Supporting information

Caging of Carbonyl Compounds as Photolabile (2,5-Dihydroxyphenyl)ethylene Glycol Acetals

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General experimental procedures

All NMR spectra were recorded on 400 MHz spectrometer in $CDCl_3$ and referenced to TMS unless otherwise noted. Flash chromatography was performed using 40-63 μm silica gel. Solutions for photolyses were prepared using HPLC grade water and methanol. Substrate concentration was kept at ca $1*10^{-2}$ M (NMR experiments) $1*10^{-3}$ M (HPLC, GC) or $1*10^{-4}$ M (UV). Irradiation of compounds **1a-e**, were carried out in mini-Rayonet photochemical reactor equipped with 1 or 2 fluorescent UV lamps (4W, 300 nm). Reaction mixtures after photolysis were analyzed by HPLC (**1b, d, e**), GC (**1c**) or NMR (**1a**). Yields of deprotection reactions were calculated using pure substrates as references. Quantum efficiencies of photochemical reactions were measured by ferrioxalate chemical actinometry.

Materials

2,5-Dimethoxybenzaldehyde, carbonyl compounds **5a-e**, and other reagents were purchased from commercial sources and used without further purification.

2,5-Dimethoxystyrene.[1] Methyltriphenyl phosphonium bromide (35.7 g, 100 mmol) was suspended in THF (300 mL) and *n*-butyllithium in hexane (2.2M, 50 mL, 110 mmol) was added dropwise under nitrogen. The resulting yellow solution was stirred for 3 h at room temperature, and then 2,5-dimethoxybenzaldehyde (16.6 g, 100 mmol) in THF (100 mL) was added dropwise. The reaction mixture was refluxed overnight, then cooled to room temperature, filtered, and washed consequently with aqueous ammonium chloride (10%, 3x100 mL) and brine (100 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and all volatiles were removed *in vacuo*. Column chromatography on the residue afforded 13 g of 2,5-dimethoxystyrene (79 mmol, 79%) as colorless oil. ^{1}H NMR: δ 3.79 (s, 3H), 3.81 (s, 3H), 5.27 (dd, 1H), 5.72 (dd, 1H), 6.80 (m, 2H), 7.03 (m, 2H); ^{13}C NMR δ 56.0, 56.5, 112.1, 112.5, 114.0, 114.9, 127.8, 131.7, 151.4, 153.9. MS: 164 (100, M+), 149 (52), 121 (66), 91 (83), 89 (16), 78 (34), 77 (39).

(2,5-Dimethoxyphenyl)ethylene glycol (**6**):[2] Glacial acetic acid (100 mL) was added to the mixture of dimethoxystyrene (13 g, 79 mmol), sodium periodate (5.14 g, 24 mmol, 30 mol%) and dry lithium bromide (1.4 g, 16 mmol, 20 mol%). The reaction mixture was stirred at 100^0C overnight, then cooled, partially concentrated *in vacuo* and poured in water (250 mL). The product was extracted with ethyl acetate (3x50 mL), and combined organic layers were washed with aqueous sodium bicarbonate (2x75 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The resulting residue was redissolved in methanol (100 mL) and stirred with potassium carbonate (16.5 g, 120 mmol) at r.t. for 20 h. The resulting mixture was then filtered and concentrated *in vacuo*. The residue redissolved in ethyl acetate (150 mL), washed with brine (3x50 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting crude product was purified by column chromatography to afford 11.1 g

of pure diol **6** (56 mmol, 79%) as a white solid. ^{1}H NMR: δ 3.65 (q, 1H), 3.72 (q, 1H), 3.77 (s, 3H), 3.79 (s, 3H), 5.02 (dd, 1H), 6.79 (m, 2H), 6.99 (d, 1H); ^{13}C NMR δ 55.97, 56.03, 66.8, 71.3, 111.7, 113.3, 113.5, 129.8, 150.8, 154.0. MS: 198 (22), 167 (100), 152 (18), 139 (59), 137 (40), 124 (36), 109 (15), 108 (12), 77 (14).

Compounds **7b-e**, **8b-e**, **1b-e** were prepared according to the procedures for syntheses of the compounds **7a**, **8a**, **1a**, respectively as described in the Experimental Section of the note.

4-(2,5-Dimethoxyphenyl)-2-phenyl-1,3-dioxolane (**7b**, 1:1 mixture of diastereomers): Colorless liquid, 85%. ^{1}H NMR: δ 3.69-3.87 (4s, 12H + 2t, 2H), 4.46 (t, 1H), 4.67 (t, 1H), 5.47 (2t, 2H), 5.98 (s, 1H), 6.08 (s, 1H), 6.79 (m, 4H), 7.12 (m, 1H), 7.19 (m, 1H), 7.40 – 7.54 (m, 5H), 7.55 – 7.59 (m, 5H). MS: 286 (100, M^+), 227 (11), 180 (48), 164 (17), 149 (40), 119 (44), 105 (39), 91 (74), 89 (16), 77 (53). HRMS: calcd. for $C_{17}H_{18}O_4Na^+$ 309.1103; found 309.1115

2-(2,5-Dimethoxyphenyl)-1,4-dioxaspiro[4.5]decane (**7c**): Colorless liquid, 72%. ^{1}H NMR: δ 1.43 – 1.75 (m, 10H), 3.59 (t, 1H), 3.76 (s, 3H), 3.79 (s, 3H), 4.43 (td, 1H), 5.33 (t, 1H), 6.76 (d, 2H), 7.16 (s, 1H); ^{13}C NMR δ 24.17, 24.24, 25.5, 35.7, 36.2, 55.95, 56.03, 70.6, 73.0, 109.9, 111.1, 112.4, 112.7, 130.4, 150.7, 154.0. MS: 278 (66, M^+), 235 (29), 180 (60), 164 (56), 151 (42), 137 (12), 121 (22), 97 (11), 91 (16), 77 (14). HRMS: calcd. for $C_{16}H_{22}O_4Na+$ 301.1410; found 301.1403

4-(2,5-Dimethoxyphenyl)-2-methyl-2-phenyl-1,3-dioxolane (**7d**, mixture of diastereomers): Colorless liquid, 63%. ^{1}H NMR: δ 1.81 (s, 3H), 3.70 (s, 3H), 3.72 (m, 1H), 3.82 (s, 3H), 4.18 (t, 1H), 5.18 (t, 1H), 6.72 – 6.78 (m, 3H), 7.27 – 7.50 (m, 5H). MS: 300 (56, M^+), 285 (15), 180 (17), 149 (12), 133 (72), 105 (100), 91 (16), 77 (36). HRMS: calcd. for $C_{18}H_{20}O_4Na^+$ 323.1259; found 323.1262

4-(2,5-Dimethoxyphenyl)-2-(2-phenyl)ethyl-1,3-dioxolane (**7e**) was used in the next step without purification.

2-(2-Phenyl-1,3-dioxolan-4-yl)benzo-1,4-quinone (**8b**, mixture of diastereomers): Yellow oil, 59%. ^{1}H NMR: δ 3.71 (m, 1H), 3.92 (dd, 1H), 4.45 (t, 1H), 4.66 (td, 1H), 5.15 (m, 2H), 5.92 (s, 1H), 5.99 (s, 1H), 6.78 (m, 4H), 6.89 (d, 1H), 7.01 (d, 2H), 7.40 – 7.43 (m, 10H). MS: 258 (8, $[M+2]^+$), 255 (9), 152 (100), 137 (15), 134 (30), 123 (54), 105 (83), 91 (47), 77 (91). HRMS: calcd. for $C_{15}H_{12}O_4Na^+$ 279.0633; found 279.0640

2-(1,4-Dioxaspiro[4.5]decan-2-yl)benzo-1,4-quinone (**8c**): Yellow oil, 77%. ^{1}H NMR: δ 1.42 – 1.72 (m, 10H), 3.64 (td, 1H), 4.45 (td, 1H), 5.02 (td, 1H), 6.76 (d, 2H), 6.93 (d, 1H); ^{13}C NMR δ 24.0, 24.1, 25.3, 35.0, 36.1, 69.3, 71.9, 111.0, 130.9, 136.6, 137.0, 148.0, 187.6, 187.8. MS: 248 (7, M+), 205 (21), 152 (19), 133 (86), 123 (6), 106 (17), 97 (6), 82 (16), 78 (15). HRMS: calcd. for $C_{14}H_{16}O_4Na^+$ 271.0946; found 271.0952

2-(2-Methyl-2-phenyl-1,3-dioxolan-4-yl)benzo-1,4-quinone (**8d**): was used in the next step without purification.

2-(2-(2-Phenyl)ethyl-1,3-dioxolan-4-yl)benzo-1,4-quinone (**8e**, mixture of diastereomers): Yellow oil, 57% over 2 steps. ^{1}H NMR: δ 2.09 (m, 2H), 2.81 (m, 2H), 3.51 (m, 1H), 4.25 (td, 1H), 5.01 (m, 1H+1H), 6.77 (d, 2h), 6.88 (d, 1H), 7.20 – 7.33 (m, 5H). MS: 286 (7, $[M+2]^+$), 180 (15), 152 (60), 133 (67), 123 (42), 105 (38), 91 (100), 77 (31). HRMS: calcd. for $C_{17}H_{16}O_4Na^+$ 307.0946; found 307.0959

4-(2,5-Dihydroxyphenyl)-2-phenyl-1,3-dioxolane (**1b**, mixture of diastereomers): white solid, 80%. ^{1}H NMR (acetone-*d6*): δ 3.77 (m, 1H+1H), 4.42 (td, 1H), 4.62 (td, 1H), 5.37 (t, 1H), 5.42 (t, 1H), 5.90 (s, 1H), 6.04 (s, 1H), 6.54 (m, 2H), 6.63 (m, 2H), 6.94 (m, 1H+1H), 7.39 – 7.69 (m, 12H); ^{13}C NMR δ 74.6, 76.2, 78.5, 79.0, 107.5, 107.7, 113.1, 113.6, 114.9, 115.0, 116.7, 116.9, 125.16, 125.23, 129.15, 129.20, 141.0, 147.3, 150.5. MS: 258 (5, M^+), 152 (100), 137 (14), 135 (23), 123 (44), 107 (13), 105 (16), 91 (10), 77 (32). HRMS: calcd. for $C_{15}H_{14}O_4Na^+$ 281.0790; found 281.0792

2-(2,5-Dihydroxyphenyl)-1,4-dioxaspiro[4.5]decane (**1c**): white solid, 70%. ^{1}H NMR (acetone-*d6*): δ 1.40 – 1.71 (m, 10H), 3.55 (t, 1H), 4.38 (td, 1H), 5.27 (t, 1H), 6.57 (dd, 1H), 6.67 (d, 1H), 6.97 (d, 1H), 7.75 (s, 1H), 7.87 (s, 1H); ^{13}C NMR δ 24.0, 24.1, 28.6, 35.4, 36.2, 70.3, 73.5, 109.3, 113.1, 114.5, 115.8, 127.7, 147.1, 150.7. MS: 250 (12, M^+), 152 (100), 135 (32), 123 (38), 107 (18), 95 (7), 77 (11), 55 (37). HRMS: calcd. for $C_{14}H_{18}O_4H^+$ 251.1283; found 251.1265

4-(2,5-Dihydroxyphenyl)-2-methyl-2-phenyl-1,3-dioxolane (**1d**, mixture of diastereomers): white solid, 75% over 2 steps. ^{1}H NMR (acetone-*d6*): δ 1.77 (s, 3H), 1.82 (s, 3.75H), 3.79 (t, 1H), 3.98 (t, 1.25H), 4.17 (t, 1.25H), 4.43 (t, 1H), 4.94 (t, 1.25H), 5.27 (t, 1H), 6.52 – 6.79 (m, 7H), 6.95 (s, br, 1H), 7.30 – 7.55 (m, 11H); ^{13}C NMR δ 24.9, 25.0, 72.2, 73.3, 75.0, 75.1, 108.8, 109.0, 113.0, 113.5, 114.7, 114.8, 116.5, 116.7, 125.0, 125.1, 129.02, 129.07, 140.5, 147.1, 150.7. MS: 272 (5, M^+), 152 (100), 135 (29), 123 (40), 107 (13), 105 (27), 95 (6), 77 (34). HRMS: calcd. for $C_{16}H_{16}O_4Na^+$ 295.0946; found 295.0956

4-(2,5-Dihydroxyphenyl)-2-(2-phenyl)ethyl-1,3-dioxolane (**1e**, mixture of diastereomers): white solid, 75%. ^{1}H NMR (acetone-*d6*): δ 2.05 (m, 2H), 2.82 (m, 2H), [3.57 (dd) + 3.66 (dd), 1H], [4.25 (t) + 4.53 (t), 1H], [5.06 (t) + 5.18 (t), 1H], 5.26 (m, 1H), 6.59 (m, 1H), 6.69 (m, 1H), [6.92 (d) + 7.00 (d), 1H], 7.15 – 7.32 (m, 5H), [7.72 (s) + 7.76 (s), 1H], [7.91 (s) + 7.95 (s), 1H]; ^{13}C NMR δ 30.25, 30.35, 36.0, 36.3, 71.3, 71.9, 73.7, 73.8, 104.0, 104.1, 112.6, 113.0, 114.5, 114.6, 115.7, 115.9, 126.0, 126.03, 128.55, 128.58, 142.1, 146.9, 150.7. MS: 286 (13, M+), 152 (100), 135 (28), 123 (61), 107 (21), 91 (42), 77 (24). HRMS: calcd. for $C_{17}H_{18}O_4Na^+$ 309.1103; found 309.1114

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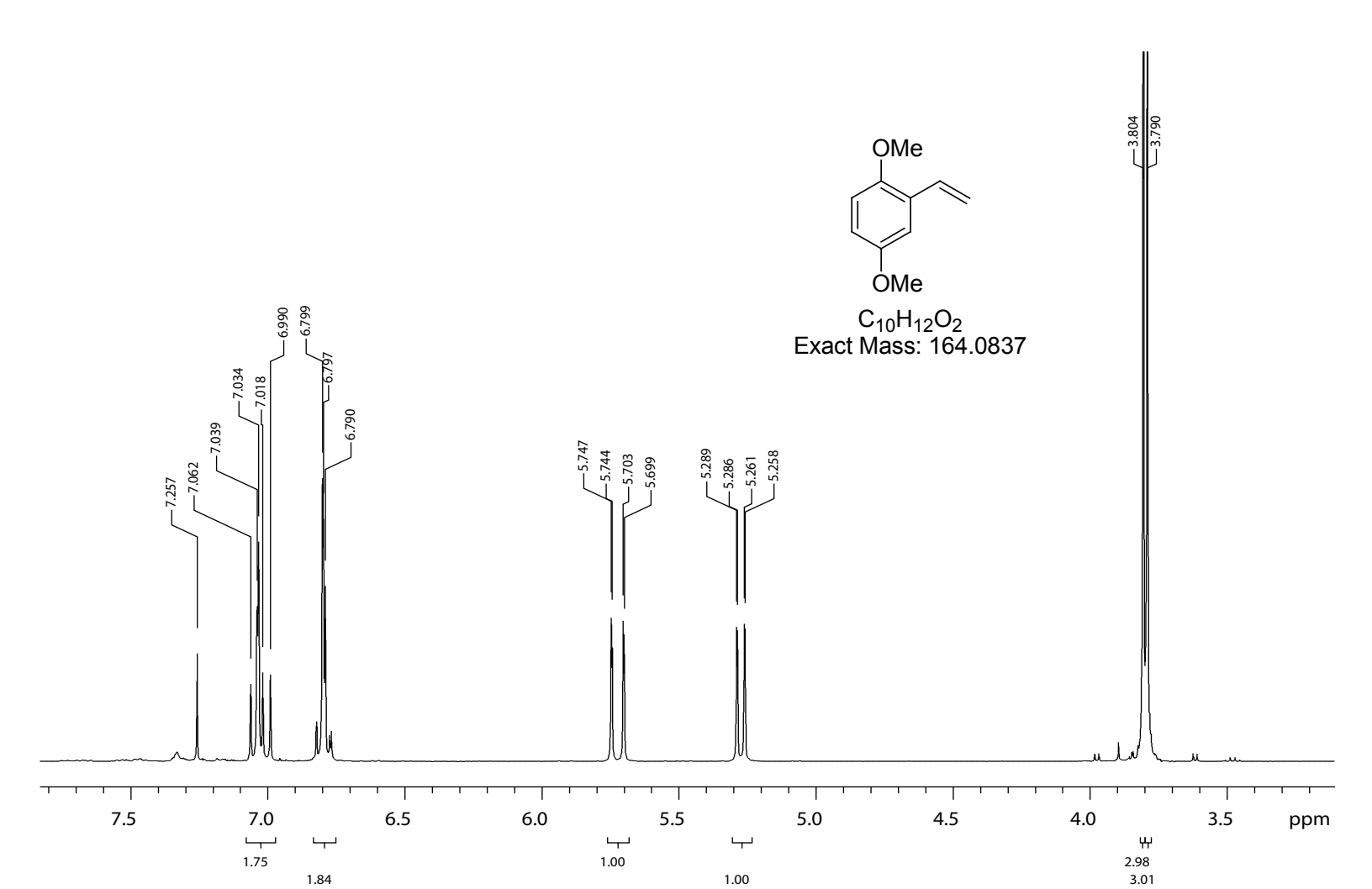
[1] Parker, K. A.; Ruder, S. M. *J. Am. Chem. Soc.* **1989**, *111*, 5948.
[2] Kappe, T.; Witoszynskyj, T. *Arch. Pharm.* **1975**, *308*, 339.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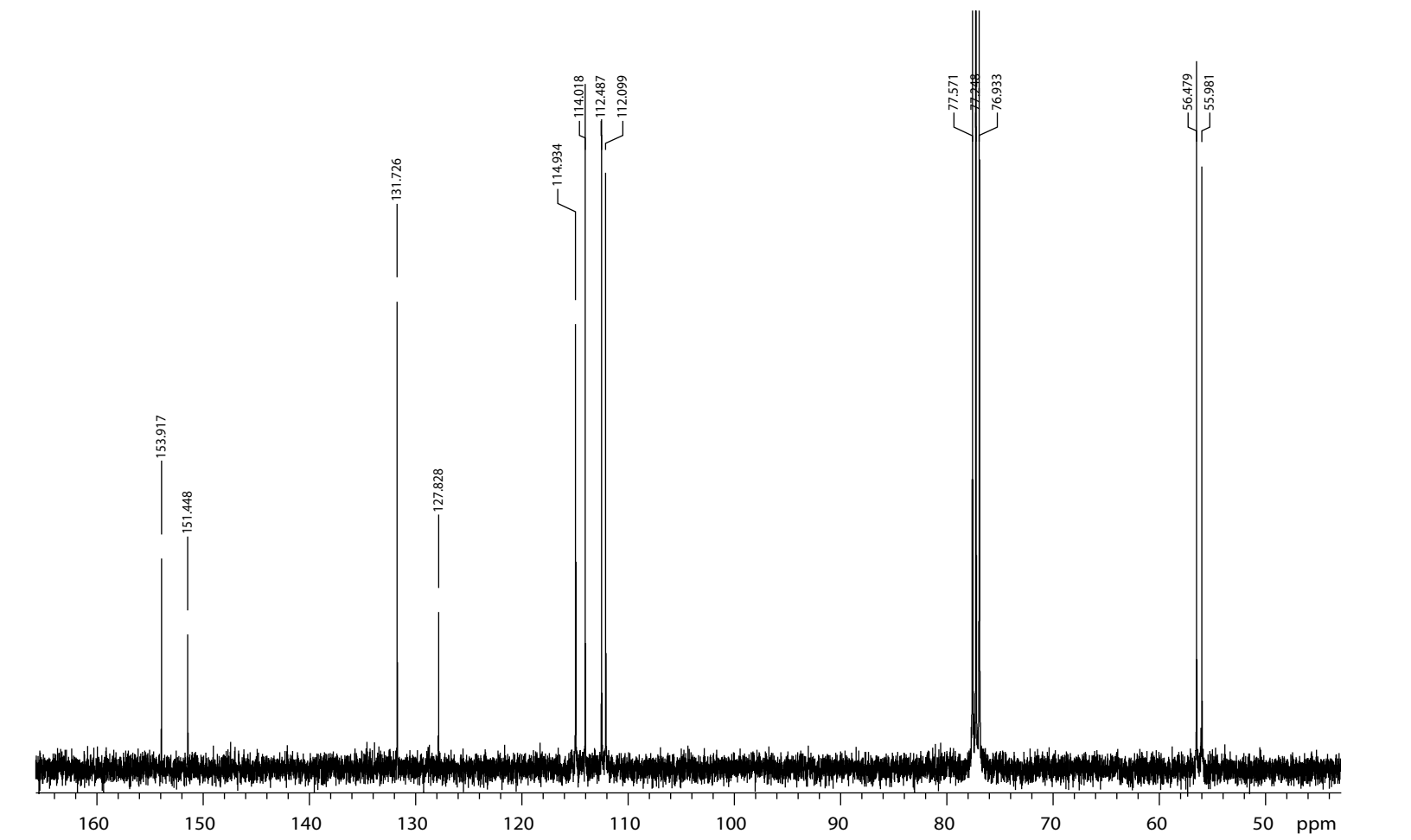
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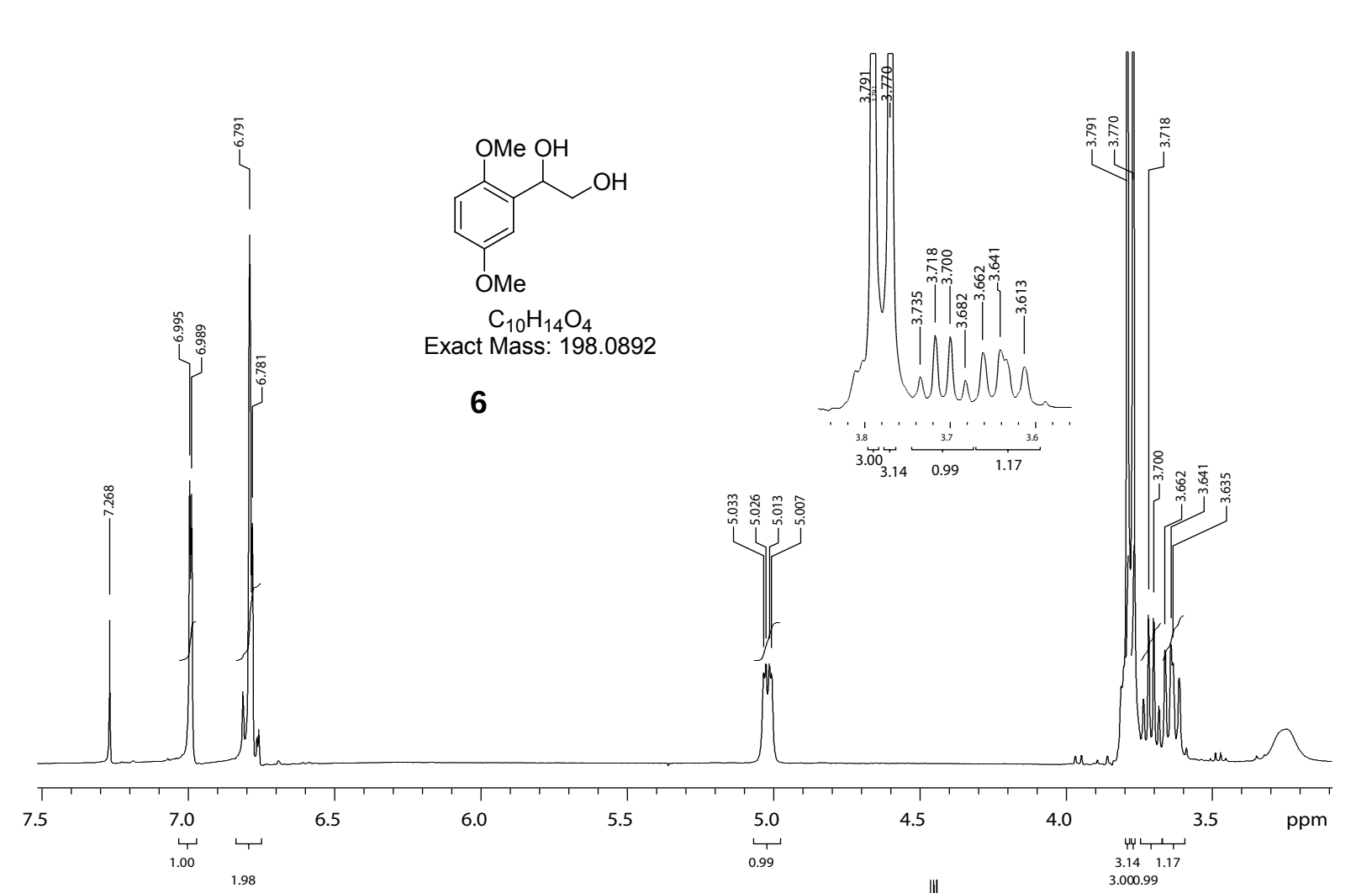
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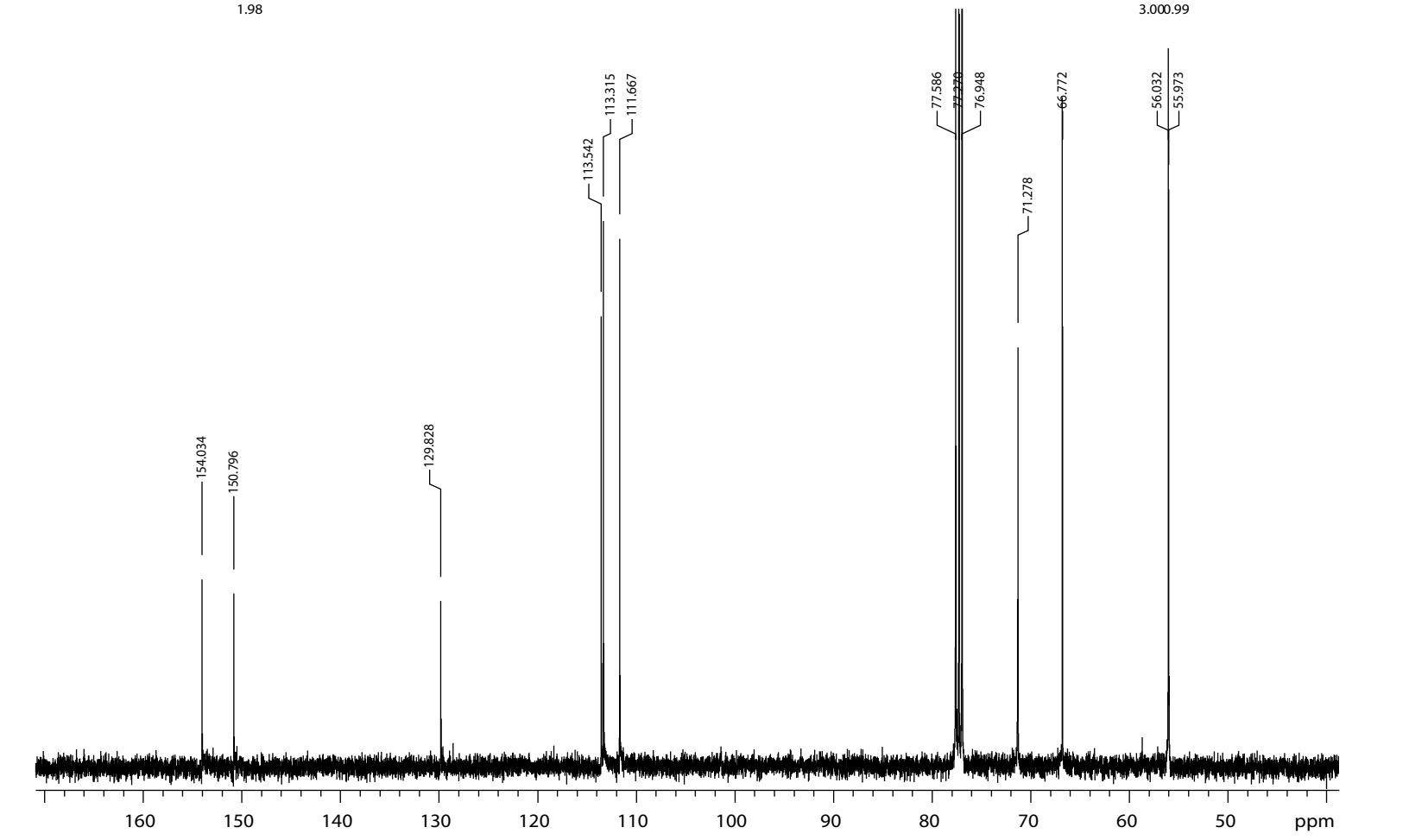
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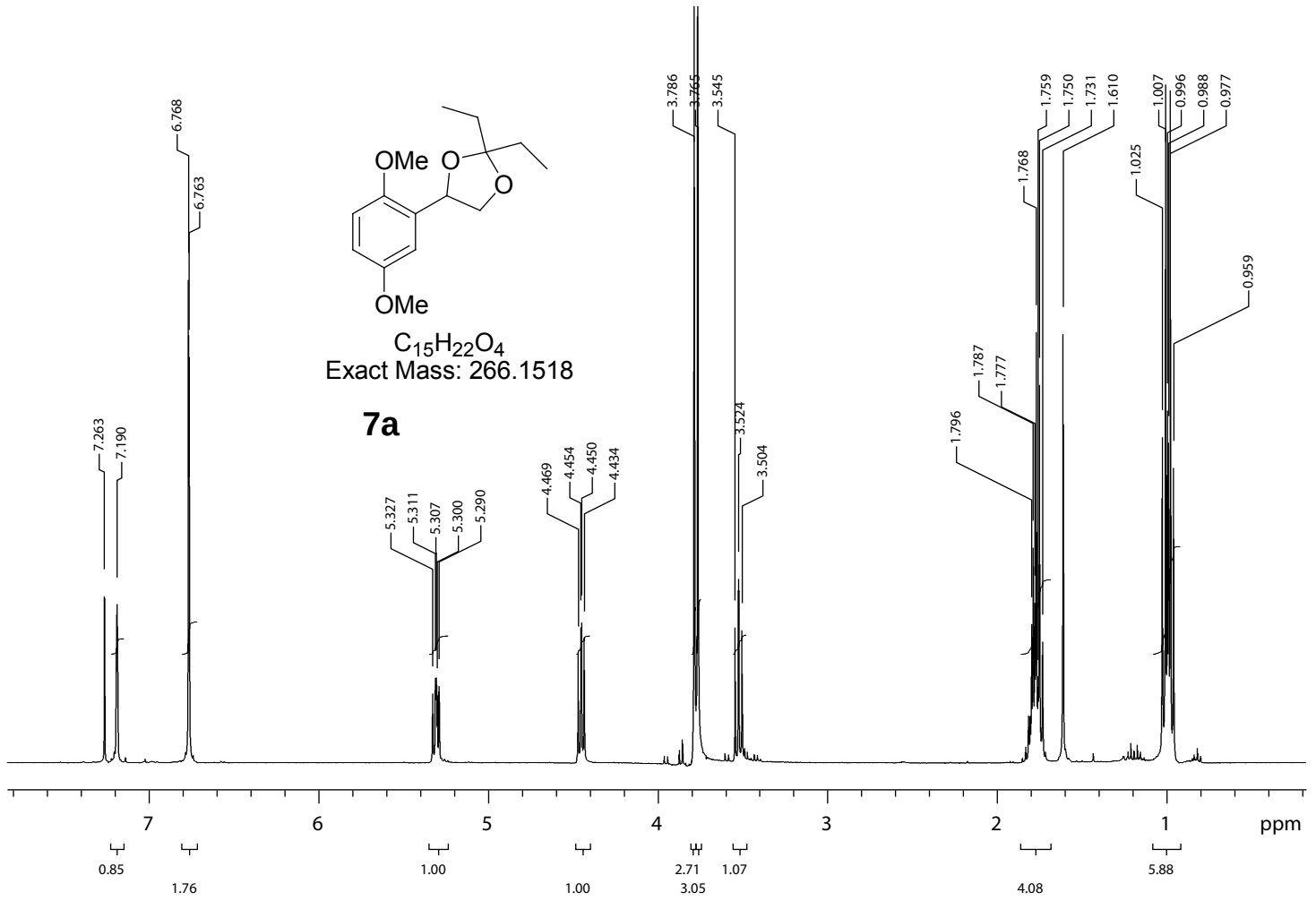
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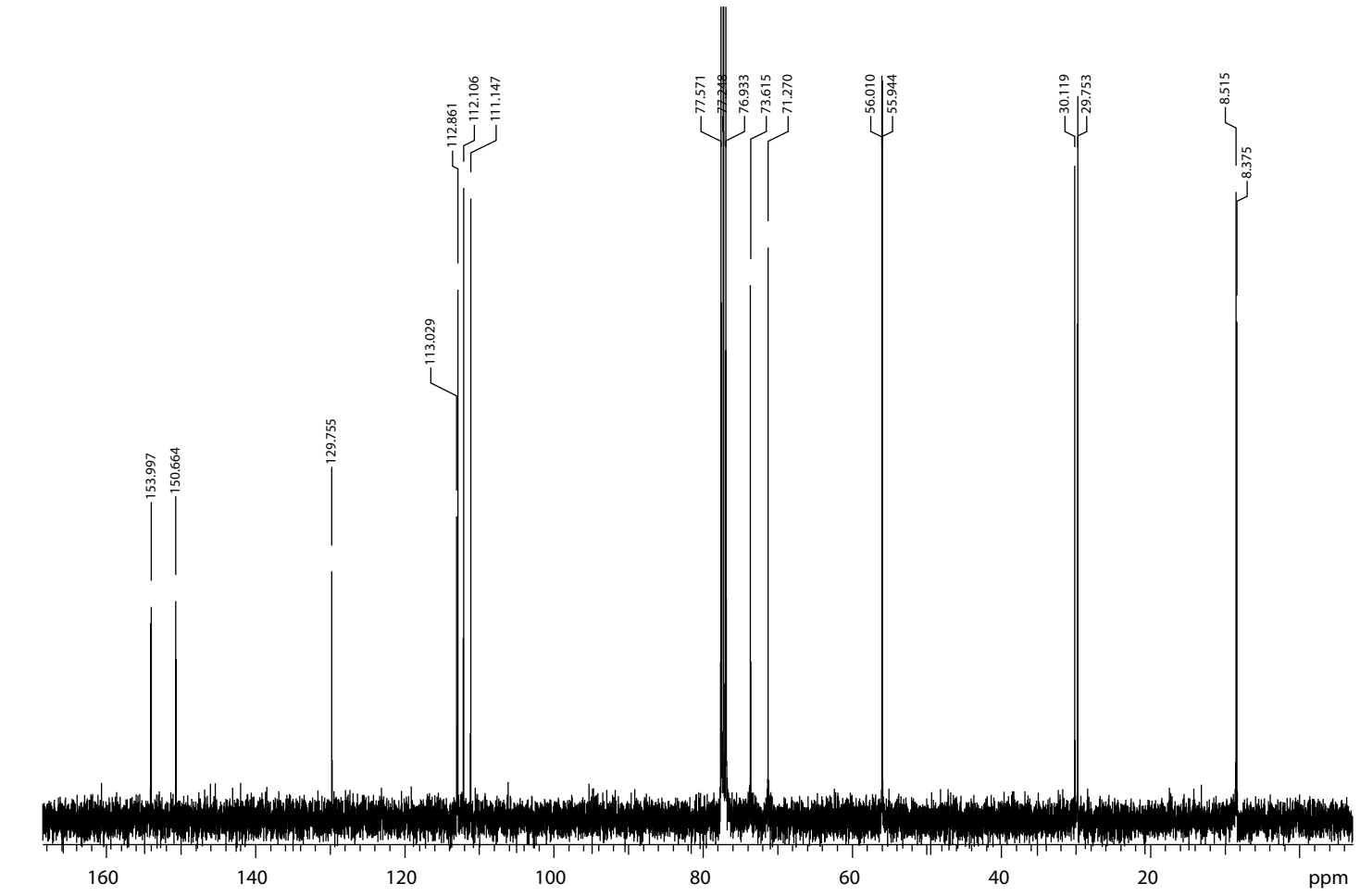
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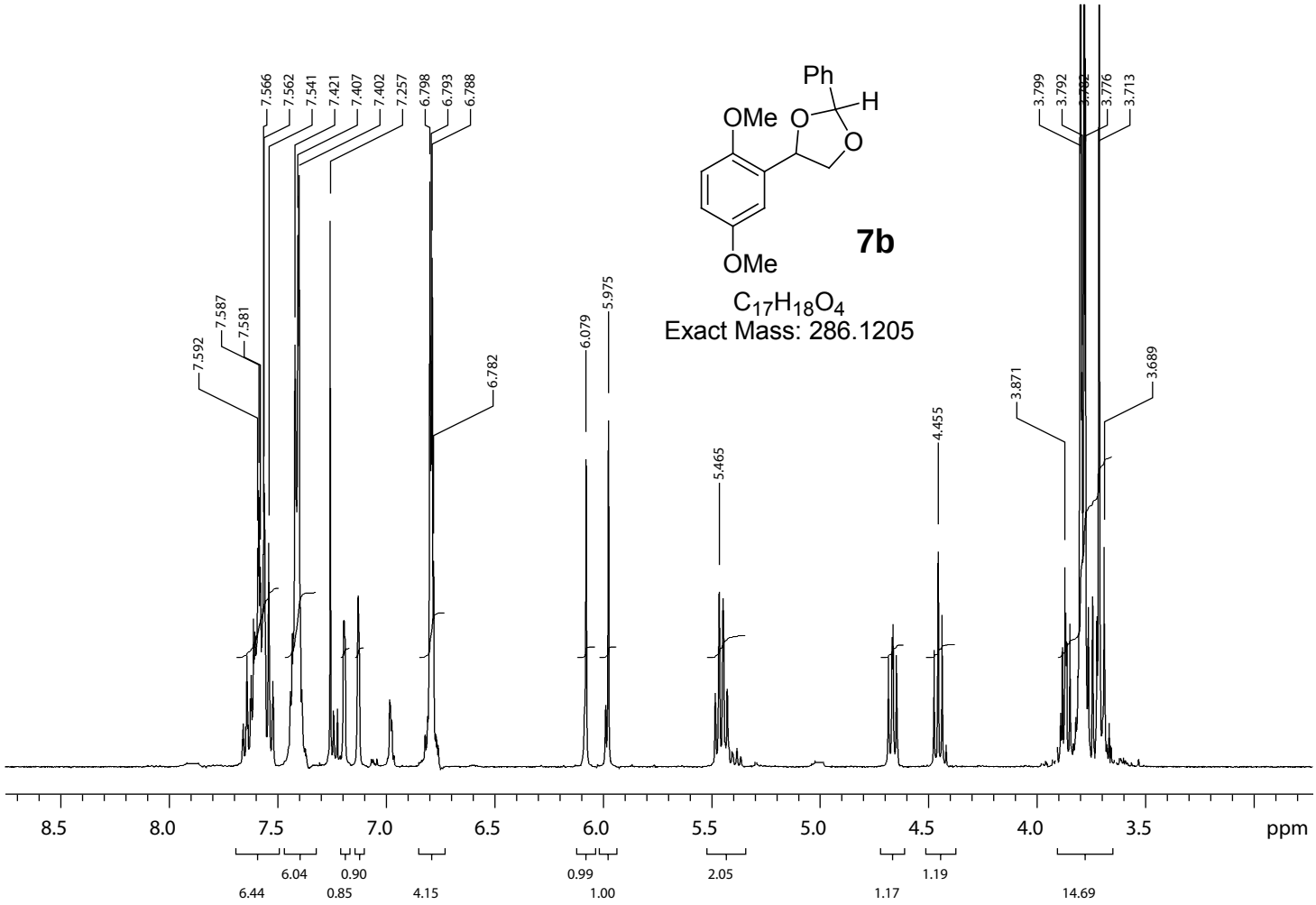
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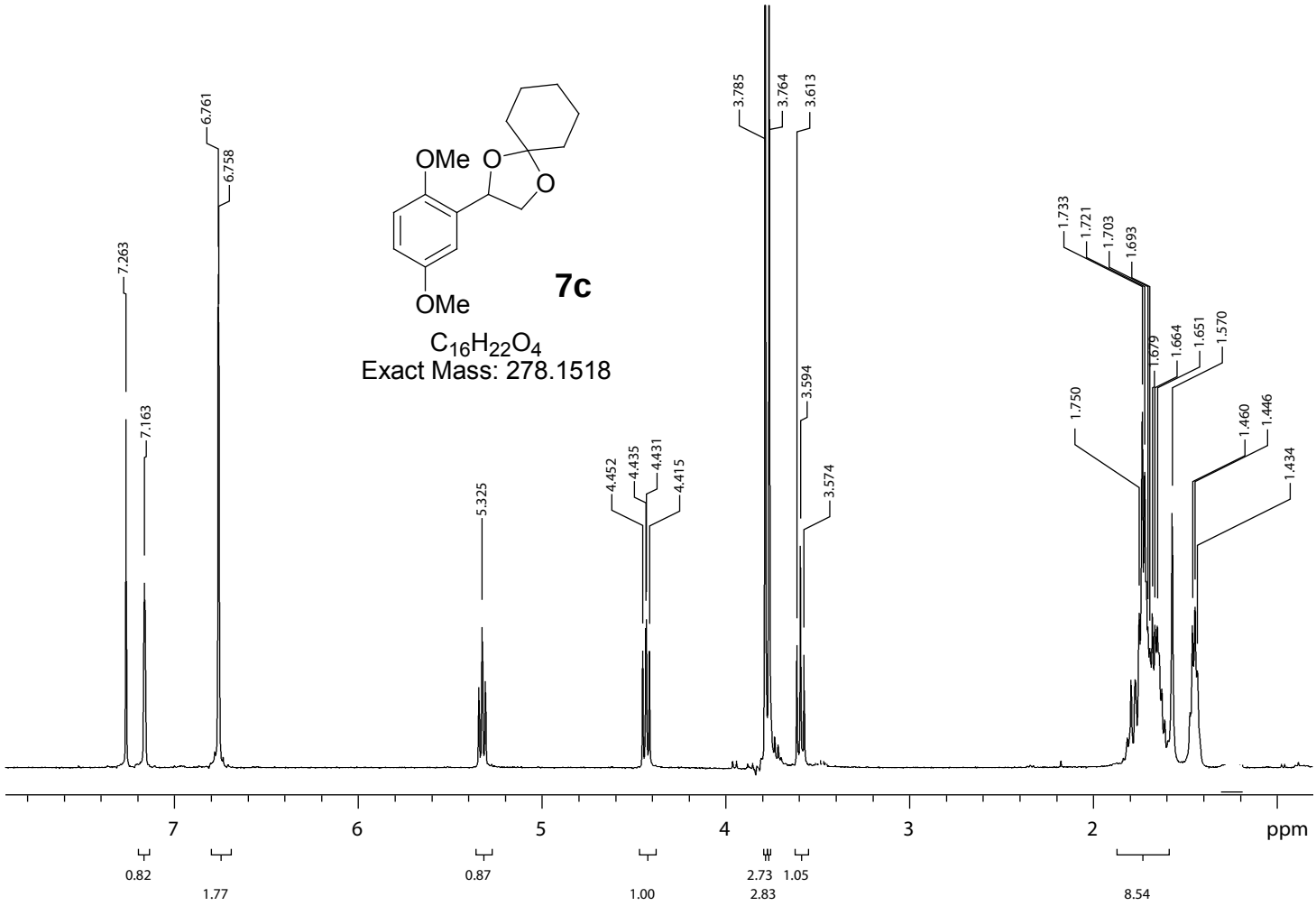
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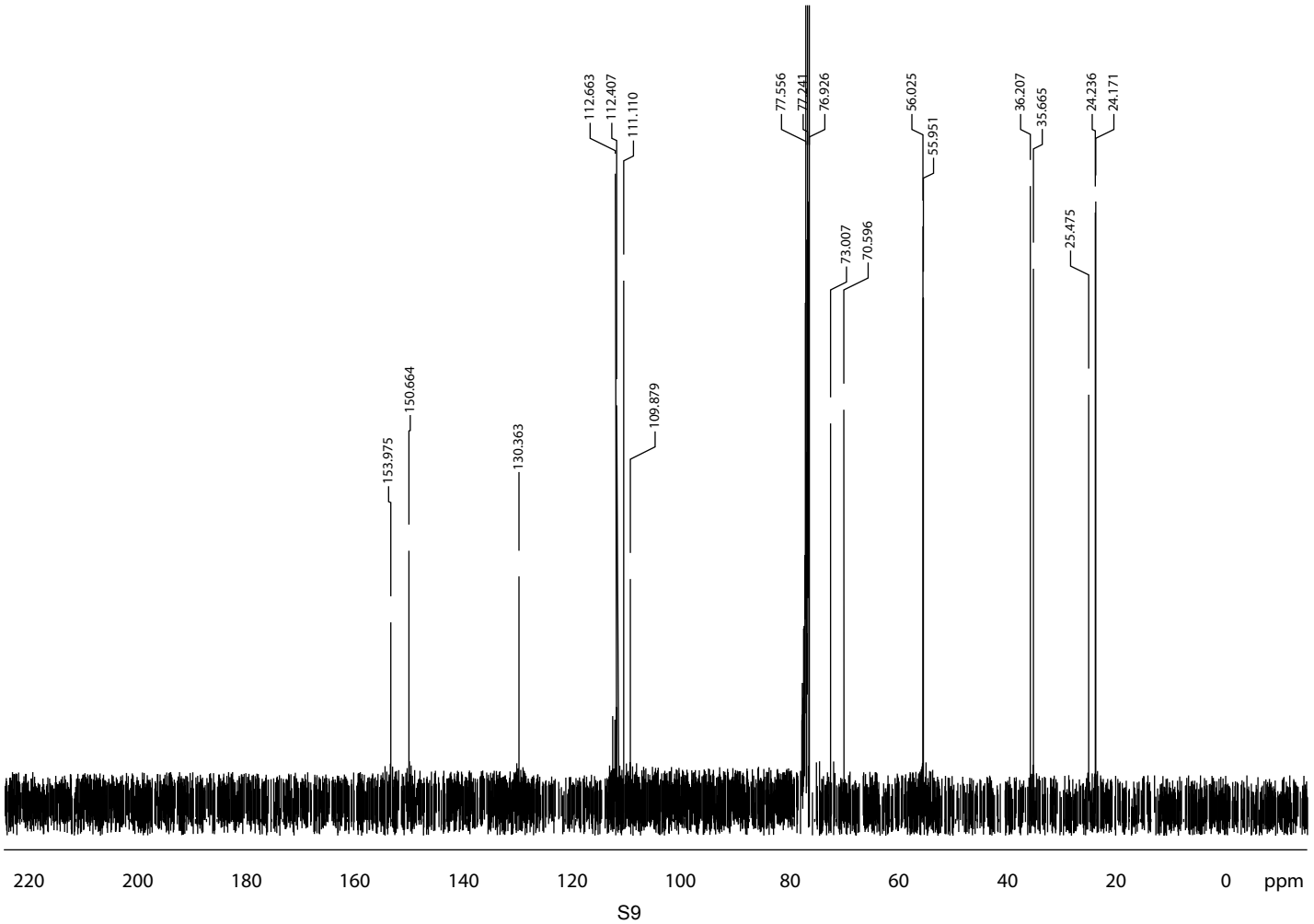
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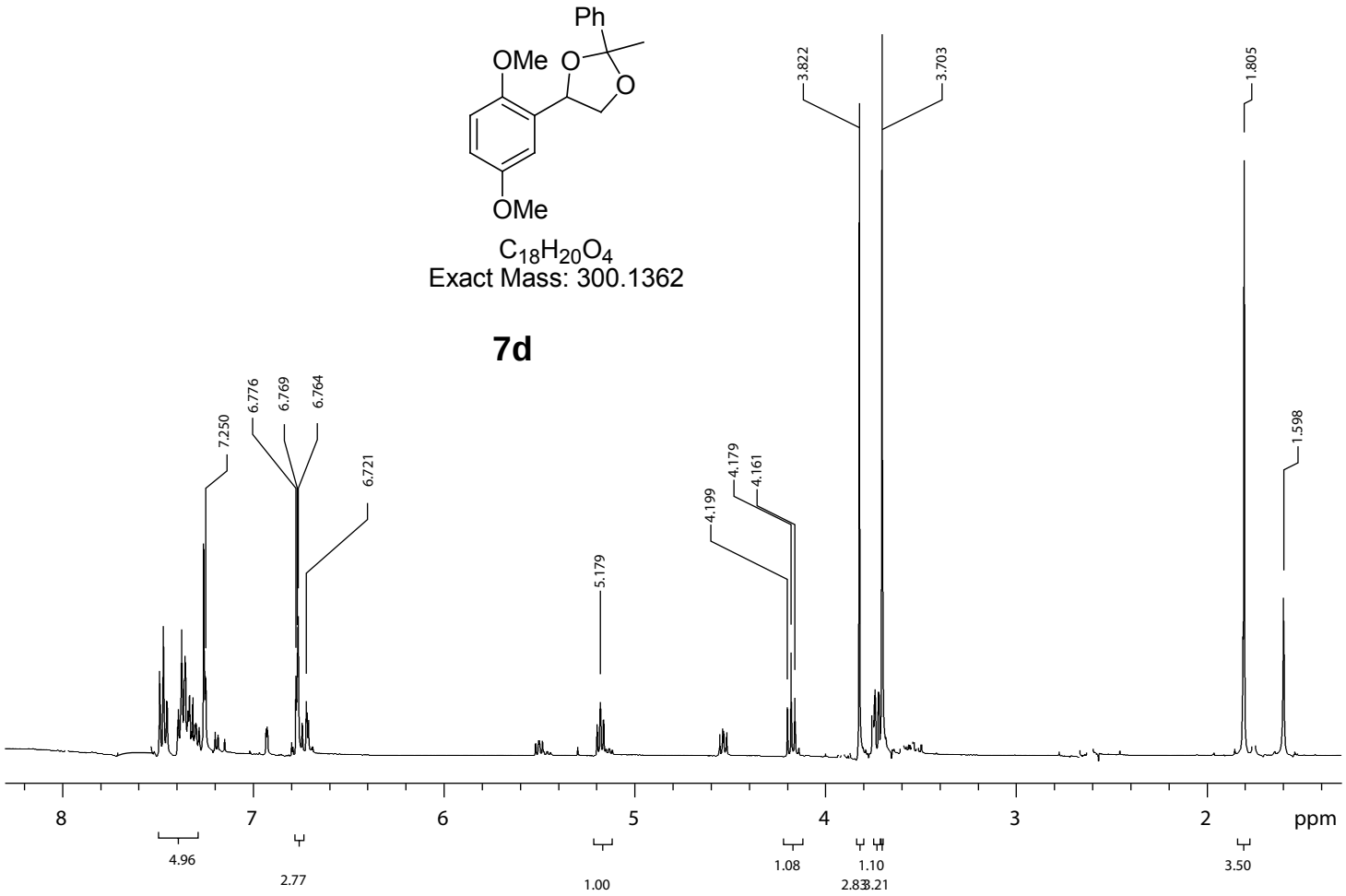
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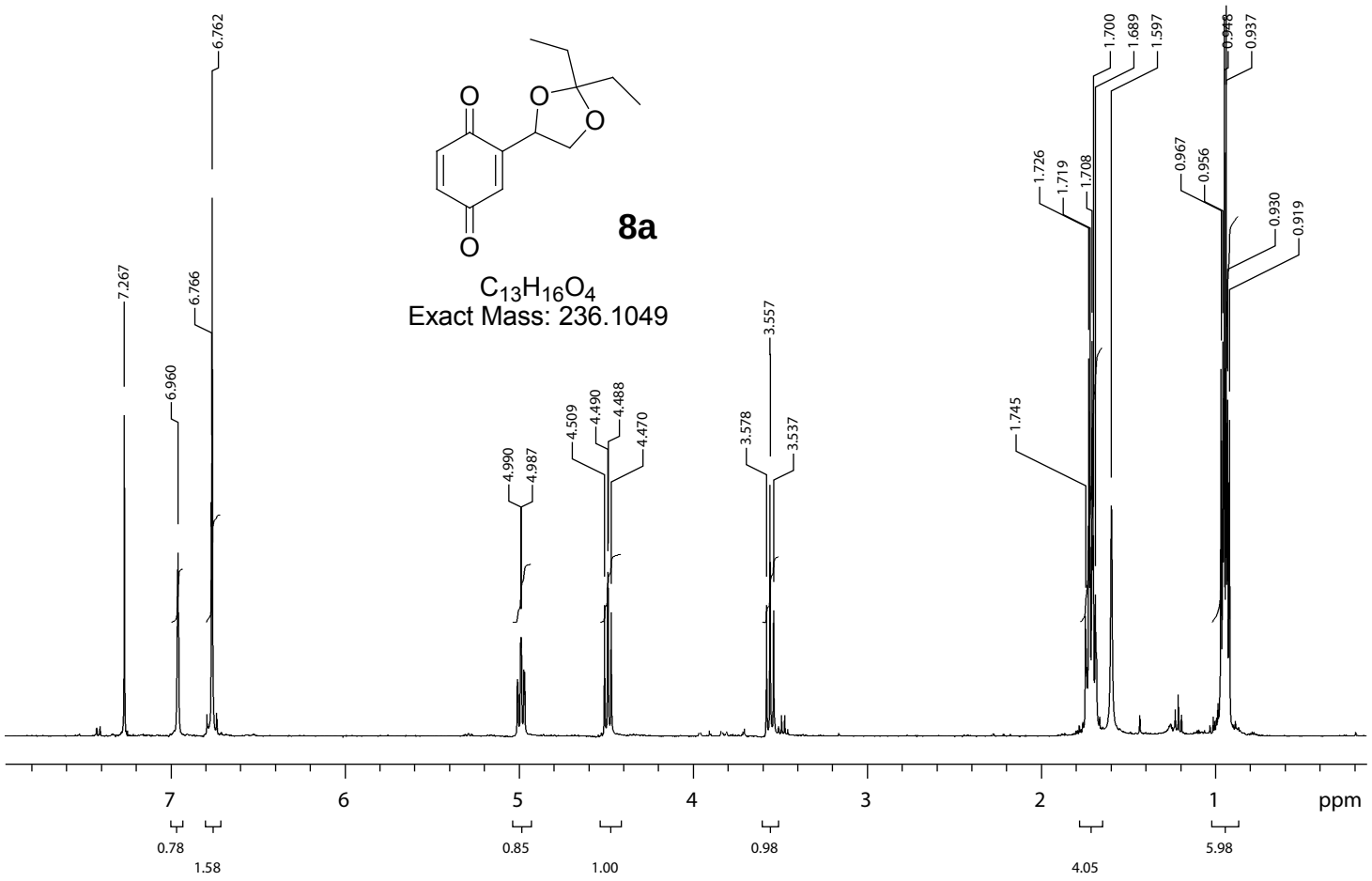
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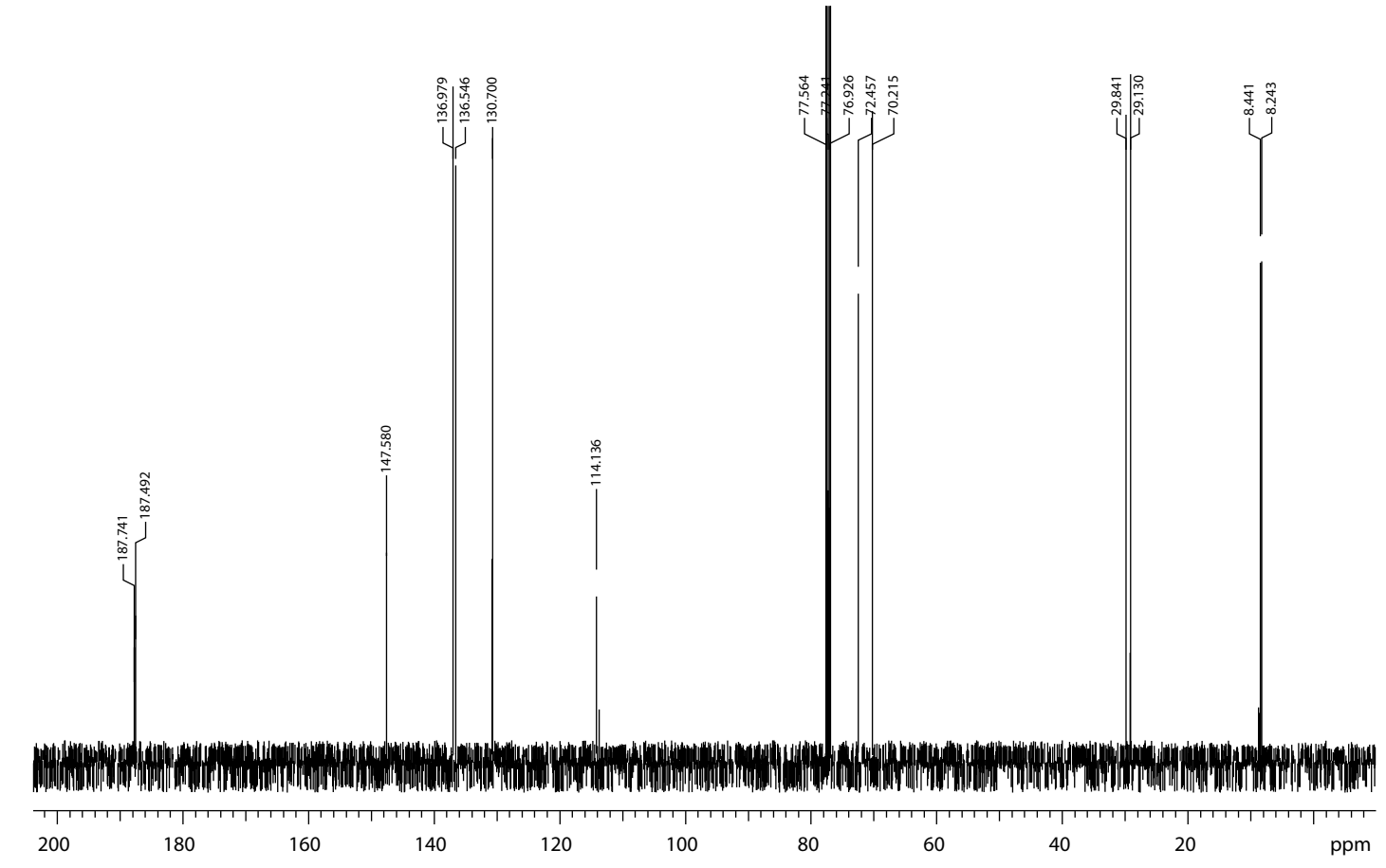
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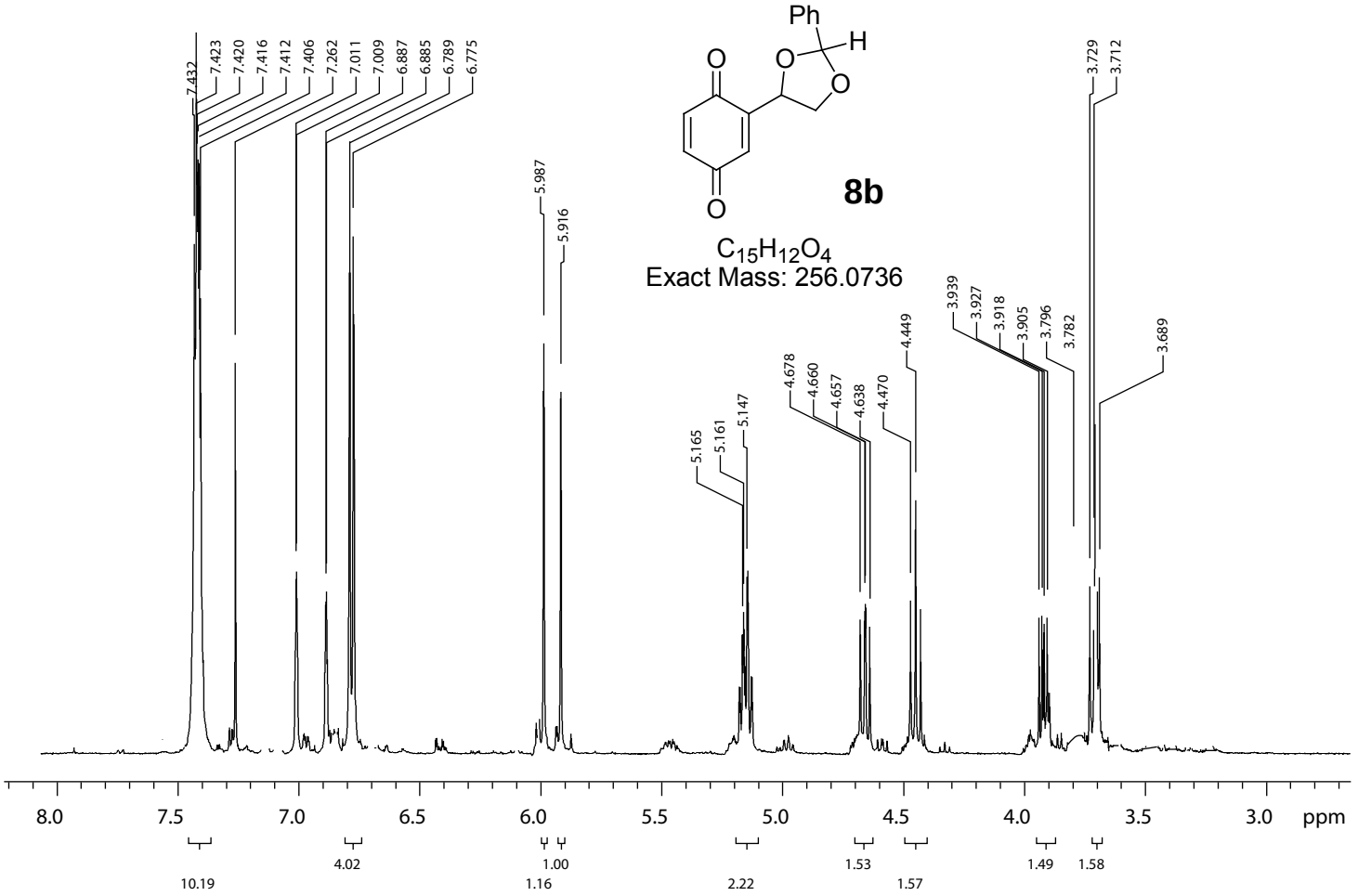
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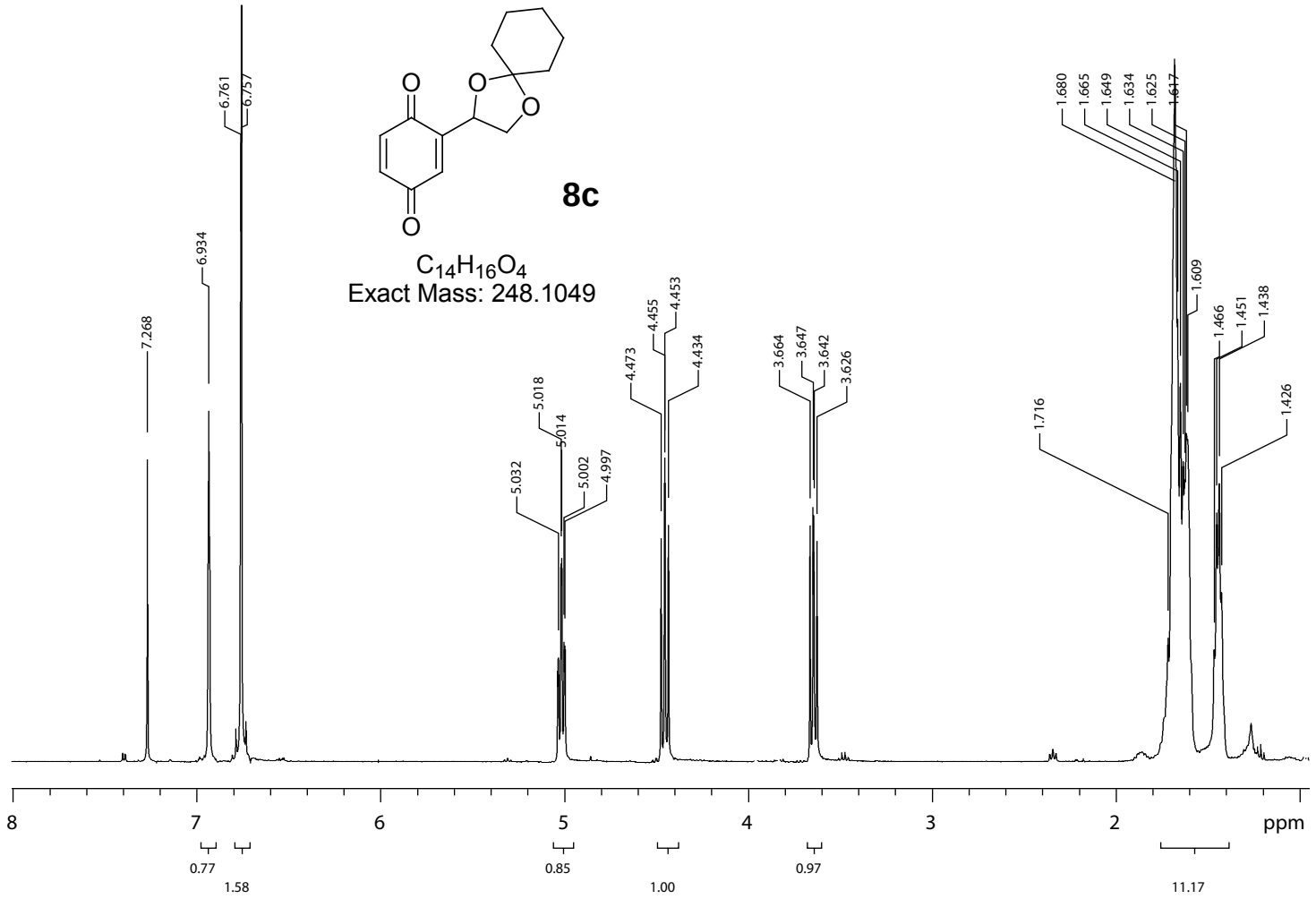
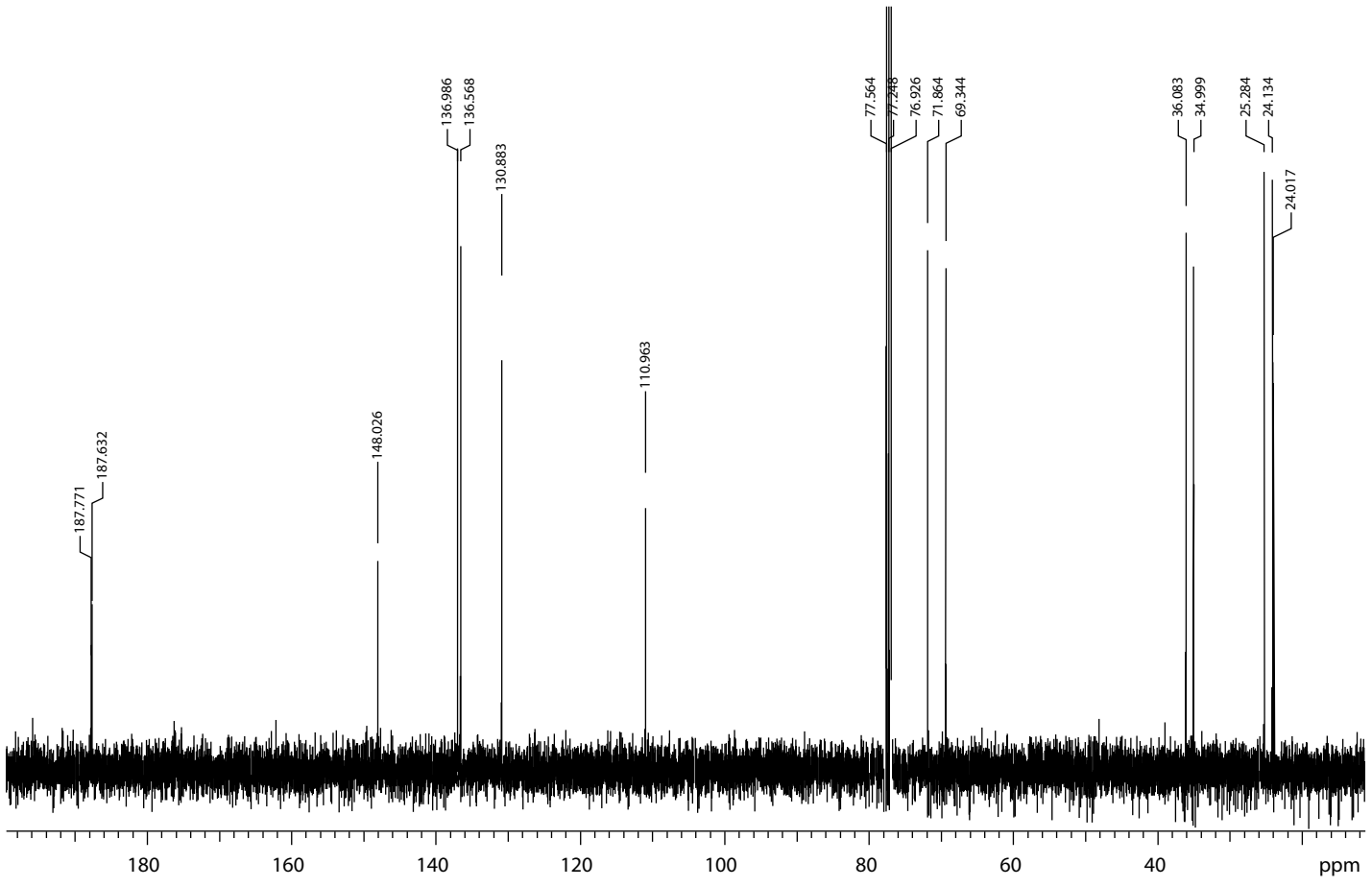
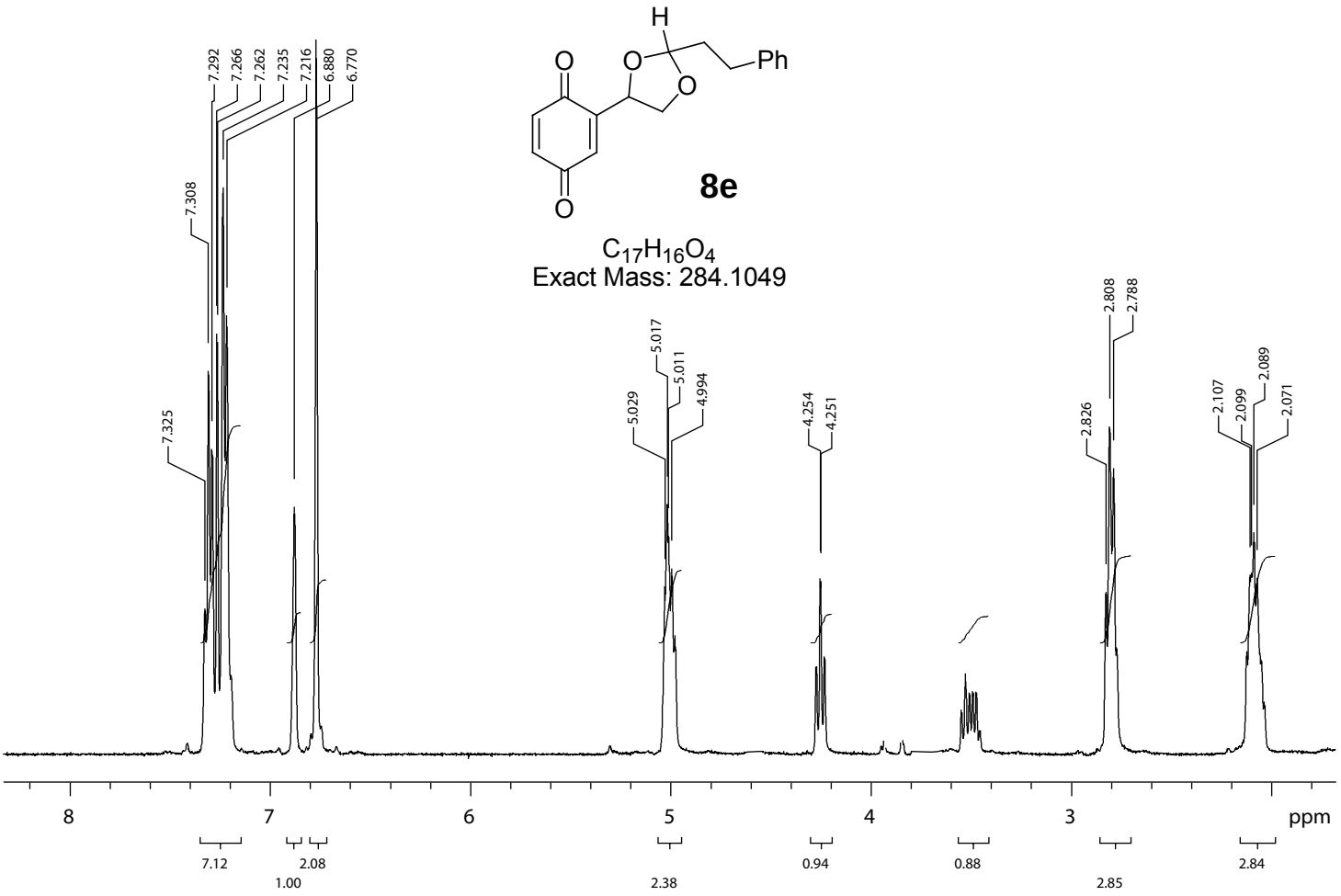
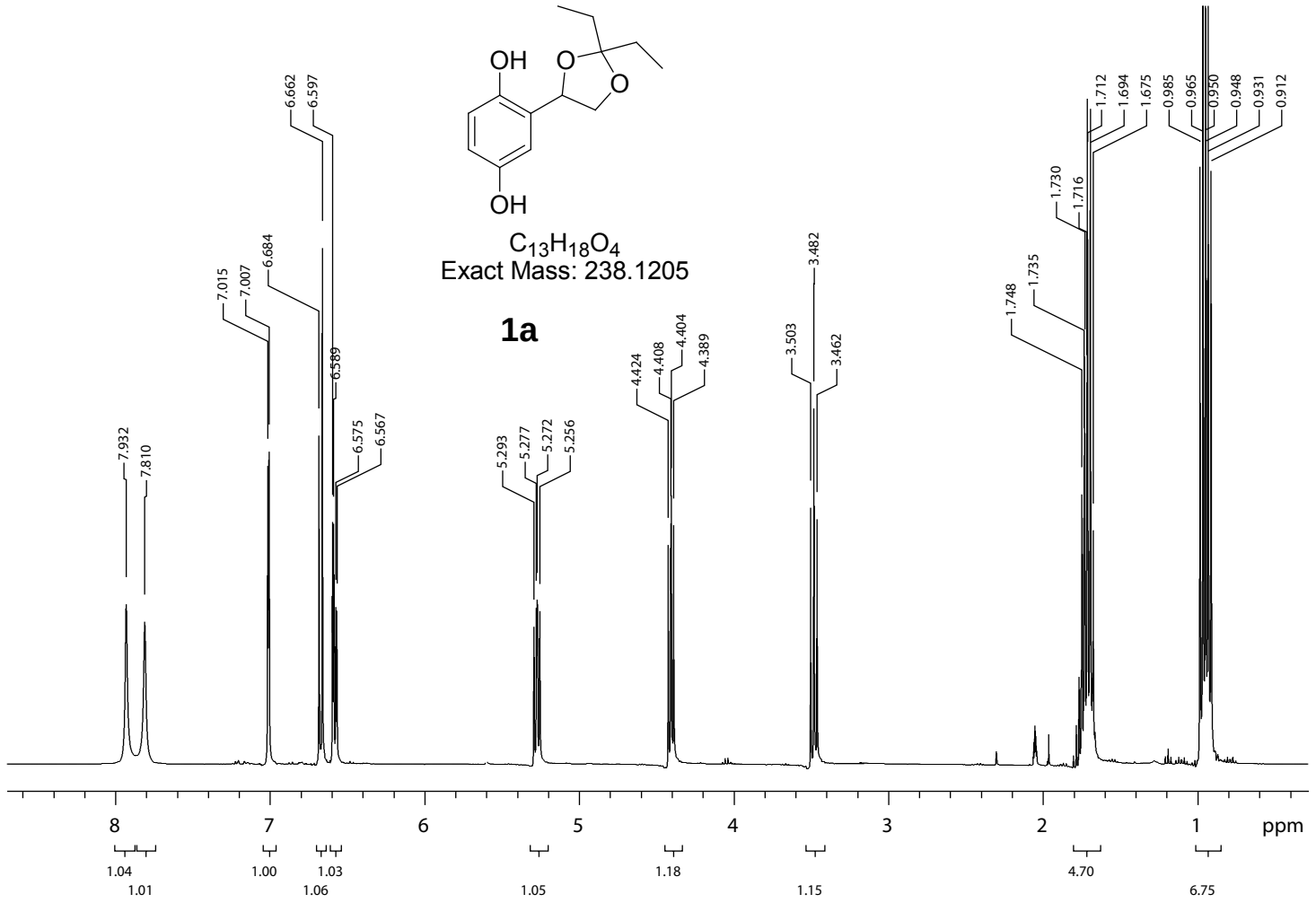
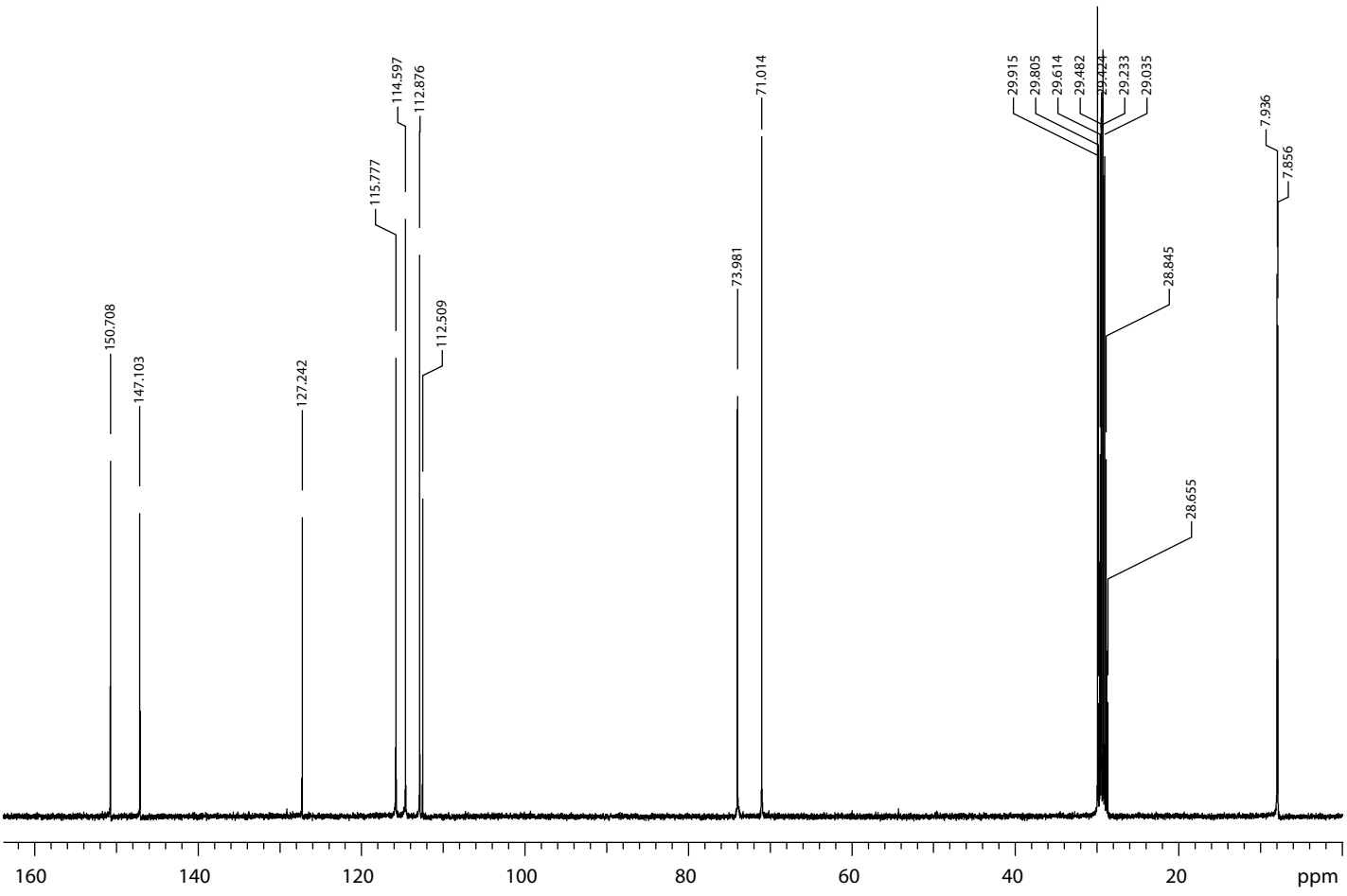
1.00
2.22
1.53
1.57
1.49
1.58

