Supporting Information

On the Regioselectivity of the intramoleclar [2+2]-Photocycloaddition of Alk-3-enyl Tetronates

Roland Weixler, Jörg P. Hehn, Thorsten Bach*

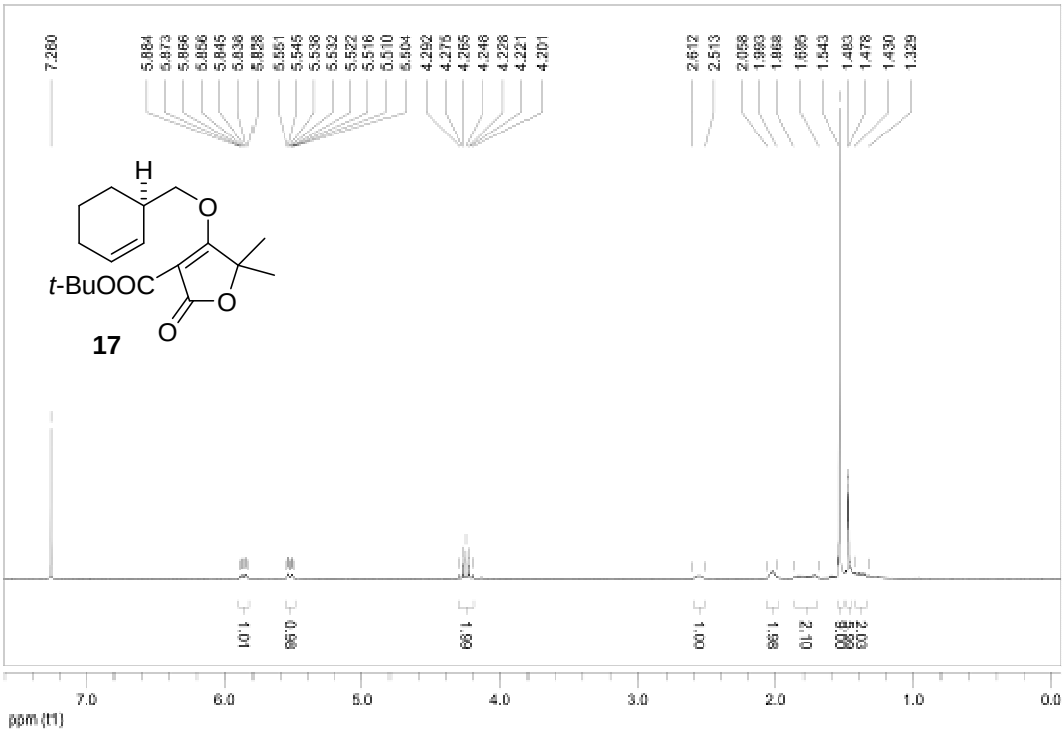
Lehrstuhl für Organische Chemie I, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

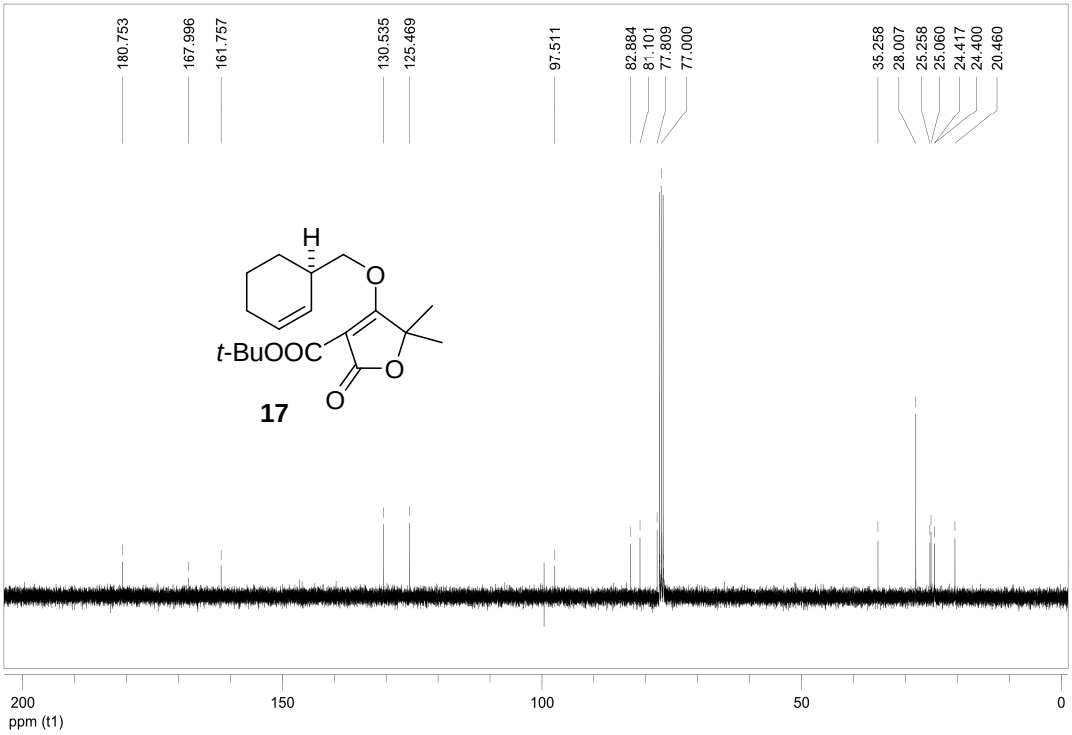
*Email: thorsten.bach@ch.tum.de

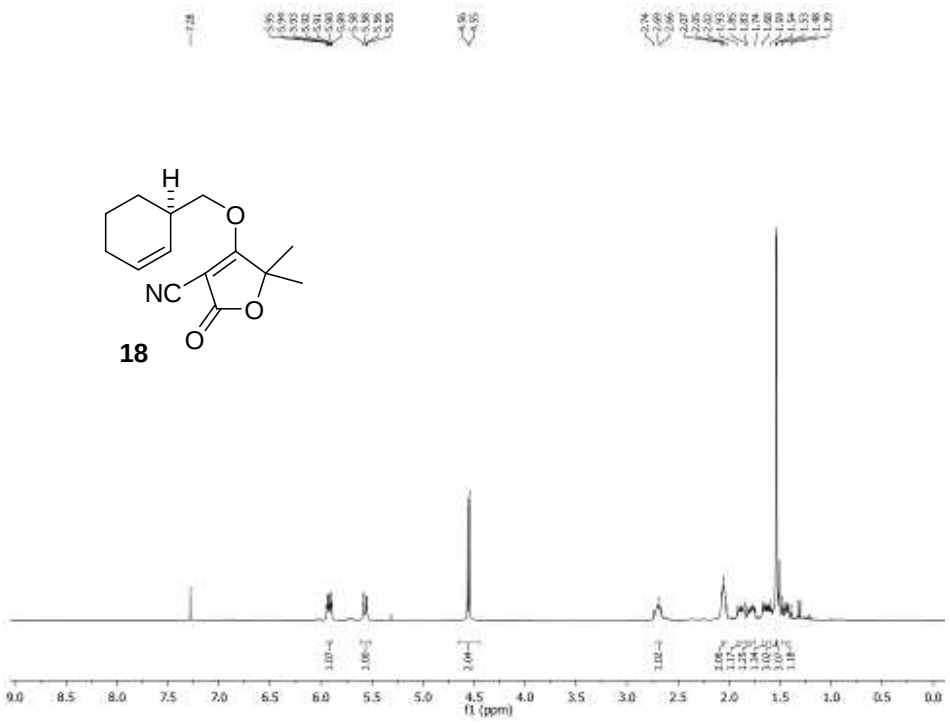
1. ^{1}H- and ^{13}C-NMR spectra of compounds **17**-**19**, **21**, **23a-b**, **25a-e**, **27**-**34d**, **37** SI 2

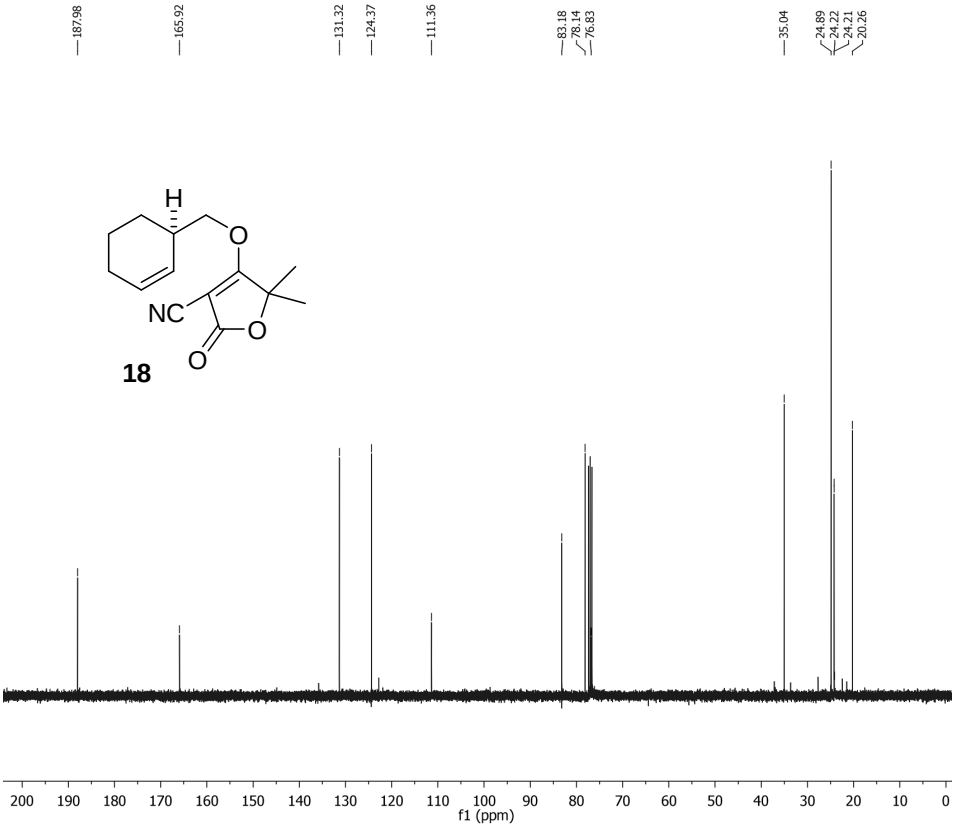
2. Structural assignment of photocycloaddition products **2**, **4**, **26**-**31**, **32a-b**, **33**, **34a,c,d** SI 26

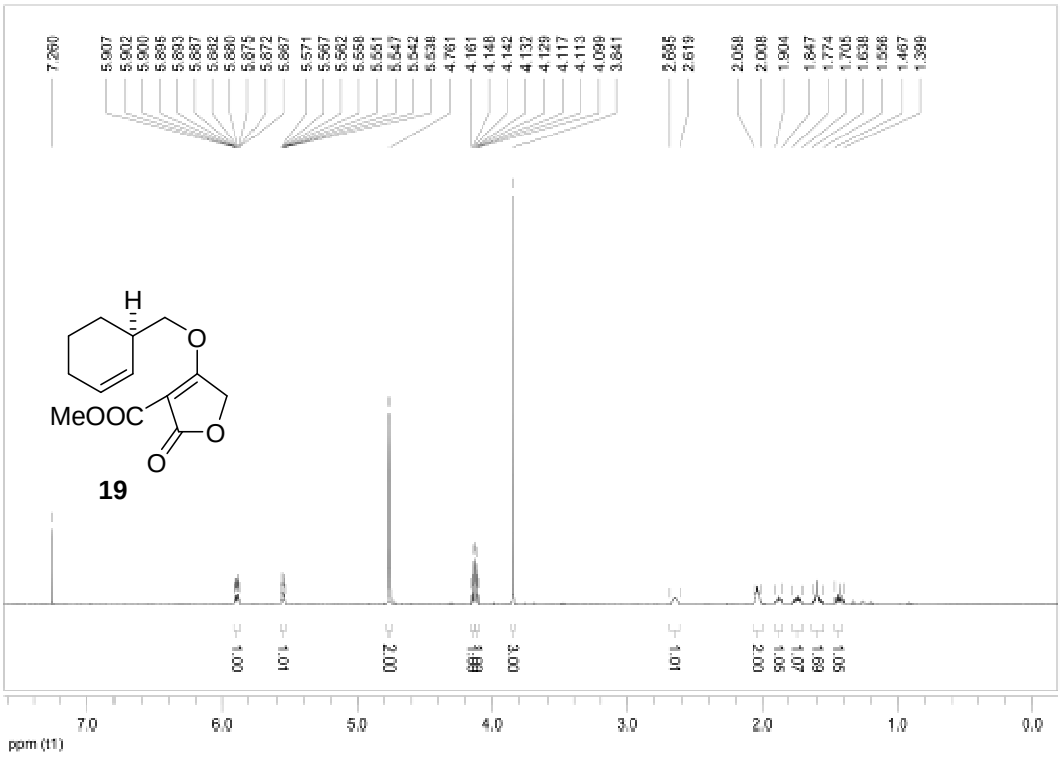
1. ^{1}H- and ^{13}C-NMR spectra of compounds **17**-**19**, **21**, **23a**-**b**, **25a**-**e**, **27**-**34d**, **37**

