Electronic Supplementary Material (ESI) for RSC Advances.

Metal-free regioselective construction of indolin-3-ones *via* hypervalent iodine oxidation of *N*-substituted indoles

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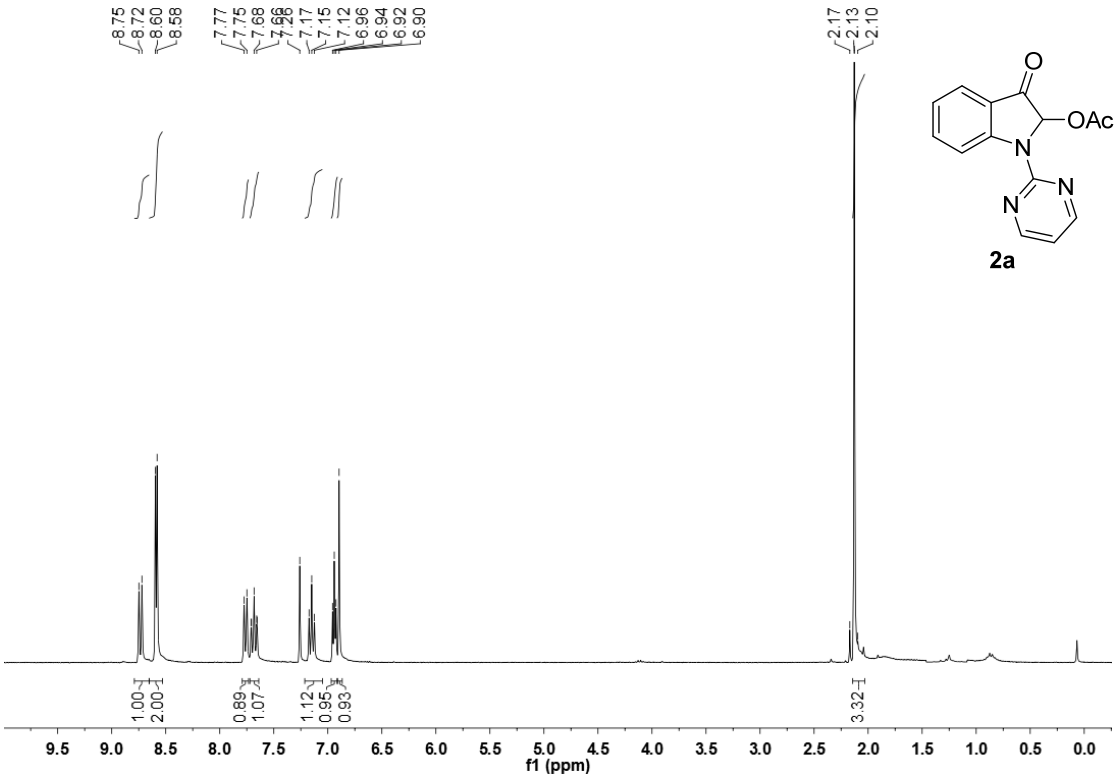
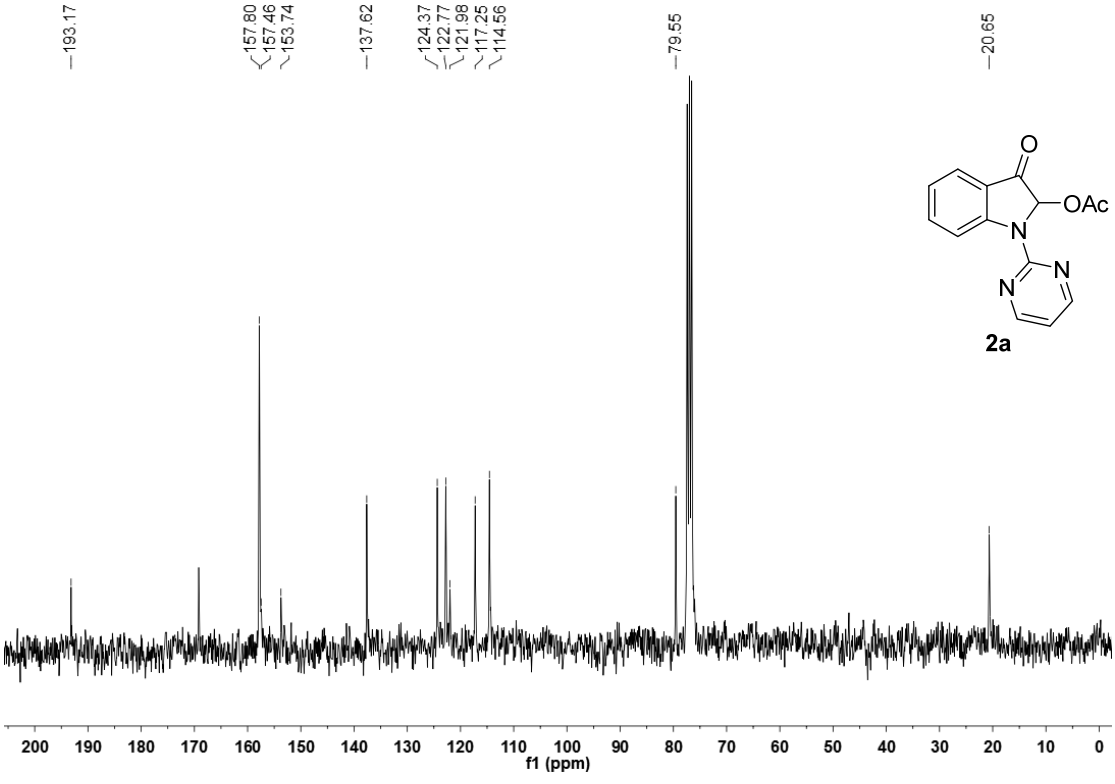
Supporting Information

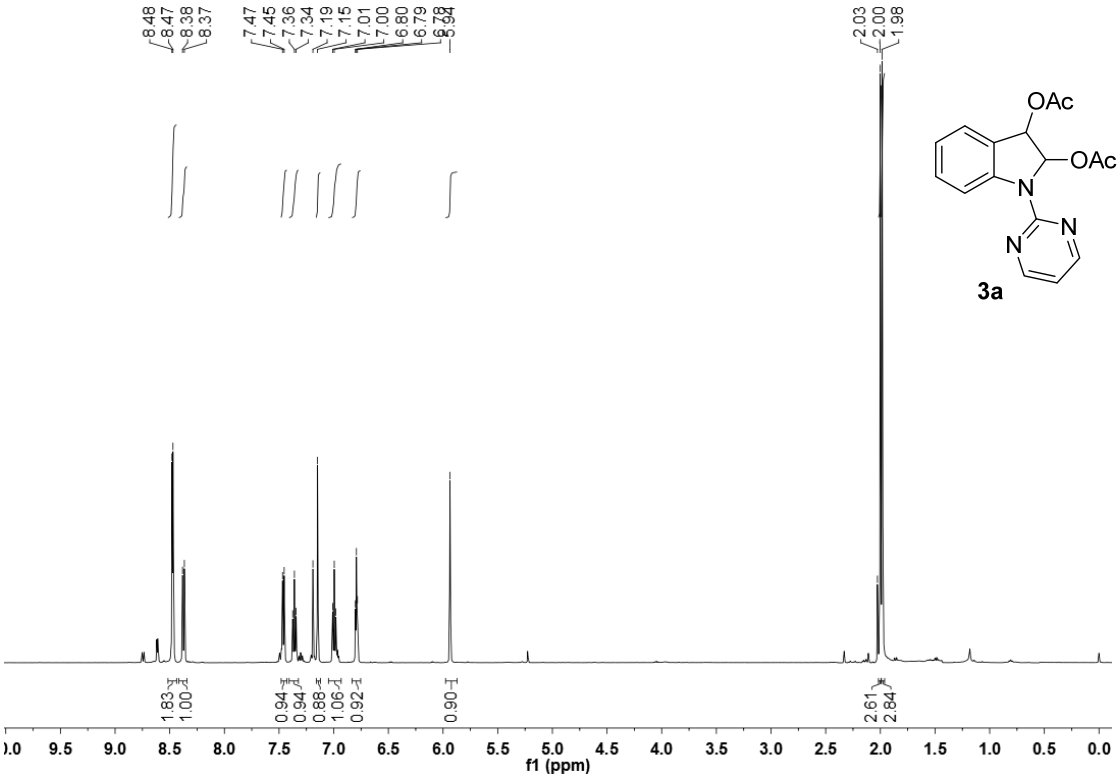
General remarks

All reagents and metal catalysts were obtained from commercial sources without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography. Mass spectra were recorded with an TSQ Quantum-LC/MS/MS of Finnigan using Electrospray ionization (ESI) techniques. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AV-300 and AV-500 spectrometer operating at 300MHz/500MHz and 75MHz/125MHz, respectively, with chemical shift values being reported in ppm relative to chloroform (δ=7.26 ppm) for ^{1}H NMR, and chloroform (δ=77.16 ppm) for ^{13}C NMR.

