Supporting Information

Divergent Total Syntheses of Rhodomyrtosones A and B

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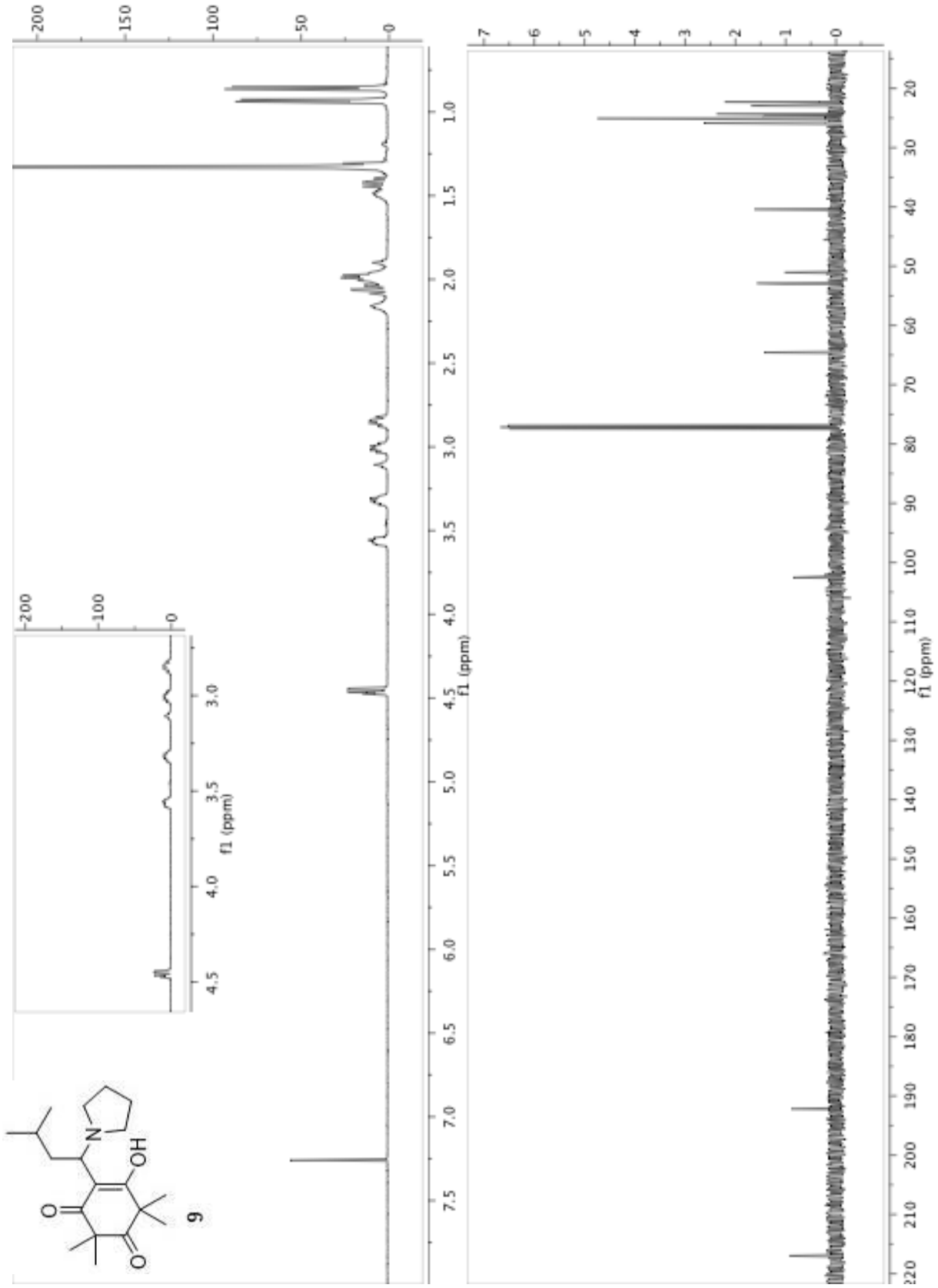
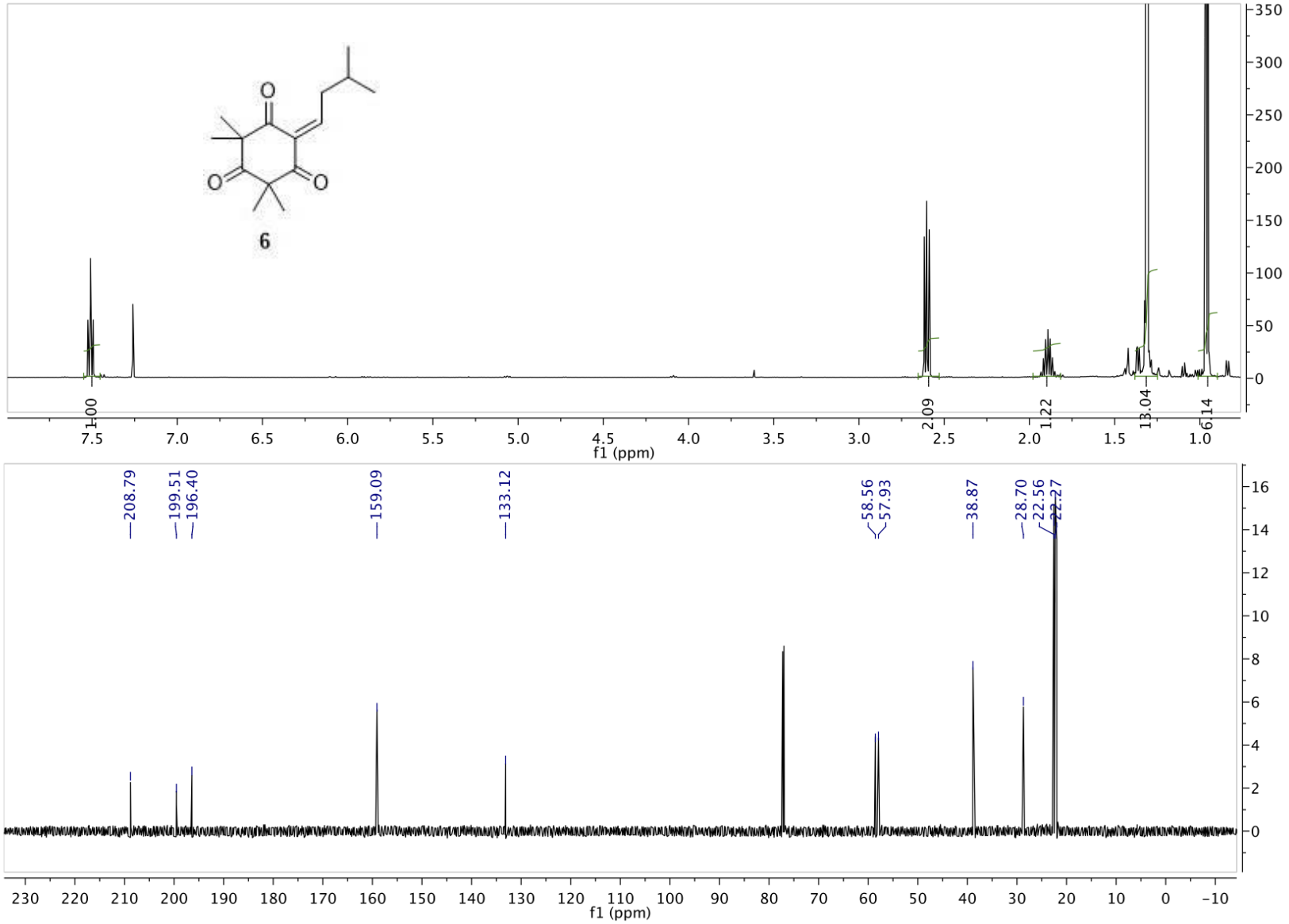
1. Select NMR Spectra

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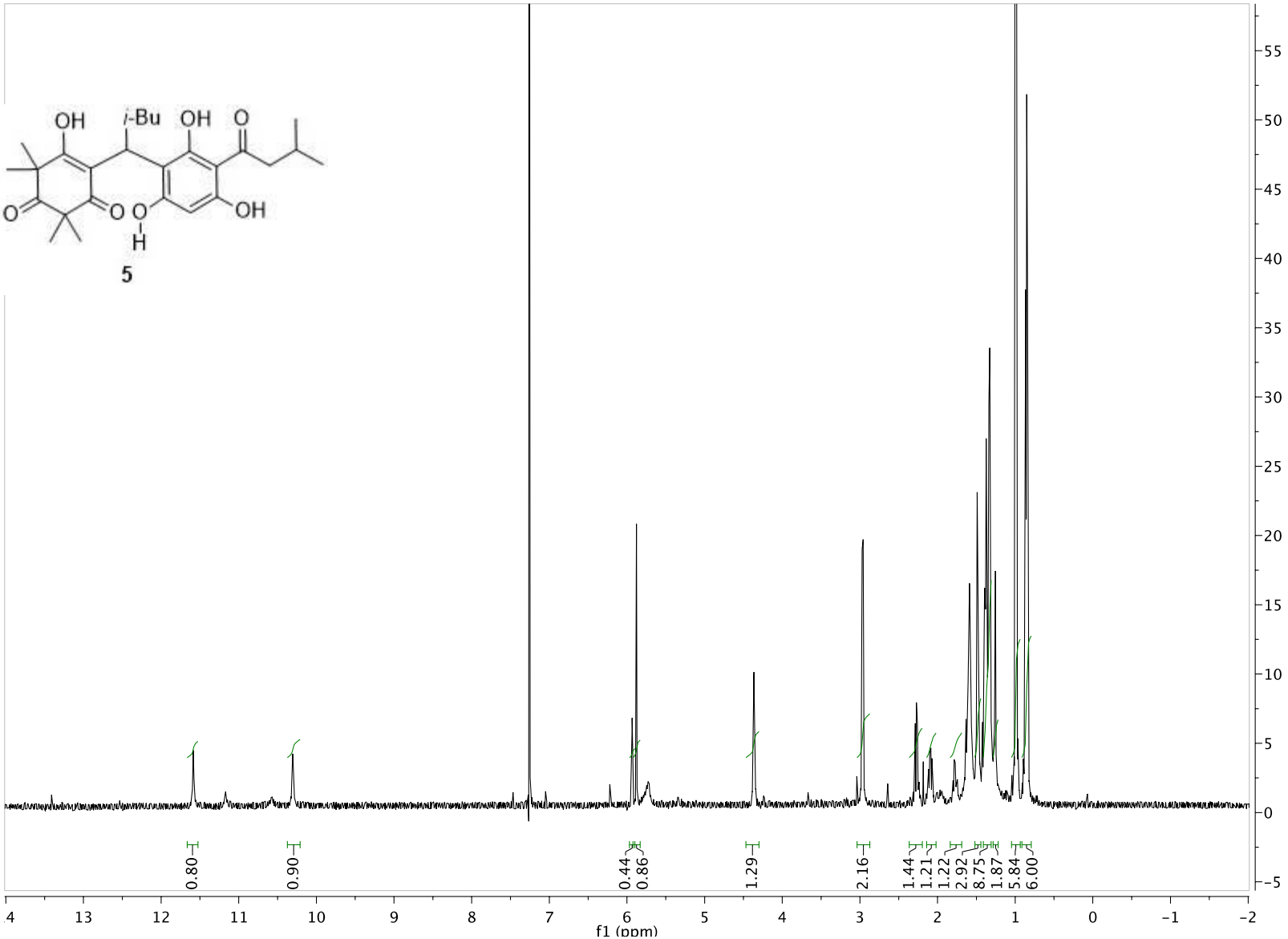
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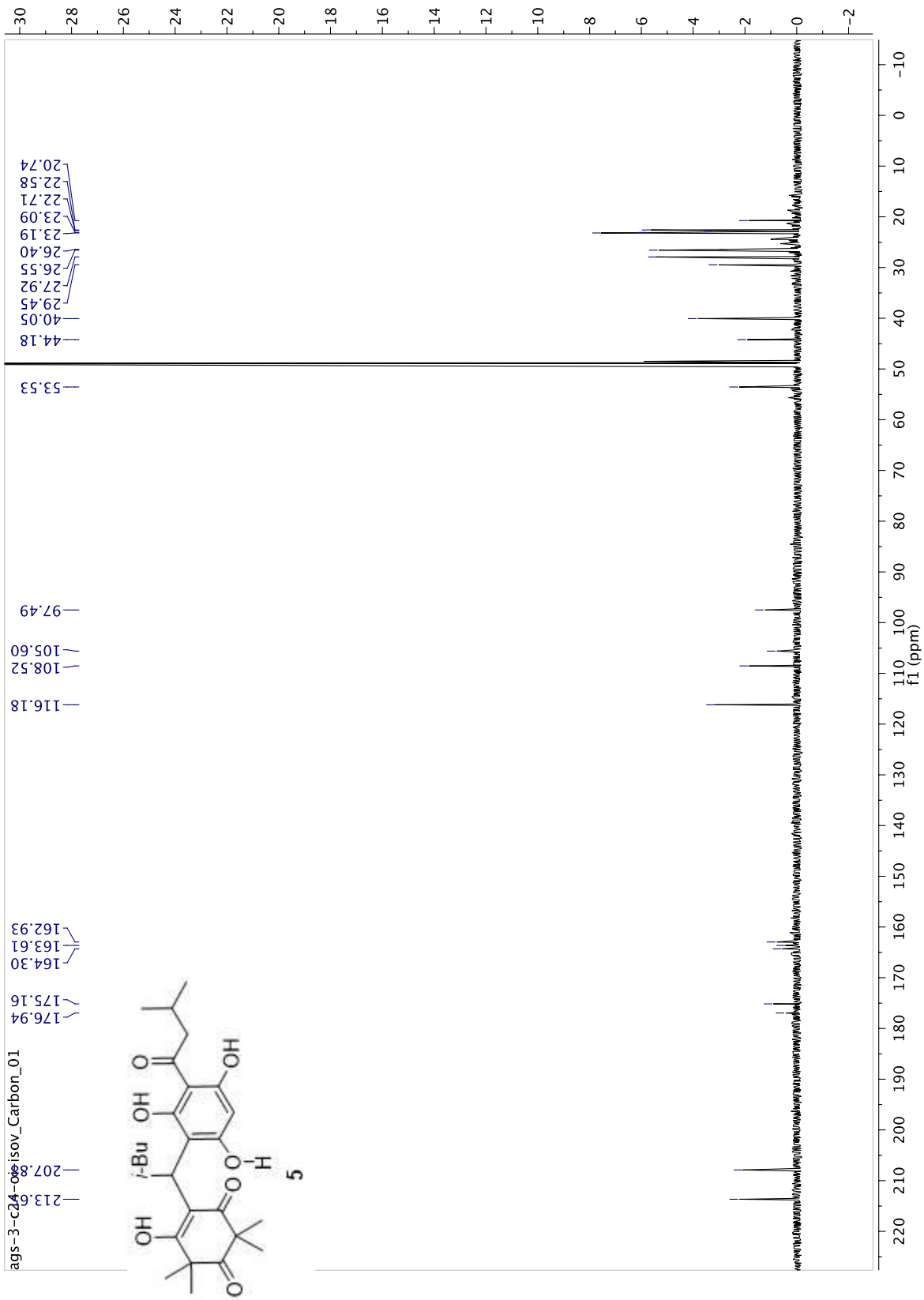
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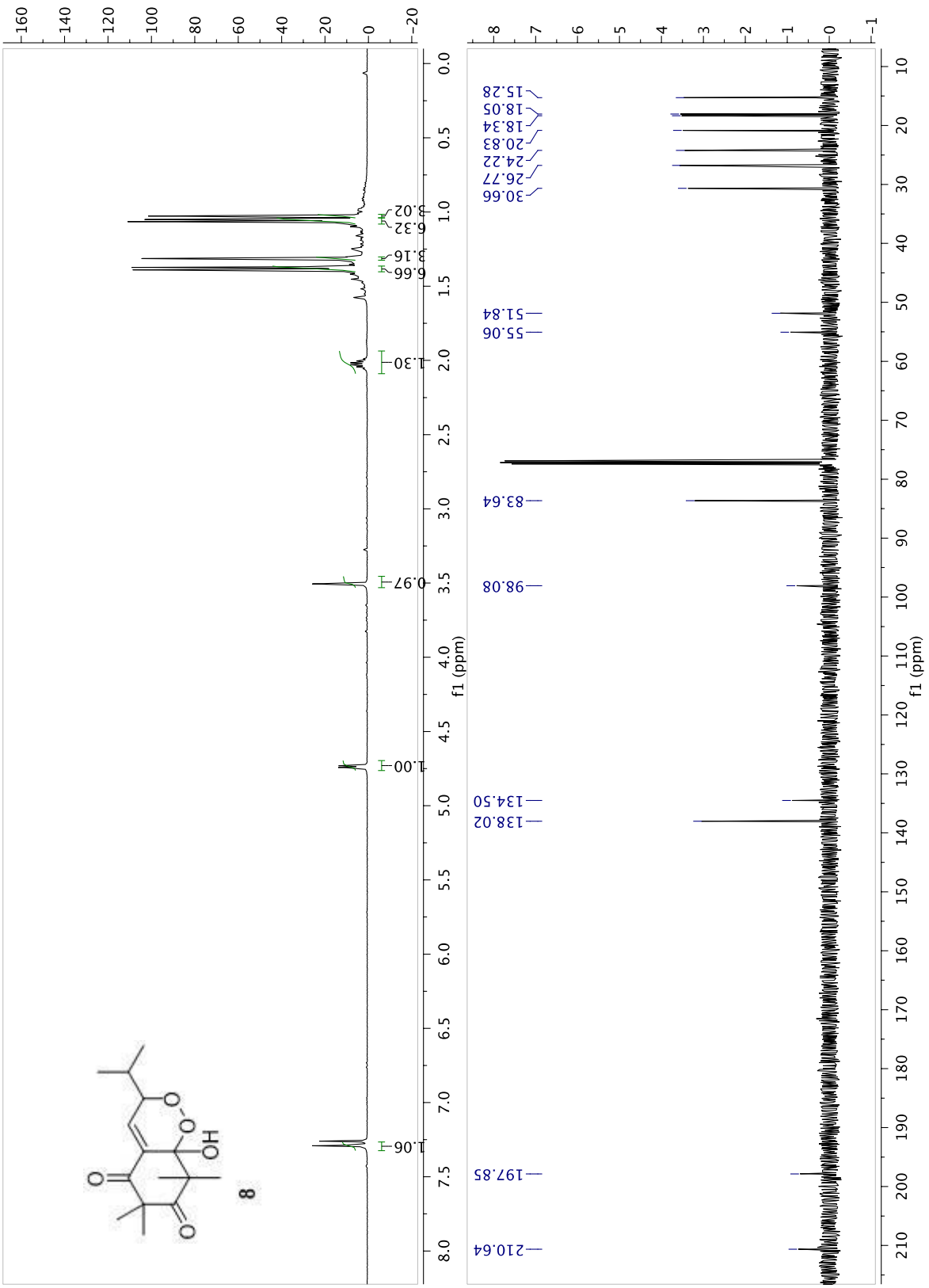
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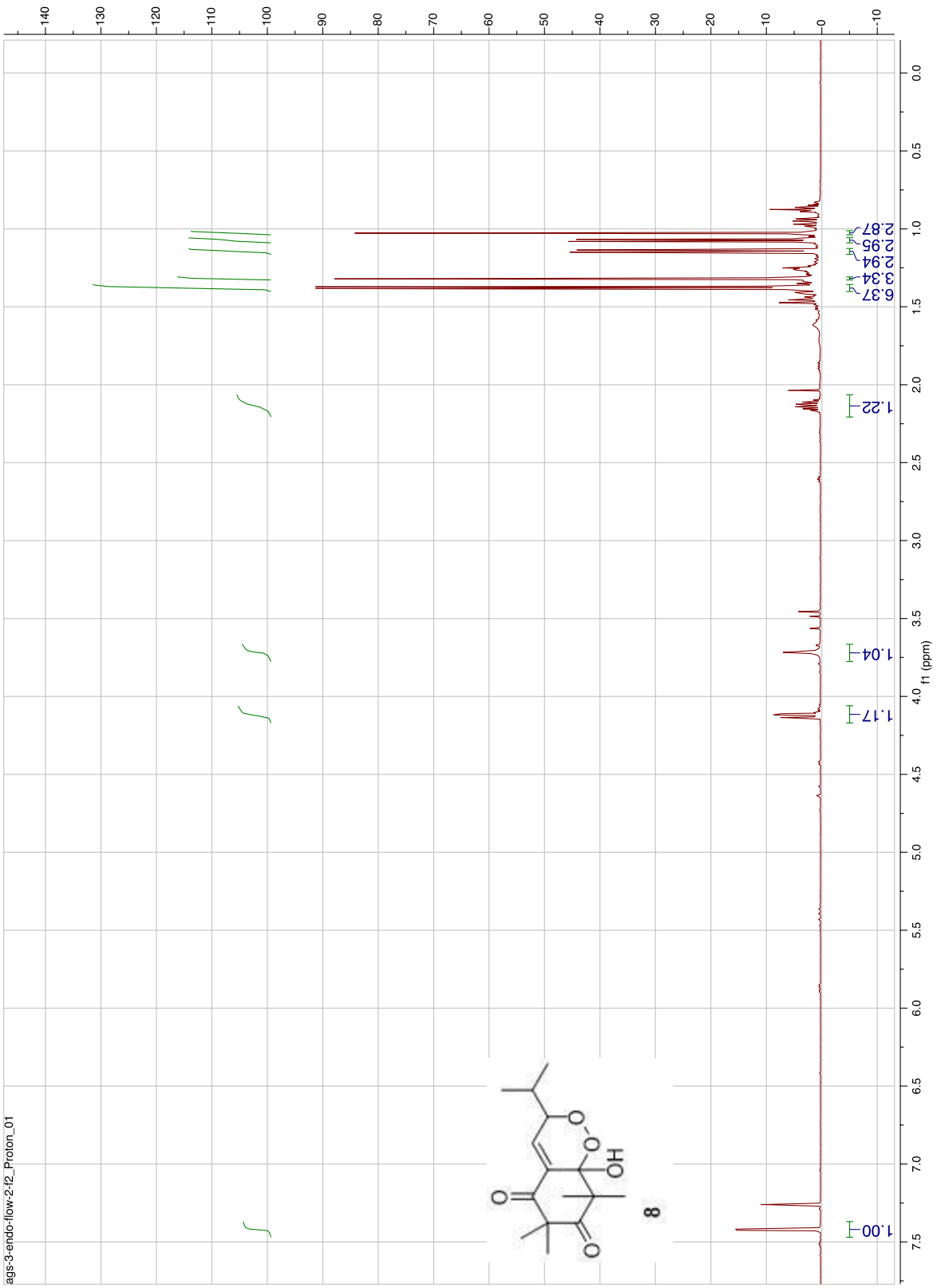
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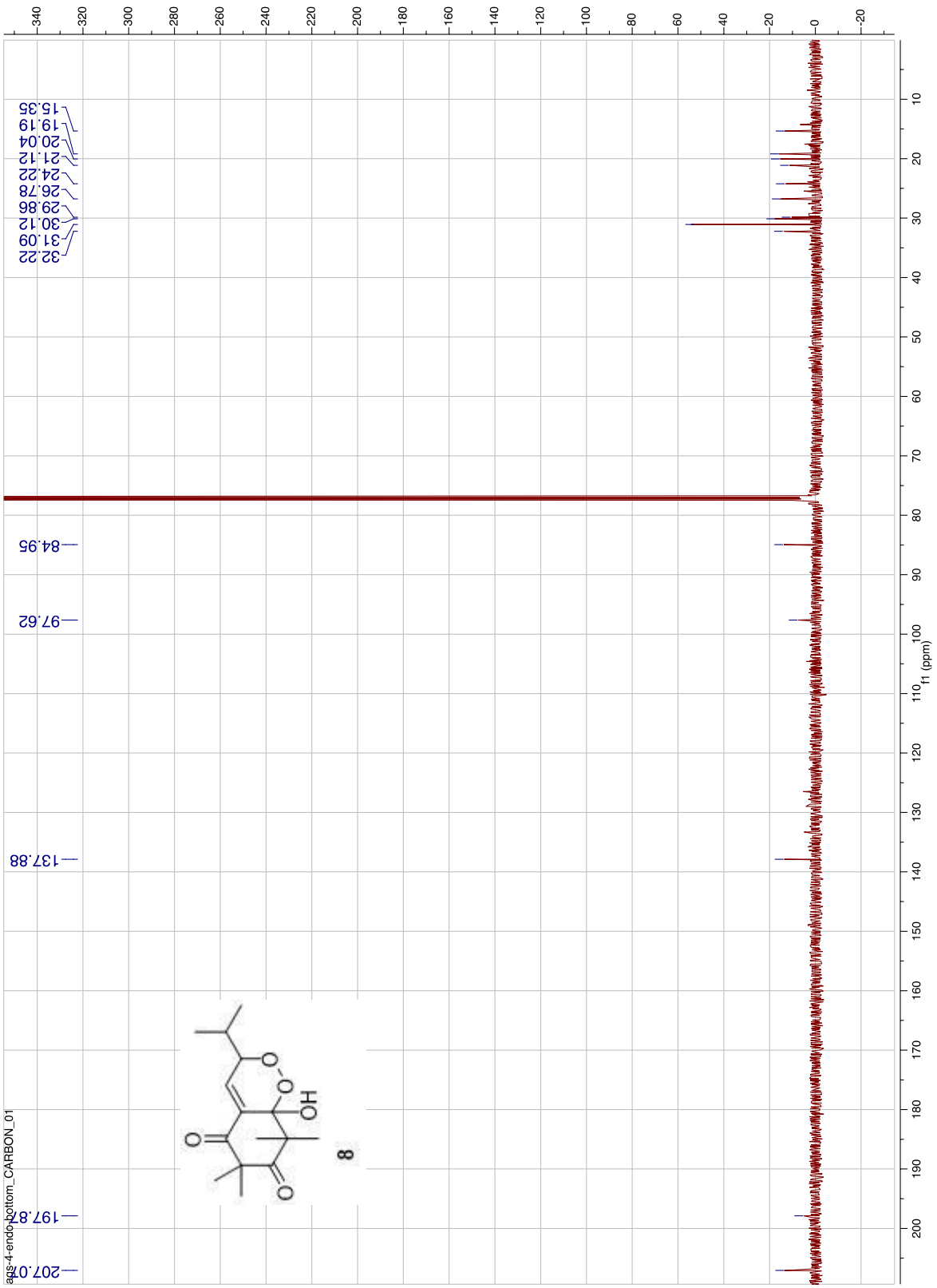
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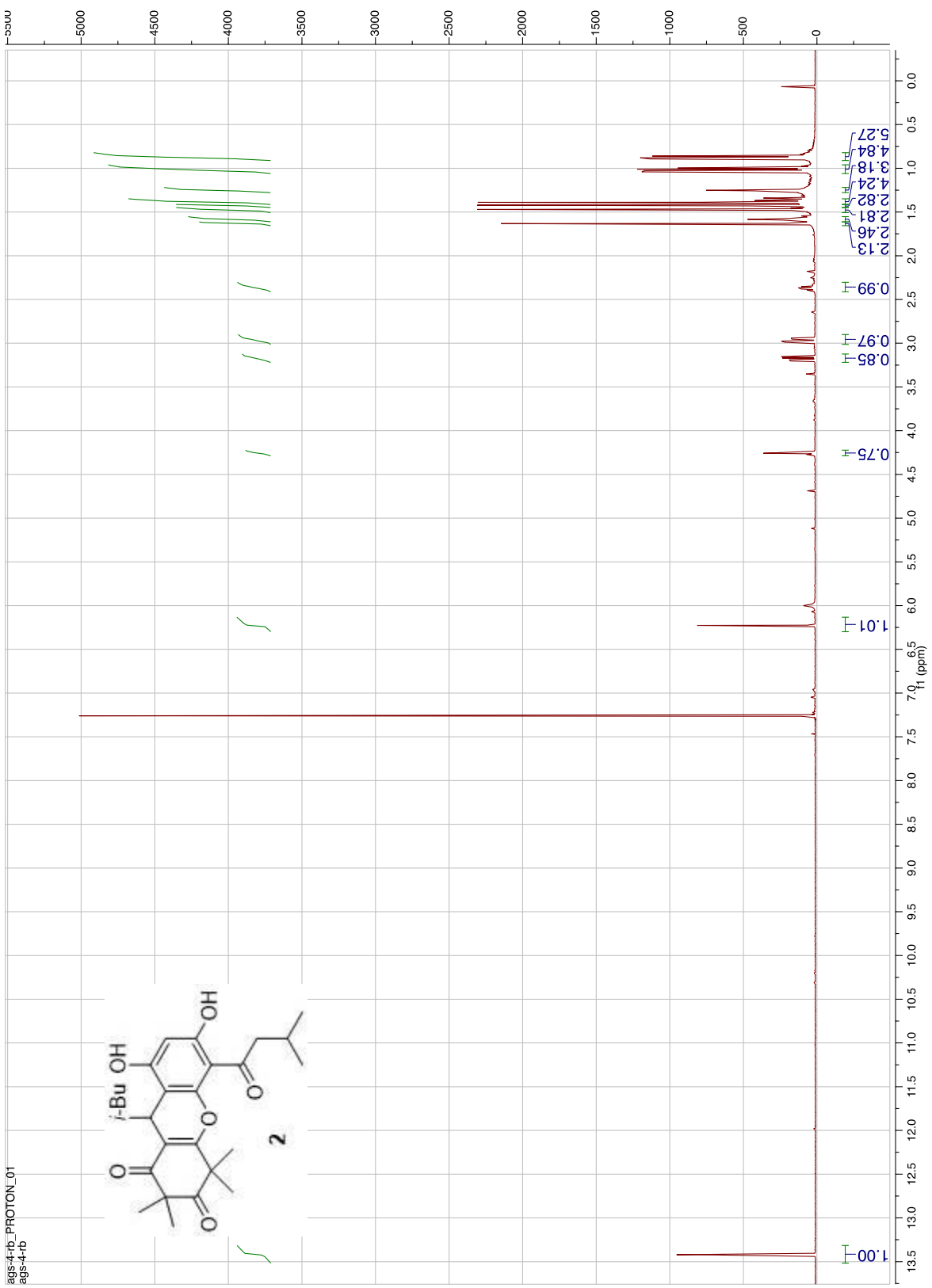
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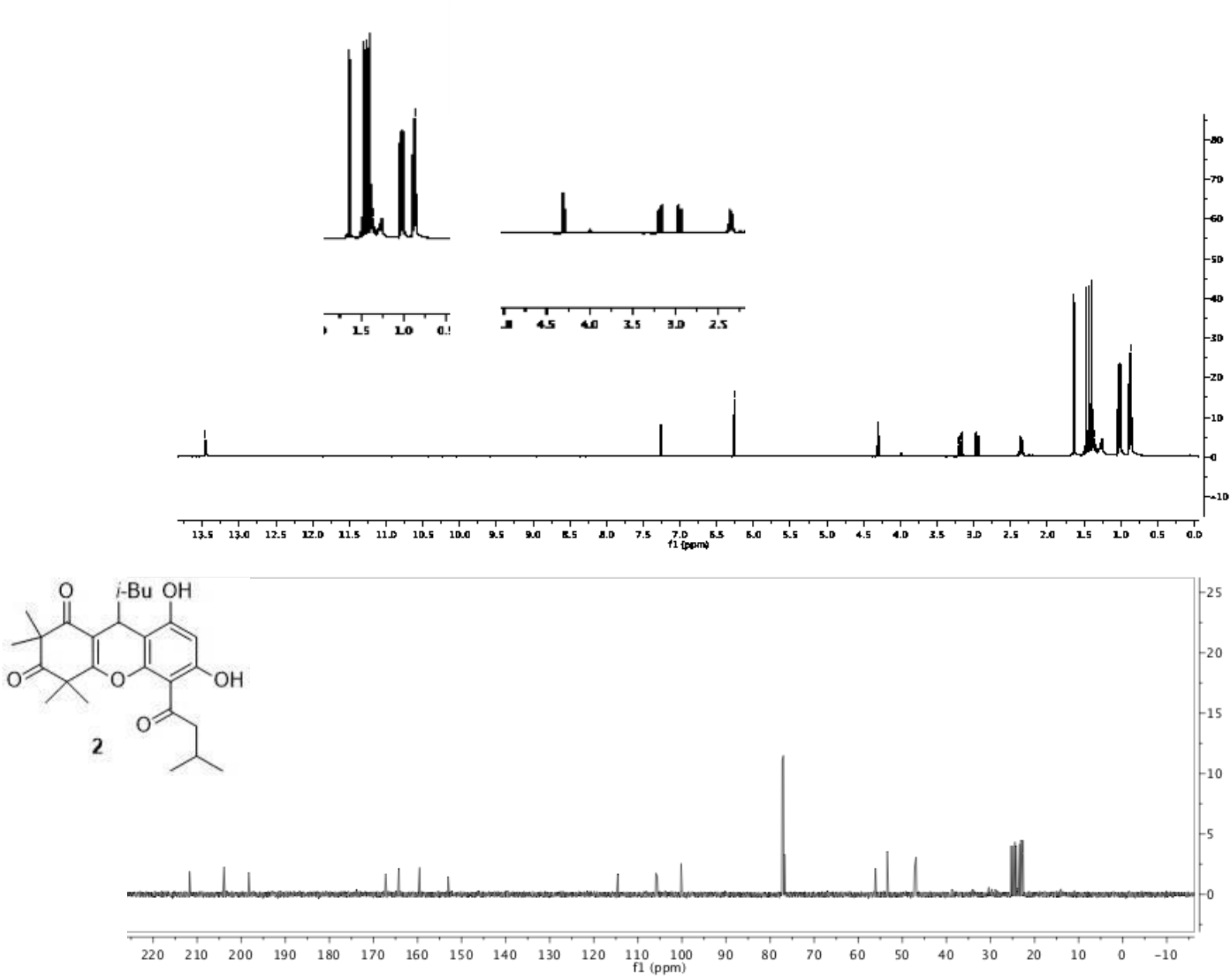
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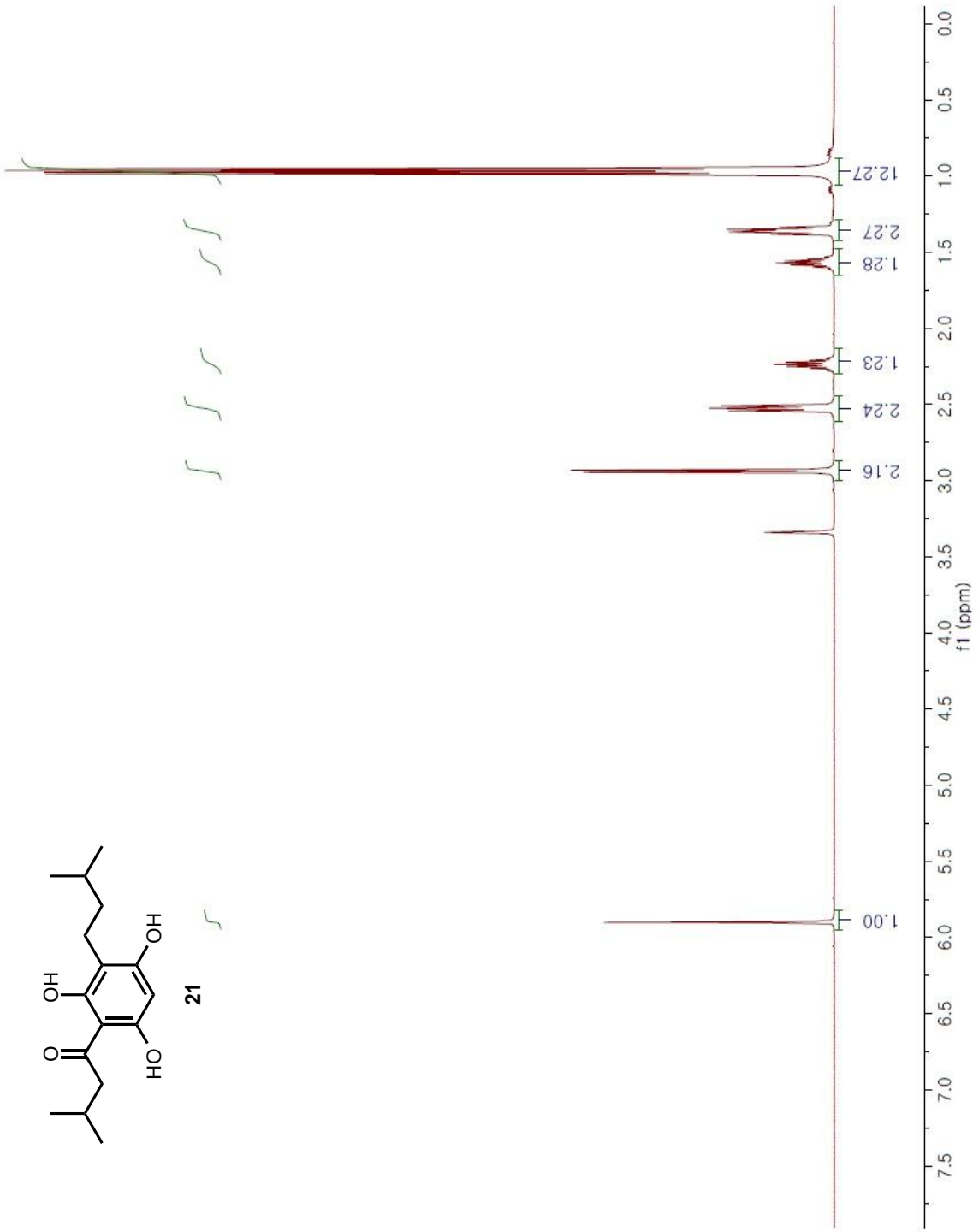
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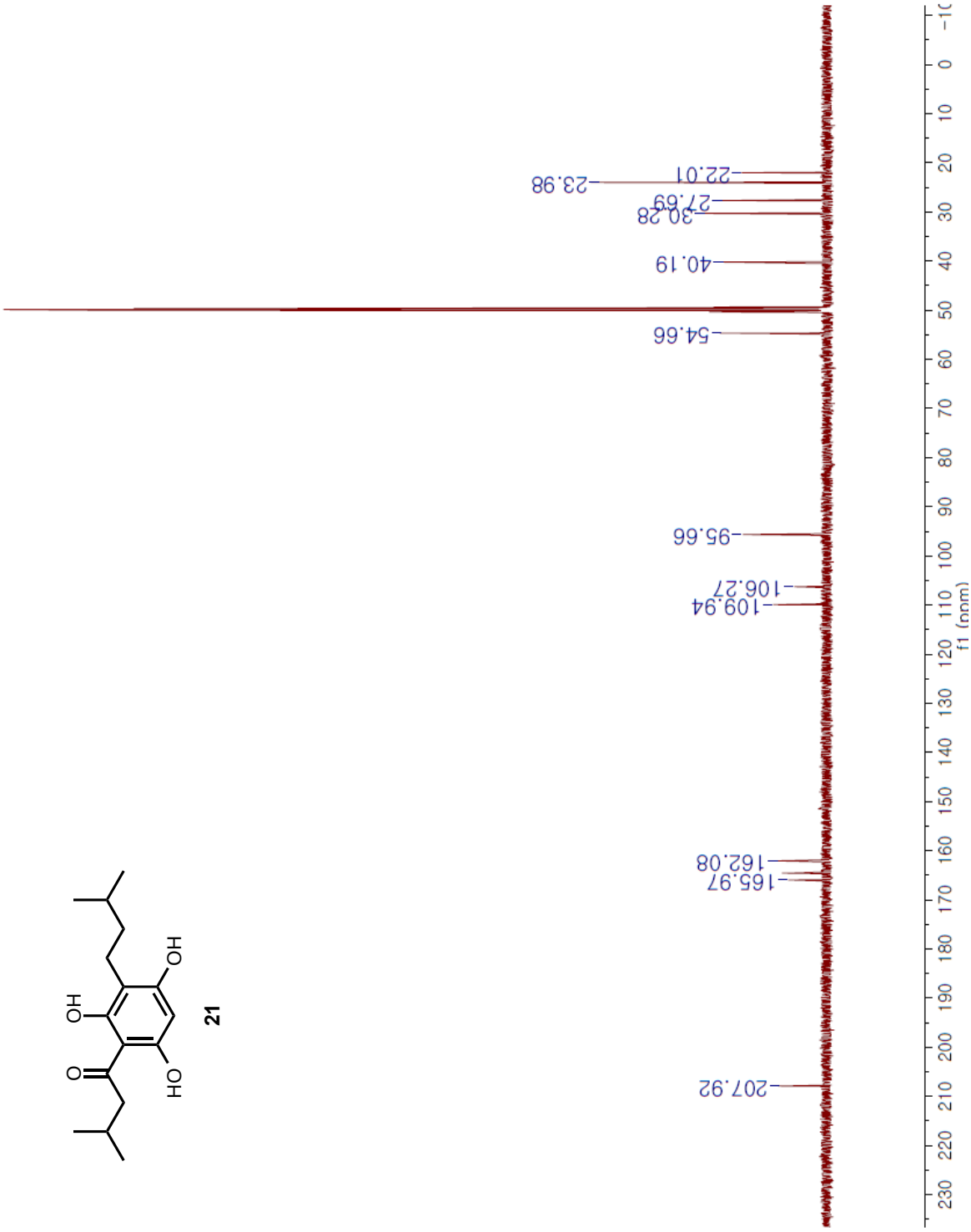
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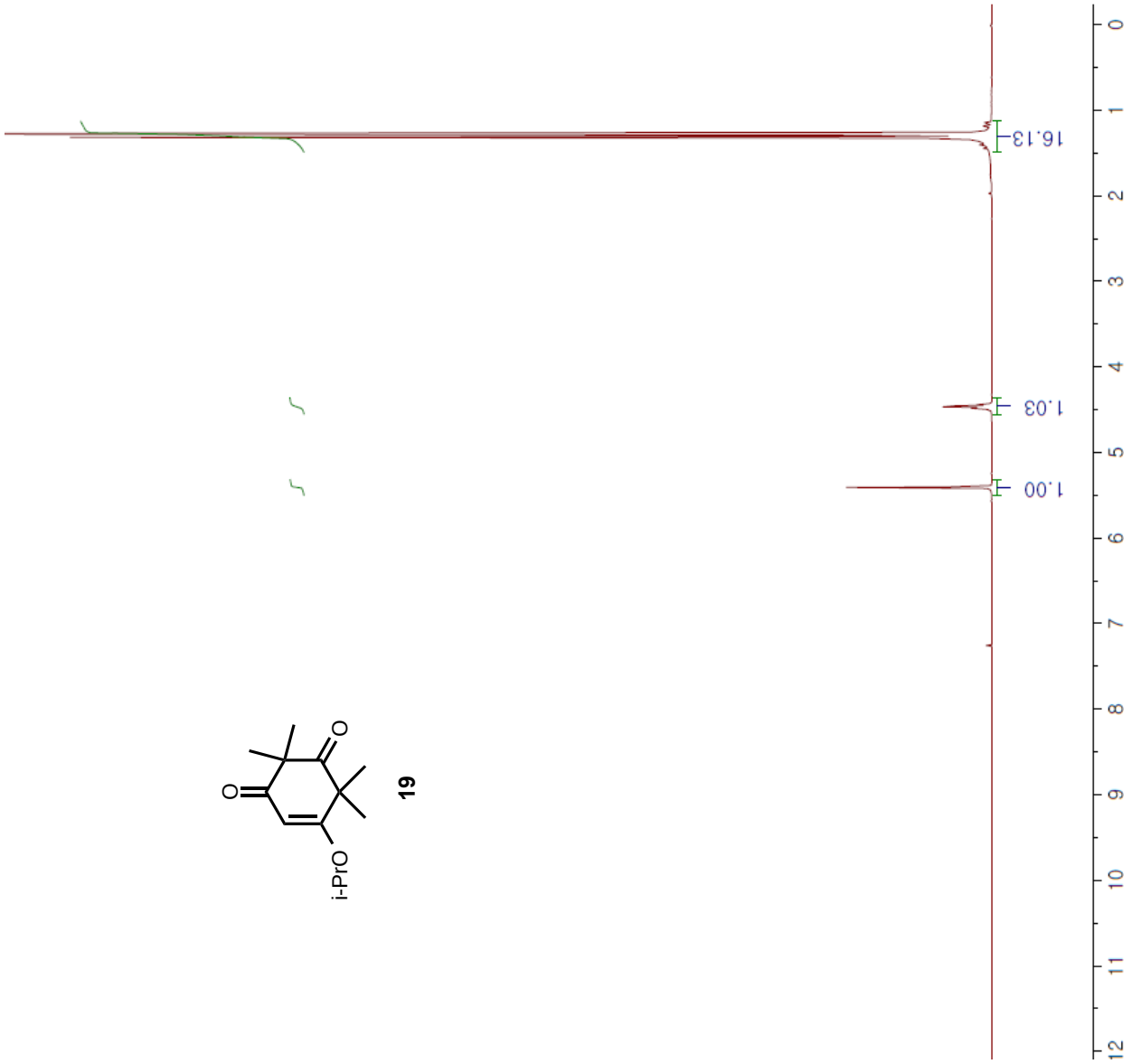
21



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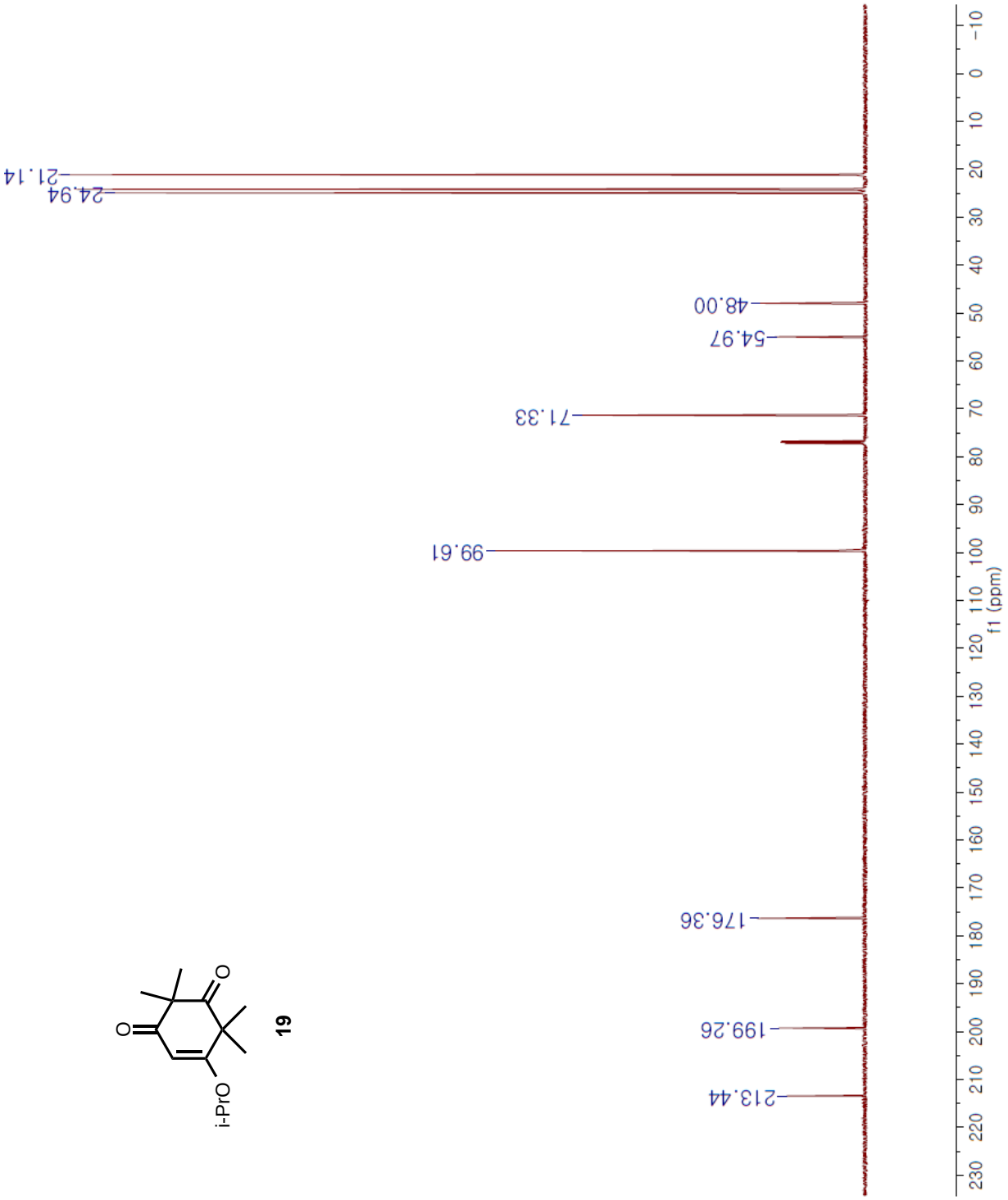
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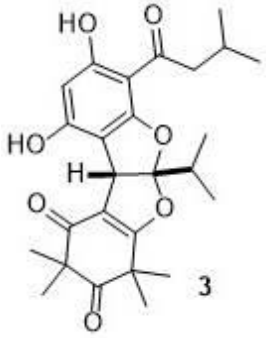

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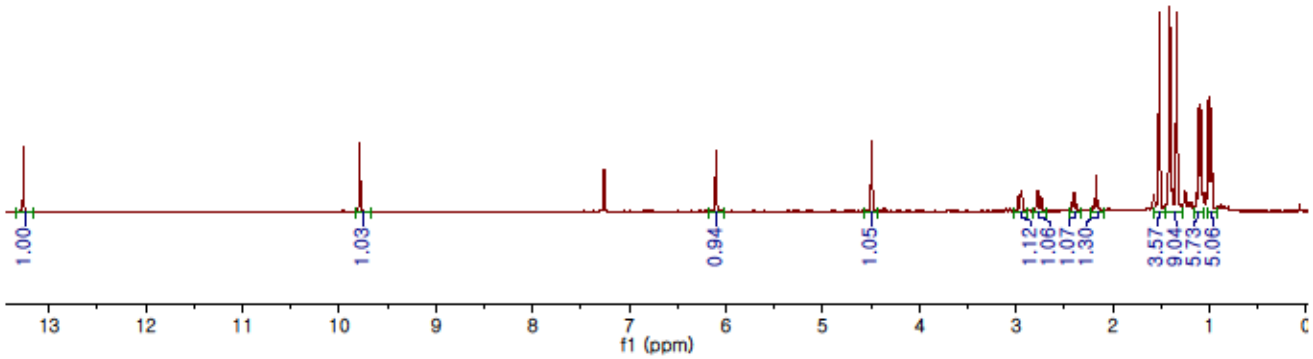

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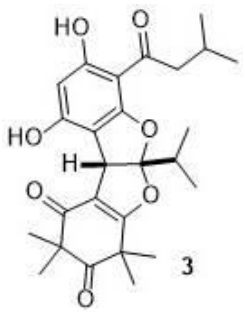
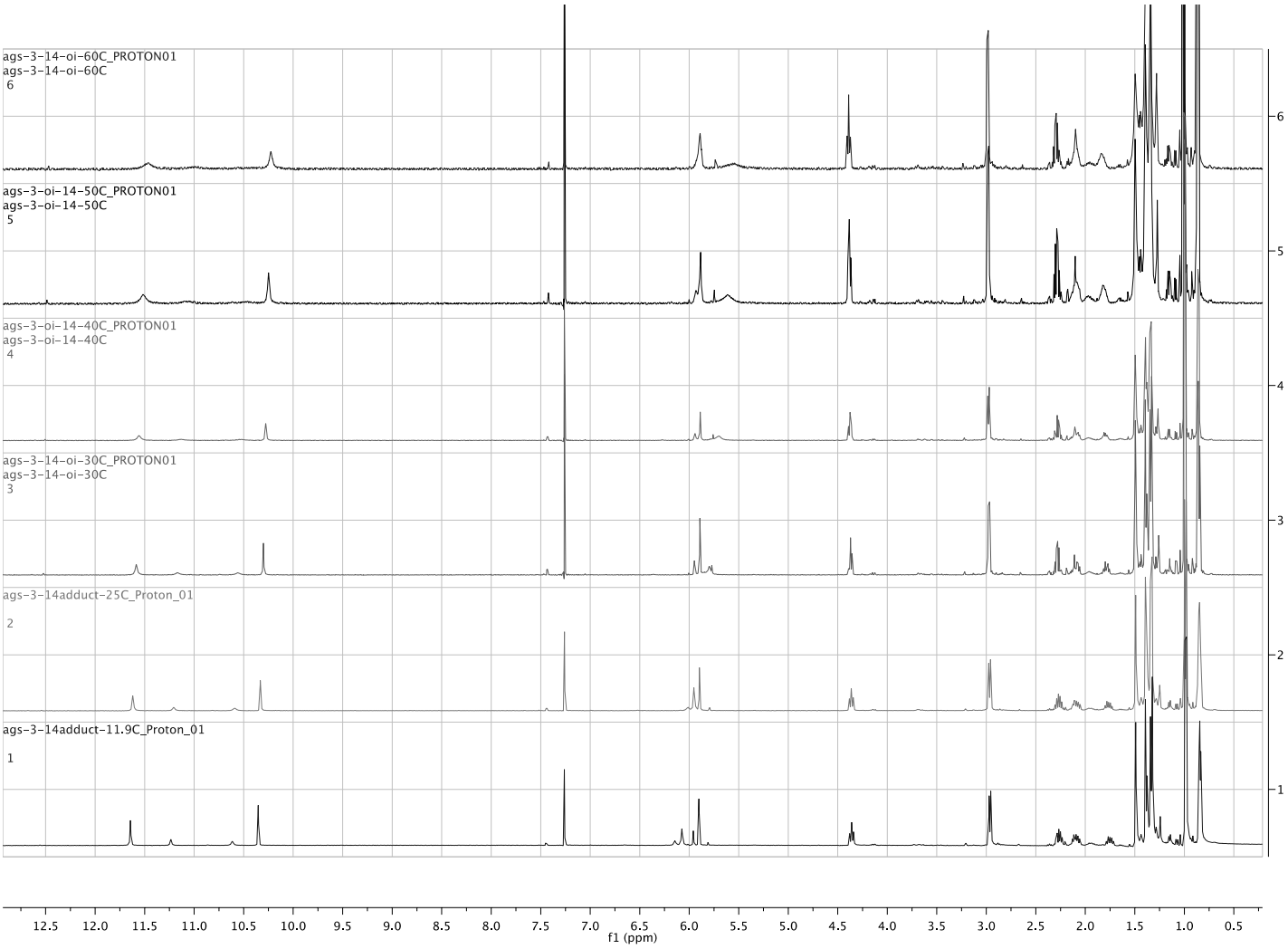


2. Variable Temperature ^{1}H NMR Studies for Compound 5



Variable temperature NMR studies were performed with compound **5** in $CDCl_3$ and the temperature was varied from 10 °C to 60 °C. The coalescence temperature was found to be 60 °C. The initial Δυ was determined to be 142.58 Hz at 10 °C. With Δυ= 142.58 Hz and T °C = 60 °C using the Shoemaker method[S1] (**Figure S1**), the rotational energy was determined to be 15 kcal/mol.

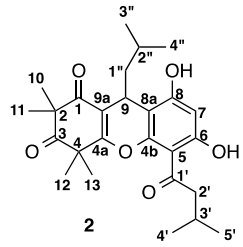
Figure S1. Equation Used for Rotational Energy Calculations.

$$\Delta G \ddagger = aT\left[9.972 + log\left(\frac{Tc}{\Delta v}\right)\right]$$

where a = 4.575 x 10^{-3} kcal/mol
where a = 1.914 x 10^{-3} kJ/mol
at coalescence temperature $kc = \pi\Delta v/\sqrt{2}$

[S1] Sandstöm, J.; Shoemaker, R. *Dynamic NMR Spectroscopy*, Academic Press, 1983.

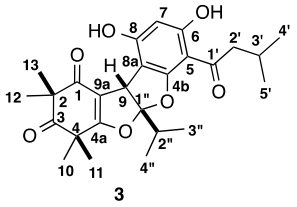
3. NMR Data Comparison for 2 and 3: Natural vs. Synthetic



2

	C ppm (mult)		H ppm (m, J Hz)	
C#	Natural **2**[a]	Synthetic **2**	Natural **2**[a]	Synthetic **2**
1	197.6 s	198.3		
2	56.1 s	56.1		
3	211.7 s	211.7		
4	47.2 s	47.2		
4a	166.9 s	167.2		
4b	153.3 s	153.0		
5	105.9 s	105.6		
6	159.0 s	159.5		
7	100.3 d	100.2	6.23 (s)	6.26 (s)
8	159.0 s	**164.2**[b]		
8a	105.9 s	105.9		
9	25.1 d	25.0	4.25 (t, 6.0)	4.3 (t, 6.06)
9a	114.5 s	114.5		
10	24.3 q	24.2	1.39 (s)	1.39 (s)
11	24.4 q	24.4	1.42 (s)	1.43 (s)
12	24.8 q	24.7	1.63 (s)	1.64 (s)
13	25.4 q	25.3	1.47 (s)	1.47 (s)
1'	204.0 s	203.9		
2'	53.6 t	53.4	3.18 (dd, 17.0, 6.5), 2.96 (dd, 17.0, 6.5)	3.18 (dd, 17.3, 7.4) 2.96 (dd, 17.3, 6.2)
3'	24.5 d	24.5	2.37 (m, 6.5)	2.36 (m, 6.57, 13.23)
4'	22.9 q	22.9	1.04 (d, 6.5)	1.02 (d, 6.64)
5'	22.6 q	22.6	1.01 (d, 6.5)	1.02 (d, 6.64)
1"	46.9 t	46.9	1.38 (obscure)	1.37 (m)
2"	24.9 d	24.7	1.38 (obscure)	1.37 (m)
3"	23.4 q	23.4	0.89 (d, 6.5)	0.87 (d, 6.37)
4"	23.1 q	23.1	0.87 (d, 6.5)	0.87 (d, 6.37)
6-OH			13.43 (s)	13.46 (s)
8-OH			6.40 (br s)	

[a] Hiranrat, A.; Mahabusarakam, W. *Tetrahedron* **2008**, *64*, 11193–11197, [b] Morkunas, M.; Dube, L.; Geotz, F.; Maier, M. E. *Tetrahedron* **2013**, *69*, 8559-8563. Hiranrat and Mahabusarakam report C-8 at 159.0 ppm. In our hands, the C-8 resonance was observed at 164.2 ppm, which is consistent with that reported by Maier and coworkers (164.3 ppm).



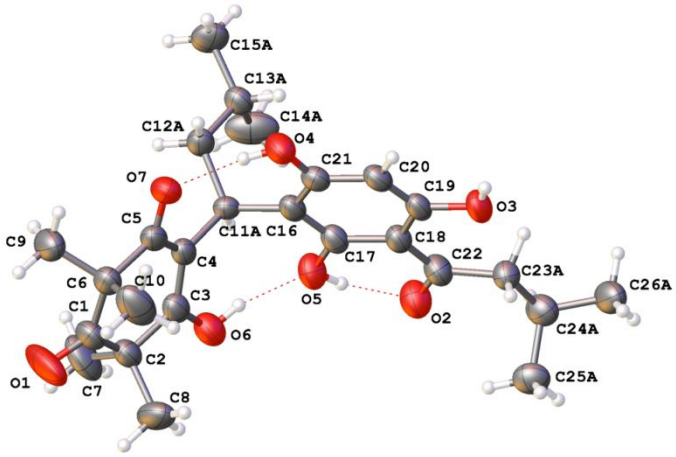
3

C#	^{13}C NMR(ppm)		^{1}H NMR (ppm, mult, J Hz)	
	Natural **3**[a]	Synthetic **3**	Natural **3**[a]	Synthetic **3**
1	198.3 s	198.4		
2	55.1 s	55.2		
3	211.1 s	211.3		
4	45.6 s	45.7		
4a	179.7 s	179.8		
4b	159.8 s	159.9		
5	101.7 s	101.8		
6	166.7 s	166.8		
7	99.6 d	99.7	6.11 (s)	6.11 (s)
8	159.6 s	159.8		
8a	104.2 s	104.3		
9	45.0 d	45.1	4.50 (s)	4.49 (s)
9a	113.2 s	113.3		
10	24.4 q	24.5	1.52 (s)	1.52 (s)
11	24.1 q	24.6	1.42 (s)	1.42 (s)
12	23.1 q	23.3	1.34 (s)	1.34 (s)
13	25.9 q	26.1	1.41 (s)	1.42 (s)
1′	203.7 s	203.8		
2′	51.5 t	51.7	2.96 (dd, 14.7, 6.6), 2.76 (dd, 14.7, 6.6)	2.96 (dd, 14.7, 6.6), 2.76 (dd, 14.7, 7.2)
3′	25.8 d	25.9	2.17 (m, 6.6)	2.17 (m, 6.6)
4′	22.8 q	22.9	1.01 (d, 6.6)	1.00 (d, 6.7)
5′	22.7 q	22.9	0.99 (d, 6.6)	1.00 (d, 6.7)
1″	129.4 s	129.5		
2″	35.4 d	35.5	2.40 (hept, 6.9)	2.40 (sept, 6.8)
3″	15.7 q	15.9	1.11 (d, 6.9)	1.11 (d, 6.8)
4″	15.6 q	15.8	1.09 (d, 6.9)	1.09 (d, 6.8)
6-OH			13.27 (s)	13.27 (s)
8-OH			9.78 (s)	9.79 (s)

[a] Hiranrat, A.; Mahabusarakam, W. *Tetrahedron* **2008**, *64*, 11193–11197.

4. X-Ray Crystallographic Data for Compound 5

X-Ray (ORTEP) for Compound 5[a]



[a] Ellipsoid contour percent probability level provided is 50% for the thermal ellipsoid plot above.

Crystals of compound **5** suitable for x-ray analysis were obtained by slow evaporation from a solution in hexanes with a couple drops of diethyl ether for solubility purposes. (Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 978312). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Table S1. Crystal Data for Compound 5

$C_{26}H_{36}O_7$	V = 2460.74 (11) Å^3
M_r = 460.55	Z = 4
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, λ = 1.54178 Å
a = 10.9488 (3) Å	μ = 0.73 mm^{-1}
b = 11.2504 (3) Å	T = 100 K
c = 20.0504 (5) Å	0.11 × 0.05 × 0.03 mm
β= 94.903 (2)°	

Table S2 . **Data Collection Parameters for Compound 5.**

Bruker Proteum-R diffractometer	9339 independent reflections
Absorption correction: multi-scan *SADABS* (Sheldrick, 1997)	6243 reflections with $I > 2\sigma(I)$
T_{min} = 0.773, T_{max} = 0.864	R_{int} = 0.052
9339 measured reflections	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table S3. Refinement Data for 5.

$R[F^2 > 2\sigma(F^2)]$ = 0.067	144 restraints
$wR(F^2)$ = 0.222	H-atom parameters constrained
S = 1.06	$\Delta\rangle_{max}$ = 0.45 e Å^{-3}
9339 reflections	$\Delta\rangle_{min}$ = -0.32 e Å^{-3}
392 parameters	

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Table S4. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Displacement Parameters (Å^2).

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	-0.22465 (18)	0.7186 (2)	0.56403 (9)	0.1130 (8)
O2	0.48108 (13)	1.04885 (13)	0.43100 (7)	0.0654 (4)
O3	0.29875 (13)	1.15970 (11)	0.25116 (7)	0.0552 (4)
H3	0.2503	1.1740	0.2173	0.083*
O4	0.01721 (14)	0.84770 (14)	0.25940 (7)	0.0630 (4)
H4	-0.0130	0.8012	0.2864	0.094*
O5	0.33160 (12)	0.89024 (12)	0.43663 (7)	0.0558 (3)
H5	0.3967	0.9289	0.4453	0.084*
O6	0.17386 (13)	0.82016 (13)	0.52131 (7)	0.0597 (4)
H6	0.2192	0.8322	0.4903	0.090*
O7	-0.11577 (13)	0.72908 (12)	0.34317 (7)	0.0587 (4)
C1	-0.1517 (2)	0.74213 (19)	0.52386 (11)	0.0637 (6)
C2	-0.0227 (2)	0.77330 (17)	0.54965 (10)	0.0562 (5)
C3	0.06408 (18)	0.78369 (15)	0.49556 (10)	0.0498 (5)
C4	0.03846 (18)	0.75459 (14)	0.42988 (9)	0.0470 (4)
C11A	0.1489 (5)	0.7450 (5)	0.3874 (3)	0.0405 (12)
H11A	0.2216	0.7328	0.4204	0.049*
C12A	0.1450 (3)	0.6332 (2)	0.34159 (15)	0.0504 (8)
H12A	0.1305	0.5622	0.3690	0.060*

H12B	0.0749	0.6407	0.3072	0.060*
C13A	0.2622 (4)	0.6142 (5)	0.3065 (2)	0.0503 (10)
H13A	0.2686	0.6829	0.2753	0.060*
C14A	0.3768 (4)	0.6153 (5)	0.3533 (2)	0.0902 (16)
H14A	0.3950	0.6969	0.3681	0.135*
H14B	0.4453	0.5842	0.3301	0.135*
H14C	0.3649	0.5654	0.3923	0.135*
C15A	0.2504 (3)	0.5027 (3)	0.26301 (19)	0.0686 (10)
H15A	0.2380	0.4333	0.2913	0.103*
H15B	0.3254	0.4919	0.2403	0.103*
H15C	0.1802	0.5111	0.2296	0.103*
C16	0.17694 (17)	0.85893 (15)	0.34956 (9)	0.0456 (4)
C17	0.27683 (16)	0.92545 (15)	0.37608 (9)	0.0458 (4)
C18	0.32439 (17)	1.02671 (15)	0.34432 (9)	0.0460 (4)
C22	0.4341 (2)	1.08423 (19)	0.37550 (10)	0.0597 (5)
C23A	0.4748 (4)	1.2016 (4)	0.34409 (18)	0.0489 (10)
H23A	0.4928	1.1865	0.2973	0.059*
H23B	0.4066	1.2595	0.3432	0.059*
C24A	0.5865 (4)	1.2547 (3)	0.38194 (19)	0.0601 (12)
H24A	0.6478	1.1902	0.3928	0.072*
C25A	0.5562 (9)	1.3140 (8)	0.4467 (4)	0.0631 (19)
H25A	0.4914	1.3731	0.4369	0.095*
H25B	0.6296	1.3532	0.4677	0.095*
H25C	0.5280	1.2538	0.4773	0.095*
C26A	0.6430 (5)	1.3473 (4)	0.3376 (3)	0.0776 (15)
H26A	0.6656	1.3091	0.2965	0.116*
H26B	0.7163	1.3815	0.3618	0.116*
H26C	0.5833	1.4105	0.3262	0.116*
C6	-0.19282 (19)	0.73947 (16)	0.44964 (10)	0.0543 (5)
C10	-0.2691 (3)	0.8511 (2)	0.43350 (15)	0.0892 (9)

H10A	-0.3384	0.8530	0.4614	0.134*
H10B	-0.2999	0.8502	0.3862	0.134*
H10C	-0.2179	0.9217	0.4426	0.134*
C9	-0.2698 (2)	0.6278 (2)	0.43530 (13)	0.0790 (7)
H9A	-0.2178	0.5573	0.4424	0.119*
H9B	-0.3056	0.6295	0.3888	0.119*
H9C	-0.3356	0.6250	0.4655	0.119*
C5	-0.08718 (19)	0.73932 (15)	0.40452 (10)	0.0509 (5)
C19	0.25960 (18)	1.06197 (15)	0.28317 (9)	0.0471 (4)
C20	0.15812 (18)	1.00107 (16)	0.25719 (9)	0.0484 (4)
H20	0.1154	1.0271	0.2166	0.058*
C21	0.11676 (17)	0.90090 (16)	0.28987 (9)	0.0482 (4)
C8	-0.0251 (3)	0.8900 (2)	0.58873 (14)	0.0875 (8)
H8A	0.0579	0.9092	0.6079	0.131*
H8B	-0.0794	0.8815	0.6249	0.131*
H8C	-0.0554	0.9540	0.5585	0.131*
C7	0.0269 (3)	0.6717 (3)	0.59697 (14)	0.0957 (9)
H7A	0.0296	0.5975	0.5715	0.144*
H7B	-0.0273	0.6617	0.6330	0.144*
H7C	0.1096	0.6919	0.6162	0.144*
C11B	0.1201 (12)	0.7385 (12)	0.3707 (7)	0.048 (4)
H11B	0.0677	0.7066	0.3315	0.057*
C12B	0.2207 (9)	0.6462 (6)	0.3908 (5)	0.078 (3)
H12C	0.1821	0.5720	0.4051	0.093*
H12D	0.2744	0.6769	0.4292	0.093*
C13B	0.3001 (15)	0.6184 (14)	0.3315 (8)	0.094 (5)
H13B	0.3438	0.6932	0.3208	0.113*
C14B	0.2264 (12)	0.5783 (13)	0.2682 (8)	0.114 (4)
H14D	0.1747	0.5107	0.2784	0.170*
H14E	0.2822	0.5544	0.2350	0.170*
H14F	0.1746	0.6439	0.2503	0.170*

C15B	0.3887 (16)	0.5367 (12)	0.3572 (10)	0.150 (6)
H15D	0.4592	0.5797	0.3788	0.224*
H15E	0.4152	0.4878	0.3207	0.224*
H15F	0.3534	0.4856	0.3902	0.224*
C23B	0.5277 (6)	1.1576 (5)	0.3422 (3)	0.0531 (15)
H23C	0.6114	1.1374	0.3614	0.064*
H23D	0.5222	1.1406	0.2936	0.064*
C24B	0.5019 (5)	1.2878 (5)	0.3538 (2)	0.0523 (16)
H24B	0.4118	1.3013	0.3444	0.063*
C25B	0.5684 (7)	1.3606 (5)	0.3037 (4)	0.0697 (19)
H25D	0.6553	1.3385	0.3070	0.105*
H25E	0.5608	1.4454	0.3137	0.105*
H25F	0.5319	1.3447	0.2582	0.105*
C26B	0.5391 (15)	1.3261 (14)	0.4264 (5)	0.071 (4)
H26D	0.6270	1.3118	0.4369	0.107*
H26E	0.4925	1.2798	0.4569	0.107*
H26F	0.5216	1.4108	0.4315	0.107*