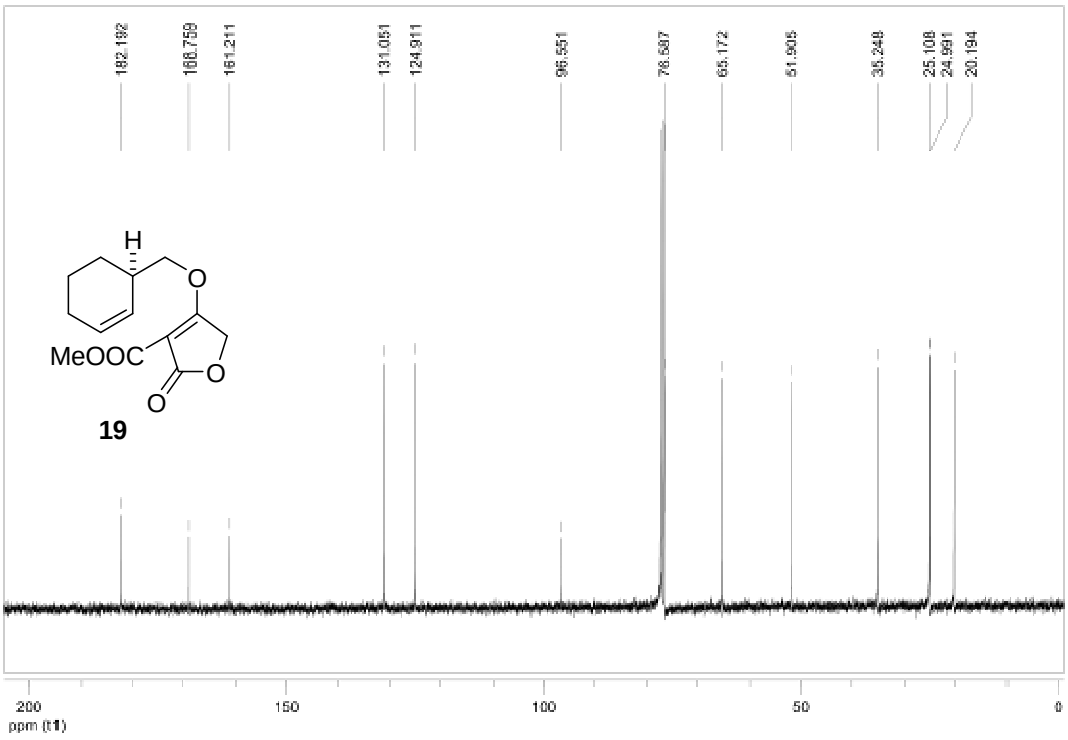


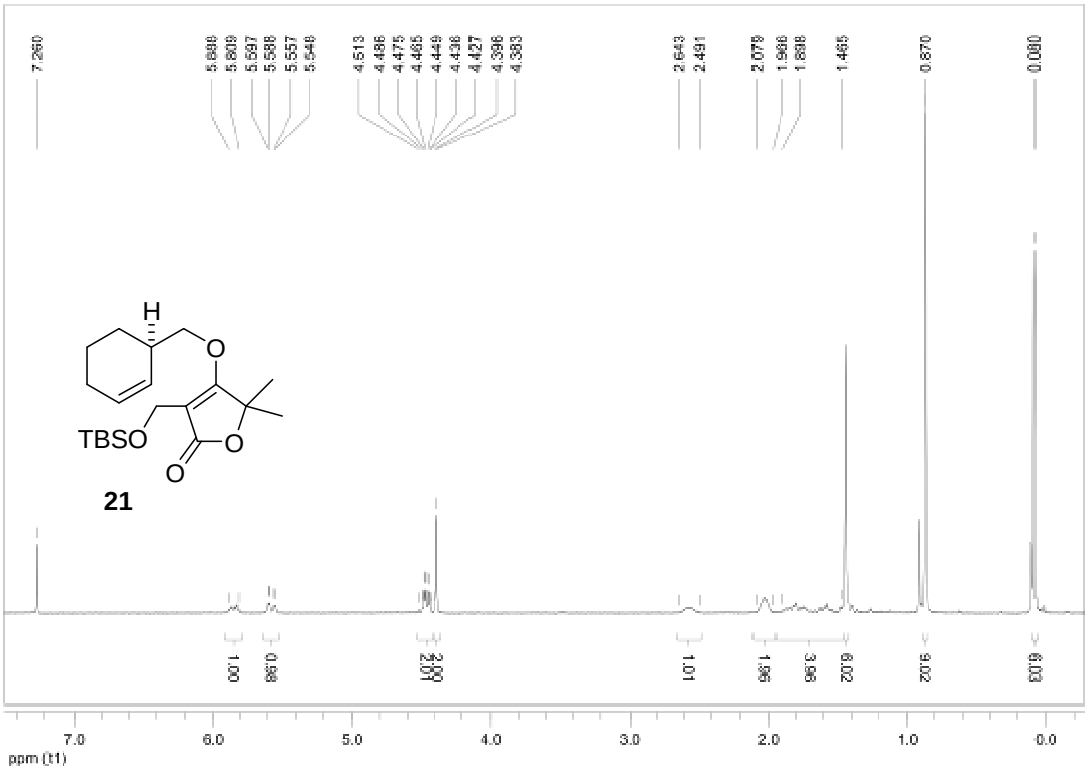



H
O
NC
O
O
18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

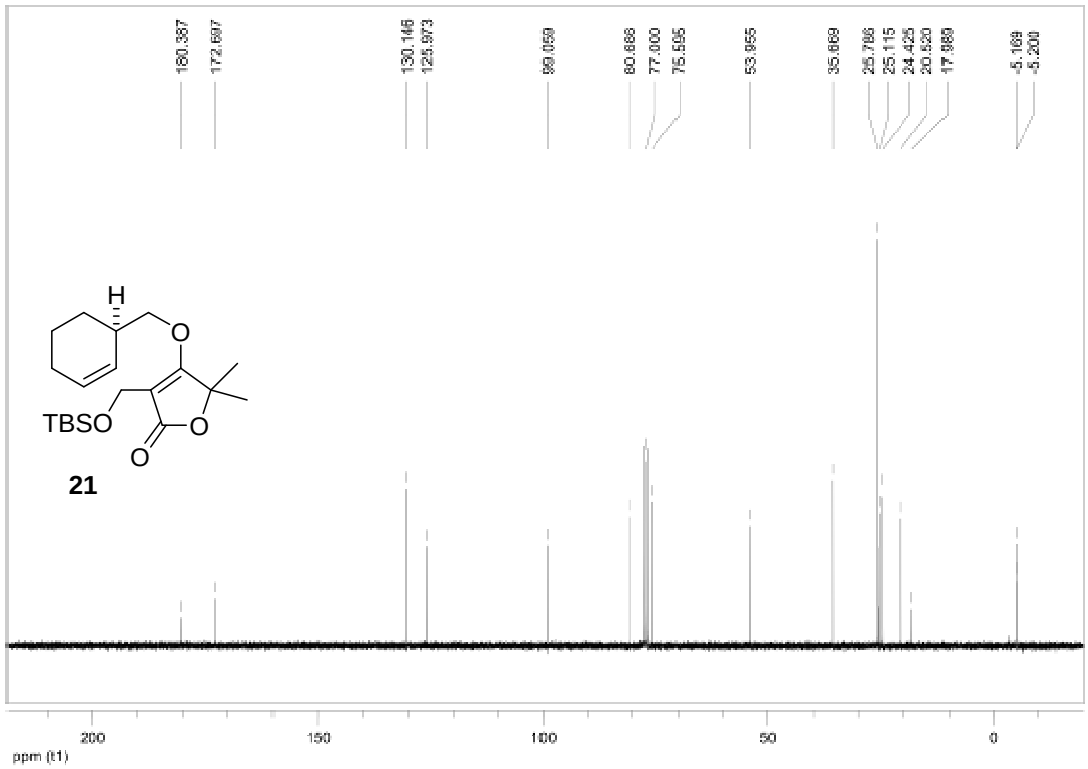

187.98
165.92
131.32
124.37
111.36
83.18
78.14
76.83
35.04
24.89
24.22
24.21
20.26
H
O
NC
O
O
18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
5.907
5.902
5.900
5.895
5.893
5.887
5.882
5.880
5.875
5.872
5.867
5.571
5.567
5.562
5.558
5.551
5.547
5.542
5.538
4.761
4.161
4.148
4.142
4.132
4.129
4.117
4.113
4.099
3.841
2.685
2.619
2.058
2.008
1.904
1.847
1.774
1.705
1.638
1.556
1.467
1.399
H
O
MeOOC
O
O
19
1.00
1.01
2.00
3.00
1.01
2.00
1.06
1.07
1.69
1.06
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

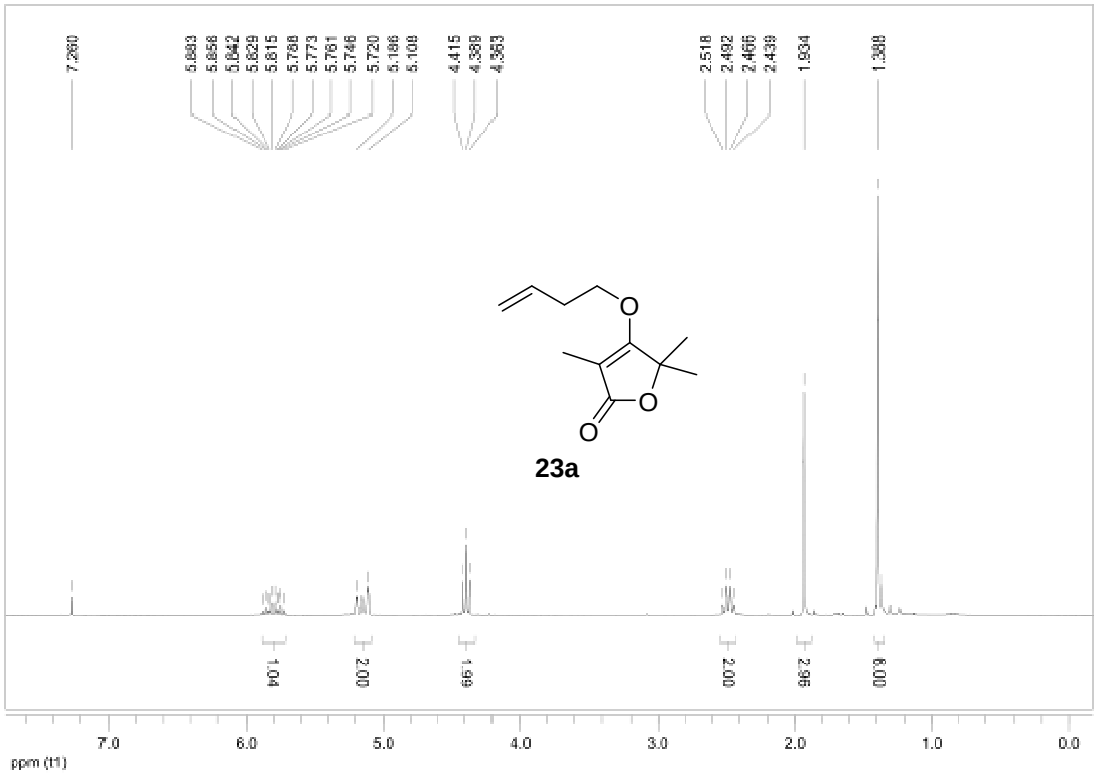

182.182
166.759
161.211
131.051
124.911
96.551
78.697
65.172
51.905
35.248
25.108
24.991
20.194
H
O
MeOOC
O
O
19
200
150
100
50
0
ppm (t1)


7.260
5.609
5.603
5.597
5.588
5.557
5.548
4.513
4.486
4.475
4.465
4.449
4.438
4.427
4.396
4.383
2.643
2.491
2.078
1.966
1.898
1.465
0.870
0.080
1.00
0.98
2.09
2.01
1.01
1.96
3.96
6.02
9.02
6.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
H
O
TBSO
O
O

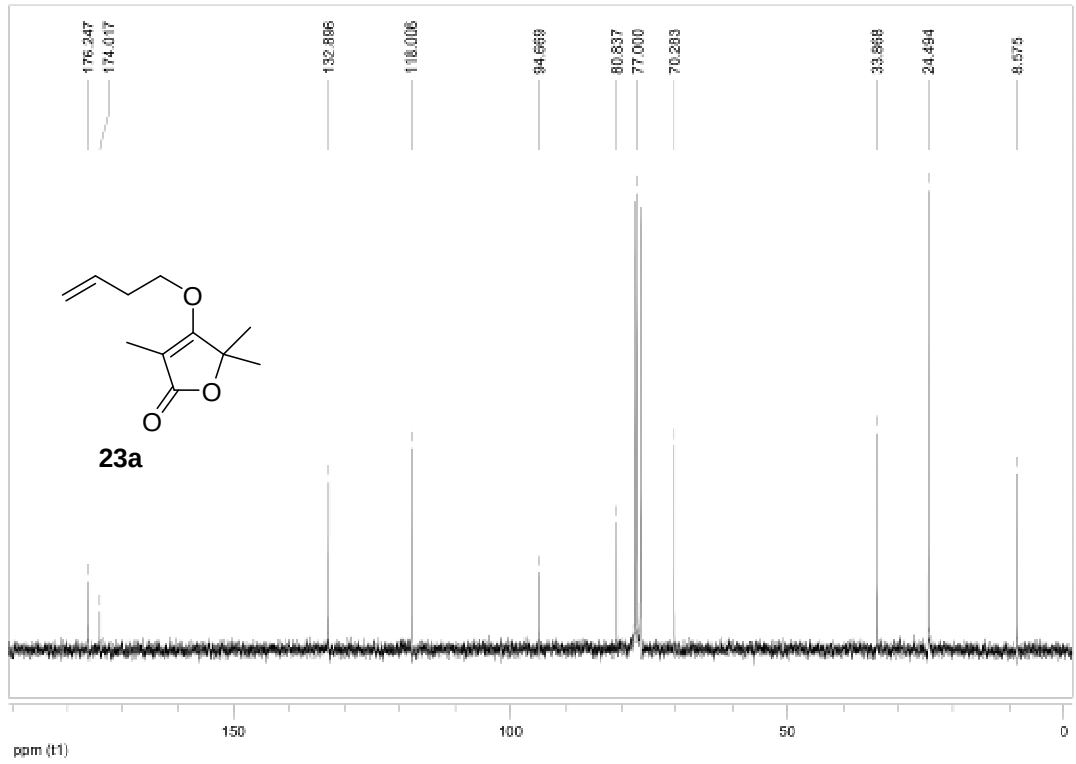
21


180.387
172.697
130.146
125.973
99.059
80.688
77.000
75.595
53.955
35.669
25.788
25.115
24.425
20.520
17.989
-5.169
-5.200
200
150
100
50
0
ppm (t1)
H
O
TBSO
O
O

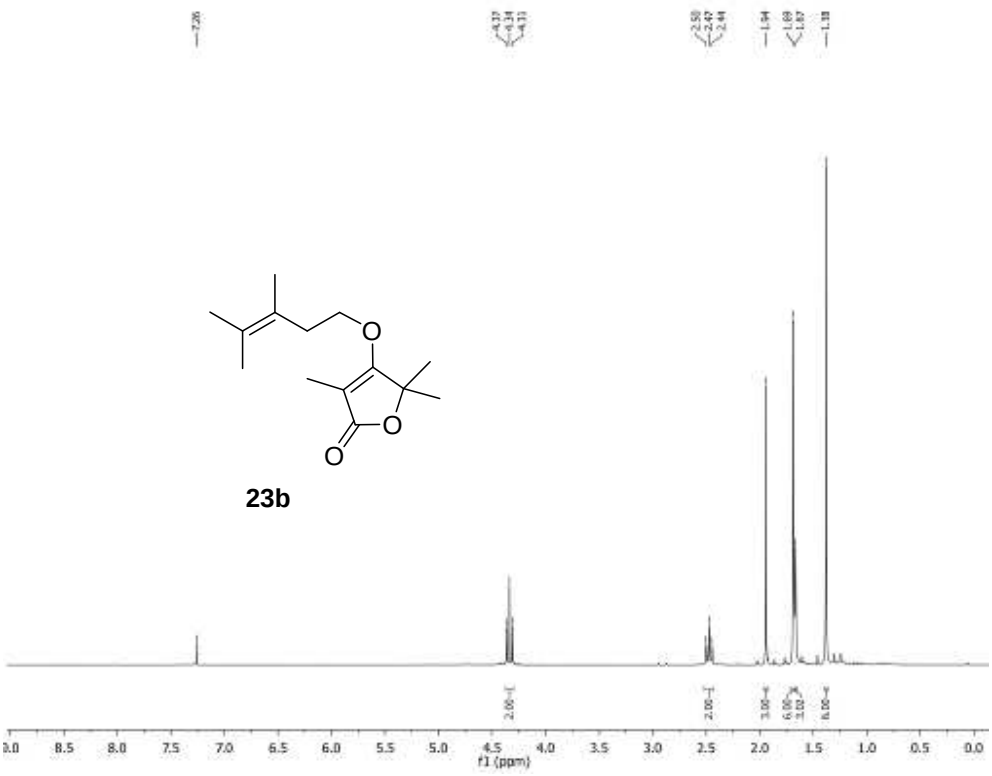
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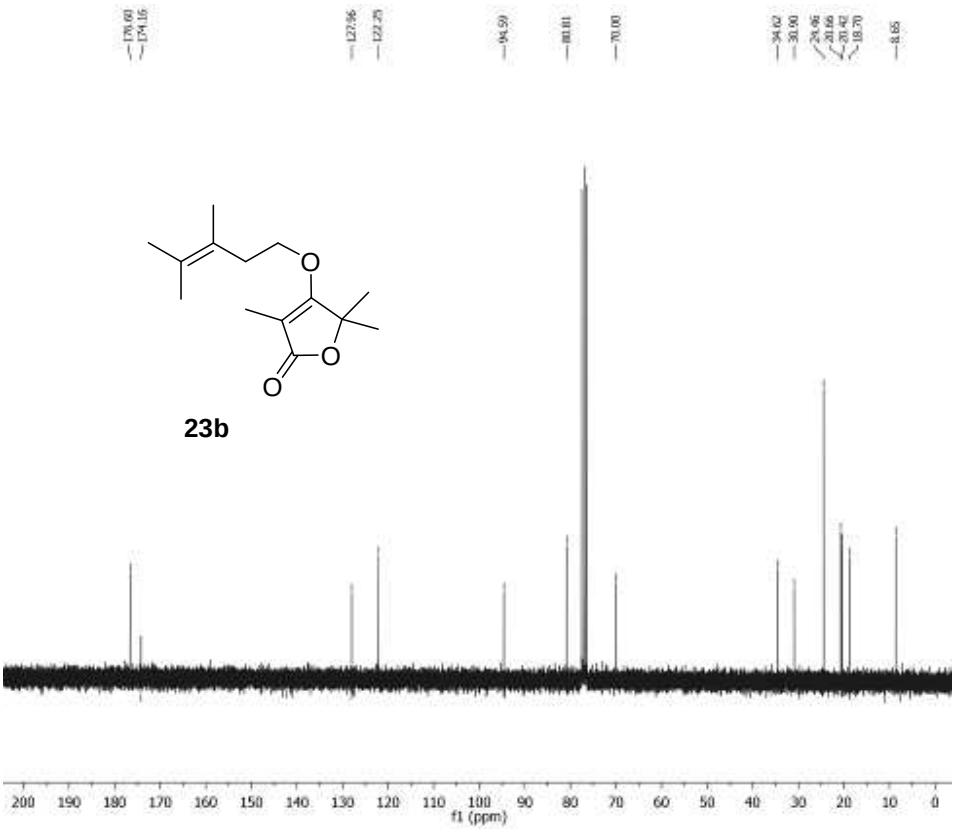

7.2860
5.8883
5.8583
5.8417
5.8292
5.8150
5.7983
5.7733
5.7617
5.7467
5.7200
5.1867
5.1092
4.4150
4.3883
4.3633
2.5183
2.4917
2.4658
2.4392
1.9342
1.3083
1.04
2.00
1.99
2.00
2.96
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

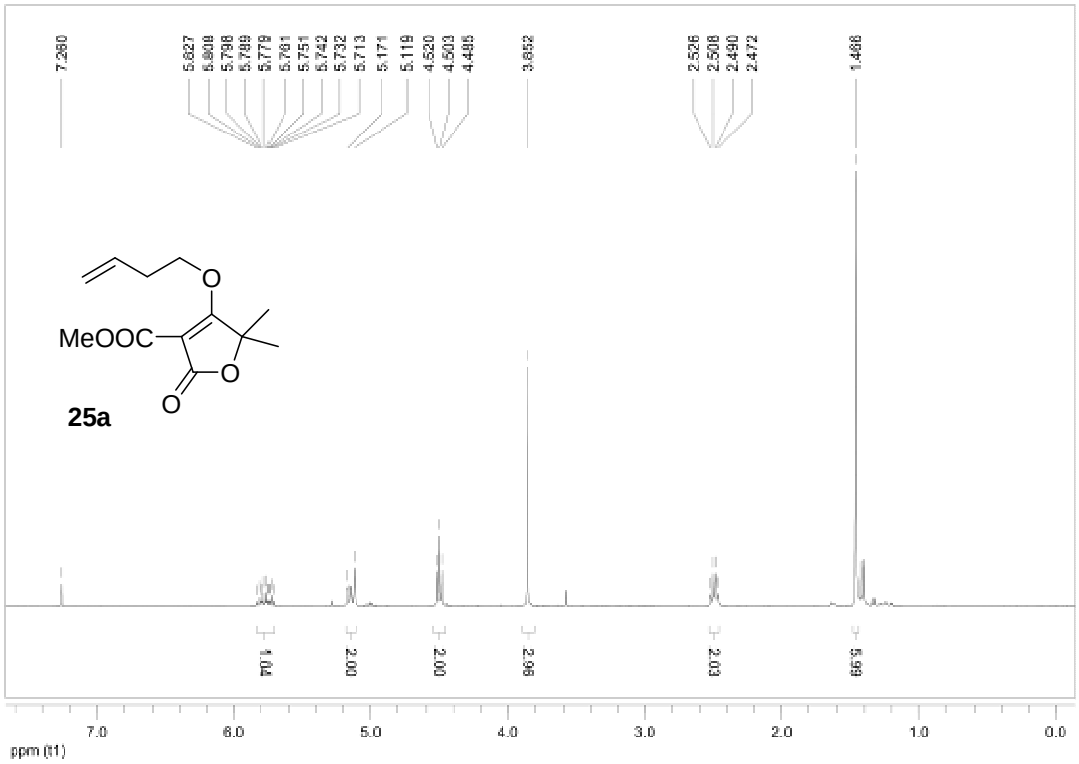
23a

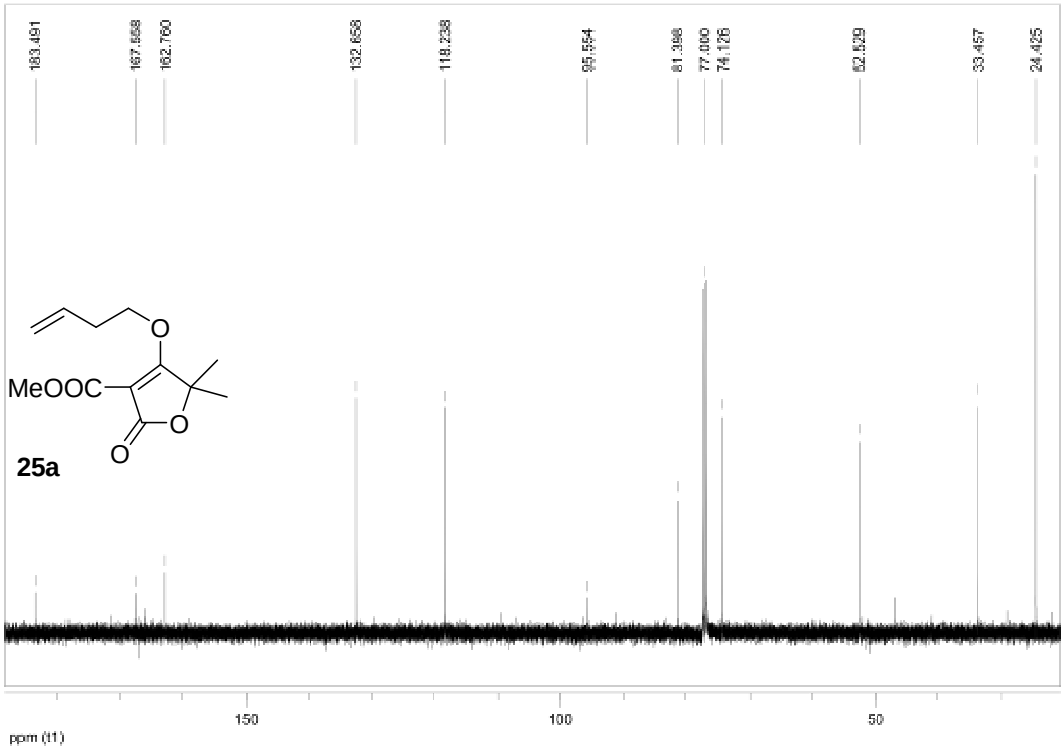

176.247
174.017
132.886
118.006
94.669
80.837
77.000
70.283
33.868
24.494
8.575
150
100
50
0
ppm (t1)

