Supporting Information for:

Enantioselective construction of *ortho*-substituted benzylic quaternary centers using a phenanthroline-Pd catalyst

Masafumi Tamura[a]

[a] Department of Pharmaceutical Sciences, Sanyo-Onoda City University, 1-1-1 Daigakudori, Sanyo-onoda, Yamaguchi 756-0884, Japan

E-mail: mtamura@rs.socu.ac.jp

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I. General experimental procedures

All reactions were carried out in oven (160 °C) and flame-dried modified Schlenk tubes with a glass stopper equipped with a Teflon-coated magnetic stirring bar under a positive pressure of dry argon. All work-up and purification procedures were carried out with reagent grade solvents in air.

For thin-layer chromatography (TLC) analysis, Pre-coated plates (TLC silica gel 60 F_{254}, Art No. 5715, 0.25 mm, Merck & Co. or NH_2 Silica Gel 60 F_{254} Plate-Wako, 0.25 mm, FUJIFILM Wako Pure Chemical Corporation) were used. For flash column chromatography, silica gel 60N (CHROMATOREX® PSQ100B, Fuji Silysia Chemical Ltd.), and amine-modified silica gel (Wakosil® 50 NH_2 (HC), FUJIFILM Wako Pure Chemical Corporation) was used. Melting point (m.p.: °C) determinations were performed using a Yanaco MP-J3 instrument are uncorrected. Optical rotations ($[\alpha]_D$) were measured on a JASCO P-2200 polarimeter. ^{1}H- and ^{13}C-NMR were measured on a JEOL JNM-ECZ S (400 MHz), JEOL JNM-ECZ R (600 MHz) spectrometer in the solvent indicated; Chemical shifts (δ) are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane, 0.00 ppm, or 7.26 ppm for $CDCl_3$), and coupling constants (*J*) are reported as hertz (Hz). Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Infrared (IR) spectra and Attenuated total reflectance Fourier-transform infrared (ATR/FTIR) spectra were recorded by using a JASCO FT/IR-4600 spectrometer. High resolution mass spectra (HRMS) (ESI, positive ion mode) were obtained with a JEOL AccuTOF^{TM} LC-plus 4G mass spectrometer and JEOL YOKUDELNA ion peak $[M+Na]^+$ (*m*/*z* 430.9141952) was used as an internal standard for mass calibration. An oil bath was used as a heat source, when reactions that require heating.

II. Experimental procedures

► Reagents and Substrates

Unless stated otherwise, reagents were used without further purification as received from commercial. CH_2Cl_2 and THF solvents (anhydrous; Kanto Chemical Co., Inc.), DCE (1,2-dichloro ethane), MeOH, EtOH, ^{i}PrOH, 1,4-dioxane, Et_2O, DMF, toluene, CCl_4, CH_3CN and DMA (*N*-Acetyl dimethylamine) were distilled prior to use according to the standard protocols. Deionized water was purified with a cartridge water purifier (ORGANO G-10D).

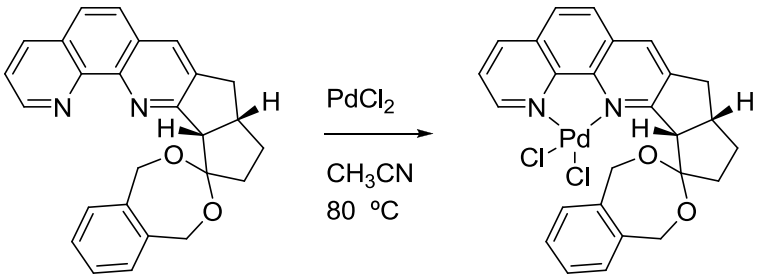
2,5-Dimethoxy-4-methyl phenylboronic acid[1] and 2,3-Dimethoxy-5-methyl phenylboronic acid[1,2] were synthesized according to the known procedures.

Other boronic acids are commercially available materials.

The substrate Methyl-3-oxocyclopent-2-ene carboxylate[3], 3-Methyl-2-cyclohepten-1-one **1c**[4]**,** 4-Methylfuran-2(5H)-one **1d**[5], 3-Ethyl-2-cyclopenten-1-one[6] from 3-Ethoxy-2-cyclopentenone and (*E*)-4-Phenylpent-3-en-2-one **4**[16] were synthesized according to the literature.

► Synthesis of Ligands and Pd-complexes

i. Synthesis of L1-$PdCl_2$



L1 **L1-$PdCl_2$**

Into an oven-dried Schlenk tube equipped with a magnetic stir-bar was charged with $PdCl_2$ (58 mg, 0.327 mmol), **L1**^{a} (129 mg, 0.327 mmol). The tube was closed with a reflux cold

finger type condenser and argon and dry CH_3CN (3.0 ml) was introduced into the Schlenk via syringe. The reaction mixture was allowed to reflux for 3 h under argon. The reaction was cooled to room temperature and filtered directly through a fritted funnel. The residue was washed with cold CH_3CN, and allowed to dry in air, yielding **L1-PdCl$_2$** (160.3 mg, 86%) as an ocher solid.

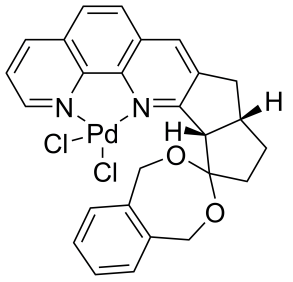
$[\alpha]_D^{24}$ = +390.88 (*c* 0.05, DMSO)

^{1}H NMR (400 MHz, DMSO-*d*) δ 9.14 (d, *J* = 5.5 Hz, 1H), 8.83 (d, *J* = 1.3 Hz, 1H), 8.59 (s, 1H), 8.12 (s, 2H), 7.93 - 7.88 (m, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.16 - 7.07 (m, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.44 (d, *J* = 15.1 Hz, 1H), 5.80 (d, *J* = 7.8 Hz, 1H), 4.84 - 4.70 (m, 3H), 3.44 - 3.36 (m, 1H), 3.06 - 3.00 (m, 1H), 2.64 - 2.61 (m, 1H), 2.19 - 2.15 (m, 1H), 2.00 - 1.96 (m, 1H), 1.81 - 1.72 (m, 2H)

^{13}C NMR (100 MHz, DMSO-*d*) δ 172.0 (C), 151.3 (CH), 147.4 (C), 146.5 (C), 145.2 (C), 140.4 (C), 139.1 (C), 138.9 (CH), 138.0 (CH), 134.4 (C), 130.2 (C), 129.9 (CH), 128.0 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.3 (CH), 125.1 (CH), 116.2 (C), 67.8 (CH_2), 67.6 (CH_2), 58.5 (CH), 36.4 (CH_2), 35.0 (CH_2), 29.0 (CH_2)

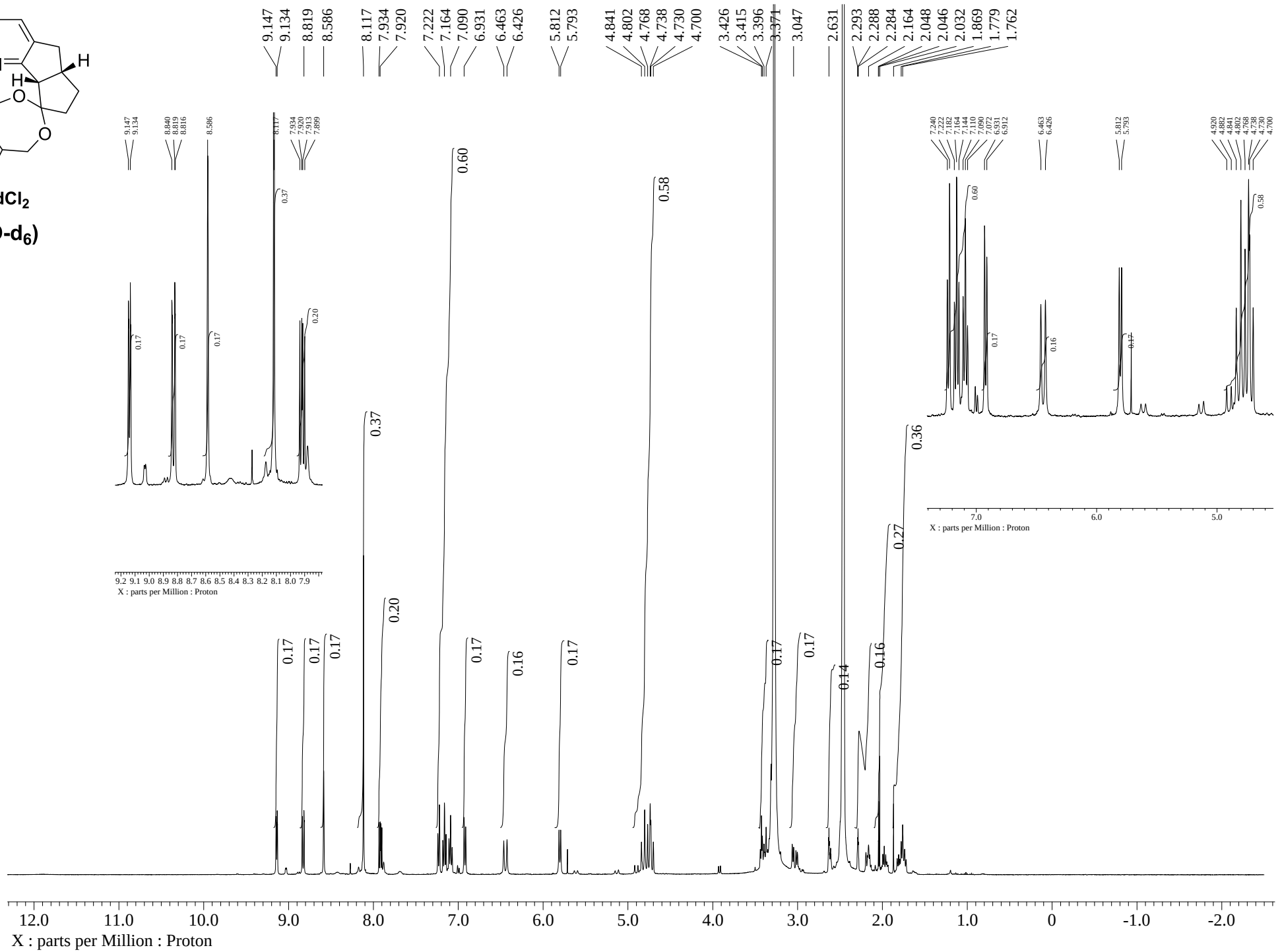
HRMS (ESI-TOF) *m/z* Calculated for $C_{26}H_{22}Cl_2N_2O_2NaPd$ $[M+Na]^+$: 592.9991, found: 592.9989

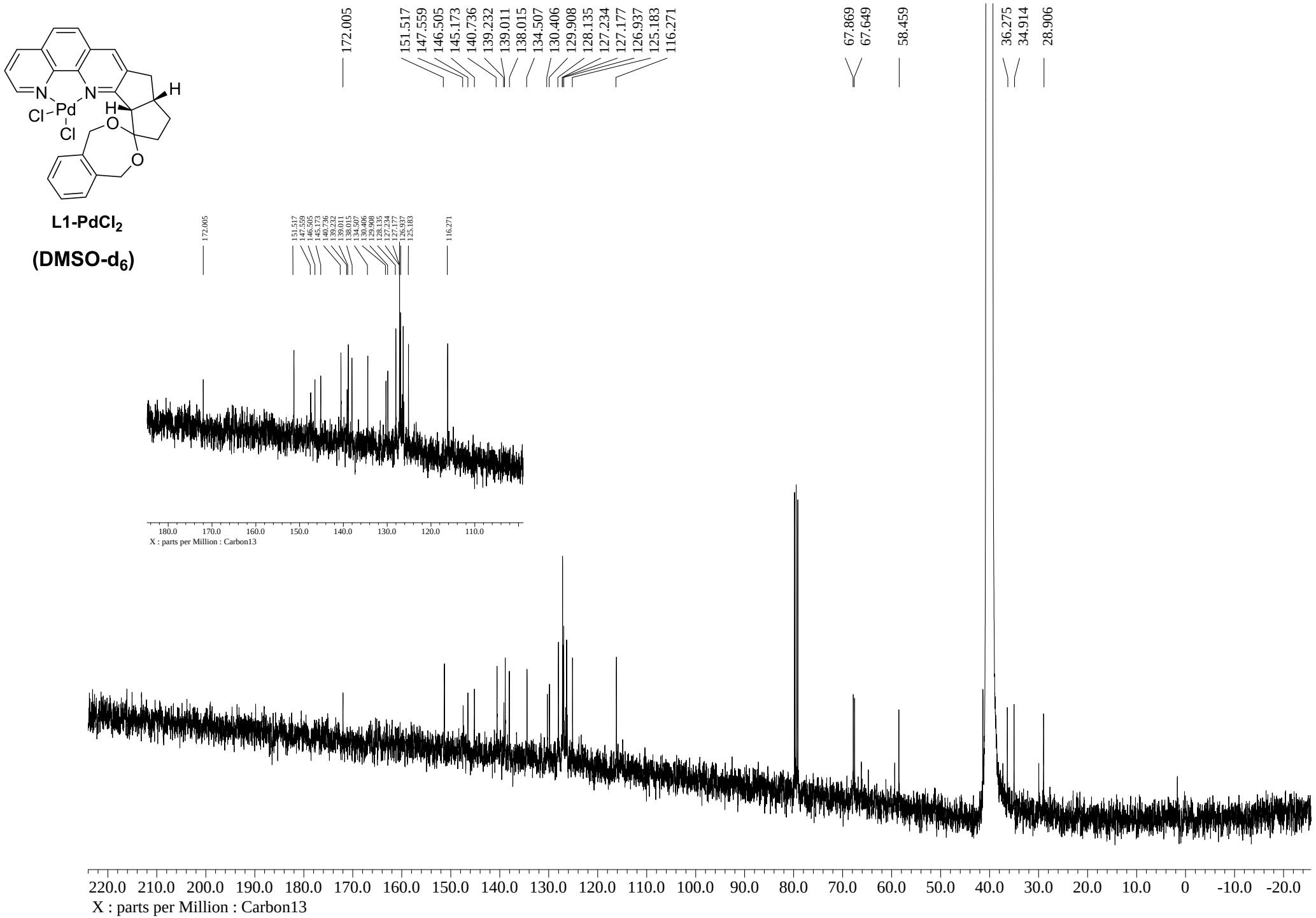
[a]**L1** was synthesized according to the literature: M. Tamura, H. Ogata, Y. Ishida, Y. Takahashi, *Tetrahedron Lett.,* 2017, **58***,* 3808.



L1-PdCl$_2$

(DMSO-d$_6$)

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146.505
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127.234
127.177
126.937
125.183
116.271
67.869
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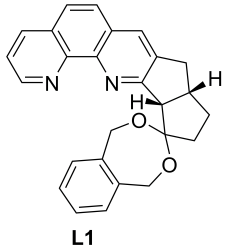
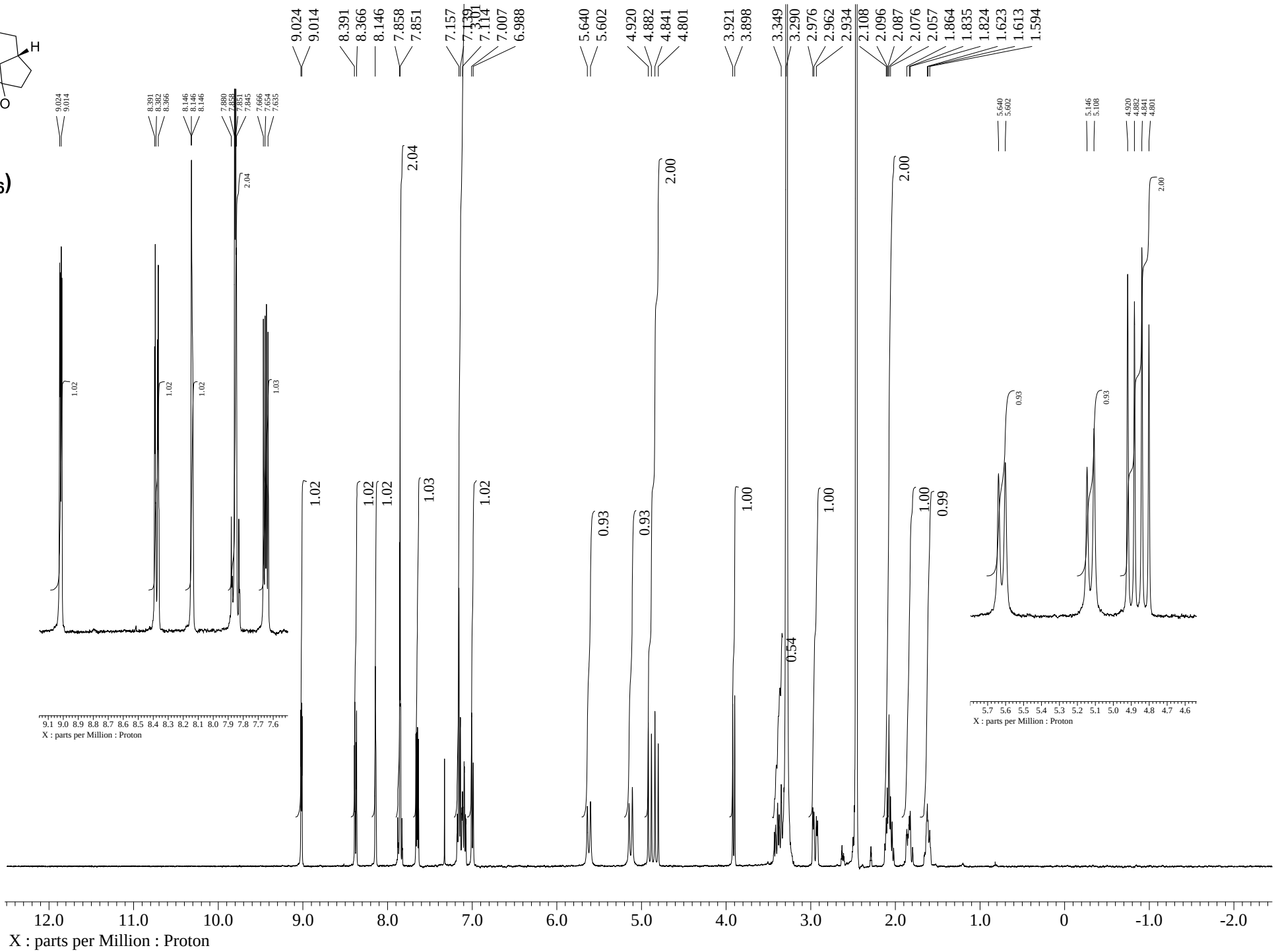
58.459
36.275
34.914
28.906
L1-PdCl2
(DMSO-d6)
X : parts per Million : Carbon13



L1

(DMSO-d_6)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7.139
7.101
7.114
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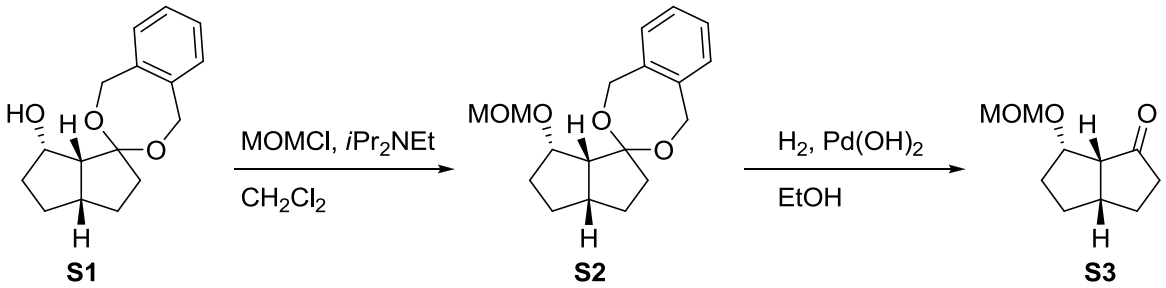
5.640
5.602
4.920
4.882
4.841
4.801
3.921
3.898
3.349
3.290
2.976
2.962
2.934
2.108
2.096
2.087
2.076
2.057
1.864
1.835
1.824
1.623
1.613
1.594
1.02
1.02
1.02
2.04
1.03
1.02
0.93
0.93
2.00
1.00
0.54
1.00
1.00
0.99
2.00
0.93
0.93
2.00
X : parts per Million : Proton
X : parts per Million : Proton
X : parts per Million : Proton

ii. Synthesis of L2 and L2-$PdCl_2$

(3a*S*,6*S*,6a*R*)-6-(methoxymethoxy) hexahydropentalen-1(2H)-one: S3



S1 **S2** **S3**

To a stirred solution of **S1**[a] (1.2 g, 4.62 mmol) in dry CH_2Cl_2 (30 ml) were added $^{i}Pr_2NEt$ (5.0 ml, 28.7 mmol) and MOMCl (1.85 g, 23 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then diluted with AcOEt and poured into water (50 ml) and extracted with AcOEt. The extract was washed with water, brine and dried over Na_2SO_4 and concentrated *in vacuo* to give a crude product. The crude product was purified by silica gel column chromatography (silica gel, 20: 1 hexane/AcOEt) to afford the **S2** (1.26 g, 90%); colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 - 7.15 (m, 2H), 7.10 - 7.04 (m, 2H), 5.00 (d, *J* = 14.6 Hz, 1H), 4.86 (dd, *J* = 5.5, 9.6 Hz, 2H), 4.76 (d, *J* = 14.6 Hz, 1H), 4.69 (dd, *J* = 3.7, 6.9 Hz, 2H), 4.17 - 4.15 (m, 1H), 3.41 (s, 3H), 2.69 - 2.50 (m, 2H), 2.19 - 1.88 (m, 5H), 1.62 - 1.41 (m, 4H)

To a solution of **S2** (1.0 g, 3.29 mmol) in EtOH (20 ml) was added $Pd(OH)_2$ (15 mg) and mixture was stirred under H_2 at room temperature. After stirring for 28 h, the catalyst was filtered off over Celite pad and filtrate was concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography (silica gel, 10: 1 hexane/AcOEt) to afford the **S3** (593 mg, 98%) as colorless oil.

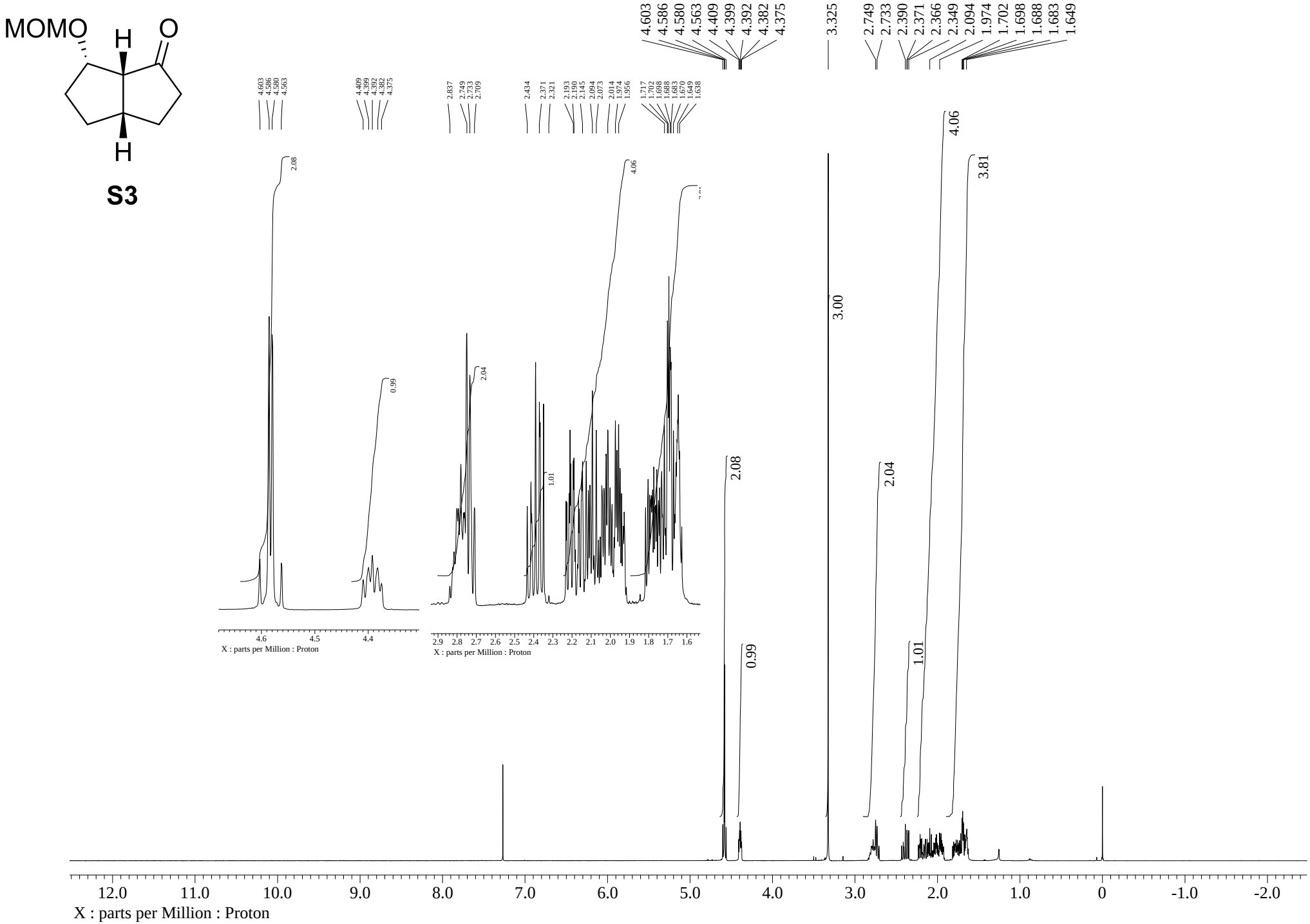
$[\alpha]_D^{23}$ = -40.02 (*c* 0.66, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.58 (q, *J* = 6.86 Hz, 2H), 4.41 - 4.38 (m, 1H), 3.32 (s, 3H), 2.84 - 2.71 (m, 2H), 2.43 - 2.32 (m, 1H), 2.23 - 1.91 (m, 4H), 1.82 - 1.63 (m, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.7 (C), 95.4 (CH_2), 79.7 (CH), 56.5 (CH), 55.4 (CH), 40.7 (CH_3), 40.2 (CH_2), 34.4 (CH_2), 31.3 (CH_2), 27.9 (CH_2)

HRMS (ESI-TOF) *m*/*z* Calculated for $C_{10}H_{16}O_3Na$ $[M+Na]^+$: 207.0997, found: 207.0994

[a]**S1** was synthesized according to the literature: M. Tamura, M. Oyamada, Y.Shirat, *Chirality.,* 2015, **27***,* 364.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O
H
S3
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4.563
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2.749
2.733
2.390
2.371
2.366
2.349
2.094
1.974
1.702
1.698
1.688
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2.04
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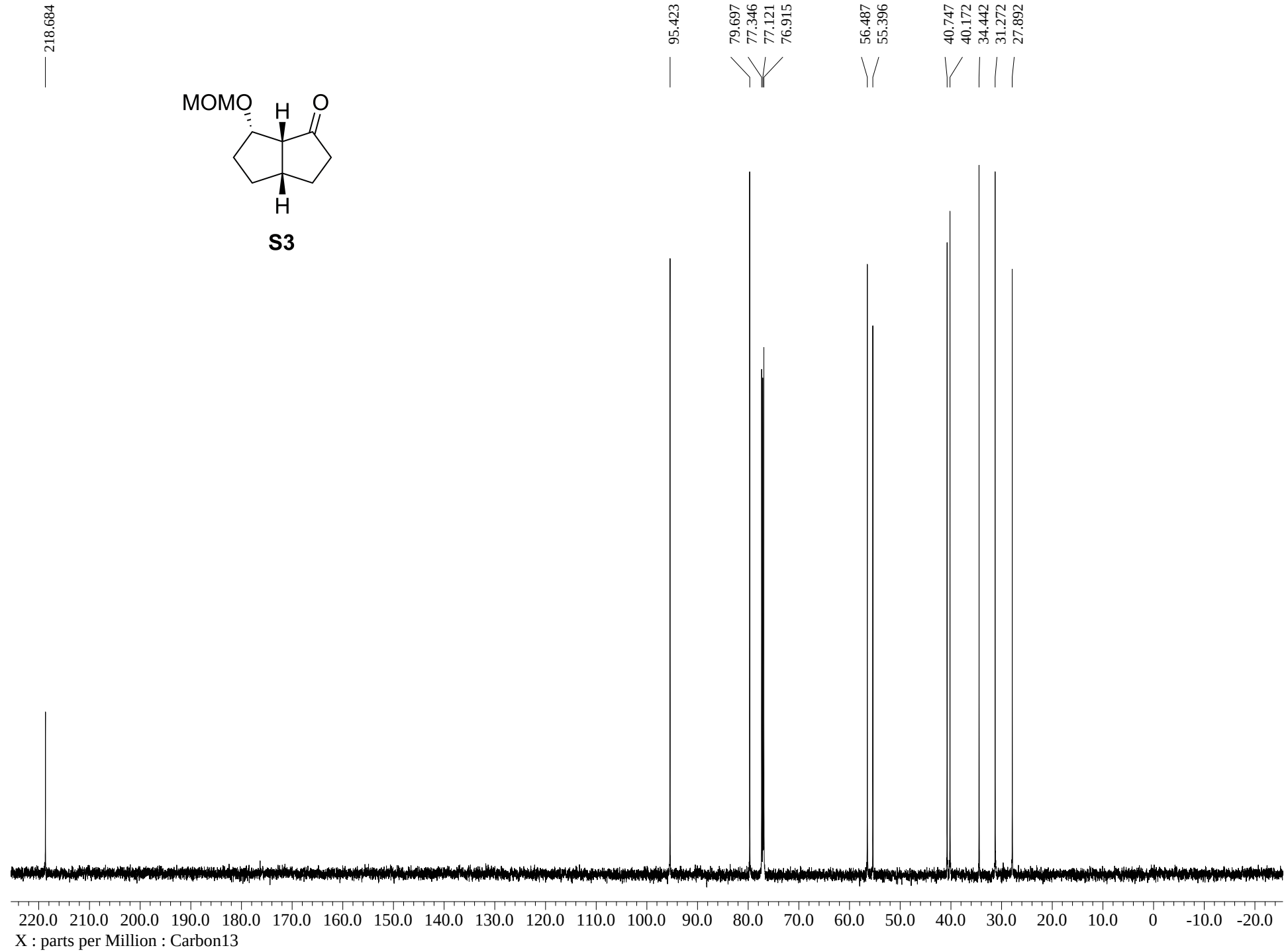
4.06
3.81
3.00
X : parts per Million : Proton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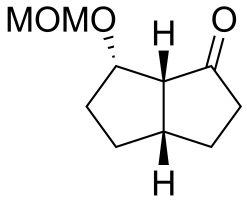
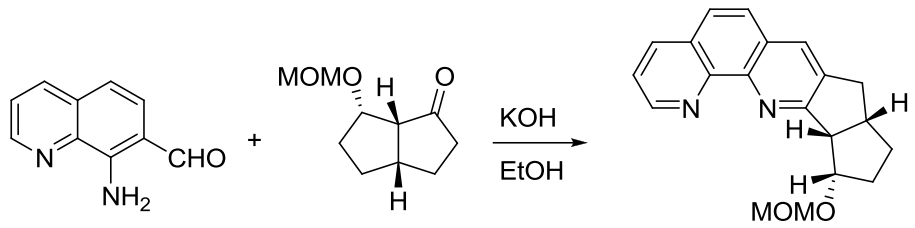
56.487
55.396
40.747
40.172
34.442
31.272
27.892
MOMO
H
O
H
S3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



S3

X : parts per Million : Carbon13

(8a*S*,11*S*,11a*S*)-11-(methoxymethoxy)-8,8a,9,10,11,11a-hexahydropentaleno[1,2-b][1,10]phenanthroline: L2



S3 **L2**

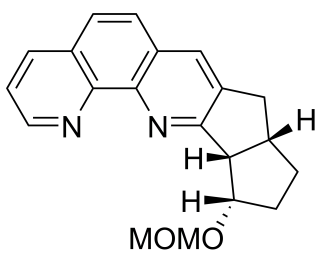
Into the round bottom flask, equipped with magnetic stir-bar under argon atmosphere was introduced a 8-Aminoquinoline-7-carbaldehyde (93.5 mg, 0.55 mmol), **S3** (100 mg, 0.55 mmol), and saturated ethanolic KOH (306 mg) in dry EtOH (10 ml), and the suspension was 80 °C for 24 h. The crude mixture was cooled to room temperature, the mixture extracted CH_2Cl_2 and washed with water and brine and dried over Na_2SO_4 and concentrated *in vacuo* to give a crude product. The crude product was purified by silica gel column chromatography (silica gel, 20: 1 CH_2Cl_2/AcOEt, followed by amine-modified silica gel, 1: 3 hexane/AcOEt) to afford the **L2** (97 mg, 55%); brown oil.

$[\alpha]_D^{24}$ = +351.68 (*c* 0.25, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (dd, *J* = 1.1, 3.9 Hz, 1H), 8.18 (d, *J* = 8.3 Hz 1H), 7.89 (s, 1H), 7.68 (dd, *J* = 7.3, 8.7 Hz, 2H), 7.54 (dd, *J* = 4.1, 7.8 Hz, 1H), 4.79 - 4.77 (m, 1H), 4.59 (d, *J* = 6.4 Hz, 1H), 4.28 (d, *J* = 6.4 Hz, 1H), 4.13 - 4.09 (m, 1H), 3.44 - 3.38 (m, 1H), 3.22 - 3.12 (m, 1H), 3.09 (s, 3H), 3.02 - 2.96 (m, 1H), 2.26 - 2.02 (m, 2H), 1.91 - 1.75 (m, 2H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.0 (C), 149.9 (CH), 146.5 (C), 145.5 (C), 139.6 (C), 135.8 (CH), 130.6 (CH), 128.3 (C), 128.0 (C), 126.9 (CH), 125.2 (CH), 122.3 (CH), 95.6 (CH_2), 80.8 (CH), 57.4 (CH), 55.2 (CH), 40.7 (CH_3), 38.6 (CH_2), 35.0 (CH_2), 31.8 (CH_2)

HRMS (ESI-TOF) *m*/*z* Calculated for $C_{20}H_{20}N_2O_2Na$ $[M+Na]^+$: 343.1422, found: 343.1428


N
N
H
H
H
MOMO

L2

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3.419 3.417 3.376 3.088 3.017
2.220 2.208 2.073 2.057 2.038 1.880 1.831 1.824 1.810 1.795
1.00 1.01 1.00 2.00 1.00 1.01 1.00 1.00 1.04 1.00 4.01 1.01 1.05 1.26 2.00
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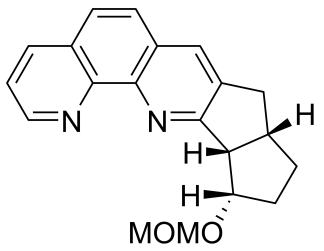
X : parts per Million : Proton
X : parts per Million : Proton


N
N
H
H
H
MOMO

L2

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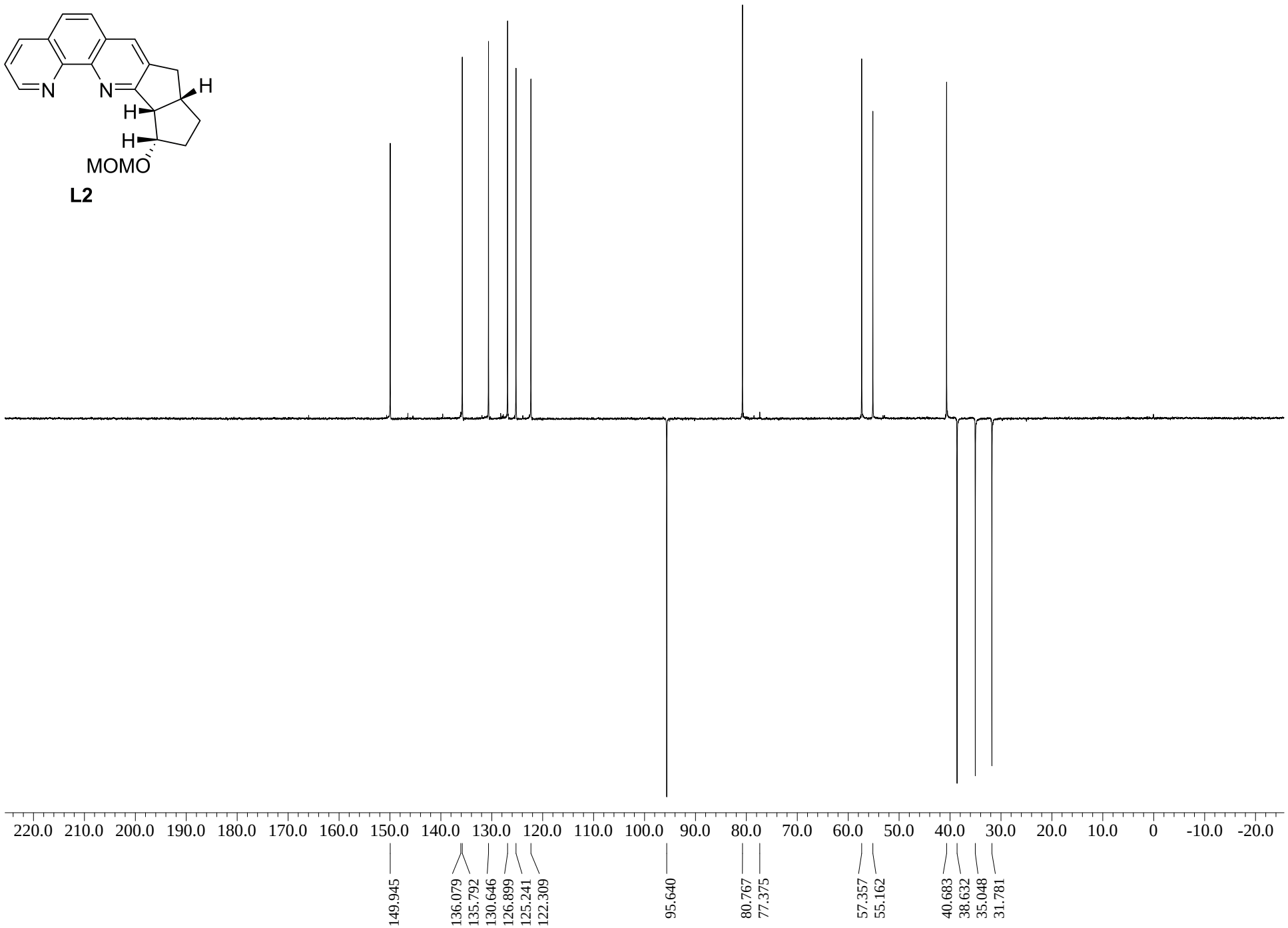
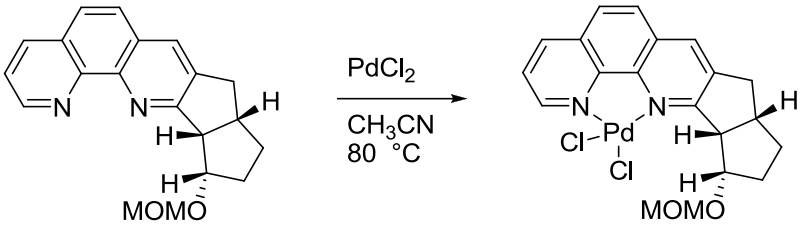
130.646
128.259
127.953
126.899
125.246
122.318
95.640
80.777
77.481
77.375
77.164
76.848
57.352
55.162
40.683
38.632
35.043
31.781
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13

L2-$PdCl_2$



L2 **L2-$PdCl_2$**

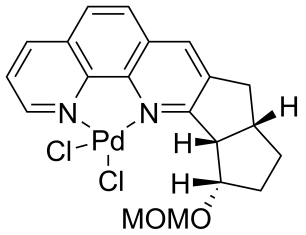
Into an oven-dried Schlenk tube equipped with a magnetic stir-bar was charged with $PdCl_2$ (27.1 mg, 0.125 mmol), **L2** (40 mg, 0.125 mmol). The tube was closed with a reflux cold finger type condenser and argon and dry CH_3CN (1.0 ml) was introduced into the Schlenk tube via syringe. The reaction mixture was allowed to reflux for 3 h under argon. The reaction was cooled to room temperature and filtered directly through a fritted funnel. The residue was washed with cold CH_3CN, and allowed to dry in air, yielding the first crop of **L2-$PdCl_2$** (56 mg, 90%) as an orange-red solid.

$[\alpha]_D^{24}$ = +431.12 (*c* 0.31, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 - 9.68 (m, 1H), 8.49 - 8.46 (m, 1H), 8.19 (d, *J* = 18.3 Hz. 1H), 7.89 - 7.84 (m, 2H), 7.75 - 7.72 (m, 1H), 5.66 - 5.63 (m, 1H), 5.02 - 5.00 (m, 1H), 4.85 - 4.84 (m, 1H), 4.55 (d, *J* = 7.6 Hz. 1H), 3.55 - 3.37 (m, 2H), 3.22 - 3.06 (m, 2H), 3.16 (s, 3H), 3.00 - 2.94 (m, 1H), 2.14 - 1.87 (m, 4H), 1.76 - 1.69 (m, 1H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3 (C), 151.1 (CH), 146.2 (CH), 138.7 (C), 133.2 (CH), 133.0 (C), 129.6 (C), 129.6 (C), 127.8 (CH), 126.2 (CH), 126.0 (CH), 123.8 (C), 97.1 (CH_2), 84.0 (CH), 78.3 (C), 56.3 (CH), 55.7 (CH), 40.4 (CH_3), 38.2 (CH_2), 38.0 (C), 34.2 (CH_2), 32.4 (C), 31.3 (CH_2), 30.0 (C)

HRMS (ESI-TOF) *m/z* Calculated for $C_{20}H_{20}Cl_2N_2O_2PdNa$ $[M+Na]^+$: 518.9834, found: 518.9854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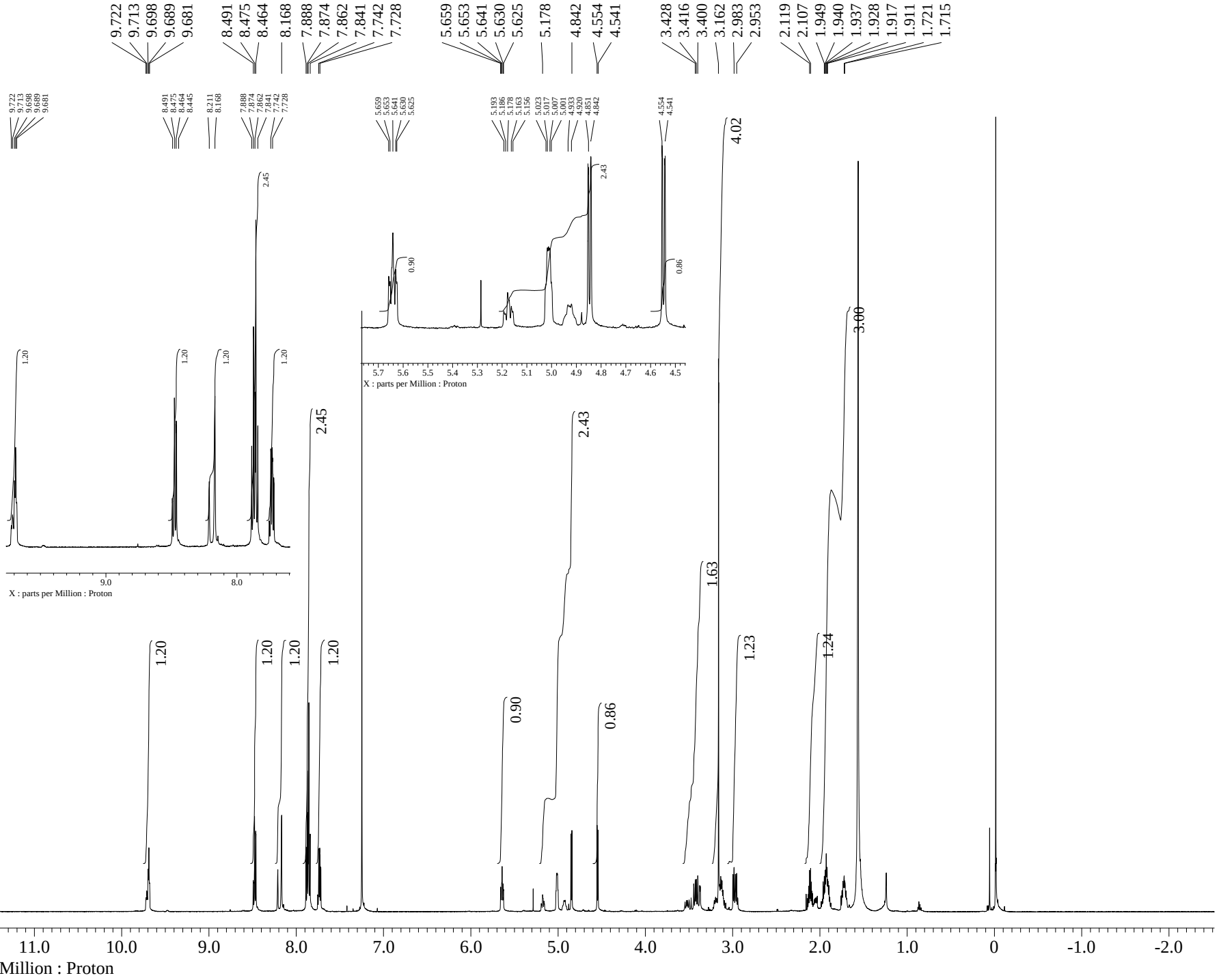
Pd
N
Cl
Cl
H
H
MOMO
H

L2-PdCl$_2$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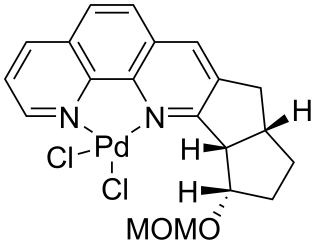
5.178
4.842
4.554 4.541
3.428 3.416 3.400 3.162 2.983 2.953
2.119 2.107 1.949 1.940 1.937 1.928 1.917 1.911 1.721 1.715
1.20 1.20 1.20 1.20 2.45 2.43 0.90 0.86 1.63 4.02 1.23 1.24 3.00
X : parts per Million : Proton


N
N
Pd
Cl
Cl
H
H
H
MOMO

L2-PdCl$_2$

173.324
151.062
146.170
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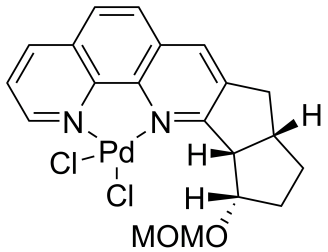
132.985
129.596
129.557
127.824
126.177
125.995
123.841
97.080
84.001
78.284
77.298
77.088
76.877
56.301
55.683
40.359
38.157
37.956
34.240
32.354
31.349
29.922
0.059
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

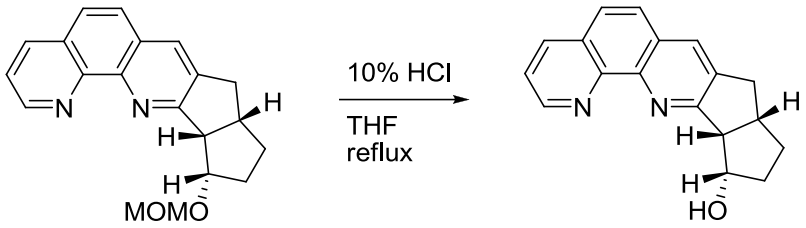

N
N
Pd
Cl
Cl
H
H
H
MOMO

L2-PdCl$_2$

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

iii Synthesis of L3

(8aS,11S,11aS)-8,8a,9,10,11,11a-hexahydropentaleno[1,2-b][1,10]phenanthrolin-11-ol: L3



L2 **L3**

To a solution of **L2** (150 mg, 0.47 mmol) in THF (10 ml) was added 10% aq. HCl (0.1 ml) and mixture was heated at reflux for 2 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2, neutralized with 6 M NaOH aqueous solution, and extracted with CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4 and concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography (silica gel, 20: 1 CH_2Cl_2/MeOH, to afford the **L3** (78 mg, 60%) as off-white solid.

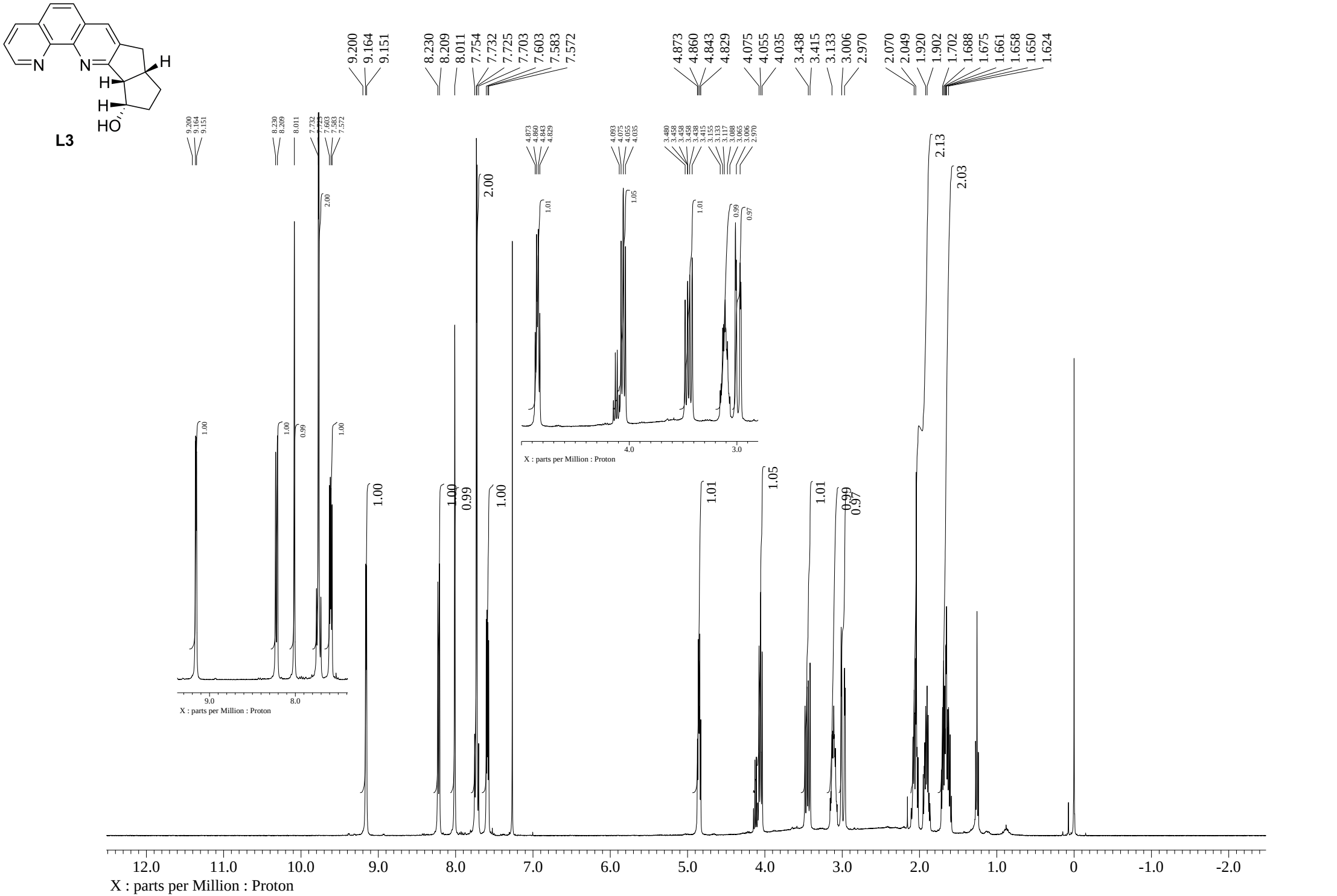
m.p. = 88 - 89 °C

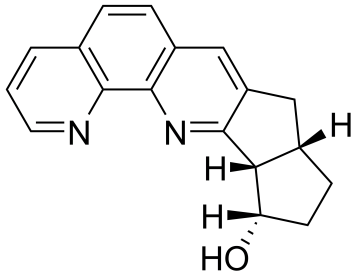
$[\alpha]_D^{24}$ = +338.67 (*c* 0.23, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (d, *J* = 4.2 Hz, 1H), 8.22 (d, *J* = 8.3 Hz 1H), 8.01 (s, 1H), 7.73 (dd, *J* = 2.8, 8.7 Hz, 2H), 7.59 (dd, *J* = 4.1, 7.8 Hz, 1H), 4.85 (dd, *J* = 7.4, 11.9 Hz, 1H), 4.07 - 4.04 (m, 1H), 3.45 (dd, *J* = 7.8, 9.1 Hz, 1H), 3.16 - 2.96 (m, 2H), 2.08 - 2.01 (m, 1H), 1.95 - 1.86 (m, 1H), 1.72 - 1.59 (m, 2H),

^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.6 (C), 150.1 (CH), 146.1 (C), 145.4 (C), 139.1 (C), 136.0 (CH), 131.8 (CH), 128.4 (C), 127.9 (C), 126.8 (CH), 125.7 (CH), 122.6 (CH), 75.1 (CH), 55.4 (CH), 40.4 (CH), 37.2 (CH_2), 35.4 (CH_2), 31.6 (CH_2)

HRMS (ESI-TOF) *m/z* Calculated for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1660, found: 299.1662


L3
9.200
9.164
9.151
8.230
8.209
8.011
7.754
7.732
7.725
7.703
7.603
7.583
7.572
4.873
4.860
4.843
4.829
4.075
4.055
4.035
3.438
3.415
3.133
3.006
2.970
2.070
2.049
1.920
1.902
1.702
1.688
1.675
1.661
1.658
1.650
1.624
2.13
2.03
2.00
1.05
1.01
1.00
0.99
0.97
X : parts per Million : Proton



L3

166.614
150.070
146.093
139.069
135.993
131.786
128.374
127.895
126.793
125.653
122.634
77.452
77.140
76.819
75.133
55.364
40.424
37.233
35.360
31.579

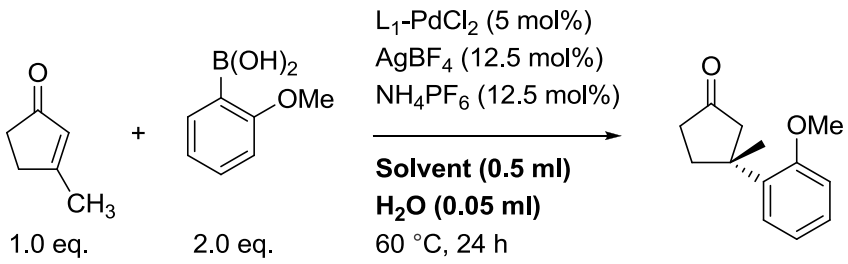
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

X : parts per Million : Carbon13

► Additional investigations of reaction conditions

Optimization Details for Pd-complex Catalyzed conjugate addition reaction

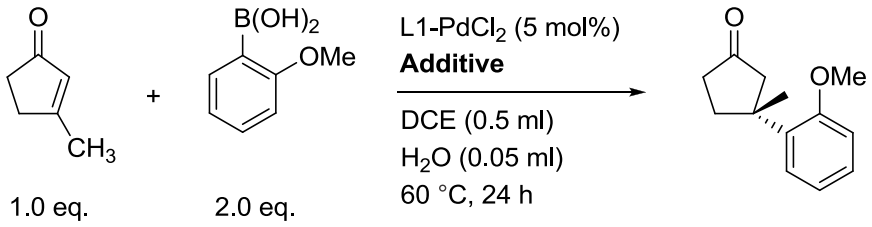
Table S1 Optimization of Solvents



1.0 eq. 2.0 eq.

Entry	Solvent	Yield (%)	e.e. (%)
1	DCE	91	98
2	MeOH : H_2O = 4:1	67	96
3	^{i}PrOH : H_2O = 4:1	23	85
4	MeOH	55	90
5	EtOH	31	85
6	H_2O	82	96
7	DMA	N.D.	-
8	THF	87	93
9	toluene	11	85
10	1,4-dioxane	14	87
11	CH_3CN	N.D.	-
12	CCl_4	52	86

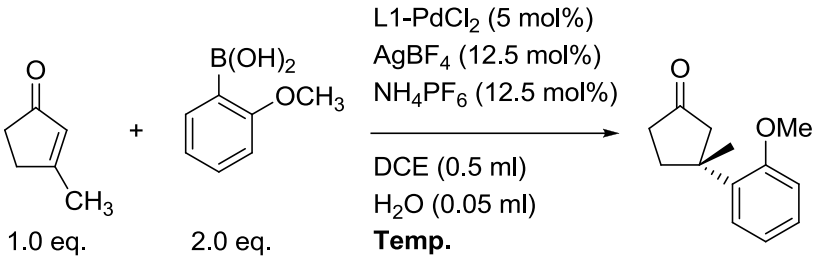
Table S2 Optimization of Additives



1.0 eq. 2.0 eq.

Entry	**Additive (mol%)**	Yield (%)	e.e. (%)
1	$AgBF_4$ (12.5 mol%), NH_4PF_6 (12.5 mol%)	90	98
2	$AgBF_4$ (12.5 mol%)	56	92
3	NH_4PF_6 (12.5 mol%)	N. R.	-
4	Ag_3PO_4 (4.2 mol%), NH_4PF_6 (12.5 mol%)	45	95
5	AgTFA (12.5 mol%), NH_4PF_6 (12.5 mol%)	78	93
6	AgOTf (12.5 mol%), NH_4PF_6 (12.5 mol%)	86	97
7	$AgPF_6$ (12.5 mol%)	90	98

Table S3 Optimization of Reaction temperature

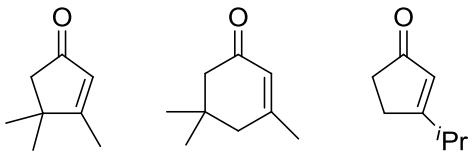


Entry	Temp.	Time (h)	Yield (%)	e.e. (%)
1	60	8	81	98
2	60	18	90	98
3	80	1	56	97
4	80	3	73	98
5	23	24	11	97
6	23	72	69	98

► Additional investigations of the substrates

Unreactive substrates and boronic acids in the Pd-catalyzed asymmetric conjugate addition reaction catalyzed by L1-$PdCl_2$.

enones:



arylboronic acids:

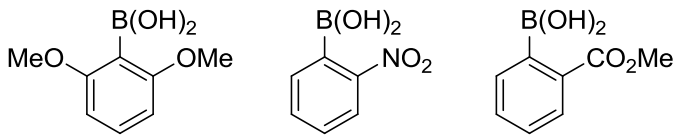


Fig. S1 Unreactive *ortho*-substituted arylboronic acids and functionalized enones.

► Palladium catalyzed conjugate additions of arylboronic acid to enones.

General Procedure A for Table 1 (using a Pd-complex):

To a 10 ml grass tube equipped with a stir bar was charged with 3-Methyl-2-cyclopent-1-one **1a** (13.4 mg, 0.14 mmol), 2-Methoxyphenyl boronic acid **2a** (42.6 mg, 0.28 mmol), **Pd-complex** (7.0×10^{-3} mmol), followed by DCE (0.5 ml) was added via syringe under argon atmosphere. To this mixture was added 0.875 M NH_4PF_6 aqueous solution (0.02 ml, 12.5 mmol) and 0.58 M $AgBF_4$ aqueous solution (0.03 ml, 12.5 mmol) via syringe and allowed to stir for 24 h at 60 °C. Upon complete consumption of the enone (monitored by TLC), the reaction mixture was allowed to cool to rt and filtered through a pad of silica eluted with Et_2O. The filtrate was dried over Na_2SO_4, concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography.

General Procedure B for Table 1 (using a Ligand/ $Pd(TFA)_2$):

To a 10 ml grass tube equipped with a stir bar was charged with 3-Methyl-2-cyclopent-1-one **1a** (13.4 mg, 0.14 mmol), 2-Methoxyphenyl boronic acid **2a** (42.6 mg, 0.28 mmol), **Ligand** (6 mol%) and $Pd(TFA)_2$ (2.1 mg, 5 mol%), followed by DCE (0.5 ml) was added by syringe under argon atmosphere. To this mixture was added 0.875 M NH_4PF_6 aqueous solution (0.02 ml, 12.5 mmol) and H_2O (0.03 ml) via syringe and allowed to stir for 24 h at 60 °C. The reaction mixture was allowed to cool to rt and filtered through a pad of silica eluted with Et_2O. The filtrate was dried over Na_2SO_4, concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography.

General Procedure for Scheme 1 and Table 2:

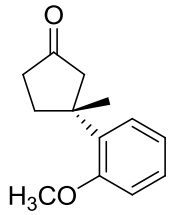
To a 10 ml grass tube equipped with a stir bar was charged with enone (0.14 mmol), arylboronic acid (0.28 mmol), **L1-PdCl₂** (4.0 mg, 7.0×10^{-3} mmol), followed by DCE (0.5 ml) was added via syringe under argon atmosphere. To this mixture was added 0.875 M NH_4PF_6 aqueous solution (0.02 ml, 12.5 mmol) and 0.58 M $AgBF_4$ aqueous solution (0.03 ml, 12.5 mmol) via syringe and allowed to stir for 24 h at 60 °C. Upon complete consumption of the enone (monitored by TLC), the reaction mixture was allowed to cool to rt and filtered through a pad of silica eluted with Et_2O. The filtrate was dried over Na_2SO_4, concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography.

General Procedure for the Synthesis of Racemic 3-Alkyl-3-arylcyclopentanones

To a 10 ml grass tube equipped with a stir bar was charged with enone (0.14 mmol), arylboronic acid (0.28 mmol), **Phen-PdCl₂**[a] (5.0 mg, 14.0×10^{-3} mmol), followed by DCE (0.6 ml) was added via syringe under argon atmosphere. To this mixture was added 0.875 M NH_4PF_6 aqueous solution (0.04 ml, 12.5 mmol) and 0.58 M $AgBF_4$ aqueous solution (0.06 ml, 12.5 mmol) via syringe and allowed to stir for 48 h at 60 °C. The reaction mixture was allowed to cool to rt and filtered through a pad of silica eluted with Et_2O. The filtrate was dried over Na_2SO_4, concentrated *in vacuo* to give a crude product. The crude residue was purified by column chromatography.

[a] **Phen-PdCl₂** was synthesized according to the literature procedure (D. İnci, R. Aydin, *J. Mol. Struct.*, 2019, **1187**, 23).

(*R*)-3-(2-methoxyphenyl)-3-methylcyclopentanone: 3a[7]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2-Methoxyphenyl boronic acid **2a** (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3a** (25.7 mg, 91%, 98% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 - 7.20 (m, 2H), 6.95 - 6.89 (m, 2H), 3.83 (s, 3H), 2.67 (d, *J* = 18.3 Hz, 1H), 2.60 (d, *J* = 18.3 Hz, 1H), 2.45 - 2.30 (m, 4H), 1.39 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 220.1 (C), 157.7 (C), 136.2 (C), 127.8 (CH), 126.4 (CH), 120.6 (CH), 111.5 (CH), 55.0 (CH_3), 52.4 (CH_2), 42.7 (C), 36.5 (CH_2), 35.0 (CH_2), 26.3 (CH_3)

*The NMR data match with those reported in literature.[7]

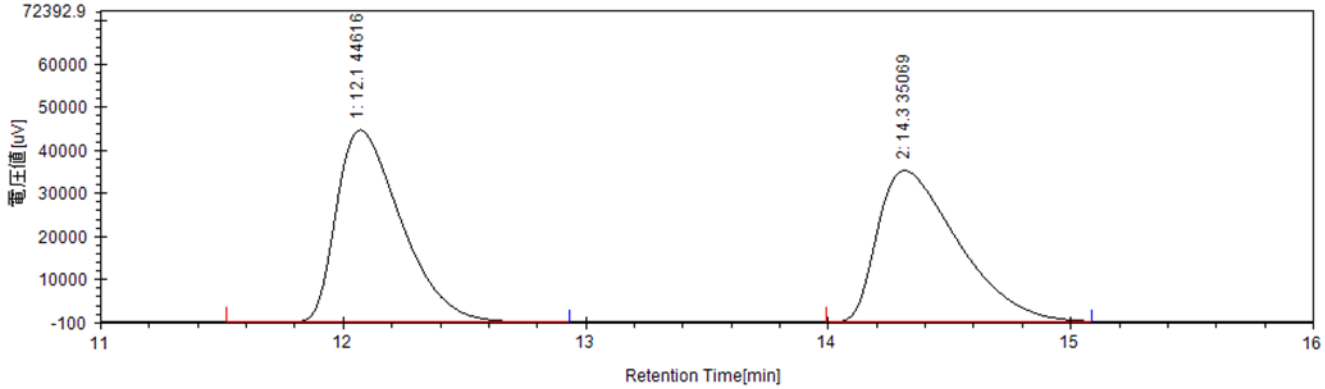
HRMS (ESI-TOF) *m/z* Calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048, found: 227.1042

$[\alpha]_D^{20}$ = +63.6 (*c* 0.46, $CHCl_3$) for a 98% ee, (Lit.[7] $[\alpha]_D^{20}$ = -21.0 (*c* 0.01, $CHCl_3$) for a 80% ee: *S* isomer)

Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 12.1 (major) and 14.9 (minor).

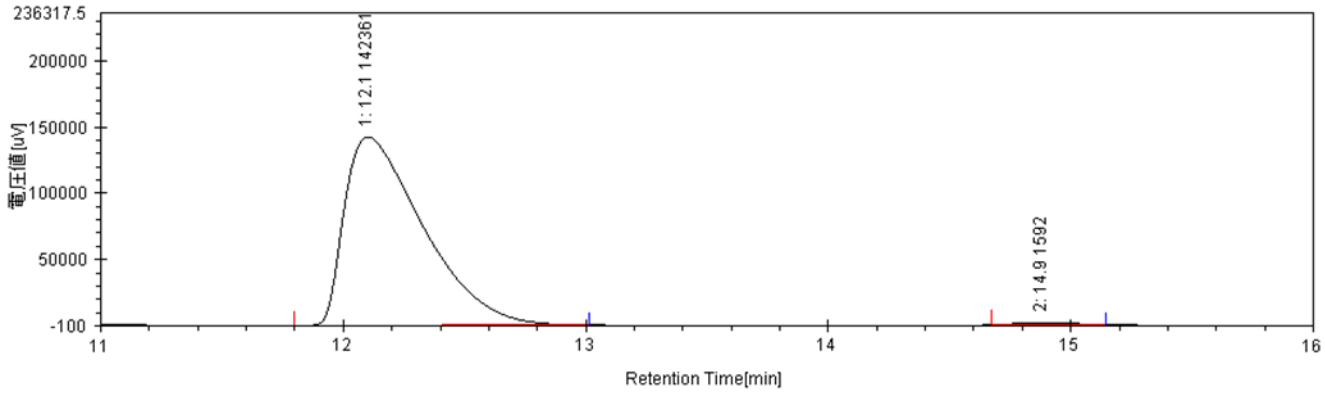
The absolute configuration was determined by comparison of the optical rotation with literature value.[7]

Racemic sample:



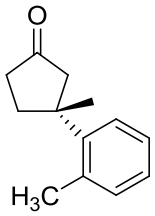
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	12.1	44616	13764.7	50.505	9782.6	1.613	***
2	14.3	35069	13489.5	49.495	8759.6	1.76	4.102

Enantiomeric sample (3a):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	12.1	142361	53283.2	99.215	6654.7	2.146	***
2	14.9	1592	421.4	0.785	17232.7	1.118	5.332

(*R*)-3-methyl-3-o-tolylcyclopentanone: 3b[7]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2-Methylphenyl boronic acid (0.28 mmol, 38.1 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3b** (19.2 mg, 73%, 94% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 - 7.12 (m, 4H), 2.74 (d, *J* = 17.4 Hz, 1H), 2.60 (d, *J* = 17.4 Hz, 1H), 2.52 - 2.35 (m, 4H), 1.38 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.9 (C), 146.6 (C), 135.7 (C), 132.6 (CH), 126.6 (CH), 126.3 (CH), 126.1 (CH), 53.0 (CH_2), 44.6 (C), 36.1 (CH_2), 36.0 (CH_2), 26.6 (CH_3), 22.6 (CH_3)

*The NMR data match with those reported in literature.[7]

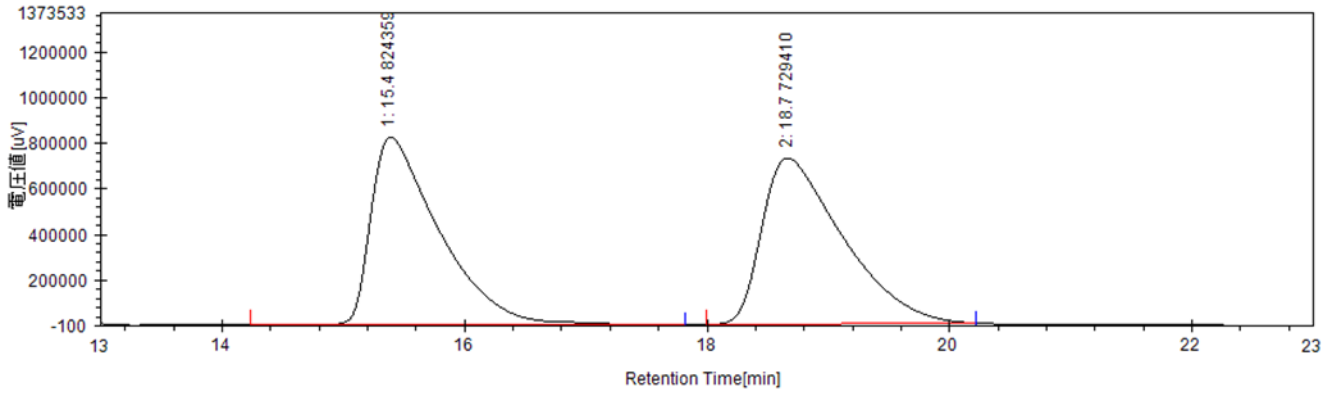
HRMS (ESI-TOF) *m/z* Calculated for $C_{13}H_{16}ONa$ $[M+Na]^+$: 211.1099, found: 211.1089

$[\alpha]_D^{24}$ = +46.38 (*c* 0.5, $CHCl_3$) for a 94% ee

Chiral HPLC analysis on a CHIRALPAK OB-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 15.5 (major) and 19.4 (minor).

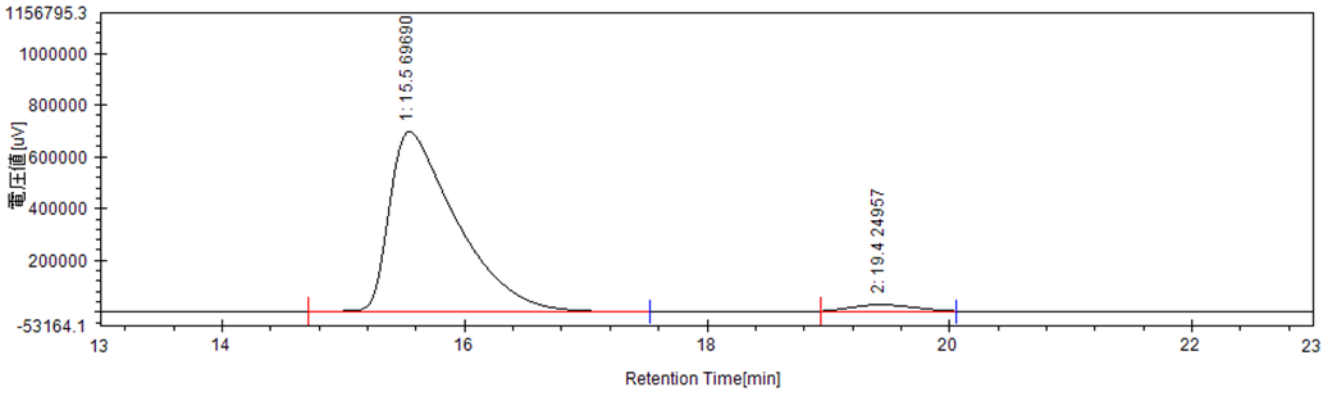
The absolute configuration was determined by comparison of the optical rotation with literature value.[7]

Racemic sample:



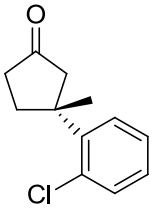
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	15.4	824359	536029.4	48.768	3857.4	2.151	***
2	18.7	729410	563103.8	51.232	3790.8	1.828	2.98

Enantiomeric sample (3b):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	15.5	696904	446952.4	96.859	3997.8	2.107	***
2	19.4	24957	14492.7	3.141	6412.6	1.139	3.986

(*R*)-3-(2-chlorophenyl)-3-methylcyclopentanone: 3c[7a]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2-Chlorophenyl boronic acid (0.28 mmol, 43.8 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3c** (29.1 mg, 80%, 98% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 - 7.16 (m, 4H), 2.91 (dd, *J* = 1.8, 18.3 Hz, 1H), 2.66 (d, *J* = 18.3 Hz, 1H), 2.55 - 2.36 (m, 4H), 1.48 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.5 (C), 144.9 (C), 133.4 (C), 131.8 (CH), 128.0 (CH), 127.7 (CH), 127.1 (CH), 52.2 (CH_2), 44.4 (C), 36.2 (CH_2), 35.2 (CH_2), 25.6 (CH_3)

*The NMR data match with those reported in literature.[7a]

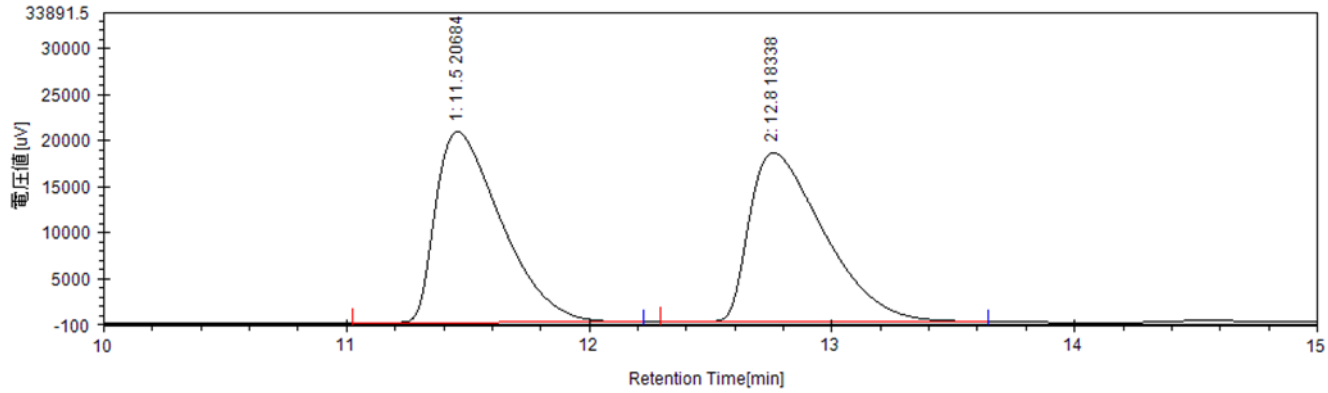
HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{13}ClONa$ $[M+Na]^+$: 231.0553, found: 227.0550

$[\alpha]_D^{20}$ = +23.66 (*c* 0.08, $CHCl_3$) for a 98% ee

Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 11.4 (major) and 13 (minor).

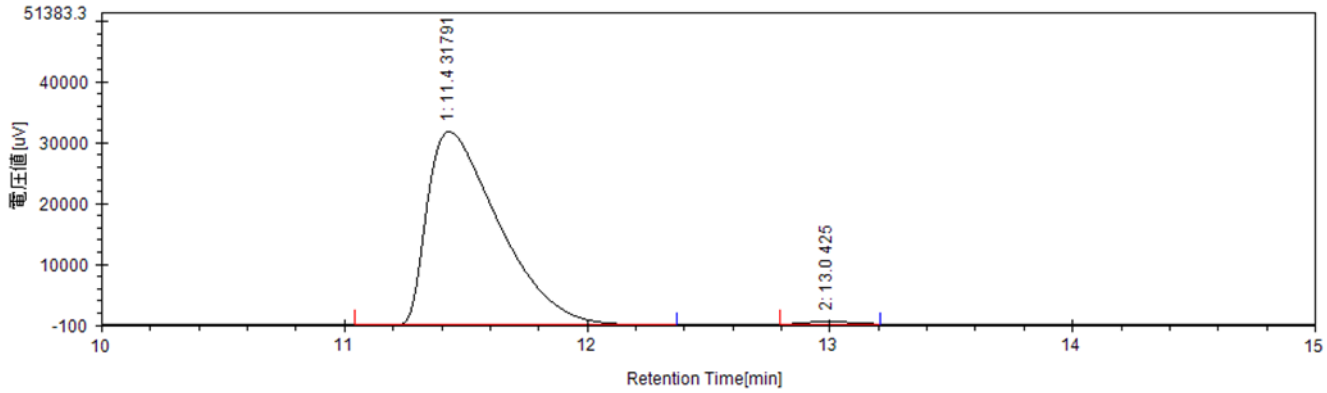
The absolute configuration was determined by comparison of the optical rotation with literature value.[7a]

Racemic sample:



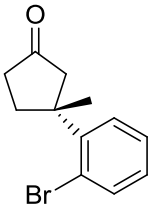
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11.5	20684	6448.9	49.729	8500.4	1.807	***
2	12.8	18338	6519.2	50.271	8141.8	1.9	2.453

Enantiomeric sample (3c):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11.4	31791	10850.9	99.111	7131.3	2.031	***
2	13	425	97.4	0.889	17786.4	1.048	3.356

(*R*)-3-(2-bromophenyl)-3-methylcyclopentanone: 3d



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2-Bromophenyl boronic acid (0.28 mmol, 56.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3d** (21 mg, 60%, 98% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.35 - 7.27 (m, 2H), 7.12 - 7.08 (m, 1H), 3.02 (dd, *J* = 1.8, 17.3 Hz, 1H), 2.67 (d, *J* = 17.8 Hz, 1H), 2.59 - 2.36 (m, 4H), 1.51 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.3 (C), 146.3 (C), 135.5 (CH), 128.2 (CH), 128.1 (CH), 127.6 (CH), 122.6 (C), 52.3 (CH_2), 45.1 (C), 36.4 (CH_2), 35.4 (CH_2), 25.7 (CH_3)

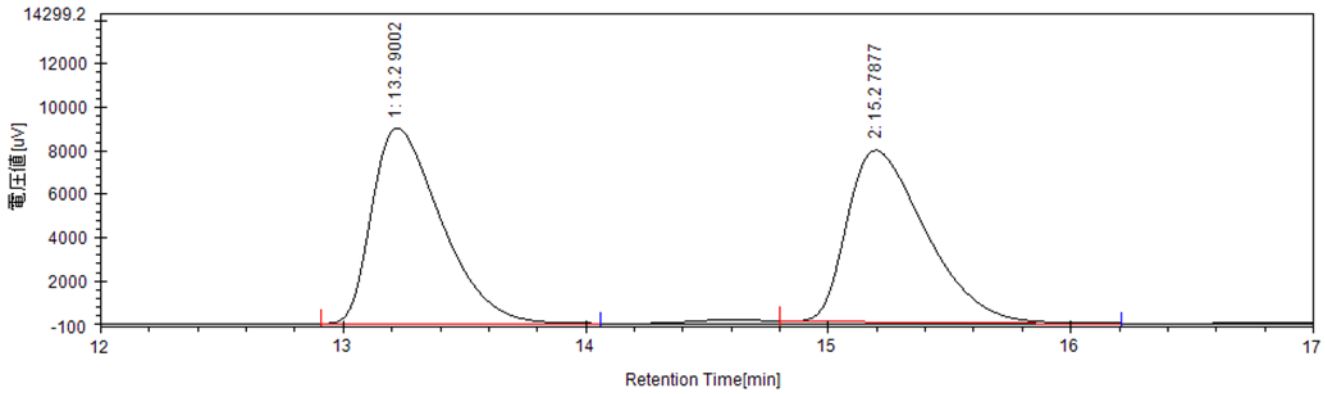
IR (neat) νmax: 1737, 1498, 1224, 1052 cm^{-1}

HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{13}BrONa$ $[M+Na]^+$: 275.0047, found: 275.0044

$[\alpha]_D^{24}$ = +56.43 (*c* 0.58, $CHCl_3$) for a 98% ee

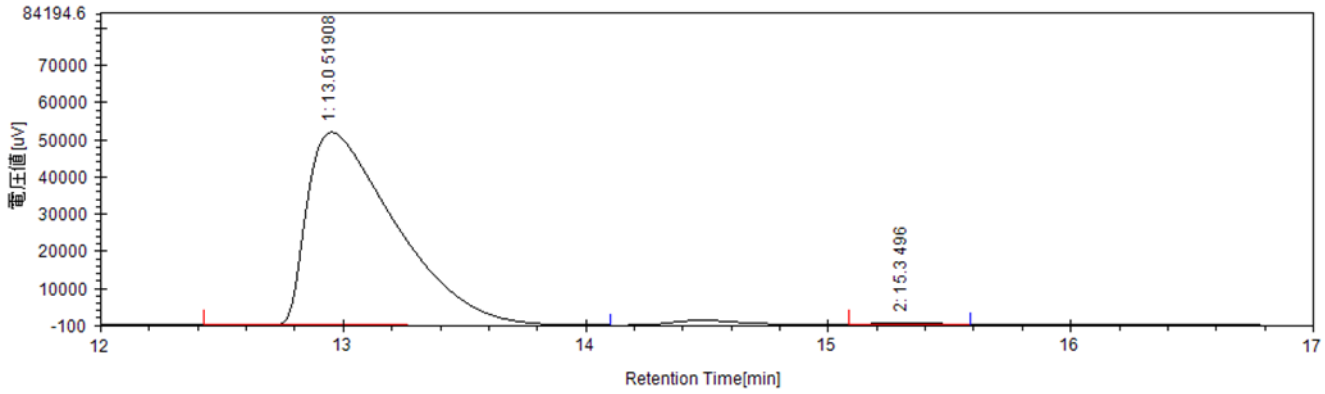
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 13 (major) and 15.3 (minor).

Racemic sample:



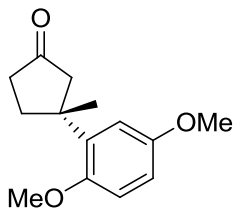
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	13.2	9002	2977.7	50.227	10275	1.569	***
2	15.2	7877	2950.8	49.773	10466.1	1.547	3.548

Enantiomeric sample (3d):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	13	51908	21965.5	99.392	5986.2	2.379	***
2	15.3	496	134.3	0.608	17908	1.111	4.196

(*R*)-3-(2,5-dimethoxyphenyl)-3-methylcyclopentanone: 3e



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2,5-Dimethoxy phenyl boronic acid (0.28 mmol, 51.0 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3e** (30.8 mg, 94%, 98% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.89 - 6.72 (m, 3H), 3.78 (s, 3H), 3.78 (s, 3H), 2.66 (d, *J* = 17.9 Hz, 1H), 2.62 (d, *J* = 17.8 Hz, 1H), 2.46 - 2.26 (m, 4H), 2.21 (s, 3H), 1.38 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 220.0 (C), 153.5 (C), 152.0 (C), 137.7 (C), 114.1 (CH), 112.1 (CH), 110.6 (CH), 55.8 (CH_3), 55.6 (CH_3), 52.3 (CH_2), 42.8 (C), 36.5 (CH_2), 34.9 (CH_2), 26.3 (CH_3)

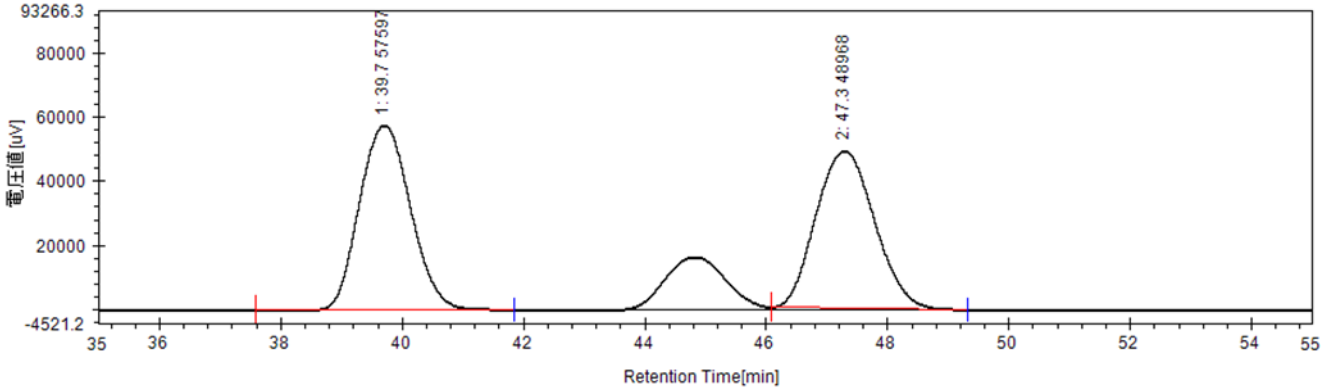
IR (neat) νmax: 1737, 1586, 1498, 1224, 1052 cm^{-1}

HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}O_3Na$ $[M+Na]^+$: 257.1154, found: 257.1155

$[\alpha]_D^{24}$ = +49.8 (*c* 0.39, $CHCl_3$) for a 98% ee

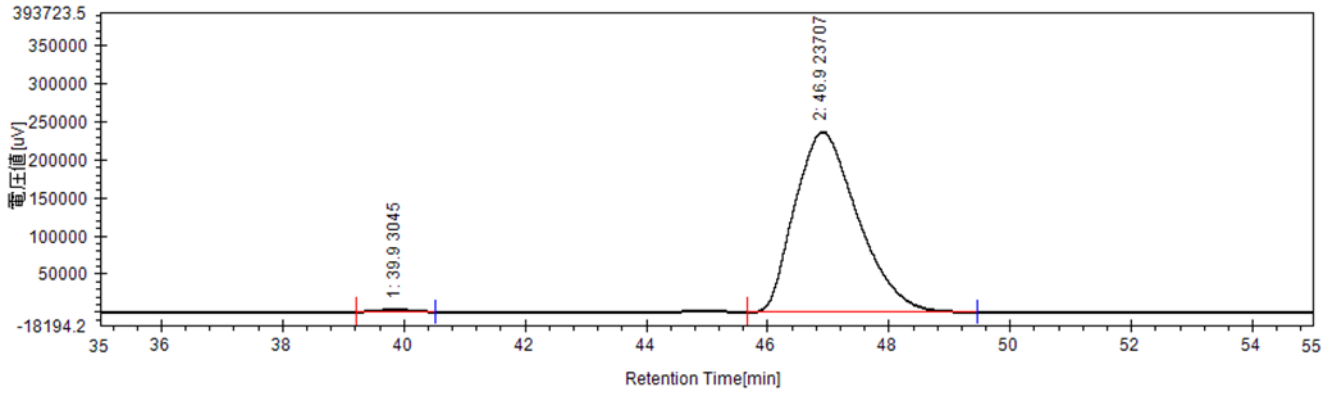
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 225 nm, retention times (min): 39.9 (minor) and 46.9 (major).

Racemic sample:



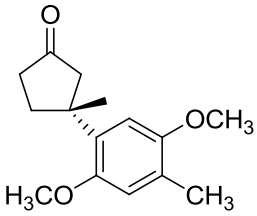
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	39.7	57597	55826.7	50.581	10195.4	1.109	***
2	47.3	48968	54543.6	49.419	10813.6	1.111	4.483

Enantiomeric sample (3e):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	39.9	3045	2330.1	0.816	14482.8	0.992	***
2	46.9	237077	283294.4	99.184	9455	1.317	4.339

(*R*)-3-(2,5-dimethoxy-4-methylphenyl)-3-methylcyclopentanone: 3f[7a]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2,5-Dimethoxy-4-methyl phenyl boronic acid (0.28 mmol, 54.9 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3f** (31.1 mg, 90%, 95% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.71 (s, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.66 (d, *J* = 18.3 Hz, 1H), 2.60 (d, *J* = 17.8 Hz, 1H), 2.44 - 2.28 (m, 4H), 2.21 (s, 3H), 1.38 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 220.1 (C), 151.5 (C), 134.2 (C), 125.6 (C), 114.8 (CH), 110.0 (CH), 56.4 (CH_3), 55.7 (CH_3), 52.5 (CH_2), 42.7 (C), 36.5 (CH_2), 35.1 (CH_2), 26.4 (CH_3), 16.0 (CH_3)

*The NMR data match with those reported in literature.[7a]

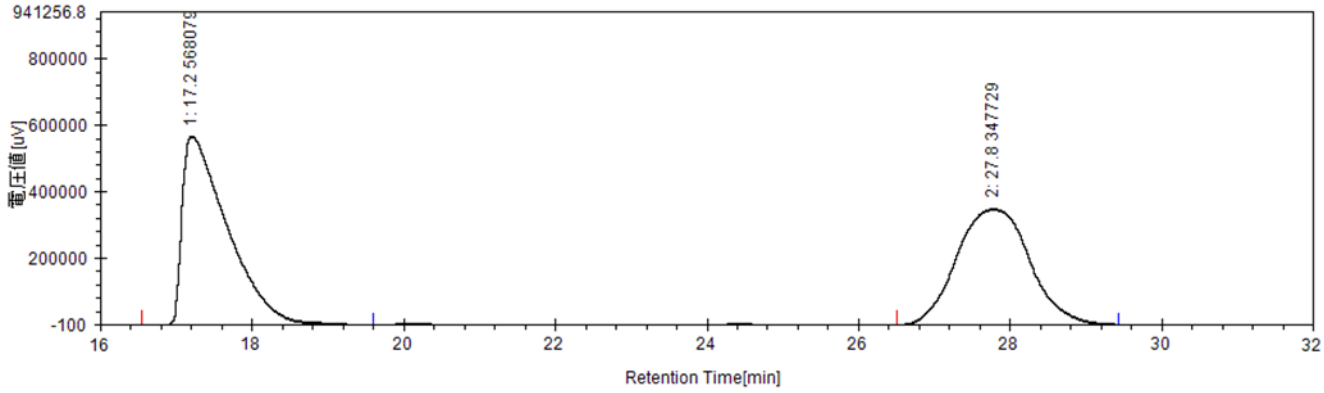
HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_3Na$ $[M+Na]^+$: 271.1310, found: 271.1314

$[\alpha]_D^{24}$ = +34.67 (*c* 0.54, $CHCl_3$) for a 95% ee

Chiral HPLC analysis on a CHIRALPAK AS-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 225 nm, retention times (min): 18 (minor) and 27.7 (major).

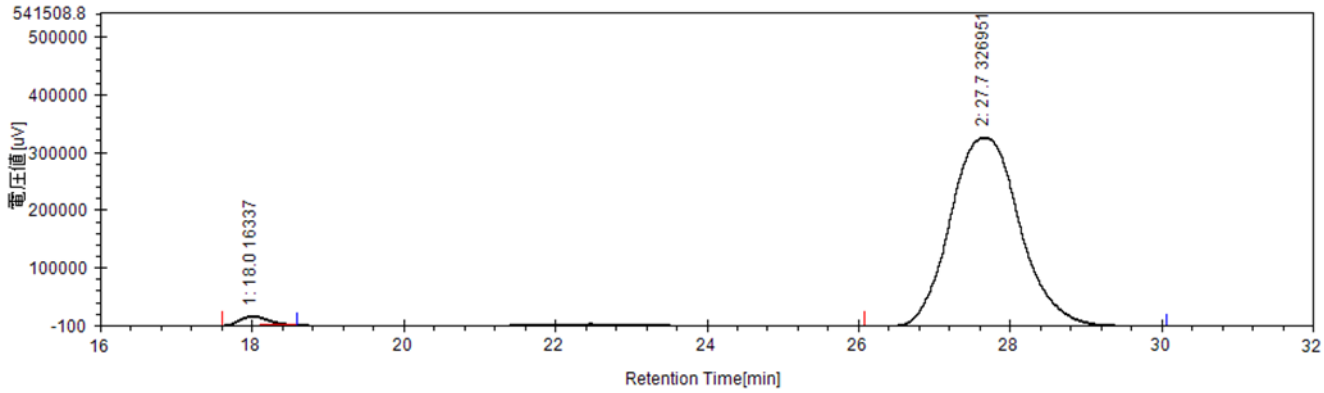
The absolute configuration was determined by comparison of the optical rotation with literature value.[7a]

Racemic sample:



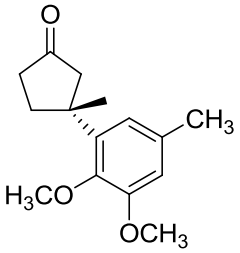
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	17.2	568079	390676.4	50.32	4142.9	3.079	***
2	27.8	347729	385708	49.68	3935	1.078	7.464

Enantiomeric sample:



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	18	16337	7197.3	2.047	10270.6	1.254	***
2	27.7	326951	344450.9	97.953	4479.1	1.123	8.2

(*R*)-3-(2,3-dimethoxy-5-methylphenyl)-3-methylcyclopentanone: 3g[7a, 8]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 2,3-Dimethoxy-5-methyl phenyl boronic acid (0.28 mmol, 54.9 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3g** (25.4 mg, 78%, 98% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.67 (d, *J* = 1.37 Hz, 1H), 6.60 (d, *J* = 1.37 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 2.71 (d, *J* = 17.8 Hz, 1H), 2.55 (d, *J* = 17.8 Hz, 1H), 2.44 - 2.26 (m, 4H), 1.36 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 219.9 (C), 153.0 (C), 145.4 (C), 141.3 (C), 133.1 (C), 118.9 (CH), 112.0 (CH), 60.5 (CH_3), 55.8 (CH_3), 52.8 (CH_2), 43.0 (C), 36.3 (CH_2), 35.4 (CH_2), 27.2 (CH_3), 21.6 (CH_3)

*The NMR data match with those reported in literature.[7a, 8]

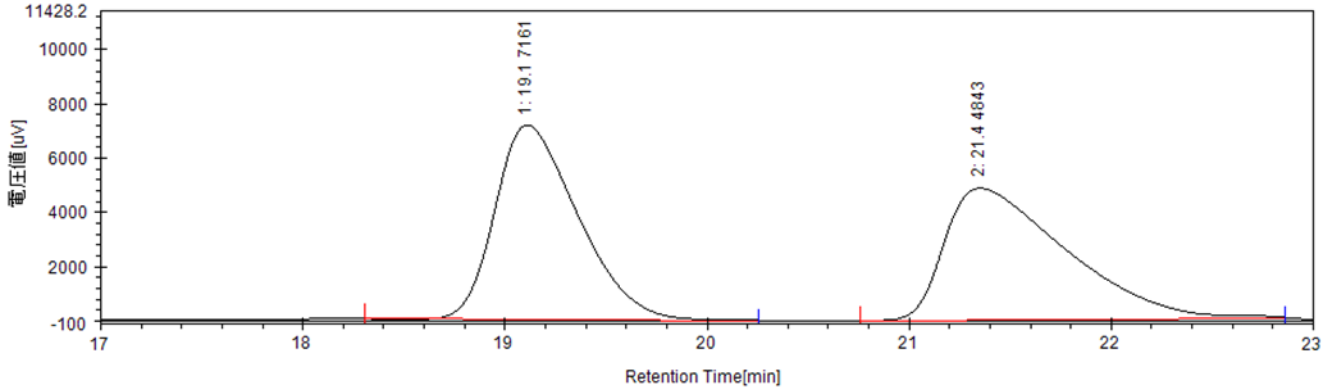
HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_3Na$ $[M+Na]^+$: 271.1310, found: 271.1317

$[\alpha]_D^{23}$ = +47.98 (*c* 0.65, $CHCl_3$) for a 98% ee

Chiral HPLC analysis on a CHIRALPAK AS-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 225 nm, retention times (min): 18.7 (major) and 21.8 (minor).

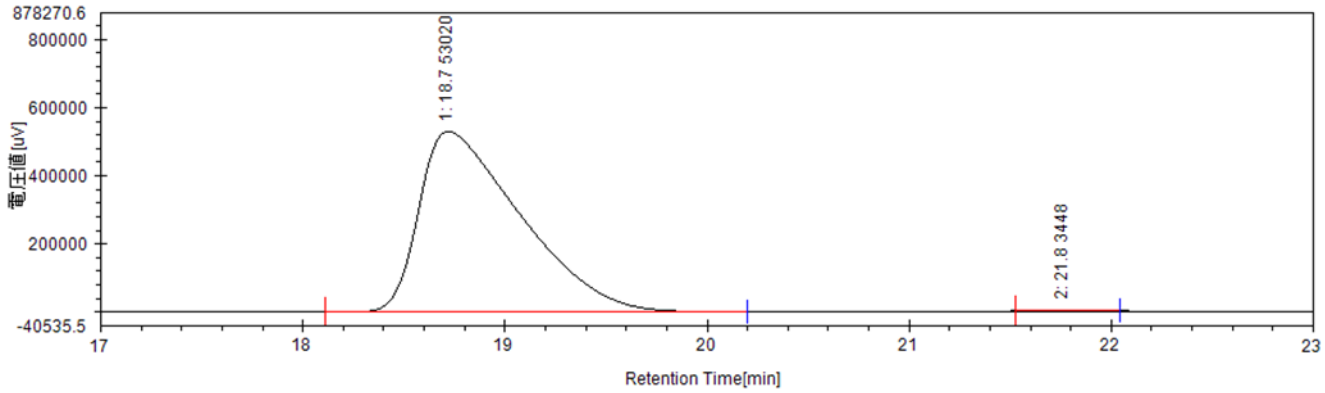
The absolute configuration was determined by comparison of the optical rotation with literature value.[7a,8]

Racemic sample:



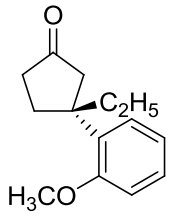
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	19.1	7161	3399.6	50.363	10374.1	1.383	***
2	21.4	4843	3350.6	49.637	6101.2	1.978	2.438

Enantiomeric sample (3g):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	18.7	530205	307660	99.646	6609.4	1.949	***
2	21.8	3448	1092.2	0.354	24350.4	1.066	4.136

(*R*)-3-ethyl-3-(2-methoxyphenyl) cyclopentanone: 3h



Synthesized according to General Procedure A from 3-Ethyl-2-cyclopentene-1-one (0.14 mmol, 15.4 mg) and 2-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3h** (28.2 mg, 92%, 96% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 - 7.20 (m, 1H), 7.12 - 7.10 (m, 1H), 6.94 - 6.88 (m, 2H), 3.81 (s, 3H), 2.75 (d, *J* = 18.3 Hz, 1H), 2.60 (d, *J* = 18.3 Hz, 1H), 2.58 - 2.23 (m, 4H), 1.90 - 1.72 (m, 2H), 0.62 (t, *J* = 7.32 Hz, 3H)

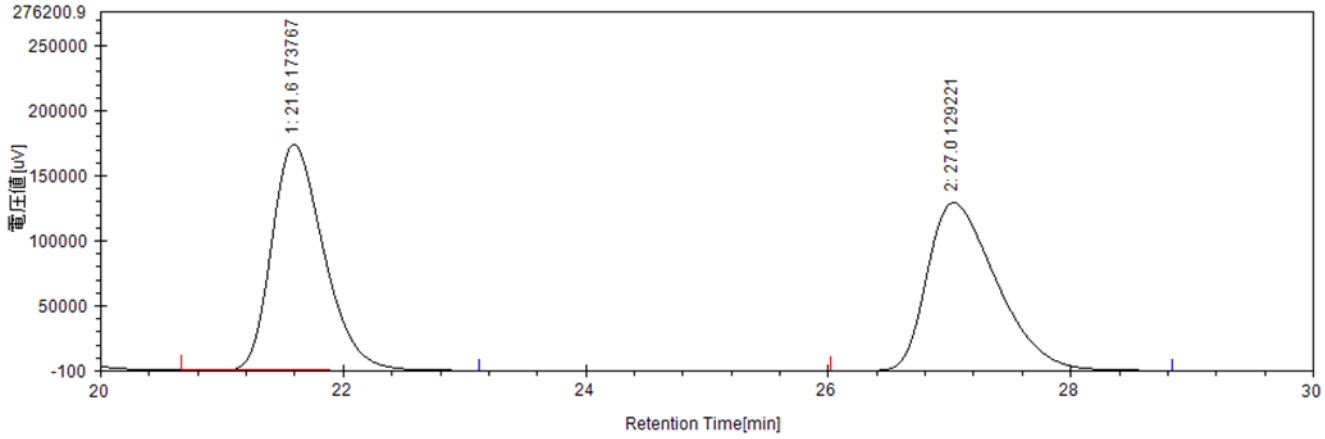
^{13}C NMR (100 MHz, Chloroform-*d*) δ 220.2 (C), 157.9 (C), 133.6 (C), 128.2 (CH), 127.8 (CH), 120.3 (CH), 111.4 (CH), 55.1 (CH_3), 51.5 (CH_2), 47.1 (C), 36.1 (CH_2), 32.3 (CH_2), 29.7 (CH_2), 9.6 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1204, found: 241.1205

$[\alpha]_D^{26}$ = +24.5 (*c* 0.20, $CHCl_3$) for a 96% ee

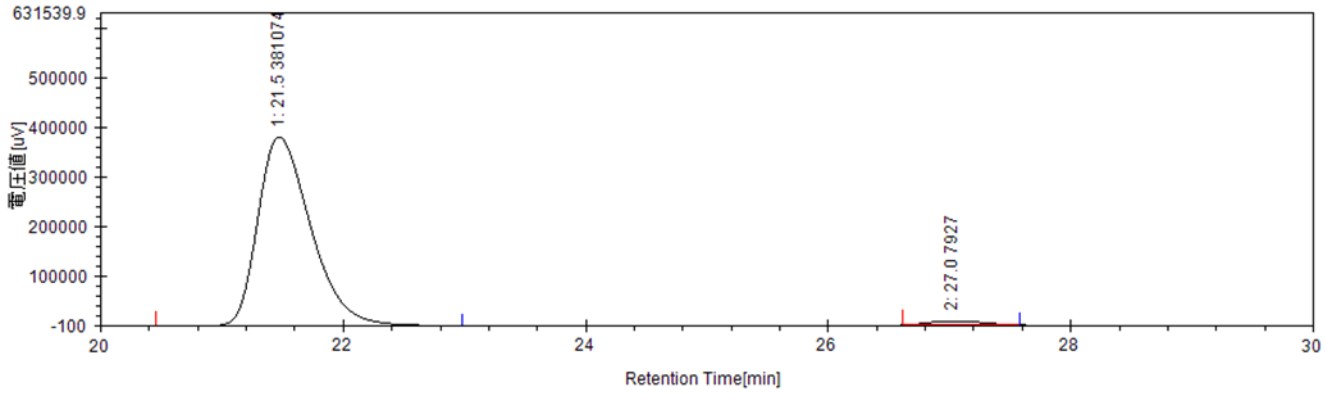
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 210 nm, retention times (min): 21.5 (major) and 27 (minor).

Racemic sample:



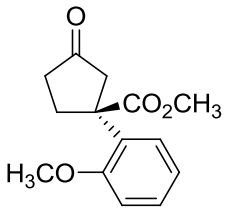
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21.6	173767	86026.7	50.196	12353.3	1.305	***
2	27	129221	85354.8	49.804	10710.4	1.481	5.989

Enantiomeric sample (3h):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21.5	381074	191570.3	97.914	11905.7	1.392	***
2	27	7927	4081.8	2.086	15497.5	1.147	6.731

(*S*)-methyl 1-(2-methoxyphenyl)-3-oxocyclopentanecarboxylate: 3i



Synthesized according to General Procedure A from Methyl-3-oxocyclopent-2-enecarboxylate (0.14 mmol, 19.6 mg) and 2-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3i** (31.6 mg, 91%, 93% ee) as a white solid. m.p. = 129 - 130 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 - 7.22 (m, 2H), 7.00 - 6.96 (m, 1H), 6.91 - 6.89 (m, 1H), 3.79 (s, 3H), 3.64 (s, 3H), 3.19 (d, *J* = 18.7 Hz, 1H), 2.44 (d, *J* = 17.8 Hz, 1H), 2.68 - 2.26 (m, 4H),

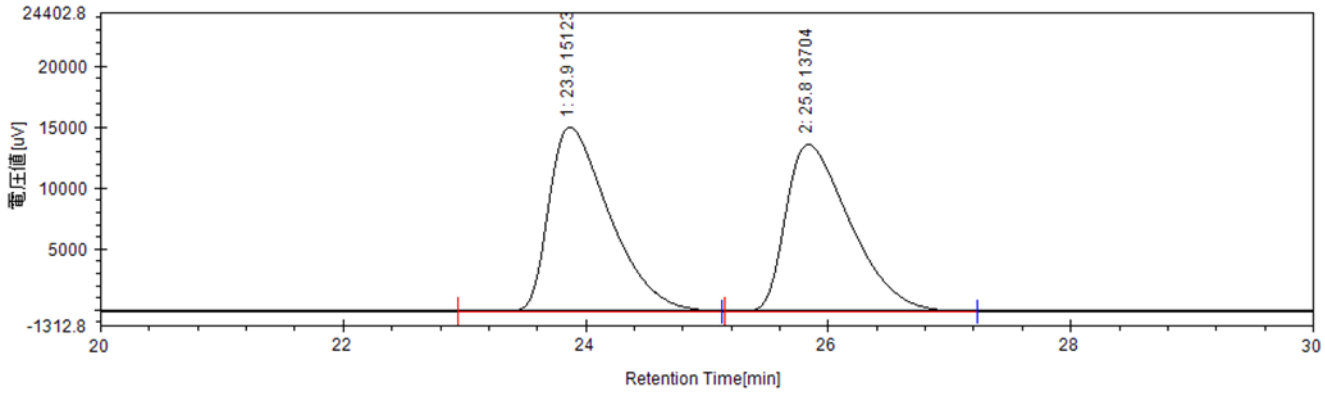
^{13}C NMR (100 MHz, Chloroform-*d*) δ 216.6 (C), 176.1 (C), 157.2 (C), 130.2 (C), 128.9 (CH), 125.9 (CH), 120.7 (CH), 111.1 (CH), 55.4 (CH_3), 52.5 (CH_3), 52.0 (C), 48.7 (CH_2), 36.1 (CH_2), 31.2 (CH_2)

HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{16}O_4Na$ $[M+Na]^+$: 271.0946, found: 271.0957

$[\alpha]_D^{24}$ = +39.9 (*c* 0.34, $CHCl_3$) for a 93% ee

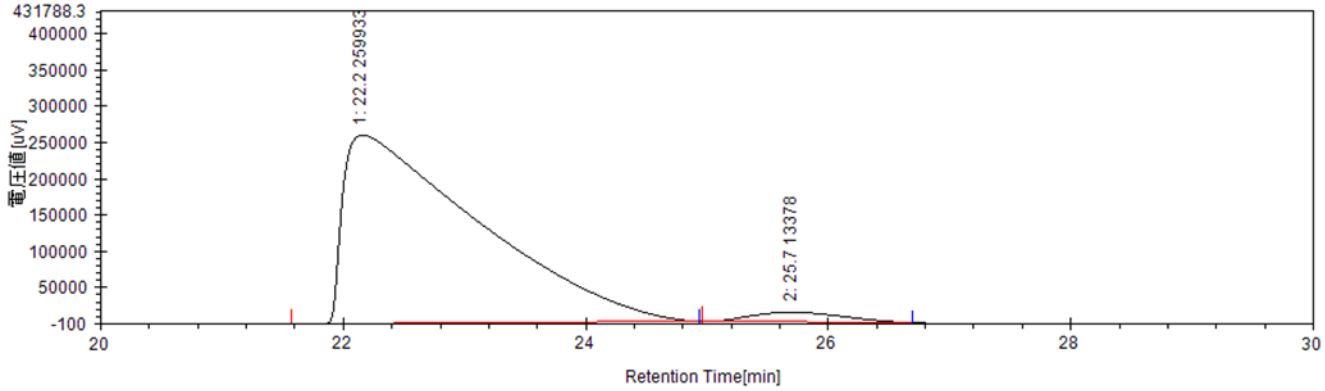
Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 22.2 (major) and 25.7 (minor).

Racemic sample:



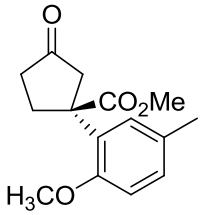
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	23.9	15123	8729	50.855	11077.5	1.71	***
2	25.8	13704	8435.4	49.145	11239.2	1.67	2.096

Enantiomeric sample (3i):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	22.2	259933	334642.1	96.61	1844.2	5.183	***
2	25.7	13378	11741.3	3.39	4779.4	1.225	2

(*S*)-methyl 1-(2-methoxy-5-methylphenyl)-3-oxocyclopentanecarboxylate: 3j



Synthesized according to General Procedure A from Methyl-3-oxocyclopent-2-enecarboxylate (0.14 mmol, 19.6 mg) and 2-Methoxy-4-methyl phenyl boronic acid (0.28 mmol, 46.5 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3j** (36.7 mg, 96%, 97% ee) as a pale-yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 9.2 Hz, 1H), 7.01 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.17 (d, *J* = 18.3 Hz, 1H), 2.66 - 2.25 (m, 4H), 2.43 (d, *J* = 18.3 Hz, 1H), 2.31 (s, 3H)

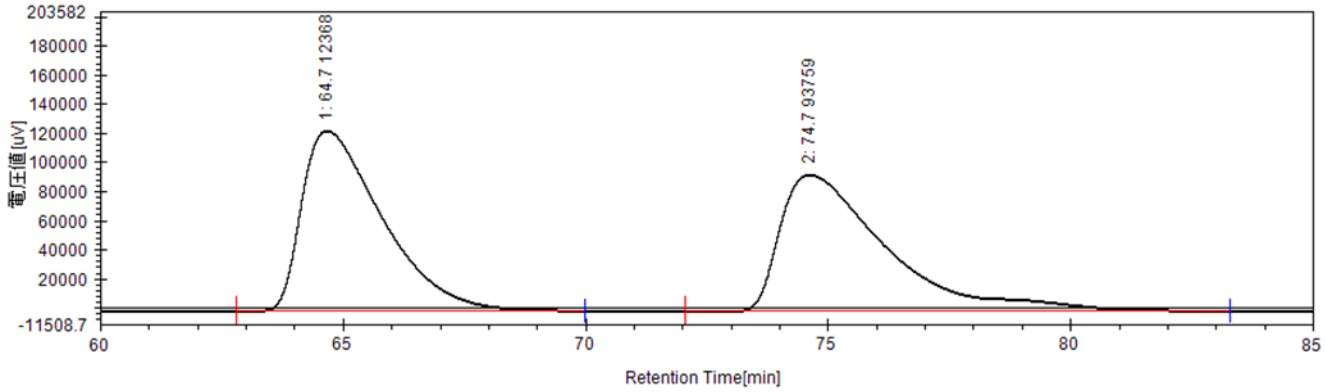
^{13}C NMR (100 MHz, Chloroform-*d*) δ 216.6 (C), 176.2 (C), 155.1 (C), 129.9 (C), 129.8 (C), 129.0 (CH), 126.7 (CH), 111.1 (CH), 55.5 (CH_3), 52.5 (CH_3), 52.0 (C), 48.8 (CH_2), 36.2 (CH_2), 31.2 (CH_2), 20.9 (CH_3)

HRMS (ESI-TOF) m/z Calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$: 285.1103, found: 229.1104

$[\alpha]_D^{24}$ = +58.3 (*c* 0.23, $CHCl_3$) for a 97% ee

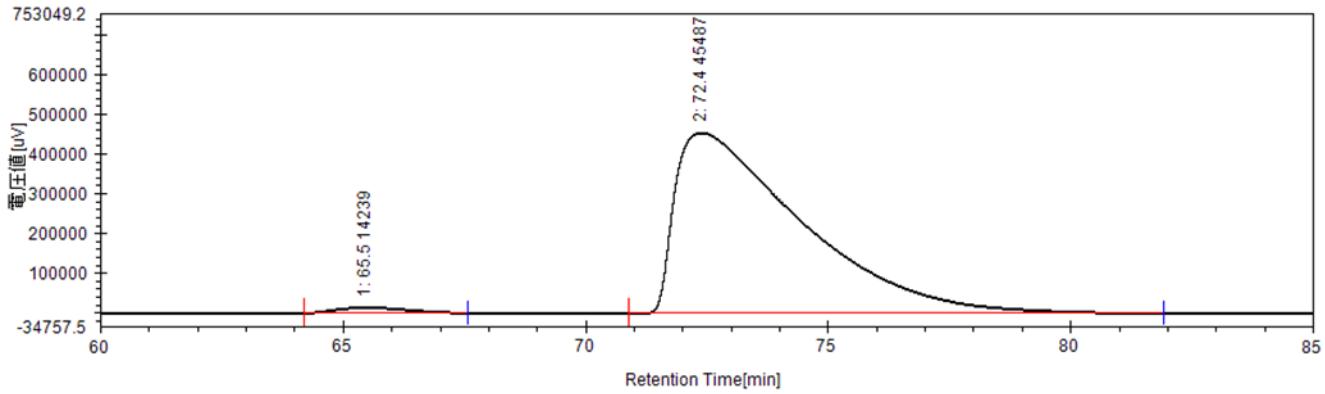
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 210 nm, retention times (min): 65.5 (minor) and 72.4 (major).

Racemic sample:



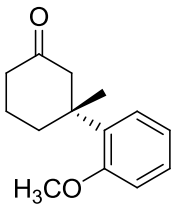
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	64.7	123686	236223.7	50.015	7545.8	1.983	***
2	74.7	93759	236079.2	49.985	6566.9	2.791	2.999

Enantiomeric sample (3j):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	65.5	14239	24037.9	1.719	8776	1.328	***
2	72.4	454879	1374490	98.281	3911.1	3.553	1.874

(*R*)-3-(2-methoxyphenyl)-3-methylcyclohexanone: 3k[7]



Synthesized according to General Procedure A from 3-Methyl-2-cyclohexen-1-one **1b** (0.14 mmol, 15.4 mg) and 2-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3k** (15.6 mg, 51%, 83% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 - 7.20 (m, 2H), 6.95 - 6.84 (m, 2H), 3.84 (s, 3H), 3.00 (d, *J* = 14.2 Hz, 1H), 2.62 - 2.54 (m, 1H), 2.45 (d, *J* = 14.2 Hz, 1H), 2.36 - 2.25 (m, 2H), 1.92 - 1.80 (m, 2H), 1.70 - 1.61 (m, 1H), 1.40 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 212.6 (C), 157.9 (C), 134.9 (C), 127.8 (CH), 127.5 (CH), 120.7 (CH), 111.9 (CH), 55.0 (CH_3), 53.4 (CH_2), 42.9 (C), 41.0 (CH_2), 35.1 (CH_2), 26.4 (CH_3), 22.2 (CH_2)

*The NMR data match with those reported in literature.[7]

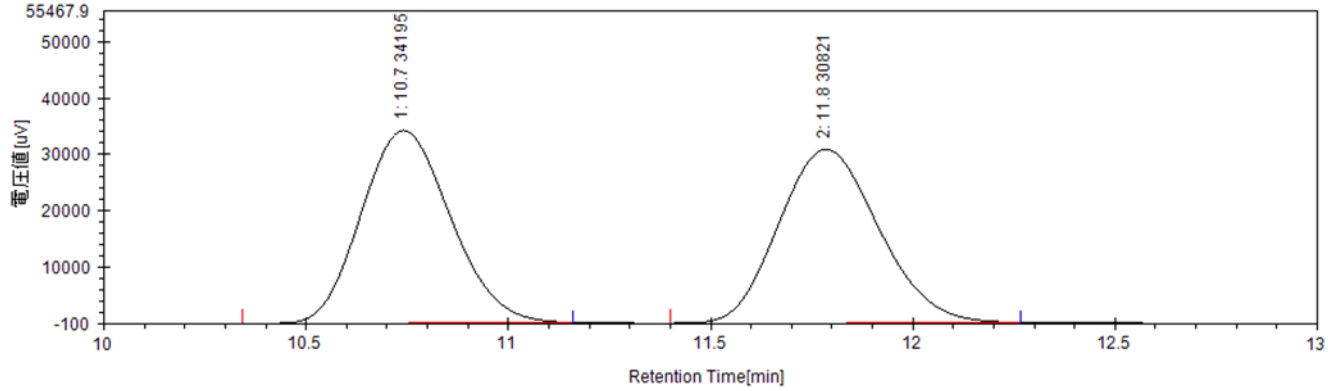
HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1204, found: 241.1205

$[\alpha]_D^{23}$ = -49.6 (*c* 0.54, $CHCl_3$) for a 83% ee

Chiral HPLC analysis on a CHIRALPAK OD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 10.8 (minor) and 11.7 (major).

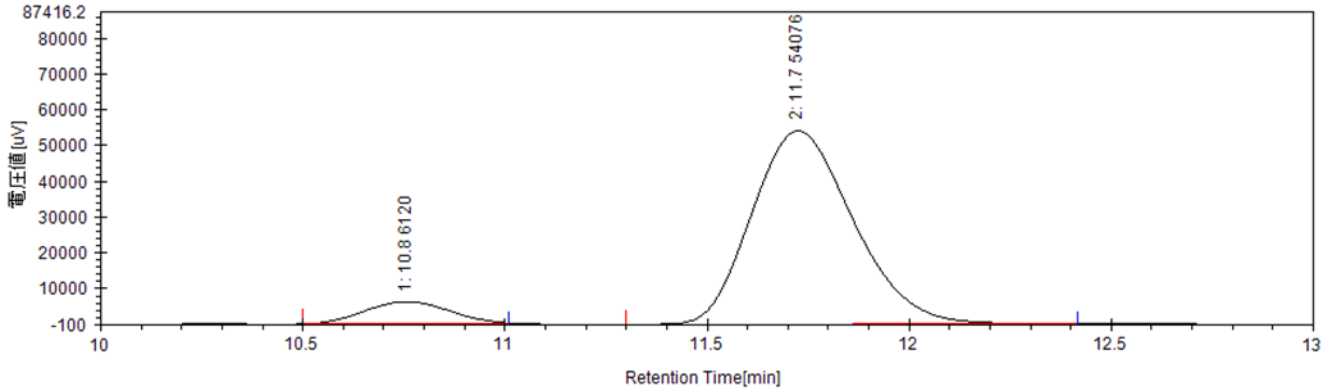
The absolute configuration was determined by comparison of the optical rotation with literature value.[7]

Racemic sample:



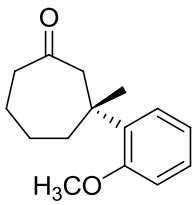
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	10.7	34195	8730.6	49.803	10998.2	1.126	***
2	11.8	30821	8799.7	50.197	10566.5	1.144	2.406

Enantiomeric sample (3k):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	10.8	6120	1468.3	8.56	11817.3	1.008	***
2	11.7	54076	15685.1	91.44	10269.2	1.204	2.258

(*R*)-3-(2-methoxyphenyl)-3-methylcycloheptanone: 3l



Synthesized according to General Procedure A from 3-Methyl-2-cyclohepten-1-one **1c** (0.14 mmol, 17.4 mg) and 2-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3l** (25.0 mg, 77%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 - 7.20 (m, 2H), 6.95 - 6.89 (m, 2H), 3.83 (s, 3H), 2.67 (d, *J* = 18.3 Hz, 1H), 2.60 (d, *J* = 18.3 Hz, 1H), 2.45 - 2.30 (m, 4H), 1.39 (s, 3H)

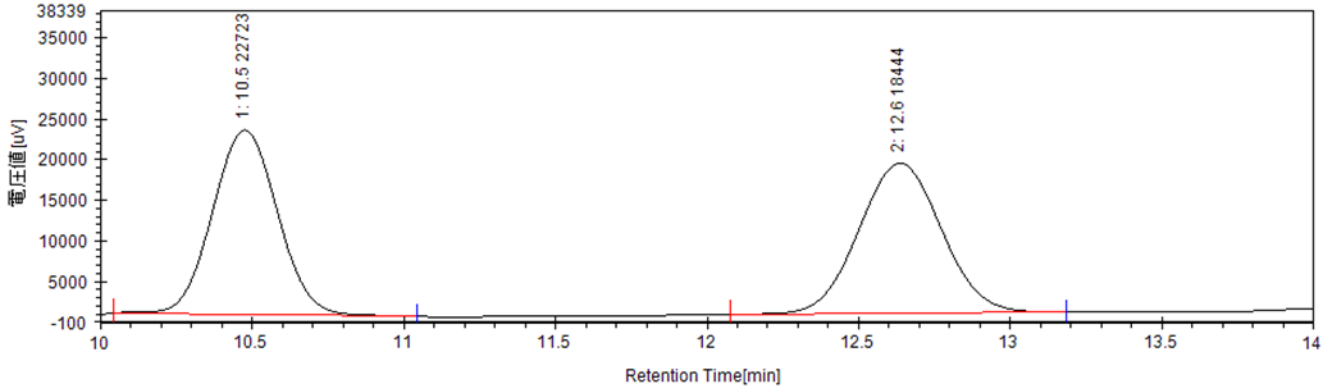
^{13}C NMR (100 MHz, Chloroform-*d*) δ 214.0 (C), 148.0 (C), 128.7 (CH), 128.6 (CH), 126.1 (CH), 125.7 (CH), 55.7 (CH_2), 44.3 (CH_2), 43.5 (CH_2), 39.9 (C), 32.0 (CH_3), 25.9 (CH_2), 24.0 (CH_2)

HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_2Na$ $[M+Na]^+$: 255.1361, found: 255.1373

$[\alpha]_D^{26}$ = -63.7 (*c* 0.37, $CHCl_3$) for a 99% ee

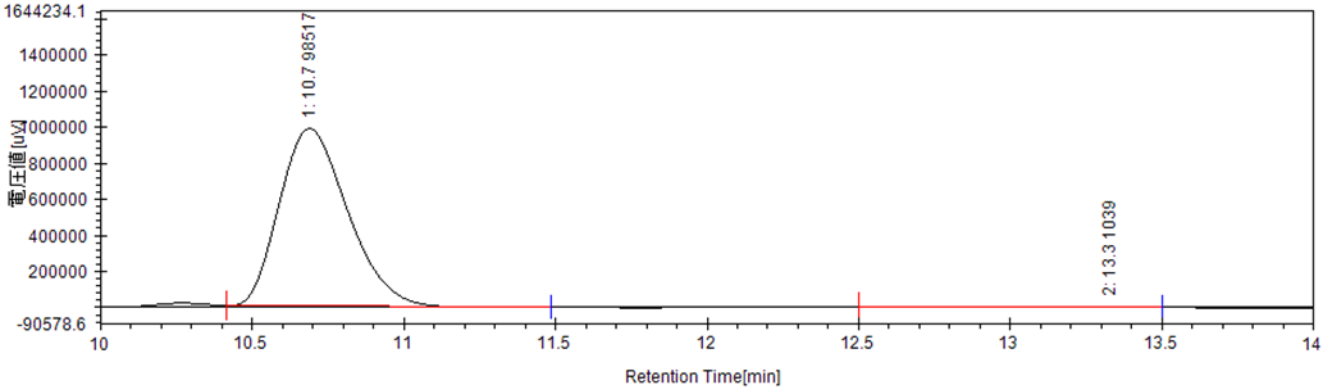
Chiral HPLC analysis on a CHIRALPAK OD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 10.7 (major) and 13.3 (minor).

Racemic sample:



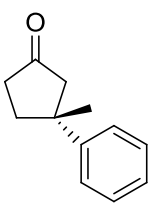
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	10.5	22723	5658.2	49.224	11210.2	1.043	***
2	12.6	18444	5836.5	50.776	9986.1	1.047	4.802

Enantiomeric sample (3l):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	10.7	985172	257291.6	99.771	10515.2	1.245	***
2	13.3	1039	590.5	0.229	8034.7	0.6	5.234

(*R*)-3-methyl-3-phenylcyclopentanone: 3n[9]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and Phenyl boronic acid (0.28 mmol, 34.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3n** (22.5 mg, 92%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 - 7.28 (m, 4H), 7.26 - 7.18 (m, 1H), 2.88 (d, *J* = 14.2 Hz, 1H), 2.44 (d, *J* = 14.2 Hz, 1H), 2.37 - 2.28 (m, 2H), 2.26 - 2.13 (m, 1H), 1.96 - 1.83 (m, 2H), 1.72 - 1.62 (m, 1H), 1.32 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.6 (C), 148.6 (C), 128.7 (CH), 126.4 (CH), 125.6 (CH), 52.3 (CH_2), 43.9 (C), 36.8 (CH_2), 35.9 (CH_2), 29.5 (CH_3)

*The NMR data match with those reported in literature.[9]

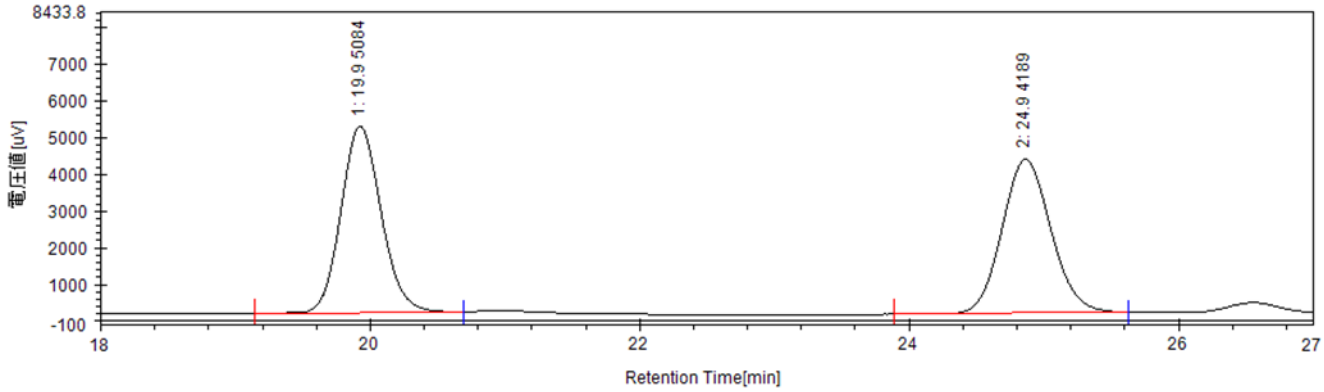
HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{14}ONa$ $[M+Na]^+$: 197.0942, found: 197.0932

$[\alpha]_D^{23}$ = +23.95 (*c* 0.17, $CHCl_3$) for a 99% ee (Lit.[9] $[\alpha]_D^{20}$ = -22.0 (*c* 0.57, $CHCl_3$) for a 72% ee)

Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 254 nm, retention times (min): 20.7 (minor) and 25.5 (major).

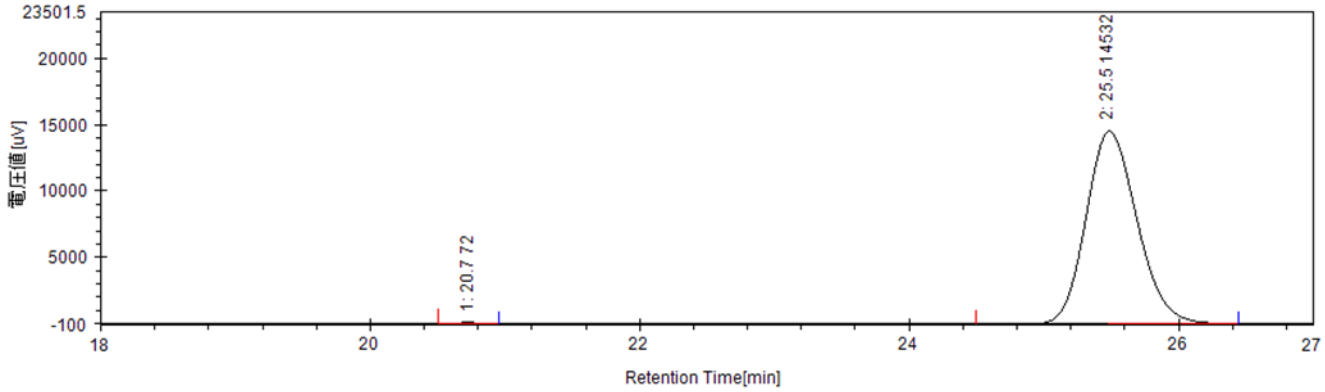
The absolute configuration was determined by comparison of the optical rotation with literature value.[9]

Racemic sample:



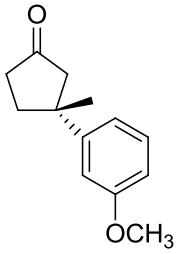
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	19.9	5081	1742.5	49.971	21835.4	1.117	***
2	24.9	4178	1744.5	50.029	22616.3	1.084	8.253

Enantiomeric sample (3n):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	20.7	72	19	0.297	35243.3	0.985	***
2	25.5	14532	6369.3	99.703	21827.3	1.175	8.417

(*R*)-3-(3-methoxyphenyl)-3-methylcyclopentanone: 3o



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 3-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3o** (26.8 mg, 94%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 - 7.25 (m, 1H), 6.89 - 6.77 (m, 3H), 3.82 (s, 3H), 2.64 (d, *J* = 17.8 Hz, 1H), 2.45 (d, *J* = 17.8 Hz, 1H), 2.45 - 2.20 (m, 4H), 1.38 (s, 3H)

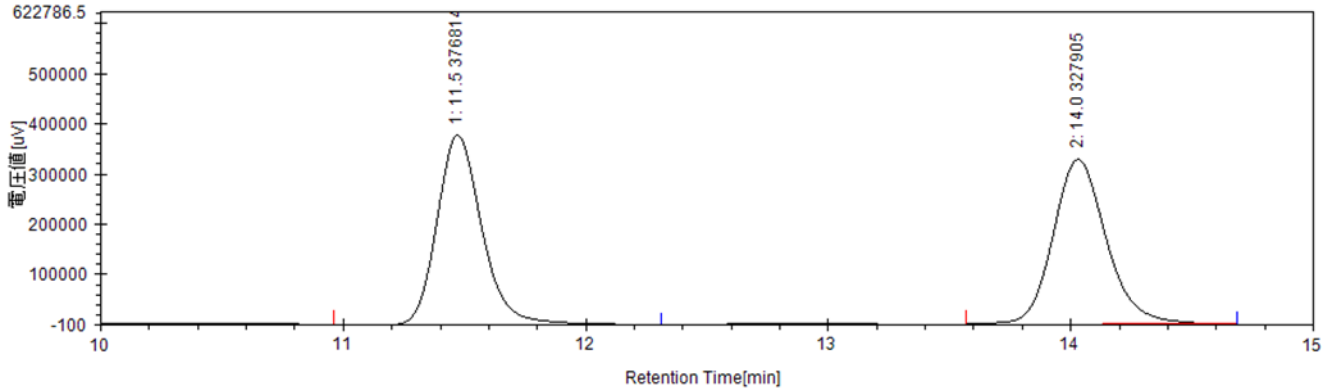
^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.5 (C), 159.8 (C), 150.3 (C), 129.6 (CH), 118.0 (CH), 112.3 (CH), 110.9 (CH), 55.3 (CH_3), 52.3 (CH_2), 43.9 (C), 36.8 (CH_2), 35.8 (CH_2), 29.4 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048, found: 227.1048

$[\alpha]_D^{23}$ = -18.53 (*c* 0.415, $CHCl_3$) for a 99% ee

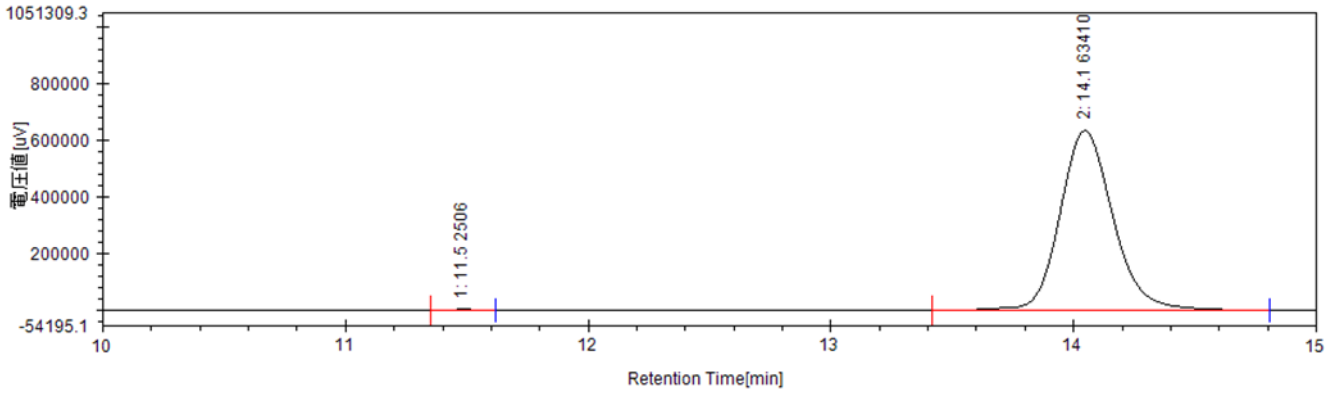
Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 0.5 ml/min, UV detection at 225 nm, retention times (min): 11.5 (minor) and 14.1 (major).

Racemic sample:



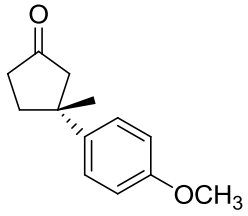
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11.5	376814	80520.8	49.107	19626.2	1.182	***
2	14	327905	83449.2	50.893	20768.3	1.154	7.154

Enantiomeric sample (3o):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11.5	2506	382.1	0.237	30544.4	1.006	***
2	14.1	634102	160846.2	99.763	21059.1	1.142	7.917

(*R*)-3-(4-methoxyphenyl)-3-methylcyclopentanone: 3p[7b]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 4-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3p** (27.1 mg, 95%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 - 7.19 (m, 2H), 6.90 - 6.84 (m, 2H), 3.80 (s, 3H), 2.63 (d, *J* = 17.8 Hz, 1H), 2.46 - 2.19 (m, 5H), 1.37 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.8 (C), 158.0 (C), 140.6 (C), 126.5 (CH), 114.0 (CH), 55.4 (CH_3), 52.6 (CH_2), 43.3 (C), 36.9 (CH_2), 36.2 (CH_2), 29.6 (CH_3)

*The NMR data match with those reported in literature.[7b]

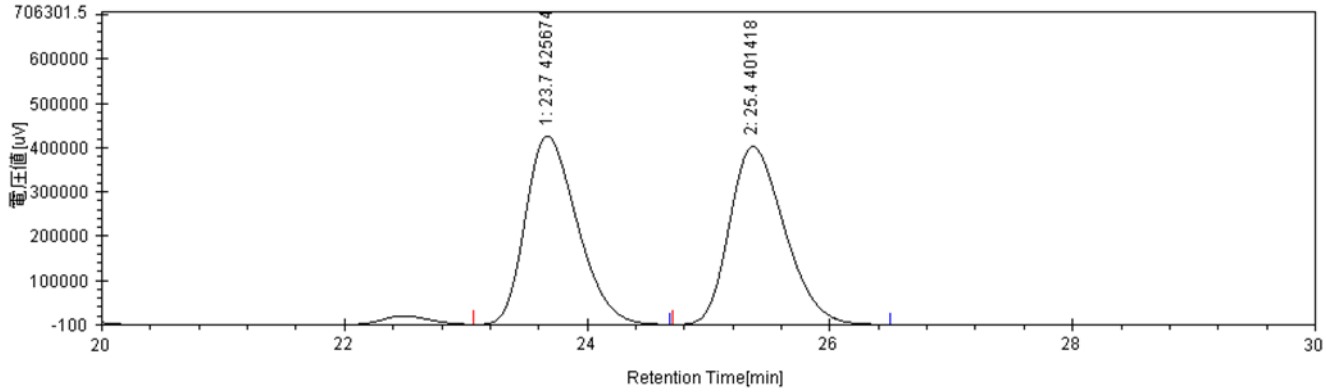
HRMS (ESI-TOF) *m/z* Calculated for $C_{13}H_{16}O_2Na$ $[M+Na]^+$: 227.1048, found: 227.1043

$[\alpha]_D^{23}$ = +3.57 (*c* 0.56, $CHCl_3$) for a 99% ee

Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 0.5 ml/min, UV detection at 225 nm, retention times (min): 23.7 (minor) and 25.3 (major).

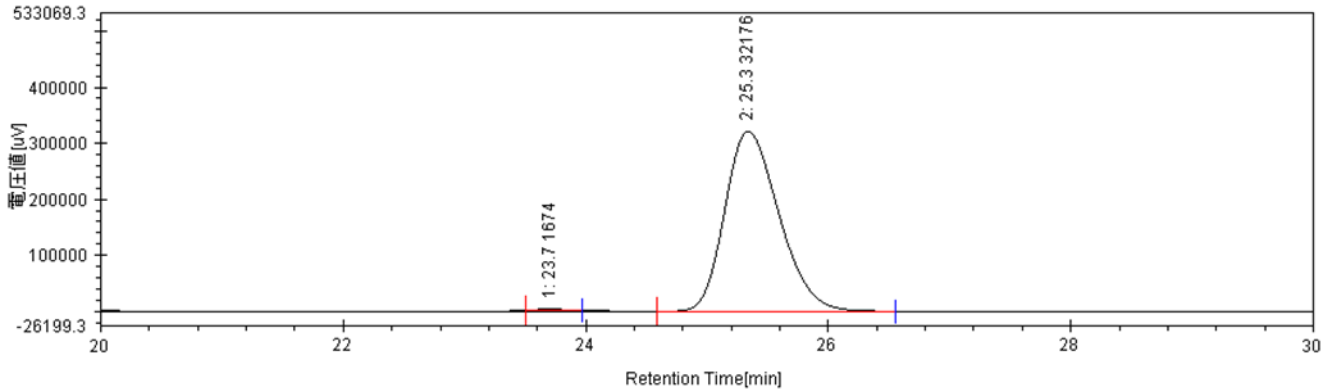
The absolute configuration was determined by comparison of the optical rotation with literature value.[7b]

Racemic sample:



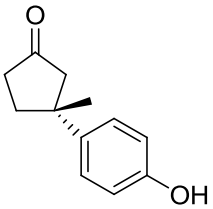
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	23.7	425674	209974.7	49.976	14615.2	1.276	***
2	25.4	401418	210180.1	50.024	14893.9	1.271	2.101

Enantiomeric sample (3p):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	23.7	1674	476.8	0.286	35973.3	1.114	***
2	25.3	321760	165957.2	99.714	15383.9	1.246	2.487

(*R*)-3-(4-hydroxyphenyl)-3-methylcyclopentanone: 3q



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 4-Hydroxyphenyl boronic acid (0.28 mmol, 38.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 5: 1) to yield **3q** (23.4 mg, 88%, 95% ee) as a white solid.

m.p. = 89 - 90 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 8.23 Hz, 2H), 6.81 (d, *J* = 8.23 Hz, 2H), 5.19 (br s, 1H), 2.63 (d, *J* = 17.84 Hz, 1H), 2.44 (d, *J* = 17.38 Hz, 1H), 2.46 - 2.20 (m, 4H), 1.36 (s, 3H)

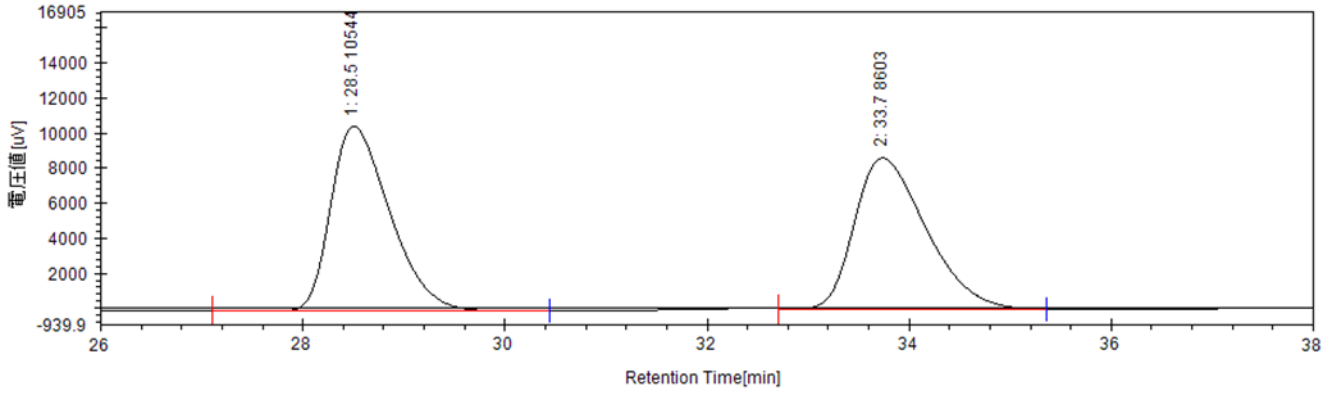
^{13}C NMR (100 MHz, Chloroform-*d*) δ 219.5 (C), 154.1 (C), 140.6 (C), 126.7 (CH), 115.4 (CH), 52.6 (CH_2), 43.3 (C), 36.9 (CH_2), 36.2 (CH_2), 29.6 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{14}O_2Na$ $[M+Na]^+$: 213.0891, found: 213.0870

$[\alpha]_D^{21}$ = -33.97 (*c* 0.415, $CHCl_3$) for a 95% ee

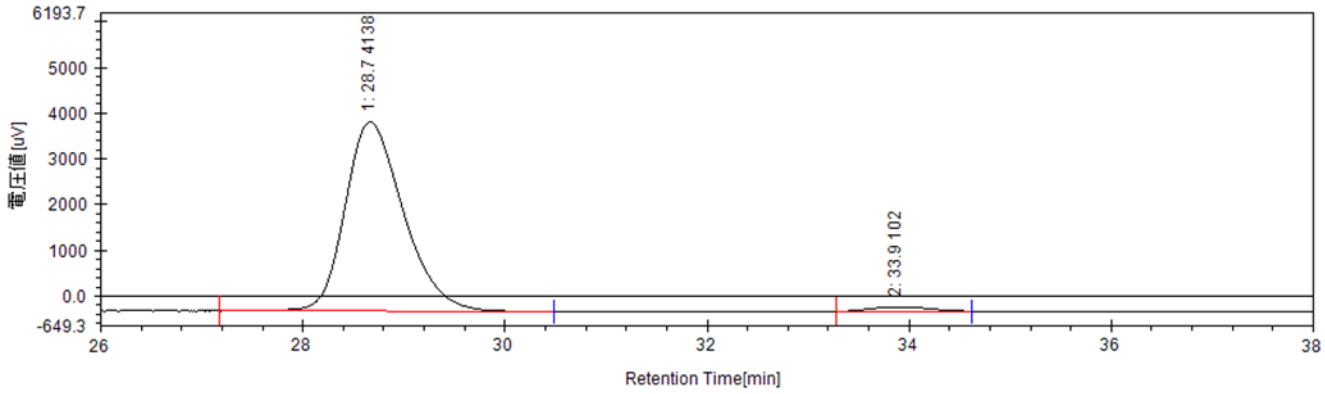
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 28.7 (major) and 33.9 (minor).

Racemic sample:



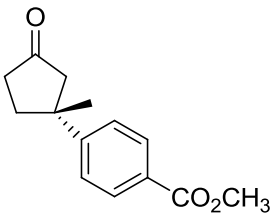
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	28.5	10544	7154.1	50.393	11324.4	1.442	***
2	33.7	8603	7042.6	49.607	10823.7	1.431	4.431

Enantiomeric sample (3q):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	28.7	4138	2775.3	97.654	12186.9	1.277	***
2	33.9	102	66.7	2.346	15126.9	1.134	4.887

(*R*)-methyl 4-(1-methyl-3-oxocyclopentyl) benzoate: 3r[10]



Synthesized according to General Procedure A from 3-Methyl-2-cyclopent-1-one **1a** (0.14 mmol, 13.4 mg) and 4-Methoxycarbonyl phenyl boronic acid (0.28 mmol, 50.4 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 10: 1) to yield **3r** (32.5 mg, 90%, 99%

ee) as a white solid.

m.p. = 94 - 95 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.69 Hz, 2H), 7.36 (d, *J* = 8.23 Hz, 2H), 3.92 (s, 3H), 2.65 (d, *J* = 17.38 Hz, 1H), 2.51 (d, *J* = 17.84 Hz, 1H), 2.50- 2.28 (m, 4H), 1.40 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 217.7 (C), 166.9 (C), 153.8 (C), 130.0 (CH), 128.4 (C), 125.6 (CH), 52.1 (CH_3), 52.0 (CH_2), 44.1 (C), 36.7 (CH_2), 35.6 (CH_2), 29.2 (CH_3)

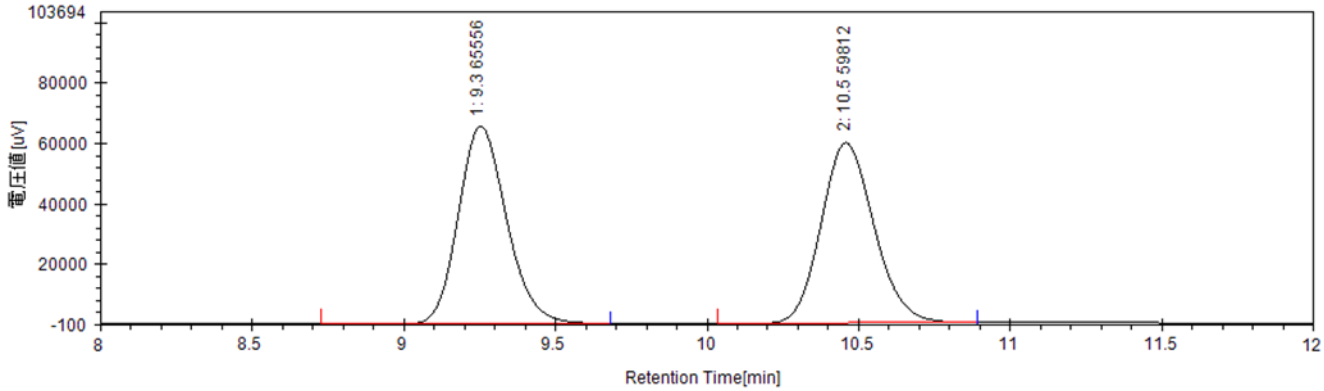
HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{16}O_3Na$ $[M+Na]^+$: 255.0997, found: 225.1001

$[\alpha]_D^{23}$ = +3.40 (*c* 1.8, EtOH) for a 99% ee

Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 1.0 ml/min, UV detection at 225 nm, retention times (min): 9.3 (minor) and 10.5 (major).

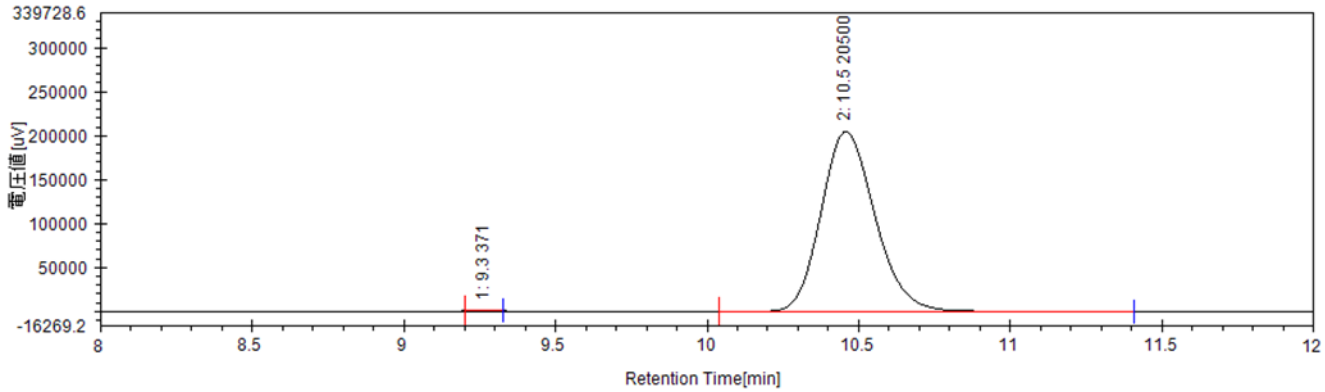
The absolute configuration was determined by comparison of the optical rotation with literature value.[10]

Racemic sample:



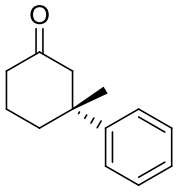
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	9.3	65556	12054.2	49.907	16558.6	1.194	***
2	10.5	59812	12099	50.093	17335.3	1.135	4.003

Enantiomeric sample (3r):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	9.3	371	29.9	0.071	67417.8	0.934	***
2	10.5	205001	42196.2	99.929	16865.8	1.164	5.14

(*R*)-3-methyl-3-phenylcyclohexanone: 3s[9a-c,11]



Synthesized according to General Procedure A from 3-Methyl-2- cyclohexen-1-one **1b** (0.14 mmol, 15.4 mg) and Phenyl boronic acid (0.28 mmol, 34.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3s** (25.5 mg, 98%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 - 7.28 (m, 4H), 7.26 - 7.18 (m, 1H), 2.88 (d, *J* = 14.2 Hz, 1H), 2.44 (d, *J* = 14.2 Hz, 1H), 2.37 - 2.28 (m, 2H), 2.26 - 2.13 (m, 1H), 1.96 - 1.83 (m, 2H), 1.72 - 1.62 (m, 1H), 1.32 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.6 (C), 147.5 (C), 128.6 (CH), 126.3 (CH), 125.7 (CH), 53.2 (CH_2), 42.9 (C), 40.9 (CH_2), 38.0 (CH_2), 29.8 (CH_3), 22.1 (CH_2)

*The NMR data match with those reported in literature.[9a-c,11]

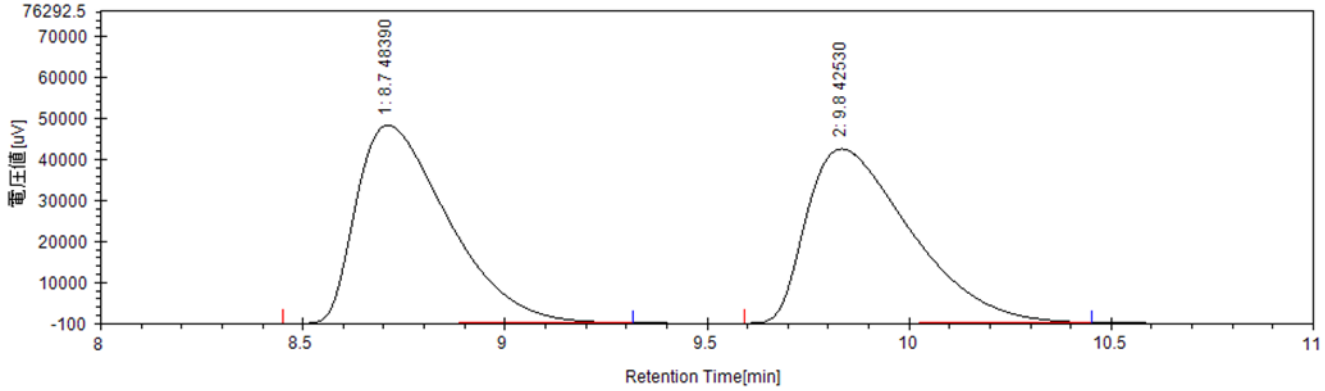
HRMS (ESI-TOF) *m/z* Calculated for $C_{13}H_{16}ONa$ $[M+Na]^+$: 211.1099, found: 211.1089

$[\alpha]_D^{23}$ = -77.1 (*c* 0.78, $CHCl_3$)

Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 225 nm, retention times (min): 8.7 (minor) and 10 (major).

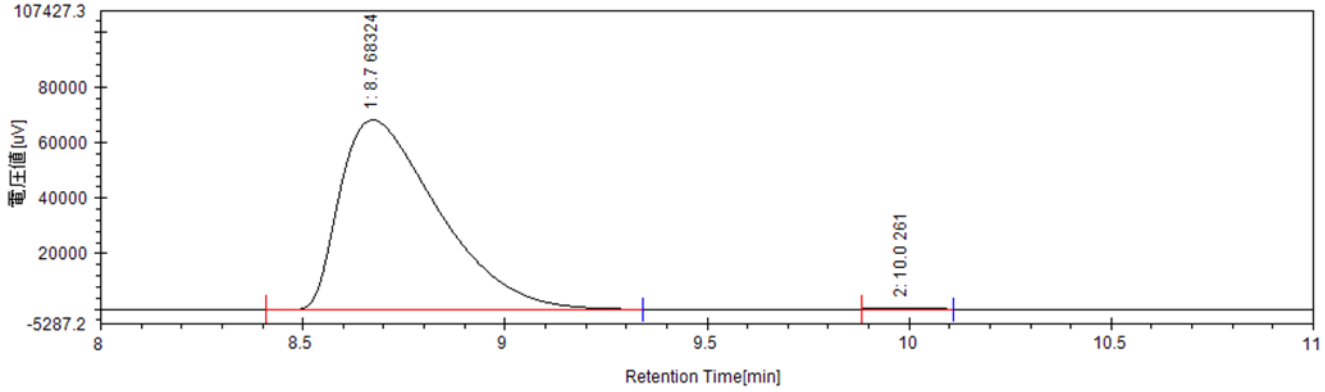
The absolute configuration was determined by comparison of the optical rotation with literature value.[9a-c,11]

Racemic sample:



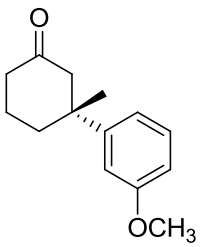
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	8.7	48390	12721.7	50.105	6957.6	1.782	***
2	9.8	42530	12668.2	49.895	6866.5	1.798	2.528

Enantiomeric sample (3s):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	8.7	68324	19247.7	99.813	6016	1.848	***
2	10	261	36.1	0.187	26666.1	1.12	3.792

(*R*)-3-(3-methoxyphenyl)-3-methylcyclohexanone: 3t[9d, e, 12]



Synthesized according to General Procedure A from 3-Methyl-2- cyclohexen-1-one **1b** (0.14 mmol, 15.4 mg) and 3-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3t** (27.5 mg, 90%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 - 7.23 (m, 1H), 6.92 - 6.87 (m, 2H), 6.76 - 6.74 (m, 1H), 3.80 (s, 3H), 2.86 (d, *J* = 14.6 Hz, 1H), 2.43 (d, *J* = 14.2 Hz, 1H), 2.33 - 2.31 (m, 2H), 2.30 - 2.14 (m, 2H), 1.94 - 1.82 (m, 2H), 1.73 - 1.63 (m, 1H), 1.31 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.4 (C), 159.8 (C), 149.4 (C), 129.6 (CH), 118.1 (CH), 112.2 (CH), 111.0 (CH), 55.3 (CH_3), 53.2 (CH_2), 43.0 (C), 40.9 (CH_2), 38.0 (CH_2), 29.8 (CH_3), 22.1 (CH_2)

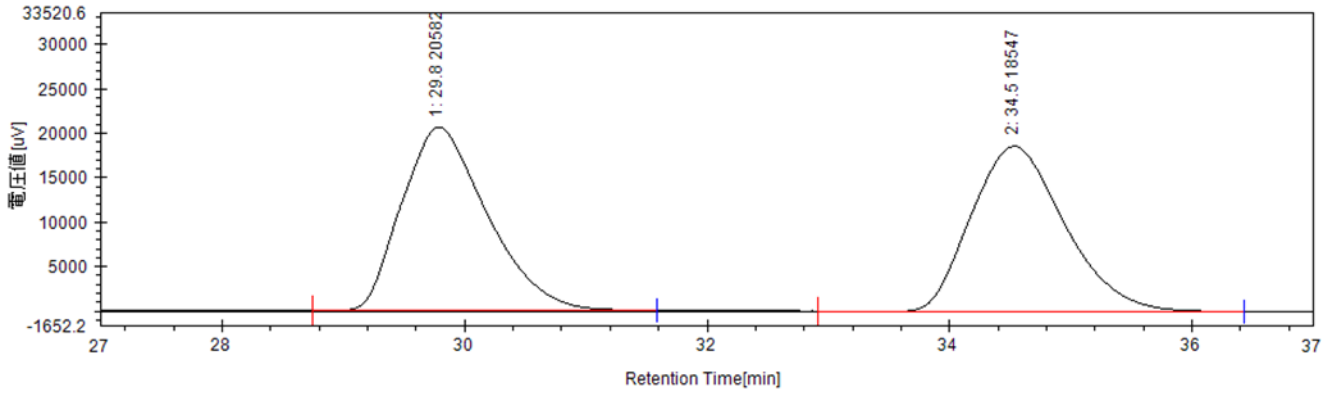
HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1204, found: 241.1204

$[\alpha]_D^{24}$ = -71.1 (*c* 0.38, $CHCl_3$) for a 99% ee

Chiral HPLC analysis on a CHIRALPAK OD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 27.9 (major) and 37.7 (minor).

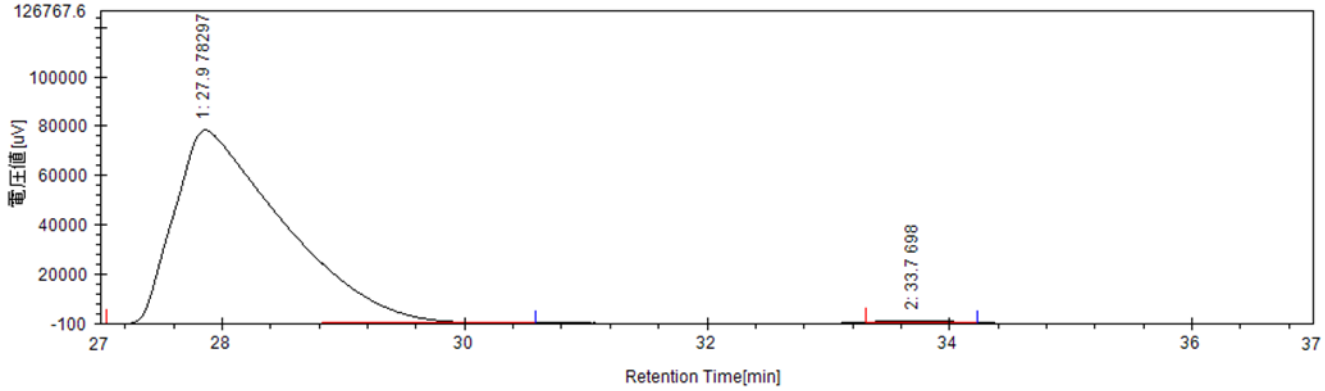
The absolute configuration was determined by comparison of the optical rotation with literature value.[9d, e, 12]

Racemic sample:



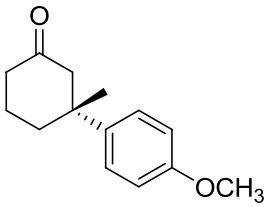
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	29.8	20582	16759	50.401	8279.1	1.333	***
2	34.5	18547	16492.5	49.599	9392.2	1.234	3.483

Enantiomeric sample (3t):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	27.9	78297	81536.1	99.529	4563.9	2.108	***
2	33.7	698	385.6	0.471	19450.9	1.137	4.484

(*R*)-3-(4-methoxyphenyl)-3-methylcyclohexanone: 3u[9d, e,12]



Synthesized according to General Procedure A from 3-Methyl-2- cyclohexen-1-one **1b** (0.14 mmol, 15.4 mg) and 4-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3u** (27.8 mg, 91%, 99% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 - 7.21 (m, 2H), 6.87 - 6.84 (m, 2H), 3.79 (s, 3H), 2.85 (d, *J* = 14.2 Hz, 1H), 2.41 (d, *J* = 14.2 Hz, 1H), 2.32 - 2.28 (m, 2H), 2.19 - 2.12 (m, 1H), 1.92 - 1.81 (m, 2H), 1.71 - 1.61 (m, 1H), 1.30 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.7 (C), 157.9 (C), 139.6 (C), 126.7 (CH), 113.9 (CH), 55.3 (CH_3), 53.4 (CH_2), 42.4 (C), 40.9 (CH_2), 38.2 (CH_2), 30.2 (CH_3), 22.1 (CH_2)

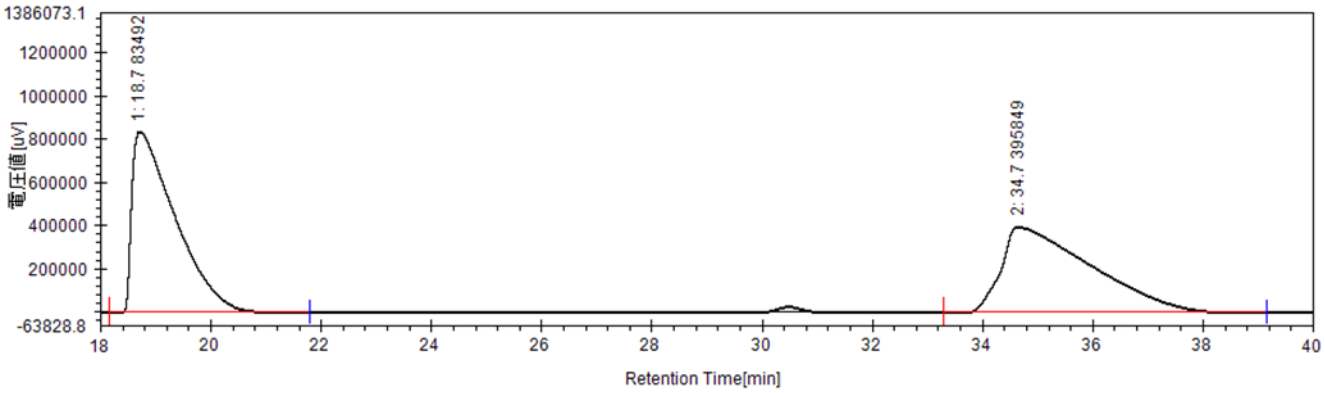
HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}O_2Na$ $[M+Na]^+$: 241.1204, found: 241.1205

$[\alpha]_D^{25}$ = -67.1 (*c* 0.79, $CHCl_3$) for a 99% ee

Chiral HPLC analysis on a CHIRALPAK AS-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 19.9 (major) and 38.4 (minor).

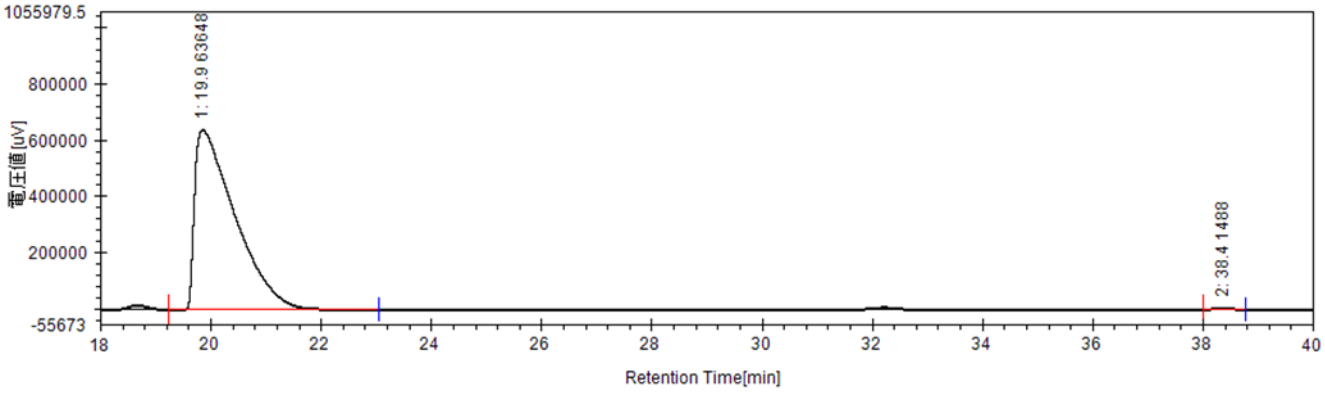
The absolute configuration was determined by comparison of the optical rotation with literature value.[9d, e,12]

Racemic sample:



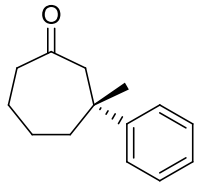
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	18.7	834926	753740.7	50.3	2754.5	3.734	***
2	34.7	395849	744739.4	49.7	2169.1	2.52	7.261

Enantiomeric sample (3u):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	19.9	636481	536814.4	99.869	3583.8	3.535	***
2	38.4	1488	703.8	0.131	33714.5	0.996	17.174

(*R*)-3-methyl-3-phenylcycloheptanone: 3v[9,11c, d]



Synthesized according to General Procedure A from 3-Methyl-2-cyclohepten-1-one **1c** (0.14 mmol, 17.4 mg) and Phenyl boronic acid (0.28 mmol, 34.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3v** (25.1 mg, 89%, 94% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 - 7.17 (m, 5H), 3.21 (d, *J* = 14.2 Hz, 1H), 2.71 (d, *J* = 14.6 Hz, 1H), 2.46 - 2.16 (m, 3H), 1.84 - 1.70 (m, 5H), 1.27 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.9 (C), 148.0 (C), 128.6 (CH), 126.0 (CH), 125.7 (CH), 55.7 (CH_2), 44.3 (CH_2), 43.5 (CH_2), 39.9 (C), 32.0 (CH_3), 25.9 (CH_2), 24.0 (CH_2)

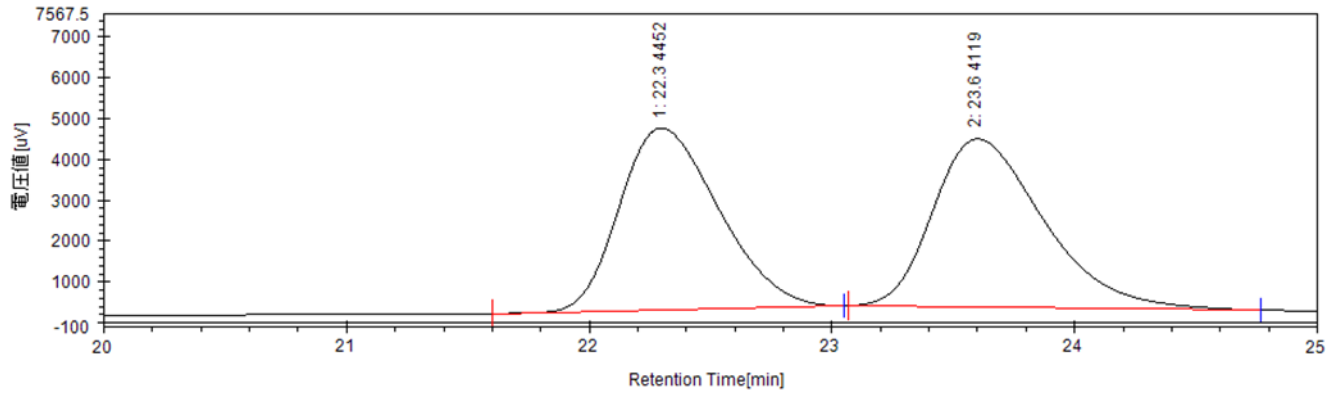
HRMS (ESI-TOF) *m/z* Calculated for $C_{14}H_{18}ONa$ $[M+Na]^+$: 225.1255, found: 225.1258

$[\alpha]_D^{24}$ = -75.1 (*c* 0.51, $CHCl_3$) for a 94% ee

Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 254 nm, retention times (min): 21.7 (major) and 23.5 (minor).

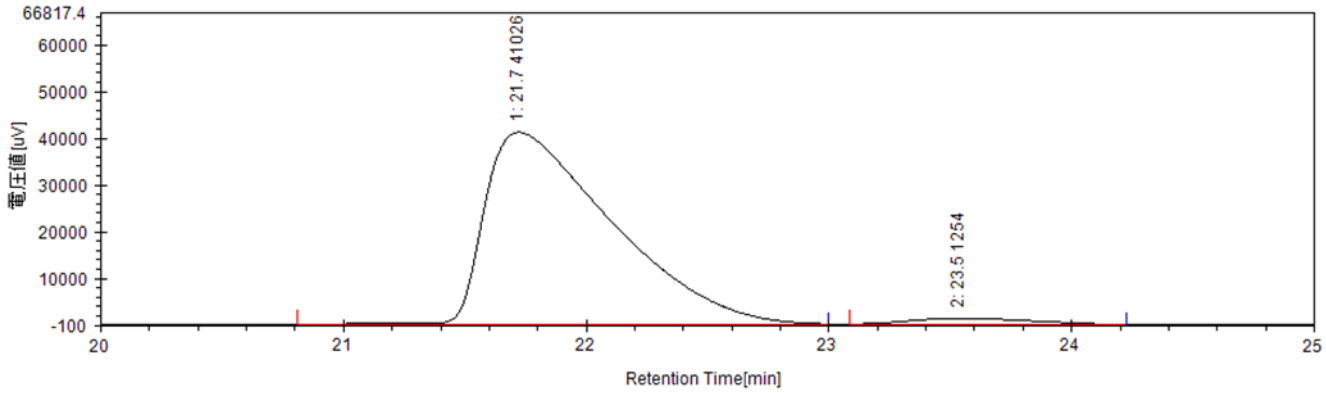
The absolute configuration was determined by comparison of the optical rotation with literature value.[9, 11c, d]

Racemic sample:



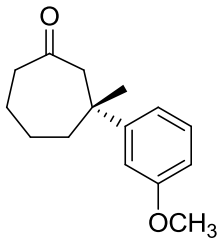
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	22.3	4452	2102.2	49.137	13765.3	1.257	***
2	23.6	4119	2176.1	50.863	13117	1.408	1.645

Enantiomeric sample (3v):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21.7	41026	24862.4	97.224	8138.1	2.317	***
2	23.5	1254	709.8	2.776	9901	1.275	1.908

(*R*)-3-(3-methoxyphenyl)-3-methylcycloheptanone: 3w



Synthesized according to General Procedure A from 3-Methyl-2-cyclohepten-1-one **1c** (0.14 mmol, 17.4 mg) and 3-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3w** (29.9 mg, 92%, 93% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 - 7.22 (m, 1H), 6.92 - 6.86 (m, 2H), 6.75 - 6.73 (m, 1H), 3.80 (s, 3H), 3.17 (d, *J* = 14.2 Hz, 1H), 2.70 (d, *J* = 14.2 Hz, 1H), 2.46 - 2.17 (m, 3H), 1.82 - 1.70 (m, 5H), 1.26 (s, 3H)

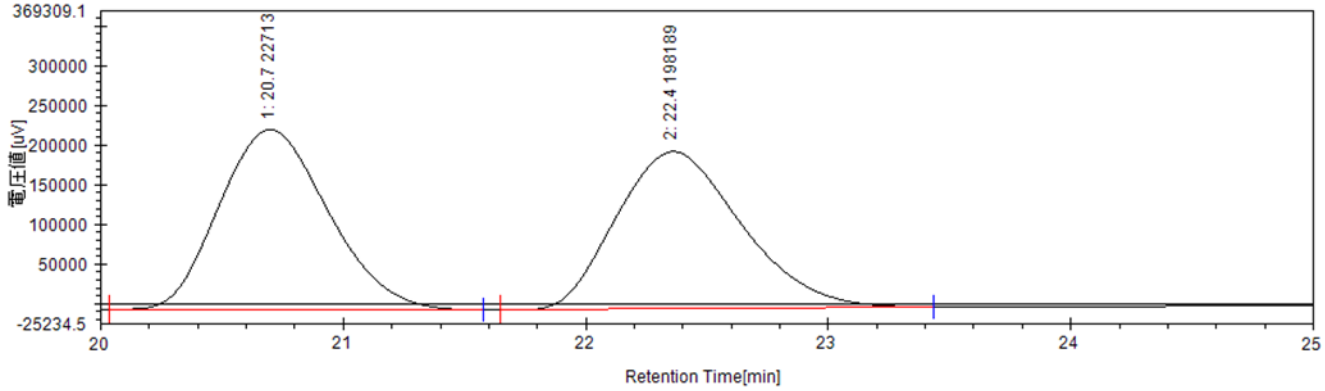
^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.9 (C), 159.8 (C), 149.8 (C), 129.6 (CH), 118.1 (CH), 112.3 (CH), 110.7 (CH), 55.8 (CH_2), 55.3 (CH_3), 44.3 (CH_2), 43.5 (CH_2), 40.0 (C), 32.0 (CH_3), 25.9 (CH_2), 24.0 (CH_2)

HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_2Na$ $[M+Na]^+$: 255.1361, found: 255.1367

$[\alpha]_D^{27}$ = -51.1 (*c* 0.35, $CHCl_3$) for a 93% ee

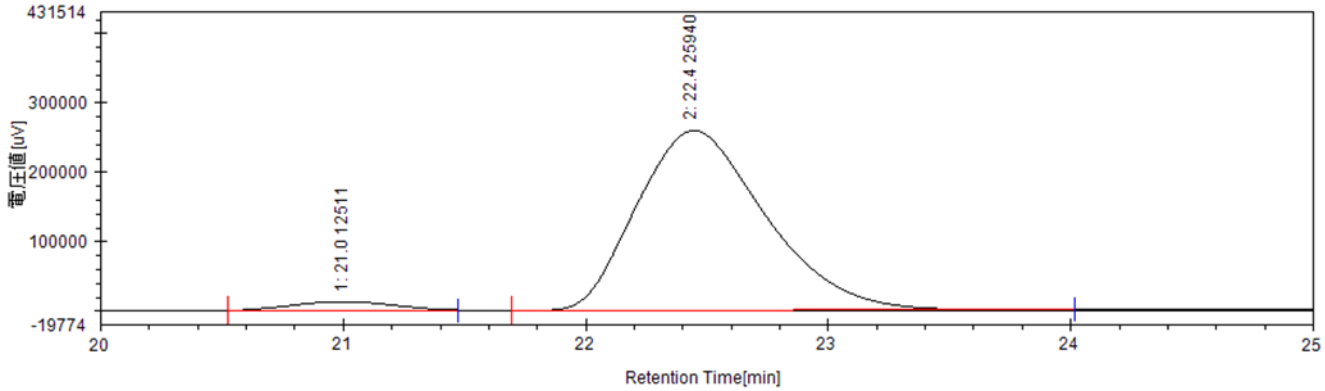
Chiral HPLC analysis on a CHIRALPAK OD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 21 (minor) and 22.4 (major).

Racemic sample:



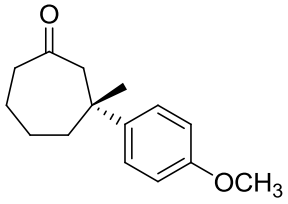
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	20.7	227134	118037.5	49.949	9751	1.165	***
2	22.4	198189	118277.2	50.051	8683.3	1.237	1.849

Enantiomeric sample (3w):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21	12511	5955.2	3.604	11195.1	1.002	***
2	22.4	259408	159270.2	96.396	8395.7	1.304	1.63

(*R*)-3-(4-methoxyphenyl)-3-methylcycloheptanone: 3x



Synthesized according to General Procedure A from 3-Methyl-2-cyclohepten-1-one **1c** (0.14 mmol, 17.4 mg) and 4-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3x** (29.2 mg, 90%, 95% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (d, *J* = 8.69 Hz, 2H), 6.85 (d, *J* = 8.69 Hz, 2H), 3.79 (s, 3H), 3.16 (d, *J* = 14.2 Hz, 1H), 2.70 (d, *J* = 14.2 Hz, 1H), 2.45 - 2.15 (m, 3H), 1.82 - 1.68 (m, 5H), 1.24 (s, 3H)

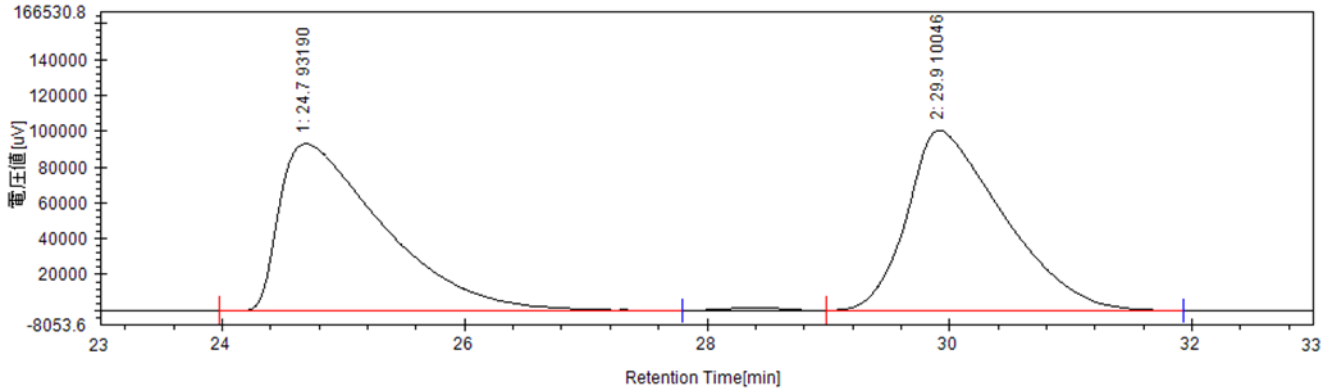
^{13}C NMR (100 MHz, Chloroform-*d*) δ 214.1 (C), 157.7 (C), 140.0 (C), 126.7 (CH), 113.9 (CH), 56.0 (CH_2), 55.3 (CH_3), 44.3 (CH_2), 43.7 (CH_2), 39.4 (C), 32.3 (CH_3), 25.9 (CH_2), 24.0 (CH_2)

HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_2Na$ $[M+Na]^+$: 255.1361, found: 255.1366

$[\alpha]_D^{26}$ = -66.3 (*c* 0.68, $CHCl_3$) for a 95% ee

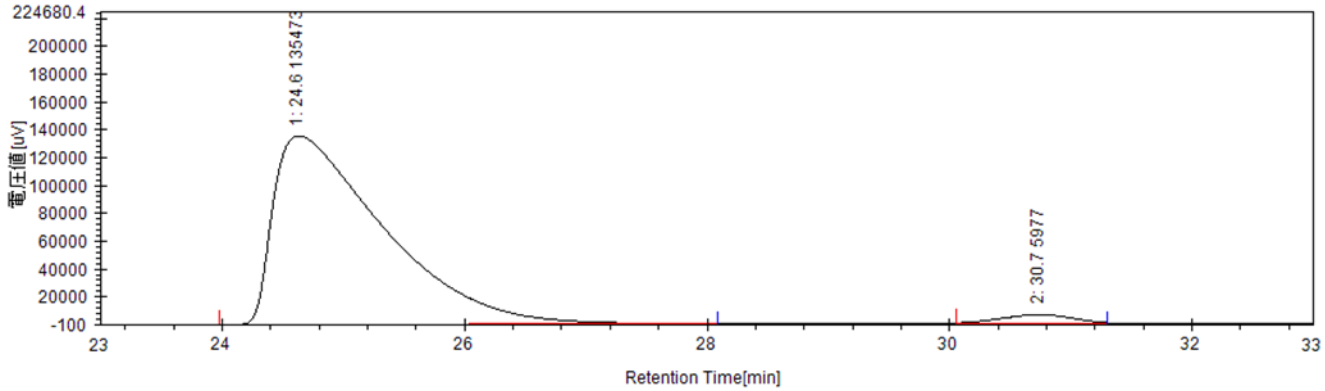
Chiral HPLC analysis on a CHIRALPAK AS-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 24.6 (major) and 30.7 (minor).

Racemic sample:



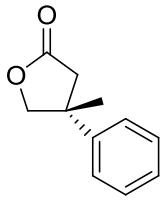
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	24.7	93190	92365.7	49.961	4145.6	2.627	***
2	29.9	100466	92509.8	50.039	7024.6	1.526	3.538

Enantiomeric sample (3x):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	24.6	135473	142799.8	97.39	3653.4	2.984	***
2	30.7	5977	3826.6	2.61	13290.3	0.91	4.542

(*R*)-4-methyl-4-phenyldihydrofuran-2(3H)-one: 3y[13]



Synthesized according to General Procedure A from 4-Methylfuran-2(5H)-one **1d** (0.14 mmol, 13.7 mg) and Phenyl boronic acid (0.28 mmol, 34.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3y** (22.1 mg, 90%, 88% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 - 7.18 (m, 5H), 4.43 (d, *J* = 8.7 Hz, 1H), 4.40 (d, *J* = 9.2 Hz, 1H), 2.92 (d, *J* = 17 Hz, 1H), 2.68 (d, *J* = 16.9 Hz, 1H), 1.53 (s, 3H)

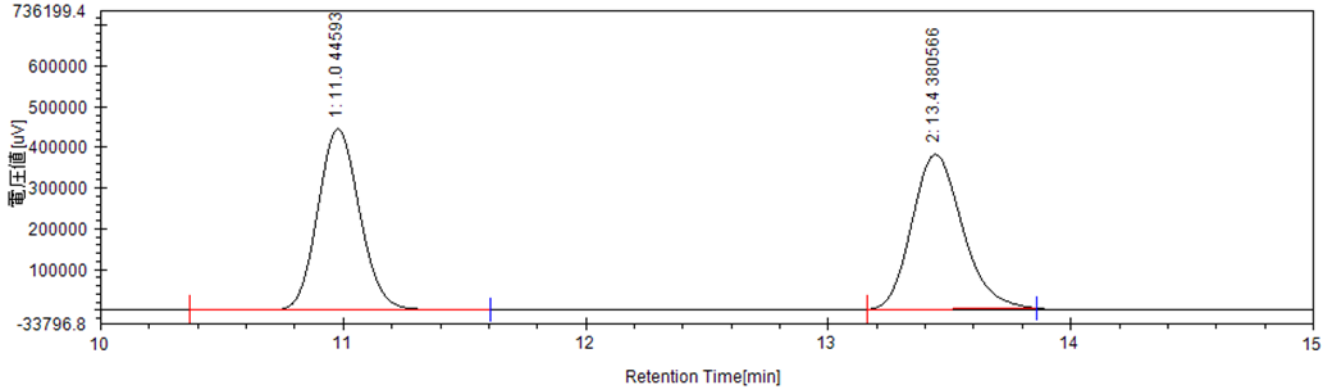
^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.2 (C), 144.4 (C), 129.1 (CH), 127.3 (CH), 125.2 (CH), 78.5 (CH_2), 44.2 (C), 42.1 (CH_2), 28.1 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{11}H_{12}O_2Na$ $[M+Na]^+$: 199.0735, found: 199.0738

$[\alpha]_D^{23}$ = +15.7 (*c* 0.67, $CHCl_3$) for a 88% ee

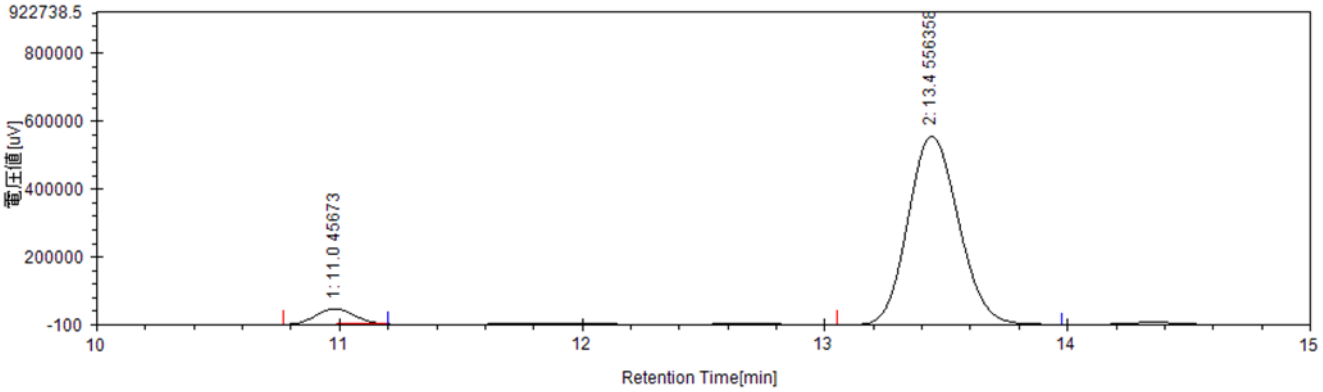
Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 0.7 ml/min, UV detection at 214 nm, retention times (min): 11 (minor) and 13.4 (major).

Racemic sample:



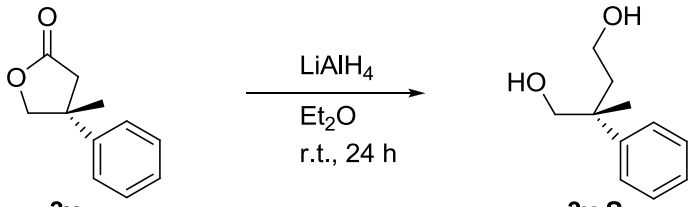
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11	445932	89022.8	49.24	19371.2	1.121	***
2	13.4	380566	91769.3	50.76	20284.8	1.197	7.139

Enantiomeric sample (3y):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	11	45673	8446.6	5.948	21613.1	1.029	***
2	13.4	556358	133567.8	94.052	19710.5	1.113	7.23

The absolute configuration was determined to be *R* by converting it to a known compound **3y-S (Scheme S1)**.[13]



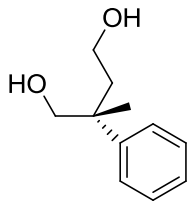
3y $[\alpha]_D^{23}$ = +15 68 (c 0.67, $CHCl_3$)

3y-S $[\alpha]_D^{23}$ = +5.04 (c 0.105, $CHCl_3$)

lit. $[\alpha]_D^{20}$ = +5.0 (c 0.9, $CHCl_3$) for *R* isomer with 98% ee

Scheme S1 Reduction of **3y** to **3y-S**.

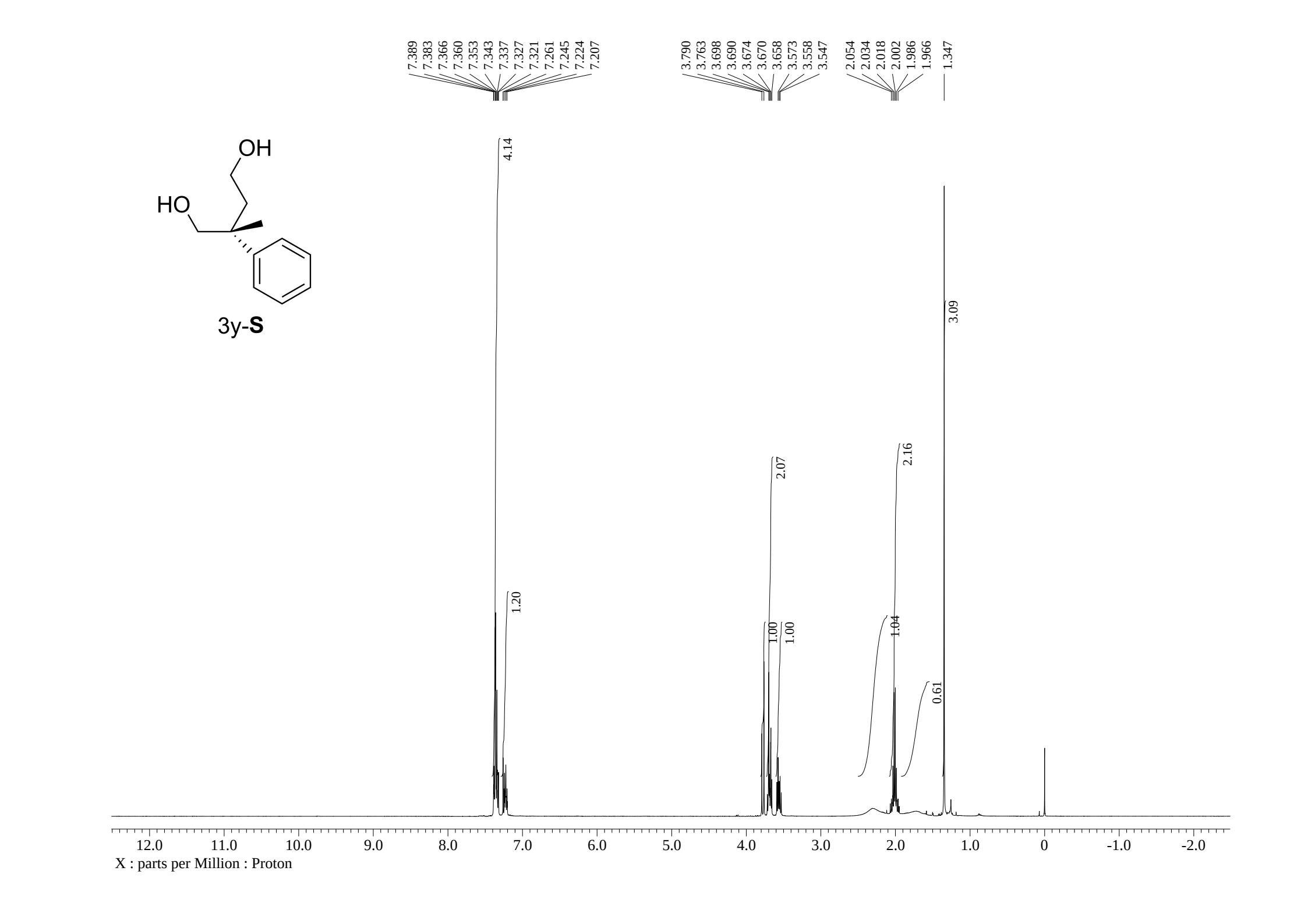
(*R*)-2-methyl-2-phenylbutane-1,4-diol: 3y-S[13e]



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 - 7.31 (m, 4H), 7.26 - 7.20 (m, 1H), 3.79 - 3.76 (m, 1H), 3.71 - 3.66 (m, 2H), 3.62 - 3.54 (m, 1H), 2.16 (br s, 1H), 2.05 - 1.98 (m, 2H), 1.63 (br s, 1H), 1.35 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.3 (C), 128.6 (CH), 126.4 (CH), 71.3 (CH_2), 59.4 (CH_2), 42.5 (C), 41.7 (CH_2), 23.4 (CH_3)

$[\alpha]_D^{23}$ = +5.04 (*c* 0.105, $CHCl_3$) (Lit.[13] $[\alpha]_D^{20}$ = +5.0 (*c* 0.9, $CHCl_3$) for a 98% ee: *R* isomer)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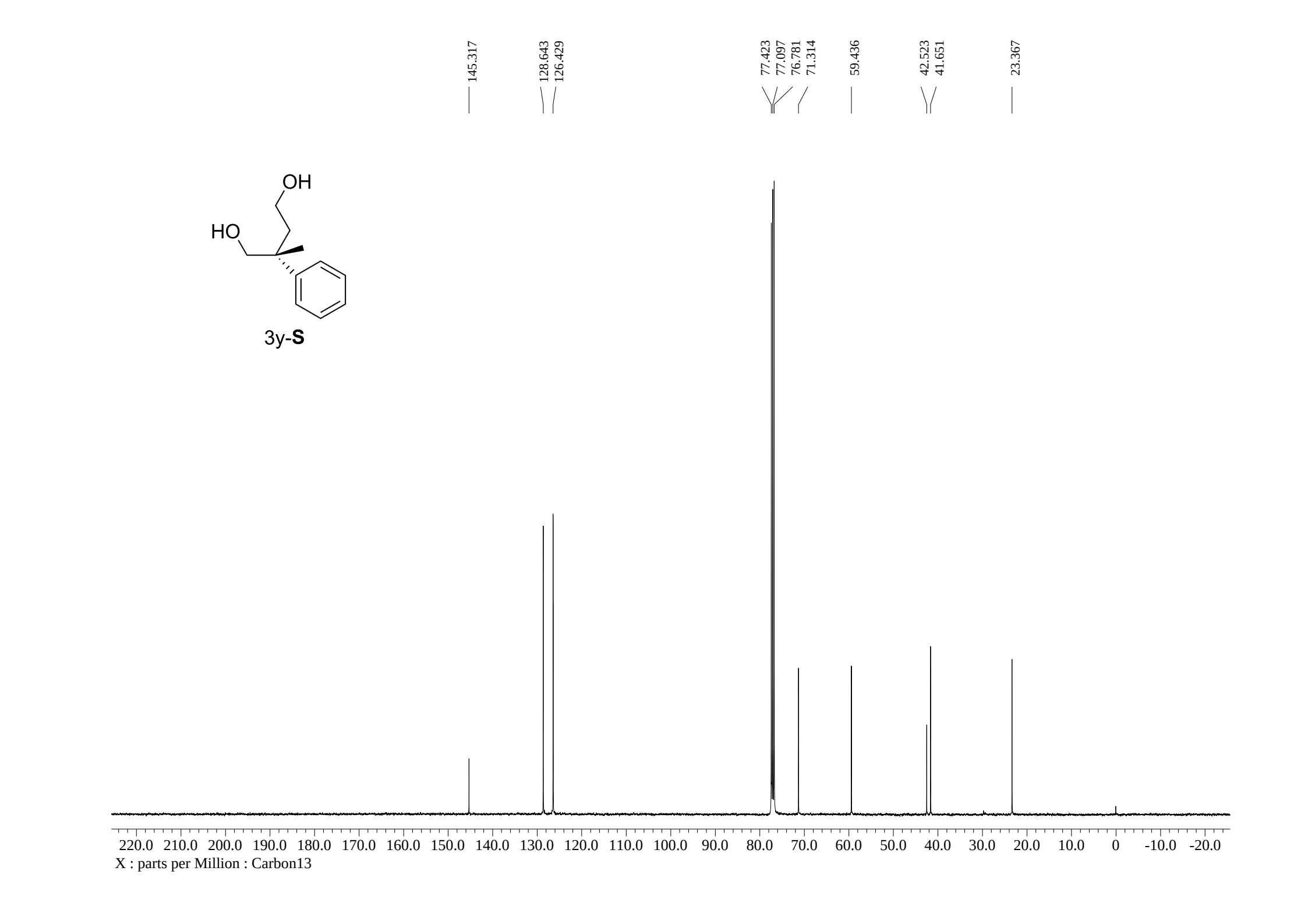
7.383
7.366
7.360
7.353
7.343
7.337
7.327
7.321
7.261
7.245
7.224
7.207
3.790
3.763
3.698
3.690
3.674
3.670
3.658
3.573
3.558
3.547
2.054
2.034
2.018
2.002
1.986
1.966
1.347
OH
HO
3y-S
4.14
1.20
1.00
2.07
1.00
1.04
2.16
0.61
3.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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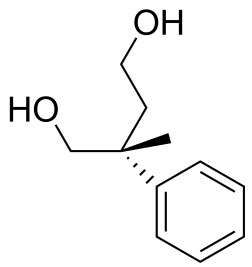
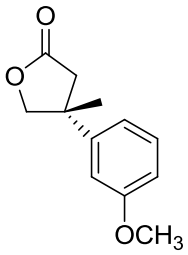
126.429
77.423
77.097
76.781
71.314
59.436
42.523
41.651
23.367
OH
HO
3y-S
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



3y-**S**

X : parts per Million : Carbon13

(*R*)-4-(3-methoxyphenyl)-4-methyldihydrofuran-2(3H)-one: 3z



Synthesized according to General Procedure A from 4-Methylfuran-2(5H)-one **1d** (0.14 mmol, 13.7 mg) and 3-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3z** (18.2 mg, 63%, 95% ee) as a colorless solid.

m.p. = 65 - 66 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 - 7.28 (m, 1H), 6.84 - 6.71 (m, 3H), 4.41 (d, *J* = 8.7 Hz, 1H), 4.38 (d, *J* = 8.7 Hz, 1H), 3.82 (s, 3H), 2.91 (d, *J* = 16.9 Hz, 1H), 2.65 (d, *J* = 16.5 Hz, 1H), 1.51 (s, 3H)

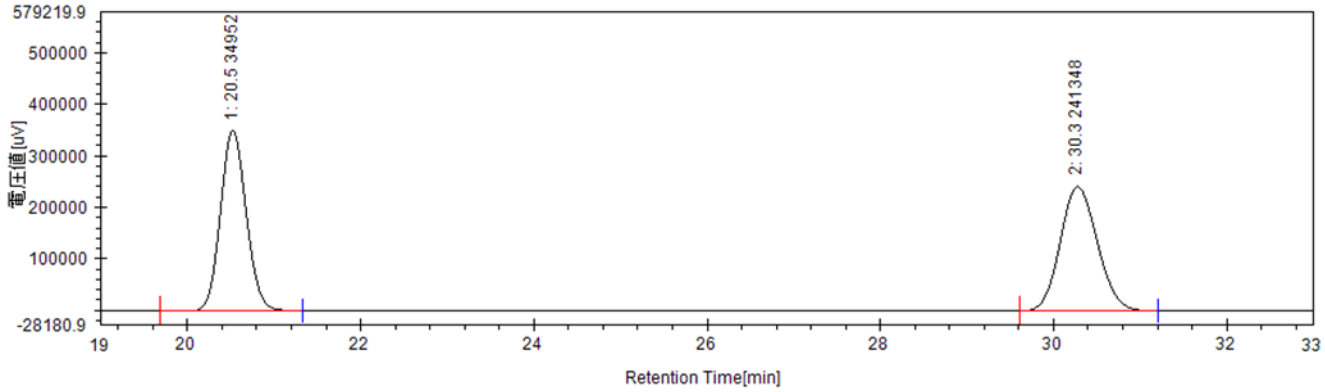
^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.2 (C), 160.1 (C), 146.0 (C), 130.2 (CH), 117.5 (CH), 112.1 (CH), 111.8 (CH), 78.4 (CH_2), 55.4 (CH_3), 44.2 (C), 42.1 (CH_2), 28.1 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{14}O_3Na$ $[M+Na]^+$: 229.0841, found: 229.0845

$[\alpha]_D^{24}$ = +13.7 (*c* 0.29, $CHCl_3$) for a 95% ee

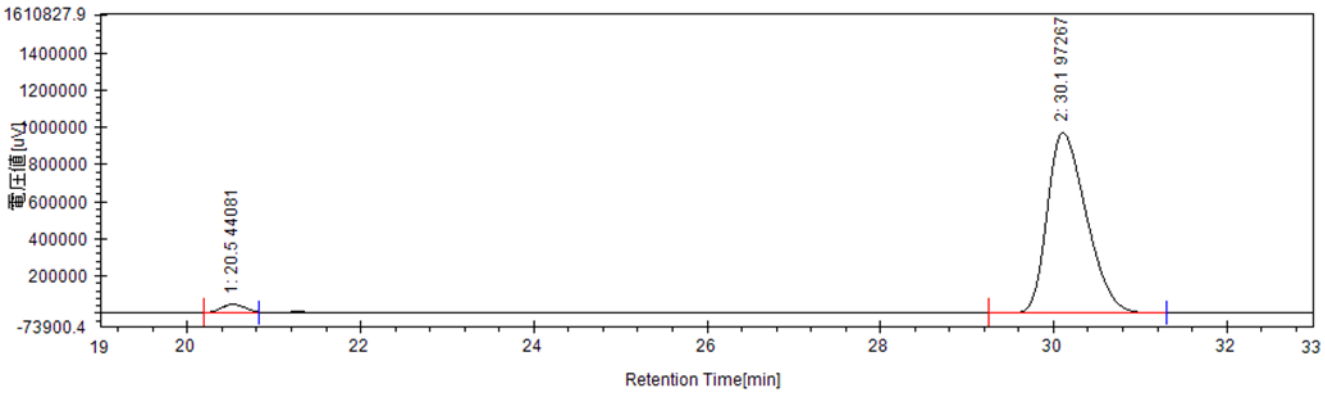
Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 0.5 ml/min, UV detection at 223 nm, retention times (min): 11 (minor) and 13.4 (major).

Racemic sample:



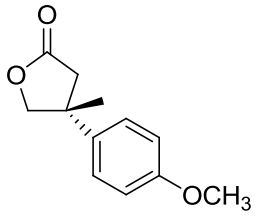
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	20.5	349522	119847.3	49.929	22808.3	1.092	***
2	30.3	241348	120189.9	50.071	23365.6	1.121	14.636

Enantiomeric sample (3z):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	20.5	44081	13553.3	2.6	26110.1	0.98	***
2	30.1	972676	507677	97.4	20970.4	1.351	14.344

(*R*)-4-(4-methoxyphenyl)-4-methyldihydrofuran-2(3H)-one: 3aa[14]



Synthesized according to General Procedure A from 4-Methylfuran-2(5H)-one **1d** (0.14 mmol, 13.7 mg) and 4-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3aa** (25.7 mg, 89%, 90% ee) as a colorless solid.

m.p. = 66 - 67 °C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.39 (d, *J* = 8.7 Hz, 1H), 4.36 (d, *J* = 8.7 Hz, 1H), 3.81 (s, 3H), 2.88 (d, *J* = 16.9 Hz, 1H), 2.64 (d, *J* = 16.4 Hz, 1H), 1.50 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.4 (C), 158.7 (C), 136.4 (C), 126.3 (CH), 114.4 (CH), 78.8 (CH_2), 55.4 (CH_3), 43.6 (C), 42.4 (CH_2), 28.0 (CH_3)

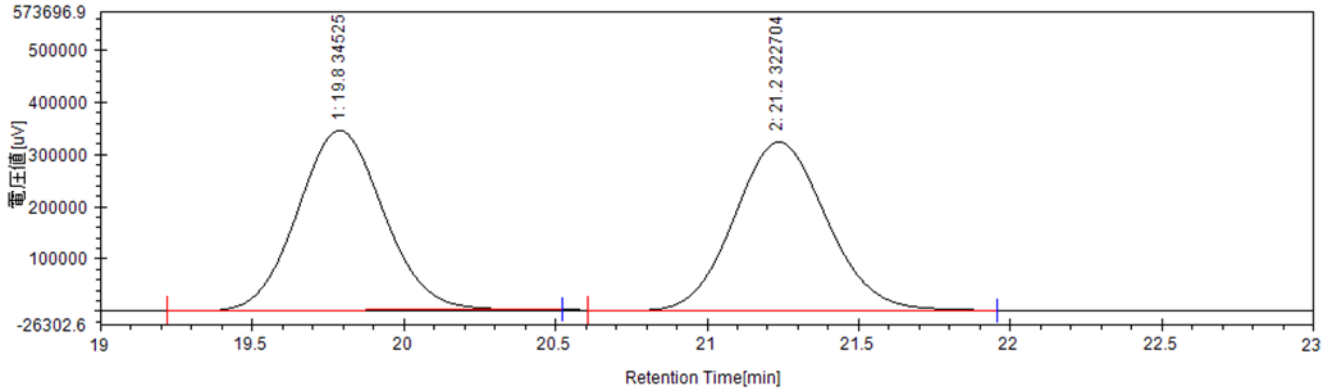
HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{14}O_3Na$ $[M+Na]^+$: 229.0841, found: 229.0846

$[\alpha]_D^{25}$ = +9.97 (*c* 0.48, $CHCl_3$) for a 90% ee

Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 9: 1, 40 °C, flow = 0.5 ml/min, UV detection at 225 nm, retention times (min): 19.9 (minor) and 21.4 (major).

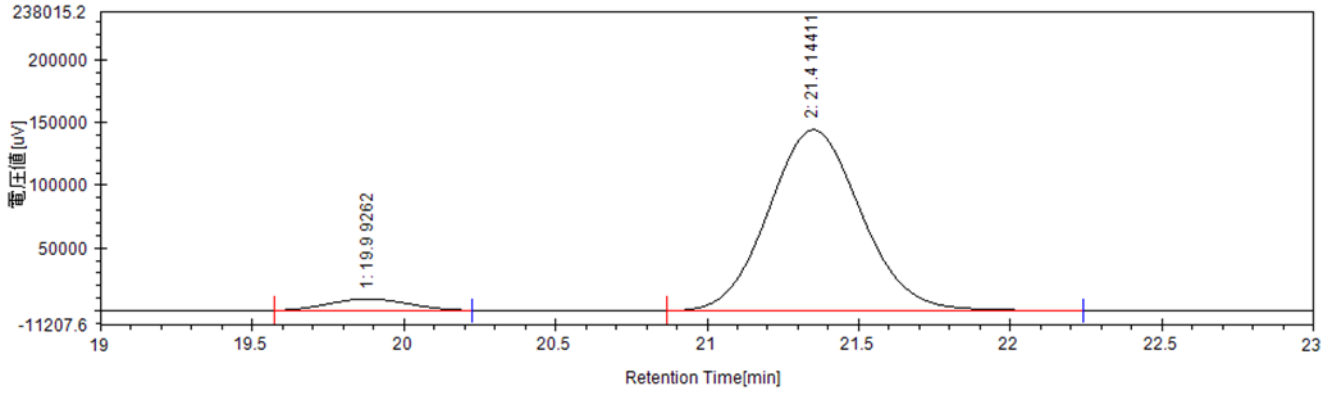
The absolute configuration was determined by comparison of the optical rotation with literature value.[14]

Racemic sample:



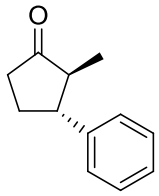
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	19.8	345259	113931	50.074	23147.6	1.058	***
2	21.2	322704	113596	49.926	23278.5	1.1	2.684

Enantiomeric sample (3aa):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	19.9	9262	2830.3	5.236	25216.2	1.041	***
2	21.4	144113	51224.8	94.764	23368.5	1.085	2.776

(2*S*,3*R*)-2-methyl-3-phenylcyclopentanone: 3ab[15]



Synthesized according to General Procedure A from 2-Methyl-2-cyclopenten-1-one **1e** (0.14 mmol, 13.7 mg) and Phenyl boronic acid (0.28 mmol, 34.2 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20: 1) to yield **3ab** as mixture of *trans* and *cis* isomer (19.0 mg, 78%, 18% ee as *trans* isomer) as a colorless oil.

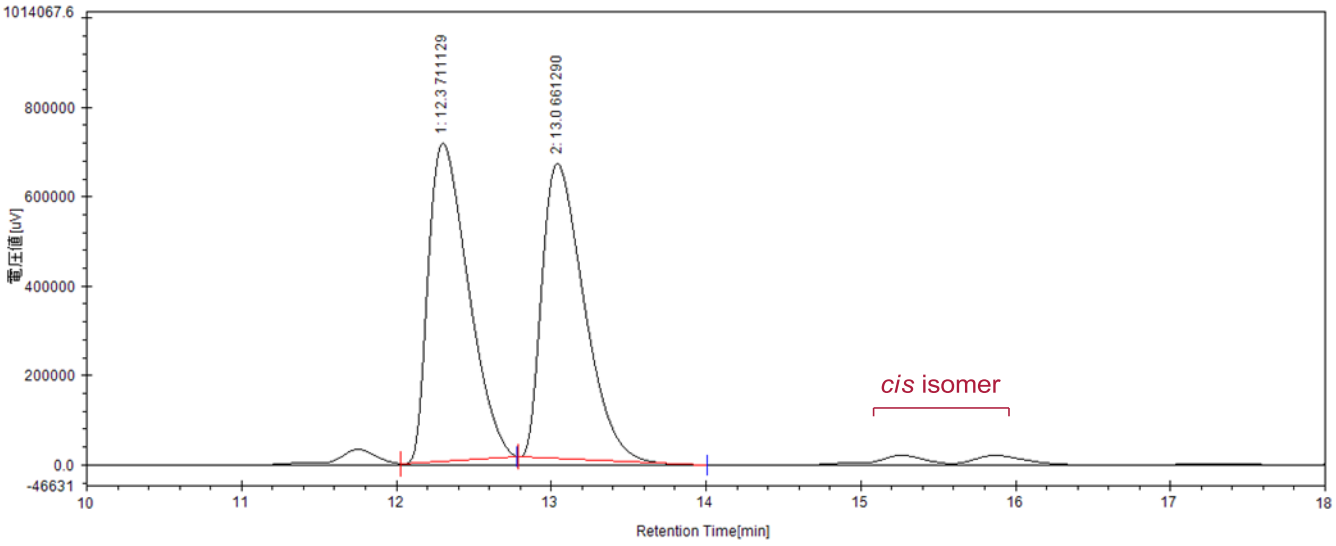
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 - 7.25 (m, 5H), 2.85 - 2.77 (m, 1H), 2.60 - 2.51 (m, 1H), 2.36 - 2.20 (m, 3H), 2.01- 1.89 (m, 1H), 1.04 (d, *J* = 6.86 Hz, 3H: *trans isomer*), 0.79 (d, *J* = 7.32 Hz, 3H: *cis isomer*)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 219.7 (C), 142.4 (C), 128.8 (CH), 127.2 (CH), 127.0 (CH), 51.5 (CH), 51.1 (CH), 37.8 (CH_2), 29.7 (CH_2), 12.3 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{12}H_{14}ONa$ $[M+Na]^+$: 197.0942, found: 197.0947

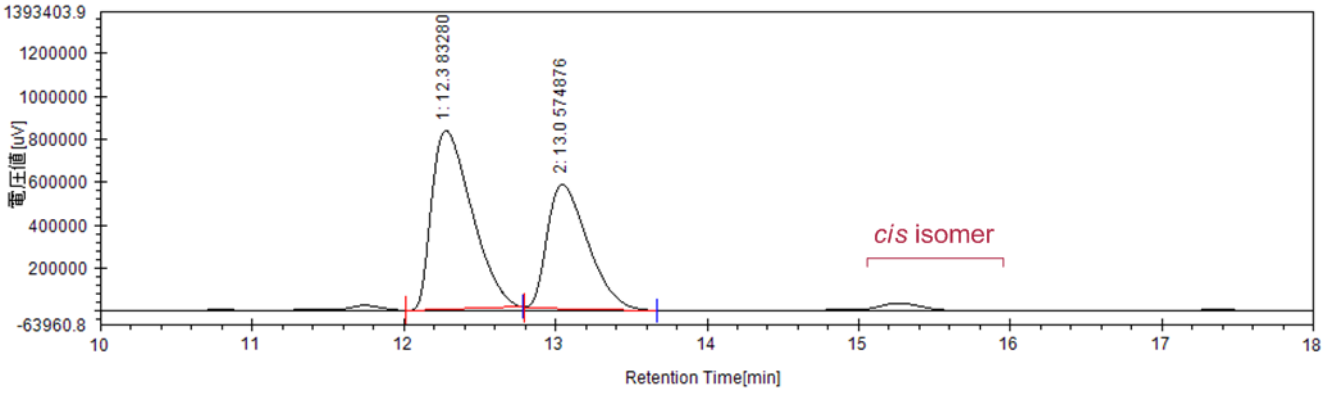
Chiral HPLC analysis on a CHIRALPAK OJ-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 210 nm, retention times (min): 12.3 (major of *trans* isomer) and 13 (minor of *trans* isomer)

Racemic sample:



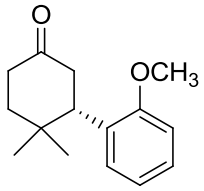
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	12.3	711129	212061.7	50.512	10330.5	1.592	***
2	13	661290	207764.1	49.488	10849.2	1.602	1.51

Enantiomeric sample (3ab):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	12.3	832528	255348	58.923	9756.4	1.676	***
2	13	574845	178011.1	41.077	11035.3	1.585	1.547

(*S*)-3-(2-methoxyphenyl)-4,4-dimethylcyclohexanone: 3ac



Synthesized according to General Procedure A from 4,4-Dimethyl-2-cyclohexen-1-one **1f** (0.14 mmol, 17.4 mg) and 2-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 20 : 1) to yield **3ac** (27.9 mg, 86%, 94% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 - 7.19 (m, 1H), 7.10 - 7.08 (m, 1H), 6.94 - 6.86 (m, 2H), 3.78 (s, 3H), 2.83 - 2.27 (m, 4H), 1.82 - 1.79 (m, 2H), 1.03 (s, 3H), 0.87 (s, 3H)

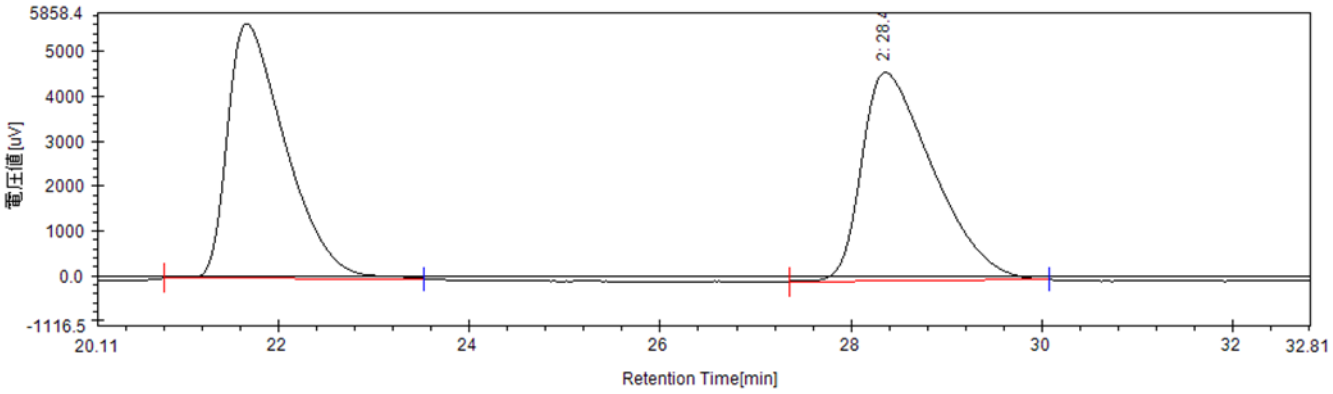
^{13}C NMR (100 MHz, Chloroform-*d*) δ 212.1 (C), 157.3 (C), 129.9 (C), 128.3 (CH), 127.6 (CH), 120.1 (CH), 110.6 (CH), 55.3 (CH_3), 43.8 (CH_2), 42.0 (C), 40.6 (CH_2), 38.5 (CH_2), 34.5 (C), 28.5 (CH_3), 20.0 (CH_3)

HRMS (ESI-TOF) *m/z* Calculated for $C_{15}H_{20}O_2Na$ $[M+Na]^+$: 255.1361, found: 255.1364

$[\alpha]_D^{24}$ = -98.9 (*c* 0.31, $CHCl_3$) for a 94% ee

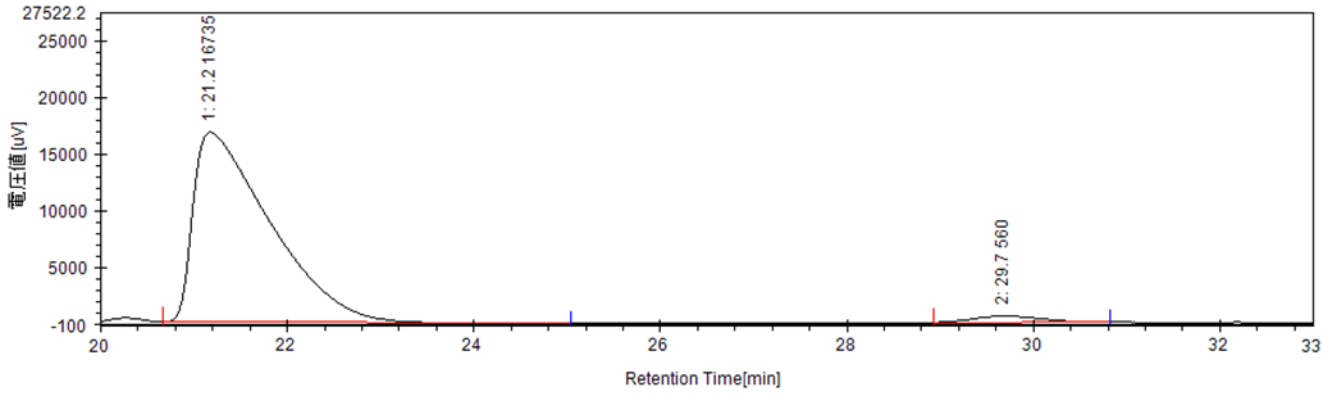
Chiral HPLC analysis on a CHIRALPAK AS-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 1.0 ml/min, UV detection at 254 nm, retention times (min): 21.2 (major) and 29.7 (minor).

Racemic sample:



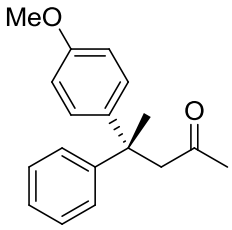
Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21.7	5678	3989.9	49.873	6198.8	1.761	***
2	28.4	4638	4010.2	50.127	6856.6	1.681	5.431

Enantiomeric sample (3ac):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	21.2	16735	15931	97.16	3176.2	2.803	***
2	29.7	560	465.6	2.84	7802.6	1.198	5.993

(*R*)-4-(4-methoxyphenyl)-4-phenylpentan-2-one: 5[17]



Synthesized according to General Procedure A from (*E*)-4-Phenylpent-3-en-2-one **4** (0.14 mmol, 22.4 mg) and 4-Methoxyphenyl boronic acid (0.28 mmol, 42.6 mg). The crude product was purified by flash chromatography (Hexane: AcOEt = 30: 1) to yield **5** (5.2 mg, 14%, 40% ee) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 - 7.25 (m, 3H), 7.20 - 7.17 (m, 2H), 7.12 - 7.08 (m, 2H), 6.83 - 6.79 (m, 2H), 3.79 (s, 3H), 3.20 (q, *J* = 0, 14.2 Hz), 1.77 (s, 3H), 1.69 (s, 3H)

^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.3 (C), 157.8 (C), 149.0 (C), 140.7 (C), 128.4 (CH), 128.2 (CH), 127.0 (CH), 126.1 (CH), 113.5 (CH), 55.3 (CH_3), 54.8 (CH_2), 45.1 (C) 32.2 (CH_3), 28.0 (CH_3)

*The NMR data match with those reported in literature.[17]

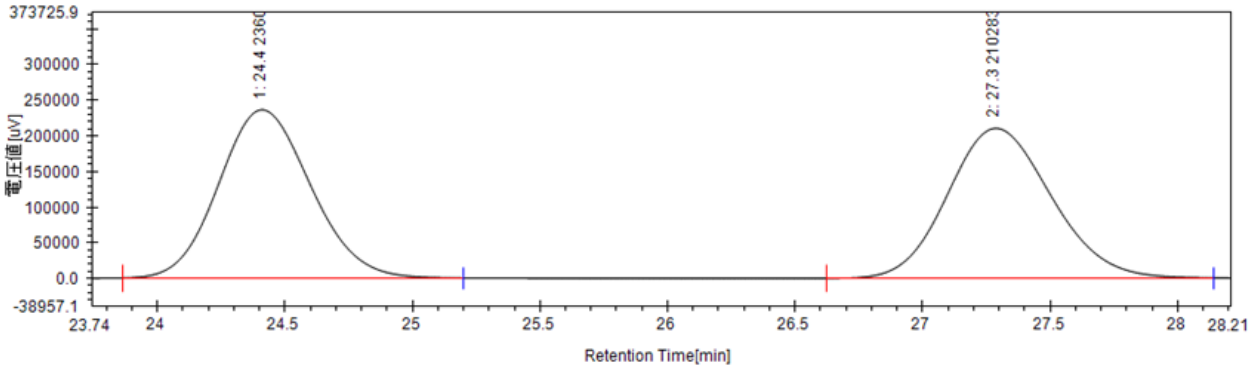
HRMS (ESI-TOF) *m/z* Calculated for $C_{18}H_{20}O_2Na$ $[M+Na]^+$: 291.1361, found: 291.1366

$[\alpha]_D^{22}$ = +6.8 (*c* 0.21, $CHCl_3$) for a 40% ee, (Lit.[17] $[\alpha]_D^{20}$ = +13 (*c* 0.29, $CHCl_3$) for a 96% ee: *S* isomer)

Chiral HPLC analysis on a CHIRALPAK AD-H column, Hexane: ^{i}PrOH = 99: 1, 40 °C, flow = 0.5 ml/min, UV detection at 220 nm, retention times (min): 24.5 (major) and 27.4 (minor).

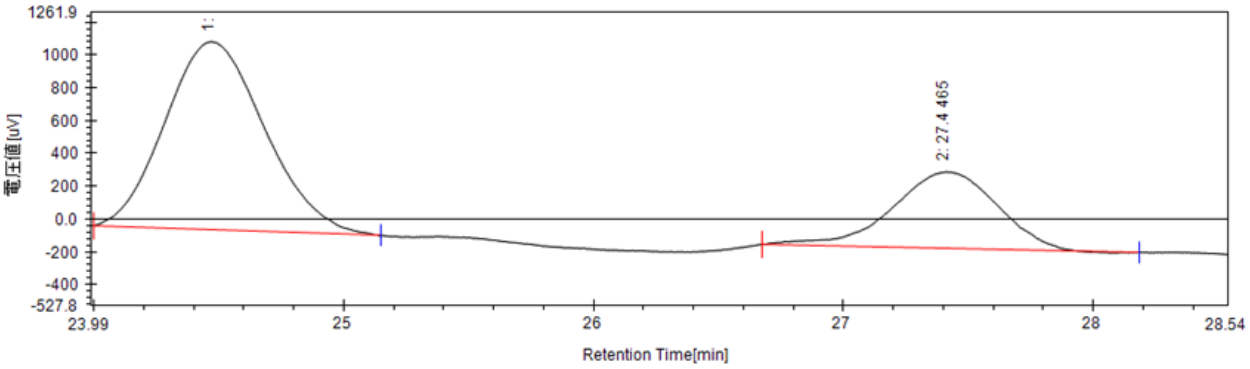
The absolute configuration was determined by comparison of the optical rotation with literature value.[17]

Racemic sample:



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	24.4	236014	98786.7	49.921	21604.6	1.113	***
2	27.3	210283	99100.3	50.079	21314	1.13	4.084

Enantiomeric sample (5):



Peak	Rt[min]	Height [uV]	Area [uV*min]	Area %	NTP	Symmetry factor	Resolution
1	24.5	1146	528.8	70.147	17586.6	1.144	***
2	27.4	465	225	29.853	20735.9	0.869	3.934

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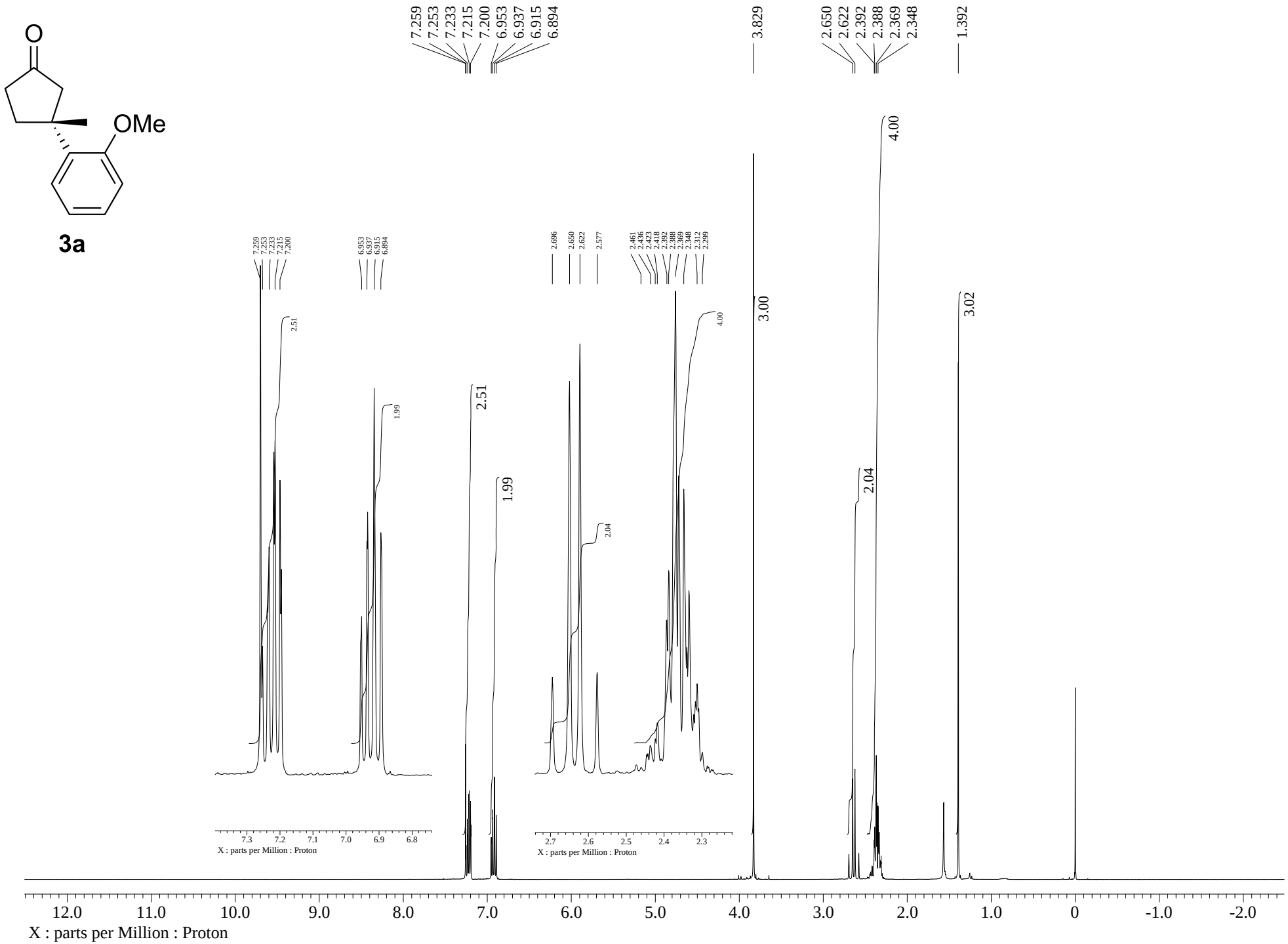
IV. ^{1}H NMR and ^{13}C NMR Spectra


O
OMe
3a
7.259
7.253
7.233
7.215
7.200
6.953
6.937
6.915
6.894
3.829
2.650
2.622
2.392
2.388
2.369
2.348
1.392
4.00
3.00
3.02
2.51
1.99
2.04
2.696
2.650
2.622
2.577
2.461
2.436
2.423
2.418
2.392
2.388
2.369
2.348
2.312
2.299
X : parts per Million : Proton
12.0
11.0
10.0
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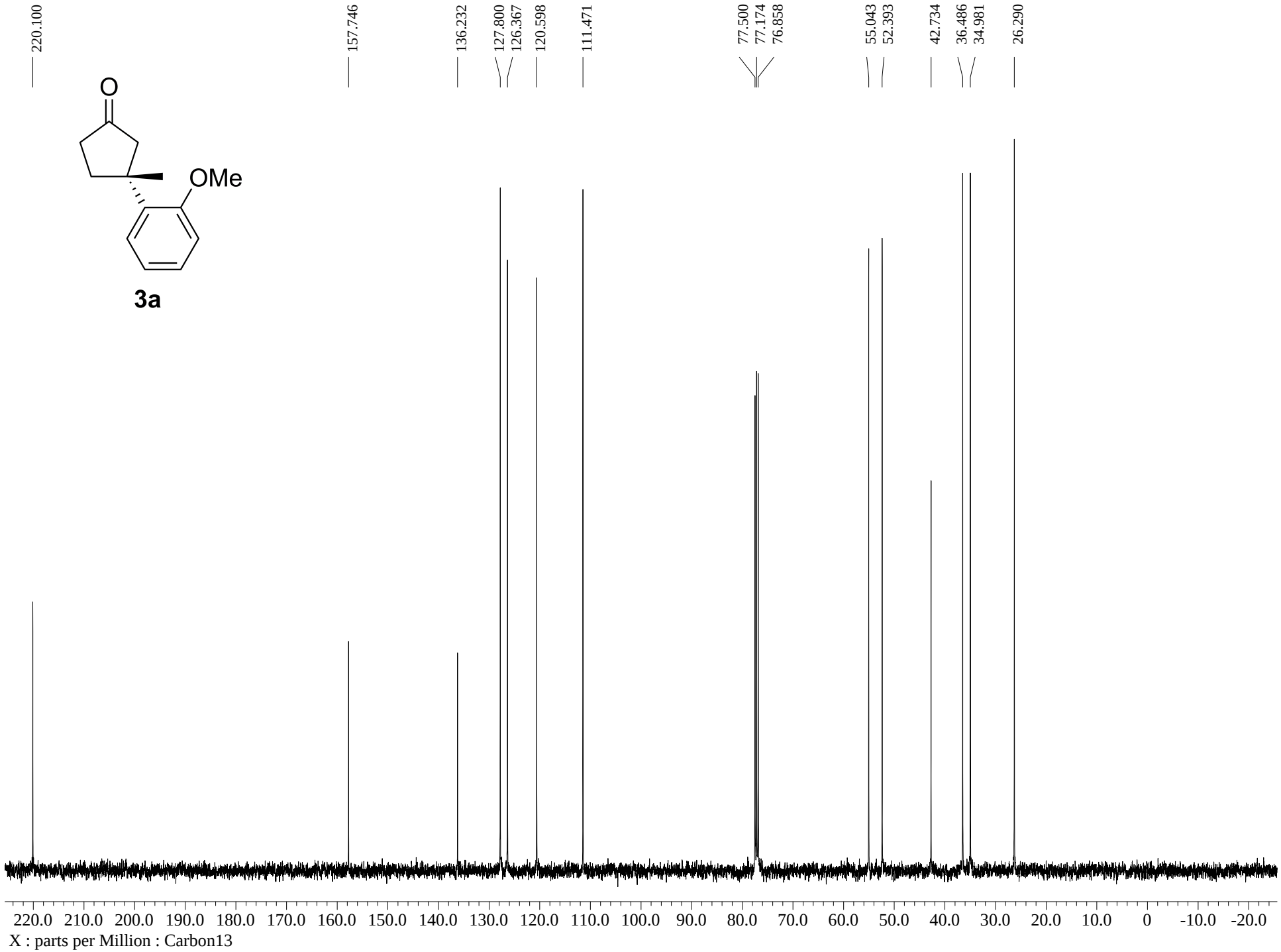
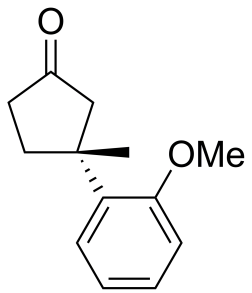
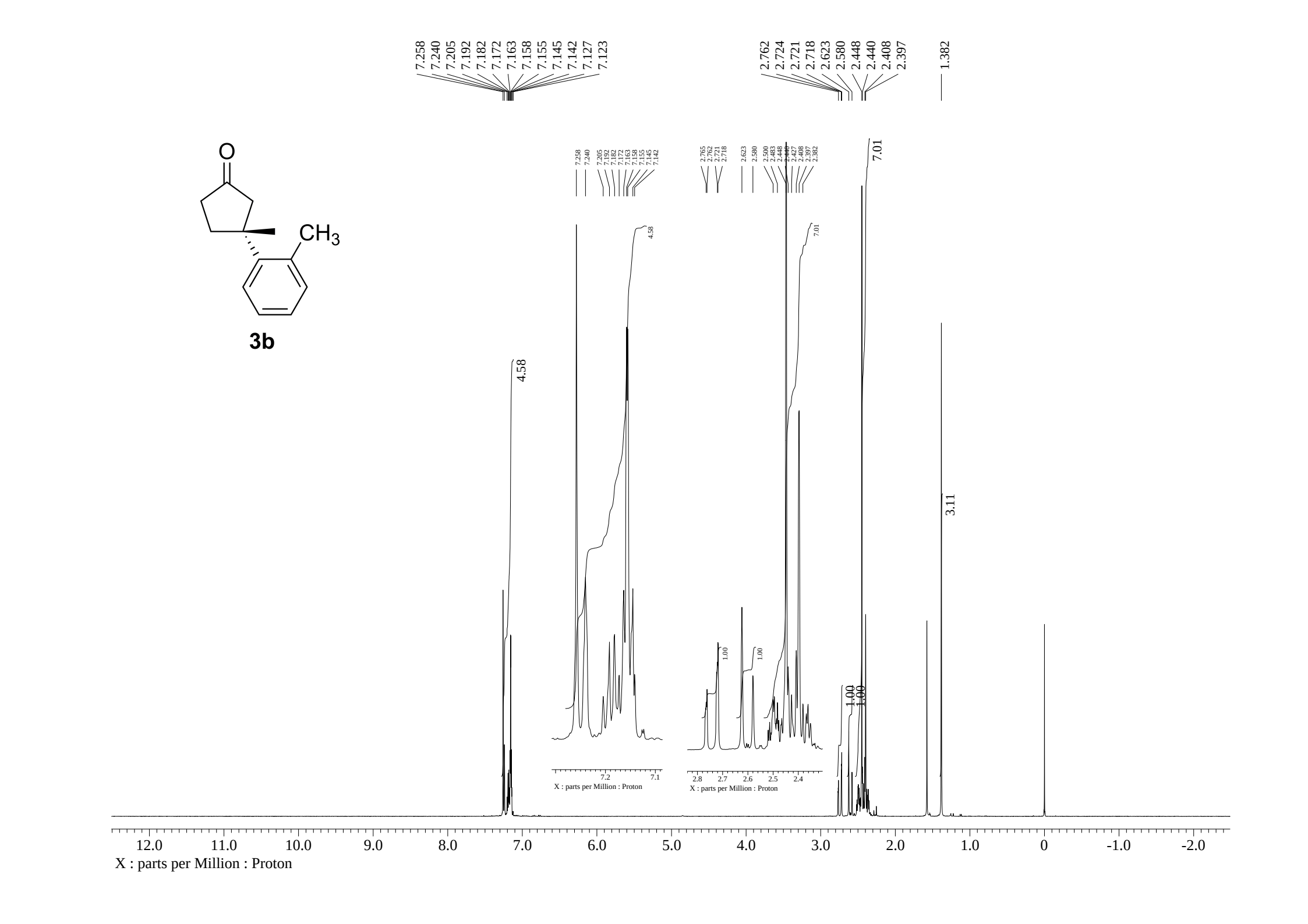
3.0
2.0
1.0
0
-1.0
-2.0

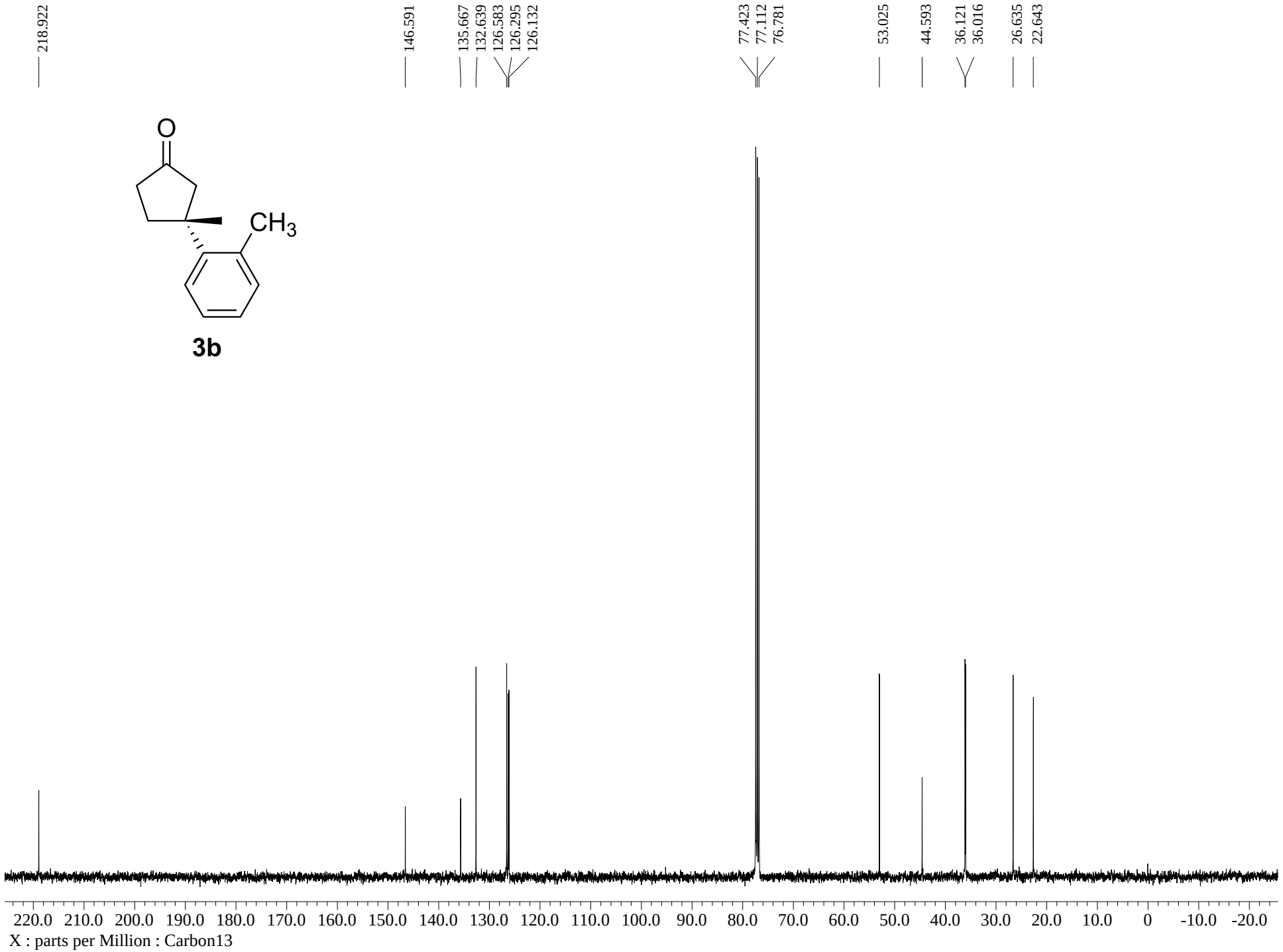

220.100
157.746
136.232
127.800
126.367
120.598
111.471
77.500
77.174
76.858
55.043
52.393
42.734
36.486
34.981
26.290
O
OMe
3a
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

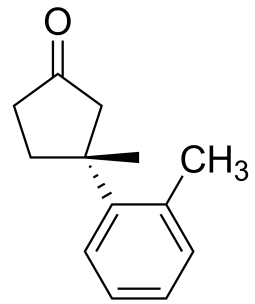


3a

X : parts per Million : Carbon13

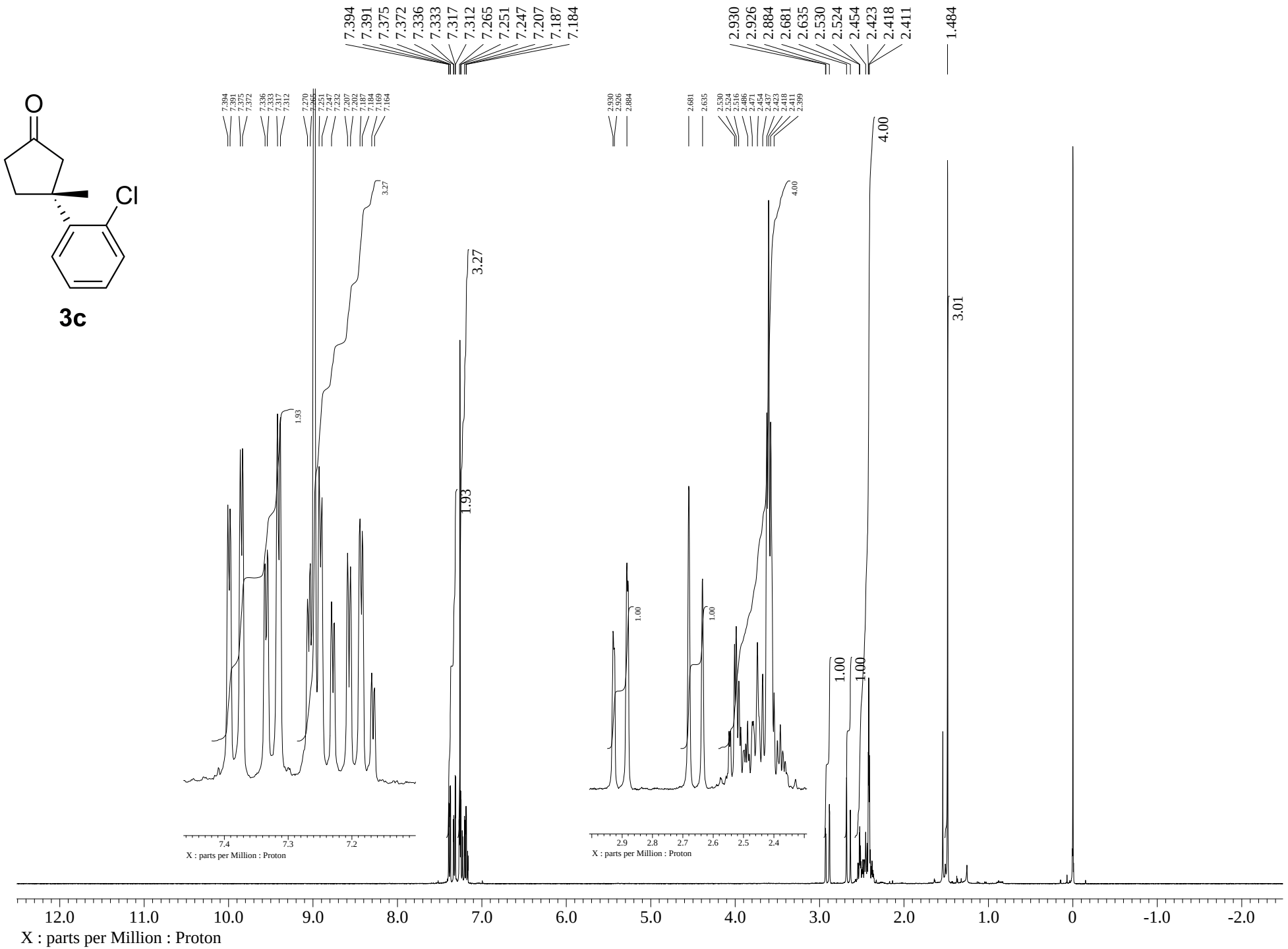

7.258
7.240
7.205
7.192
7.182
7.172
7.163
7.158
7.155
7.145
7.142
7.127
7.123
2.762
2.724
2.721
2.718
2.623
2.580
2.448
2.440
2.408
2.397
1.382
O
CH3
3b
4.58
7.01
3.11
1.00
1.00
1.00
1.00
7.2
7.1
2.8
2.7
2.6
2.5
2.4
X : parts per Million : Proton
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

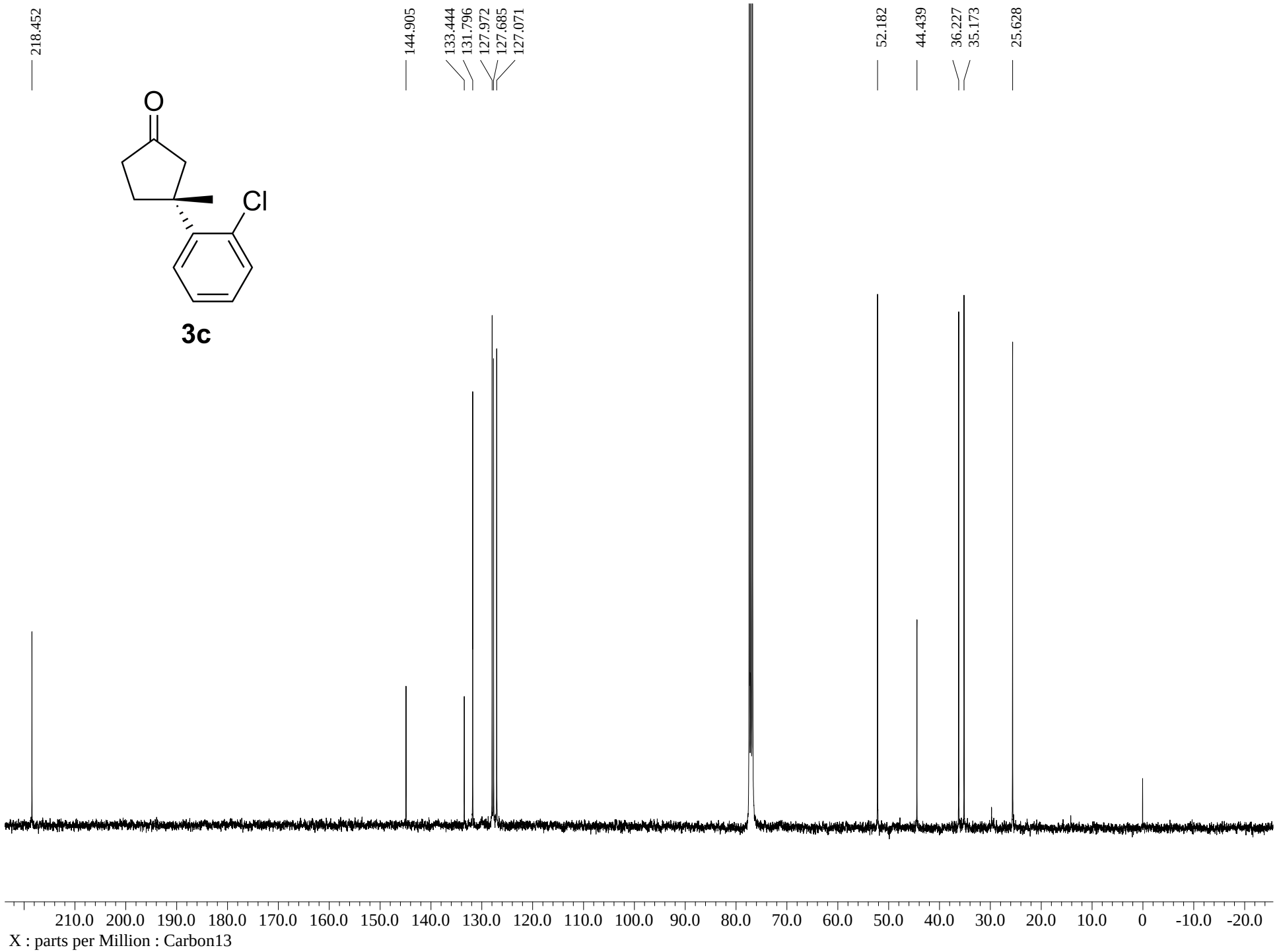

218.922
146.591
135.667
132.639
126.583
126.295
126.132
77.423
77.112
76.781
53.025
44.593
36.121
36.016
26.635
22.643
O
CH3
3b
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

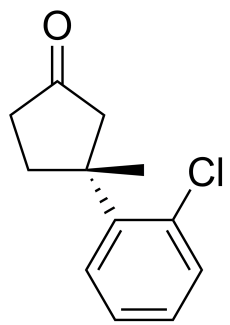


3b

X : parts per Million : Carbon13

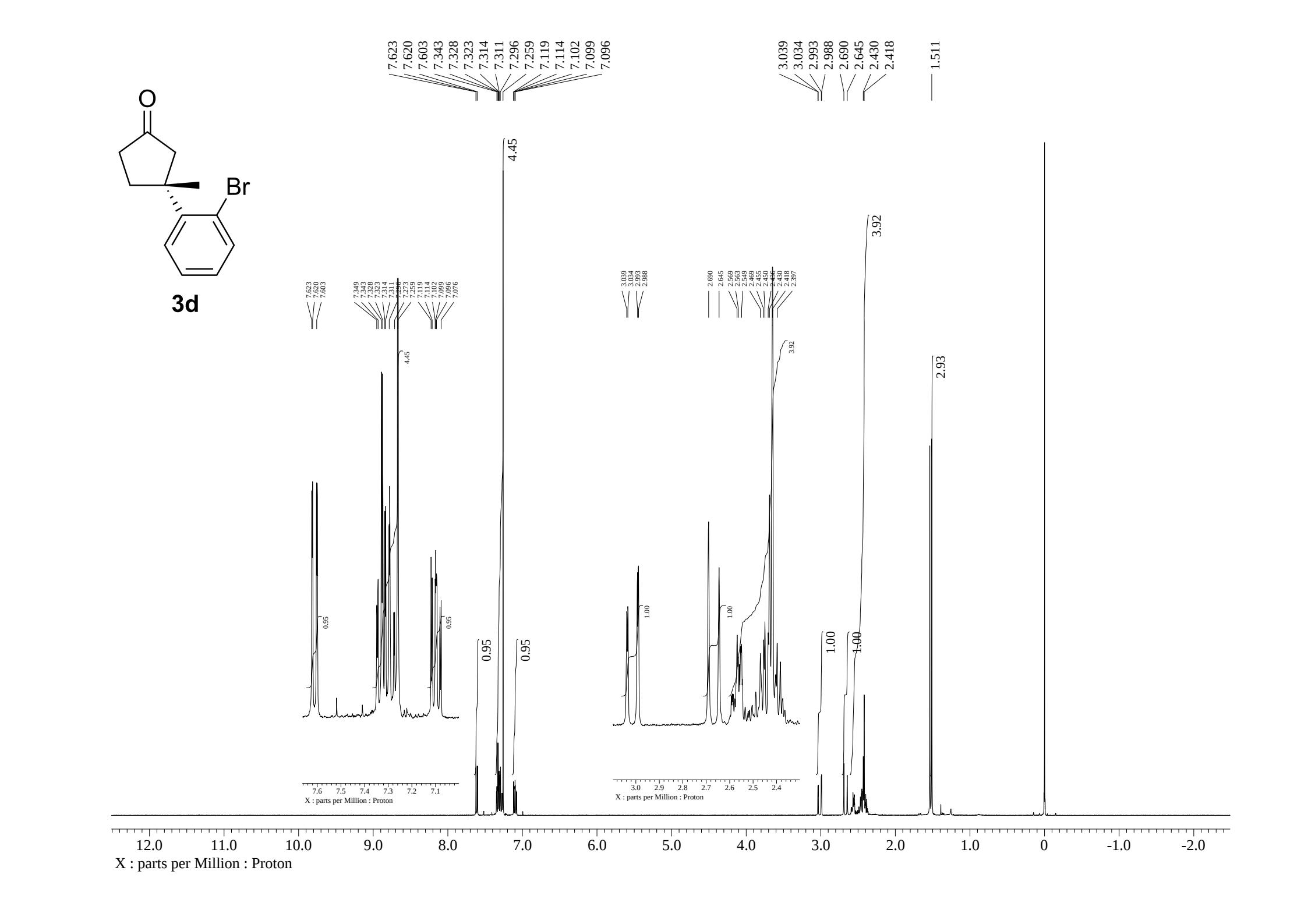

7.394
7.391
7.375
7.372
7.336
7.333
7.317
7.312
7.265
7.251
7.247
7.207
7.187
7.184
2.930
2.926
2.884
2.681
2.635
2.530
2.524
2.454
2.423
2.418
2.411
1.484
O
Cl
3c
3.27
1.93
4.00
3.01
1.00
1.00
1.00
1.00
X : parts per Million : Proton
X : parts per Million : Proton
X : parts per Million : Proton

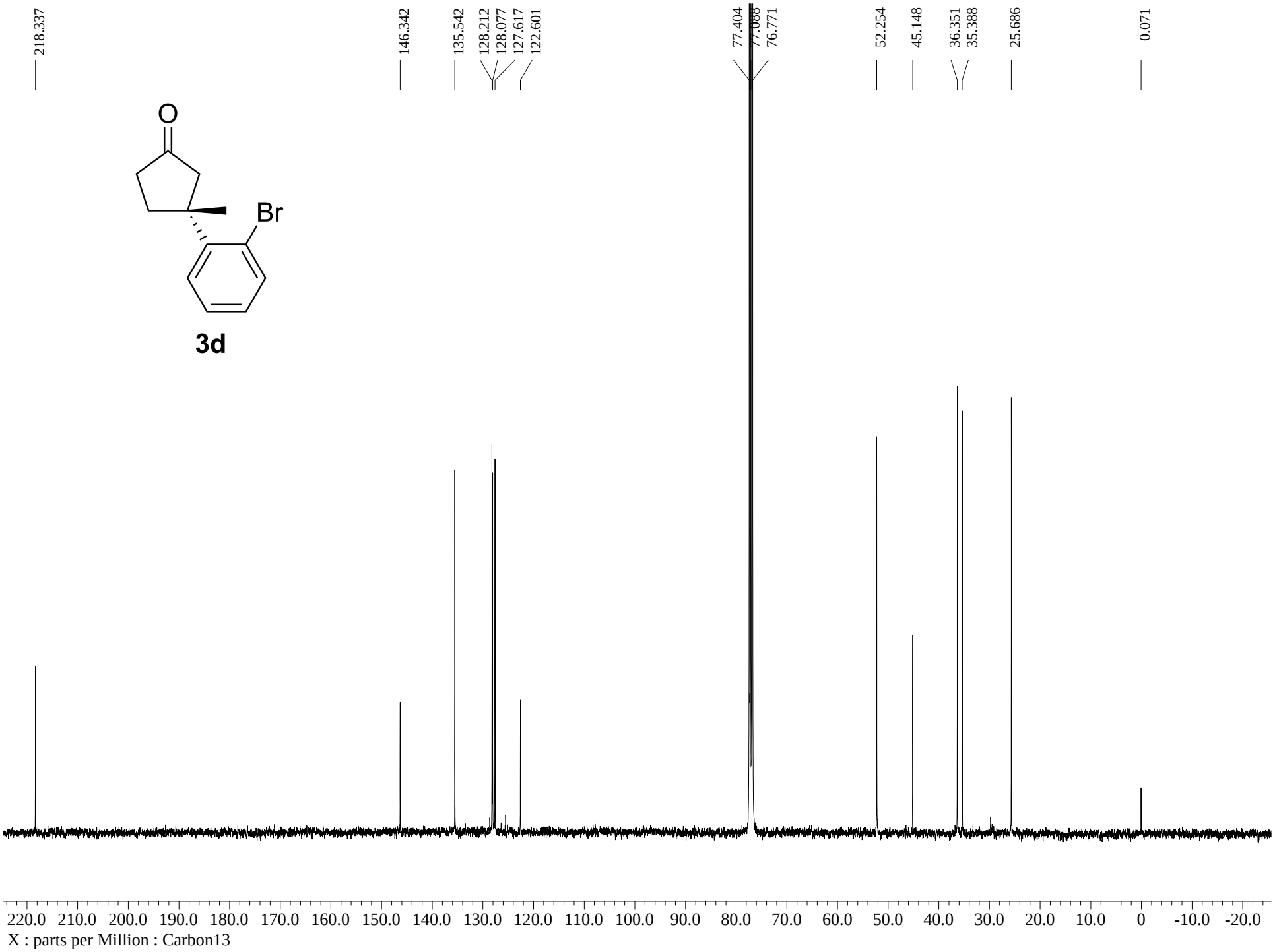

218.452
144.905
133.444
131.796
127.972
127.685
127.071
52.182
44.439
36.227
35.173
25.628
O
Cl
3c
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

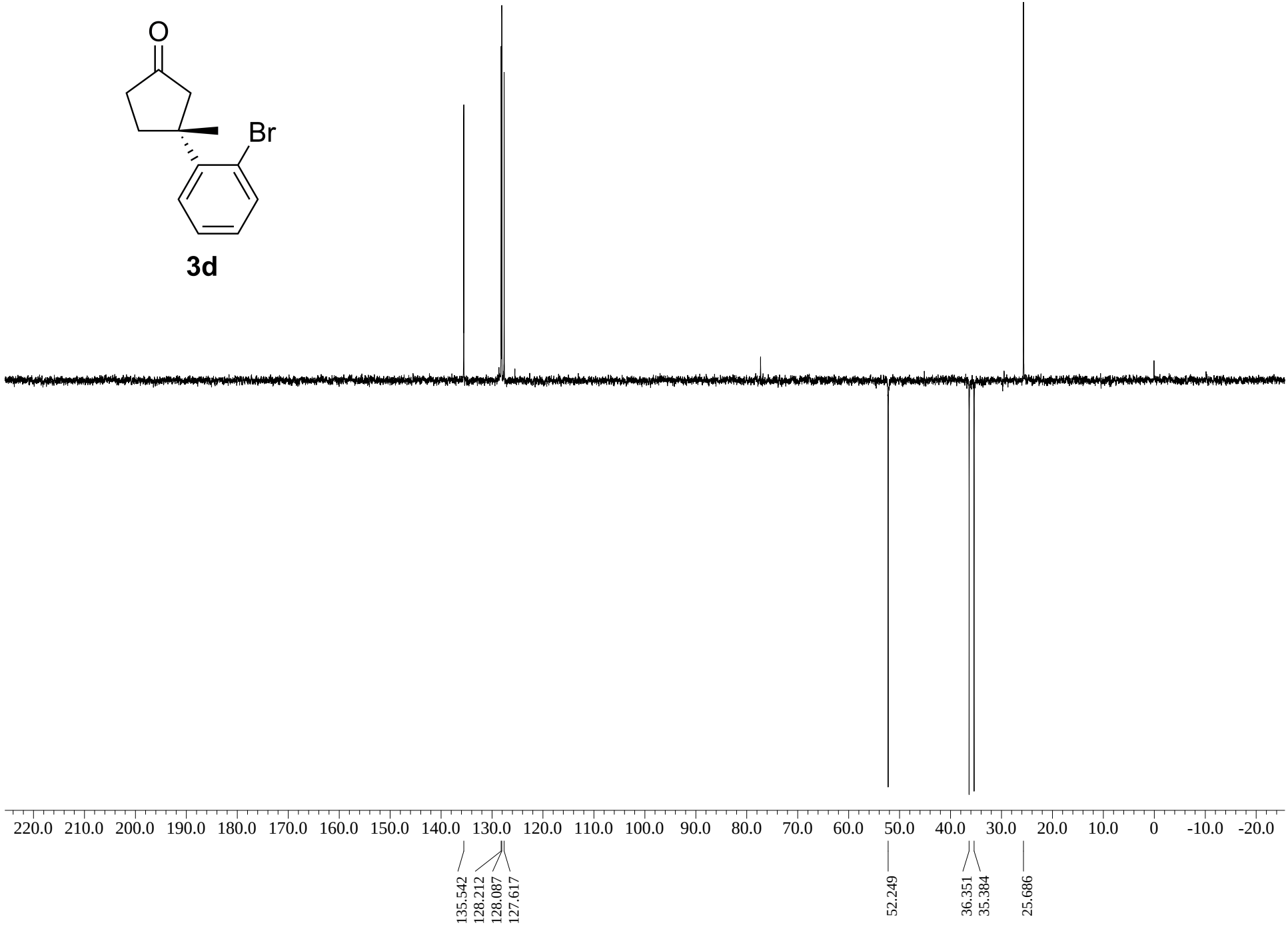


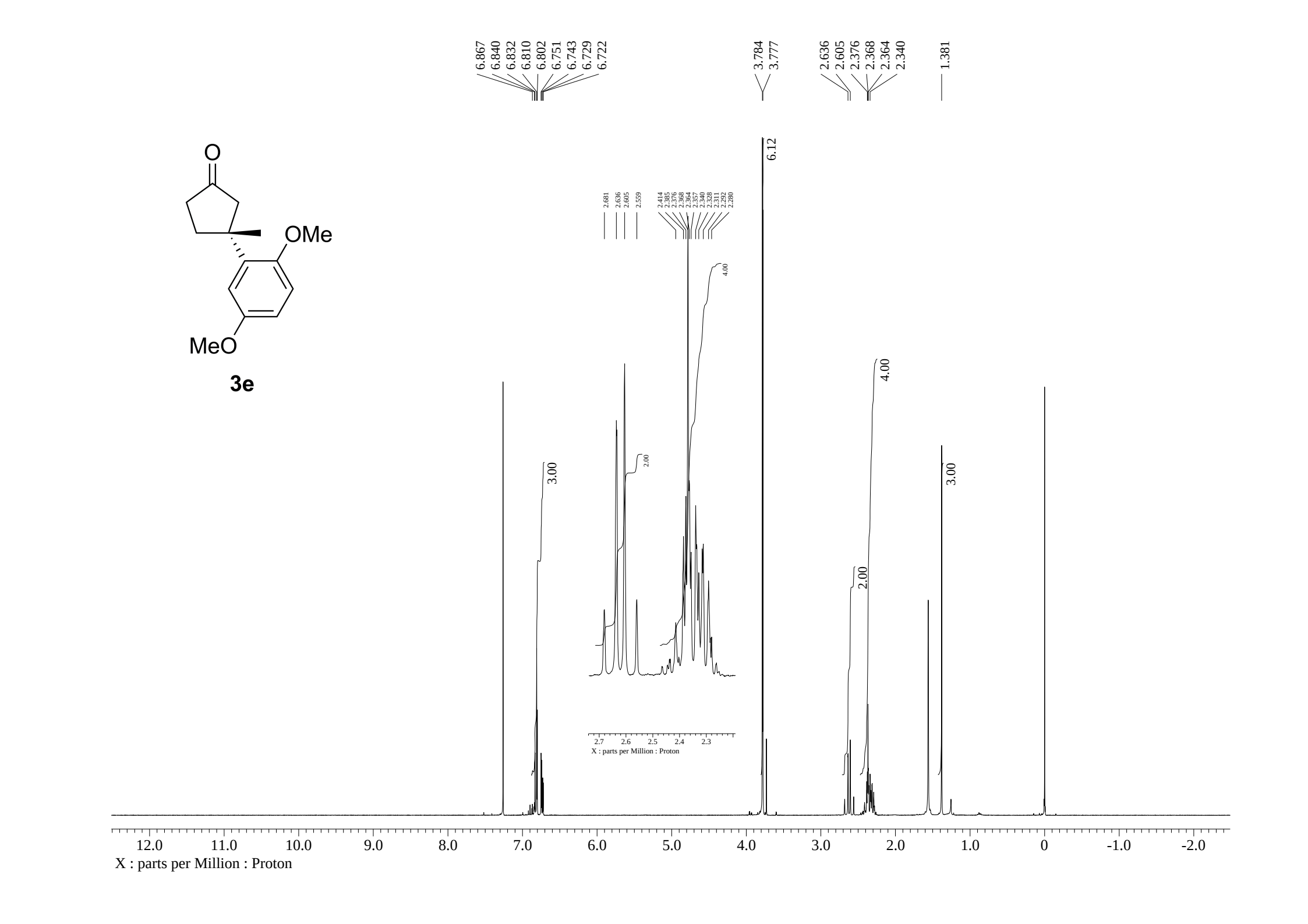
3c

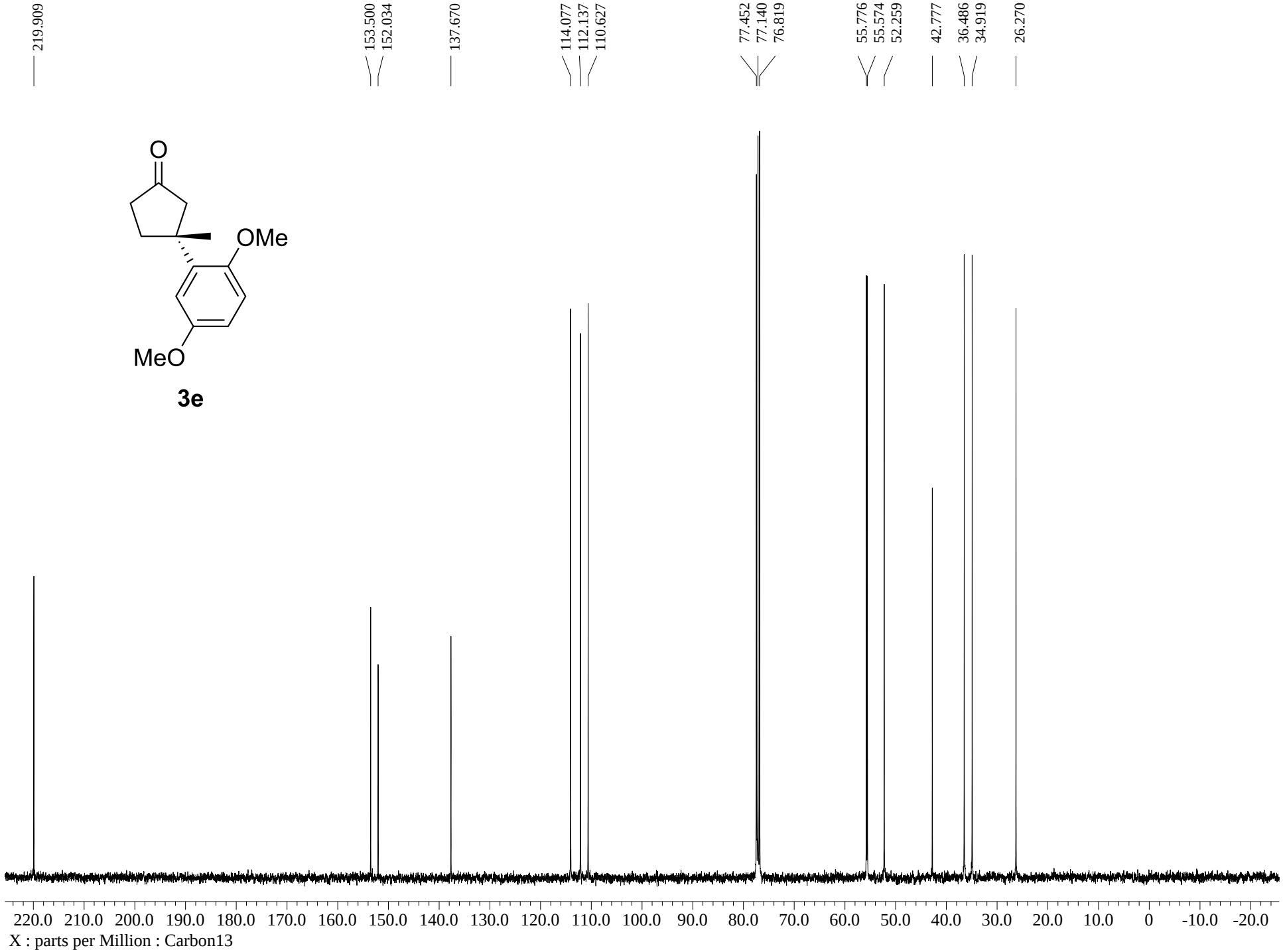
X : parts per Million : Carbon13


O
Br
3d
7.623
7.620
7.603
7.343
7.328
7.323
7.314
7.311
7.296
7.259
7.119
7.114
7.102
7.099
7.096
3.039
3.034
2.993
2.988
2.690
2.645
2.430
2.418
1.511
4.45
3.92
2.93
0.95
0.95
1.00
1.00
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton


218.337
146.342
135.542
128.212
128.077
127.617
122.601
77.404
77.088
76.771
52.254
45.148
36.351
35.388
25.686
0.071
O
Br
3d
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13


O
Br
3d
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
135.542
128.212
128.087
127.617
52.249
36.351
35.384
25.686
X : parts per Million : Carbon13


6.867
6.840
6.832
6.810
6.802
6.751
6.743
6.729
6.722
3.784
3.777
2.636
2.605
2.376
2.368
2.364
2.340
1.381
6.12
4.00
3.00
2.00
3.00
2.00
4.00
2.681
2.636
2.605
2.559
2.414
2.385
2.376
2.368
2.364
2.357
2.340
2.328
2.311
2.292
2.280
2.7
2.6
2.5
2.4
2.3
X : parts per Million : Proton
O
OMe
MeO
3e
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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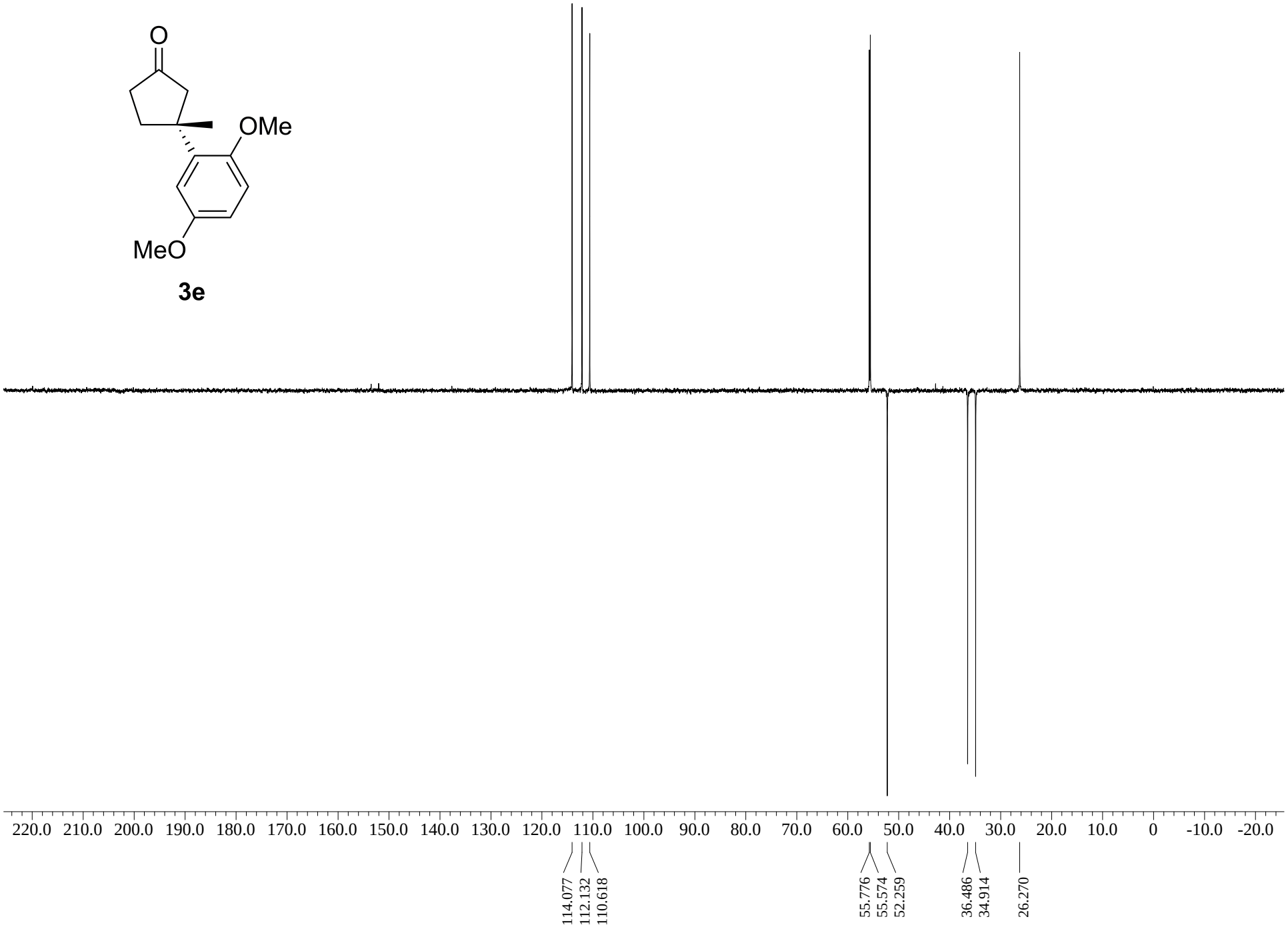
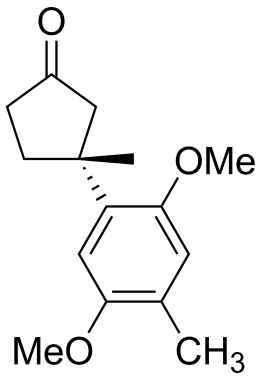
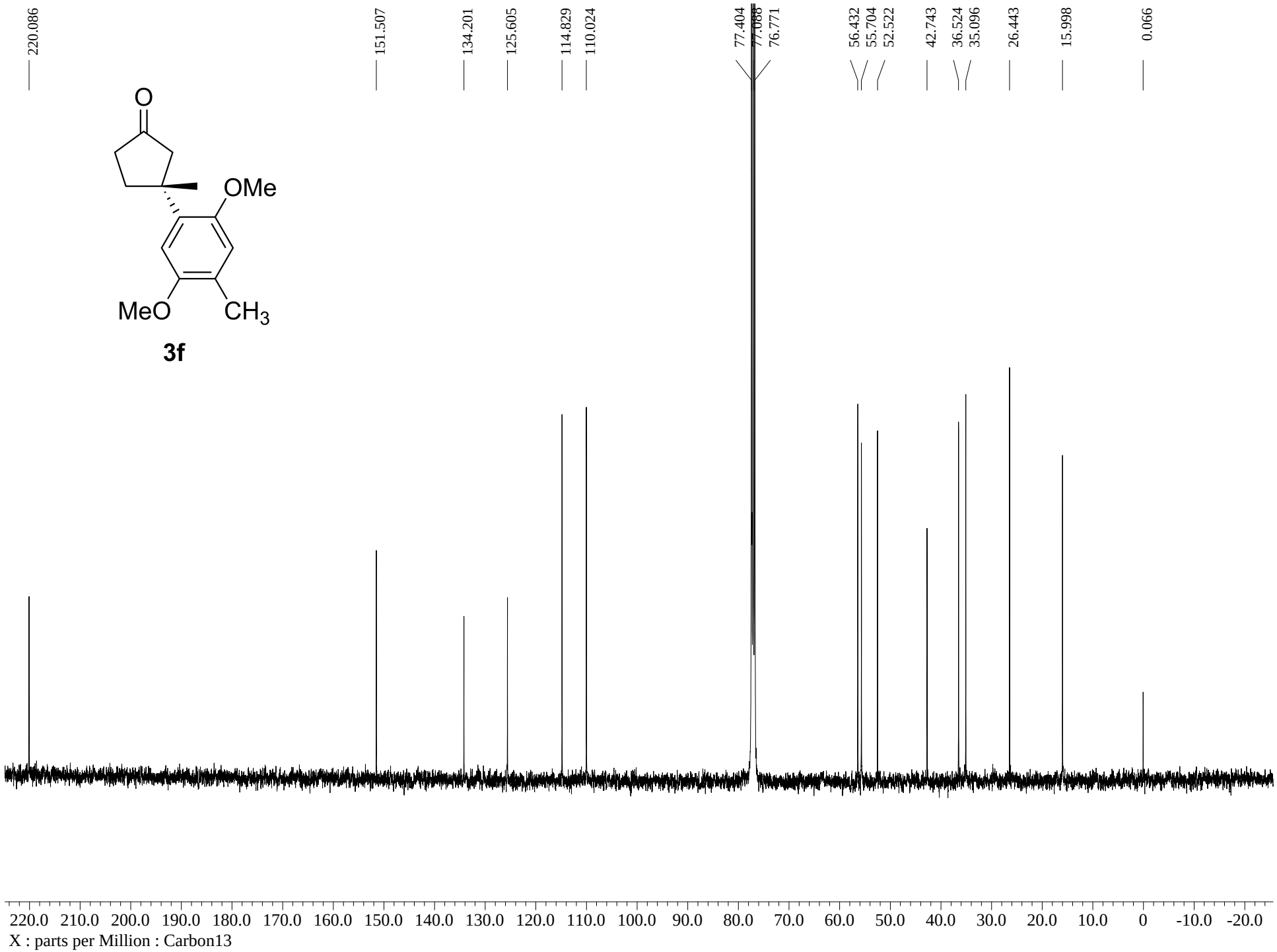
152.034
137.670
114.077
112.137
110.627
77.452
77.140
76.819
55.776
55.574
52.259
42.777
36.486
34.919
26.270
O
OMe
MeO
3e
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13


O
OMe
MeO
3e
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
114.077
112.132
110.618
55.776
55.574
52.259
36.486
34.914
26.270
X : parts per Million : Carbon13


O
OMe
MeO
CH3

3f

6.713
3.797
3.778
2.633
2.618
2.380
2.366
2.350
2.324
2.213
1.384
6.13
3.99
3.01
2.00
2.04
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton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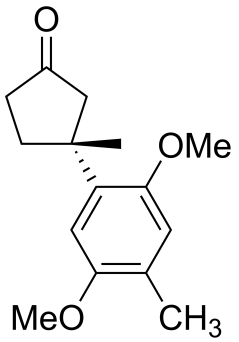
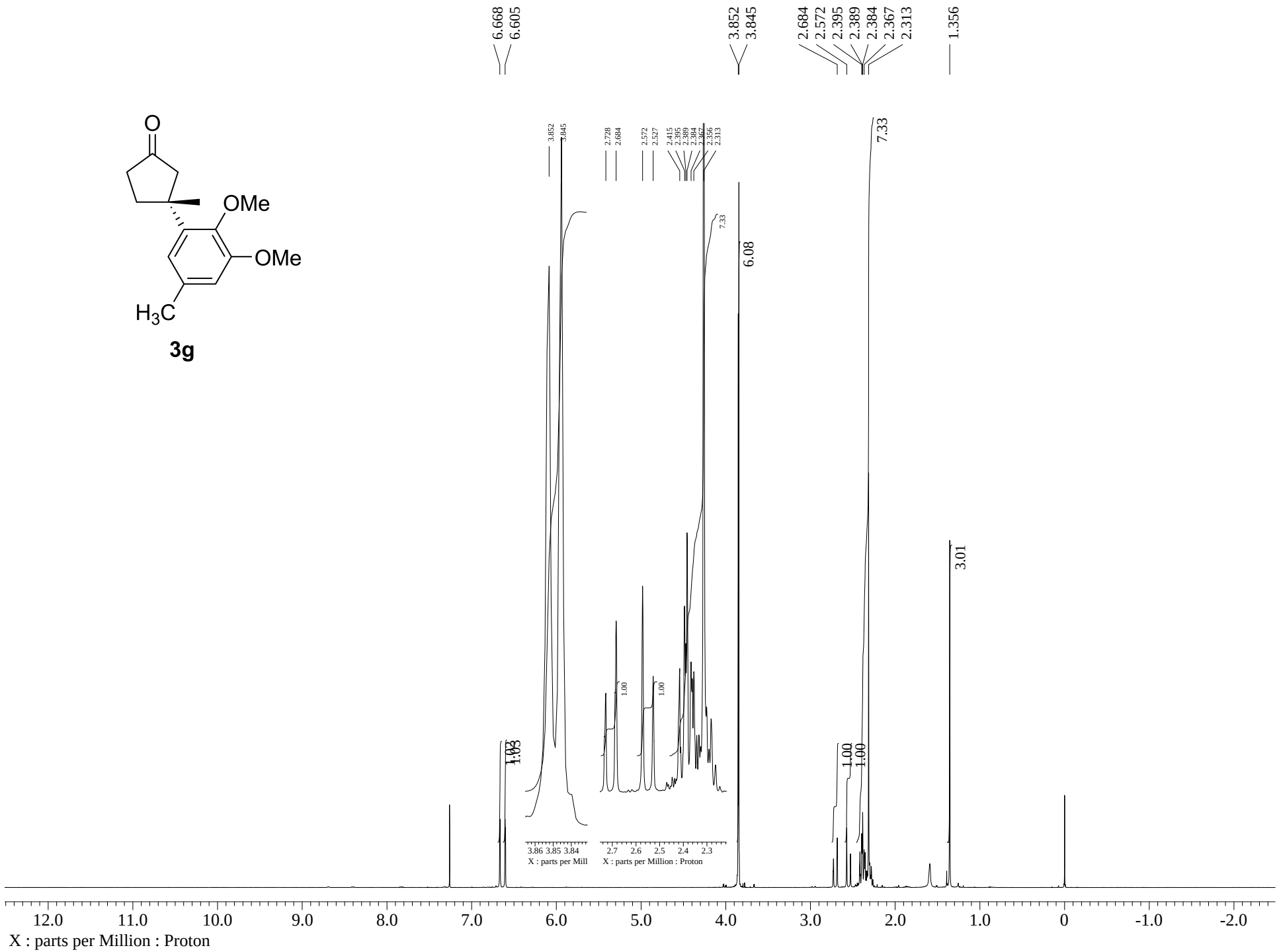
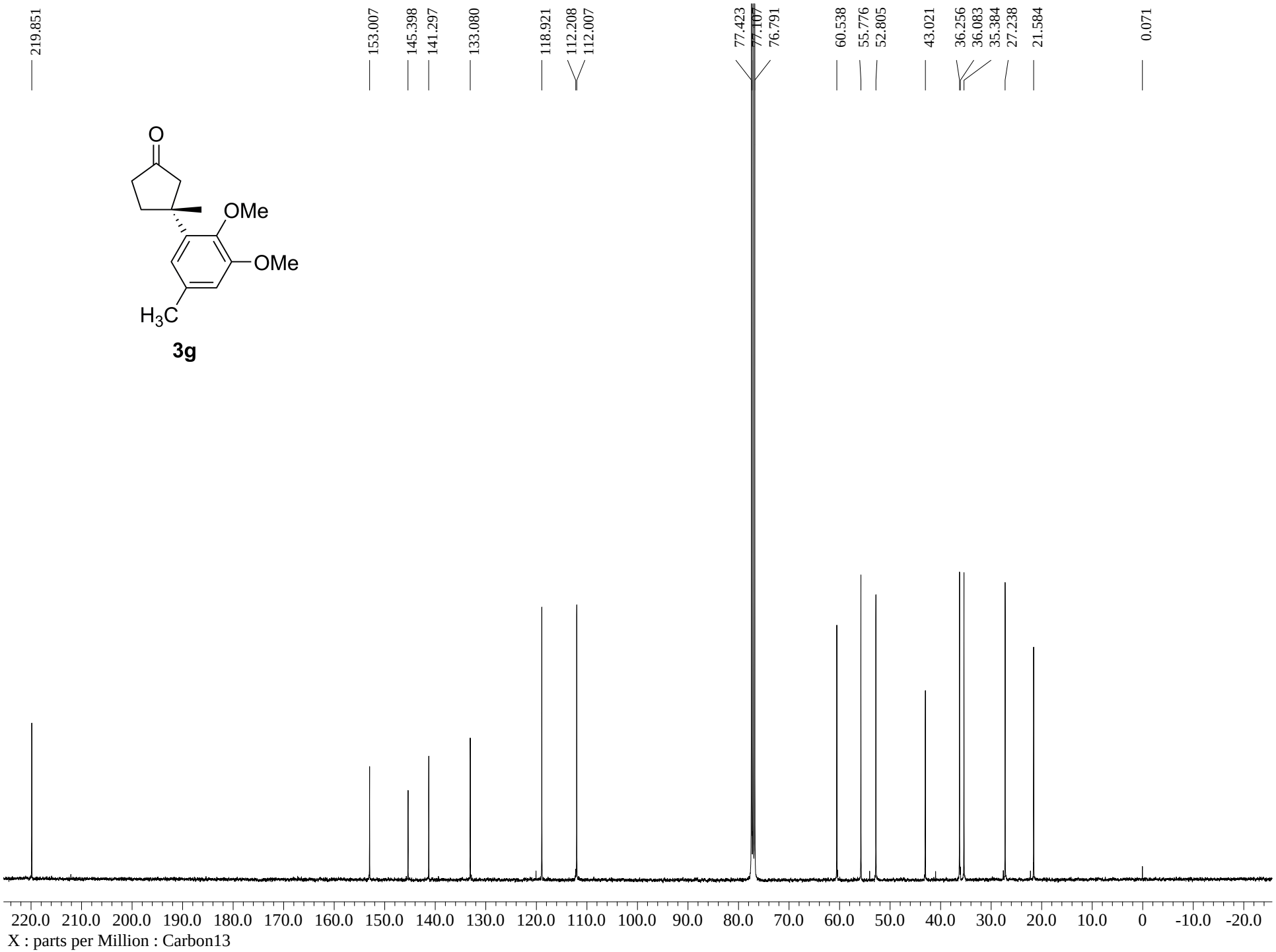
125.605
114.829
110.024
77.404
77.088
76.771
56.432
55.704
52.522
42.743
36.524
35.096
26.443
15.998
0.066
O
OMe
MeO
CH3
3f
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



3f

X : parts per Million : Carbon13


6.668
6.605
3.852
3.845
2.684
2.572
2.395
2.389
2.384
2.367
2.313
1.356
O
OMe
OMe
H3C
3g
7.33
6.08
3.01
1.00
1.00
3.86 3.85 3.84
X : parts per Mill
2.7 2.6 2.5 2.4 2.3
X : parts per Million : Proton
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton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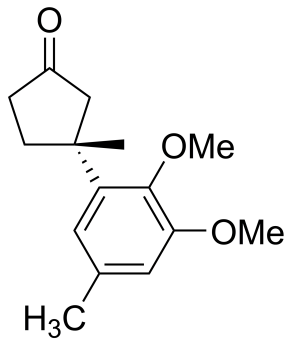
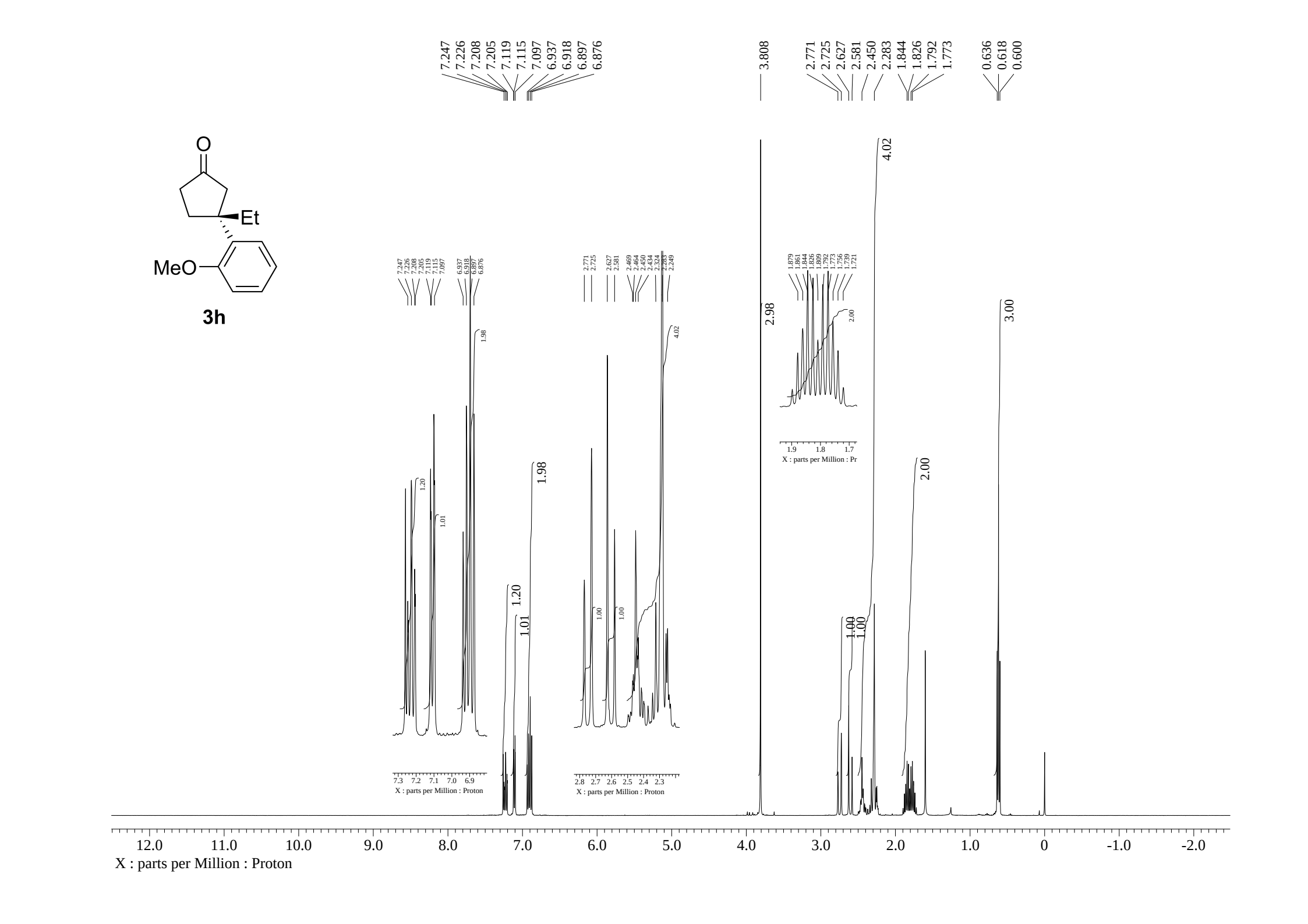
141.297
133.080
118.921
112.208
112.007
77.423
77.107
76.791
60.538
55.776
52.805
43.021
36.256
36.083
35.384
27.238
21.584
0.071
O
OMe
OMe
H3C
3g
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



3g

X : parts per Million : Carbon13


O
Et
MeO
3h
7.247
7.226
7.208
7.205
7.119
7.115
7.097
6.937
6.918
6.897
6.876
3.808
2.771
2.725
2.627
2.581
2.450
2.283
1.844
1.826
1.792
1.773
0.636
0.618
0.600
2.98
4.02
3.00
2.00
1.98
1.20
1.01
1.00
1.00
X : parts per Million : Proton
12.0
11.0
10.0
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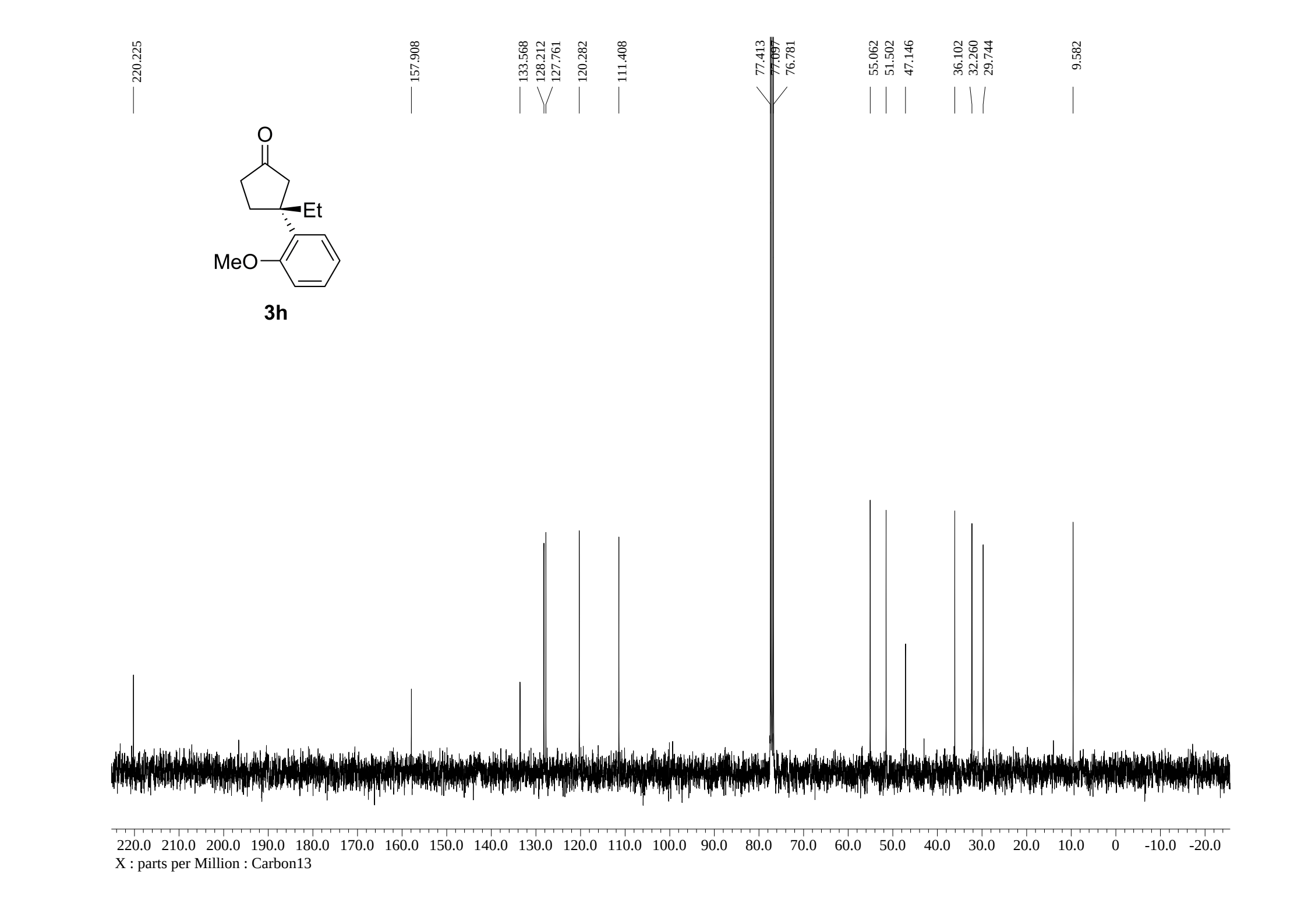
3.0
2.0
1.0
0
-1.0
-2.0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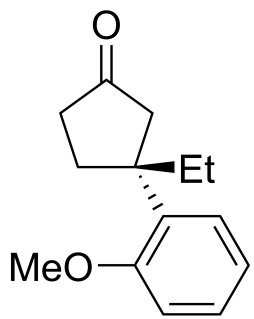
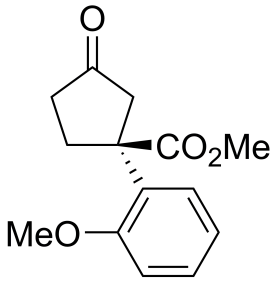
128.212
127.761
120.282
111.408
77.413
77.097
76.781
55.062
51.502
47.146
36.102
32.260
29.744
9.582
O
Et
MeO
3h
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



3h

X : parts per Million : Carbon13


O
CO2Me
MeO

3i

7.305
7.301
7.285
7.281
7.239
7.235
7.219
7.216
6.999
6.979
6.977
6.961
6.957
6.906
6.885
3.792
3.639
3.214
3.167
2.628
2.622
2.606
2.561
2.466
2.438
2.421
2.348
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5.04
2.87
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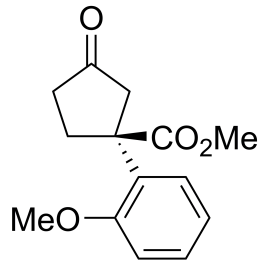
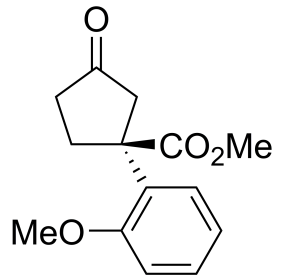
1.00
0.92
0.87
0.82
0.80
X : parts per Million : Proton


O
CO2Me
MeO

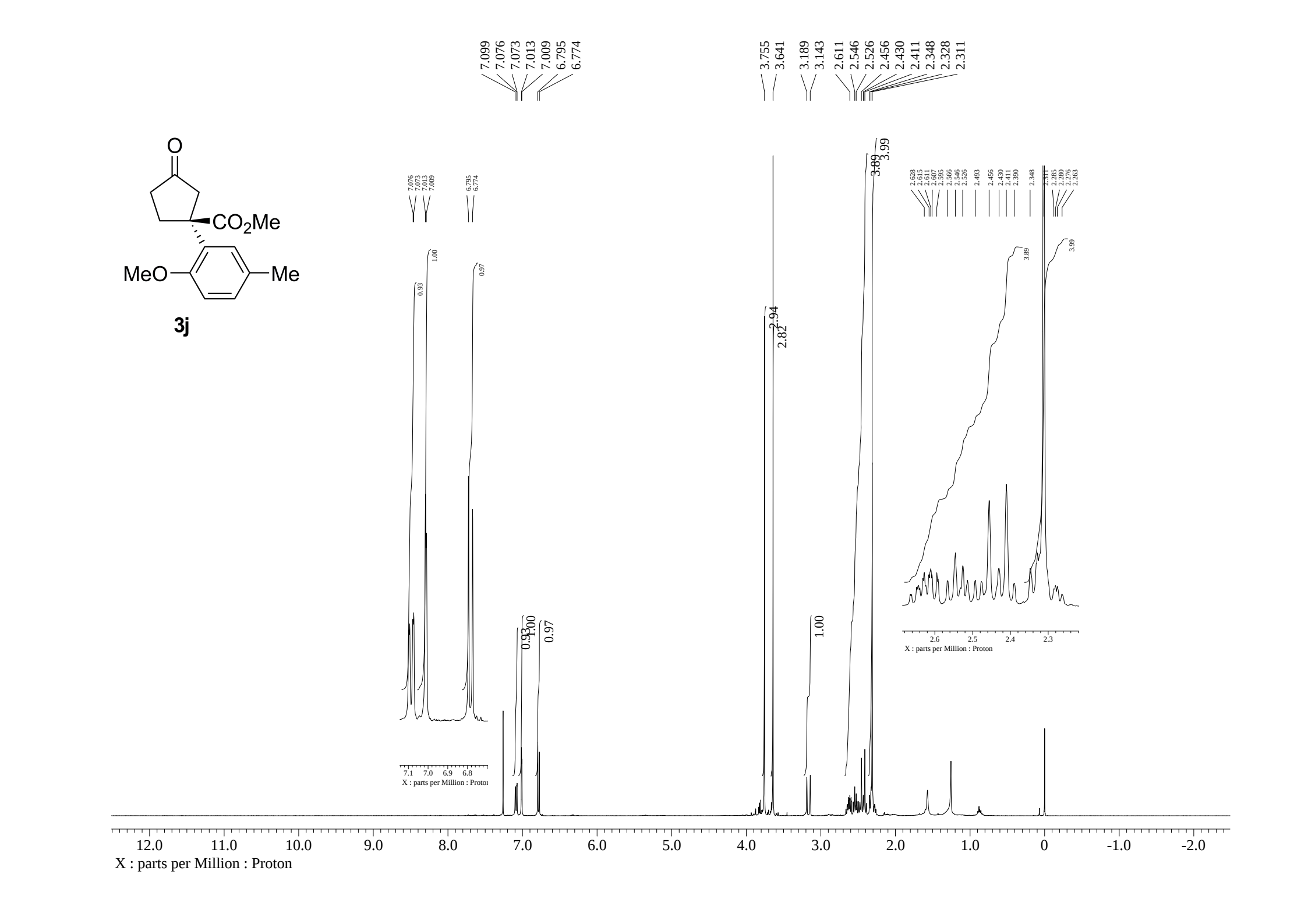
3i

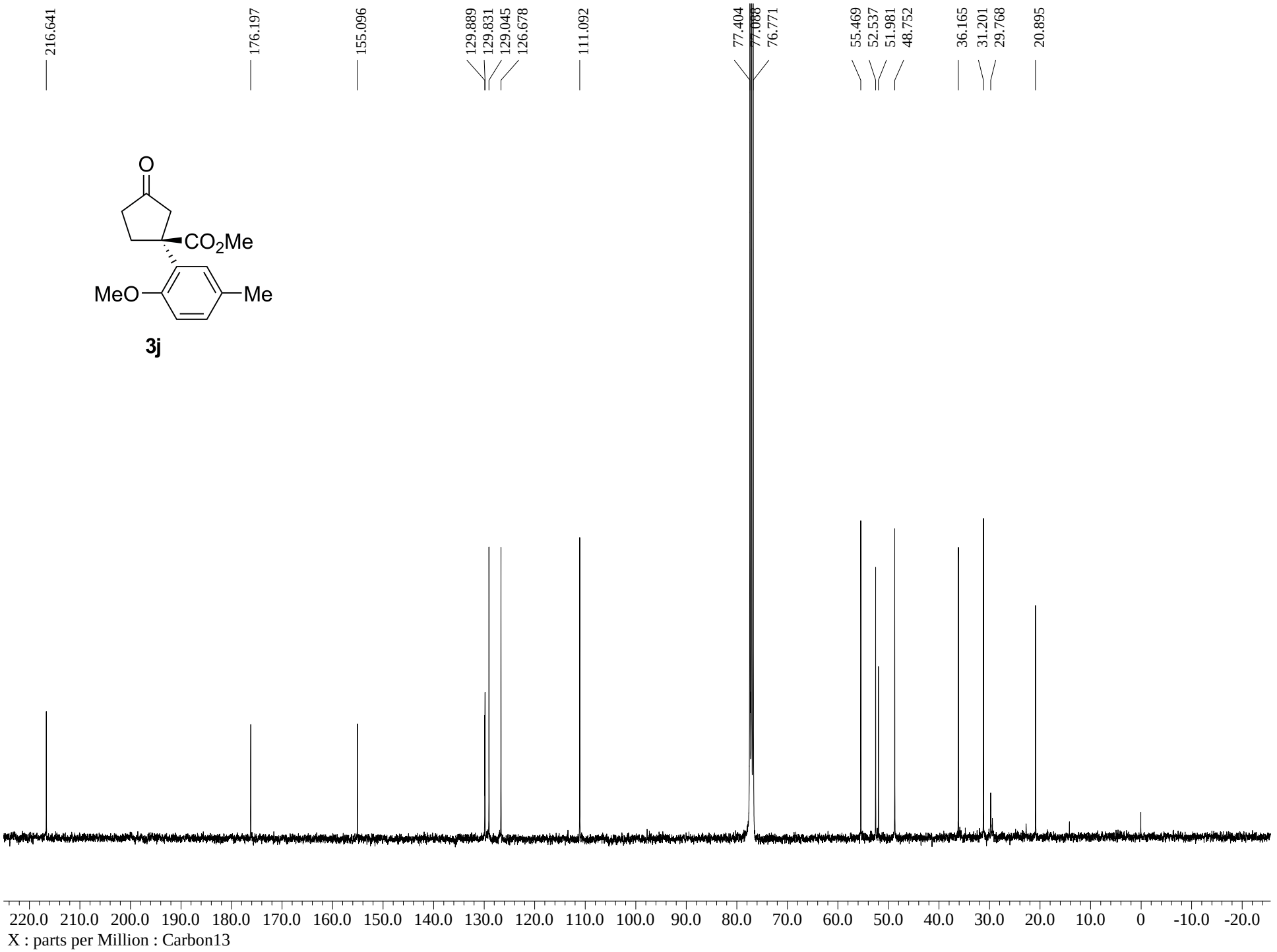
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
216.574
176.116
157.190
130.176
128.892
125.888
120.703
111.126
77.404
77.088
76.771
55.368
52.537
52.038
48.718
36.145
31.196
X : parts per Million : Carbon13

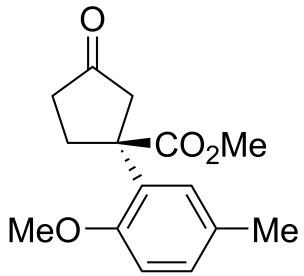


3i

X : parts per Million : Carbon13

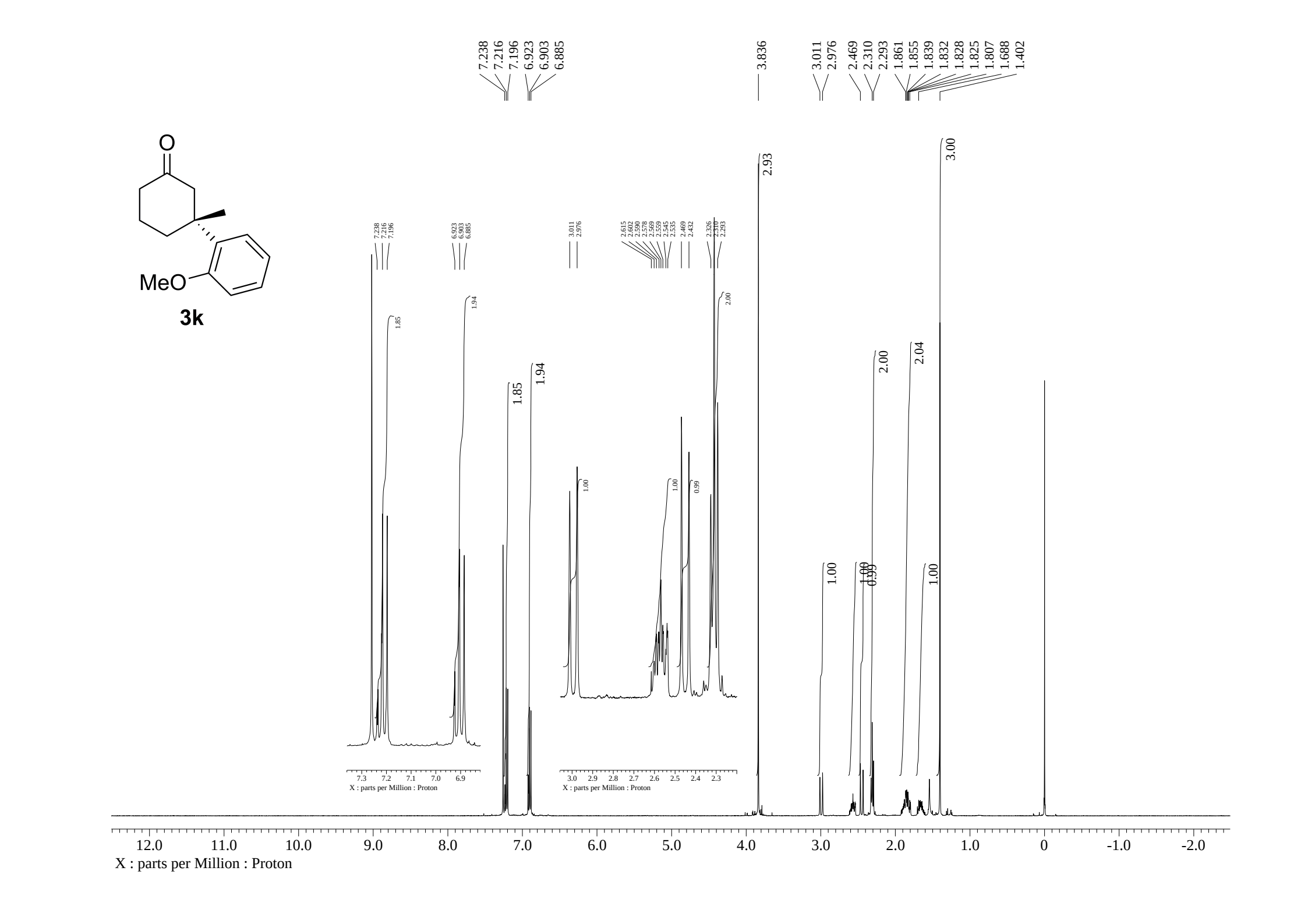

O
CO2Me
MeO
Me
3j
7.099
7.076
7.073
7.013
7.009
6.795
6.774
3.755
3.641
3.189
3.143
2.611
2.546
2.526
2.456
2.430
2.411
2.348
2.328
2.311
2.94
2.82
1.00
0.97
3.89
3.99
X : parts per Million : Proton

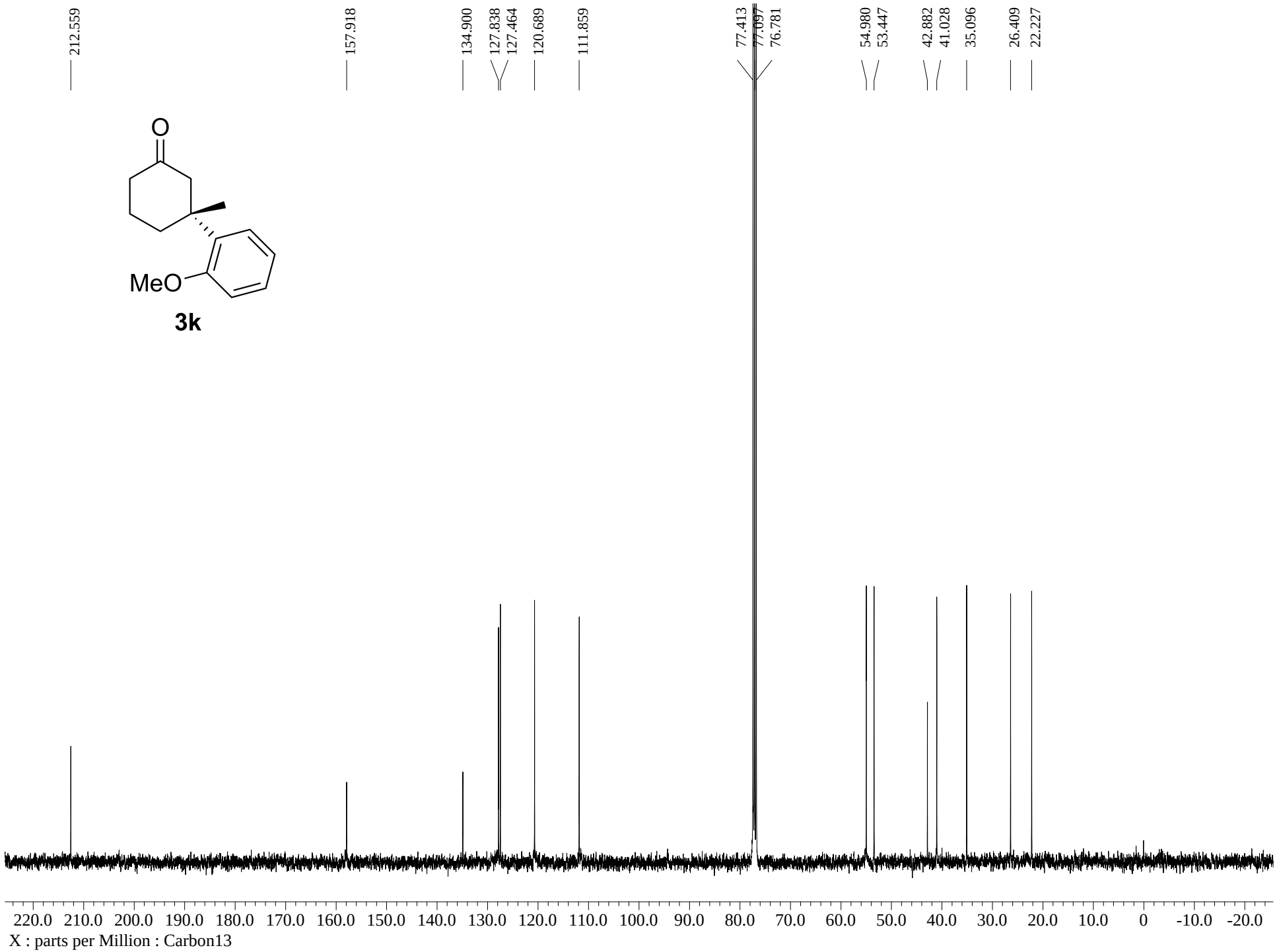

216.641
176.197
155.096
129.889
129.831
129.045
126.678
111.092
77.404
77.088
76.771
55.469
52.537
51.981
48.752
36.165
31.201
29.768
20.895
O
CO2Me
MeO
Me
3j
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

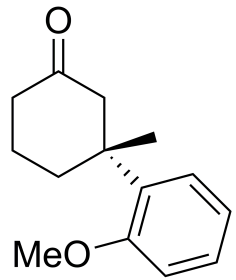


3j

X : parts per Million : Carbon13

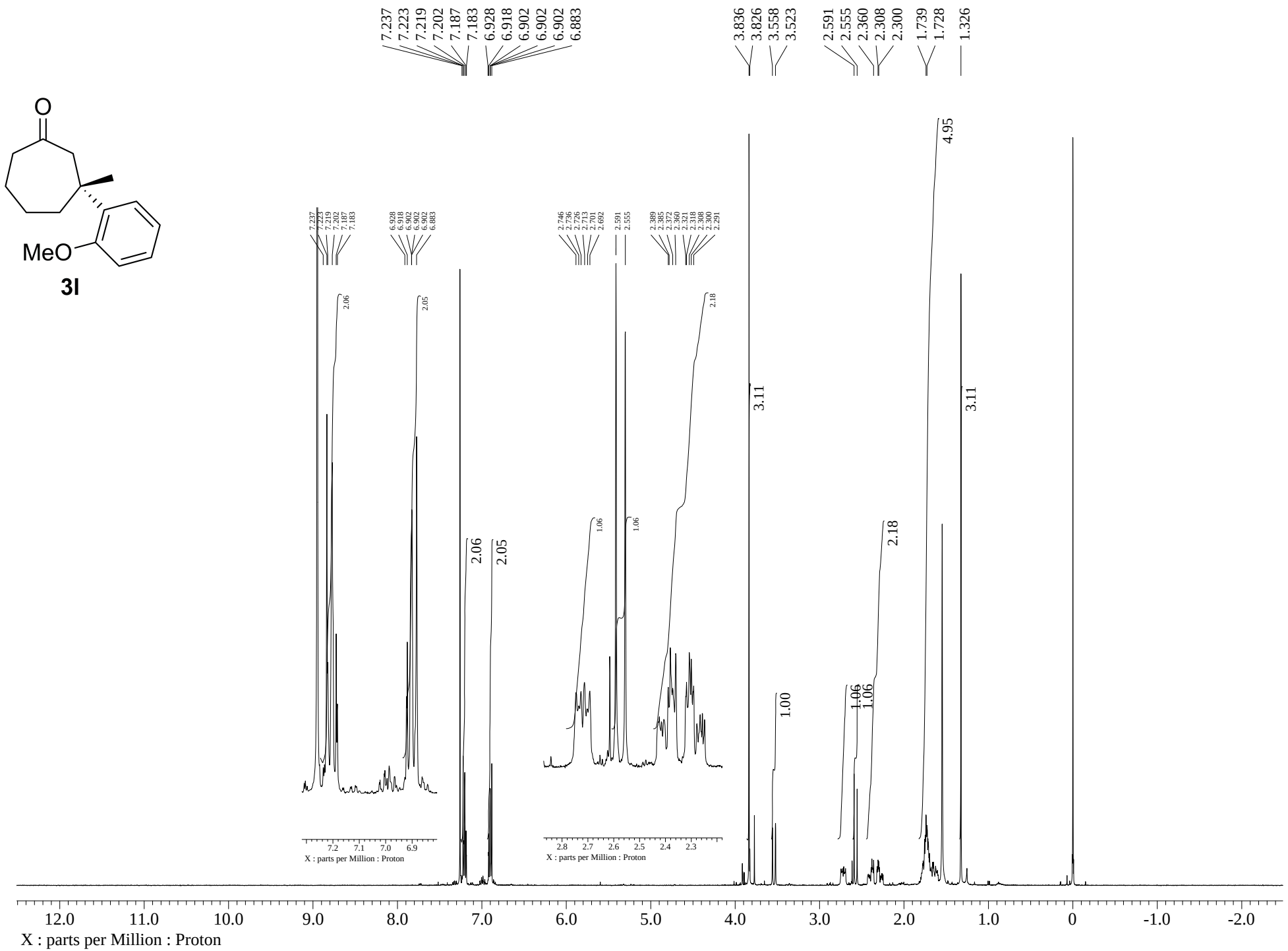

7.238
7.216
7.196
6.923
6.903
6.885
3.836
3.011
2.976
2.469
2.310
2.293
1.861
1.855
1.839
1.832
1.828
1.825
1.807
1.688
1.402
O
MeO
3k
2.93
3.00
1.85
1.94
2.00
2.04
1.00
1.00
0.99
1.00
X : parts per Million : Proton

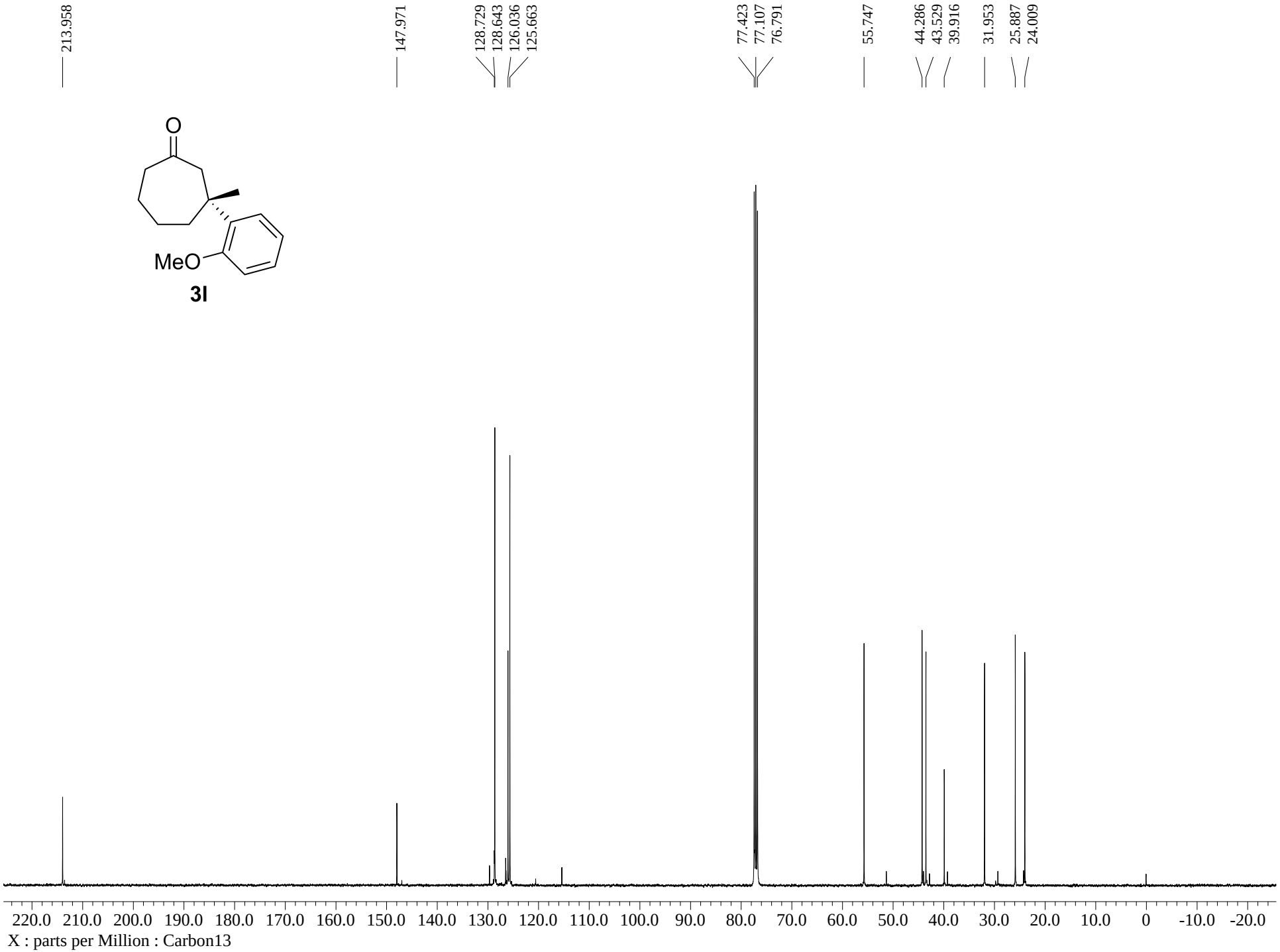

212.559
157.918
134.900
127.838
127.464
120.689
111.859
77.413
77.097
76.781
54.980
53.447
42.882
41.028
35.096
26.409
22.227
O
MeO
3k
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

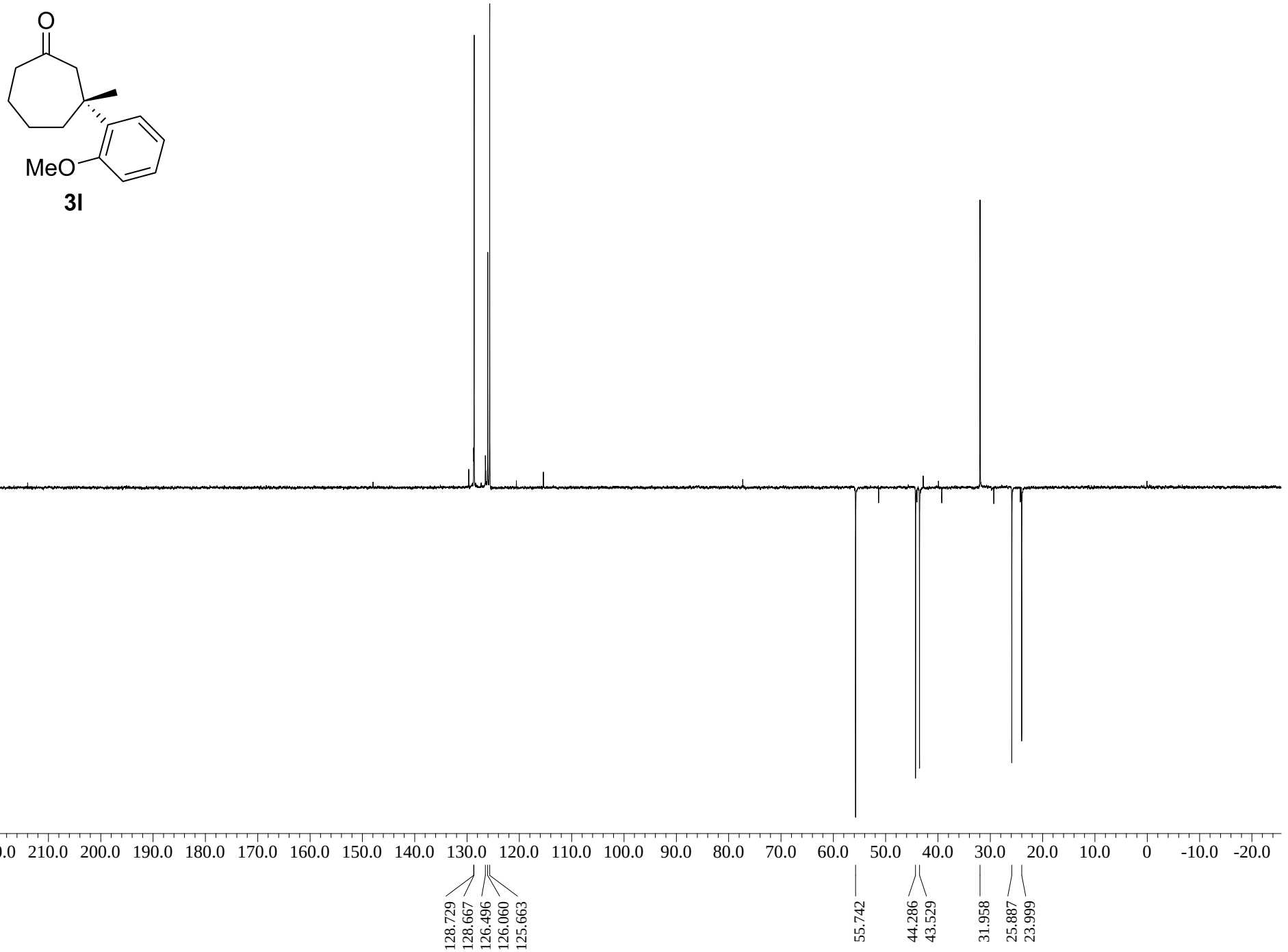


3k

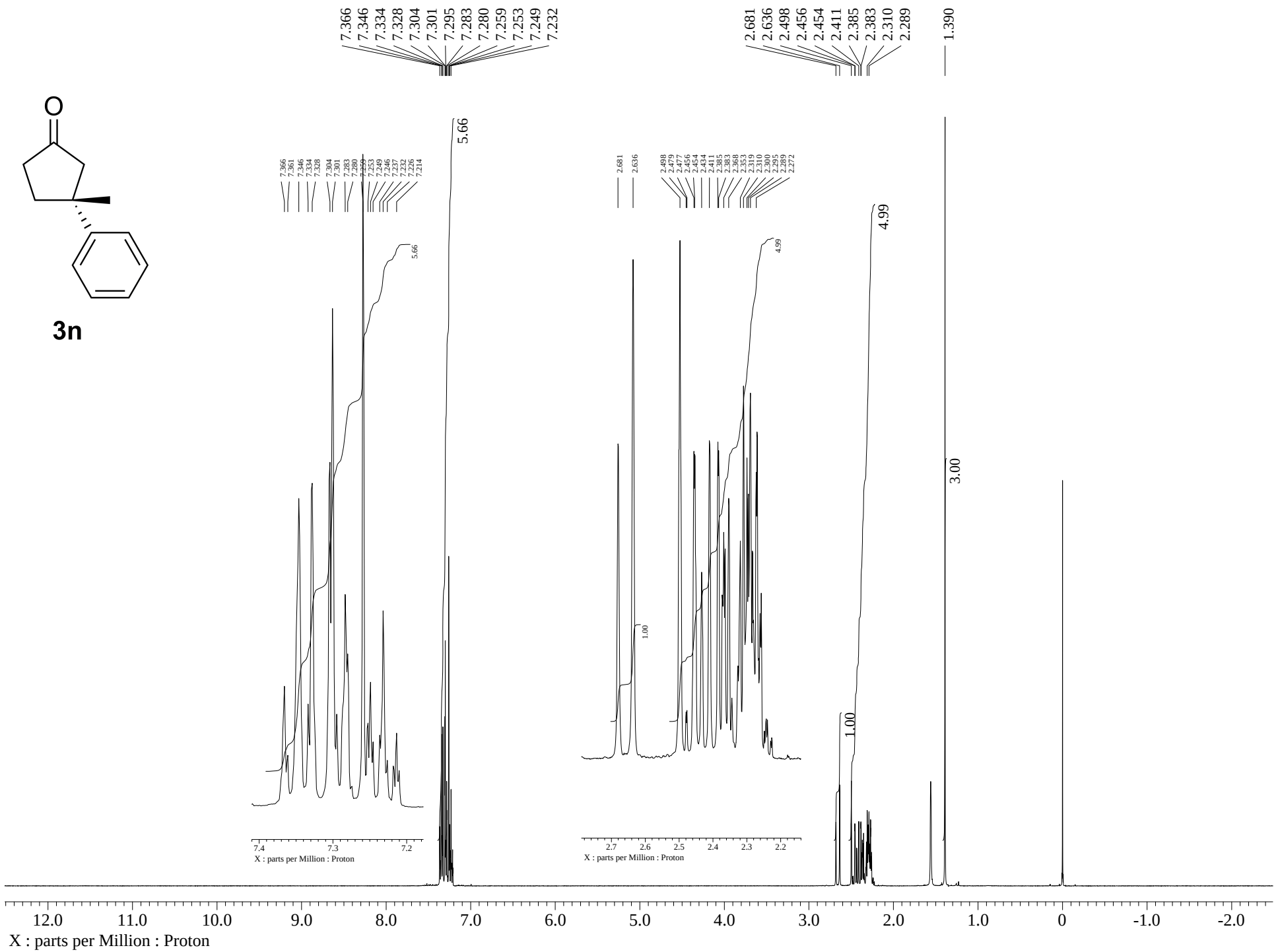
X : parts per Million : Carbon13

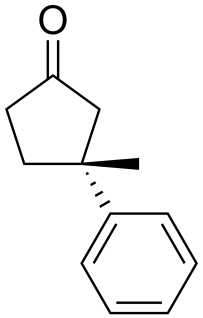

7.237
7.223
7.219
7.202
7.187
7.183
6.928
6.918
6.902
6.902
6.902
6.883
3.836
3.826
3.558
3.523
2.591
2.555
2.360
2.308
2.300
1.739
1.728
1.326
O
MeO
3I
4.95
3.11
3.11
2.06
2.05
2.18
1.00
1.06
1.06
1.06
1.06
2.06
2.05
2.18
X : parts per Million : Proton
X : parts per Million : Proton
X : parts per Million : Proton


213.958
147.971
128.729
128.643
126.036
125.663
77.423
77.107
76.791
55.747
44.286
43.529
39.916
31.953
25.887
24.009
O
MeO
3l
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



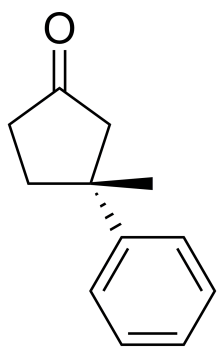
X : parts per Million : Carbon13


7.366
7.346
7.334
7.328
7.304
7.301
7.295
7.283
7.280
7.259
7.253
7.249
7.232
2.681
2.636
2.498
2.456
2.454
2.411
2.385
2.383
2.310
2.289
1.390
5.66
4.99
1.00
3.00
O
3n
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0



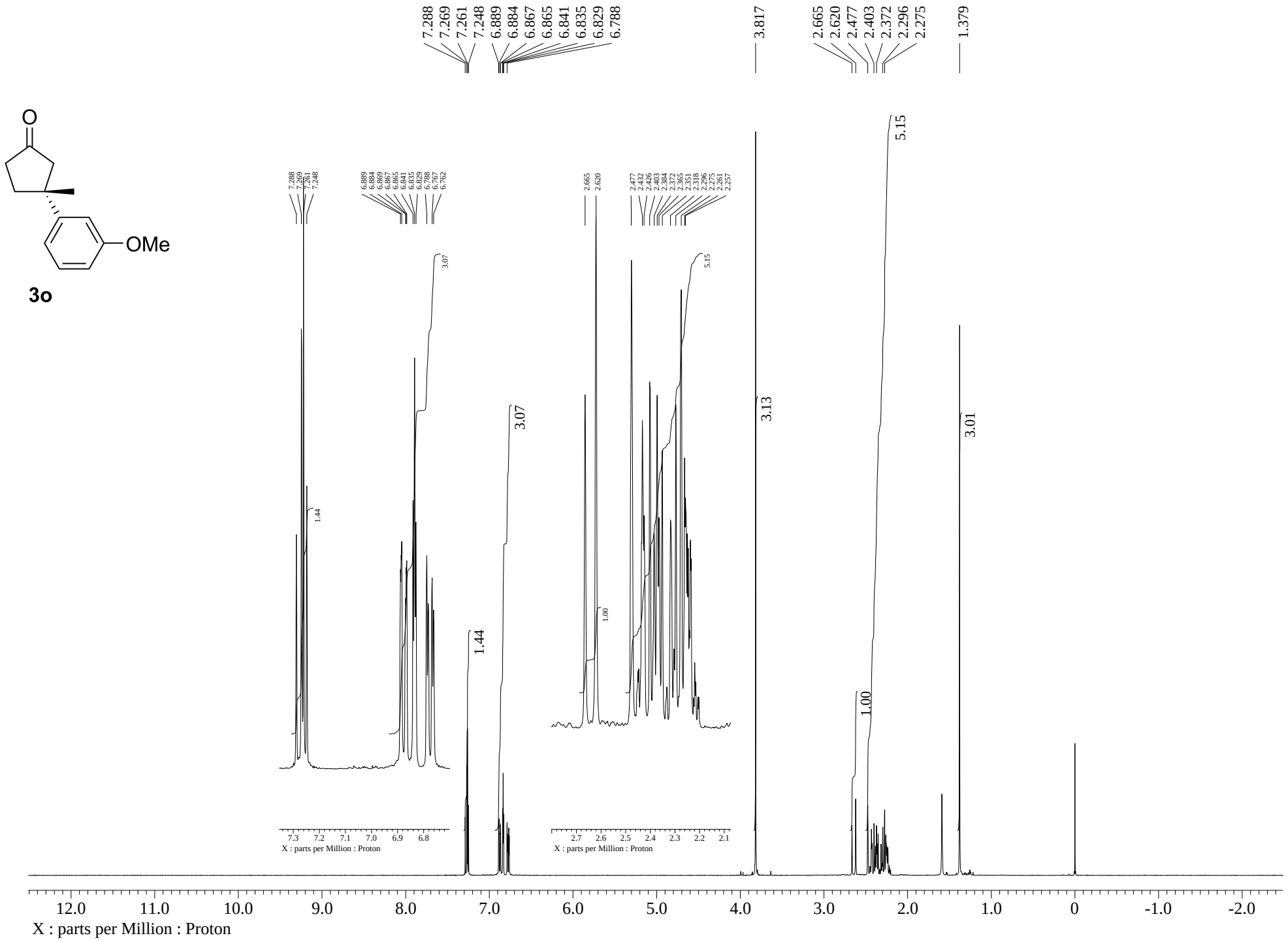
3n

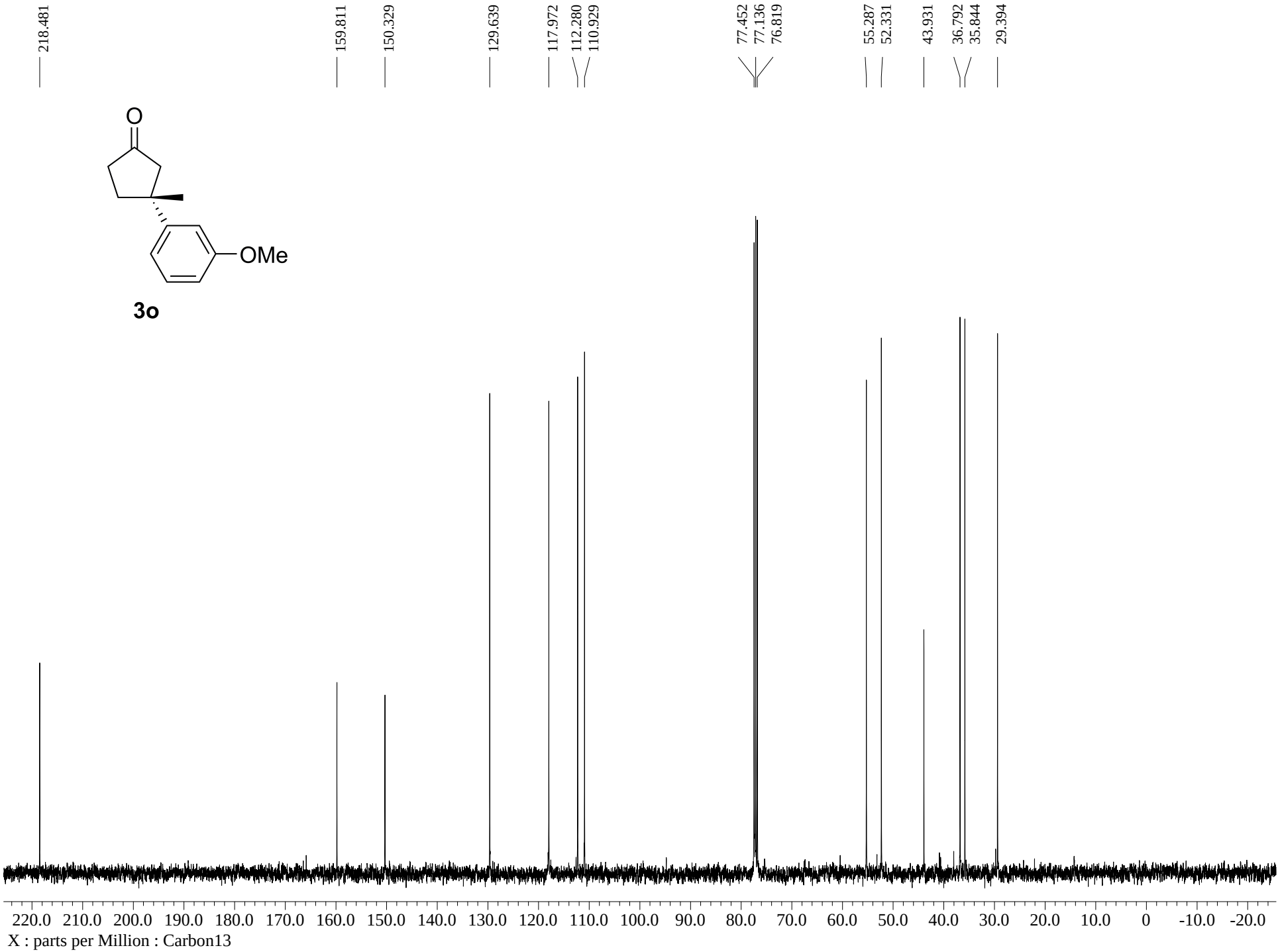
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
218.562
148.565
128.652
126.405
125.528
77.481
77.164
76.839
52.326
43.893
36.802
35.882
29.495
X : parts per Million : Carbon13

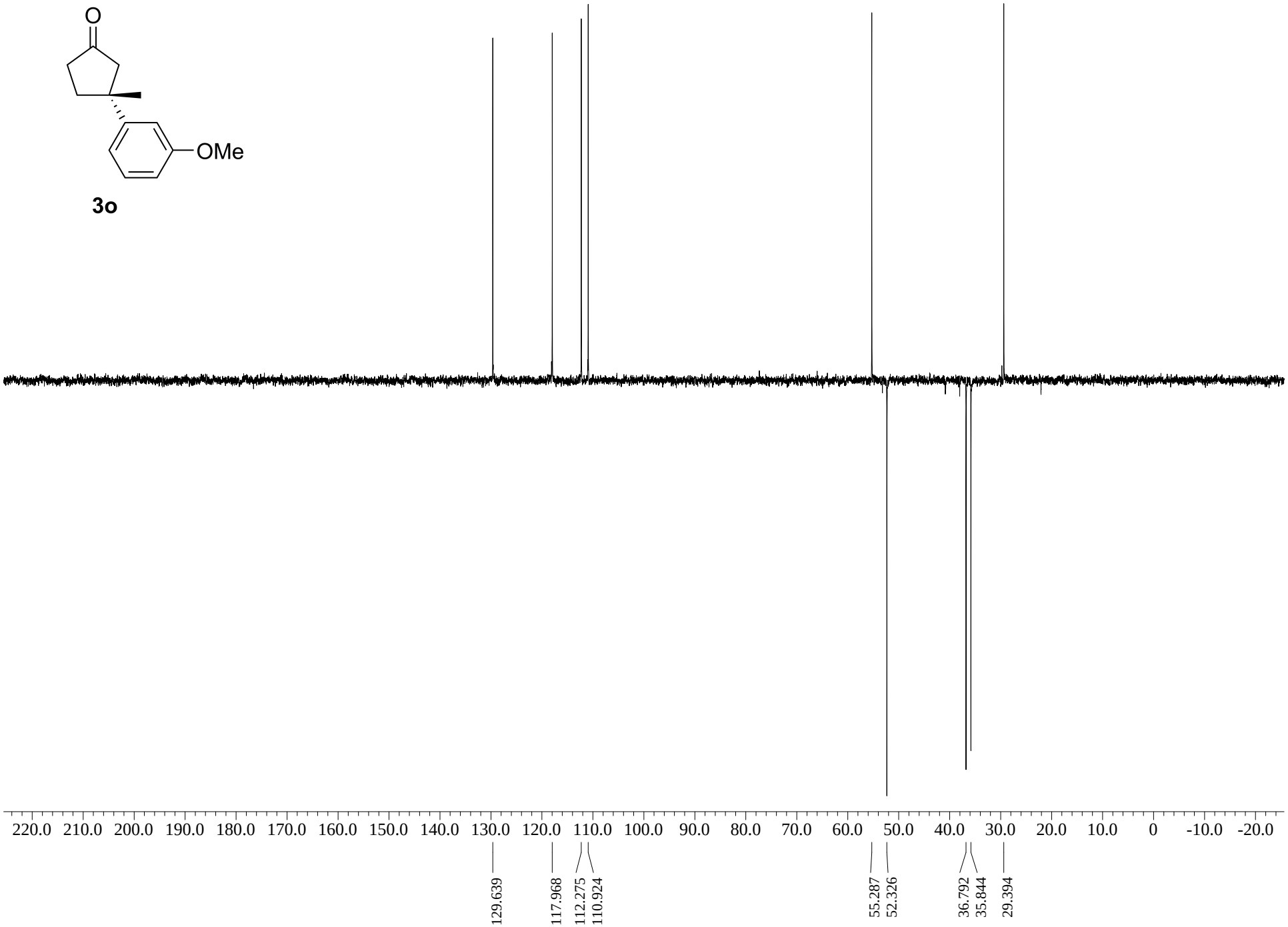


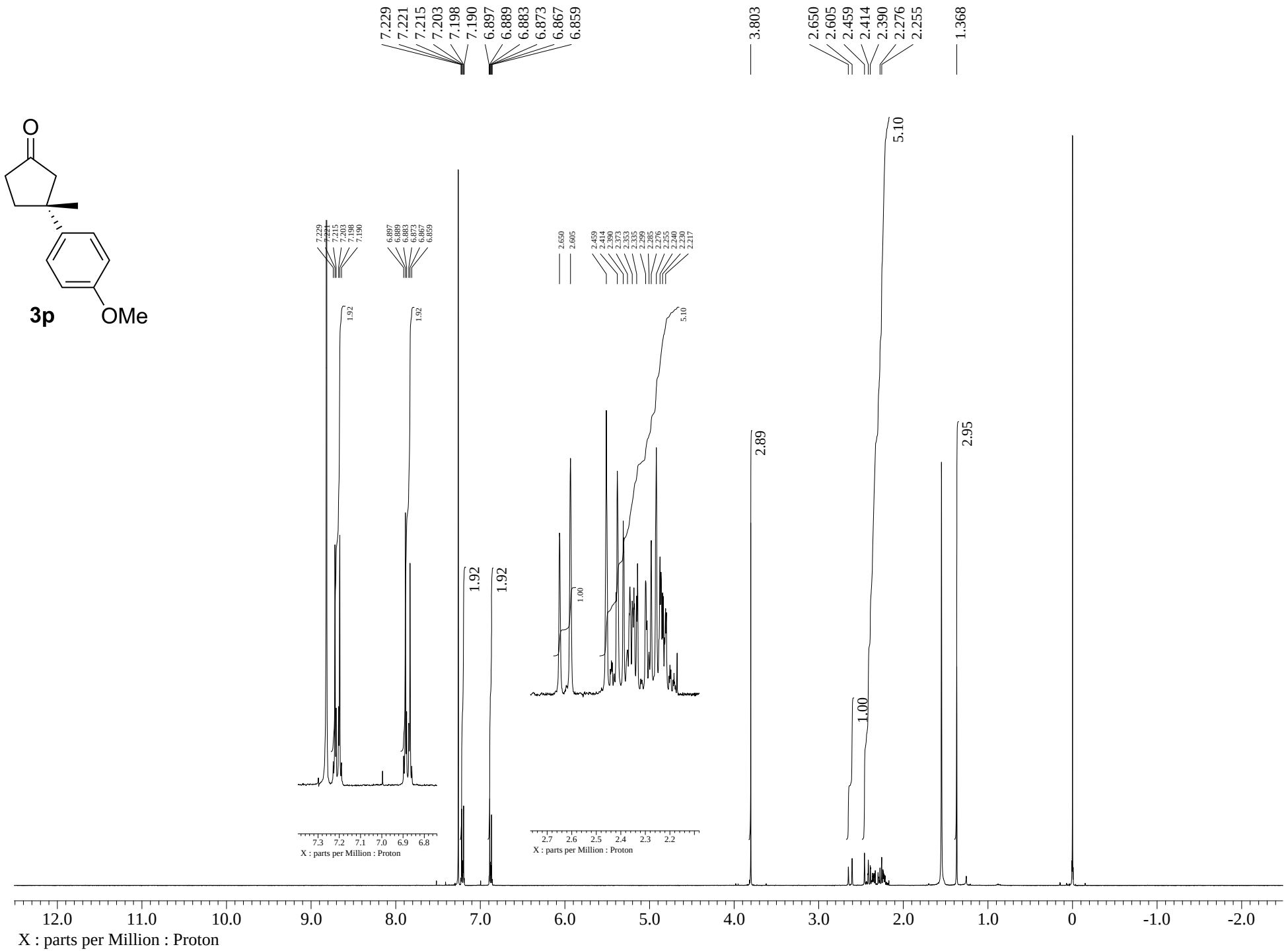
3n

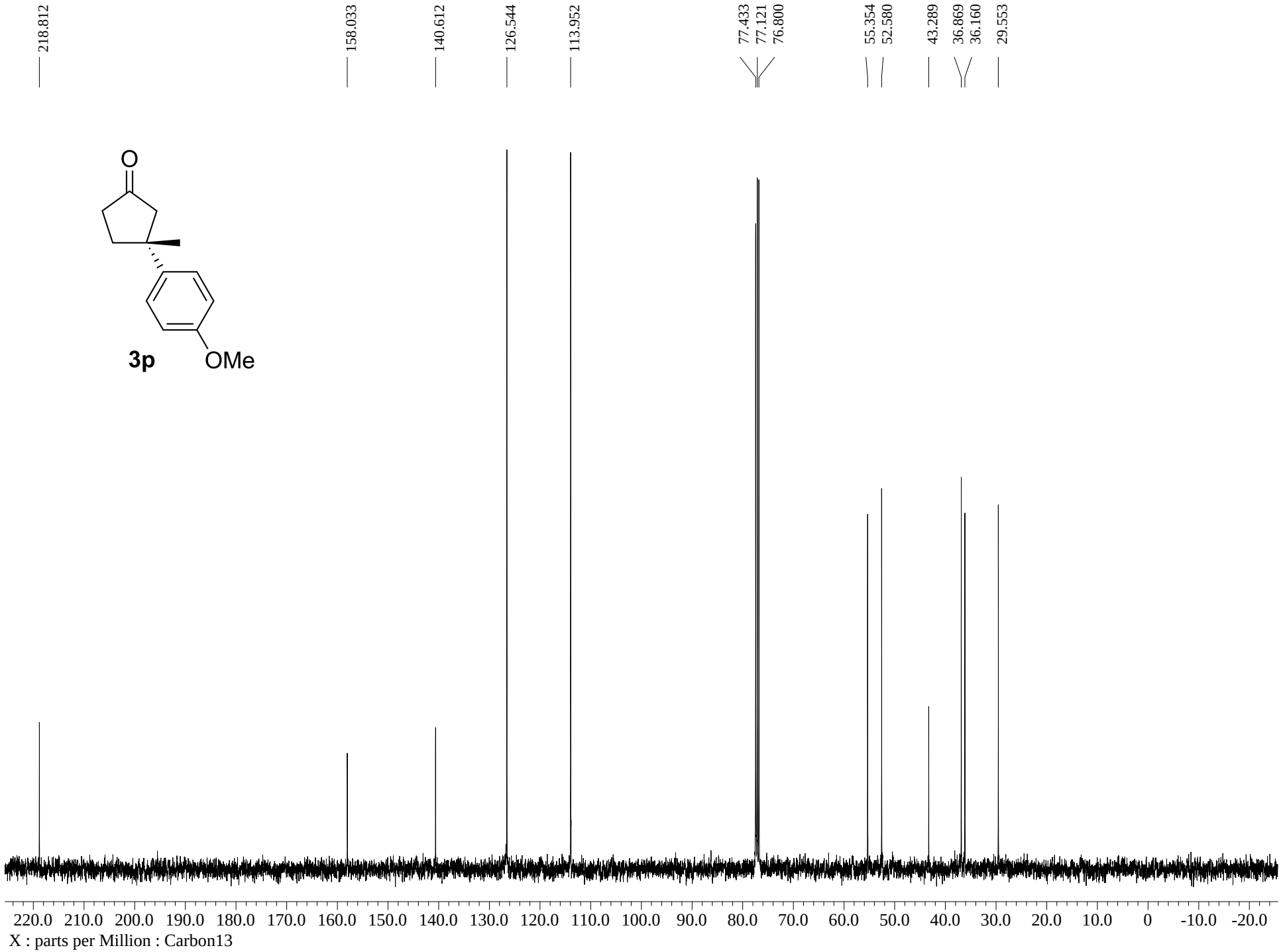
X : parts per Million : Carbon13

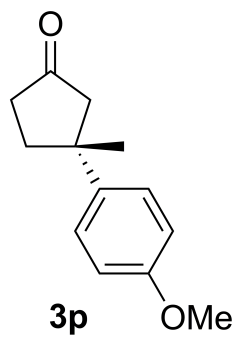

O
OMe
3o
7.288
7.269
7.261
7.248
6.889
6.884
6.867
6.865
6.841
6.835
6.829
6.788
3.817
2.665
2.620
2.477
2.403
2.372
2.296
2.275
1.379
5.15
3.13
3.07
3.01
1.44
1.00
X : parts per Million : Proton


218.481
159.811
150.329
129.639
117.972
112.280
110.929
77.452
77.136
76.819
55.287
52.331
43.931
36.792
35.844
29.394
O
OMe
3o
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

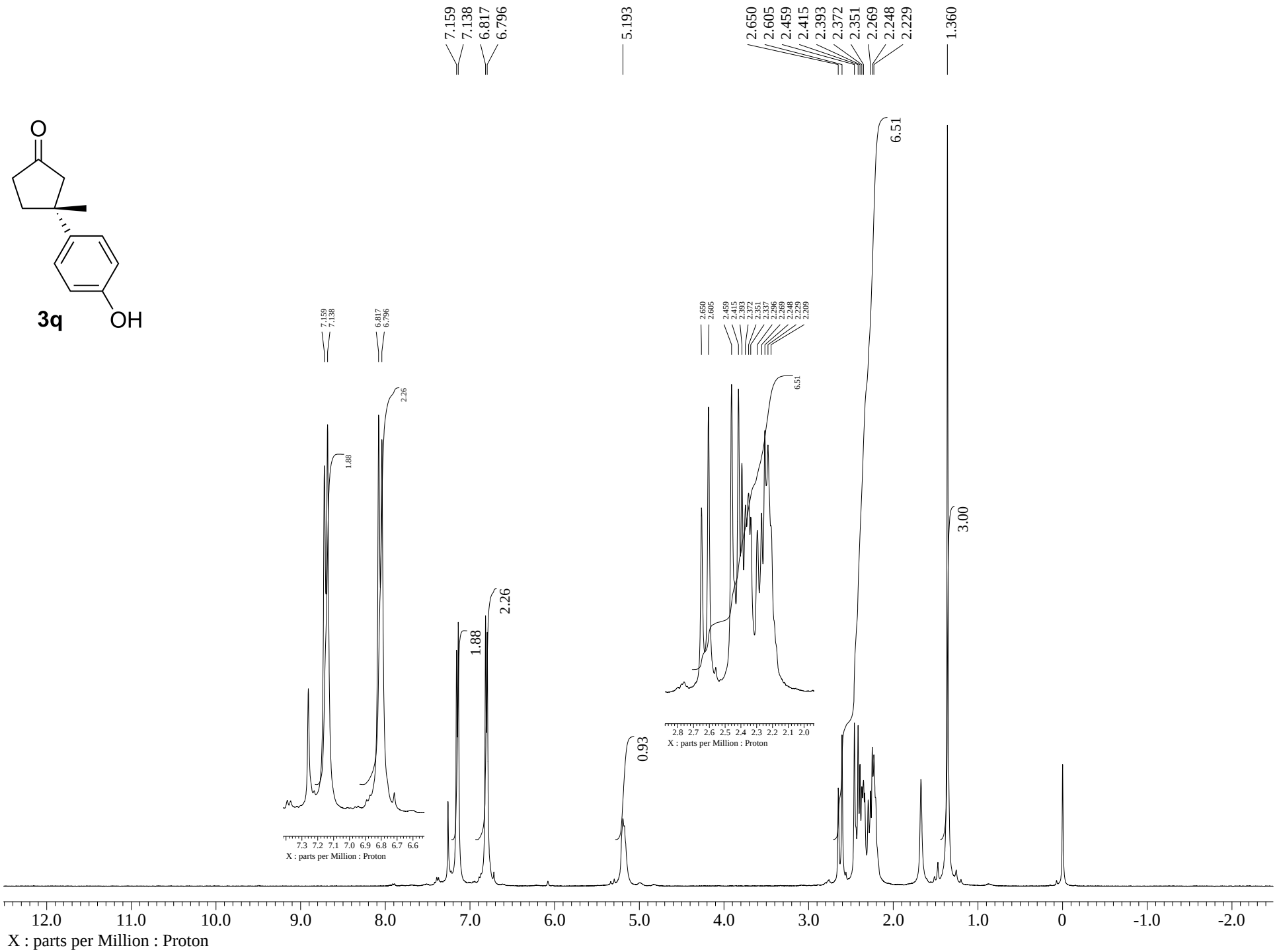

O
OMe
3o
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
129.639
117.968
112.275
110.924
55.287
52.326
36.792
35.844
29.394
X : parts per Million : Carbon13

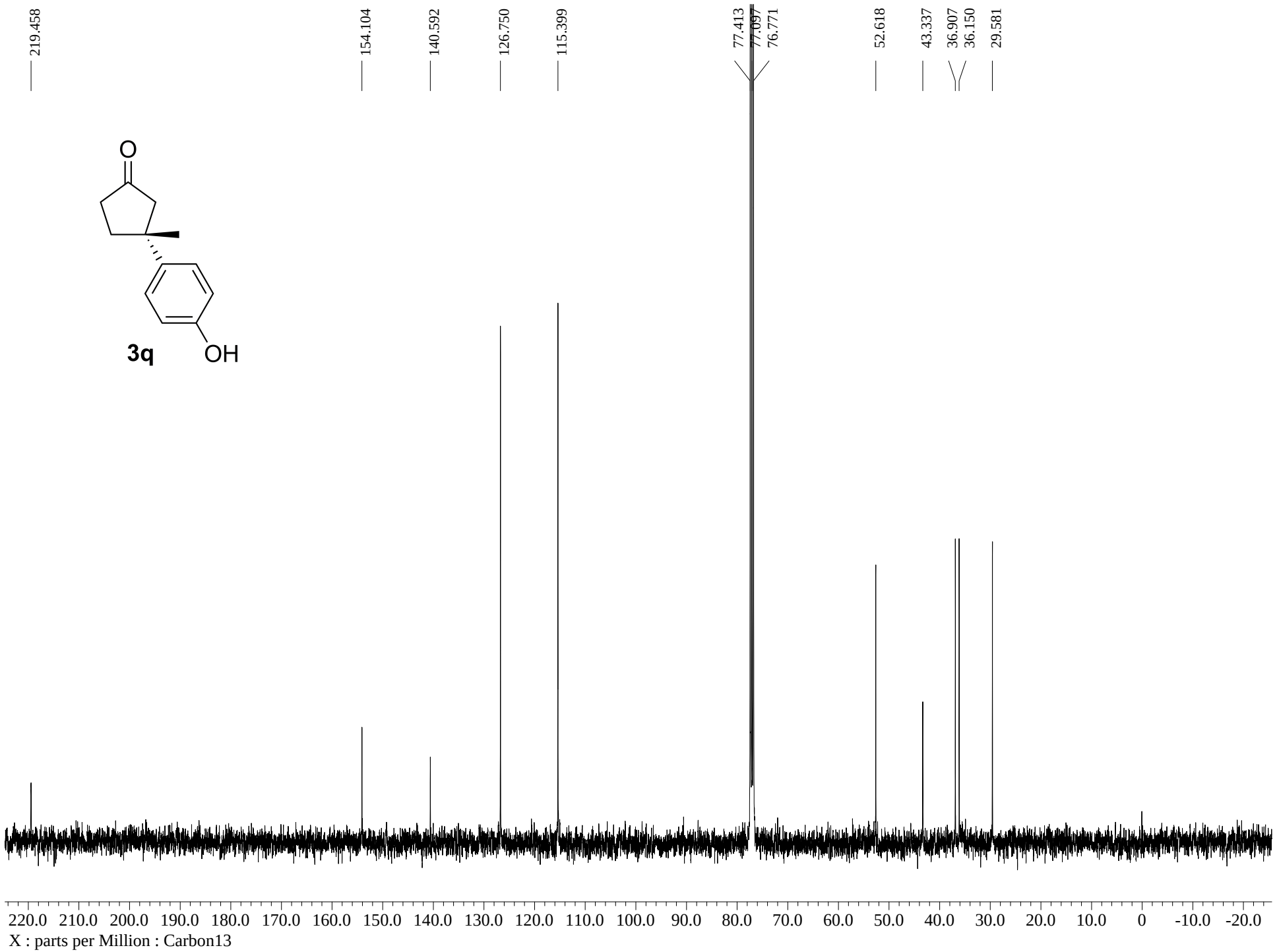

7.229
7.221
7.215
7.203
7.198
7.190
6.897
6.889
6.883
6.873
6.867
6.859
3.803
2.650
2.605
2.459
2.414
2.390
2.276
2.255
1.368
O
3p
OMe
1.92
1.92
1.92
1.00
5.10
2.89
2.95
X : parts per Million : Proton
X : parts per Million : Proton

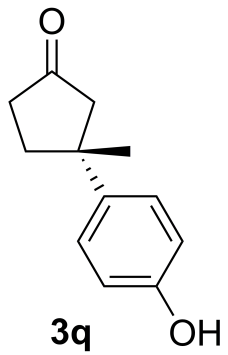

218.812
158.033
140.612
126.544
113.952
77.433
77.121
76.800
55.354
52.580
43.289
36.869
36.160
29.553
O
3p
OMe
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13


7.159
7.138
6.817
6.796
5.193
2.650
2.605
2.459
2.415
2.393
2.372
2.351
2.269
2.248
2.229
1.360
6.51
3.00
2.26
1.88
0.93
3q
OH
X : parts per Million : Proton


219.458
154.104
140.592
126.750
115.399
77.413
77.097
76.771
52.618
43.337
36.907
36.150
29.581
O
OH
3q
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

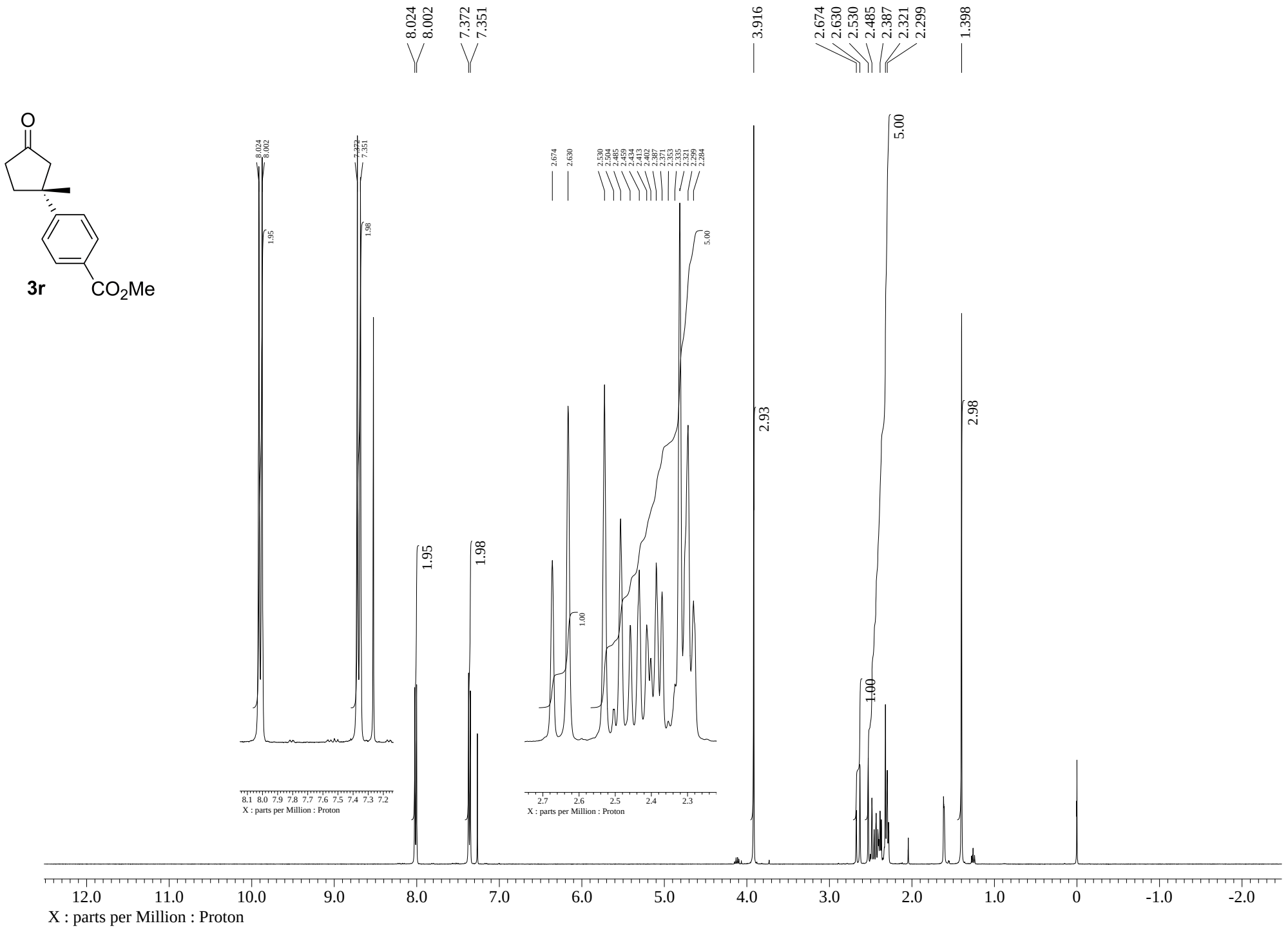


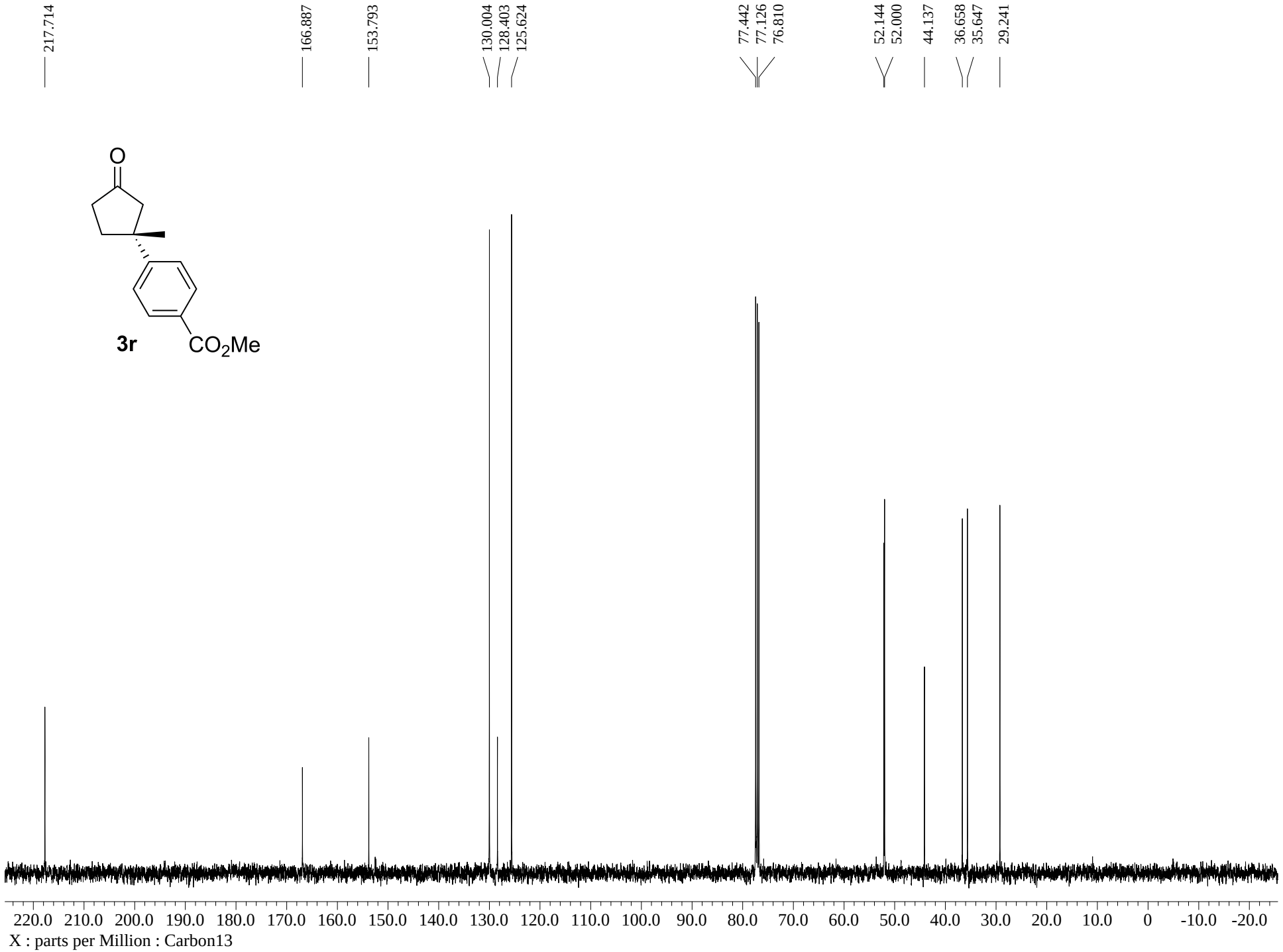
3q

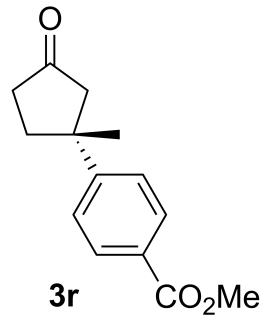
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0

126.745 115.399 52.613 36.907 36.150 29.576

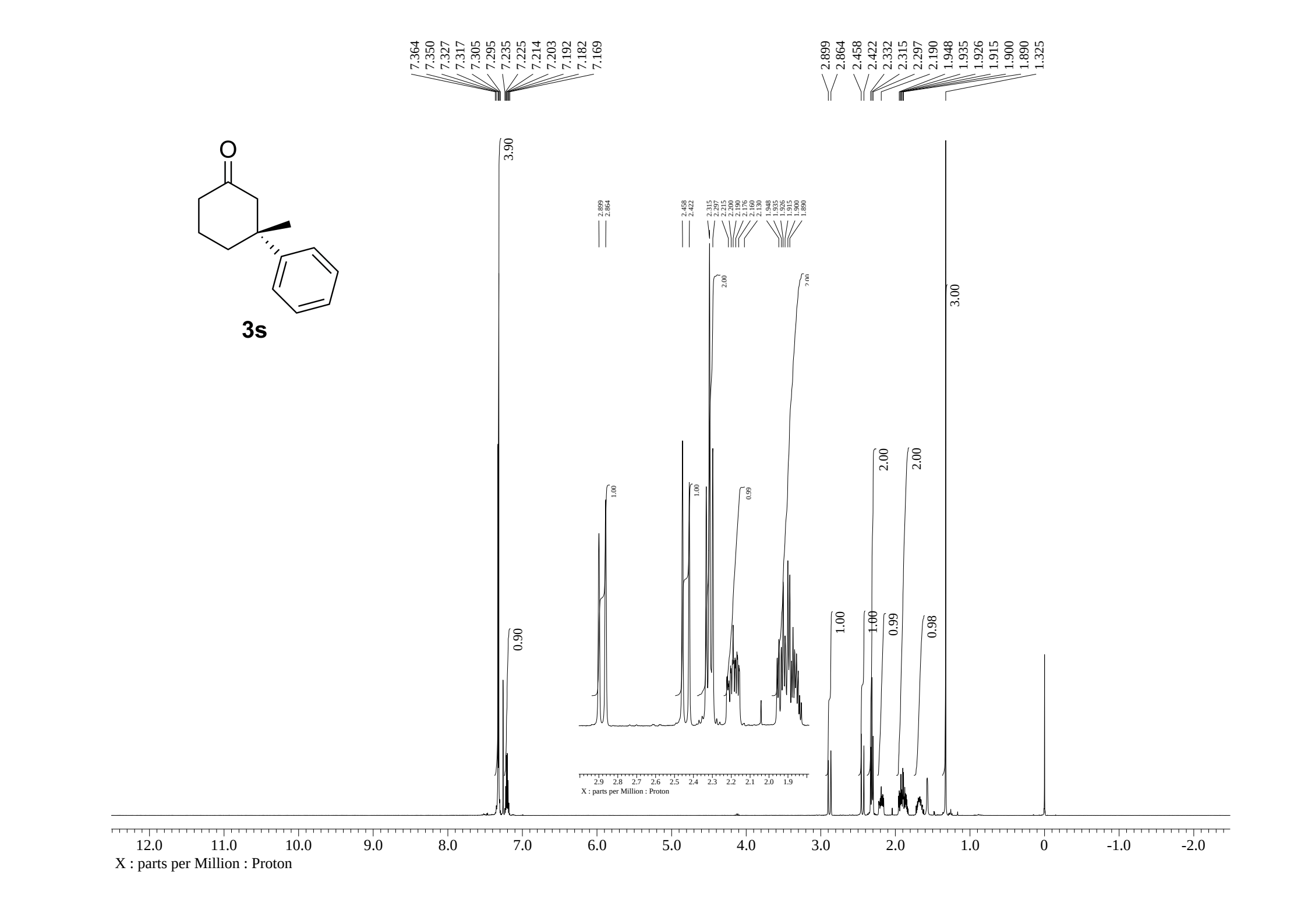
X : parts per Million : Carbon13

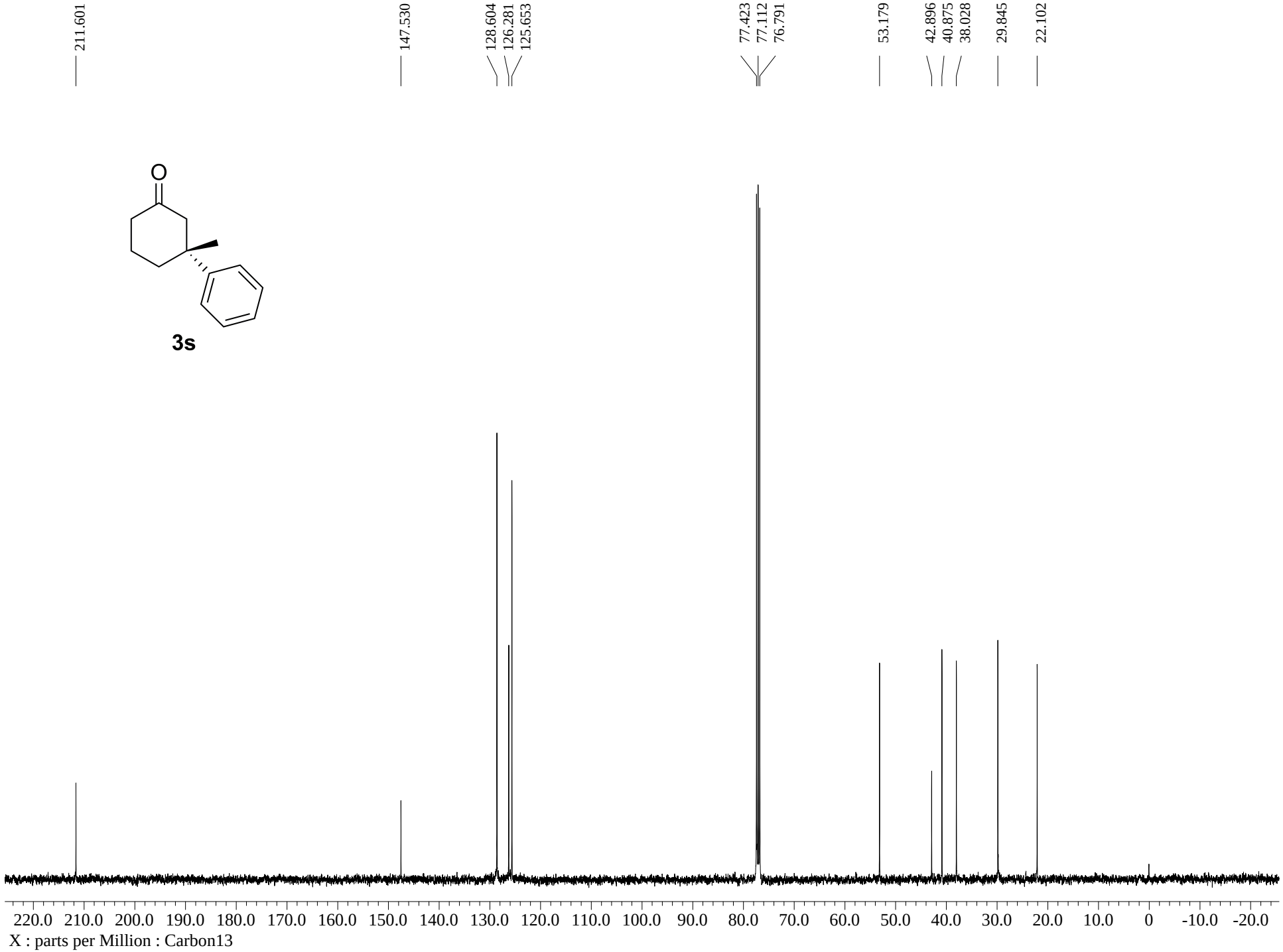

8.024
8.002
7.372
7.351
3.916
2.674
2.630
2.530
2.485
2.387
2.321
2.299
1.398
O
3r
CO2Me
1.95
1.98
2.93
5.00
1.00
2.98
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0

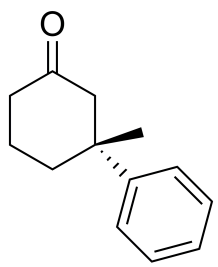

217.714
166.887
153.793
130.004
128.403
125.624
77.442
77.126
76.810
52.144
52.000
44.137
36.658
35.647
29.241
O
3r
CO2Me
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13

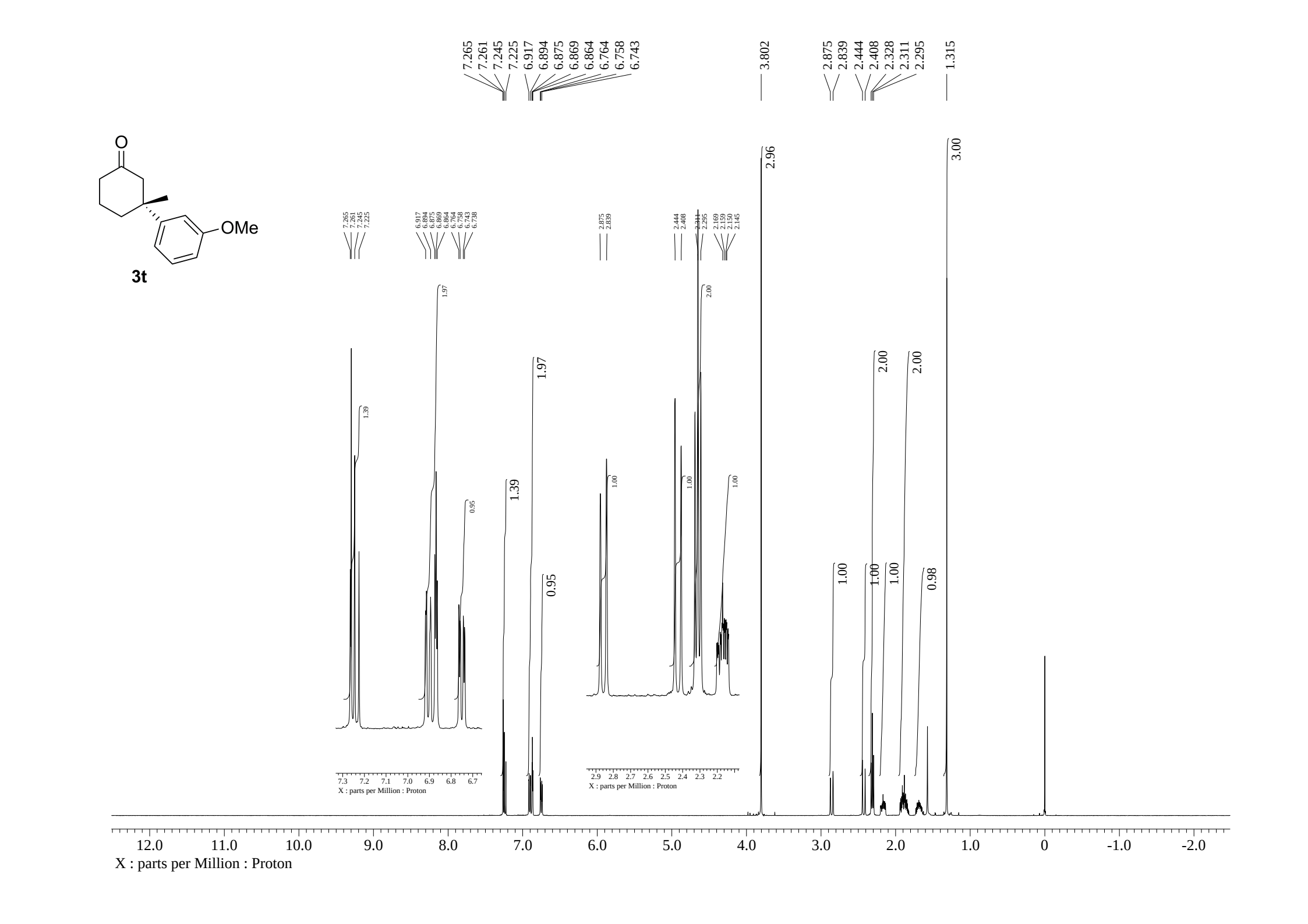

7.364
7.350
7.327
7.317
7.305
7.295
7.235
7.225
7.214
7.203
7.192
7.182
7.169
2.899
2.864
2.458
2.422
2.332
2.315
2.297
2.190
1.948
1.935
1.926
1.915
1.900
1.890
1.325
O
3s
3.90
0.90
1.00
2.00
2.00
1.00
1.00
0.99
0.98
3.00
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

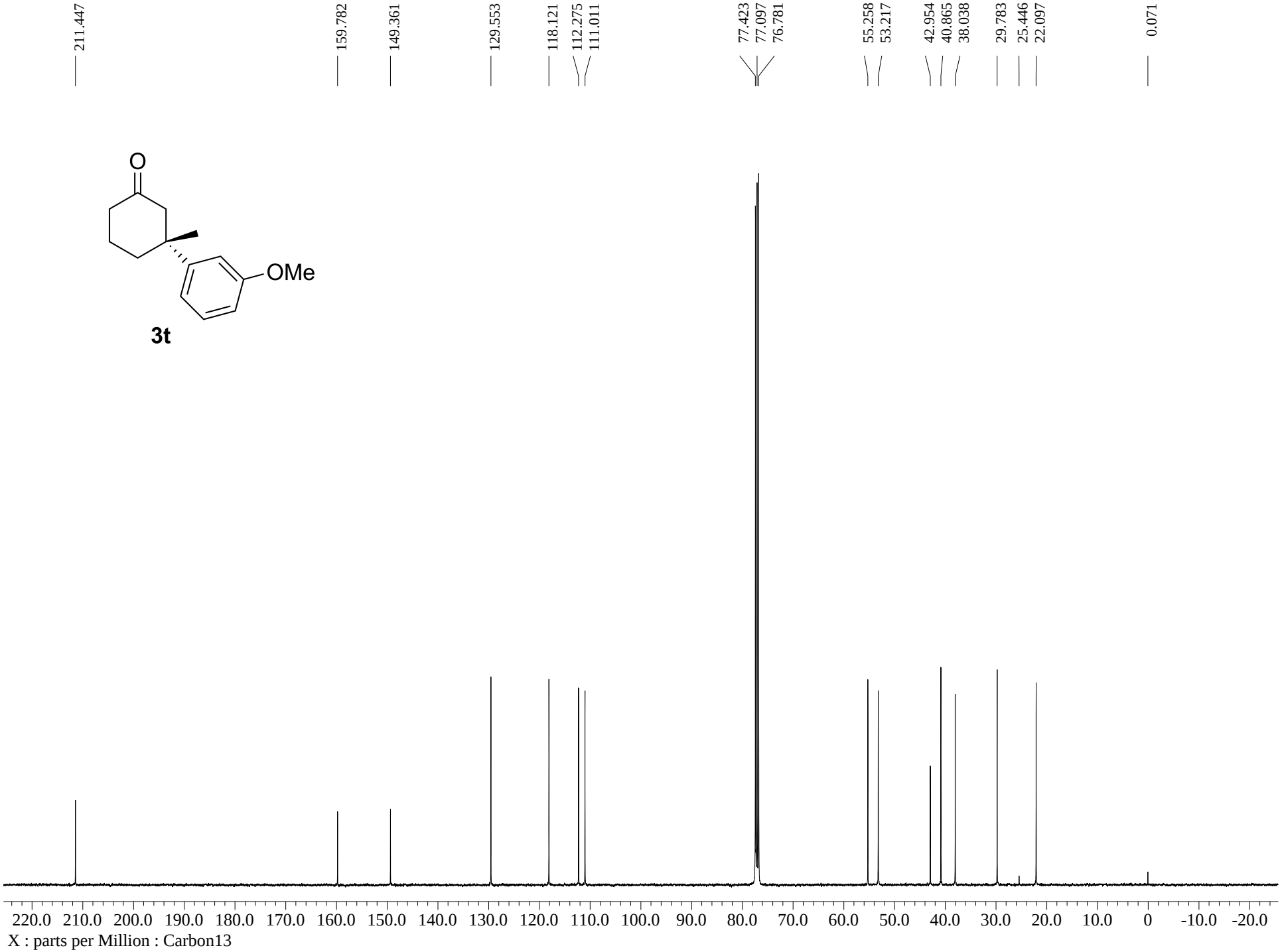

211.601
147.530
128.604
126.281
125.653
77.423
77.112
76.791
53.179
42.896
40.875
38.028
29.845
22.102
O
3s
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

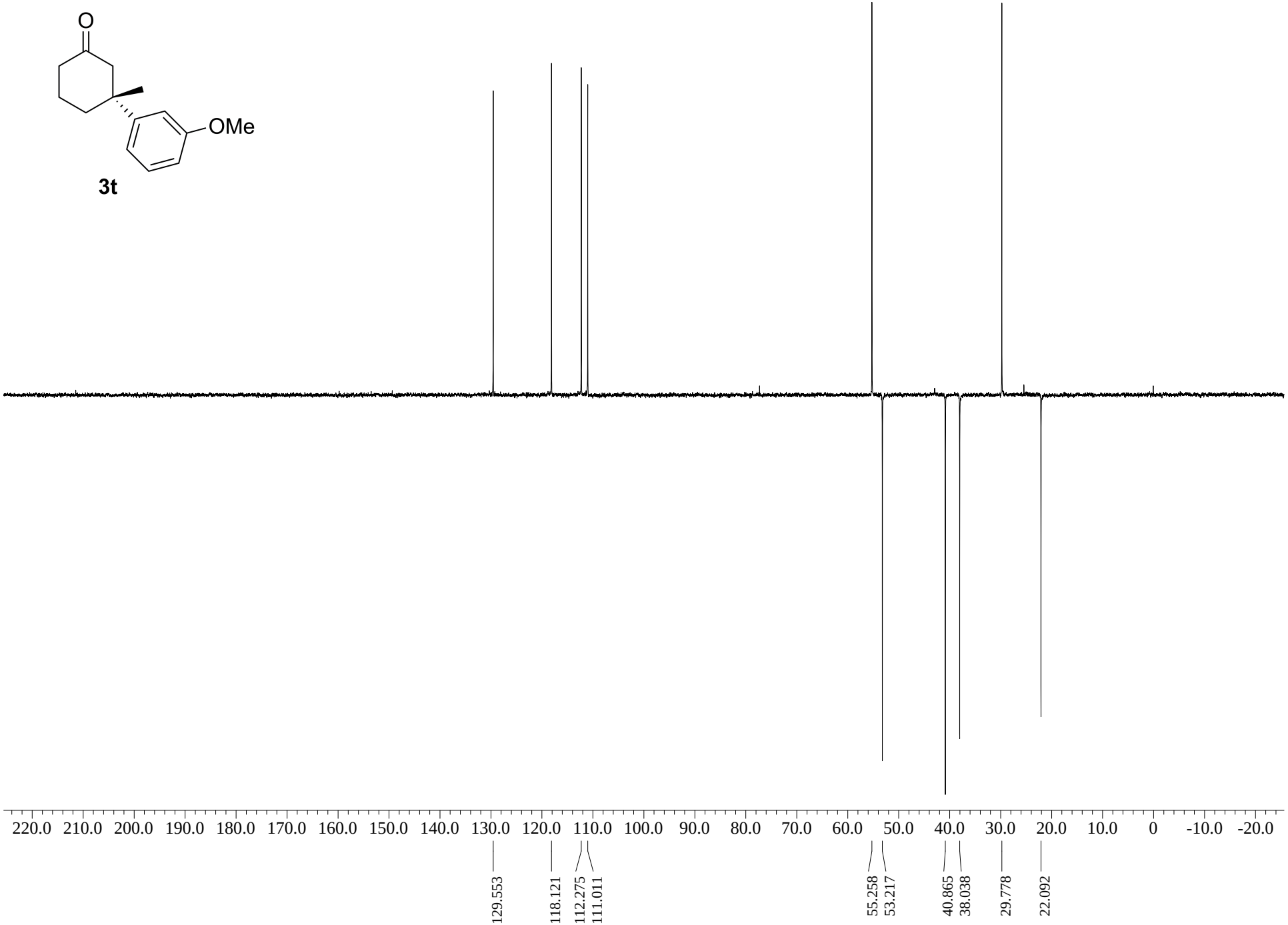


3s

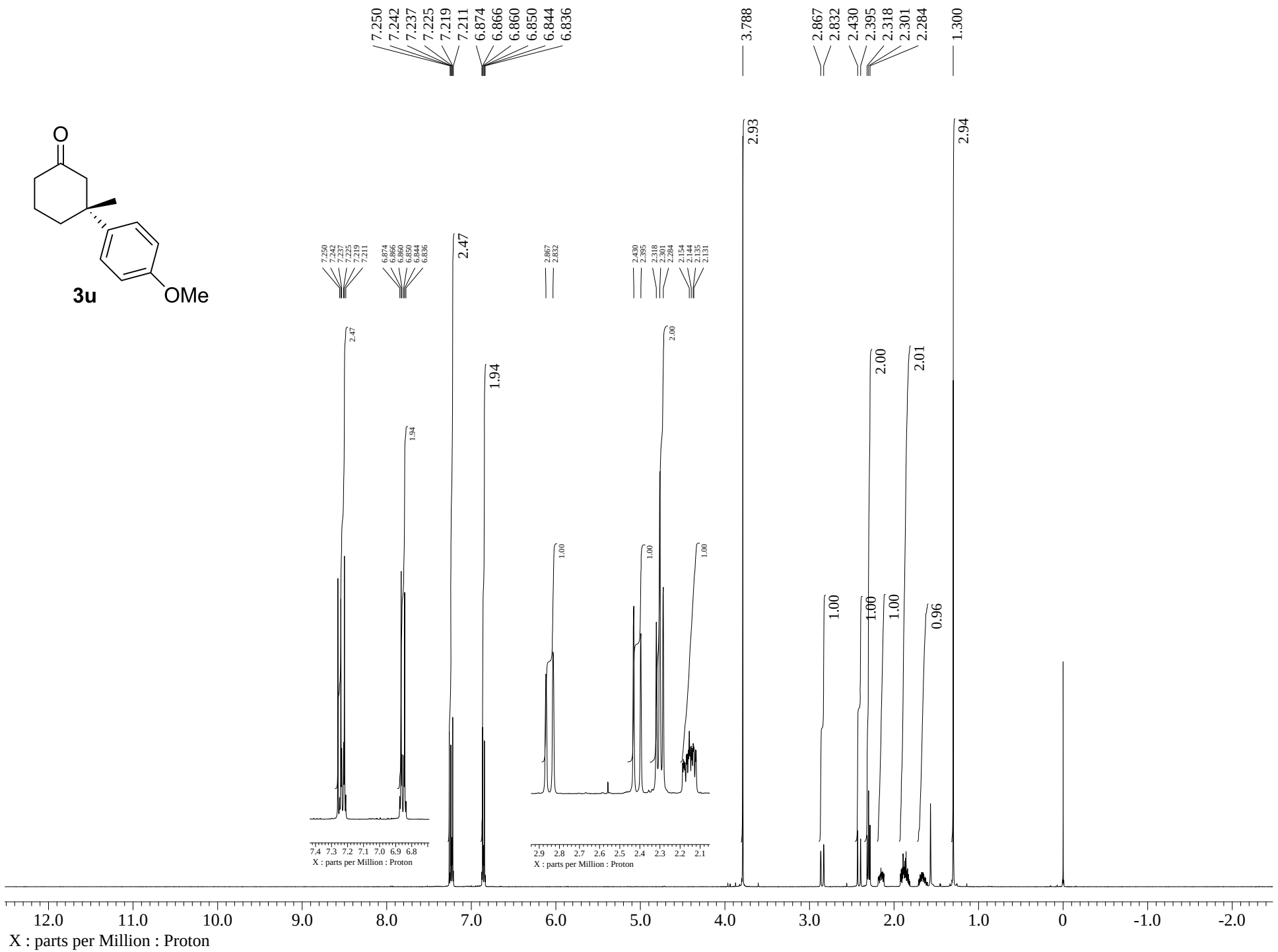
X : parts per Million : Carbon13

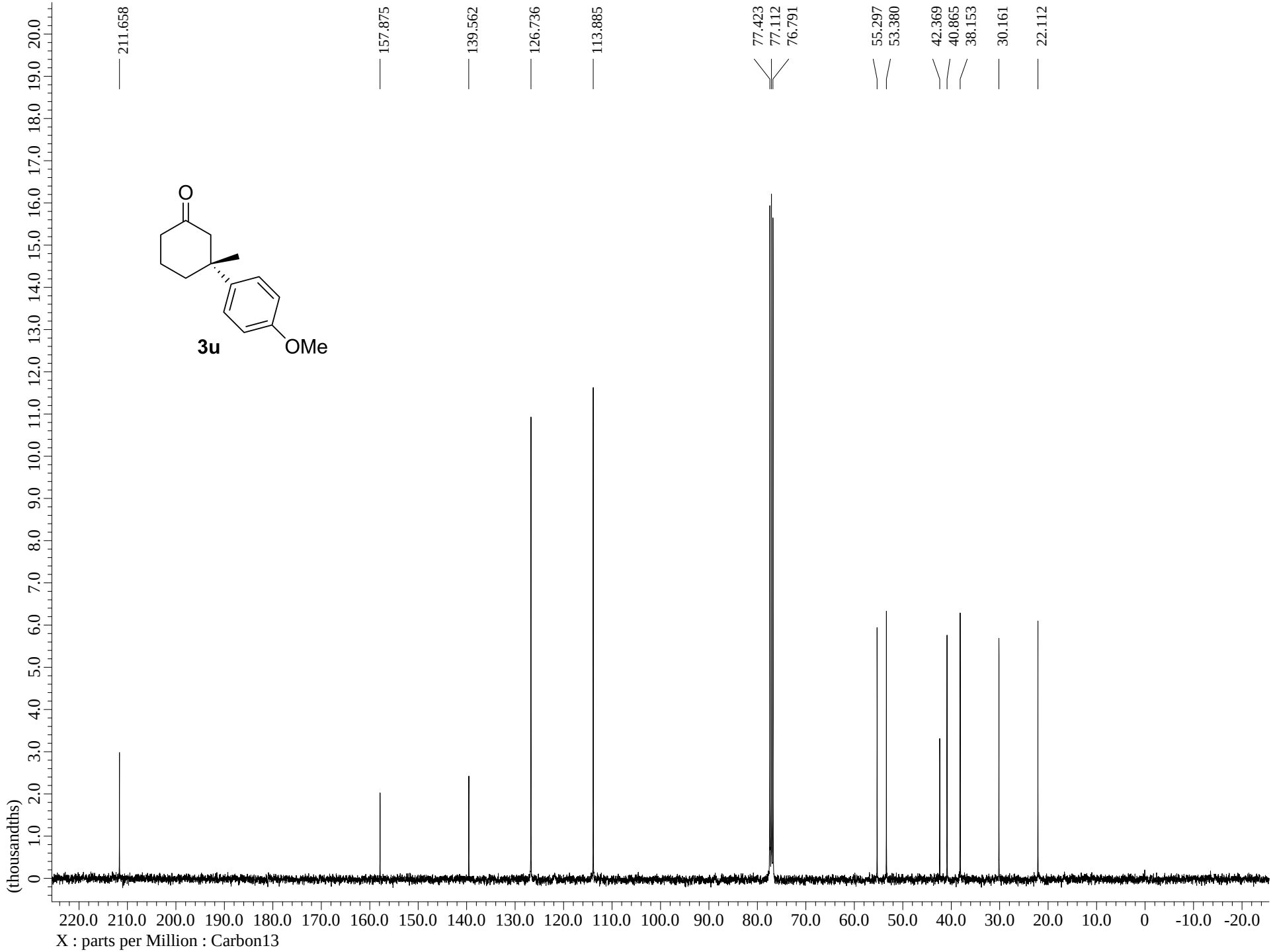

O
OMe
3t
7.265
7.261
7.245
7.225
6.917
6.894
6.875
6.869
6.864
6.764
6.758
6.743
3.802
2.875
2.839
2.444
2.408
2.328
2.311
2.295
1.315
2.96
3.00
2.00
2.00
1.39
1.97
0.95
1.00
1.00
1.00
0.98
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0

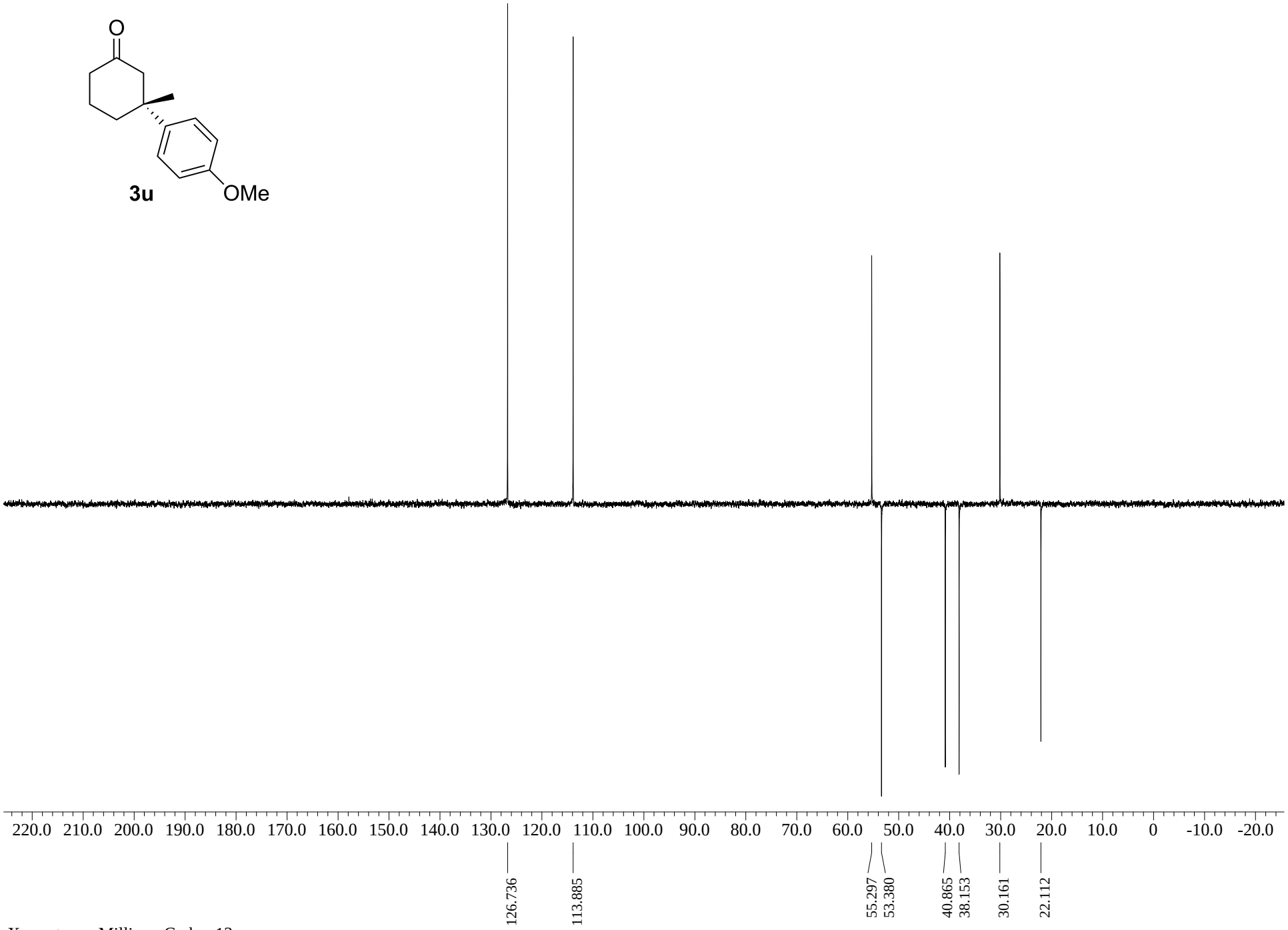

211.447
159.782
149.361
129.553
118.121
112.275
111.011
77.423
77.097
76.781
55.258
53.217
42.954
40.865
38.038
29.783
25.446
22.097
0.071
O
OMe
3t
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



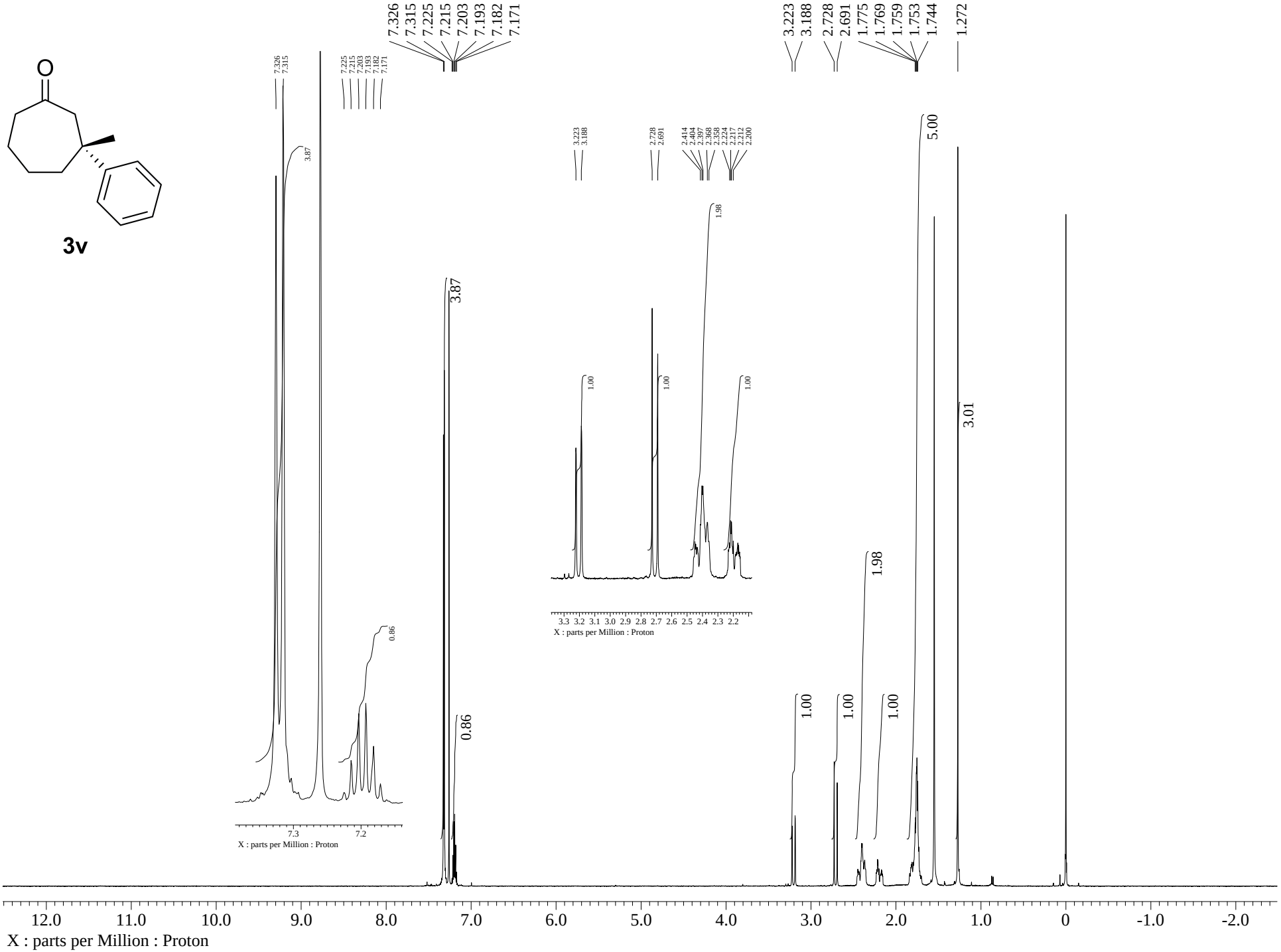
X : parts per Million : Carbon13

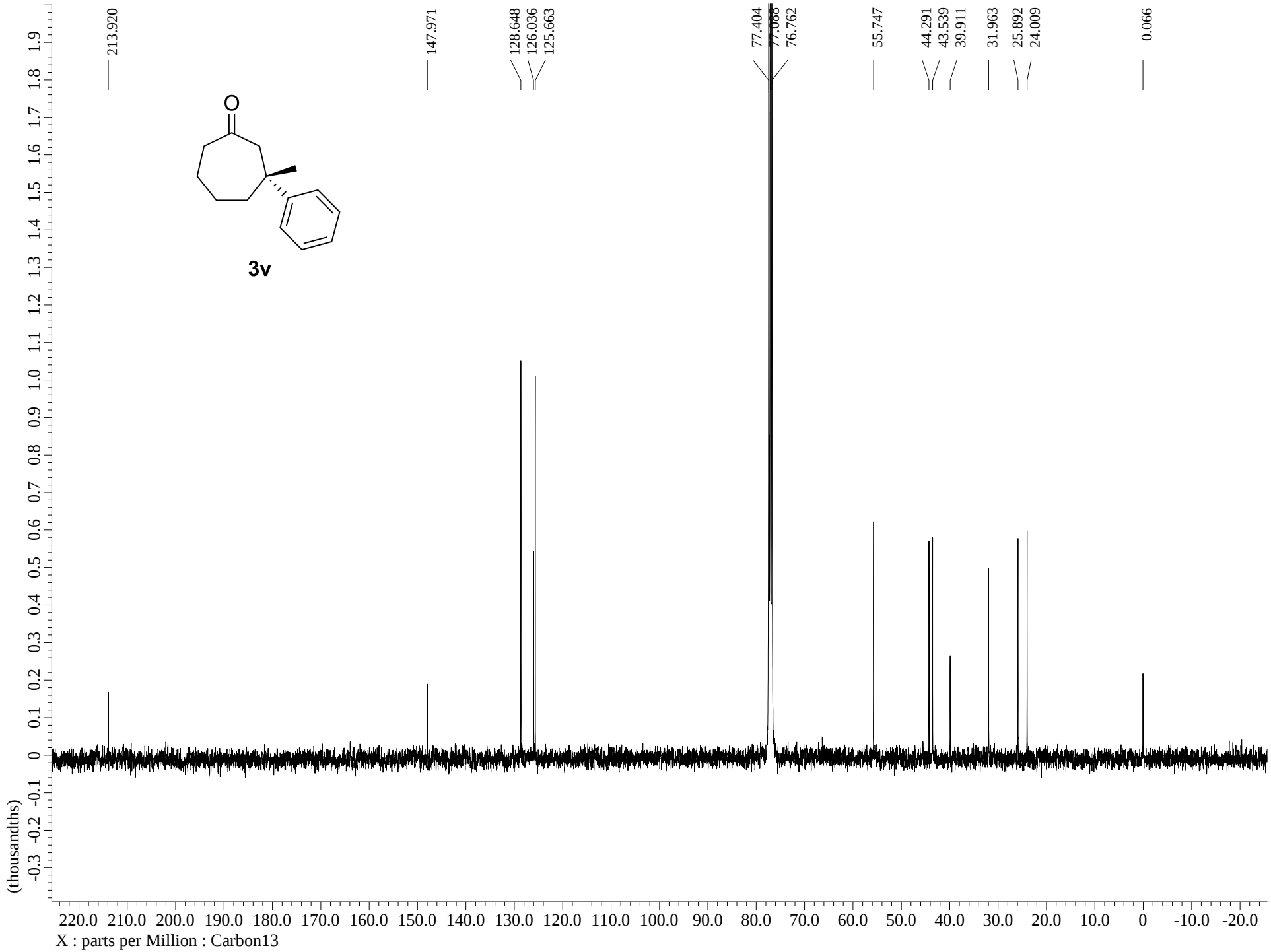

7.250
7.242
7.237
7.225
7.219
7.211
6.874
6.866
6.860
6.850
6.844
6.836
3.788
2.867
2.832
2.430
2.395
2.318
2.301
2.284
1.300
O
3u
OMe
2.93
2.94
2.47
1.94
2.00
2.01
1.00
1.00
1.00
0.96
2.154
2.144
2.135
2.131
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

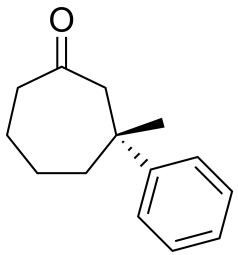

211.658
157.875
139.562
126.736
113.885
77.423
77.112
76.791
55.297
53.380
42.369
40.865
38.153
30.161
22.112
O
3u
OMe
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13

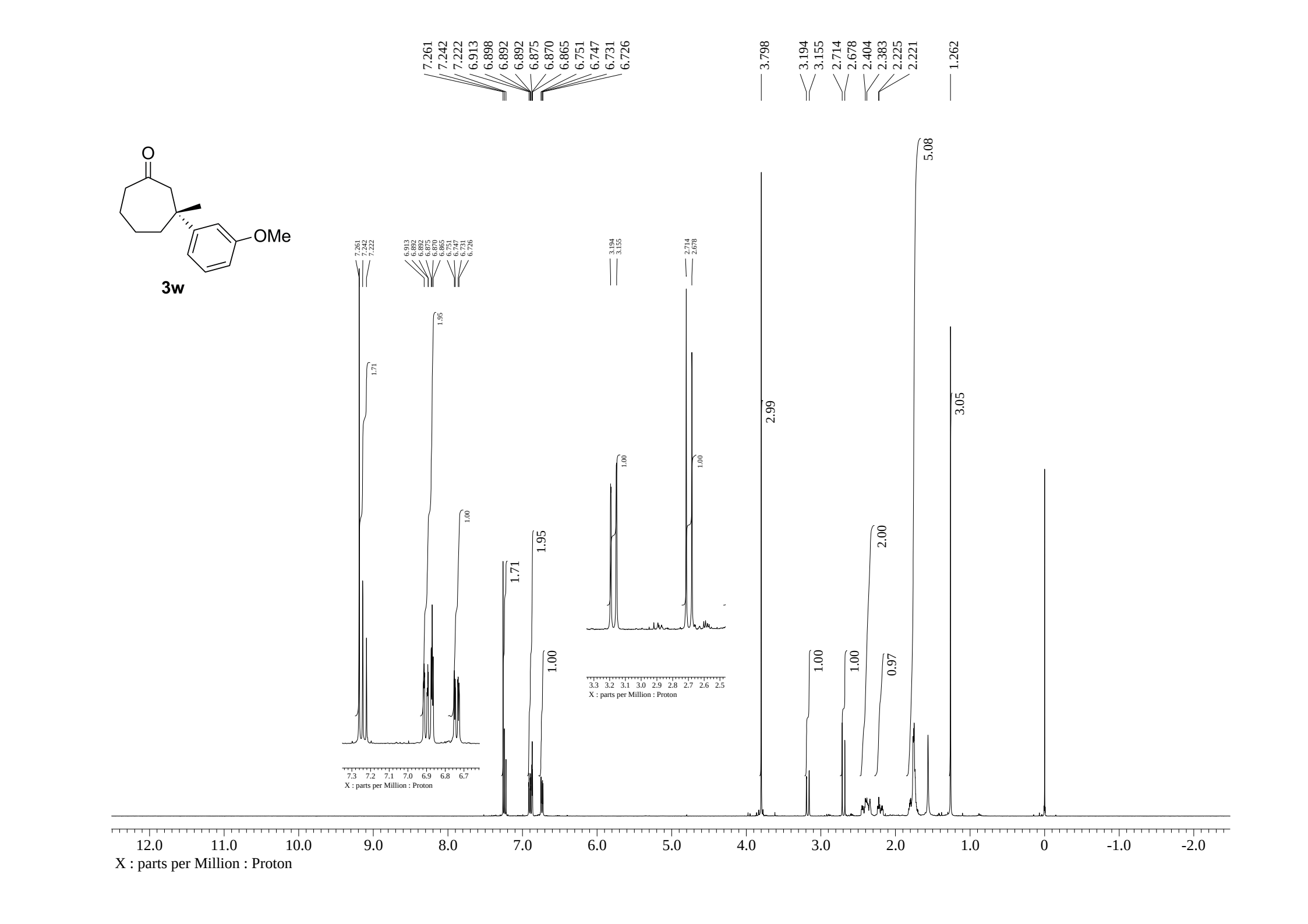

3v
7.326
7.315
7.225
7.215
7.203
7.193
7.182
7.171
3.223
3.188
2.728
2.691
1.775
1.769
1.759
1.753
1.744
1.272
3.87
0.86
1.00
1.98
5.00
3.01
X : parts per Million : Proton

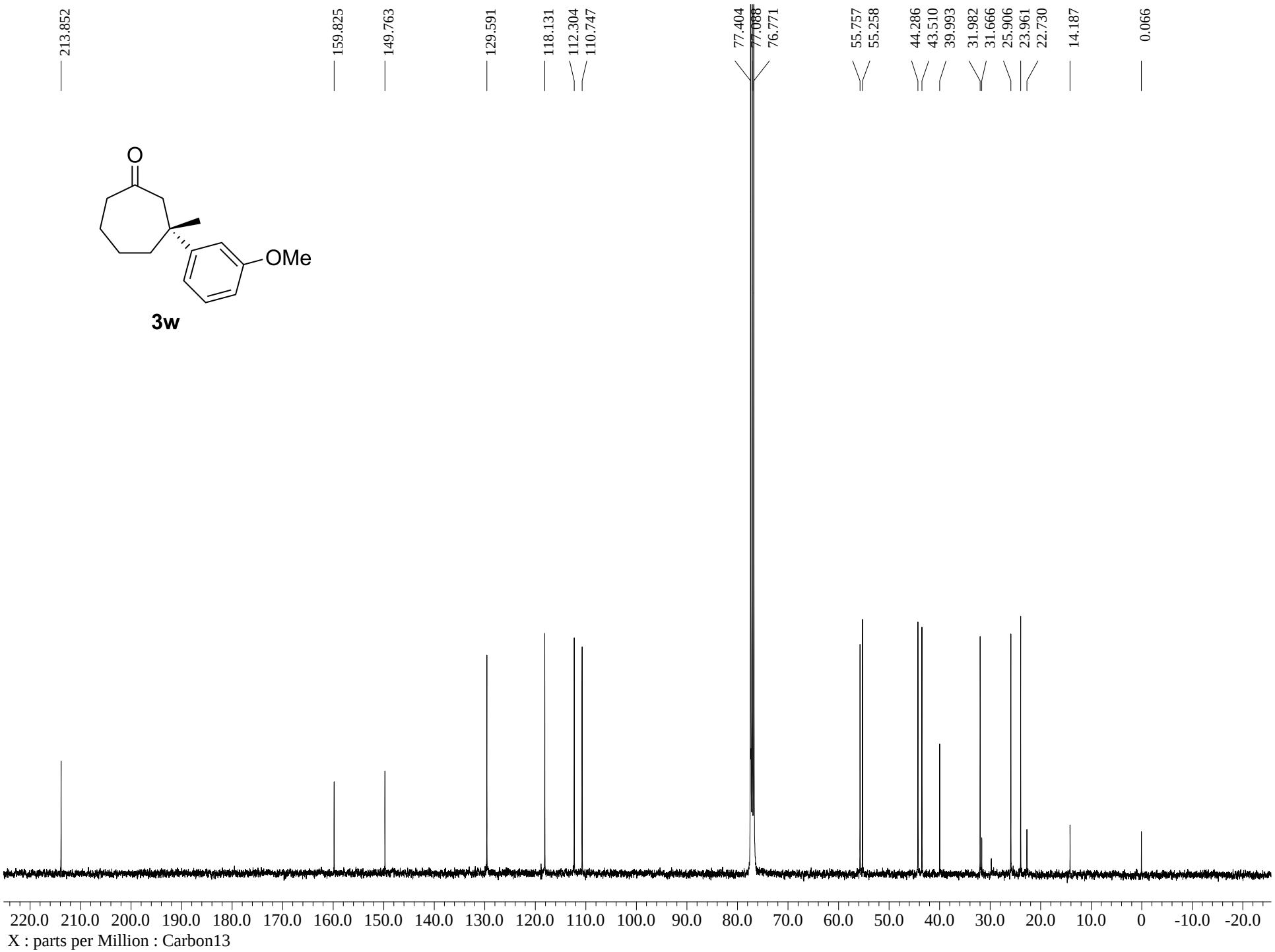

213.920
147.971
128.648
126.036
125.663
77.404
77.068
76.762
55.747
44.291
43.539
39.911
31.963
25.892
24.009
0.066
O
3v
(thousandths)
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

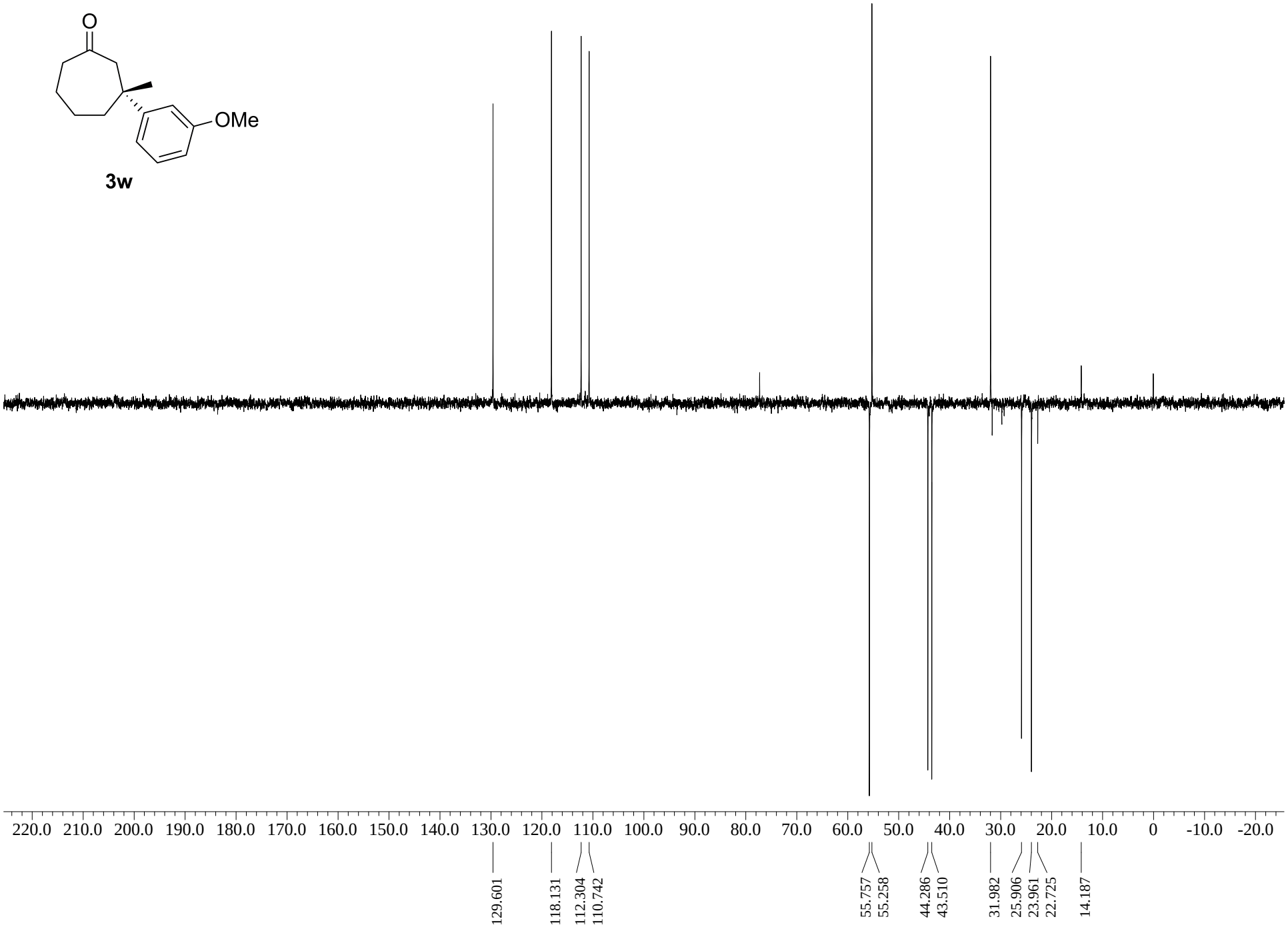


3v

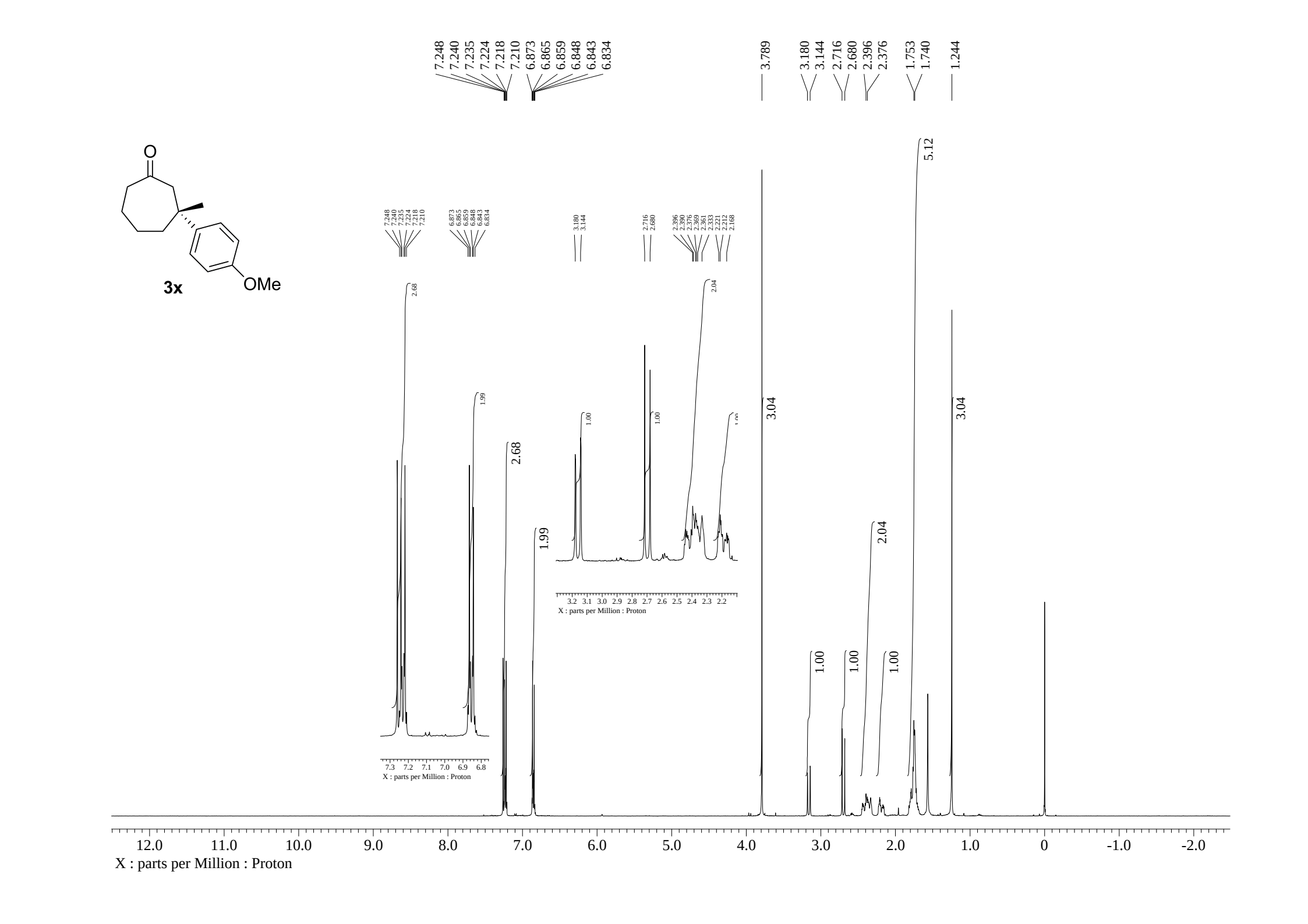
X : parts per Million : Carbon13

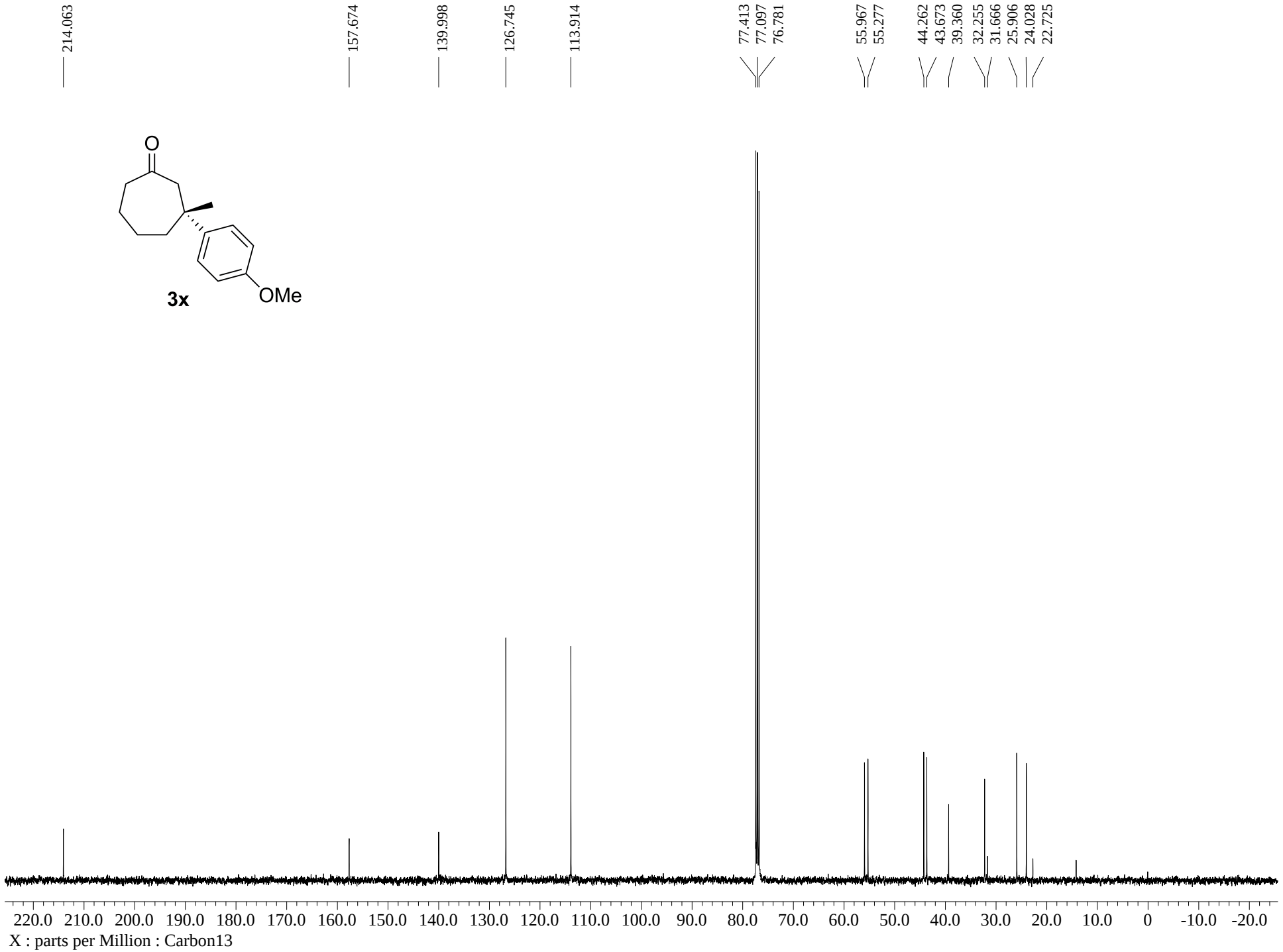

7.261
7.242
7.222
6.913
6.898
6.892
6.892
6.875
6.870
6.865
6.751
6.747
6.731
6.726
3.798
3.194
3.155
2.714
2.678
2.404
2.383
2.225
2.221
1.262
O
OMe
3w
5.08
2.99
3.05
1.71
1.95
1.00
2.00
0.97
X : parts per Million : Proton

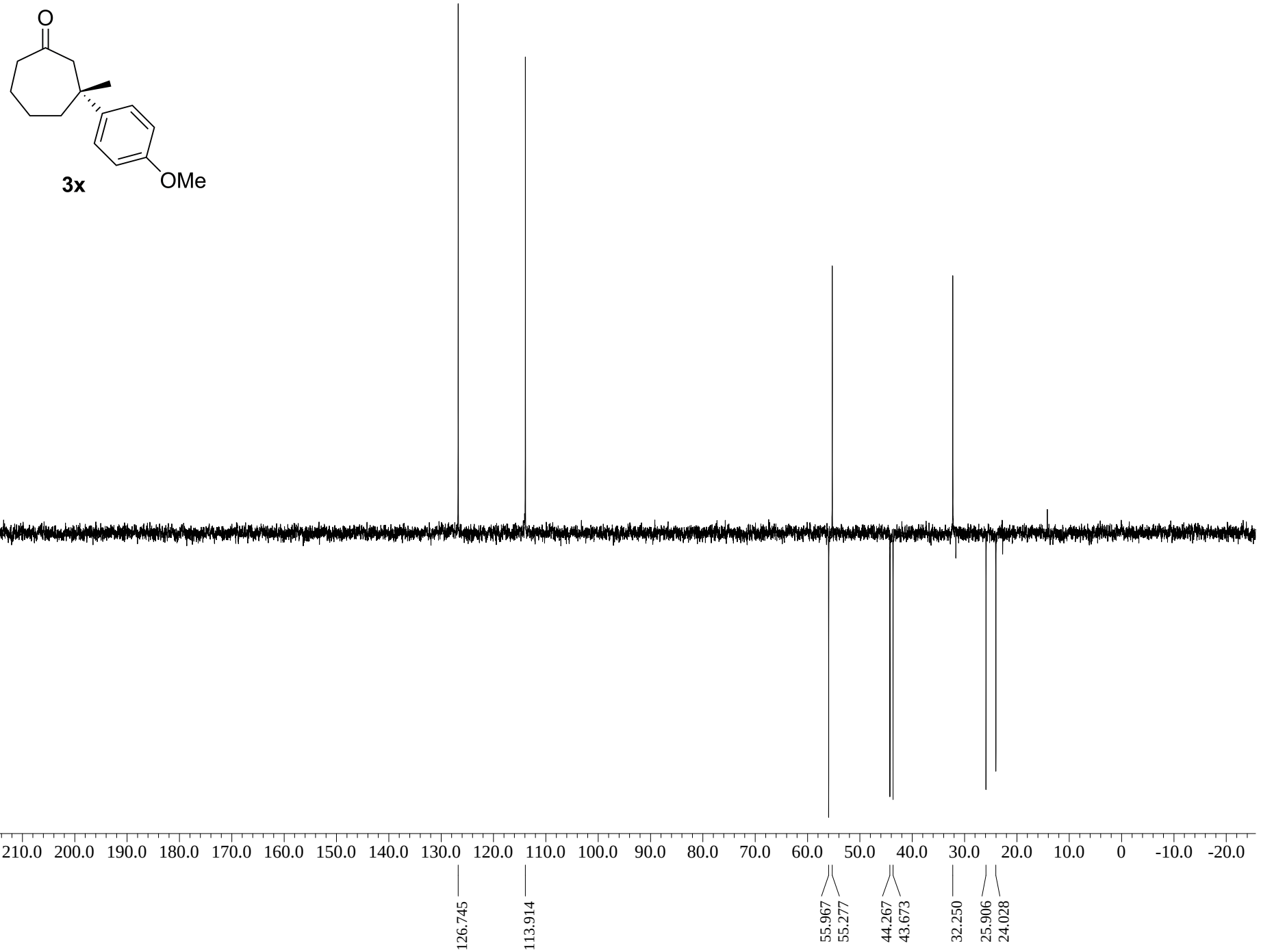

213.852
159.825
149.763
129.591
118.131
112.304
110.747
77.404
77.088
76.771
55.757
55.258
44.286
43.510
39.993
31.982
31.666
25.906
23.961
22.730
14.187
0.066
O
OMe
3w
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



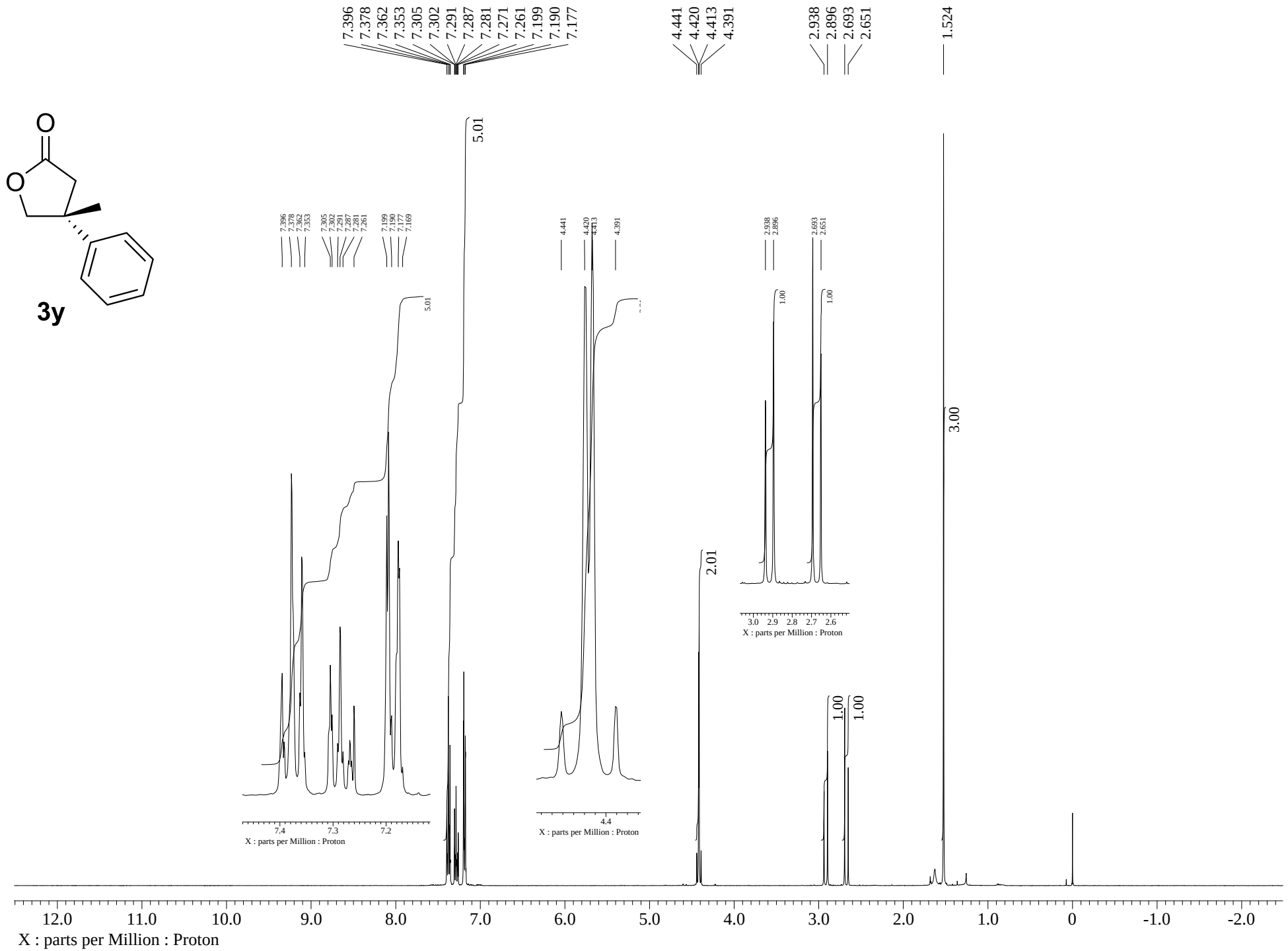
X : parts per Million : Carbon13

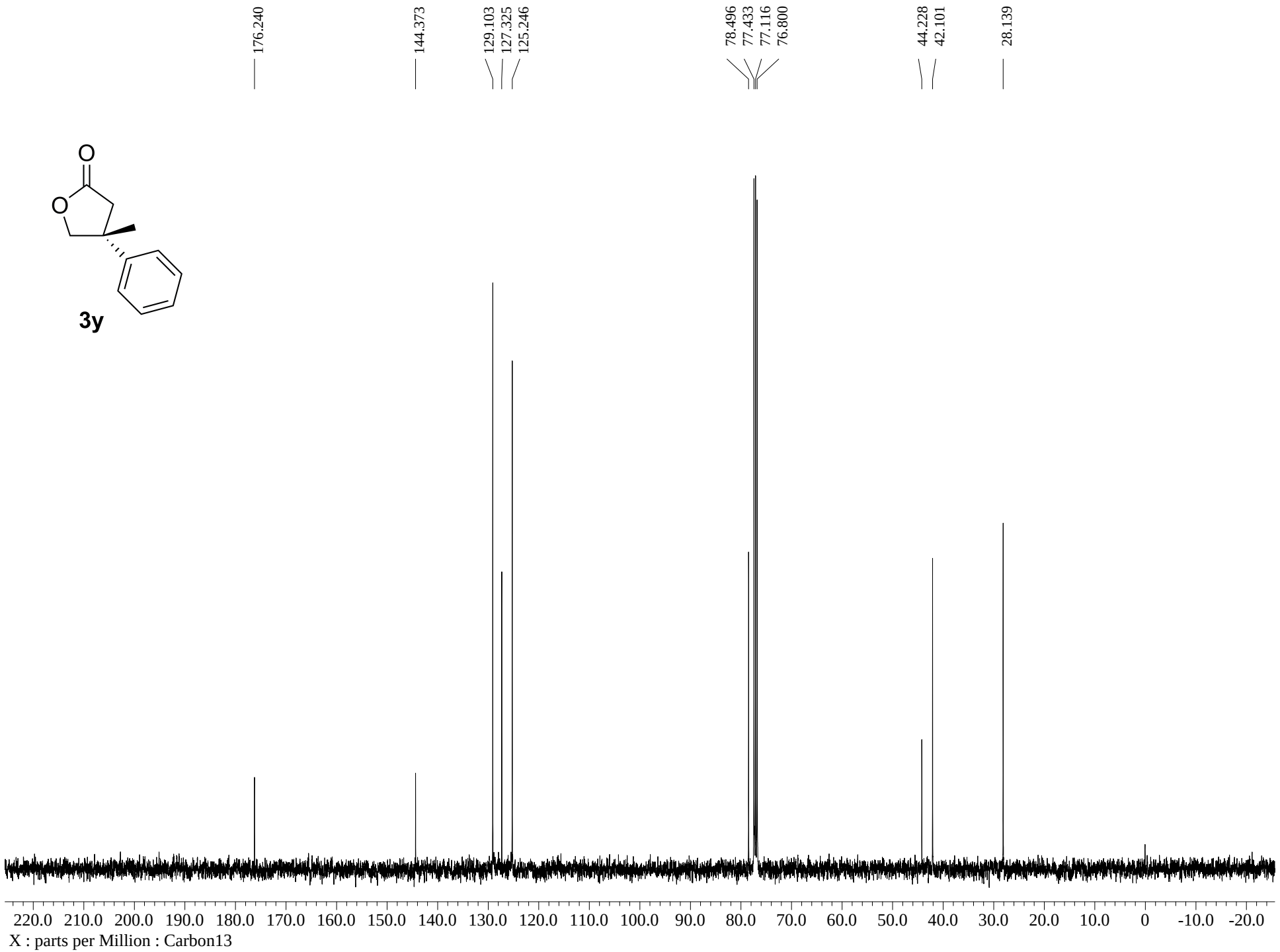

7.248
7.240
7.235
7.224
7.218
7.210
6.873
6.865
6.859
6.848
6.843
6.834
3.789
3.180
3.144
2.716
2.680
2.396
2.376
1.753
1.740
1.244
O
OMe
3x
5.12
3.04
3.04
2.68
2.04
1.99
1.00
1.00
1.00
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : Proton

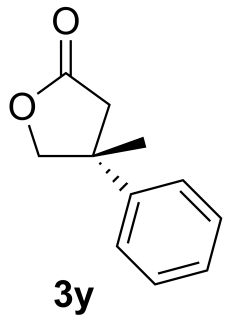

214.063
157.674
139.998
126.745
113.914
77.413
77.097
76.781
55.967
55.277
44.262
43.673
39.360
32.255
31.666
25.906
24.028
22.725
O
OMe
3x
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13

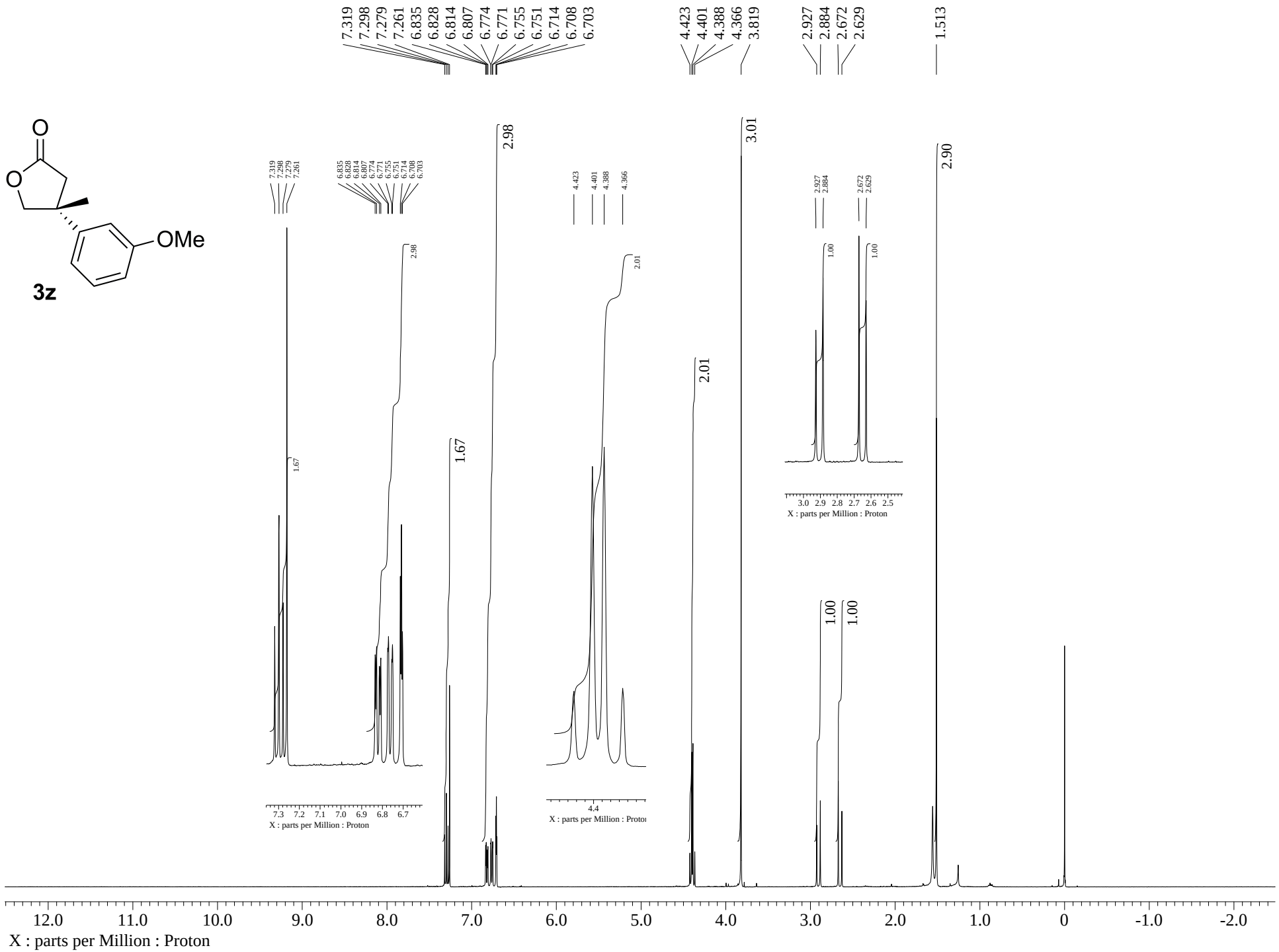

7.396
7.378
7.362
7.353
7.305
7.302
7.291
7.287
7.281
7.271
7.261
7.199
7.190
7.177
4.441
4.420
4.413
4.391
2.938
2.896
2.693
2.651
1.524
5.01
2.01
1.00
1.00
3.00
3y
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0

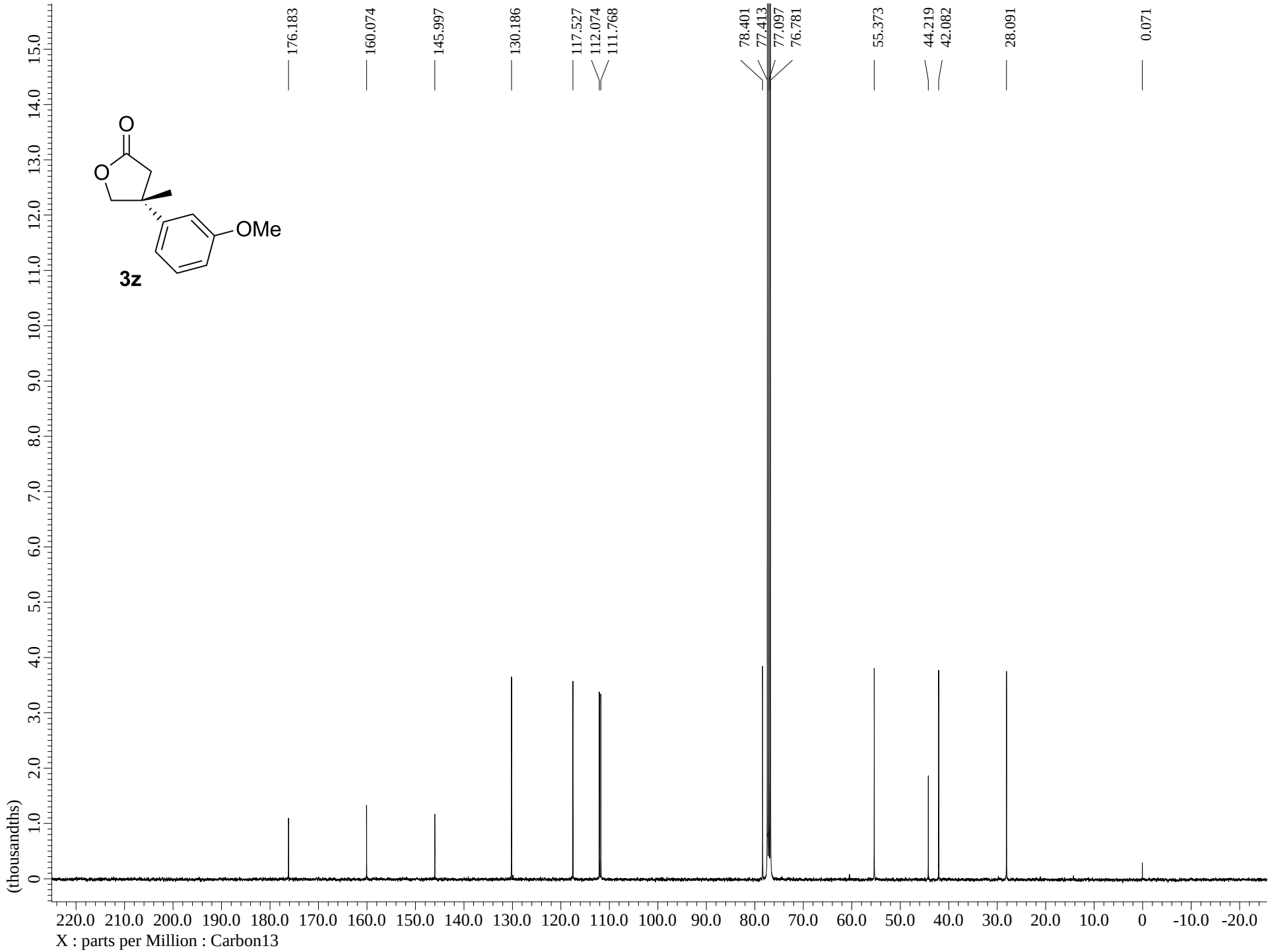

176.240
144.373
129.103
127.325
125.246
78.496
77.433
77.116
76.800
44.228
42.101
28.139
O
O
3y
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

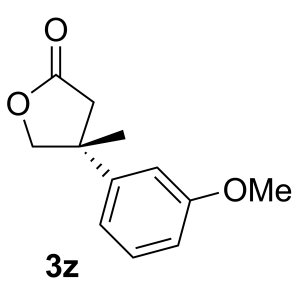


3y

X : parts per Million : Carbon13

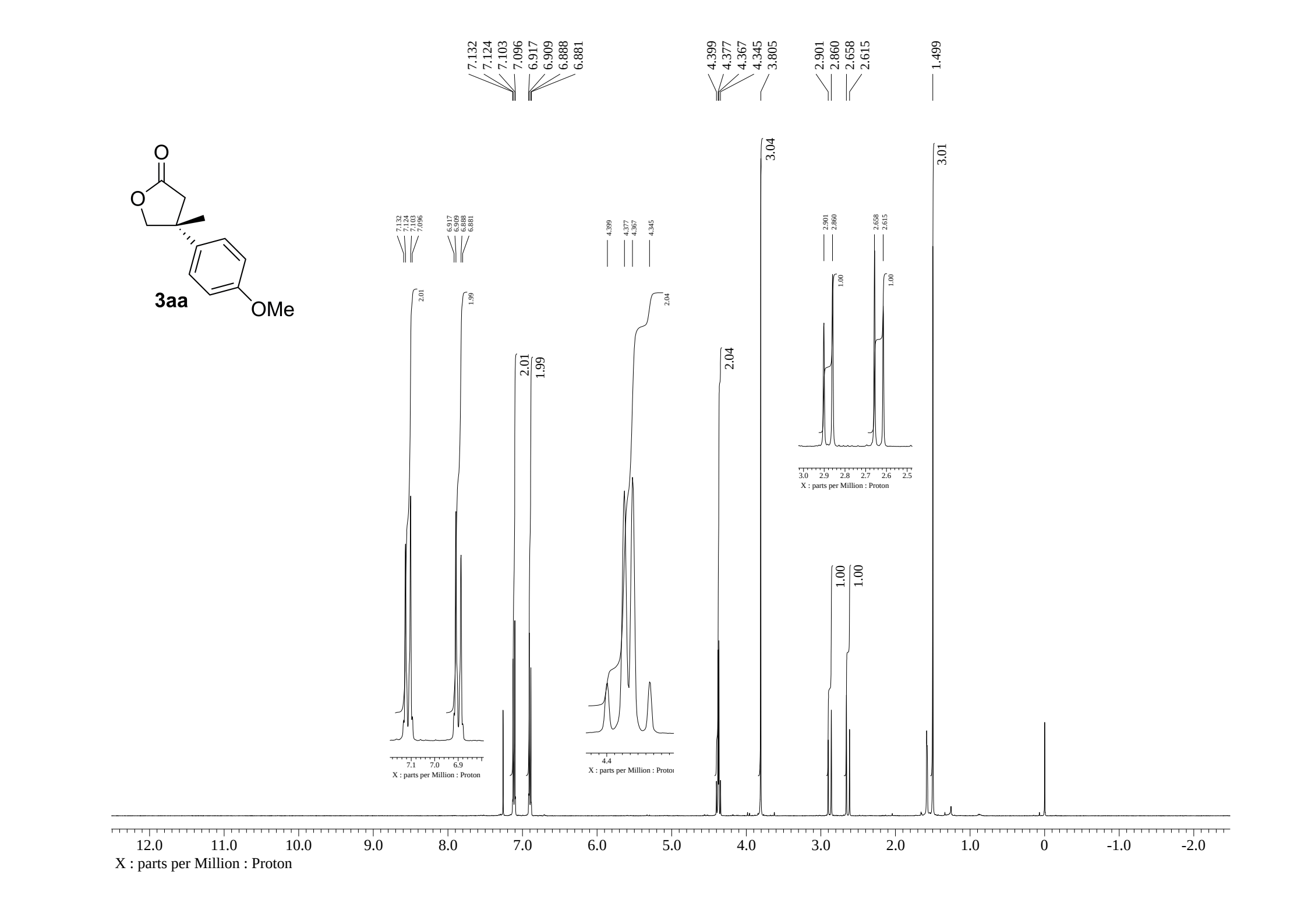

7.319
7.298
7.279
7.261
6.835
6.828
6.814
6.807
6.774
6.771
6.755
6.751
6.714
6.708
6.703
4.423
4.401
4.388
4.366
3.819
2.927
2.884
2.672
2.629
1.513
O
O
OMe
3z
1.67
2.98
1.67
2.01
3.01
1.00
1.00
2.90
7.3 7.2 7.1 7.0 6.9 6.8 6.7
X : parts per Million : Proton
4.4
X : parts per Million : Proton
3.0 2.9 2.8 2.7 2.6 2.5
X : parts per Million : Proton
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
X : parts per Million : Proton

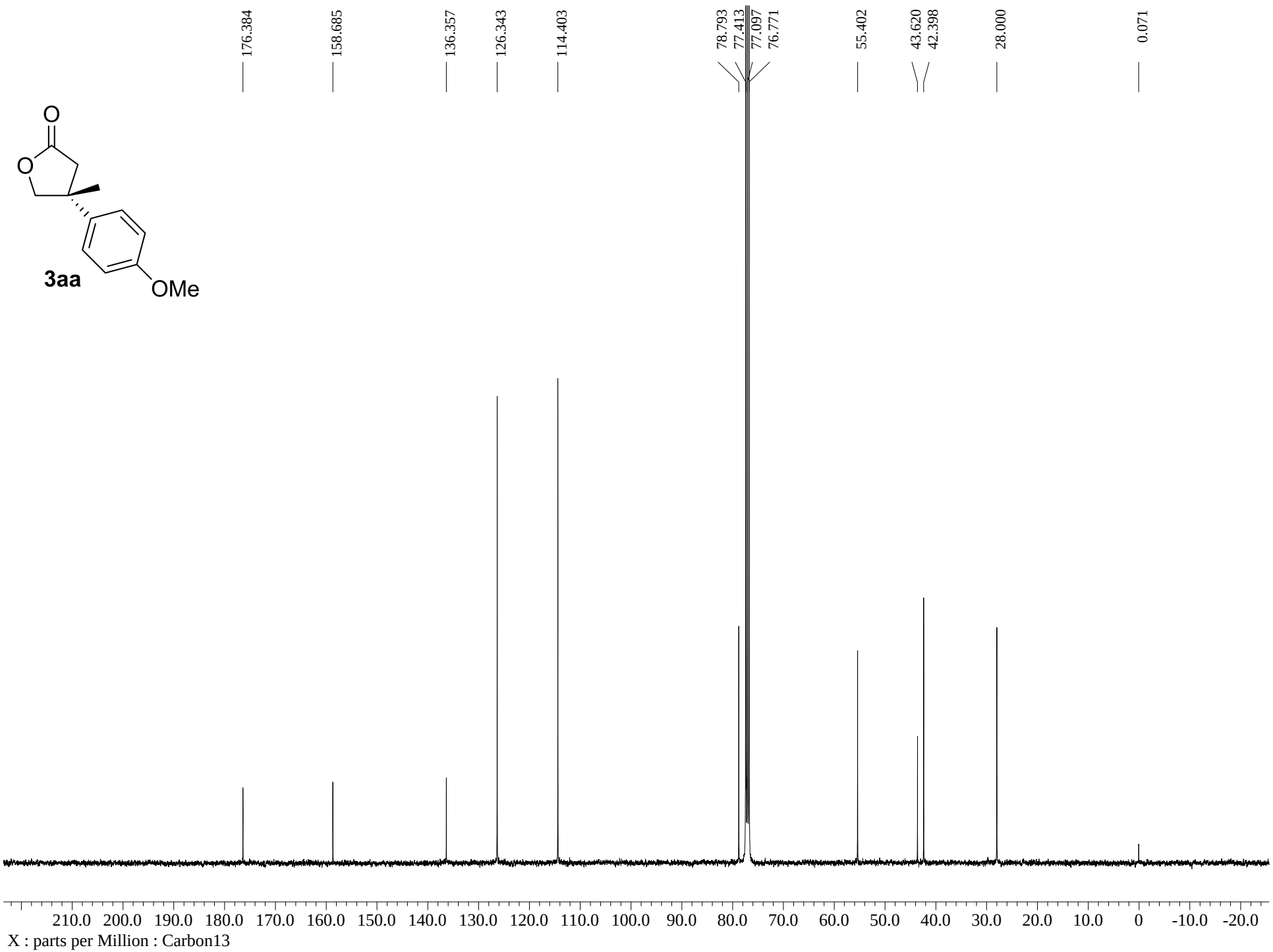

176.183
160.074
145.997
130.186
117.527
112.074
111.768
78.401
77.413
77.097
76.781
55.373
44.219
42.082
28.091
0.071
O
O
OMe
3z
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

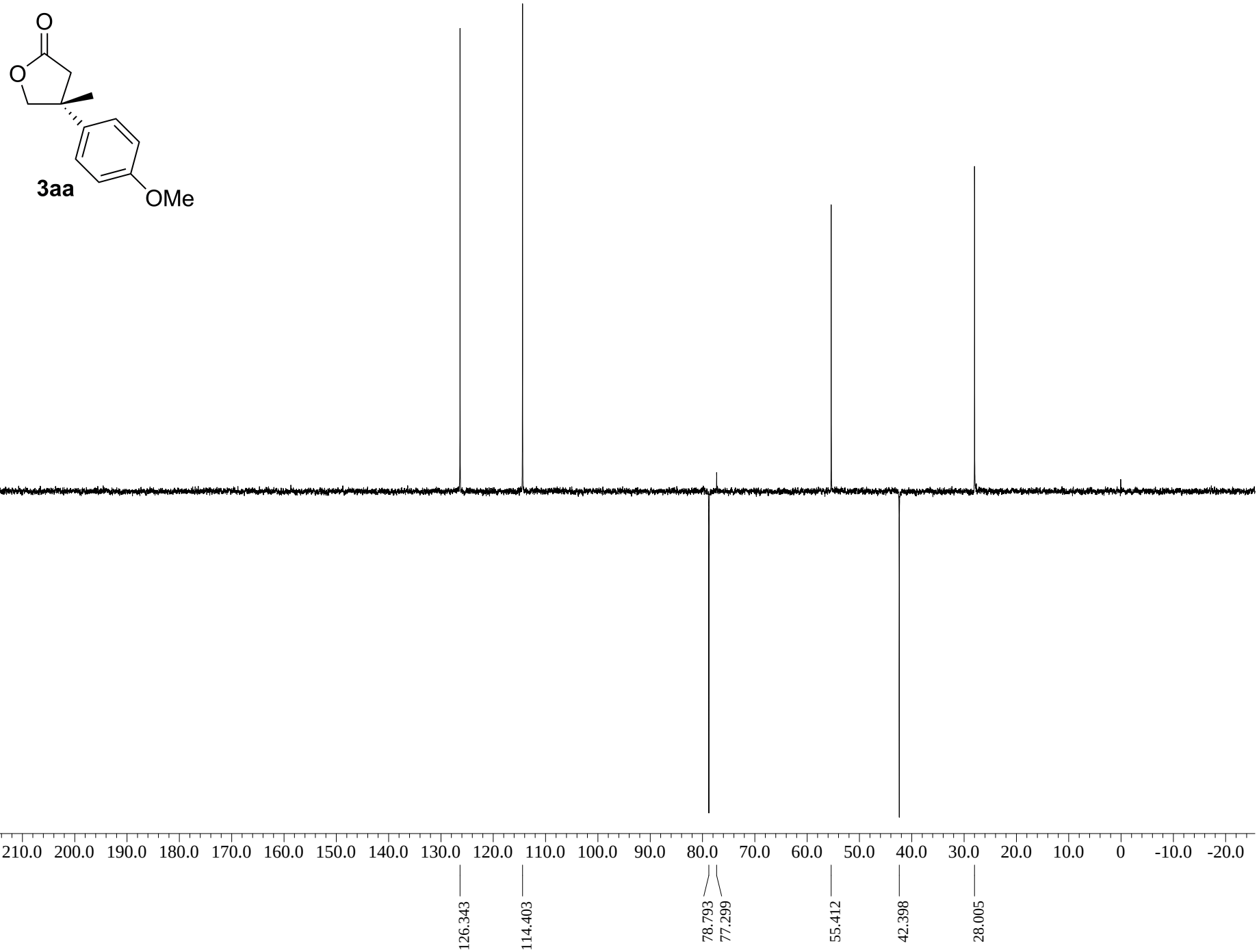


3z

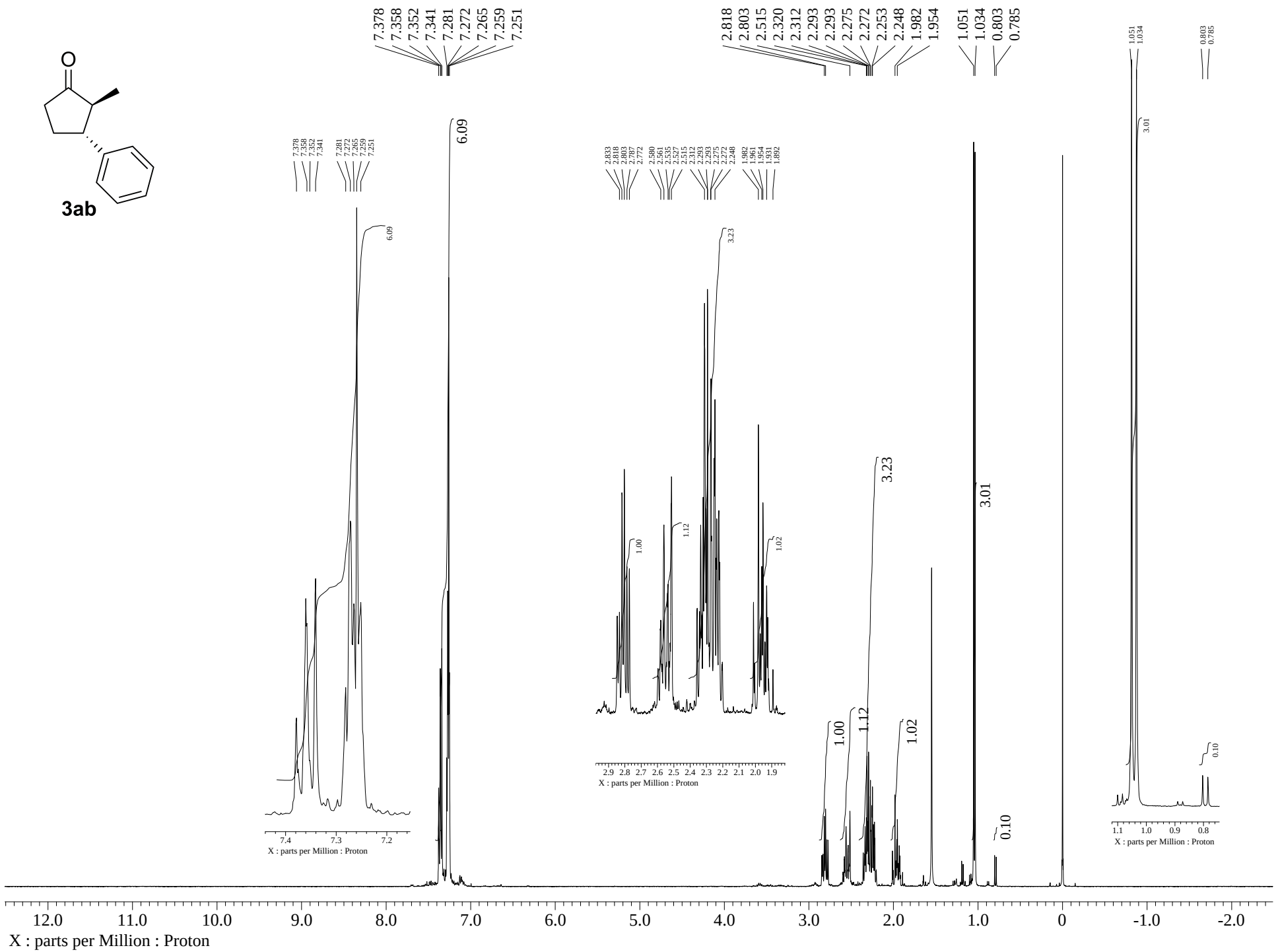
X : parts per Million : Carbon13

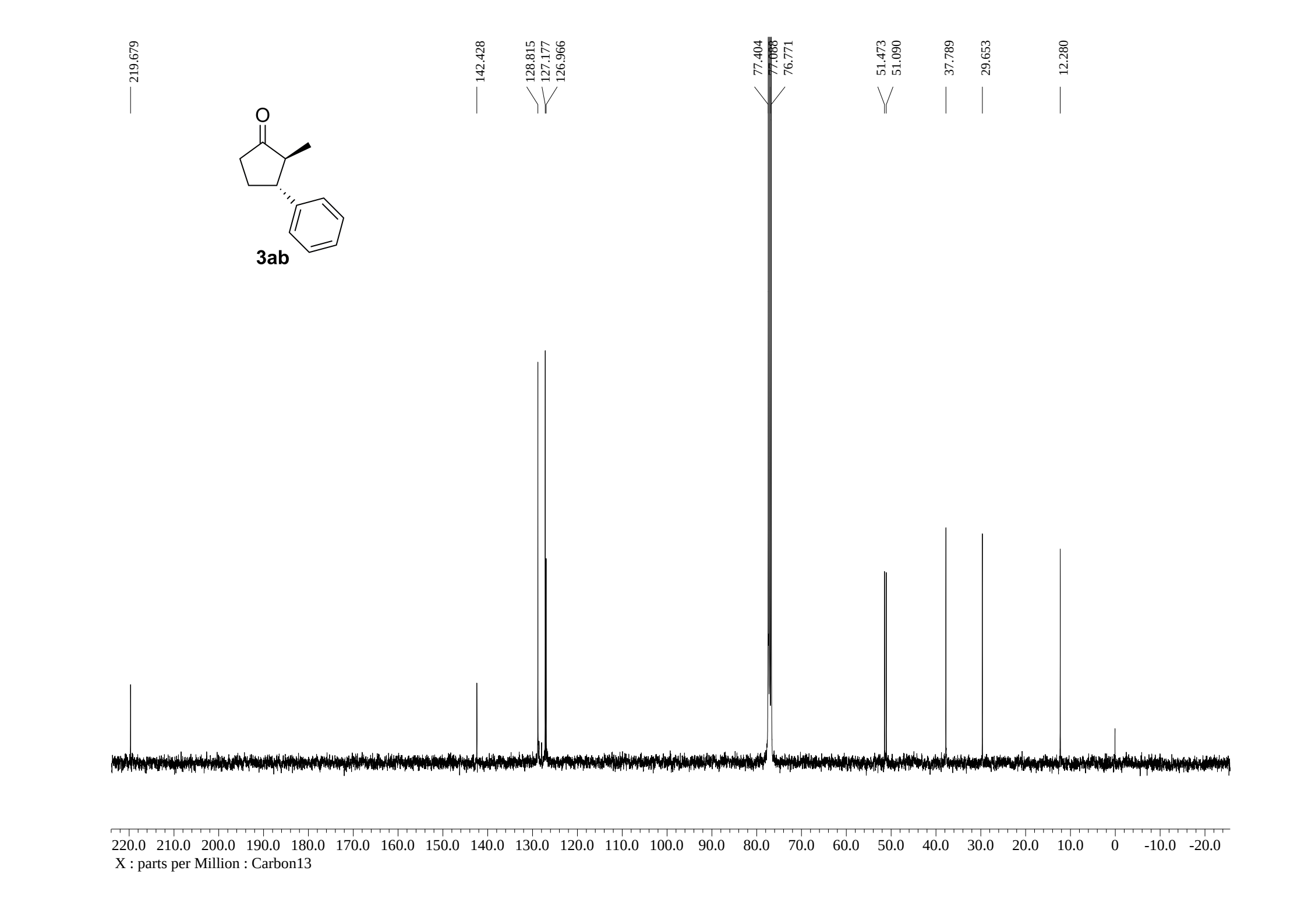

7.132
7.124
7.103
7.096
6.917
6.909
6.888
6.881
4.399
4.377
4.367
4.345
3.805
2.901
2.860
2.658
2.615
1.499
3.04
3.01
2.04
2.01
1.99
1.00
1.00
O
O
3aa
OMe
X : parts per Million : Proton
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0

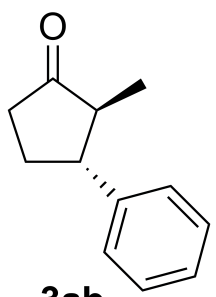

176.384
158.685
136.357
126.343
114.403
78.793
77.413
77.097
76.771
55.402
43.620
42.398
28.000
0.071
O
O
3aa
OMe
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13

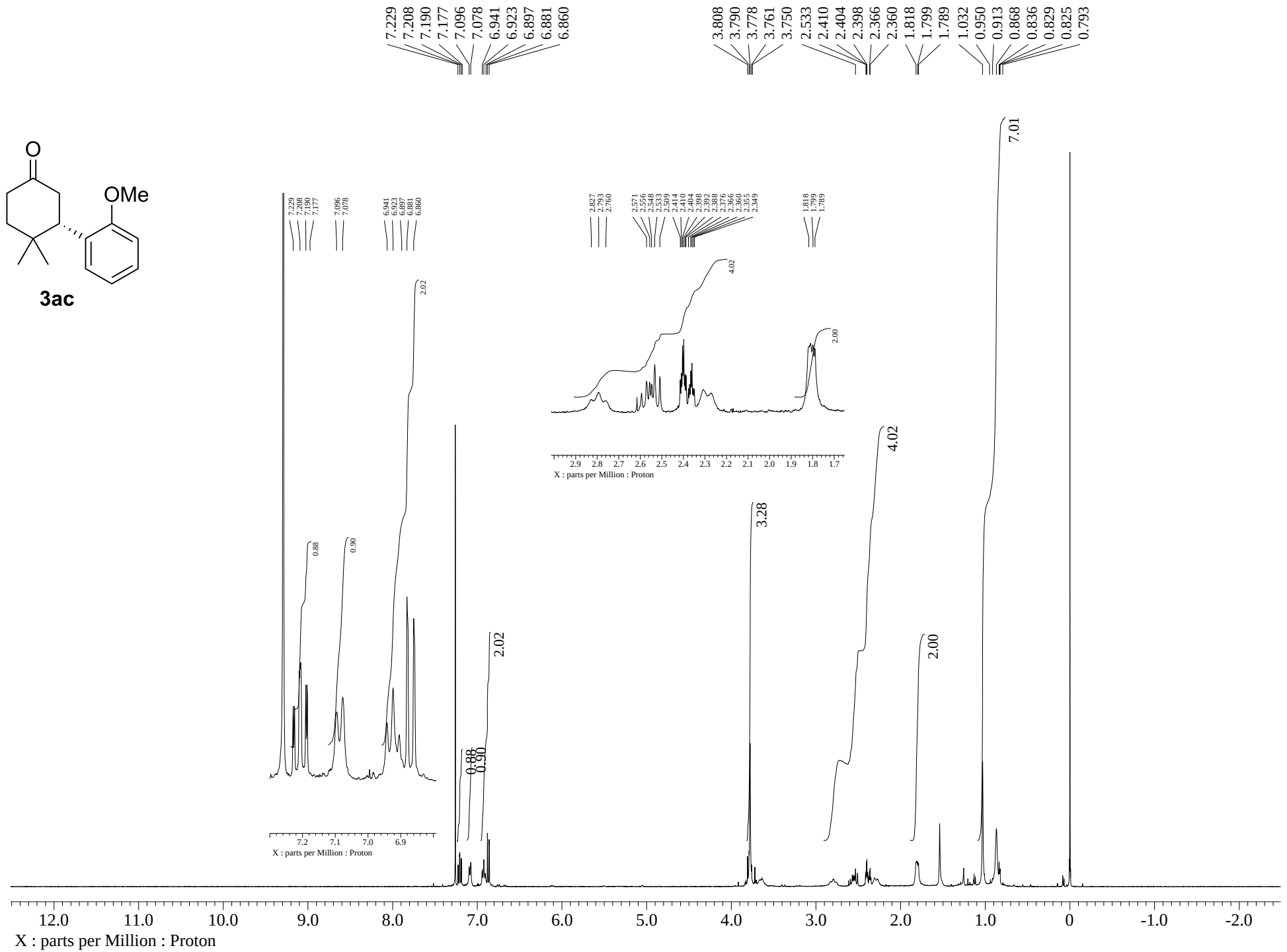

3ab
7.378
7.358
7.352
7.341
7.281
7.272
7.265
7.259
7.251
2.818
2.803
2.515
2.320
2.312
2.293
2.293
2.275
2.272
2.253
2.248
1.982
1.954
1.051
1.034
0.803
0.785
6.09
3.23
3.01
1.00
1.12
1.02
0.10
X : parts per Million : Proton

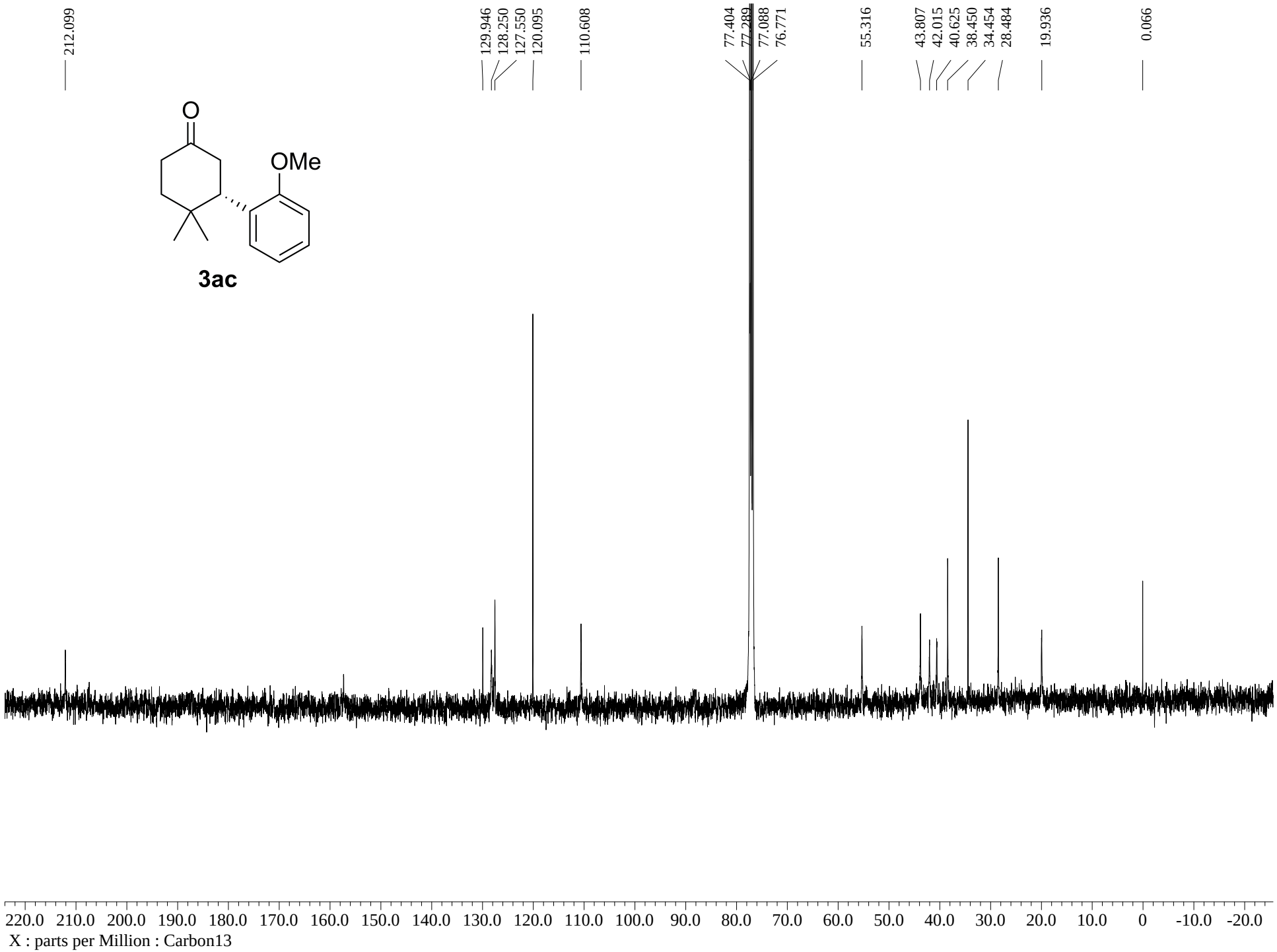

219.679
142.428
128.815
127.177
126.966
77.404
77.088
76.771
51.473
51.090
37.789
29.653
12.280
O
3ab
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

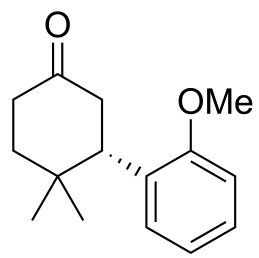


3ab

X : parts per Million : Carbon13

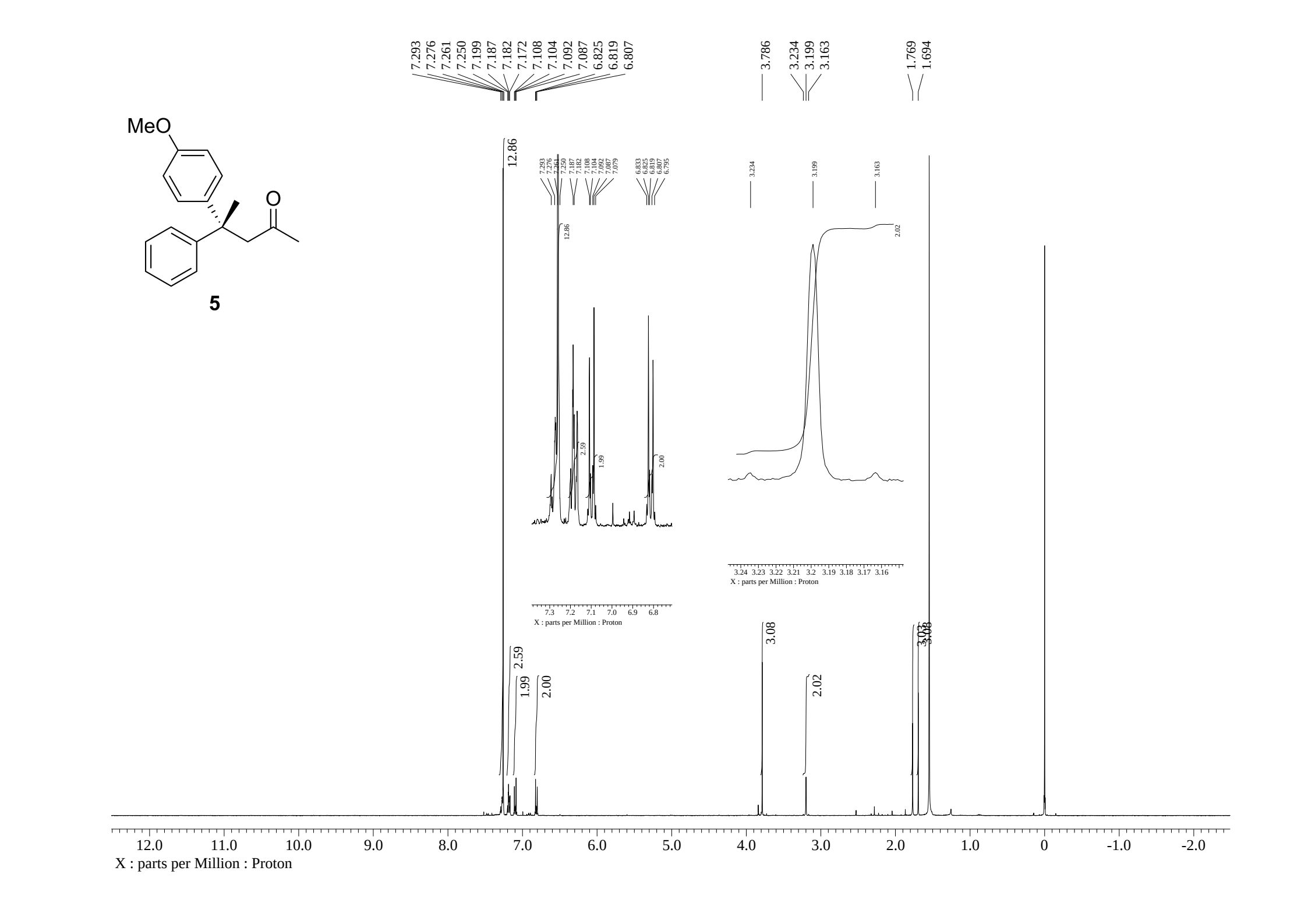

7.229
7.208
7.190
7.177
7.096
7.078
6.941
6.923
6.897
6.881
6.860
3.808
3.790
3.778
3.761
3.750
2.533
2.410
2.404
2.398
2.366
2.360
1.818
1.799
1.789
1.032
0.950
0.913
0.868
0.836
0.829
0.825
0.793
O
OMe
3ac
7.01
4.02
3.28
2.02
2.00
0.88
0.90
X : parts per Million : Proton

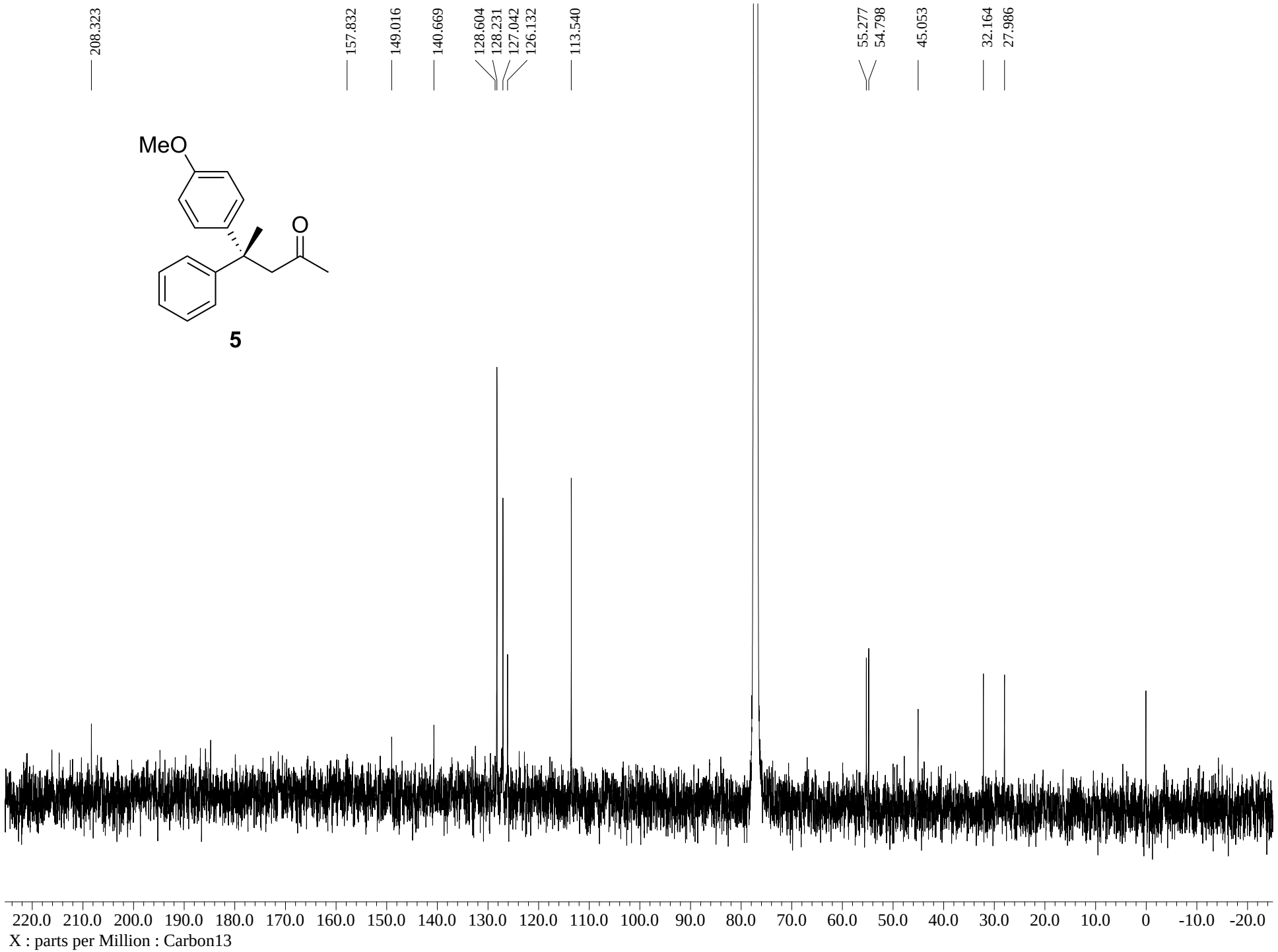

212.099
129.946
128.250
127.550
120.095
110.608
77.404
77.289
77.088
76.771
55.316
43.807
42.015
40.625
38.450
34.454
28.484
19.936
0.066
O
OMe
3ac
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13

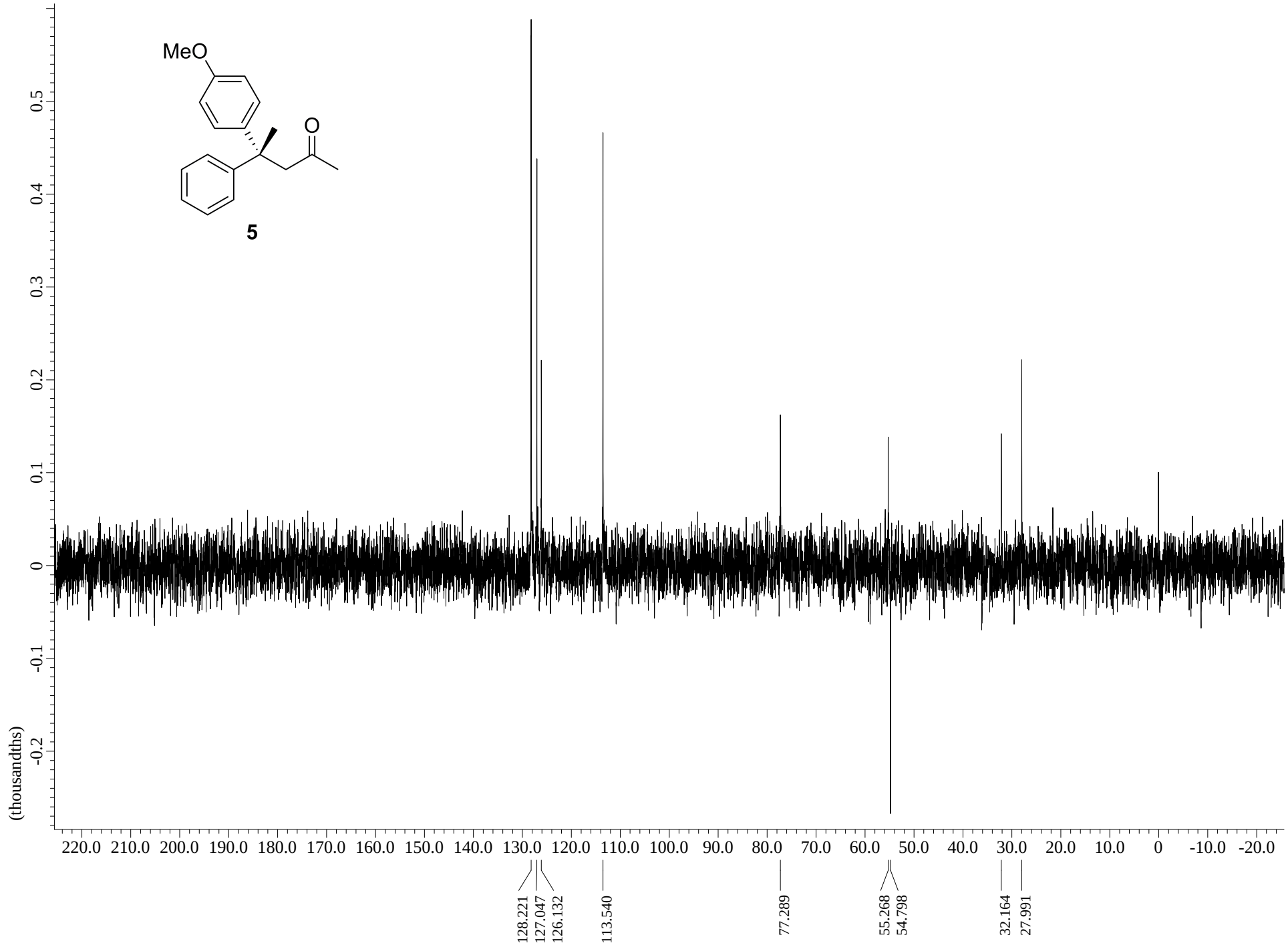


3ac

X : parts per Million : Carbon13


MeO
O
5
7.293
7.276
7.261
7.250
7.199
7.187
7.182
7.172
7.108
7.104
7.092
7.087
6.825
6.819
6.807
3.786
3.234
3.199
3.163
1.769
1.694
12.86
2.59
1.99
2.00
3.08
2.02
X : parts per Million : Proton


208.323
157.832
149.016
140.669
128.604
128.231
127.042
126.132
113.540
55.277
54.798
45.053
32.164
27.986
MeO
O
5
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
X : parts per Million : Carbon13



X : parts per Million : Carbon13