Supporting Information

Substrate-dependent Divergent Outcome from Catalytic Reactions of Silyl-protected Enoldiazoacetates With Nitrile Oxides: Azabicyclo[3.1.0]hexanes or 5-Arylaminofuran-2(3*H*)-ones

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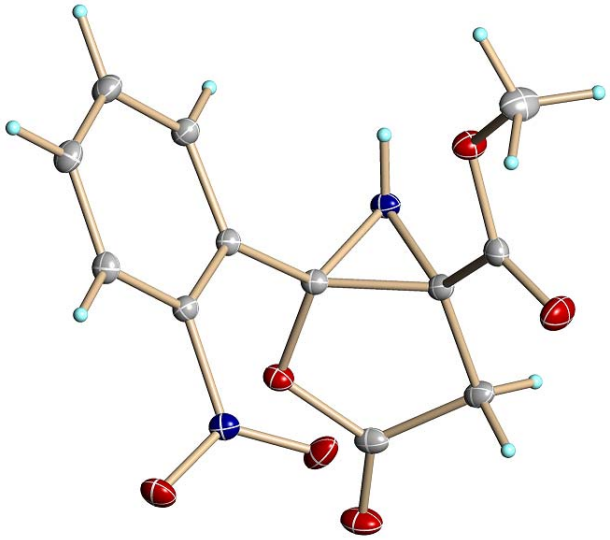
Crystallographic data for compound 4g

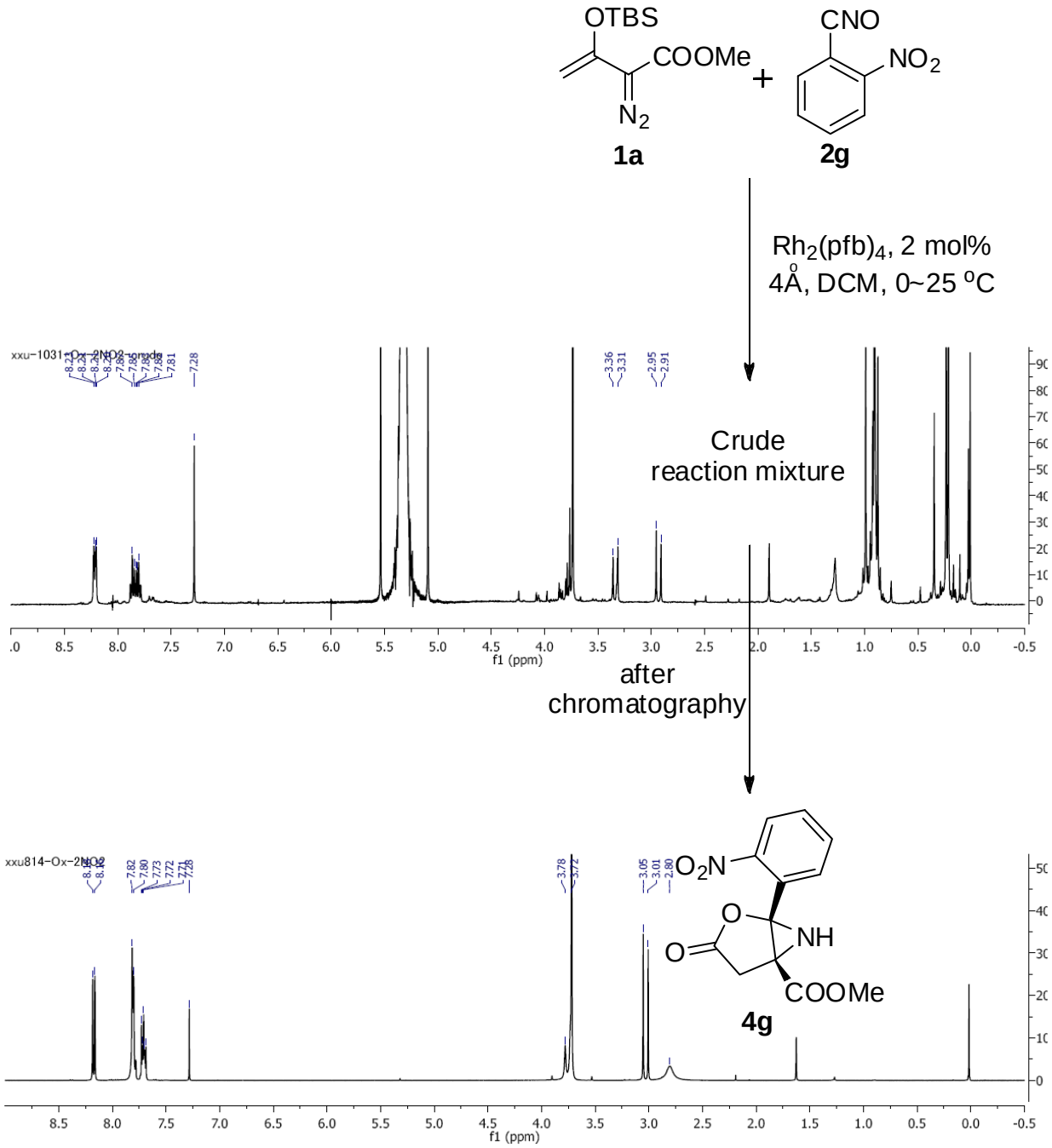


A clear colourless prism-like specimen of $C_{12}H_{10}N_2O_6$, approximate dimensions 0.10 mm × 0.28 mm × 0.50 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Smart Apex2, CCD system equipped with a graphite monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

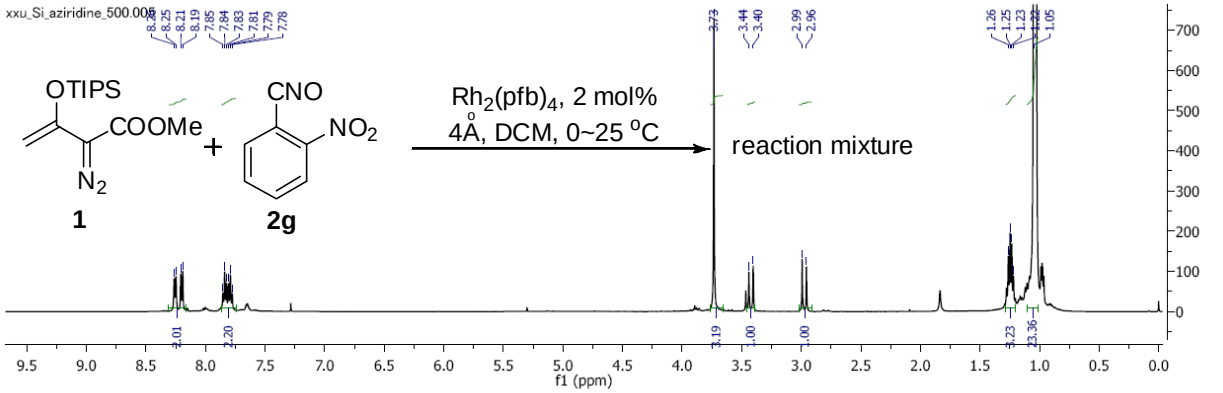
The total exposure time was 12.63 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 17592 reflections to a maximum θ angle of 30.00° (0.71 Å resolution), of which 3452 were independent (average redundancy 5.096, completeness = 100.0%, R_{int} = 1.93%, R_{sig} = 1.48%) and 3196 (92.58%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.8882(5) Å, b = 20.8439(15) Å, c = 8.2554(6) Å, β = 90.0280(10)°, V = 1185.29(15) Å^3, are based upon the refinement of the XYZ-centroids of 9934 reflections above 20 σ(I) with 4.934° < 2θ < 62.18°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9440 and 0.9880.

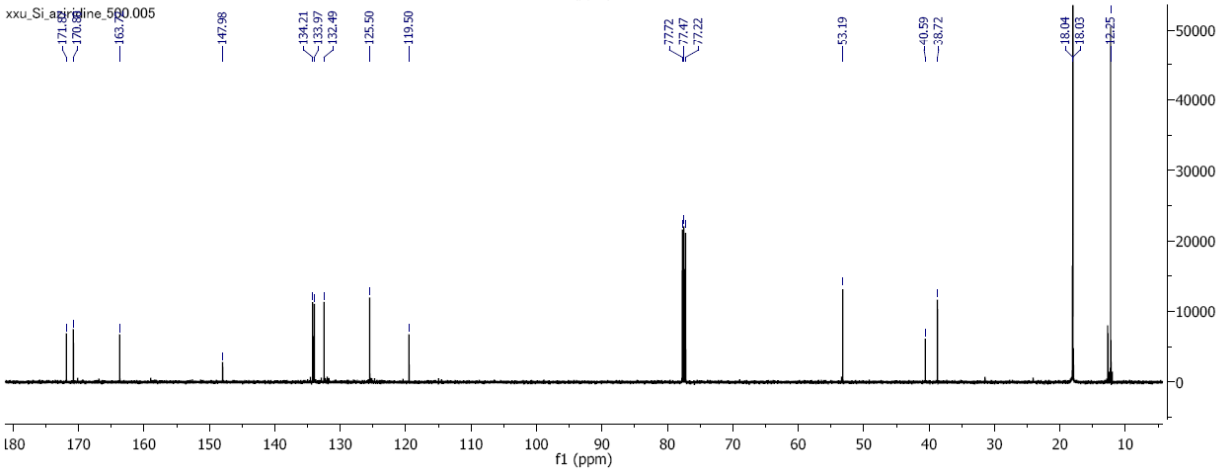
The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{12}H_{10}N_2O_6$. The final anisotropic full-matrix least-squares refinement on F^2 with 221 variables converged at R_1 = 3.50%, for the observed data and wR_2 = 7.14% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.455 e$^-$/Å^3 and the largest hole was -0.228 e$^-$/Å^3 with an RMS deviation of 0.045 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.559 g/cm^3 and F(000), 576 e$^-$

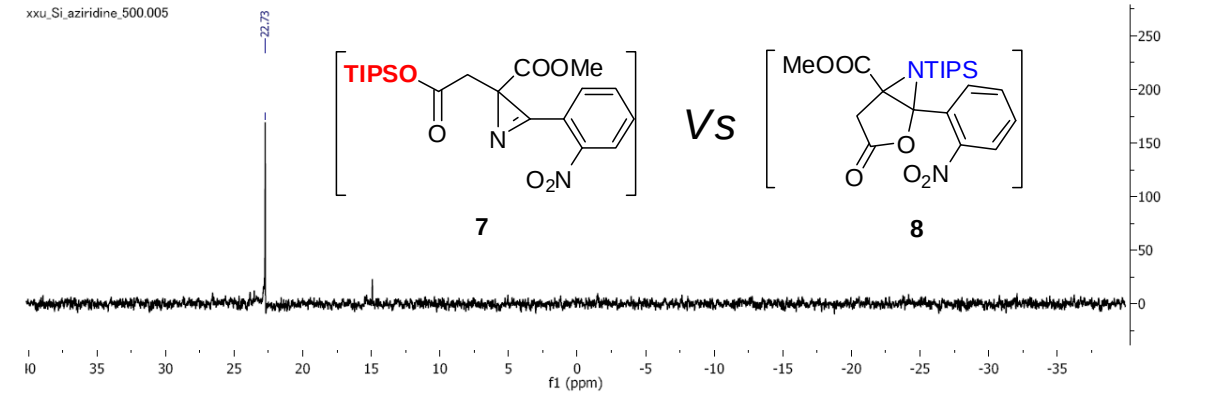
^{1}H NMR spectra comparison of 4g with the reaction mixture (pre-4g)

