Supporting Information

Ionic Rhodium Catalyzed Reductive N-Heterocyclization of 2-Nitrovinylarenes

Kazumi Okuro, Joanna Gurnham, and Howard Alper*

Centre for Catalysis Research and Innovation, Department of Chemistry,
University of Ottawa, 10 Marie Curie, Ottawa, K1N 6N5, Canada

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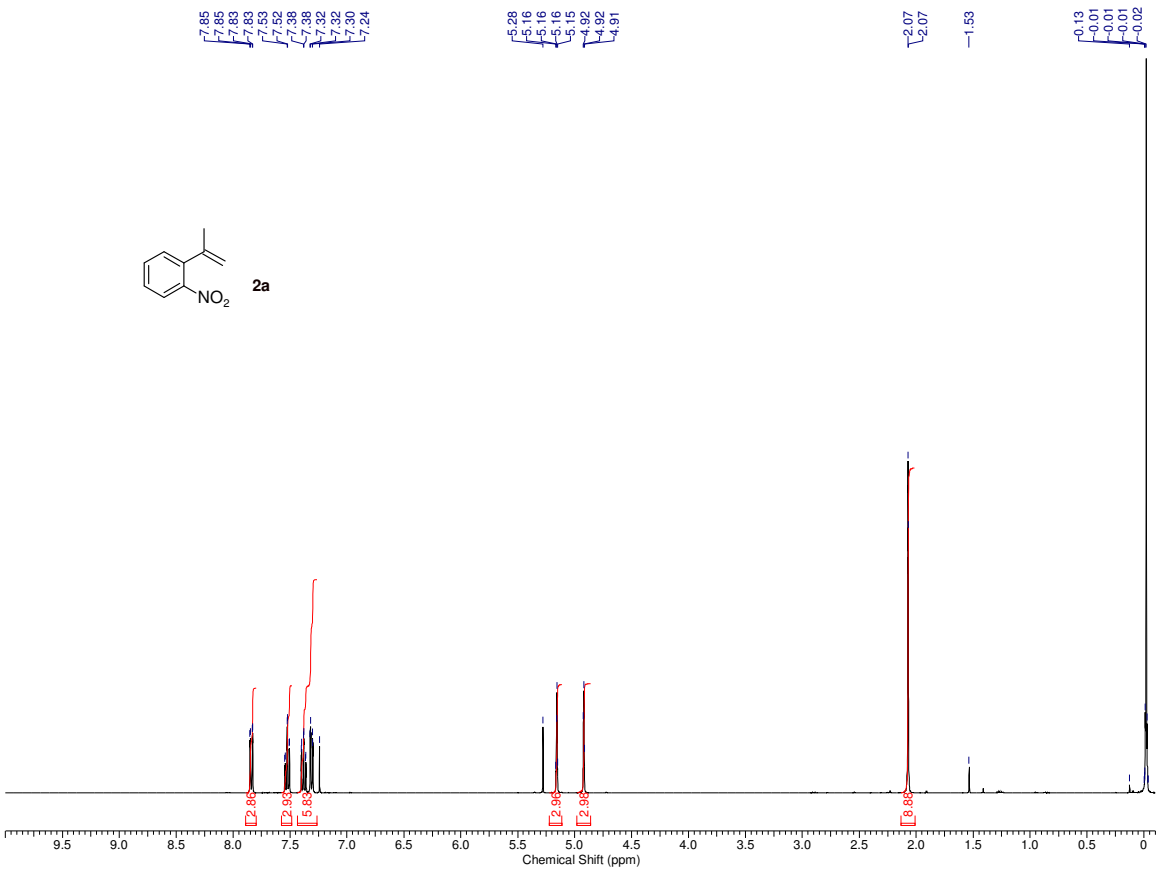
General:

The ionic diamine rhodium complex **1** was prepared from $[Rh(COD)Cl]_2$ as previously described.[1] 2-Nitrocinnamaldehyde **2k** and 2-nitrochalcone **2p** were purchased from Alfa Aesar and were used without further purification.

Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded in $CDCl_3$, containing TMS as an internal standard, on a Bruker Avance 400 MHz. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are given in Hz. Mass spectra were determined using a VG 7070E spectrometer.

General Procedure for the Reductive N-Cyclization of 2:

The 2-nitrovinylarenes (1.0 mmol), complex **1** (0.05 mmol, 25.6 mg) and THF (3 mL) were placed into a glass liner, equipped with a magnetic stirring bar. The glass liner was then inserted into a 45 mL autoclave. The autoclave was flushed five times with carbon monoxide and pressurized to 100 psi. The autoclave was heated at 100 ^oC with stirring. After the reaction, the autoclave was cooled to rt prior to the release of carbon monoxide. The solvent was evaporated under reduced pressure, and the product was purified by silica gel column chromatography with n-hexane and diethyl ether as the eluant.