Al_2O_3/CuI/PANI nanocomposite catalyzed green synthesis of biologically active 2-substituted benzimidazole derivatives

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***Correspondence:**

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Electronic Supplementary Information (ESI) includes SEM and XRD of recycled Al_2O_3/CuI/PANI nanocatalyst; Green chemistry metric calculations, ^1H NMR and ^{13}C NMR spectra of all compounds.

Total No of Pages: 20, Total No of Tables: 0, Total number of Figures: 2.

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1. General Remarks

Chemicals and solvents were purchased from Sigma Adrich, Alfa-Aesar and Merck India Pvt. ^{1}H and ^{13}C spectra were recorded on a Jeol Spectrospin spectrometer at 400 MHz and 100 MHz respectively by keeping TMS as internal standard. CHNS Analyser was recorded on model Vario Micro Cube at USIC (University Science Instrument Centre), University of Delhi, Delhi, India. Mass spectral data were recorded on MALDI MS - ABI Sciex 5800 TOF/ TOF System with LC-MALDI. The X-ray diffractometer (Model No. D8 DISCOVER) at 2θ range of 10–90° with Cu Kα radiation. Chemical shift values were recorded in terms of δ and coupling constants (J) are in hertz (Hz). FTIR spectra were obtained on IRAffinity-1S Fourier Transform Infrared Spectrophotometer. Scanning Electron microscopy (SEM) measurement was performed on JEOL JSM 6610 at USIC, University of Delhi. Transmission electron microscopy (TEM) was obtained on a TECNAI G20 HR-TEM 200kV at SAIF (sophisticated analytical instrumentation facility), AIIMS, New Delhi, India. The elemental composition and electronic structure analysis were obtained from X-ray photoelectron spectra (XPS) of PHI 5000 Versa Probe III instrument at Institute Instrumentation Centre, Indian Institute of Technology, Roorkee – 247 667 (Uttarakhand), India. BET experiment was performed on BET Surface Area Measurement Equipment, IISC Bangalore.

2. SEM and XRD of recycled Al_2O_3/CuI/PANI nanocatalyst

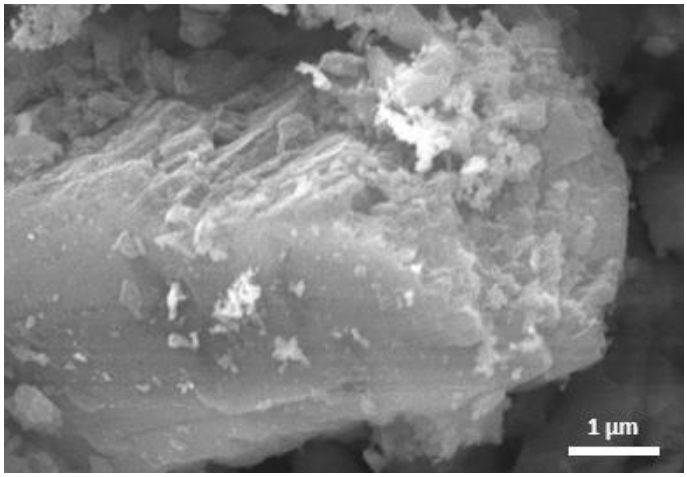


Figure S1: SEM image of recycled Al_2O_3/CuI/PANI nanocomposites

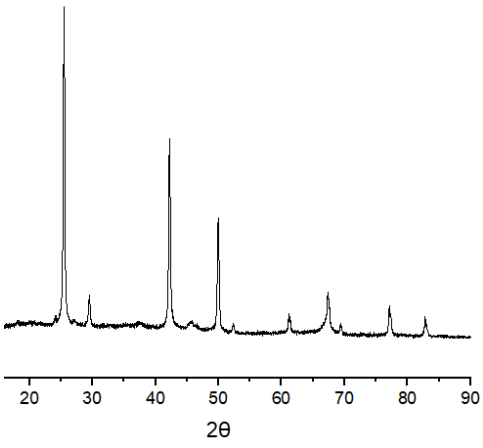
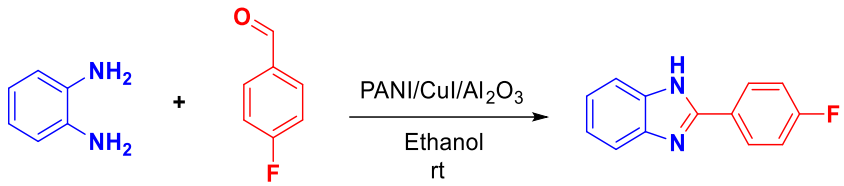


Figure S2: XRD of recycled Al_2O_3/CuI/PANI nanocomposites

3. Calculation of Green chemistry metrices for 3i of our method



FW	108.14 g/mol	124.11 g/mol	212.23 g/mol
m.mol	**0.5 mmol**	**0.5 mmol**	**0.47 mmol**
amount	**62 mg**	**54 mg**	**99 mg**

E-factor:

The ideal value of E-factor is zero.

E-factor = [total mass of raw materials - the total mass of product]/ mass of product.

E-factor of i = [(62 + 54)-99]/99

= 0.17.

Process mass intensity (PMI):

PMI= ∑ (mass of stoichiometric reactants)/[mass of product]

= (62+ 54)/ 99

= 1.17.

Reaction mass efficiency (RME):

RME = [mass of product /∑ (mass of stoichiometric reactants)] × 100

= [99 / (62+ 54)] × 100

= 85.34%

Carbon efficiency (CE):

CE denotes the percentage of carbon in the reactants that remains in the product.

CE= [Amount of carbon in product/ Total carbon present in reactants] x 100

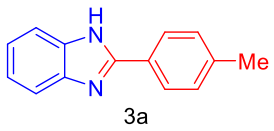
= [no. of moles of product x no. of carbons in product / (moles of a x carbons in 1i + moles of 2 carbons in 2)] x 100

