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


**ELECTRONIC SUPPORTING INFORMATION**

# Photochemical Generation and Trapping of 3-Oxacyclohexyne

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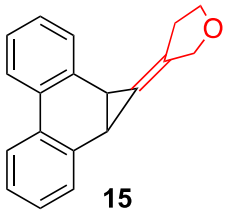
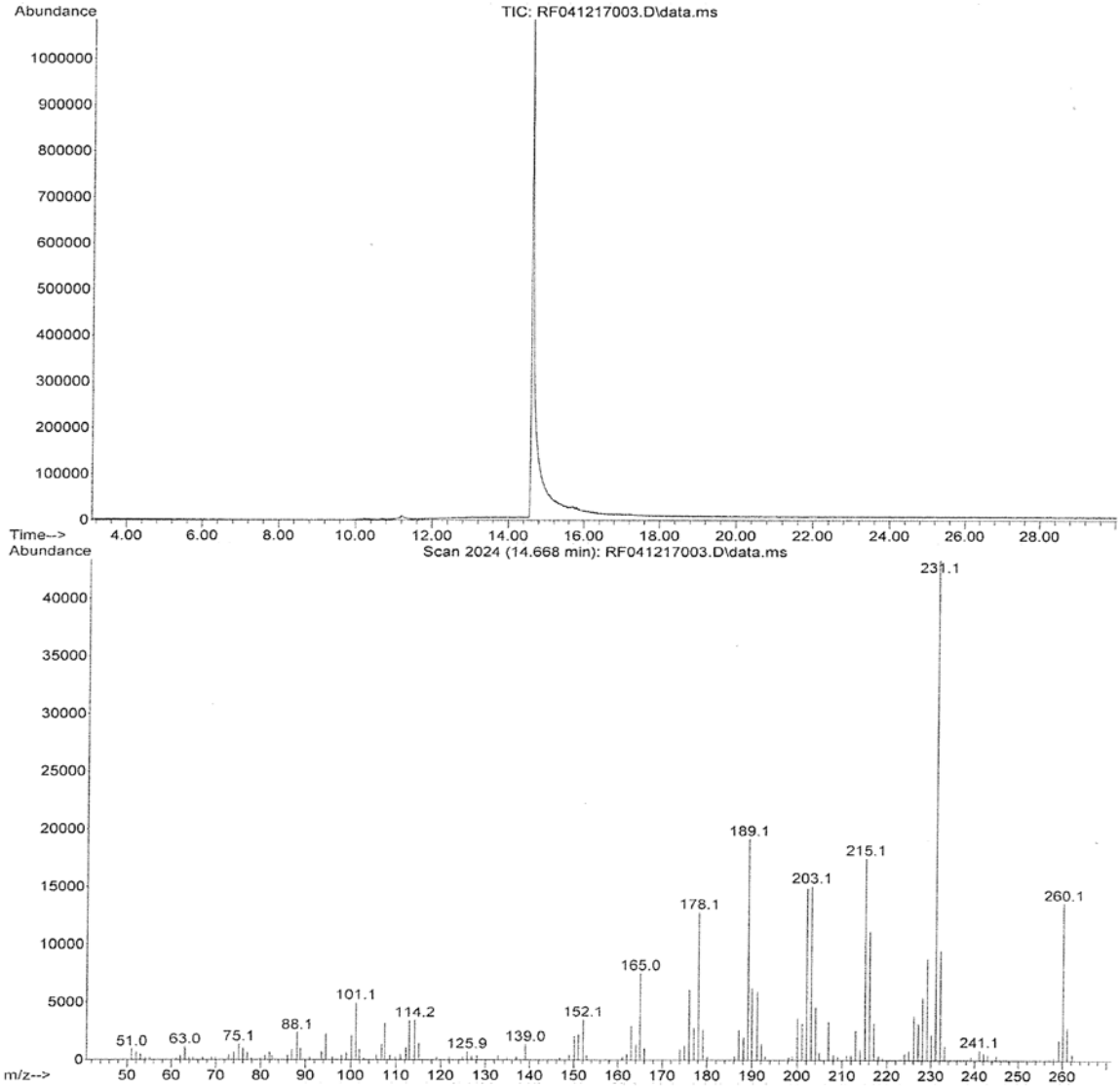

O

**15**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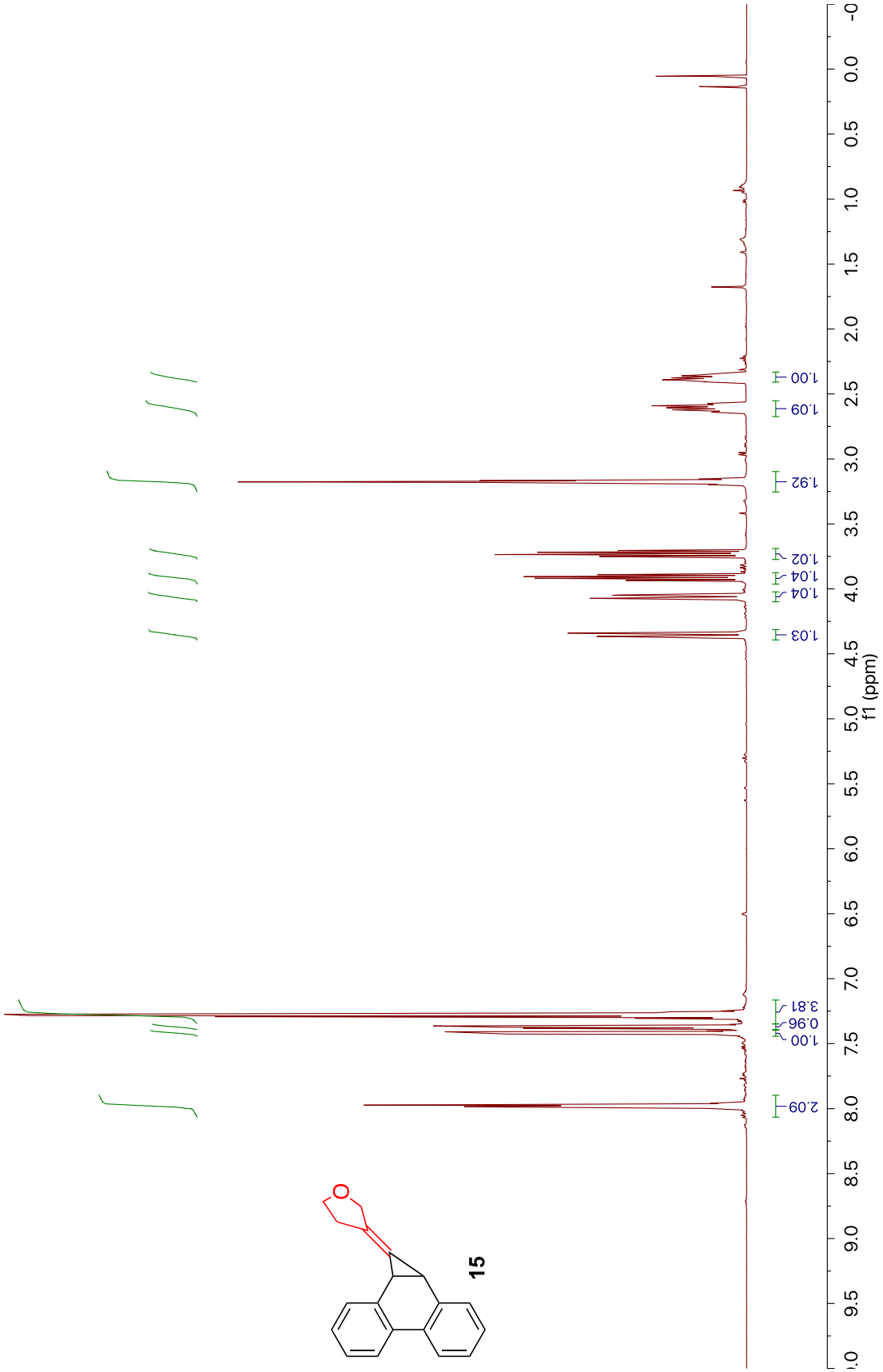
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1.02
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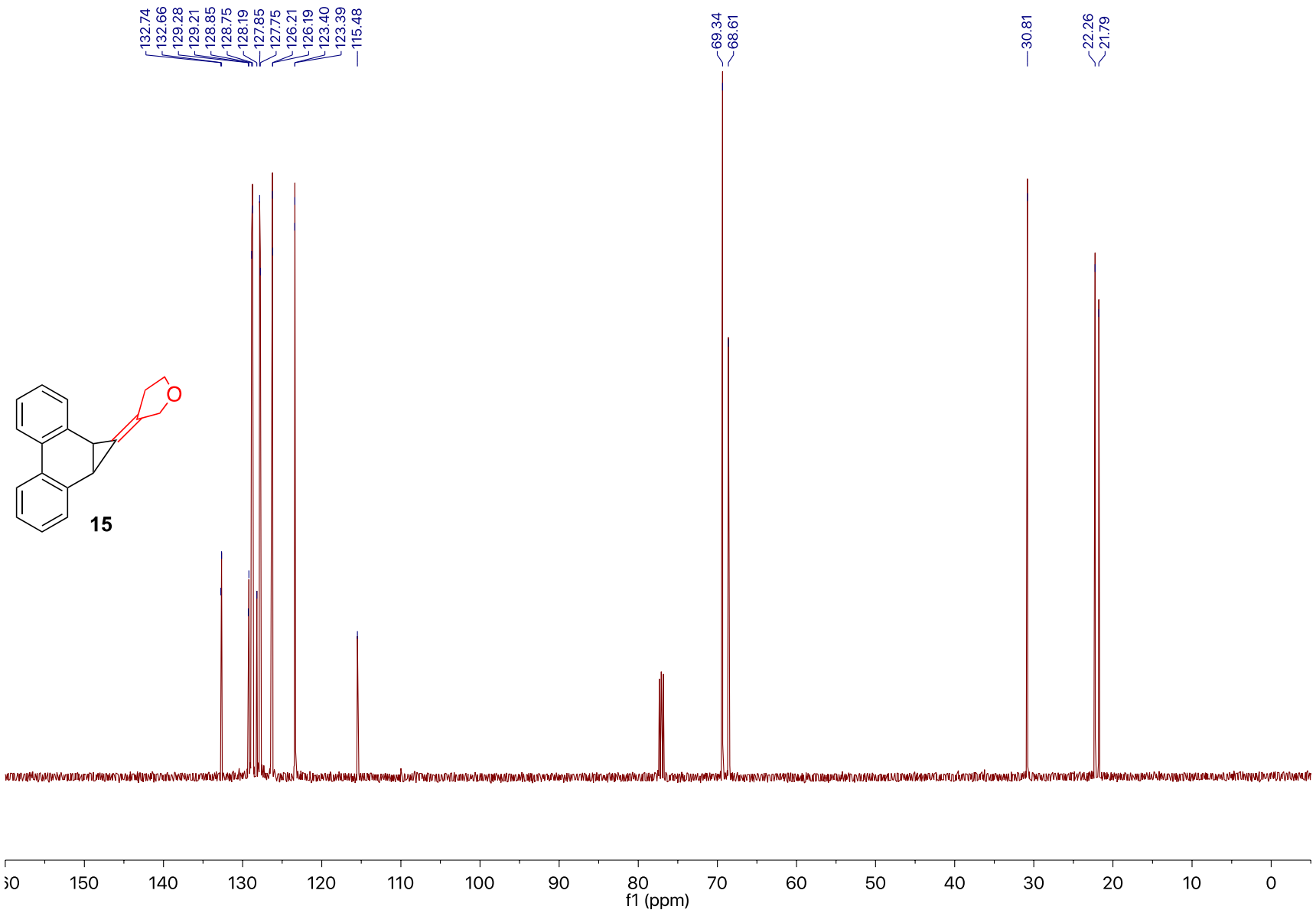
1.00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22.26
21.79
O
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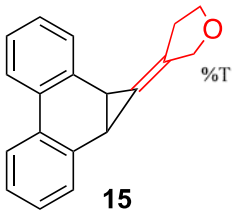
f1 (ppm)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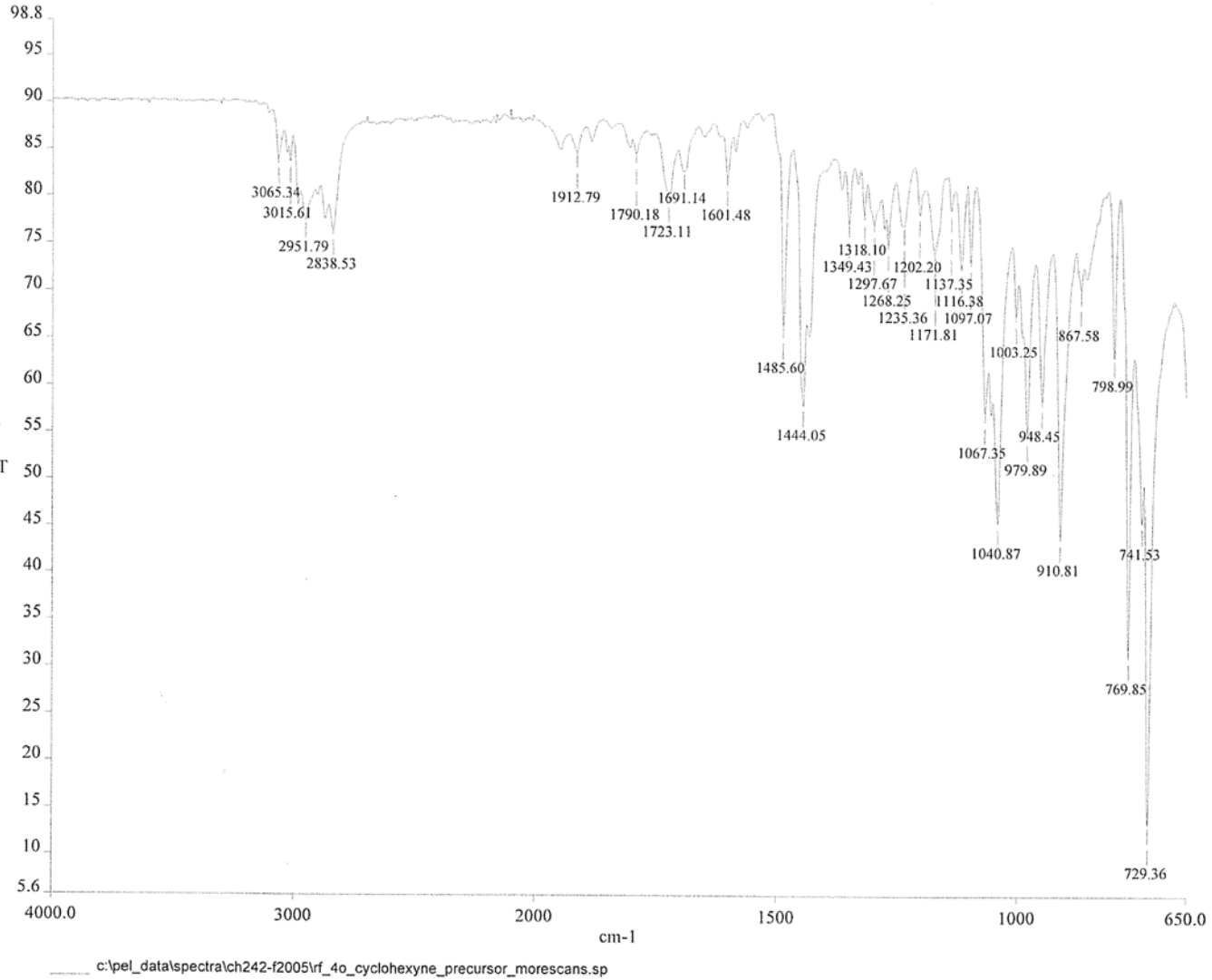
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5.6
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2838.53
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1790.18
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1691.14
1601.48
1485.60
1444.05
1318.10
1349.43
1297.67
1268.25
1235.36
1171.81
1202.20
1137.35
1116.38
1097.07
1067.35
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1003.25
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867.58
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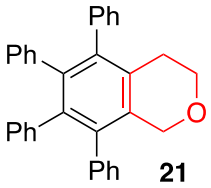
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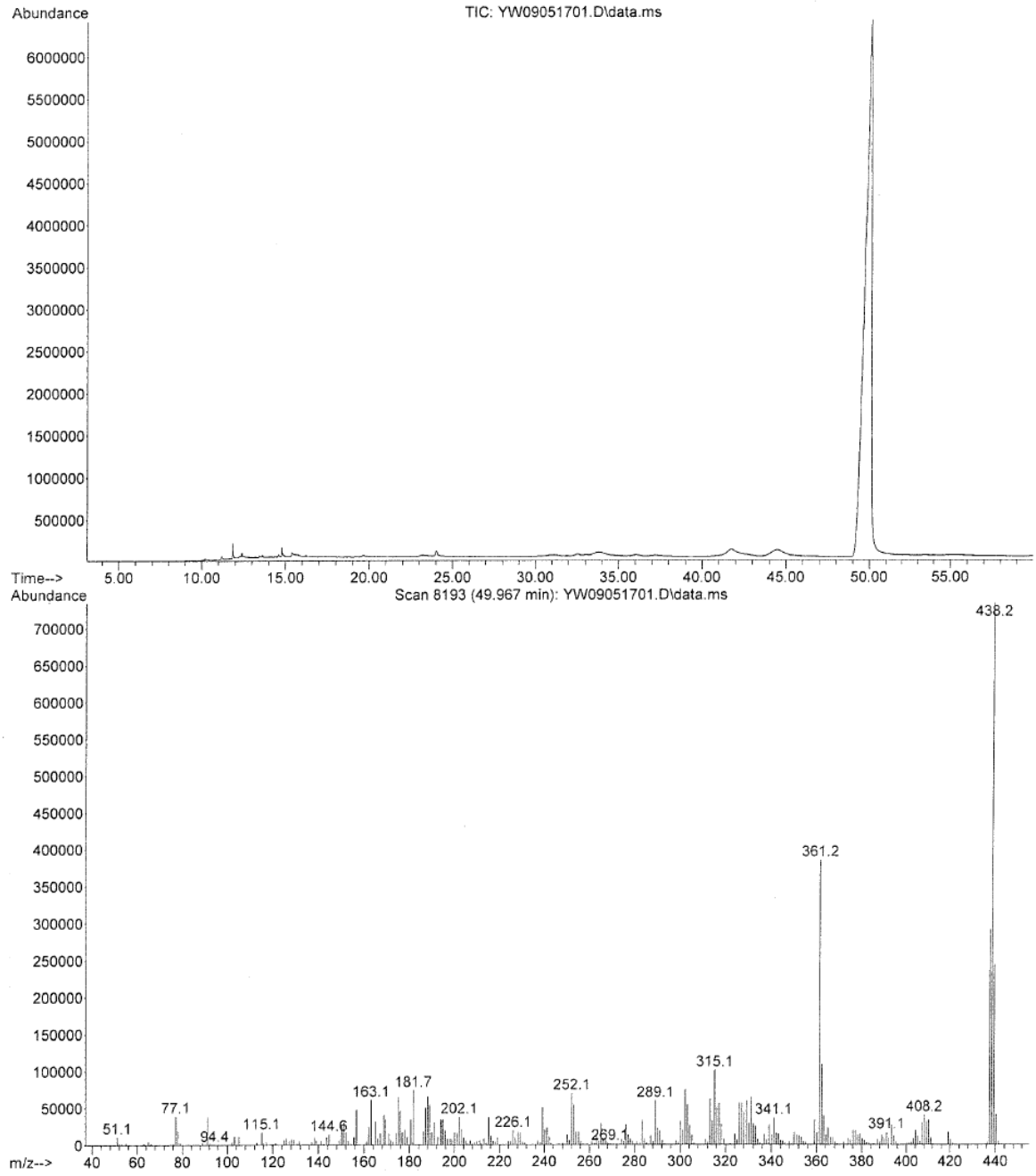
Ph
Ph
Ph
O

