Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoinduced difunctionalization of 2,3-dihydrofuran for the efficient synthesis of 2,3-disubstituted tetrahydrofurans

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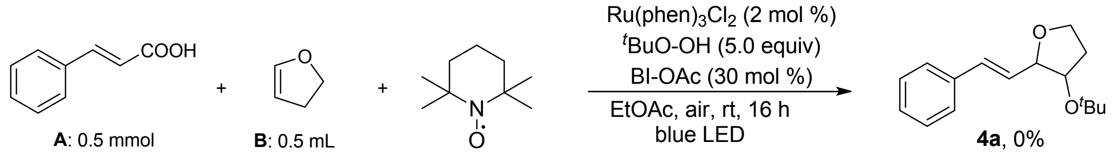
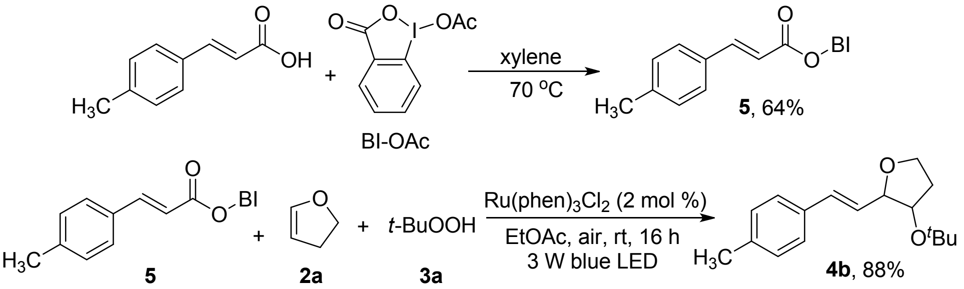
1. Mechanism study

1.1 Free radical-trapping experiment



Cinnamic acid (**1a**, 74.0 mg, 0.50 mmol), 2,3-dihydrofuran (**2a**, 0.50 mL), TBHP (**3a**, 70 % solution in H_2O, 321.4 mg, 2.50 mmol), BI-OAc (45.9 mg, 0.15 mmol), $Ru(phen)_3Cl_2$ (2.0 mol %) and (2,2,6,6-tetramethylpiperidine)-1-oxyl (TEMPO, 156.3 mg, 1.0 mmol) were dissolved in EtOAc (2.0 mL) in an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated using blue LED (450–455 nm, 3 W) at room temperature in air for 16 h. After the reaction was carried out, no desired product **4a** was observed.

1.2 Typical procedure for the synthesis of 5 and the reaction of 5 with 2a and 3



To a 50 mL round-bottom flask, BI-OAc (612 mg, 2.0 mmol) and 4-Methylcinnamic acid (389.3 mg, 2.4 mmol) were dissolved in xylene (20 mL) and the flask was heated in 70 °C under reduced pressure. When the xylene was removed, petroleum ether was used to wash the solid for 3 times and the white solid was filtered and dried in *vacuum*, affording pure **5** in 64% yield.

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was **5** (211.5 mg, 0.50 mmol), 2,3-dihydrofuran (**2a**, 0.50 mL), TBHP (**3a**, 70 % solution in H_2O, 321.4 mg, 2.50 mmol), $Ru(phen)_3Cl_2$ (2.0 mol %) and EtOAc (2.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 3 W) irradiation at room temperature in air with stirring for 16 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 50:1 to 20:1) to give the desired product **4b** in 88 % yield.

Characterization data of 5

1-((3-(*p*-tolyl)acryloyl)-1,2-benziodoxol-3-(1H)-one (5): White solid. 249.2 mg, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08–8.02 (m, 2H), 7.81 (d, J = 16.0 Hz, 1H), 7.48–7.44 (m, 3H), 7.24–7.19 (m, 3H), 6.44 (d, J = 16.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.66, 171.24, 147.26, 141.89, 141.32, 133.59, 133.37, 131.96, 131.33, 129.70, 128.41, 127.98, 116.11, 94.60, 21.50.

1.3 Determination of CO_2 during the reaction by FT-IR

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with cinnamic acid (**1a**, 74.0 mg, 0.50 mmol), 2,3-dihydrofuran (**2a**, 0.50 mL), TBHP (**3a**, 70 % solution in H_2O, 321.4 mg, 2.50 mmol), BI-OAc (45.9 mg, 0.15 mmol), and EtOAc (2.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 3 W) irradiation at room temperature in air with stirring for 16 h. After completion of the reaction, the resulting gas from the reaction mixture was directly determined by a Bruker Tensor 27 FT-IR, and the concentration of CO_2 was found to be 2394.95 ppm (Figure S1).

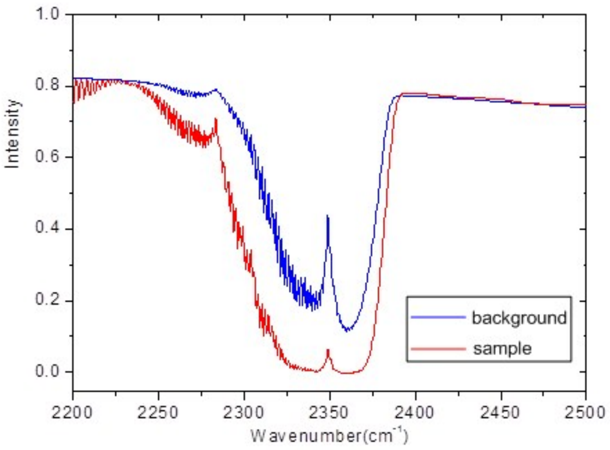


Figure S1. FT-IR analysis of the resulting gas by a Bruker Tensor 27 FT-IR

1.4 Determination of BI-OH during the reaction by HRMS

A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with cinnamic acid (**1a**, 74.0 mg, 0.50 mmol), 2,3-dihydrofuran (**2a**, 0.50 mL), TBHP (**3a**, 70 % solution in H_2O, 321.4 mg, 2.50 mmol), BI-OAc (45.9 mg, 0.15 mmol), and EtOAc (2.0 mL). The reaction vessel was exposed to blue LED (450–455 nm, 3 W) irradiation at room temperature in air with stirring for 16 h. After completion of the reaction, the reaction mixture was directly identified by the HRMS analysis, and BI-OH was founded (Figure S2).

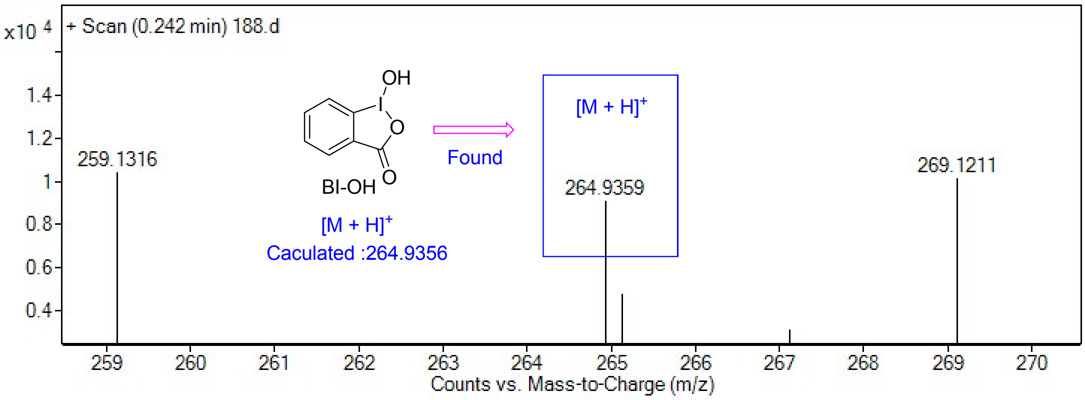
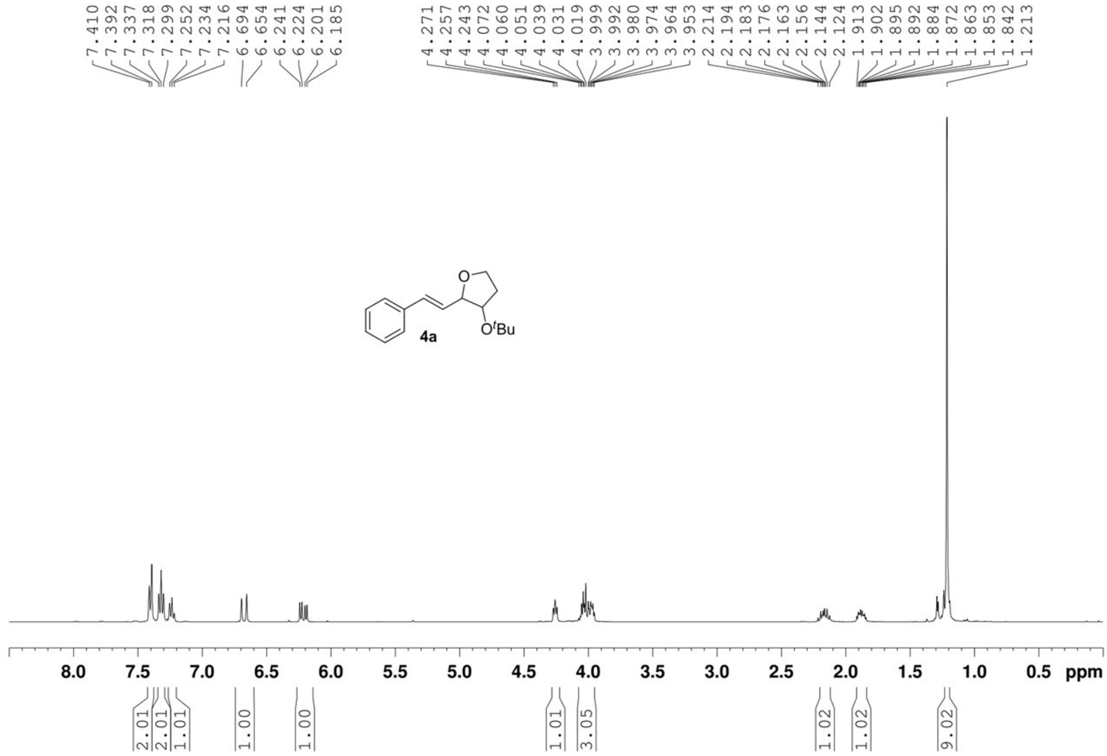
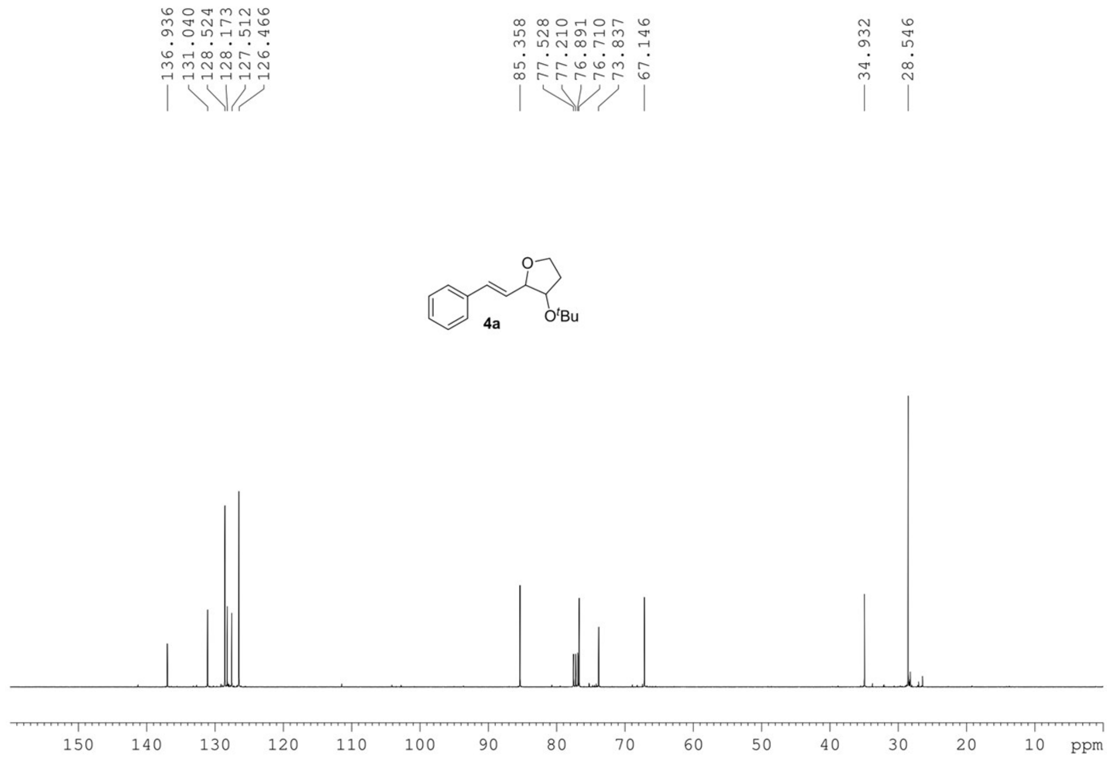
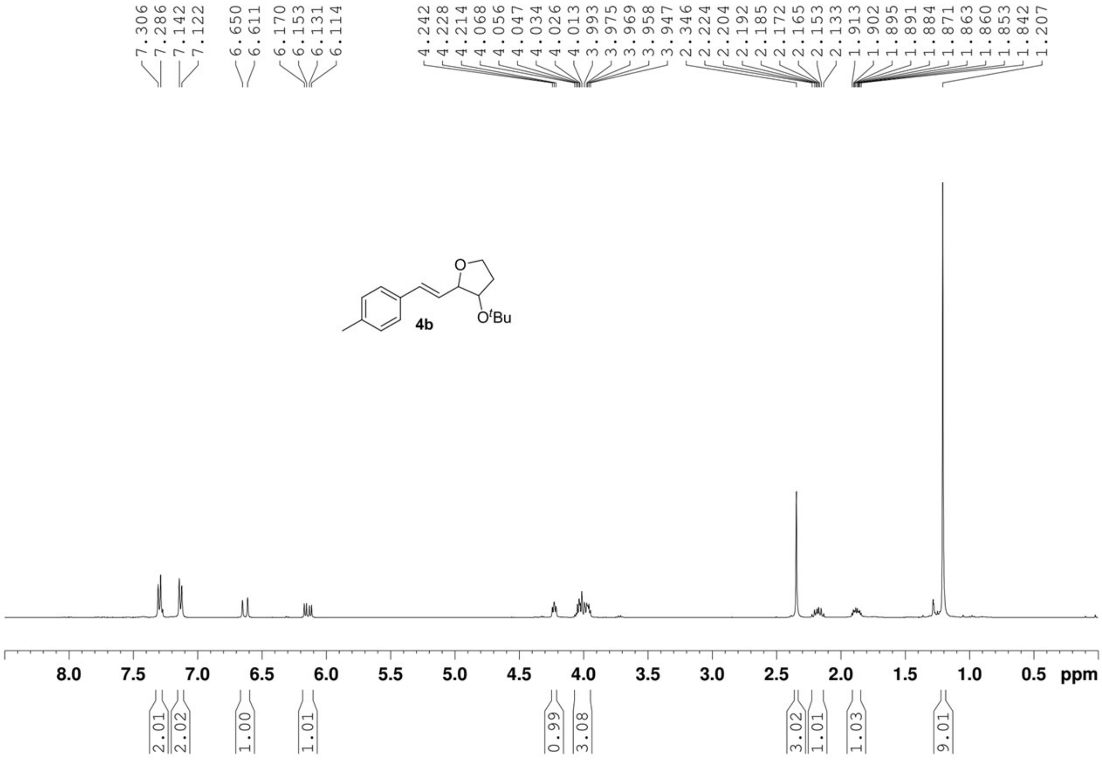


Figure S2. HRMS analysis of BI-OH.

