Supporting Information

DDQ-Catalyzed Reactions Employing MnO_2 as a Stoichiometric Oxidant

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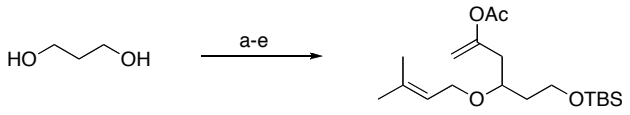
General Experimental:

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz respectively, a Bruker Avance 400 spectrometer at 300 MHz and 100 MHz respectively, a Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, a Bruker Avance 600 spectrometer at 600 MHz and 151 MHz if specified. The chemical shifts are given in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^1H NMR: $CDCl_3$ = 7.27 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23. Data are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; dd = doublet of doublets; dt = doublet of triplets; br = broad. High resolution and low resolution mass spectra were recorded on a VG 7070 spectrometer. Infrared (IR) spectra were collected on a Mattson Cygnus 100 spectrometer. Samples for IR were prepared as a thin film on a NaCl plate by dissolving the compound in CH_2Cl_2 and then evaporating the CH_2Cl_2. Manganese dioxide was purchased from Strem and used after activation by heating to 125 °C for 48 h. Methylene chloride was distilled under N_2 from CaH_2. Nitromethane was dried over 4 Å molecular sieves. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60F-254 plates. Visualization was done under UV (254 nm). Flash chromatography was done using ICN SiliTech 32-63 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, pentane and hexanes (commercial mixture) were purchased from EM Science and used as is for chromatography. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

General procedure for the oxidation reactions:
The reaction substrate (1 eq), 2,6-dichloropyridine (2 eq), MnO_2 (6 eq) and 4 Å molecular sieves (2 mass eq) were suspended in anhydrous nitromethane to give a ~0.1 M solution (substrate concentration). The mixture was stirred at room temperature for 15 minutes, followed by the addition of DDQ (0.05 eq). The mixture was stirred at rt for 10 h and a second portion of DDQ (0.05 eq) was added. After an additional 14 h the last portion of DDQ (0.05 eq) was added. The reaction was monitored by TLC and, upon starting material consumption, was quenched by Et_3N. The mixture was concentrated and purified by flash chromatography to give the desired product.

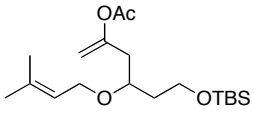
General procedure for the deprotection of *p*-methoxy benzyl ethers:
To the substrate (1 eq) and MnO_2 (6 eq) in anhydrous nitromethane (~0.2 M) was added MeOH

(8 eq) and DDQ (0.05 eq). The mixture was stirred at 60 °C for 10 h and a second portion of DDQ (0.05 eq) was added. After an additional 18 h the last portion of DDQ (0.05 eq) was added. The reaction was monitored by TLC and, upon starting material consumption, was quenched by Et_3N. The mixture was concentrated and purified by flash chromatography to give the desired alcohol.



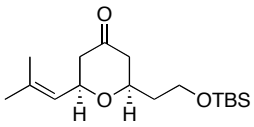
Reagents and conditions
a) NaH, TBSCl, THF, 93%. b) SO_3•Py, DMSO, Et_3N, CH_2Cl_2, 69%. c) Propargyl bromide, Zn, 1,2-diiodoethane, THF, 49%. d) NaH, DMF, then prenyl bromide, 81%. e) HOAc, $[(p\text{-cymene})RuCl_2]_2$, Fur_3P, Na_2CO_3, PhMe, 55%.

Scheme 1. The preparation of substrate **1**.



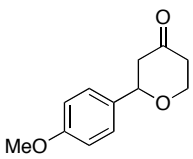
6-((*tert*-Butyldimethylsilyl)oxy)-4-((3-methylbut-2-en-1-yl)oxy)hex-1-en-2-yl acetate (1)

^1H NMR (400 MHz, $CDCl_3$) δ 5.36-5.32 (m, 1H), 4.82 (s, 2H), 4.04 (dd, *J* = 7.0, 11.0 Hz, 1H), 3.96-3.92 (m, 1H), 3.77-3.62 (m, 3H), 2.50 (dd, *J* = 6.4, 10.9 Hz, 1H), 2.41 (dd, *J* = 5.8, 14.7 Hz, 1H), 2.14 (s, 3H), 1.74 (s, 3H), 1.73-1.70 (m, 2H), 1.68 (s, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 169.3, 153.8, 136.9, 121.5, 103.8, 73.1, 66.2, 59.6, 38.8, 37.8, 26.1, 26.0, 21.3, 18.5, 18.2, -5.1, -5.2; IR (neat) 2927, 2859, 1759, 1651, 1254, 1200, 1094, 1020, 835, 773 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{36}O_4Si$ [M^+] 356.2383, found 356.2376.



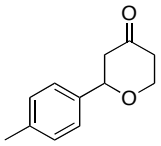
(2*R*,6*R*)-2-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-6-(2-methylprop-1-en-1-yl)dihydro-2*H*-pyran-4(3*H*)-one (2)

The general oxidation procedure was followed with **1** (42 mg, 0.12 mmol), 2,6-dichloropyridine (35 mg, 0.23 mmol), MnO_2 (61 mg, 0.70 mmol), 4 Å molecular sieves (60 mg), and DDQ (3 x 1.4 mg, 0.018 mmol) in 1.1 mL nitromethane. The reaction was stirred at room temperature for 48 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (30% CH_2Cl_2 in hexane to 5% EtOAc in hexane) to give the desired product (29 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.23-5.21 (m, 1H), 4.34-4.25 (m, 1H), 3.86-3.75 (m, 2H), 3.72-3.67 (m, 1H), 2.39-2.25 (m, 4H), 1.89-1.79 (m, 1H), 1.74 (s, 3H), 1.72-1.69 (m, 1H), 1.67 (s, 3H), 0.87 (s, 9H), 0.03 (s, 6H); ^{13}C (100 MHz, $CDCl_3$) δ 207.6, 137.4, 124.7, 74.3, 73.8, 59.0, 48.2, 48.1, 39.5, 26.1, 25.9, 18.6, 18.4, -5.2, -5.3; IR (neat) 2953, 2927, 2859, 1724, 1469, 1385, 1361, 1325, 1253, 1146, 1098, 1025, 940, 901, 835, 777 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{32}O_3Si$ [M^+] 312.2121, found 312.2124.



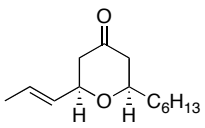
2-(4-Methoxyphenyl)dihydro-2*H*-pyran-4(3*H*)-one (4)

The general oxidation procedure was followed with **3**[1] (35 mg, 0.14 mmol), 2,6-dichloropyridine (41 mg, 0.28 mmol), MnO_2 (75 mg, 0.84 mmol), 4 Å molecular sieves (40 mg), and DDQ (3 x 1.6 mg, 0.021 mmol) in 1.4 mL anhydrous nitromethane. The reaction was stirred at rt for 41 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (15% EtOAc in hexane) to give the desired product (22 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 4.60 (dd, *J* = 3.5, 10.5 Hz, 1H), 4.40 (ddd, *J* = 1.5, 7.5, 11.5 Hz, 1H), 3.83 (td, *J* = 2.5, 11.5 Hz, 1H), 3.81 (s, 3H), 2.75-2.68 (m, 2H), 2.65-2.59 (m, 1H), 2.42 (dm, *J* = 14.5 Hz, 1H). These data are consistent with reported literature values.[1]



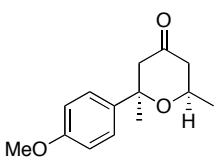
2-*p*-Tolyldihydro-2*H*-pyran-4(3*H*)-one (6)

The general oxidation procedure was followed with **5**[1] (49 mg, 0.21 mmol), 2,6-dichloropyridine (46 mg, 0.31 mmol), MnO_2 (109 mg, 1.3 mmol), 4 Å molecular sieves (80 mg), and DDQ (3 x 2.4 mg, 0.032 mmol) in 2.0 mL anhydrous nitromethane. The reaction was stirred at room temperature for 44 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (30% CH_2Cl_2 in hexane to 7% EtOAc in hexane) to give the desired product (33 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.61 (dd, *J* = 5.5, 9.0 Hz, 1H), 4.42 (ddd, *J* = 1.5, 7.5, 11.5 Hz, 1H), 3.83 (td, *J* = 3.0, 11.5 Hz, 1H), 2.72 (ddd, *J* = 7.5, 9.5, 14.5 Hz, 1H), 2.64 (m, 2H), 2.43 (dm, *J* = 14.5 Hz, 1H), 2.35 (s, 3H). These data are consistent with reported literature values.[1]



(2*R*,6*R*)-2-Hexyl-6-((*E*)-prop-1-en-1-yl)dihydro-2*H*-pyran-4(3*H*)-one (8)

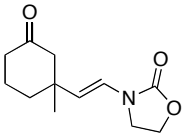
The general oxidation procedure was followed with **7**[2] (26 mg, 0.097 mmol), 2,6-dichloropyridine (22 mg, 0.15 mmol), MnO_2 (51 mg, 0.58 mmol), 4 Å molecular sieves (40 mg), and DDQ (3 x 1.1 mg, 0.015 mmol) in 1.0 mL anhydrous nitromethane. The reaction was stirred at room temperature for 40 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (30% CH_2Cl_2 in hexanes to 5% EtOAc in hexanes) to give the desired product (20 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (ddq, *J* = 0.9, 12.8, 15.4 Hz, 1H), 5.54 (ddq, *J* = 1.5, 6.1, 15.3 Hz, 1H), 4.06-3.99 (m, 1H), 3.58 (ddt, *J* = 2.7, 6.9, 14.3 Hz, 1H), 2.37-2.33 (m, 3H), 2.28-2.18 (m, 1H), 1.72-1.66 (m, 3H), 1.54-1.27 (m, 10H), 0.87 (t, *J* = 6.6 Hz, 3H). These data are consistent with reported literature values.[2]



(2*R*,6*R*)-2-(4-Methoxyphenyl)-2,6-dimethyl-tetrahydropyran-4-one (10)

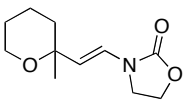
The general oxidation procedure was followed with **9**[3] (46 mg, 0.17 mmol), 2,6-dichloropyridine (49 mg, 0.33 mmol), MnO_2 (86 mg, 0.99 mmol), 4 Å molecular sieves (80 mg), and DDQ (4 x 1.9 mg, 0.034 mmol) in 1.6 mL anhydrous nitromethane. The reaction was stirred at room temperature for 48 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash

chromatography (30% CH_2Cl_2 in hexane to 7% EtOAc in hexane) to give the desired product (29 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.27-4.17 (m, 1H), 3.81 (s, 3H), 2.72-2.61 (m, 2H), 2.46-2.40 (m, 1H), 2.29 (dd, *J* = 11.0, 14.1 Hz, 1H), 1.48 (s, 3H), 1.42 (d, *J* = 6.0 Hz, 3H). These data are consistent with reported literature values.[3]



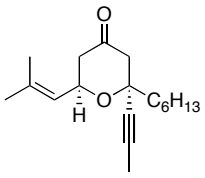
(*E*)-3-(2-(1-Methyl-3-oxocyclohexyl)vinyl)oxazolidin-2-one (12)

The general oxidation procedure was followed with **11**[4] (27 mg, 0.1 mmol), 2,6-dichloropyridine (22 mg, 0.15 mmol), MnO_2 (53 mg, 0.6 mmol), 4 Å molecular sieves (50 mg), and DDQ (3 x 1.2 mg, 0.015 mmol) in 1.0 mL anhydrous nitromethane. The reaction was stirred at room temperature for 36 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (40% hexane in EtOAc) to give the desired product (15 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.65 (d, *J* = 14.7 Hz, 1H), 4.76 (d, *J* = 14.7 Hz, 1H), 4.46-4.41 (m, 2H), 3.69-3.64 (m, 2H), 2.39-2.22 (m, 4H), 1.95-1.86 (m, 2H), 1.83-1.65 (m, 2H), 1.13 (s, 3H). These data are consistent with reported literature values.[4]



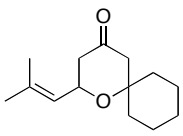
(*E*)-3-(2-(2-Methyltetrahydro-2H-pyran-2-yl)vinyl)oxazolidin-2-one (14)

The general oxidation procedure was followed with **13**[4] (21 mg, 0.1 mmol), 2,6-dichloropyridine (22 mg, 0.15 mmol), MnO_2 (53 mg, 0.6 mmol), 4 Å molecular sieves (30 mg), and DDQ (3 x 1.2 mg, 0.015 mmol) in 1.0 mL anhydrous nitromethane. The reaction was stirred at room temperature for 24 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (40% hexane in EtOAc) to give the desired product (18 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (d, *J* = 14.8 Hz, 1H), 4.83 (d, *J* = 14.9 Hz, 1H), 4.49-4.44 (m, 2H), 3.75-3.62 (m, 4H), 1.80-1.74 (m, 1H), 1.68-1.47 (m, 5H), 1.30 (s, 3H). These data are consistent with reported literature values.[4]



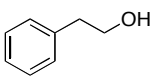
(2*R*,6*R*)-2-Hexyl-6-(2-methylprop-1-enyl)-2-(prop-1-ynyl)dihydro-2*H*-pyran-4(3*H*)-one (16)

The general oxidation procedure was followed with **15**[3] (35 mg, 0.11 mmol), 2,6-dichloropyridine (24 mg, 0.16 mmol), MnO_2 (57 mg, 0.66 mmol), 4 Å molecular sieves (70 mg), and DDQ (3 x 1.4 mg, 0.017 mmol) in 1.1 mL anhydrous nitromethane. The reaction was stirred at room temperature for 40 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (30% CH_2Cl_2 in hexane to 5% EtOAc in hexane) to give the desired product (21 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.24 (d, *J* = 6.8 Hz, 1H), 4.92 (ddd, *J* = 3.1, 7.9, 11.0 Hz, 1H), 2.49 (dd, *J* = 1.6, 13.7 Hz, 1H), 2.41 (d, *J* = 13.7 Hz, 1H), 2.35-2.32 (m, 1H), 2.28 (dd, *J* = 11.0, 14.2 Hz, 1H), 1.85 (s, 3H), 1.75 (s, 3H), 1.71 (d, *J* = 0.8 Hz, 3H), 1.58-1.29 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H). These data are consistent with reported literature values.[3]



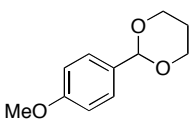
2-(2-Methylprop-1-enyl)-1-oxaspiro[5.5]undecan-4-one (18)

The general oxidation procedure was followed with **17**[3] (38 mg, 0.14 mmol), 2,6-dichloropyridine (31 mg, 0.21 mmol), MnO_2 (74 mg, 0.85 mmol), 4 Å molecular sieves (60 mg), and DDQ (3 x 1.7 mg, 0.021 mmol) in 1.4 mL anhydrous nitromethane. The reaction was stirred at room temperature for 30 h then was quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (30% CH_2Cl_2 in hexane to 15% Et_2O in hexane) to give the desired product (26 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$) δ 5.26 (d, J = 8.0 Hz, 1H), 4.56 (dt, J = 4.4, 9.2 Hz, 1H), 2.33-2.29 (m, 4H), 1.82-1.72 (m, 5H), 1.70 (s, 3H), 1.57-1.29 (m, 8H). These data are consistent with reported literature values.[3]



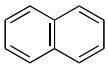
2-Phenylethanol

The General procedure for the deprotection of *p*-methoxy benzyl ethers was followed: **3** (60 mg, 0.25 mmol), MnO_2 (129 mg, 1.48 mmol), MeOH (60 µL), nitromethane (1.3 mL) and DDQ (3 x 2.8 mg, 0.037 mmol). The reaction was stirred at 60 °C for 48 h and then quenched by Et_3N. The crude was purified by flash chromatography (10% to 15% EtOAc in hexane) to give the desired product (27 mg, 90%).



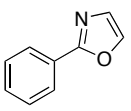
2-(4-Methoxyphenyl)-1,3-dioxane

5 (45 mg, 0.23 mmol), MnO_2 (120 mg, 1.4 mmol), $NaHCO_3$ (39 mg, 0.46 mmol) and 4 Å molecular sieves (80 mg) were dissolved in 1.5 mL anhydrous nitromethane, followed by DDQ (3 x 2.6 mg, 15% eq). The reaction was stirred at room temperature for 40 h and then quenched by Et_3N. The crude mixture was concentrated and purified by flash chromatography (10% EtOAc in hexane) to give the desired product (42 mg, 94%).



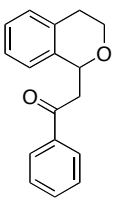
Naphthalene

7 (46 mg, 0.35 mmol) and MnO_2 (185 mg, 2.1 mmol) were dissolved in 2.5 mL anhydrous nitromethane, followed by DDQ (2 x 4.0 mg, 10% eq). The reaction was stirred at room temperature for 24 h. The crude mixture was concentrated and purified by flash chromatography (hexane) to give the desired product (43 mg, 96%).



