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SUPPLEMENTARY MATERIAL

Ilimaquinone and 5-*epi*-ilimaquinone: Beyond a Simple Diastereomeric Ratio, Biosynthetic Considerations from NMR-Based Analysis

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Content:

Geographic data (WGS 84) and depth of sampling sites of sponges (S: South ; W : West; E: East)

Dactylospongia elegans					
archipelago	**date**	**island**	**latitude**	**longitude**	**depth (m)**
Marquesas	08/29/2009	Nuku Hiva	8°56,173 S	140°05,593 W	6-10
Marquesas	08/30/2009	Nuku Hiva	8°57,661 S	140°10,149 W	12-18
Marquesas	09/11/2009	Tahuata	9°59,917 S	139°07,879 W	10-40
Marquesas	09/12/2009	Fatu Hiva	10°28,311 S	138°40,698 W	10-22
Dactylospongia metachromia					
archipelago	**date**	**atoll/island**	**latitude**	**longitude**	**depth (m)**
Fiji	05/18/2007	Ngele Levu	16°11,010 S	179°44,381 E	8-25
Fiji	05/12/2007	Vanua Levu	16°18,847 S	178°54,595 E	12-13
Gambier	29/09/2010	Kouaku	23°12,950 S	134°51,406 W	15-23
Gambier	07/10/2010	outer reef (SW)	23°16,683 S	134°56,109 W	30
Gambier	07/10/2010	Lagoon (S)	23°16,301 S	134°56,474 W	16-17
Tuamotu	04/28/2011	Hereheretue	19°52,477 S	145°00,404 W	40-63
Tuamotu	04/29/2011	Anuanuraro	20°24,924 S	143°32,629 W	50-63
Tuamotu	04/30/2011	Tematangi	21°42,220 S	140°40,935 W	10-60
Tuamotu	05/01/2011	Tematangi	21°40,946 S	140°41,407 W	20-70
Tuamotu	05/01/2011	Tematangi	21°42,590 S	140°34,021 W	20-60
Tuamotu	05/09/2011	Makemo	16°39,386 S	143°34,856 W	13
Tuamotu	05/17/2011	Fakarava	16°04,095 S	145°41,936 W	6-25
Tuamotu	05/19/2011	Fakarava	16°07,738 S	145°49,121 W	10-35
Tuamotu	05/21/2011	Toau	16°02,085 S	145°55,231 W	20-50
Tuamotu	05/23/2011	Rangiroa	15°05,150 S	147°56,531 W	15-30
Tuamotu	05/24/2011	Rangiroa	14°55,927 S	147°43,329 W	15-46
Tuamotu	05/25/2011	Rangiroa	14°57,569 S	147°38,039 W	35-45
Tuamotu	07/11/2013	Rangiroa	14°58,209 S	147°37,375 W	7-37
Tuamotu	07/12/2013	Rangiroa	14°56,054 S	147°42,492 W	7-57
Tuamotu	05/28/2011	Tikehau	15°05,391 S	148°16,152 W	10-35
Society	05/31/2011	Tetiaroa	17°02,252 S	149°33,707 W	15-30

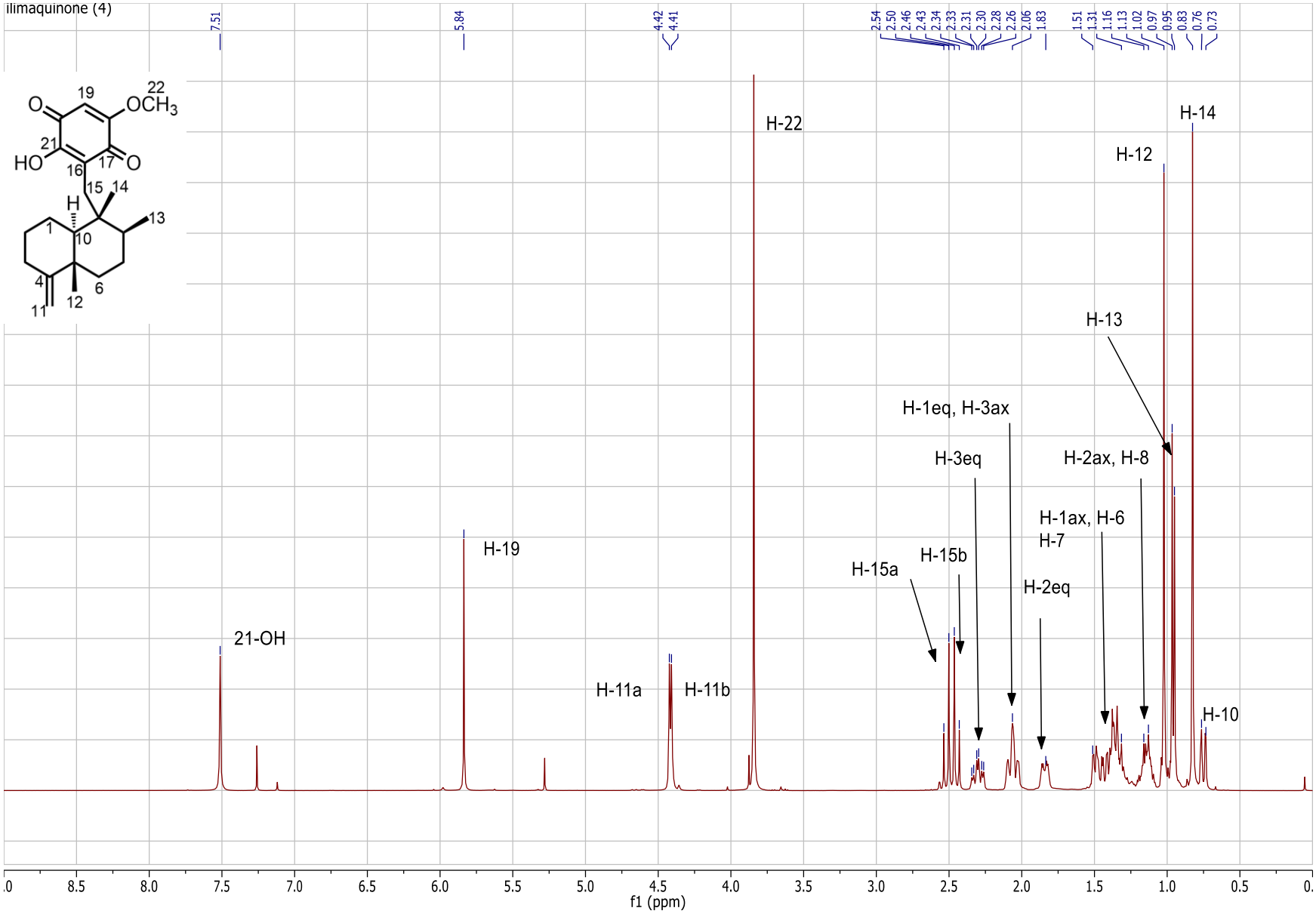
Ilimaquinone (4): Yellow solid; *m/z* $[M+Na]^+$ 381.2035, (calculated for $C_{22}H_{30}O_4Na$, 381.2042); IR (film) ν_{max} (cm^{-1}): 2921, 1641. R_f: 0.45 (SiO_2, CH_2Cl_2), 0.7 ($SiO_2/AgNO_3$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (s, OH), 5.83 (s, 1H), 4.42 (br s, 1H), 4.40 (br s, 1H), 3.84 (s, 3H), 2.52 (d, 1H, J=13.7 Hz), 2.45 (d, 1H, J=13.7 Hz), 2.30 (m, 1H), 2.02-2.09 (m, 2H), 1.84 (m, 1H), 1.31-1.51 (m, 5H), 1.11-1.19 (m, 2H), 1.02 (s, 3H), 0.95 (d, 3H, J=6.4 Hz), 0.82 (s, 3H), 0.75 (dd, 1H, J=12; 1.8 Hz).^{13}C Jmod NMR (100 MHz, $CDCl_3$) δ (ppm) : 182.3 (C-17), 182 (C-20), 161.6 (C-18), 160.4 (C-4), 153.3 (C-21), 117.3 (C-16), 102.4 (C-11), 101.9 (C-19), 56.8 (C-22), 50.0 (C-10), 43.2 (C-9), 40.4 (C-5), 38.0 (C-8), 36.6 (C-6), 32.9 (C-3), 32.3 (C-15), 28.6 (C-2), 27.9 (C-7), 23.1 (C-1), 20.5 (C-12), 17.8 (C-13), 17.3 (C-14).

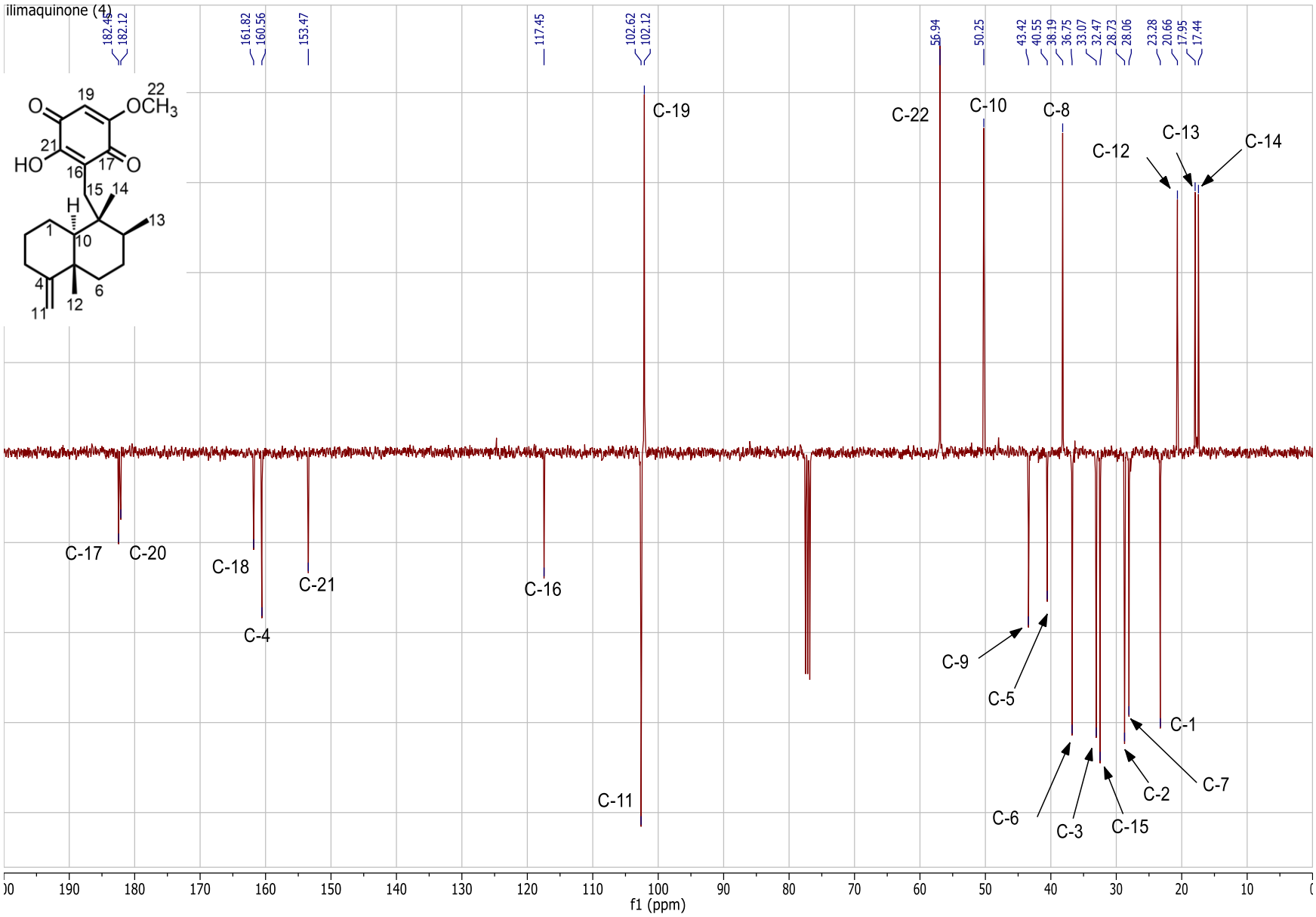
5-*Epi*-ilimaquinone (5): Yellow solid; *m/z* $[M+Na]^+$ 381.2035, (calculated for $C_{22}H_{30}O_4Na$, 381.2042); IR (film) ν_{max} (cm^{-1}): 2929, 1641. R_f: 0.45 (SiO_2, CH_2Cl_2), 0.5 ($SiO_2/AgNO_3$, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (s, OH), 5.88 (s, 1H), 4.69 (br s, 1H), 4.66 (br s, 1H), 3.87 (s, 3H), 2.59 (d, 1H, J=13.7 Hz), 2.49 (d, 1H, J=13.7 Hz), 2.43 (m, 1H), 2.16-2.08 (m, 2H), 2.0 (m, 1H), 1.91-1.63 (m, 3H), 1.48 (m, 1H), 1.23-1.17 (m, 3H), 1.1 (dd, 1H, J=13.9, 3.2 Hz), 1.05 (s, 3H), 0.92 (d, 3H, J=6.2 Hz), 0.87 (s, 3H). ^{13}C Jmod NMR (100 MHz, $CDCl_3$) δ (ppm) : 182.4 (C-17, C-20), 161.7 (C-18), 153.5 and 153.3 (C-4, C-21), 117.6 (C-16), 105.7 (C-11), 102.0 (C-19), 56.8 (C-22), 48.5 (C-10), 44.9 (C-9), 39.5 (C-5 , C-8), 37.9 (C-6), 33.2 (C-12), 32.7 (C-15), 32.0 (C-3), 27.8 (C-7), 24.9 (C-2), 22.5 (C-1), 18.6 (C-14), 18.2 (C-13).

Isospongiaquinone (**7**): orange-yellow solid; *m/z* $[M+Na]^+$ 381.2046, (calculated for $C_{22}H_{30}O_4Na$, 381.2042), IR (film), ν_{max} (cm^{-1}): 2965, 1642. R_f: 0.45 (SiO_2, CH_2Cl_2), 0.76 ($SiO_2/AgNO_3$, CH_2Cl_2), ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 (s, OH), 5.85 (s, 1H), 5.13 (br s, 1H), 3.85 (s, 3H), 2.61 (d, J = 13.7 Hz, 1H), 2.49 (d, J = 13.7 Hz, 1H), 2.06-1.97 (m, 2H), 1.87 (m, 1H), 1.62 (dt, J = 12.6, 3.0, 1H), 1.52 (br s, 3H), 1.44 (m, 1H), 1.34 (m, 2H), 1.21 (m, 1H), 1.03 (br s, 1H), 0.99 (br s, 4H), 0.96 (d, J = 6.2 Hz, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.3 (C-20), 182 (C-17), 161.8 (C-18), 153.2 (C-21), 144.0 (C-4), 120.9 (C-3), 117.6 (C-16), 101.9 (C-19), 56.8 (C-22), 47.9 (C-10), 43.0 (C-9), 38.5 (C-5), 37.8 (C-8), 36.0 (C-6), 32.3 (C-15), 27.9 (C-7), 27.0 (C-2), 20.1 (C-12), 19.8 (C-1), 18.1 (C-11), 17.6 (C-13), 17.3 (C-14).

5-*epi*-isospongiaquinone (14): orange-yellow solid, *m/z* $[M+Na]^+$ 381.2041, (calculated for $C_{22}H_{30}O_4Na$, 381.2042), IR, ν_{max} (cm^{-1}): 2925, 1642. R_f: 0.45 (SiO_2, CH_2Cl_2), 0.66 ($SiO_2/AgNO_3$, CH_2Cl_2), ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (s, OH), 5.86 (s, 1H), 5.39 (br s, 1H), 3.86 (s, 3H), 2.60 (d, J = 13.2 Hz, 1H), 2.47 (d, J = 13.2 Hz, 1H), 2.11 (br d, J = 12.5 Hz, 1H), 1.97 (dt, J = 16.8 ; 4.7 Hz, 1H), 1.82-1.72 (m, 3H), 1.50 (m, 1H), 1.43-1.35 (m, 3H), 1.14 (td, J = 13 ; 4.5 Hz, 1H), 1.02 (s, 3H), 0.99 (s, 3H), 0.95 (d, J = 6.7 Hz, 3H), 0.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.4 (C-20), 182.1 (C-17), 161.6 (C-18), 153.8 (C-21), 146.3 (C-4), 114.9 (C-3), 118.4 (C-16), 102.0 (C-19), 56,8 (C-22), 41,8 (C-8), 41.3 (C-6), 40.9 (C-5), 36,5 (C-10), 36.4 (C-9), 32,7 (C-15), 31.6 (C-2), 30.6 (C-7), 29.7 (C-11), 28.0 (C-12), 22.8 (C-1), 16,6 (C-13), 16.0 (C-14).

Neomamanuthaquinone (**15**): yellow solid; *m/z* $[M+Na]^+$ 381.2039, (calculated for $C_{22}H_{30}O_4Na$, 381.2042), IR, v_{max} (cm^{-1}): 2925, 1642. R_f: 0.45 (SiO_2, CH_2Cl_2), 0.73 ($SiO_2/AgNO_3$, CH_2Cl_2), ^1H NMR(400 MHz, $CDCl_3$) δ (ppm): 7.34 (s, OH), 5.84 (s, 1H), 3.85 (s, 3H), 2.70 (d, J = 13.2 Hz, 1H), 2.56 (d, J = 13.2 Hz, 1H), 2.13-1.97 (m, 3H), 1.90-1.85 (m, 2H), 1.60-1.53 (m, 3H), 1.43-1.32 (m, 3H), 0.99 (s, 3H), 0.95 (s, 3H), 0.81 (s, 3H), 0.77 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.6 (C-20), 182.1 (C-17), 161.4 (C-18), 152.8 (C-21), 135.0 (C-5), 131.3 (C-10), 117.9 (C-16), 102.0 (C-19), 56.8 (C-22), 42.8 (C-9), 39.9 (C-3), 34.5 (C-8), 34.2 (C-4), 32.2 (C-15), 28.9 (C-12), 28.0 (C-11), 26.5 (C-7), 25.8 (C-1), 22.0 (C-14), 20.7 (C-6), 20.0 (C-2), 15.4 (C-13).


ilimaquinone (4)
7.51
5.84
4.42
4.41
2.54
2.50
2.46
2.43
2.34
2.33
2.31
2.30
2.28
2.26
2.06
1.83
1.51
1.31
1.16
1.13
1.02
0.97
0.95
0.83
0.76
0.73
H-22
H-14
H-12
H-13
H-1eq, H-3ax
H-3eq
H-2ax, H-8
H-1ax, H-6
H-7
H-19
H-15b
H-15a
H-2eq
21-OH
H-11a
H-11b
H-10
f1 (ppm)


ilimaquinone (4)
182.45
182.12
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160.56
153.47
117.45
102.62
102.12
56.94
50.25
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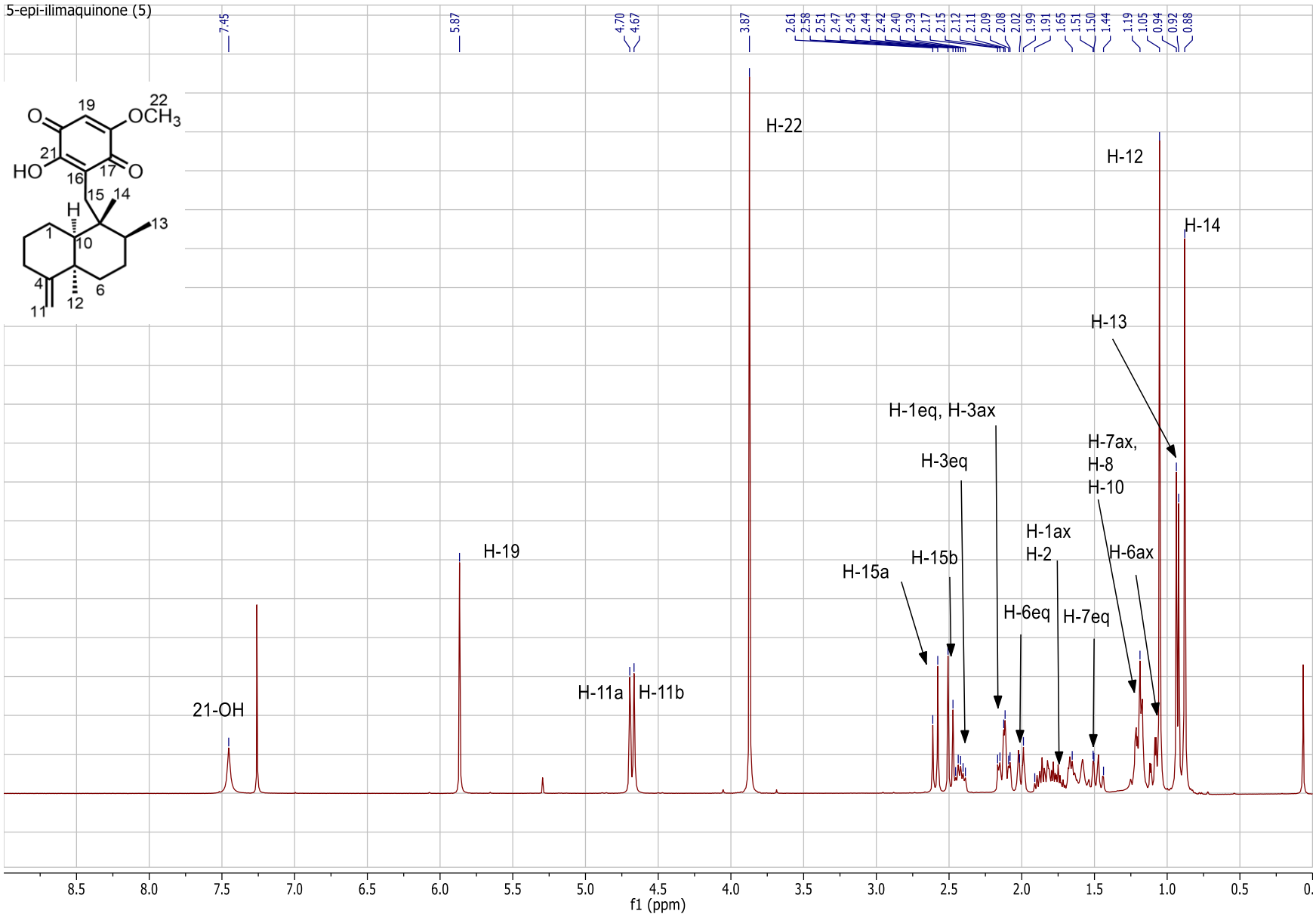
40.55
38.19
36.75
33.07
32.47
28.73
28.06
23.28
20.66
17.95
17.44
C-19
C-22
C-10
C-8
C-12
C-13
C-14
C-17
C-20
C-18
C-21
C-16
C-4
C-9
C-5
C-1
C-7
C-2
C-11
C-6
C-3
C-15
f1 (ppm)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4.67
3.87
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2.58
2.51
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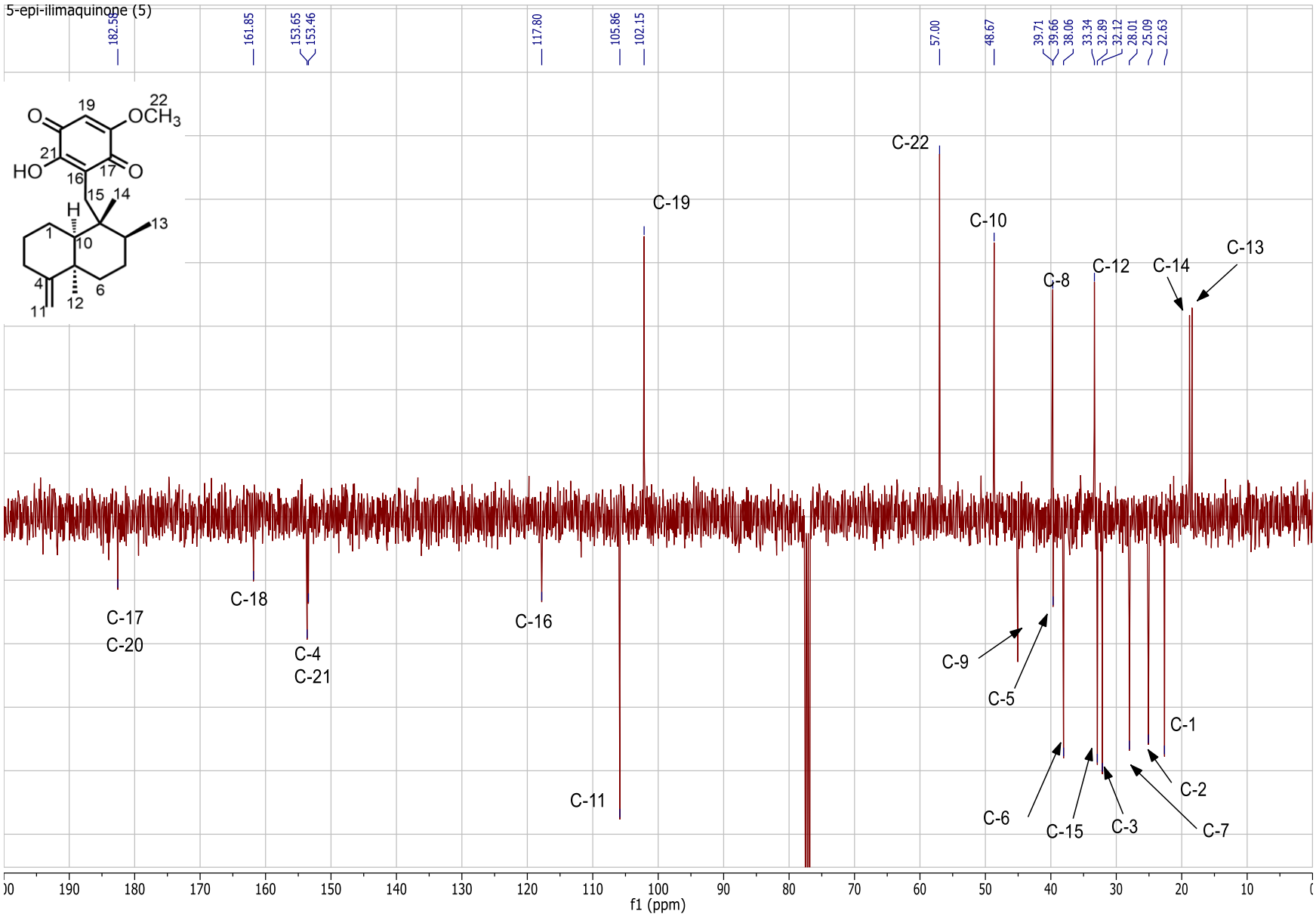
2.45
2.44
2.42
2.40
2.39
2.17
2.15
2.12
2.11
2.09
2.08
2.02
1.99
1.91
1.65
1.51
1.50
1.44
1.19
1.05
0.94
0.92
0.88
H-22
H-12
H-14
H-13
H-1eq, H-3ax
H-7ax,
H-8
H-10
H-3eq
H-1ax
H-2
H-6ax
H-19
H-15b
H-15a
H-6eq
H-7eq
H-11a
H-11b
21-OH
f1 (ppm)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153.46
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105.86
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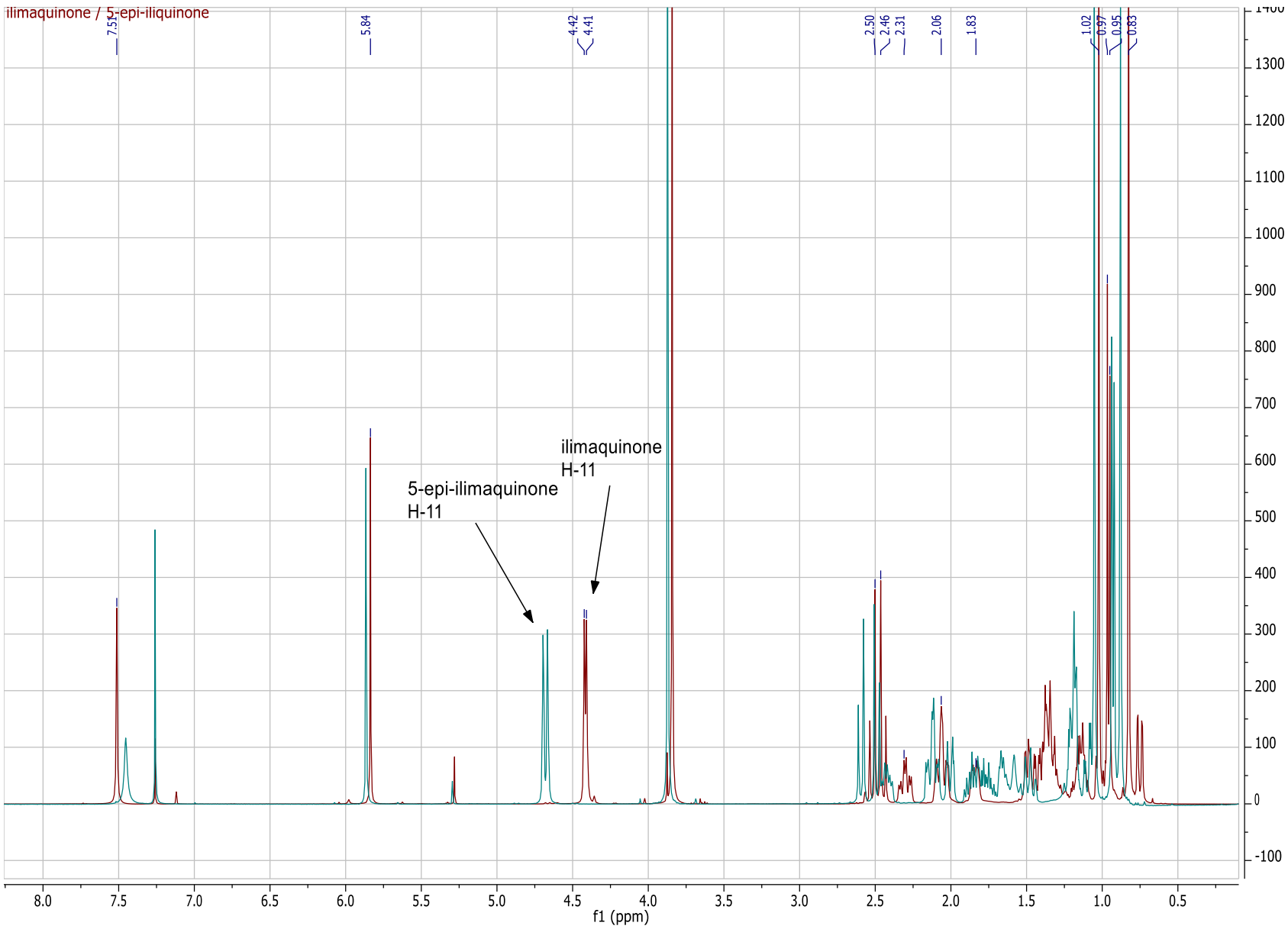
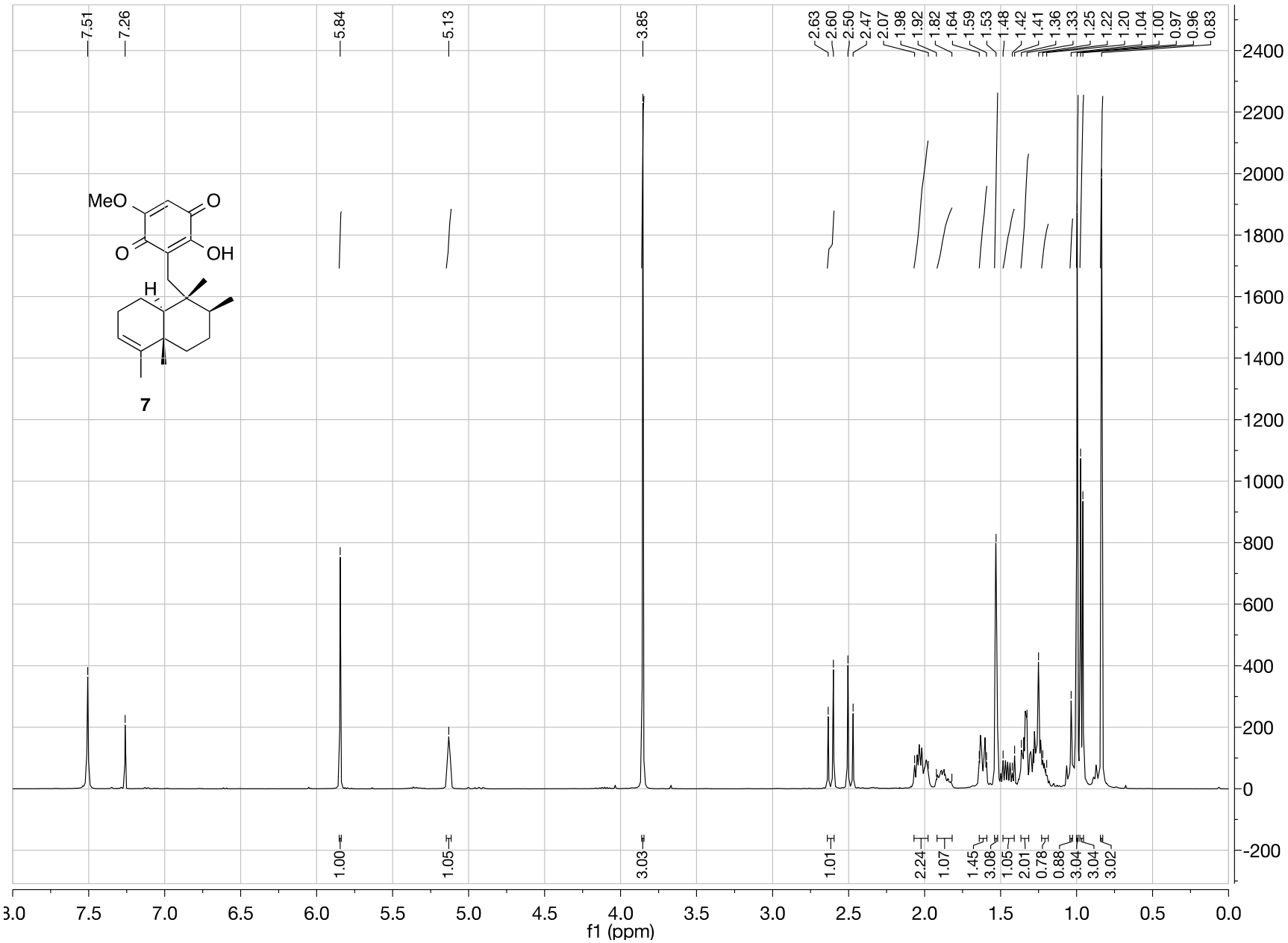
C-6
C-15
C-3
C-7
f1 (ppm)


ilimaquinone / 5-epi-iliquinone
7.51
5.84
4.42
4.41
2.50
2.46
2.31
2.06
1.83
1.02
0.97
0.95
0.83
ilimaquinone
H-11
5-epi-ilimaquinone
H-11
f1 (ppm)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5.13
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2.07
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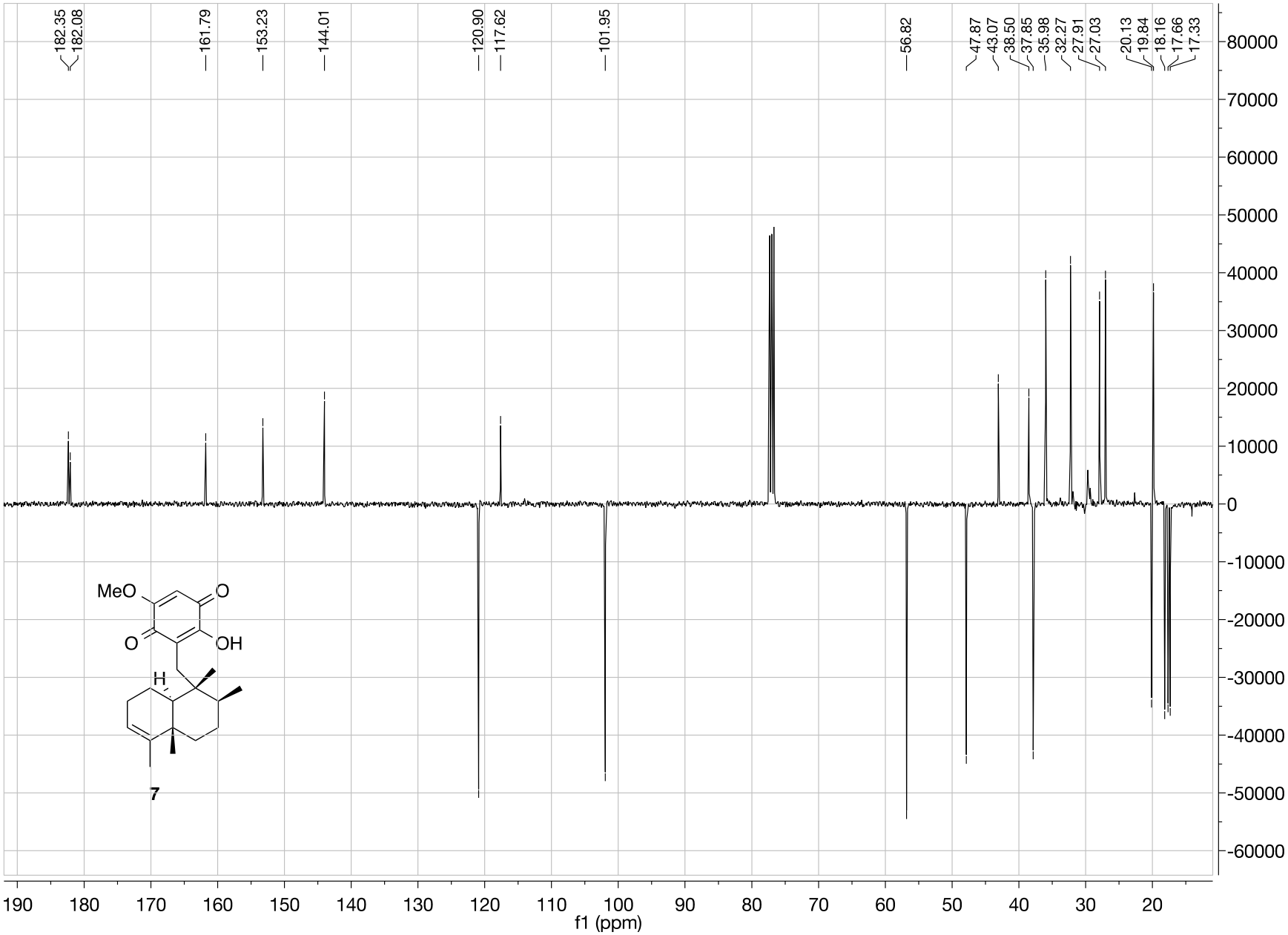
1.48
1.42
1.41
1.36
1.33
1.25
1.22
1.20
1.04
1.00
0.97
0.96
0.83
MeO
O
O
OH
H
7
1.00
1.05
3.03
1.01
2.24
1.07
1.45
3.08
1.05
2.01
0.78
0.88
3.04
3.04
3.02
f1 (ppm)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153.23
144.01
120.90
117.62
101.95
56.82
47.87
43.07
38.50
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35.98
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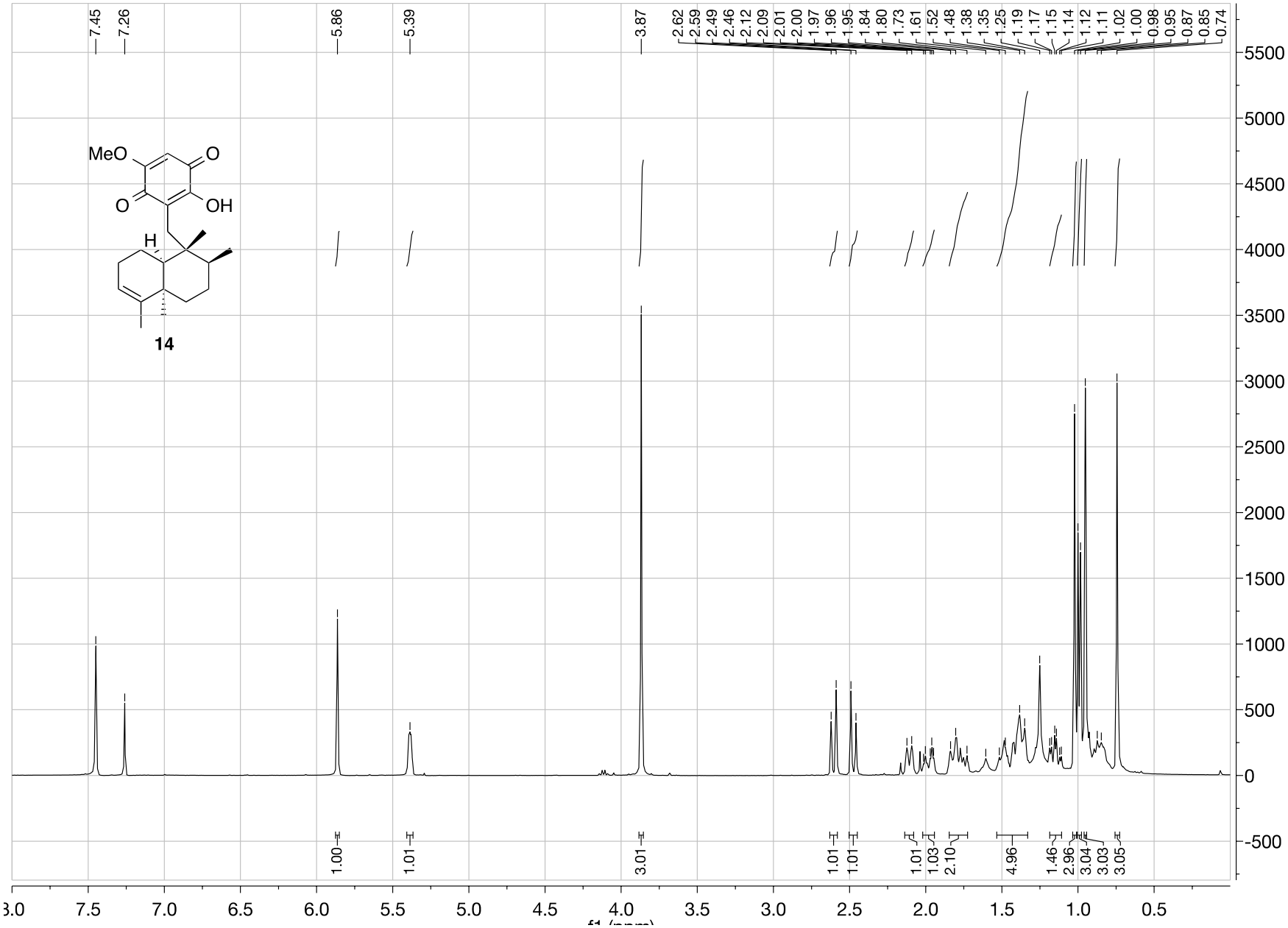
MeO
O
O
OH
H
7
f1 (ppm)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1.25
1.19
1.17
1.15
1.14
1.12
1.11
1.02
1.00
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0.95
0.87
0.85
0.74