2. ^{1}H and ^{13}C NMR spectra of the product



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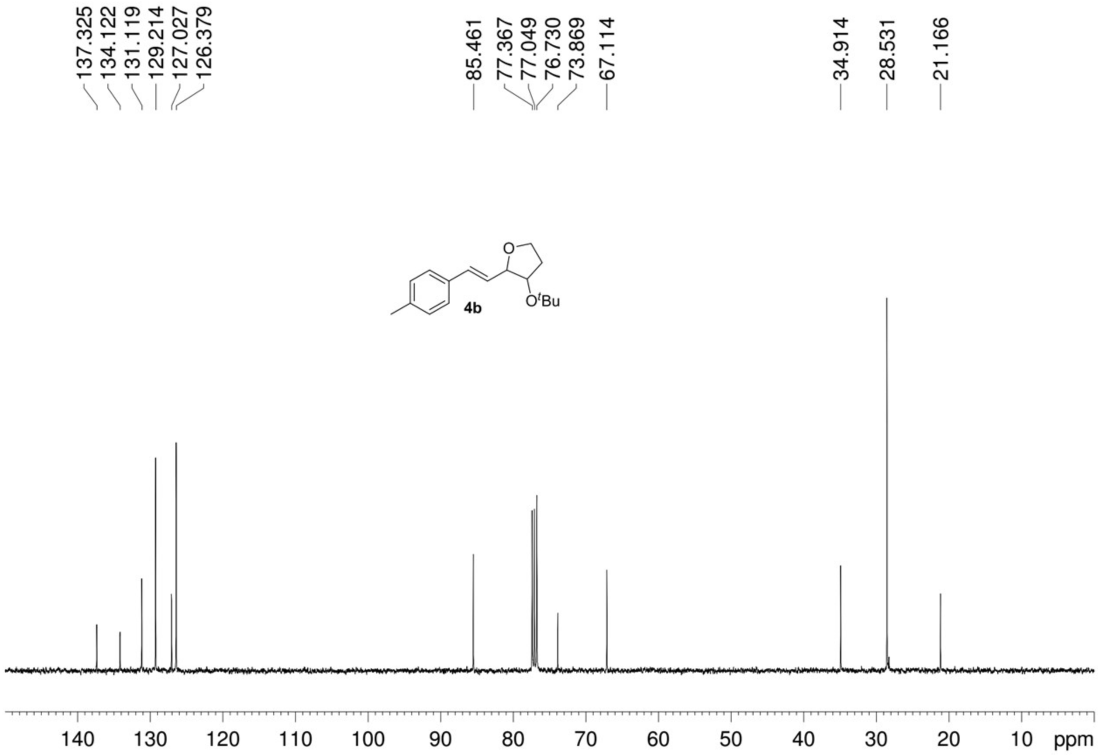
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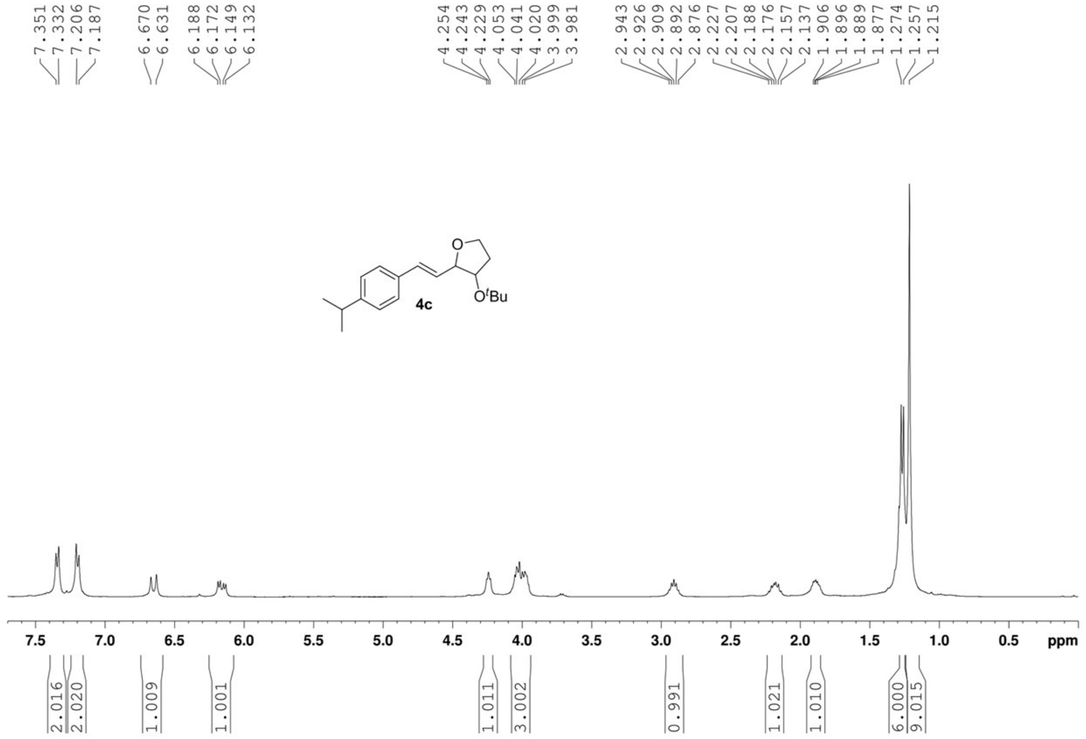
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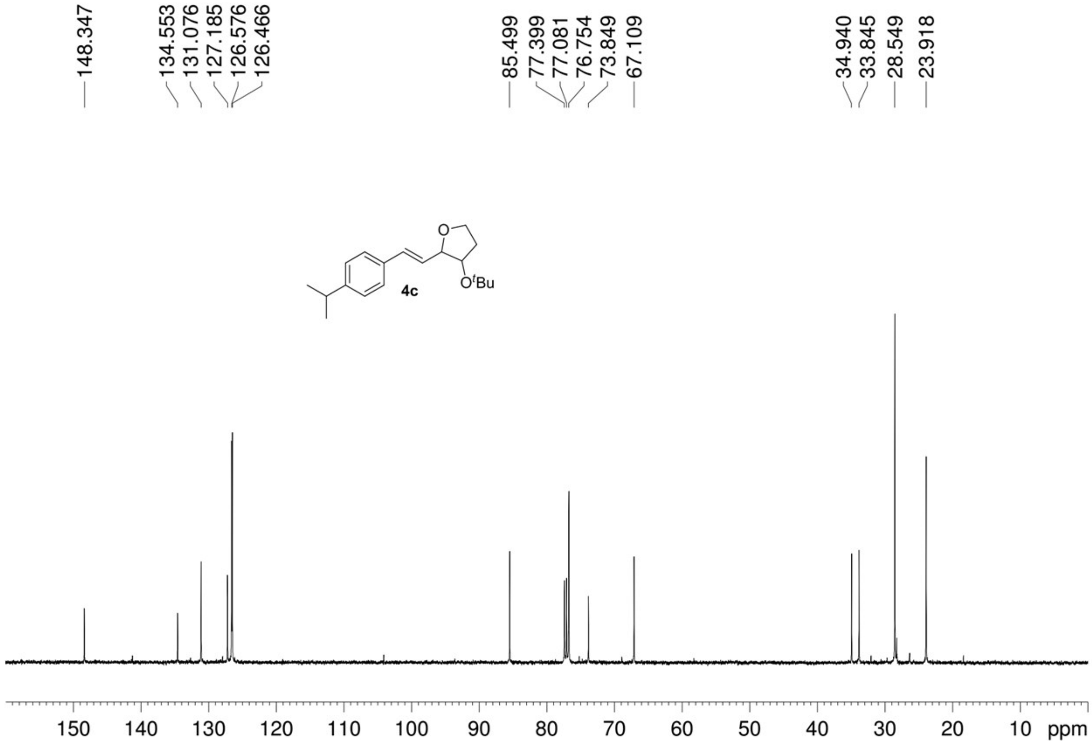
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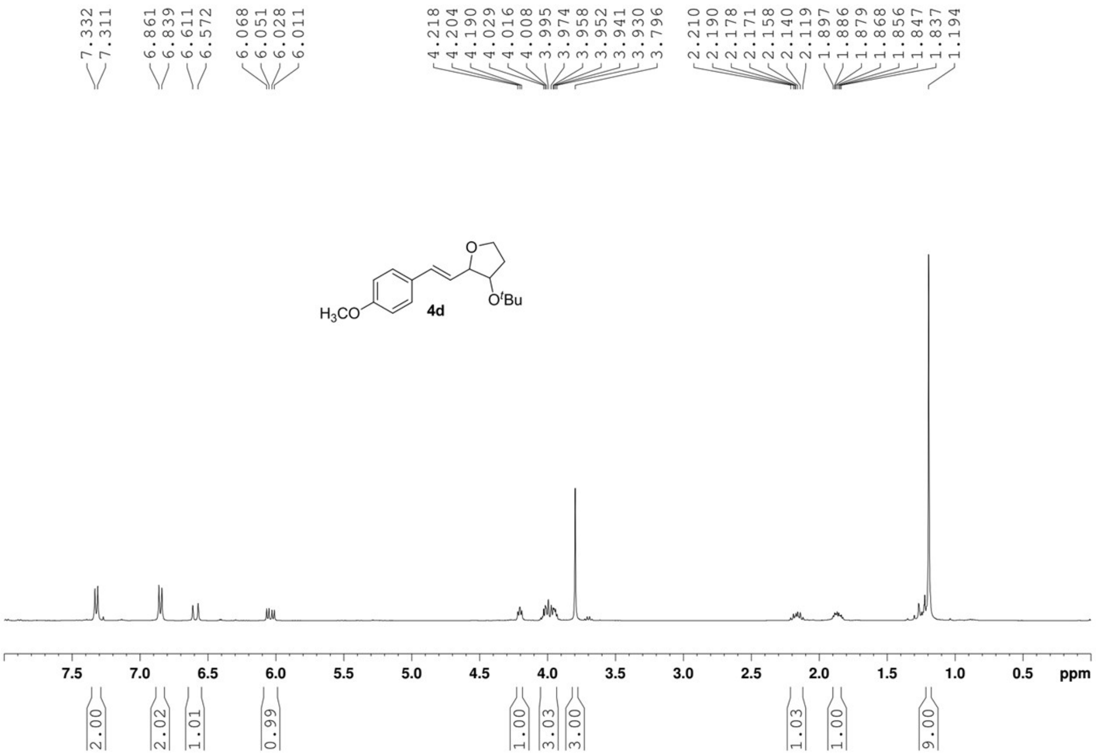
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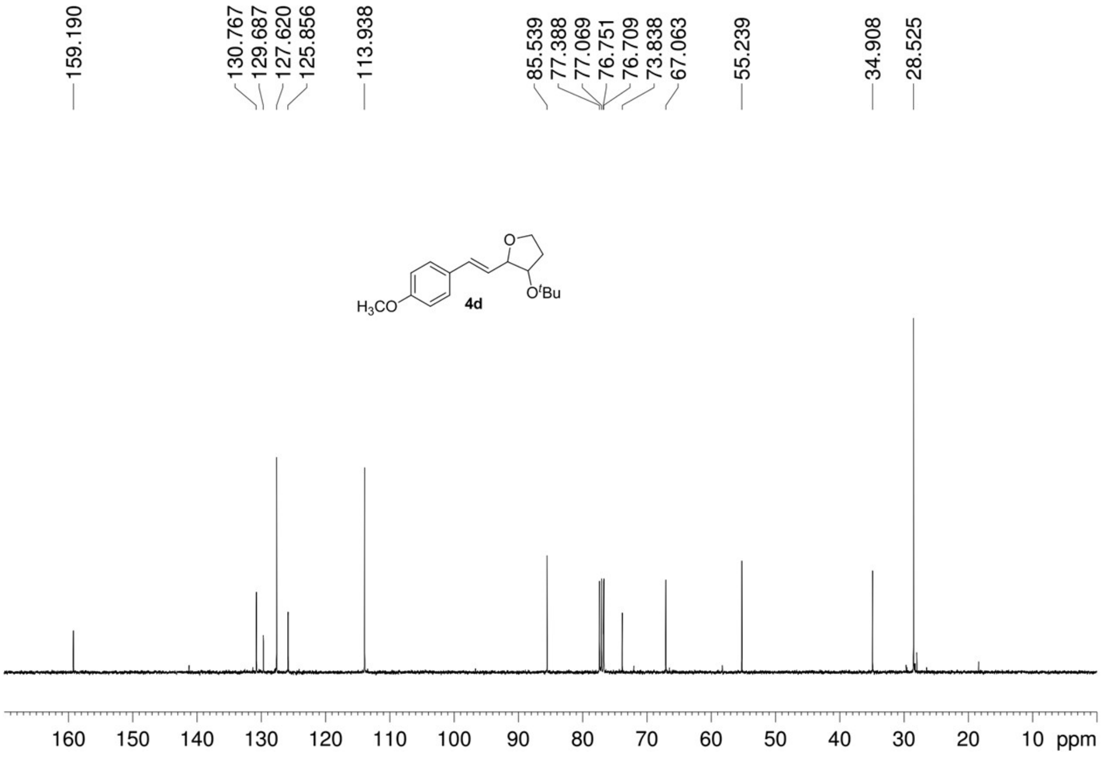
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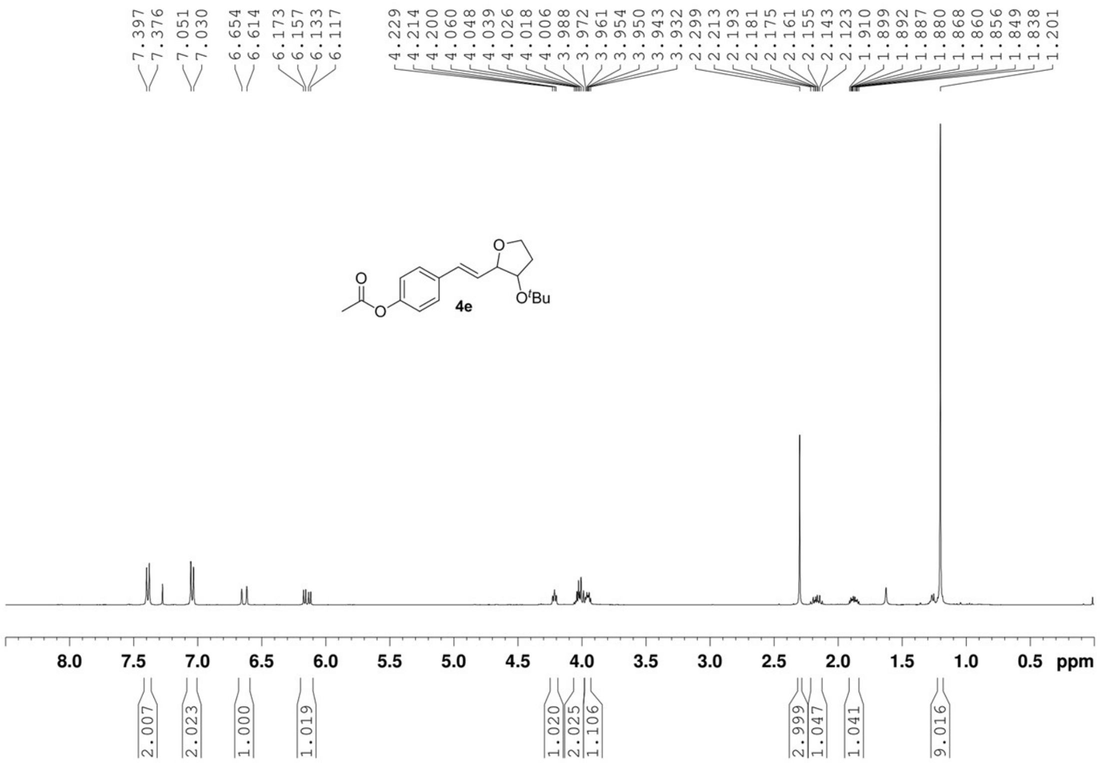
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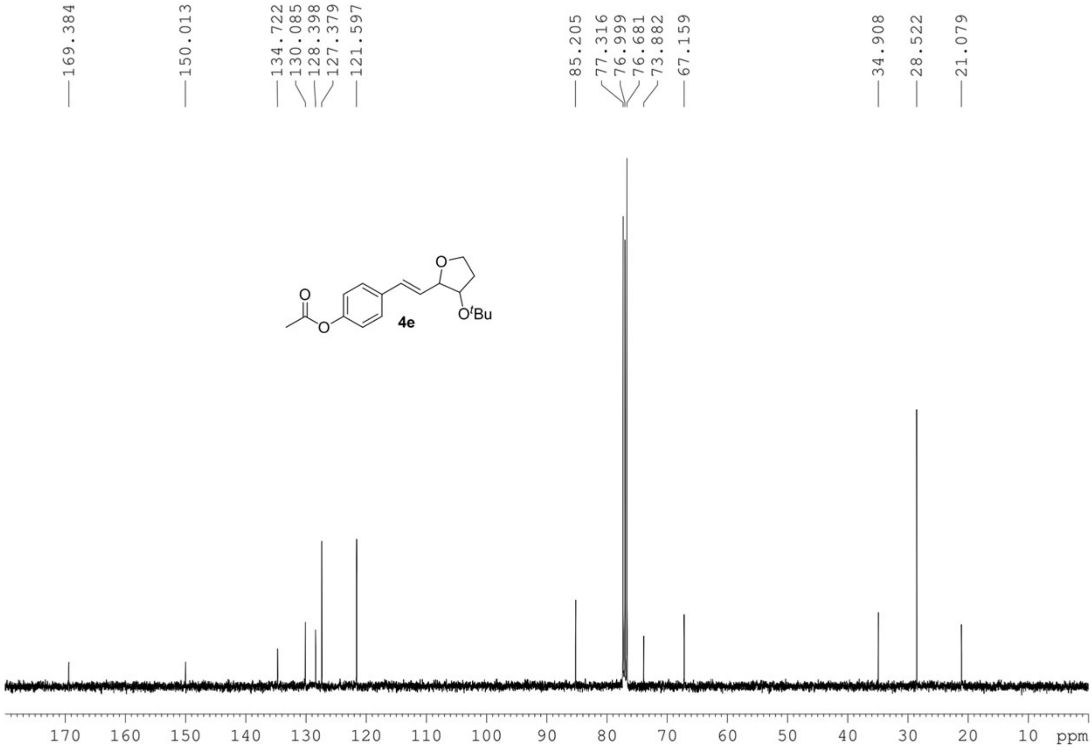
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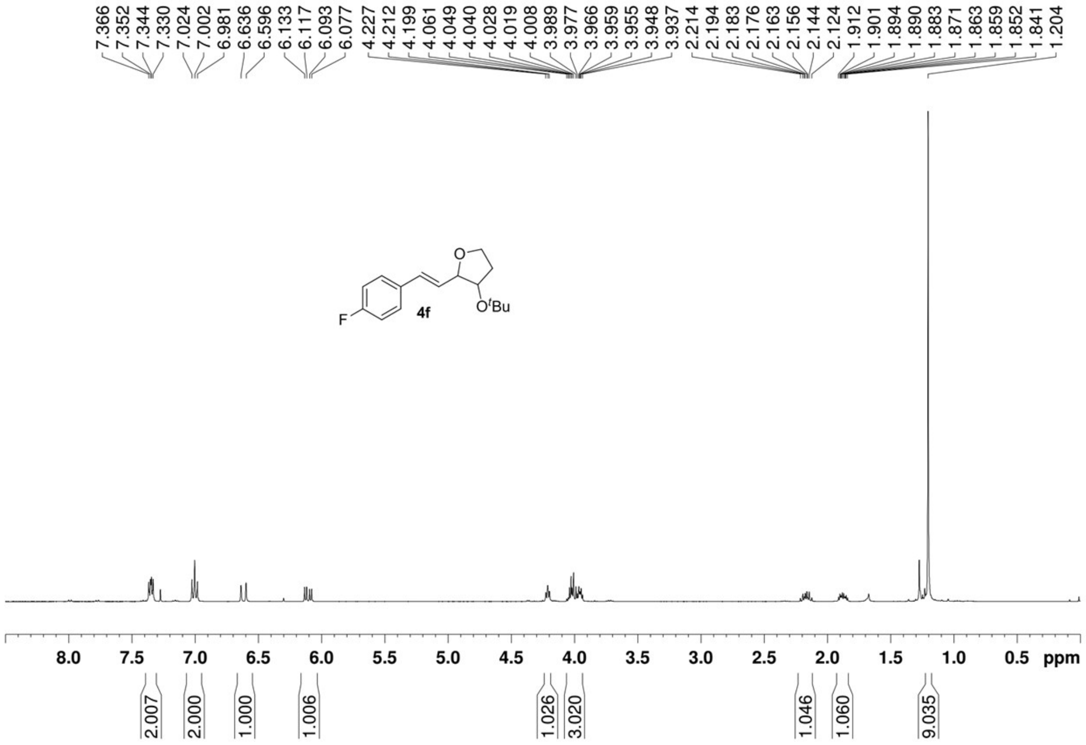
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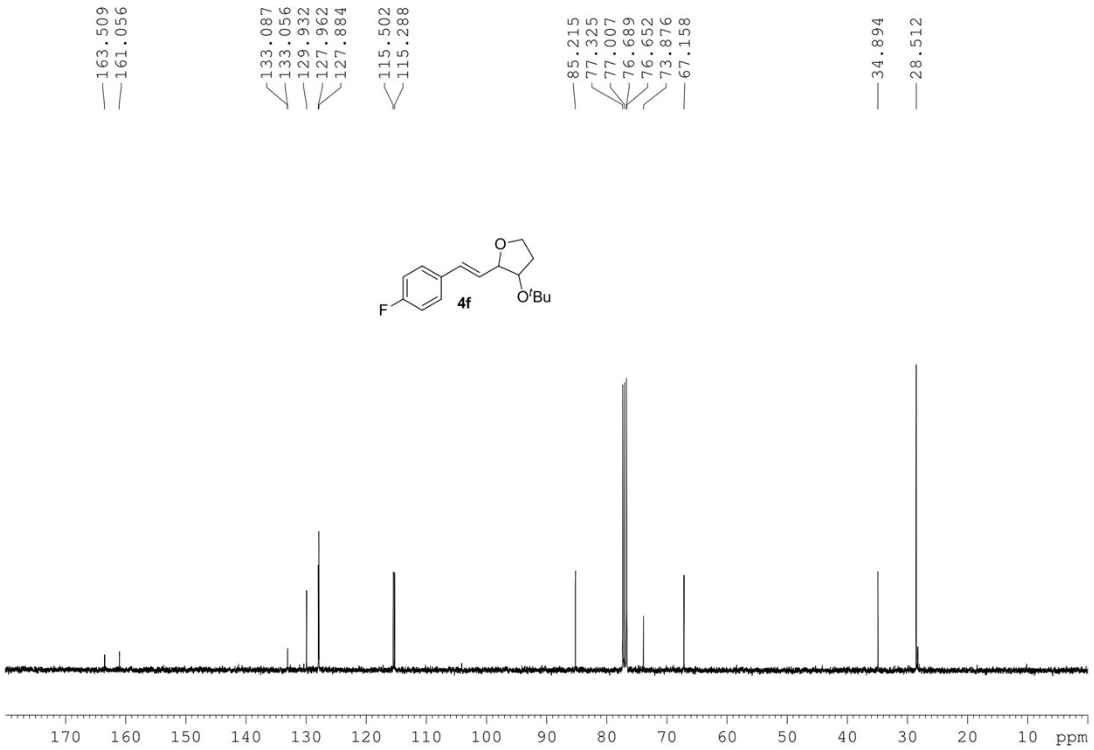
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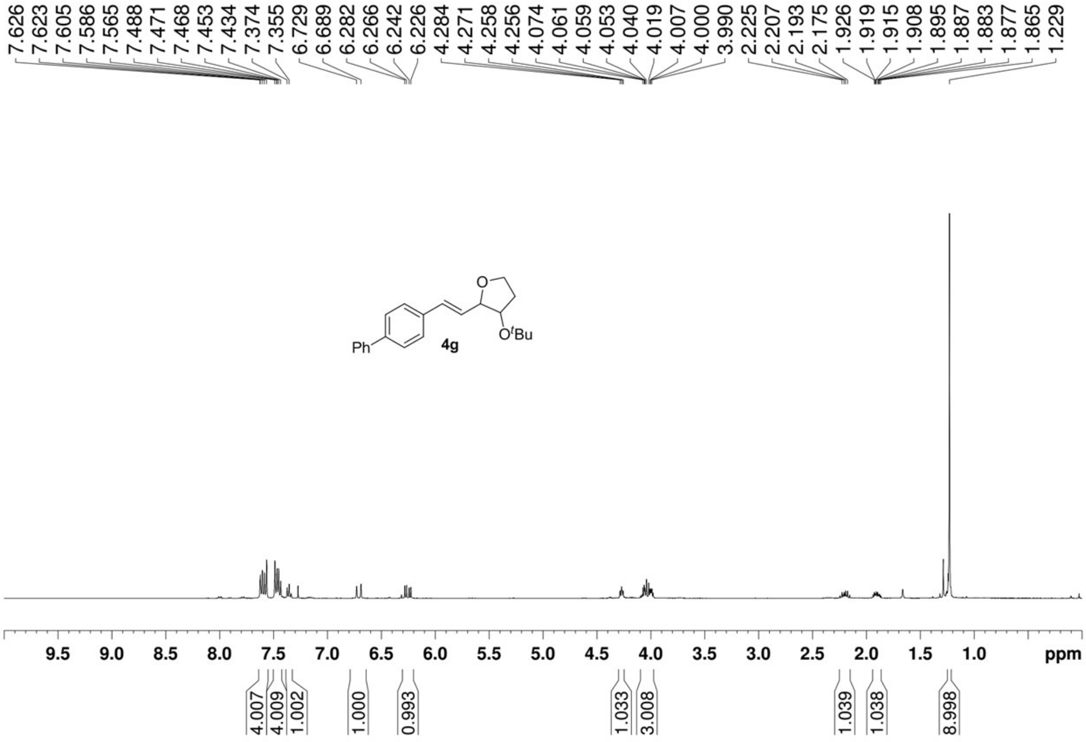
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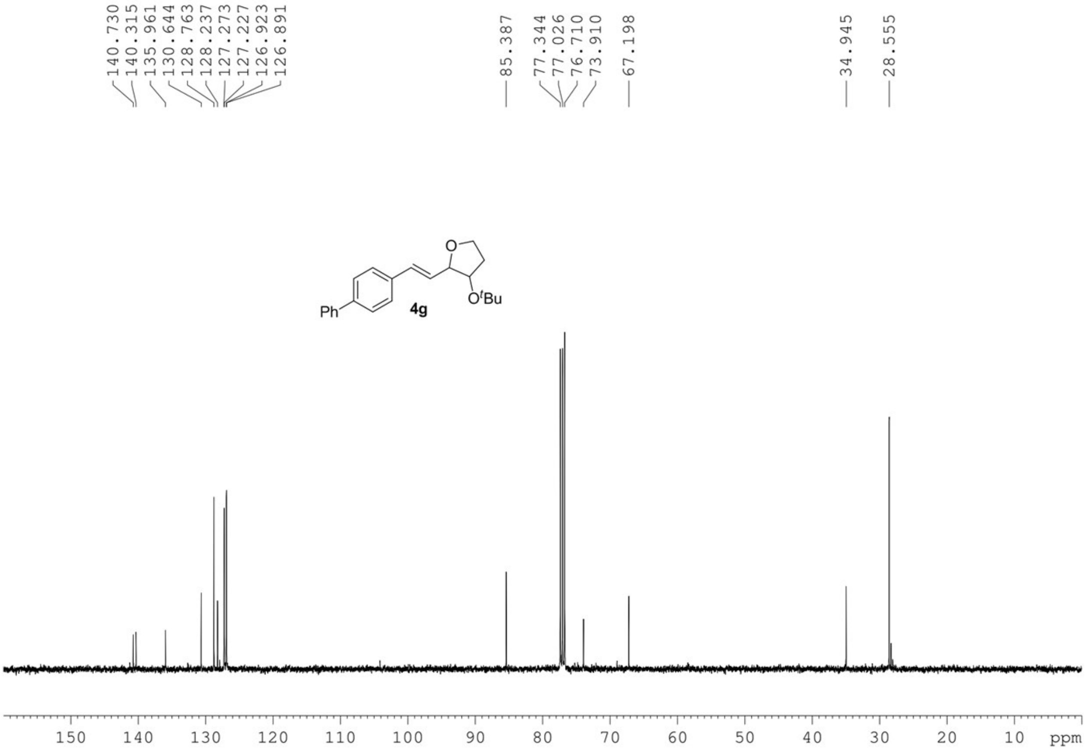
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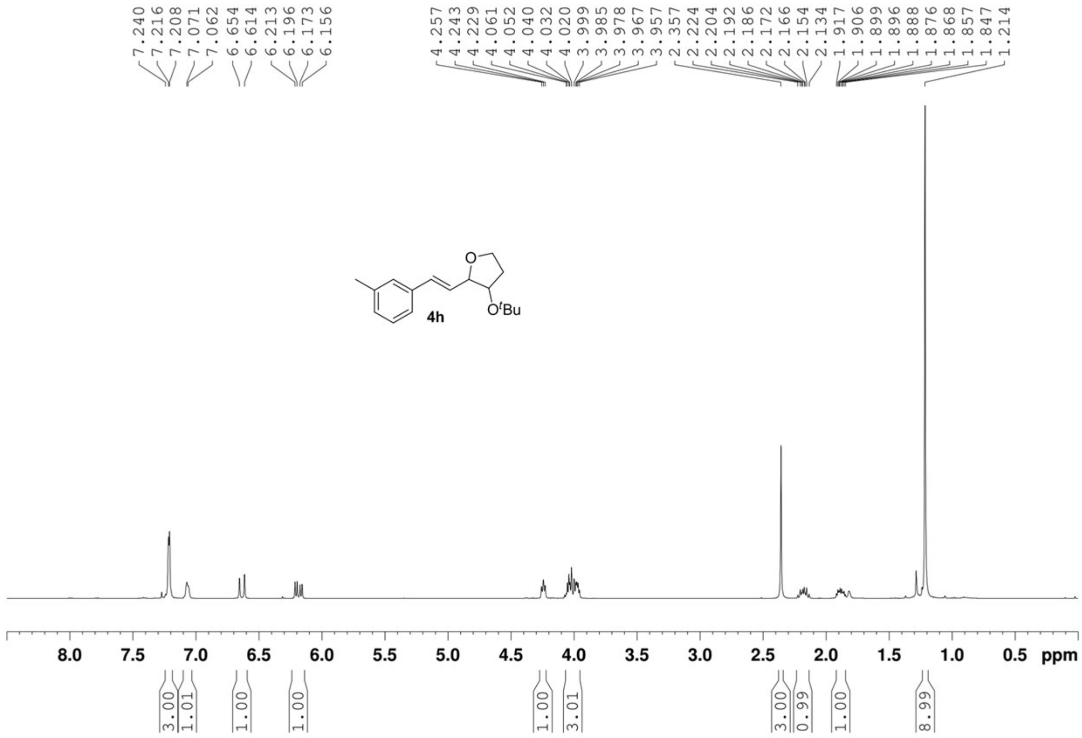
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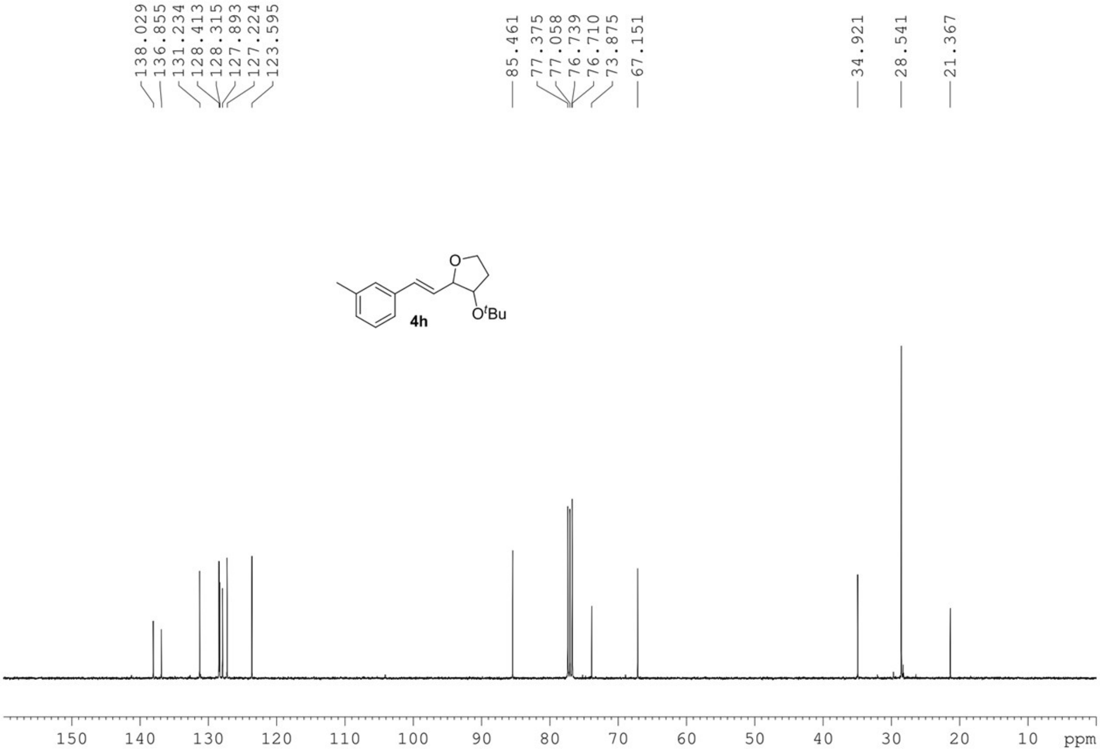
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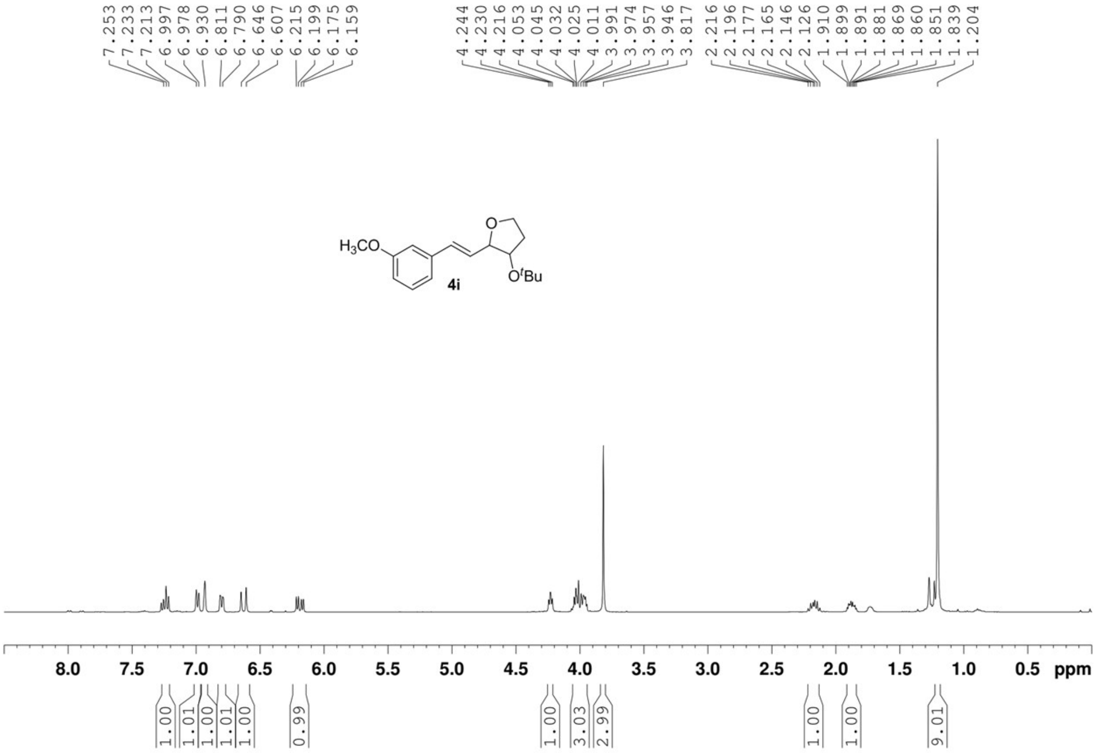
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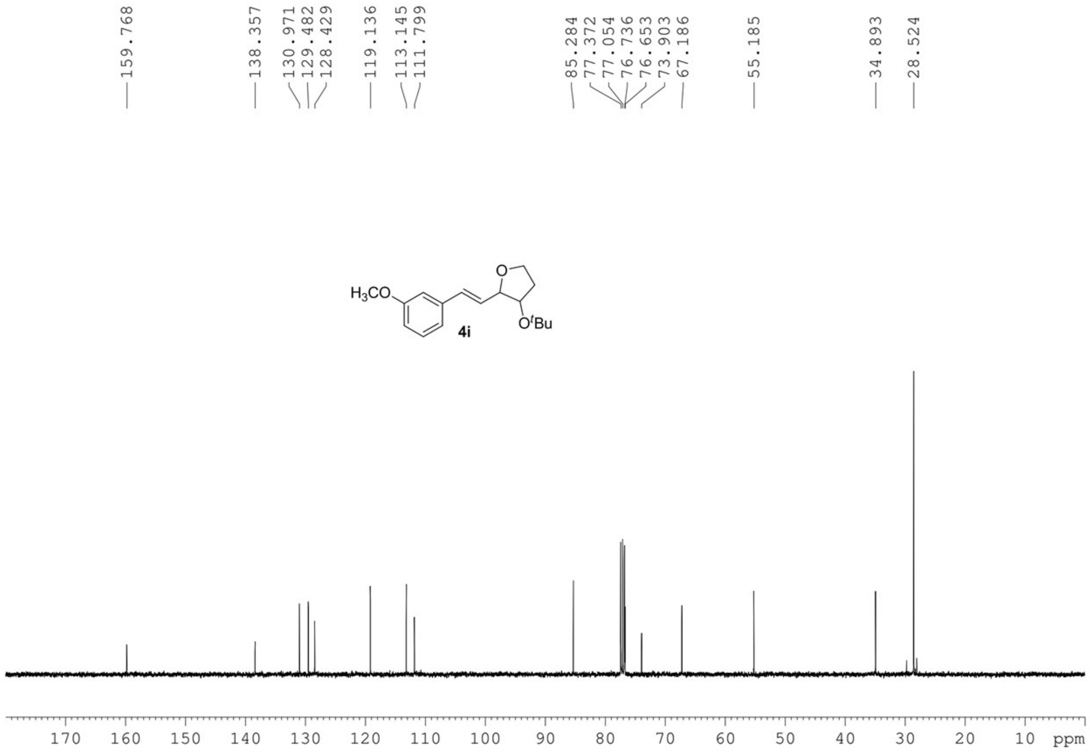
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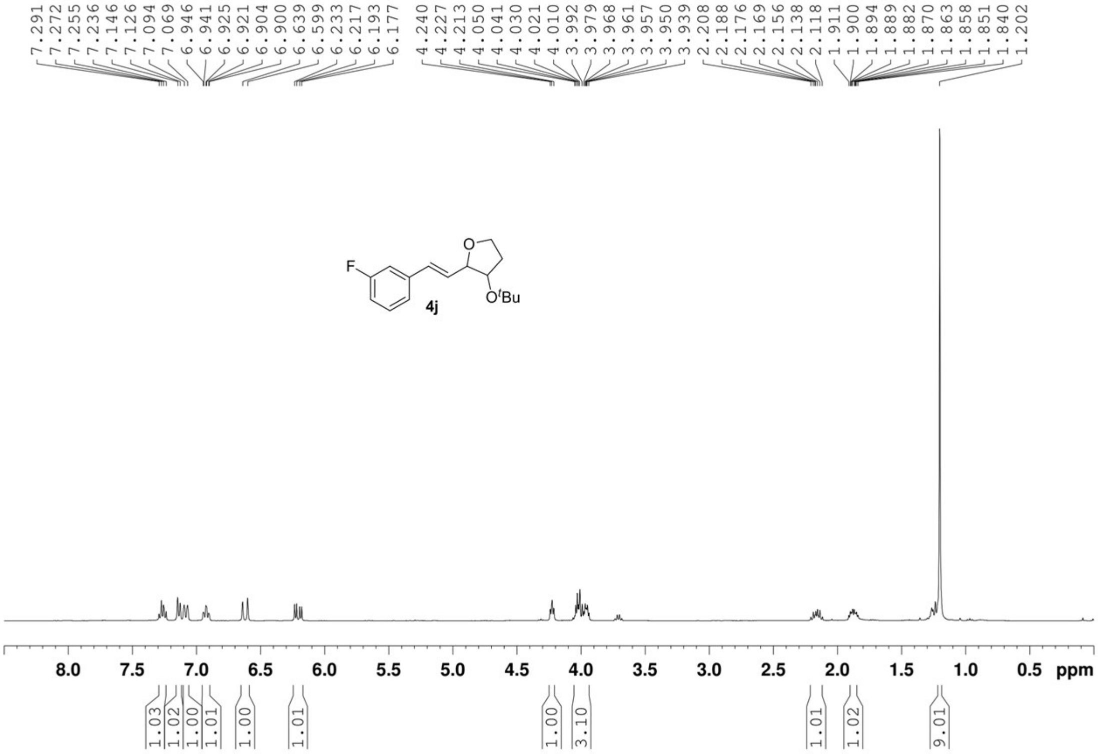
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O^tBu
4j
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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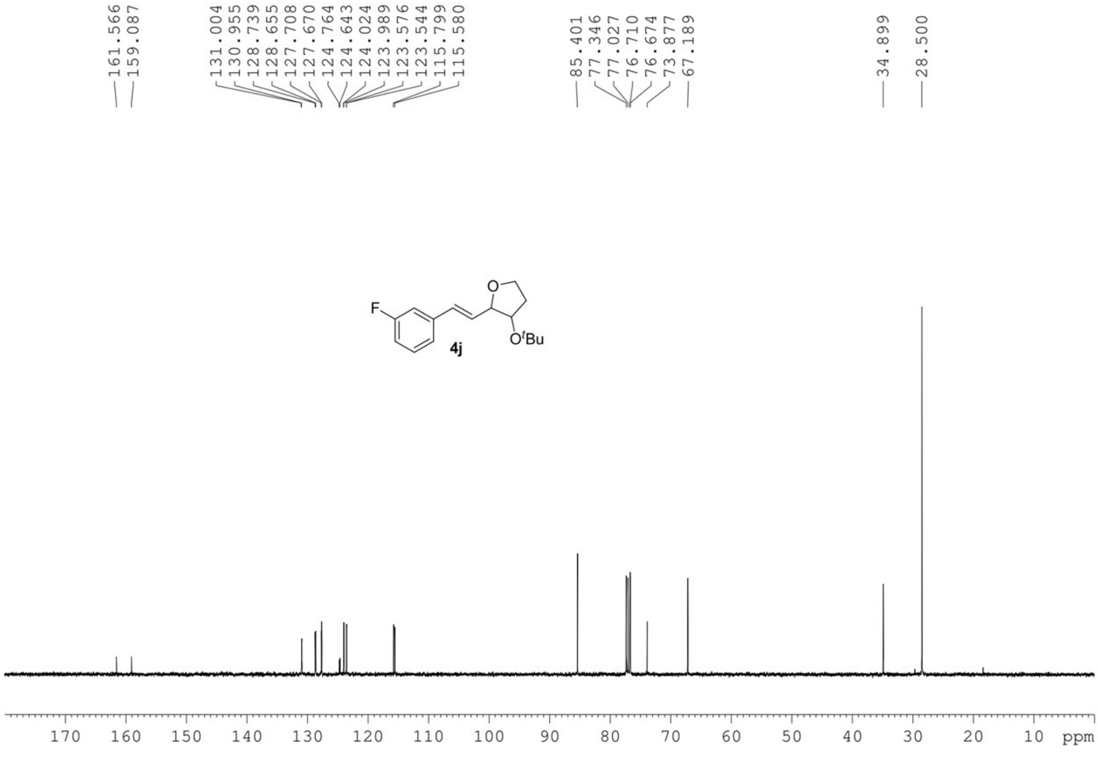
161.566 159.087
131.004 130.955 128.739 128.655 127.708 127.670 124.764 124.643 124.024 123.989 123.576 123.544 115.799 115.580
85.401 77.346 77.027 76.710 76.674 73.877 67.189
34.899 28.500
F
O
O^tBu
4j
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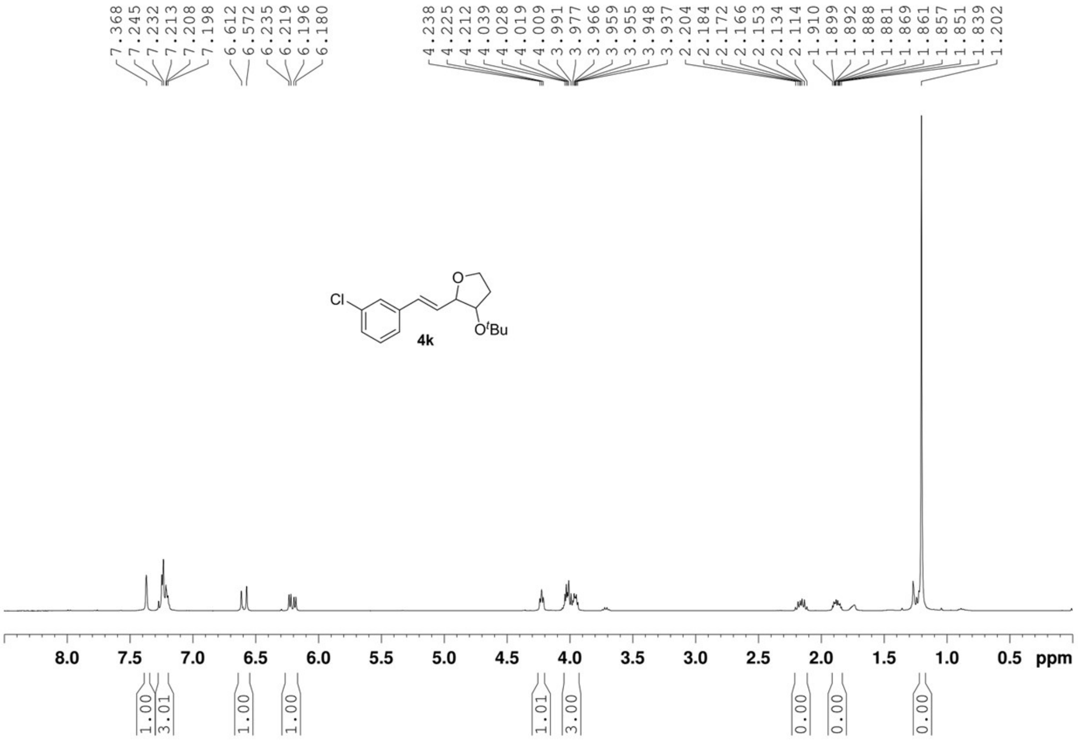
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6.572
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6.219
6.196
6.180
4.238
4.225
4.212
4.039
4.028
4.019
4.009
3.991
3.977
3.966
3.959
3.955
3.948
3.937
2.204
2.184
2.172
2.166
2.153
2.134
2.114
1.910
1.899
1.892
1.888
1.881
1.869
1.861
1.857
1.851
1.839
1.202
Cl
O
O^{t}Bu
4k
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
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ppm
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1.01
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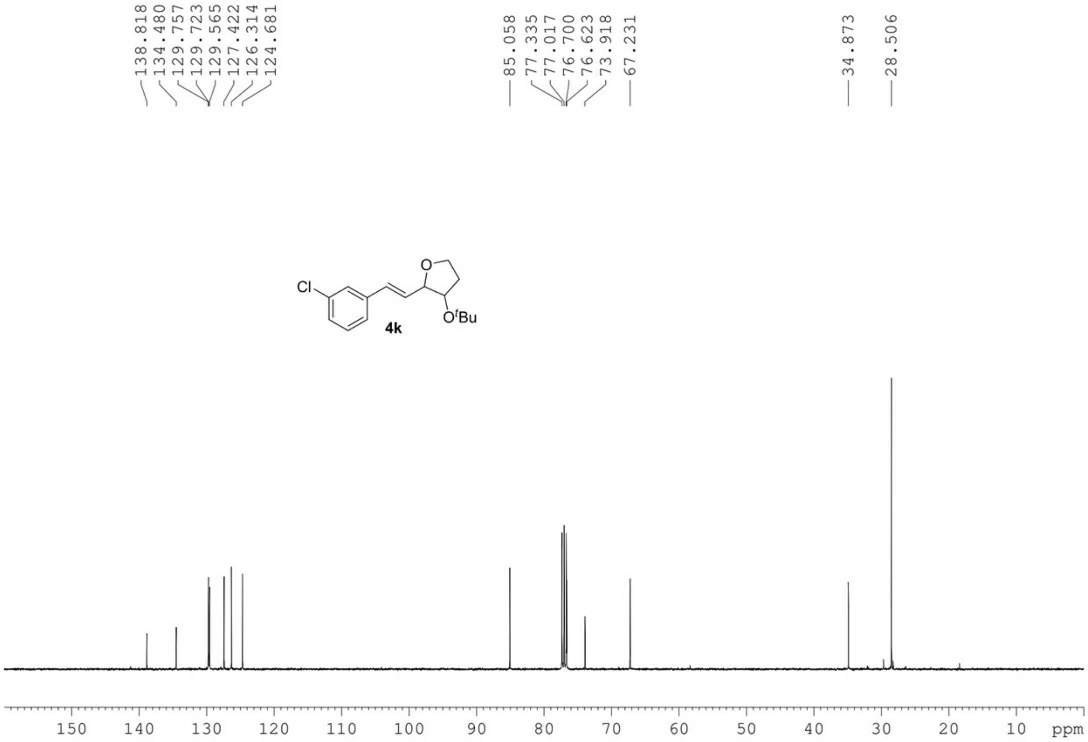
0.00