**21**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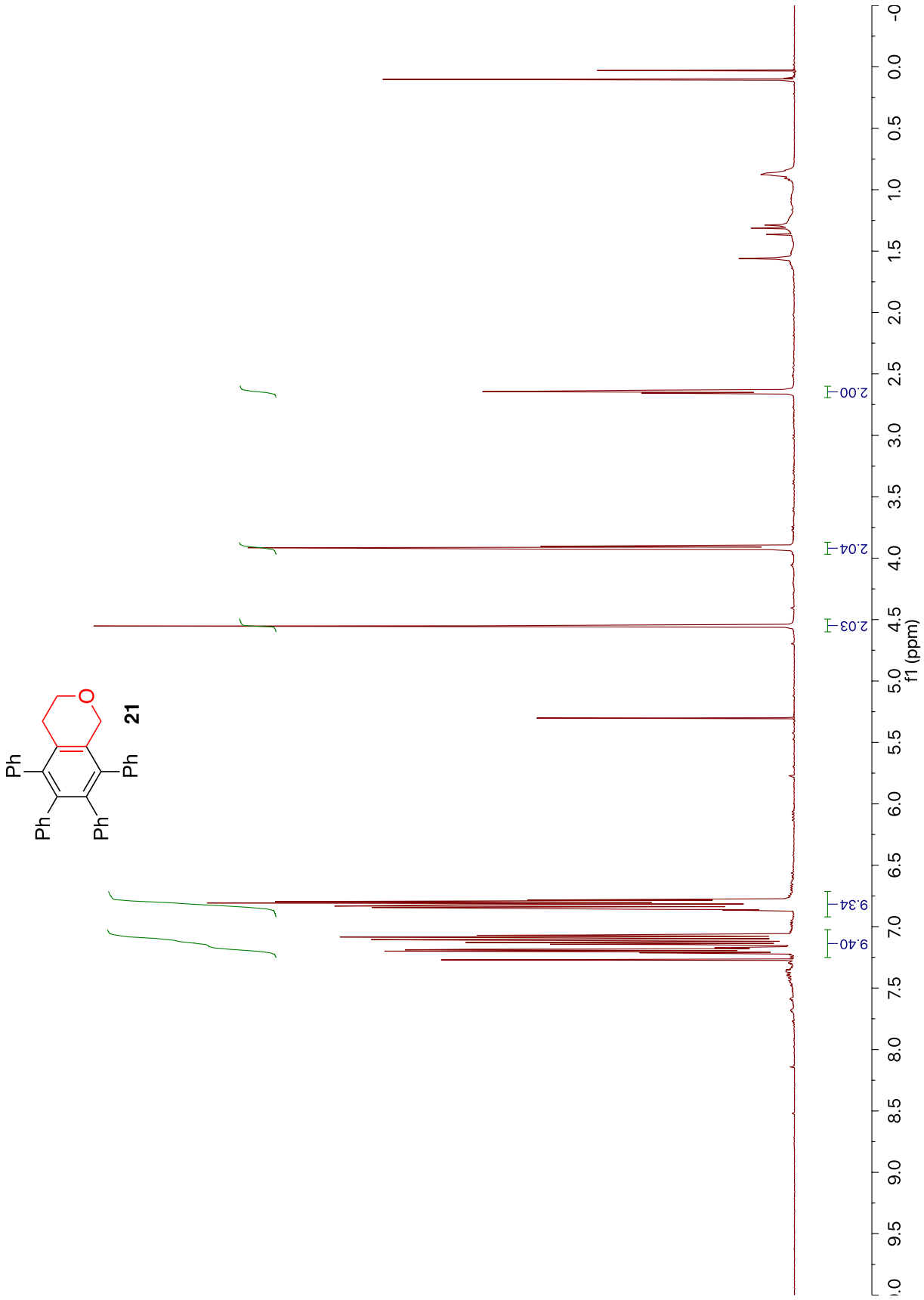
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Ph
Ph
Ph
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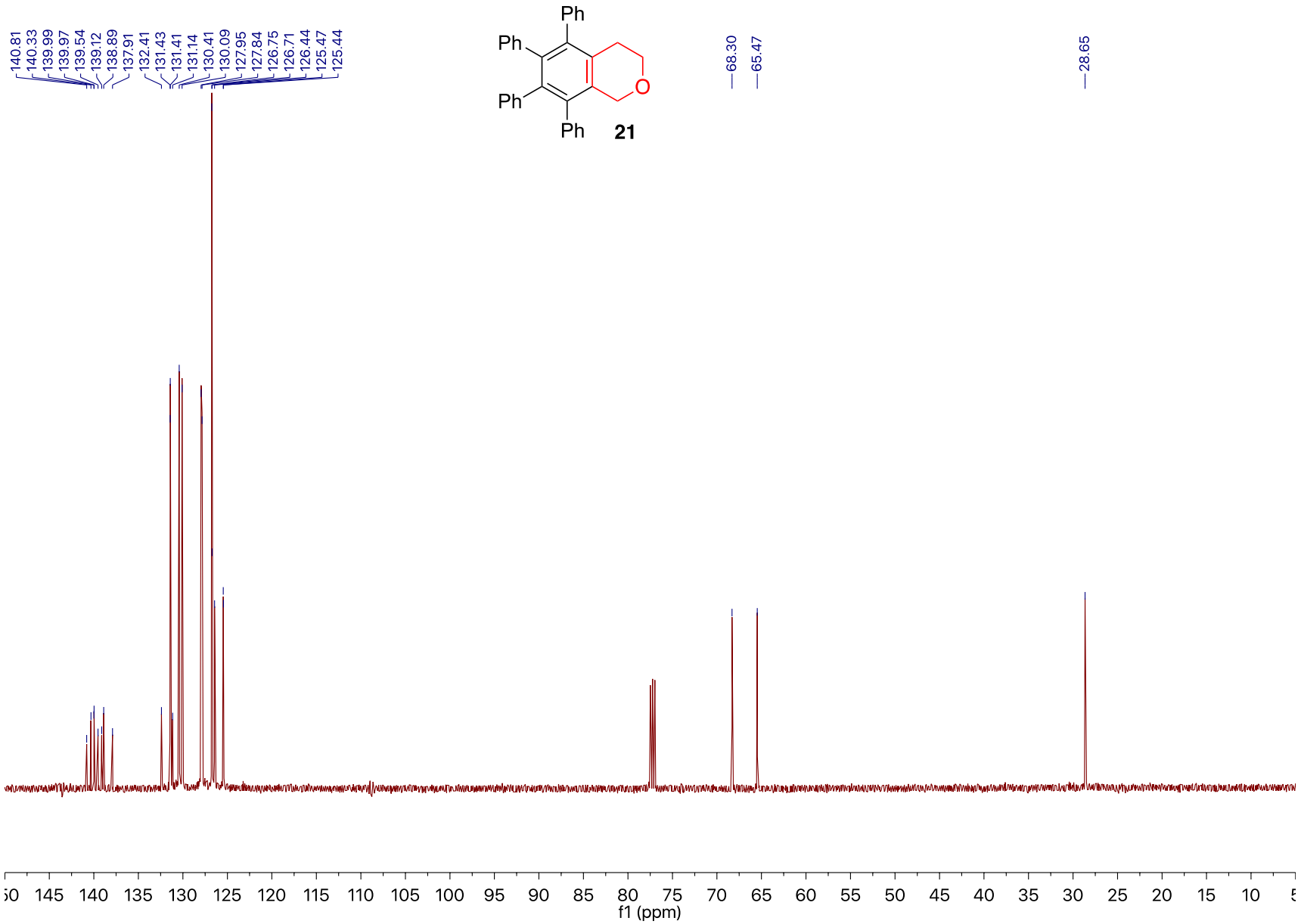
f1 (ppm)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131.14
130.41
130.09
127.95
127.84
126.75
126.71
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125.47
125.44
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Ph
Ph
Ph
O
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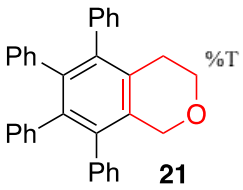
f1 (ppm)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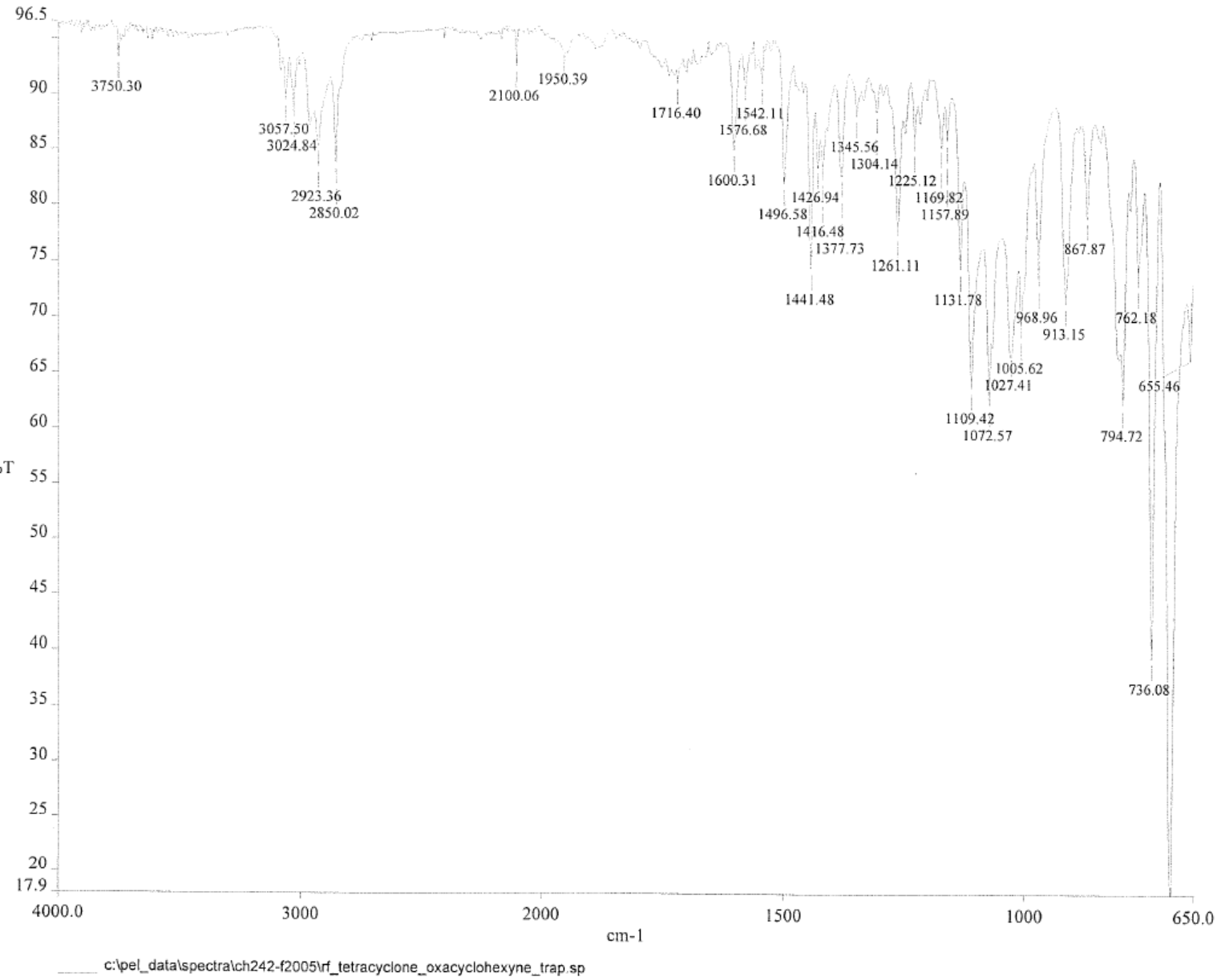
Ph
Ph
Ph
O