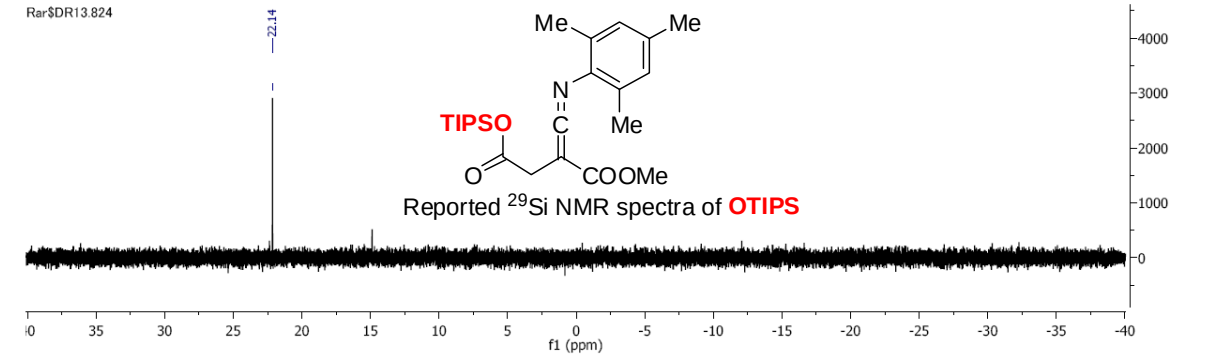


NMR spectra of reaction mixture with TIPS-enoldiazoacetate









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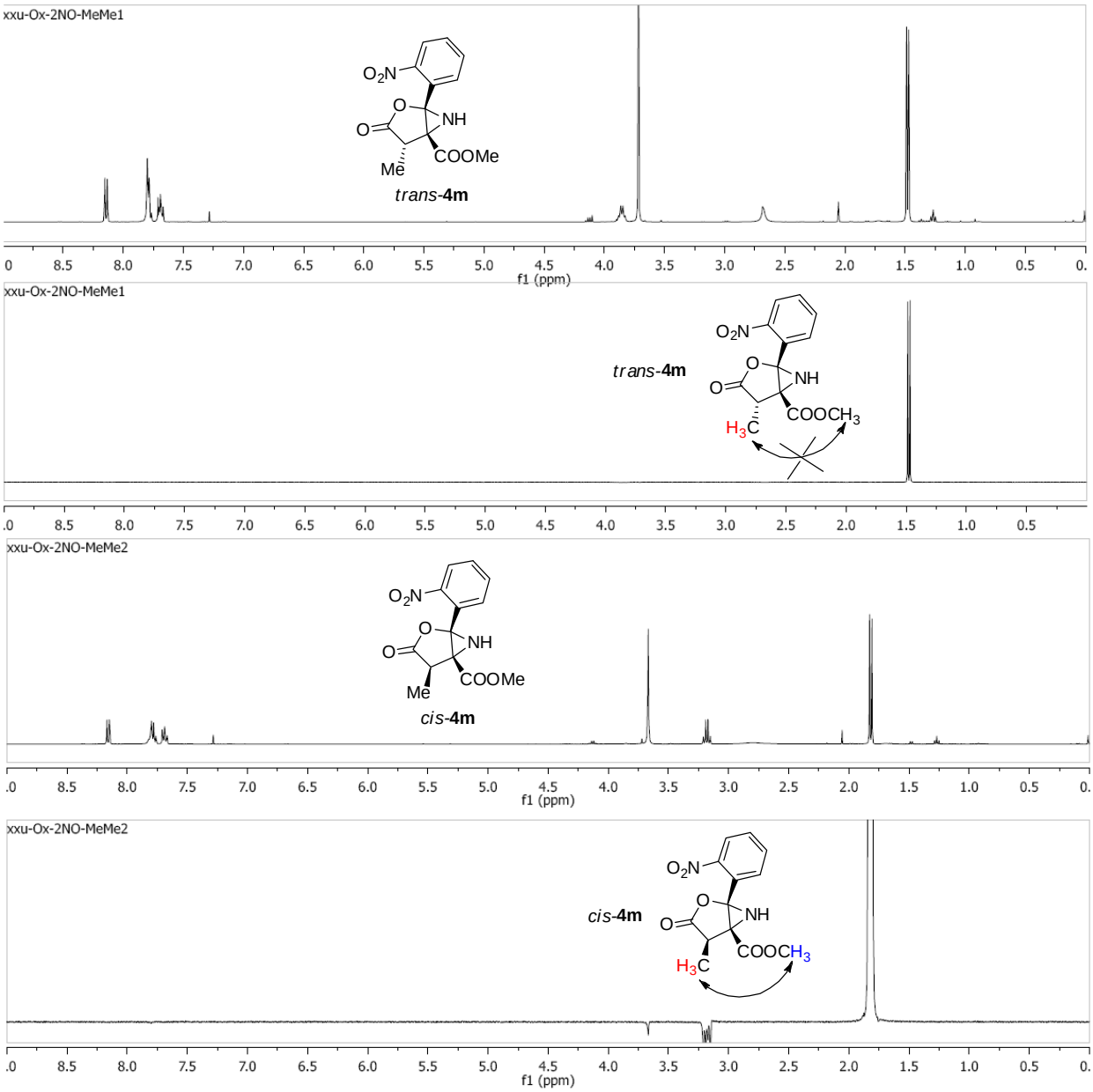
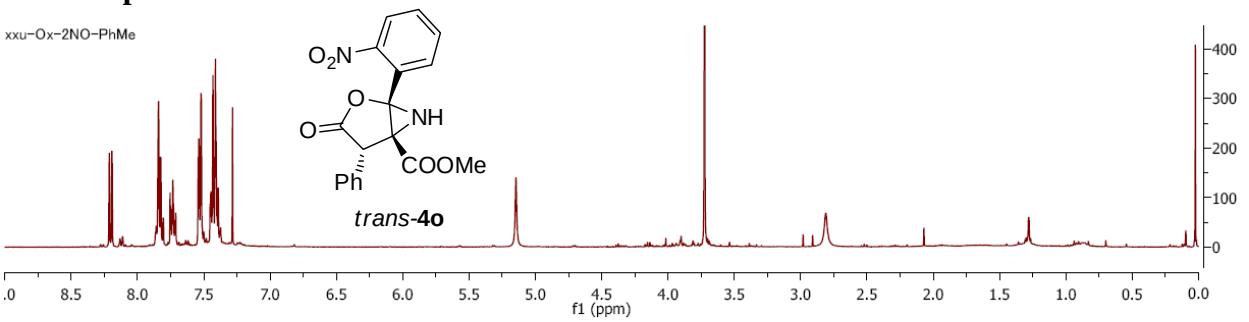
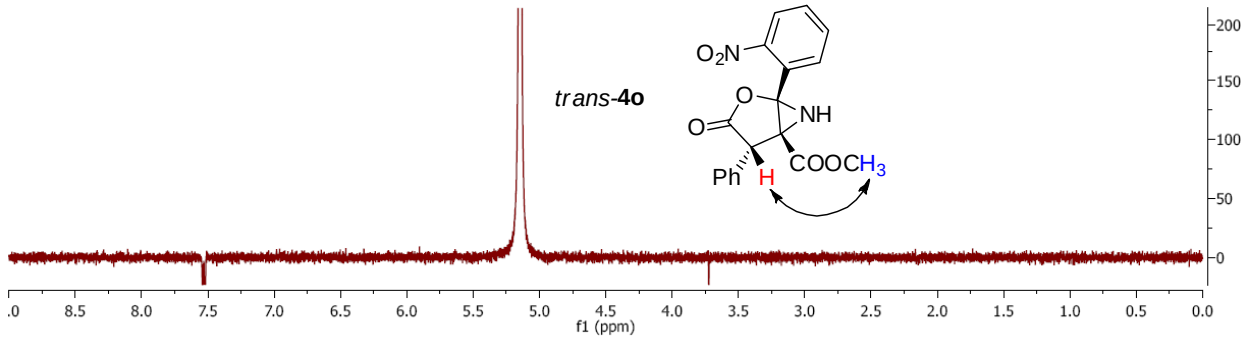
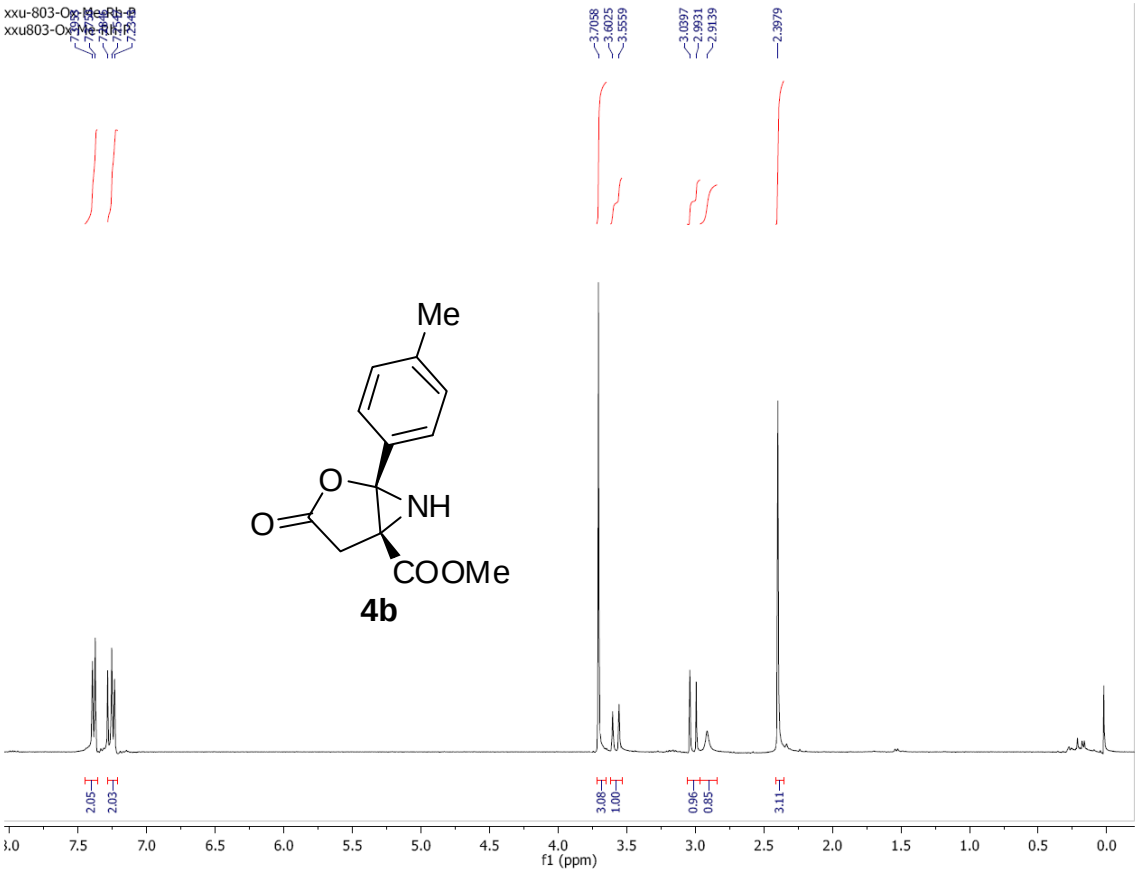


1D-Noe spectra of *trans*-4o



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xxu803-Ox-Me-Rh-P
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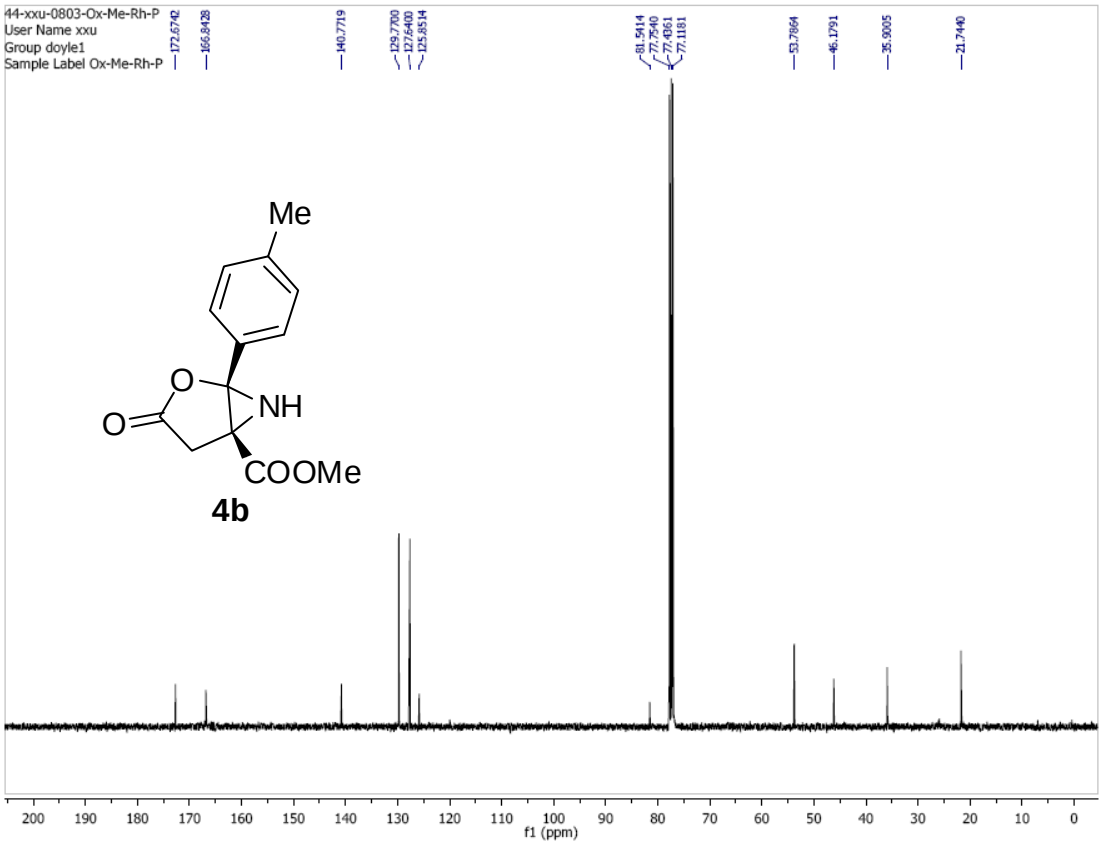
NH
O
COOMe
4b
f1 (ppm)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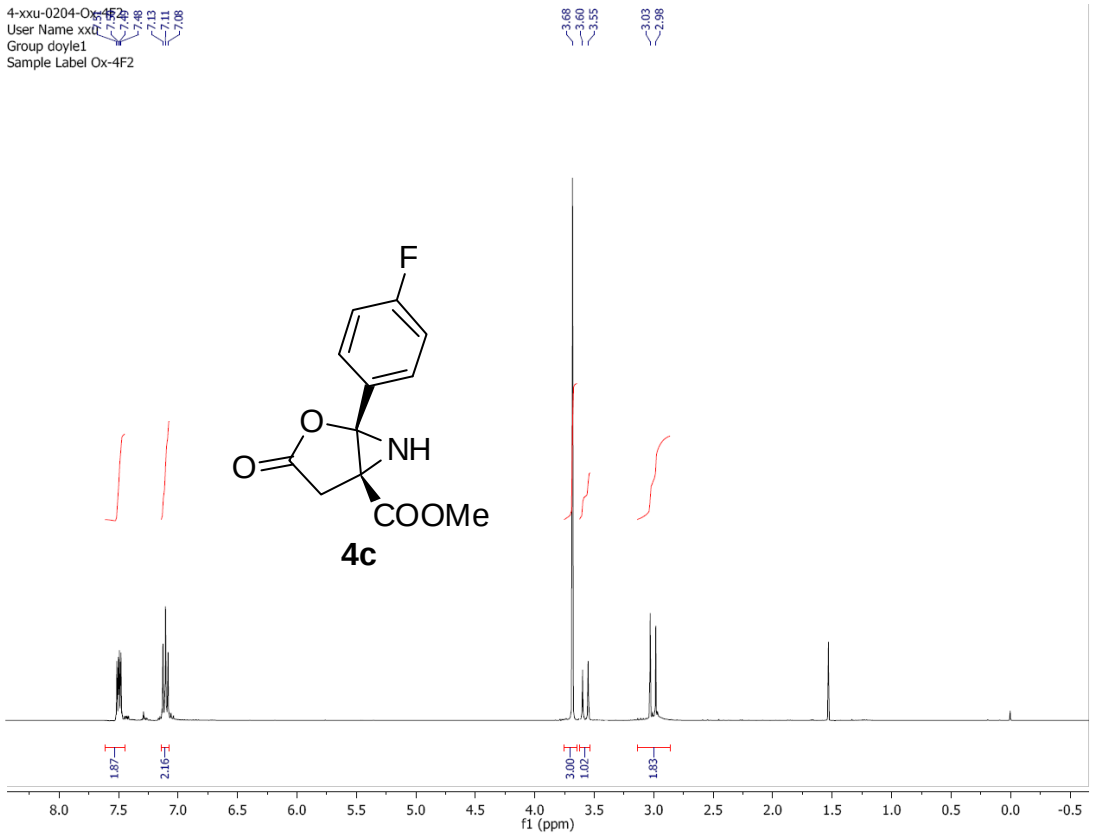
NH
O
COOMe
4b
f1 (ppm)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Sample Label Ox-4F2
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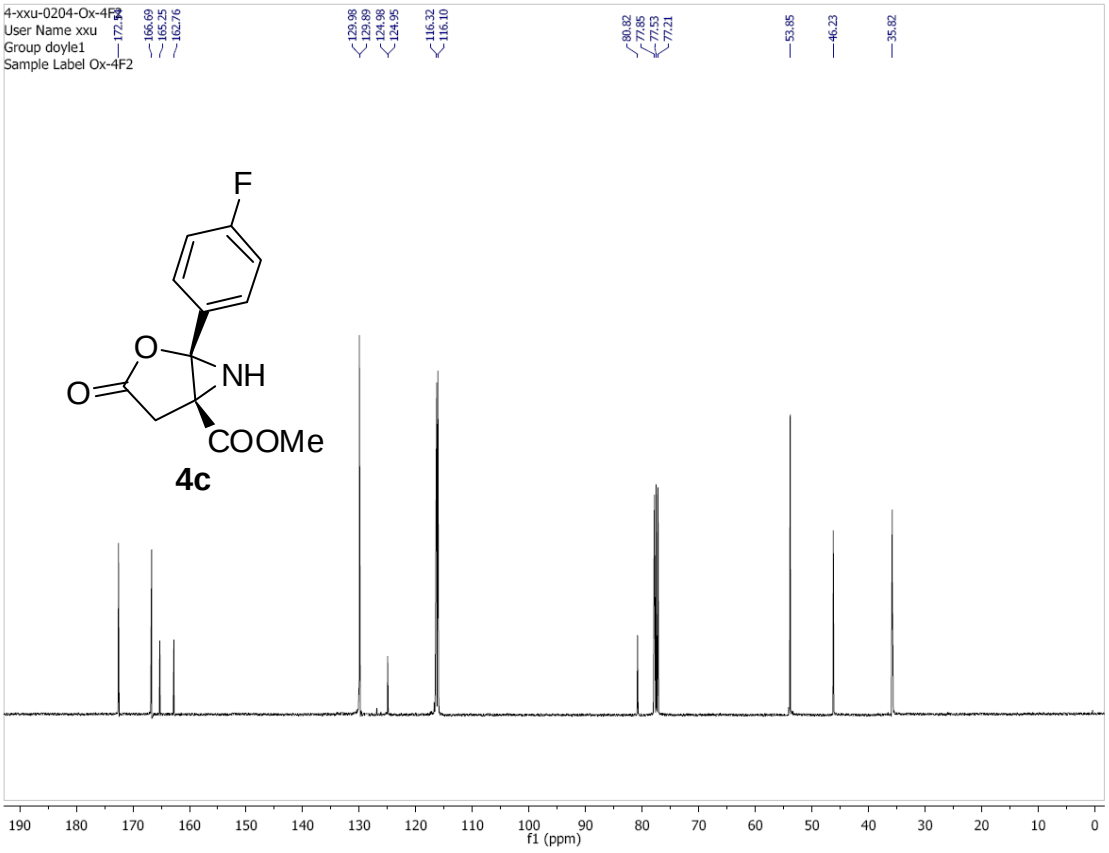
7.13
7.11
7.08
3.68
3.60
3.55
3.03
2.98
F
O
NH
O
COOMe
4c
1.87
2.16
3.00
1.02
1.83
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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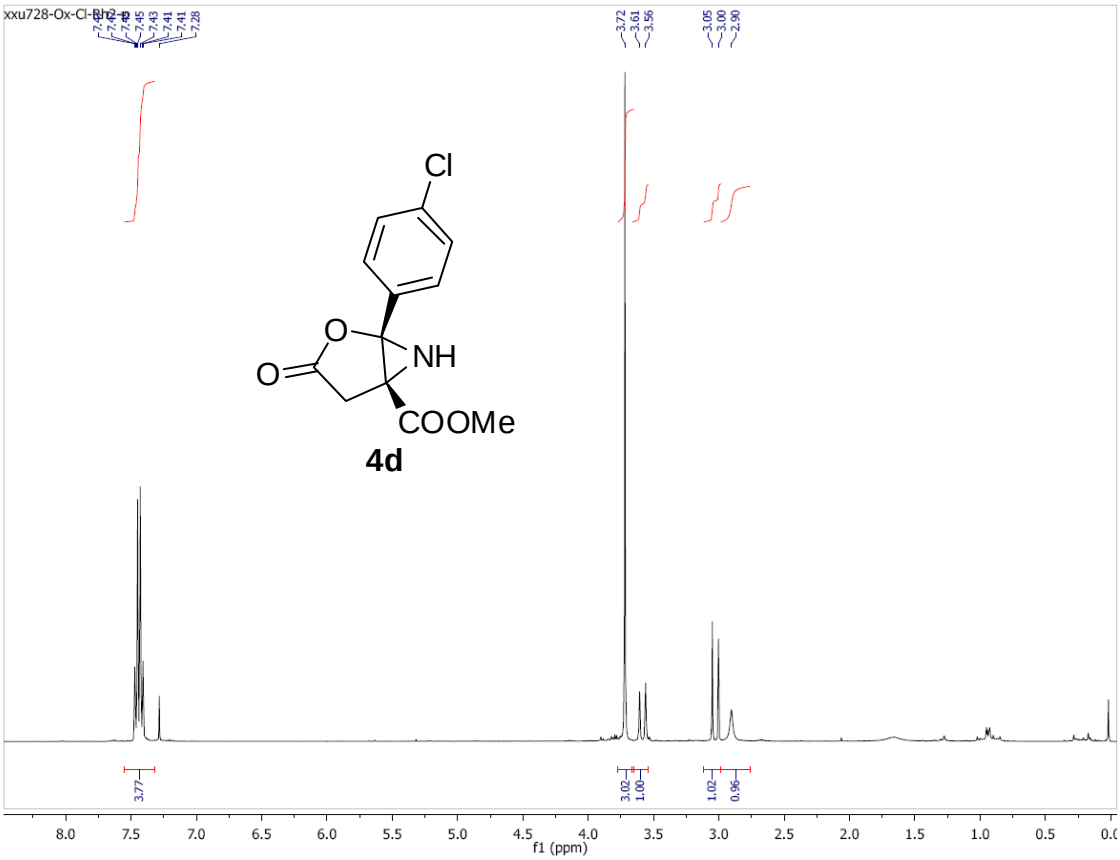
124.98
124.95
116.32
116.10
80.82
77.85
77.53
77.21
53.85
46.23
35.82
F
O
NH
O
COOMe
4c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.45
7.43
7.41
7.41
7.28
3.72
3.61
3.56
3.05
3.00
2.90
Cl
O
NH
O
COOMe
4d
3.77
3.02
1.00
1.02
0.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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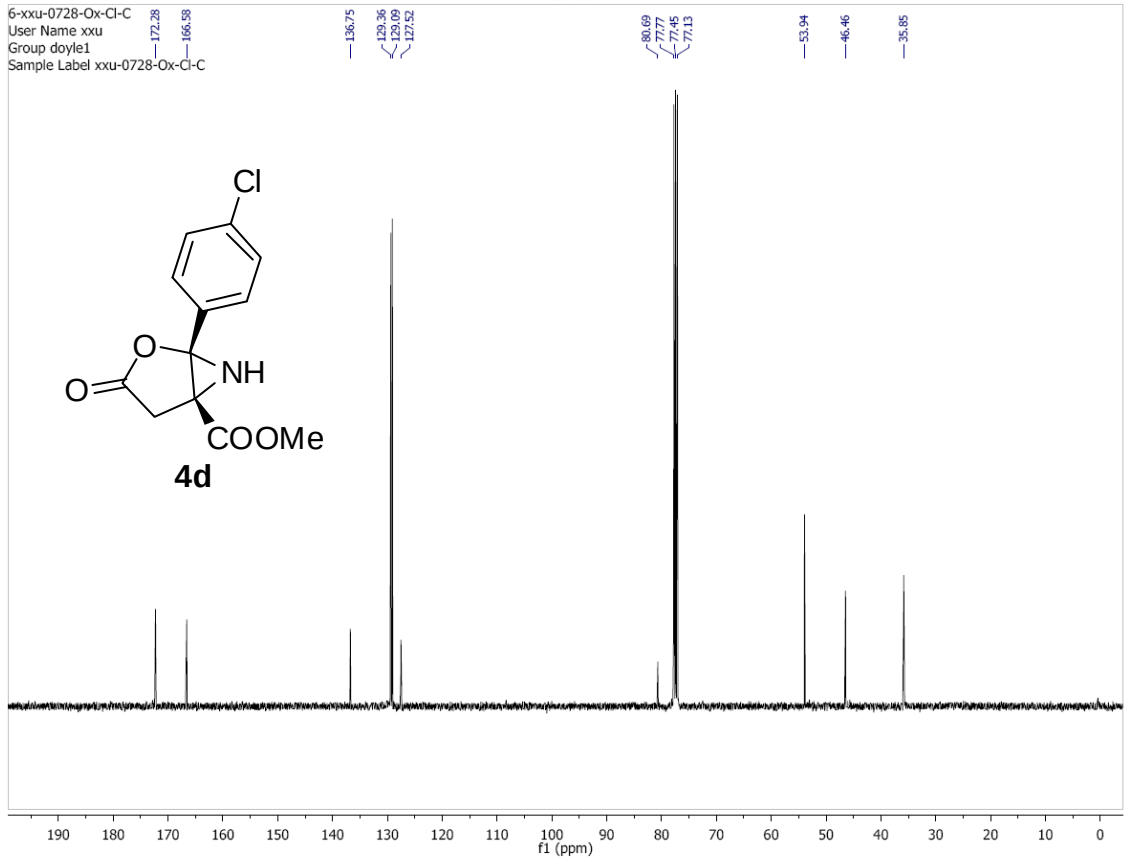
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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Group doyle1
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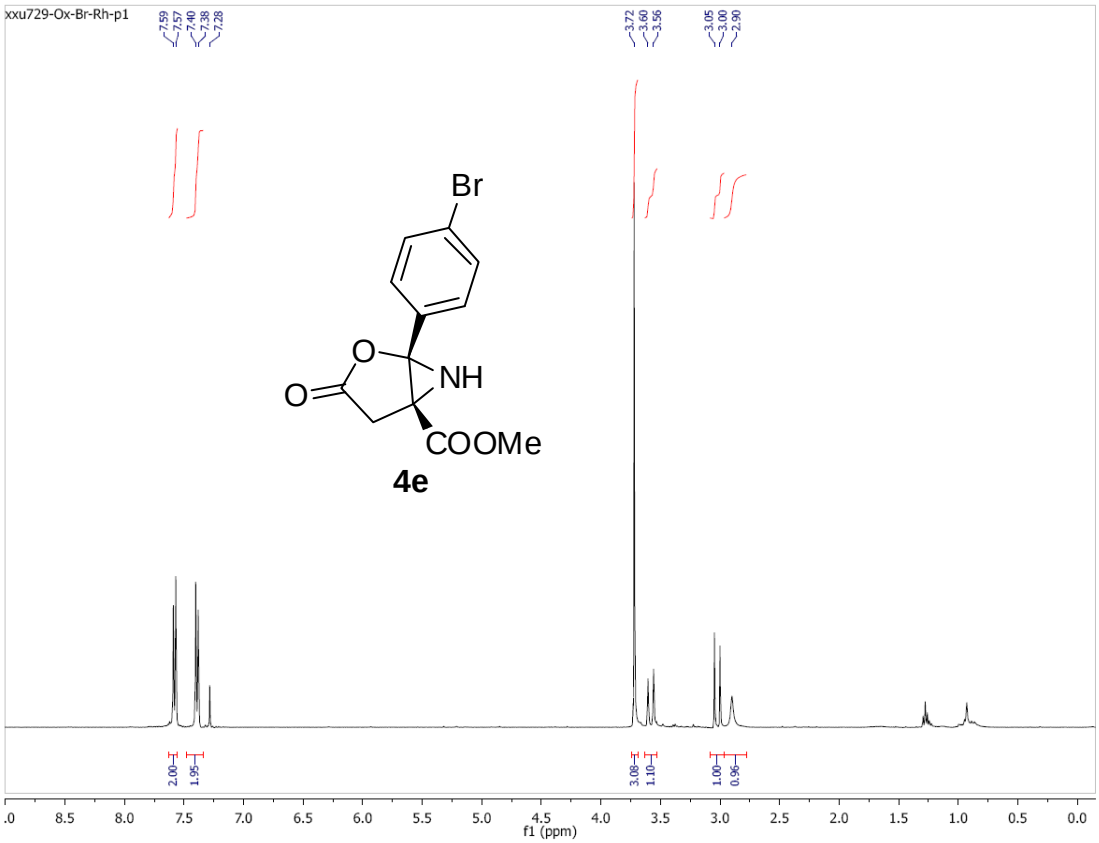
166.58
136.75
129.36
129.09
127.52
80.69
77.77
77.45
77.13
53.94
46.46
35.85
Cl
O
NH
O
COOMe
4d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.38
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3.05
3.00
