Synthesis

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Supporting Information

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Supporting Information

Ni-catalyzed C-F/N-H annulation of 2-(2-fluoroaryl)-*N*-heteroaromatic compounds with alkynes: Activation of C-F bonds

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1. X-ray structure of 3af

To provide further evidence, compound **3af** was crystalized from acetone and structural and crystallographic information for compound **3af** is given below.

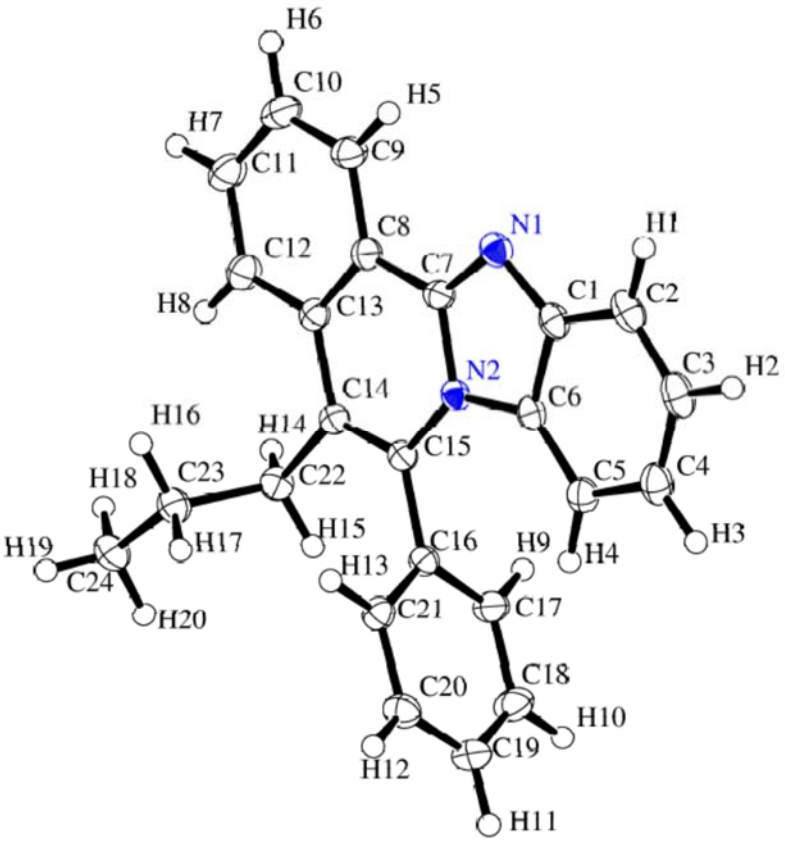


Figure S1. The structure of **3af** was determined by the X-ray diffraction. Hydrogen atoms are not labelled for clarity. Thermal ellipsoids are drawn at the 50% probability level.

CCDC 2046289 contains supplementary crystallographic data for compound **3af**. A colorless prism crystal of $C_{24}H_{20}N_2$ having approximate dimensions of 0.700 x 0.600 x 0.300 mm was mounted on a glass fiber. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Kα radiation. The data were collected at a temperature of -150 ± 1 ℃ to a maximum 2θ value of 61.6°. A total of 592 oscillation images were collected. A sweep of data was done using w scans from 16.0 to 42.0° in 0.50° step, at χ = -114.0° and φ = -102.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was 5.34°. A second sweep was performed using w scans from 0.0 to 26.0° in 0.50° step, at χ = -99.0° and φ = -30.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was -5.18°. Another sweep was performed using w scans from -3.0 to 28.0° in 0.50° step, at χ = -99.0° and φ = 0.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was -5.18°. Another sweep was performed using w scans from -26.0 to 23.0° in 0.50° step, at χ = -99.0° and φ = 120.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was 5.34°. Another sweep was performed using w scans from -26.0 to 27.0° in 0.50° step, at χ = -99.0° and φ = 150.0°. The exposure rate was 2.5 [sec./°]. The detector swing

angle was -5.18°. Another sweep was performed using w scans from -20.0 to 5.0° in 0.50° step, at χ = -99.0° and φ = -150.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was -5.18°. Another sweep was performed using ω scans from -23.0 to 38.0° in 0.50° step, at χ = -99.0° and φ = -180.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was 5.34°. Another sweep was performed using ω scans from 49.0 to 74.0° in 0.50° step, at χ = 38.0° and φ = -180.0°. The exposure rate was 2.5 [sec./°]. The detector swing angle was 5.34°. The crystal-to-detector distance was 35.00 mm. Readout was performed in the 0.172 mm pixel mode.

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL97[3].

Table S1. Crystal Data

Empirical Formula	$C_{24}H_{20}N_2$
Formula Weight	336.44
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.700 x 0.600 x 0.300 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.7325(4) Å
	b = 15.4375(6) Å
	c = 11.7681(4) Å
	β = 100.832(3)°
	V = 1736.60(12) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.287 g/cm^3
F_{000}	712.00
m(MoKα)	0.754 cm^{-1}

[1] Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. Completion and refinement of crystal structures with SIR92. *J. Appl. Cryst.* **26**, 343–350 (1993).
[2] Crystal Structure Analysis Package, Rigaku Corporation (2000-2016). Tokyo 196-8666, Japan.
[3] Sheldrick, G. M. A Short History of SHELX. *Acta Cryst.* **A64**, 112–122 (2008).

Table S2. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation	MoKa (λ = 0.71073 Å)
	multi-layer mirror monochromated
Voltage, Current	50kV, 1mA
Temperature	-150.0 °C
Detector Aperture	83.8 x 70.0 mm
Data Images	592 exposures
ω oscillation Range (χ = -114.0, φ = -102.0)	16.0 - 42.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	5.34°
ω oscillation Range (χ = -99.0, φ = -30.0)	0.0 - 26.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	-5.18°
ω oscillation Range (χ = -99.0, φ = 0.0)	-3.0 - 28.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	-5.18°
ω oscillation Range (χ = -99.0, φ = 120.0)	-26.0 - 23.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	5.34°
ω oscillation Range (χ = -99.0, φ = 150.0)	-26.0 - 27.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	-5.18°
ω oscillation Range (χ = -99.0, φ = -150.0)	-20.0 - 5.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	-5.18°
ω oscillation Range (χ = -99.0, φ = -180.0)	-23.0 - 38.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	5.34°
ω oscillation Range (χ = 38.0, φ = -180.0)	49.0 - 74.0°
Exposure Rate	2.5 sec./°
Detector Swing Angle	5.34°
Detector Position	35.00 mm
Pixel Size	0.172 mm
$2\theta_{max}$	61.6°
No. of Reflections Measured	Total: 17745
	Unique: 4481 (R_{int} = 0.0334)

Corrections	Lorentz-polarization Absorption (trans. factors: 0.580 - 0.978)

Table S3. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$S\ w\ (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(F_o^2) + (0.0761 \cdot P)^2 + 0.2112 \cdot P]$ where $P = (Max(F_o^2,0) + 2\ F_c^2)/3$
$2\theta_{max}$ cutoff	61.6°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4481
No. Variables	315
Reflection/Parameter Ratio	14.23
Residuals: R1 (I>2.00σ(I))	0.0456
Residuals: R (All reflections)	0.0534
Residuals: wR2 (All reflections)	0.1300
Goodness of Fit Indicator	1.102
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.23 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.39 $e^-/Å^3$

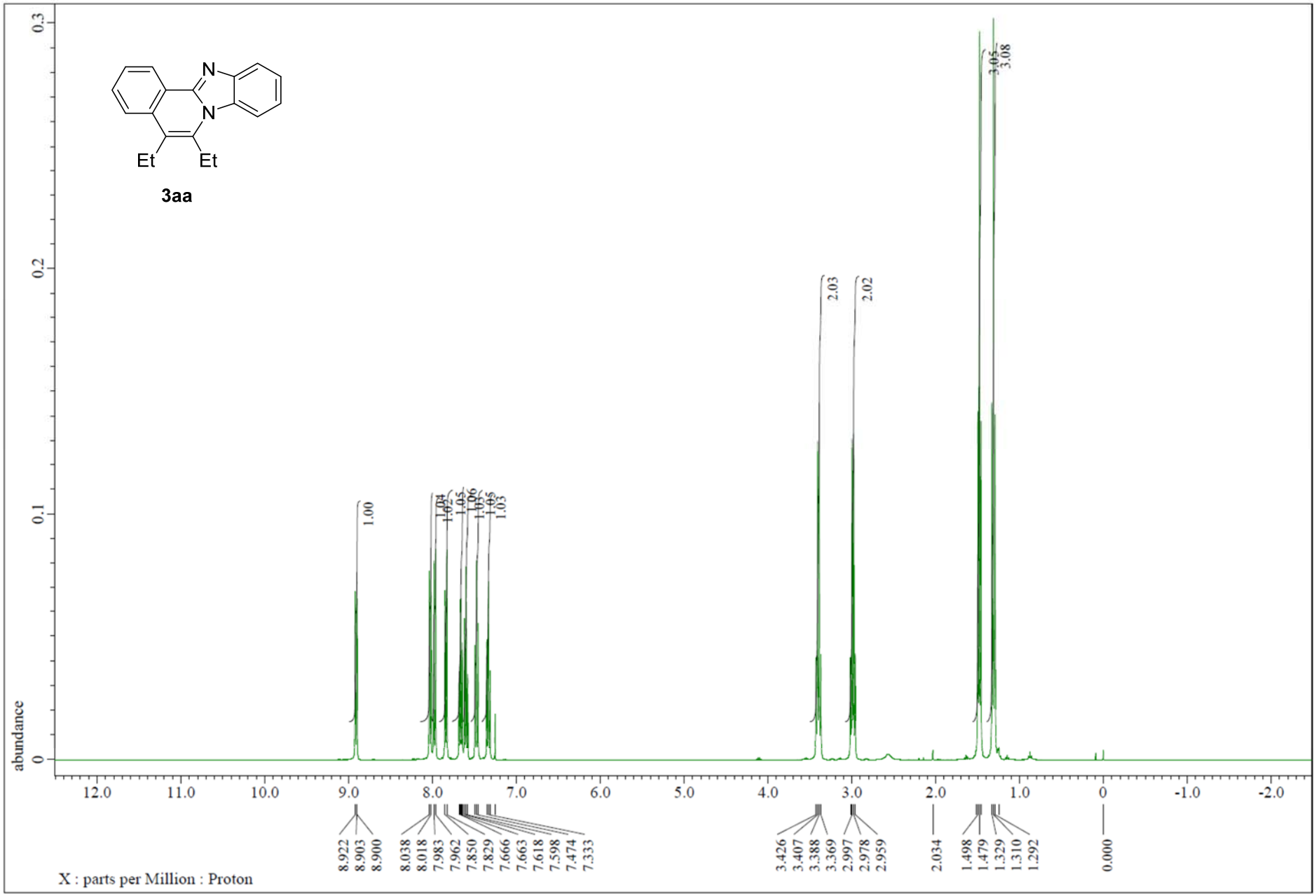
Table S4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
N1	C1	1.3793(14)	N1	C7	1.3182(13)
N2	C6	1.4008(13)	N2	C7	1.3902(14)
N2	C15	1.4047(12)	C1	C2	1.4028(15)
C1	C6	1.4052(14)	C2	C3	1.3778(19)
C3	C4	1.3991(18)	C4	C5	1.3844(15)
C5	C6	1.3957(16)	C7	C8	1.4362(15)
C8	C9	1.4012(15)	C8	C13	1.4080(14)
C9	C10	1.3745(17)	C10	C11	1.3943(17)
C11	C12	1.3768(18)	C12	C13	1.4104(16)
C13	C14	1.4568(15)	C14	C15	1.3543(14)
C14	C22	1.5084(14)	C15	C16	1.4876(15)
C16	C17	1.3911(16)	C16	C21	1.3941(16)
C17	C18	1.3876(16)	C18	C19	1.3861(19)
C19	C20	1.3853(17)	C20	C21	1.3847(17)
C22	C23	1.5309(16)	C23	C24	1.5206(15)

Table S5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C1	N1	C7	104.50(9)	C6	N2	C7	105.82(8)
C6	N2	C15	131.65(9)	C7	N2	C15	122.52(8)
N1	C1	C2	128.14(10)	N1	C1	C6	111.58(9)
C2	C1	C6	120.28(10)	C1	C2	C3	117.95(11)
C2	C3	C4	121.20(10)	C3	C4	C5	121.96(12)
C4	C5	C6	116.91(11)	N2	C6	C1	104.56(9)
N2	C6	C5	133.75(9)	C1	C6	C5	121.67(9)
N1	C7	N2	113.53(9)	N1	C7	C8	127.54(10)
N2	C7	C8	118.92(9)	C7	C8	C9	120.32(9)
C7	C8	C13	118.76(10)	C9	C8	C13	120.91(10)
C8	C9	C10	120.15(10)	C9	C10	C11	119.81(11)
C10	C11	C12	120.57(11)	C11	C12	C13	121.12(10)
C8	C13	C12	117.43(10)	C8	C13	C14	119.76(9)
C12	C13	C14	122.81(9)	C13	C14	C15	120.37(9)
C13	C14	C22	119.15(9)	C15	C14	C22	120.46(10)
N2	C15	C14	119.64(10)	N2	C15	C16	115.94(8)
C14	C15	C16	124.37(9)	C15	C16	C17	121.16(10)
C15	C16	C21	119.31(10)	C17	C16	C21	119.47(10)
C16	C17	C18	119.96(12)	C17	C18	C19	120.19(11)
C18	C19	C20	120.10(11)	C19	C20	C21	119.86(11)
C16	C21	C20	120.37(10)	C14	C22	C23	113.86(9)
C22	C23	C24	112.20(10)				