0.00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76.623
73.918
67.231
34.873
28.506
Cl
O
O^{t}Bu
4k
150
140
130
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110
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70
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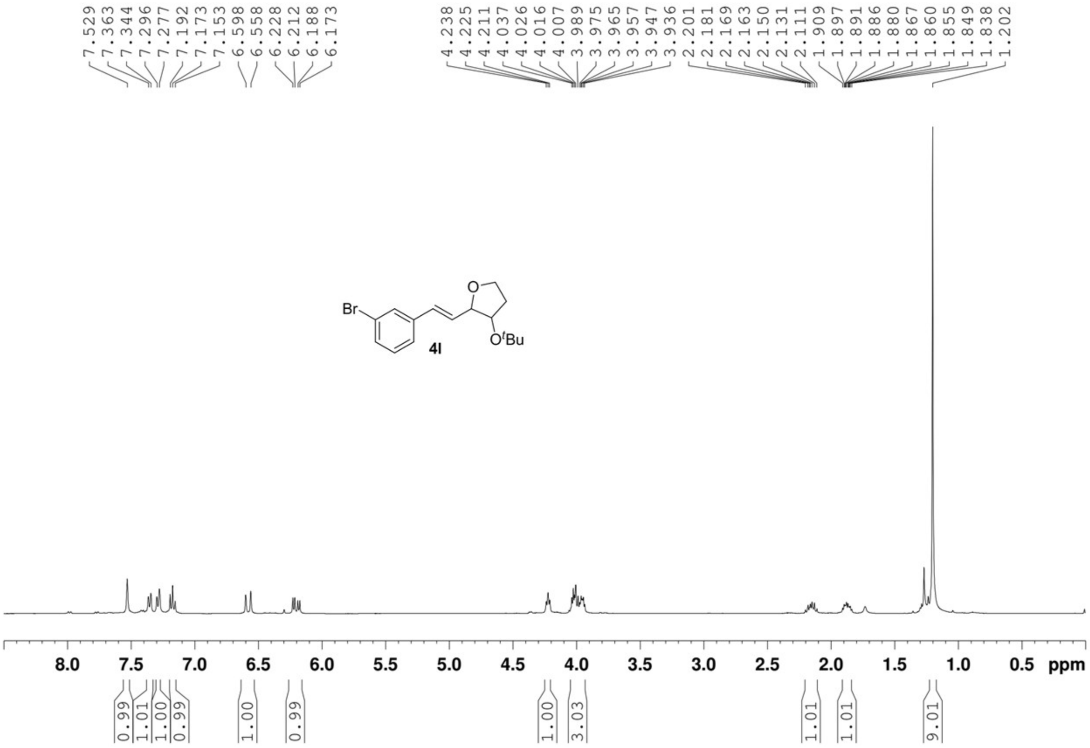
40
30
20
10
ppm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6.228
6.212
6.188
6.173
4.238
4.225
4.211
4.037
4.026
4.016
4.007
3.989
3.975
3.965
3.957
3.947
3.936
2.201
2.181
2.169
2.163
2.150
2.131
2.111
1.909
1.897
1.891
1.886
1.880
1.867
1.860
1.855
1.849
1.838
1.202
Br
O
O^{t}Bu
4l
8.0
7.5
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
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1.00
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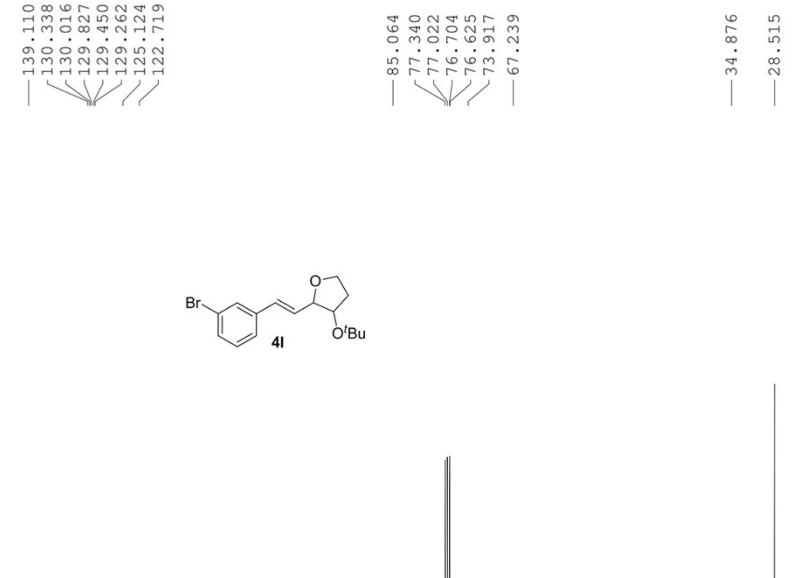
1.01
9.01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122.719
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76.704
76.625
73.917
67.239
34.876
28.515
Br
O
O^{t}Bu
4l
150
140
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120
110
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90
80
70
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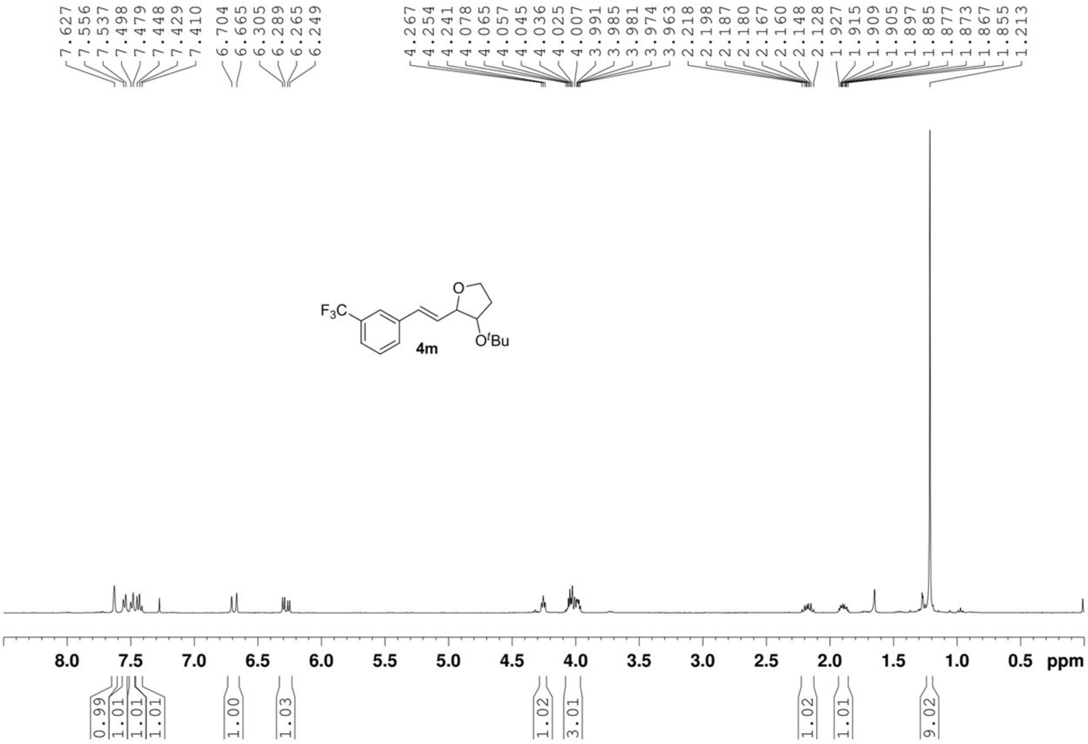
50
40
30
20
10
ppm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7.410
6.704
6.665
6.305
6.289
6.265
6.249
4.267
4.254
4.241
4.078
4.065
4.057
4.045
4.036
4.025
4.007
3.991
3.985
3.981
3.974
3.963
2.218
2.198
2.187
2.180
2.167
2.160
2.148
2.128
1.927
1.915
1.909
1.905
1.897
1.885
1.877
1.873
1.867
1.855
1.213
F3C
O
O^tBu
4m
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
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1.01
1.01
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1.02
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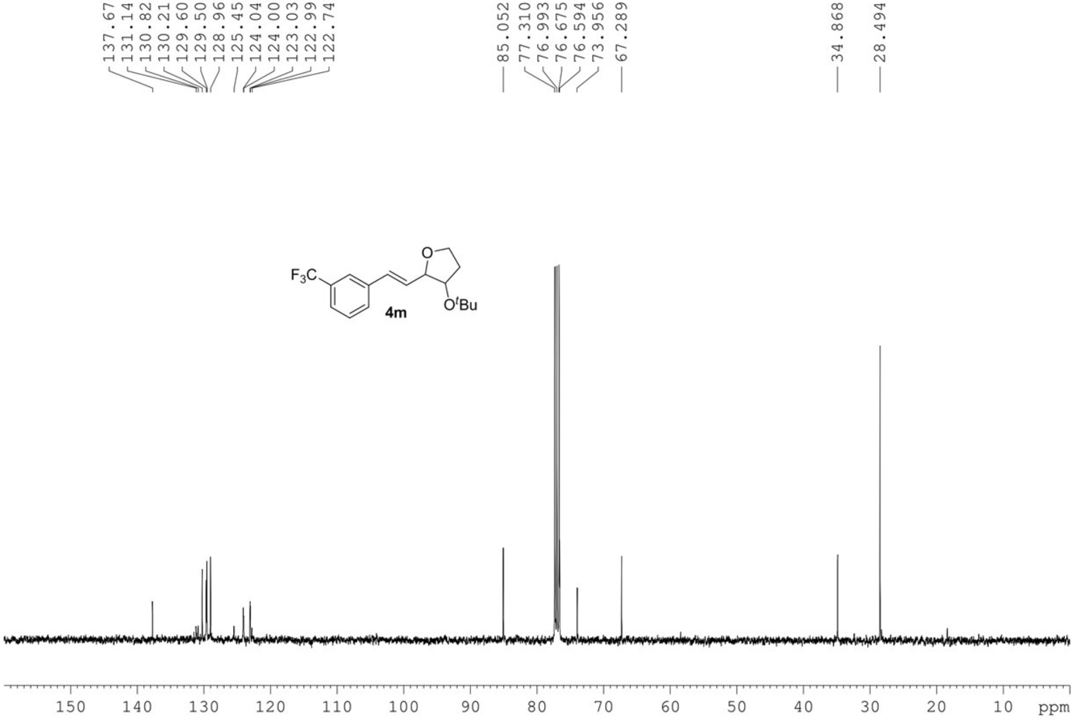
1.02
1.01
9.02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124.004
123.031
122.992
122.747
85.052
77.310
76.993
76.675
76.594
73.956
67.289
34.868
28.494
F3C
O
O^tBu
4m
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140
130
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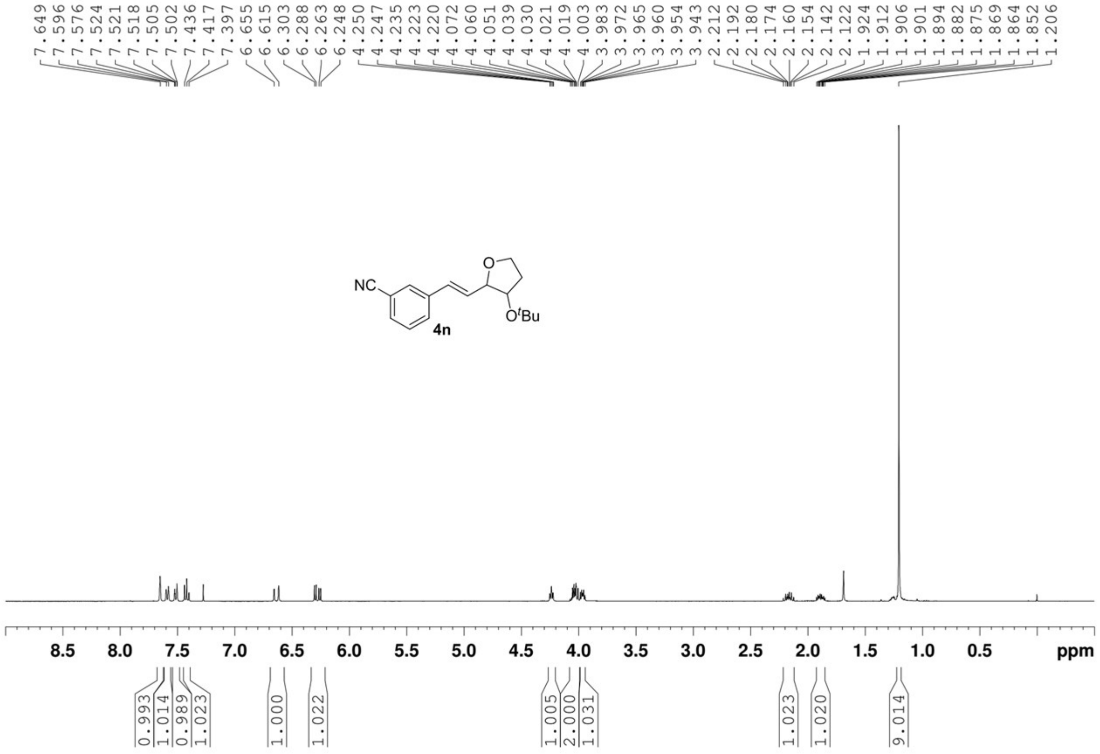
30
20
10
ppm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7.502
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7.417
7.397
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6.615
6.303
6.288
6.263
6.248
4.250
4.247
4.235
4.223
4.220
4.072
4.060
4.051
4.039
4.030
4.021
4.019
4.003
3.983
3.972
3.965
3.960
3.954
3.943
2.212
2.192
2.180
2.174
2.160
2.154
2.142
2.122
1.924
1.912
1.906
1.901
1.894
1.882
1.875
1.869
1.864
1.852
1.206
NC
O
O^tBu
4n
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
