Electronic Supplementary Information

Brønsted Acidic Reduced Graphene Oxide as a Sustainable Carbocatalyst: A Selective Method for the Synthesis of C-2 Substituted Benzimidazole

Murugan Karthik, Palaniswamy Suresh*

Supramolecular and Catalysis Lab, Dept. of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, India
*ghemistry@gmail.com, suresh.chem@mkuniversity.org

Table of Contents

1. Synthesis of Reduced Graphene Oxide (RGO)

Graphene oxide (GO) was prepared by modified Hummers and Offmann method.[2] In a typical synthesis, 2.5 g of graphite powder was added to 115 mL of concentrated H_2SO_4 in an ice bath. Then, $NaNO_3$ (2.5 g) and $KMnO_4$ (15.0 g) were added gradually under stirring, and the temperature of the mixture was kept below 5 ºC, and the mixture was stirred for 4 h. After that, the mixture was stirred at room temperature for 12 h, and then diluted with 200 mL of double distilled (DD) water by keeping the mixture in an ice bath. After adding 500 mL of DD water, the mixture was transferred to an oil bath and maintained at 98 ºC for 1 h. Then the reaction was terminated by adding 15 mL of 30 % H_2O_2 aqueous solution followed by 5 % HCl solution to remove sulfate. Finally, the resulting graphite oxide was repeatedly washed with DD water and then dialyzed for three days to remove residual salts and acids with periodically changing the water. Then it was dried in a vacuum oven at 45 ºC for 24 h to obtain graphite oxide. Before using it in reactions, it was exfoliated by sonication in water gave graphene oxide (GO). The resulting GO suspension (400 mL, 1.0 mg/mL in DD H_2O) was reduced with Sodium borohydride (0.960 g) at 100 ºC for 24 h followed by washing with deionized water several times. The obtained black precipitate was dialyzed for 24 h to get a purified reduced graphene oxide.