2. Copies of ^{1}H and ^{13}C NMR Spectra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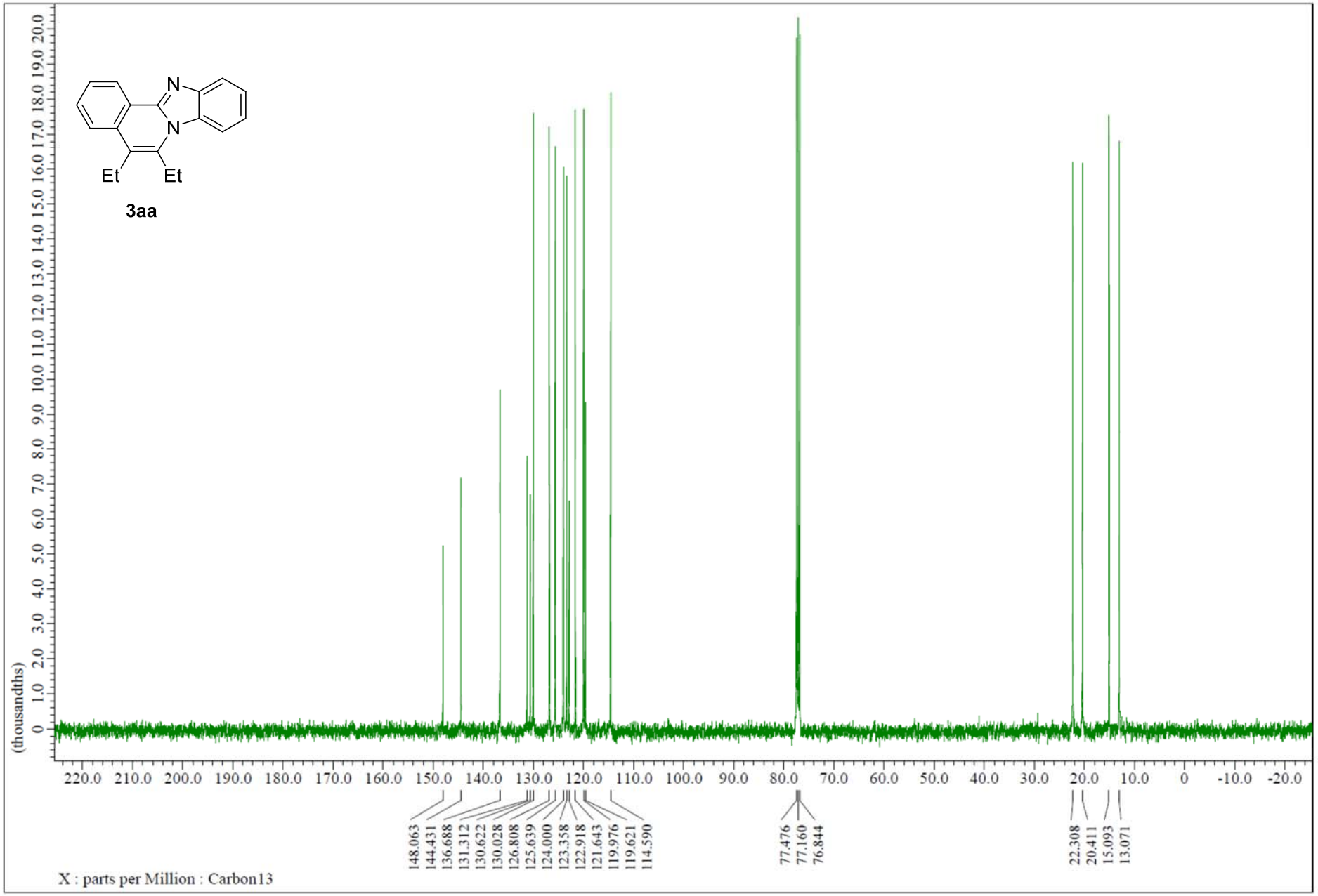
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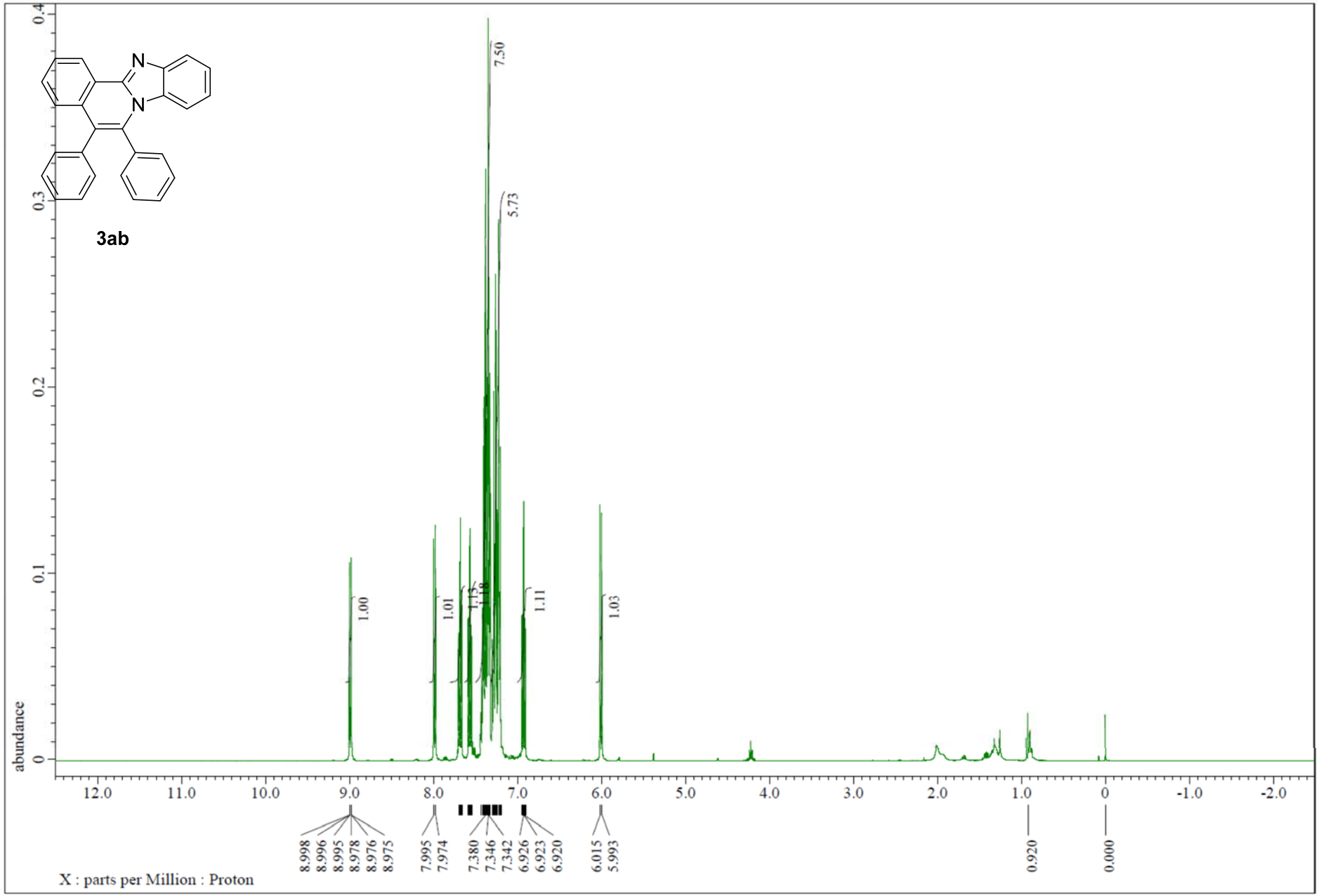
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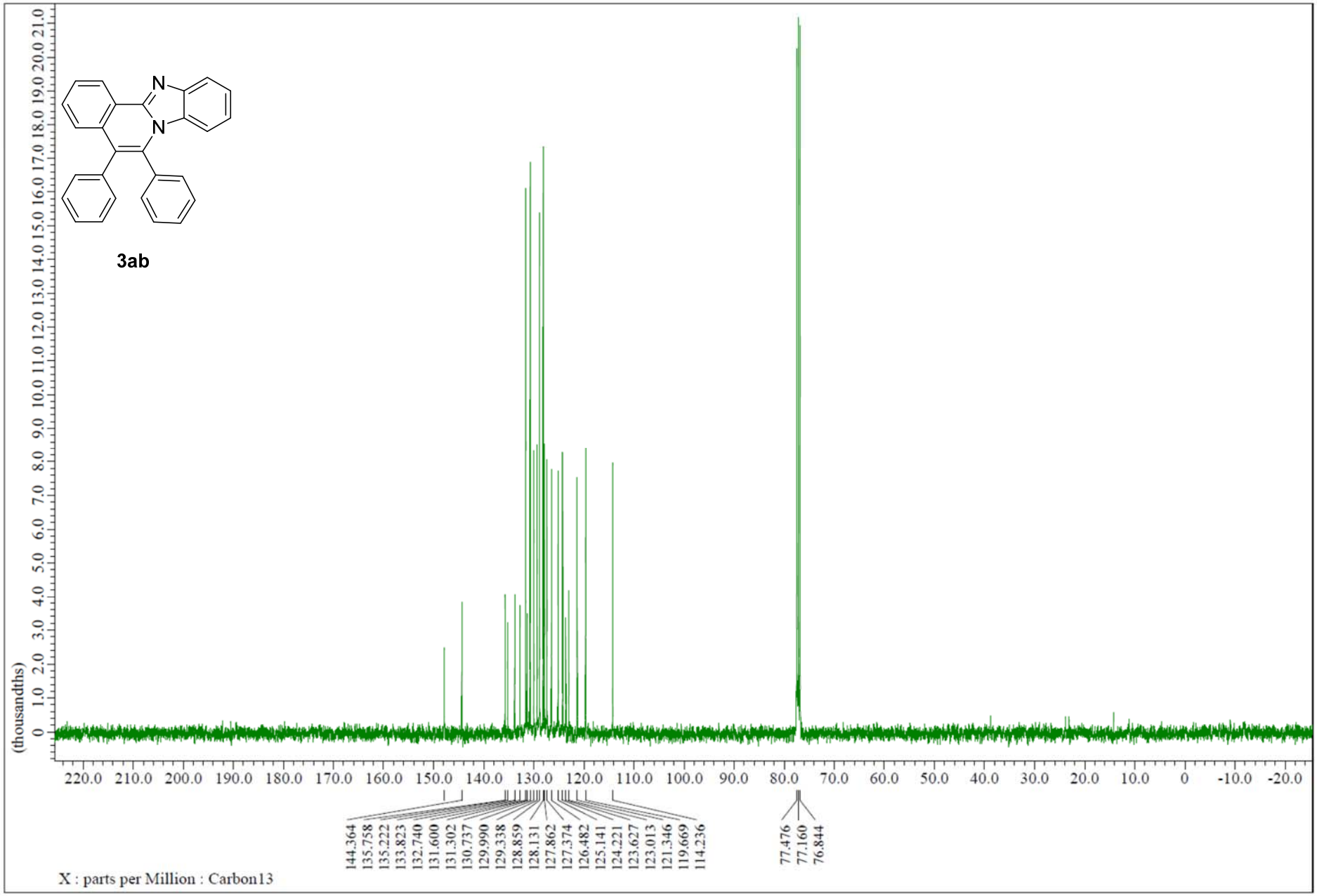
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220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
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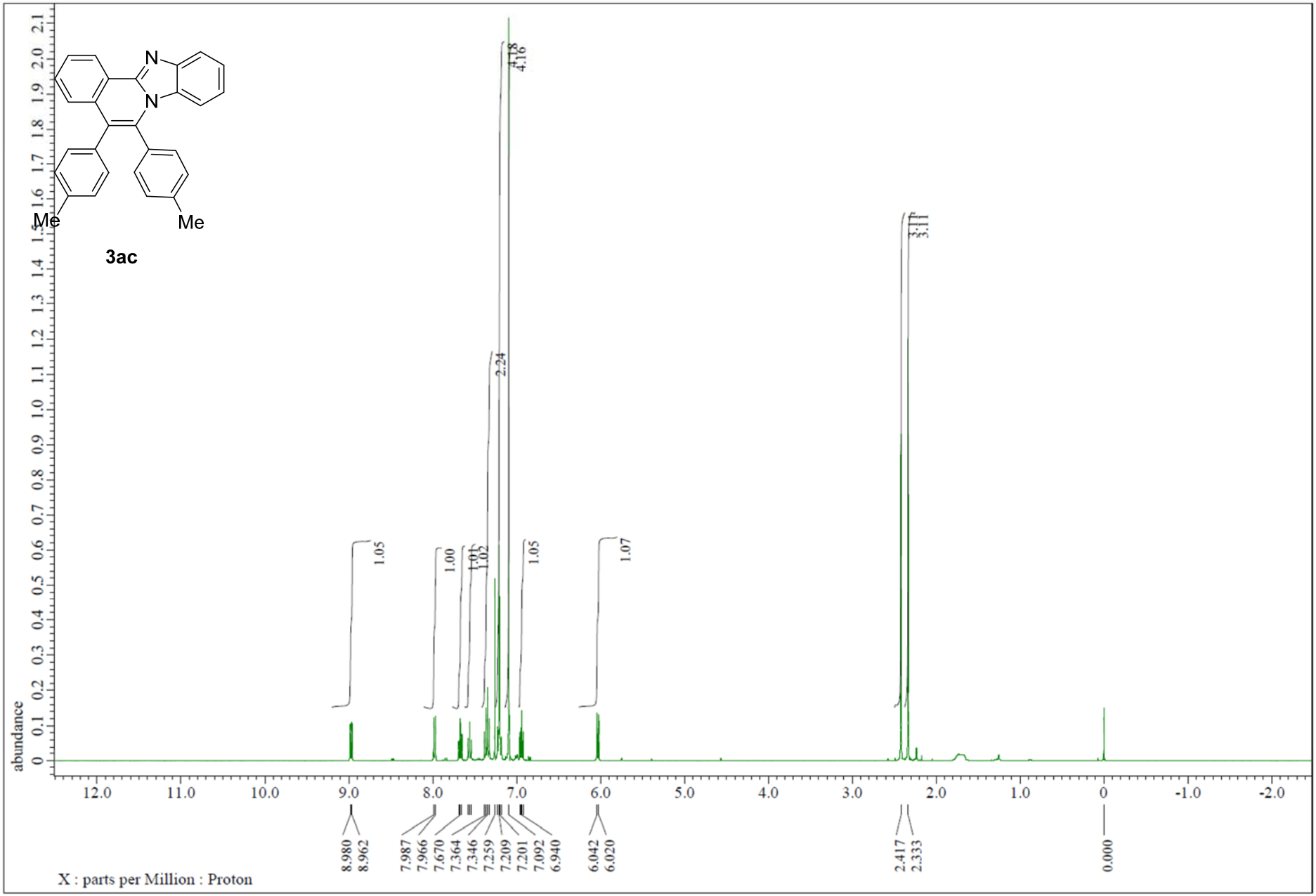
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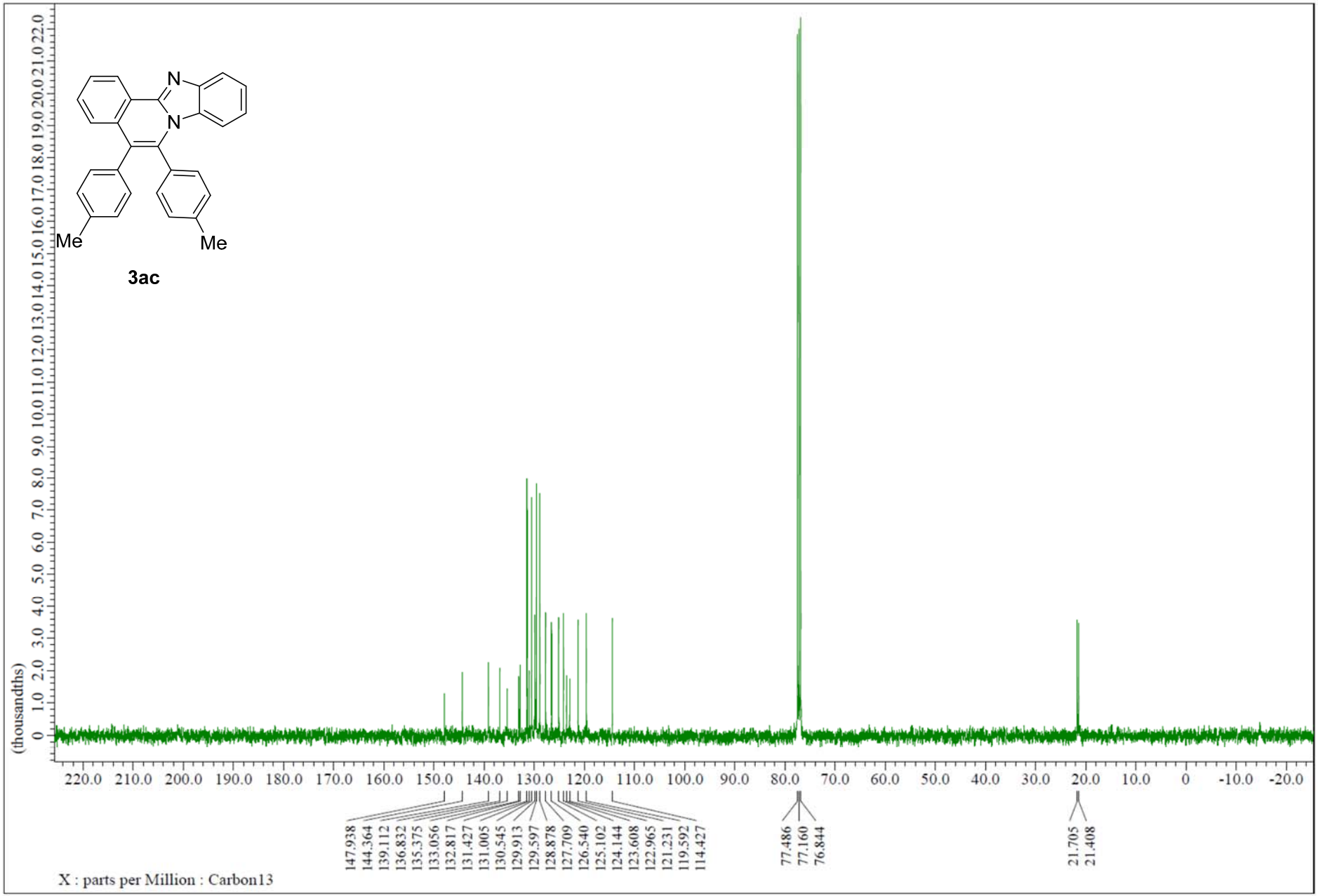
1.07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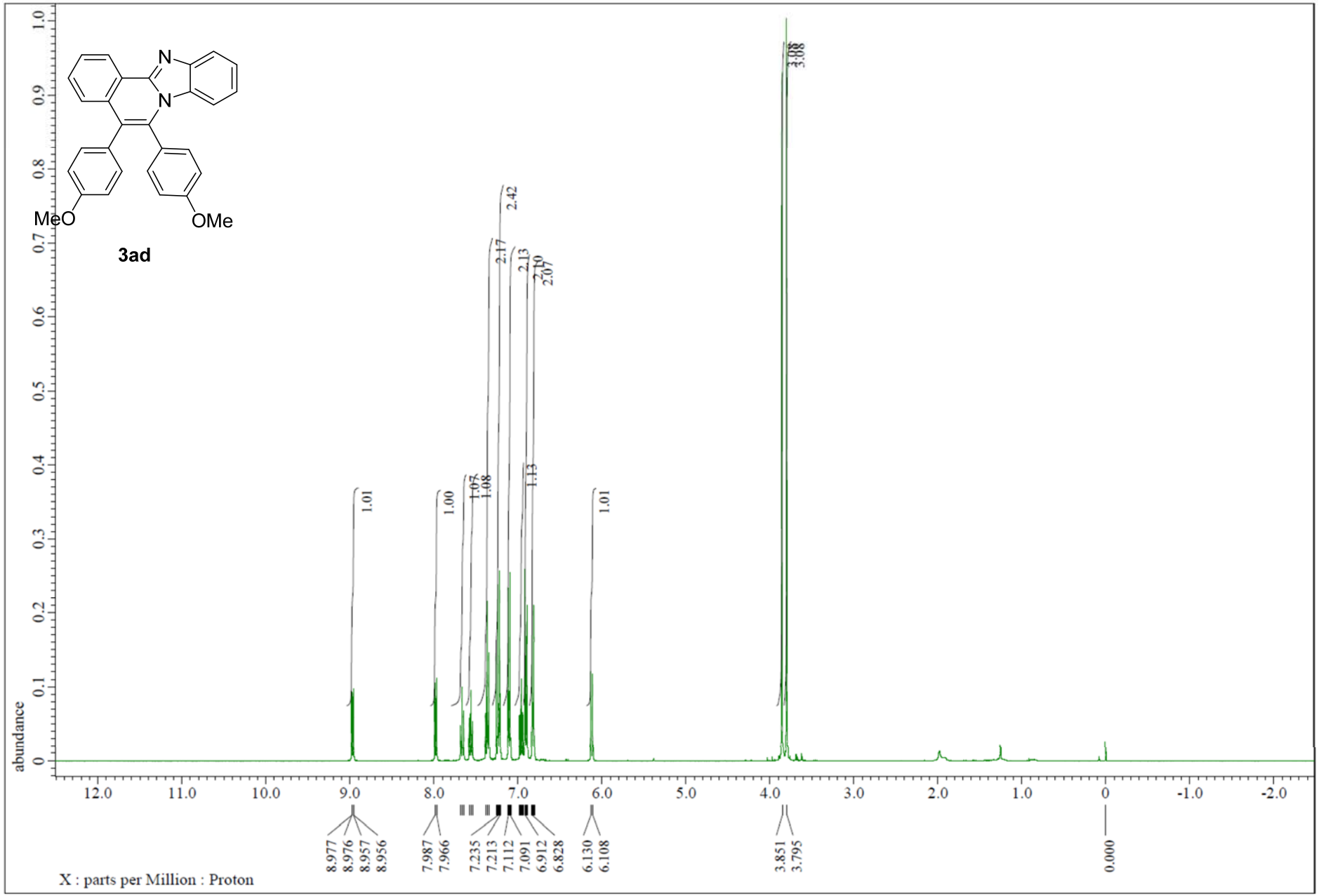
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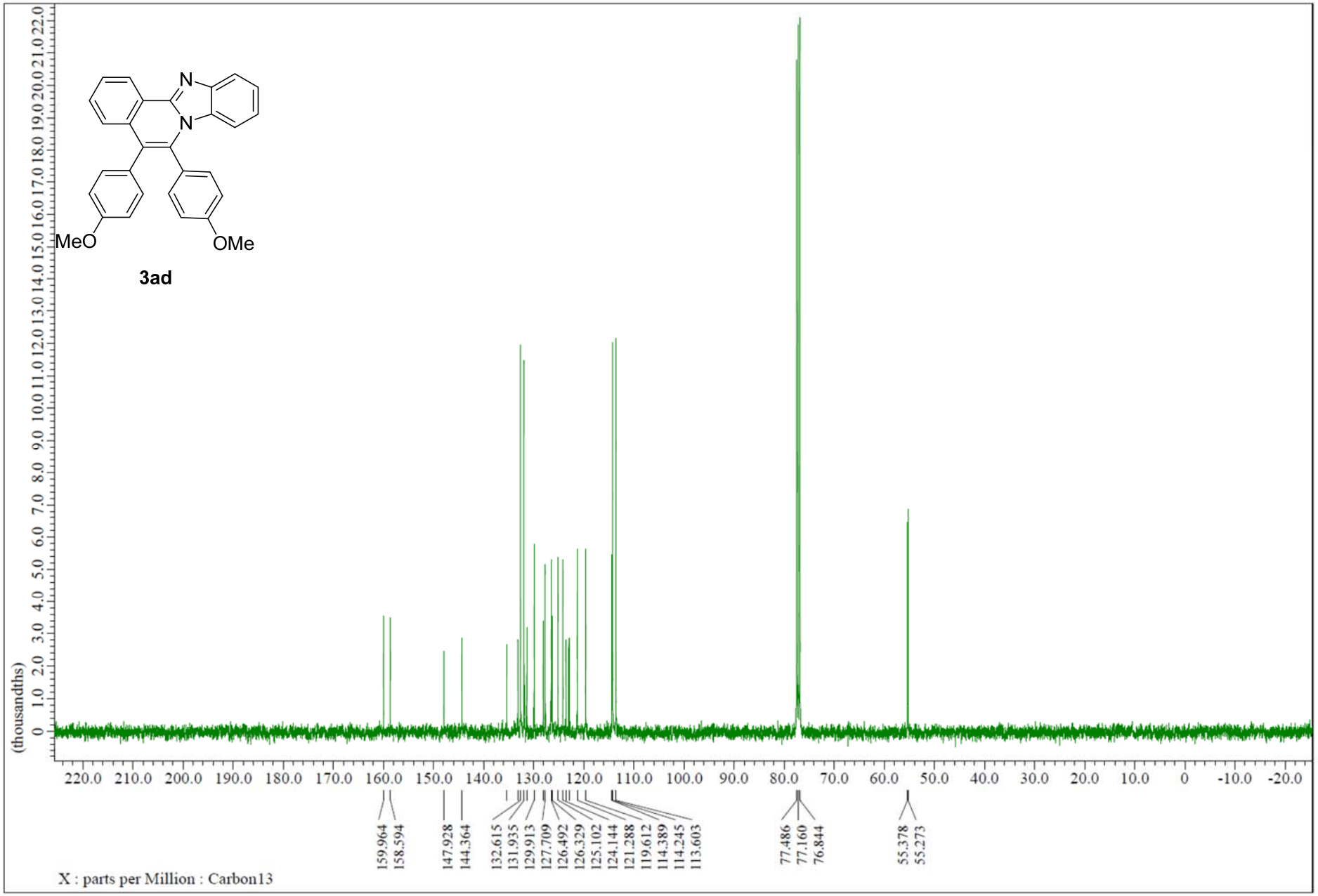
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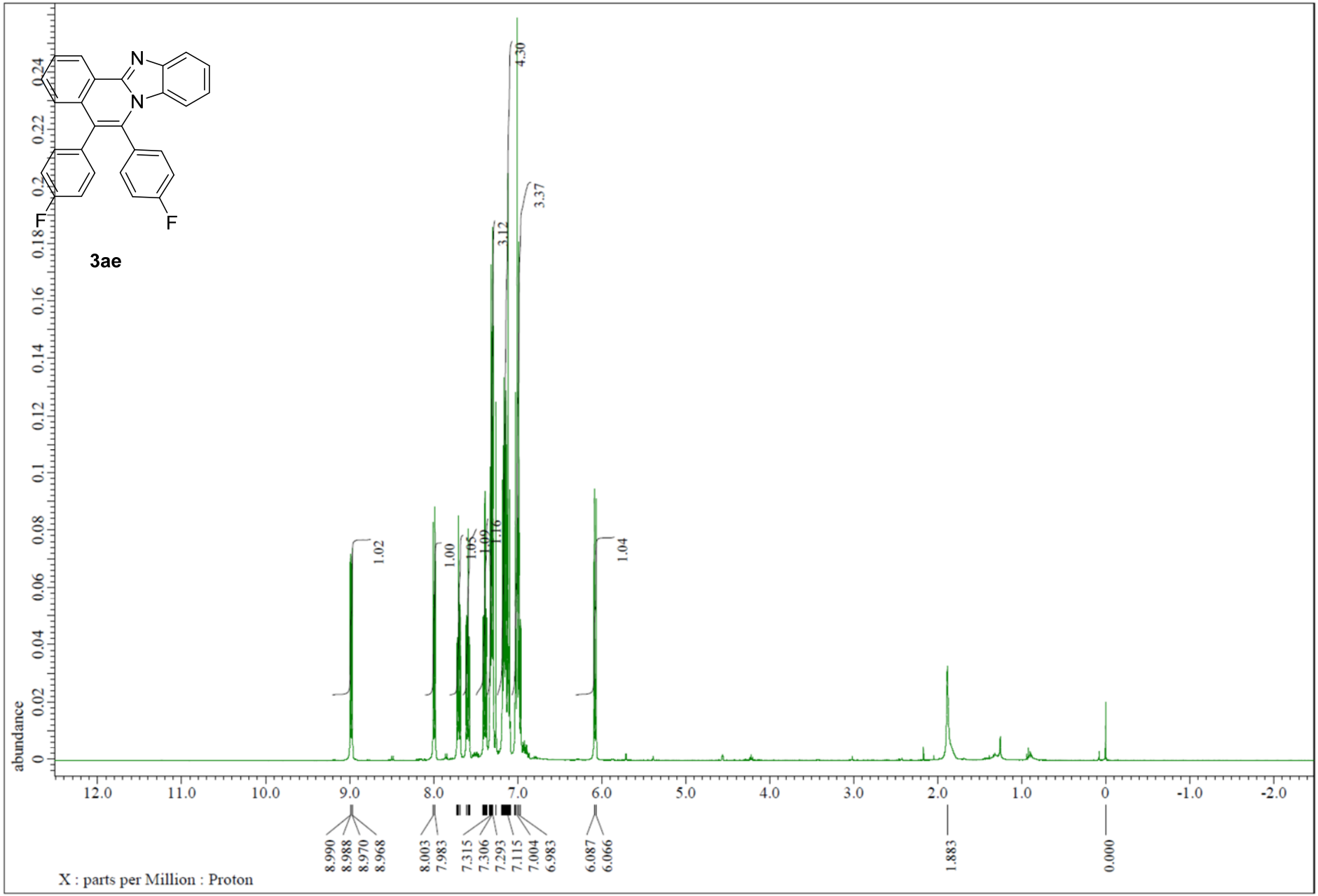
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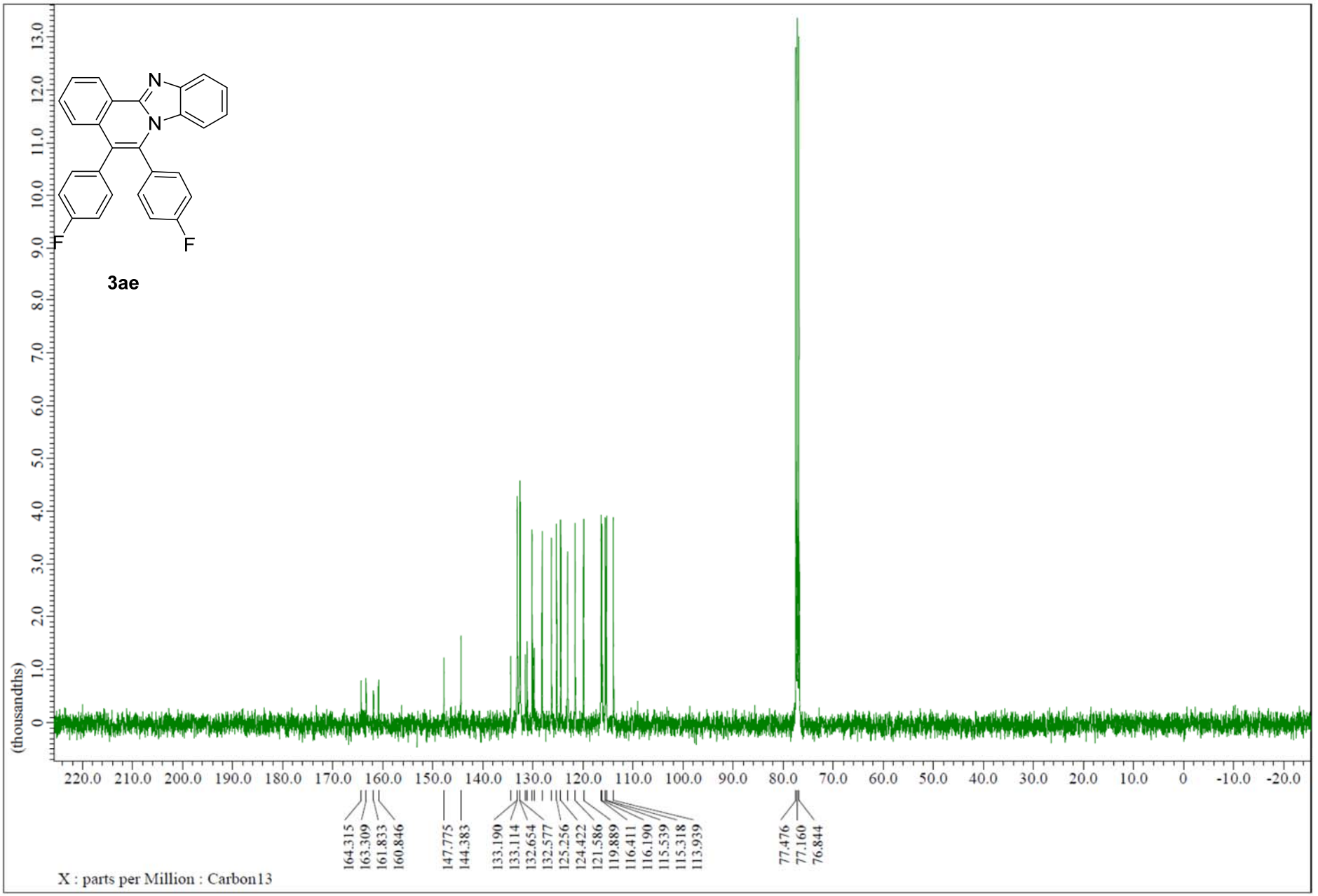
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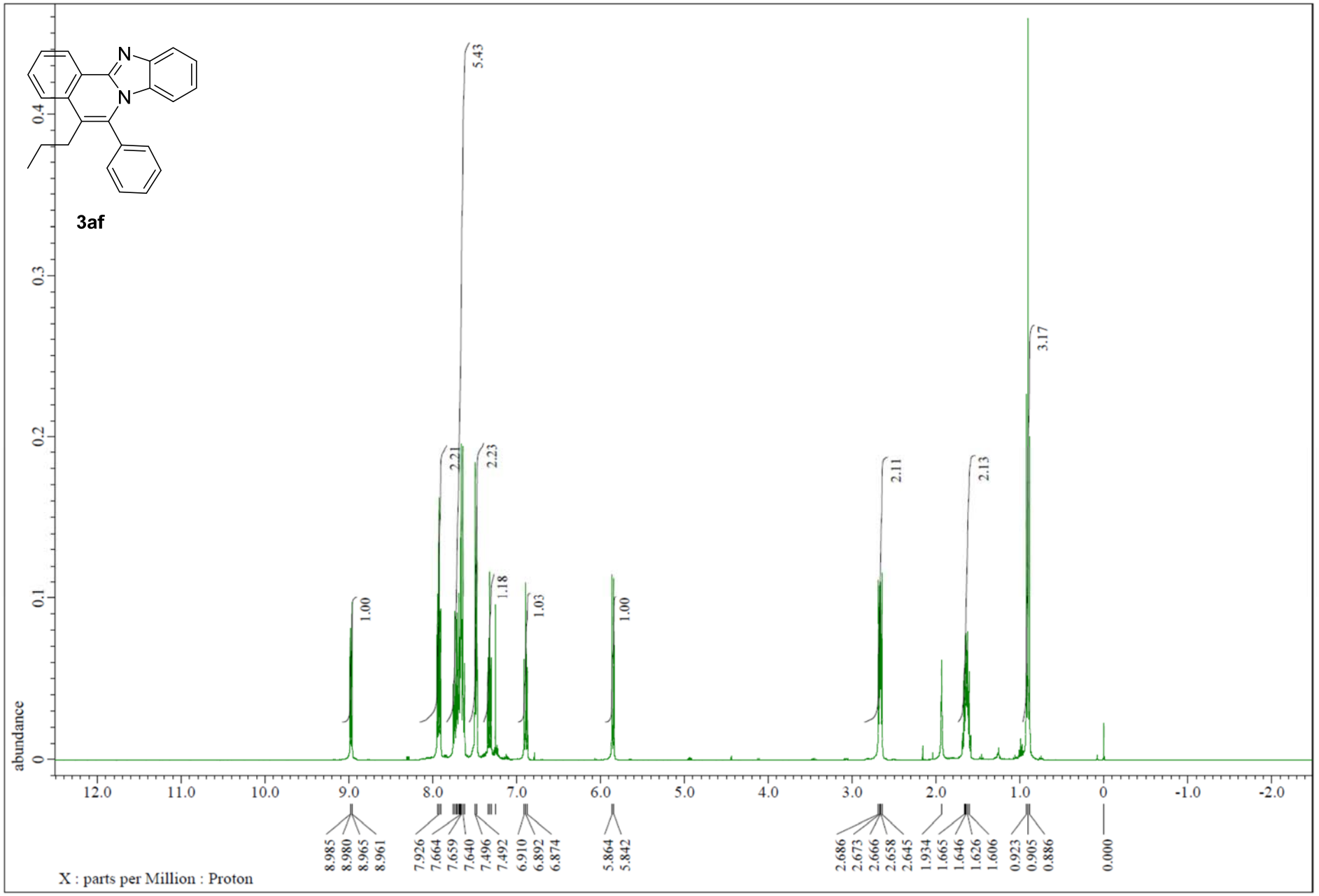
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1.00
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2.13
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8.965
8.961
7.926
7.664
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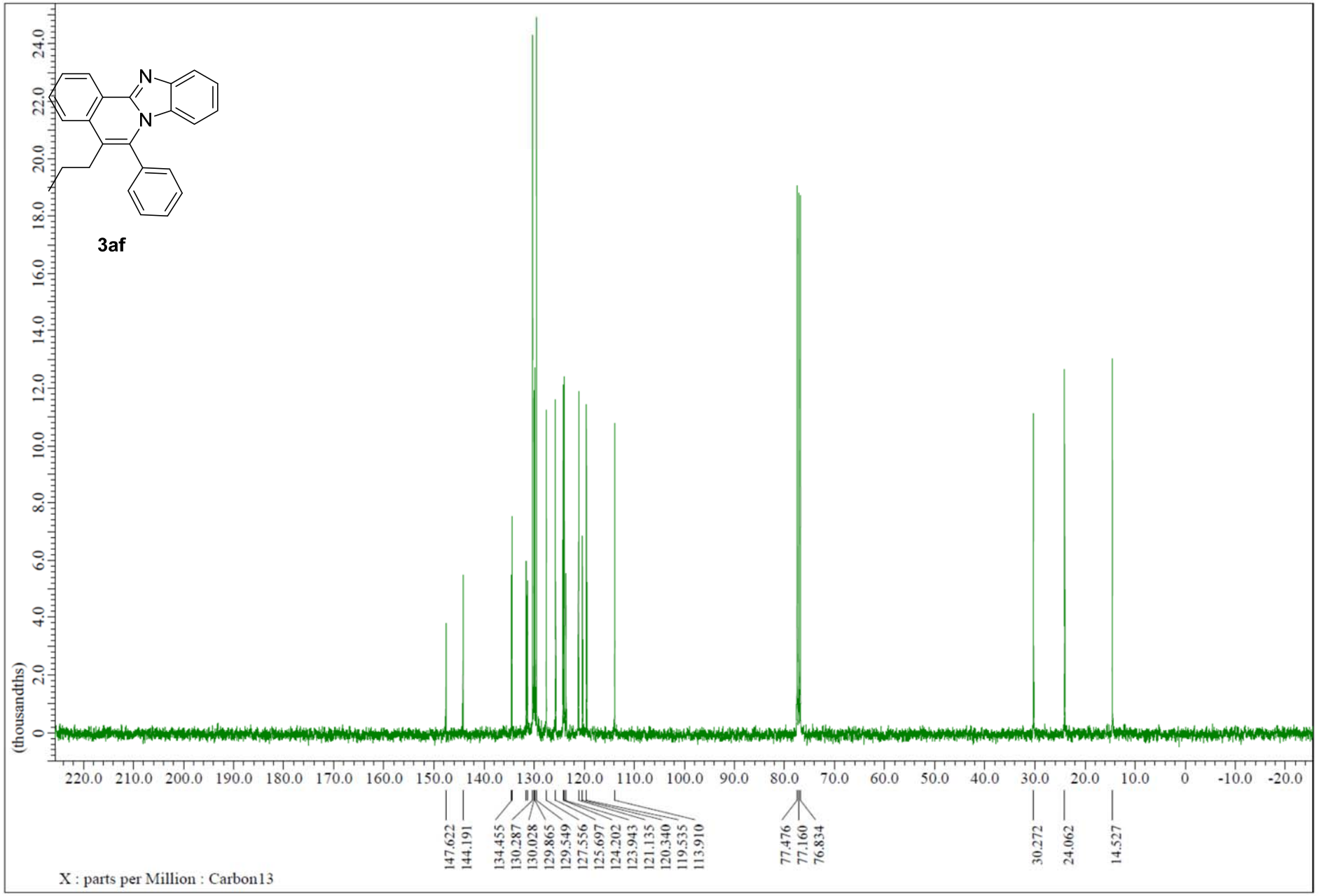
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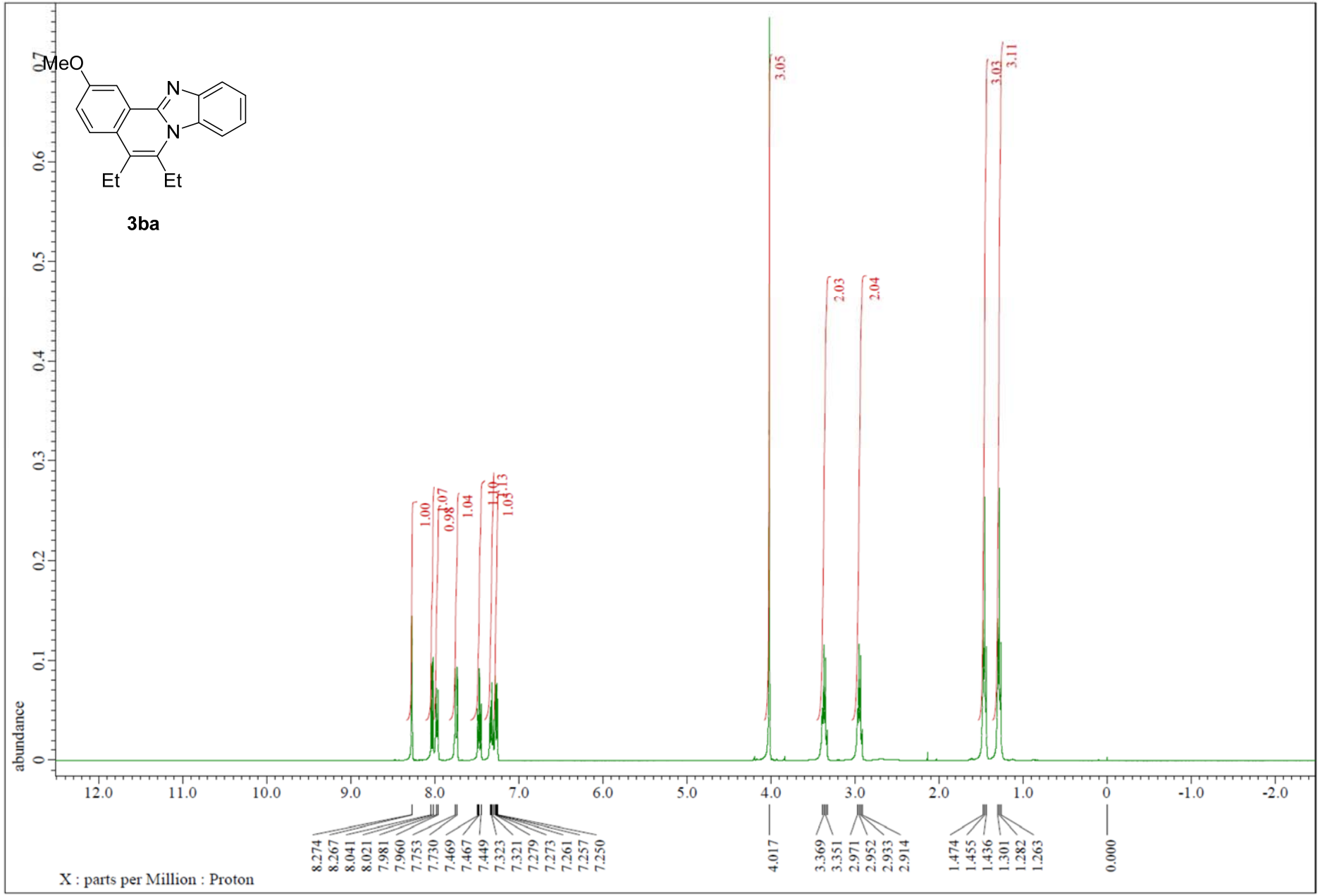
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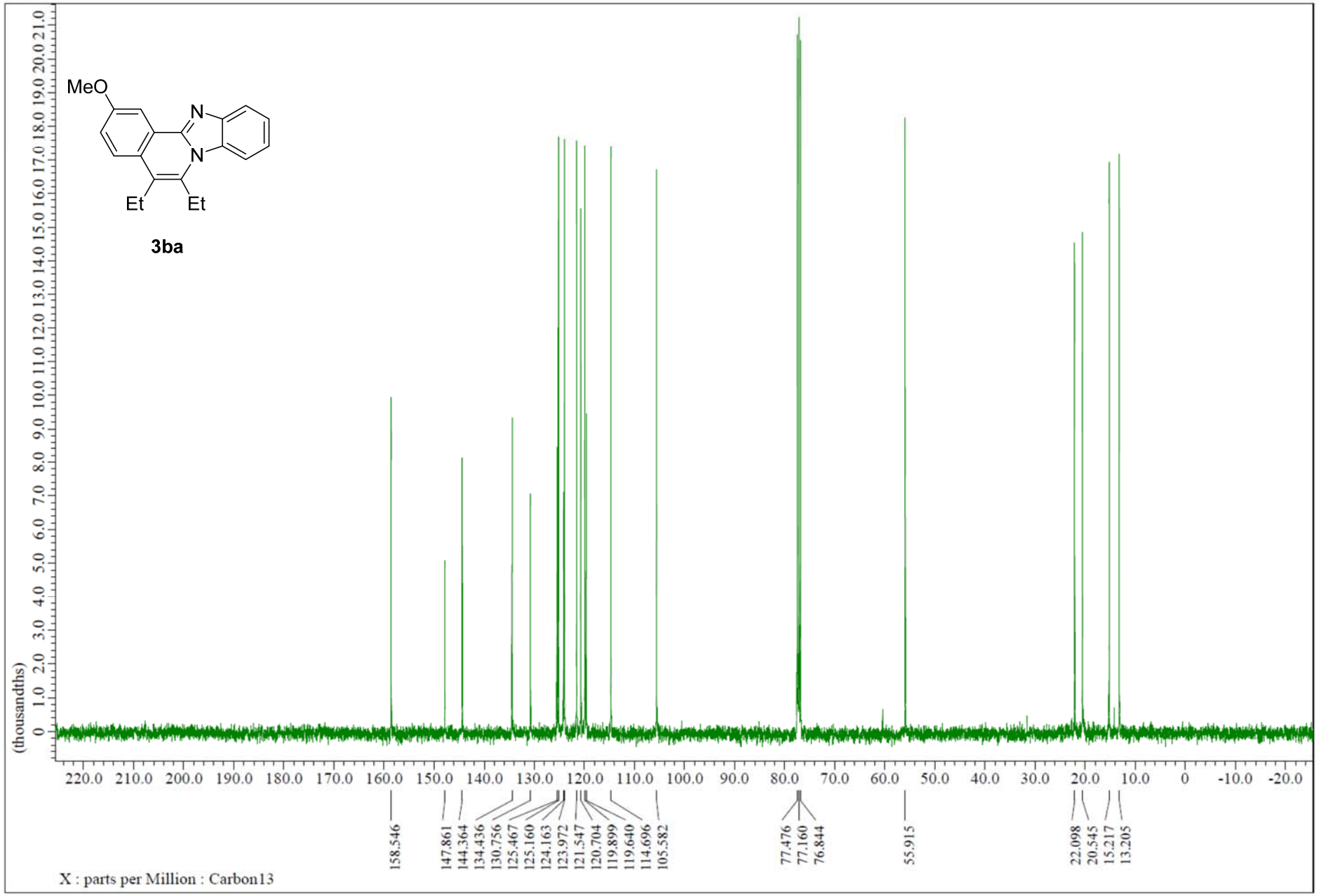
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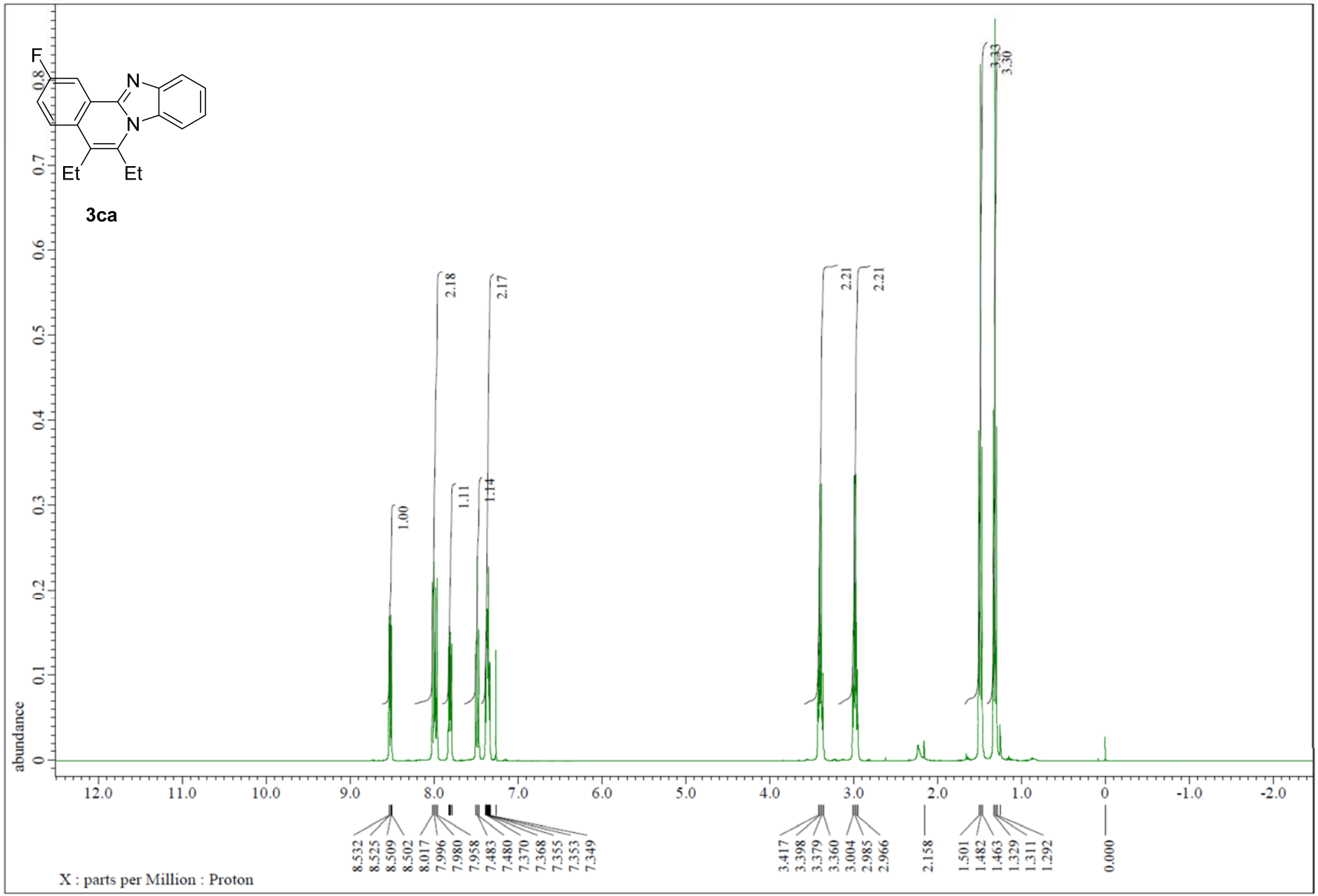
F
N
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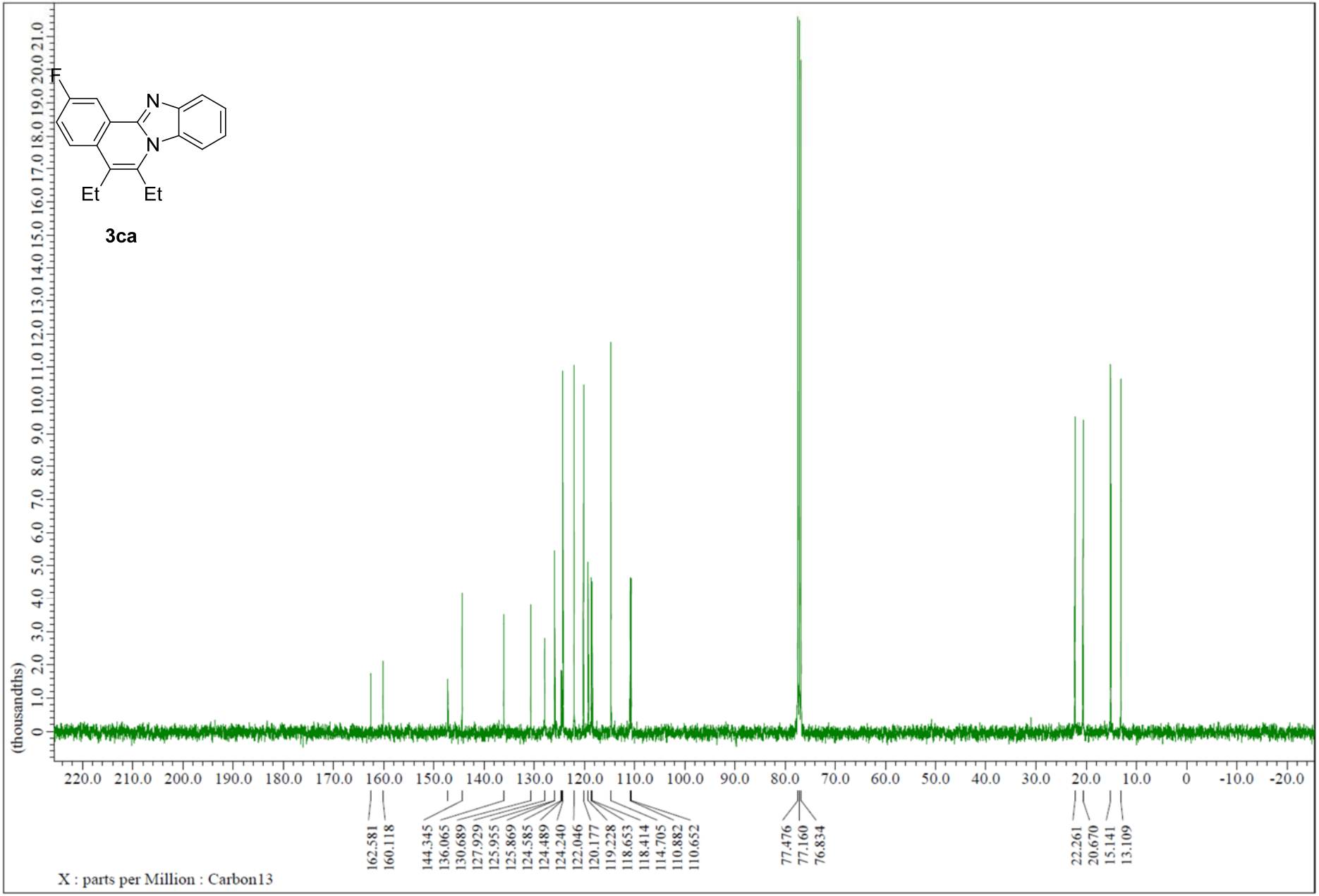
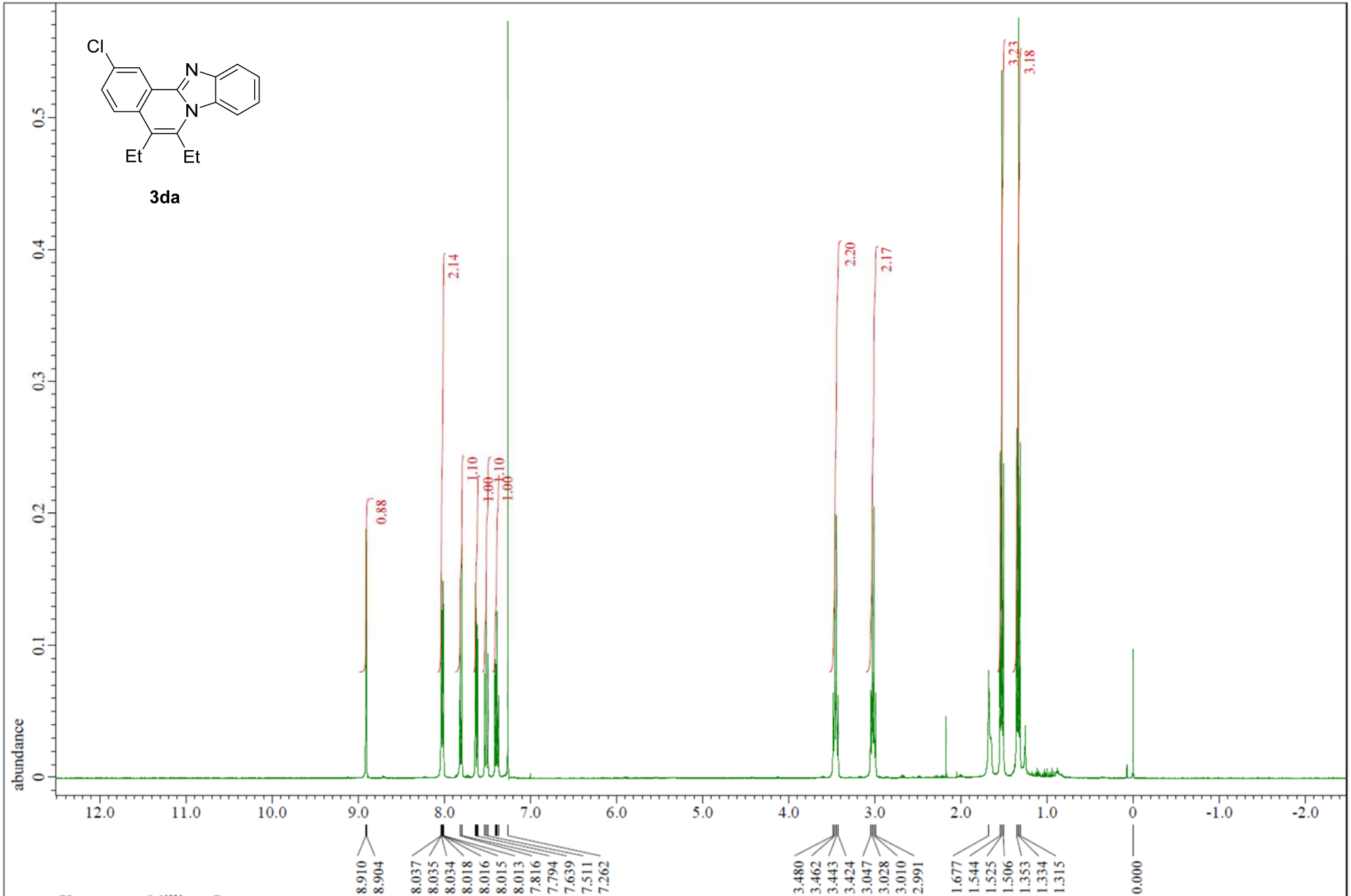
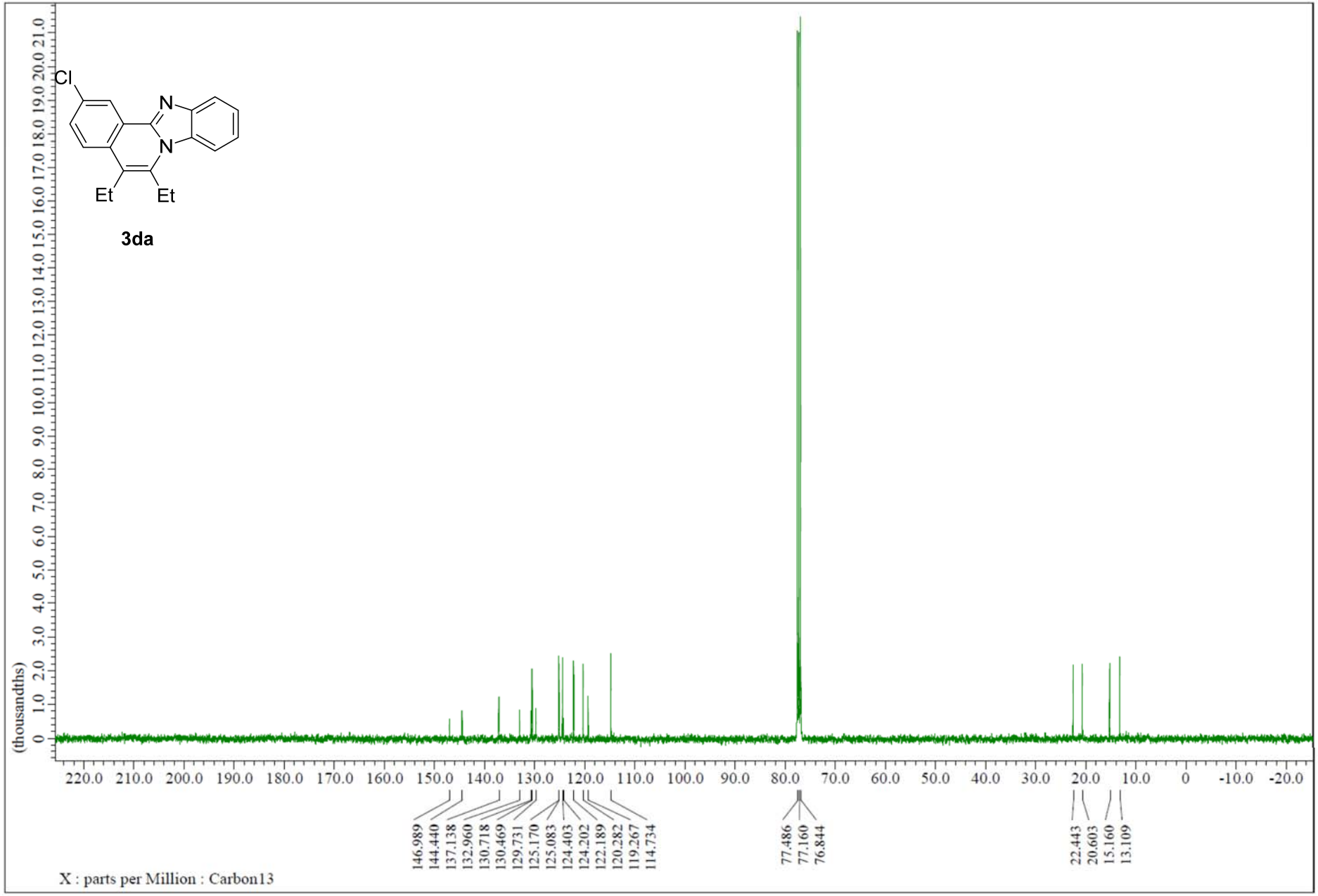
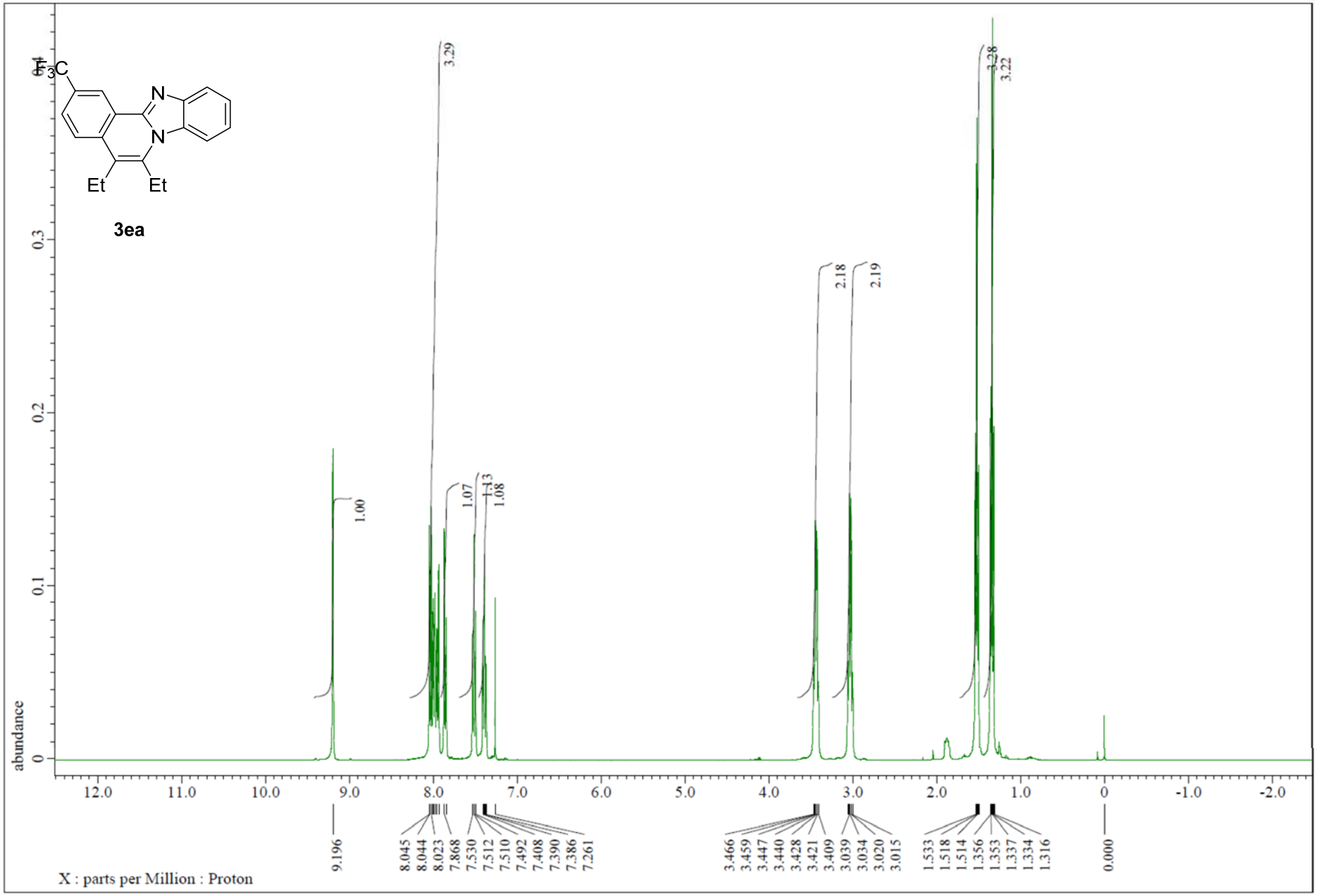
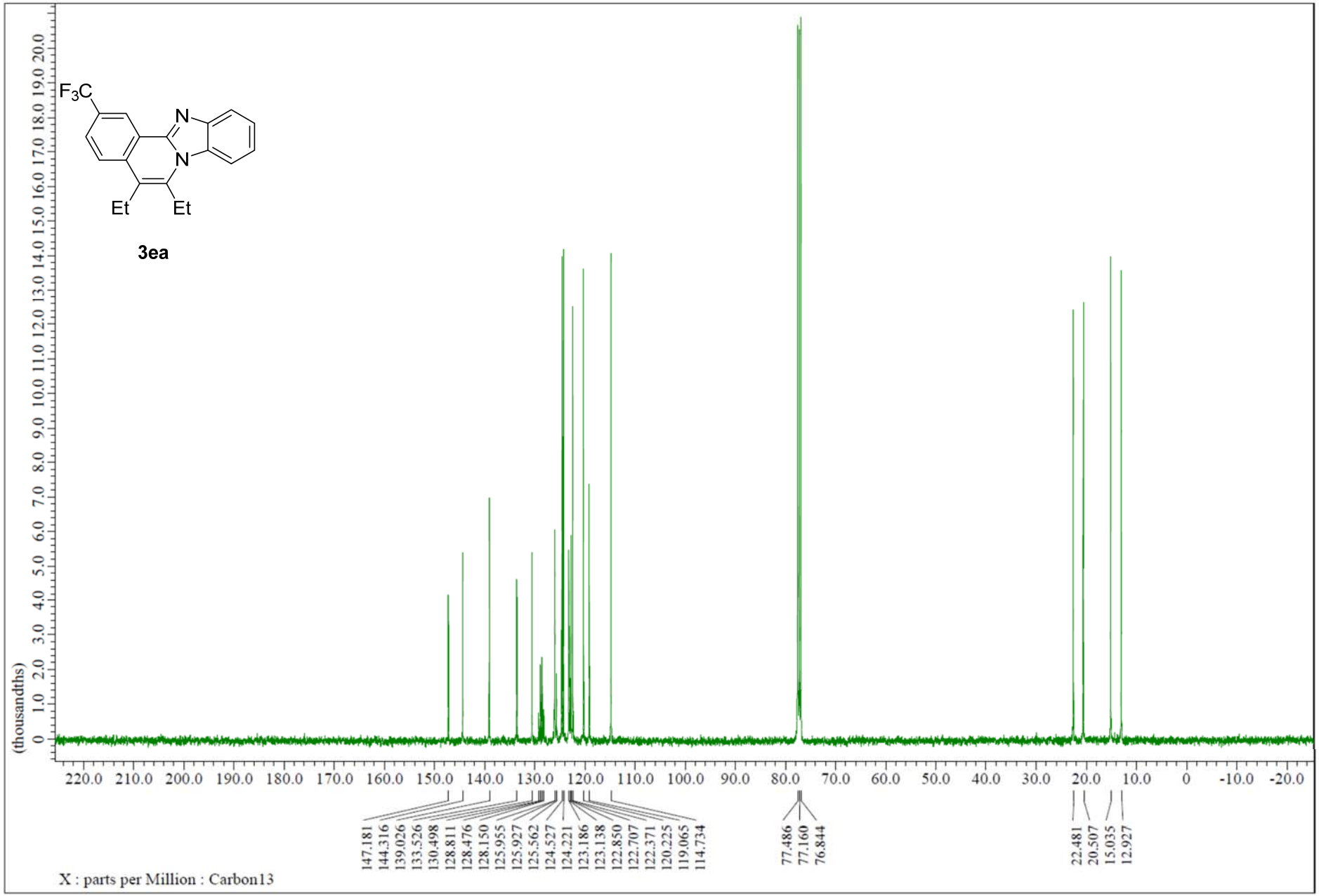
8.525
8.509
8.502
8.017
7.996
7.980
7.958
7.483
7.480
7.370
7.368
7.355
7.353
7.349
3.417
3.398
3.379
3.360
3.004
2.985
2.966
2.158
1.501
1.482
1.463
1.329
1.311
1.292
0.000

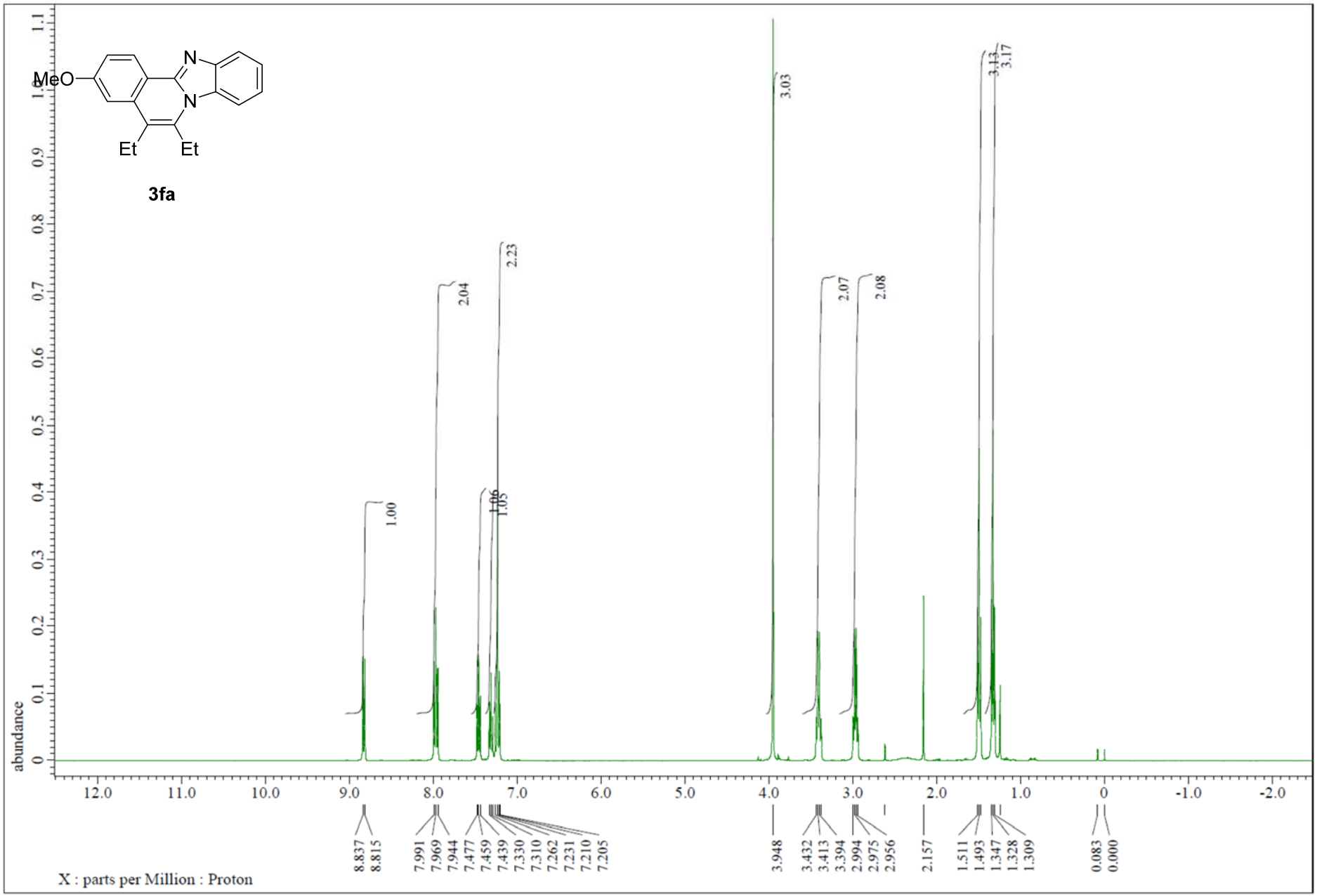

F
N
N
Et
Et
3ca
(thousandths)
X : parts per Million : Carbon13
162.581
160.118
144.345
136.065
130.689
127.929
125.955
125.869
124.585
124.489
124.240
122.046
120.177
119.228
118.653
118.414
114.705
110.882
110.652
77.476
77.160
76.834
22.261
20.670
15.141
13.109

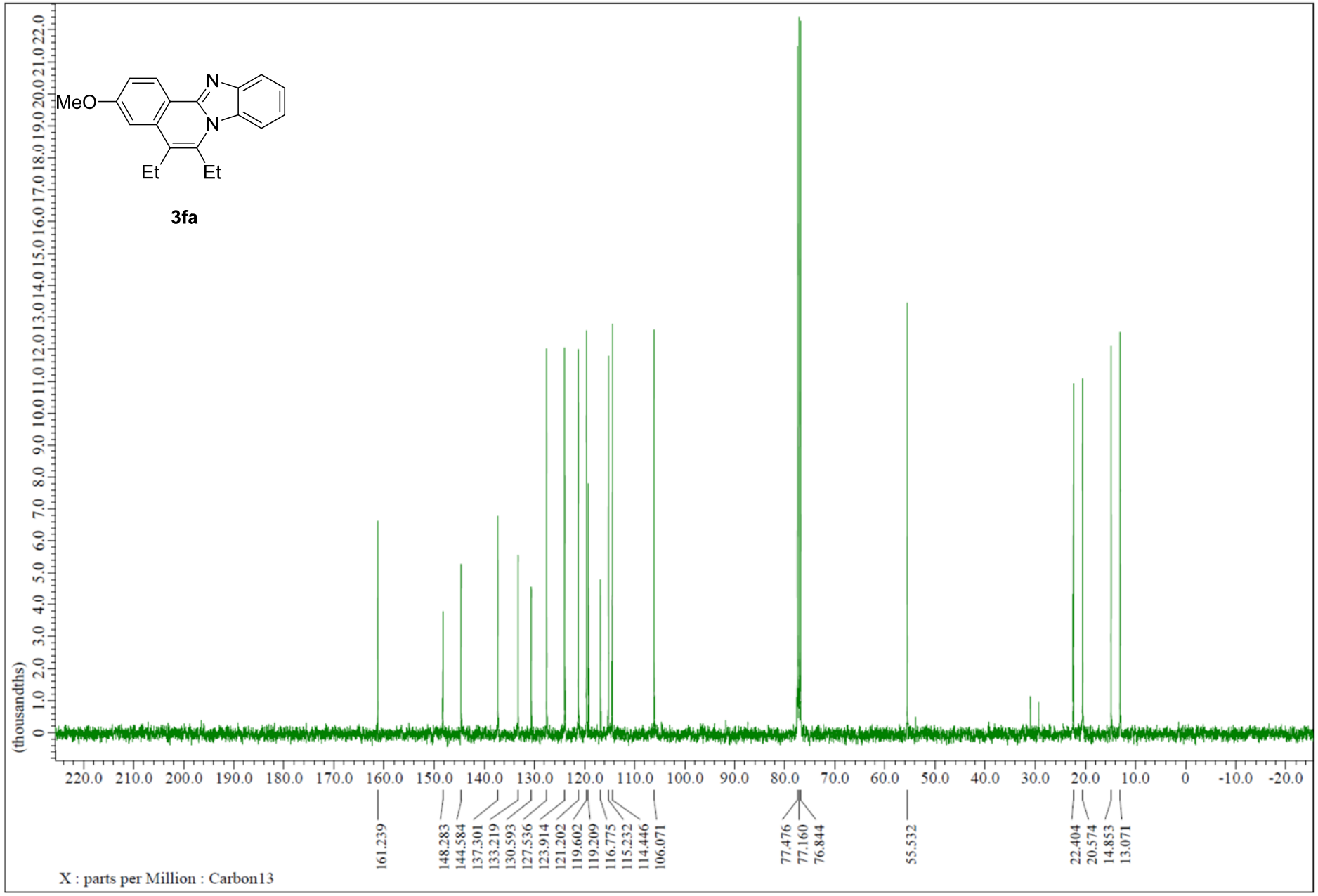

Cl
N
N
Et
Et
3da
abundance
0.5
0.4
0.3
0.2
0.1
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
0.88
2.14
1.10
1.00
1.10
1.00
2.20
2.17
3.23
3.18
8.910
8.904
8.037
8.035
8.034
8.018
8.016
8.015
8.013
7.816
7.794
7.639
7.511
7.262
3.480
3.462
3.443
3.424
3.047
3.028
3.010
2.991
1.677
1.544
1.525
1.506
1.353
1.334
1.315
0.000

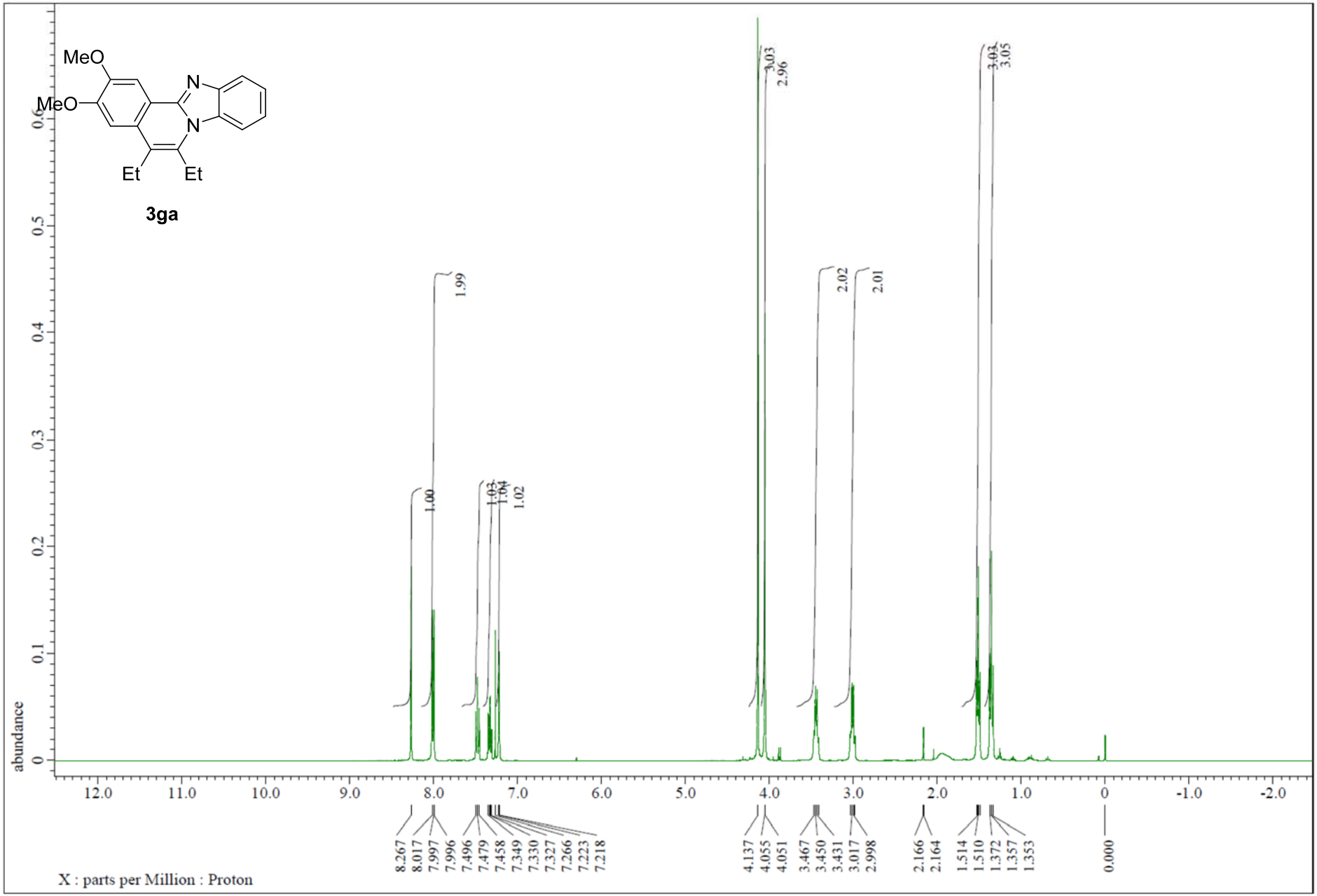

Cl
N
N
Et
Et
3da
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
146.989
144.440
137.138
132.960
130.718
130.469
129.731
125.170
125.083
124.403
124.202
122.189
120.282
119.267
114.734
77.486
77.160
76.844
22.443
20.603
15.160
13.109
X : parts per Million : Carbon13

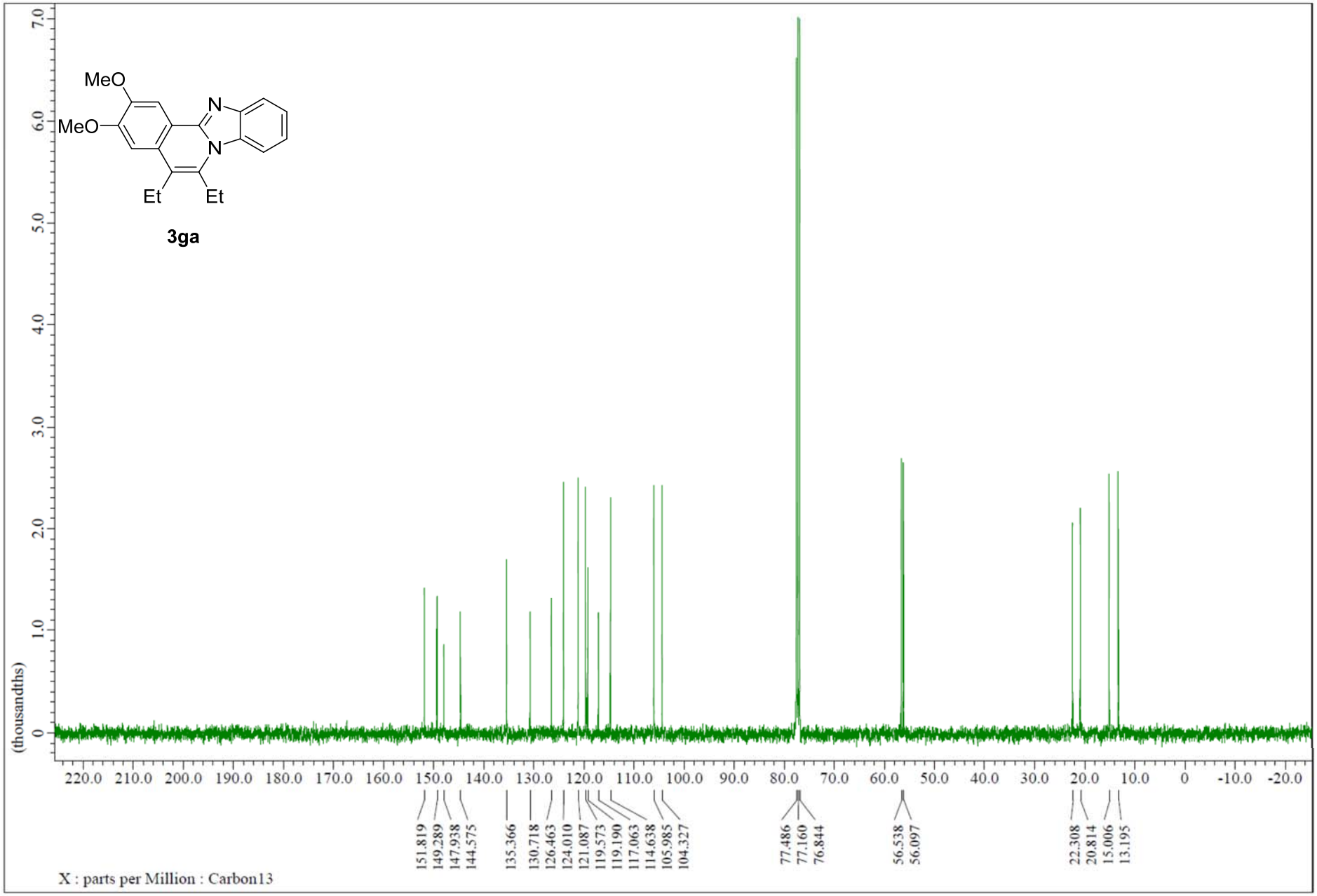

F3C
N
N
Et
Et
3ea
abundance
X : parts per Million : Proton
3.29
3.28
3.22
2.18
2.19
1.00
1.07
1.13
1.08
9.196
8.045
8.044
8.023
7.868
7.530
7.512
7.510
7.492
7.408
7.390
7.386
7.261
3.466
3.459
3.447
3.440
3.428
3.421
3.409
3.039
3.034
3.020
3.015
1.533
1.518
1.514
1.356
1.353
1.337
1.334
1.316
0.000

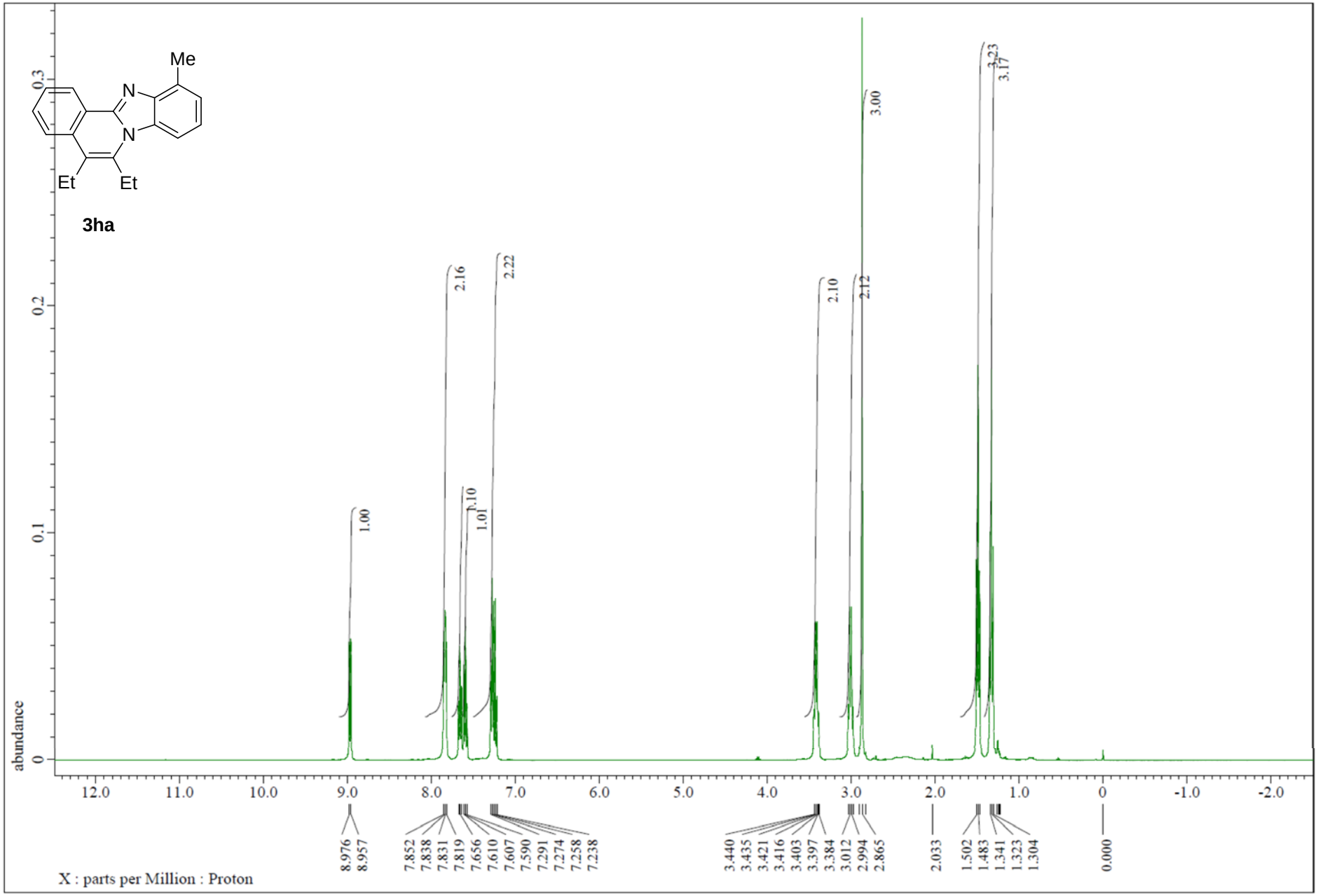

F3C
N
N
Et
Et
3ea
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.181
144.316
139.026
133.526
130.498
128.811
128.476
128.150
125.955
125.927
125.562
124.527
124.221
123.186
123.138
122.850
122.707
122.371
120.225
119.065
114.734
77.486
77.160
76.844
22.481
20.507
15.035
12.927
X : parts per Million : Carbon13

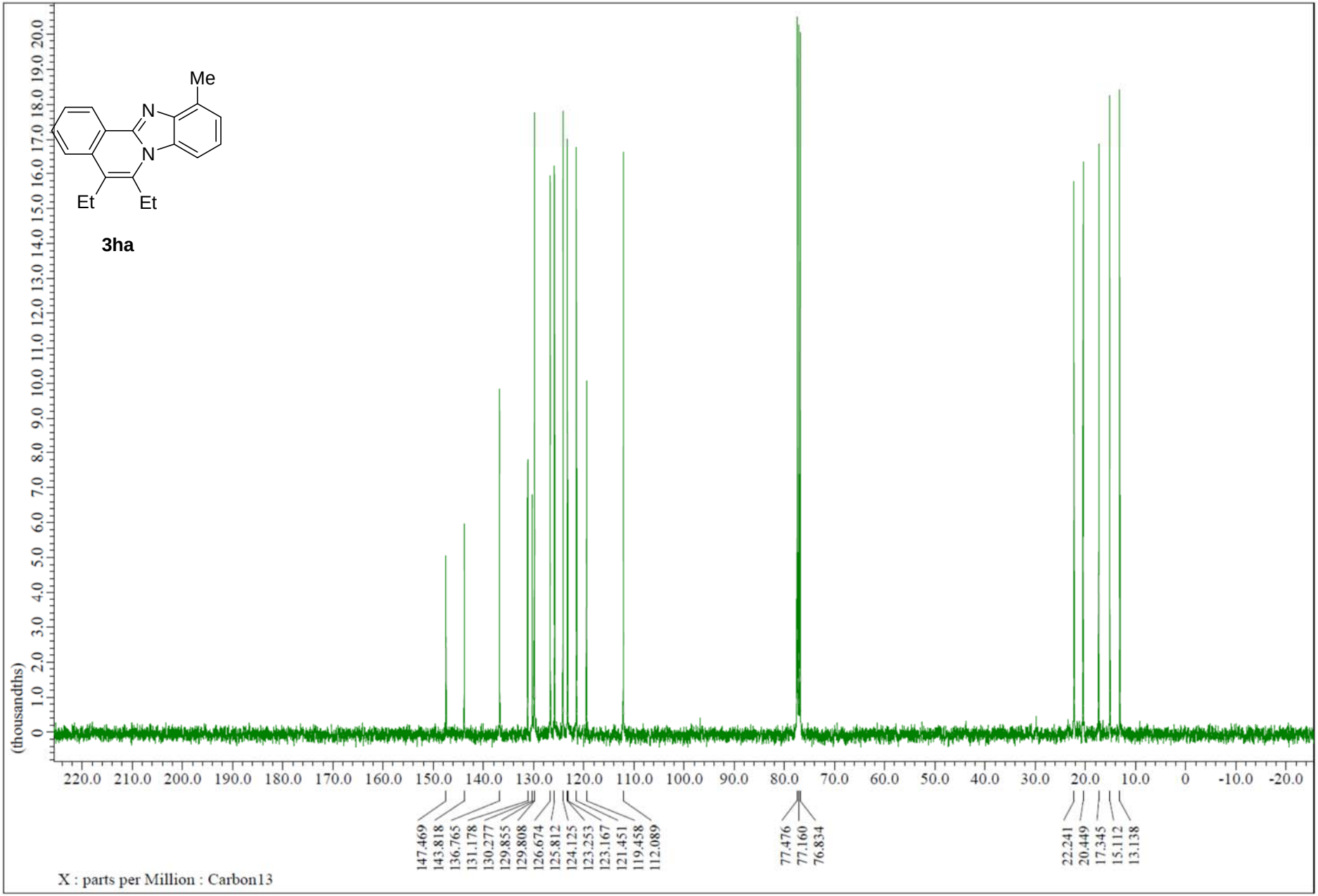

MeO
N
N
Et
Et
3fa
abundance
X : parts per Million : Proton
1.00
2.04
1.06
1.05
2.23
3.03
2.07
2.08
3.13
3.17
8.837
8.815
7.991
7.969
7.944
7.477
7.459
7.439
7.330
7.310
7.262
7.231
7.210
7.205
3.948
3.432
3.413
3.394
2.994
2.975
2.956
2.157
1.511
1.493
1.347
1.328
1.309
0.083
0.000

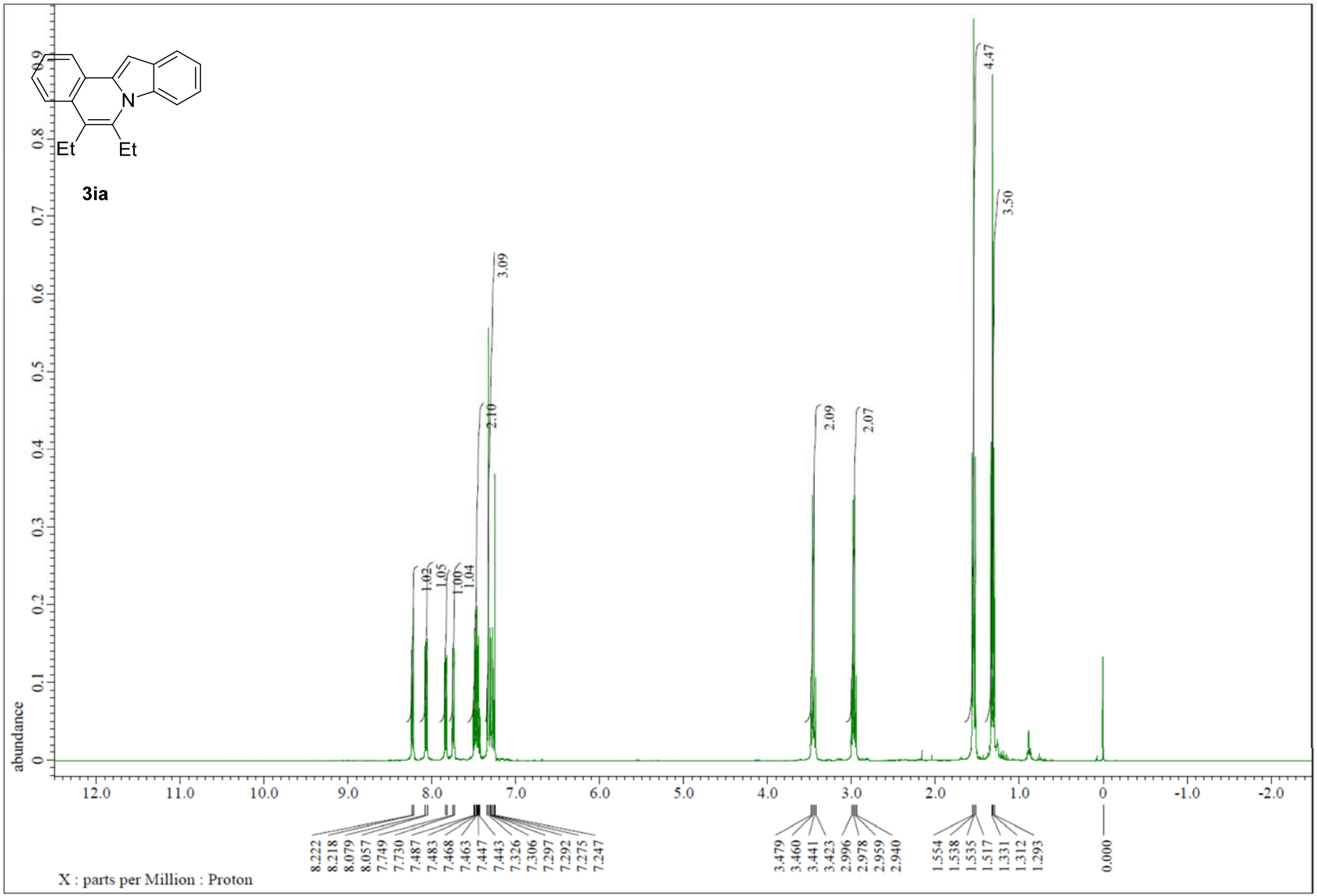

MeO
N
N
Et
Et
3fa
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
161.239
148.283
144.584
137.301
133.219
130.593
127.536
123.914
121.202
119.602
119.209
116.775
115.232
114.446
106.071
77.476
77.160
76.844
55.532
22.404
20.574
14.853
13.071
X : parts per Million : Carbon13

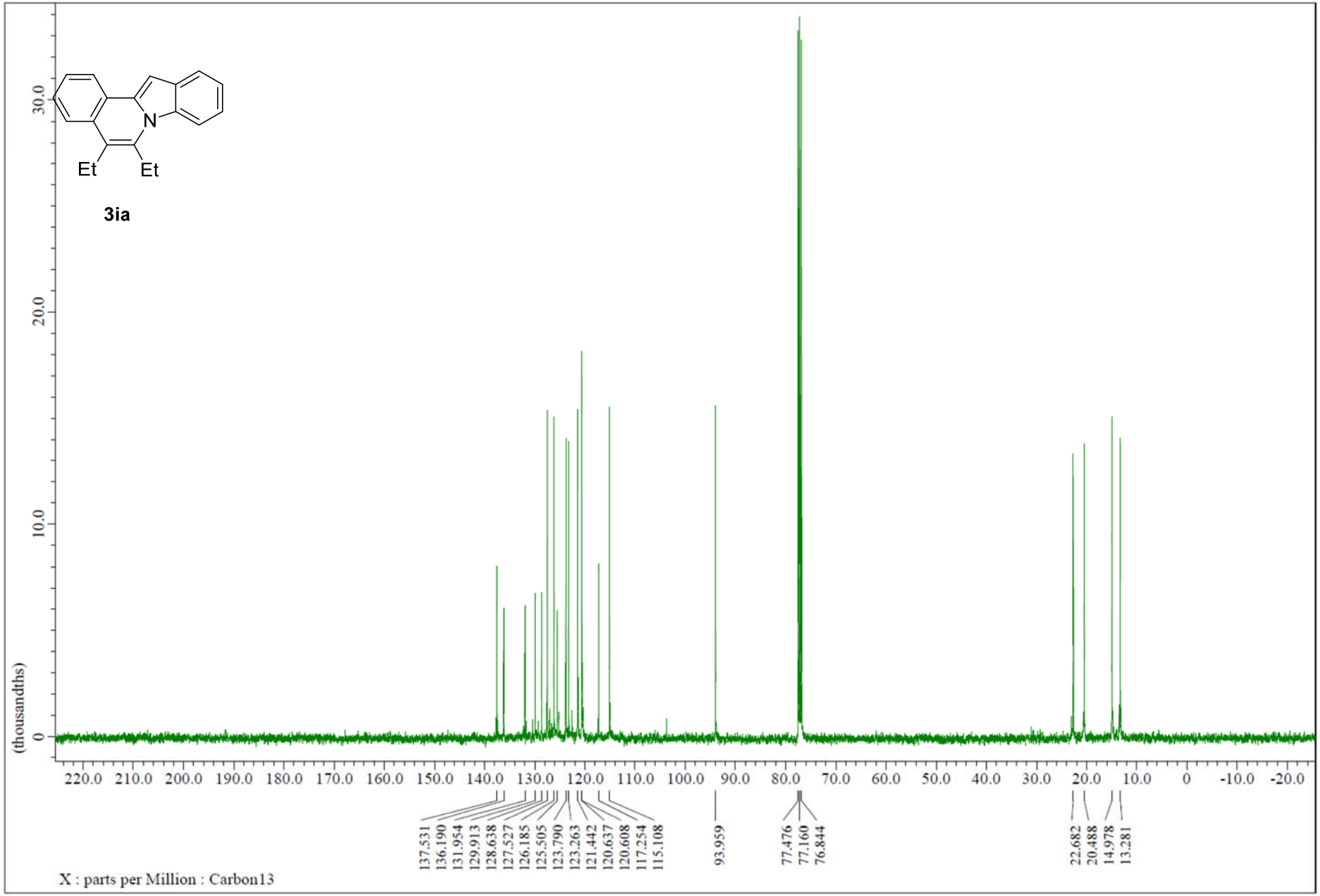

MeO
MeO
N
N
Et
Et
3ga
abundance
X : parts per Million : Proton
1.00
1.99
1.03
1.04
1.02
3.03
2.96
2.02
2.01
3.03
3.05
8.267
8.017
7.997
7.996
7.496
7.479
7.458
7.349
7.330
7.327
7.266
7.223
7.218
4.137
4.055
4.051
3.467
3.450
3.431
3.017
2.998
2.166
2.164
1.514
1.510
1.372
1.357
1.353
0.000


MeO
MeO
N
N
Et
Et
3ga
(thousandths)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
151.819
149.289
147.938
144.575
135.366
130.718
126.463
124.010
121.087
119.573
119.190
117.063
114.638
105.985
104.327
77.486
77.160
76.844
56.538
56.097
22.308
20.814
15.006
13.195
X : parts per Million : Carbon13


Me
N
N
Et
Et
3ha
abundance
X : parts per Million : Proton
1.00
1.10
1.01
2.16
2.22
2.10
2.12
3.00
3.23
3.17
8.976
8.957
7.852
7.838
7.831
7.819
7.656
7.610
7.607
7.590
7.291
7.274
7.258
7.238
3.440
3.435
3.421
3.416
3.403
3.397
3.384
3.012
2.994
2.865
2.033
1.502
1.483
1.341
1.323
1.304
0.000


Me
N
N
Et
Et
3ha
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
147.469
143.818
136.765
131.178
130.277
129.855
129.808
126.674
125.812
124.125
123.253
123.167
121.451
119.458
112.089
77.476
77.160
76.834
22.241
20.449
17.345
15.112
13.138
X : parts per Million : Carbon13


Et
Et
N
3ia
abundance
X : parts per Million : Proton
1.02
1.05
1.00
1.04
2.10
3.09
2.09
2.07
4.47
3.50
8.222
8.218
8.079
8.057
7.749
7.730
7.487
7.483
7.468
7.463
7.447
7.443
7.326
7.306
7.297
7.292
7.275
7.247
3.479
3.460
3.441
3.423
2.996
2.978
2.959
2.940
1.554
1.538
1.535
1.517
1.331
1.312
1.293
0.000


Et
Et
N
3ia
(thousandths)
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
137.531
136.190
131.954
129.913
128.638
127.527
126.185
125.505
123.790
123.263
121.442
120.637
120.608
117.254
115.108
93.959
77.476
77.160
76.844
22.682
20.488
14.978
13.281
X : parts per Million : Carbon13