Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information for:

New Molecular Design for Blue BODIPYs

Zhiyuan Wu,[a] Hikaru Fujita,[a] Nikki Cecil M. Magdaong,[b] James R. Diers,[c] Don Hood,[b] Srinivasarao Allu,[a] Dariusz M. Niedzwiedzki,[d] Christine Kirmaier,[b] David F. Bocian,[c,*] Dewey Holten,[b,*] and Jonathan S. Lindsey[a,*]

[a] Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204

[b] Department of Chemistry
Washington University
St. Louis, Missouri 63130-4889

[c] Department of Chemistry
University of California
Riverside, California 92521-0403

[d] Department of Energy, Environmental & Chemical Engineering
and Center for Solar Energy and Energy Storage
Washington University
St. Louis, Missouri 63130-4889

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Table S1. Summary of crystal data for dihydrodipyrrin–complexes.

	1-BBu_2	**2-BBu_2**	**2-BF_2**
CCDC registry	1900105	1900106	1900107
Formula	$C_{23}H_{37}BN_2O_2$	$C_{23}H_{36}BBrN_2O_2$	$C_{15}H_{18}BBrF_2N_2O_2$
Formula Weight (g/mol)	384.35	463.26	387.03
Crystal Dimensions (mm)	0.232 × 0.264 × 0.370	0.184 × 0.298 × 0.425	0.212 × 0.326 × 0.418
Crystal System	monoclinic	hexagonal	triclinic
Space Group	P 1 21/n 1	P 65	P -1
Temperature, K	180(2)	100(2)	100(2)
a, Å	11.8186(2)	9.6838(2)	7.1235(2)
b, Å	9.1192(2)	9.6838(2)	11.0063(3)
c, Å	22.4535(5)	43.5738(8)	11.5158(3)
α, deg	90	90	66.4695(11)
β, deg	103.9509(8)	90	84.0270(12)
γ, deg	90	120	83.5531(13)
V, $Å^3$	2348.57(8)	3538.73(16)	820.83(4)
Number of reflections to determine final unit cell	281	378	246
Min and Max 2θ for cell determination (deg)	3.815, 45.38	17.95, 63.19	4.280, 66.43
Z	4	6	2
F (000)	840	1464	392
ρ (g/cm)	1.087	1.304	1.566
λ, Å, (MoKα)	0.71073	0.71073	0.71073
μ, (mm^{-1})	0.068	1.763	2.533
Max 2θ for data collection (deg)	47.64	66.32	73.08
Measured fraction of data	0.998	1.000	0.998
Number of reflections measured	32991	185013	52690
Unique reflections measured	3604	8999	8056
R_{merge}	2.14%	4.74%	2.70%
Number of parameters in least-squares	392	268	212
R_1	0.0441	0.0331	0.0237
wR_2	0.1140	0.0773	0.0588
R_1 (all data)	0.0561	0.0347	0.0303
wR_2 (all data)	0.1252	0.0779	0.0608

Table S2. Molar absorption coefficient of dihydrodipyrrin complexes.

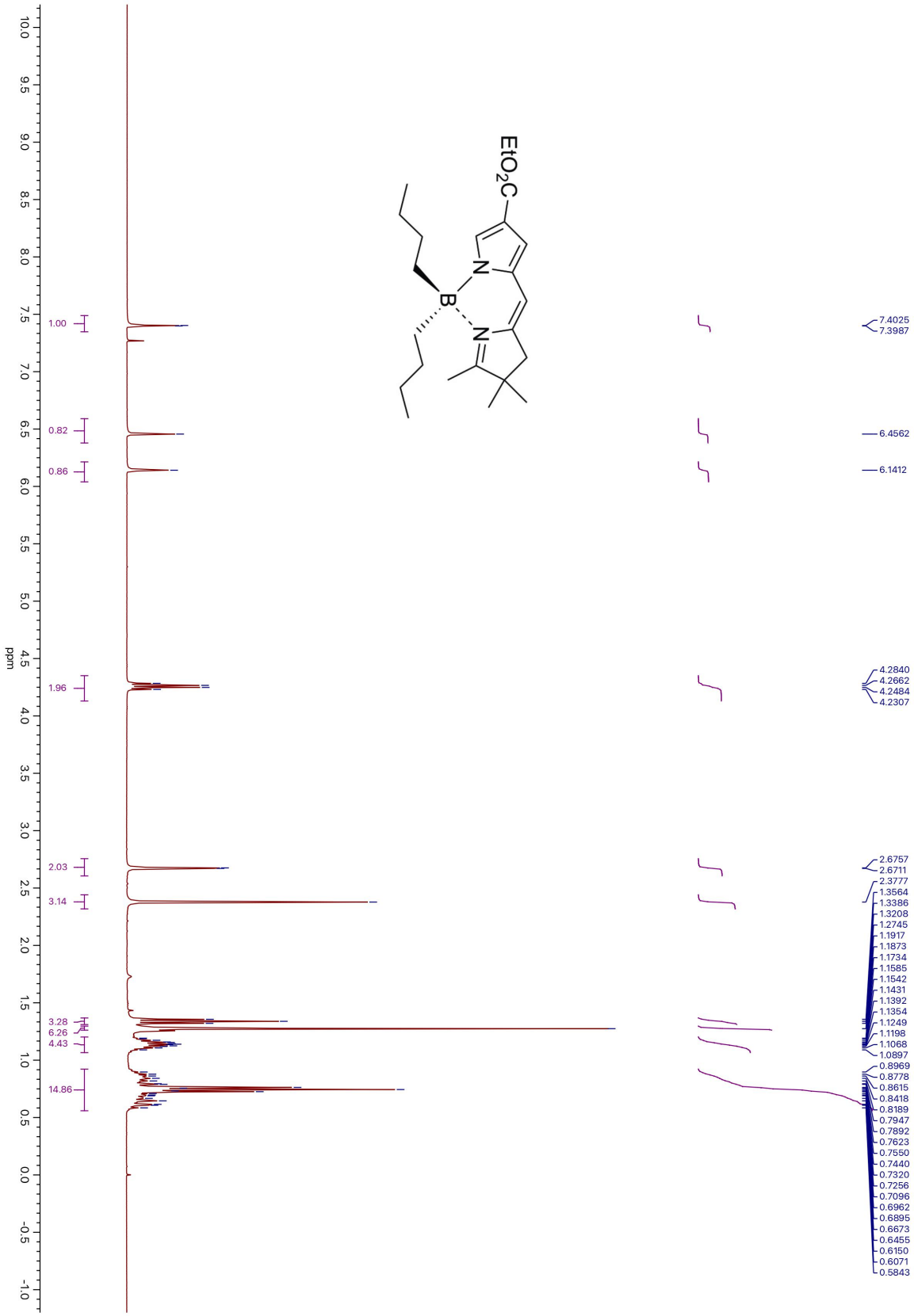
Compound	Abs (nm) in toluene	ε ($M^{-1}\cdot cm^{-1}$) in toluene	Abs (nm) in acetonitrile	ε ($M^{-1}\cdot cm^{-1}$) in acetonitrile
1-BBu$_2$	398	1.1×10^4	377	1.1×10^4
2	332	2.5×10^4	322	2.3×10^4
2-BBu$_2$	399	8.6×10^3	375	9.1×10^3
2-BF$_2$	400	1.1×10^4	–	–
3-BBu$_2$	408	1.1×10^4	–	–
3-BF$_2$	400	1.3×10^4	–	–
4-BBu$_2$	436	1.5×10^4	–	–

Fluorescence yields were determined against two standards using several different excitation wavelengths and the results were averaged. Single excited-state lifetimes were determined on two transient absorption spectrometers and by fluorescence decay and the results were averaged. The values and averages are given in Table S3.

Table S3. Photophysical properties.[a]

Cmpd	Solvent	Φ_f vs pyranine	Φ_f vs **BDPY1**	Φ_f avg	τ_S Helios TA (ns)	τ_S EOS TA (ns)	τ_S TCSPC (ns)	τ_S (ns)
1-BBu$_2$	toluene	0.89	0.84	0.87 ± 0.04	8.0	6.6	7.9	7.5 ± 0.8
1-BBu$_2$	MeCN	0.87	0.90	0.88 ± 0.04		9.0	8.6	8.8 ± 0.3
1-BBu$_2$	DMSO	0.88	0.92	0.90 ± 0.04		7.7	8.0	7.9 ± 0.2
2-BBu$_2$	toluene	0.81	0.81	0.81 ± 0.01	7.2	6.4	7.3	7.0 ± 0.5
2-BF$_2$	toluene	0.43	0.41	0.42 ± 0.01	5.1	4.8	4.8	4.9 ± 0.2
3-BBu$_2$	toluene	0.91	0.85	0.88 ± 0.03	6.2	7.4	7.5	7.0 ± 0.7
3-BF$_2$	toluene	0.4	0.36	0.38 ± 0.04	5.0	4.8	4.8	4.9 ± 0.1
4-BBu$_2$	toluene	0.3	0.29	0.30 ± 0.04	3.9	3.8	3.9	3.9 ± 0.1

[a]All data were acquired at room temperature. MeCN is acetonitrile and DMSO is dimethylsulfoxide. Fluorescence yields were determined for deoxygenated samples relative to standards pyranine (Φ_f = 1.0 in 0.10 M NaOH[23]) and 5-mesityldipyrrinatoboron difluoride (**BDPY1**) (Φ_f = 0.93 in toluene[24]) and averaged. Singlet excited-state lifetimes (τ_S) were determined via transient absorption (TA) spectroscopy using Helios (–2 ps to 7 ns) and EOS (–2 ns to 40 ns) spectrometers and via fluorescence decay using time correlated single photon counting (TCSPC) and the resulting three values were averaged.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4.0
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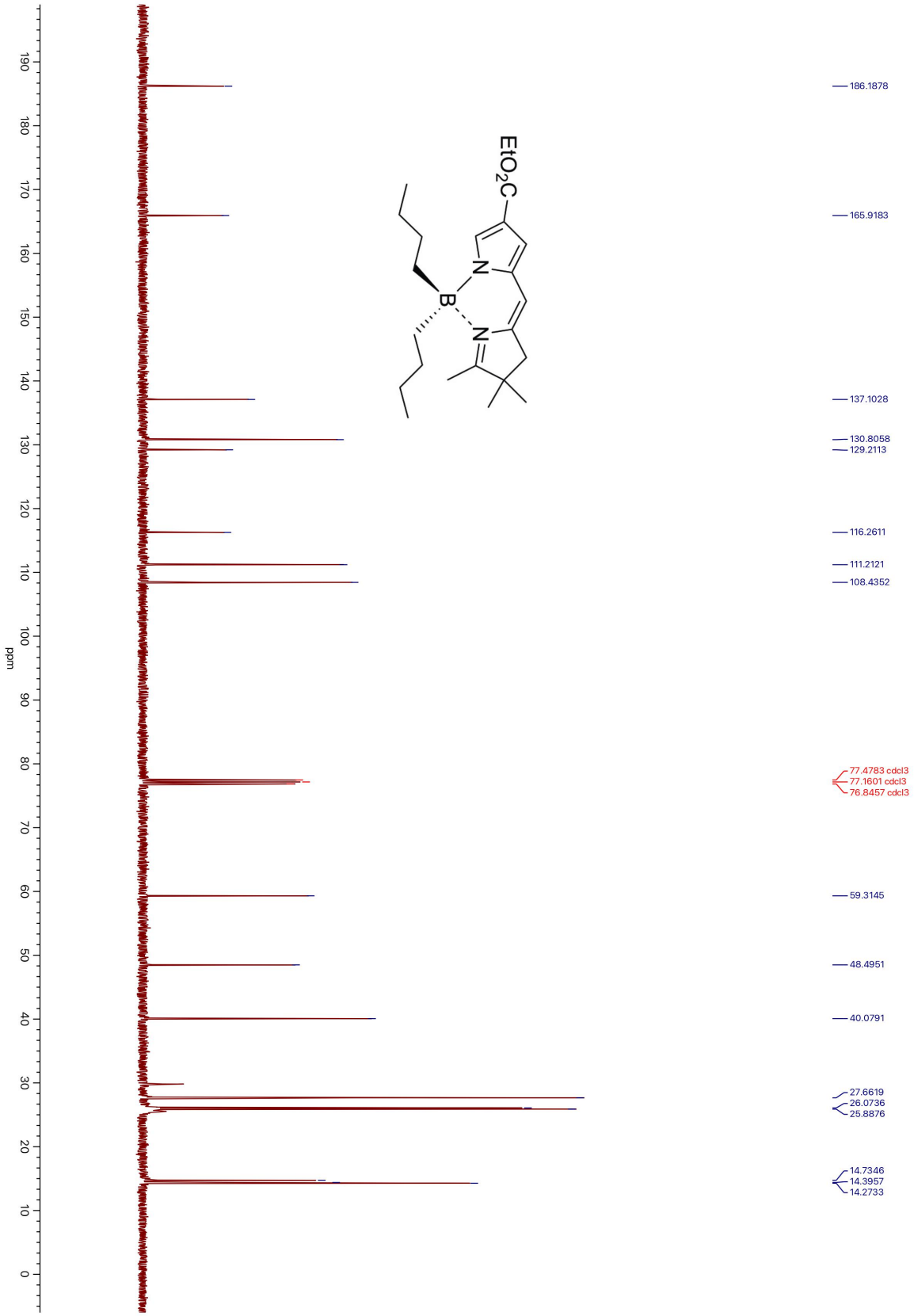
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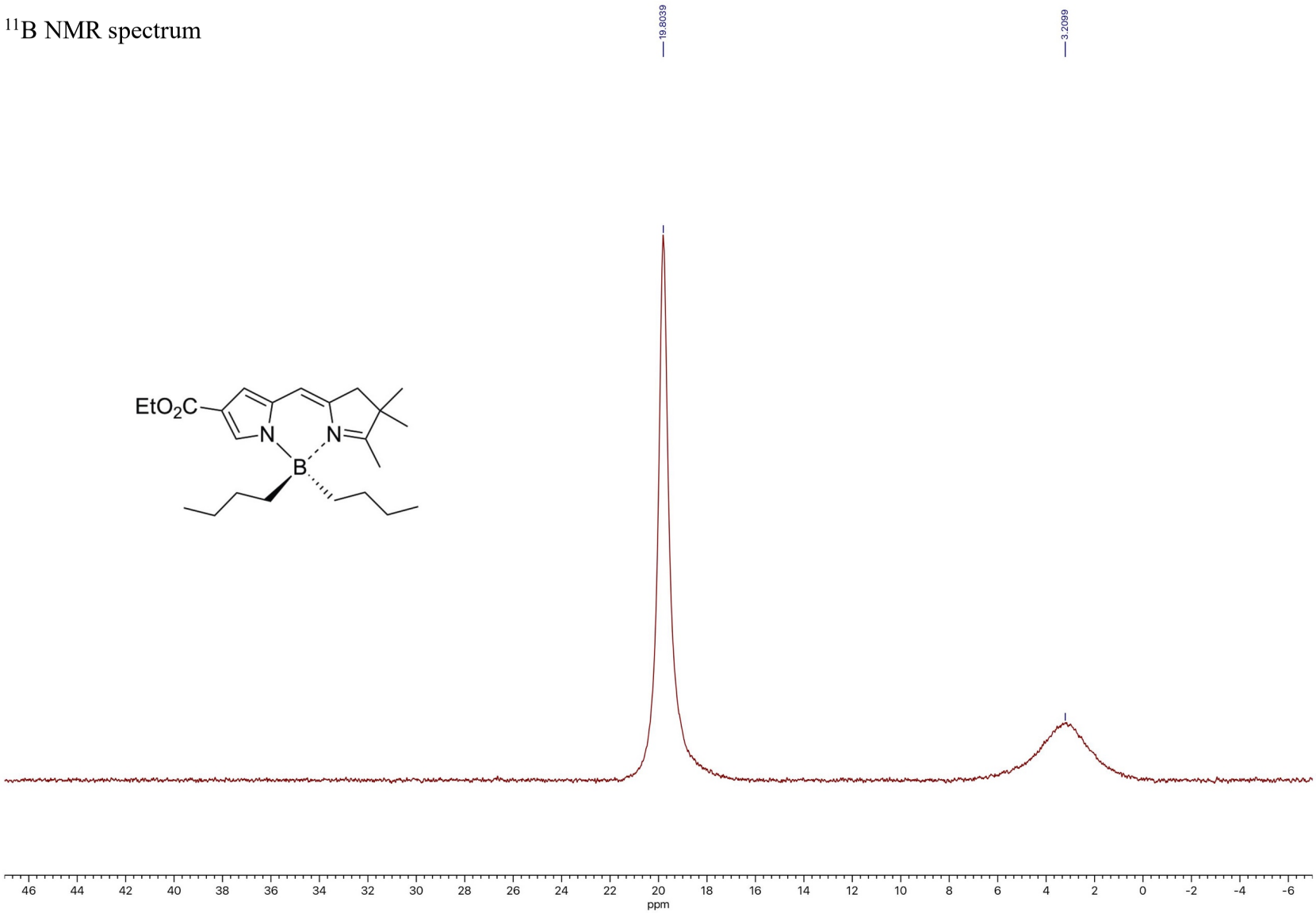
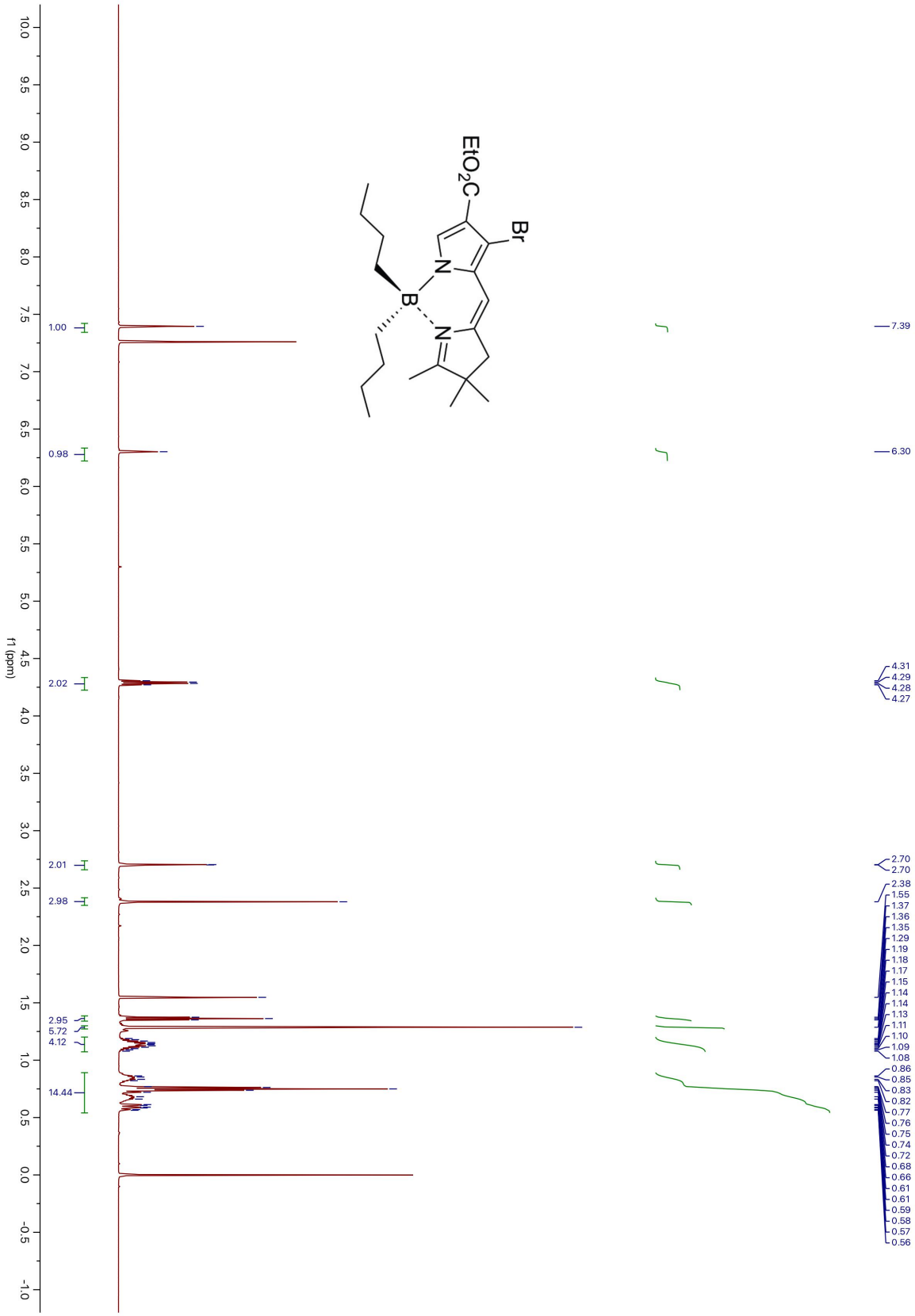
^{11}B NMR spectrum

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4.31
4.29
4.28
4.27
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2.70
2.38
1.55
1.37
1.36
1.35
1.29
1.19
1.18
1.17
1.15
1.14
1.14
1.13
1.11
1.10
1.09
1.08
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0.85
0.83
0.82
0.77
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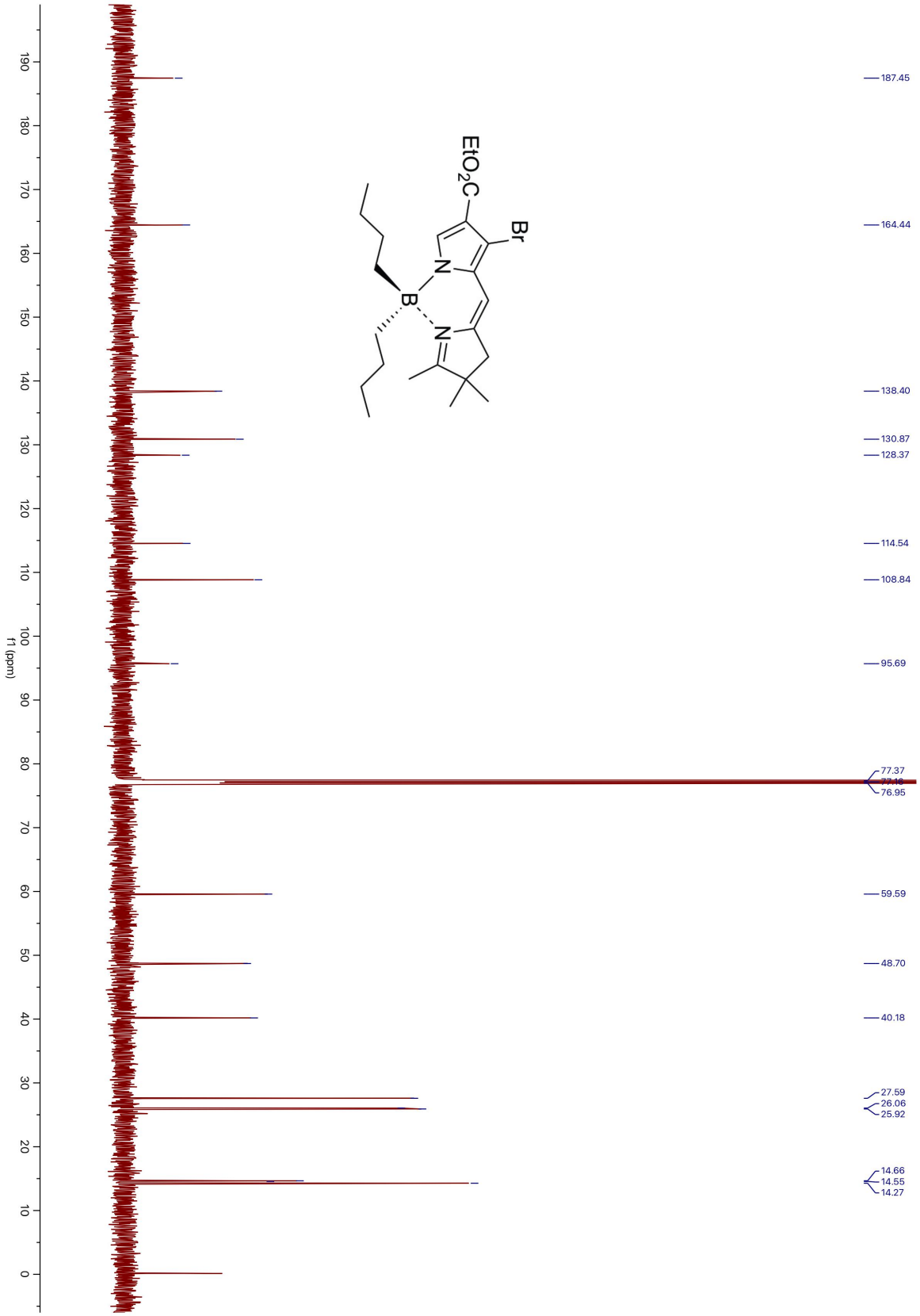
0.56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N
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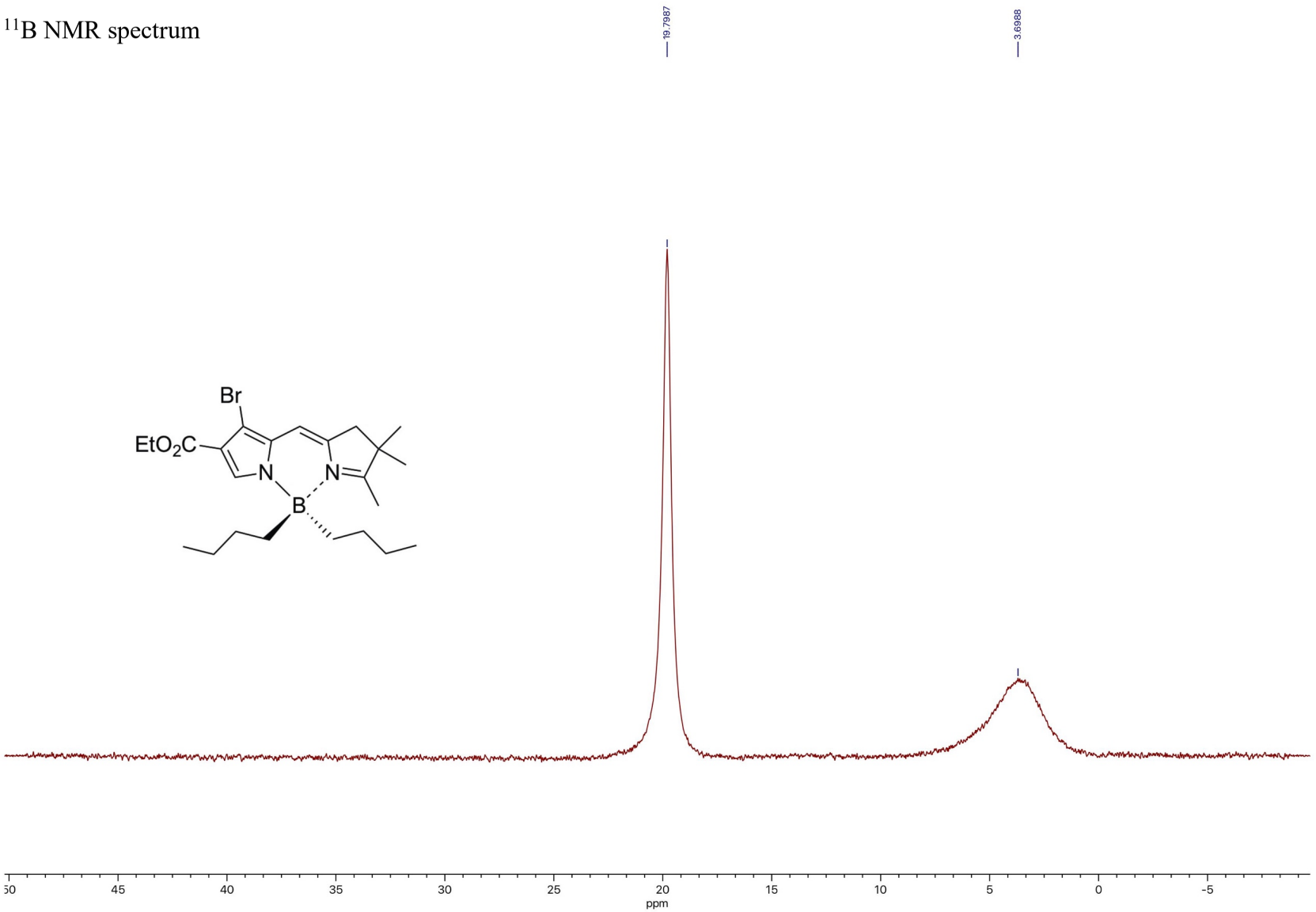
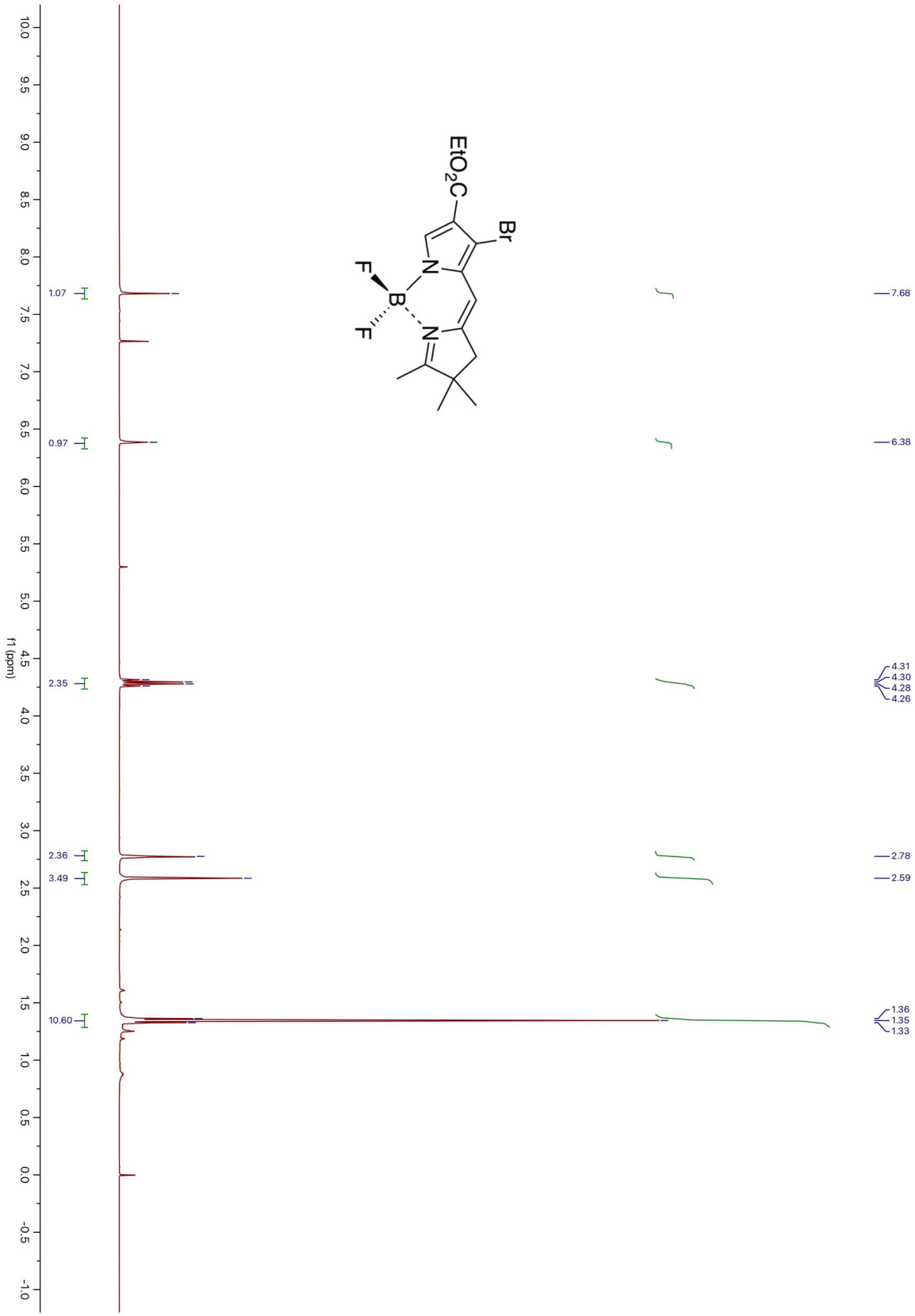
14.66
14.55
14.27

^{11}B NMR spectrum

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Br
F
B
F
N
N
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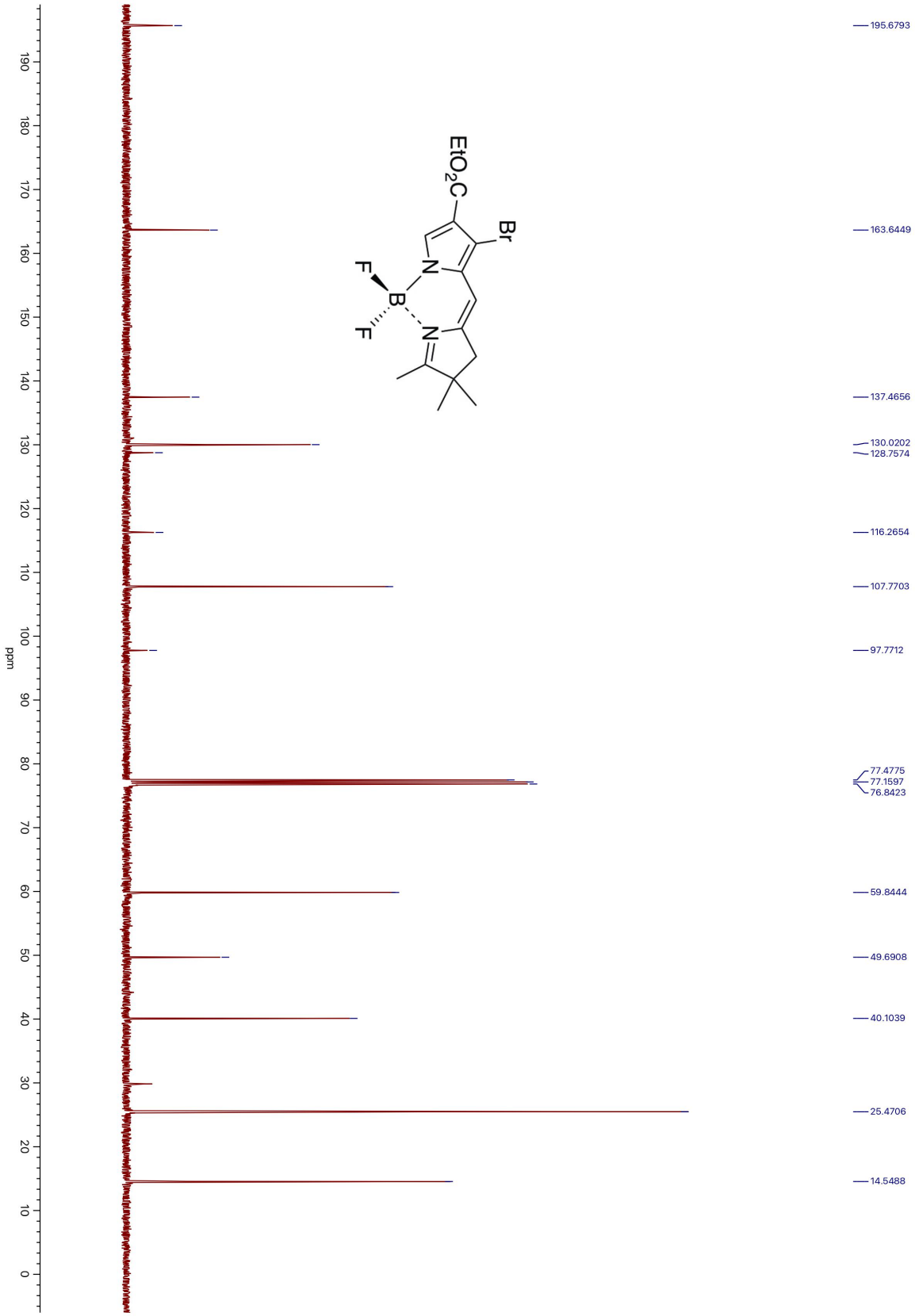
1.35
1.33
f1 (ppm)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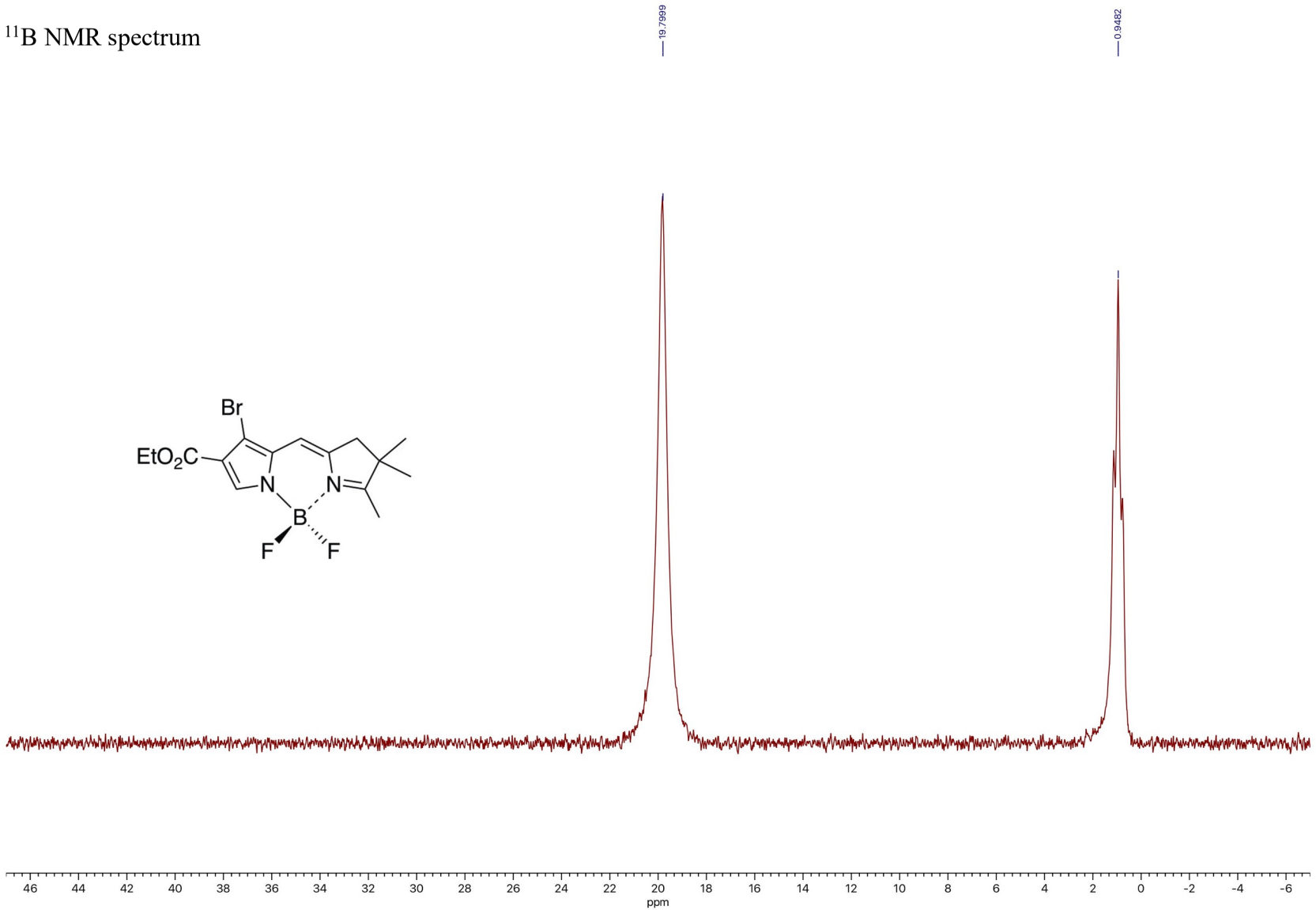
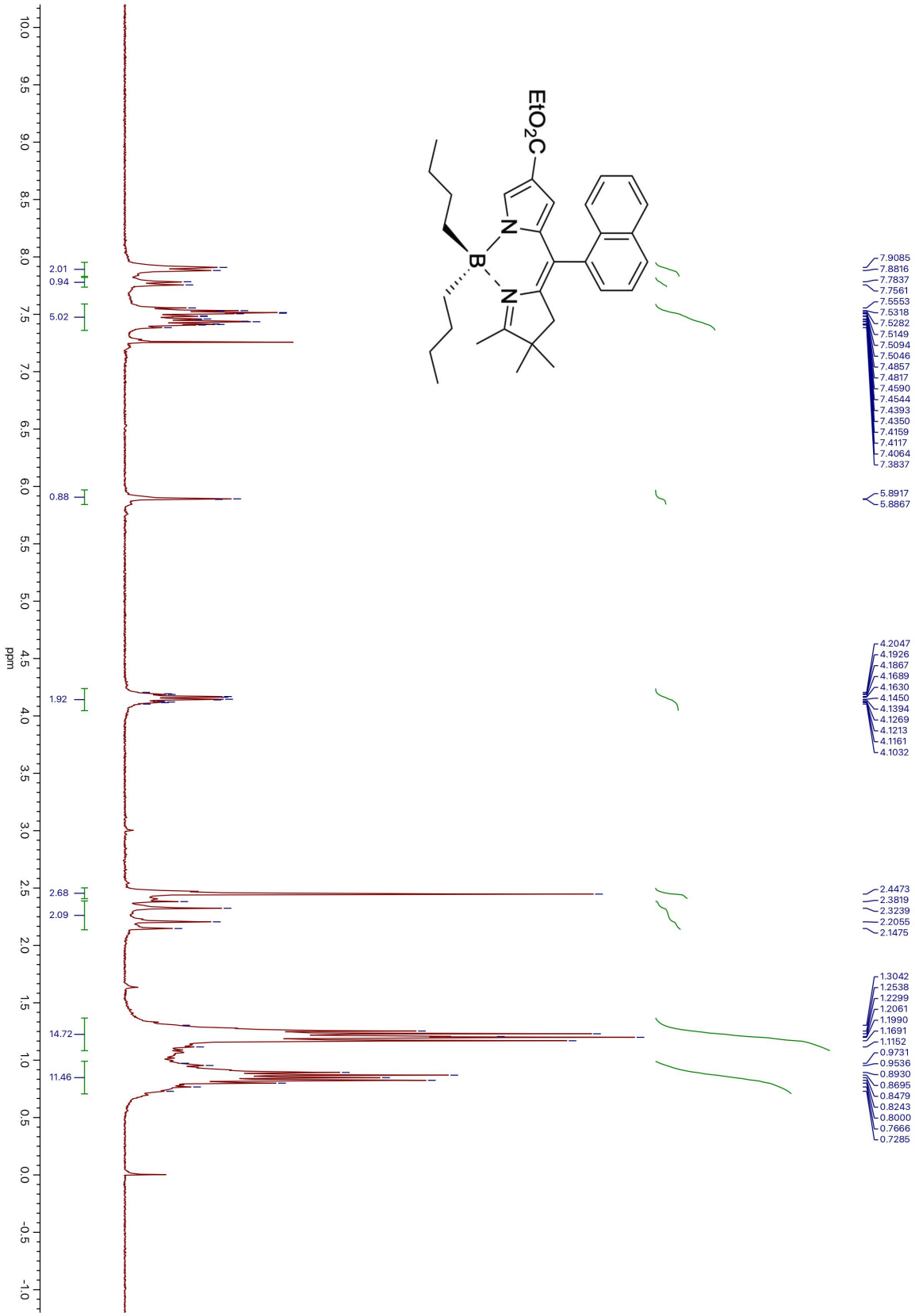
ppm
EtO2C
Br
F
F
B
N
N

^{11}B NMR spectrum

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7.7561
7.5553
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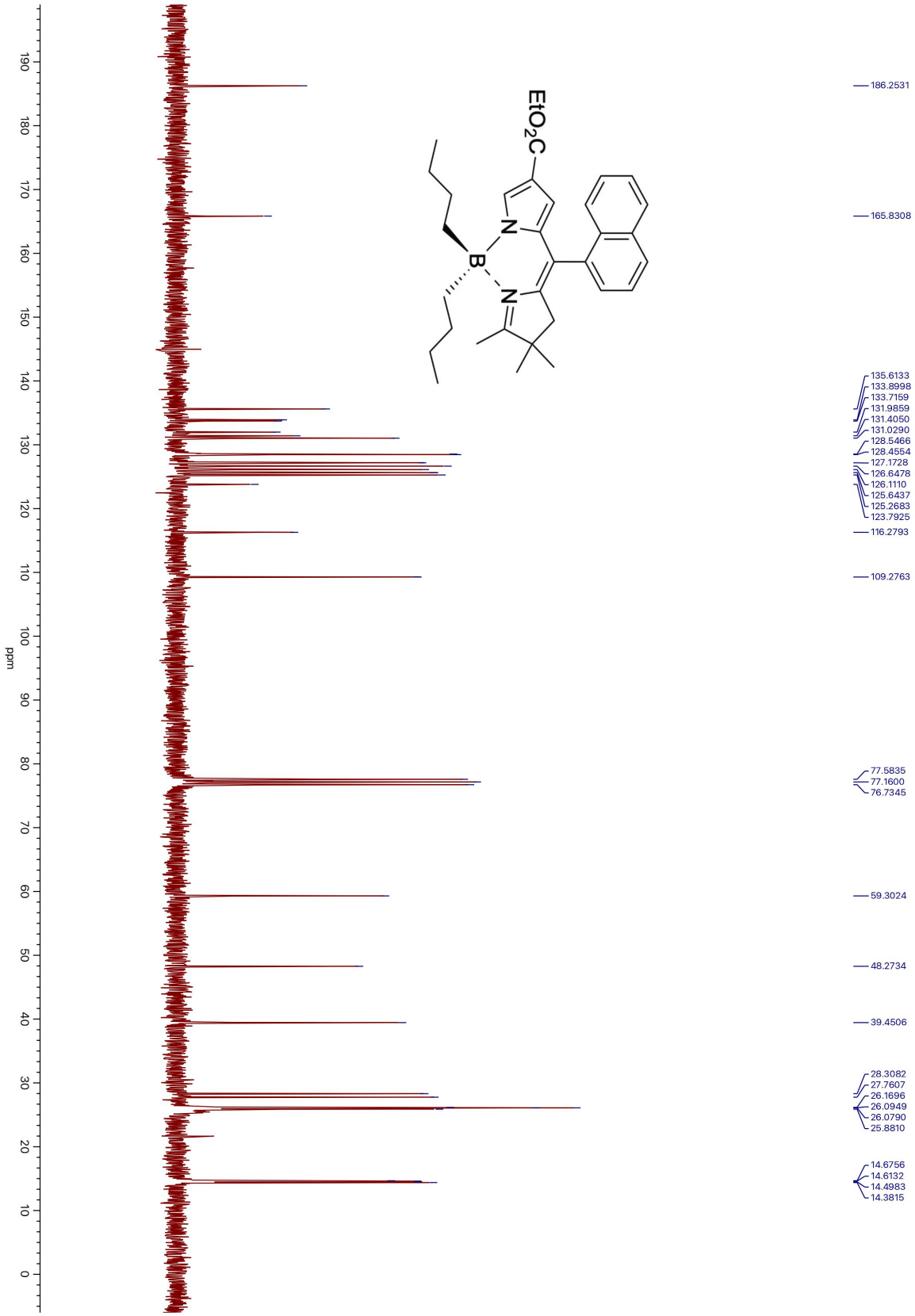
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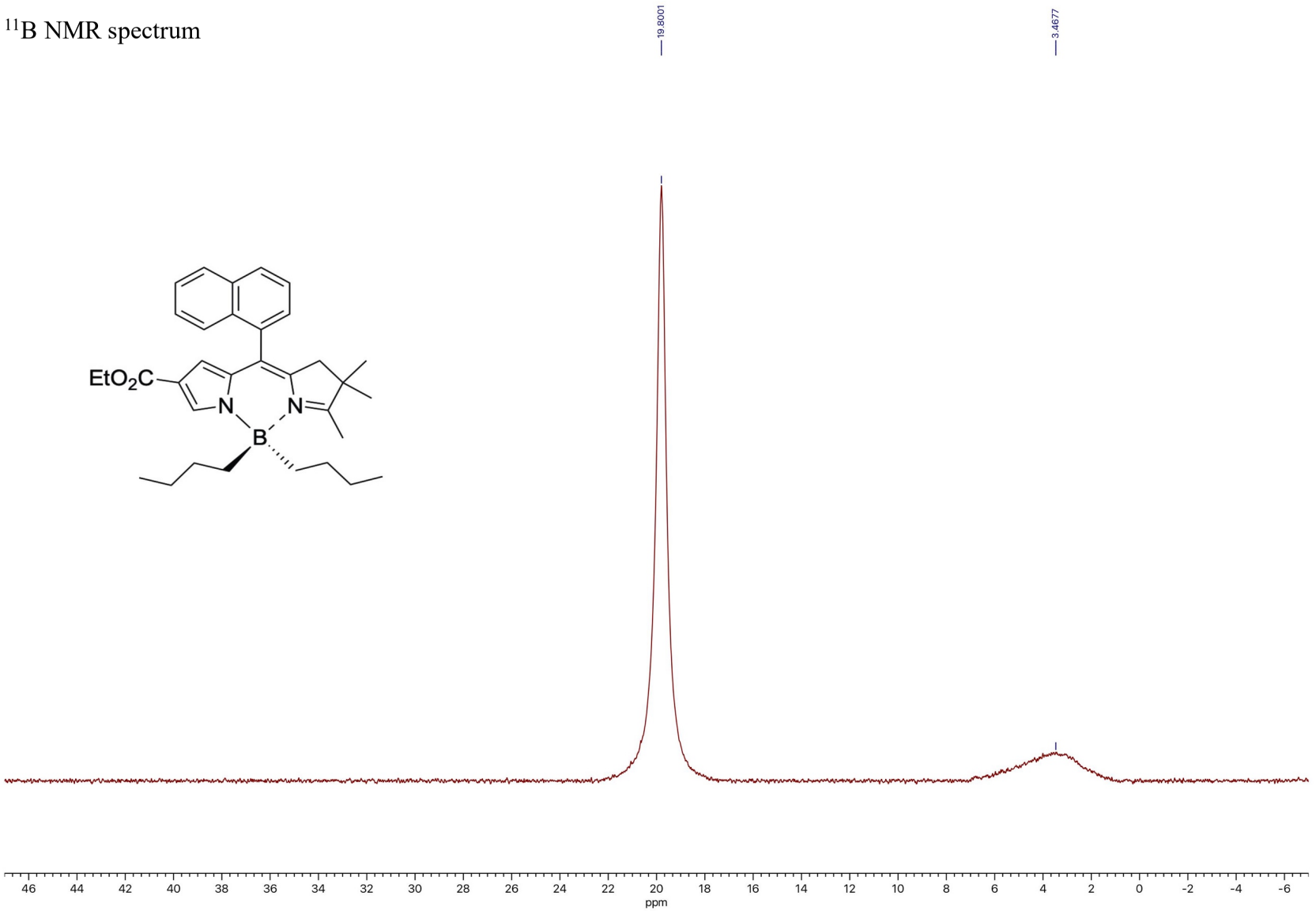
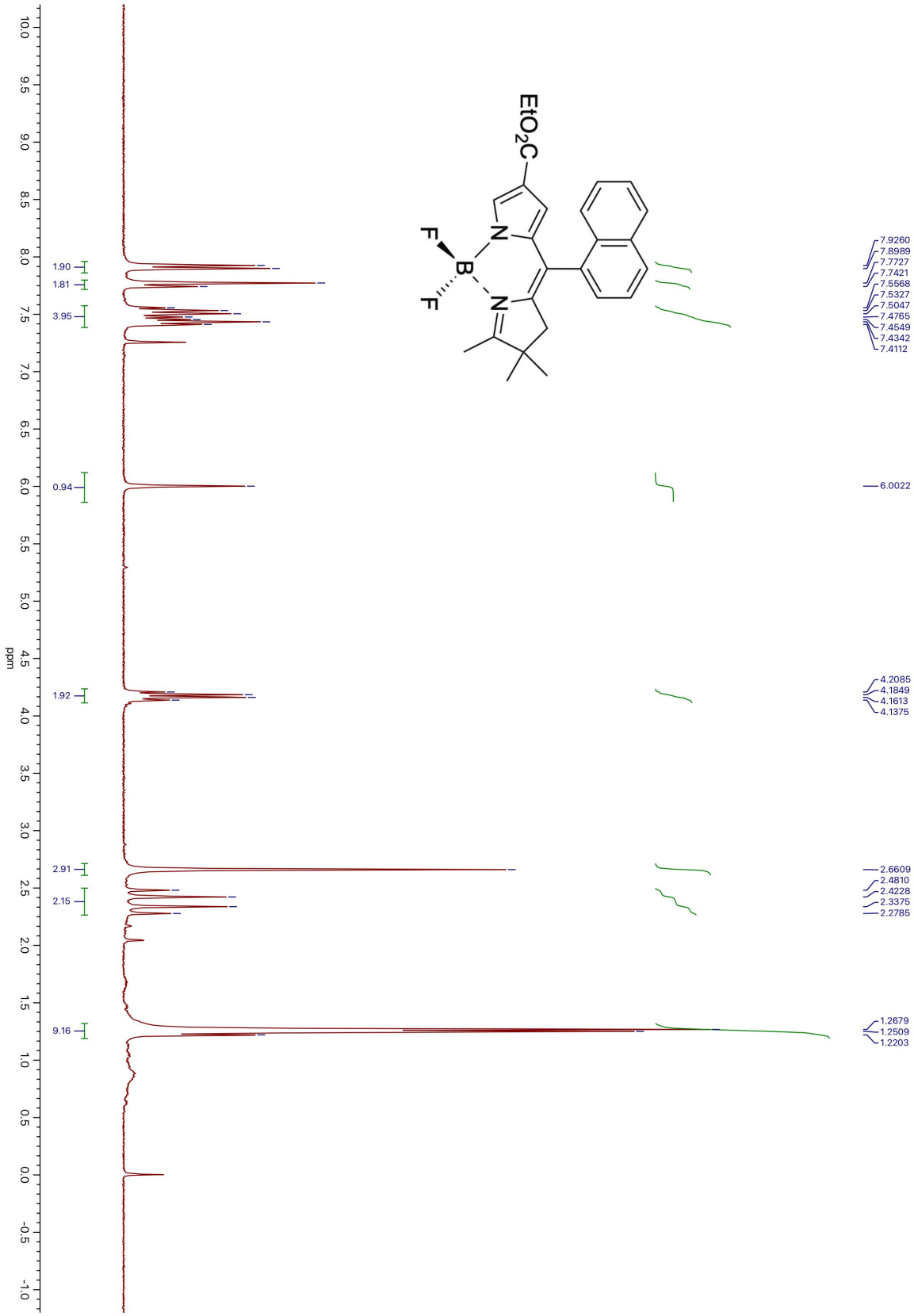
^{11}B NMR spectrum

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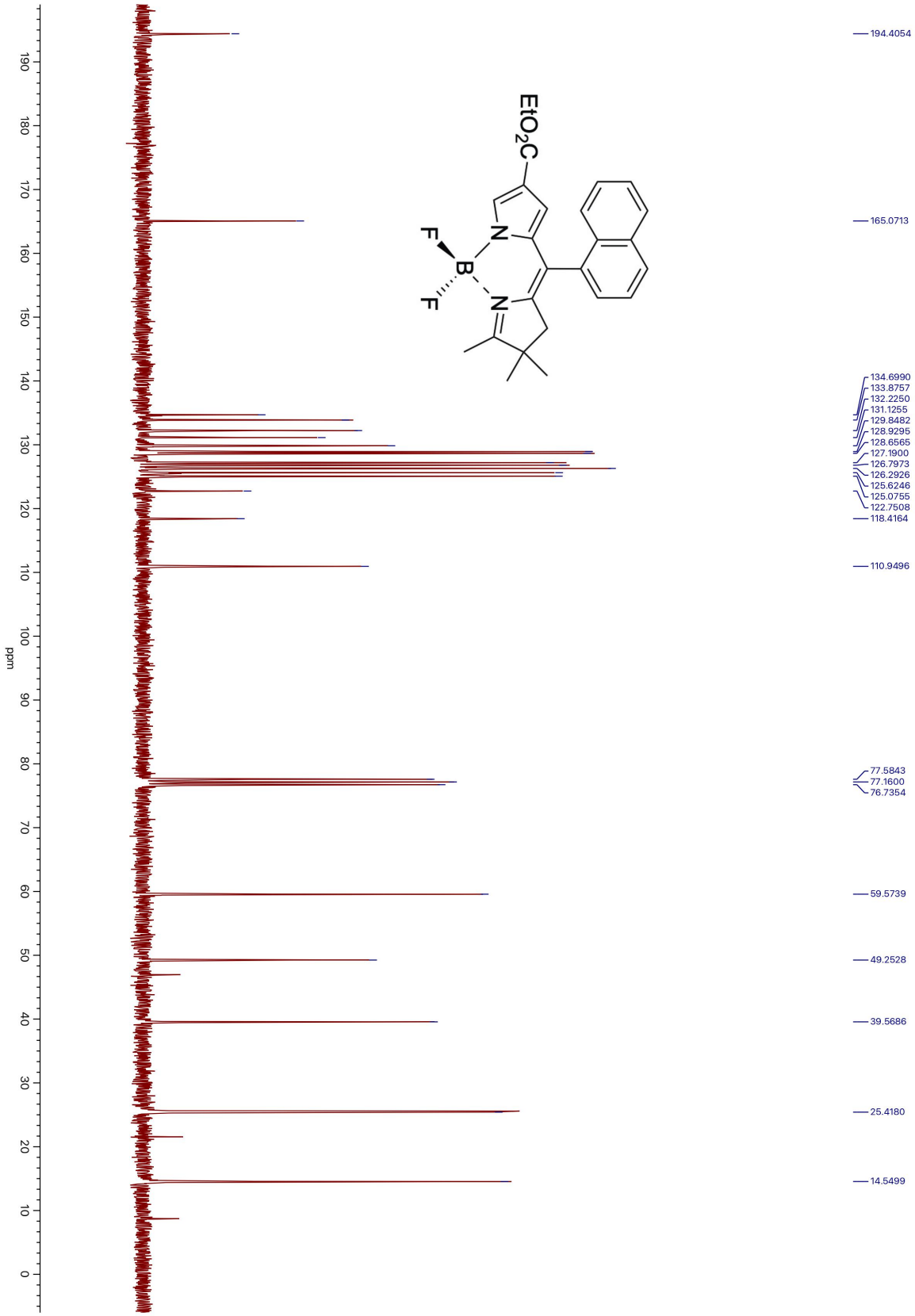
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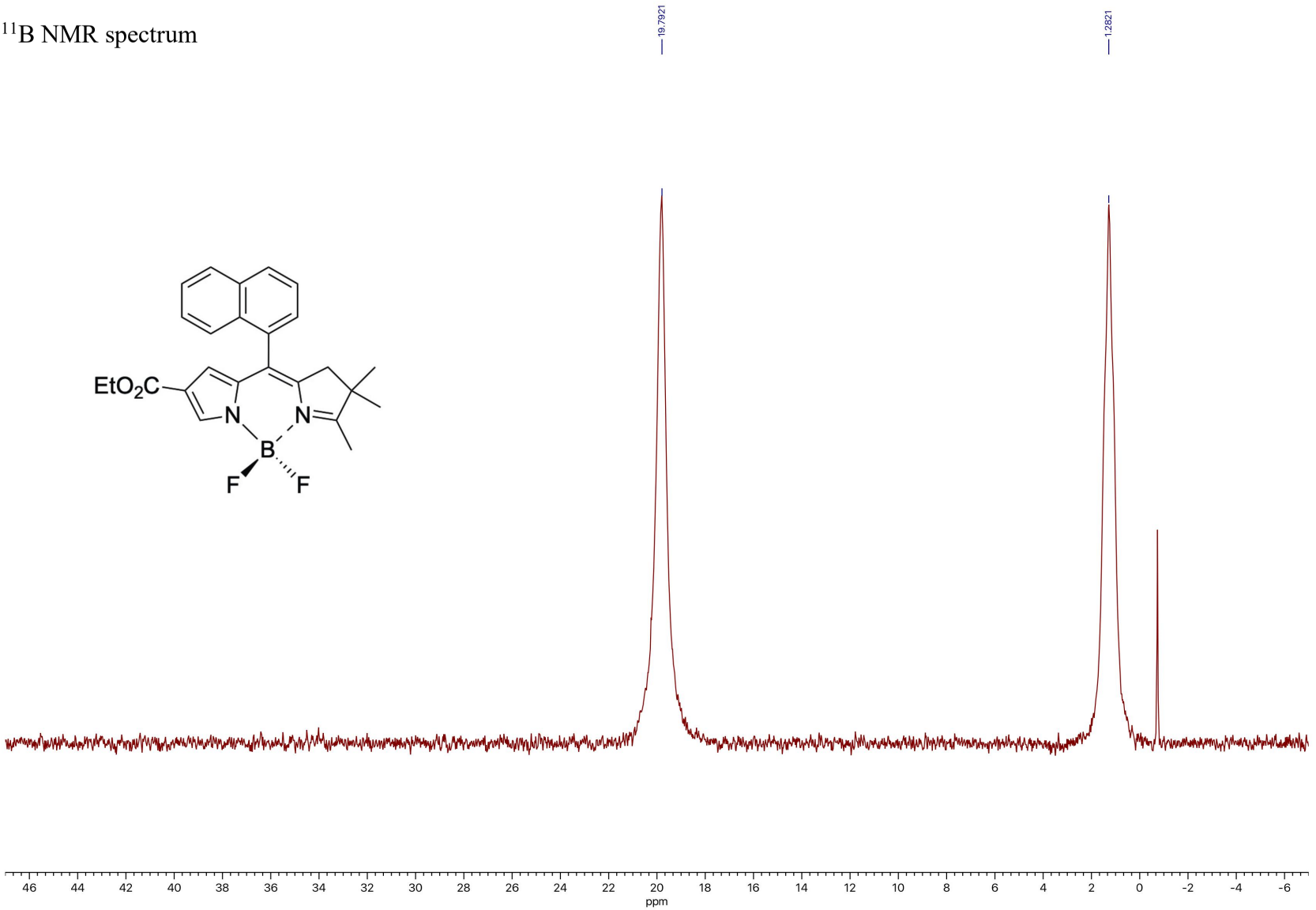
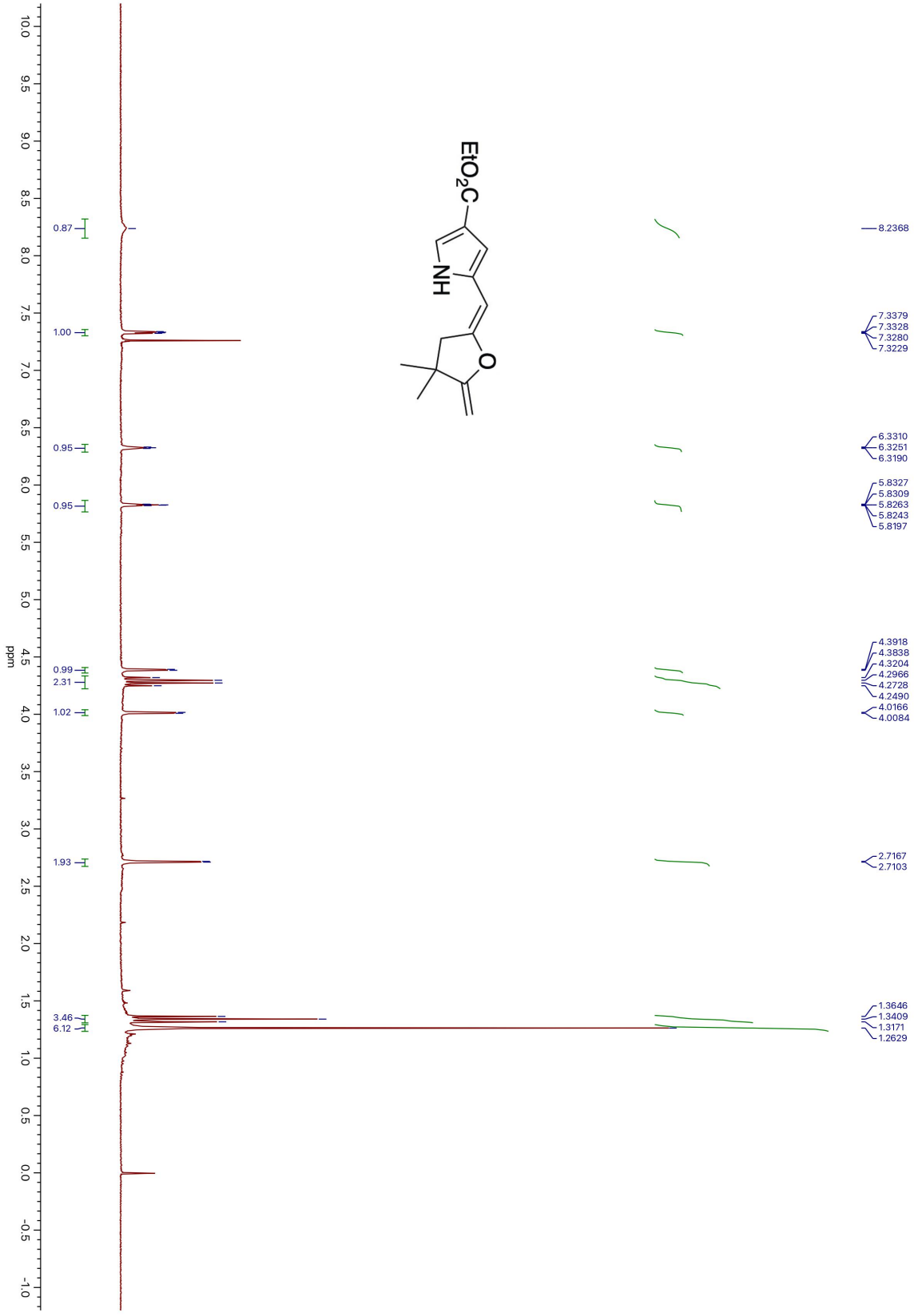
EtO2C
N
B
F
F
N

^{11}B NMR spectrum

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8.0
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7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
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1.00
0.95
0.95
0.99
2.31
1.02
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7.3280
7.3229
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5.8309
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5.8243
5.8197
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4.3204
4.2966
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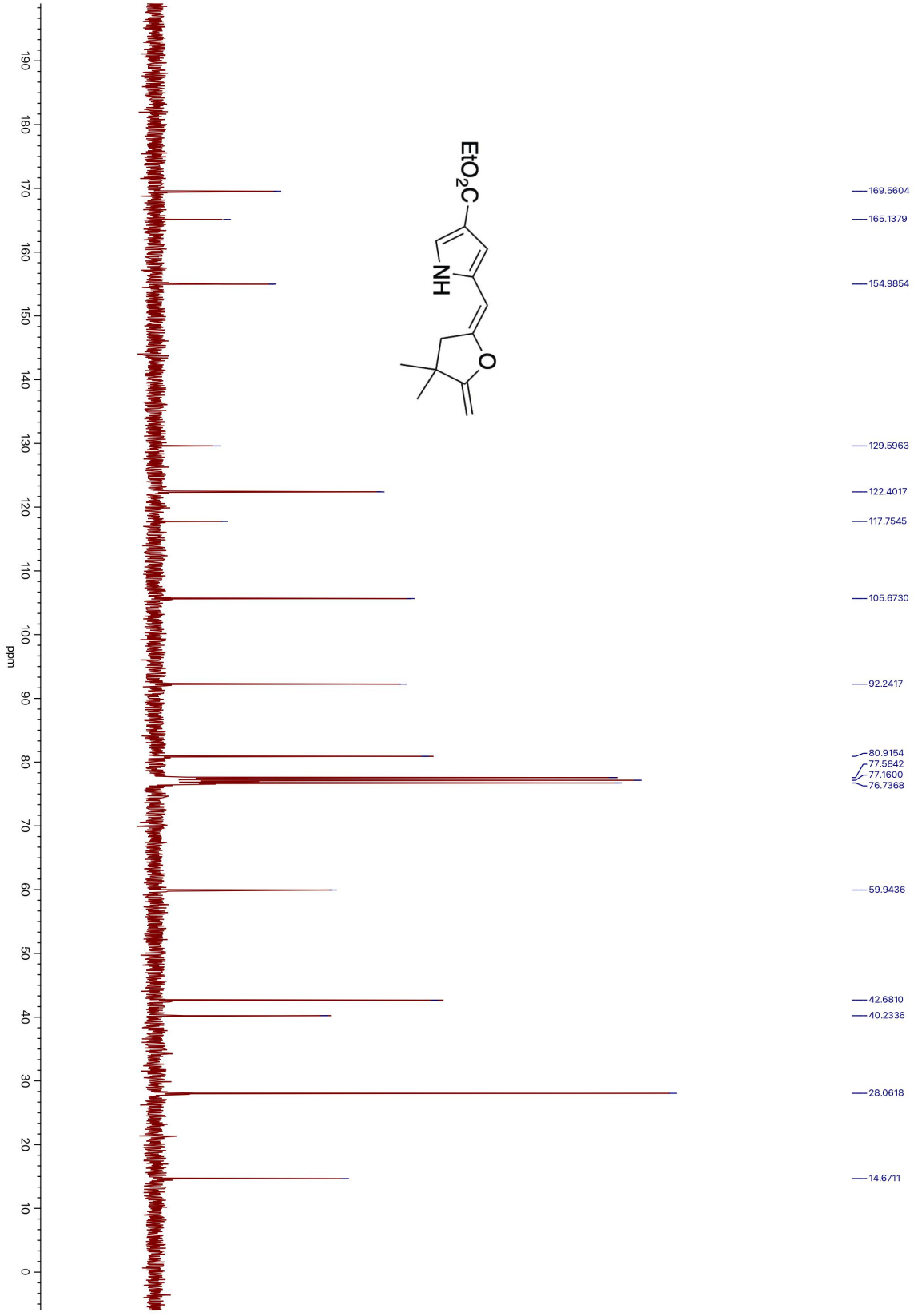
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O
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