Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

for

Direct Conversion of Allyl Arenes to Aryl Ethylketones via TBHP-mediated Palladium-Catalyzed Tandem Isomerization-Wacker Oxidation of Terminal Alkenes**

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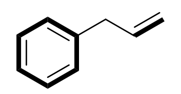
General procedure and compound's characterization

Experimental Procedure and Spectral data

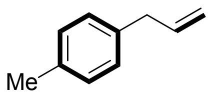
General Considerations.

^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz respectively, and the chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization . HRMS was carried out on a MAT 95XP (Thermo). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

Substrates.



1a



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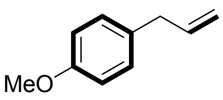
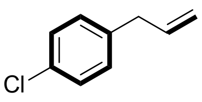
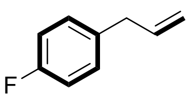


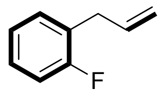
1c



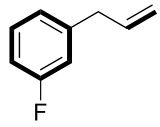
1d



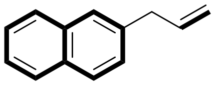
1e



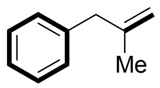
1f



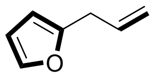
1g



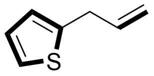
1h



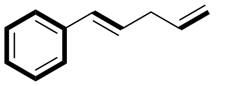
1i



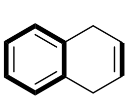
1j



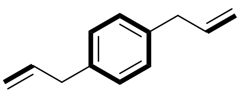
1k



1l



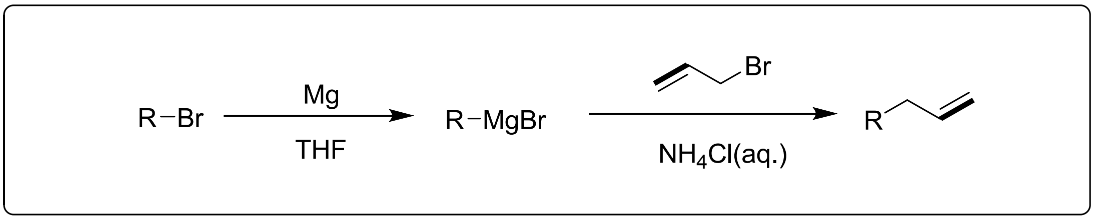
1m



1o

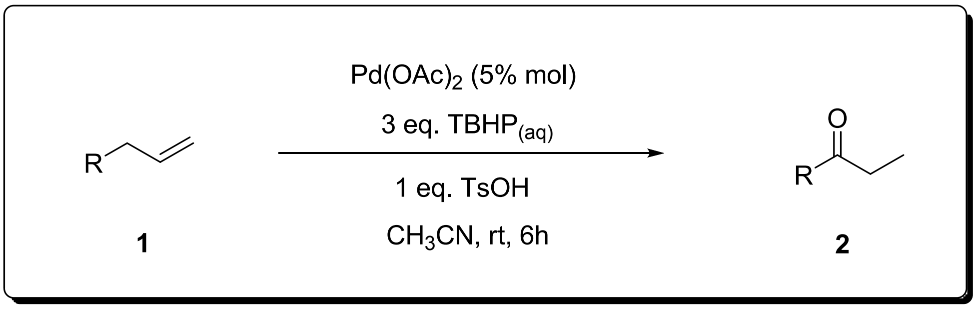
Substrates **1a**, **1j** and **1m** were purchased from Aldrich.

Other substrates were synthesized through Grignard reaction: The aryl bromide was reacted with magnesium in THF using I_2 as initiator. After finishing the reaction, the combined organics added to the THF solution of allyl bromide with magnetic stirring. After 1 hour, NH_4Cl (aq.) was added to the reaction mixture, washing with water and then concentrated for further purification.



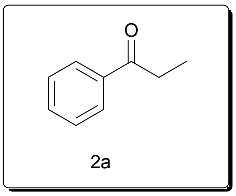
TBHP-mediated palladium-catalyzed tandem isomerization -Wacker oxidation of terminal alkenes

Typical procedure for TBHP-mediated palladium-catalyzed tandem isomerization-Wacker oxidation of allyl arenes to form aryl ethylketones (Table 1):



$Pd(OAc)_2$ (0.025 mmol, 6 mg) and TsOH (0.5 mmol, 86 mg) was mixed with CH_3CN (2 mL) in a glass vial or round-bottom flask equipped with a magnetic stirring bar. Then, substrate **1** (0.5 mmol) and TBHP (1.5 mmol, 0.21 mmol) was added. The mixture was stirred at room temperature for 6 h. After reaction finishing, 5 mL of ethyl acetate was added and removal of the CH_3CN with brine, the residue was purified by flash chromatography on silica gel to obtain the desired product **2** using light petroleum ether/ethyl acetate(15:1, v/v) as eluent, which furnished the aryl ethylketones.

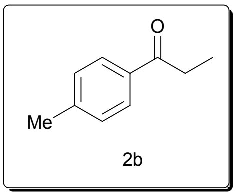
Characterization data for all prepared compounds:



2a

propiophenone (2a) [1]

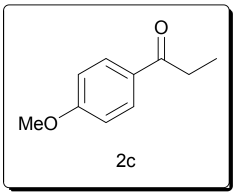
MS (EI) m/z: 134.07; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.89 (d, 2H), 7.46 (m, 1H), 7.37 (m, 1H), 2.90 (q, 2H), 1.16 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=200.5, 138.8, 132.8, 128.5, 127.9, 31.7, 8.14 ppm.



2b

1-p-tolylpropan-1-one (2b) [1]

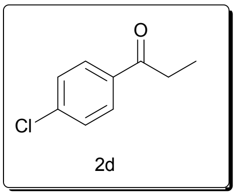
MS (EI) m/z: 148.09; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.81 (d, 2H), 7.18 (d, 2H), 2.90 (q, 2H), 2.34 (s, 3H) , 1.18 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=200.0, 143.4, 134.4, 129.1, 128.0, 31.5, 21.4, 8.2 ppm.



2c

1-(4-methoxyphenyl)propan-1-one (2c) [1]

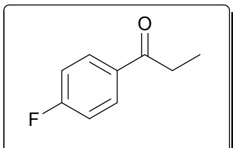
MS (EI) m/z: 164.08; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.89 (d, 2H), 6.87 (d, 2H), 3.80 (s, 2H), 2.88 (q, 2H) , 1.17 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=199.0, 163.2, 130.0, 129.8, 113.5, 55.2, 31.2, 8.2 ppm;



2d

1-(4-chlorophenyl)propan-1-one (2d) [2]

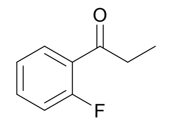
MS (EI) m/z: 168.03; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.89 (d, 2H), 7.41 (d, 2H), 2.96 (q, 2H) , 1.21 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.4, 139.2, 135.2, 129.4, 128.8, 31.7, 8.1 ppm;



2e

1-(4-fluorophenyl)propan-1-one (2e) [3]

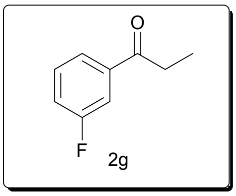
MS (EI) m/z: 152.06; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.97 (q, 2H), 7.41 (t, 2H), 2.94 (q, 2H) , 1.20 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.7, 165.8 (d, $J_{C\text{-}F}$ = 252.3 Hz), 133.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.4(d, $J_{C\text{-}F}$ = 9.1 Hz), 115.3(d, $J_{C\text{-}F}$ = 11.7 Hz),31.4, 7.9 ppm.



2f

1-(2-fluorophenyl)propan-1-one (2f) [1]

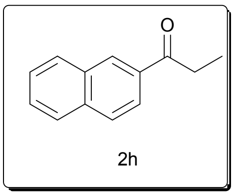
MS (EI) m/z: 152.06; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.86 (t, 1H), 7.48 (m, 1H), 7.20 (t, 1H), 7.11 (t 1H), 2.98 (q, 2H), 1.20 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 162.8 (d, $J_{C\text{-}F}$ = 252.3 Hz), 134.2 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 125.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.2 Hz) 116.5(d, $J_{C\text{-}F}$ = 24.0 Hz), 36.4(d, $J_{C\text{-}F}$ = 7.4 Hz), 7.9(d, $J_{C\text{-}F}$ = 2.0 Hz) ppm.



2g

1-(3-fluorophenyl)propan-1-one (2g) [4]

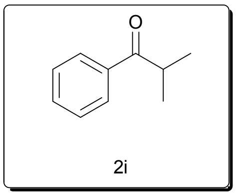
MS (EI) m/z: 152.06; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.71 (t, 1H), 7.61 (t, 1H), 7.42 (m, 1H), 7.22 (t, 1H), 2.96 (q, 2H), 1.21 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=199.1 (d, Hz), 162.8 (d, $J_{C\text{-}F}$ = 246.1 Hz), 138.9 (d, $J_{C\text{-}F}$ = 6.0 Hz), 130.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 123.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 119.6 (d, $J_{C\text{-}F}$ = 21.3 Hz) 114.4(d, $J_{C\text{-}F}$ = 22.0 Hz), 31.8, 7.9 ppm.



2h

1-(naphthalen-2-yl)propan-1-one (2h) [3]

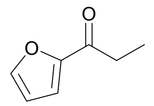
MS (EI) m/z: 184.09; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 8.48 (s, 1H), 8.05 (d, 1H), 7.98 (d, 1H), 7.90 (m, 2H), 7.55-7.64 (m, 2H), 2.94 (q, 2H), 1.20 (t, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 31.8, 8.1 ppm



2i

2-methyl-1-phenylpropan-1-one (2i) [1]

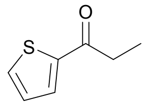
MS (EI) m/z: 148.09; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.91 (d, 2H), 7.46 (m, 1H), 7.38 (t, 1H), 3.34-3.54 (m, 1H), 1.15 (t, 6H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ=204.2, 136.1, 132.7, 128.6, 128.2, 35.2, 19.1 ppm.



2j

1-(furan-2-yl)propan-1-one (2j) [5]

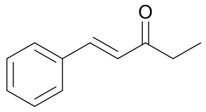
MS (EI) m/z: 124.05; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.41 (s, 1H), 7.00 (d, 1H), 6.34 (t, 1H), 2.89 (q, 2H), 1.15 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=186.4, 152.6, 146.4, 117.3, 112.1, 25.7, 8.1 ppm.



2k

1-(thiophen-2-yl)propan-1-one (2k) [6]

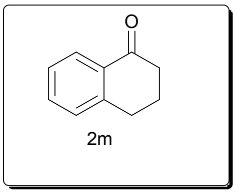
MS (EI) m/z: 140.03; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69 (d, 1H), 7.62 (d, 2H), 7.11 (t, 1H), 2.87 (q, 2H), 1.12 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.6, 144.5, 133.8, 132.6, 128.2, 26.8, 8.2 ppm.



2l

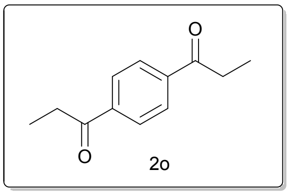
(E)-1-phenylpent-1-en-3-one (2l) [1]

MS (EI) m/z: 160.09; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.55 (m, 2H), 7.53 (d, *J*=16.4 Hz, 1H), 7.42 (t, 3H), 6.74 (d, *J*=16.4 Hz, 1H), 2.82 (q, 2H), 1.10 (t, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.4, 143.5, 134.4, 130.5, 129.0, 128.3, 127.2, 27.5, 8.0 ppm.



3,4-dihydronaphthalen-1(2H)-one (2m) [7]

MS (EI) m/z: 146.07; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.99 (d, 1H), 7.40 (d, 1H), 9.19-7.26 (m, 2H), 2.90 (t, 2H), 2.58 (t, 2H), 2.06 (d, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=198.1, 144.4, 133.3, 132.5, 128.8, 127.0, 126.5, 39.1, 29.6, 23.2 ppm.



1,1'-(1,4-phenylene)bis(propan-1-one) (2o)

^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.01 (s, 4H), 2.90 (q, 4H), 1.15 (t, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=199.6, 139.4, 129.0, 31.9, 8.2 ppm; HRMS EI (m/z): calcd for $C_{12}H_{14}O_2$, 190.0997; found, 190.0994.

Reference:

[1] N. Ahlsten, H. Lundberg and B. Martín-Matute, *Green Chem.* **2012**, *12*, 1628.

[2] B. Lastra-Barreira, J. Díez, P. Crochet , *Green Chem.* **2009**, *11*, 1681.

[3] L. Menéndez-Rodríguez, P. Crochet, V. Cadierno, *J. Mol. Cat. A: Chemical*, **2013**, *366*, 390.

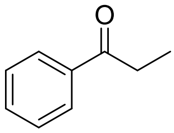
[4] A. V. R. Rao, R. Rao, J. S. Yadav, M, Khagga, *Synth. Commun.*, **2013**, 43, 1661.

[5] J. Boudreau, M. Doucette, A. N. Ajjou Tetradron Letters. **2006**, *47*, 1695.

[6] A. Poirel , A. De Nicola , P. Retailleau , R. Ziessel, *J. Org. Chem.* **2012**, *77*, 7512.

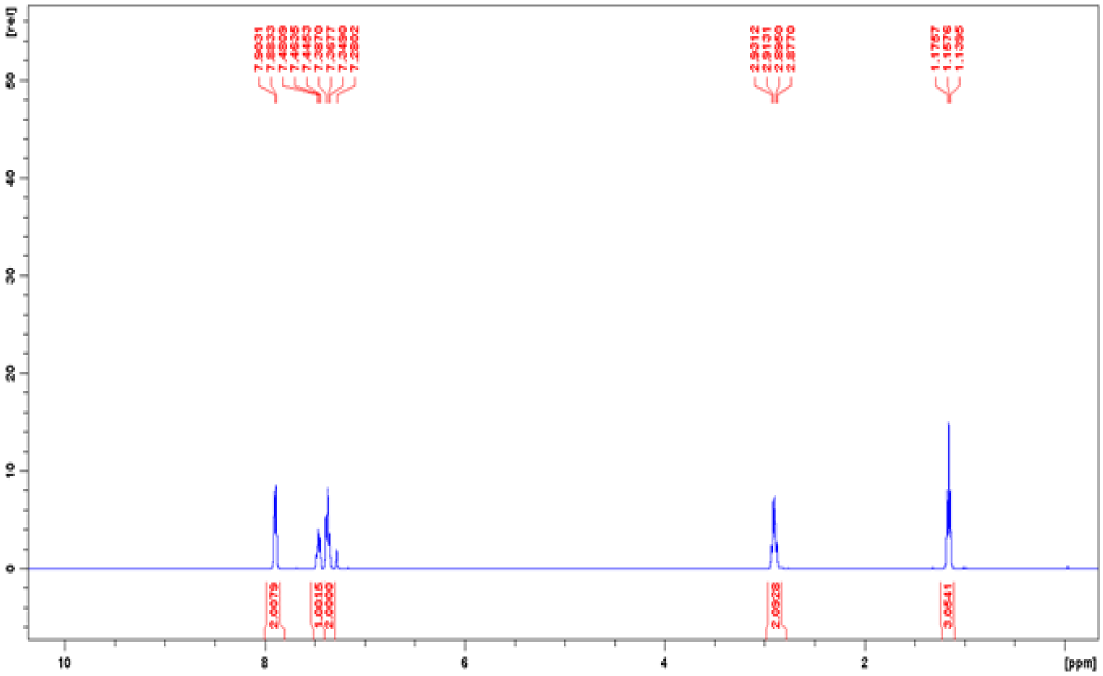
[7] B. Landers , C. Berini , C. Wang , O. Navarro, *J. Org. Chem.* **2011**, *76*, 1390.

NMR Spectra

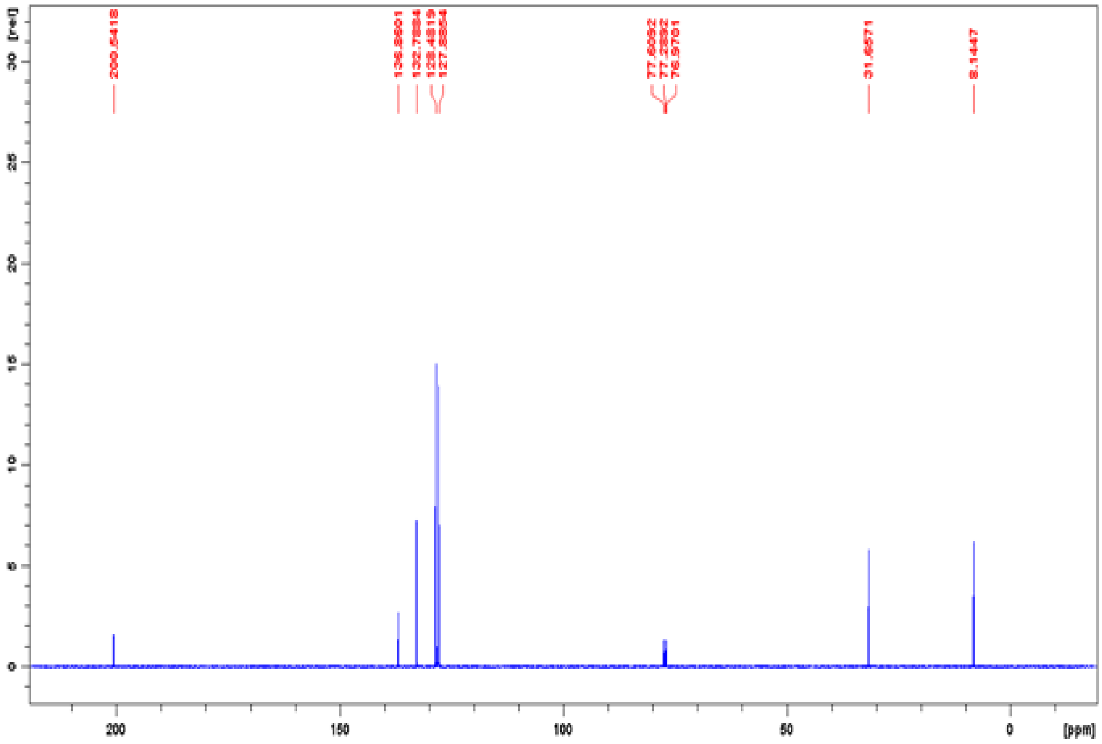


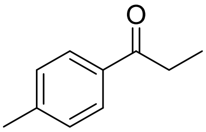
2a

^{1}H



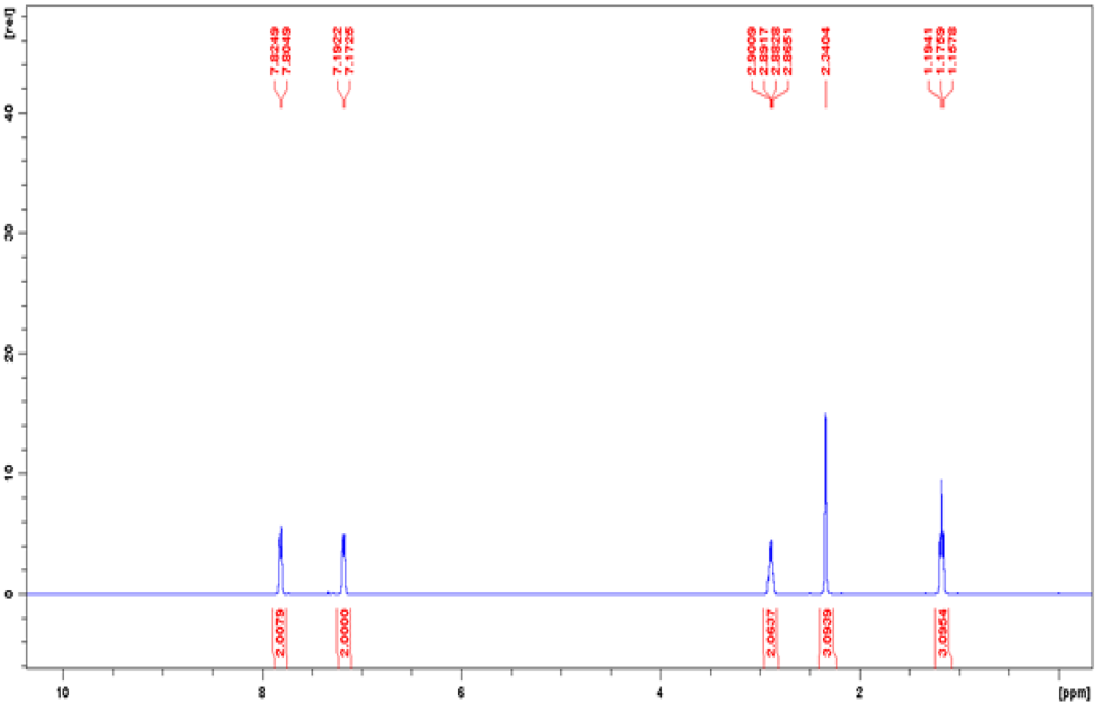
^{13}C




O

2b

^{1}H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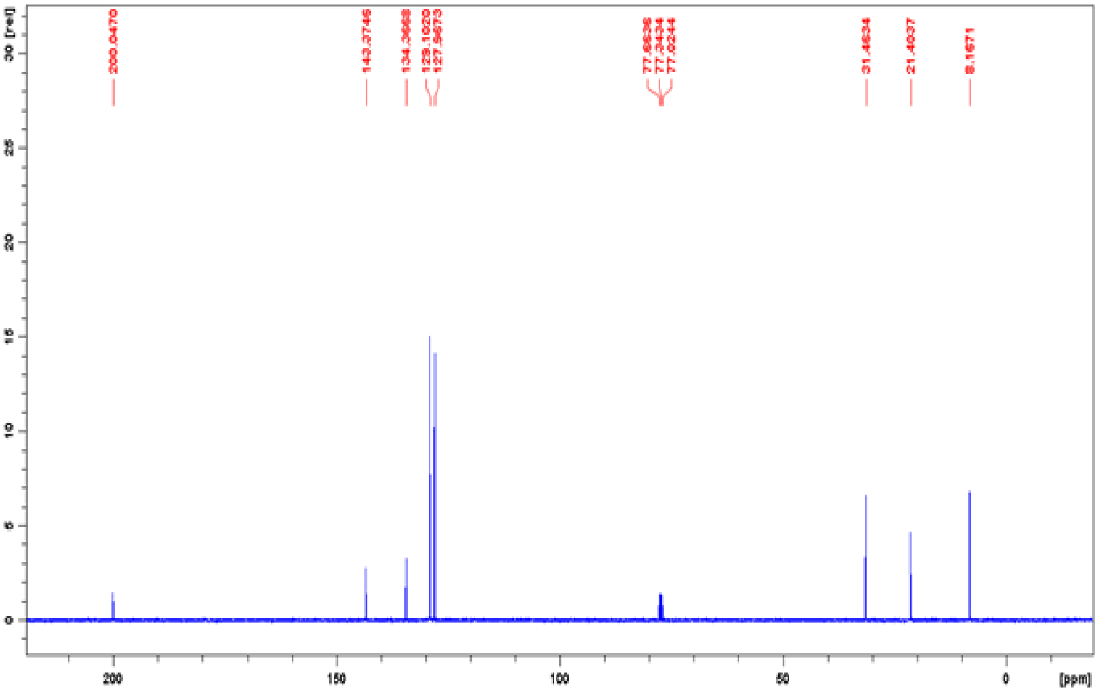
10
8
6
4
2
[ppm]

^{13}C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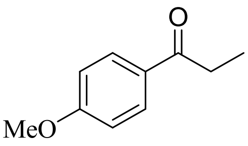
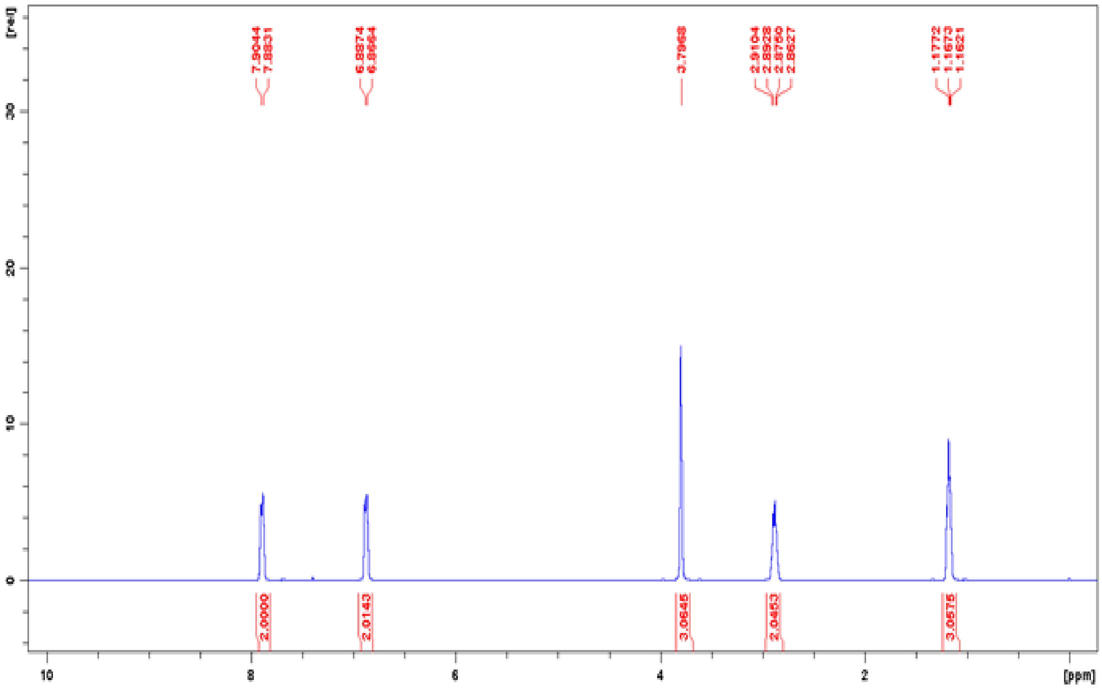
0
[ppm]


O
MeO

2c

^{1}H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1.1621
[rel]
30
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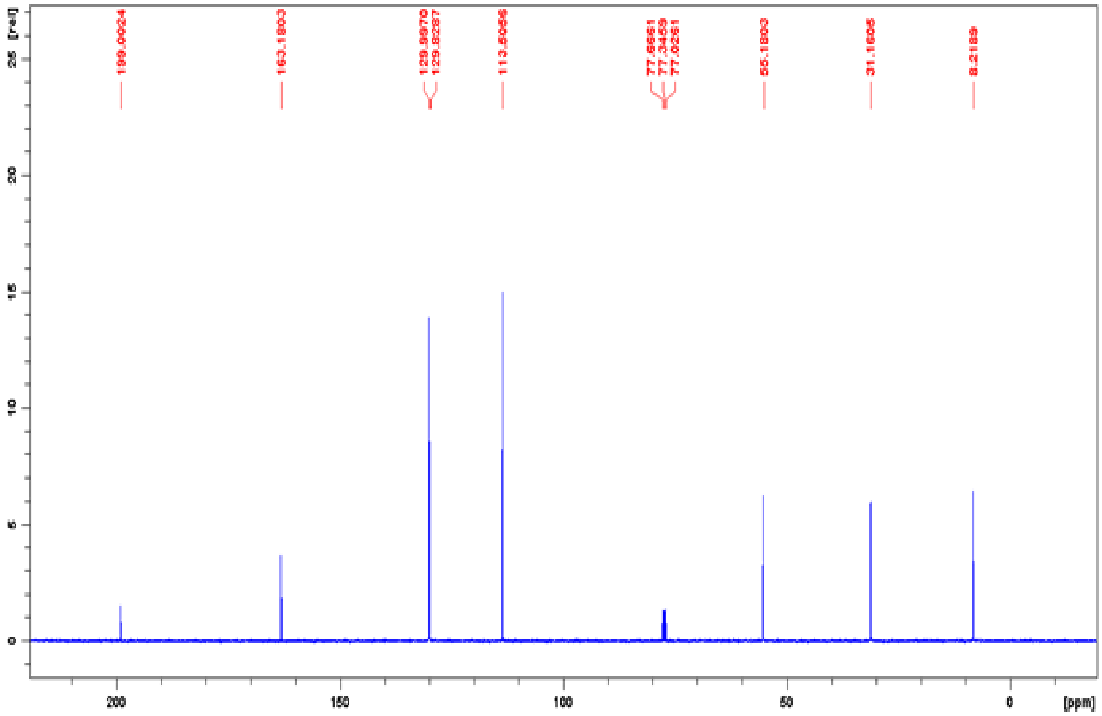
2.0143
3.0645
2.0453
3.0575
10
8
6
4
2
[ppm]

^{13}C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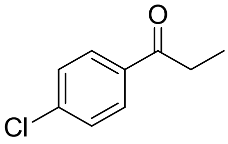
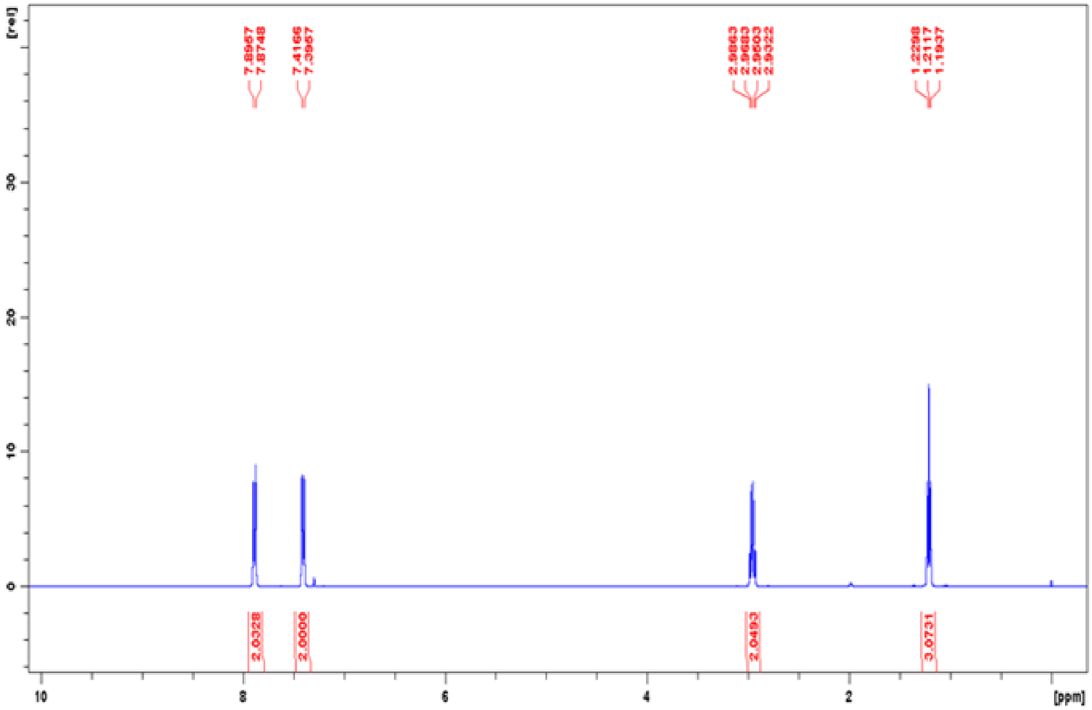
163.1803
129.9970
129.8287
113.5056
77.6651
77.3459
77.0261
55.1803
31.1605
8.2189
25 [rel]
20
15
10
5
0
200
150
100
50
0
[ppm]

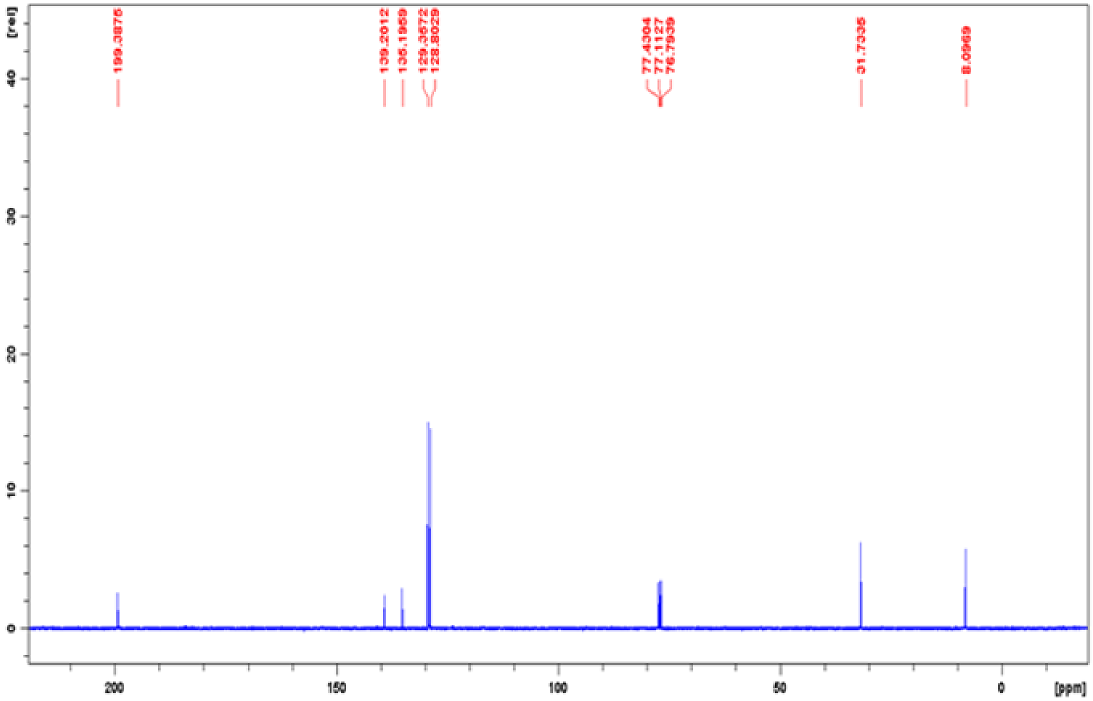

O
Cl

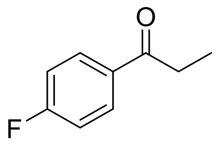
2d

^{1}H


[rel]
7.8957
7.8748
7.4166
7.3957
2.9863
2.9683
2.9503
2.9322
1.2298
1.2117
1.1937
30
20
10
0
2.0328
2.0000
2.0493
3.0731
10
8
6
4
2
[ppm]

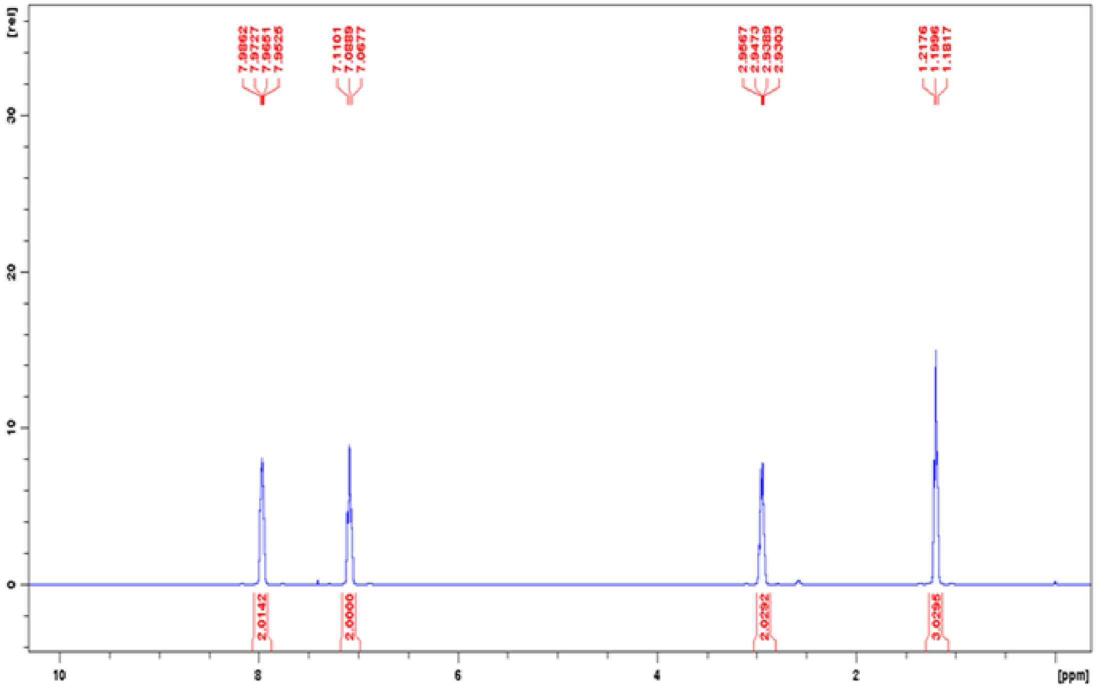
^{13}C


[rel]
199.3876
139.2012
135.1959
129.3572
128.8029
77.4304
77.1127
76.7939
31.7335
8.0969
40
30
20
10
0
200
150
100
50
0
[ppm]


O
F

2e

^{1}H


[rel]
30
20
10
0
7.9862
7.9727
7.9651
7.9525
7.1101
7.0889
7.0677
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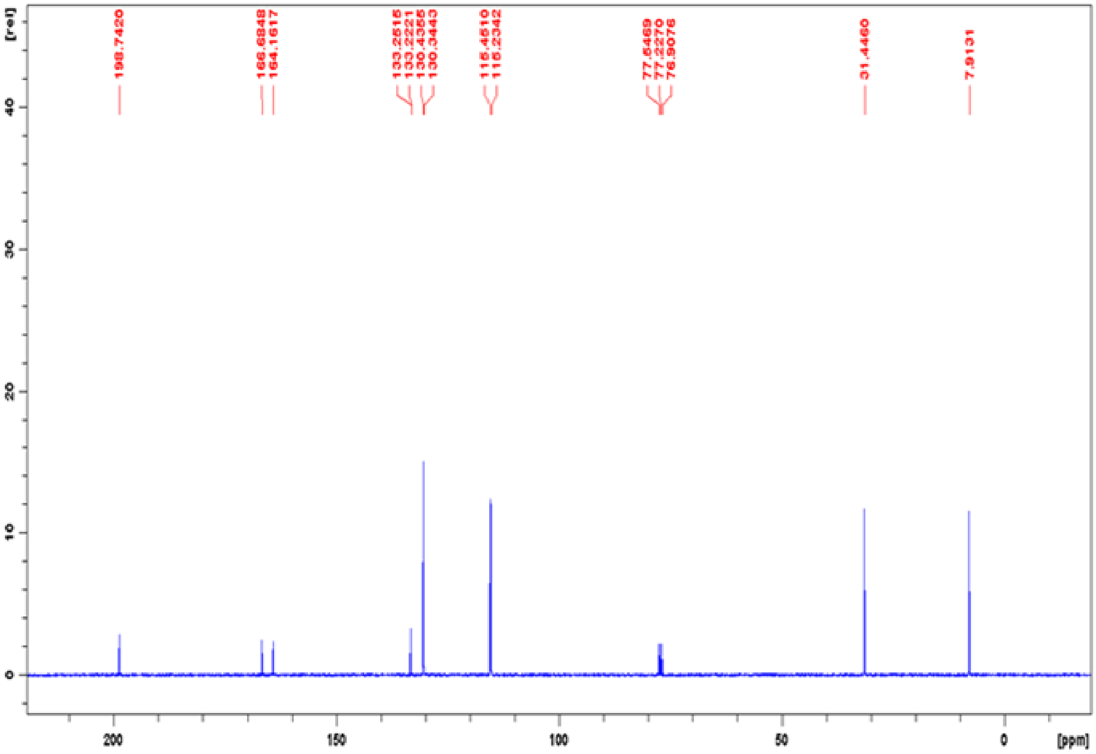
2.9473
2.9389
2.9303
1.2176
1.1996
1.1817
2.0142
2.0000
2.0292
3.0295
10
8
6
4
2
[ppm]

^{13}C


[rel]
40
30
20
10
0
198.7420
166.6848
164.1617
133.2516
133.2221
130.4355
130.3443
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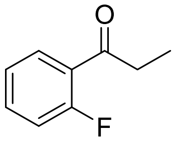
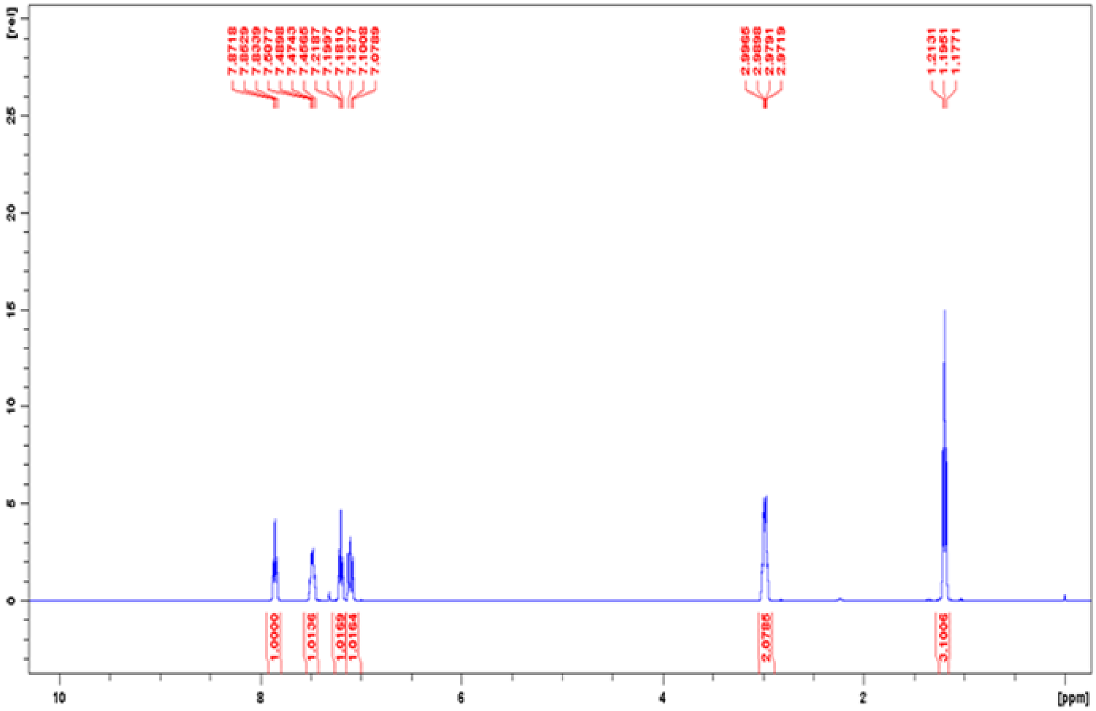
115.2342
77.5469
77.2270
76.9076
31.4460
7.9131
200
150
100
50
0
[ppm]

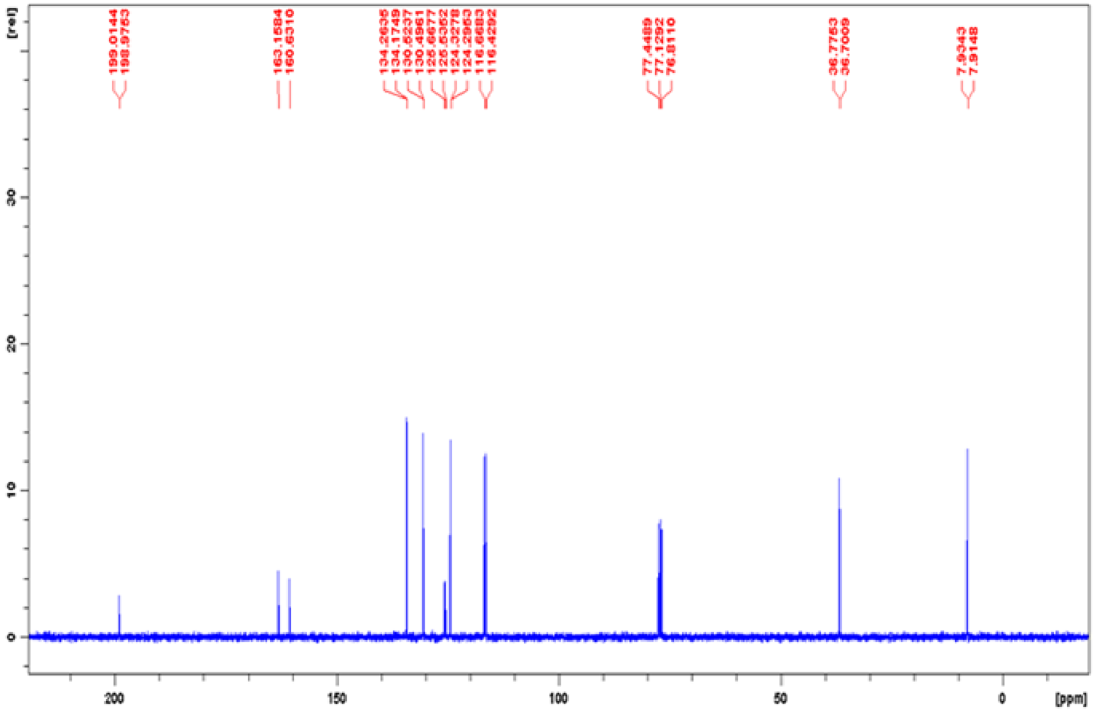

O
F

2f

^{1}H


[rel]
25
20
15
10
5
0
7.8718
7.8529
7.8339
7.5077
7.4898
7.4743
7.4565
7.2187
7.1997
7.1810
7.1277
7.1008
7.0789
2.9965
2.9898
2.9791
2.9719
1.2131
1.1951
1.1771
1.0000
1.0136
1.0162
1.0164
2.0786
3.1006
10
8
6
4
2
[ppm]

^{13}C


[rel]
30
20
10
0
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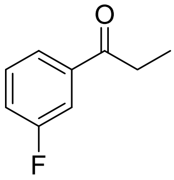
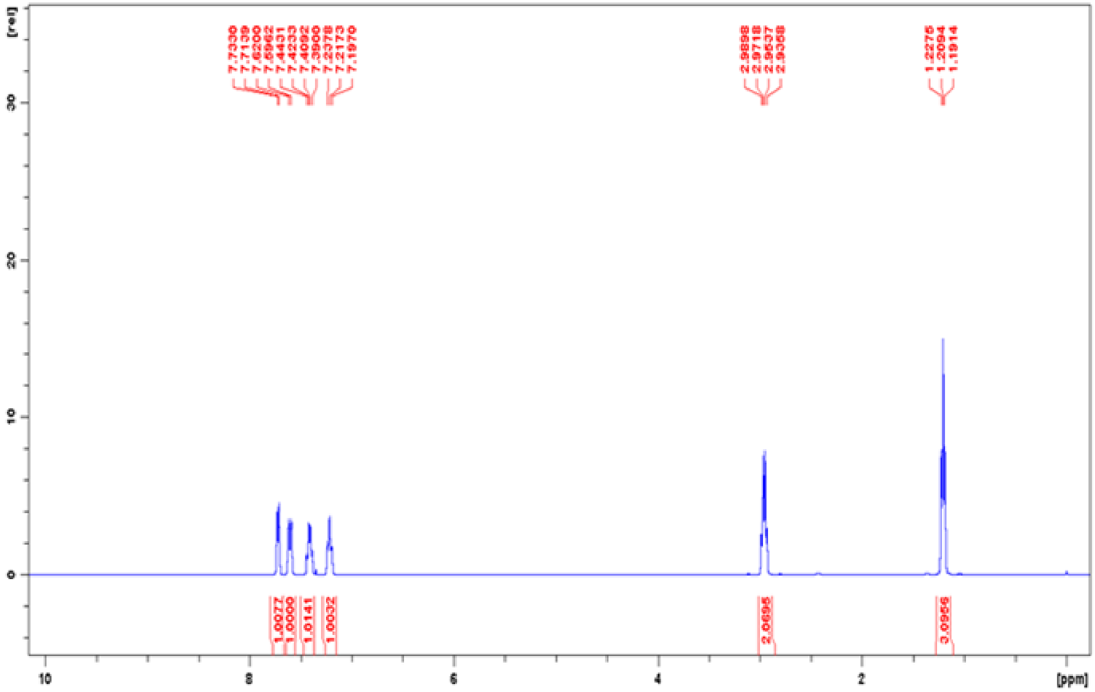
198.9763
163.1584
160.6310
134.2635
134.1749
130.5237
130.4961
125.6677
125.5352
124.3278
124.2953
116.6683
116.4292
77.4489
77.1292
76.8110
36.7753
36.7009
7.9343
7.9148
200
150
100
50
0
[ppm]

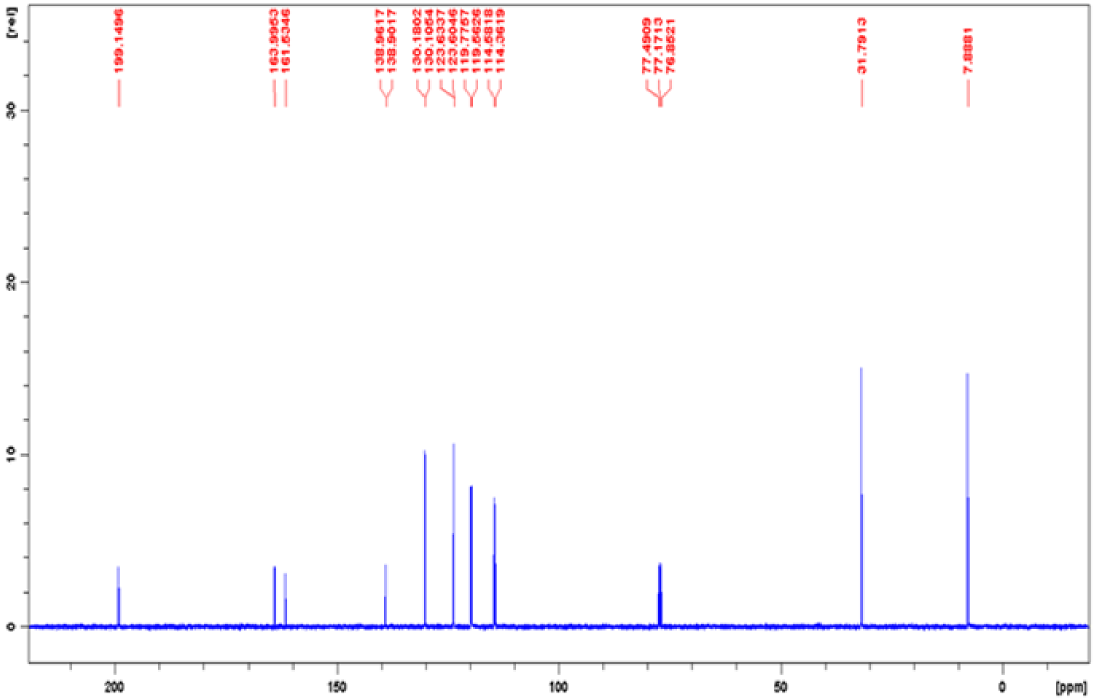

O
F

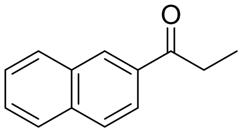
2g

^{1}H


[rel]
7.7330
7.7139
7.6200
7.5962
7.4431
7.4233
7.4092
7.3900
7.2378
7.2173
7.1970
2.9898
2.9718
2.9537
2.9358
1.2275
1.2094
1.1914
30
20
10
0
1.0077
1.0000
1.0141
1.0032
2.0695
3.0956
10
8
6
4
2
[ppm]

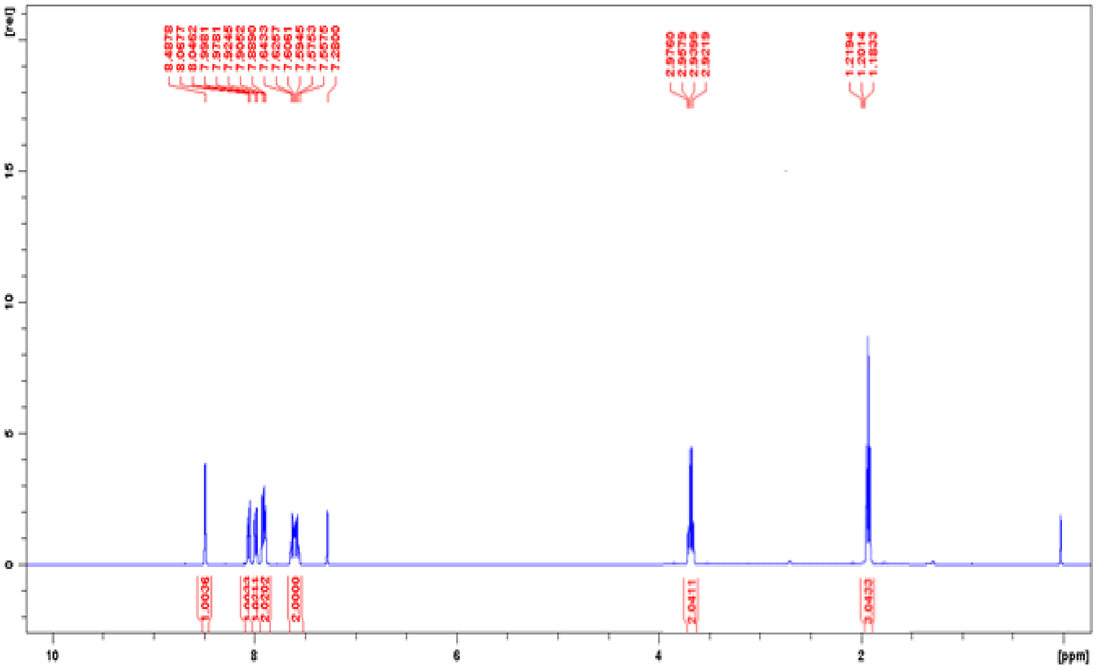
^{13}C


[rel]
199.1496
163.9953
161.5346
138.9617
138.9017
130.1802
130.1054
123.6337
123.6046
119.7757
119.5626
114.5818
114.3619
77.4909
77.1713
76.8521
31.7913
7.8881
30
20
10
0
200
150
100
50
0
[ppm]

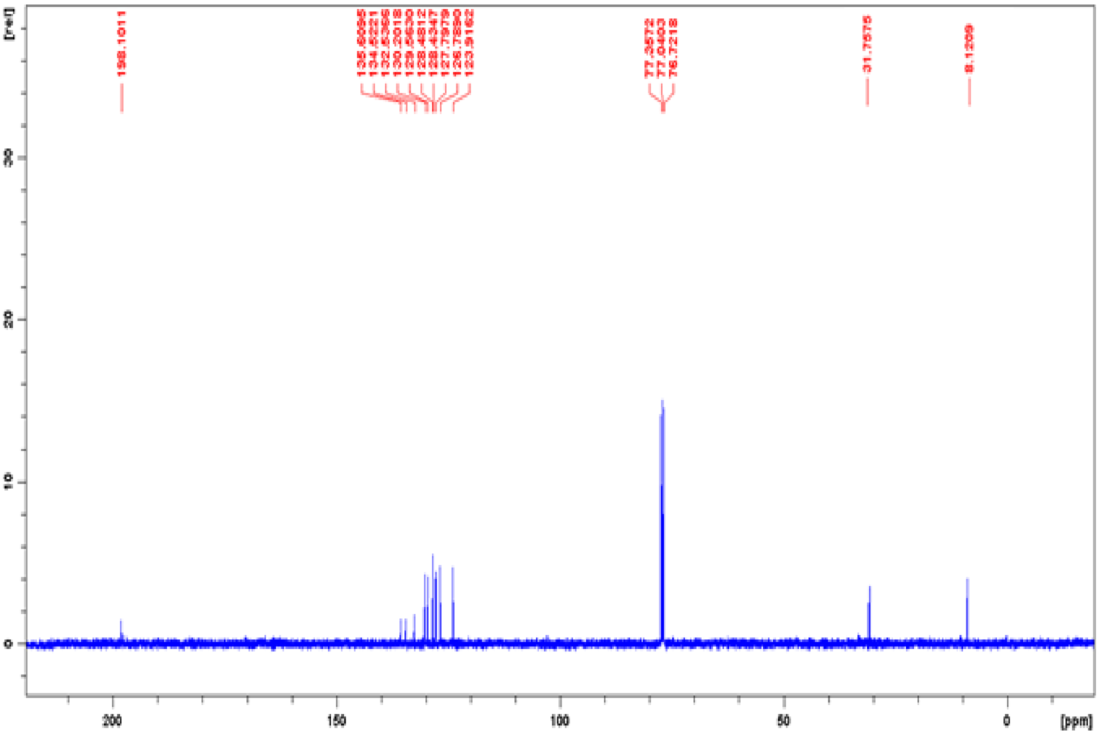


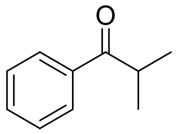
2h

^{1}H


[rel]
15
10
5
0
8.4878
8.0677
8.0462
7.9981
7.9781
7.9245
7.9052
7.8890
7.6433
7.6257
7.6061
7.5945
7.5753
7.5575
7.2800
2.9760
2.9579
2.9399
2.9219
1.2194
1.2014
1.1833
1.0036
1.0033
1.0211
2.0202
2.0000
2.0411
3.0433
10
8
6
4
2
[ppm]

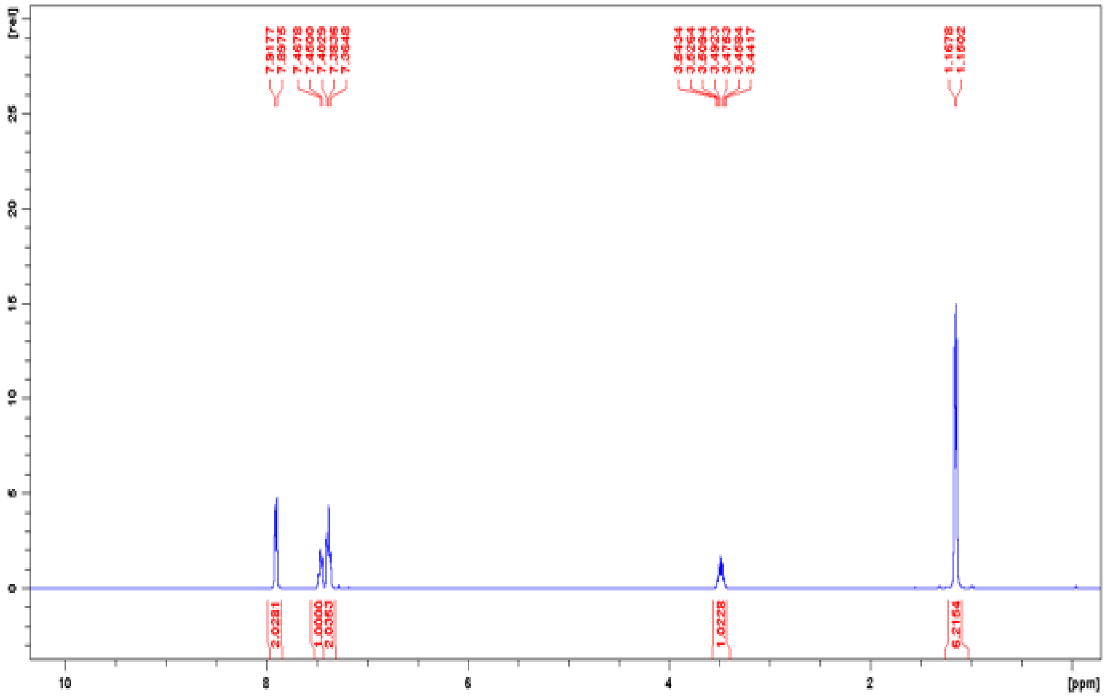
^{13}C


[rel]
30
20
10
0
198.1011
135.6085
134.5221
132.5366
130.2018
129.5530
128.4512
128.4347
127.7979
126.7890
123.9162
77.3572
77.0403
76.7218
31.7575
8.1209
200
150
100
50
0
[ppm]



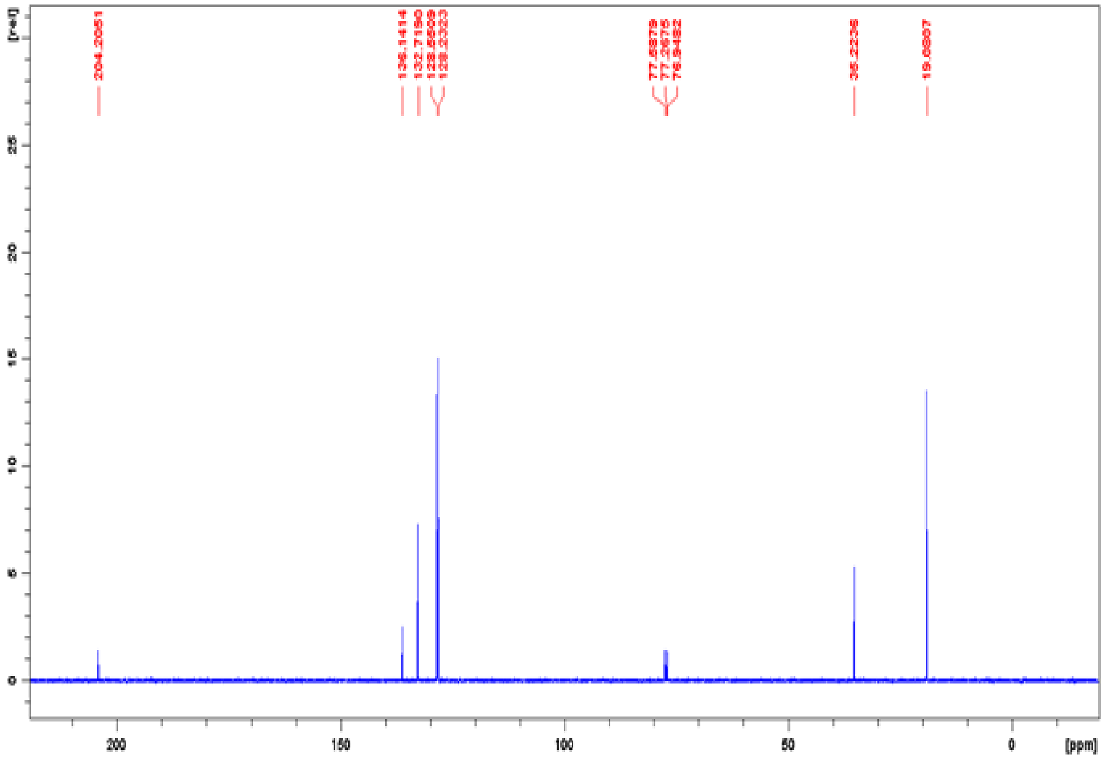
2i

^{1}H

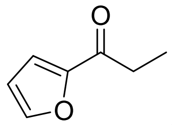


[rel]
25
20
15
10
5
0
7.9177
7.8975
7.4678
7.4500
7.4029
7.3836
7.3648
3.5434
3.5264
3.5094
3.4923
3.4753
3.4584
3.4417
1.1678
1.1502
2.0281
1.0000
2.0353
1.0228
6.2164
10
8
6
4
2
[ppm]

^{13}C

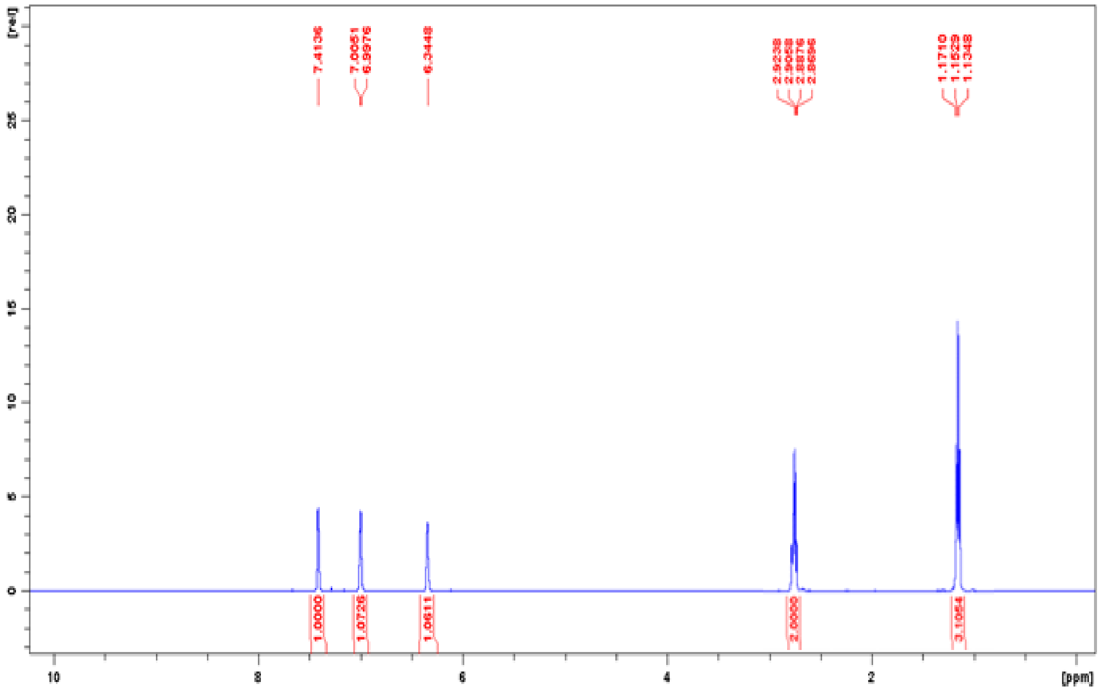


[rel]
25
20
15
10
5
0
204.2051
136.1414
132.7190
128.5509
128.2323
77.5879
77.2675
76.9482
35.2236
19.0807
200
150
100
50
0
[ppm]



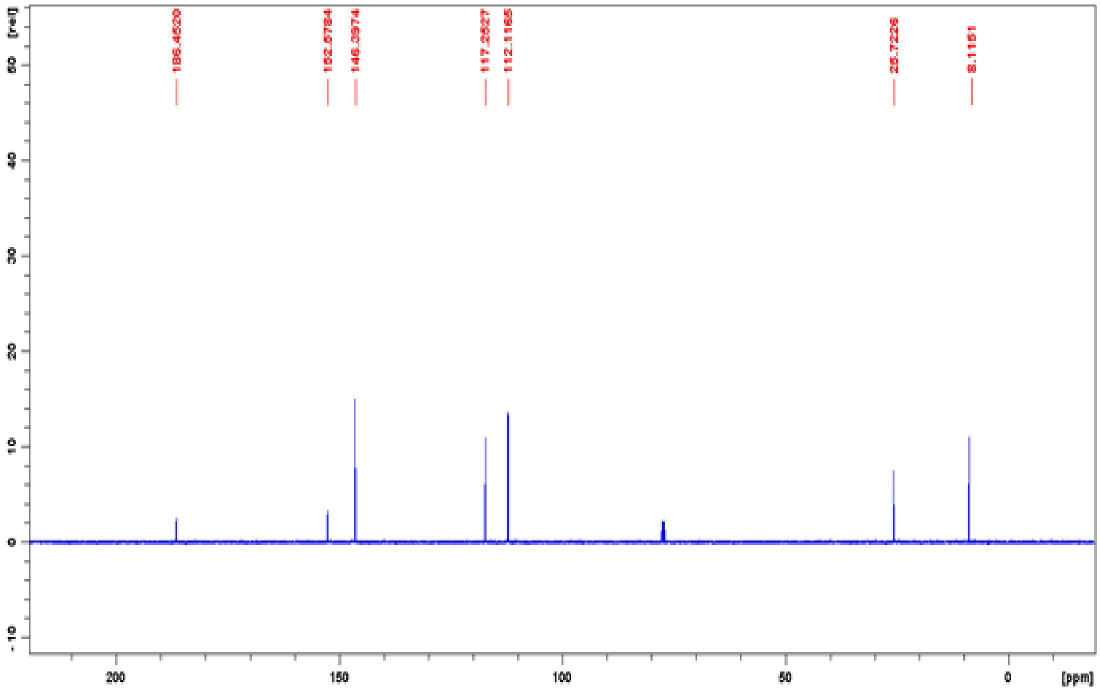
2j

^{1}H

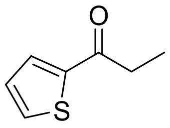


[rel]
25
20
15
10
5
0
7.4136
7.0051
6.9976
6.3449
2.9238
2.9058
2.8876
2.8696
1.1710
1.1529
1.1348
1.0000
1.0726
1.0611
2.0000
3.1064
10
8
6
4
2
[ppm]

^{13}C

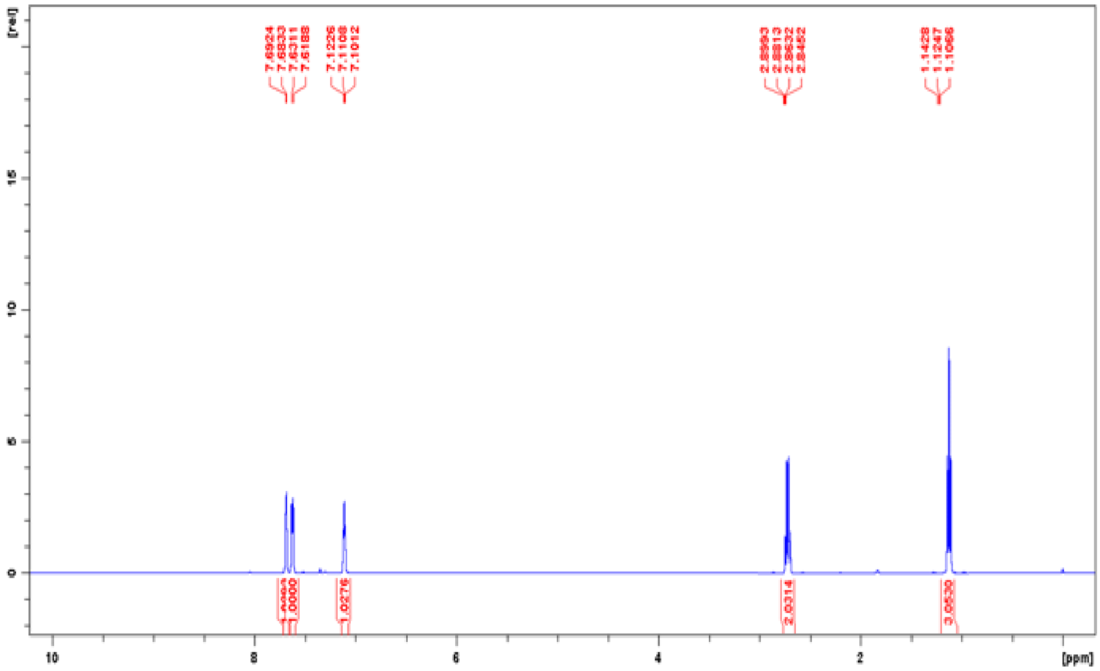


[rel]
50
40
30
20
10
0
-10
185.4520
152.5784
146.3974
117.2527
112.1165
25.7226
8.1161
200
150
100
50
0
[ppm]

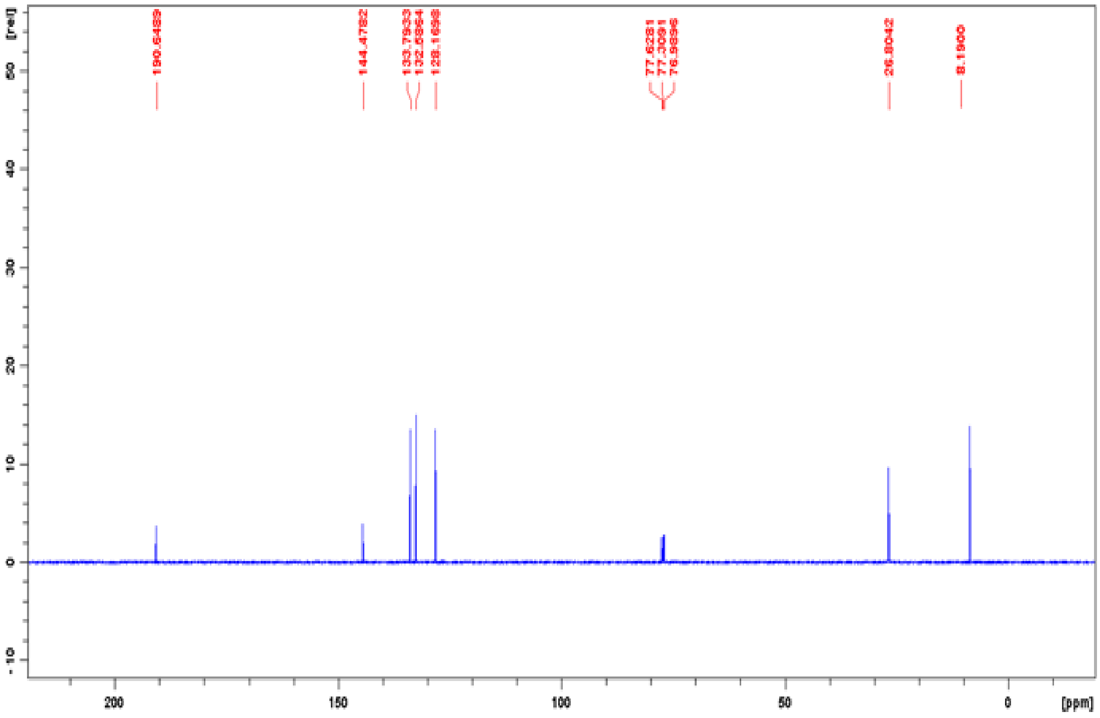

O
S

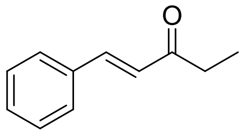
2k

^{1}H


7.6924
7.6833
7.6311
7.6188
7.1226
7.1108
7.1012
2.8993
2.8813
2.8632
2.8452
1.1428
1.1247
1.1066
1.0000
1.0276
2.0314
3.0530
[rel]
15
10
5
0
10
8
6
4
2
[ppm]

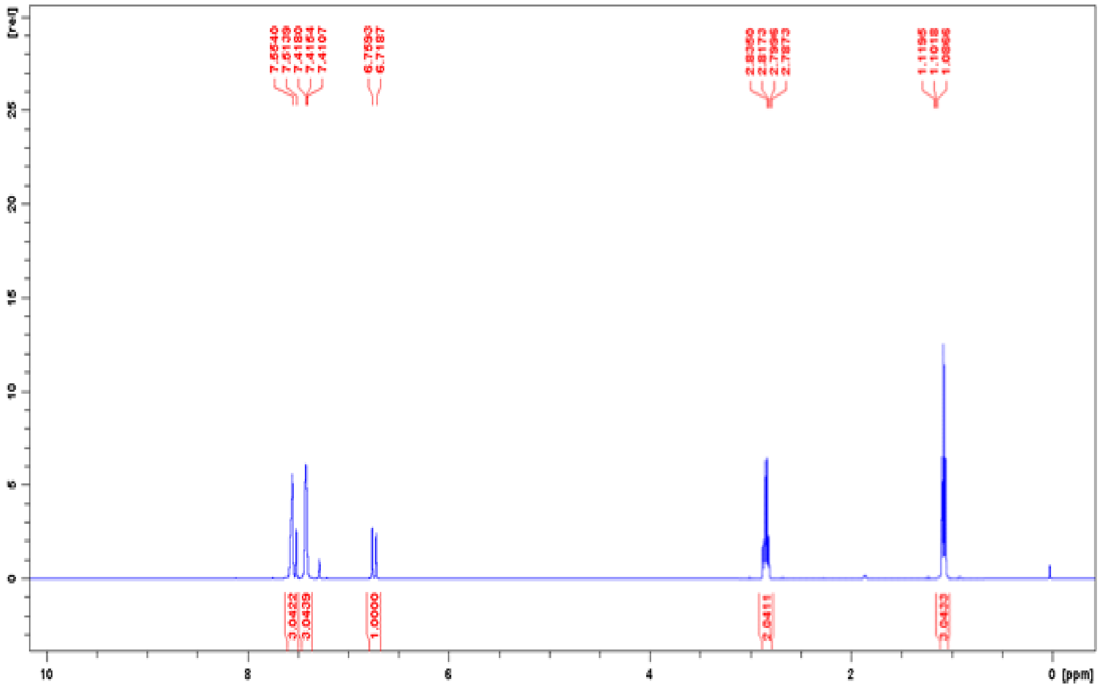
^{13}C


190.6489
144.4782
133.7933
132.5854
128.1698
77.6281
77.3091
76.9896
26.8042
8.1900
[rel]
50
40
30
20
10
0
-10
200
150
100
50
0
[ppm]

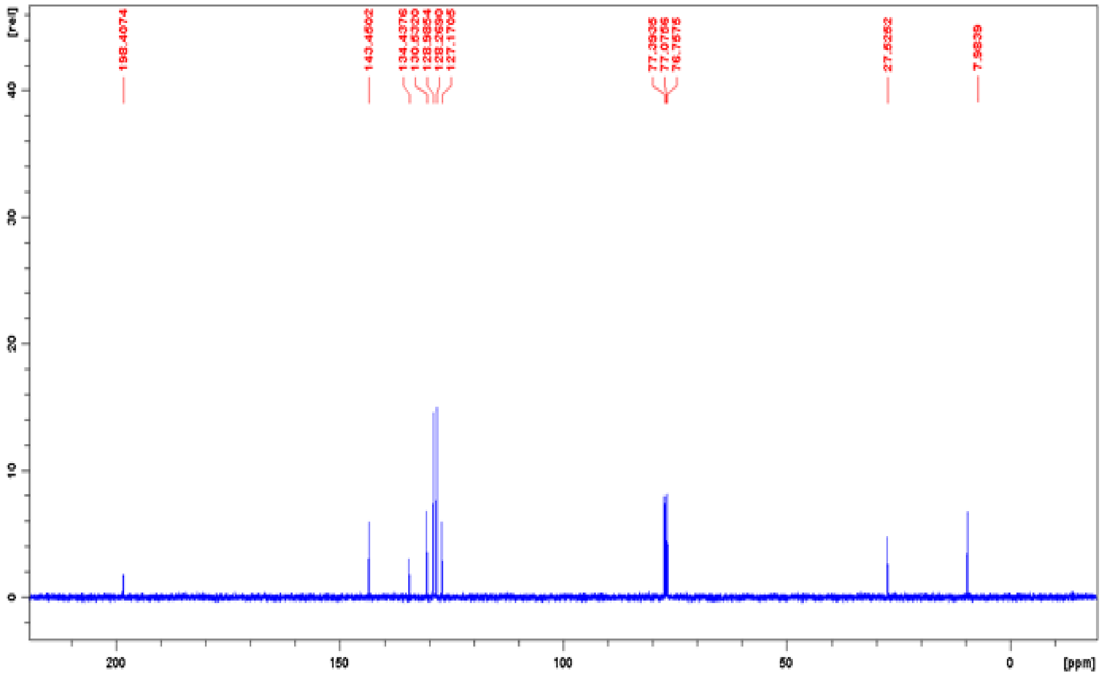


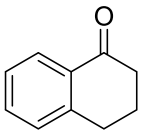
2l

^{1}H


7.5540
7.5139
7.4180
7.4154
7.4107
6.7593
6.7187
2.8350
2.8173
2.7996
2.7873
1.1195
1.1018
1.0866
3.0422
3.0439
1.0000
2.0411
3.0432
[rel]
25
20
15
10
5
0
10
8
6
4
2
0 [ppm]

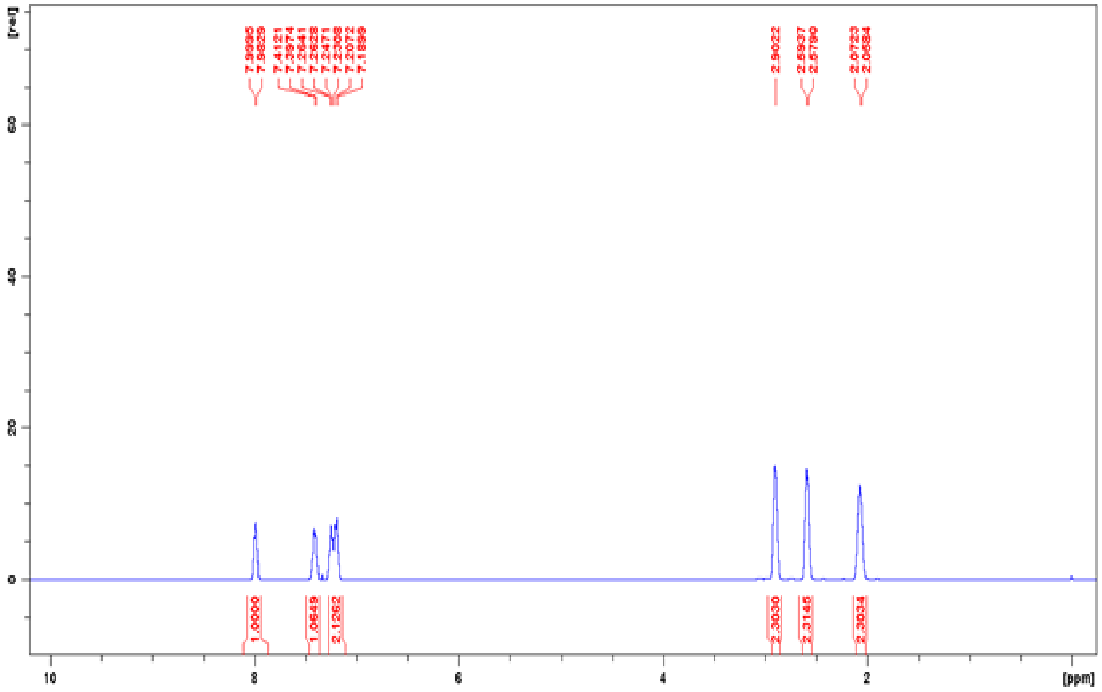
^{13}C


198.4074
143.4502
134.4376
130.5320
128.9854
128.2590
127.1705
77.3935
77.0756
76.7575
27.5252
7.9839
[rel]
40
30
20
10
0
200
150
100
50
0
[ppm]



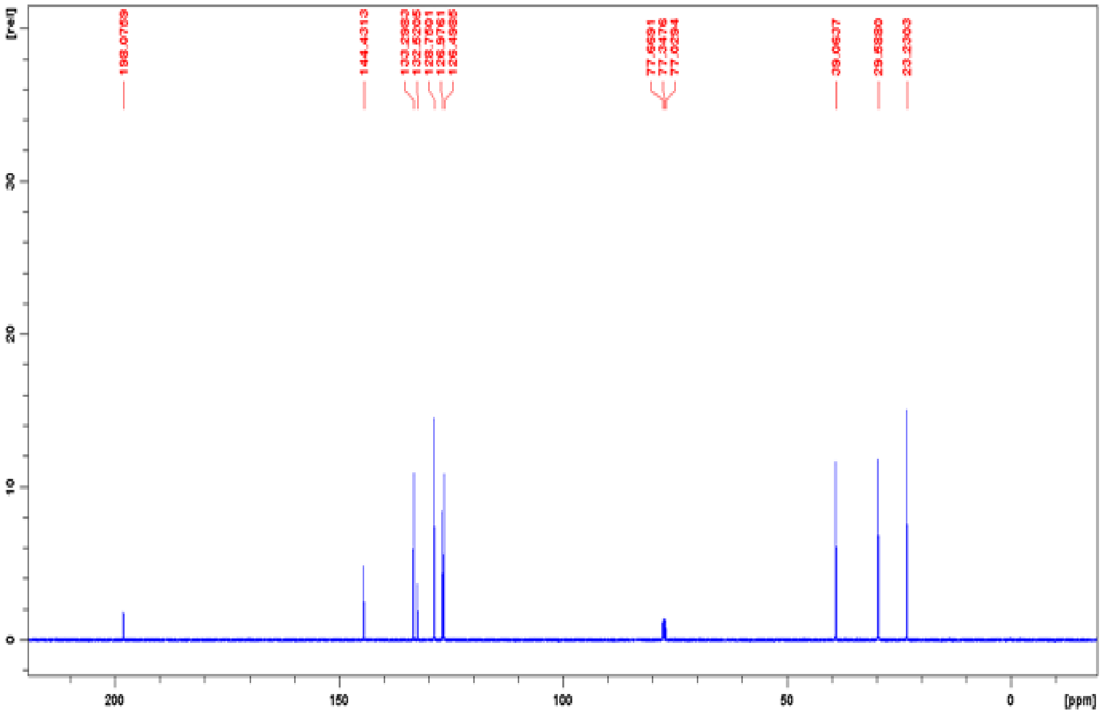
2m

^{1}H



7.9995
7.9829
7.4121
7.3874
7.2841
7.2628
7.2471
7.2308
7.2072
7.1899
2.9022
2.5937
2.5790
2.0723
2.0584
1.0000
1.0549
2.1262
2.3030
2.3145
2.3034
[rel]
60
40
20
0
10
8
6
4
2
[ppm]

^{13}C



198.0759
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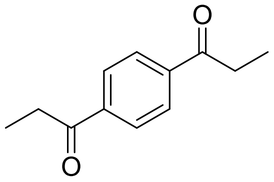
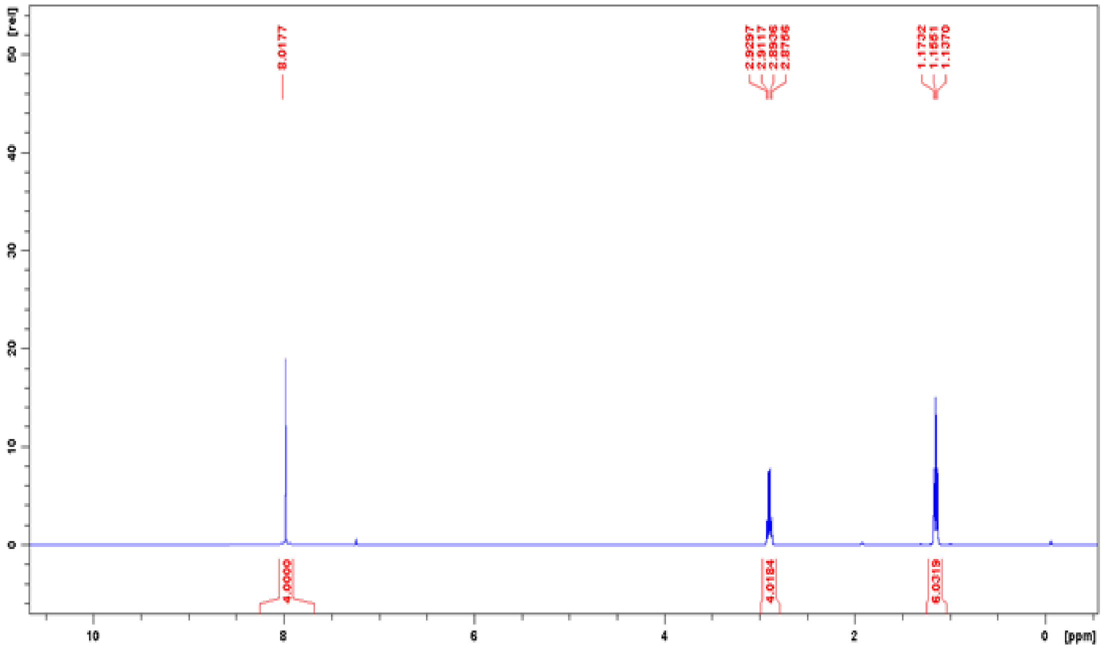
133.2983
132.5205
128.7591
126.9761
126.4985
77.6691
77.3476
77.0294
39.0637
29.5880
23.2303
[rel]
30
20
10
0
200
150
100
50
0
[ppm]

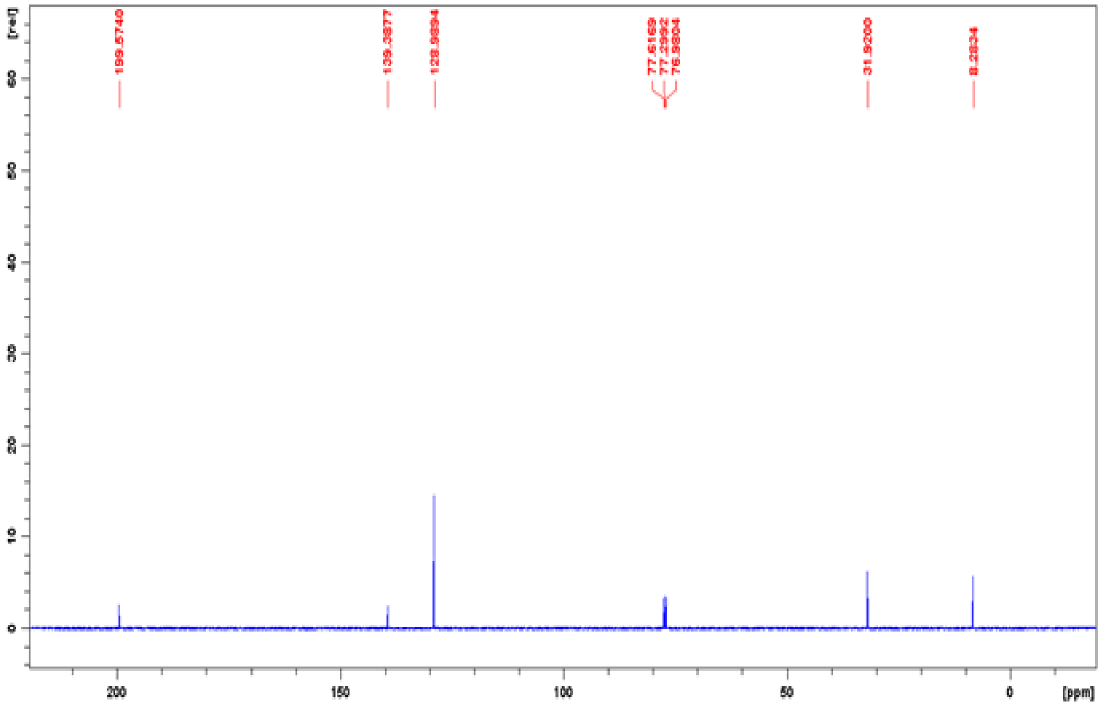


2o

^{1}H


8.0177
2.9297
2.9117
2.8936
2.8756
1.1732
1.1551
1.1370
4.0000
4.0184
6.0319
[rel]
50
40
30
20
10
0
10
8
6
4
2
0
[ppm]

^{13}C


199.5740
139.3877
128.3894
77.5169
77.2992
76.9804
31.9200
8.2834
[rel]
60
50
40
30
20
10
0
200
150
100
50
0
[ppm]