2. Characterization of G-SO_3H

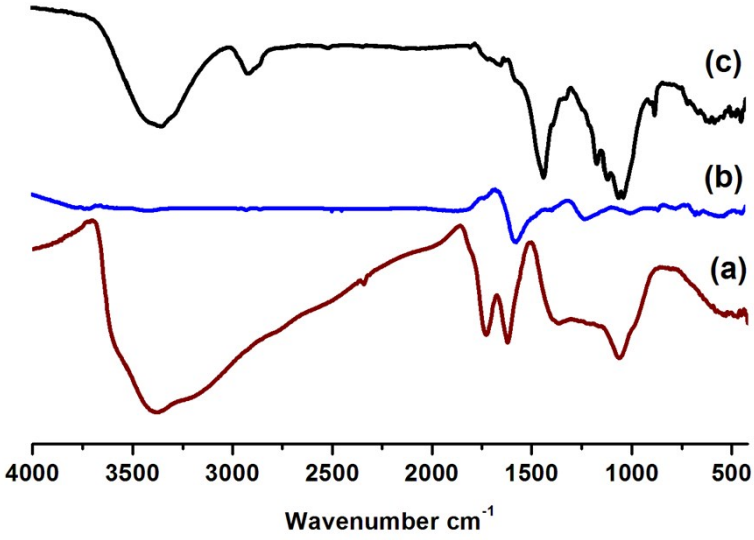


Fig. S1 FT-IR Spectra a) GO, b) RGO, c) G-SO_3H

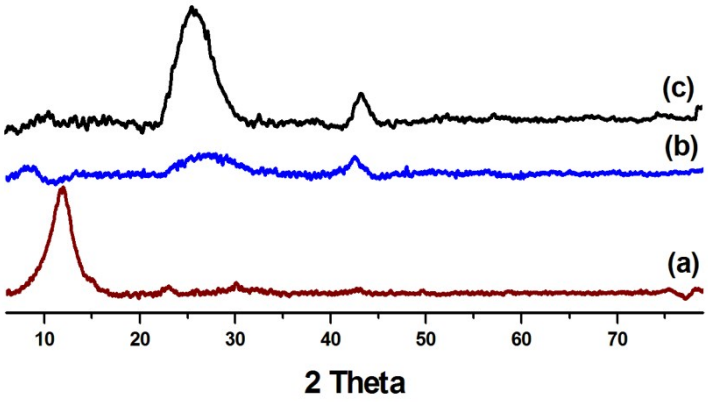


Fig. S2 PXRD Pattern of a) GO, b) RGO, c) G-SO_3H

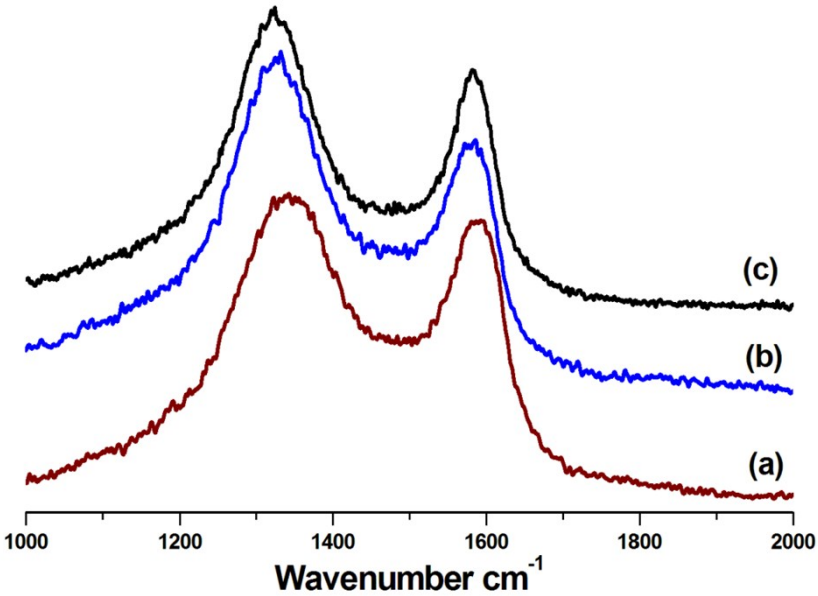


Fig. S3 Raman spectra of a) GO, b) RGO, c) G-SO_3H

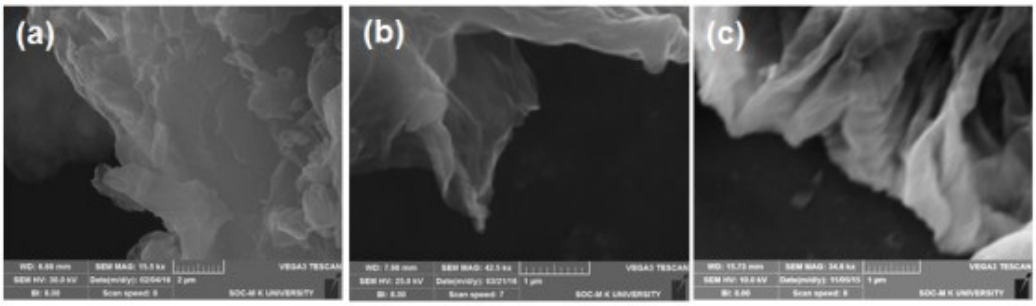


Fig.S4 SEM Images of a) GO b) RGO c) G-SO_3H

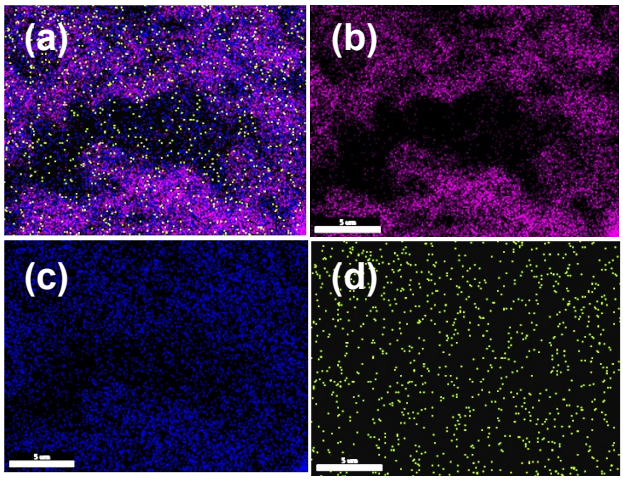


Fig.S5 SEM elemental mapping of a) G-SO_3H, b) C, c) O, d) S

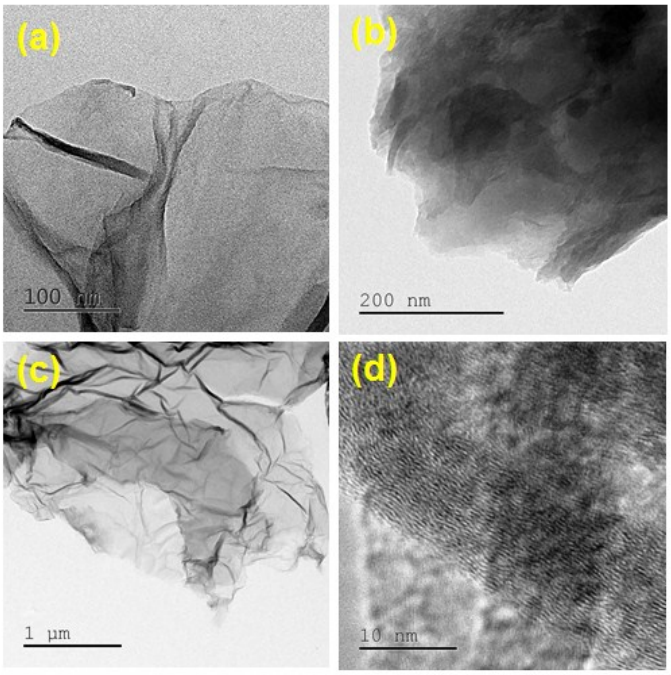


Fig. S6 TEM images of a) GO, b) RGO, c & d) G-SO_3H

3. Pyridine Absorption Study

Synthesis of Graphene Sulfonic Acid-Pyridine (G-SO_3H-Py)

G-SO_3H (20 mg) was dispersed in 2 mL of 1,4-dioxane *via* sonication. Then 2 mL (0.025 mol) of pyridine was added dropwise to the dispersed solution. The resulting mixture was sonicated for 1 h and further allow to vigorous stirring for 24 h at room temperature. The resulting black precipitate was separated by centrifugation and washed with excess of dichloromethane, dried under vacuum at 60 °C for further use. The resulting pyridine chemisorbed graphene sulfonic acid was denoted as G-SO_3H-Py.

General Procedure for G-SO_3H-Py Catalysed Benzimidazole Synthesis

In a typical procedure 6 mg of G-SO_3H-Py catalyst was dispersed in 2 mL of 1,4-dioxane under sonication. Then 0.5 mmol of the benzen-1,2-diamine was added followed by the addition of 0.5 mmol of benzaldehyde and allowed to stir at room temperature. The progress of the reaction was monitored by TLC.

4. LC-MS Analysis of Products

In the present work, benzimidazole was synthesised through the condensation between benzene-1,2-diamine (0.5 mmol, 1eq) and benzaldehyde (0.5 mmol, 1eq) using G-SO_3H as a Brønsted acid catalyst in 2 mL of 1,4-dioxane at 80 ˚C. The course of the reaction was monitored through LC-MS analysis using UV-vis. and ESI-Mass detectors. Due to the poor stability of the diimine, analysis and its formation was confirmed using LC-MS analysis. One of the representative HPLC chromatogram and corresponding ESI- mass spectra are given below. (Table-1, Entry 11).