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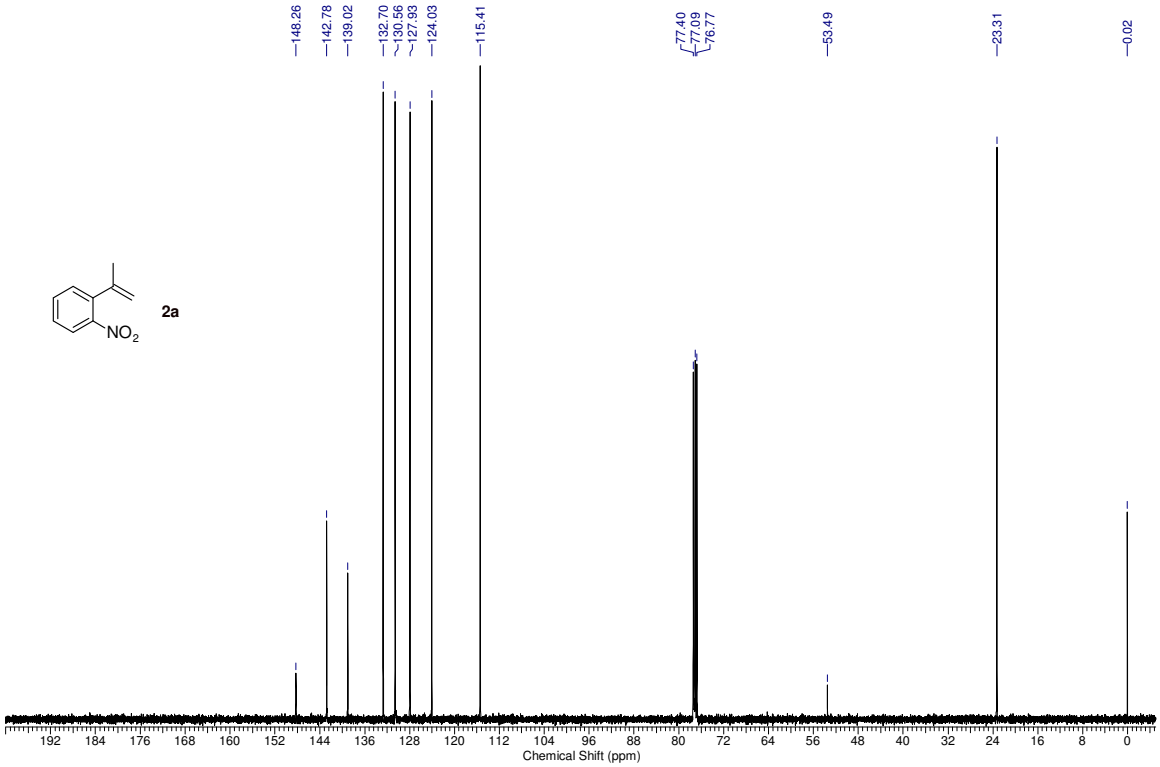
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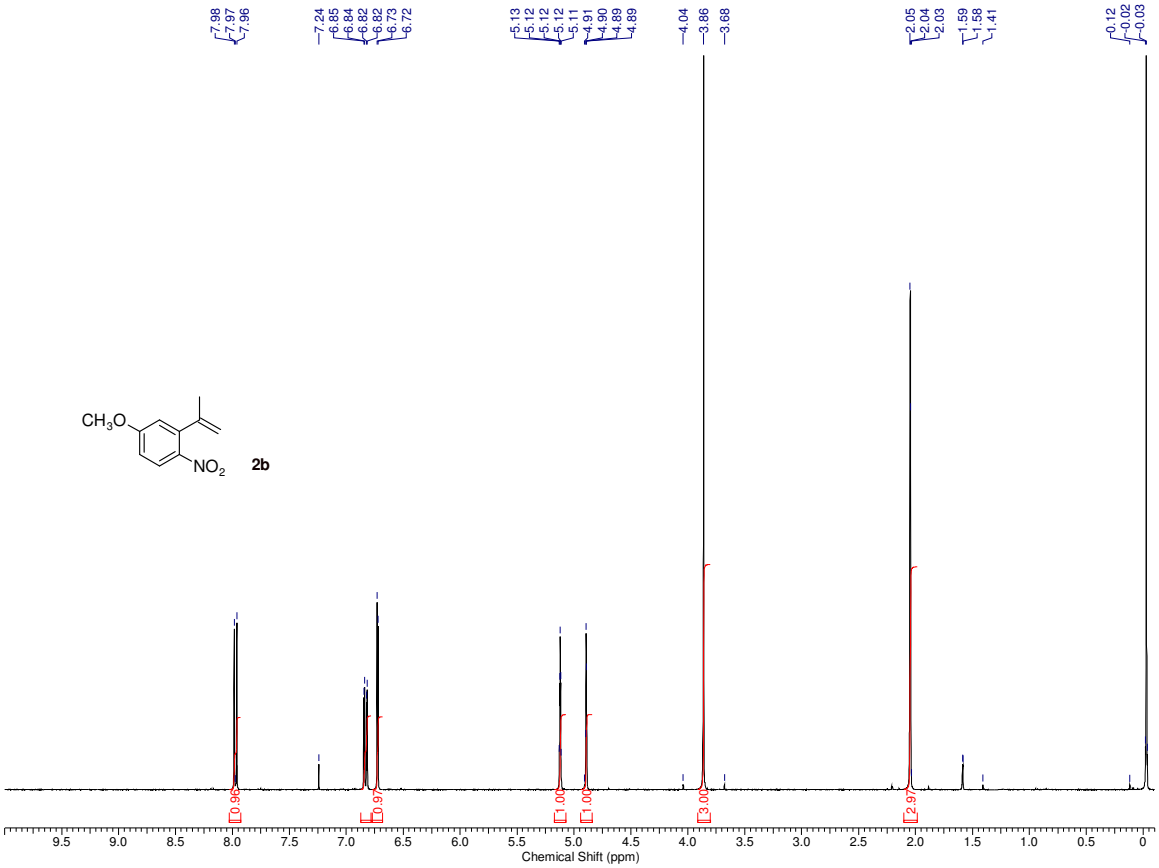
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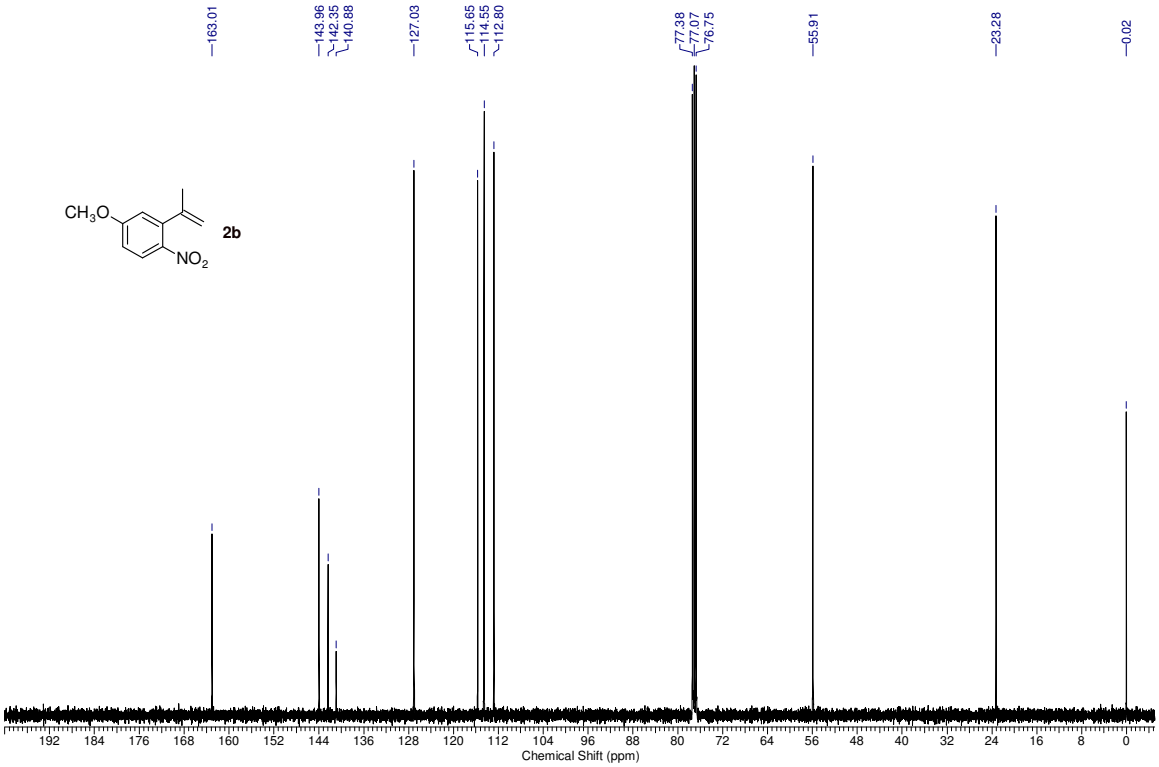
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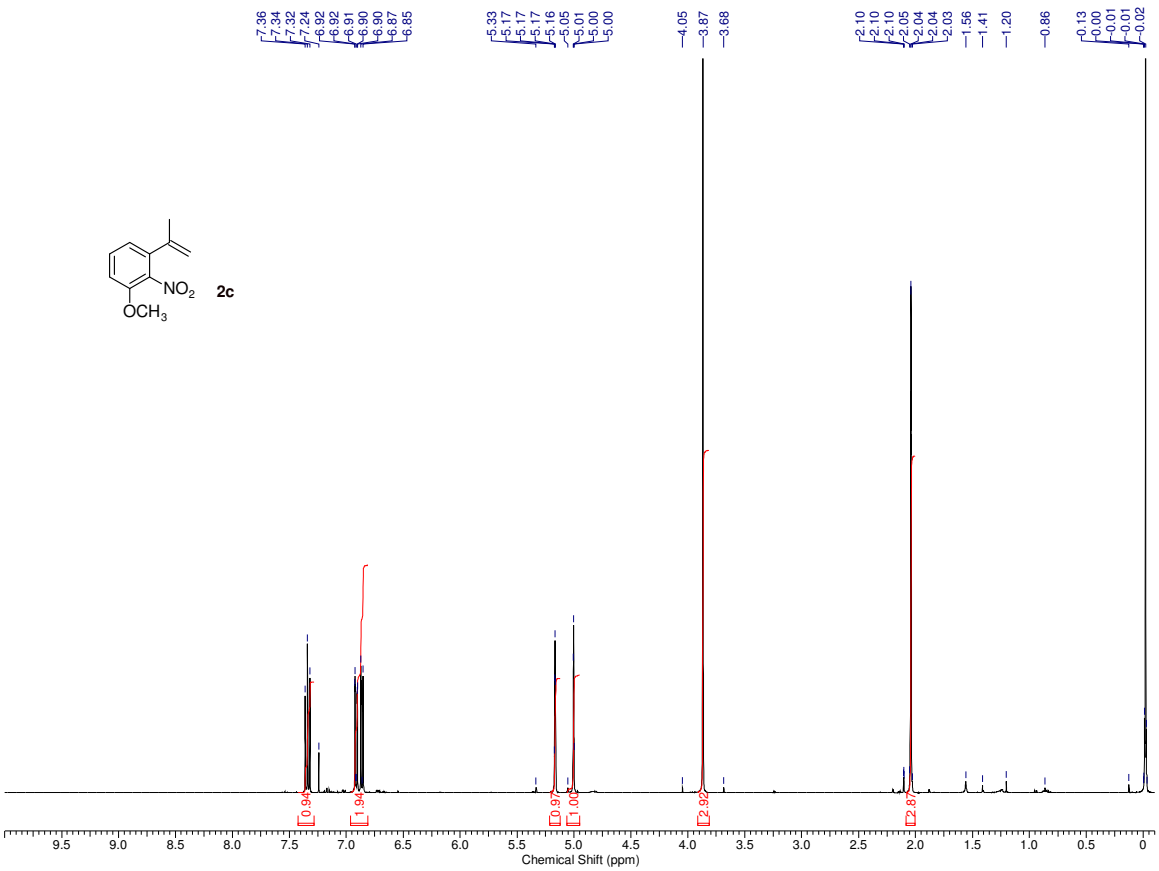
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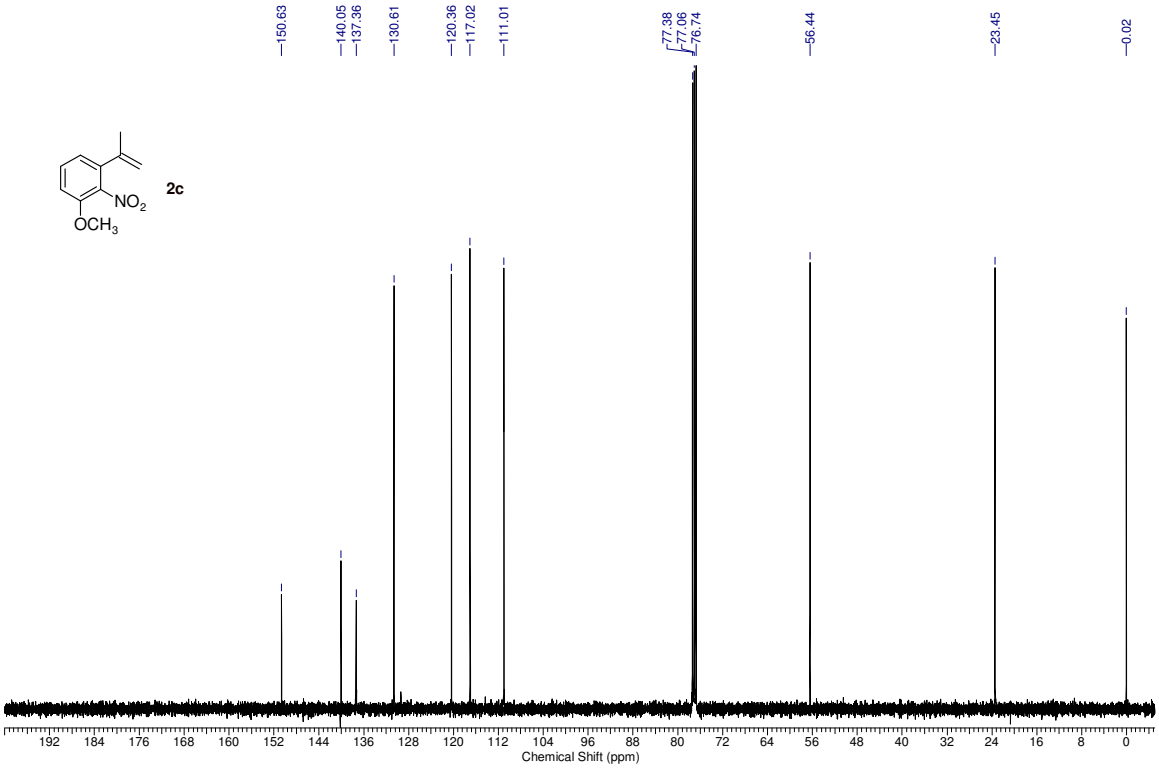
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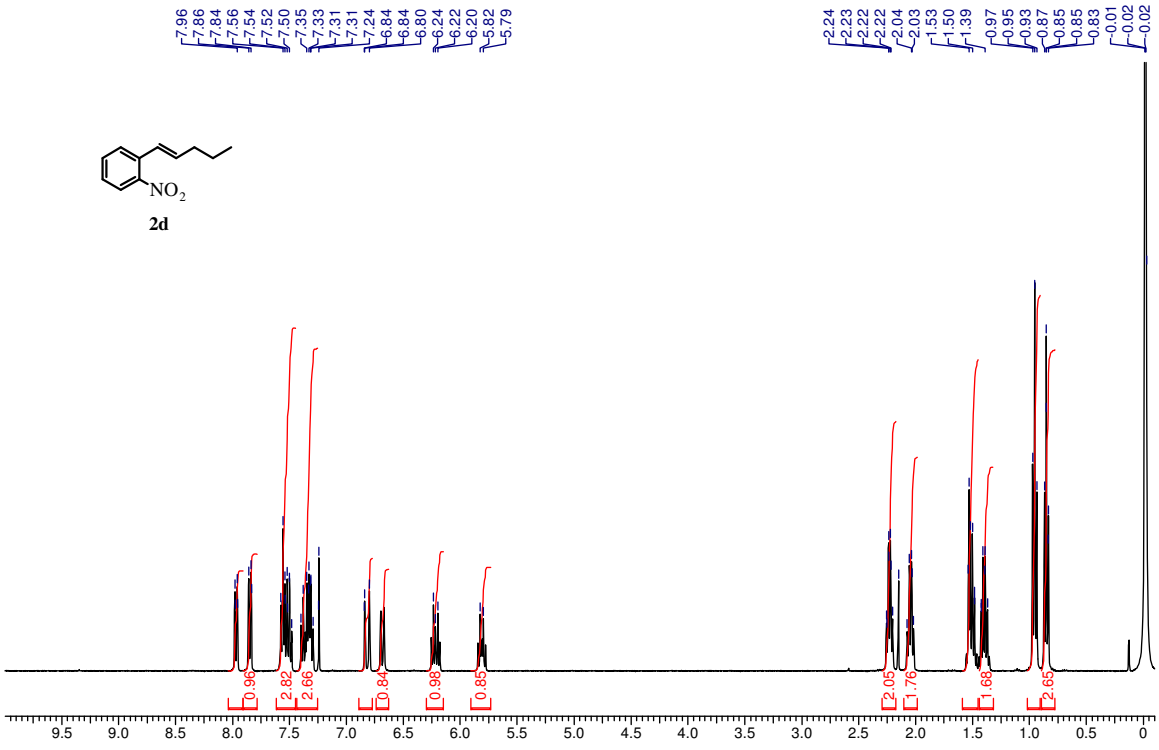
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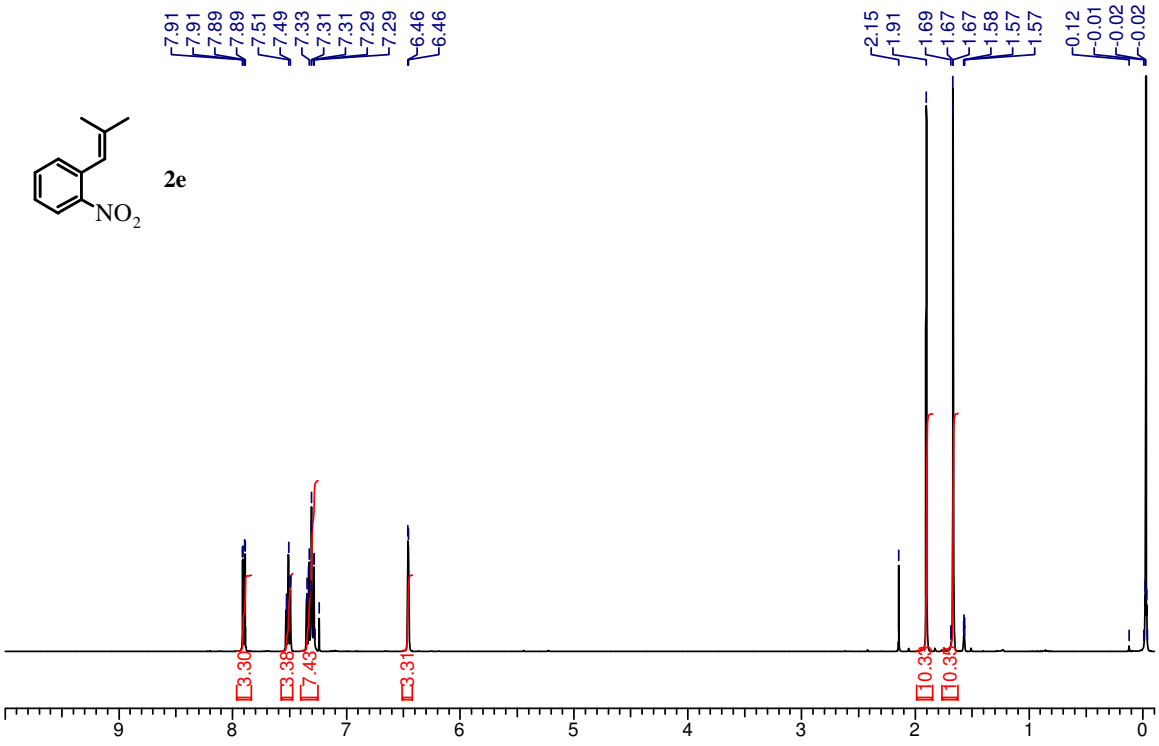
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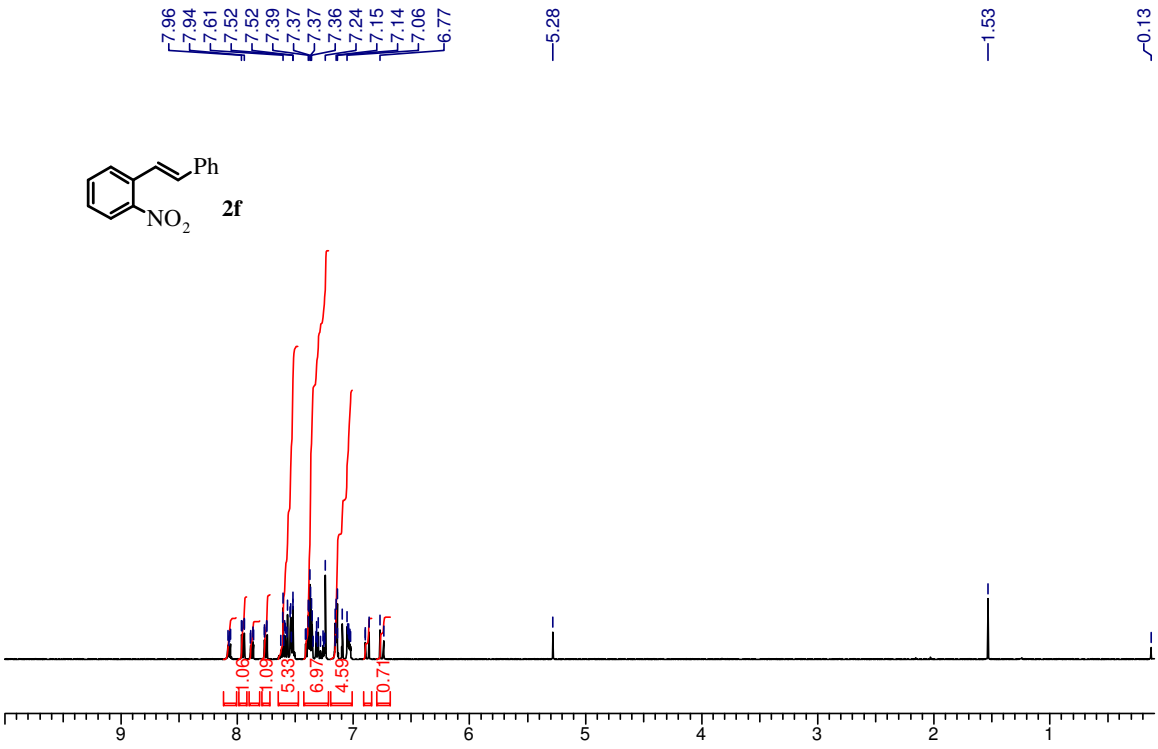
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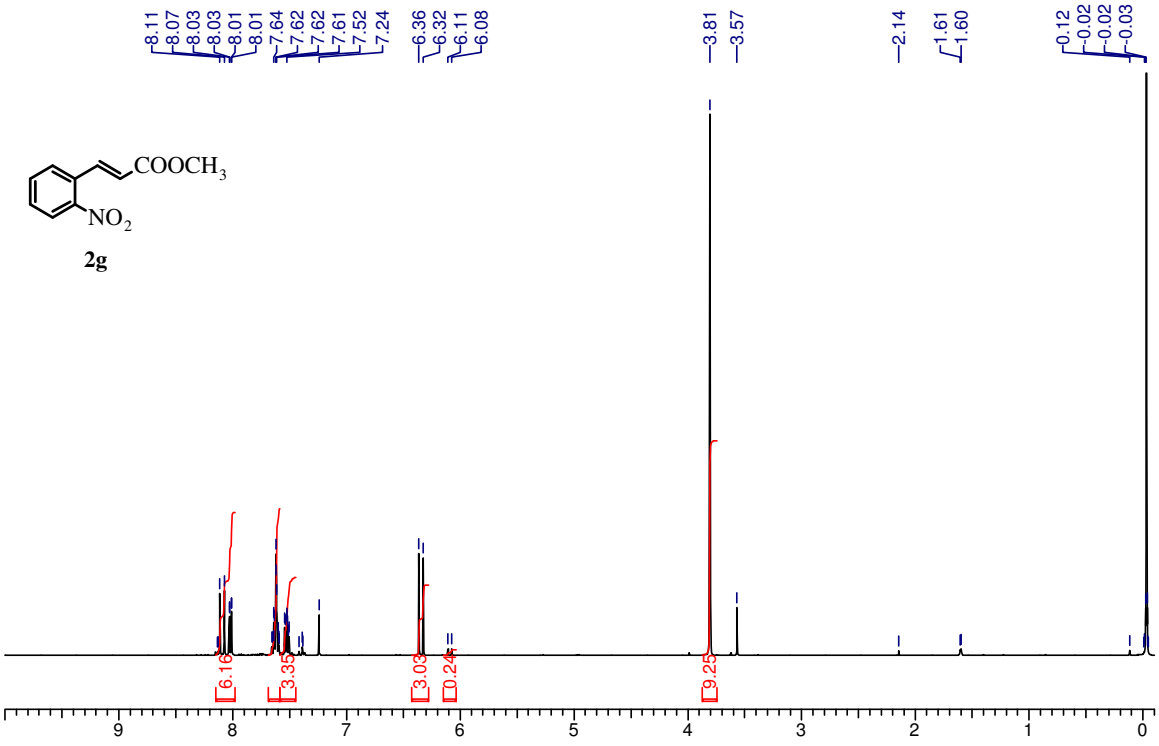
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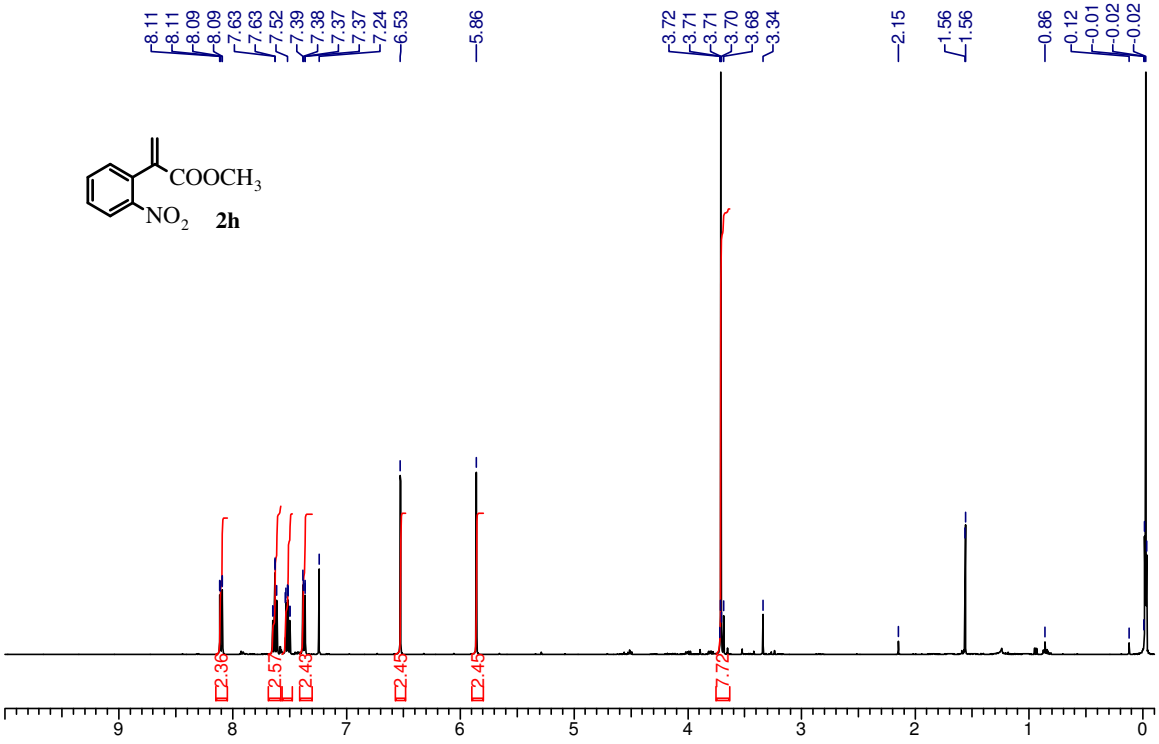
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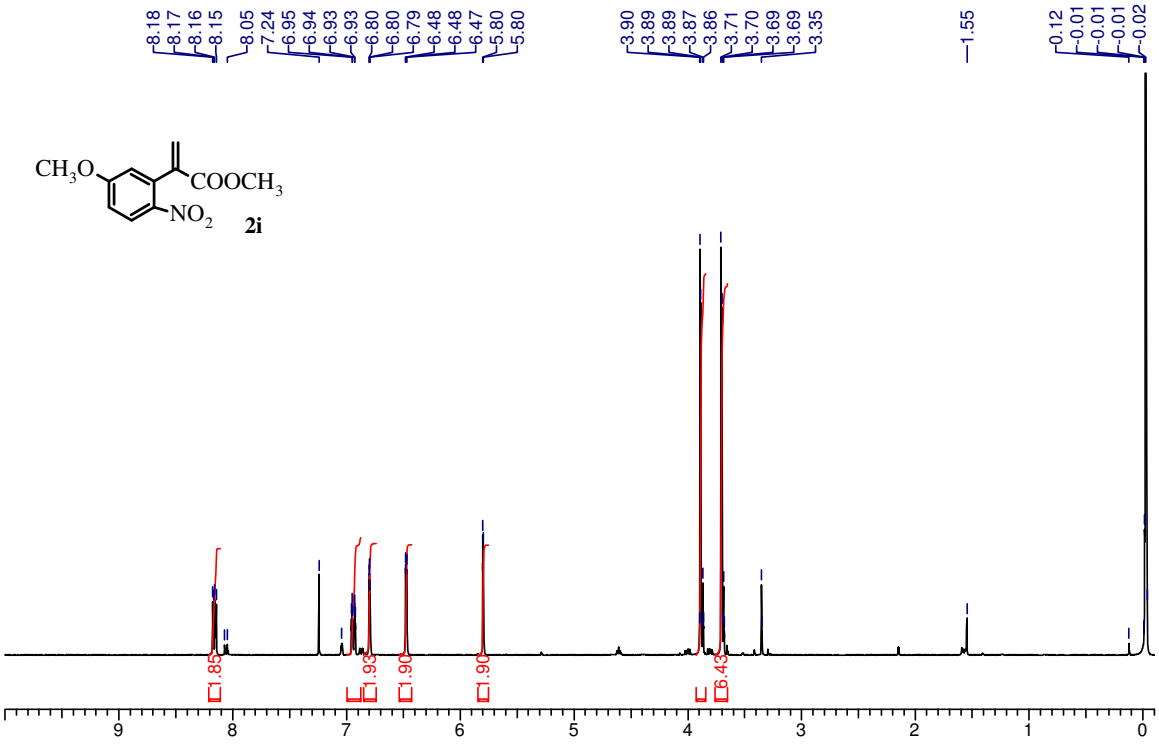
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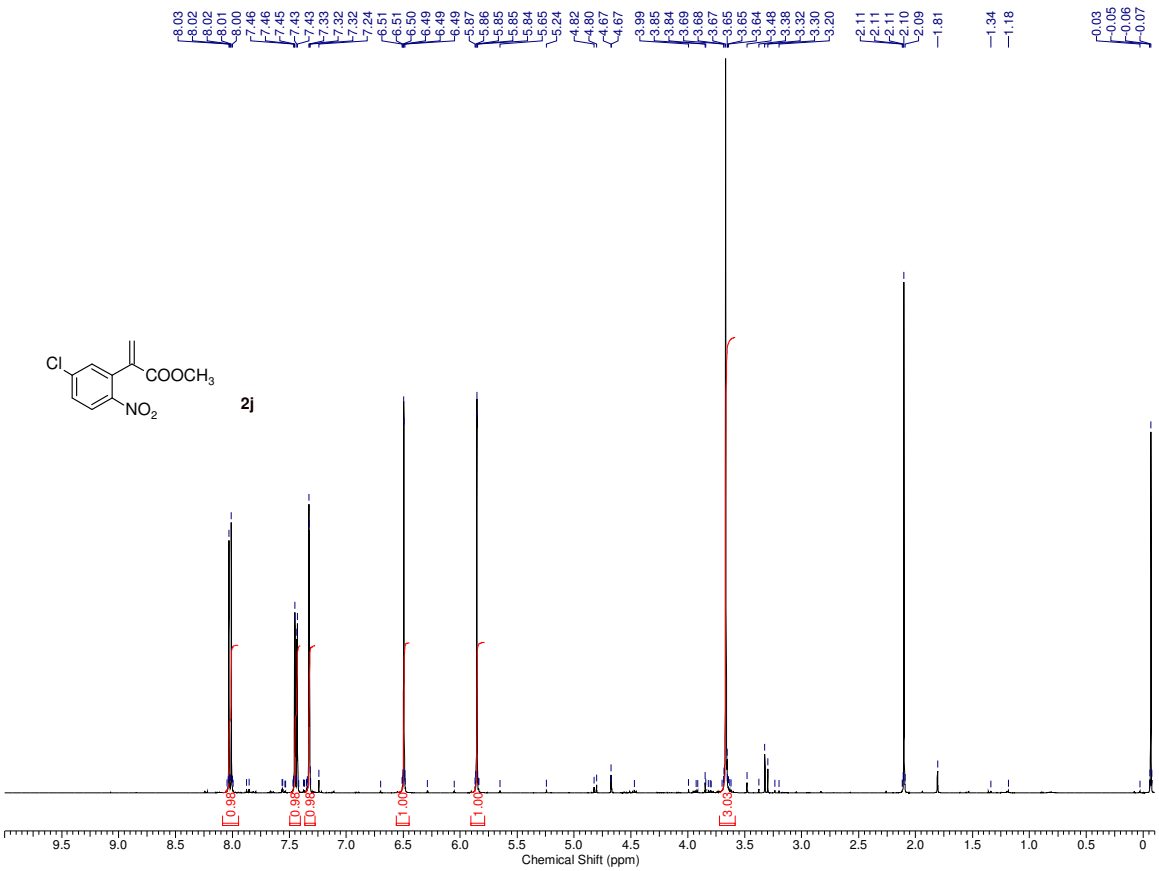
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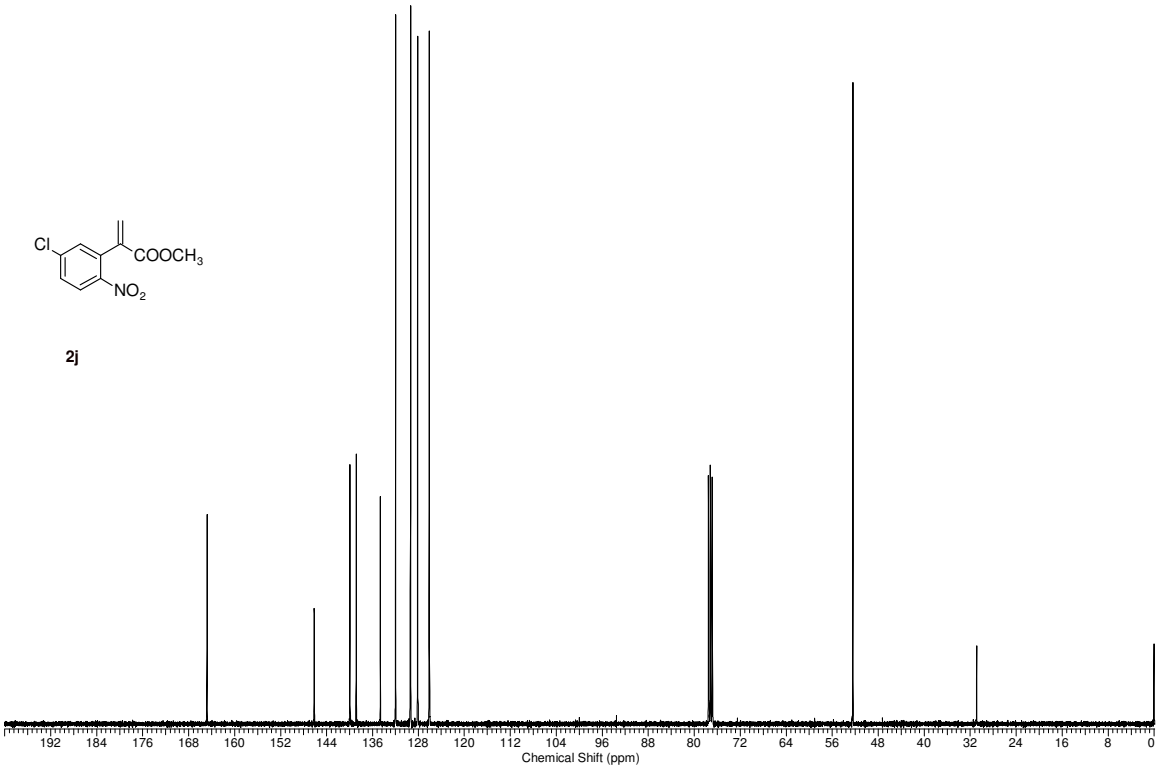
