Electronic Supplementry Information

Synthesis of imidazopyridine-fused indoles *via* one-pot sequential Knoevenagel condensation and cross dehydrogenative coupling

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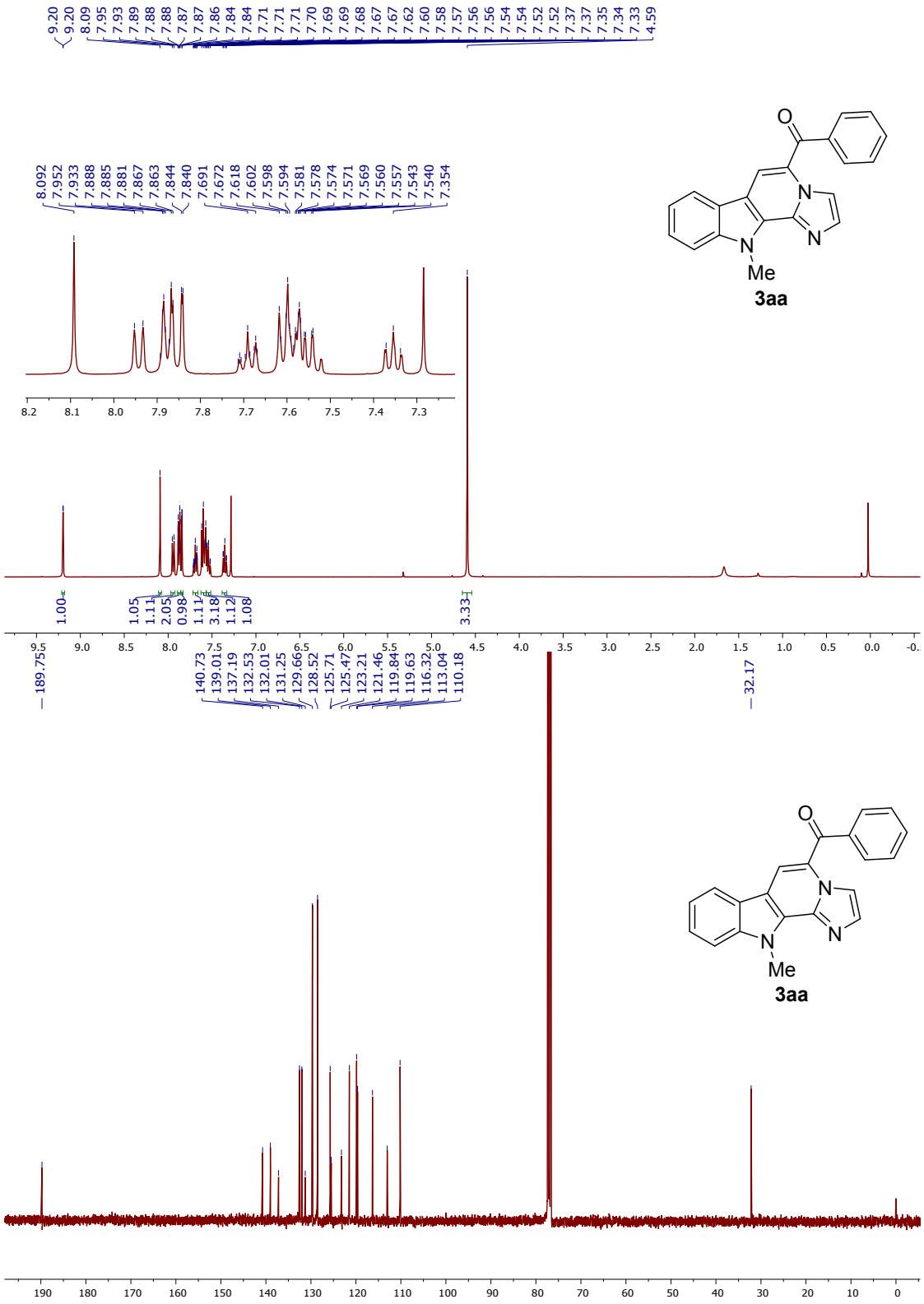
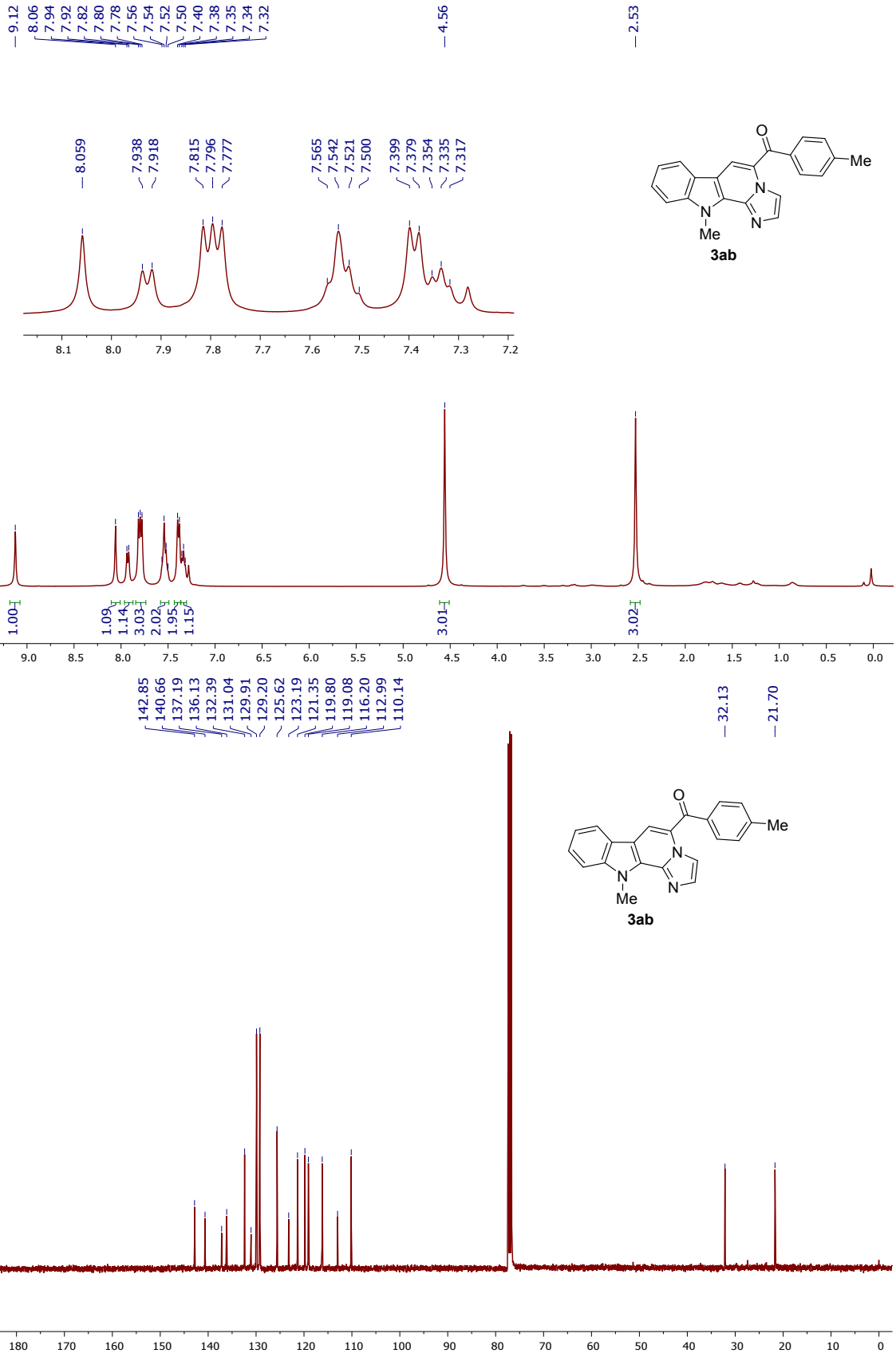
Content

Copies of ^{1}H and ^{13}C NMR spectra of products

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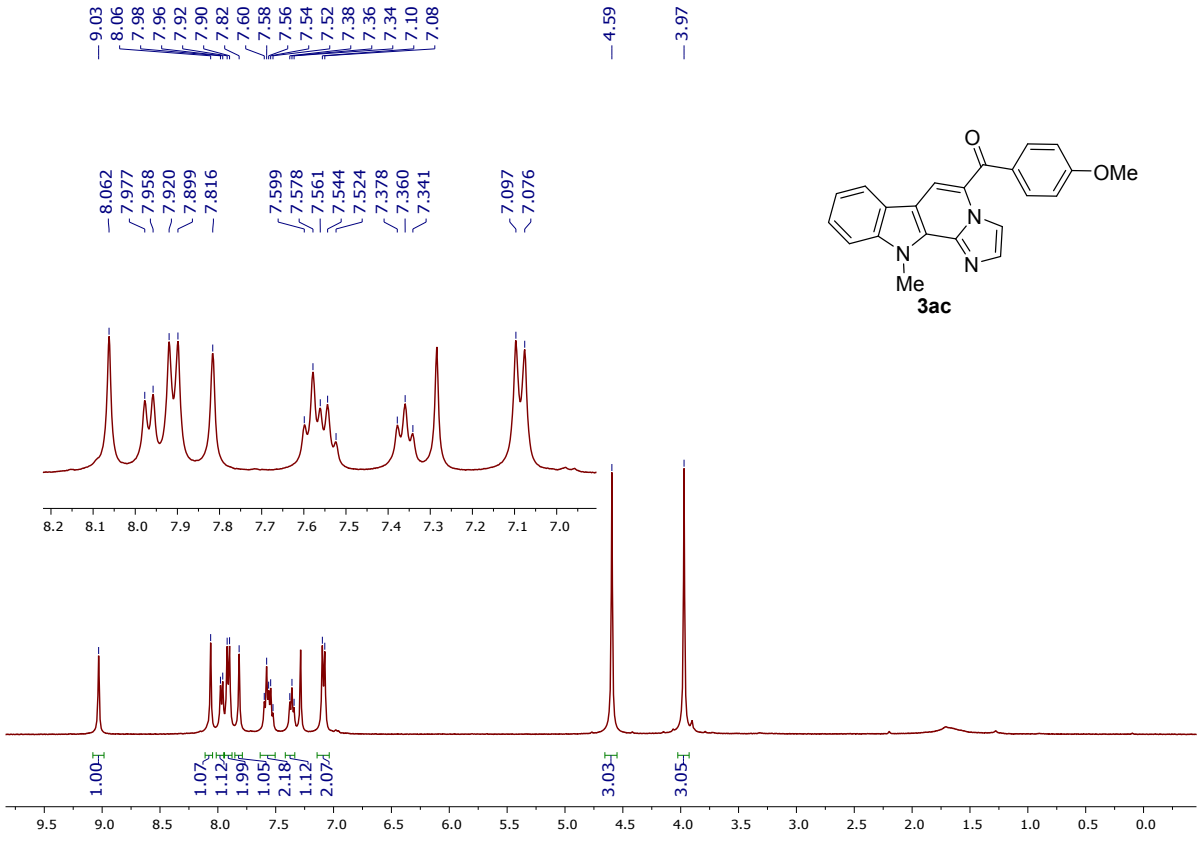
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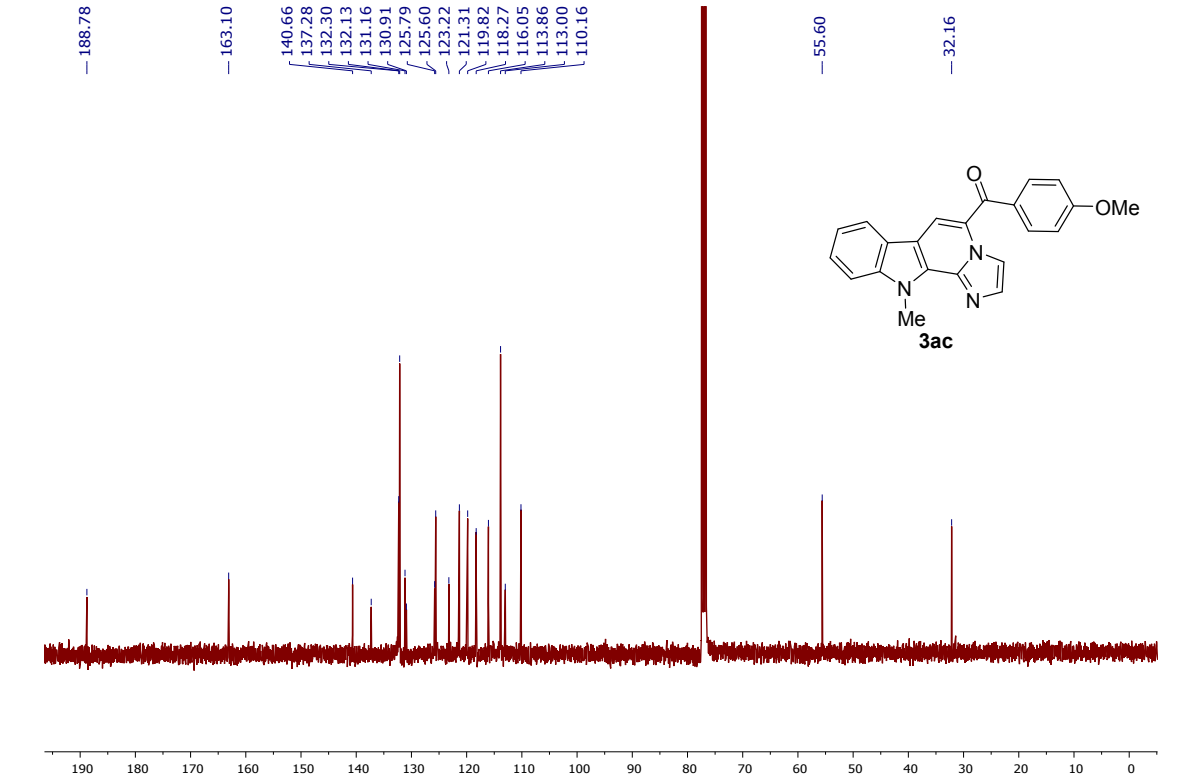
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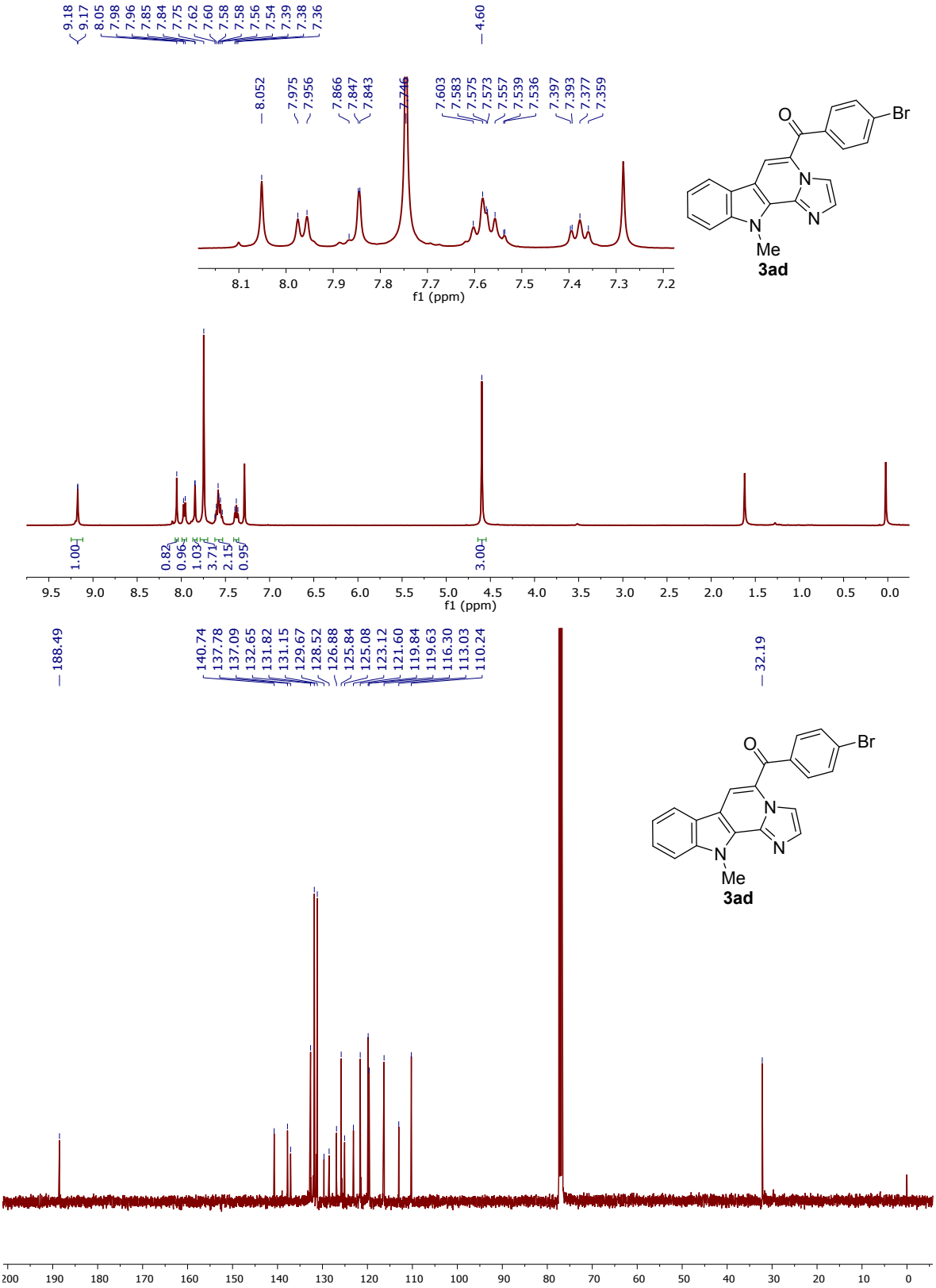
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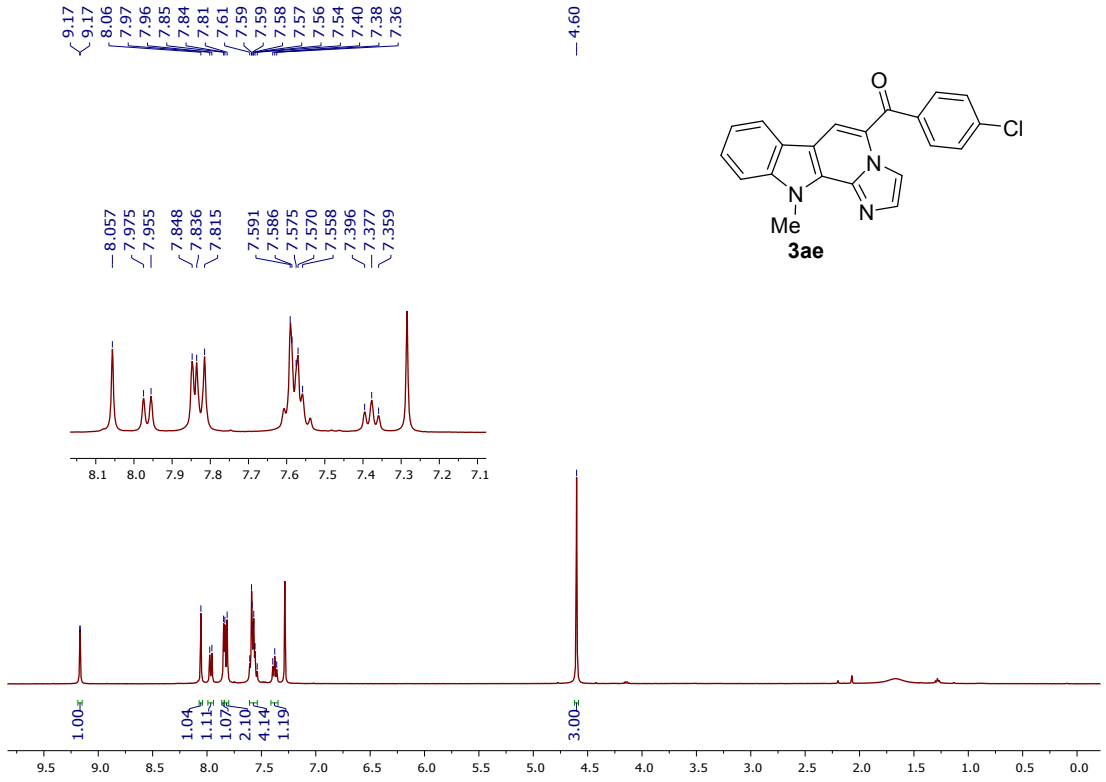
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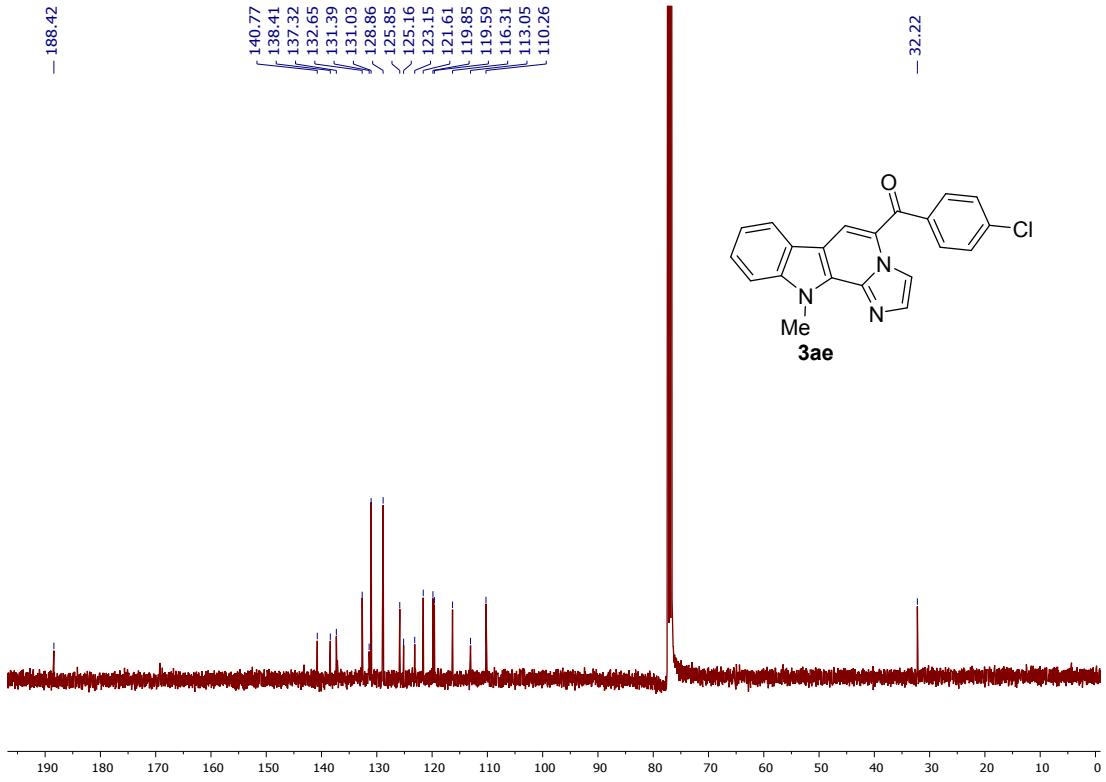
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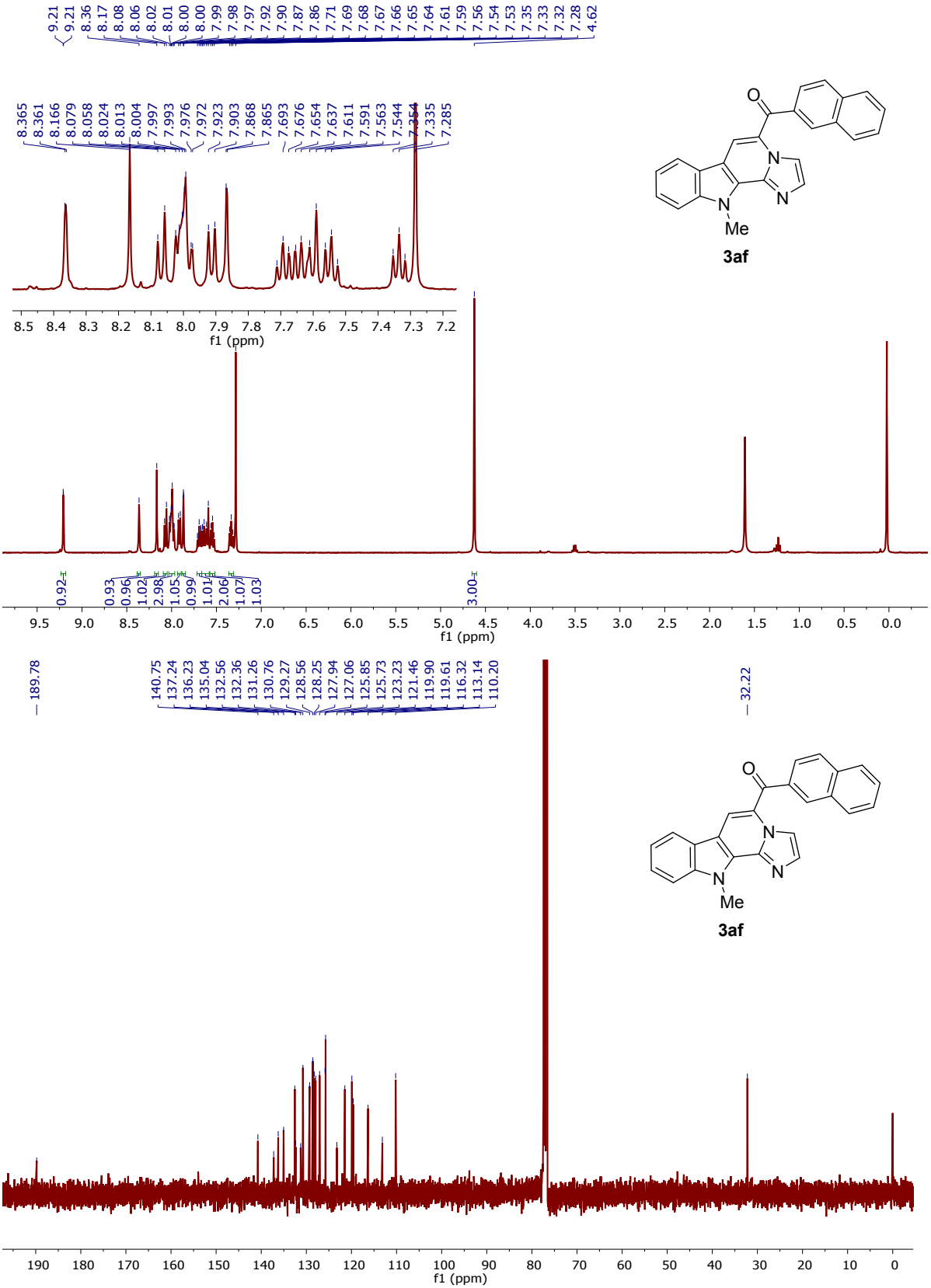
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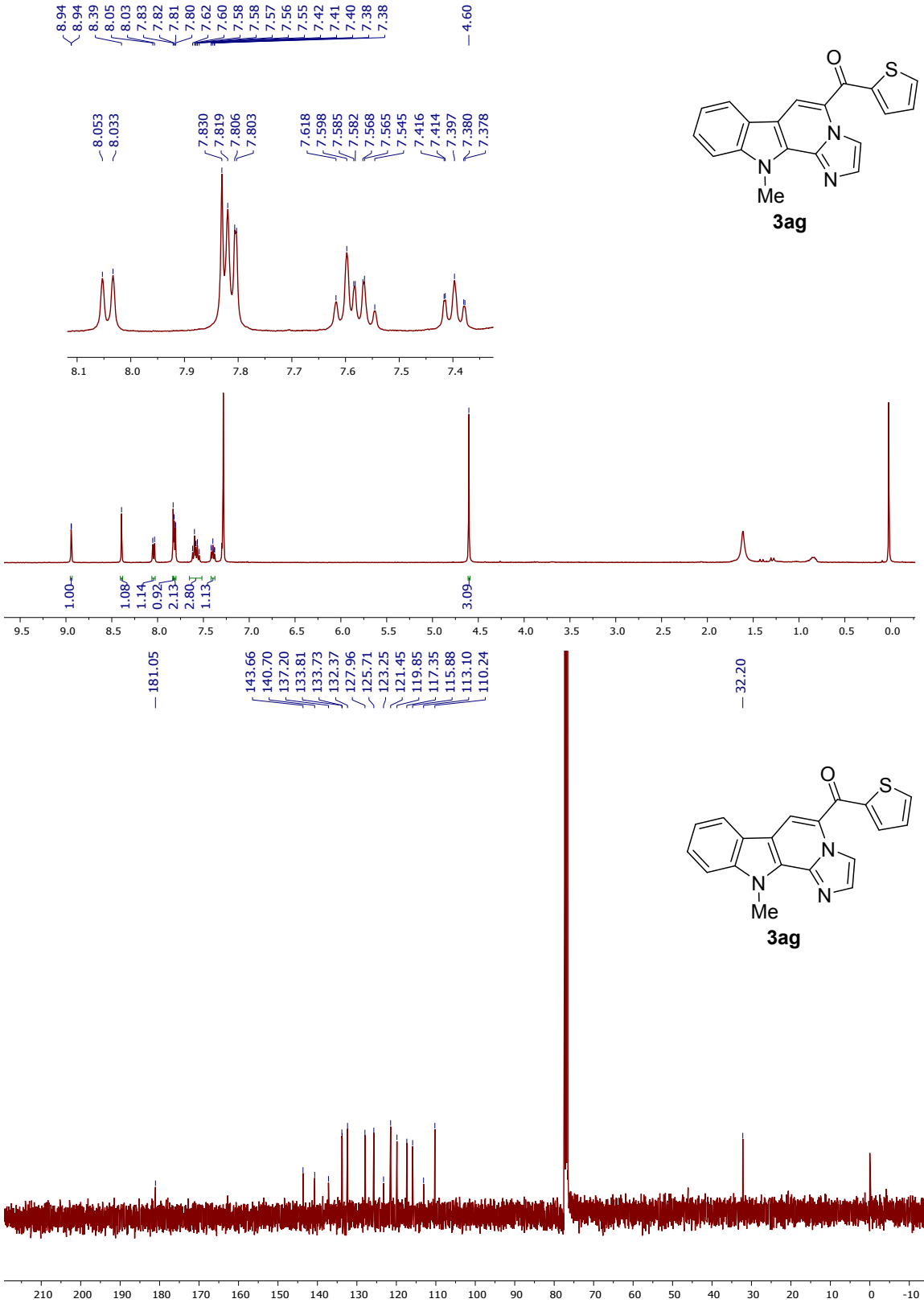
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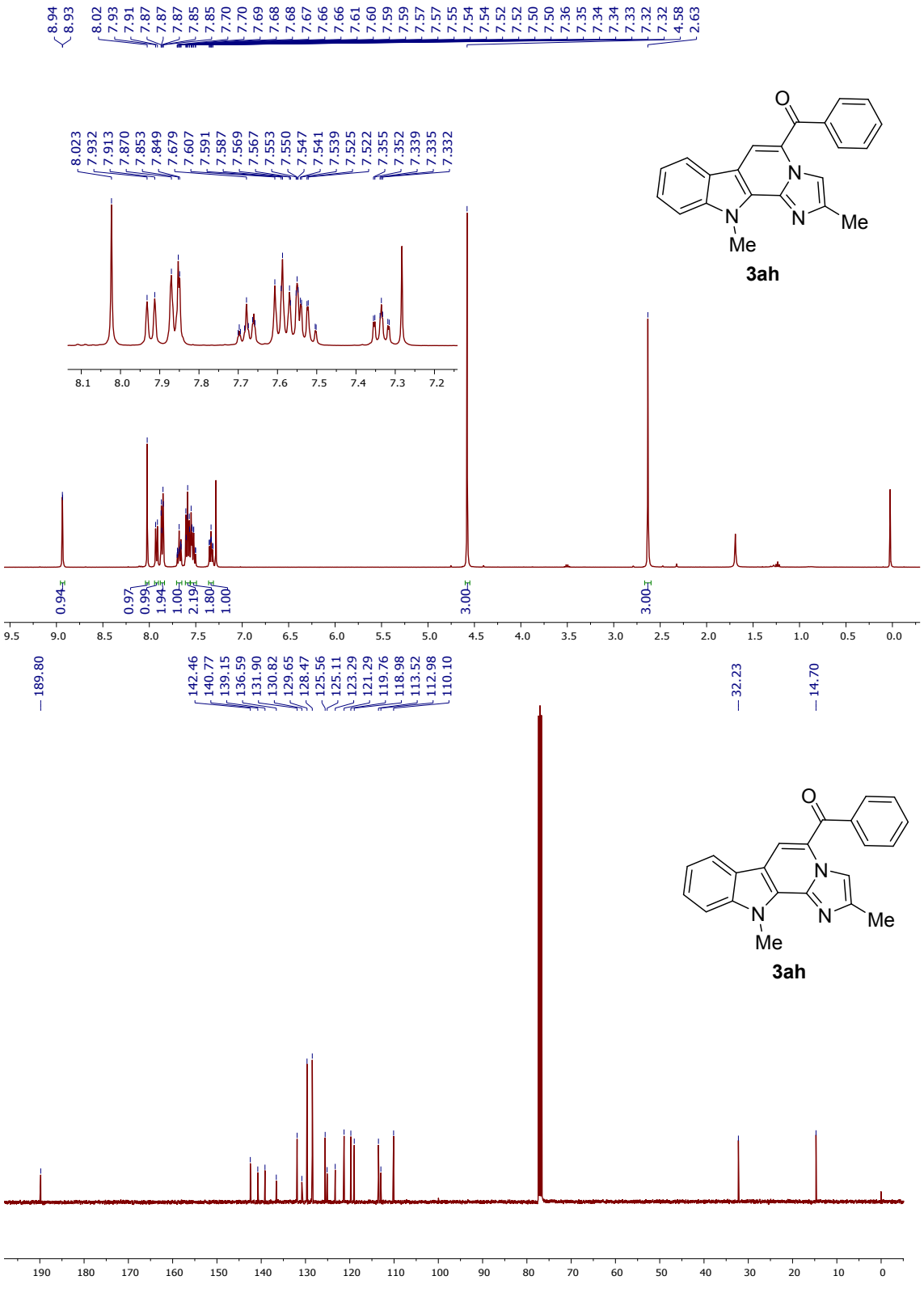
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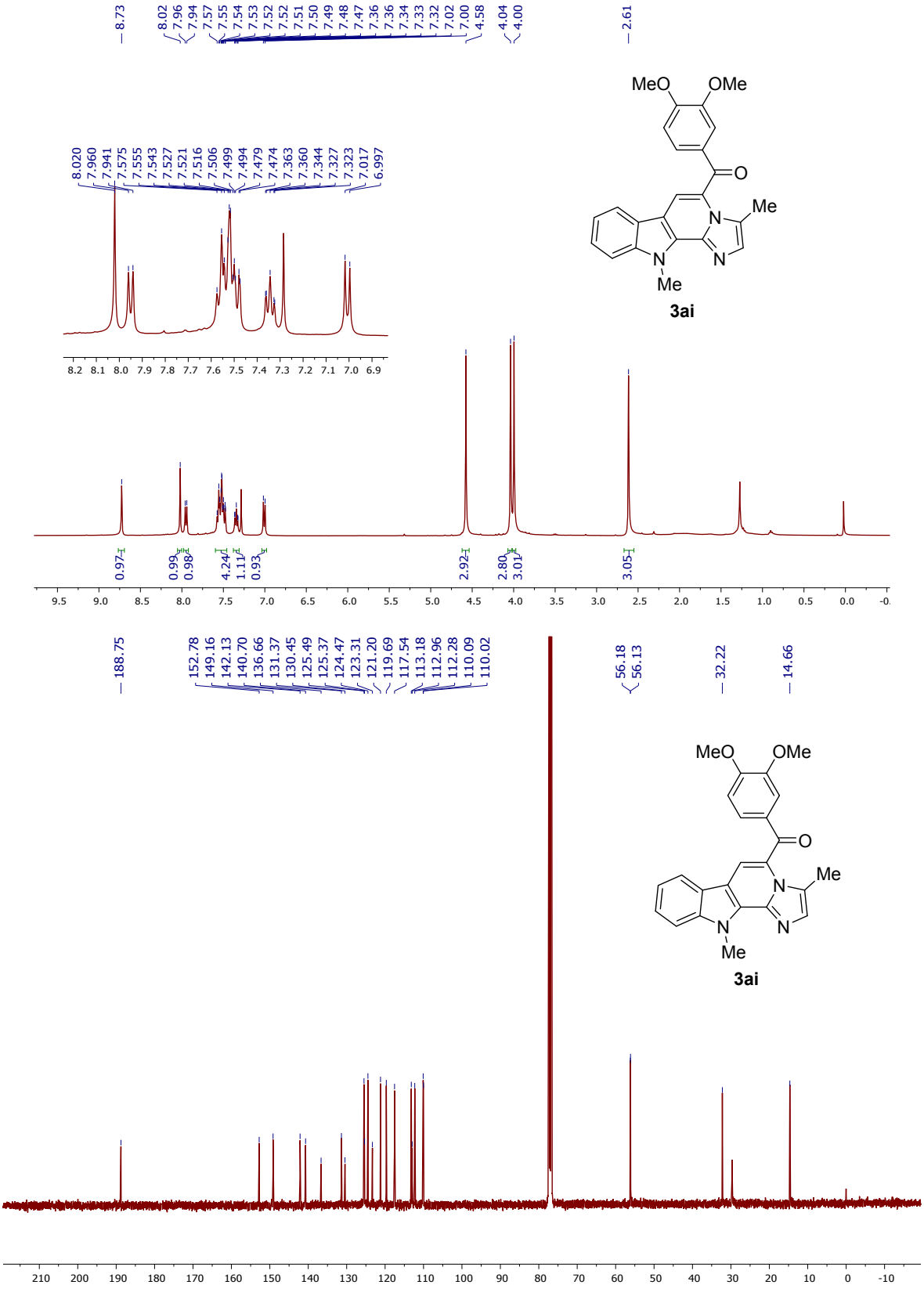
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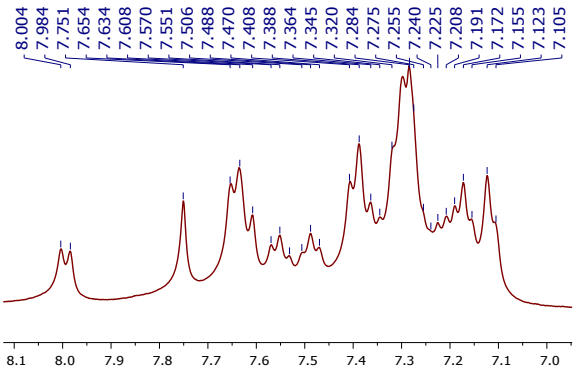
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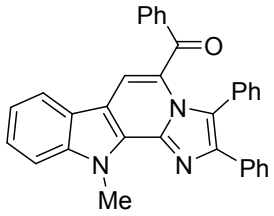
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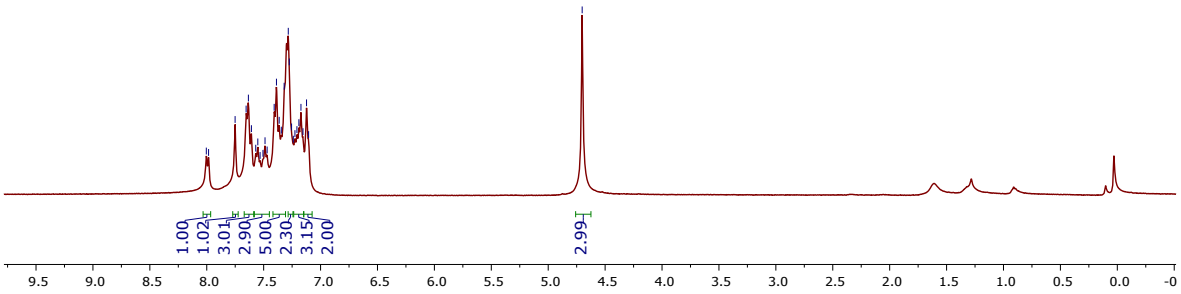
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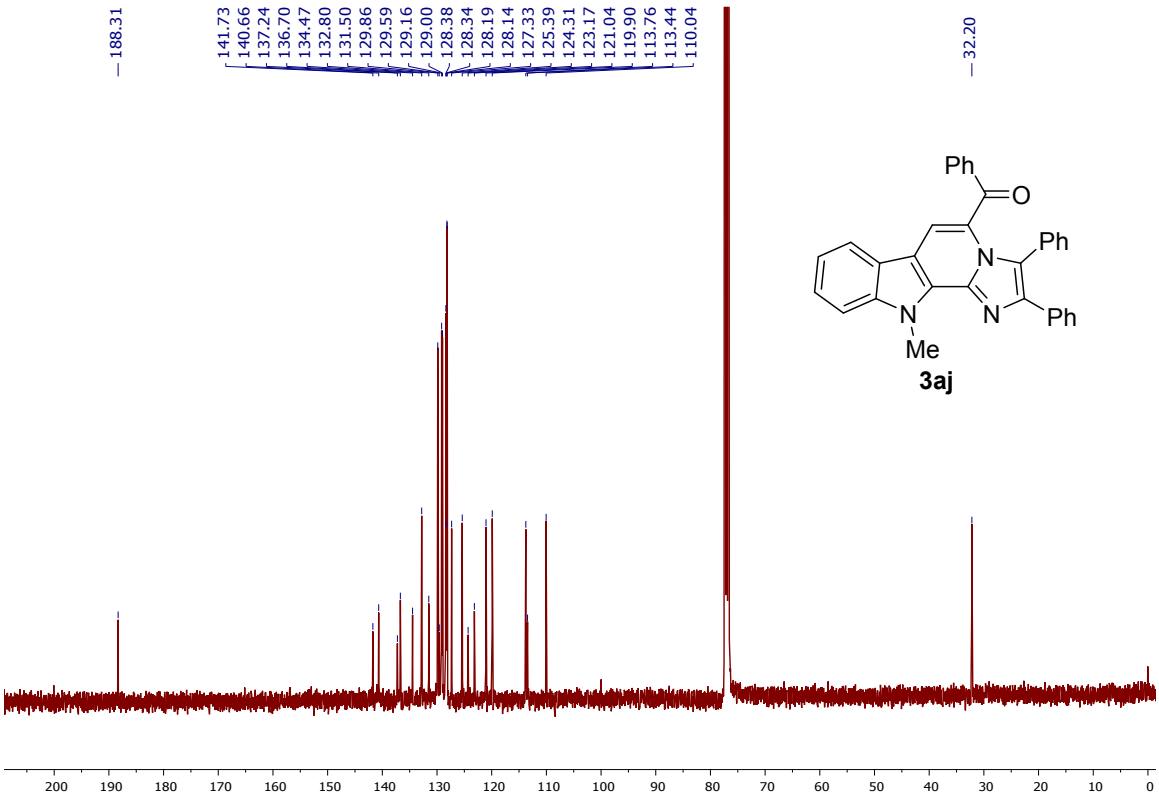
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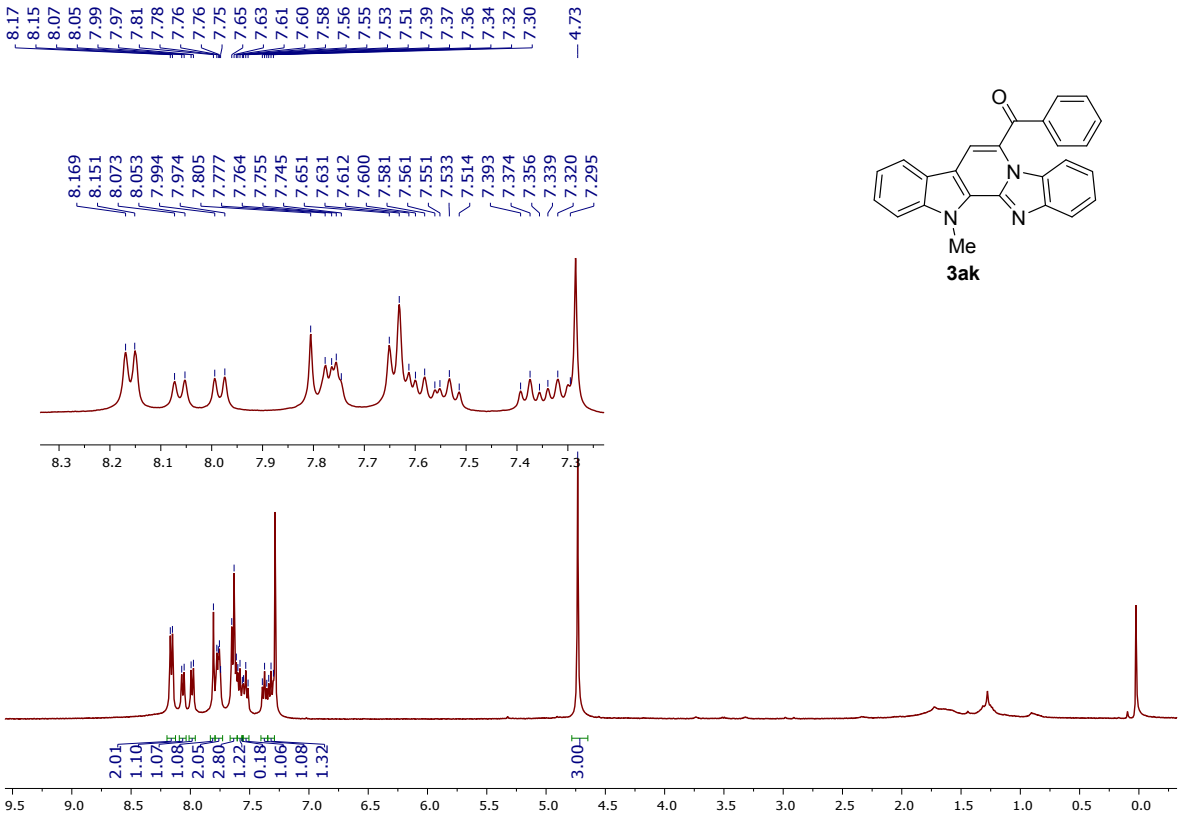
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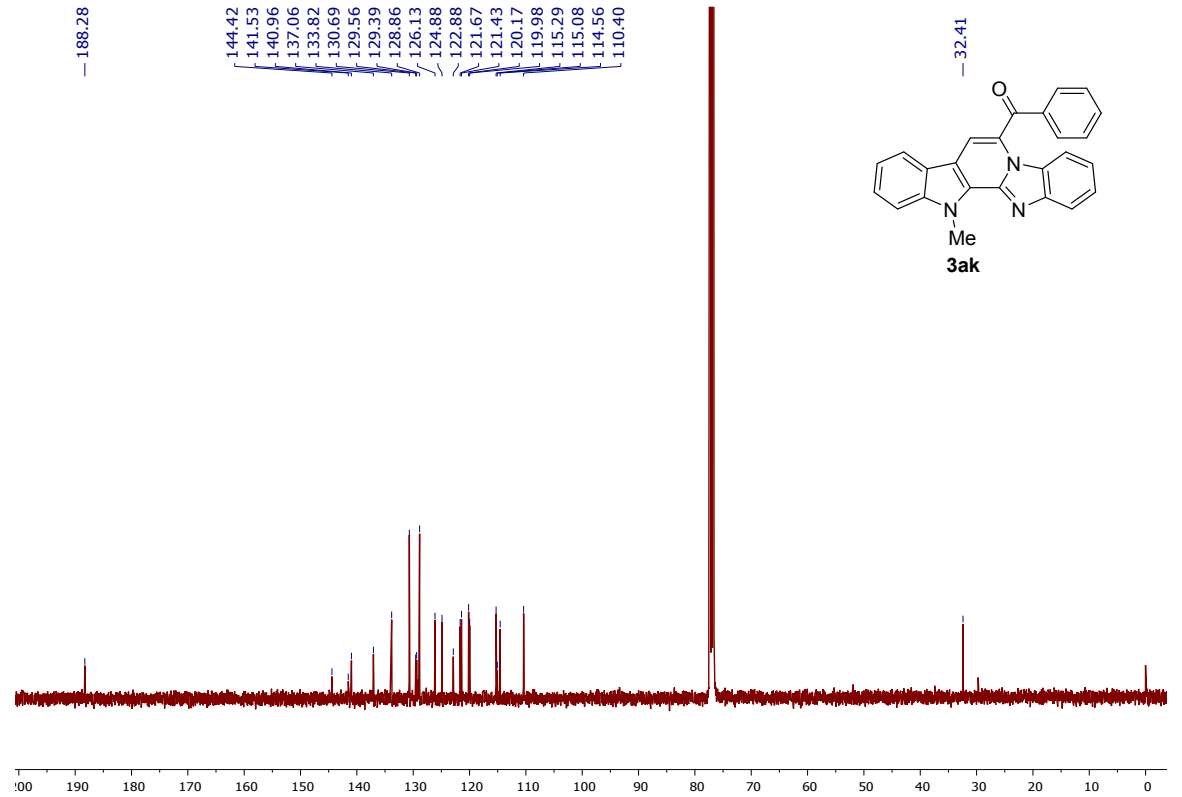
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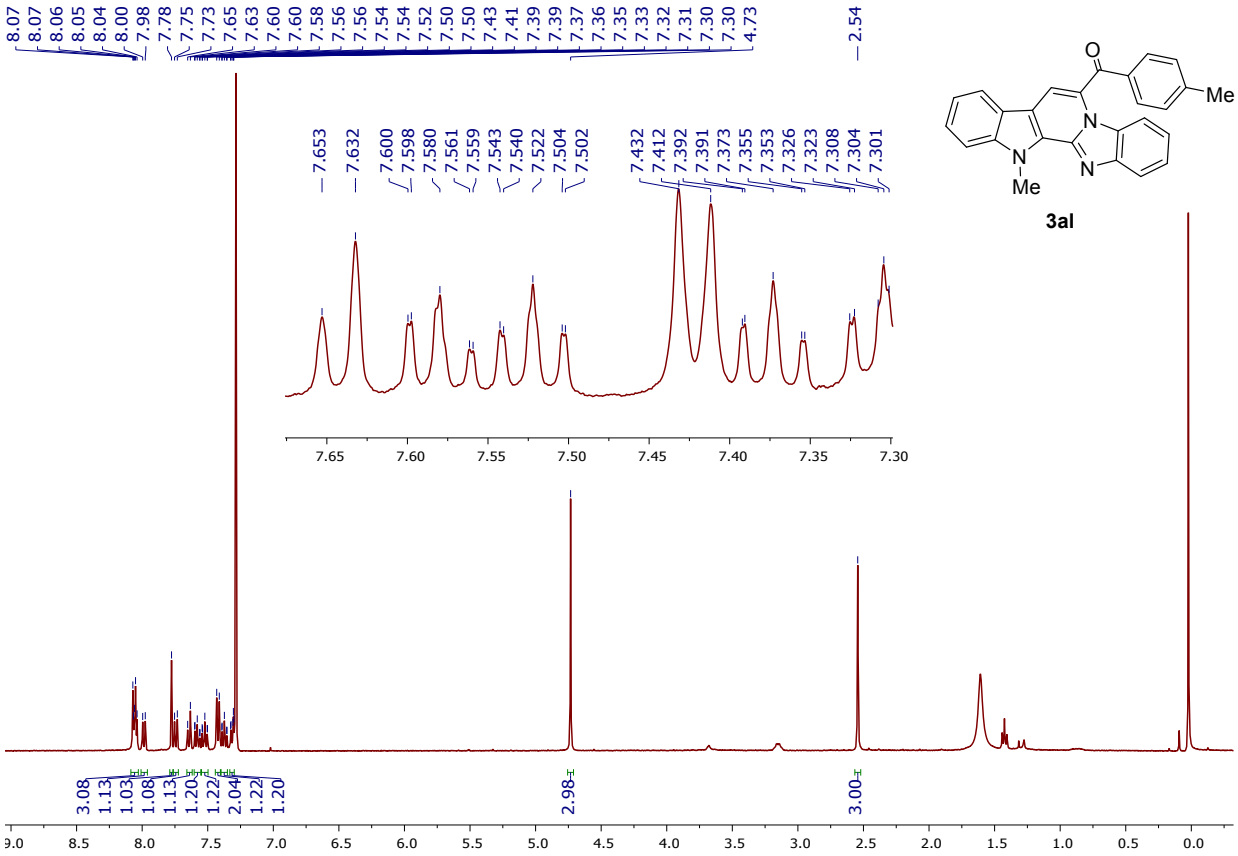
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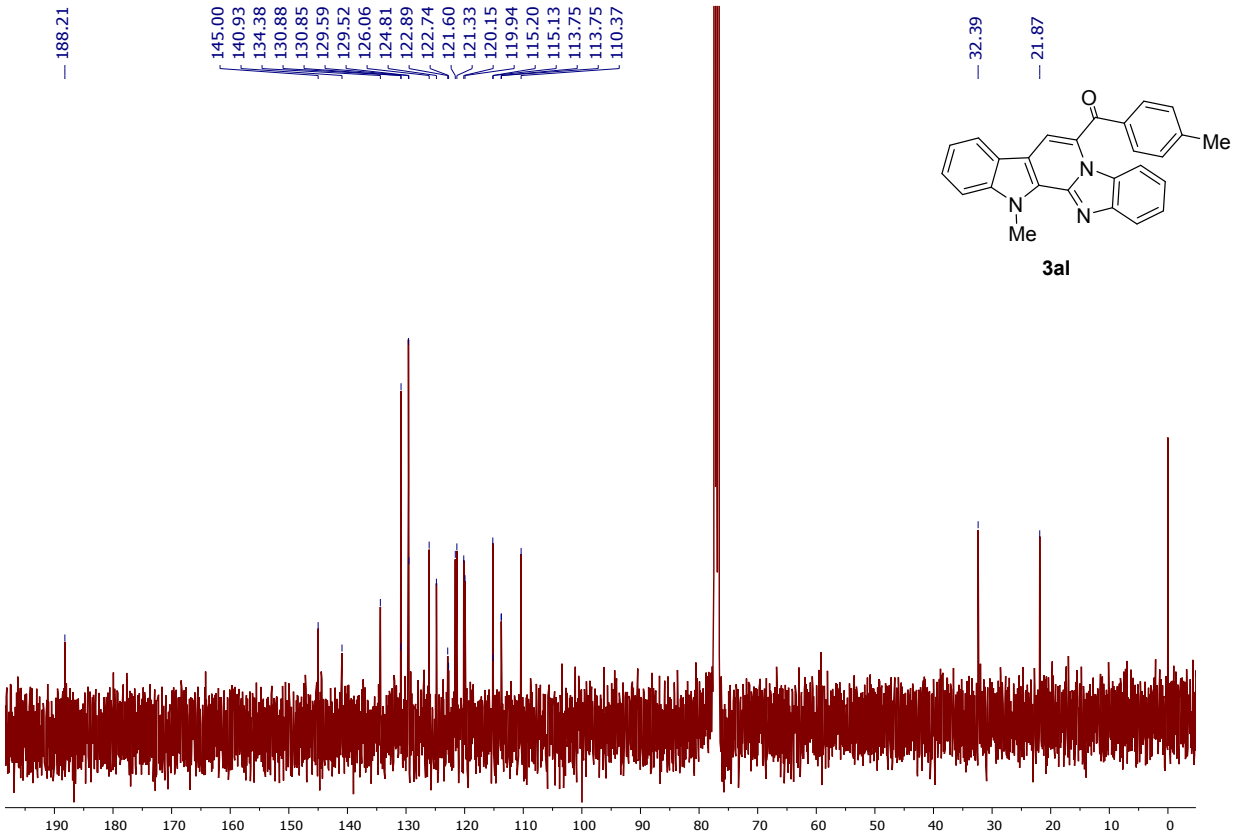
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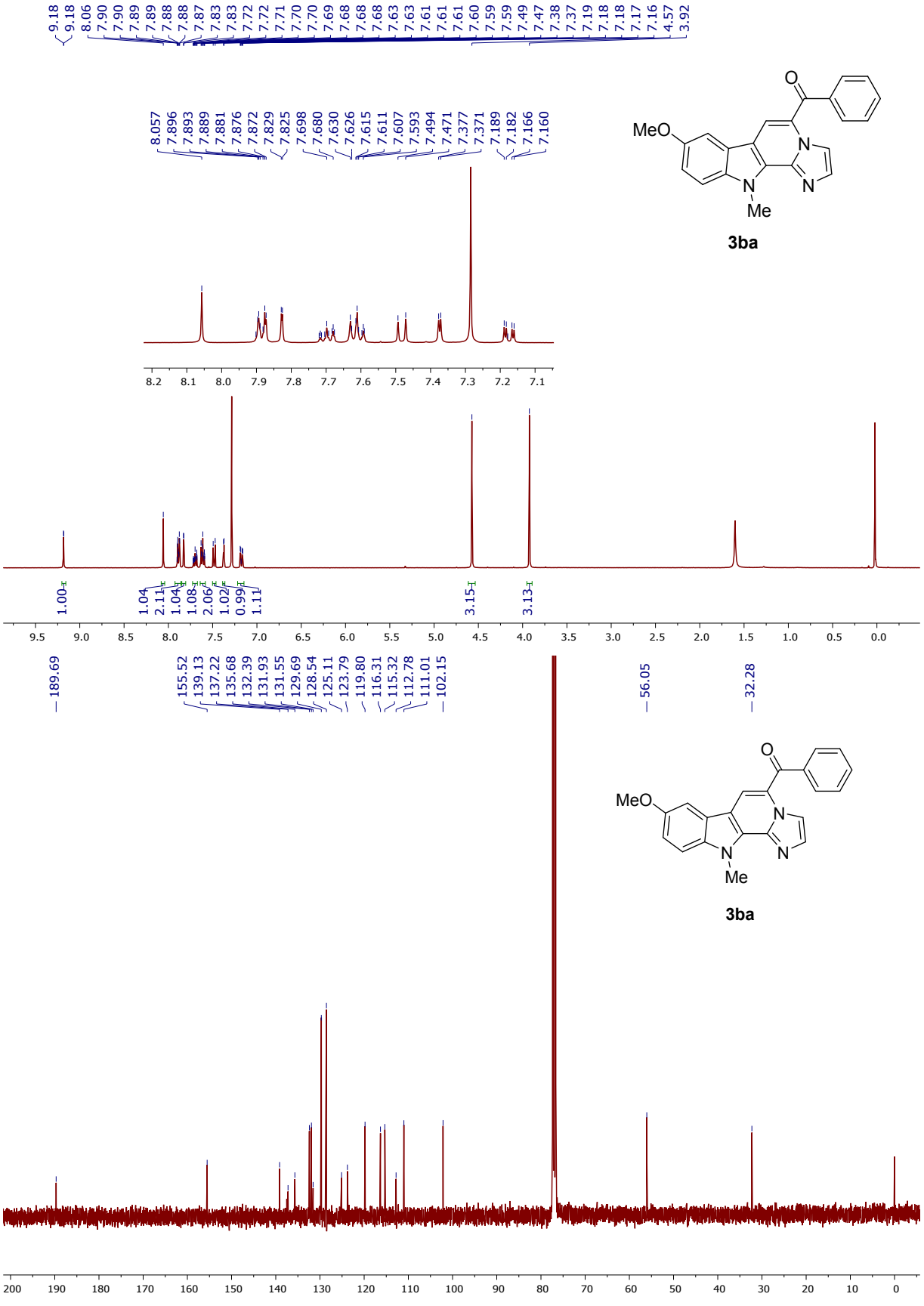
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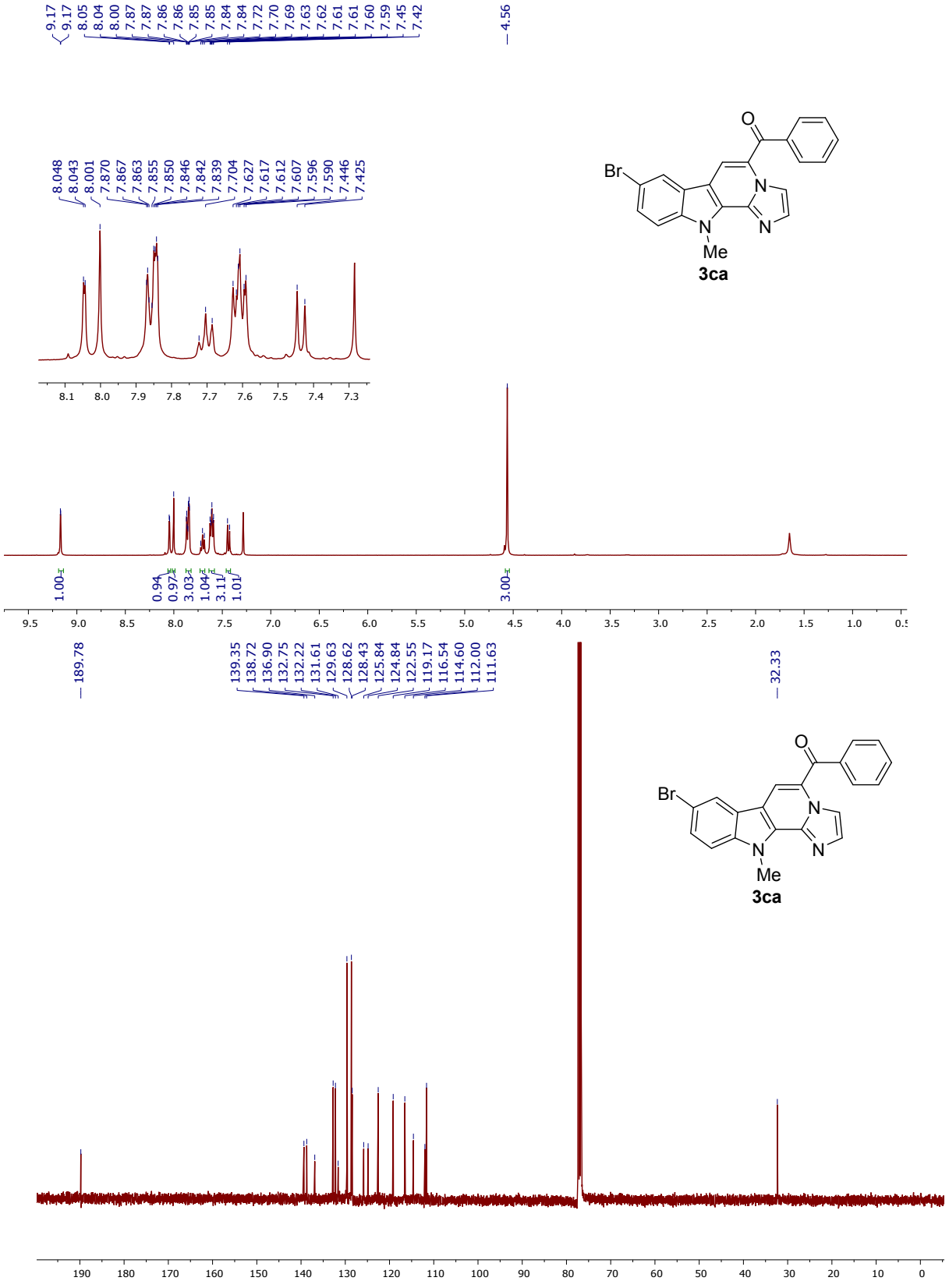
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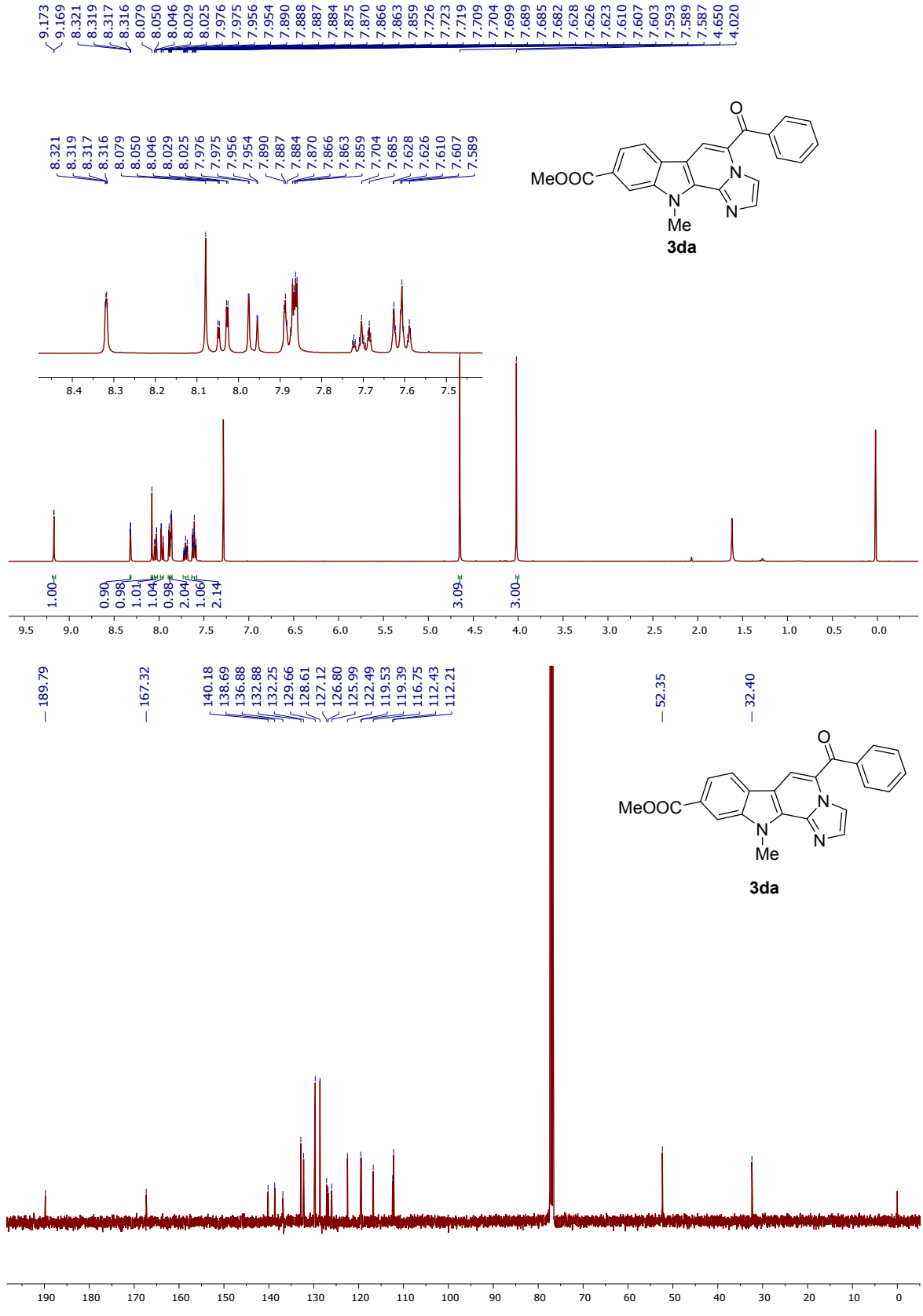
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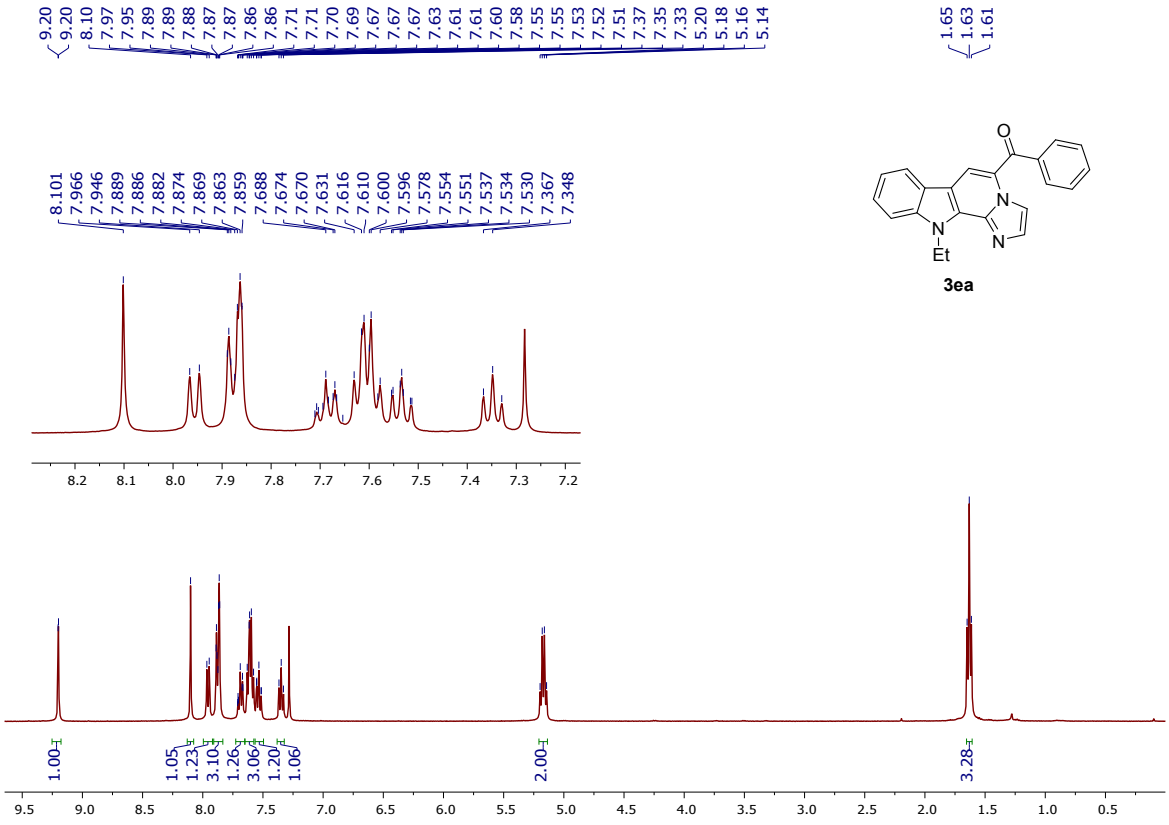
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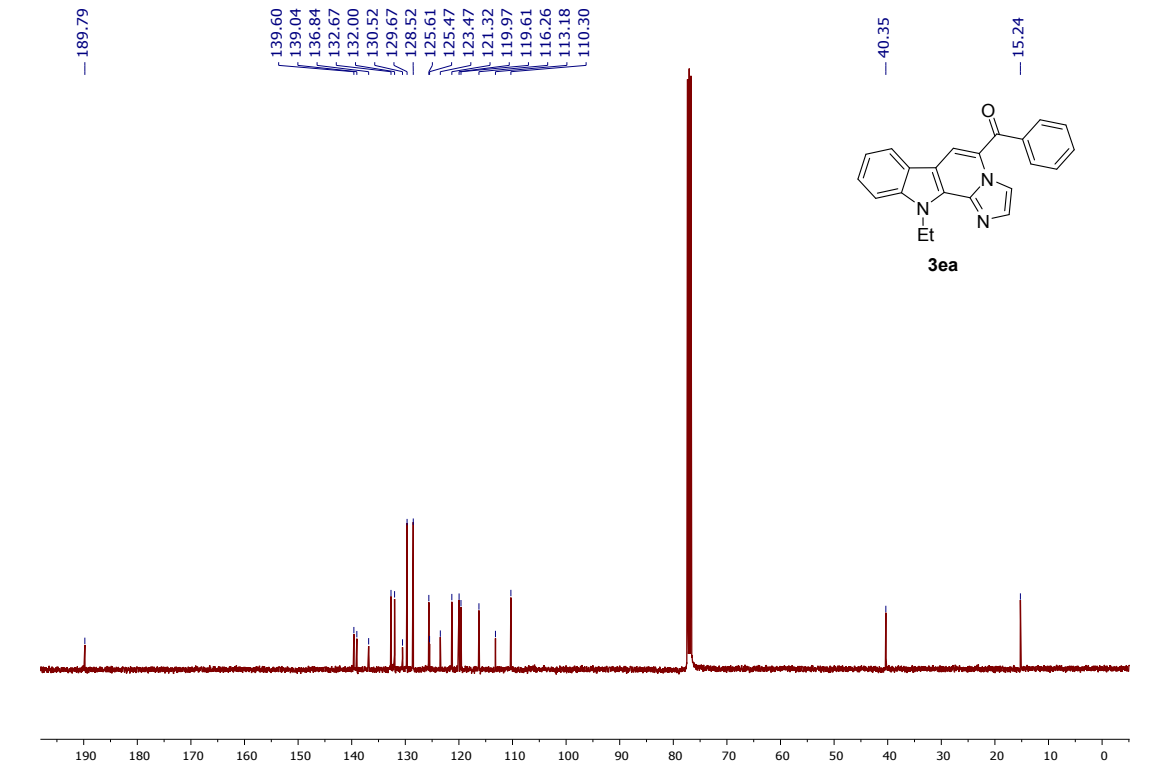
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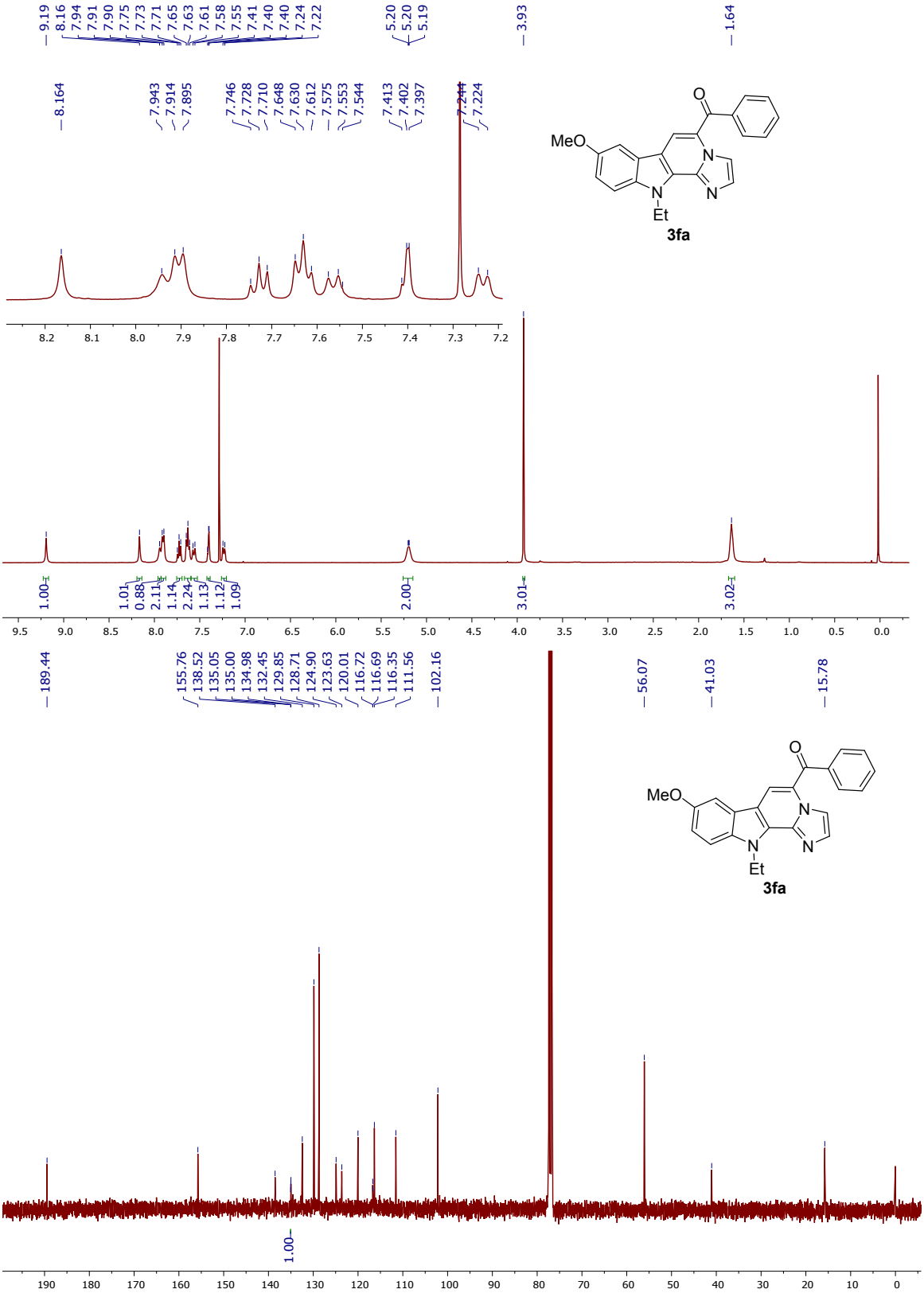
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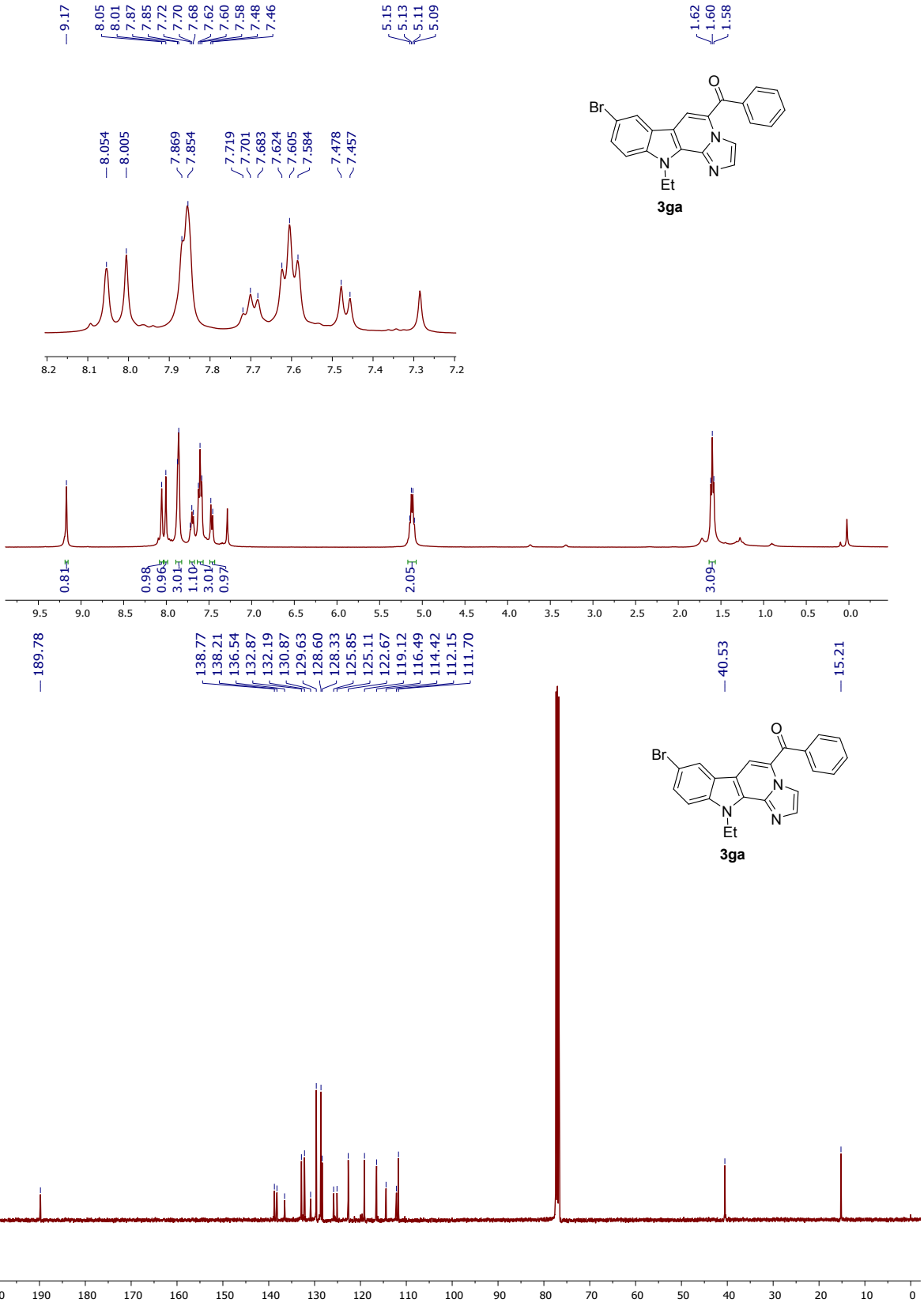
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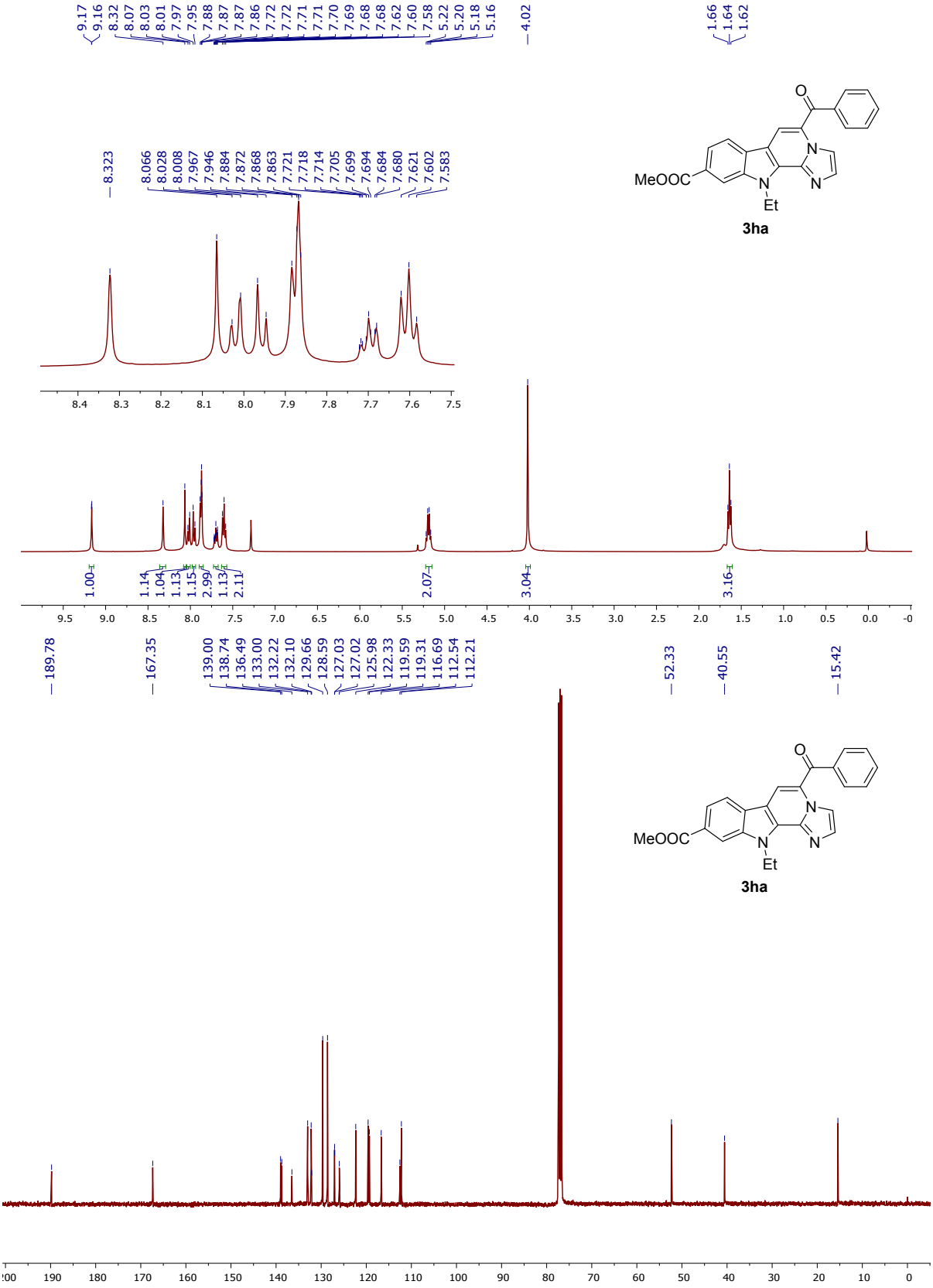
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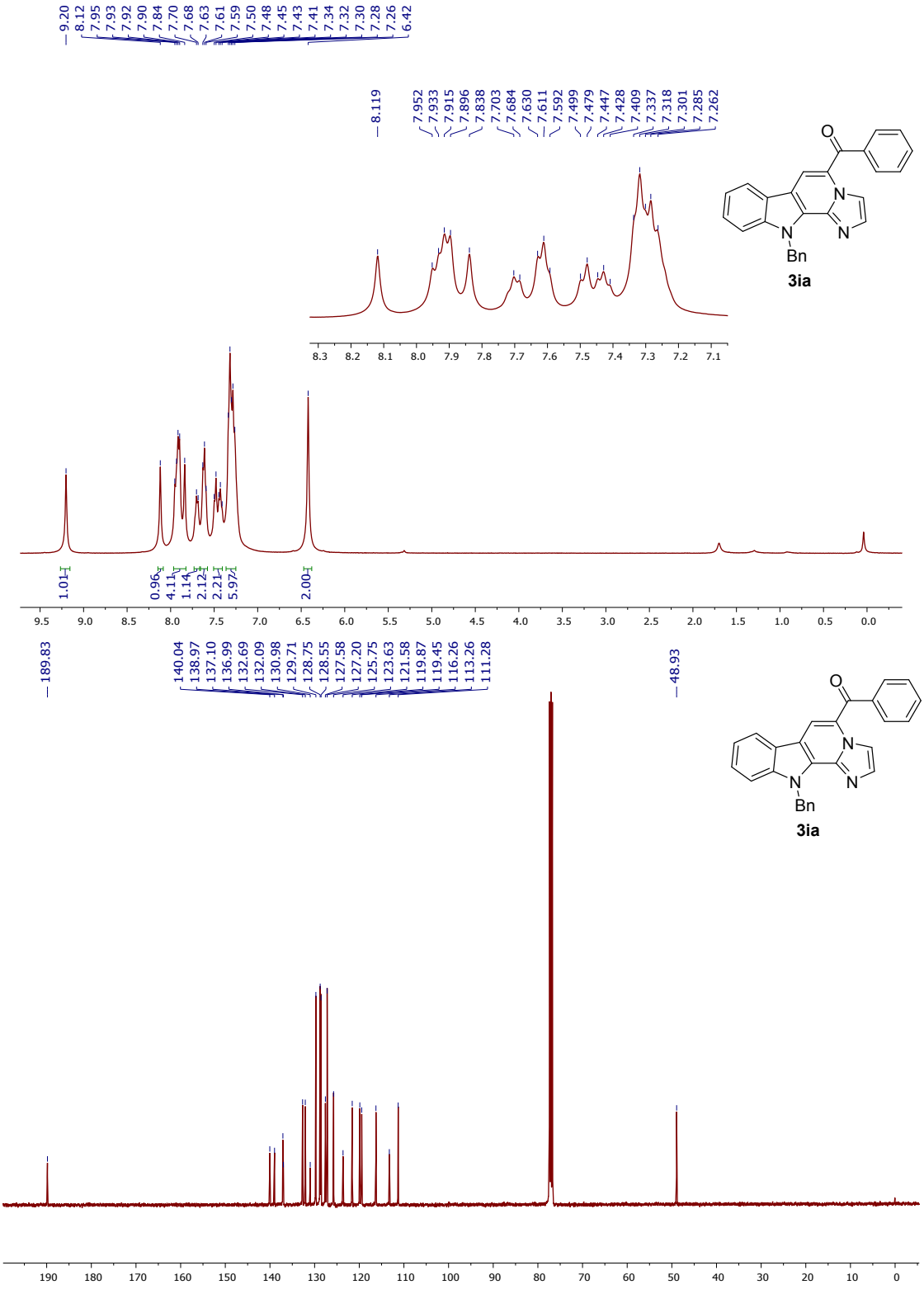
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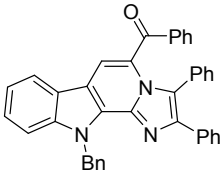
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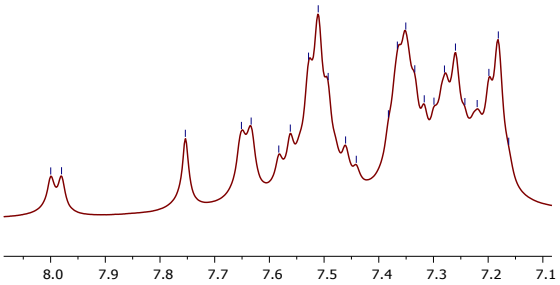
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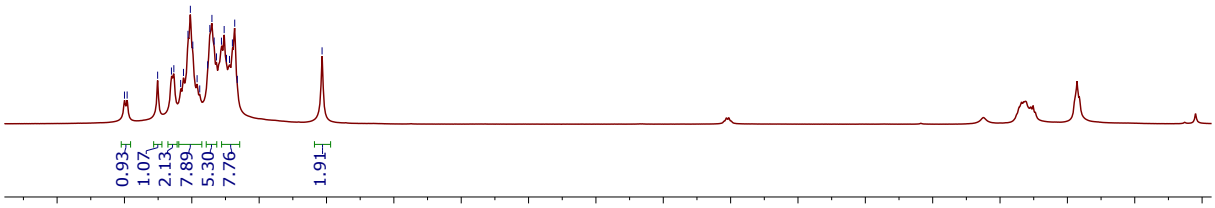
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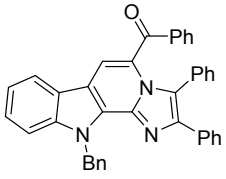
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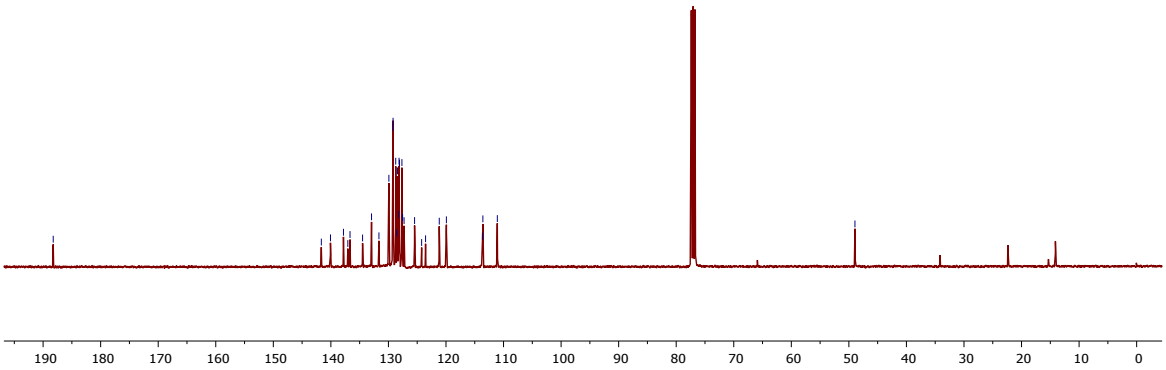
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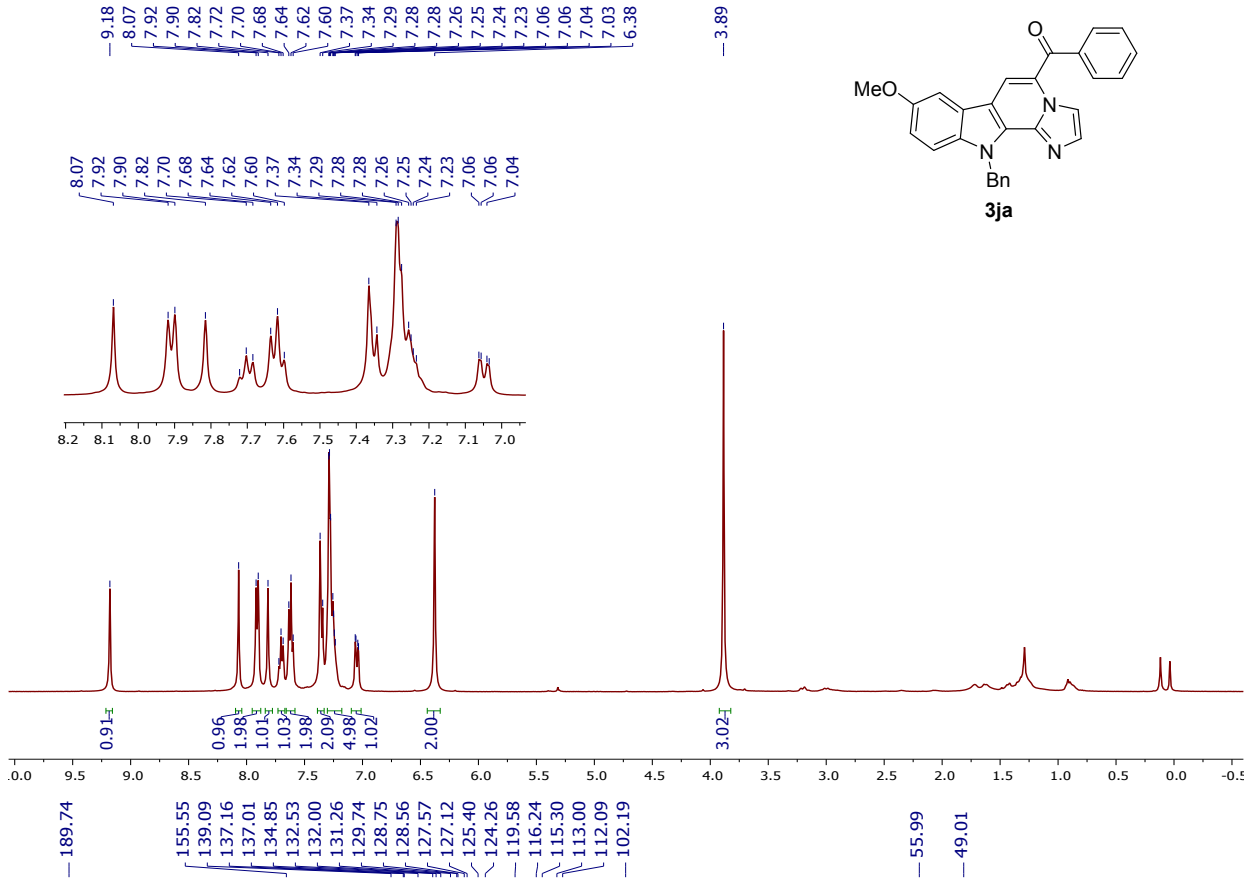
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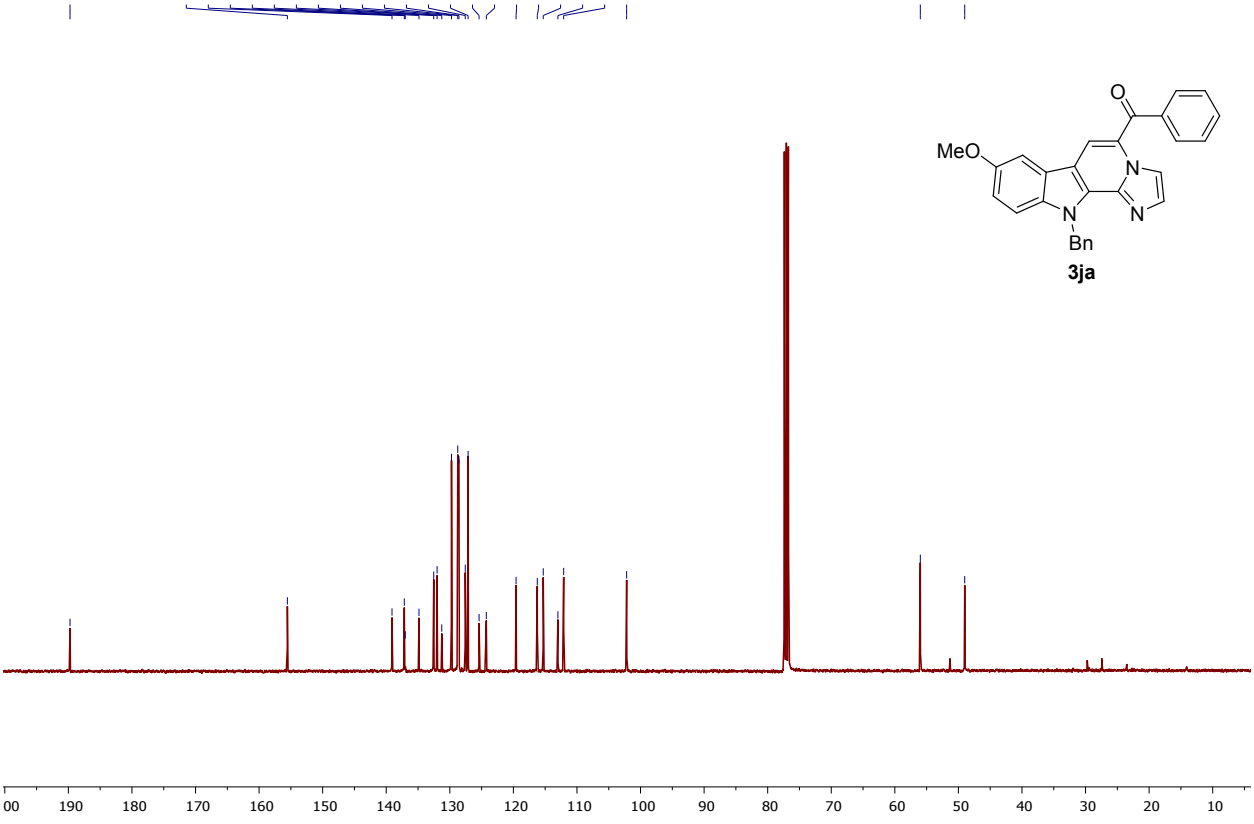
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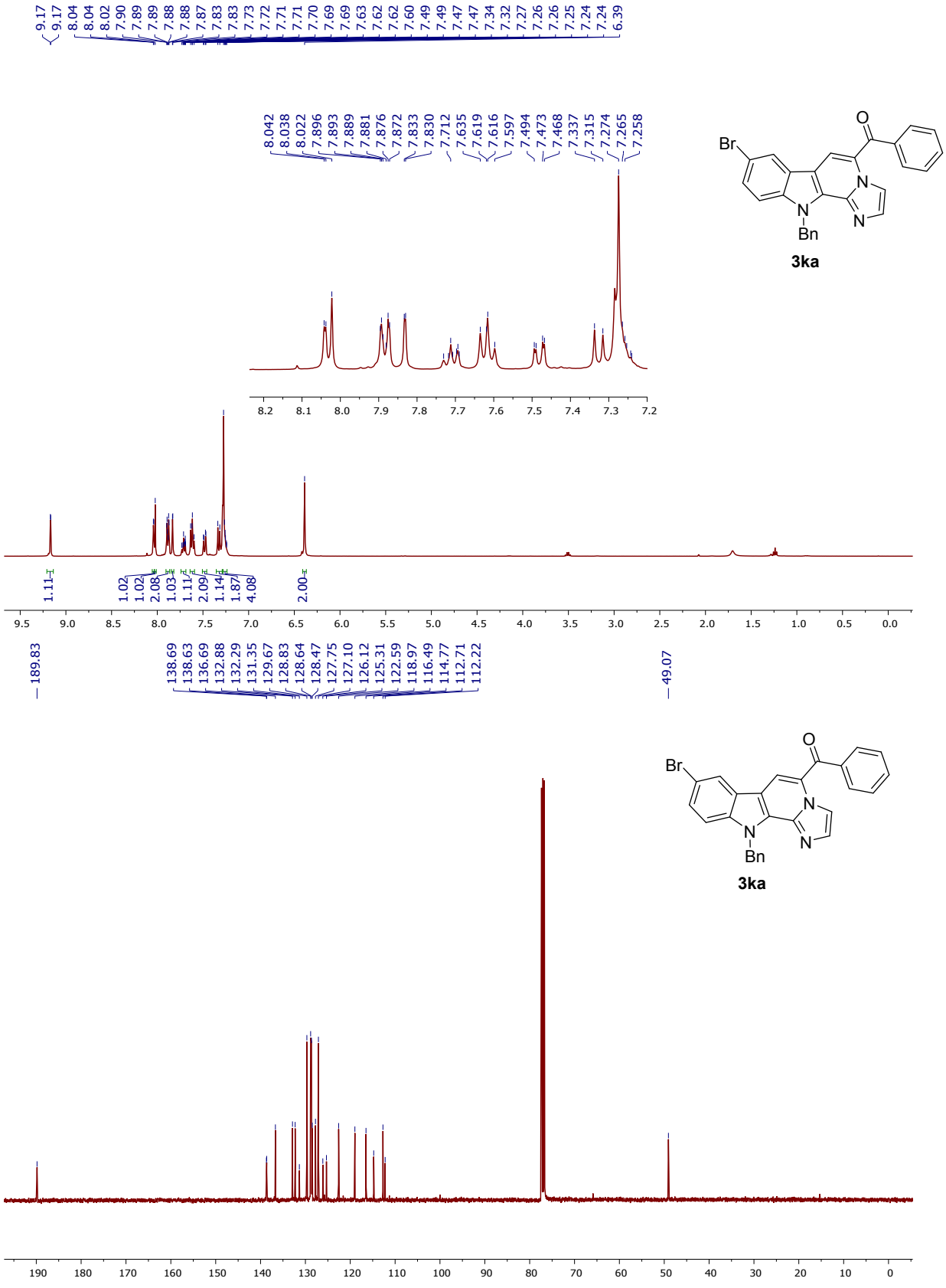
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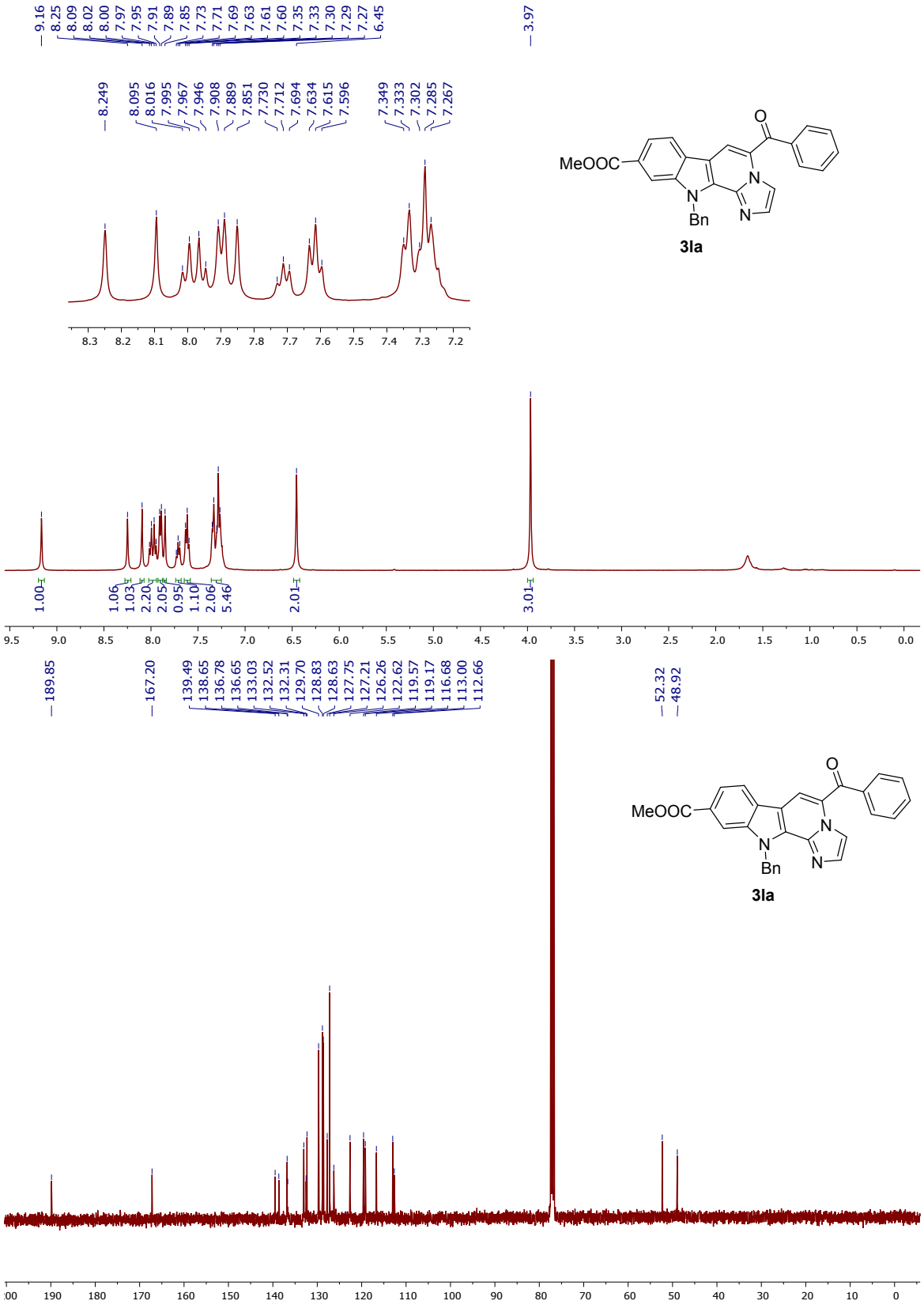
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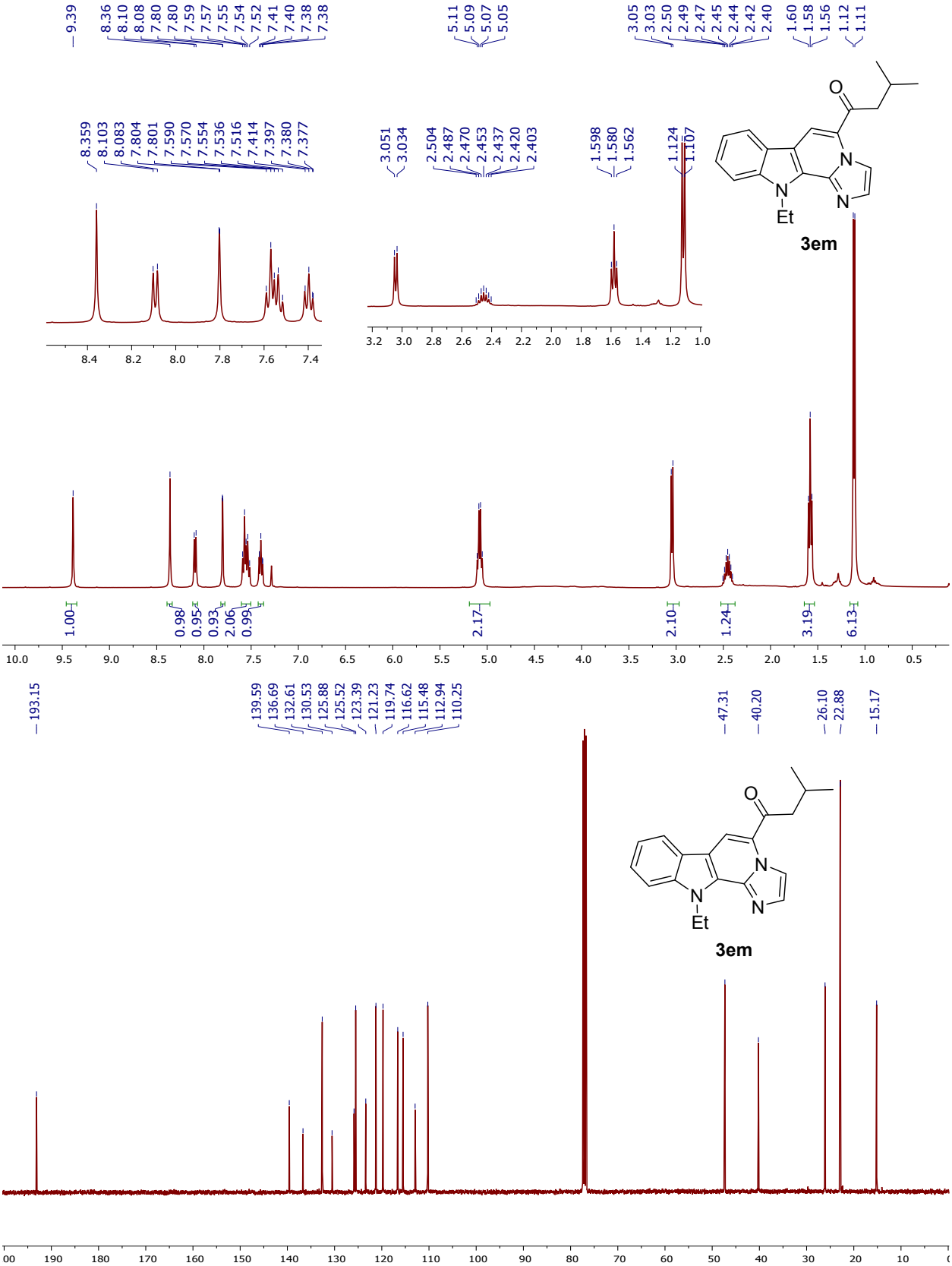
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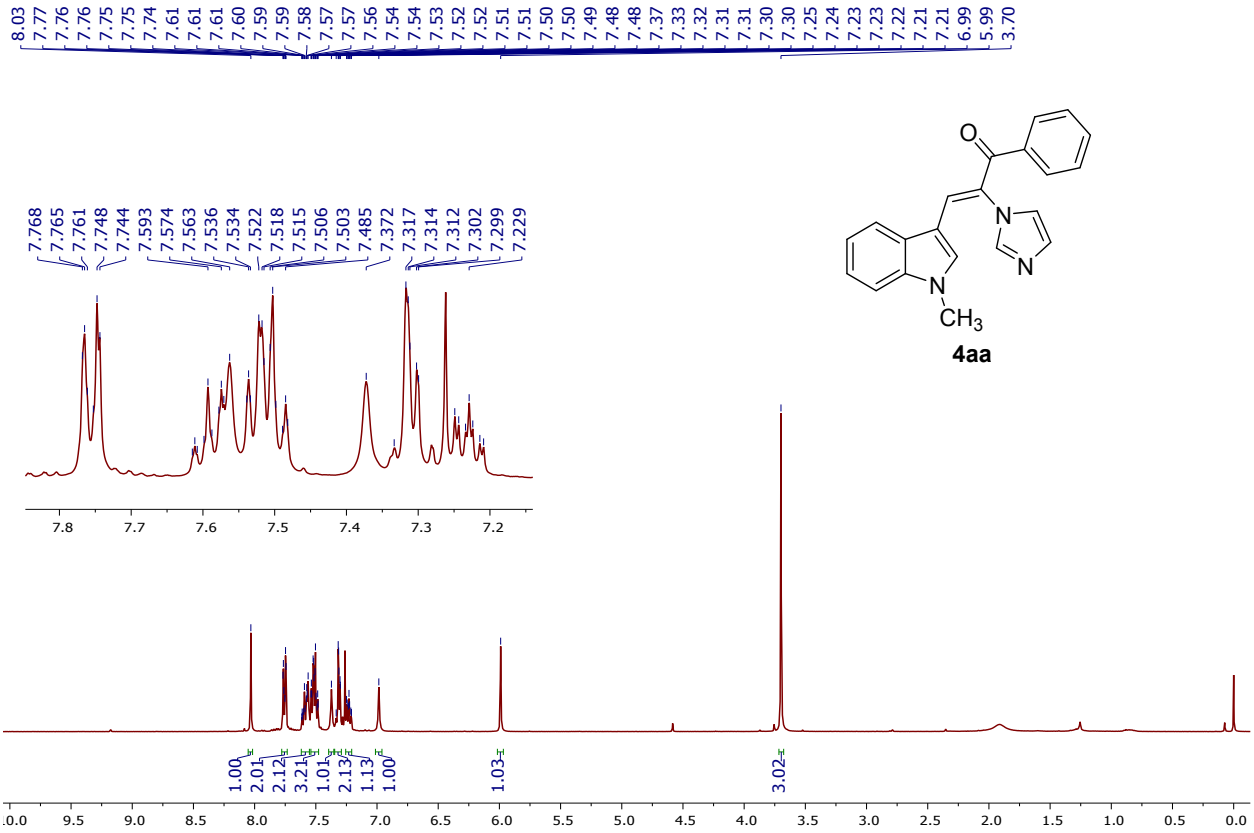
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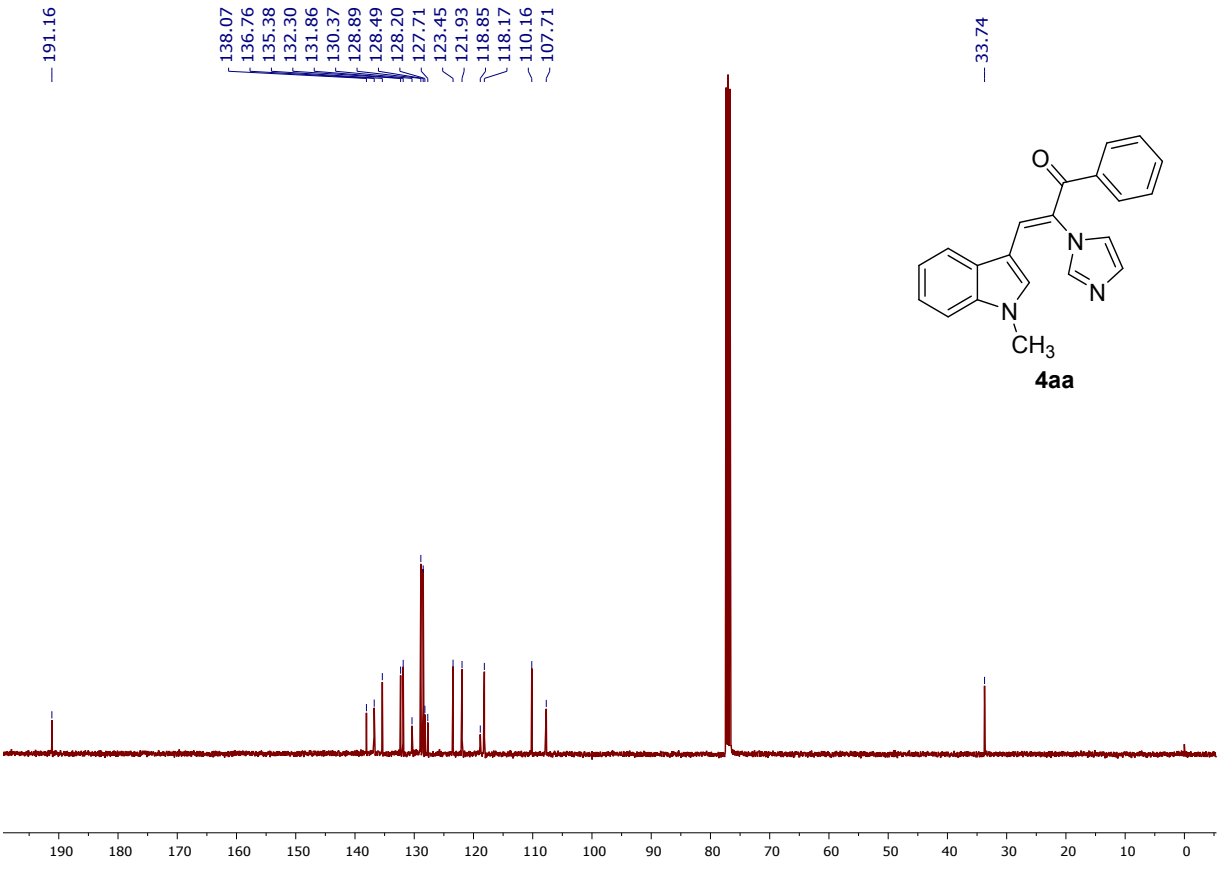
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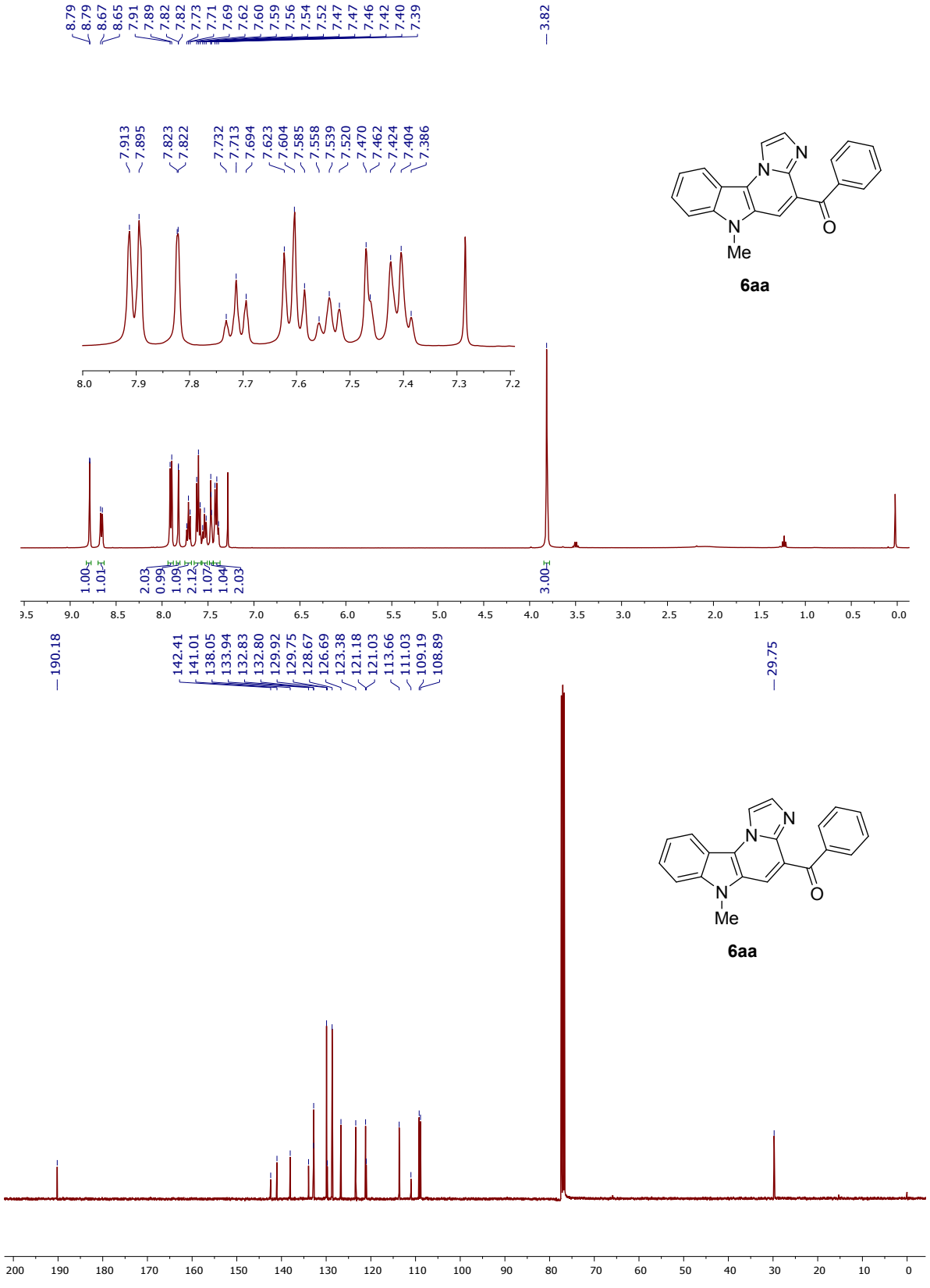
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7.59
7.56
7.54
7.52
7.47
7.47
7.46
7.42
7.40
7.39
3.82
7.913
7.895
7.823
7.822
7.732
7.713
7.694
7.623
7.604
7.585
7.558
7.539
7.520
7.470
7.462
7.424
7.404
7.386
N
N
N
O
Me
6aa
1.00
1.01
2.03
0.99
1.09
2.12
1.07
1.04
2.03
3.00
190.18
142.41
141.01
138.05
133.94
132.83
132.80
129.92
129.75
128.67
126.69
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121.03
113.66
111.03
109.19
108.89
29.75
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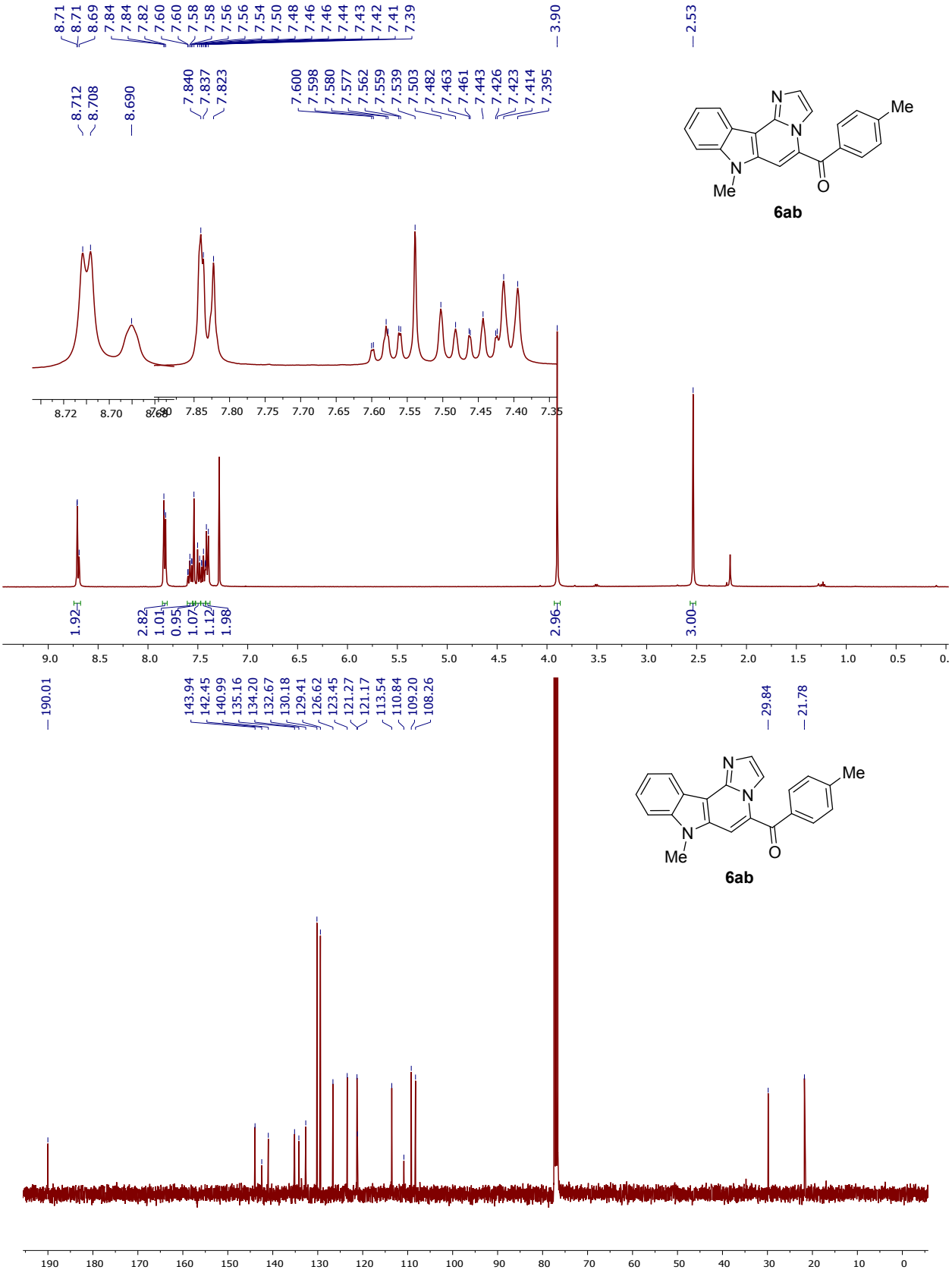
N
N
O
Me
6aa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7.60
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7.54
7.50
7.48
7.46
7.46
7.44
7.43
7.42
7.41
7.39
3.90
2.53
8.712
8.708
8.690
7.840
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7.823
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7.559
7.539
7.503
7.482
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7.395
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N
N
Me
Me
O
6ab
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7.60
7.55
7.50
7.45
7.40
7.35
1.92
2.82
1.01
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1.07
1.12
1.98
2.96
3.00
9.0
8.5
8.0
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6.5
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3.5
3.0
2.5
2.0
1.5
1.0
0.5
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135.16
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129.41
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121.27
121.17
113.54
110.84
109.20
108.26
29.84
21.78
N
N
N
Me
Me
O
6ab
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120
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90
80
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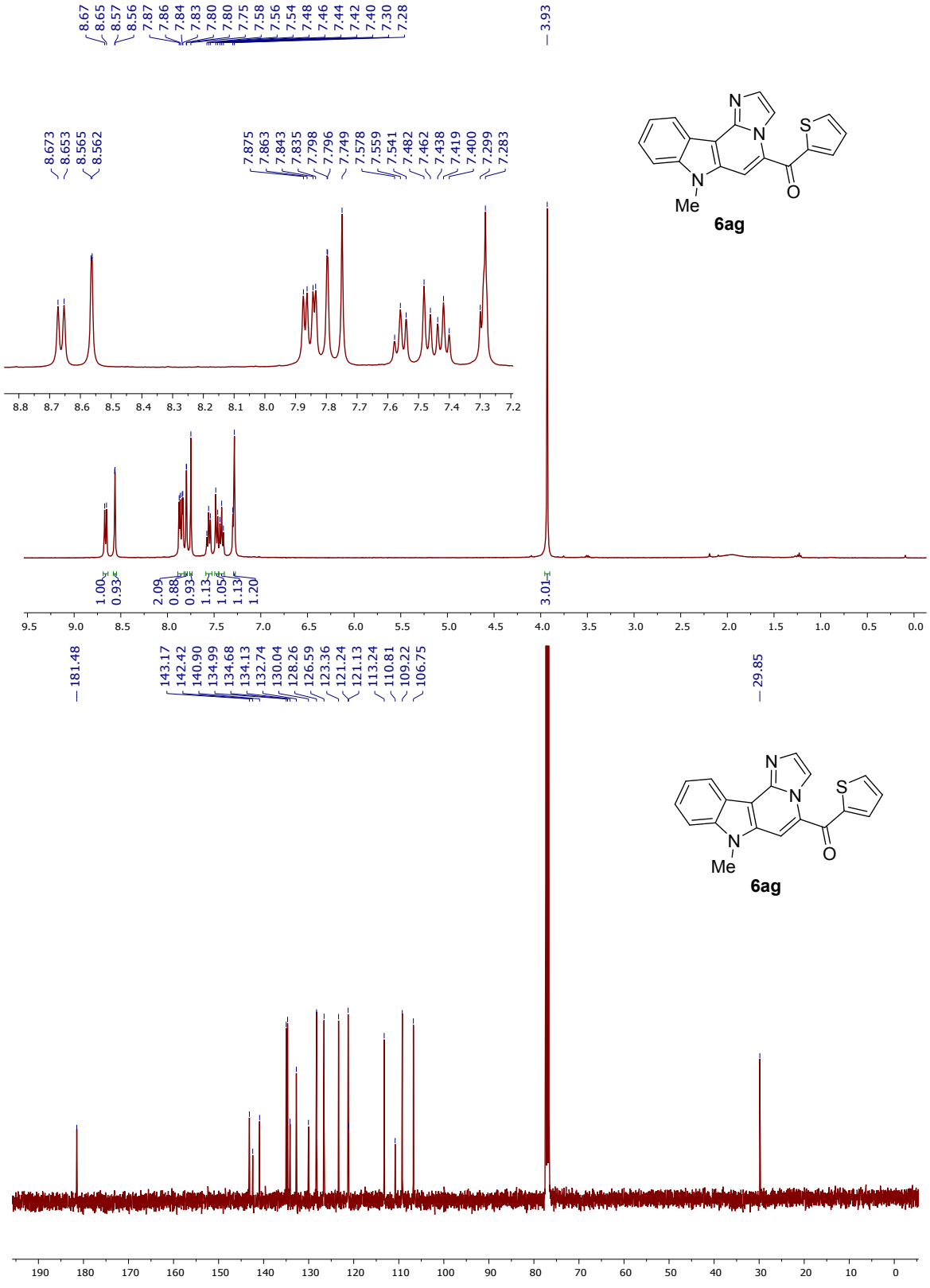
20
10
0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7.56
7.54
7.48
7.46
7.44
7.42
7.40
7.30
7.28
3.93
8.673
8.653
8.565
8.562
7.875
7.863
7.843
7.835
7.798
7.796
7.749
7.578
7.559
7.541
7.482
7.462
7.438
7.419
7.400
7.299
7.283
N
N
S
N
Me
O
6ag
1.00
0.93
2.09
0.88
0.93
1.13
1.05
1.13
1.20
3.01
181.48
143.17
142.42
140.90
134.99
134.68
134.13
132.74
130.04
128.26
126.59
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109.22
106.75
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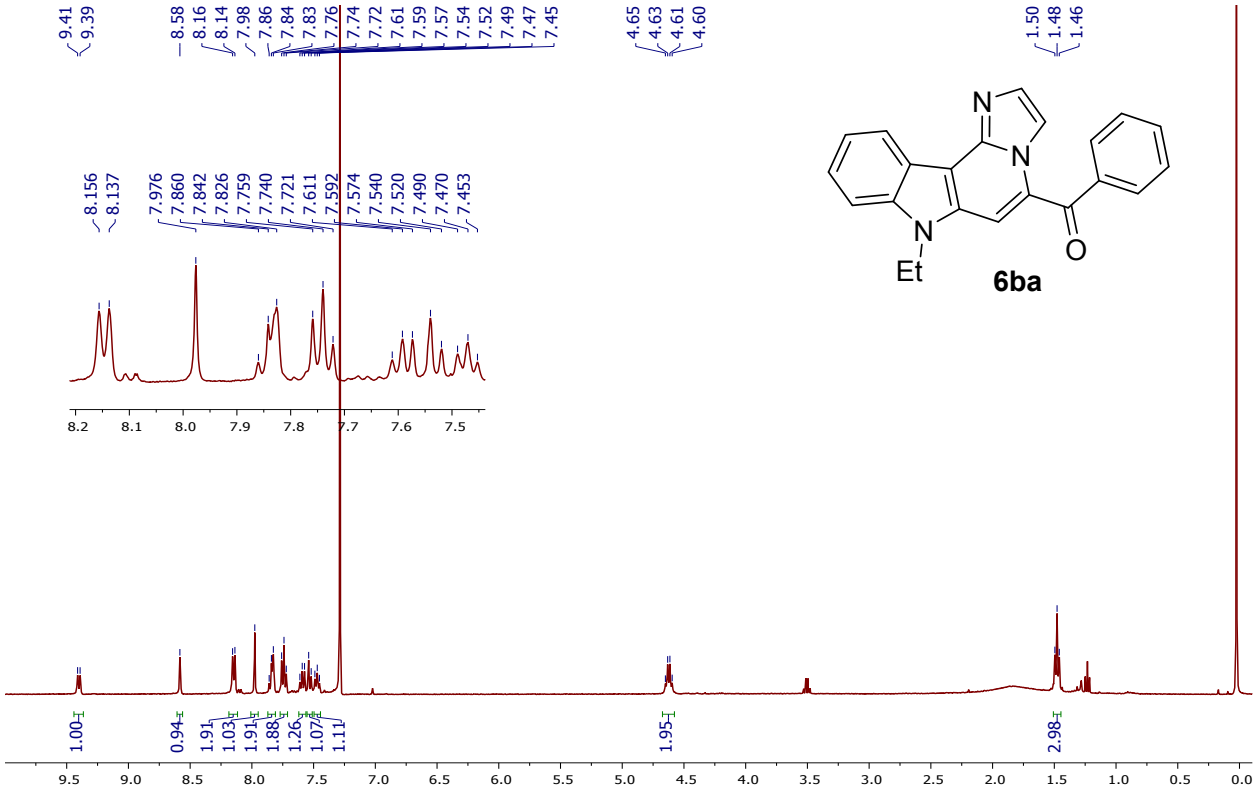
N
N
S
N
Me
O
6ag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7.84
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7.61
7.59
7.57
7.54
7.52
7.49
7.47
7.45
4.65
4.63
4.61
4.60
1.50
1.48
1.46
8.156
8.137
7.976
7.860
7.842
7.826
7.759
7.740
7.721
7.611
7.592
7.574
7.540
7.520
7.490
7.470
7.453
N
N
N
Et
O
6ba
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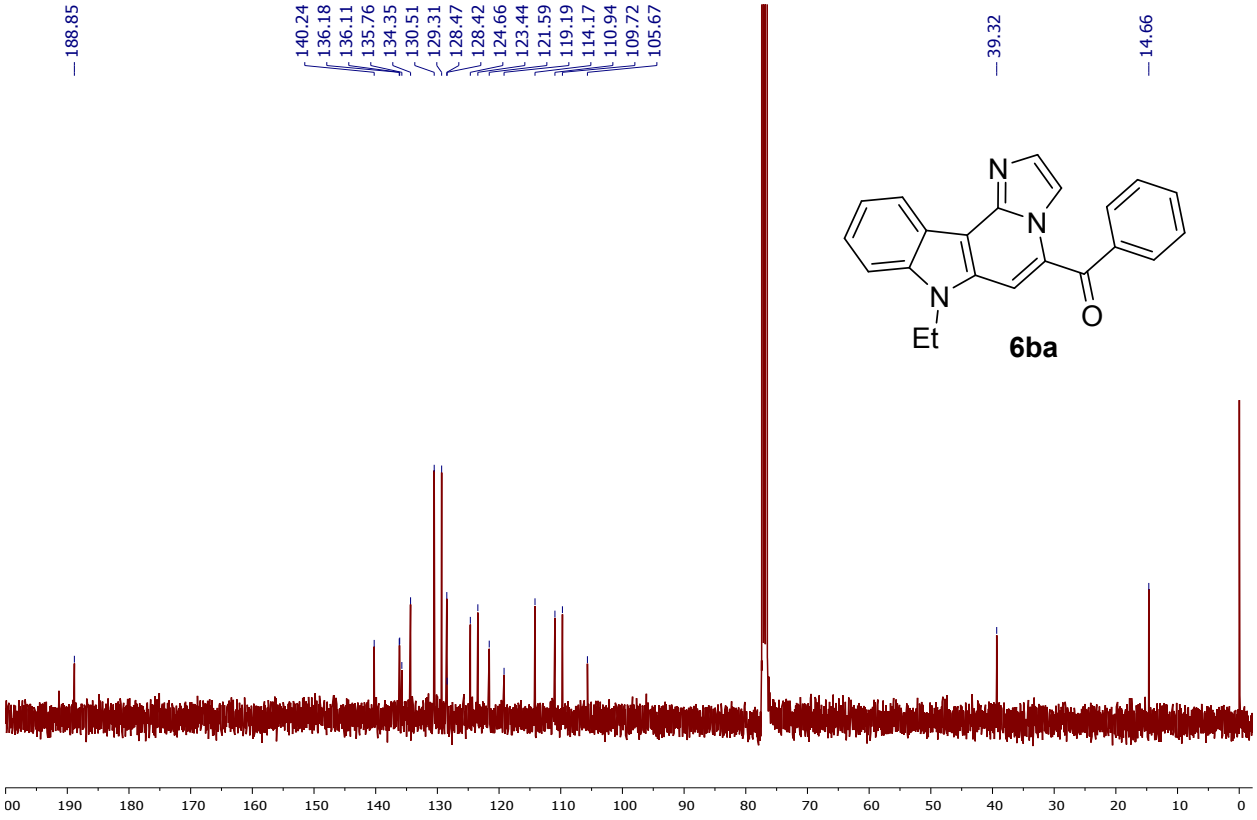
0.94
1.91
1.03
1.91
1.88
1.26
1.07
1.11
1.95
2.98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136.18
136.11
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134.35
130.51
129.31
128.47
128.42
124.66
123.44
121.59
119.19
114.17
110.94
109.72
105.67
39.32
14.66
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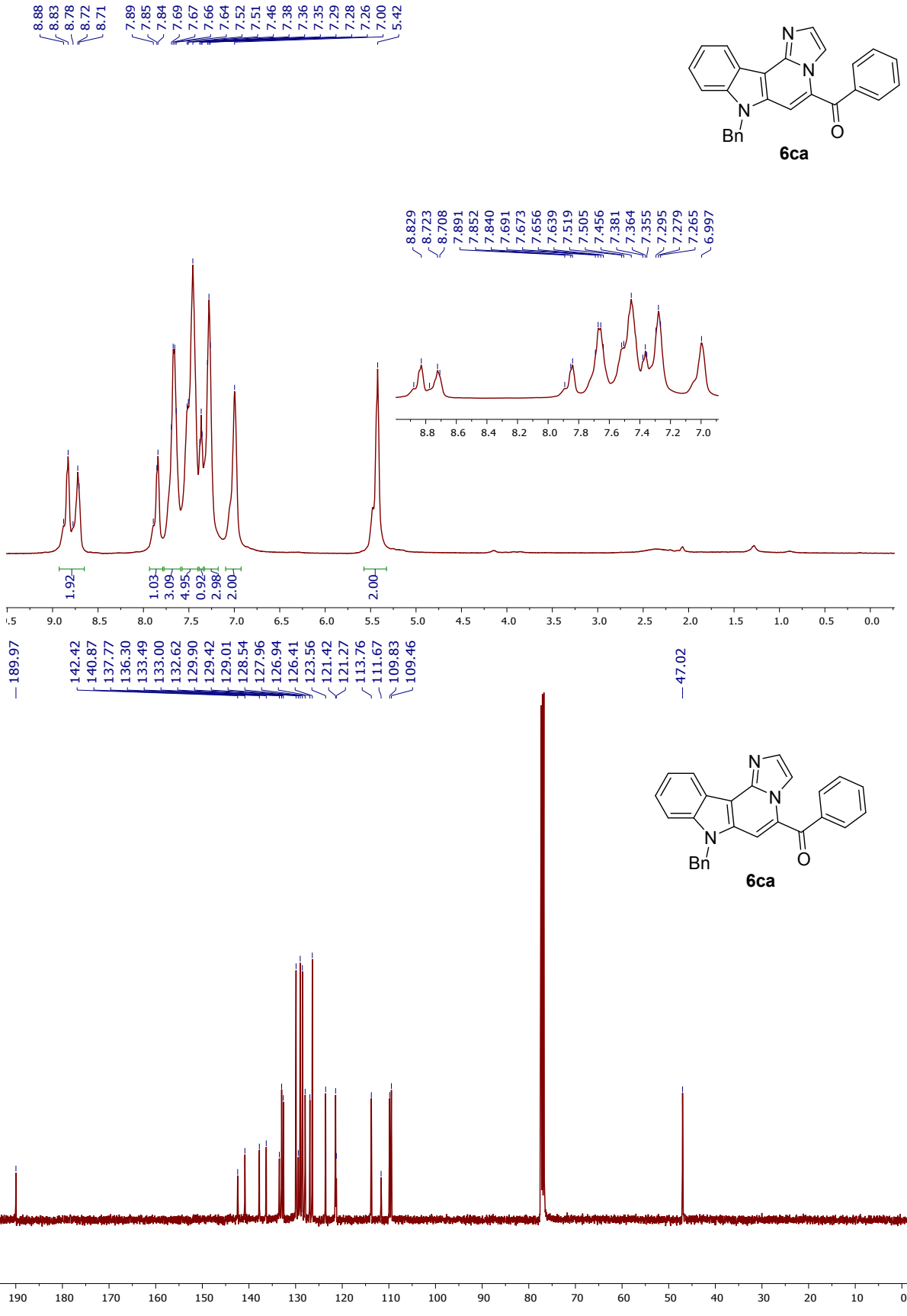
N
N
Et
O
6ba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7.84
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7.67
7.66
7.64
7.52
7.51
7.46
7.38
7.36
7.35
7.29
7.28
7.26
7.00
5.42
N
N
N
Bn
O
6ca
8.829
8.723
8.708
7.891
7.852
7.840
7.691
7.673
7.656
7.639
7.519
7.505
7.456
7.381
7.364
7.355
7.295
7.279
7.265
6.997
1.92
1.03
3.09
4.95
0.92
2.98
2.00
2.00
189.97
142.42
140.87
137.77
136.30
133.49
133.00
132.62
129.90
129.42
129.01
128.54
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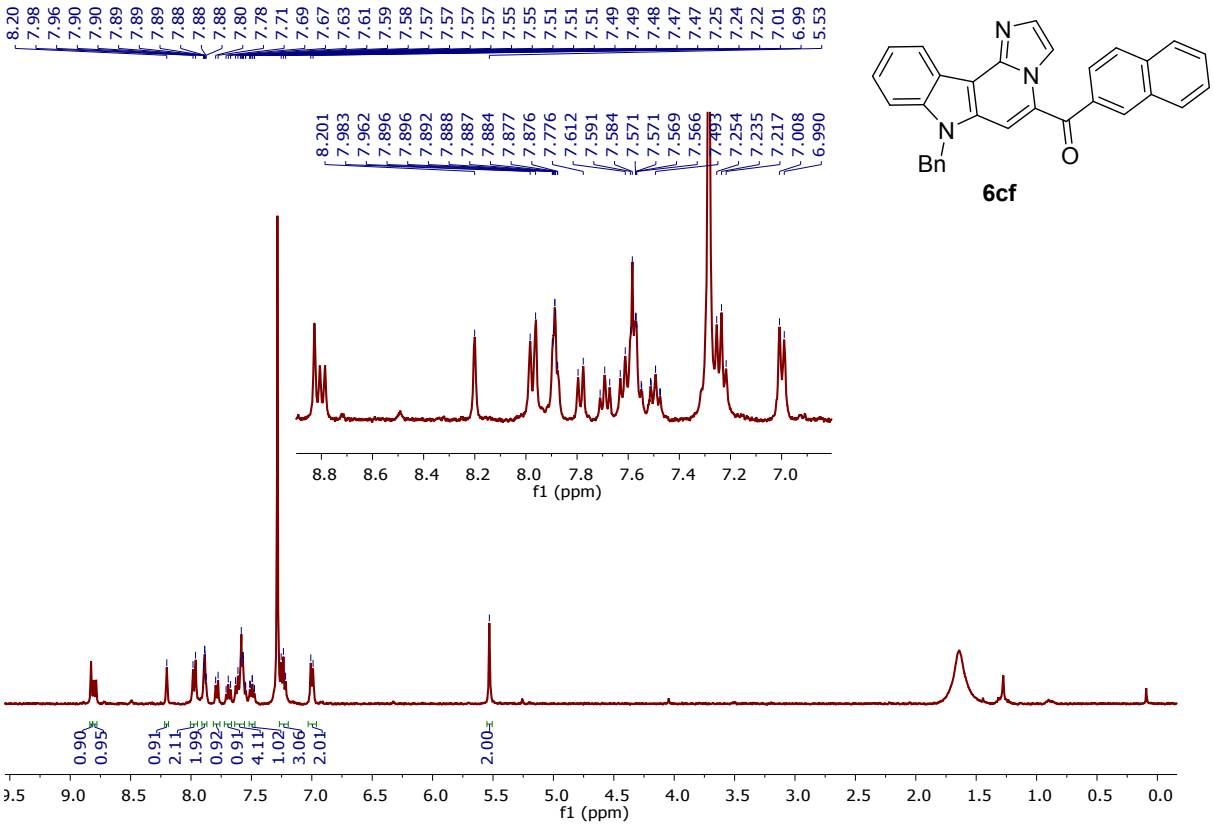
111.67
109.83
109.46
47.02
6ca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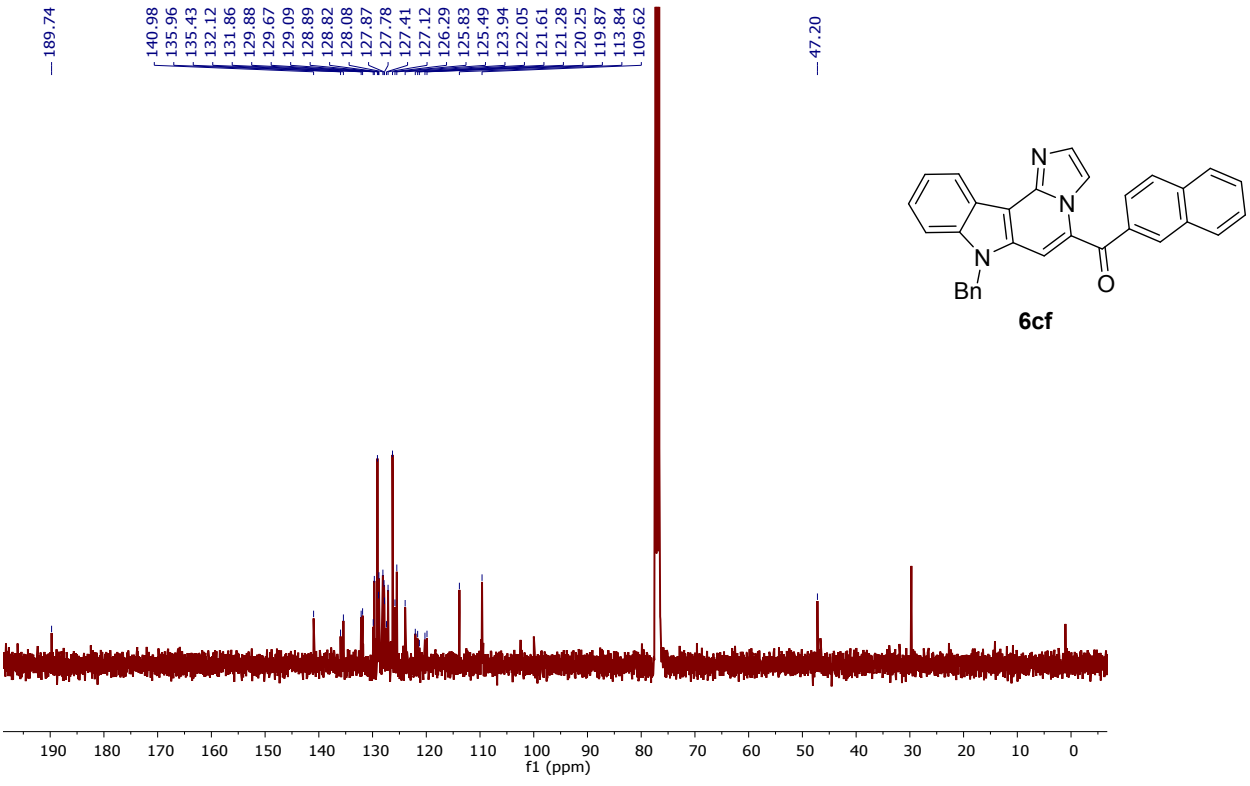
8.201 7.983 7.962 7.896 7.896 7.892 7.888 7.887 7.884 7.877 7.876 7.776 7.612 7.591 7.584 7.571 7.571 7.569 7.566 7.493 7.254 7.235 7.217 7.008 6.990
f1 (ppm)
0.90 0.95 0.91 2.11 1.99 0.92 0.91 4.11 1.02 3.06 2.01 2.00
f1 (ppm)
N
N
N
Bn
O
6cf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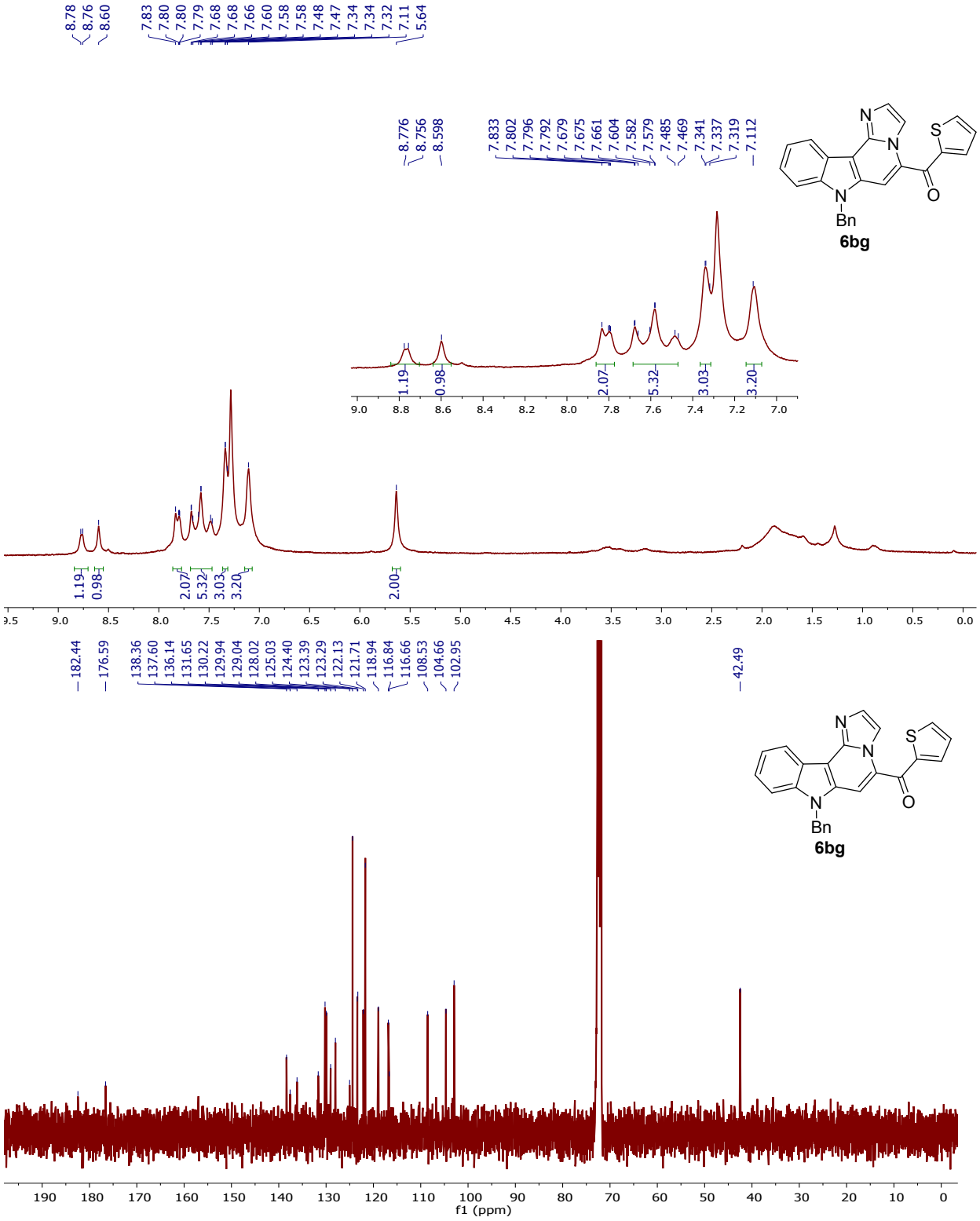
140.98 135.96 135.43 132.12 131.86 129.88 129.67 129.09 128.89 128.82 128.08 127.87 127.78 127.41 127.12 126.29 125.83 125.49 123.94 122.05 121.61 121.28 120.25 119.87 113.84 109.62
47.20
f1 (ppm)
N
N
N
Bn
O
6cf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7.83
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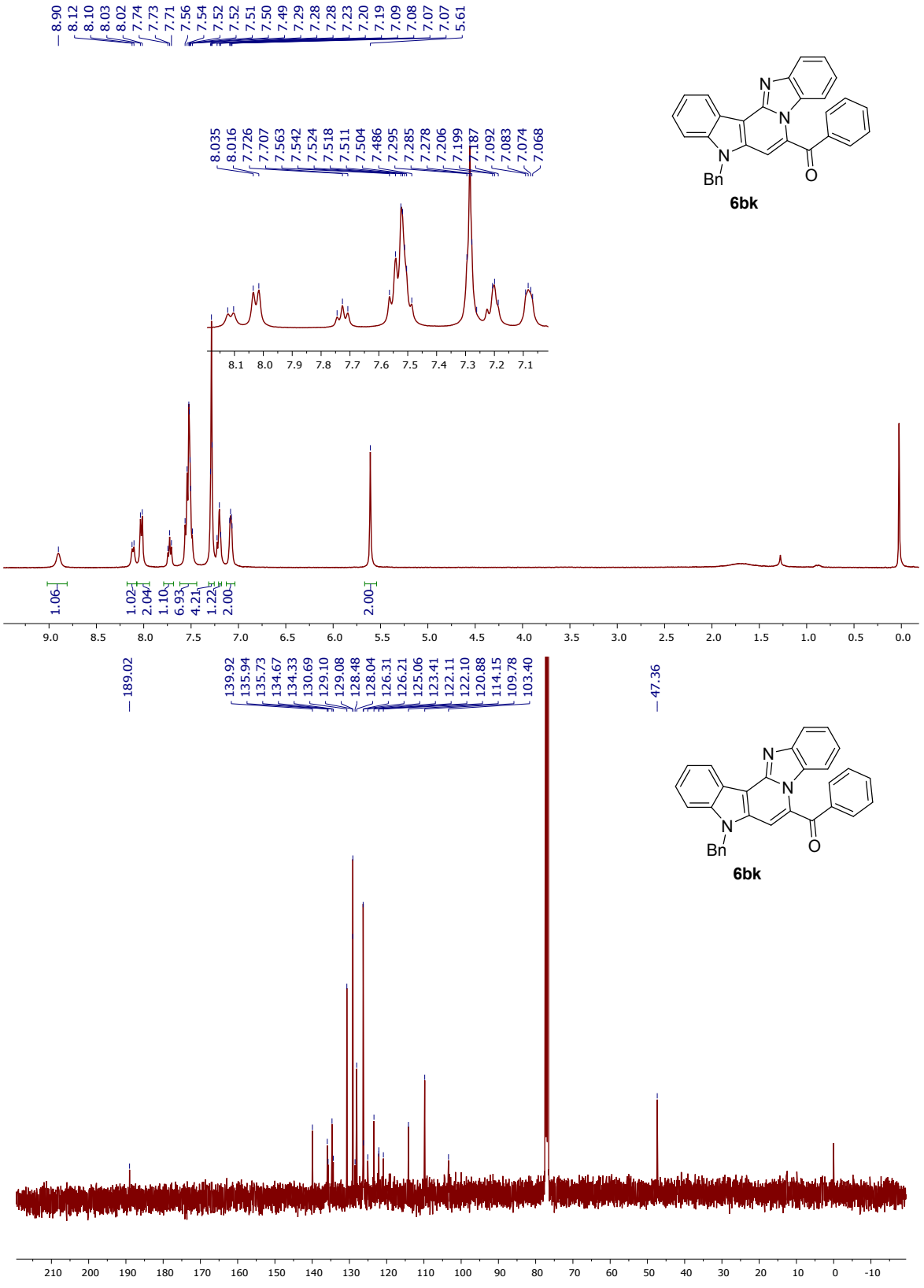
7.80
7.79
7.68
7.68
7.66
7.60
7.58
7.58
7.48
7.47
7.34
7.34
7.32
7.11
5.64
8.776
8.756
8.598
7.833
7.802
7.796
7.792
7.679
7.675
7.661
7.604
7.582
7.579
7.485
7.469
7.341
7.337
7.319
7.112
N
N
S
N
O
Bn
6bg
1.19
0.98
2.07
5.32
3.03
3.20
2.00
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
182.44
176.59
138.36
137.60
136.14
131.65
130.22
129.94
129.04
128.02
125.03
124.40
123.39
123.29
122.13
121.71
118.94
116.84
116.66
108.53
104.66
102.95
42.49
N
N
S
N
O
Bn
6bg
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.71
7.56
7.54
7.52
7.52
7.51
7.50
7.49
7.29
7.28
7.28
7.23
7.20
7.19
7.09
7.08
7.07
7.07
5.61
8.035
8.016
7.726
7.707
7.563
7.542
7.524
7.518
7.511
7.504
7.486
7.295
7.285
7.278
7.206
7.199
7.187
7.092
7.083
7.074
7.068
N
N
N
Bn
O
6bk
1.06
1.02
2.04
1.10
6.93
4.21
1.22
2.00
2.00
189.02
139.92
135.94
135.73
134.67
134.33
130.69
129.10
129.08
128.48
128.04
126.31
126.21
125.06
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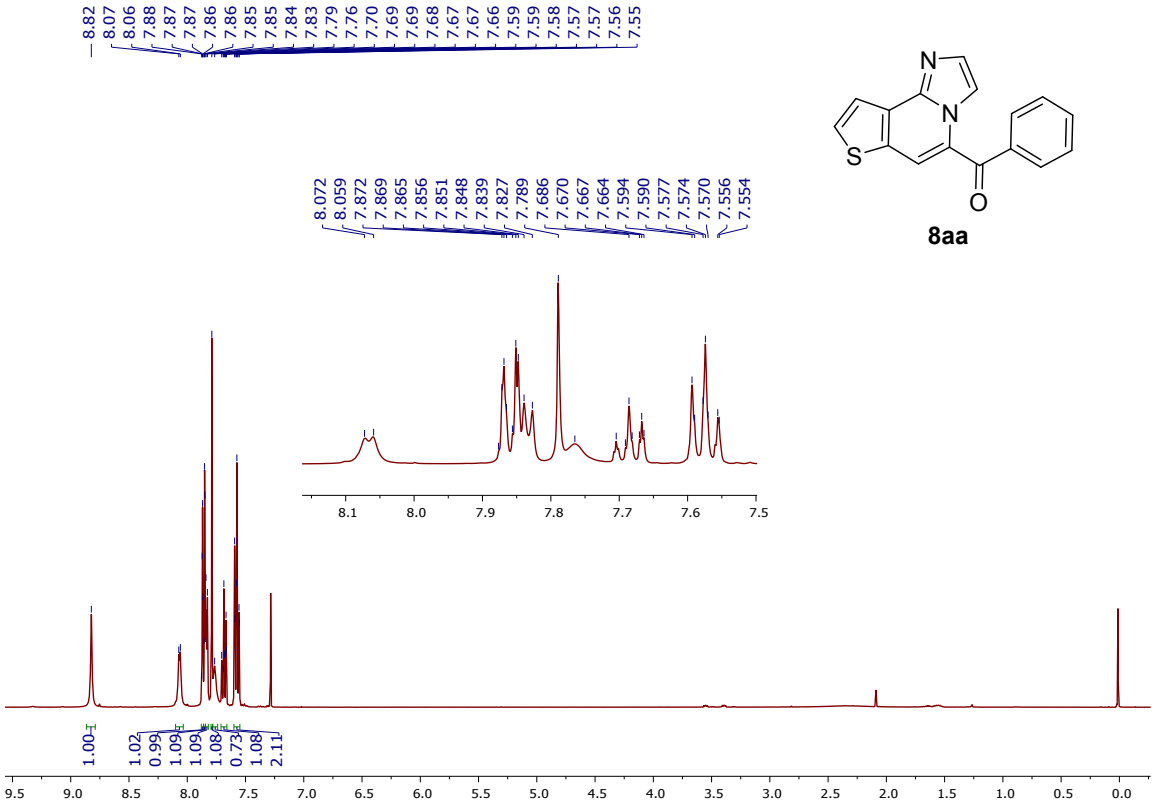
122.10
120.88
114.15
109.78
103.40
47.36
N
N
N
Bn
O
6bk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8.06
7.88
7.87
7.87
7.86
7.86
7.85
7.85
7.84
7.83
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7.76
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7.69
7.69
7.68
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7.67
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7.57
7.56
7.55
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7.686
7.670
7.667
7.664
7.594
7.590
7.577
7.574
7.570
7.556
7.554
N
N
S
O
8aa
1.00
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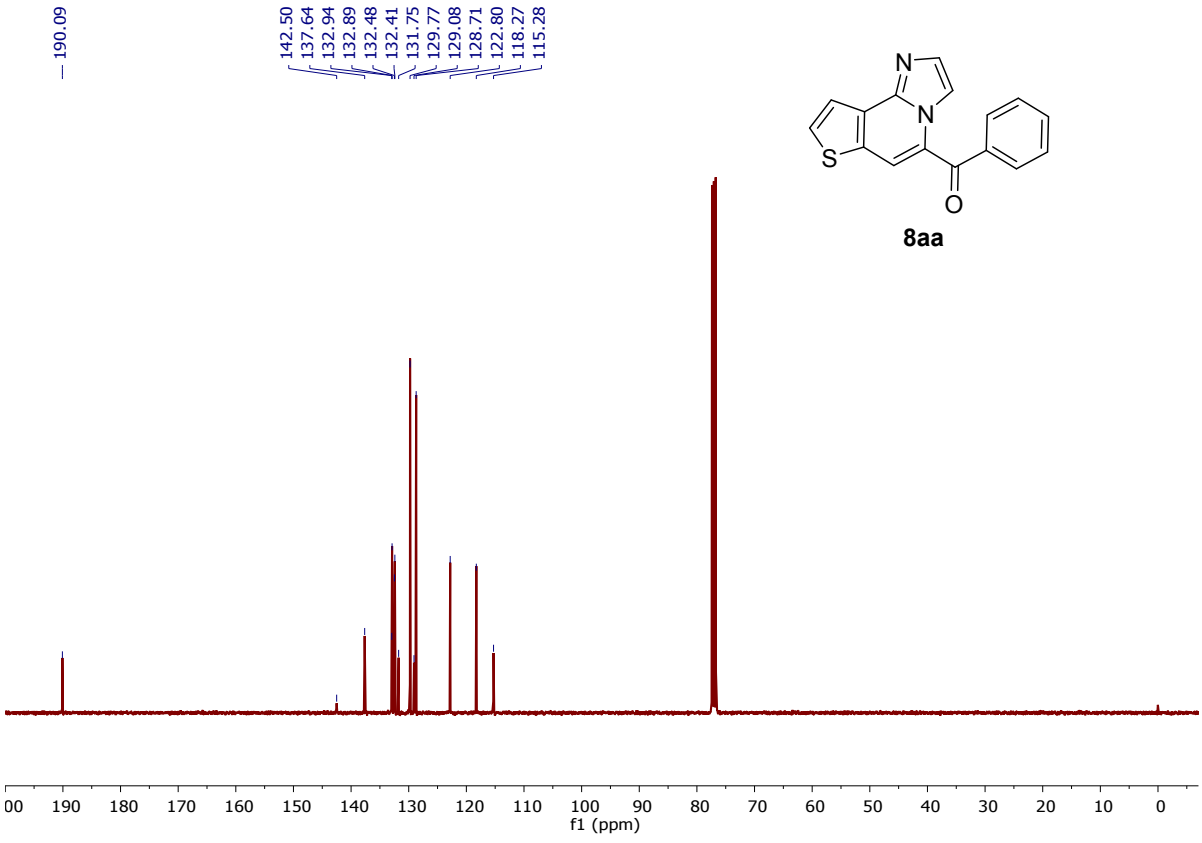
1.09
1.08
0.73
1.08
2.11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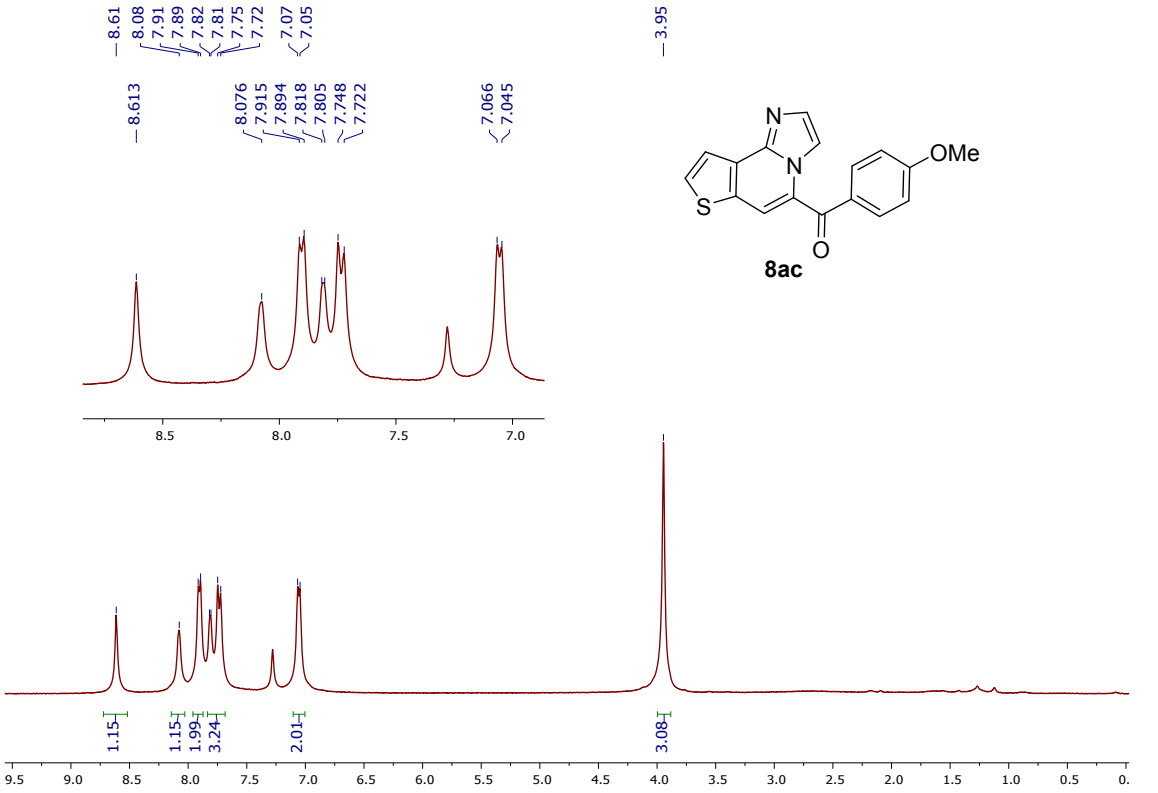
142.50
137.64
132.94
132.89
132.48
132.41
131.75
129.77
129.08
128.71
122.80
118.27
115.28
N
N
S
O
8aa
f1 (ppm)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7.72
7.07
7.05
3.95
8.613
8.076
7.915
7.894
7.818
7.805
7.748
7.722
7.066
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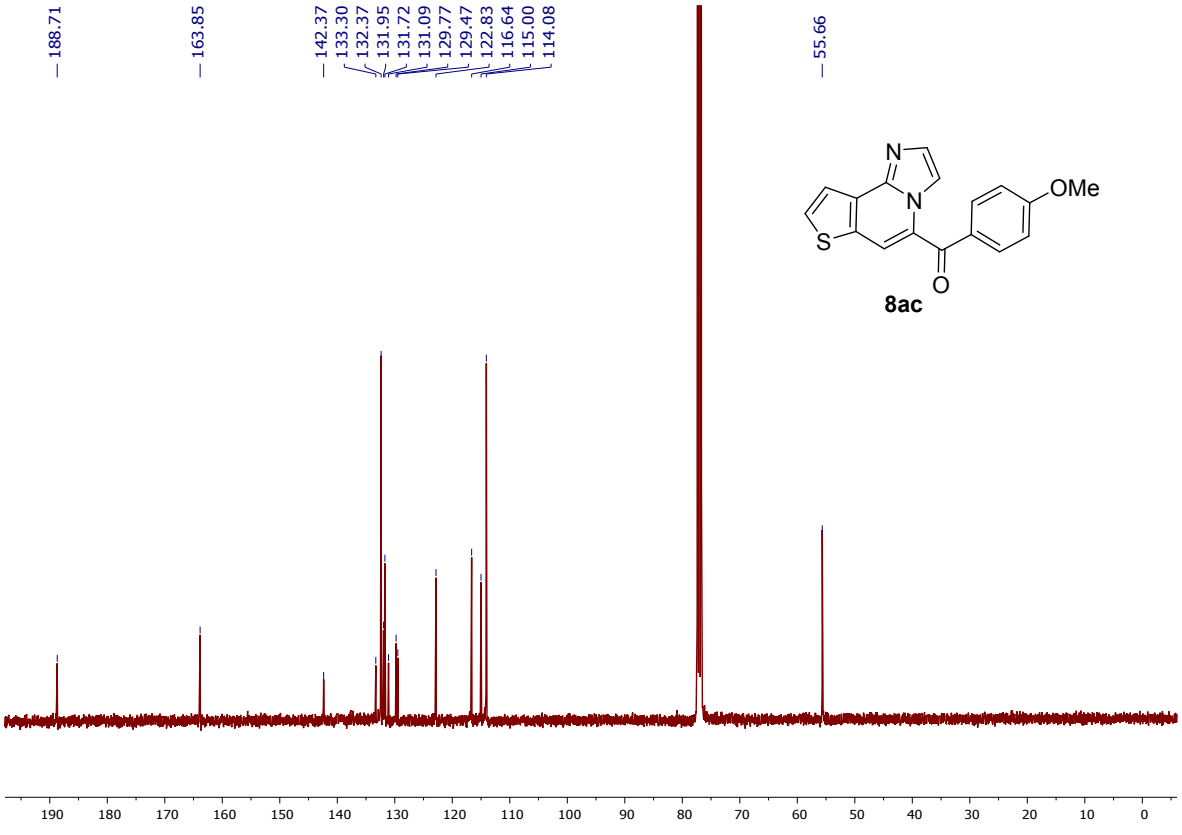
N
N
S
OMe
O
8ac
1.15
1.15
1.99
3.24
2.01
3.08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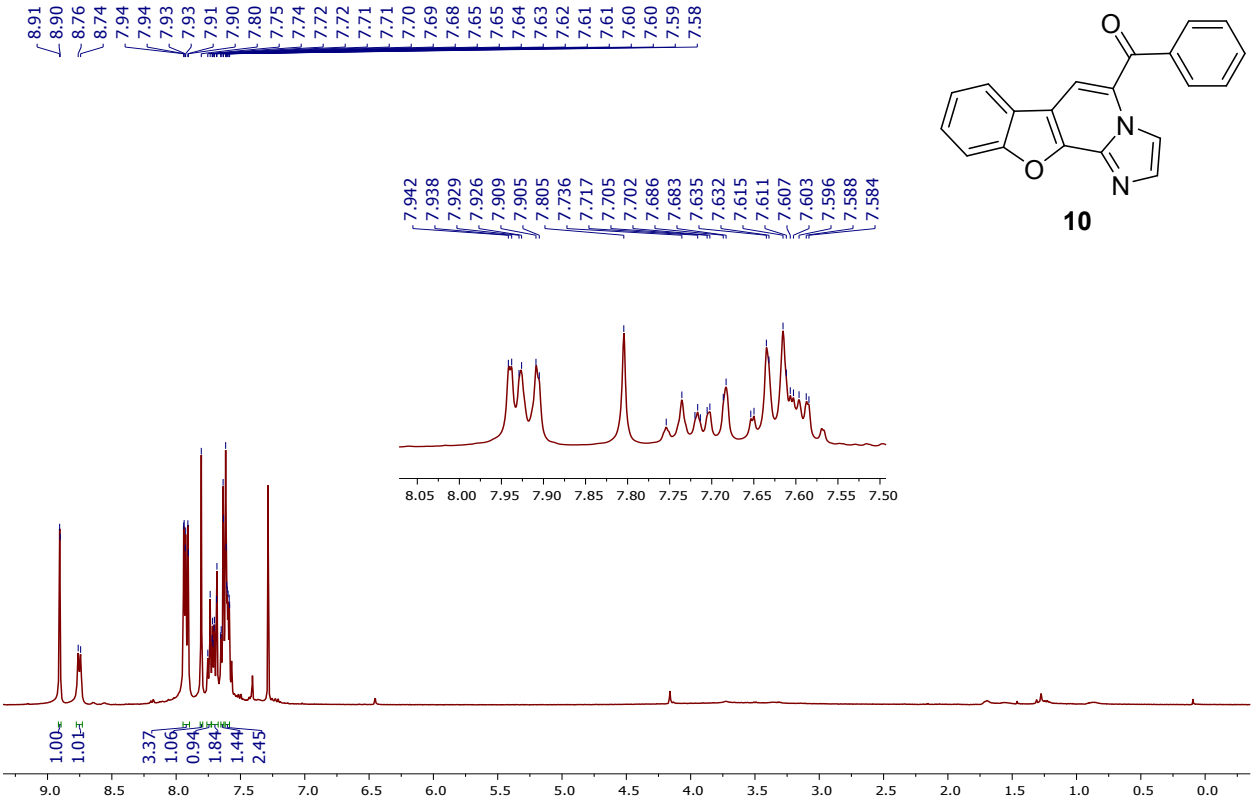
114.08
55.66
N
N
S
OMe
O
8ac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7.94
7.93
7.93
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7.90
7.80
7.75
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7.72
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7.71
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7.64
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7.62
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7.58
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7.683
7.635
7.632
7.615
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7.596
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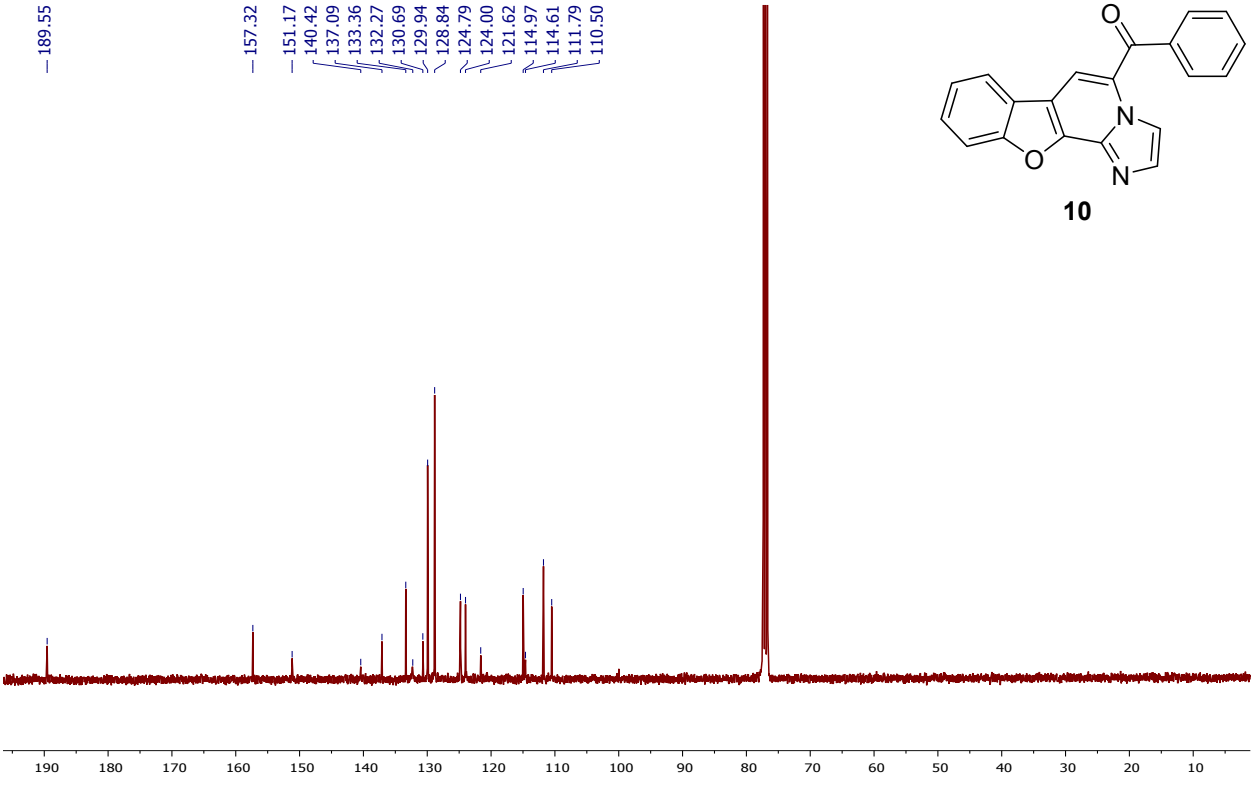
8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50
1.00
1.01
3.37
1.06
0.94
1.84
1.44
2.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
O
N
O
N
10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140.42
137.09
133.36
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130.69
129.94
128.84
124.79
124.00
121.62
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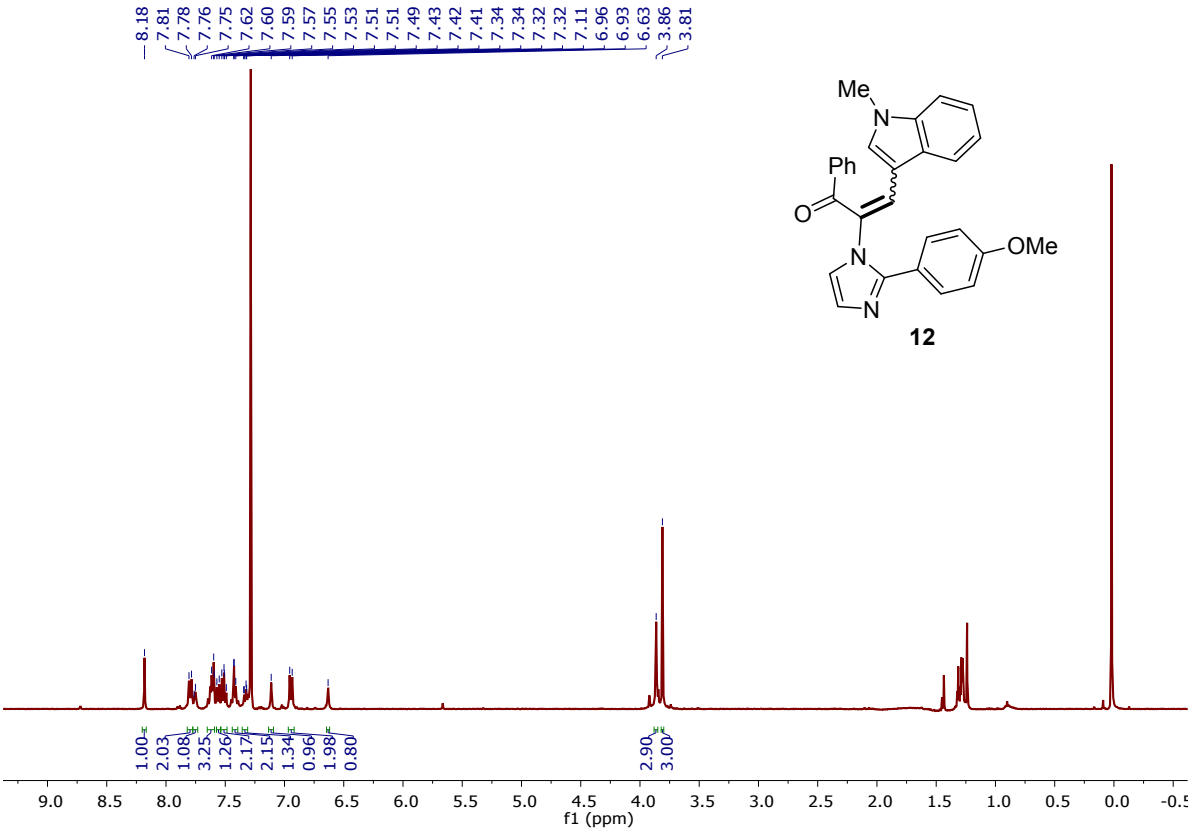
114.61
111.79
110.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
O
N
O
N
10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7.75
7.62
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7.57
7.55
7.53
7.51
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7.49
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7.42
7.41
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7.34
7.32
7.32
7.11
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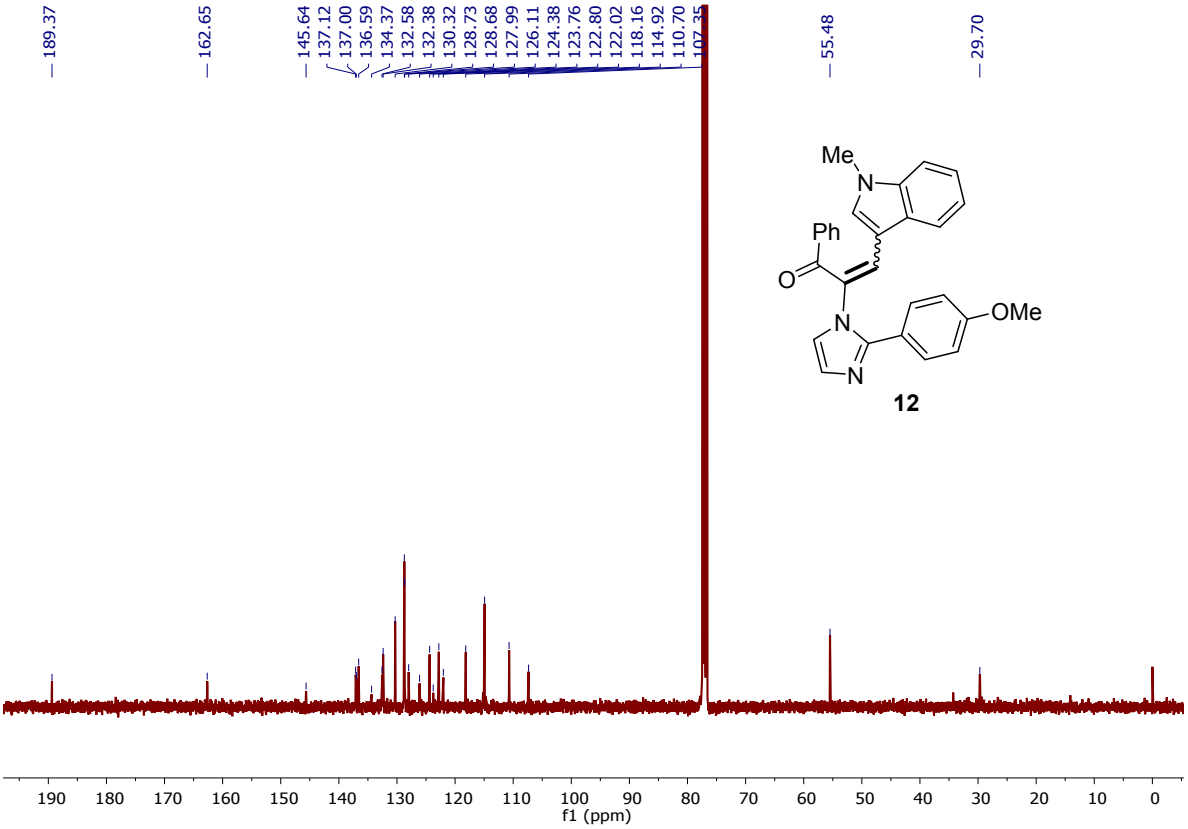
6.63
3.86
3.81
1.00
2.03
1.08
3.25
1.26
2.17
2.15
1.34
0.96
1.98
0.80
2.90
3.00
f1 (ppm)

Me
N
Ph
O
N
OMe
N

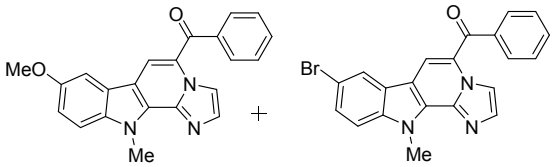
12


189.37
162.65
145.64
137.12
137.00
136.59
134.37
132.58
132.38
130.32
128.73
128.68
127.99
126.11
124.38
123.76
122.80
122.02
118.16
114.92
110.70
107.35
55.48
29.70
f1 (ppm)

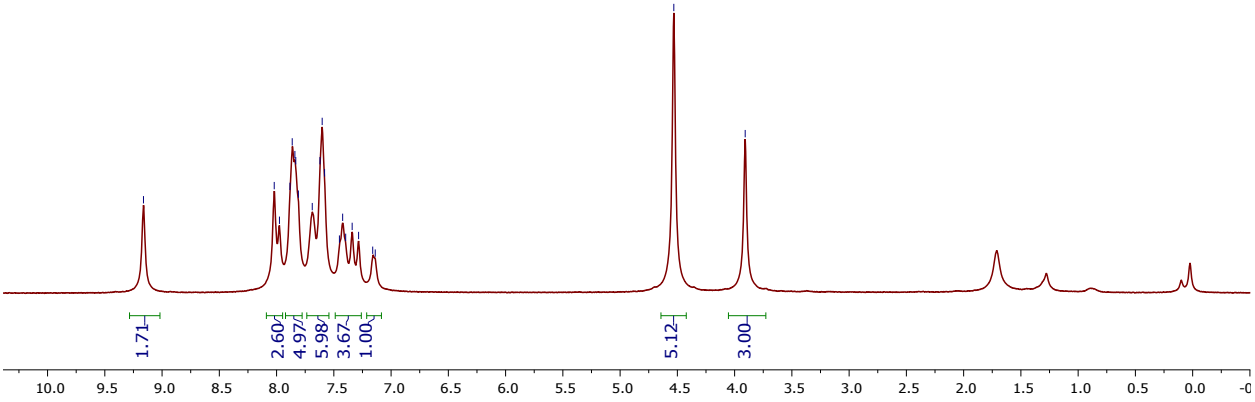
Me
N
Ph
O
N
OMe
N

12

Competitive study: ^{1}H NMR of **3ab** and **3ac** mixture



3ba : 3ca = 1:0.7



X-ray crystallographic data of compound 3ha and 4aa

The single crystals of the compound **3ha** ($C_{24}H_{19}N_3O_3$) and compound **4aa** ($C_{21}H_{17}N_3O$) were obtained as greenish yellow and yellow crystal blocks respectively from ethyl acetate solutions. The 3ha and 4aa crystallized in monoclinic crystal system with $P2_1/n$ and $P2_1$ space groups respectively. The crystal structures information of **3ha** and **4aa** are deposited into the Cambridge Crystallographic Data Center and the CCDC numbers for the **3ha** and **4aa** are 1821802 and 1821644 respectively. In the compound **4aa**, the indole and imidazole groups are *cis* to each other around C9=C9 (1.353(3) Å) double bond. The torsional angle between indole ring and olefin group C10-C9-C7-C8 = 5.93° and between the olefin group and imidazole ring C9-C10-N2-C11 = 72.99°, forcing the imidazole ring slightly perpendicular to the indole ring. In the compound 3ha, all the four fused rings are almost planar along with the two carbons of two carbonyl groups, however the phenyl group substitution forming torsional angle of C11-C18-C19-C20 = 47.26°.

Crystal structure of compound 3ha (Exp 159) and 4aa (Exp 164)

The crystal data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. The crystals were kept at 93(2) K during data collection using MoKα (λ = 0.71073) radiation. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimization.

Single crystal structure, cell parameters and structure data of compound 3ha (Exp159):

The single crystals of the compound **3ha** were obtained as yellow blocks. The crystal structure of this is given below.

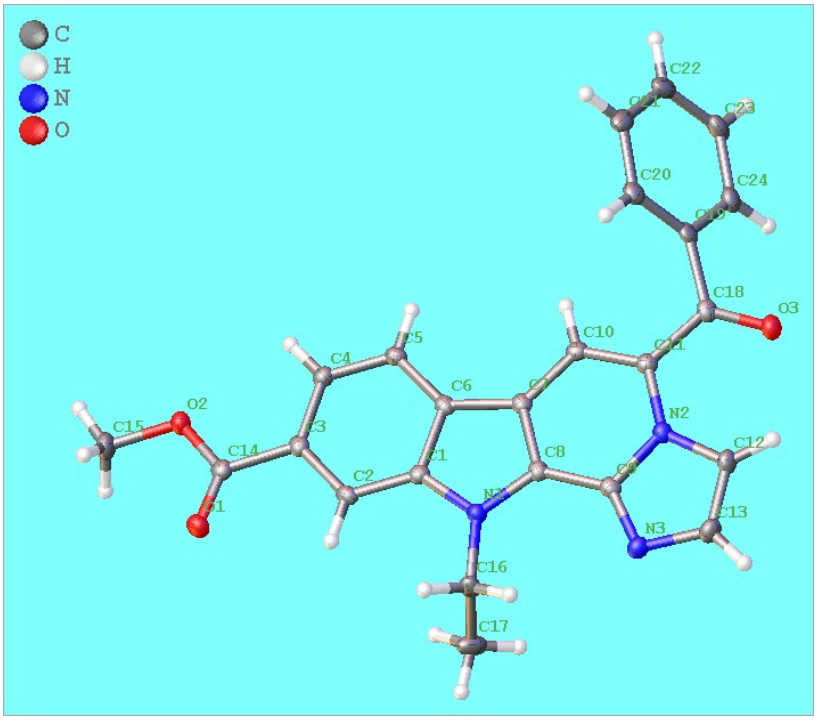


Figure S1. Crystal structure of **3ha**

Table S1: Crystal data and structure refinement for 3ha.

Identification code	exp_159_VNS176	ρ_{calc}g/cm^3	1.421
Empirical formula	$C_{24}H_{19}N_3O_3$	μ/mm^{-1}	0.096
Formula weight	397.42	F(000)	832.0
Temperature/K	93(2)	Crystal size/mm^3	0.3 × 0.2 × 0.1
Crystal system	monoclinic	Radiation	MoKα (λ = 0.71073)
Space group	$P2_1/n$	2Θ range for data collection/°	10.078 to 49.992
a/Å	9.4056(12)	Index ranges	$-11 \le h \le 9$, $-8 \le k \le 8$, $-31 \le l \le 33$
b/Å	7.0317(8)	Reflections collected	10670
c/Å	28.179(3)	Independent reflections	3247 [R_{int} = 0.0183, R_{sigma} = 0.0205]
α/°	90	Data/restraints/parameters	3247/0/273
β/°	94.395(10)	Goodness-of-fit on F^2	1.039
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0324, wR_2 = 0.0821
Volume/Å^3	1858.2(4)	Final R indexes [all data]	R_1 = 0.0407, wR_2 = 0.0862
Z	4	Largest diff. peak/hole/eÅ^{-3}	0.18/-0.20

Table S2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3ha. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O2		8630.4(13)	3388.1(3)	19.4(2)
O1	5883.7(10)	9751.7(14)	3178.7(3)	22.2(2)
O3	3781.1(10)	5176.3(13)	6827.3(3)	21.7(2)
N2	2870.8(11)	6805.5(14)	5936.9(4)	14.7(2)
N1	3282.9(11)	8238.7(15)	4688.9(4)	14.8(2)
N3	1007.1(11)	7683.4(15)	5430.3(4)	18.3(3)
C10	5270.4(13)	6552.2(17)	5742.3(4)	14.6(3)
C6	5631.9(14)	7531.2(17)	4864.3(4)	14.0(3)
C5	7047.9(14)	7370.1(17)	4758.8(4)	15.7(3)
C7	4865.4(14)	7183.3(17)	5277.5(4)	14.3(3)
C2	4965.7(14)	8660.7(17)	4056.0(4)	15.2(3)
C4	7410.6(14)	7846.5(17)	4310.2(4)	15.8(3)
C8	3447.9(14)	7632.4(17)	5150.3(4)	14.2(3)
C1	4609.9(13)	8179.6(17)	4507.1(4)	14.1(3)
C12	1666.6(14)	6705.1(19)	6182.7(5)	18.5(3)
C9	2399.0(14)	7413.3(17)	5478.9(4)	15.1(3)
C11	4301.6(13)	6387.3(17)	6076.3(4)	15.0(3)
C3	6377.4(13)	8492.5(17)	3959.1(4)	15.2(3)
C14	6726.7(14)	9026.3(18)	3471.8(4)	16.5(3)
C18	4677.1(14)	5693.9(18)	6563.5(4)	16.5(3)

C19	6217.7(14)	5572.2(19)	6735.9(4)	17.2(3)
C13	572.8(14)	7245.2(19)	5868.0(5)	20.2(3)
C16	1980.7(14)	8877.9(19)	4422.7(5)	19.2(3)
C20	7181.0(14)	7035(2)	6680.7(4)	19.8(3)
C24	6666.7(15)	3959(2)	6992.4(5)	21.6(3)
C23	8063.5(15)	3800(2)	7177.7(5)	26.0(3)
C15	8430.9(15)	9054(2)	2911.6(5)	25.1(3)
C22	9021.6(15)	5256(2)	7118.1(5)	26.7(3)
C21	8575.3(15)	6878(2)	6872.2(5)	24.4(3)
C17	1319.8(15)	7328(2)	4107.8(5)	31.4(4)

Table S3: Anisotropic Displacement Parameters ($Å^2×10^3$) for 3ha. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	18.3(5)	24.4(5)	16.0(5)	2.0(4)	4.0(4)	0.4(4)
O1	21.5(5)	27.7(5)	17.3(5)	4.4(4)	0.2(4)	1.5(4)
O3	21.9(5)	26.5(5)	17.1(5)	3.2(4)	4.7(4)	-0.3(4)
N2	16.9(6)	13.5(5)	13.7(5)	-0.7(4)	1.8(4)	0.4(4)
N1	15.1(6)	15.8(5)	13.5(5)	0.0(4)	1.1(4)	0.5(4)
N3	15.6(6)	19.8(6)	19.8(6)	0.3(5)	2.5(4)	0.0(5)
C10	15.5(6)	11.7(6)	16.3(6)	-2.1(5)	-1.0(5)	-0.2(5)
C6	18.7(7)	10.0(6)	13.3(6)	-2.2(5)	0.0(5)	-0.7(5)
C5	16.4(7)	14.6(6)	15.7(6)	-0.6(5)	-1.8(5)	0.9(5)
C7	17.2(6)	10.7(6)	14.8(6)	-1.9(5)	0.6(5)	-0.6(5)
C2	18.7(7)	11.9(6)	14.5(6)	-0.3(5)	-1.7(5)	0.4(5)
C4	14.8(6)	14.9(6)	17.8(6)	-1.1(5)	2.2(5)	0.0(5)
C8	18.0(7)	10.2(6)	14.5(6)	-1.4(5)	1.3(5)	-1.2(5)
C1	15.0(6)	11.1(6)	16.1(6)	-2.5(5)	0.9(5)	-0.7(5)
C12	19.4(7)	20.4(6)	16.5(6)	-0.2(5)	6.0(5)	-0.1(5)
C9	18.7(7)	11.4(6)	15.1(6)	-1.9(5)	-0.1(5)	0.0(5)
C11	16.7(7)	11.9(6)	16.3(6)	-2.1(5)	0.5(5)	0.1(5)
C3	18.5(7)	11.9(6)	15.3(6)	-1.8(5)	1.5(5)	-1.9(5)
C14	17.7(7)	14.2(6)	17.5(7)	-1.5(5)	1.3(5)	-2.1(5)
C18	21.9(7)	13.2(6)	14.6(6)	-2.4(5)	3.3(5)	0.0(5)
C19	20.9(7)	22.1(7)	8.9(6)	-1.4(5)	2.7(5)	1.5(6)
C13	15.9(7)	23.1(7)	22.2(7)	0.3(6)	5.6(5)	1.1(5)
C16	15.5(6)	25.0(7)	17.3(7)	4.5(5)	1.7(5)	5.4(6)
C20	23.8(7)	23.5(7)	12.3(6)	-1.9(5)	2.0(5)	0.3(6)
C24	25.0(7)	26.3(7)	14.1(6)	2.7(6)	5.4(5)	1.4(6)
C23	25.5(8)	37.3(8)	15.5(7)	7.1(6)	2.9(6)	9.0(6)
C15	24.7(7)	32.8(8)	18.8(7)	2.9(6)	8.4(6)	-1.1(6)
C22	19.5(7)	47.6(9)	12.8(6)	-2.5(6)	0.1(5)	4.7(7)
C21	22.5(7)	35.0(8)	16.0(7)	-6.2(6)	2.7(5)	-5.9(6)

C17	17.7(7)	51.1(10)	24.7(8)	-9.7(7)	-2.7(6)	2.0(7)

Table S4: Bond Lengths for 3ha.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	C14	1.3340(16)	C5	C4	1.3757(18)
O2	C15	1.4406(16)	C7	C8	1.3902(18)
O1	C14	1.2126(16)	C2	C1	1.3810(18)
O3	C18	1.2212(16)	C2	C3	1.3810(18)
N2	C12	1.3740(17)	C4	C3	1.4078(18)
N2	C9	1.3989(17)	C8	C9	1.4124(18)
N2	C11	1.4039(17)	C12	C13	1.3600(19)
N1	C8	1.3657(16)	C11	C18	1.4742(18)
N1	C1	1.3857(16)	C3	C14	1.4845(18)
N1	C16	1.4575(16)	C18	C19	1.4950(18)
N3	C9	1.3195(17)	C19	C20	1.3876(19)
N3	C13	1.3639(17)	C19	C24	1.3928(19)
C10	C7	1.4075(18)	C16	C17	1.509(2)
C10	C11	1.3641(18)	C20	C21	1.384(2)
C6	C5	1.3913(18)	C24	C23	1.381(2)
C6	C7	1.4368(17)	C23	C22	1.382(2)
C6	C1	1.4131(18)	C22	C21	1.383(2)

Table S5: Bond Angles for 3ha.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O2	C15	114.51(10)	N2	C9	C8	116.75(11)
C12	N2	C9	105.39(11)	N3	C9	N2	112.45(11)
C12	N2	C11	131.12(11)	N3	C9	C8	130.80(12)
C9	N2	C11	123.48(11)	N2	C11	C18	119.08(11)
C8	N1	C1	107.63(10)	C10	C11	N2	117.76(11)
C8	N1	C16	128.03(11)	C10	C11	C18	123.07(12)
C1	N1	C16	124.34(10)	C2	C3	C4	120.74(12)
C9	N3	C13	103.71(11)	C2	C3	C14	116.46(11)
C11	C10	C7	121.42(12)	C4	C3	C14	122.80(12)
C5	C6	C7	135.02(12)	O2	C14	C3	113.01(11)
C5	C6	C1	118.95(12)	O1	C14	O2	123.16(12)
C1	C6	C7	106.03(11)	O1	C14	C3	123.84(12)
C4	C5	C6	119.04(12)	O3	C18	C11	122.57(12)
C10	C7	C6	133.71(12)	O3	C18	C19	118.82(11)
C8	C7	C10	119.83(12)	C11	C18	C19	118.59(11)
C8	C7	C6	106.45(11)	C20	C19	C18	123.10(12)
C3	C2	C1	117.74(12)	C20	C19	C24	119.17(12)
C5	C4	C3	121.18(12)	C24	C19	C18	117.58(12)
N1	C8	C7	110.69(11)	C12	C13	N3	112.88(12)

N1	C8	C9	128.62(12)	N1	C16	C17	111.85(11)
C7	C8	C9	120.69(12)	C21	C20	C19	120.28(13)
N1	C1	C6	109.21(11)	C23	C24	C19	120.28(13)
C2	C1	N1	128.44(11)	C24	C23	C22	120.29(13)
C2	C1	C6	122.35(12)	C23	C22	C21	119.72(13)
C13	C12	N2	105.57(12)	C22	C21	C20	120.25(14)

Table S6: Torsion Angles for 3ha.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	C18	C19	C20	-134.35(13)	C1	C6	C7	C10	-179.18(13)
O3	C18	C19	C24	41.04(17)	C1	C6	C7	C8	-0.02(13)
N2	C12	C13	N3	0.23(15)	C1	C2	C3	C4	0.16(18)
N2	C11	C18	O3	12.07(19)	C1	C2	C3	C14	-179.81(11)
N2	C11	C18	C19	-169.61(11)	C12	N2	C9	N3	-0.07(14)
N1	C8	C9	N2	-178.47(11)	C12	N2	C9	C8	-179.94(11)
N1	C8	C9	N3	1.7(2)	C12	N2	C11	C10	177.30(12)
C10	C7	C8	N1	179.10(11)	C12	N2	C11	C18	0.66(19)
C10	C7	C8	C9	-1.73(18)	C9	N2	C12	C13	-0.09(13)
C10	C11	C18	O3	-164.38(12)	C9	N2	C11	C10	-1.29(17)
C10	C11	C18	C19	13.94(18)	C9	N2	C11	C18	-177.93(11)
C6	C5	C4	C3	0.09(19)	C9	N3	C13	C12	-0.27(15)
C6	C7	C8	N1	-0.20(14)	C11	N2	C12	C13	-178.87(12)
C6	C7	C8	C9	178.96(11)	C11	N2	C9	N3	178.82(11)
C5	C6	C7	C10	0.7(3)	C11	N2	C9	C8	-1.04(17)
C5	C6	C7	C8	179.90(13)	C11	C10	C7	C6	178.35(13)
C5	C6	C1	N1	-179.71(11)	C11	C10	C7	C8	-0.72(18)
C5	C6	C1	C2	-0.01(18)	C11	C18	C19	C20	47.26(17)
C5	C4	C3	C2	-0.17(19)	C11	C18	C19	C24	-137.35(12)
C5	C4	C3	C14	179.79(11)	C3	C2	C1	N1	179.57(12)
C7	C10	C11	N2	2.18(18)	C3	C2	C1	C6	-0.07(18)
C7	C10	C11	C18	178.67(11)	C18	C19	C20	C21	176.29(12)
C7	C6	C5	C4	-179.92(13)	C18	C19	C24	C23	-177.34(12)
C7	C6	C1	N1	0.23(13)	C19	C20	C21	C22	0.35(19)
C7	C6	C1	C2	179.93(11)	C19	C24	C23	C22	1.2(2)
C7	C8	C9	N2	2.53(17)	C13	N3	C9	N2	0.20(14)
C7	C8	C9	N3	-177.30(12)	C13	N3	C9	C8	-179.96(13)
C2	C3	C14	O2	-173.04(11)	C16	N1	C8	C7	-178.64(11)
C2	C3	C14	O1	7.15(18)	C16	N1	C8	C9	2.3(2)
C4	C3	C14	O2	7.00(17)	C16	N1	C1	C6	178.68(11)
C4	C3	C14	O1	-172.82(12)	C16	N1	C1	C2	-1.0(2)
C8	N1	C1	C6	-0.36(13)	C20	C19	C24	C23	-1.76(19)
C8	N1	C1	C2	179.97(12)	C24	C19	C20	C21	0.97(18)
C8	N1	C16	C17	-99.19(15)	C24	C23	C22	C21	0.1(2)

C1	N1	C8	C7	0.35(14)	C23	C22	C21	C20	-0.9(2)
C1	N1	C8	C9	-178.73(12)	C15	O2	C14	O1	-2.75(18)
C1	N1	C16	C17	81.98(15)	C15	O2	C14	C3	177.43(11)
C1	C6	C5	C4	0.00(18)					

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_159_VNS176.

Atom	*x*	*y*	*z*	U(eq)
H10	6218.95	6240.96	5823.48	18
H5	7739.22	6946.6	4988.16	19
H2	4277.97	9083.68	3825.37	18
H4	8355.25	7739.96	4237.5	19
H12	1611.25	6343.53	6498.25	22
H13	-371.62	7308.96	5943.24	24
H16A	2196.55	9962.31	4227.91	23
H16B	1301.02	9286.21	4643.9	23
H20	6888.37	8126.75	6514.19	24
H24	6022.84	2985.71	7038.97	26
H23	8361.08	2708.97	7343.29	31
H15A	7867.87	8275.32	2689.34	38
H15B	9424.14	8797.73	2884.91	38
H15C	8239.94	10370.63	2843.05	38
H22	9962.38	5144.41	7242.82	32
H21	9214.63	7866.06	6835.51	29
H17A	2020.28	6831.6	3910.41	47
H17B	534.24	7841.09	3910.6	47
H17C	984.22	6326.63	4301.92	47

Single crystal structure, cell parameters and structure data of compound 4aa

The single crystals of the compound 3ha were obtained as yellow blocks. The crystal structure of this is given below.

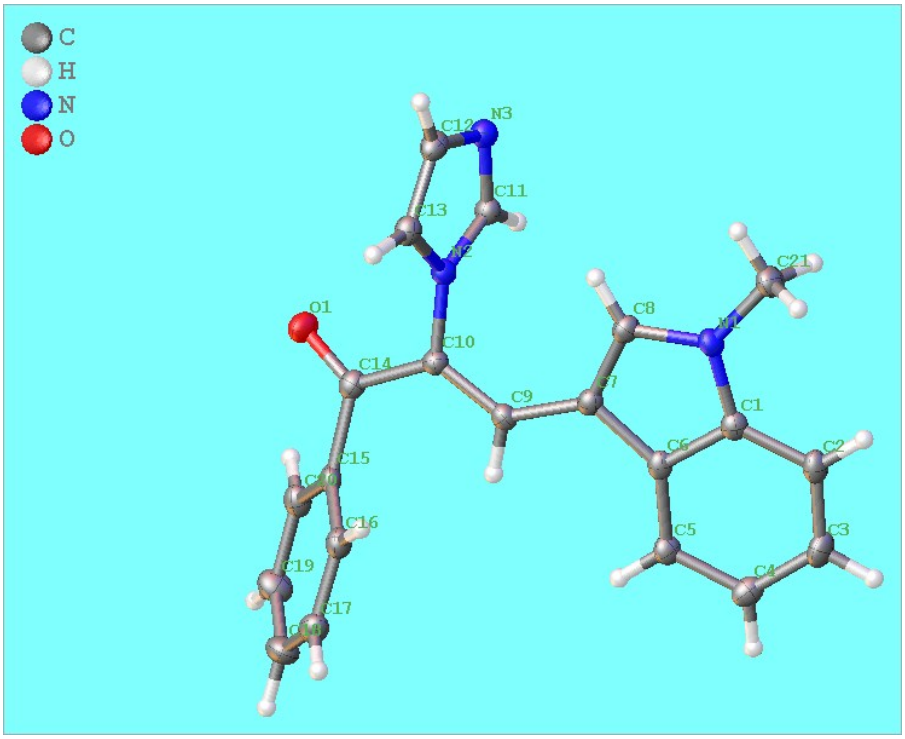


Table S8: Crystal data and structure refinement for 4aa.

Identification code	exp_164-vns139	ρ_{calc}g/cm^3	1.298
Empirical formula	$C_{21}H_{17}N_3O$	μ/mm^{-1}	0.082
Formula weight	327.38	F(000)	344.0
Temperature/K	93(2)	Crystal size/mm^3	0.2 × 0.1 × 0.1
Crystal system	monoclinic	Radiation	MoKα (λ = 0.71073)
Space group	$P2_1$	2Θ range for data collection/°	10.332 to 49.994
a/Å	8.8630(6)	Index ranges	-10 ≤ h ≤ 10, -8 ≤ k ≤ 7, -14 ≤ l ≤ 16
b/Å	6.9410(4)	Reflections collected	5002
c/Å	14.0380(10)	Independent reflections	2563 [R_{int} = 0.0401, R_{sigma} = 0.0447]
α/°	90	Data/restraints/parameters	2563/1/227
β/°	104.114(7)	Goodness-of-fit on F^2	1.067
γ/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0311, wR_2 = 0.0821
Volume/Å^3	837.52(10)	Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0838
Z	2	Largest diff. peak/hole/eÅ^{-3}	0.13/-0.14

Table S9: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement

Parameters (Å^2×10^3) for 4aa. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	-2037.2(19)	-6169(3)	-7106.5(13)	28.3(4)
N2	-4970(2)	-7226(3)	-8037.3(13)	17.4(4)
N3	-5361(2)	-8825(3)	-9440.3(14)	22.1(5)
N1	-9833(2)	-5242(3)	-8857.7(13)	19.6(4)
C8	-8338(2)	-5816(3)	-8502.5(16)	19.1(5)
C14	-3080(3)	-5306(3)	-6855.5(17)	19.7(5)
C5	-8485(3)	-1101(4)	-7380.7(17)	20.2(5)
C13	-5025(3)	-9140(4)	-7807.2(17)	20.3(5)
C4	-9782(3)	89(4)	-7561.0(18)	23.6(5)
C7	-7501(3)	-4430(4)	-7876.9(16)	18.3(5)
C1	-10022(3)	-3435(3)	-8477.7(17)	19.2(5)
C15	-2697(3)	-3854(3)	-6039.5(16)	18.5(5)
C11	-5157(3)	-7114(3)	-9026.9(16)	19.4(5)
C9	-5894(3)	-4397(3)	-7351.4(16)	17.4(5)
C6	-8589(2)	-2885(3)	-7853.4(16)	17.6(5)
C17	-3004(3)	-2438(4)	-4532.9(17)	25.4(5)
C21	-11051(3)	-6287(4)	-9538.5(18)	25.2(6)
C10	-4718(3)	-5624(3)	-7376.2(16)	17.2(5)
C12	-5283(3)	-10097(4)	-8678.0(17)	22.4(5)
C2	-11336(3)	-2252(4)	-8665.0(17)	22.6(5)
C3	-11189(3)	-494(4)	-8199.8(18)	25.1(6)
C20	-1470(3)	-2600(4)	-6028.6(17)	23.8(5)
C18	-1803(3)	-1170(4)	-4533.2(19)	29.9(6)
C16	-3468(3)	-3770(4)	-5286.7(17)	22.4(5)
C19	-1044(3)	-1249(4)	-5290.6(19)	29.5(6)

Table S10: Anisotropic Displacement Parameters (Å^2×10^3) for 4aa. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	16.8(8)	32.5(10)	34.9(9)	-9.4(8)	4.9(7)	1.9(8)
N2	13.9(9)	20.2(11)	18.2(9)	-1.2(8)	3.9(7)	-1.0(8)
N3	18.4(9)	24.8(11)	22.6(10)	-2.7(9)	3.9(8)	0.6(8)
N1	15.6(9)	23.6(11)	18.7(9)	-1.2(8)	2.3(8)	-1.5(8)
C8	16.9(11)	19.7(12)	22.0(11)	1.5(10)	7.4(9)	0.9(9)
C14	18.4(12)	18.9(12)	22.7(12)	1.9(10)	6.6(9)	-0.1(10)
C5	15.4(11)	22.7(12)	22.8(11)	0(1)	5.2(9)	-2.4(10)
C13	17.5(11)	21.7(13)	22.3(12)	2.4(10)	6.1(9)	-0.5(9)
C4	23.2(12)	19.5(13)	30.6(13)	0.2(11)	11.3(10)	-0.2(10)
C7	17.0(11)	20.5(12)	18.2(10)	1.0(9)	5.9(9)	1.1(9)
C1	17.5(11)	22.1(13)	18.8(11)	2.1(9)	6.0(9)	-0.7(9)

C15	14.9(11)	19.1(12)	19.1(11)	1.1(9)	-0.4(9)	2.1(9)
C11	18.2(11)	20.5(12)	19.5(11)	1.1(10)	4.8(9)	0.8(9)
C9	17.0(11)	19.3(11)	15.8(10)	0.6(9)	3.8(9)	-2.3(9)
C6	14.4(10)	21.6(12)	17.4(10)	4.0(9)	5.5(9)	-0.4(9)
C17	26.3(13)	29.2(14)	21.4(11)	-0.3(10)	7(1)	4.3(11)
C21	18.7(12)	28.8(14)	26.5(12)	-3.0(11)	2.1(10)	-1.6(11)
C10	17.7(11)	16.7(12)	17.6(11)	0.4(9)	4.7(9)	-0.4(9)
C12	17.3(11)	18.8(12)	30.8(13)	-1.3(10)	5.5(10)	-1.3(9)
C2	15.8(11)	29.3(14)	22.5(11)	4.6(10)	4.3(9)	1.3(10)
C3	17.1(12)	27.7(14)	31.6(13)	5.9(11)	8.1(10)	4.3(10)
C20	19.3(12)	29.4(14)	22.2(12)	2.5(11)	4.3(10)	-0.3(11)
C18	31.3(14)	30.1(14)	25.6(12)	-8.2(11)	1.6(11)	-0.8(12)
C16	17.4(11)	23.8(13)	24.8(12)	1.4(10)	2.7(10)	0.8(10)
C19	27.0(13)	30.0(14)	30.2(13)	-3.9(11)	4.2(10)	-8.5(11)

Table S11: Bond Lengths for 4aa.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C14	1.223(3)	C13	C12	1.361(3)
N2	C13	1.371(3)	C4	C3	1.406(3)
N2	C11	1.361(3)	C7	C9	1.436(3)
N2	C10	1.430(3)	C7	C6	1.448(3)
N3	C11	1.314(3)	C1	C6	1.409(3)
N3	C12	1.376(3)	C1	C2	1.397(3)
N1	C8	1.357(3)	C15	C20	1.391(3)
N1	C1	1.389(3)	C15	C16	1.393(3)
N1	C21	1.449(3)	C9	C10	1.353(3)
C8	C7	1.389(3)	C17	C18	1.381(4)
C14	C15	1.501(3)	C17	C16	1.390(3)
C14	C10	1.474(3)	C2	C3	1.375(4)
C5	C4	1.388(3)	C20	C19	1.380(4)
C5	C6	1.397(3)	C18	C19	1.391(4)

Table S12: Bond Angles for 4aa.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	N2	C10	127.53(19)	C20	C15	C14	117.3(2)
C11	N2	C13	107.04(19)	C20	C15	C16	119.5(2)
C11	N2	C10	125.41(19)	C16	C15	C14	123.1(2)
C11	N3	C12	105.13(19)	N3	C11	N2	111.7(2)
C8	N1	C1	108.80(19)	C10	C9	C7	130.6(2)
C8	N1	C21	126.8(2)	C5	C6	C7	134.4(2)
C1	N1	C21	124.4(2)	C5	C6	C1	118.7(2)
N1	C8	C7	110.6(2)	C1	C6	C7	106.8(2)
O1	C14	C15	120.2(2)	C18	C17	C16	120.6(2)

O1	C14	C10	120.4(2)	N2	C10	C14	114.63(18)
C10	C14	C15	119.38(19)	C9	C10	N2	120.46(19)
C4	C5	C6	119.0(2)	C9	C10	C14	124.4(2)
C12	C13	N2	105.6(2)	C13	C12	N3	110.5(2)
C5	C4	C3	120.7(2)	C3	C2	C1	117.0(2)
C8	C7	C9	130.3(2)	C2	C3	C4	121.7(2)
C8	C7	C6	105.74(19)	C19	C20	C15	120.2(2)
C9	C7	C6	124.0(2)	C17	C18	C19	119.4(2)
N1	C1	C6	108.0(2)	C17	C16	C15	119.8(2)
N1	C1	C2	129.2(2)	C20	C19	C18	120.4(2)
C2	C1	C6	122.8(2)				

Table S13: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4aa.

Atom	*x*	*y*	*z*	U(eq)
H8	-7930.7	-6977.03	-8656.53	23
H5	-7560.24	-717.14	-6951.52	24
H13	-4909.5	-9673.17	-7185.72	24
H4	-9719.6	1285.89	-7256	28
H11	-5142.52	-5969.53	-9368.71	23
H9	-5615.11	-3361.61	-6924.03	21
H17	-3506.47	-2400.3	-4023.75	31
H21A	-10689.87	-7559.39	-9634.69	38
H21B	-11315.97	-5620	-10156.06	38
H21C	-11951.96	-6373.28	-9275.85	38
H12	-5391.1	-11426.19	-8748.19	27
H2	-12268.75	-2635.42	-9085.59	27
H3	-12041.26	330.09	-8310.39	30
H20	-933.3	-2672.04	-6520.31	29
H18	-1504.93	-270.9	-4031.37	36
H16	-4291.2	-4602.48	-5288.35	27
H19	-245.29	-385.96	-5299.68	35

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