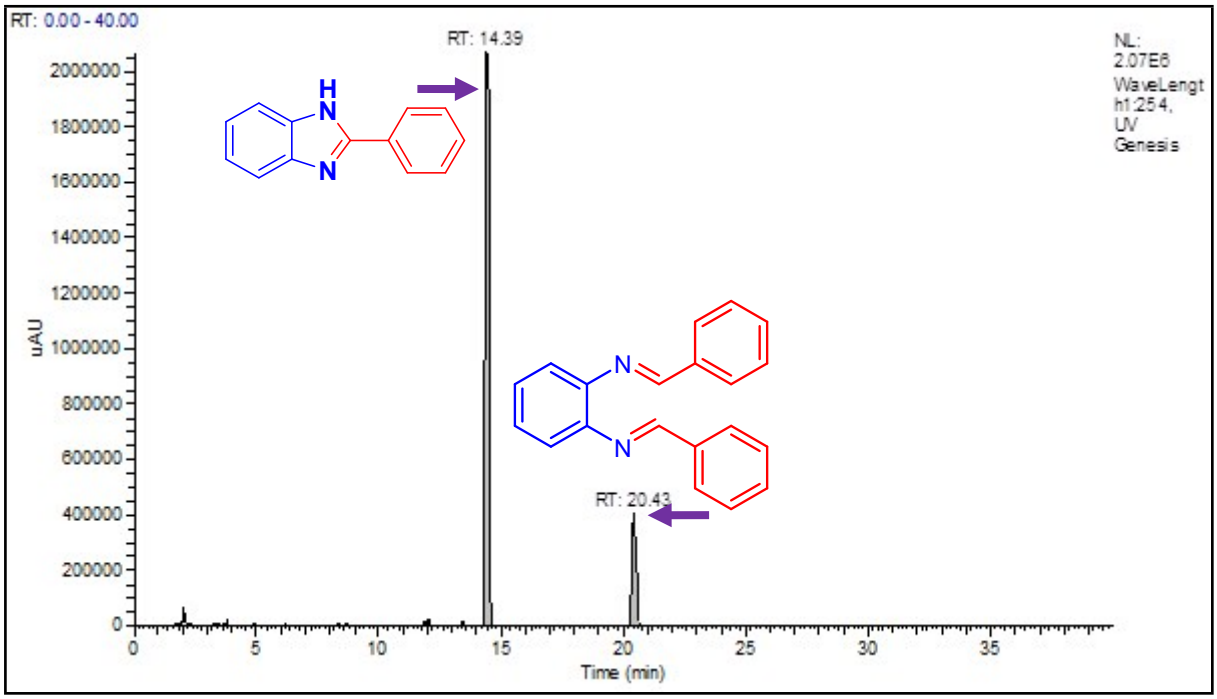


Fig. S7 LC-MS chromatogram of crude product

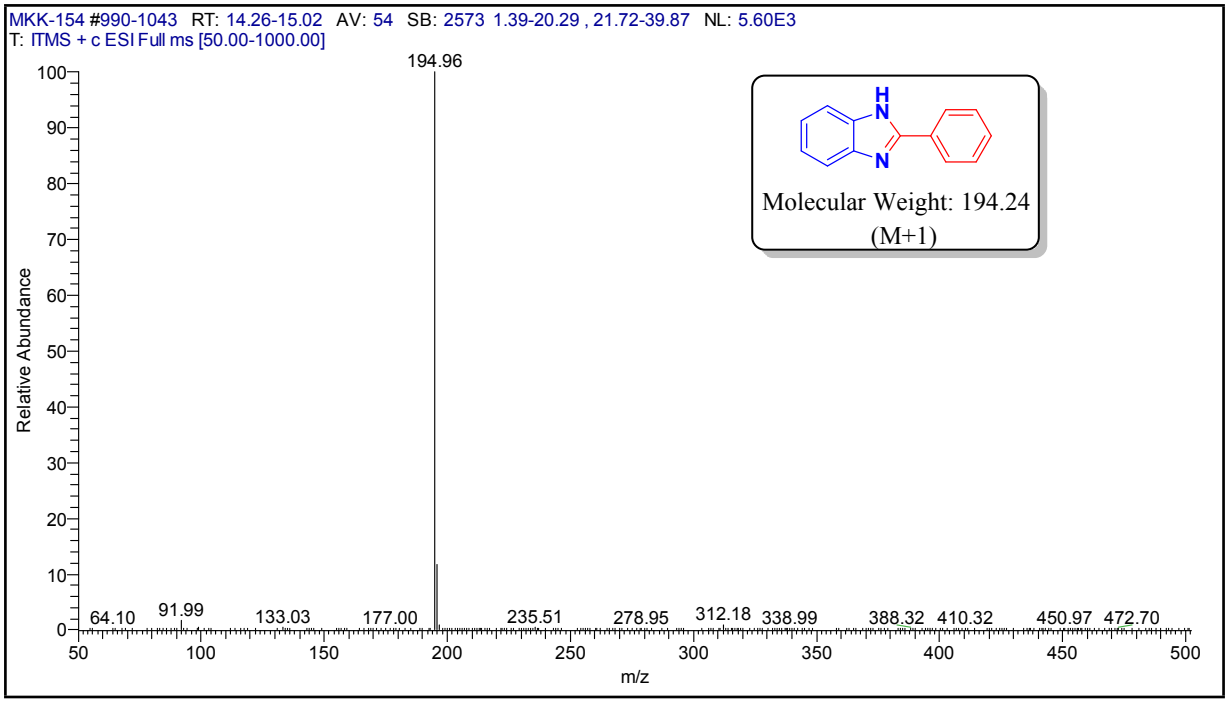


Fig. S8 Mass of 2-Phenyl-1*H*-benzo[*d*]imidazole at RT -14.3 min

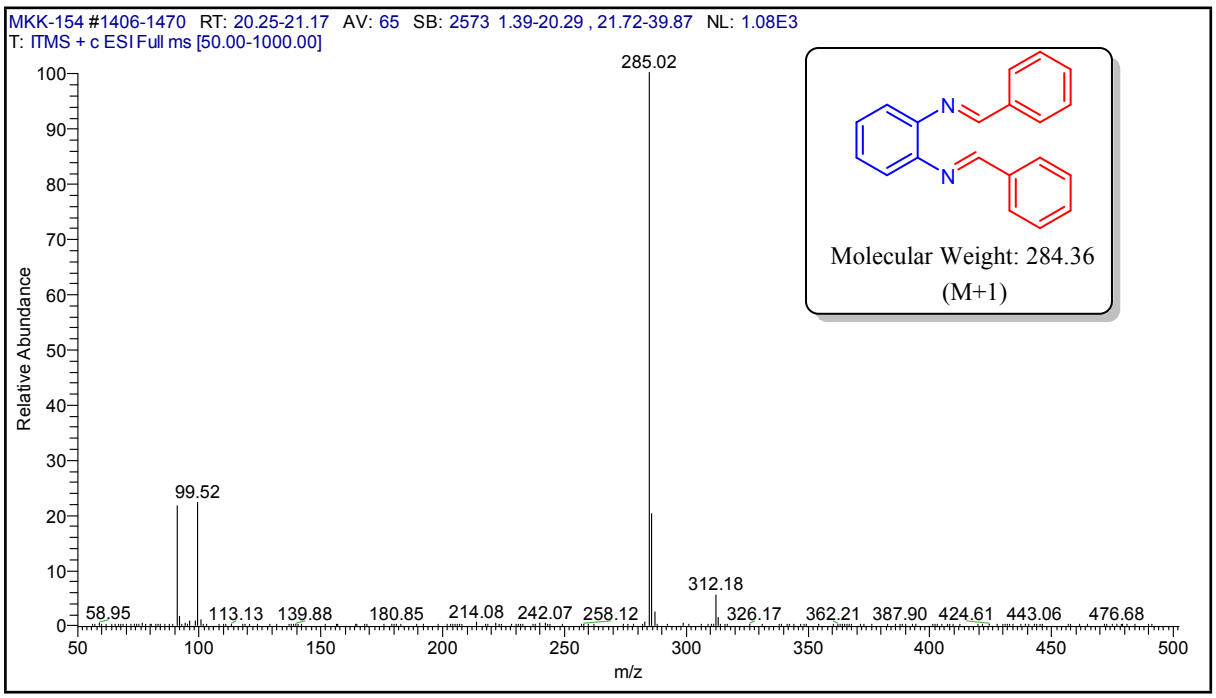
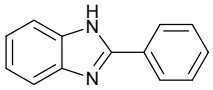
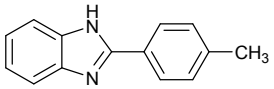
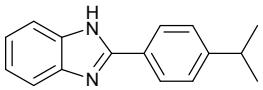
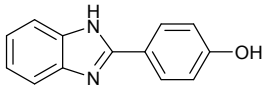
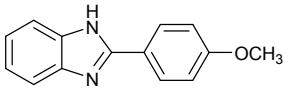
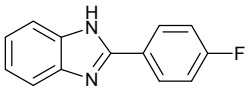
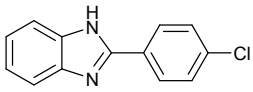
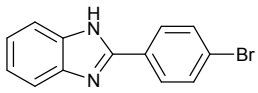
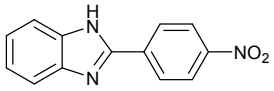
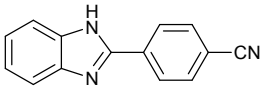
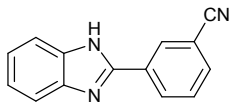
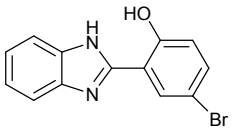
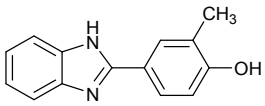
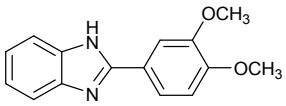
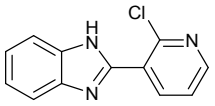
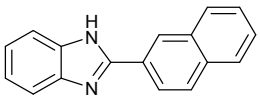
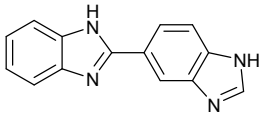