2-Phenyloxazole

9 (60 mg, 0.41 mmol) and MnO_2 (213 mg, 2.5 mmol) were dissolved in 4.0 mL anhydrous benzene, followed by DDQ (4 x 4.7 mg, 20% eq). The reaction was stirred at 80 °C for 48 h. The crude mixture was concentrated and purified by flash chromatography (20% EtOAc in hexane) to give the desired product (51 mg, 86%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.72 (s, 1H), 7.49-7.44 (m, 3H), 7.25 (s, 1H). These data are consistent with reported literature values.[5]



2-(Isochroman-1-yl)-1-phenylethanone

Isochroman (27 mg, 0.2 mmol), acetophenone (72 mg, 0.6 mmol) and MnO_2 (105 mg, 1.2 mmol) were dissolved in 0.25 mL anhydrous nitromethane, followed by DDQ (4 x 2.3 mg, 20% eq). The reaction was stirred at 100 °C for 48 h. The crude mixture was concentrated and purified by flash chromatography (40% CH_2Cl_2 in hexane to 10% EtOAc in hexane) to give the desired product (21 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-8.01 (m, 2H), 7.59 (tt, *J* = 1.4, 8.6 Hz, 1H), 7.51-7.45 (m, 2H), 7.23-7.10 (m, 4H), 5.52 (dd, *J* = 3.4, 8.5 Hz, 1H), 4.13 (ddd, *J* = 3.7, 5.4, 11.3 Hz, 1H), 3.82 (ddd, *J* = 3.8, 9.5, 13.4 Hz, 1H), 3.63 (dd, *J* = 8.7, 16.2 Hz, 1H), 3.33 (dd, *J* = 3.6, 16.2 Hz, 1H), 3.03 (ddd, *J* = 6.0, 10.0, 16.2 Hz, 1H), 2.73 (td, *J* = 3.2, 15.8 Hz, 1H). These data are consistent with reported literature values.[6]

Procedure for the large scale oxidation:

To MnO_2 (16.4 g, 189 mmol) in 30 mL anhydrous nitromethane was added **24** (4.1 g, 31.5 mmol) in 10 mL anhydrous nitromethane dropwise under N_2, followed by the addition of DDQ (2 x 357 mg, 3.15 mmol). The reaction was stirred at room temperature for 16 h. After filtration through a Celite pad with Et_2O, the crude mixture was concentrated and purified by flash chromatography (hexane) to give the desired product (3.8 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 4H), 7.63-7.61 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 133.7, 128.1, 126.0.

References:

1. Jung, H. H.; Floreancig, P. E. *Tetrahedron*. **2009**, *65*, 10830.
2. Tu, W; Liu, L; Floreancig, P. E. *Angew. Chem. Int. Ed.* **2008**, *47*, 4184.
3. Liu, L; Floreancig, P. E. *Angew. Chem. Int. Ed.* **2010**, *49*, 5894.
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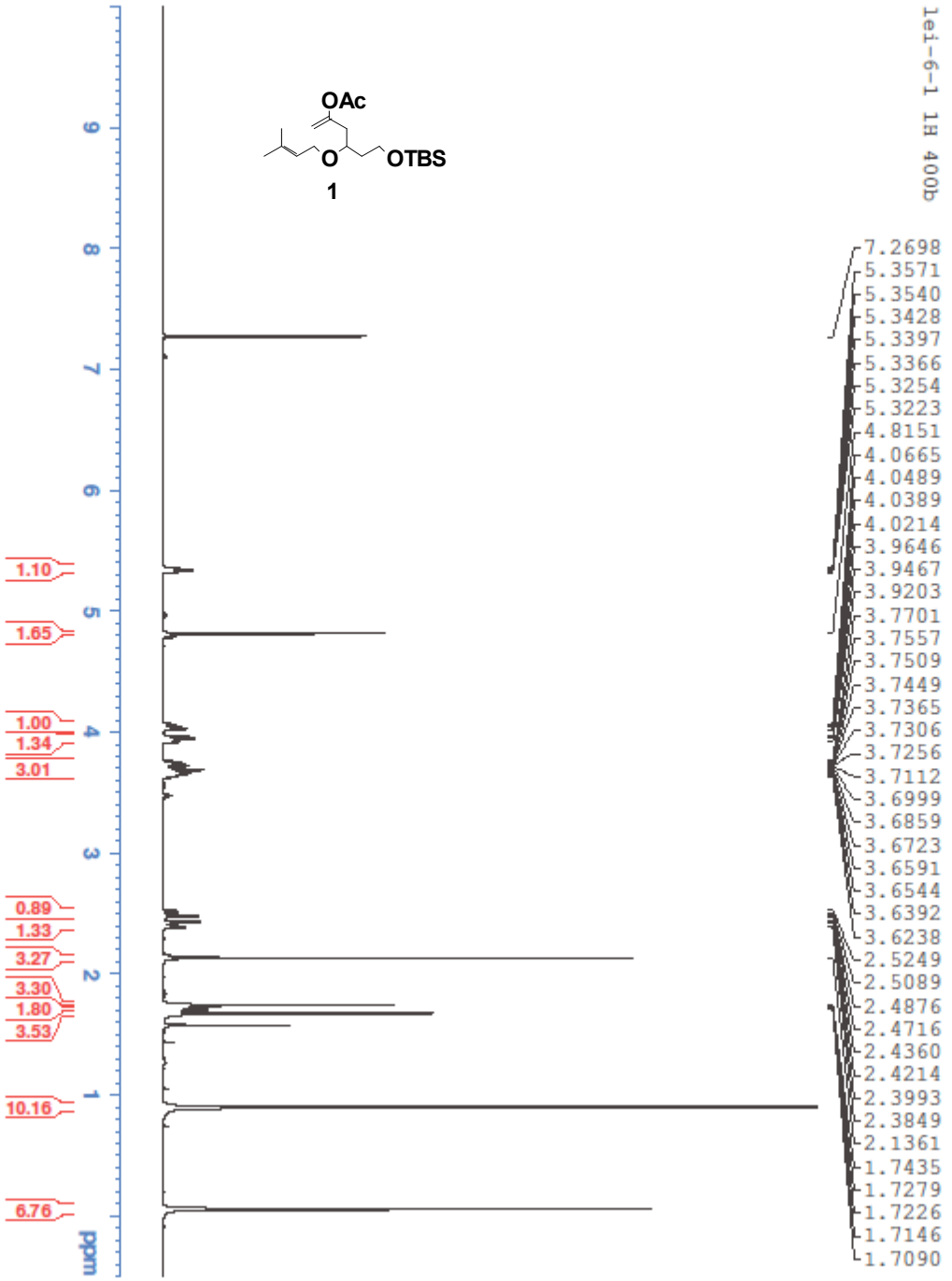
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O
OTBS
1
1ei-6-1 1H 400b
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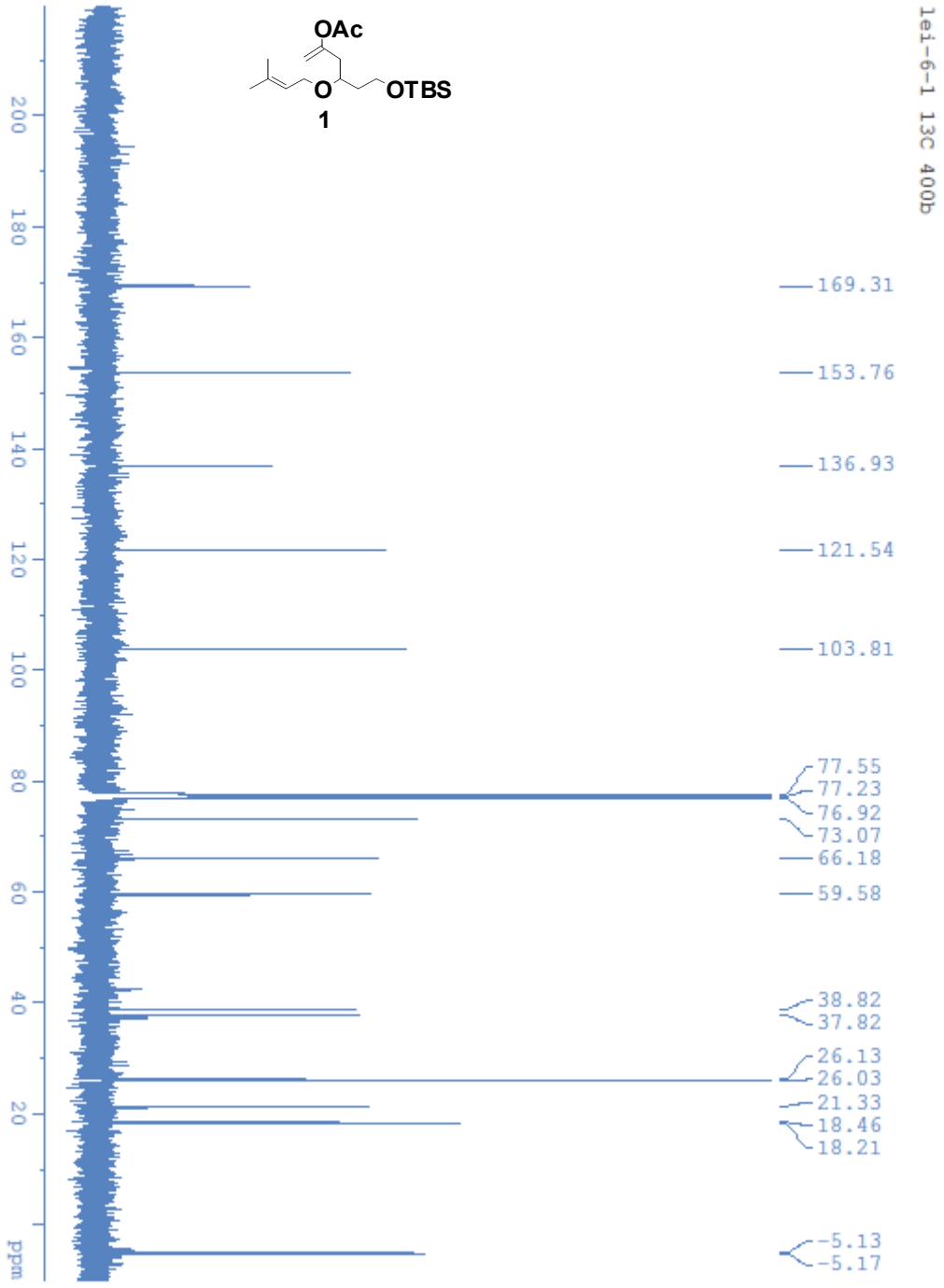
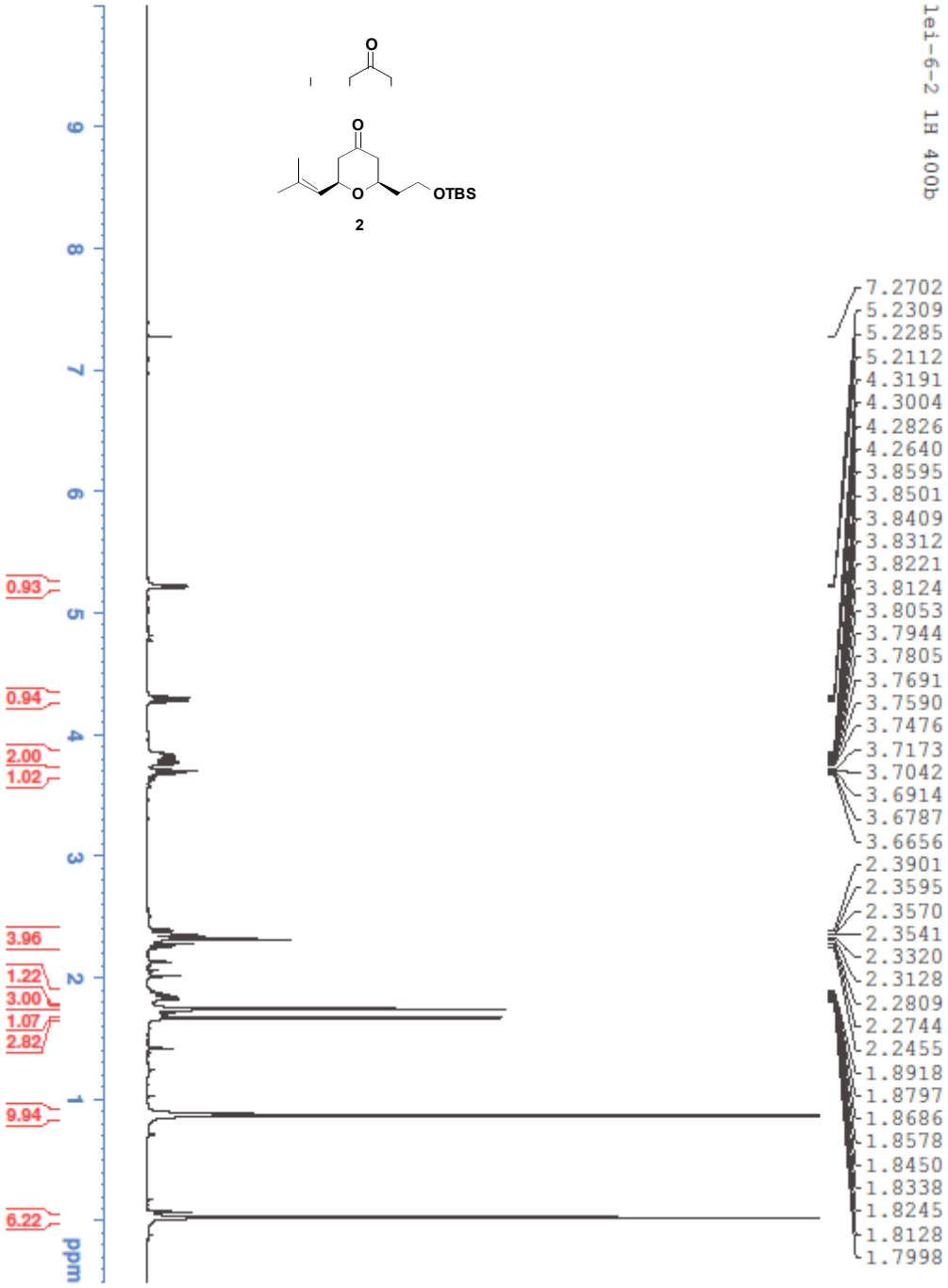
5.3571
5.3540
5.3428
5.3397
5.3366
5.3254
5.3223
4.8151
4.0665
4.0489
4.0389
4.0214
3.9646
3.9467
3.9203
3.7701
3.7557
3.7509
3.7449
3.7365
3.7306
3.7256
3.7112
3.6999
3.6859
3.6723
3.6591
3.6544
3.6392
3.6238
2.5249
2.5089
2.4876
2.4716
2.4360
2.4214
2.3993
2.3849
2.1361
1.7435
1.7279
1.7226
1.7146
1.7090
1.10
1.65
1.00
1.34
3.01
0.89
1.33
3.27
3.30
1.80
3.53
10.16
6.76
ppm


OAc
O
OTBS
1
lei-6-1 13C 400b
200
180
160
140
120
100
80
60
40
20
ppm
169.31
153.76
136.93
121.54
103.81
77.55
77.23
76.92
73.07
66.18
59.58
38.82
37.82
26.13
26.03
21.33
18.46
18.21
-5.13
-5.17


lei-6-2 1H 400b
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O
O
OTBS
2
7.2702
5.2309
5.2285
5.2112
4.3191
4.3004
4.2826
4.2640
3.8595
3.8501
3.8409
3.8312
3.8221
3.8124
3.8053
3.7944
3.7805
3.7691
3.7590
3.7476
3.7173
3.7042
3.6914
3.6787
3.6656
2.3901
2.3595
2.3570
2.3541
2.3320
2.3128
2.2809
2.2744
2.2455
1.8918
1.8797
1.8686
1.8578
1.8450
1.8338
1.8245
1.8128
1.7998
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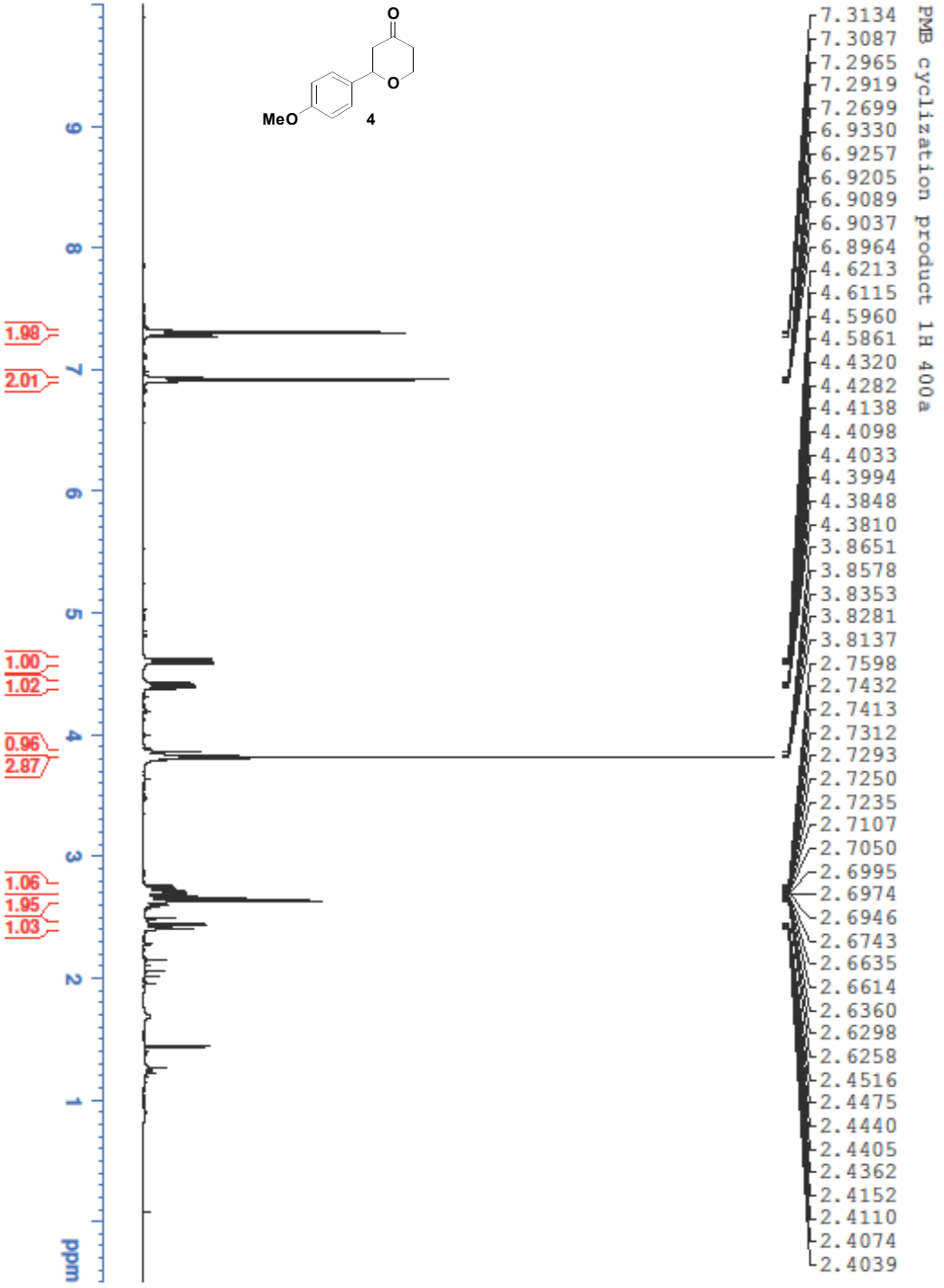
0.94
2.00
1.02
3.96
1.22
3.00
1.07
2.82
9.94
6.22
ppm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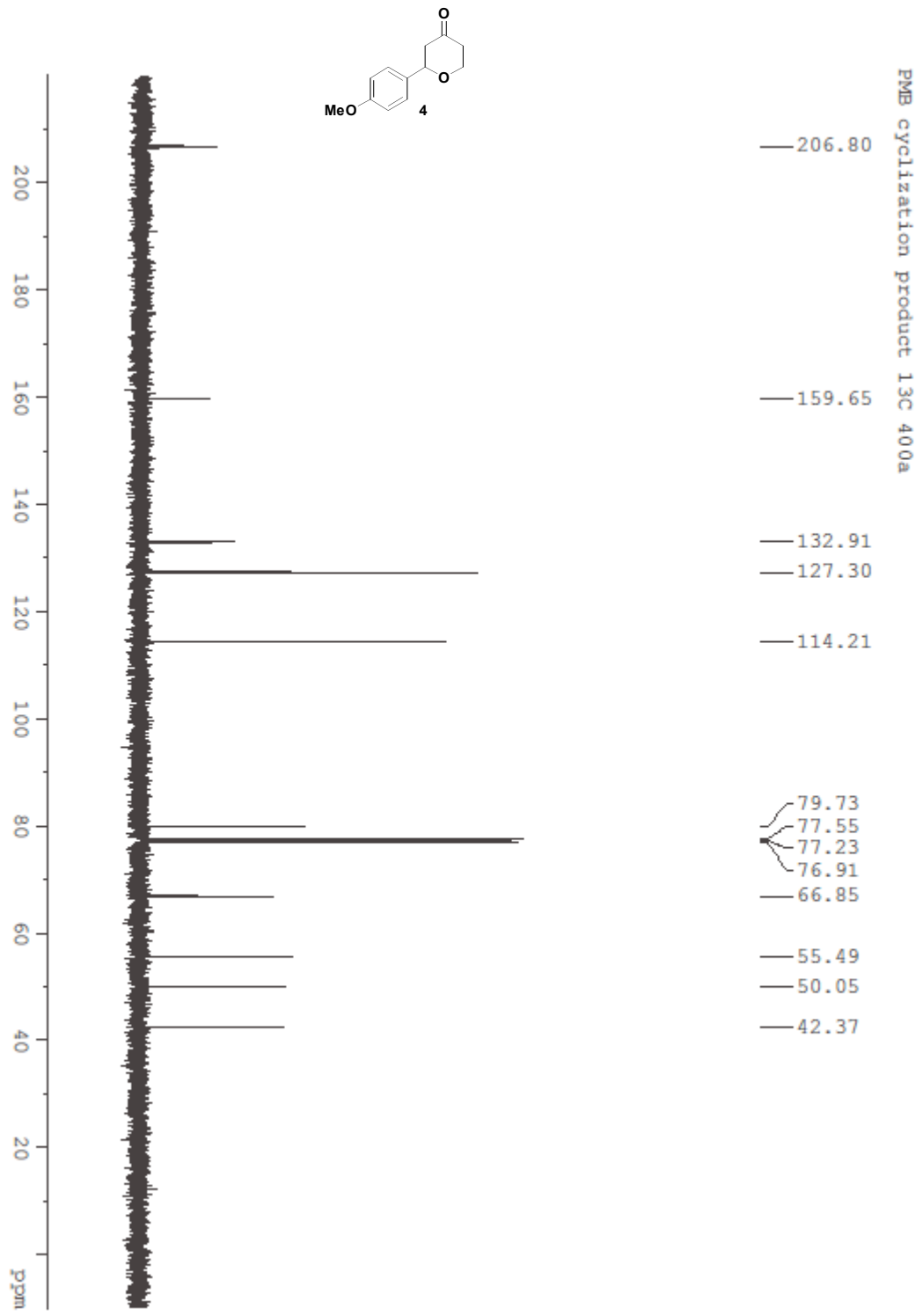
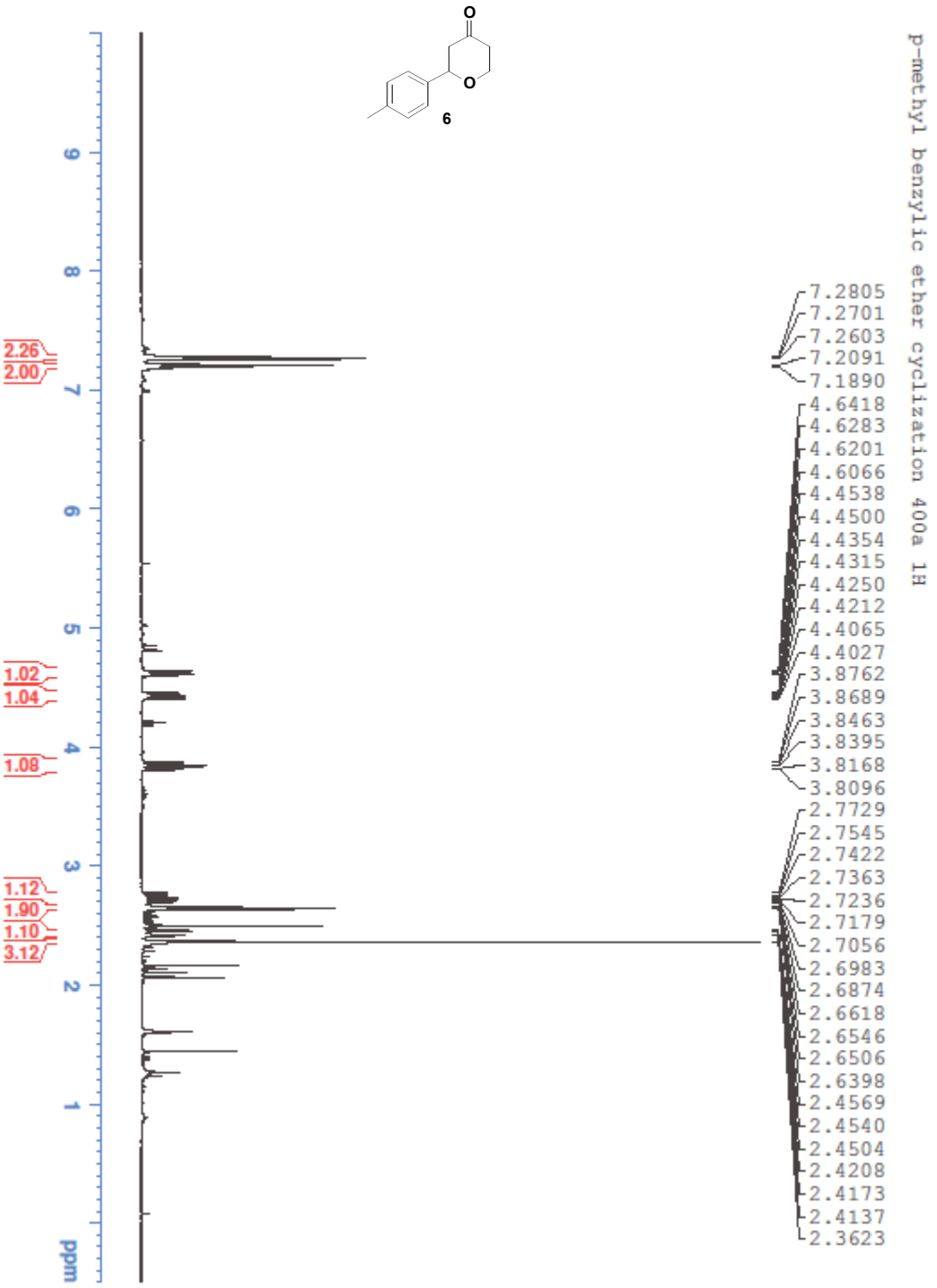
7.2965
7.2919
7.2699
6.9330
6.9257
6.9205
6.9089
6.9037
6.8964
4.6213
4.6115
4.5960
4.5861
4.4320
4.4282
4.4138
4.4098
4.4033
4.3994
4.3848
4.3810
3.8651
3.8578
3.8353
3.8281
3.8137
2.7598
2.7432
2.7413
2.7312
2.7293
2.7250
2.7235
2.7107
2.7050
2.6995
2.6974
2.6946
2.6743
2.6635
2.6614
2.6360
2.6298
2.6258
2.4516
2.4475
2.4440
2.4405
2.4362
2.4152
2.4110
2.4074
2.4039
MeO
4
O
O
1.98
2.01
1.00
1.02
0.96
2.87
1.06
1.95
1.03
ppm


PMB cyclization product 13C 400a
MeO
4
206.80
159.65
132.91
127.30
114.21
79.73
77.55
77.23
76.91
66.85
55.49
50.05
42.37
200
180
160
140
120
100
80
60
40
20
ppm


p-methyl benzylic ether cyclization 400a 1H
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7.2701
7.2603
7.2091
7.1890
4.6418
4.6283
4.6201
4.6066
4.4538
4.4500
4.4354
4.4315
4.4250
4.4212
4.4065
4.4027
3.8762
3.8689
3.8463
3.8395
3.8168
3.8096
2.7729
2.7545
2.7422
2.7363
2.7236
2.7179
2.7056
2.6983
2.6874
2.6618
2.6546
2.6506
2.6398
2.4569
2.4540
2.4504
2.4208
2.4173
2.4137
2.3623
2.26
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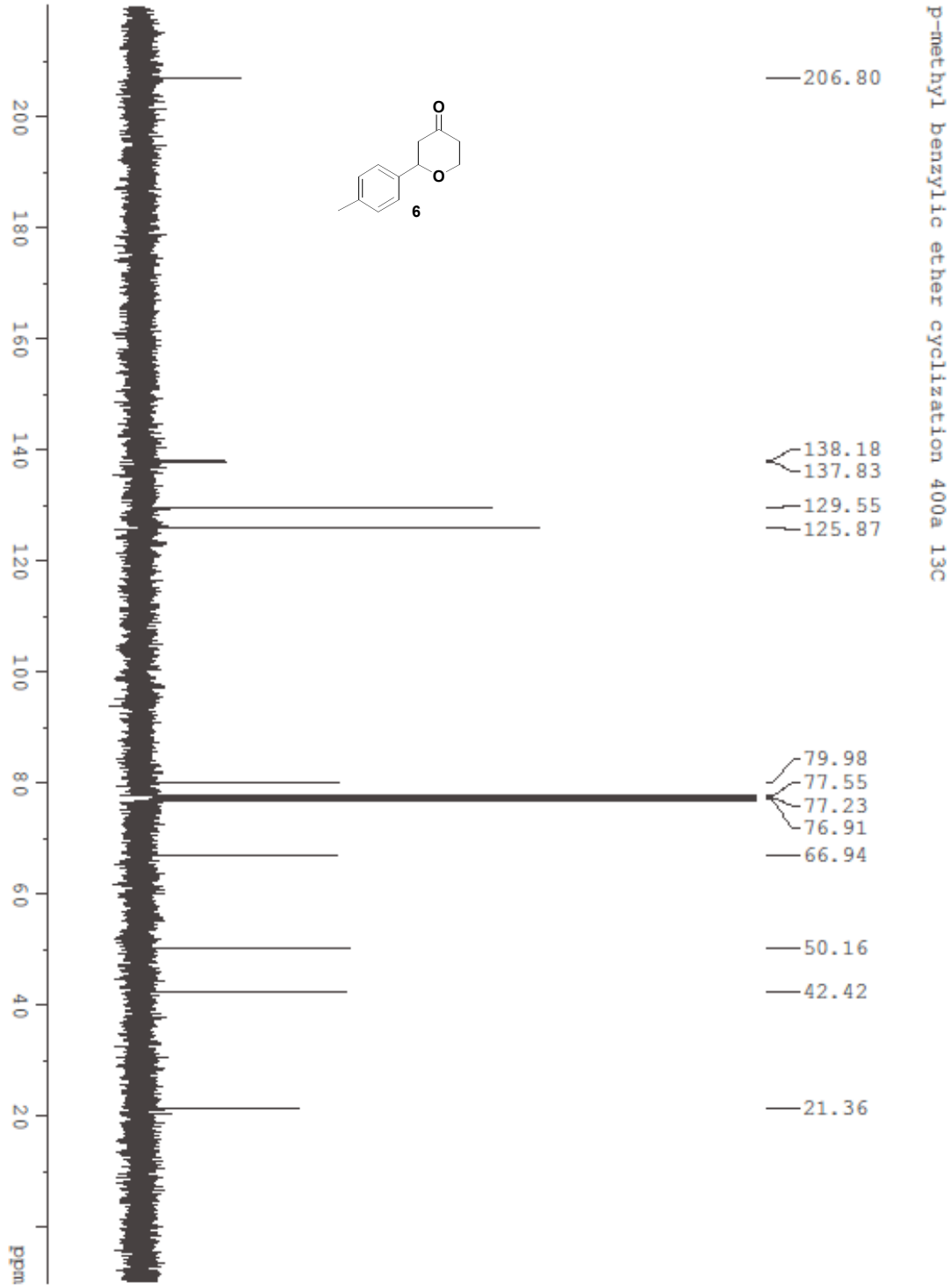
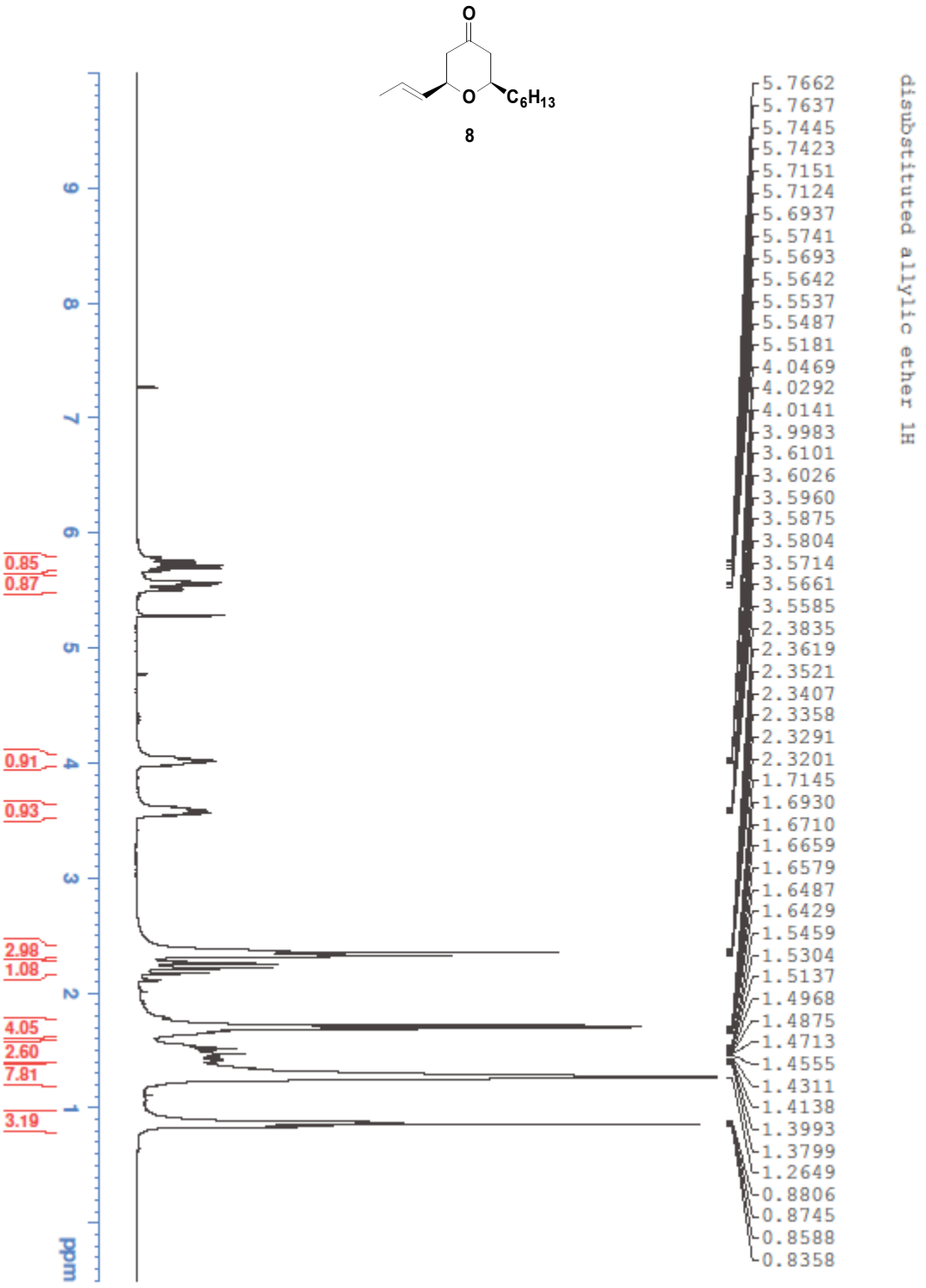
1.02
1.04
1.08
1.12
1.90
1.10
3.12
ppm
O
O
6


p-methyl benzylic ether cyclization 400a 13C
206.80
138.18
137.83
129.55
125.87
79.98
77.55
77.23
76.91
66.94
50.16
42.42
21.36
O
O
6
200
180
160
140
120
100
80
60
40
20
ppm