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NH
O
COOMe
4e
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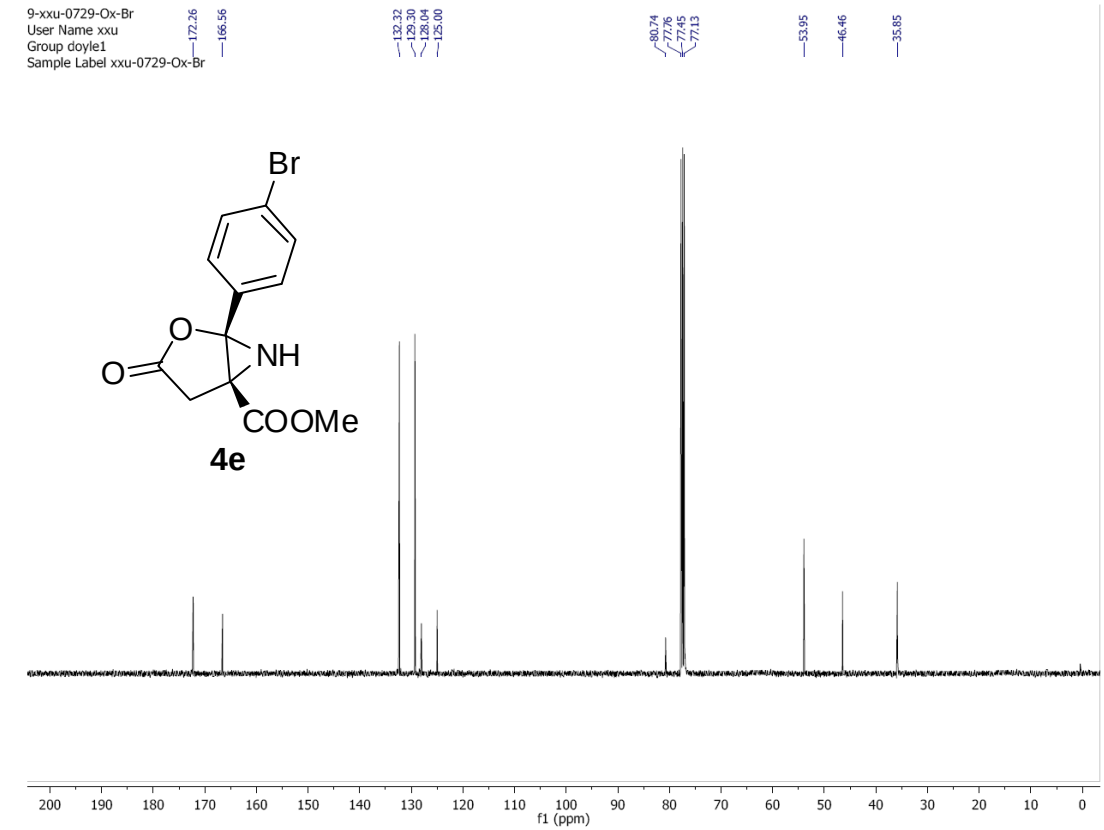
1.95
3.08
1.10
1.00
0.96
f1 (ppm)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Group doyle1
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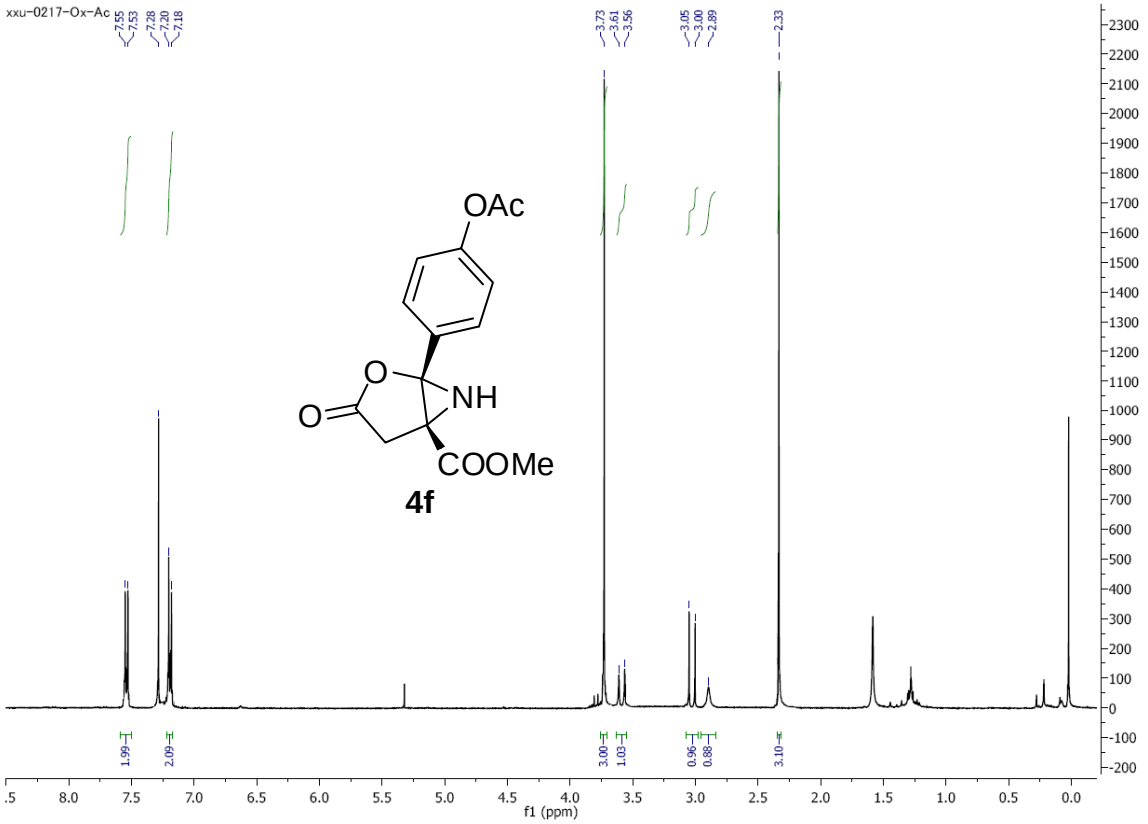
132.32
129.30
128.04
125.00
80.74
77.76
77.45
77.13
53.95
46.46
35.85
Br
O
NH
O
COOMe
4e
f1 (ppm)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7.53
7.28
7.20
7.18
3.73
3.61
3.56
3.05
3.00
2.89
2.33
OAc
O
NH
O
COOMe
4f
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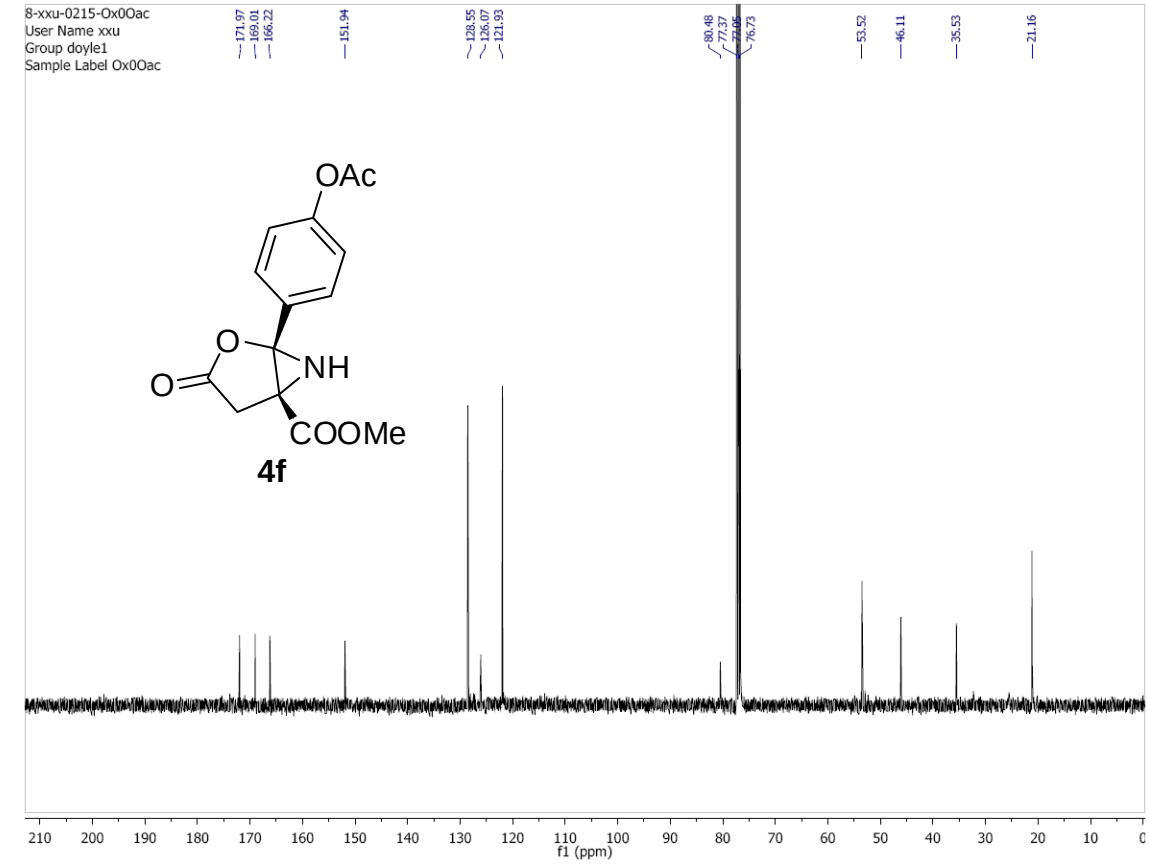
2.09
3.00
1.03
0.96
0.88
3.10
f1 (ppm)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Group doyle1
Sample Label Ox0Oac
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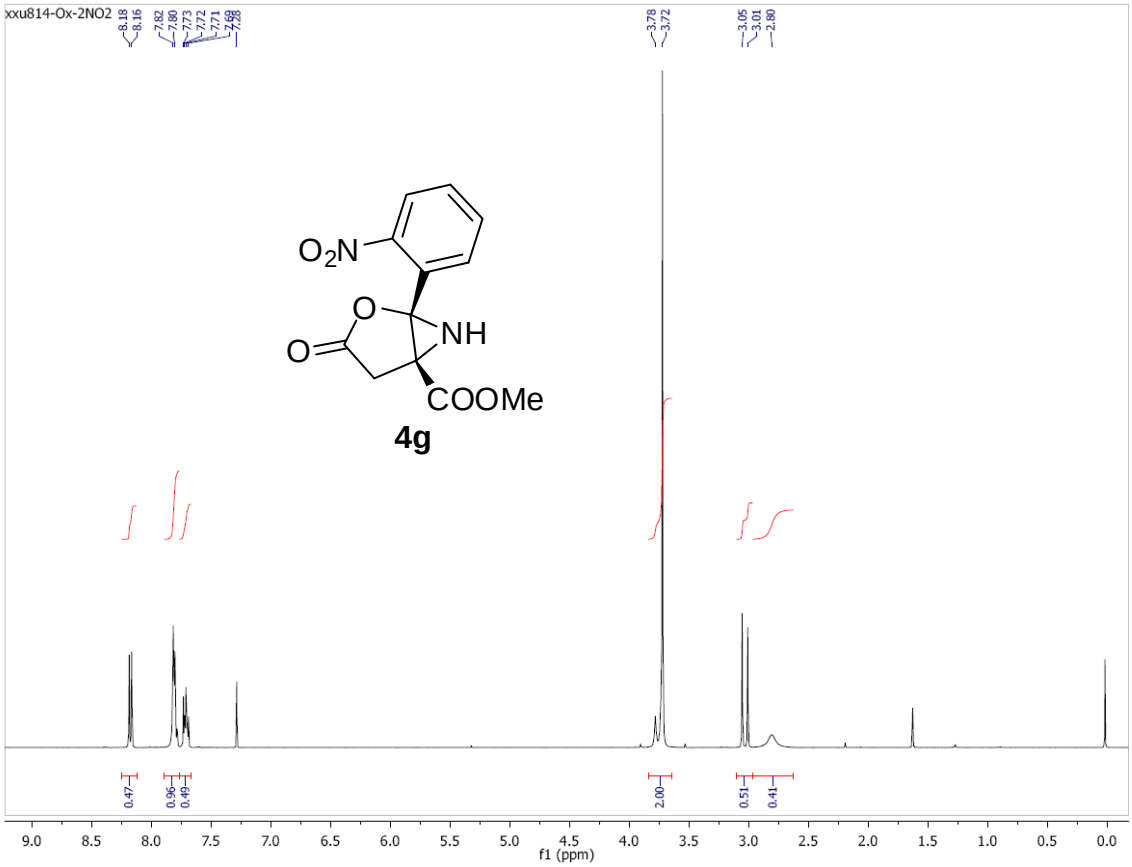
166.22
151.94
128.55
126.07
121.93
80.48
77.37
77.05
76.73
53.52
46.11
35.53
21.16
OAc
O
NH
O
COOMe
4f
f1 (ppm)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7.82
7.80
7.73
7.72
7.71
3.78
3.72
3.05
3.01
2.80
O2N
O
NH
O
COOMe
4g
0.47
0.96
0.49
2.00
0.51
0.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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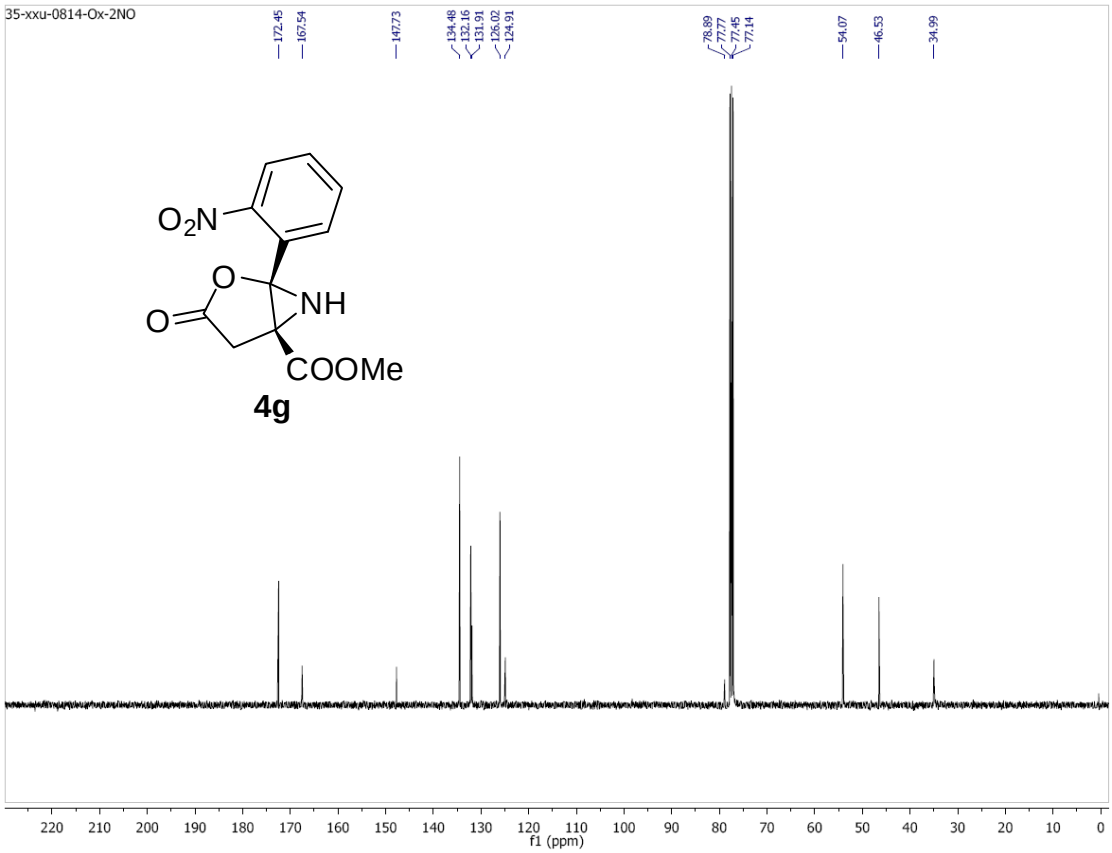
1.0
0.5
0.0
f1 (ppm)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126.02
124.91
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77.77
77.45
77.14
54.07
46.53
34.99
O2N
O
NH
O
COOMe
4g
220
210
200
190
180
170
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50
