Electronic Supplementary Information (ESI†)

Nano Zirconia Catalysed One Pot Synthesis of Some Novel Substituted Imidazoles under Solvent Free Conditions

Shivam Bajpai, Sundaram Singh*, Vandana Srivastava

Indian Institute of Technology (BHU), Varanasi – 221 005, U.P., India.

Table of Contents

1. General remarks

All chemicals were procured from Aldrich, USA, and E. Merck, Germany and used as such. *N*-substituted isatins were prepared by earlier reported procedures. TLC was carried out on SiO_2 gel (HF254, 200 mesh). The solvent system employed was ethyl acetate: n-hexane (1: 1) and the spots were identified by placing the plate in Iodine chamber. IR spectra were recorded on a PerkinElmer FT/IR version10.03.05 spectrometer. NMR spectra were run on a JEOL AL300 FTNMR spectrometer; chemical shifts are given in δ ppm, relative to TMS as internal standard. **Elemental microanalysis was performed on Exeter Analytical Inc Model CE-440 CHN Analyzer.** Melting points were measured in open capillaries and are uncorrected. An XRD spectrum was recorded on a Scifert X-Ray Diffraction System. TEM image was taken from TECNAI G2, FEI. SEM image was recorded from Scanning Electron Microscope, QUANTA 200 F. BET surface area analysis was carried by Smart Sorb-93 manufactured by Smart Instruments Pvt. Ltd.

2. Typical procedure for the synthesis of ZrO_2 NPs[1]

0.075 M solution of $ZrOCl_2.8H_2O$ was prepared and then precipitated with NH_4OH (25%) with continuous stirring on a magnetic stirrer till the PH raises in the range of 10 to 10.5.This resulted in the formation of precipitate of zirconium hydroxide. The precipitate was filtered and washed with double distilled water until traces of chloride ion were completely removed from the filtrate. Complete removal of chloride ion from filtrate was checked by titrating it with $AgNO_3$ solution using potassium chromate as indicator. Now, the precipitate was dried in oven at 80 – 90 ^{0}C for 24 h. and calcinated at 600 ^{0}C for 3 h in order to formation of white nano zirconia powder.

3. IR spectra of ZrO_2 NPs

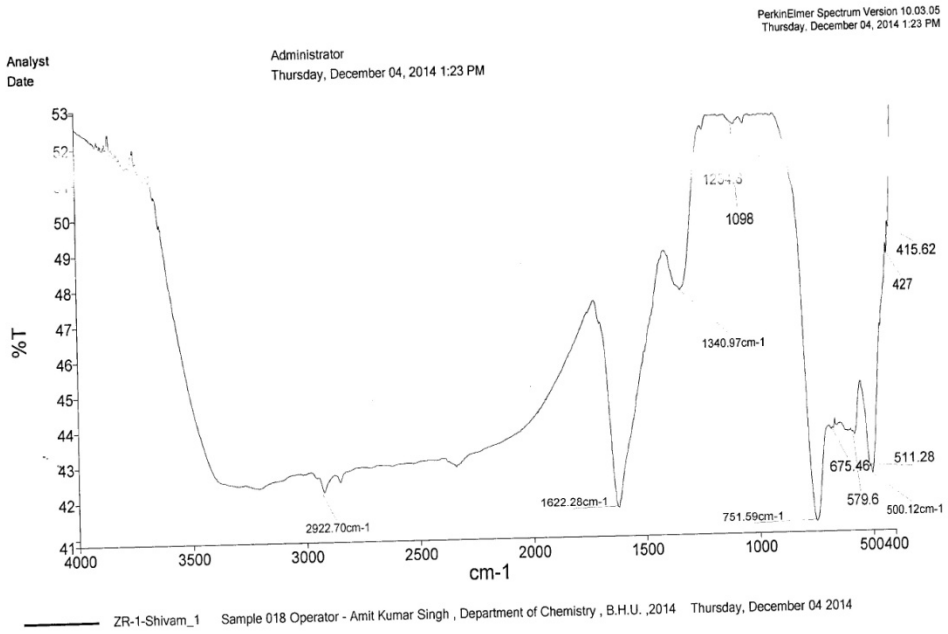

Figure A: FT-IR spectrum of ZrO_2 NPs

4. SEM image of ZrO_2 NPs

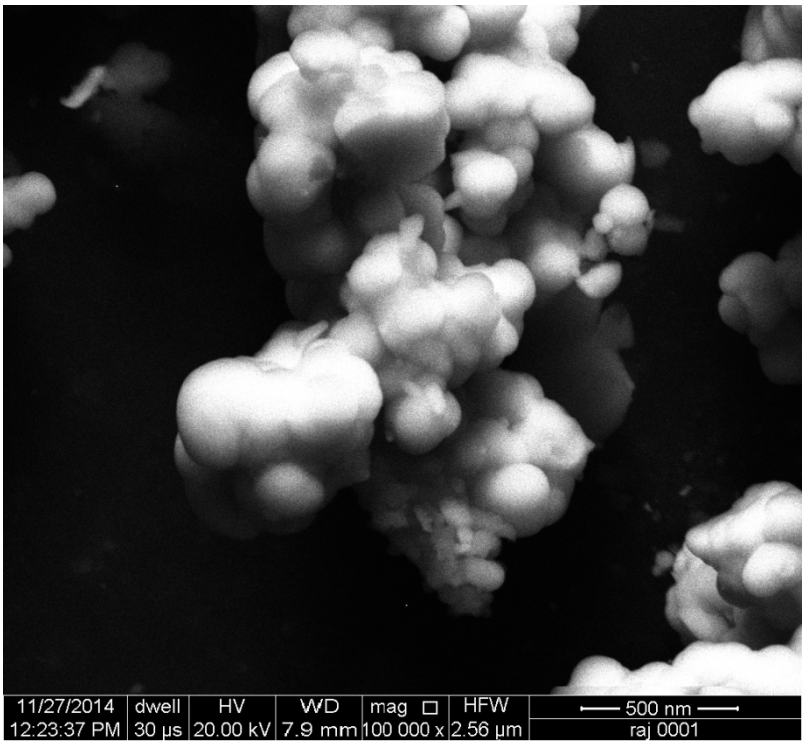

Figure B: SEM image of ZrO_2 NPs

5. BET surface area analysis data of ZrO_2 NPs

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Surface Area Analyser **From Smart Instruments Co.Pvt.Ltd**	**Model: Smart Sorb 92/93** **WebSite: www.smartinstrument.com**
Run Time:01:01 pm	Date:November 4 2014
% of N2 :30.06 Sample Name : I Wt of Tube (gms) :24.0721 Sample Wt (gms) :.1225 Sample Loss : 2.2 % Regeneration Temp.(deg.C) : 300 Time for regeneration (min.) :75	Room temp.in Deg.C:28 Wt of Tube+Sample (gms) :24.1946 Sample Wt after Reg. (gms) : .1198
Desorption count : 30706.4 Injection count : 22306.2 Injected volume (cc) : 1.4	

Surface Area in (Sq.m/gm) : 44.70

Remarks: SHIVAM | | |

Graph For Sample : I

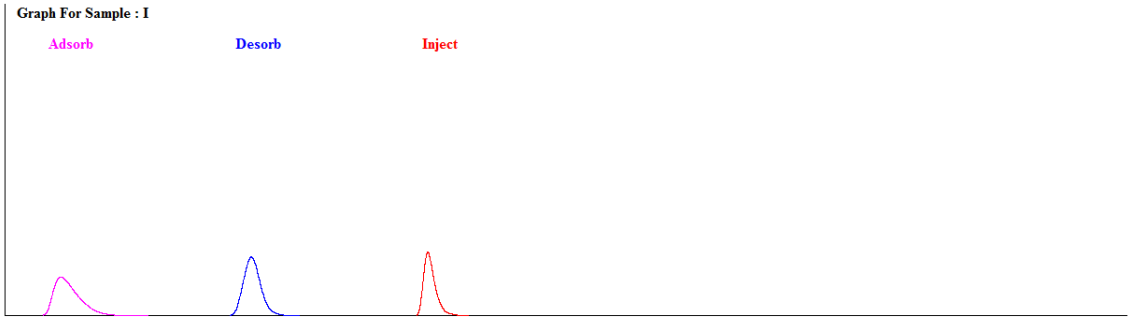


Figure C: BET surface area of ZrO_2 NPs

6. SEM image of bulk ZrO_2

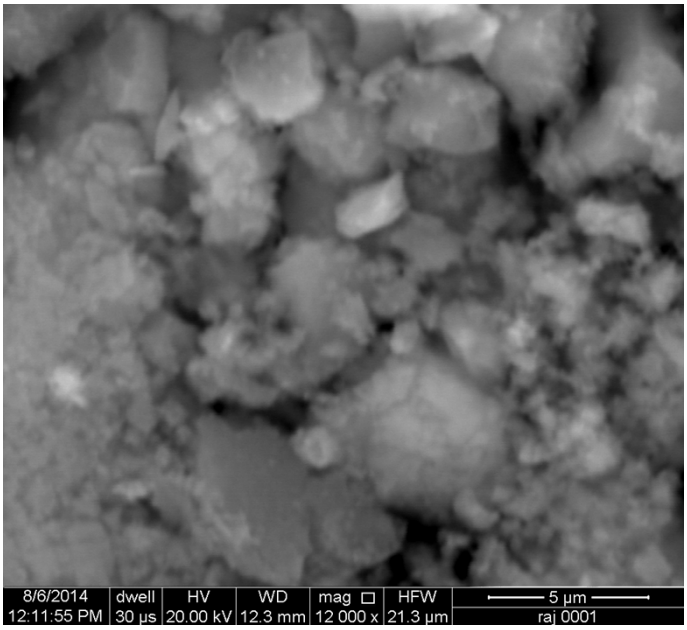


Figure D: SEM image of bulk ZrO_2

7. BET surface area analysis data of bulk ZrO_2

IIT BHU

Surface Area Analyser **From Smart Instruments Co.Pvt.Ltd**	**Model: Smart Sorb 92/93** **WebSite: www.smartinstrument.com**
Run Time:01:41 pm	Date:November 4 2014
% of N2 :30.06	Room temp.in Deg.C:28
Sample Name : I Wt of Tube (gms) :23.8081 Sample Wt (gms) :.1555 Sample Loss : 7.6 % Regeneration Temp.(deg.C) : 300 Time for regeneration (min.) :75	Wt of Tube+Sample (gms) :23.9636 Sample Wt after Reg. (gms) : .1437
Desorption count : 4081 Injection count : 2270.4 Injected volume (cc) : 0.2	

Surface Area in (Sq.m/gm) : 6.95

Remarks: SHIVAM | | |

Graph For Sample : I

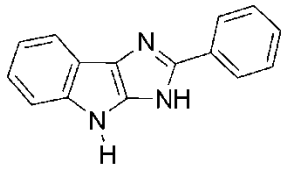
Figure E: BET surface area of bulk ZrO_2

8. General procedure for the synthesis of substituted imidazoles 4a-s

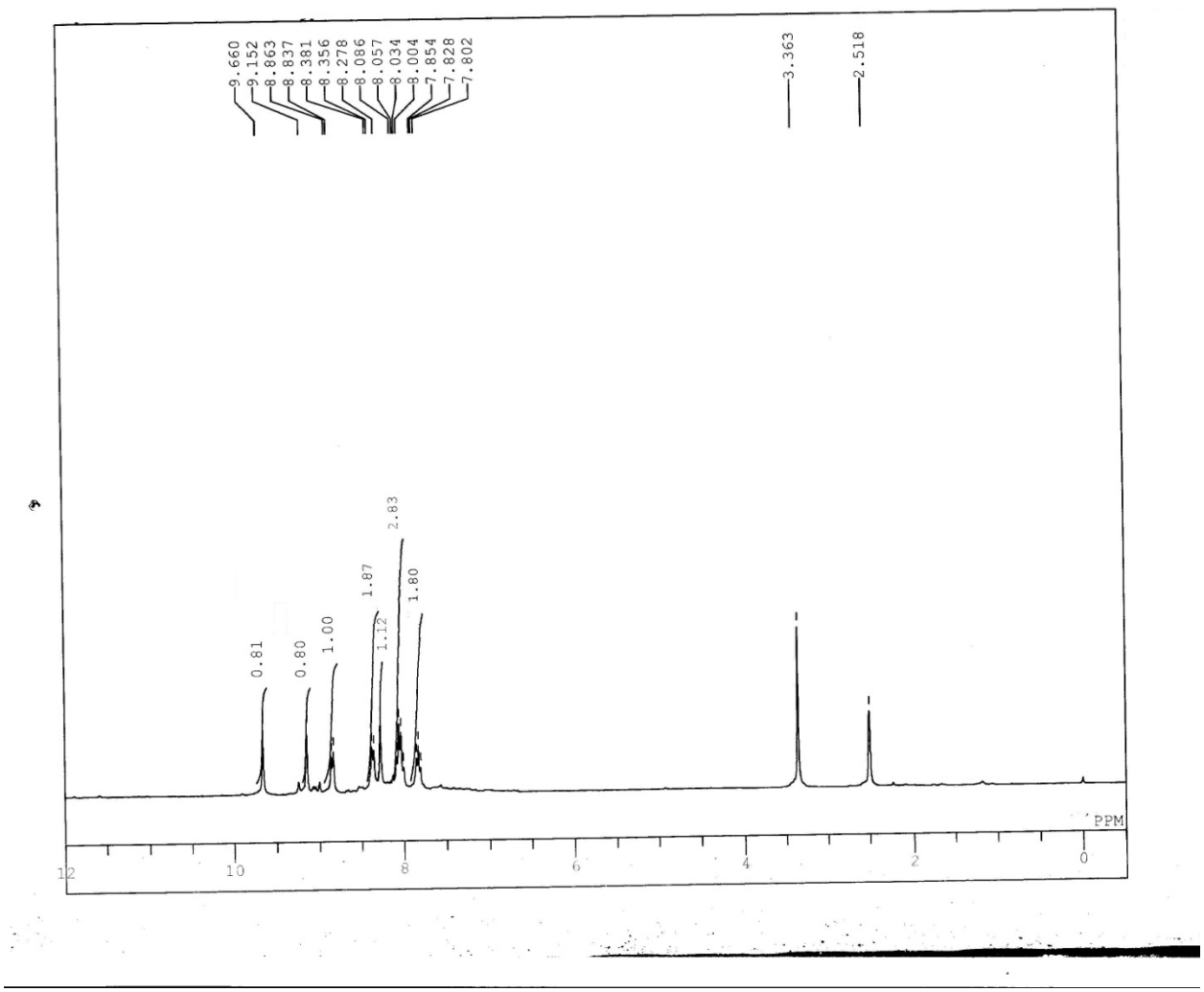
To a mixture of isatin derivatives **1a-g** (1 mmol), ammonium acetate **2** (5 mmol), substituted aromatic aldehydes **3a-f** (1 mmol), 15 mol% of ZrO_2 NPs was added [**Scheme 1**]. The mixture was heated and stirred at 110 ^{0}C for 30 min. The progress of the reaction was monitored by thin layered chromatography (n-hexane: ethyl acetate, 1:1). After completion, 20 ml acetone was added to the reaction mixture; the catalyst was removed by filtration and washed with xylene and acetone. Then, 50 ml of double distilled water is added to the liquid portion. This resulted in the formation of precipitate of products **4a-s**. The precipitate was filtered, dried and recrystallized with ethanol.

9. Characterization data and ^{1}H & ^{13}C spectra of substituted imidazoles 4a-s

9.1. 2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4a)



Brown solid, IR (KBr) υ: 3400, 3209, 3019, 2964, 1660, 1614, 1567, 1484, 1316, 1210, 1171, 1010, 877, 742, 653, 580 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 7.80- 8.86 (m, 9H, aromatic protons), 9.15 (s, 1H, NH), 9.66 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 124.0, 126.7, 127.5, 130.2, 130.7, 132.0, 133.7, 135.5, 139.1, 148.2, 160.9 ppm. Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.24; H, 4.74; N, 18.01 Found C, 77.20; H, 4.76; N, 18.03.


9.660
9.152
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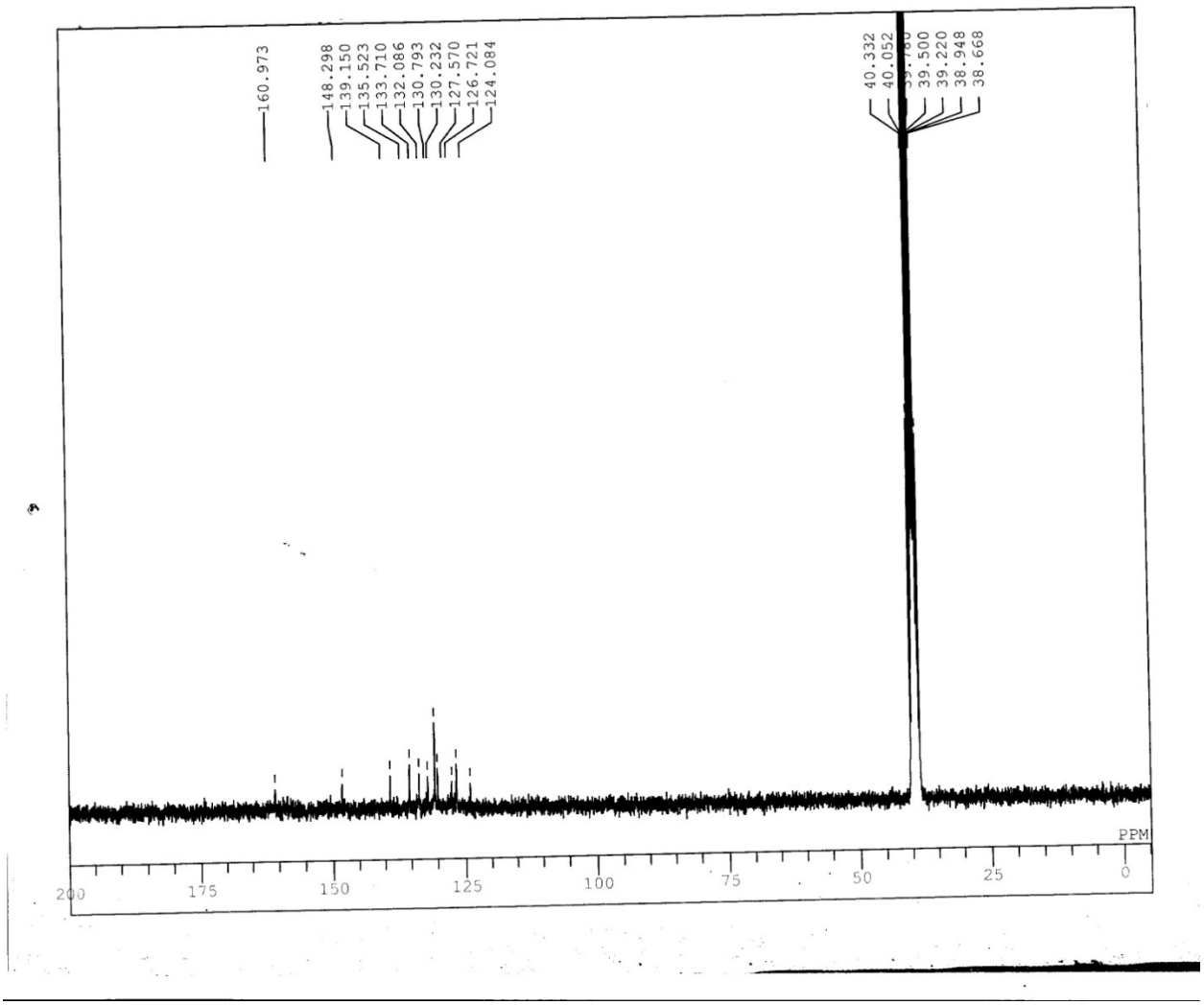
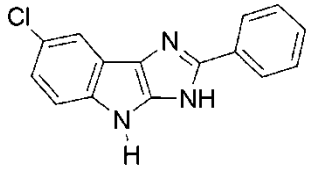
8.837
8.381
8.356
8.278
8.086
8.057
8.034
8.004
7.854
7.828
7.802
3.363
2.518
0.81
0.80
1.00
1.87
1.12
2.83
1.80
PPM
12
10
8
6
4
2
0