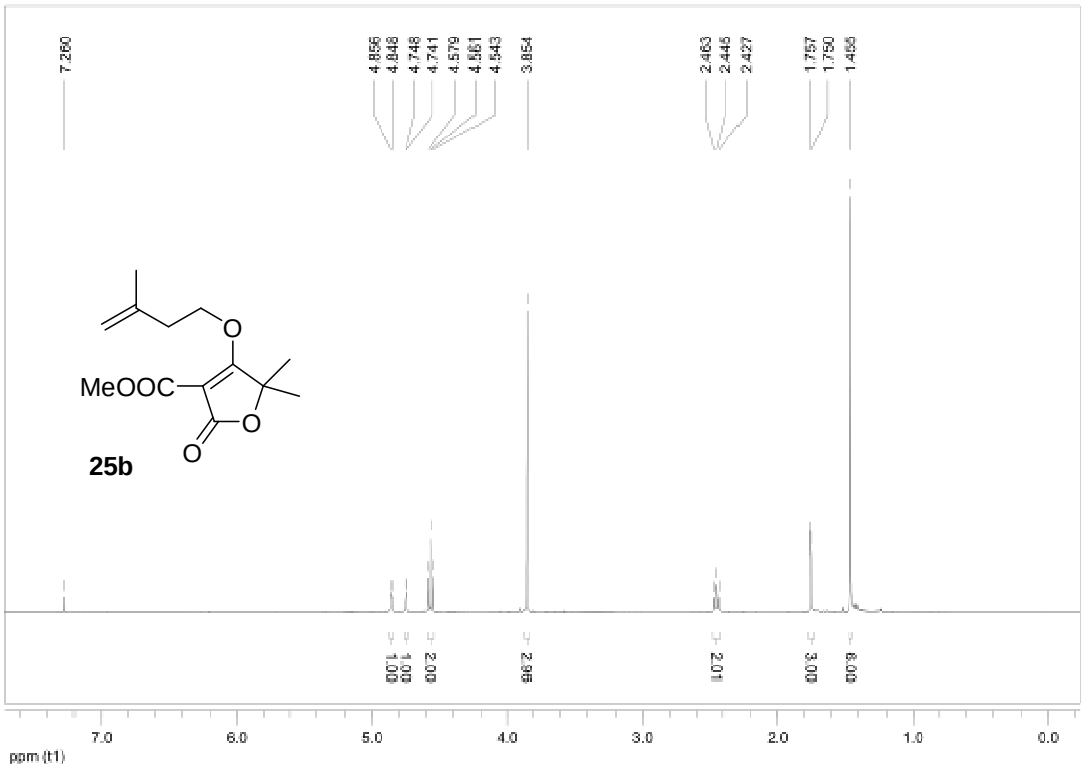
23a

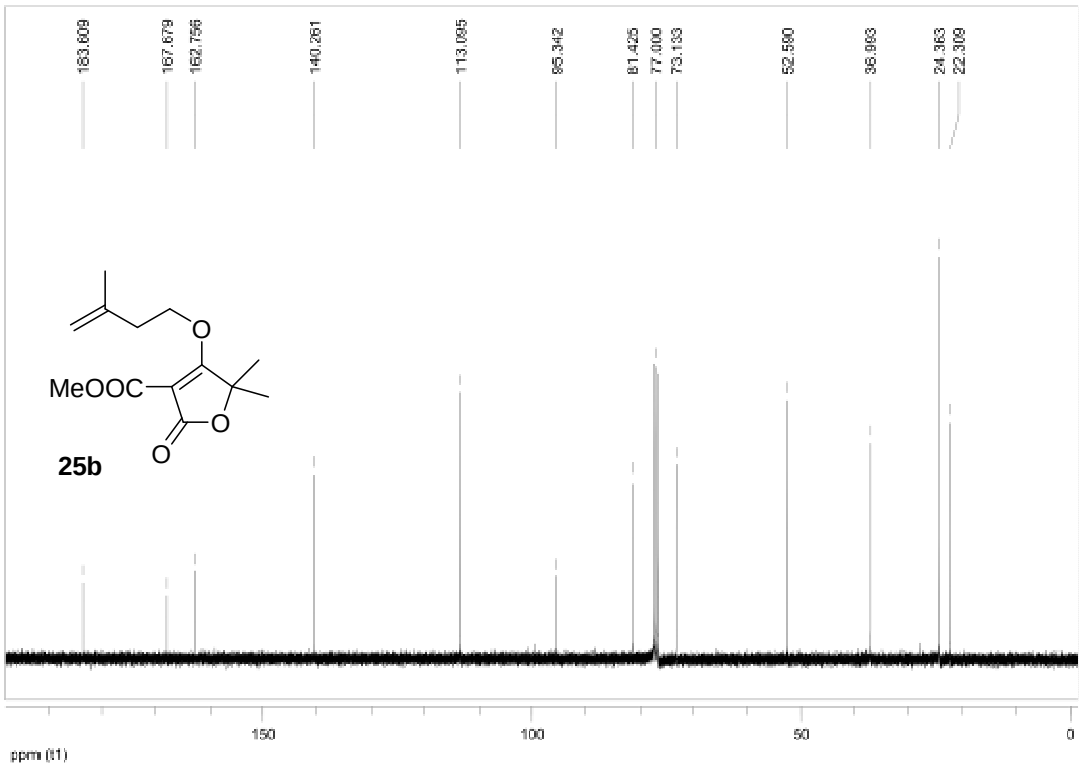

O
O
O
23b
f1 (ppm)

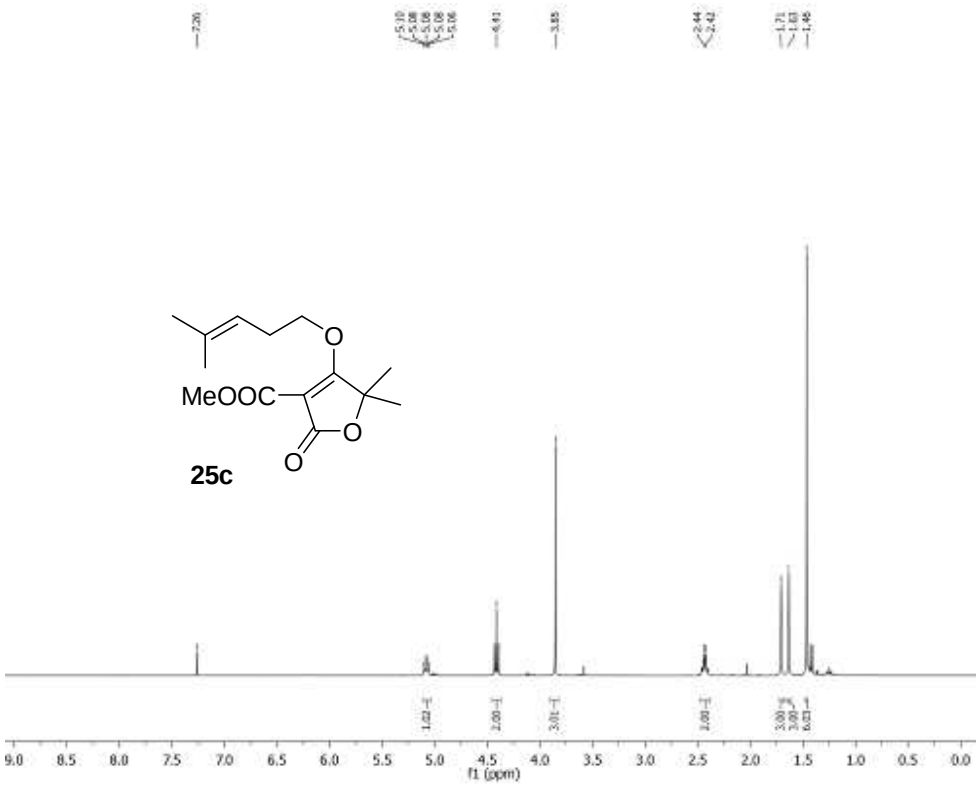

O
O
O
23b
f1 (ppm)

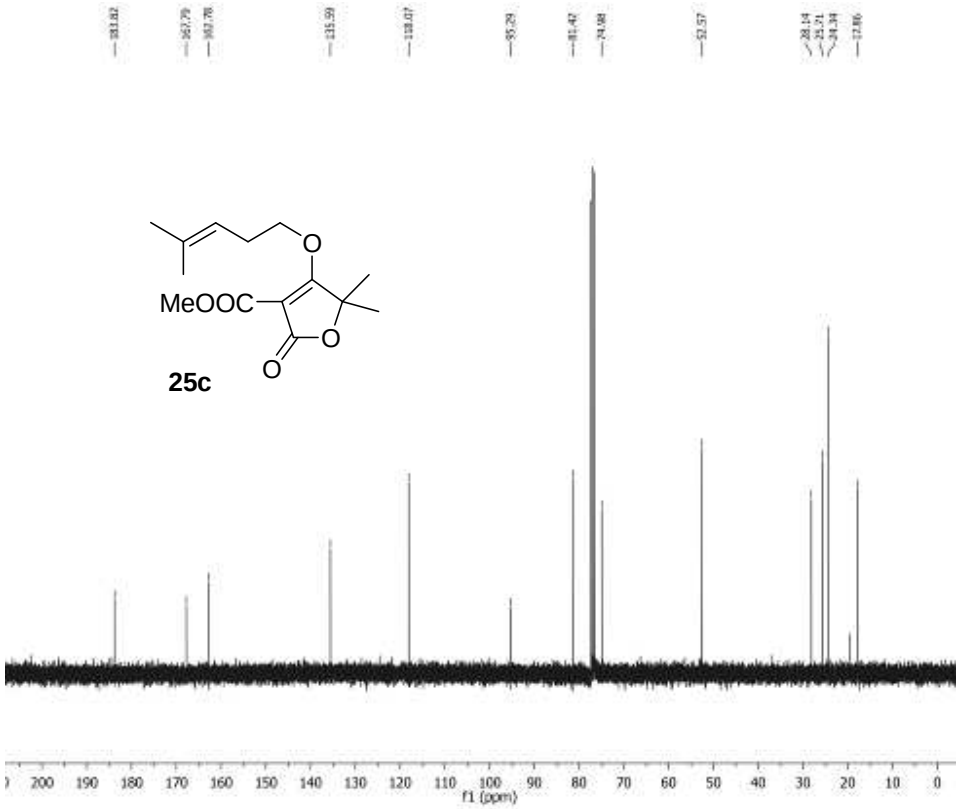

7.260
5.827
5.808
5.798
5.789
5.779
5.761
5.751
5.742
5.732
5.713
5.171
5.119
4.520
4.503
4.485
3.852
2.536
2.508
2.490
2.472
1.468
MeOOC
O
O
O
25a
1.04
2.00
2.00
2.98
2.03
6.99
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

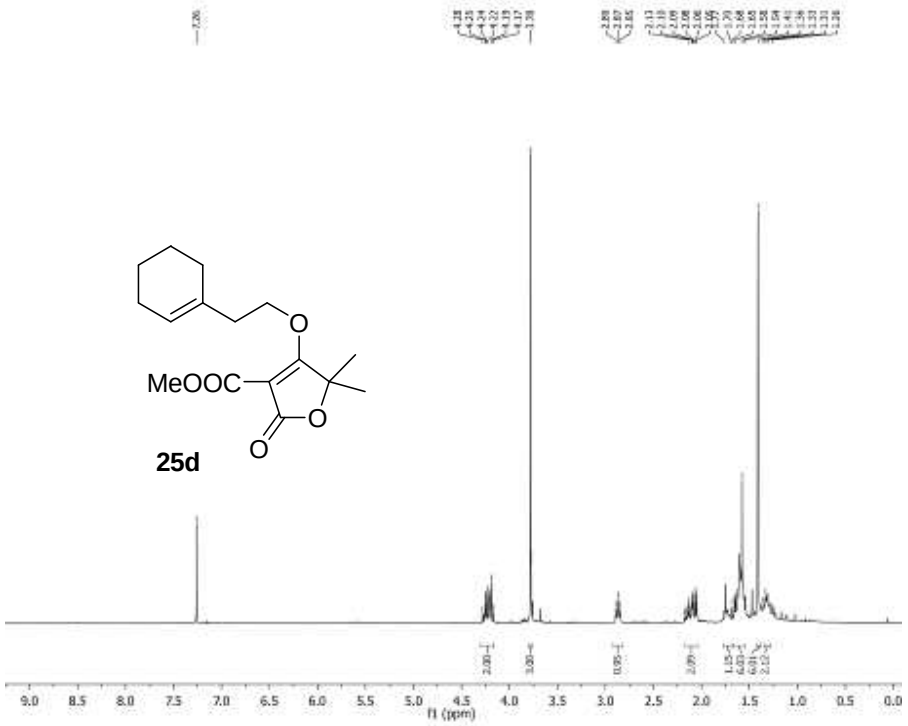

183.491
167.658
162.760
132.658
118.238
95.554
81.398
77.000
74.126
62.529
33.457
24.425
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150
100
50
ppm (t1)

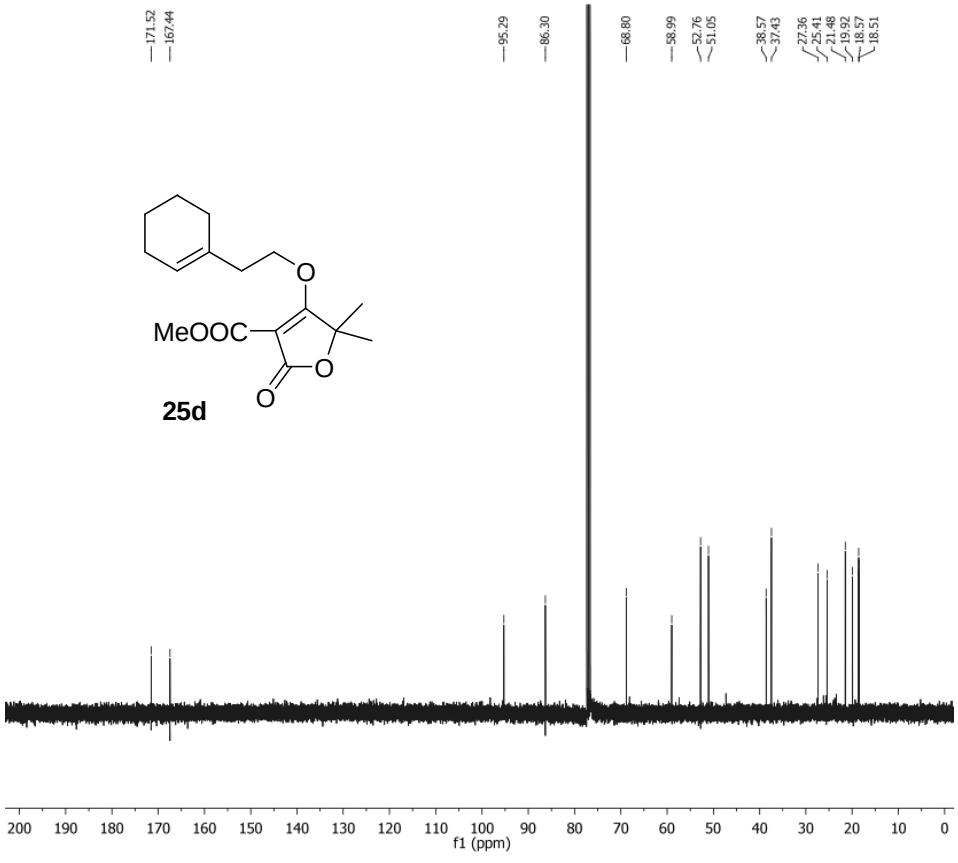

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4.848
4.748
4.741
4.579
4.561
4.543
3.854
2.463
2.445
2.427
1.757
1.750
1.455
MeOOC
O
O
O
25b
1.00
1.00
2.00
2.98
2.01
3.00
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

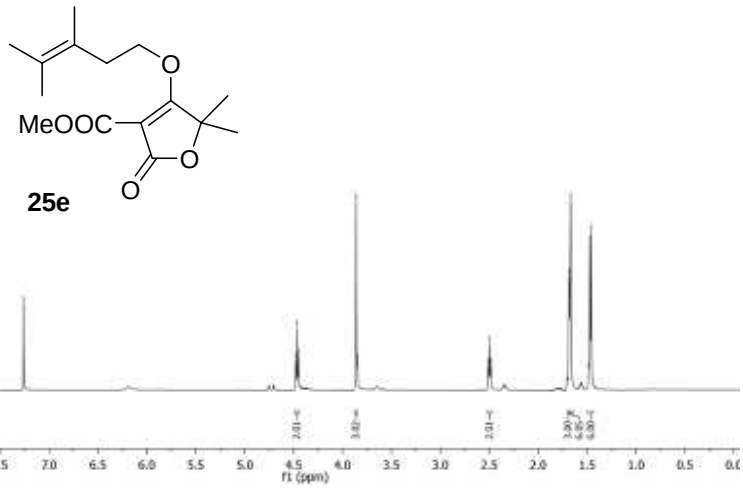

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167.679
162.756
140.261
113.095
85.342
81.425
77.000
73.133
52.590
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24.363
22.309
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O
O
25b
150
100
50
0
ppm (t1)

