Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Total synthesis and confirmation of the revised structures of Jiangrines A, C and D

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Table S1. Comparison of ^{1}H NMR data for natural jiangrine A with those of synthetic 1

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	9.66, s	9.77, s	+0.11
2	--	--	--
3	--	--	--
4	6.13, d (2.4)	6.23, d (2.4)	+0.10
5	6.74, d (2.4)	6.84, d (2.4)	+0.10
6	4.90, d (6.6)	5.00, d (6.4)	+0.10
7	3.67, m	3.76, td (6.4, 4.0)	+0.09
8a	3.57,dd (11.1, 4.1)	3.67, dd (11.2, 4.0)	+0.10
8b	3.50,dd (11.1, 6.0)	3.61, dd (11.2, 6.4)	+0.11
1’	--	--	--
2’, 6’	6.82, d (8.4)	6.93, d (8.8)	+0.11
3’, 5’	6.56, d (8.4)	6.66, d (8.4)	+0.10
4’	--	--	--
7’	2.80, t (7.2)	2.89, t (7.2)	+0.09
8’	4.33, t (7.2)	4.44, t (7.2)	+0.11

$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample

Table S2. Comparison of ^{13}C NMR data for natural jiangrine A with those of synthetic 1

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	181.2	181.2	0.0
2	141.1	141.1	0.0
3	128.8	128.8	0.0
4	109.7	109.7	0.0
5	132.4	132.5	+0.1
6	69.4	69.4	0.0
7	76.4	76.4	0.0
8	64.5	64.5	0.0
1’	130.4	130.4	0.0
2’, 6’	130.9	130.9	0.0
3’, 5’	116.2	116.2	0.0
4’	157.4	157.1	-0.3
7’	38.1	38.1	0.0
8’	52.4	52.4	0.0

$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample

Table S3. Comparison of ^{1}H NMR data for natural jiangrine C with those of synthetic 2

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	9.75, s	9.76, d (0.6)	+0.01
2	--	--	--
3	--	--	--
4	6.10, d (1.8)	6.11 d (2.4)	+0.01
5	6.81, d (1.8)	6.82, d (2.4)	+0.01
6	4.60, d (6.7)	4.60, d (6.8)	0.00
7	3.71, q (5.4)	3.72, td (6.0, 4.0)	+0.01
8a	3.51, dd (11.4, 3.6)	3.52, dd (11.2, 4.0)	+0.01
8b	3.32, m	3.34, m	+0.02
1’	--	--	--
2’, 6’	6.87, d (7.8)	6.88, d (8.4)	+0.01
3’, 5’	6.63, d (7.8)	6.64, d (8.8)	+0.01
4’	--	--	--
7’	2.89, t (7.2)	2.90, t (7.2)	+0.01
8’	4.54, t (7.2)[1]	4.47, t (7.0)	+0.02
6-OCH_3	3.26, s	3.27, s	+0.01

$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample. [1]: The original data of the chemical shift was not read correctly, which didn’t match the original 1H NMR spectrum of natural sample. The correct chemical shift should be 4.45.

Table S4. Comparison of ^{13}C NMR data for natural jiangrine C with those of synthetic 2

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	180.9	180.9	0.0
2	137.7	137.6	-0.1
3	129.5	129.4	-0.1
4	110.0	110.0	0.0
5	132.9	132.9	0.0
6	79.0	79.0	0.0
7	76.9	76.9	0.0
8	63.9	63.9	0.0
1’	130.3	130.2	-0.1
2’, 6’	130.9	130.9	0.0
3’, 5’	116.2	116.2	0.0
4’	157.1	157.1	0.0
7’	37.9	37.9	0.0
8’	52.4	52.4	0.0
6-OCH_3	57.1	57.1	0.0

$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample

Table S5. Comparison of ^{1}H NMR data for natural jiangrine D with those of synthetic 3

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	9.73, s	9.74, d (0.6)	+0.01
2	--	--	--
3	--	--	--
4	6.13, d (2.4)	6.14 d (2.4)	+0.01
5	6.83, d (2.4)	6.84, d (2.4)	+0.01
6	4.61, d (5.8)	4.62, d (5.8)	+0.01
7	3.79, q (5.4)	3.80, td (6.0, 4.4)	+0.01
8a	3.59, dd (10.8, 4.2)	3.60, dd (11.2, 4.4)	+0.01
8b	3.55, dd (10.8, 5.4)	3.55, dd (11.2, 6.4)	0.00
1’	--	--	--
2’, 6’	6.89, d (8.4)	6.90, d (8.4)	+0.01
3’, 5’	6.64, d (8.4)	6.65, d (8.4)	+0.01
4’	--	--	--
7’	2.89, t (7.2)	2.90, t (7.2)	+0.01
8’	4.54, t (7.2) [1]	4.46, t (7.2)	+0.01
6-OCH_3	3.26, s	3.27, s	+0.01

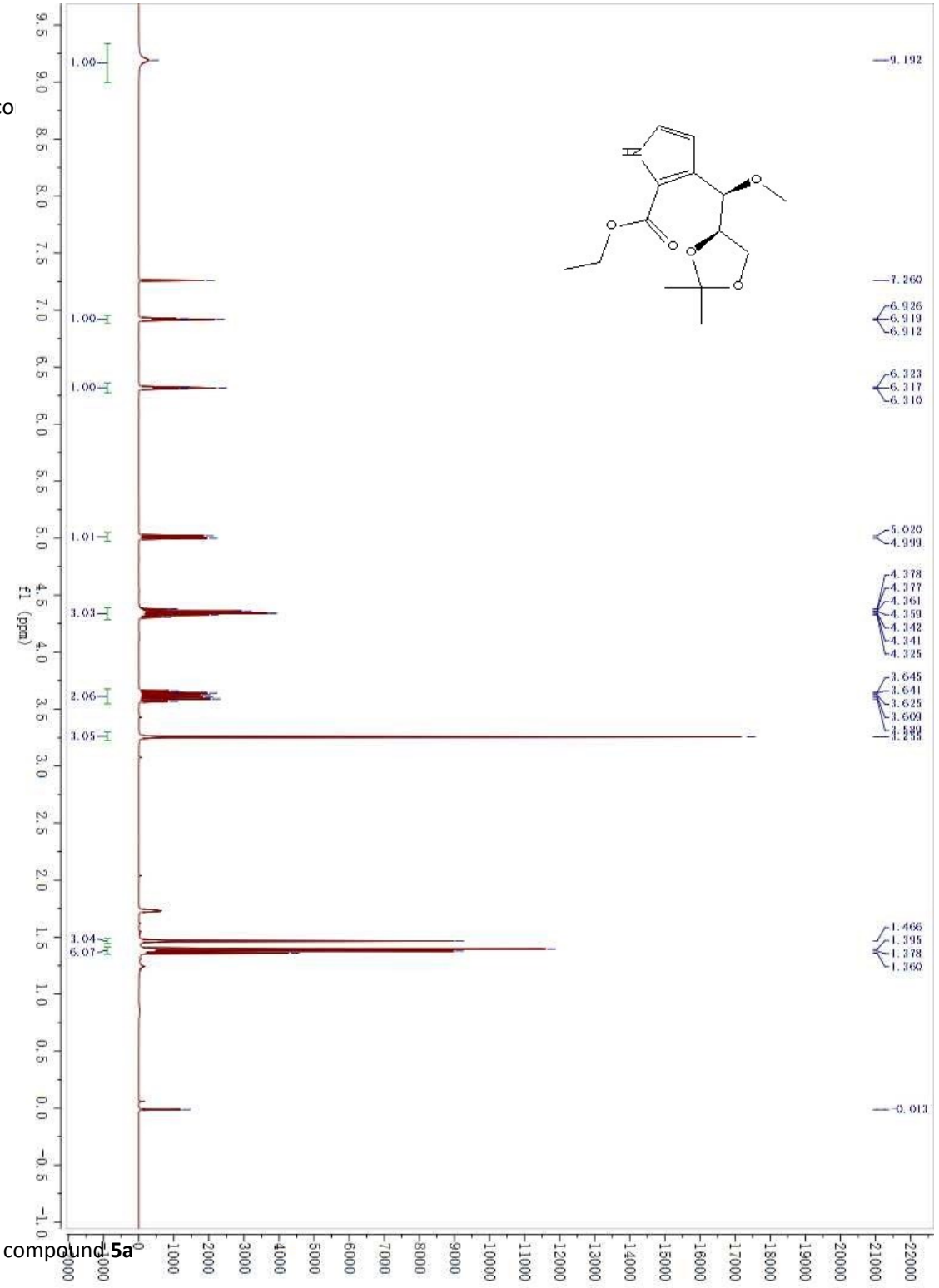
$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample. [1]: The original data of the chemical shift was not read correctly, which didn’t match the original ^{1}H NMR spectrum of natural sample. The correct chemical shift should be 4.45.

Table S6. Comparison of ^{13}C NMR data for natural jiangrine D with those of synthetic 3

position	natural (600 MHz, CD_3OD)	Synthetic (400 MHz, CD_3OD)	$\Delta\ \delta$ (ppm)
1	181.3	181.3	0.0
2	137.7	137.7	-0.1
3	129.9	130.0	+0.1
4	110.3	110.3	0.0
5	132.7	132.7	0.0
6	79.1	79.1	0.0
7	75.7	75.7	0.0
8	64.2	64.2	0.0
1’	130.2	130.3	+0.1
2’, 6’	130.9	130.9	0.0
3’, 5’	116.2	116.2	0.0
4’	157.1	157.1	0.0
7’	38.0	37.9	-0.1
8’	52.4	52.4	0.0
6-OCH_3	57.1	57.1	0.0

$\Delta\ \delta$ = the chemical shift of synthetic sample minus the chemical shift of natural sample

^{1}HNMR spectra of co



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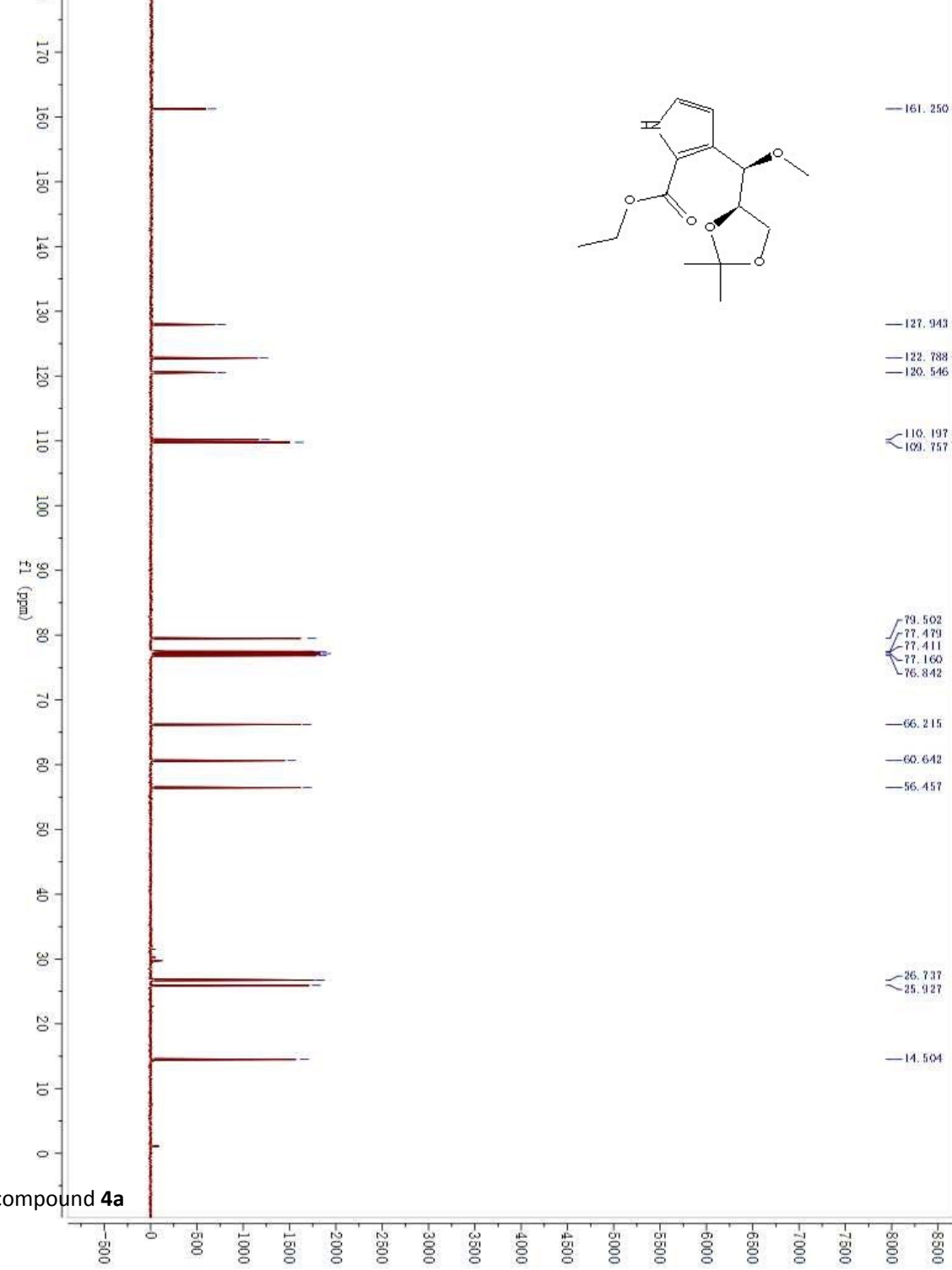

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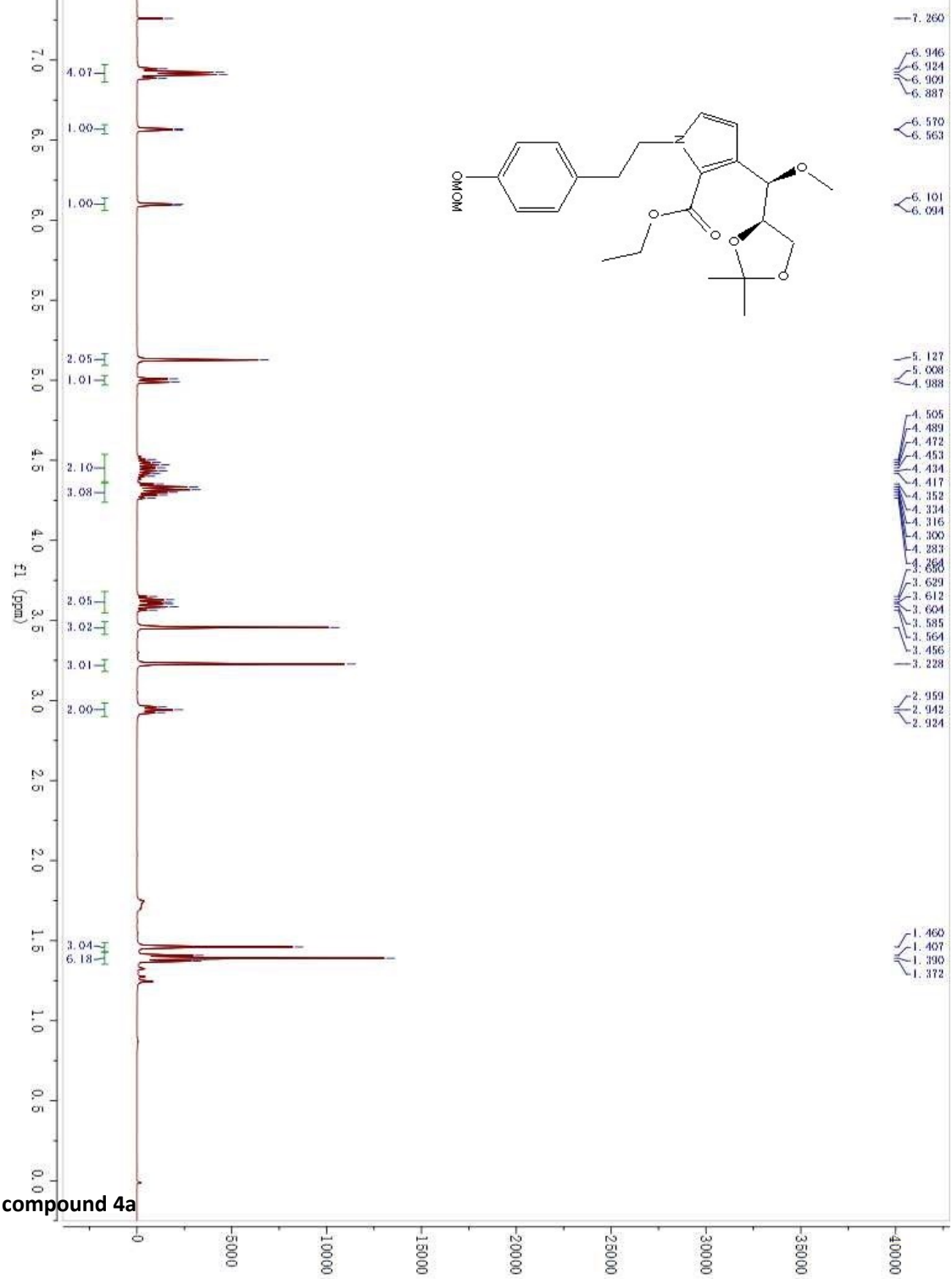

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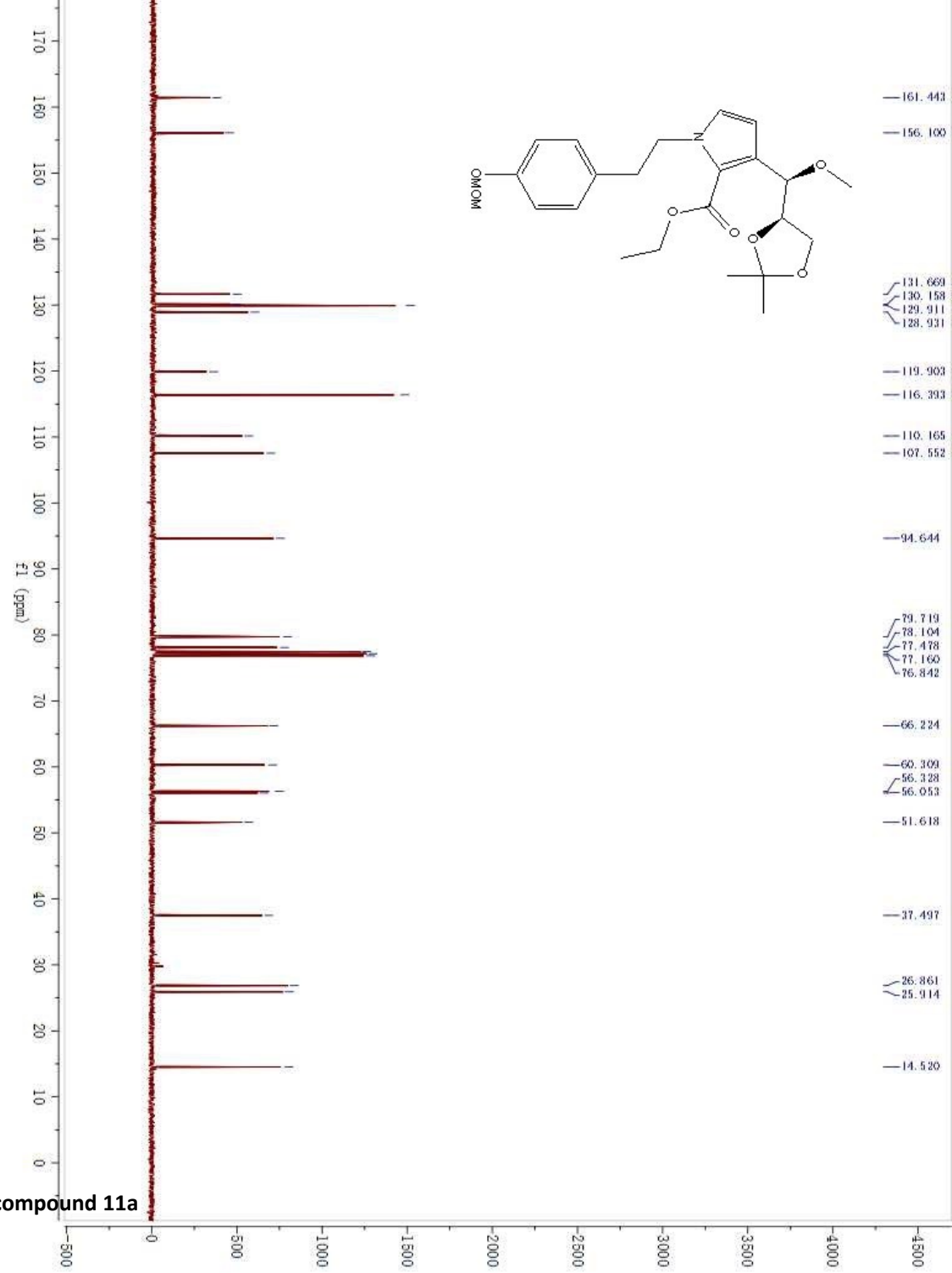

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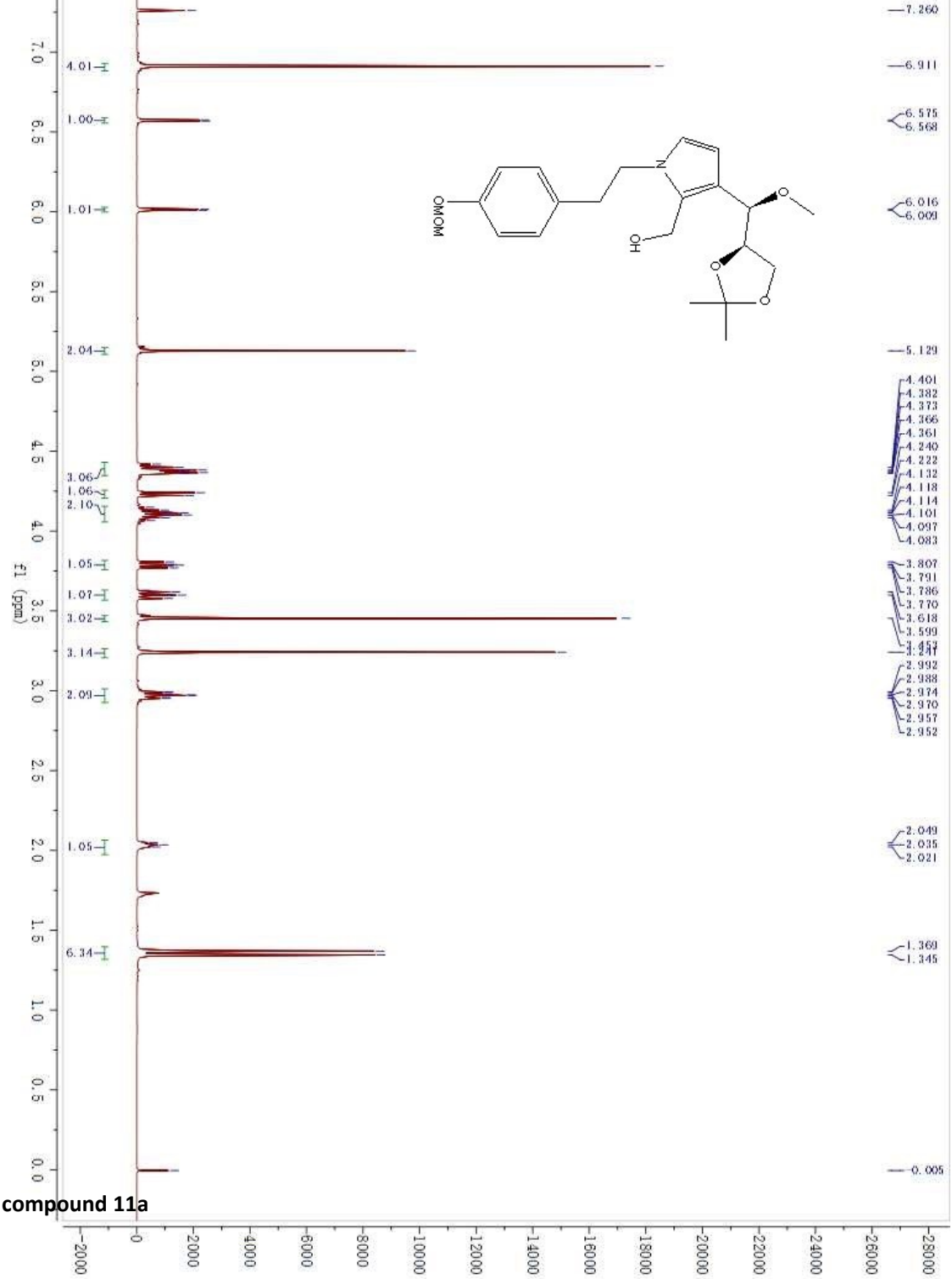

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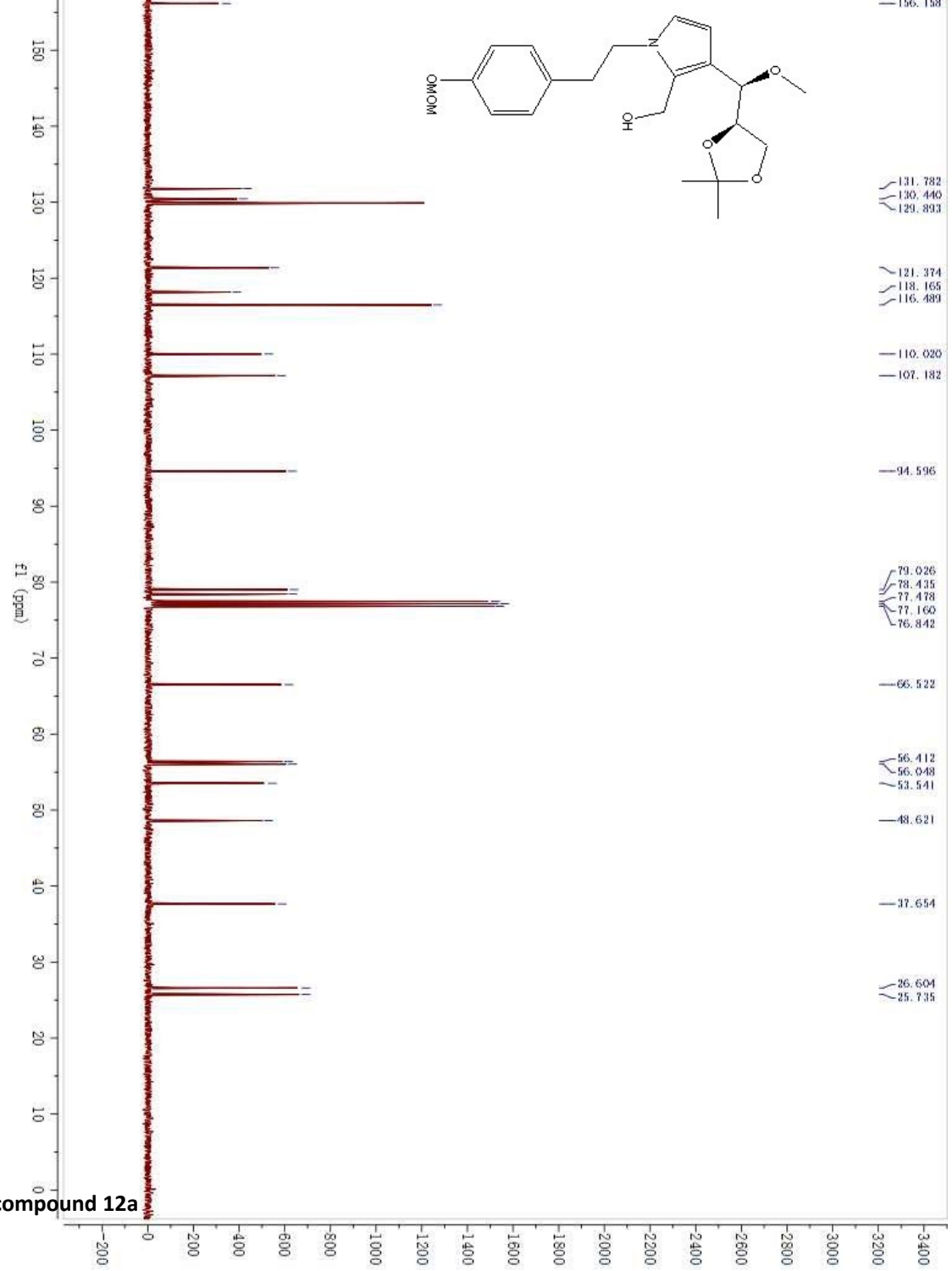

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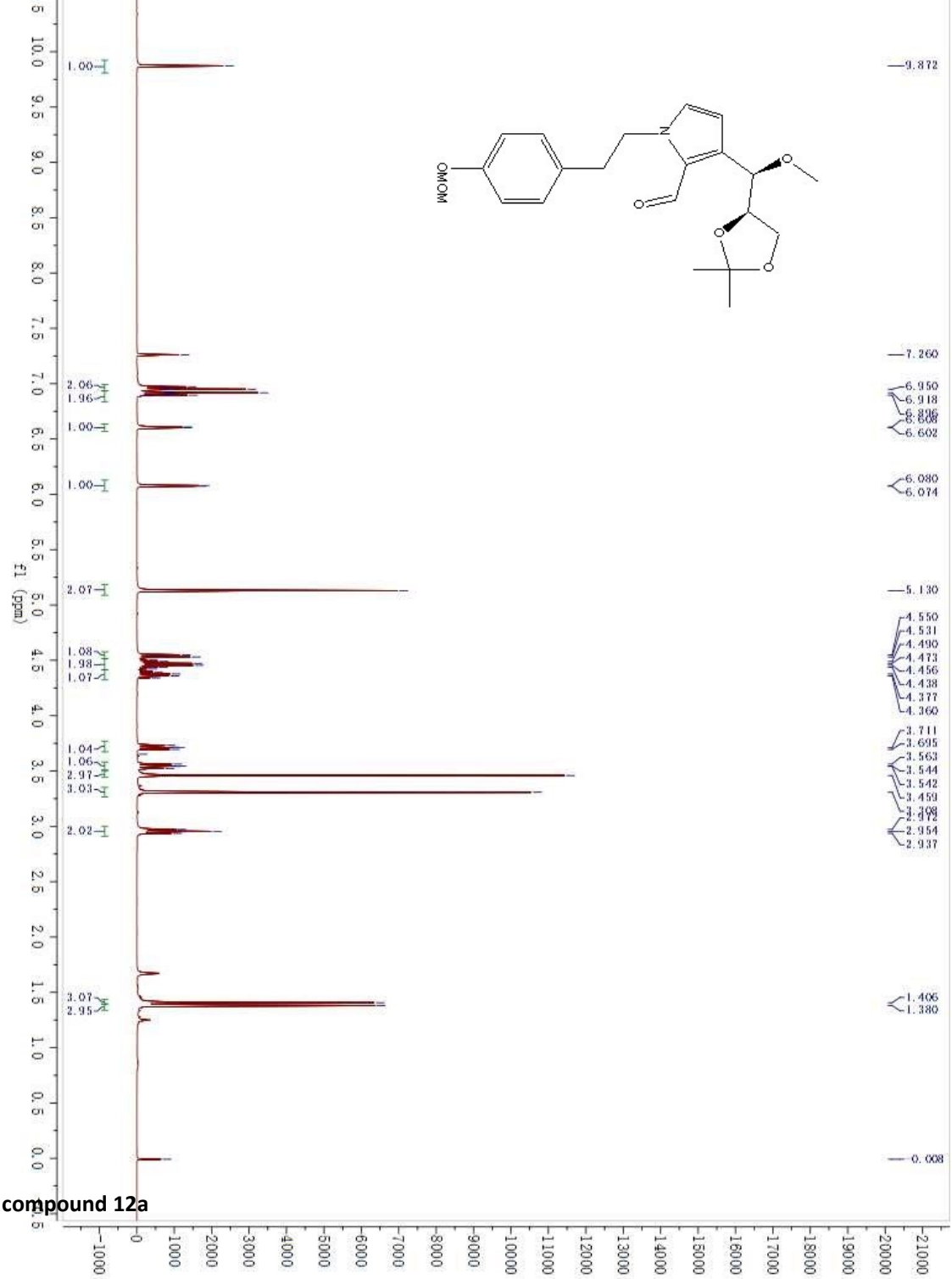

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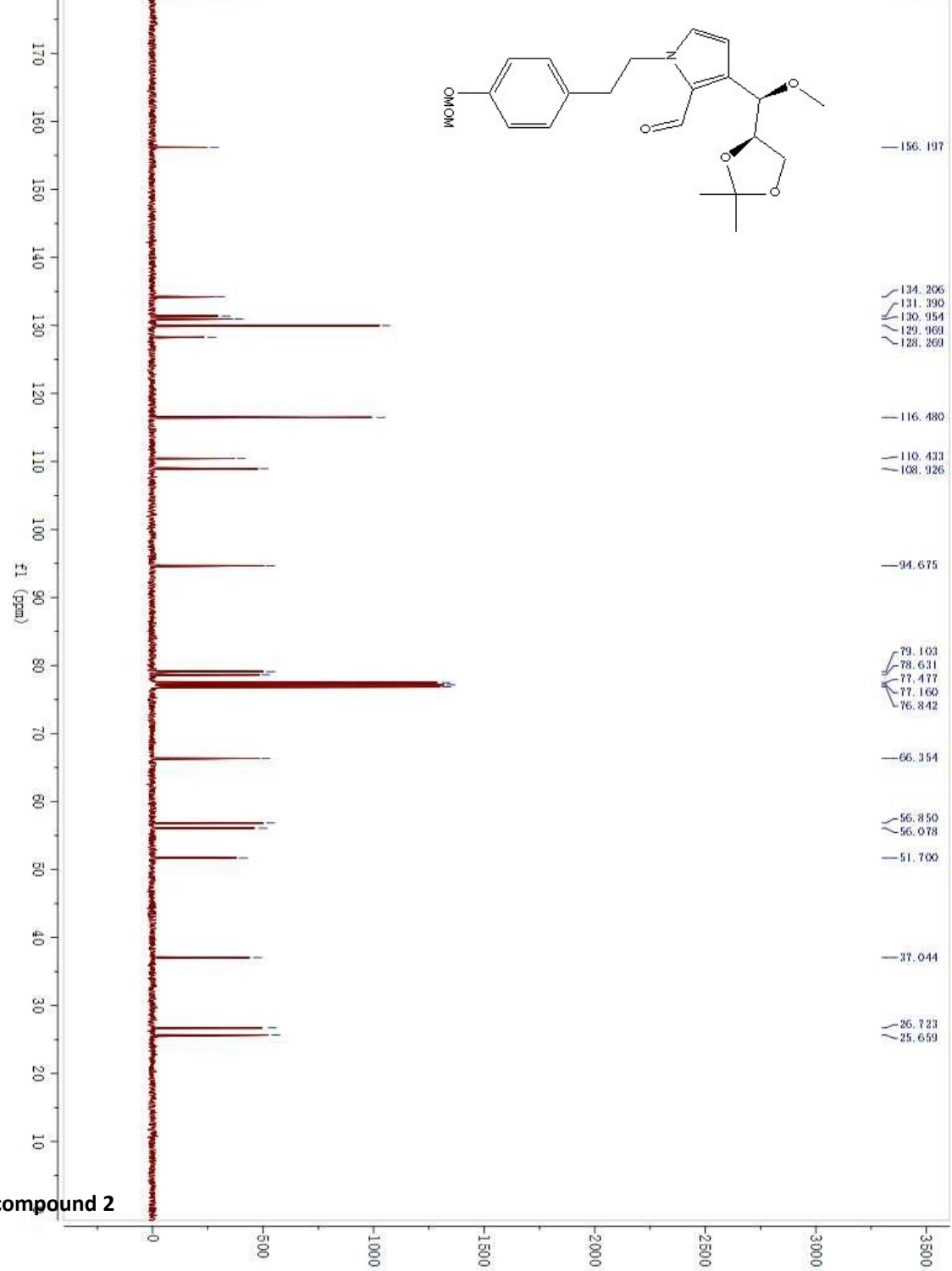

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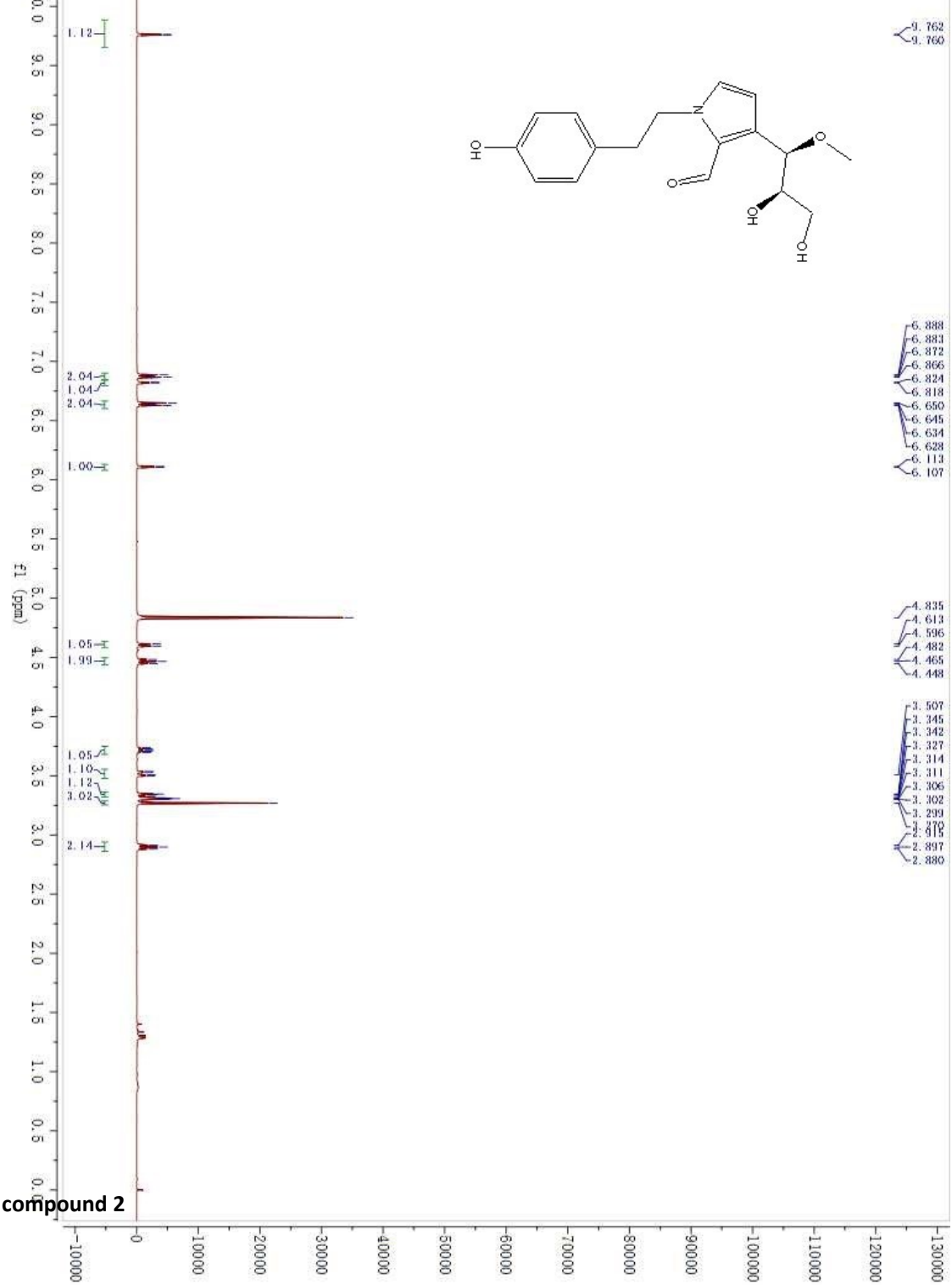

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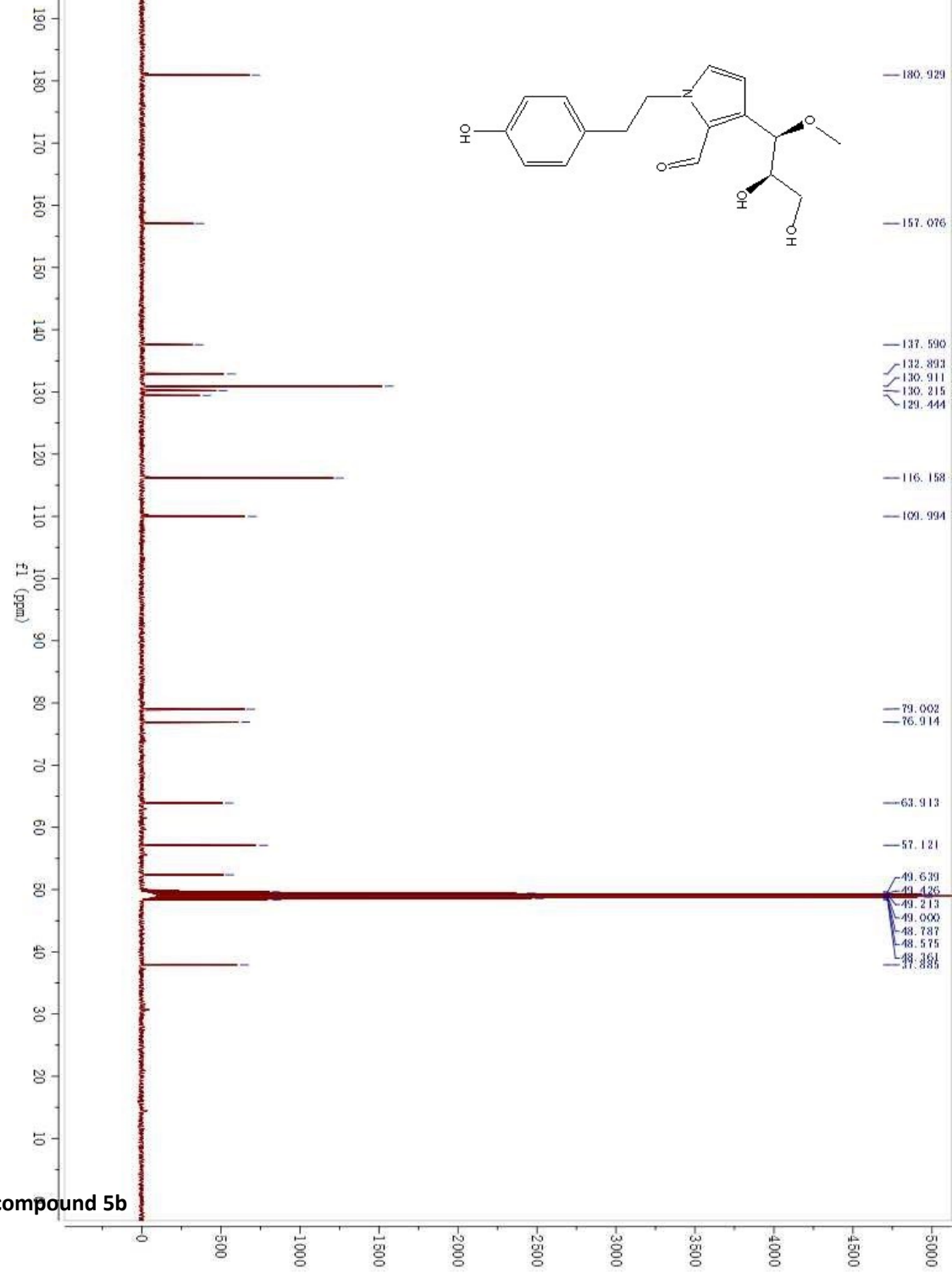

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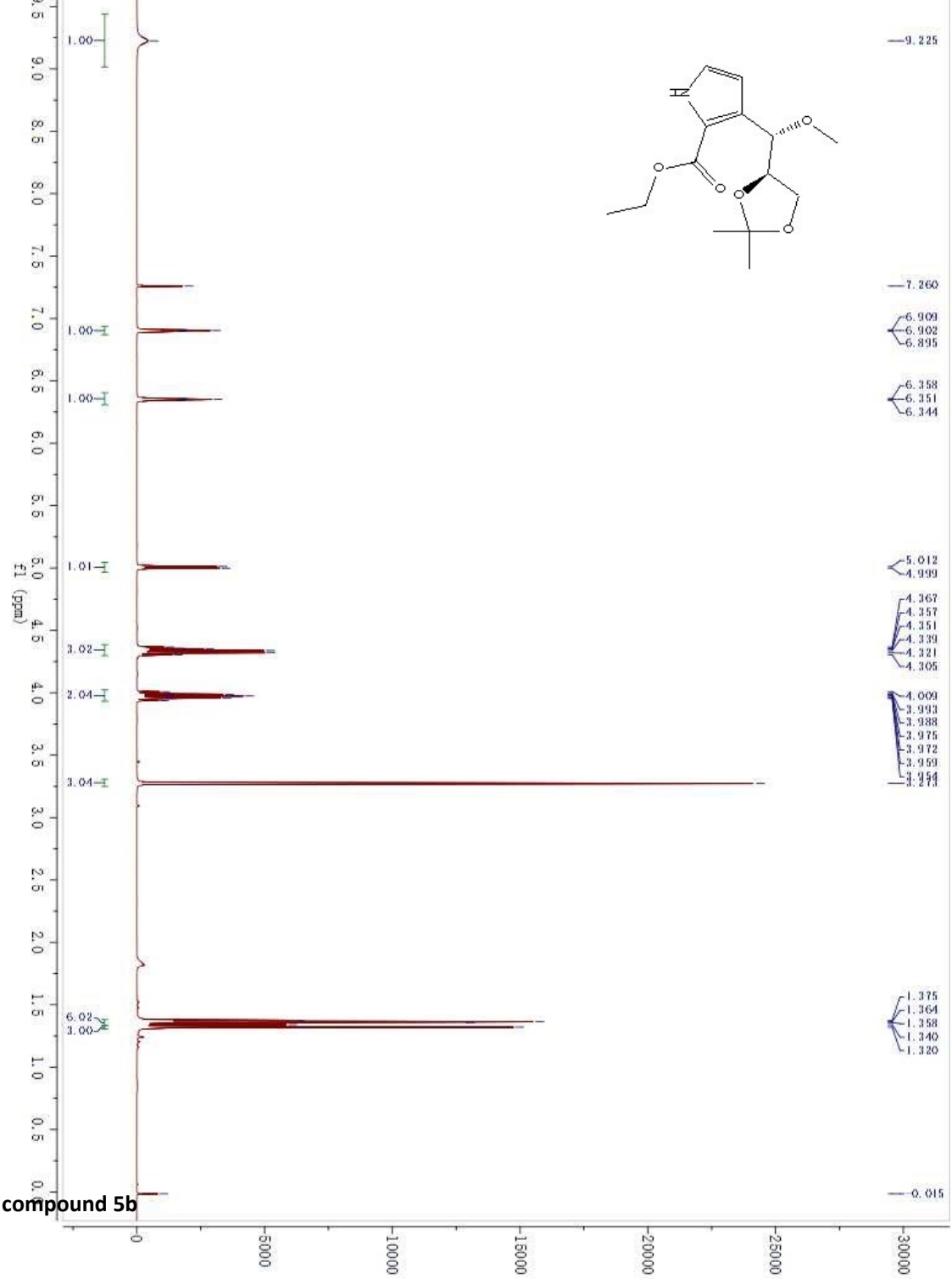

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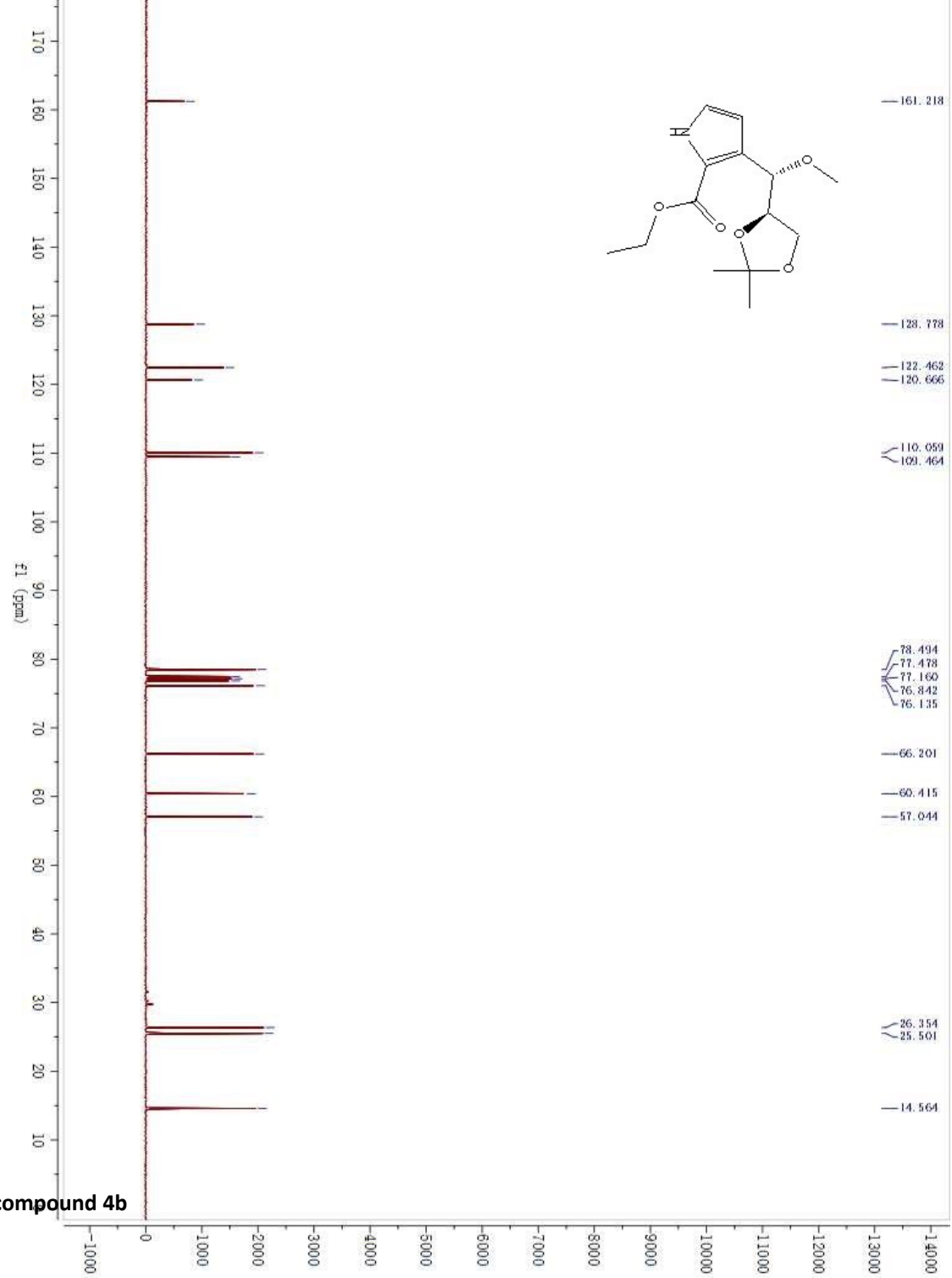

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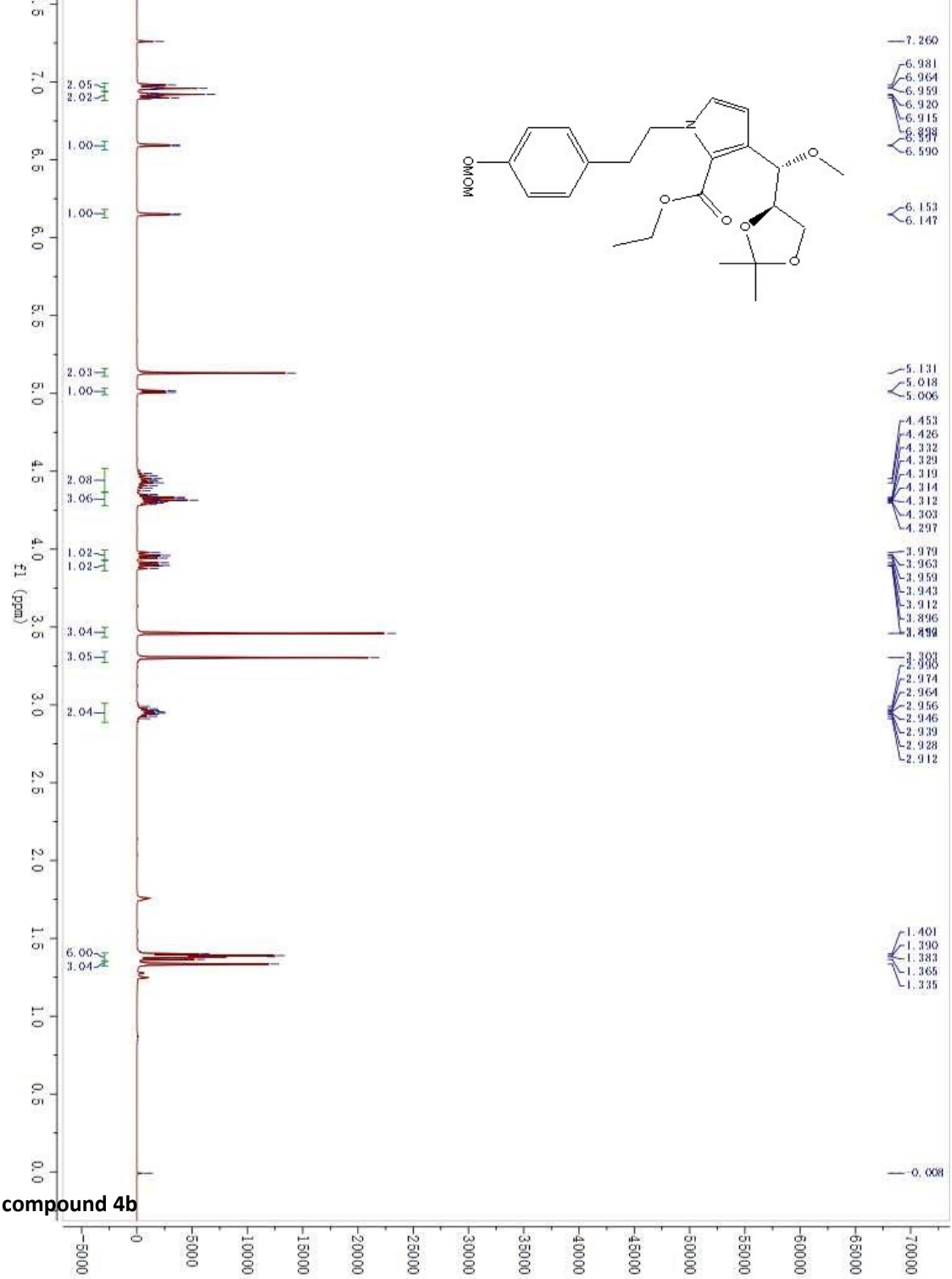

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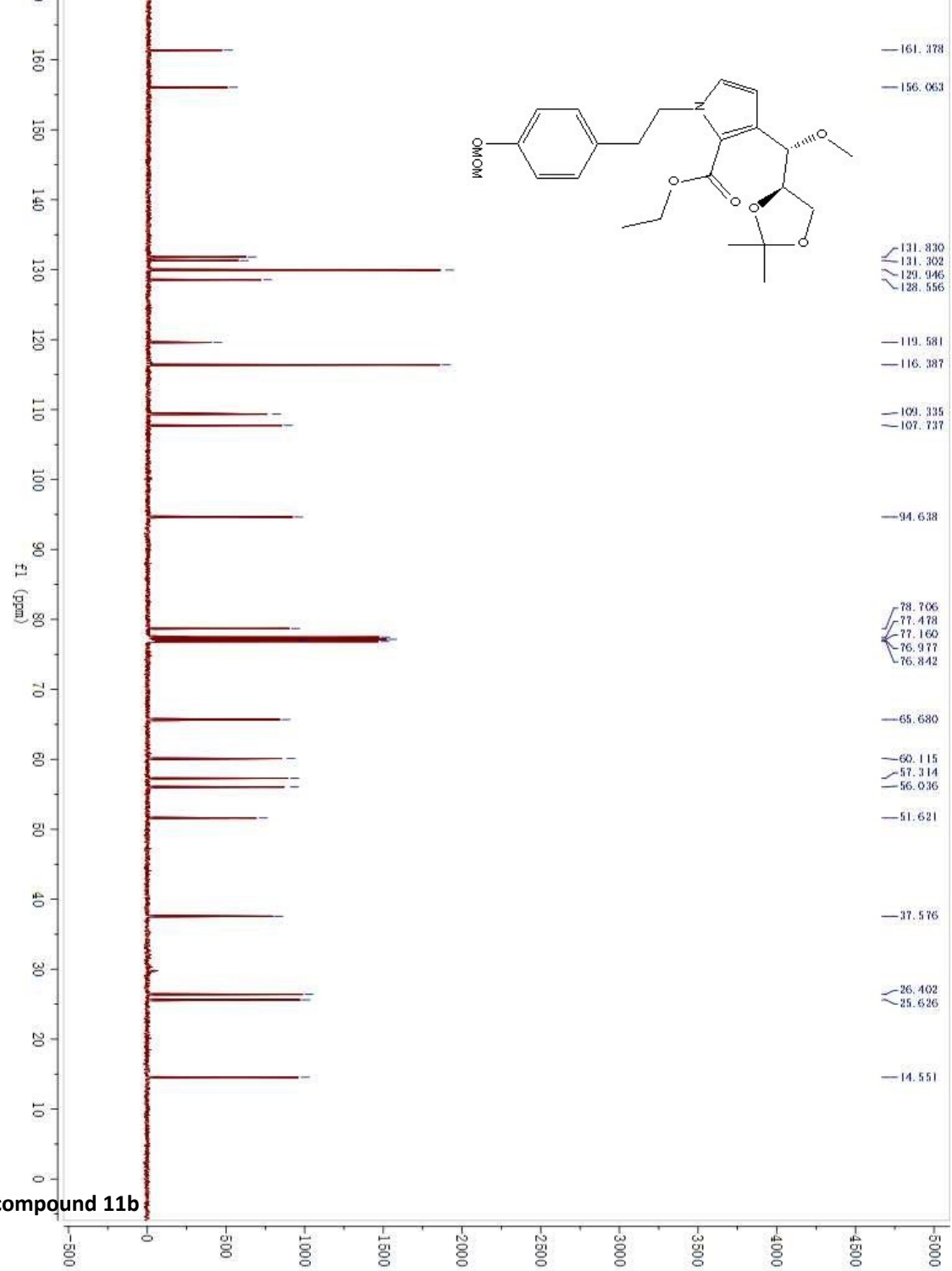

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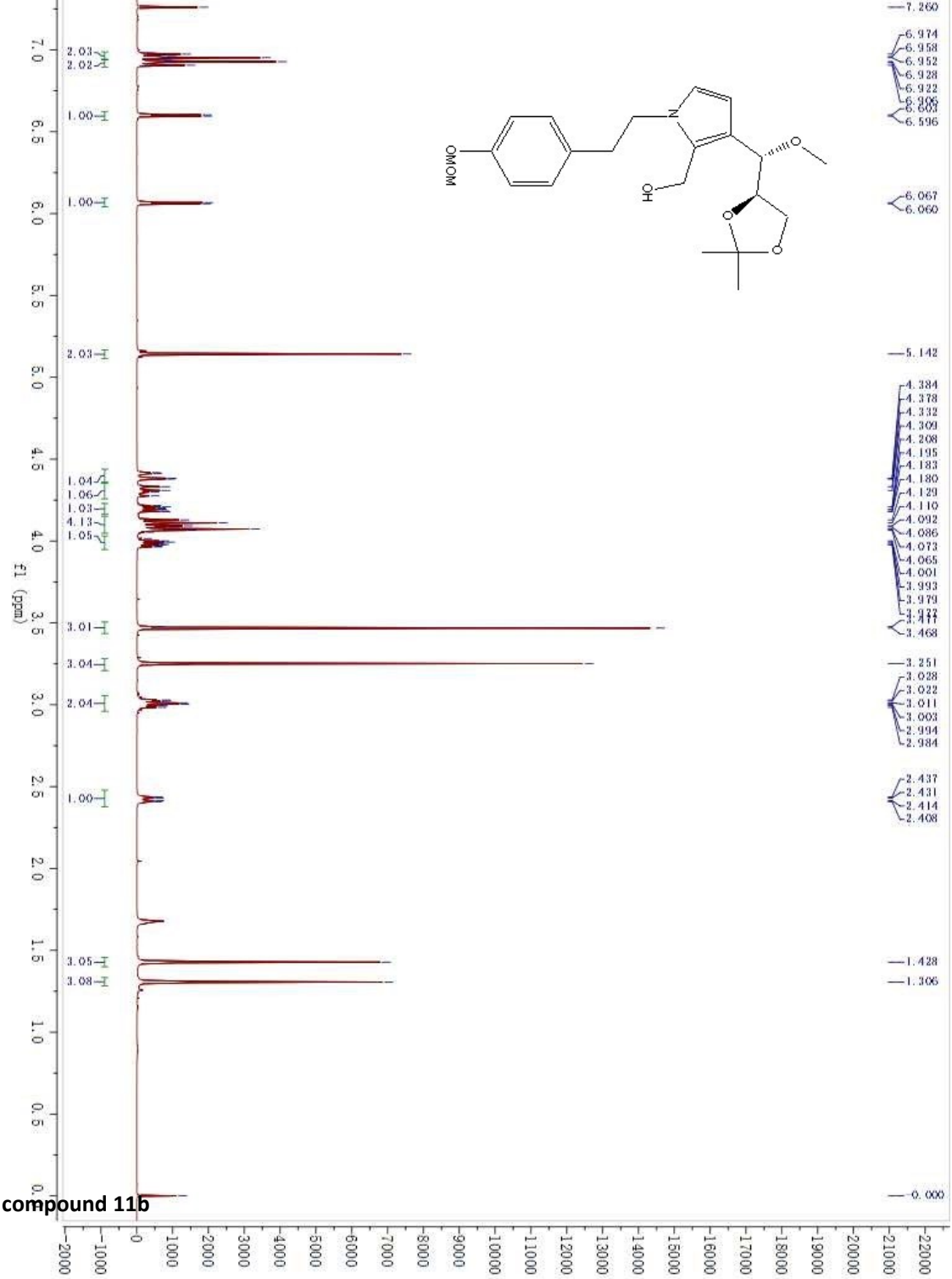

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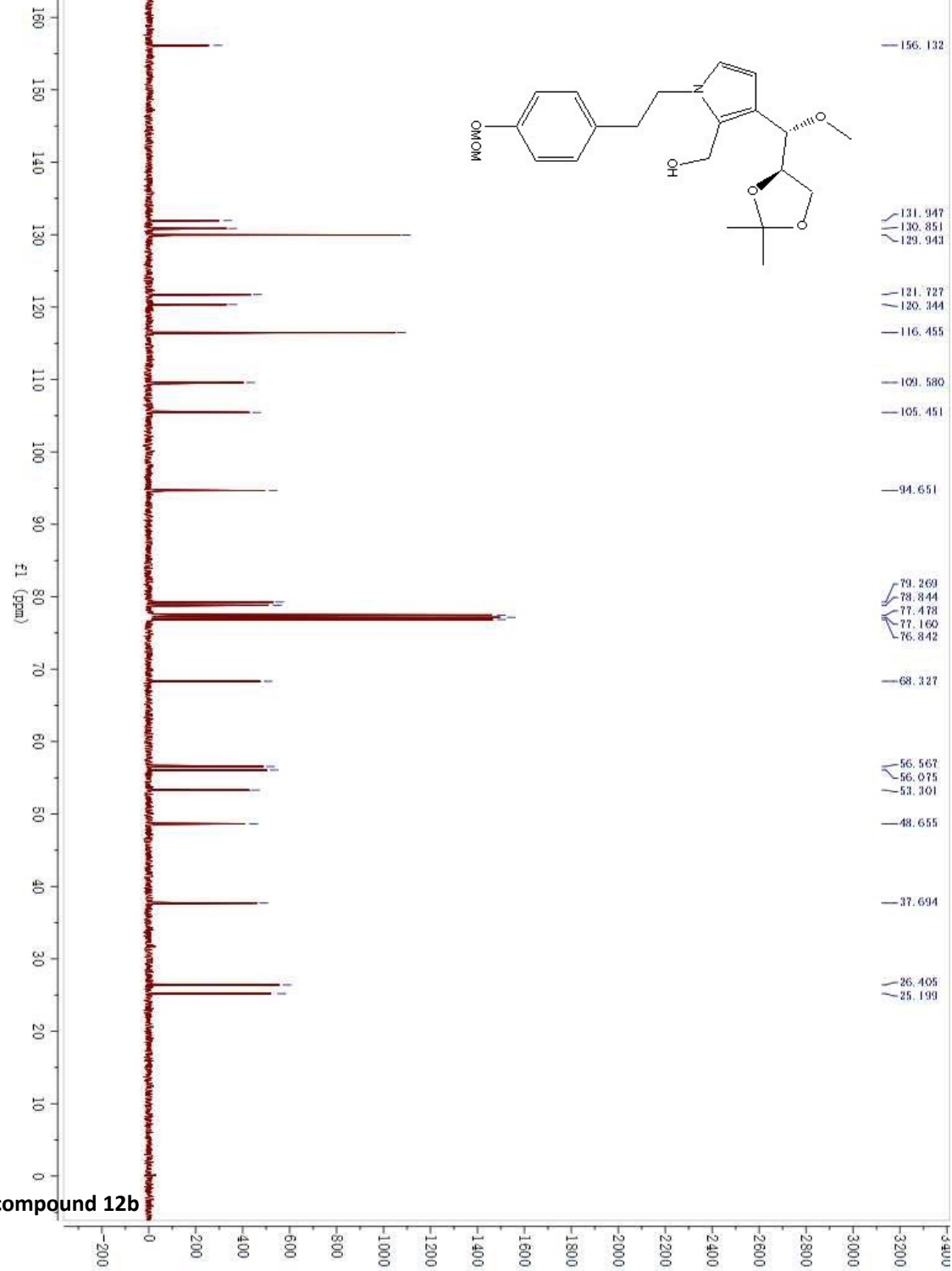

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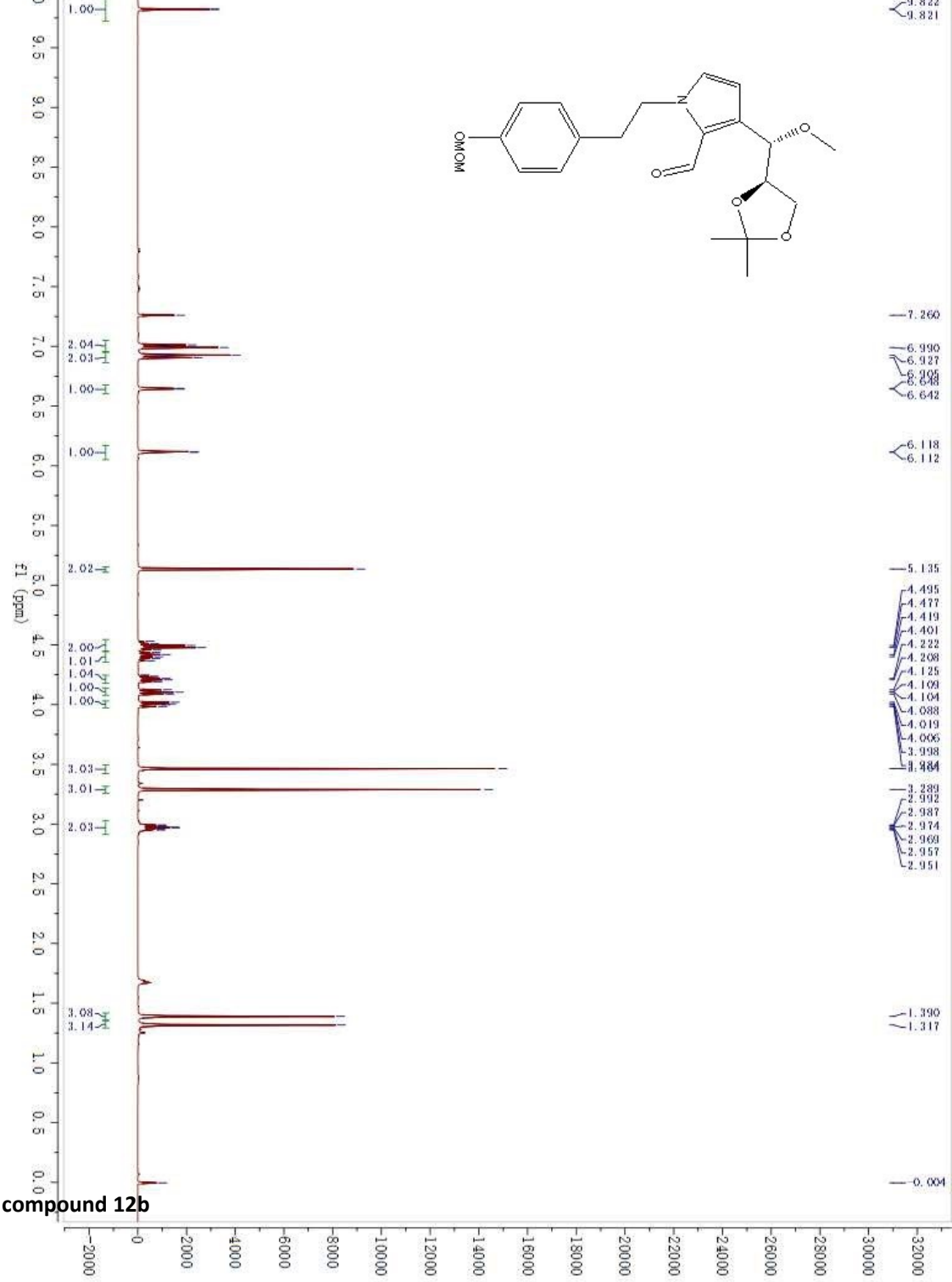
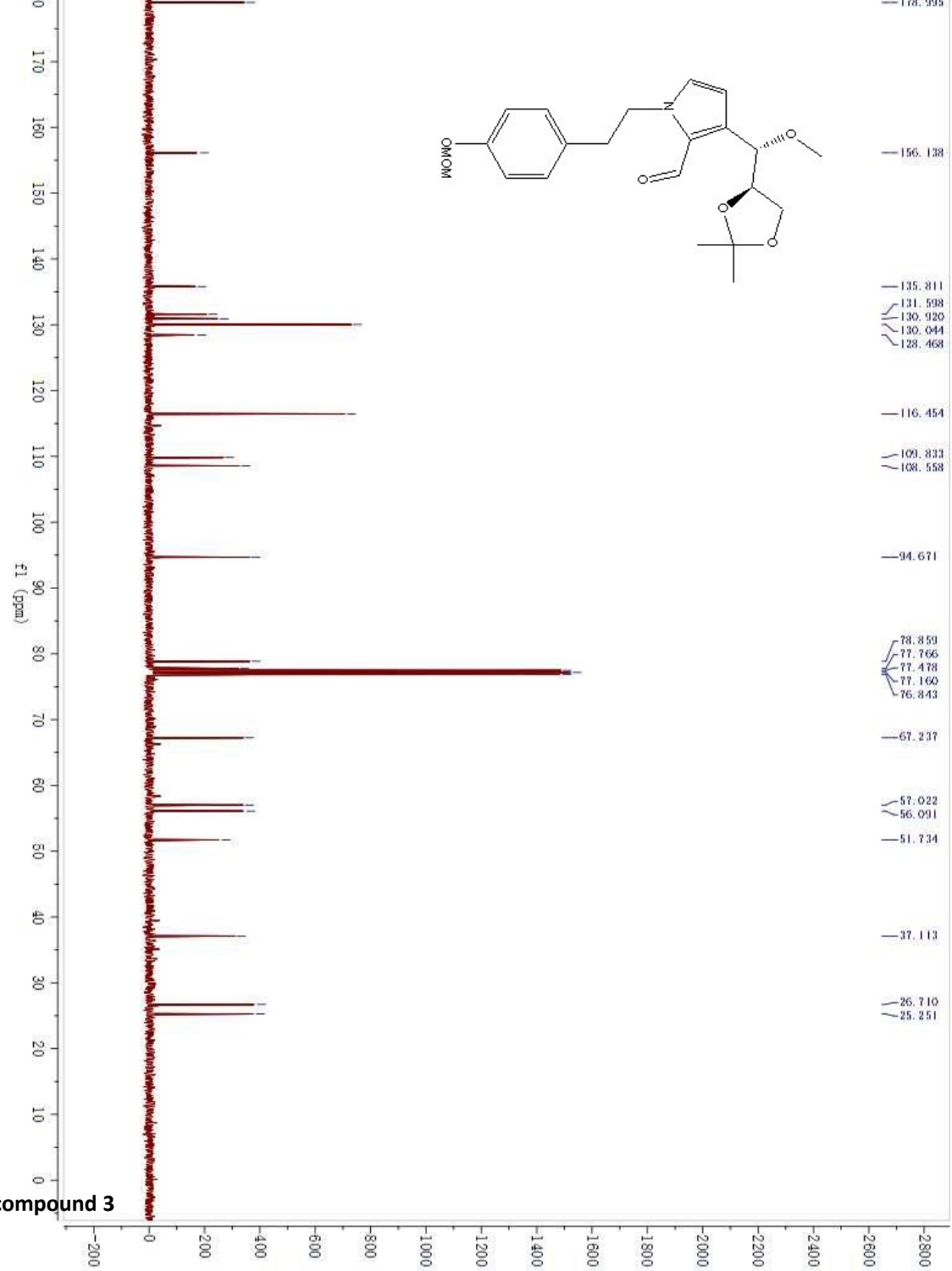


^{13}C NMR spectra of compound 12b



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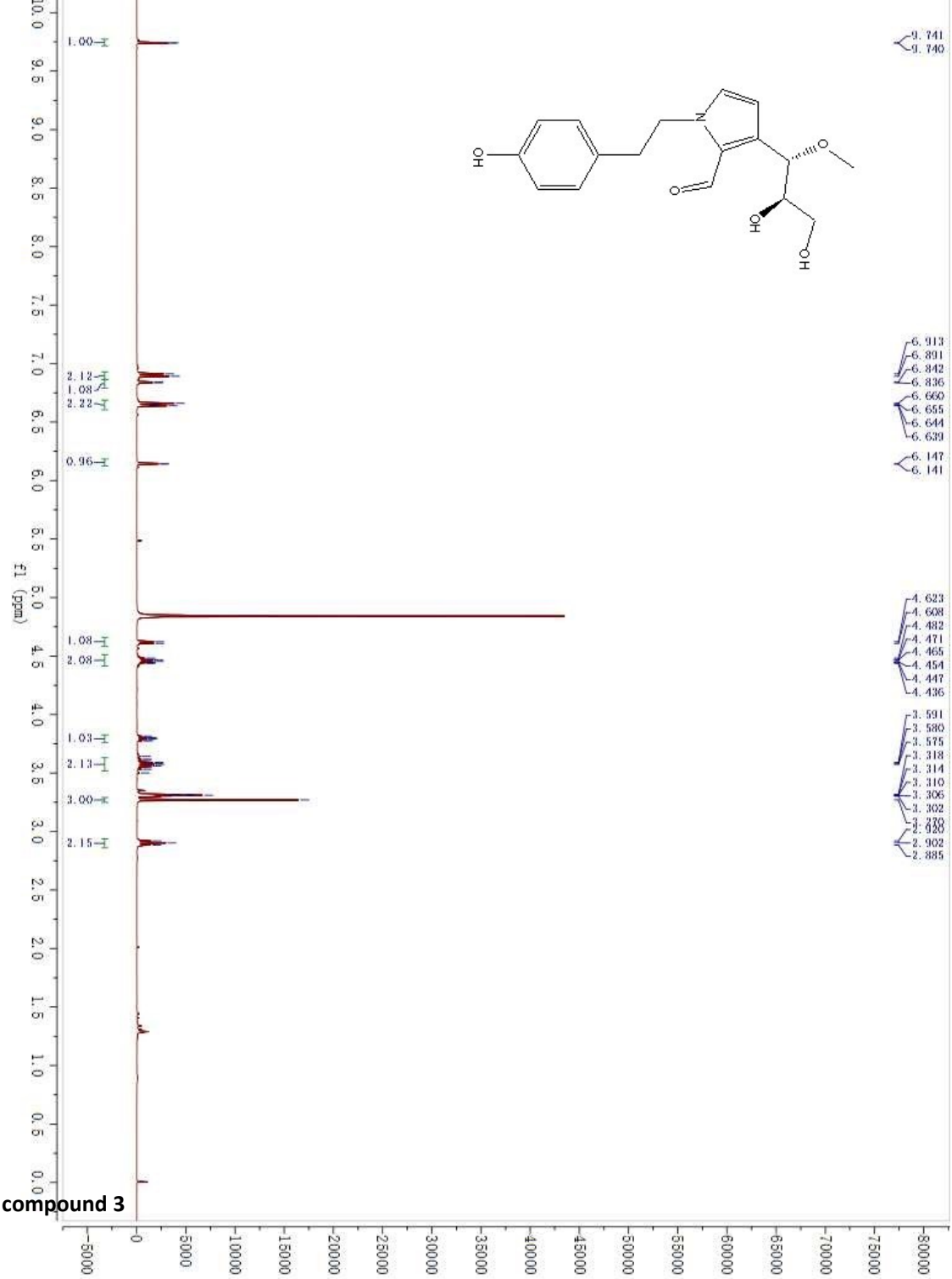

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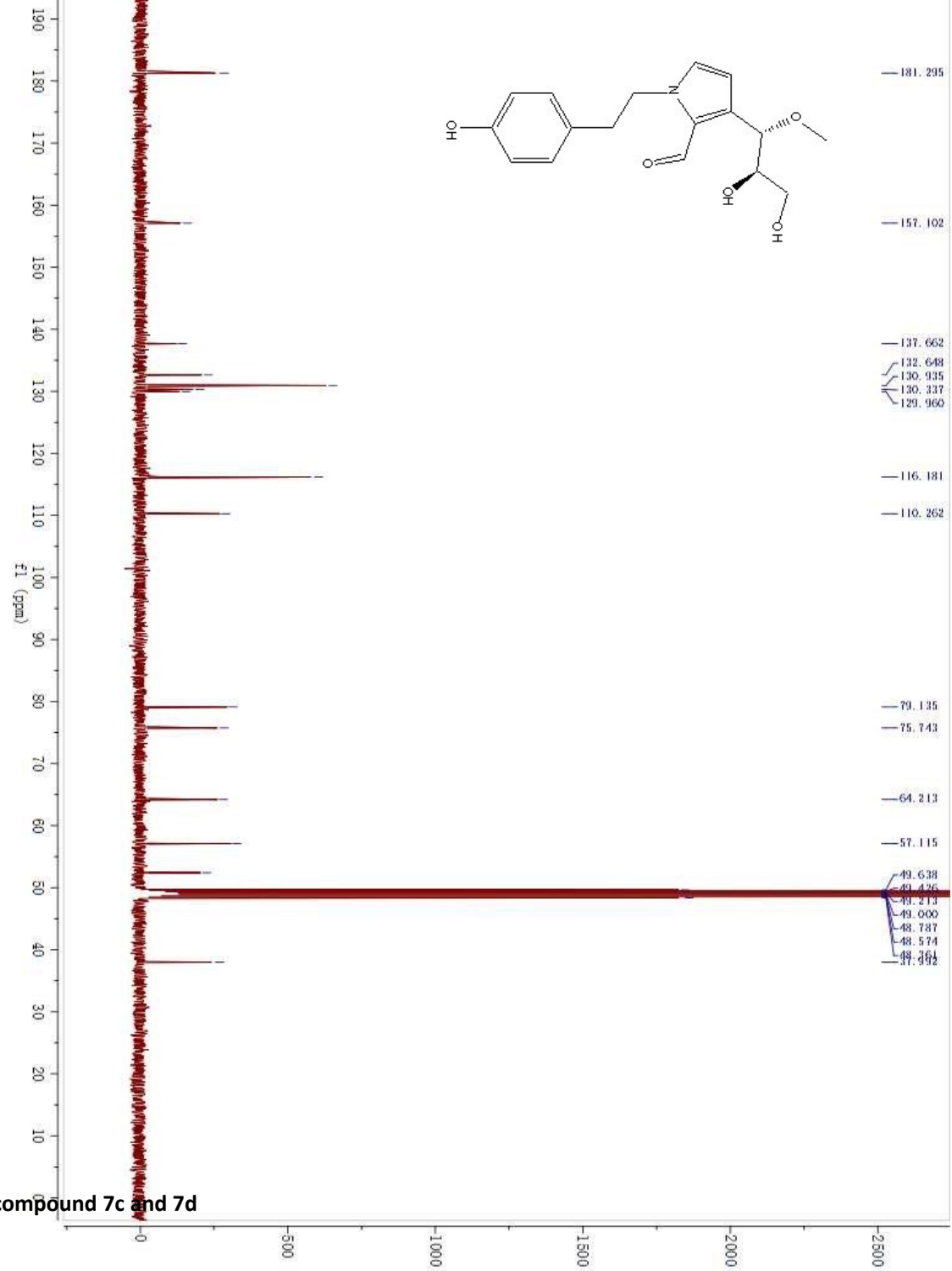

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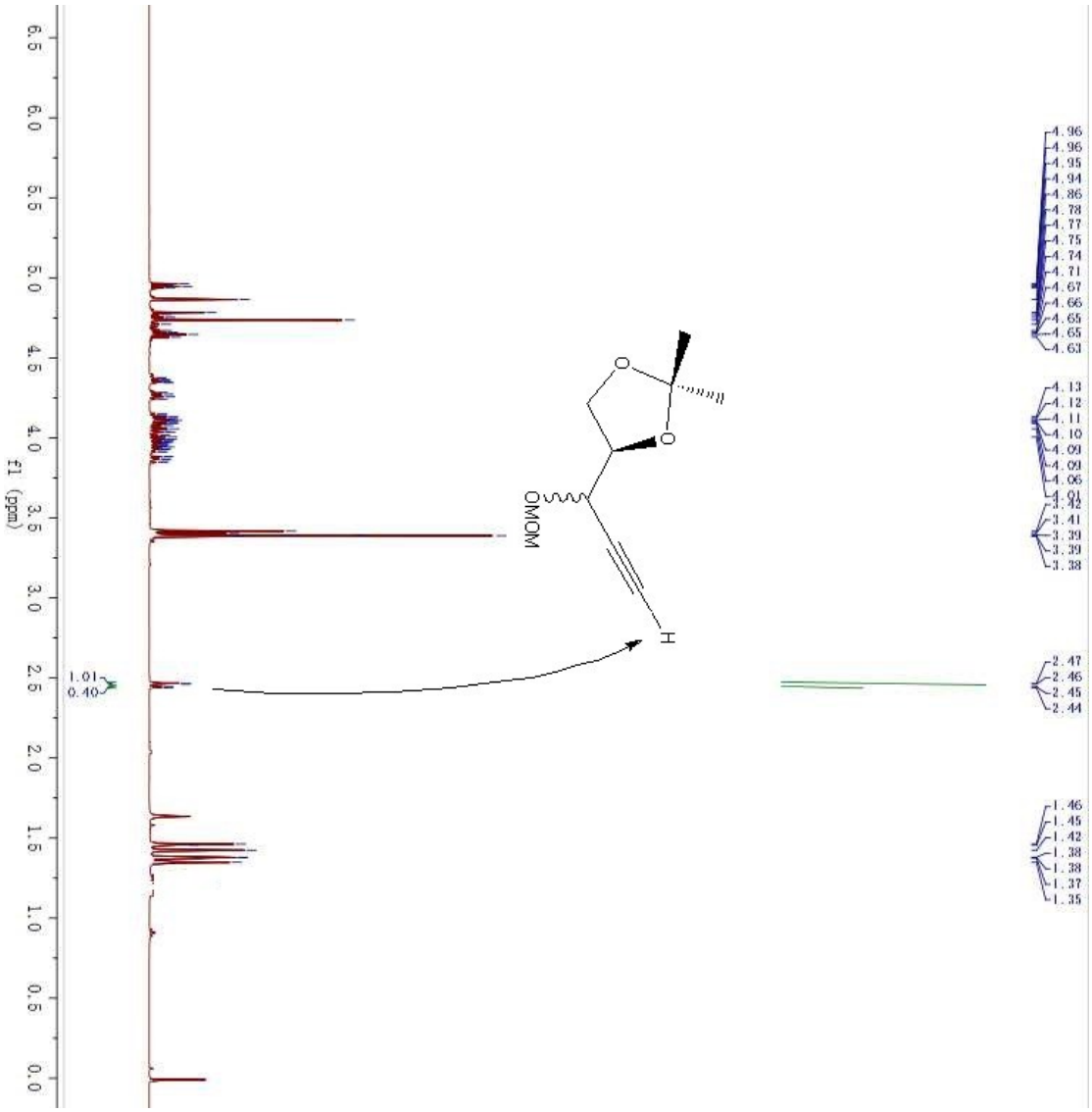

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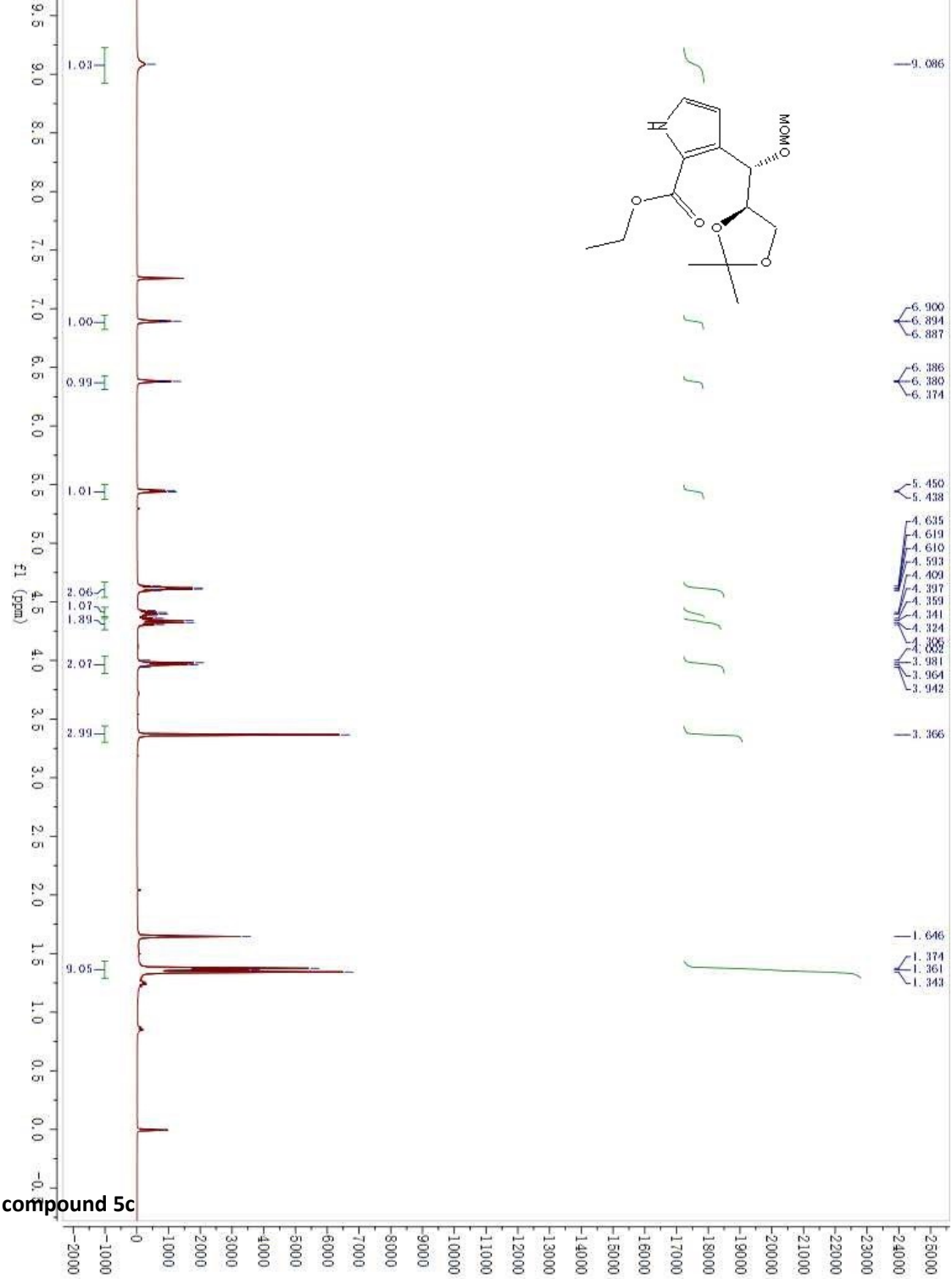

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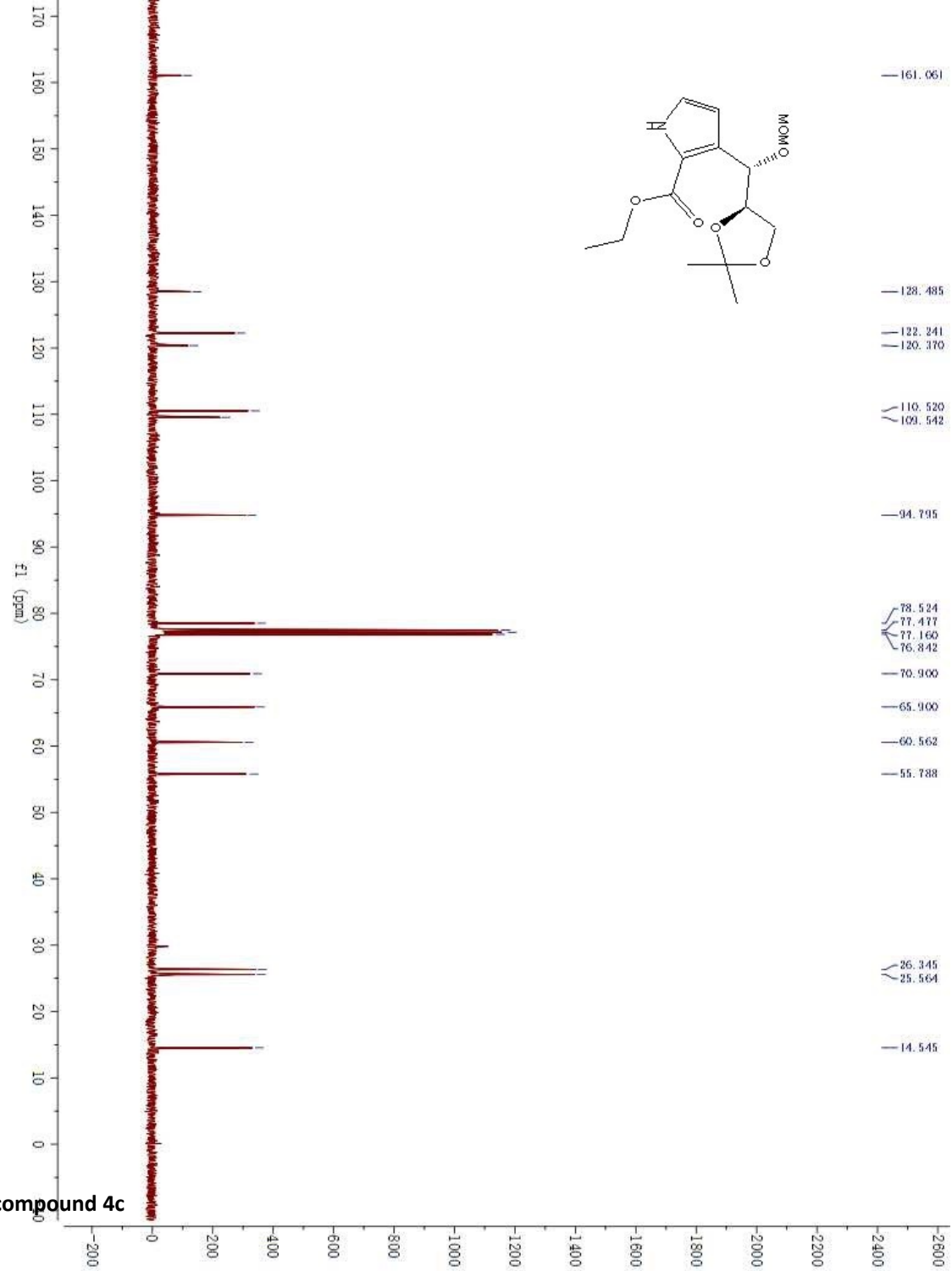

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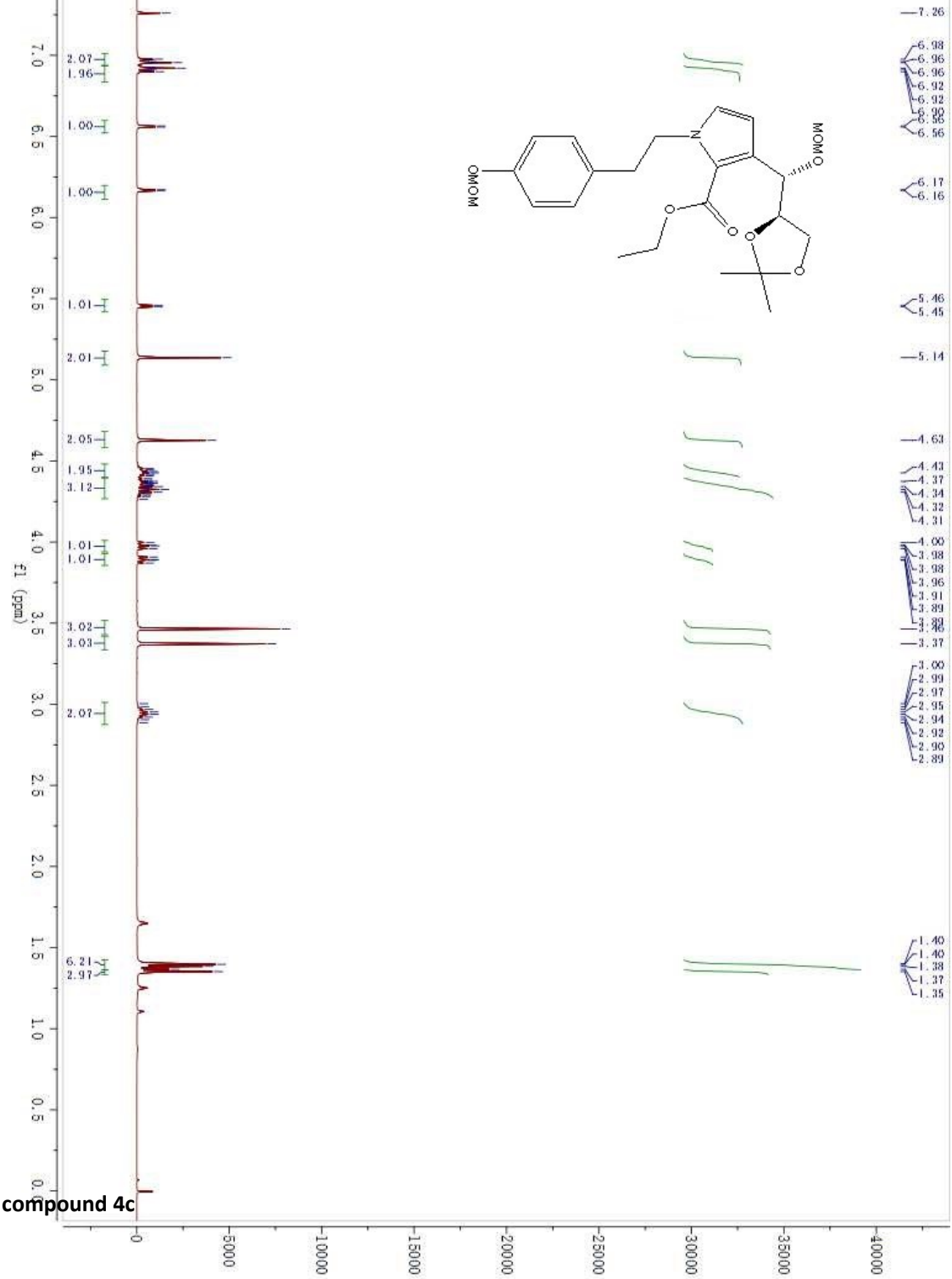

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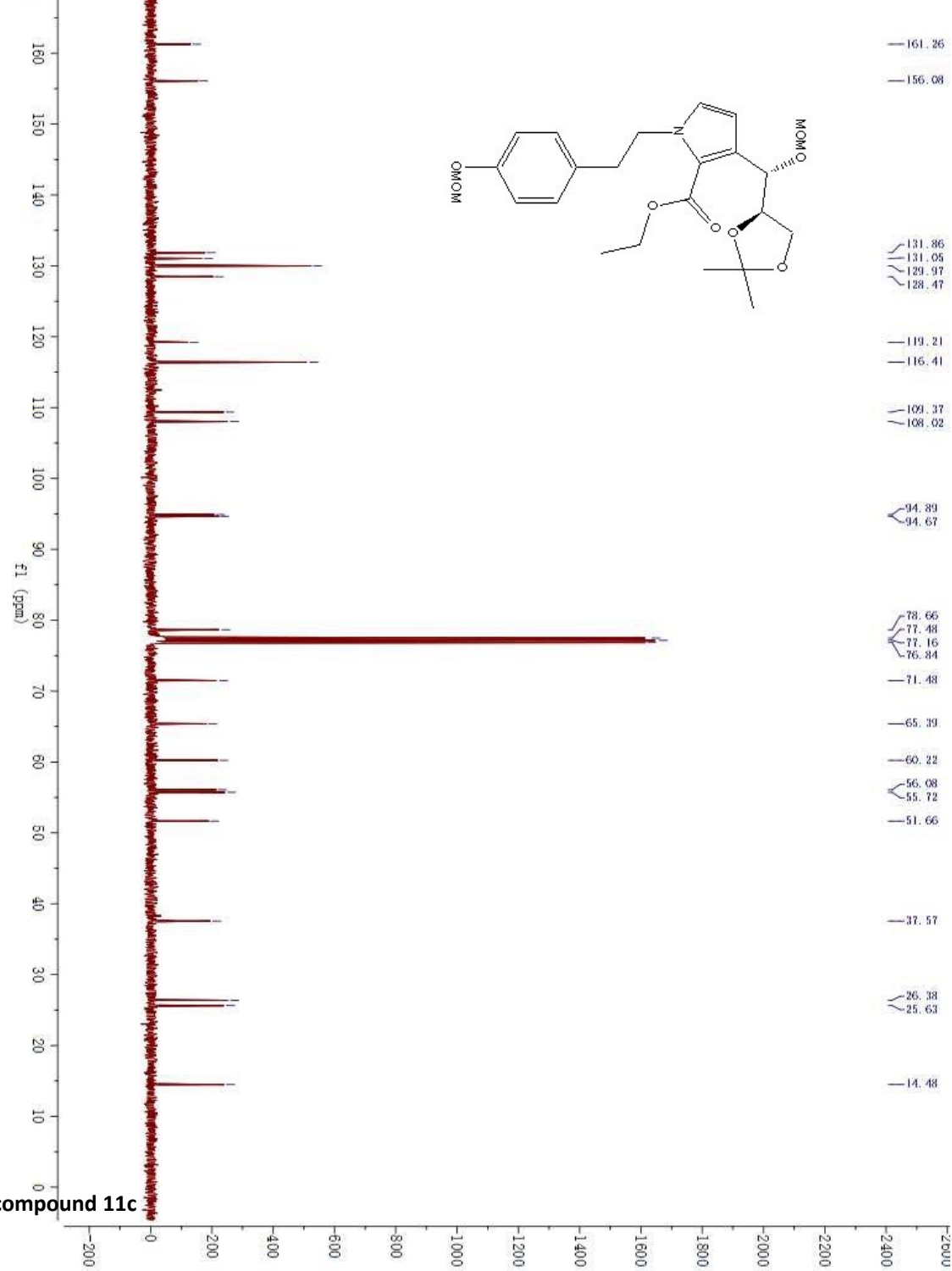

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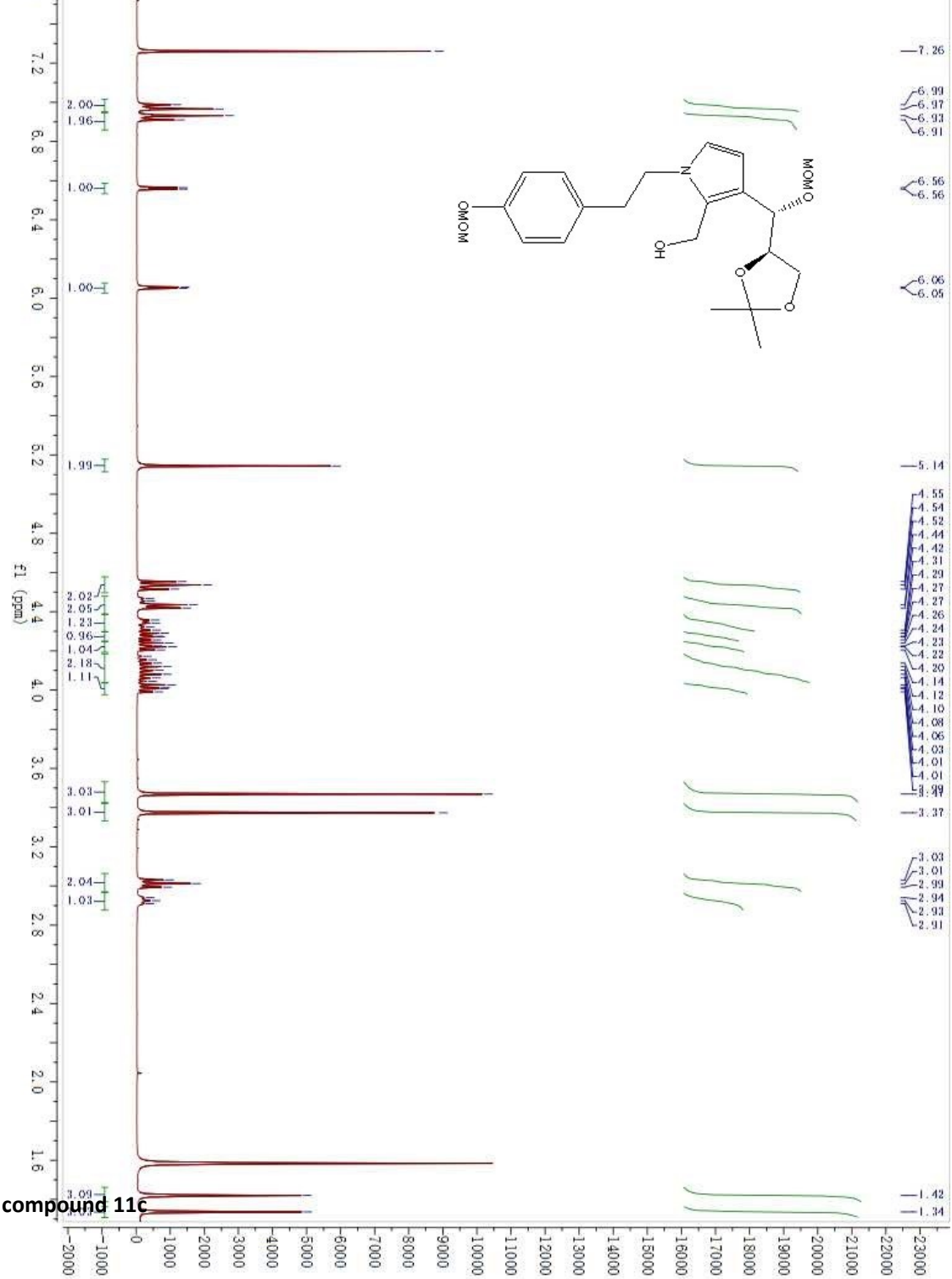
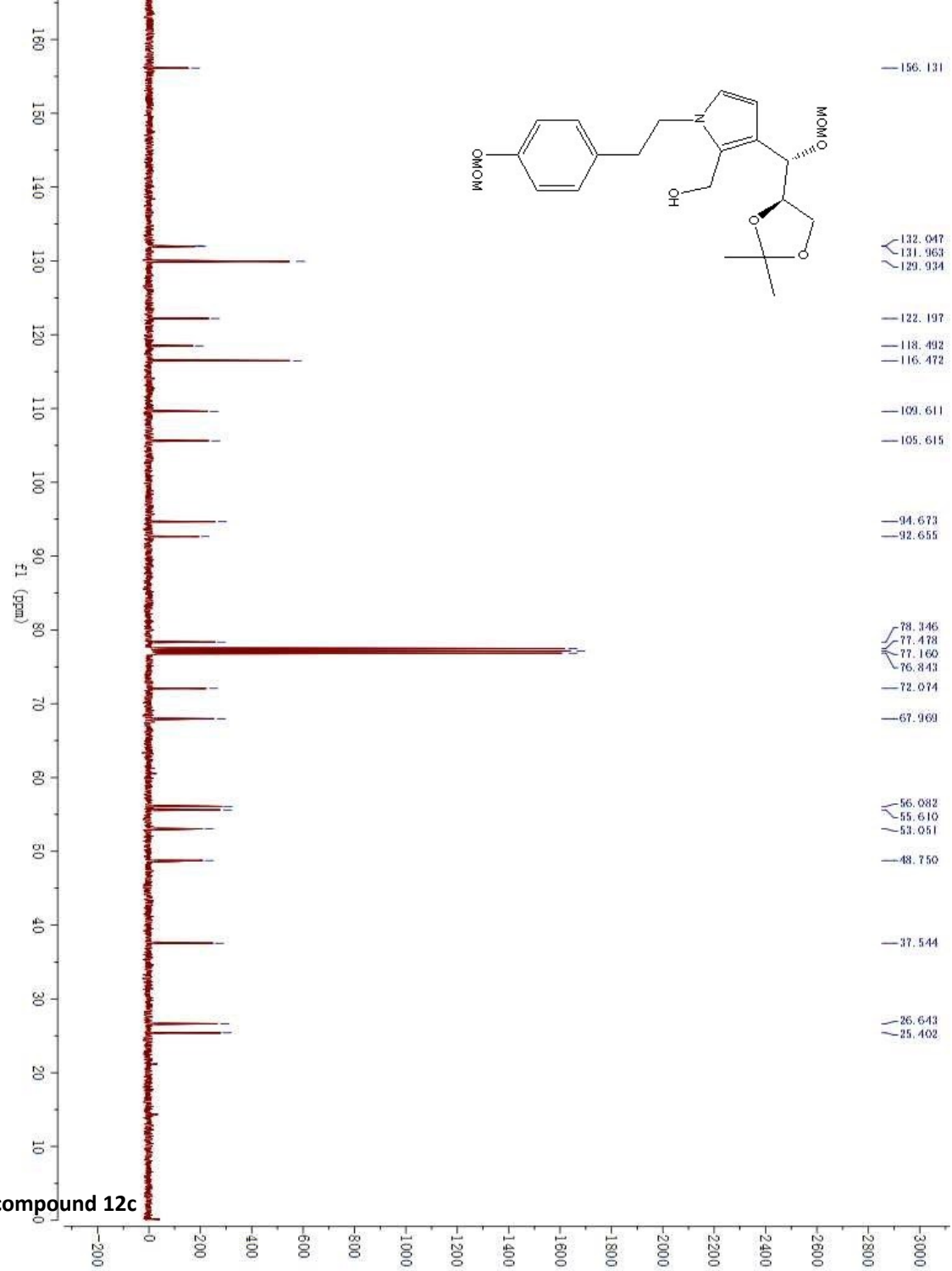


^{13}C NMR spectra of compound 11c



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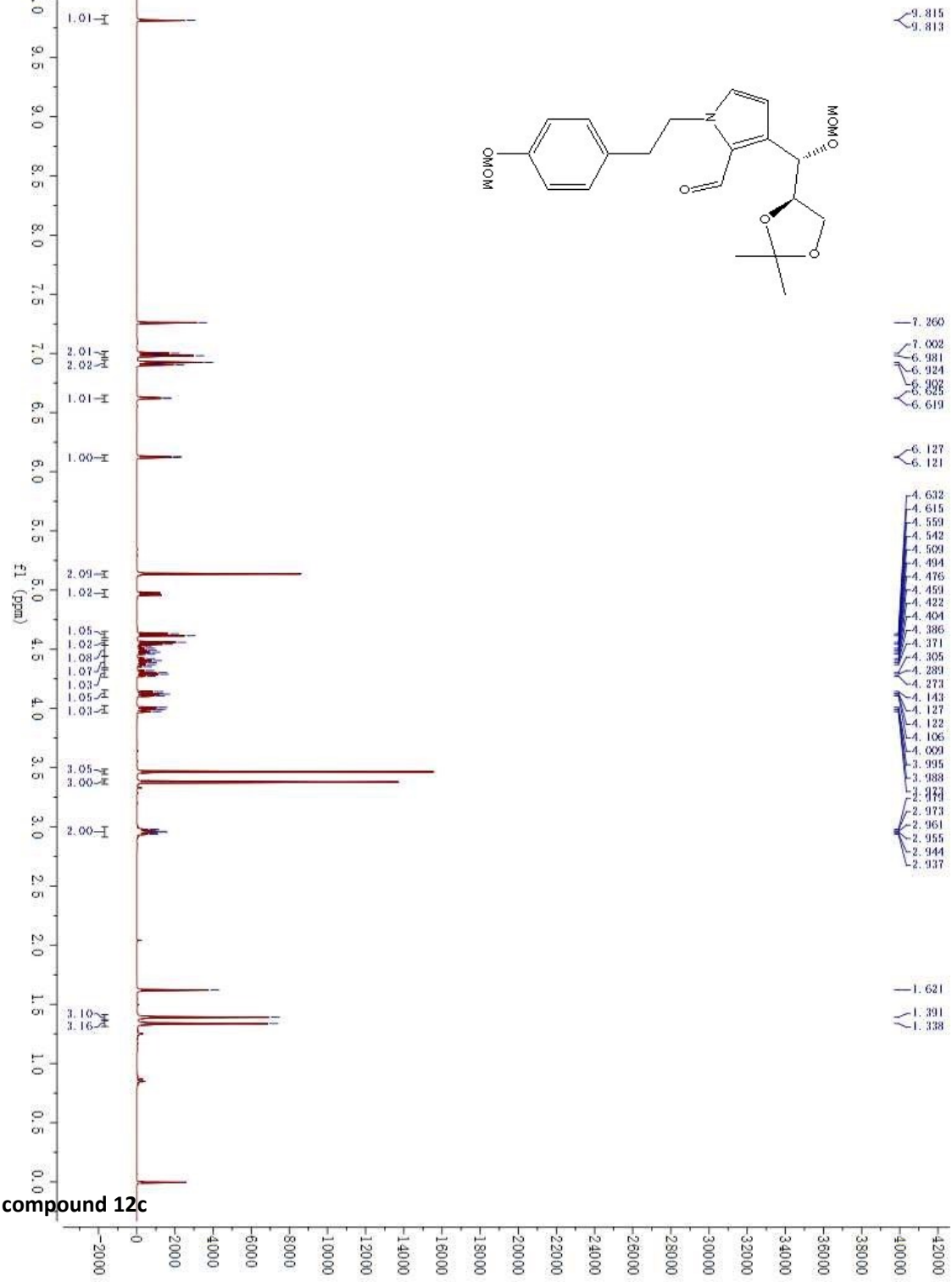
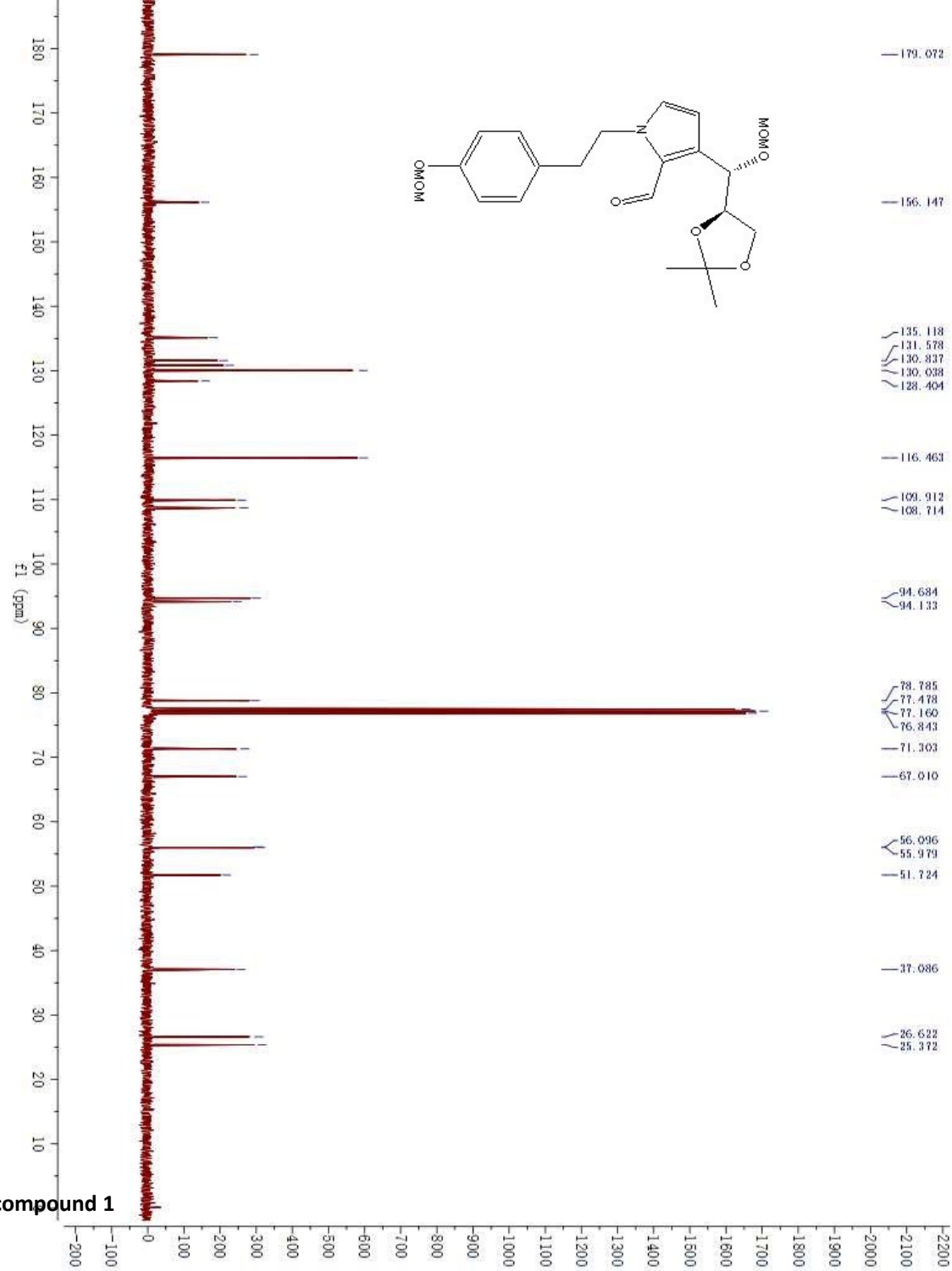


^{13}C NMR spectra of compound 12c



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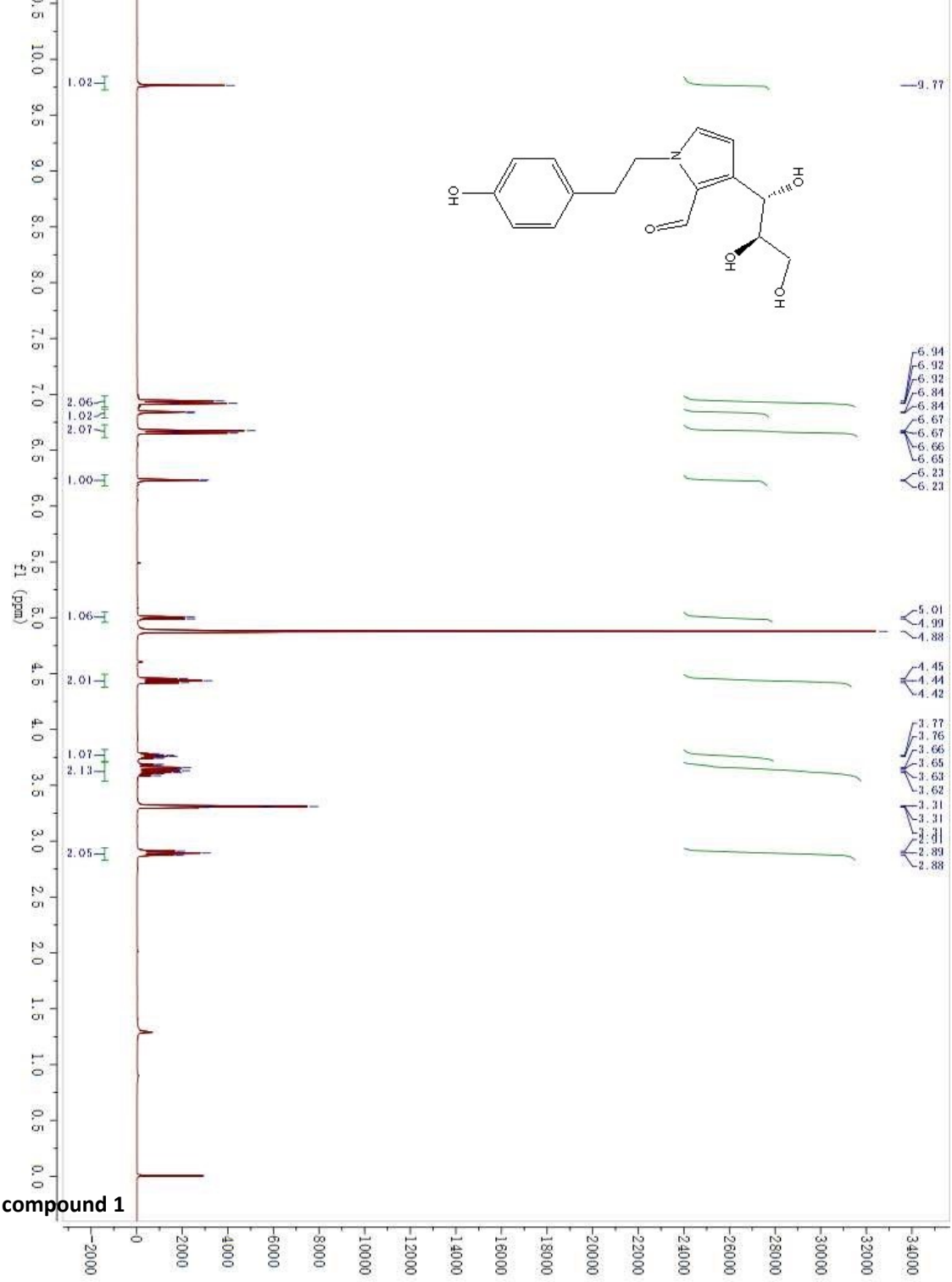

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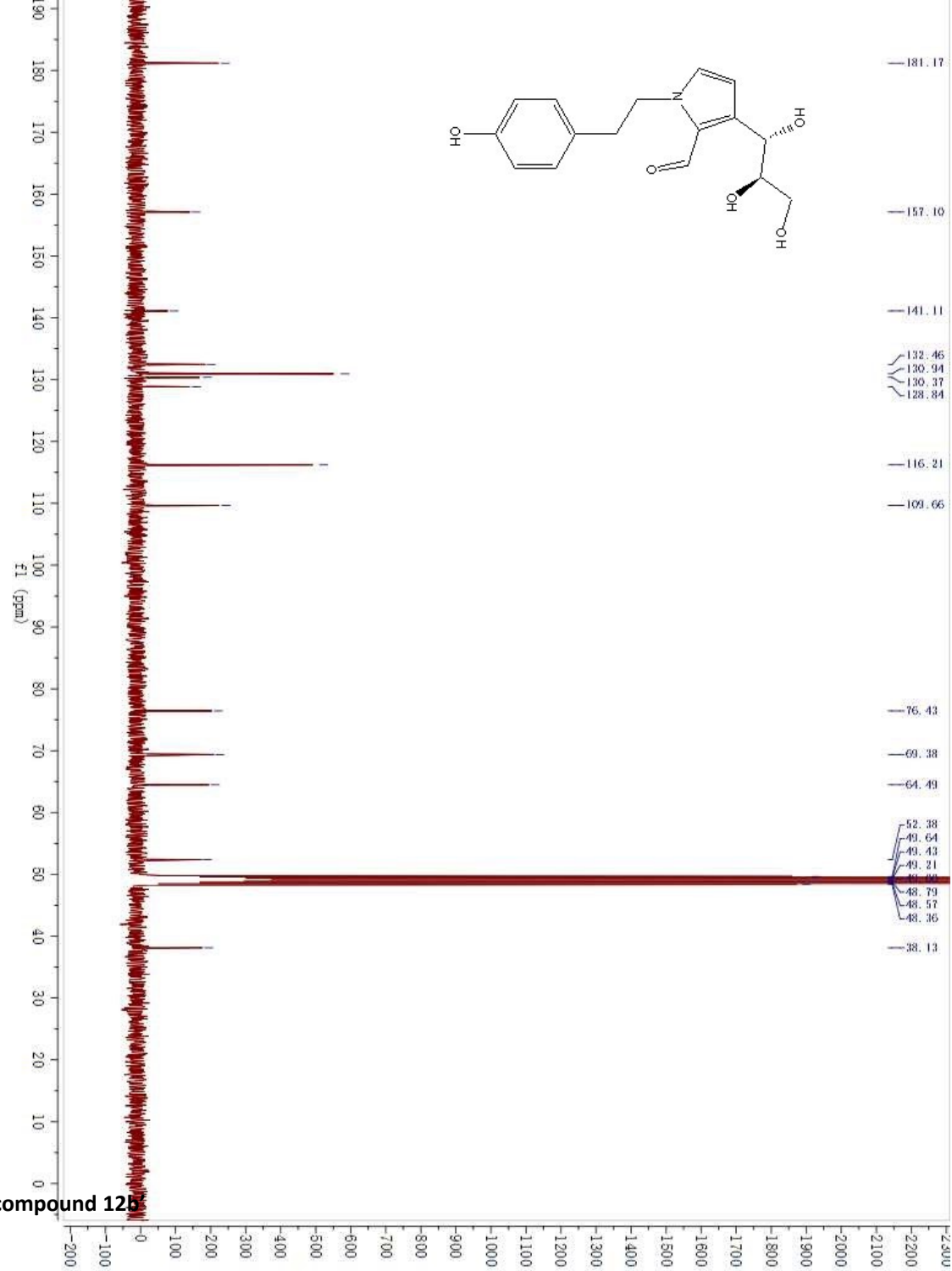

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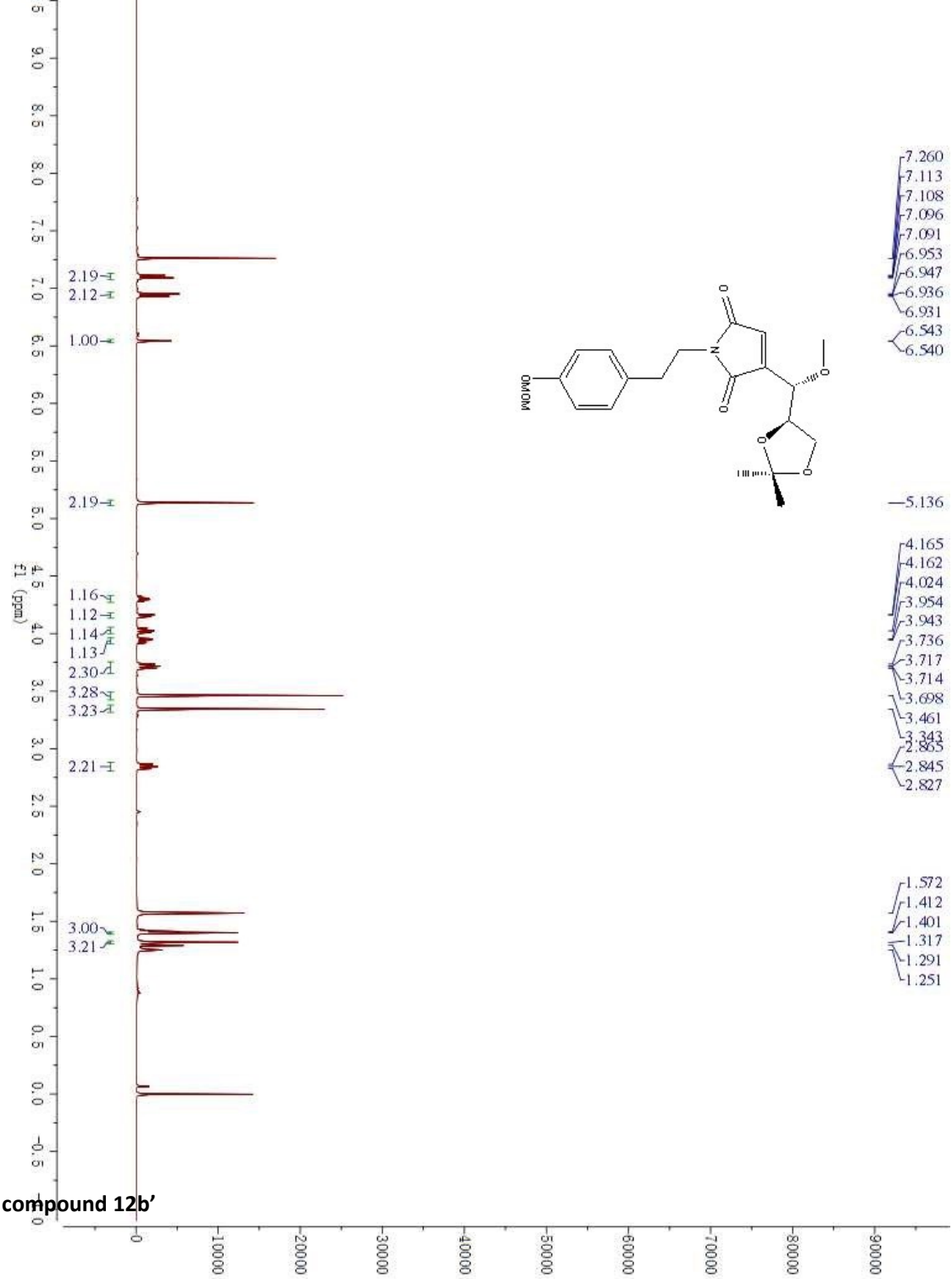
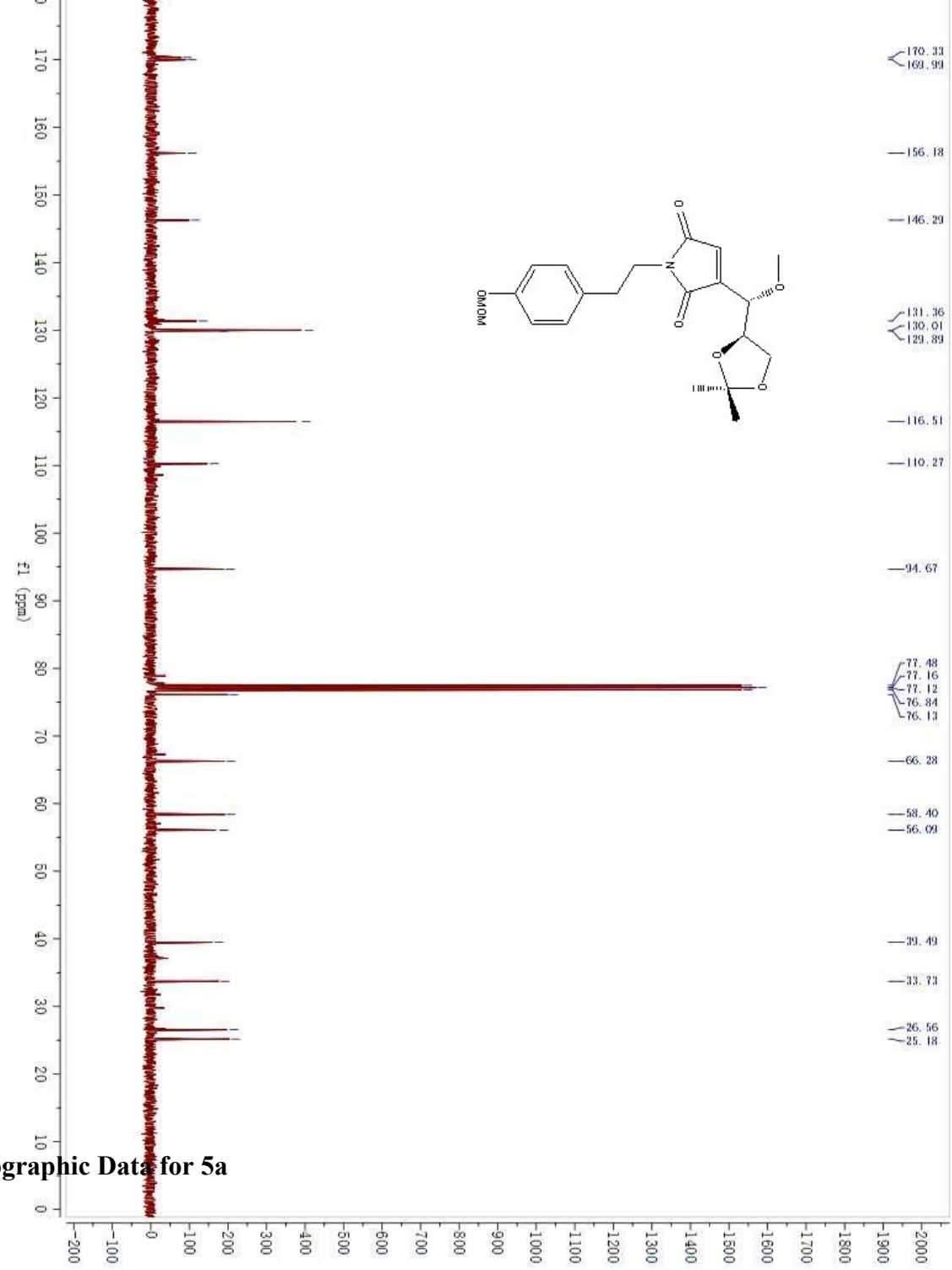
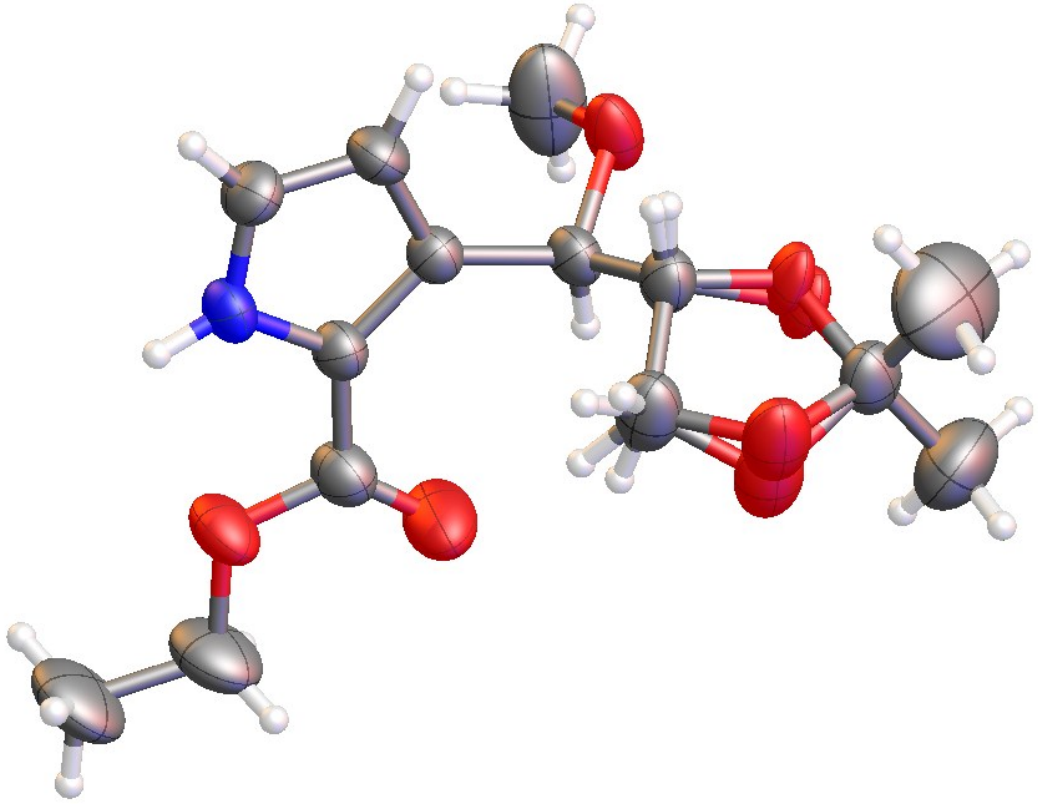


^{13}C NMR spectra of compound 12b'



X-Ray Crystallographic Data for 5a



Structure deposited at the Cambridge Crystallographic Data Centre (CCDC 1510892)

Crystal data and structure refinement for CCDC 1510892

Empirical formula	$C_{14}H_{21}N_1O_5$
Formula weight	283.32
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.4821(4)
b/Å	13.9447(9)
c/Å	14.9797(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1562.92(18)
Z	4
ρ_{calc}g/cm^3	1.204
m/mm^{-1}	0.091
F(000)	608.0
Crystal size/mm^3	0.4 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	6.086 to 52.738
Index ranges	$-6 \leq h \leq 9$, $-15 \leq k \leq 17$, $-18 \leq l \leq 12$
Reflections collected	4877
Independent reflections	2994 [Rint = 0.0182, Rsigma = 0.0438]
Data/restraints/parameters	2994/0/192
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R1 = 0.0523, wR2 = 0.1052
Final R indexes [all data]	R1 = 0.0786, wR2 = 0.1210
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.24