= [0.47 x 13 / (0.5 x 7 + 0.5 x 6)] x 100

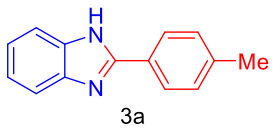
= [6.11 / (3.5 + 3)] x 100

= 94%

4. ^{1}H and ^{13}C Spectra of compounds



3a



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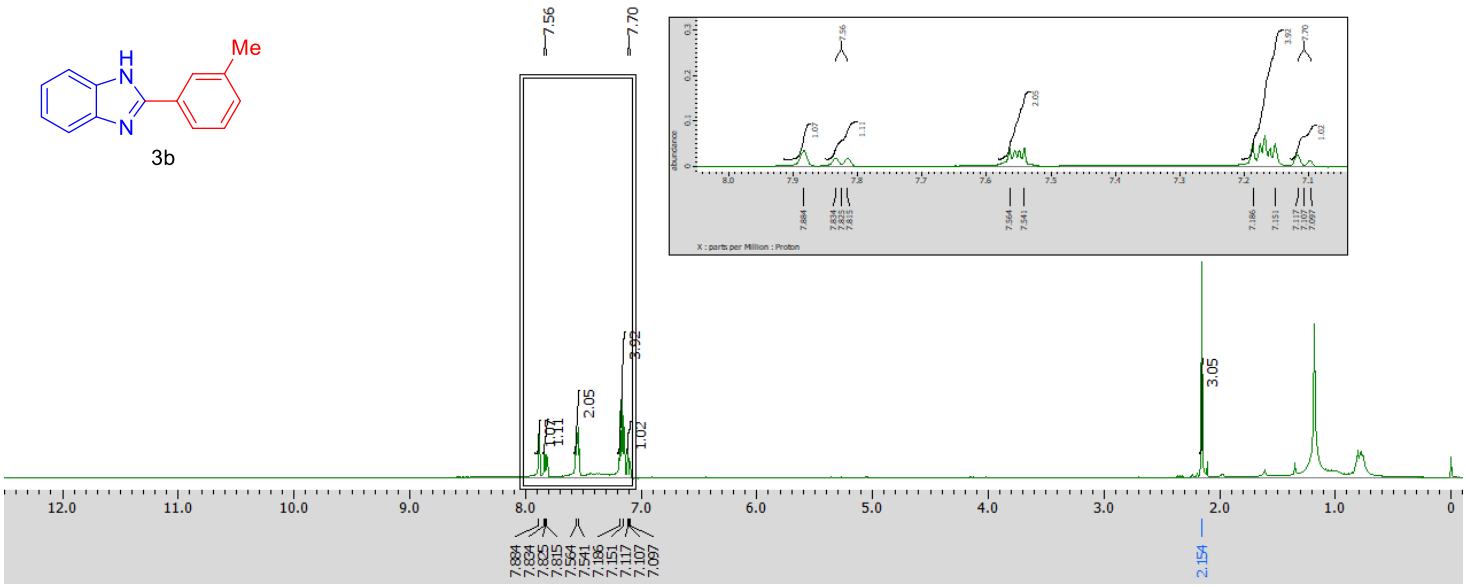
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N
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7.70
3.92
2.05
1.11
1.07
1.02
3.05
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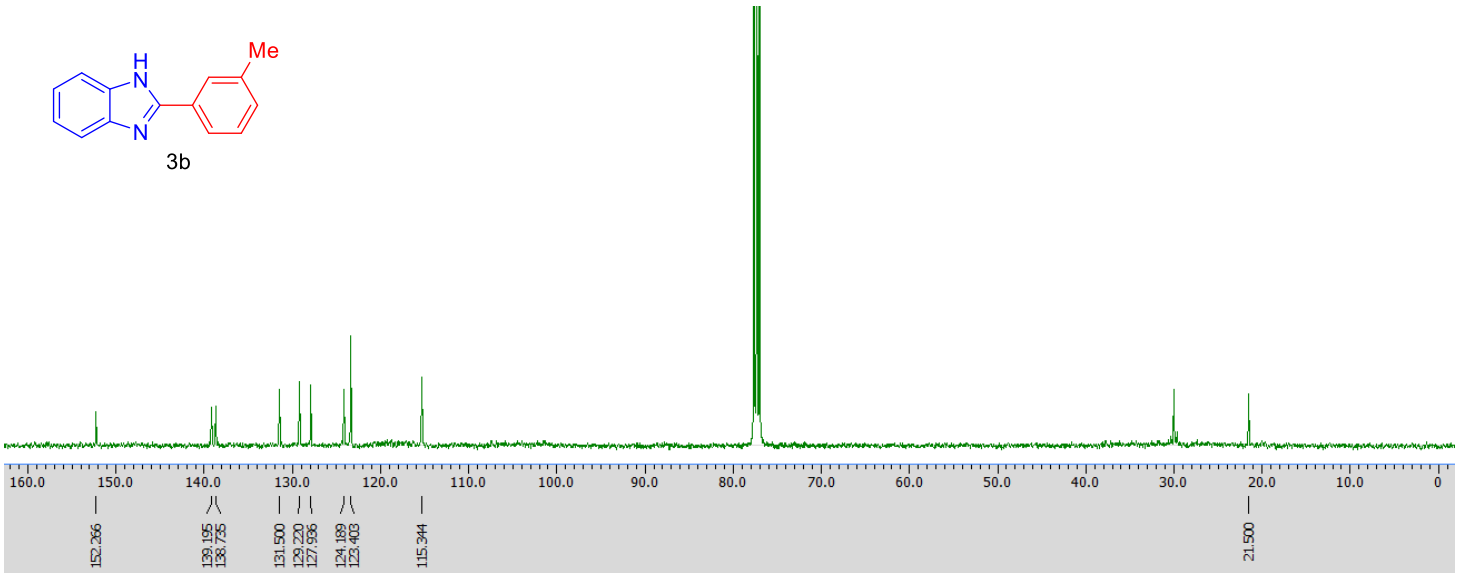
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.884
7.834
7.825
7.815
7.564
7.541
7.186
7.151
7.117
7.107
7.097
X : parts per Million : Proton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N
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60.0
50.0
40.0
30.0
20.0
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123.403