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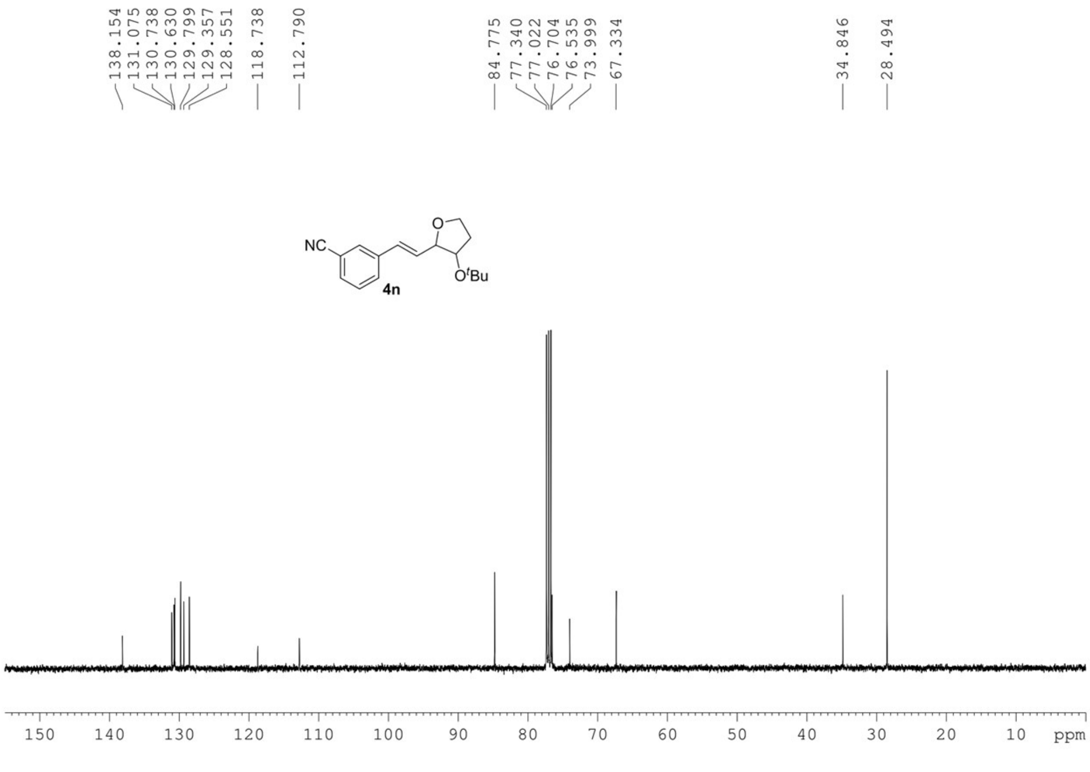
1.022
1.005
2.000
1.031
1.023
1.020
9.014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112.790
84.775
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76.704
76.535
73.999
67.334
34.846
28.494
NC
O
O^tBu
4n
150
140
130
120
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70
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40
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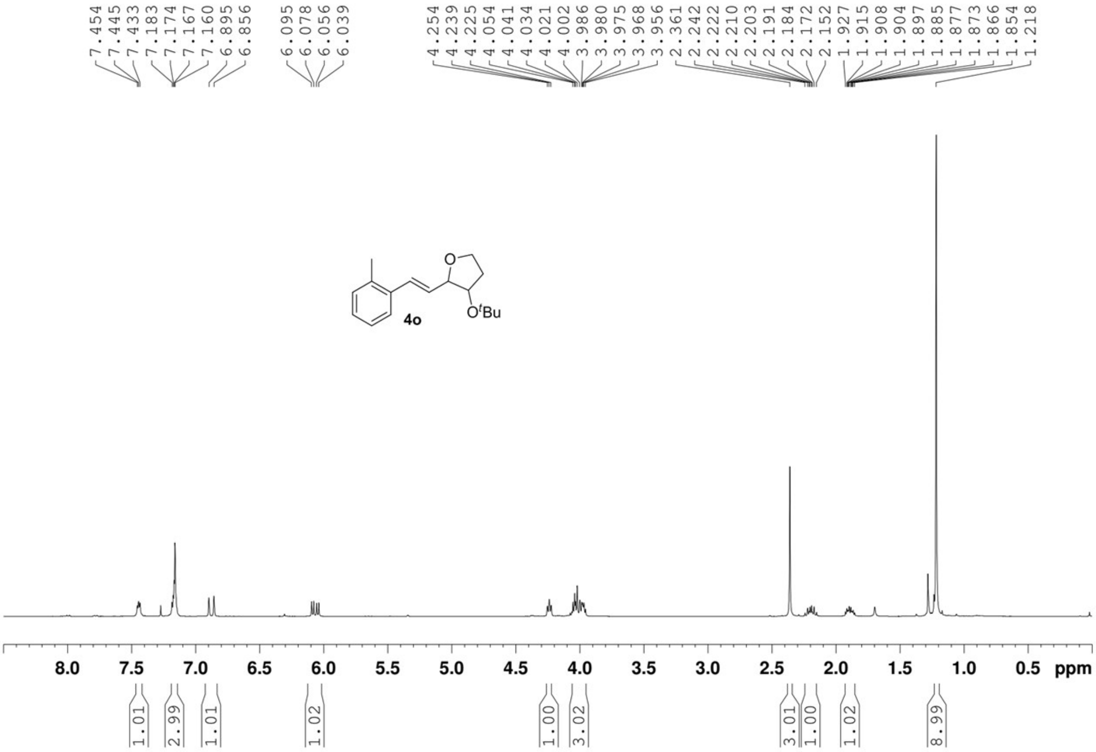
20
10
ppm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6.095
6.078
6.056
6.039
4.254
4.239
4.225
4.054
4.041
4.034
4.021
4.002
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3.980
3.975
3.968
3.956
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2.242
2.222
2.210
2.203
2.191
2.184
2.172
2.152
1.927
1.915
1.908
1.904
1.897
1.885
1.877
1.873
1.866
1.854
1.218
O
O^{t}Bu
4o
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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3.02
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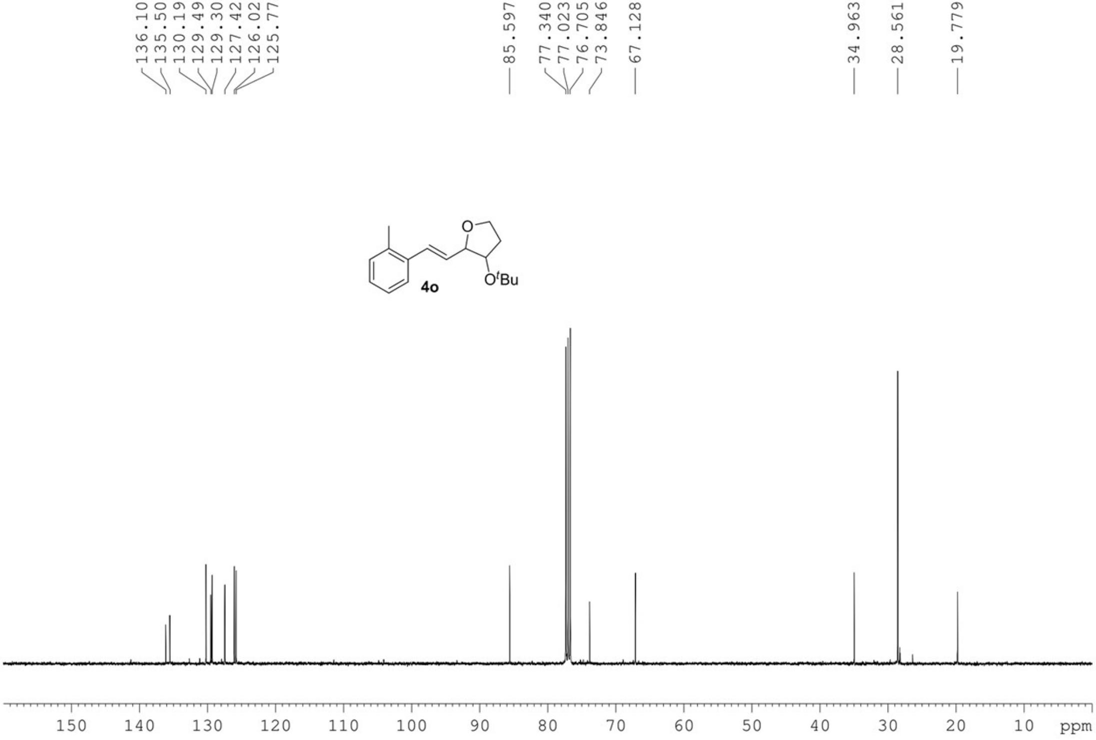
1.02
8.99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73.846
67.128
34.963
28.561
19.779
O
O^{t}Bu
4o
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140
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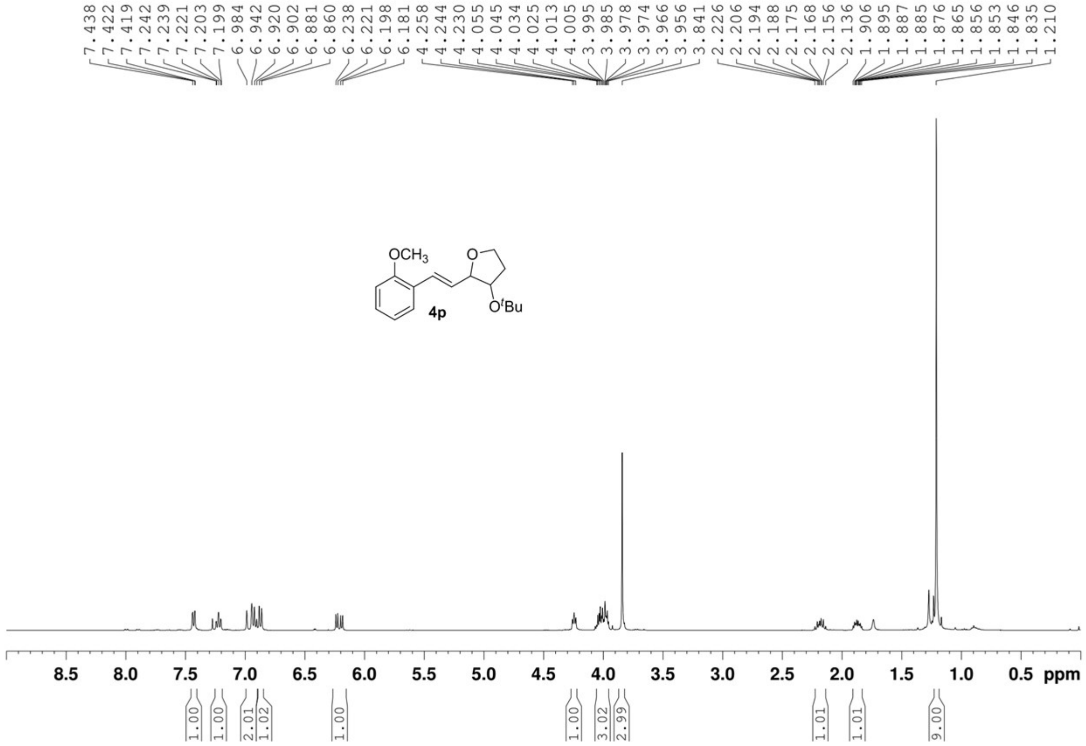
30
20
10
ppm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6.881
6.860
6.238
6.221
6.198
6.181
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4.244
4.230
4.055
4.045
4.034
4.025
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4.005
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1.835
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O
O^tBu
4p
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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 ppm
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2.01
1.02
1.00
1.00
3.02
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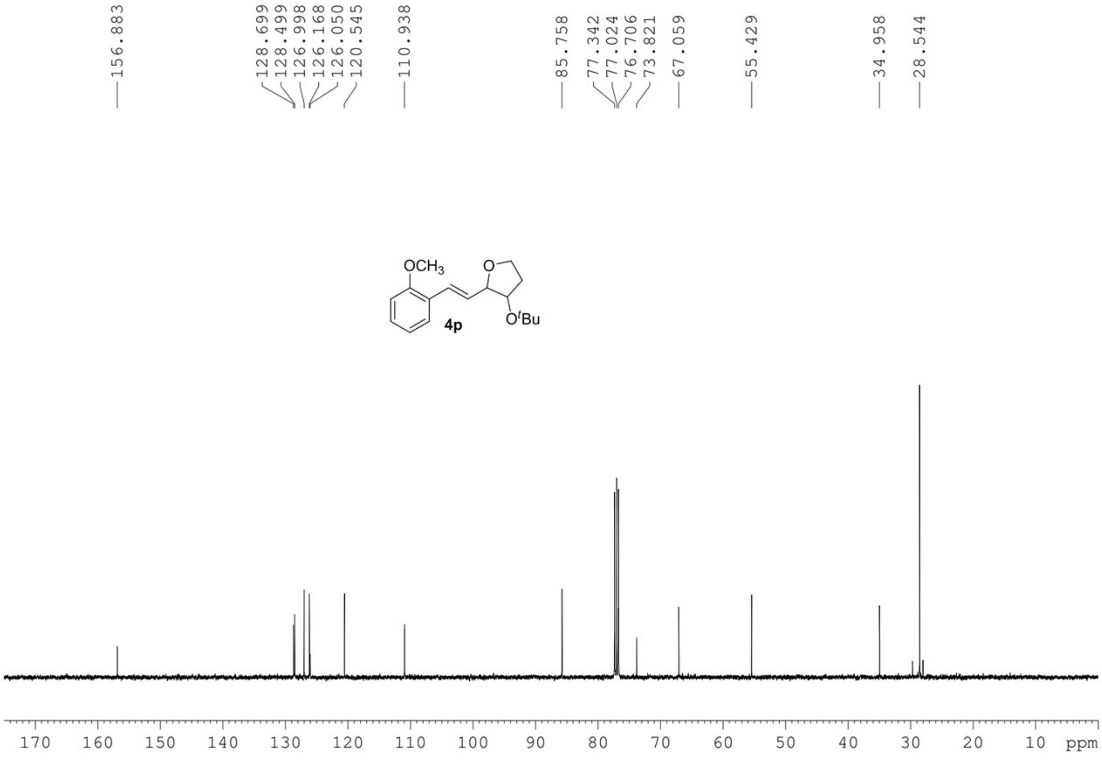
1.01
9.00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28.544
OCH3
O
O^tBu
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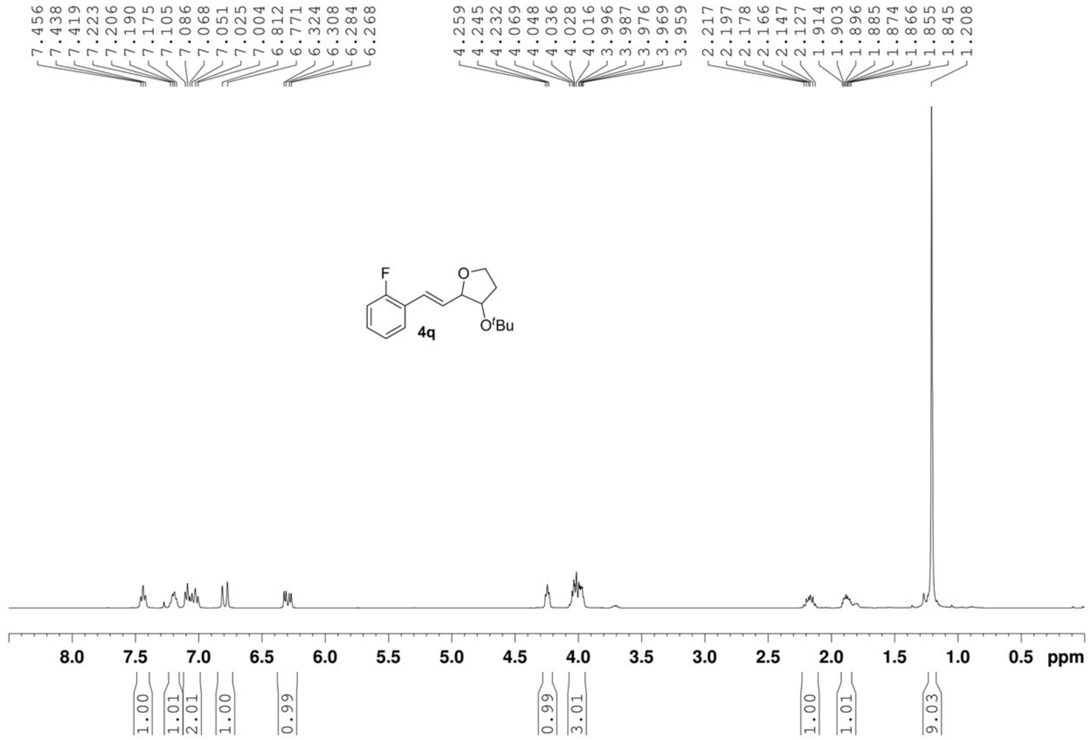
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6.308
6.284
6.268
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4.036
4.028
4.016
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3.969
3.959
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2.197
2.178
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2.147
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1.903
1.896
1.885
1.874
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1.855