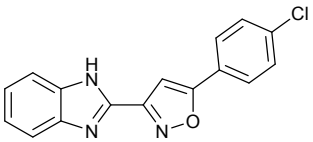
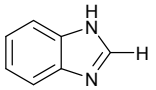
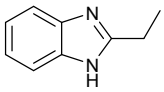
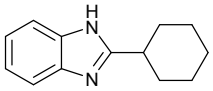
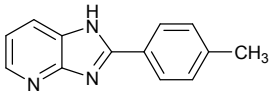
Fig. S9 Mass of (1E,1'E)-N,N'-(1,2-Phenylene)*bis*(1-phenylmethanimine) at RT -20.3 min

NMR and Mass data

2-phenyl-1*H*-benzo[*d*]imidazole (4a) ^{1}H NMR (300 MHz, $CDCl_3$+DMSO) δ: 12.65 (s, 1H), 8.19 (d, *J* = 6.9 Hz, 2H), 7.69 (s, 1H), 7.49 (dd, *J* = 14.9, 7.3 Hz, 4H), 7.21 (dd, *J* = 5.8, 2.9 Hz, 2H). (**Fig. S10)** ^{13}C NMR (75 MHz, $CDCl_3$+DMSO) δ: 150.51, 129.10, 128.50, 127.51, 125.44, 121.32, 120.49, 117.65. (**Fig. S11)** Mass (ESI): 194.06 (M+1) (**Fig. S54)**	
2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (4b) ^{1}H NMR (400 MHz, DMSO) δ: 12.81 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 6.8, Hz, 1H), 7.50 (d, *J* = 6.8, Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 5.2 Hz, 2H), 2.46 (s, 3H). (**Fig. S12)** ^{13}C NMR (100 MHz, DMSO) δ: 151.86, 144.32, 140.00, 135.43, 129.96, 127.94, 126.86, 122.78, 122.01, 119.18, 111.64, 21.43. (**Fig. S13)** Mass (ESI): 207.12 (M-1) (**Fig. S55)**	
2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole (4c) ^{1}H NMR (300 MHz, DMSO) δ: 12.85 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.18 (dd, *J* = 5.6, 3.1 Hz, 2H), 2.96 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). (**Fig. S14)** ^{13}C NMR (75 MHz, DMSO) δ: 151.42, 150.39, 127.87, 126.92, 126.55, 121.70, 118.77, 111.23. (**Fig. S15)** Mass (ESI): 237.15 (M+1) (**Fig. S56)**	
4-(1*H*-benzo[*d*]imidazol-2-yl)phenol (4d) ^{1}H NMR (300 MHz, DMSO) δ: 9.99 (s, 1H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.53 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.15 (dd, *J* = 6.0, 3.2 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.55 (s, 1H). (**Fig. S16)** ^{13}C NMR (75 MHz, DMSO) δ: 163.19, 159.28, 151.84, 139.28, 128.28, 121.77, 121.05, 115.79. (**Fig. S17)** Mass (ESI): 211.11 (M+1) (**Fig. S57)**	
2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (4e) ^{1}H NMR (400 MHz, DMSO) δ: 12.72 (s, 1H), 8.12-8.02 (m, *J* = 8.4, 2H), 7.61 (d, *J* = 6.8, Hz, 1H), 7.48 (d, *J* = 6.8, Hz, 1H), 7.19-7.08 (m, 4H), 3.83 (s, 3H). (**Fig. S18)** ^{13}C NMR (100 MHz, DMSO) δ: 161.07, 151.82, 146.70, 135.97, 128.47, 123.19, 122.86, 122.52, 121.89, 118.95, 114.83, 111.48, 55.79. (**Fig. S19)** Mass (ESI): 225.09 (M+1) (**Fig. S58)**	
2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (4f) ^{1}H NMR (300 MHz, DMSO+$CDCl_3$) δ: 8.25-8.18 (m, 2H), 7.60 (s,	