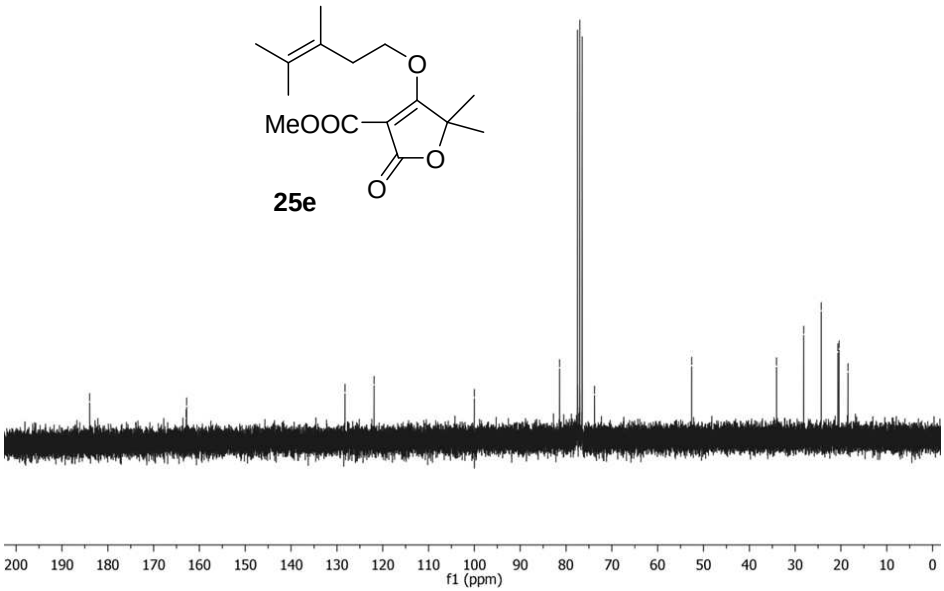

MeOOC
O
O
O
25c
f1 (ppm)

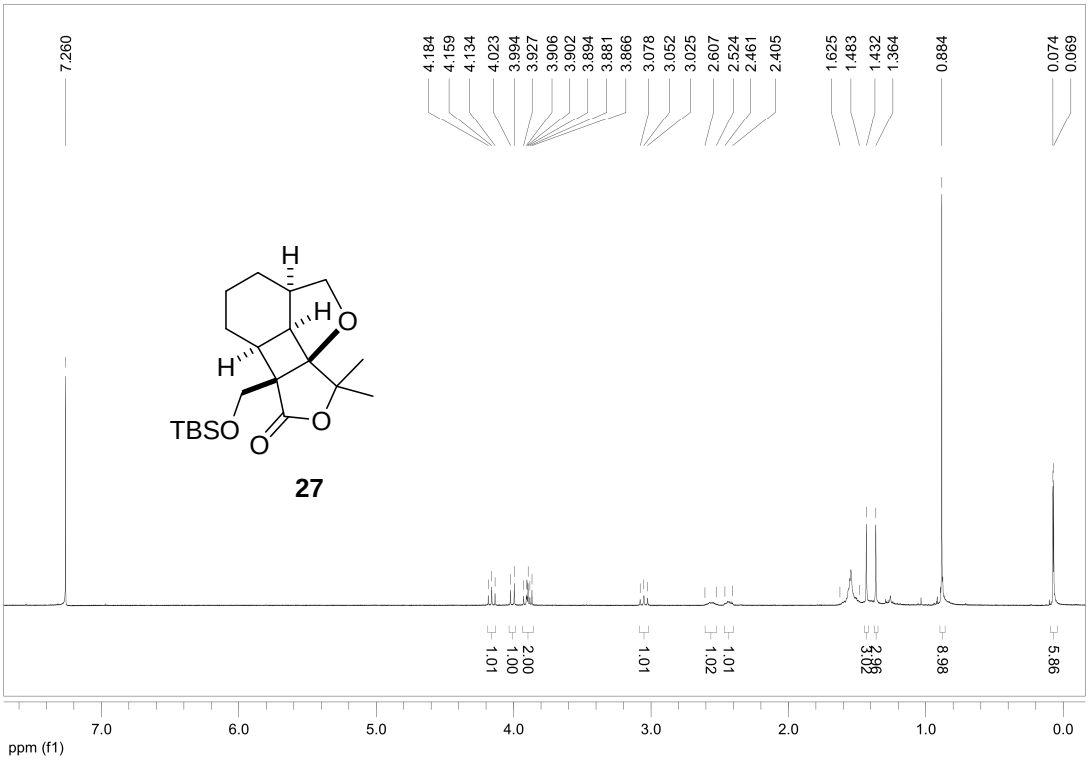

MeOOC
O
O
O
25c
f1 (ppm)


MeOOC
O
O
O
25d
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 0.0
f1 (ppm)

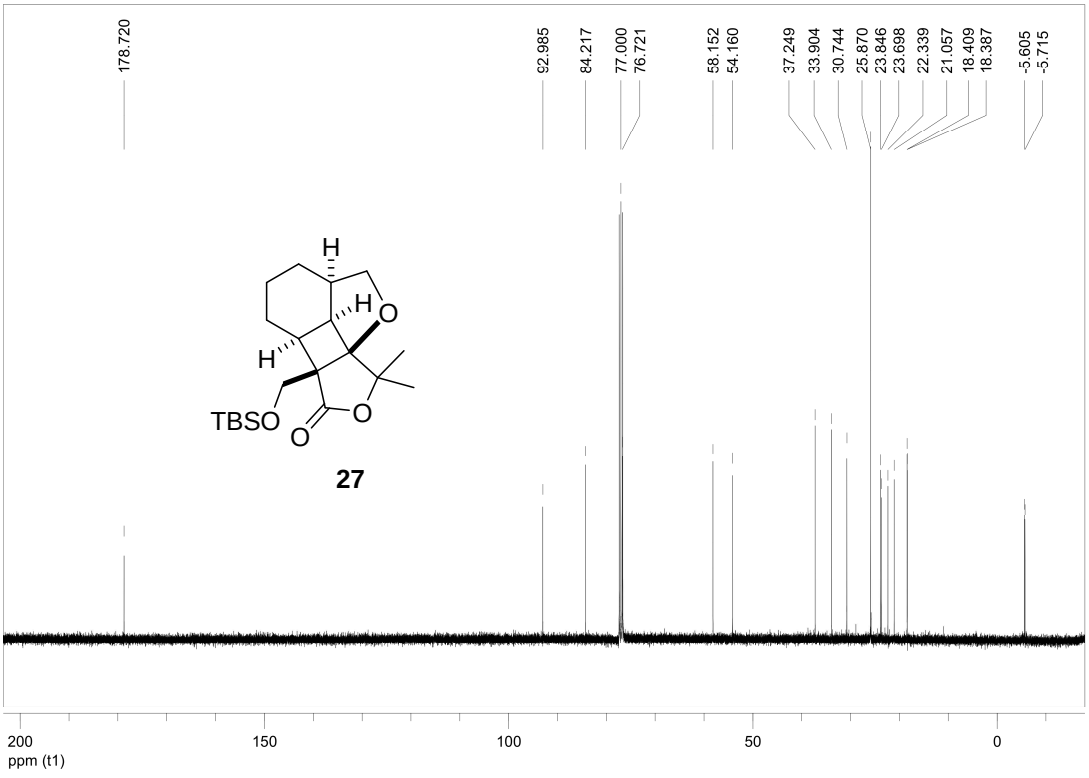

171.52
167.44
95.29
86.30
68.80
58.99
52.76
51.05
38.57
37.43
27.36
25.41
21.48
19.92
18.57
18.51
MeOOC
O
O
O
25d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeOOC
O
O
O
25e
f1 (ppm)

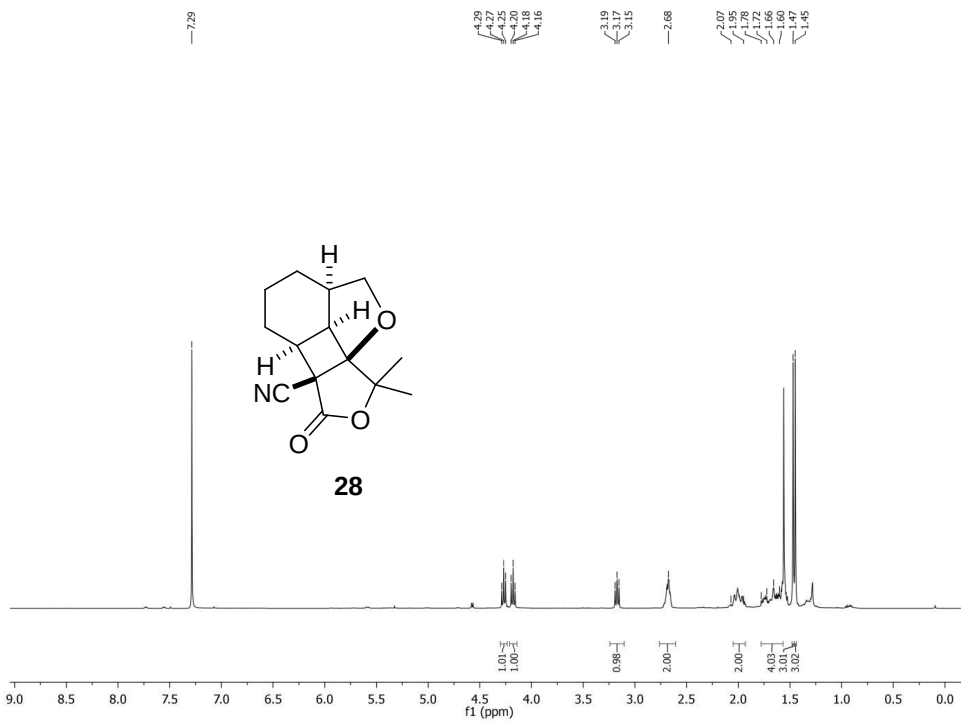

MeOOC
O
O
O
25e
f1 (ppm)


7.260
4.184
4.159
4.134
4.023
3.994
3.927
3.906
3.902
3.894
3.881
3.866
3.078
3.052
3.025
2.607
2.524
2.461
2.405
1.625
1.483
1.432
1.364
0.884
0.074
0.069
1.01
1.00
2.00
1.01
1.02
1.01
3.02
2.98
8.98
5.86
7.0
6.0
5.0
4.0
3.0
2.0
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ppm (f1)
H
H
O
H
TBSO
O
O
O

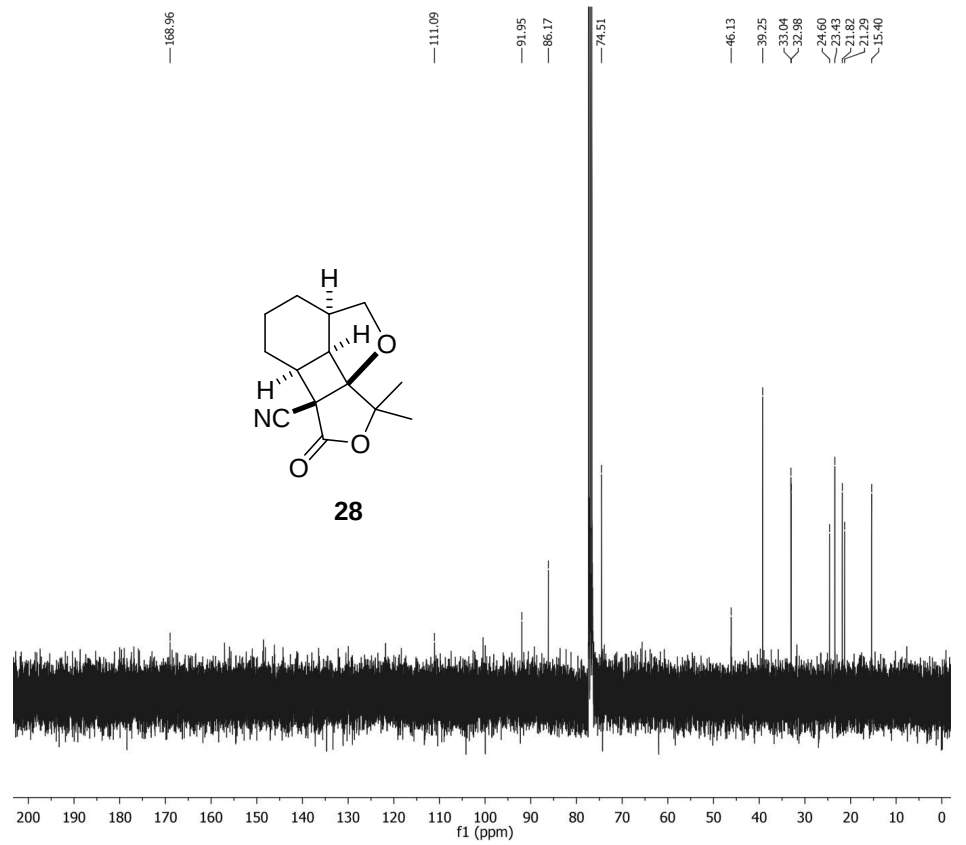
27


178.720
92.985
84.217
77.000
76.721
58.152
54.160
37.249
33.904
30.744
25.870
23.846
23.698
22.339
21.057
18.409
18.387
-5.605
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200
150
100
50
0
ppm (t1)
H
H
O
H
TBSO
O
O
O

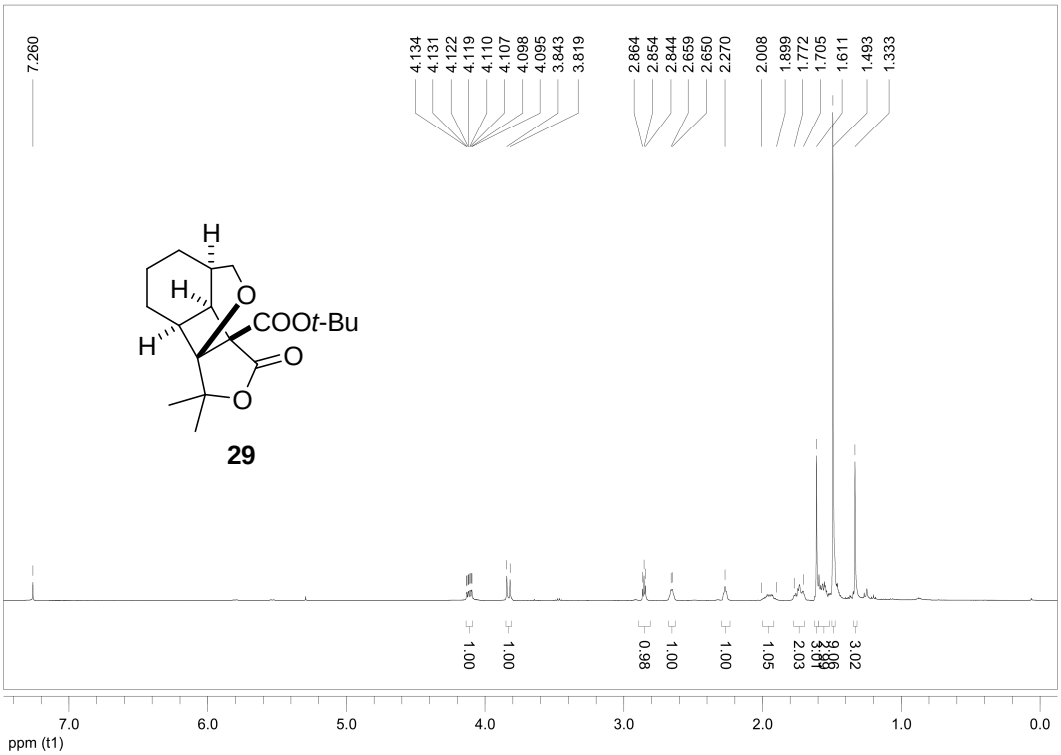
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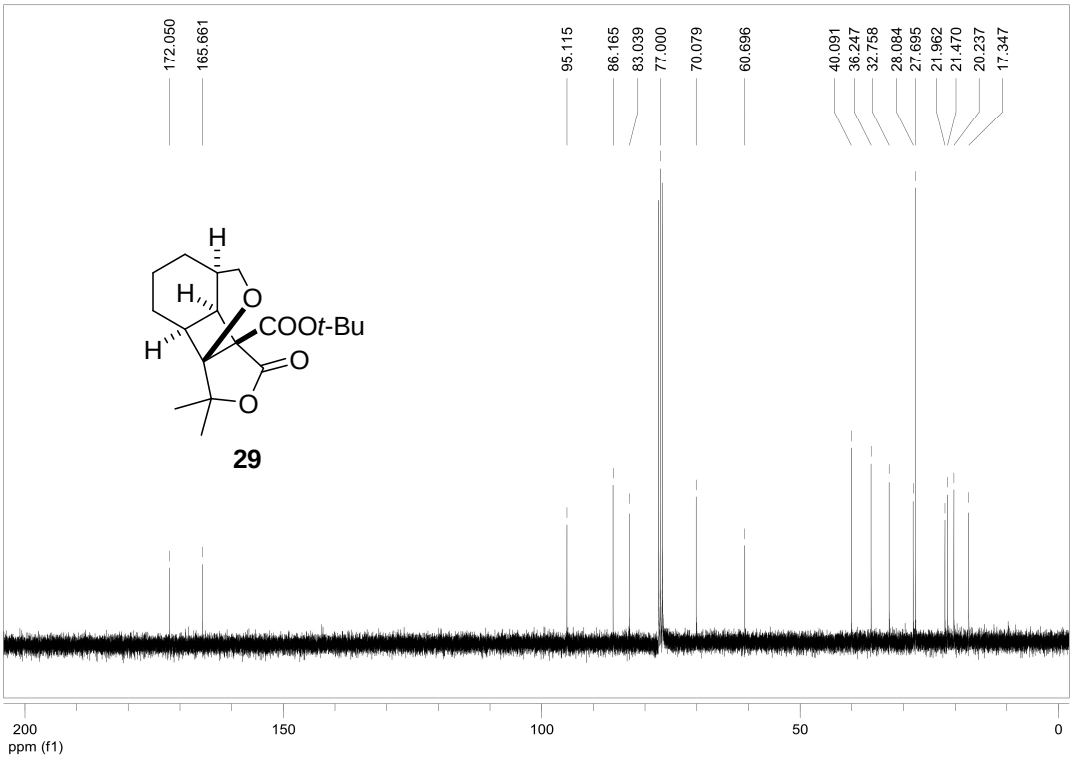