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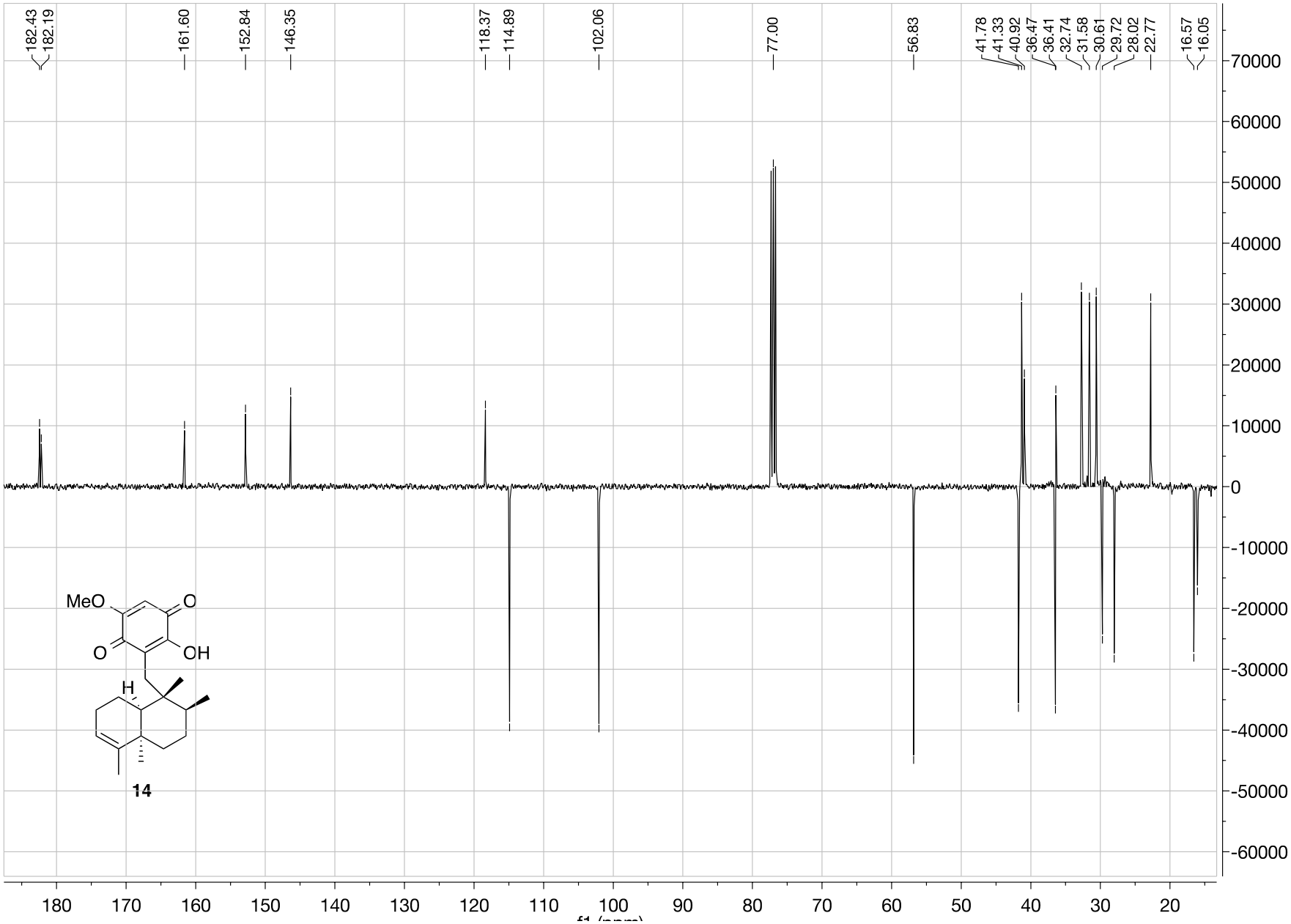
O
O
OH
H
14
1.00
1.01
3.01
1.01
1.01
1.01
1.03
2.10
4.96
1.46
2.96
3.04
3.03
3.05
f1 (ppm)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114.89
102.06
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56.83
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40.92
36.47
36.41
32.74
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28.02
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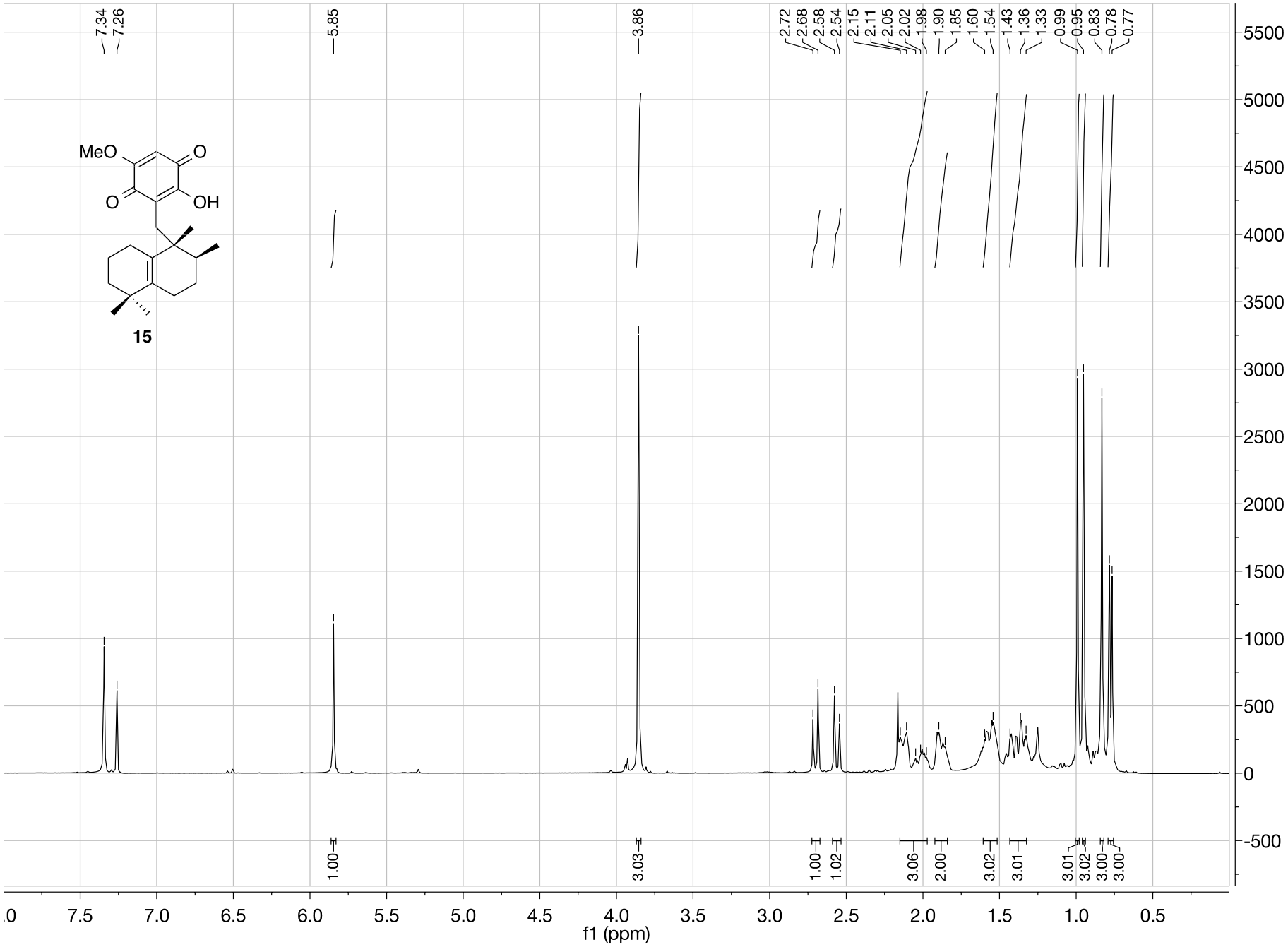
16.57
16.05
MeO
O
O
OH
H
14
f1 (ppm)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2.68
2.58
2.54
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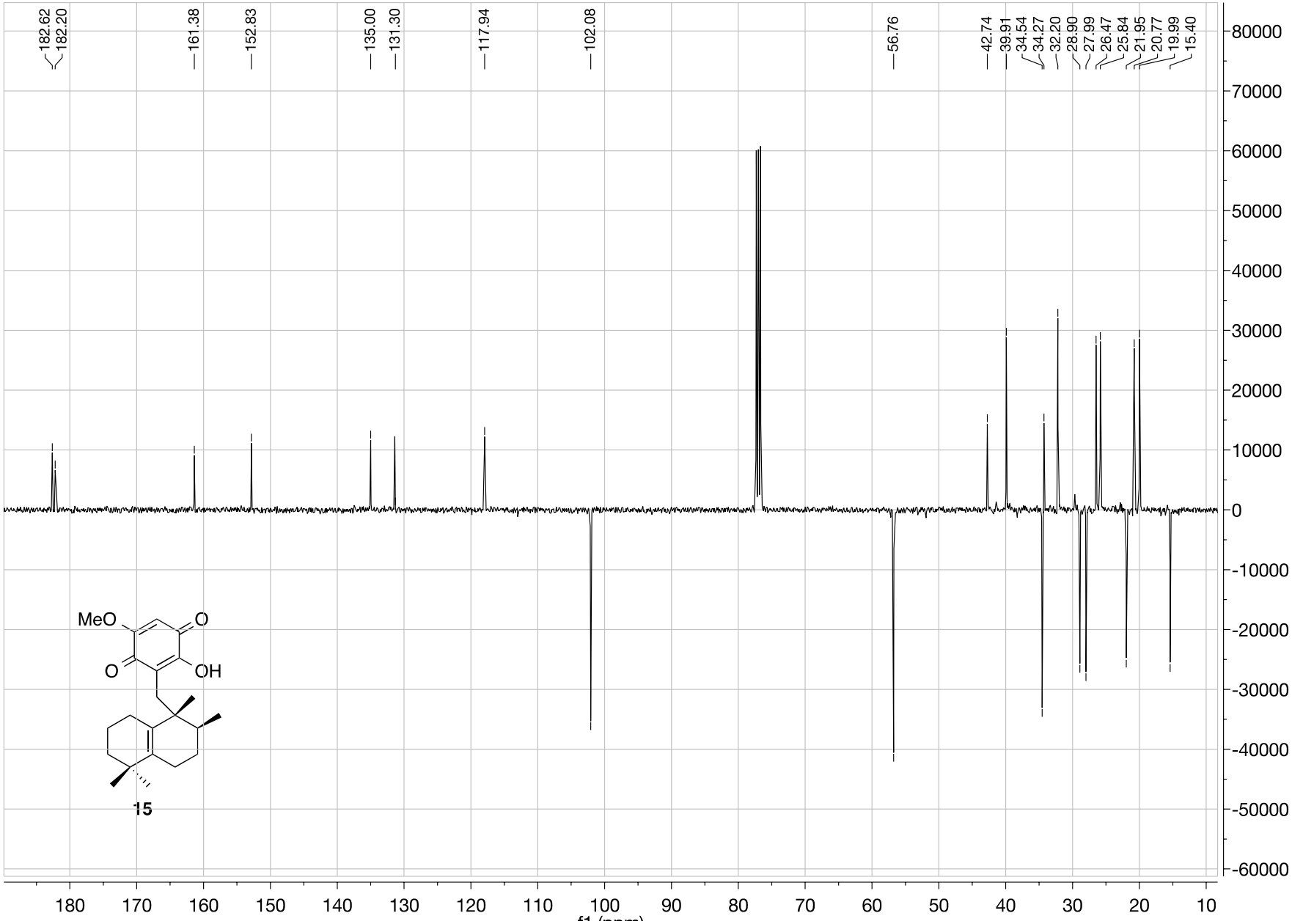
2.11
2.05
2.02
1.98
1.90
1.85
1.60
1.54
1.43
1.36
1.33
0.99
0.95
0.83
0.78
0.77
MeO
O
O
OH
15
1.00
3.03
1.00
1.02
3.06
2.00
3.02
3.01
3.01
3.02
3.00
3.00
f1 (ppm)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34.27
32.20
28.90
27.99
26.47
25.84
21.95
20.77
19.99
15.40
MeO
O
O
OH
15
f1 (ppm)