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F
O
4q
O^{t}Bu
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5.5
5.0
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4.0
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3.0
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2.0
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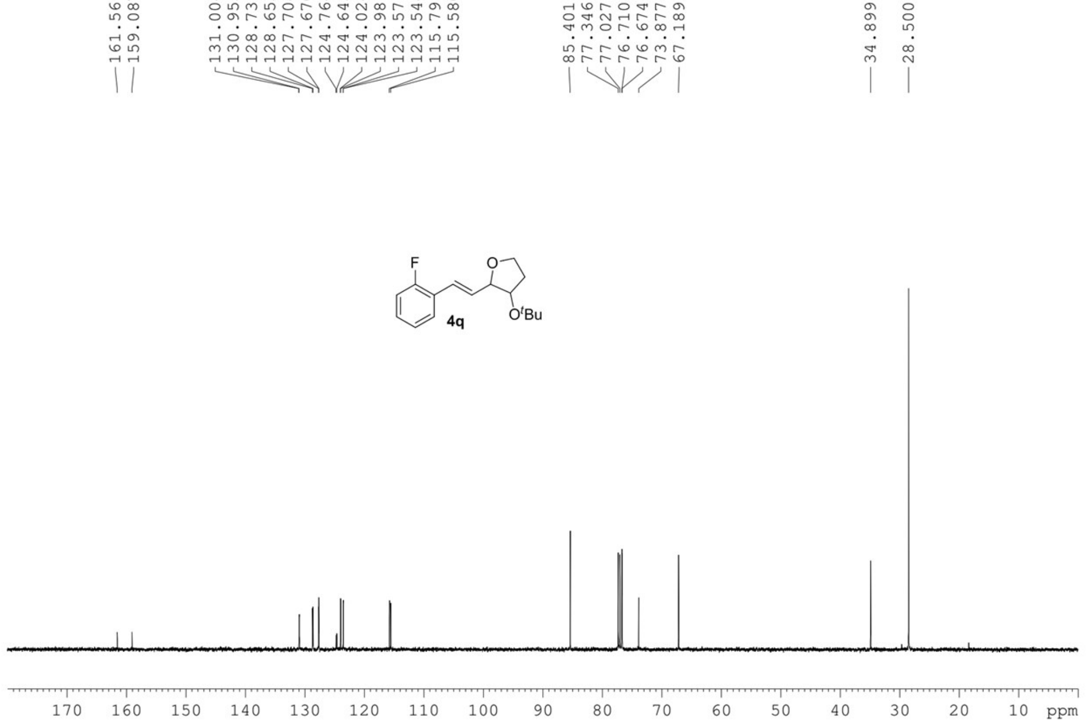
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123.576
123.544
115.799
115.580
85.401
77.346
77.027
76.710
76.674
73.877
67.189
34.899
28.500
F
O
4q
O^{t}Bu
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140
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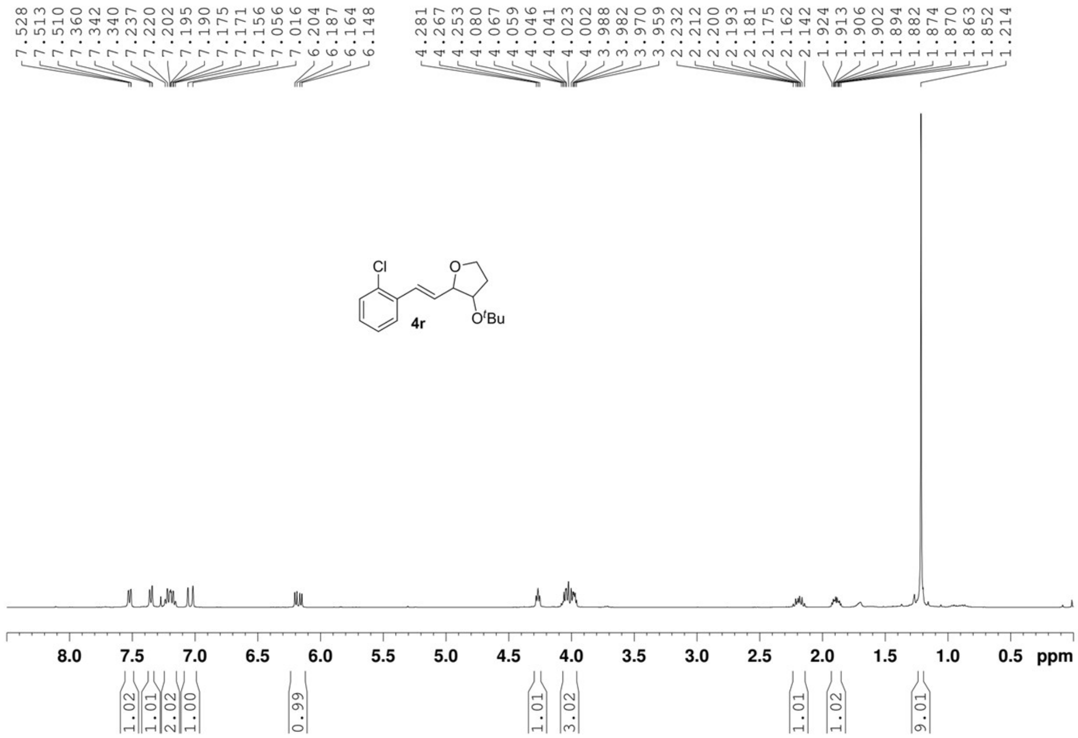
ppm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7.156
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7.016
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6.148
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4.267
4.253
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4.067
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4.041
4.023
4.002
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2.181
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1.902
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Cl
O
O^{t}Bu
4r
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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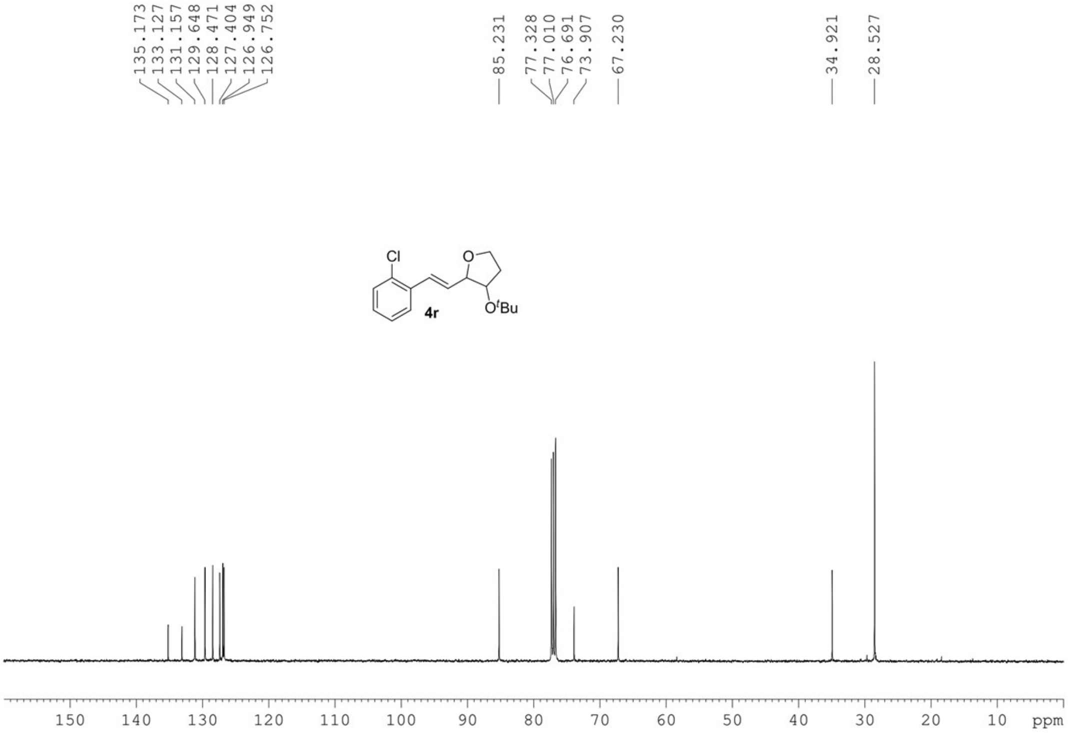
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73.907
67.230
34.921
28.527
Cl
O
O^{t}Bu
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70
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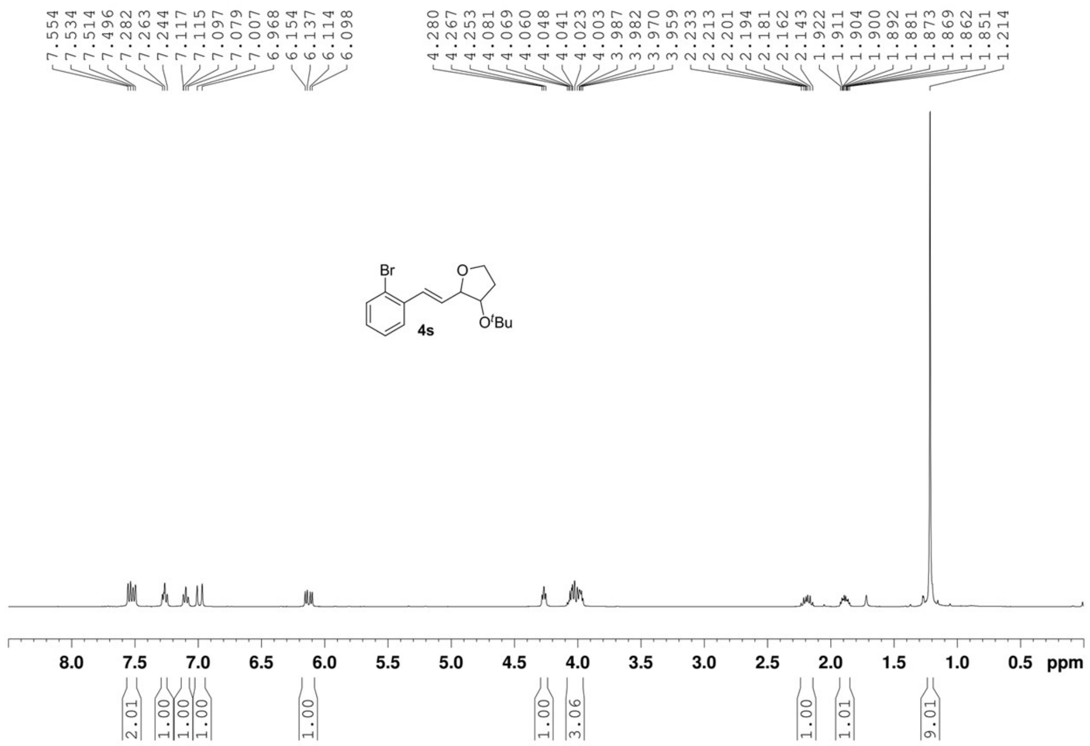
20
10
ppm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4.253
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4.041
4.023
4.003
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2.143
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1.911
1.904
1.900
1.892
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1.873
1.869
1.862
1.851
1.214
Br
O
O^{t}Bu
4s
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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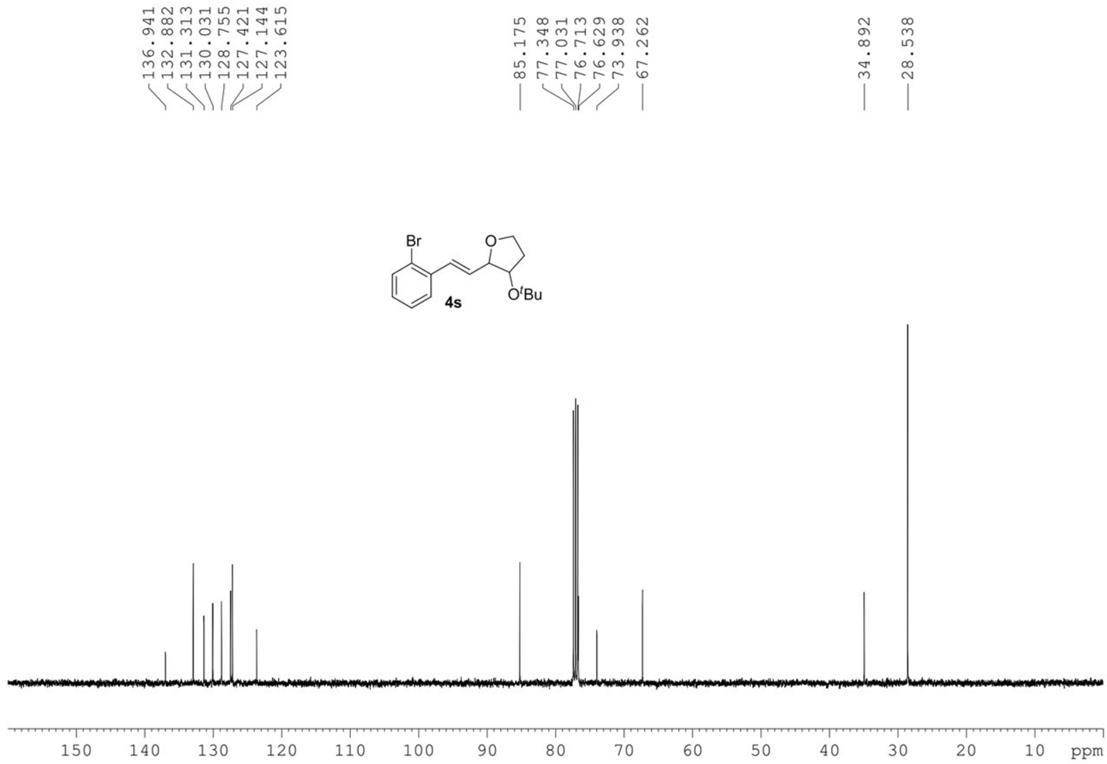
9.01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76.629
73.938
67.262
34.892
28.538
Br
O
O^{t}Bu
4s
150
140
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120
110
100
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70
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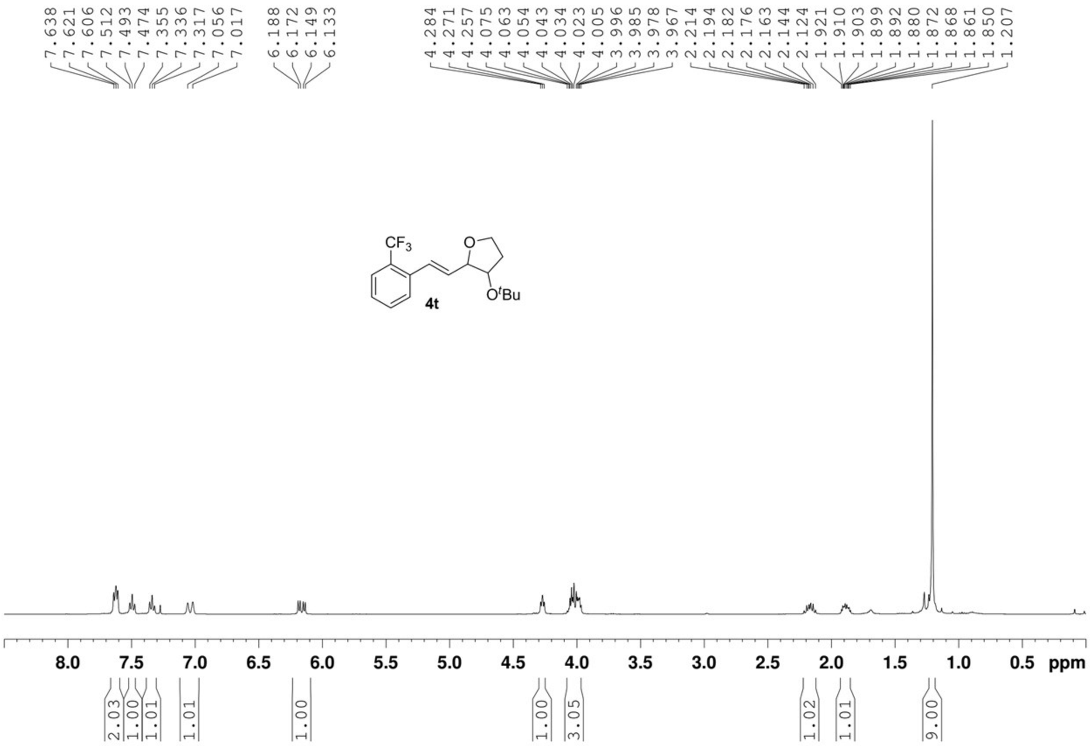
10
ppm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6.172
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4.043
4.034
4.023
4.005
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1.899