7.29
4.29
4.27
4.25
4.20
4.18
4.16
3.19
3.17
3.15
2.68
2.07
1.95
1.78
1.72
1.66
1.60
1.47
1.45
H
H
O
H
NC
O
O
1.01
1.00
0.98
2.00
2.00
4.03
3.01
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

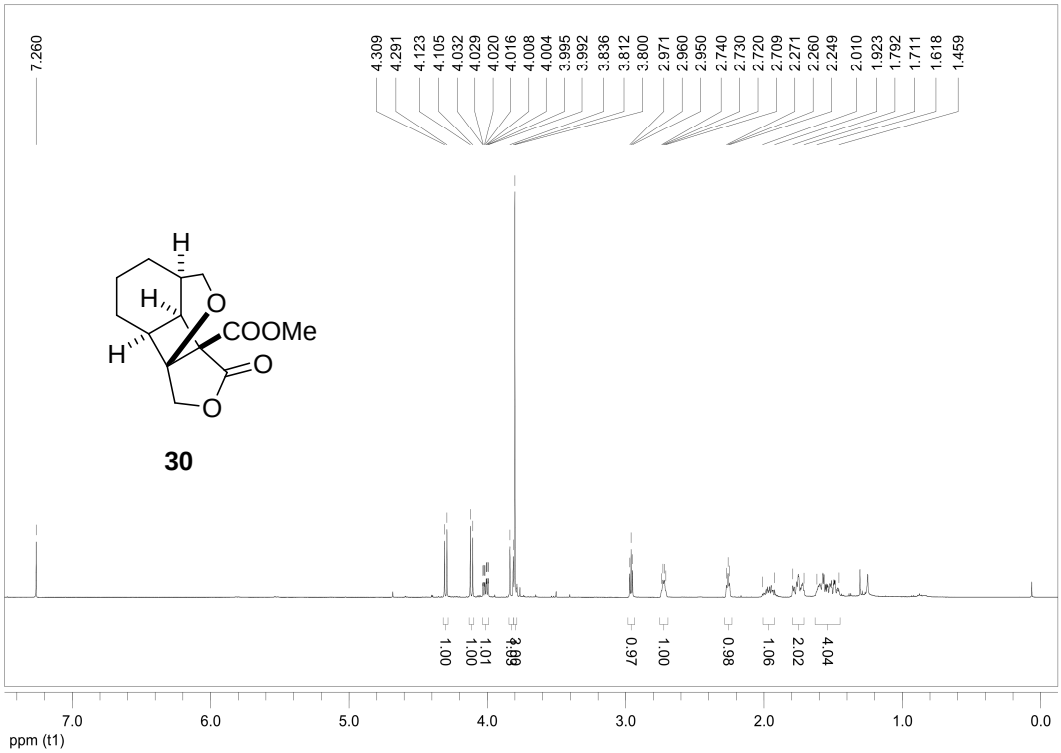
28


168.96
111.09
91.95
86.17
74.51
46.13
39.25
33.04
32.98
24.60
23.43
21.82
21.29
15.40
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O
H
NC
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

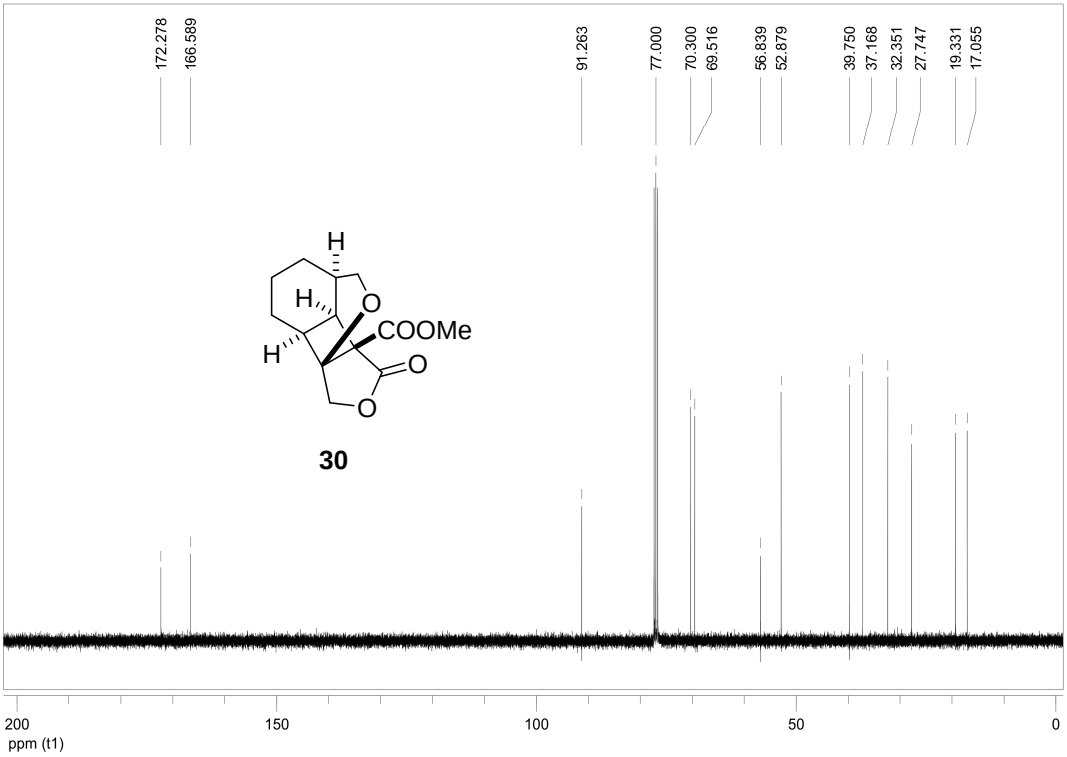
28


7.260
4.134
4.131
4.122
4.119
4.110
4.107
4.098
4.095
3.843
3.819
2.864
2.854
2.844
2.659
2.650
2.270
2.008
1.899
1.772
1.705
1.611
1.493
1.333
COOt-Bu
29
1.00
1.00
0.98
1.00
1.00
1.05
2.03
3.02
7.0
6.0
5.0
4.0
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2.0
1.0
0.0
ppm (t1)

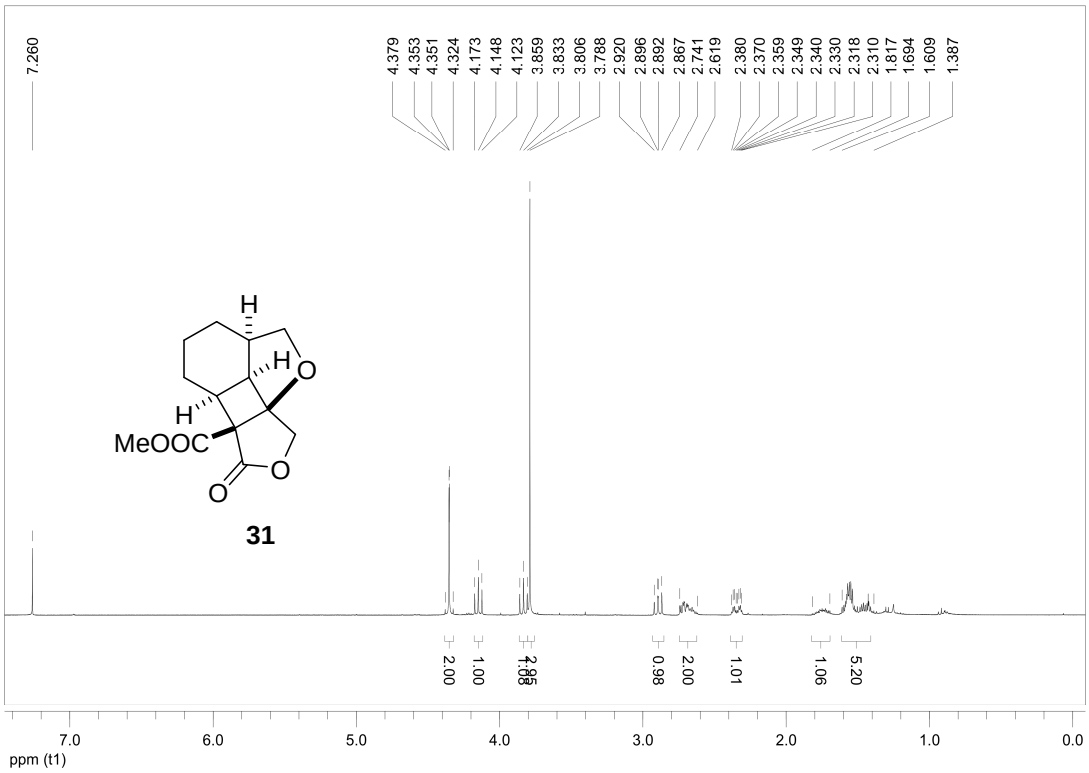

172.050
165.661
95.115
86.165
83.039
77.000
70.079
60.696
40.091
36.247
32.758
28.084
27.695
21.962
21.470
20.237
17.347
COOt-Bu
29
200
150
100
50
0
ppm (f1)


7.260
4.309
4.291
4.123
4.105
4.032
4.029
4.020
4.016
4.008
4.004
3.995
3.992
3.836
3.812
3.800
2.971
2.960
2.950
2.740
2.730
2.720
2.709
2.271
2.260
2.249
2.010
1.923
1.792
1.711
1.618
1.459
H
H
O
COOMe
H
O
O
1.00
1.00
1.01
0.97
1.00
0.98
1.06
2.02
4.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

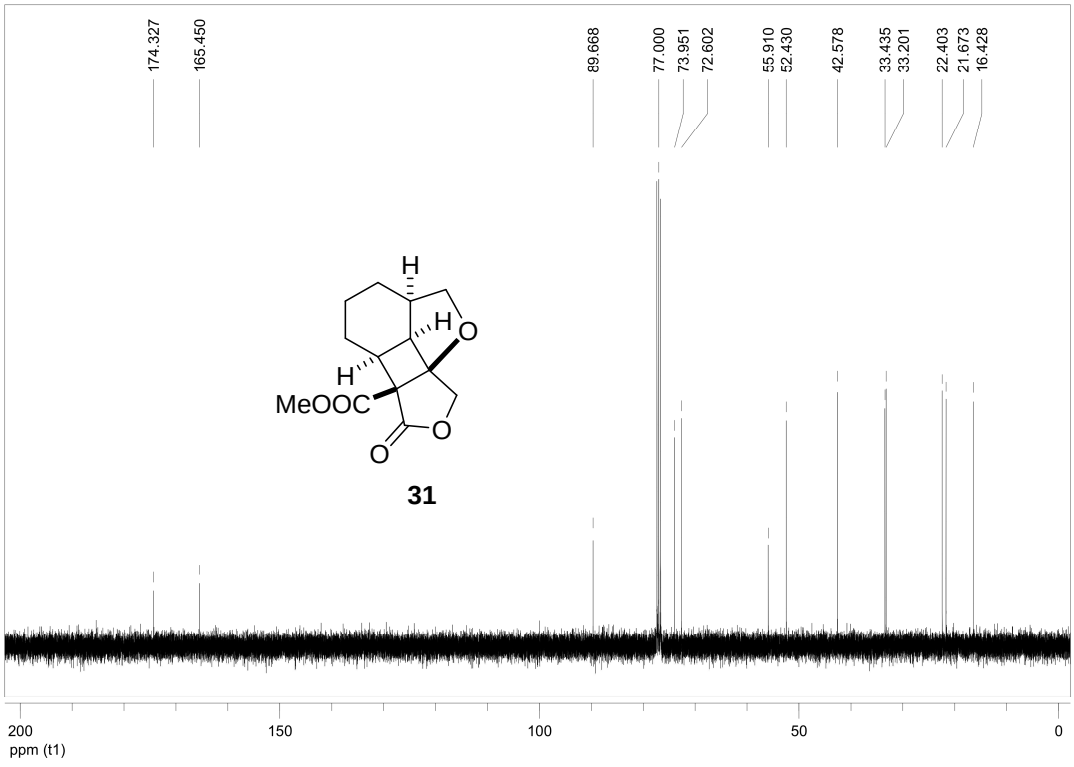
30


172.278
166.589
91.263
77.000
70.300
69.516
56.839
52.879
39.750
37.168
32.351
27.747
19.331
17.055
H
H
O
COOMe
H
O
O
200
150
100
50
0
ppm (t1)

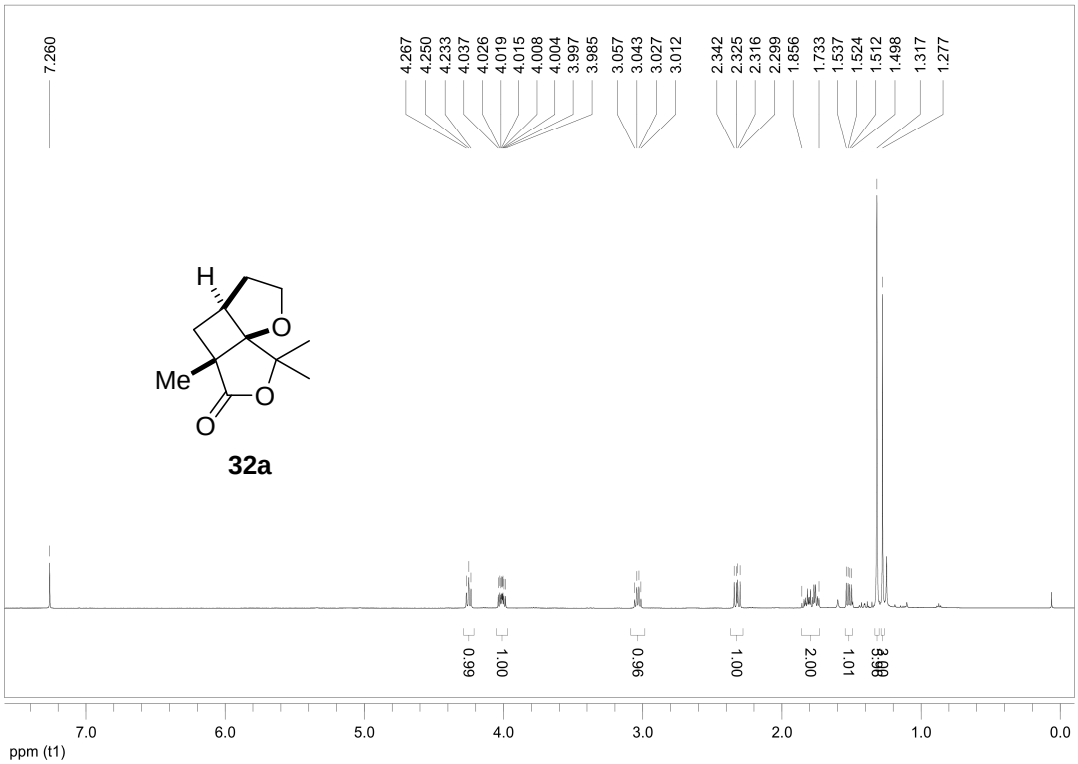
30

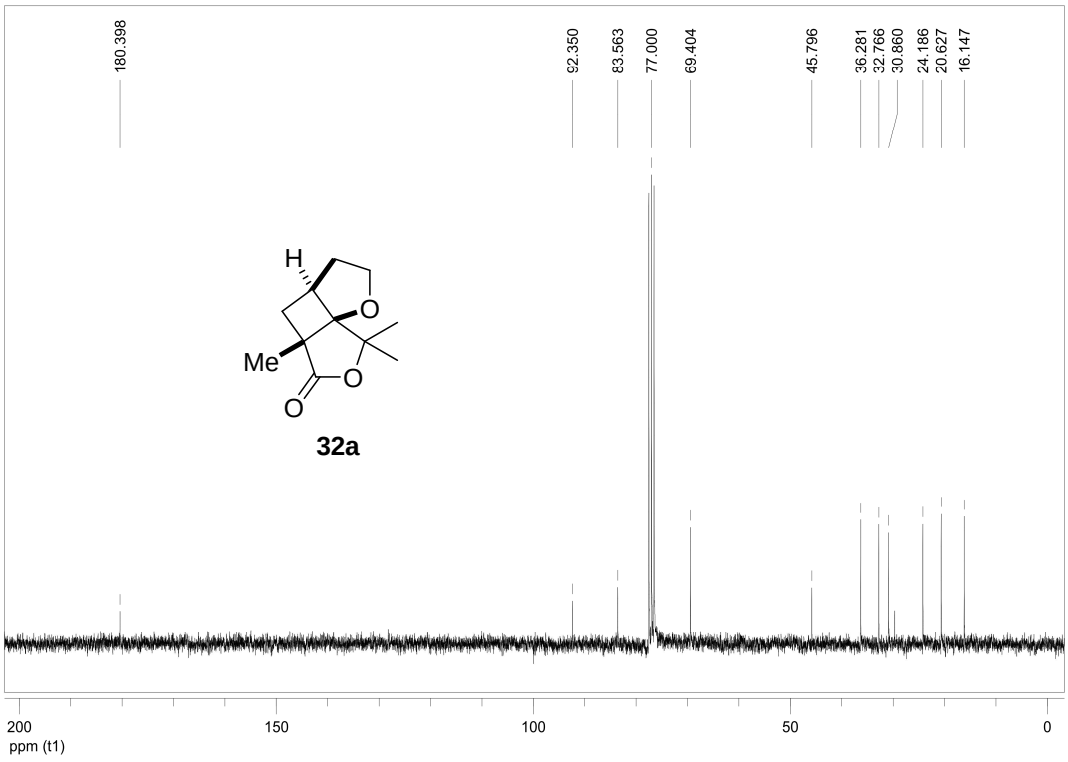

7.260
4.379
4.353
4.351
4.324
4.173
4.148
4.123
3.859
3.833
3.806
3.788
2.920
2.896
2.892
2.867
2.741
2.619
2.380
2.370
2.359
2.349
2.340
2.330
2.318
2.310
1.817
1.694
1.609
1.387
H
H
O
H
MeOOC
O
O
2.00
1.00
2.05
0.98
2.00
1.01
1.06
5.20
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