2H), 7.24-7.17 (m, 4H), 7.16 (s, 1H). (**Fig. S20)** ^{13}C NMR (75 MHz, DMSO+$CDCl_3$) δ: 164.27, 160.97, 150.16, 128.00, 127.95, 125.91, 121.38, 114.97, 114.68. (**Fig. S21)** Mass (ESI): 211.08 (M-1) (**Fig. S59)**	
2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole (4g) ^{1}H NMR (300 MHz, DMSO) δ: 13.00 (s, 1H), 8.19 (d, *J* = 8.6 Hz, 2H), 7.68-7.62 (m, 3H), 7.53 (s, *J* = 8.0 Hz, 1H), 7.22 (s, 2H). (**Fig. S22)** ^{13}C NMR (100 MHz, DMSO) δ: 150.61, 144.24, 135.48, 134.93, 129.51, 128.59, 123.22, 122.28, 119.41, 111.87. (**Fig. S23)** Mass (ESI): 229.04 (M+1) (**Fig. S60)**	
2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole (4h) ^{1}H NMR (300 MHz, DMSO) δ: 13.02 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.60 (s, 2H), 7.21 (s, 2H). (**Fig. S24)** ^{13}C NMR (75 MHz, DMSO) δ: 151.07, 132.83, 130.24, 129.21, 124.11. (**Fig. S25)** Mass (ESI): 275.03 (M+2) (**Fig. S61)**	
2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole (4i) ^{1}H NMR (300 MHz, DMSO+$CDCl_3$) δ: 8.44 (d, *J* = 9.0 Hz, 2H), 8.34 (d, *J* = 9.0 Hz, 2H), 7.65 (s, 2H), 7.30-7.23 (m, 2H), 4.09 (s, 1H). (**Fig. S26)** ^{13}C NMR (75 MHz, DMSO+$CDCl_3$) δ: 148.22, 146.92, 138.48, 135.21, 126.41, 122.92, 122.06, 114.52. (**Fig. S27)** Mass (ESI): 238.10 (M-1) (**Fig. S62)**	
4-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile (4j) ^{1}H NMR (400 MHz, DMSO) δ: 13.20 (s, 1H), 8.34 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz 2H), 7.7-7.6 (m, 2H), 7.26 (s, 2H). (**Fig. S28)** ^{13}C NMR (100 MHz, DMSO) δ: 149.83, 134.73, 133.43, 127.44, 123.69, 122.80, 119.77, 119.07, 112.34. (**Fig. S29)** Mass (ESI): 218.12 (M-1) (**Fig. S63)**	
3-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile (4k) ^{1}H NMR (300 MHz, DMSO) δ: 13.11 (s, 1H), 8.55 (m, 1H), 8.51-8.47(m, 1H), 7.98-7.95 (m, 1H), 7.80-7.75 (m, 1H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H) 7.25 (s, 2H). (**Fig. S30)** ^{13}C NMR (75 MHz, DMSO) δ: 149.65, 144.05,135.46, 133.54, 131.81, 131.36, 130.81, 130.18, 123.61, 122.54, 119.65, 118.85, 112.62, 112.04 (**Fig. S31)** Mass (ESI): 220.09 (M+1) (**Fig. S64)**	

2-(1*H*-benzo[*d*]imidazol-2-yl)-4-bromophenol (4l) ^{1}H NMR (300 MHz, DMSO) δ: 13.28 (s, 2H), 8.29 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 6.0 Hz, 1H), 7.62 (d, *J* = 6.6 Hz, 1H), 7.54-7.50 (m, 1H), 7.31 (s, 2H).7.02 (d, *J* = 8.7 Hz, 1H). (**Fig. S32)** ^{13}C NMR (100 MHz, DMSO) δ: 157.59, 150.70, 134.46, 128.90, 124.06, 123.14, 119.93, 118.56, 115.11, 112.20, 110.61. (**Fig. S33)** Mass (ESI): 291.04 (M+2) (**Fig. S65)**	
4-(1*H*-benzo[*d*]imidazol-2-yl)-2-methylphenol (4m) ^{1}H NMR (300 MHz, DMSO) δ: 9.91 (s, 1H), 8.13 (s, 1H), 7.91 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.14 (dd, *J* = 5.9, 3.1 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 2.20 (s, 3H). (**Fig. S34)** ^{13}C NMR (75 MHz, DMSO) δ: 158.28, 152.70, 139.90, 130.03, 126.41, 125.32, 122.59, 121.39, 115.74, 115.37, 16.93. (**Fig. S35)** Mass (ESI): 225.10 (M+1) (**Fig. S66)**	
2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole (4n) ^{1}H NMR (300 MHz, DMSO+$CDCl_3$) δ: 7.84-7.72 (m, 2H), 7.57 (s, 2H), 7.19 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 3.94 (d, *J* = 10.1 Hz, 6H). (**Fig. S36)** ^{13}C NMR (75 MHz, DMSO+$CDCl_3$) δ: 151.10, 149.42, 148.08, 138.53, 122.08, 121.02, 118.68, 113.77, 110.29, 109.02, 54.81. (**Fig. S37)** Mass (ESI): 255.27 (M+1) (**Fig. S67)**	
2-(2-chloropyridin-3-yl)-1*H*-benzo[*d*]imidazole (4o) ^{1}H NMR (300 MHz, DMSO) δ: 8.88-8.85 (m, 1H), 7.90-7.88 (m, 1H), 7.82-7.79 (m, 2H), 7.45-7.42 (m, 2H), 6.67-6.62 (m, 1H), (**Fig. S38)** ^{13}C NMR (75 MHz, DMSO) δ: 160.55 146.70, 143.47, 141.47, 133.02, 125.81, 125.35, 114.84, 113.48, 106.69. (**Fig. S39)** Mass (ESI): 227.12 (M-2) (**Fig. S68)**	
2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole (4p) ^{1}H NMR (300 MHz, DMSO+$CDCl_3$) δ: 8.72 (s, 1H), 8.33 (d, *J* = 10.1 Hz, 1H), 7.98 (dt, *J* = 16.9, 9.2 Hz, 3H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 9.2, 4.4 Hz, 3H), 7.27-7.16 (m, 2H). (**Fig. S40)** ^{13}C NMR (75 MHz, DMSO+$CDCl_3$) δ: 149.90, 142.42, 133.55, 131.96, 131.82, 131.34, 126.72, 126.08, 125.27, 125.16, 124.35, 122.41. (**Fig. S41)** Mass (ESI): 243.15 (M-1) (**Fig. S69)**	
1*H*,1'*H*-2,5'-bibenzo[*d*]imidazole (4q) ^{1}H NMR (300 MHz, DMSO) δ: 12.78 (s, 2H), 8.38 (s, 1H), 8.34 (s, 1H), 8.13-8.07 (m, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.59-7.56 (m, 2H), 7.21-7.16 (m, 2H). (**Fig. S42)**	

^{13}C NMR (100 MHz, DMSO) δ: 152.76, 144.60, 124.56, 122.24, 121.34, 116.03. (**Fig. S43)** Mass (ESI): 235.10 (M+1) (**Fig. S70)**	
3-(1*H*-benzo[*d*]imidazol-2-yl)-5-(4-chlorophenyl)isoxazole (4r) ^{1}H NMR (300 MHz, DMSO) δ: 13.27 (s, 1H), 8.01(d, *J* = 8.5 Hz, 2H) 7.73-7.62 (m, 5H), 7.29-7.26 (m, 2H). (**Fig. S44)** ^{13}C NMR (75 MHz, DMSO) δ: 169.57, 157.01, 142.25, 135.97, 129.91, 128.12, 125.68, 123.50, 100.61. (**Fig. S45)** Mass (ESI): 294.11 (M-1) (**Fig. S71)**	
1*H*-benzo[*d*]imidazole (4s) ^{1}H NMR (300 MHz, DMSO+$CDCl_3$) δ: 8.07 (s, 1H), 7.60 (s, 2H), 7.25-7.14 (m, 2H). (**Fig. S46)** ^{13}C NMR (75 MHz, DMSO+$CDCl_3$) δ: 141.50, 138.39, 122.66, 115.80. (**Fig. S47)** Mass (ESI): 118.10 (M+1) (**Fig. S72)**	
2-ethyl-1*H*-benzo[*d*]imidazole (4t) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.25 (ddd, *J* = 17.6, 6.0, 3.1 Hz, 2H), 3.80 (s, 1H), 2.99 (q, *J* = 7.6 Hz, 2H), 1.41 (t, *J* = 7.6 Hz, 3H). (**Fig. S48)** ^{13}C NMR (75 MHz, $CDCl_3$) δ: 156.18, 137.56, 122.61, 114.46 22.22, 12.22. (**Fig. S49)** Mass (ESI): 147.07 (M+1) (**Fig. S73)**	
2-cyclohexyl-1*H*-benzo[*d*]imidazole (4u) ^{1}H NMR (400 MHz, $CDCl_3$+DMSO) δ: 7.49-7.17 (m, 2H), 7.15-7.05 (m, 2H), 2.87-2.85 (m, 2H), 2.84-2.83 (m, 2H), 2.82-2.79 (m, 3H), 2.78-2.77 (m, 3H). (**Fig. S50)** ^{13}C NMR (75 MHz, $CDCl_3$+DMSO) δ: 157.61, 136.87, 119.59, 112.85, 29.87, 24.16. (**Fig. S51)** Mass (ESI): 199.16 (M-1) (**Fig. S74)**	
2-(*p*-tolyl)-1*H*-imidazo[4,5-*b*]pyridine (4v) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.49 (s, 1H), 7.96 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.36-7.16 (m, 3H), 6.67 (dd, *J* = 7.6, 5.0 Hz, 1H), 2.43 (s, 3H). (**Fig. S52)** ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.37, 154.56, 145.90, 142.20, 133.42, 132.37, 129.52, 128.78, 123.32, 114.02, 21.63. (**Fig. S53)** Mass (ESI): 208.08 (M-1) (**Fig. S75)**	

NMR Spectrum of Substituted benzimidazole

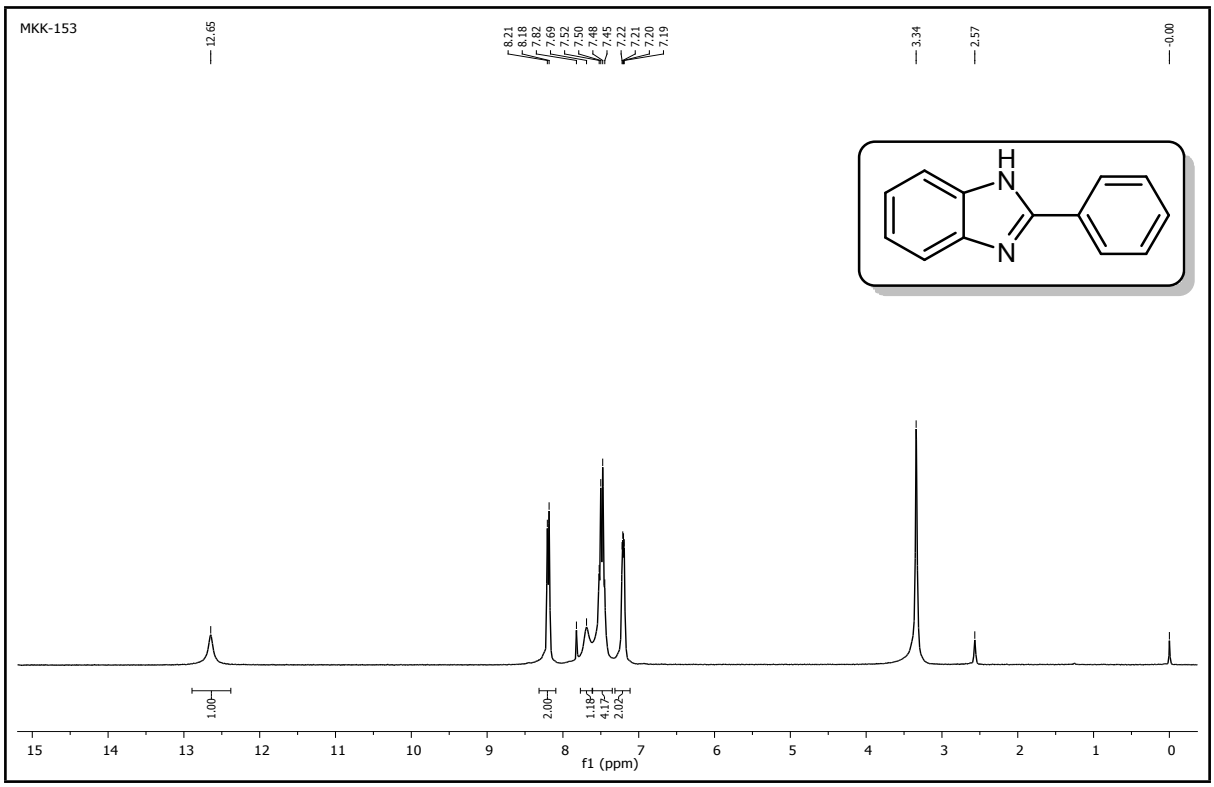


Fig. S10 ^{1}H NMR Spectrum of 2-phenyl-1*H*-benzo[*d*]imidazole. **(4a)** (300 MHz, $CDCl_3$+DMSO)

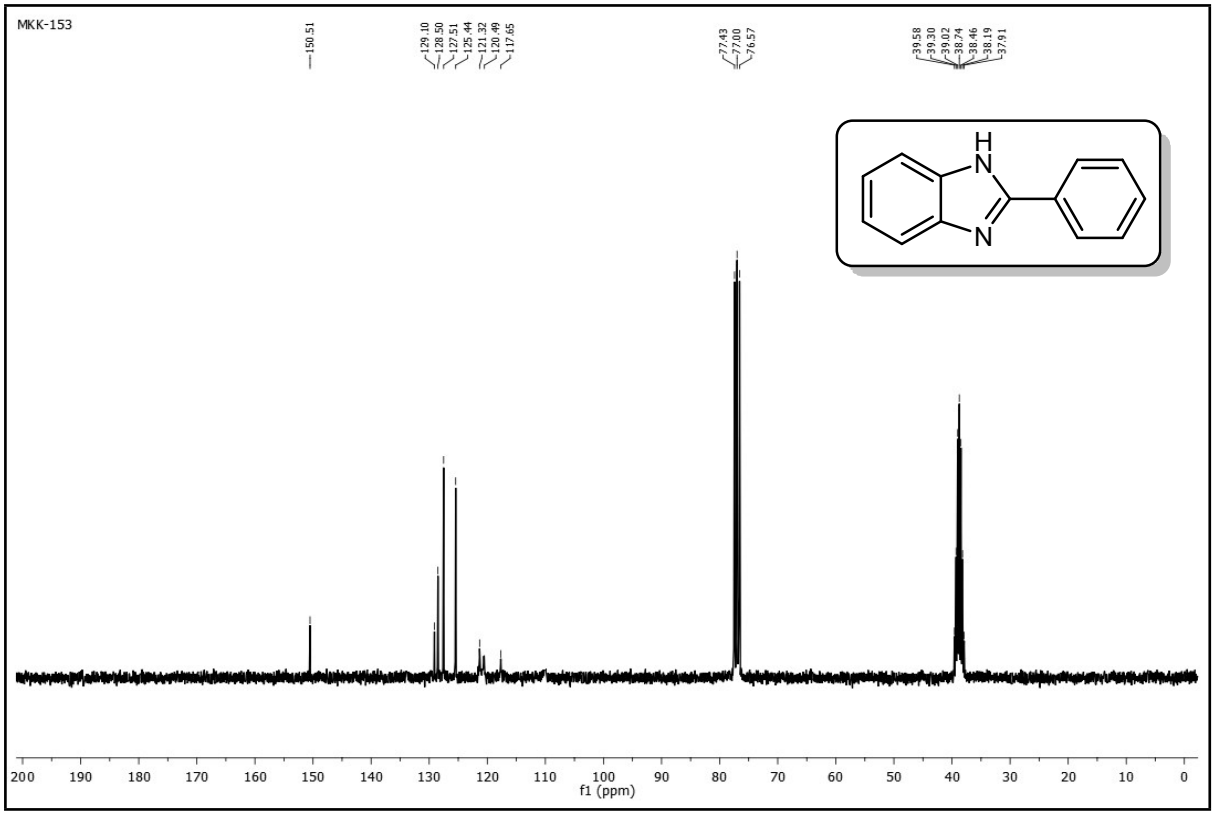


Fig. S11 ^{13}C NMR Spectrum of 2-phenyl-1*H*-benzo[*d*]imidazole **(4a)** (75 MHz, $CDCl_3$+DMSO),

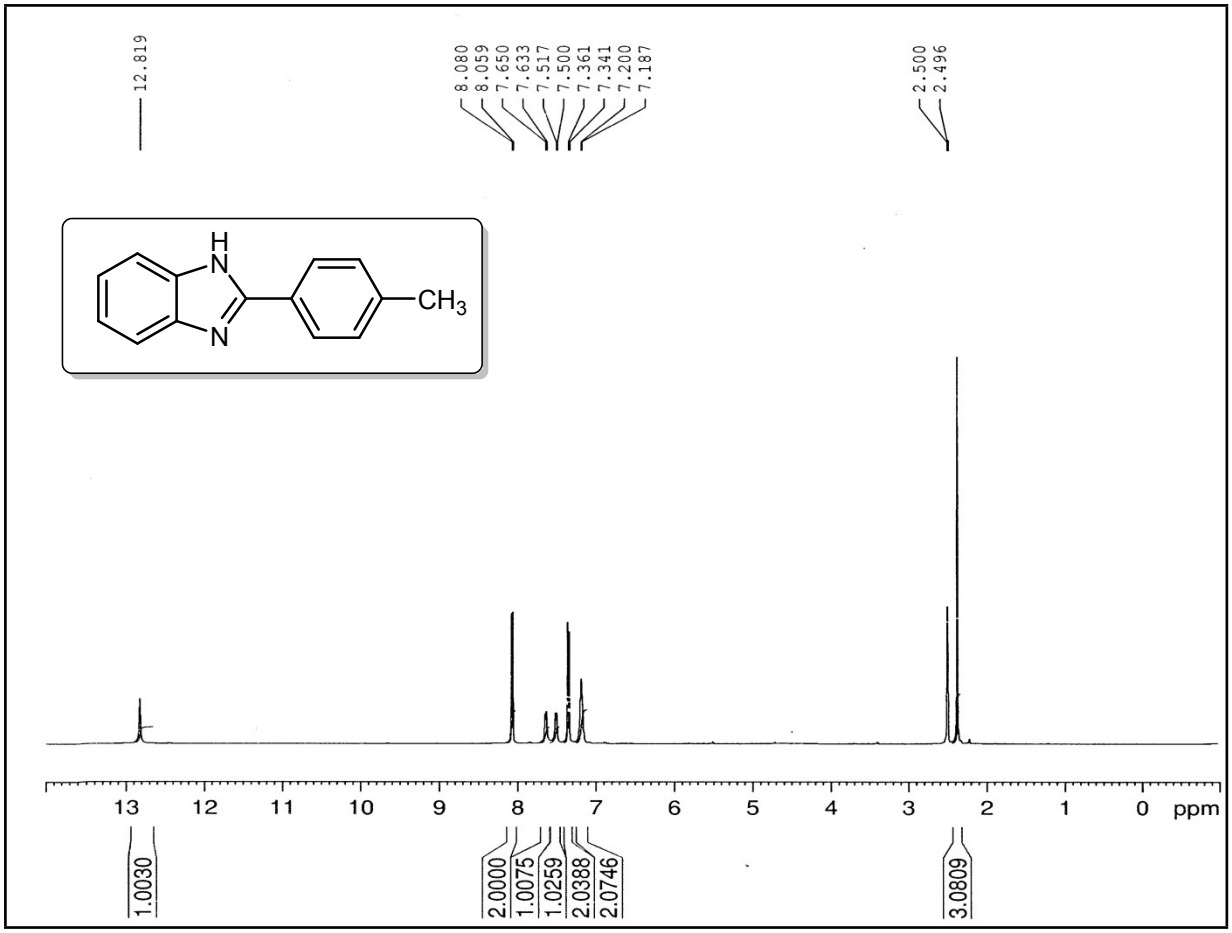


Fig. S12 ^{1}H NMR Spectrum of 2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole **(4b)** (400 MHz, DMSO)