**21**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3024.84
2923.36
2850.02
2100.06
1950.39
1716.40
1600.31
1576.68
1542.11
1496.58
1441.48
1426.94
1416.48
1377.73
1345.56
1304.14
1261.11
1225.12
1169.82
1157.89
1131.78
1109.42
1072.57
1027.41
1005.62
968.96
913.15
867.87
794.72
762.18
736.08
655.46
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cm-1
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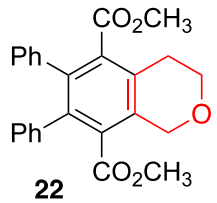
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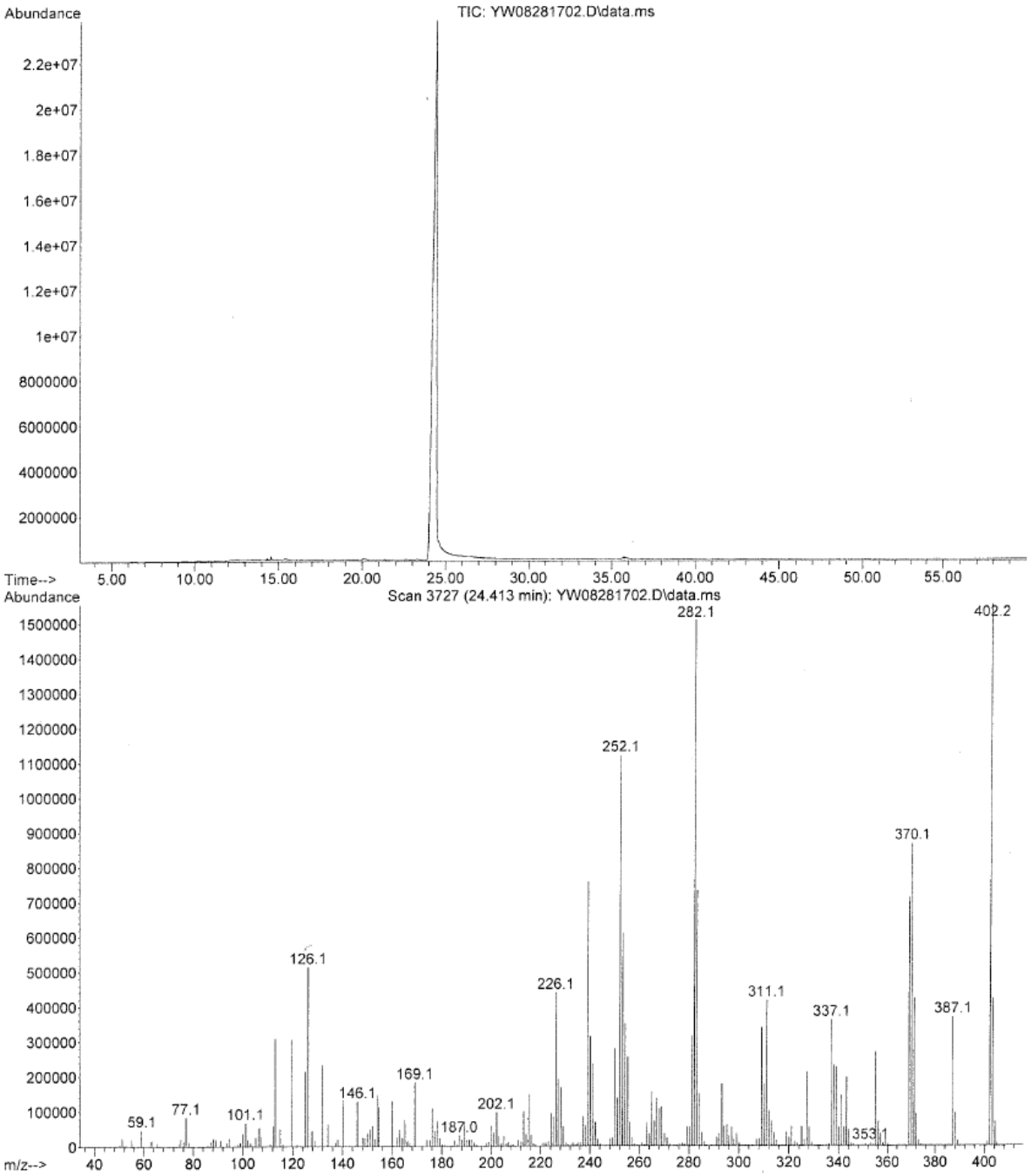
Ph
Ph
O
CO2CH3