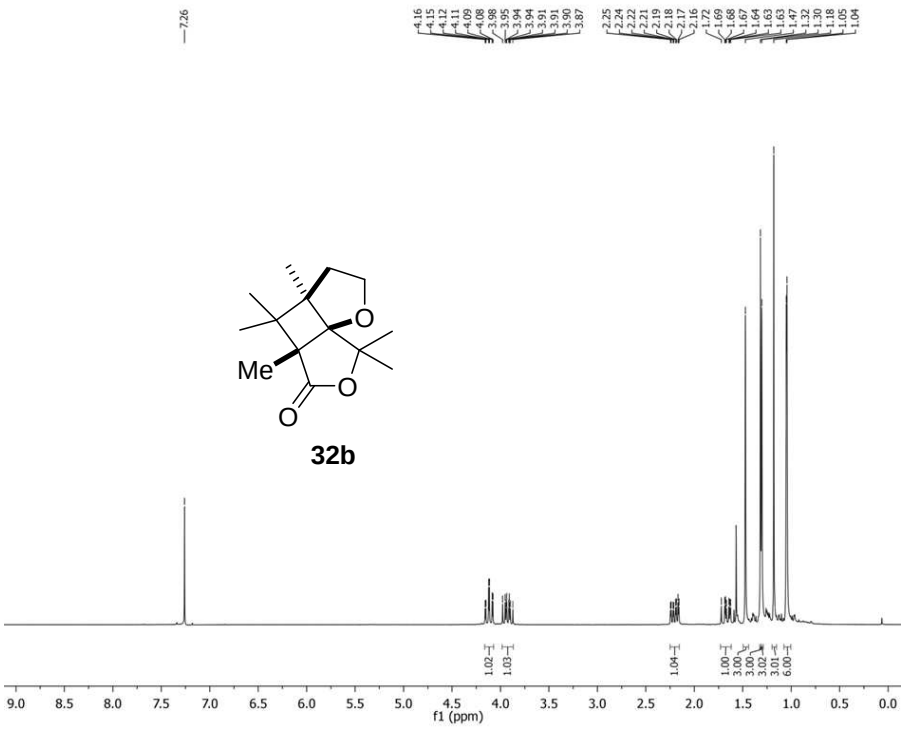
31

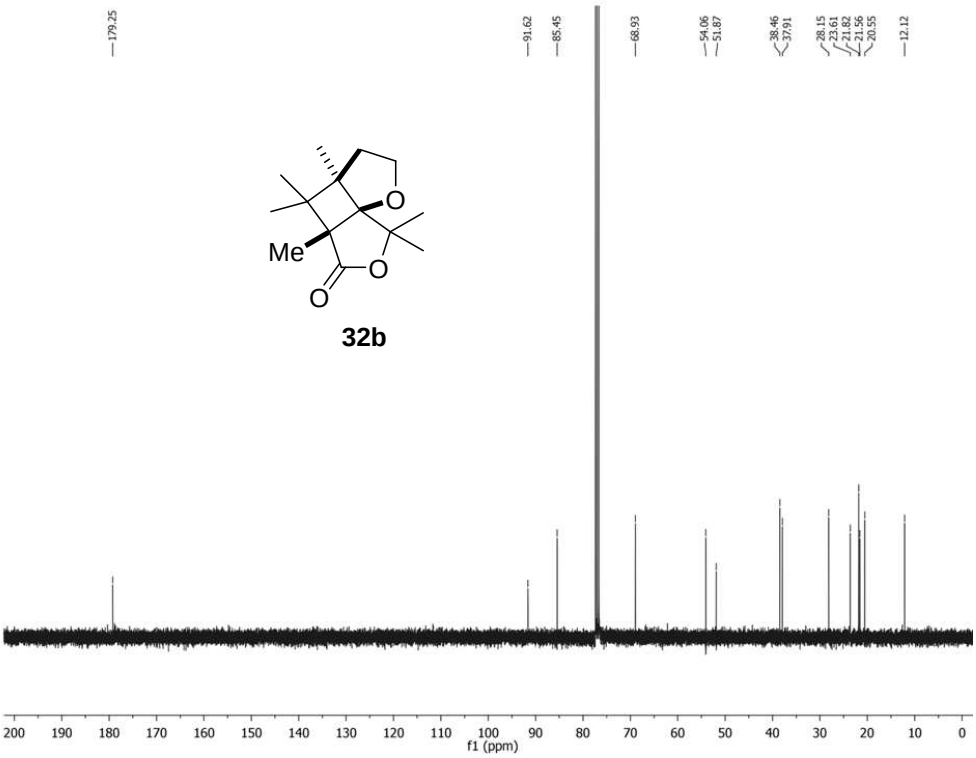

174.327
165.450
89.668
77.000
73.951
72.602
55.910
52.430
42.578
33.435
33.201
22.403
21.673
16.428
H
H
O
H
MeOOC
O
O
200
150
100
50
0
ppm (t1)

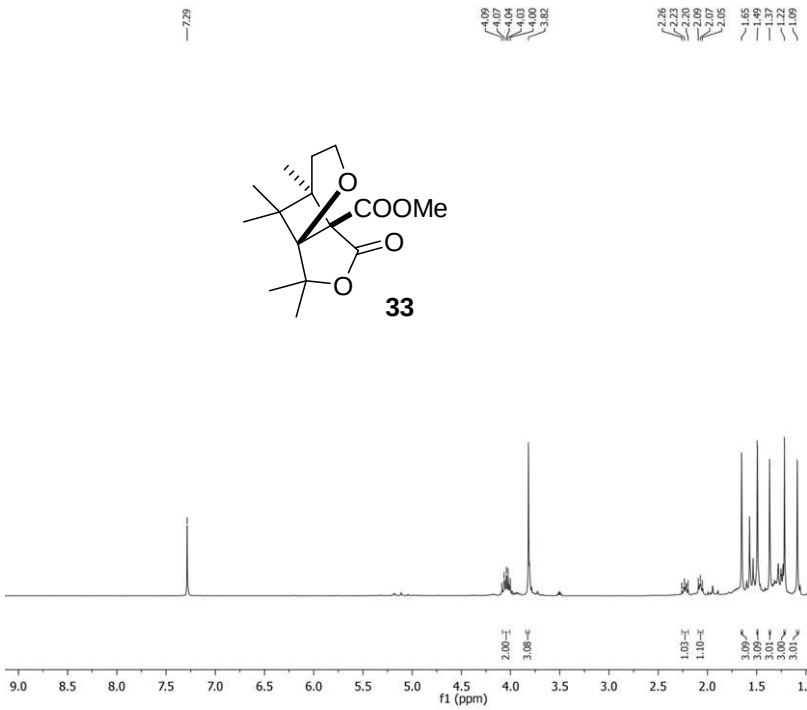
31

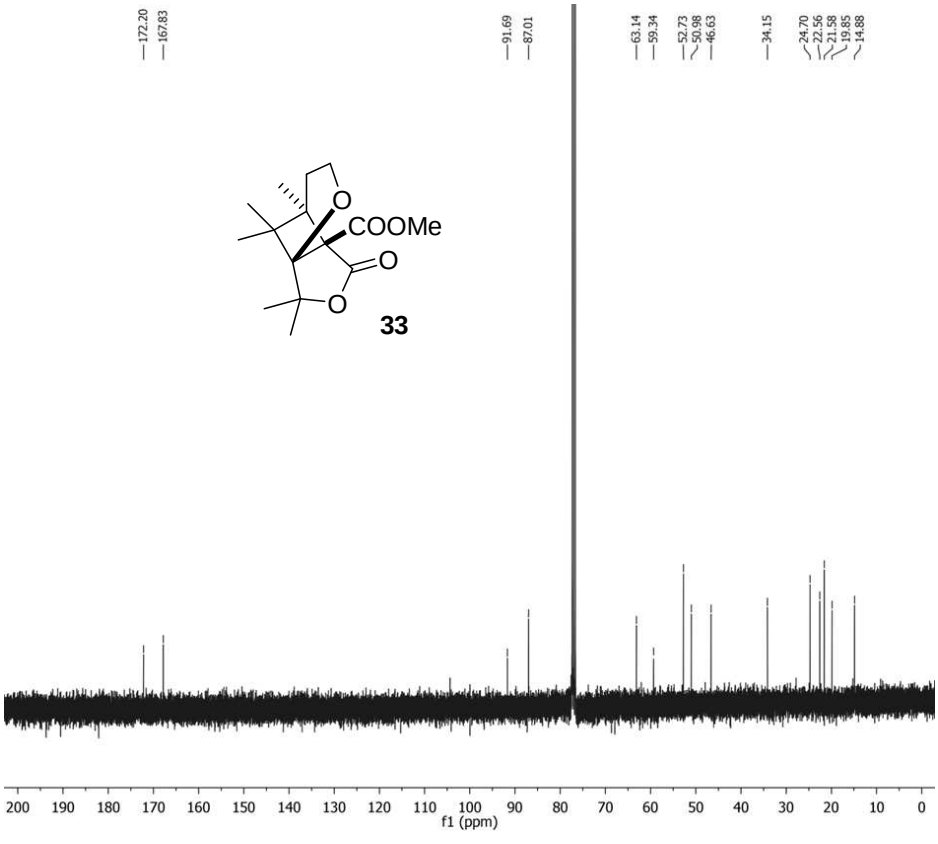

7.260
4.267
4.250
4.233
4.037
4.026
4.019
4.015
4.008
4.004
3.997
3.985
3.057
3.043
3.027
3.012
2.342
2.325
2.316
2.299
1.856
1.733
1.537
1.524
1.512
1.498
1.317
1.277
H
O
Me
O
O
32a
0.99
1.00
0.96
1.00
2.00
1.01
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

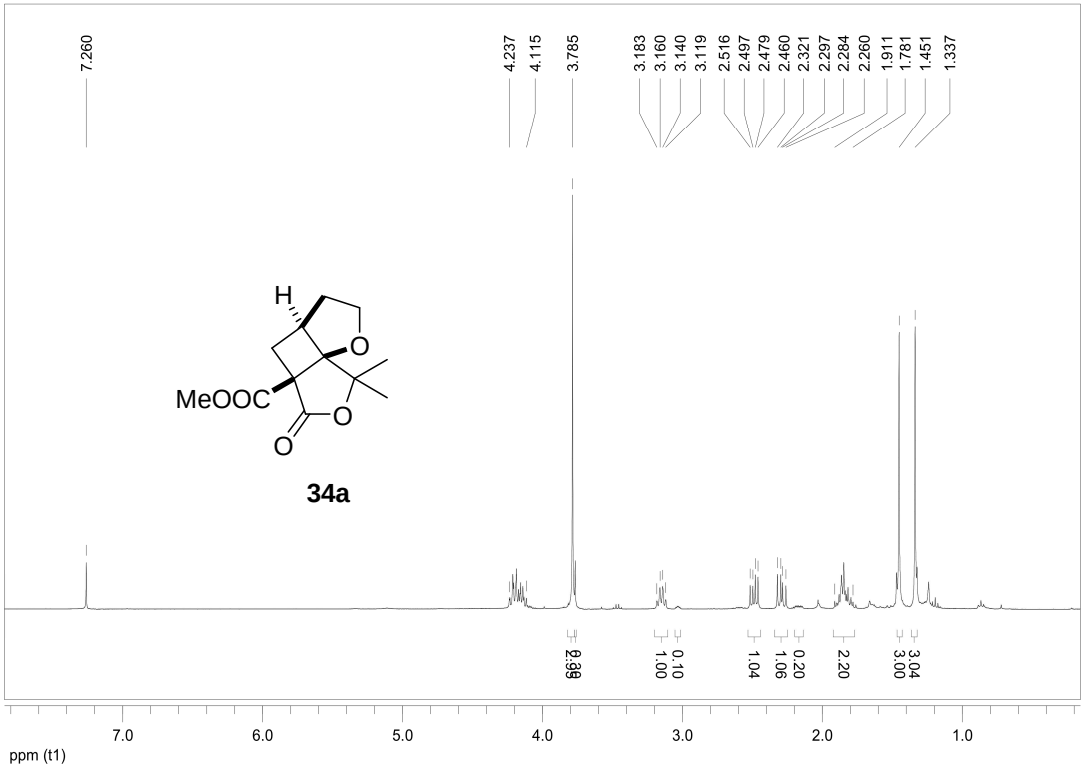

180.398
92.350
83.563
77.000
69.404
45.796
36.281
32.766
30.860
24.186
20.627
16.147
H
O
Me
O
O
32a
200
150
100
50
0
ppm (t1)

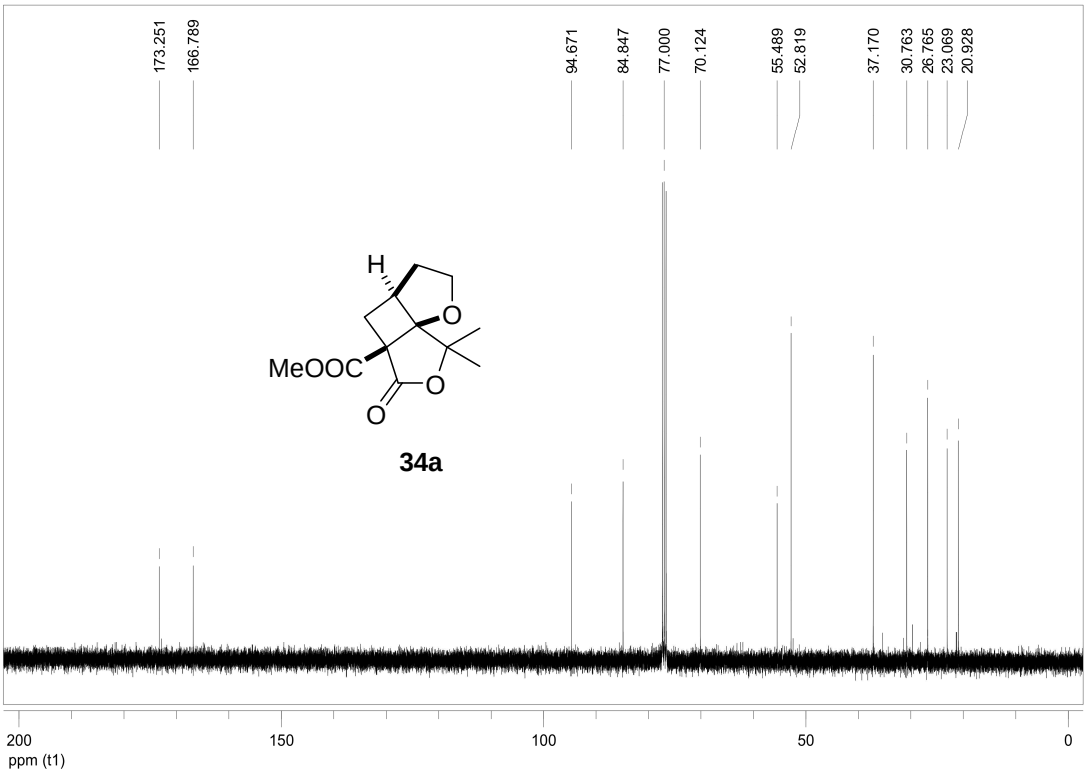

Me
O
O
O
32b
f1 (ppm)

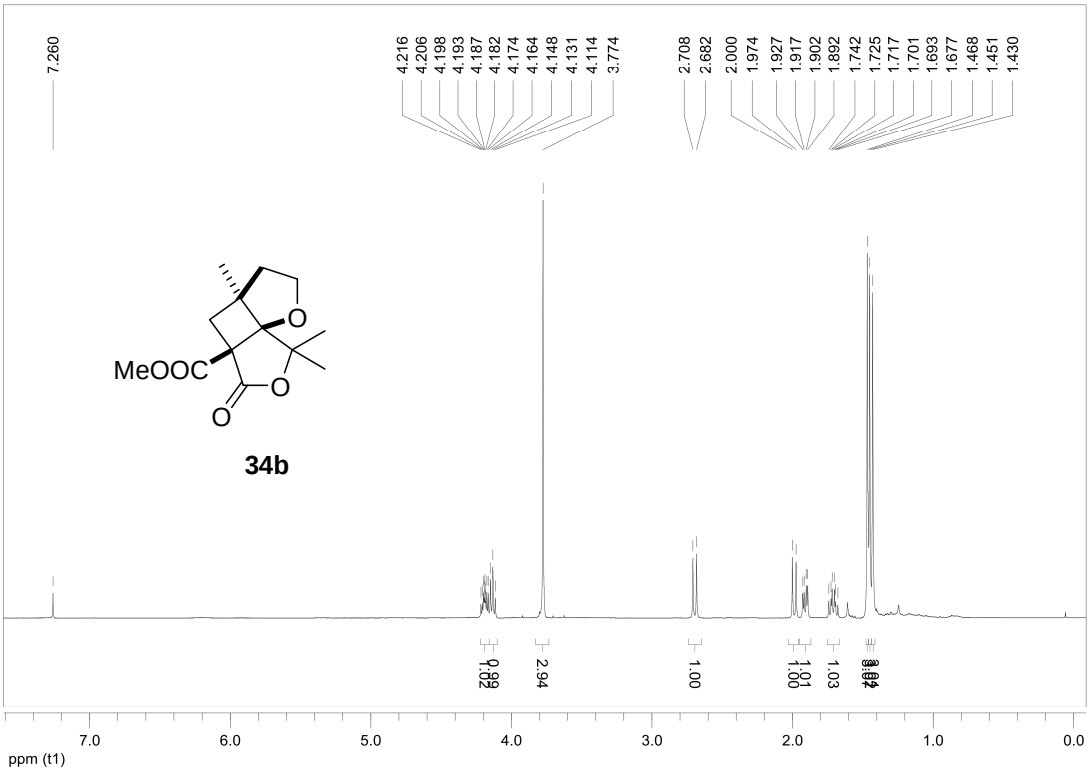

Me
O
O
O
32b
f1 (ppm)

