Supporting Information

Copper-Catalyzed Enantioselective Hetero-Diels-Alder Reaction of Danishefsky's Diene with Glyoxals

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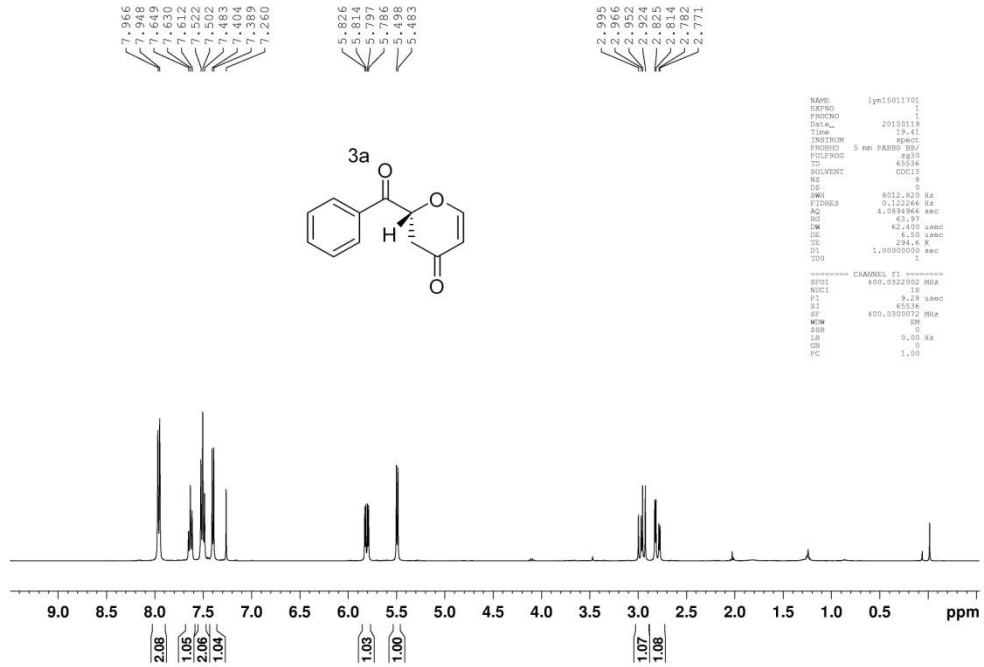

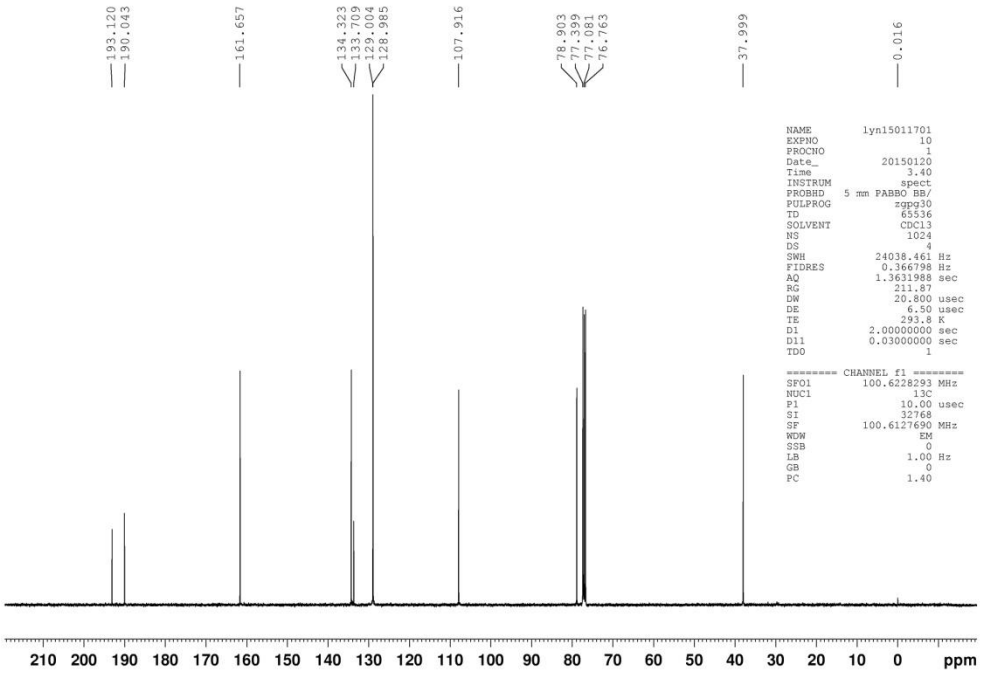

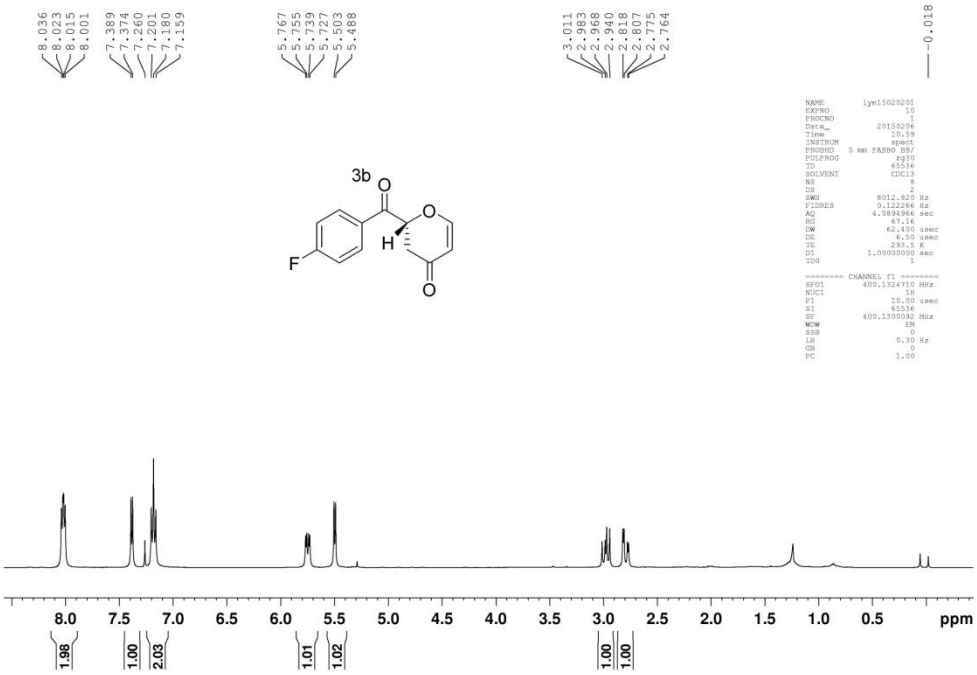
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5.727
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3.011
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H
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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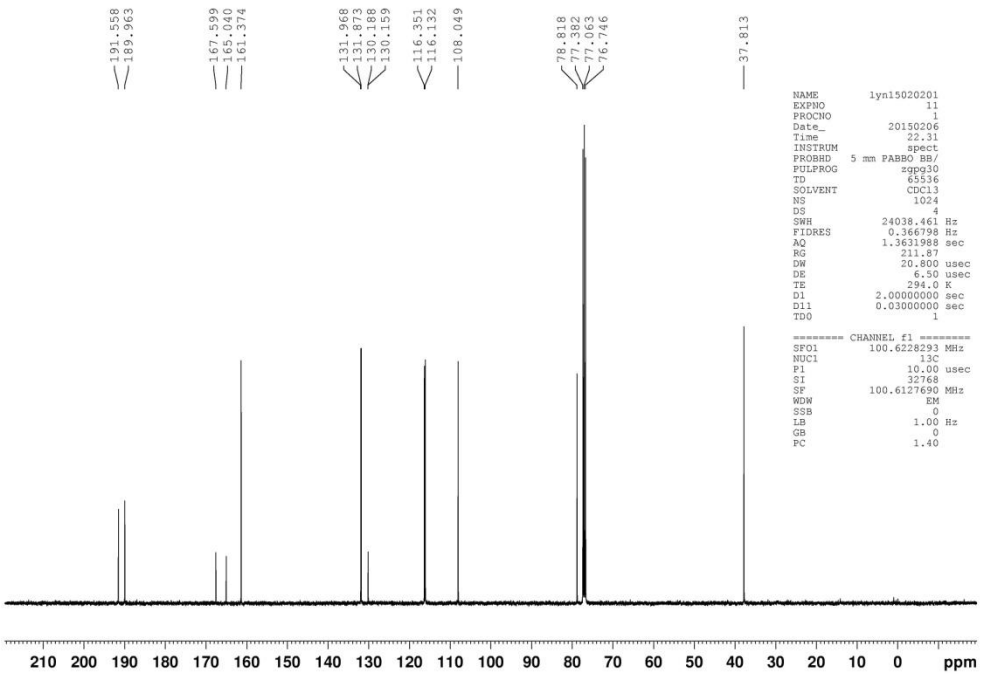
1.02
1.00
1.00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D11 0.03000000 sec
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LB 1.00 Hz
GB 0
PC 1.40
210
200
190
180
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140
130
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110
100
90
80
70
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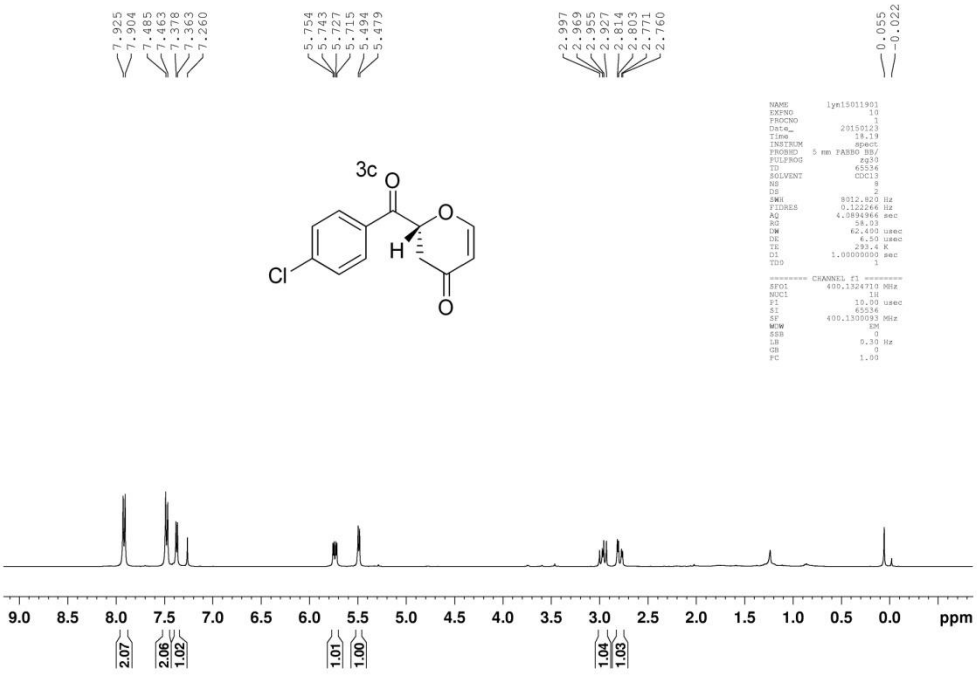
50
40
30
20
10
0
ppm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2.997
2.969
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2.803
2.771
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3c
O
O
H
Cl
O
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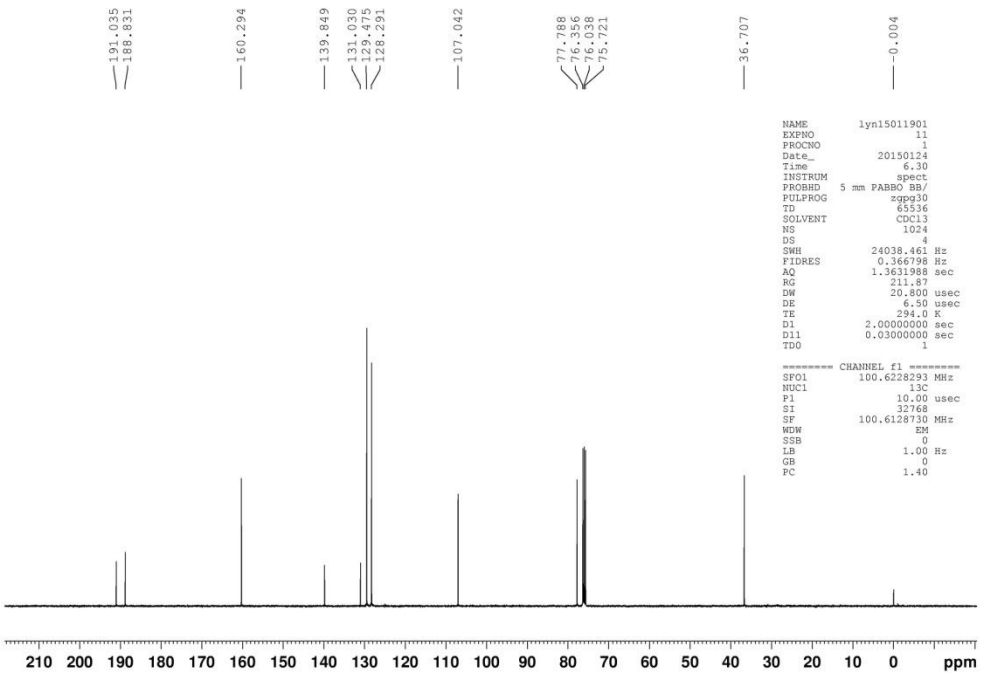
1.02
1.01
1.00
1.04
1.03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FIDRES 0.366798 Hz
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DE 6.50 usec
TE 294.0 K
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D11 0.03000000 sec
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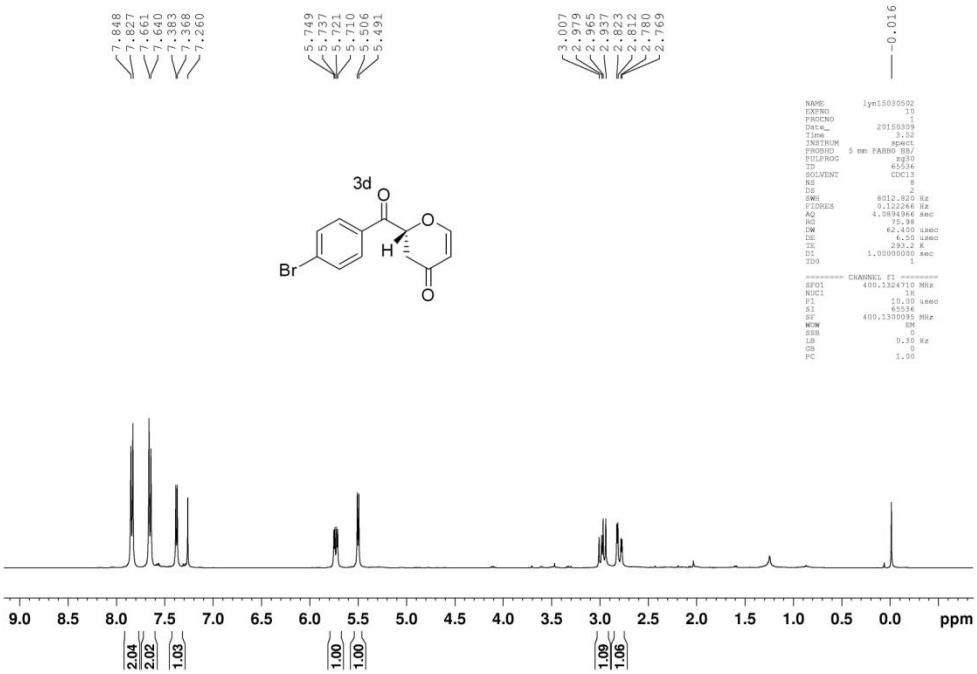
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2.822
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3d
Br
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PULPROG zg30
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SI 65536
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GB 0
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1.03
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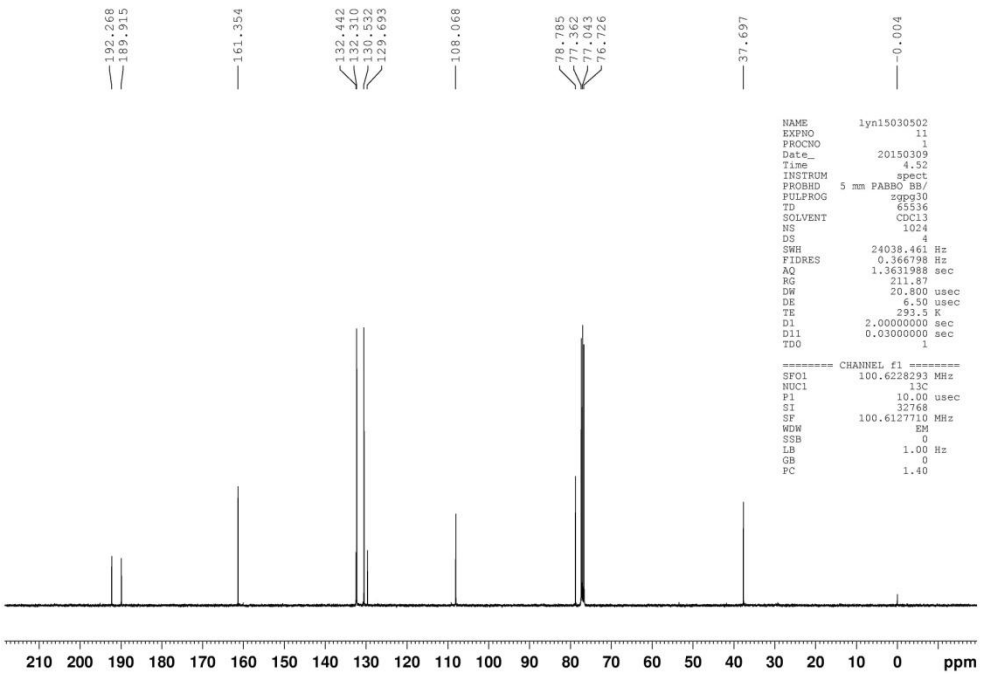
1.06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PULPROG zgpg30
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FIDRES 0.366798 Hz
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RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
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SI 32768
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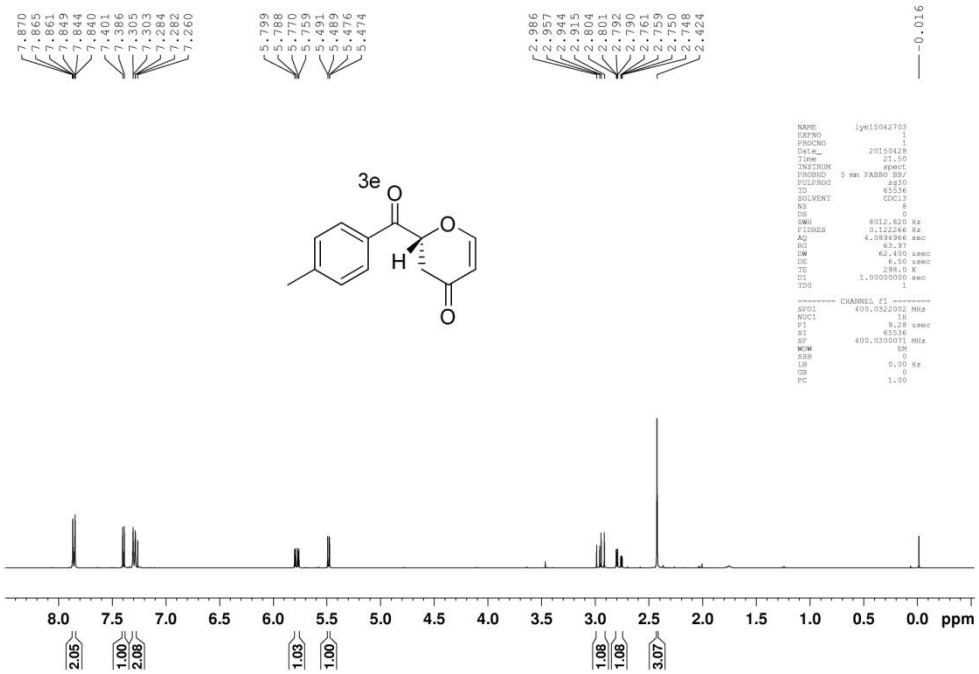
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2.944
2.915
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2.792
2.790
2.761
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O
H
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LB 0.00 Hz
GB 0
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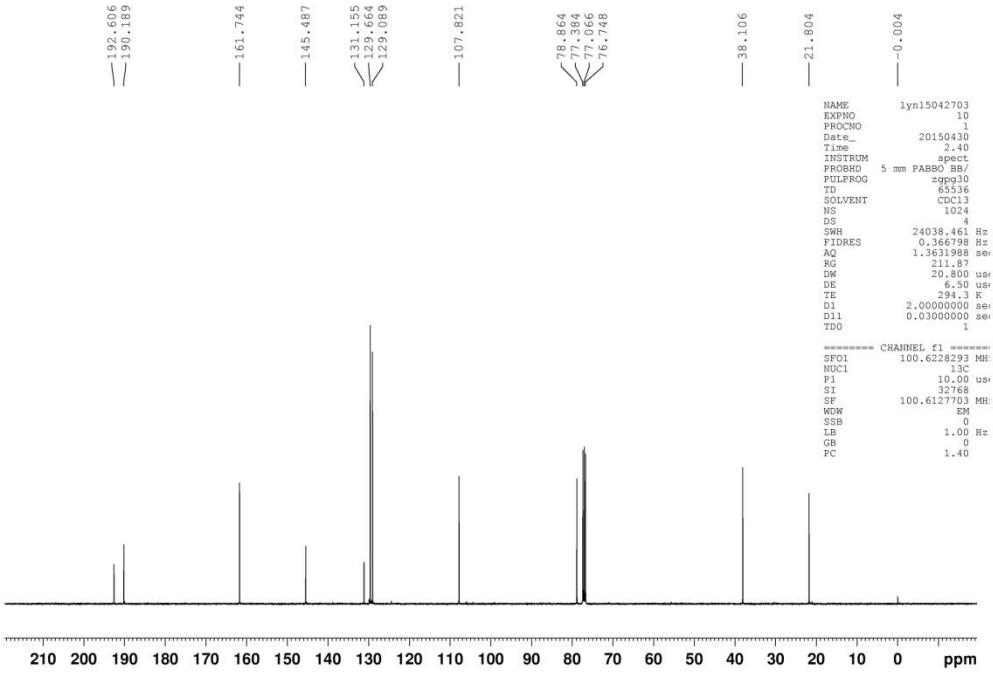
1.08
1.08
3.07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77.066
76.748
38.106
21.804
-0.004
NAME lyn15042703
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PROCNO 1
Date_ 20150430
Time 2.40
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PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 se
RG 211.87
DW 20.800 us
DE 6.50 us
TE 294.3 K
D1 2.00000000 se
D11 0.03000000 se
TD0 1
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NUC1 13C
P1 10.00 us
SI 32768
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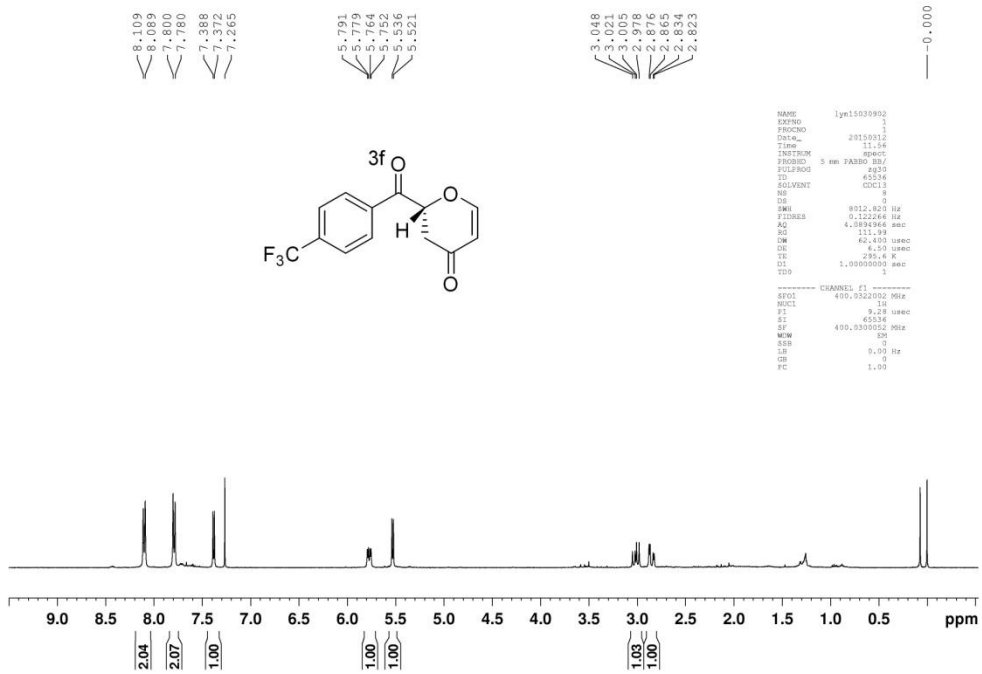
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5.521
3.048
3.021
3.005
2.978
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2.834
2.823
0.000
3f
O
O
H
F3C
O
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PROCNO 1
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Time 11.54
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PULPROG zg30
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DE 6.50 usec
TE 295.6 K
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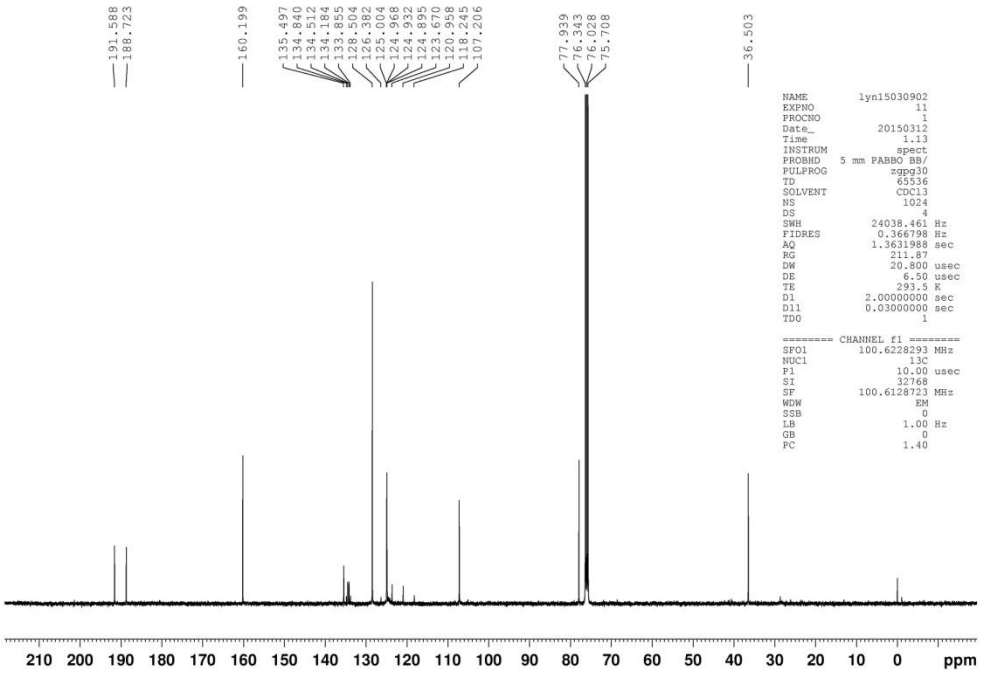
1.00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124.895
123.670
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77.939
76.343
76.028
75.708
36.503
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Time 1.13
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
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GB 0
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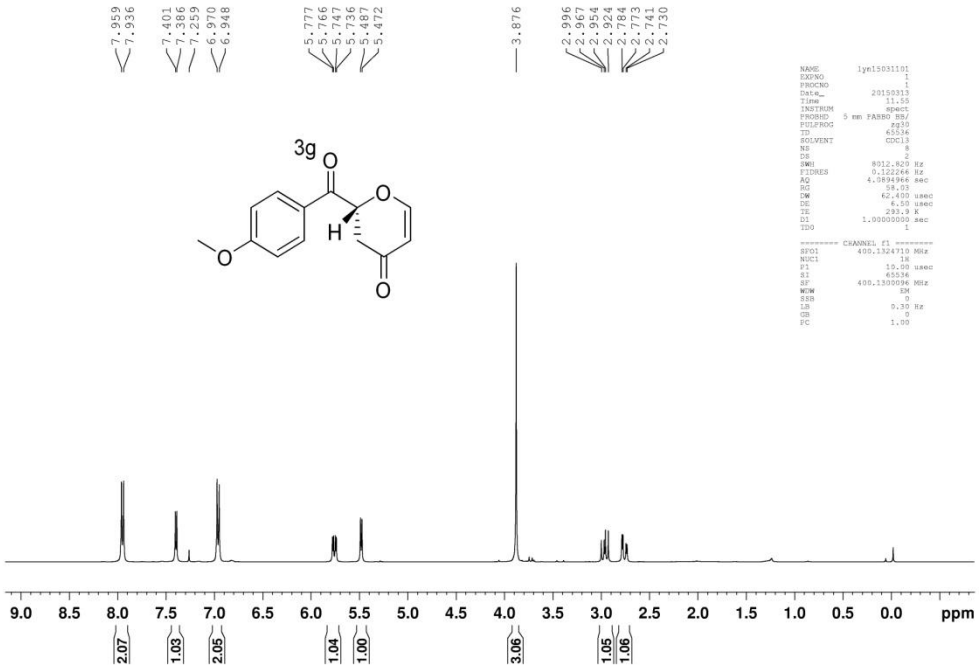
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O
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H
O
O
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PROCNO 1
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Time 11.55
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PULPROG zg30
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FIDRES 0.122266 Hz
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RG 58.03
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DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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NUC1 1H
P1 10.00 usec
SI 65536
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
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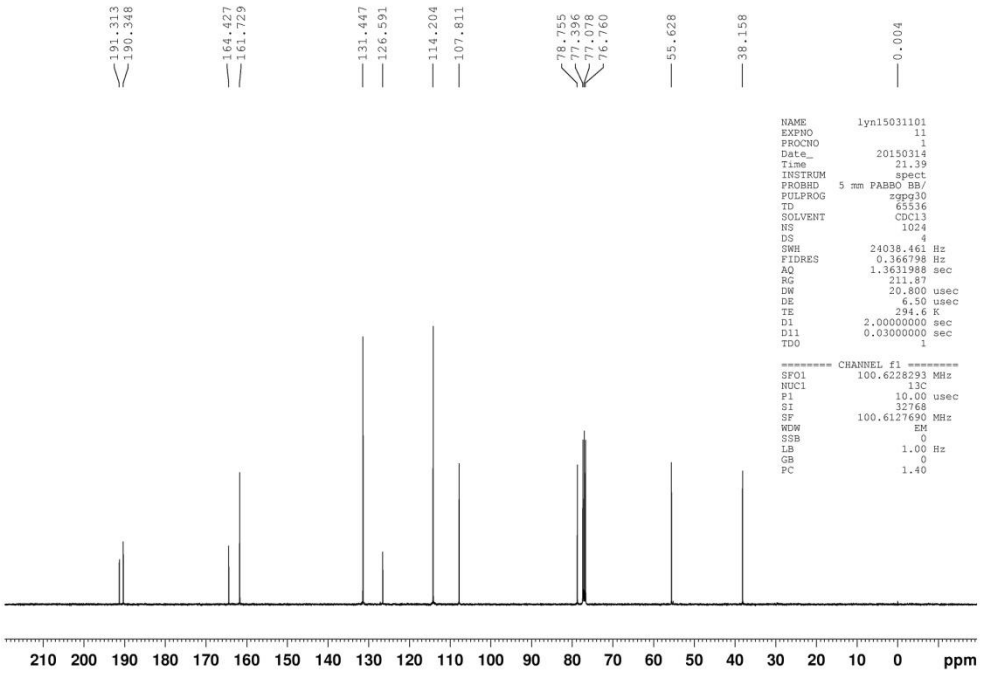
1.03
2.05
1.04
1.00
3.06
1.05
1.06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190.348
164.427
161.729
131.447
126.591
114.204
107.811
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77.396
77.078
76.760
55.628
38.158
0.004
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Time 21.39
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 294.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.61276690 MHz
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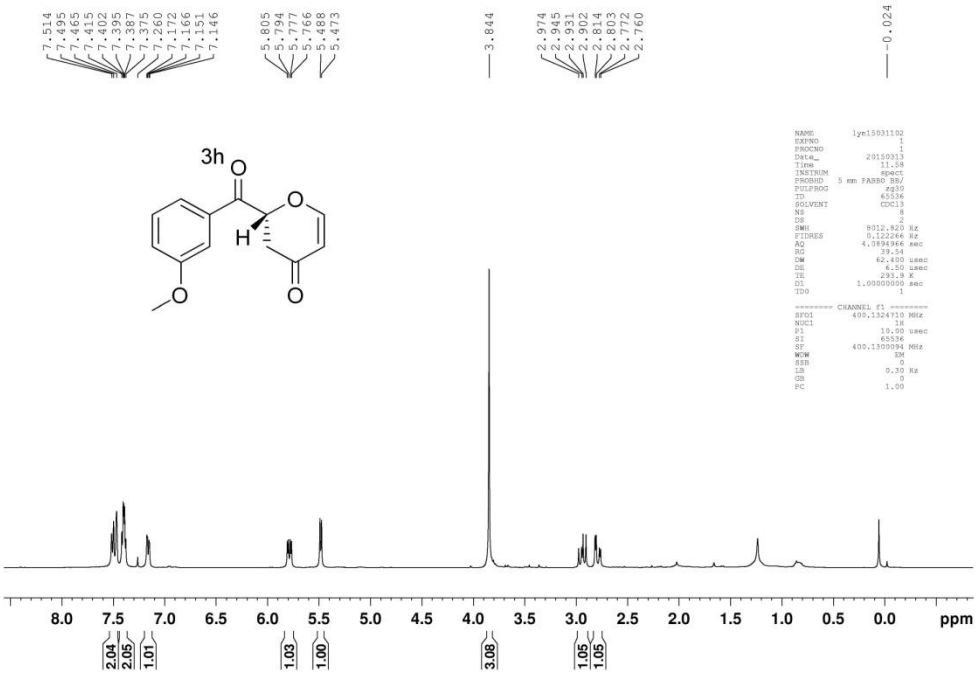
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7.415
7.402
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7.146
5.805
5.794
5.777
5.766
5.488
5.473
3.844
2.974
2.945
2.931
2.902
2.814
2.803
2.772
2.760
-0.024
3h
O
O
H
O
O
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SOLVENT CDCl3
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 39.54
DW 62.400 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
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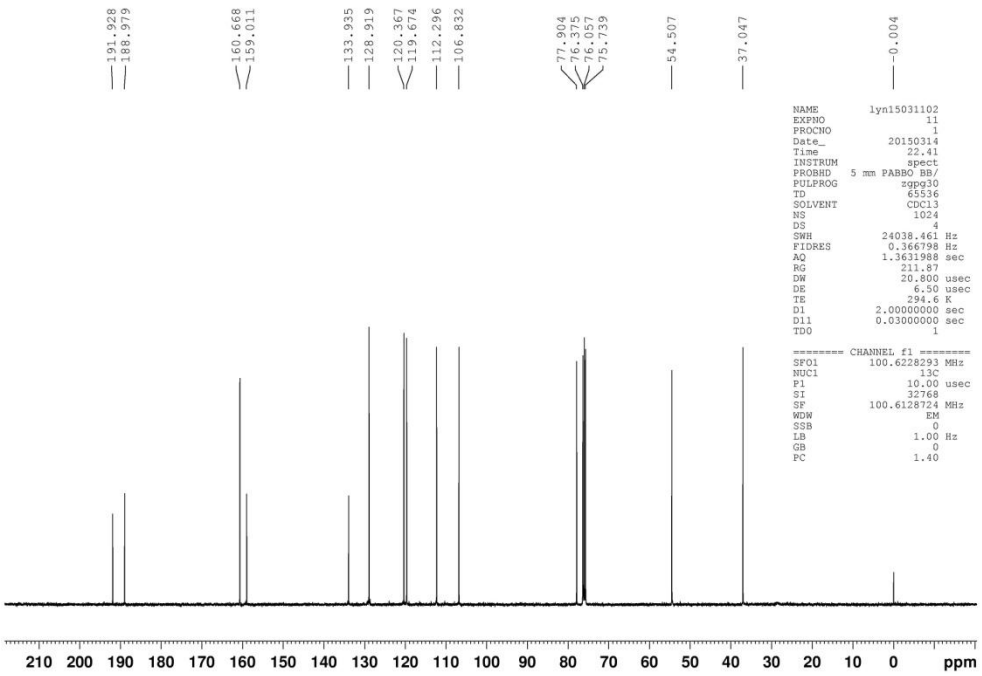
2.05
1.01
1.03
1.00
3.08
1.05
1.05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76.057
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 294.6 K
D1 2.00000000 sec
D11 0.03000000 sec
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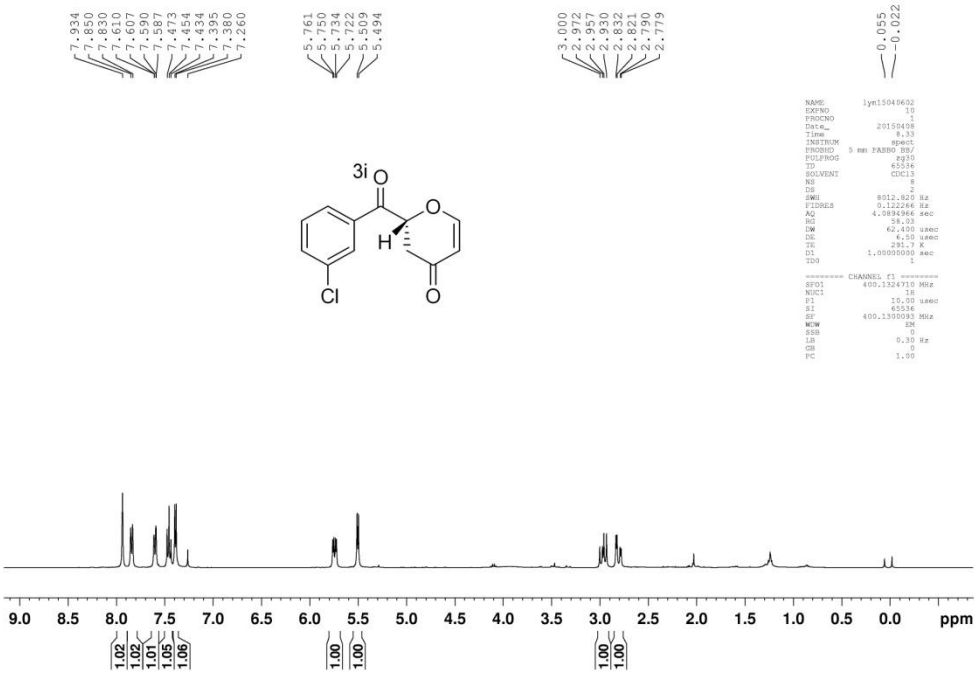
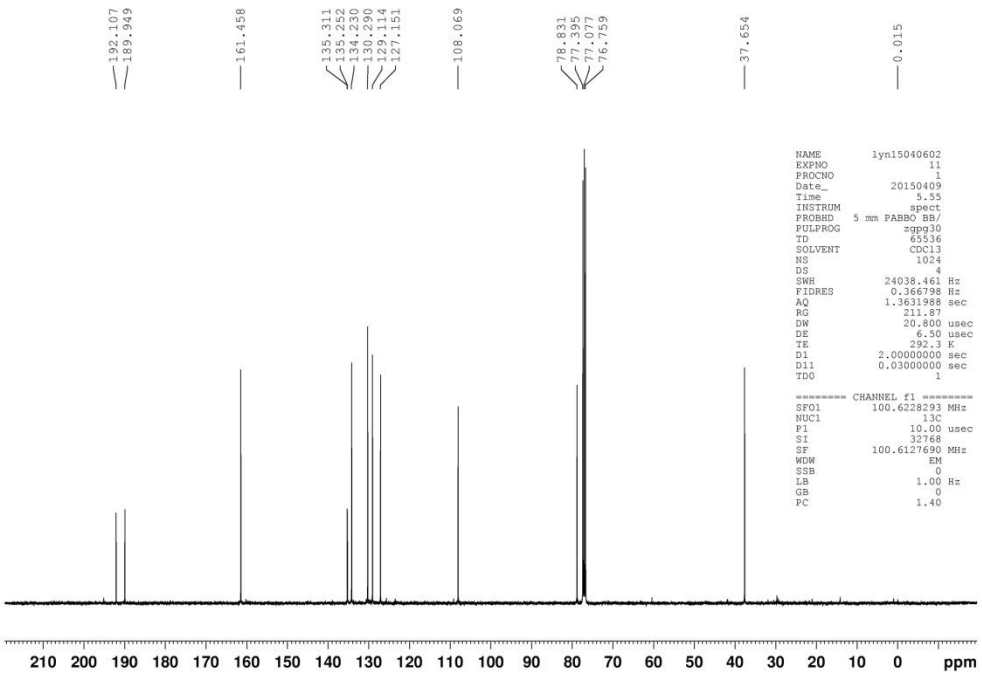
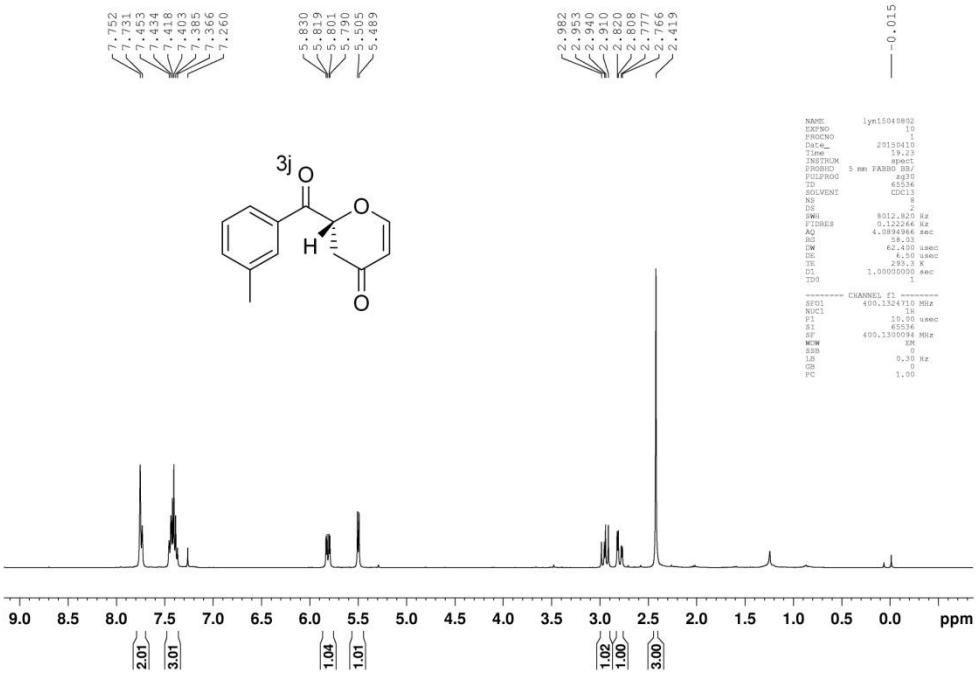
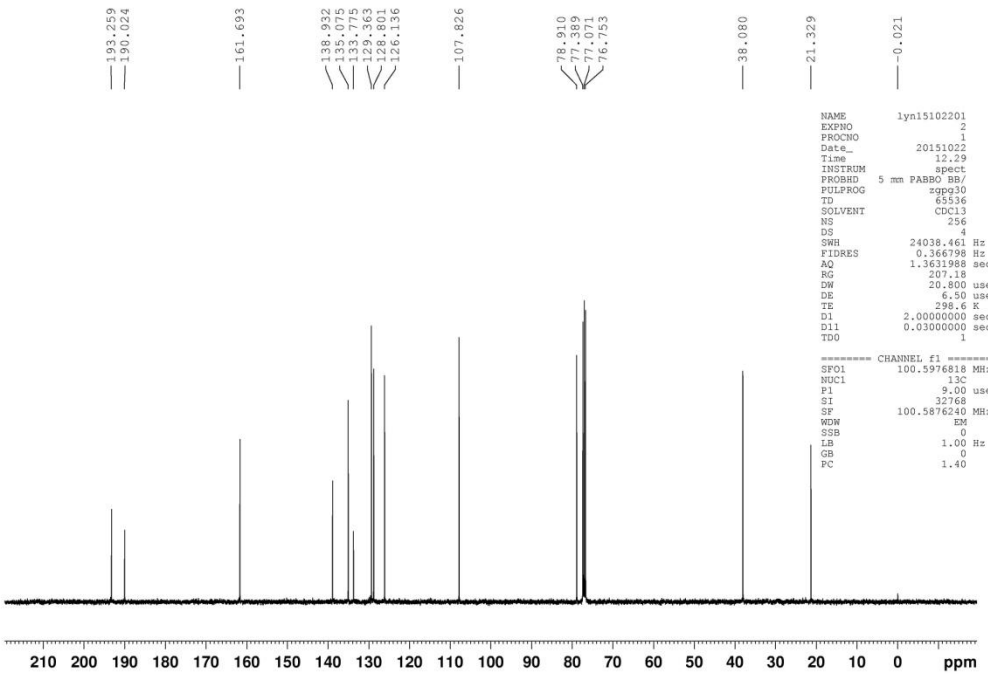
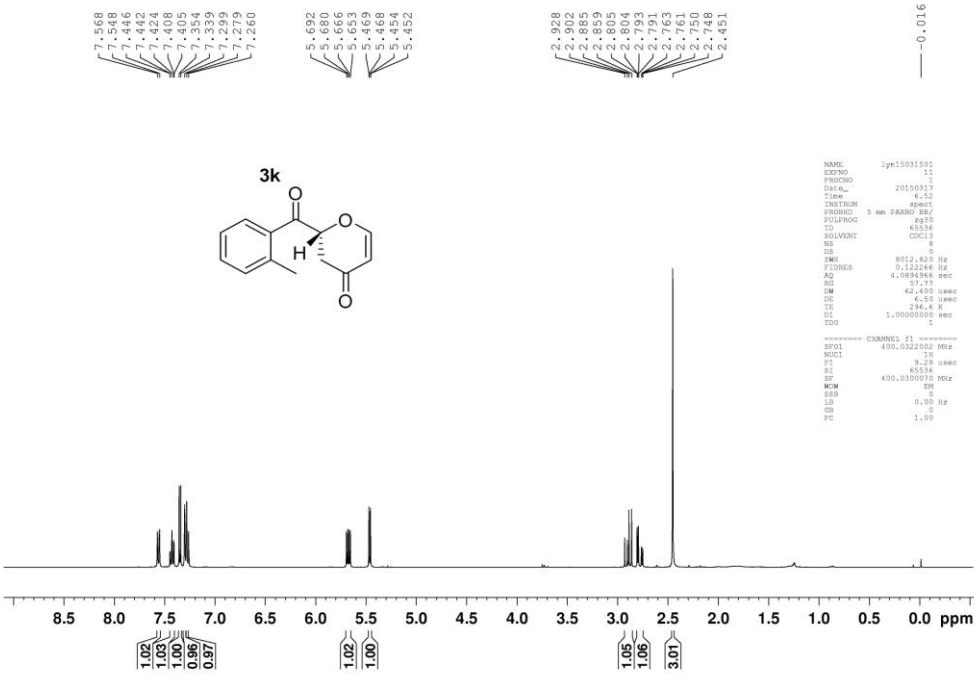
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6128724 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