**22**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202.1
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77.1
101.1
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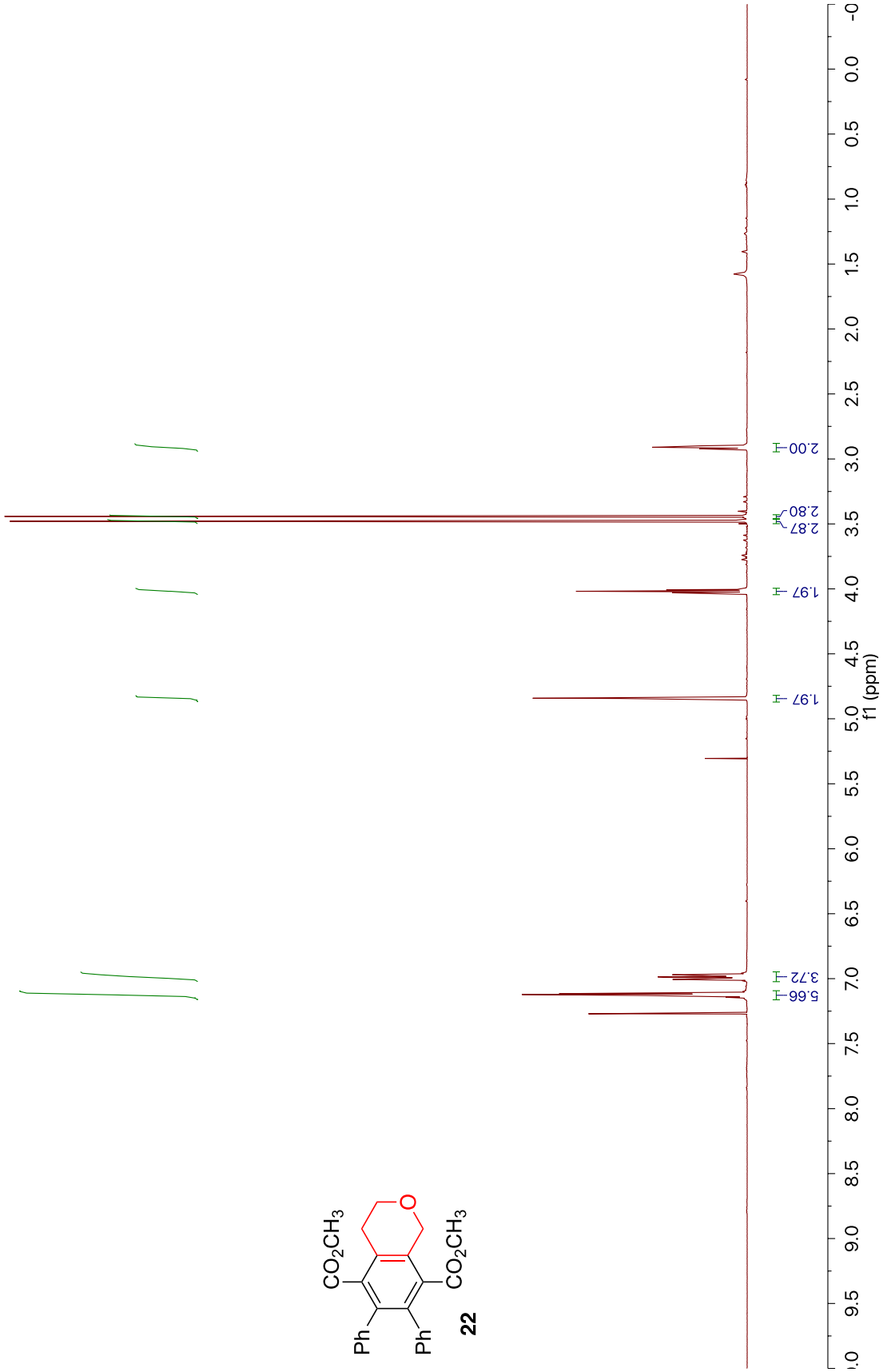


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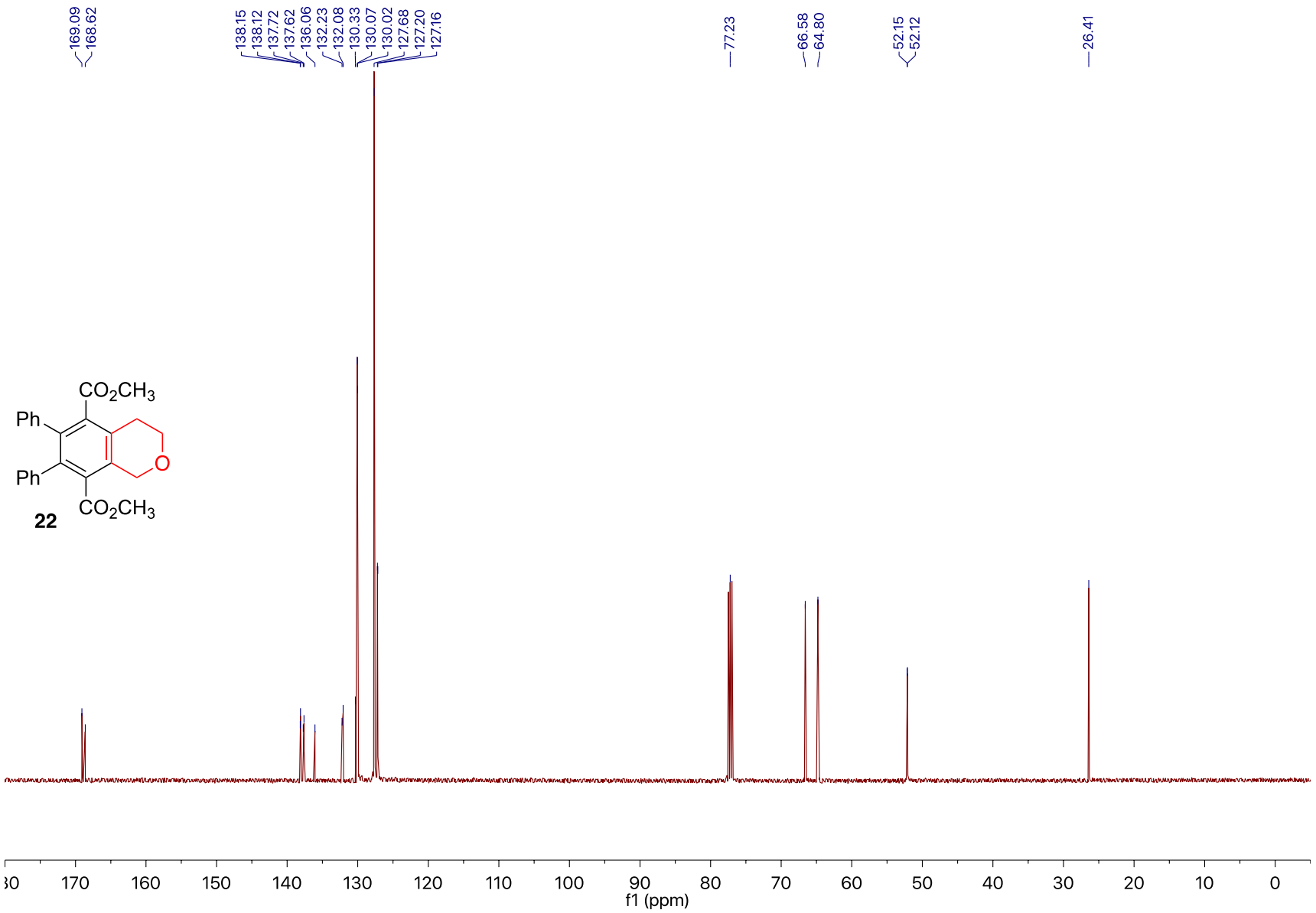
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137.62
136.06
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132.08
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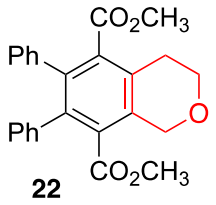
127.68
127.20
127.16
77.23
66.58
64.80
52.15
52.12
26.41
CO2CH3
Ph
Ph
O
CO2CH3
22
f1 (ppm)