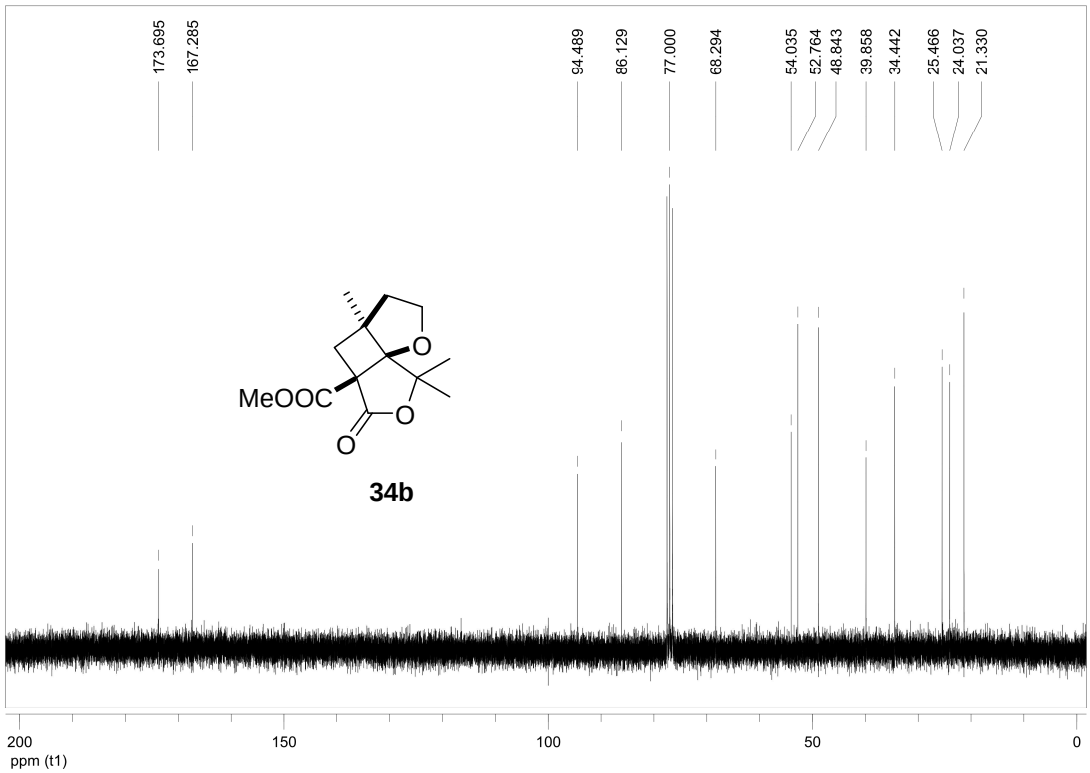

7.29
4.09
4.07
4.04
4.03
4.00
3.82
2.26
2.23
2.20
2.09
2.07
2.05
1.65
1.49
1.37
1.22
1.09
O
COOMe
O
O
33
2.00
3.08
1.03
1.10
3.09
3.04
3.01
3.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

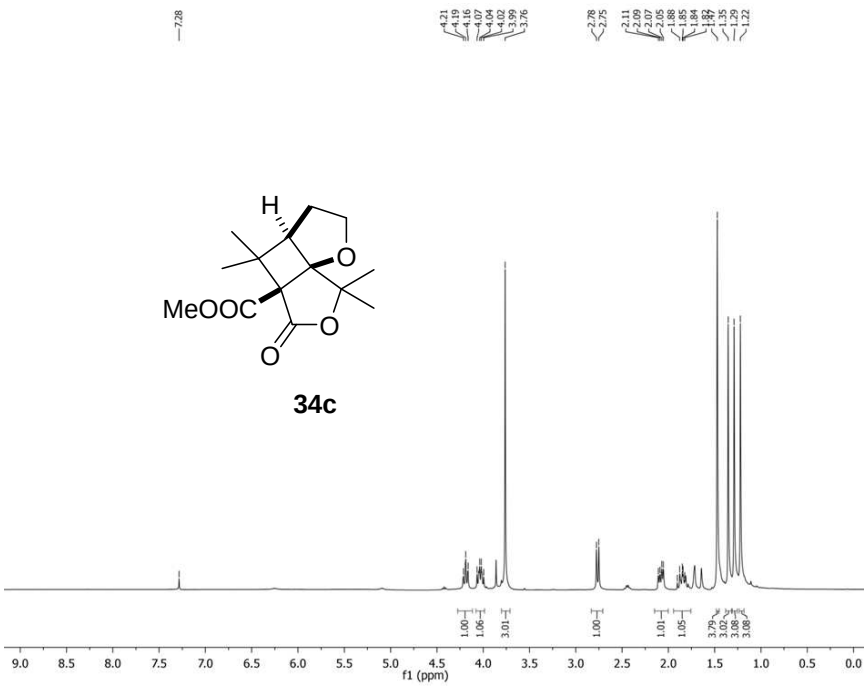

172.20
167.83
91.69
87.01
63.14
59.34
52.73
50.98
46.63
34.15
24.70
22.56
21.58
19.85
14.88
O
COOMe
O
O
33
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.260
4.237
4.115
3.785
3.183
3.160
3.140
3.119
2.516
2.497
2.479
2.460
2.321
2.297
2.284
2.260
1.911
1.781
1.451
1.337
MeOOC
34a
2.99
0.10
1.00
1.04
1.06
0.20
2.20
3.00
3.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

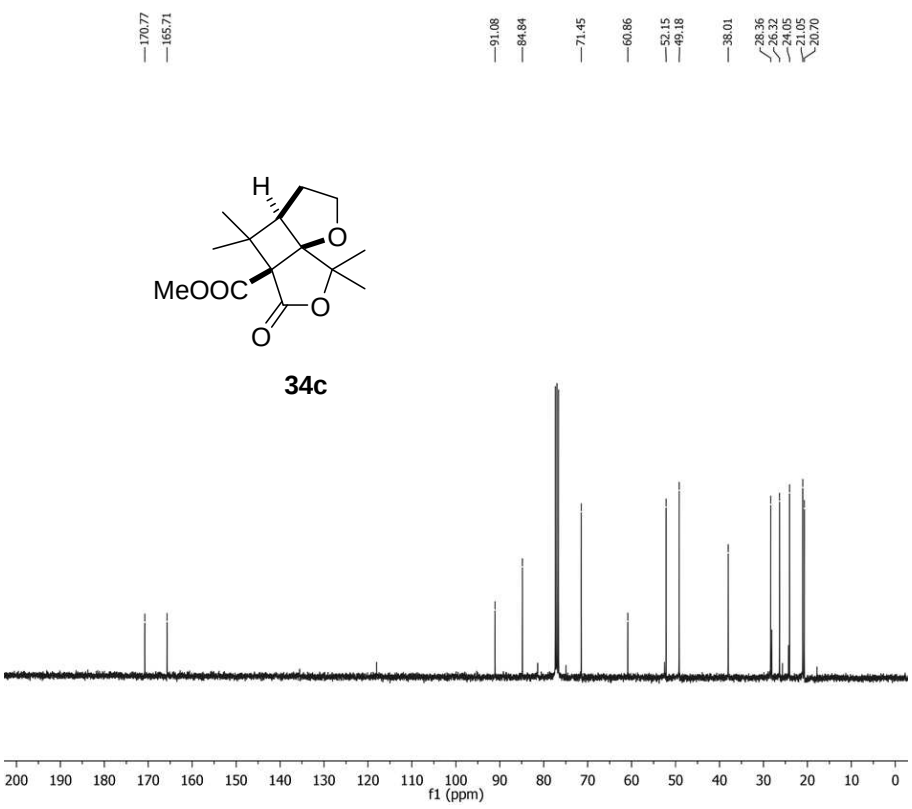

173.251
166.789
94.671
84.847
77.000
70.124
55.489
52.819
37.170
30.763
26.765
23.069
20.928
MeOOC
34a
200
150
100
50
0
ppm (t1)


7.260
4.216
4.206
4.198
4.193
4.187
4.182
4.174
4.164
4.148
4.131
4.114
3.774
2.708
2.682
2.000
1.974
1.927
1.917
1.902
1.892
1.742
1.725
1.717
1.701
1.693
1.677
1.468
1.451
1.430
MeOOC
O
O
O
34b
0.98
2.94
1.00
1.01
1.00
1.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

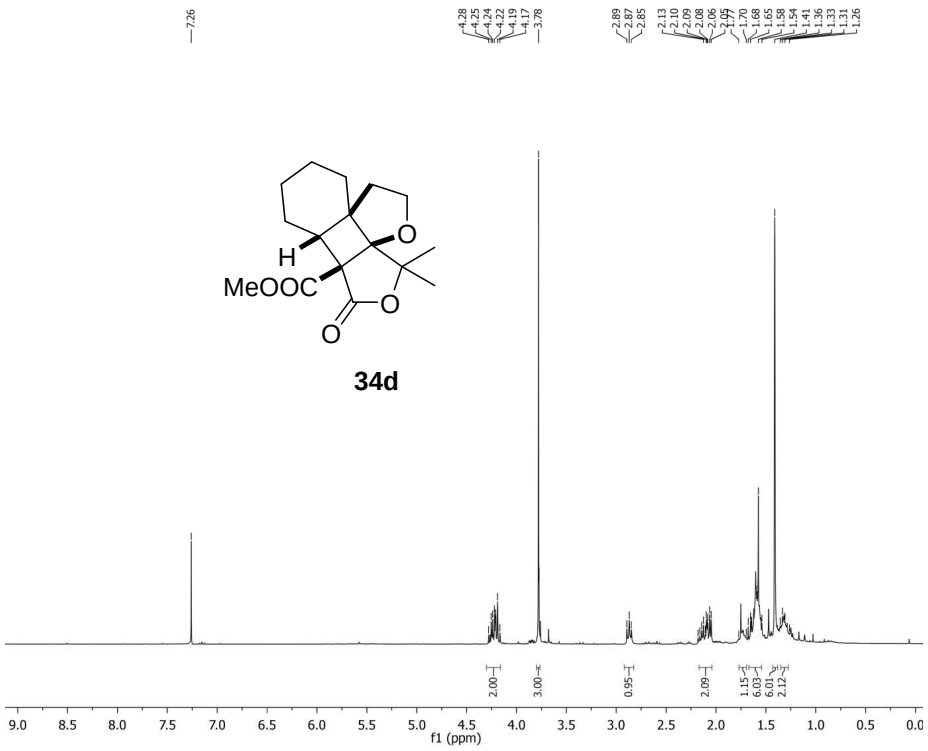

173.695
167.285
94.489
86.129
77.000
68.294
54.035
52.764
48.843
39.858
34.442
25.466
24.037
21.330
MeOOC
O
O
O
34b
200
150
100
50
0
ppm (t1)


7.28
4.21
4.19
4.16
4.07
4.04
4.02
3.99
3.76
2.78
2.75
2.11
2.09
2.07
2.05
1.88
1.85
1.84
1.35
1.29
1.22
H
O
MeOOC
O
O
1.00
1.06
3.01
1.00
1.01
1.05
3.79
3.02
3.08
3.08
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 0.0
f1 (ppm)

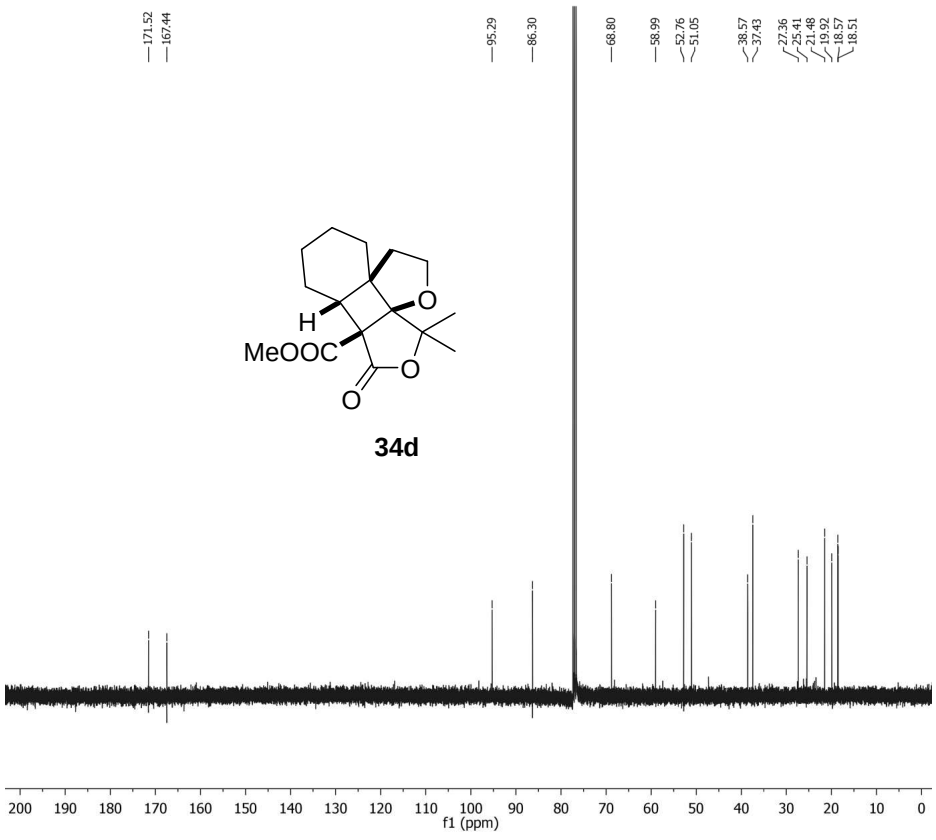
34c


170.77
165.71
91.08
84.84
71.45
60.86
52.15
49.18
38.01
28.36
26.32
24.05
21.05
20.70
H
O
MeOOC
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

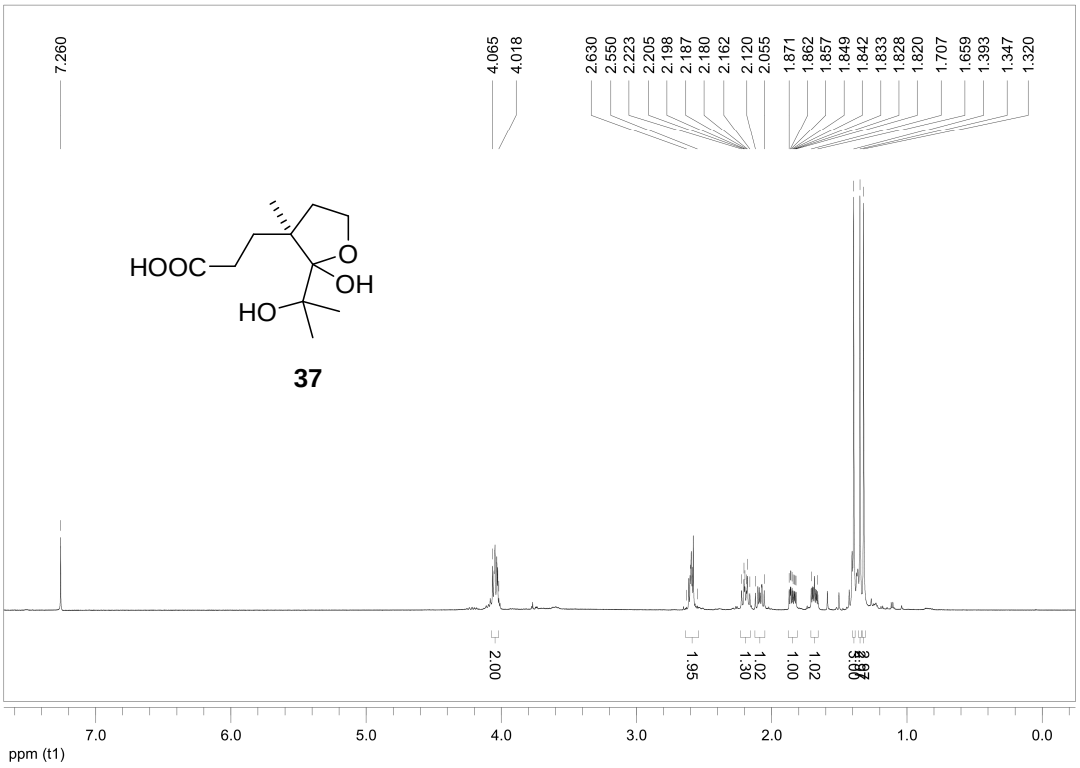
34c

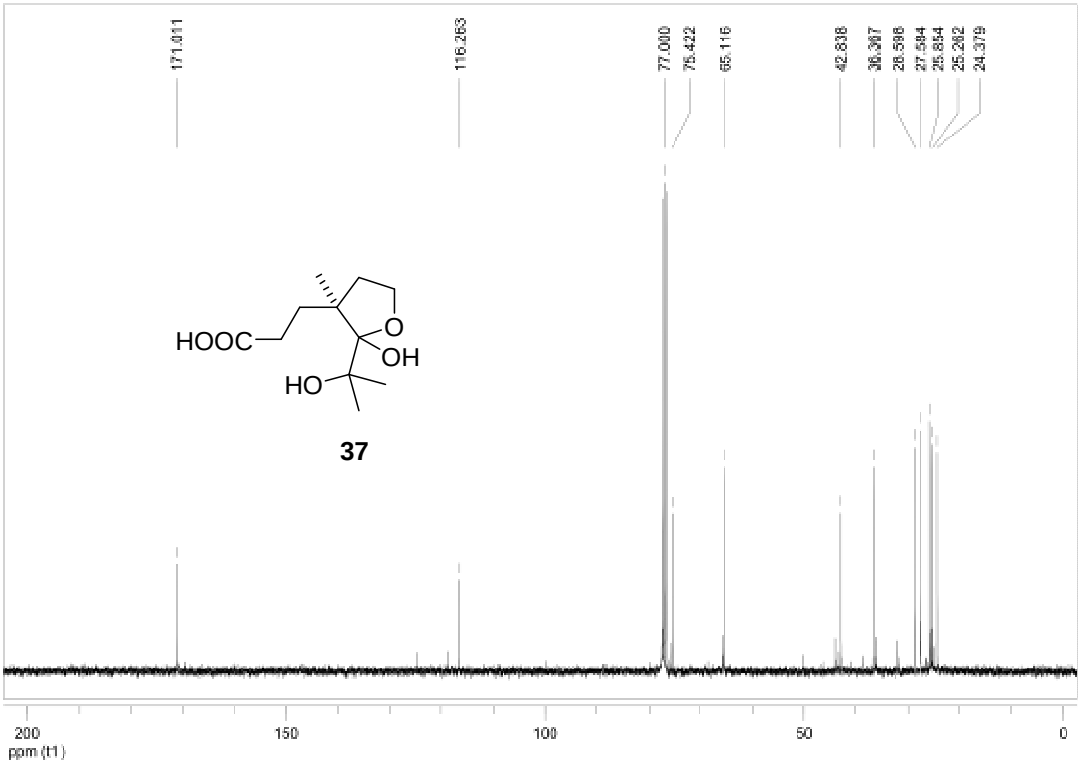

7.26
4.28
4.25
4.24
4.22
4.19
4.17
3.78
2.89
2.87
2.85
2.13
2.10
2.09
2.08
2.06
1.70
1.68
1.65
1.58
1.54
1.41
1.36
1.33
1.31
1.26
H
MeOOC
O
O
O
2.00
3.00
0.95
2.09
1.15
6.03
6.01
2.12
f1 (ppm)

34d


171.52
167.44
95.29
86.30
68.80
58.99
52.76
51.05
38.57
37.43
27.36
25.41
21.48
19.92
18.57
18.51
H
MeOOC
O
O
O
f1 (ppm)

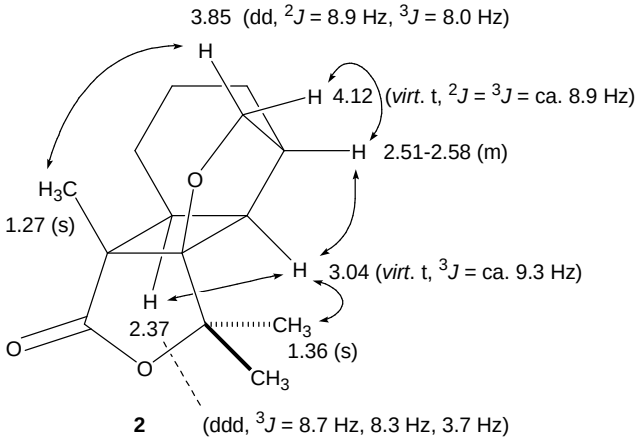
34d


7.260
4.065
4.018
2.630
2.550
2.223
2.205
2.198
2.187
2.180
2.162
2.120
2.055
1.871
1.862
1.857
1.849
1.842
1.833
1.828
1.820
1.707
1.659
1.393
1.347
1.320
HOOC
O
OH
HO
37
2.00
1.95
1.02
1.30
1.00
1.02
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


171.011
116.263
77.000
76.422
65.116
42.838
36.387
28.598
27.584
25.854
25.282
24.379
HOOC
O
OH
HO
37
200
150
100
50
0
ppm (t1)

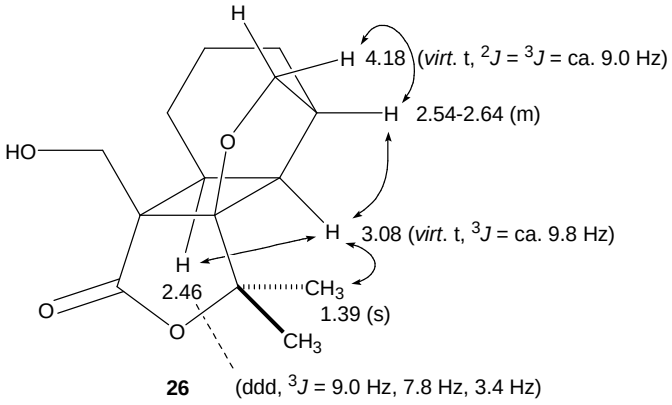
2. Structural assignments of photocycloaddition products **2**, **4**, **26**-**29**, **32a**-**b**, **33**, **34a,c,c**

Double ended arrows indicate NOE contacts



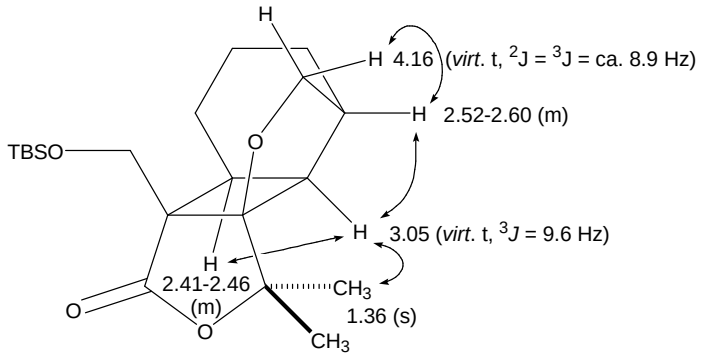
2

for experimental details and analytical data, see: Hehn, J. P.; Herdtweck, E.; Bach, T. *Org. Lett.* **2011**, *13*, 1892-1895.

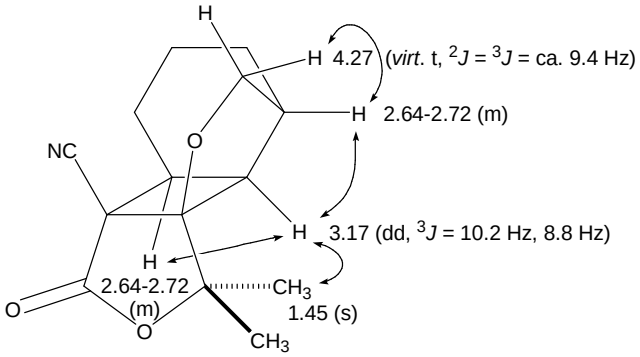


26

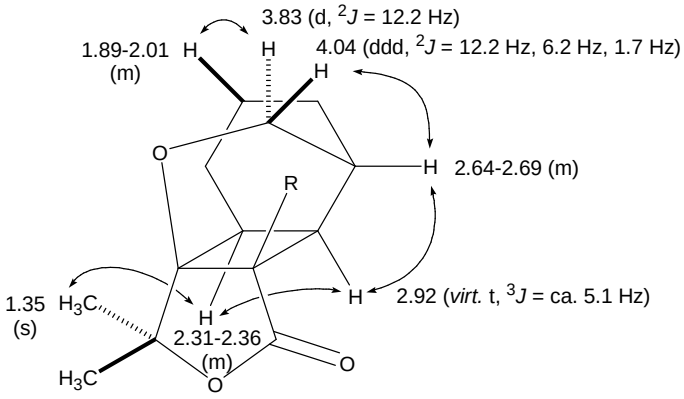
for experimental details and analytical data, see: Hehn, J. P.; Herdtweck, E.; Bach, T. *Org. Lett.* **2011**, *13*, 1892-1895.



27

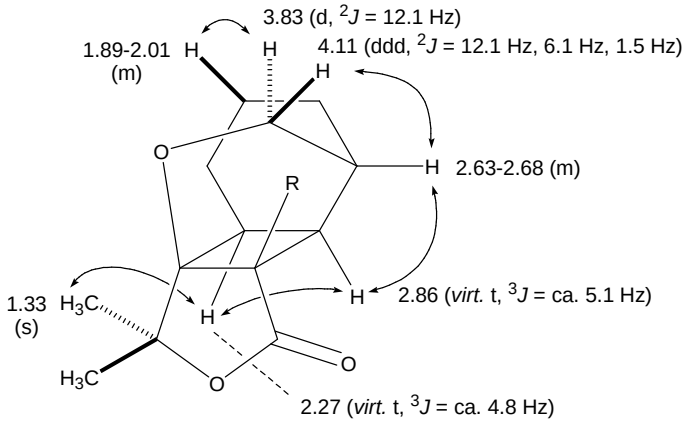


28

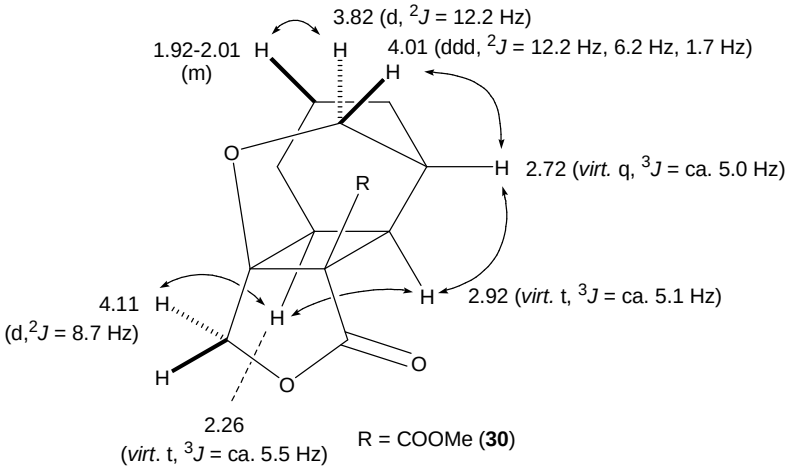


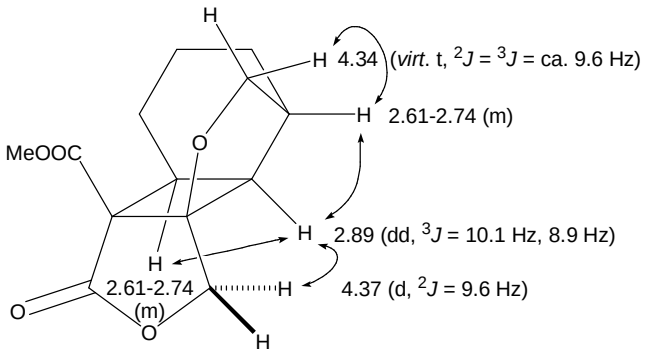
R = COOMe (**4**)

for experimental details and analytical data, see: Hehn, J. P.; Herdtweck, E.; Bach, T. *Org. Lett.* **2011**, *13*, 1892-1895.

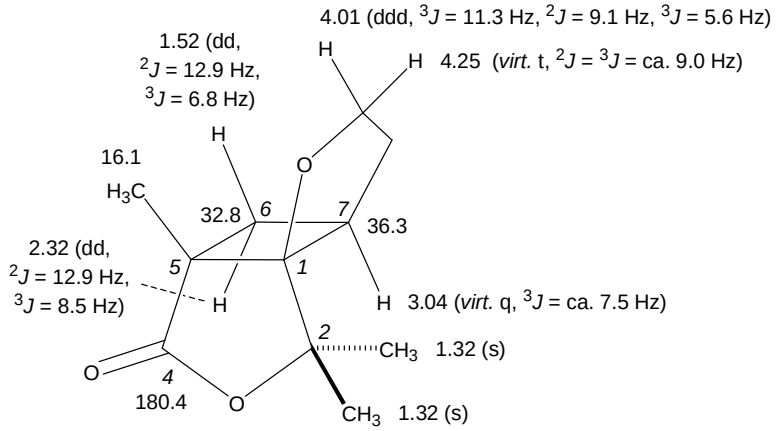


R = COO*t*-Bu (**29**)


3.82 (d, ^2J = 12.2 Hz)
1.92-2.01 (m)
4.01 (ddd, ^2J = 12.2 Hz, 6.2 Hz, 1.7 Hz)
2.72 (*virt.* q, ^3J = ca. 5.0 Hz)
2.92 (*virt.* t, ^3J = ca. 5.1 Hz)
4.11 (d, ^2J = 8.7 Hz)
2.26 (*virt*. t, ^3J = ca. 5.5 Hz)
R = COOMe (**30**)


4.34 (*virt*. t, ^2J = ^3J = ca. 9.6 Hz)
2.61-2.74 (m)
MeOOC
2.89 (dd, ^3J = 10.1 Hz, 8.9 Hz)
2.61-2.74 (m)
4.37 (d, ^2J = 9.6 Hz)

31



32a

Characteristic HMBC signals for compound **32a**:

C1 ↔ C7-**H**

C2 ↔ C7-**H**

C5-**C**H_3 does not couple with C7-**H**

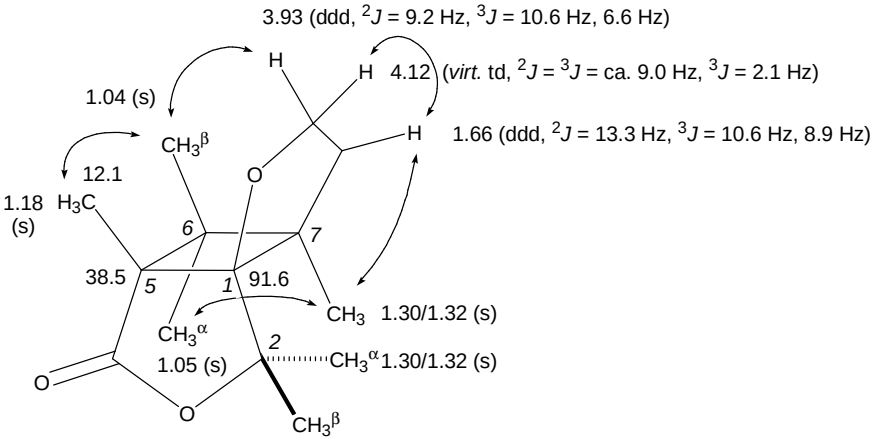
C4 does not couple with C7-**H**

C5-**C**H_3 ↔ C6-$\mathbf{H_2}$

C4 ↔ C6-$\mathbf{H_2}$

C6 ↔ C5-C$\mathbf{H_3}$

C7 does not couple with C5-C$\mathbf{H_3}$



32b

Characteristic HMBC signals for compound **32b**:

C1 ↔ C7-C**H$_3$**

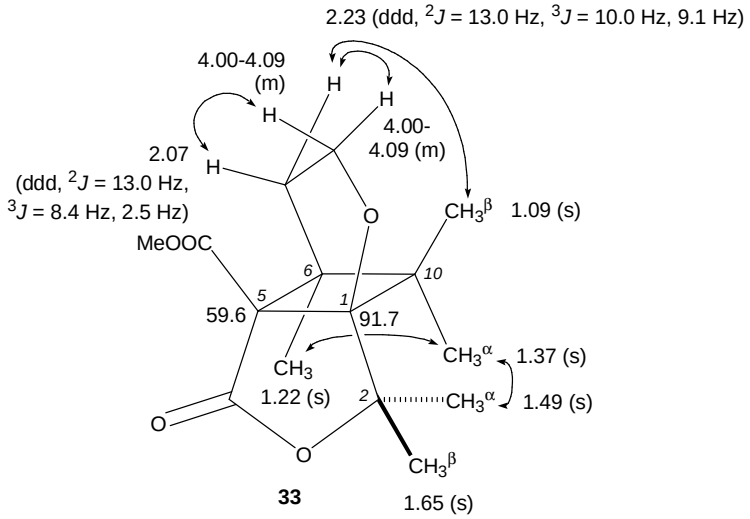
C1 does not couple with C6-C**H$_3^{\alpha}$**

C1 does not couple with C6-C**H$_3^{\beta}$**

C5 ↔ C6-C**H$_3^{\alpha}$**

C5 ↔ C6-C**H$_3^{\beta}$**

C5 does not couple with C7-C**H$_3^{\beta}$**



Characteristic HMBC signals for compound **33**:

C1 ↔ C10-C**H**$_3^{\alpha}$

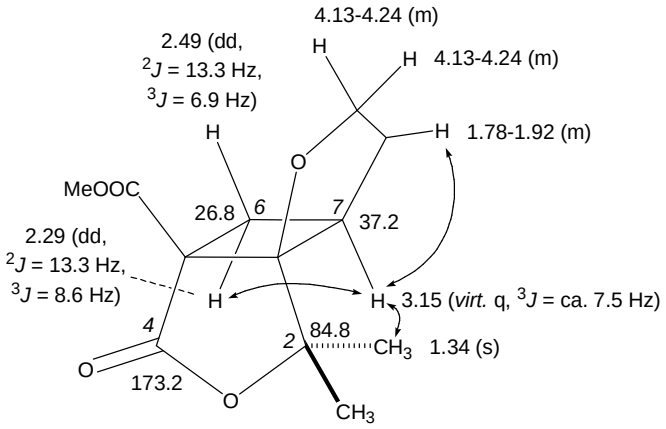
C1 ↔ C10-C**H**$_3^{\beta}$

C1 does not couple with C6-C**H**$_3$

C5 ↔ C6-C**H**$_3$

C5 does not couple with C10-C**H**$_3^{\alpha}$

C5 does not couple with C10-C**H**$_3^{\alpha}$



34a

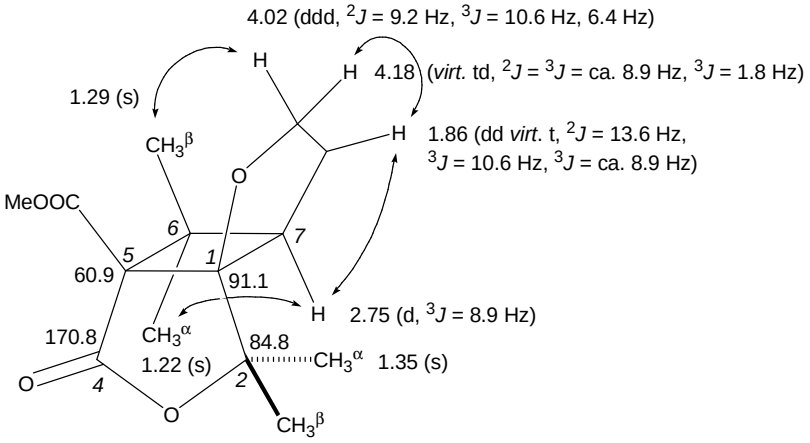
Characteristic HMBC signals for compound **34a**:

C2 ↔ C7-**H**

C2 does not couple with C6-$\mathbf{H_2}$

C4 ↔ C6-$\mathbf{H_2}$

C4 does not couple with C7-**H**



34c

Characteristic HMBC signals for compound **34c**:

C1 ↔ C7-**H**

C2 ↔ C7-**H**

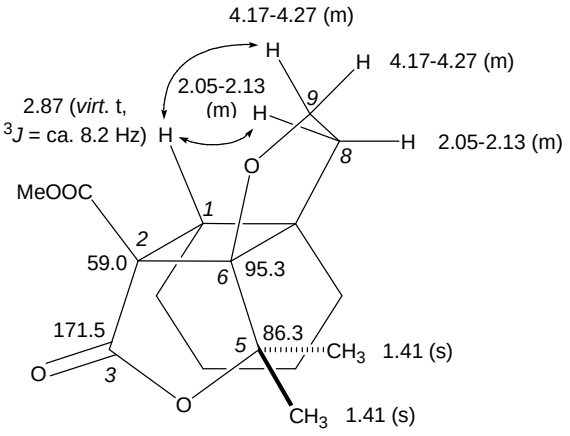
C4 does not couple with C7-**H**

C5 ↔ C6-C**H**$_3^{\alpha}$

C5 ↔ C6-C**H**$_3^{\beta}$

C1 does not couple with C6-C**H**$_3^{\alpha}$

C1 does not couple with C6-C**H**$_3^{\beta}$



34d

Characteristic HMBC signals for compound **34d**:

C2 ↔ C1-**H**

C2 does not couple with C8-**H**

C2 does not couple with C9-**H**

C6 ↔ C8-**H**

C6 ↔ C9-**H**

C3 ↔ C1-**H**

C5 does not couple with C1-**H**

C6 does not couple with C1-**H**