O
O
C6H13
8
disubstituted allylic ether 1H
5.7662
5.7637
5.7445
5.7423
5.7151
5.7124
5.6937
5.5741
5.5693
5.5642
5.5537
5.5487
5.5181
4.0469
4.0292
4.0141
3.9983
3.6101
3.6026
3.5960
3.5875
3.5804
3.5714
3.5661
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2.3407
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2.3291
2.3201
1.7145
1.6930
1.6710
1.6659
1.6579
1.6487
1.6429
1.5459
1.5304
1.5137
1.4968
1.4875
1.4713
1.4555
1.4311
1.4138
1.3993
1.3799
1.2649
0.8806
0.8745
0.8588
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0.85
0.87
0.91
0.93
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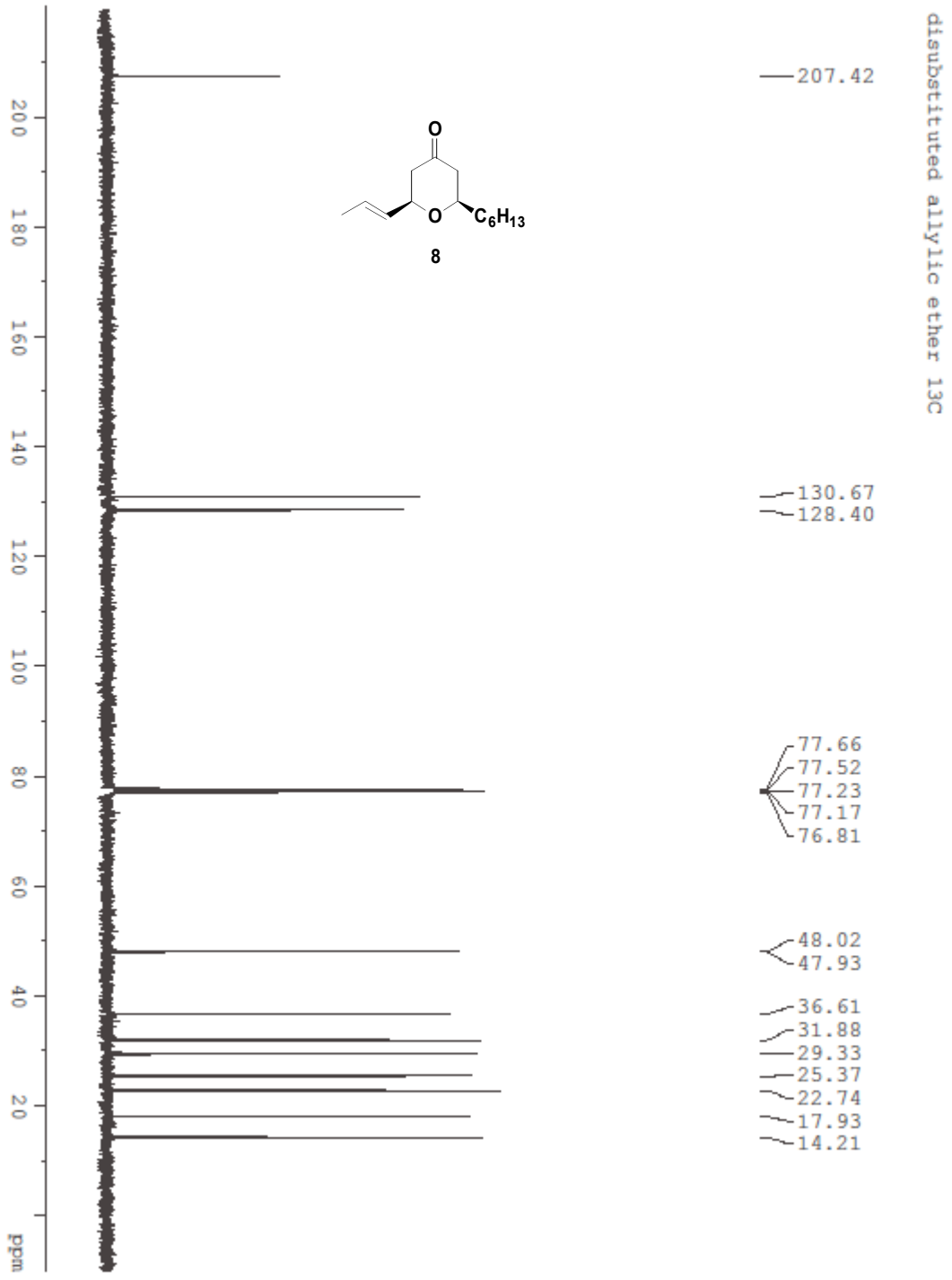
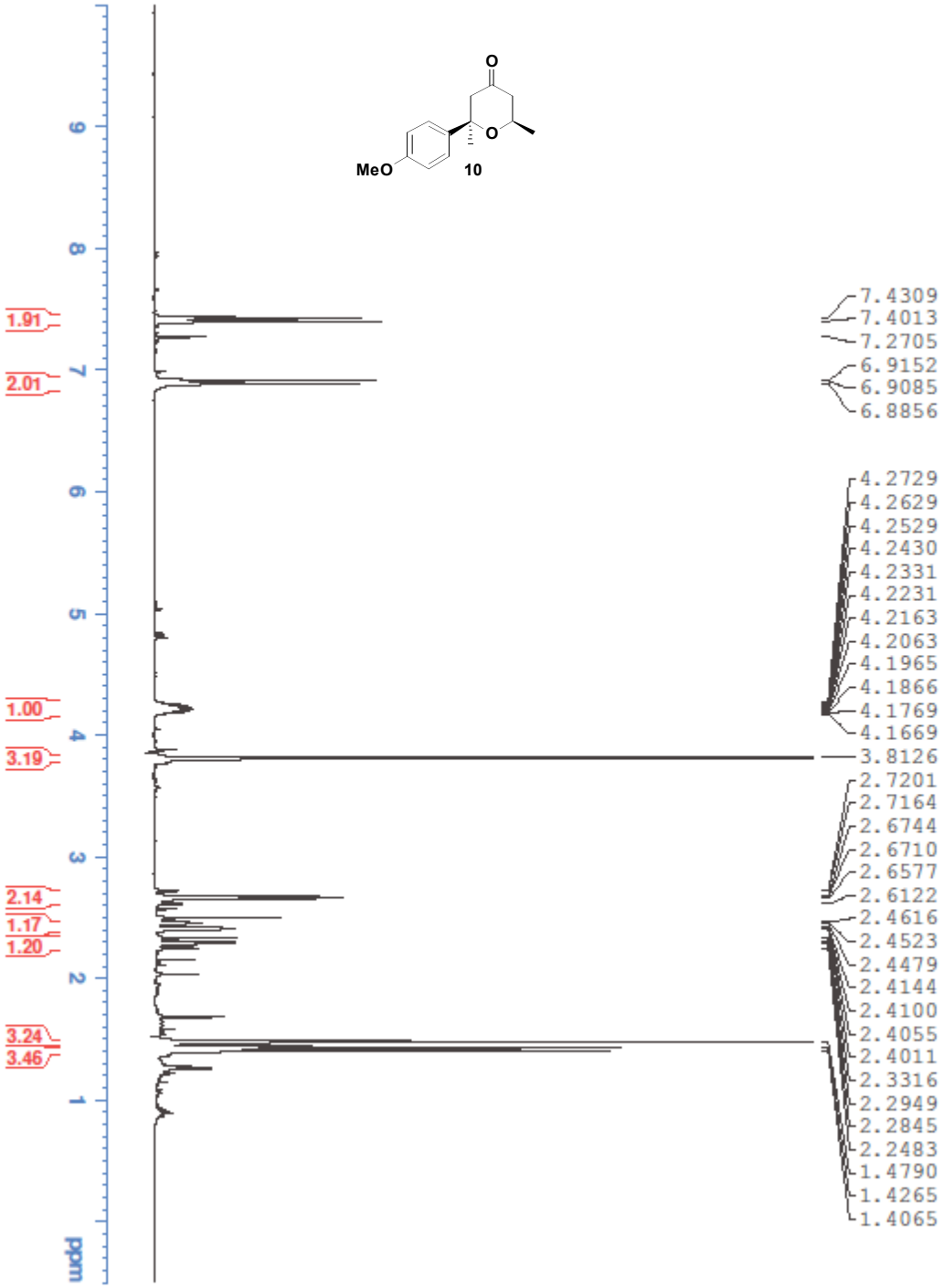
1.08
4.05
2.60
7.81
3.19
ppm


disubstituted allylic ether 13C
207.42
130.67
128.40
77.66
77.52
77.23
77.17
76.81
48.02
47.93
36.61
31.88
29.33
25.37
22.74
17.93
14.21
O
O
C6H13
8
200
180
160
140
120
100
80
60
40
20
ppm


O
O
MeO
10
1.91
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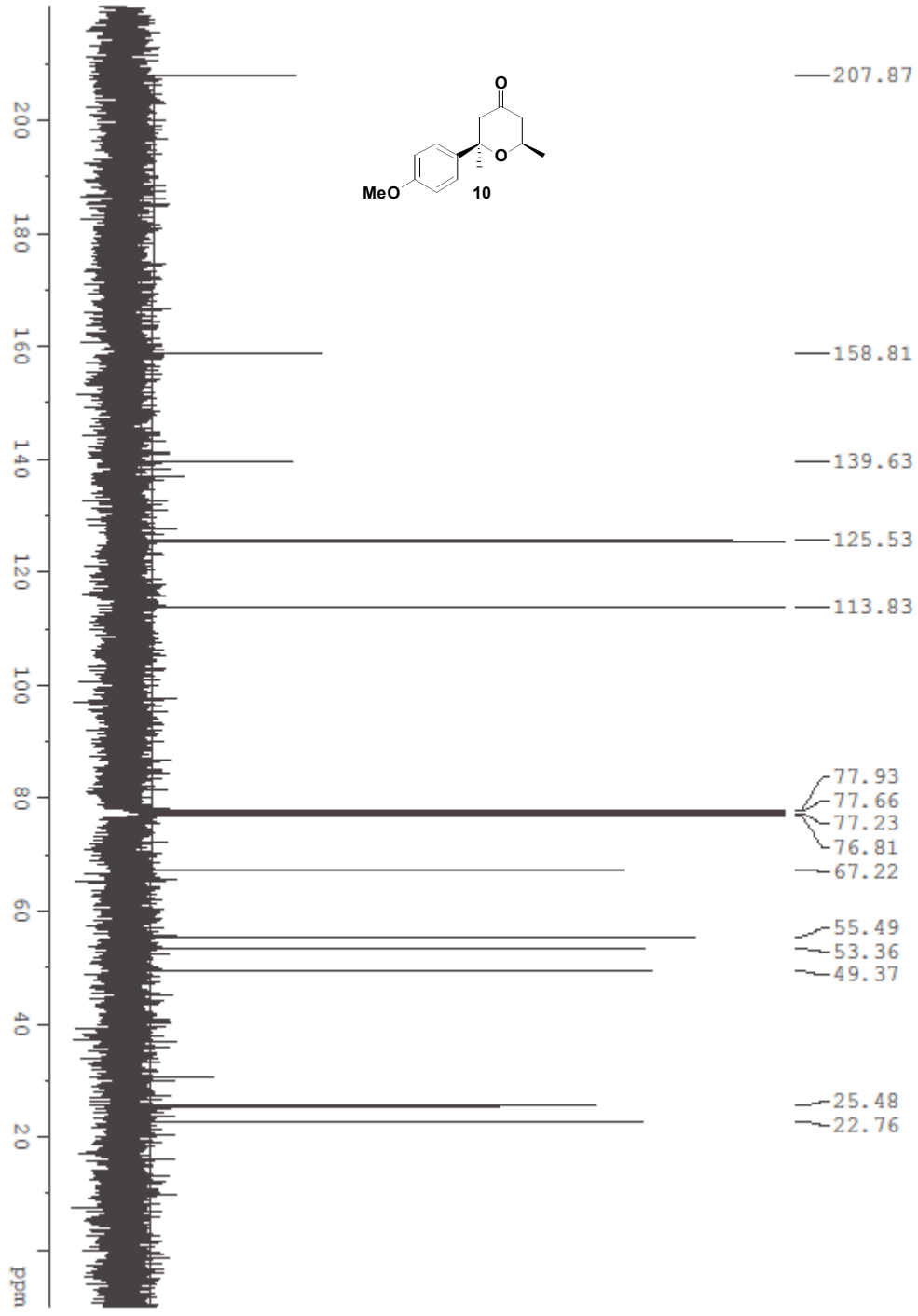
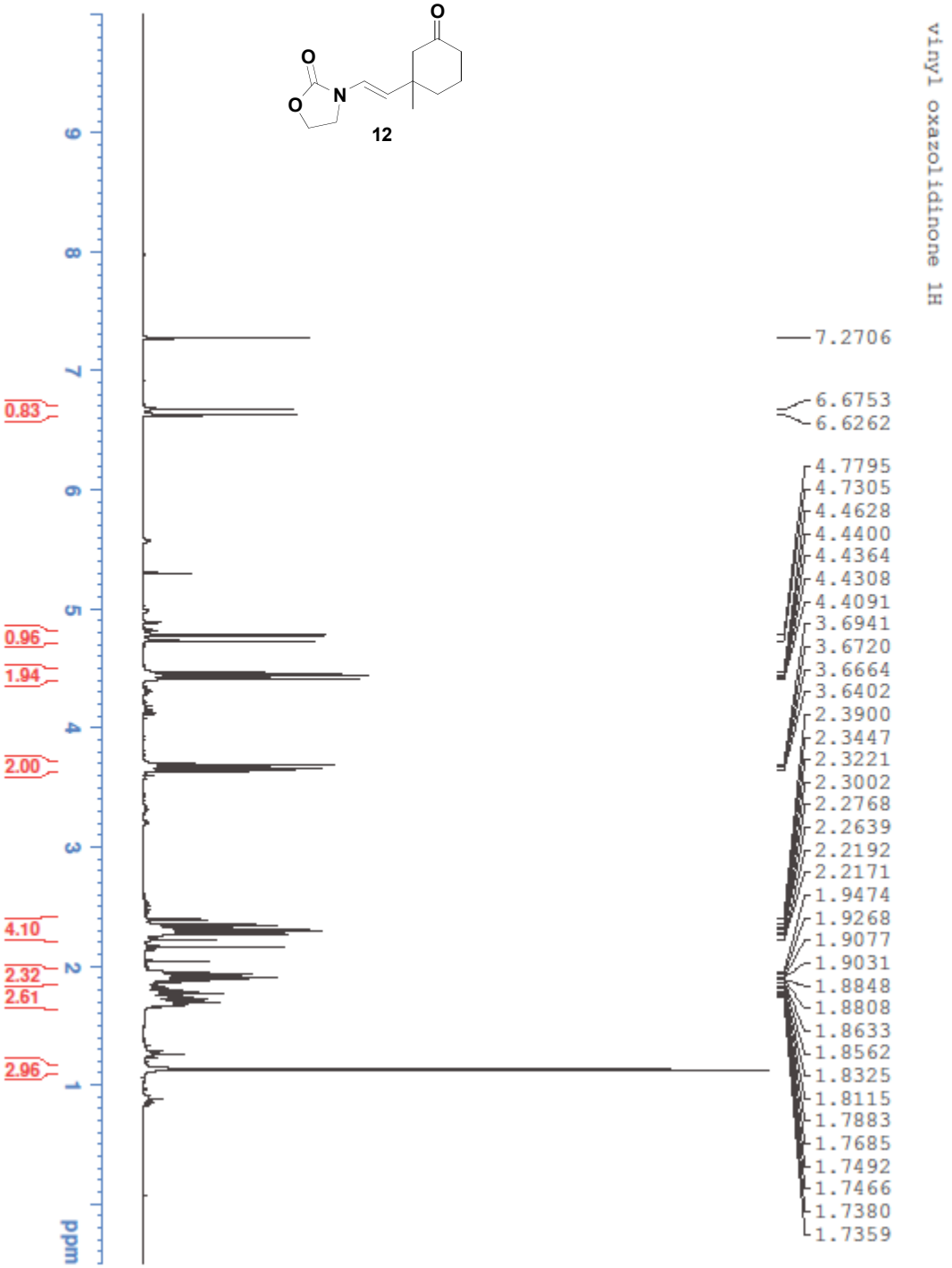
1.00
3.19
2.14
1.17
1.20
3.24
3.46
ppm
7.4309
7.4013
7.2705
6.9152
6.9085
6.8856
4.2729
4.2629
4.2529
4.2430
4.2331
4.2231
4.2163
4.2063
4.1965
4.1866
4.1769
4.1669
3.8126
2.7201
2.7164
2.6744
2.6710
2.6577
2.6122
2.4616
2.4523
2.4479
2.4144
2.4100
2.4055
2.4011
2.3316
2.2949
2.2845
2.2483
1.4790
1.4265
1.4065


O
O
MeO
10
207.87
158.81
139.63
125.53
113.83
77.93
77.66
77.23
76.81
67.22
55.49
53.36
49.37
25.48
22.76
200
180
160
140
120
100
80
60
40
20
ppm


vinyl oxazolidinone 1H
12
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6.6262
4.7795
4.7305
4.4628
4.4400
4.4364
4.4308
4.4091
3.6941
3.6720
3.6664
3.6402
2.3900
2.3447
2.3221
2.3002
2.2768
2.2639
2.2192
2.2171
1.9474
1.9268
1.9077
1.9031
1.8848
1.8808
1.8633
1.8562
1.8325
1.8115
1.7883
1.7685
1.7492
1.7466
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1.7359
0.83
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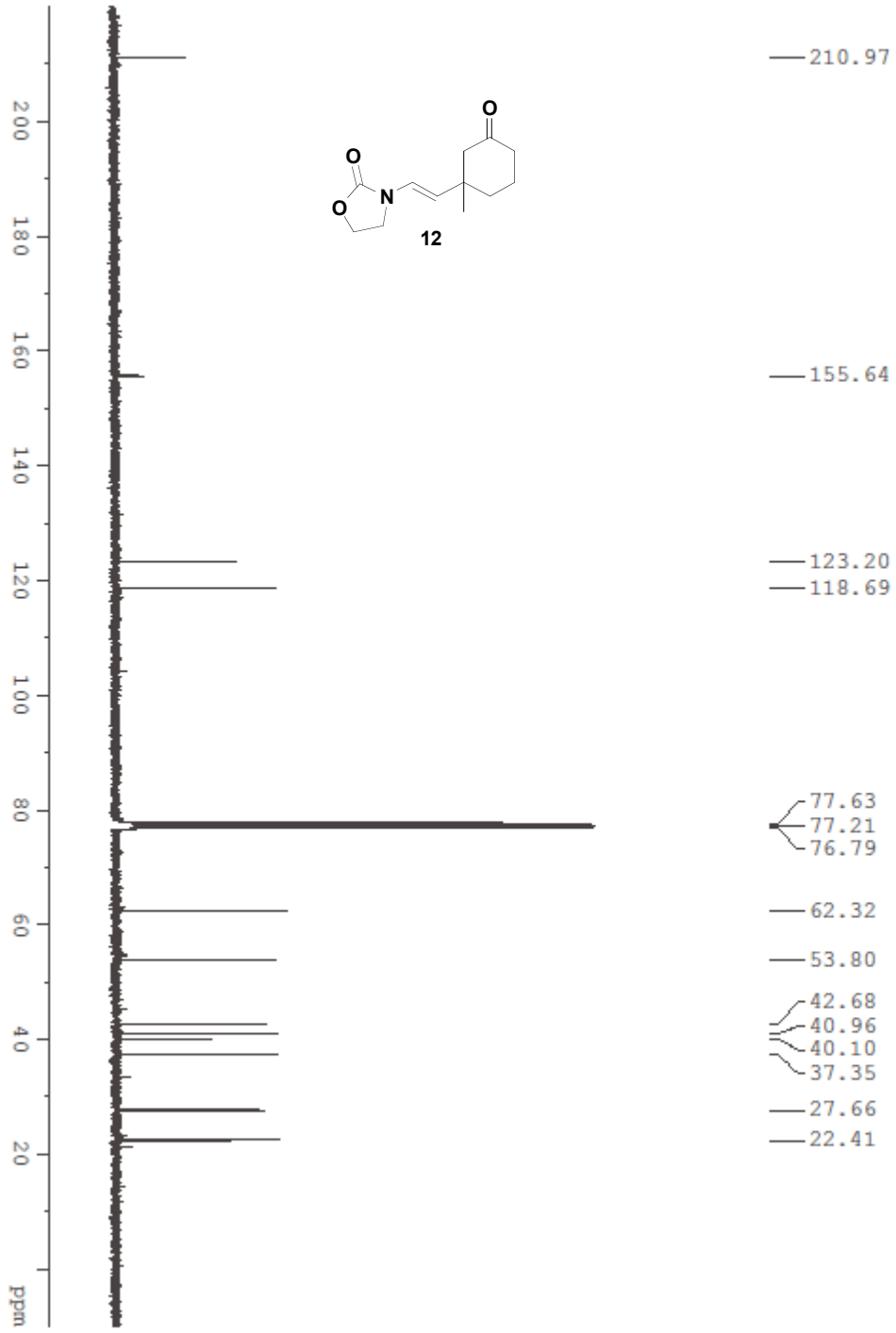
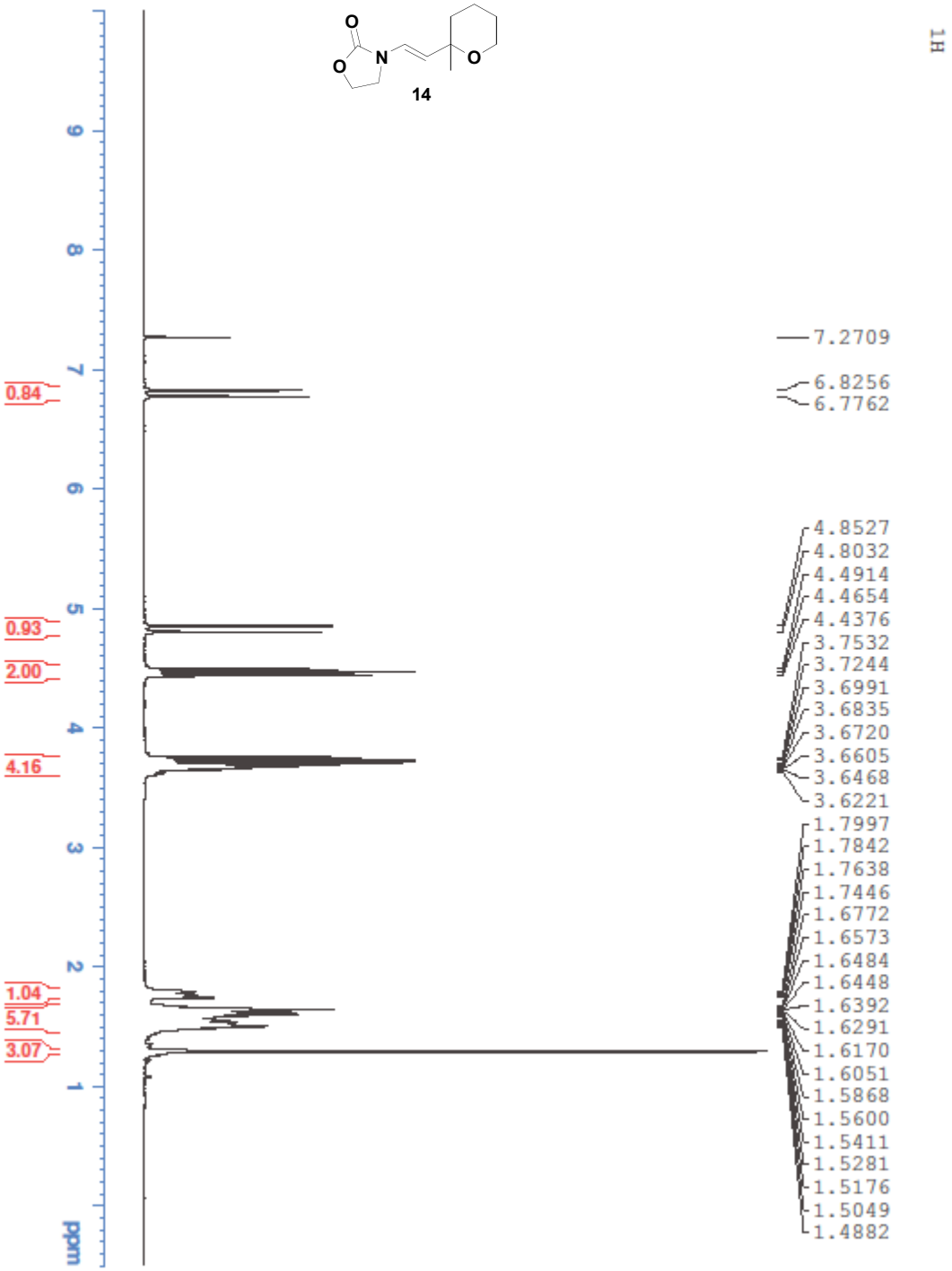
1.94
2.00
4.10
2.32
2.61
2.96
ppm


210.97
155.64
123.20
118.69
77.63
77.21
76.79
62.32
53.80
42.68
40.96
40.10
37.35
27.66
22.41
200
180
160
140
120
100
80
60
40
20
ppm
O
O
N
O
12


14
1H
7.2709
6.8256
6.7762
4.8527
4.8032
4.4914
4.4654
4.4376
3.7532
3.7244
3.6991
3.6835
3.6720
3.6605
3.6468
3.6221
1.7997
1.7842
1.7638
1.7446
1.6772
1.6573
1.6484
1.6448
1.6392
1.6291
1.6170
1.6051
1.5868
1.5600
1.5411
1.5281
1.5176
1.5049
1.4882
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0.93
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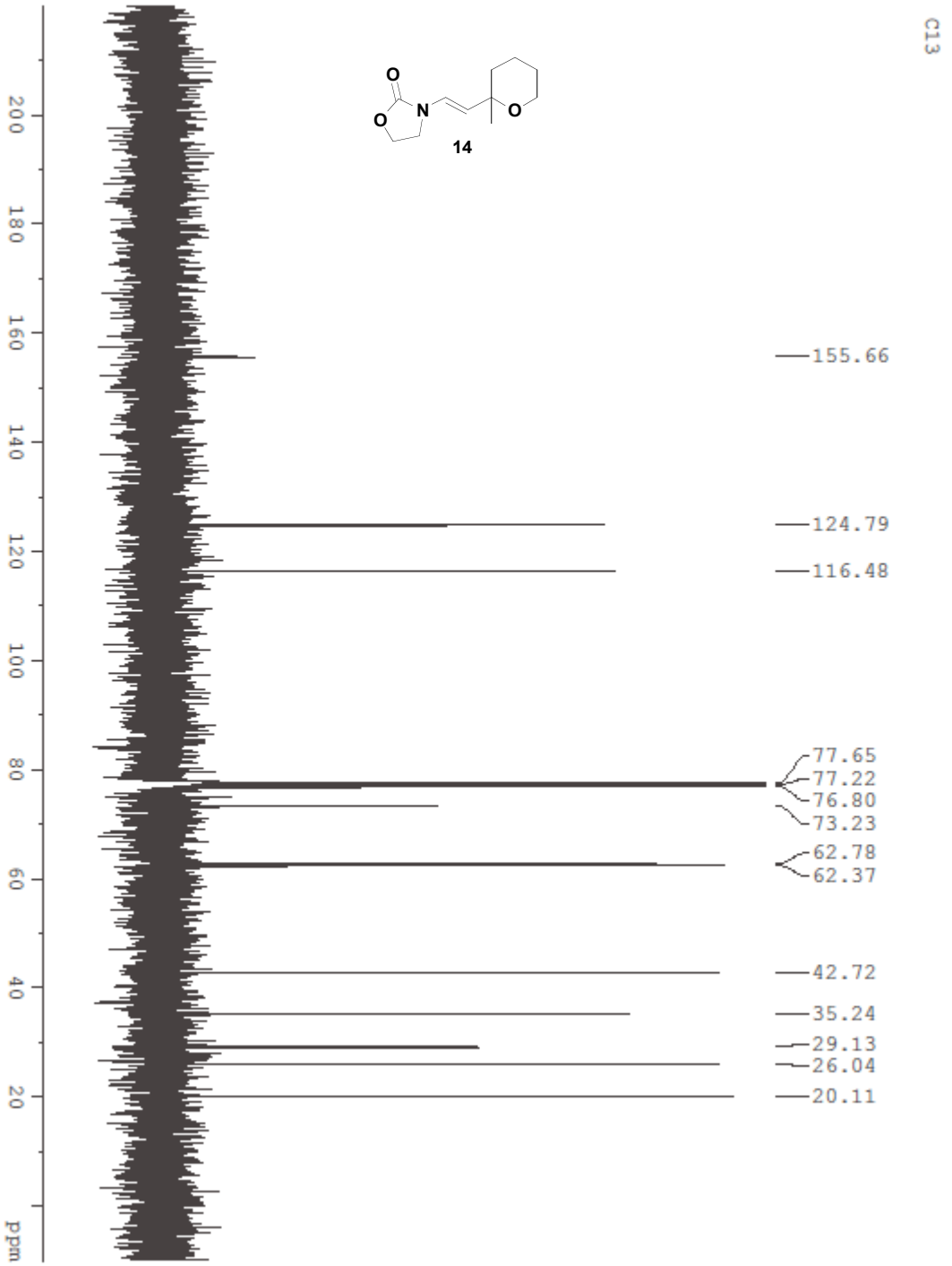
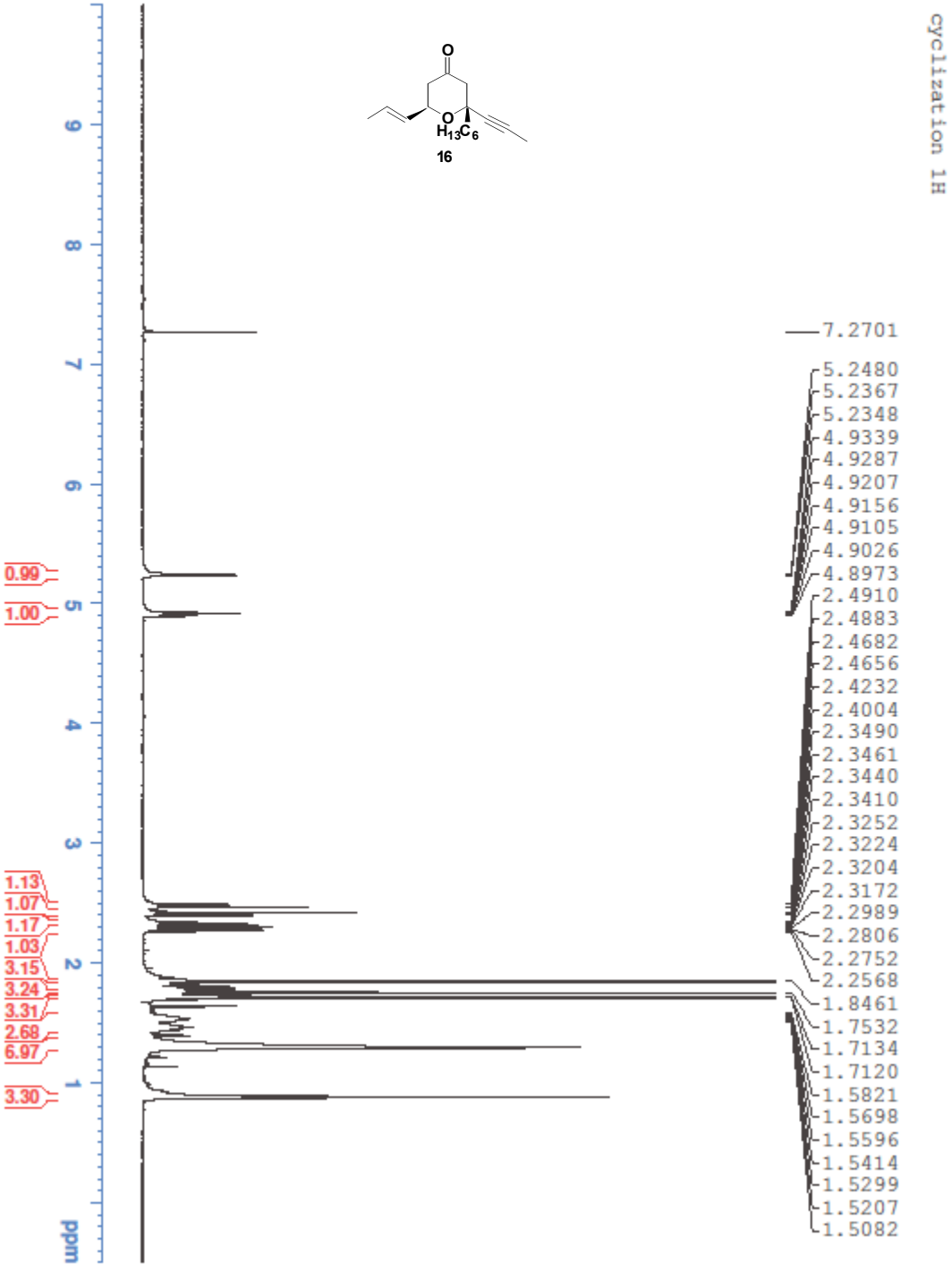
4.16
1.04
5.71
3.07
ppm


C13
14
155.66
124.79
116.48
77.65
77.22
76.80
73.23
62.78
62.37
42.72
35.24
29.13
26.04
20.11
200
180
160
140
120
100
80
60
40
20
ppm


cyclization 1H
16
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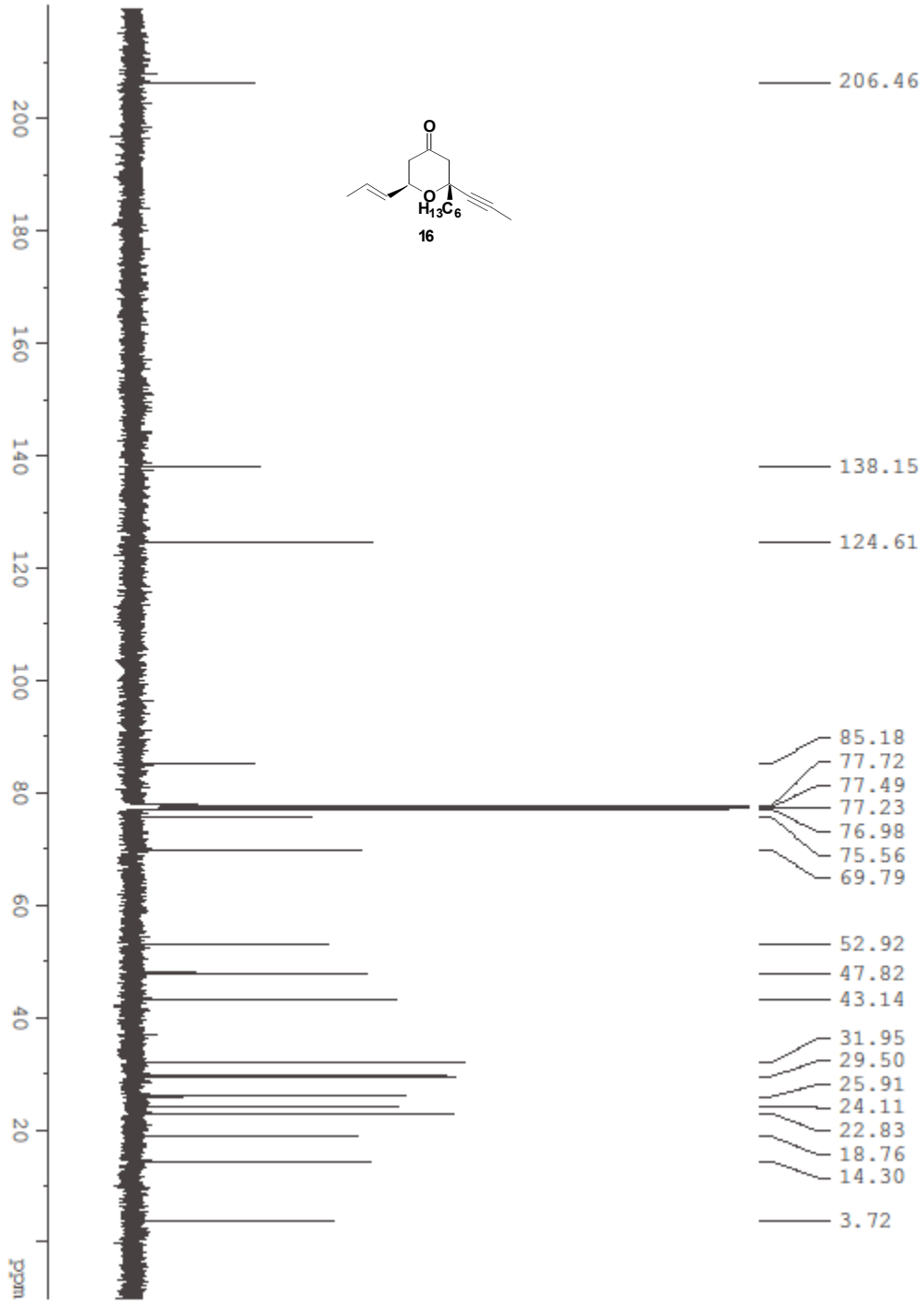
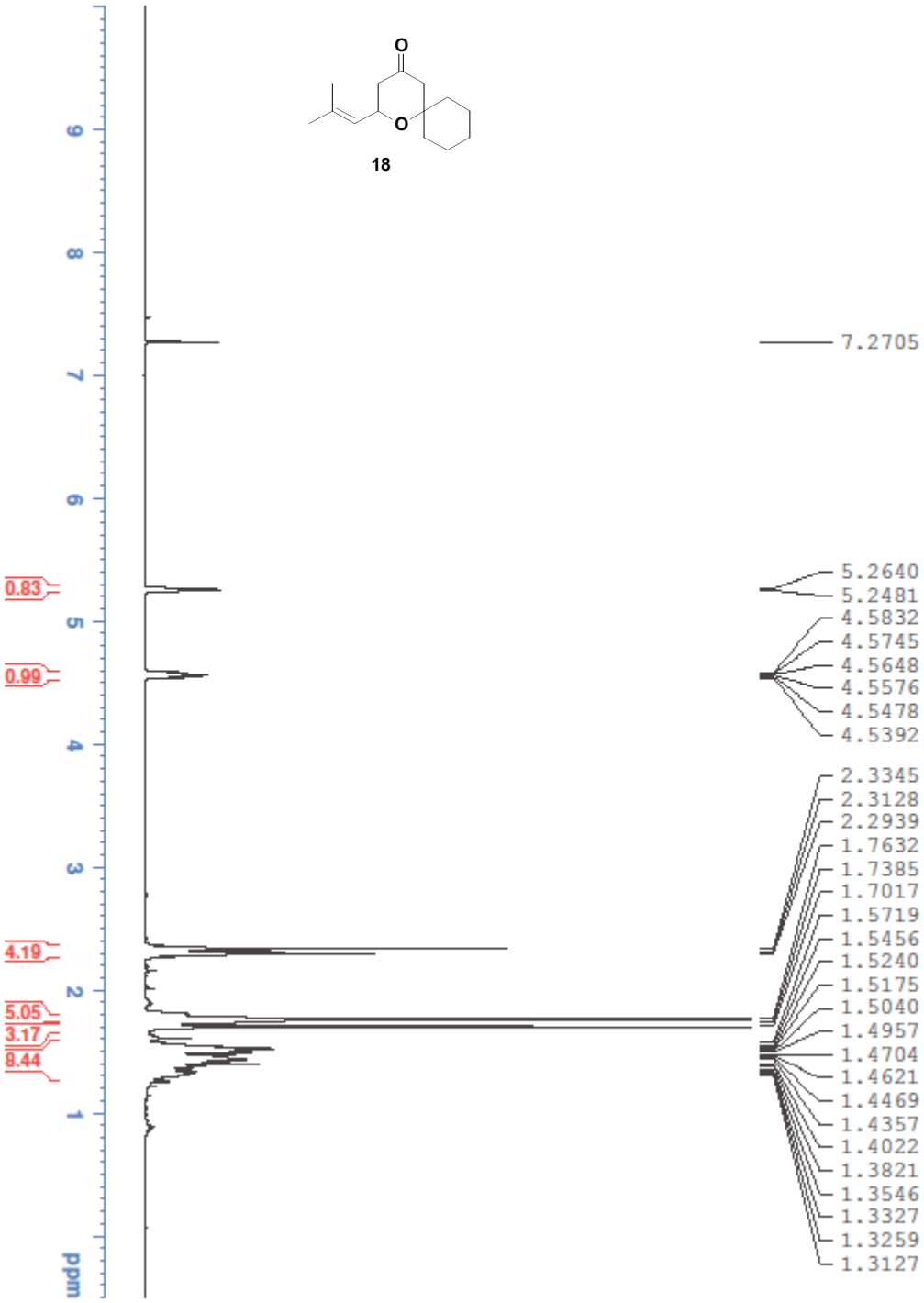
5.2480
5.2367
5.2348
4.9339
4.9287
4.9207
4.9156
4.9105
4.9026
4.8973
2.4910
2.4883
2.4682
2.4656
2.4232
2.4004
2.3490
2.3461
2.3440
2.3410
2.3252
2.3224
2.3204
2.3172
2.2989
2.2806
2.2752
2.2568
1.8461
1.7532
1.7134
1.7120
1.5821
1.5698
1.5596
1.5414
1.5299
1.5207
1.5082
0.99
1.00
1.13
1.07
1.17
1.03
3.15
3.24
3.31
2.68
6.97
3.30
ppm


206.46
138.15
124.61
85.18
77.72
77.49
77.23
76.98
75.56
69.79
52.92
47.82
43.14
31.95
29.50
25.91
24.11
22.83
18.76
14.30
3.72
ppm
O
O
H13C6
16


O
O
18
9
8
7
6
5
4
3
2
1
ppm
0.83
0.99
4.19
5.05
3.17
8.44
7.2705
5.2640
5.2481
4.5832
4.5745
4.5648
4.5576
4.5478
4.5392
2.3345
2.3128
2.2939
1.7632
1.7385
1.7017
1.5719
1.5456
1.5240
1.5175
1.5040
1.4957
1.4704
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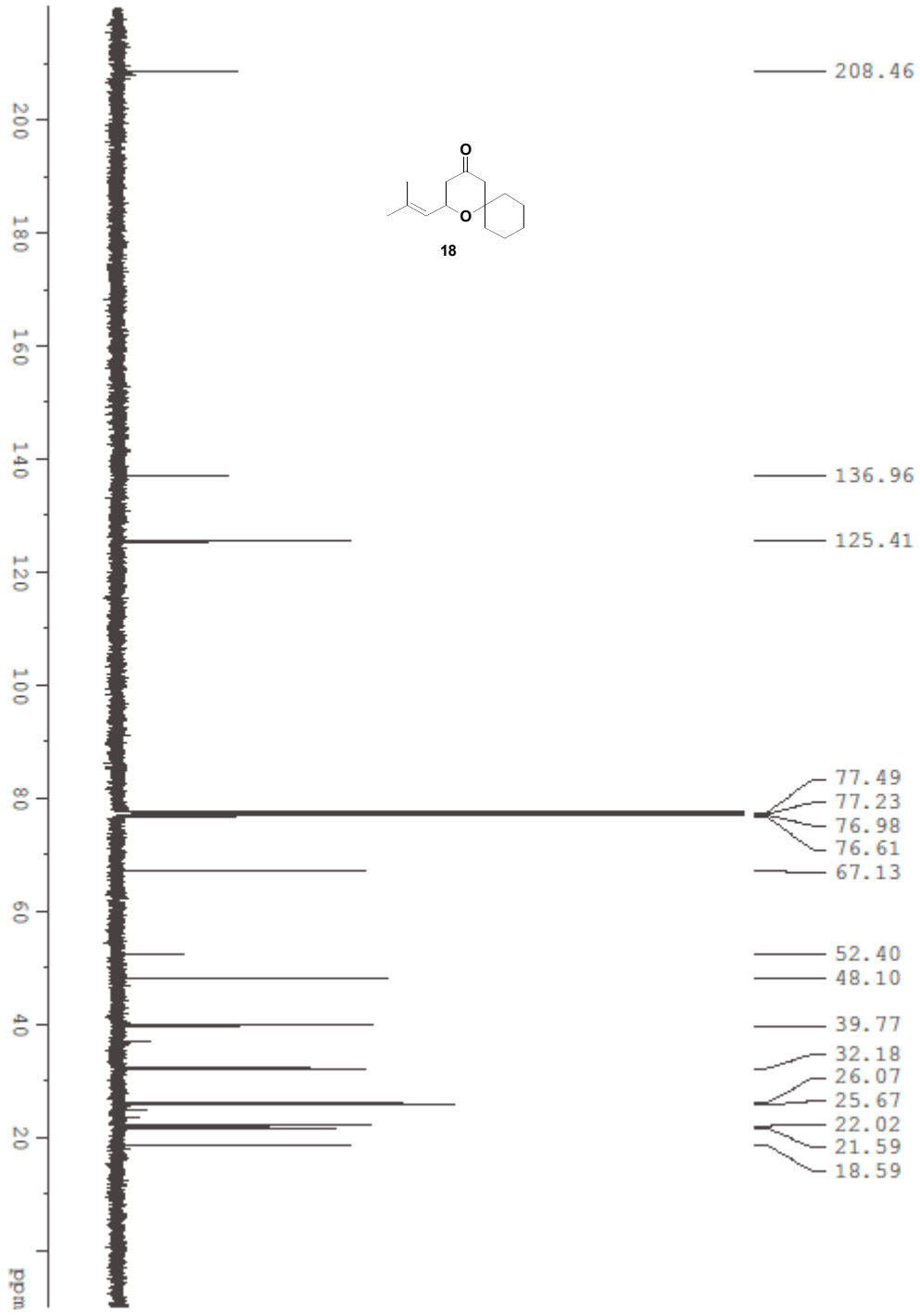
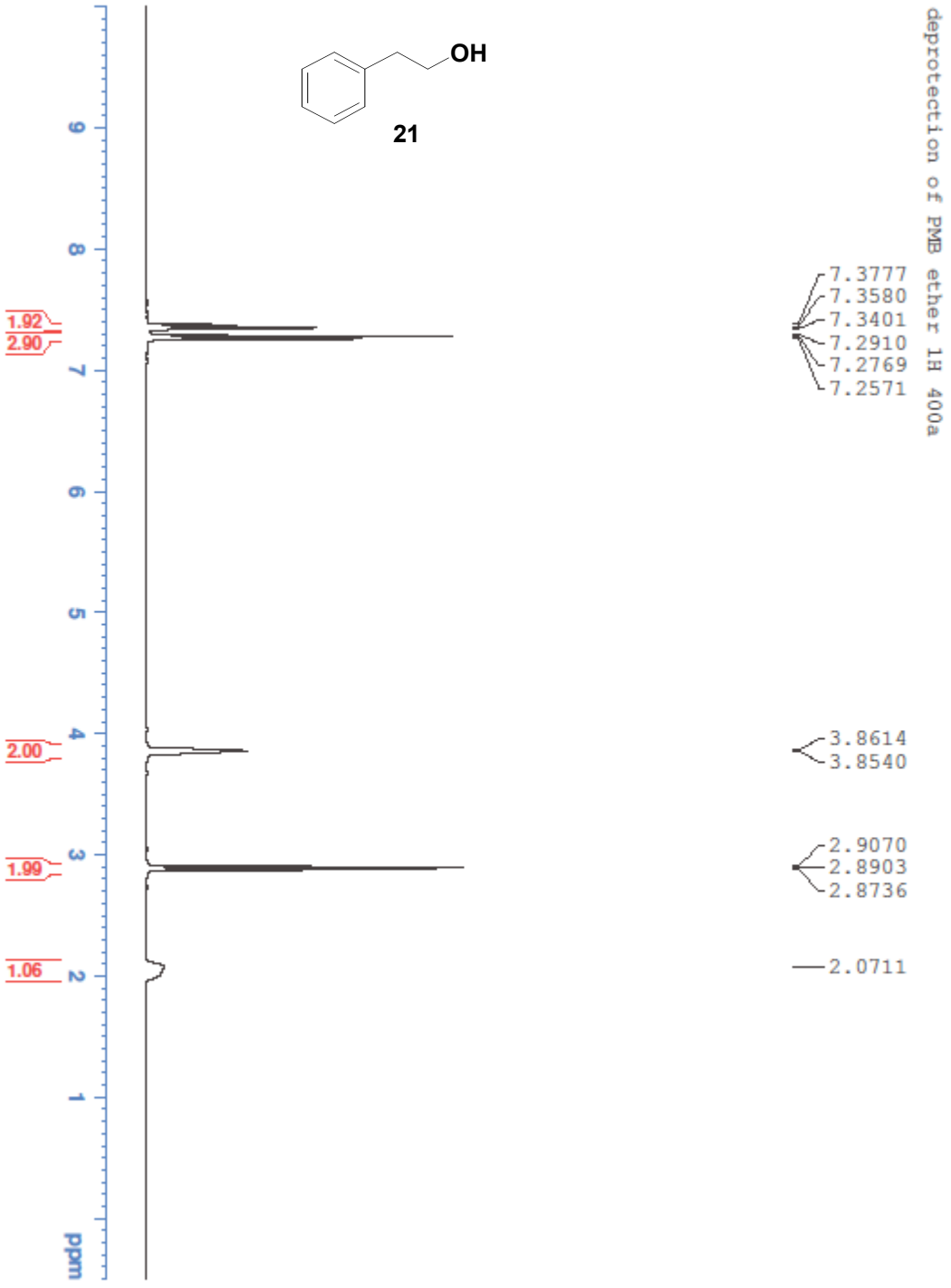
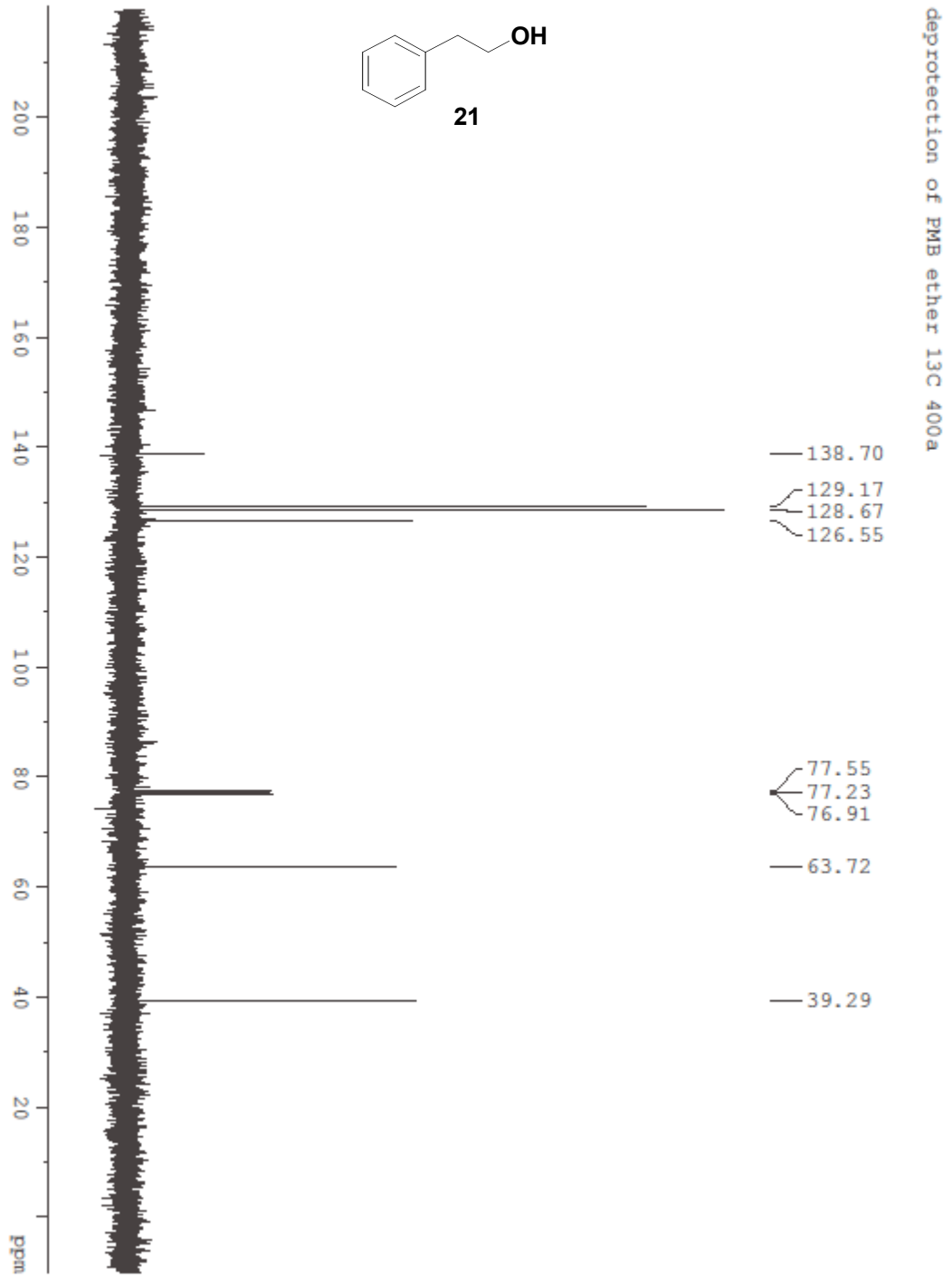
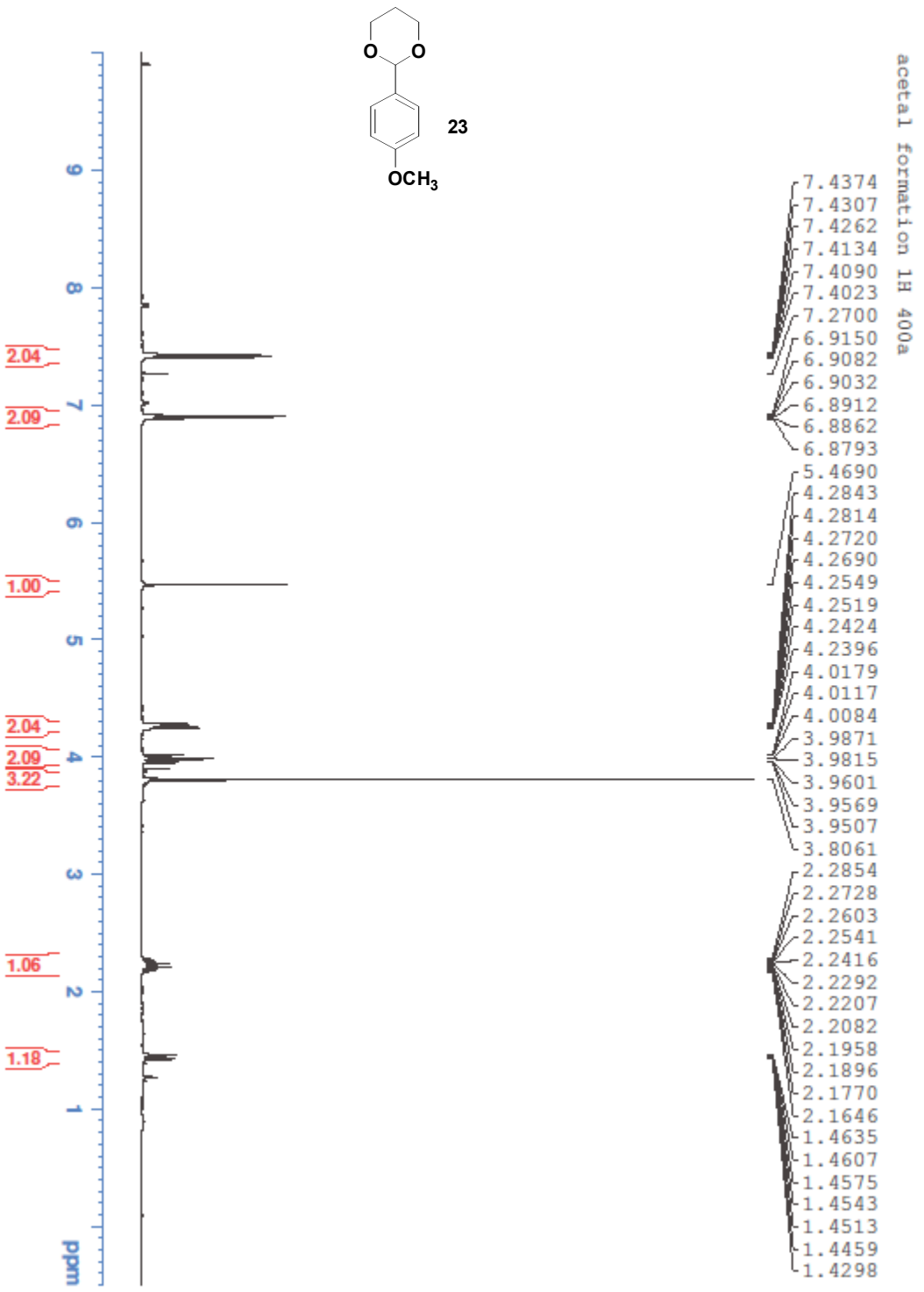
1.4469
1.4357
1.4022
1.3821
1.3546
1.3327
1.3259
1.3127


208.46
136.96
125.41
77.49
77.23
76.98
76.61
67.13
52.40
48.10
39.77
32.18
26.07
25.67
22.02
21.59
18.59
200
180
160
140
120
100
80
60
40
20
ppm
O
O
18


OH
21
deprotection of PMB ether 1H 400a
7.3777
7.3580
7.3401
7.2910
7.2769
7.2571
3.8614
3.8540
2.9070
2.8903
2.8736
2.0711
1.92
2.90
2.00
1.99
1.06
ppm


OH
21
deprotection of PMB ether 13C 400a
138.70
129.17
128.67
126.55
77.55
77.23
76.91
63.72
39.29
200
180
160
140
120
100
80
60
40
20
ppm


23
OCH3
acetal formation 1H 400a
7.4374
7.4307
7.4262
7.4134
7.4090
7.4023
7.2700
6.9150
6.9082
6.9032
6.8912
6.8862
6.8793
5.4690
4.2843
4.2814
4.2720
4.2690
4.2549
4.2519
4.2424
4.2396
4.0179
4.0117
4.0084
3.9871
3.9815
3.9601
3.9569
3.9507
3.8061
2.2854
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2.2541
2.2416
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2.2207
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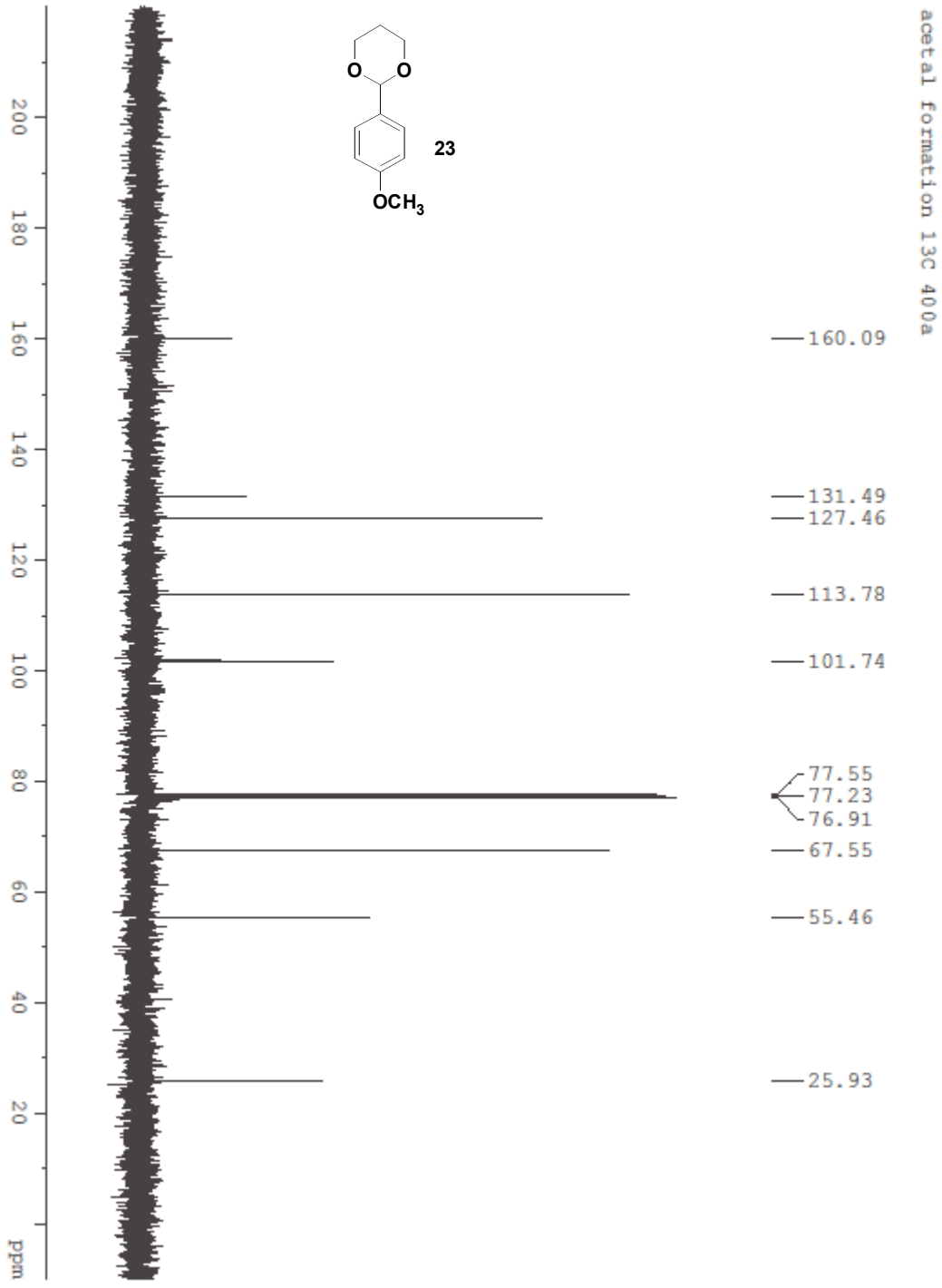
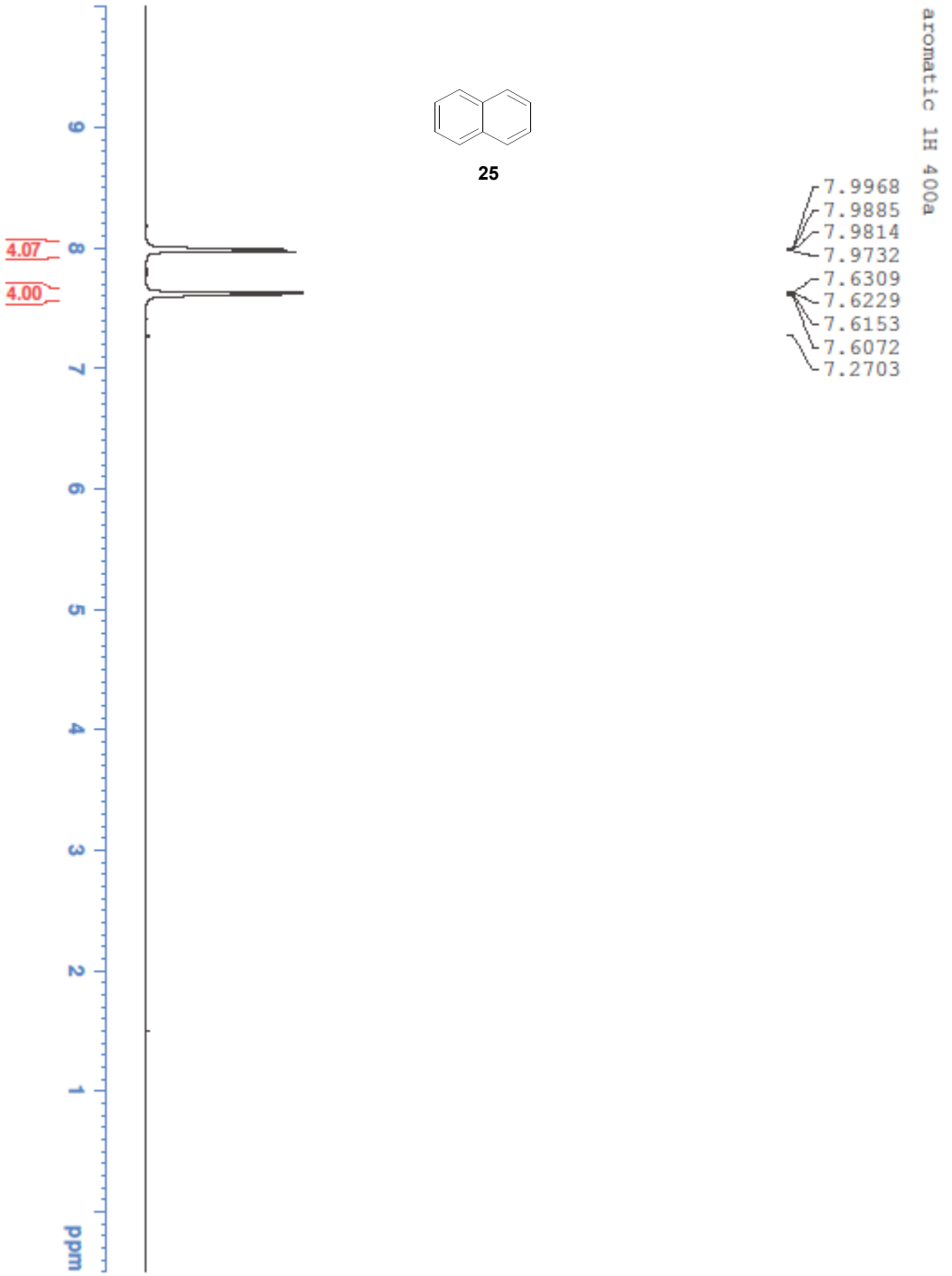
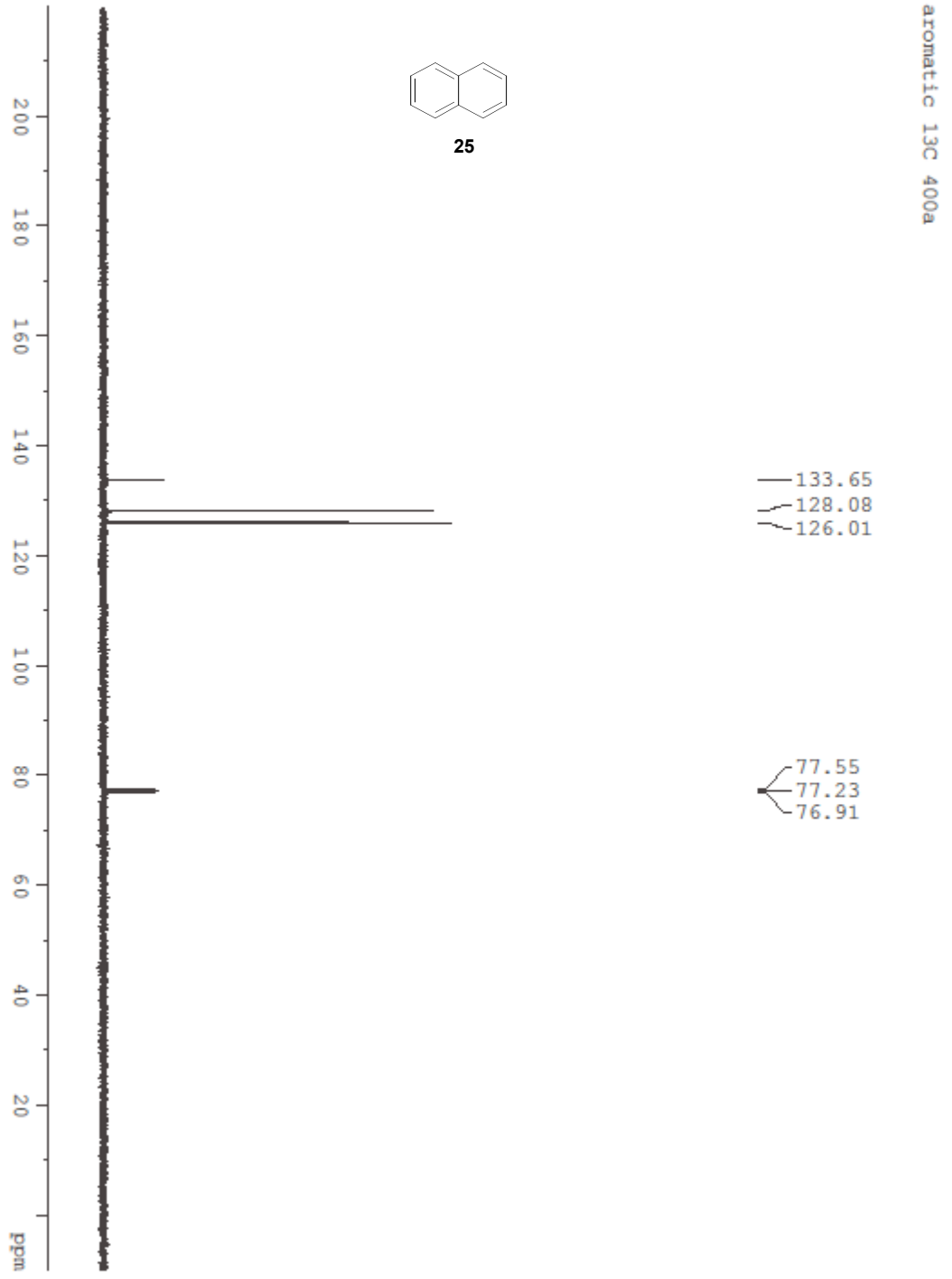
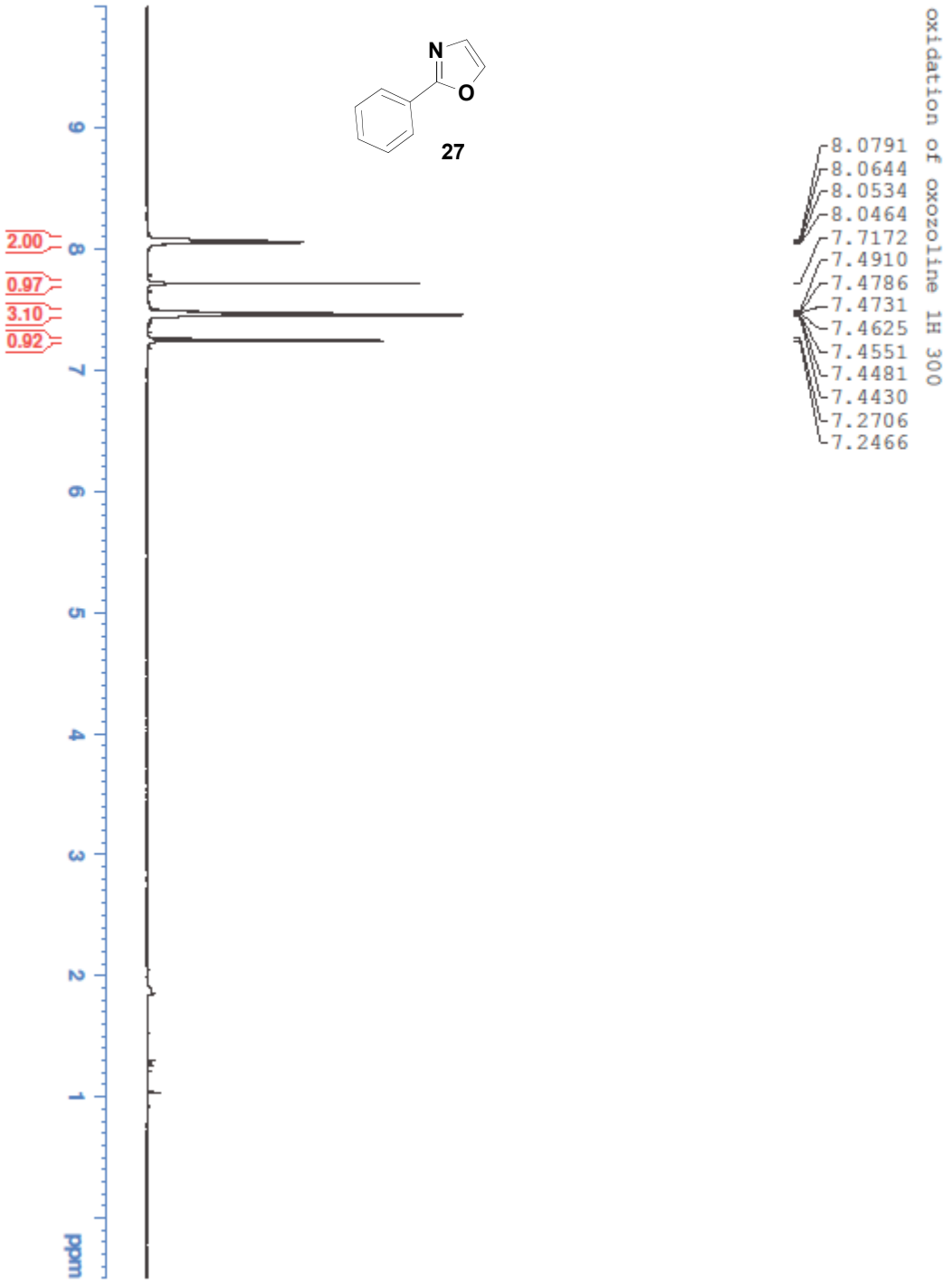
2.1896
2.1770
2.1646
1.4635
1.4607
1.4575
1.4543
1.4513
1.4459
1.4298
2.04
2.09
1.00
2.04
2.09
3.22
1.06
1.18
ppm

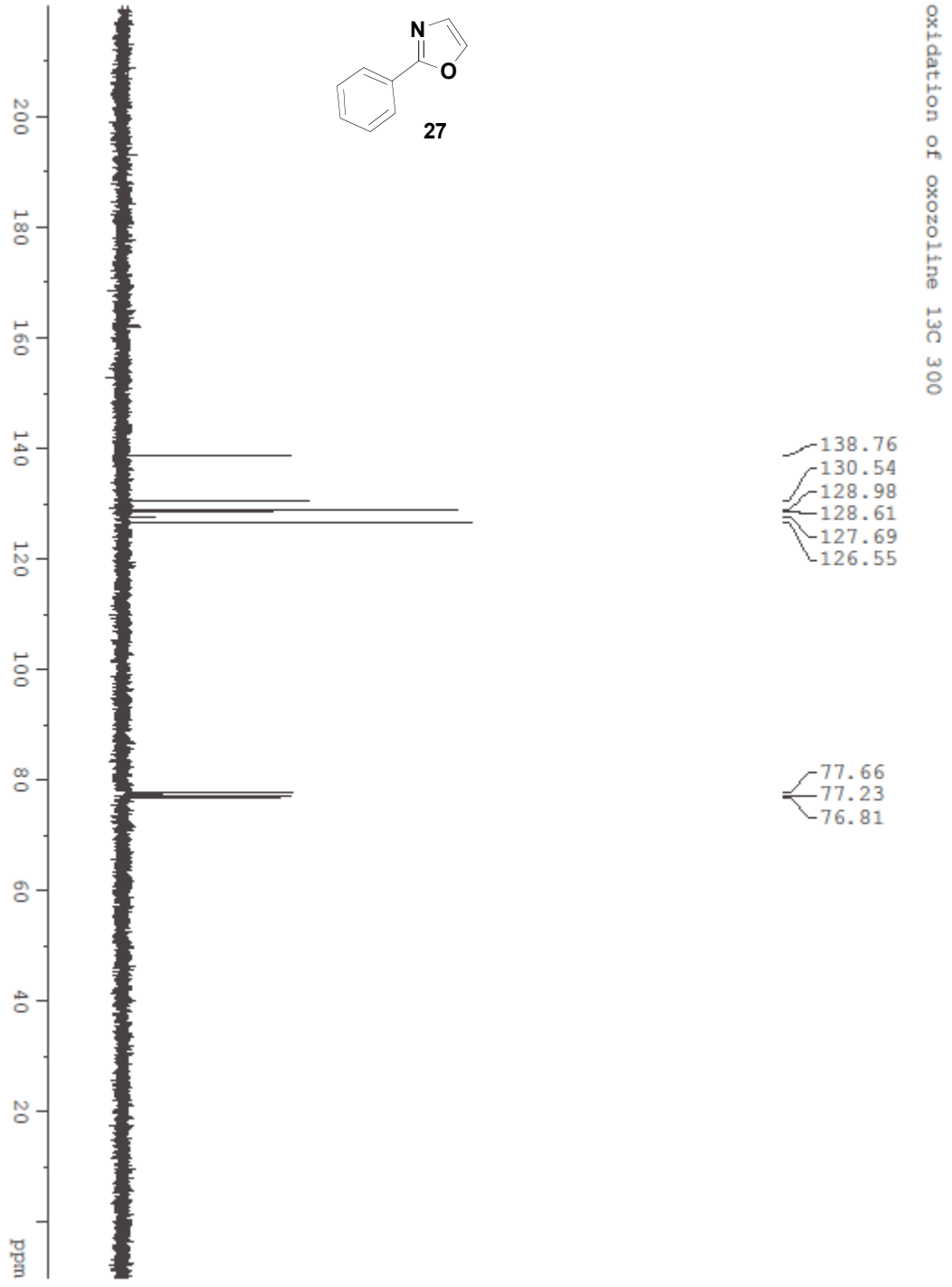

acetal formation 13C 400a
23
OCH3
160.09
131.49
127.46
113.78
101.74
77.55
77.23
76.91
67.55
55.46
25.93
200
180
160
140
120
100
80
60
40
20
ppm

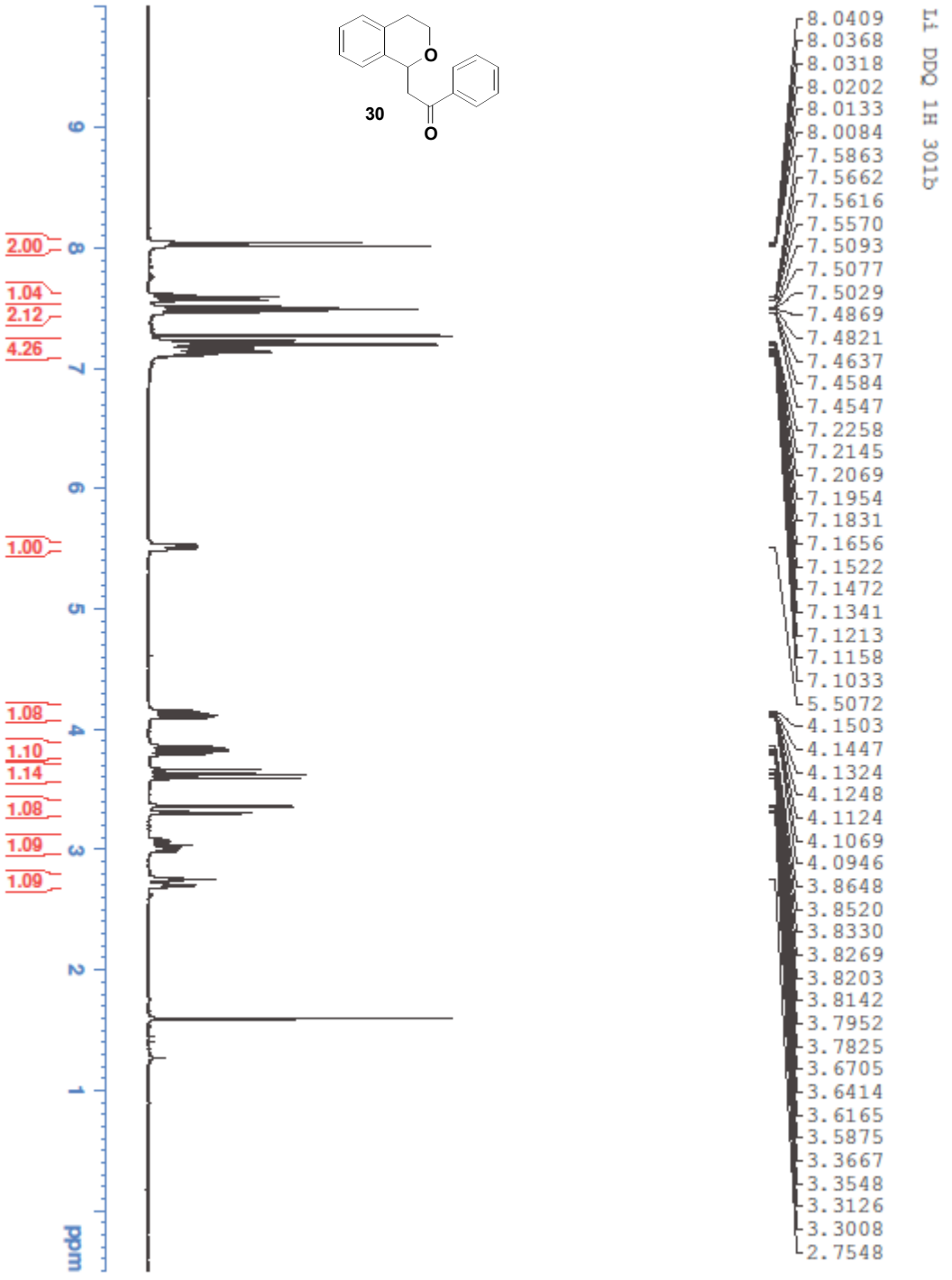

aromatic 1H 400a
7.9968
7.9885
7.9814
7.9732
7.6309
7.6229
7.6153
7.6072
7.2703
4.07
4.00
9
8
7
6
5
4
3
2
1
ppm

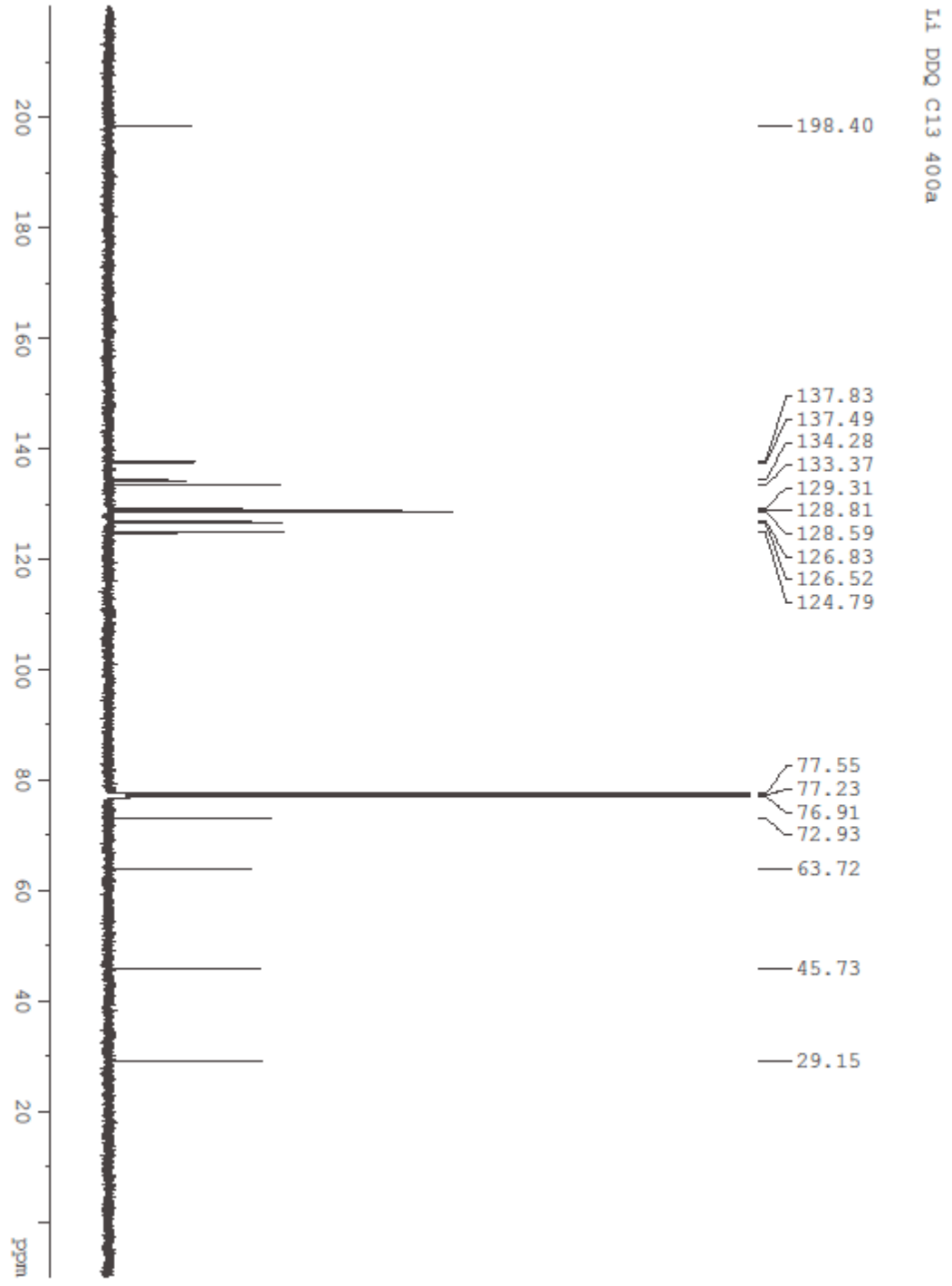
25


aromatic 13C 400a
25
133.65
128.08
126.01
77.55
77.23
76.91
200
180
160
140
120
100
80
60
40
20
ppm


oxidation of oxozoline 1H 300
8.0791
8.0644
8.0534
8.0464
7.7172
7.4910
7.4786
7.4731
7.4625
7.4551
7.4481
7.4430
7.2706
7.2466
N
O
27
2.00
0.97
3.10
0.92
9
8
7
6
5
4
3
2
1
ppm


oxidation of oxozoline 13C 300
N
O
27
138.76
130.54
128.98
128.61
127.69
126.55
77.66
77.23
76.81
200
180
160
140
120
100
80
60
40
20
ppm


30
O
O
2.00
1.04
2.12
4.26
1.00
1.08
1.10
1.14
1.08
1.09
1.09
ppm
1 2 3 4 5 6 7 8 9
Li DDQ 1H 301b
8.0409
8.0368
8.0318
8.0202
8.0133
8.0084
7.5863
7.5662
7.5616
7.5570
7.5093
7.5077
7.5029
7.4869
7.4821
7.4637
7.4584
7.4547
7.2258
7.2145
7.2069
7.1954
7.1831
7.1656
7.1522
7.1472
7.1341
7.1213
7.1158
7.1033
5.5072
4.1503
4.1447
4.1324
4.1248
4.1124
4.1069
4.0946
3.8648
3.8520
3.8330
3.8269
3.8203
3.8142
3.7952
3.7825
3.6705
3.6414
3.6165
3.5875
3.3667
3.3548
3.3126
3.3008
2.7548


Li DDQ C13 400a
198.40
137.83
137.49
134.28
133.37
129.31
128.81
128.59
126.83
126.52
124.79
77.55
77.23
76.91
72.93
63.72
45.73
29.15
200
180
160
140
120
100
80
60
40
20
ppm