Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supplementary Information

Synthesis and C2-functionalization of indoles with allylic acetates under rhodium catalysis

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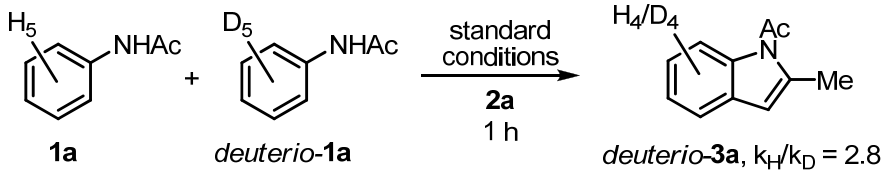
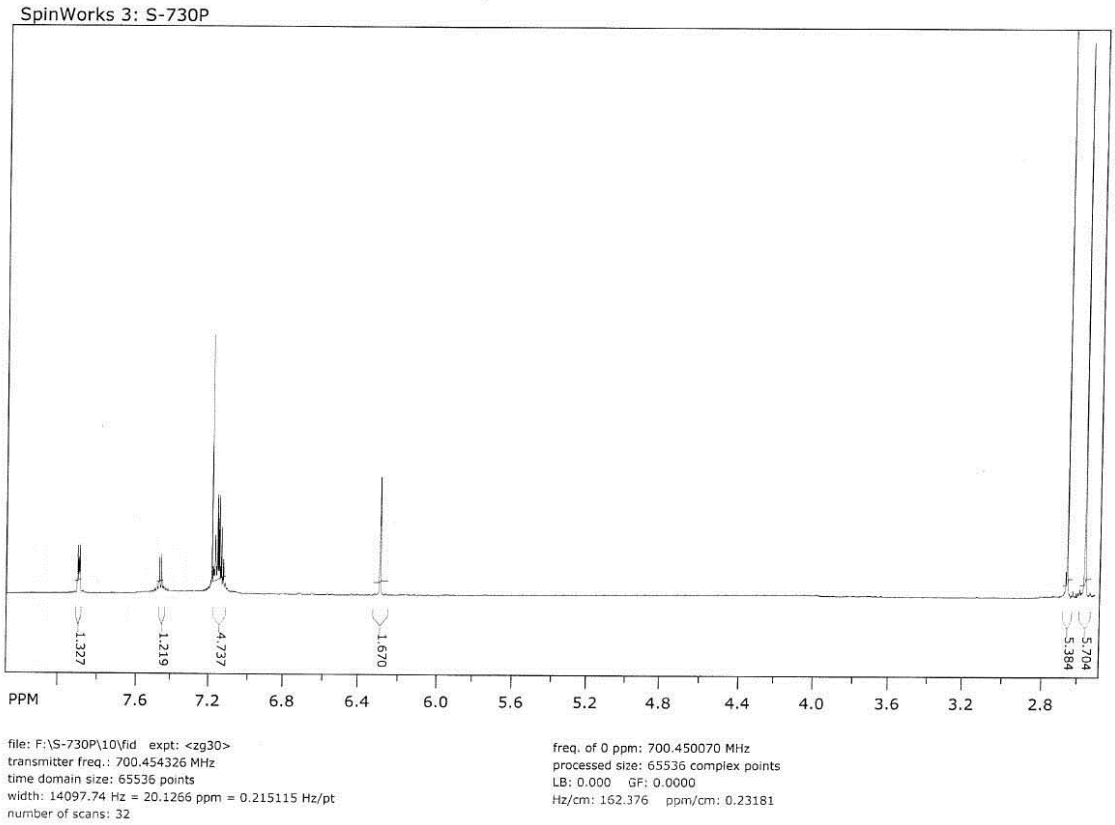
^{1}H NMR and ^{13}C NMR copies of all products ---------- S6–S36

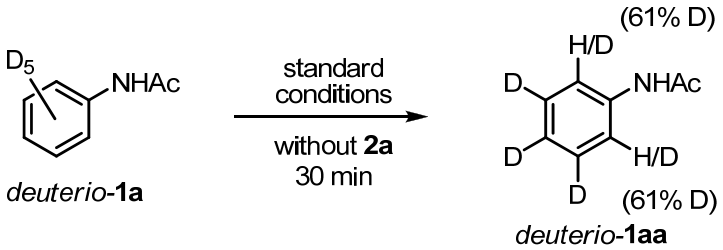
Mechanistic Studies

a) Kinetic Isotope Effect

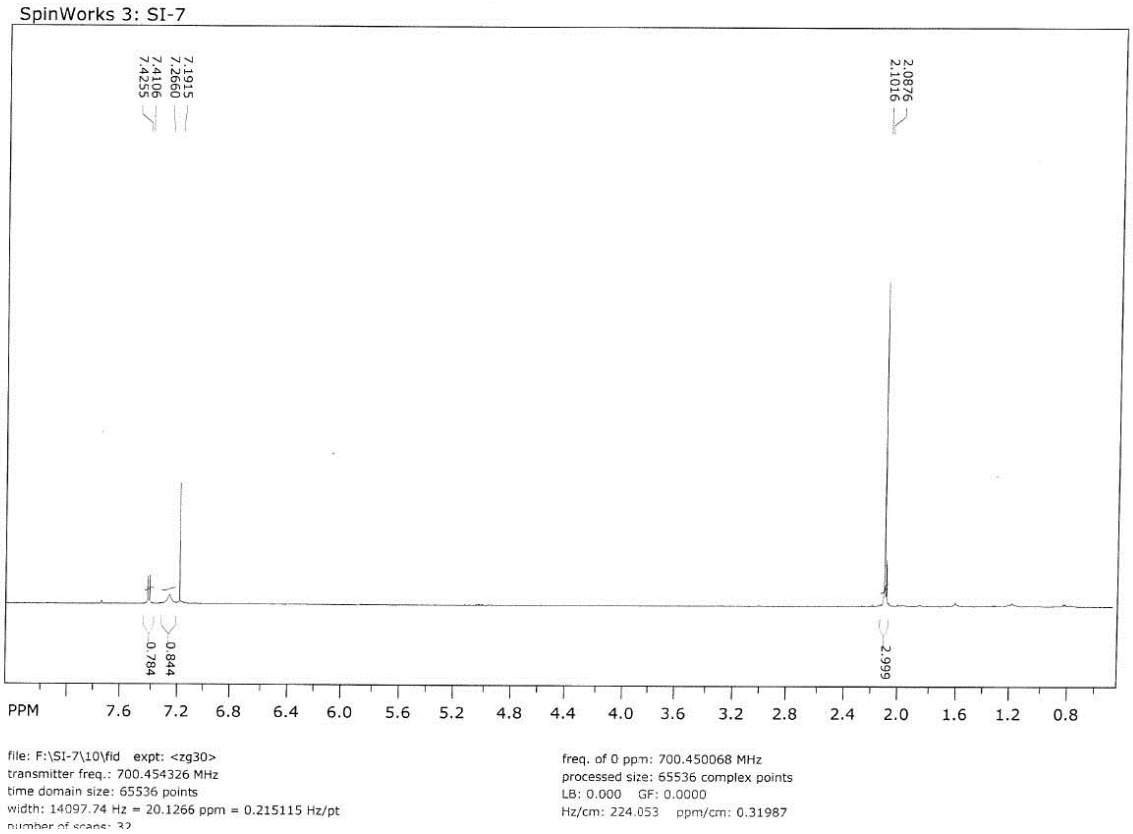




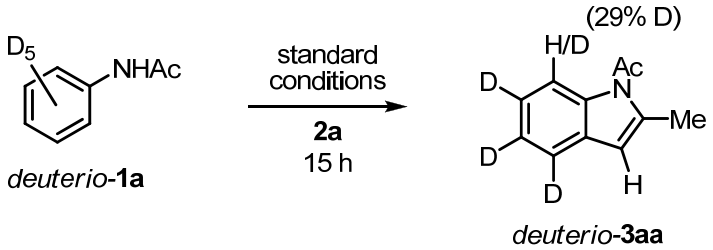
b) Reversibility of deuterio-1a without allyl acetate (2a)

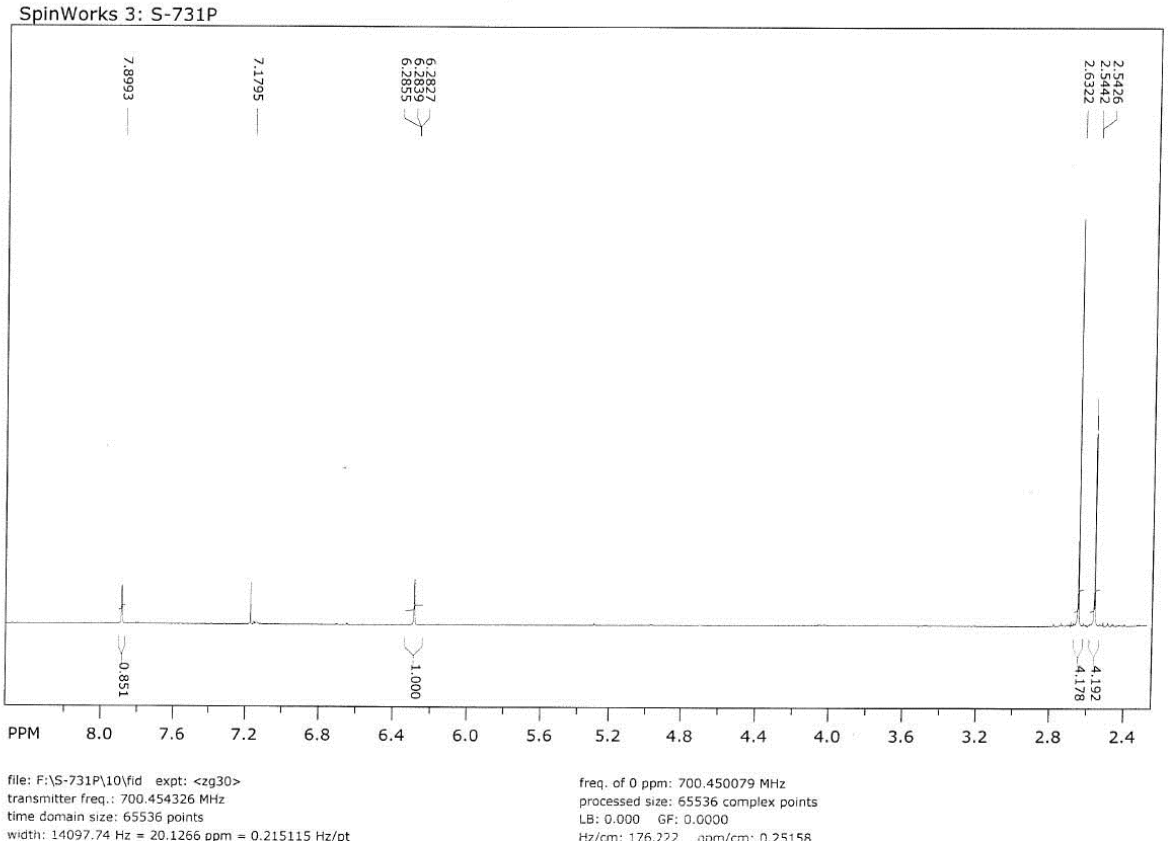


^{1}H NMR (700 MHz, $CDCl_3$)

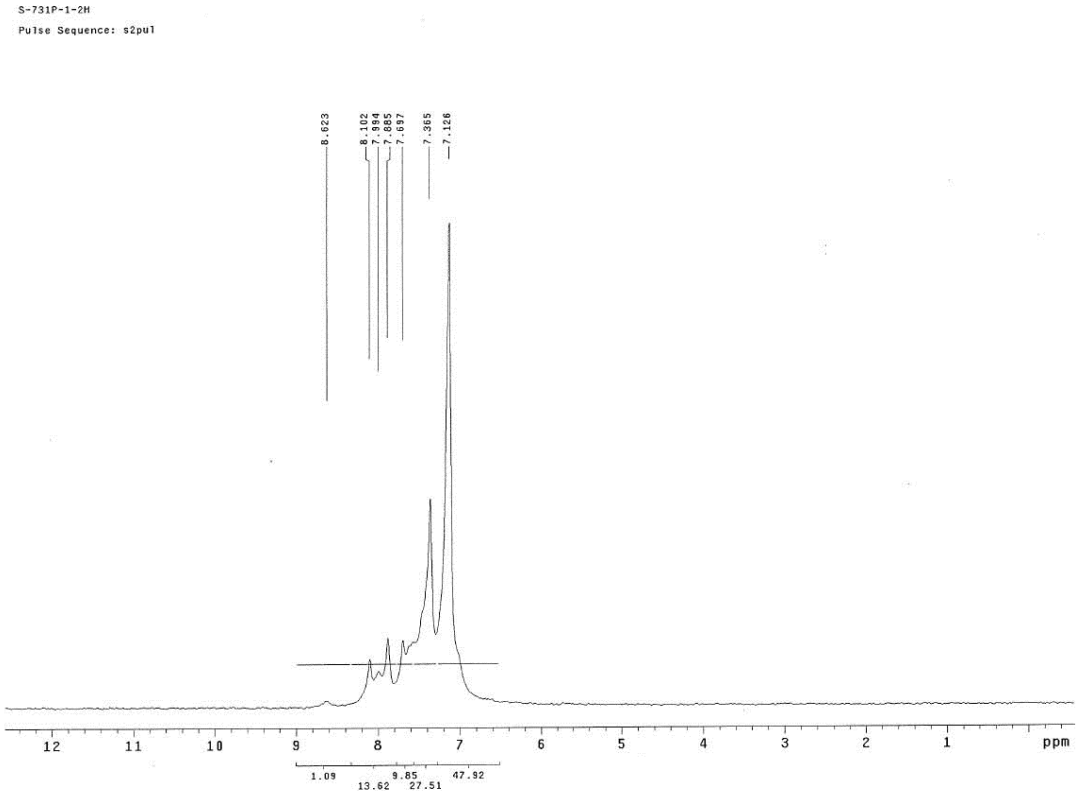


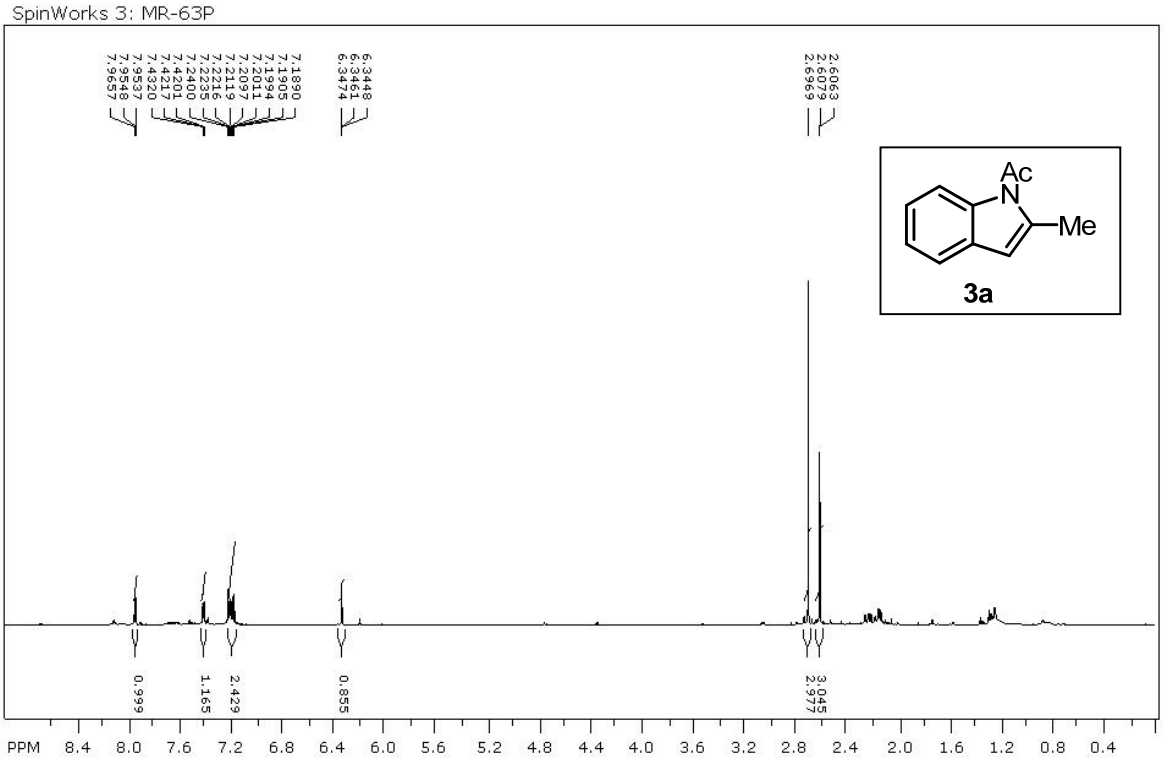
c) Reversibility of deuterio-1a with allyl acetate (2a)





^{2}H NMR (700 MHz, $CHCl_3$)

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7.9548
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7.4320
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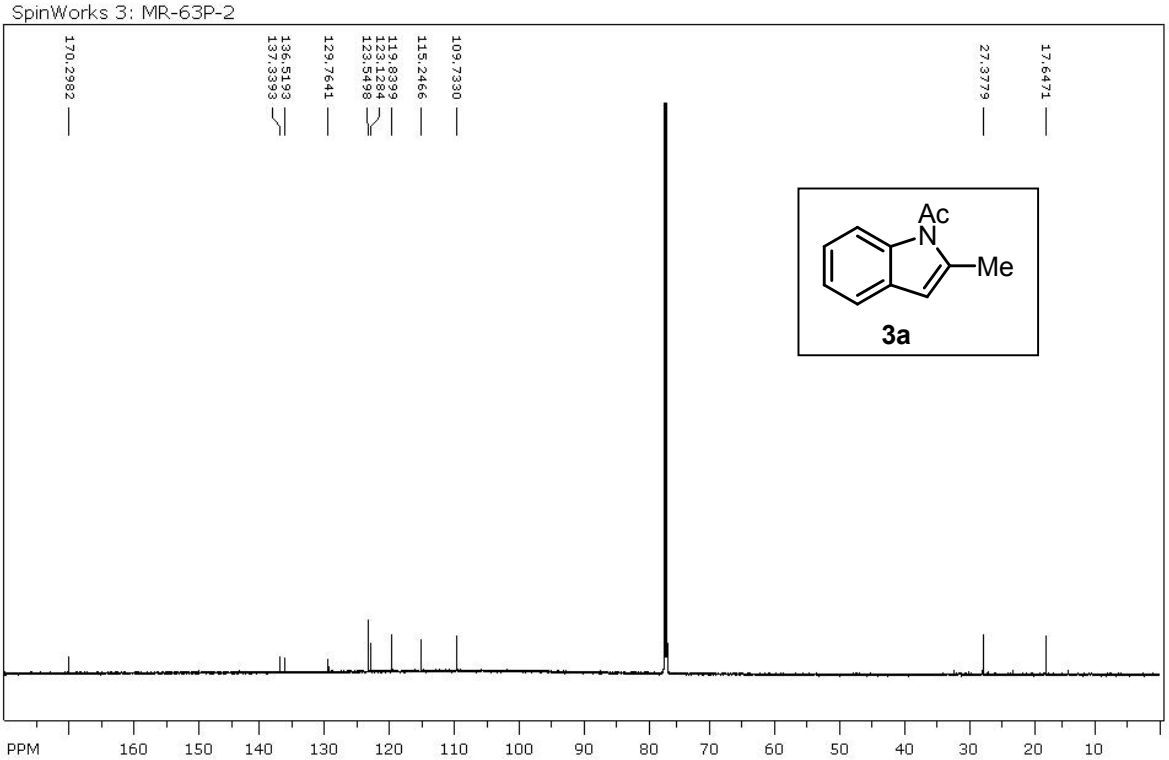
7.2216
7.2119
7.2097
7.2011
7.1994
7.1905
7.1890
6.3474
6.3461
6.3448
2.6967
2.6079
2.6063
0.999
1.165
2.429
0.855
3.045
2.977
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Ac
N
Me
3a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17.6471
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Ac
N
Me
3a

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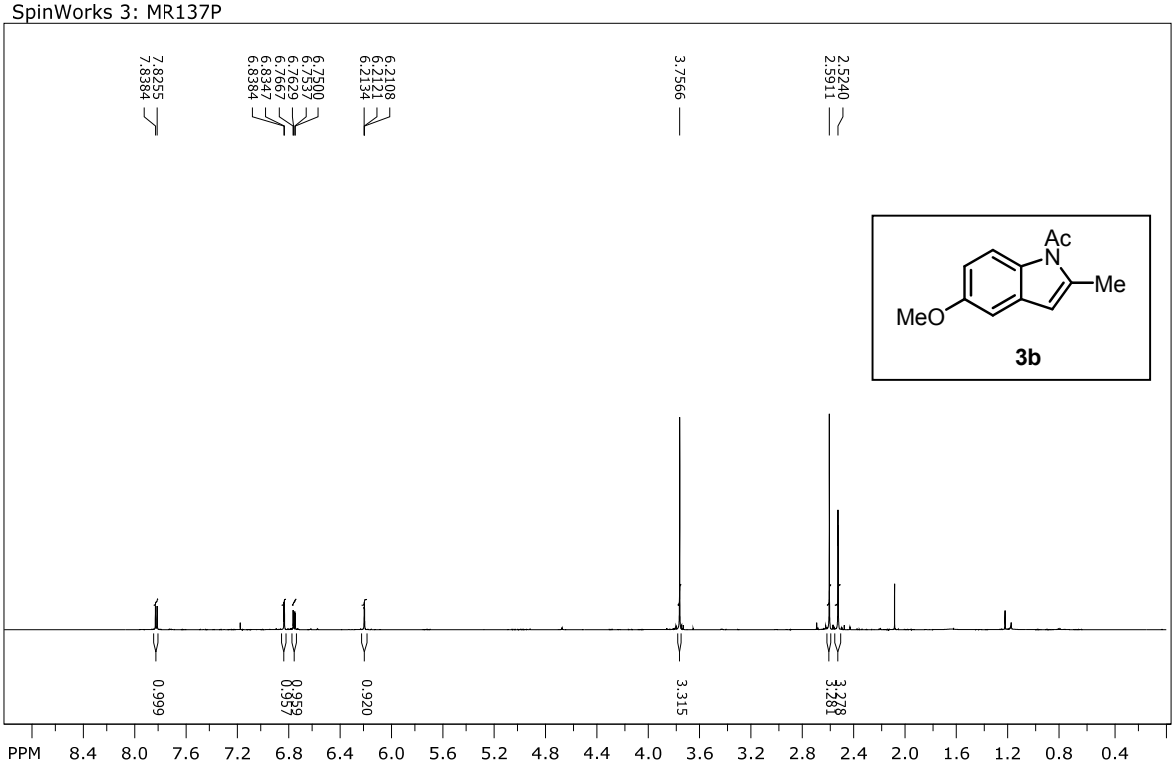

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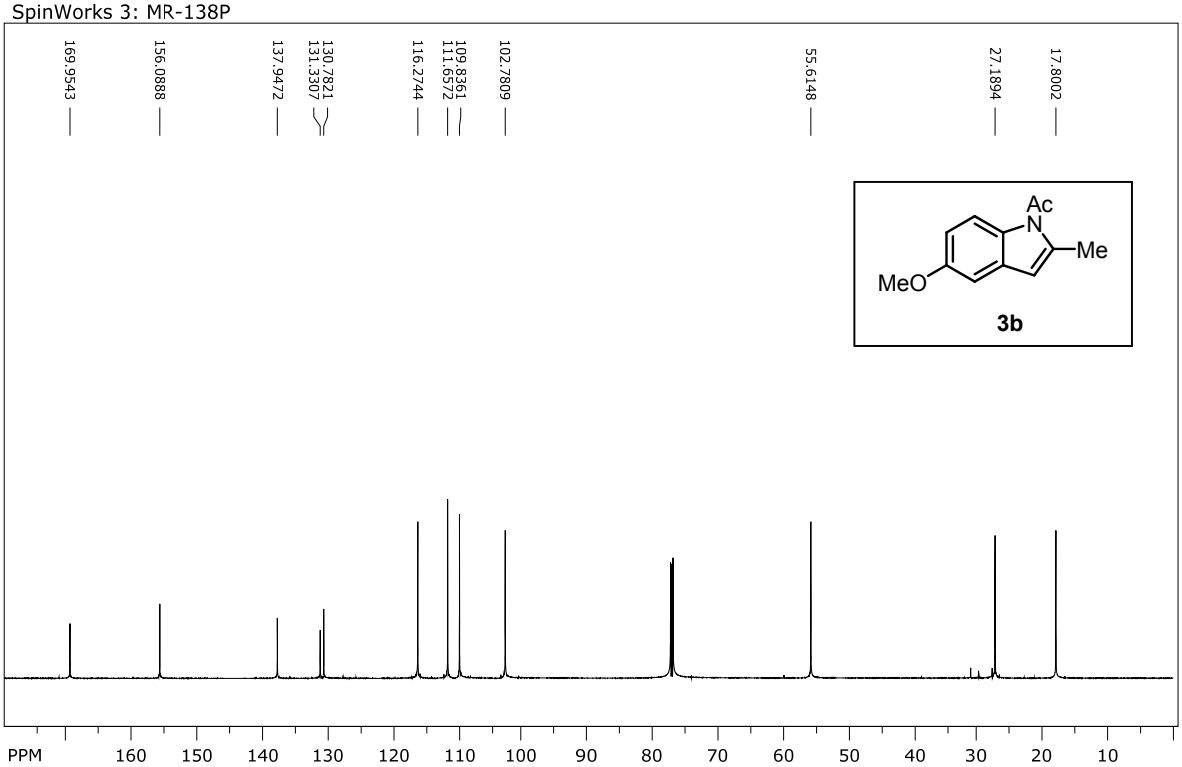

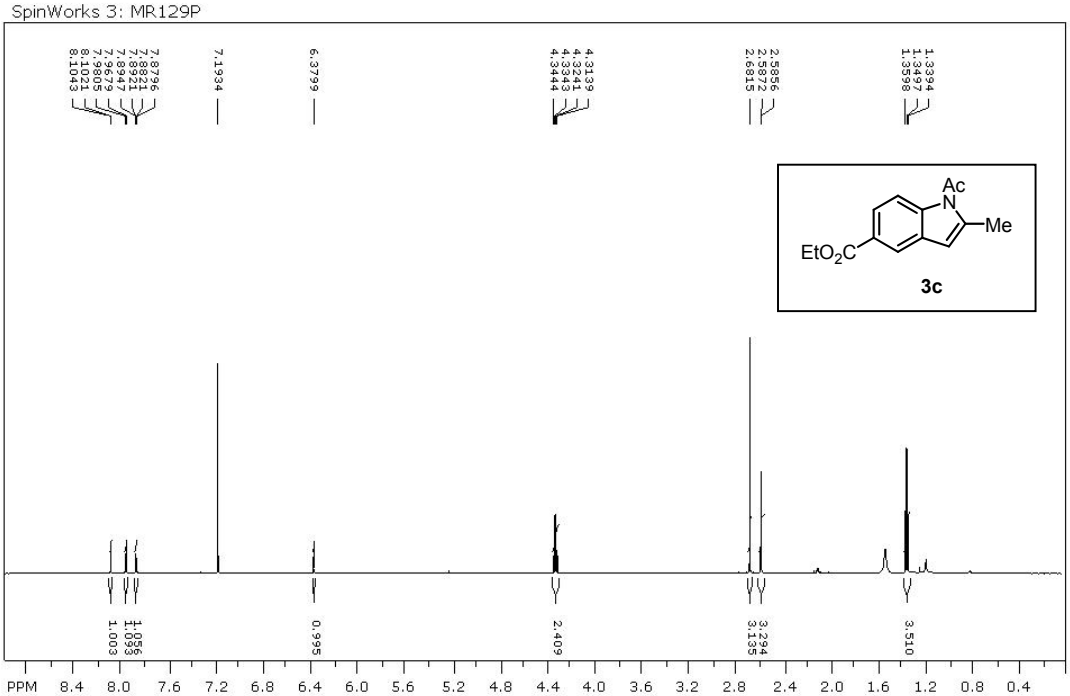
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7.8796
7.1934
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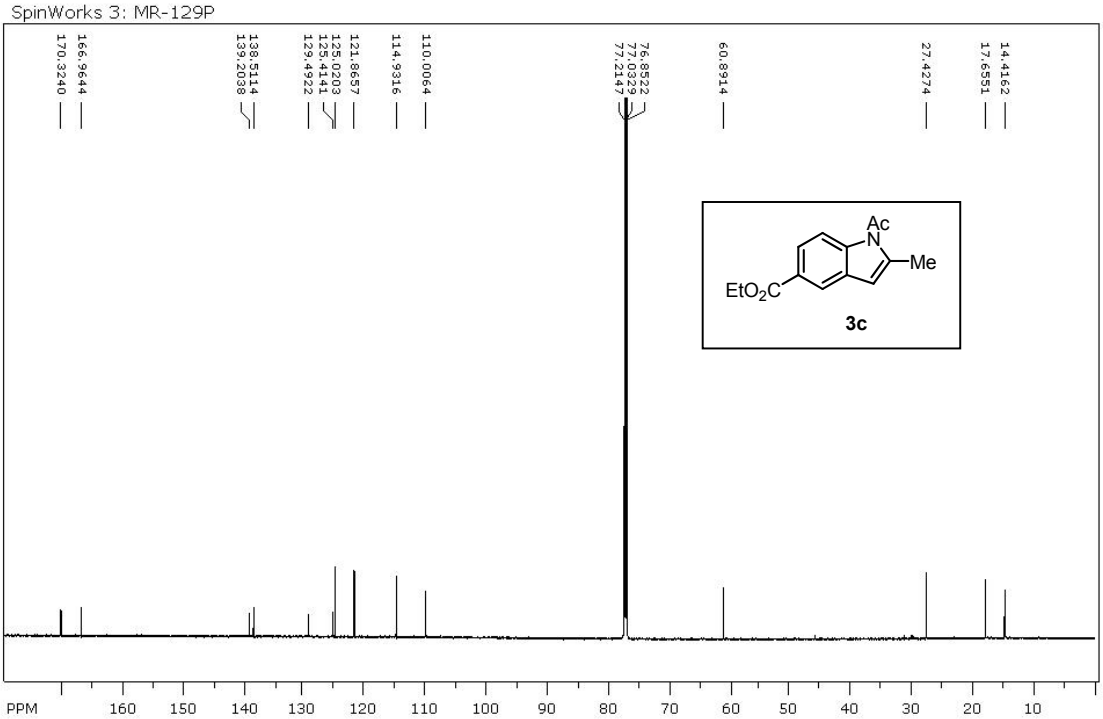
4.3444
4.3343
4.3239
2.6815
2.5872
2.5856
1.3558
1.3497
1.3394
1.003
1.093
1.056
0.995
2.409
3.135
3.294
3.510
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Ac
N
Me
EtO2C
3c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77.2147
77.0329
76.8522
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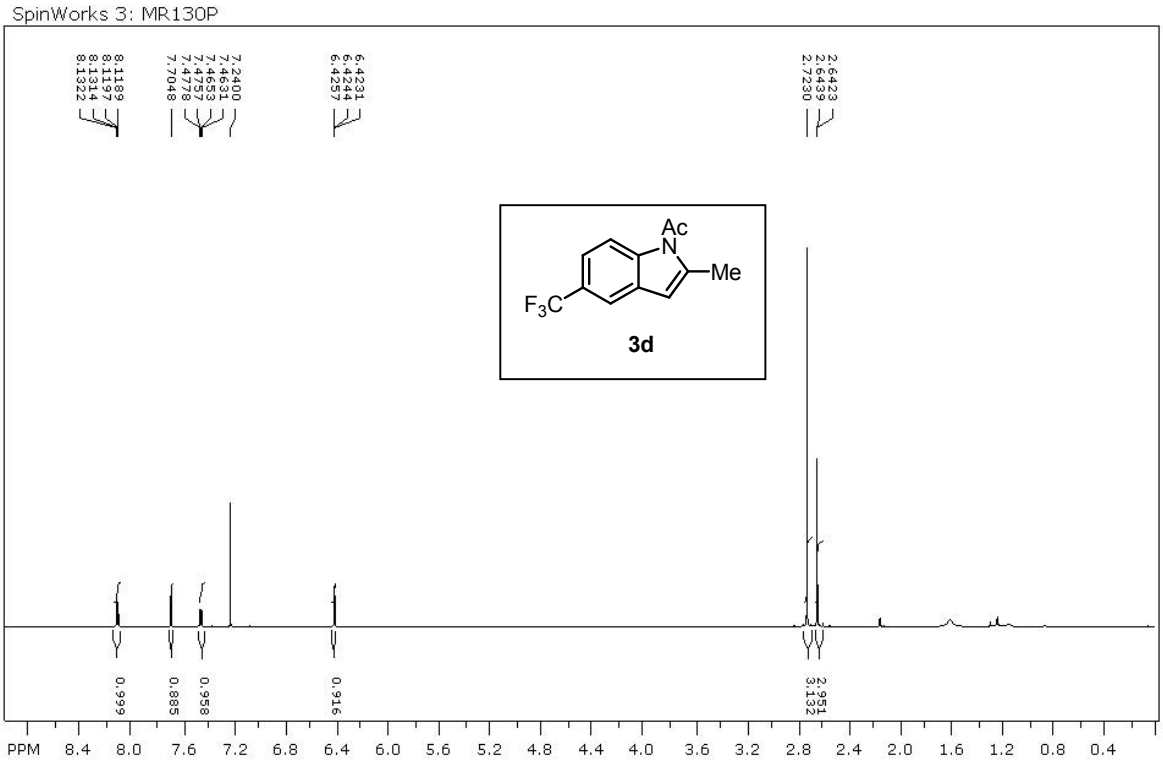
Ac
N
Me
EtO2C
3c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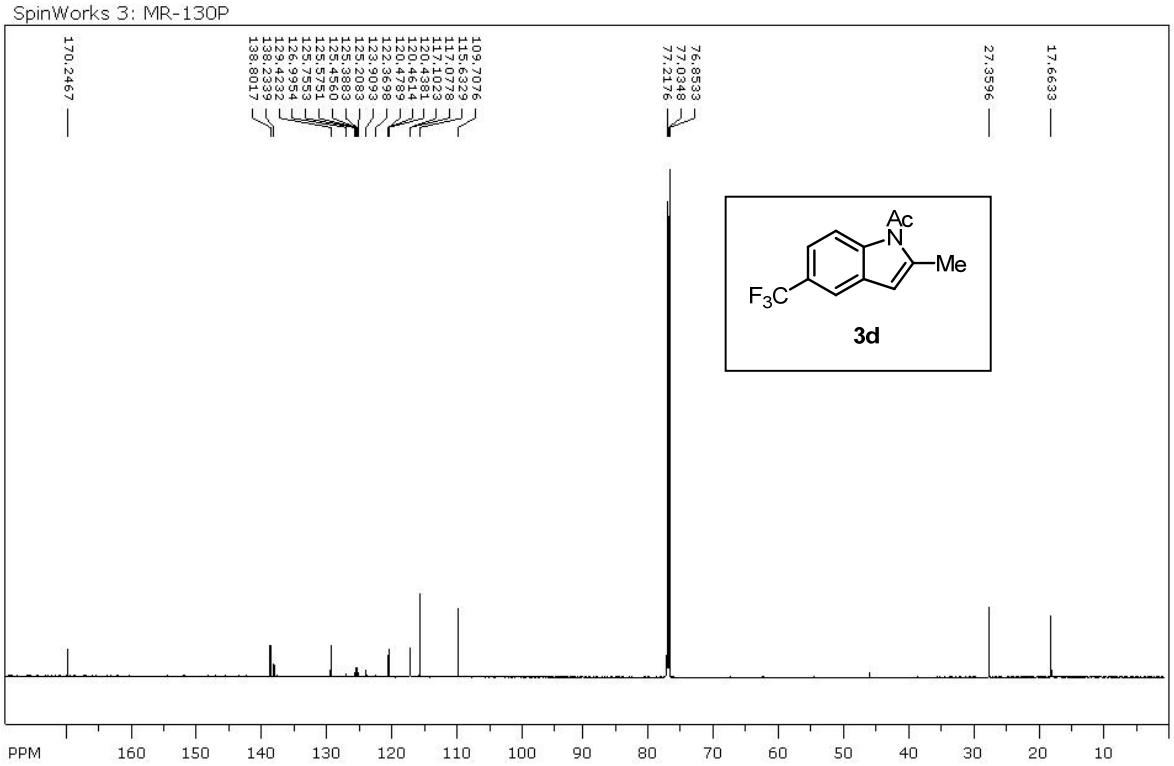
6.4257
6.4244
6.4231
2.7230
2.6439
2.6423
Ac
N
Me
F3C
3d
0.999
0.885
0.958
0.916
3.132
2.951
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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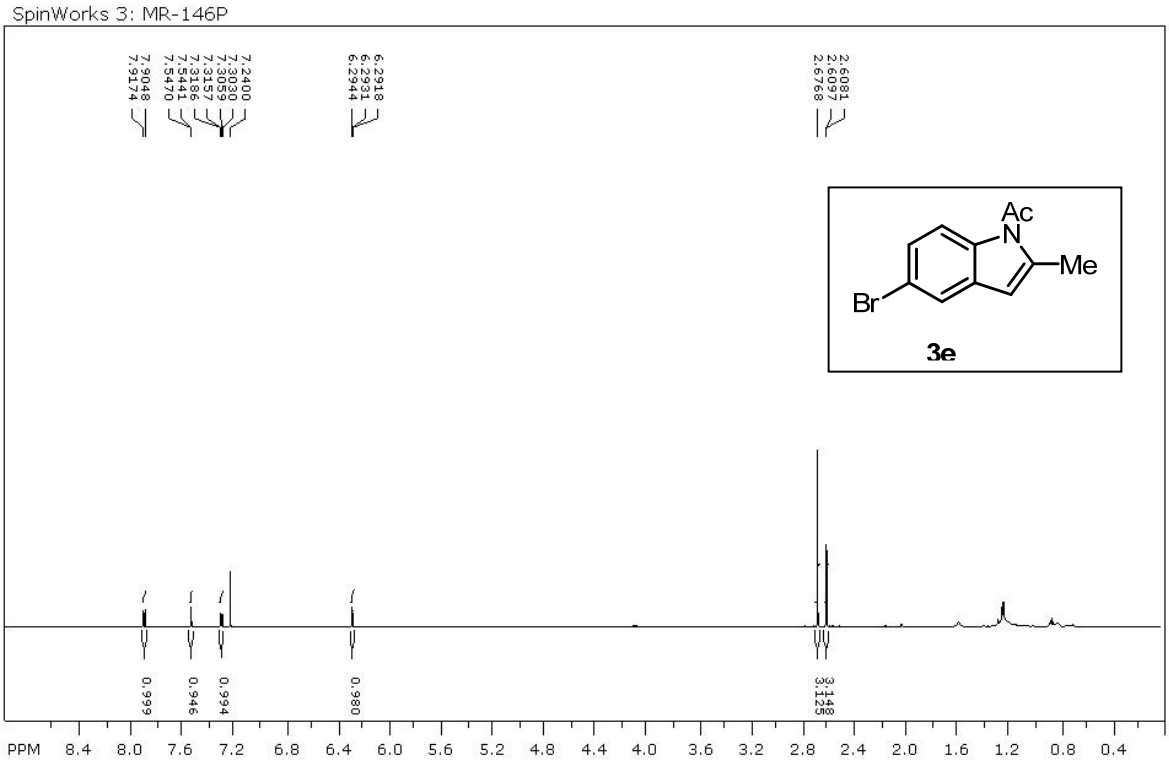
125.5751
125.4560
125.3883
125.2083
123.9093
122.3698
120.4789
120.4614
120.4381
117.0778
115.6329
109.7076
77.2176
77.0348
76.8533
27.3596
17.6633
Ac
N
Me
F3C
3d
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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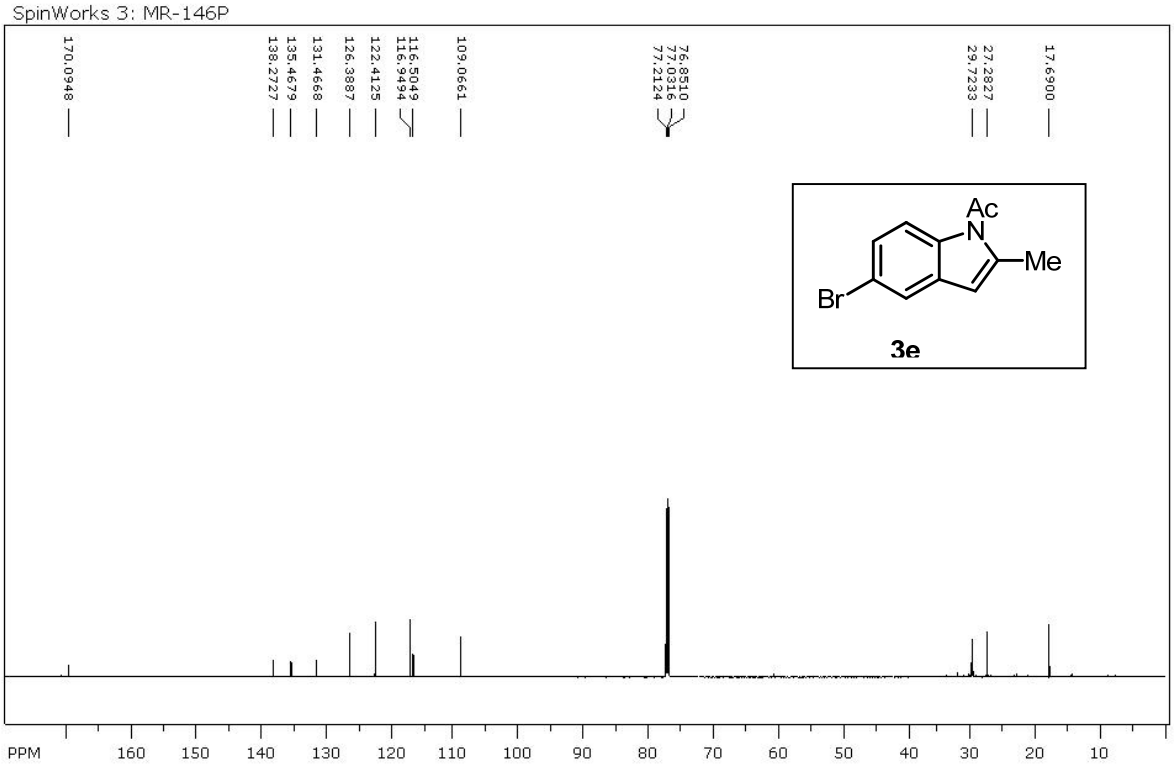
7.3030
7.2400
6.2818
6.2931
6.2944
2.6081
2.6097
2.6768
Ac
N
Me
Br
3e
0.999
0.946
0.994
0.980
3.148
3.125
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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76.8510
77.0316
77.2124
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27.2827
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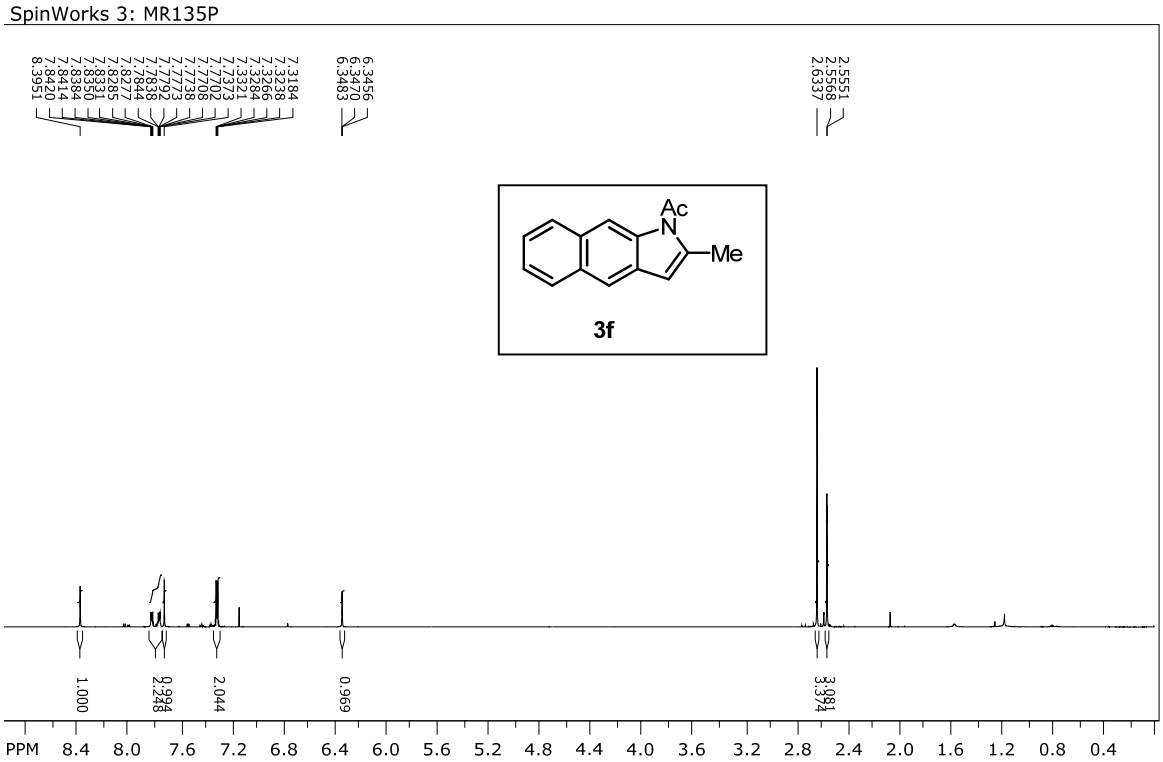
Ac
N
Me
Br
3e
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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7.8277
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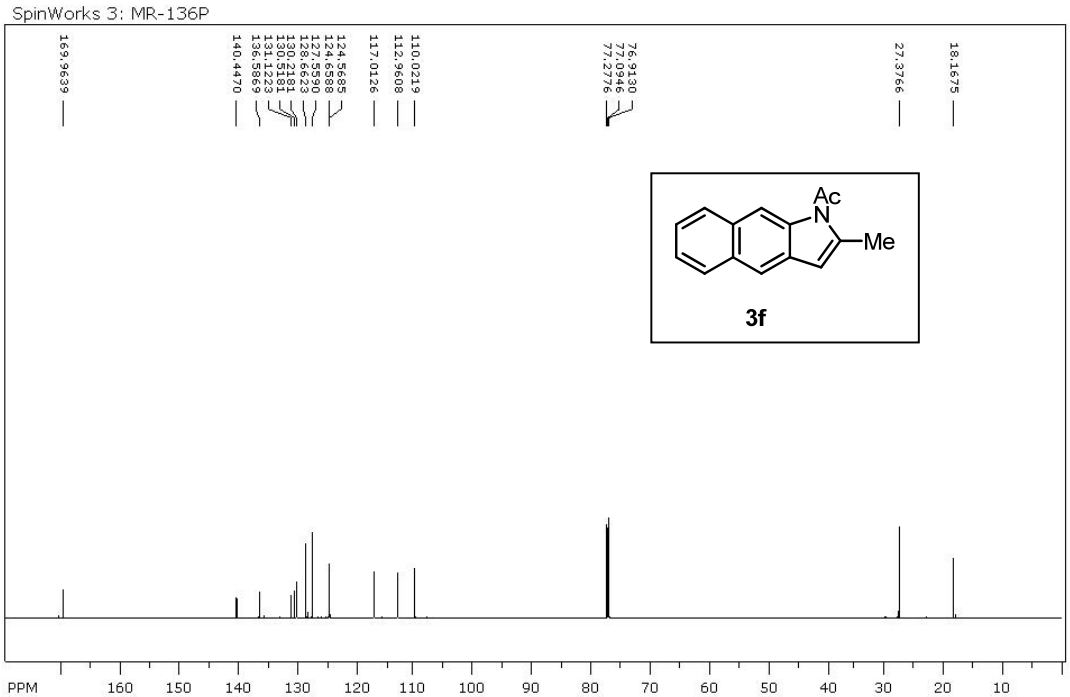
7.7792
7.7778
7.7773
7.7708
7.7703
7.3321
7.3284
7.3266
7.3238
7.3184
6.3483
6.3449
6.3456
2.6337
2.5569
2.5551
Ac
N
Me
3f
1.000
2.248
0.994
2.044
0.969
3.374
3.081
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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124.5685
117.0126
112.9608
110.0219
77.2776
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76.9130
27.3766
18.1675
Ac
N
Me
3f
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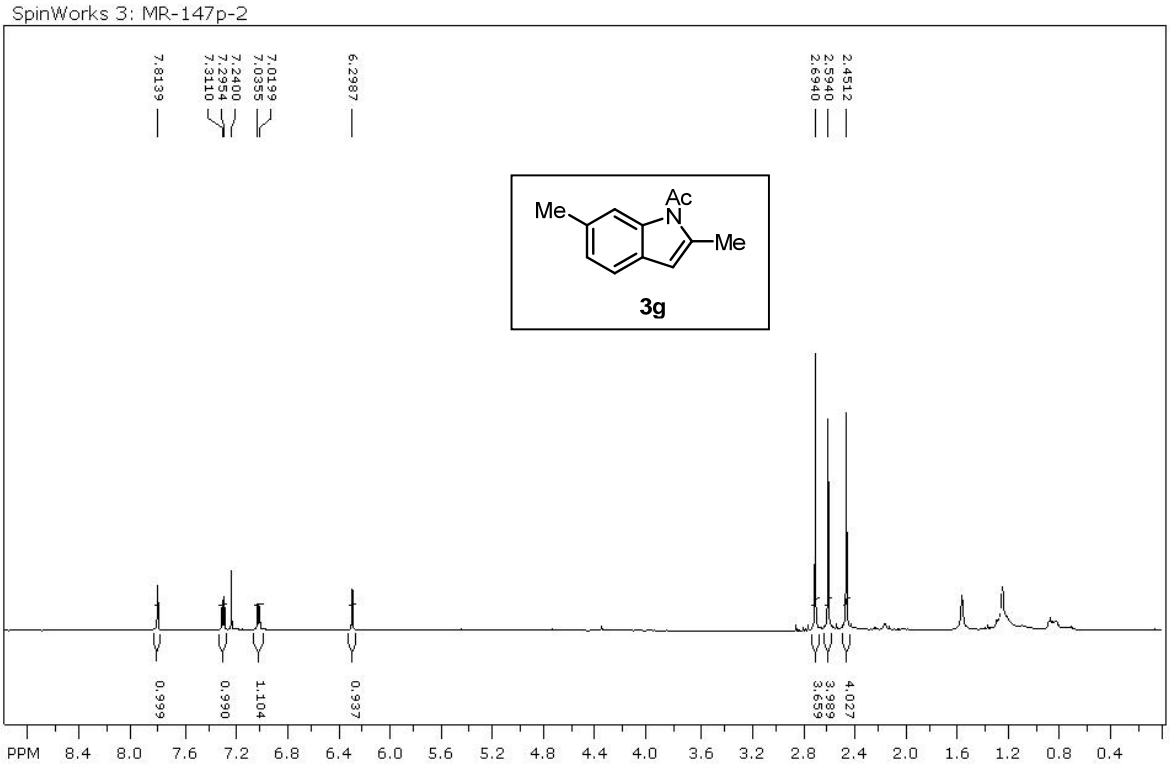
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6.2987
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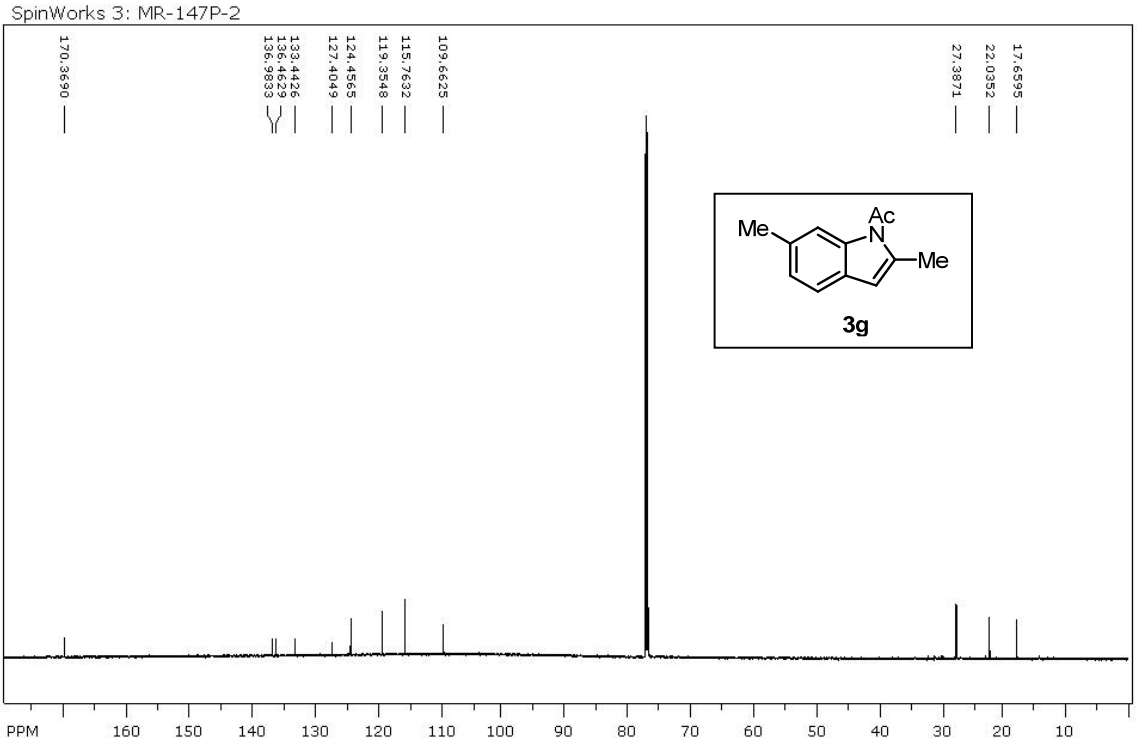
2.5940
2.4512
Me
Ac
N
Me
3g
0.999
0.990
1.104
0.937
3.659
3.989
4.027
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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115.7632
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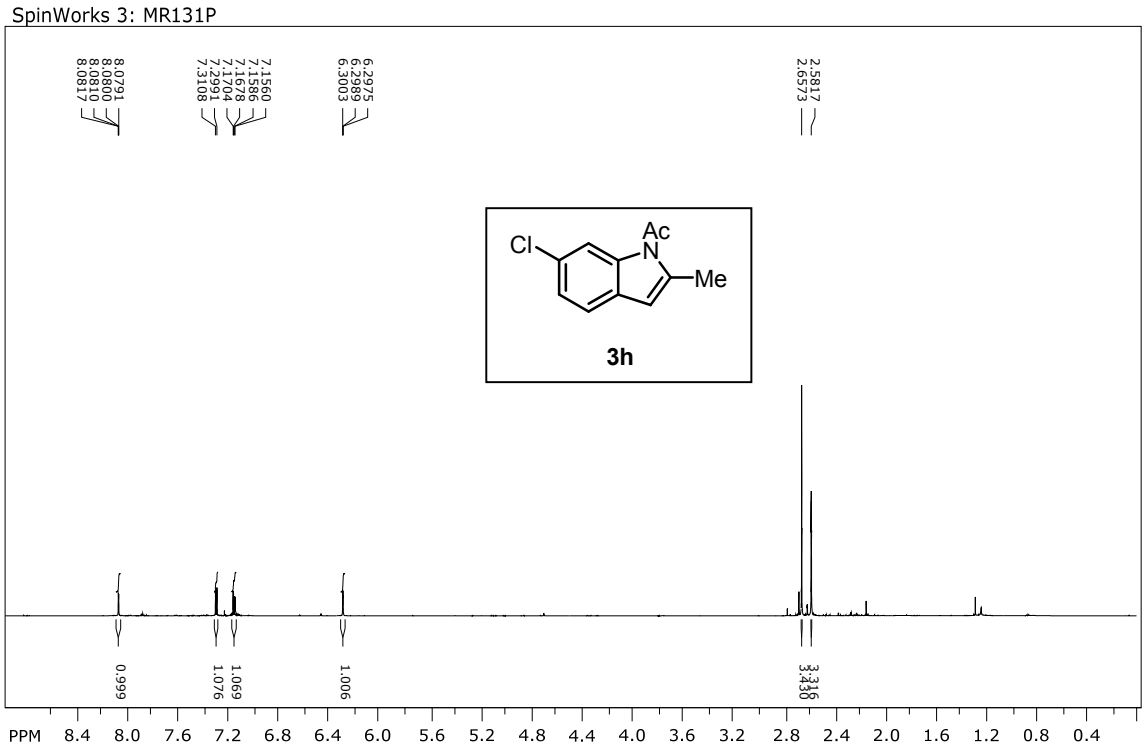
N
Me
3g
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10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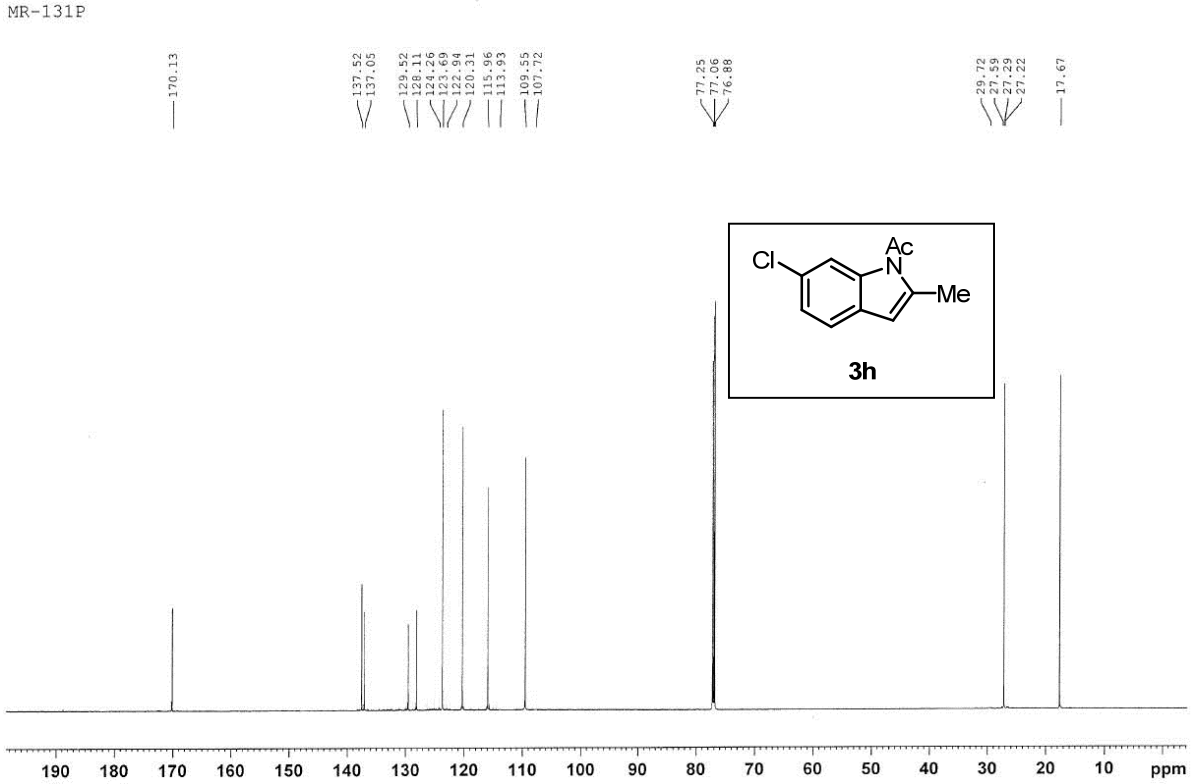
7.1560
6.3003
6.2989
6.2975
2.6573
2.5817
Cl
Ac
N
Me
3h
0.999
1.076
1.069
1.006
3.316
3.430
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4