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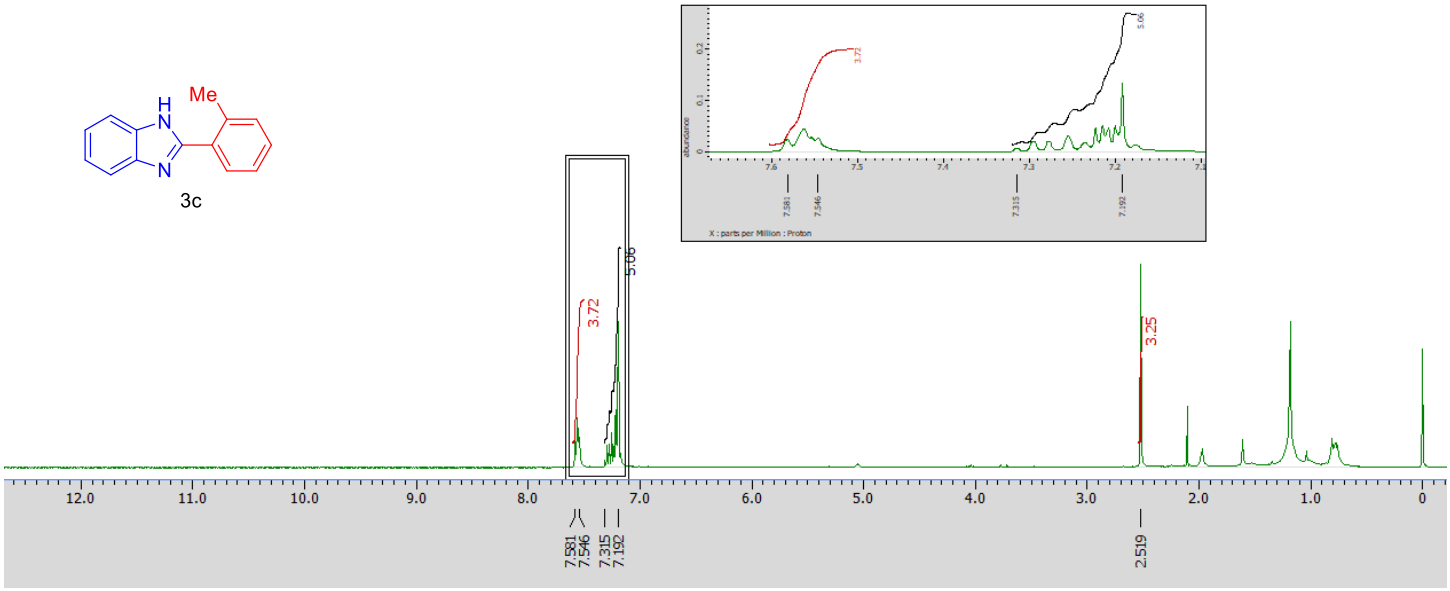
21.500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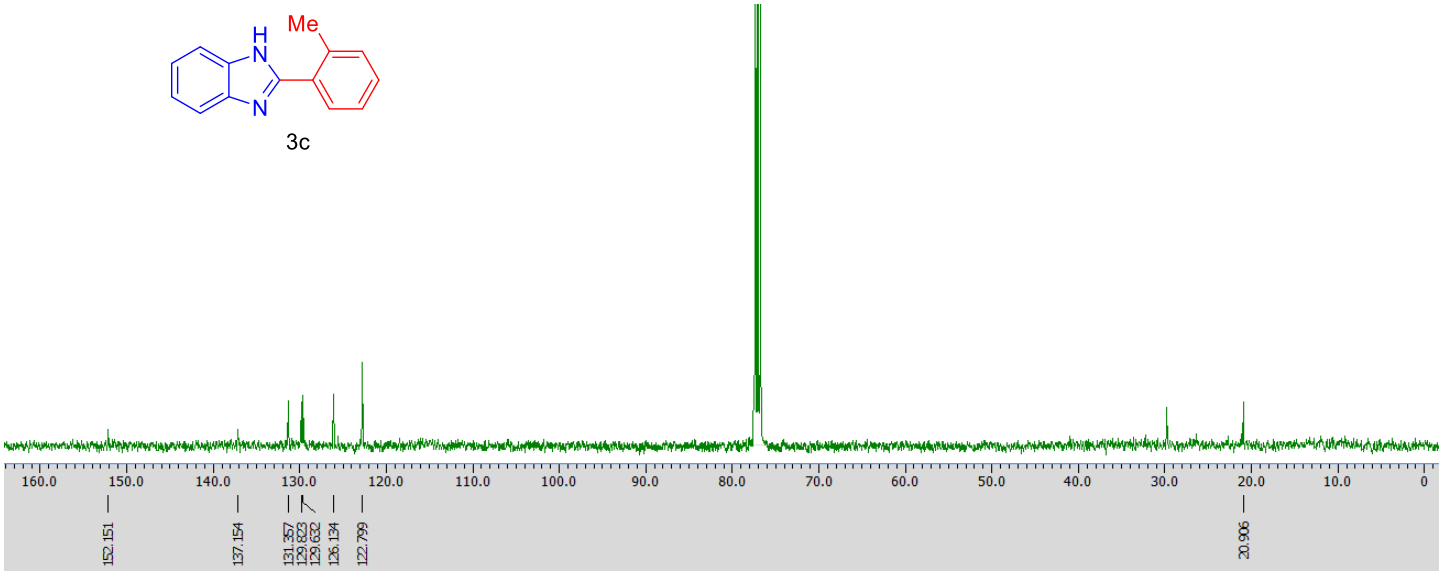
7.192
2.519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60.0
50.0
40.0
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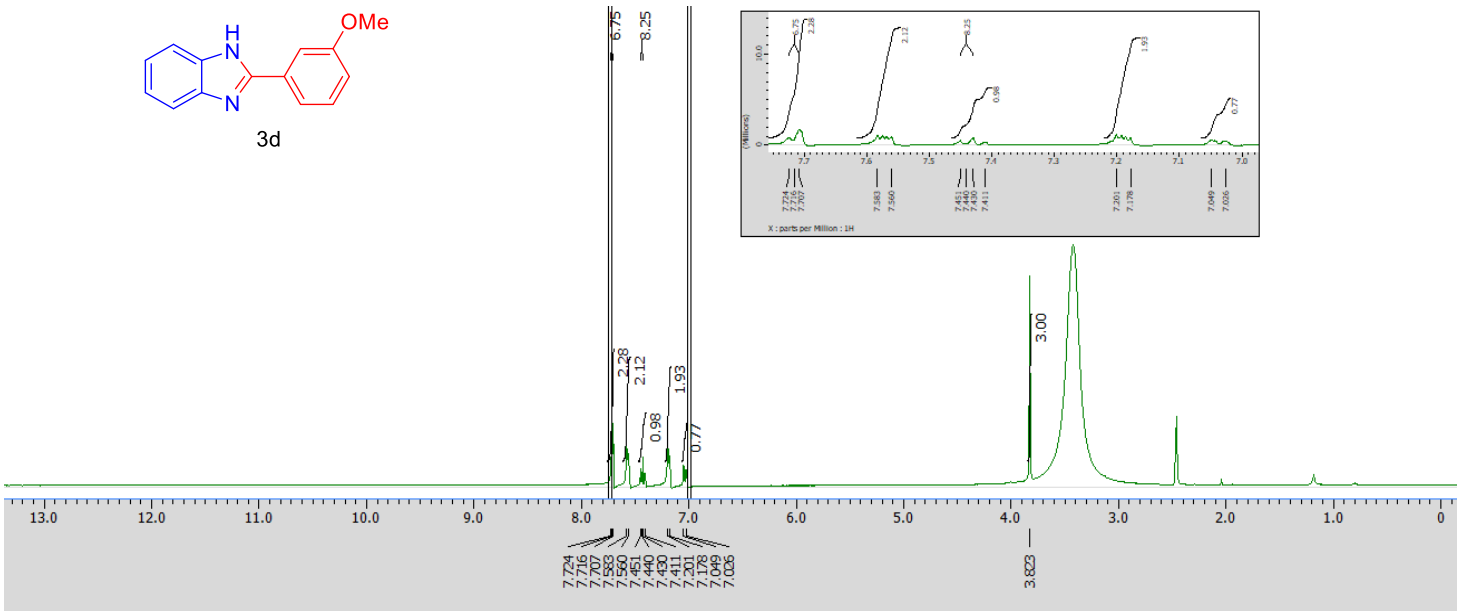
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N
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7.724
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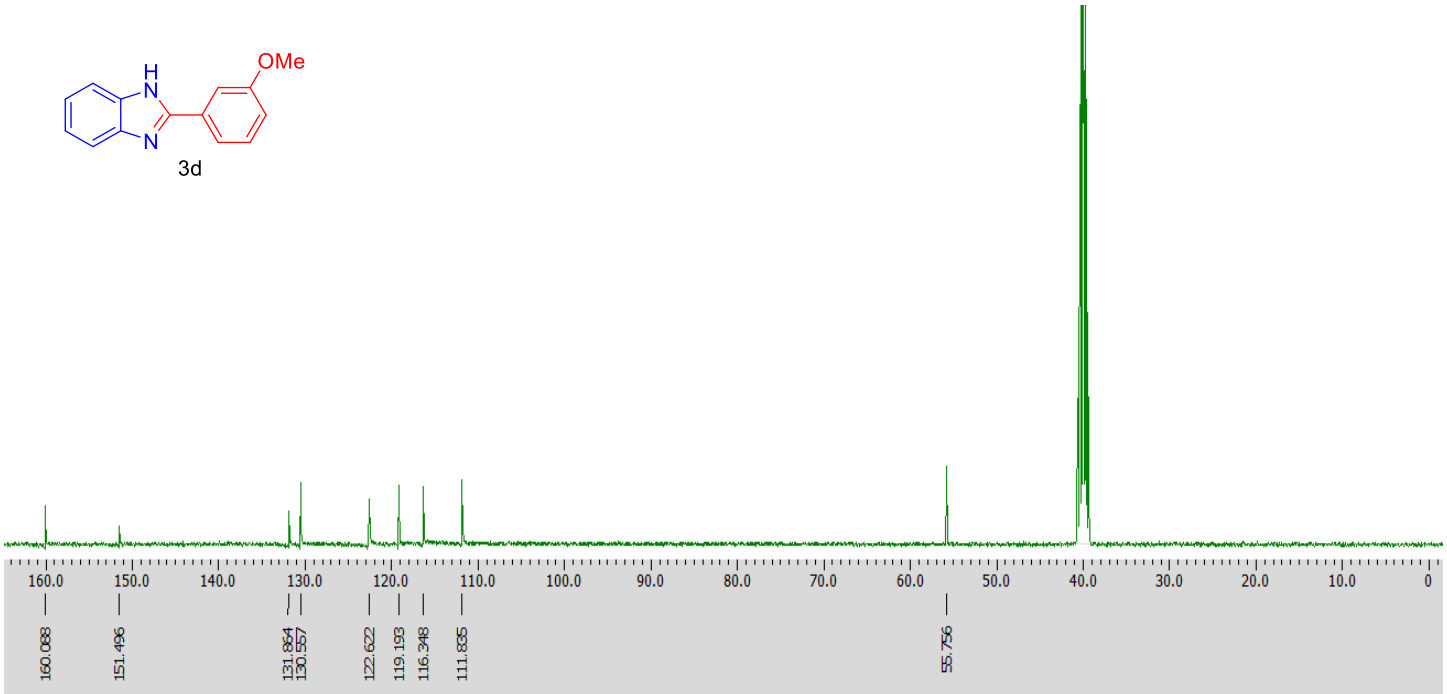
7.026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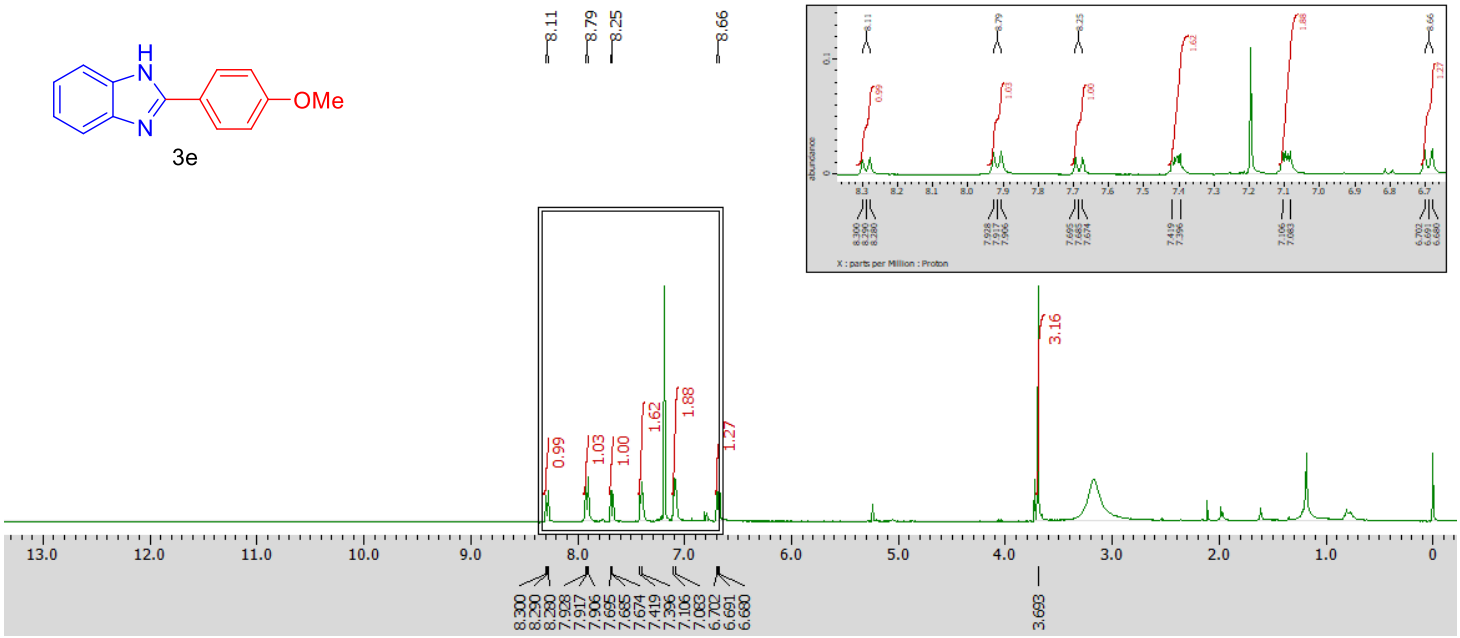
55.756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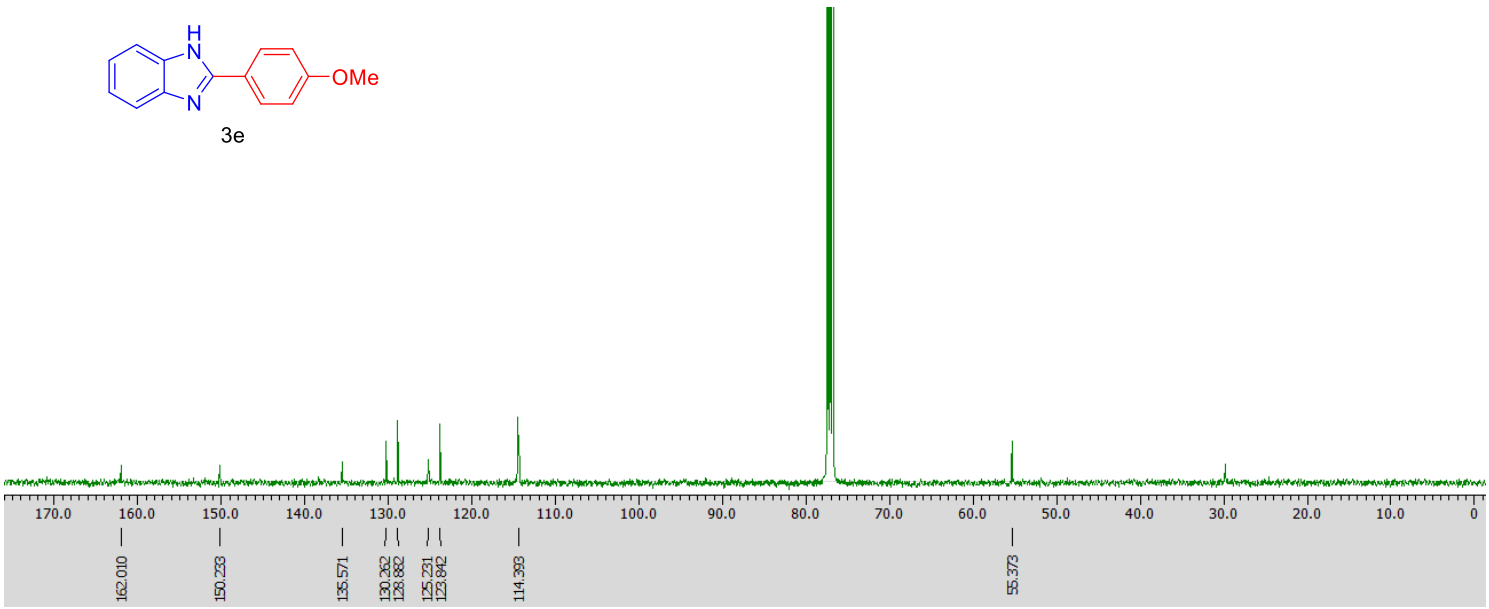
3.16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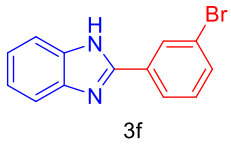
H
N
N
Br

3f

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3.65
1.98
1.00
1.01
0.91
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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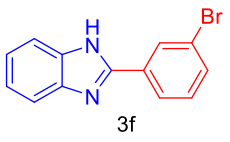
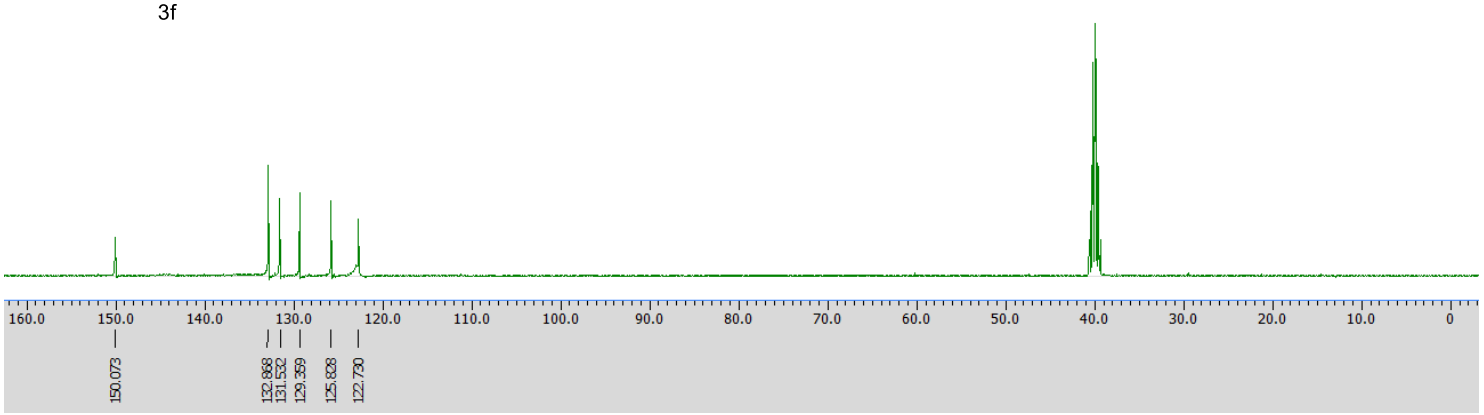
7.221


H
N
N
Br

3f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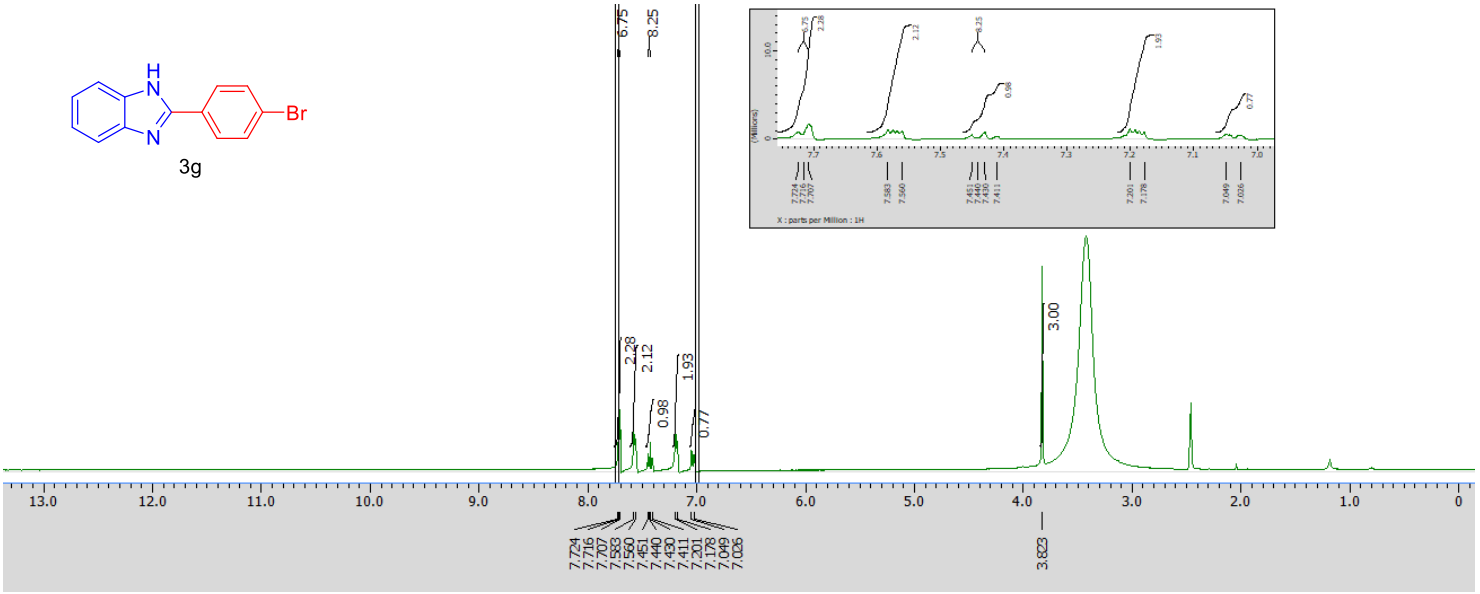
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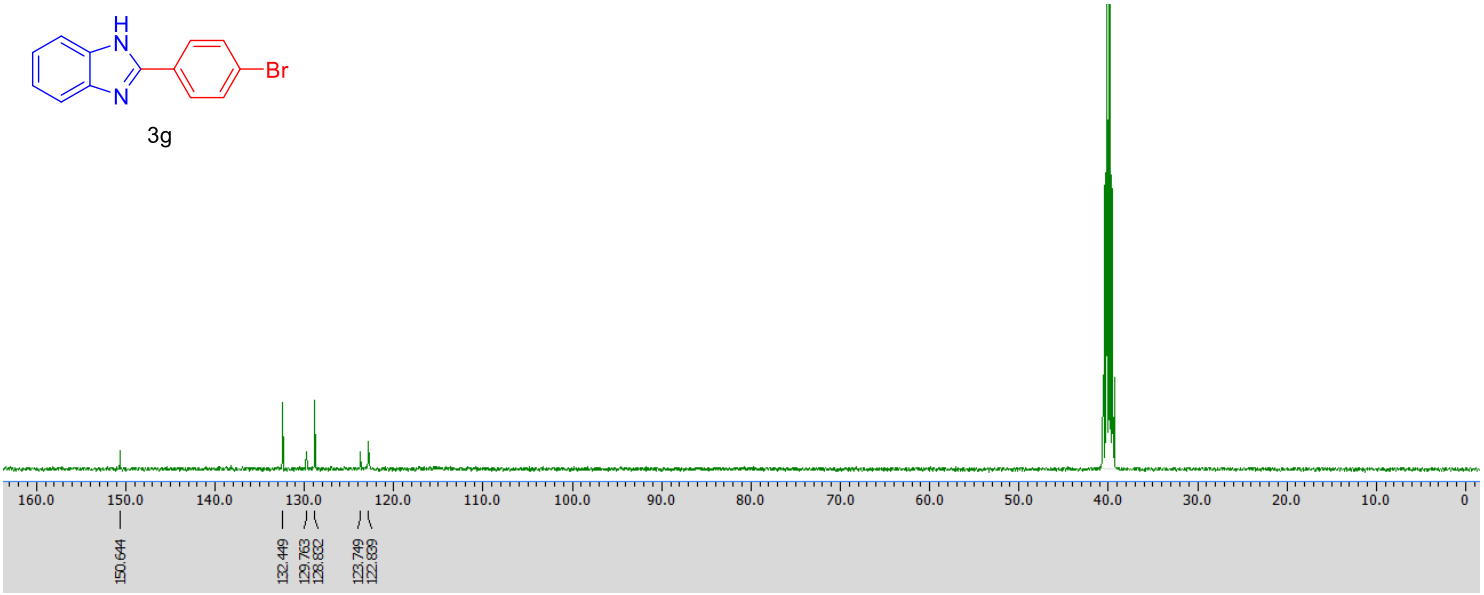
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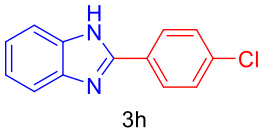
H
N
N
Cl

3h

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8.0
7.0
6.0
5.0
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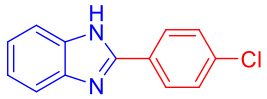
7.215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N
N
Cl

3h

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70.0
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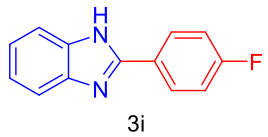

3i

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2.09
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1.00
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12.0
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10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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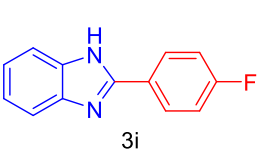
7.207



3i

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40.0
30.0
20.0
10.0
0
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150.860
144.225
135.489
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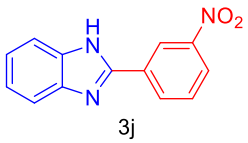
NO2
H
N
N

3j

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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
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0
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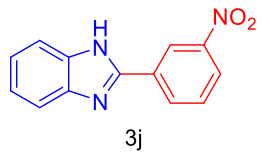
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H
N
N

3j

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60.0
50.0
40.0
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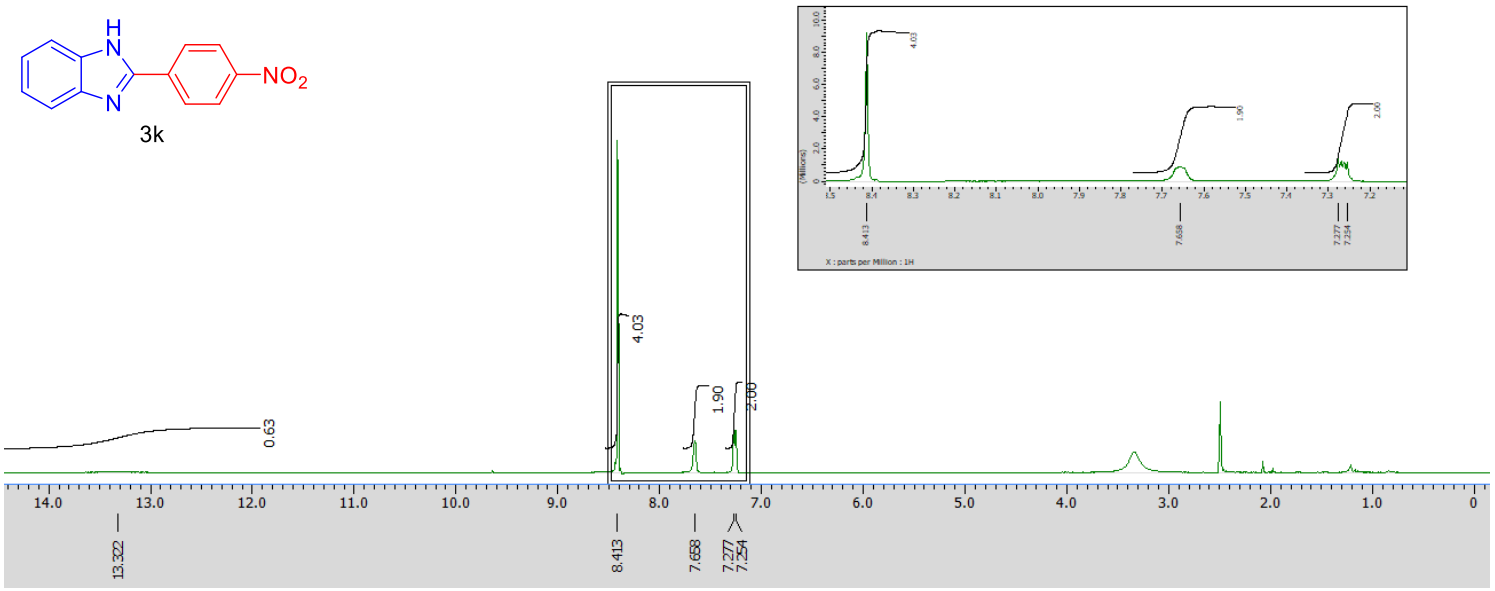
121.315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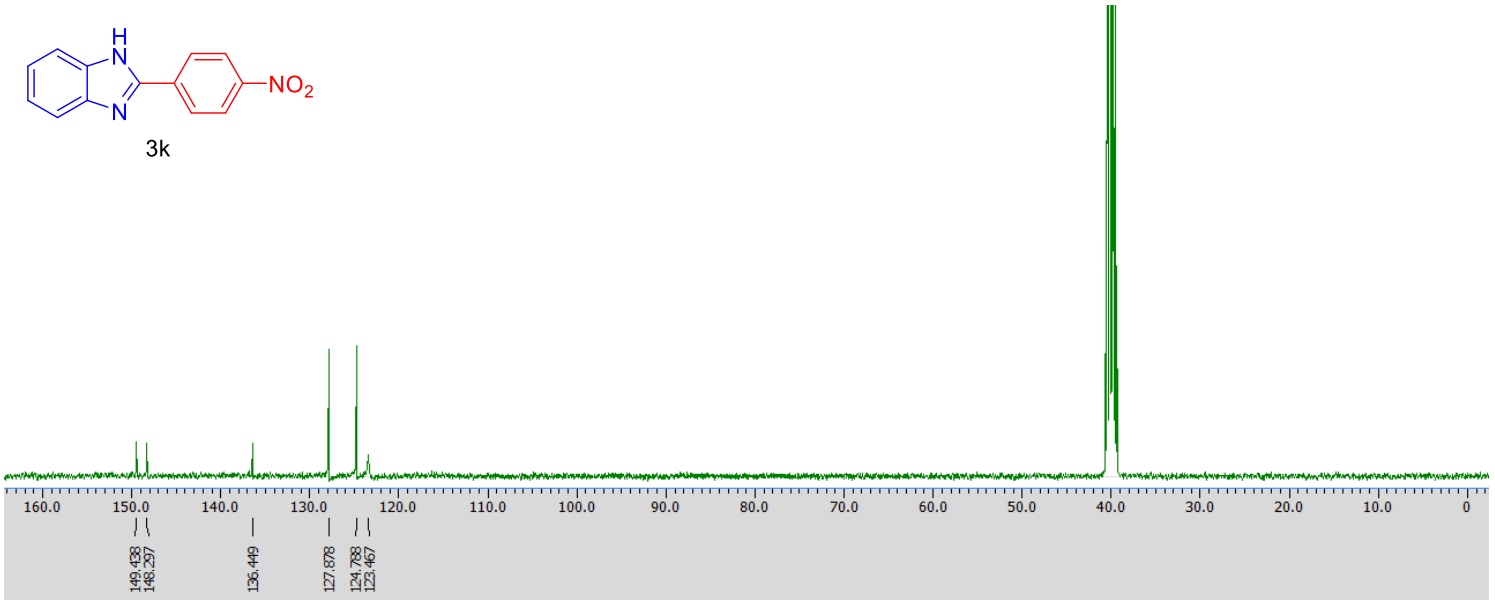
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123.467

3l

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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
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2.0
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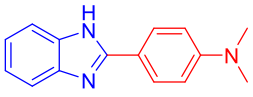

3l

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120.0
110.0
100.0
90.0
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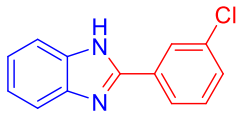
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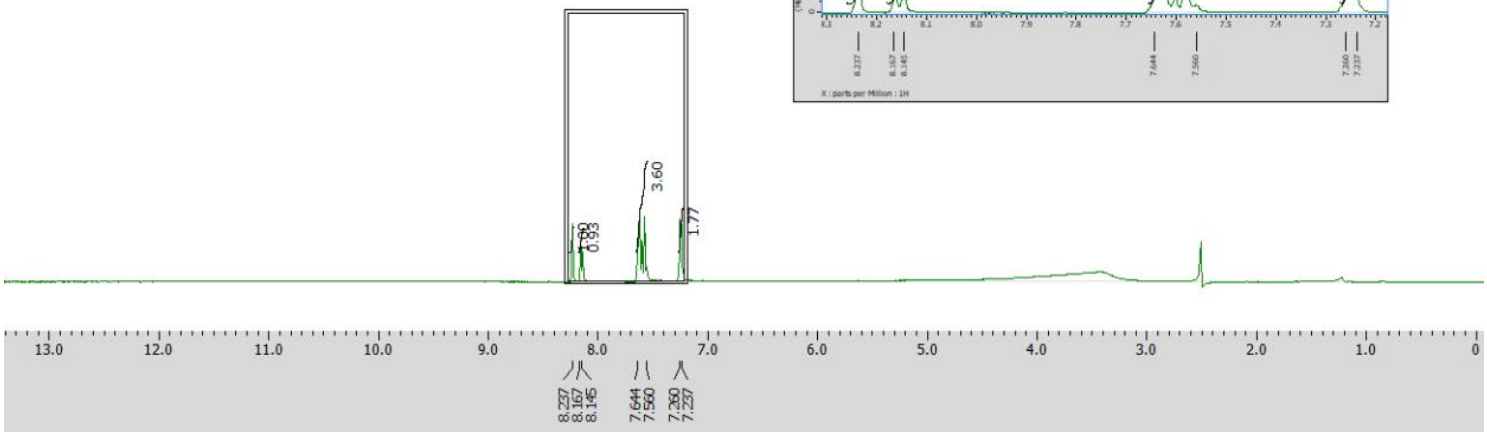
N
Cl

3m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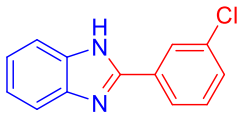
7.260
7.237


H
N
N
Cl

3m

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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
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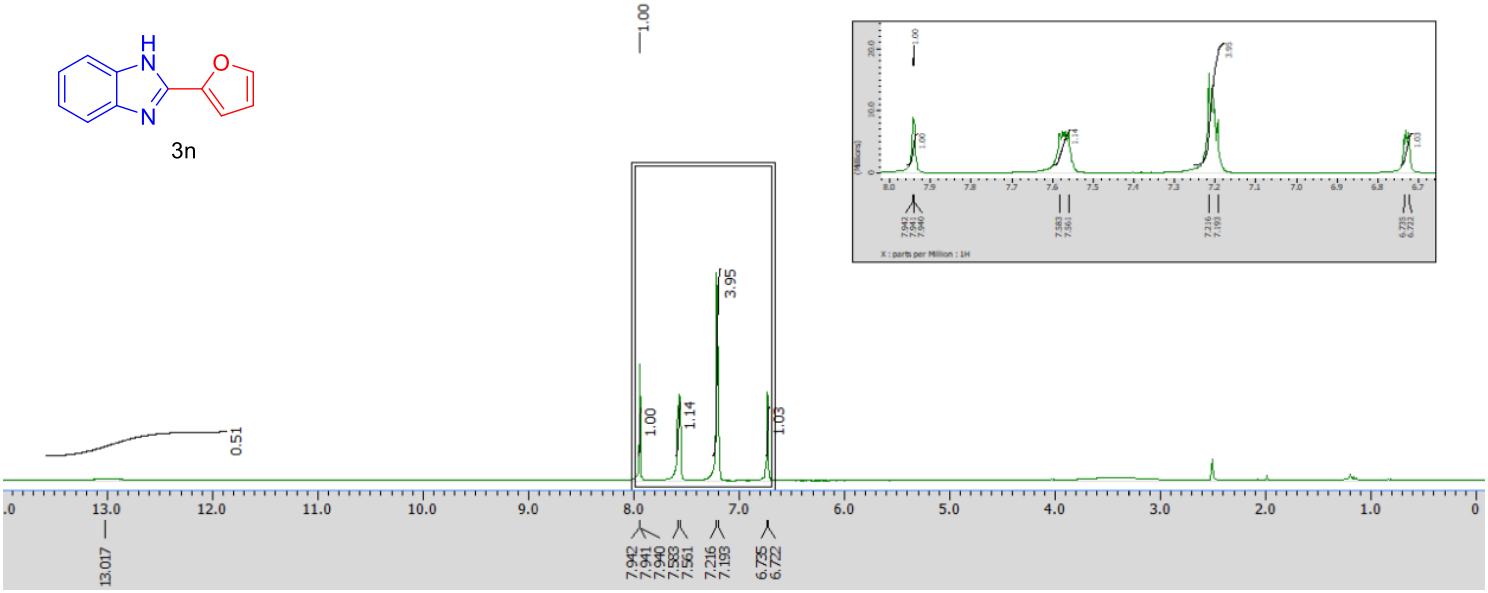
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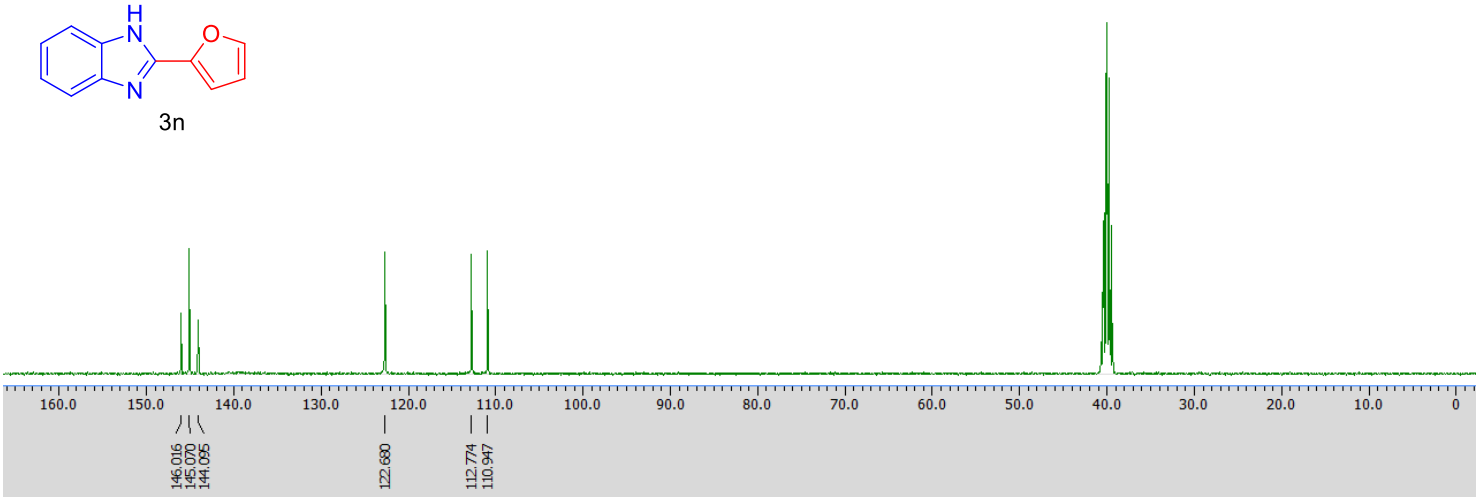
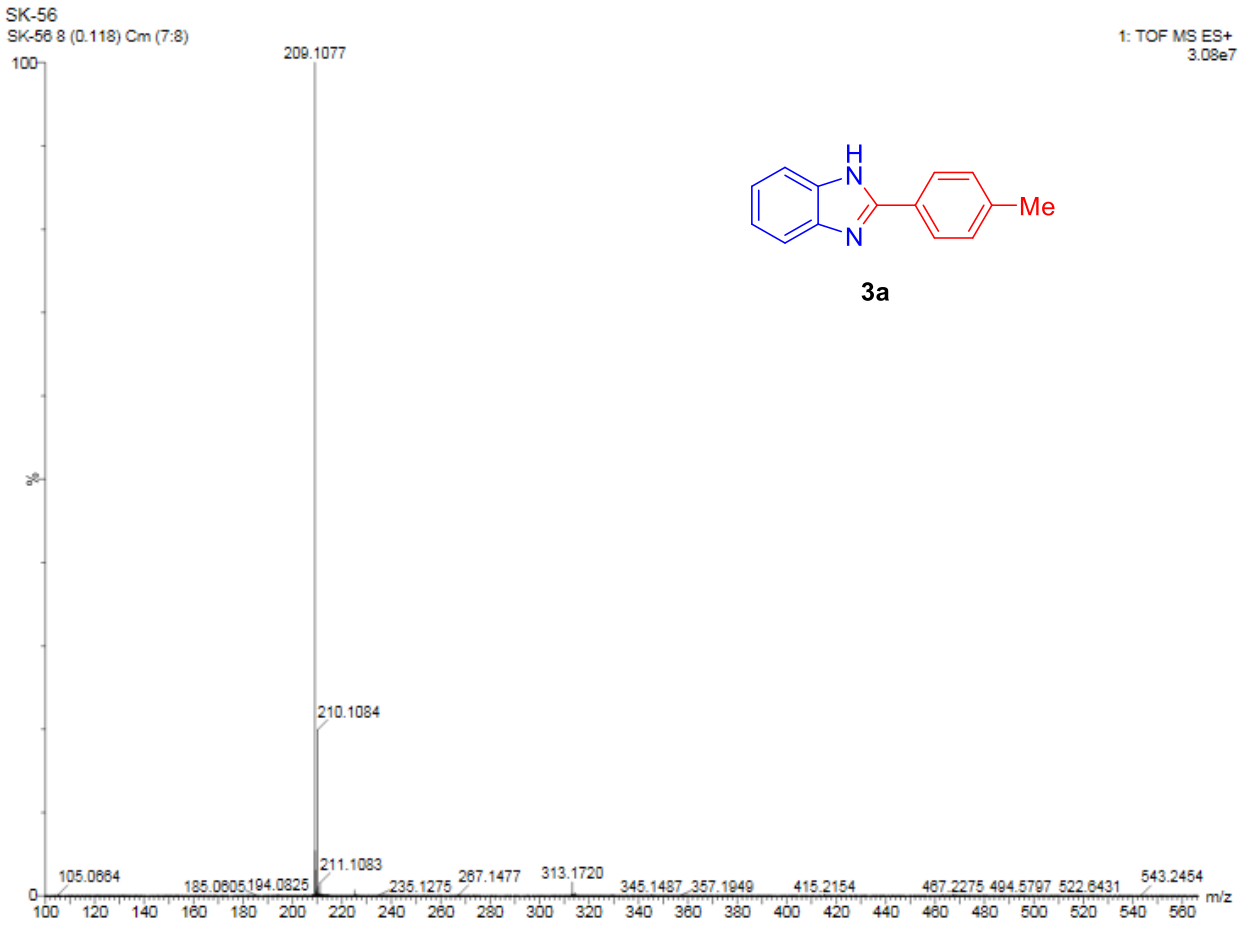
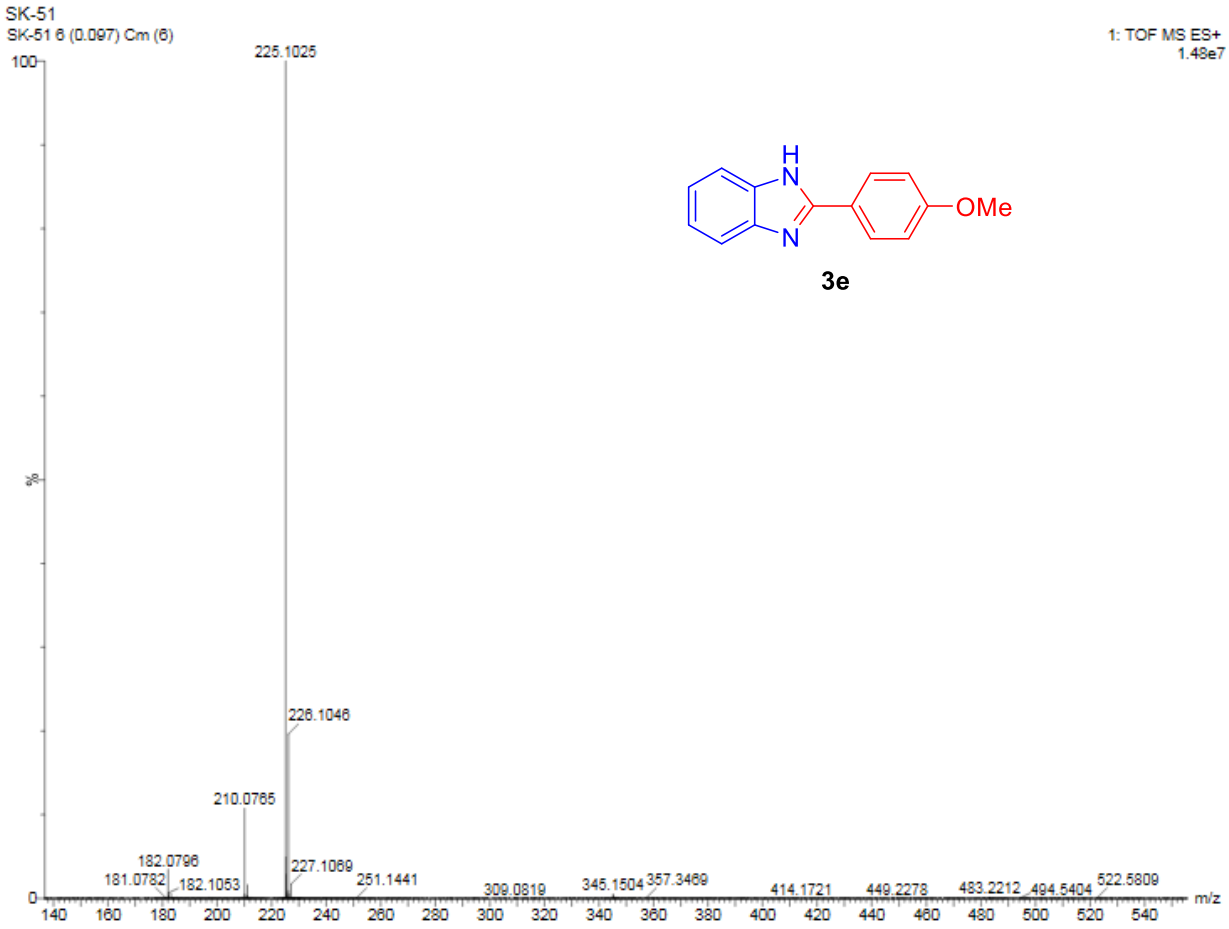
1.00
1.03
0.51
13.017
7.942
7.941
7.940
7.583
7.561
7.216
7.199
6.735
6.722


3n
146.016
145.070
144.095
122.680
112.774
110.947

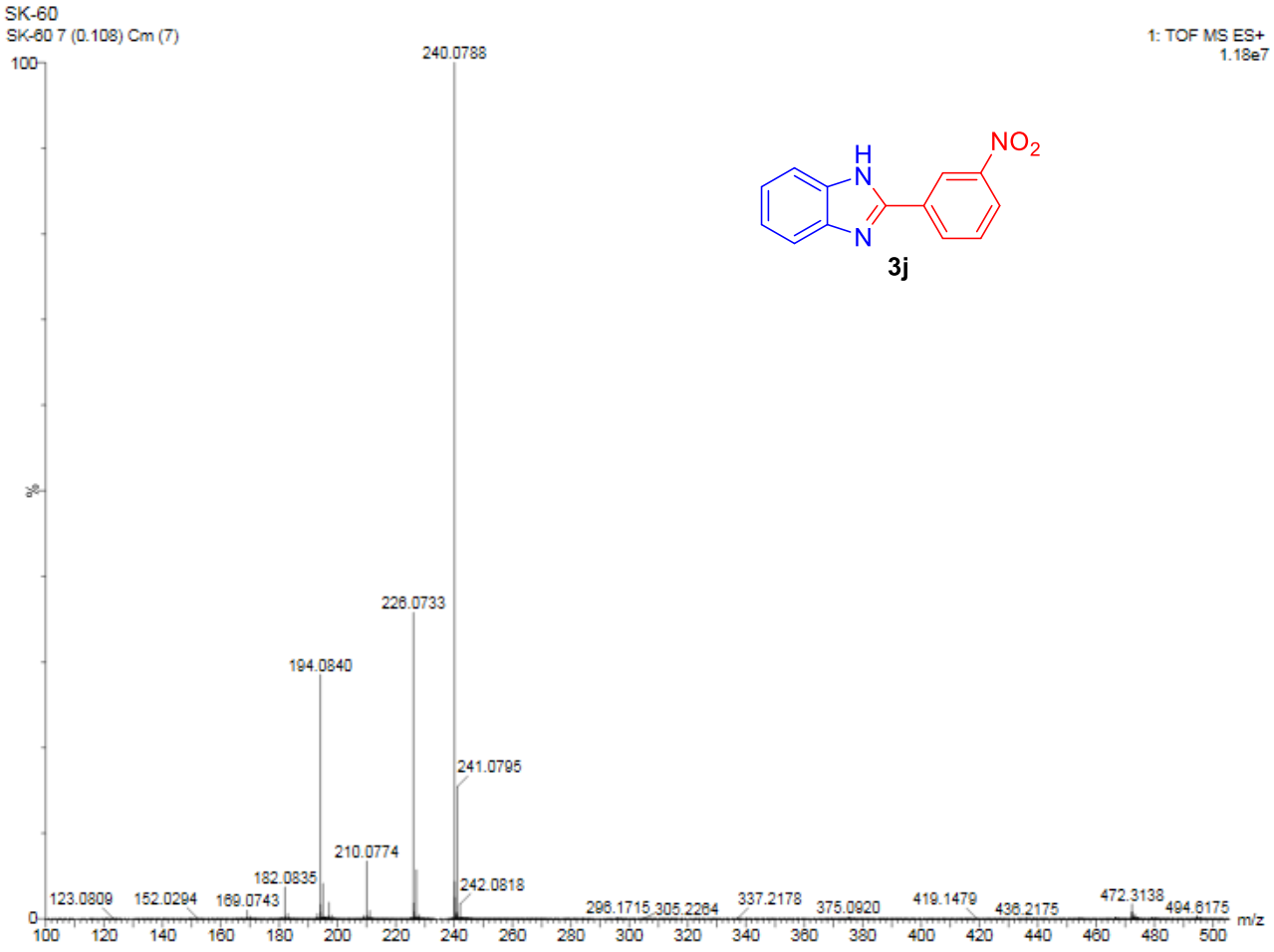
Mass Spectra of Selected Compounds

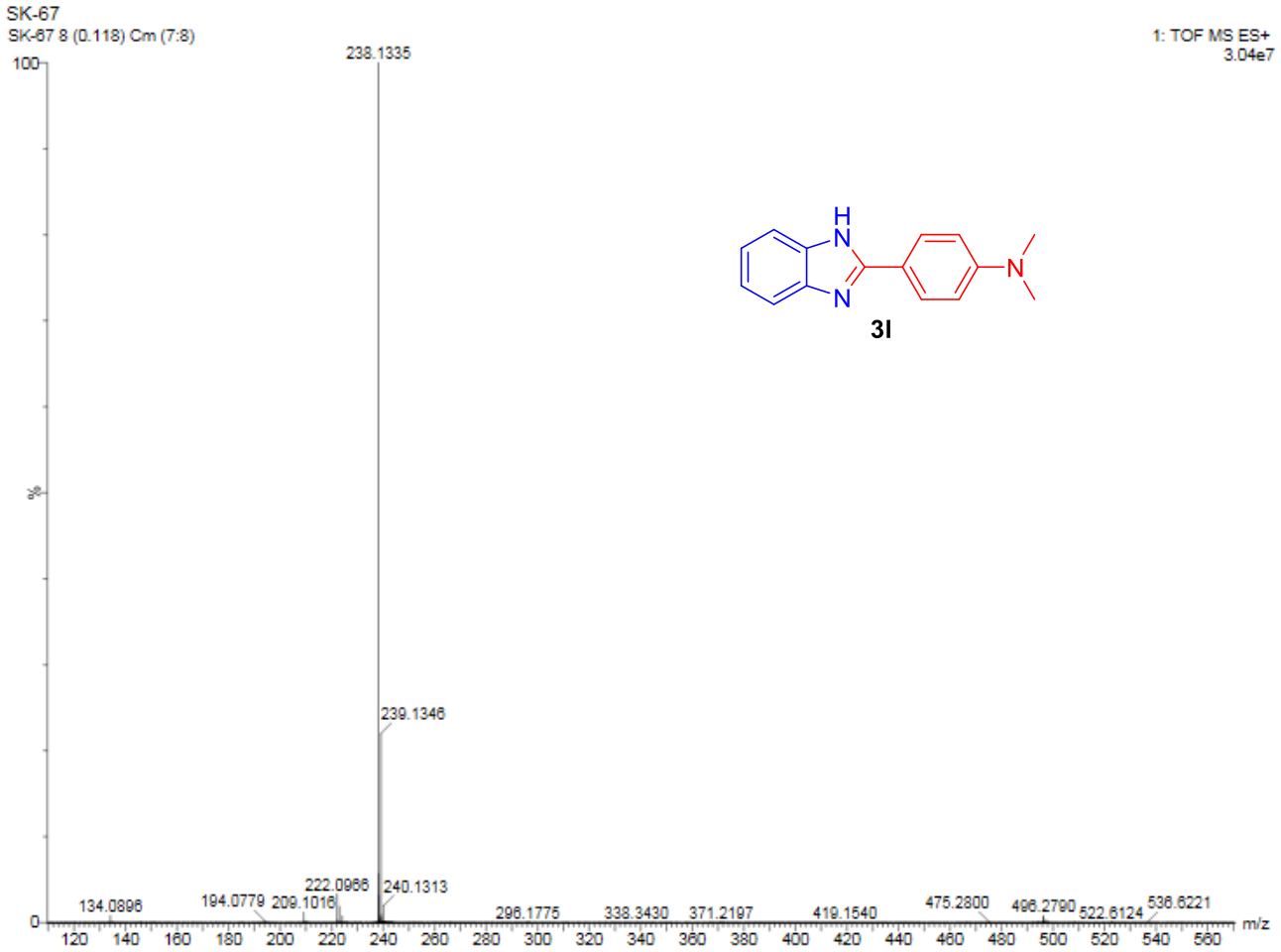


3a

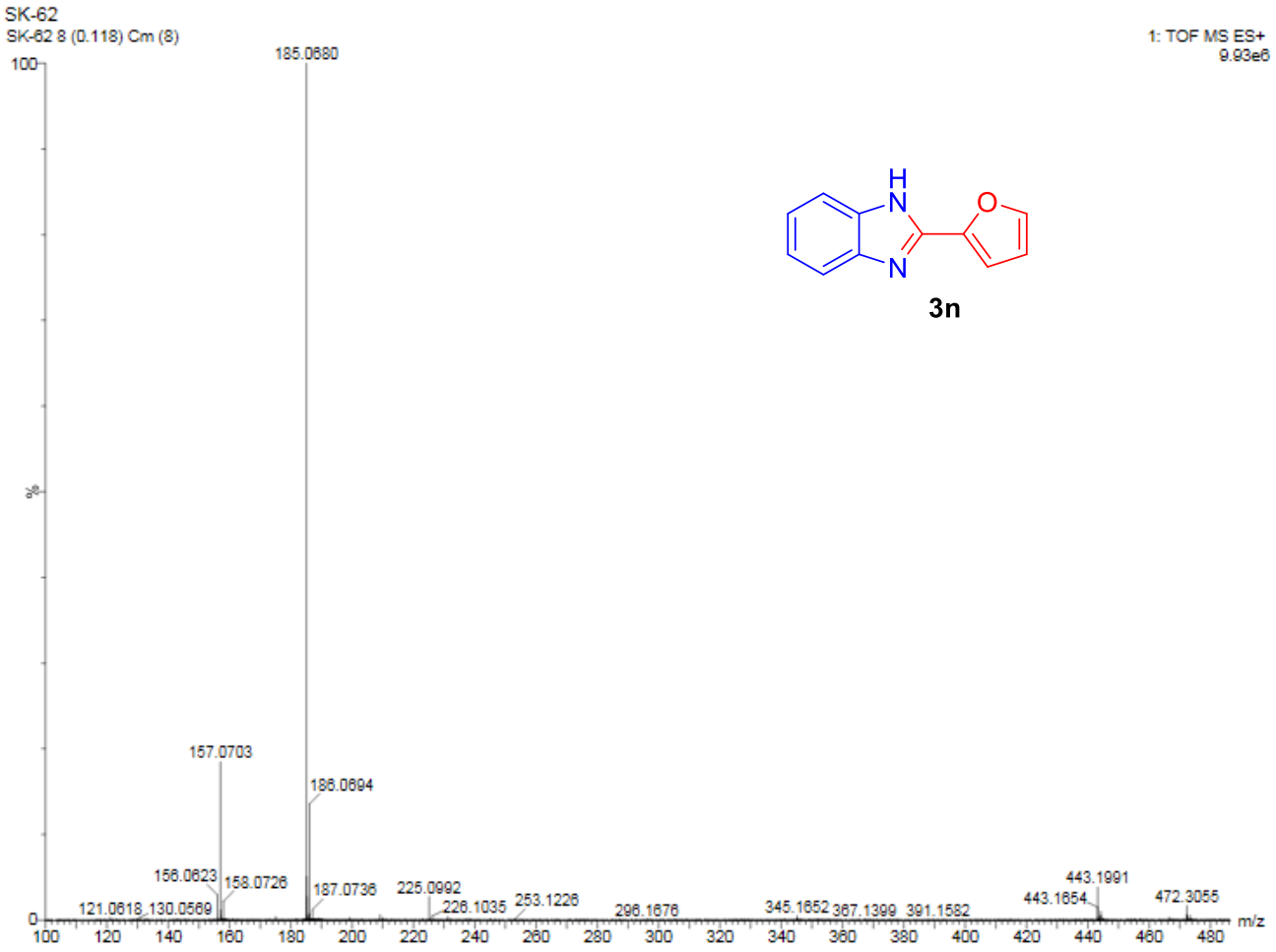

SK-51
SK-51 6 (0.097) Cm (6)
1: TOF MS ES+
1.48e7
100
%
0
225.1025
226.1046
210.0765
182.0796
181.0782
182.1053
227.1069
251.1441
309.0819
345.1504
357.3469
414.1721
449.2278
483.2212
494.5404
522.5809
m/z
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
H
N
N
OMe

3e


SK-60
SK-60 7 (0.108) Cm (7)
1: TOF MS ES+
1.18e7
100
%
0
240.0788
226.0733
194.0840
241.0795
210.0774
182.0835
242.0818
123.0809
152.0294
169.0743
296.1715
305.2264
337.2178
375.0920
419.1479
436.2175
472.3138
494.6175
m/z
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
NO2
H
N
N
3j


SK-67
SK-67 8 (0.118) Cm (7:8)
1: TOF MS ES+
3.04e7
100
%
0
238.1335
239.1346
240.1313
222.0966
209.1016
194.0779
134.0896
296.1775
338.3430
371.2197
419.1540
475.2800
496.2790
522.6124
536.6221
m/z
120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
H
N
N
N

3l


SK-62
SK-62 8 (0.118) Cm (8)
1: TOF MS ES+
9.93e6
185.0680
100
%
0
157.0703
186.0694
156.0623
158.0726
187.0736
225.0992
121.0618
130.0569
226.1035
253.1226
296.1676
345.1652
367.1399
391.1582
443.1991
443.1654
472.3055
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
m/z
H
N
N
O
3n