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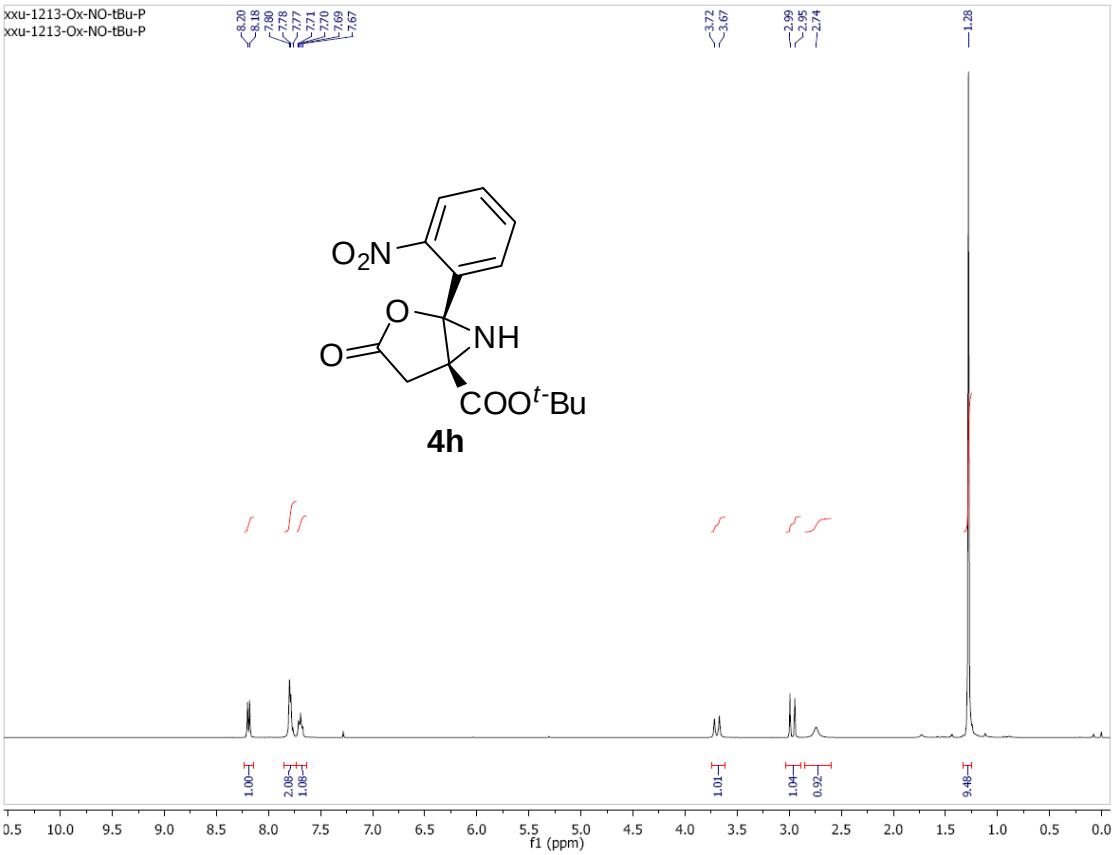
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xxu-1213-Ox-NO-tBu-P
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8.18
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7.78
7.77
7.71
7.70
7.69
7.67
3.72
3.67
2.99
2.95
2.74
1.28
O2N
O
NH
O
COOt-Bu
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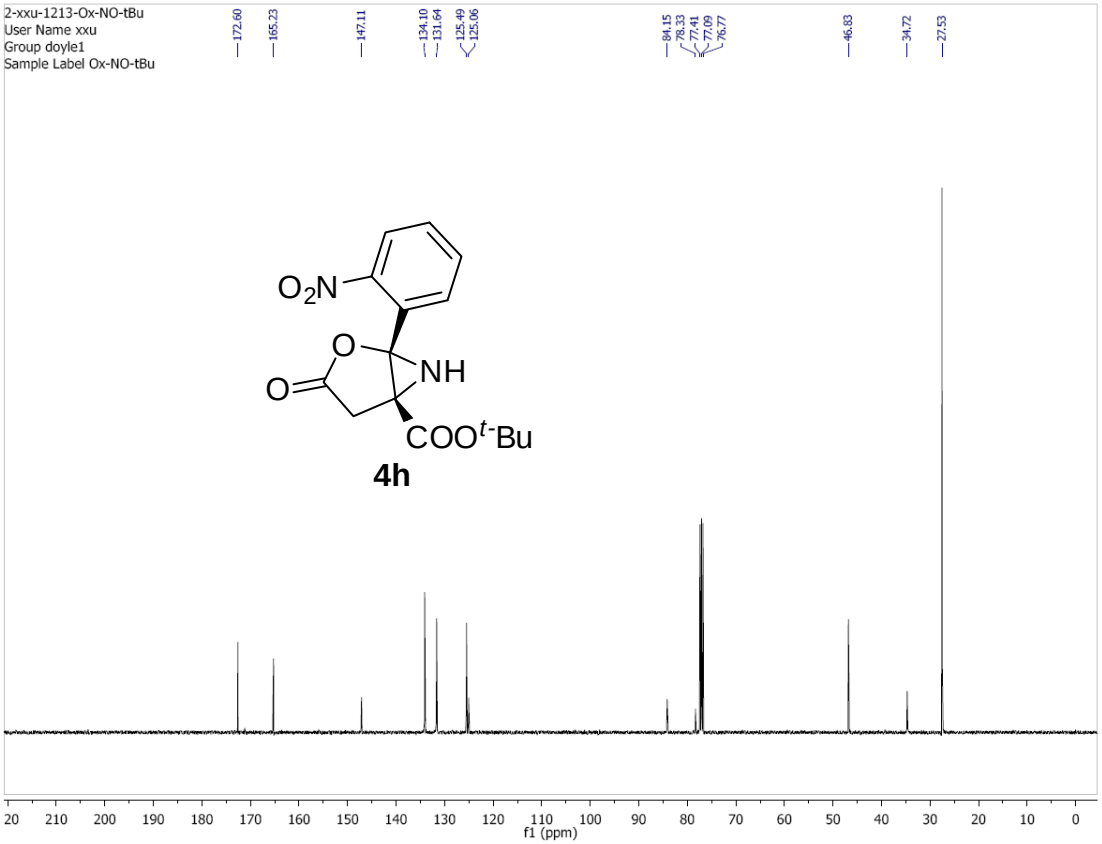
2.08
1.08
1.01
1.04
0.92
9.48
f1 (ppm)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Sample Label Ox-NO-tBu
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147.11
134.10
131.64
125.49
125.06
84.15
78.33
77.41
77.09
76.77
46.83
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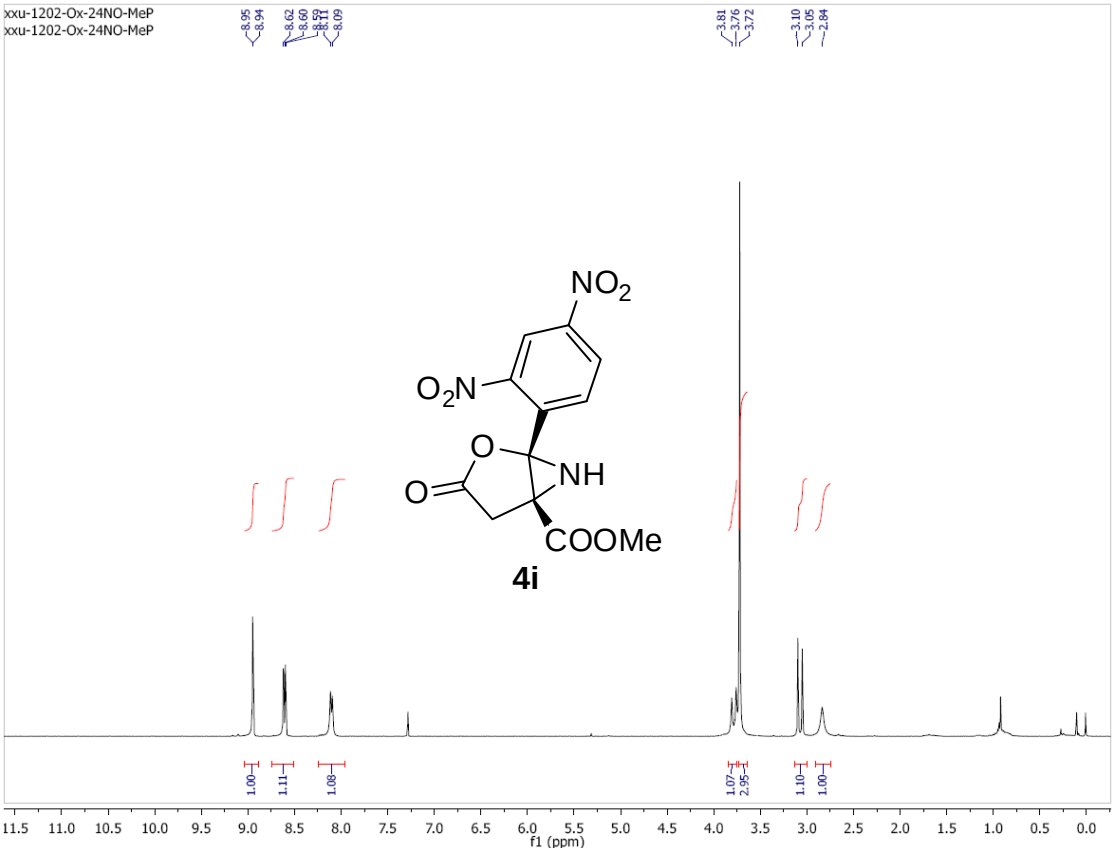
27.53
O2N
O
NH
O
COOt-Bu
4h
f1 (ppm)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8.09
3.81
3.76
3.72
3.10
3.05
2.84
NO2
O2N
O
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COOMe
4i
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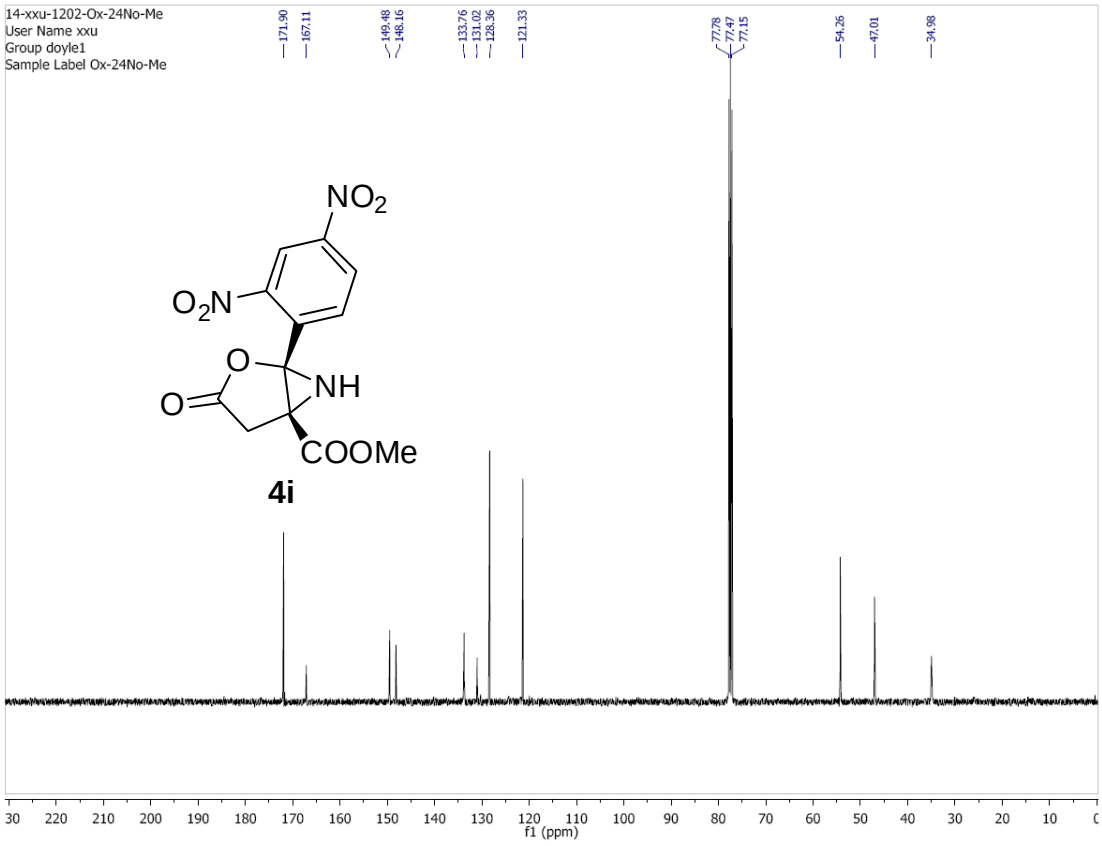
2.95
1.10
1.00
f1 (ppm)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Sample Label Ox-24No-Me
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149.48
148.16
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131.02
128.36
121.33
77.78
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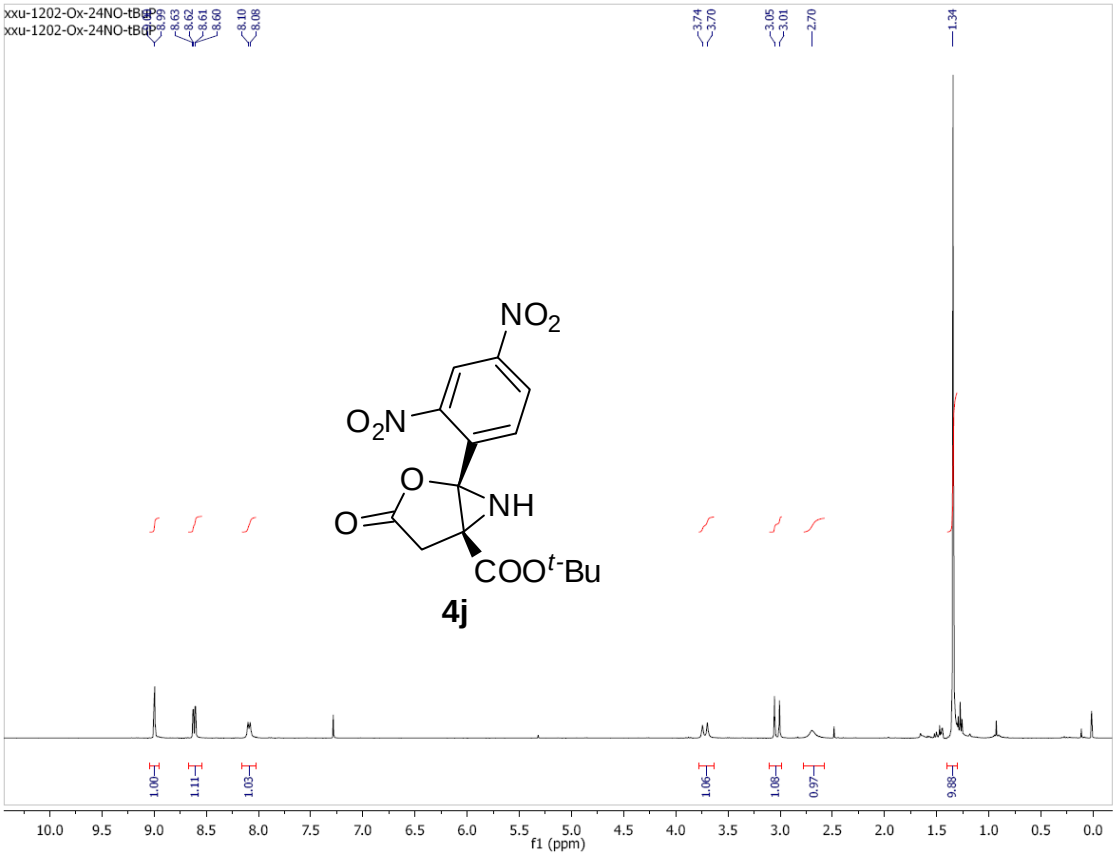
O
NH
O
COOMe
4i
f1 (ppm)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xxu-1202-Ox-24NO-tBuP
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8.63
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8.61
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3.74
3.70
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3.01
2.70
1.34
NO2
O2N
O
NH
O
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4j
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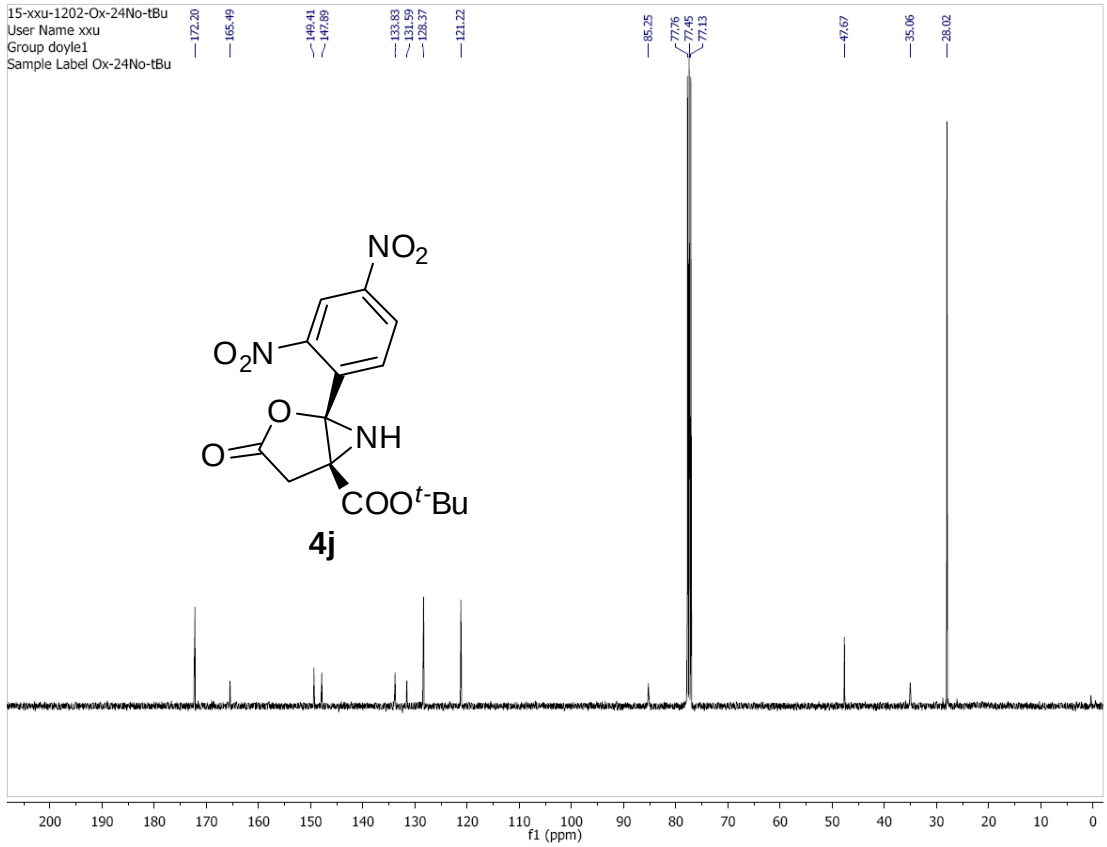
1.08
0.97
9.88
f1 (ppm)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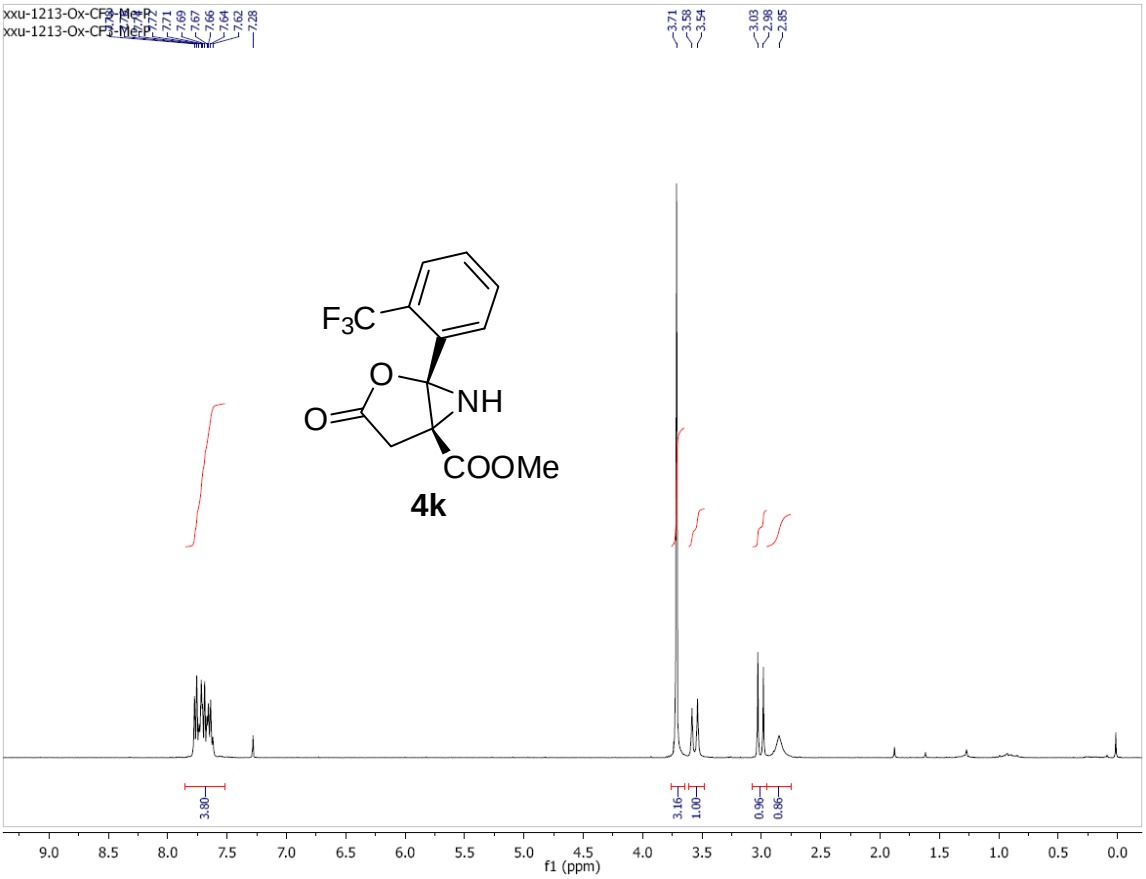
133.83
131.59
128.37
121.22
85.25
77.76
77.45
77.13
47.67
35.06
28.02
NO2
O2N
O
NH
O
COO^{t}-Bu
4j
f1 (ppm)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7.69
7.67
7.66
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7.62
7.28
3.71
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3.54
3.03
2.98
2.85
F3C
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NH
O
COOMe
4k
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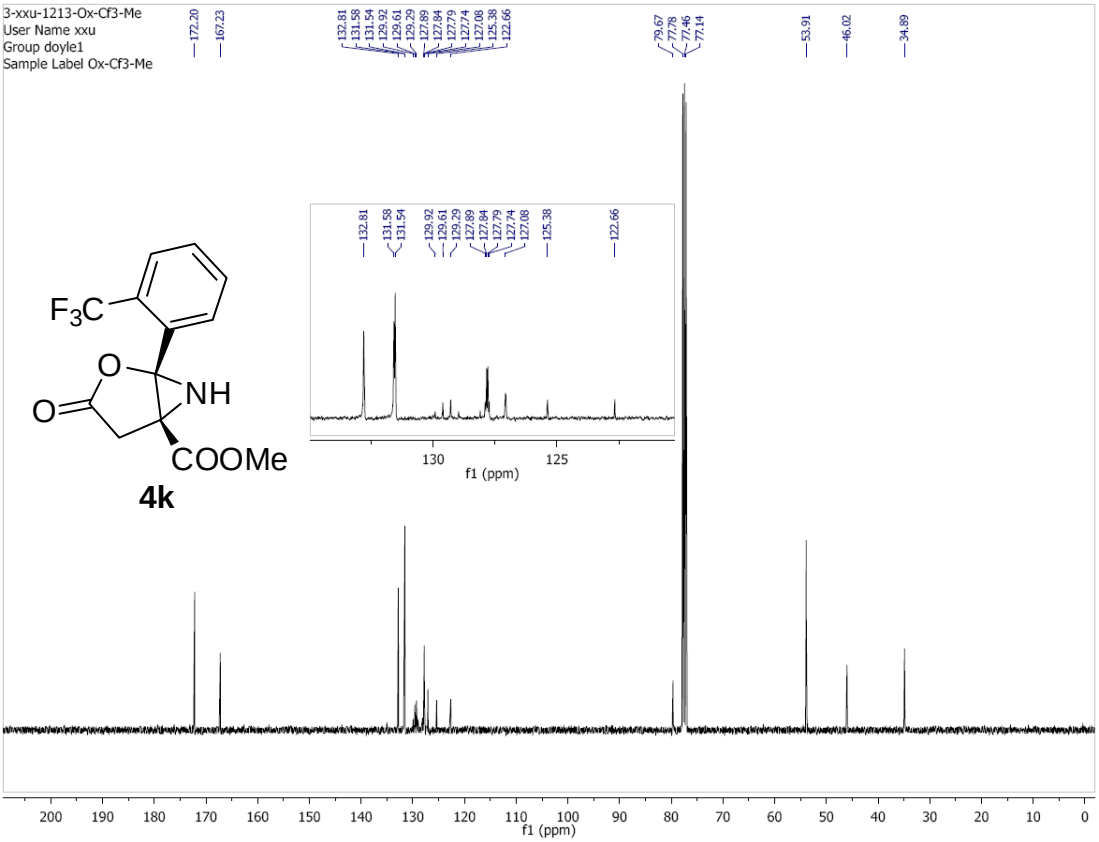
1.00
0.96
0.86
f1 (ppm)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132.81
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131.54
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129.61
129.29
127.89
127.84
127.79
127.74
127.08
125.38
122.66
79.67
77.78
77.46
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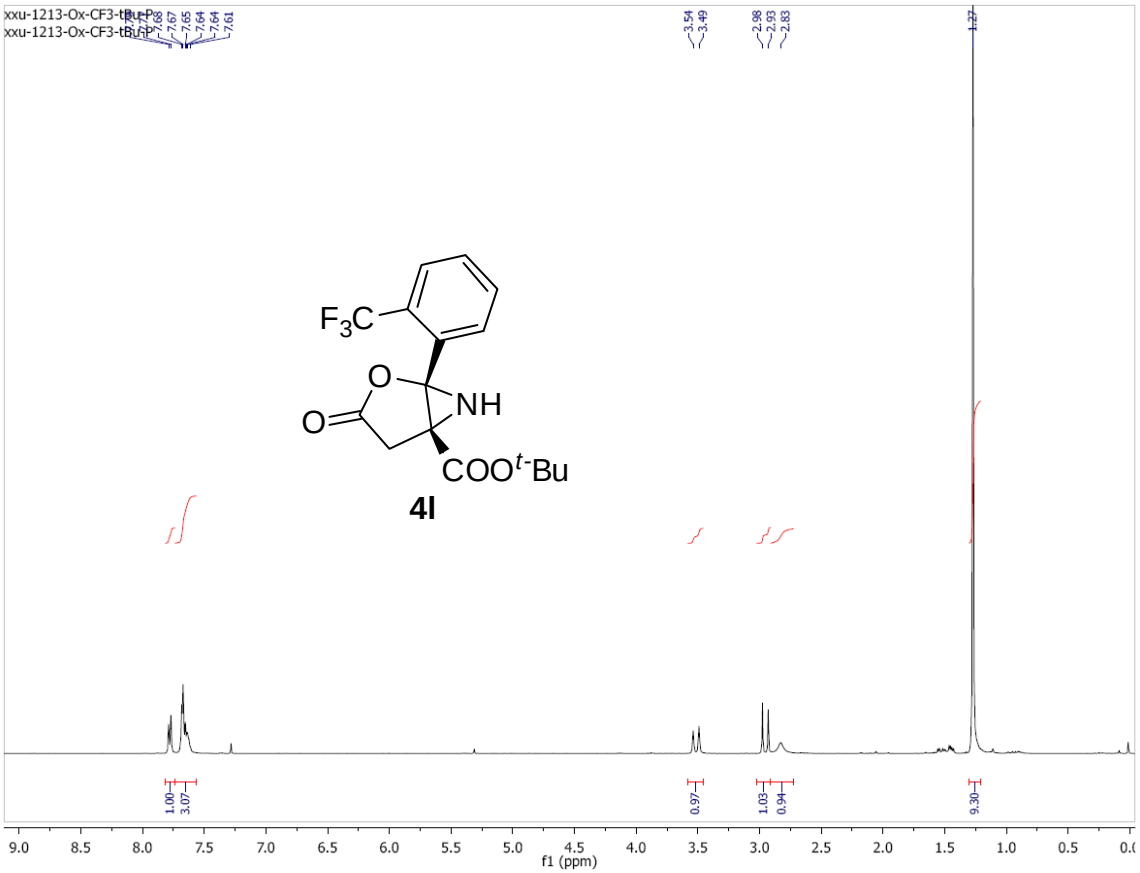
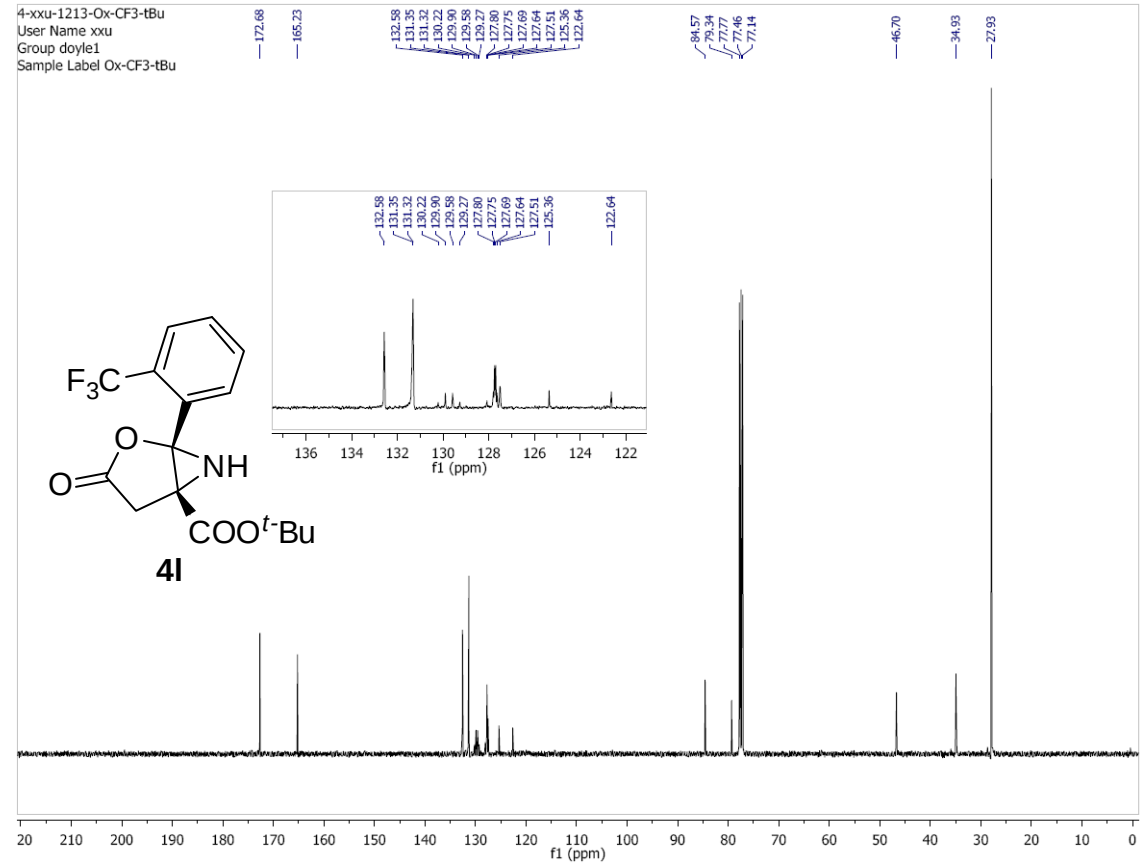
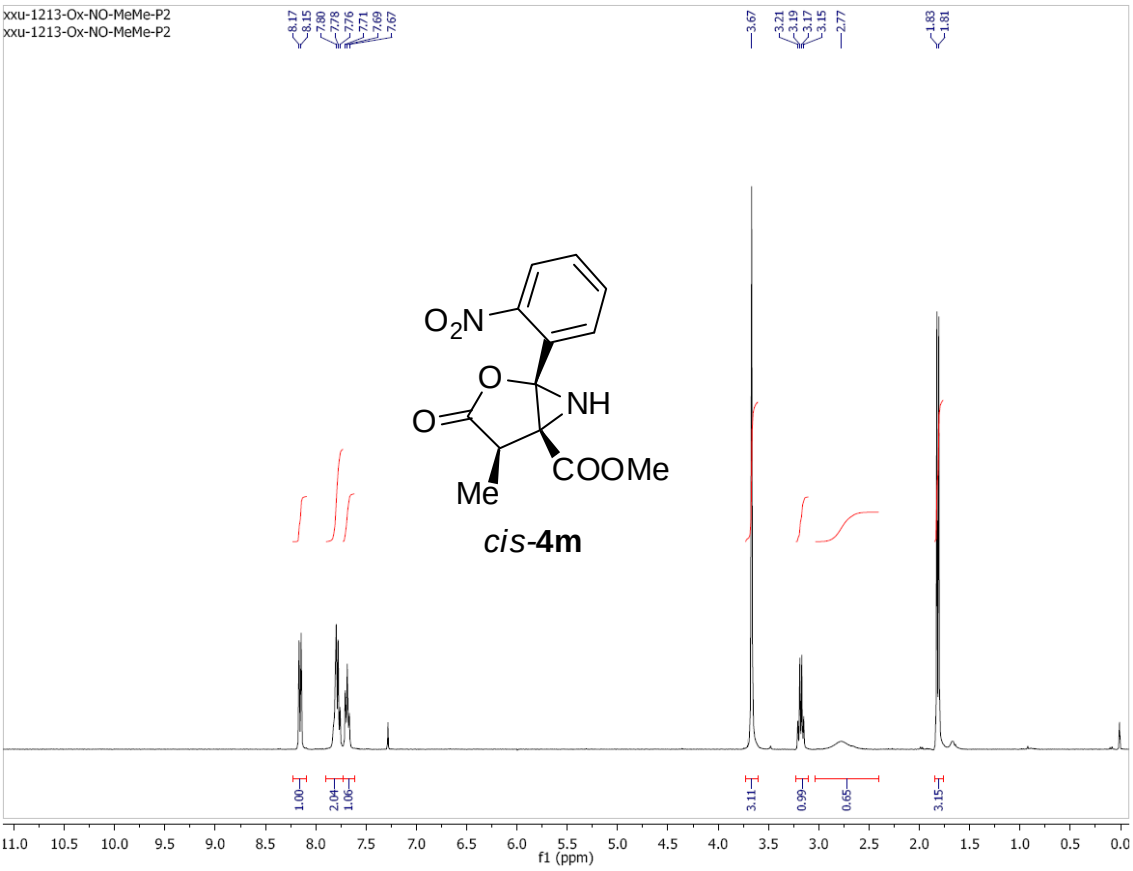
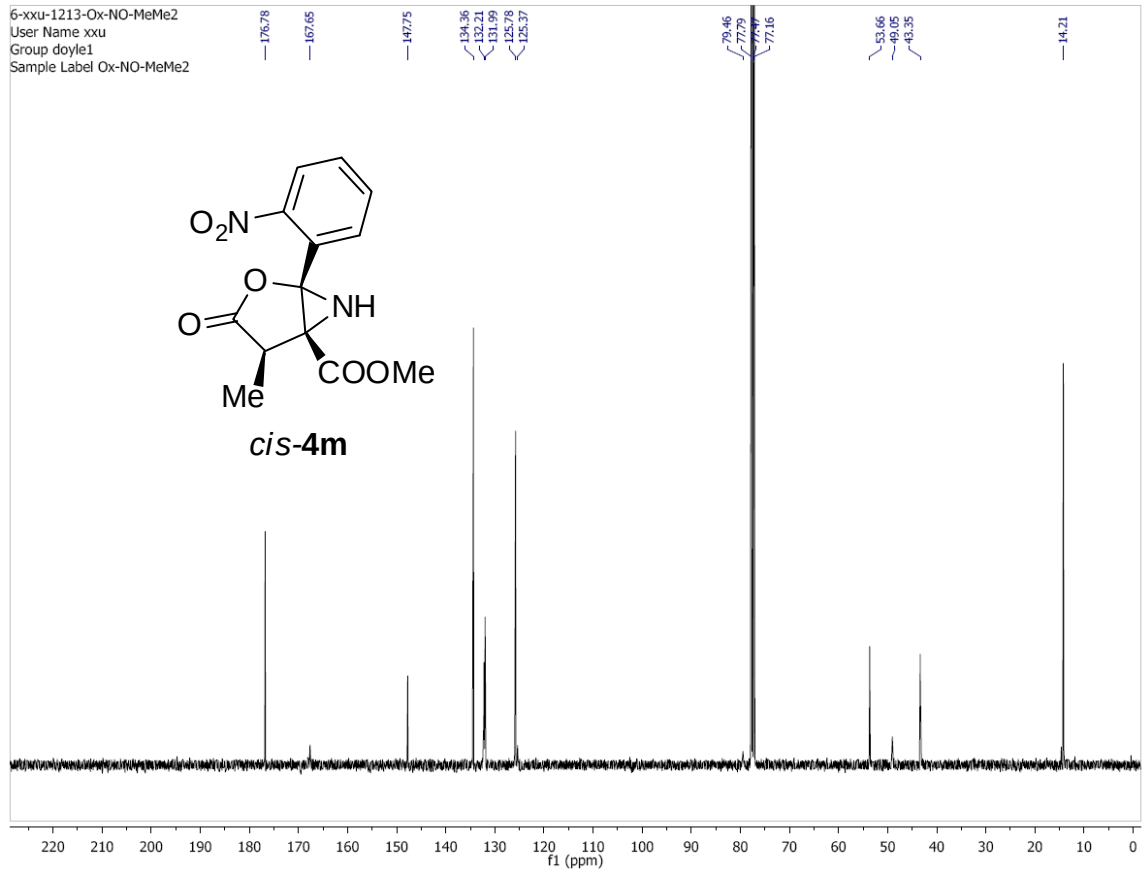
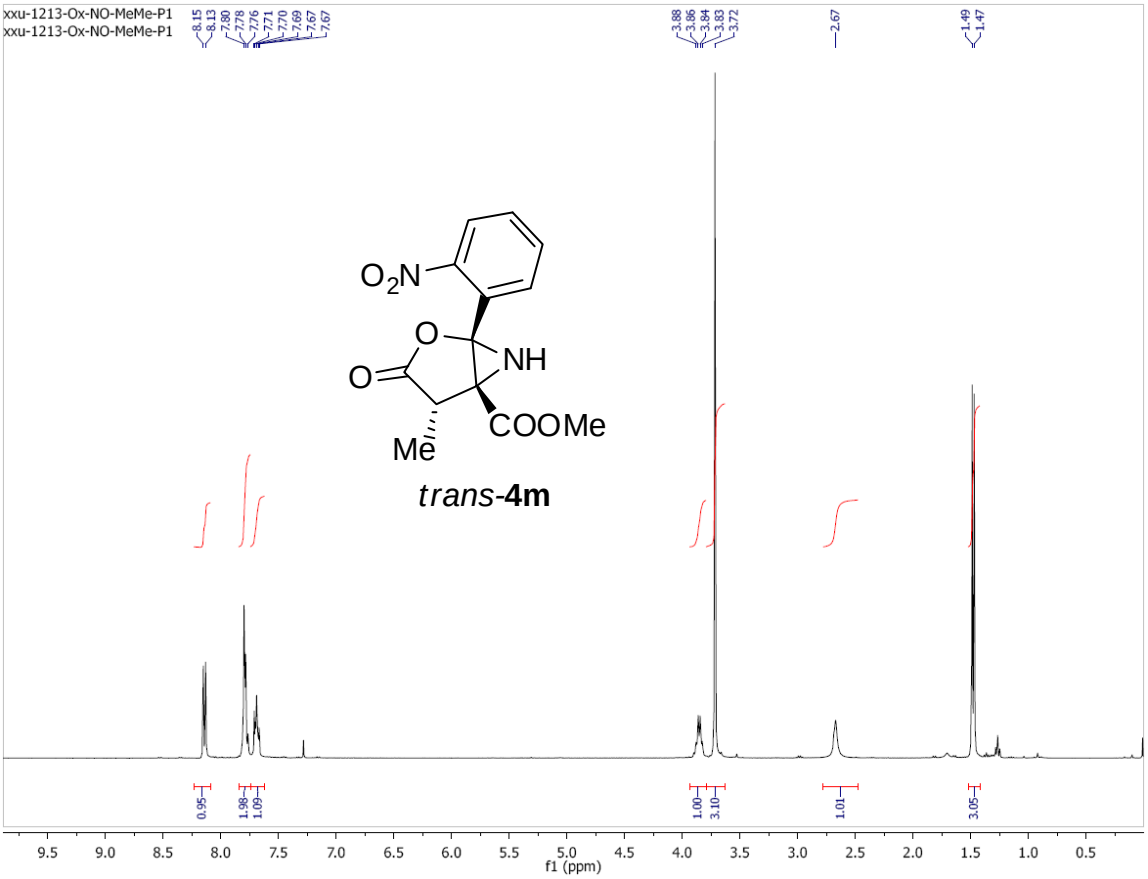
NH
O
COOMe
4k
130
125
f1 (ppm)

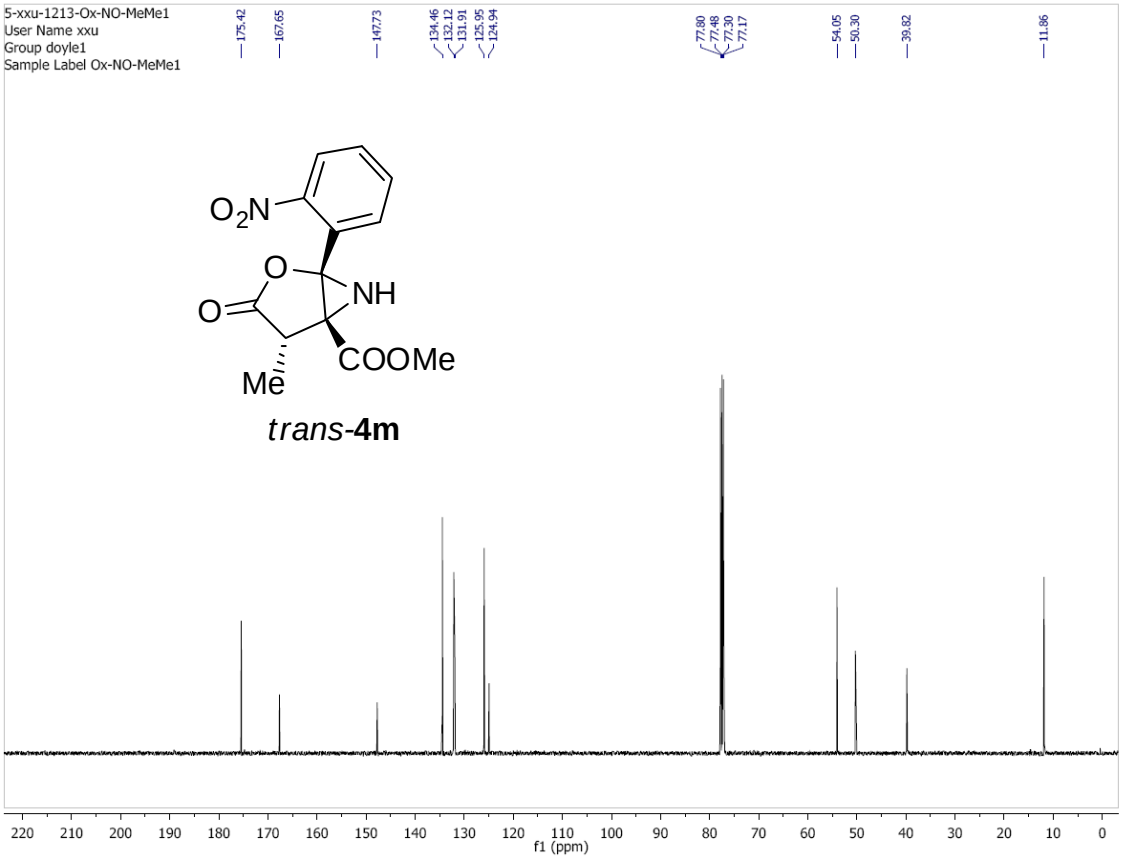

xxu-1213-Ox-CF3-tBu-Pr
xxu-1213-Ox-CF3-tBu-PP
7.77
7.68
7.67
7.65
7.64
7.64
7.61
3.54
3.49
2.98
2.93
2.83
1.27
F3C
O
NH
O
COO^{t}-Bu
4l
1.00
3.07
0.97
1.03
0.94
9.30
f1 (ppm)

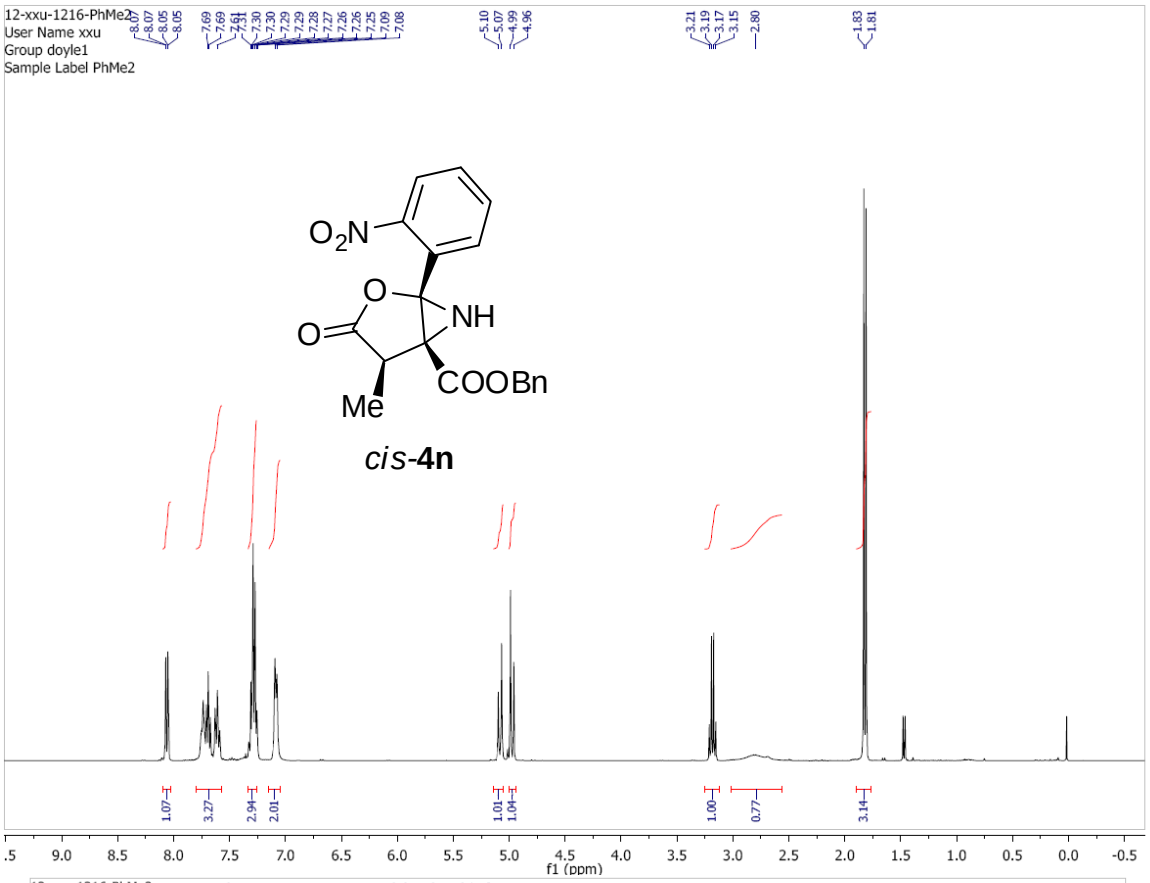

4-xxu-1213-Ox-CF3-tBu
User Name xxu
Group doyle1
Sample Label Ox-CF3-tBu
172.68
165.23
132.58
131.35
131.32
130.22
129.90
129.58
129.27
127.80
127.75
127.69
127.64
127.51
125.36
122.64
84.57
79.34
77.77
77.46
77.14
46.70
34.93
27.93
F3C
O
NH
O
COO^{t}-Bu
4l
f1 (ppm)

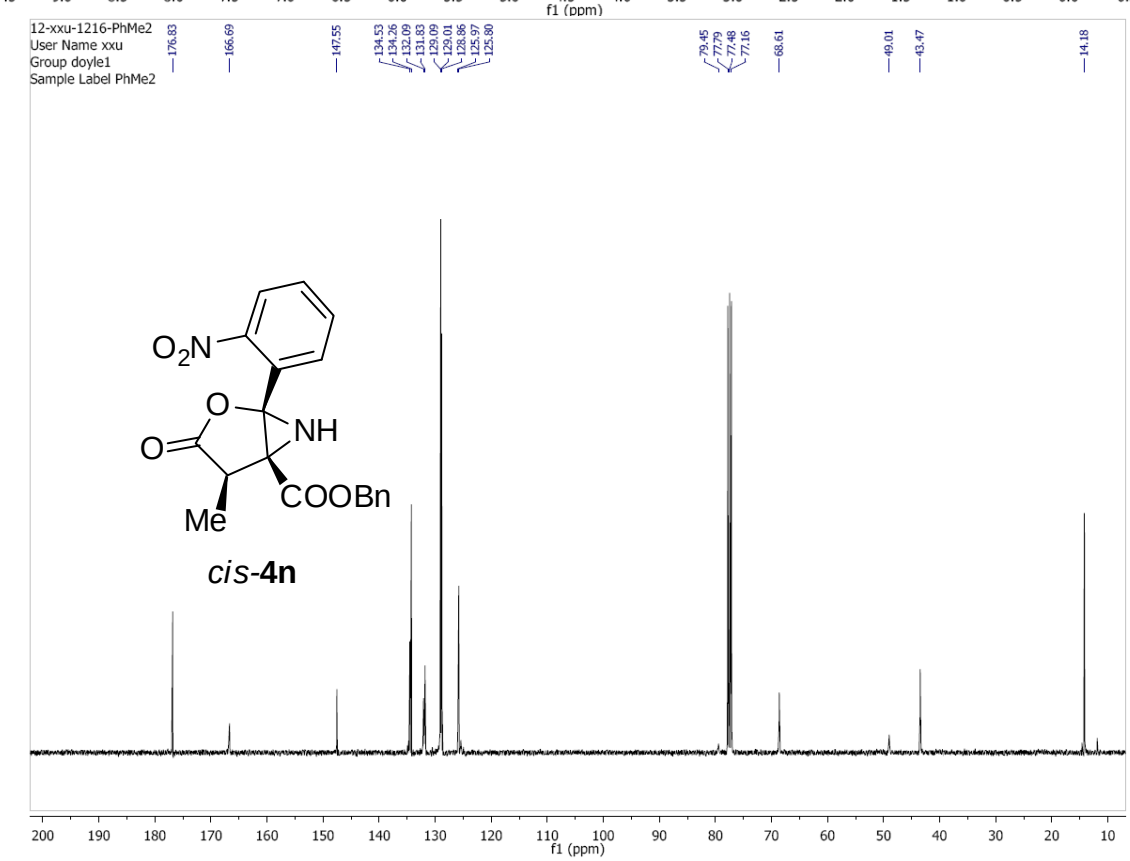

xxu-1213-Ox-NO-MeMe-P2
xxu-1213-Ox-NO-MeMe-P2
8.17
8.15
7.80
7.78
7.76
7.71
7.69
7.67
3.67
3.21
3.19
3.17
3.15
2.77
1.83
1.81
1.00
2.04
1.06
3.11
0.99
0.65
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O2N
O
NH
O
COOMe
Me
cis-4m

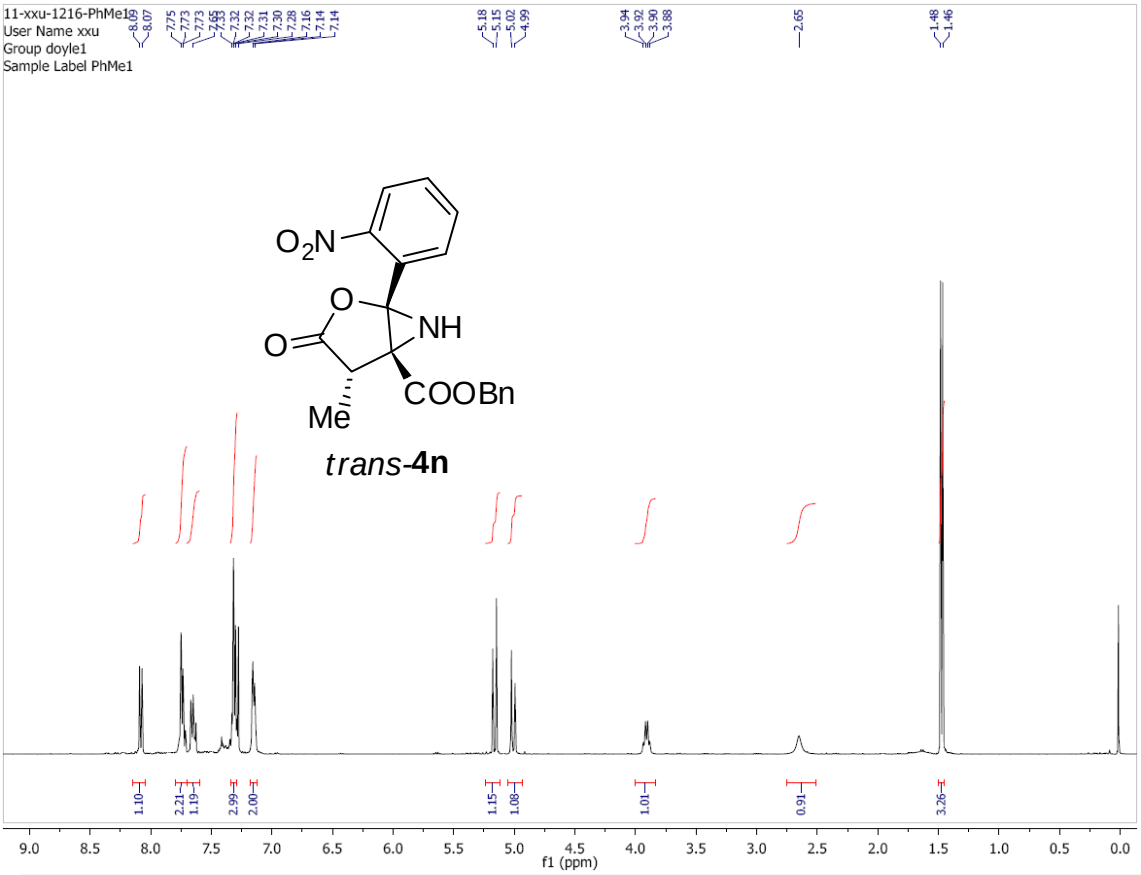

6-xxu-1213-Ox-NO-MeMe2
User Name xxu
Group doyle1
Sample Label Ox-NO-MeMe2
176.78
167.65
147.75
134.36
132.21
131.99
125.78
125.37
79.46
77.79
77.47
77.16
53.66
49.05
43.35
14.21
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O2N
O
NH
O
COOMe
Me
cis-4m