1.892
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1.861
1.850
1.207
CF3
O
O^tBu
4t
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
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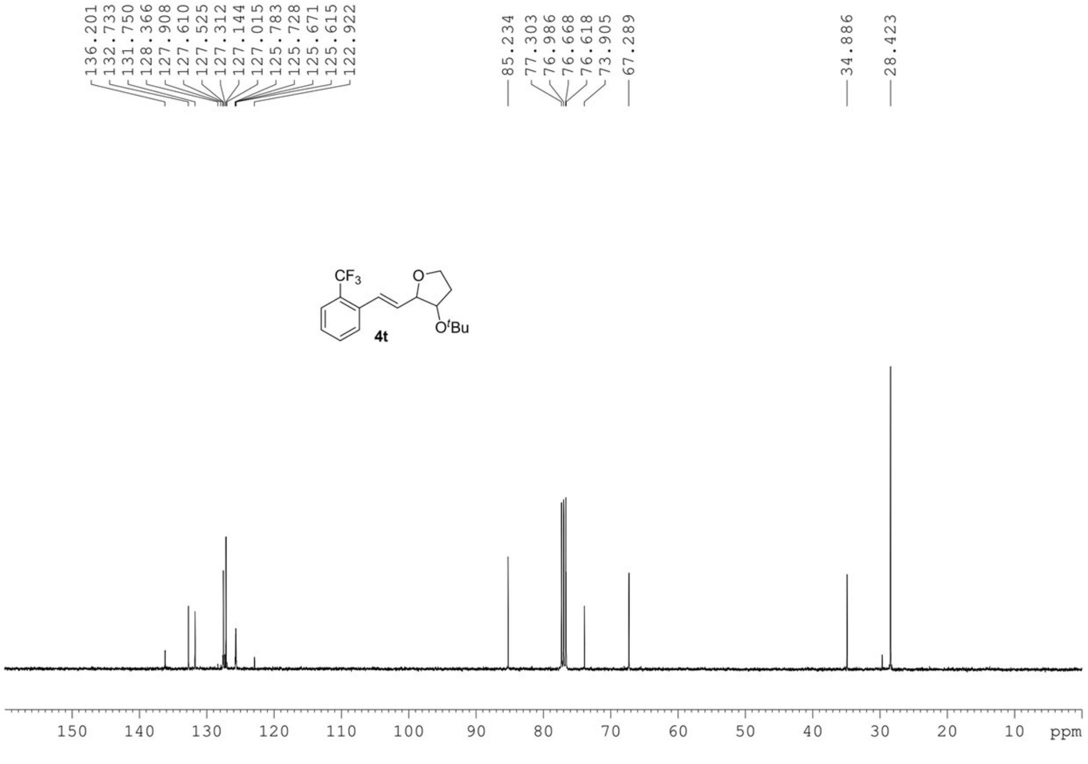
9.00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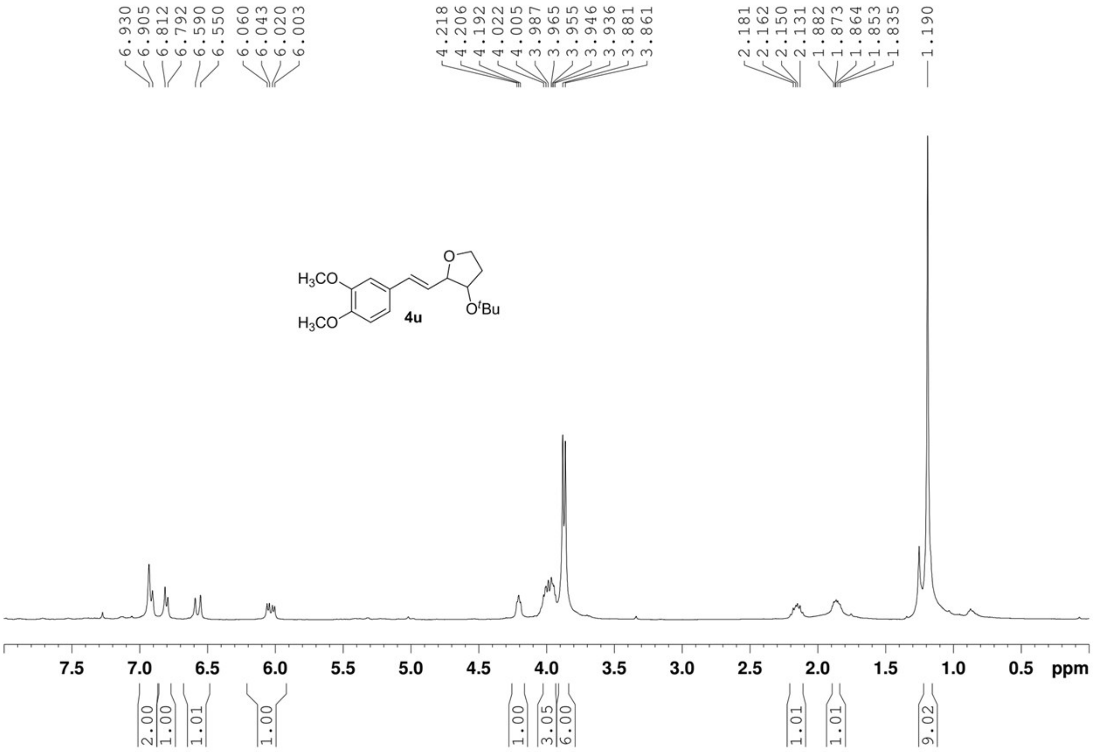
125.671
125.615
122.922
85.234
77.303
76.986
76.668
76.618
73.905
67.289
34.886
28.423
CF3
O
O^tBu
4t
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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6.003
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4.192
4.022
4.005
3.987
3.965
3.955
3.946
3.936
3.881
3.861
2.181
2.162
2.150
2.131
1.882
1.873
1.864
1.853
1.835
1.190
H_3CO
H_3CO
4u
O^tBu
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
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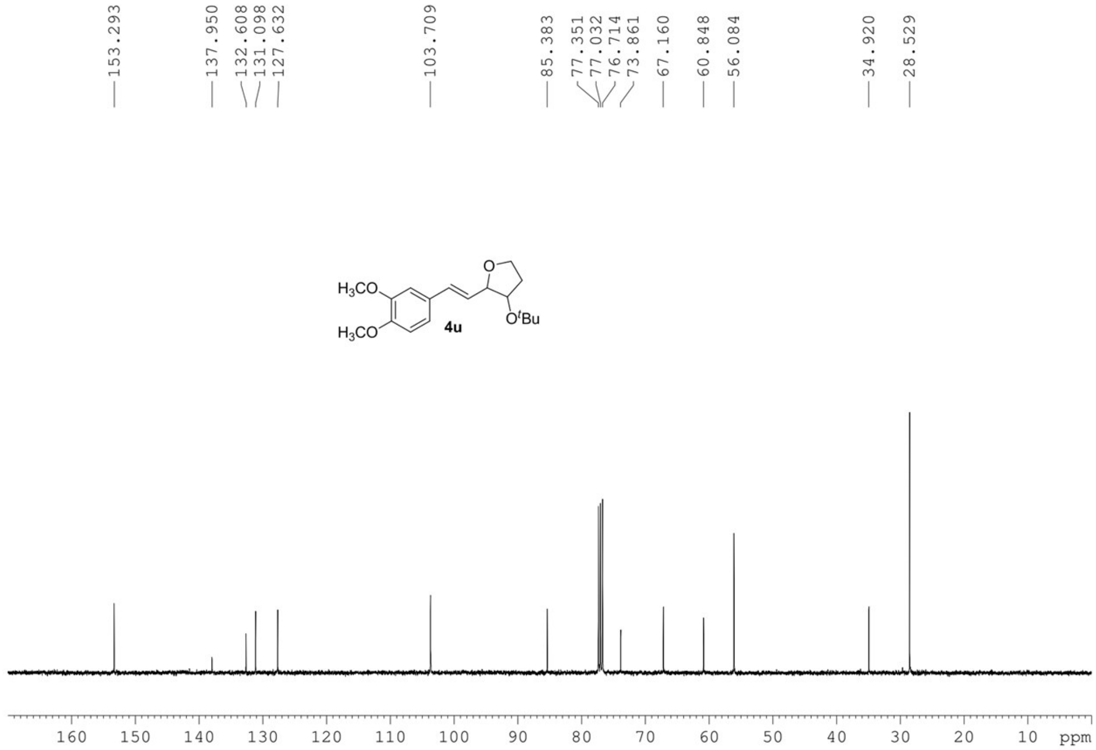
1.01
9.02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131.098
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77.351
77.032
76.714
73.861
67.160
60.848
56.084
34.920
28.529
H_3CO
H_3CO
4u
O^tBu
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150
140
130
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110
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70
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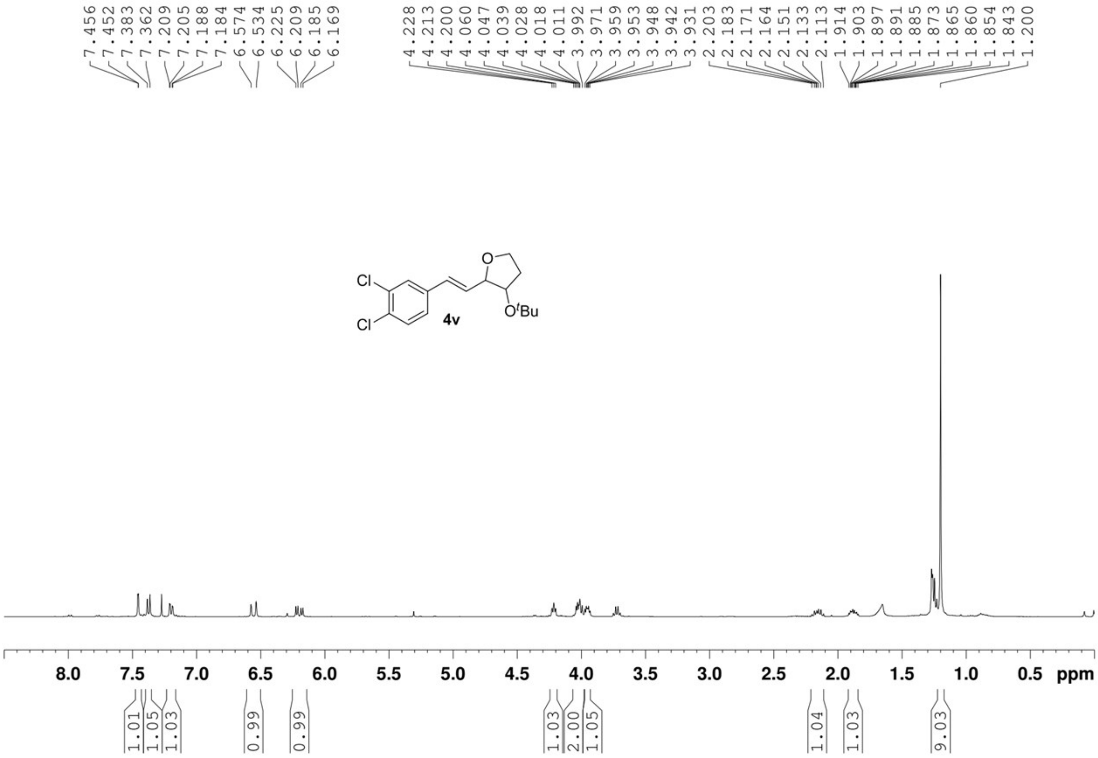
30
20
10
ppm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4.228 4.213 4.200 4.060 4.047 4.039 4.028 4.018 4.011 3.992 3.971 3.959 3.953 3.948 3.942 3.931
2.203 2.183 2.171 2.164 2.151 2.133 2.113 1.914 1.903 1.897 1.891 1.885 1.873 1.865 1.860 1.854 1.843 1.200
Cl
Cl
O
O^tBu
4v
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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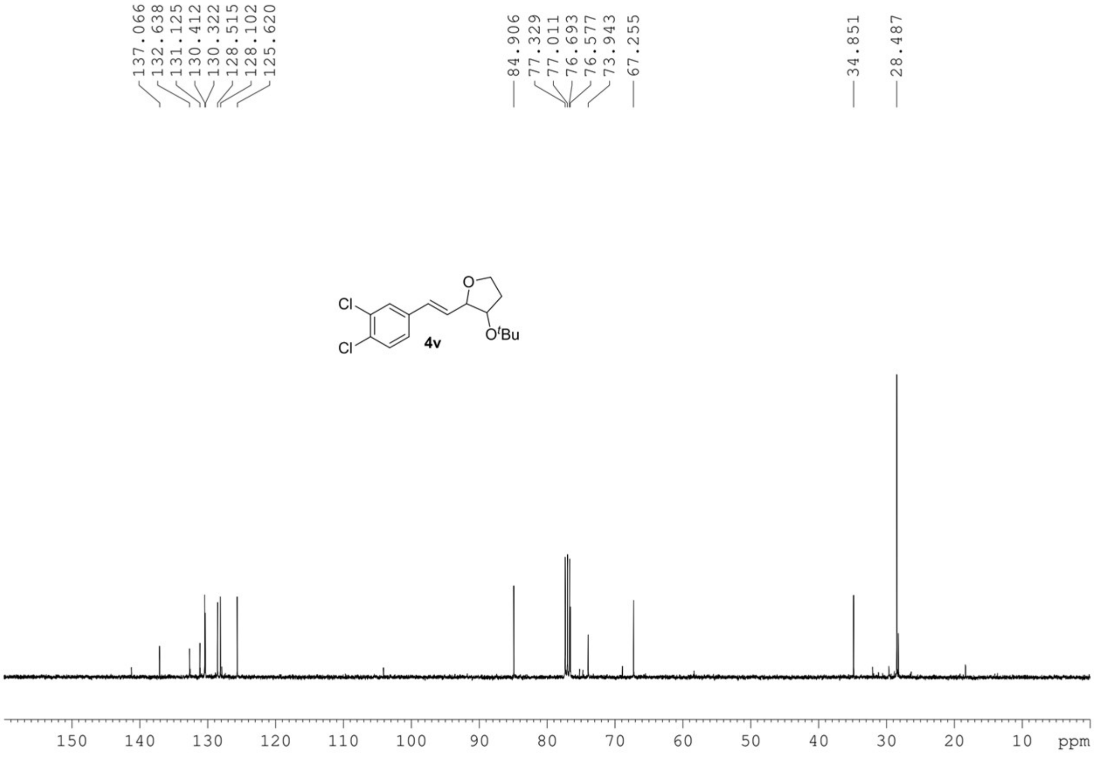
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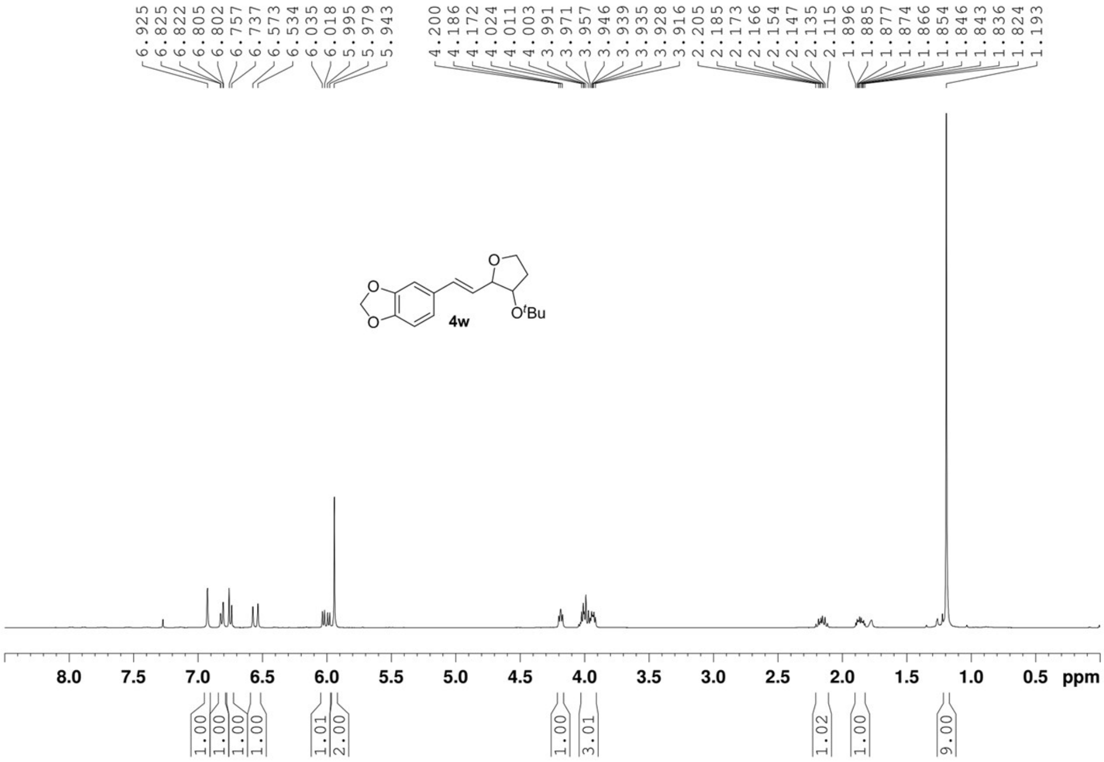
84.906 77.329 77.011 76.693 76.577 73.943 67.255
34.851 28.487
Cl
Cl
O
O^tBu
4v
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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6.573
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6.035
6.018
5.995
5.979
5.943
4.200
4.186
4.172
4.024
4.011
4.003
3.991
3.971
3.957
3.946
3.939
3.935
3.928
3.916
2.205
2.185
2.173
2.166
2.154
2.147
2.135
2.115
1.896
1.885
1.877
1.874
1.866
1.854
1.846
1.843
1.836
1.824
1.193
4w
O^tBu
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
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1.00
1.00
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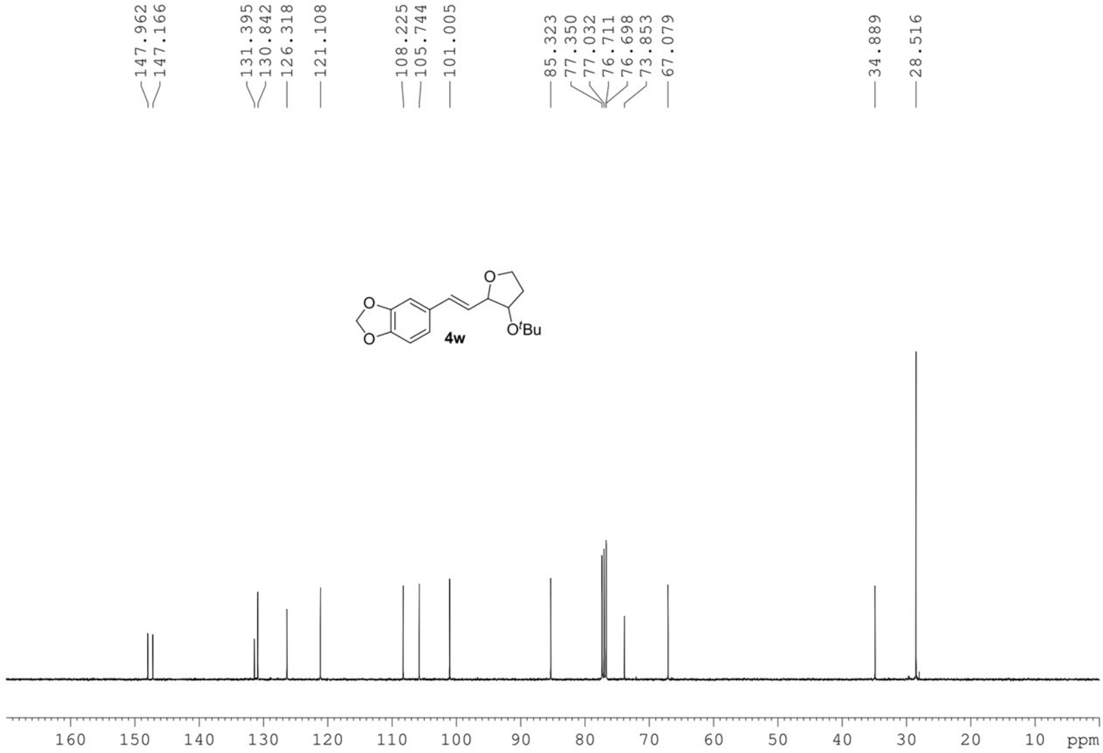
2.00
1.00
3.01
1.02
1.00
9.00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105.744