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



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2.00
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OAc
OAc
N
N
N
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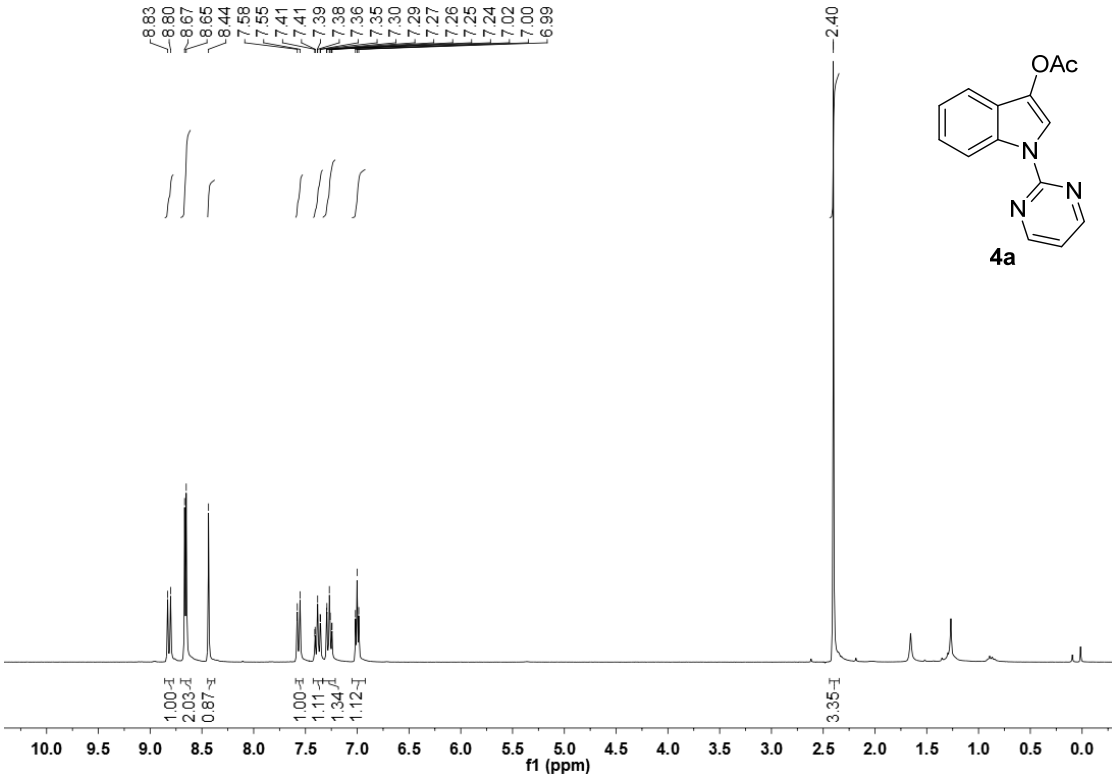
f1 (ppm)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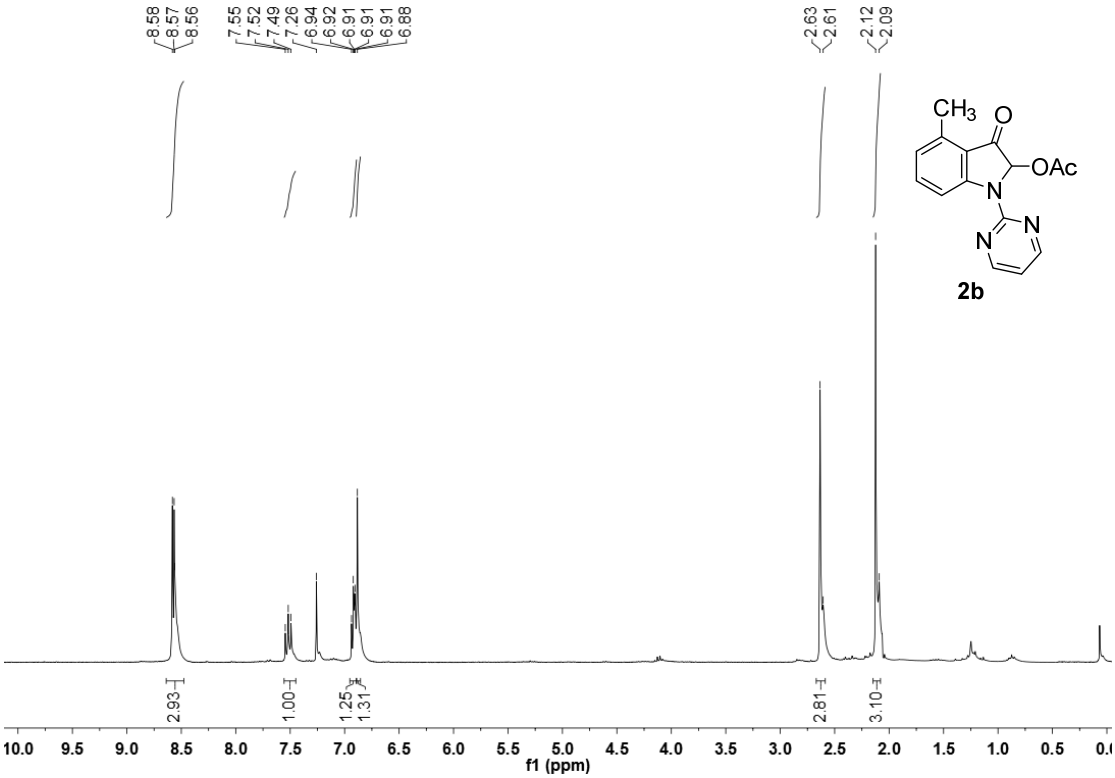
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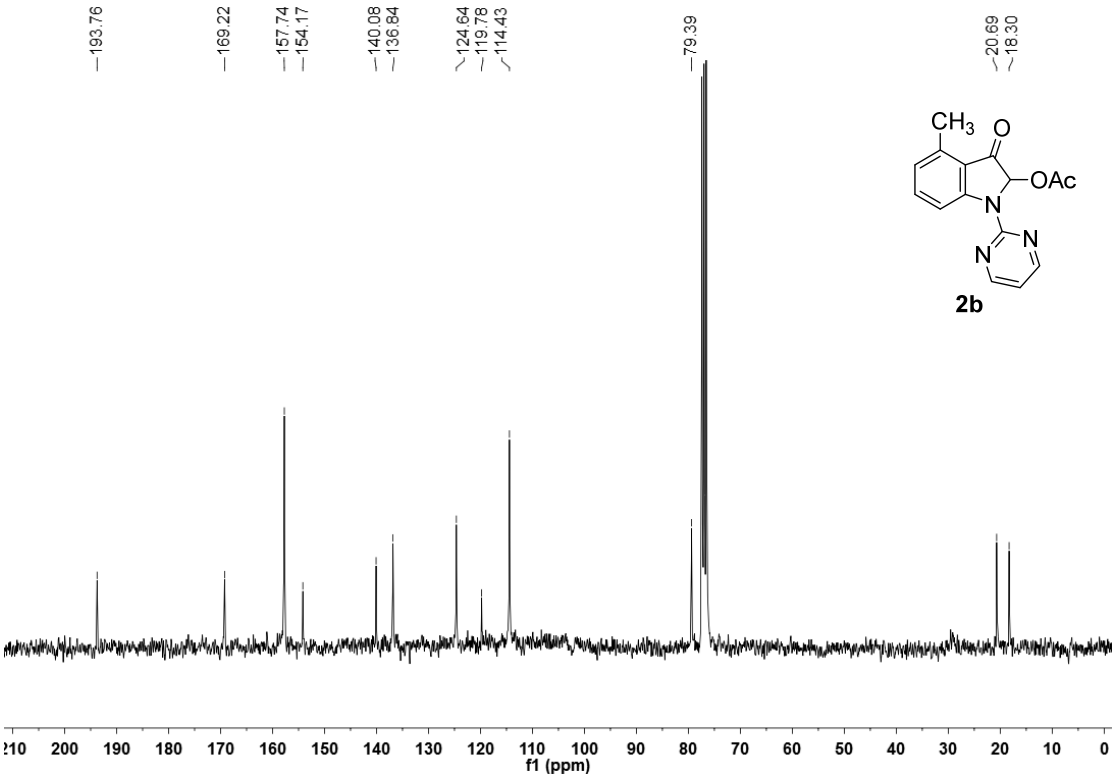
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N
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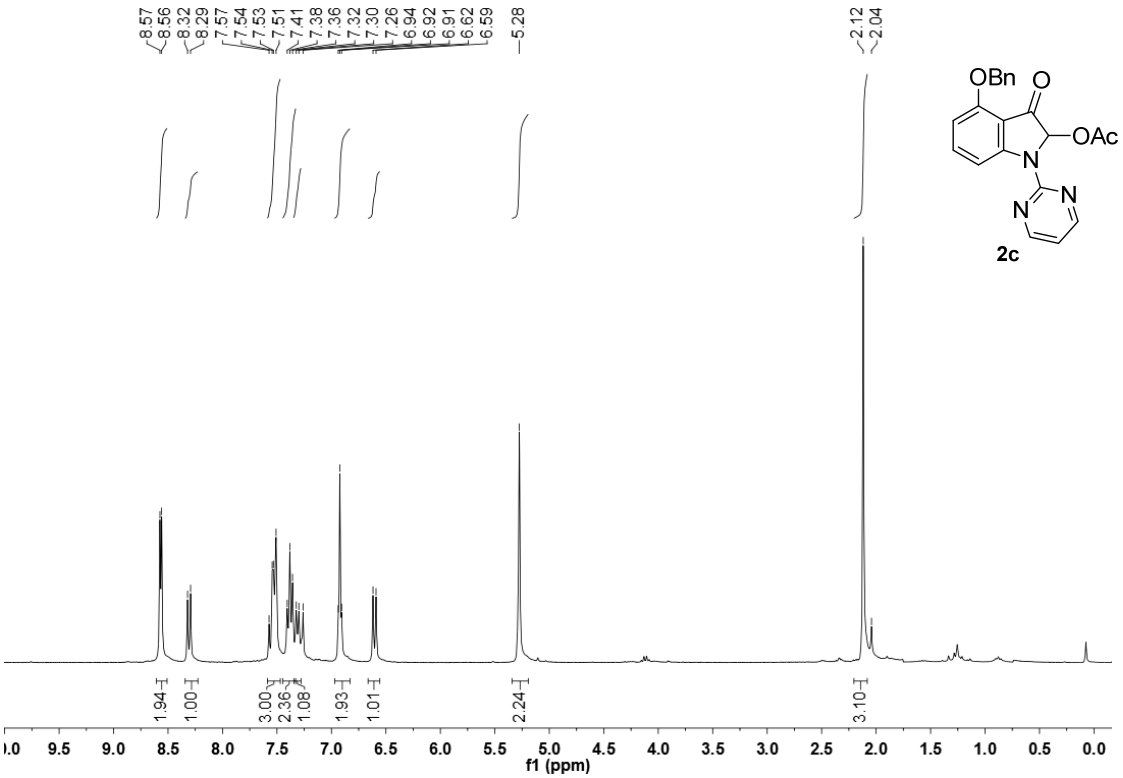
N
2b
f1 (ppm)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6.92
6.91
6.62
6.59
5.28
2.12
2.04
OBn
O
OAc
N
N
N
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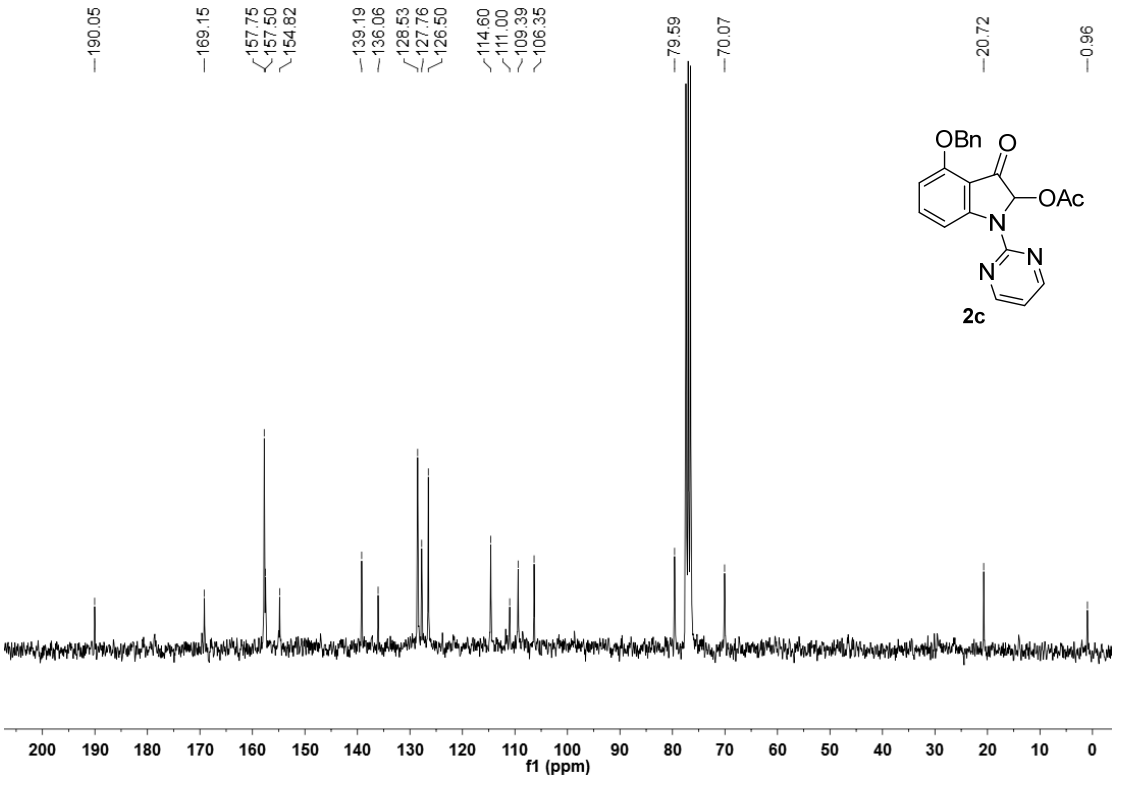
f1 (ppm)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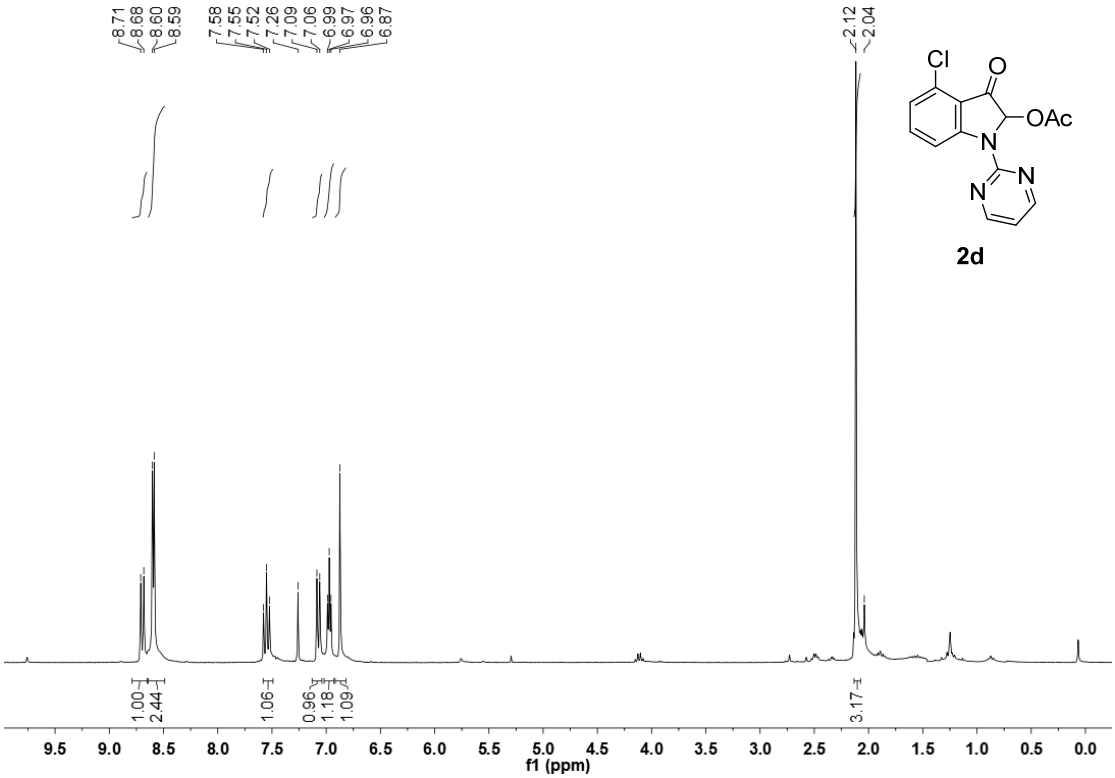
f1 (ppm)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2.04
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Cl
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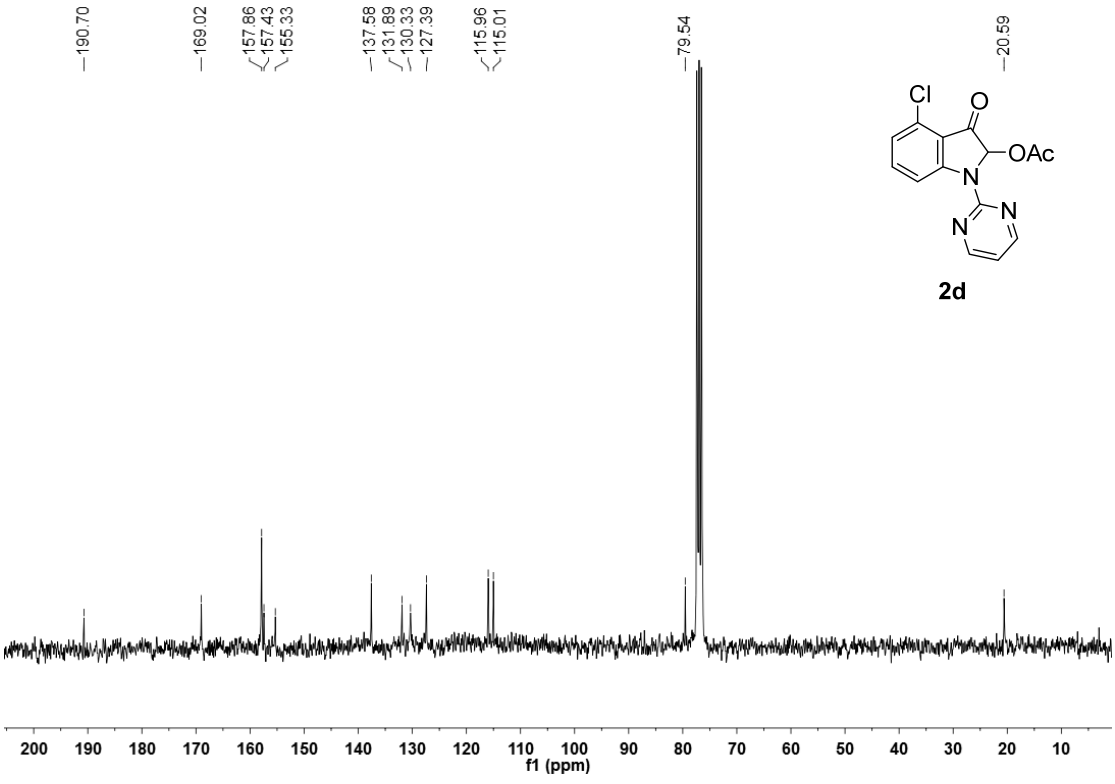
N
N

2d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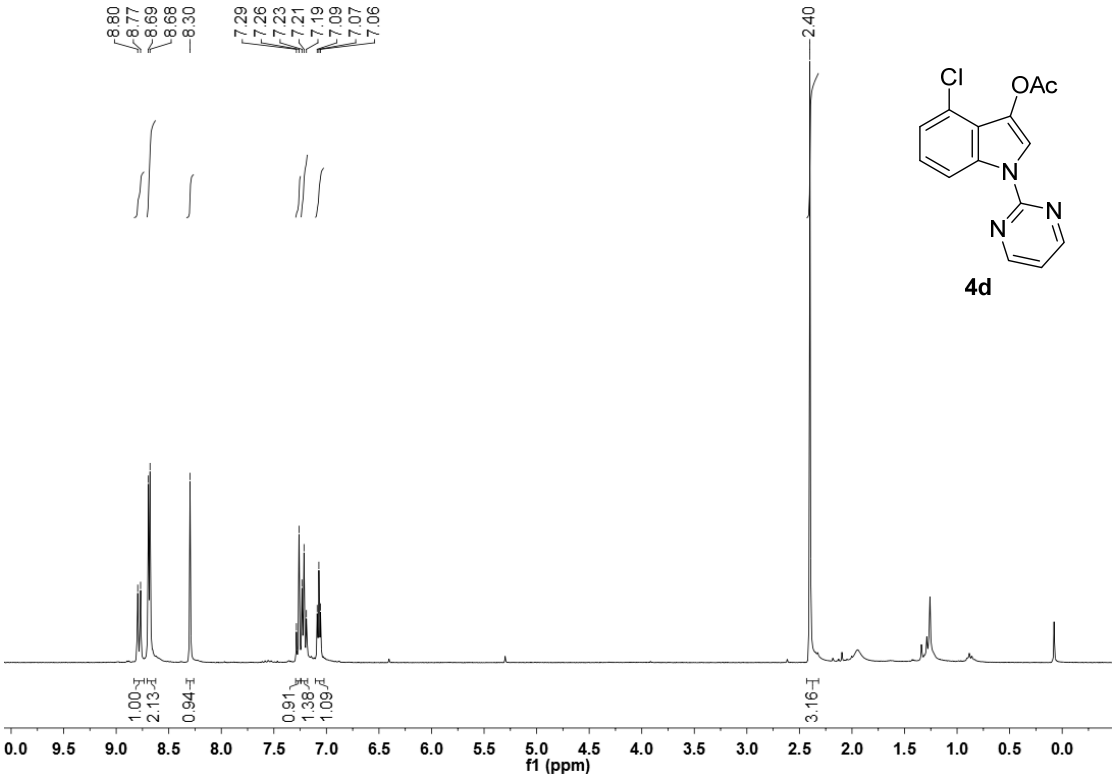
f1 (ppm)
Cl
O
OAc
N
N
N

2d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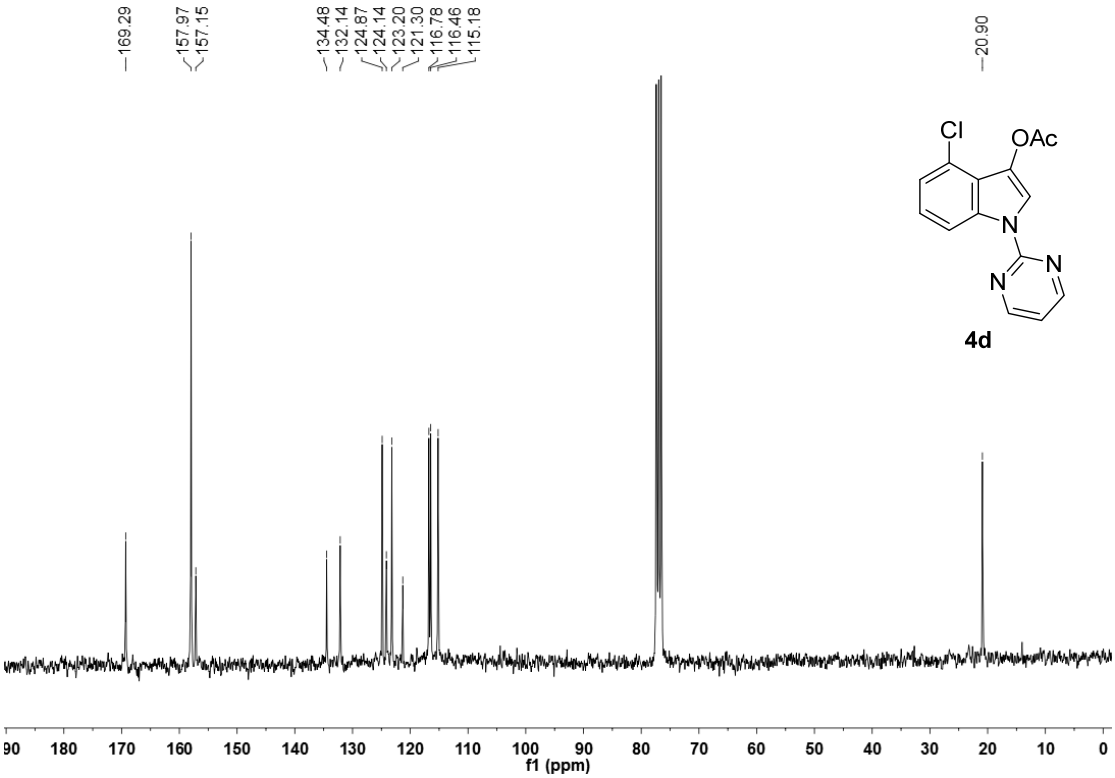
4d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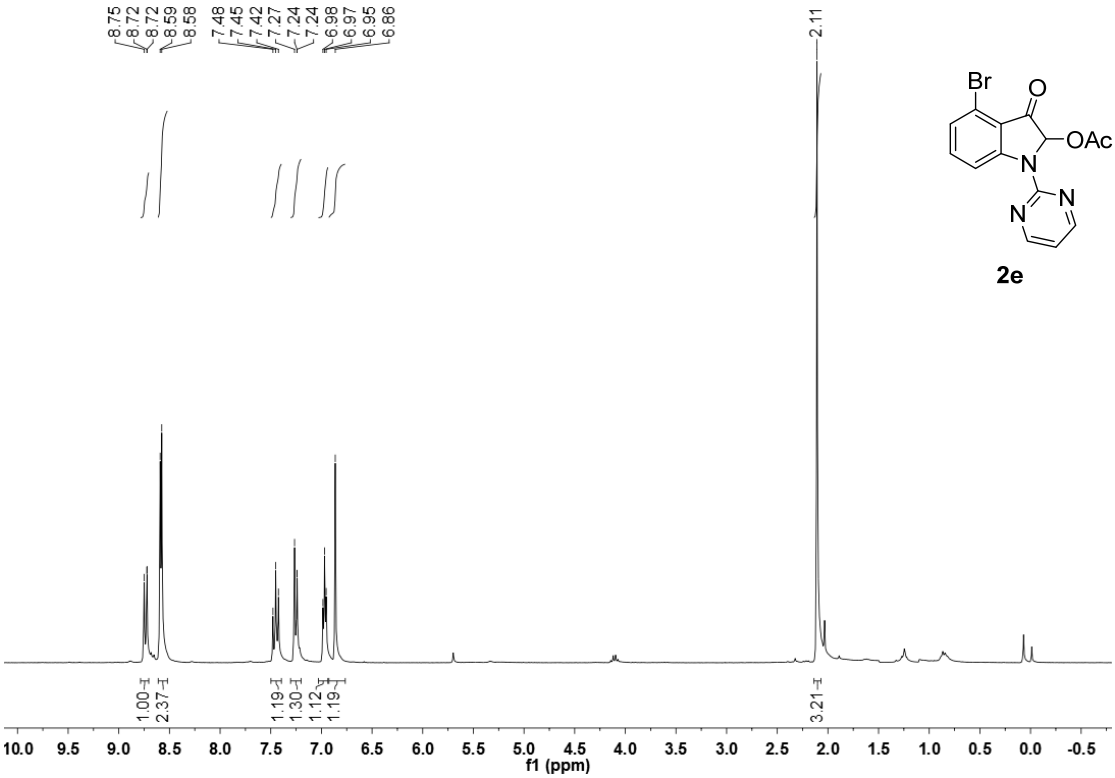
f1 (ppm)

4d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Br
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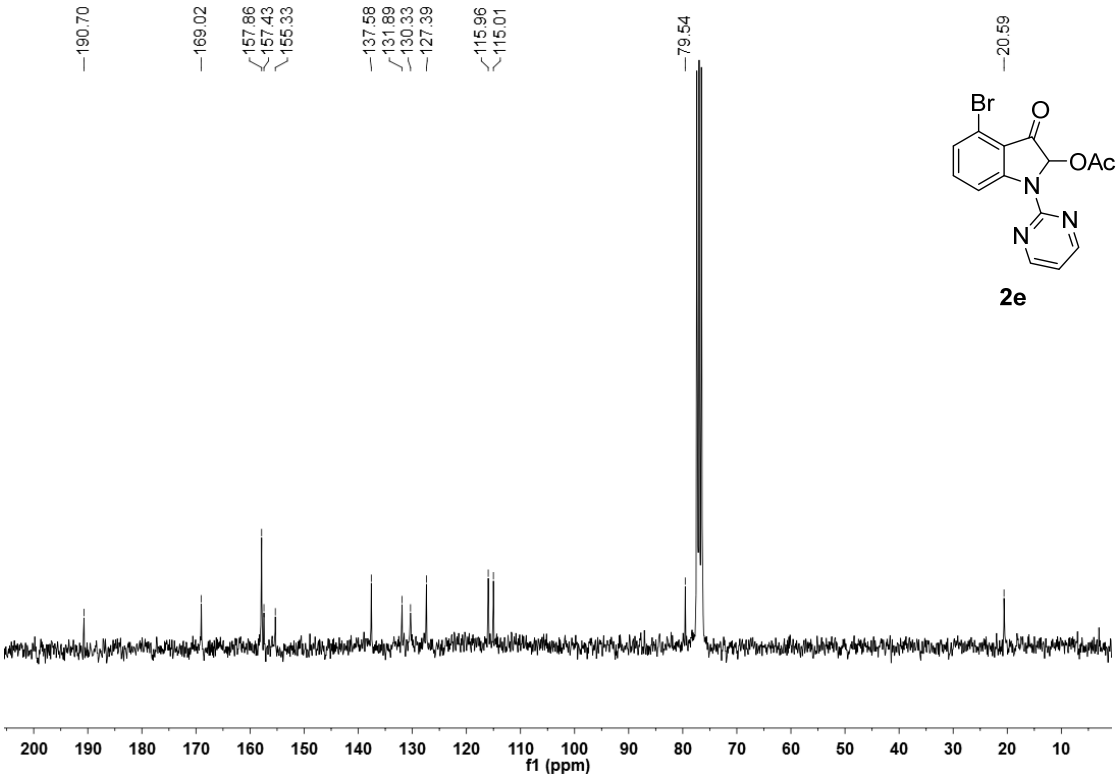
f1 (ppm)

2e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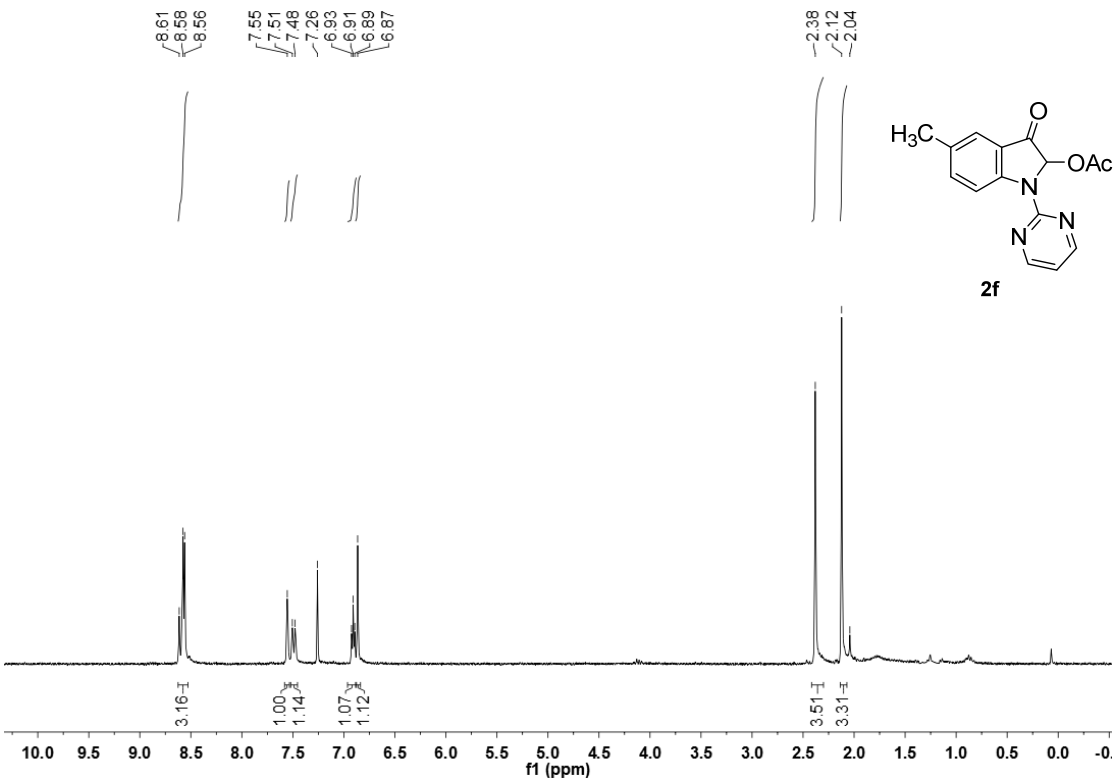
N
N
N
f1 (ppm)

2e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O
H3C
OAc
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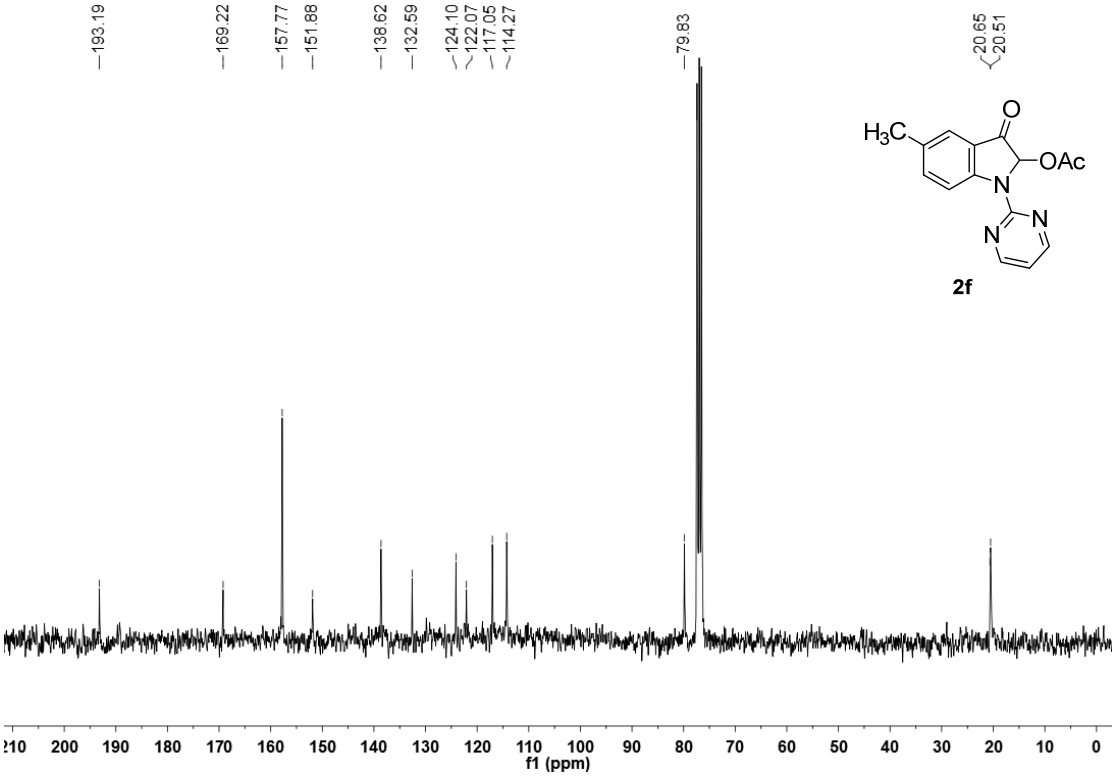
N
N

2f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f1 (ppm)

O
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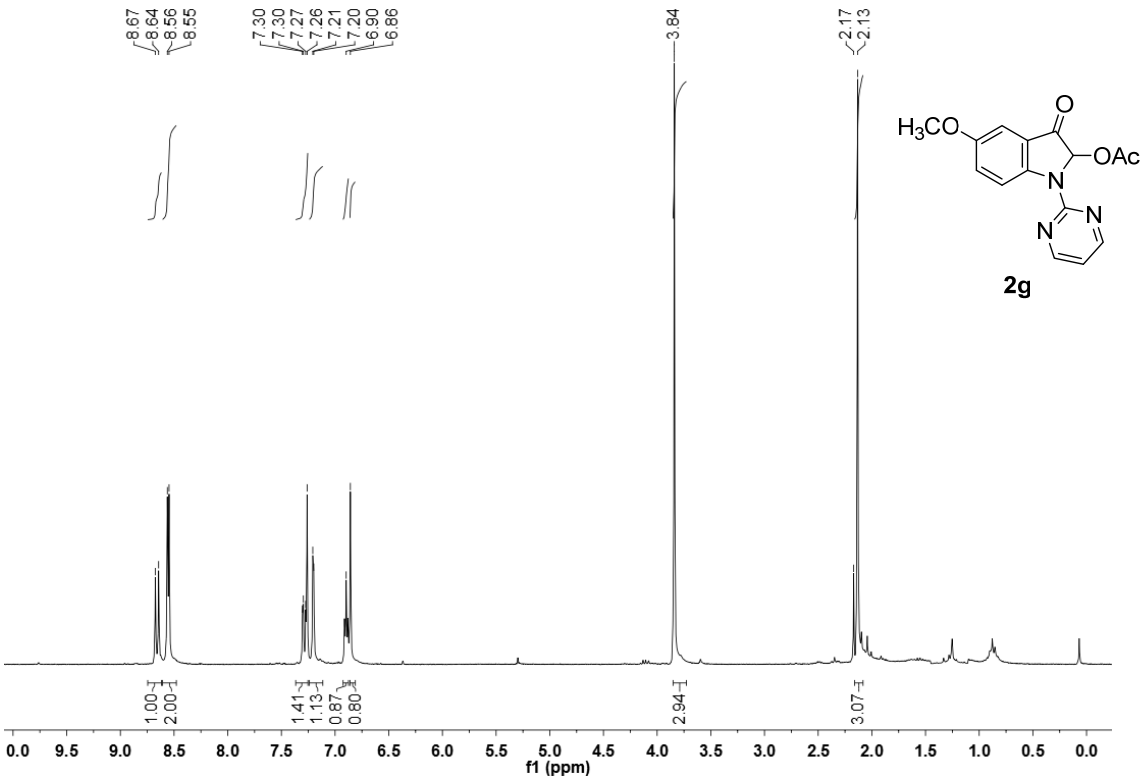
N
N

2f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2.00
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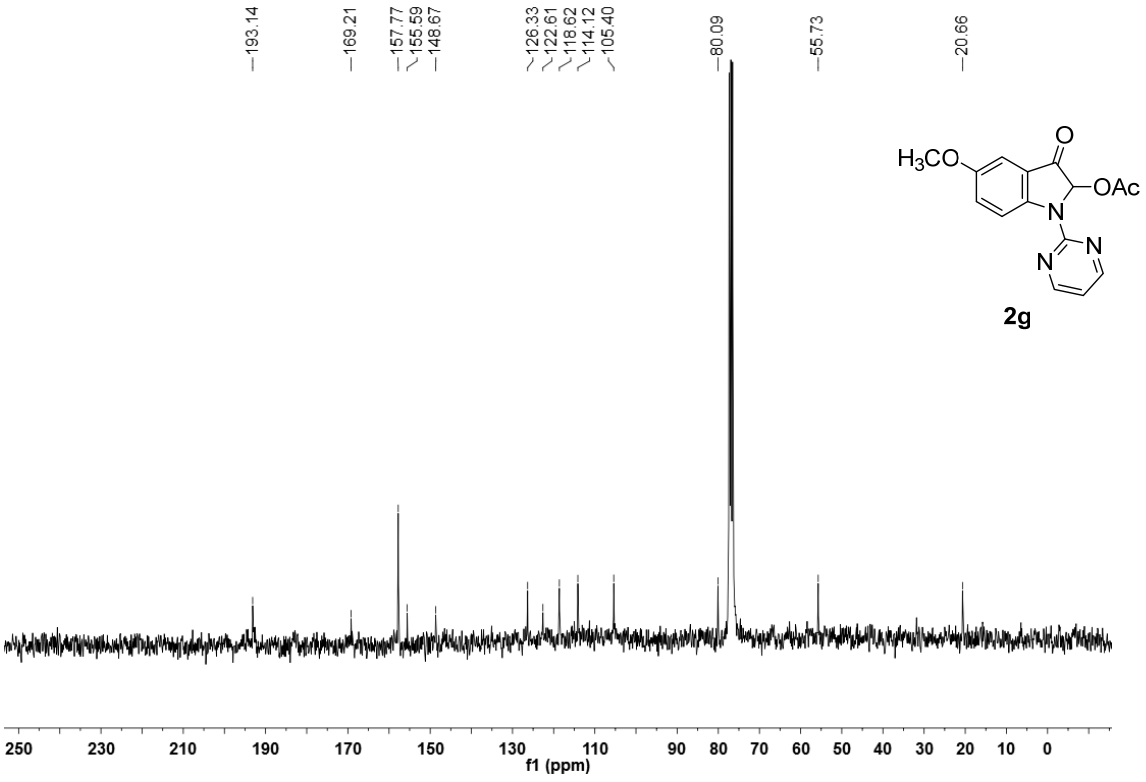
2g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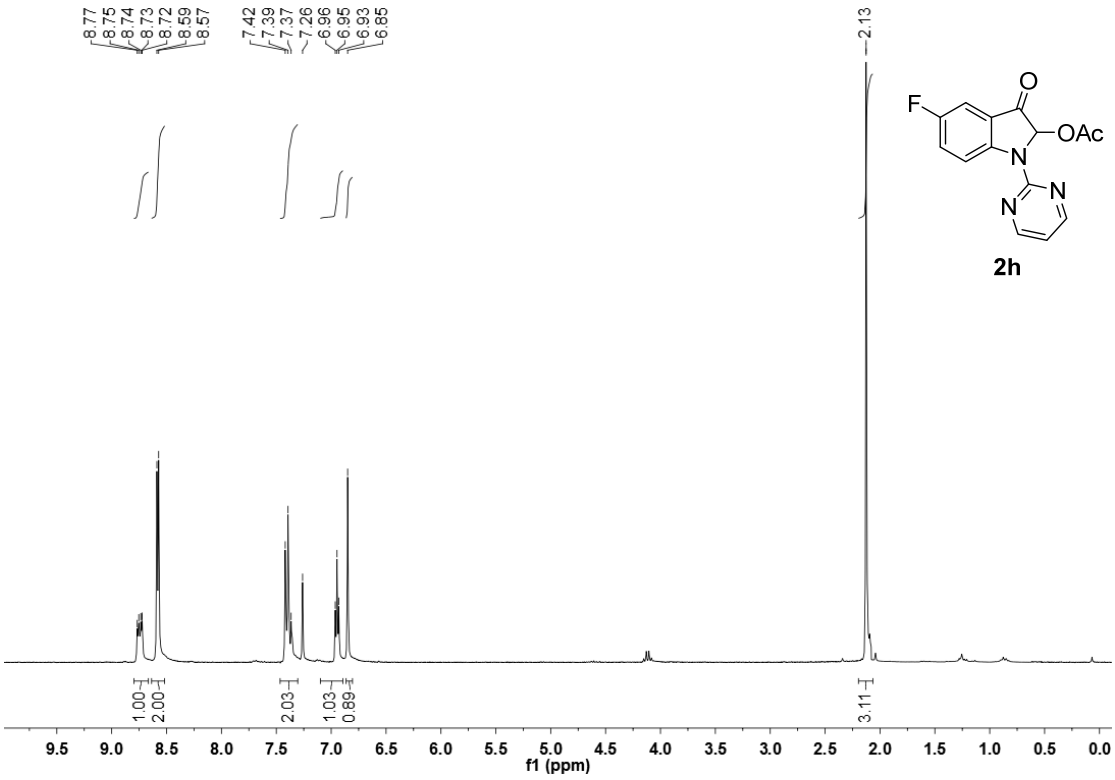
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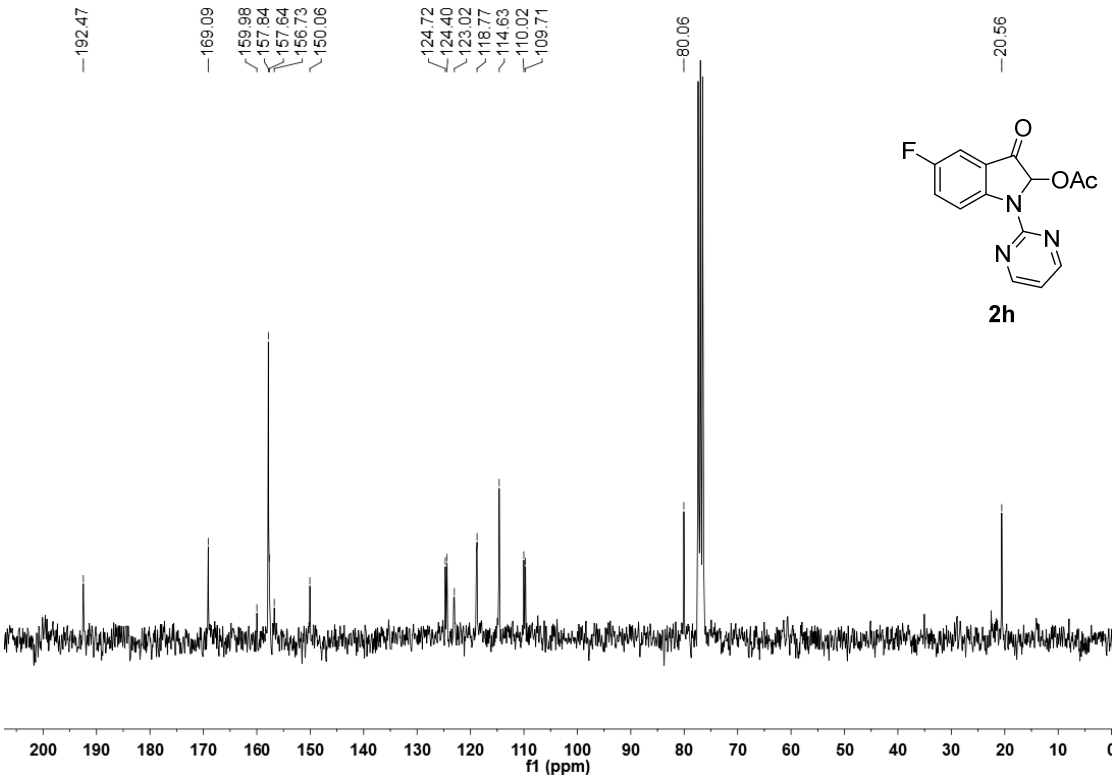
6.93
6.85
2.13
F
O
OAc
N
N
N
1.00
2.00
2.03
1.03
0.89
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2h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110.02
109.71
80.06
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N
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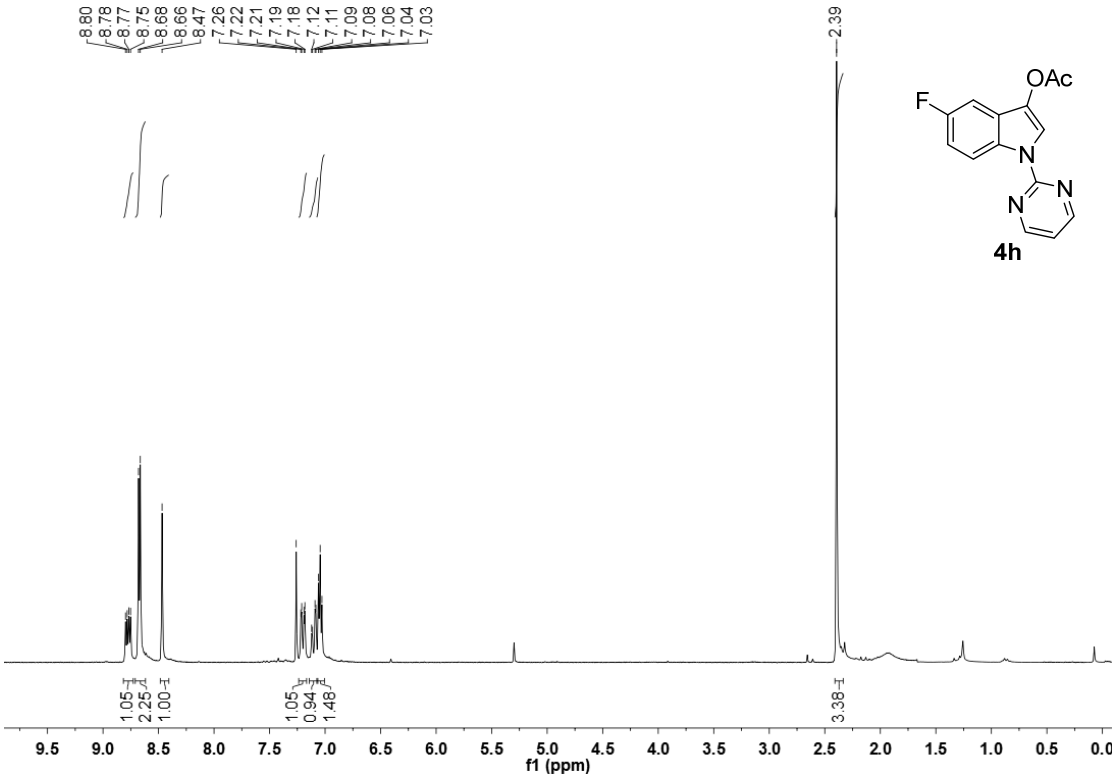
f1 (ppm)

2h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7.04
7.03
2.39
1.05
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1.00
1.05
0.94
1.48
3.38
9.5 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
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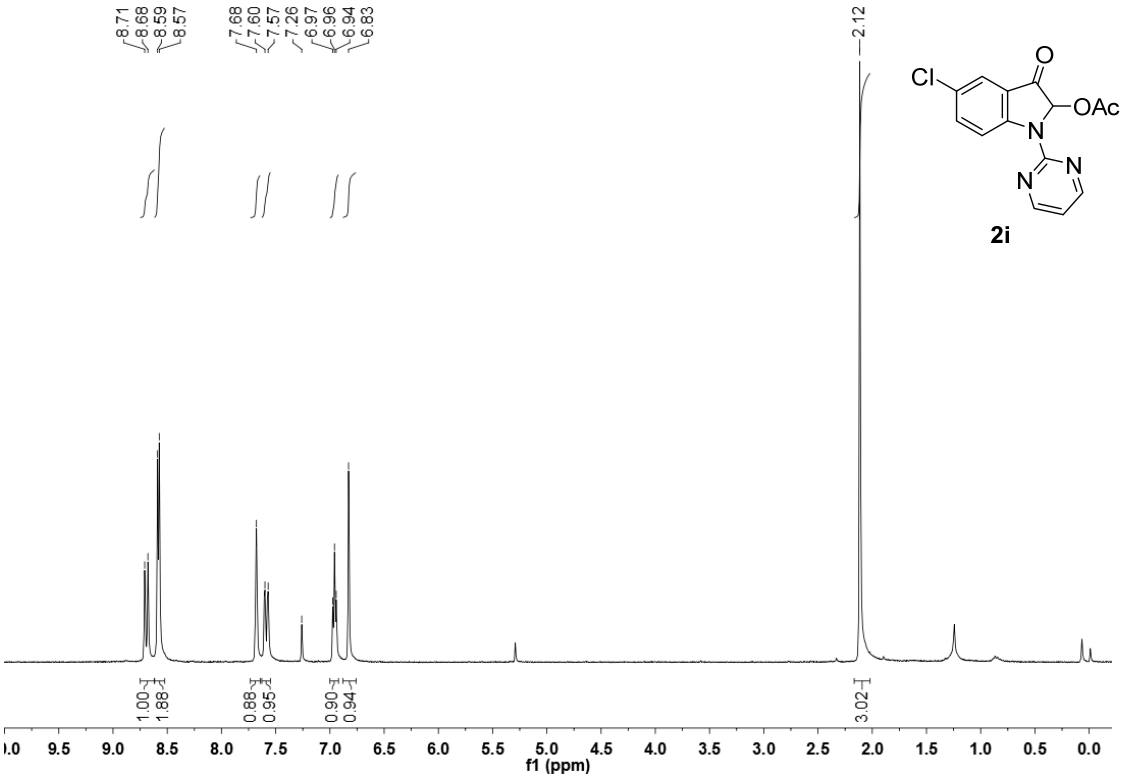
N

4h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1.00
1.88
0.88
0.95
0.90
0.94
3.02
9.5 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
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N

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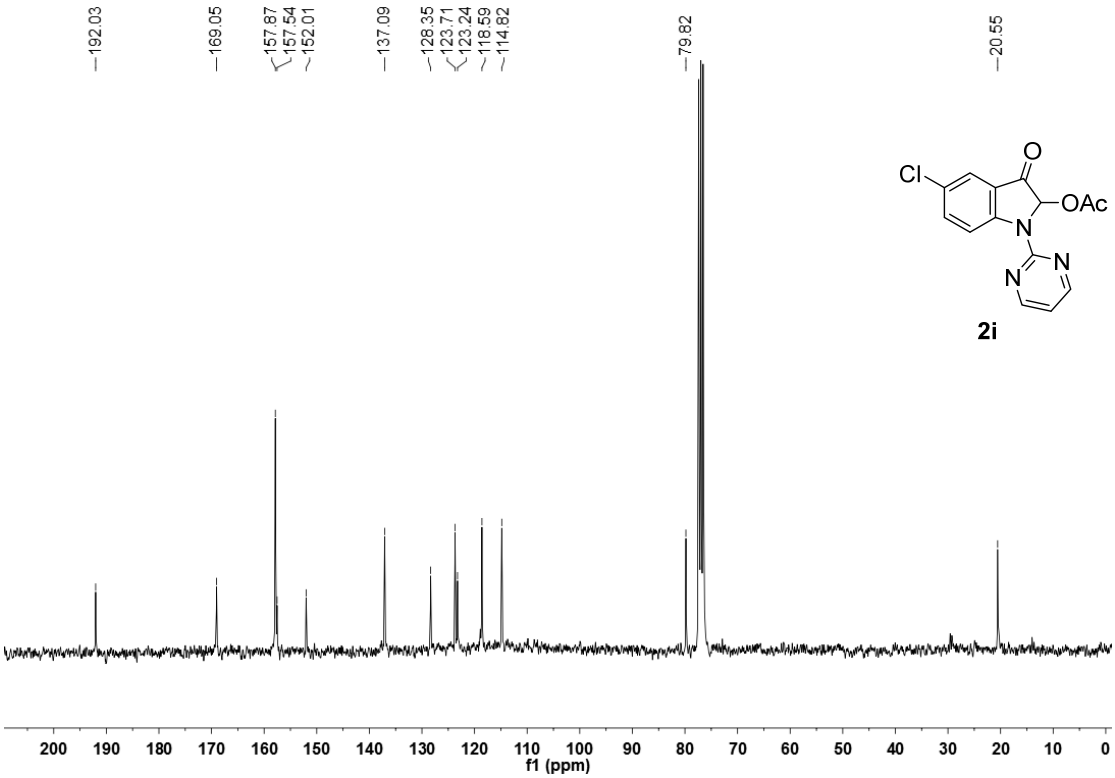
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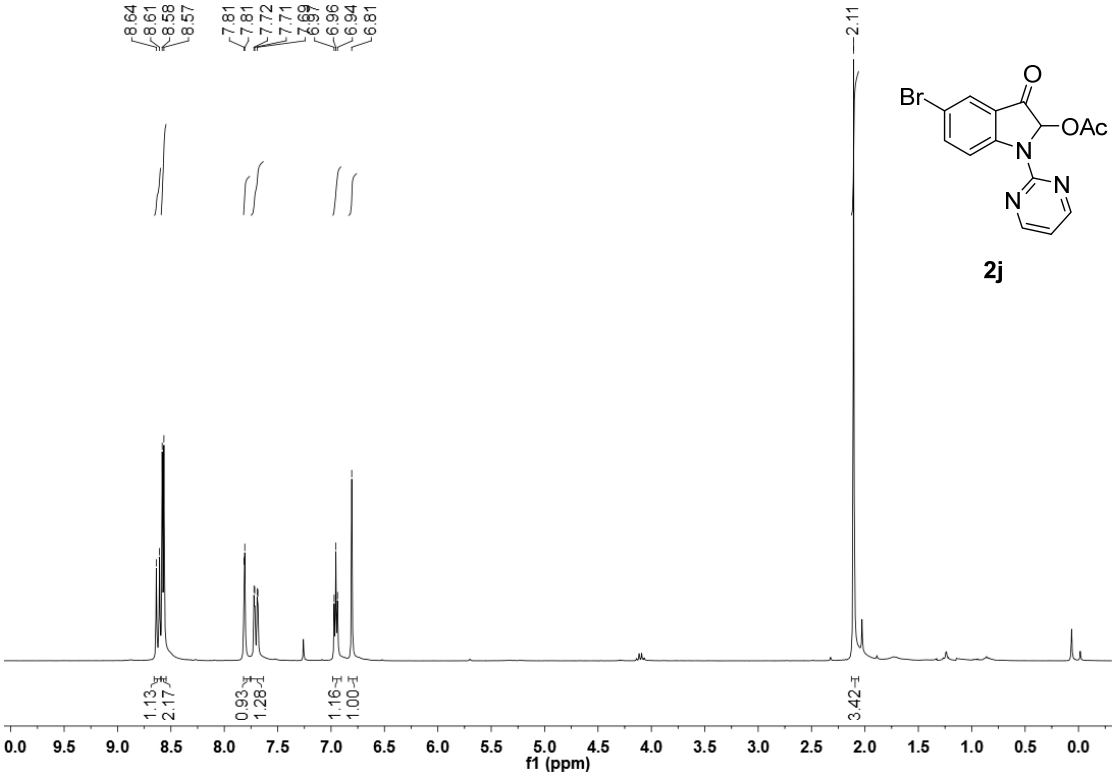
2i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2.11
Br
O
OAc
N
N
N
1.13
2.17
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1.28
1.16
1.00
3.42
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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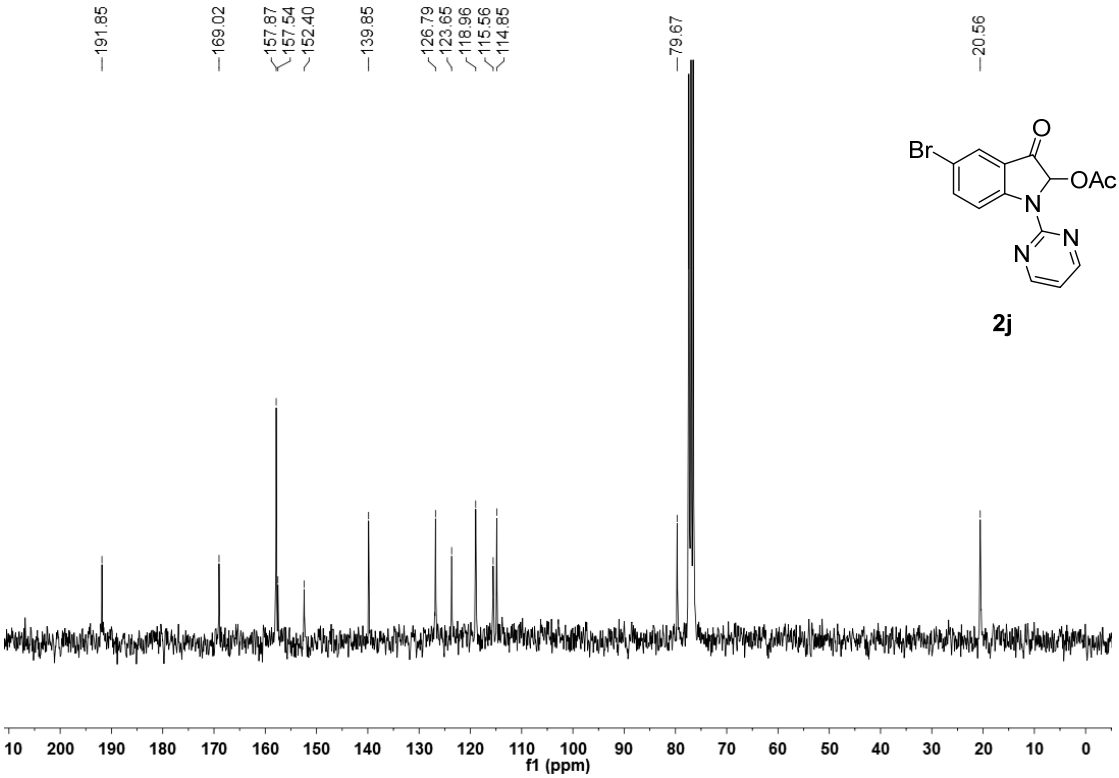
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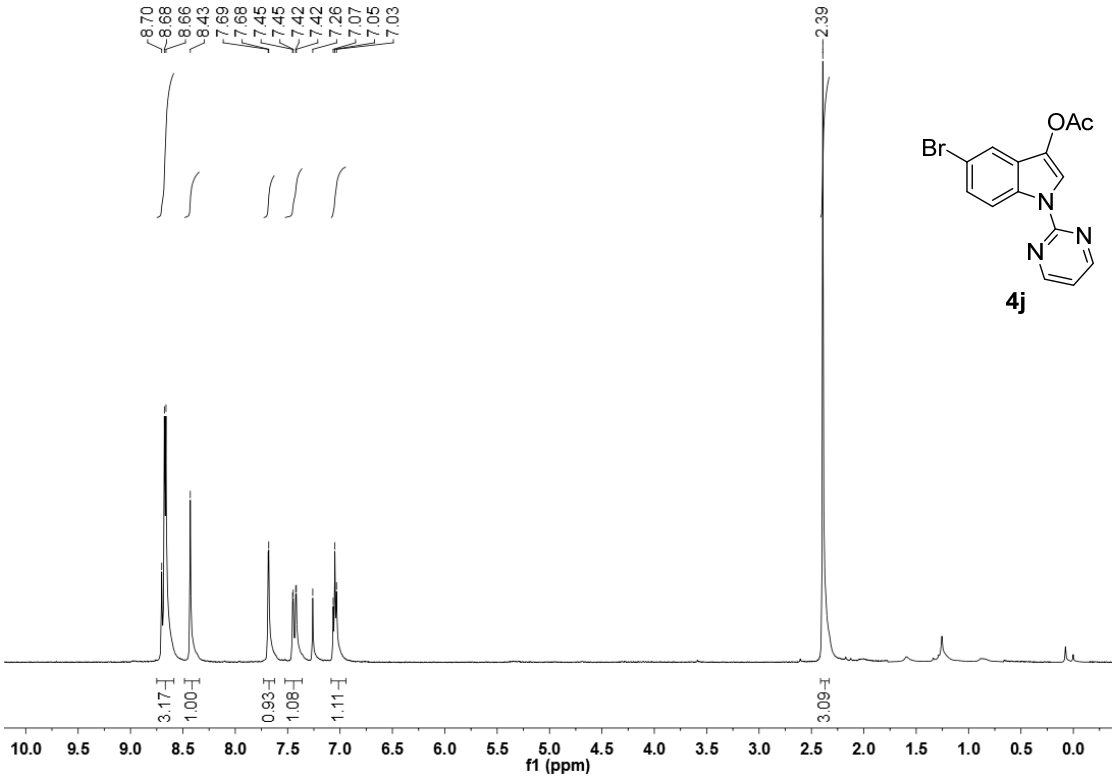
f1 (ppm)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7.03
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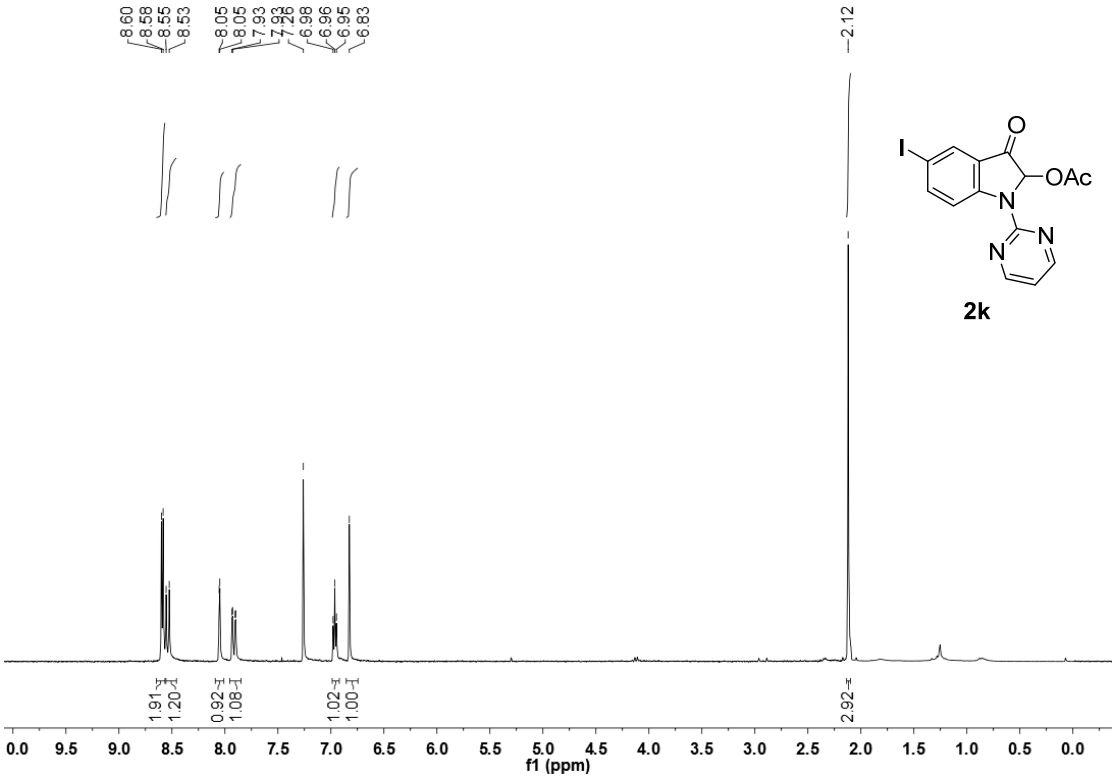
f1 (ppm)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2.12
1.91
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f1 (ppm)

O
I
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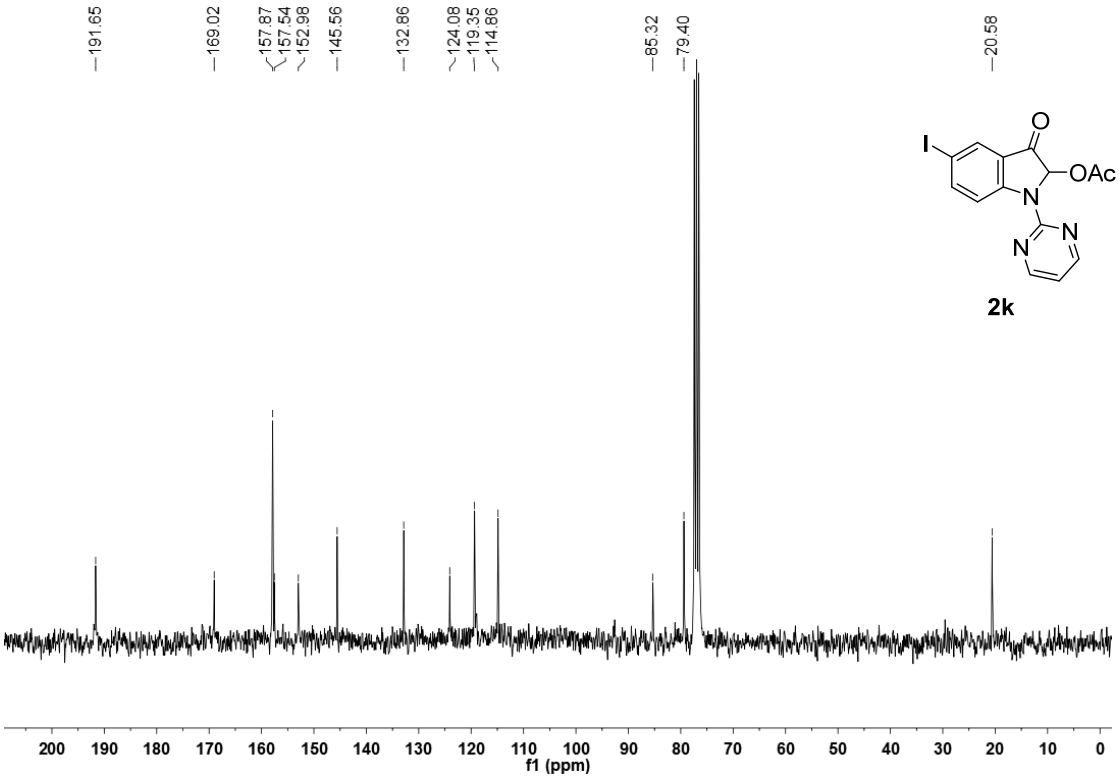
N
N

2k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f1 (ppm)

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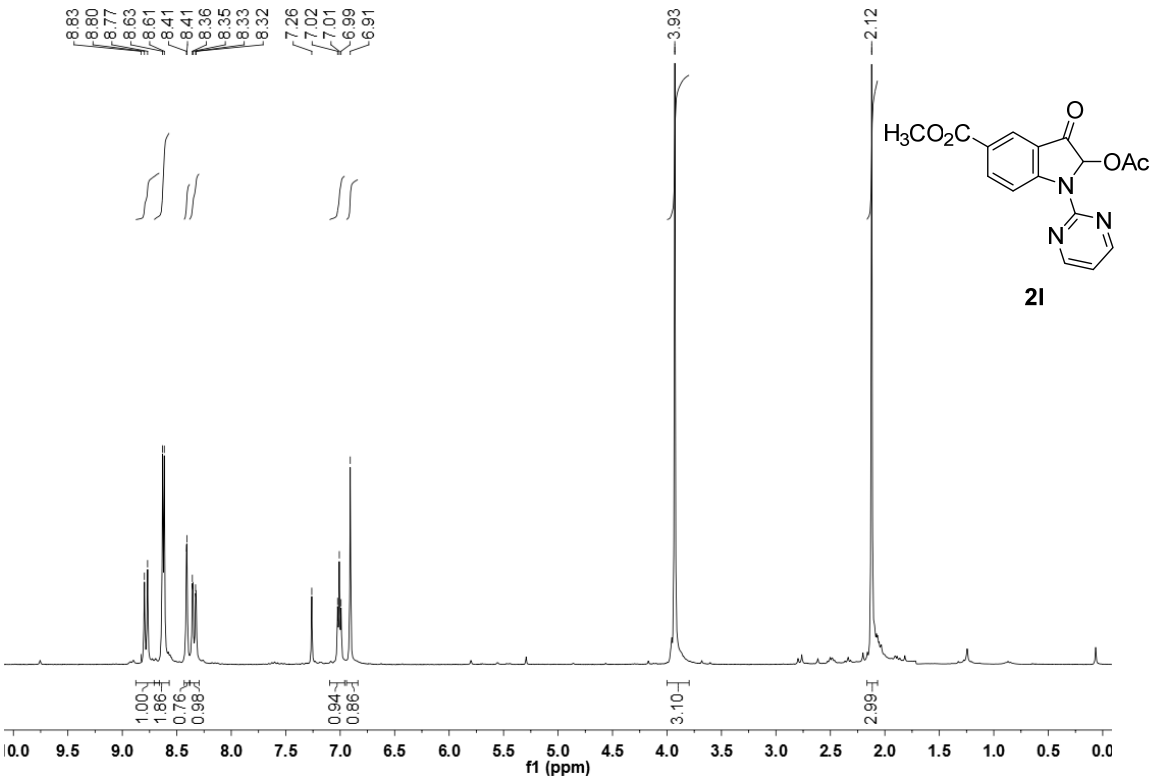
N
N

2k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7.01
6.99
6.91
3.93
2.12
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H3CO2C
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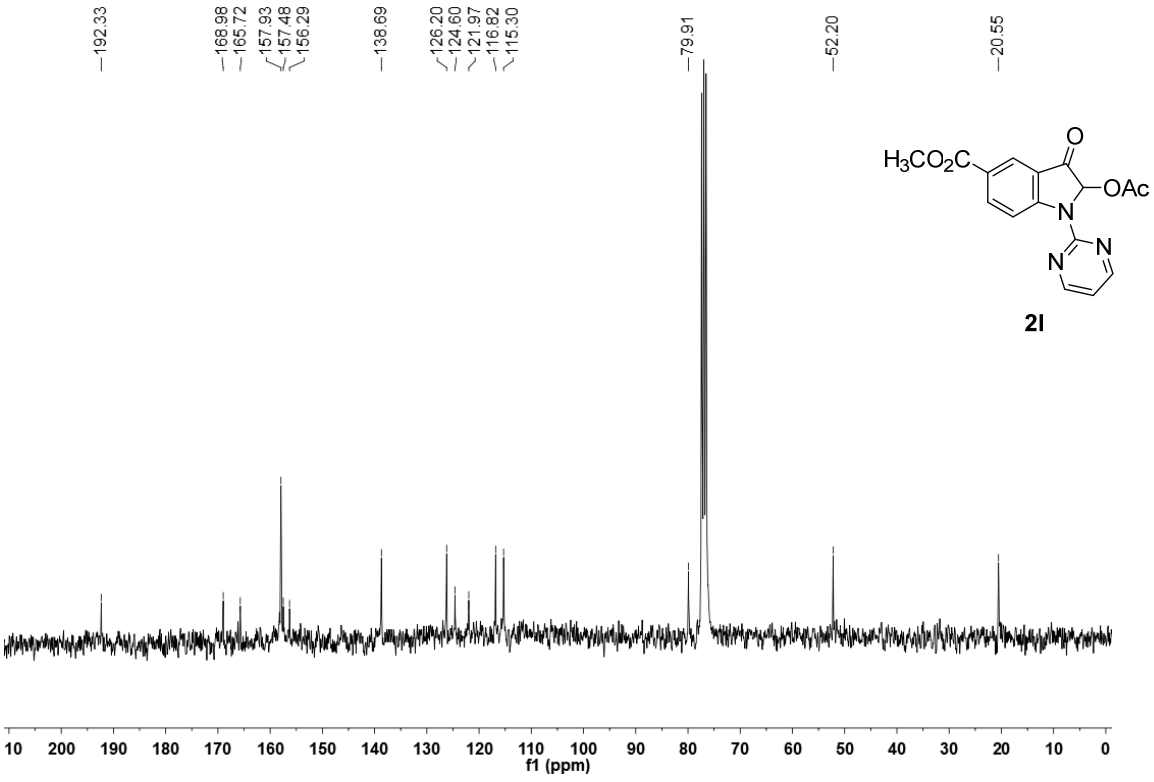
N
2l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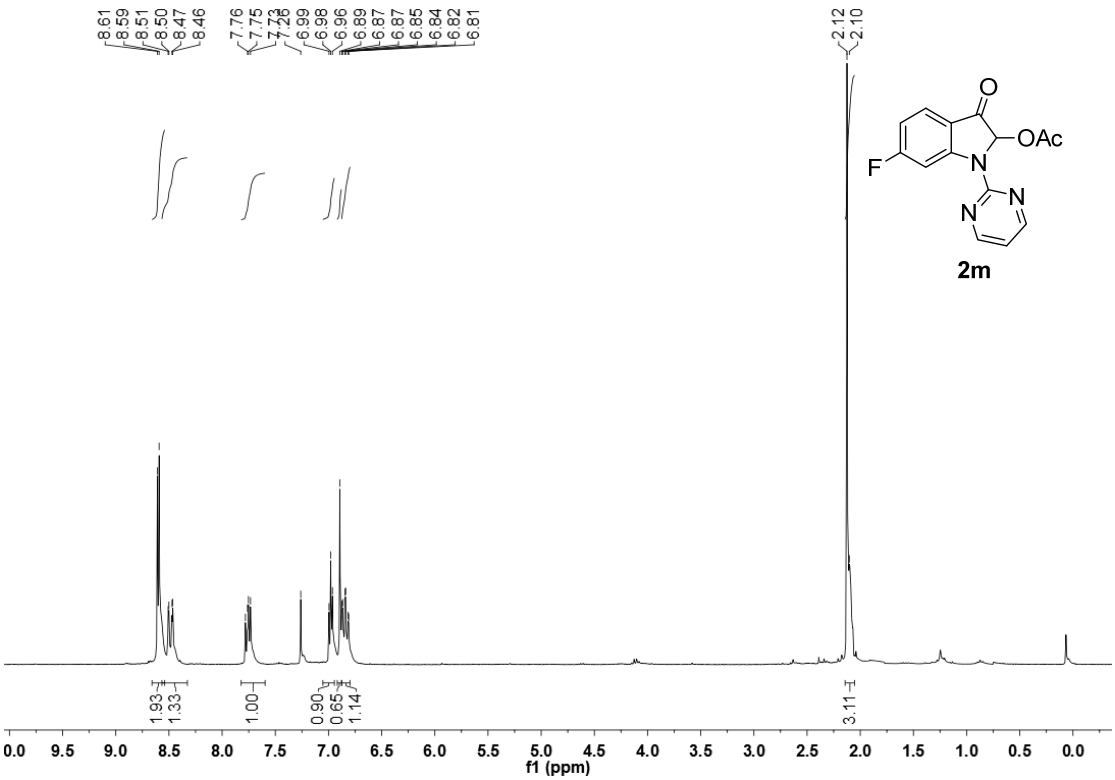
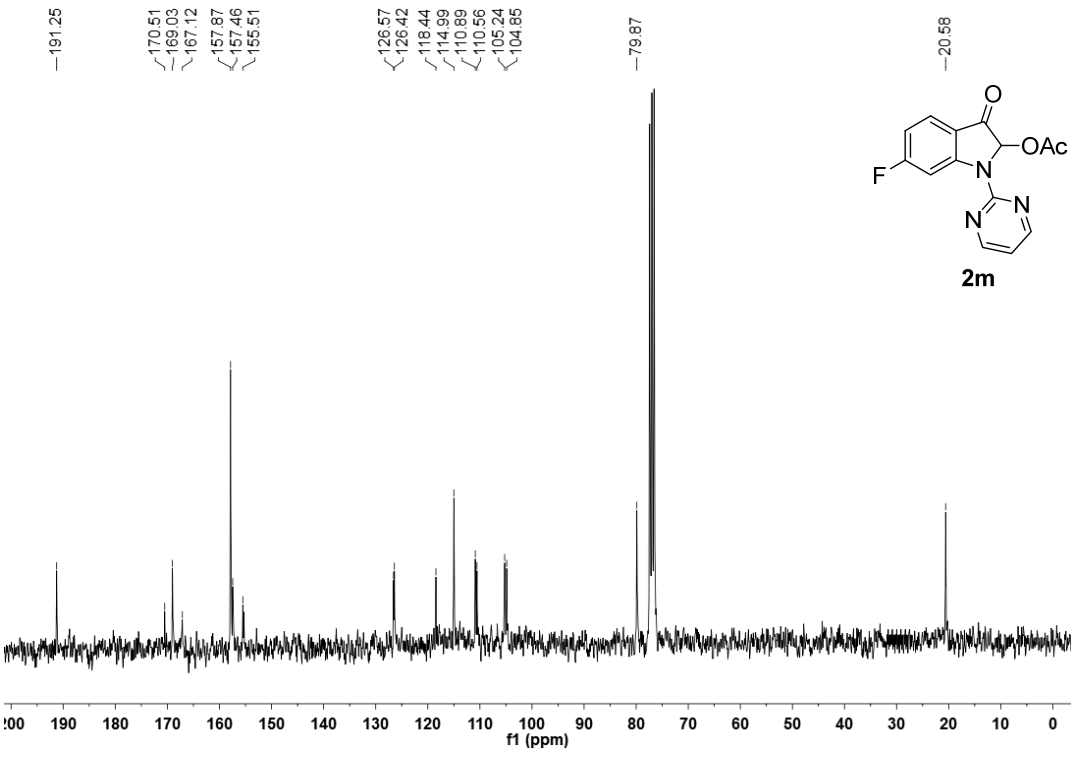
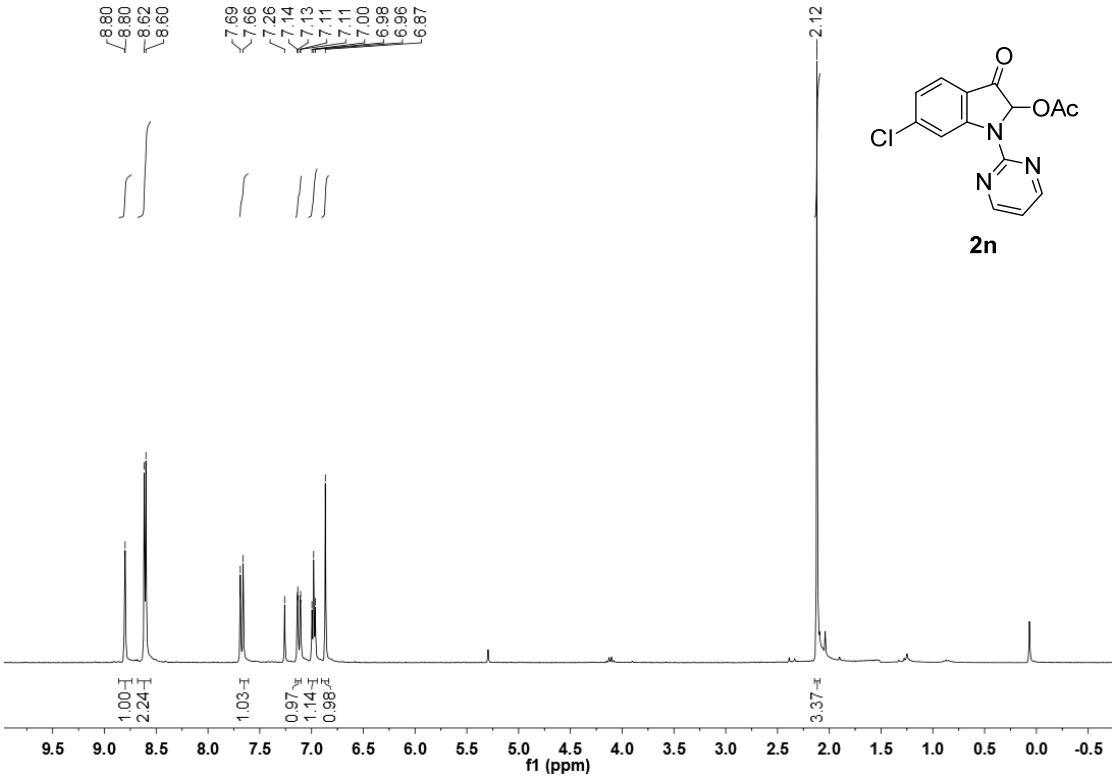
79.91
52.20
20.55
f1 (ppm)
O
H3CO2C
OAc
N
N
N
2l


8.61
8.59
8.51
8.50
8.47
8.46
7.76
7.75
7.73
7.26
6.99
6.98
6.96
6.89
6.87
6.87
6.85
6.84
6.82
6.81
2.12
2.10
O
OAc
F
N
N
N
1.93
1.33
1.00
0.90
0.65
1.14
3.11
f1 (ppm)

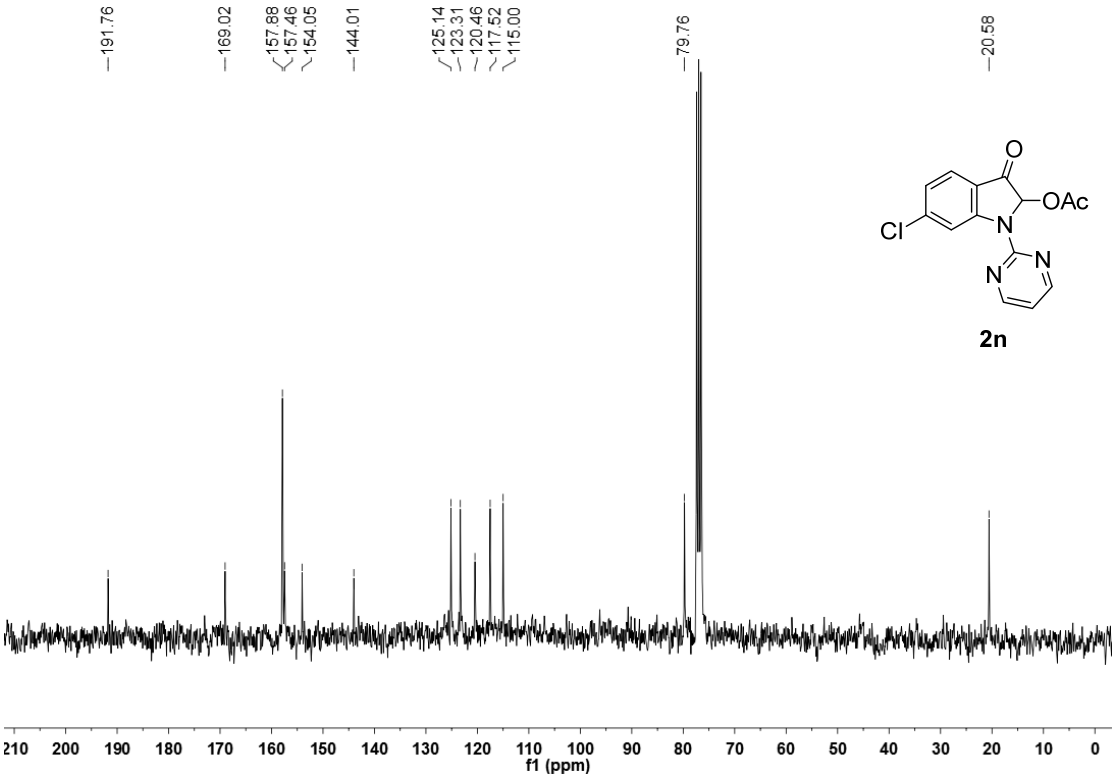
2m


191.25
170.51
169.03
167.12
157.87
157.46
155.51
126.57
126.42
118.44
114.99
110.89
110.56
105.24
104.85
79.87
20.58
O
OAc
F
N
N
N
f1 (ppm)

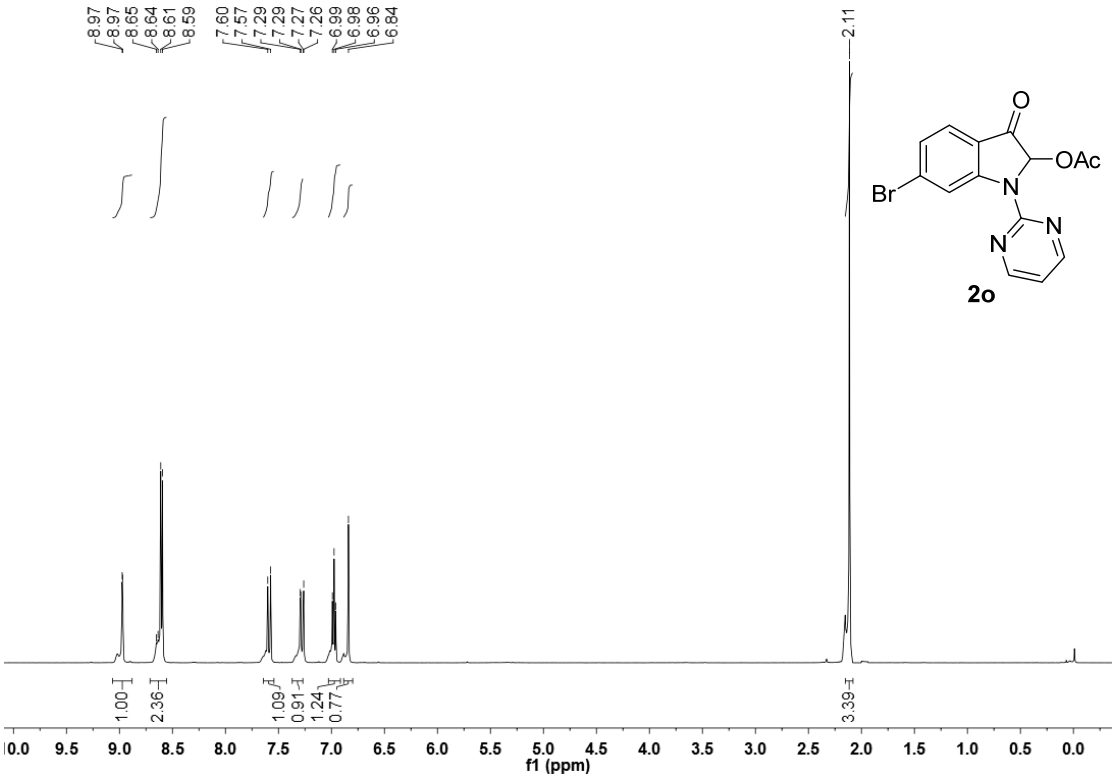
2m

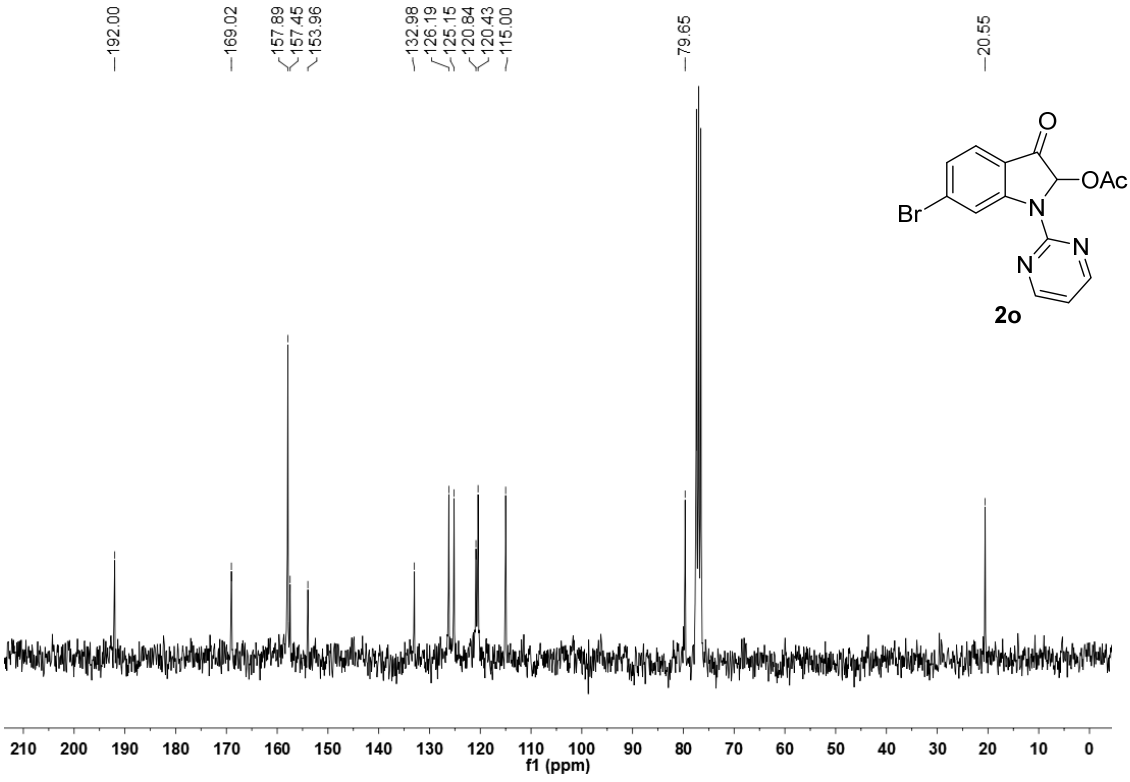

8.80
8.80
8.62
8.60
7.69
7.66
7.26
7.14
7.13
7.11
7.11
7.00
6.98
6.96
6.87
2.12
1.00
2.24
1.03
0.97
1.14
0.98
3.37
f1 (ppm)
O
OAc
Cl
N
N
N

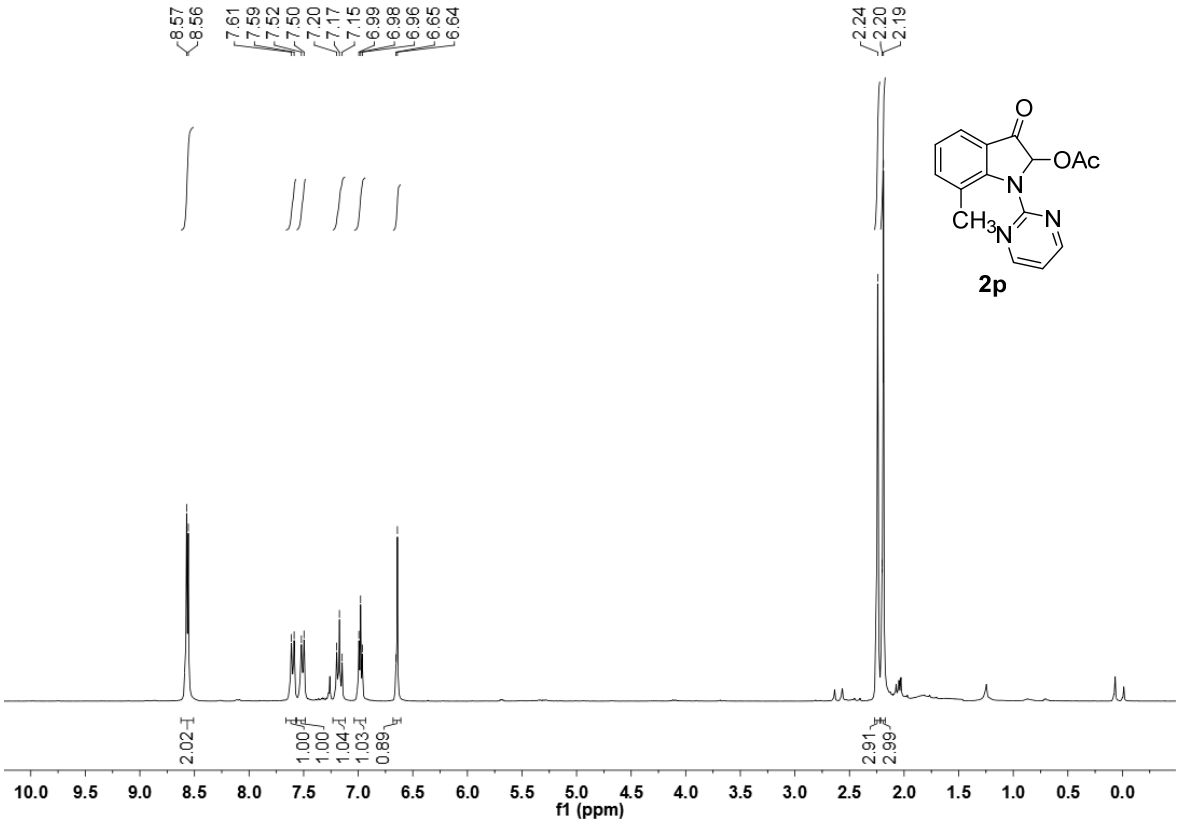
2n

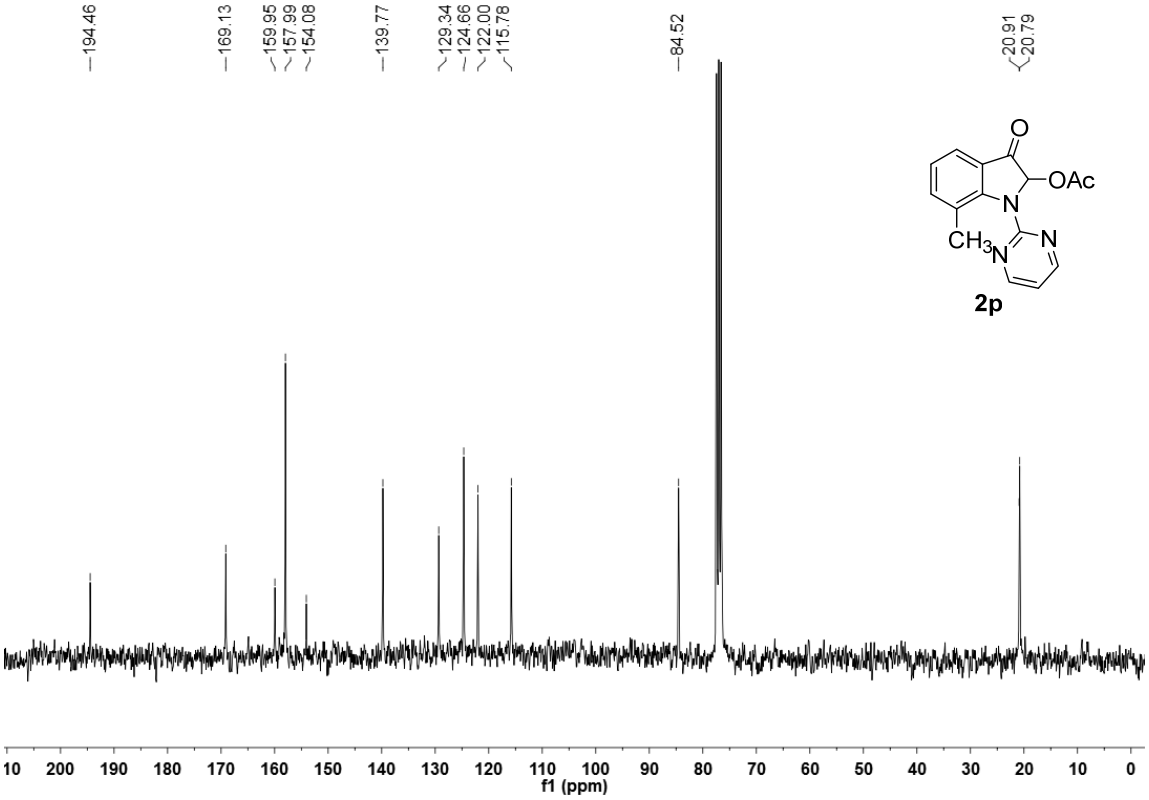

191.76
169.02
157.88
157.46
154.05
144.01
125.14
123.31
120.46
117.52
115.00
79.76
20.58
f1 (ppm)
O
OAc
Cl
N
N
N

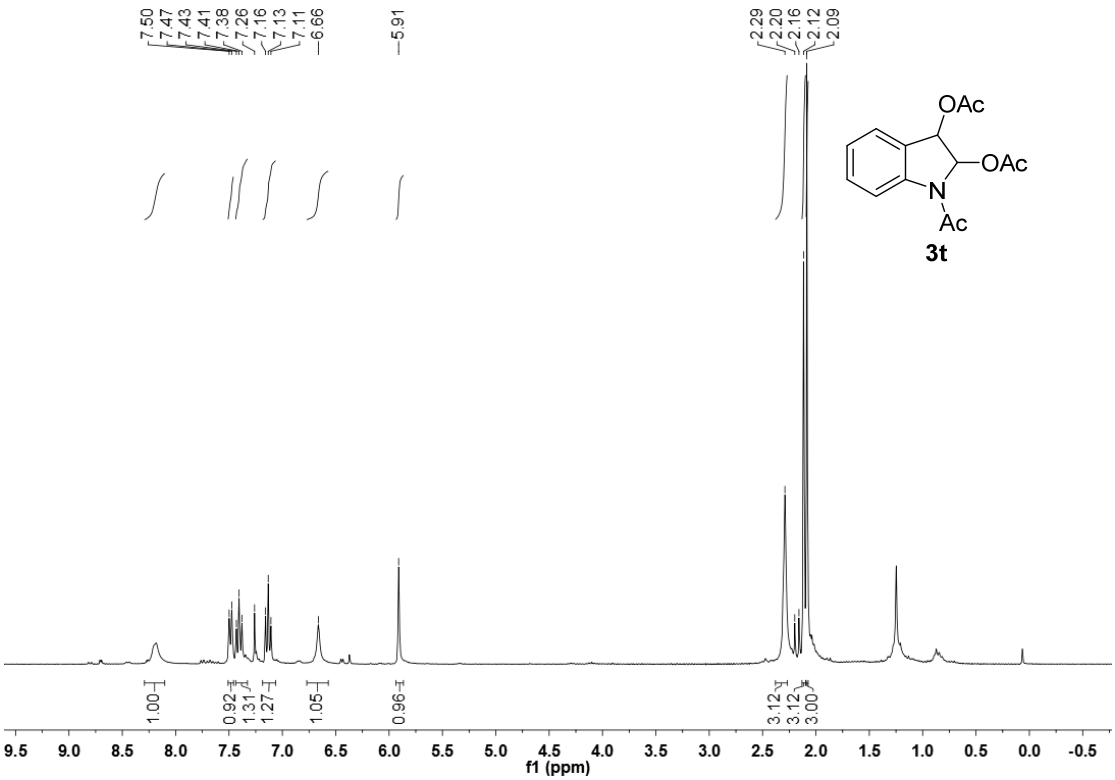
2n

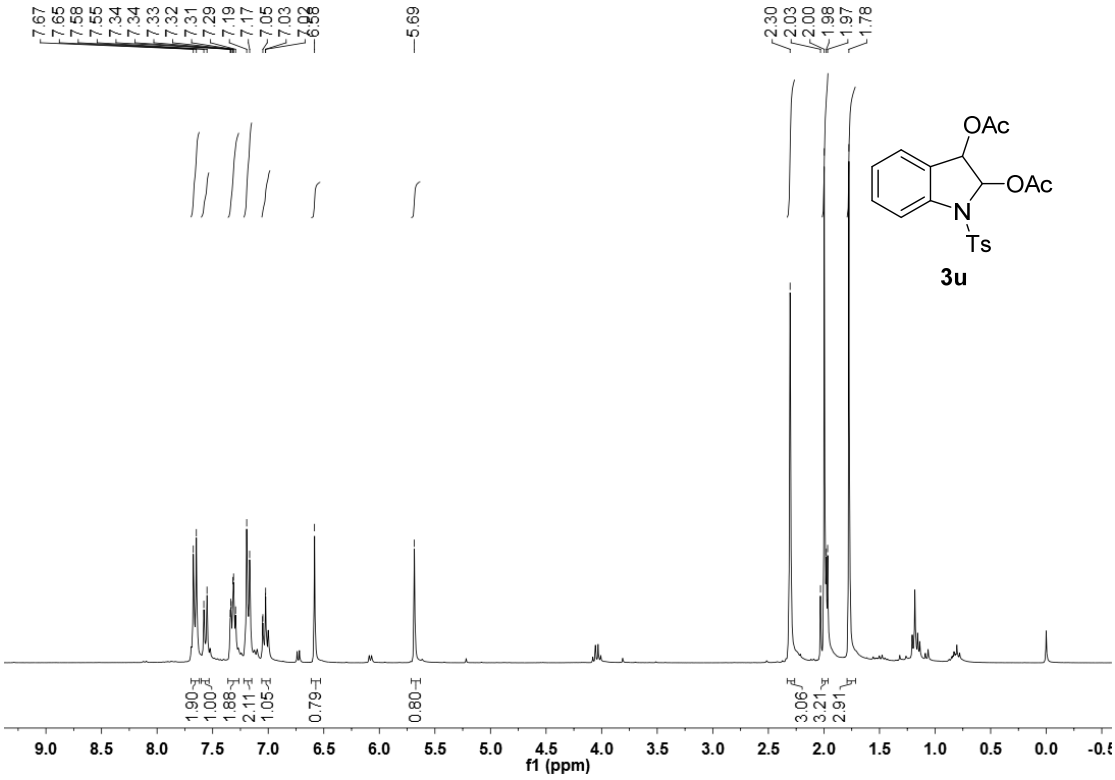

8.97
8.97
8.65
8.64
8.61
8.59
7.60
7.57
7.29
7.29
7.27
7.26
6.99
6.98
6.96
6.84
2.11
1.00
2.36
1.09
0.91
1.24
0.77
3.39
f1 (ppm)
O
OAc
Br
N
N
N
2o

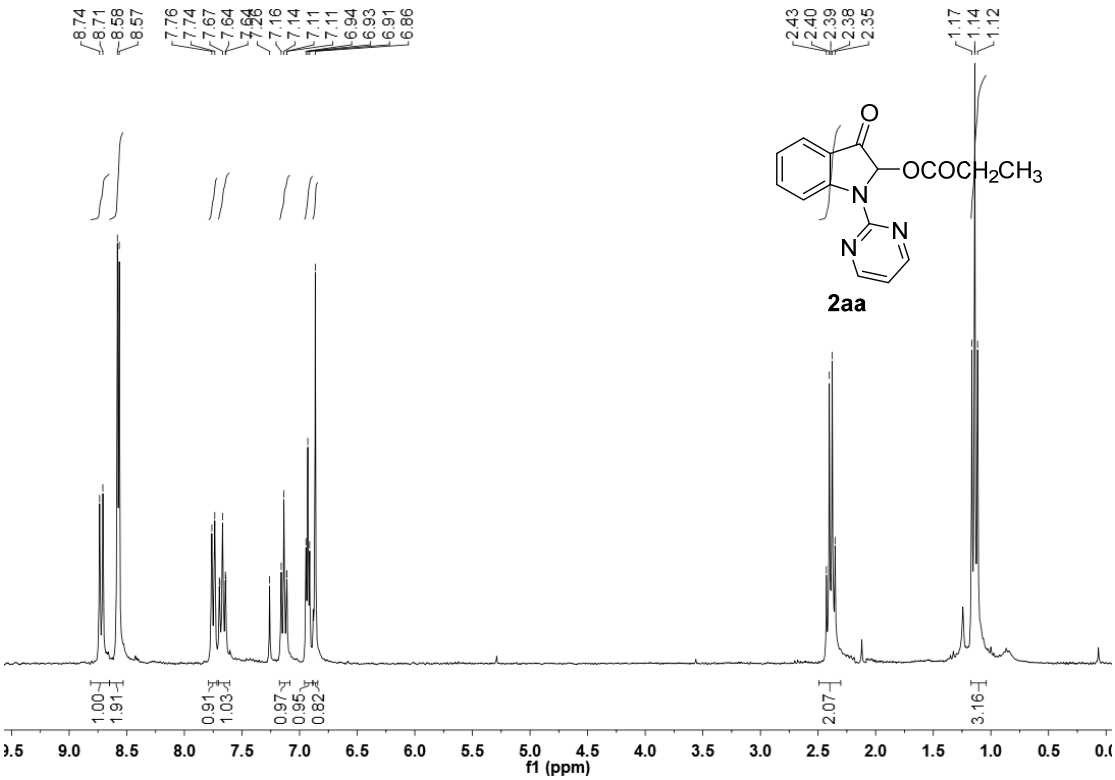

192.00
169.02
157.89
157.45
153.96
132.98
126.19
125.15
120.84
120.43
115.00
79.65
20.55
f1 (ppm)
O
OAc
Br
N
N
N
2o

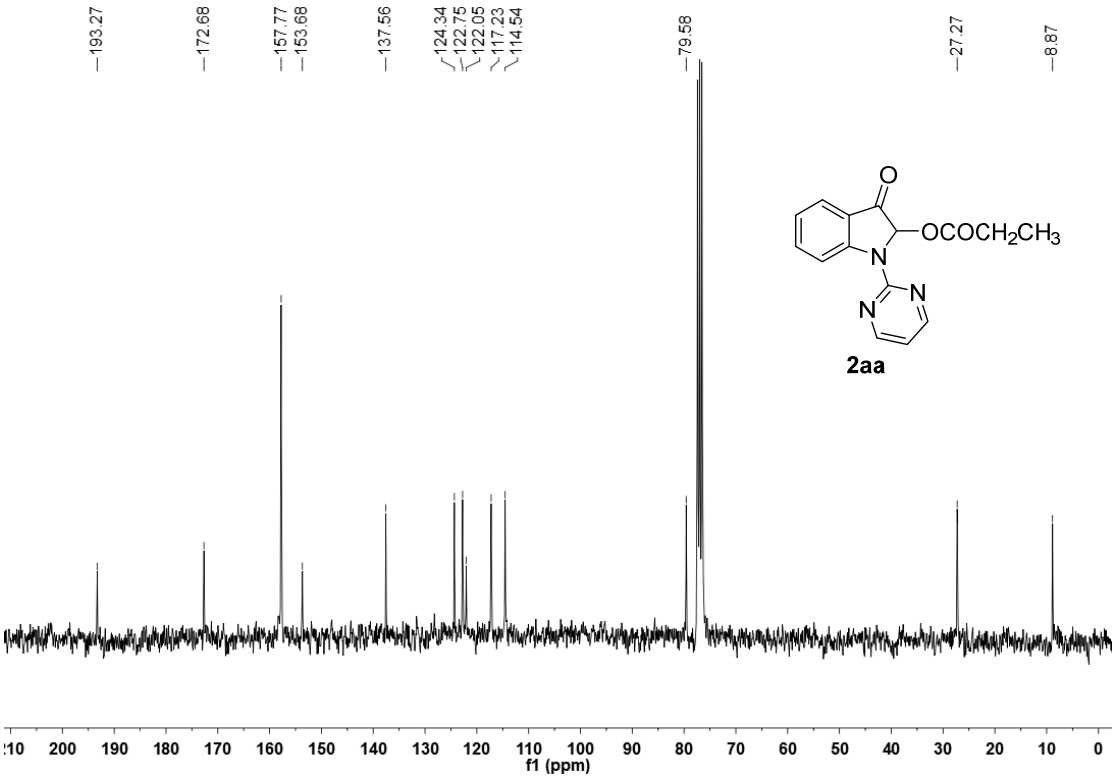

8.57
8.56
7.61
7.59
7.52
7.50
7.20
7.17
7.15
6.99
6.98
6.96
6.65
6.64
2.24
2.20
2.19
O
OAc
N
CH3
N
N
2p
2.02
1.00
1.00
1.04
1.03
0.89
2.91
2.99
f1 (ppm)

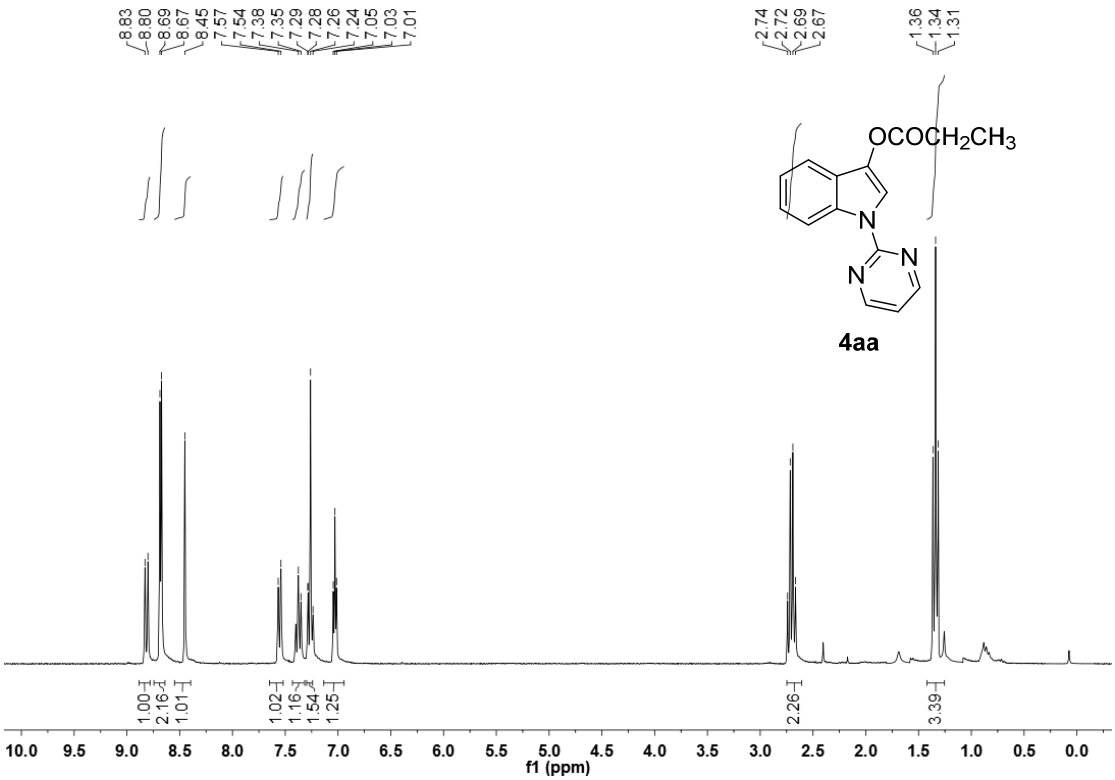

194.46
169.13
159.95
157.99
154.08
139.77
129.34
124.66
122.00
115.78
84.52
20.91
20.79
O
OAc
N
CH3
N
N
2p
f1 (ppm)


7.50
7.47
7.43
7.41
7.38
7.26
7.16
7.13
7.11
6.66
5.91
2.29
2.20
2.16
2.12
2.09
OAc
OAc
N
Ac
3t
1.00
0.92
1.31
1.27
1.05
0.96
3.12
3.12
3.00
f1 (ppm)

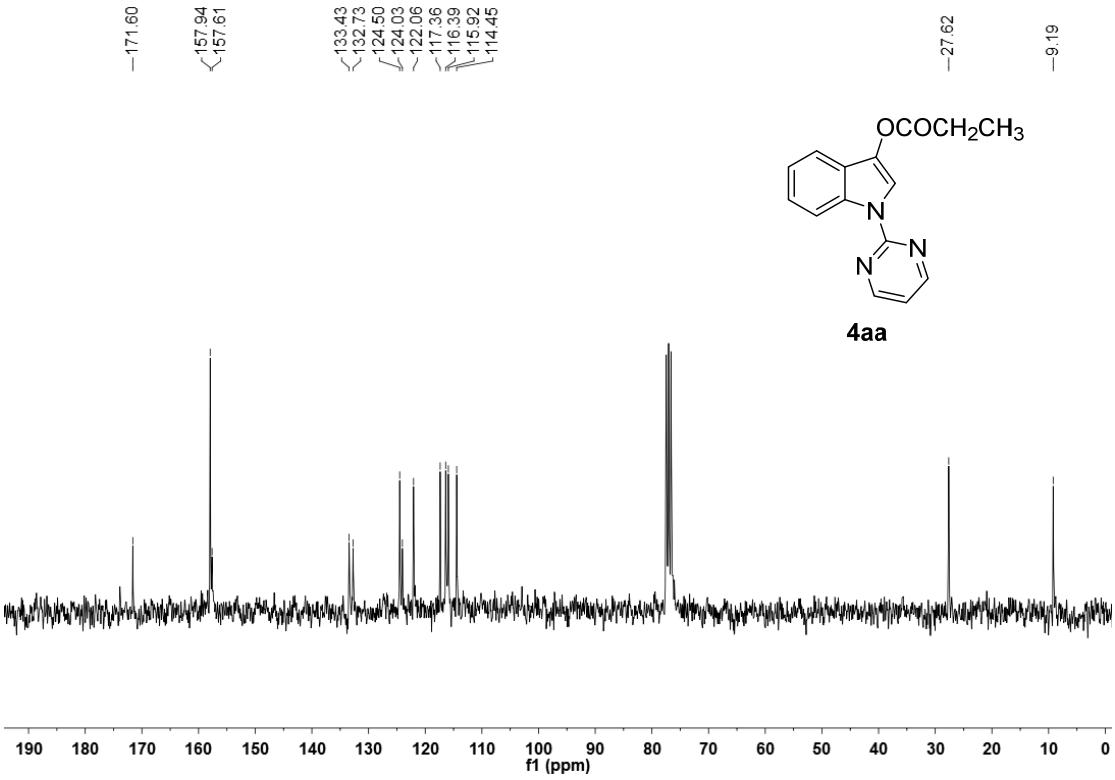

7.67
7.65
7.58
7.55
7.34
7.34
7.33
7.32
7.31
7.29
7.19
7.17
7.05
7.03
6.92
6.88
5.69
2.30
2.03
2.00
1.98
1.97
1.78
OAc
OAc
N
Ts
3u
1.90
1.00
1.88
2.11
1.05
0.79
0.80
3.06
3.21
2.91
f1 (ppm)


8.74
8.71
8.58
8.57
7.76
7.74
7.67
7.64
7.26
7.16
7.14
7.11
6.94
6.93
6.91
6.86
2.43
2.40
2.39
2.38
2.35
1.17
1.14
1.12
O
OCOCH2CH3
N
N
N
2aa
1.00
1.91
0.91
1.03
0.97
0.95
0.82
2.07
3.16
f1 (ppm)

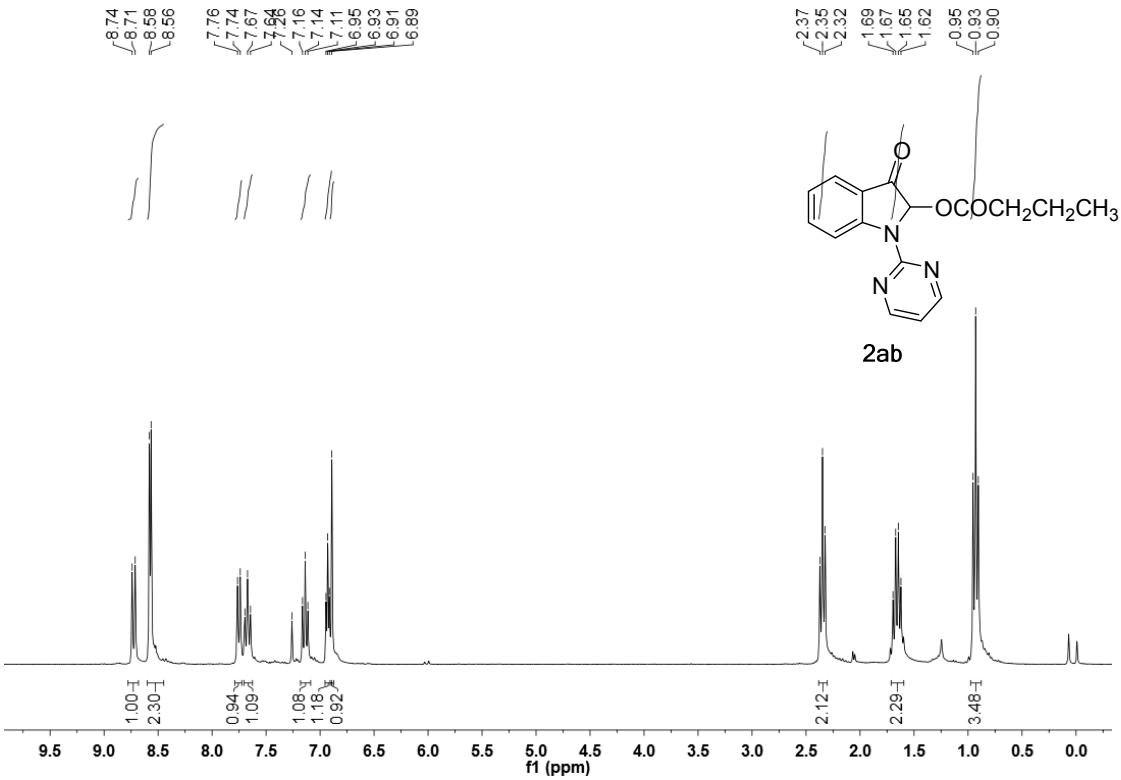

193.27
172.68
157.77
153.68
137.56
124.34
122.75
122.05
117.23
114.54
79.58
27.27
8.87
O
OCOCH2CH3
N
N
N
2aa
f1 (ppm)


8.83
8.80
8.69
8.67
8.45
7.57
7.54
7.38
7.35
7.29
7.28
7.26
7.24
7.05
7.03
7.01
2.74
2.72
2.69
2.67
1.36
1.34
1.31
OCOCH2CH3
N
N
N
1.00
2.16
1.01
1.02
1.16
1.54
1.25
2.26
3.39
10.0 9.5 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
f1 (ppm)

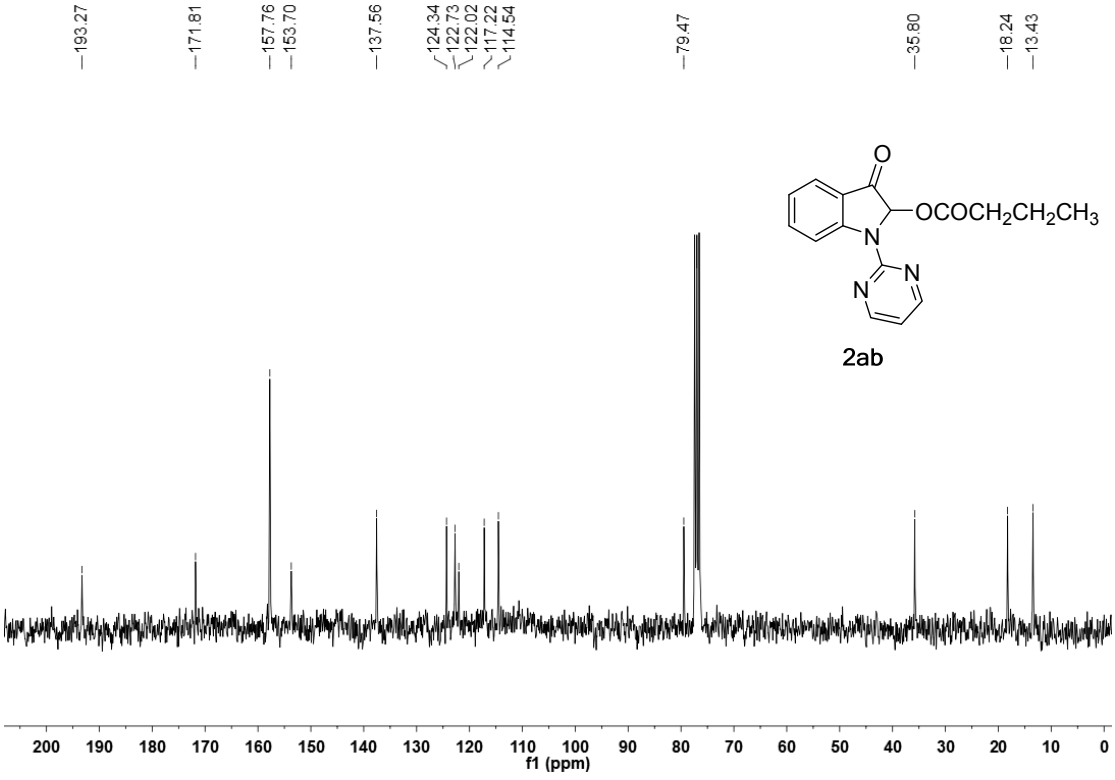
4aa


171.60
157.94
157.61
133.43
132.73
124.50
124.03
122.06
117.36
116.39
115.92
114.45
27.62
9.19
OCOCH2CH3
N
N
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

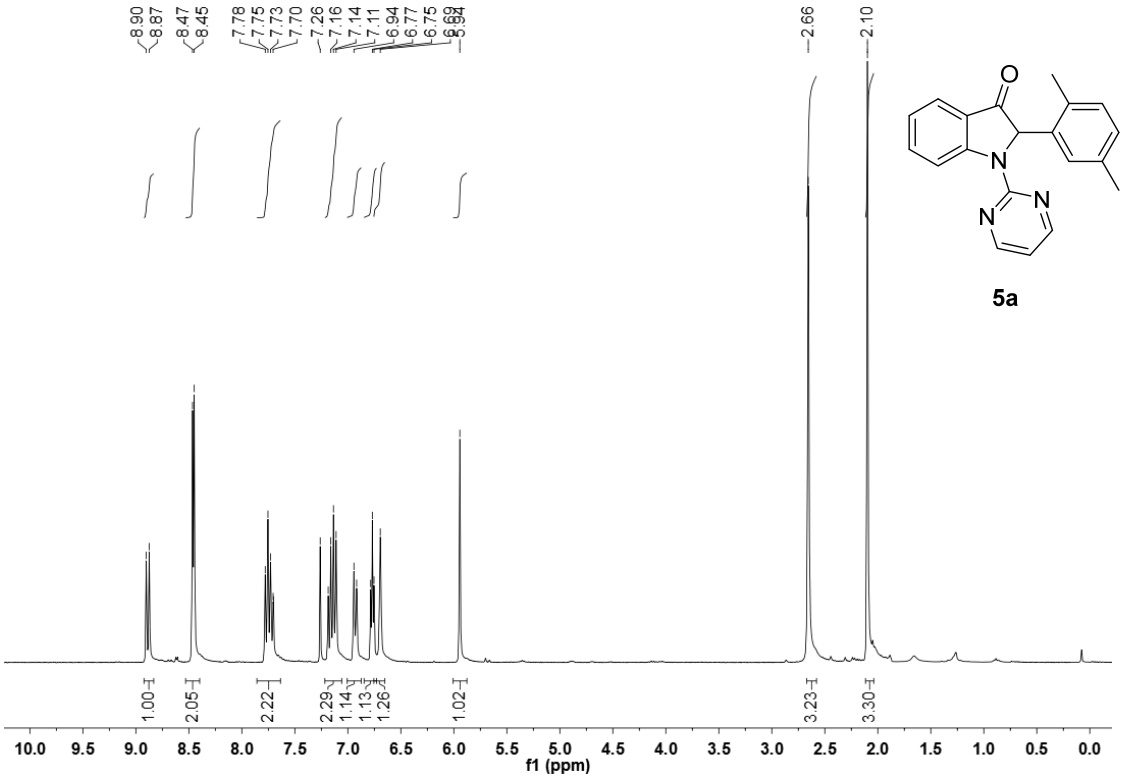
4aa


8.74
8.71
8.58
8.56
7.76
7.74
7.67
7.64
7.26
7.16
7.14
7.11
6.95
6.93
6.91
6.89
2.37
2.35
2.32
1.69
1.67
1.65
1.62
0.95
0.93
0.90
O
OCOCH2CH2CH3
N
N
N
1.00
2.30
0.94
1.09
1.08
1.18
0.92
2.12
2.29
3.48
9.5 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
f1 (ppm)

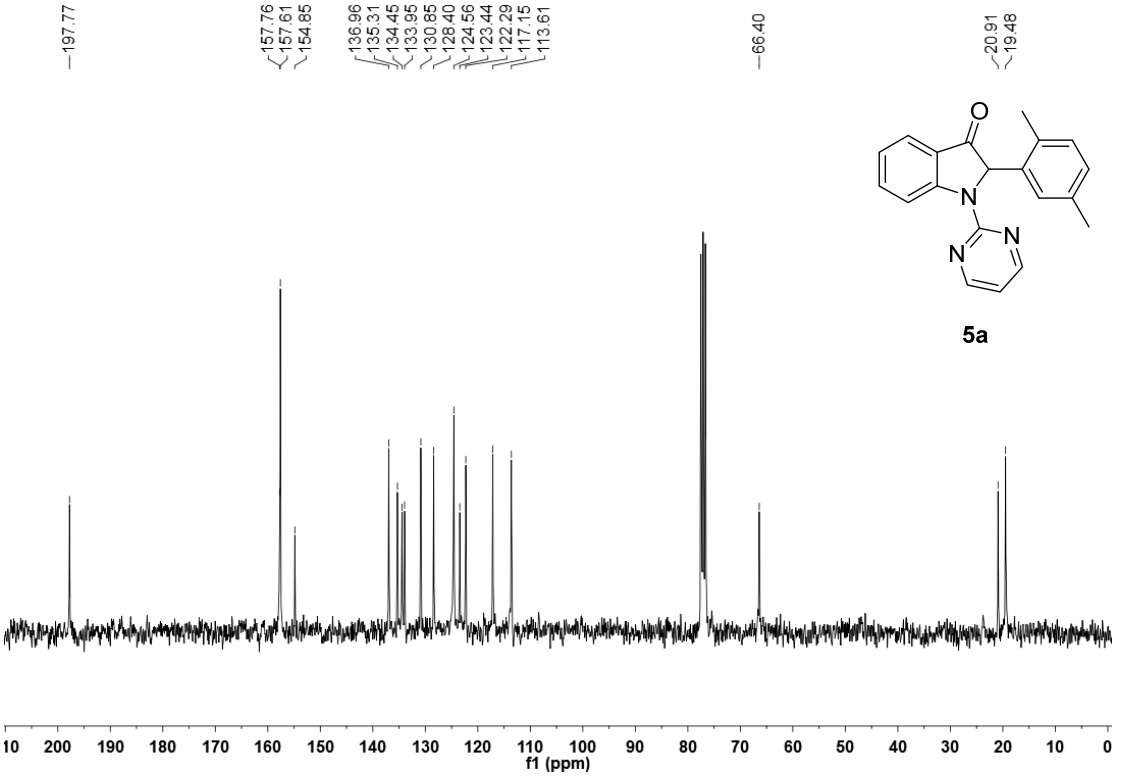
2ab


193.27
171.81
157.76
153.70
137.56
124.34
122.73
122.02
117.22
114.54
79.47
35.80
18.24
13.43
O
OCOCH2CH2CH3
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2ab


8.90
8.87
8.47
8.45
7.78
7.75
7.73
7.70
7.26
7.16
7.14
7.11
6.94
6.77
6.75
2.66
2.10
1.00
2.05
2.22
2.29
1.14
1.13
1.26
1.02
3.23
3.30
10.0 9.5 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
f1 (ppm)
O
N
N
N

5a


197.77
157.76
157.61
154.85
136.96
135.31
134.45
133.95
130.85
128.40
124.56
123.44
122.29
117.15
113.61
66.40
20.91
19.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
N
N
N

5a