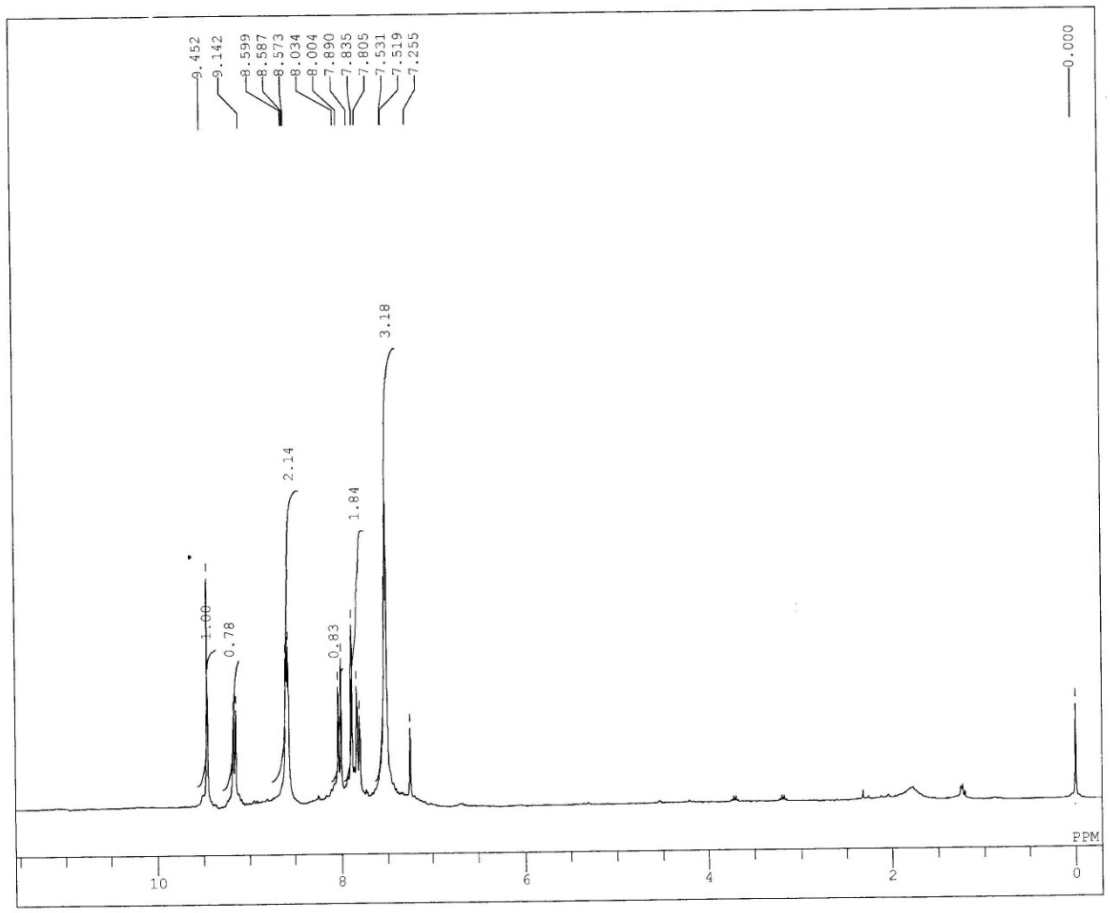


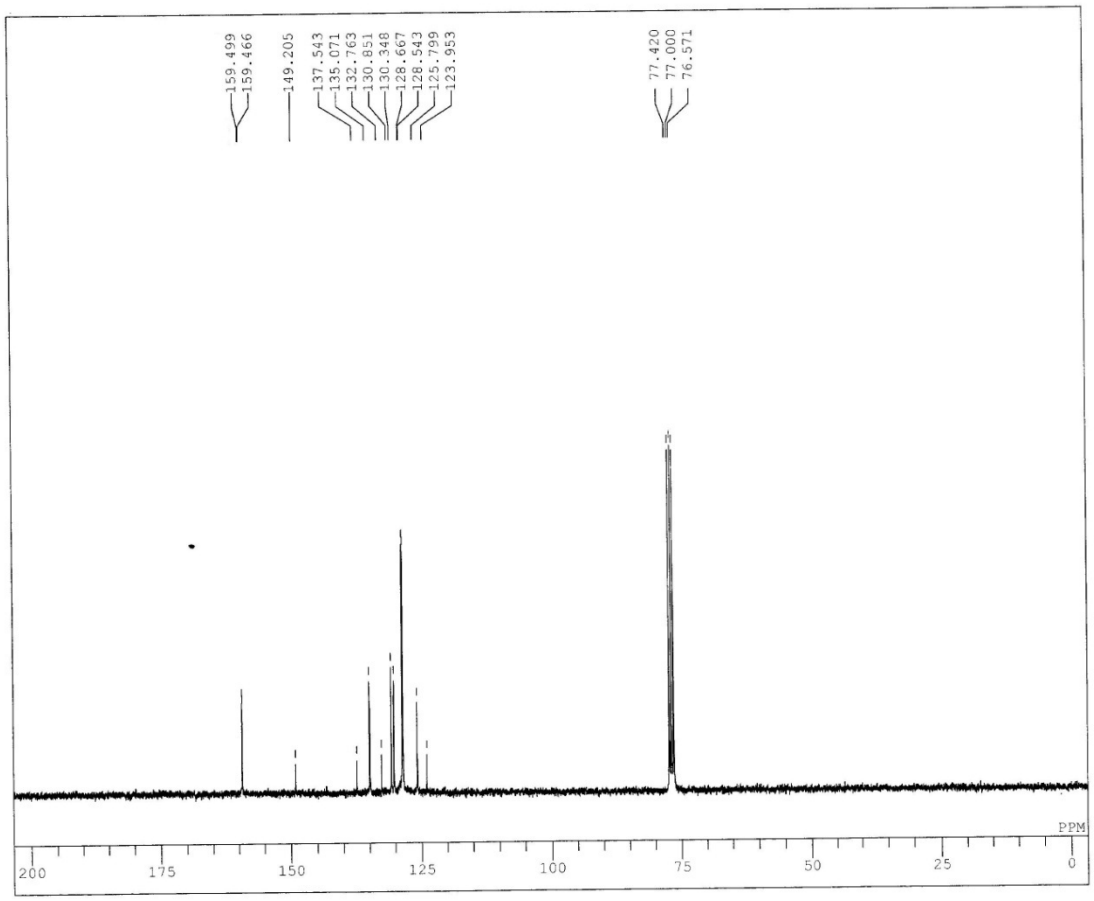
9.2. 7-chloro-2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4b)



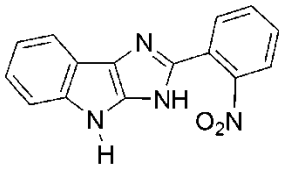
Brown solid, IR (KBr) υ: 3364, 3190, 2981, 2964, 1648, 1609, 1559, 1447, 1311, 1199, 1143, 1019, 872, 744, 651, 566 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51- 8.59 (m, 8H, aromatic protons), 9.14 (s, 1H, NH), 9.45 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 123.9,

125.7, 128.5, 128.6, 130.3, 130.8, 132.7, 135.0, 137.5, 149.2, 159.4 ppm. Anal. Calcd for $C_{15}H_{10}ClN_3$: C, 67.28; H, 3.78; N, 15.72. Found C, 67.32; H, 3.76; N, 15.70

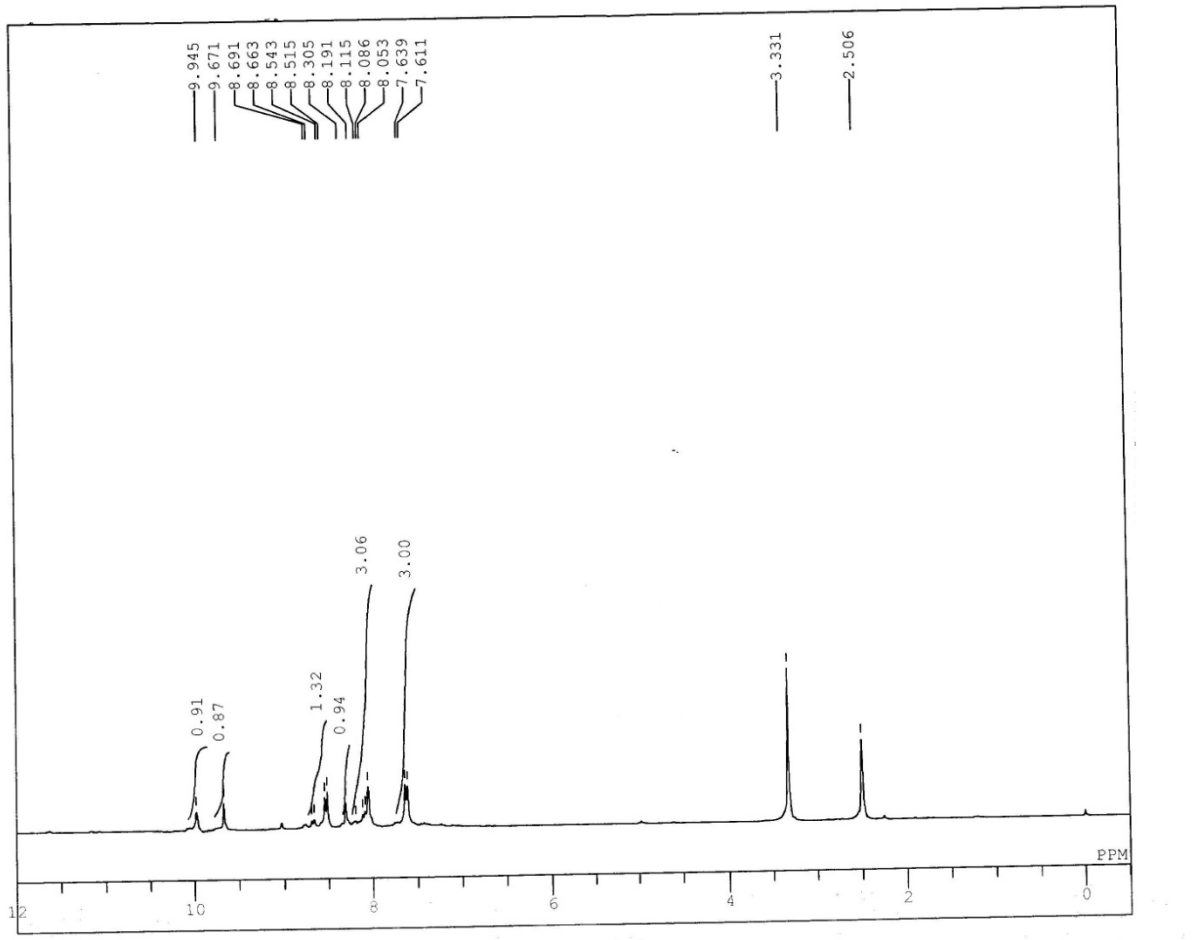




9.3. 2-(2-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4c)



Brown solid, IR (KBr) υ: 3332, 3201, 2995, 2917, 1658, 1623, 1549, 1485, 1348, 1280, 1176, 1068, 864, 708, 667, 544 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 7.61- 8.69 (m, 8H, aromatic protons), 9.67 (s, 1H, NH), 9.94 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 123.8, 126.7, 128.8, 129.8, 130.1, 131.8, 135.4, 135.8, 135.9, 148.3, 160.7 ppm. Anal. Calcd for $C_{15}H_{10}N_4O_2$: C, 64.74; H, 3.62; N, 20.13 Found C, 64.69; H, 3.65; N, 20.14.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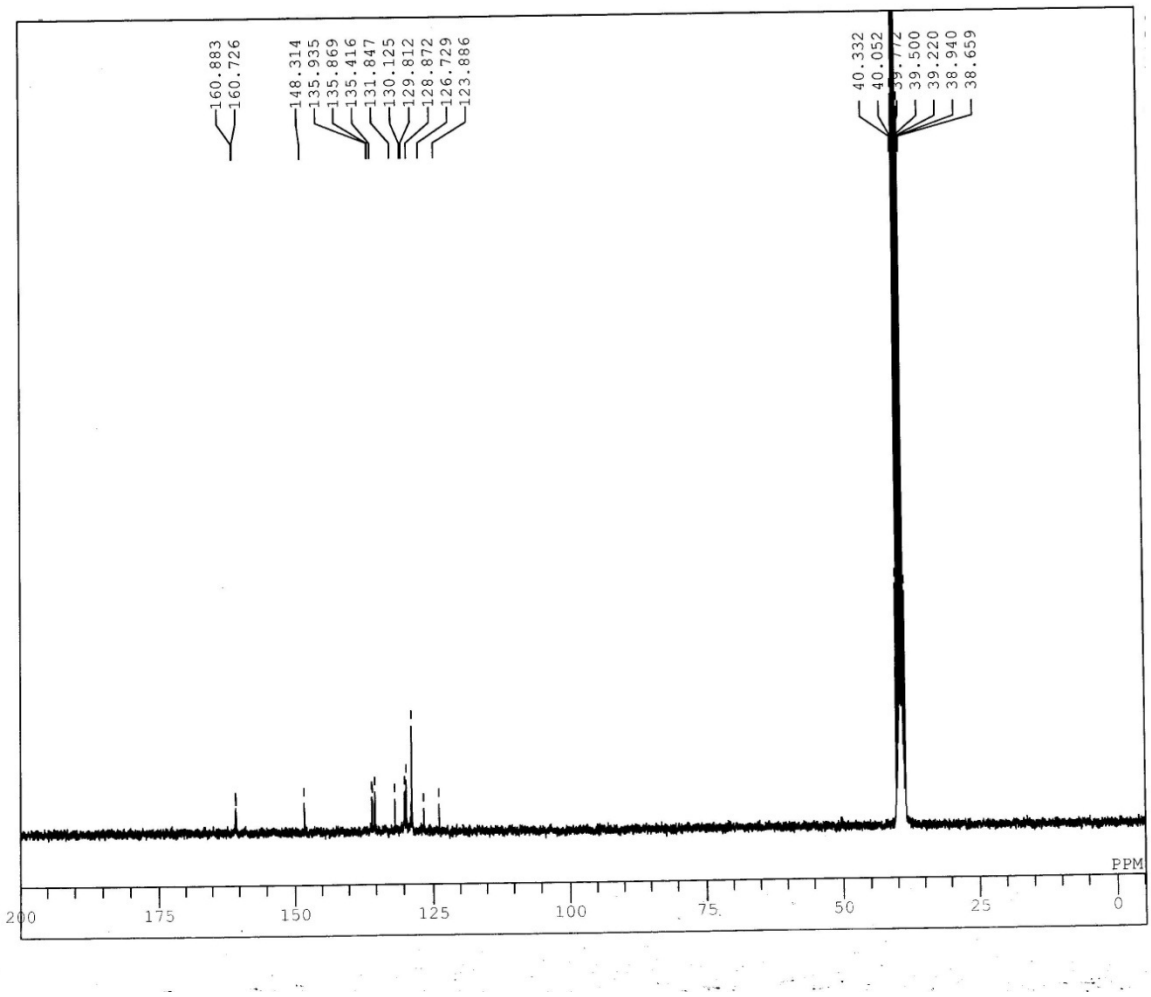
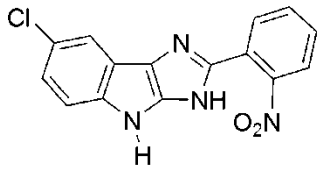
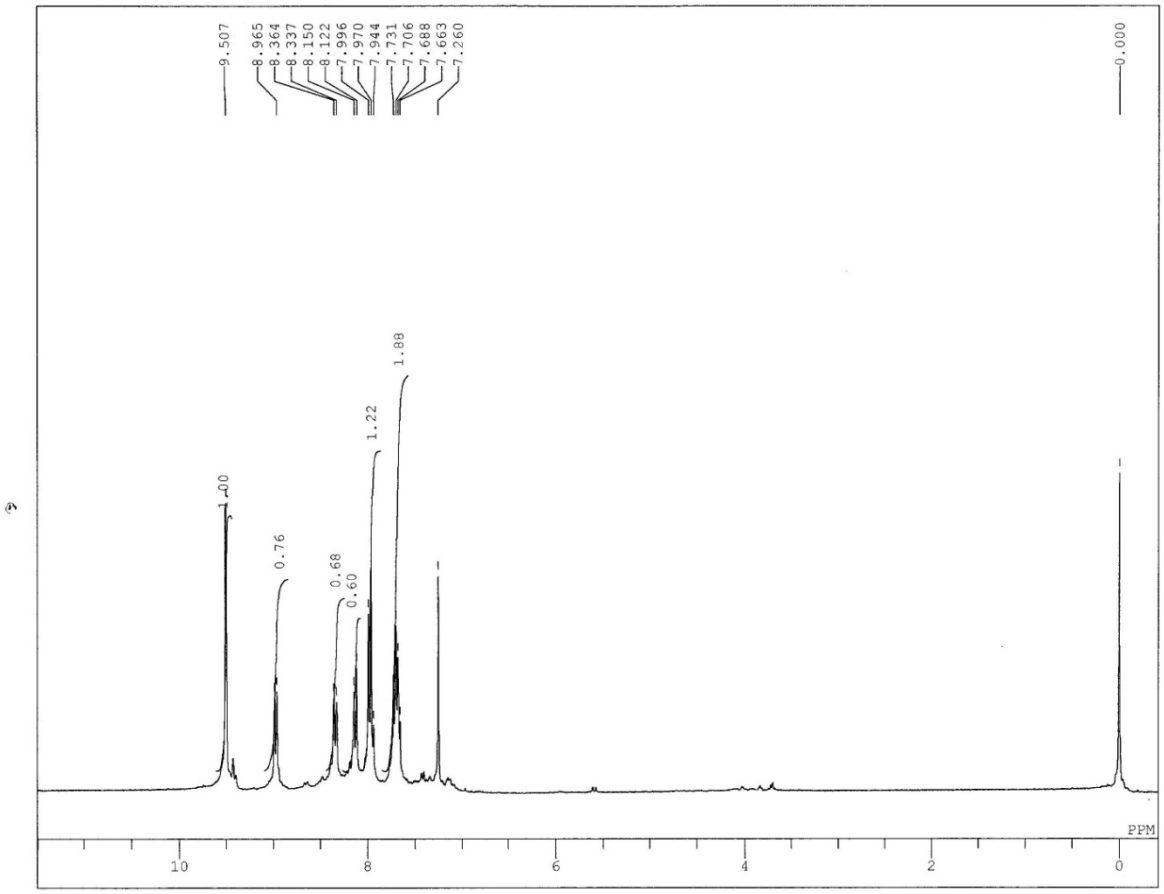
9.671
8.691
8.663
8.543
8.515
8.305
8.191
8.115
8.086
8.053
7.639
7.611
3.331
2.506
0.91
0.87
1.32
0.94
3.06
3.00
PPM
12
10
8
6
4
2
0



9.4. 7-chloro-2-(2-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4d)



Brown solid, IR (KBr) υ: 3399, 3229, 2916, 2885, 1645, 1600, 1539, 1457, 1329, 1253, 1162, 1027, 885, 703, 647, 553 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66- 8.36 (m, 7H, aromatic protons), 8.96 (s, 1H, NH), 9.50 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 123.4, 123.8, 124.8, 127.1, 128.0, 128.6, 129.4, 133.9, 134.1, 134.4, 139.7, 148.7, 150.4, 160.6 ppm. Anal. Calcd for $C_{15}H_9ClN_4O_2$: C, 57.60; H, 2.91; N, 17.91 Found C, 57.51; H, 3.0; N, 17.94.


9.507
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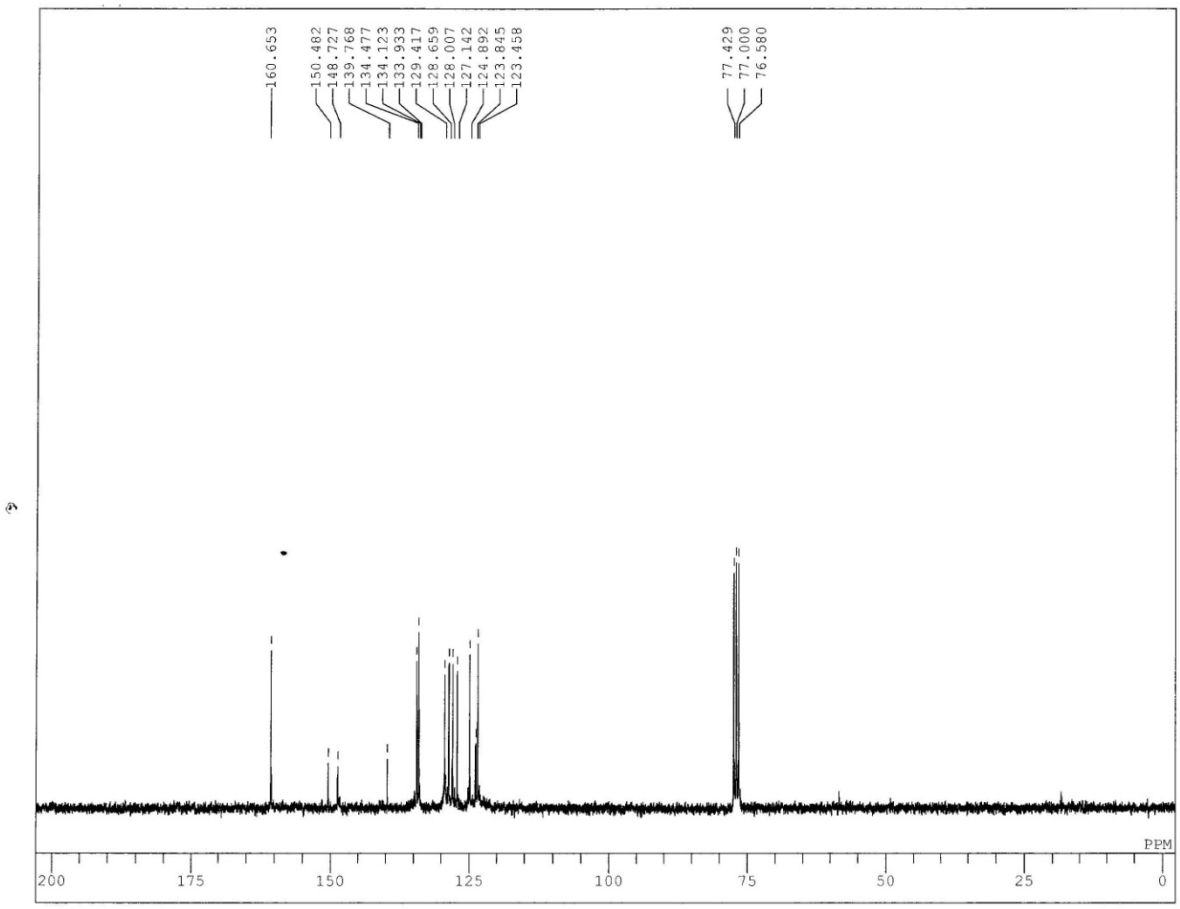
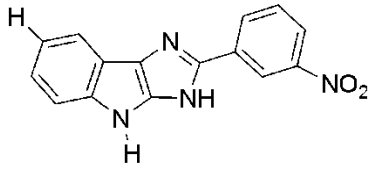
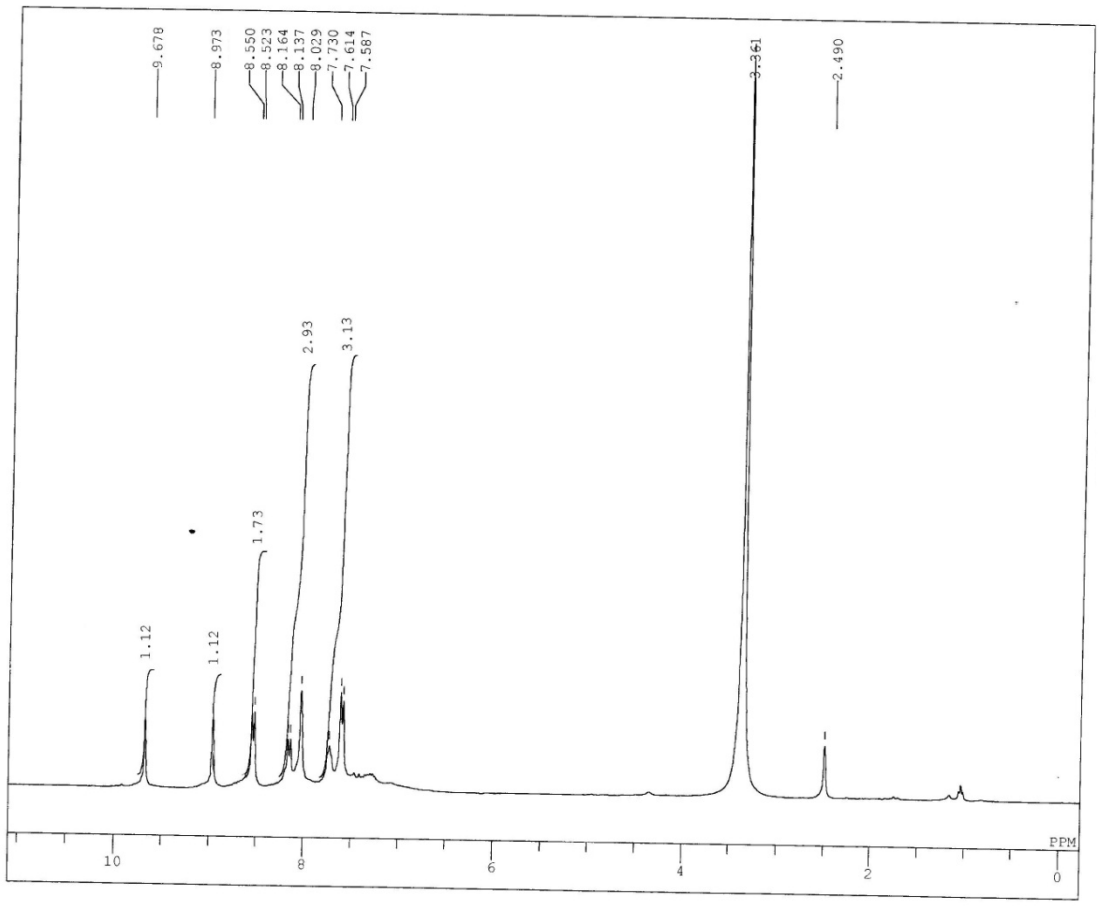
8.364
8.337
8.150
8.122
7.996
7.970
7.944
7.731
7.706
7.688
7.663
7.260
0.000
1.00
0.76
0.68
0.60
1.22
1.88
PPM
10
8
6
4
2
0



9.5. 2-(3-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4e)



Brown solid, IR (KBr) υ: 3315, 3194, 3066, 2978, 1662, 1623, 1572, 1482, 1353, 1286, 1135, 1025, 832, 797, 661, 542 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 7.58- 8.55 (m, 8H, aromatic protons), 8.97 (s, 1H, NH), 9.67 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 122.3, 123.6, 125.2, 127.9, 128.4, 129.7, 130.4, 134.4, 134.5, 135.2, 139.0, 147.6, 161.7 ppm. Anal. Calcd for $C_{15}H_{10}N_4O_2$: C, 64.70; H, 3.63; N, 20.16 Found C, 64.51; H, 3.72; N, 20.23.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8.137
8.029
7.730
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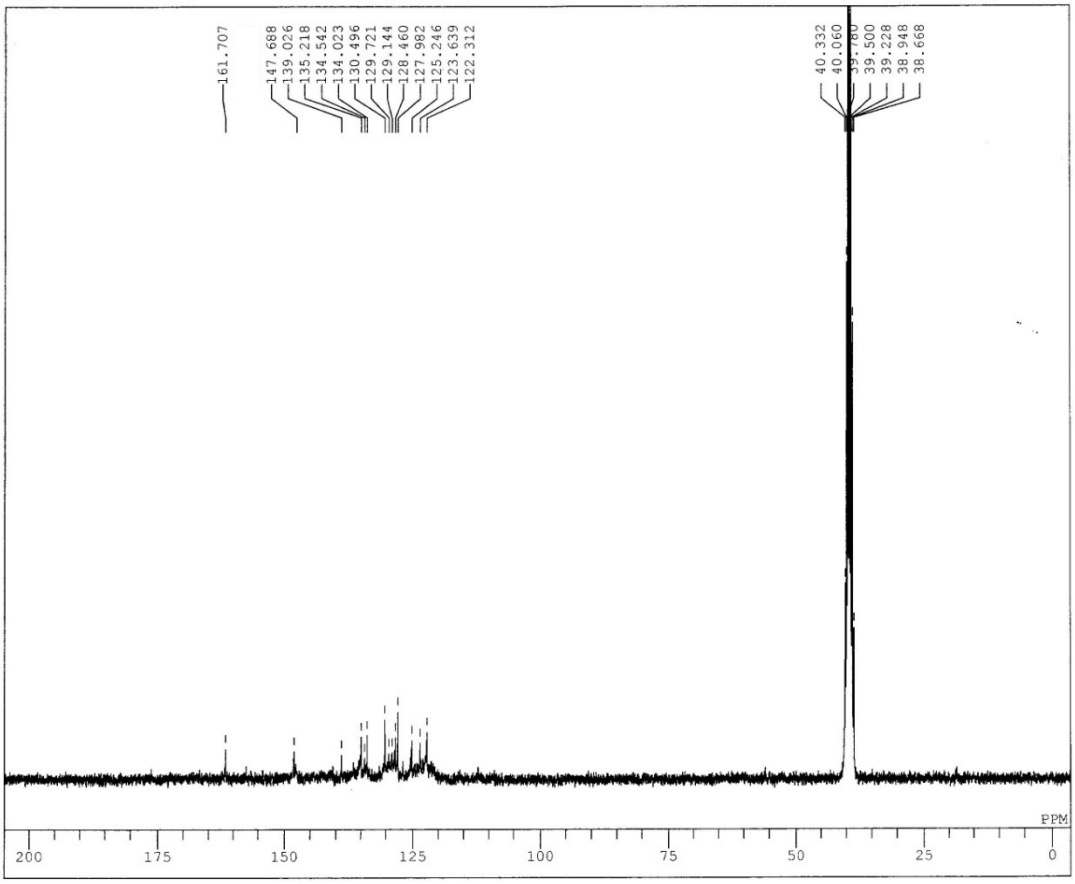
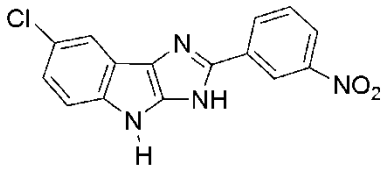
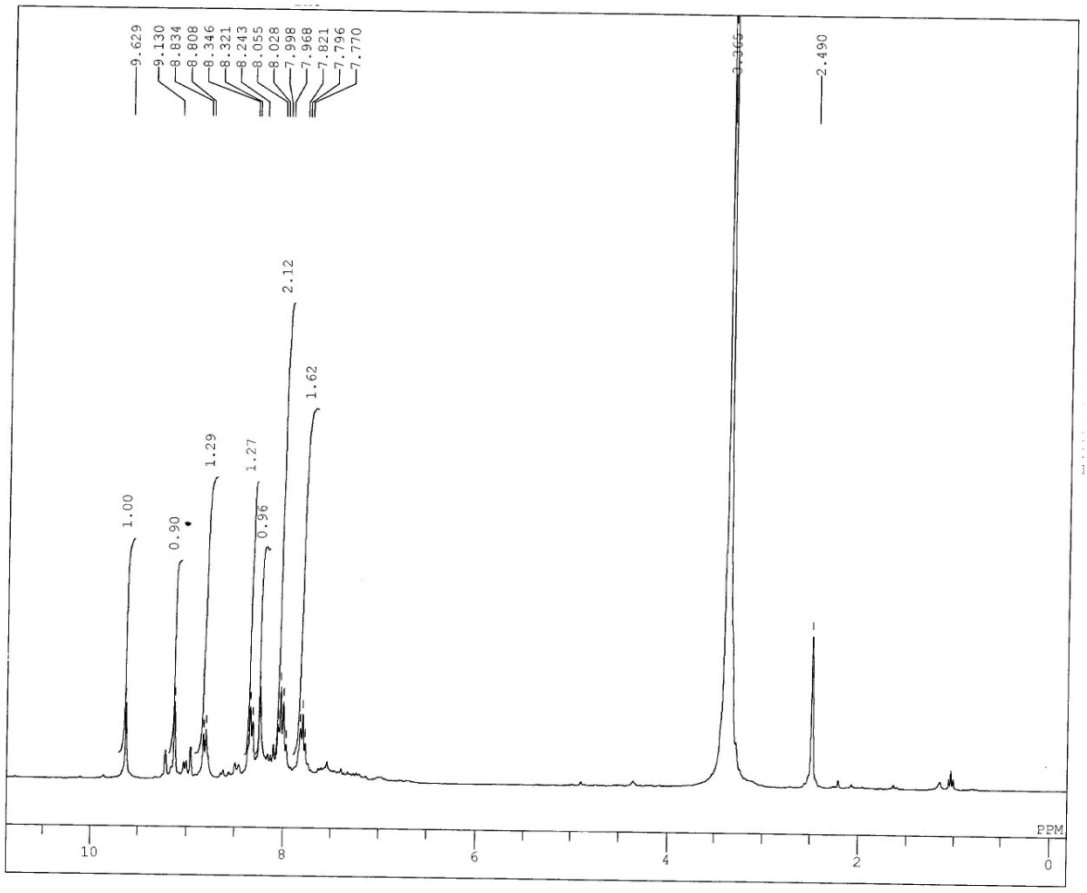
3.13
PPM
10
8
6
4
2
0



9.6. 7-chloro-2-(3-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4f)



Brown solid, IR (KBr) υ: 3385, 3211, 3003, 2959, 1646, 1603, 1538, 1458, 1367, 1248, 1122, 1022, 831, 741, 635, 564 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 7.77- 8.83 (m, 7H, aromatic protons), 9.13 (s, 1H, NH), 9.62 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 124.0, 126.6, 127.5, 127.6, 130.2, 130.7, 132.0, 133.6, 135.4, 139.1, 148.2, 160.8, 160.9 ppm. Anal. Calcd for $C_{15}H_9ClN_4O_2$: C, 57.61; H, 2.90; N, 17.92 Found C, 57.67; H, 2.90; N, 17.90.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9.130
8.834
8.808
8.346
8.321
8.243
8.055
8.028
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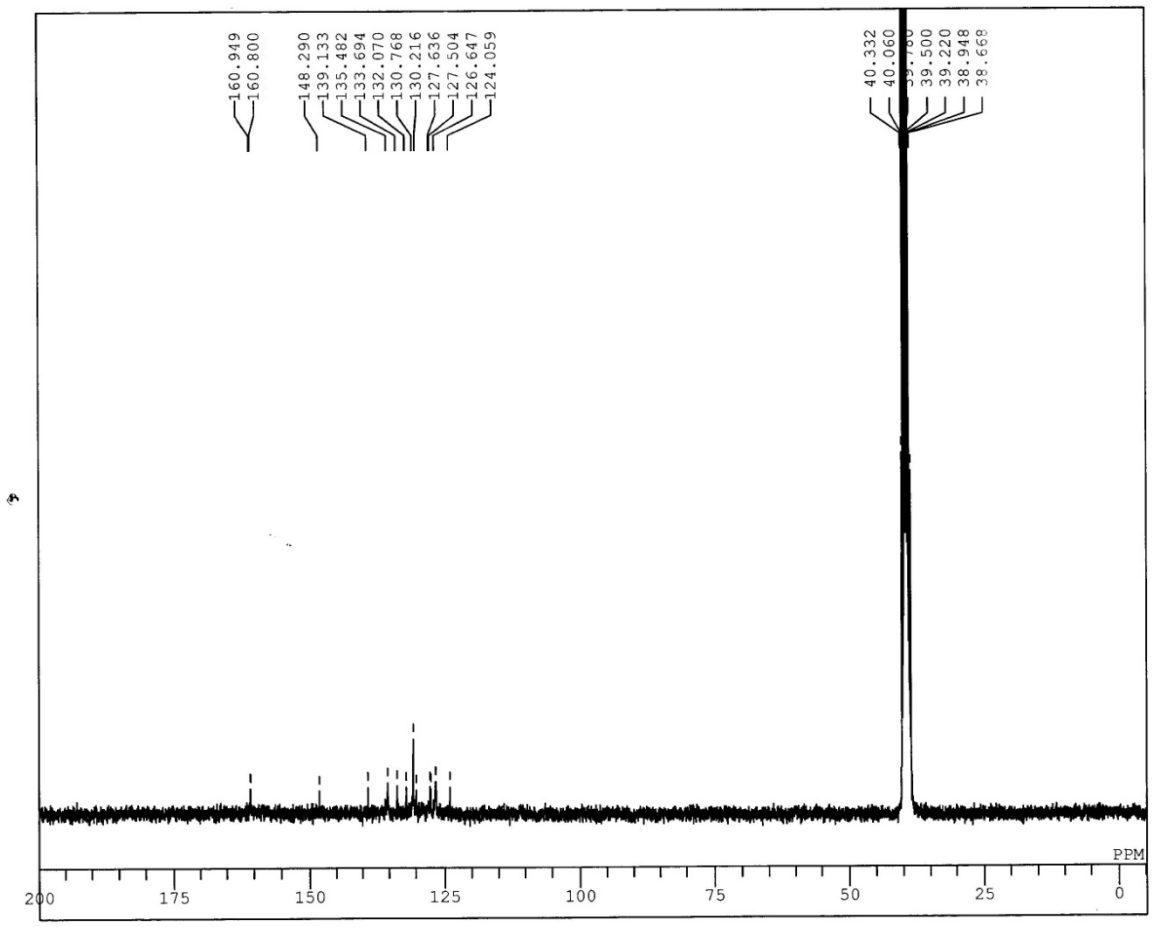
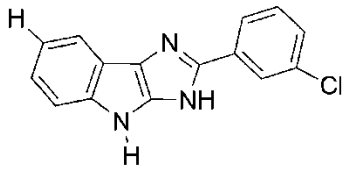
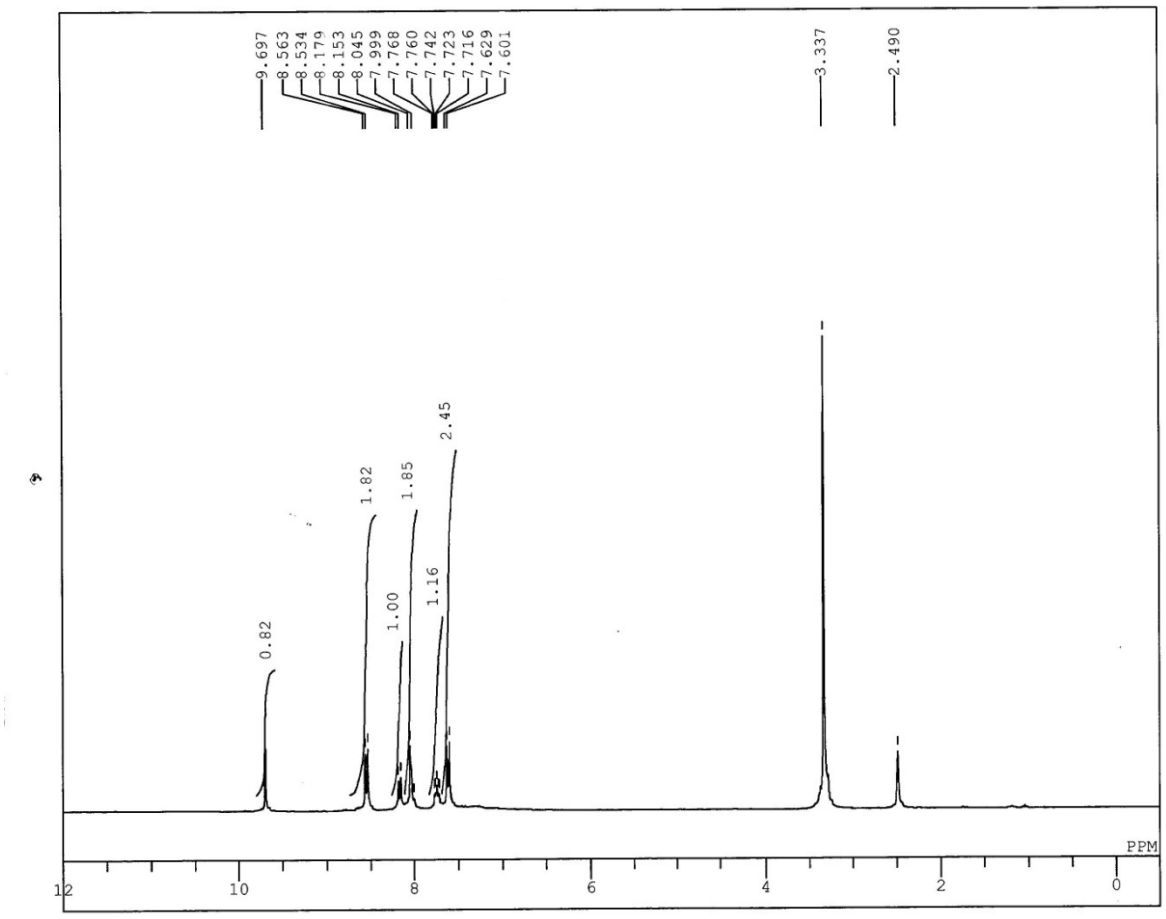
7.968
7.821
7.796
7.770
3.365
2.490
2.12
1.62
1.29
1.27
1.00
0.90
0.96
PPM
10
8
6
4
2
0



9.7. 2-(3-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4g)



Brown solid, IR (KBr) υ: 3405, 3217, 2948, 2909, 1671, 1617, 1568, 1454, 1371, 1283, 1134, 1018, 892, 754, 641, 577 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 7.60- 8.56 (m, 9H, aromatic protons and 1H, NH), 9.69 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 123.8, 126.6, 128.8, 128.7, 130.1, 131.0, 131.6, 135.2, 137.0, 148.4, 160.6 ppm. Anal. Calcd for $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.77; N, 15.70 Found C, 67.29; H, 3.75; N, 15.70.


9.697
8.563
8.534
8.179
8.153
8.045
7.999
7.768
7.760
7.742
7.723
7.716
7.629
7.601
3.337
2.490
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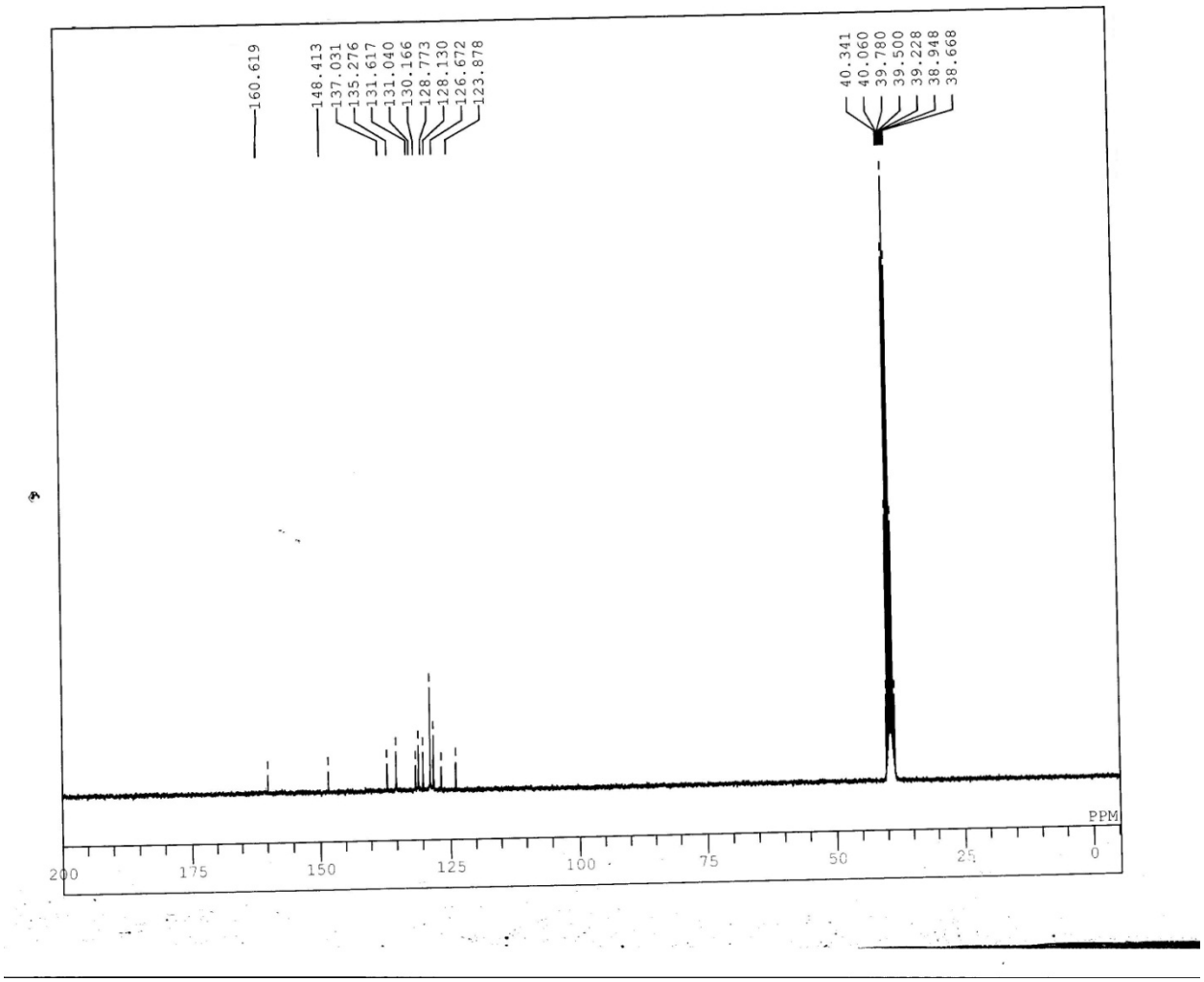
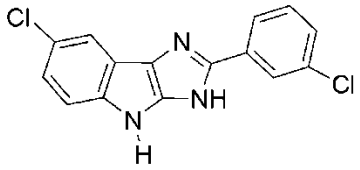
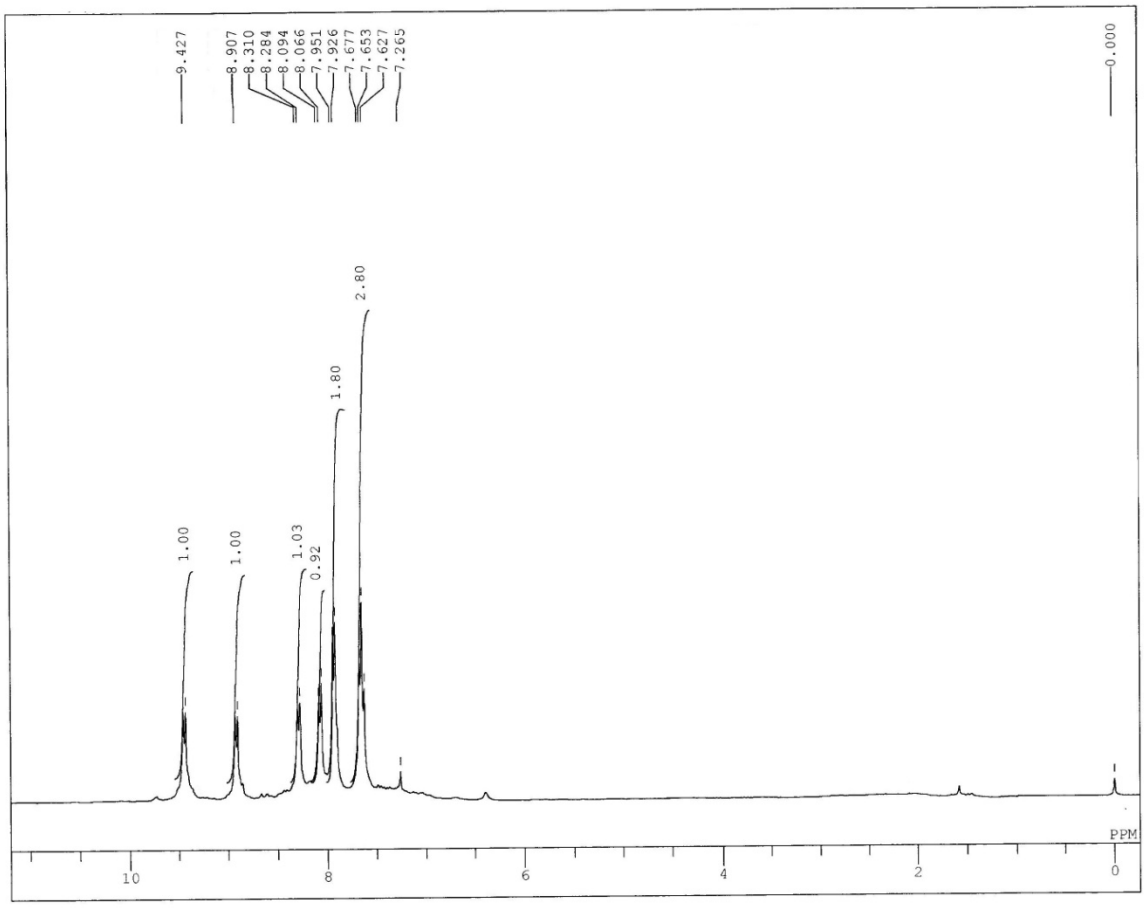
1.00
1.85
1.16
2.45
PPM
12
10
8
6
4
2
0

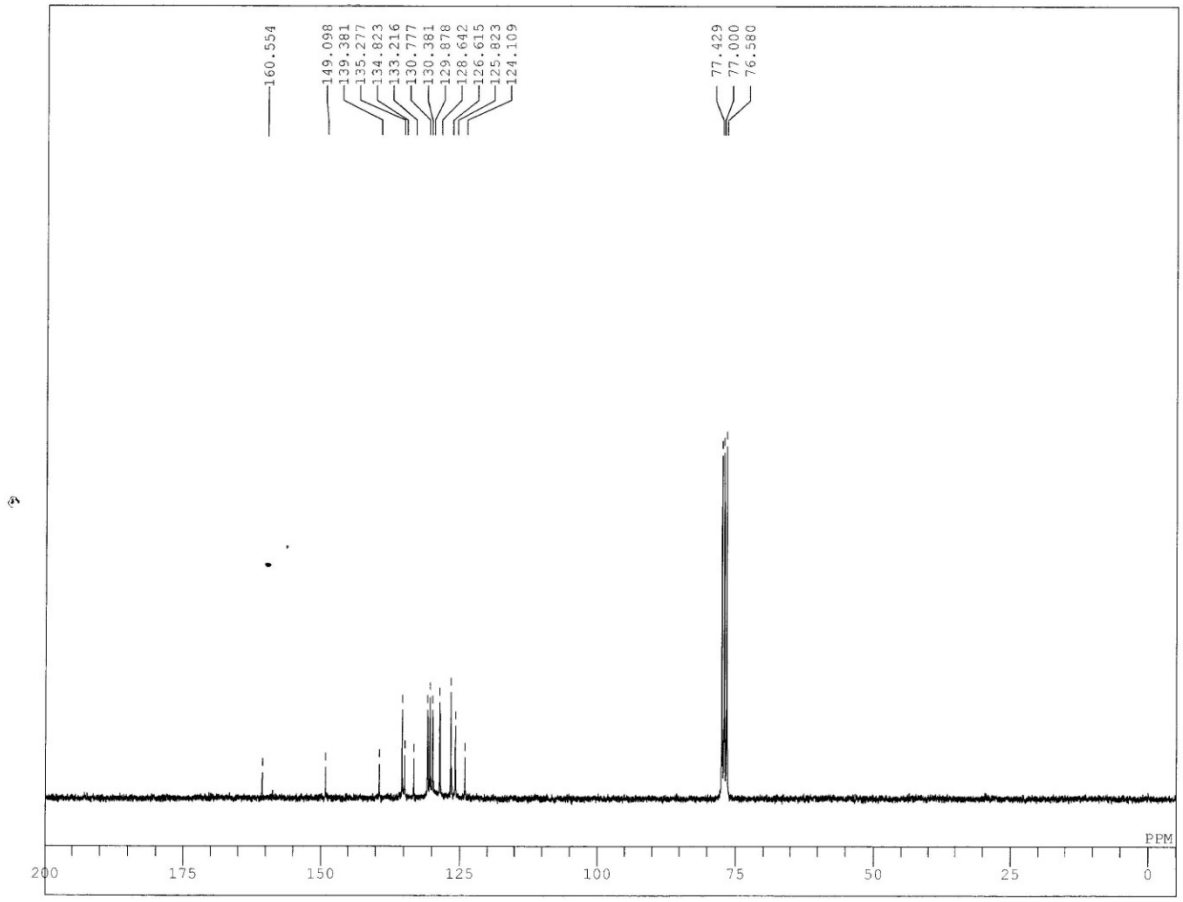


9.8. 7-chloro-2-(3-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4h)

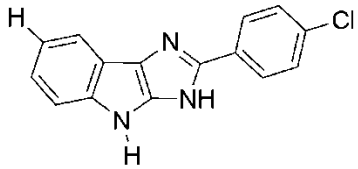


Brown solid, IR (KBr) υ: 3398, 3227, 2977, 2893, 1664, 1605, 1551, 1477, 1358, 1242, 1163, 1011, 844, 743, 650, 567 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.62- 8.31 (m, 7H, aromatic protons), 8.90 (s, 1H, NH), 9.42 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 124.1, 125.8, 126.6, 128.6, 129.8, 130.3, 130.7, 133.2, 134.8, 135.2, 139.3, 149.0, 160.5 ppm. Anal. Calcd for $C_{15}H_9C_{l2}N_3$: C, 59.62; H, 3.00; N, 13.91 Found C, 59.52; H, 3.05; N, 13.89.

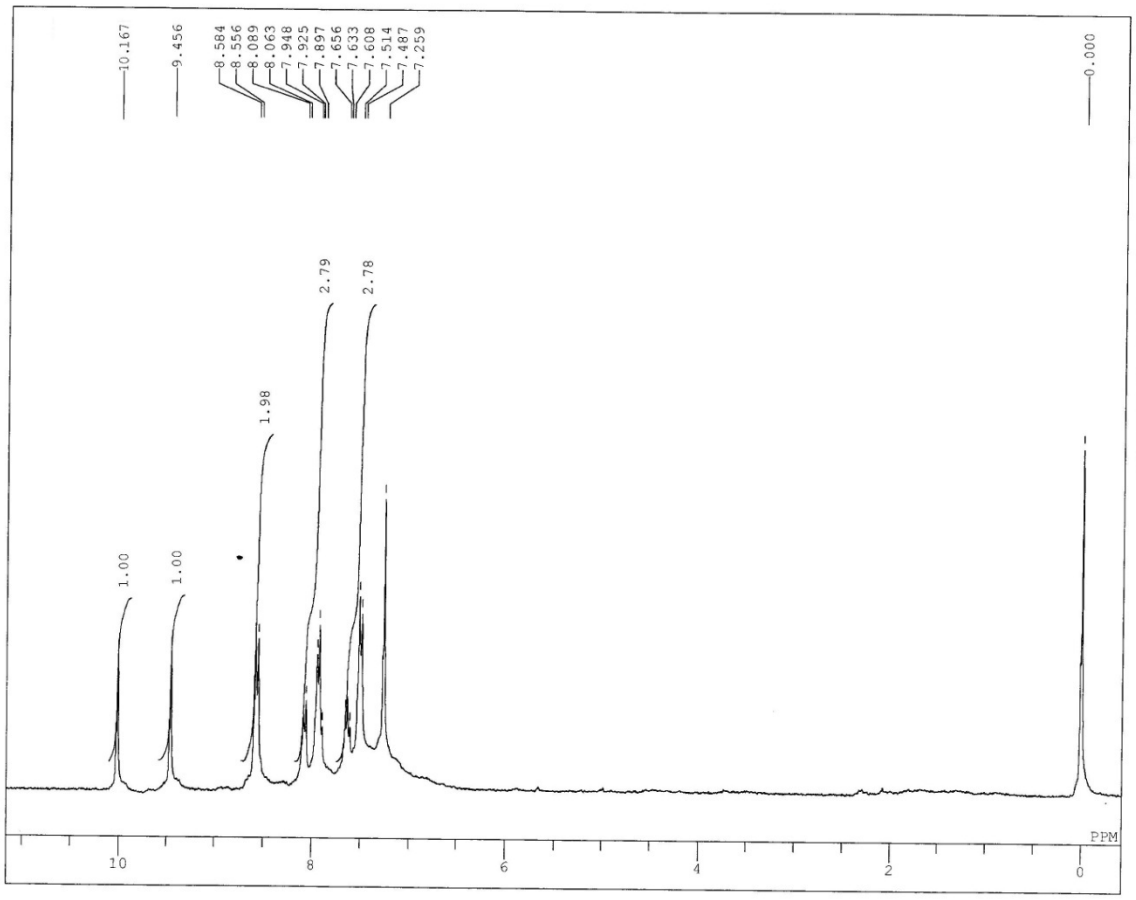

9.427
8.907
8.310
8.284
8.094
8.066
7.951
7.926
7.677
7.653
7.627
7.265
0.000
1.00
1.00
1.03
0.92
1.80
2.80
PPM
10
8
6
4
2
0

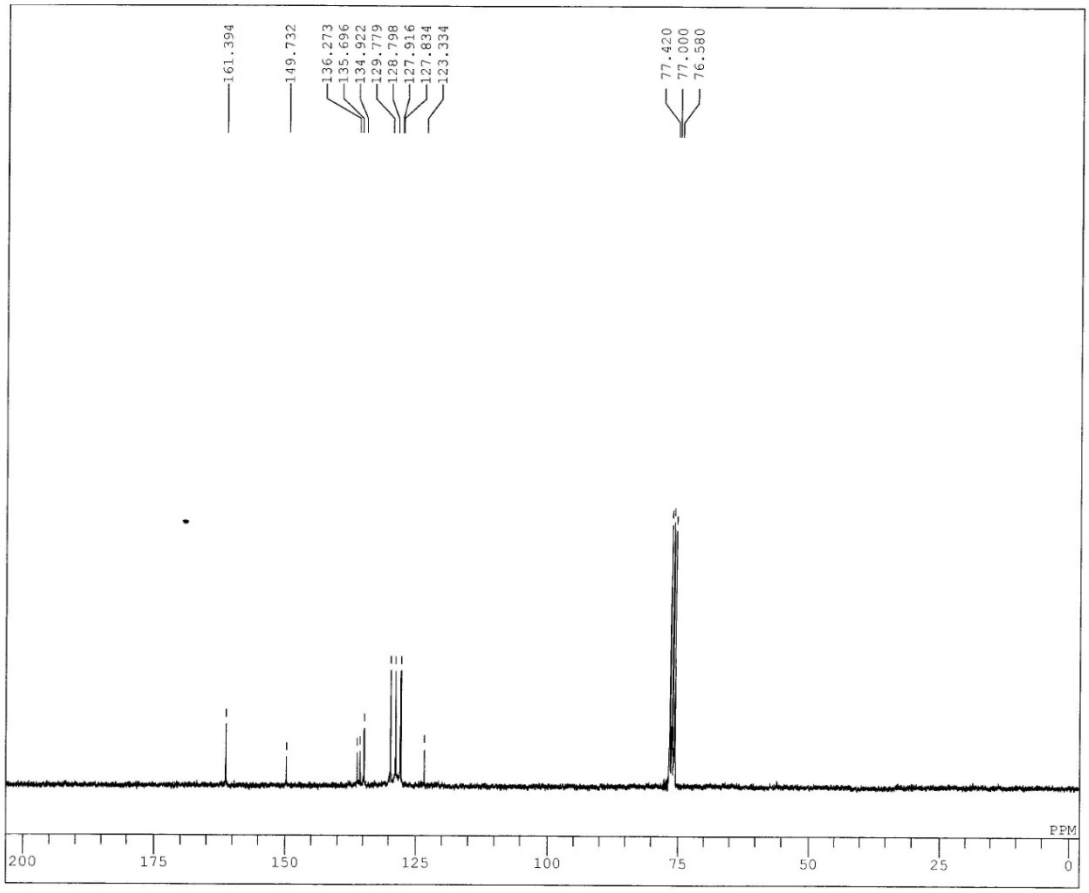


9.9. 2-(4-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4i)

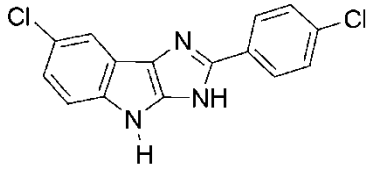


Brown solid, IR (KBr) υ: 3362, 3255, 3015, 2882, 1669, 1620, 1565, 1482, 1375, 1235, 1140, 1026, 890, 777, 663, 526 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48- 8.58 (m, 8H, aromatic protons), 9.45 (s, 1H, NH), 10.16 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 123.3, 127.8, 127.9, 128.7, 129.7, 134.9, 135.6, 136.2, 149.7, 161.3 ppm. Anal. Calcd for $C_{15}H_{10}ClN_3$: C, 67.30; H, 3.77; N, 15.70 Found C, 67.31; H, 3.75; N, 15.73.

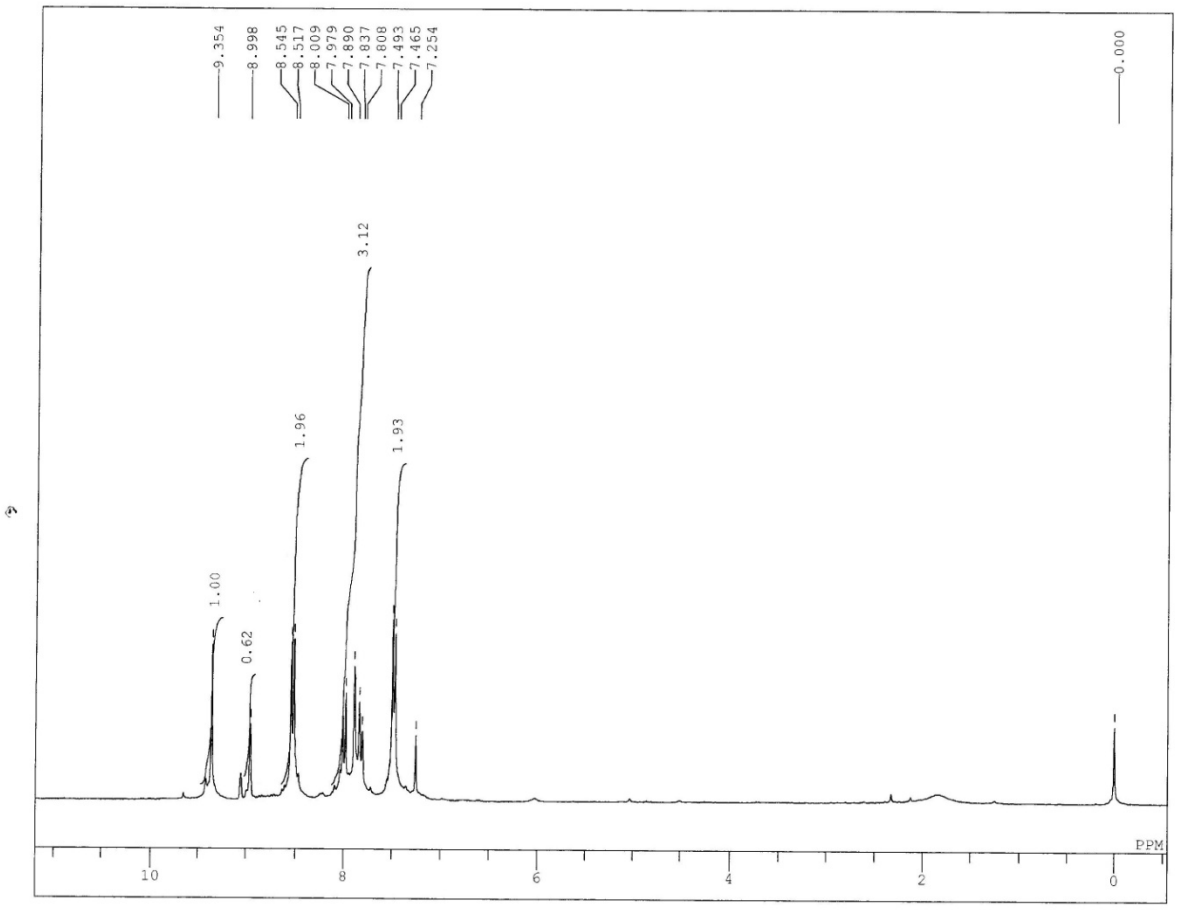

10.167
9.456
8.584
8.556
8.089
8.063
7.948
7.925
7.897
7.656
7.633
7.608
7.514
7.487
7.259
0.000
2.79
2.78
1.98
1.00
1.00
PPM
10
8
6
4
2
0

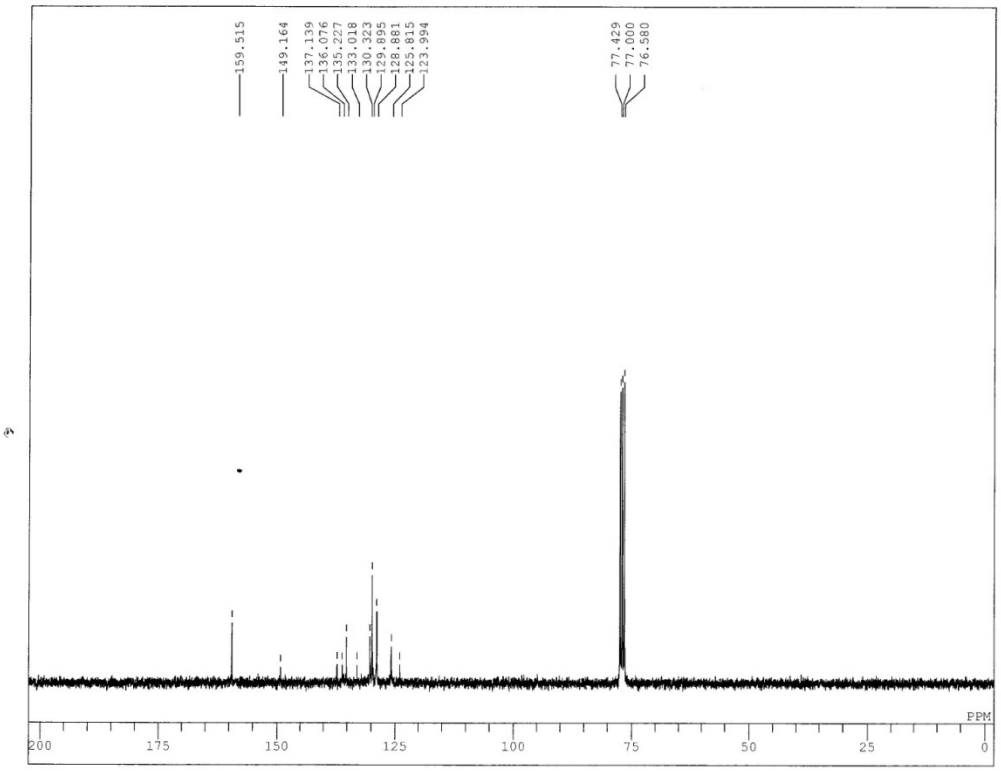


9.10. 7-chloro-2-(4-chlorophenyl)-3,4-dihydroimidazo[4,5-b]indole (4j)

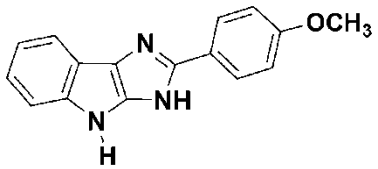


Brown solid, IR (KBr) υ: 3386, 3233, 3047, 2960, 1657, 1612, 1558, 1435, 1348, 1282, 1153, 1019, 871, 742, 654, 552 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46- 8.54 (m, 7H, aromatic protons), 8.99 (s, 1H, NH), 9.35 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 123.9, 125.8, 128.8, 129.8, 130.3, 133.0, 135.2, 136.0, 137.1, 149.1, 159.5 ppm. Anal. Calcd for $C_{15}H_9Cl_2N_3$: C, 59.62; H, 3.00; N, 13.91 Found C, 59.55; H, 3.10; N, 13.90.

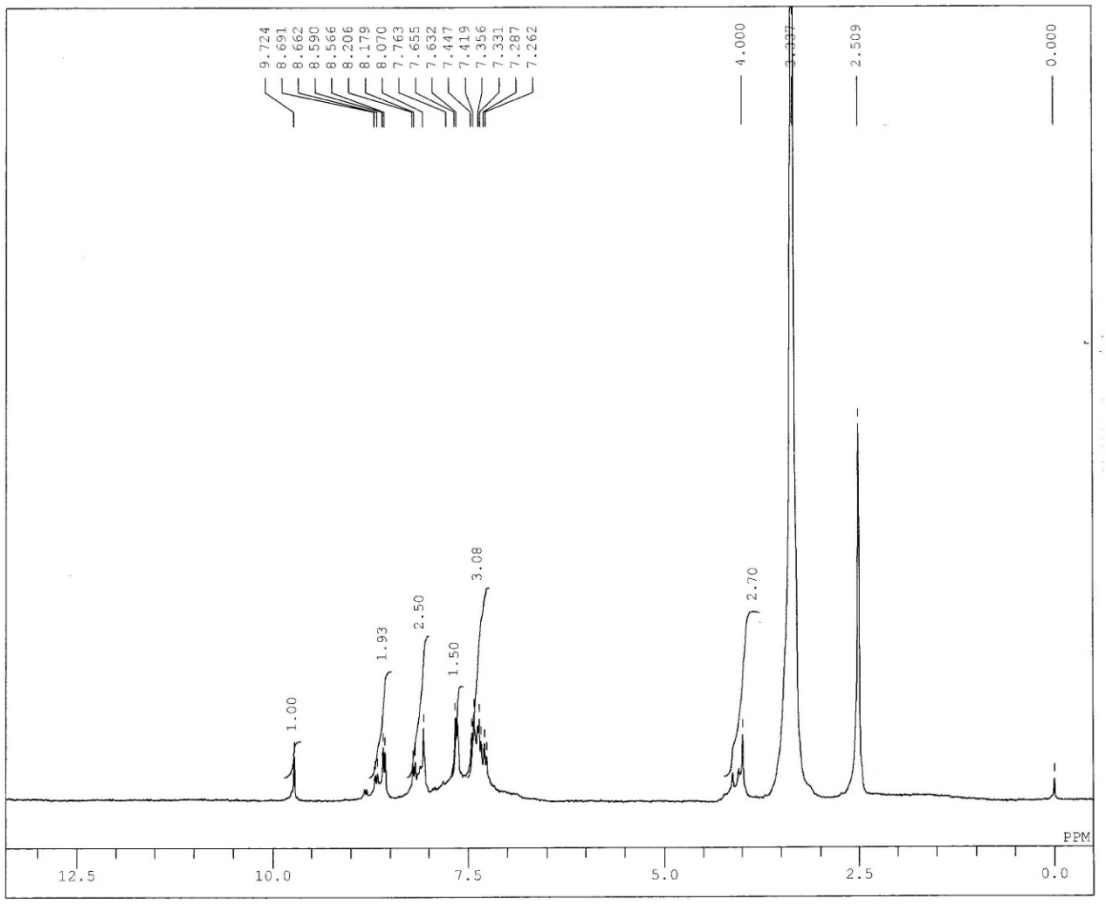

9.354
8.998
8.545
8.517
8.009
7.979
7.890
7.837
7.808
7.493
7.465
7.254
0.000
3.12
1.96
1.93
1.00
0.62
PPM
10
8
6
4
2
0

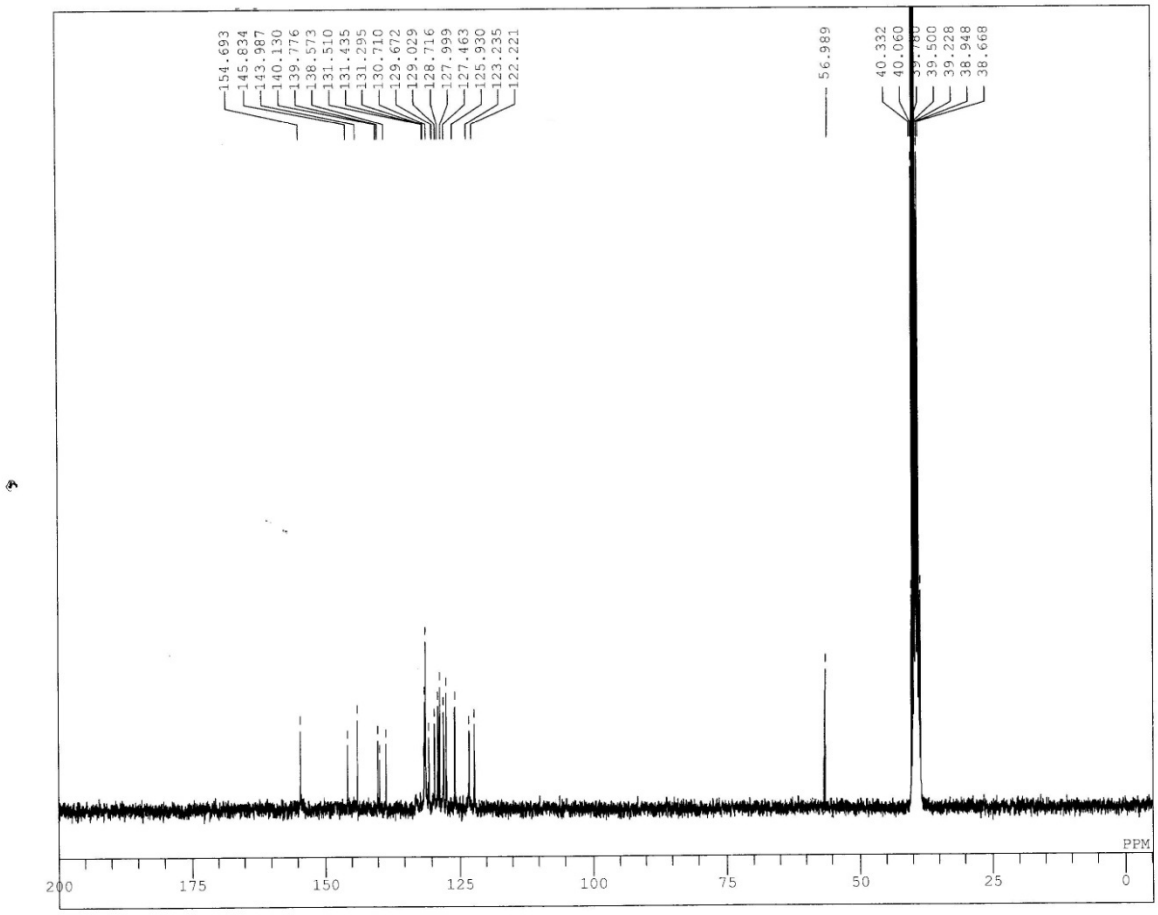


9.11. 2-(4-methoxyphenyl)-3,4-dihydroimidazo[4,5-b]indole (4k)

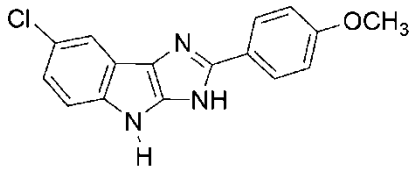


Brown solid, IR (KBr) υ: 3351, 3138, 3001, 2944, 2881, 1667, 1619, 1575, 1450, 1371, 1284, 1157, 1021, 863, 743, 654, 534 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 4.00 (s, 3H, CH_3), 7.26-8.69 (m, 9H, aromatic protons and 1H, NH), 9.72 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 56.9, 122.2, 123.2, 125.9, 127.7, 127.4, 127.9, 128.7, 129.0, 129.6, 130.7, 131.2, 131.4, 131.5, 138.5, 139.7, 140.1, 143.9, 145.8, 154.6 ppm. Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96 Found C, 72.91; H, 5.04; N, 15.95.


9.724
8.691
8.662
8.590
8.566
8.206
8.179
8.070
7.763
7.655
7.632
7.447
7.419
7.396
7.331
7.287
7.262
4.000
3.337
2.509
0.000
1.00
1.93
2.50
1.50
3.08
2.70
PPM
12.5
10.0
7.5
5.0
2.5
0.0

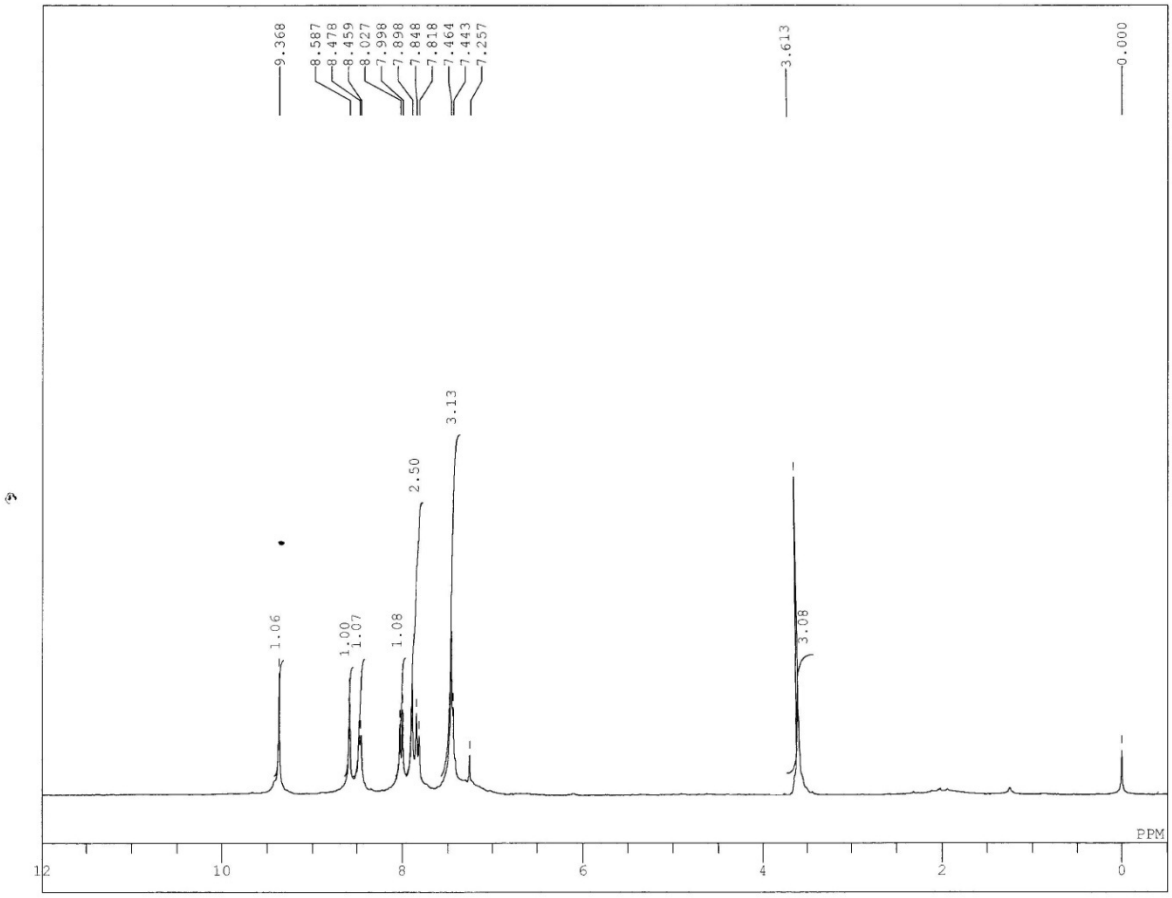


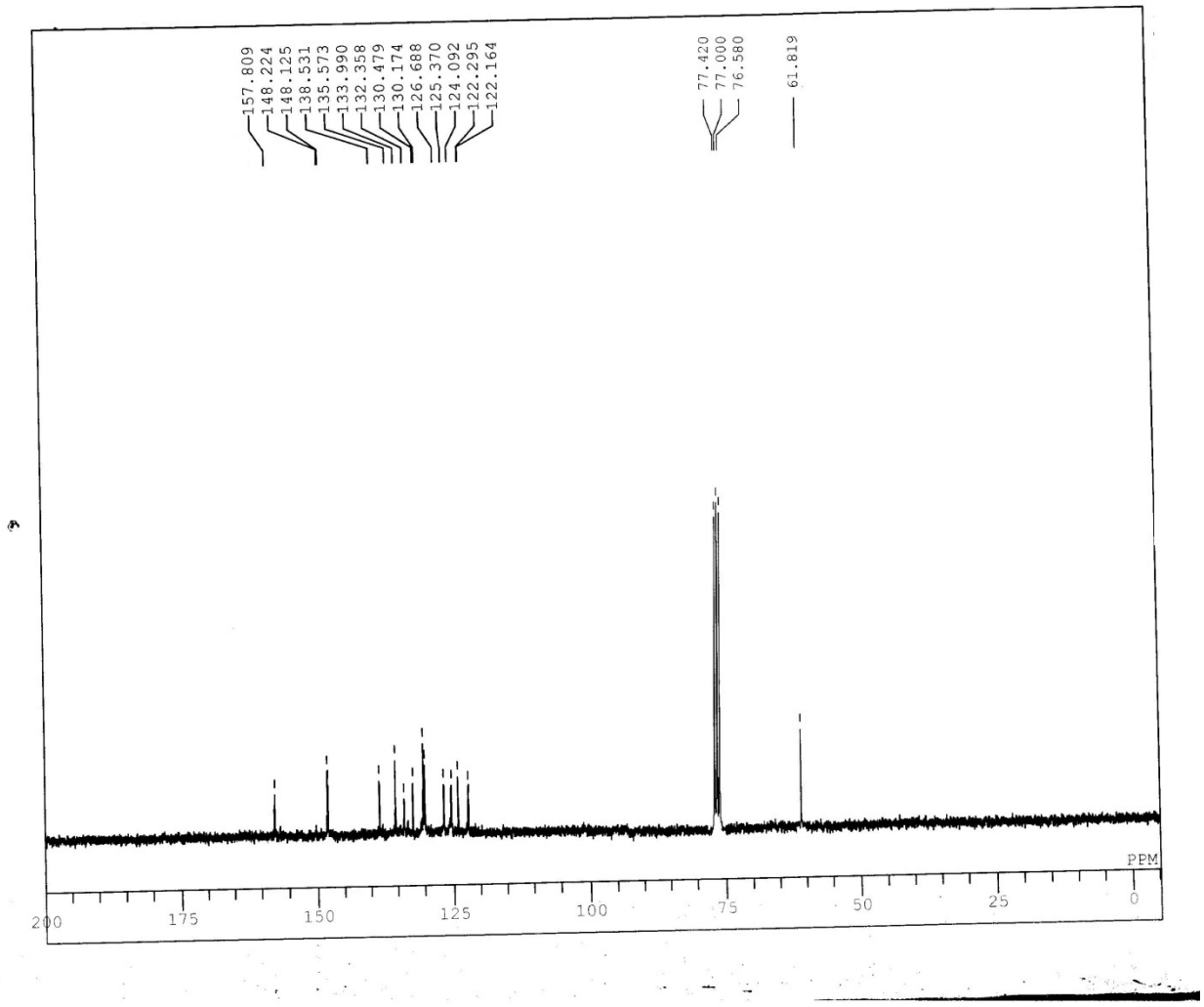
9.12. 7-chloro-2-(4-methoxyphenyl)-3,4-dihydroimidazo[4,5-b]indole (4l)



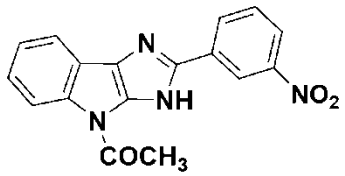
Brown solid, IR (KBr) υ: 3370, 3259, 2991, 2911, 1675, 1614, 1558, 1480, 1436 1377, 1291, 1186, 1049, 869, 745, 651, 522 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.61 (s, 3H, CH_3), 7.44-8.47 (m, 8H, aromatic protons), 8.58 (s, 1H, NH), 9.36 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz,

$CDCl_3$) δ: 61.8, 122.16, 122.29, 124.0, 125.3, 126.6, 130.1, 130.4, 132.3, 133.9, 135.5, 138.5, 148.1, 148.2, 157.8 ppm. Anal. Calcd for $C_{16}H_{12}ClN_3O$: C, 64.54; H, 4.06; N, 14.11 Found C, 64.70; H, 4.00; N, 14.10.



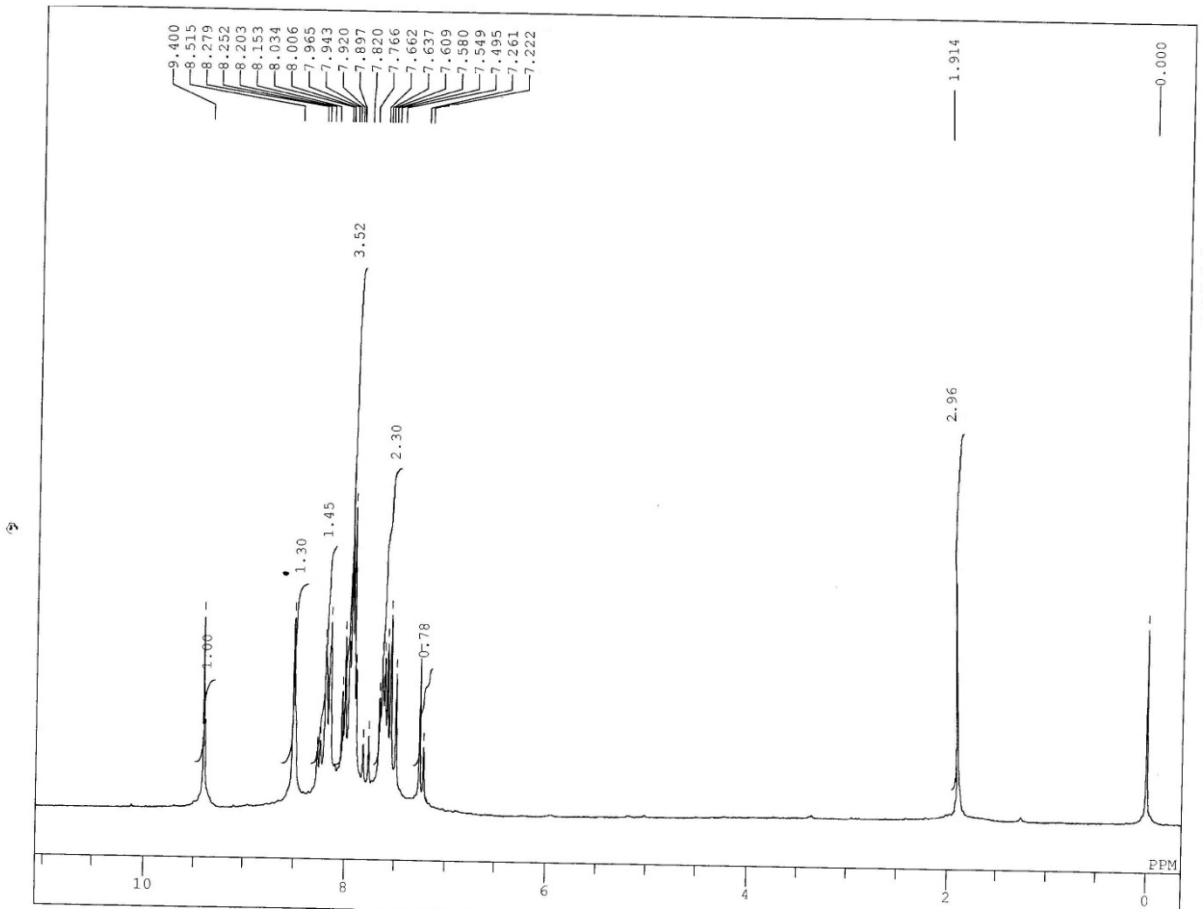


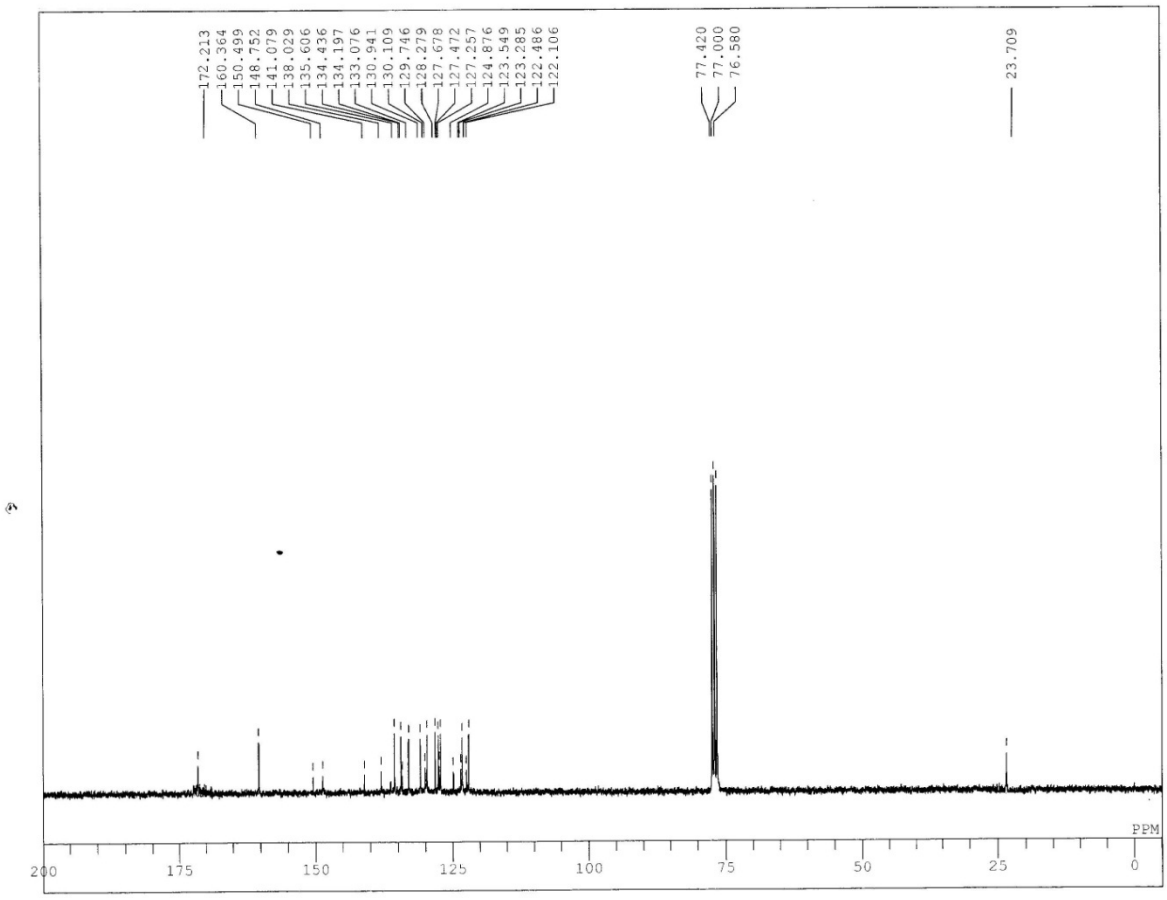
9.13. 1-(2-(3-nitrophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4m)



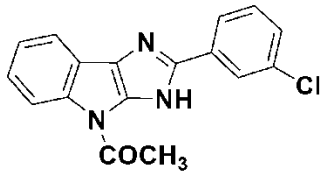
Brown solid, IR (KBr) υ: 3389, 3266, 2978, 2935, 1694, 1645, 1616, 1571, 1467, 1346, 1224, 1133, 1021, 823, 744, 641, 572 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.91 (s, 3H, CH_3), 7.22-8.51 (m, 8H, aromatic protons), 9.40 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 23.7,

122.1, 122.4, 123.2, 123.5, 124.8, 127.2, 127.4, 127.6, 128.2, 129.7, 130.1, 130.9, 133.0, 134.1, 134.4, 135.6, 138.0, 141.0, 148.7, 150.4, 160.3, 172.2 ppm. Anal. Calcd for $C_{17}H_{12}N_4O_3$: C, 63.75; H, 3.78; N, 17.49 Found C, 63.68; H, 3.88; N, 17.52.



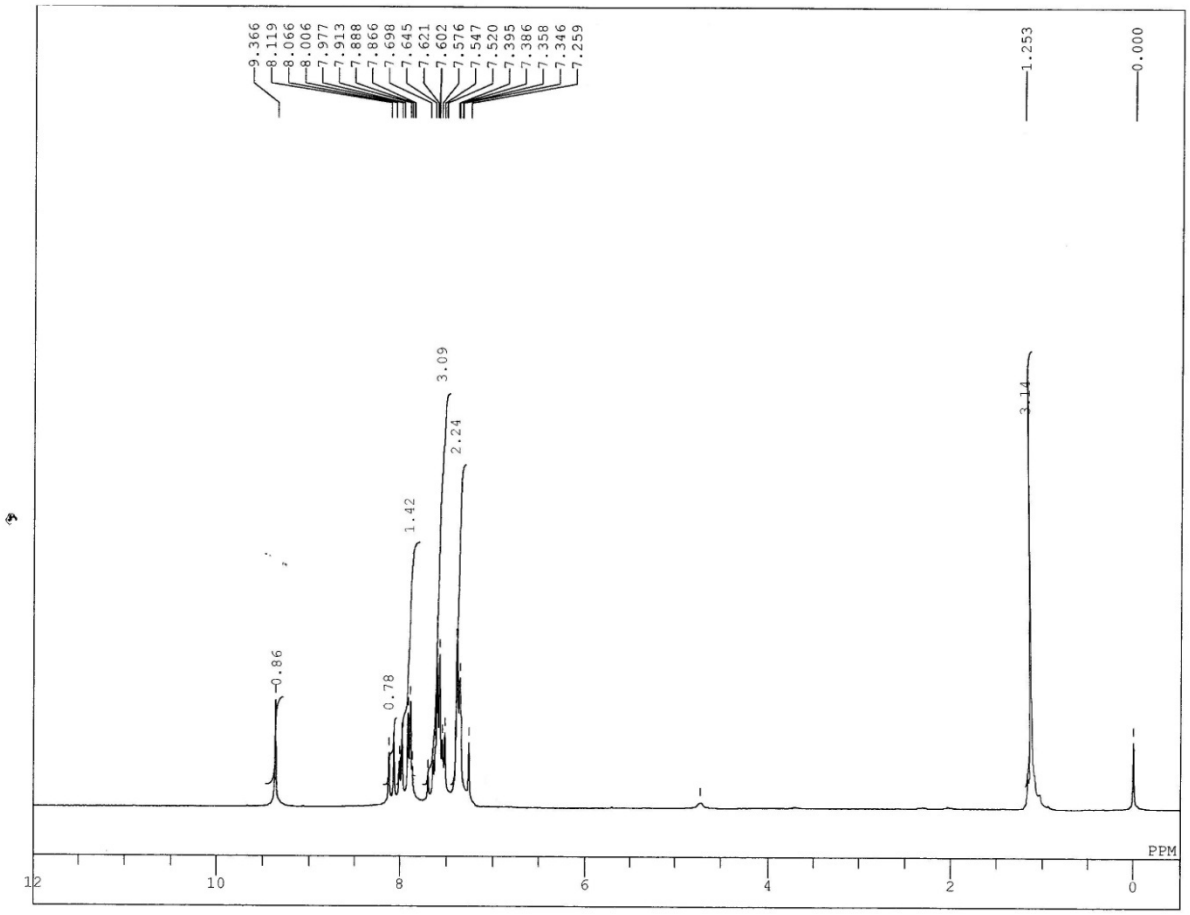


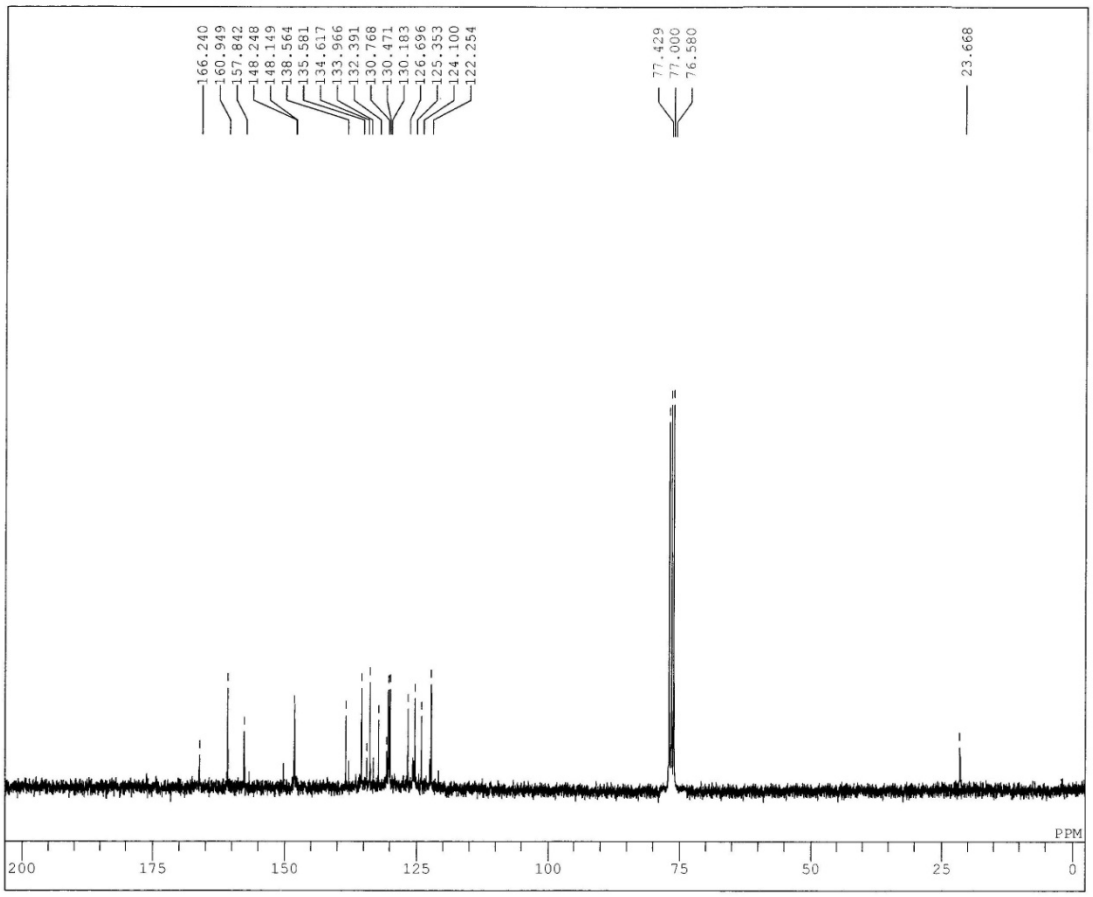
9.14. 1-(2-(3-chlorophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4n)



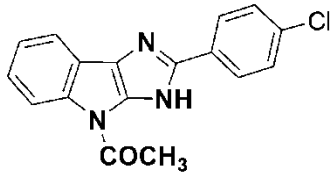
Brown solid, IR (KBr) υ: 3367, 3215, 2947, 2923, 1692, 1662 1607, 1580, 1477, 1359, 1272, 1144, 1042, 807, 735, 653, 546 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (s, 3H, CH_3), 7.34-8.11 (m, 8H, aromatic protons), 9.36 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 23.6, 122.5, 124.1, 125.3, 126.6, 130.1, 130.4, 130.7, 132.3, 133.9, 134.6, 135.5, 138.5, 148.1, 148.2,

157.8, 160.9, 166.2 ppm. Anal. Calcd for $C_{17}H_{12}ClN_3O$: C, 65.92; H, 3.90; N, 13.57 Found C, 66.01; H, 3.95; N, 13.47.



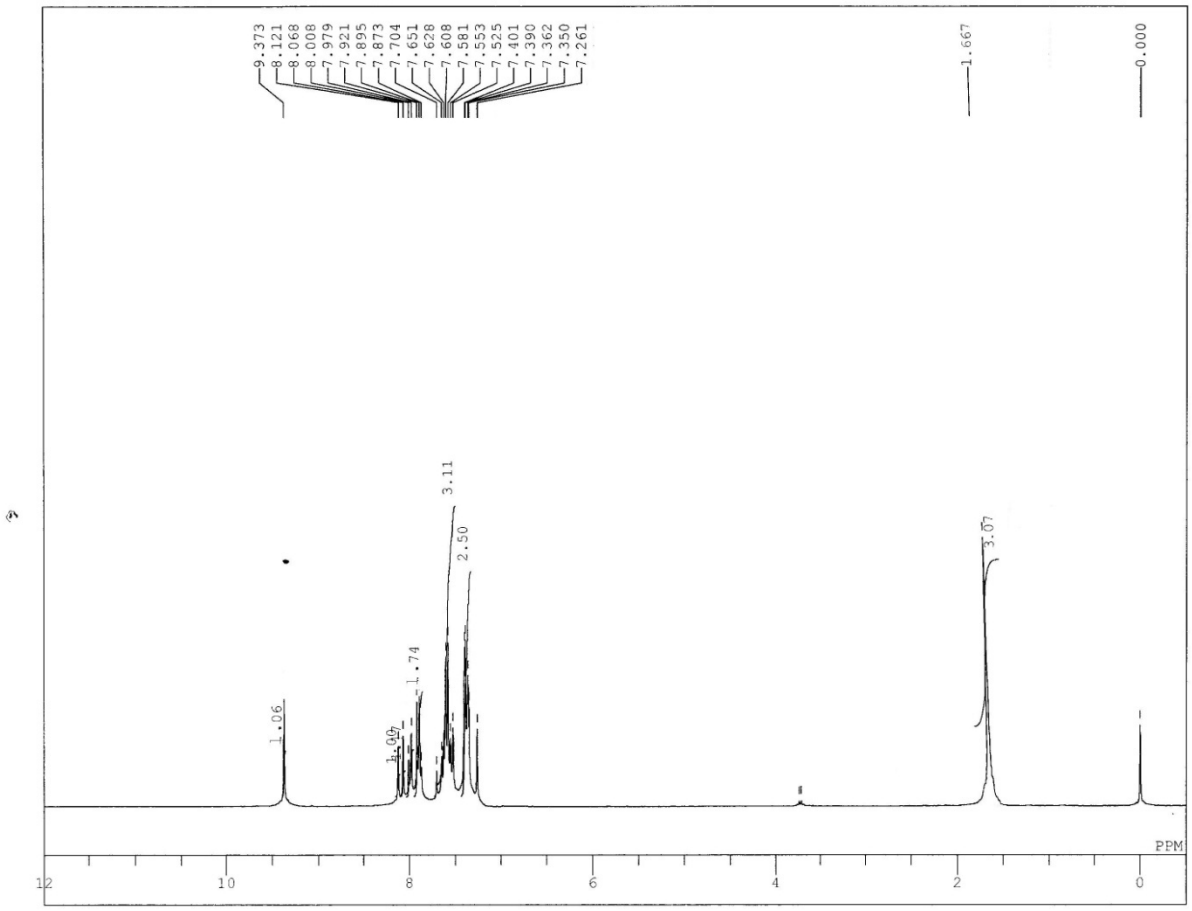


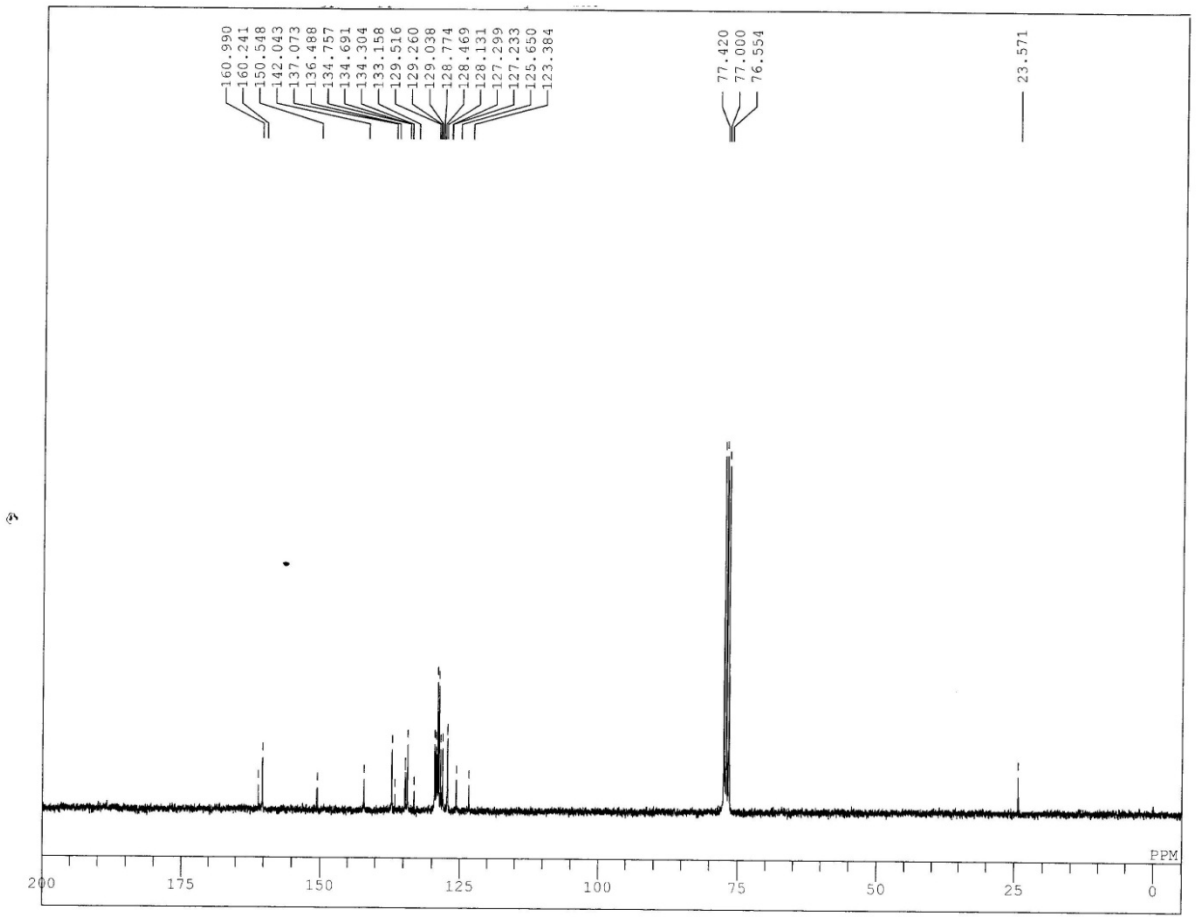
9.15. 1-(2-(4-chlorophenyl)imidazo[4,5-b]indol-4(3H)-yl)ethanone (4o)



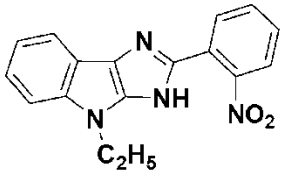
Brown solid, IR (KBr) υ: 3350, 3285, 3011, 2935, 1685, 1654 1611, 1572, 1485, 1455, 1343, 1284, 1132, 1062, 899, 783, 659, 531 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.66 (s, 3H, CH_3), 7.35- 8.12 (m, 8H, aromatic protons), 9.37 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 23.5, 123.3, 125.6, 127.2, 128.1, 128.4, 128.7, 129.0, 129.2, 129.5, 133.1, 134.3, 134.6, 134.7,

136.4, 137.0, 142.0, 150.5, 160.2, 160.9 ppm. Anal. Calcd for $C_{17}H_{12}ClN_3O$: C, 65.92; H, 3.90; N, 13.57 Found C, 65.99; H, 3.93; N, 13.54.



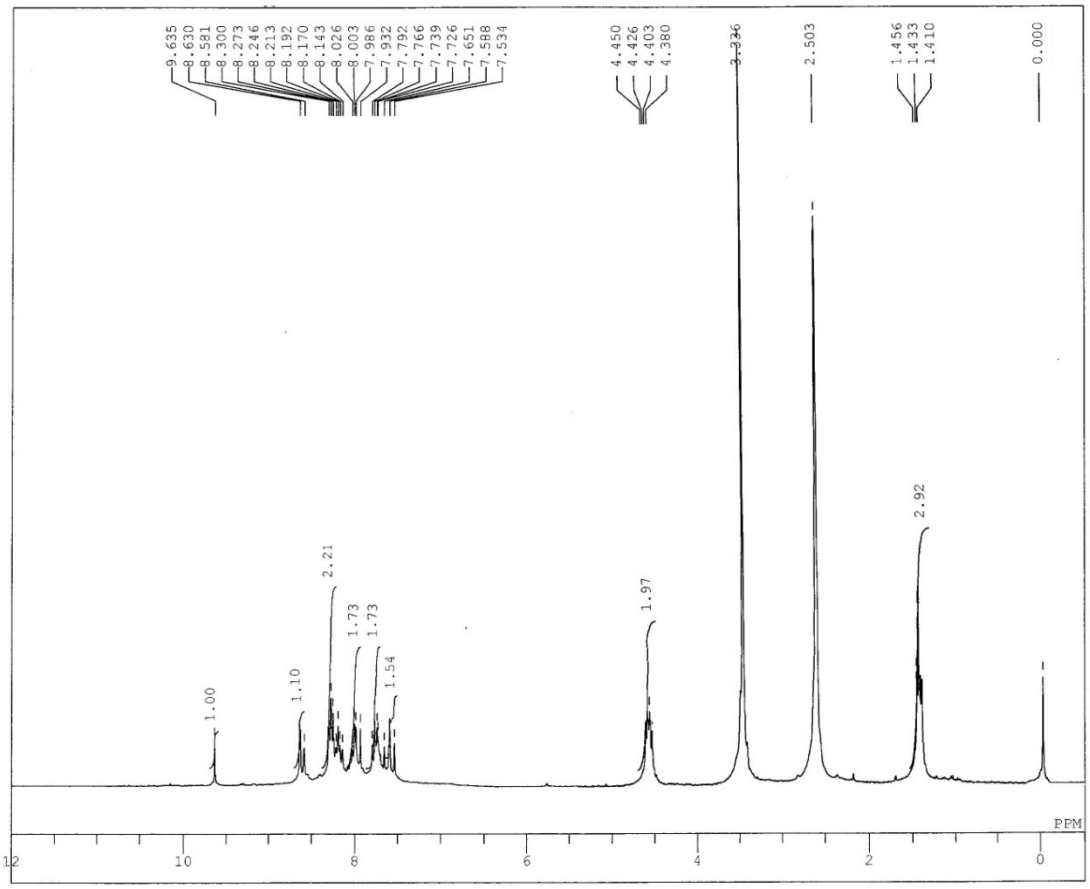


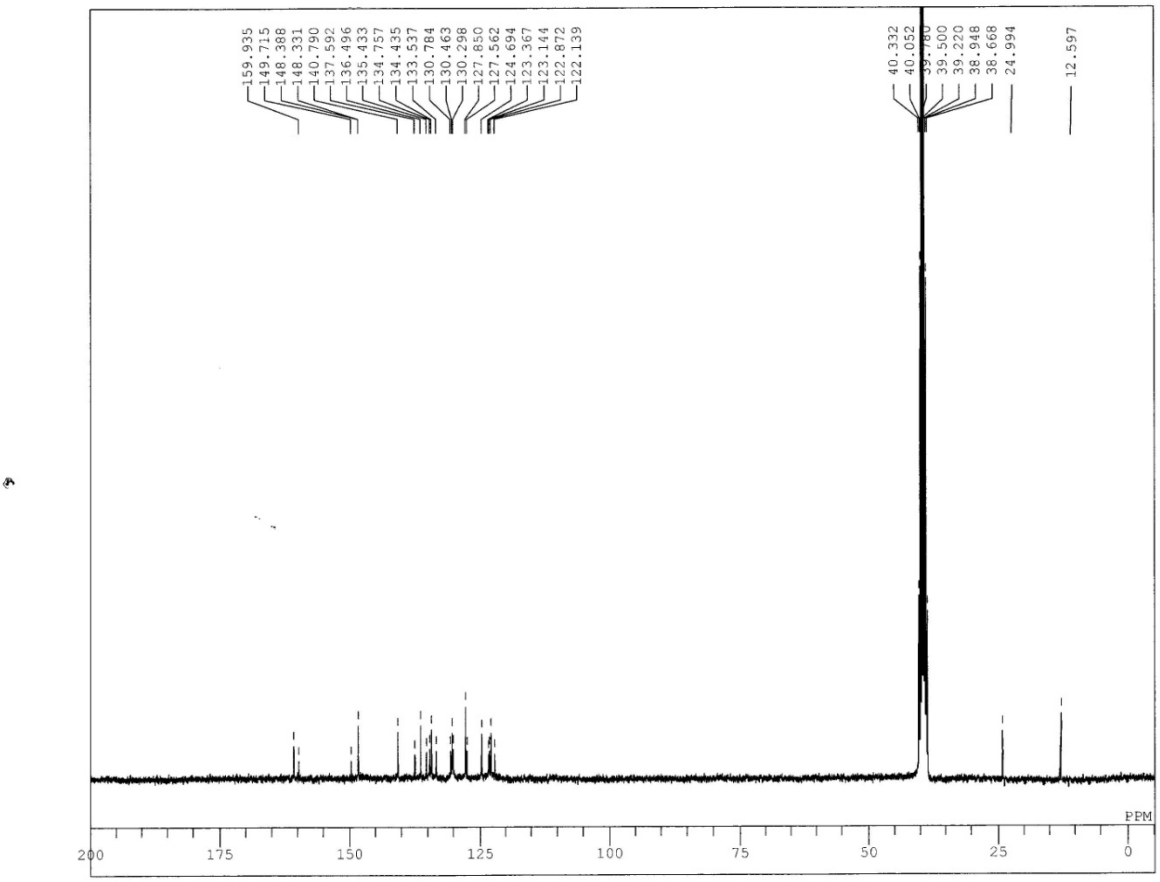
9.16. 4-ethyl-2-(2-nitrophenyl)-3,4-dihydroimidazo[4,5-b]indole (4p)



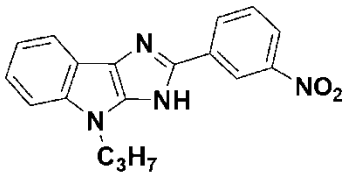
Brown solid, IR (KBr) υ: 3416, 3199, 3012, 2999, 2942, 2872, 1654, 1607, 1561, 1441, 1453 1351, 1283, 1192, 1021, 861, 741, 657, 526 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 1.41-1.45 (t, *J*= 6.6, 3H, CH_3), 4.38-4.45 (q, *J*=6.9, 2H, CH_2), 7.53- 8.63 (m, 8H, aromatic protons), 9.63 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 12.5, 24.9, 122.1, 122.8, 123.1, 124.6, 127.5, 127.8, 130.2, 130.4, 130.7, 133.5, 134.4, 137.7, 135.4, 136.4, 137.5, 140.7, 148.3, 149.7, 159.9.

ppm. Anal. Calcd for $C_{17}H_{14}N_4O_2$: C, 66.66; H, 4.61; N, 18.29 Found C, 66.74; H, 4.65; N, 18.20.



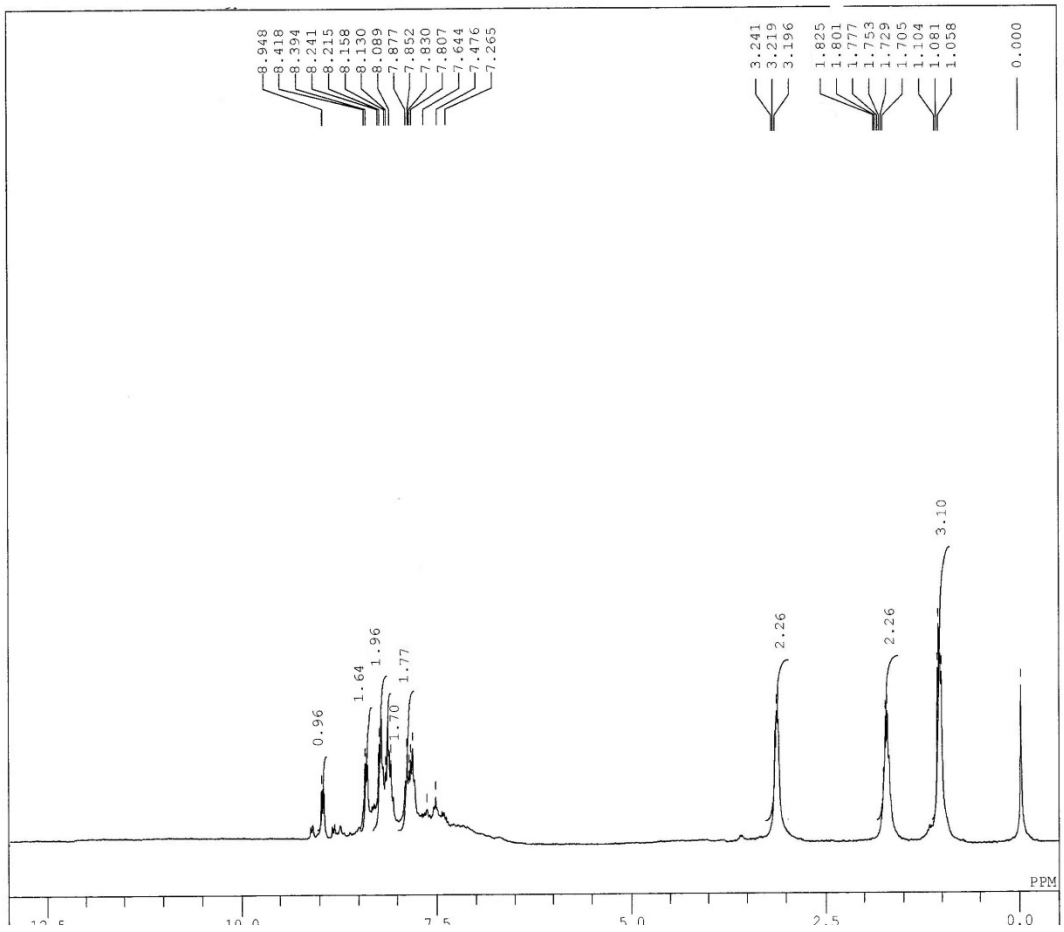


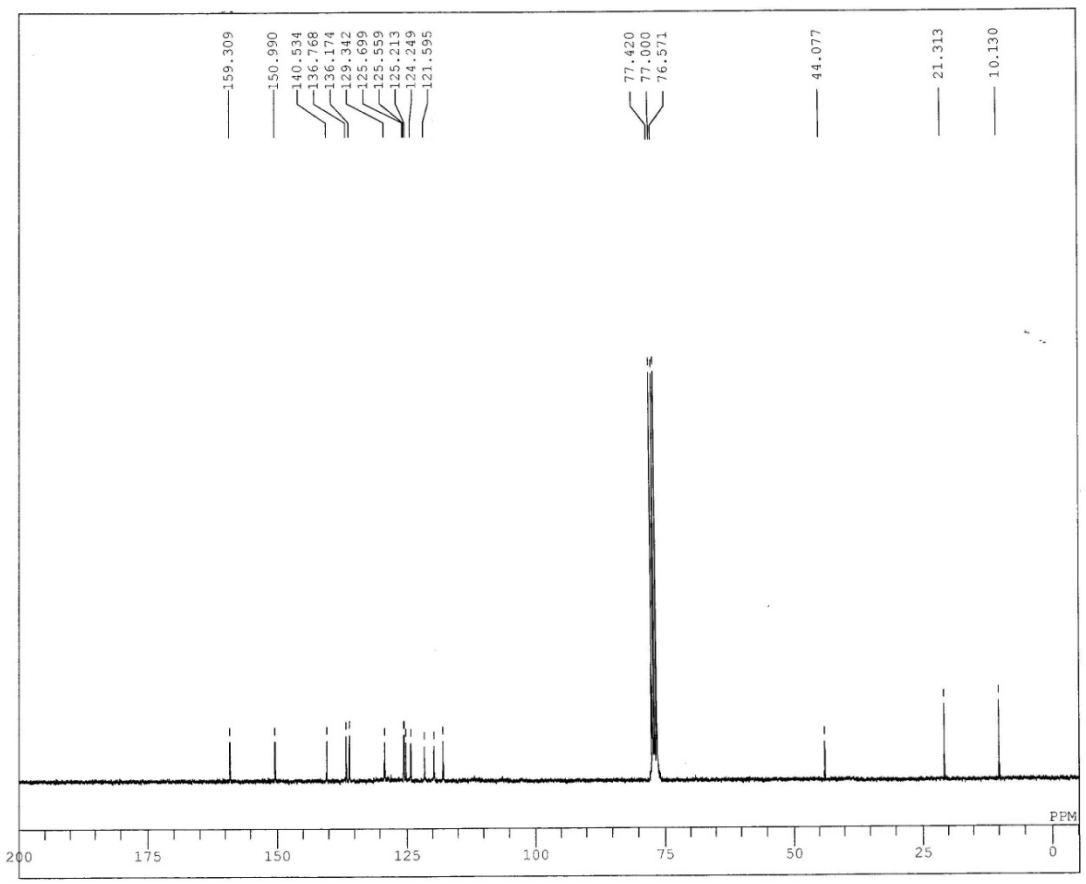
9.17. 2-(3-nitrophenyl)-4-propyl-3,4-dihydroimidazo[4,5-b]indole (4q)



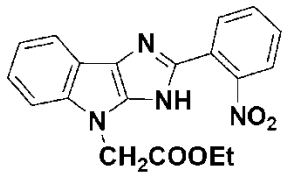
Brown solid, IR (KBr) υ: 3400, 3301, 3221, 3135, 3009, 2951, 2912, 2865, 1664, 1616, 1571, 1478, 1422, 1371, 1271, 1181, 1037, 873, 739, 649, 536 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.05-1.10 (t, *J*= 6.9, 3H, CH_3), 1.70-1.82 (m, 2H, CH_2), 3.19-3.24 (t, *J*=6.6, 2H, CH_2), 7.47- 8.41 (m, 8H, aromatic protons), 8.94 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$) δ: 10.1, 21.3,

44.0, 121.5, 124.2, 125.2, 125.5, 125.6, 129.3, 136.1, 136.7, 140.5, 150.9, 159.3 ppm. Anal. Calcd for $C_{18}H_{16}N_4O_2$ C, 67.49; H, 5.03; N, 17.49 Found C, 67.44; H, 5.10; N, 17.52.



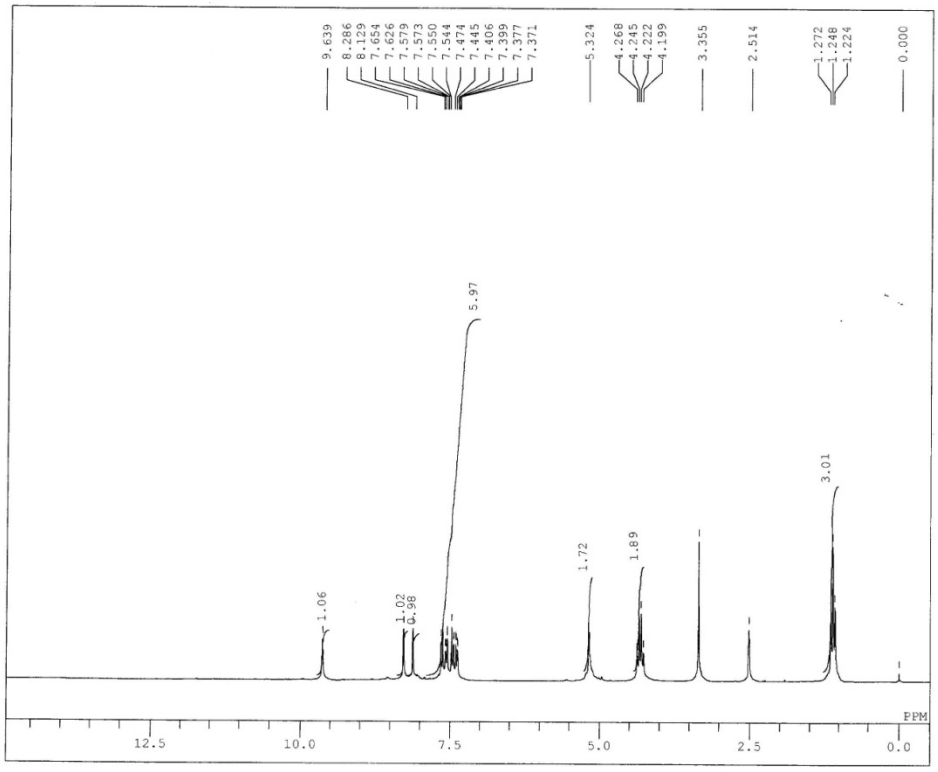


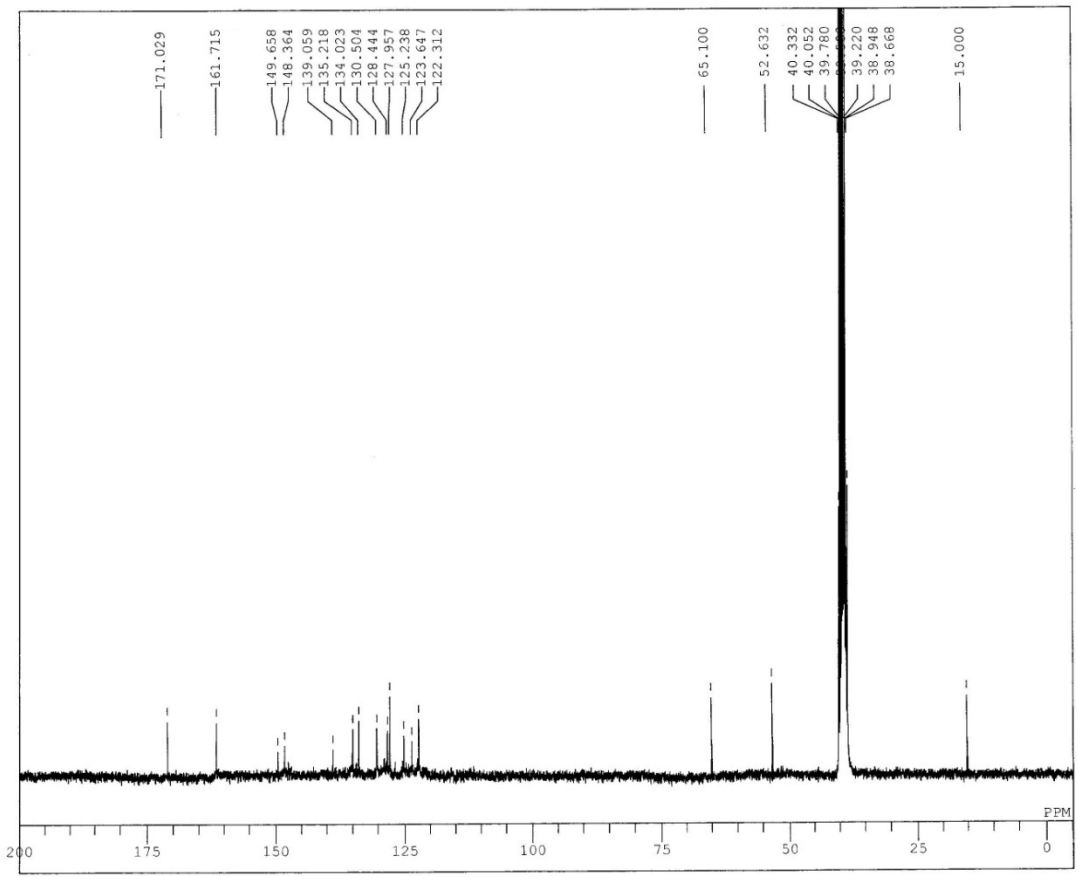
9.18. Ethyl 2-(2-(2-nitrophenyl)imidazo[4,5-b]indol-4(3H)-yl)acetate (4r)



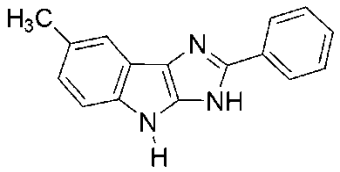
Brown solid, IR (KBr) υ: 3389, 3255, 3129, 3116, 3027, 2969, 2913, 2847, 1735, 1657, 1618, 1569, 1435, 1353, 1264, 1158, 1049, 854, 751, 651, 546 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 1.22- 1.27 (t, *J*= 7.2, 3H, CH_3), 4.19- 4.26 (q, *J*=6.9, 2H, CH_2), 5.32 (s, 2H, CH_2), 7.37- 8.28 (m, 8H, aromatic protons), 9.63 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 15.0, 52.6, 65.1, 122.3, 123.6, 125.2, 127.9, 128.4, 130.5, 134.0, 135.2, 139.0, 148.3, 149.6, 161.7, 171.0

ppm. Anal. Calcd for $C_{19}H_{16}N_4O_4$: C, 62.63; H, 4.43; N, 15.38 Found C, 62.71; H, 4.51; N, 15.30.

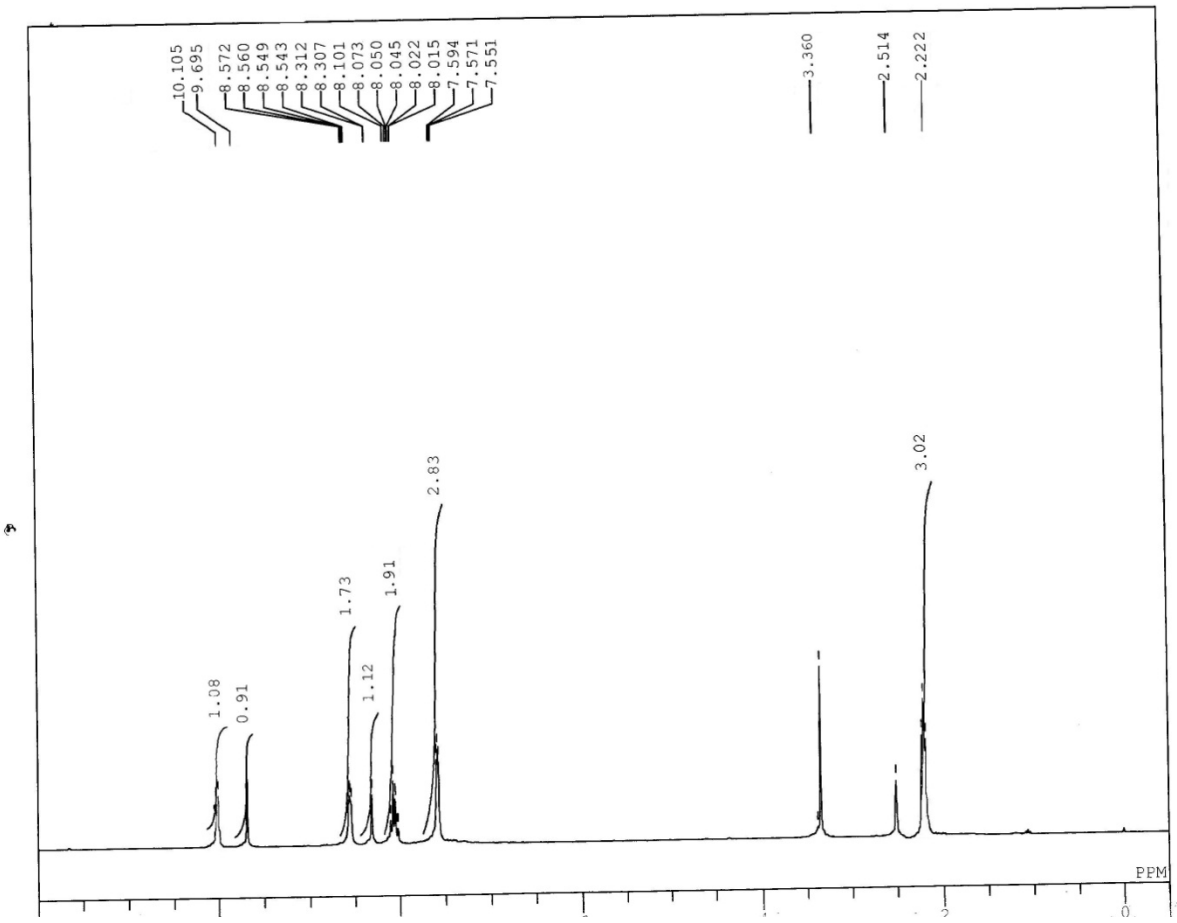


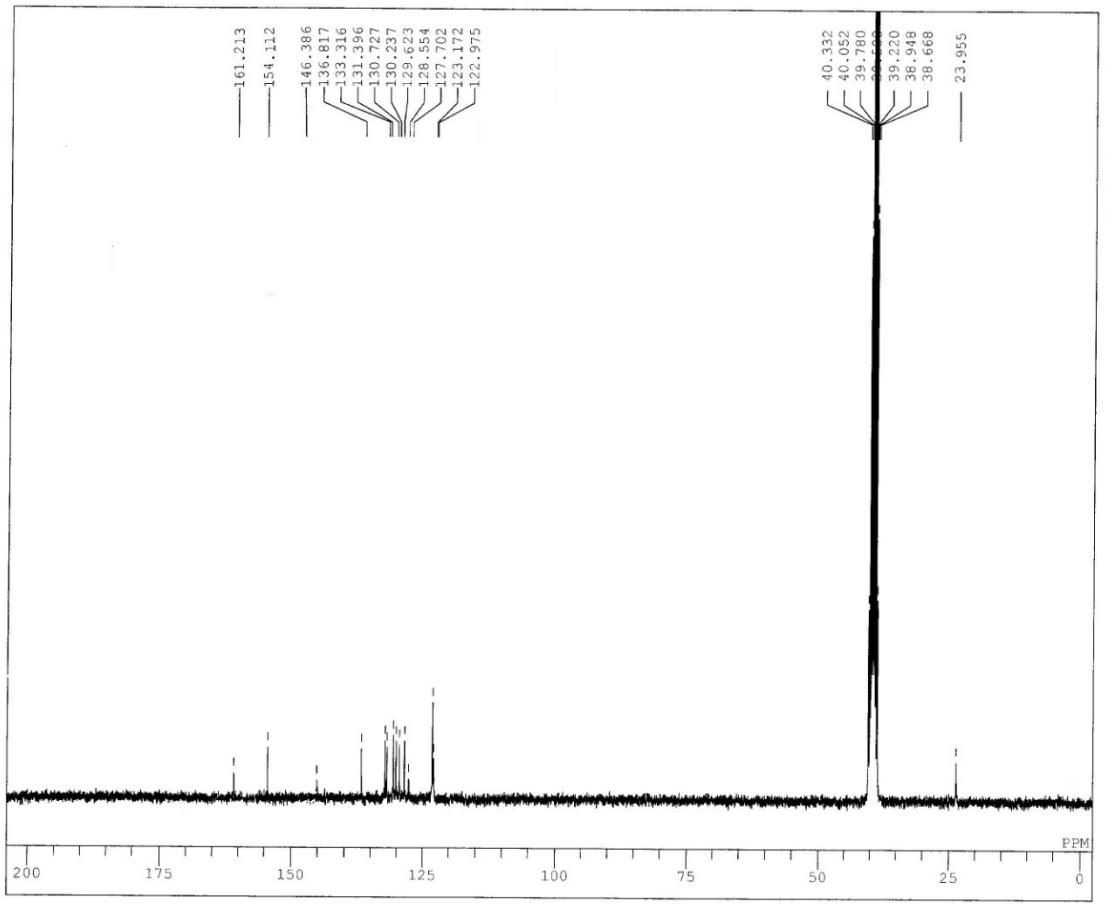

171.029
161.715
149.658
148.364
139.059
135.218
134.023
130.504
128.444
127.957
125.238
123.647
122.312
65.100
52.632
40.332
40.052
39.780
39.220
38.948
38.668
15.000
PPM
200
175
150
125
100
75
50
25
0

9.19. 7-methyl-2-phenyl-3,4-dihydroimidazo[4,5-b]indole (4s)



Brownish white solid, IR (KBr) υ: 3398, 3242, 2963, 2931, 1648, 1607, 1559, 1451, 1311, 1232, 1142, 1027, 813, 741, 655, 534 cm^{-1}. ^{1}H NMR (300 MHz, DMSO) δ: 2.22 (s, 3H, CH_3), 7.55-8.57 (m, 8H, aromatic protons), 9.69 (s, 1H, NH), 10.10 (s, 1H, NH) ppm. ^{13}C NMR (75.45 MHz, DMSO) δ: 23.9, 122.9, 123.1, 127.7, 128.5, 129.6, 130.2, 130.7, 131.3, 133.3, 136.8, 146.3, 154.1, 161.2, ppm. Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99 Found C, 77.64; H, 5.34; N, 17.02.





1. D. Gusain, S. N. Upadhyay, Y. C. Shrama, *RSC Adv.*, **4**, 2014, 18755-18762.