101.005
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77.032
76.711
76.698
73.853
67.079
34.889
28.516
4w
O^tBu
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150
140
130
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90
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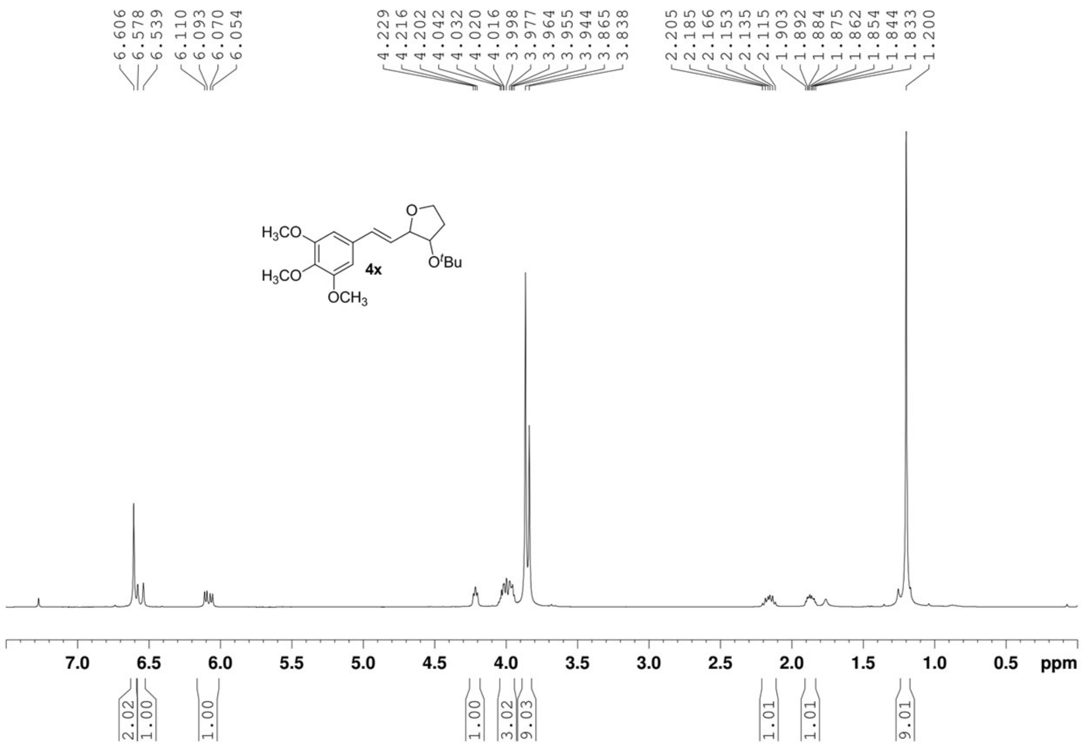
20
10
ppm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6.070
6.054
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4.202
4.042
4.032
4.020
4.016
3.998
3.977
3.964
3.955
3.944
3.865
3.838
2.205
2.185
2.166
2.153
2.135
2.115
1.903
1.892
1.884
1.875
1.862
1.854
1.844
1.833
1.200
H3CO
H3CO
OCH3
O
OtBu
4x
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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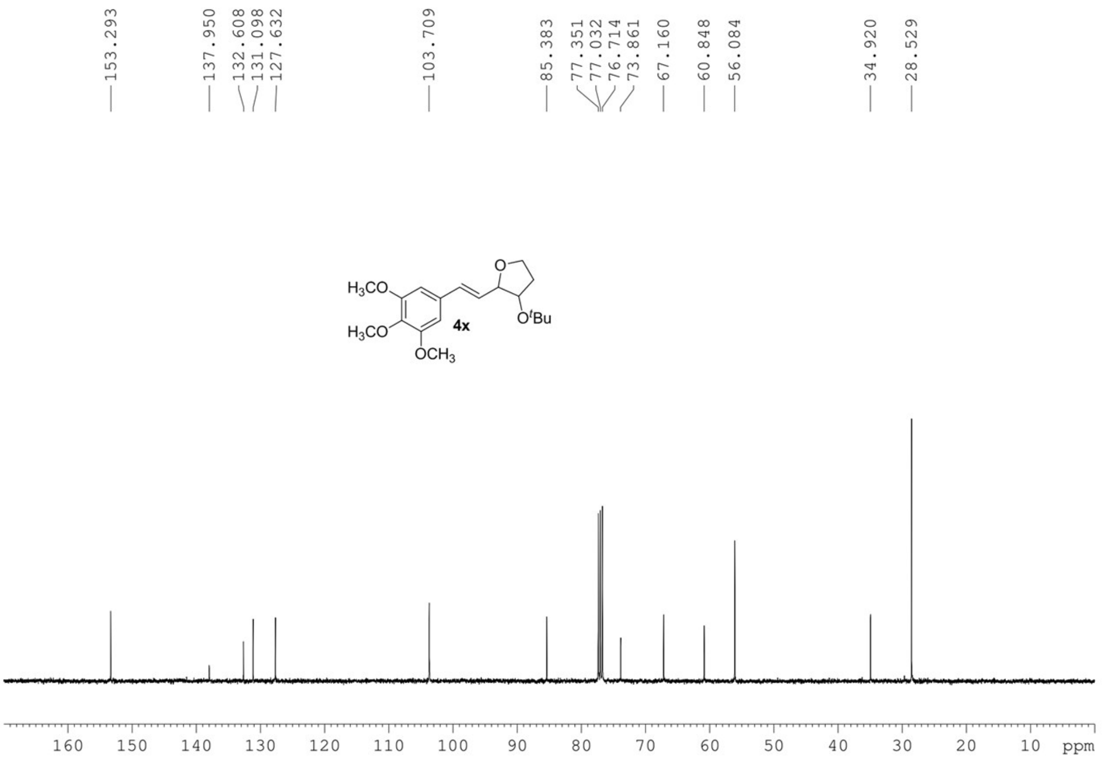
9.01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127.632
103.709
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77.351
77.032
76.714
73.861
67.160
60.848
56.084
34.920
28.529
H3CO
H3CO
OCH3
O
OtBu
4x
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150
140
130
120
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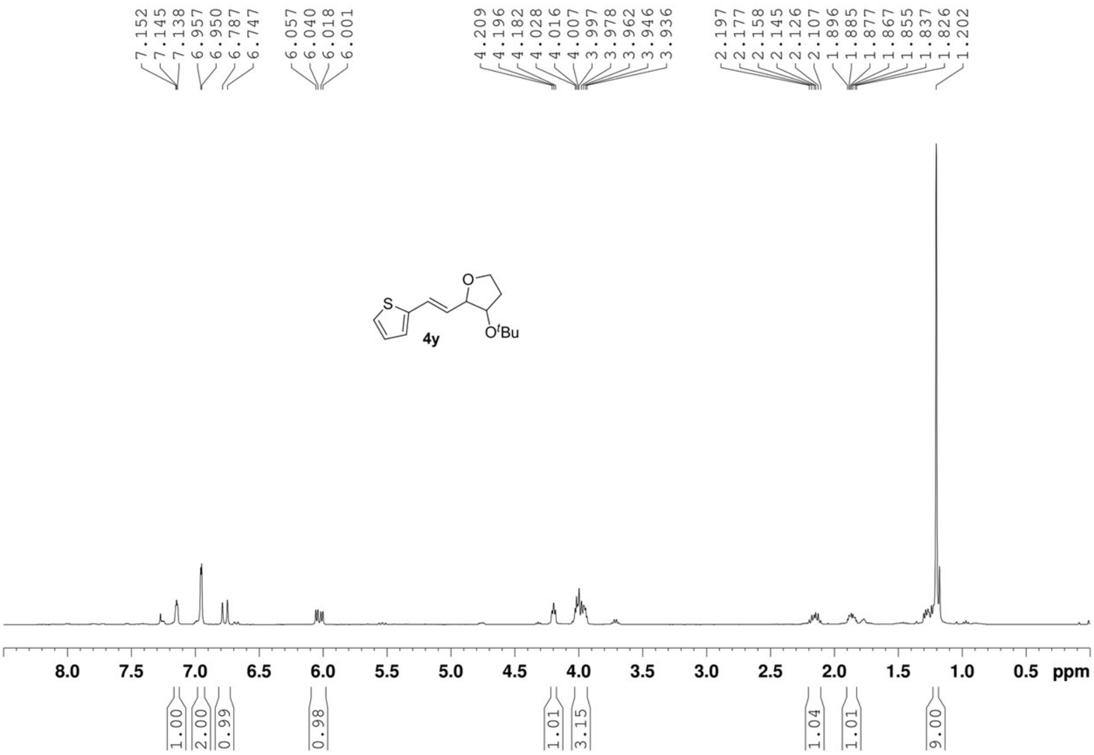
100
90
80
70
60
50
40
30
20
10
ppm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6.787
6.747
6.057
6.040
6.018
6.001
4.209
4.196
4.182
4.028
4.016
4.007
3.997
3.978
3.962
3.946
3.936
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2.177
2.158
2.145
2.126
2.107
1.896
1.885
1.877
1.867
1.855
1.837
1.826
1.202
S
O
4y
O^tBu
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
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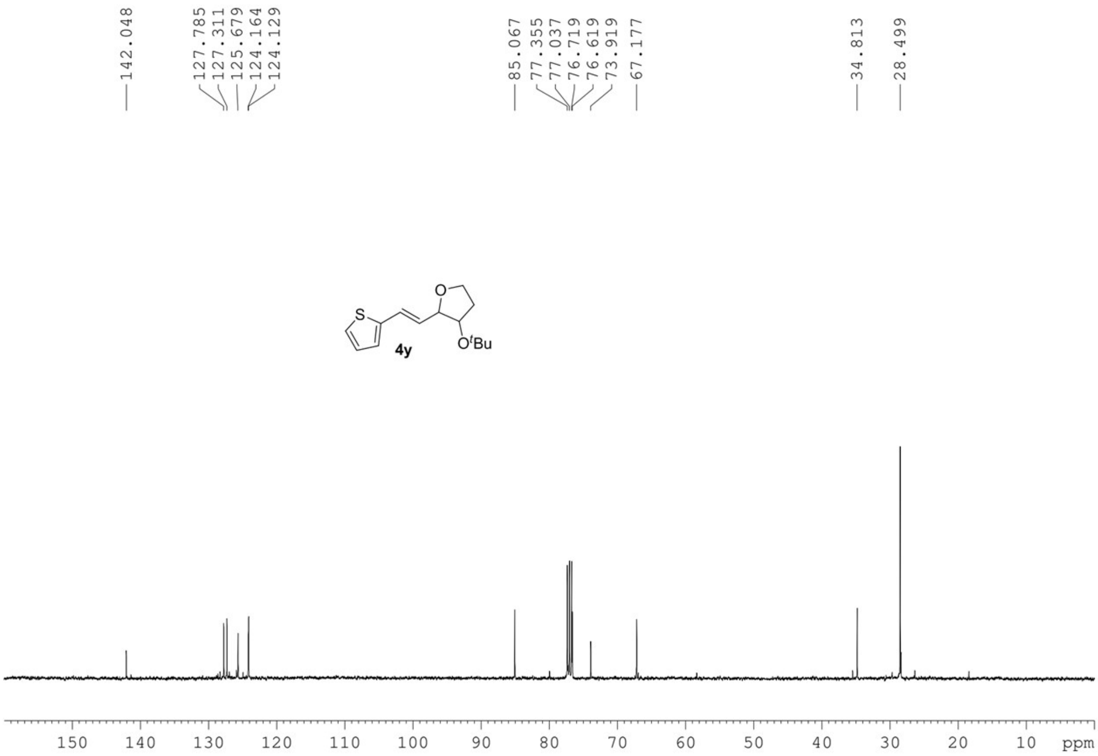
1.01
9.00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77.355
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76.719
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67.177
34.813
28.499
S
O
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150
140
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30
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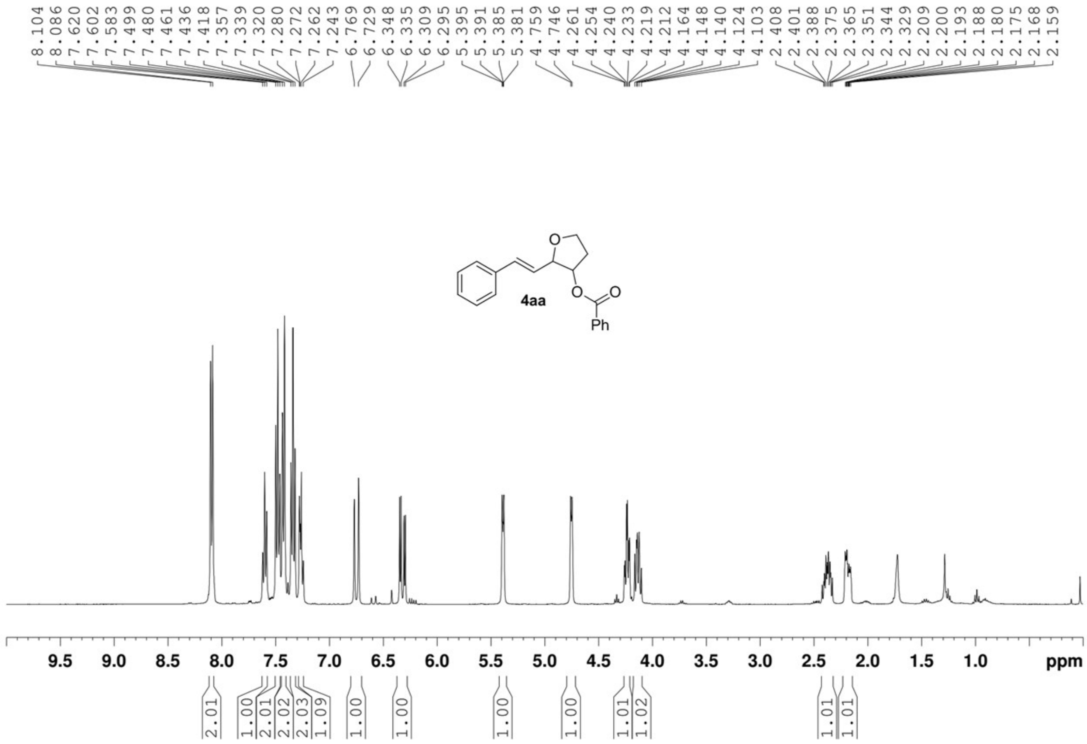
ppm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7.320
7.280
7.272
7.262
7.243
6.769
6.729
6.348
6.335
6.309
6.295
5.395
5.391
5.385
5.381
4.759
4.746
4.261
4.254
4.240
4.233
4.219
4.212
4.164
4.148
4.140
4.124
4.103
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2.401
2.388
2.375
2.365
2.351
2.344
2.329
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2.200
2.193
2.188
2.180
2.175
2.168
2.159
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O
O
Ph
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9.0
8.5
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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
ppm
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1.00
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2.02
2.03
1.09
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1.00
1.00
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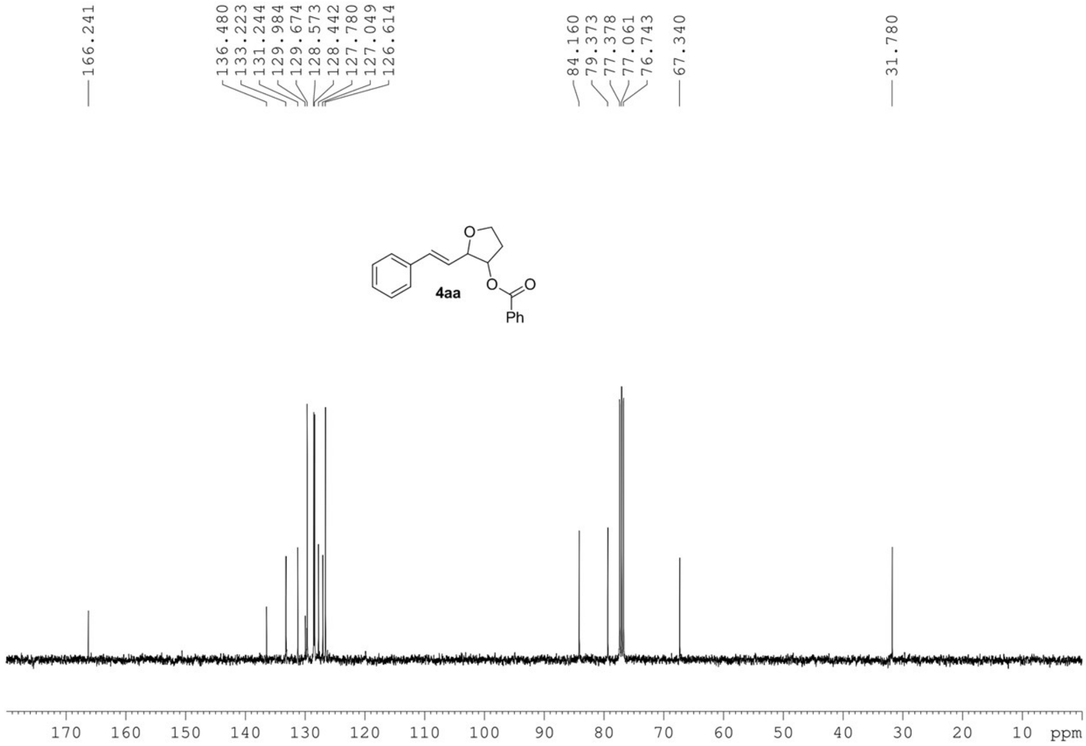
1.01
1.01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127.049
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79.373
77.378
77.061
76.743
67.340
31.780
O
O
O
Ph
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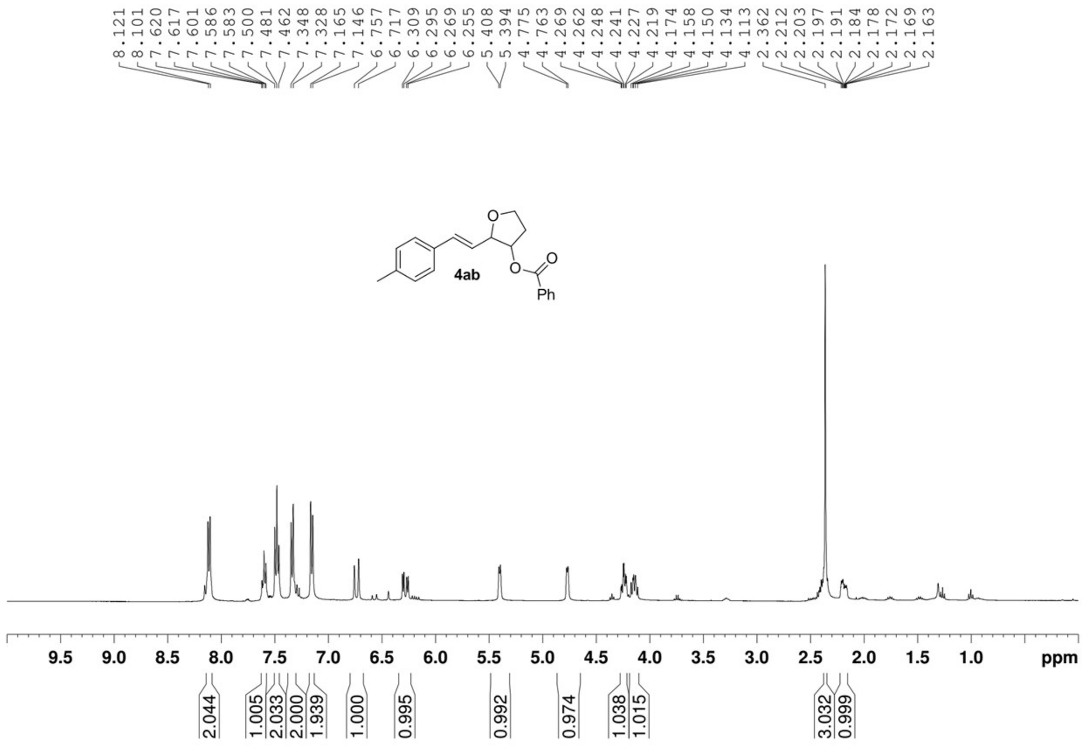
ppm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7.348
7.328
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6.717
6.309
6.295
6.269
6.255
5.408
5.394
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4.763
4.269
4.262
4.248
4.241
4.227
4.219
4.174
4.158
4.150
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2.191
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2.172
2.169
2.163
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2.5
2.0
1.5
1.0
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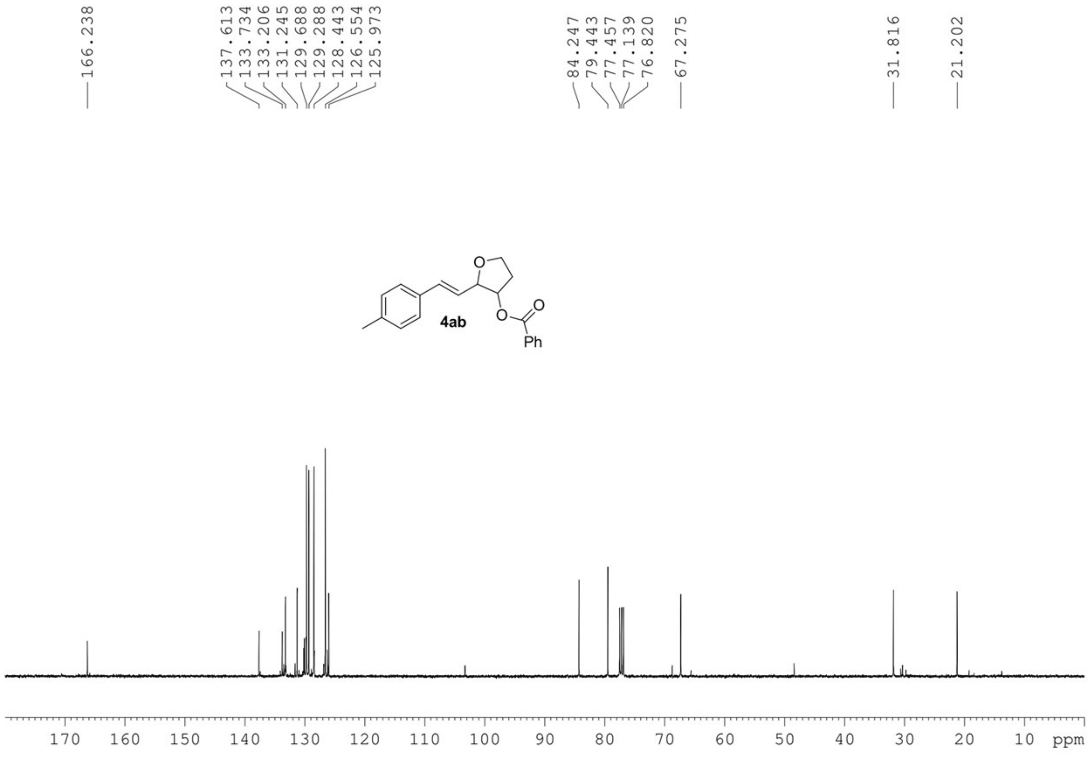
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77.457
77.139
76.820
67.275
31.816
21.202
O
O
O
Ph
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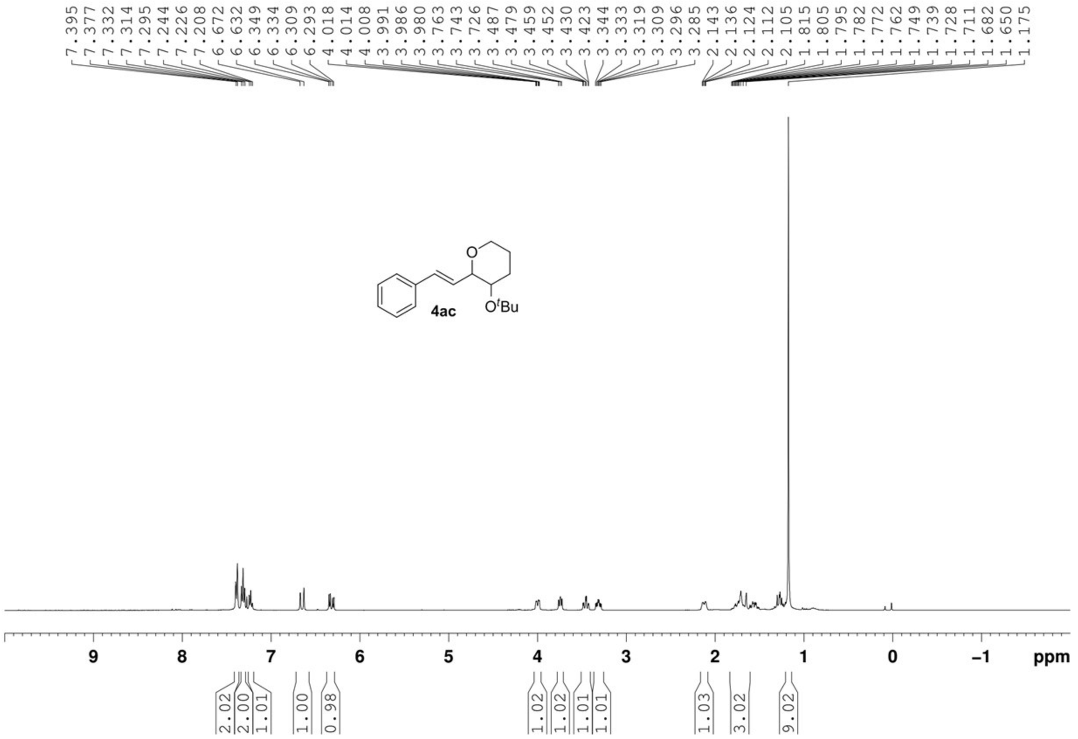
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3.333
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3.309
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3.285
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2.136
2.124
2.112
2.105
1.815
1.805
1.795
1.782
1.772
1.762
1.749
1.739
1.728
1.711
1.682
1.650
1.175
O
O^tBu
4ac
9
8
7
6
5
4
3
2
1
0
–1
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1.01
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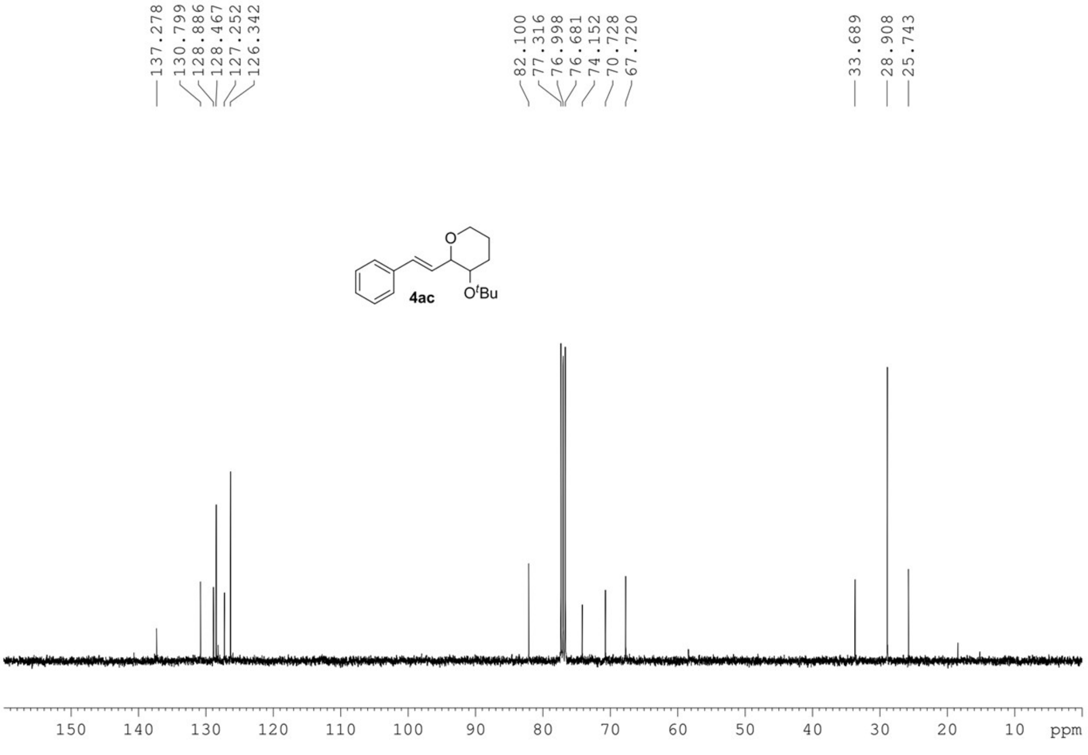
1.03
3.02
9.02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25.743
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70
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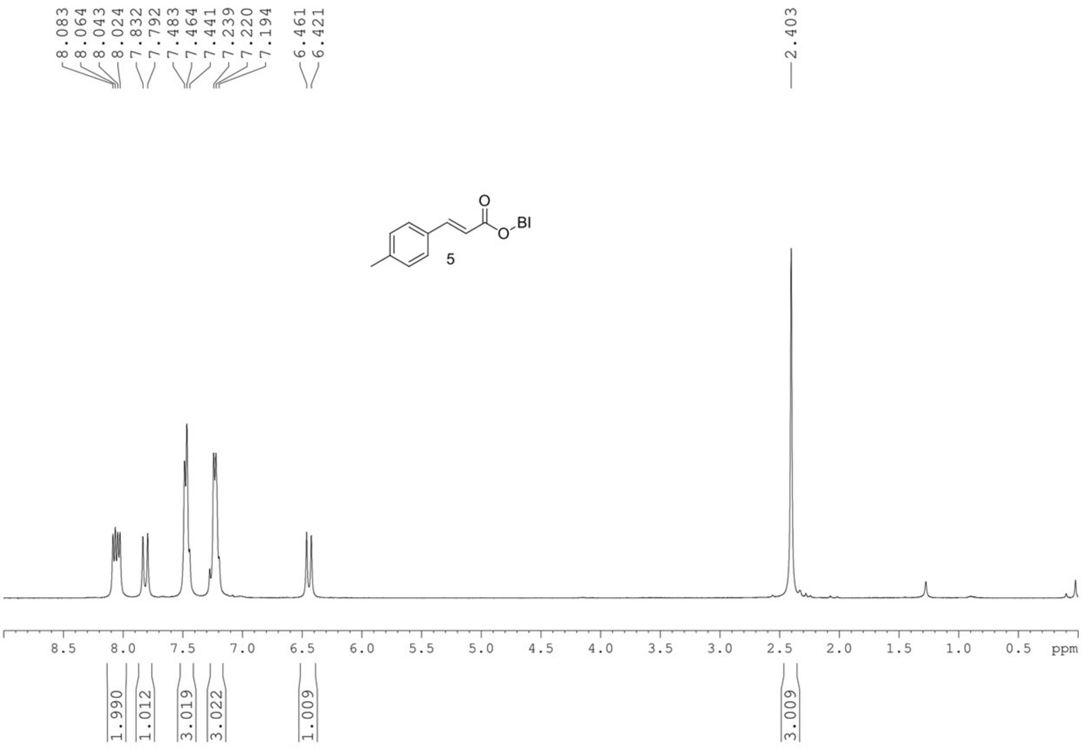
30
20
10
ppm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6.421
2.403
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O
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7.5
7.0
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6.0
5.5
5.0
4.5
4.0
3.5
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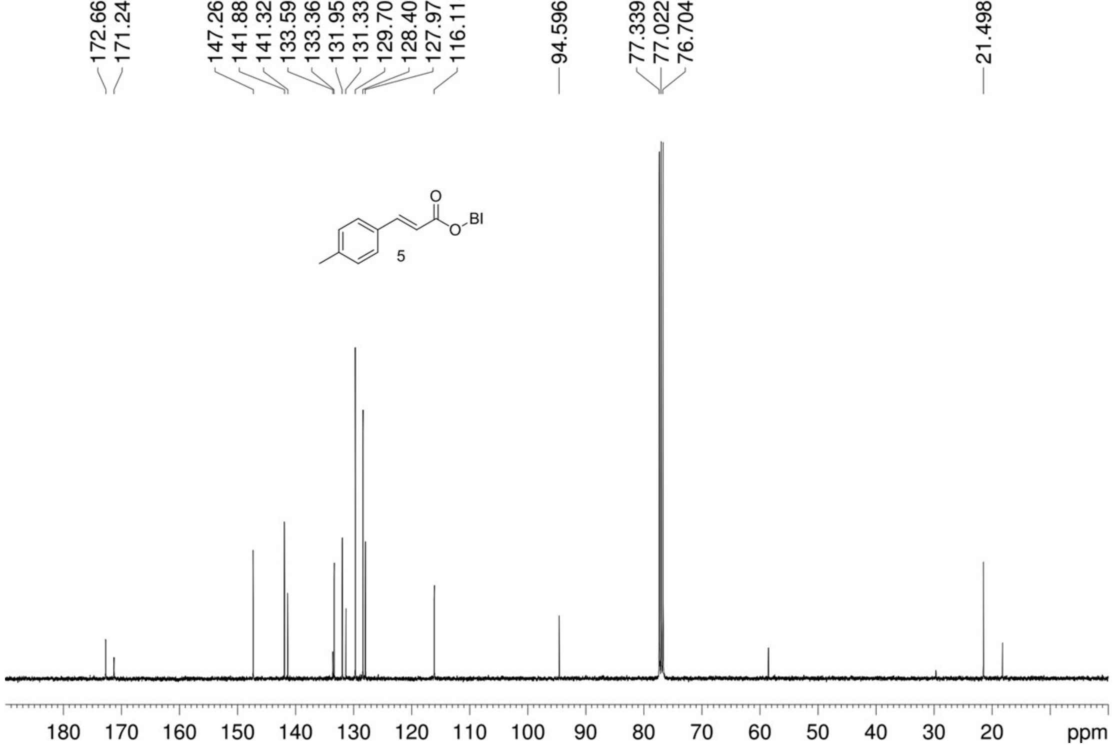
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94.596
77.339
77.022
76.704
21.498
O
O
BI
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180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm