Wacker-type Oxidation of Alkynes into 1,2-Diketones Using Molecular Oxygen

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Experimental Section

General. All reactions were carried out under oxygen atmosphere. $PdBr_2$ and $CuBr_2$ were purchased from Alfa-Aesar Chemicals and used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were registered on Varian 400M spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300-400 mesh. IR, X-ray, EA, MS and HRMS were performed by the State-authorized Analytical Center in Soochow University.

General procedures for oxidation of alkynes:

Alkyne (0.2 mmol), $PdBr_2$ (0.01 mmol), and $CuBr_2$ (0.02 mmol) were added to an oven-dried Schlenck tube under air. The septum-sealed tube was evacuated and refilled with O_2 thrice. Dioxane (2.0 mL) and H_2O (0.4 mL) were added via syringe. The reaction mixture was heated in an oil bath at designated temperature for 24 h. After the reaction completed, the product was obtained by silica gel chromatography with Petroleum/Ethyl acetate mixtures.

1,2-diphenylethane-1,2-dione (2a).[1] Yellow solid; mp: 94-95 °C; Yield: 97%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (t, 4H, *J* = 8.0 Hz), 7.64 (t, 2H, *J* = 7.6 Hz), 7.97 (d, 4H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.9, 129.8, 132.8, 134.9, 194.5; MS ($C_{14}H_{10}O_2$): 210; IR (KBr, cm^{-1}): ν 1660.

4-(2-oxo-2-phenylacetyl)benzonitrile (2b).[2] Yellow solid; mp: 111-112 °C; Yield: 89%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (t, 2H, *J* = 7.6 Hz), 7.71 (t, 2H, *J* = 7.6 Hz), 7.84 (d, 2H, *J* = 8.0 Hz), 7.99 (d, 2H, *J* = 8.2 Hz), 8.11 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 117.5, 117.7, 129.1, 129.9, 130.0, 132.2, 132.6, 135.3, 135.7, 192.2, 192.8; MS ($C_{15}H_9NO_2$): 235; IR (KBr, cm^{-1}): ν 1661, 1683, 2227.

1-(4-bromophenyl)-2-phenylethane-1,2-dione (2c).[2] Yellow solid; mp: 86-87 °C; Yield: 97%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51 (t, 2H, *J* = 8.0 Hz), 7.64-7.68 (m, 3H), 7.83 (d, 2H, *J* = 8.0 Hz), 7.96 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 128.9, 129.8, 130.3, 131.1, 131.5, 132.2, 132.5, 135.0, 193.1, 193.7; MS ($C_{16}H_9BrO_2$): 288 (M^+, ^{79}Br), 290 (M^+, ^{81}Br); IR (KBr, cm^{-1}): ν 1668.

1-(4-methoxyphenyl)-2-phenylethane-1,2-dione (2d)[2] Yellow oil; Yield: 90%; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 6.96 (d, 2H, *J* = 8.0 Hz), 7.46-7.51 (m, 2H), 7.61-7.63 (m, 1H), 7.92-7.98 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.5, 114.3, 125.8, 128.9, 129.7, 132.2, 133.0, 134.7, 164.9, 193.1, 194.8; MS ($C_{15}H_{12}O_3$): 240; IR (KBr, cm^{-1}): ν 1677.

1-phenyl-2-o-tolylethane-1,2-dione (2e)[3] Yellow solid; mp: 56-57 °C; Yield: 77%; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.70 (s, 3H), 7.25-7.34 (m, 2H), 7.46-7.52 (m, 3H), 7.63-7.65 (m, 2H), 7.97 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.9, 126.0, 128.9, 129.8, 131.6, 132.5, 132.9, 133.0, 133.8, 134.7, 141.3, 194.8, 196.7; MS ($C_{15}H_{12}O_2$): 224; IR (KBr, cm^{-1}): ν 1658, 1673.

1-phenyl-2-(3-(trifluoromethyl)phenyl)ethane-1,2-dione (2f)[4] Yellow solid; mp: 69-70 °C; Yield: 93%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.54 (m, 2H), 7.62-7.70 (m, 2H), 7.90 (d, 1H, *J* = 10.4 Hz), 7.96-8.00 (m, 2H) , 8.14 (d, 1H, *J* = 10.4 Hz) , 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 100

MHz): δ 121.5, 125.1, 126.27, 126.32, 126.37, 126.43, 129.1, 129.2, 129.7, 129.96, 130.01, 131.0, 131.08, 131.12, 131.2, 131.4, 131.9, 132.5, 133.2, 133.4, 135.2, 192.6, 193.3; MS ($C_{15}H_9F_3O_2$): 278; IR (KBr, cm^{-1}): ν 1668.

1-(phenanthren-9-yl)-2-phenylethane-1,2-dione (2g) Yellow solid; mp: 117-119 °C; Yield: 89%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.81 (m, 8H), 8.10-8.24 (m, 3H), 8.58-8.69 (m, 2H), 9.39-9.42 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 122.6, 122.8, 126.6, 127.2, 127.4, 127.6, 128.18, 128.21, 129.0, 129.2, 130.0, 130.46, 130.54, 130.7, 132.8, 133.2, 134.7, 138.7, 194.4, 197.0; MS ($C_{22}H_{14}O_2$): 310; IR (KBr, cm^{-1}): ν 1665; Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14%; H, 4.55%. Found: C, 84.77%; H, 4.45%.

4-(2-oxo-2-phenylacetyl)benzaldehyde (2h)[5] Yellow solid; mp: 64-67 °C; Yield: 90%; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49 (t, 2H, *J* = 10.0 Hz), 7.64 (t, 1H, *J* = 10.0 Hz), 7.93 (d, 2H, *J* = 11.2 Hz), 7.97 (d, 2H, *J* = 11.2 Hz), 8.09 (d, 2H, *J* = 10.0 Hz), 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 129.0, 129.8, 130.2, 132.3, 135.2, 136.7, 139.8, 191.3, 193.3, 193.5; MS ($C_{15}H_{10}O_3$): 238; IR (KBr, cm^{-1}): ν 1666, 1691.

1-(4-(hydroxy(phenyl)methyl)phenyl)-2-phenylethane-1,2-dione (2i) Yellow solid; mp: 99-101 °C; Yield: 89%; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.68 (brs, 1H), 5.85 (s, 1H), 7.27-7.33 (m, 5H), 7.47-7.53 (m, 4H), 7.63-7.67 (m, 1H), 7.89-7.95 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 75.4, 126.5, 126.7, 127.8, 128.5, 128.9, 129.7, 129.9, 131.5, 132.5, 134.9, 142.7, 151.1, 194.2, 194.6; MS ($C_{21}H_{16}O_3$ + Na): 339; IR (KBr, cm^{-1}): ν 1672, 3533; Anal. Calcd. for $C_{21}H_{16}O_3$: C, 79.73%; H, 5.10%, Found: C, 79.48%; H, 5.14%.

1-(4-benzoylphenyl)-3,3-dimethylbutane-1,2-dione (2j) Yellow solid; mp: 85-86 °C; Yield: 80%; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (s, 9H), 7.49 (t, 2H, *J* = 7.2 Hz), 7.62 (t, 1H, *J* = 7.2 Hz), 7.79 (d, 2H, *J* = 7.2 Hz), 7.86 (d, 2H, *J* = 8.0 Hz), 7.93 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.1, 42.7, 128.5, 129.3, 130.08, 130.11, 133.2, 135.1, 136.5, 142.4, 194.5, 195.6, 210.2; HRMS: Anal. Calcd. For $C_{19}H_{18}O_3$: 294.1256, Found: 294.1252; IR (KBr, cm^{-1}): ν 1654, 1681.

1-(4-nitrophenyl)hexane-1,2-dione (2k) Yellow solid; mp: 65-66 °C; Yield: 73%; ^1H NMR($CDCl_3$, 400MHz): δ 0.96 (t, 3H, *J* = 7.2 Hz), 1.39-1.45 (m, 2H), 1.68-1.71 (m, 2H), 2.94 (t, 2H, *J* = 7.2 Hz), 8.20 (d, 2H, *J* = 8.8 Hz), 8.33 (d, 2H, *J* = 8.8Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.7, 22.2, 24.9, 38.0, 123.8, 131.3, 136.7, 150.9, 189.4, 201.5; MS ($C_{12}H_{13}ON_4$): 235; HRMS: Anal. Calcd. For $C_{12}H_{13}NO_4$: 235.0845, Found: 235.0850; IR (KBr, cm^{-1}): ν 1686, 1712.

methyl 4-(2-cyclohexyl-2-oxoacetyl)benzoate (2l) Yellow solid; mp: 73-74 °C; Yield: 67%; ^1H NMR($CDCl_3$, 400MHz): δ 1.24-1.48 (m, 5H), 1.70-1.95 (m, 5H), 3.11-3.16 (m, 1H), 3.97 (s, 3H), 8.00 (d, 2H, *J* = 7.6 Hz), 8.15 (d, 2H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.2, 25.7, 27.1, 45.7, 52.5, 129.8, 129.9, 134.9, 135.7, 165.9, 193.1, 205.2; MS ($C_{16}H_{18}O_4$): 274; IR (KBr, cm^{-1}): ν 1679, 1728; Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06%; H, 6.61%, Found: C, 70.32%; H, 6.39%.

1-cyclohexyl-4-phenylbutane-1,2-dione (2m) Yellow oil; Yield: 41%; ^1H NMR($CDCl_3$, 400MHz): δ 1.17-1.37 (m, 5H), 1.61-1.79 (m, 5H), 2.91 (t, 2H, *J* = 7.6 Hz), 3.07 (t, 2H, *J* = 7.6 Hz), 3.11-3.15 (m, 1H), 7.18-7.20 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.4, 25.8, 27.7, 29.1, 38.3, 43.1, 126.2, 128.2, 128.4, 140.3, 199.4, 202.1; MS ($C_{16}H_{20}O_2$): 244; IR (KBr, cm^{-1}): ν 1708; Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65%; H, 8.25%. Found: C, 78.89%; H, 8.01%.

References:

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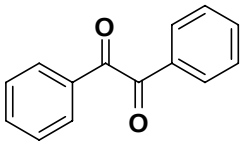

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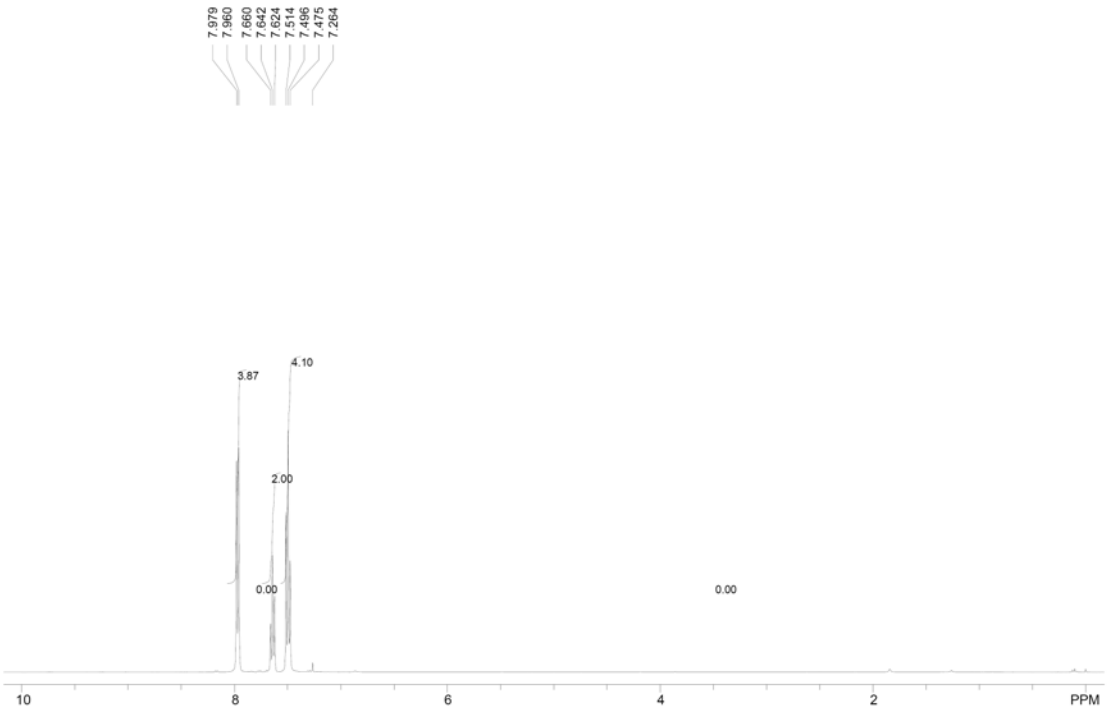
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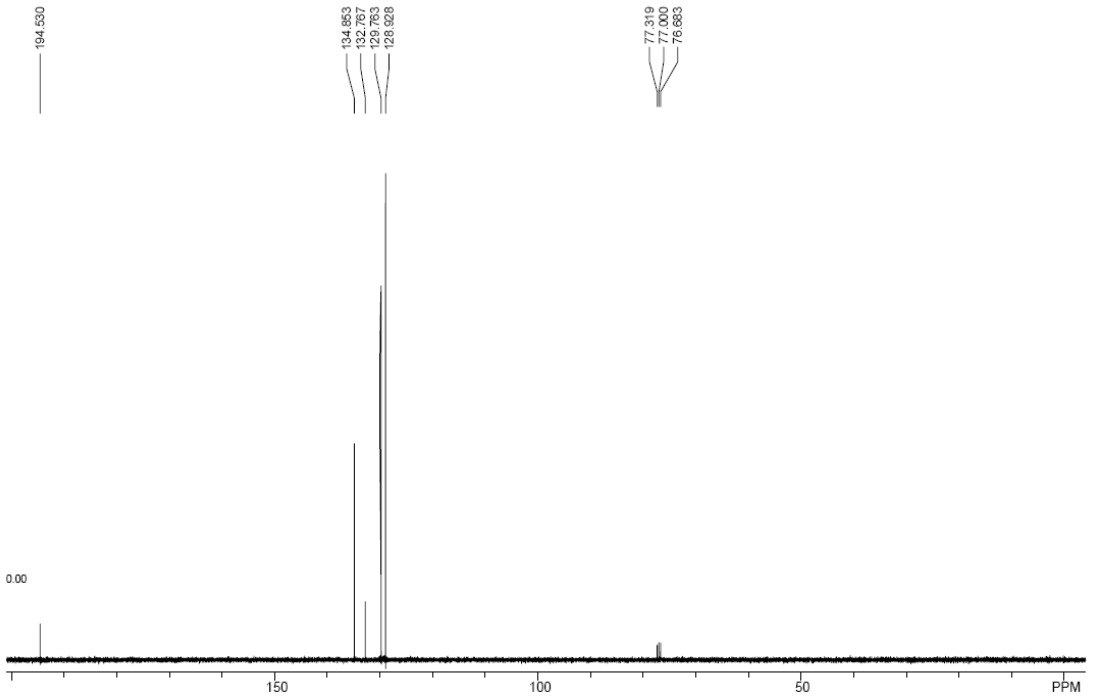
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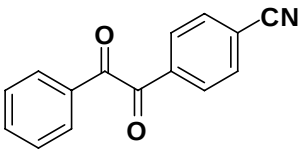
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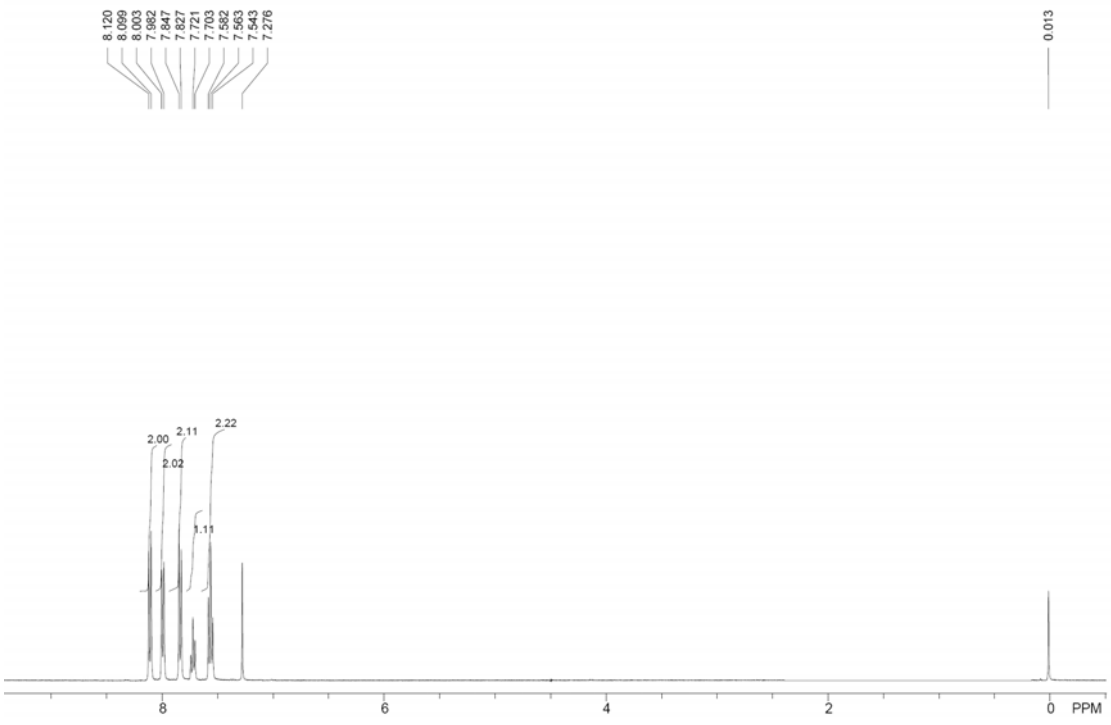
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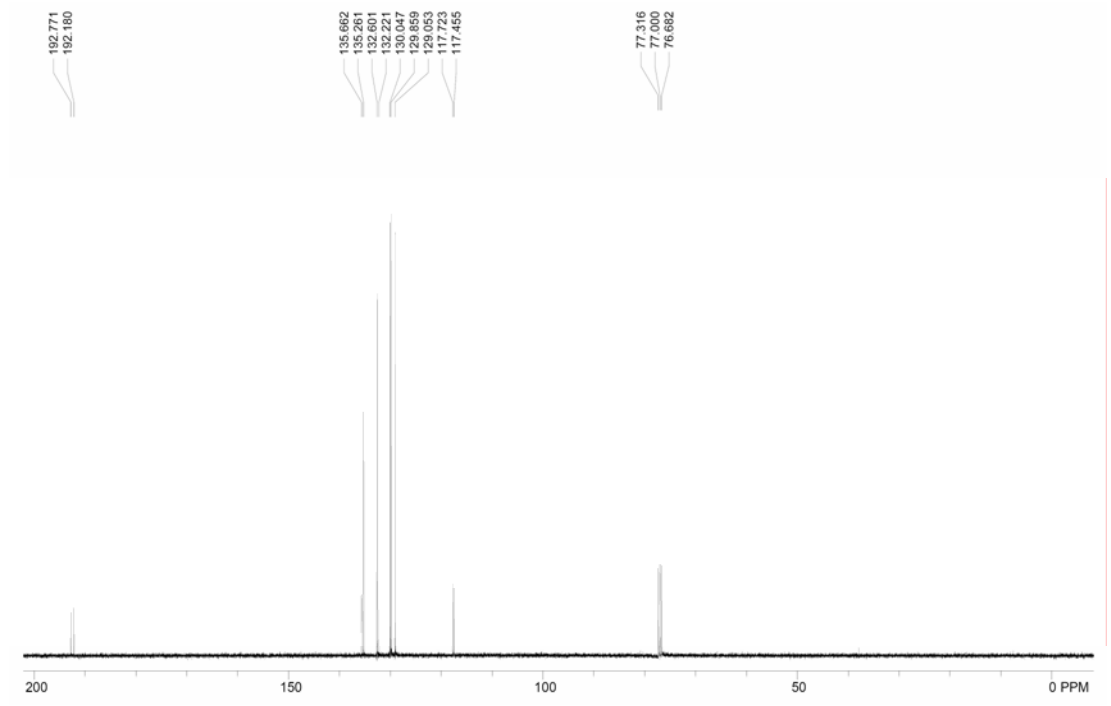
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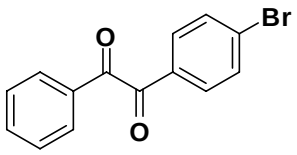
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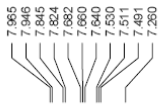
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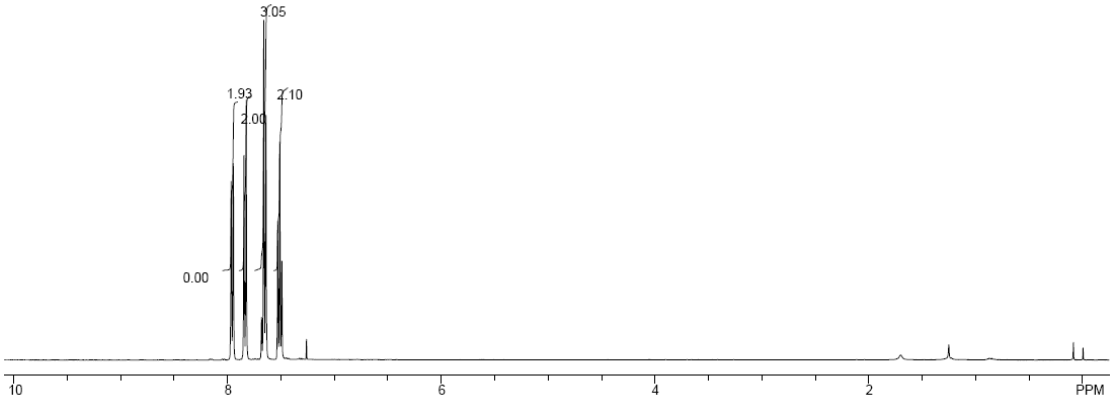
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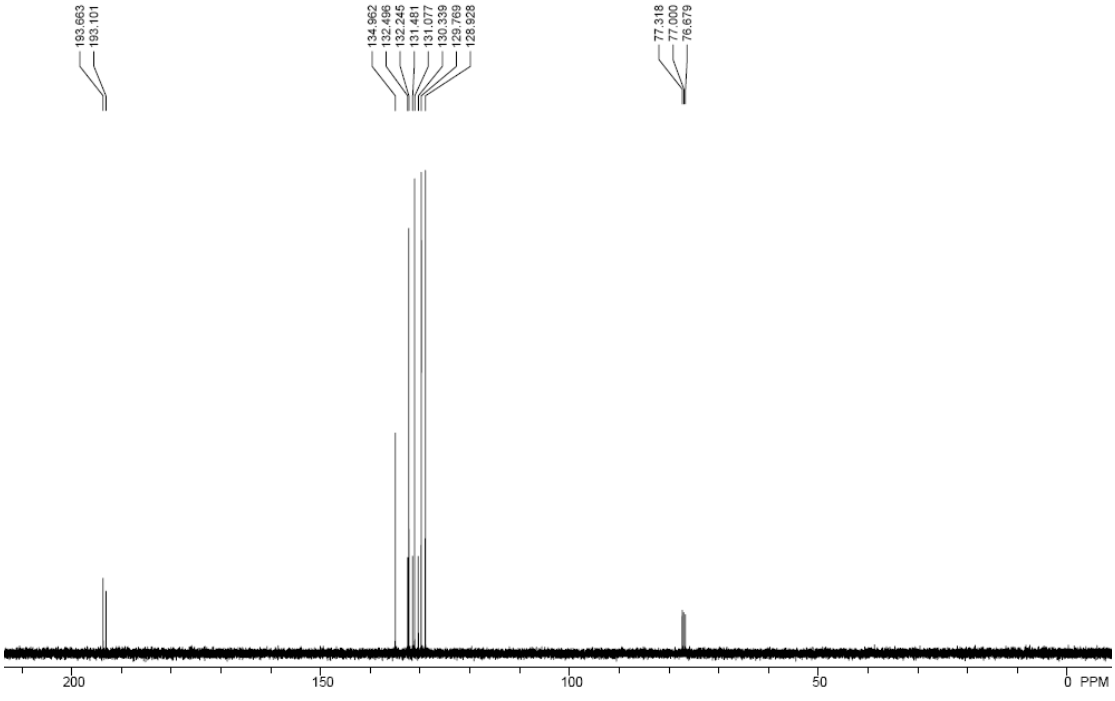
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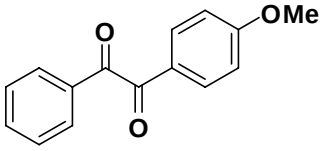
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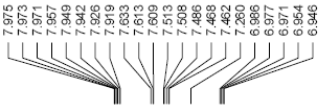
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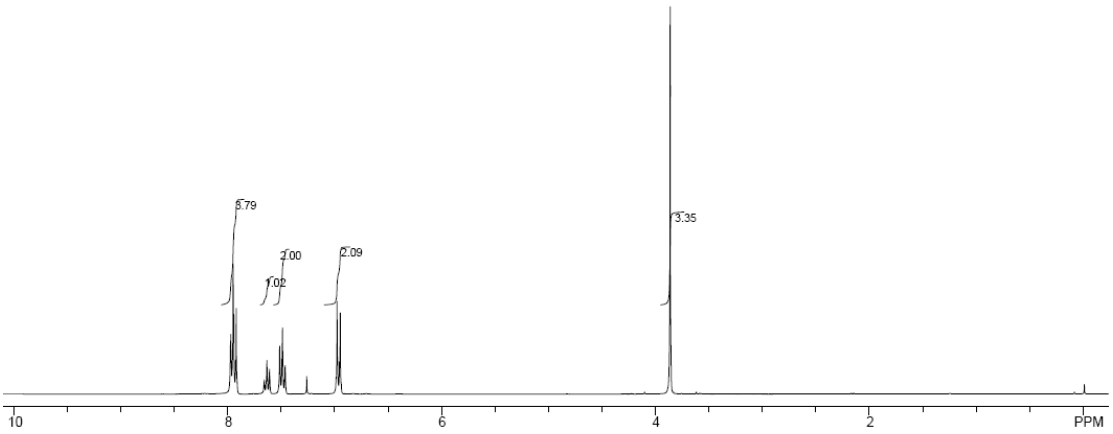
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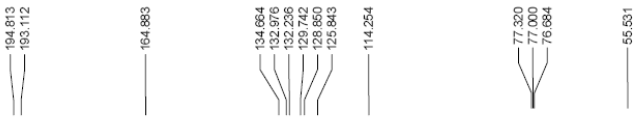
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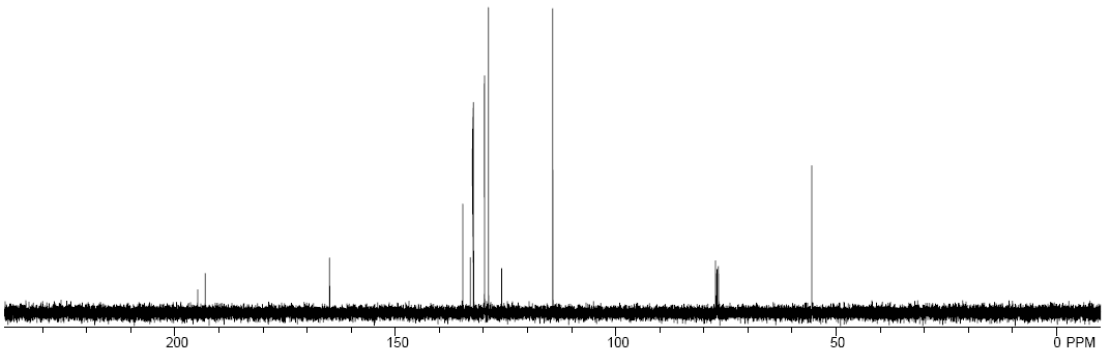
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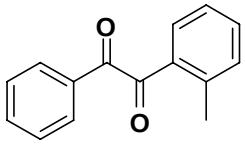

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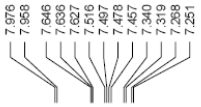
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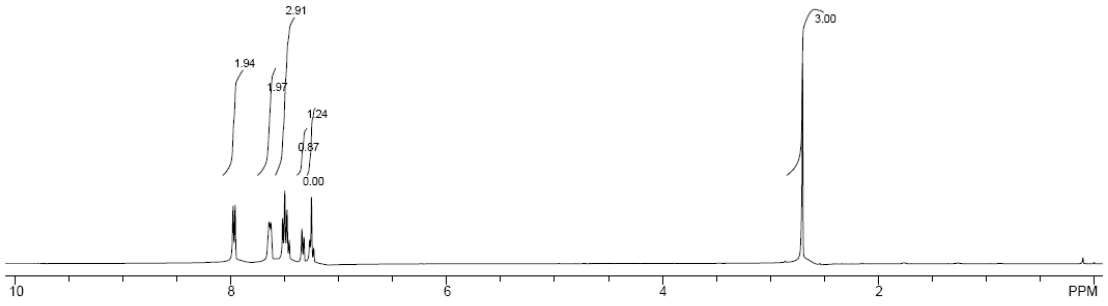
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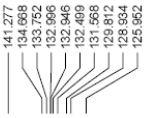
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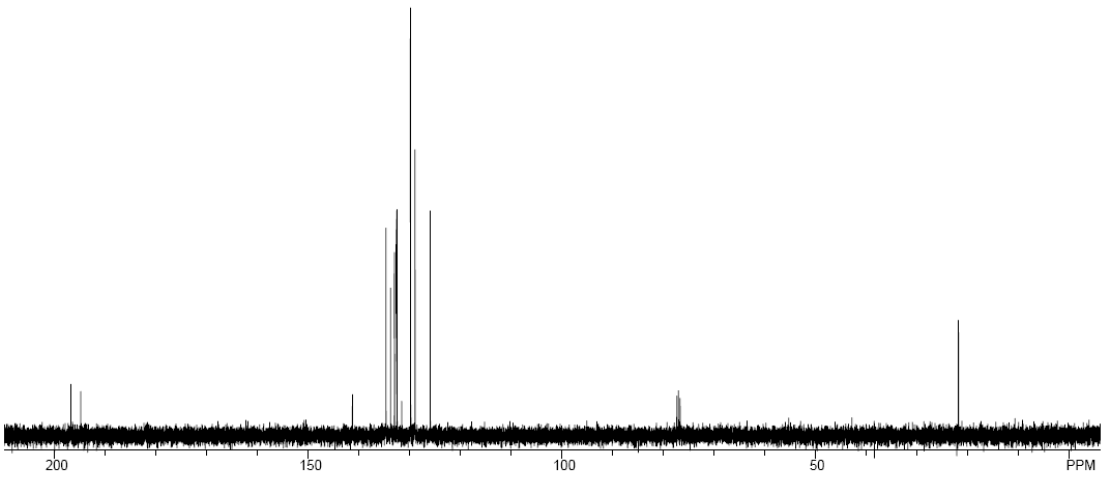
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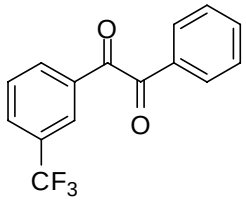
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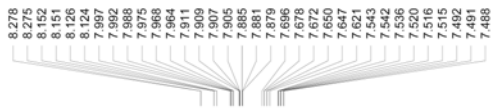
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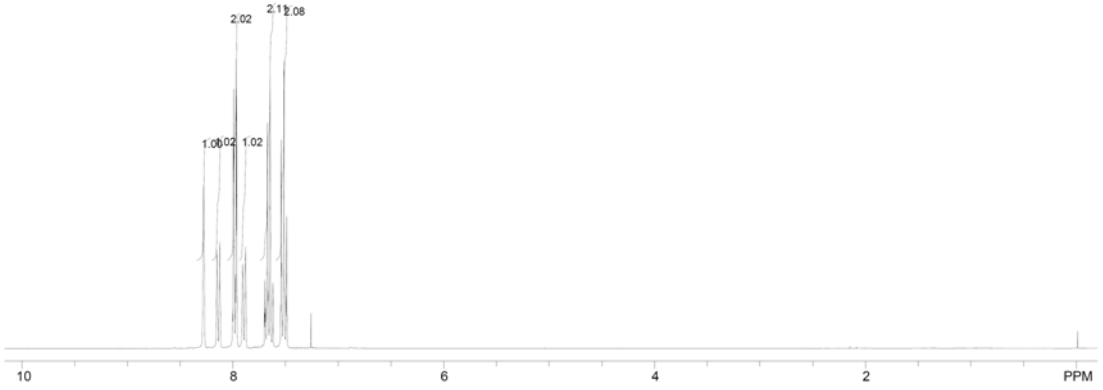
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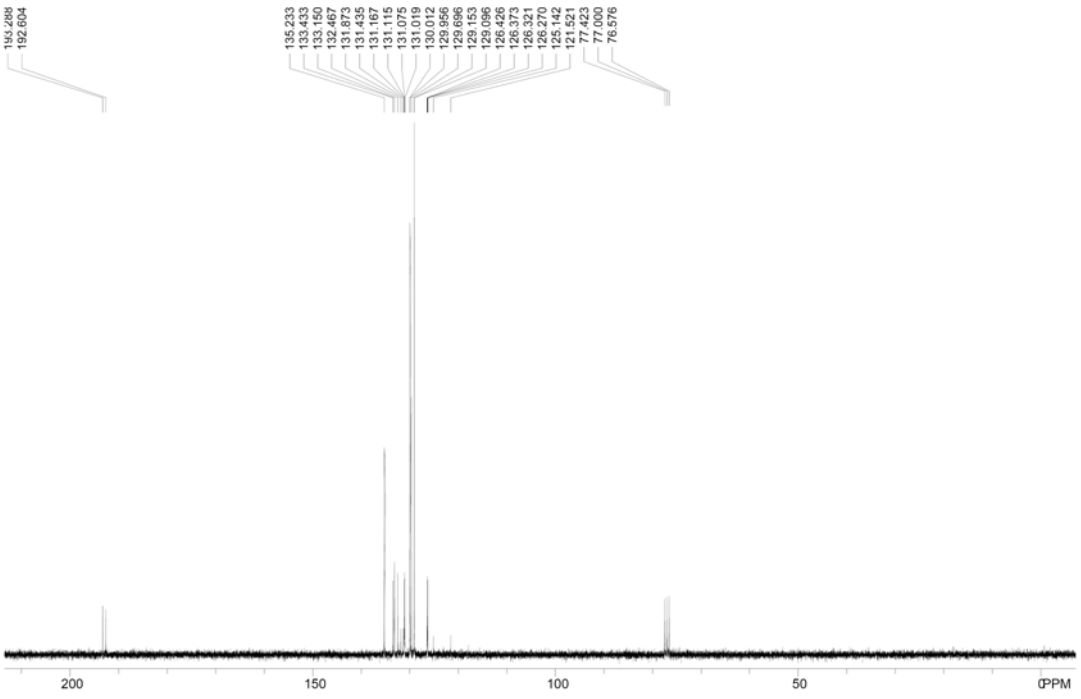
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131.435
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131.115
131.075
131.019
130.012
129.956
129.696
129.153
129.096
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76.576
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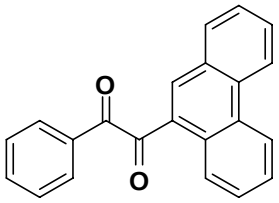
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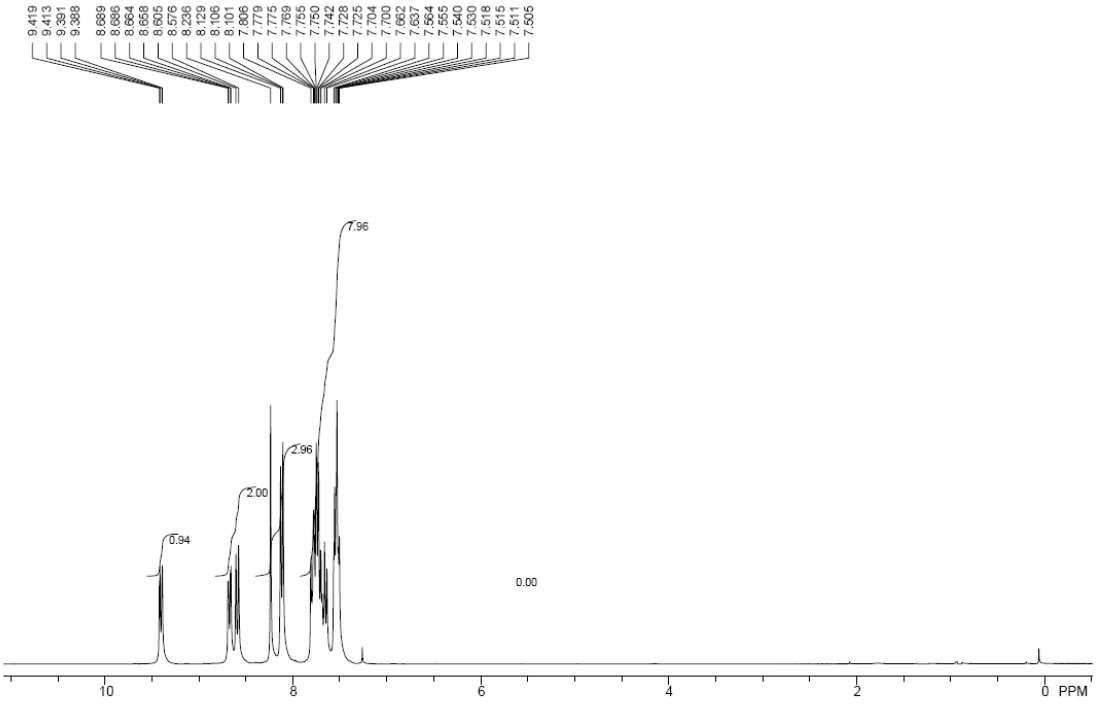
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8.658
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8.576
8.236
8.129
8.106
8.101
7.806
7.779
7.775
7.769
7.755
7.750
7.742
7.728
7.725
7.704
7.700
7.662
7.637
7.564
7.555
7.540
7.530
7.518
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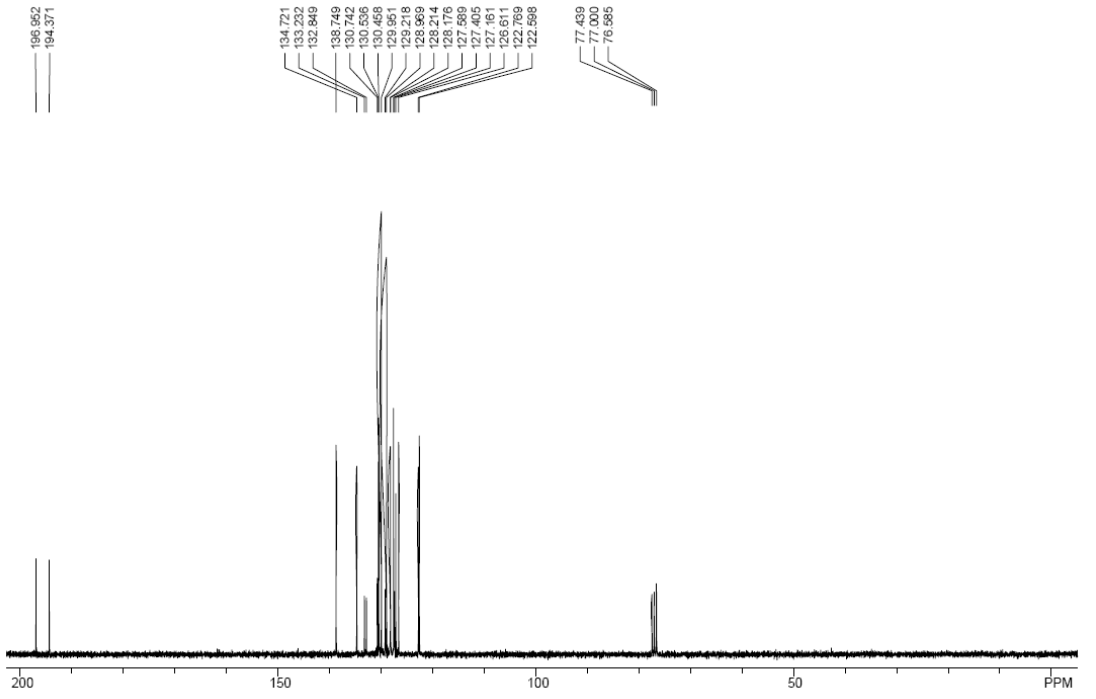
0.00
10
8
6
4
2
0 PPM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128.214
128.176
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122.598
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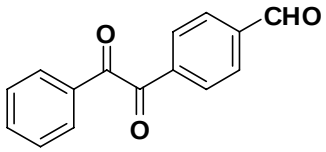
50
PPM


CHO
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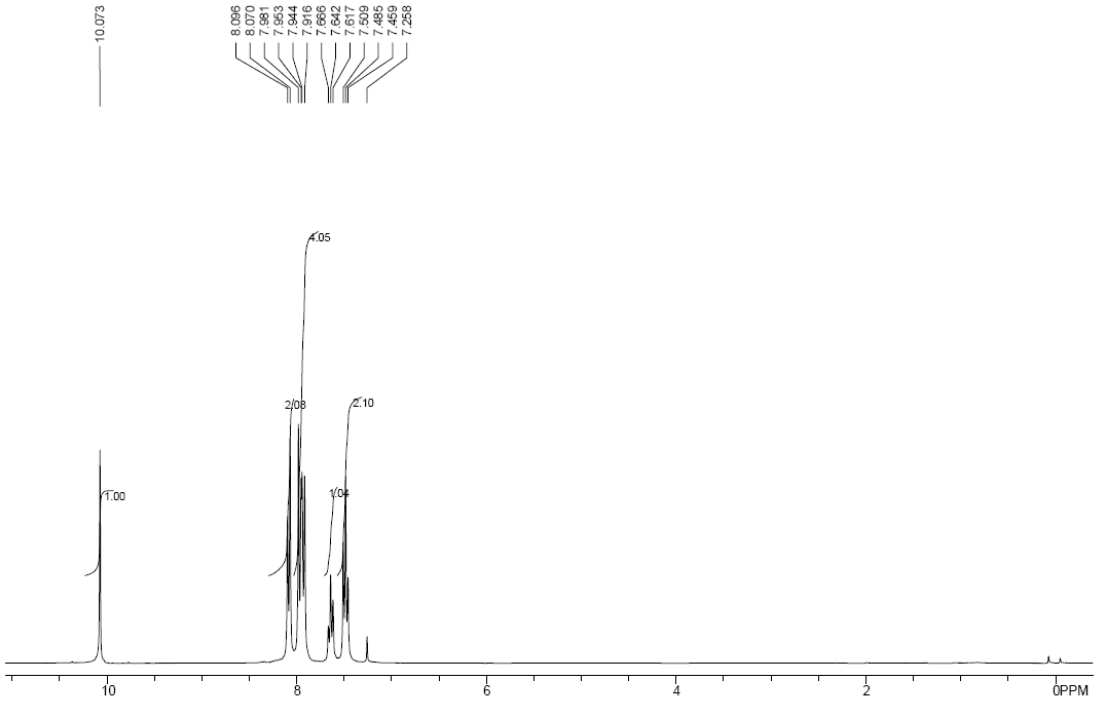
2h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8.070
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7.944
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7.666
7.642
7.617
7.509
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7.459
7.258
4.05
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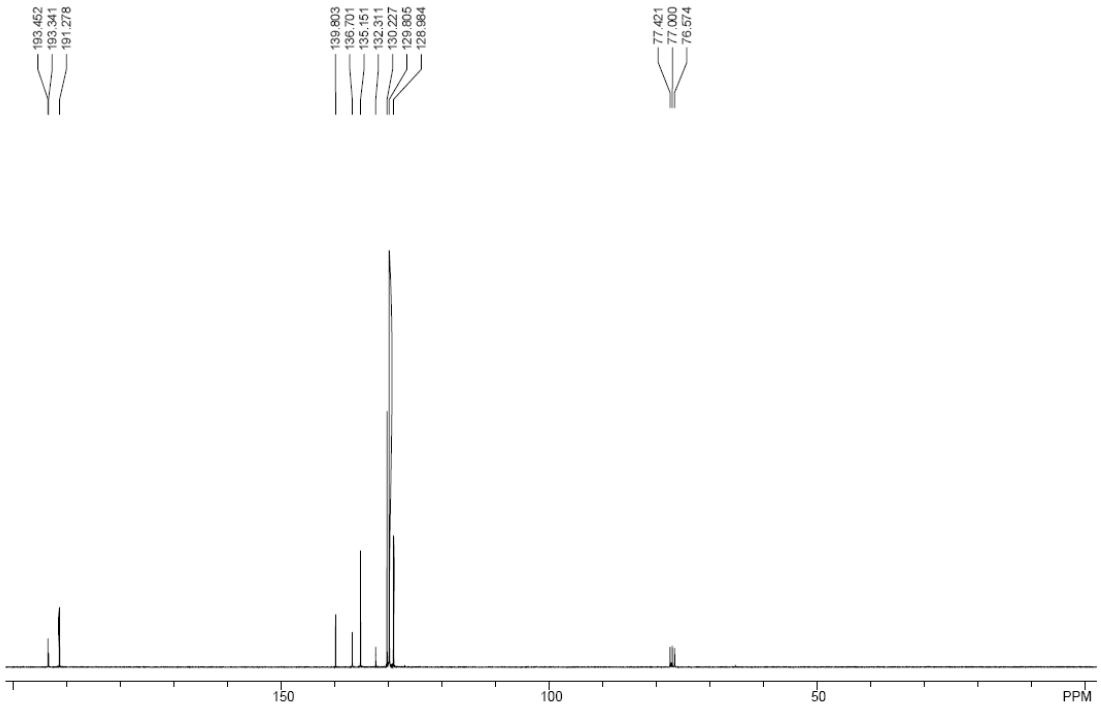
2.10
1.00
1.04
10
8
6
4
2
0PPM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191.278
139.803
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132.311
130.227
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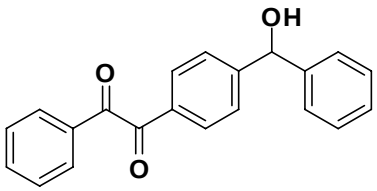
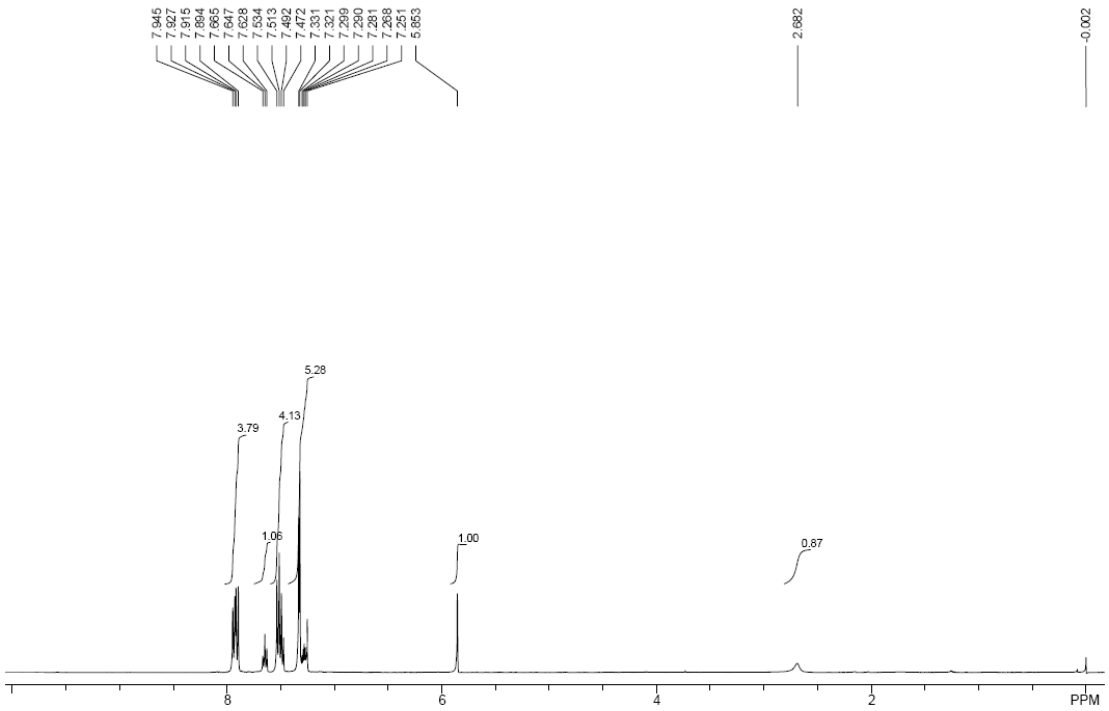
77.000
76.574
150
100
50
PPM


OH
O
O

2i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7.628
7.534
7.513
7.492
7.472
7.331
7.321
7.299
7.290
7.281
7.268
7.251
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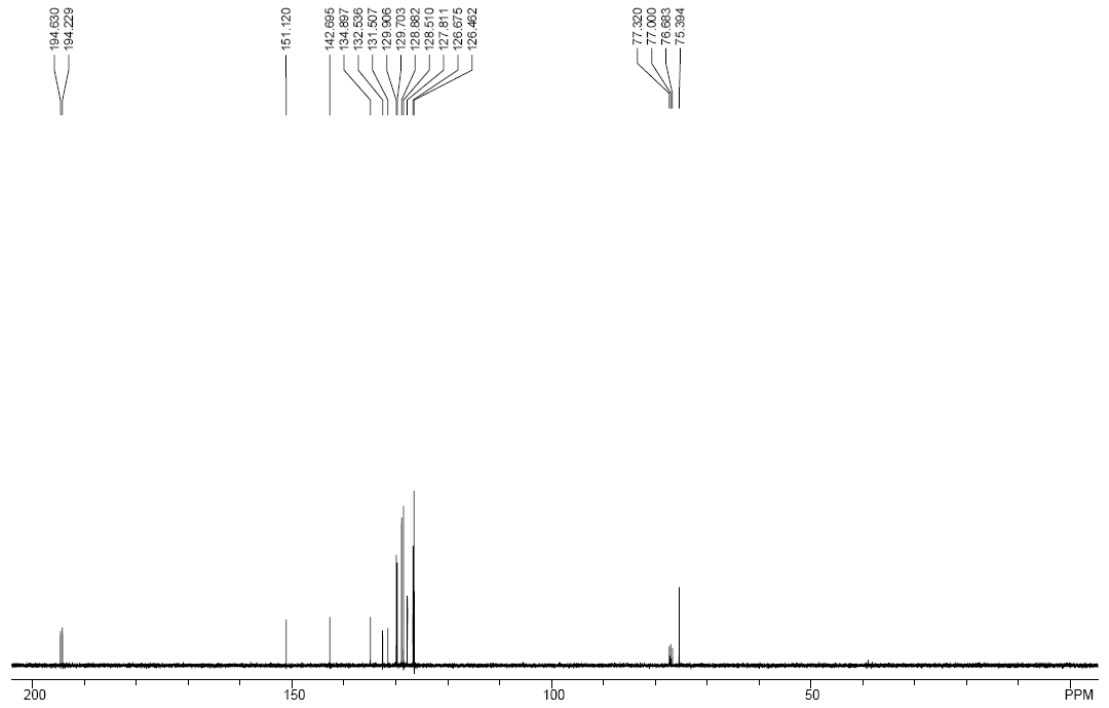
5.28
4.13
3.79
1.06
1.00
0.87
8
6
4
2
PPM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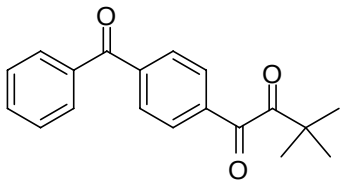
194.229
151.120
142.695
134.897
132.536
131.507
129.906
129.703
128.882
128.510
127.811
126.675
126.462
77.320
77.000
76.683
75.394
200
150
100
50
PPM



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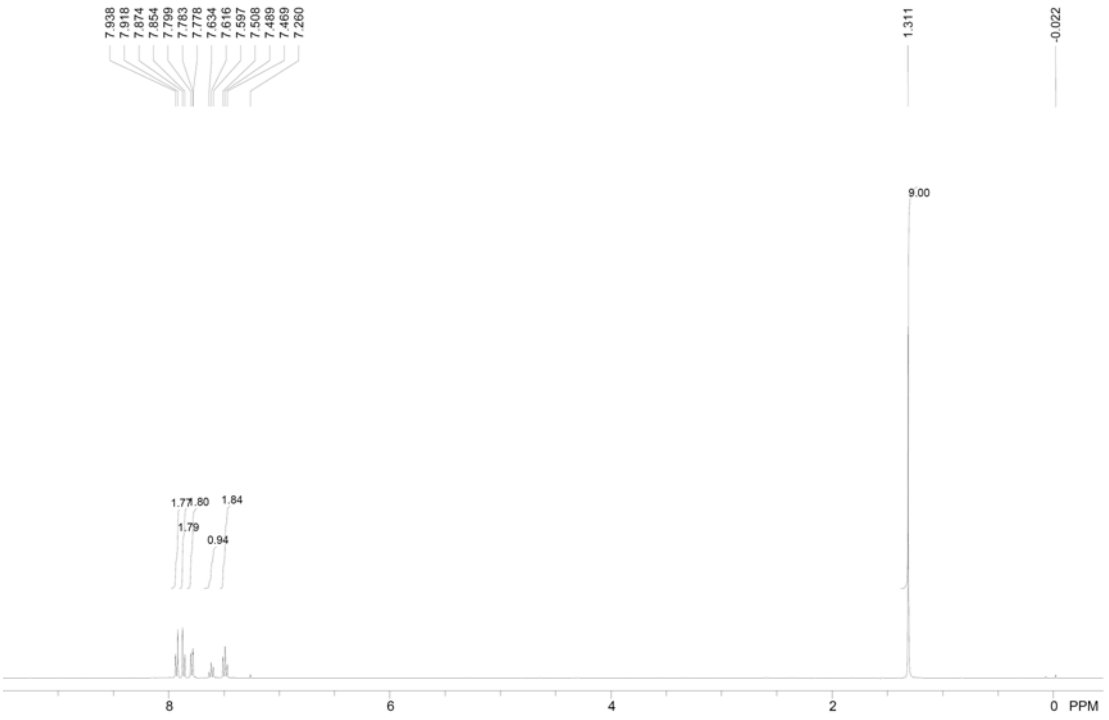
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7.874
7.854
7.799
7.783
7.778
7.634
7.616
7.597
7.508
7.489
7.469
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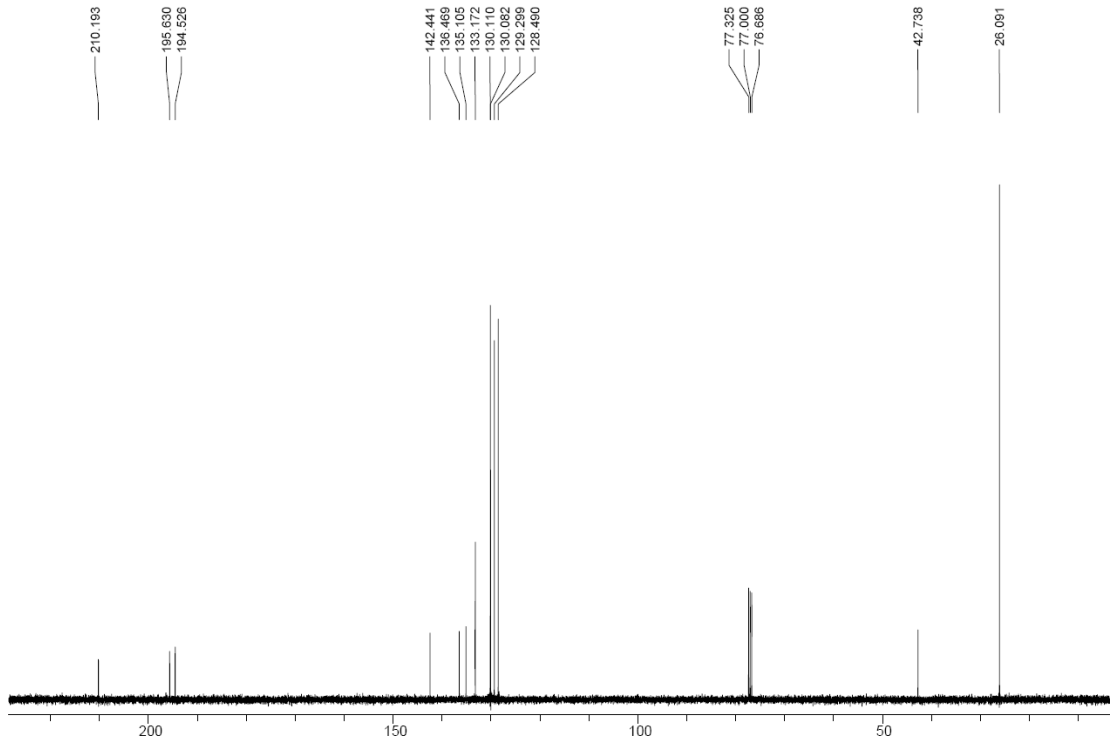
9.00
1.77
1.80
1.84
1.79
0.94
8
6
4
2
0 PPM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142.441
136.469
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133.172
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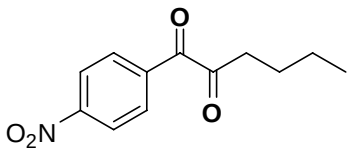
129.299
128.490
77.325
77.000
76.686
42.738
26.091
200
150
100
50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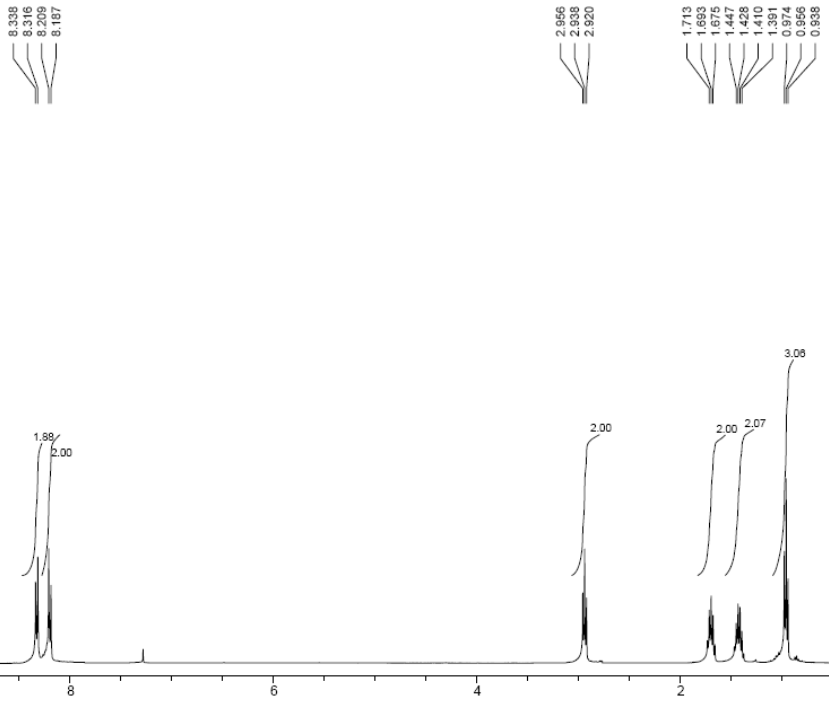
O
O2N

2k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2.920
1.713
1.693
1.675
1.447
1.428
1.410
1.391
0.974
0.956
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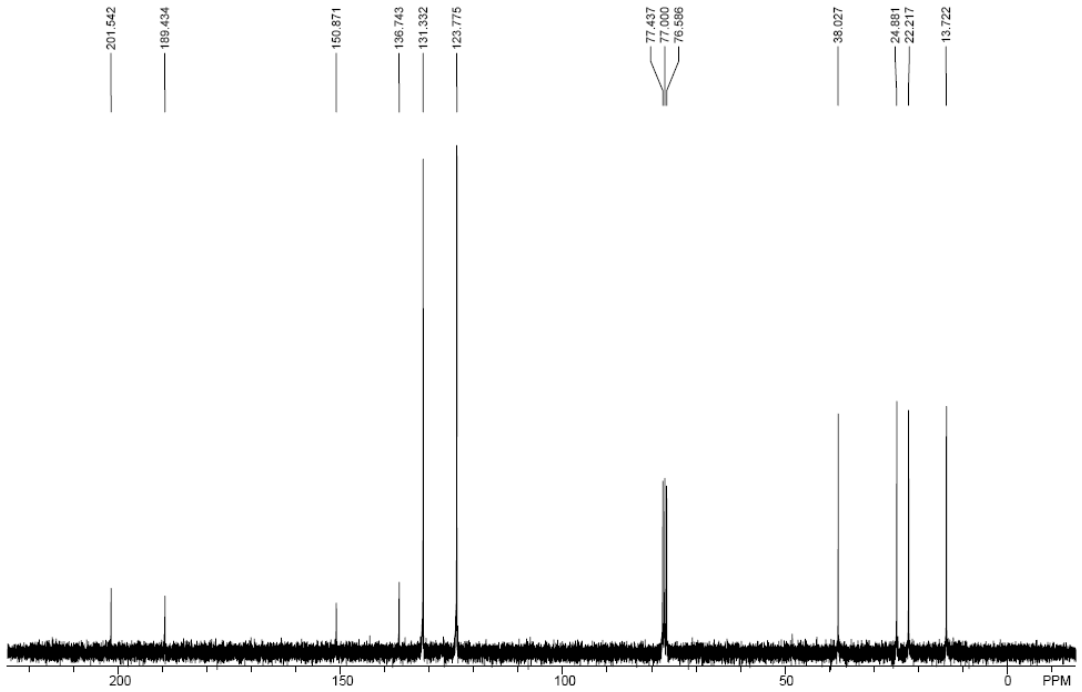
2.00
2.00
2.00
2.07
3.06
10
8
6
4
2
0
PPM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131.332
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13.722
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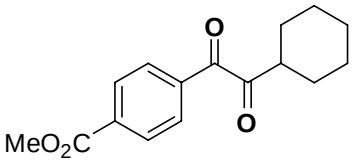
100
50
0
PPM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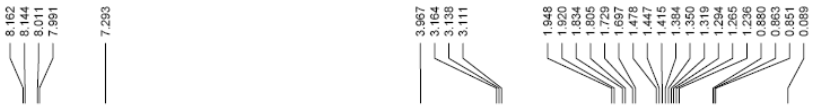
O
MeO2C

2l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3.967
3.164
3.138
3.111
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1.920
1.834
1.805
1.729
1.697
1.478
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1.350
1.319
1.294
1.265
1.236
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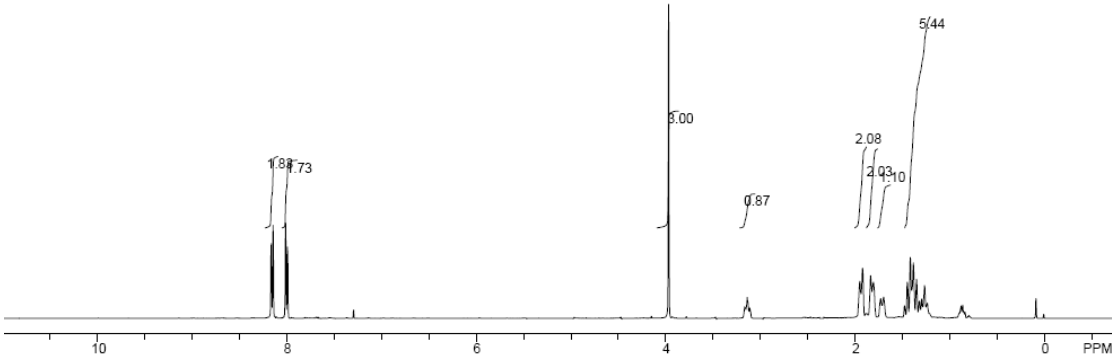
0.863
0.851
0.089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2.03
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1.73
0.87
10
8
6
4
2
0
PPM


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165.911
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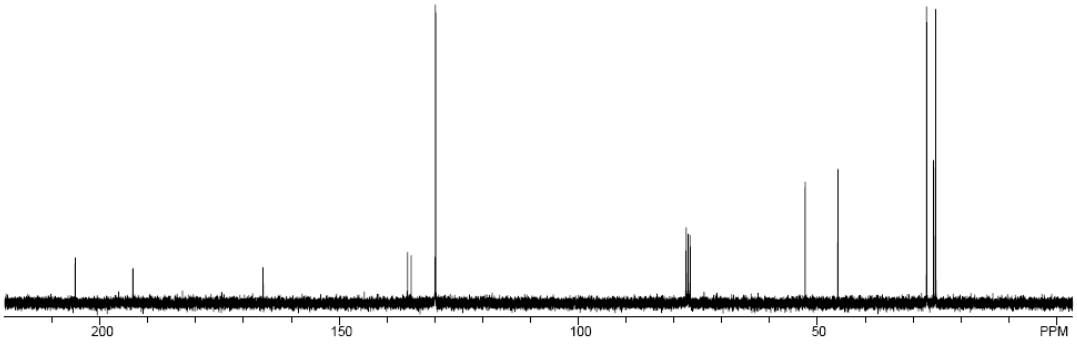
77.000
76.575
52.532
45.668
27.117
25.657
25.225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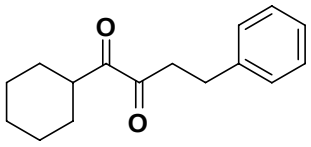
150
100
50
PPM



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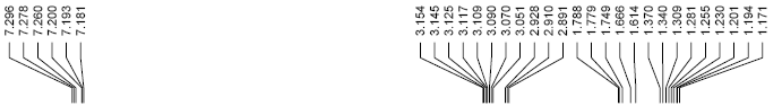
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3.145
3.125
3.117
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3.090
3.070
3.051
2.928
2.910
2.891
1.788
1.779
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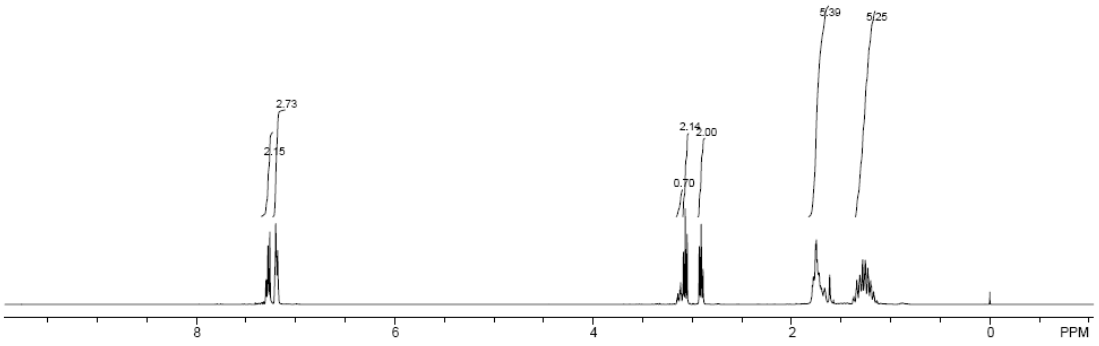
1.194
1.171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8
6
4
2
0
PPM


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29.067
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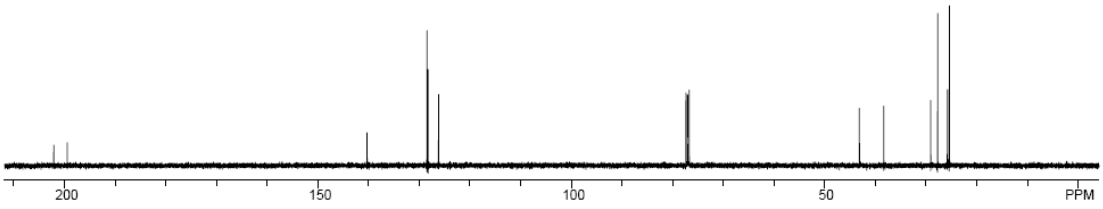
25.791
25.405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PPM