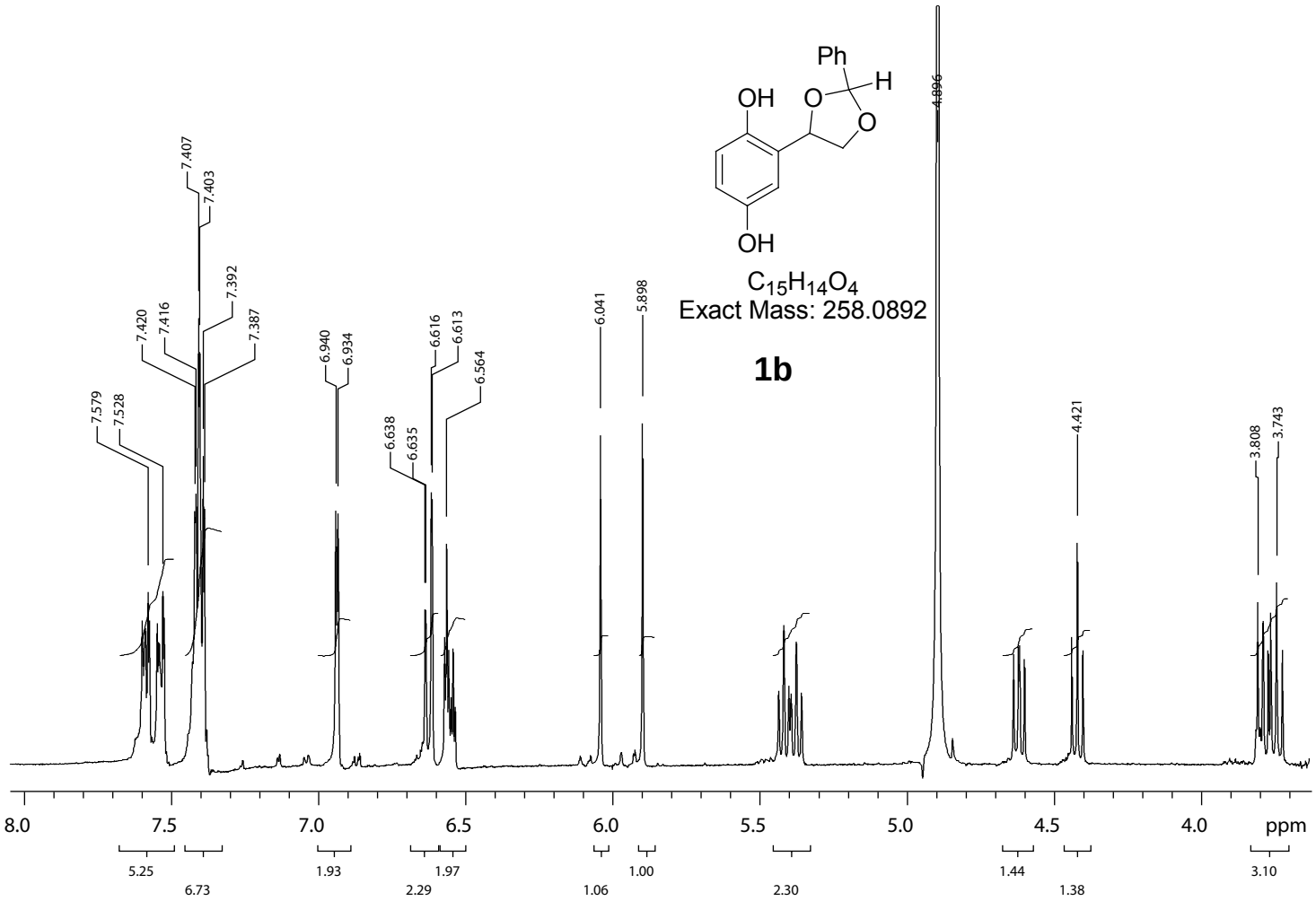

8c
C14H16O4
Exact Mass: 248.1049
6.761
6.757
6.934
7.268
5.032
5.018
5.014
5.002
4.997
4.473
4.455
4.453
4.434
3.664
3.647
3.642
3.626
1.716
1.680
1.665
1.649
1.634
1.625
1.617
1.609
1.466
1.451
1.438
1.426
8
7
6
5
4
3
2
ppm
0.77
1.58
0.85
1.00
0.97
11.17

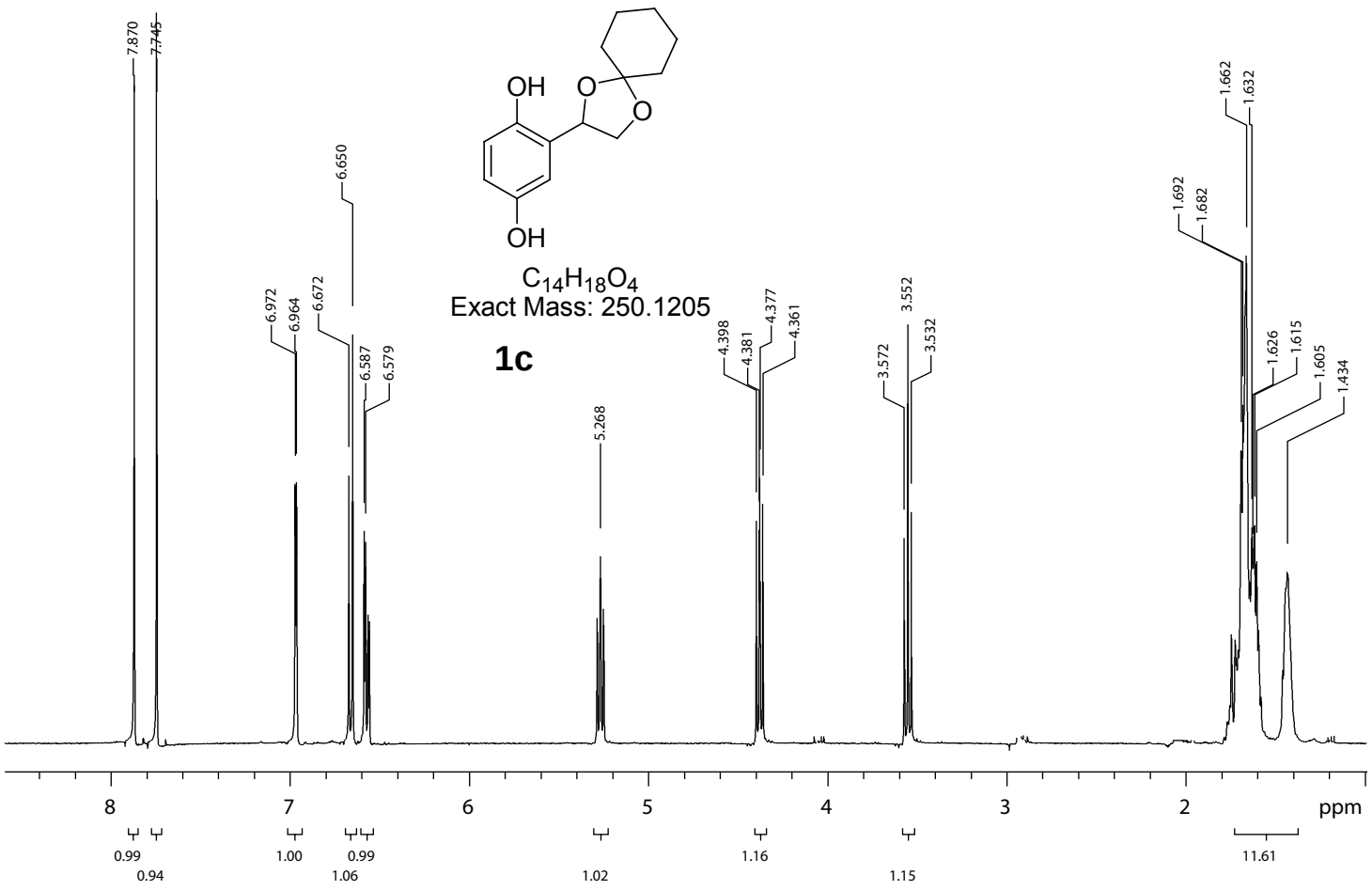

136.986
136.568
130.883
110.963
148.026
187.771
187.632
77.564
77.248
76.926
71.864
69.344
36.083
34.999
25.284
24.134
24.017
180
160
140
120
100
80
60
40
ppm

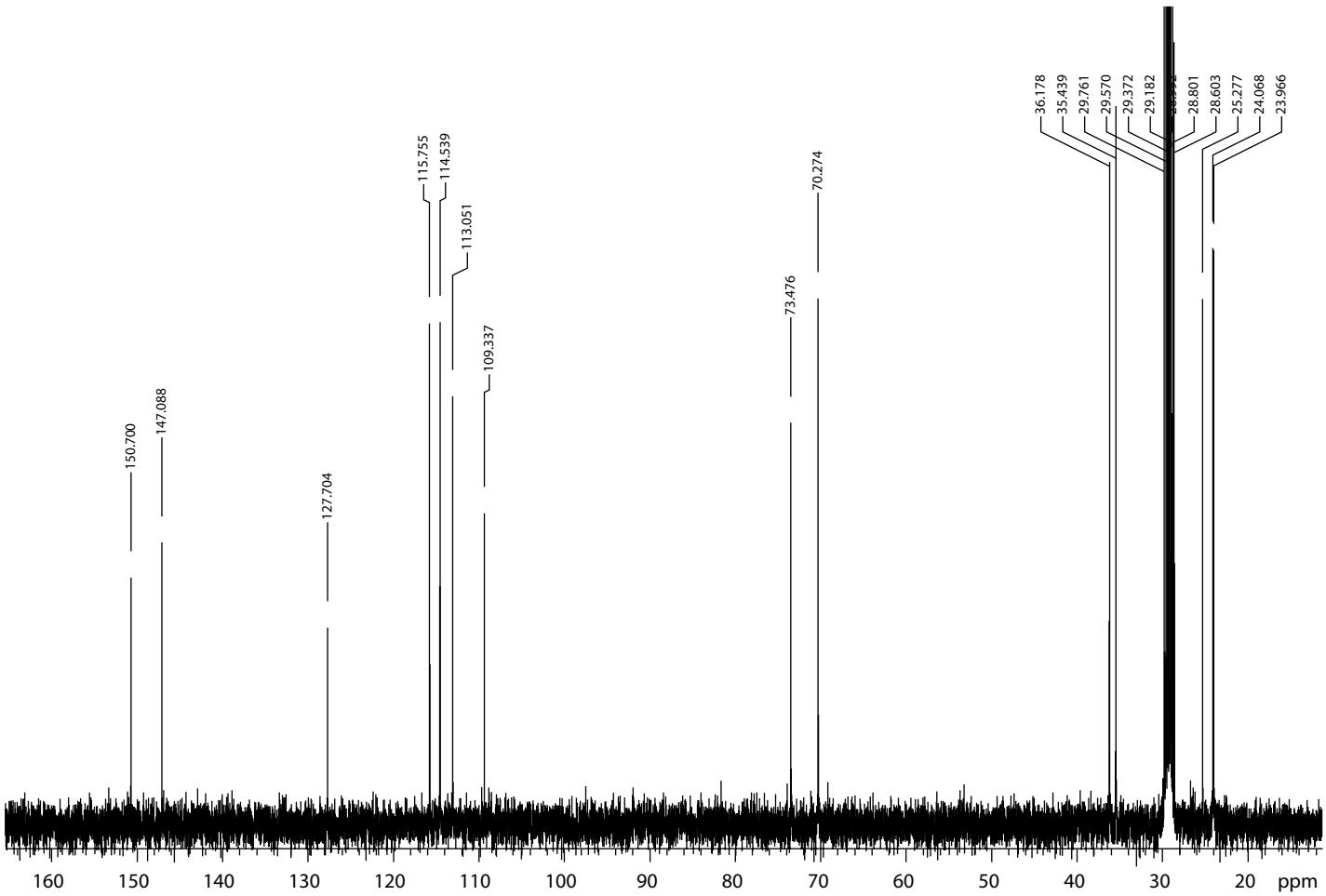

H
O
O
O
Ph
O
8e
C17H16O4
Exact Mass: 284.1049
7.292
7.266
7.262
7.235
7.216
6.880
6.770
7.308
7.325
5.029
5.017
5.011
4.994
4.254
4.251
2.826
2.808
2.788
2.107
2.099
2.089
2.071
8
7
6
5
4
3
ppm
7.12
2.08
1.00
2.38
0.94
0.88
2.85
2.84

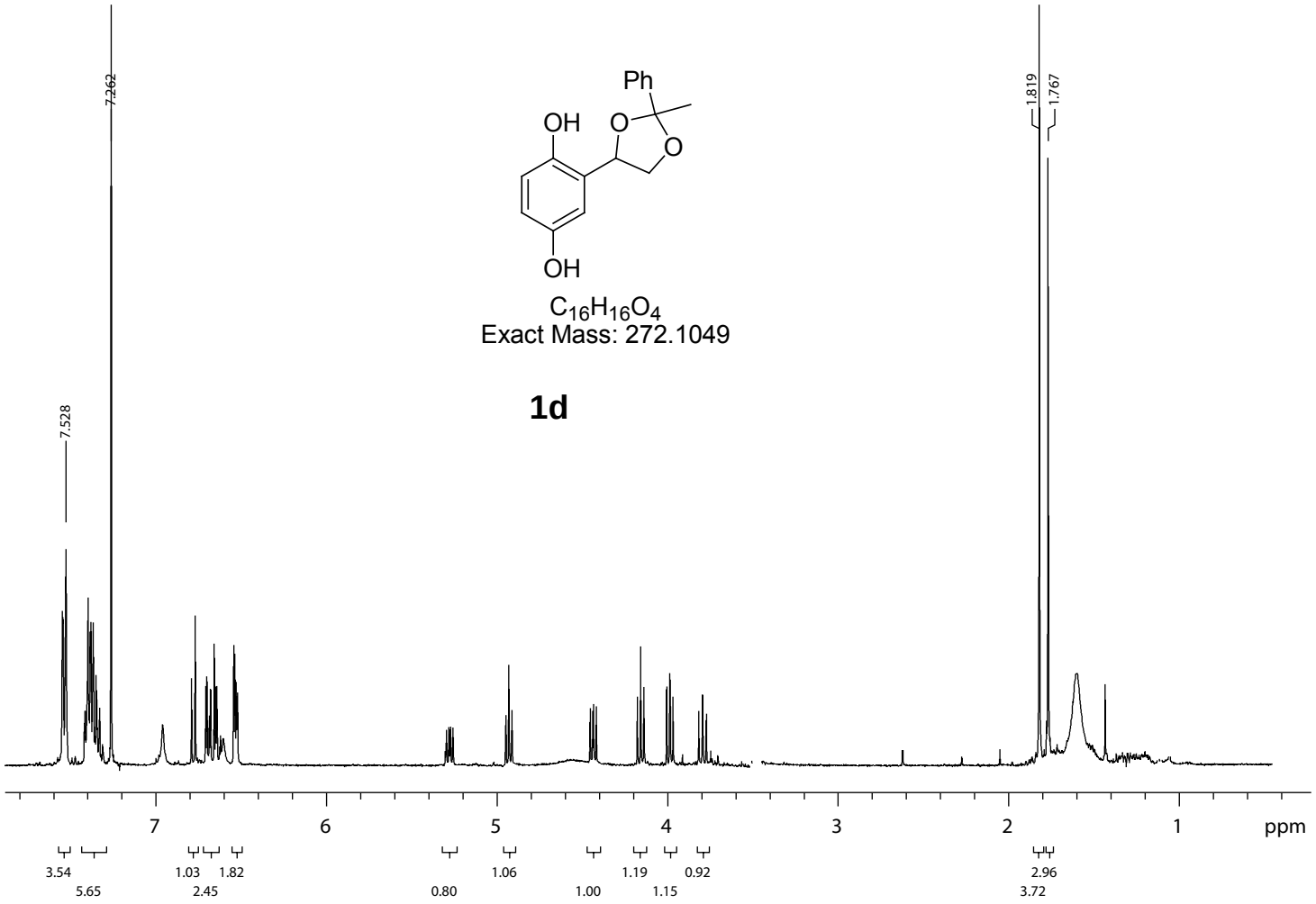

OH
O
O
OH
$C_{13}H_{18}O_4$
Exact Mass: 238.1205
1a
7.932
7.810
7.015
7.007
6.684
6.662
6.597
6.589
6.575
6.567
5.293
5.277
5.272
5.256
4.424
4.408
4.404
4.389
3.503
3.482
3.462
1.748
1.735
1.730
1.716
1.712
1.694
1.675
0.985
0.965
0.950
0.948
0.931
0.912
8
7
6
5
4
3
2
1
ppm
1.04
1.01
1.00
1.03
1.06
1.05
1.18
1.15
4.70
6.75


150.708
147.103
127.242
115.777
114.597
112.876
112.509
73.981
71.014
29.915
29.805
29.614
29.482
29.424
29.233
29.035
28.845
28.655
7.936
7.856
160
140
120
100
80
60
40
20
ppm


Ph
H
OH
O
O
OH
$C_{15}H_{14}O_4$
Exact Mass: 258.0892
1b
7.579
7.528
7.420
7.416
7.407
7.403
7.392
7.387
6.940
6.934
6.638
6.635
6.616
6.613
6.564
6.041
5.898
4.896
4.421
3.808
3.743
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm
5.25
6.73
1.93
2.29
1.97
1.06
1.00
2.30
1.44
1.38
3.10

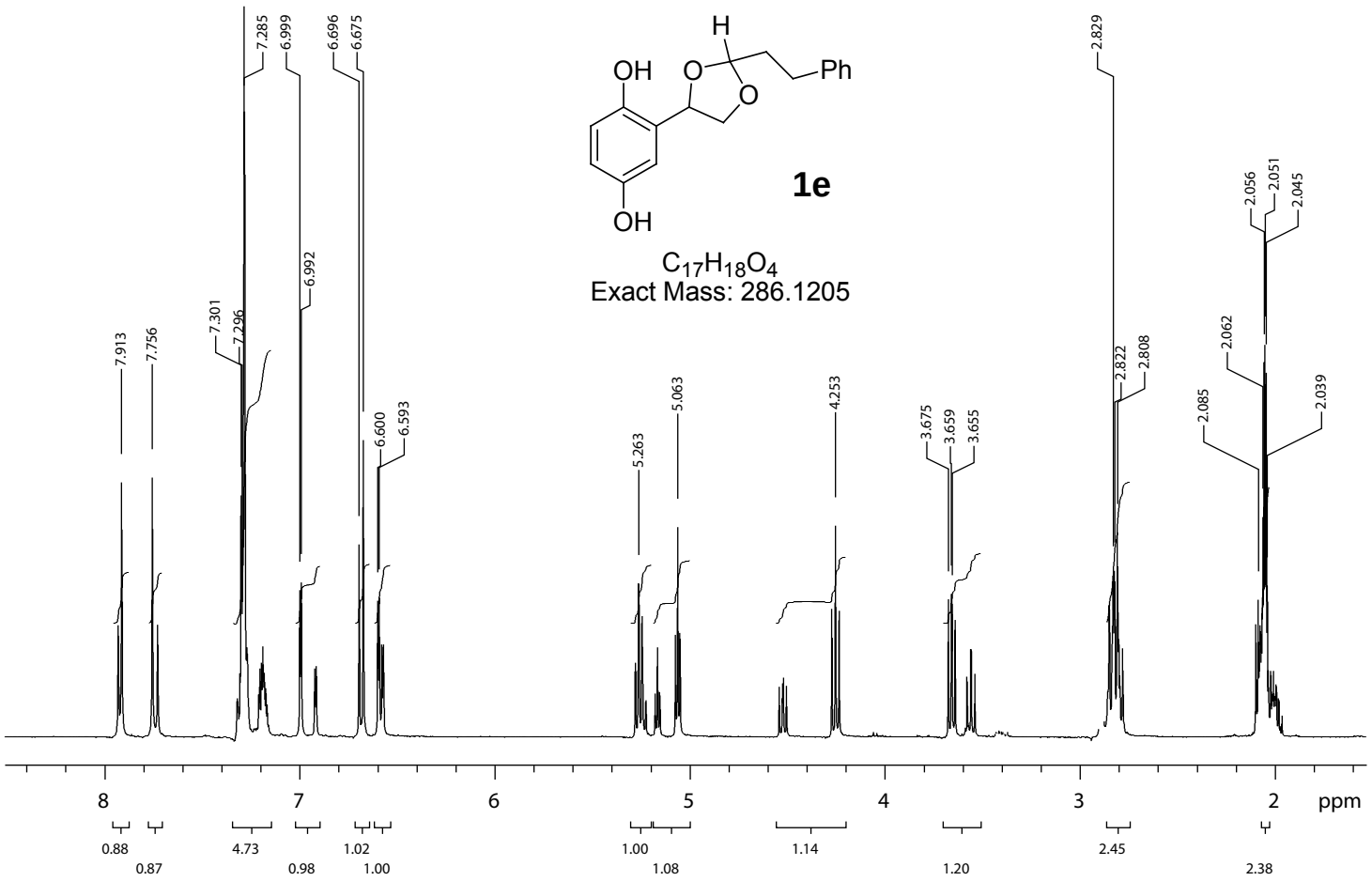

OH
O
O
OH
$C_{14}H_{18}O_4$
Exact Mass: 250.1205
1c
7.870
7.745
6.972
6.964
6.672
6.650
6.587
6.579
5.268
4.398
4.381
4.377
4.361
3.572
3.552
3.532
1.692
1.682
1.662
1.632
1.626
1.615
1.605
1.434
8
7
6
5
4
3
2
ppm
0.99
0.94
1.00
0.99
1.06
1.02
1.16
1.15
11.61

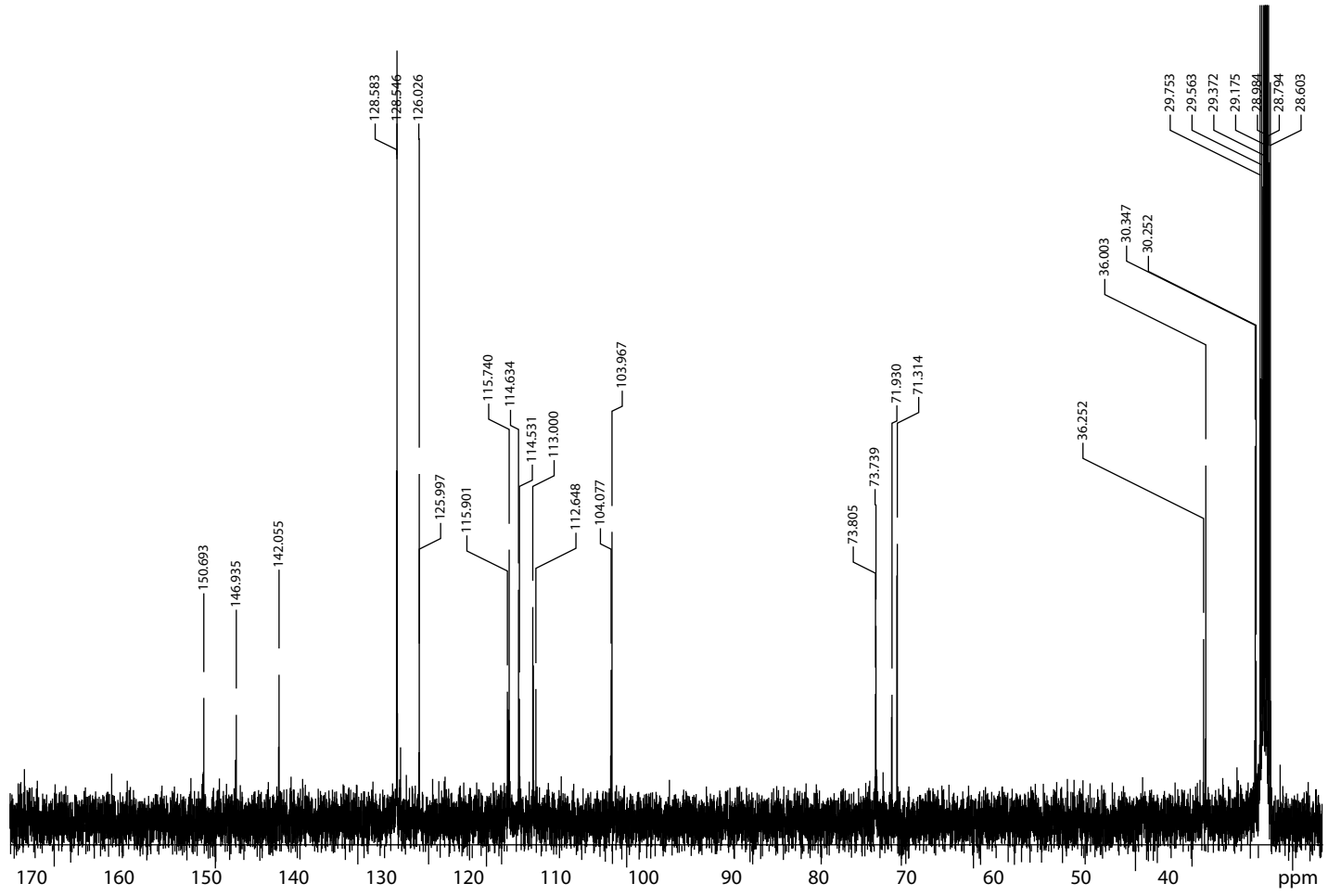

150.700
147.088
127.704
115.755
114.539
113.051
109.337
73.476
70.274
36.178
35.439
29.761
29.570
29.372
29.182
28.801
28.603
25.277
24.068
23.966
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



$C_{16}H_{16}O_4$
Exact Mass: 272.1049

1d


H
OH
O
O
Ph
OH
1e
C17H18O4
Exact Mass: 286.1205
7.913
7.756
7.301
7.296
7.285
6.999
6.992
6.696
6.675
6.600
6.593
5.263
5.063
4.253
3.675
3.659
3.655
2.829
2.822
2.808
2.085
2.062
2.056
2.051
2.045
2.039
8
7
6
5
4
3
2
ppm
0.88
0.87
4.73
0.98
1.02
1.00
1.00
1.08
1.14
1.20
2.45
2.38


150.693
146.935
142.055
128.583
128.546
126.026
125.997
115.901
115.740
114.634
114.531
113.000
112.648
104.077
103.967
73.805
73.739
71.930
71.314
36.252
36.003
30.347
30.252
29.753
29.563
29.372
29.175
28.984
28.794
28.603
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm