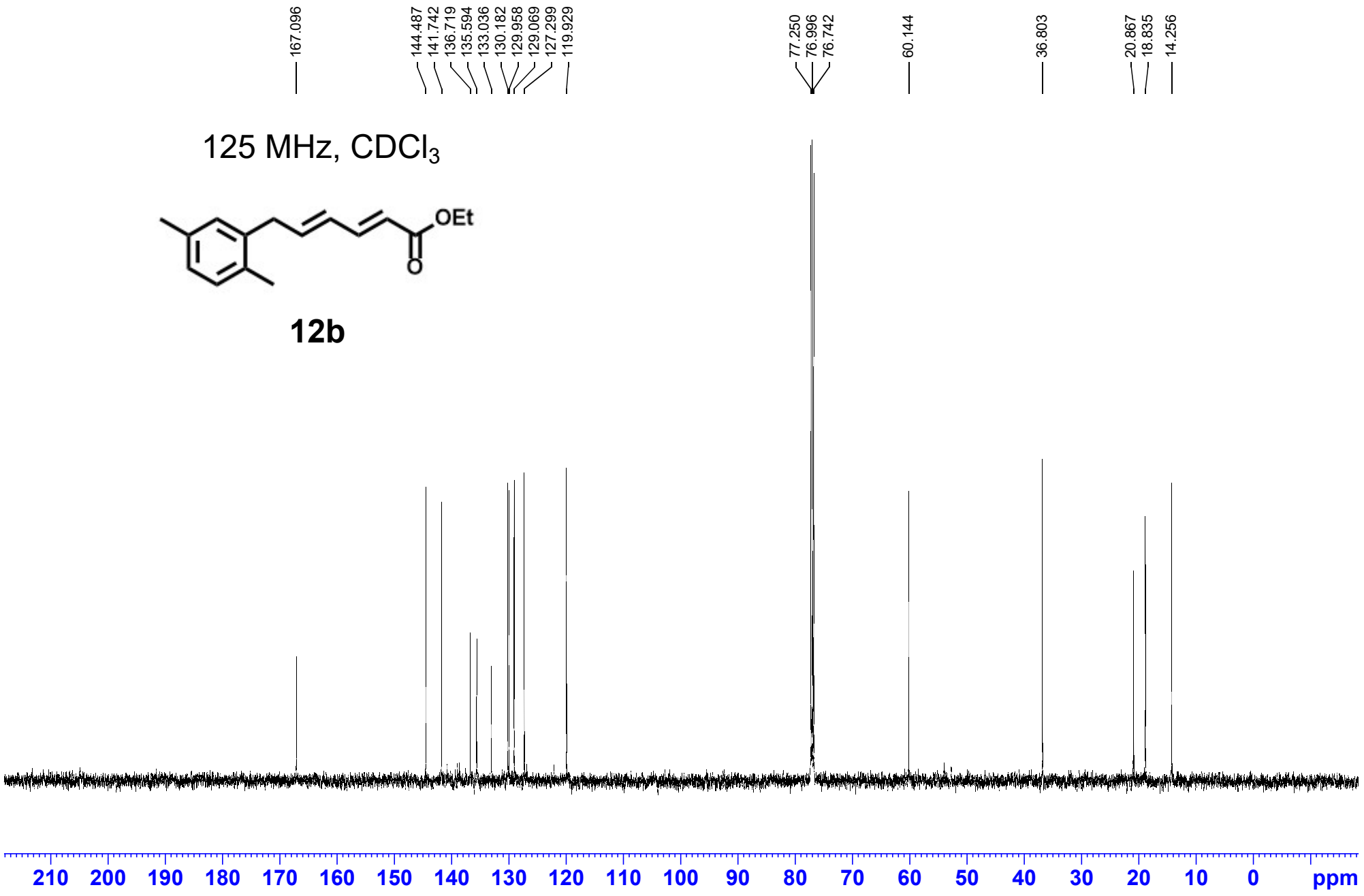
pmp.031 21, 13C, sorbate + mesitylene adduct, 500/125, 1/15/22



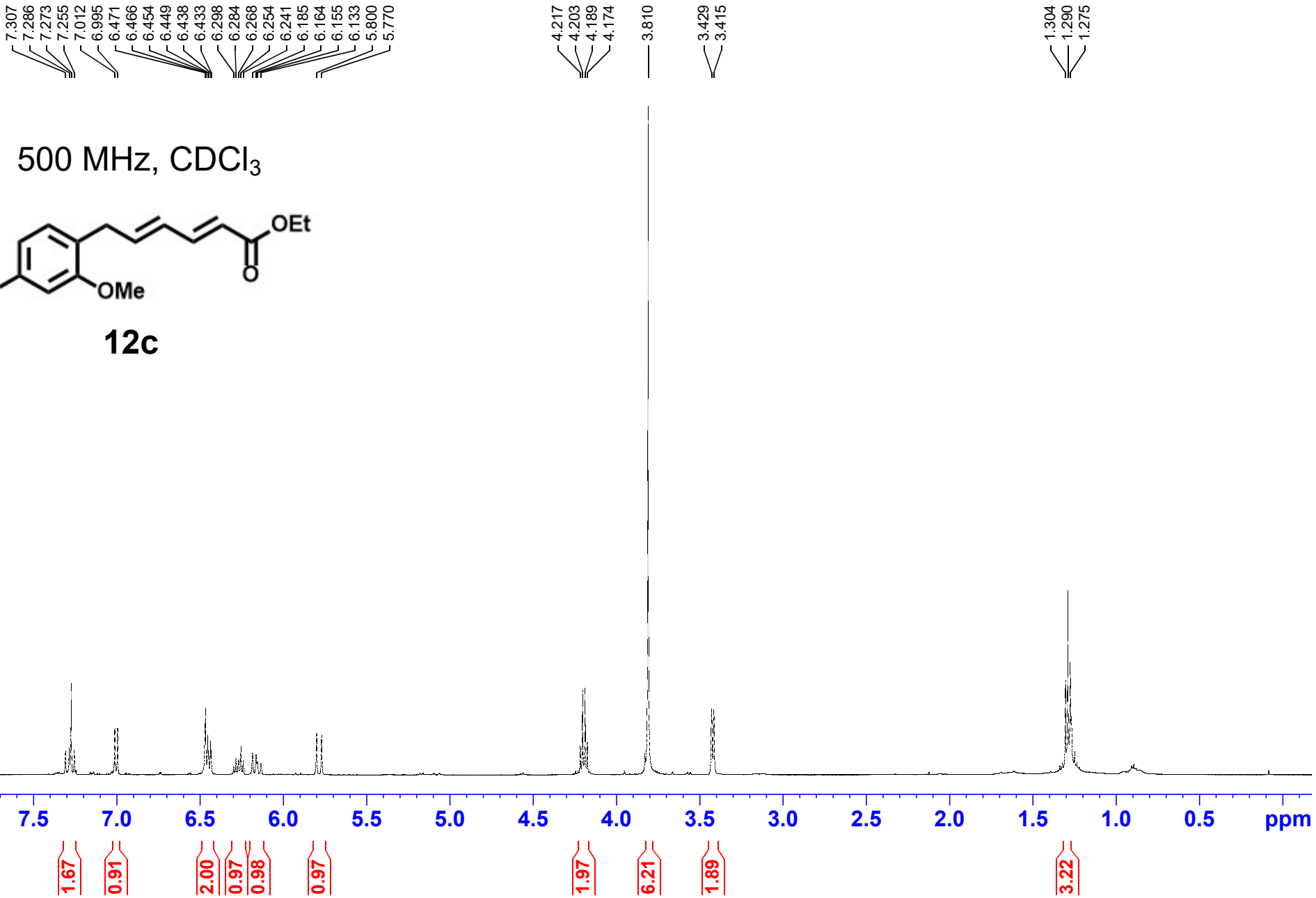
pmp.040 20, sorbate + p-xylene, 1H, 500, 1/24/22



pmp.040 21, sorbate + p-xylene, 13C, 500/125, 1/24/22



pmp.057 20, 1H, sorbate + 13-MeO2Ph, 1H, 500, 1/17/22

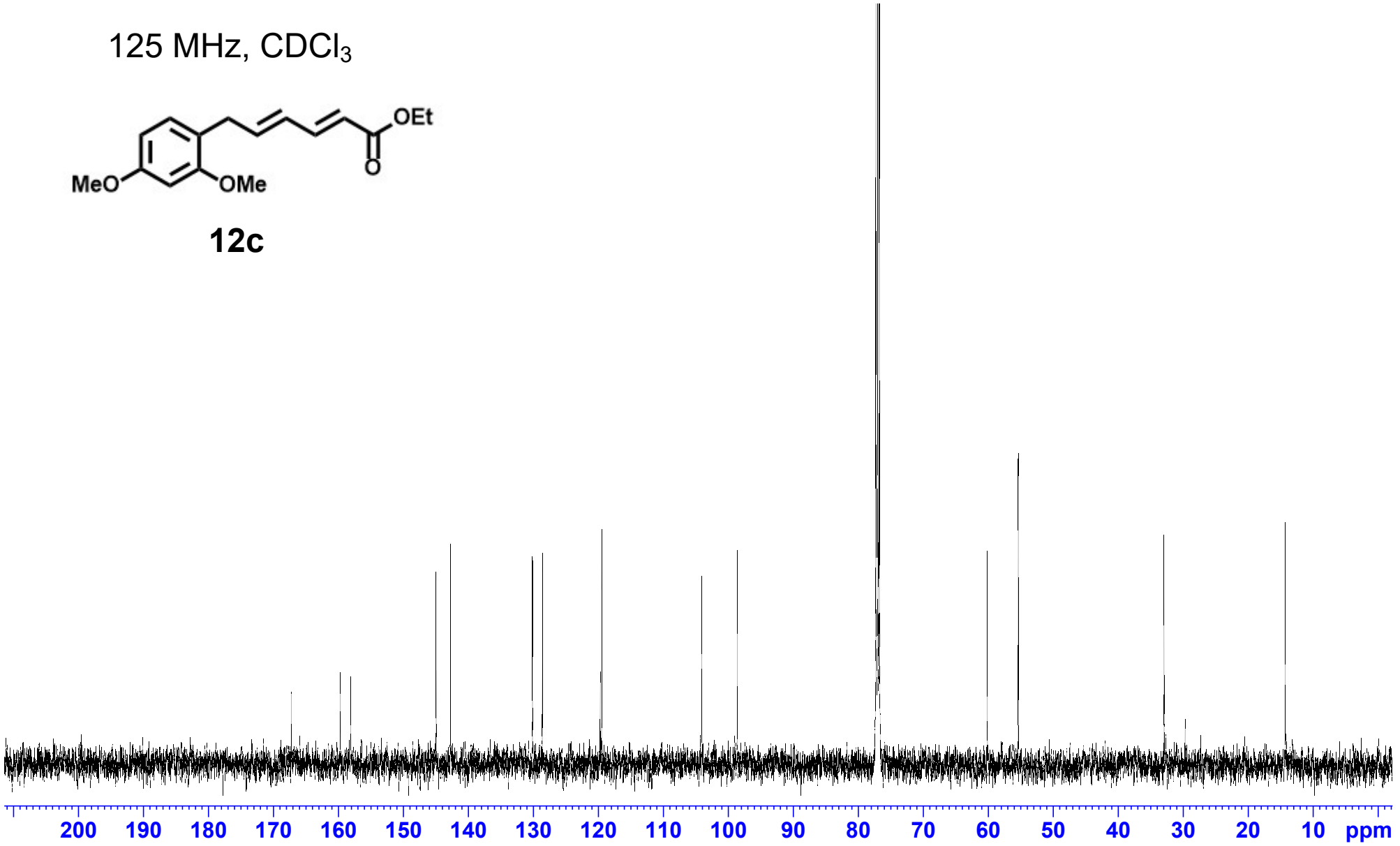


pmp.057 21, 13C, sorbate + 1,3-MeO2Ph, 500/125, 1/17/22

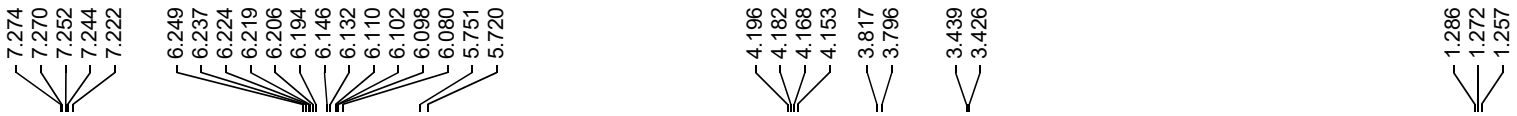
167.243
159.680
158.103
144.950
142.731
130.117
128.607
119.694
119.473
104.065
98.618
77.250
76.997
76.743
60.119
55.350
32.932
14.288

125 MHz, $CDCl_3$

12c

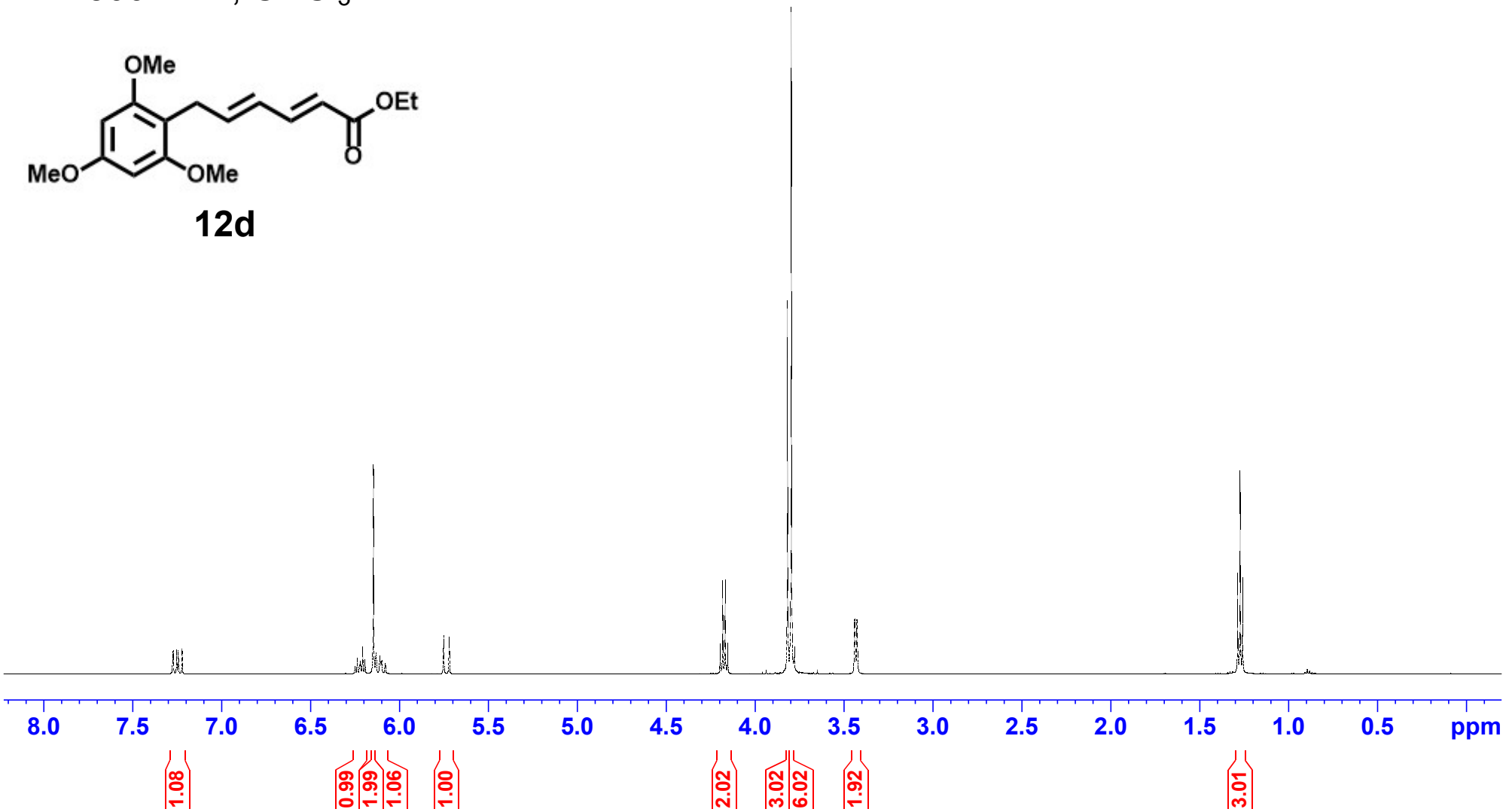


pmp.069 20, 1H, sorbate + 135-MeO3Ph, 1H, 500, 1/15/22



500 MHz, $CDCl_3$

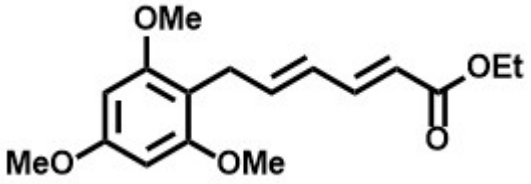
12d



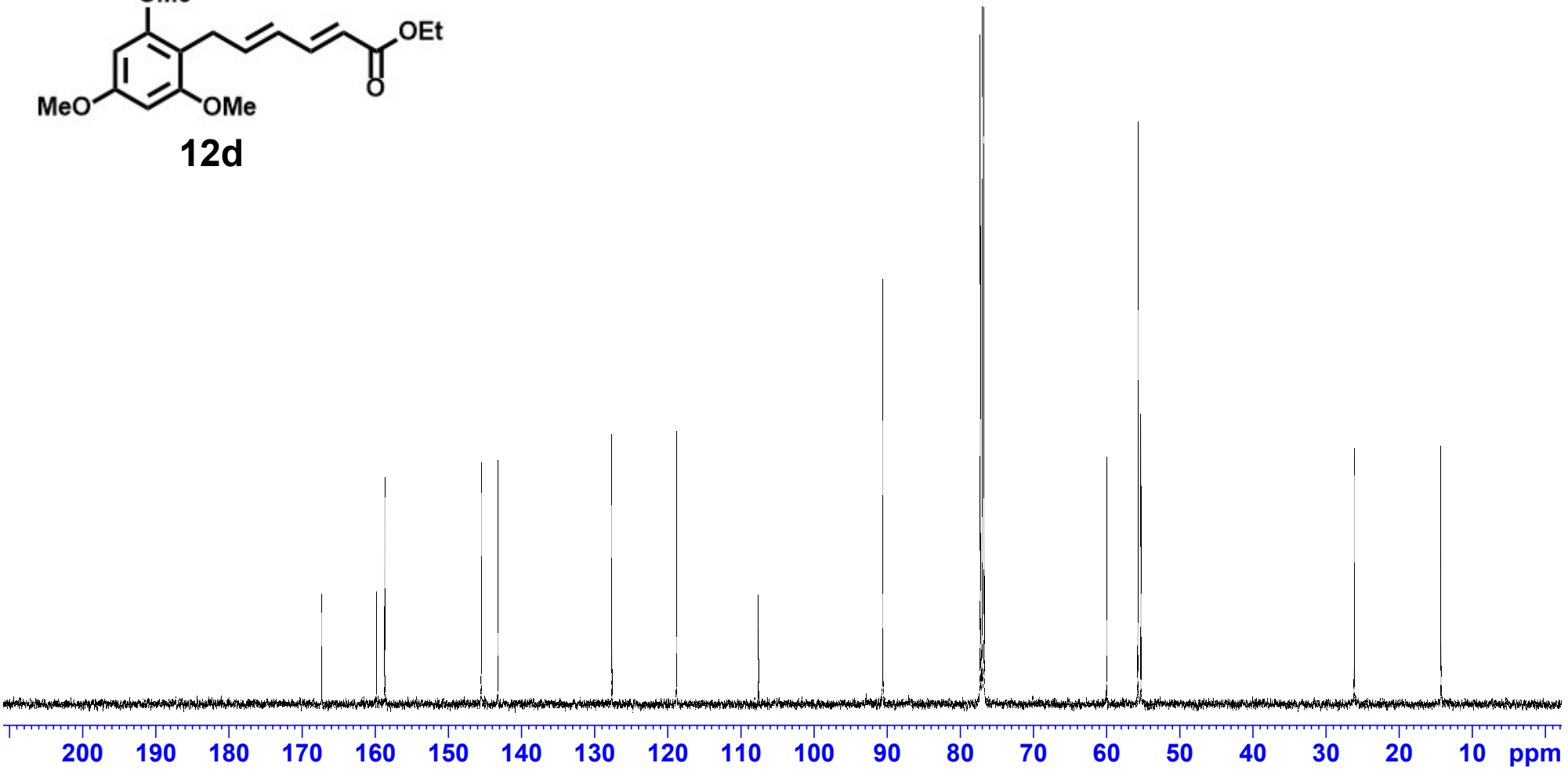
pmp.069 21, 13C, sorbate + 135-MeO3Ph, 500/125, 1/15/22

167.304
159.820
158.679
145.478
143.205
127.636
118.765
107.582
90.583
77.250
76.996
76.742
59.958
55.678
55.280
26.112
14.260

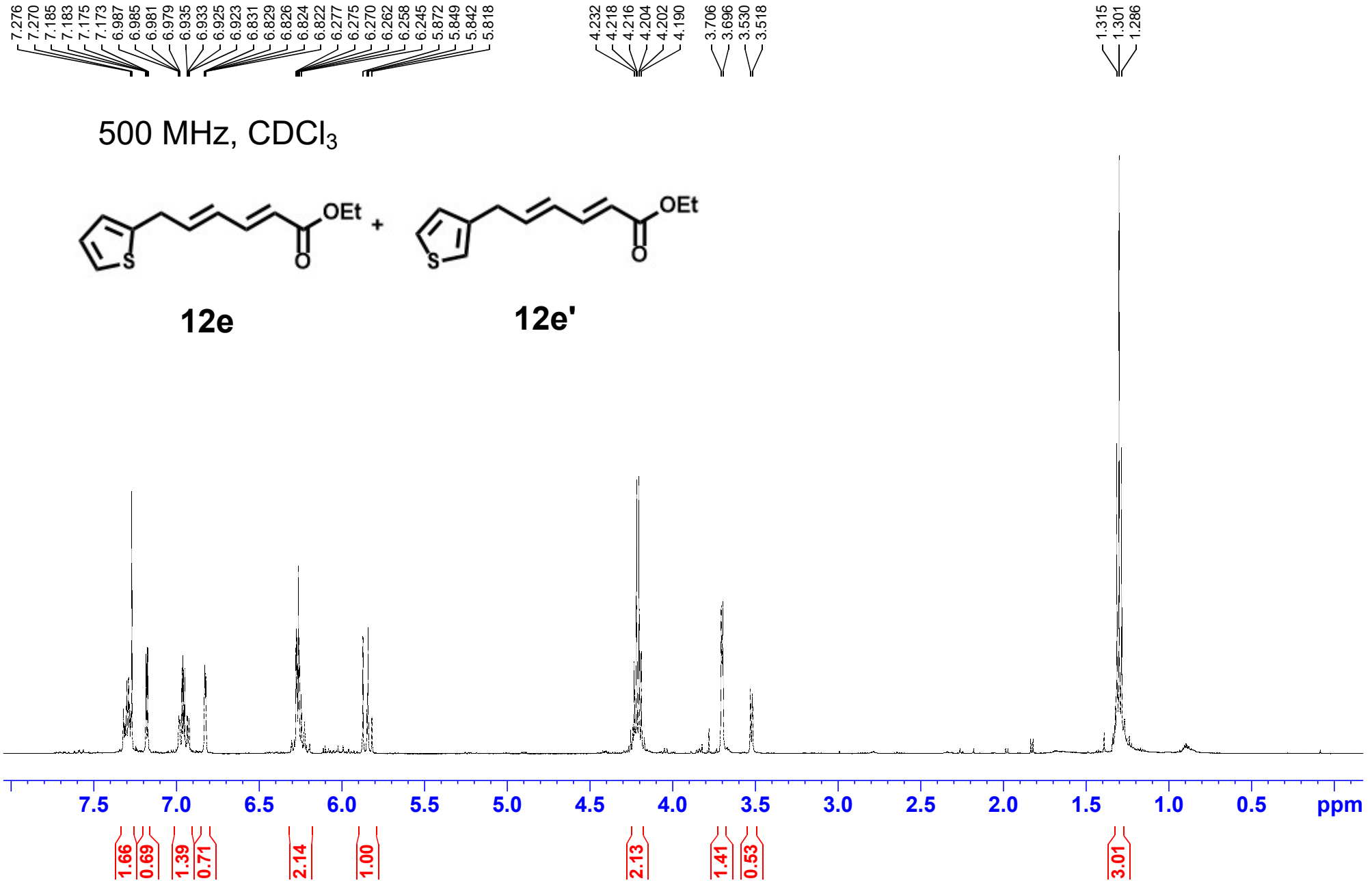
125 MHz, $CDCl_3$



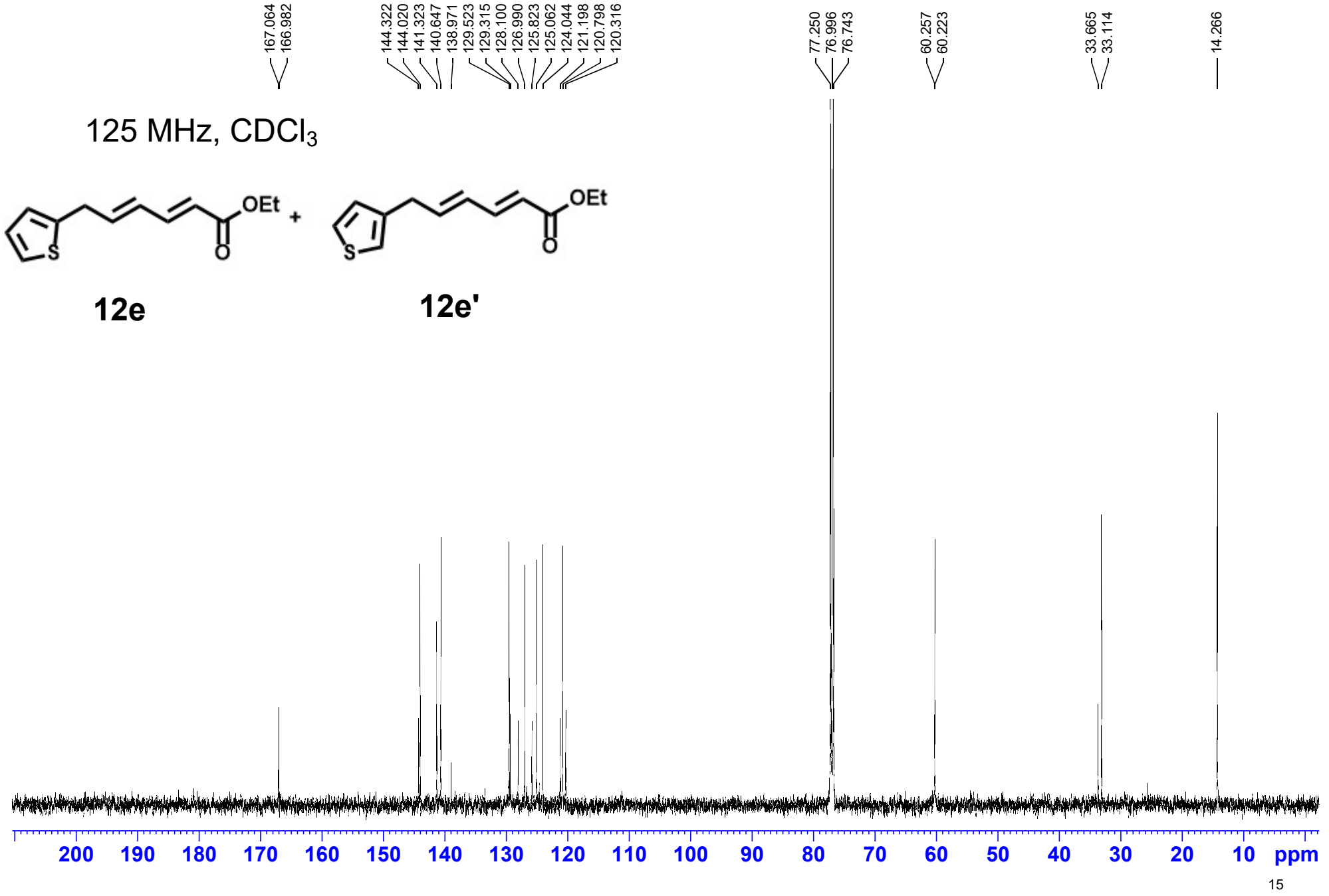
12d



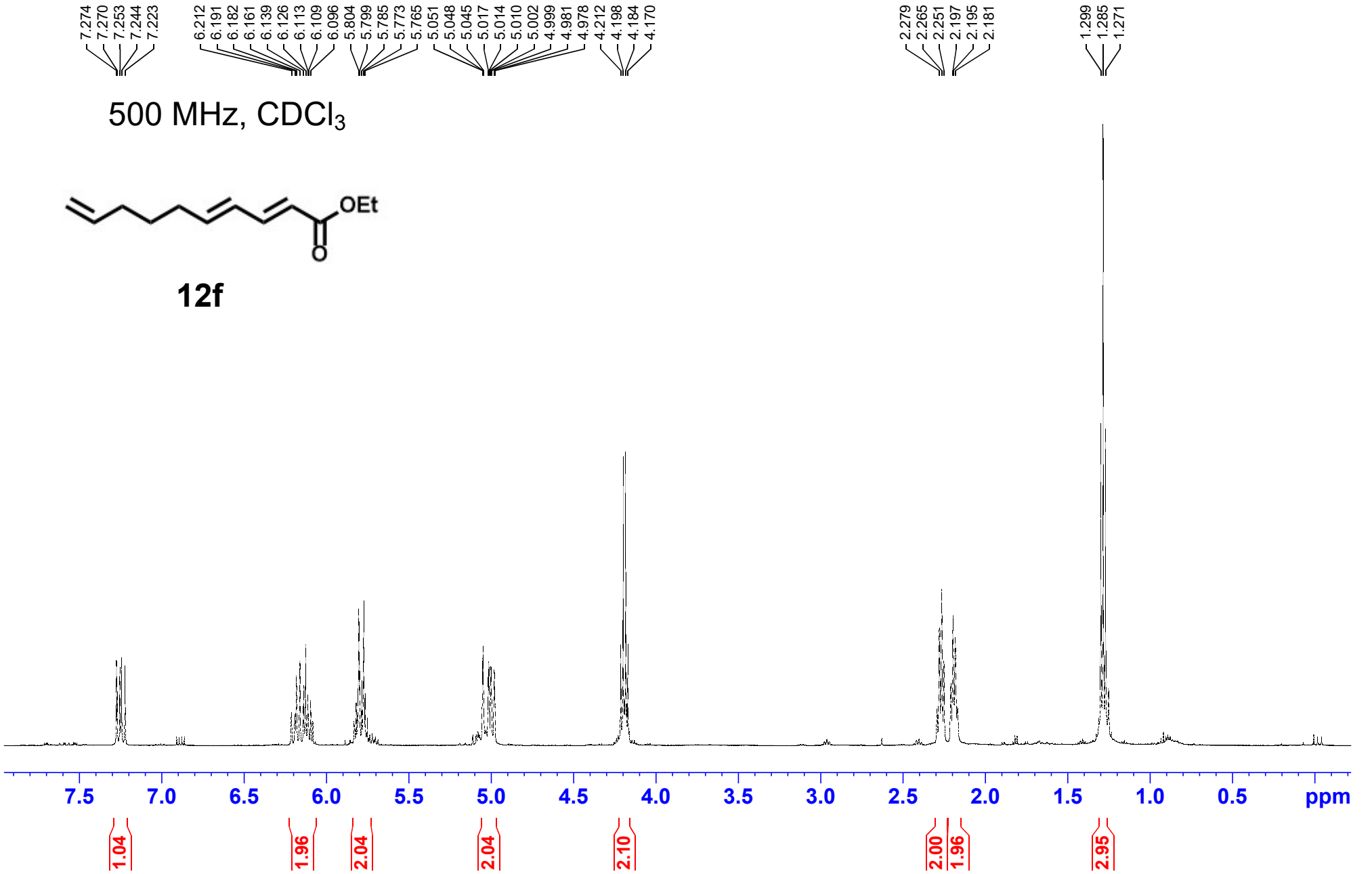
pmp.074 20, sorbate + thiophene, 1H, 500, 1/22/22



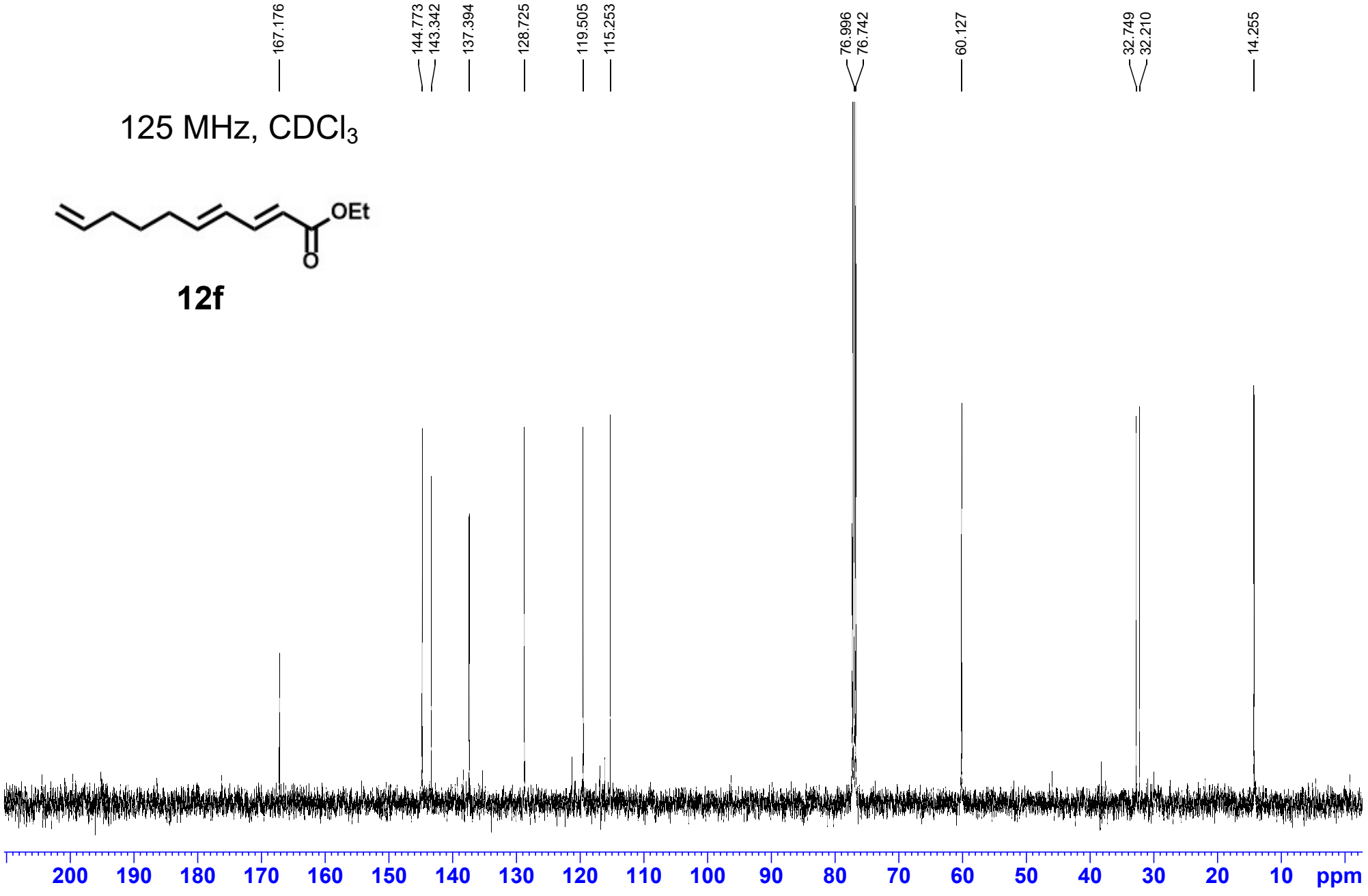
pmp.074 21, sorbate + thiophene, 13C, 500/125, 1/22/22



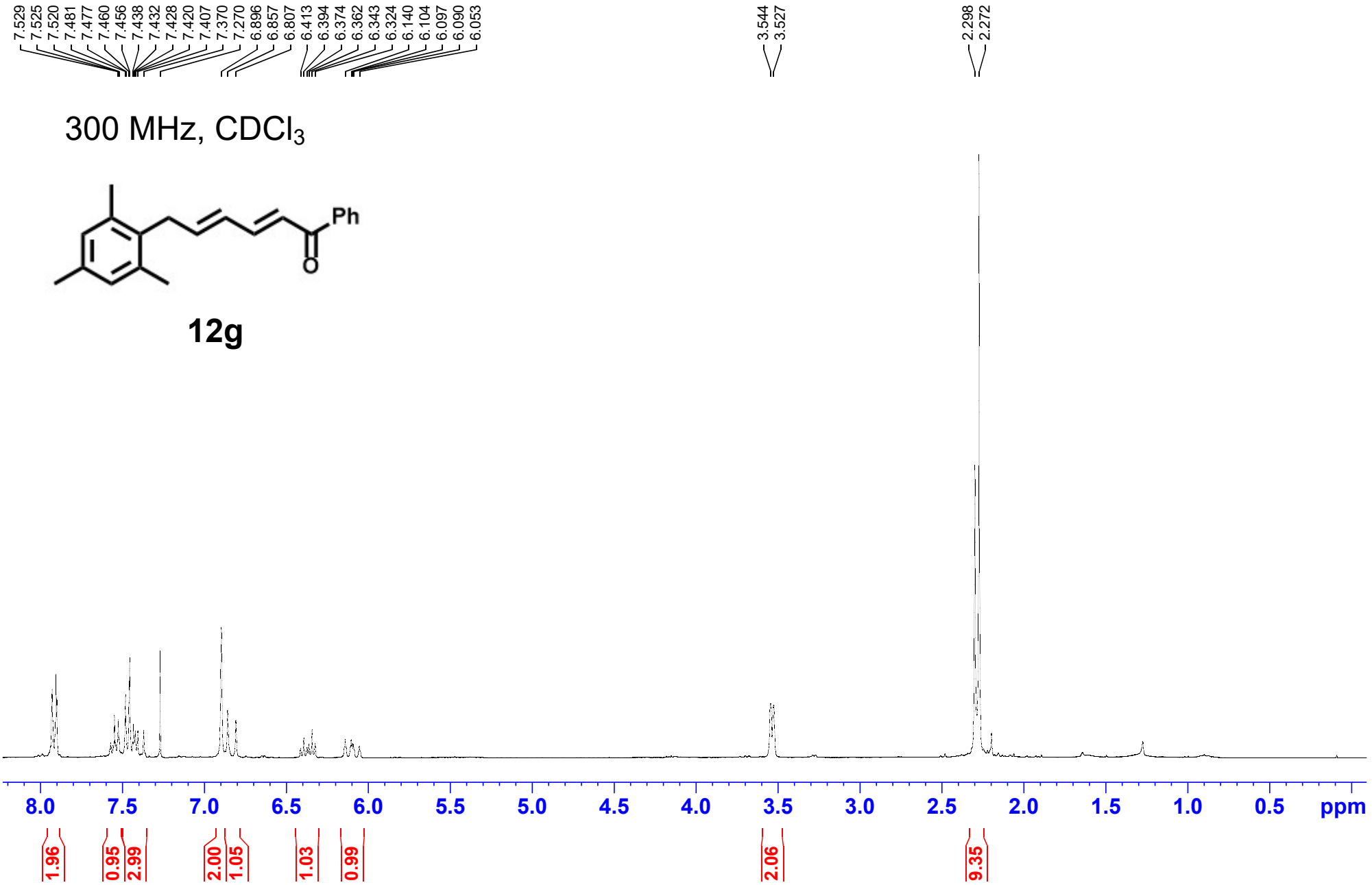
pmp.079 30, sorbate + allylTMS, 1H, 500, 3/20/22



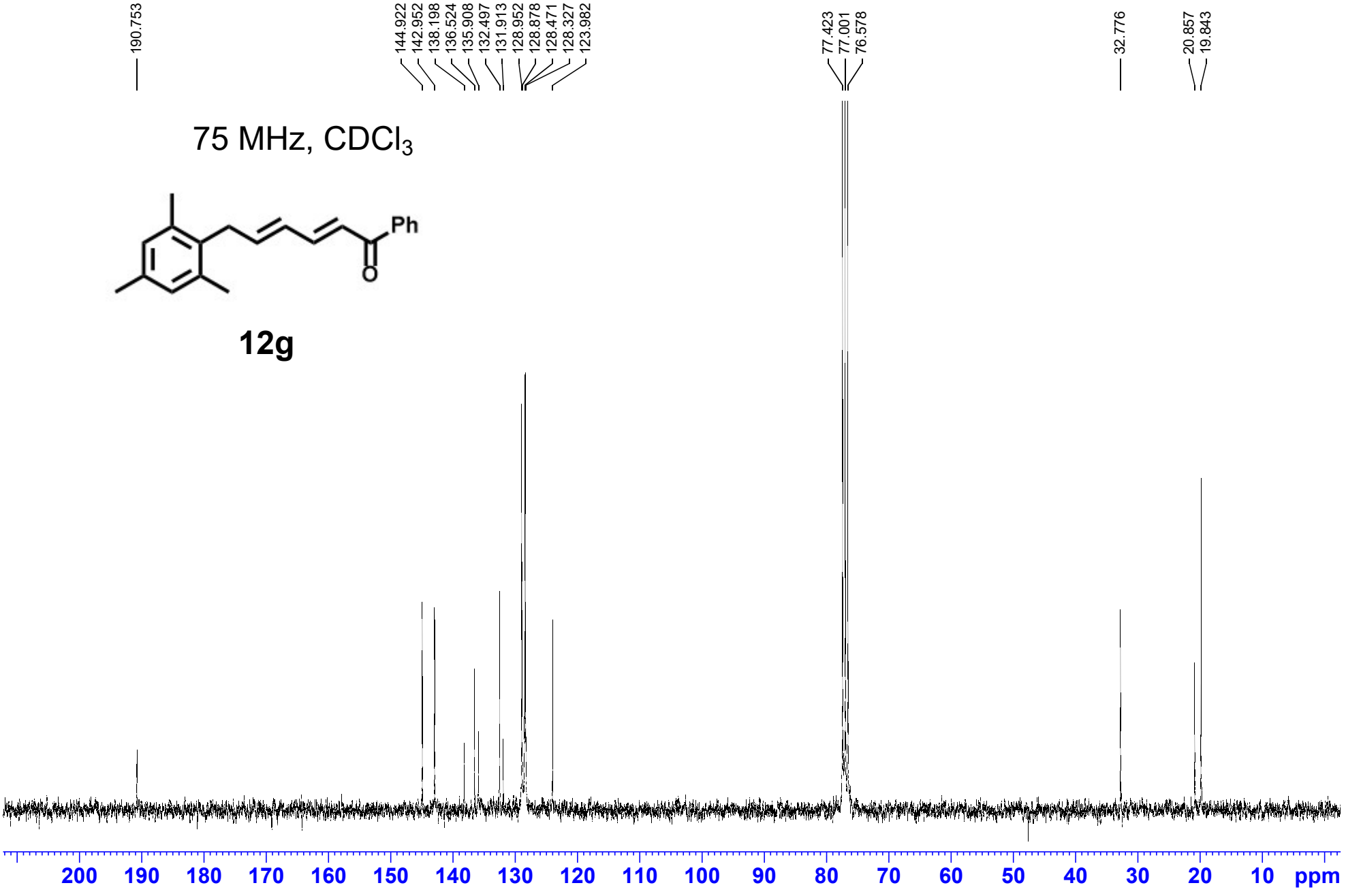
pmp.079 30, sorbate + allylTMS, 13C, 500/125, 3/20/22



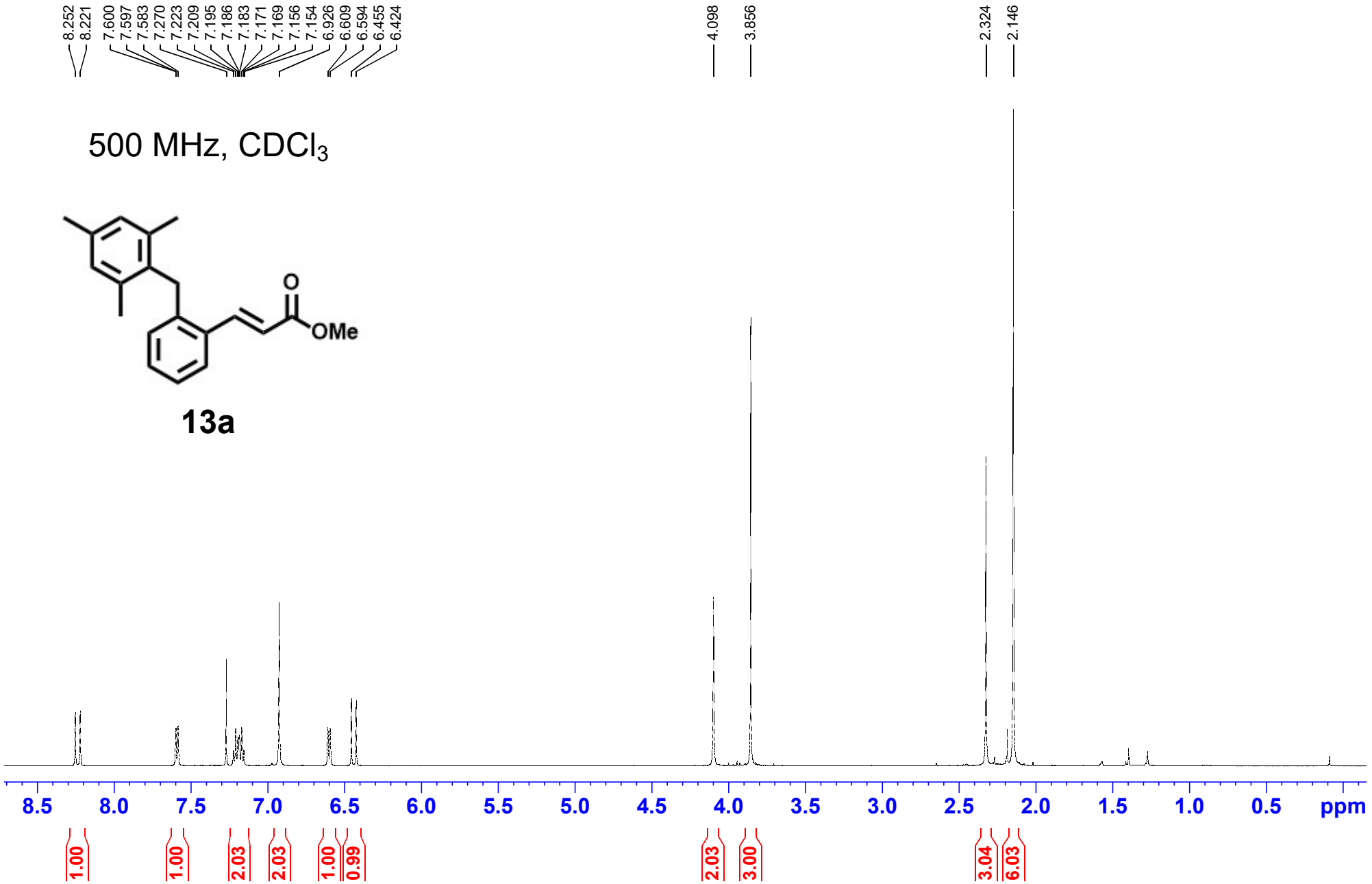
pmp.100 20, 1H, Ph ket + mesitylene, 300US, 2/4/22



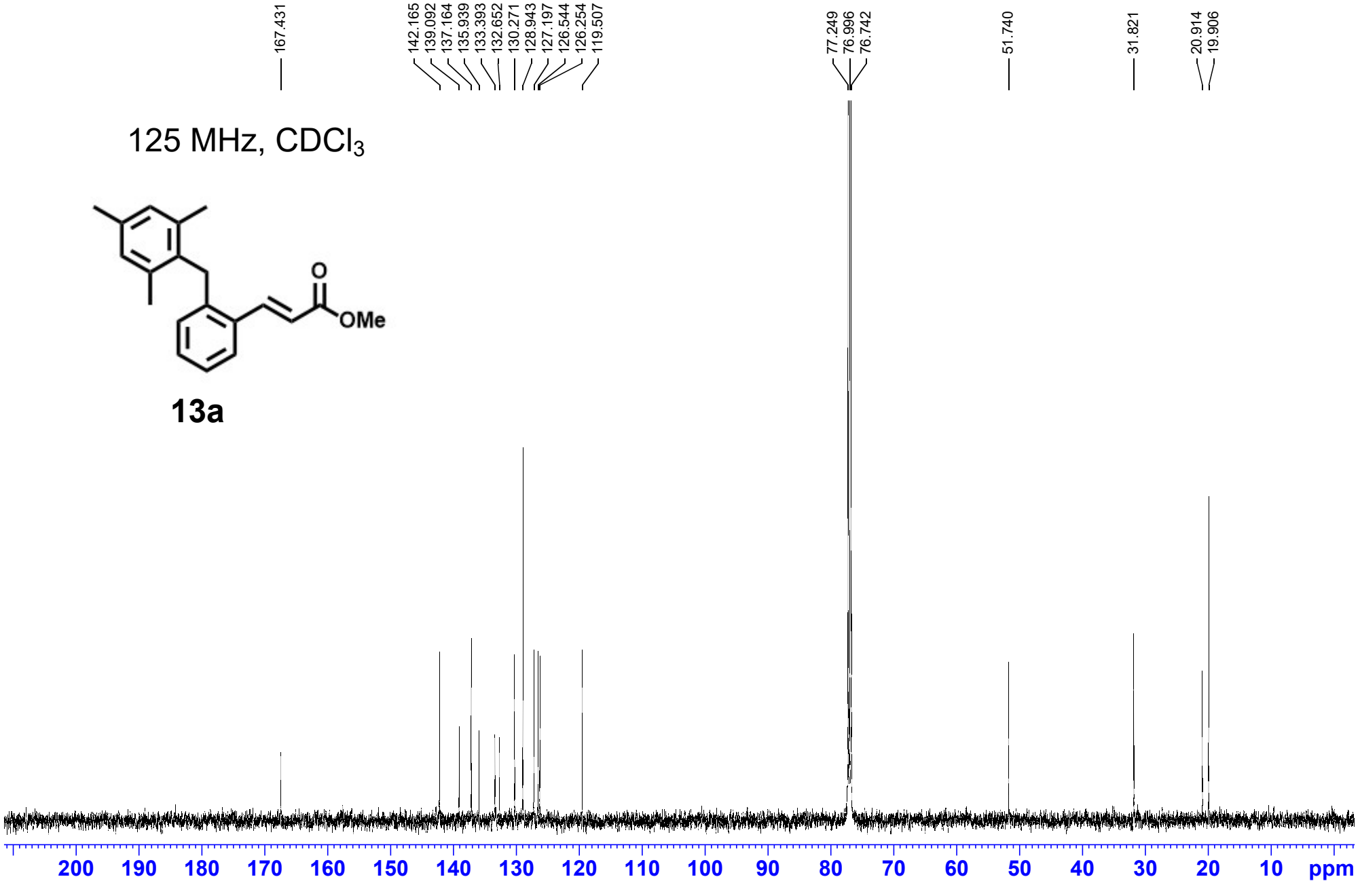
pmp.100 21, 13C, Ph ketone + mesitylene, 300US/75, 2/4/21



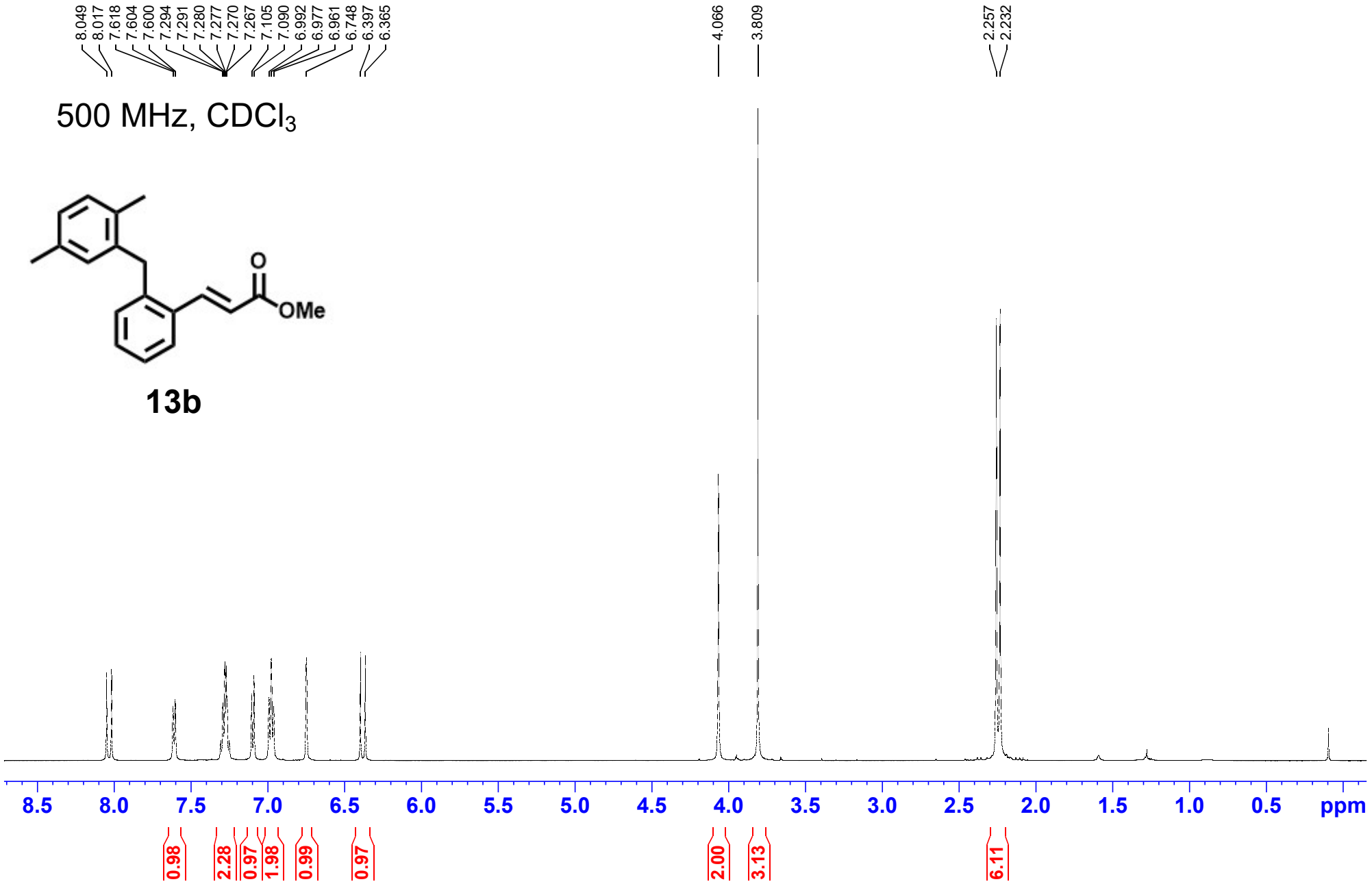
pmp.148 20, phenyl fused + mesitylene, 1H, 500, 1/20/22



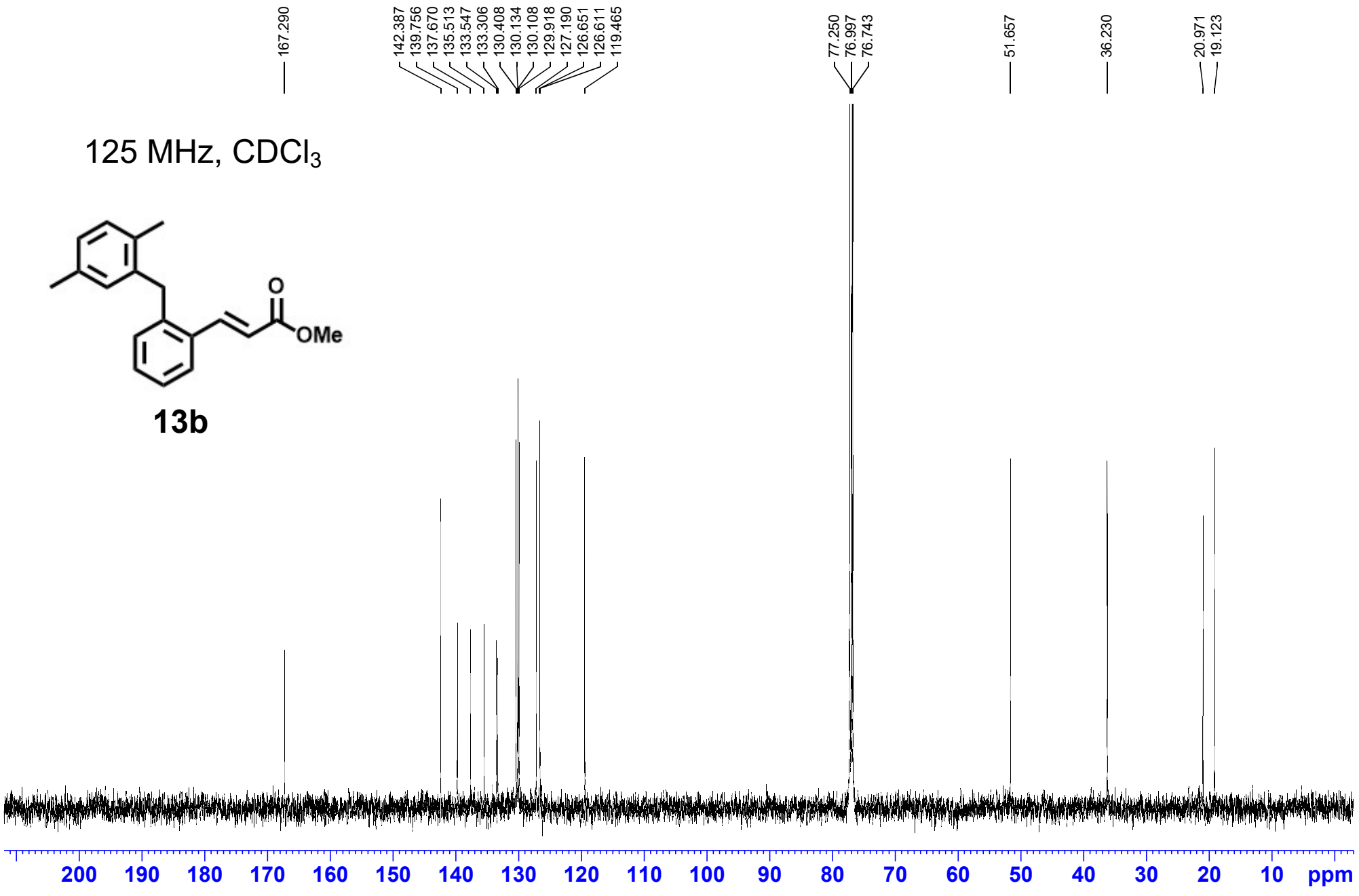
pmp.148 21, phenyl fused + mesitylene, 13C, 500/125, 1/20/22



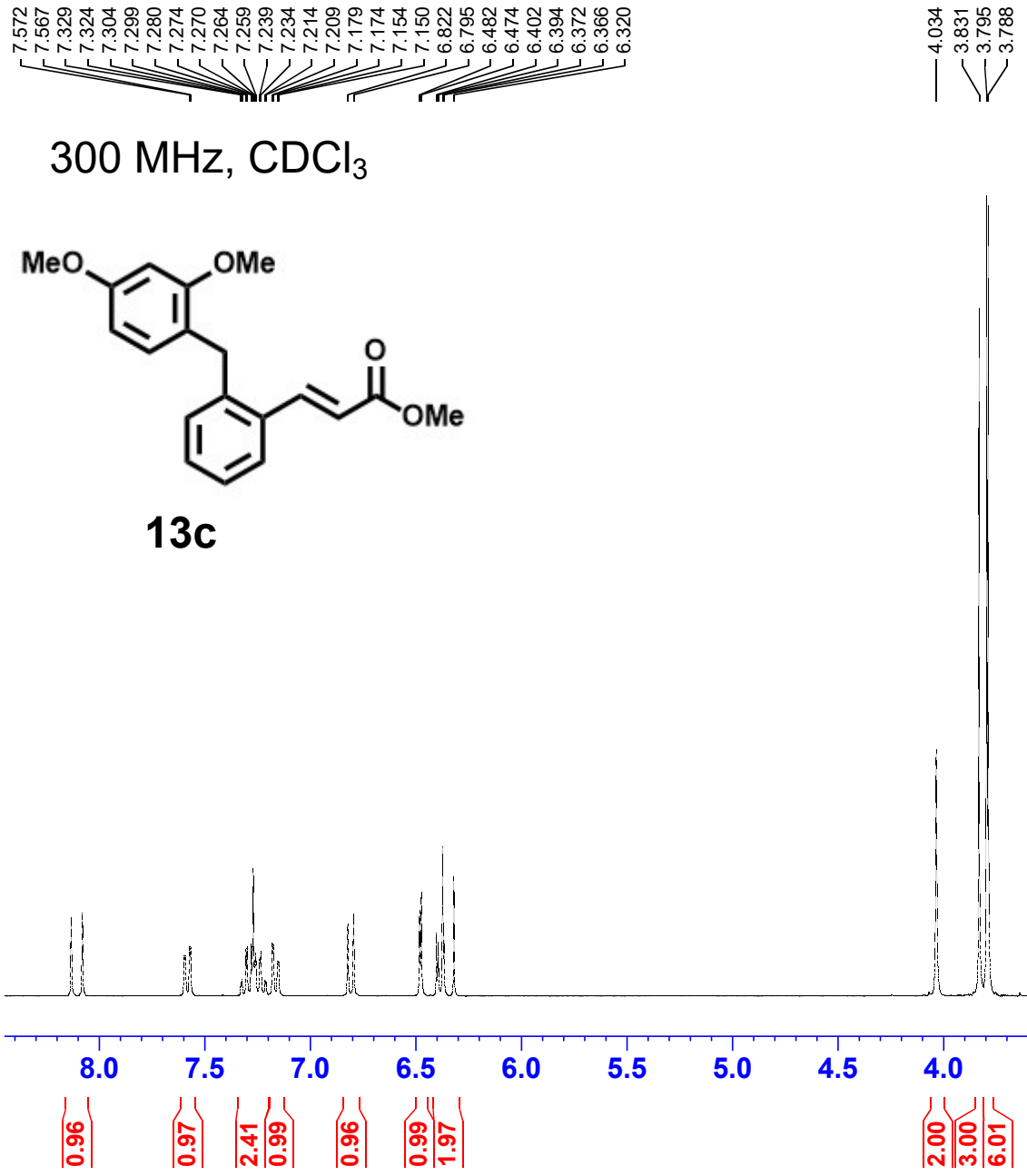
pmp.150 20, phenyl fused + p-xylene, 1H, 500, 1/19/22



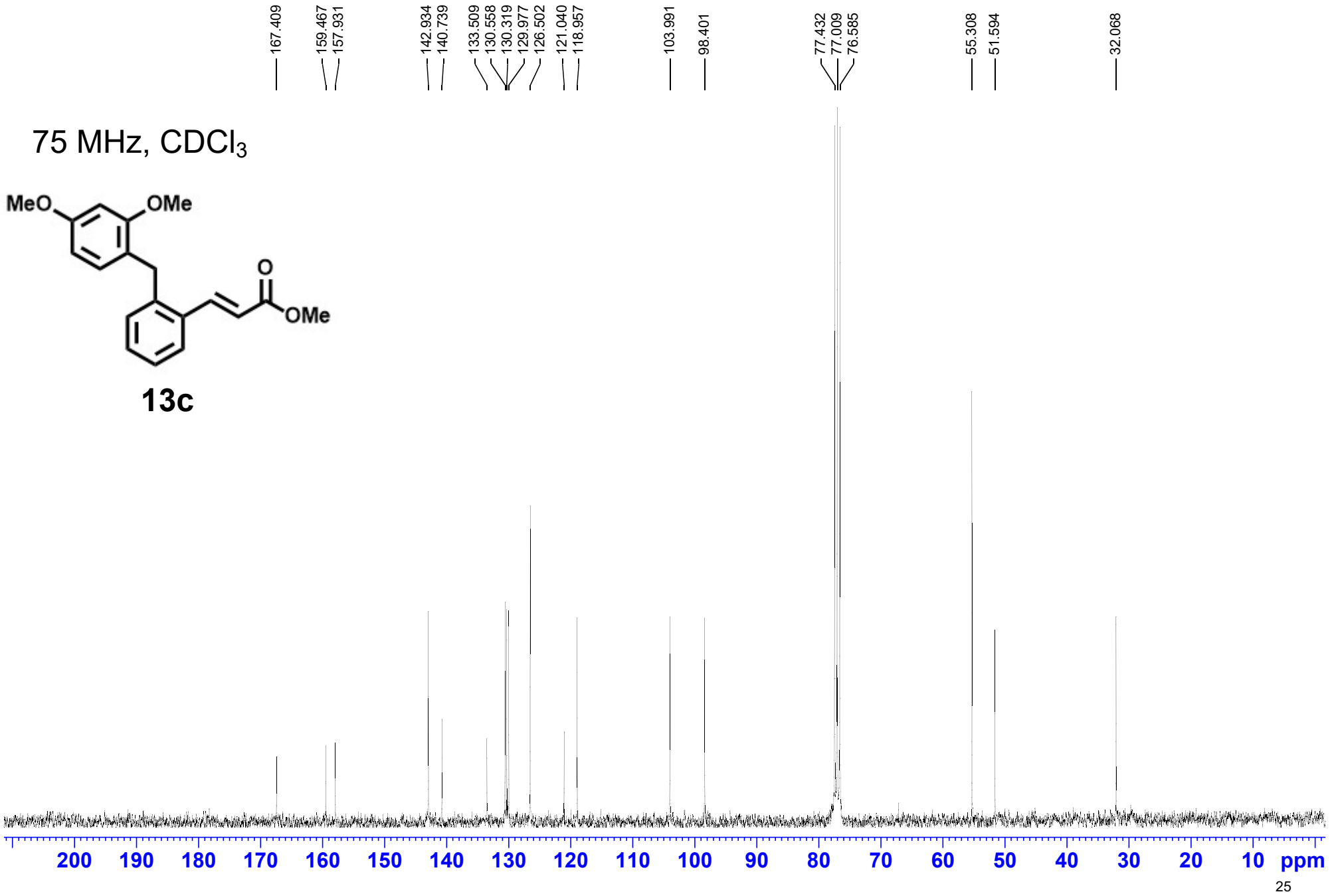
pmp.150 21, phenyl fused + p-xylene, 13C, 500/125, 1/19/22



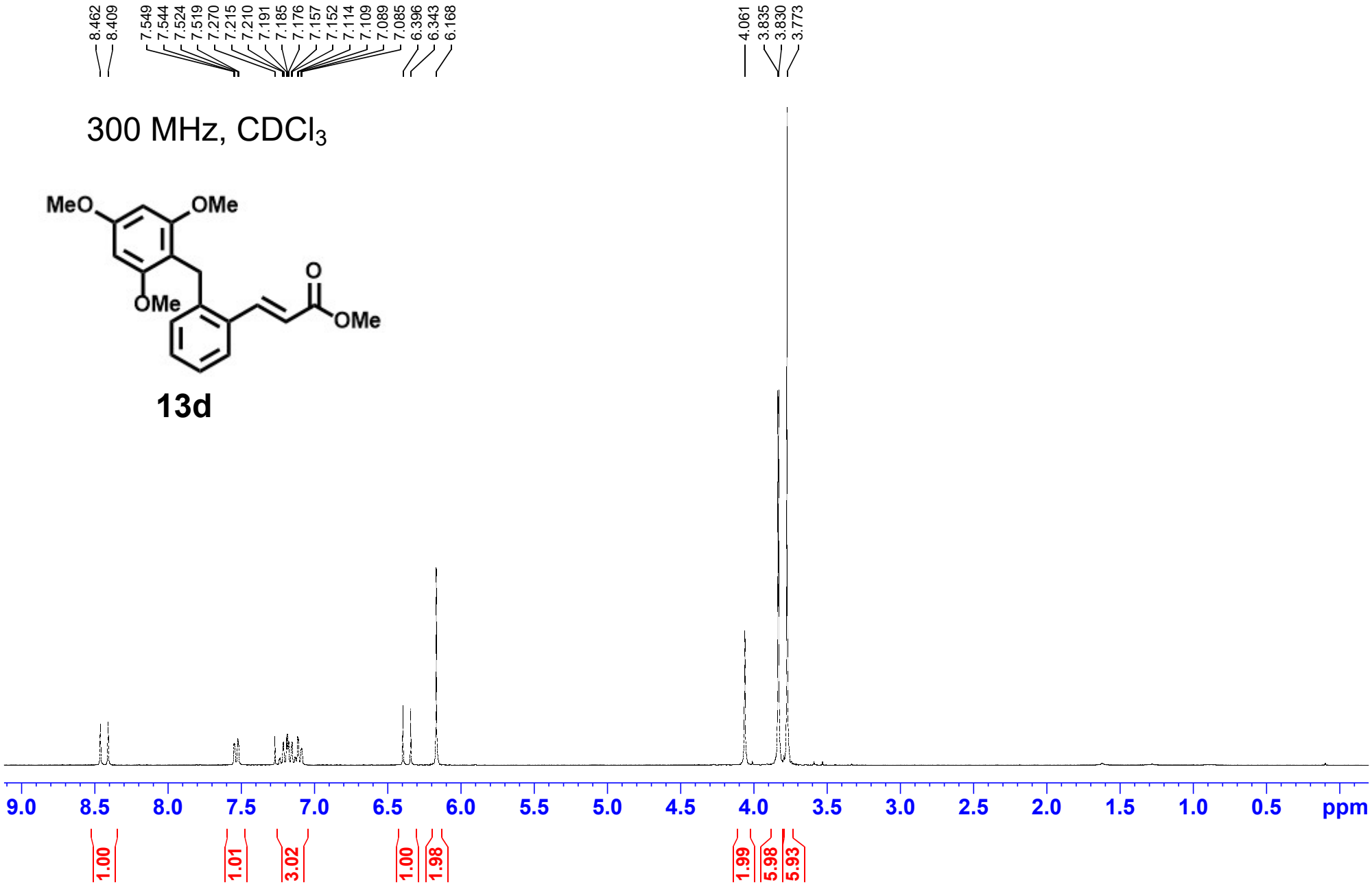
pmp.141 20, 1H, benzo + 1,3-MeO2Ph, B82-300, 1/26/22



pmp.141 21, 13C, benzo + 1,3-MeO2Ph, B82-300/75, 1/26/22



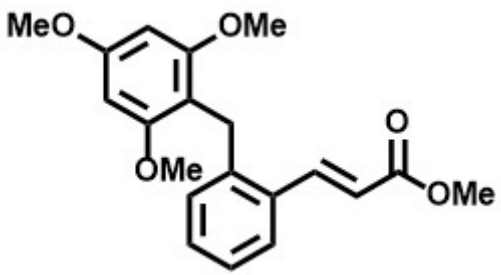
pmp.149 20, 1H, aryl fused substrate + 135-MeO3Ph, B82-300, 1/18/22



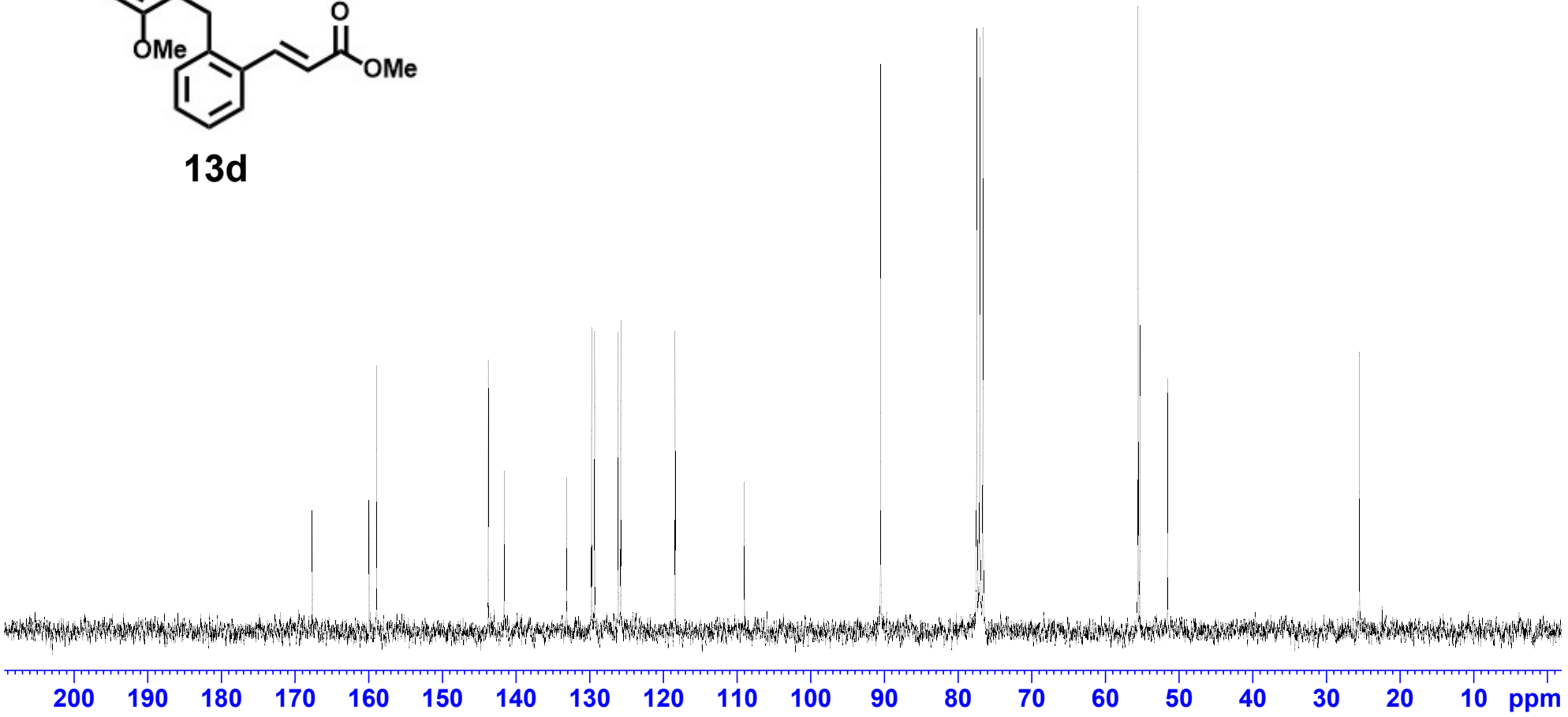
pmp.149 20, 13C, aryl fused substrate + 135-MeO3Ph, B82-300/75, 1/18/22

167.653
159.924
158.912
143.756
141.594
133.117
129.720
129.304
126.135
125.761
118.397
108.981
90.487
77.428
77.006
76.583
55.548
55.280
51.544
25.485

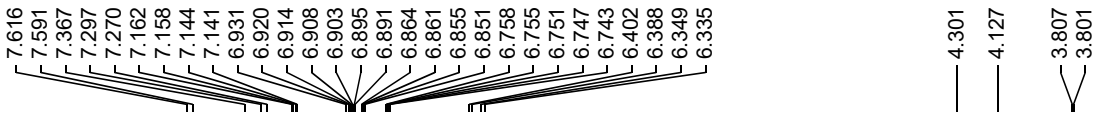
75 MHz, $CDCl_3$



13d

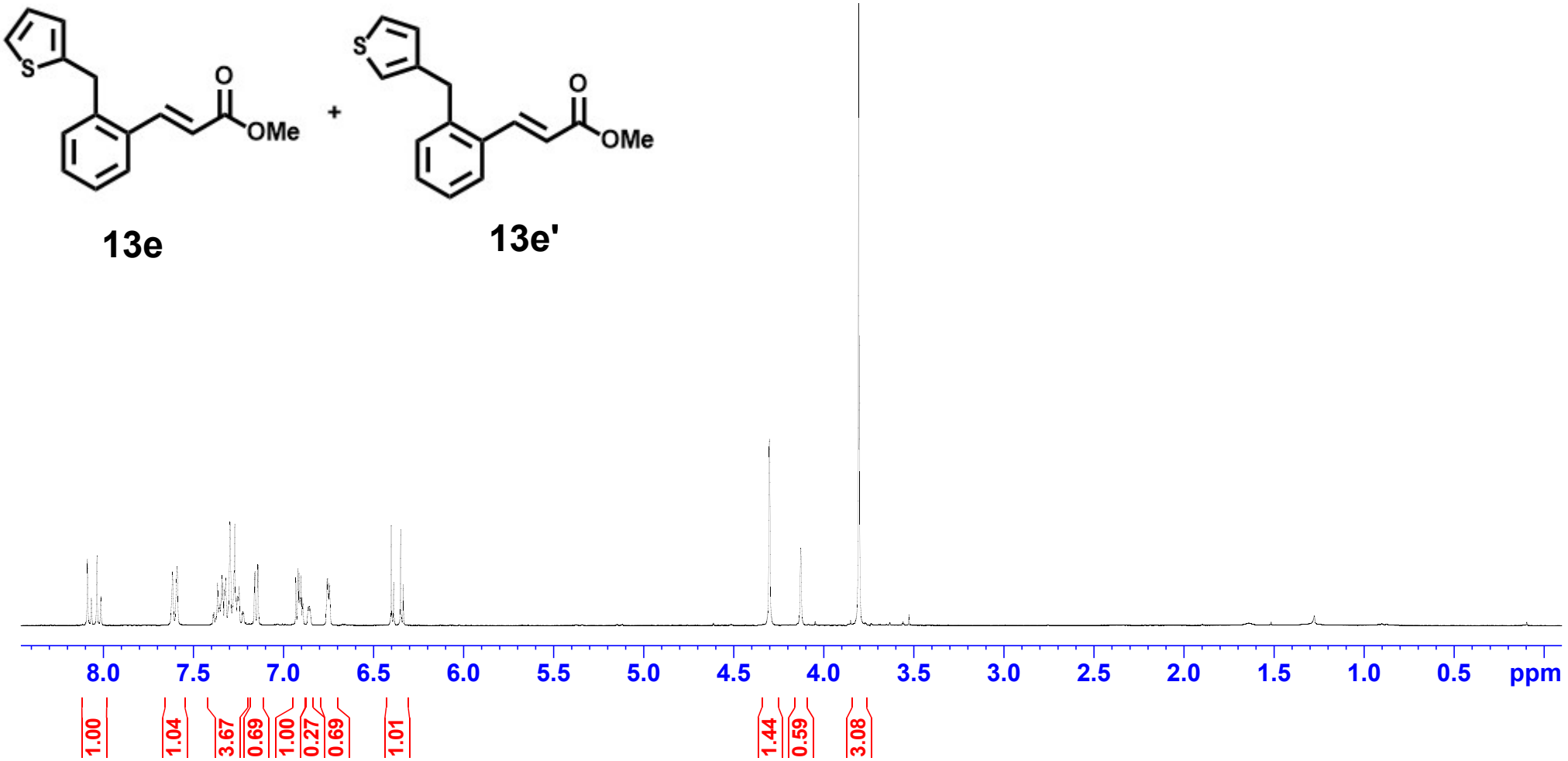


pmp.0147 20, benzo fused+ thiophene, DPX300, 2/2/22

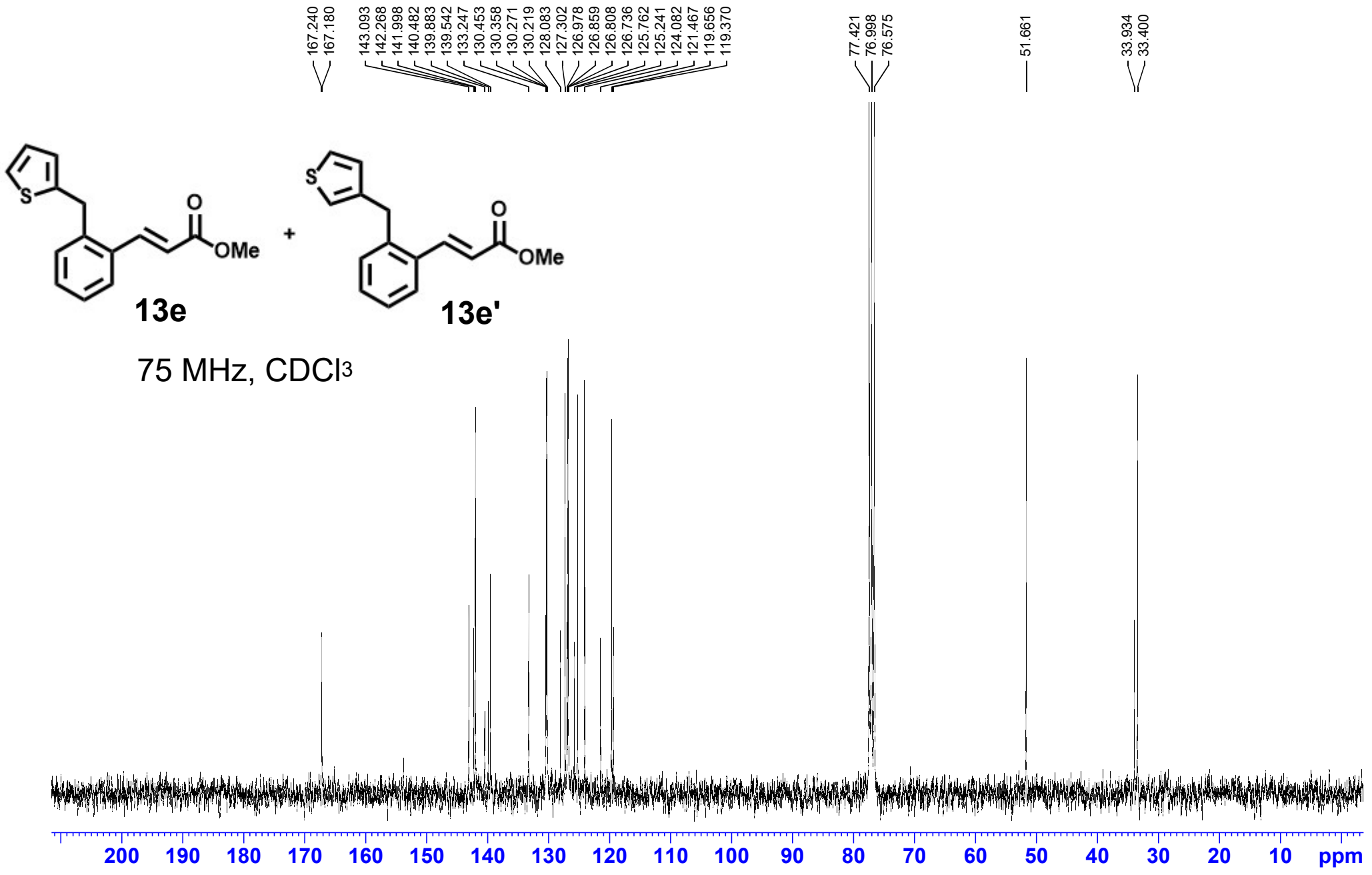


300 MHz, $CDCl_3$

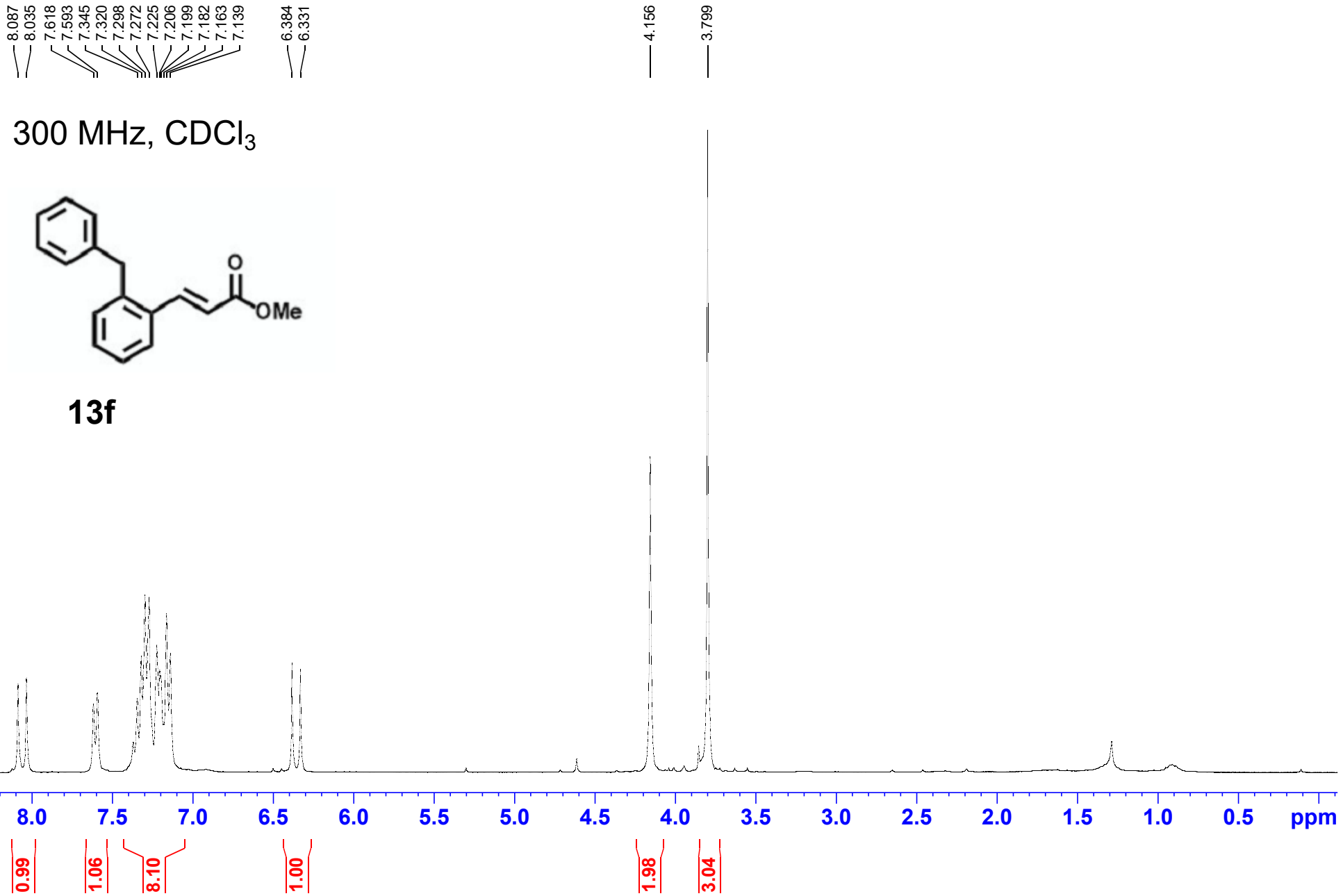
13e **13e'**



pmp.147 21, 13C, benzo fused + thiophene, DPX 300/75, 2/2/22



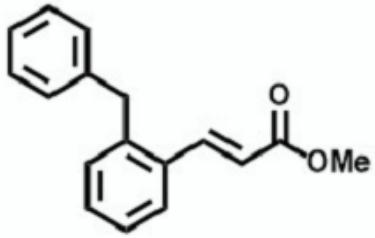
jrg.1487 2, aryl spaced cpd + GaCl3 + benzene



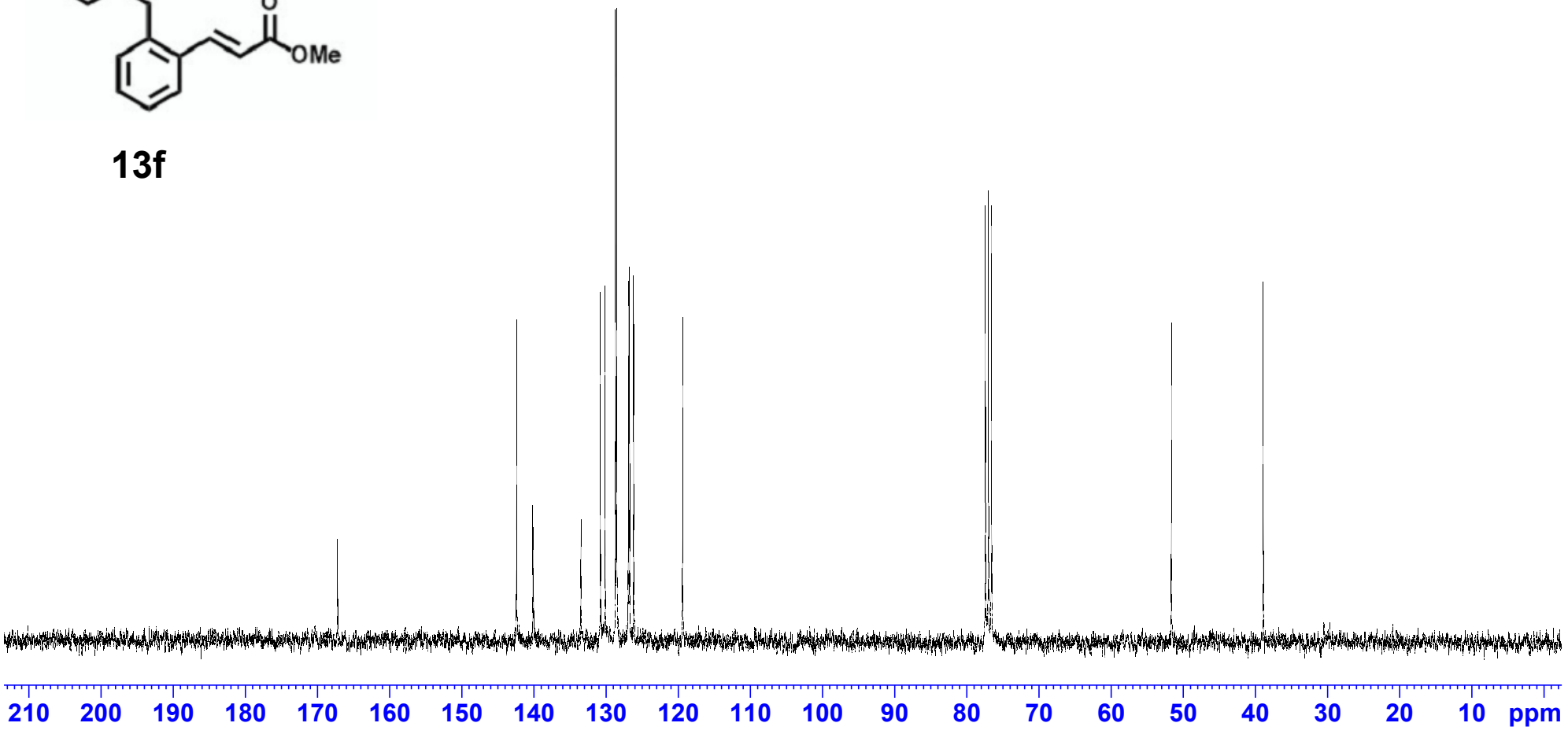
jrg.1487 21, 13C, aryl spaced substrate, Ph subst prod, 300 US/75

167.221
142.400
140.147
140.053
133.472
130.785
130.138
128.694
128.519
126.902
126.738
126.180
119.376
77.424
77.001
76.577
51.623
38.916

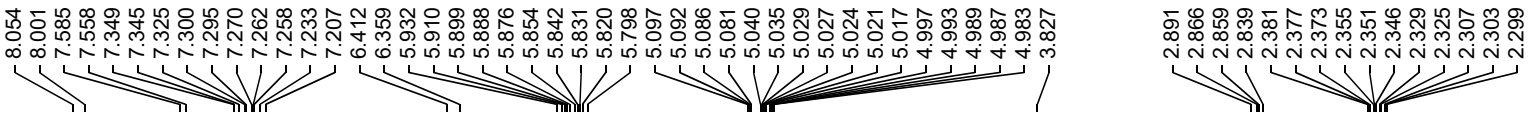
75 MHz, $CDCl_3$



13f

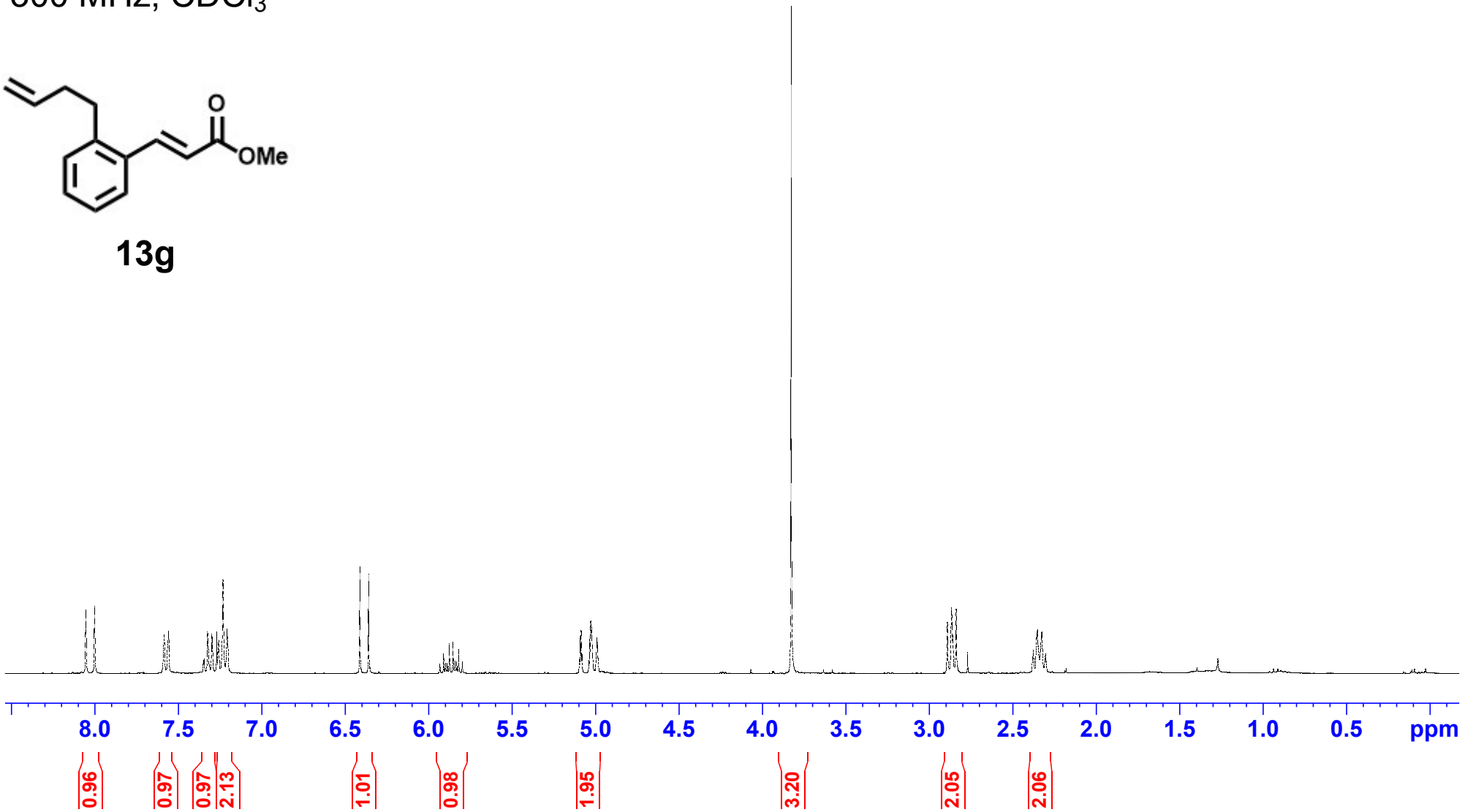


pmp.153 20, 1H, benzo + allylTMS, B82-300, 2/1/22



300 MHz, $CDCl_3$

13g

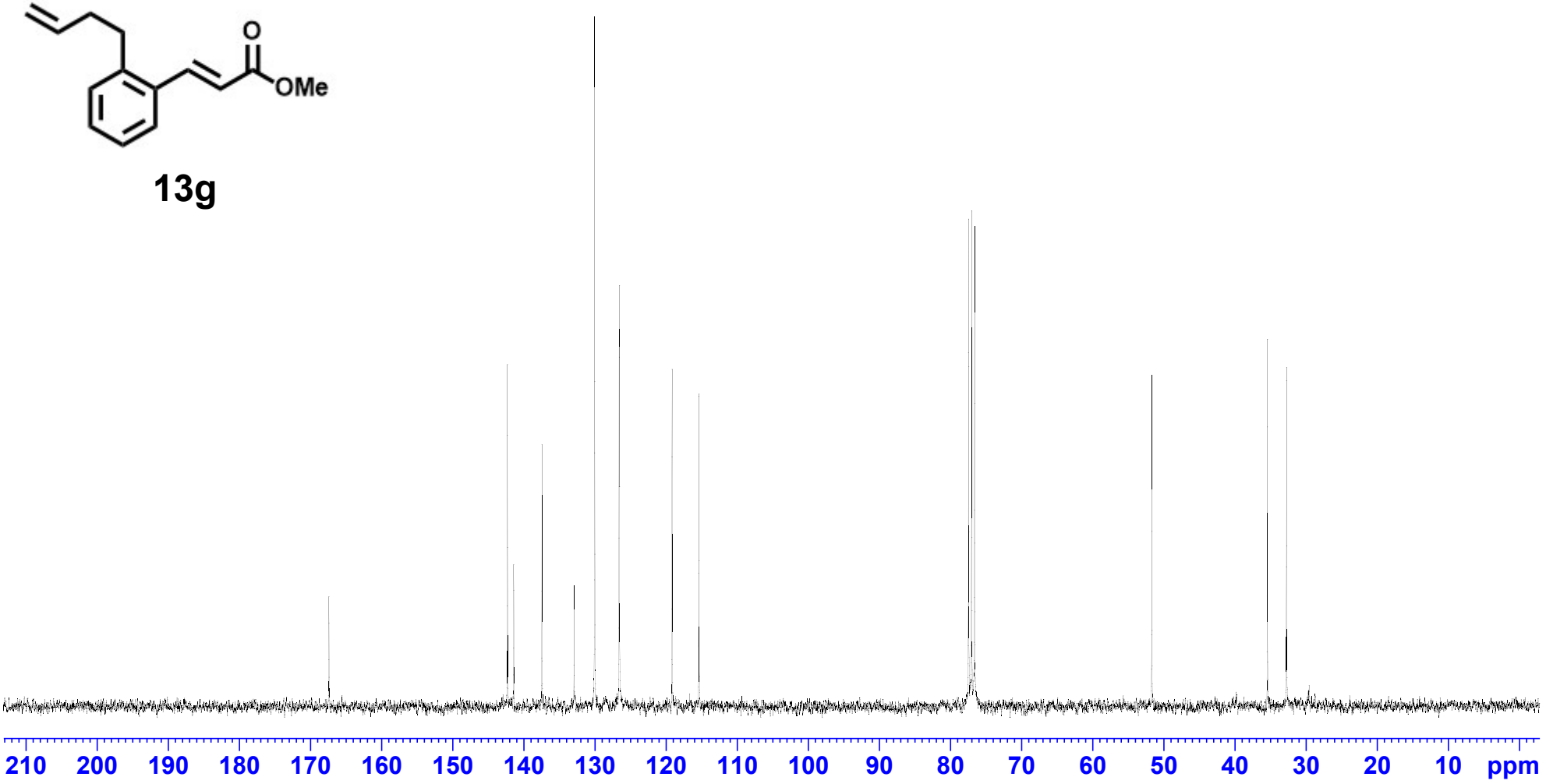


pmp.153 21, 13C, benzo fused + allylTMS, B-82 300/75, 2/1/22

167.394
142.293
141.408
137.429
132.922
130.020
126.585
126.536
119.131
115.361
77.431
77.008
76.585
51.667
35.413
32.710

75 MHz, $CDCl_3$

13g



jrg.1491 20, pages Ph spaced substarte + InCl3 + propiophen Si enol, rflx, B82-300

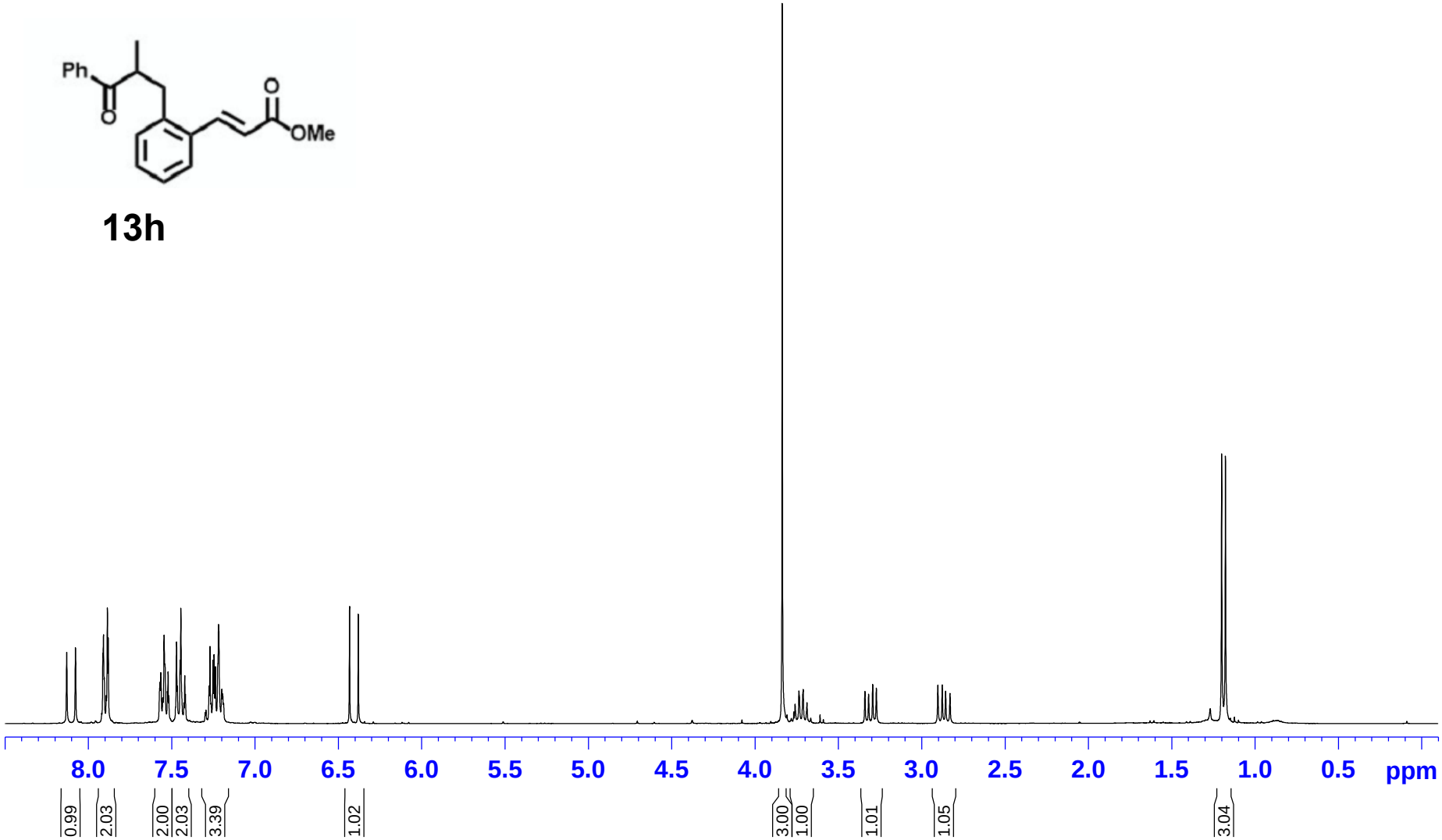
7.885 7.880 7.571 7.566 7.546 7.522 7.471 7.466 7.450 7.445 7.422 7.275 7.270 7.252 7.246 7.238 7.219 7.199 7.194 6.433 6.380

3.837 3.759 3.737 3.711 3.688 3.341 3.318 3.294 3.272 2.903 2.877 2.856 2.830

1.200 1.177

300 MHz, $CDCl_3$

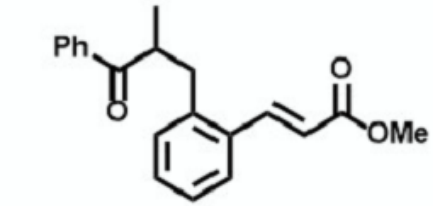
13h



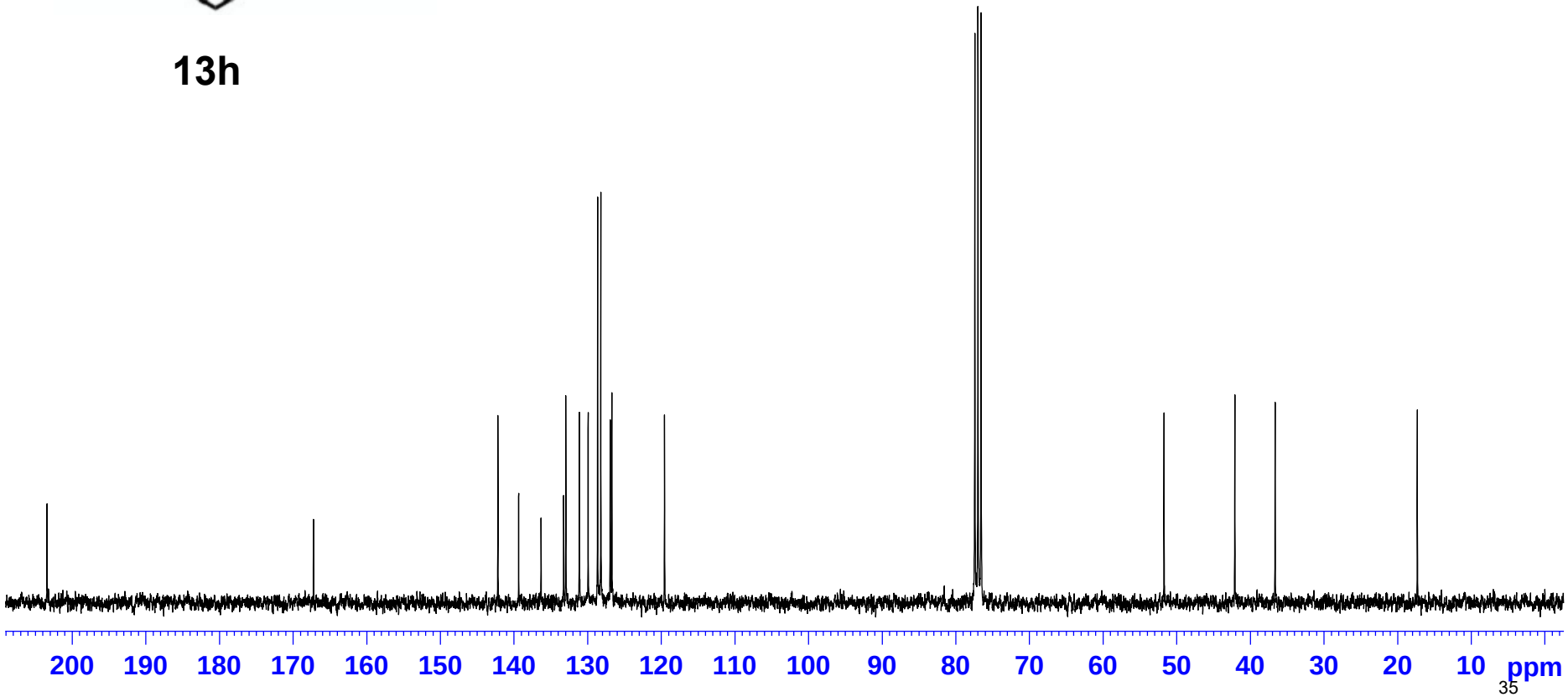
jrg.1491 21, pages Ph spaced substarte + InCl3 + propiophen Si enol, B82-300/75MHz,

203.421 167.222 142.212 139.393 136.348 133.275 132.985 131.153 129.952 128.665 128.233 126.959 126.735 119.581 77.429 77.007 76.583 51.729 42.120 36.643 17.329

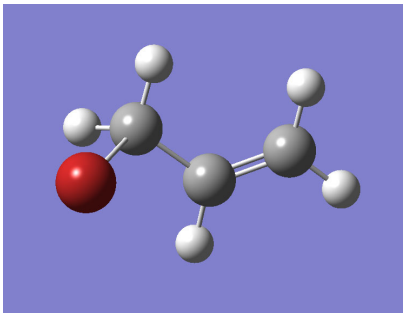
300 MHz, $CDCl_3$



13h



Allyl bromide **7**

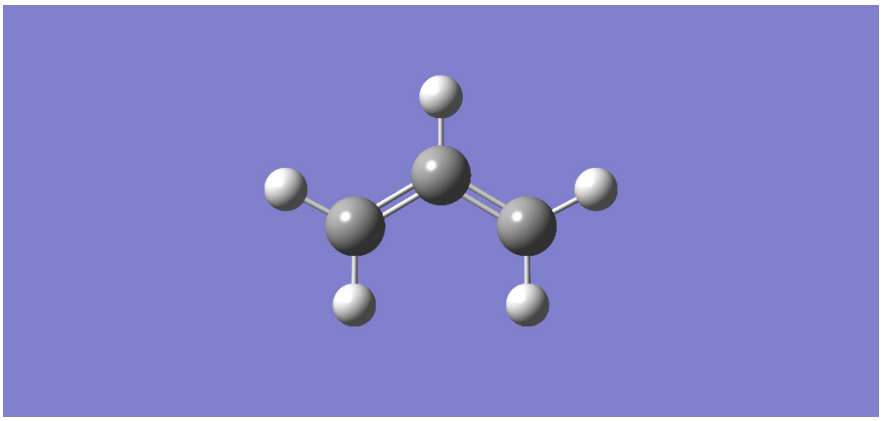


```
%chk=propene3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

propene

0 1
 Br                -4.15384620     0.07692308     0.00000000
 C                 -6.06384620     0.07692308     0.00000000
 H                 -6.42051255     0.55052859     0.89072270
 H                 -6.42051255     0.61150859    -0.85551590
 C                 -6.57717980    -1.37411828    -0.05067148
 H                 -5.88025262    -2.18553040    -0.07900646
 C                 -7.90857136    -1.62687438    -0.05949811
 H                 -8.60997214    -0.81937431    -0.08917306
 H                 -8.25957734    -2.63740676    -0.03671404
```

Allyl Cation **7+**

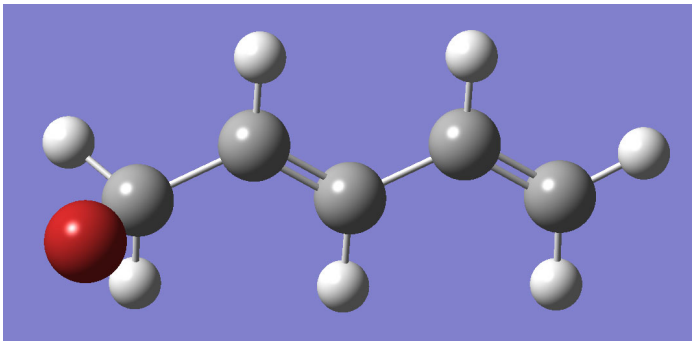


```
%chk=propeneion3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

propene

1 1
 C                  -6.06384620     0.07692308     0.00000000
 H                  -6.42051255     0.55052859     0.89072270
 H                  -6.42051255     0.61150859    -0.85551590
 C                  -6.57717980    -1.37411828    -0.05067148
 H                  -5.88025262    -2.18553040    -0.07900646
 C                  -7.90857136    -1.62687438    -0.05949811
 H                  -8.60997214    -0.81937431    -0.08917306
 H                  -8.25957734    -2.63740676    -0.03671404
```

Pentadienyl bromide **8a**

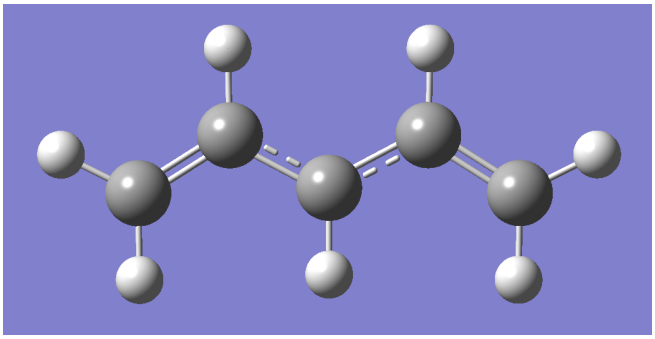


```
%chk=pentadiene3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for pentadiene

0 1
 C                   -1.84615387    0.69230768    0.00000000
 H                   -1.31299012   -0.23539724    0.00000000
 C                   -1.17087956    1.86728498    0.00000000
 H                   -1.70404331    2.79498990    0.00000000
 C                    0.36912044    1.86728498    0.00000000
 H                    0.90228419    0.93958006    0.00000000
 C                    1.05136384    3.03822946    0.00000000
 H                    0.52372137    3.96908575    0.00000000
 H                    2.12134496    3.03187216    0.00000000
 C                   -3.38615387    0.69230768    0.00000000
 H                   -3.74282021    1.19501568    0.87462780
 H                   -3.74282072    1.19840360   -0.87267157
 Br                  -4.02281996   -1.10845440   -0.00349202
```

Pentadienyl cation **8a+**

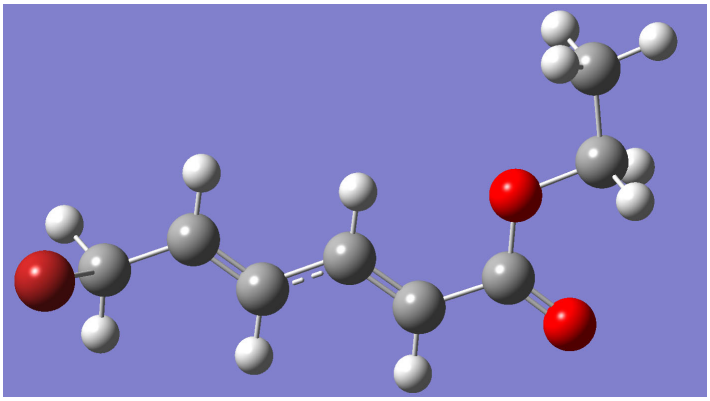


```
%chk=pentadieneion3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for pentadiene ion

1 1
 C                  -4.35233144   -0.33678756    0.00000000
 H                  -3.81916769   -1.26449248    0.00000000
 C                  -3.67705713    0.83818974    0.00000000
 H                  -4.21022088    1.76589466    0.00000000
 C                  -2.13705713    0.83818974    0.00000000
 H                  -1.60389338   -0.08951518    0.00000000
 C                  -1.45481373    2.00913422    0.00000000
 H                  -1.98245620    2.93999051    0.00000000
 H                  -0.38483262    2.00277692    0.00000000
 C                  -5.89233144   -0.33678756    0.00000000
 H                  -6.24899779    0.16930856   -0.87267166
 H                  -6.24899829    0.16592023    0.87462771
```

Pentadienyl bromide with ester **8b**

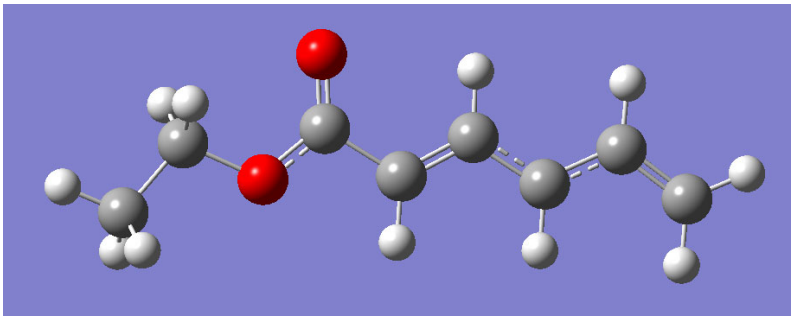


```
%chk=ethylester3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

Optimization for ethyl ester

0 1
 C                    -0.41450776      0.25906735      0.00000000
 C                    -1.95450776      0.25906735      0.00000000
 H                    -2.48767150      1.18677227      0.00000000
 C                    -2.63675116     -0.91187713      0.00000000
 H                    -2.10910869     -1.84273341      0.00000000
 C                    -4.17672398     -0.90272737      0.00000000
 H                    -4.70436645      0.02812891      0.00000000
 C                    -4.86591238     -2.06959771      0.00000000
 H                    -4.34380982     -3.00357250      0.00000000
 O                     0.21253267      1.35011770      0.00000000
 O                     0.29803819     -0.98076259      0.00000000
 C                     1.70460386     -0.72295222     -0.00261381
 H                     1.96290100     -0.16271150     -0.87686373
 H                     1.96607541     -0.16231271      0.87043600
 C                     2.47128794     -2.05853986     -0.00370136
 H                     3.52375390     -1.86563275     -0.00519748
 H                     2.21264423     -2.61897836      0.87031930
 H                     2.21016152     -2.61898132     -0.87698159
 C                    -6.40580366     -2.05129852      0.00000000
 H                    -6.75645322     -1.54286225      0.87374908
 H                    -6.75644971     -1.54252396     -0.87355355
 Br                   -7.06382257     -3.84437157     -0.00034910
```

Pentadienyl cation with ester **8a+**

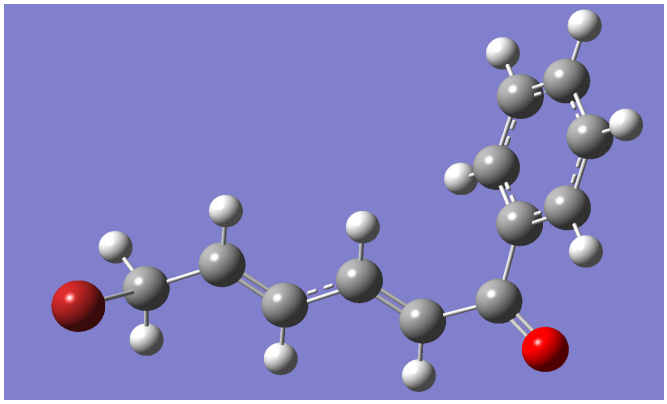


```
%chk=ethylesterion2dcm.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for ethyl ester ion (no Br)

1 1
 C                  -2.07665031   -0.71377475   -1.85499308
 H                  -3.02055188   -1.17783702   -1.65853435
 H                  -1.36637849   -1.45926666   -2.14594972
 C                  -1.58063216   -0.00071868   -0.58333392
 H                  -1.40534453    1.05472597   -0.59785424
 C                  -1.36538336   -0.70540626    0.55405362
 H                  -1.53890475   -1.76104112    0.57467801
 C                  -0.86933885    0.01561205    1.82120492
 H                  -0.69581746    1.07124692    1.80058053
 C                  -0.65183749   -0.68230884    2.96233008
 H                  -0.82358650   -1.73809665    2.98905783
 C                  -0.15578412    0.04664626    4.22492879
 O                   0.04829000    1.28815179    4.20067296
 O                   0.07372218   -0.68979624    5.42903813
 C                   0.52679830    0.19927053    6.45333413
 H                  -0.21657108    0.94835583    6.62989340
 H                   1.43760273    0.66692810    6.14247776
 C                   0.77374500   -0.59447336    7.74970907
 H                   1.11276075    0.07077228    8.51614013
 H                  -0.13705969   -1.06213038    8.06056550
 H                   1.51711376   -1.34355914    7.57314922
```

Pentadienyl bromide with phenyl ketone **8c**

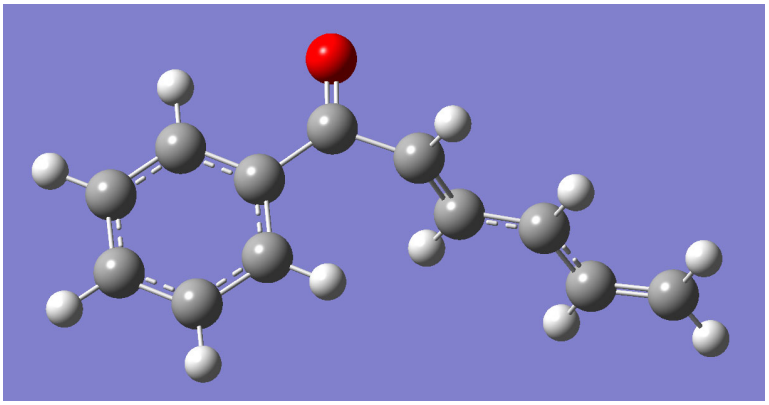


```
%chk=phenylketone3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for phenyl ketone

0 1
 Br                -5.61538468   -0.64102563    0.00000000
 C                 -7.52538468   -0.64102563    0.00000000
 H                 -7.88205103   -0.10644012   -0.85551590
 H                 -7.88205153   -1.64921670   -0.03520681
 C                 -8.03871755    0.04061221    1.28197473
 H                 -7.34178996    0.42177894    1.99884561
 C                 -9.37010899    0.15934678    1.50528168
 H                -10.07184814   -0.21986927    0.79207950
 C                 -9.87480633    0.84240444    2.78992670
 H                 -9.17306717    1.22162049    3.50312888
 C                -11.20467161    0.96485059    3.02021412
 H                -11.91119756    0.58759861    2.31070581
 C                -11.70071560    1.64930395    4.30748408
 O                -12.93412979    1.76644640    4.52779671
 C                -10.68384649    2.19226475    5.32864557
 C                 -9.31585579    2.06363210    5.08672303
 C                -11.13041427    2.81272736    6.49532954
 C                 -8.39471245    2.55477838    6.01165114
 H                 -8.96411222    1.57373472    4.16720206
 C                -10.20911971    3.30495673    7.42017356
 H                -12.20856866    2.91435312    6.68607633
 C                 -8.84144221    3.17596780    7.17860134
 H                 -7.31643193    2.45286562    5.82133187
 H                -10.56151092    3.79448432    8.33976989
 H                 -8.11496624    3.56319355    7.90770025
```

Pentadienyl cation with phenyl ketone **8c+**



```
%chk=phenylketoneion3.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for phenyl ketone ion

1 1
 C                  -7.52538468   -0.64102563    0.00000000
 H                  -7.88205103   -0.10644012   -0.85551590
 H                  -7.88205153   -1.64921670   -0.03520681
 C                  -8.03871755    0.04061221    1.28197473
 H                  -7.34178996    0.42177894    1.99884561
 C                  -9.37010899    0.15934678    1.50528168
 H                 -10.07184814   -0.21986927    0.79207950
 C                  -9.87480633    0.84240444    2.78992670
 H                  -9.17306717    1.22162049    3.50312888
 C                 -11.20467161    0.96485059    3.02021412
 H                 -11.91119756    0.58759861    2.31070581
 C                 -11.70071560    1.64930395    4.30748408
 O                 -12.93412979    1.76644640    4.52779671
 C                 -10.68384649    2.19226475    5.32864557
 C                  -9.31585579    2.06363210    5.08672303
 C                 -11.13041427    2.81272736    6.49532954
 C                  -8.39471245    2.55477838    6.01165114
 H                  -8.96411222    1.57373472    4.16720206
 C                 -10.20911971    3.30495673    7.42017356
 H                 -12.20856866    2.91435312    6.68607633
 C                  -8.84144221    3.17596780    7.17860134
 H                  -7.31643193    2.45286562    5.82133187
 H                 -10.56151092    3.79448432    8.33976989
 H                  -8.11496624    3.56319355    7.90770025
```

Et 4-bromocrotonate **9**

```
%chk=butene-ethylester.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for butene with ethyl ester

0 1
 Br                -4.15384620    0.07692308    0.00000000
 C                 -6.06384620    0.07692308    0.00000000
 H                 -6.42051255    0.55052859    0.89072270
 H                 -6.42051255    0.61150859   -0.85551590
 C                 -6.57717980   -1.37411828   -0.05067148
 H                 -5.88025262   -2.18553040   -0.07900646
 C                 -7.90857136   -1.62687438   -0.05949811
 H                 -8.60997214   -0.81937431   -0.08917306
 C                 -8.41375754   -3.08128547   -0.02670608
 O                 -9.81702773   -3.35633174   -0.03577927
 O                 -7.58885778   -4.03096591    0.00819387
 C                -10.02631220   -4.77085091   -0.02043243
 H                 -9.59208165   -5.18606084    0.86497400
 H                 -9.56710181   -5.20871108   -0.88200327
 C                -11.53758231   -5.06639550   -0.03821057
 H                -11.69419467   -6.12479801   -0.02569323
 H                -11.99695675   -4.62766303    0.82282889
 H                -11.97163339   -4.65207125   -0.92411975
```

Gamma carbonyl cation with ester **9+**

```
%chk=butene-ethylesterion.chk
%mem=1024MB
%nprocs=8
# opt b3lyp/6-311++g(d,p)  scrf=(solvent=dichloromethane)

optimization for butene with ethyl ester

1 1
 C                  -6.06384620    0.07692308    0.00000000
 H                  -6.42051255    0.55052859    0.89072270
 H                  -6.42051255    0.61150859   -0.85551590
 C                  -6.57717980   -1.37411828   -0.05067148
 H                  -5.88025262   -2.18553040   -0.07900646
 C                  -7.90857136   -1.62687438   -0.05949811
 H                  -8.60997214   -0.81937431   -0.08917306
 C                  -8.41375754   -3.08128547   -0.02670608
 O                  -9.81702773   -3.35633174   -0.03577927
 O                  -7.58885778   -4.03096591    0.00819387
 C                 -10.02631220   -4.77085091   -0.02043243
 H                  -9.59208165   -5.18606084    0.86497400
 H                  -9.56710181   -5.20871108   -0.88200327
 C                 -11.53758231   -5.06639550   -0.03821057
 H                 -11.69419467   -6.12479801   -0.02569323
 H                 -11.99695675   -4.62766303    0.82282889
 H                 -11.97163339   -4.65207125   -0.92411975
```