Supporting Information

Copper(II)-Catalyzed Benzylic C(sp^3)-H Aerobic Oxidation of (Hetero)Aryl Acetimidates: Synthesis of Aryl α-Ketoesters

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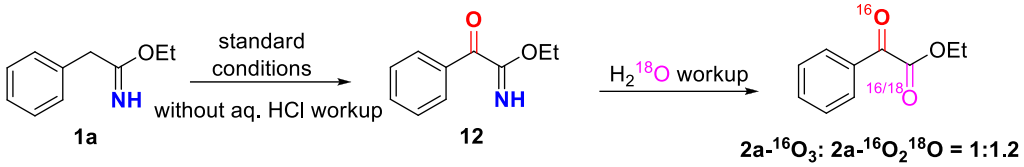
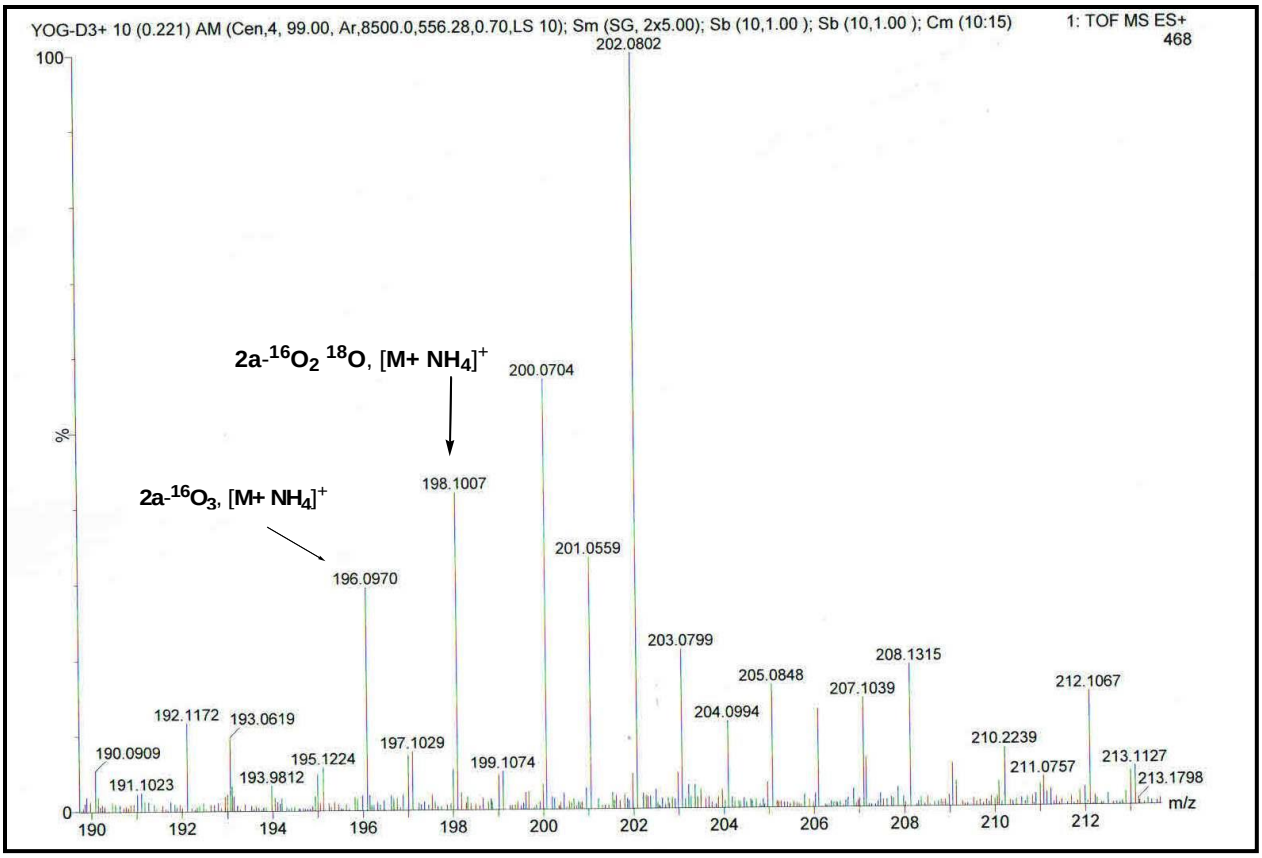
1. Control Experiments.

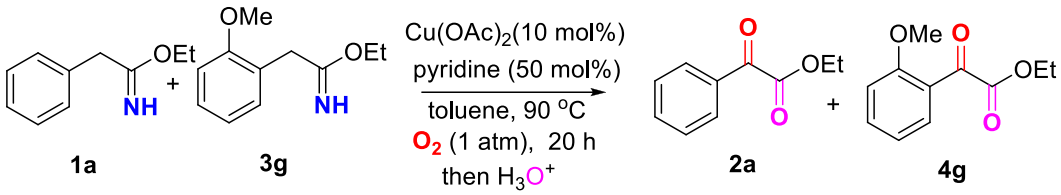
(A) ^{18}O labeling experiment with $H_2{}^{18}O$



Imidates **1a** (81 mg, 0.5 mmol) and **3g** (96 mg, 0.5 mmol), anhydrous $Cu(OAc)_2$ (0.05 mmol, 9.18 mg), pyridine (0.25 mmol, 20 μL) and anhydrous toluene (2.5 mL) were placed in a 25 mL round-bottom flask. The flask was sealed with a rubber septum and degassed and refilled with O_2 (3 times), the reaction flask was heated at 90 °C in a preheated oil bath for 20 hours under oxygen atmosphere. The reaction mixture was treated with 400 mol% $H_2{}^{18}O$ and stirred at room temperature for 2.0 hours, the ^{18}O labeling products were observed (2a-$^{16}O_3$:2a-$^{16}O_2{}^{18}O$ =1:1.2 by HMRS analysis)(Scheme 6d, of text). The HRMS value obtained at (m/z = 196.0970 and 198.1007) $[M+NH_4]^+$ clearly support that the one oxygen atom of ketoester originate from the water.



(B) Competition experiments.



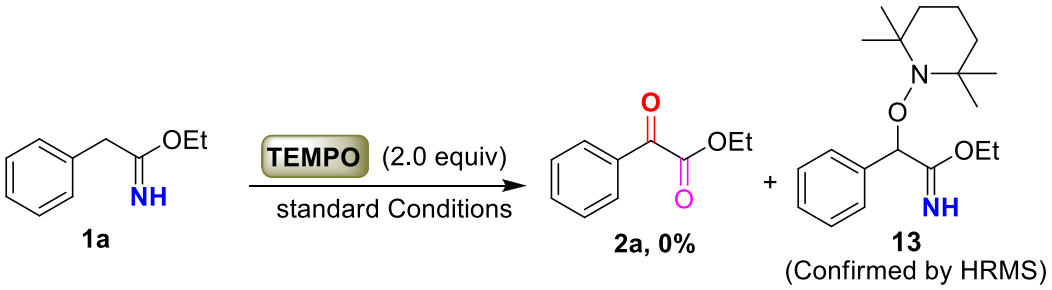
Imidates **1a** (81 mg, 0.5 mmol) and **3g** (96 mg, 0.5 mmol), anhydrous $Cu(OAc)_2$ (0.05 mmol, 9.18 mg), pyridine (0.25 mmol, 20 μL) and anhydrous toluene (2.5 mL) were placed in a 25 mL round-bottom flask. The flask was sealed with a rubber septum and degassed and refilled with O_2 (3 times). Then, the reaction flask was heated at 90 °C in a preheated oil bath for the different time intervals (5, 10, 15 and 20 hours). After the different time interval, the reaction mixture was treated with 10% HCl solution (10 mL) and stirred at room temperature for 30 min. The resulting

solution was extracted with ethyl acetate (10 mL × 3), and the combined organic layer was washed with brine solution (10 mL) and concentrated in *vacuo*. The crude residue was purified using silica gel column chromatography with hexanes and EtOAc (98:02) as the eluent to afford the corresponding product and the ratio of the products are given in the table.

Table S1. Competition experiments in different time interval.

Entry	Reaction time (hours)	Yield (%)		Ratio of products
		2a	**4g**	**2a**:**4g**
1	5	11	18	1:1.6
2	10	20	28	1:1.4
3	15	25	34	1:1.4
4	20	31	46	1:1.5

(C) Experimental procedure for radical capture experiment with TEMPO.



Imidates (0.5 mmol), anhydrous $Cu(OAc)_2$ (0.05 mmol, 9.18 mg), pyridine (0.25 mmol, 20 μL), radical scavenger (2,2,6,6-tetramethyl-1-piperidin-1-yl)oxyl (TEMPO) (1.00 mmol, 2.0 equiv) and anhydrous toluene (2.5 mL) were placed in a 25 mL round bottom flask. The reaction flask was sealed with the rubber septum and degassed and refilled with O_2 (3 times). The reaction flask was allowed to heat at 90 ^{o}C in the preheated oil bath for 20 h. Upon completion of the

reaction (monitored by TLC), no product formation and observed a new spot on TLC, which correspond to a TEMPO-benzylimidate adduct **13.** This was confirmed by performing HRMS analysis of crude reaction mixture. The appearance of a peak at 319.2398 $[M+H]^+$ correspond to TEMPO-benzylimidate adduct.

Display Report

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Comment			

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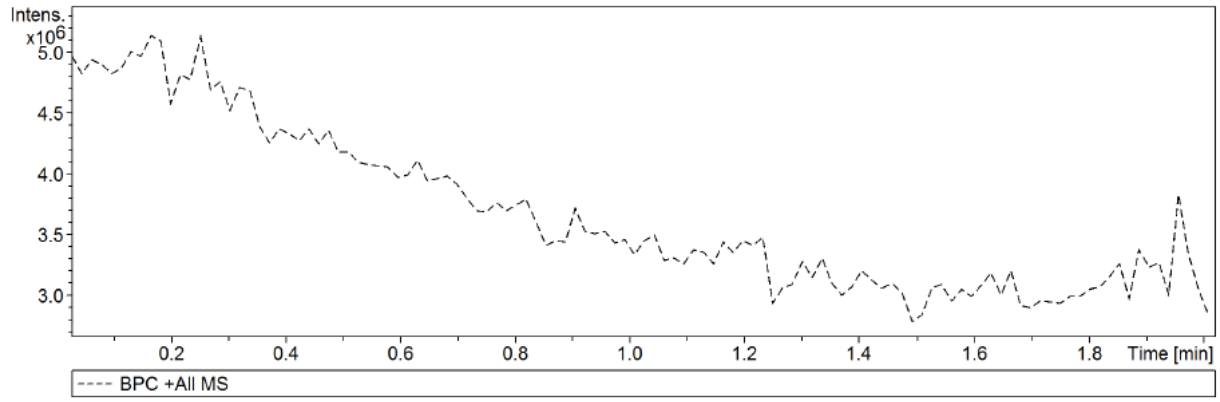
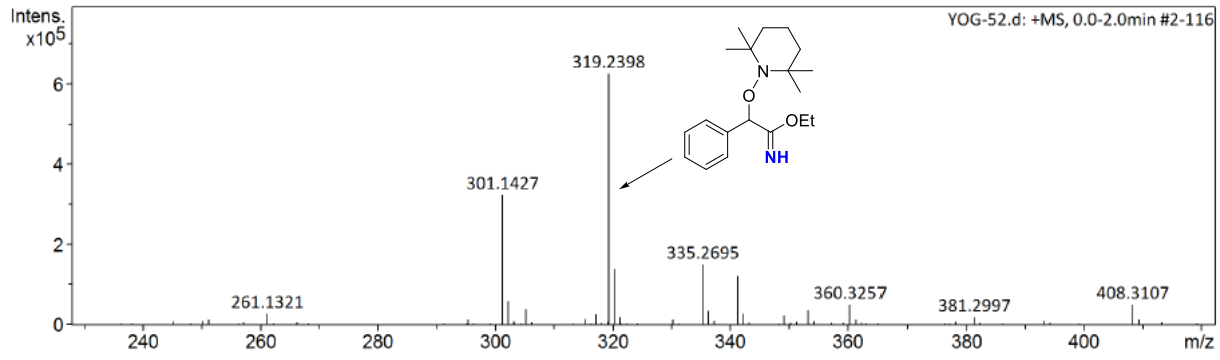
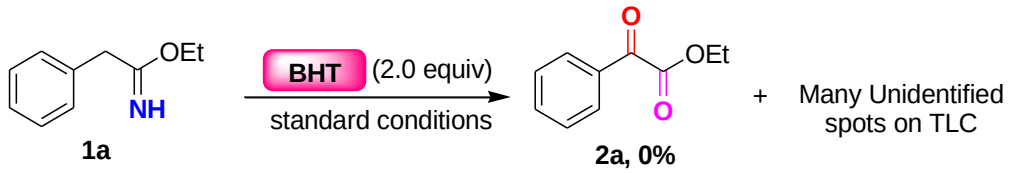




(D) Experimental procedure for the reaction with BHT.



Imidates (0.5 mmol), anhydrous $Cu(OAc)_2$ (0.05 mmol, 9.18 mg), anhydrous pyridine (0.25 mmol, 20 μL), 2,6-di-*tert*-butyl-4-methylphenol (BHT) (1.00 mmol, 2.0 equiv) and anhydrous toluene (2.5 mL) were placed in a 25 mL round bottom flask. The reaction flask was sealed with the rubber septum and degassed and refilled with O_2 (3 times) and the reaction mixture was allowed to heat at 90 ^oC in the preheated oil bath for 20 h under oxygen atmosphere. Many unidentified spots were observed *via* TLC analysis, which was inseparable through the column chromatography.

(E) EPR analysis.

The aliquot from the reaction mixture was subjected to EPR experiments [**1a**, Cu (II), O_2 balloon (1atm)] and EPR spectra recorded (Fig S1). Then in aliquot of reaction mixture, DMPO was added and EPR spectra recorded. The EPR signal corresponding to DMPO-superoxide adduct was identified (Fig S2). The calculated hyperfine splitting are g_0 (2.0037), α^H(15.0 G), and α^N (14.4 G). These results indicate that superoxide adduct **B**, which could be combined with DMPO (Fig S2). Interestingly, the above EPR signal (DMPO-superoxide adducts) was disappeared with

the addition of superoxide dismutase (SOD) at room temperature (Fig S3). These results (Fig S1, S2 & Fig S3) clearly support that this transformation must have proceeded via a radical pathway.

Table S2. The EPR Experiments in different reaction conditions.

entry	Reaction condition	DMPO signals	Figure No.
1	Standard condition	none	S1
2	Standard condition+ DMPO	DMPO-(OH) signal appear	S2
3	Standard condition + SOD + DMPO	none	S3

EPR Spectra of the reaction mixture (1a, [Cu], O_2)

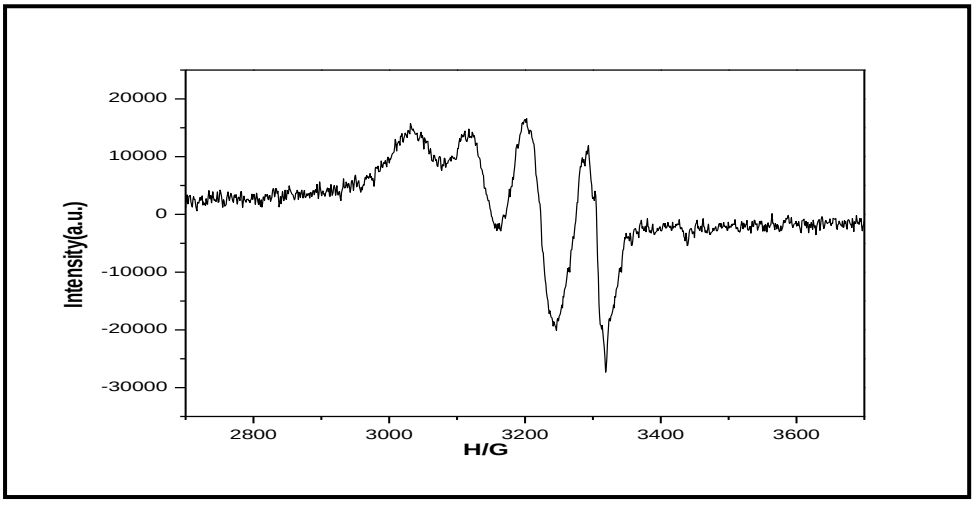


Figure S1. EPR spectra (X band, 9.4 GHz, 25 ^oC) of the reaction mixture: Benzylimidate (**1a**) (82 mg, 0.5 mmol), $Cu(OAc)_2$ (9.18 mg, 0.05 mmol) in toluene (2.5 mL) under O_2 balloon (1 atm). The reaction mixture was stirred at 90 ^oC for 1 h. 0.02 mL of this reaction mixture was taken out in a small tube at 25 ^oC. The reaction mixture was analysed by EPR at 25 ^oC.

EPR Spectra of the reaction mixture (1a, [Cu], O_2) + DMPO

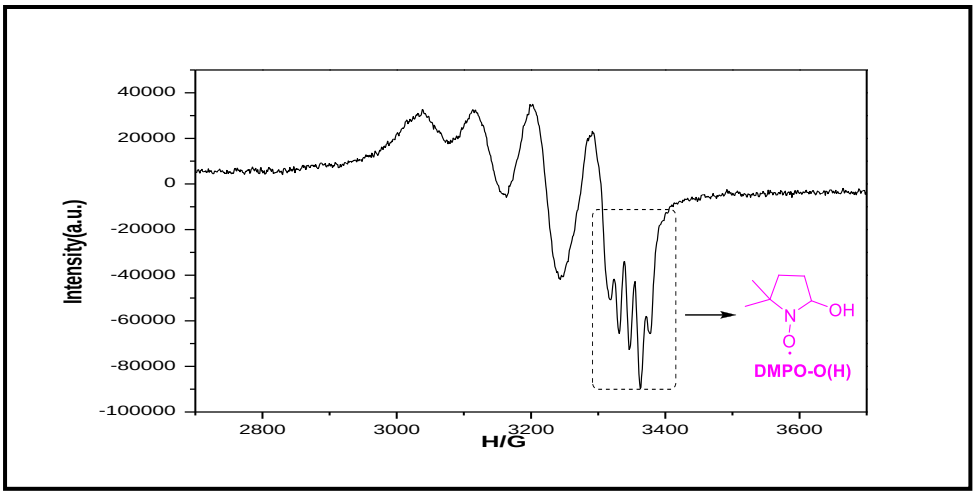


Figure S2. EPR spectra (X band, 9.4 GHz, 25 ^{o}C) of the reaction mixture: Benzylimidate (**1a**) (82.0 mg, 0.5 mmol), $Cu(OAc)_2$ (9.18 mg, 0.05 mmol) in toluene (2.5 mL) under O_2 balloon (1 atm). The reaction mixture was stirred at 90 ^{o}C for 1 h. 0.02 mL of this reaction mixture was taken out in a small tube, followed by the addition of 0.01 mL DMPO (5×10^{-2}M) at 25 ^{o}C. The reaction mixture was analysed by EPR. There are 4 classical peaks, which are corresponding to the signals [DMPO-O(H)]. The calculated hyperfine splitting are g_0 (2.0037), α^H (15.0 G).

EPR Spectra of the reaction mixture (1a, [Cu], O_2) + SOD+ DMPO

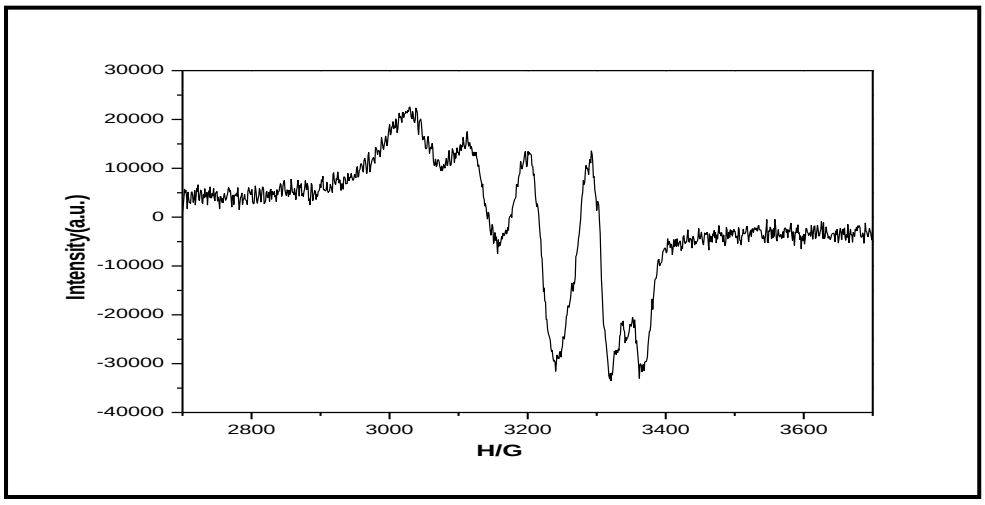


Figure S3. EPR spectra (X band, 9.4 GHz, 25 ^{o}C) of the reaction mixture: Benzylimidate (**1a**) (82 mg, 0.5 mmol), $Cu(OAc)_2$ (9.18 mg, 0.05 mmol) in toluene (2.5 mL) under O_2 balloon (1 atm). The reaction mixture was stirred at 90 ^{o}C for 1 h. 0.02 mL of this reaction mixture was taken out in a small tube, mixed well with 0.01 mL SOD solvent (5×10^{-2}M) at 25 ^{o}C, followed by the addition of 0.01 mL DMPO (5×10^{-2}M). The reaction mixture was analysed by EPR at 25 ^{o}C.

(F) Detection of intermediates using TLC and HRMS analysis:

Display Report

Analysis Info

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Acquisition Parameter

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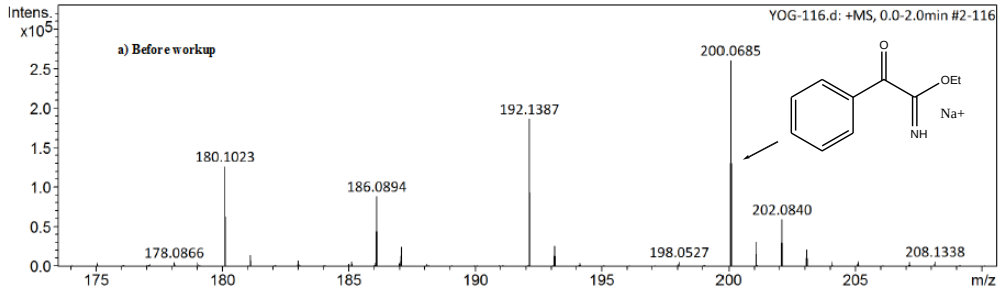
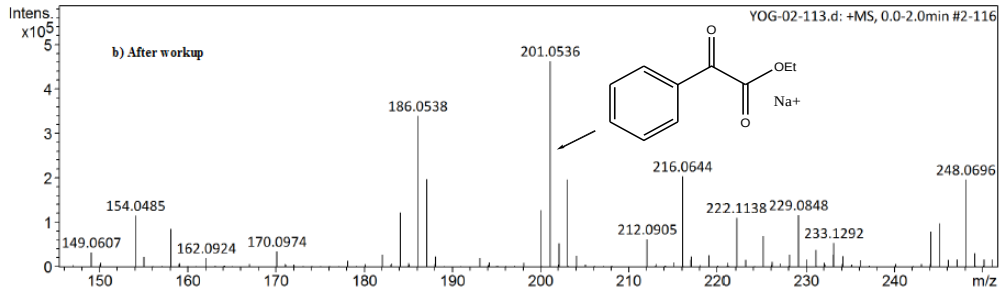
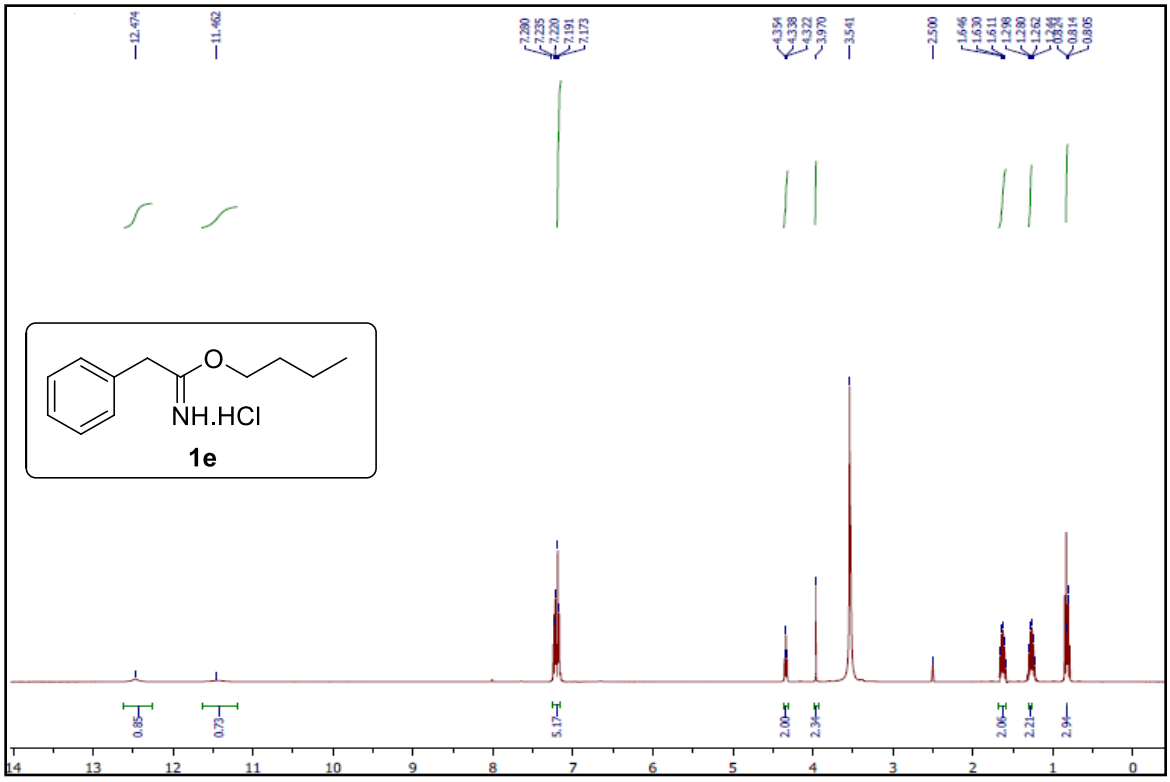
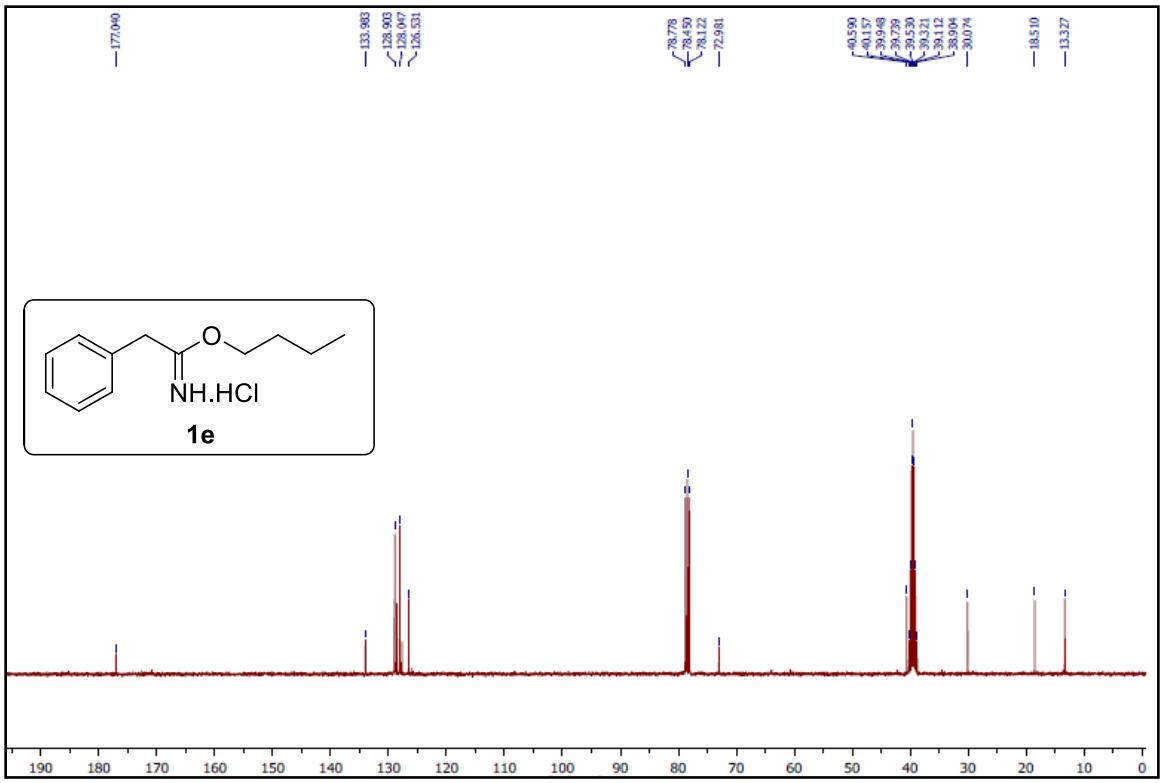
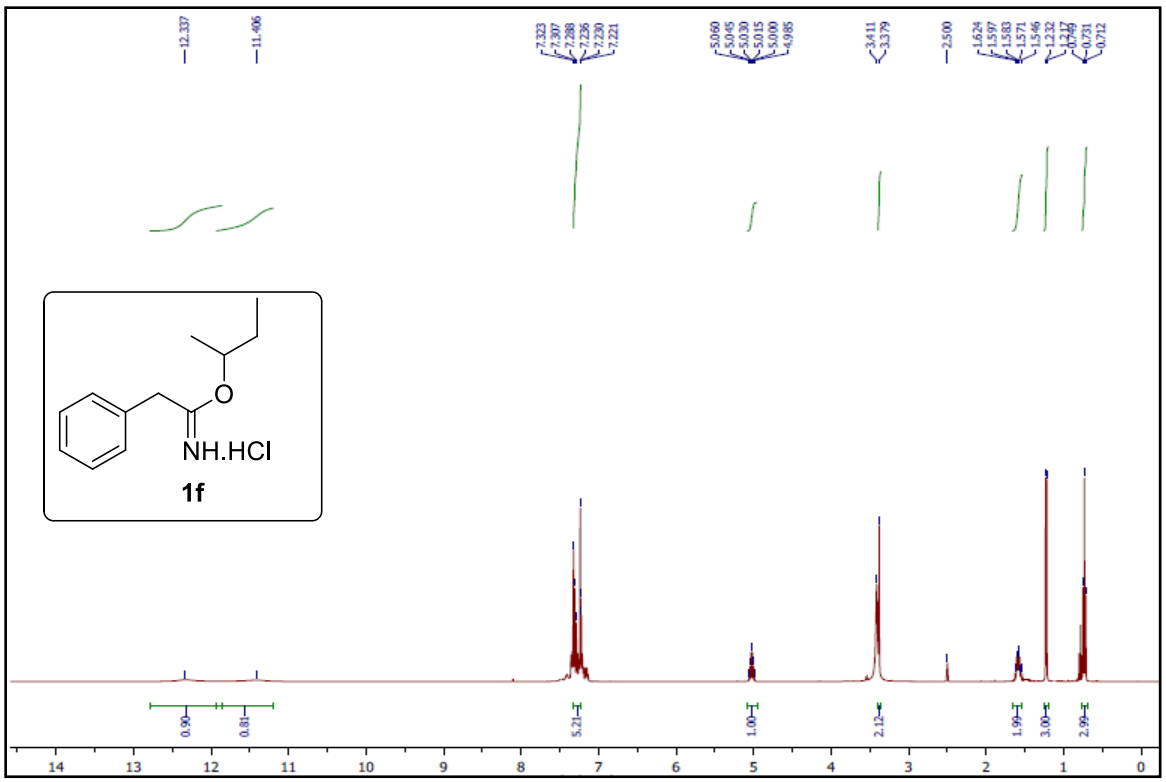




2 (A). Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of starting material.



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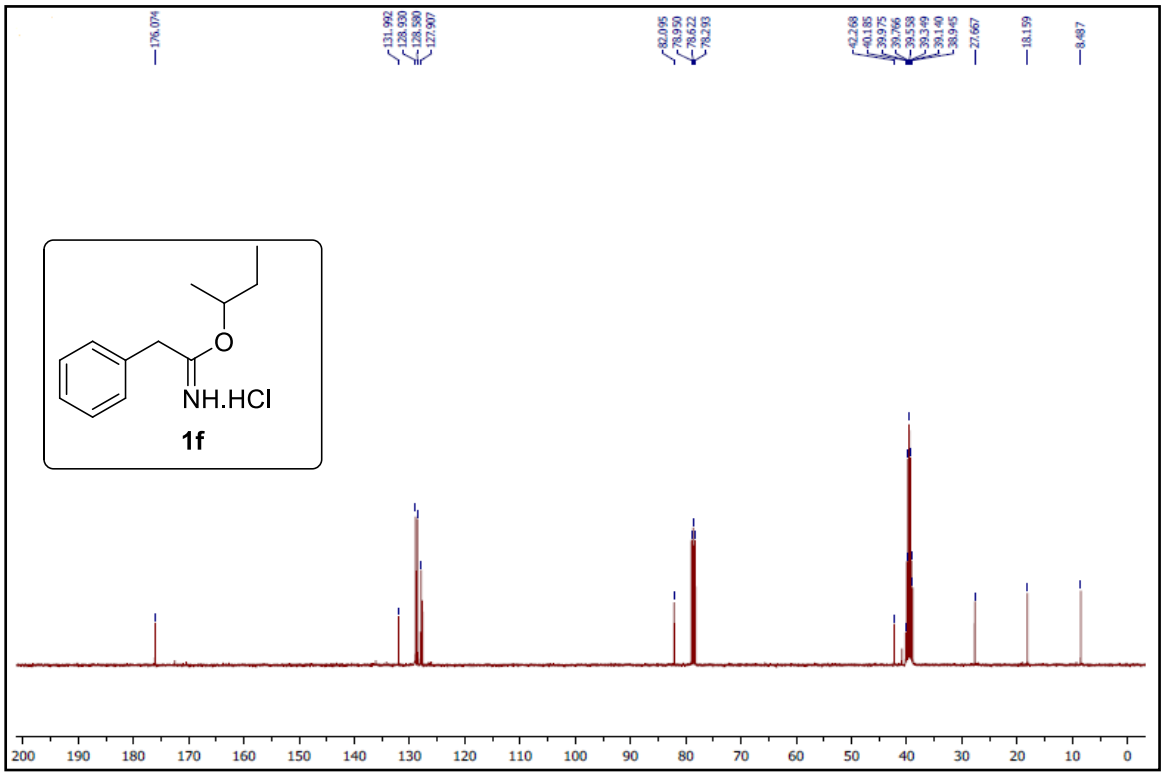
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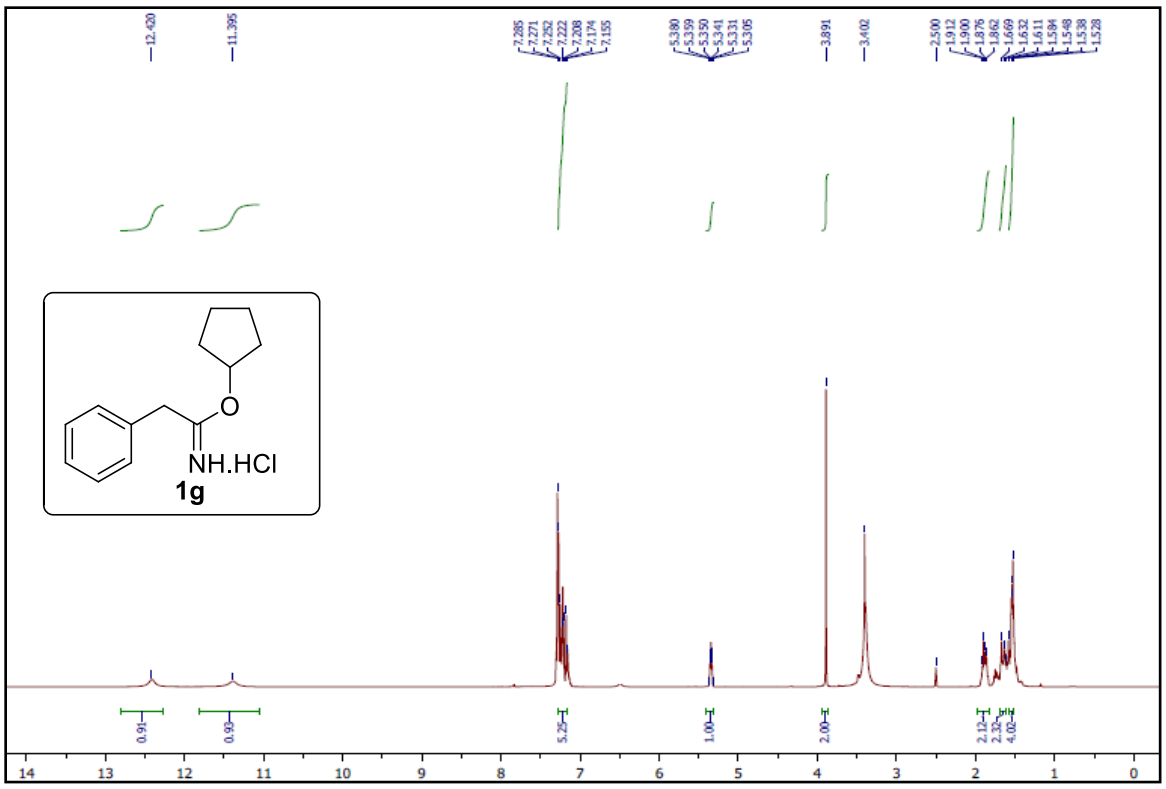
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5.331
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1.528
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2.00
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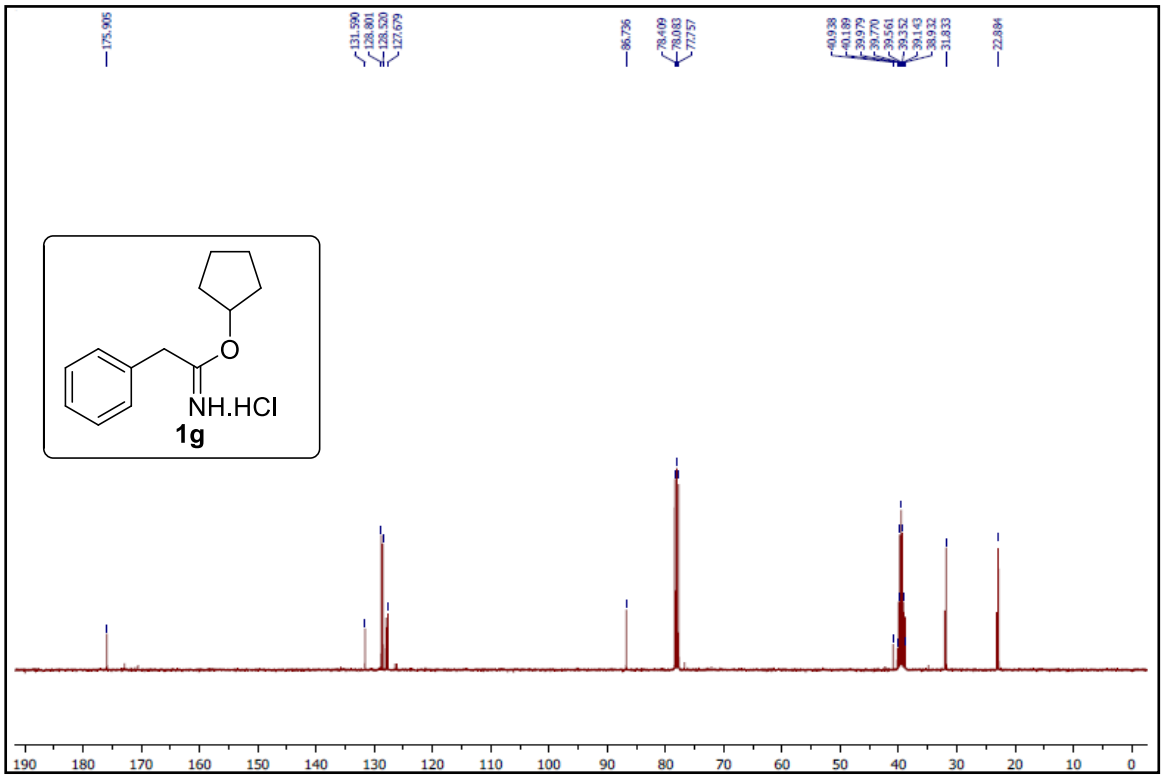
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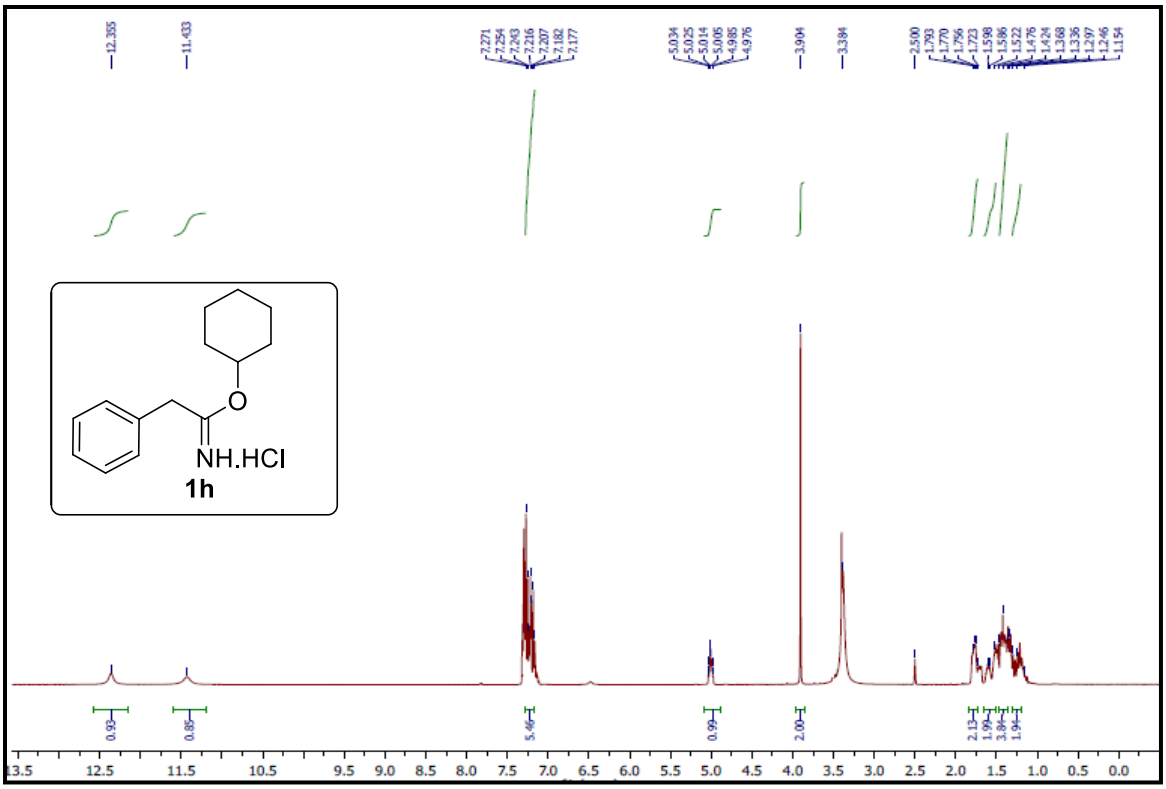
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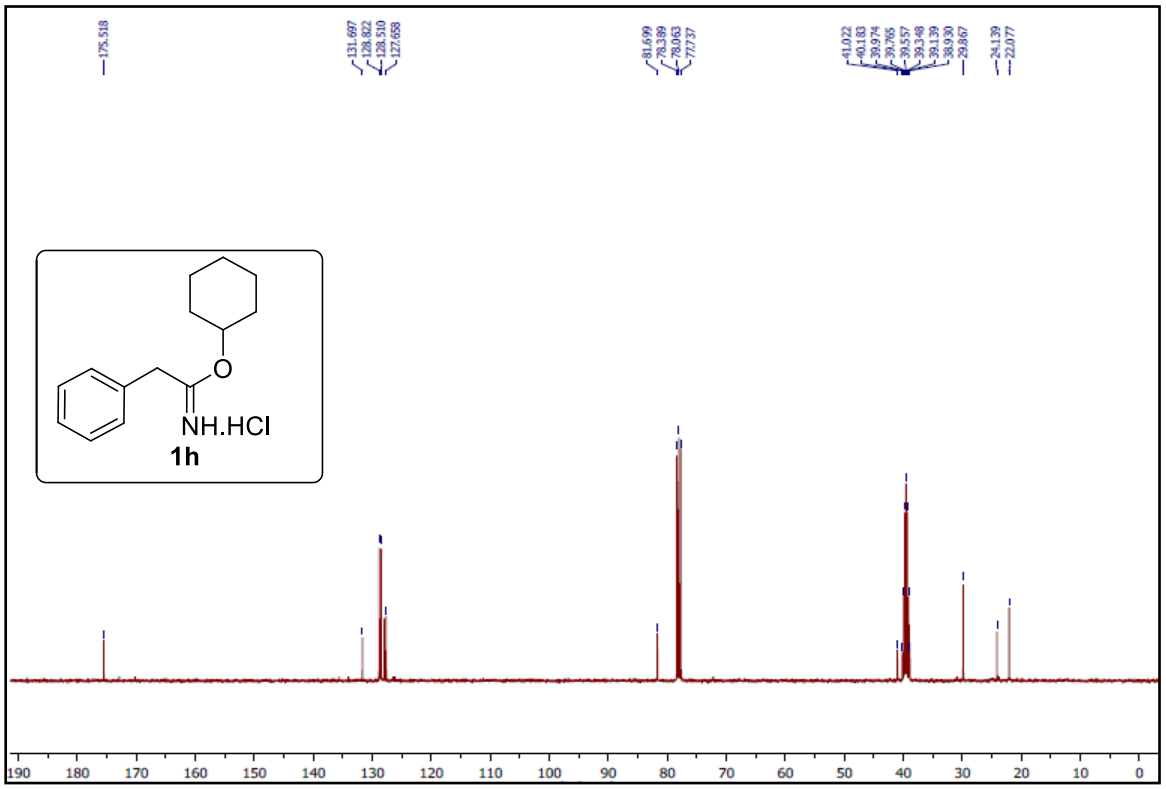
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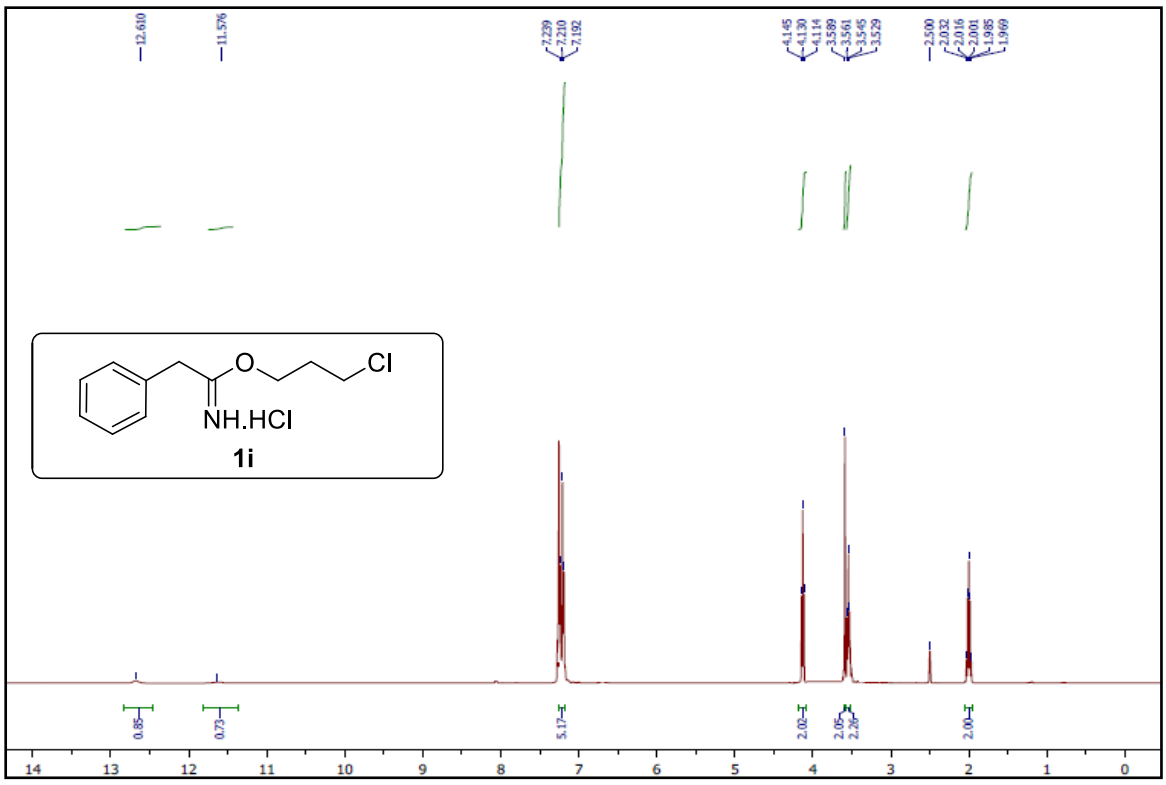
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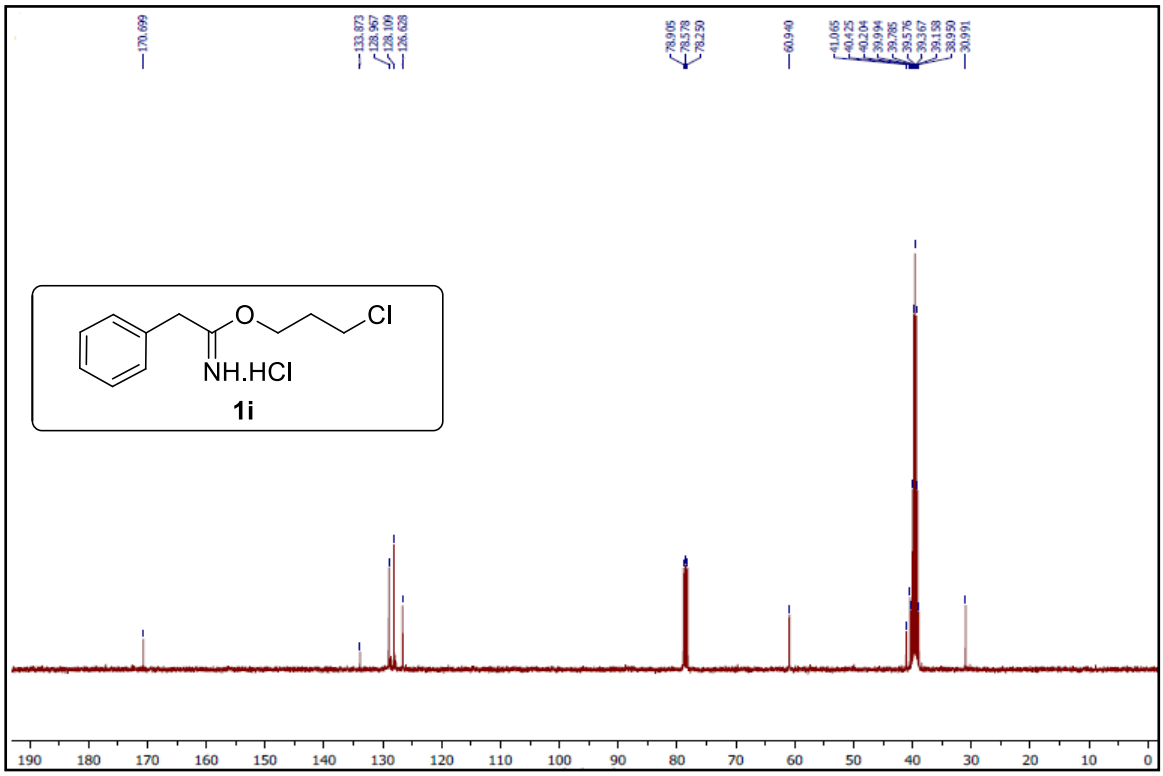
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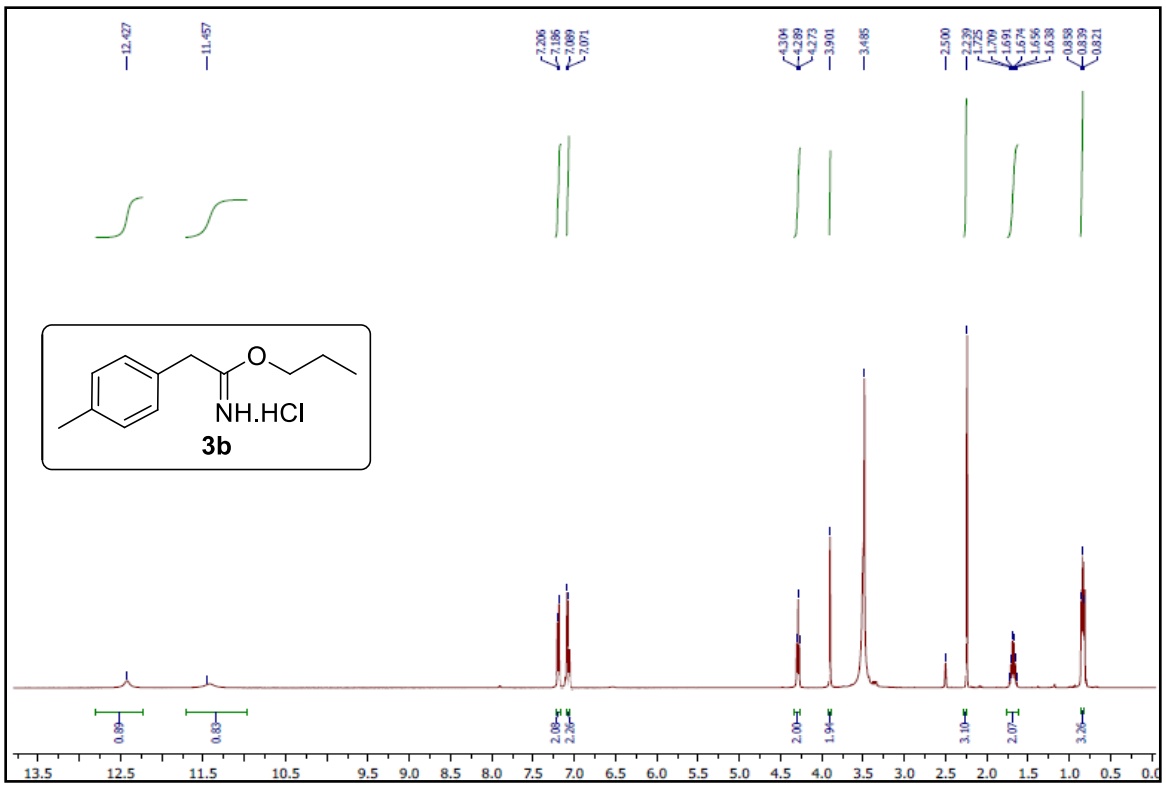
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1.656
1.638
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2.00
1.94
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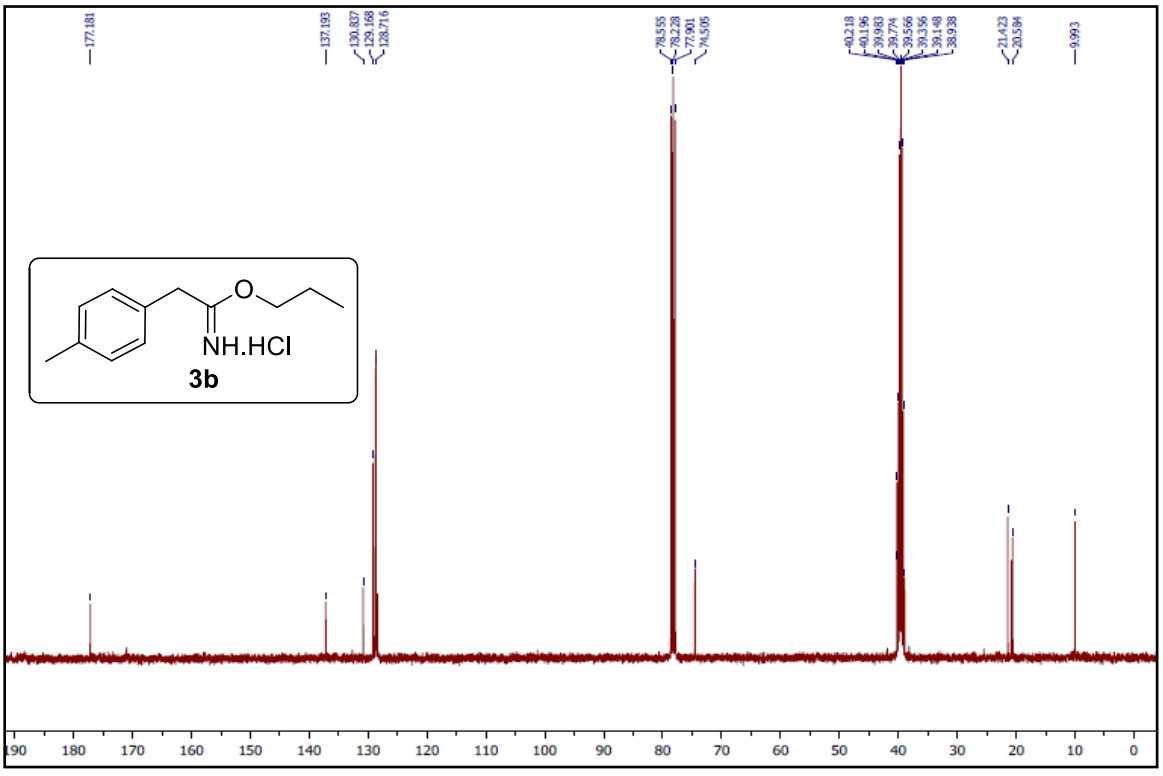
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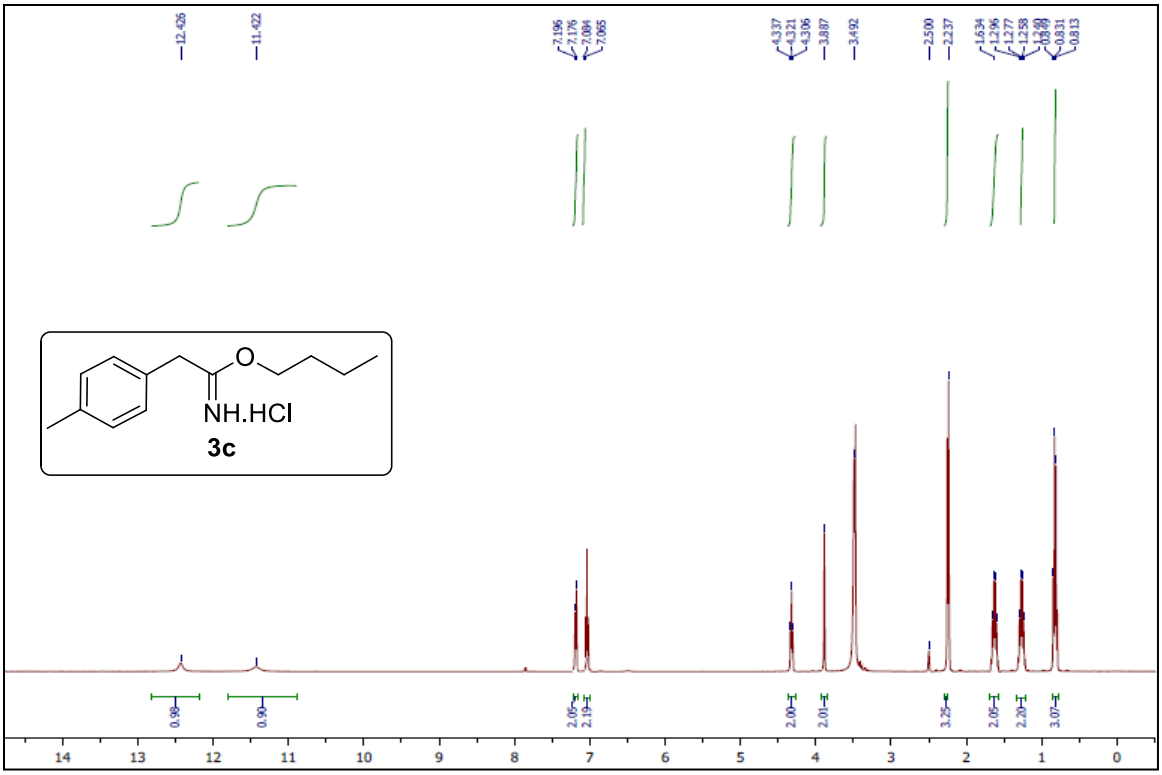
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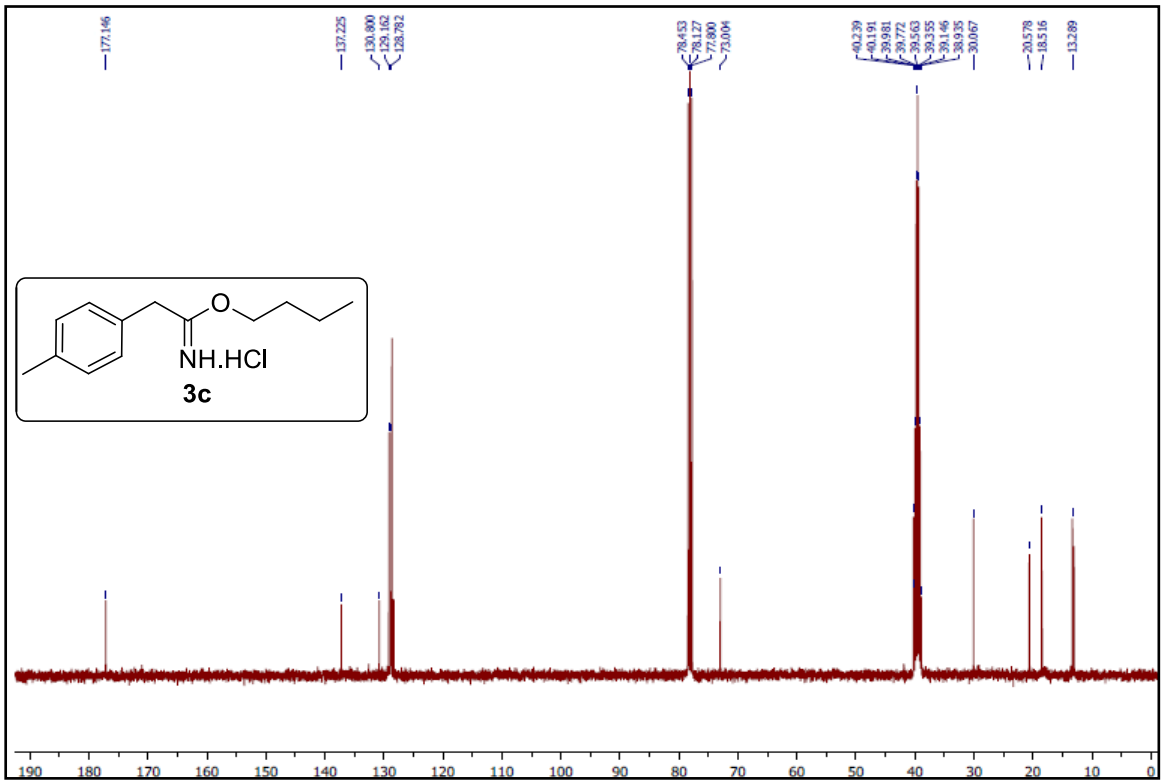
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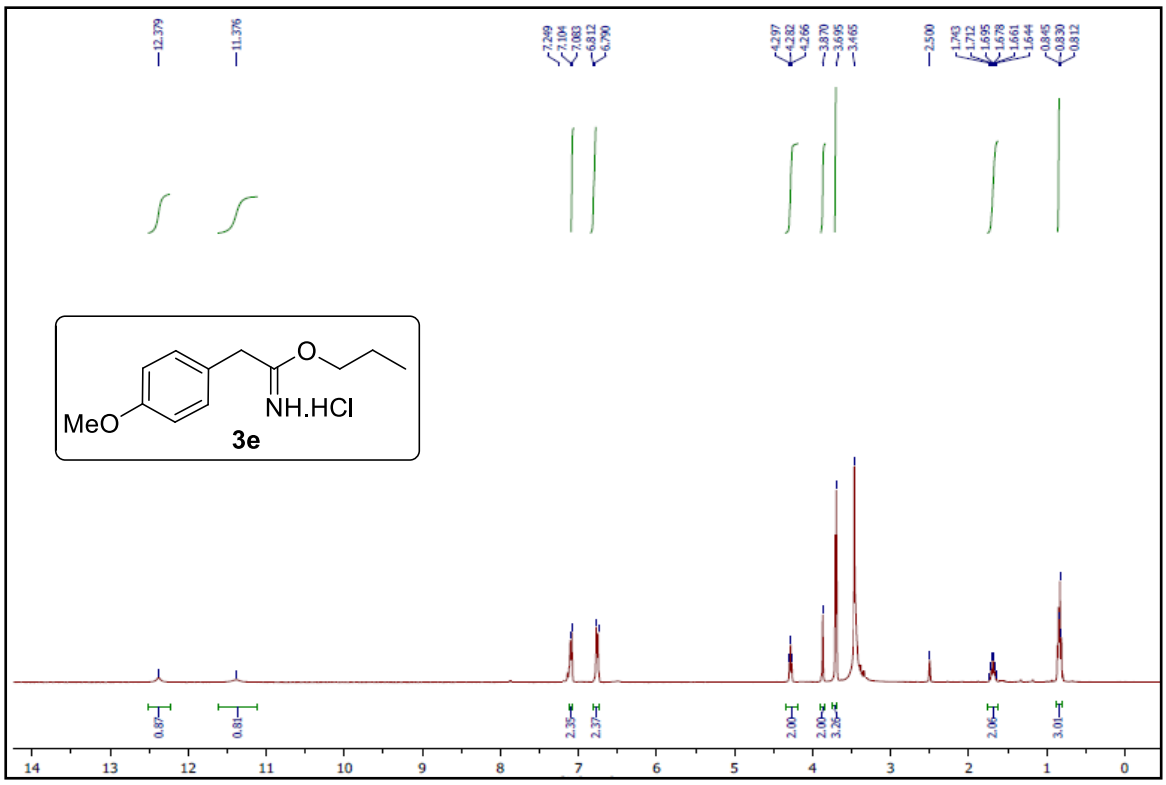
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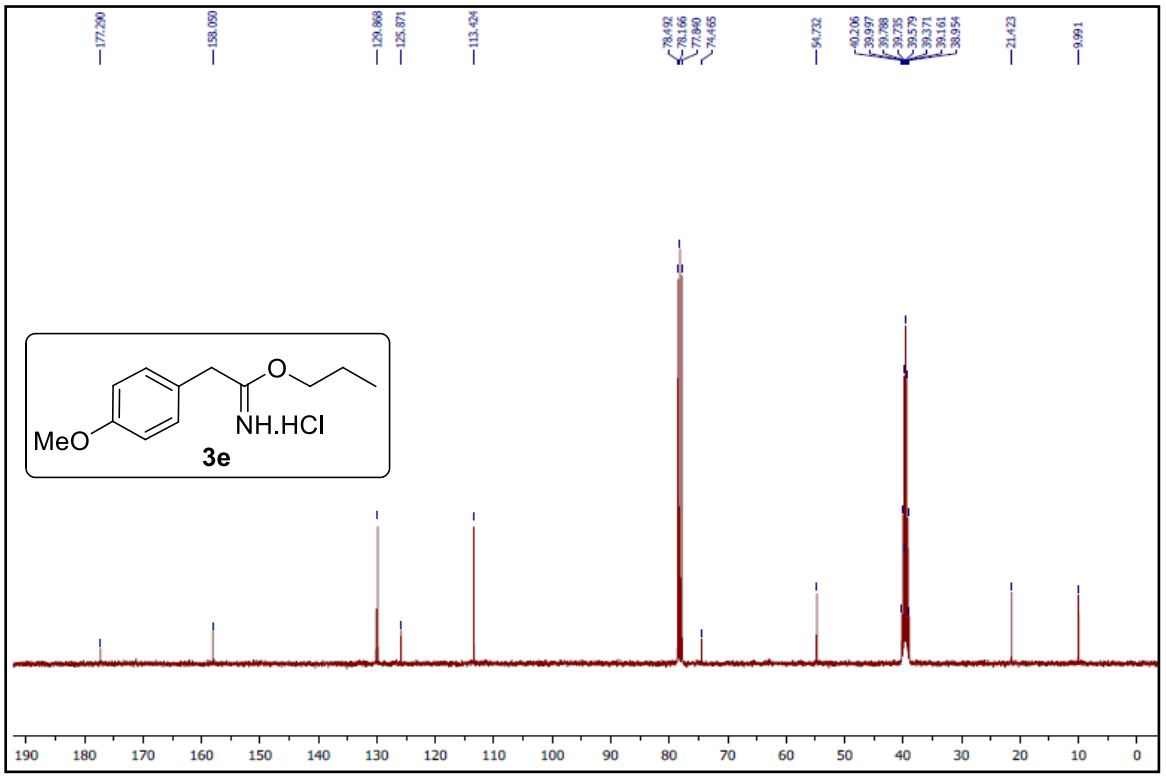
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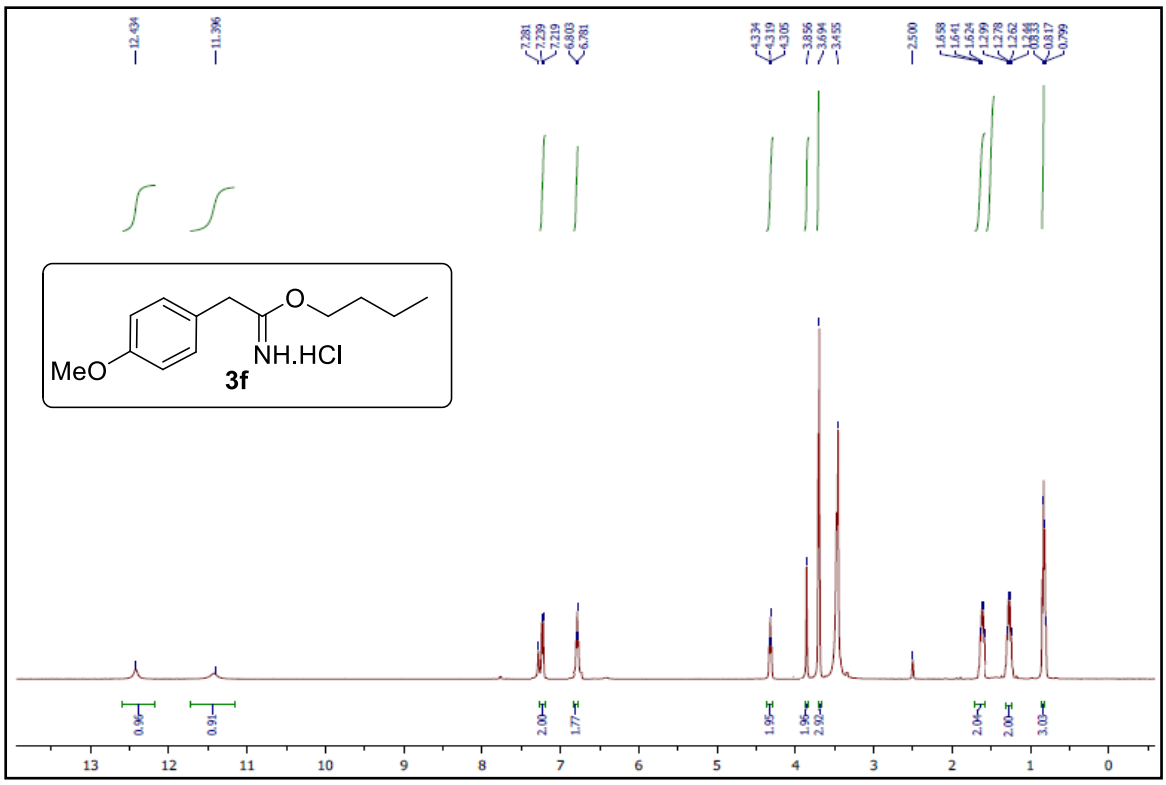
NH.HCl
3e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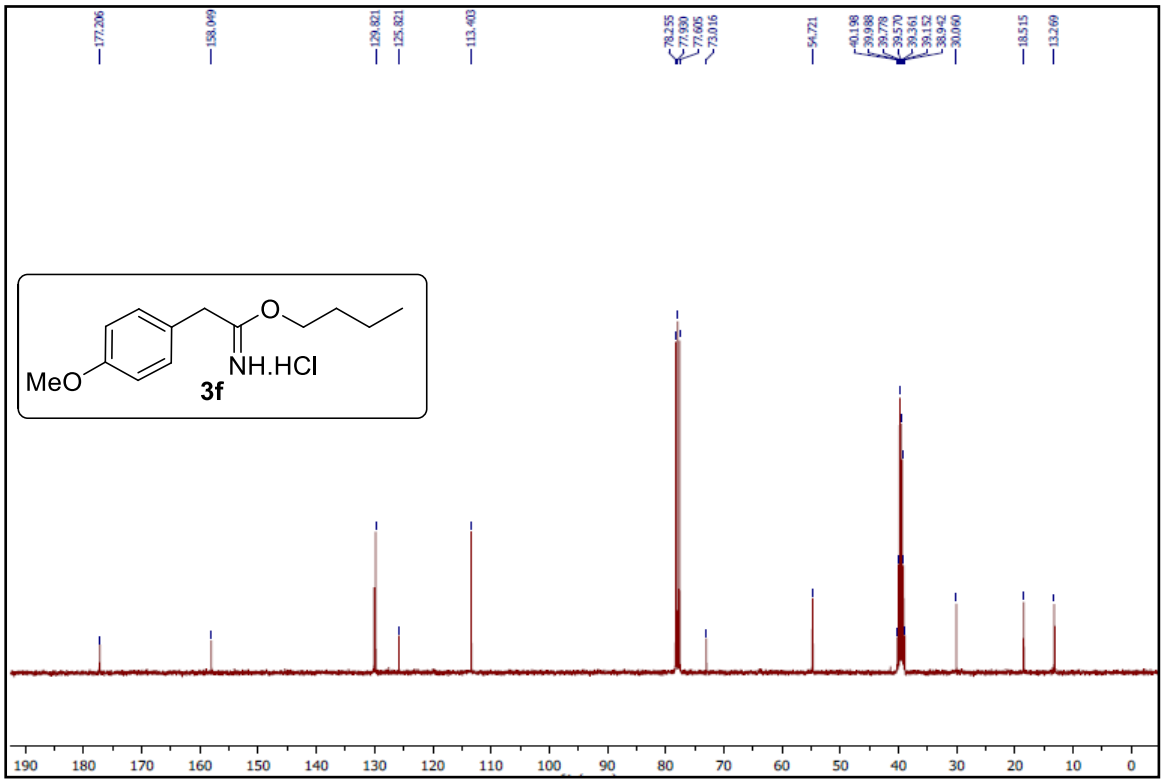
O
NH.HCl
3f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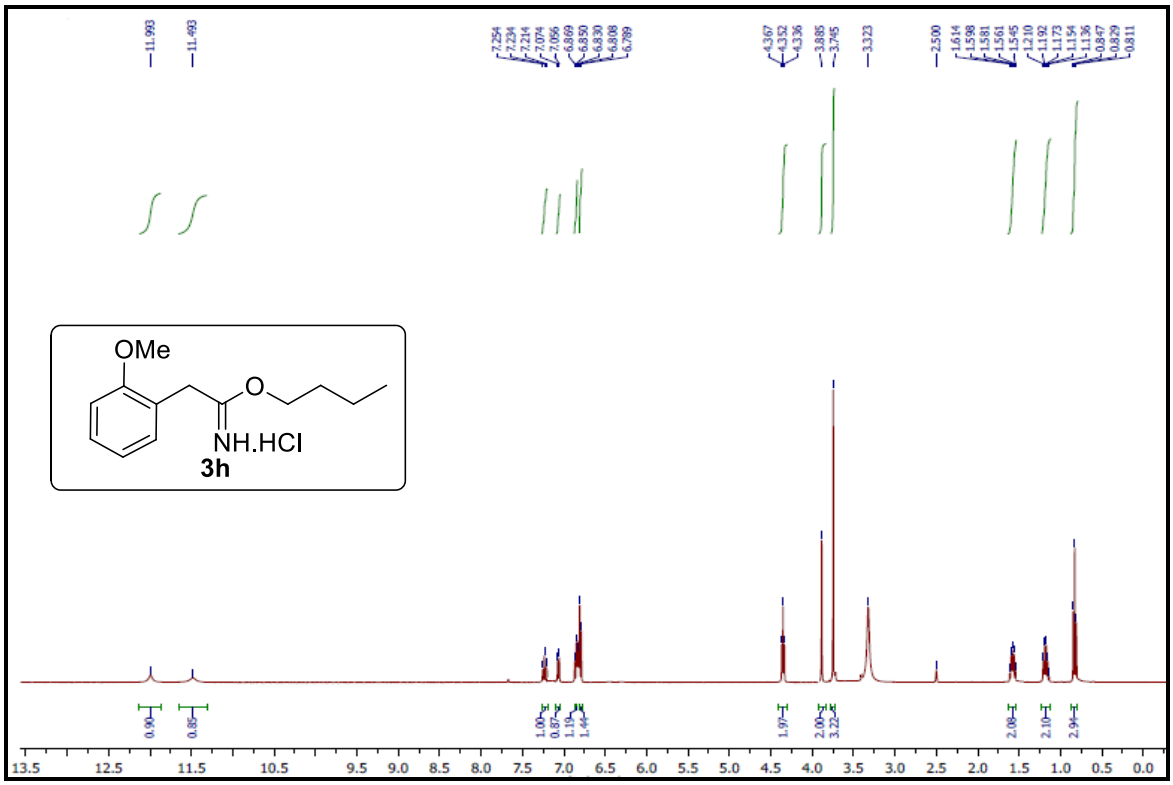
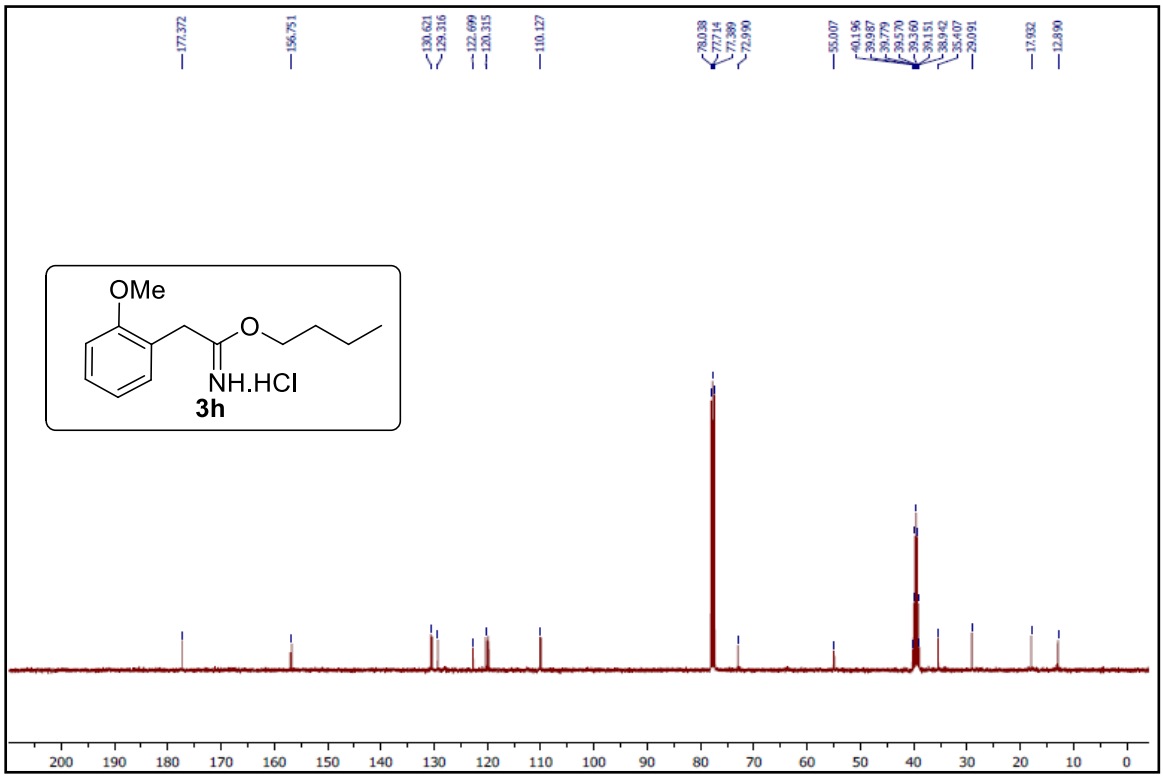
O
NH.HCl
3f


OMe
O
NH.HCl
3h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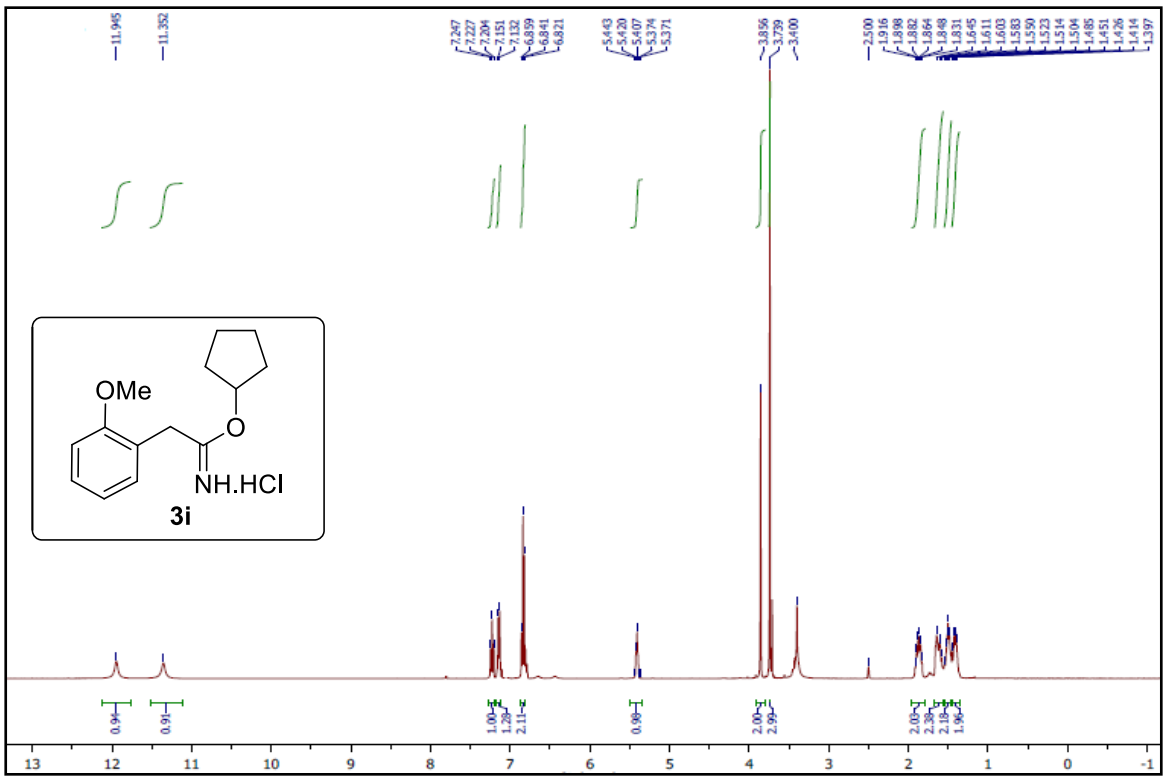
O
NH.HCl
3h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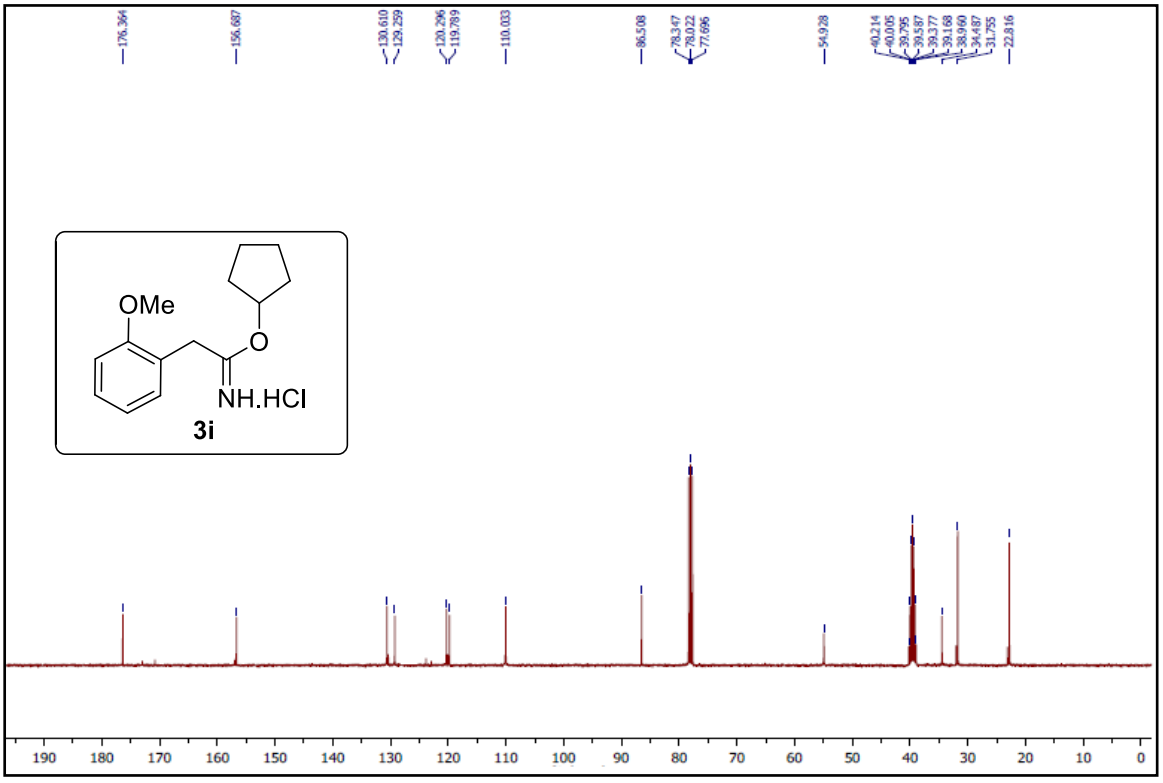
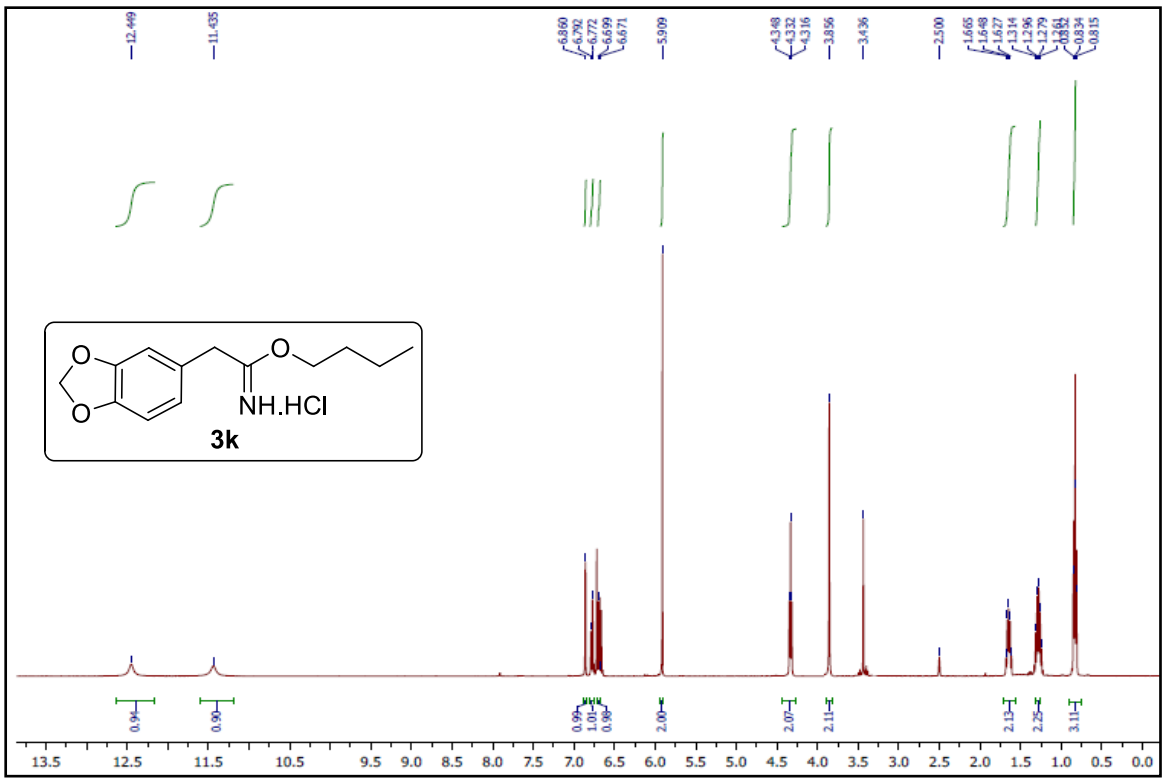
O
NH.HCl
3i


OMe
O
NH.HCl
3i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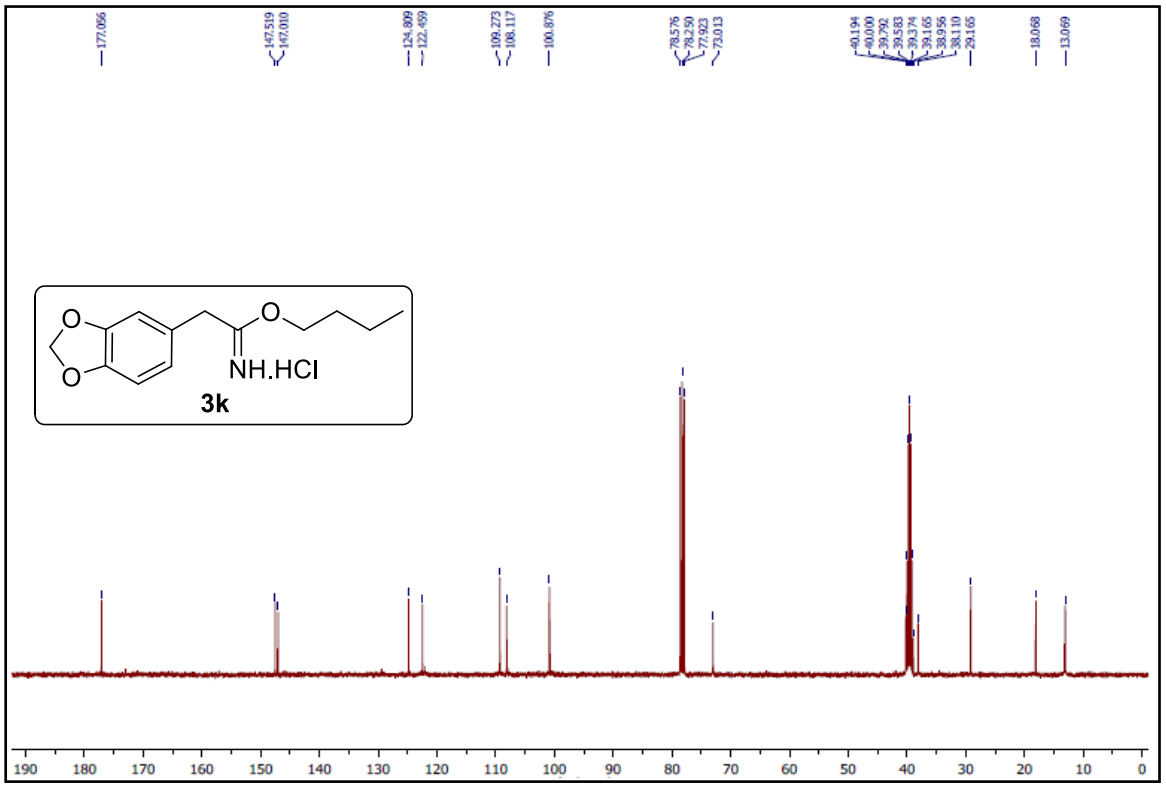
6.772
6.699
6.671
5.909
4.348
4.332
4.316
3.856
3.436
2.500
1.665
1.648
1.627
1.314
1.296
1.279
0.834
0.815
NH.HCl
3k


177.066
147.519
147.010
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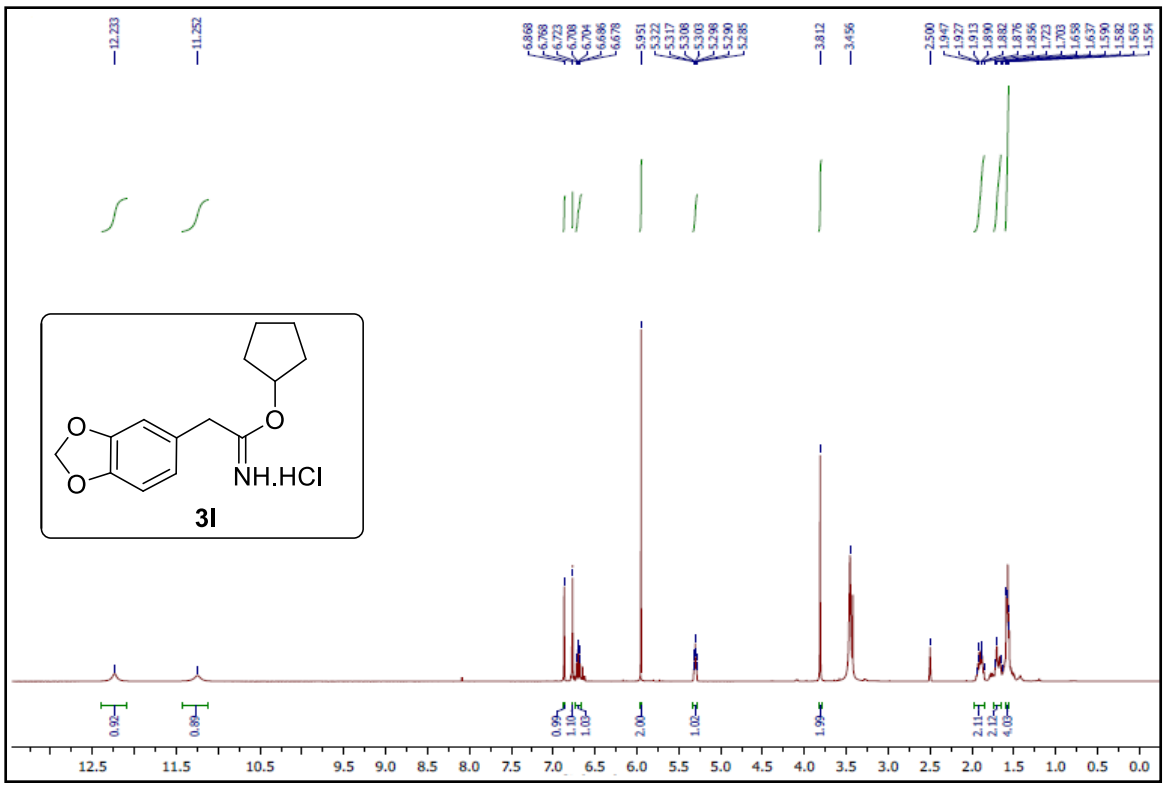
122.459
109.273
108.117
100.876
78.576
78.250
77.923
73.013
60.194
60.000
39.792
39.583
39.374
39.165
38.956
38.110
29.165
18.068
13.069
NH.HCl
3k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11.252
6.868
6.768
6.723
6.708
6.704
6.686
6.678
5.951
5.322
5.317
5.308
5.303
5.298
5.290
5.285
3.812
3.456
2.500
1.947
1.927
1.913
1.890
1.882
1.876
1.856
1.723
1.703
1.658
1.637
1.590
1.582
1.563
1.554
O
O
O
NH.HCl
3l
0.92
0.89
0.99
1.10
1.02
2.00
1.02
1.99
2.11
2.12
4.03
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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2.0
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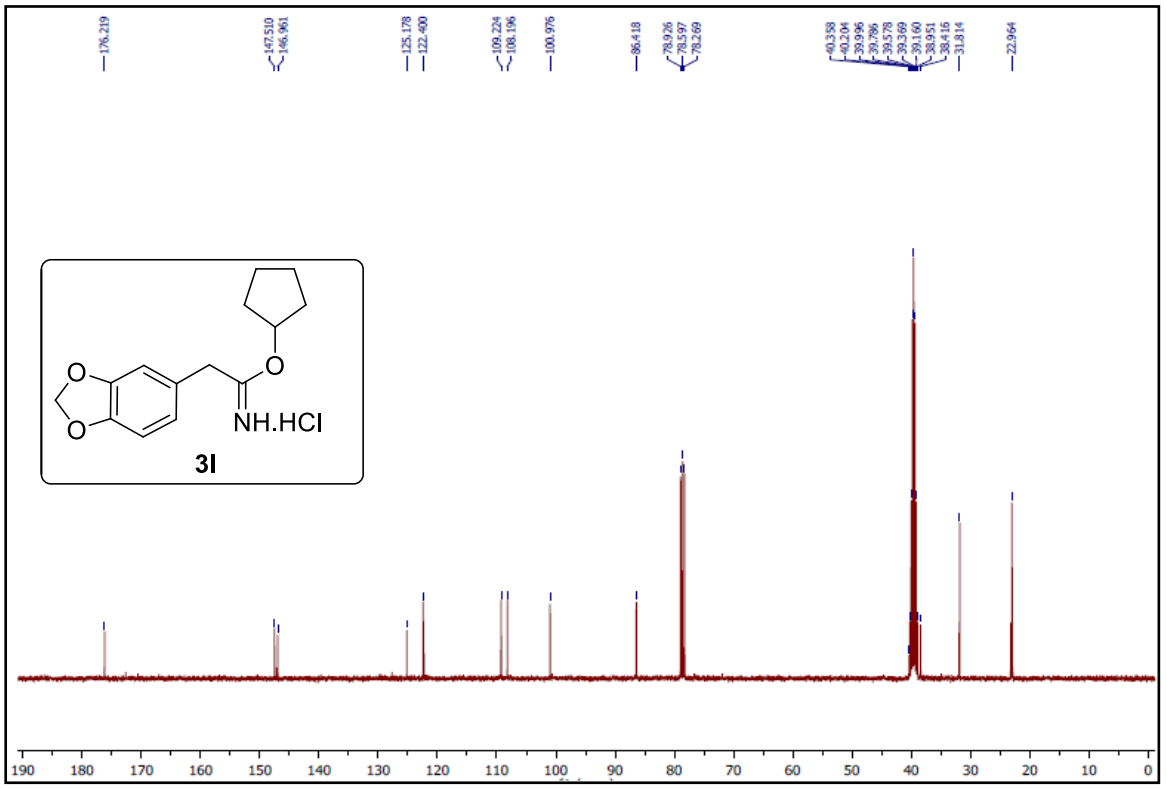
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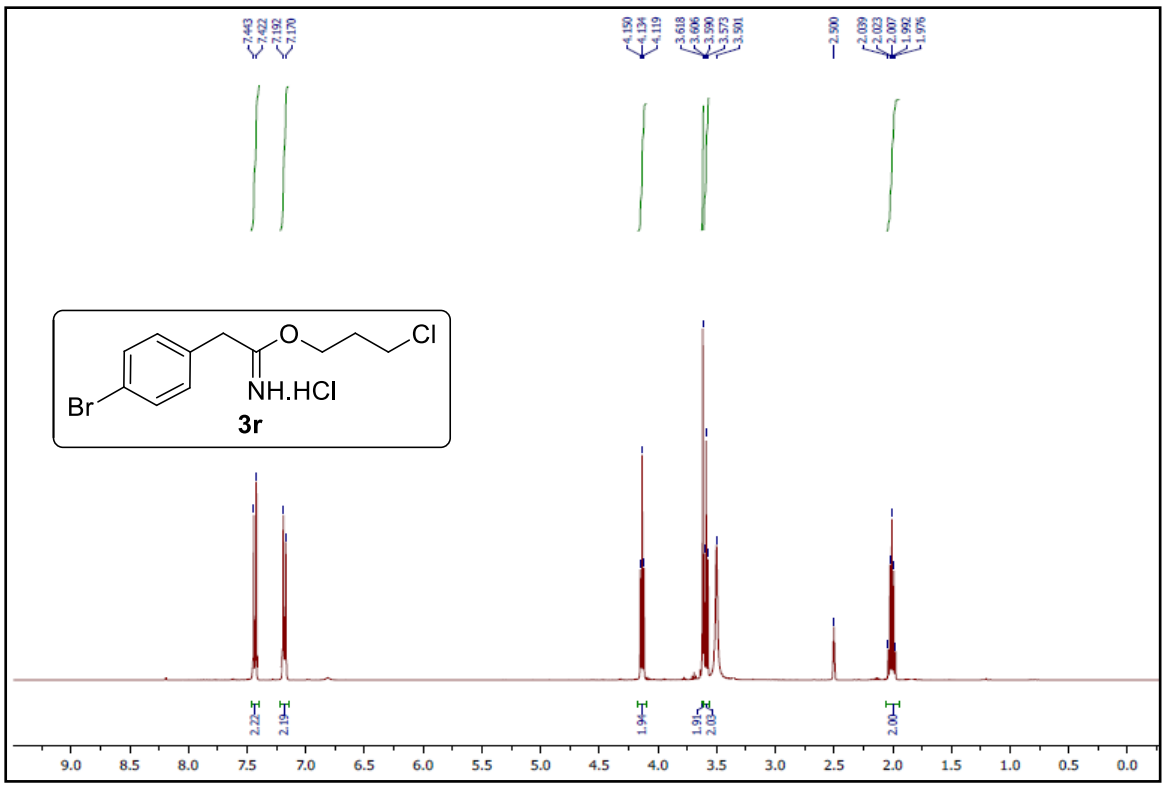
146.961
125.178
122.400
109.224
108.196
100.976
86.418
78.926
78.597
78.269
40.358
40.204
39.996
39.786
39.578
39.369
39.160
38.951
38.416
31.814
22.964
O
O
O
NH.HCl
3l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.443
7.422
7.192
7.170
4.150
4.134
4.119
3.618
3.606
3.590
3.573
3.501
2.500
2.039
2.023
2.007
1.992
1.976
O
Cl
NH.HCl
Br
3r
2.22
2.19
1.94
1.91
2.02
2.00
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
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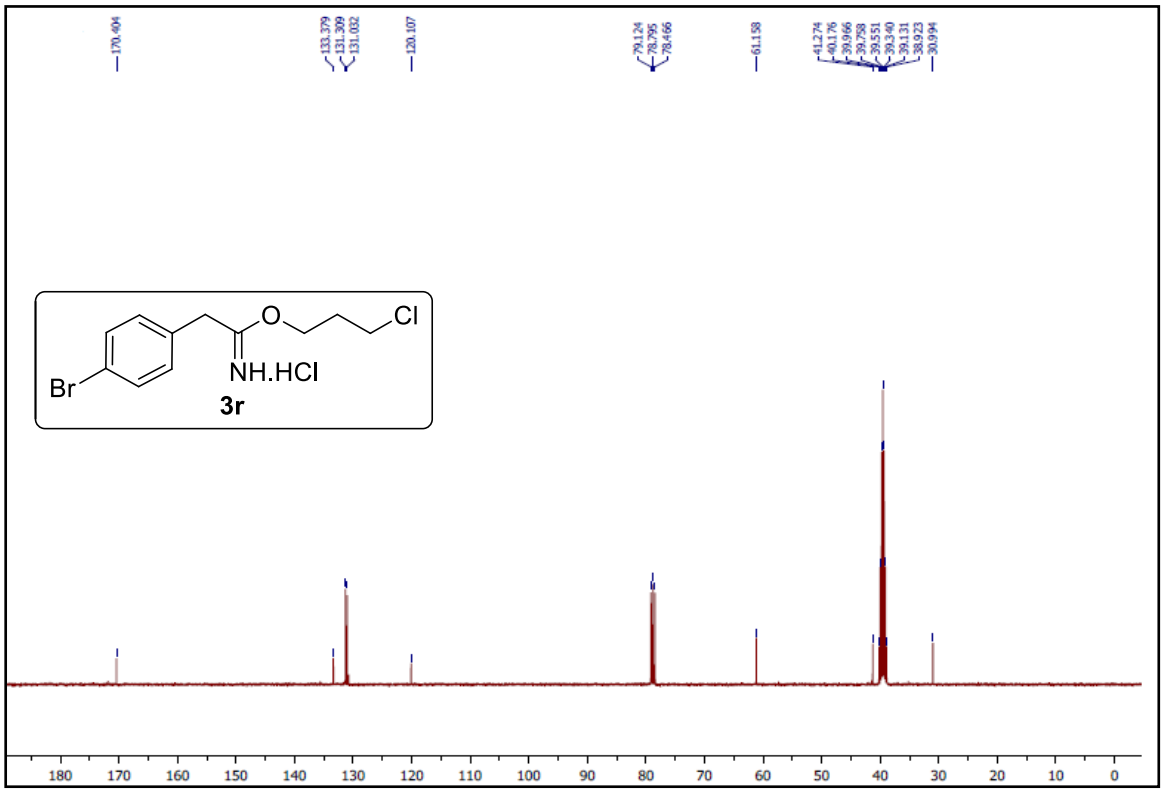
0.5
0.0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133.379
131.309
131.032
120.107
79.124
78.795
78.466
61.158
41.274
40.176
39.966
39.758
39.551
39.340
39.131
38.923
30.994
O
Cl
NH.HCl
Br
3r
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170
160
150
140
130
120
110
100
90
80
70
60
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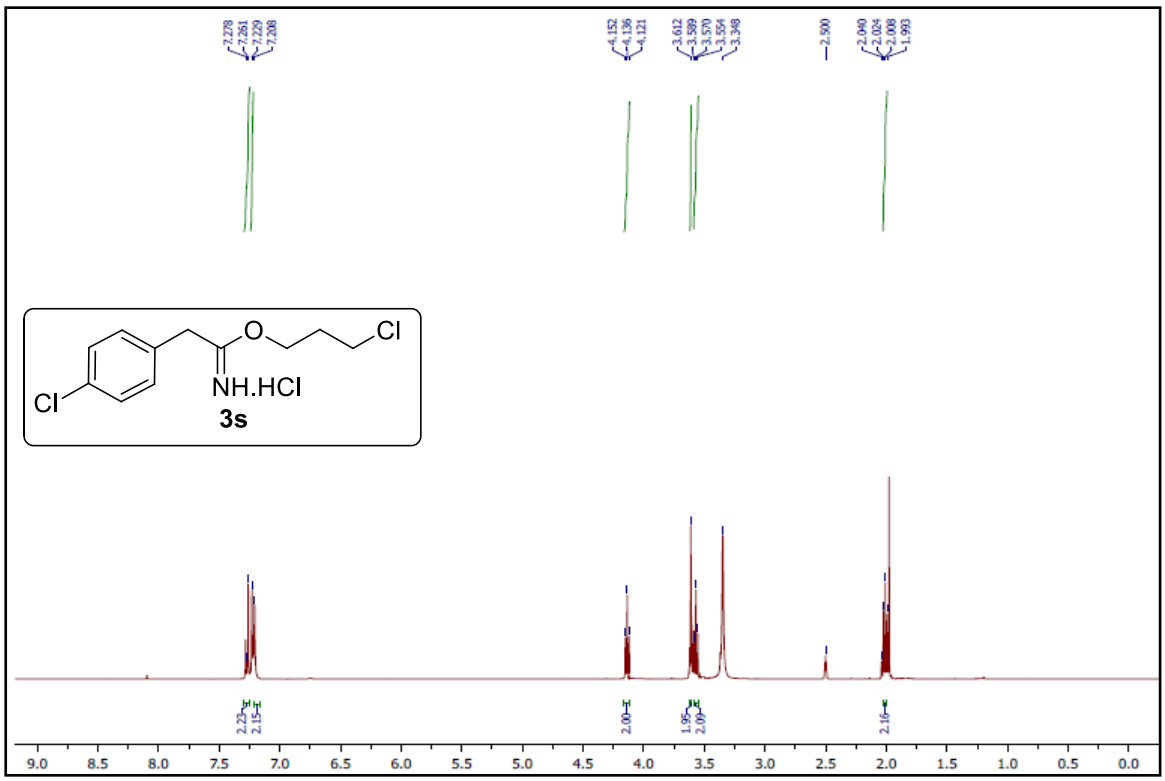
40
30
20
10
0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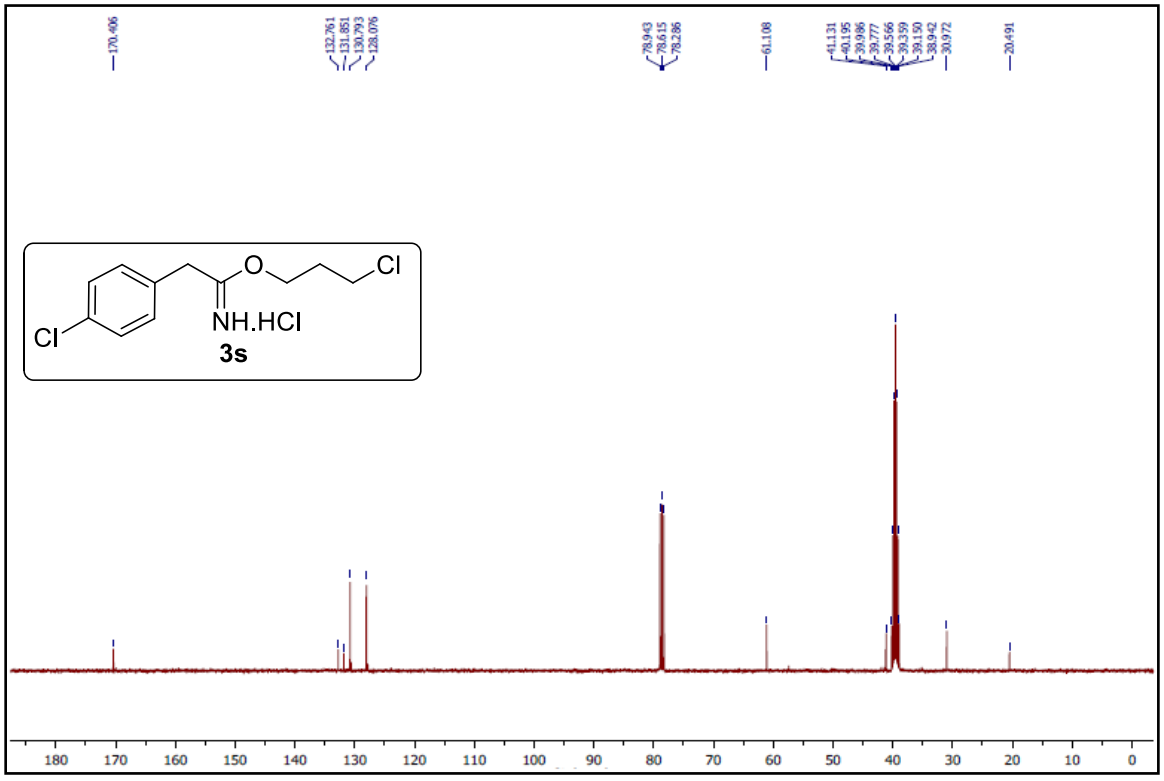
7.261
7.229
7.208
4.152
4.136
4.121
3.612
3.589
3.570
3.554
3.348
2.500
2.040
2.024
2.008
1.993
Cl
O
Cl
NH.HCl
3s
2.23
2.15
2.00
1.95
2.00
2.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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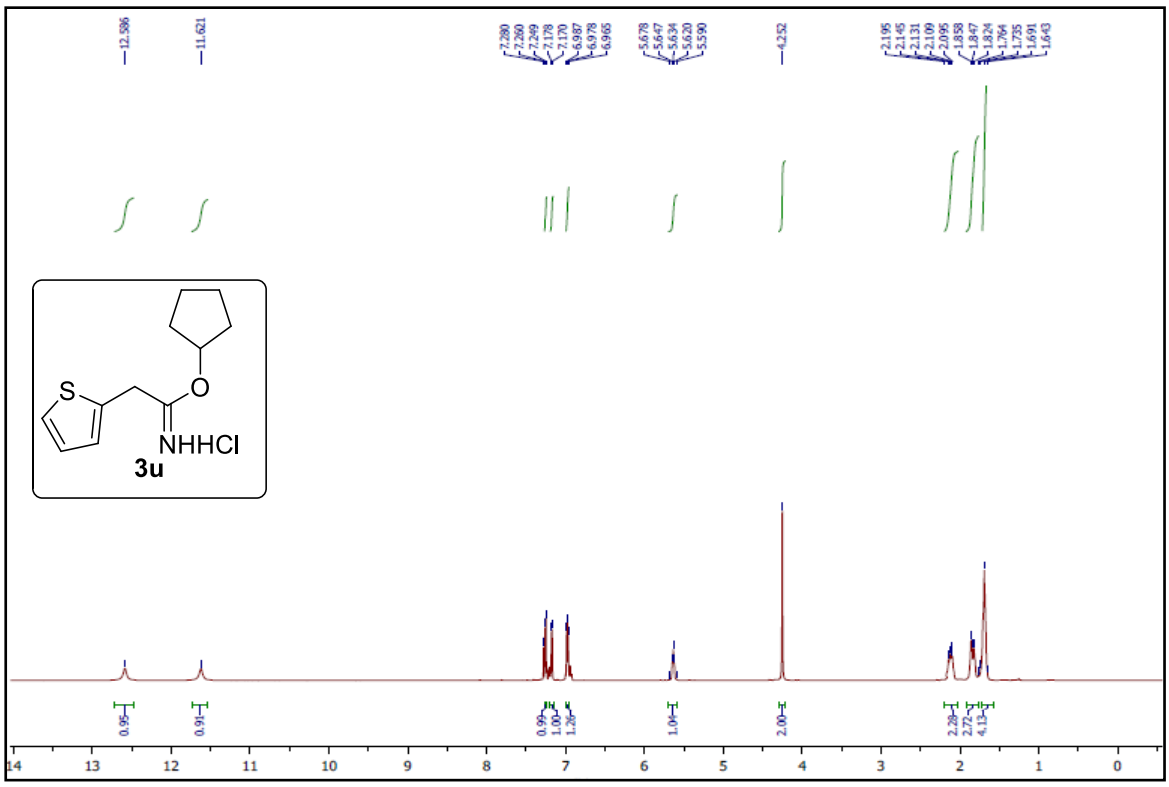
132.761
131.851
130.793
128.076
78.943
78.615
78.286
61.108
41.131
40.195
39.986
39.777
39.566
39.359
39.150
38.942
30.972
20.491
Cl
O
Cl
NH.HCl
3s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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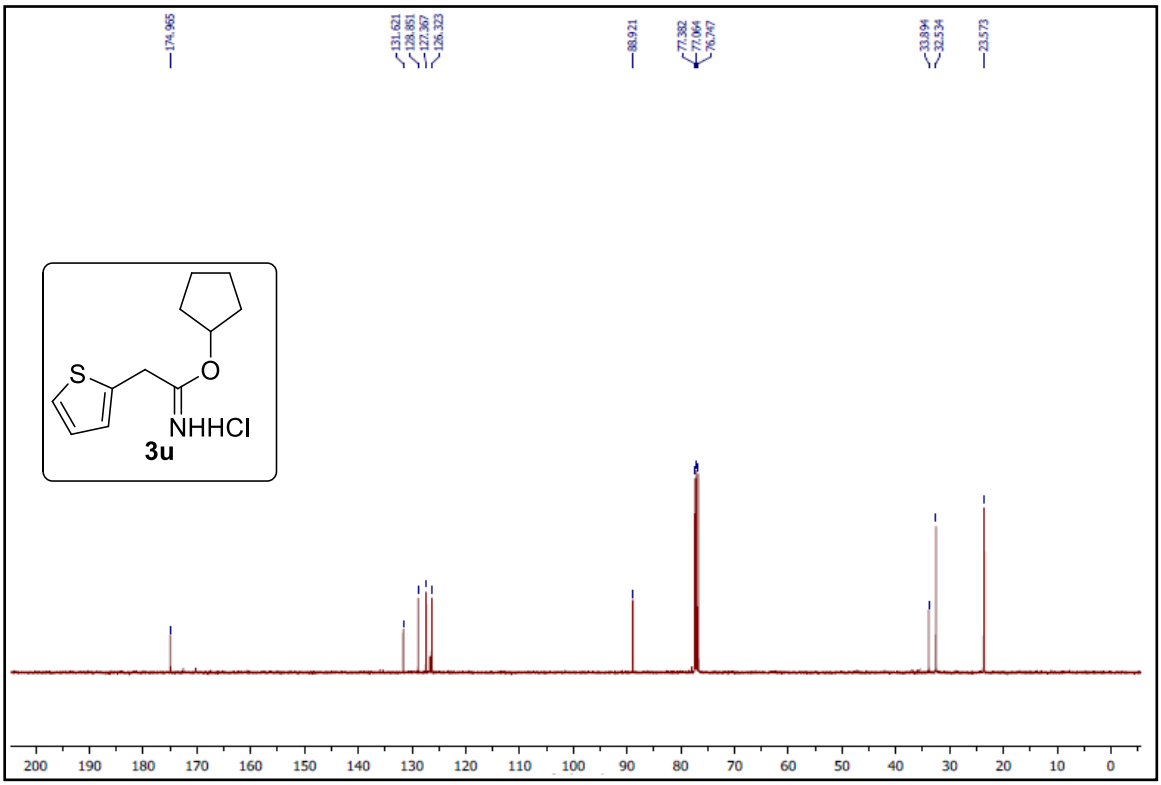
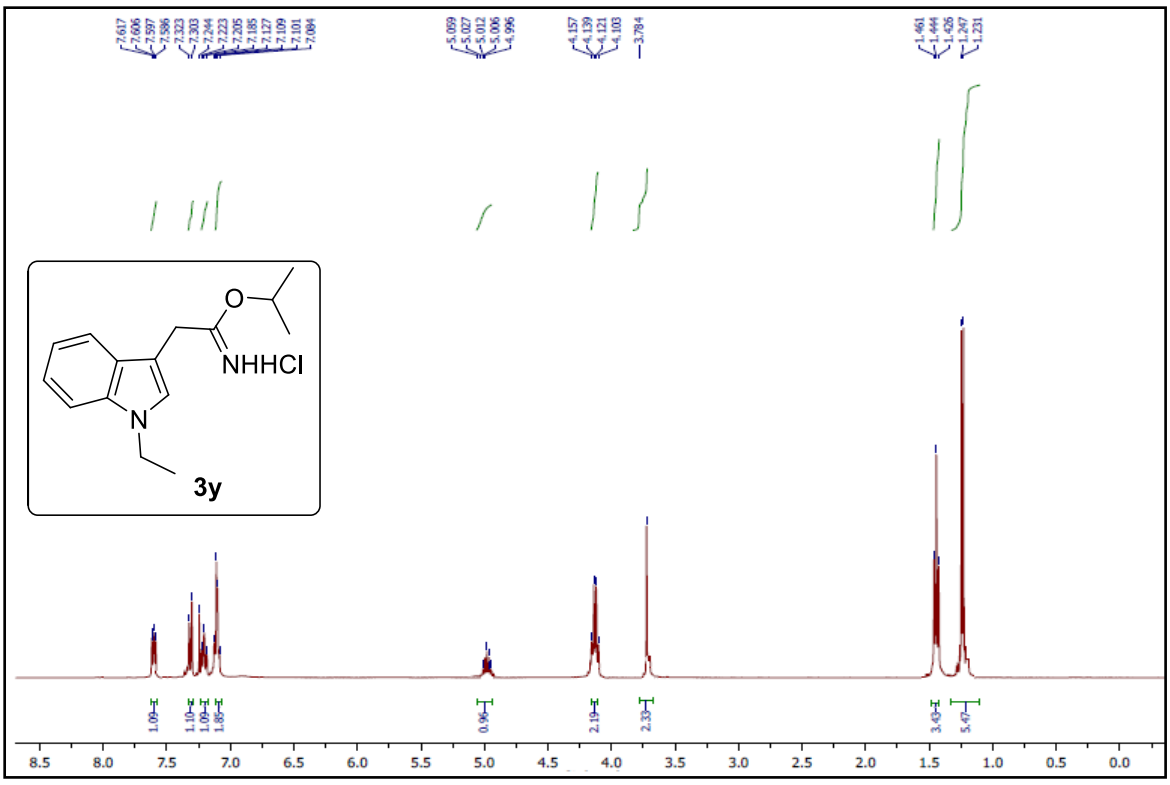
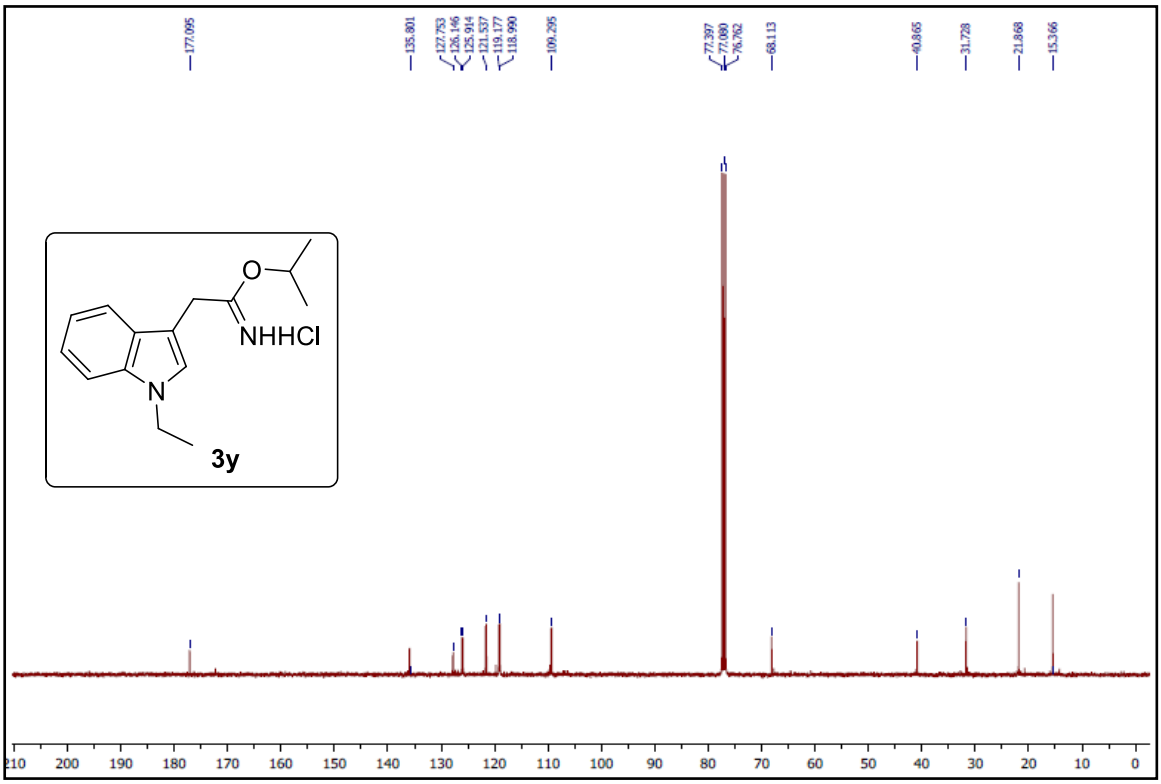
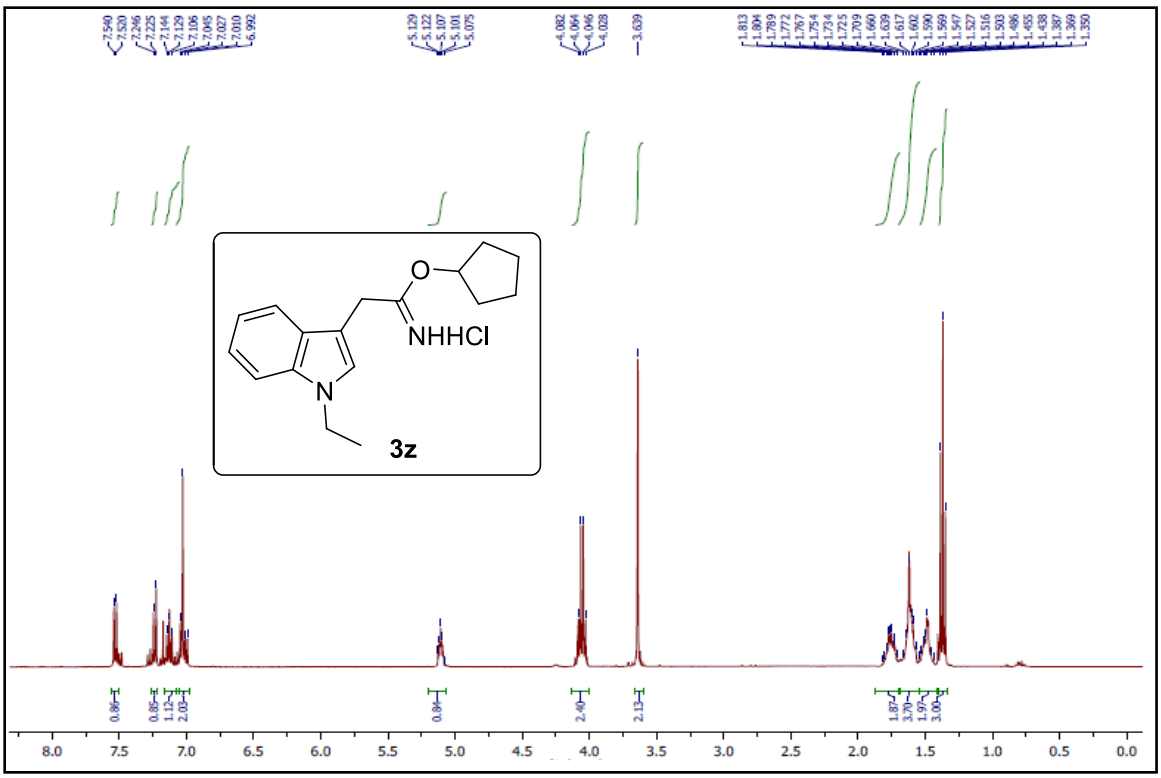
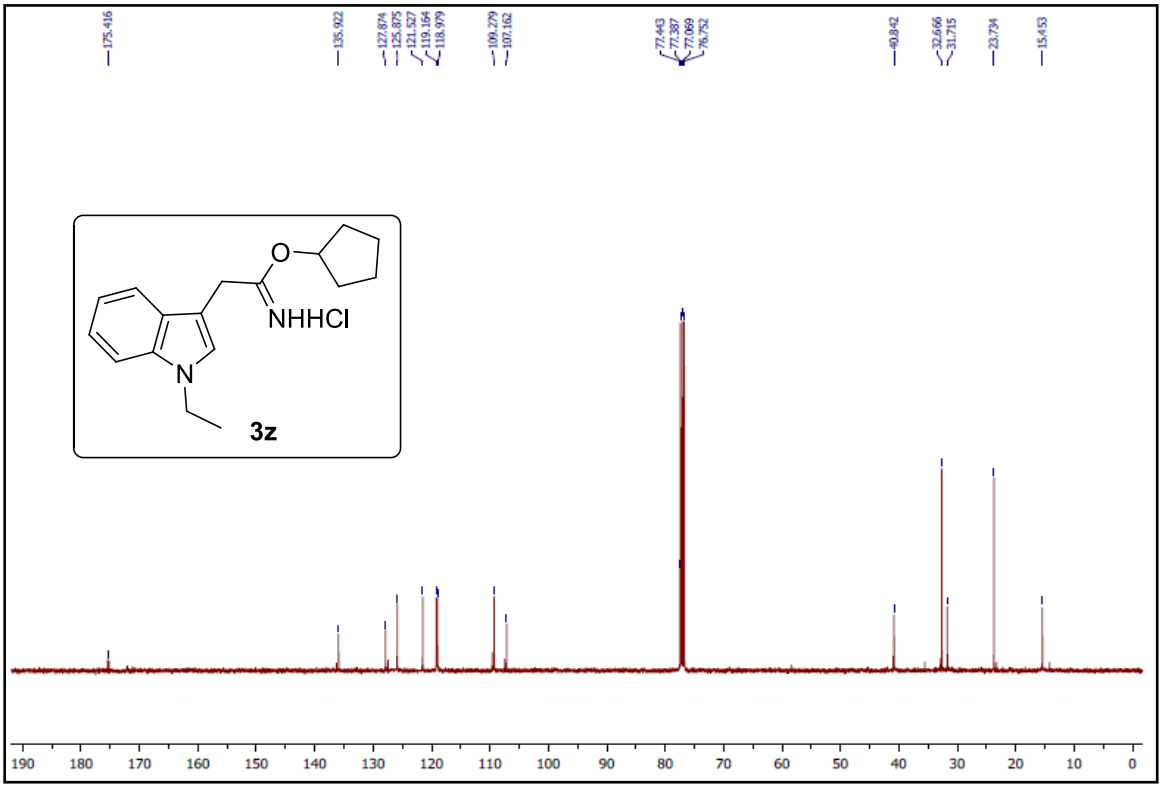
7.380
7.360
7.249
7.178
7.170
6.987
6.978
6.965
5.678
5.647
5.634
5.620
5.590
4.252
2.195
2.145
2.131
2.109
2.095
1.858
1.847
1.824
1.764
1.735
1.691
1.643
S
O
NHHCl
3u
0.95
0.91
0.99
1.00
1.26
1.04
2.00
2.28
2.72
4.13
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0


174.965
131.621
128.651
127.387
126.323
88.921
77.382
77.064
76.747
33.894
32.534
23.573
S
O
NHHCl
3u
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

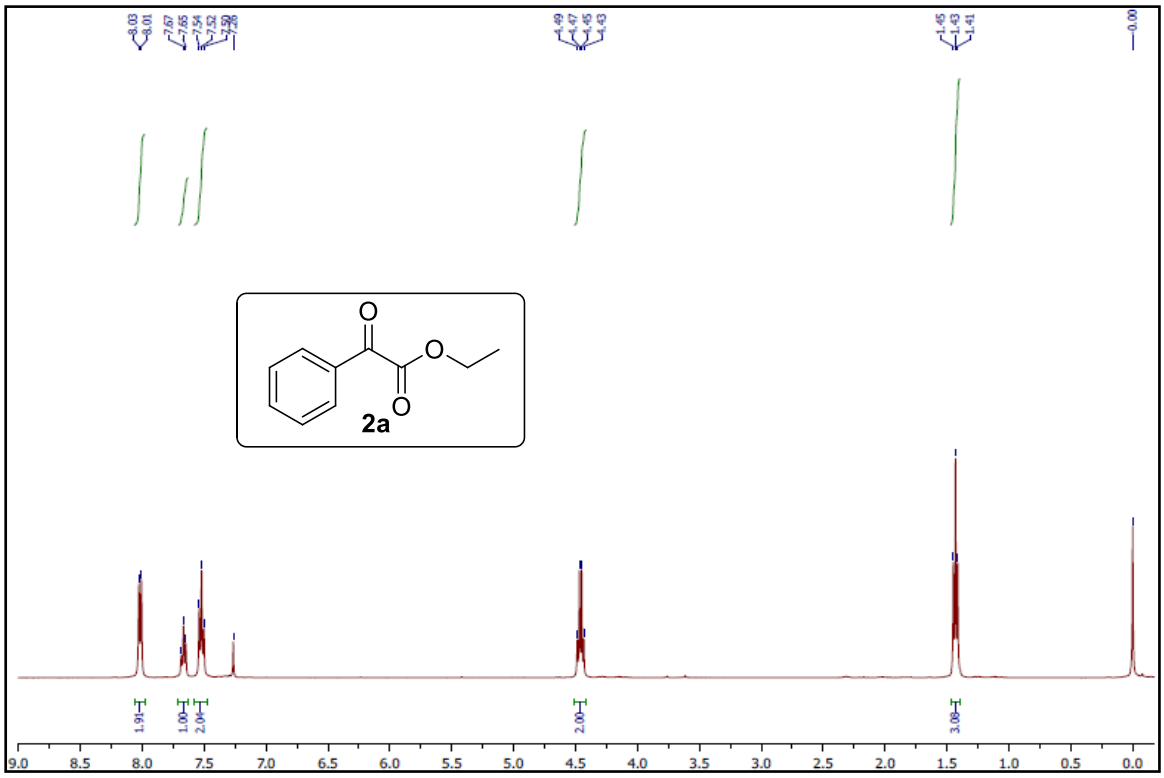

NHHCl
3y

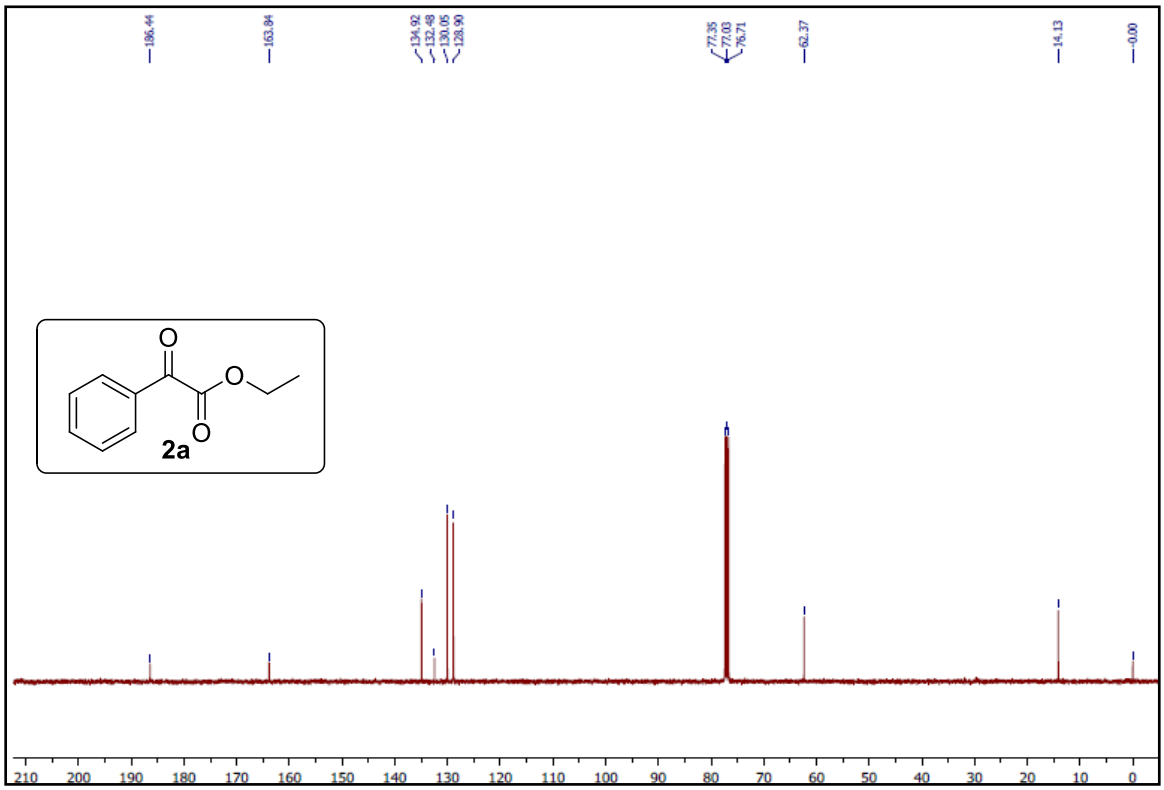

NHHCl
3y

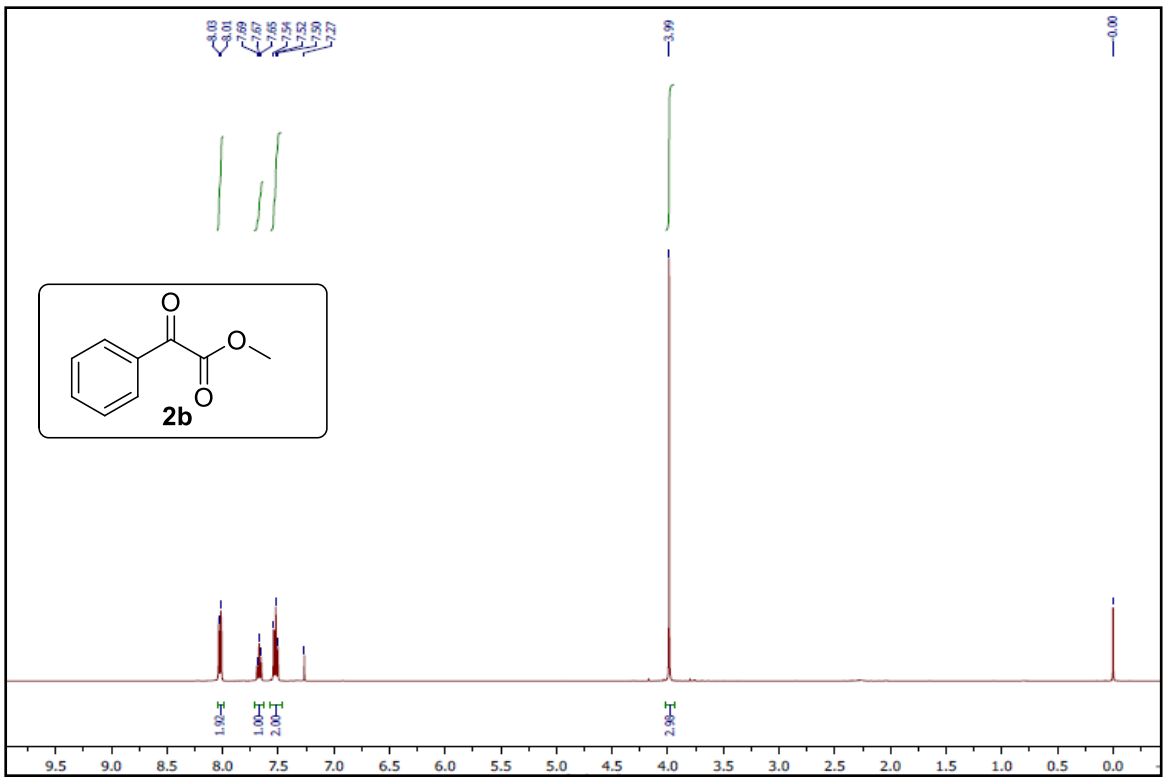

NHHCl
3z


NHHCl
3z

2 (B). Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of products.



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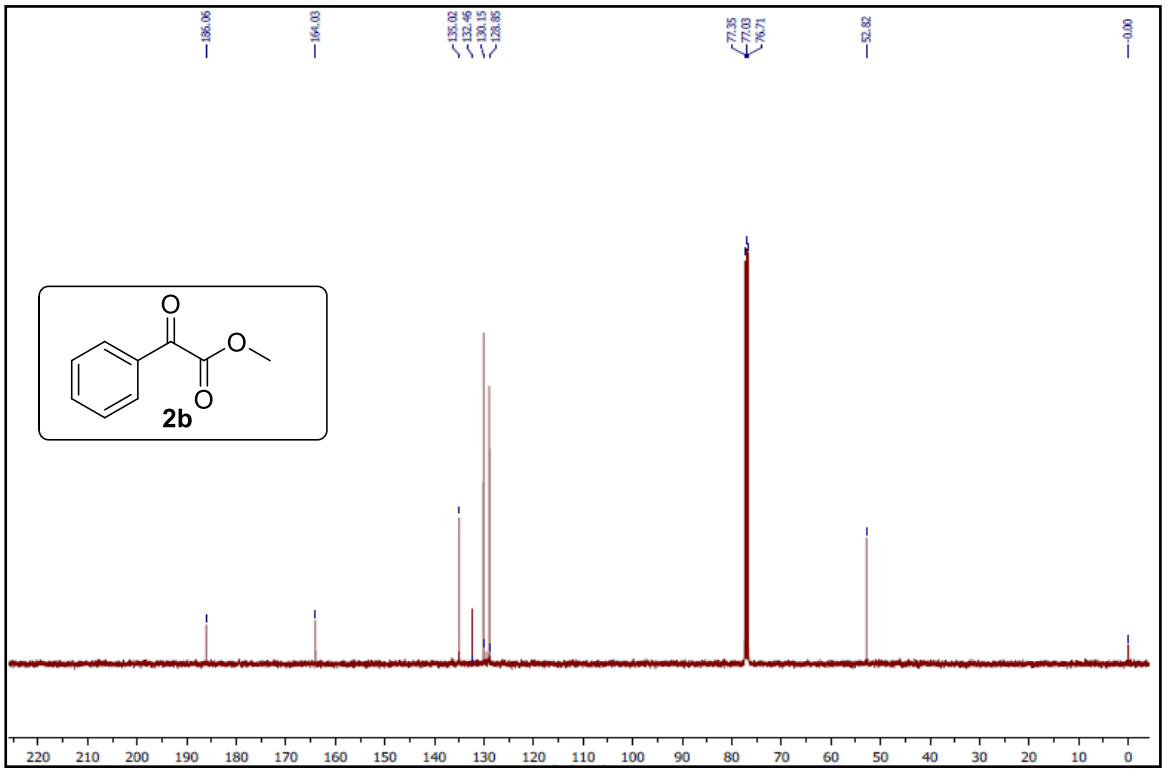
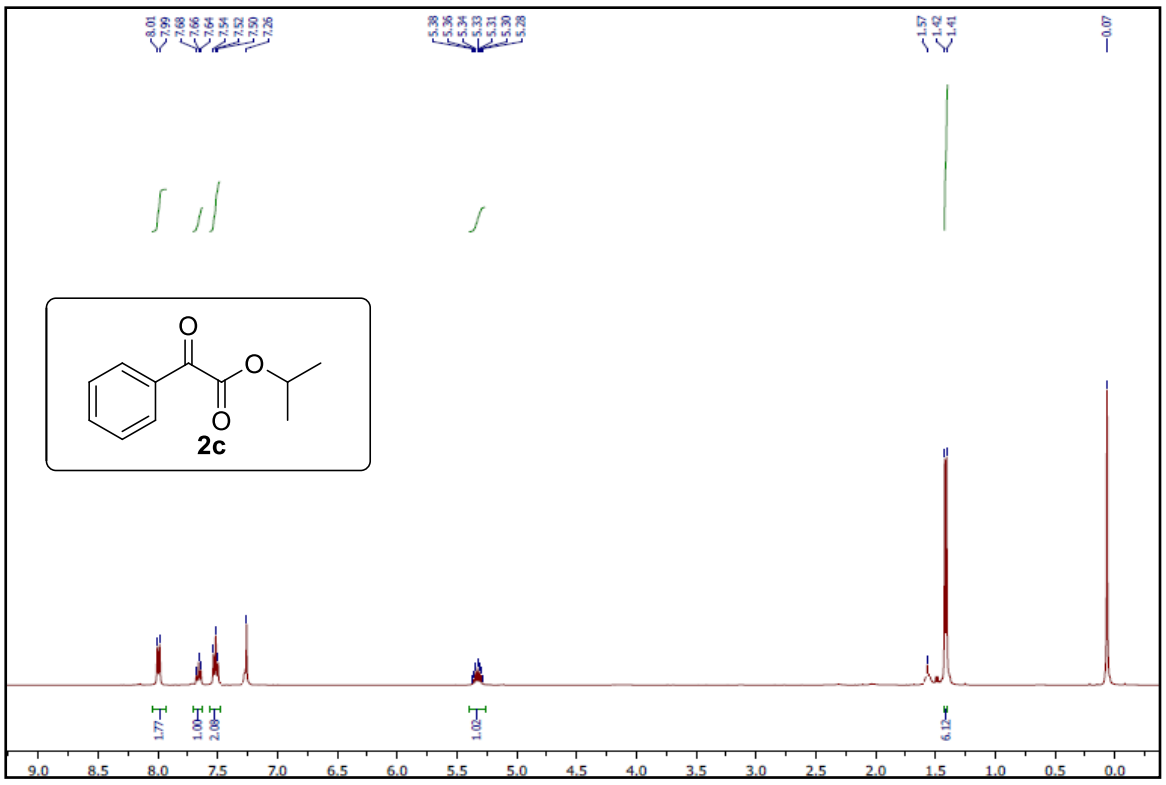
8.01
7.69
7.67
7.65
7.54
7.52
7.50
7.27
3.99
0.00
2b
1.92
1.00
2.00
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


186.06
164.03
135.02
132.46
130.15
128.85
77.35
77.03
76.71
52.82
0.00
2b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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7.99
7.68
7.66
7.64
7.54
7.52
7.50
7.26
5.38
5.36
5.34
5.33
5.31
5.30
5.28
1.57
1.42
1.41
0.07
O
O
O
2c
1.77
1.00
2.00
1.02
6.12
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
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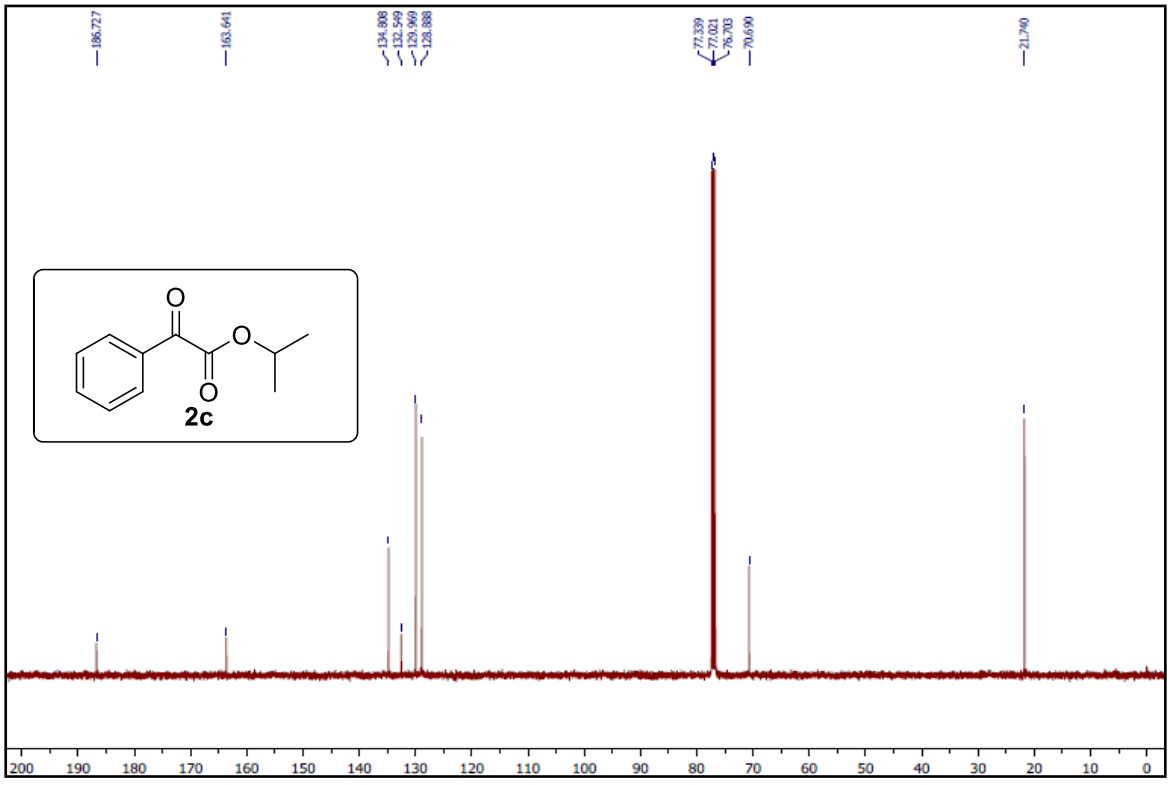
1.0
0.5
0.0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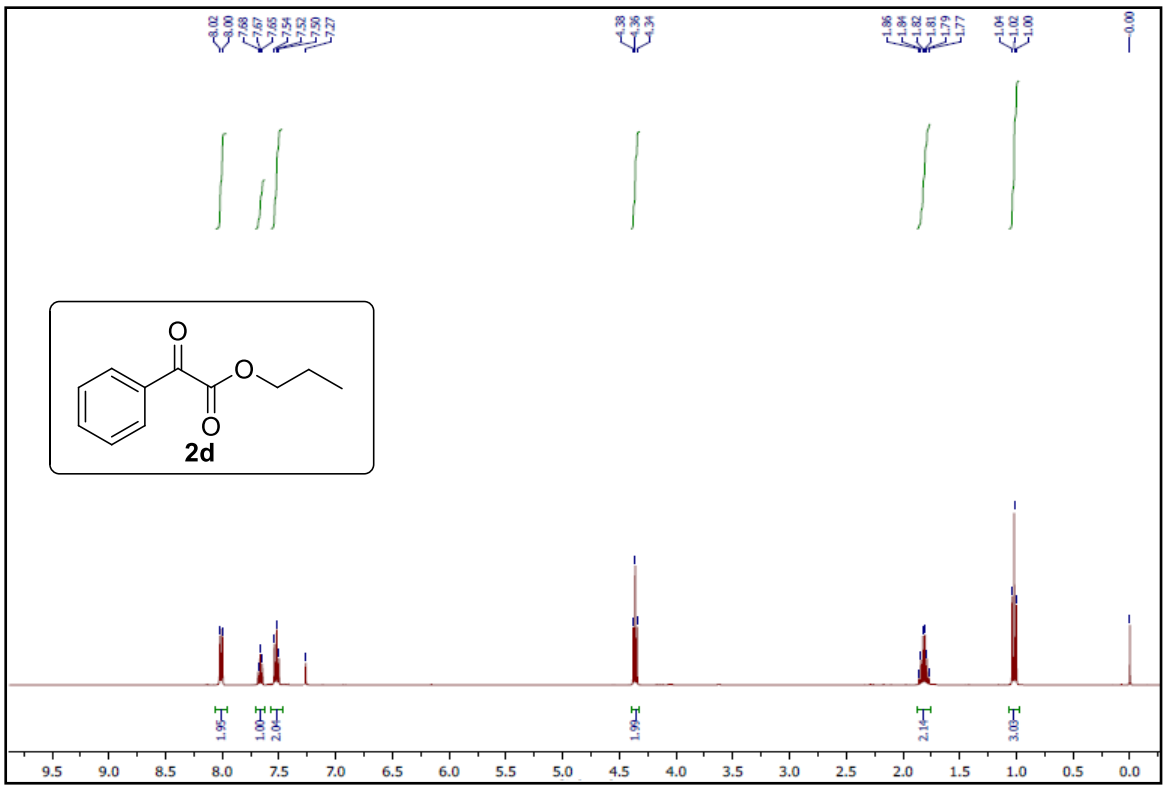
132.549
129.999
128.888
77.339
77.021
76.703
70.690
21.740
O
O
O
2c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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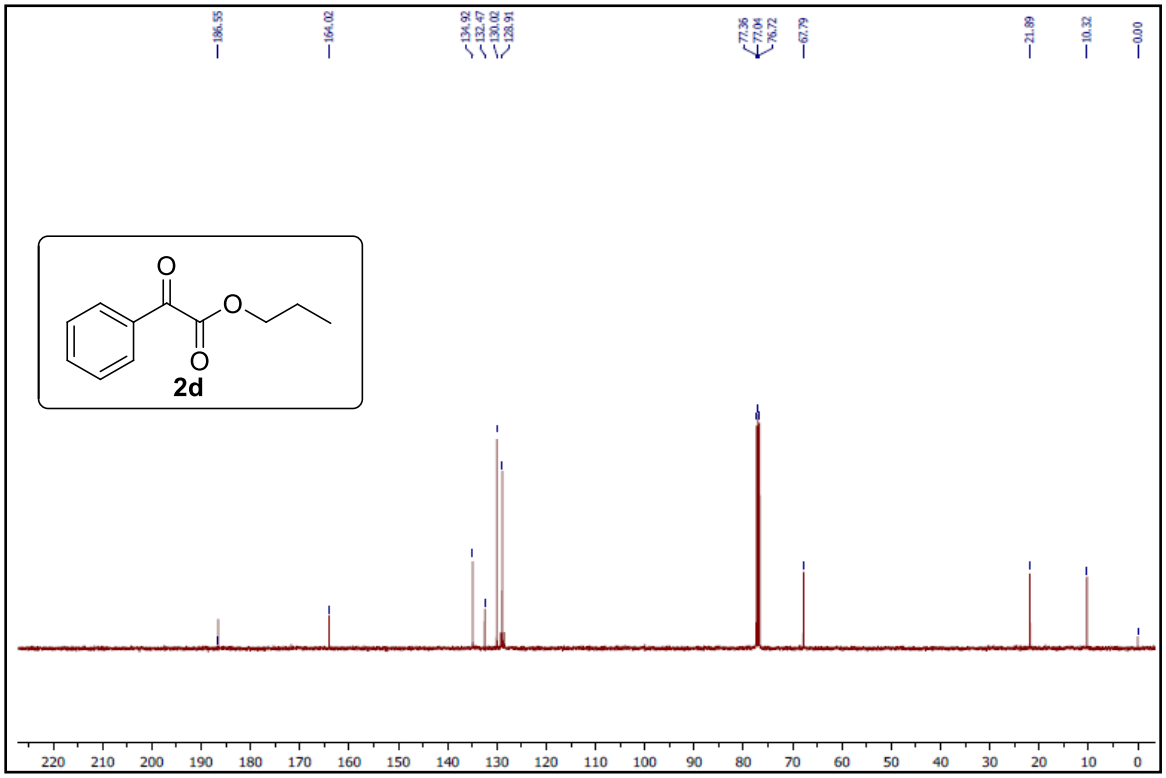
8.00
7.68
7.67
7.65
7.54
7.52
7.50
7.27
4.38
4.36
4.34
1.86
1.84
1.82
1.81
1.79
1.77
1.04
1.02
1.00
0.00
O
O
O
2d
1.99
1.00
2.04
1.99
2.14
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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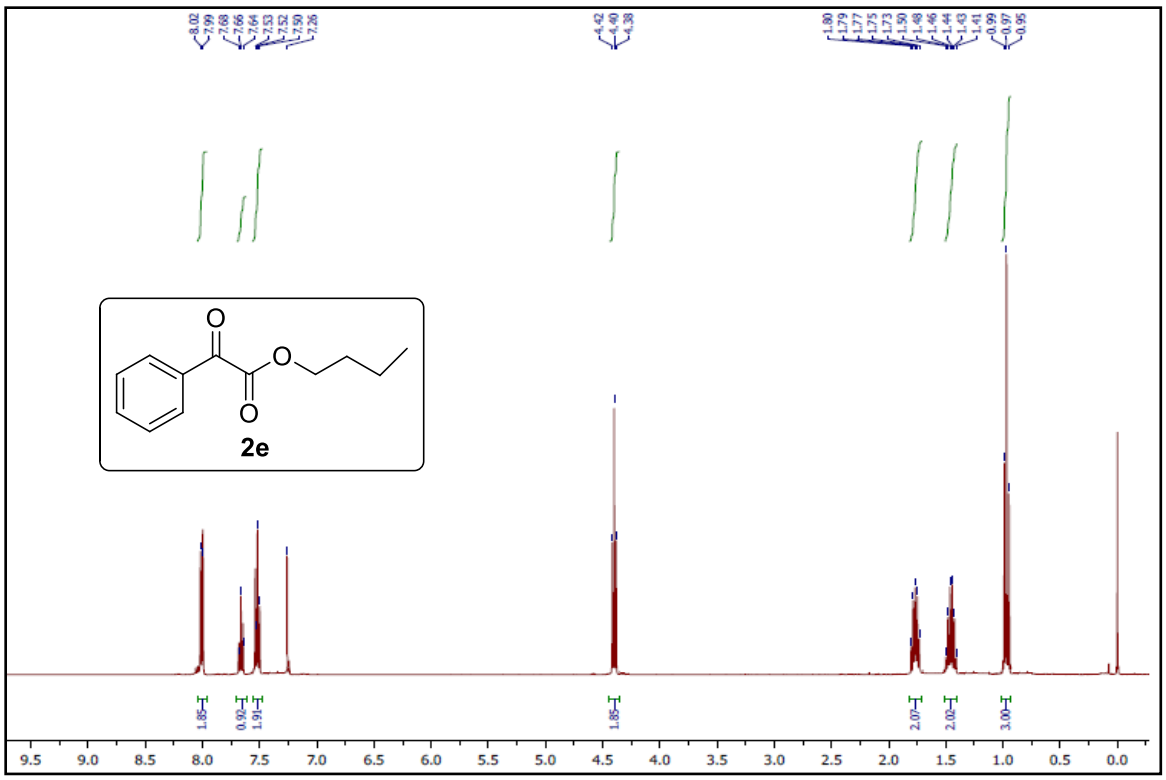
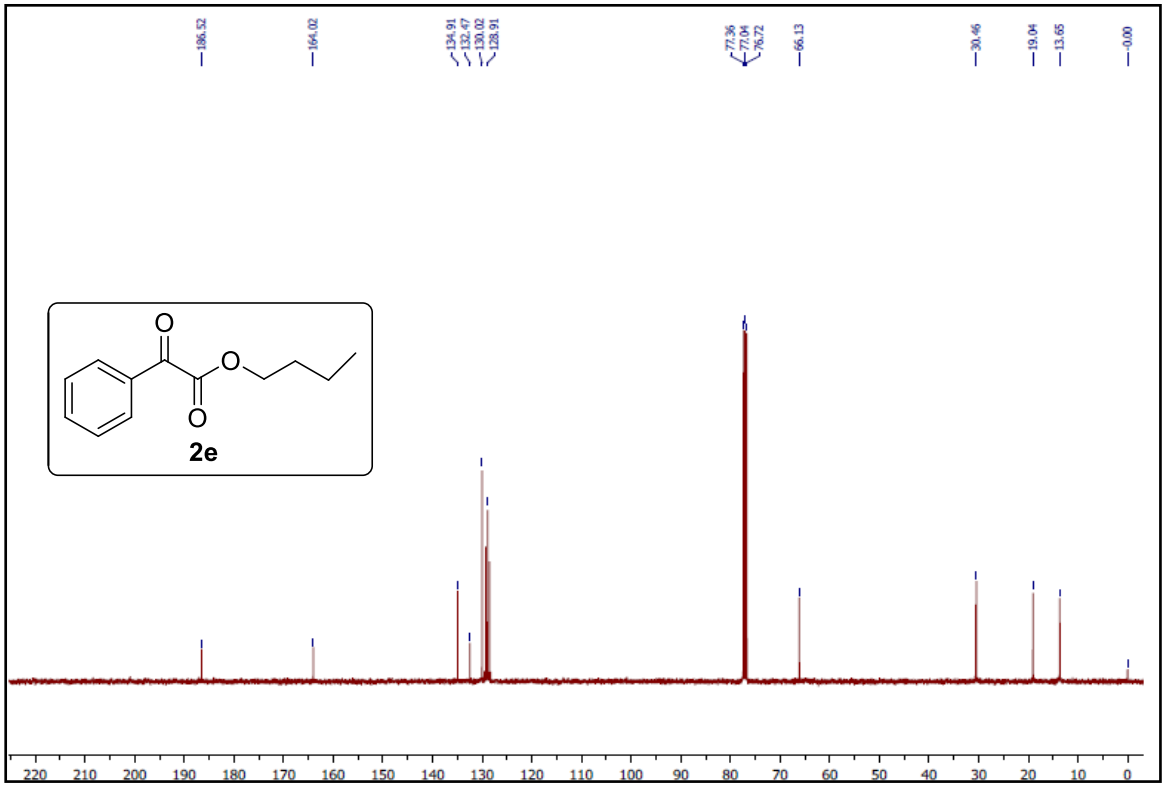
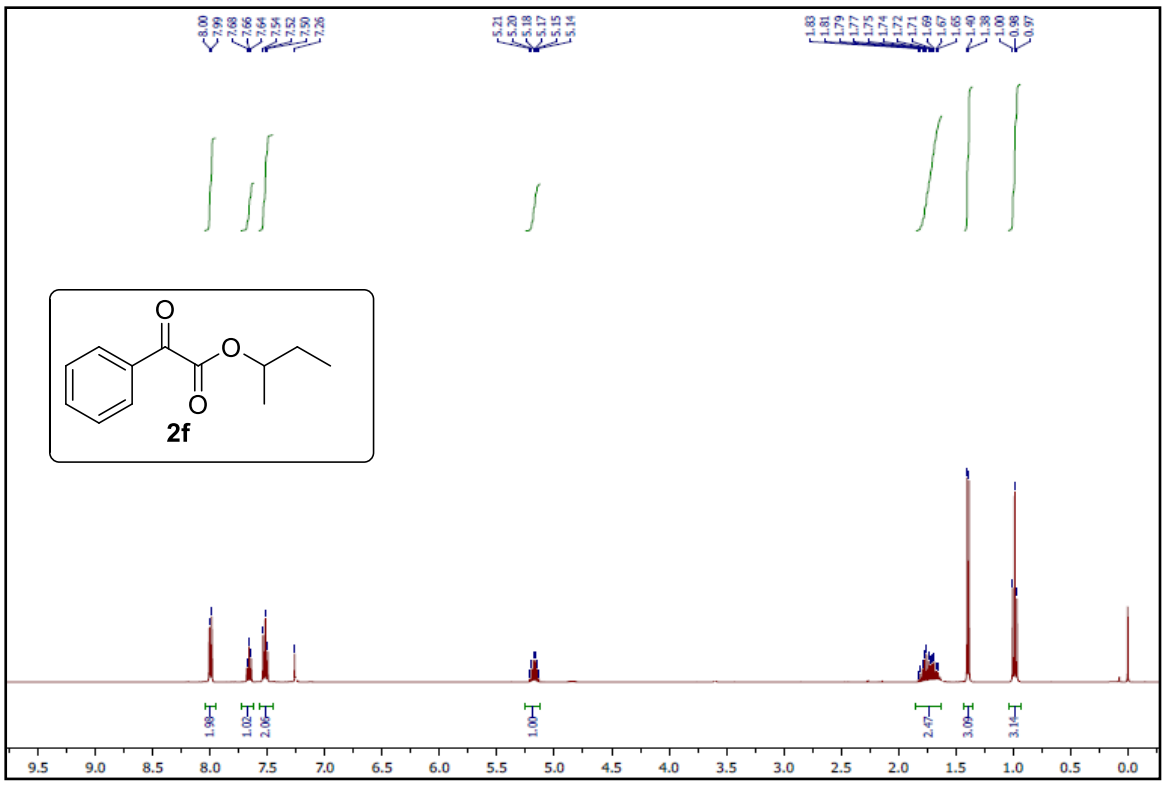
134.92
132.47
130.02
128.91
77.36
77.04
76.72
67.79
21.89
10.32
0.00
O
O
O
2d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


2e


2e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7.99
7.68
7.66
7.64
7.54
7.52
7.50
7.26
5.21
5.20
5.18
5.17
5.15
5.14
1.83
1.81
1.79
1.77
1.75
1.74
1.72
1.71
1.69
1.67
1.65
1.49
1.38
1.00
0.98
0.97
O
O
O
2f
1.98
1.02
2.06
1.00
2.47
3.09
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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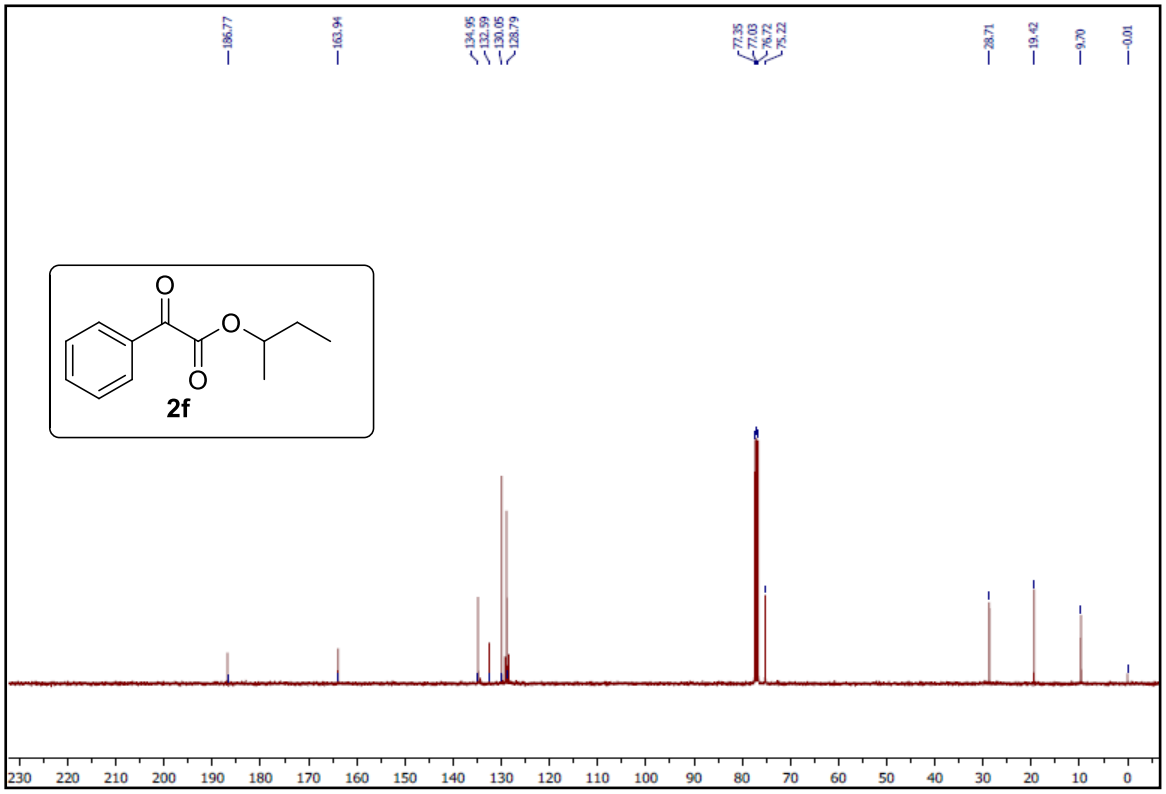
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130.05
128.79
77.35
77.03
76.72
75.22
28.71
19.42
9.70
-0.01
O
O
O
2f
230
220
210
200
190
180
170
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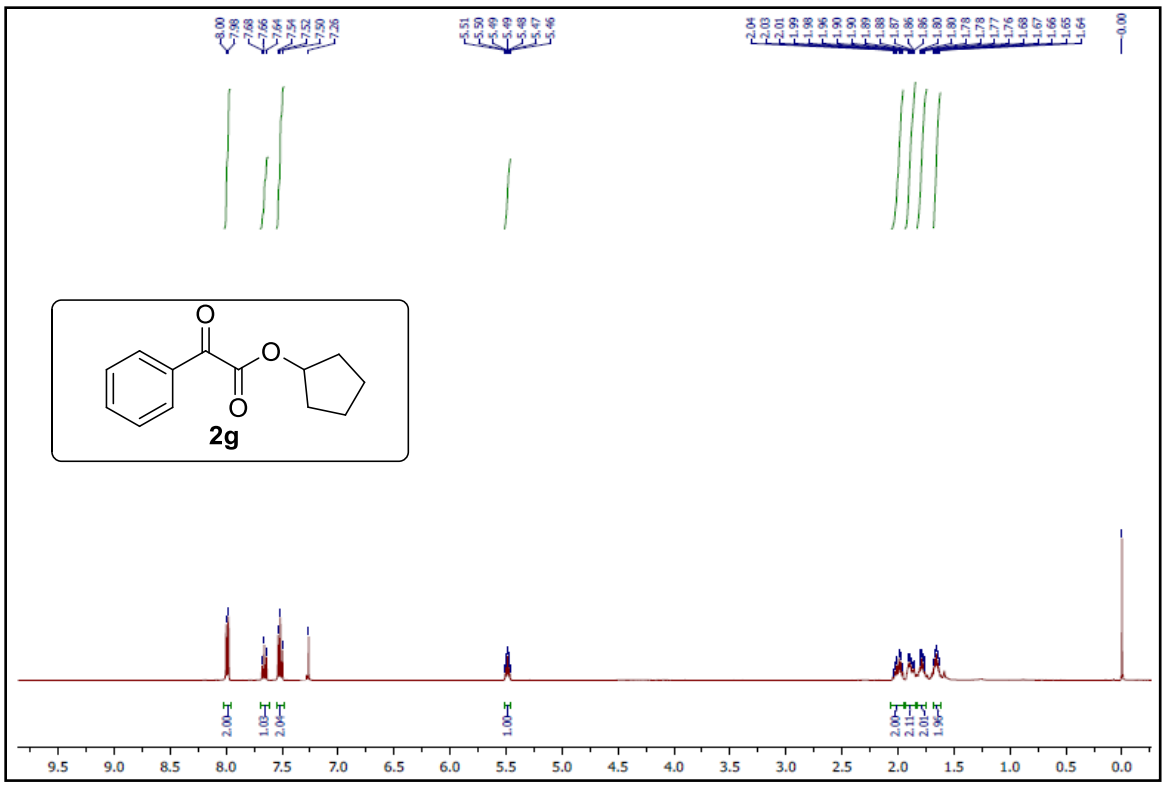
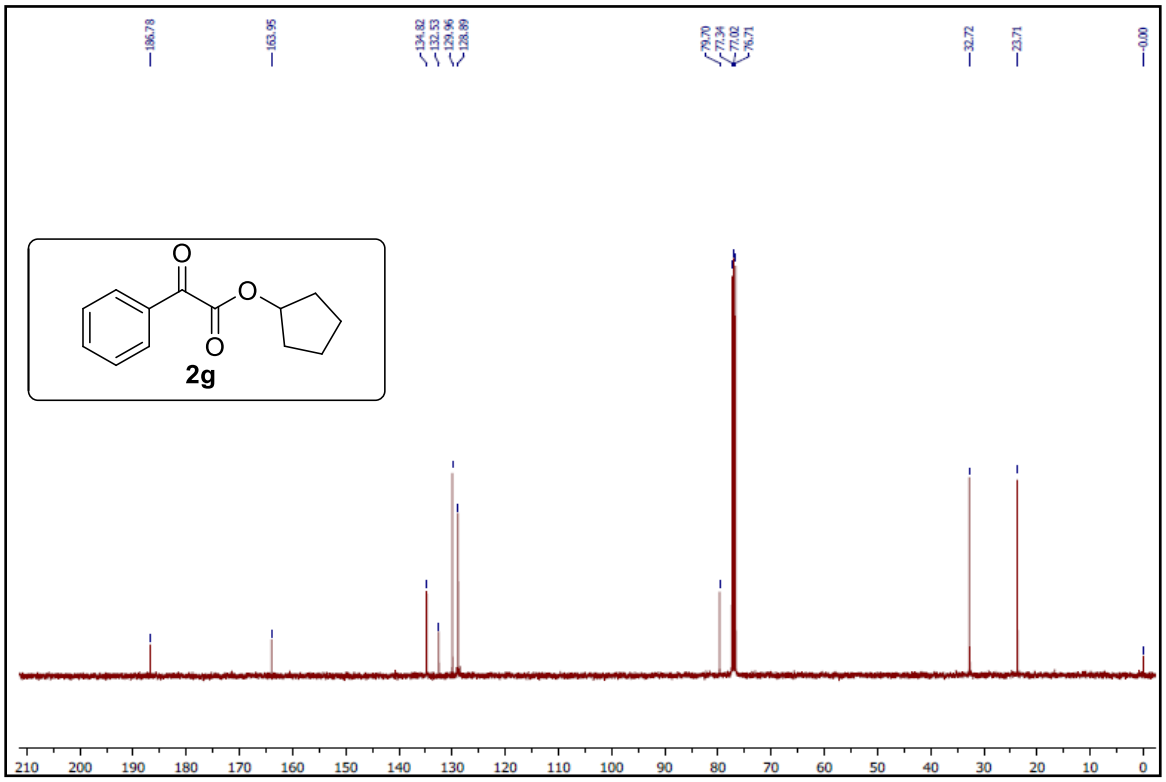
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


2g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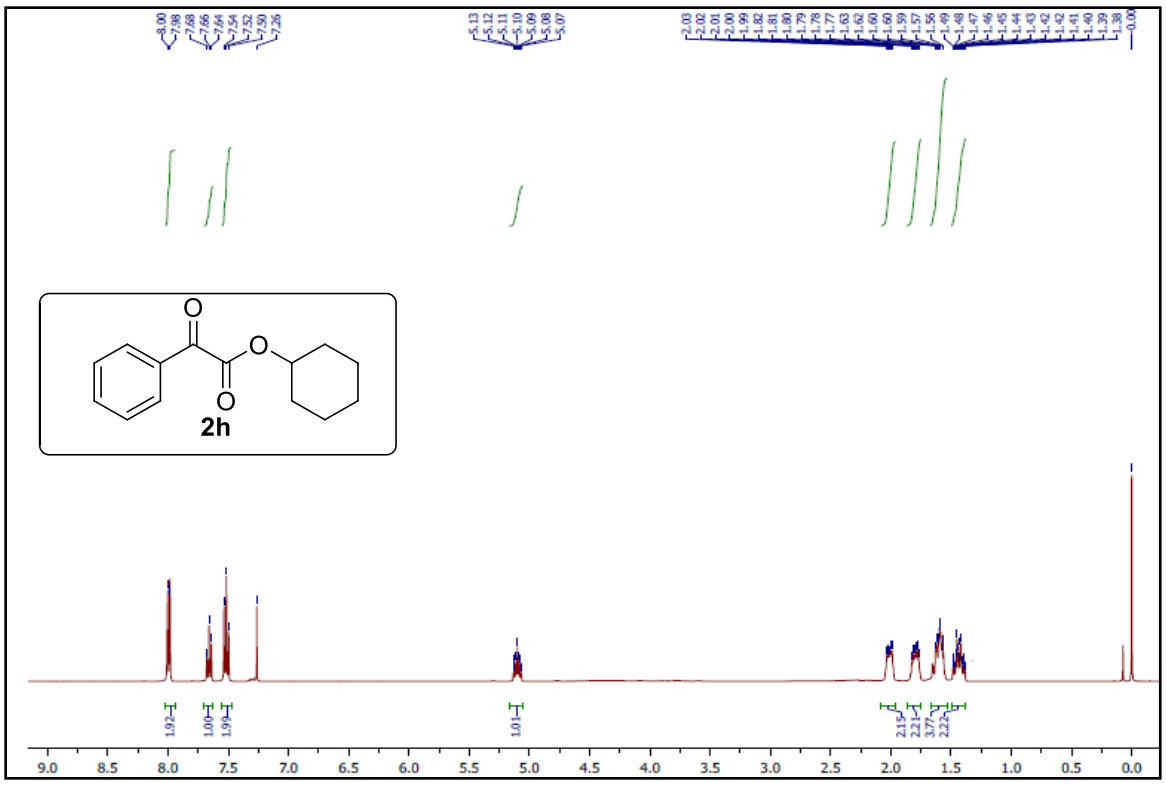
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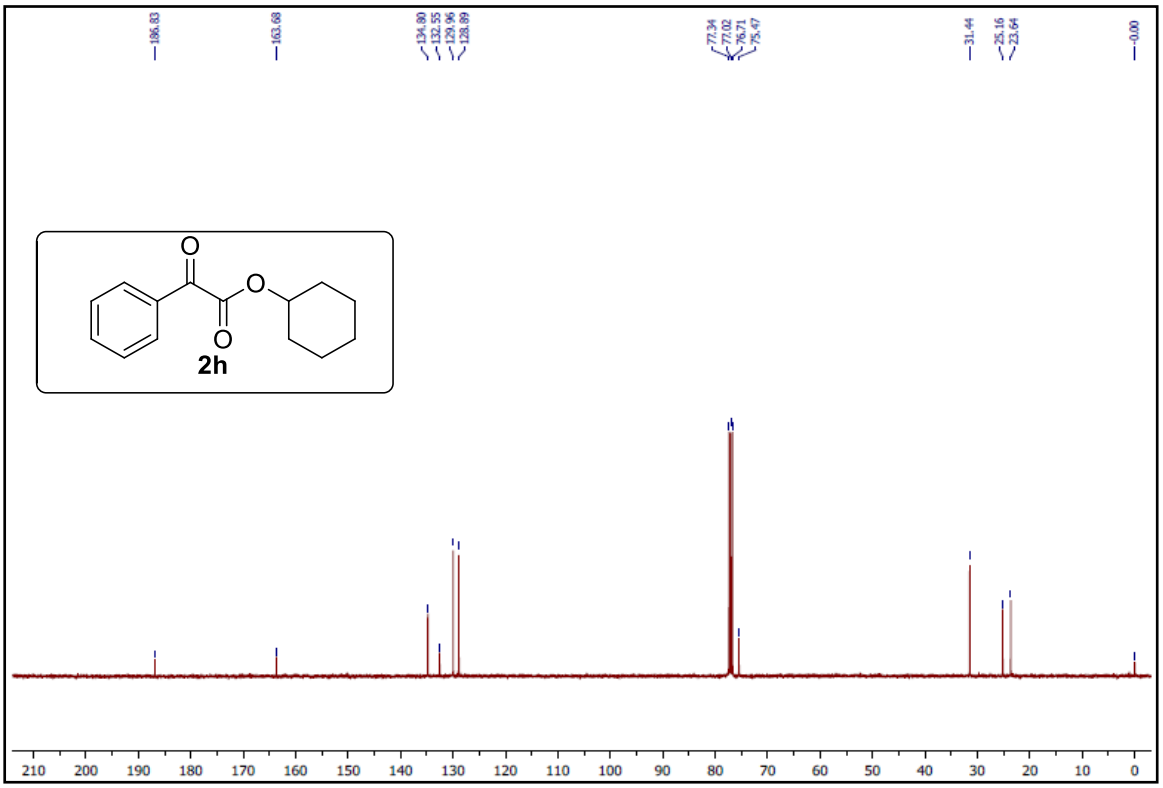
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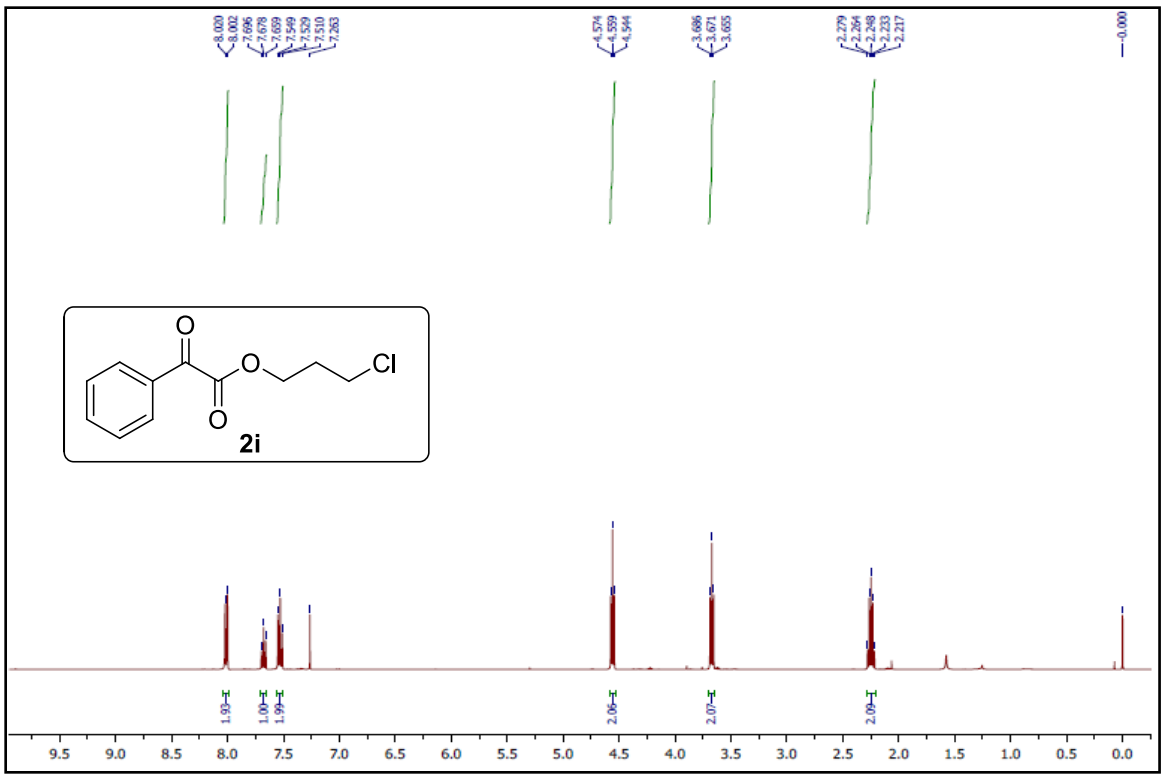
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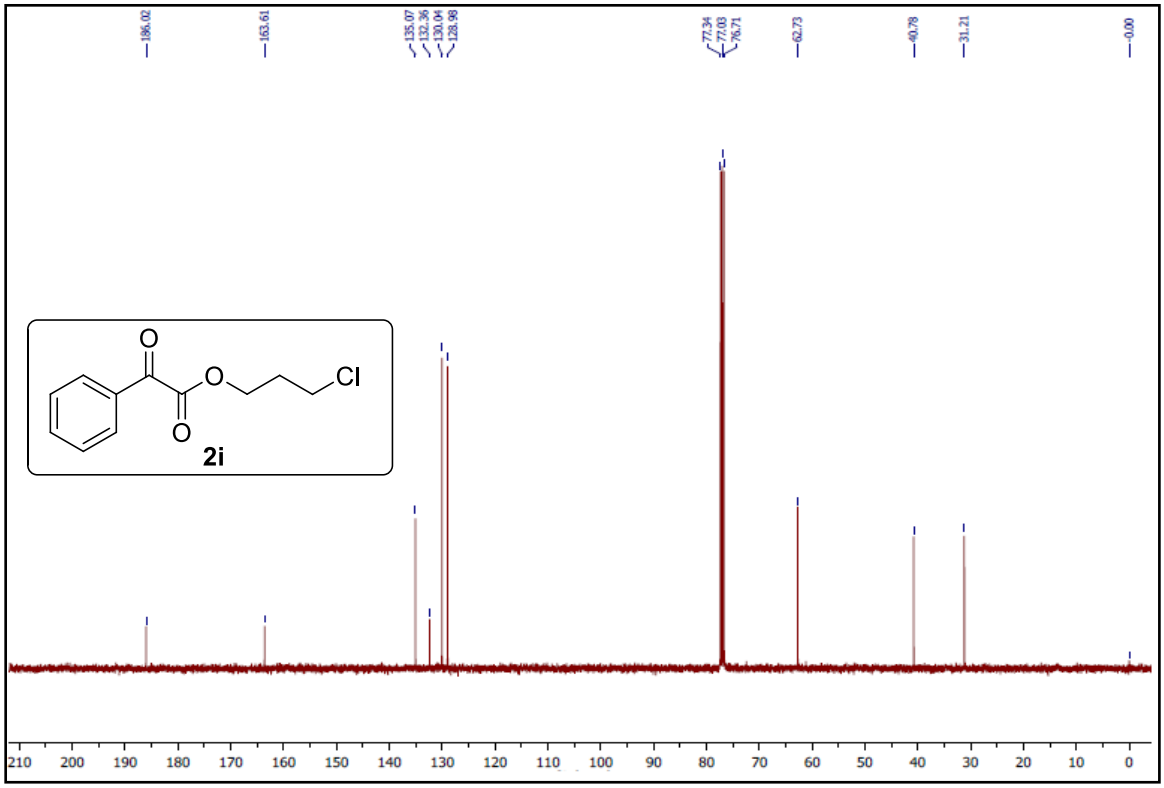
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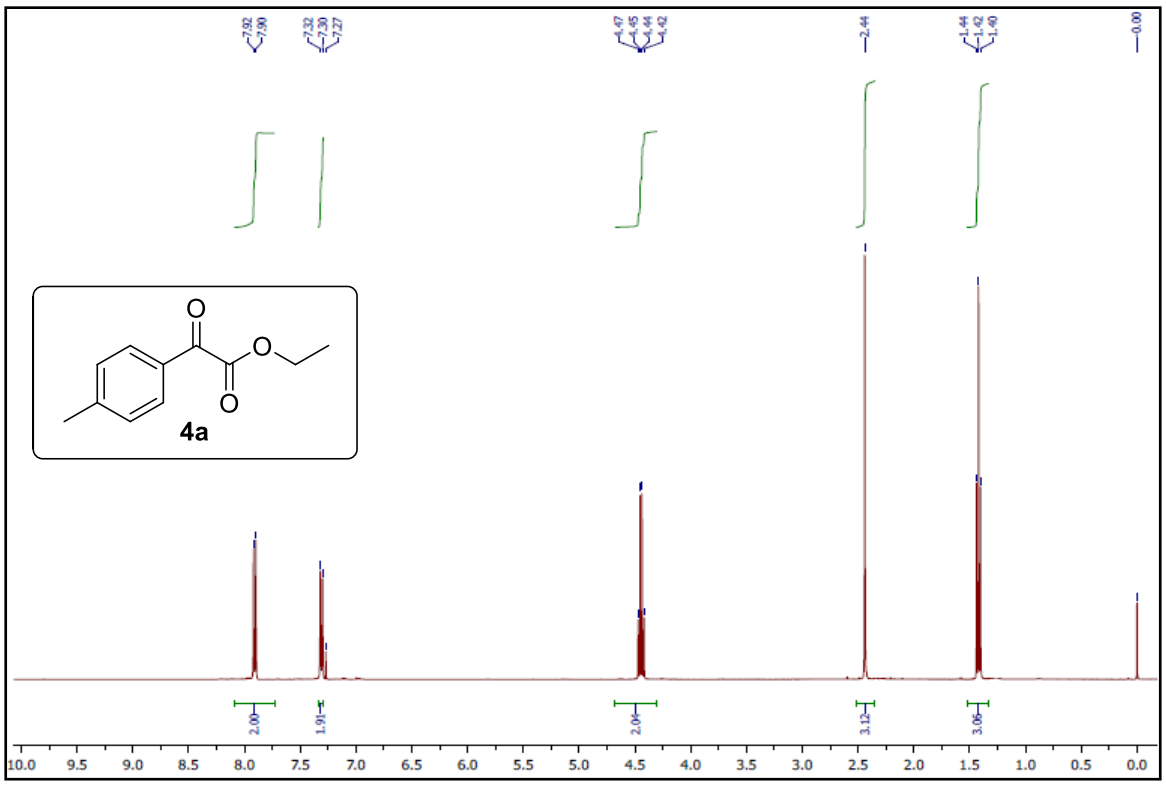
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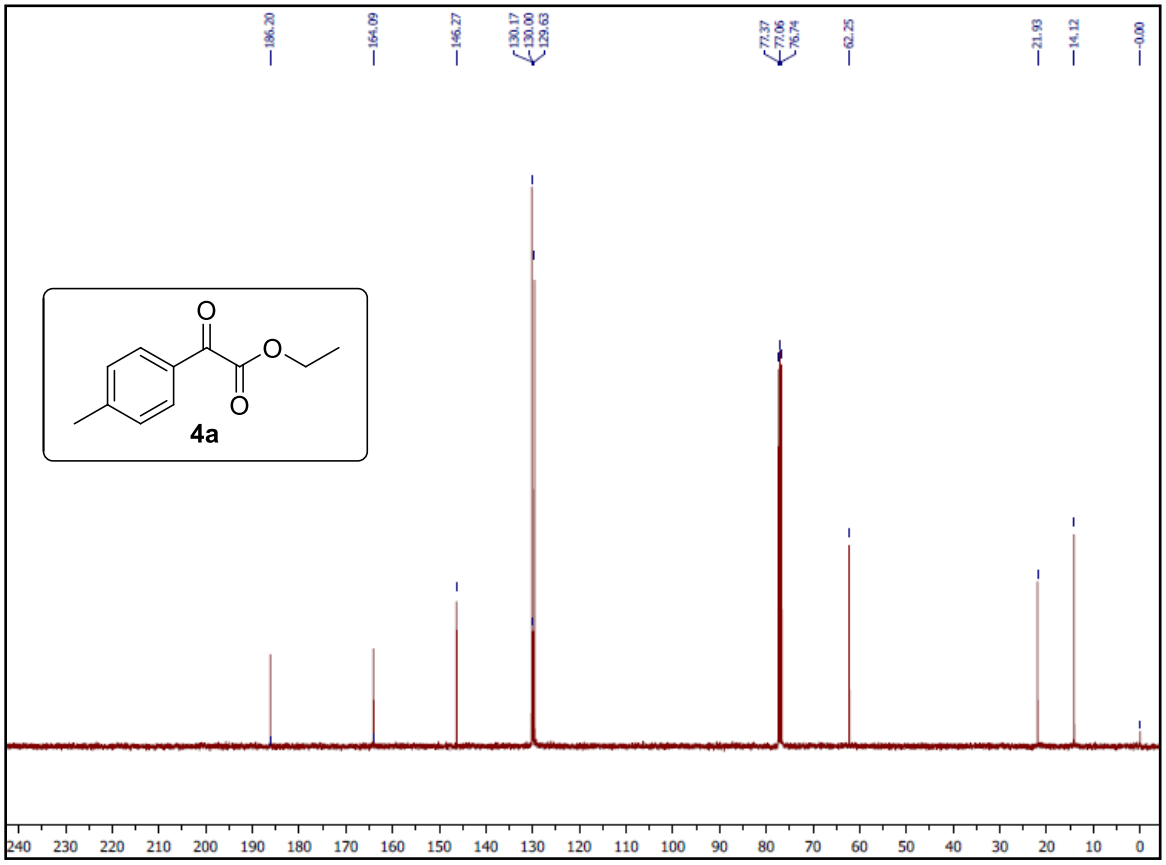
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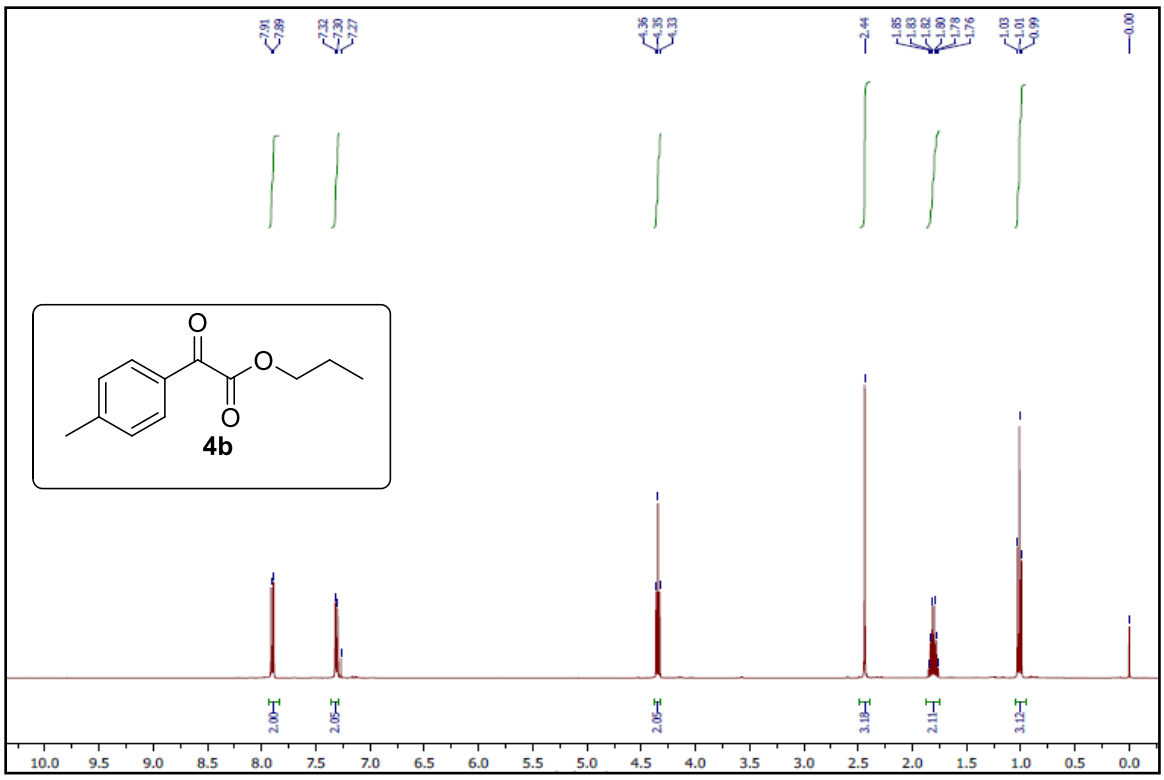
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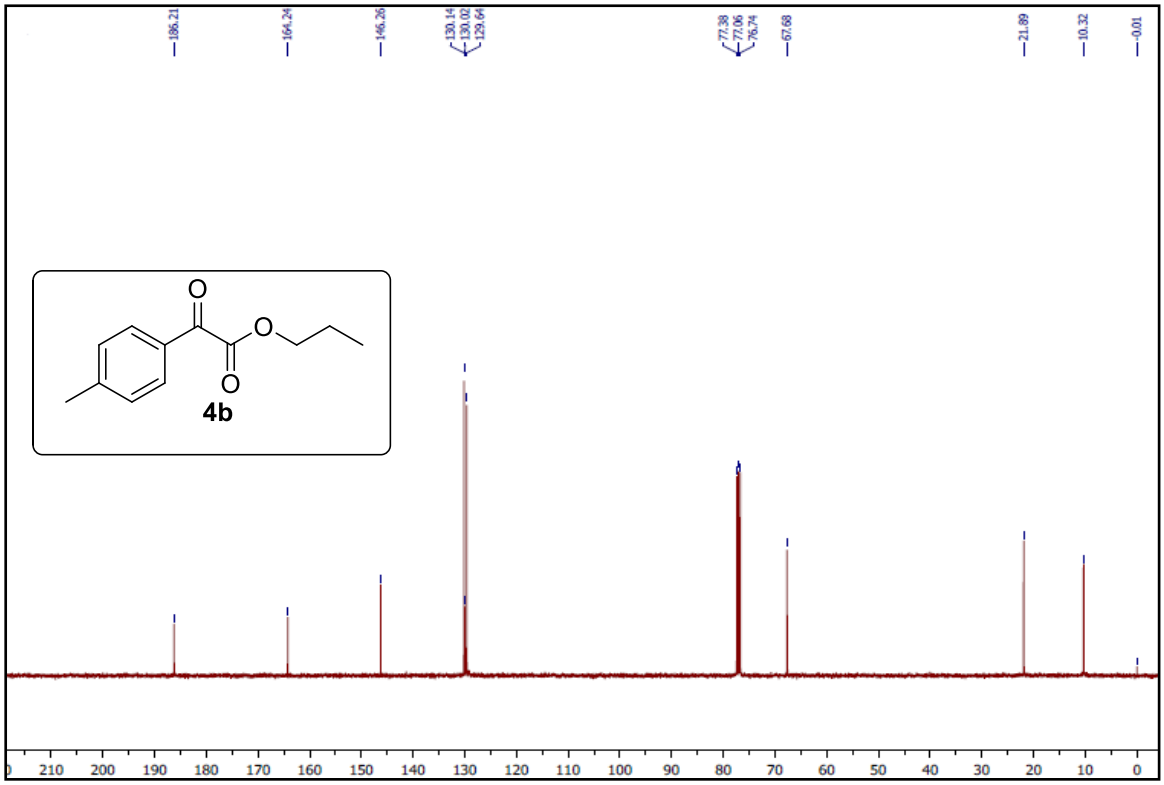
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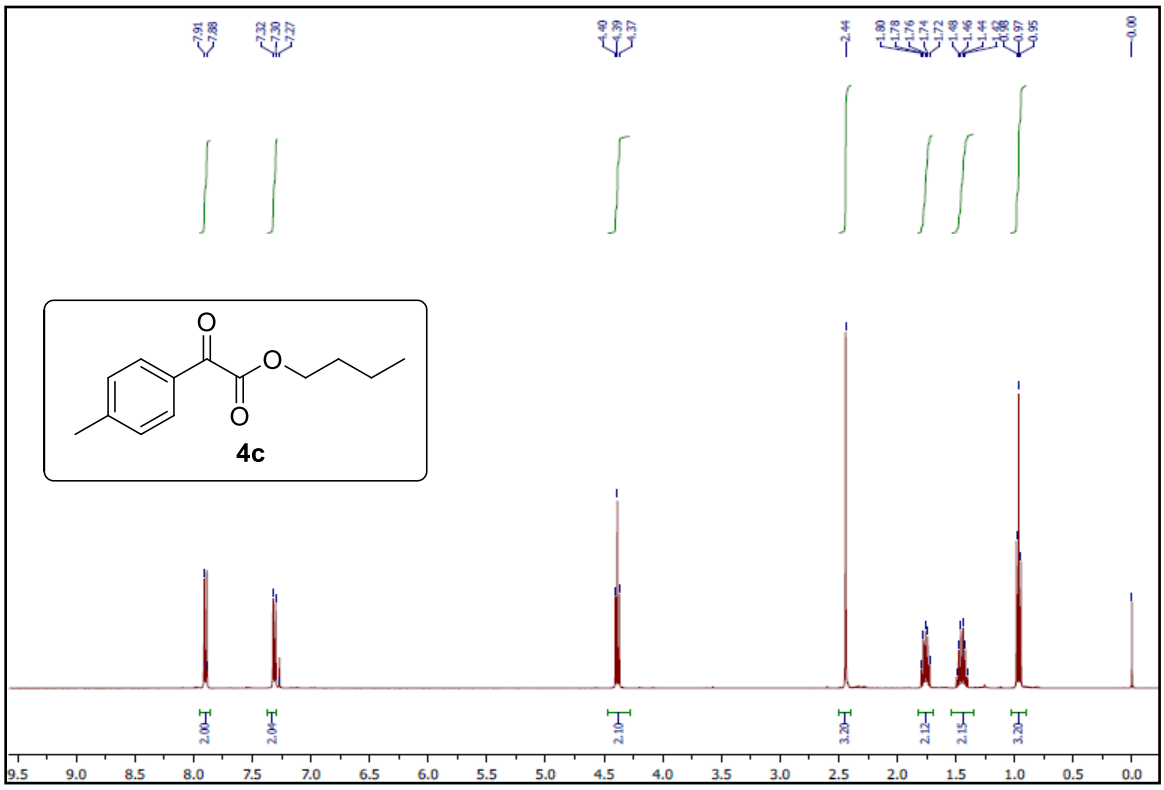
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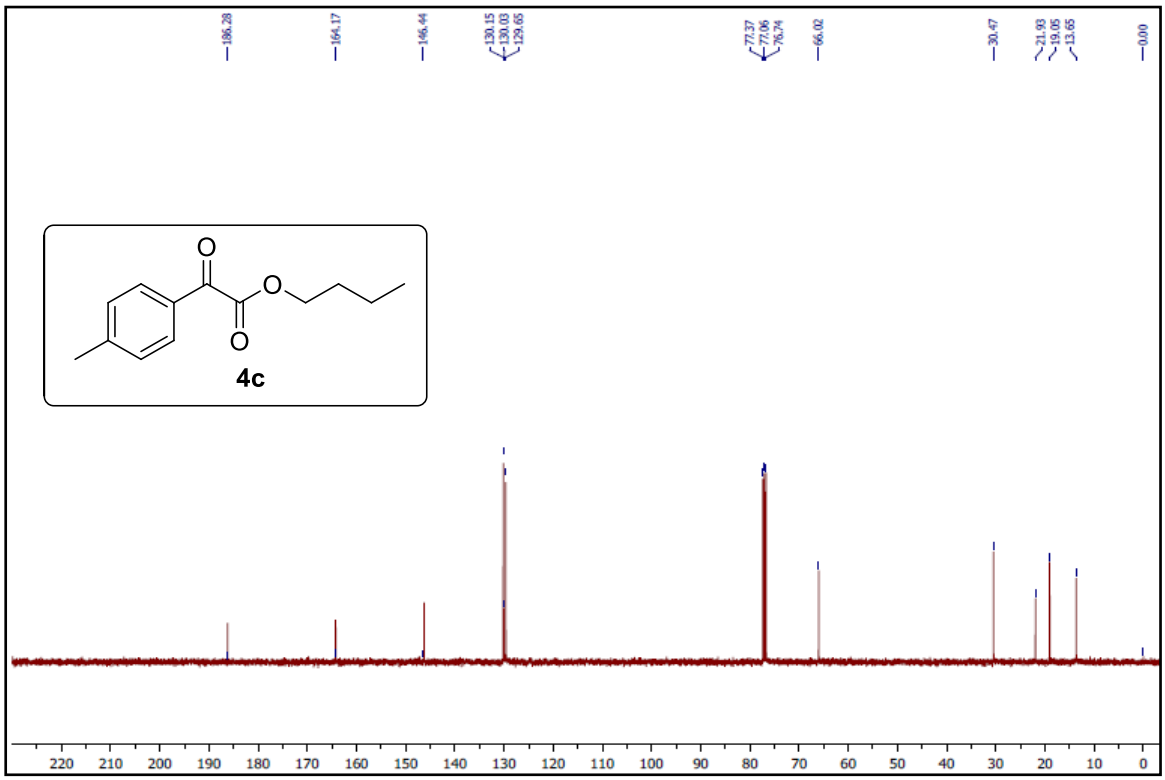
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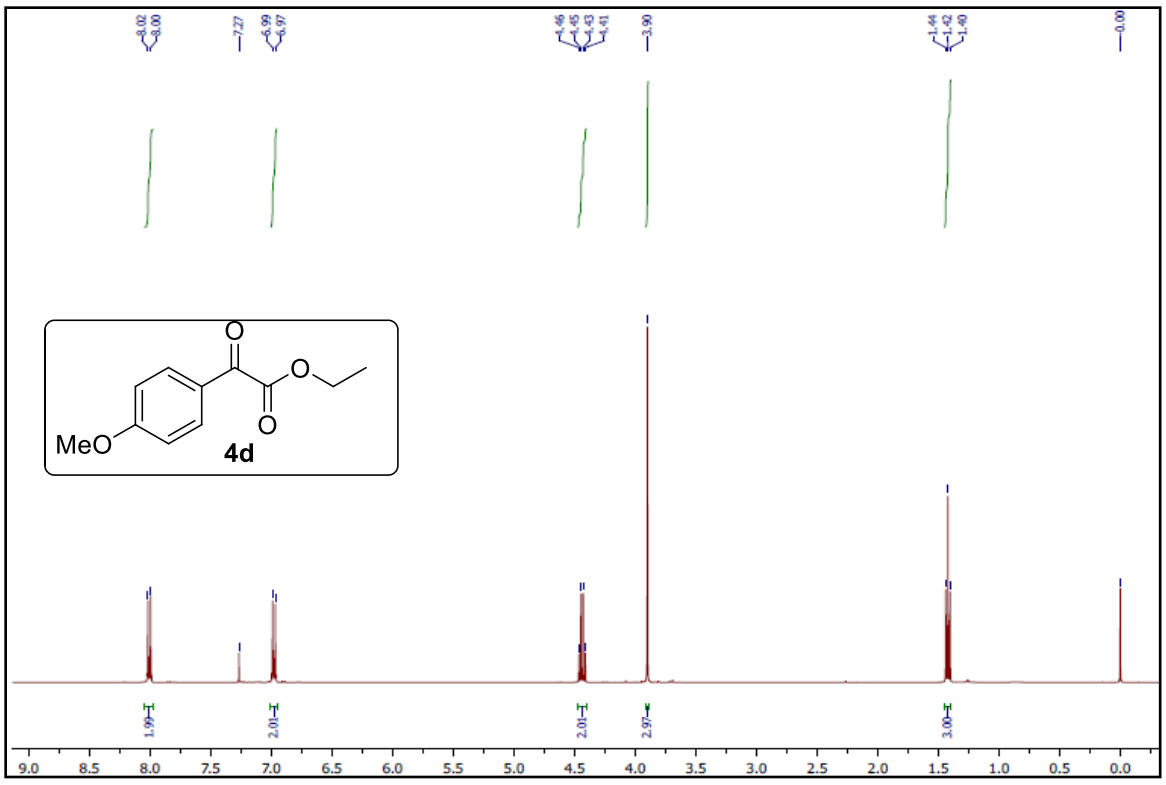
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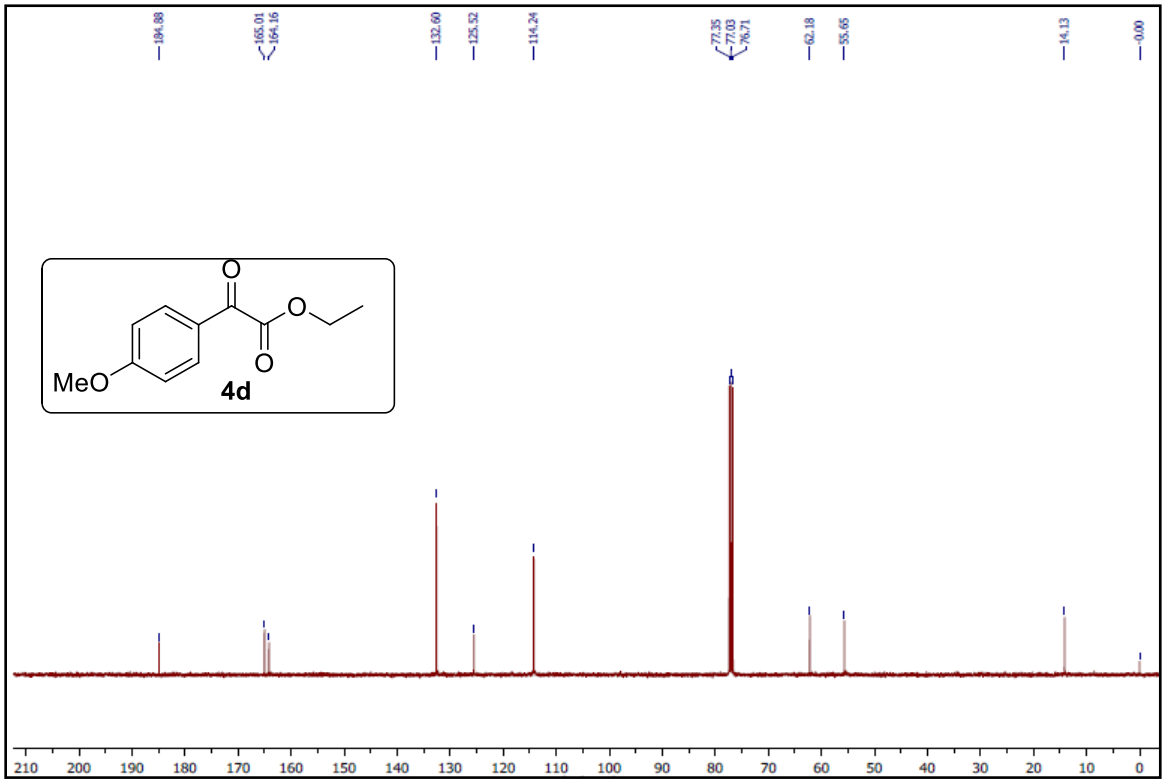
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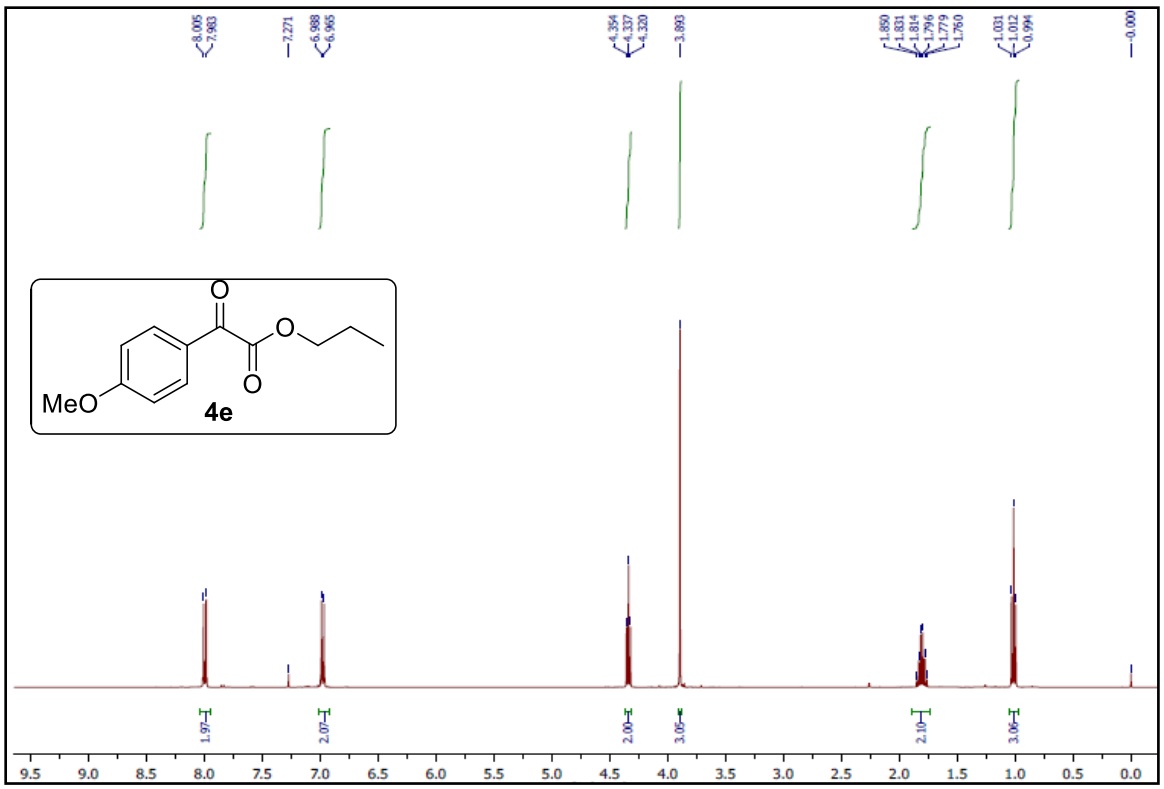
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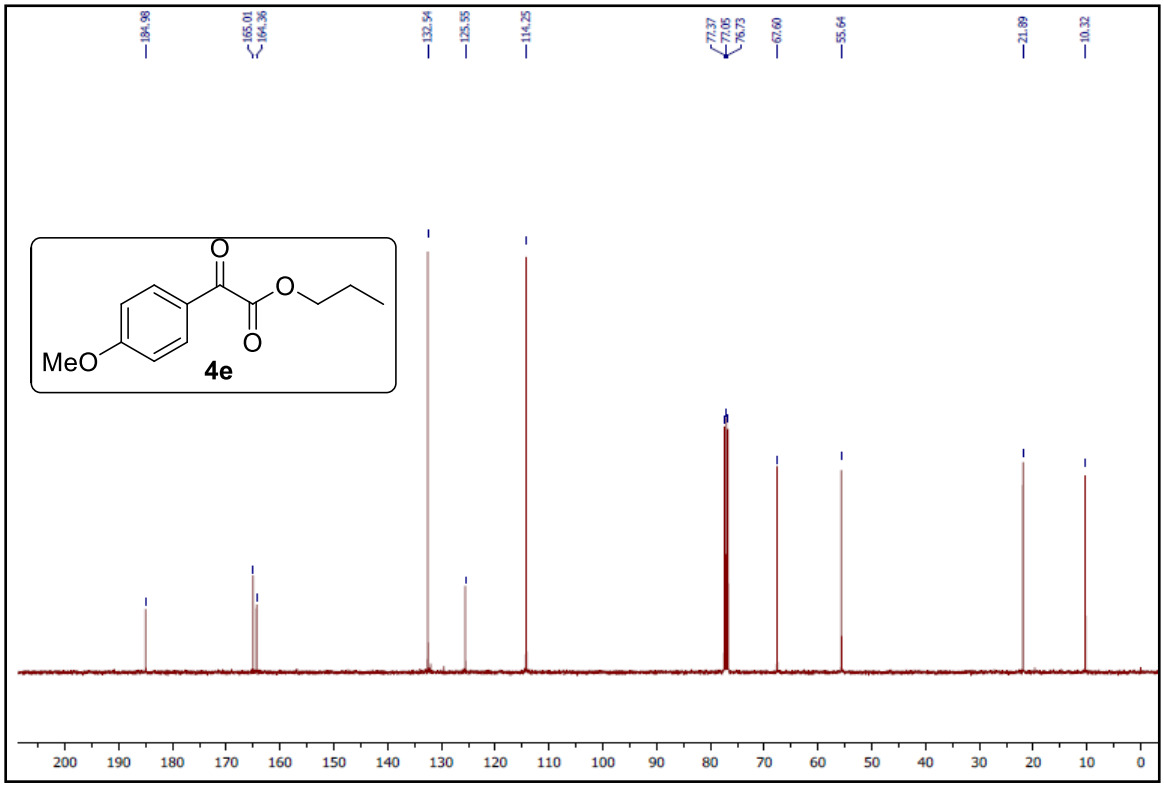
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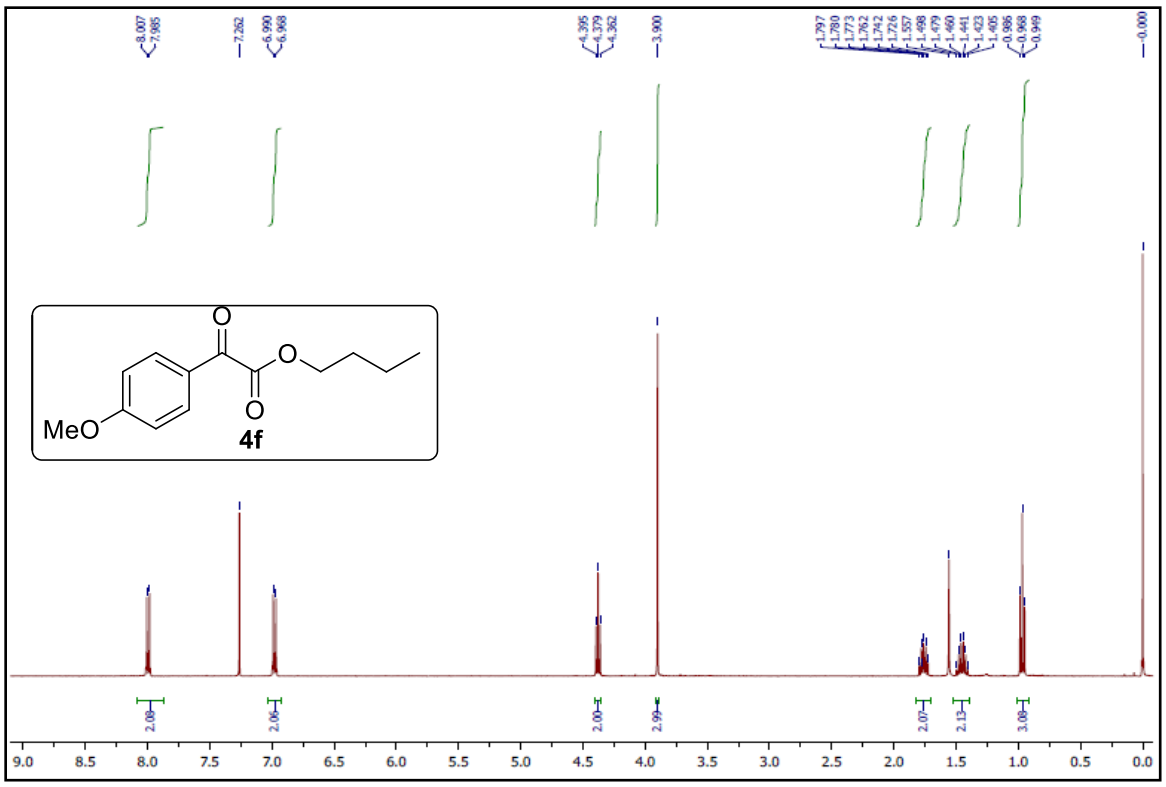
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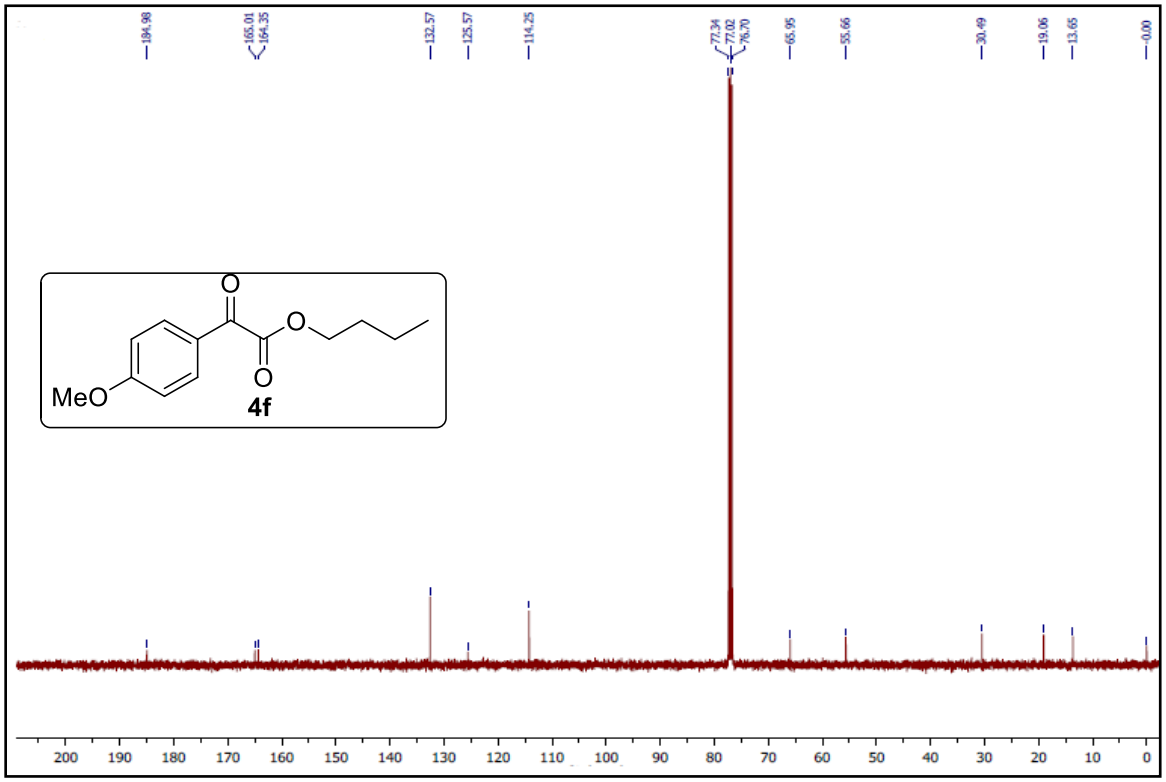
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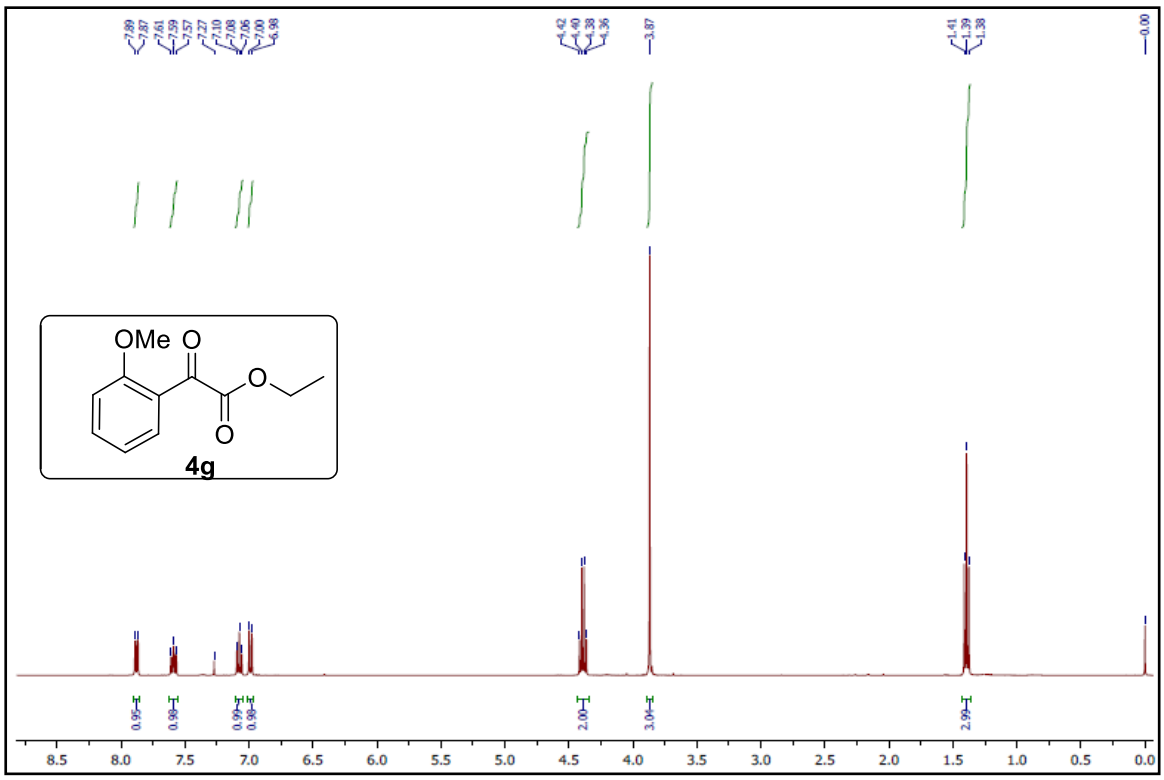
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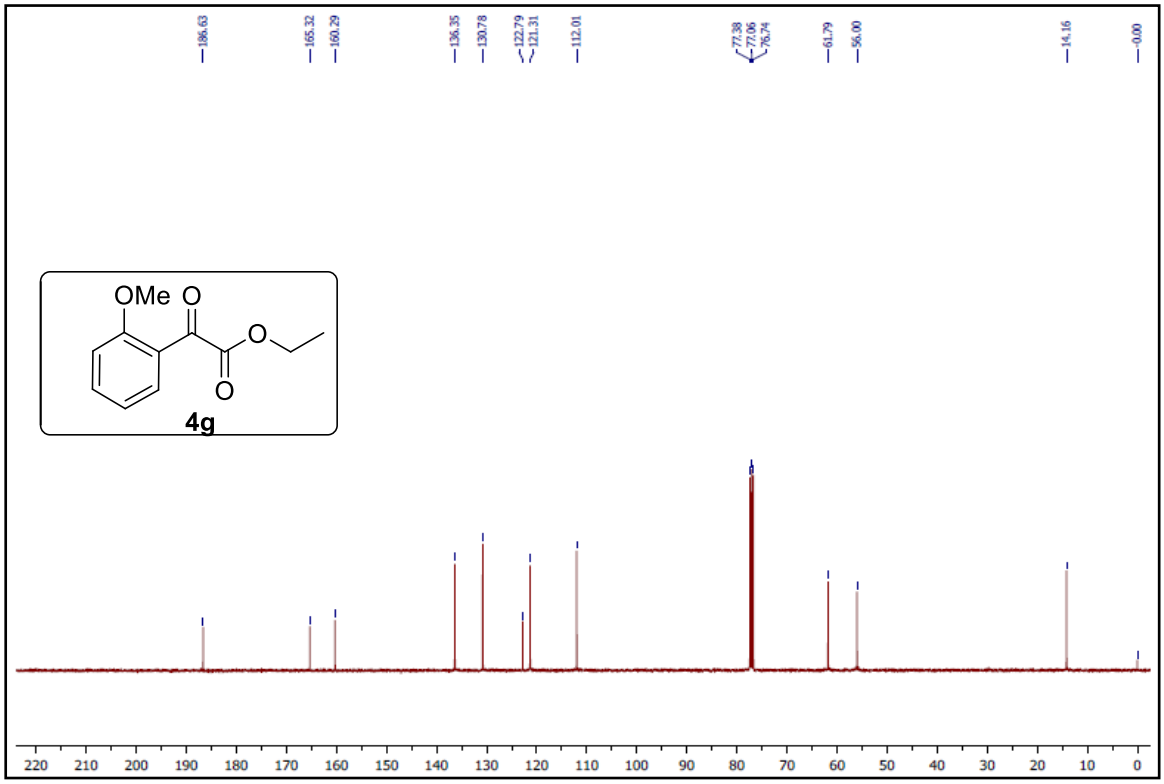
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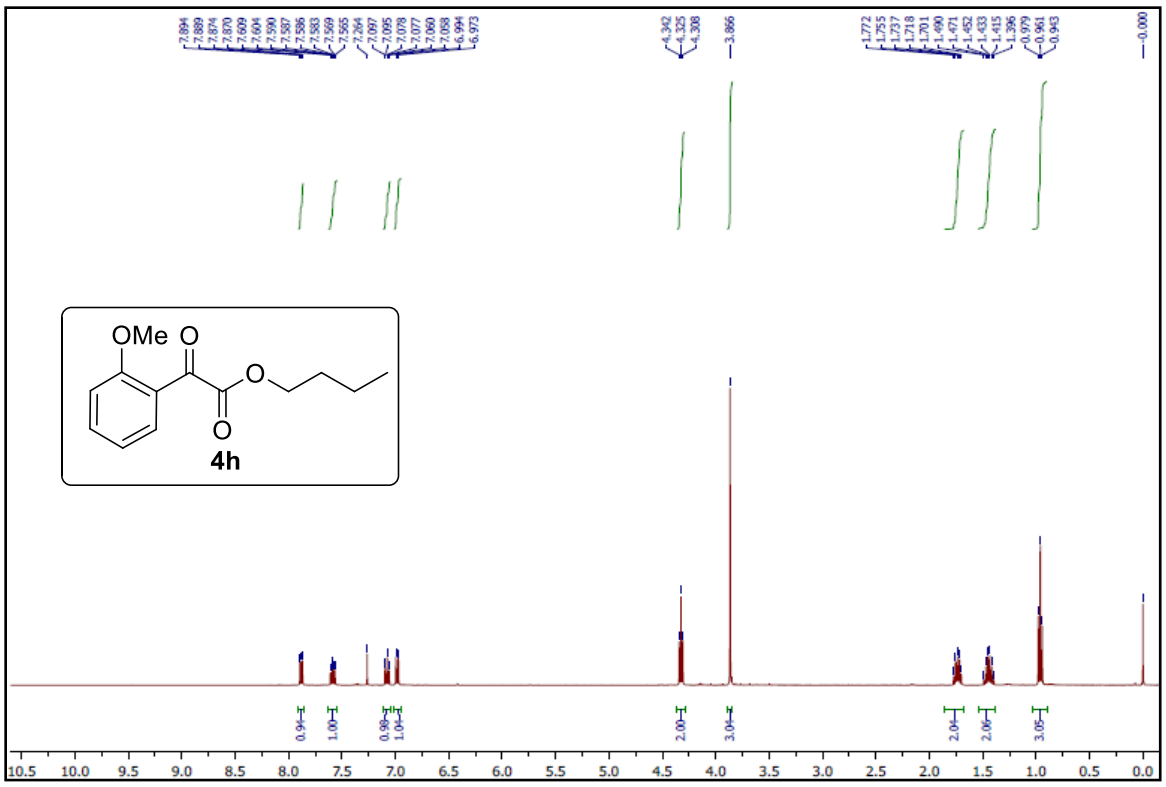
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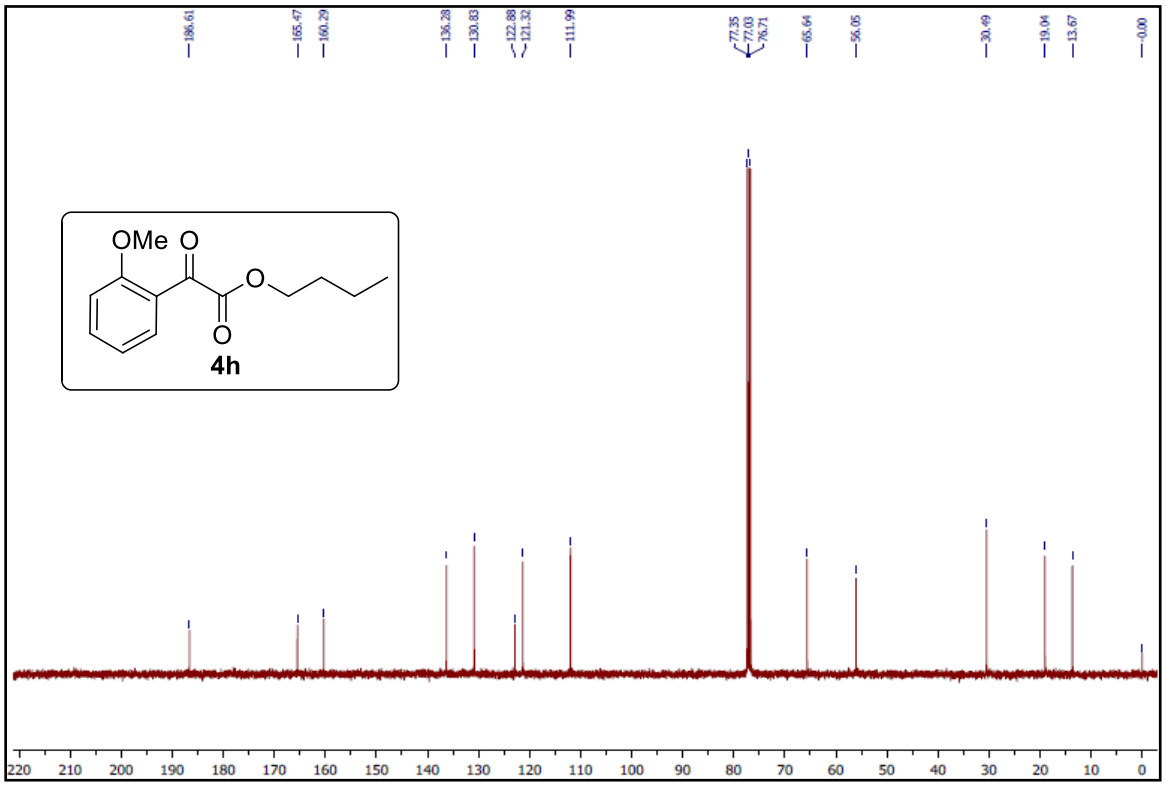
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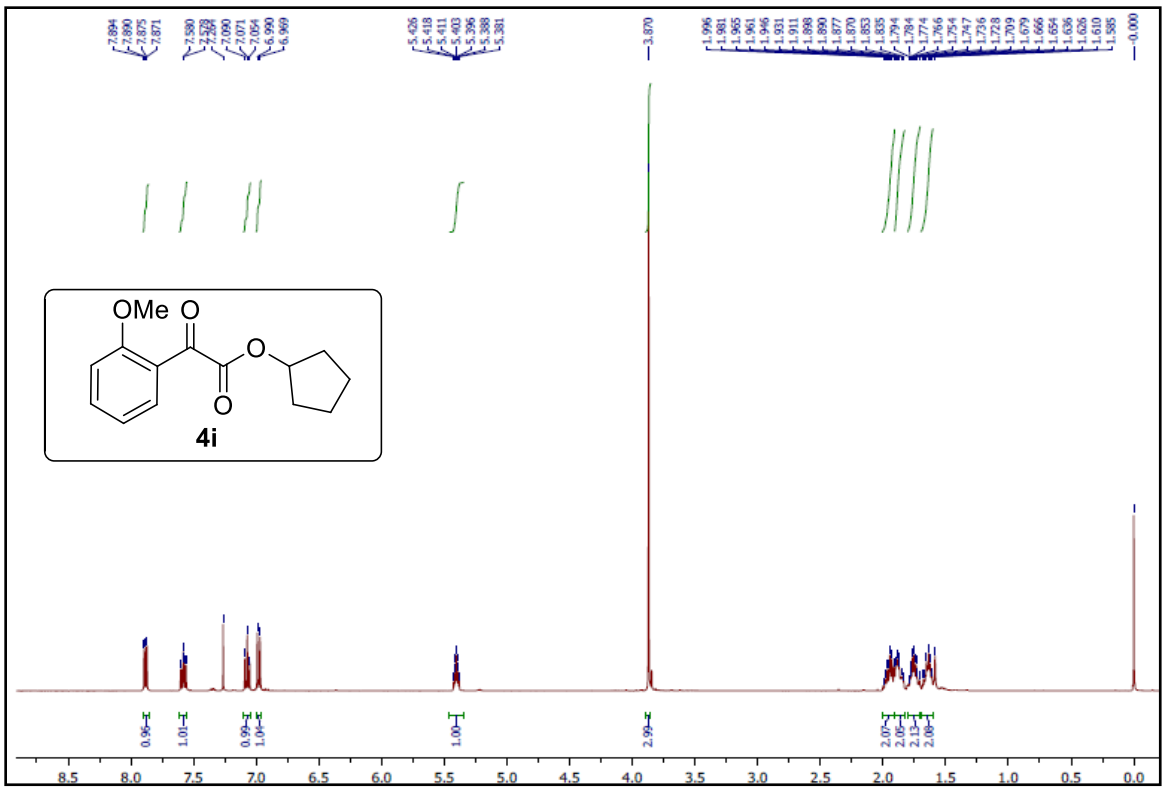
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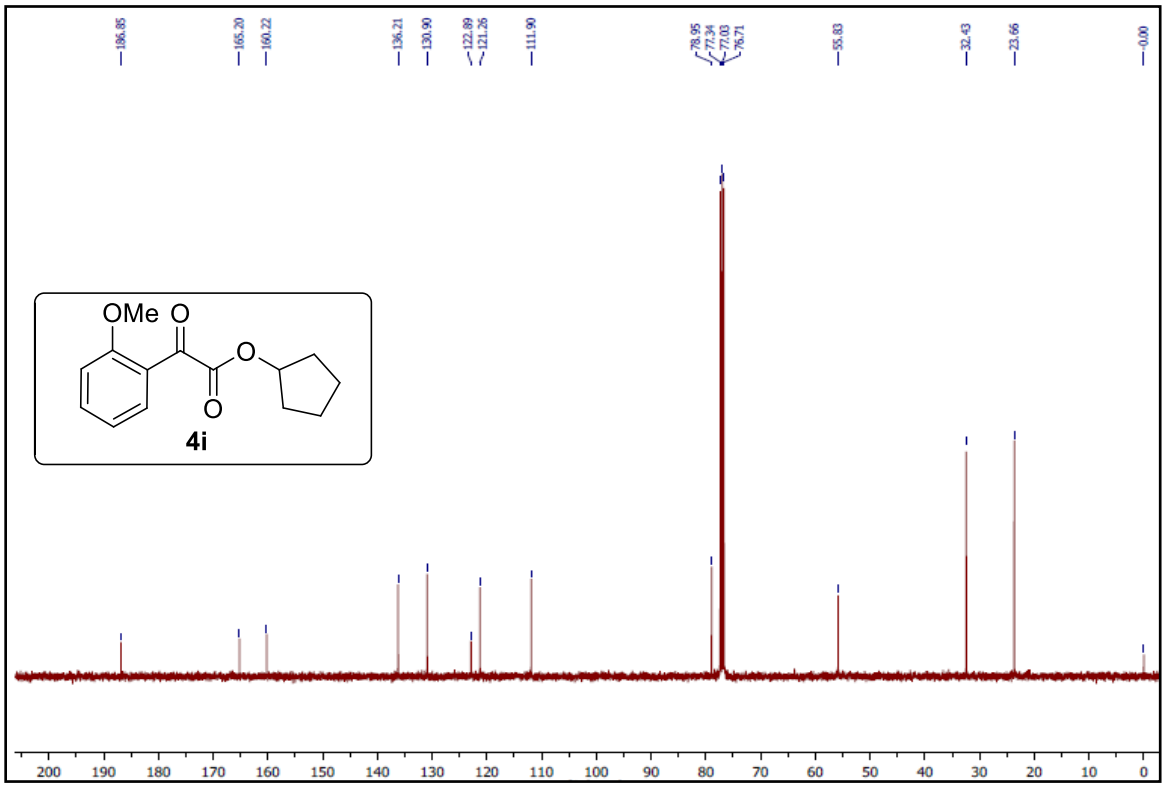
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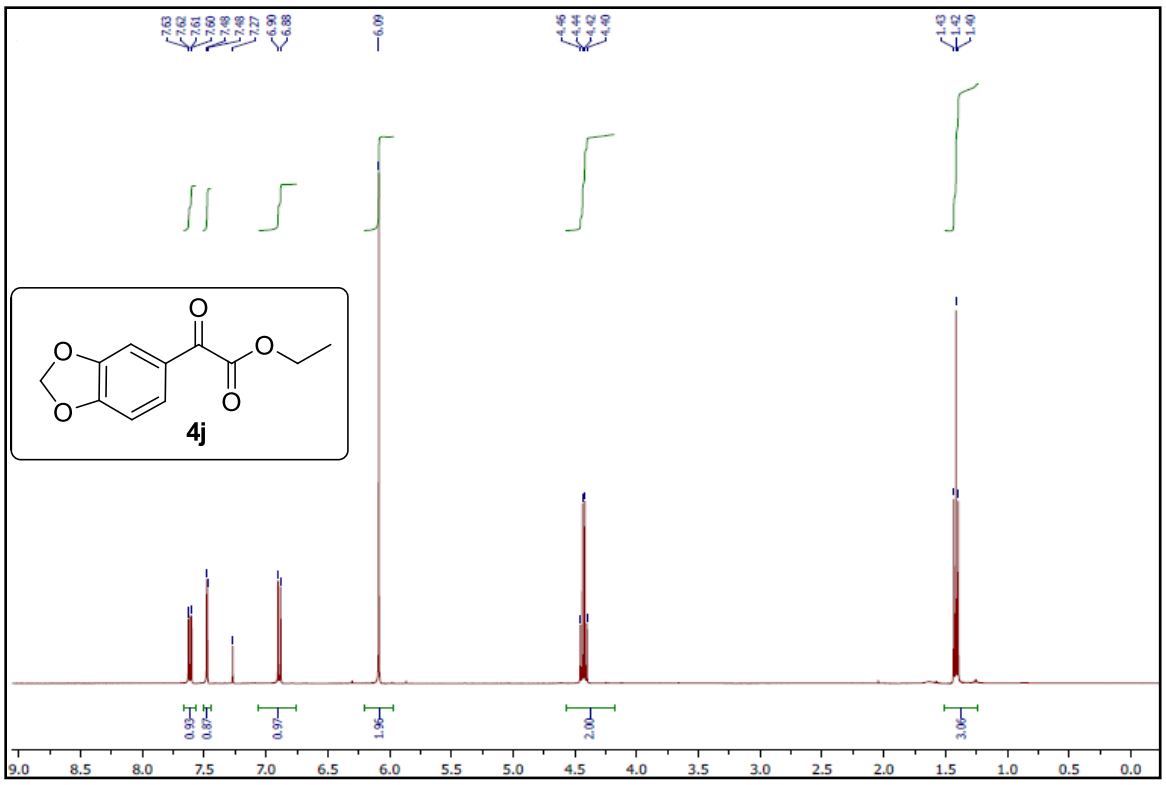
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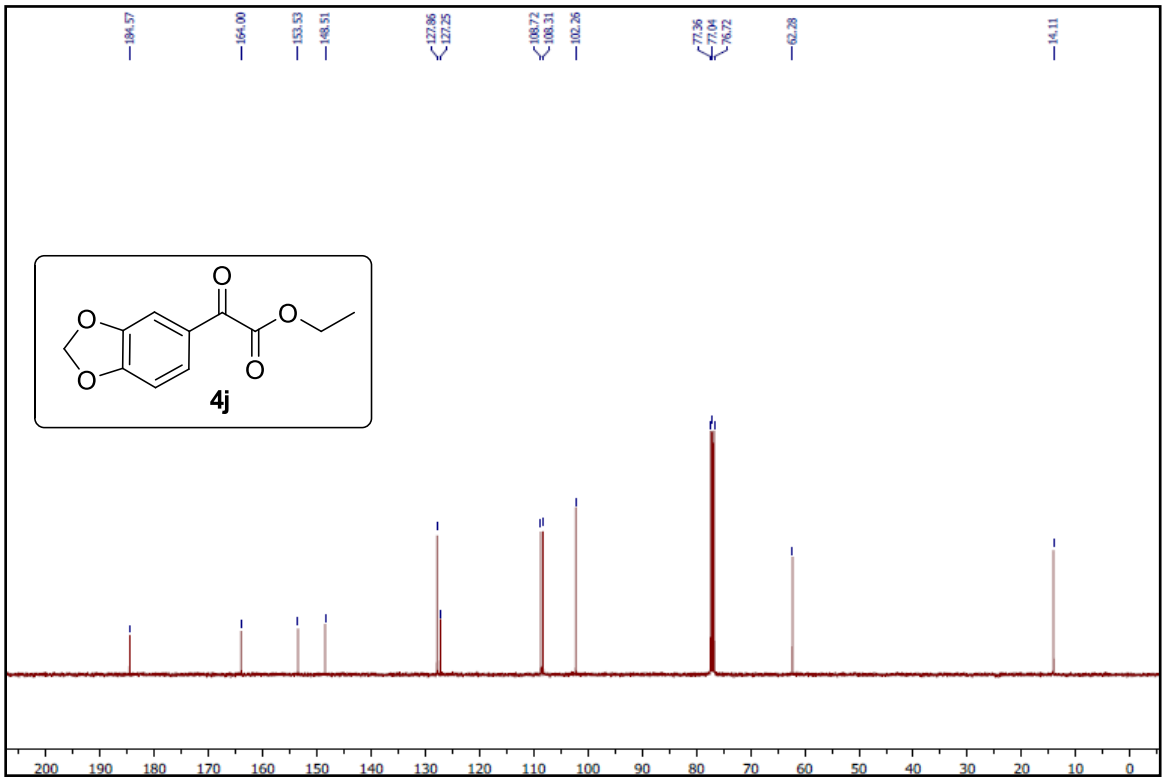
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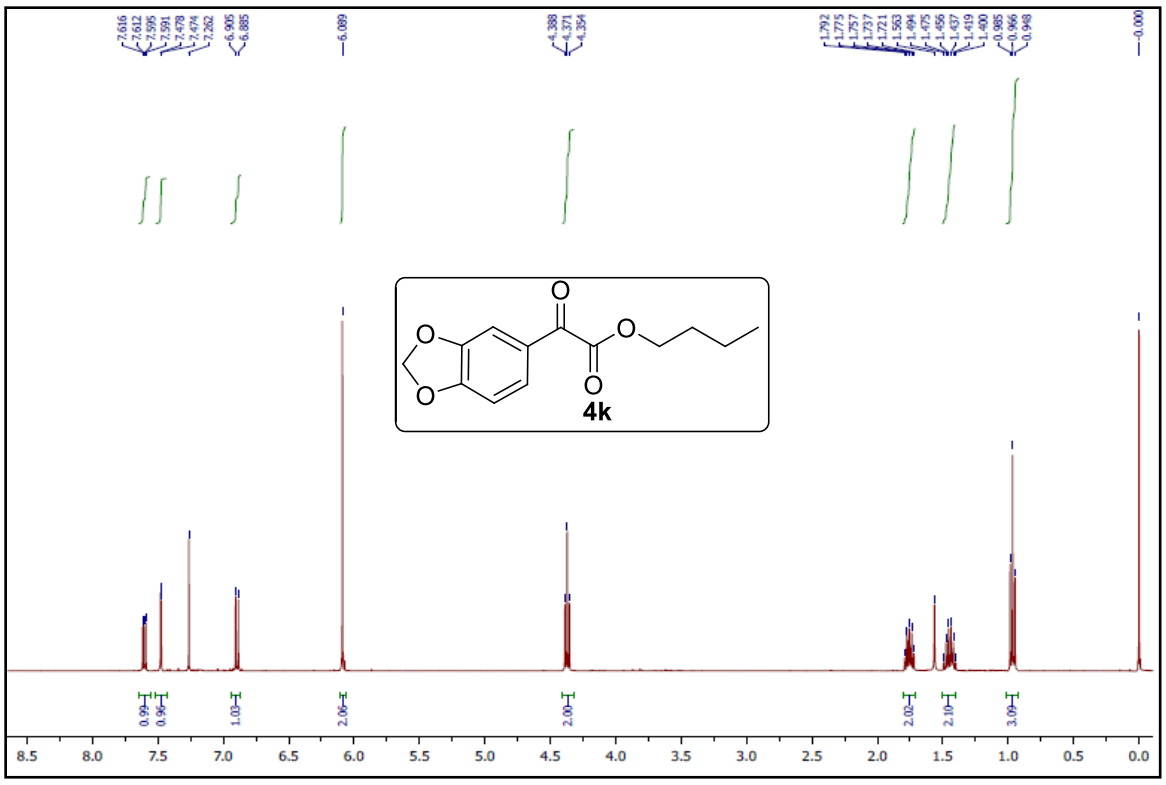
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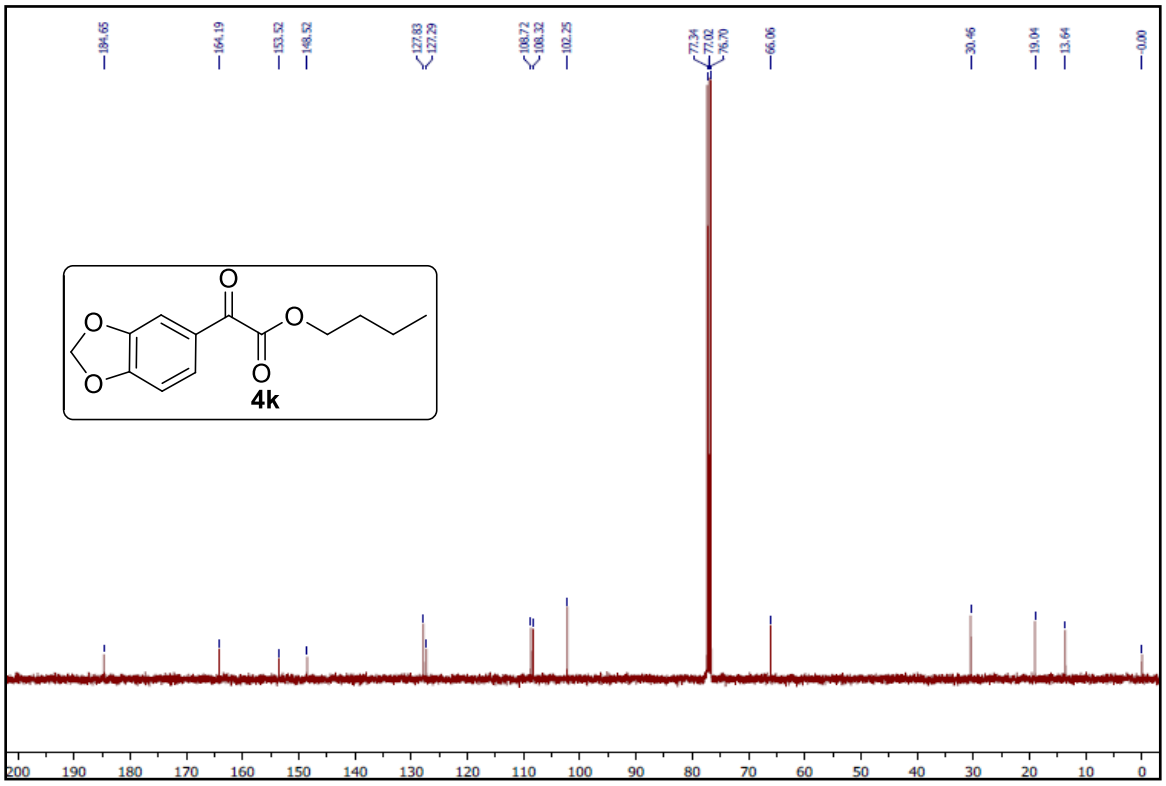
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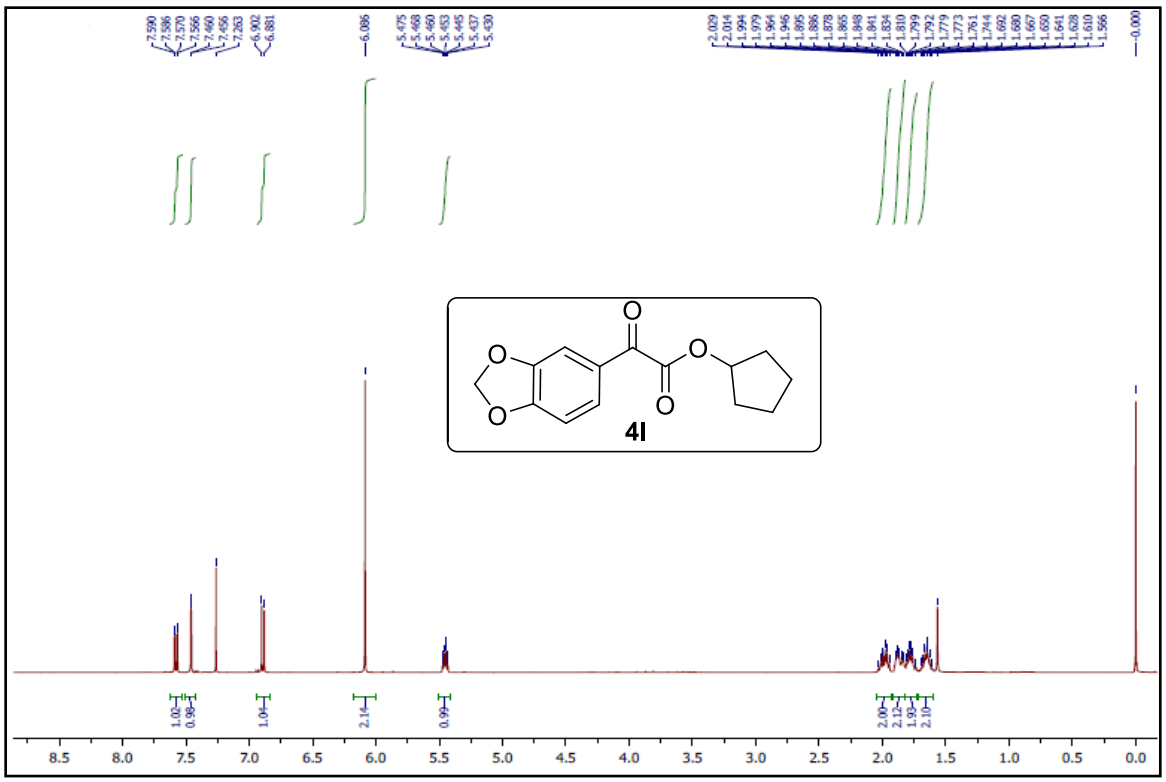
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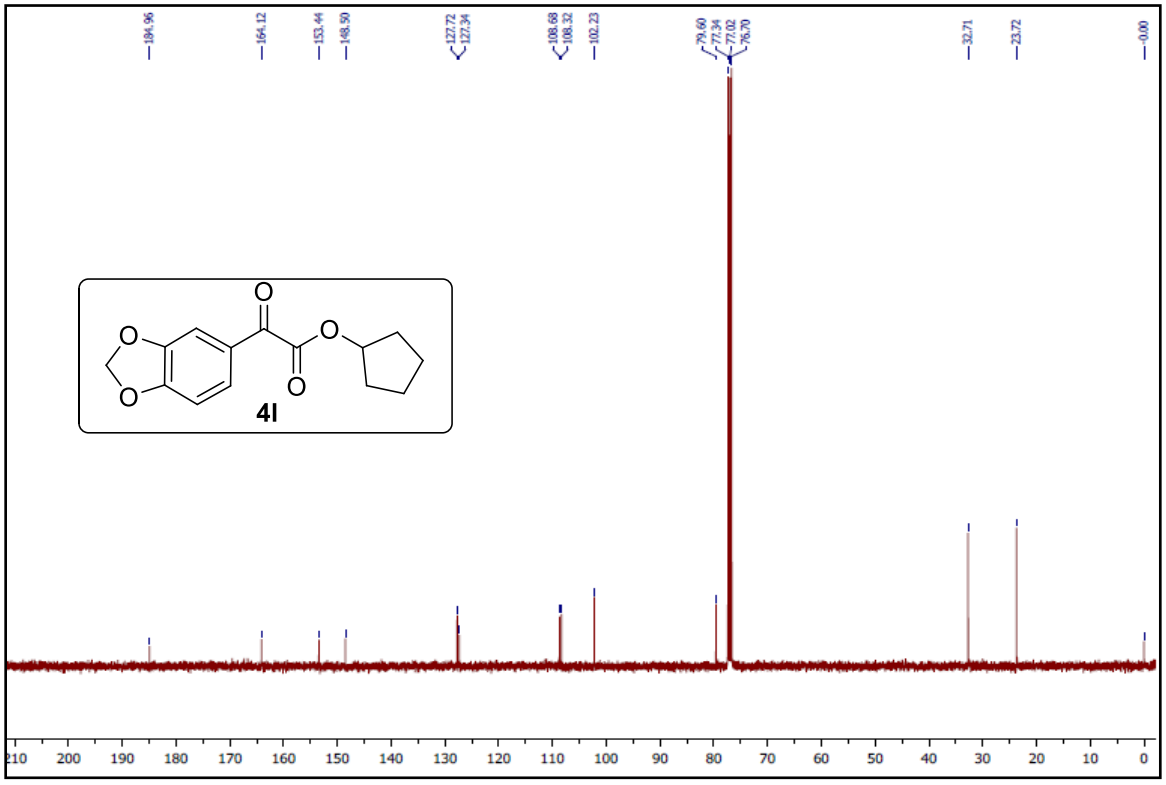
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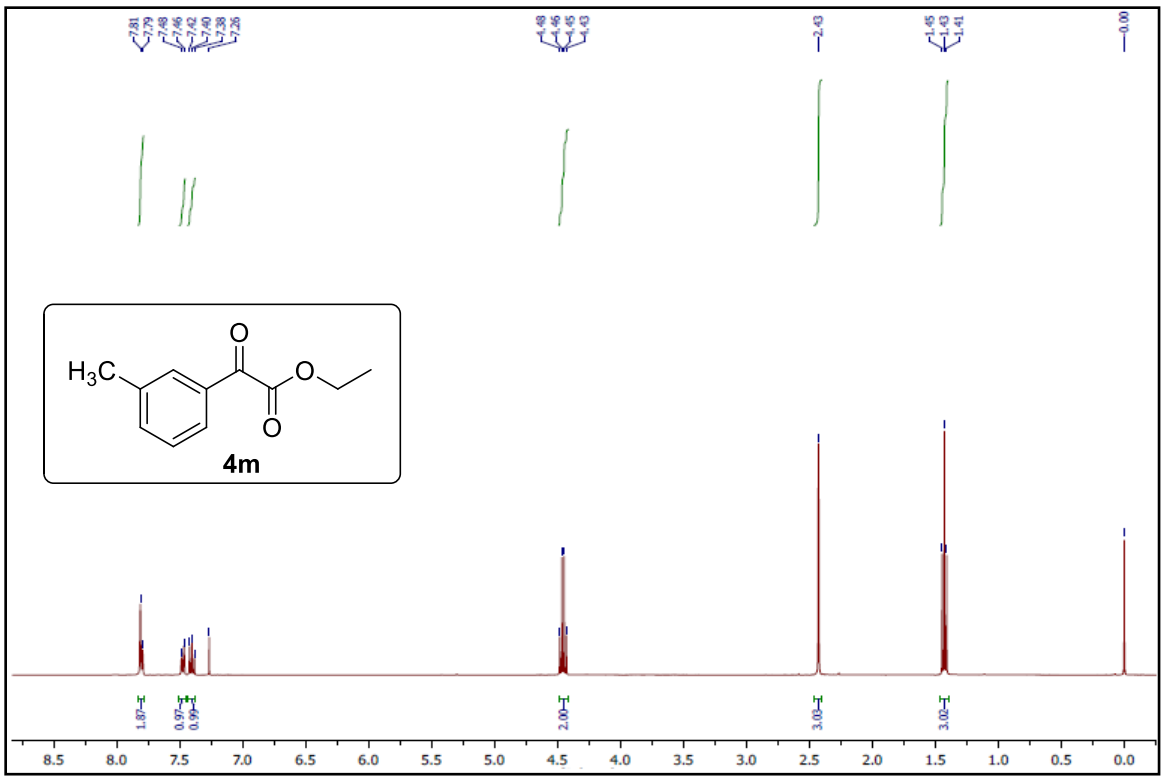
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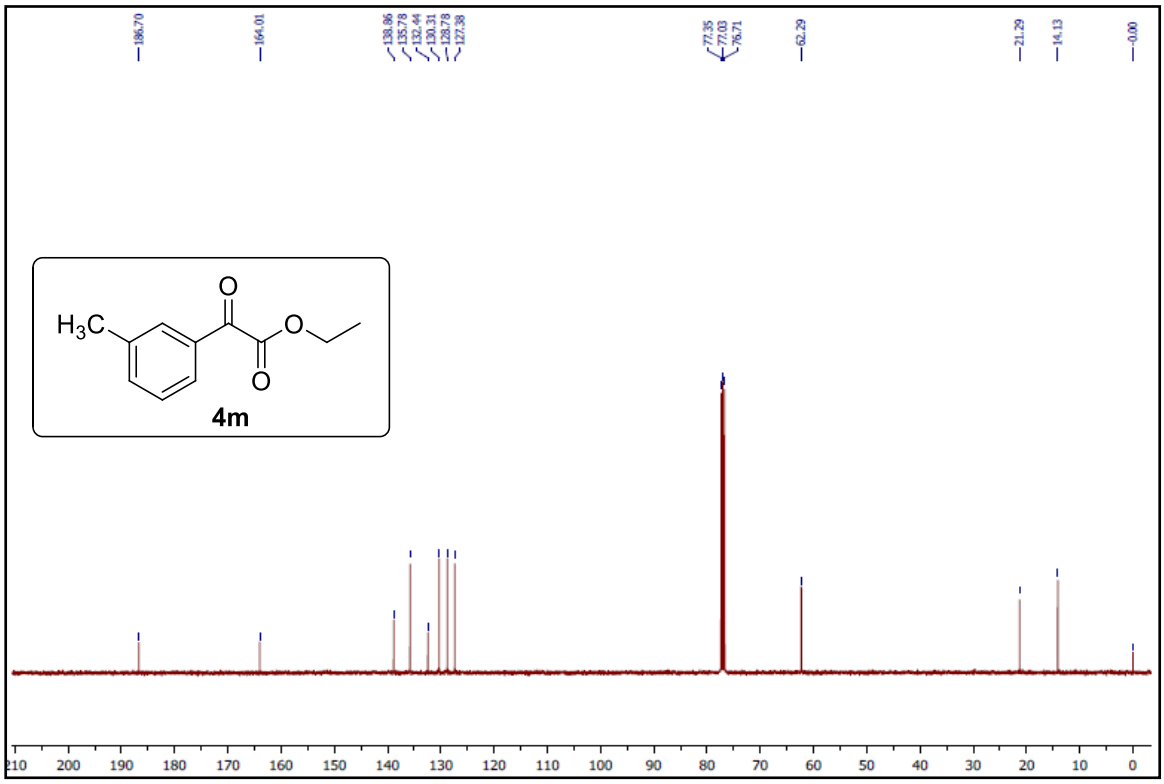
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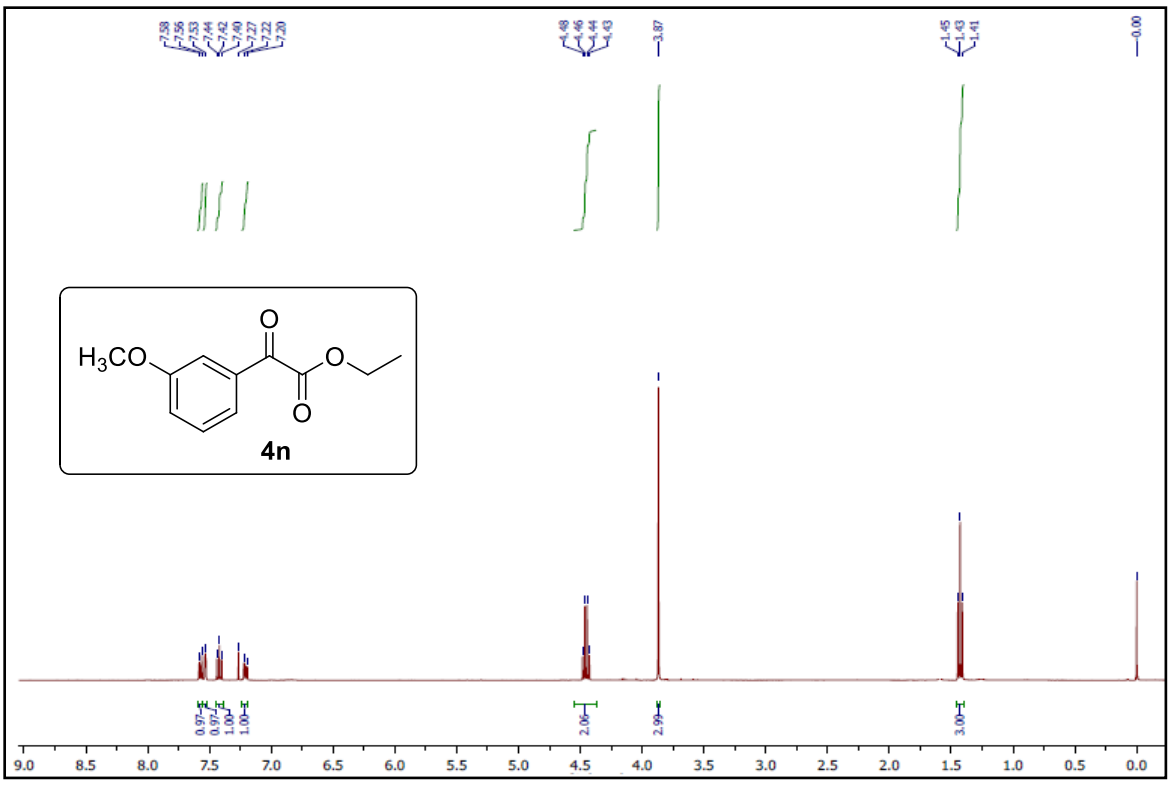
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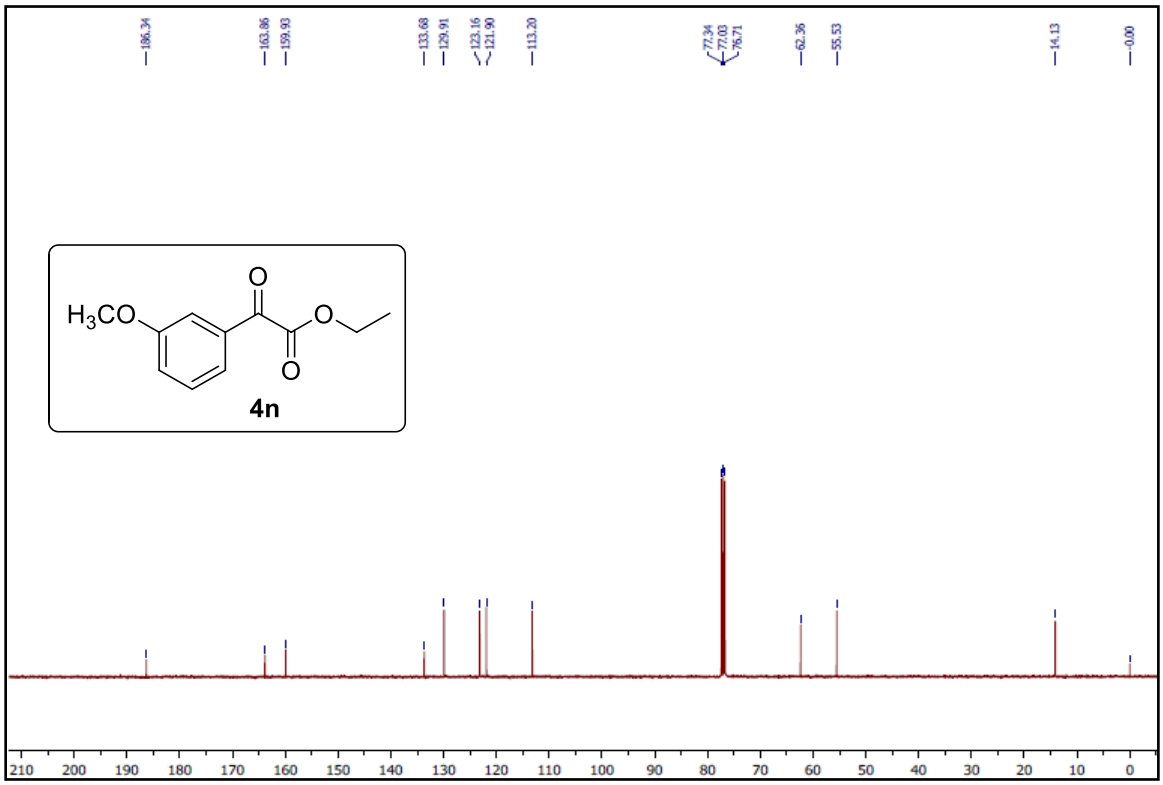
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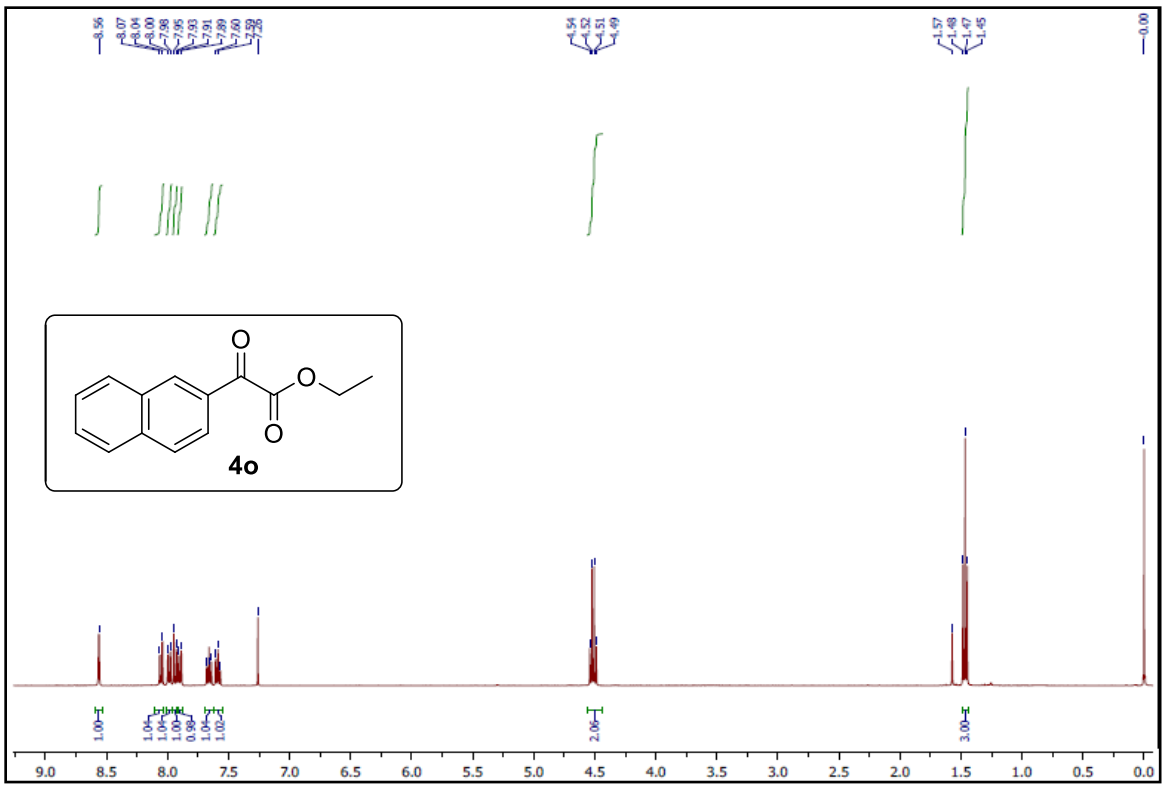
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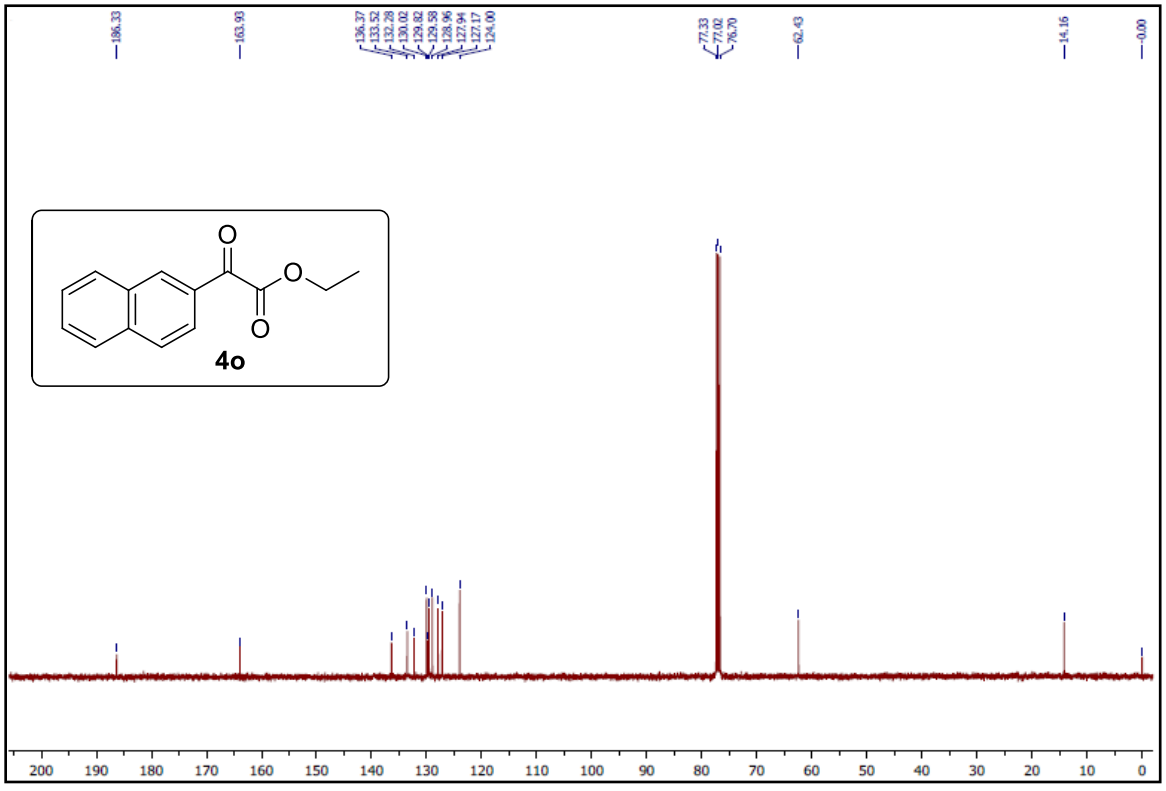
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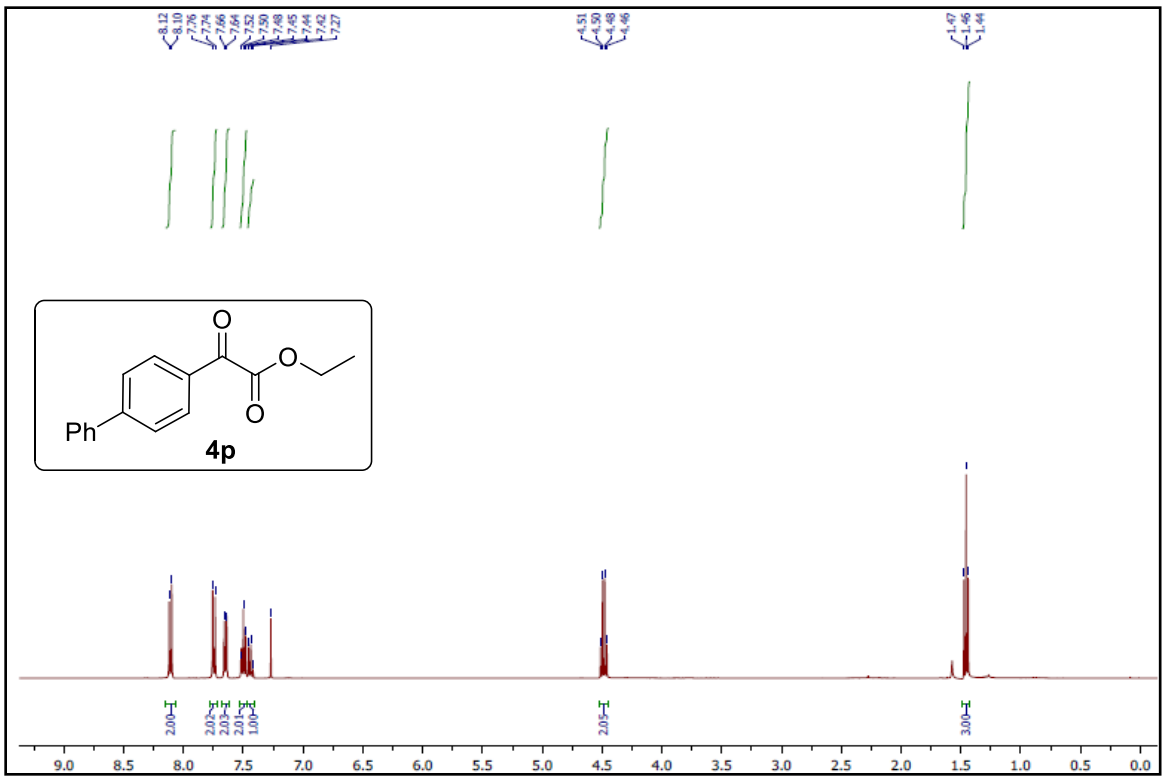
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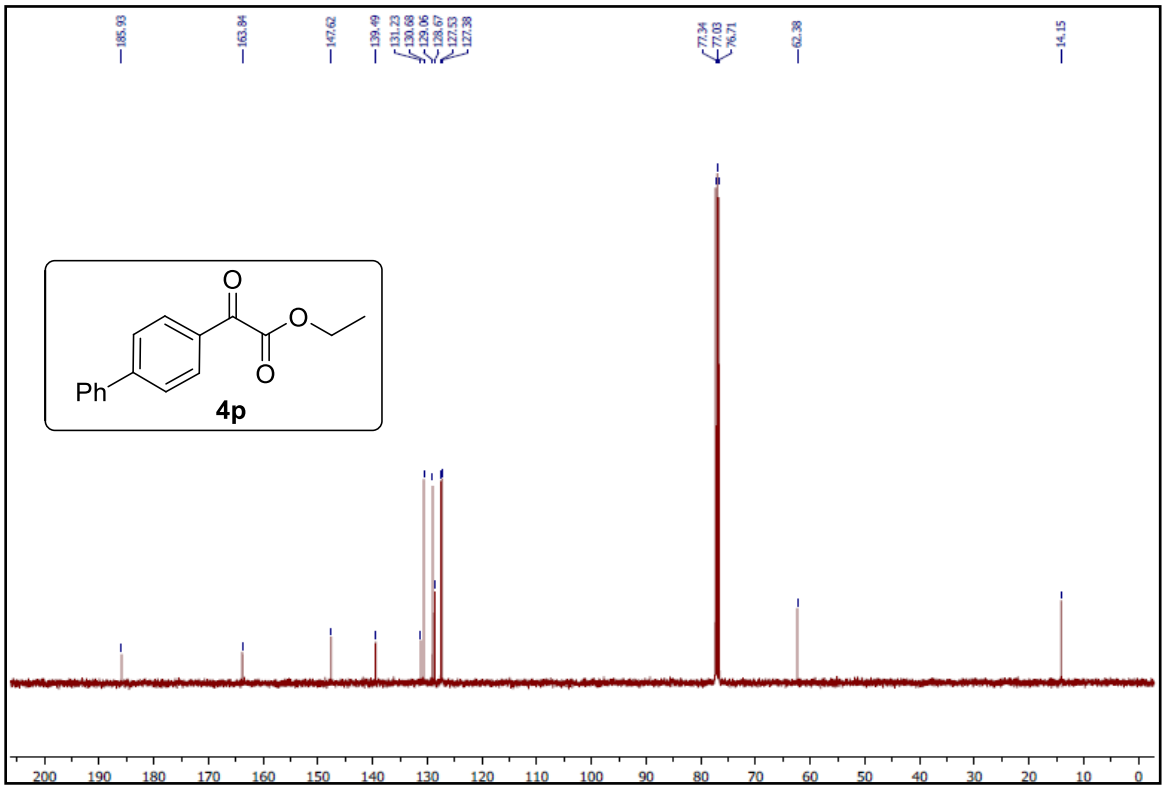
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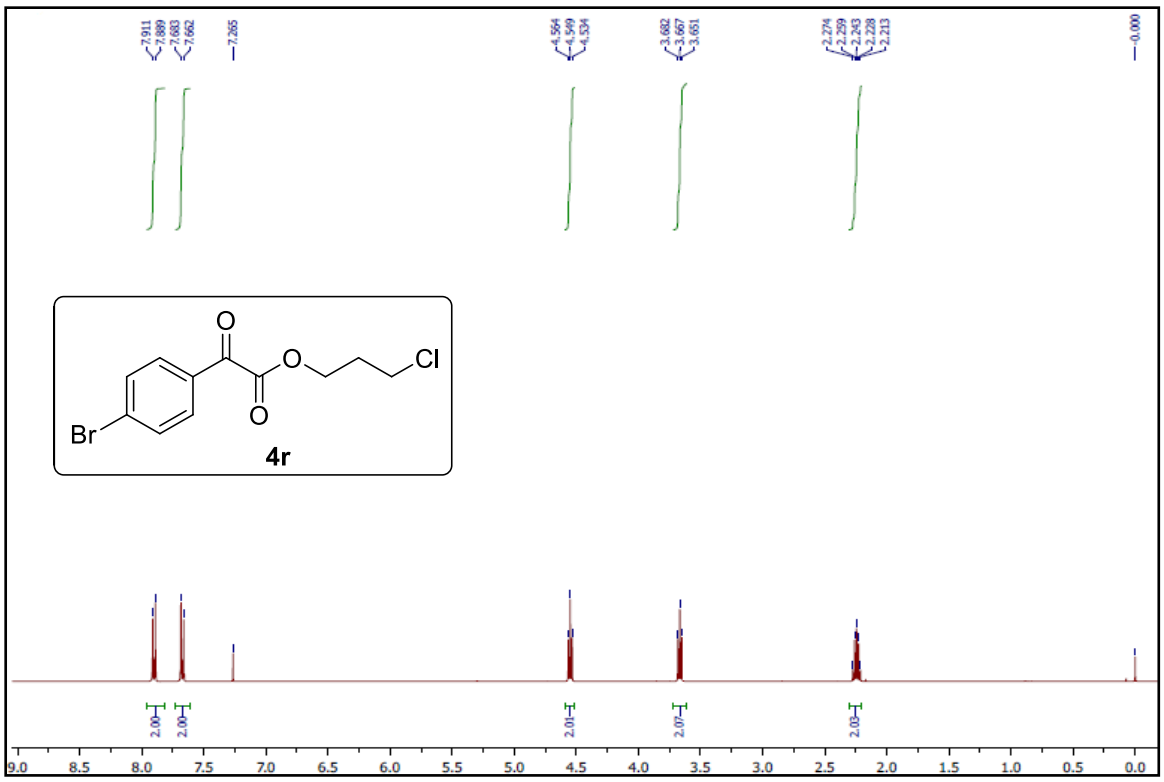
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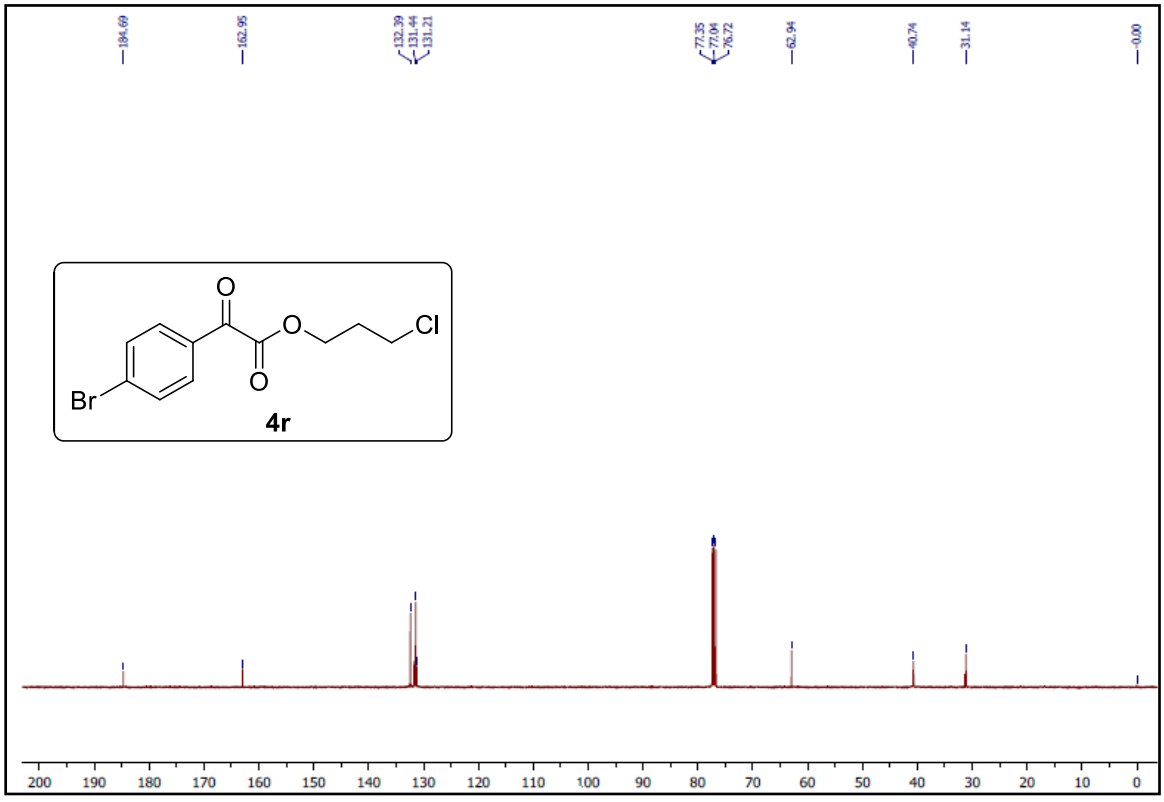
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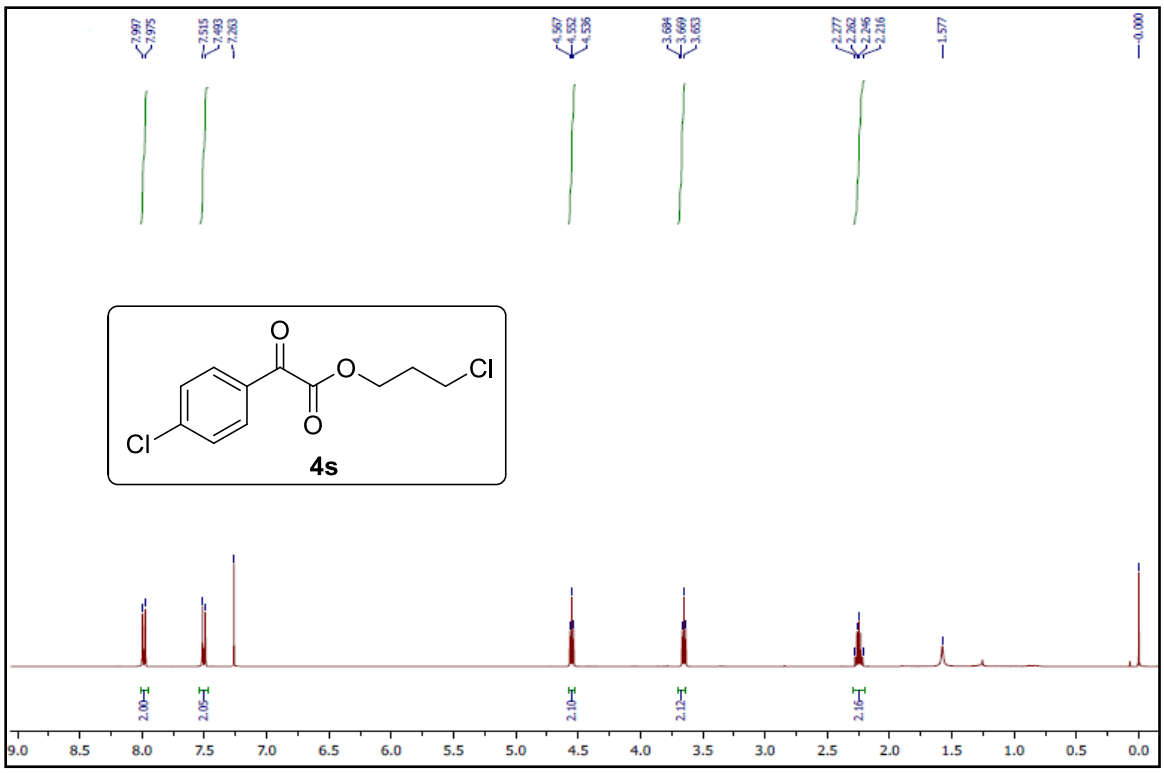
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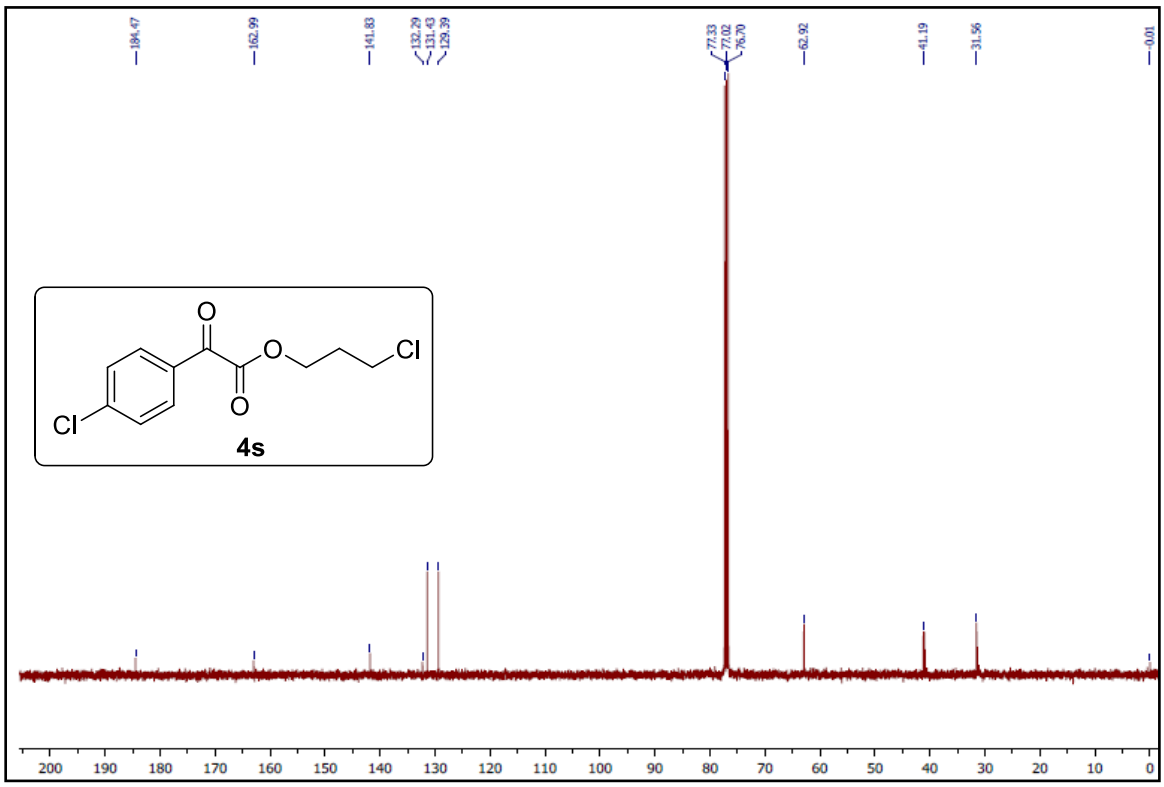
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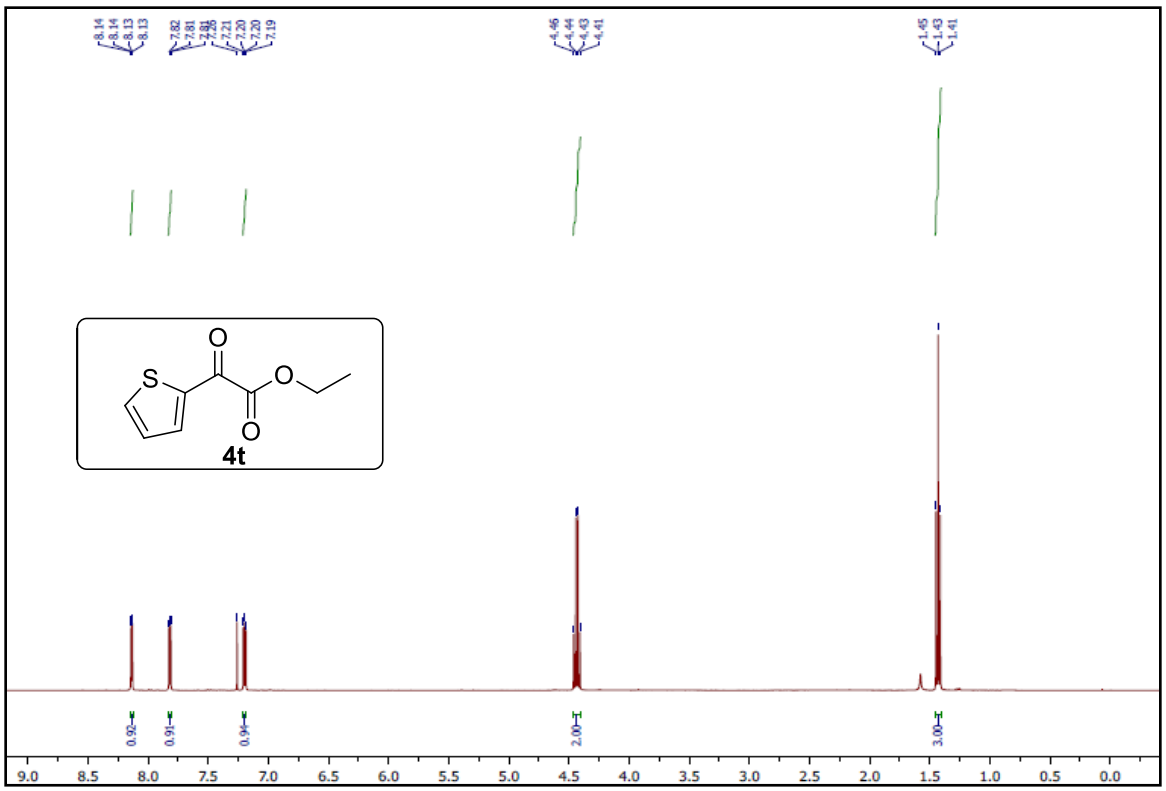
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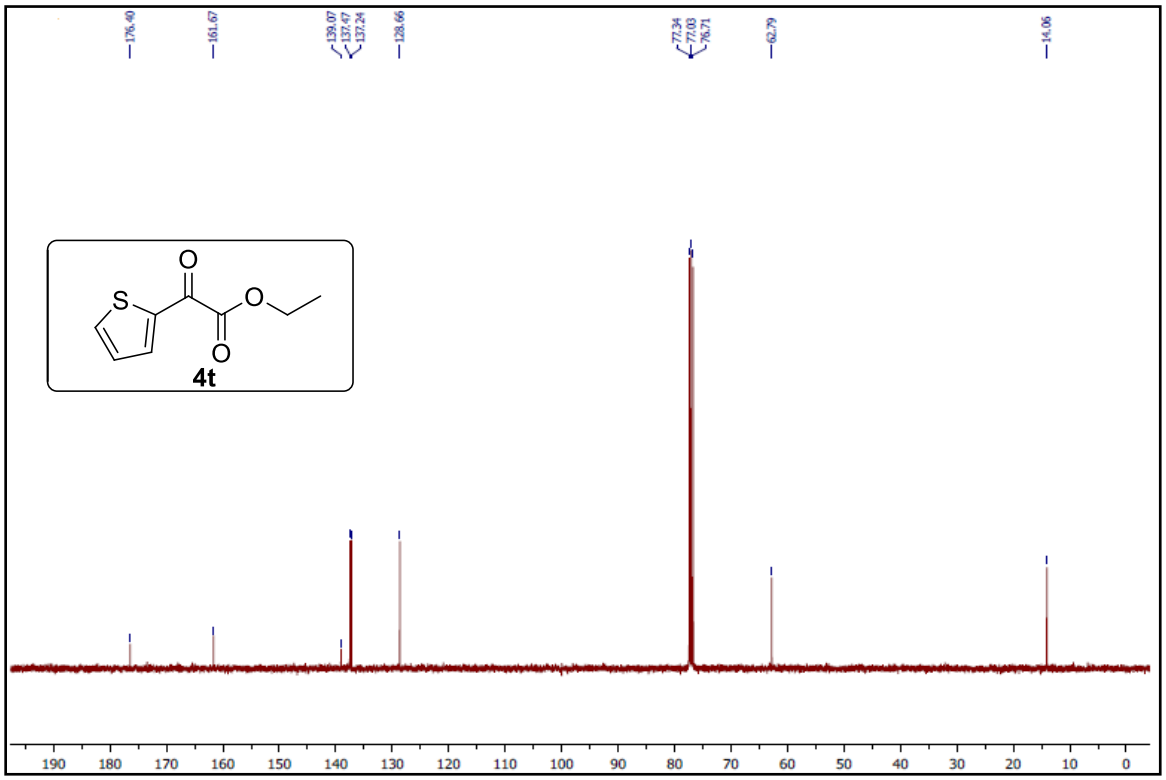
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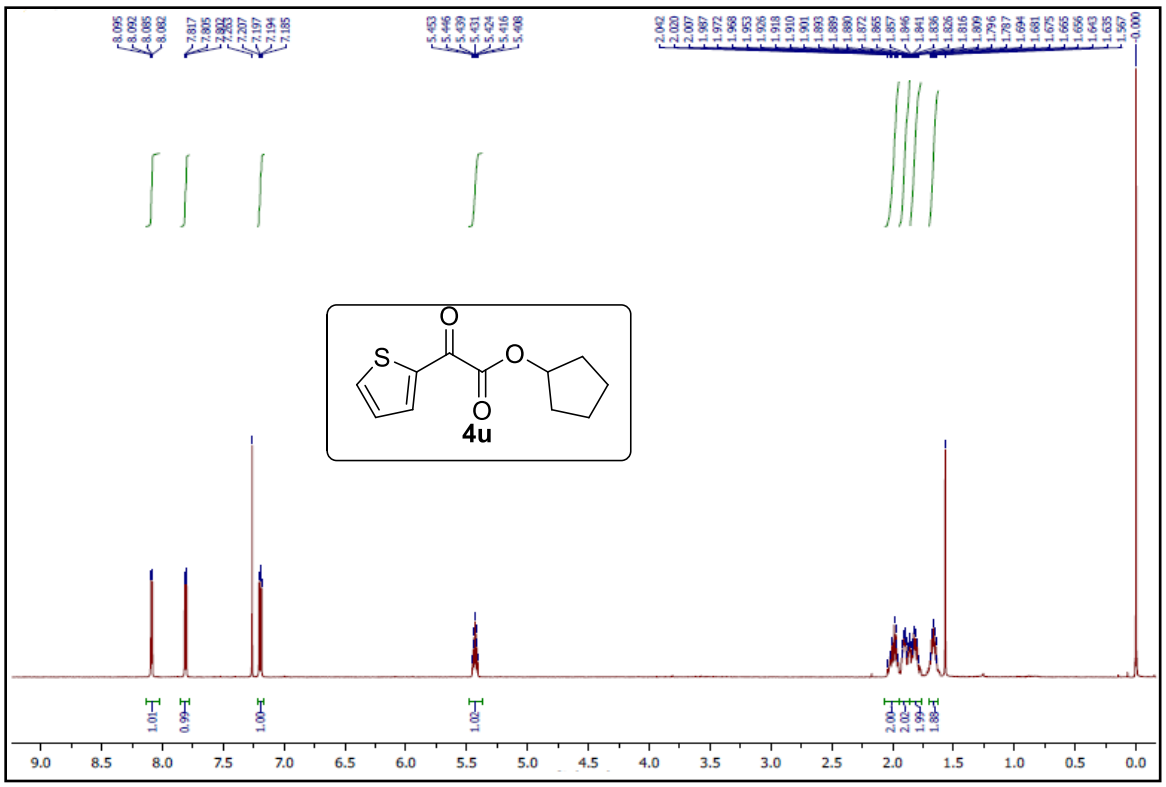
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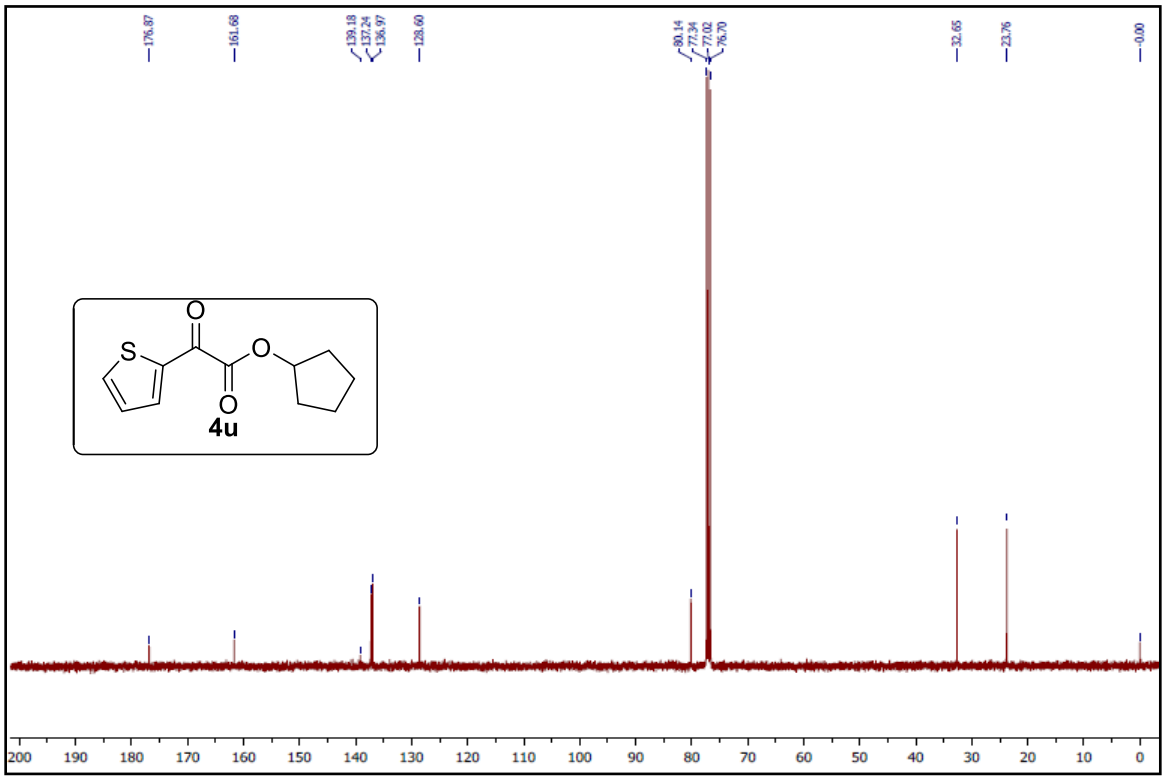
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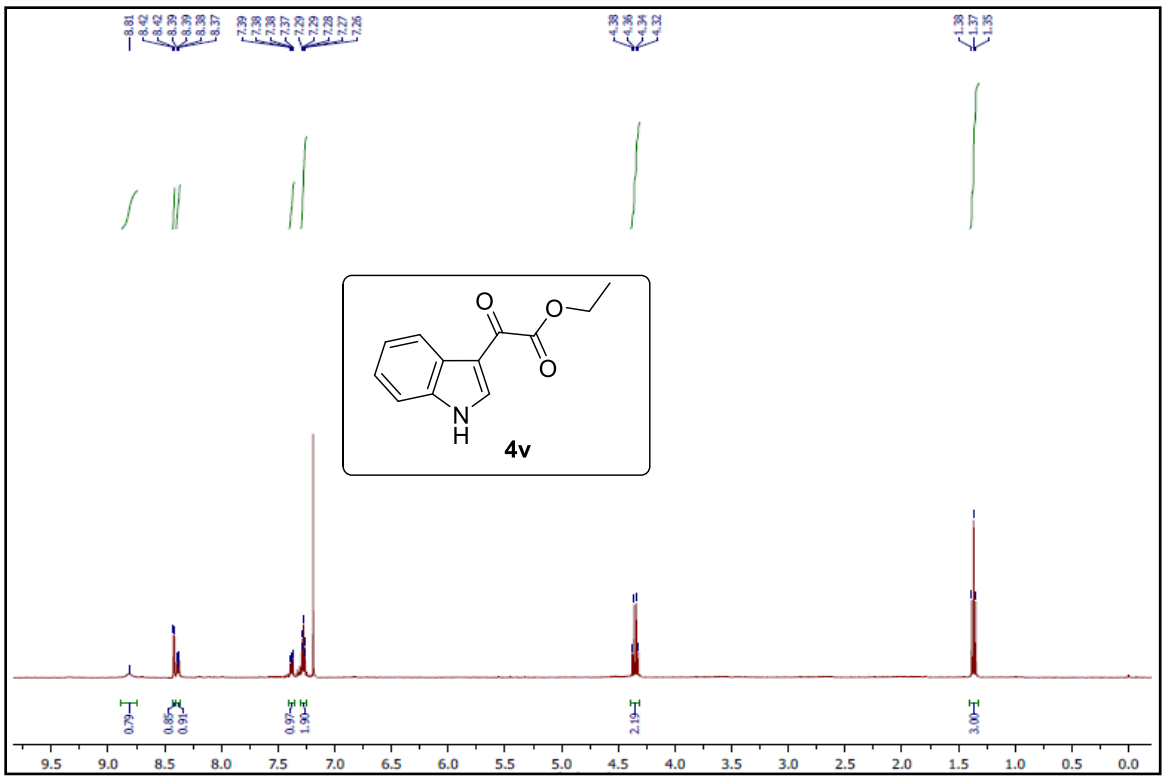
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4v
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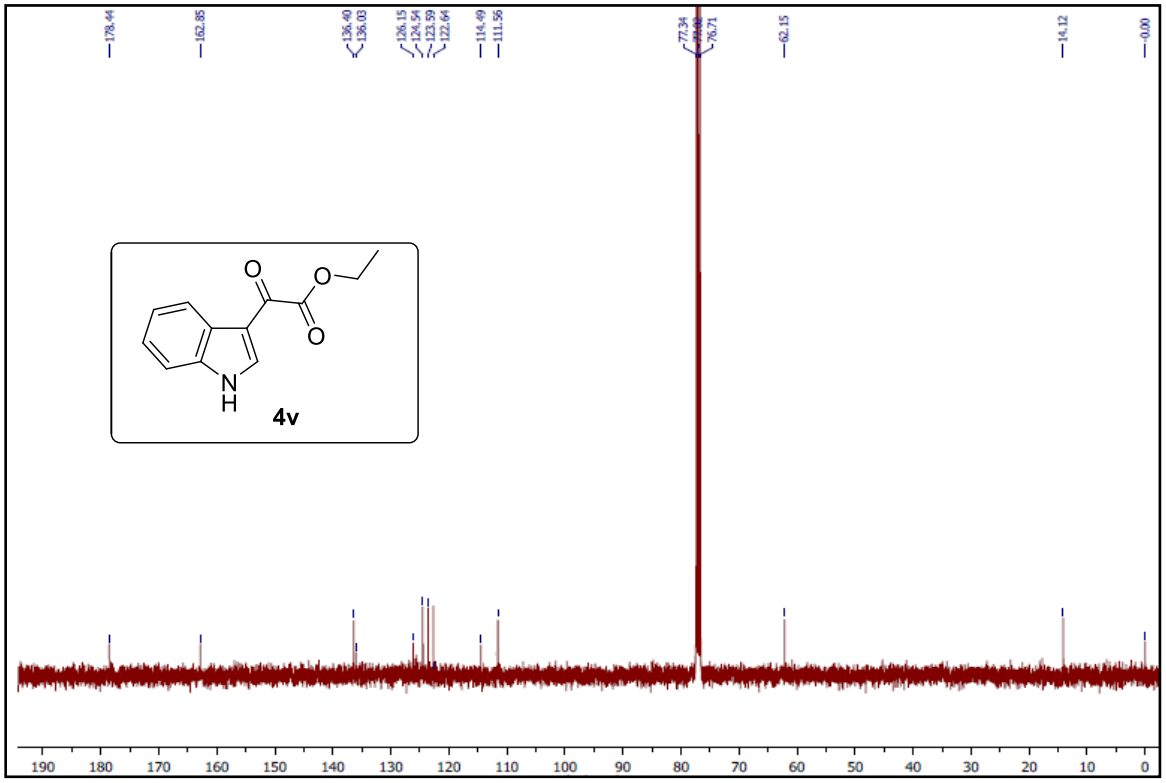
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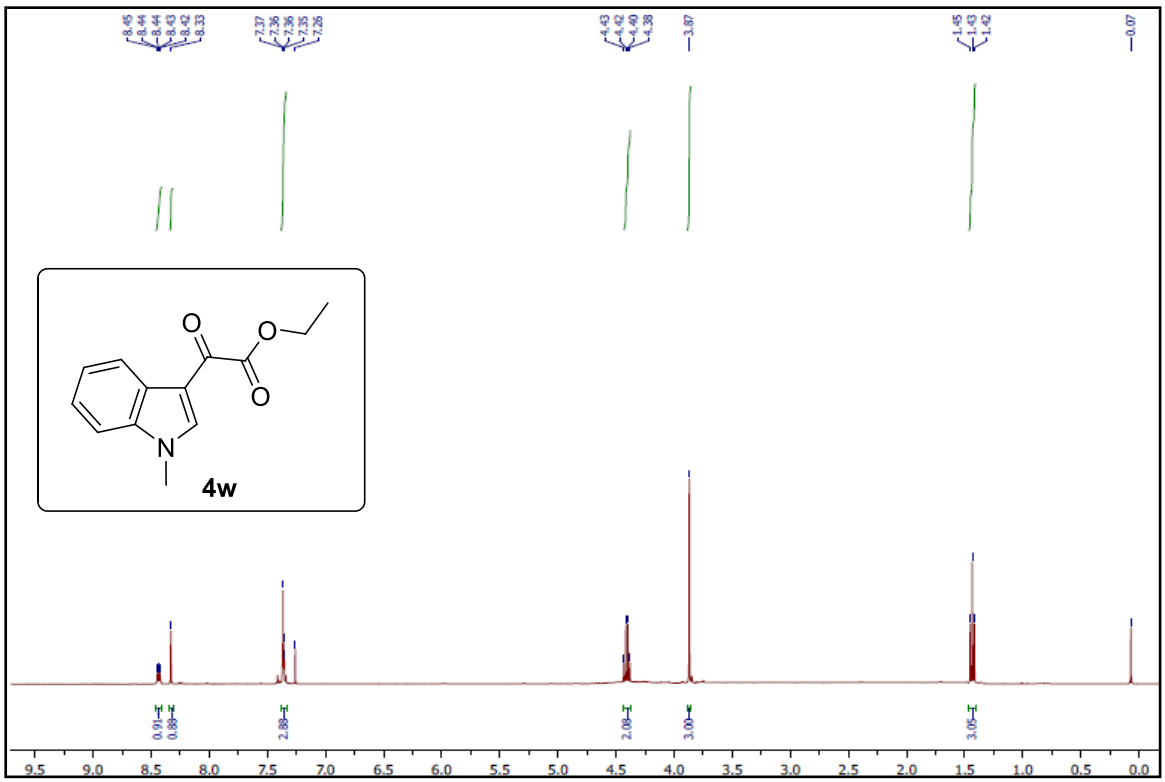
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3.00
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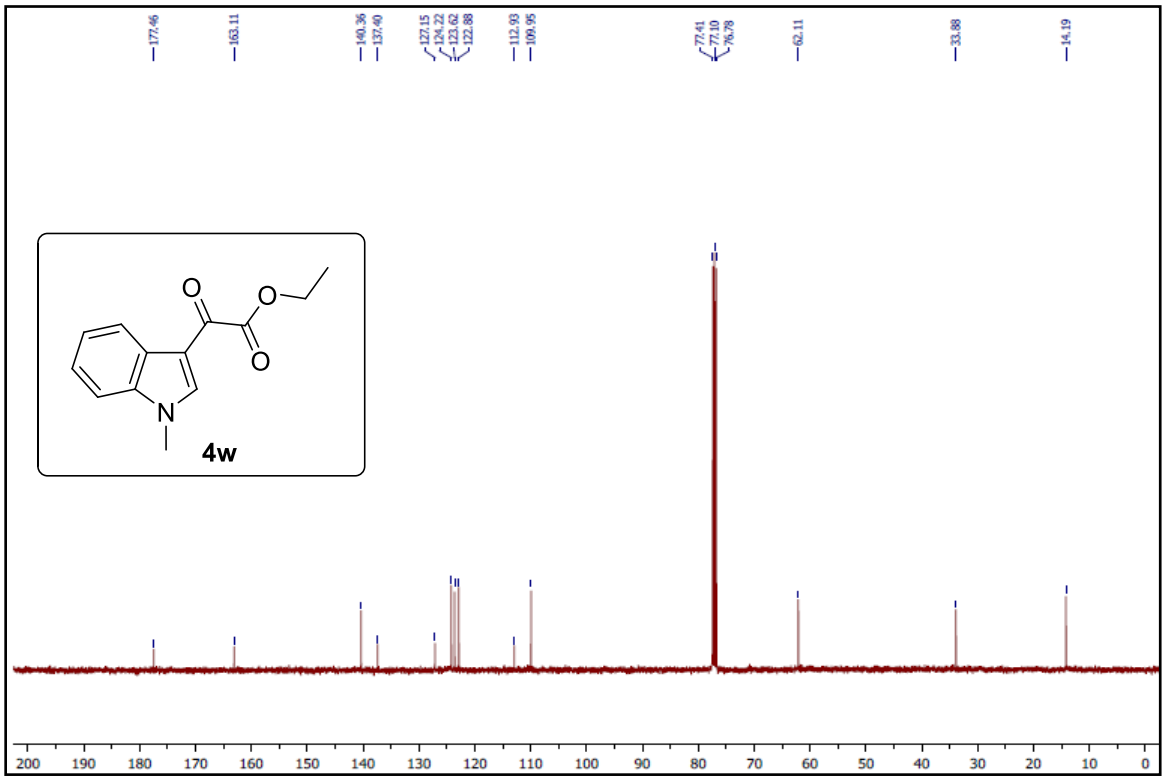
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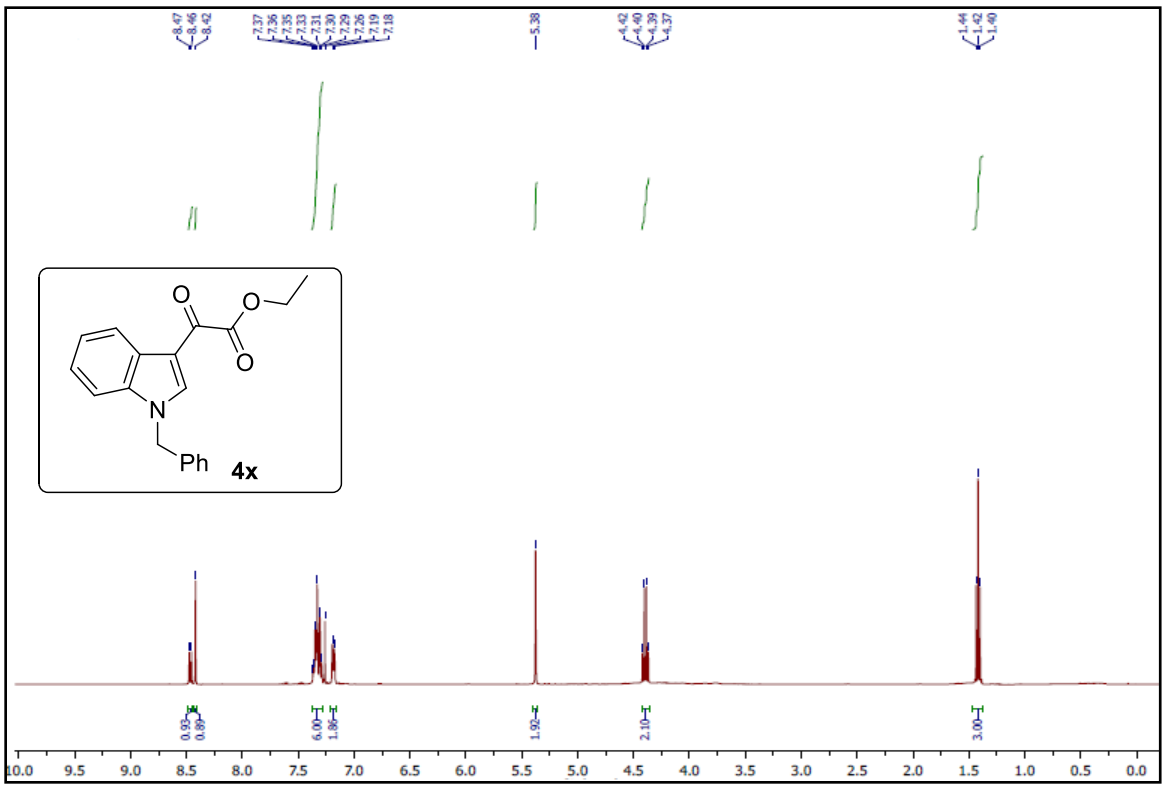
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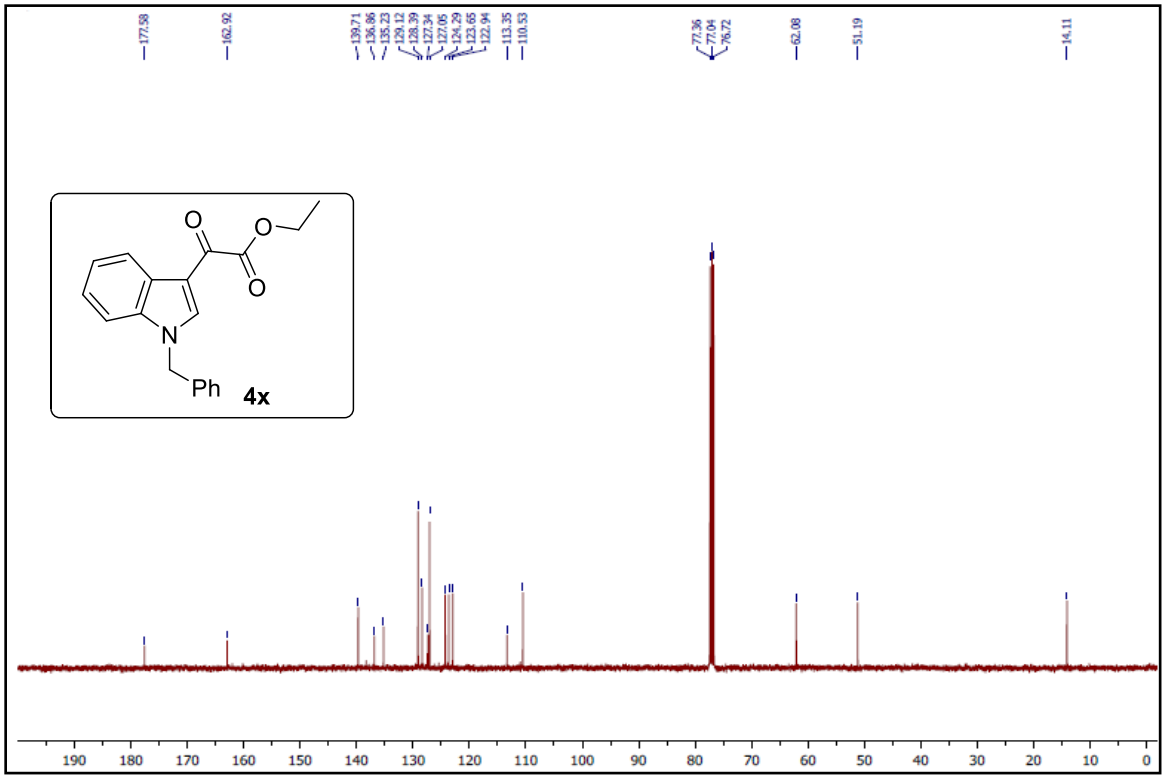
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N
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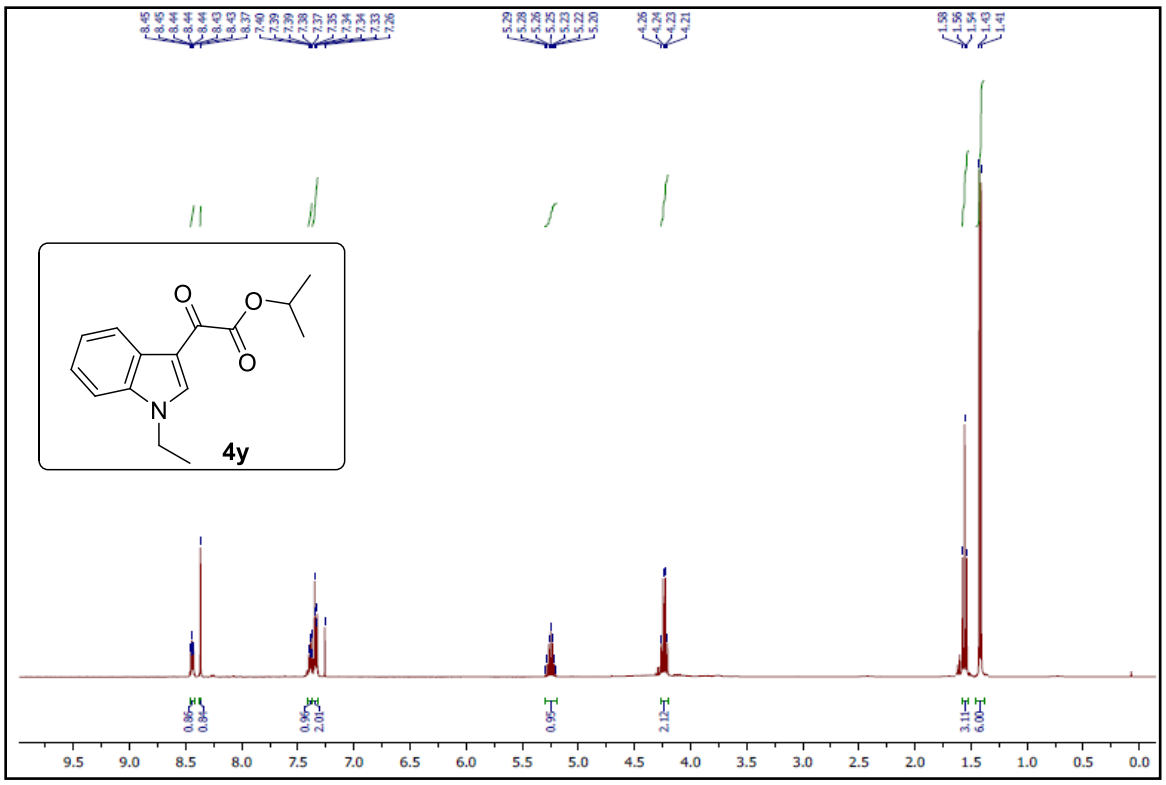
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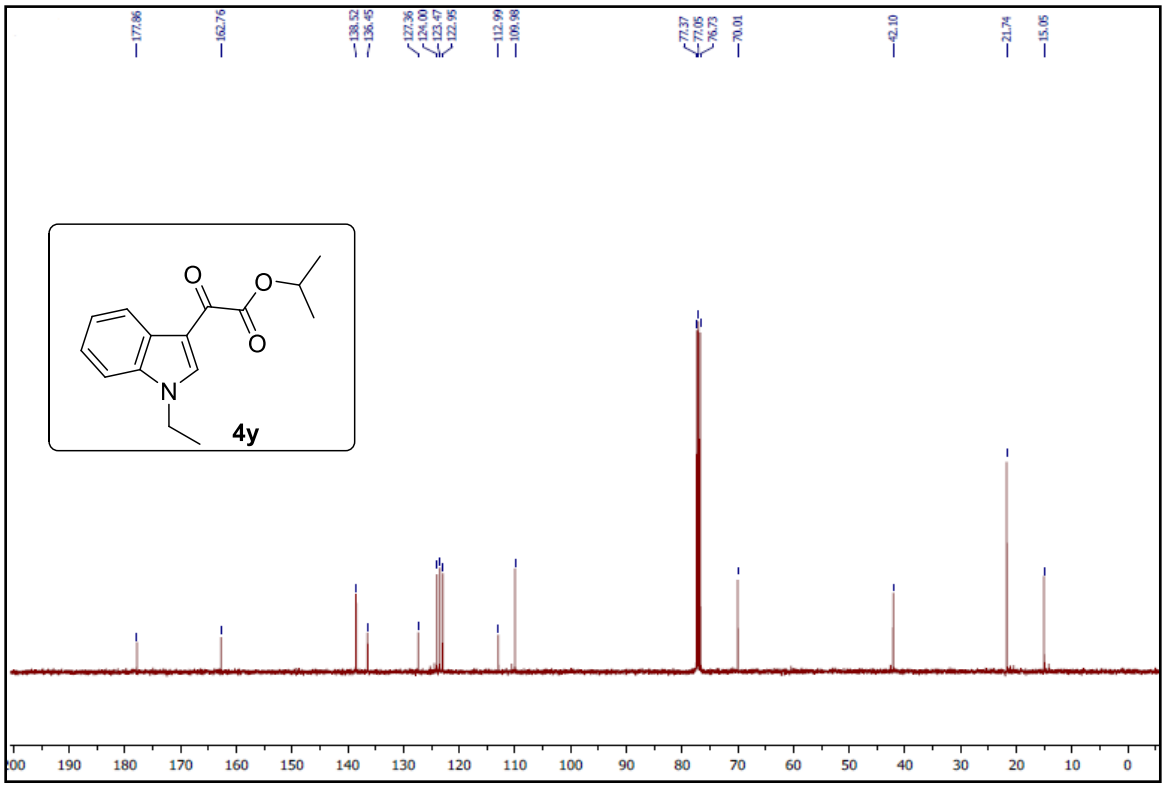
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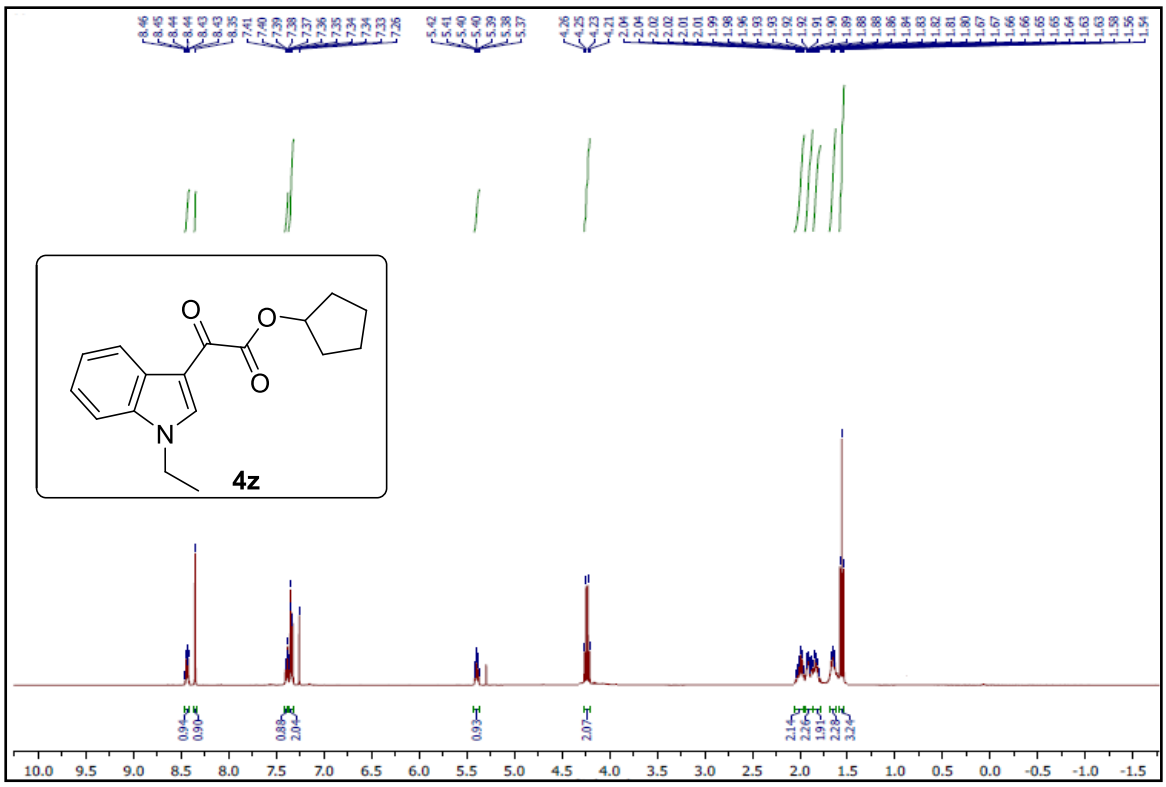
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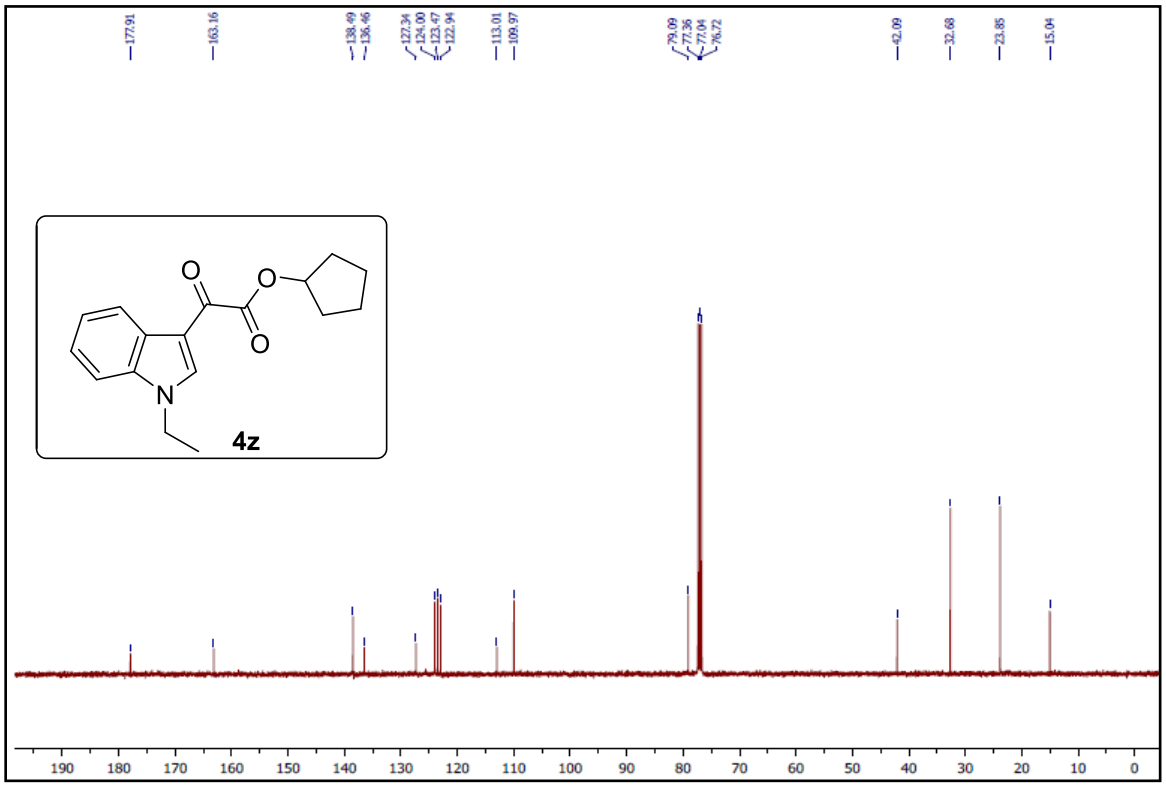
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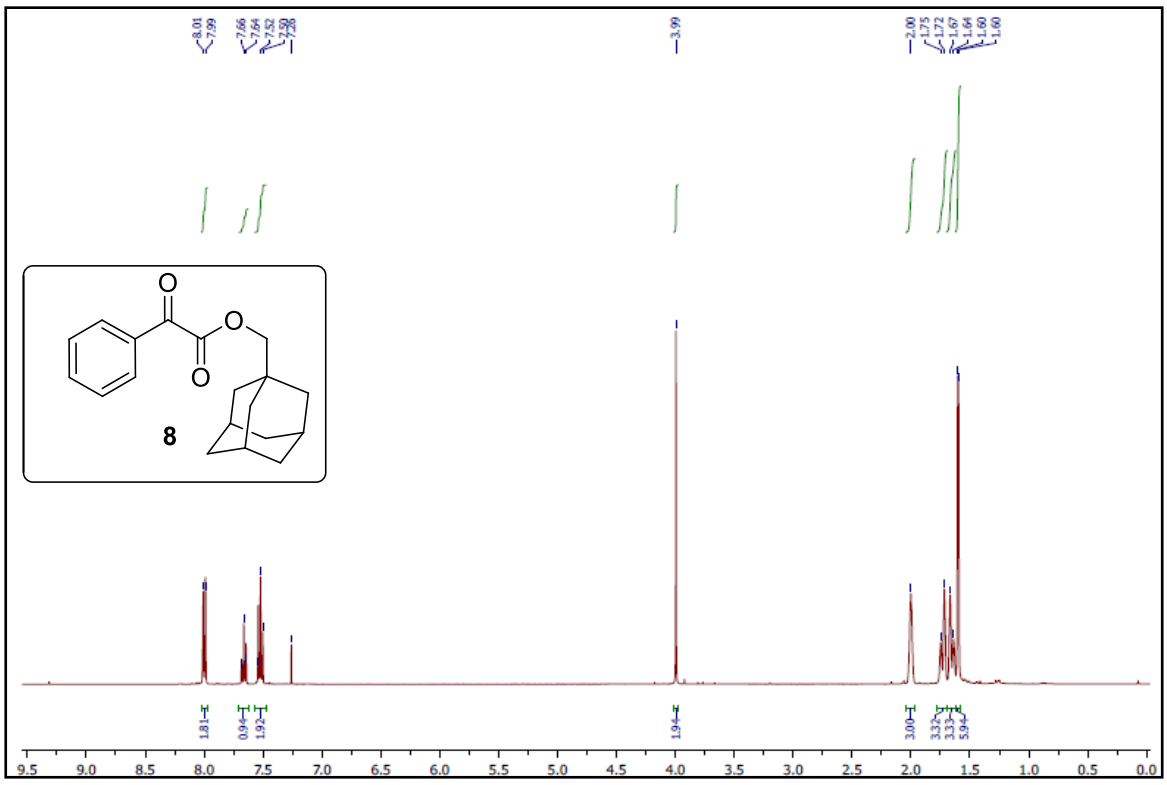
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1.92
1.94
3.00
3.32
3.33
5.94
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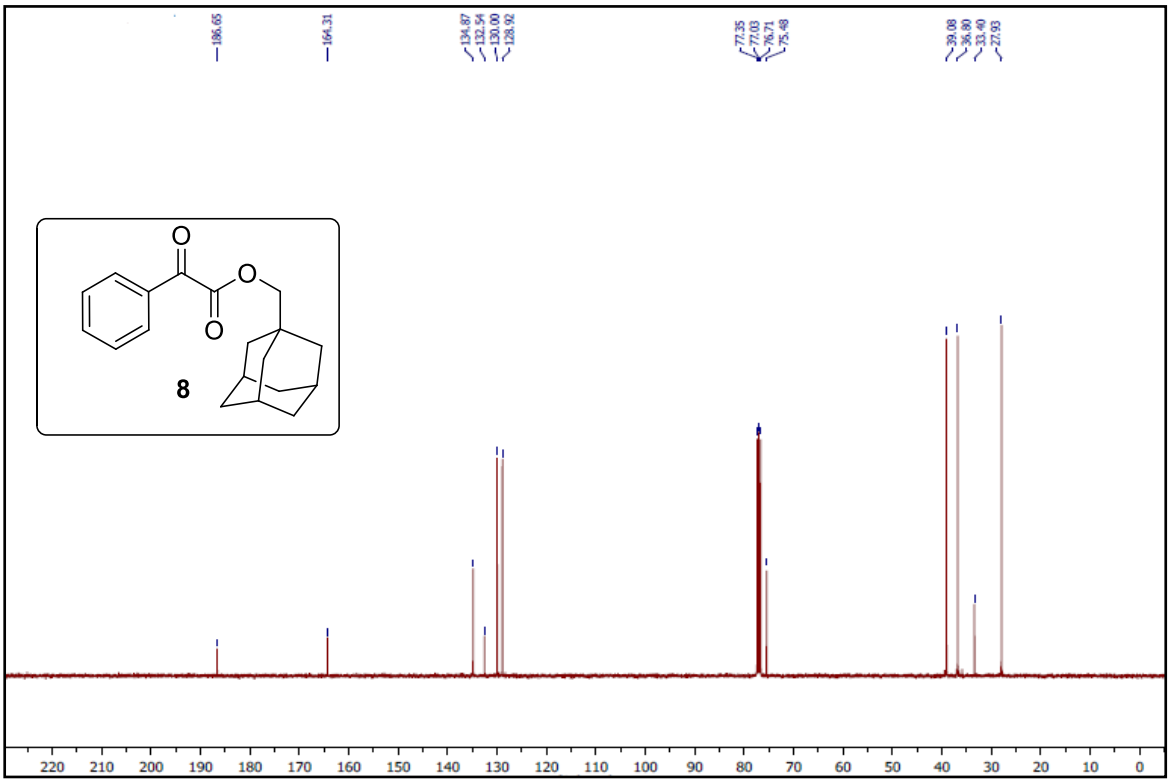
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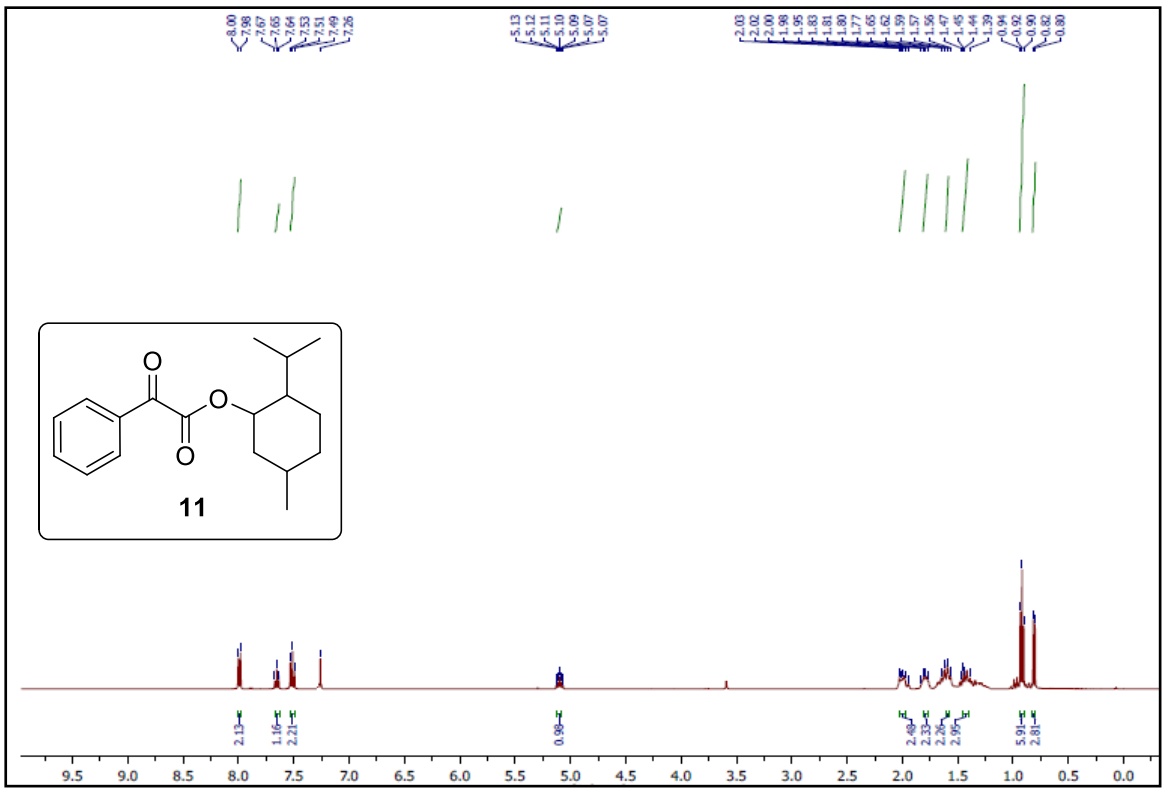
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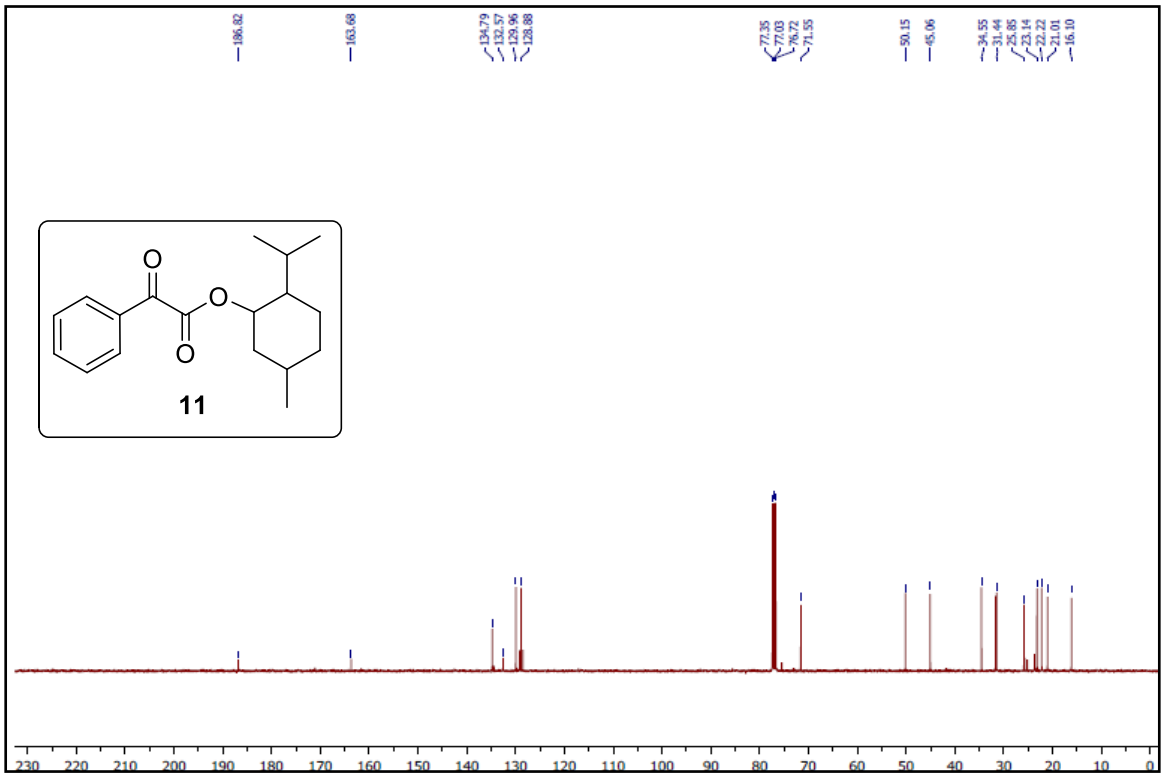
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