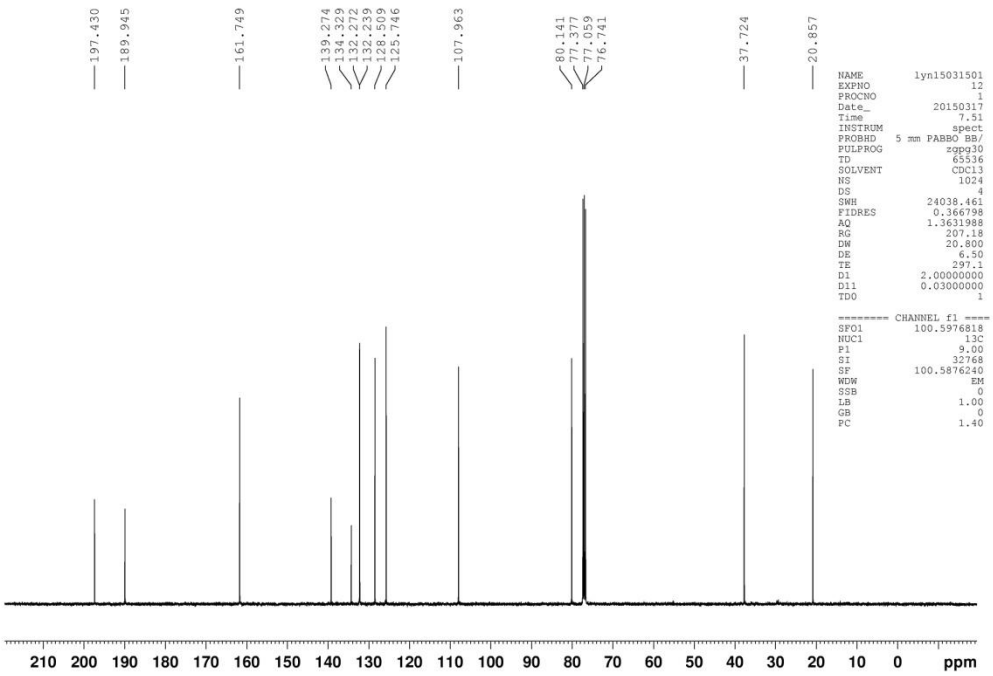

7.934
7.850
7.830
7.610
7.607
7.590
7.587
7.473
7.454
7.434
7.395
7.380
7.260
5.761
5.750
5.734
5.722
5.509
5.494
3.000
2.972
2.957
2.930
2.832
2.821
2.790
2.779
0.055
-0.022
3i
O
O
H
Cl
O
NAME lyn15040602
EXPNO 10
PROCNO 1
Date_ 20150408
Time 8.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894964 sec
RG 58.03
DW 62.400 usec
DE 6.50 usec
TE 291.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
1.02
1.02
1.01
1.05
1.06
1.00
1.00
1.00
1.00

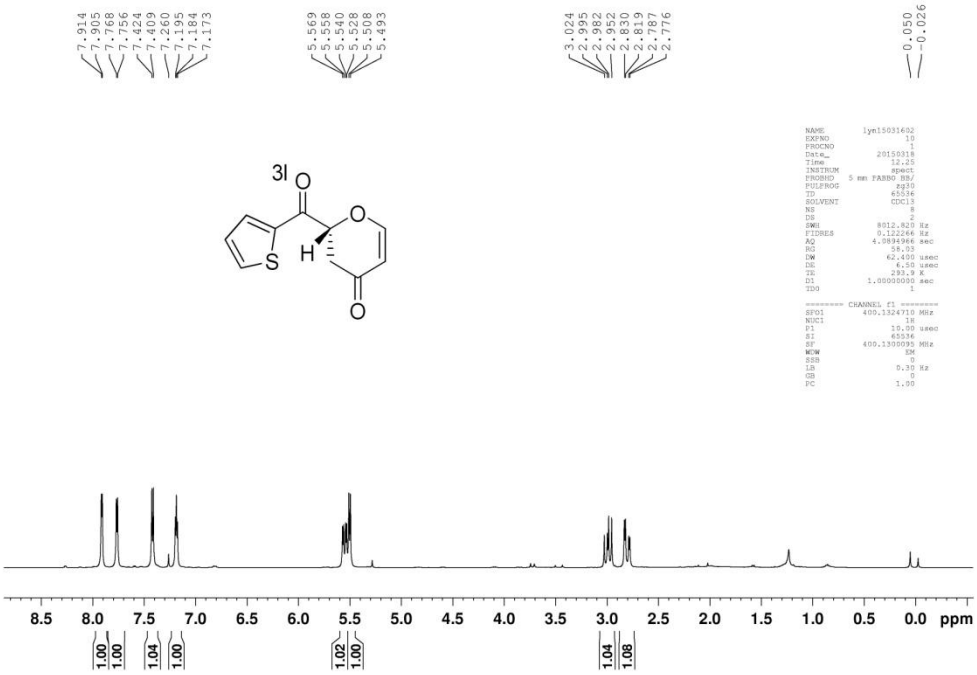

192.107
189.949
161.458
135.311
135.252
134.230
130.290
129.114
127.151
108.069
78.831
77.395
77.077
76.759
37.654
0.015
NAME lyn15040602
EXPNO 11
PROCNO 1
Date_ 20150409
Time 5.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 292.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

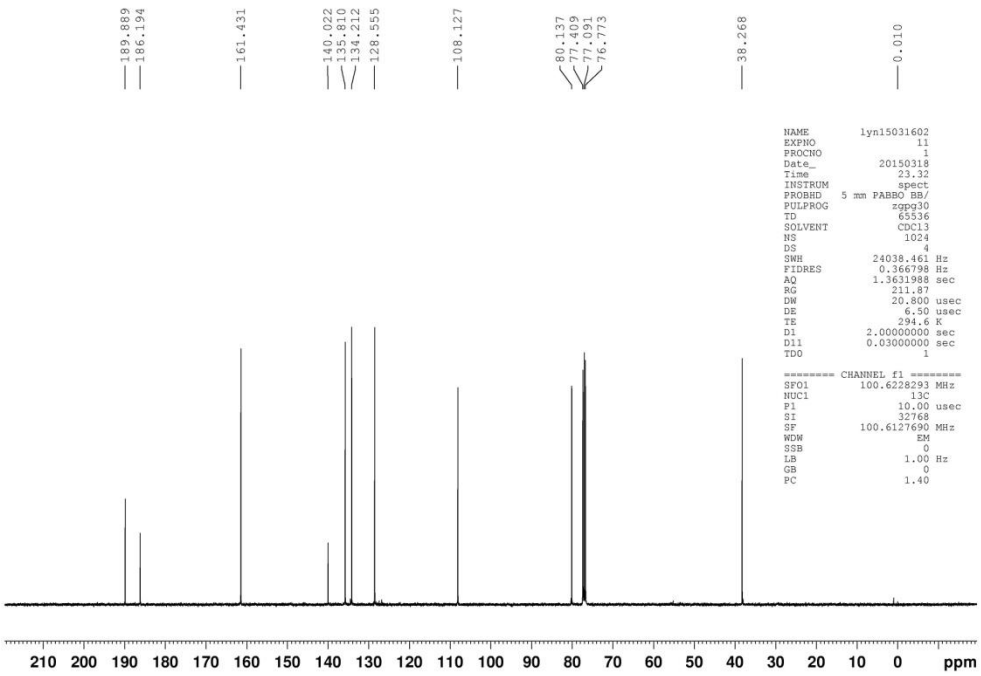

7.752
7.731
7.453
7.434
7.418
7.403
7.385
7.366
7.260
5.830
5.819
5.801
5.790
5.505
5.489
2.982
2.953
2.940
2.910
2.820
2.808
2.777
2.766
2.419
-0.015
3j
O
O
H
O
NAME lyn15040802
EXPNO 10
PROCNO 1
Date_ 20150410
Time 19.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 58.23
DW 62.450 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
2.01
3.01
1.04
1.01
1.02
1.00
3.00

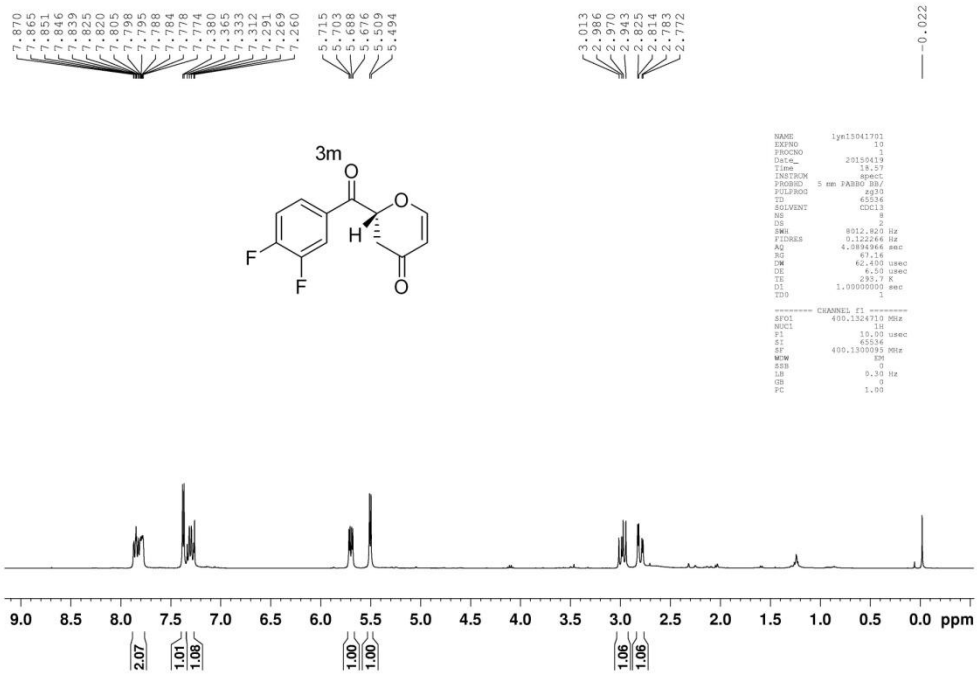

193.259
190.024
161.693
138.932
135.075
133.775
129.363
128.801
126.136
107.826
78.910
77.389
77.071
76.753
38.080
21.329
-0.021
NAME lyn15102201
EXPNO 2
PROCNO 1
Date_ 20151022
Time 12.29
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 207.18
DW 20.800 use
DE 6.50 use
TE 298.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ======
SFO1 100.5976818 MHz
NUC1 13C
P1 9.00 use
SI 32768
SF 100.5876240 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

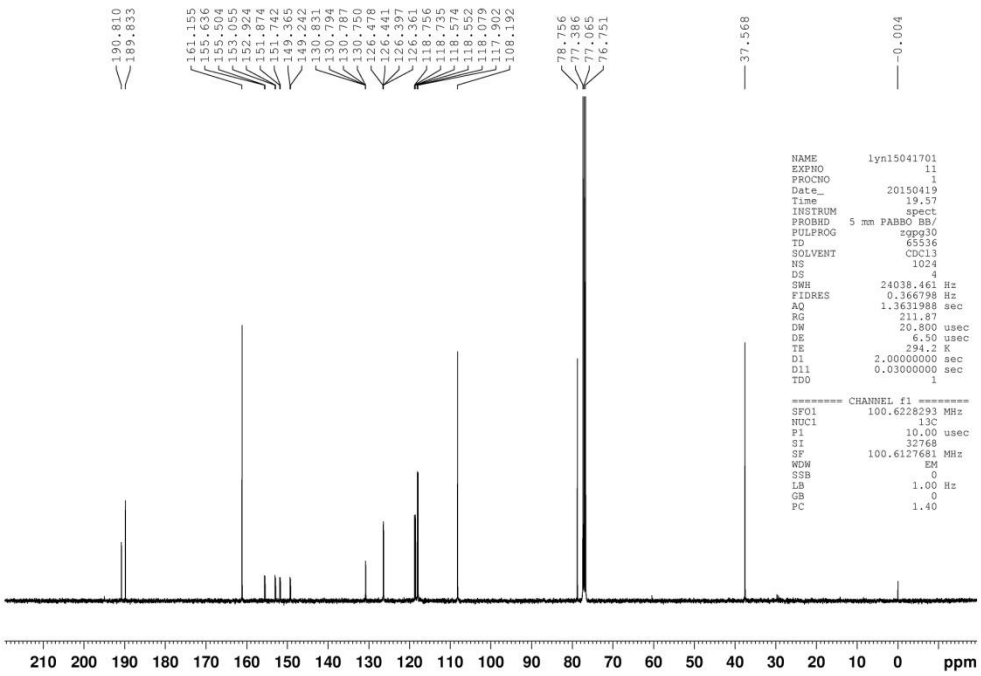

7.568
7.548
7.446
7.442
7.424
7.408
7.405
7.354
7.339
7.299
7.279
7.260
5.692
5.680
5.666
5.653
5.469
5.468
5.454
5.452
2.928
2.902
2.885
2.859
2.805
2.804
2.793
2.791
2.763
2.761
2.750
2.748
2.451
-0.016
3k
O
O
H
O
NAME lyn15031501
EXPNO 11
PROCNO 1
Date_ 20150317
Time 6.52
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 57.77
DW 62.400 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.0322002 MHz
NUC1 1H
P1 9.28 usec
SI 65536
SF 400.0300070 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
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 ppm
1.02
1.03
1.00
0.96
0.97
1.02
1.00
1.05
1.06
3.01

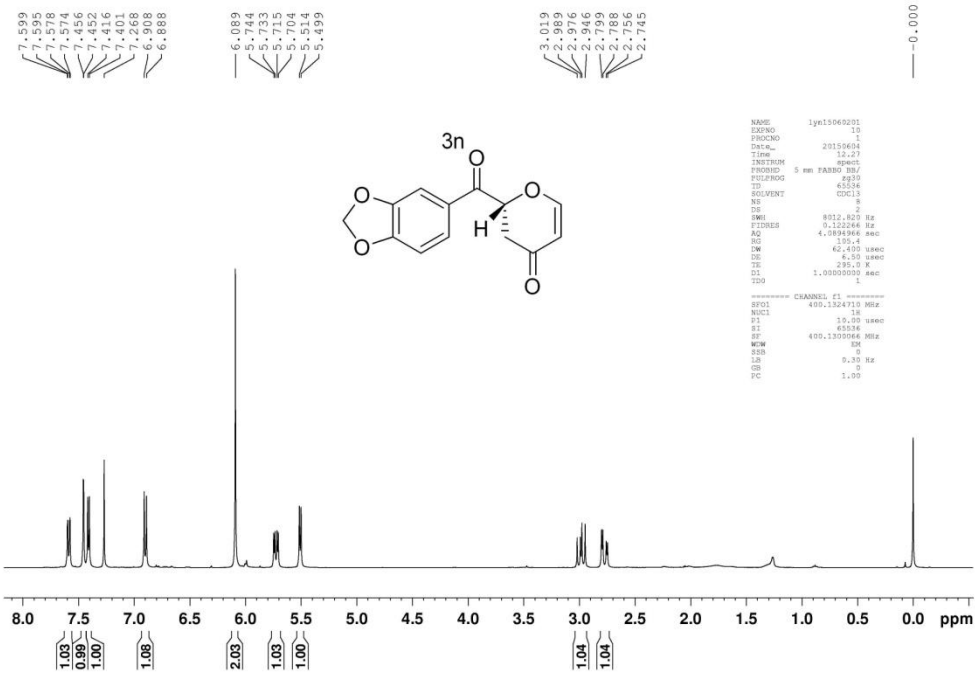

197.430
189.945
161.749
139.274
134.329
132.272
132.239
128.509
125.746
107.963
80.141
77.377
77.059
76.741
37.724
20.857
NAME lyn15031501
EXPNO 12
PROCNO 1
Date_ 20150317
Time 7.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461
FIDRES 0.366798
AQ 1.3631988
RG 207.18
DW 20.800
DE 6.50
TE 297.1
D1 2.00000000
D11 0.03000000
TD0 1
======== CHANNEL f1 ====
SFO1 100.5976818
NUC1 13C
P1 9.00
SI 32768
SF 100.5876240
WDW EM
SSB 0
LB 1.00
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

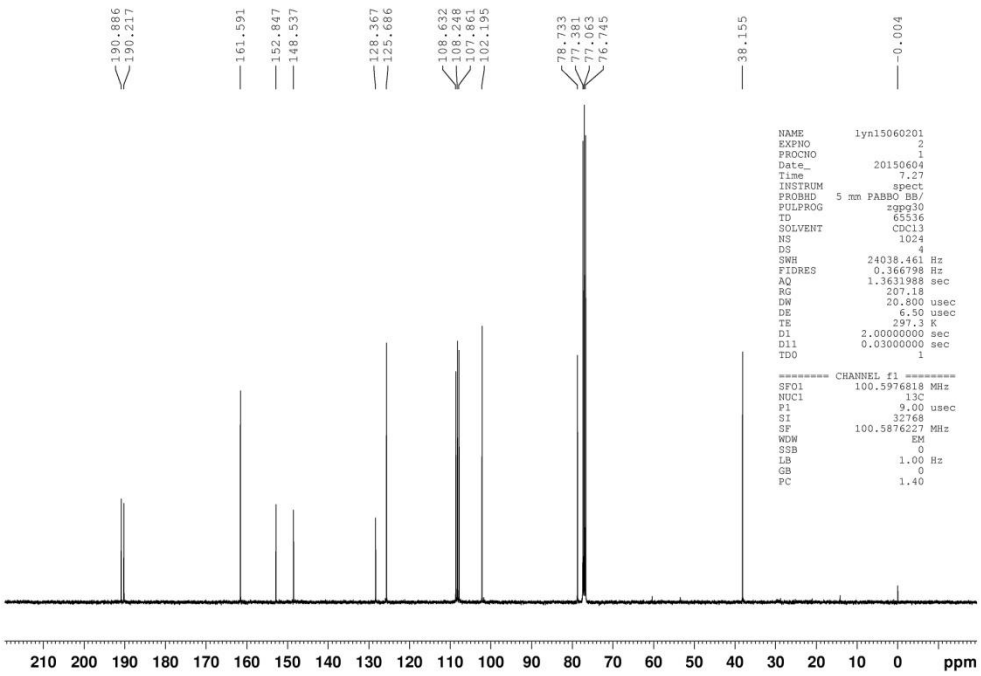

7.914
7.905
7.768
7.756
7.424
7.409
7.260
7.195
7.184
7.173
5.569
5.558
5.540
5.528
5.508
5.493
3.024
2.995
2.982
2.952
2.830
2.819
2.787
2.776
0.050
-0.026
3l
O
O
S
H
O
NAME lyn15031602
EXPNO 10
PROCNO 1
Date_ 20150318
Time 12.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 58.03
DW 62.400 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
1.00
1.00
1.04
1.00
1.02
1.00
1.04
1.08

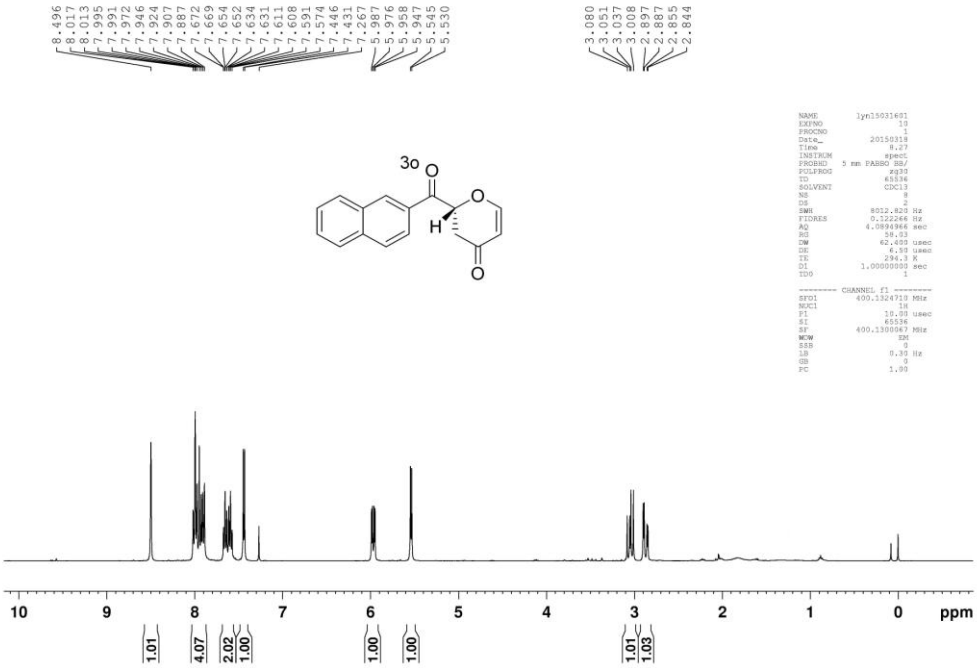

189.889
186.194
161.431
140.022
135.810
134.212
128.555
108.127
80.137
77.409
77.091
76.773
38.268
0.010
NAME lyn15031602
EXPNO 11
PROCNO 1
Date_ 20150318
Time 23.32
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 294.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

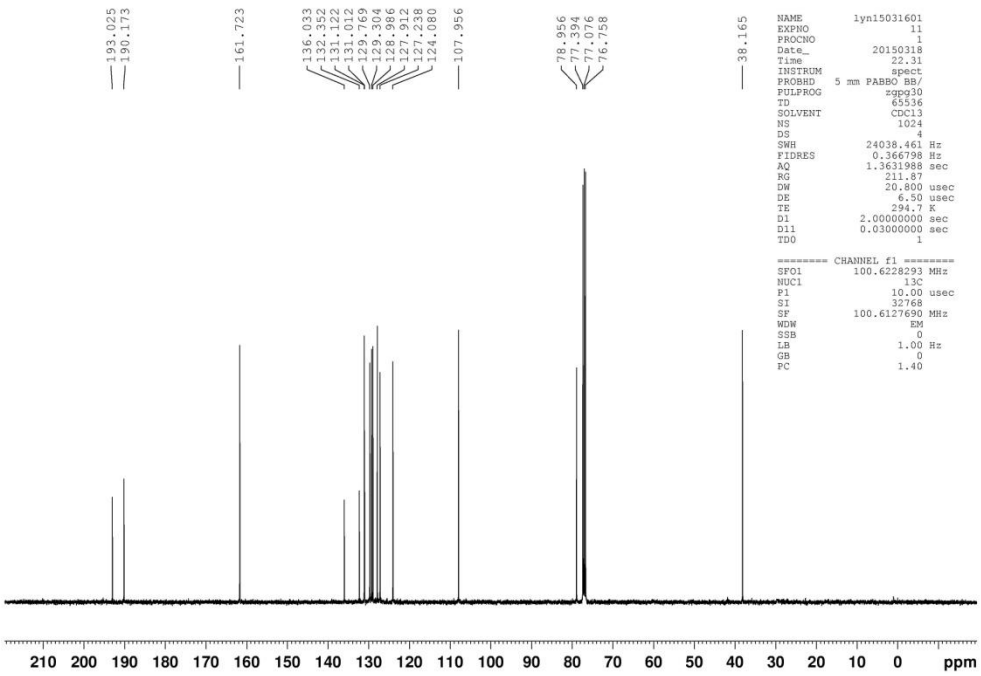

7.870
7.865
7.851
7.846
7.839
7.825
7.820
7.805
7.798
7.795
7.788
7.784
7.778
7.774
7.380
7.365
7.333
7.312
7.291
7.269
7.260
5.715
5.703
5.688
5.676
5.509
5.494
3.013
2.986
2.970
2.943
2.825
2.814
2.783
2.772
0.022
3m
O
O
H
F
F
O
NAME lyn15041701
EXPNO 10
PROCNO 1
Date_ 20150419
Time 18.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 67.16
DW 62.400 usec
DE 6.50 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
2.07
1.01
1.08
1.00
1.00
1.06
1.06

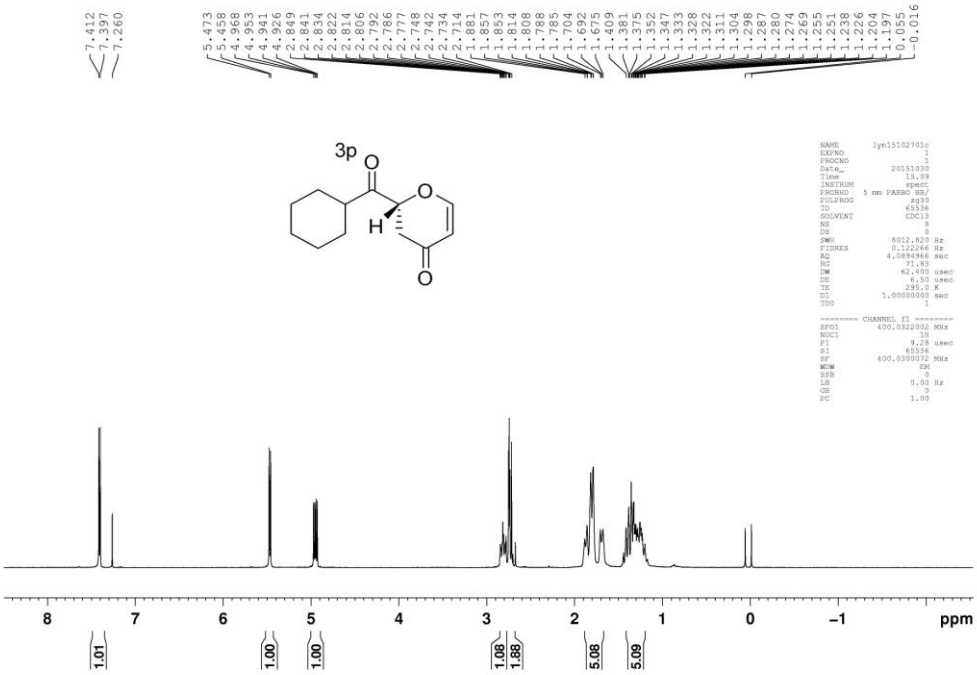

190.810
189.833
161.155
155.636
155.504
153.055
152.924
151.874
151.742
149.365
149.242
130.931
130.794
130.787
130.750
126.478
126.441
126.397
126.361
118.756
118.735
118.574
118.552
118.079
117.902
108.192
78.756
77.386
77.065
76.751
37.568
0.004
NAME lyn15041701
EXPNO 11
PROCNO 1
Date_ 20150419
Time 19.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 294.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127681 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.599
7.595
7.578
7.574
7.456
7.452
7.416
7.401
7.268
6.908
6.888
6.089
5.744
5.733
5.715
5.704
5.514
5.499
3.019
2.989
2.976
2.946
2.799
2.788
2.756
2.745
-0.000
3n
O
O
O
O
H
O
NAME lyn15060201
EXPNO 10
PROCNO 1
Date_ 20150604
Time 12.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 155.4
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
1.03
0.99
1.00
1.08
2.03
1.03
1.00
1.04
1.04


190.886
190.217
161.591
152.847
148.537
128.367
125.686
108.632
108.248
107.861
102.195
78.733
77.381
77.063
76.745
38.155
-0.004
NAME lyn15060201
EXPNO 2
PROCNO 1
Date_ 20150604
Time 7.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 207.18
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.5976818 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.5876227 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.496
8.017
8.013
7.995
7.991
7.972
7.946
7.924
7.907
7.887
7.672
7.669
7.654
7.652
7.634
7.631
7.611
7.608
7.591
7.574
7.446
7.431
7.267
5.987
5.976
5.958
5.947
5.545
5.530
3.080
3.051
3.037
3.008
2.897
2.887
2.855
2.844
3o
O
O
H
O
NAME lyn15031601
EXPNO 10
PROCNO 1
Date_ 20150318
Time 8.27
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 58.03
DW 62.400 usec
DE 6.50 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 18.00 usec
SI 65536
SF 400.1300047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
4.07
2.02
1.00
1.00
1.00
1.01
1.03


193.025
190.173
161.723
136.033
132.352
131.122
131.012
129.769
129.304
128.986
127.912
127.238
124.080
107.956
78.956
77.394
77.076
76.758
38.165
NAME lyn15031601
EXPNO 11
PROCNO 1
Date_ 20150318
Time 22.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 211.87
DW 20.800 usec
DE 6.50 usec
TE 294.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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2.822
2.814
2.806
2.792
2.786
2.777
2.748
2.742
2.734
2.714
1.881
1.857
1.853
1.814
1.808
1.788
1.785
1.704
1.692
1.675
1.409
1.381
1.375
1.352
1.347
1.333
1.328
1.322
1.311
1.304
1.298
1.287
1.280
1.274
1.269
1.255
1.251
1.238
1.226
1.204
1.197
0.055
-0.016
3p
O
O
H
O
NAME lyn15102701c
EXPNO 1
PROCNO 1
Date_ 20151030
Time 18.39
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122264 Hz
AQ 4.0894966 sec
RG 71.83
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.0322092 MHz
NUC1 1H
P1 9.28 usec
SI 65536
SF 400.0300072 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
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–1
ppm
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1.00
1.00
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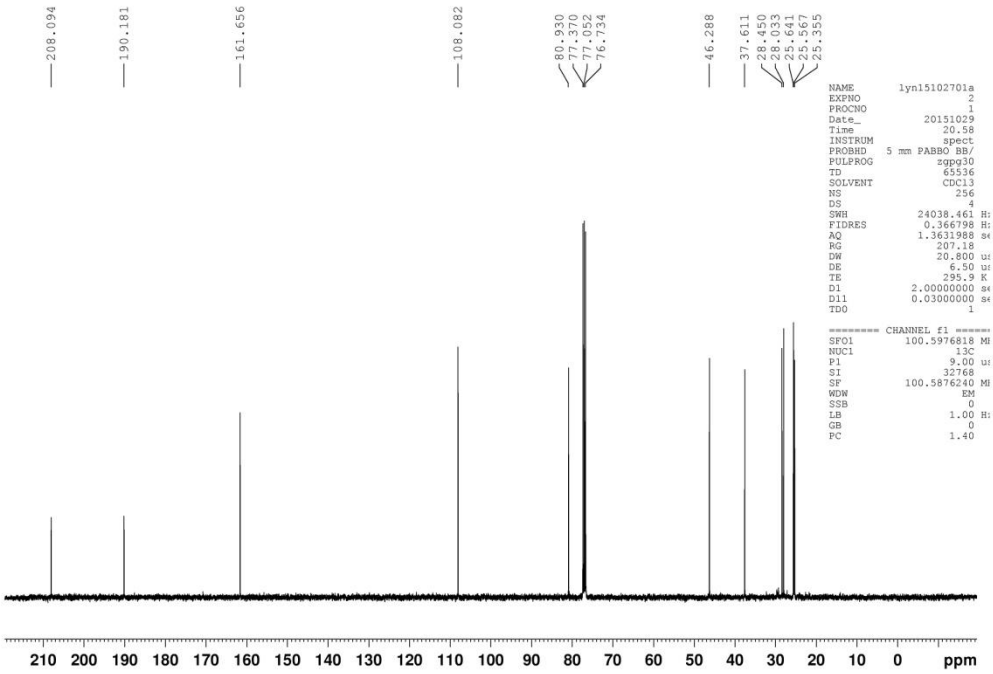
5.08
5.09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NAME lyn15102701a
EXPNO 2
PROCNO 1
Date_ 20151029
Time 20.58
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PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 H
FIDRES 0.366798 H
AQ 1.3631988 s
RG 207.18
DW 20.800 u
DE 6.50 u
TE 295.9 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ====
SFO1 100.5976818 M
NUC1 13C
P1 9.00 u
SI 32768
SF 100.5876240 M
WDW EM
SSB 0
LB 1.00 H
GB 0
PC 1.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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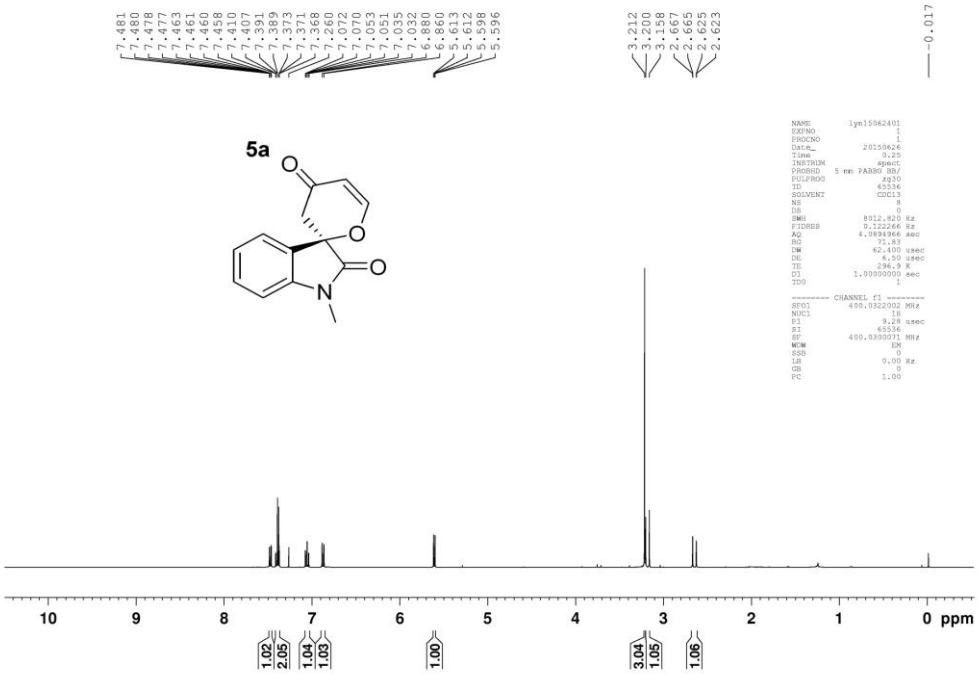
30
20
10
0
ppm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7.371
7.368
7.260
7.072
7.070
7.053
7.051
7.035
7.032
6.880
6.860
5.613
5.612
5.598
5.596
3.212
3.200
3.158
2.667
2.665
2.625
2.623
-0.017
5a
NAME lyn15062401
EXPNO 1
PROCNO 1
Date_ 20150626
Time 0.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8912.820 Hz
FIDRES 0.122266 Hz
AQ 4.5894966 sec
RG 71.83
DW 62.400 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.0322002 MHz
NUC1 1H
P1 9.28 usec
SI 65536
SF 400.0300071 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
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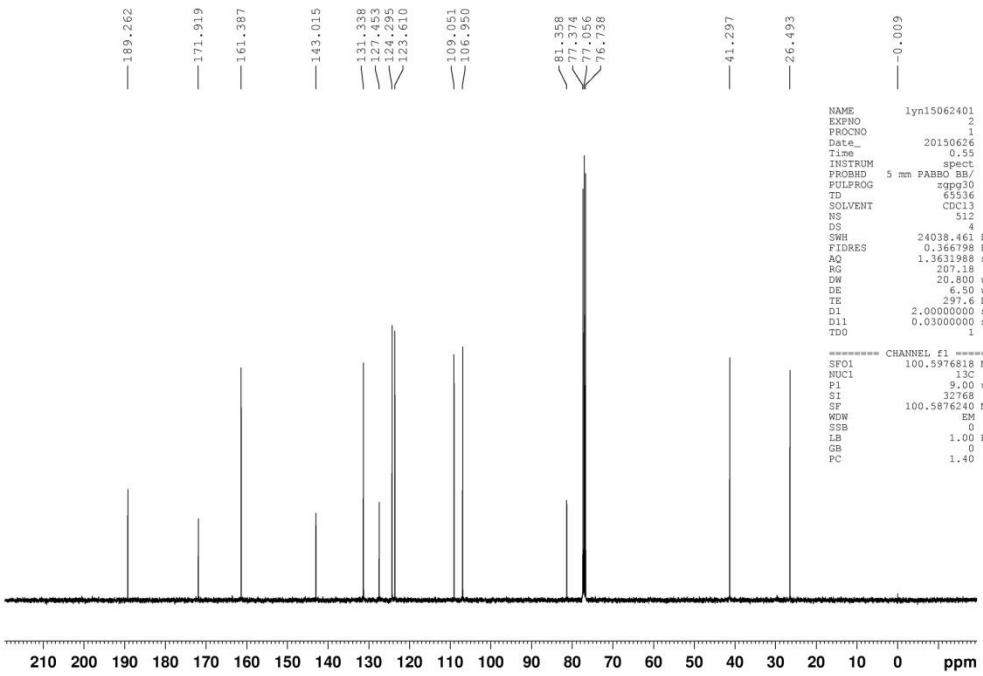
1.02
2.05
1.04
1.03
1.00
3.04
1.05
1.06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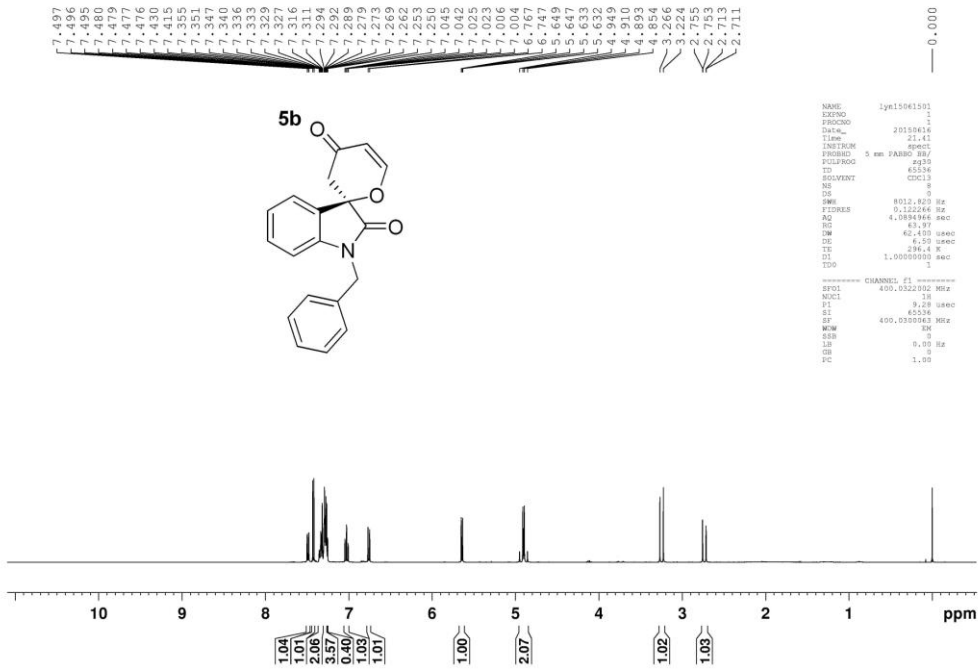
77.056
76.738
41.297
26.493
-0.009
NAME lyn15062401
EXPNO 2
PROCNO 1
Date_ 20150626
Time 0.55
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 H
FIDRES 0.366798 H
AQ 1.3631988 s
RG 207.18
DW 20.800 u
DE 6.50 u
TE 297.6 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 ======
SFO1 100.5976818 M
NUC1 13C
P1 9.00 u
SI 32768
SF 100.5876240 M
WDW EM
SSB 0
LB 1.00 H
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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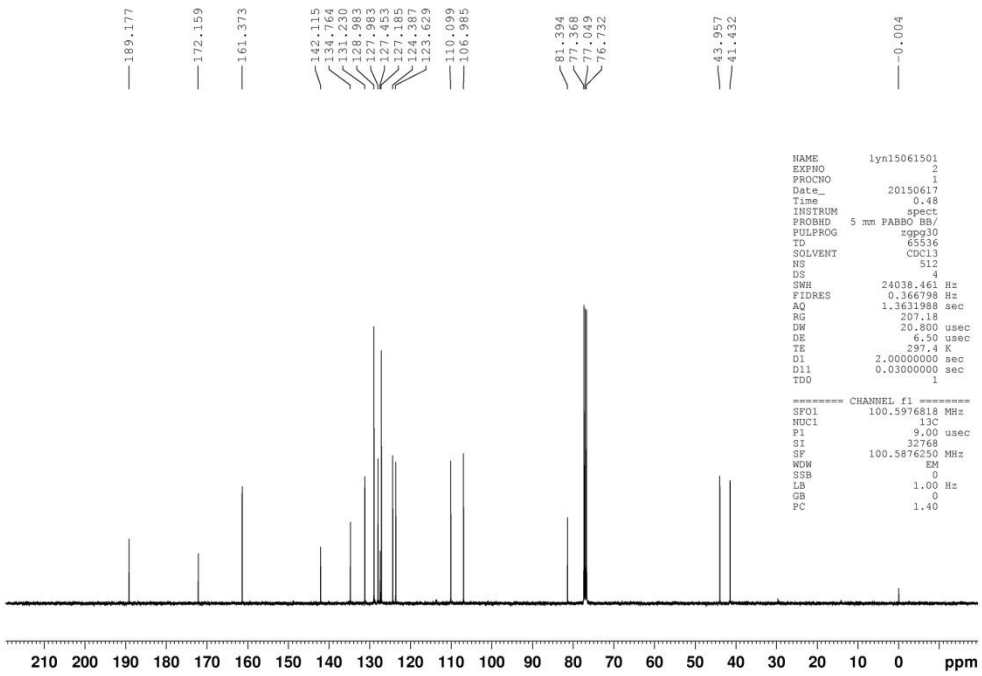
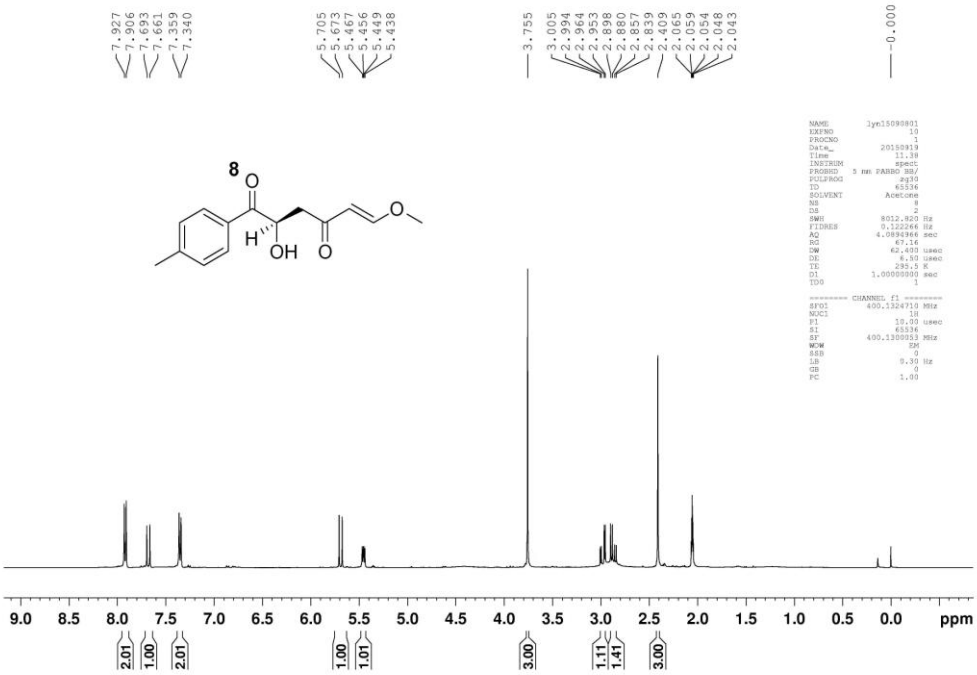
0.000
5b
NAME lyn15061501
EXPNO 1
PROCNO 1
Date_ 20150616
Time 21.41
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 63.97
DW 62.400 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.0322002 MHz
NUC1 1H
P1 9.28 usec
SI 65536
SF 400.0300063 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 ppm
1.04 1.01 2.06 3.57 0.40 1.03 1.01 1.00 2.07 1.02 1.03


189.177 172.159 161.373 142.115 134.764 131.230 128.983 127.983 127.453 127.185 124.387 123.629 110.099 106.985 81.394 77.368 77.049 76.732 43.957 41.432 -0.004
NAME lyn15061501
EXPNO 2
PROCNO 1
Date_ 20150617
Time 0.48
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 512
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 207.18
DW 20.800 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.5976818 MHz
NUC1 13C
P1 9.00 usec
SI 32768
SF 100.5876250 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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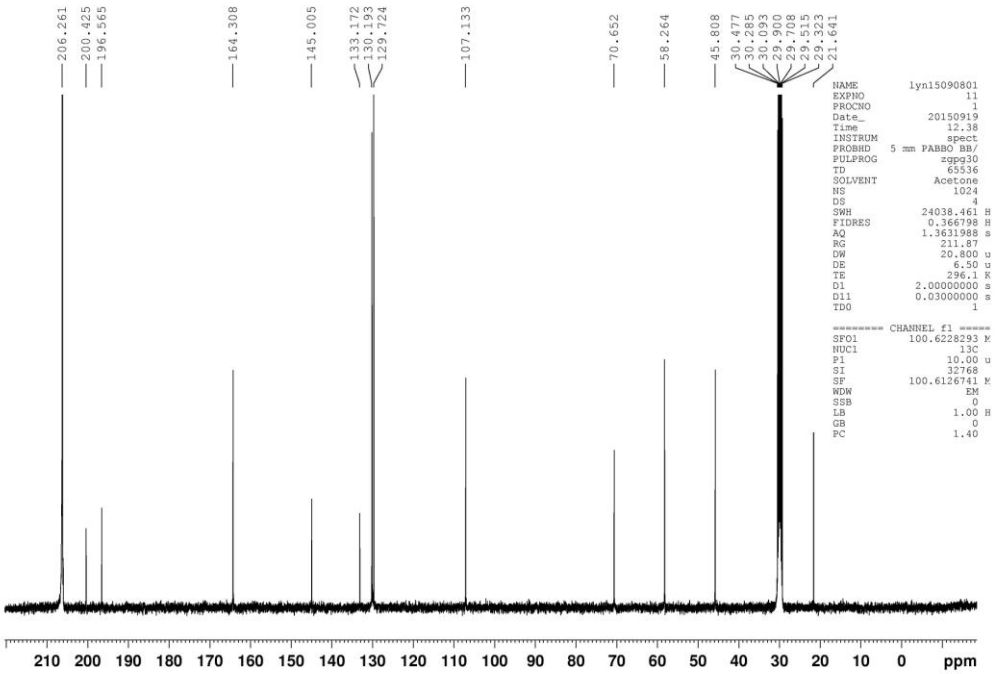
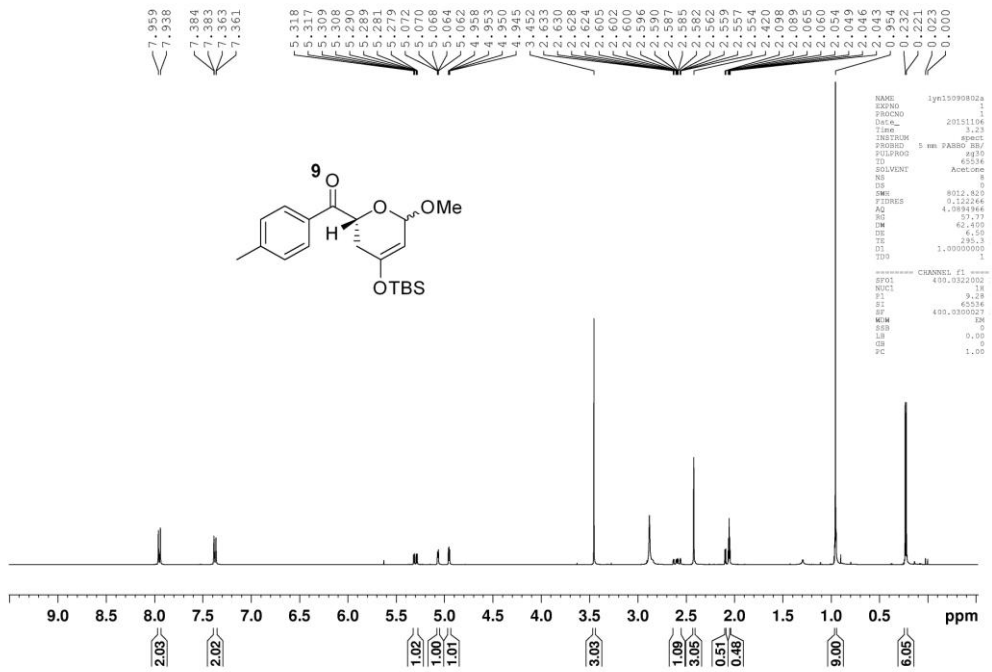
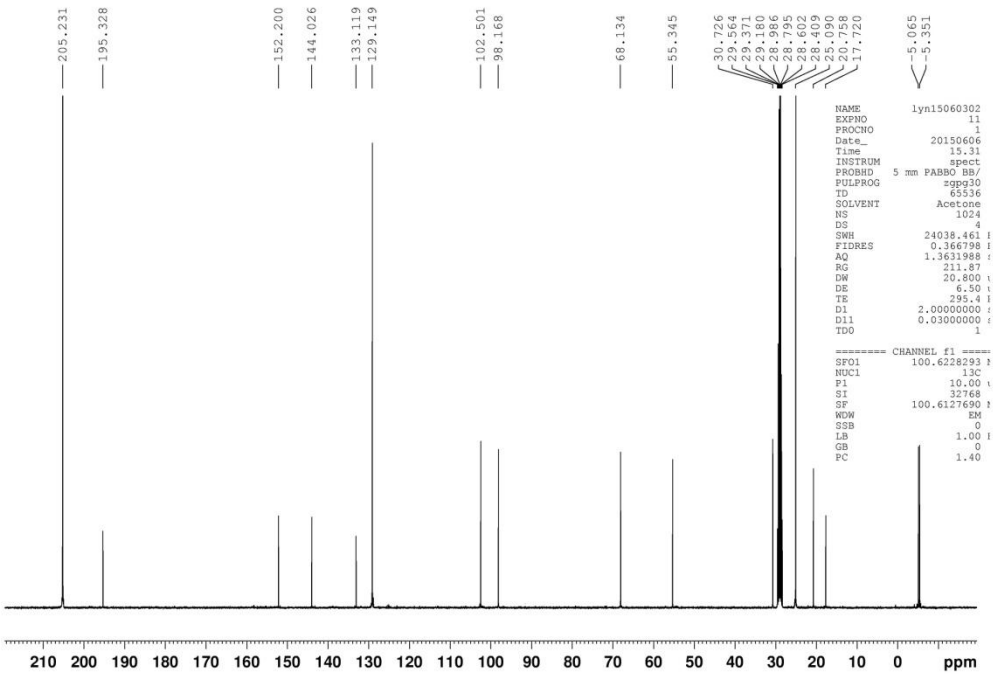
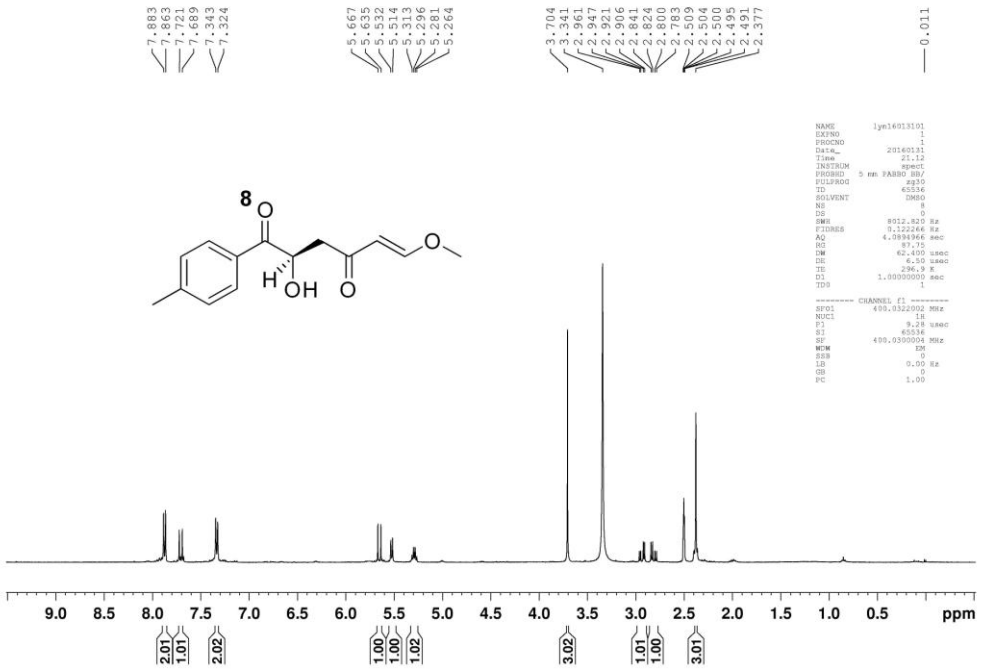
2.964
2.953
2.898
2.880
2.857
2.839
2.409
2.165
2.059
2.054
2.048
2.043
-0.000
8
O
H
OH
O
O
NAME lyn15090801
EXPNO 10
PROCNO 1
Date_ 20150919
Time 11.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 8
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 67.16
DW 62.400 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 10.00 usec
SI 65536
SF 400.1300053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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 ppm
2.01
1.00
2.01
1.00
1.01
3.00
1.11
1.41
3.00


206.261
200.425
196.565
164.308
145.005
133.172
130.193
129.724
107.133
70.652
58.264
45.808
30.477
30.285
30.093
29.900
29.708
29.515
29.323
21.641
NAME lyn15090801
EXPNO 11
PROCNO 1
Date_ 20150919
Time 12.38
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 1024
DS 4
SWH 24038.461 H
FIDRES 0.366798 H
AQ 1.3631988 s
RG 211.87
DW 20.800 u
DE 6.50 u
TE 296.1 K
D1 2.00000000 s
D11 0.03000000 s
TD0 1
======== CHANNEL f1 =====
SFO1 100.6228293 M
NUC1 13C
P1 10.00 u
SI 32768
SF 100.6126741 M
WDW EM
SSB 0
LB 1.00 H
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





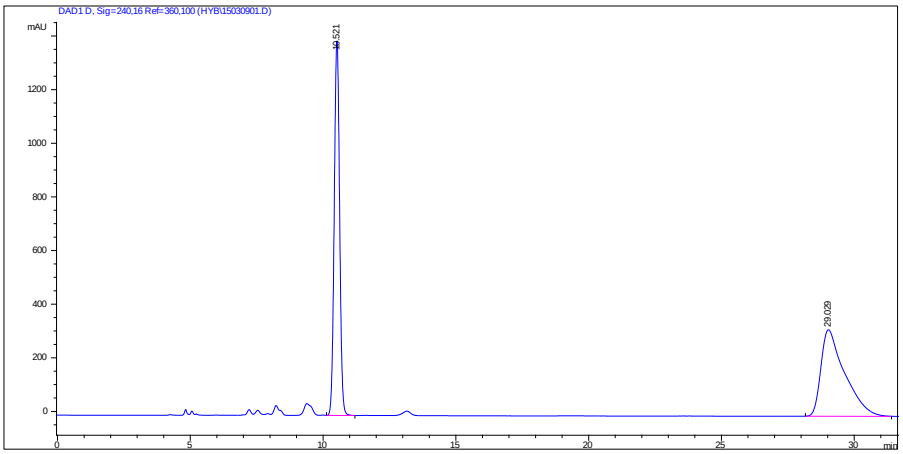
The ^{1}H NMR copy of this compound **8** in $(CD_3)_2SO$



Part II HPLC data

3a

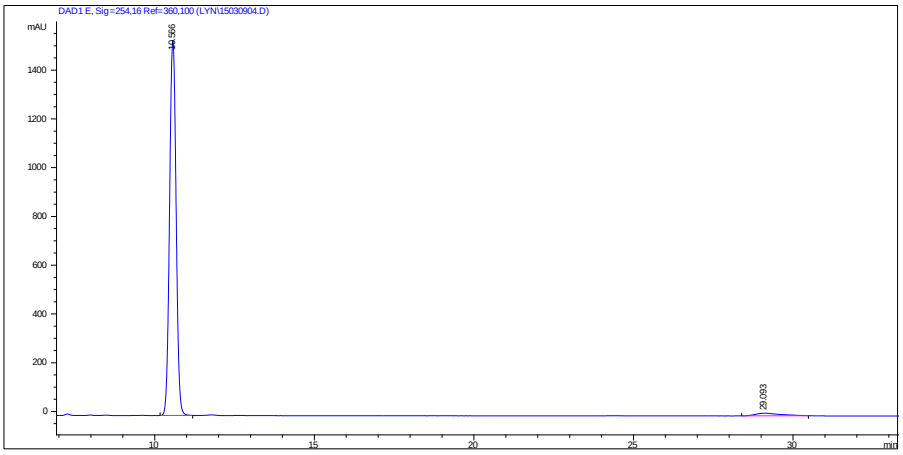
Racemic sample



Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.521	VB	0.2201	1.96510e4	1396.95081	49.6131
2	29.029	BB	0.8754	1.99575e4	322.77548	50.3869

Asymmetric version:

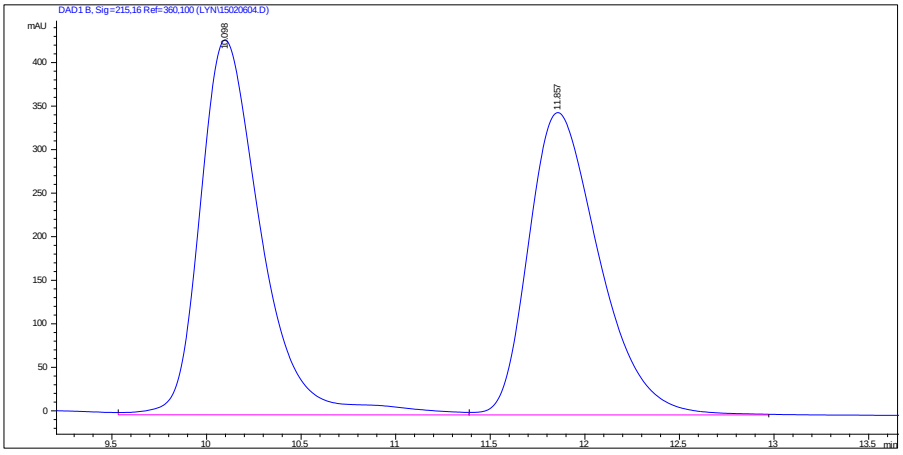


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.566	BB	0.2233	2.17943e4	1538.38623	97.2800
2	29.093	BB	0.6945	609.38611	10.86264	2.7200

3b

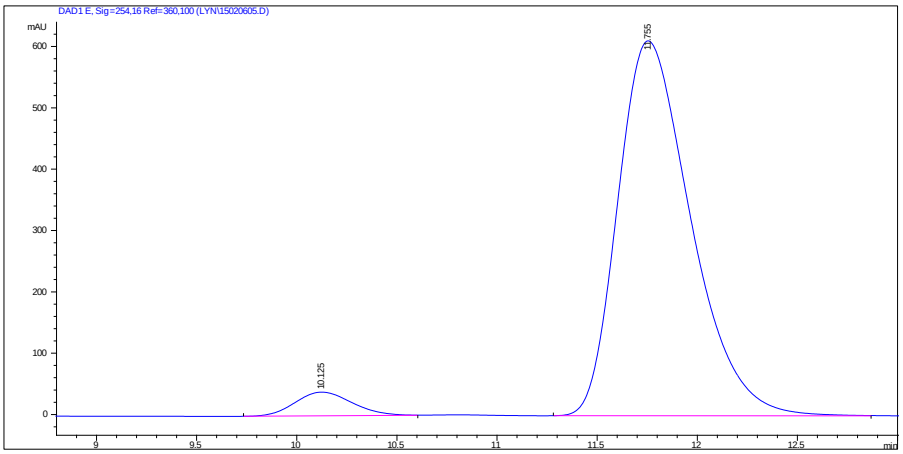
Racemic sample



Signal 2: DAD1 B, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.098	VV	0.3404	9687.53613	430.68527	51.8424
2	11.857	VB	0.4005	8998.97266	347.11163	48.1576

Asymmetric version:

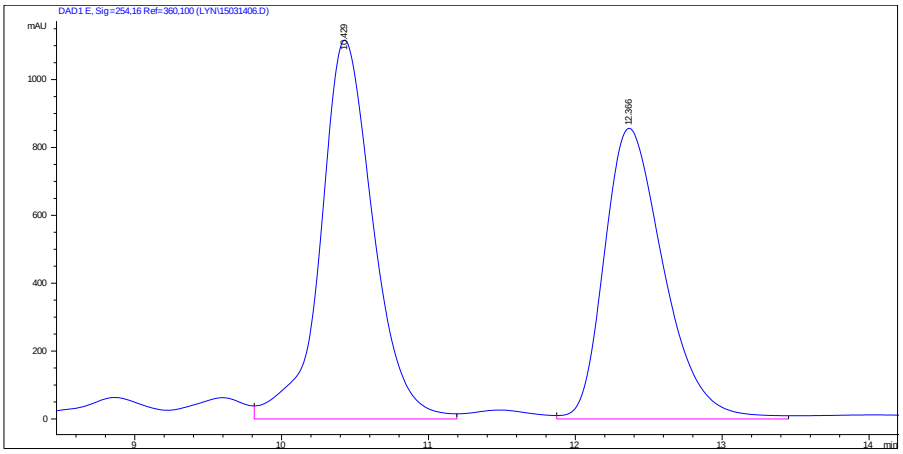


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.125	PV	0.3095	767.95483	38.70024	4.7281
2	11.755	PB	0.3914	1.54746e4	611.13477	95.2719

3c

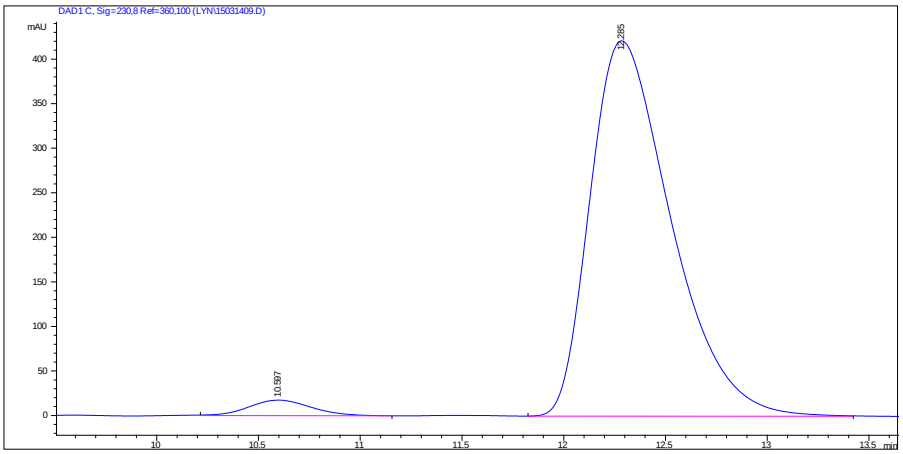
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.429	VV	0.3783	2.77881e4	1116.60852	53.5327
2	12.366	VB	0.4345	2.41205e4	856.59686	46.4673

Asymmetric version:

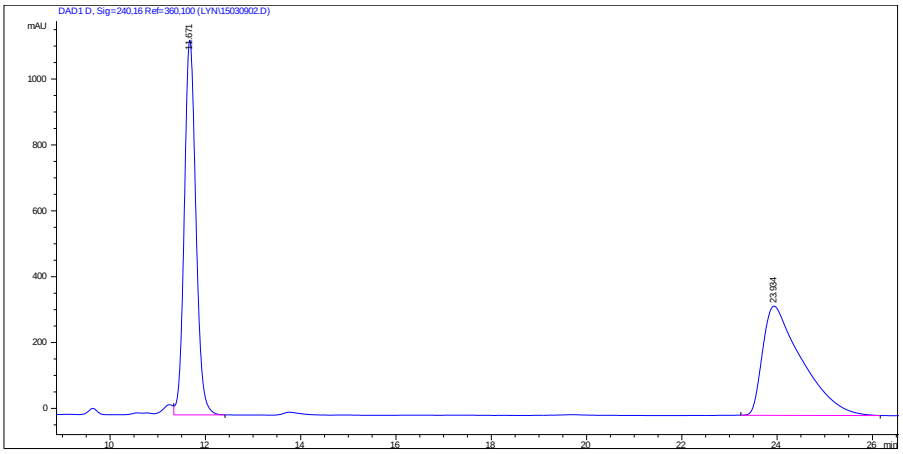


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.597	BP	0.3268	371.22302	17.40598	3.0871
2	12.285	PB	0.4248	1.16539e4	421.22025	96.9129

3d

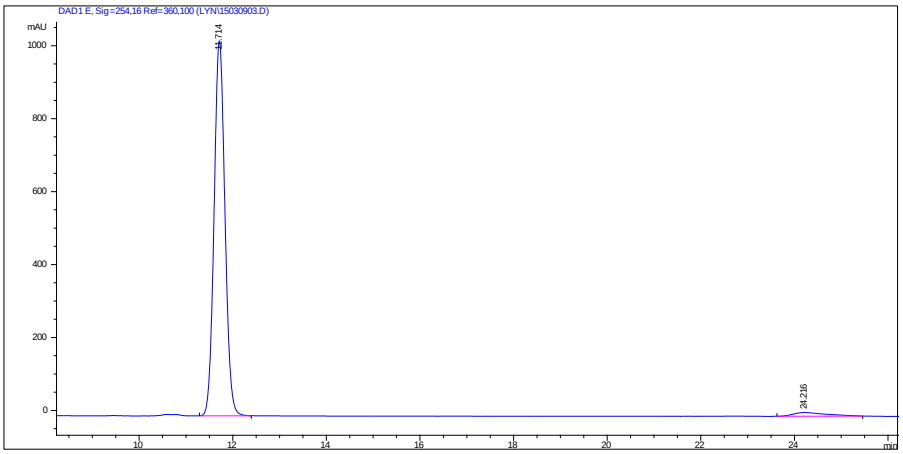
Racemic sample



Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.671	VB	0.2596	1.92682e4	1137.72498	50.4680
2	23.934	BB	0.8052	1.89109e4	331.67847	49.5320

Asymmetric version:

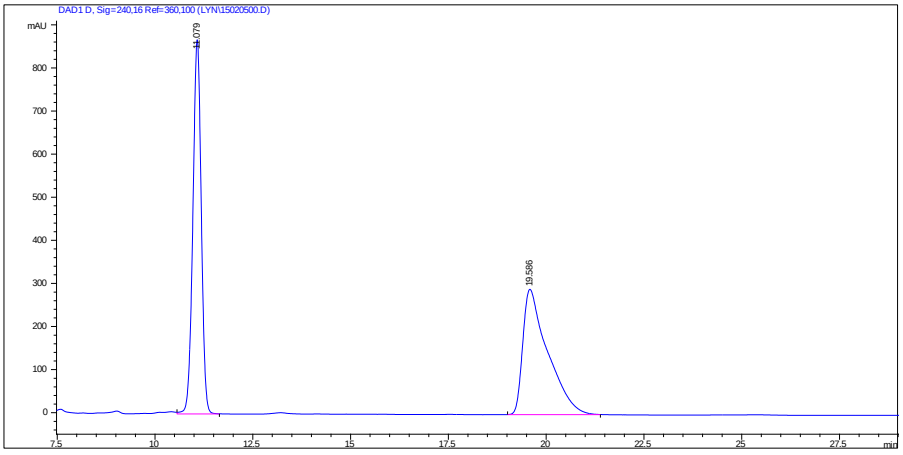


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.714	BB	0.2499	1.65632e4	1028.28687	96.9675
2	24.216	BB	0.6405	517.99200	10.30356	3.0325

3e (the product of **1e** with **2a**)

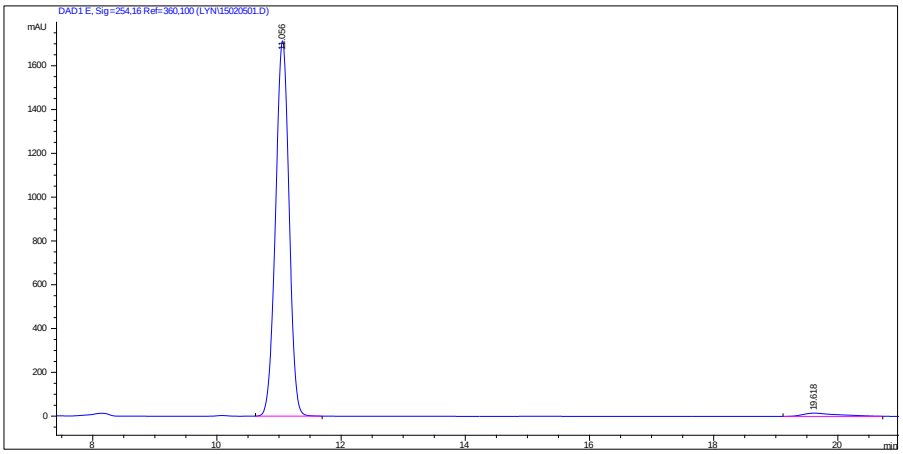
Racemic sample



Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.079	VB	0.2296	1.29214e4	868.34955	50.1709
2	19.586	BB	0.6190	1.28334e4	290.74463	49.8291

Asymmetric version:

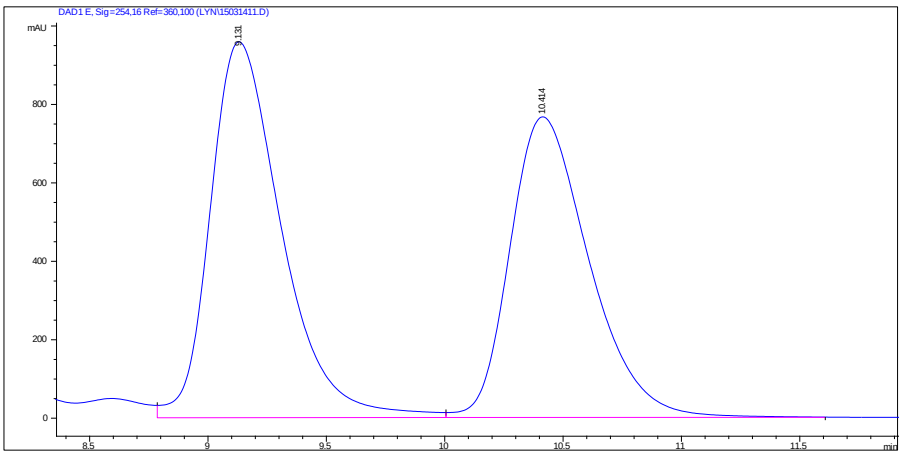


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.056	BB	0.2365	2.59291e4	1713.55005	97.7541
2	19.618	BB	0.5468	595.72827	14.76253	2.2459

3f

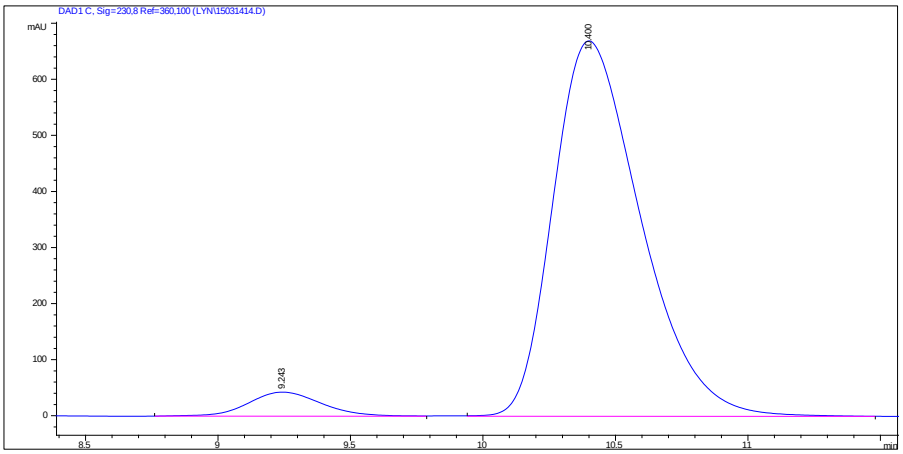
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.131	VV	0.3181	2.00553e4	958.54431	52.9712
2	10.414	VB	0.3570	1.78054e4	766.54028	47.0288

Asymmetric version:

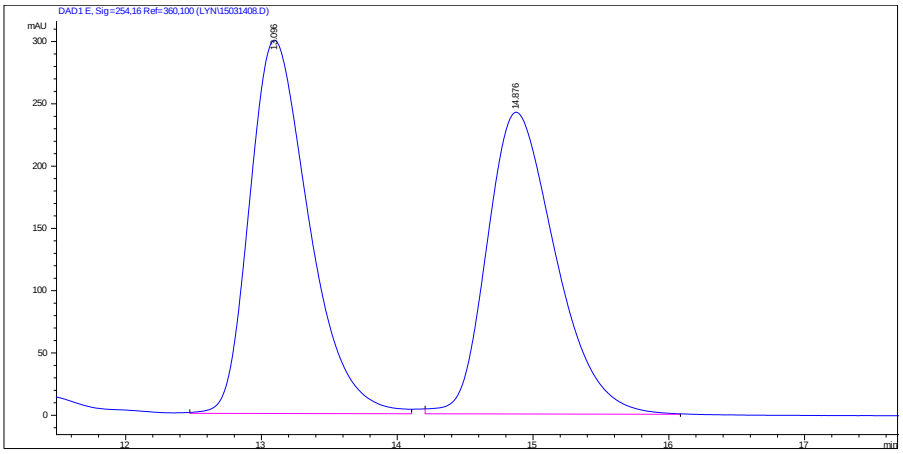


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.243	BB	0.2972	830.58038	43.02282	5.1048
2	10.400	BB	0.3550	1.54399e4	669.72467	94.8952

3g

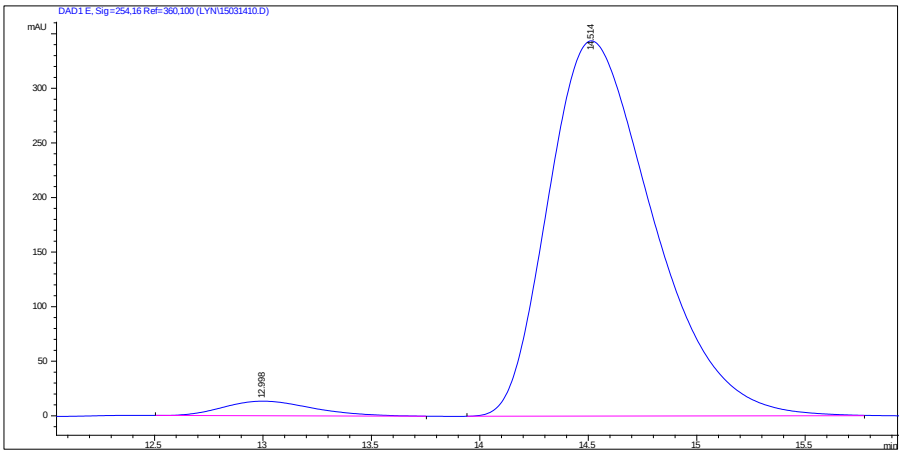
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.096	BB	0.4645	9109.72949	299.77536	51.7400
2	14.876	BB	0.5432	8497.00000	242.23282	48.2600

Asymmetric version:

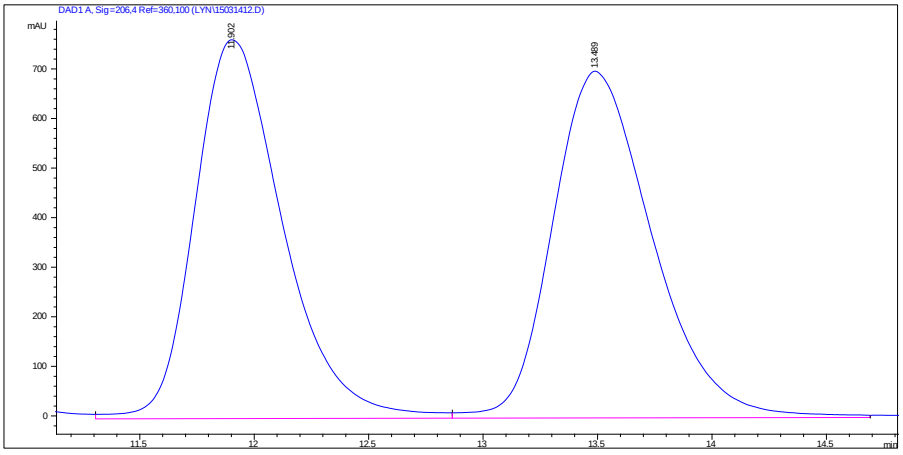


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.998	PB	0.4342	385.99319	13.39294	3.2321
2	14.514	BB	0.5241	1.15565e4	343.83163	96.7679

3h

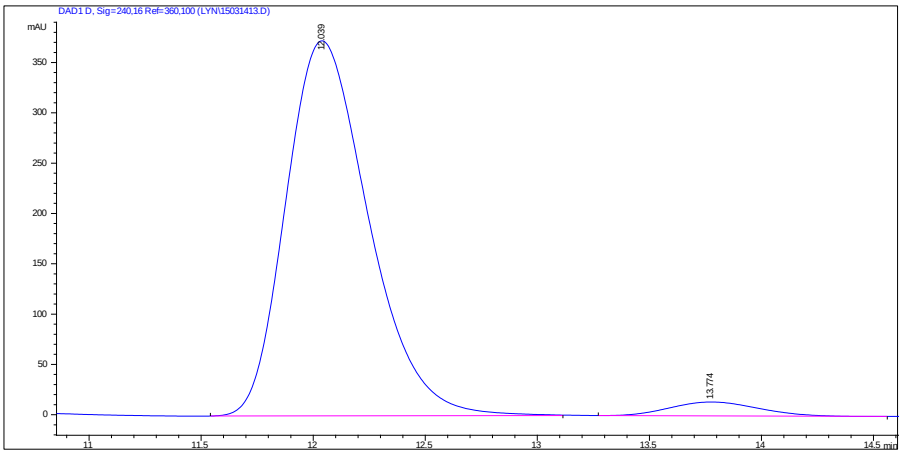
Racemic sample



Signal 1: DAD1 A, Sig=206,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.902	VV	0.4065	2.04718e4	764.23077	49.1114
2	13.489	VV	0.4717	2.12126e4	699.70520	50.8886

Asymmetric version:

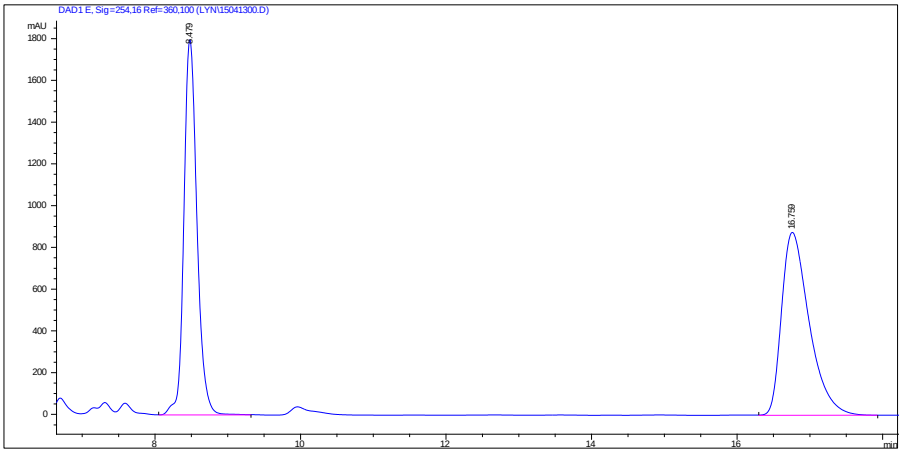


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.039	BB	0.3975	9568.49121	372.70026	96.2185
2	13.774	PP	0.4153	376.05804	13.82640	3.7815

3i

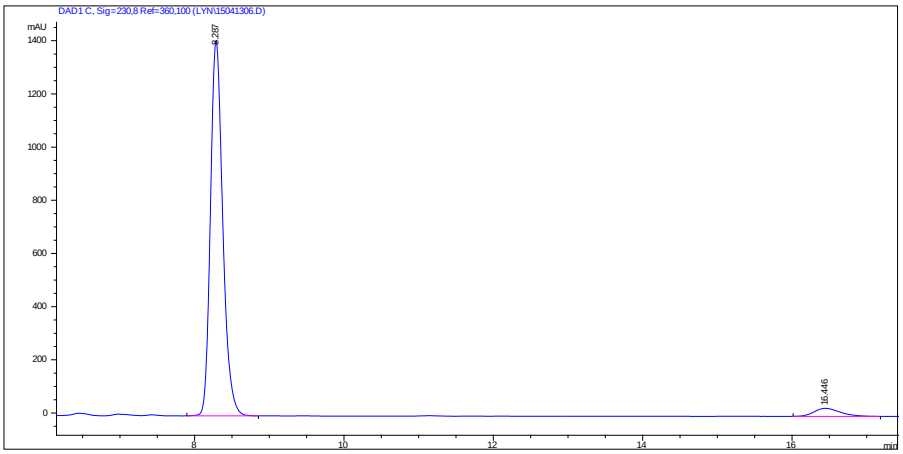
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.479	VB	0.1917	2.24459e4	1796.76819	49.3056
2	16.759	BB	0.4034	2.30782e4	875.90588	50.6944

Asymmetric version:

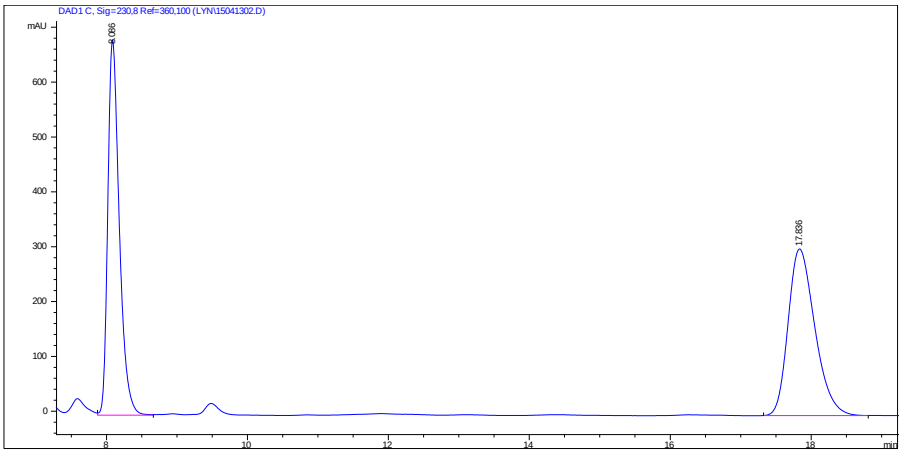


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.287	BB	0.1776	1.61558e4	1410.82239	95.6410
2	16.446	BB	0.3706	736.32678	30.18789	4.3590

3j

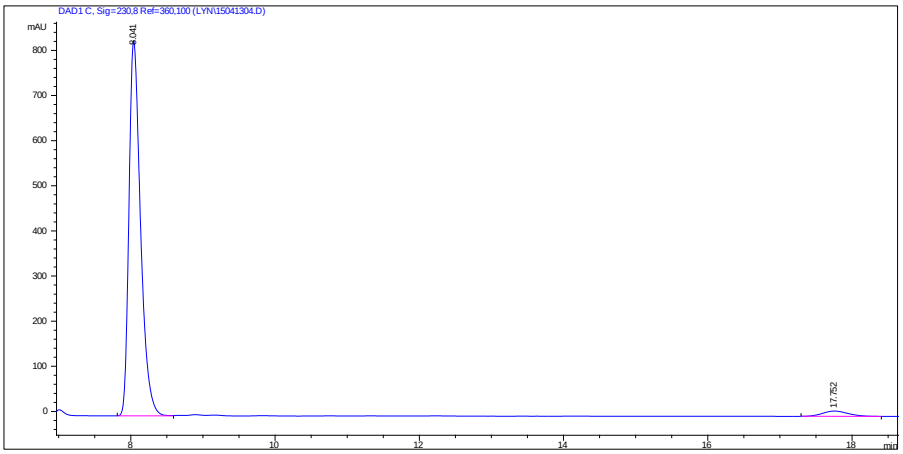
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.086	VB	0.1724	7761.13623	684.13861	49.2025
2	17.836	BB	0.4057	8012.72510	303.80225	50.7975

Asymmetric version:

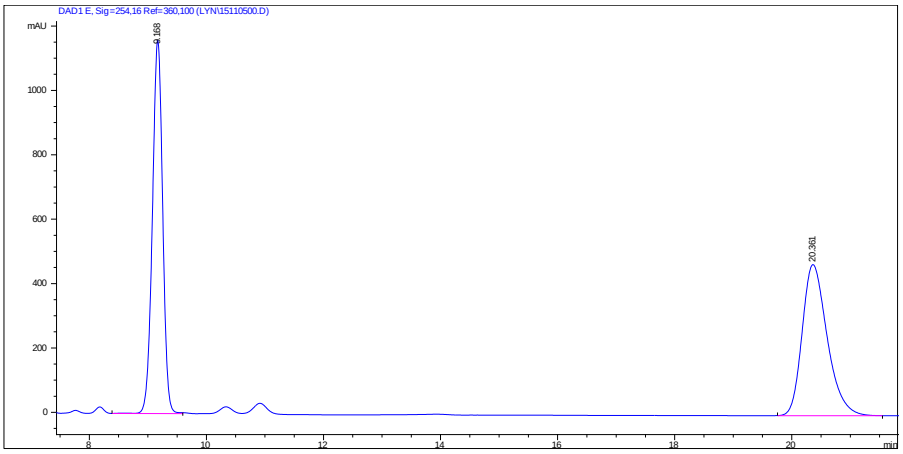


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.041	BB	0.1698	9251.20508	831.37354	96.9217
2	17.752	BB	0.3804	293.82388	11.72181	3.0783

3k

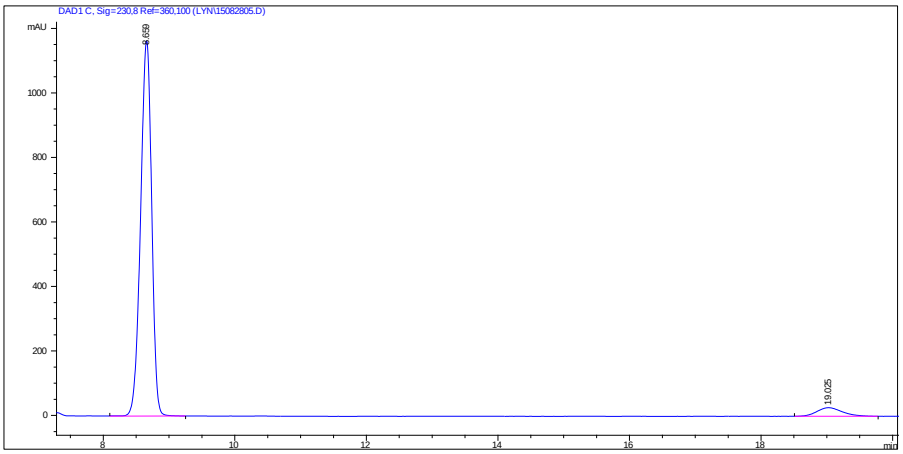
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.168	VB	0.1882	1.41396e4	1159.84839	50.3536
2	20.361	BB	0.4565	1.39410e4	469.45822	49.6464

Asymmetric version:

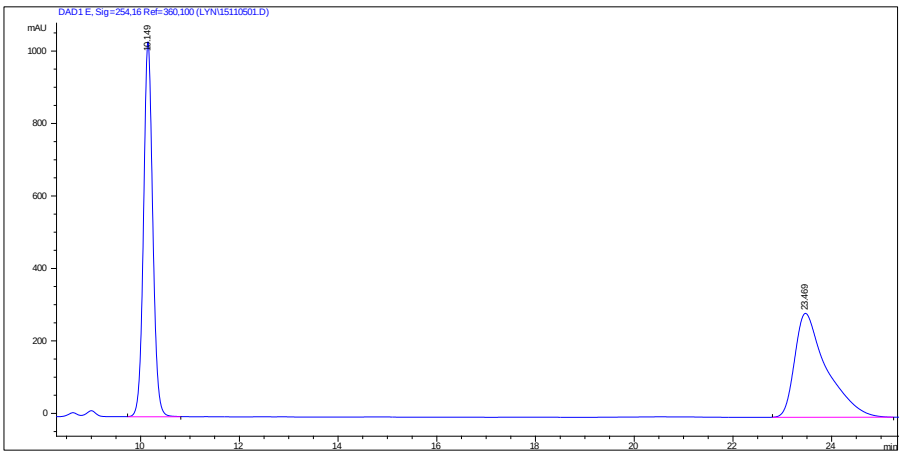


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.659	BP	0.1845	1.36091e4	1163.31519	94.9780
2	19.025	BB	0.4101	719.58899	26.73173	5.0220

3l

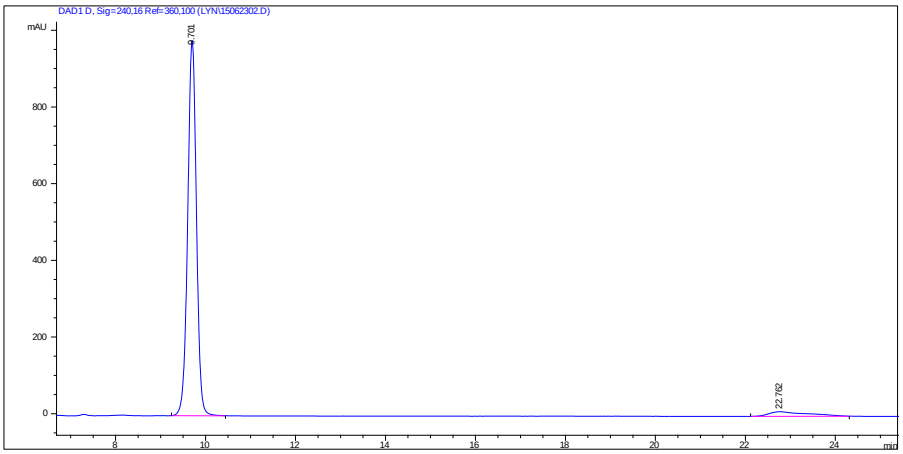
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.149	BB	0.1994	1.34259e4	1034.75476	51.1758
2	23.469	BB	0.6429	1.28090e4	286.87366	48.8242

Asymmetric version:

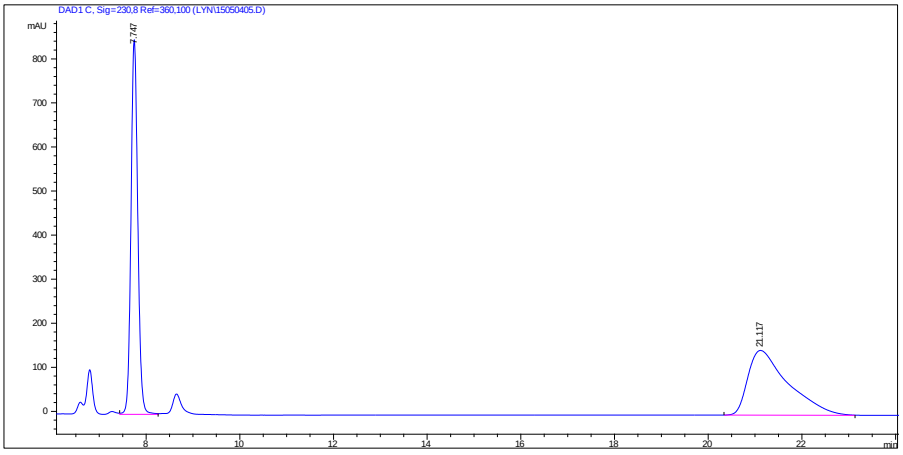


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.701	BB	0.2076	1.32102e4	978.21857	94.7571
2	22.762	BB	0.7872	730.91980	12.02336	5.2429

3m

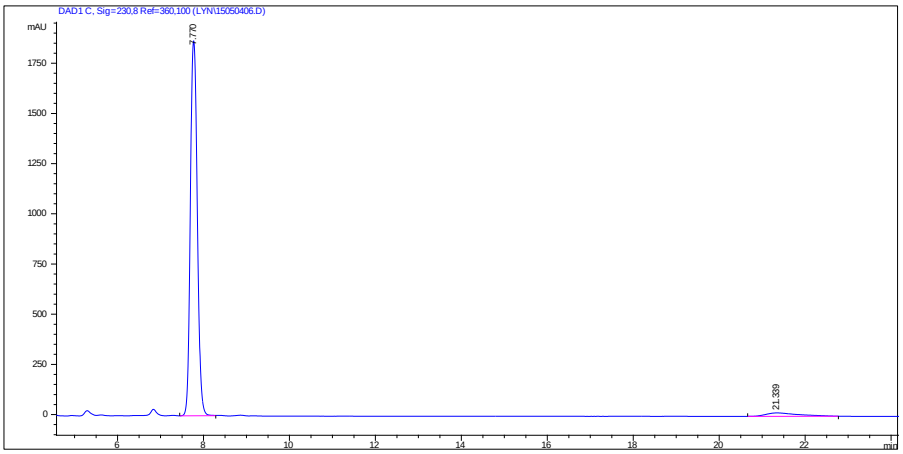
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.747	VB	0.1554	8561.06445	850.54309	49.5144
2	21.117	BB	0.8597	8728.99805	146.81039	50.4856

Asymmetric version:

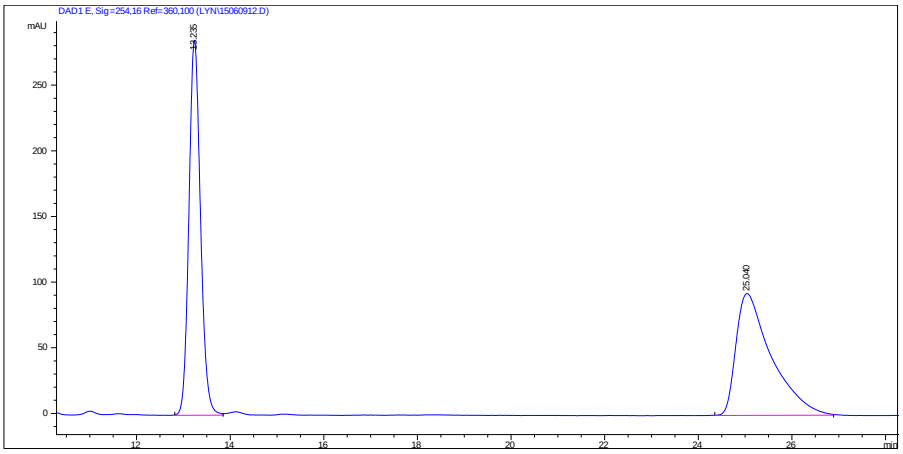


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.770	VB	0.1765	2.09021e4	1868.23242	95.7855
2	21.339	BB	0.7313	919.67297	17.04858	4.2145

3n

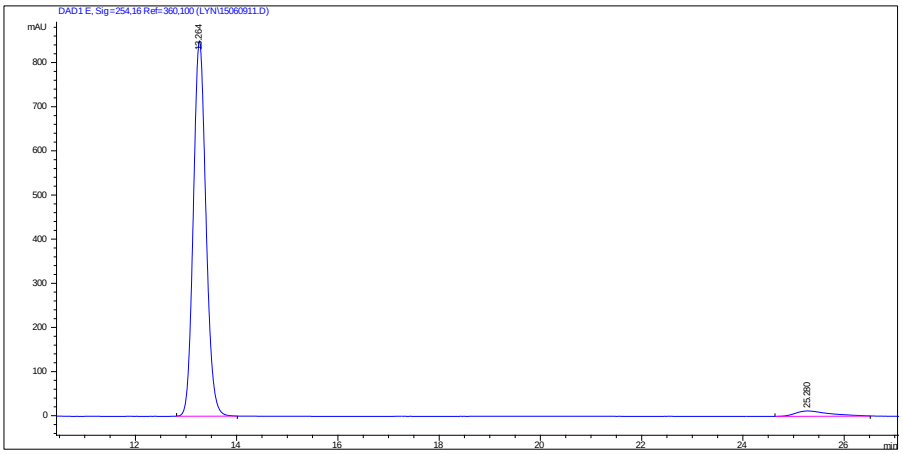
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.235	BB	0.2645	4908.40137	285.61188	50.2345
2	25.040	BB	0.7440	4862.57910	92.69225	49.7655

Asymmetric version:

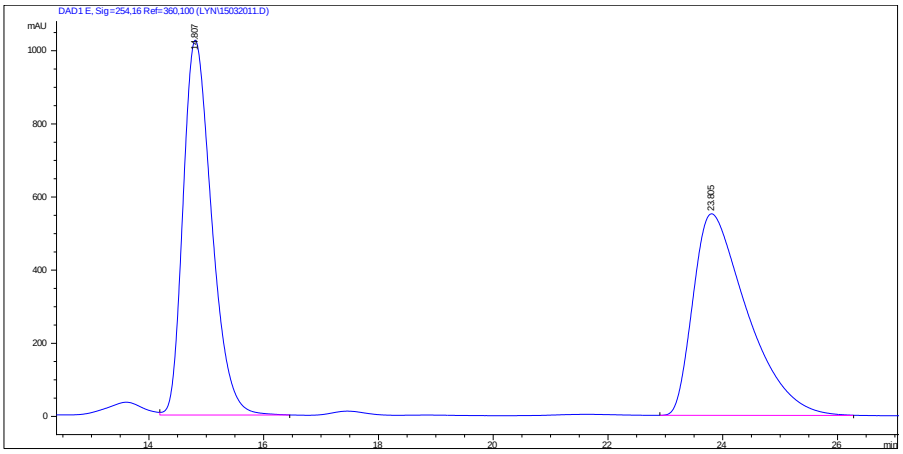


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.264	BB	0.2681	1.47335e4	850.72620	96.2678
2	25.280	BB	0.6435	571.20807	11.99699	3.7322

3o

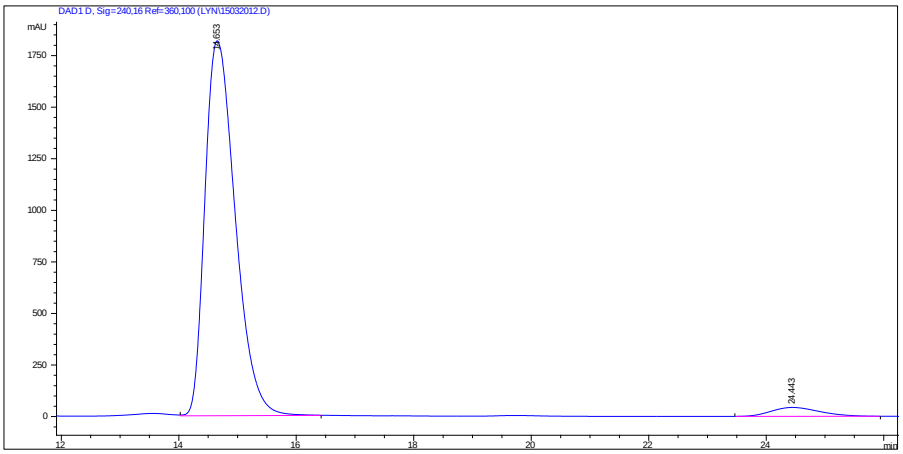
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.807	VB	0.5372	3.54297e4	1025.27173	49.5182
2	23.805	PB	0.9702	3.61191e4	551.39532	50.4818

Asymmetric version:

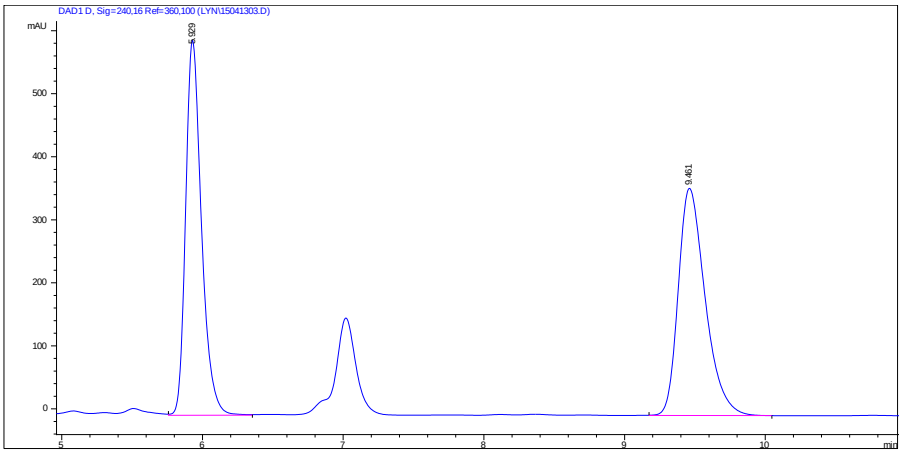


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.653	VB	0.5588	6.52323e4	1817.29456	96.3375
2	24.443	BB	0.8504	2479.99341	43.15519	3.6625

3p

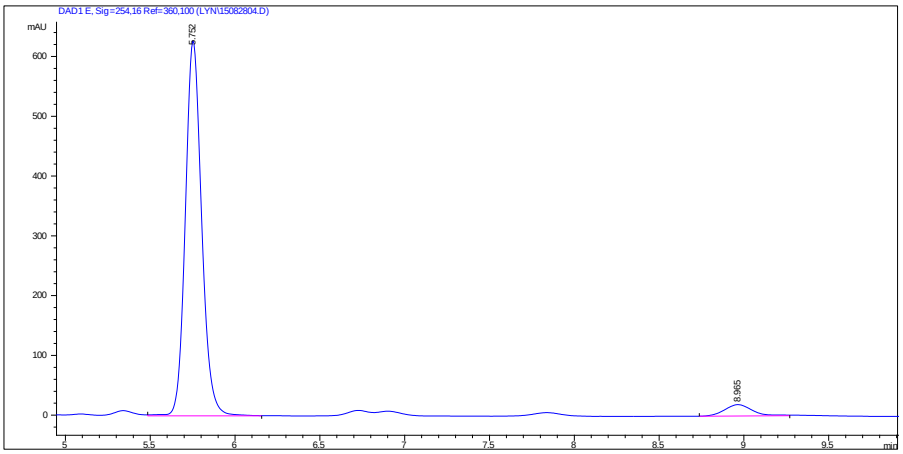
Racemic sample



Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.929	VB	0.1191	4649.16016	595.36285	49.2668
2	9.461	BB	0.2029	4787.54932	360.51605	50.7332

Asymmetric version:

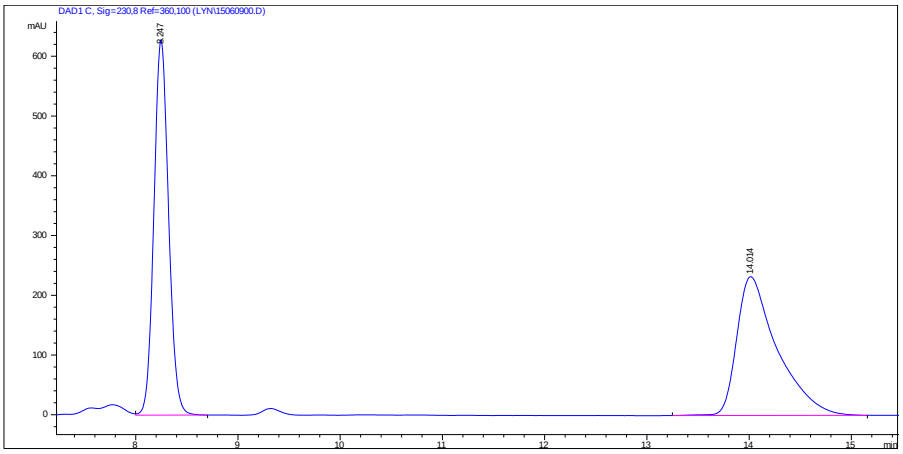


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.752	VB	0.1020	4196.63281	627.80042	95.0962
2	8.965	PB	0.1728	216.40656	19.01407	4.9038

3e (the product of **1e** with **2b**)

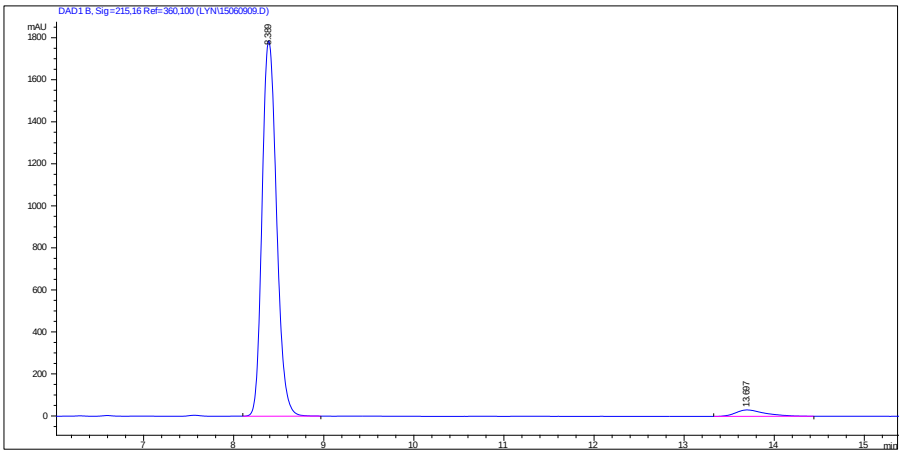
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.247	VB	0.1544	6267.85645	628.20105	49.5661
2	14.014	BB	0.3982	6377.59961	232.38318	50.4339

Asymmetric version:

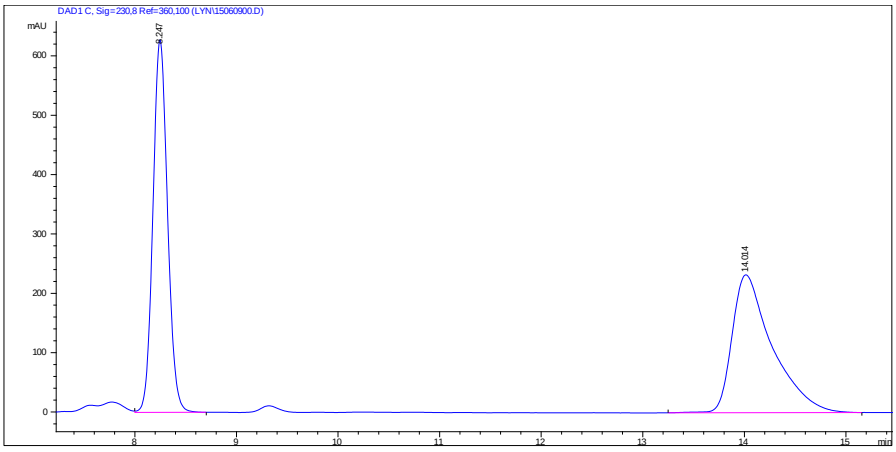


Signal 2: DAD1 B, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.389	VB	0.1743	1.99518e4	1786.80371	96.6607
2	13.697	PP	0.3335	689.25854	30.51258	3.3393

3e (on a gram scale)

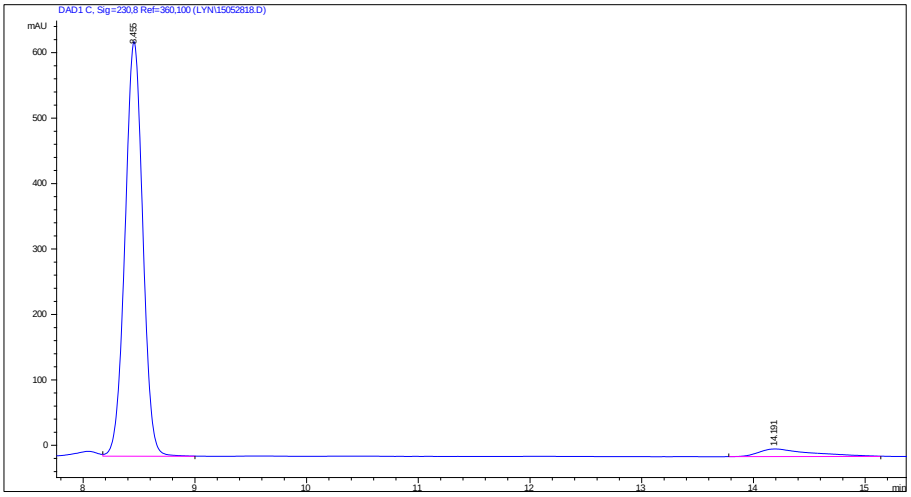
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Heiqht [mAU]	Area %
1	8.247	VB	0.1544	6267.85645	628.20105	49.5661
2	14.014	BB	0.3982	6377.59961	232.38318	50.4339

Asymmetric version:

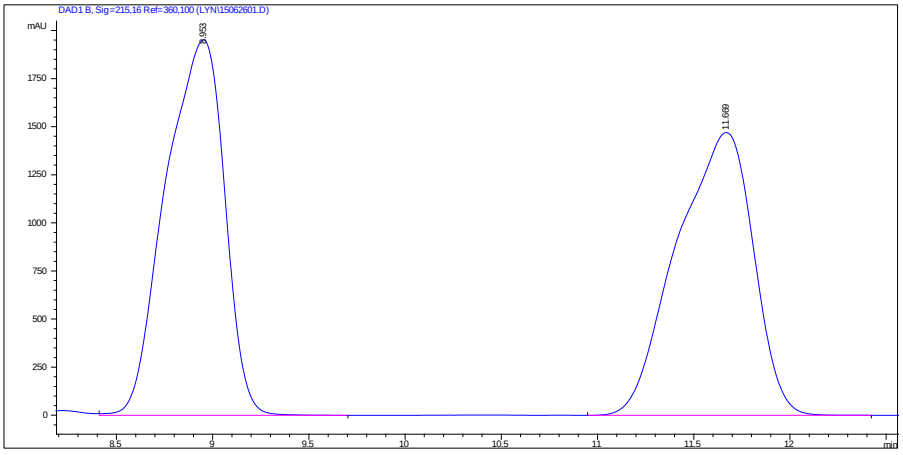


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.455	VB	0.1707	6990.48193	633.58875	94.7996
2	14.191	BB	0.4522	383.47641	11.64519	5.2004

5a

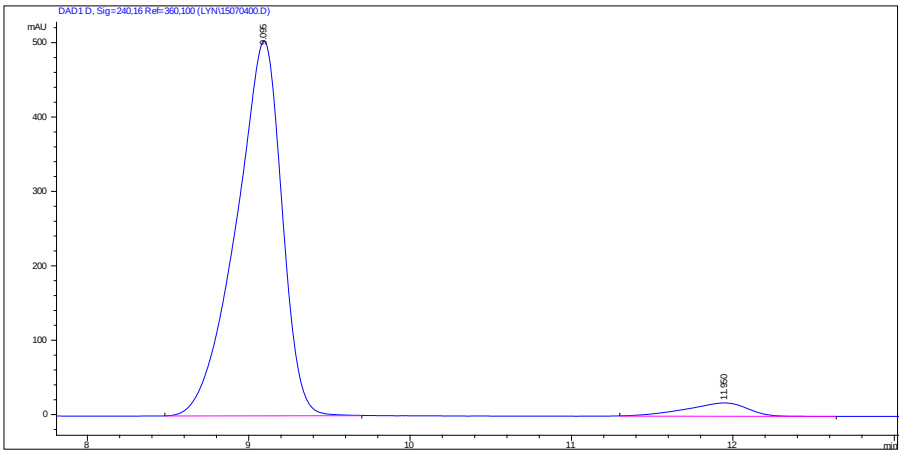
Racemic sample



Signal 2: DAD1 B, Sig=215,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.953	VB	0.3025	4.16029e4	1952.99536	50.5883
2	11.669	VB	0.3926	4.06353e4	1469.77734	49.4117

Asymmetric version:

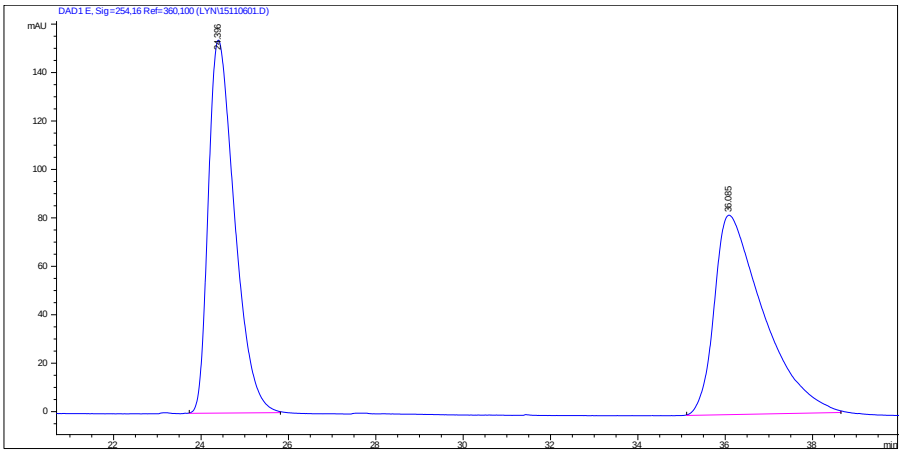


Signal 4: DAD1 D, Sig=240,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.095	BB	0.2859	9936.77734	504.16934	95.4247
2	11.950	BP	0.3944	476.44077	17.90617	4.5753

5b

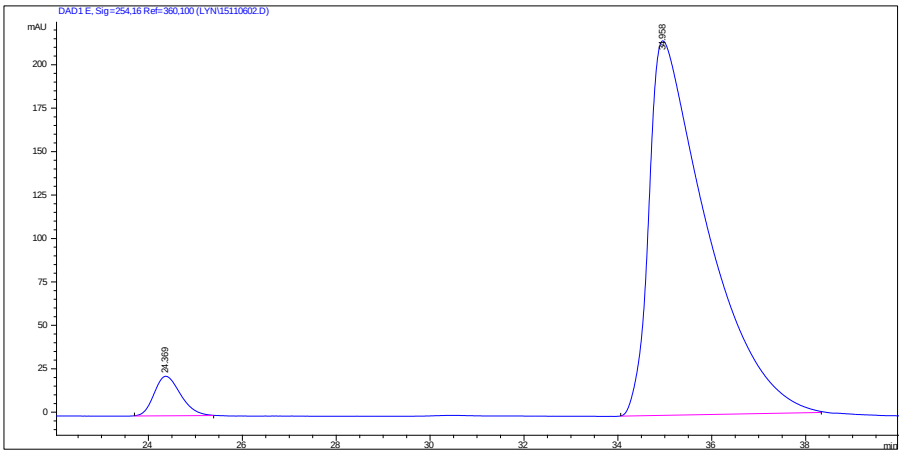
Racemic sample



Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.396	BB	0.6403	6447.68311	154.04562	50.0294
2	36.085	BB	1.1124	6440.09668	82.35015	49.9706

Asymmetric version:

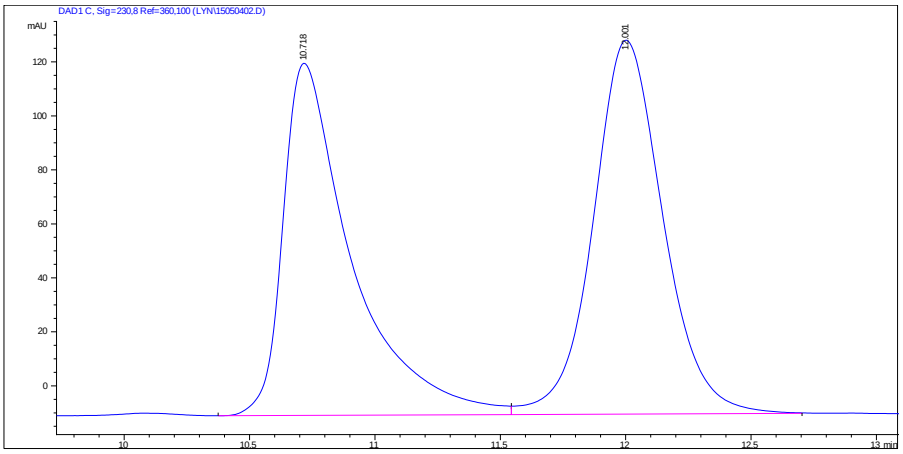


Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.369	BB	0.5783	893.58014	22.74741	4.5821
2	34.958	BB	1.1890	1.86078e4	215.58382	95.4179

8

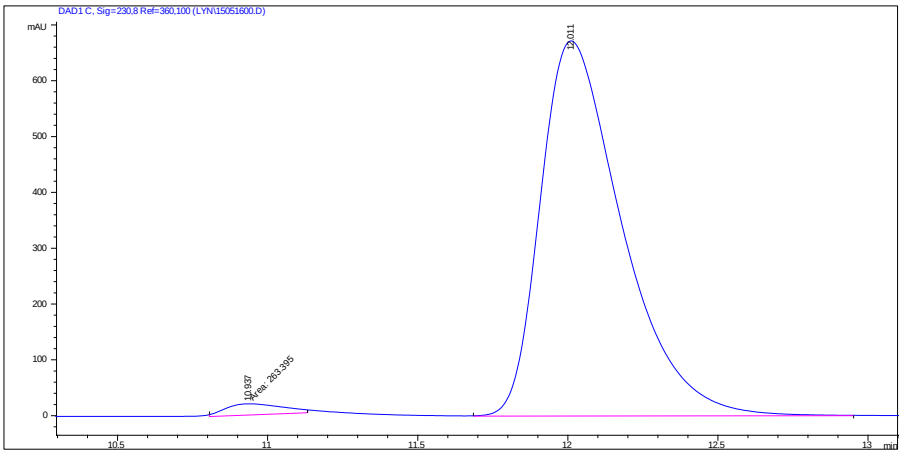
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.718	VV	0.2736	2478.13550	130.45532	48.0321
2	12.001	VB	0.2958	2681.19629	138.52663	51.9679

Asymmetric version:

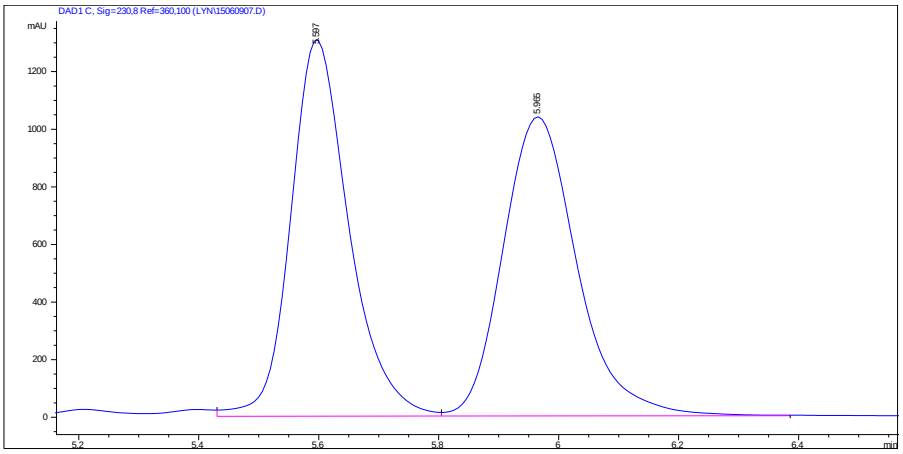


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.937	MM	0.2179	263.39484	20.14396	2.0291
2	12.011	BB	0.2888	1.27176e4	671.98730	97.9709

9

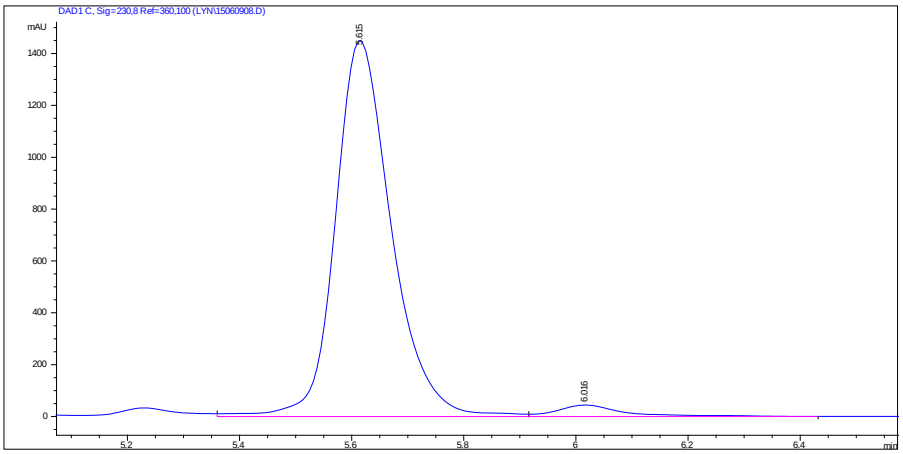
Racemic sample



Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.597	VV	0.1024	8793.47363	1308.19861	49.7290
2	5.965	VB	0.1318	8889.30469	1038.77307	50.2710

Asymmetric version:

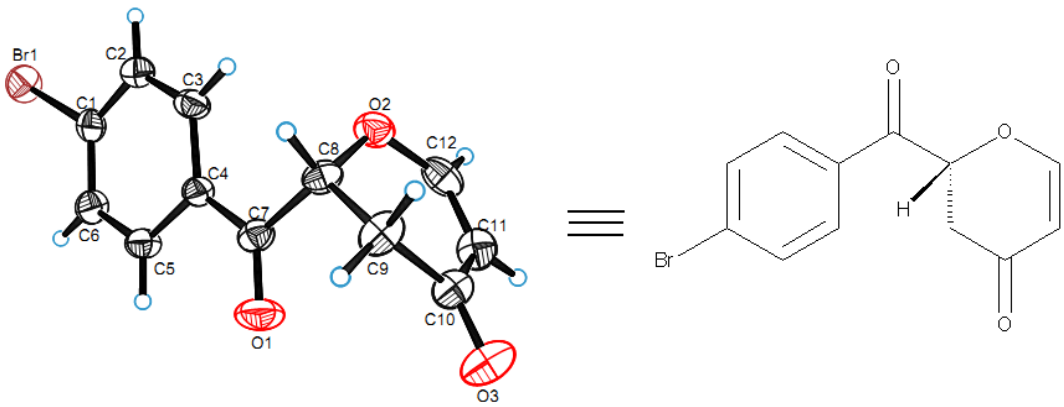


Signal 3: DAD1 C, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.615	VV	0.1049	1.00718e4	1452.53955	96.3728
2	6.016	VB	0.1232	379.07559	44.56753	3.6272

Part III Crystal data

A single crystal for X-ray analysis of **3d** was obtained by recrystallation from $CHCl_3$/petroleum ether



CCDC 1437133

Table 1 Crystal data and structure refinement for 3d.

Identification code	**3d**
Empirical formula	$C_{12}H_9BrO_3$
Formula weight	281.10
Temperature/K	290(2)

Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.3040(3)
b/Å	6.0907(3)
c/Å	16.9947(10)
α/°	90
β/°	91.708(5)
γ/°	90
Volume/$Å^3$	548.77(5)
Z	2
ρ_{calc}g/cm^3	1.701
μ/mm^{-1}	5.028
F(000)	280.0
Crystal size/mm^3	0.320 × 0.310 × 0.280
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/ °	10.416 to 138.44
Index ranges	$-6 \leq h \leq 6$, $-3 \leq k \leq 7$, $-20 \leq l \leq 19$
Reflections collected	1854
Independent reflections	1377 [R_{int} = 0.0562, R_{sigma} = 0.0525]
Data/restraints/parameters	1377/1/145
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1676
Final R indexes [all data]	R_1 = 0.0667, wR_2 = 0.1681
Largest diff. peak/hole / e $Å^{-3}$	0.81/-0.89
Flack parameter	-0.01(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3d. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	19219(2)	23195(3)	4405.5(6)	64.5(5)
O2	16423(15)	16283(15)	1216(5)	56(2)
O3	11307(17)	11236(18)	985(7)	75(3)
C11	12480(20)	14890(20)	722(7)	55(3)
C4	16206(18)	17230(20)	2929(6)	42(2)
O1	13328(18)	14354(18)	2721(6)	77(3)
C9	15390(20)	12386(19)	1445(8)	52(3)
C10	12854(19)	12740(19)	1048(7)	50(3)
C1	17970(19)	20769(19)	3804(6)	45(2)
C2	19250(19)	20180(20)	3150(6)	46(2)
C6	15890(20)	19690(20)	4051(6)	52(3)

C5	14988(18)	17850(20)	3627(6)	47(3)
C8	16510(20)	14495(18)	1770(7)	44(2)
C12	14200(30)	16420(20)	785(7)	58(3)
C3	18350(16)	18370(30)	2718(5)	47(2)
C7	15183(18)	15280(20)	2520(6)	44(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3d. The Anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	76.7(8)	55.1(7)	61.8(7)	-10.2(8)	1.1(5)	-7.0(8)
O2	62(5)	50(5)	56(4)	2(4)	10(4)	-14(4)
O3	54(5)	58(6)	111(8)	-9(6)	-9(5)	-9(5)
C11	50(6)	56(8)	59(7)	1(6)	-2(5)	15(6)
C4	35(4)	50(6)	42(5)	8(5)	0(4)	-2(4)
O1	78(6)	78(7)	78(6)	-19(5)	29(5)	-43(5)
C9	44(6)	35(5)	76(7)	-10(6)	-7(5)	12(5)
C10	43(5)	45(9)	61(6)	-9(5)	2(4)	5(5)
C1	47(5)	41(6)	44(5)	11(5)	-5(4)	8(5)
C2	42(5)	47(6)	51(5)	1(5)	4(4)	0(5)
C6	54(6)	58(8)	45(5)	-19(6)	6(4)	-4(6)
C5	47(5)	45(8)	51(5)	-7(6)	11(4)	-8(5)
C8	39(5)	36(6)	59(6)	-2(5)	2(4)	-2(4)
C12	78(8)	46(7)	51(6)	13(6)	18(6)	8(7)
C3	40(4)	52(7)	50(4)	17(7)	7(3)	1(7)
C7	41(5)	39(6)	52(5)	3(5)	-1(4)	-4(5)

Table 4 Bond Lengths for 3d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C1	1.904(12)	O1	C7	1.194(13)
O2	C12	1.371(16)	C9	C10	1.501(15)
O2	C8	1.440(14)	C9	C8	1.512(15)
O3	C10	1.232(15)	C1	C6	1.361(15)
C11	C12	1.308(19)	C1	C2	1.369(15)
C11	C10	1.432(18)	C2	C3	1.397(19)
C4	C3	1.390(14)	C6	C5	1.409(16)
C4	C5	1.420(14)	C8	C7	1.550(15)
C4	C7	1.469(16)			

Table 5 Bond Angles for 3d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	O2	C8	113.9(9)	C1	C2	C3	117.6(10)

C12	C11	C10	122.2(11)	C1	C6	C5	119.4(10)
C3	C4	C5	118.6(11)	C6	C5	C4	119.0(10)
C3	C4	C7	125.2(10)	O2	C8	C9	113.6(9)
C5	C4	C7	116.0(9)	O2	C8	C7	107.3(9)
C10	C9	C8	112.2(9)	C9	C8	C7	112.5(9)
O3	C10	C11	124.2(11)	C11	C12	O2	125.9(12)
O3	C10	C9	121.1(11)	C4	C3	C2	121.9(10)
C11	C10	C9	114.6(10)	O1	C7	C4	122.9(10)
C6	C1	C2	123.4(11)	O1	C7	C8	119.0(11)
C6	C1	Br1	118.7(8)	C4	C7	C8	118.0(9)
C2	C1	Br1	117.8(8)				

Table 6 Torsion Angles for 3d.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C12	C11	C10	O3	-178.2(12)	C10	C9	C8	C7	73.7(13)
C12	C11	C10	C9	-1.6(17)	C10	C11	C12	O2	-6.4(19)
C8	C9	C10	O3	-155.3(12)	C8	O2	C12	C11	-14.7(16)
C8	C9	C10	C11	27.9(14)	C5	C4	C3	C2	-3.4(17)
C6	C1	C2	C3	0.0(17)	C7	C4	C3	C2	-178.1(11)
Br1	C1	C2	C3	179.0(9)	C1	C2	C3	C4	1.2(17)
C2	C1	C6	C5	1.0(17)	C3	C4	C7	O1	-179.8(12)
Br1	C1	C6	C5	-178.0(9)	C5	C4	C7	O1	5.4(17)
C1	C6	C5	C4	-3.1(17)	C3	C4	C7	C8	-3.2(16)
C3	C4	C5	C6	4.3(16)	C5	C4	C7	C8	-178.0(10)
C7	C4	C5	C6	179.5(10)	O2	C8	C7	O1	118.1(12)
C12	O2	C8	C9	41.7(12)	C9	C8	C7	O1	-7.5(15)
C12	O2	C8	C7	-83.3(11)	O2	C8	C7	C4	-58.7(12)
C10	C9	C8	O2	-48.4(13)	C9	C8	C7	C4	175.7(9)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3d.

Atom	*x*	*y*	*z*	U(eq)
H11	10965	15203	456	66
H9A	16529	11762	1069	62
H9B	15220	11341	1871	62
H2	20668	20950	2998	56
H6	15067	20171	4496	63
H5	13618	17056	3802	57
H8	18280	14213	1913	53
H12	13892	17723	513	70
H3	19210	17928	2276	56

checkCIF (basic structural check) running

Checking for embedded fcf data in CIF ...
Found embedded fcf data in CIF. Extracting fcf data from uploaded CIF, please wait.

checkCIF/PLATON (basic structural check)

Structure factors have been supplied for datablock(s) shelxl

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary

Please wait while processing .... Interpreting this report

Structure factor report

Datablock: shelxl

Bond precision: C-C = 0.0160 A Wavelength=1.54184

Cell: a=5.3040(3) b=6.0907(3) c=16.9947(10)
alpha=90 beta=91.708(5) gamma=90

Temperature: 290 K

	Calculated	Reported
Volume	548.77(5)	548.77(5)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C12 H9 Br O3	?
Sum formula	C12 H9 Br O3	C12 H9 Br O3
Mr	281.09	281.10
Dx,g cm-3	1.701	1.701
Z	2	2

Mu (mm-1)	5.028	5.028
F000	280.0	280.0
F000'	279.36	
h,k,lmax	6,7,20	6,7,20
Nref	2058[1133]	1377
Tmin,Tmax	0.250,0.245	0.647,1.000
Tmin'	0.160	

Correction method= # Reported T Limits: Tmin=0.647 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.22/0.67 Theta(max)= 69.220

R(reflections)= 0.0661(1325) wR2(reflections)= 0.1681(1377)

S = 1.027 Npar= 145

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.016 Ang.
PLAT915_ALERT_3_B Low Friedel Pair Coverage ....(No Flack x Check) 31 %

Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.967 Note
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ..... 7.49 Note
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note
C12 H9 Br O3
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 35 Report
PLAT913_ALERT_3_C Missing # of Very Strong Reflections in FCF .... 5 Note

---

Alert level G

PLAT791_ALERT_4_G The Model has Chirality at C8 (Chiral SPGR) R Verify
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Th(Min) ... 1 Report
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 12 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
0 ALERT type 2 Indicator that the structure model may be wrong or deficient
7 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Validation response form

Please find below a validation response form (VRF) that can be filled in and pasted into your CIF.

```
# start Validation Reply Form
_vrf_PLAT029_shelxl
;
PROBLEM: _diffrn_measured_fraction_theta_full Low .......        0.967 Note
RESPONSE: ...
;
_vrf_PLAT090_shelxl
;
PROBLEM: Poor Data / Parameter Ratio (Zmax > 18) ........         7.49 Note
RESPONSE: ...
;
_vrf_PLAT790_shelxl
;
PROBLEM: Centre of Gravity not Within Unit Cell: Resd.   #             1 Note
RESPONSE: ...
;
_vrf_PLAT911_shelxl
;
PROBLEM: Missing # FCF Refl Between THmin & STh/L=   0.600           35 Report
RESPONSE: ...
;
_vrf_PLAT913_shelxl
;
PROBLEM: Missing # of Very Strong Reflections in FCF ....             5 Note
RESPONSE: ...
;
# end Validation Reply Form
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or

experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

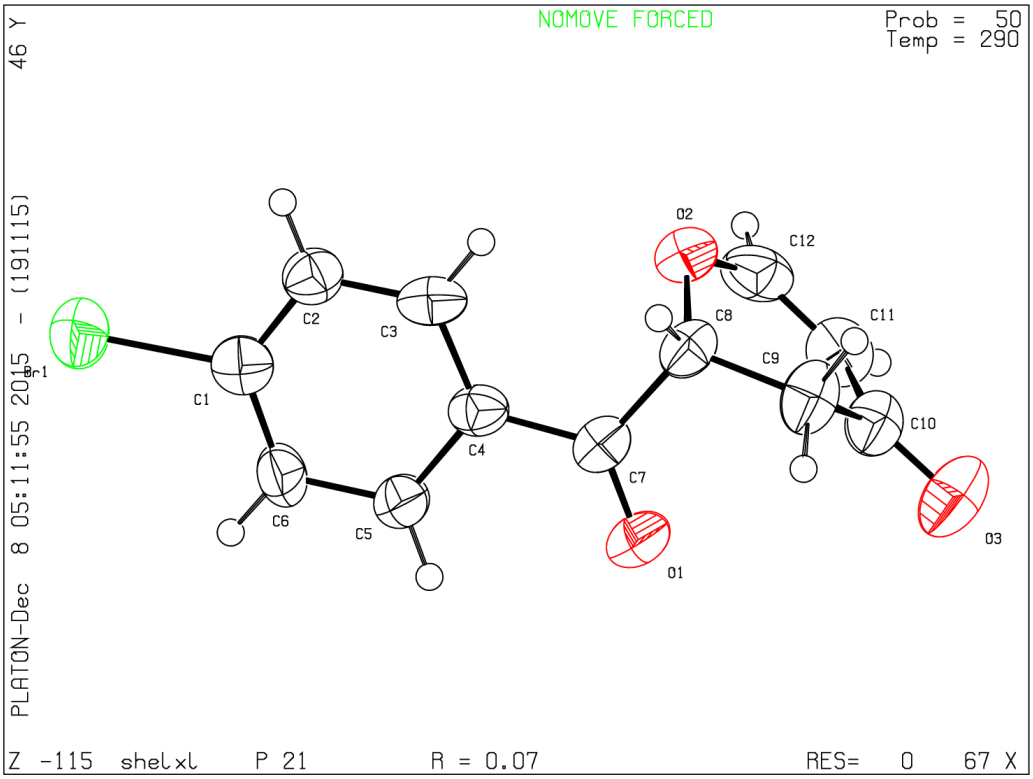
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checksare run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock shelxl- ellipsoid plot



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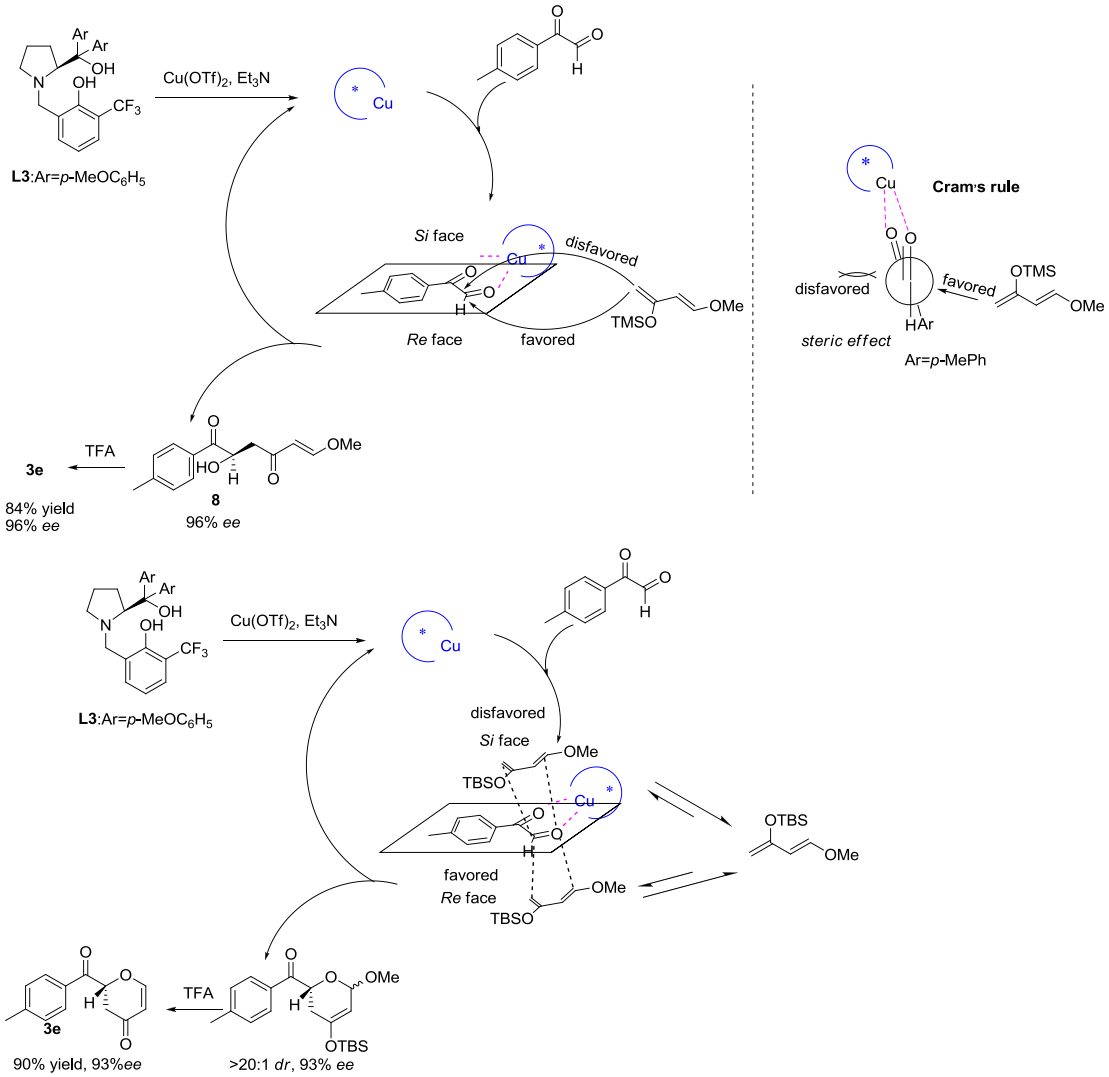
Part IV **The explanation of the HDA Reaction**

A plausible reaction pathway was proposed in scheme 1 in Supporting Information. The catalyst was generated in situ through stirring the solution of $Cu(OTf)_2$, Ligand **L3**, and Et_3N in CPME for 2h. The catalyst could coordinate with the double carbonyl groups of **1e**, resulting in the attack of Danishefsky's diene from the favored *Re* face due to the steric effect of the ligand. Then, the asymmetric hetero-Diels-Alder reaction of Danishefsky's diene with glyoxals afforded the product **3e**.

Scheme 1. The plausible mechanism of the HDA Reaction