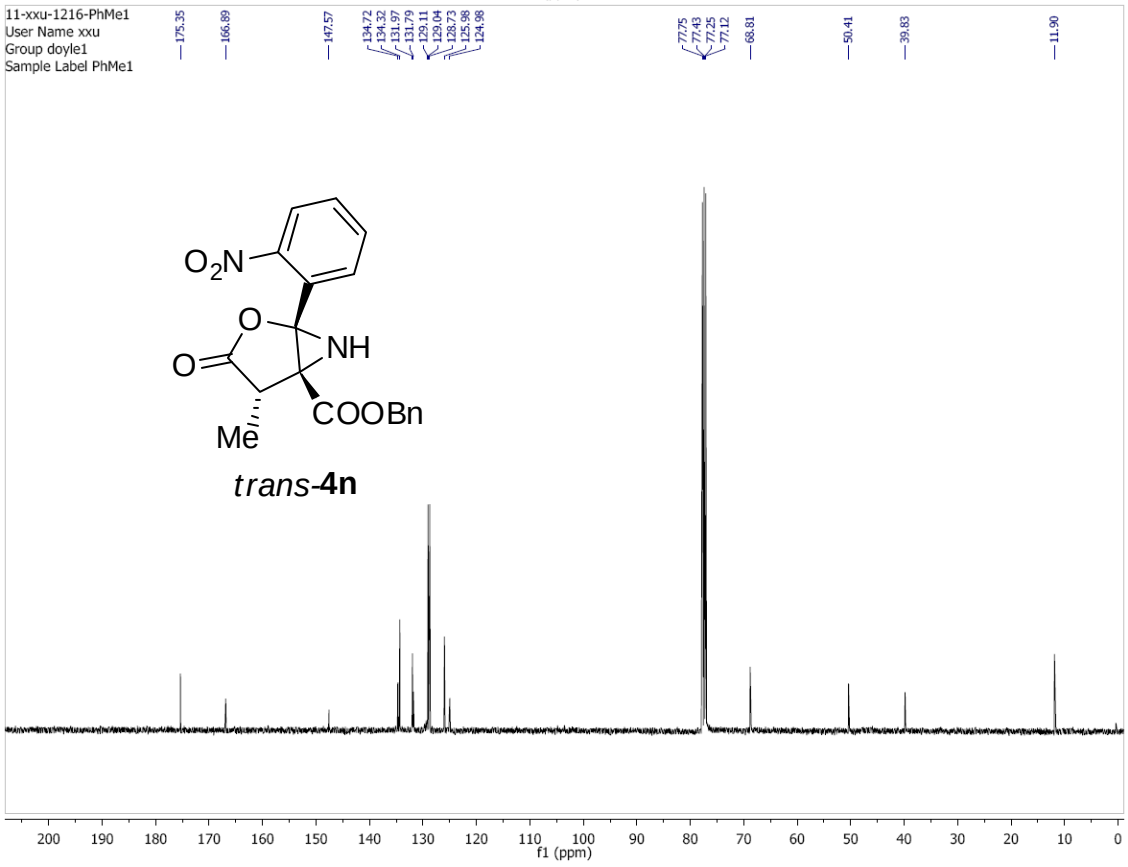

xxu-1213-Ox-NO-MeMe-P1
xxu-1213-Ox-NO-MeMe-P1
8.15
8.13
7.80
7.78
7.76
7.71
7.70
7.69
7.67
7.67
3.88
3.86
3.84
3.83
3.72
2.67
1.49
1.47
O2N
O
NH
O
COOMe
Me
trans-4m
0.95
1.98
1.09
1.00
3.10
1.01
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

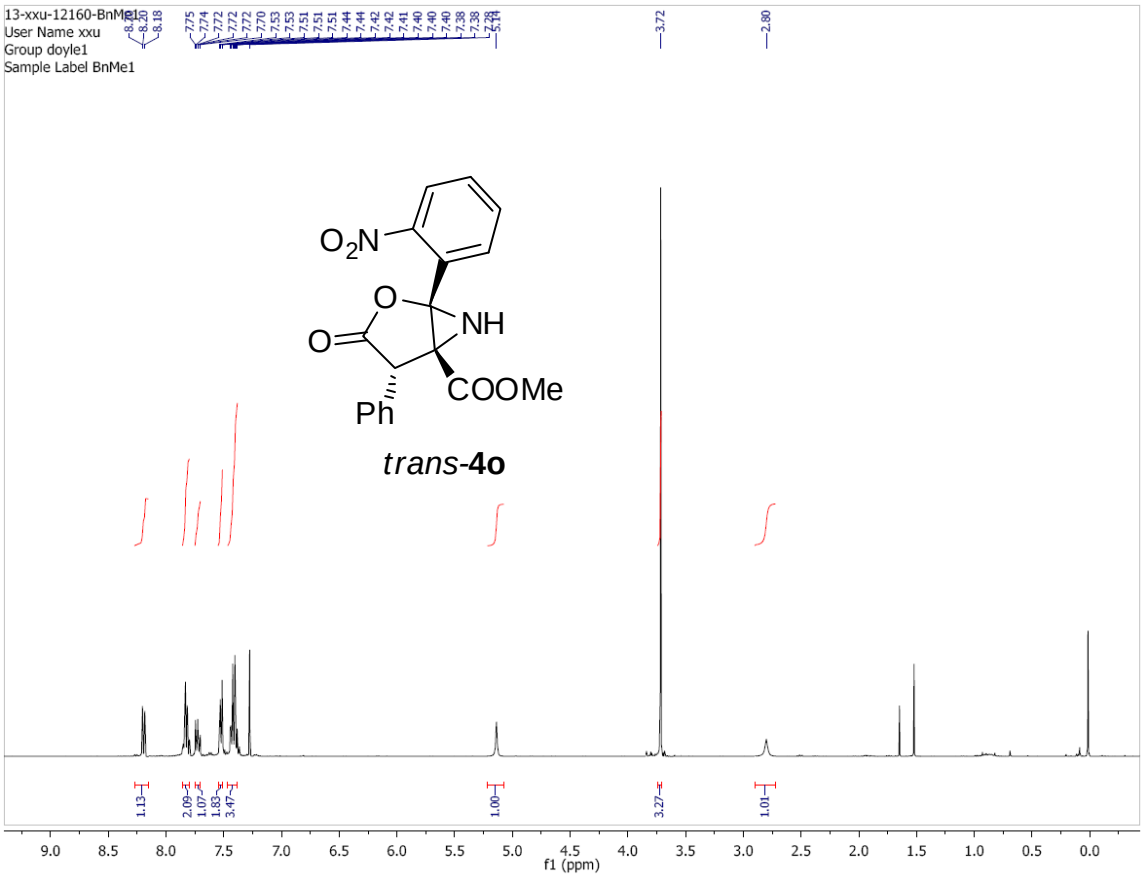

5-xxu-1213-Ox-NO-MeMe1
User Name xxu
Group doyle1
Sample Label Ox-NO-MeMe1
175.42
167.65
147.73
134.46
132.12
131.91
125.95
124.94
77.80
77.48
77.30
77.17
54.05
50.30
39.82
11.86
O2N
O
NH
O
COOMe
Me
trans-4m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

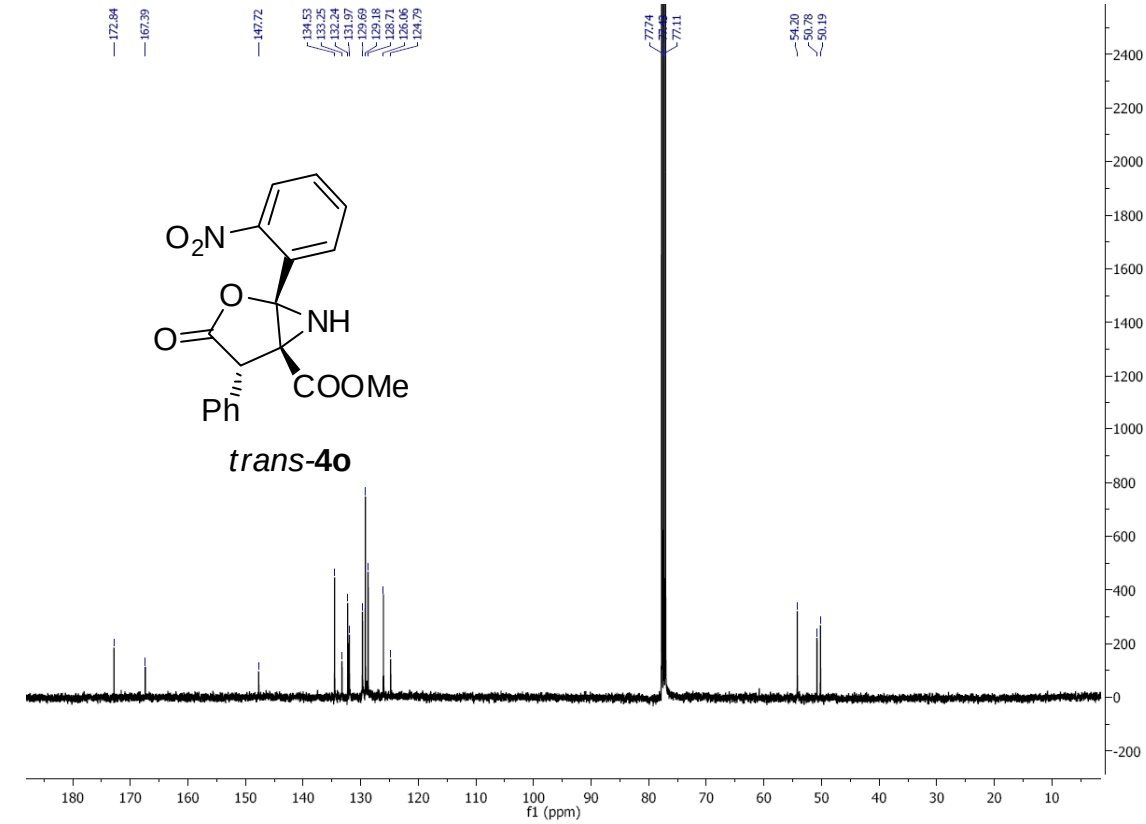

12-xxu-1216-PhMe2
User Name xxu
Group doyle1
Sample Label PhMe2
O2N
O
NH
O
COOBn
Me
cis-4n
f1 (ppm)

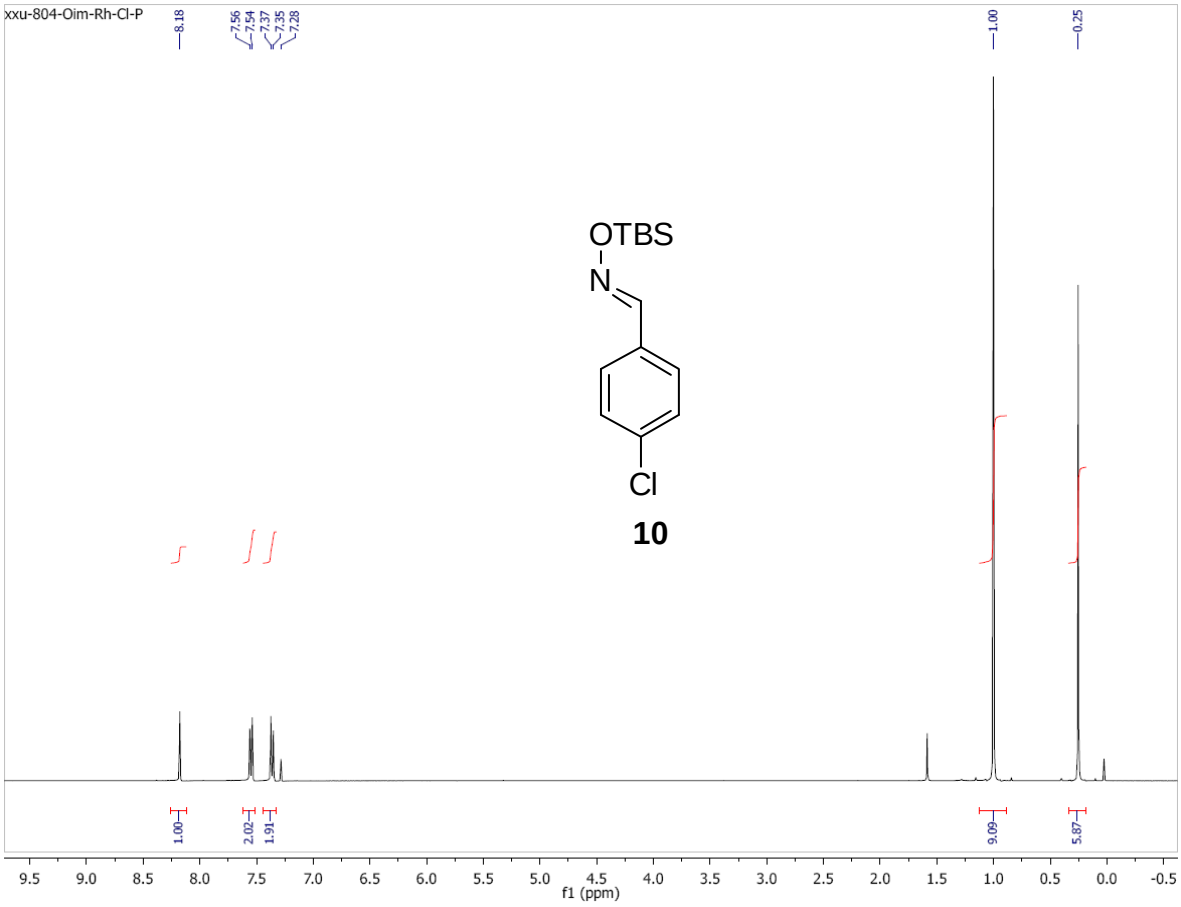

12-xxu-1216-PhMe2
User Name xxu
Group doyle1
Sample Label PhMe2
O2N
O
NH
O
COOBn
Me
cis-4n
f1 (ppm)

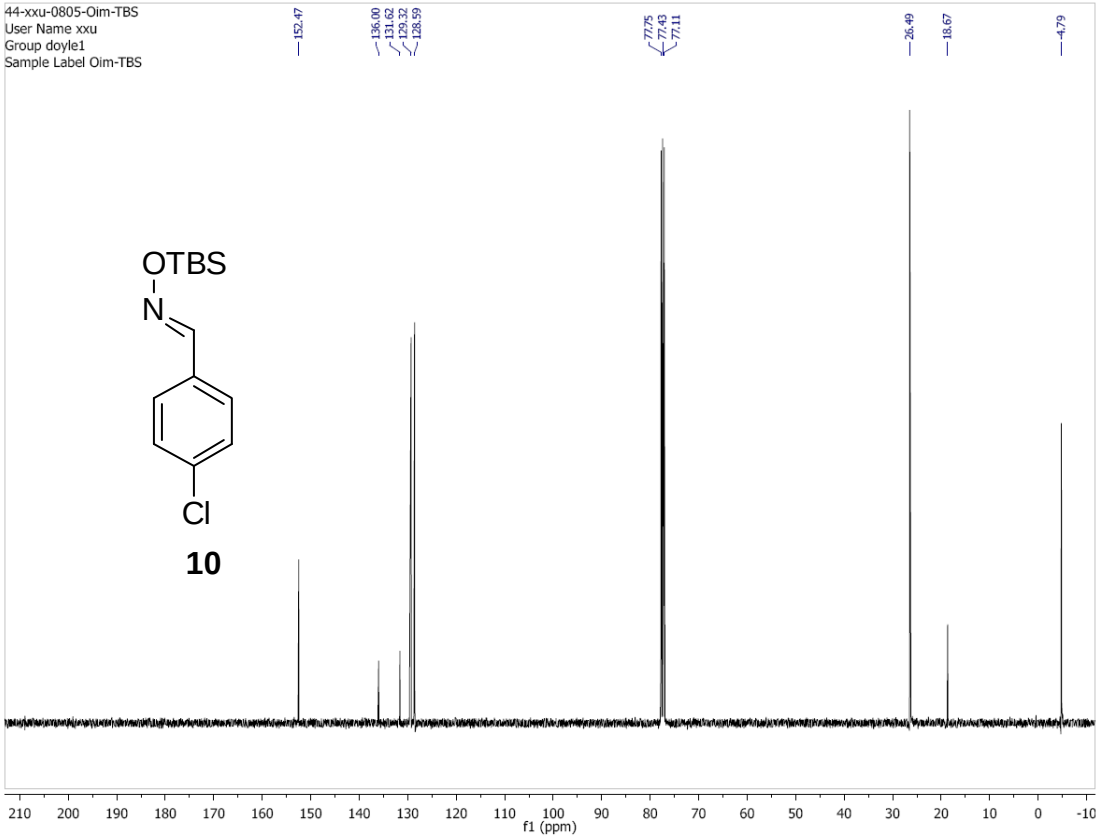

11-xxu-1216-PhMe1
User Name xxu
Group doyle1
Sample Label PhMe1
O2N
O
NH
O
COOBn
Me
trans-4n
f1 (ppm)


11-xxu-1216-PhMe1
User Name xxu
Group doyle1
Sample Label PhMe1
O2N
O
NH
O
COOBn
Me
trans-4n
f1 (ppm)


13-xxu-12160-BnMe1
User Name xxu
Group doyle1
Sample Label BnMe1
O2N
O
NH
O
COOMe
Ph
trans-4o
f1 (ppm)


O2N
O
NH
O
COOMe
Ph
trans-4o
f1 (ppm)


xxu-804-Oim-Rh-Cl-P
8.18
7.56
7.54
7.37
7.35
7.28
1.00
0.25
OTBS
N
Cl
10
1.00
2.02
1.91
9.09
5.87
f1 (ppm)


44-xxu-0805-Oim-TBS
User Name xxu
Group doyle1
Sample Label Oim-TBS
152.47
136.00
131.62
129.32
128.59
77.75
77.43
77.11
26.49
18.67
-4.79
OTBS
N
Cl
10
f1 (ppm)