Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

A Tandem Reaction of Organozinc Reagent Prepared from Palladium-catalyzed Umpolung Method: Diastereoselective Formation of Cyclohexene Derivatives Bearing Three Adjacent Stereocenters

Mutsumi SADA, Kenichi Nomura, and Seijiro MATSUBARA*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoutodaigaku-Katsura, Nishikyo, Kyoto 615-8510, Japan

Contents

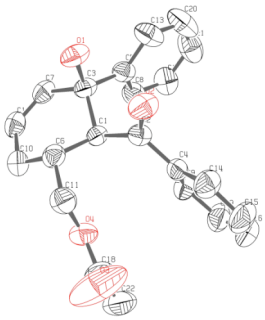
Instrumentation and Chemicals

Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer using tetramethylsilane for ^{1}H NMR as an internal standard (δ = 0 ppm), $CDCl_3$ for ^{13}C NMR as an internal standard (δ = 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Kyoto University Elemental Analysis Center. Infrared (IR) spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Melting points were determined using a YANAKO MP-500D. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and an aqueous vanillin solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–100 μm).

Unless otherwise noted, commercially available reagents were used without purification. Tetrahydrofuran, Dehydrated stabilizer free —Super— was purchased from Kanto Chemical Co., stored under argon, and used as it is.

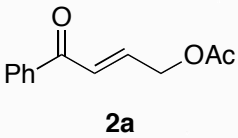
X-ray Christallographic Analysis

ORTEP drawing: **4a**



Empirical formula	C22 H22 O4	
Formula weight	350.40	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.0102(6) Å	α = 81.280(2)°.
	b = 10.0194(9) Å	β = 83.245(2)°.
	c = 15.9053(15) Å	γ = 75.899(2)°.
Volume	914.94(15) $Å^3$	
Z	2	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	372	
Crystal size	1.00 x 0.50 x 0.20 mm^3	
Theta range for data collection	2.11 to 27.04°.	
Index ranges	-7<=h<=6, -12<=k<=8, -19<=l<=20	
Reflections collected	5637	
Independent reflections	3892 [R(int) = 0.0150]	
Completeness to theta = 27.04°	96.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3892 / 0 / 237	
Goodness-of-fit on F^2	0.823	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1829	
R indices (all data)	R1 = 0.0625, wR2 = 0.1990	
Largest diff. peak and hole	0.295 and -0.219 $e.Å^{-3}$	

^{1}H NMR and ^{13}C NMR Spectra of the Substrate and the Products



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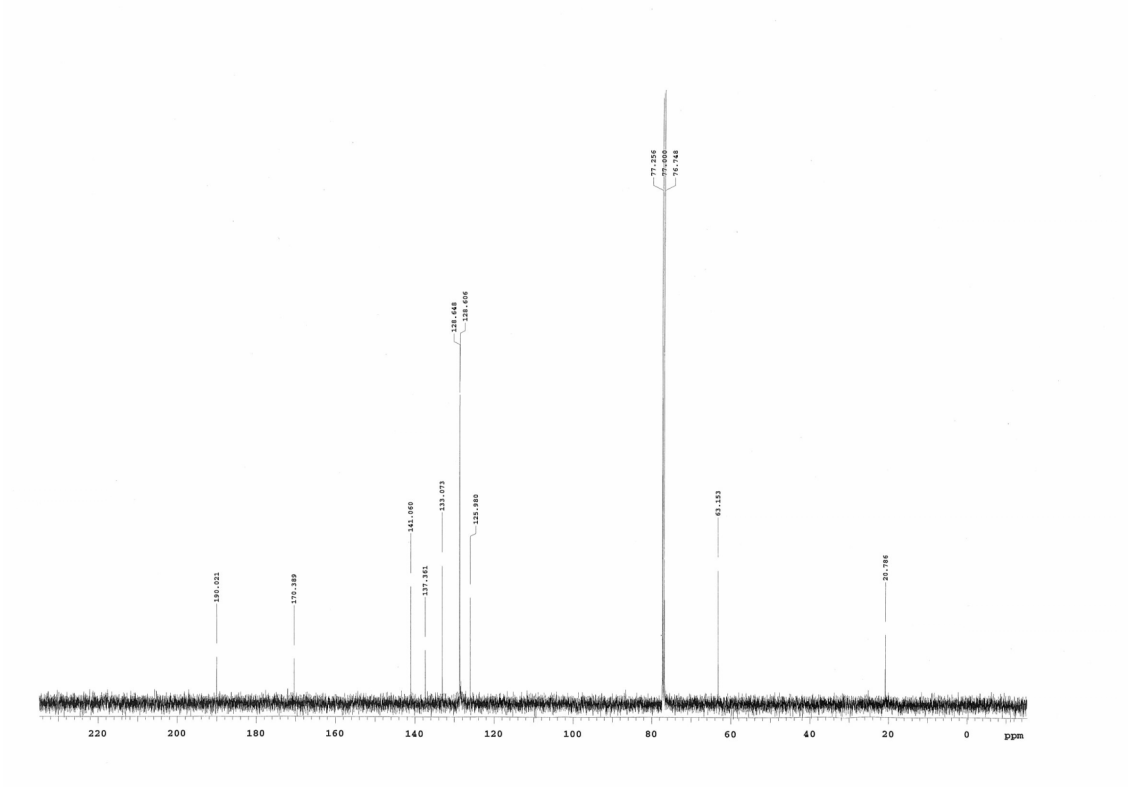
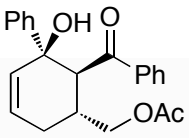
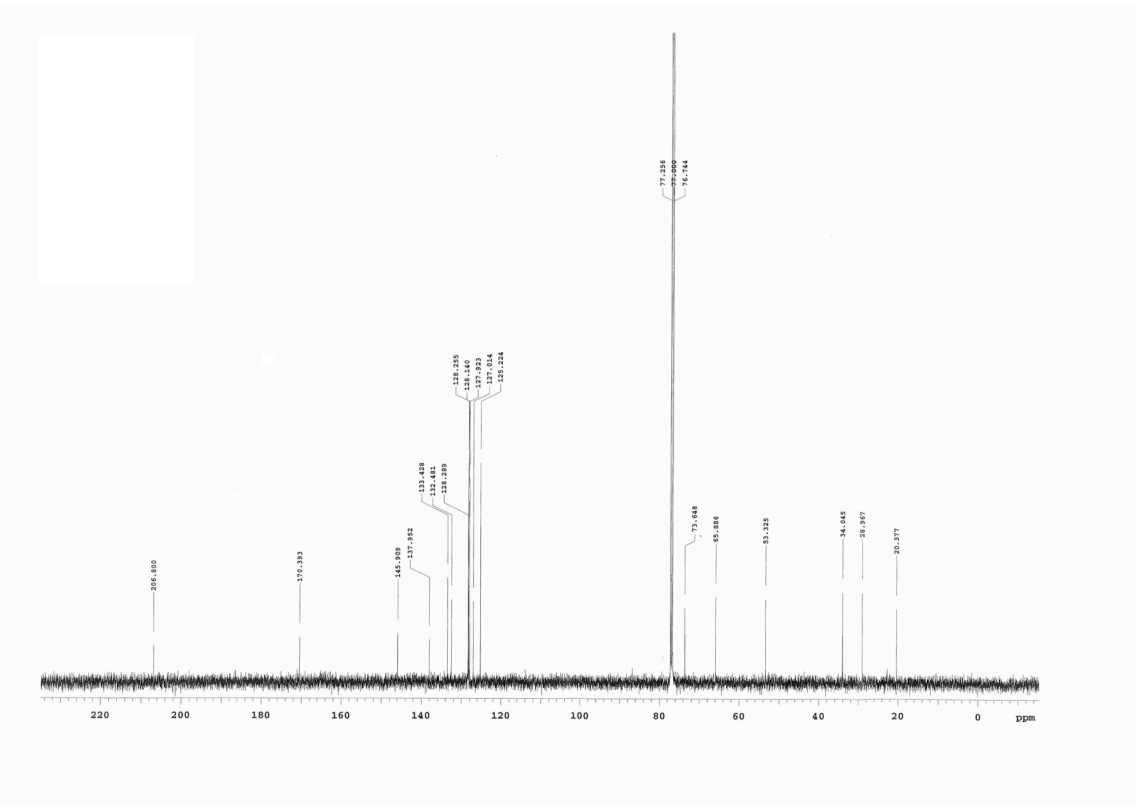



Ph
OH
O
Ph
OAc

4a

10
9
8
7
6
5
4
3
2
1
0
ppm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77.000
76.744
73.648
65.886
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180
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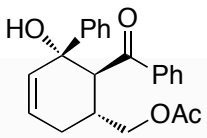
140
120
100
80
60
40
20
0
ppm


HO
Ph
O
Ph
OAc

4'a

10
9
8
7
6
5
4
3
2
1
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ppm
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3.84
1.83
5.20
1.13
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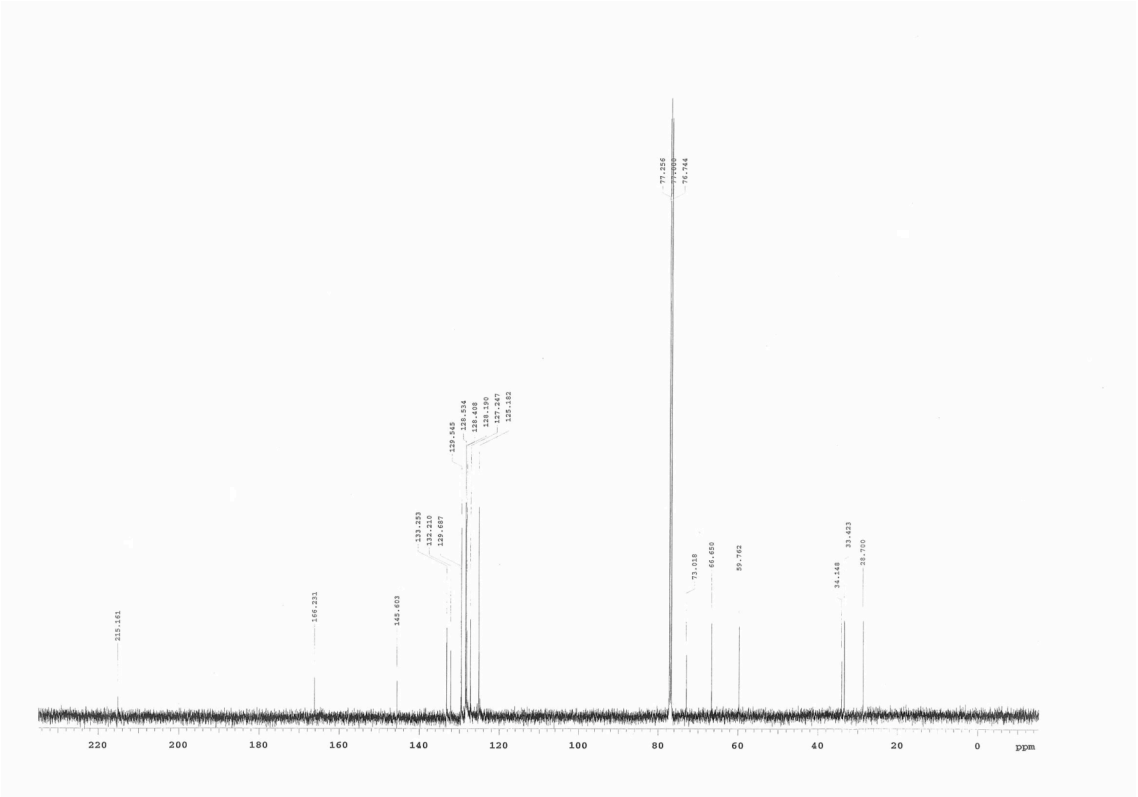
0.99
1.87
1.16
1.21
1.30
1.44
3.09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59.762
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33.423
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166.231
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137.293
132.210
129.687
128.565
128.334
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126.182
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200
180
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140
120
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60
40
20
0
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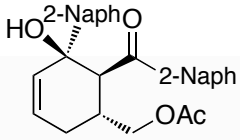
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2-Naph
O
2-Naph
OAc

4b

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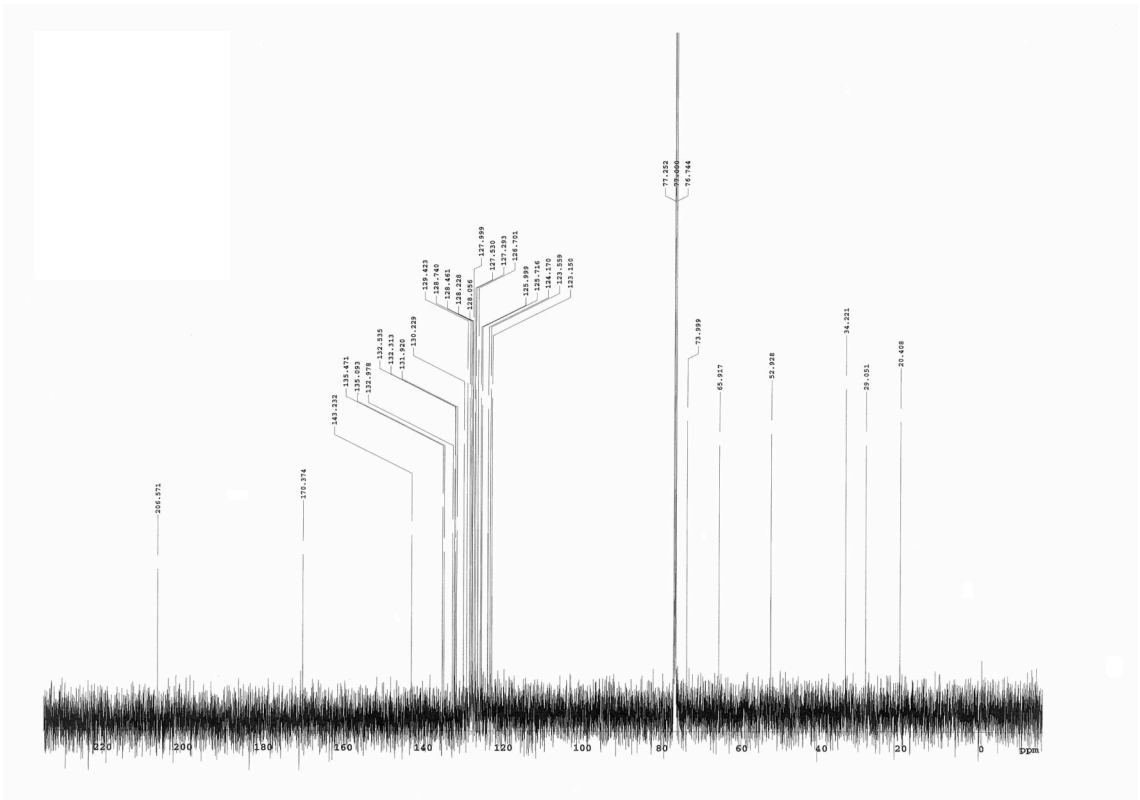
9
8
7
6
5
4
3
2
1
0
ppm
2.04
3.12.07
7.12 1.00
1.00
1.02
0.91
1.04
2.07
1.13
1.14
1.11
3.11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128.228
128.056
127.999
127.530
127.301
126.701
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125.714
124.170
123.965
123.150
77.252
77.000
76.744
73.999
65.917
50.928
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29.051
20.408
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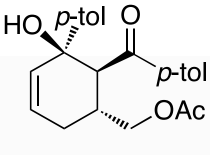
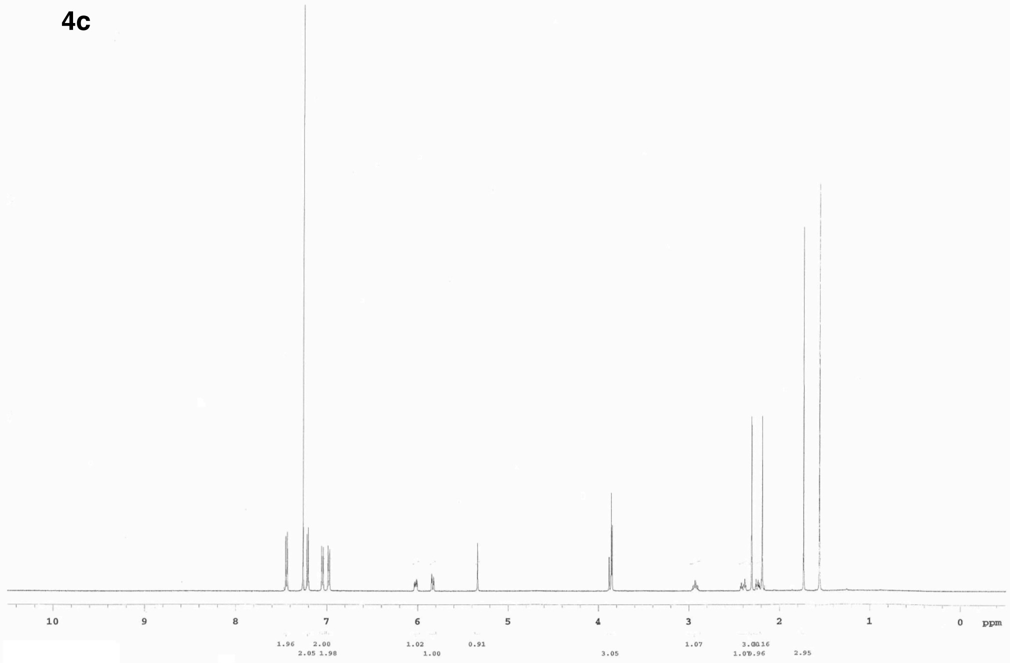
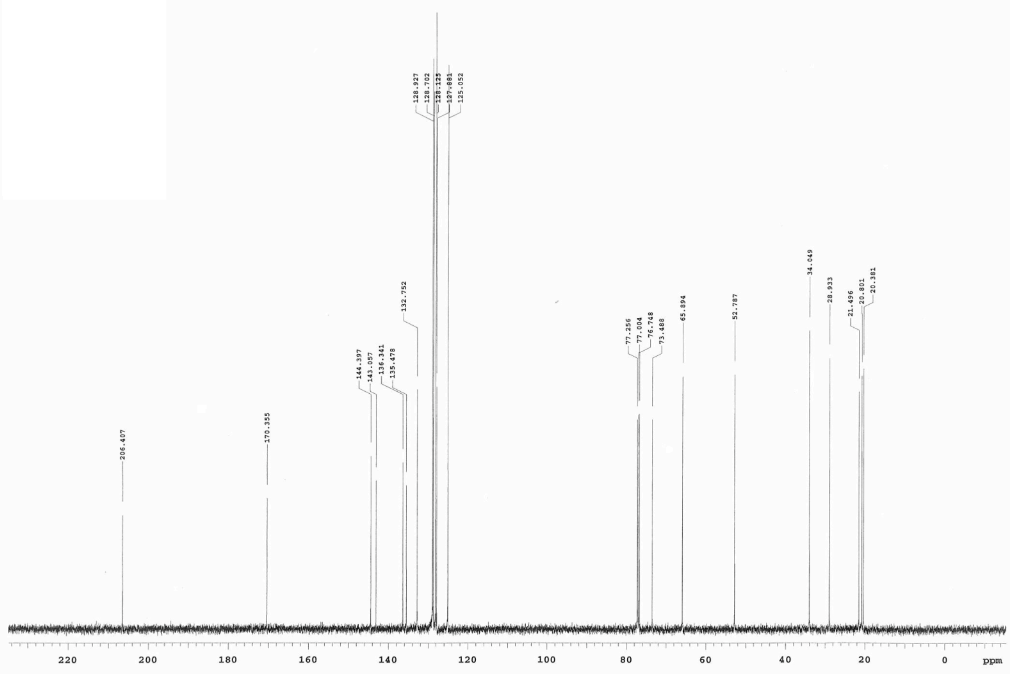
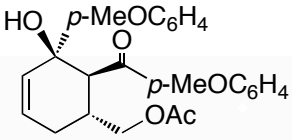
200
180
160
140
120
100
80
60
40
20
0
ppm



4c






HO
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O
p-MeOC6H4
OAc

4d

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.07
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1.00
1.02
0.97
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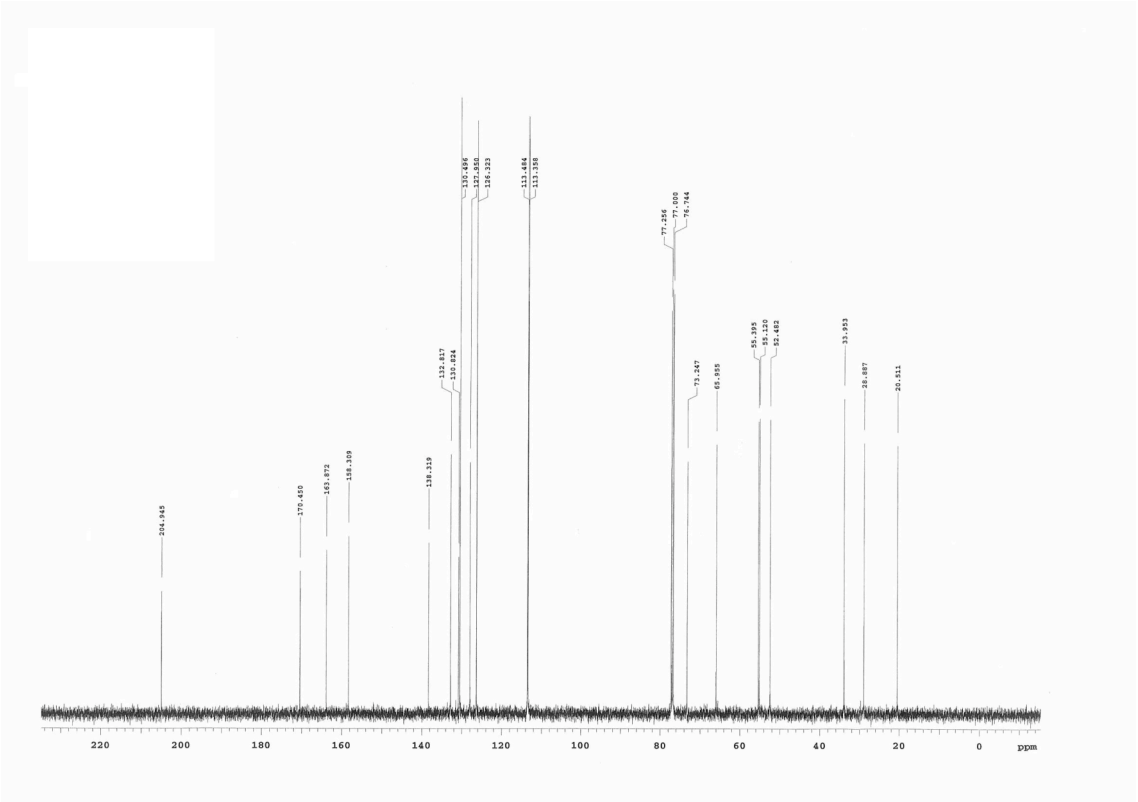
3.03
3.06
1.16
1.13
1.13
3.00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77.000
76.744
73.267
65.955
55.395
55.120
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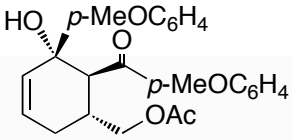
140
120
100
80
60
40
20
0
ppm


HO
p-MeOC6H4
O
p-MeOC6H4
OAc

4'd

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9
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7
6
5
4
3
2
1
0
ppm
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1.91
2.84
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1.00
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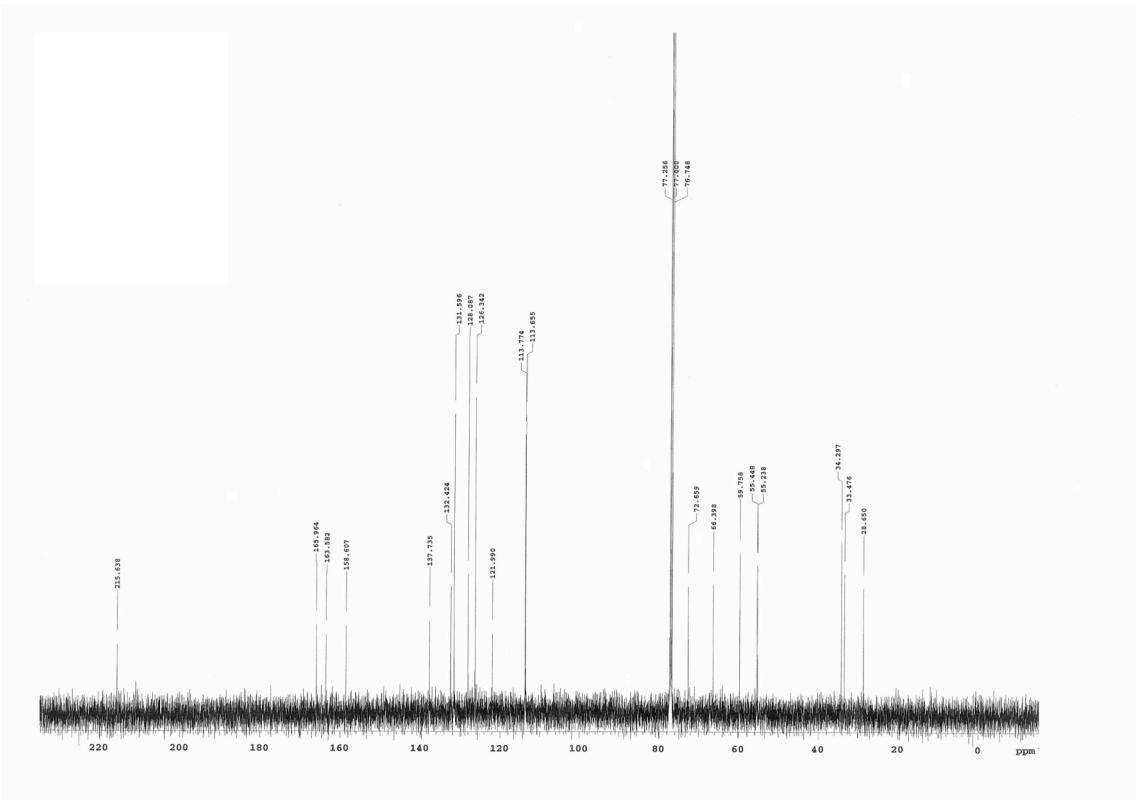
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132.424
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130.087
126.342
121.990
113.774
113.455
77.256
77.000
76.748
72.659
66.398
59.758
55.448
55.238
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180
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140
120
100
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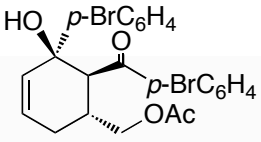
60
40
20
0
ppm


HO
p-BrC6H4
O
p-BrC6H4
OAc

4e

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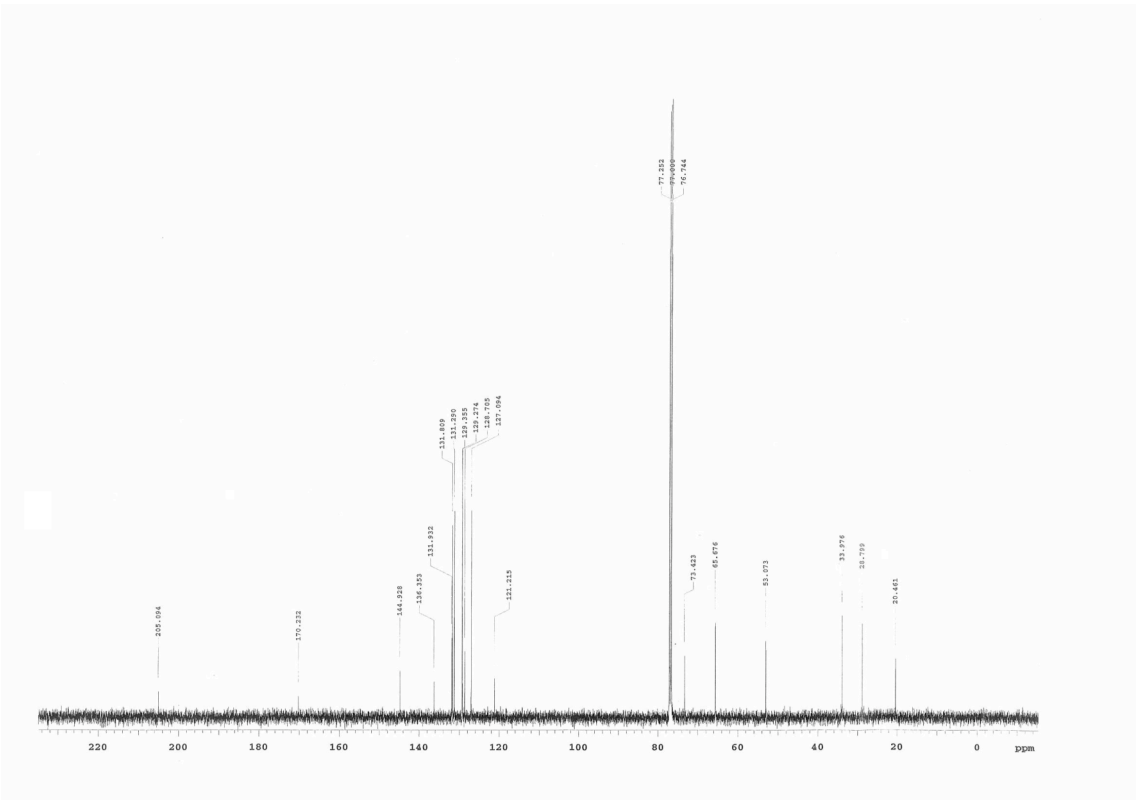
8
7
6
5
4
3
2
1
0
ppm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180
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140
120
100
80
60
40
20
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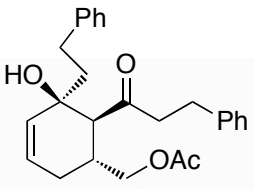
ppm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HO
O
Ph
OAc

4f

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6
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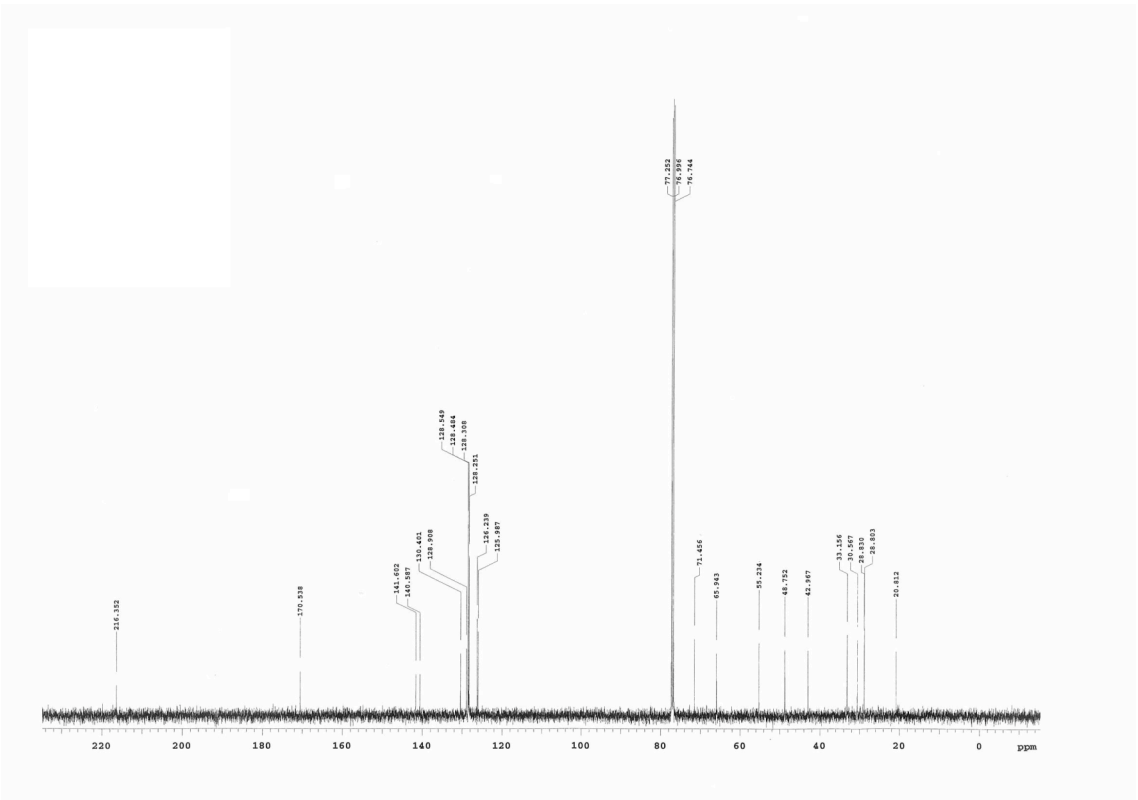
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60
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20
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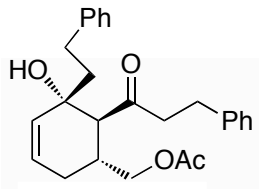
ppm


Ph
HO
O
Ph
OAc

4'f

10
9
8
7
6
5
4
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2
1
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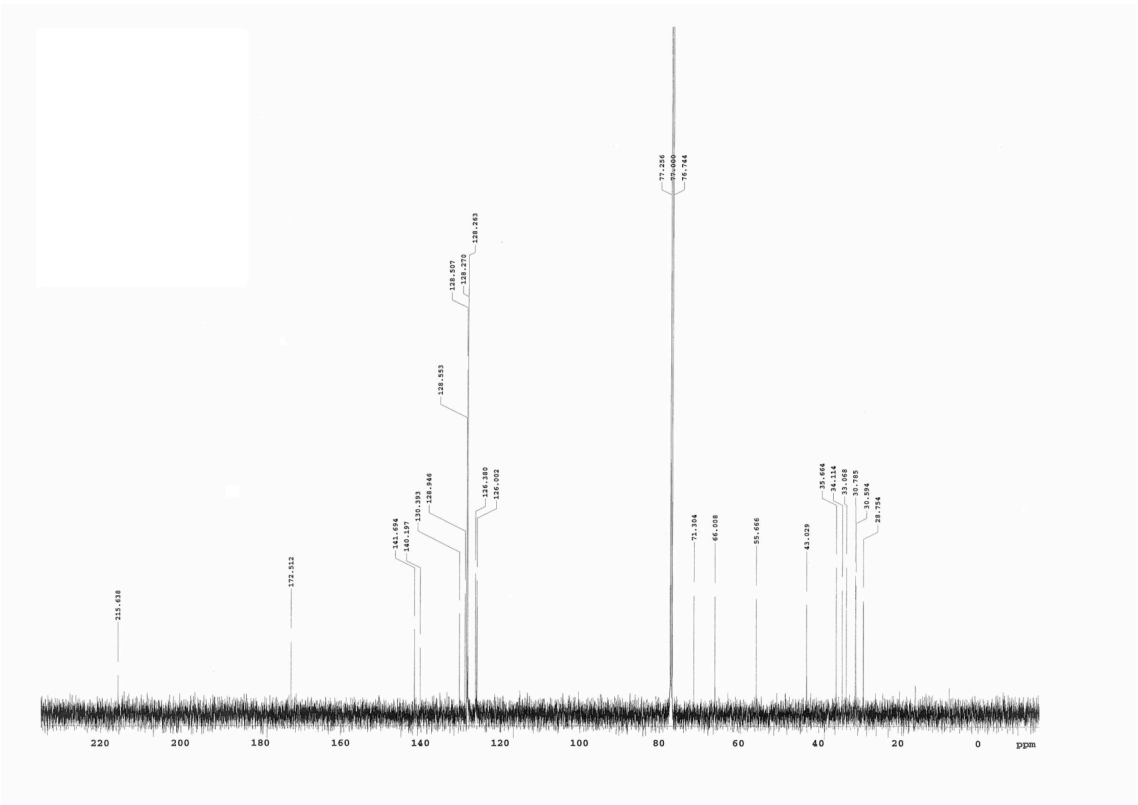
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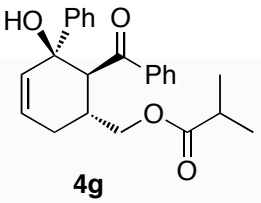
HO
Ph
O
Ph
O
O

4g

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9
8
7
6
5
4
3
2
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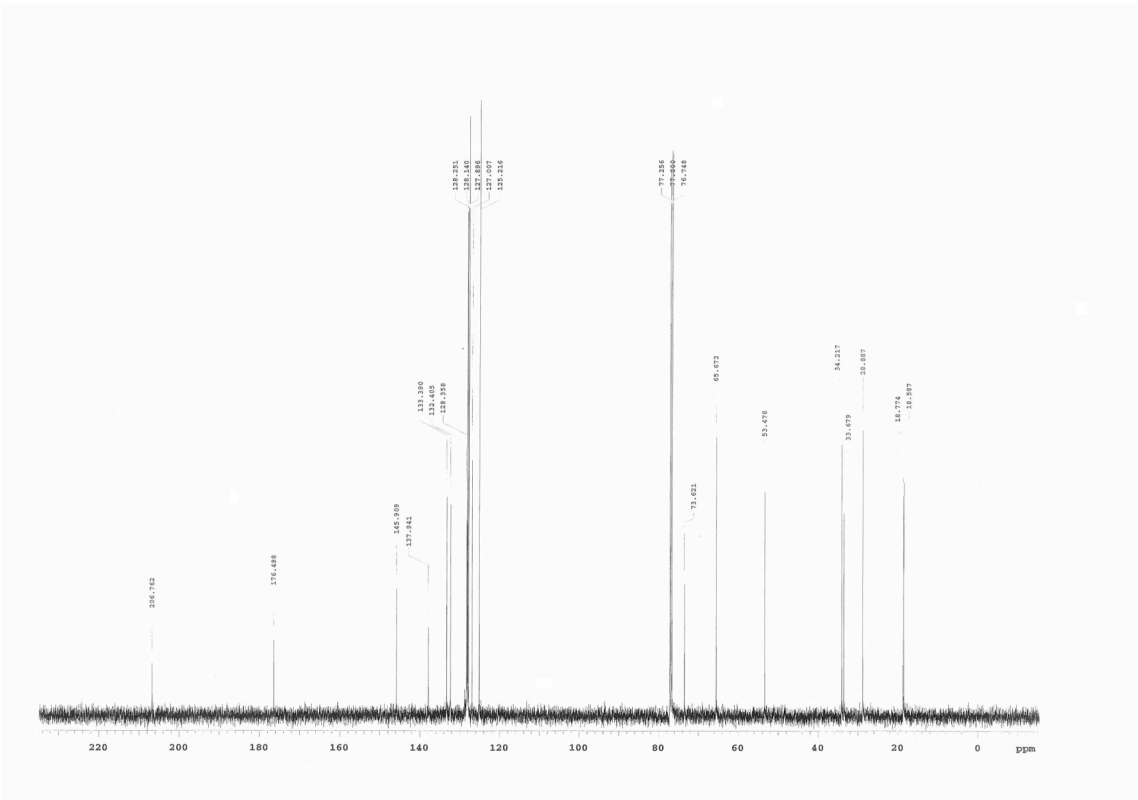
0
ppm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100
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60
40
20
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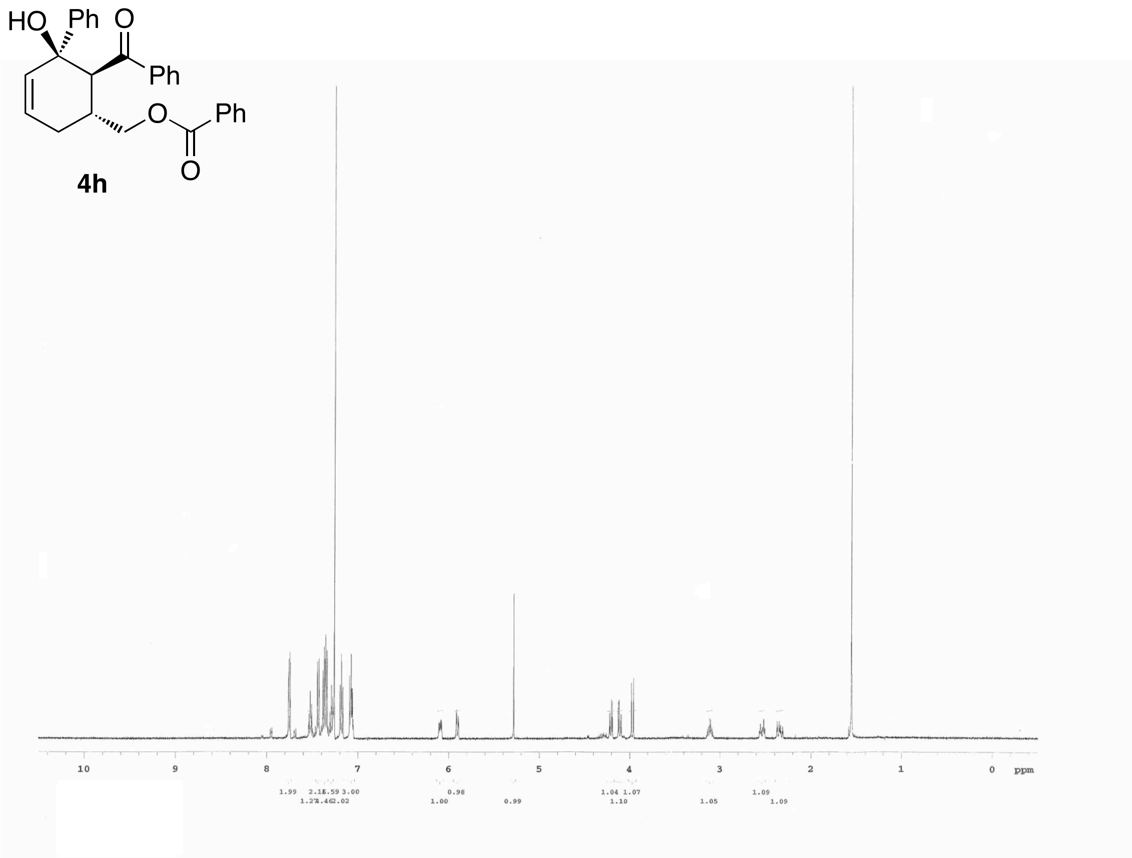
ppm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O
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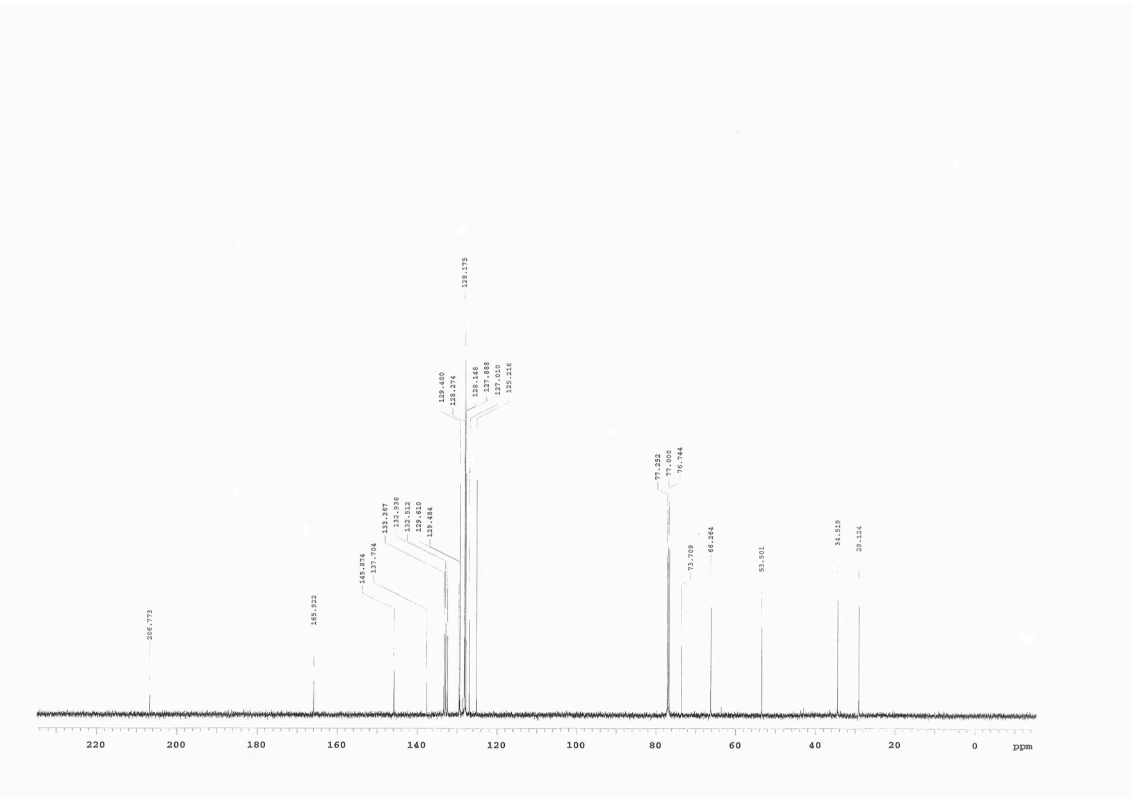
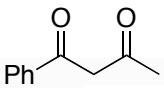
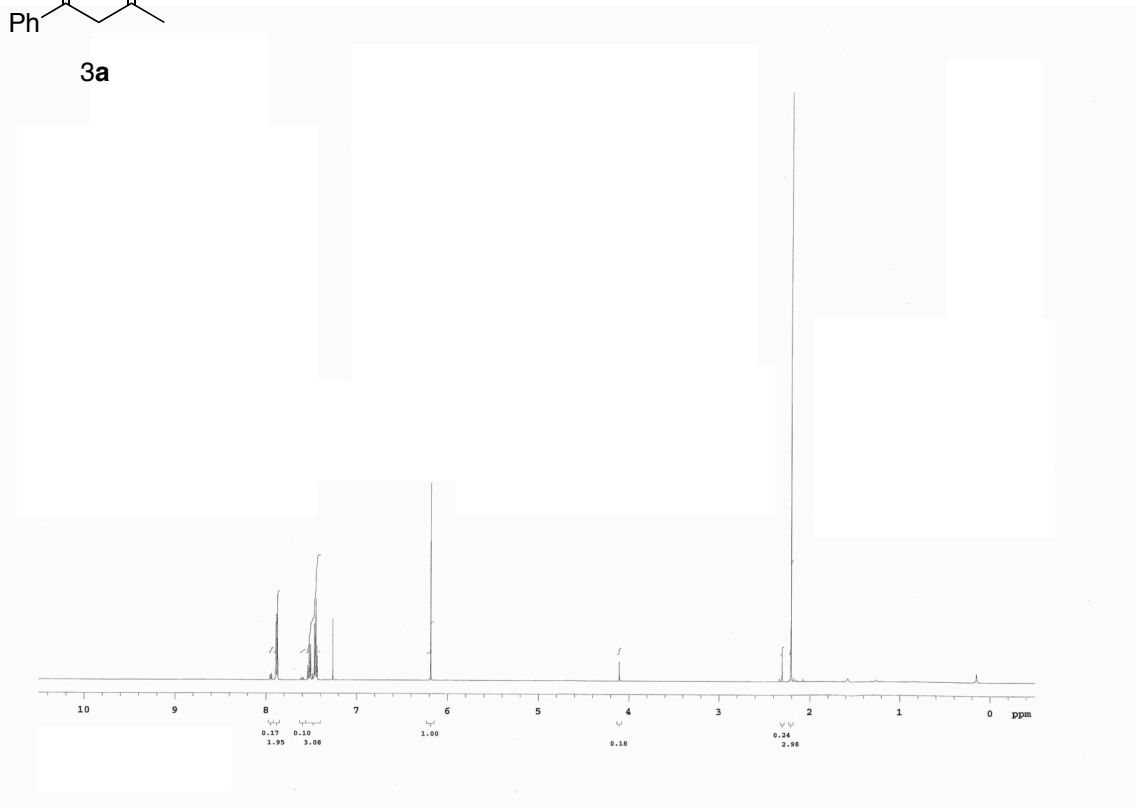
O
4h




O
O
Ph

3a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8
7
6
5
4
3
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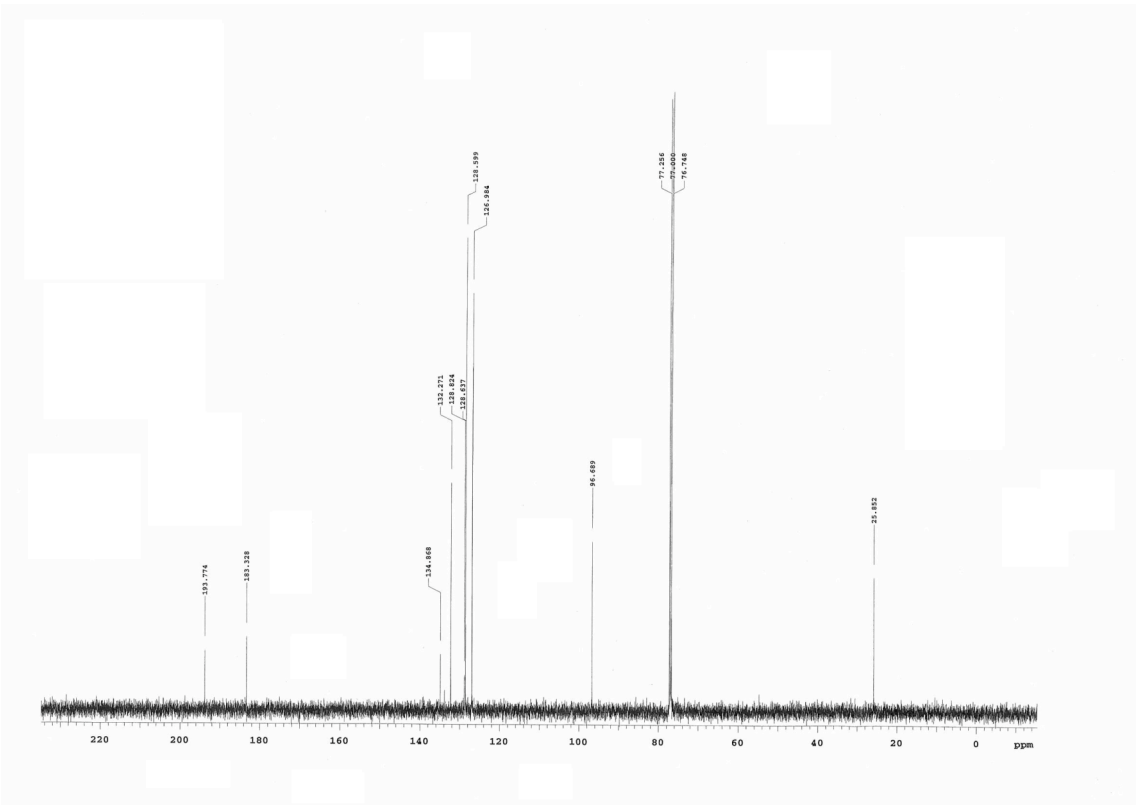
0.18
0.24
2.98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183.328
134.868
132.271
128.624
128.037
126.984
96.689
77.256
77.000
76.746
25.852
220
200
180
160
140
120
100
80
60
40
20
0
ppm