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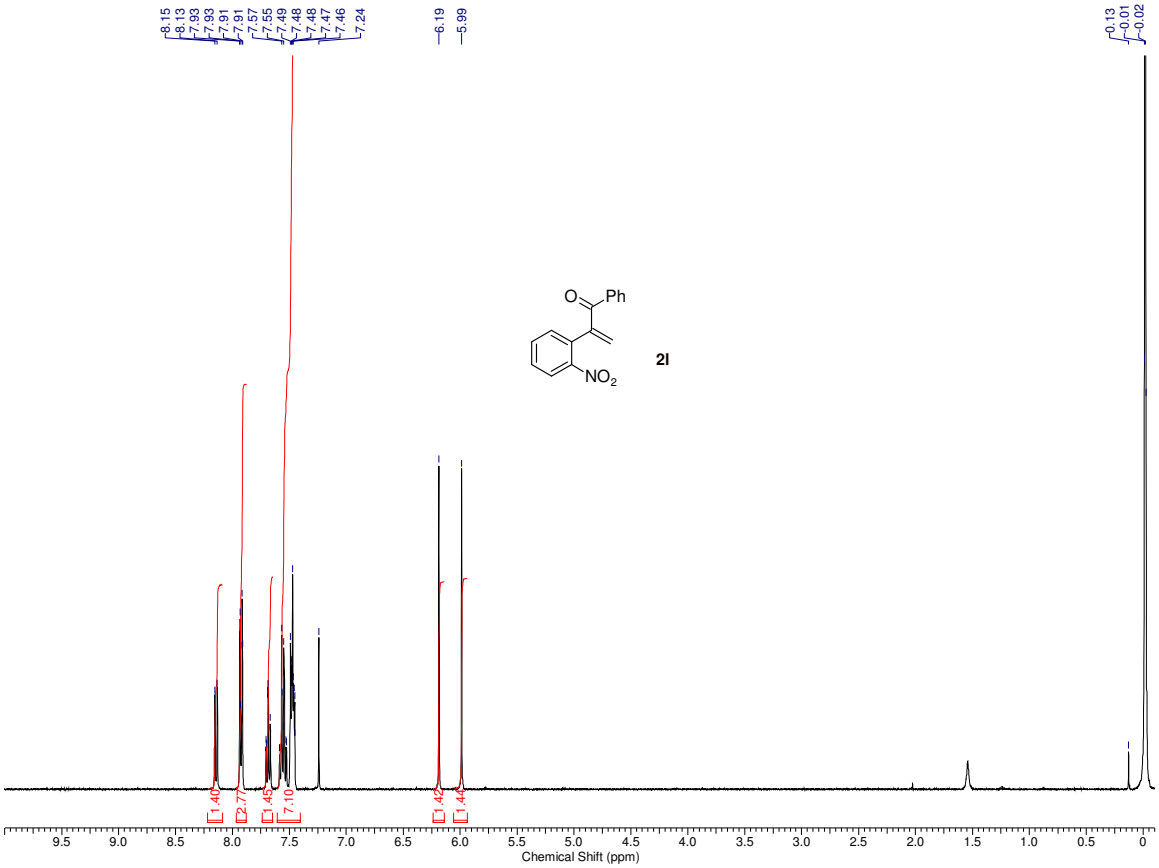
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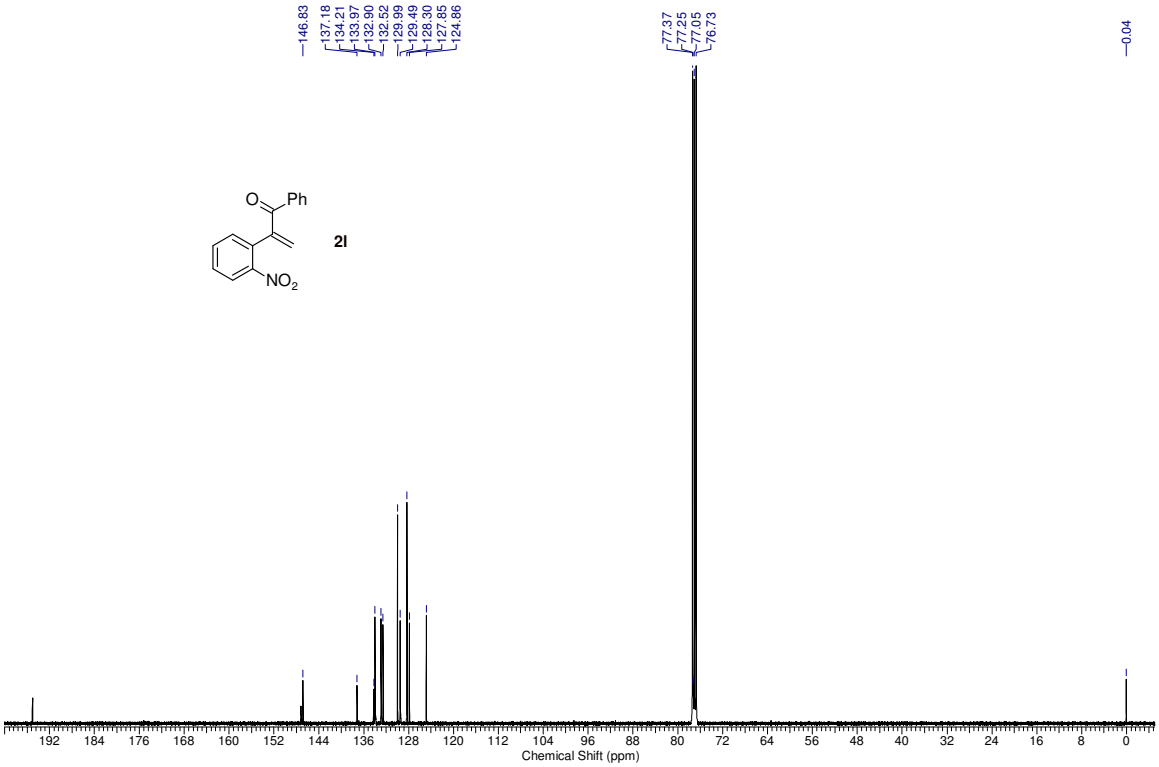
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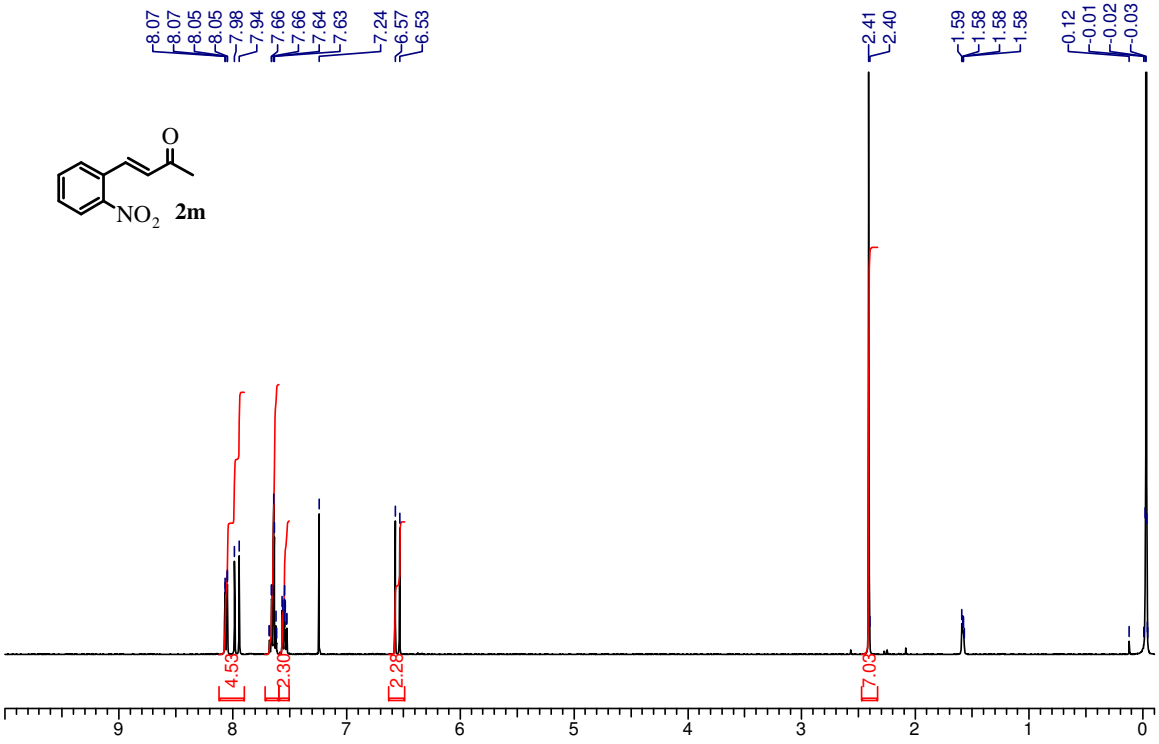
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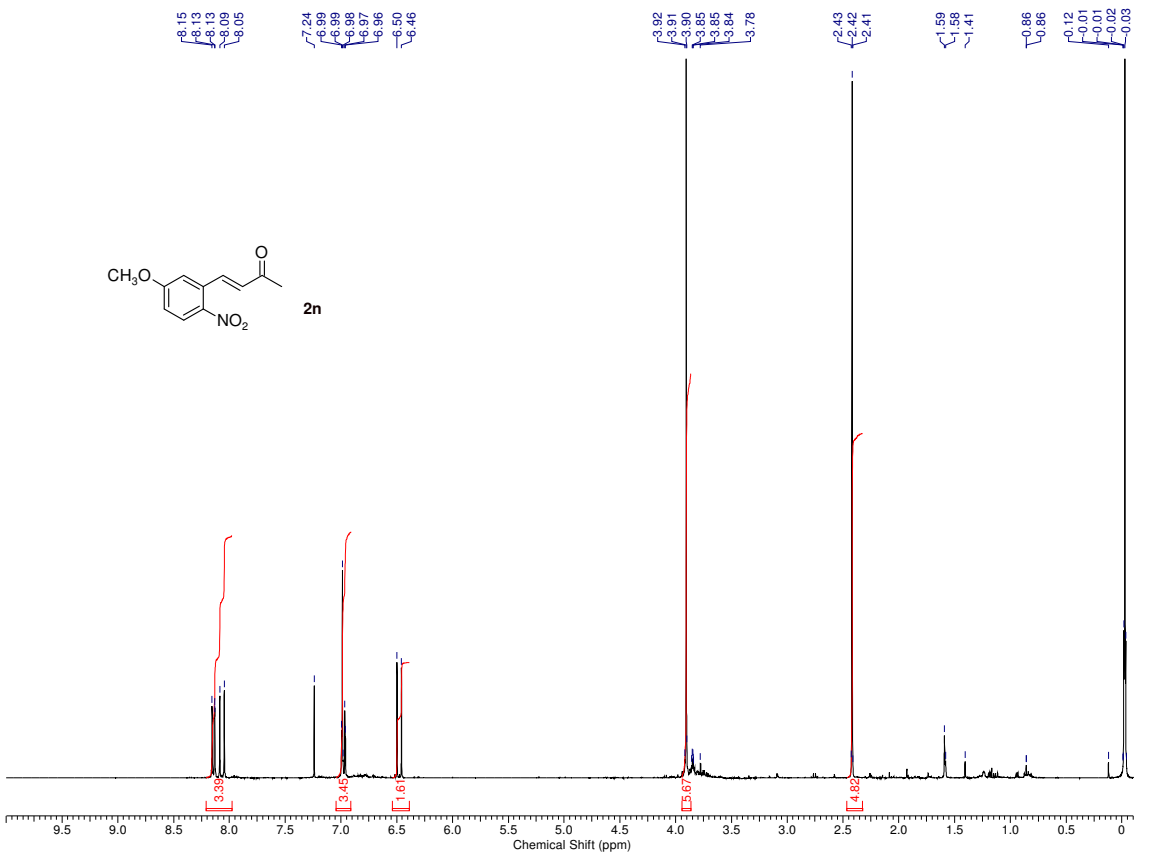
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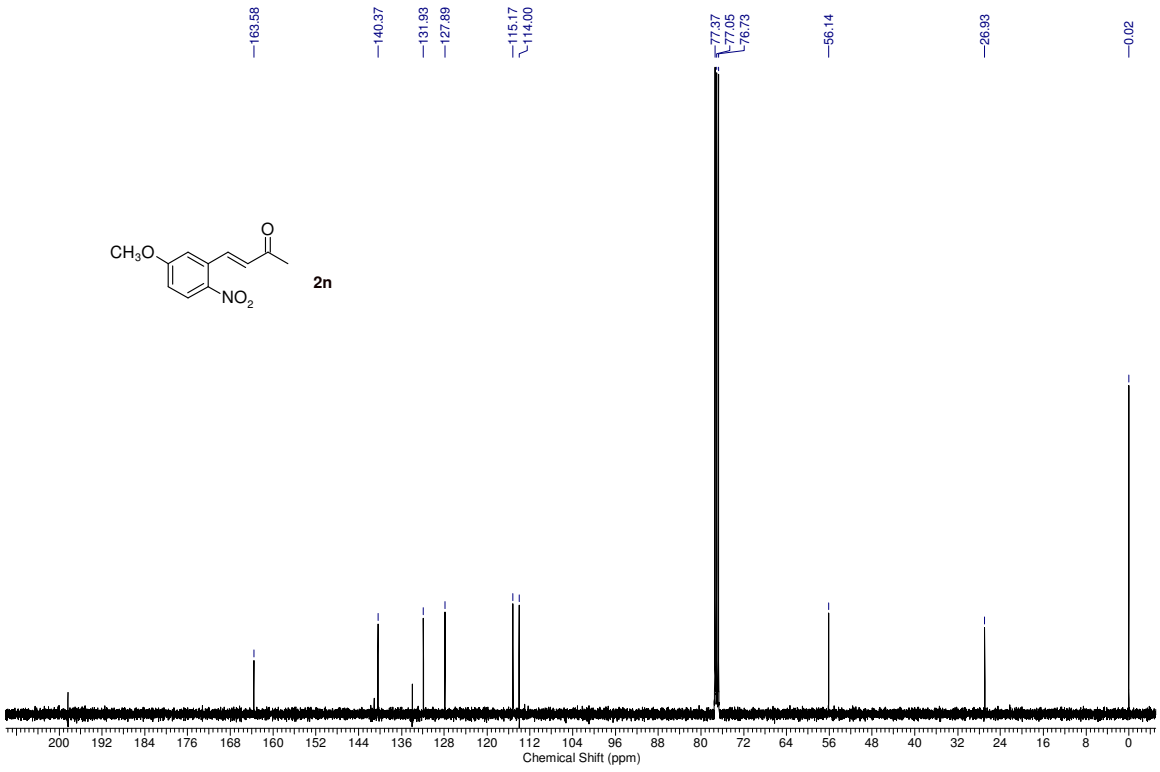
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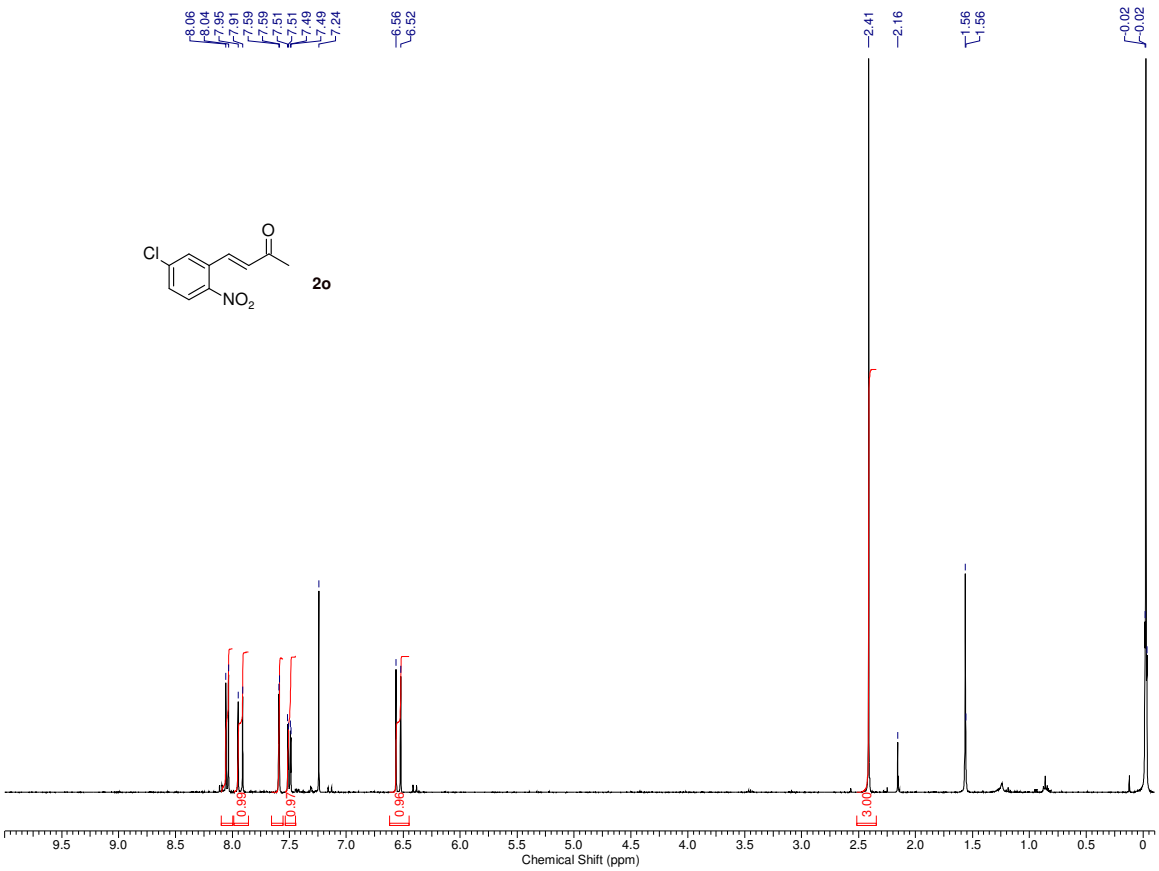
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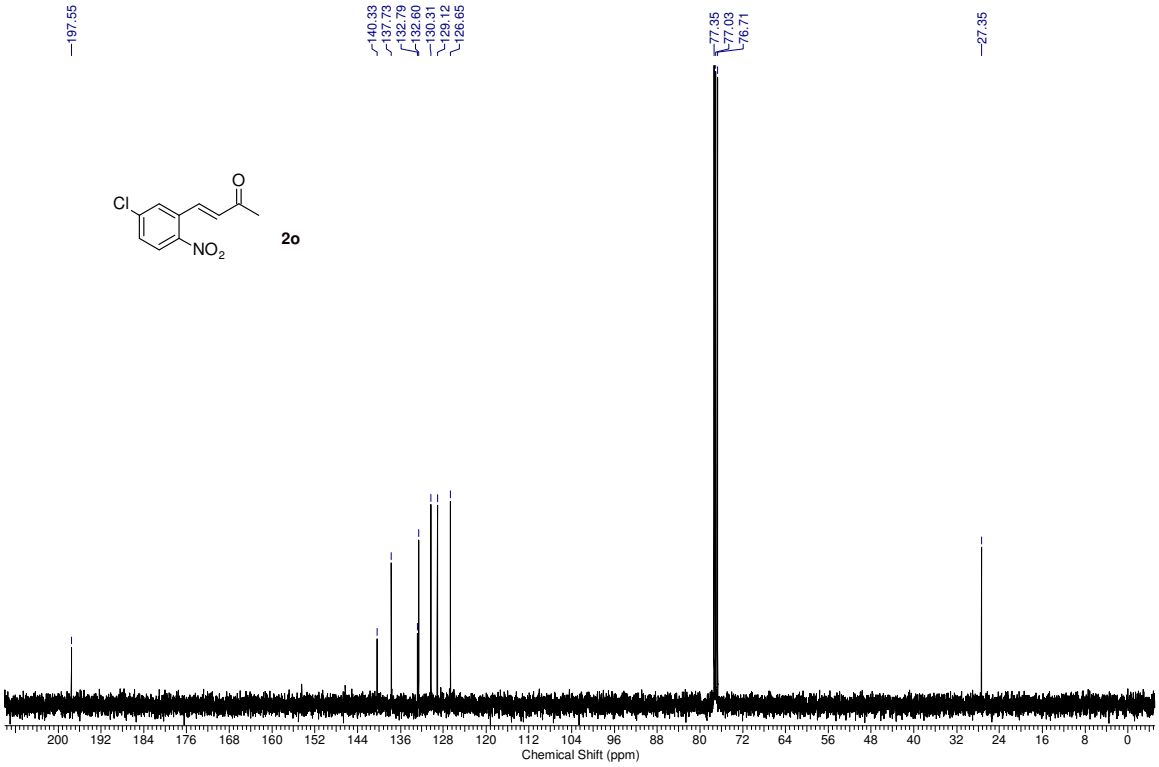
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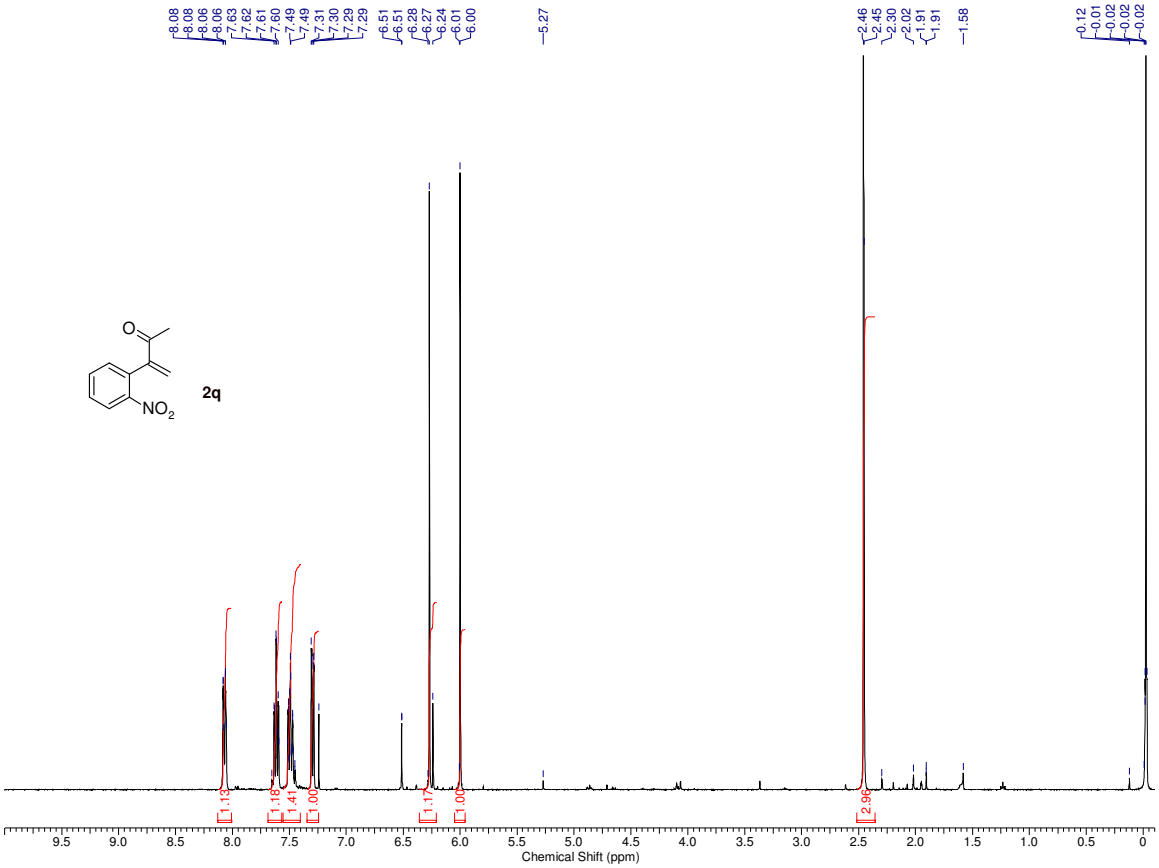
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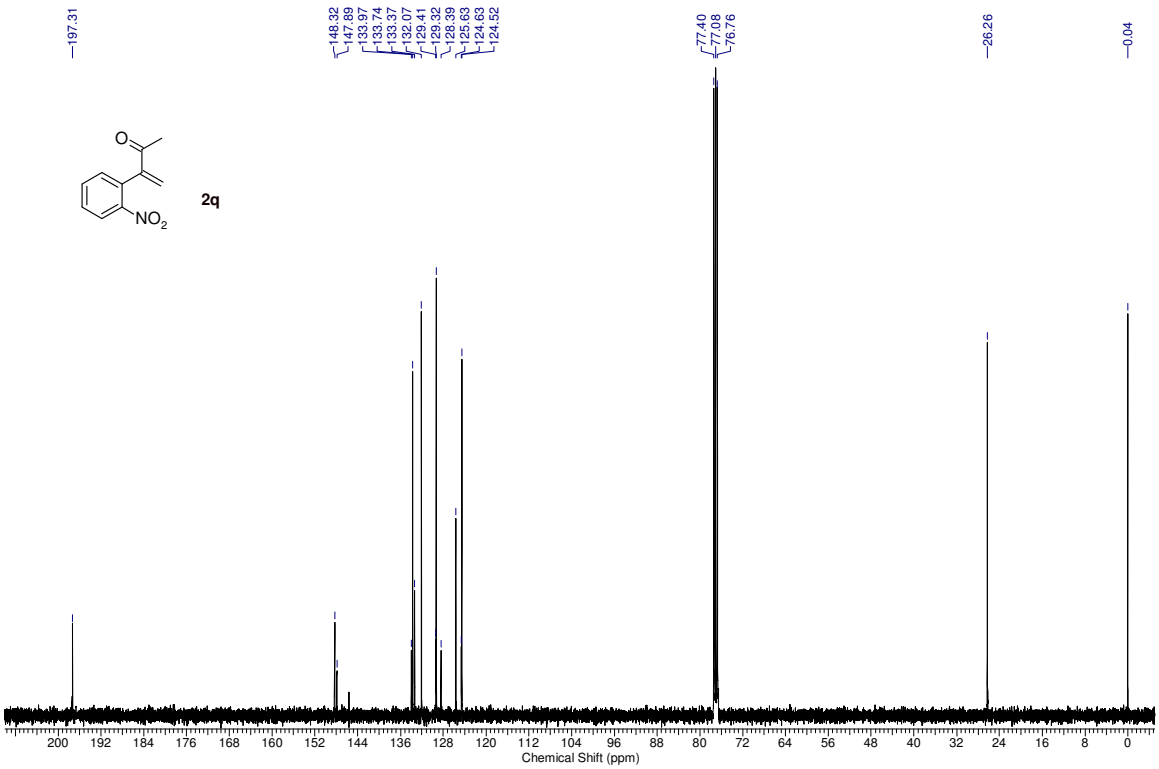
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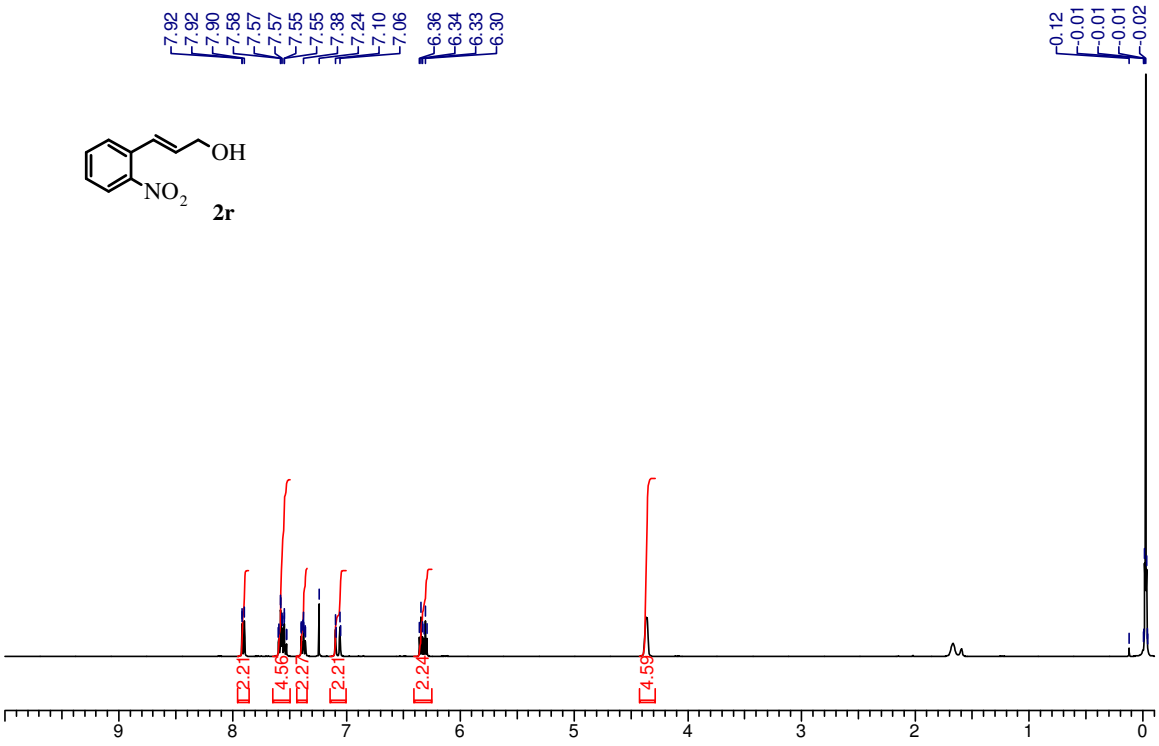
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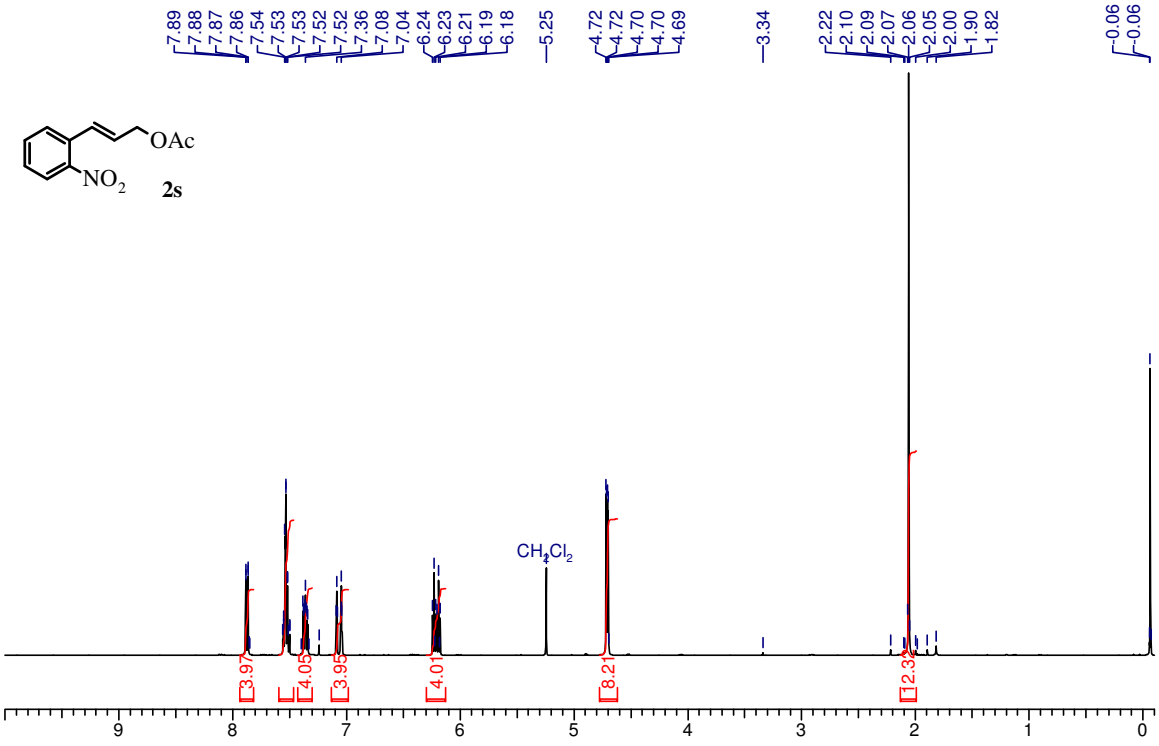
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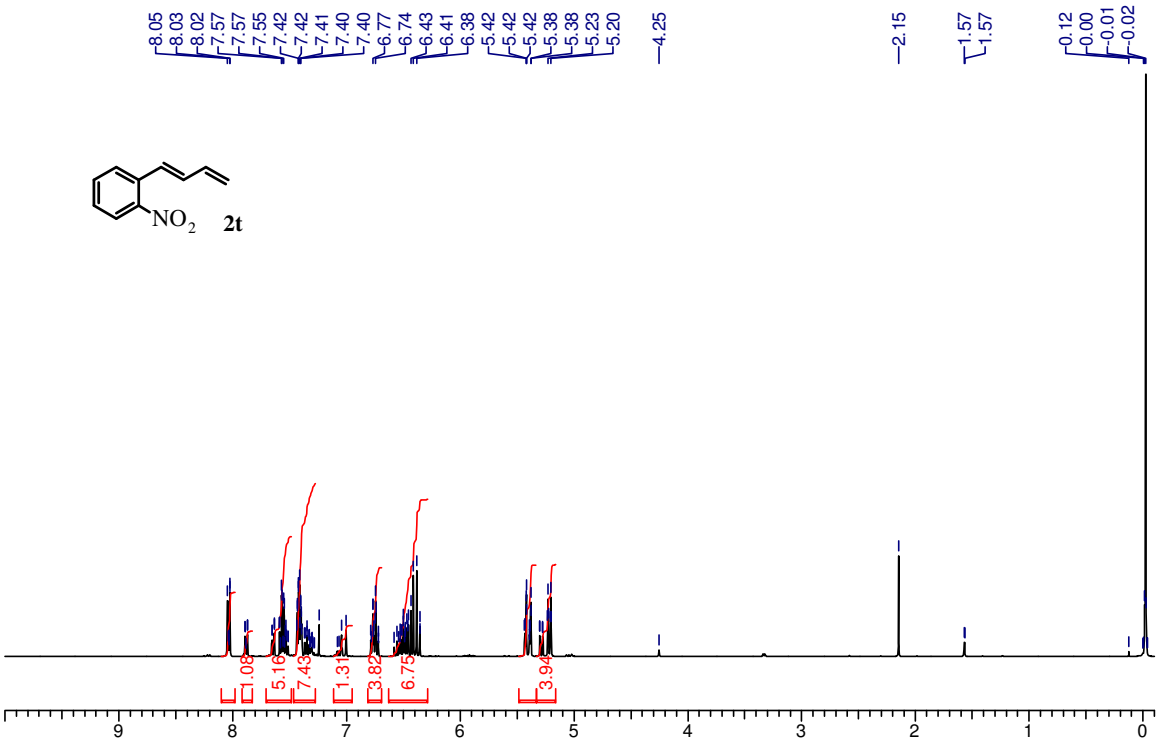
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5.42
5.42
5.42
5.38
5.38
5.23
5.20
4.25
2.15
1.57
1.57
0.12
0.00
-0.01
-0.02
NO2
2t
1.08
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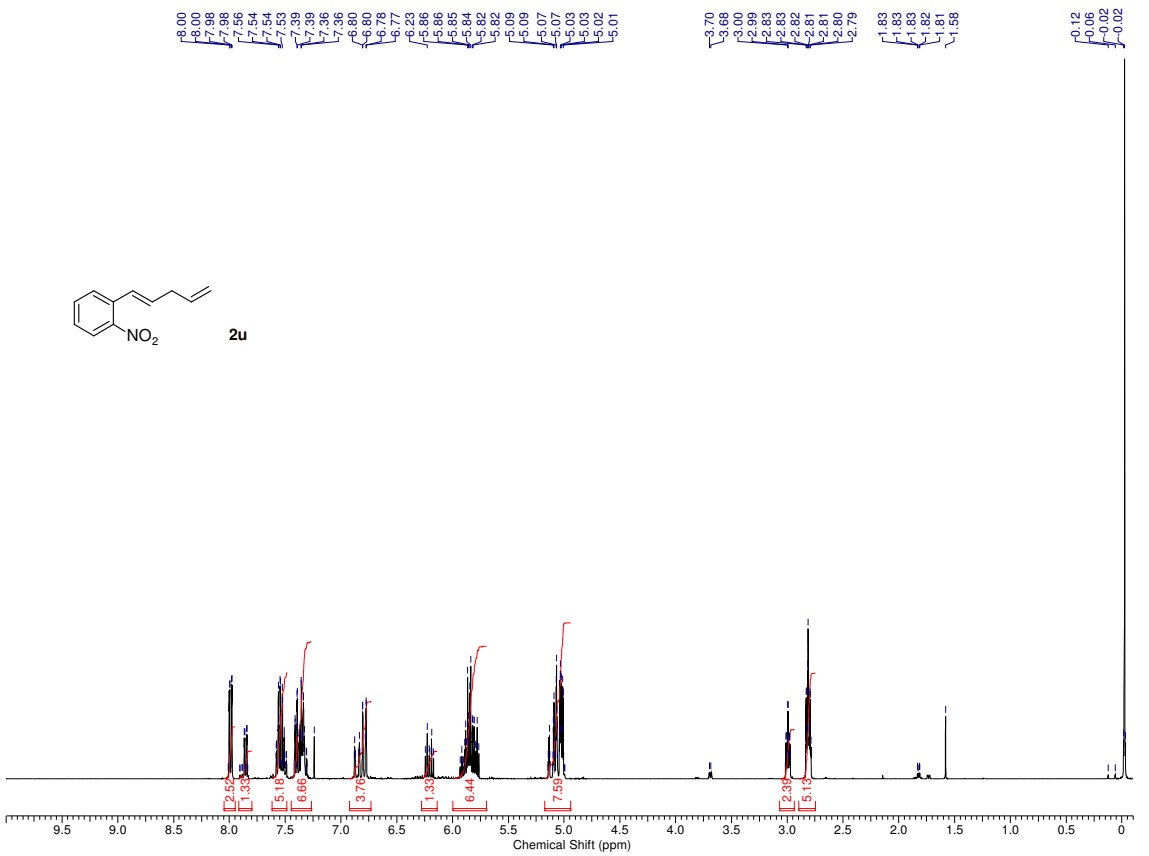
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6.80
6.80
6.78
6.77
6.23
5.86
5.86
5.85
5.84
5.82
5.82
5.09
5.09
5.07
5.07
5.03
5.03
5.02
5.01
3.70
3.68
3.00
2.99
2.83
2.83
2.82
2.81
2.81
2.80
2.79
1.83
1.83
1.83
1.82
1.81
1.58
0.12
0.06
-0.02
-0.02
NO2
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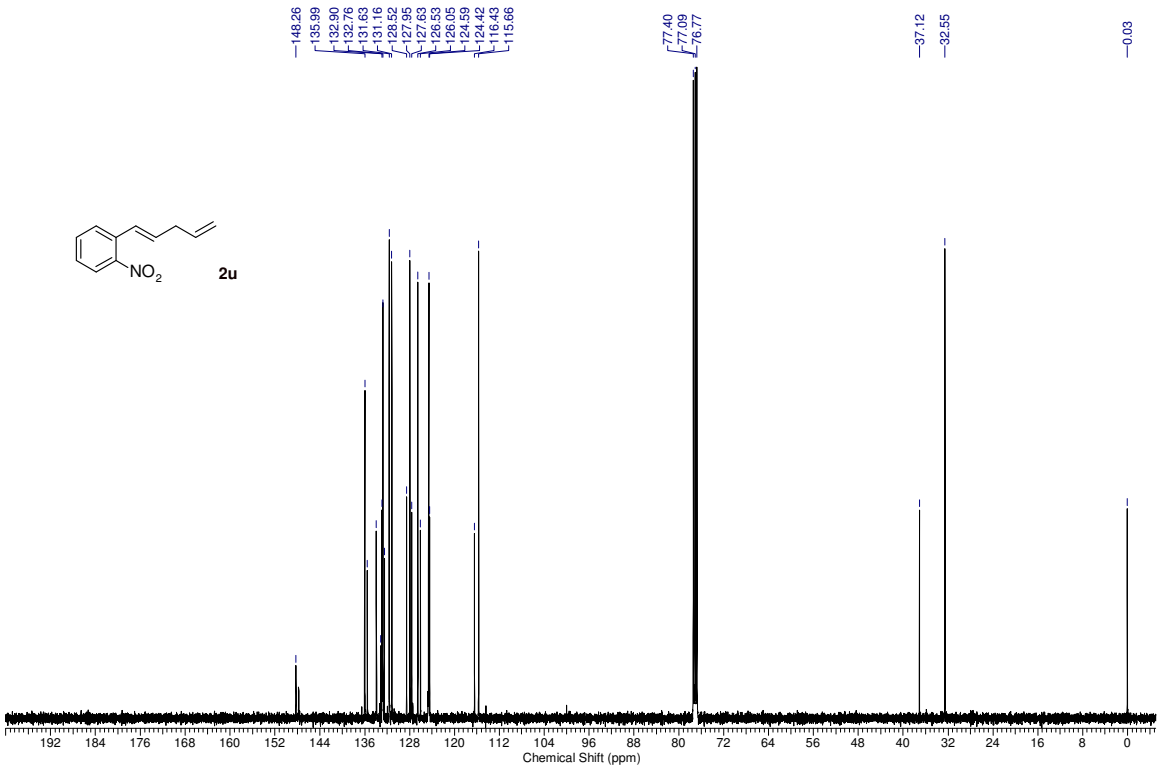
Chemical Shift (ppm)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126.05
124.59
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77.09
76.77
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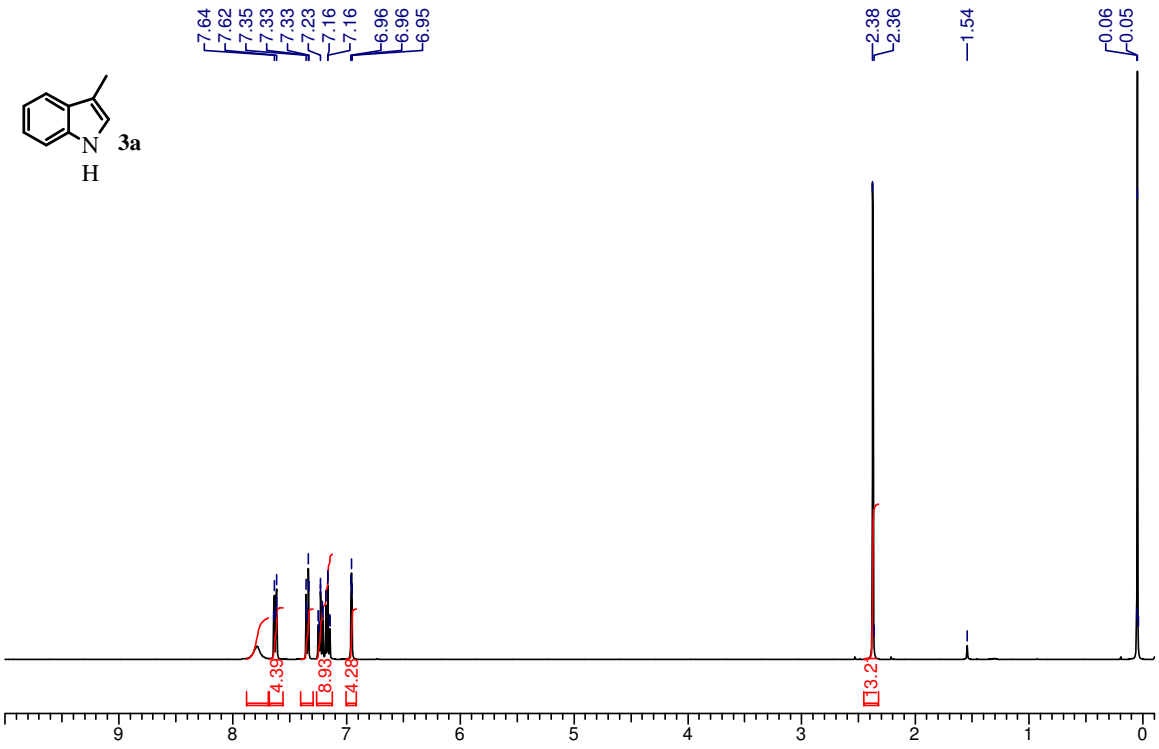
NO2
2u
Chemical Shift (ppm)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6.96
6.95
2.38
2.36
1.54
0.06
0.05
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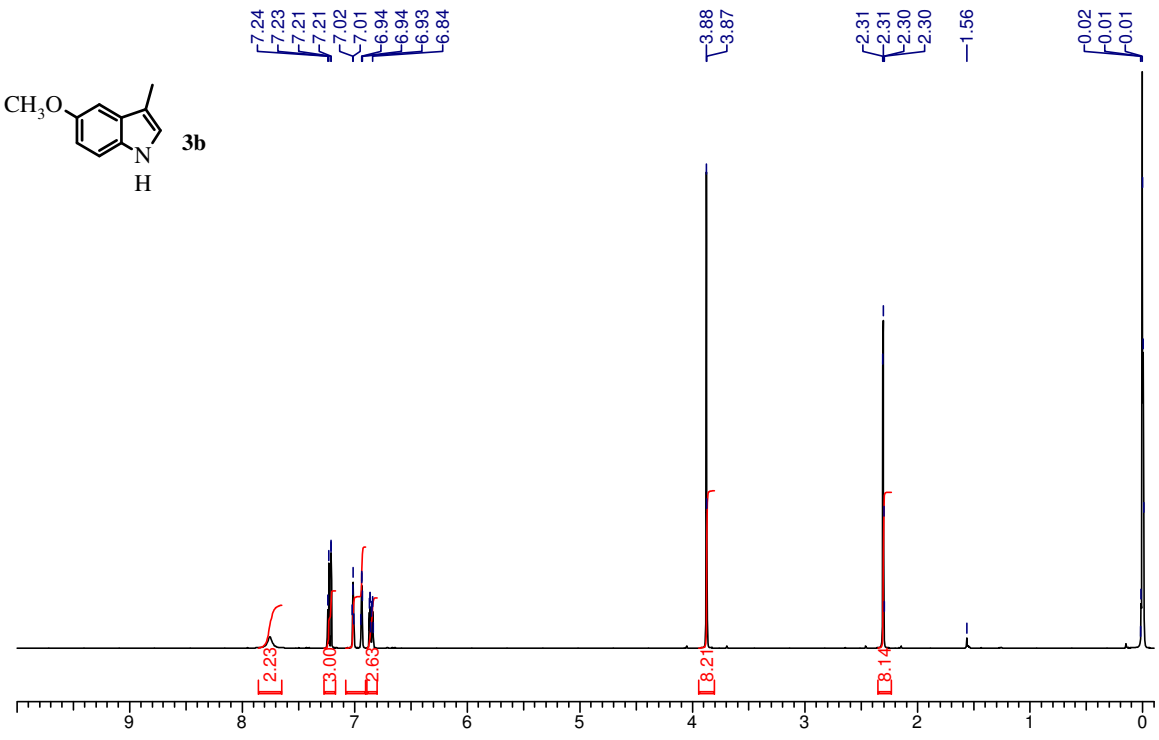
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7.21
7.02
7.01
6.94
6.94
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6.84
3.88
3.87
2.31
2.31
2.30
2.30
1.56
0.02
0.01
0.01
CH3O
3b
N
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2.63
8.21
8.14
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7
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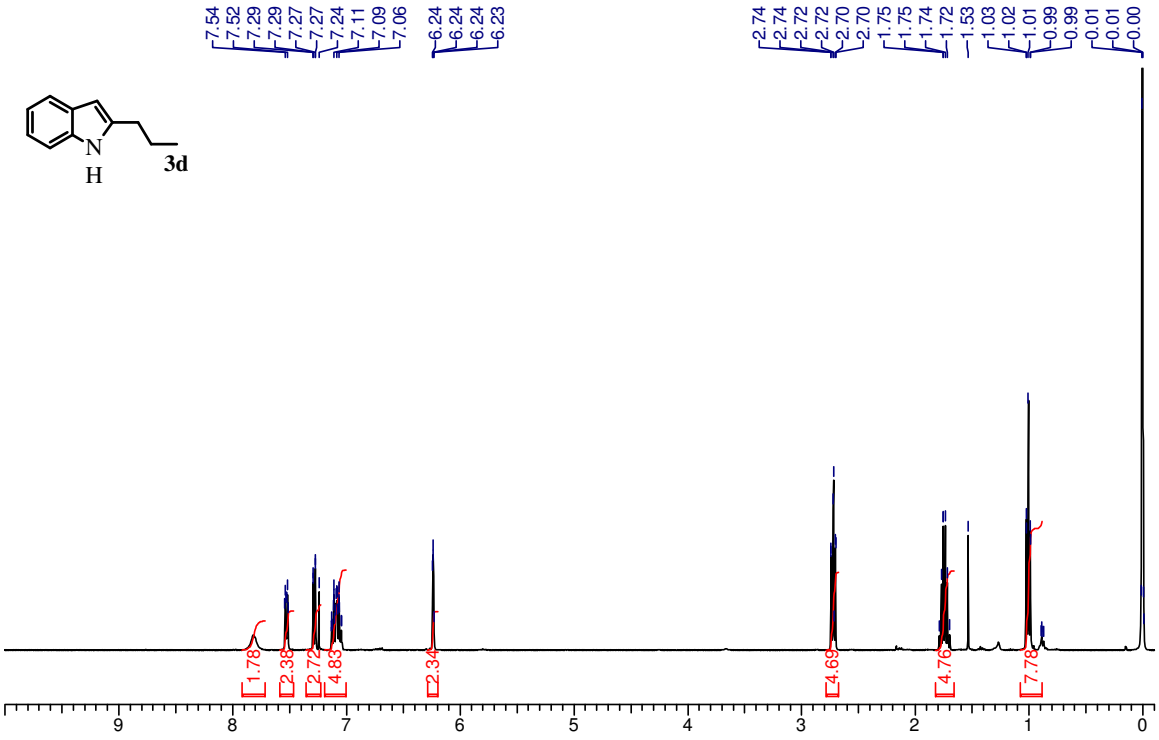
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7.06
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6.24
6.24
6.23
2.74
2.74
2.72
2.72
2.70
2.70
1.75
1.75
1.74
1.72
1.53
1.03
1.02
1.01
0.99
0.99
0.01
0.01
0.00
N
H
3d
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2.38
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4.76
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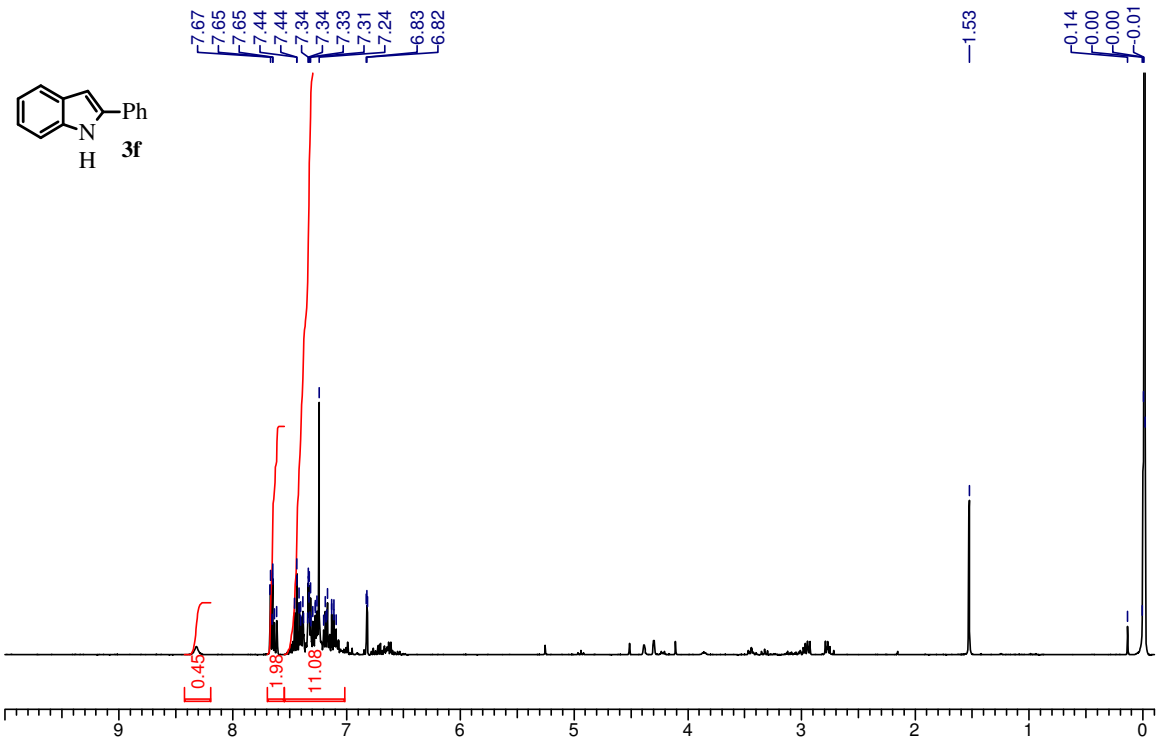
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7.65
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7.44
7.34
7.34
7.33
7.31
7.24
6.83
6.82
1.53
0.14
0.00
0.00
0.01
N
H
Ph
3f
0.45
1.98
11.08
9
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7
6
5
4
3
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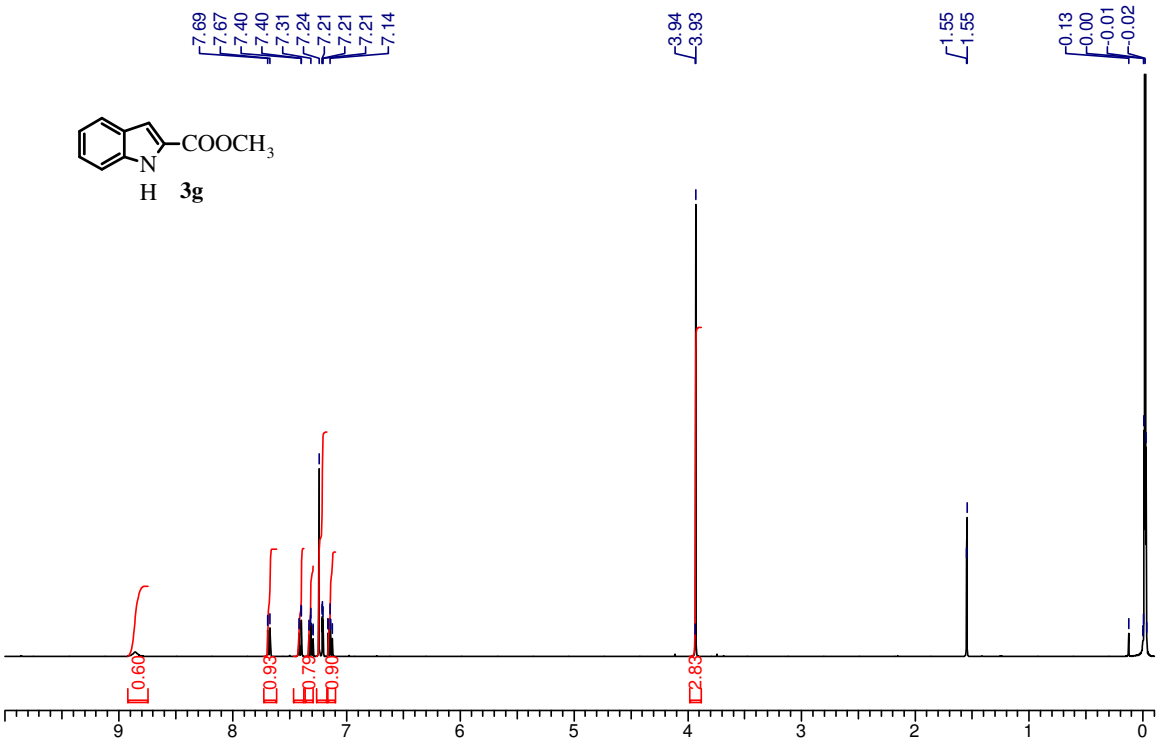
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7.31
7.24
7.21
7.21
7.21
7.14
3.94
3.93
1.55
1.55
0.13
0.00
-0.01
-0.02
COOCH3
N
H
3g
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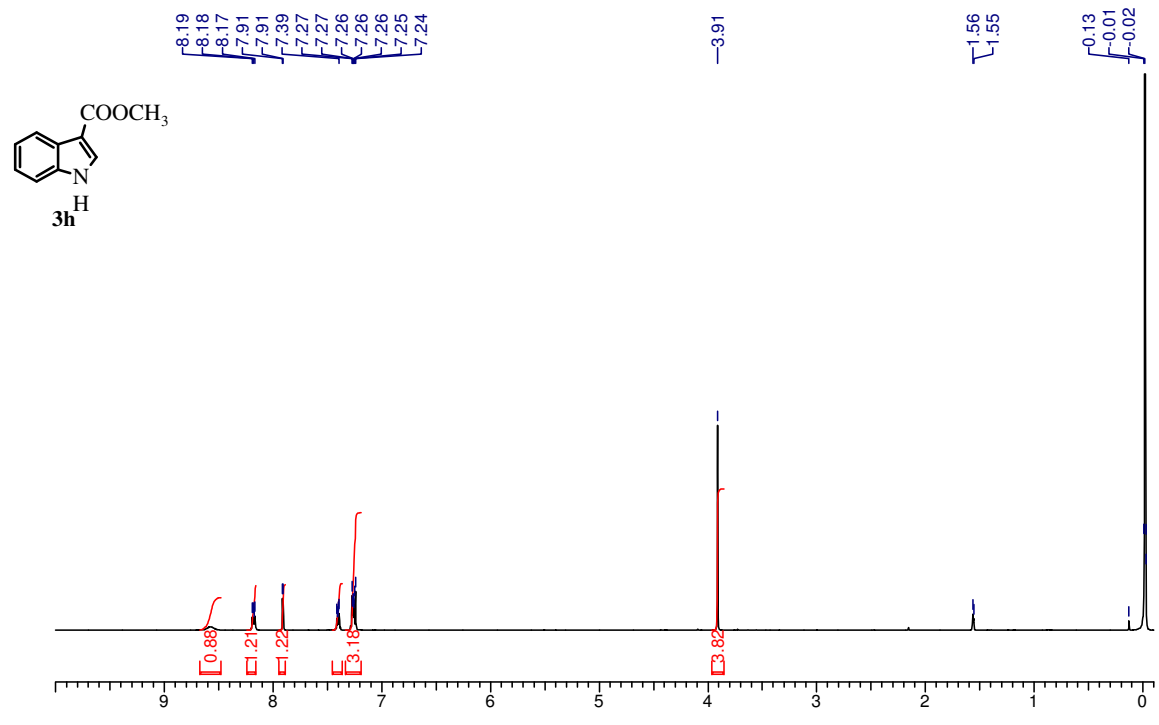
0.99
0.79
0.90
2.83
9
8
7
6
5
4
3
2
1
0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8.17
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7.39
7.27
7.27
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7.26
7.26
7.25
7.24
3.91
1.56
1.55
0.13
0.01
-0.02
COOCH3
N
H
3h
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1.21
1.22
3.18
3.82
9
8
7
6
5
4
3
2
1
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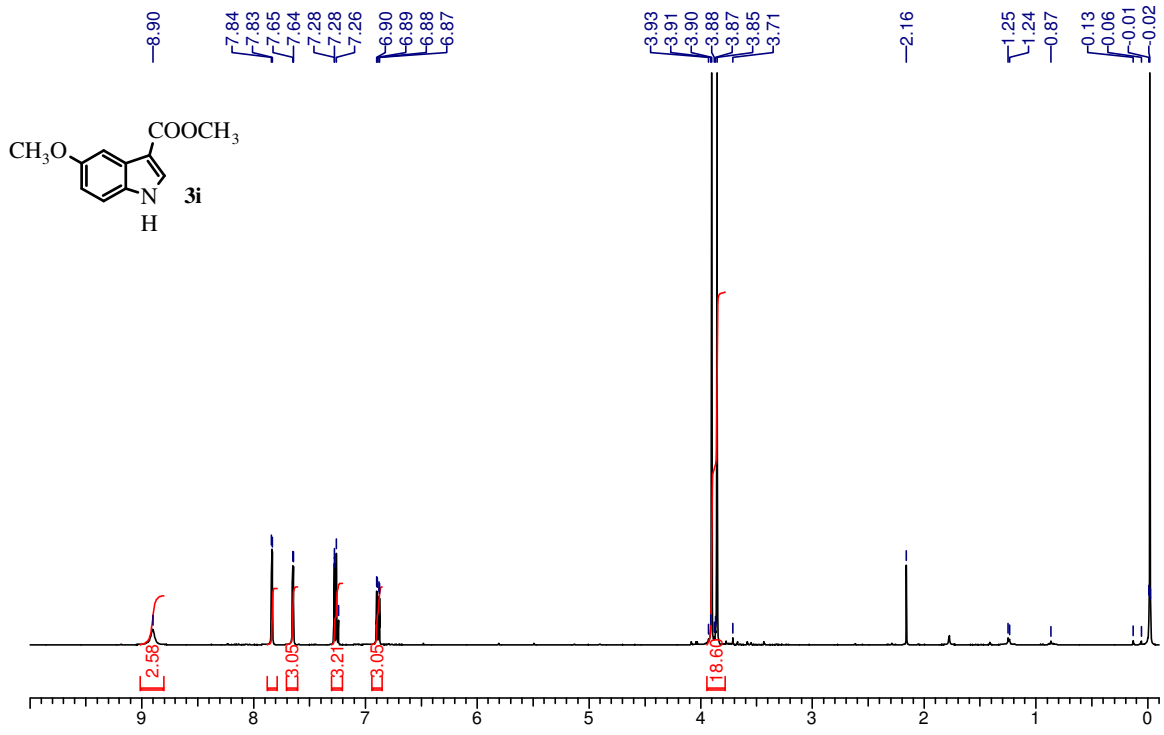
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7.83
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7.28
7.28
7.26
6.90
6.89
6.88
6.87
3.93
3.91
3.90
3.88
3.87
3.85
3.71
2.16
1.25
1.24
0.87
0.13
0.06
0.01
0.02
COOCH3
CH3O
N
H
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3.21
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7
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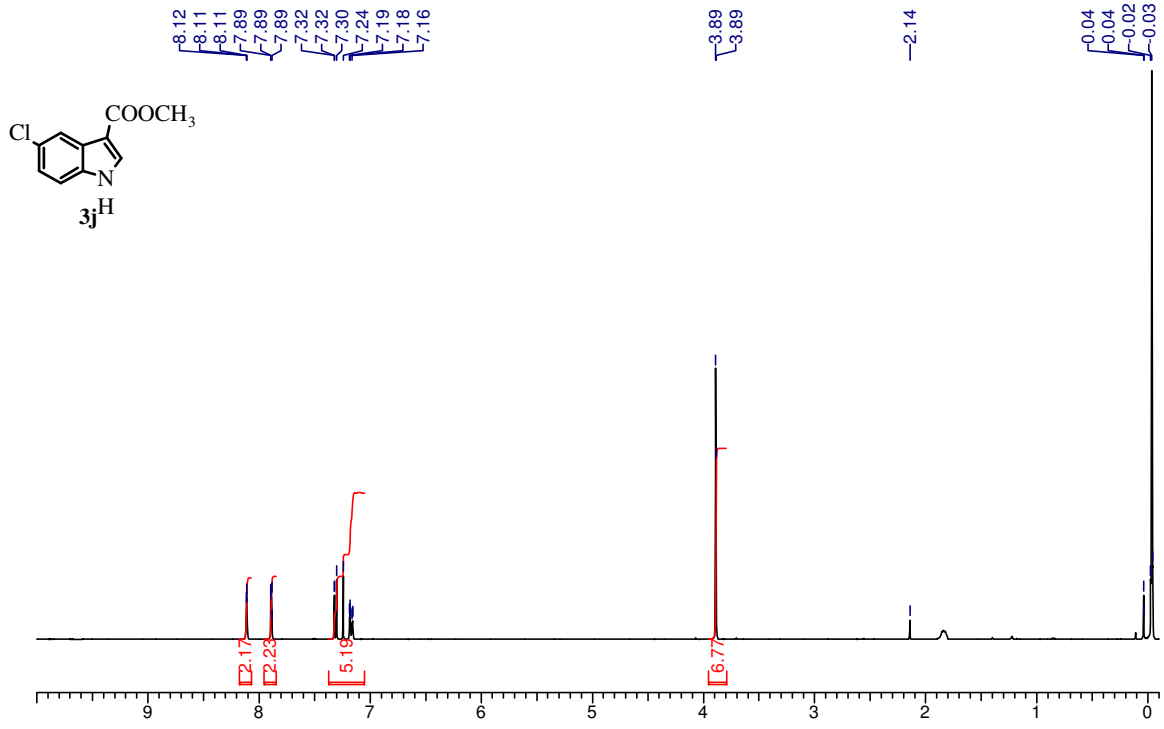
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8.11
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7.89
7.89
7.32
7.32
7.30
7.24
7.19
7.18
7.16
3.89
3.89
2.14
0.04
0.04
0.02
0.03
COOCH3
Cl
N
H
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2.17
2.23
5.19
6.77
9
8
7
6
5
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3
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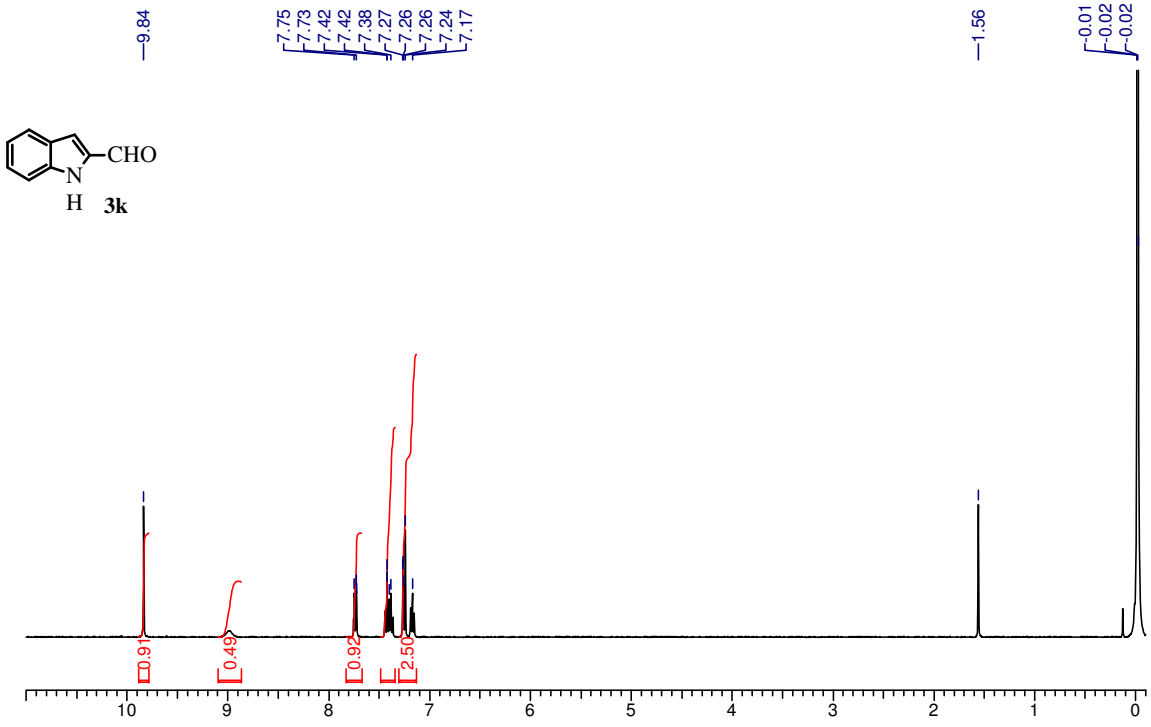
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7.73
7.42
7.42
7.38
7.27
7.26
7.26
7.24
7.17
1.56
0.01
0.02
0.02
CHO
N
H
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0.49
0.92
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7
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5
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1
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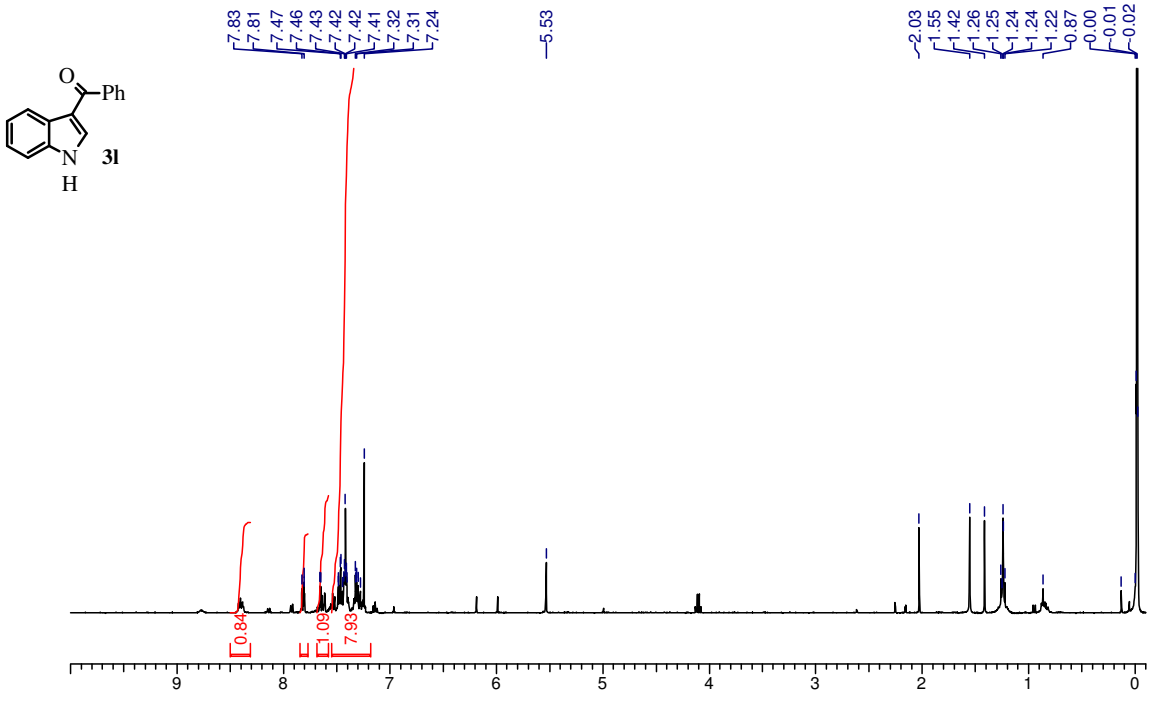
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7.42
7.42
7.41
7.32
7.31
7.24
5.53
2.03
1.55
1.42
1.26
1.25
1.24
1.24
1.22
0.87
0.00
0.01
0.02
O
Ph
N
H
3l
0.84
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7.93
9
8
7
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3
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1
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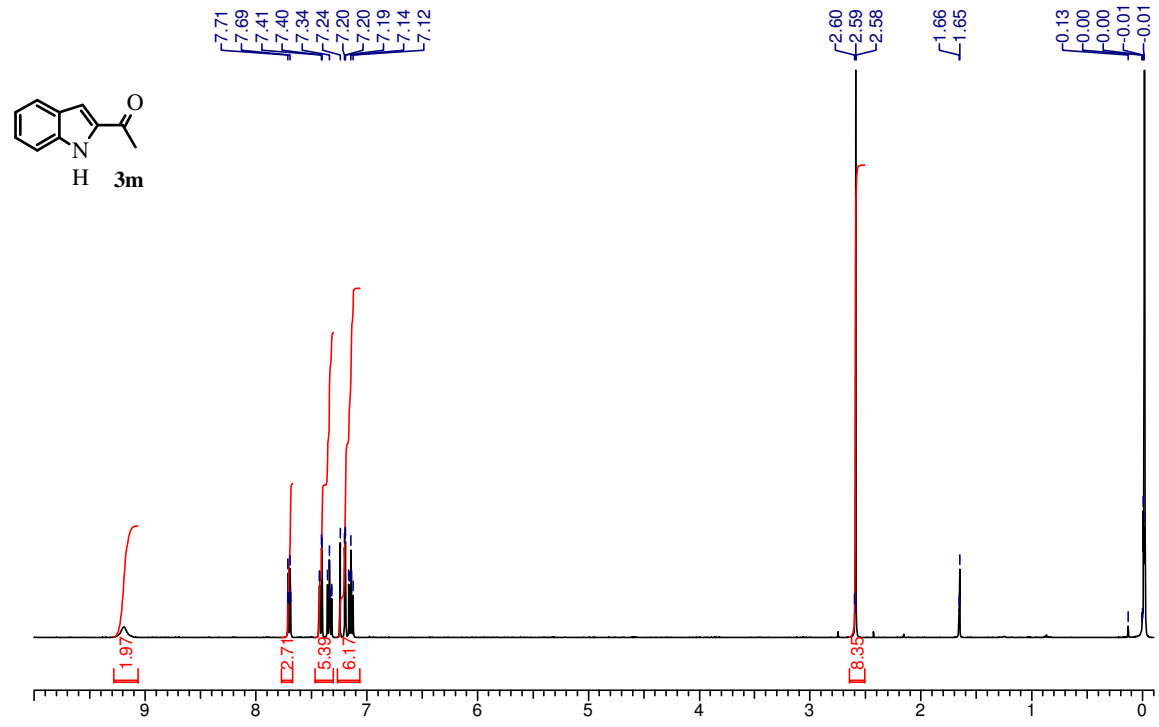
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7.24
7.20
7.20
7.19
7.14
7.12
2.60
2.59
2.58
1.66
1.65
0.13
0.00
0.00
-0.01
-0.01
O
N
H
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5.39
6.17
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7
6
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1
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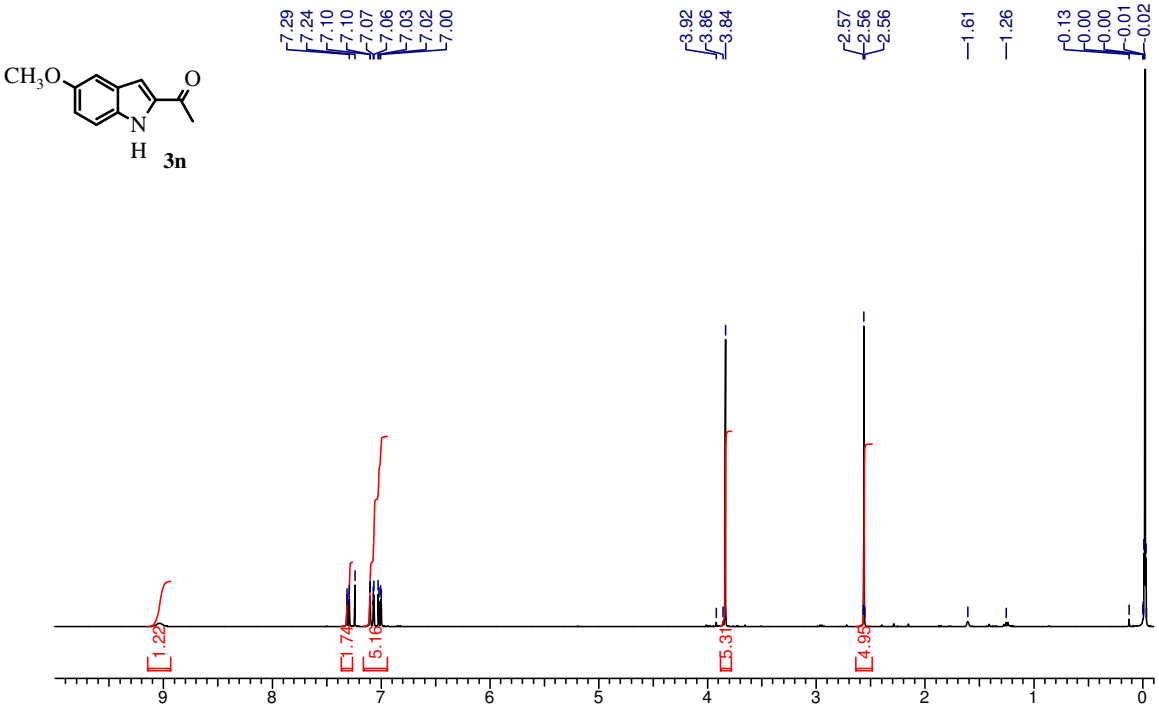
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7.10
7.07
7.06
7.03
7.02
7.00
3.92
3.86
3.84
2.57
2.56
2.56
1.61
1.26
0.13
0.00
0.00
-0.01
-0.02
CH3O
O
N
H
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5.16
5.31
4.95
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7
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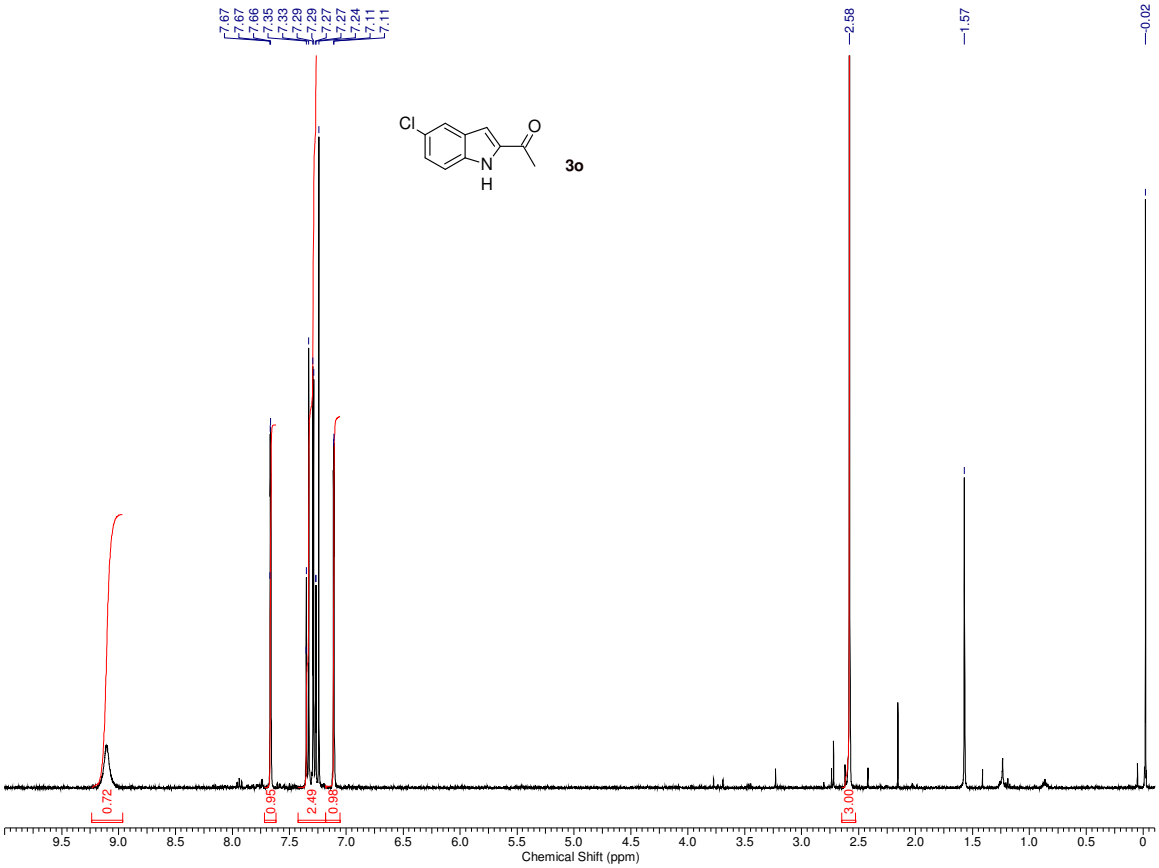
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7.29
7.29
7.27
7.27
7.24
7.11
7.11
2.58
1.57
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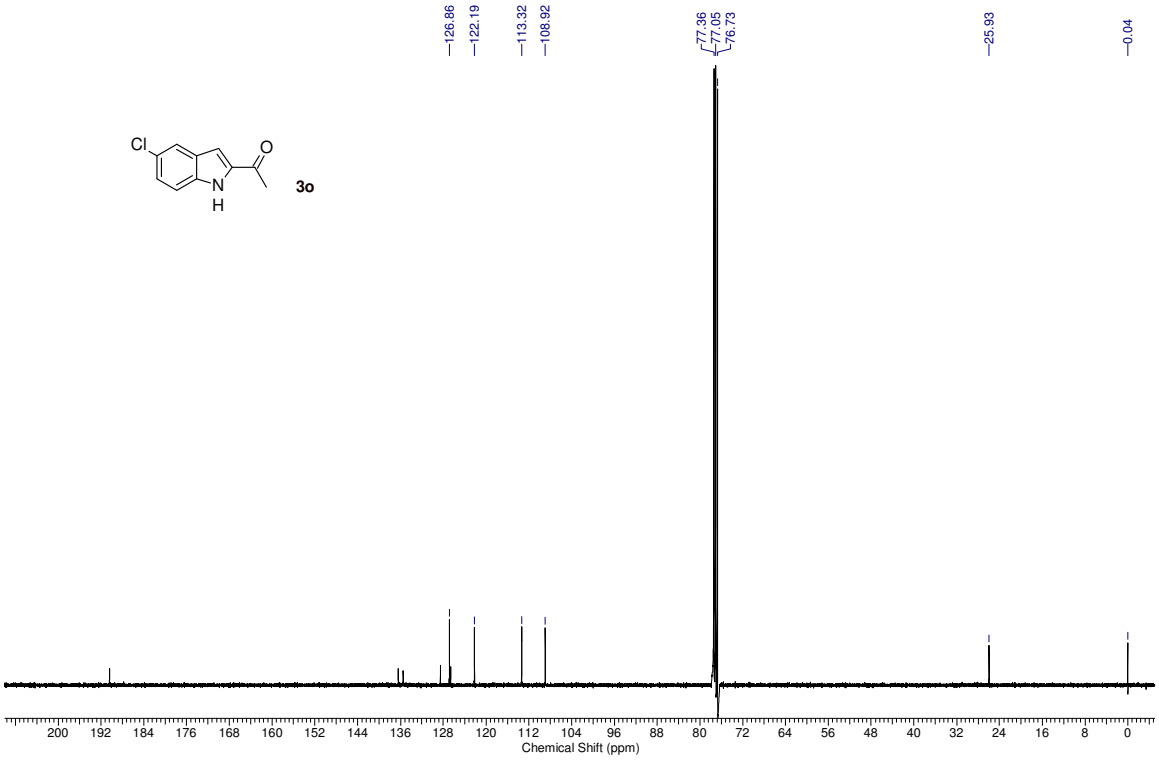
Cl
O
N
H
3o
0.72
0.95
2.49
0.98
3.00
Chemical Shift (ppm)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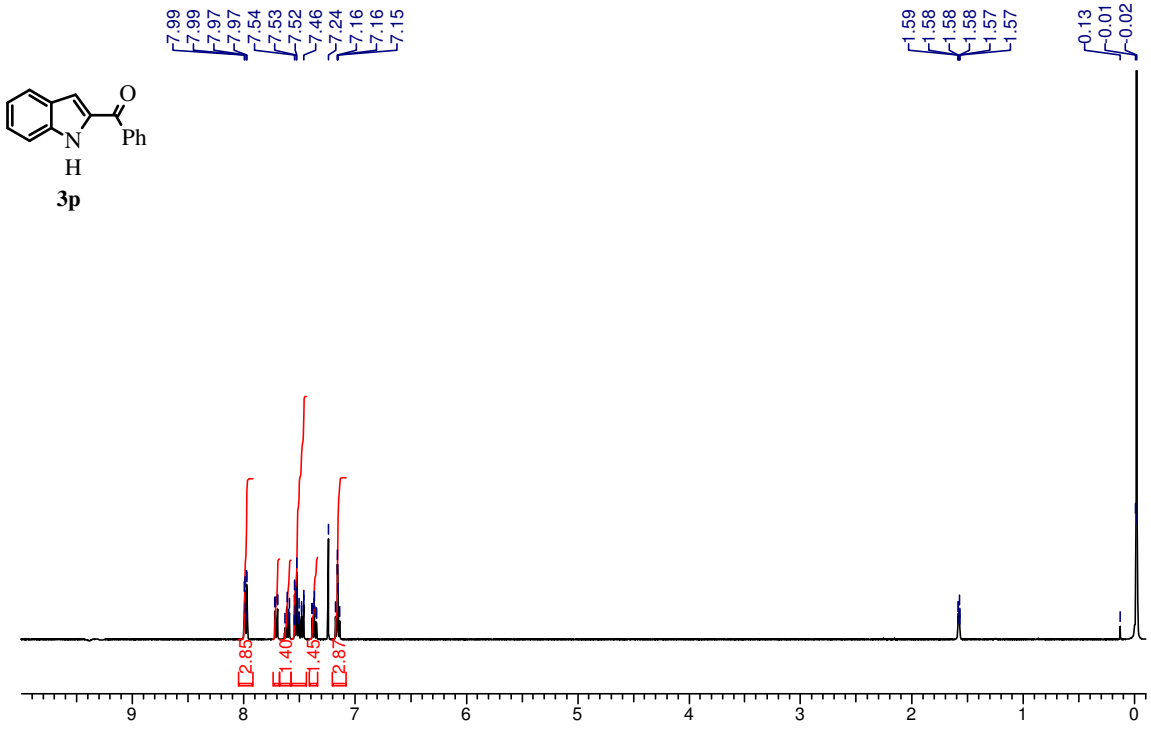
0.04
Cl
O
N
H
3o
Chemical Shift (ppm)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7.16
7.15
1.59
1.58
1.58
1.58
1.57
1.57
0.13
0.01
0.02
O
Ph
N
H
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7
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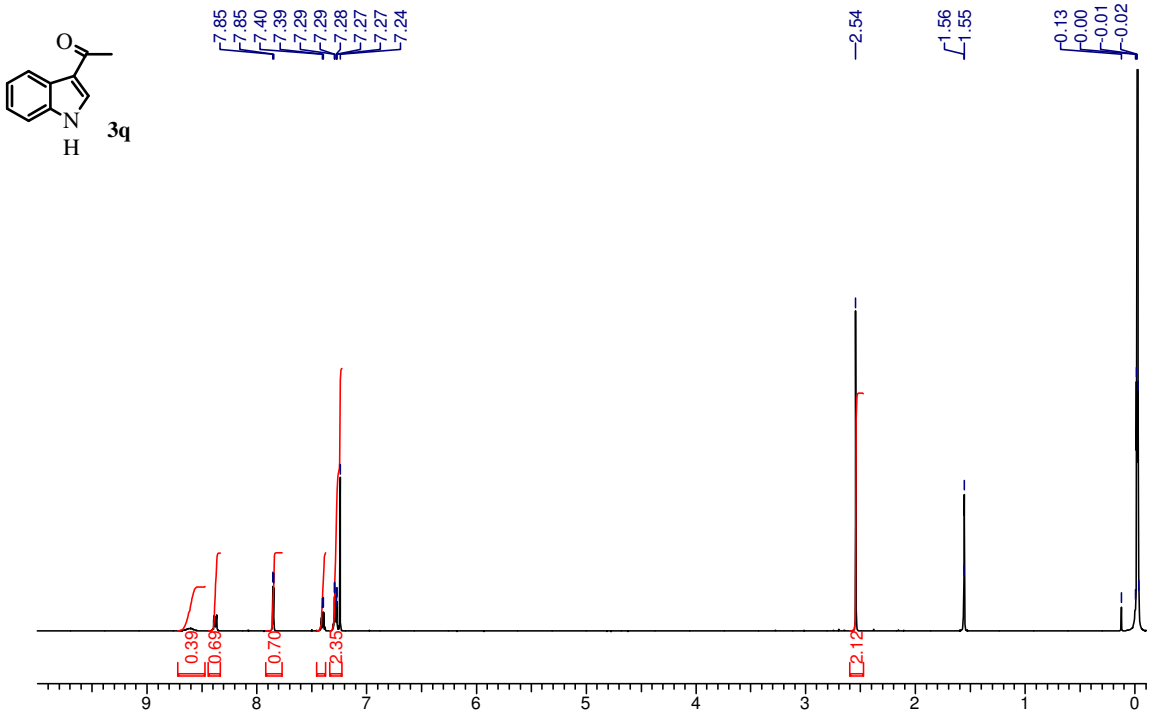
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7.24
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1.55
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0.01
0.02
O
N
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7
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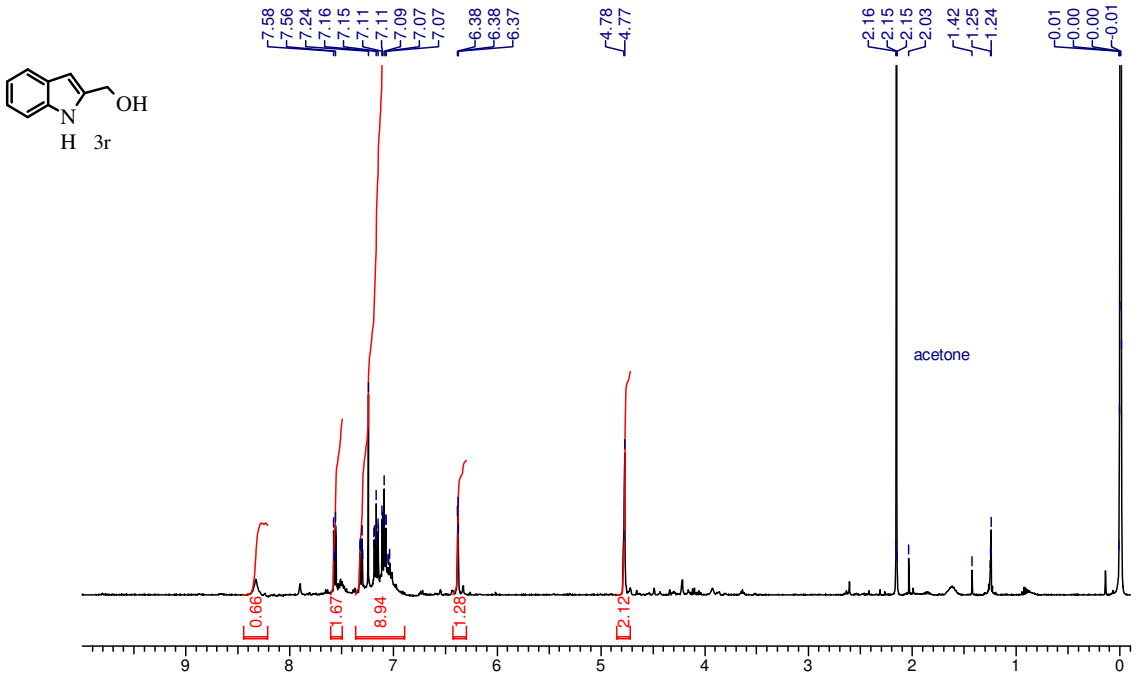
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7.09
7.07
7.07
6.38
6.38
6.37
4.78
4.77
2.16
2.15
2.15
2.03
1.42
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0.00
0.00
-0.01
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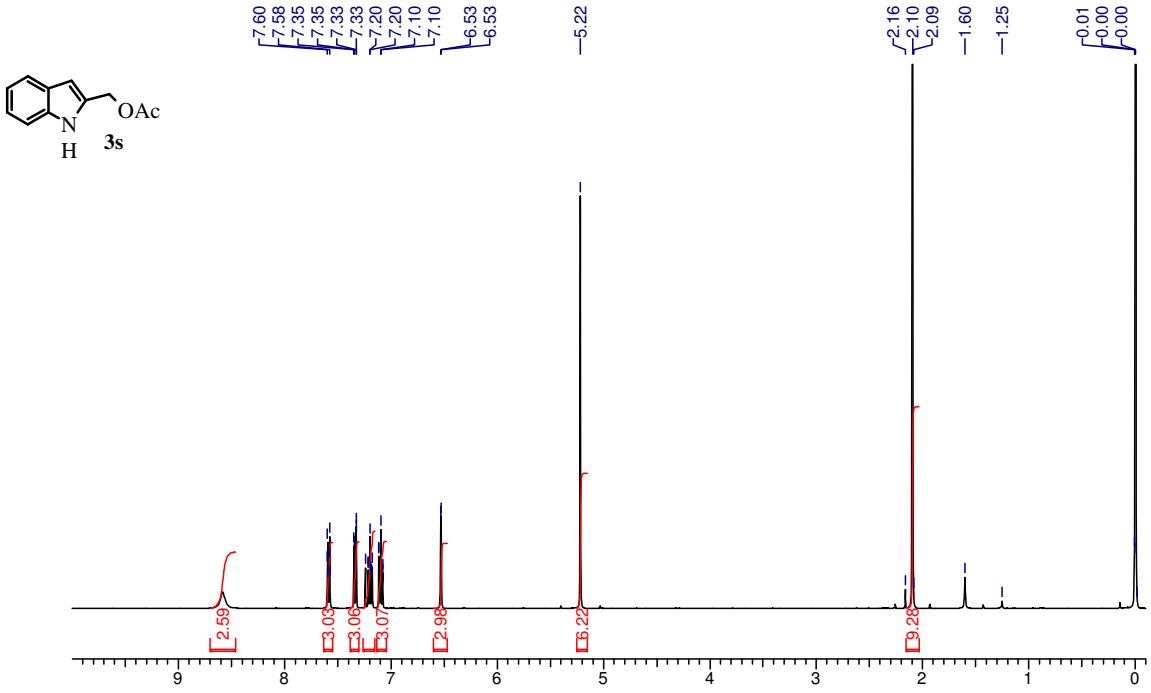
8.94
1.28
2.12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6.53
6.53
5.22
2.16
2.10
2.09
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3.06
3.07
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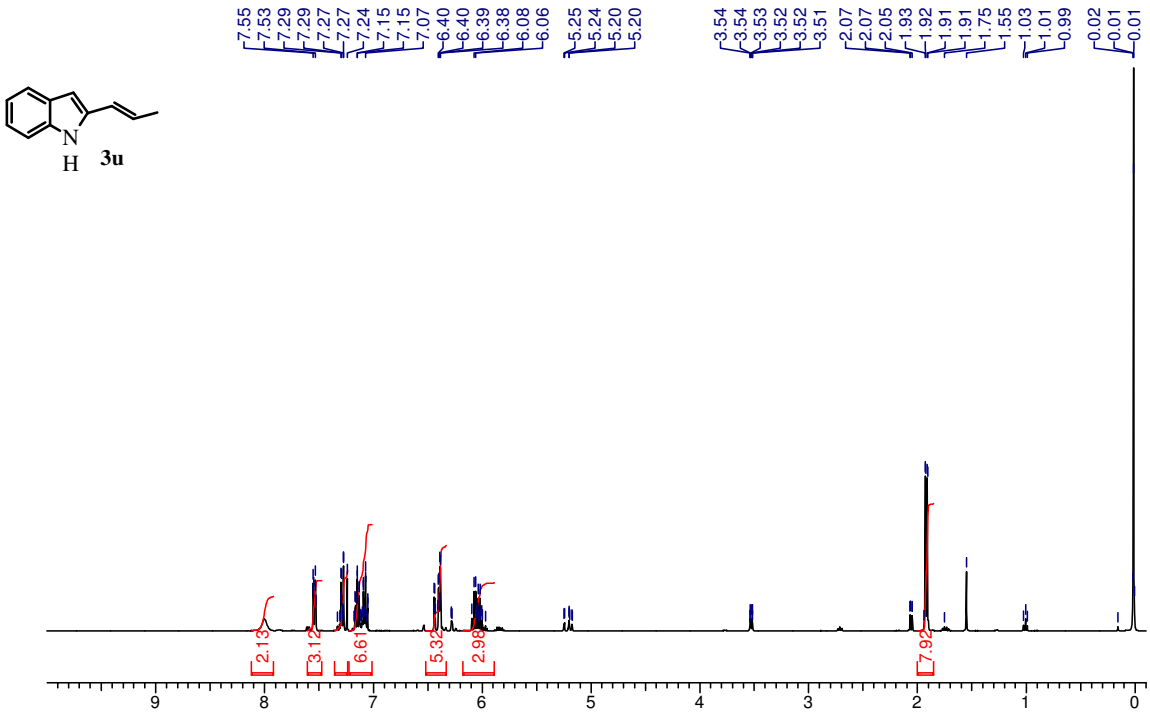
9.28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6.39
6.38
6.08
6.06
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5.24
5.20
5.20
3.54
3.54
3.53
3.52
3.52
3.51
2.07
2.07
2.05
1.93
1.92
1.91
1.91
1.75
1.55
1.03
1.01
0.99
0.02
0.01
0.01
2.13
3.12
6.61
5.32
2.99
7.92
9
8
7
6
5
4
3
2
1
0

N
H **3u**