MR-131P
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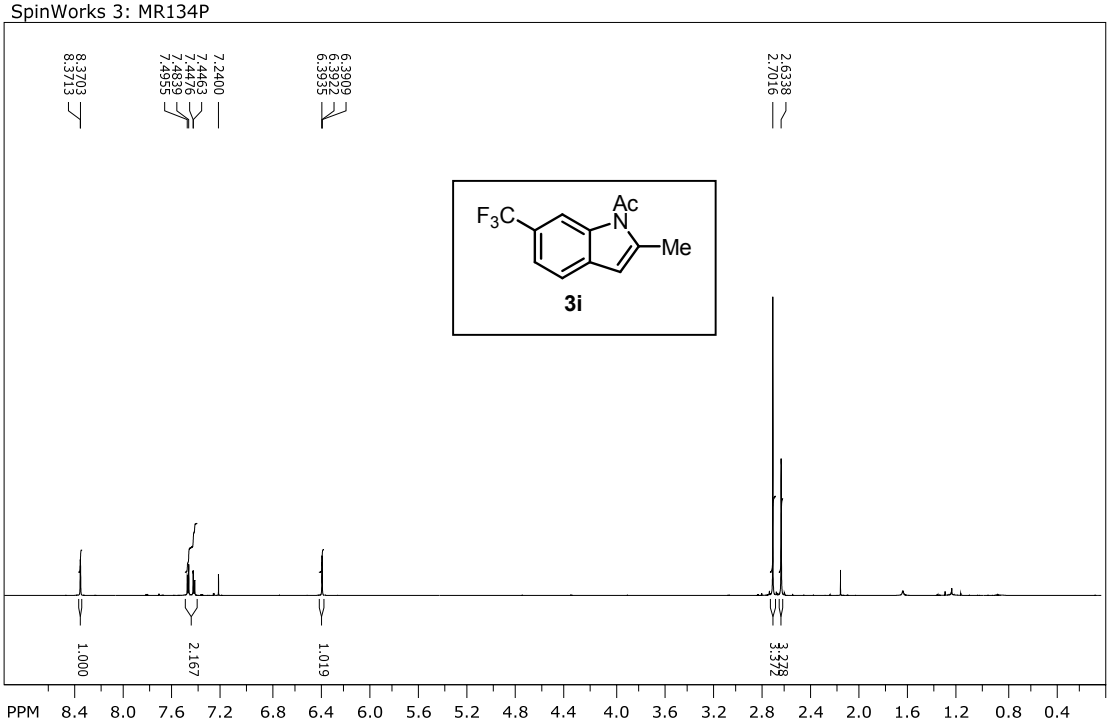
137.05
129.52
128.11
124.26
123.69
122.94
120.31
115.96
113.93
109.55
107.72
77.25
77.06
76.88
29.72
27.59
27.29
27.22
17.67
Cl
Ac
N
Me
3h
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

SpinWorks 3: MR134P



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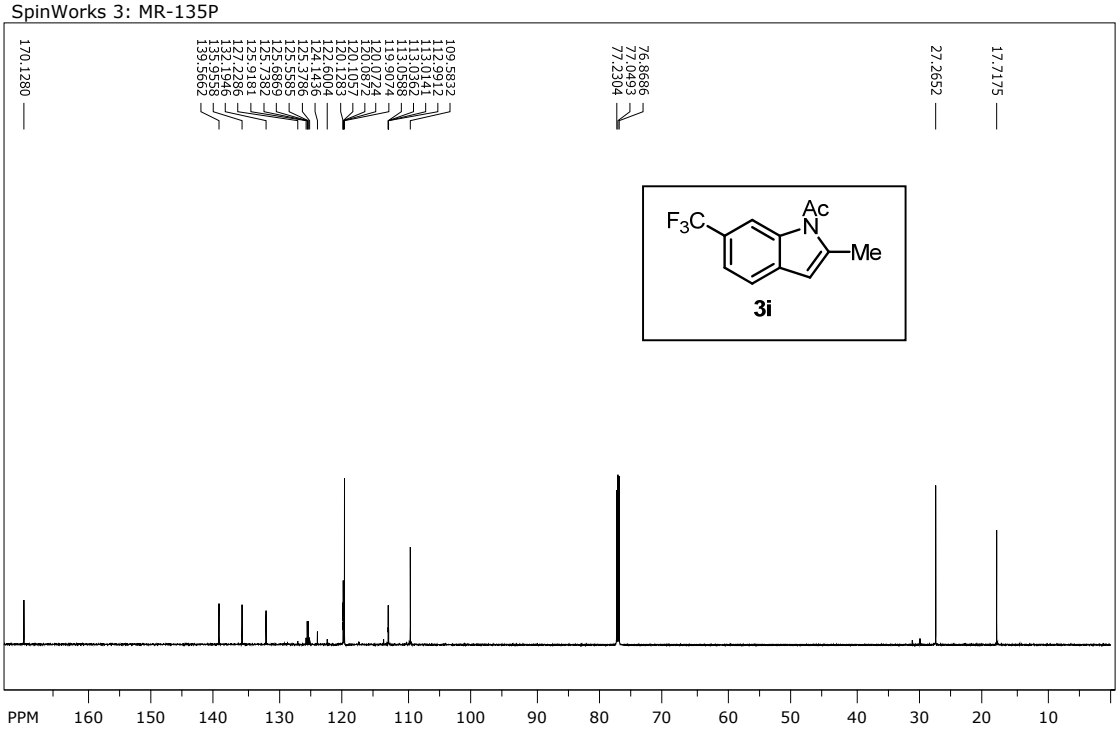

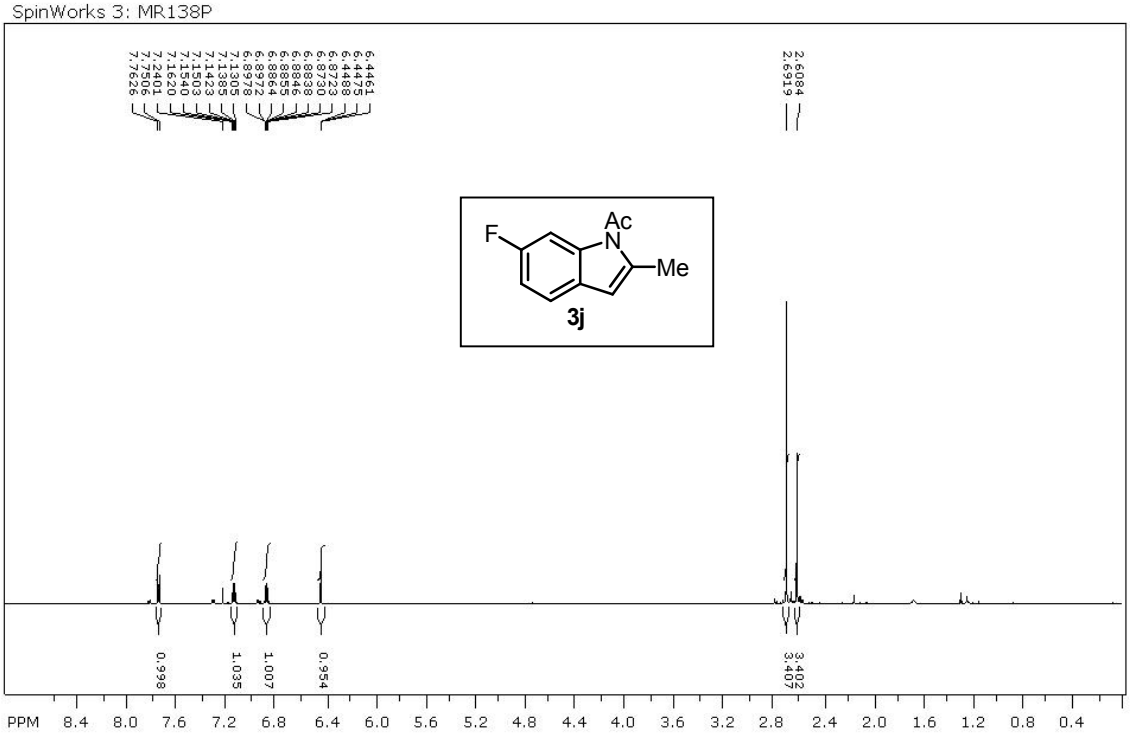
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7.1385
7.1305
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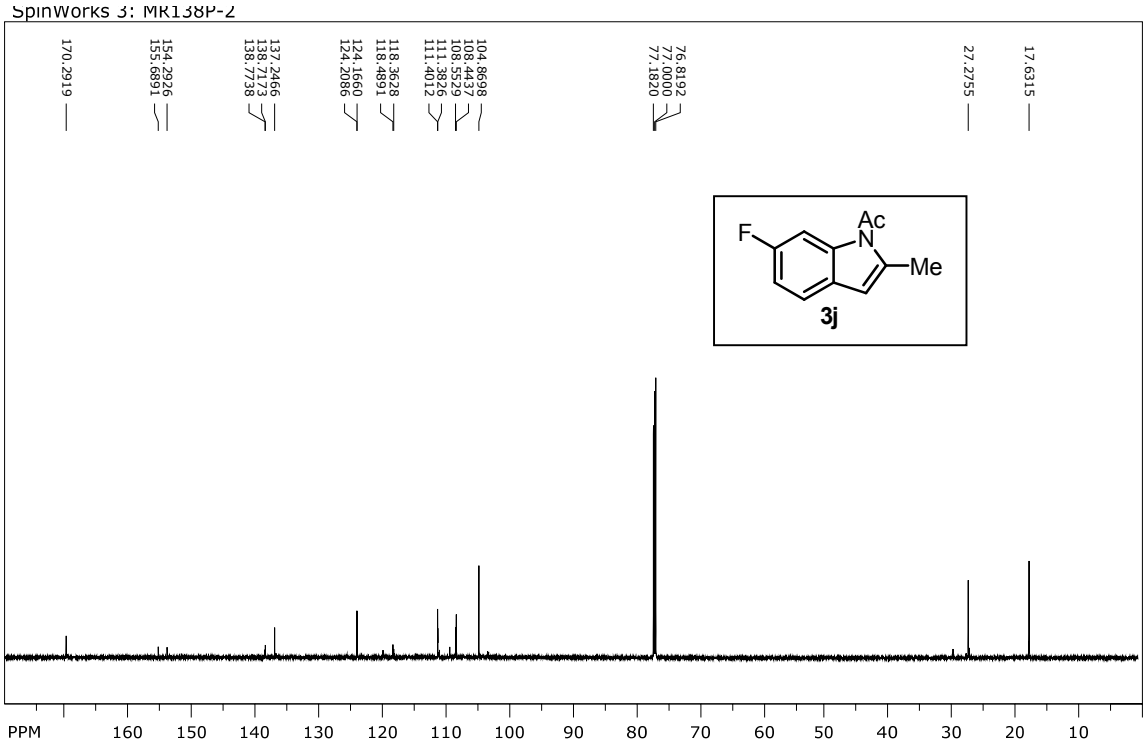
6.8972
6.8864
6.8855
6.8838
6.8730
6.8723
6.4488
6.4475
6.4461
2.6919
2.6084
F
Ac
N
Me
3j
0.998
1.035
1.007
0.954
3.407
3.402
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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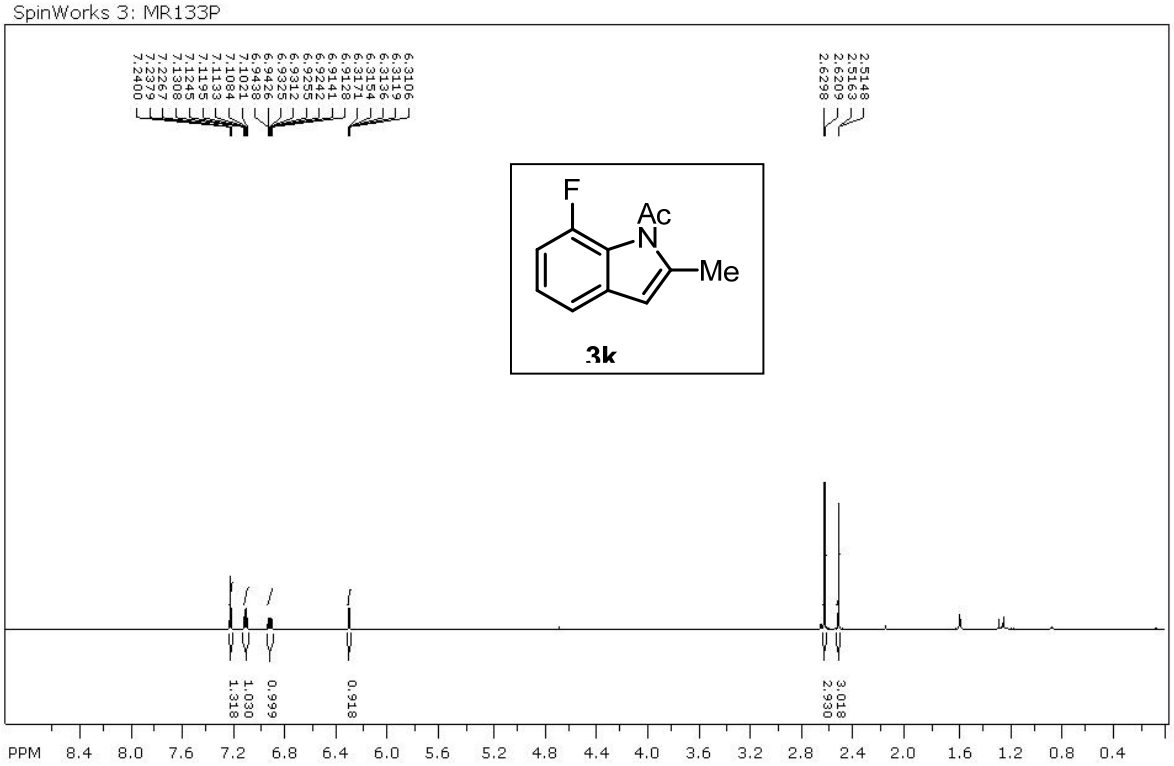
154.2926
138.7738
138.7173
137.2466
124.2086
124.1660
118.4891
118.3628
111.4012
111.3826
108.5529
108.4437
104.8698
77.1820
77.0000
76.8192
27.2755
17.6315
F
Ac
N
Me
3j
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

SpinWorks 3: MR133P



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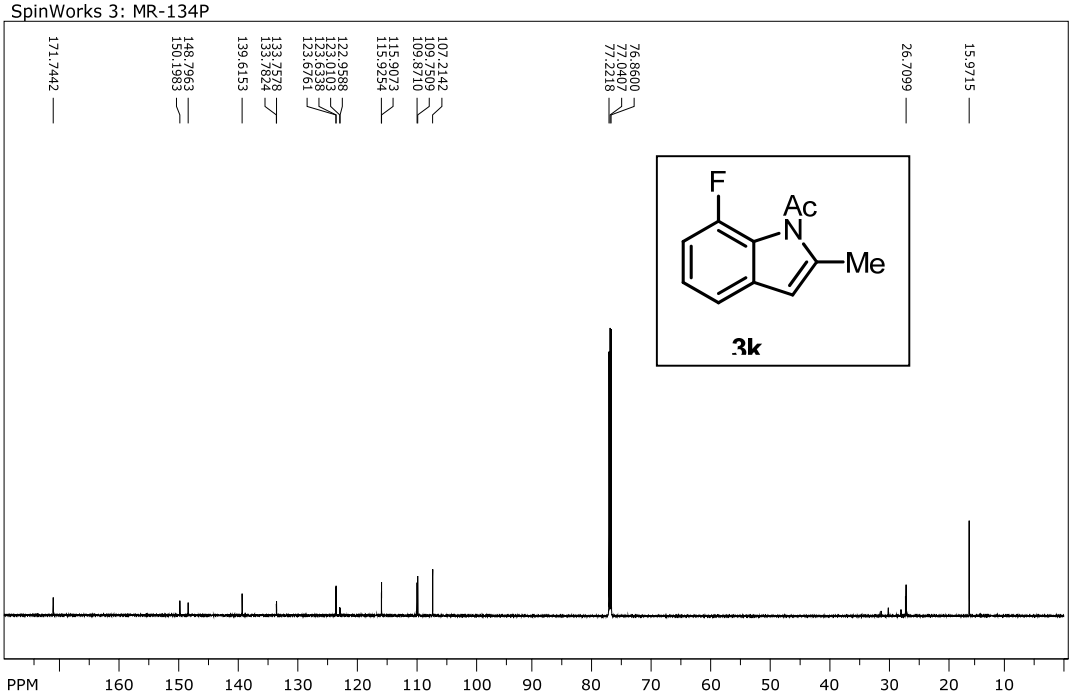

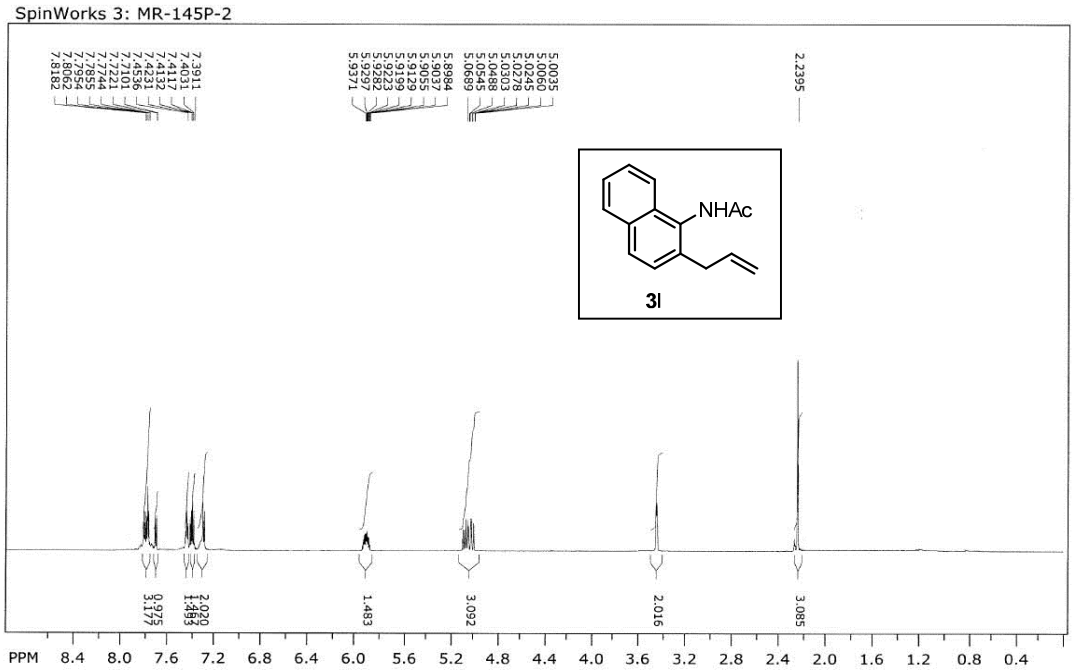
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7.4031
7.4117
7.4231
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5.0303
5.0278
5.0245
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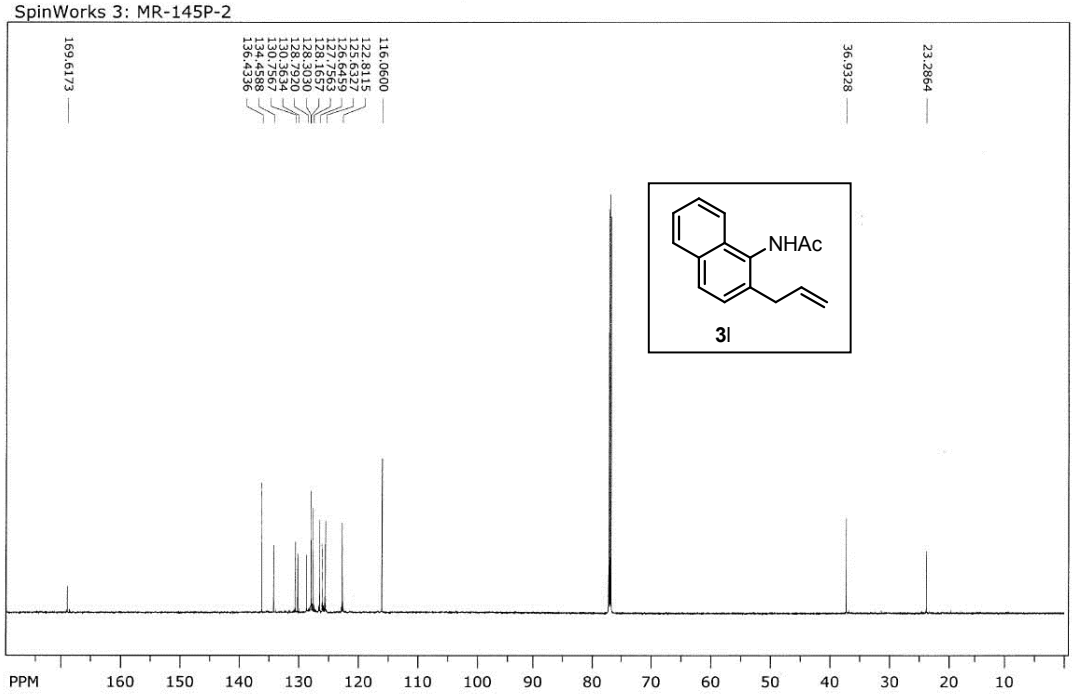
5.0035
2.2395
NHAc
3l
3.177
0.975
2.020
1.493
1.483
3.092
2.016
3.085
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4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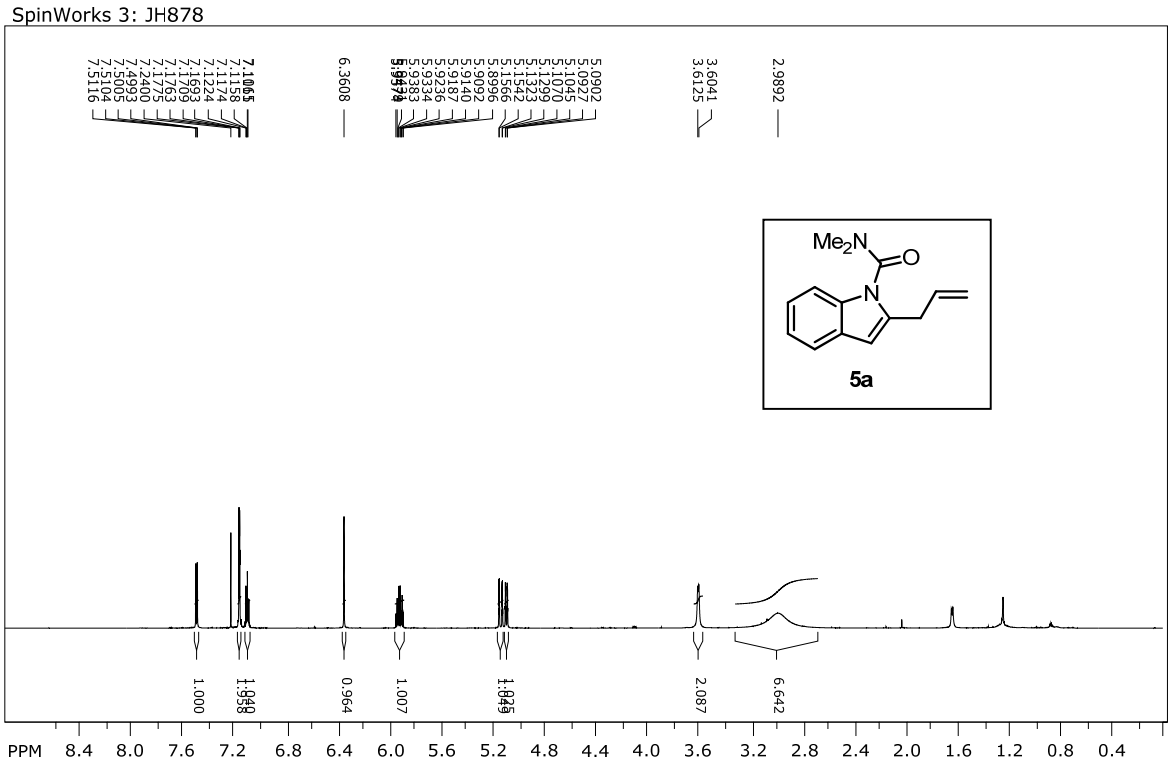
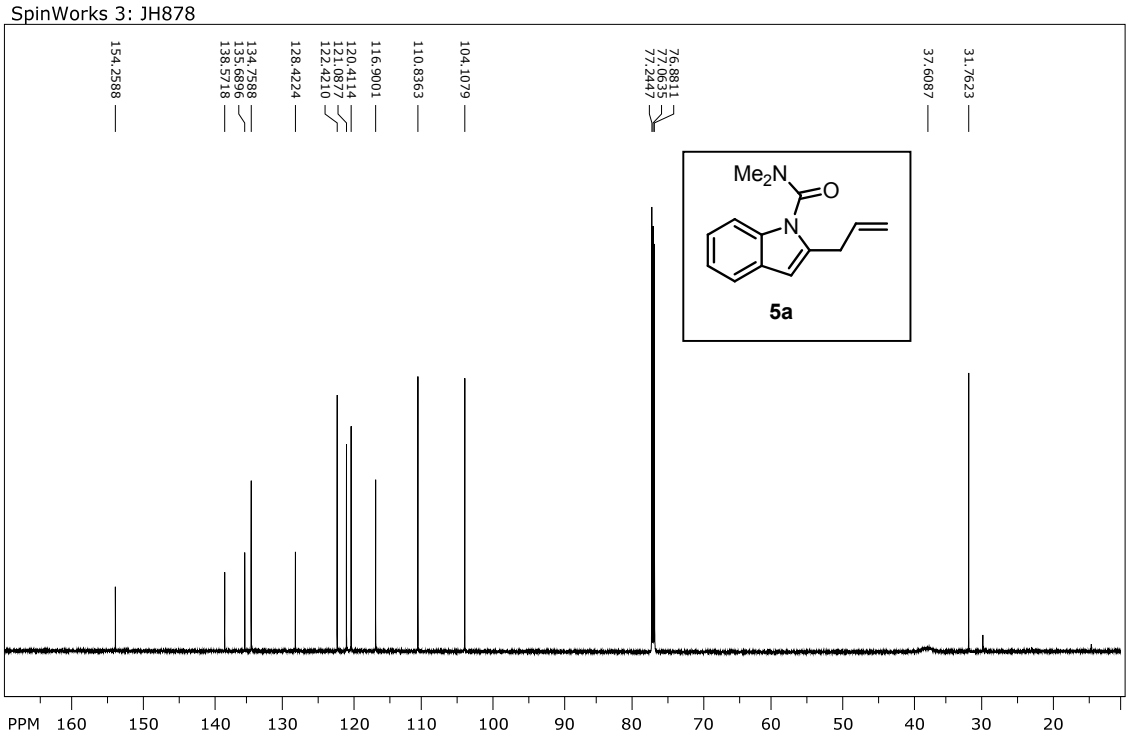
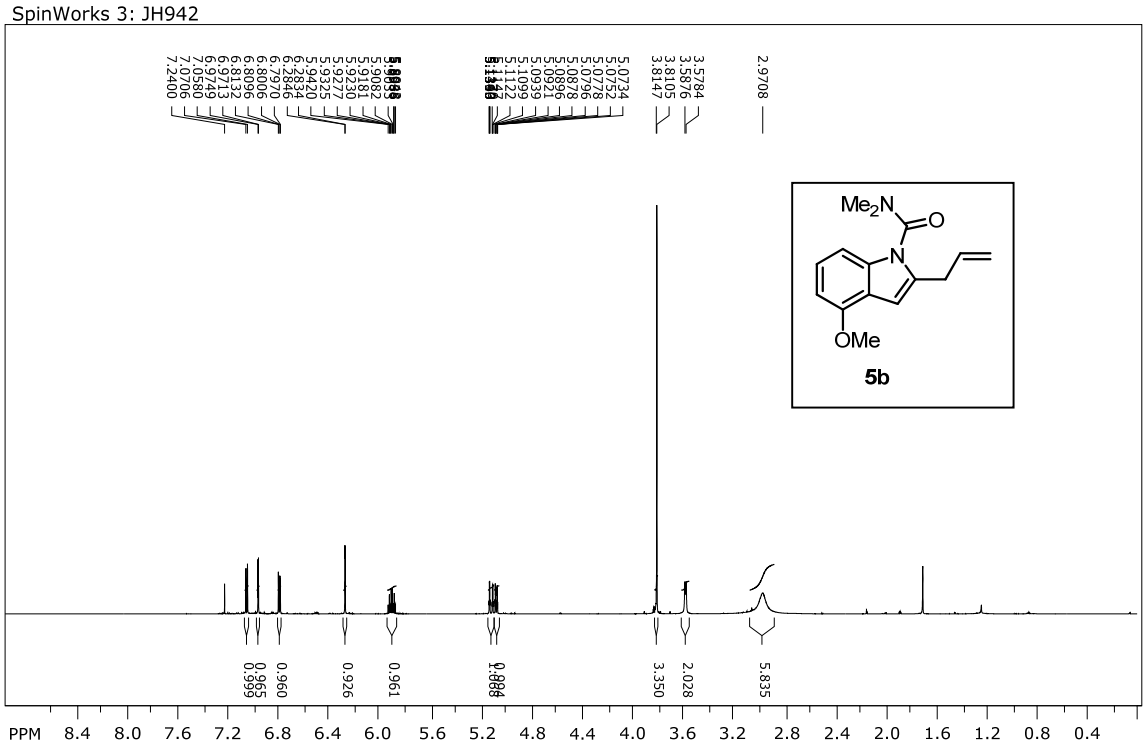
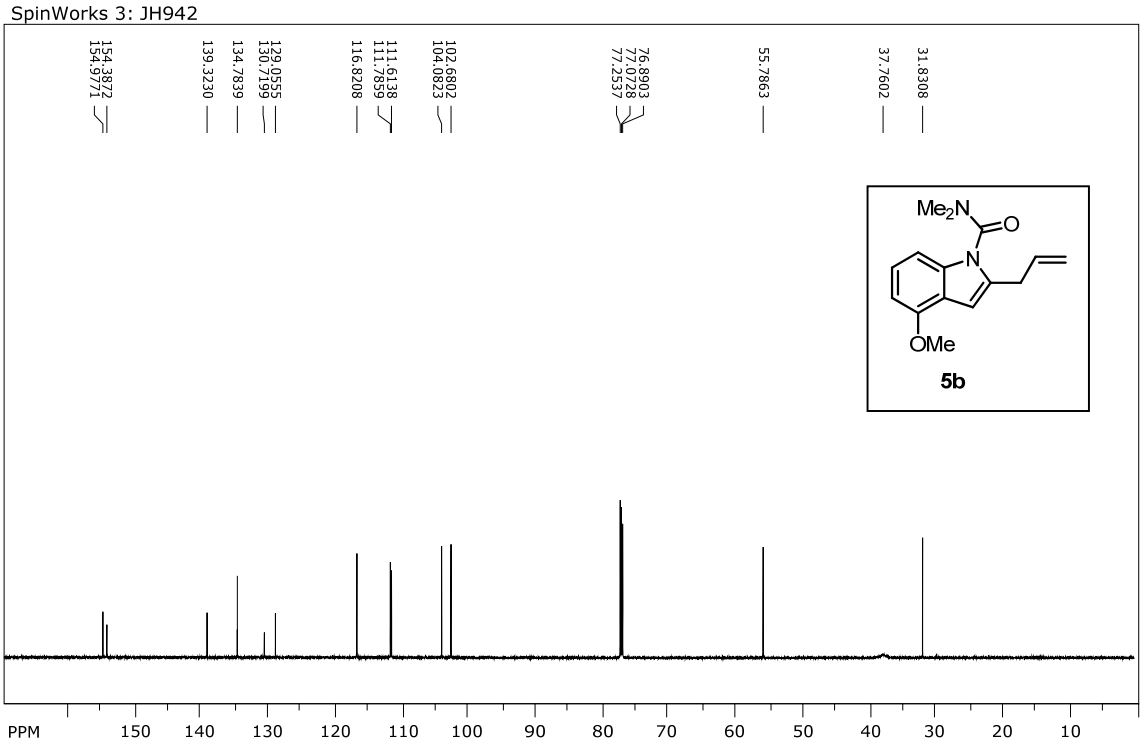
128.1653
126.6459
125.6327
122.8115
116.0600
36.9328
23.2864
NHAc
3l
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

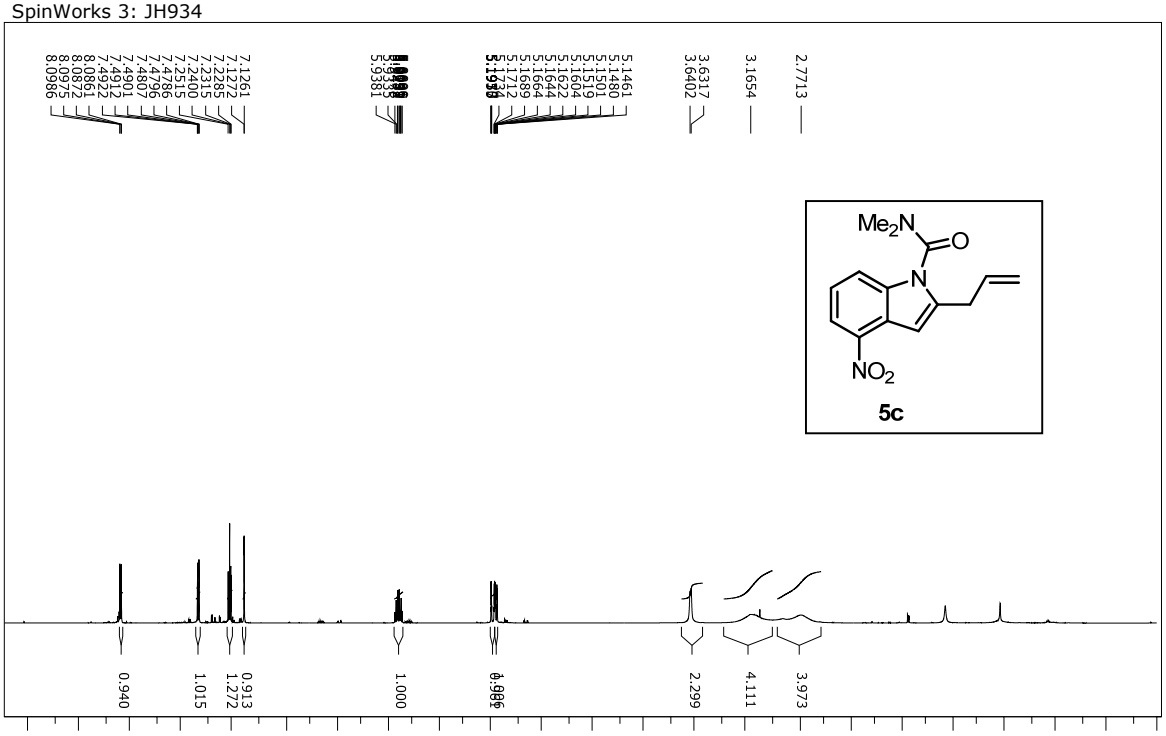

SpinWorks 3: JH878
7.5116
7.5104
7.5005
7.4993
7.2400
7.1795
7.1789
7.1683
7.1224
7.1174
7.1158
7.1065
6.3608
5.9374
5.9334
5.9236
5.9187
5.9140
5.8996
5.1566
5.1542
5.1323
5.1299
5.1070
5.1045
5.0927
5.0902
3.6125
3.6041
2.9892
Me2N
O
N
5a
1.000
1.958
0.964
1.007
1.049
2.087
6.642
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4


SpinWorks 3: JH878
154.2588
138.5718
135.6896
134.7588
128.4224
122.4210
121.0877
120.4114
116.9001
110.8363
104.1079
77.2447
77.0635
76.8811
37.6087
31.7623
Me2N
O
N
5a
PPM 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

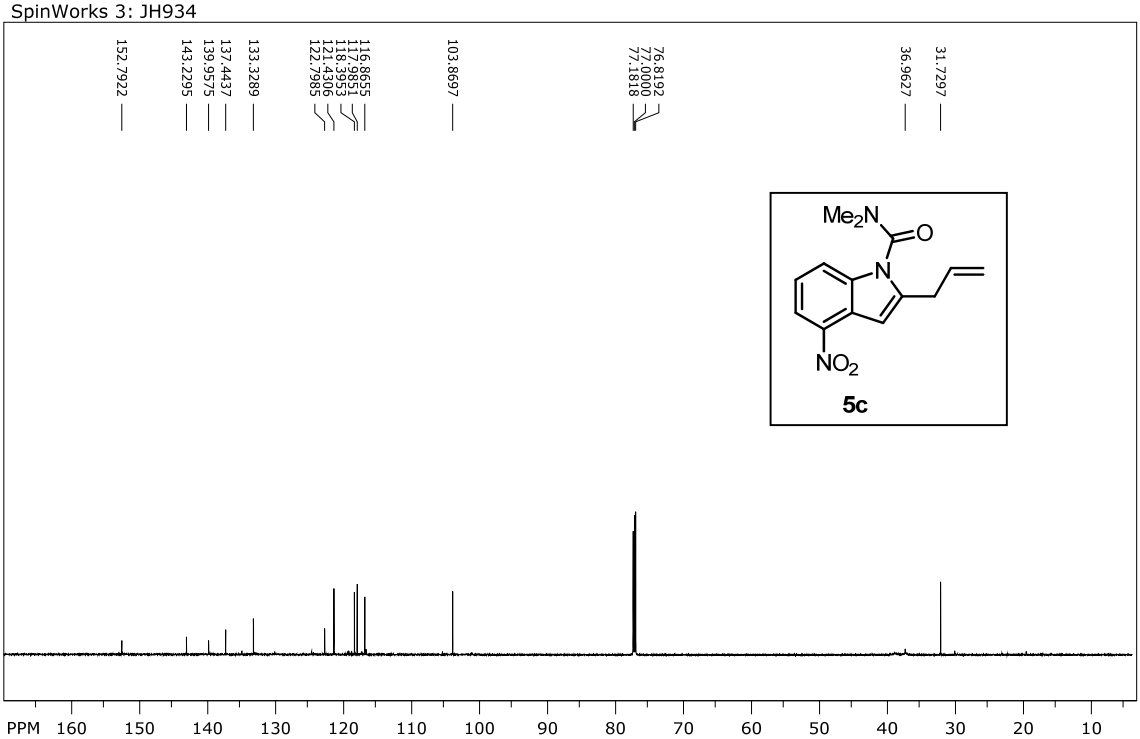

SpinWorks 3: JH942
7.2400
7.0706
7.0580
6.9749
6.9713
6.8132
6.8096
6.8006
6.7876
6.2834
5.9420
5.9325
5.9277
5.9230
5.9181
5.9082
5.0734
5.0778
5.0796
5.0878
5.0896
5.0921
5.0939
5.1099
5.1122
3.8147
3.8105
3.5876
3.5784
2.9708
0.999
0.965
0.960
0.926
0.961
0.884
3.350
2.028
5.835
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Me2N
O
N
OMe
5b


SpinWorks 3: JH942
154.3872
154.9771
139.3230
134.7839
129.0555
130.7199
116.8208
111.6138
111.7859
102.6802
104.0823
76.8903
77.0728
77.2537
55.7863
37.7602
31.8308
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Me2N
O
N
OMe
5b

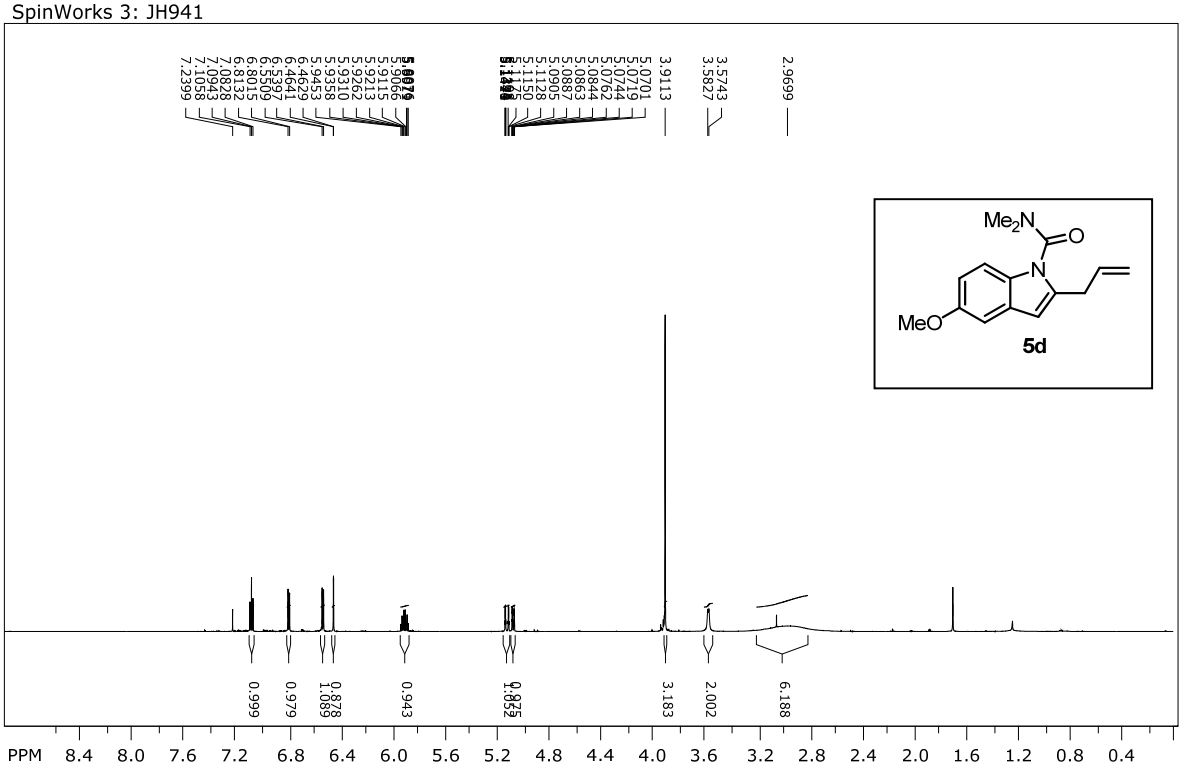
SpinWorks 3: JH934



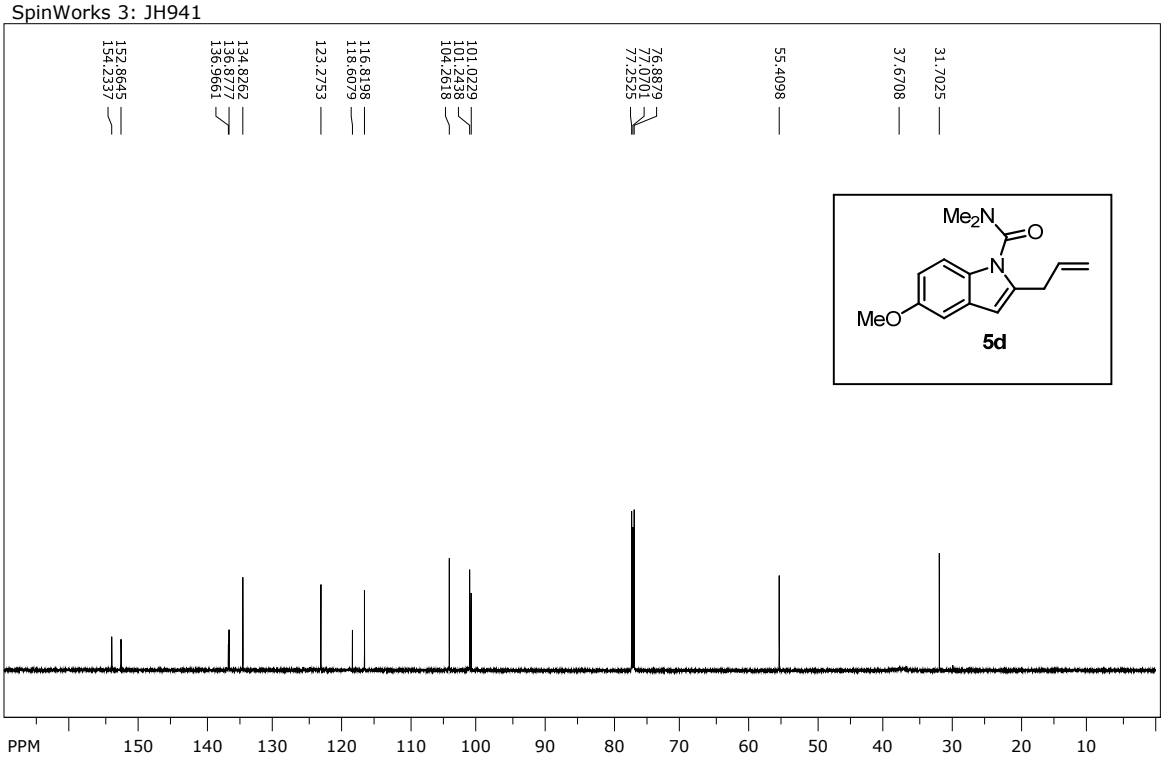
SpinWorks 3: JH934



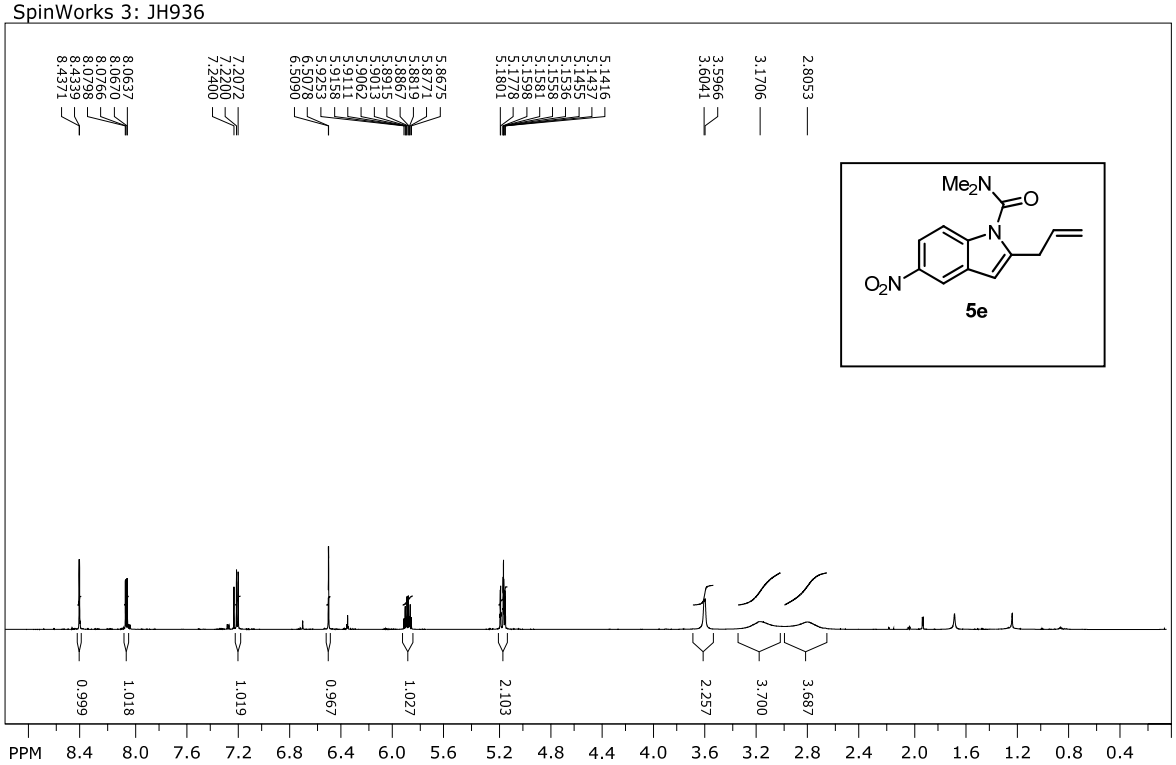
SpinWorks 3: JH941



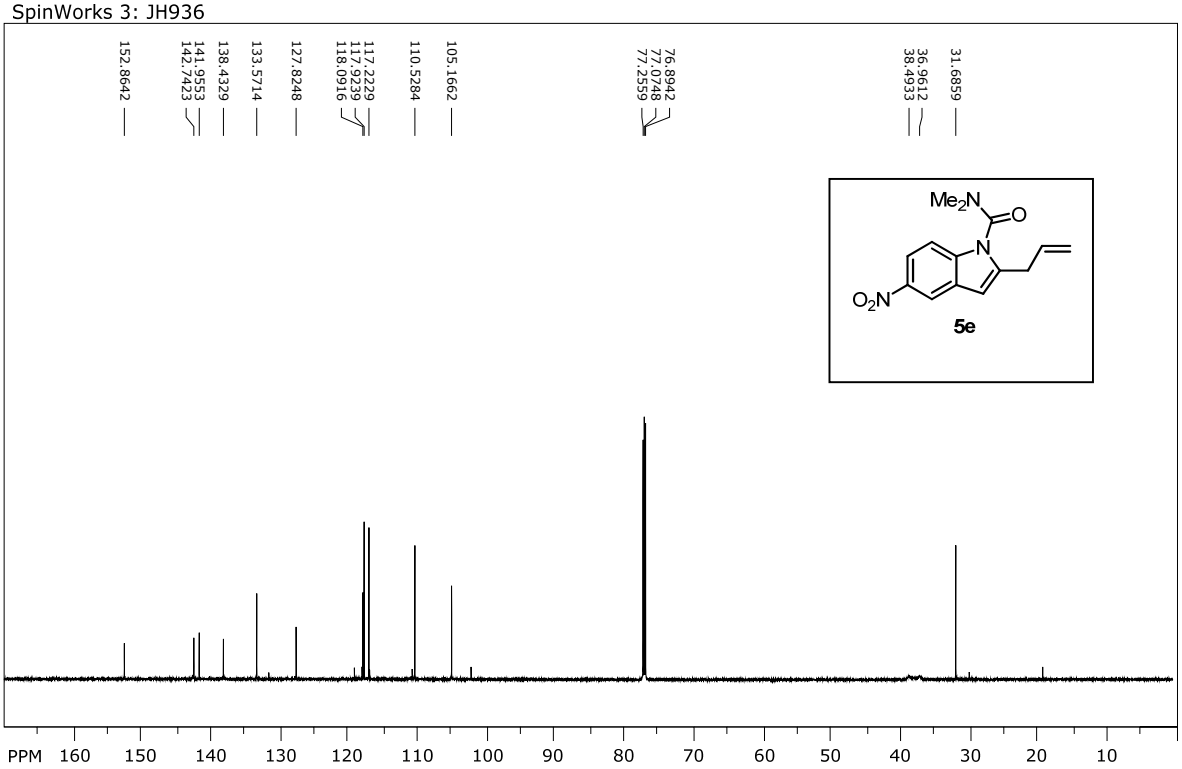
SpinWorks 3: JH941

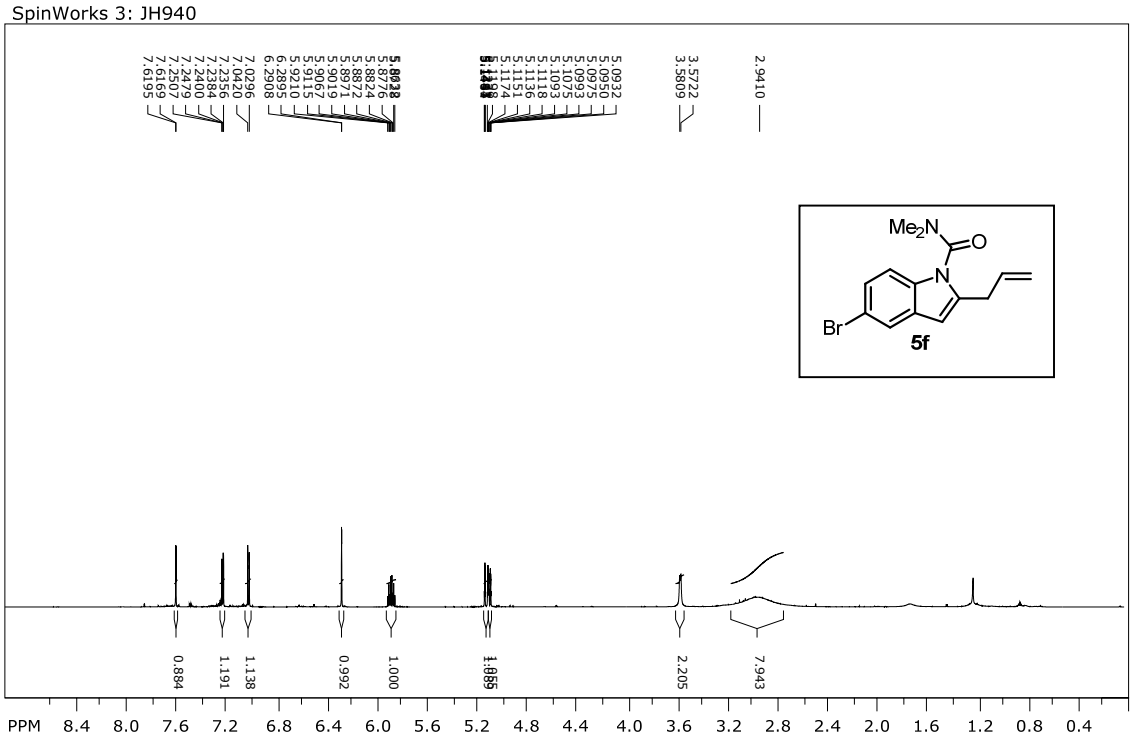


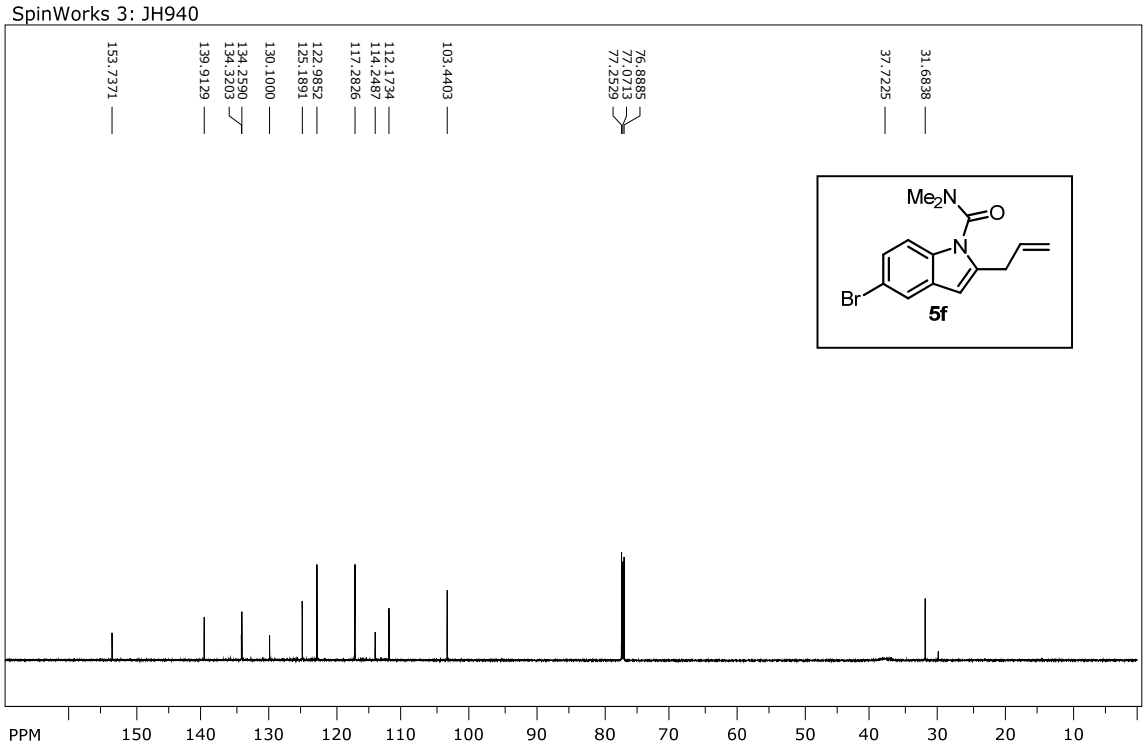
SpinWorks 3: JH936

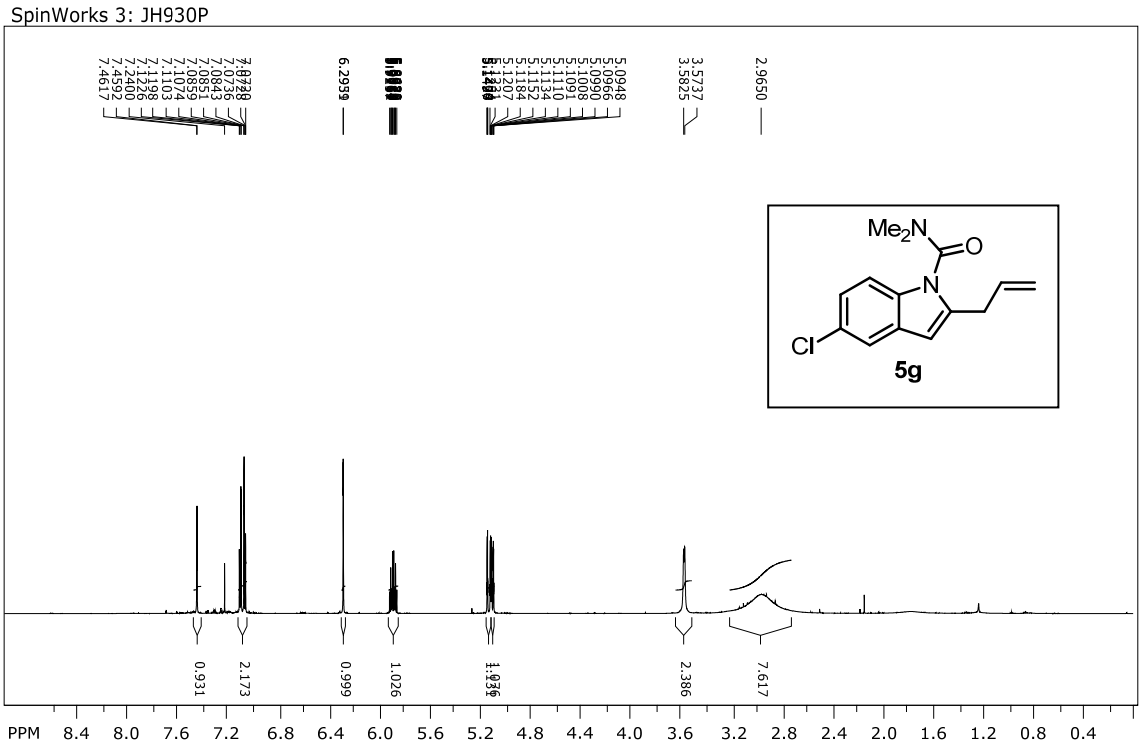


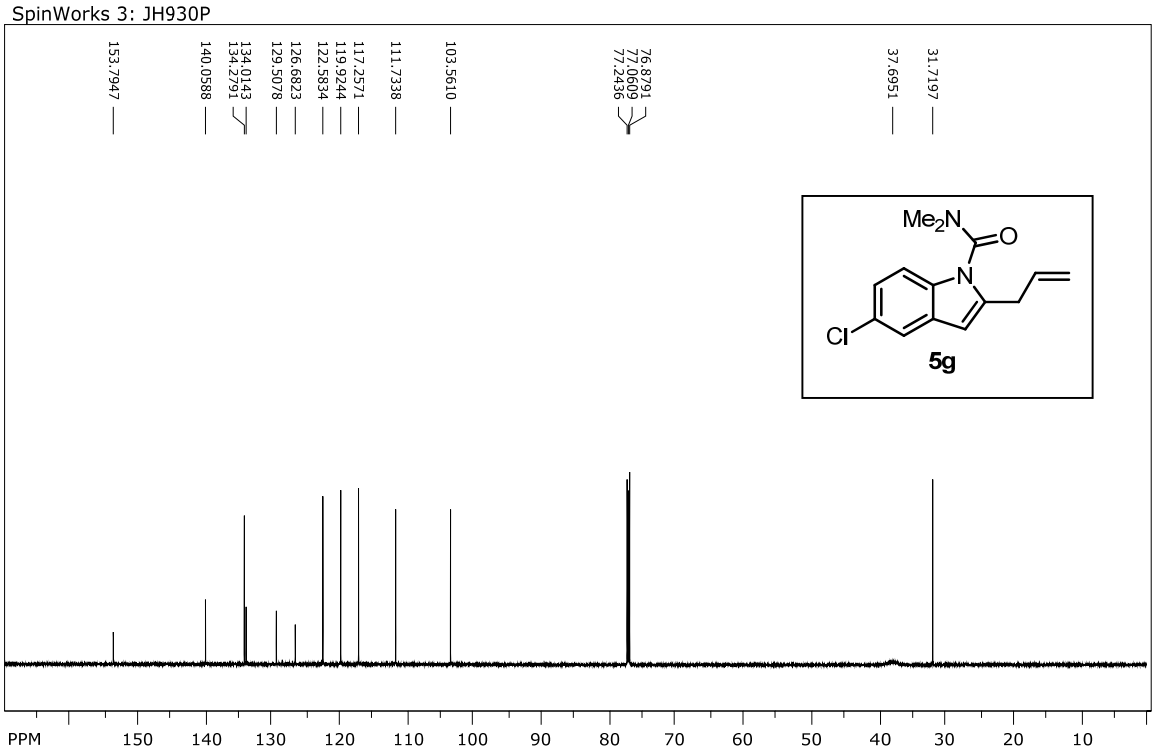
SpinWorks 3: JH936

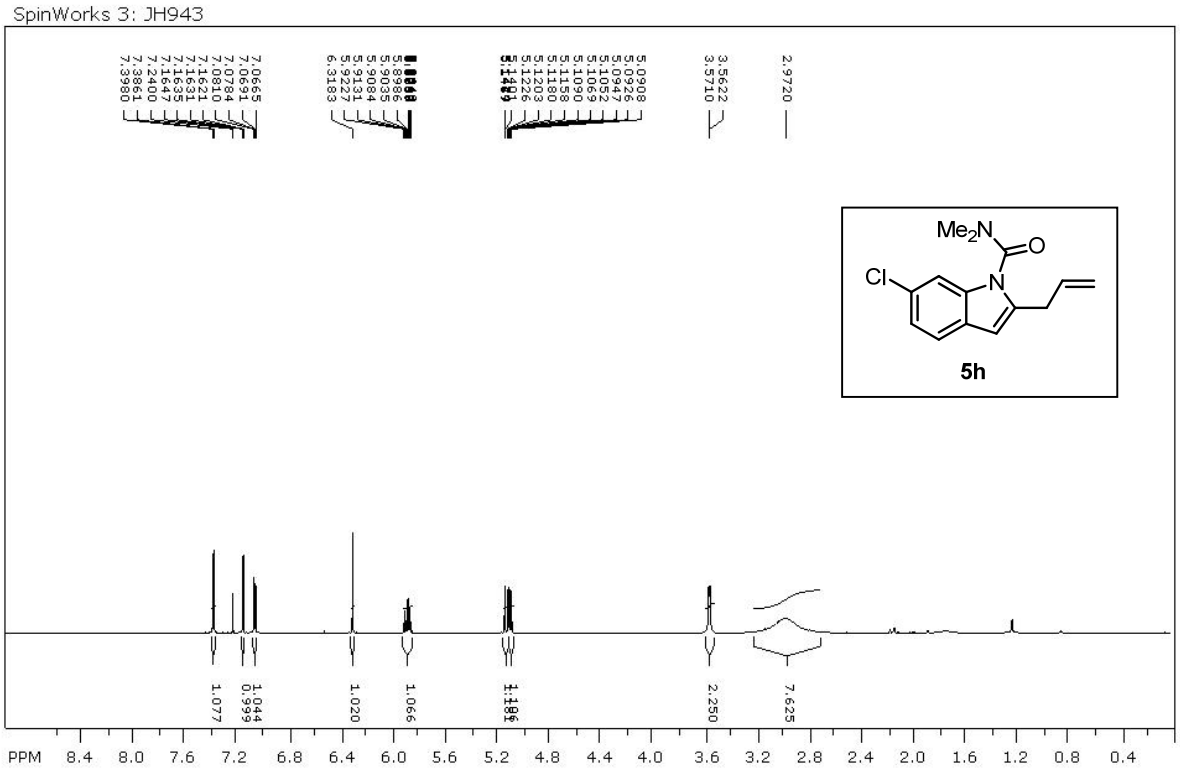


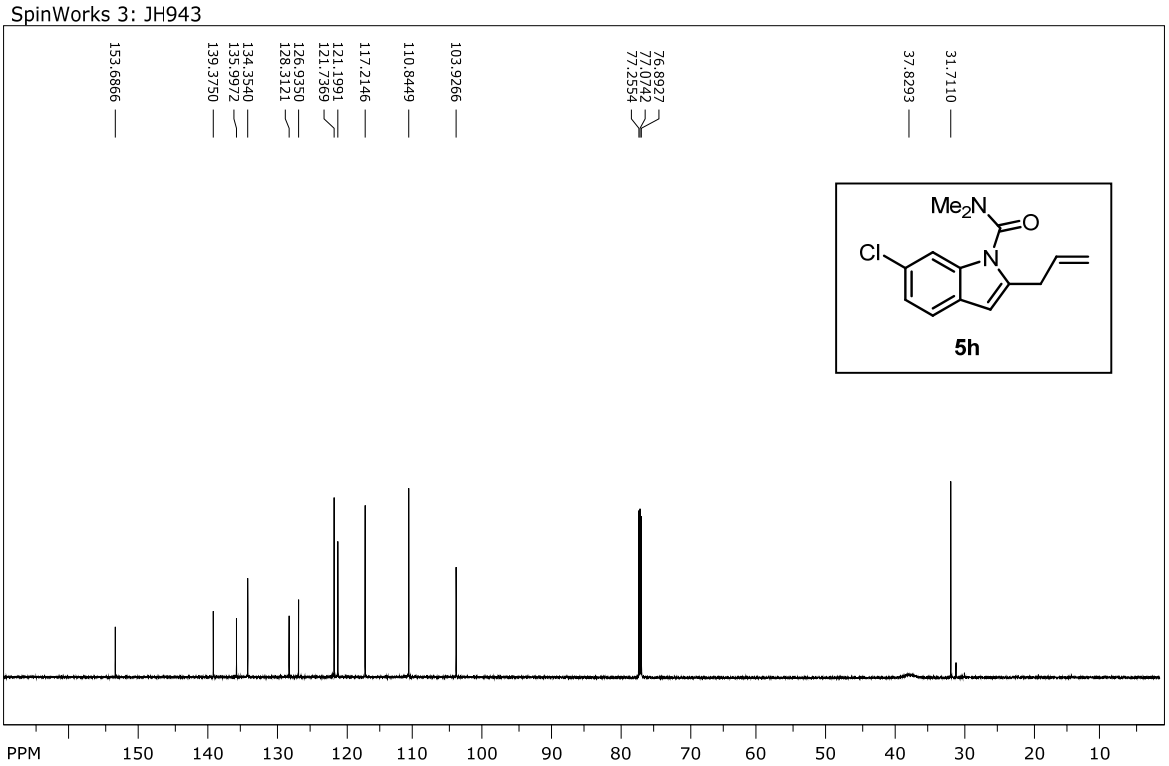

SpinWorks 3: JH940
7.6195
7.6169
7.2507
7.2400
7.2384
7.2356
7.0420
7.0296
6.2908
6.2895
5.9210
5.9115
5.9067
5.9019
5.8971
5.8872
5.8824
5.0932
5.0950
5.0973
5.0993
5.1075
5.1093
5.1118
5.1136
5.1151
5.1174
3.5722
3.5809
2.9410
Me2N
O
N
Br
5f
0.884
1.191
1.138
0.992
1.000
2.205
7.943
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

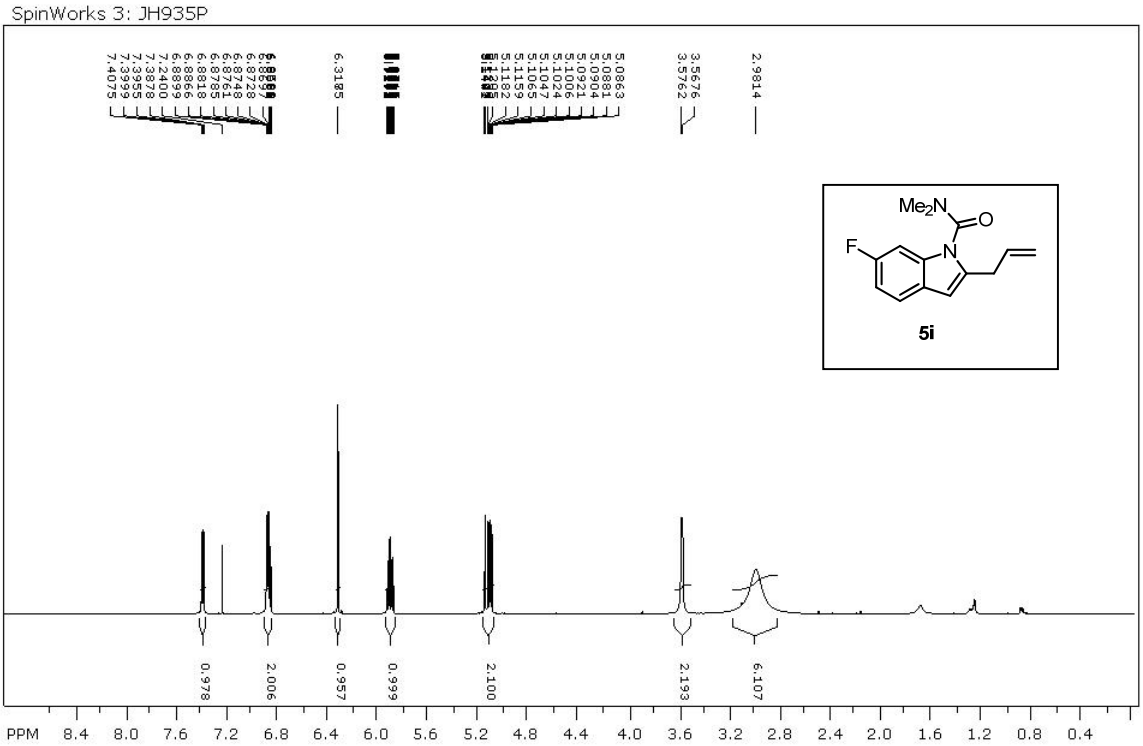

SpinWorks 3: JH940
153.7371
139.9129
134.3203
134.2590
130.1000
125.1891
122.9852
117.2826
114.2487
112.1734
103.4403
77.2529
77.0713
76.8885
37.7225
31.6838
Me2N
O
N
Br
5f
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

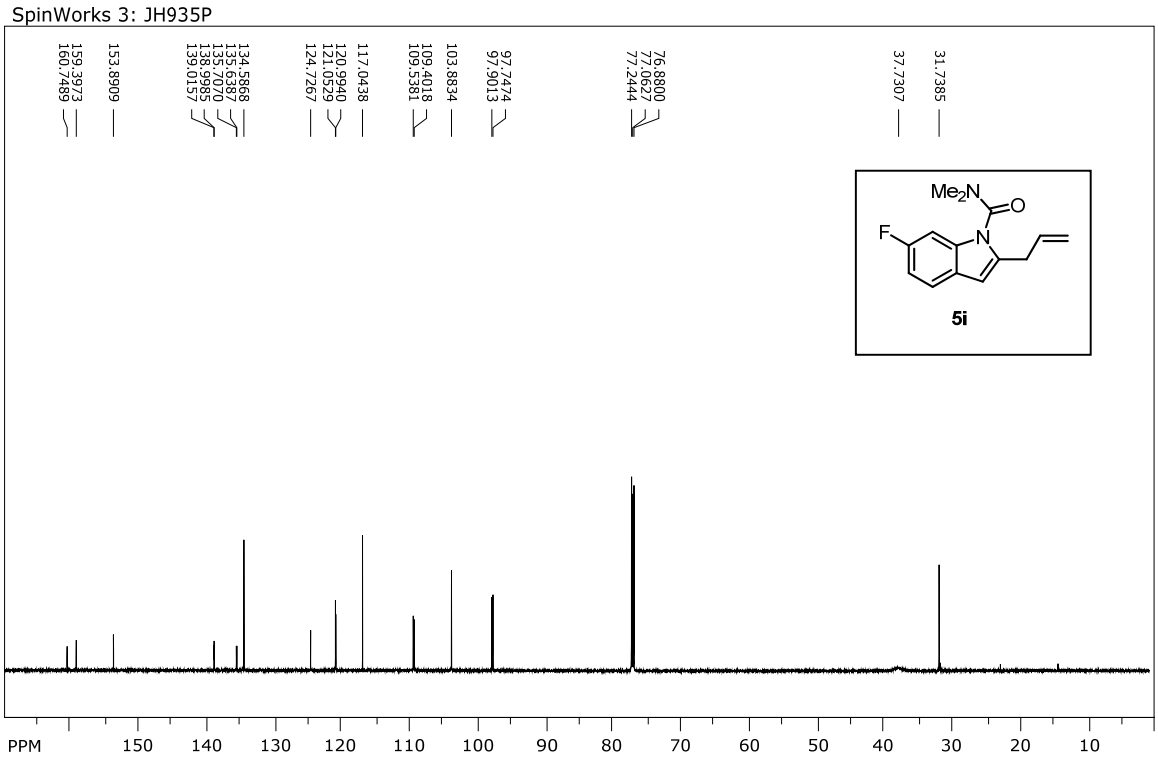

SpinWorks 3: JH930P
7.4617
7.4569
7.1226
7.1198
7.1103
7.1074
7.0859
7.0851
7.0849
7.0778
6.2959
5.0948
5.0966
5.1090
5.1068
5.1091
5.1110
5.1134
5.1152
5.1184
5.1207
3.5737
3.5825
2.9650
Me2N
O
N
Cl
5g
0.931
2.173
0.999
1.026
2.386
7.617
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4


SpinWorks 3: JH930P
153.7947
140.0588
134.0143
134.2791
129.5078
126.6823
122.5834
119.9244
117.2571
111.7338
103.5610
76.8791
77.0609
77.2436
37.6951
31.7197
Me2N
O
N
Cl
5g
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

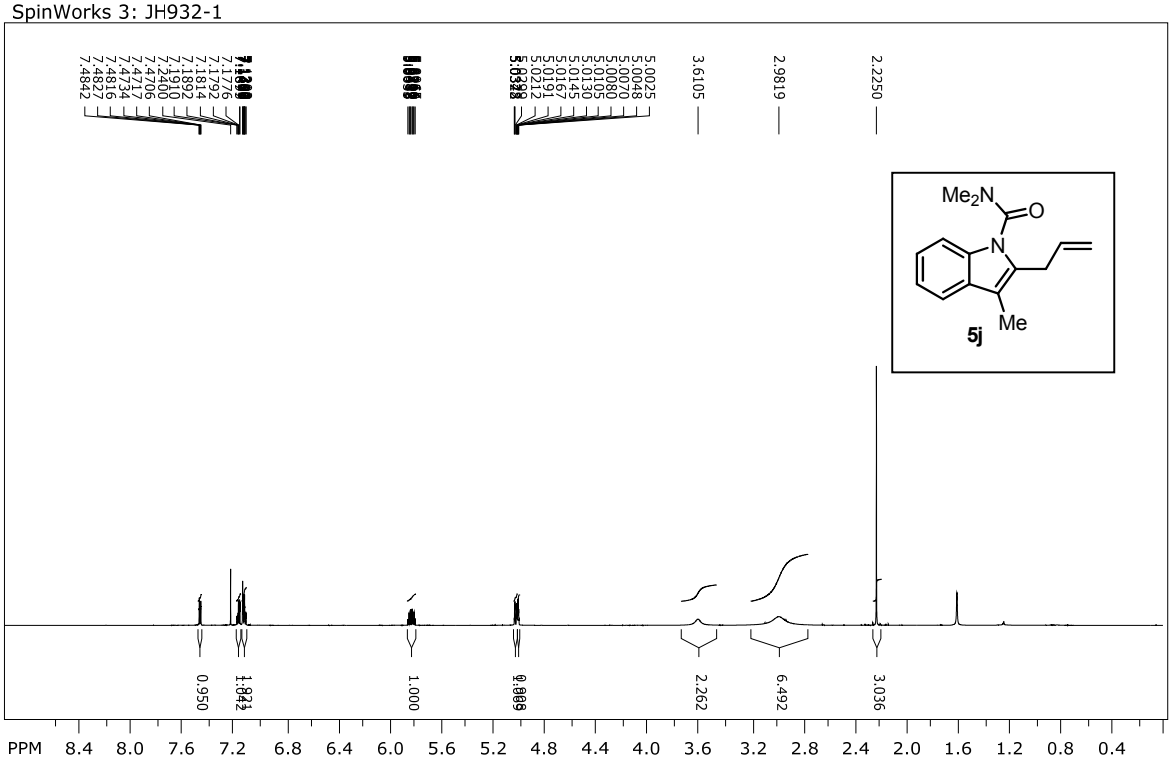

SpinWorks 3: JH943
7.0665
7.0691
7.0284
7.0210
7.1831
7.1635
7.1647
7.2400
7.3861
7.3980
6.3183
5.9227
5.9131
5.9084
5.0908
5.0926
5.0947
5.1052
5.1069
5.1090
5.1158
5.1200
5.1226
3.5622
3.5710
2.9720
1.077
0.999
1.044
1.020
1.066
2.250
7.625
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Me2N
O
Cl
N
5h


SpinWorks 3: JH943
153.6866
139.3750
135.9972
134.3540
128.3121
126.9350
121.7369
121.1991
117.2146
110.8449
103.9266
76.8927
77.0742
77.2554
37.8293
31.7110
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Me2N
O
Cl
N
5h

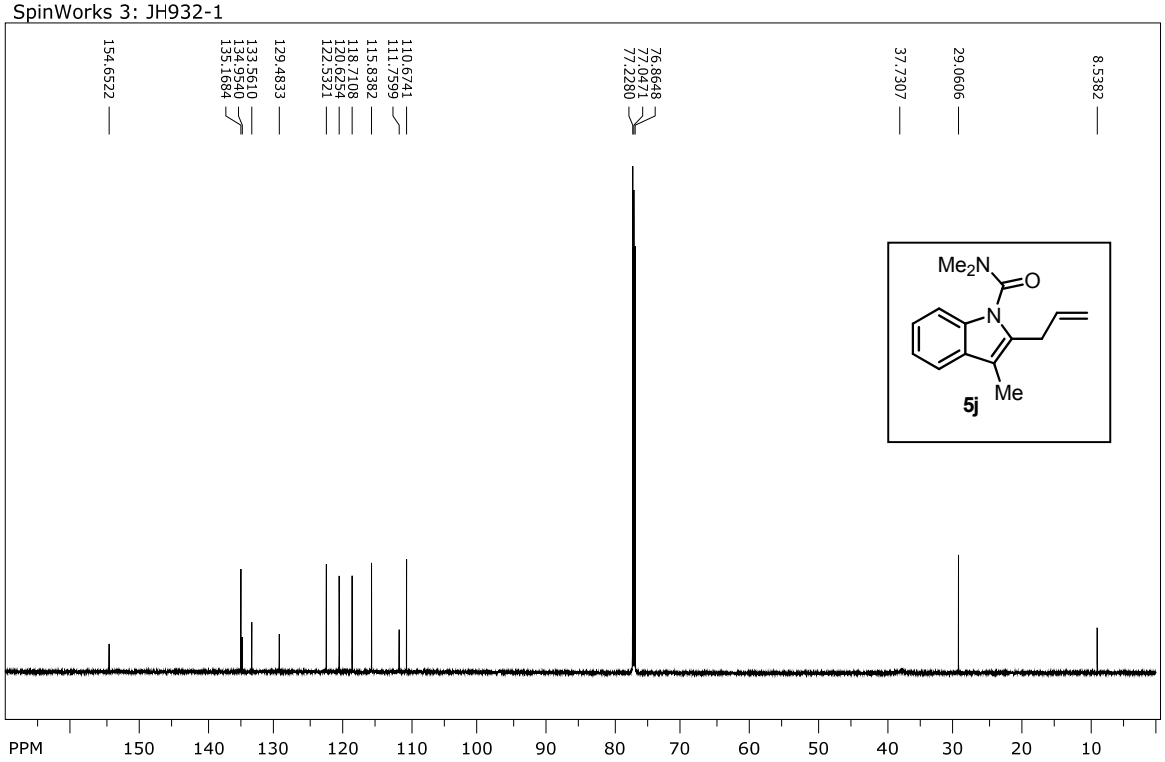

SpinWorks 3: JH935P
7.4075
7.3999
7.3955
7.3925
7.2490
6.8899
6.8866
6.8818
6.8785
6.8761
6.8748
6.8728
6.3185
5.0863
5.0881
5.0904
5.0921
5.1047
5.1065
5.1159
5.1182
3.5676
3.5762
2.9814
0.978
2.006
0.957
0.999
2.100
2.193
6.107
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Me2N
O
N
F
5i

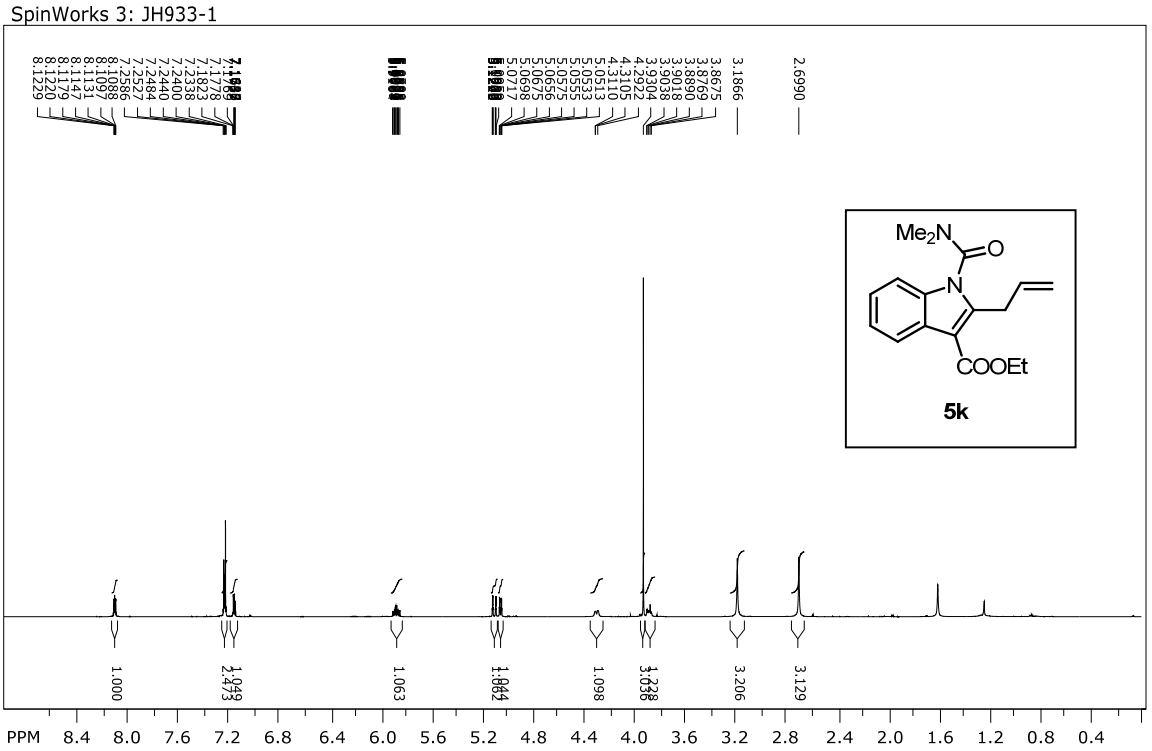

SpinWorks 3: JH935P
159.3973
160.7489
153.8909
139.0157
138.9985
135.7070
135.6387
134.5868
124.7267
121.0529
120.9940
117.0438
109.5381
109.4018
103.8834
97.9013
97.7474
77.2444
77.0627
76.8800
37.7307
31.7385
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Me2N
O
N
F
5i

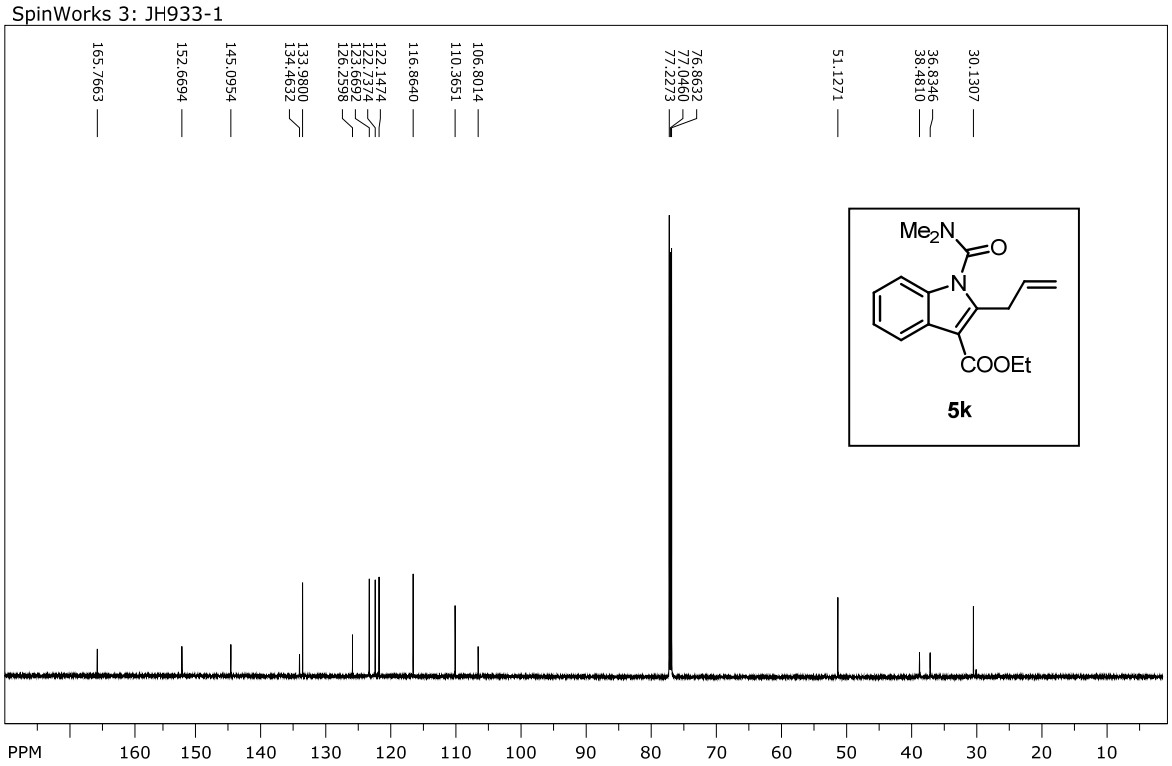
SpinWorks 3: JH932-1



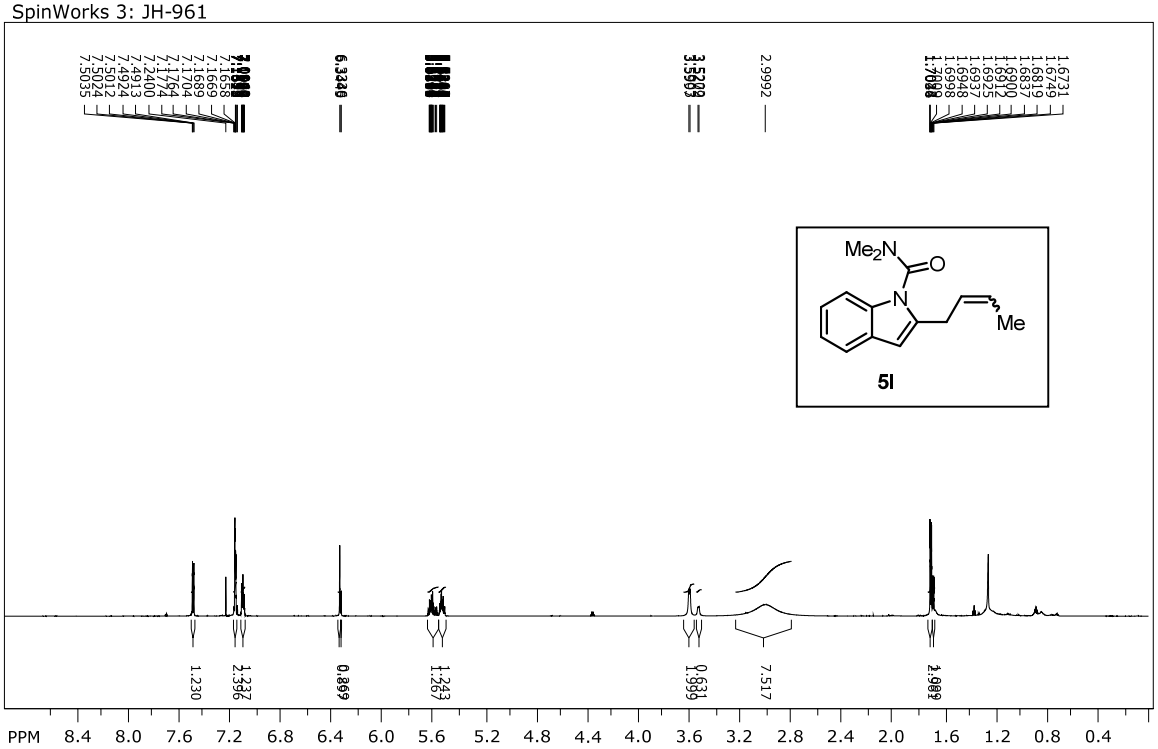
SpinWorks 3: JH932-1



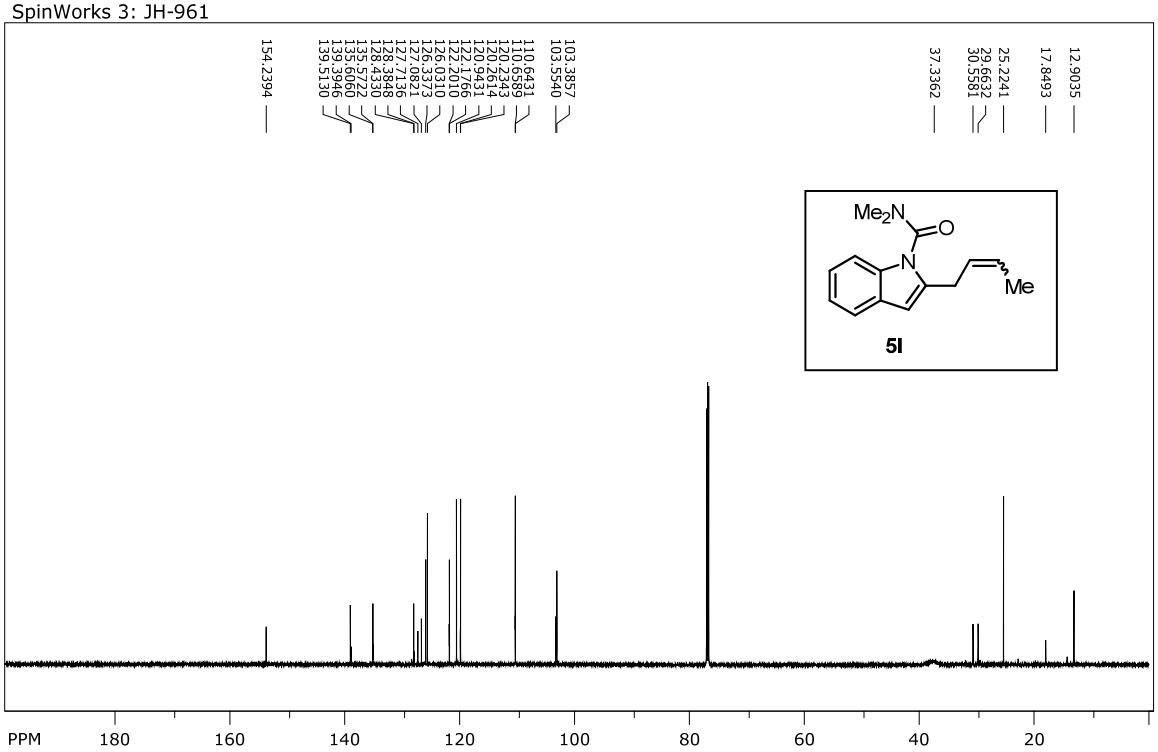

SpinWorks 3: JH933-1
Me2N
O
N
COOEt
5k
PPM


SpinWorks 3: JH933-1
Me2N
O
N
COOEt
5k
PPM

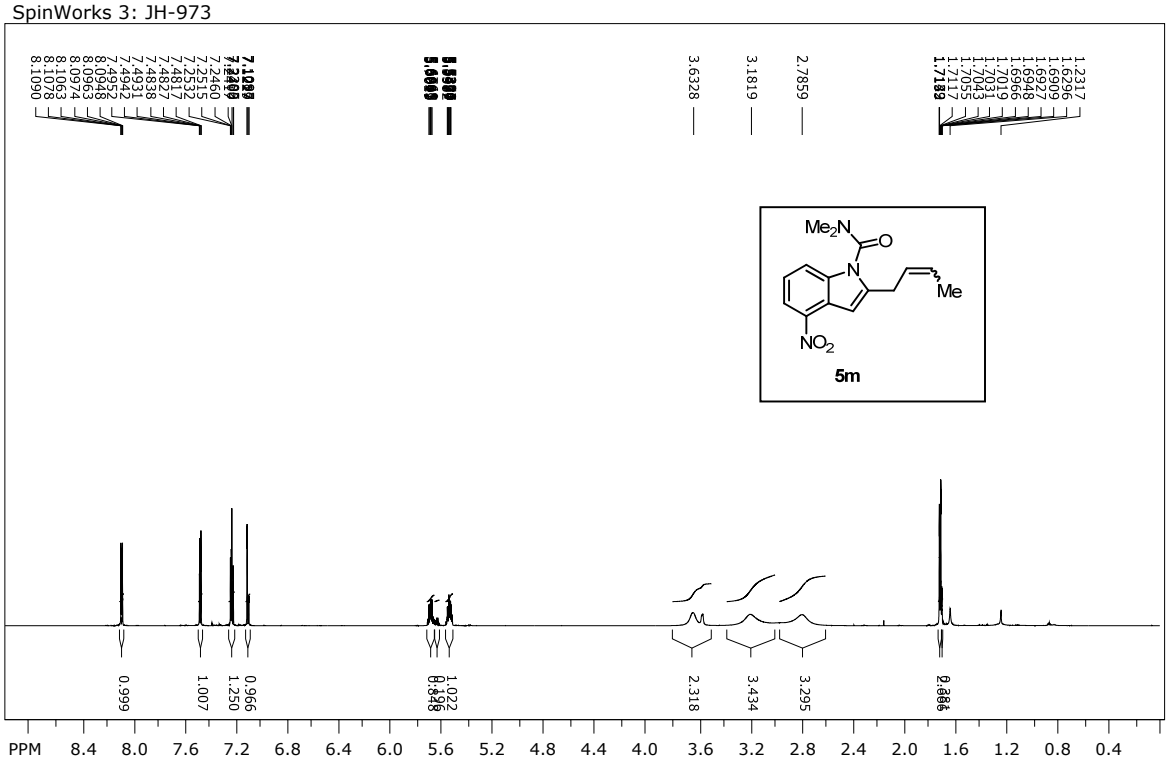
SpinWorks 3: JH-961



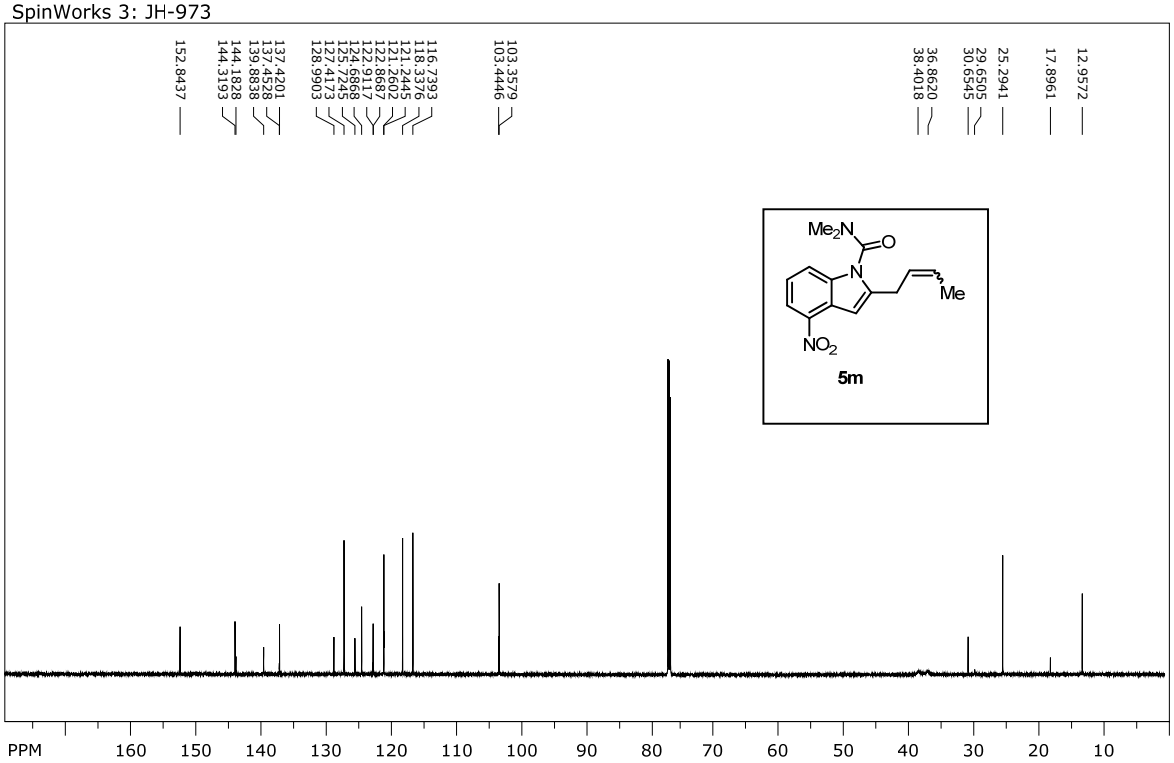
SpinWorks 3: JH-961



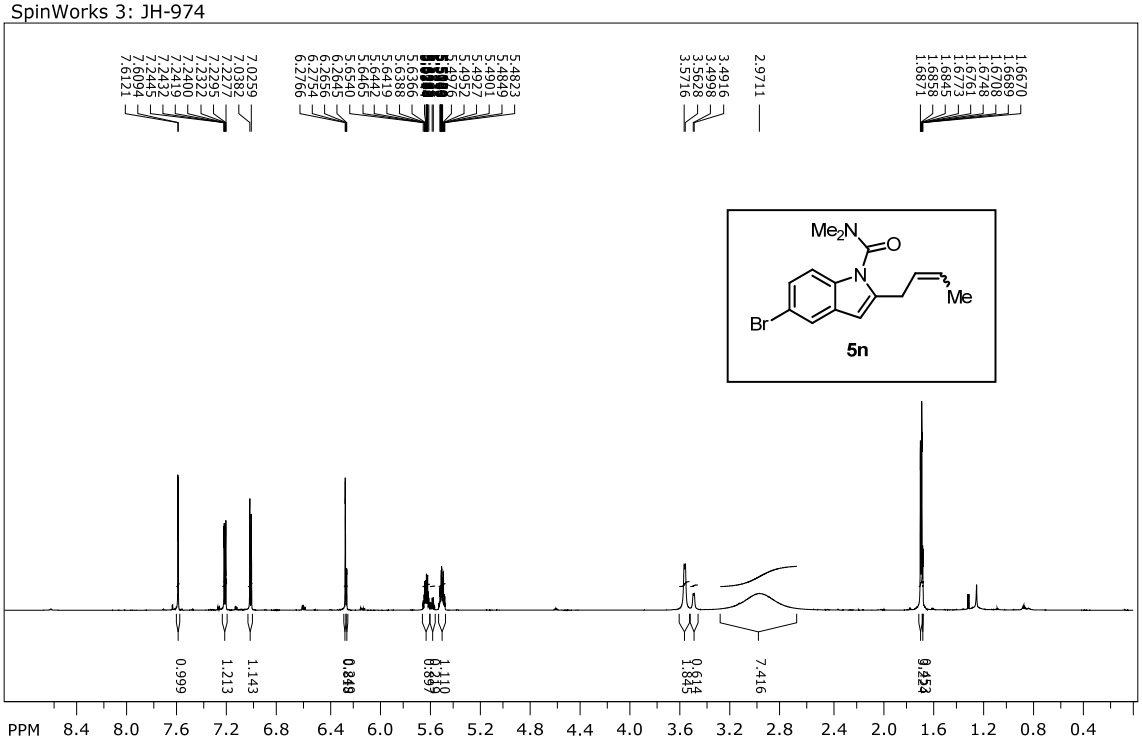
SpinWorks 3: JH-973



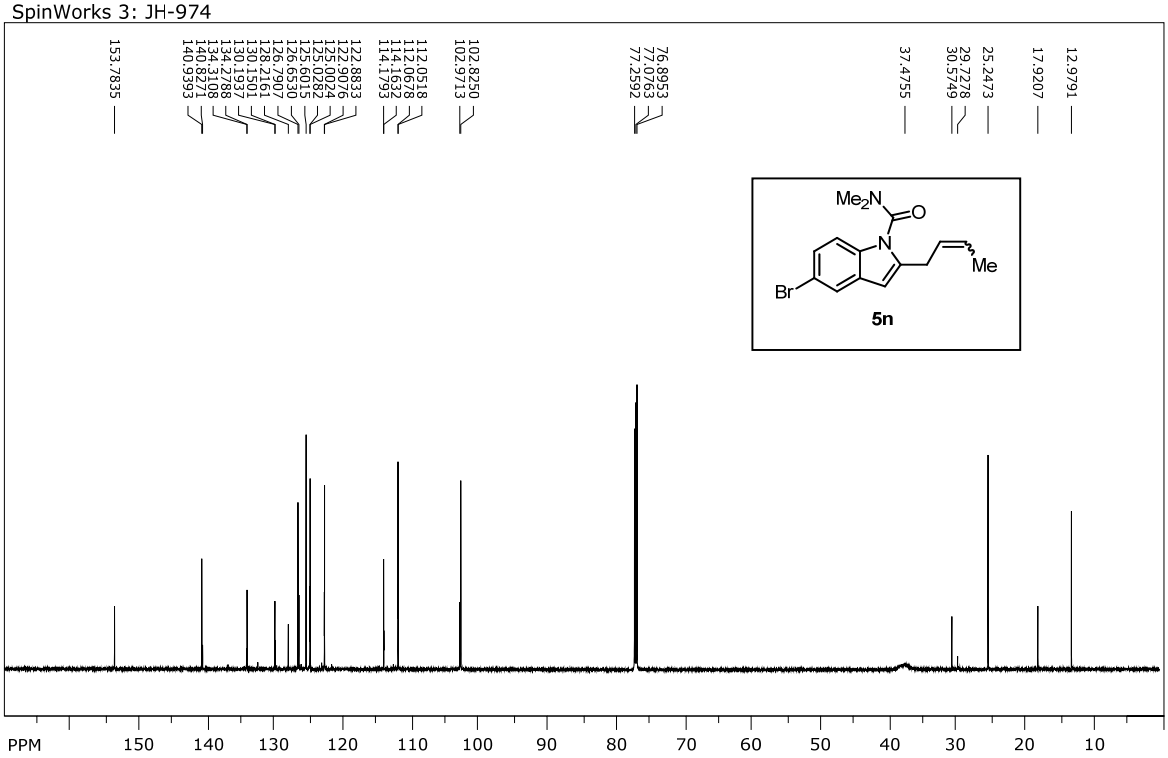
SpinWorks 3: JH-973



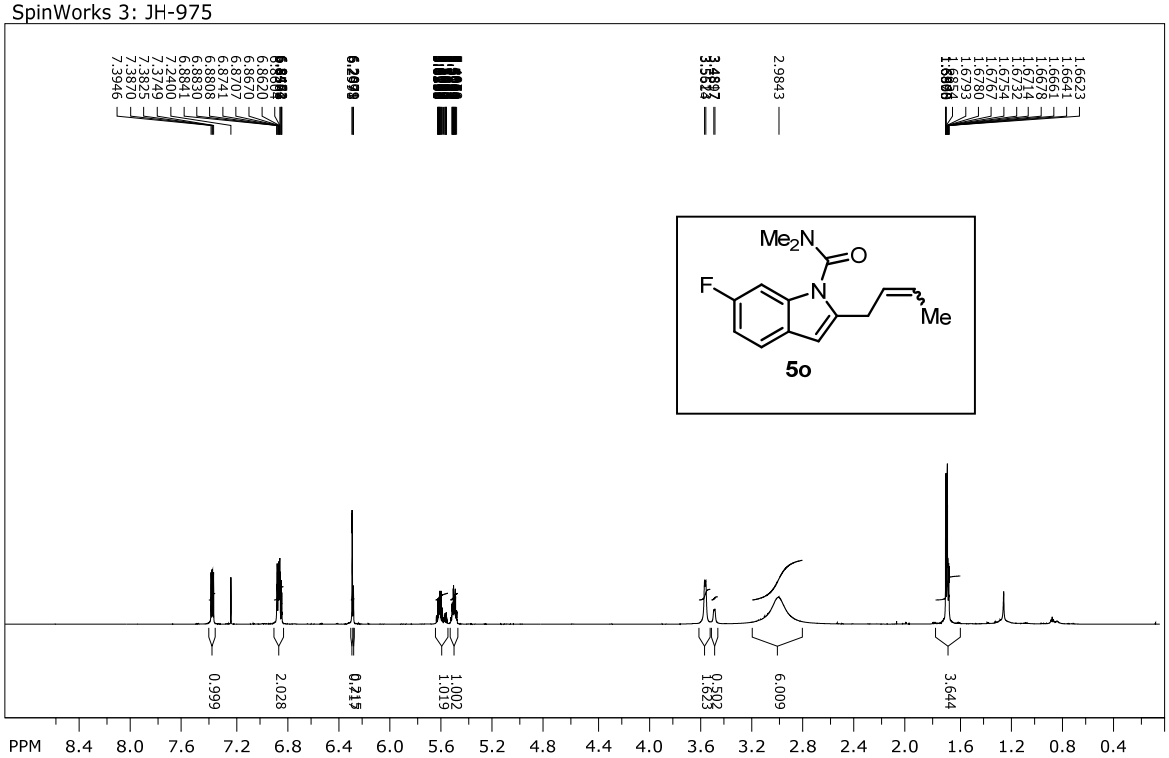
SpinWorks 3: JH-974



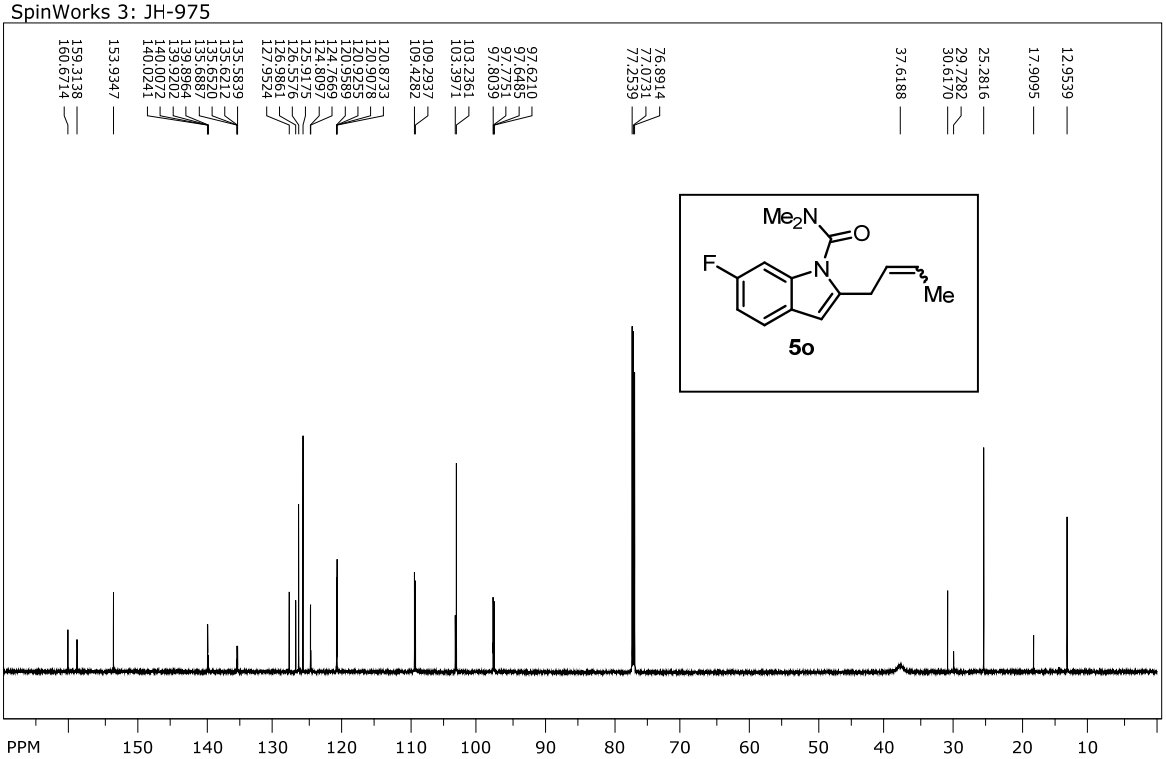
SpinWorks 3: JH-974

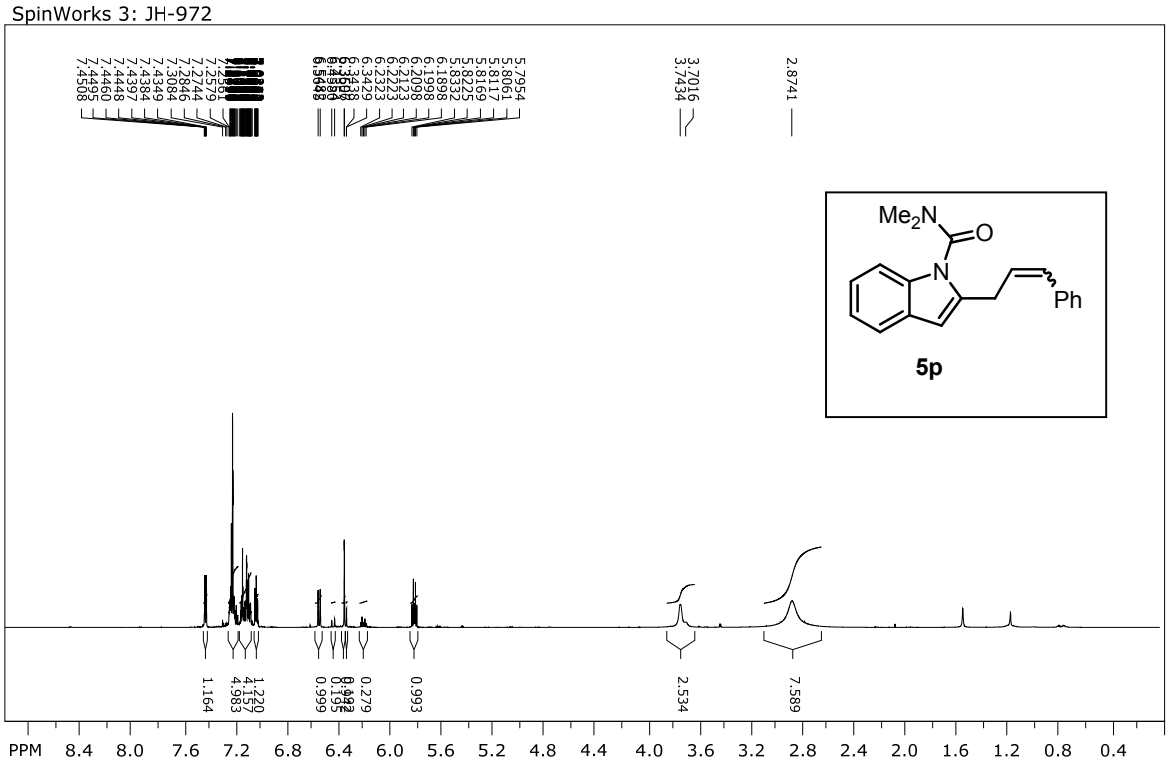


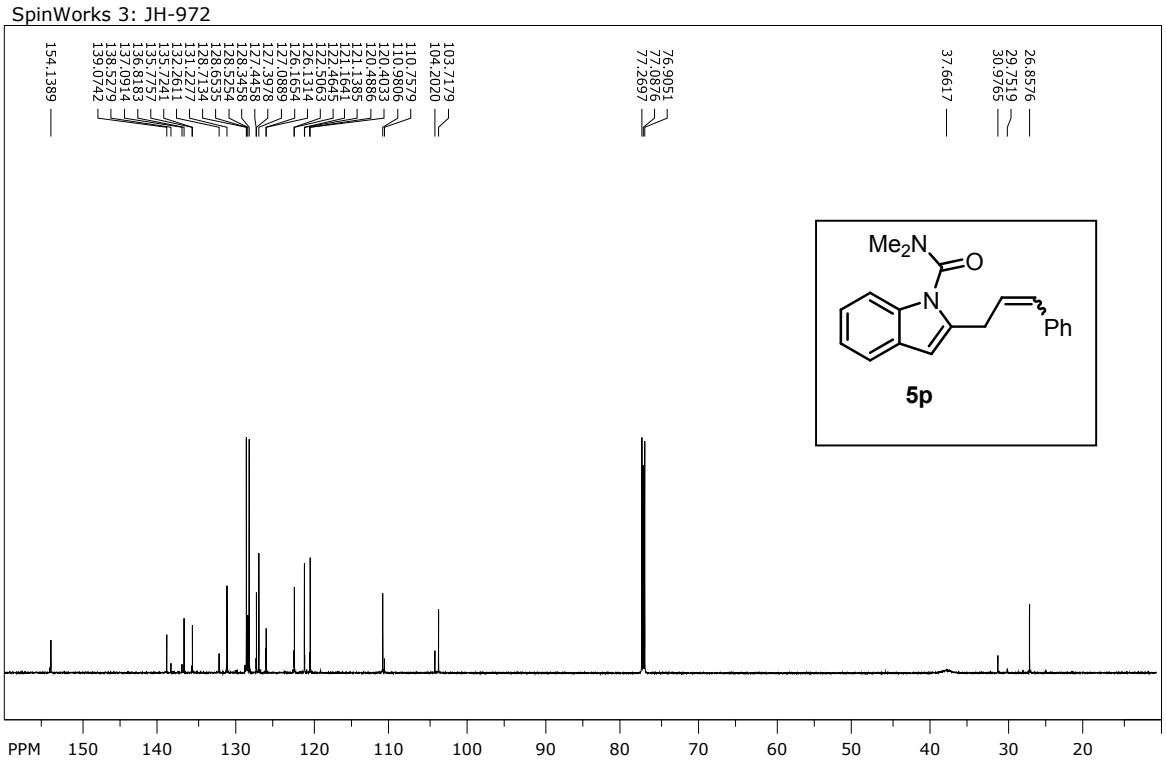
SpinWorks 3: JH-975



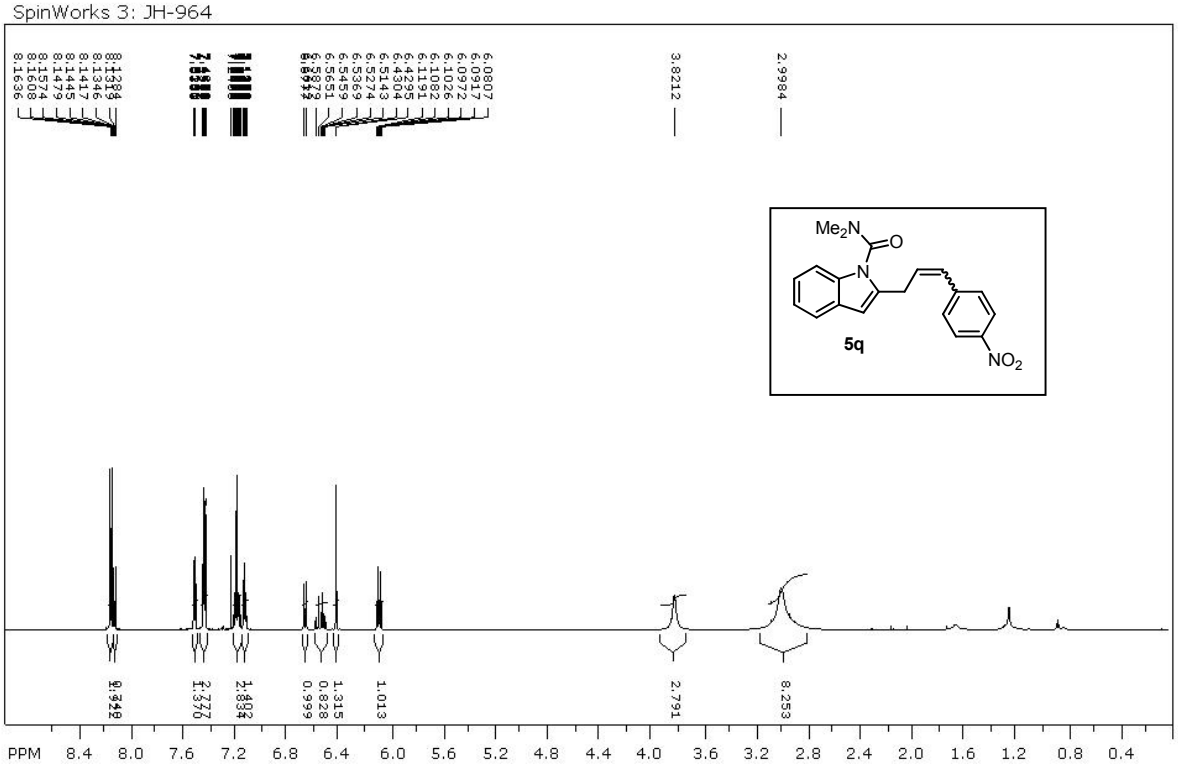
SpinWorks 3: JH-975



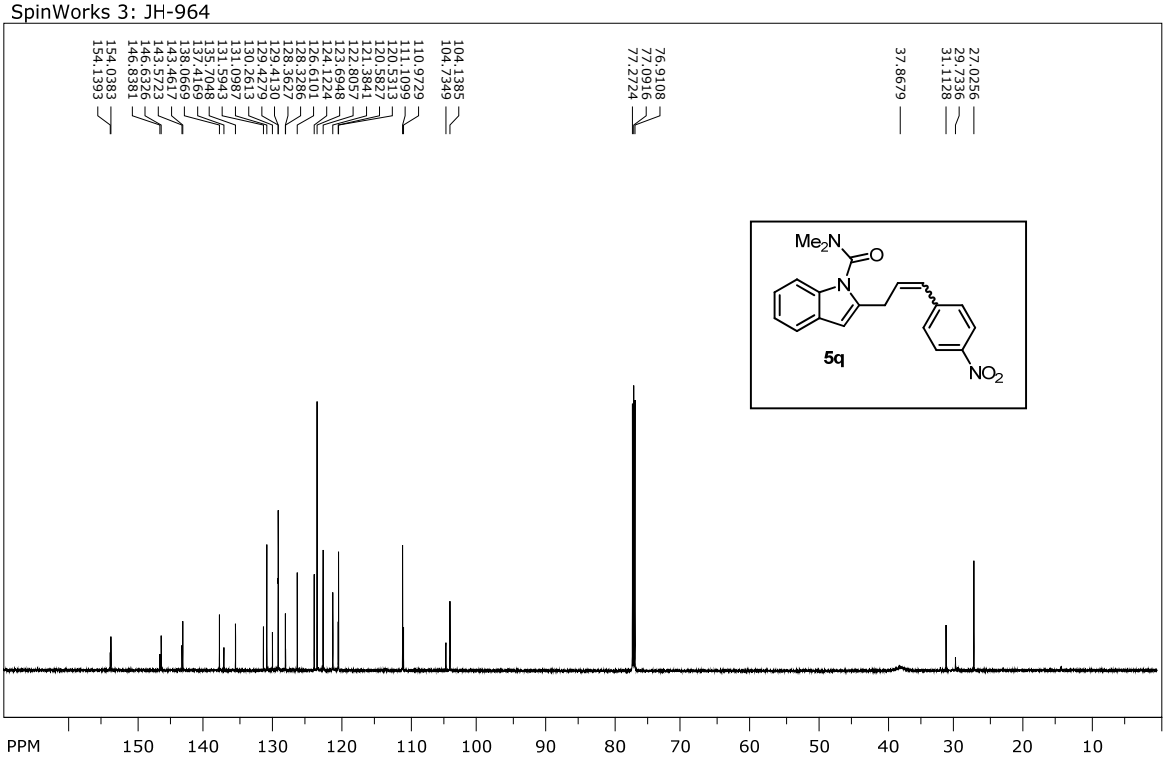

SpinWorks 3: JH-972
5.7954
5.8061
5.8117
5.8169
5.8225
5.8332
6.1898
6.1998
6.2098
6.2223
6.2323
6.3429
6.3438
3.7016
3.7434
2.8741
7.4508
7.4495
7.4460
7.4448
7.4397
7.4384
7.4349
7.3084
7.2646
7.2744
7.2791
Me2N
O
N
Ph
5p
1.164
4.983
1.220
4.157
0.999
0.279
0.993
2.534
7.589
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4

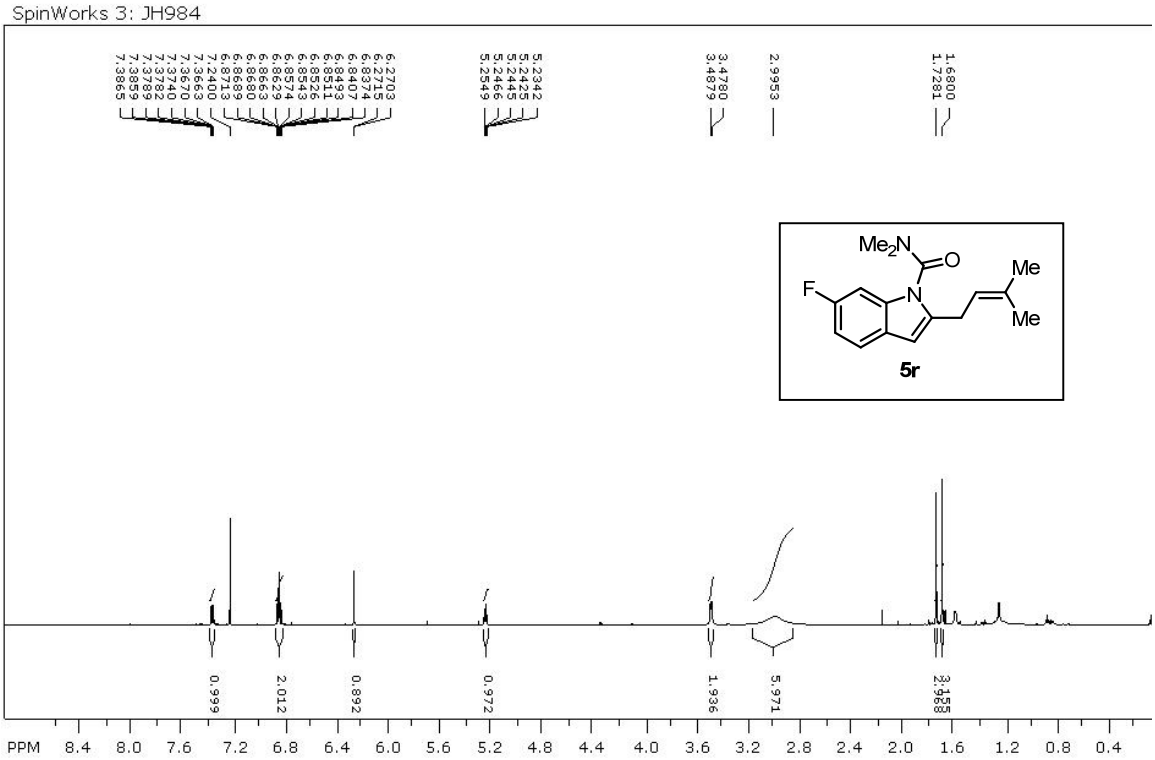

SpinWorks 3: JH-972
154.1389
139.0742
138.5279
137.0914
136.8183
135.7757
135.7241
132.2611
131.2277
128.7134
128.6535
128.5458
127.4458
127.3978
127.0889
126.1654
126.1314
122.5063
122.4645
121.1641
121.1385
120.4886
120.4033
110.9806
110.7579
104.2020
103.7179
77.2697
77.0876
76.9051
37.6617
30.9765
29.7519
26.8576
Me2N
O
N
Ph
5p
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20

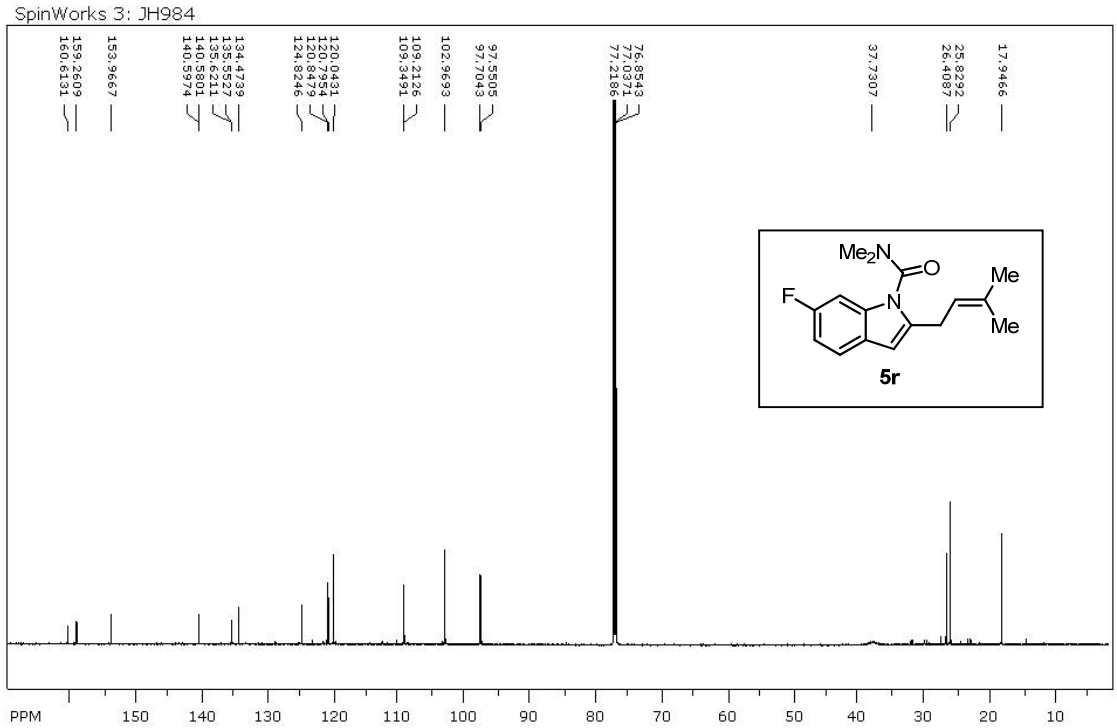
SpinWorks 3: JH-964

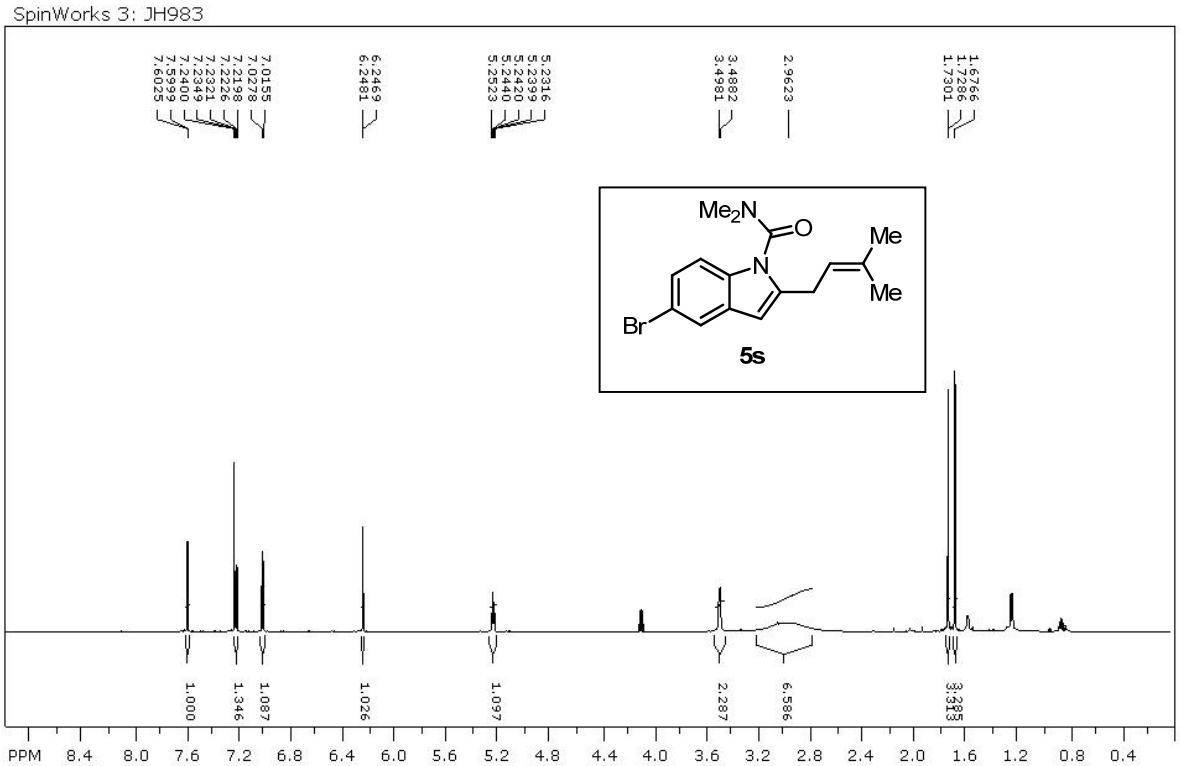


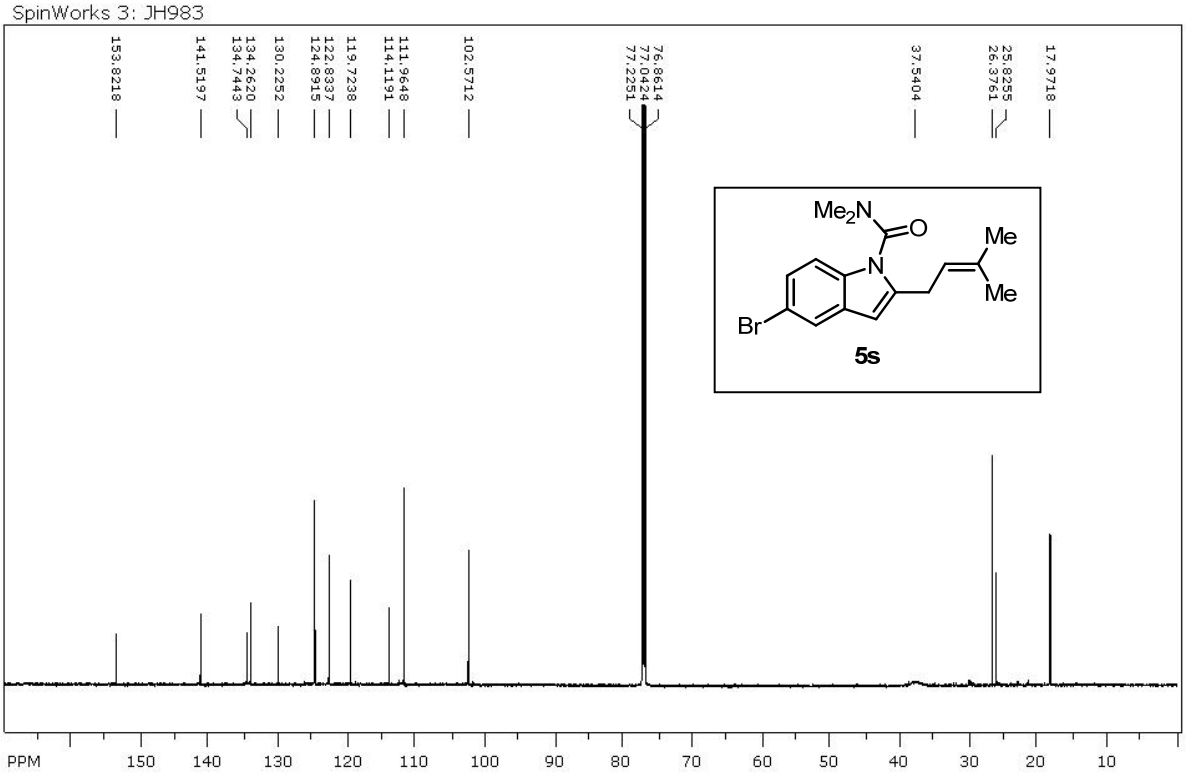
SpinWorks 3: JH-964




SpinWorks 3: JH984
7.3865
7.3859
7.3789
7.3782
7.3740
7.3670
7.3663
7.2400
7.8713
6.8689
6.8668
6.8623
6.8574
6.8543
6.8526
6.8511
6.8493
6.8407
6.8374
6.2715
6.2703
5.2549
5.2466
5.2445
5.2425
5.2342
3.4879
3.4780
2.9953
1.7281
1.6800
0.999
2.012
0.892
0.972
1.936
5.971
3.158
PPM
8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Me2N
O
F
N
Me
Me
5r


SpinWorks 3: JH984
160.6131
159.2609
153.9667
140.5974
135.6211
135.5527
134.4739
124.8246
120.8479
120.7994
120.0431
109.3491
109.2126
102.9693
97.7043
97.5505
77.2186
77.0371
76.8543
37.7307
26.4087
25.8292
17.9466
PPM
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Me2N
O
F
N
Me
Me
5r


SpinWorks 3: JH983
7.6025
7.5999
7.2400
7.2349
7.2321
7.2226
7.2198
7.0278
7.0155
6.2481
6.2469
5.2523
5.2440
5.2420
5.2399
5.2316
3.4981
3.4882
2.9623
1.7301
1.7286
1.6766
1.000
1.346
1.087
1.026
1.097
2.287
6.586
3.285
3.313
PPM 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
Me2N
O
N
Me
Me
Br
5s


SpinWorks 3: JH983
153.8218
141.5197
134.2620
134.7443
130.2252
124.8915
122.8337
119.7238
114.1191
111.9648
102.5712
77.2251
77.0424
76.8614
37.5404
26.3761
25.8255
17.9718
PPM 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Me2N
O
N
Me
Me
Br
5s