CO2CH3
Ph
Ph
O
CO2CH3

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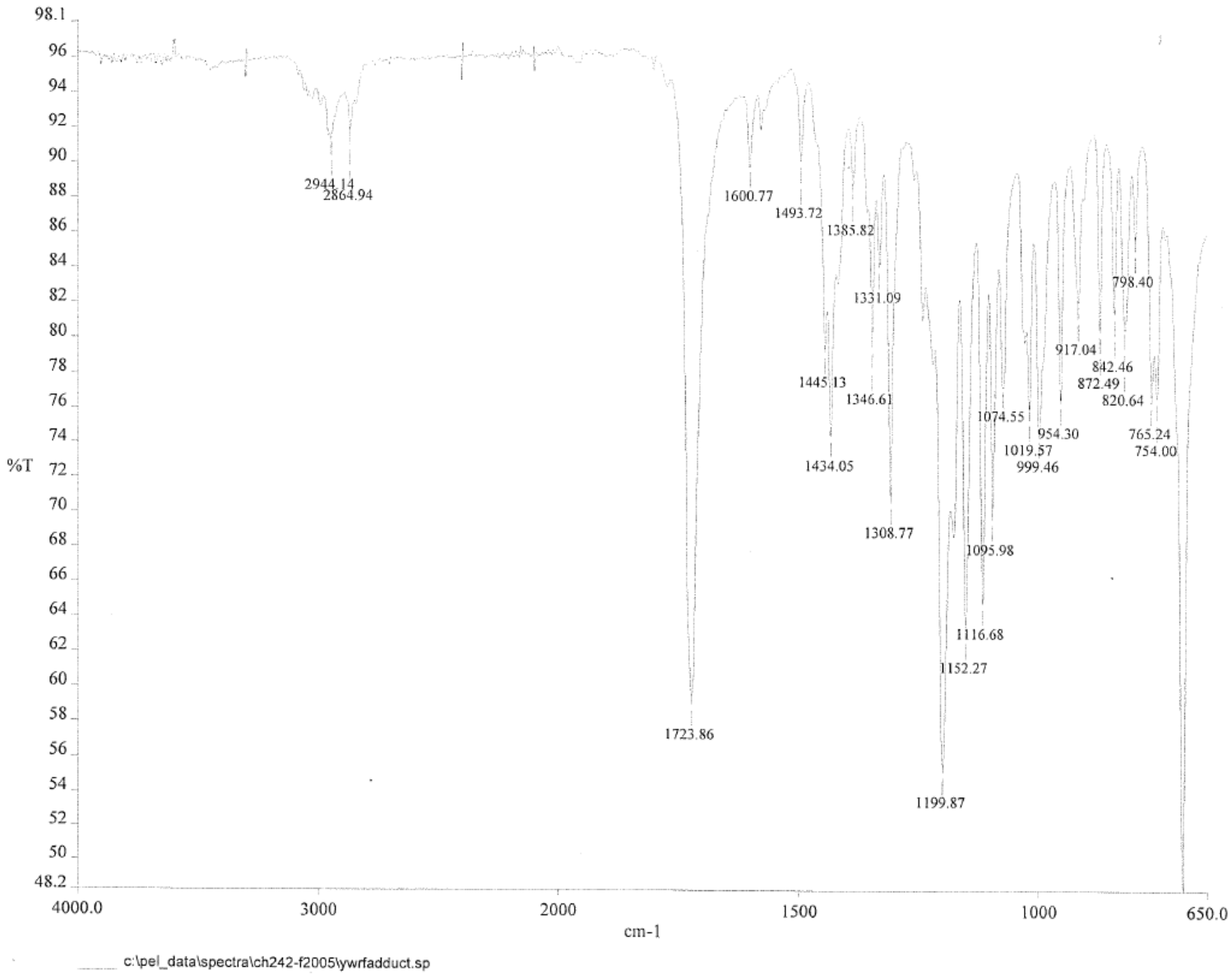
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60
58
56
54
52
50
48.2
%T
2944.14
2864.94
1600.77
1493.72
1385.82
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1308.77
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cm-1
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## Cartesian coordinates and energies for (R/U)B3LYP/6-31+G* optimized structures

Singlet carbene **16**

Charge = 0 Multiplicity = 1
C,0,-0.0170079807,1.2020444166,0.0732488676
C,0,0.0026475134,-1.2660274367,0.138527328
C,0,-0.320733033,-0.6443857086,-1.2377960299
H,0,-1.0128196739,1.6685944378,0.0818085622
H,0,0.7430239029,1.9512046498,0.3028296055
H,0,1.0017181333,-1.7143580172,0.1386415441
H,0,-0.7239711584,-2.0209839578,0.4508031237
H,0,0.1177625933,-1.1896148368,-2.0770726937
H,0,-1.4097666362,-0.5661373312,-1.3813646128
C,0,-0.0029653008,-0.0122843043,2.3287156835
C,0,-0.0057380751,-0.0128911958,1.0259928322
O,0,0.2701117152,0.6491072842,-1.2030702104

Zero-point correction= 0.096909 (Hartree/Particle)
Thermal correction to Energy= 0.102596
Thermal correction to Enthalpy= 0.103541
Thermal correction to Gibbs Free Energy= 0.067476
Sum of electronic and zero-point Energies= -269.120236
Sum of electronic and thermal Energies= -269.114548
Sum of electronic and thermal Enthalpies= -269.113604
Sum of electronic and thermal Free Energies= -269.149668

Triplet carbene **16**

Charge = 0 Multiplicity = 3
C,0,0.0118674271,1.174063384,0.0732055731
C,0,0.0126793431,-1.2407120536,0.1150771175
C,0,-0.34424675,-0.6642446293,-1.2646278315
H,0,-0.9423982952,1.7223362132,0.1801824832
H,0,0.8225864619,1.8796150455,0.2956121757
H,0,1.0329341526,-1.659667554,0.1184835604
H,0,-0.6590966458,-2.0225705516,0.4831149353
H,0,0.1172918078,-1.1852885171,-2.1062556975
H,0,-1.4356220876,-0.6434660883,-1.4104748395
C,0,-0.1655626981,0.0309394505,2.4013579096
C,0,0.0145730242,-0.0174870102,1.001992993
O,0,0.17725626,0.6707503108,-1.2464043793

Zero-point correction= 0.094522 (Hartree/Particle)
Thermal correction to Energy= 0.100171
Thermal correction to Enthalpy= 0.101115
Thermal correction to Gibbs Free Energy= 0.064464
Sum of electronic and zero-point Energies= -269.055512
Sum of electronic and thermal Energies= -269.049862
Sum of electronic and thermal Enthalpies= -269.048918

Sum of electronic and thermal Free Energies= -269.085570
S**2 before annihilation 2.0128, after 2.0000

3-Oxacyclohexyne **7**

Charge = 0 Multiplicity = 1
C,0,0.1363959973,-1.5298632392,0.0962866696
C,0,-0.4192438148,1.4947695568,0.120270603
C,0,0.9616270535,0.7459940065,-0.1661541669
H,0,0.7970260541,-1.8864127324,0.8985547149
H,0,-0.0807520582,-2.3555452209,-0.5841753533
H,0,-0.8607392233,1.8939360142,-0.8002944822
H,0,-0.2314246475,2.3278154134,0.8073876196
H,0,1.53124105,1.3176675348,-0.9043282248
H,0,1.5194204218,0.705305311,0.7813992244
C,0,-1.174820917,0.3698102338,0.6620462501
C,0,-1.0688917655,-0.8529103869,0.6663743528
O,0,0.8249648395,-0.5473284812,-0.7182401973

Zero-point correction= 0.097938 (Hartree/Particle)
Thermal correction to Energy= 0.103260
Thermal correction to Enthalpy= 0.104204
Thermal correction to Gibbs Free Energy= 0.069621
Sum of electronic and zero-point Energies= -269.135180
Sum of electronic and thermal Energies= -269.129858
Sum of electronic and thermal Enthalpies= -269.128914
Sum of electronic and thermal Free Energies= -269.163498

TS for **16** (singlet) to **7** by 1,2-shift of bond ***a***

Charge = 0 Multiplicity = 1
C,0,-0.1352158303,-1.2794242798,0.1165558497
C,0,-0.0571296662,1.393199524,-0.1179942634
C,0,1.2431495826,0.5831495621,0.1751432172
H,0,-0.092645417,-1.4882777736,1.1879782994
H,0,-0.3545123127,-2.1580444023,-0.4808010929
H,0,-0.0135943558,1.8503907762,-1.1135171666
H,0,-0.1981616771,2.1864501609,0.6251476313
H,0,2.1284803538,1.007432801,-0.301713943
H,0,1.405907831,0.5170087671,1.2606257783
C,0,-1.9336988103,-0.5809865143,-0.0667707612
C,0,-1.097596782,0.3636463082,-0.0544596437
O,0,1.0398200841,-0.7113069295,-0.3710669051

Zero-point correction= 0.096473 (Hartree/Particle)
Thermal correction to Energy= 0.101686
Thermal correction to Enthalpy= 0.102630
Thermal correction to Gibbs Free Energy= 0.067917
Sum of electronic and zero-point Energies= -269.104030
Sum of electronic and thermal Energies= -269.098818
Sum of electronic and thermal Enthalpies= -269.097873
Sum of electronic and thermal Free Energies= -269.132586

****** 1 imaginary frequencies (negative Signs) ******
Frequencies -- -361.0977

TS for **16** (singlet) to **7** by 1,2-shift of bond ***b***

Charge = 0 Multiplicity = 1
C,0,-0.0276842229,-1.3886630199,0.0985364045
C,0,-0.1577247842,1.3329774684,-0.1604108494
C,0,1.1425834198,0.6027015967,0.2262490352
H,0,0.0948850349,-1.8475590727,1.0913657018
H,0,-0.2337178356,-2.1725156541,-0.636258863
H,0,-0.1624059831,1.6206328198,-1.2116772241
H,0,-0.272370415,2.2081914353,0.4807483319
H,0,2.0032349052,1.1283235627,-0.1989226376
H,0,1.2476684659,0.5747473076,1.3218772676
C,0,-1.8174454761,0.6725325152,0.0445641813
C,0,-1.0574376844,-0.3283770621,0.1061933181
O,0,1.1752175753,-0.7197538968,-0.3031376664

Zero-point correction= 0.096182 (Hartree/Particle)
Thermal correction to Energy= 0.101421
Thermal correction to Enthalpy= 0.102365
Thermal correction to Gibbs Free Energy= 0.067590
Sum of electronic and zero-point Energies= -269.097952
Sum of electronic and thermal Energies= -269.092712
Sum of electronic and thermal Enthalpies= -269.091768
Sum of electronic and thermal Free Energies= -269.126543

****** 1 imaginary frequencies (negative Signs) ******
Frequencies -- -410.1475

## Summary output of (R/U)CCSD(T)/cc-pVTZ//B3LYP/6-31+G* calculations

Singlet carbene **16**

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C5H6O1\DMTHAMAT\02-May-2017\0\
\# ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\SInglet carbene\\0,1\C,0
,-0.063381,-1.22231,0.086606\C,0,-0.064202,1.237676,-0.124329\C,0,1.30
2838,0.604489,0.215606\H,0,-0.059705,-1.609875,1.115763\H,0,-0.33121,-
2.021351,-0.607223\H,0,-0.077106,1.607075,-1.155115\H,0,-0.338548,2.05
5147,0.547926\H,0,2.14512,1.090279,-0.2829\H,0,1.471047,0.606848,1.303
92\C,0,-2.285799,0.050245,0.028447\C,0,-0.983837,0.014419,0.001878\O,0
,1.219586,-0.729404,-0.271452\\Version=EM64L-G09RevA.02\State=1-A\HF=-
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268.6867461\MP4SDQ=-268.6970787\CCSD=-268.6960371\CCSD(T)=-268.7443365
\RMSD=8.122e-09\PG=C01 [X(C5H6O1)]\\@

T1 Diagnostic = 0.01493500

3-Oxacyclohexyne **7**

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C5H6O1\DMTHAMAT\03-May-2017\0\
\# ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\Oxacyclohexyne Far Bond
shift\\0,1\C,0,-1.511649,0.031204,0.072699\C,0,1.549633,0.255874,-0.11
649\C,0,0.673675,-1.028711,0.246898\H,0,-1.901363,-0.156433,1.082704\H
,0,-2.334617,-0.009805,-0.643523\H,0,1.958932,0.191672,-1.131401\H,0,2
.38272,0.325213,0.592403\H,0,1.170782,-1.921589,-0.142751\H,0,0.611817
,-1.088268,1.343836\C,0,0.512284,1.275133,0.005864\C,0,-0.714353,1.295
831,0.040774\O,0,-0.618227,-1.039597,-0.324967\\Version=EM64L-G09RevA.
02\State=1-A\HF=-267.6307753\MP2=-268.6857351\MP3=-268.7031533\MP4D=-2
68.7300084\MP4DQ=-268.6996778\MP4SDQ=-268.7120094\CCSD=-268.7103038\CC
SD(T)=-268.7648722\RMSD=3.811e-09\PG=C01 [X(C5H6O1)]\\@

T1 Diagnostic = 0.01702020

TS for **16** (singlet) to **7** by 1,2-shift of bond ***a***

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C5H6O1\DMTHAMAT\02-May-2017\0\
\# ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\TS for Near Bond shift\\
0,1\C,0,-0.732199,-1.031932,0.144721\C,0,0.670304,1.245756,-0.076981\C
,0,1.392887,-0.108193,0.201465\H,0,-0.794866,-1.243137,1.214694\H,0,-1
.364028,-1.67825,-0.455252\H,0,0.932025,1.628367,-1.070508\H,0,0.94804
2,1.997002,0.671274\H,0,2.369586,-0.179202,-0.280444\H,0,1.505714,-0.2
55986,1.285239\C,0,-1.941566,0.473433,-0.020424\C,0,-0.745183,0.873572
,-0.010163\O,0,0.56726,-1.123075,-0.349589\\Version=EM64L-G09RevA.02\S
tate=1-A\HF=-267.612566\MP2=-268.6470272\MP3=-268.6729353\MP4D=-268.69
76876\MP4DQ=-268.6687433\MP4SDQ=-268.6794734\CCSD=-268.6775306\CCSD(T)

=-268.7301465\RMSD=3.257e-09\PG=C01 [X(C5H6O1)]\\@

T1 Diagnostic = 0.01357317

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TS for **16** (singlet) to **7** by 1,2-shift of bond ***b***

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1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C5H6O1\DMTHAMAT\01-May-2017\0\
\# ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\TS for Far Bond shift\\0
,1\C,0,0.881993,-1.107277,0.067354\C,0,-0.974749,0.891945,-0.149236\C,
0,0.487945,1.164861,0.250333\H,0,1.268005,-1.403098,1.054675\H,0,1.234
212,-1.820089,-0.684071\H,0,-1.159905,1.134701,-1.195522\H,0,-1.630365
,1.469697,0.503909\H,0,0.806913,2.132427,-0.149476\H,0,0.581747,1.1840
06,1.347174\C,0,-1.815566,-0.689078,0.012836\C,0,-0.589047,-0.9635,0.0
72617\O,0,1.369492,0.190081,-0.300014\\Version=EM64L-G09RevA.02\State=
1-A\HF=-267.6074946\MP2=-268.6406776\MP3=-268.6671741\MP4D=-268.691725
9\MP4DQ=-268.6632251\MP4SDQ=-268.6737313\CCSD=-268.6720446\CCSD(T)=-26
8.7240053\RMSD=5.110e-09\PG=C01 [X(C5H6O1)]\\@

T1 Diagnostic = 0.01404773