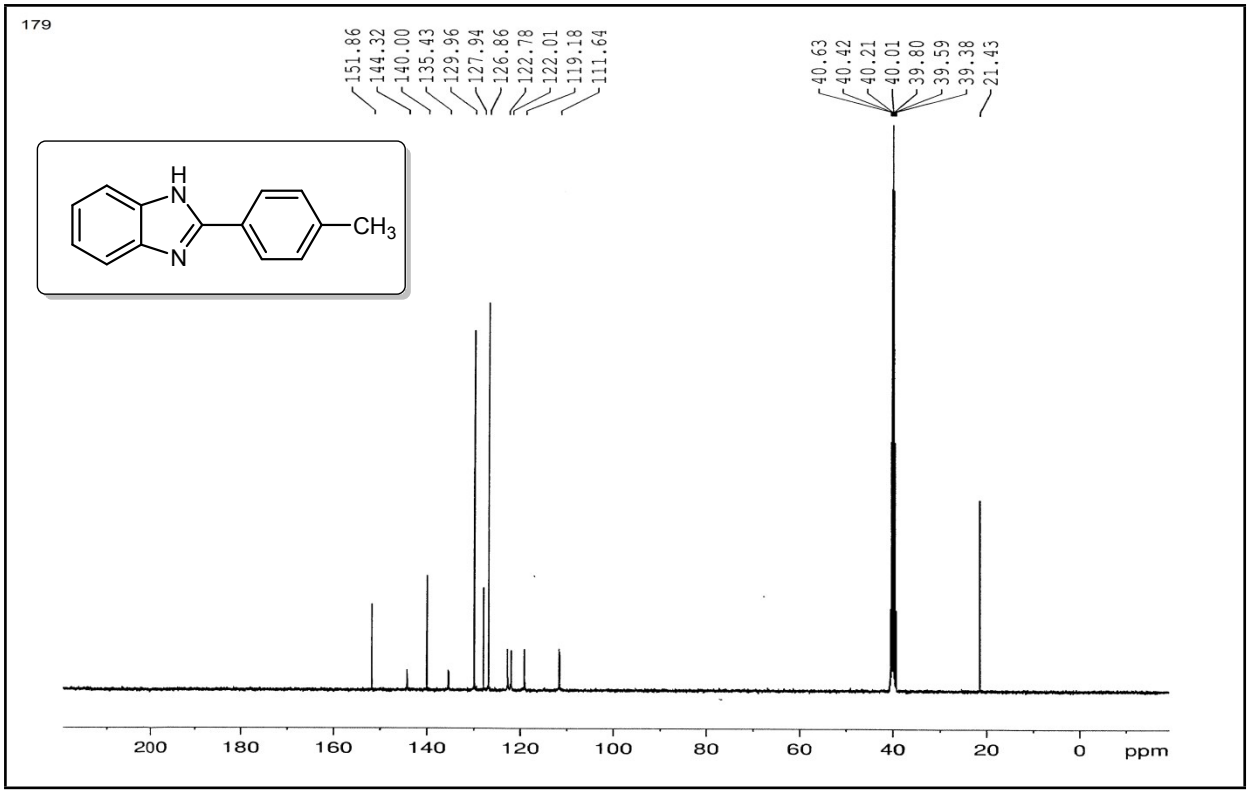


Fig. S13 ^{13}C NMR Spectrum of 2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole **(4b)** (100 MHz, DMSO)

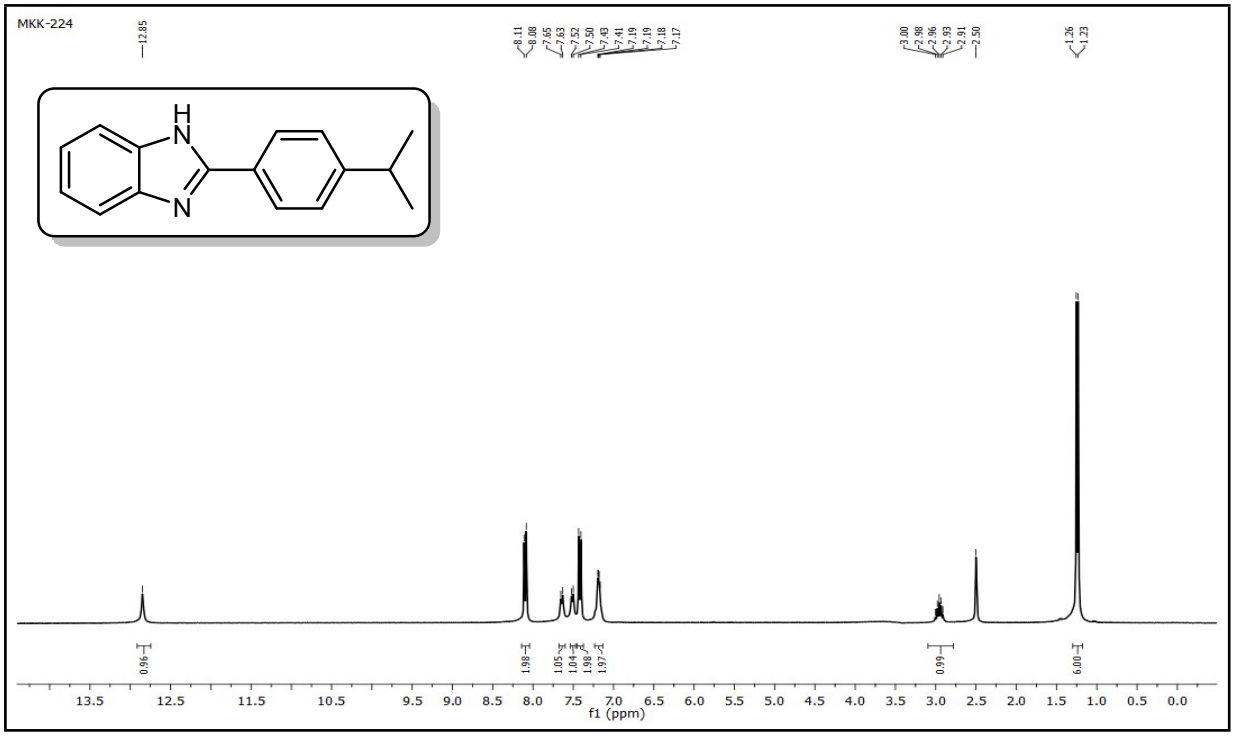


Fig. S14 ^{1}H NMR Spectrum of 2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **(4c)** (300 MHz, DMSO)

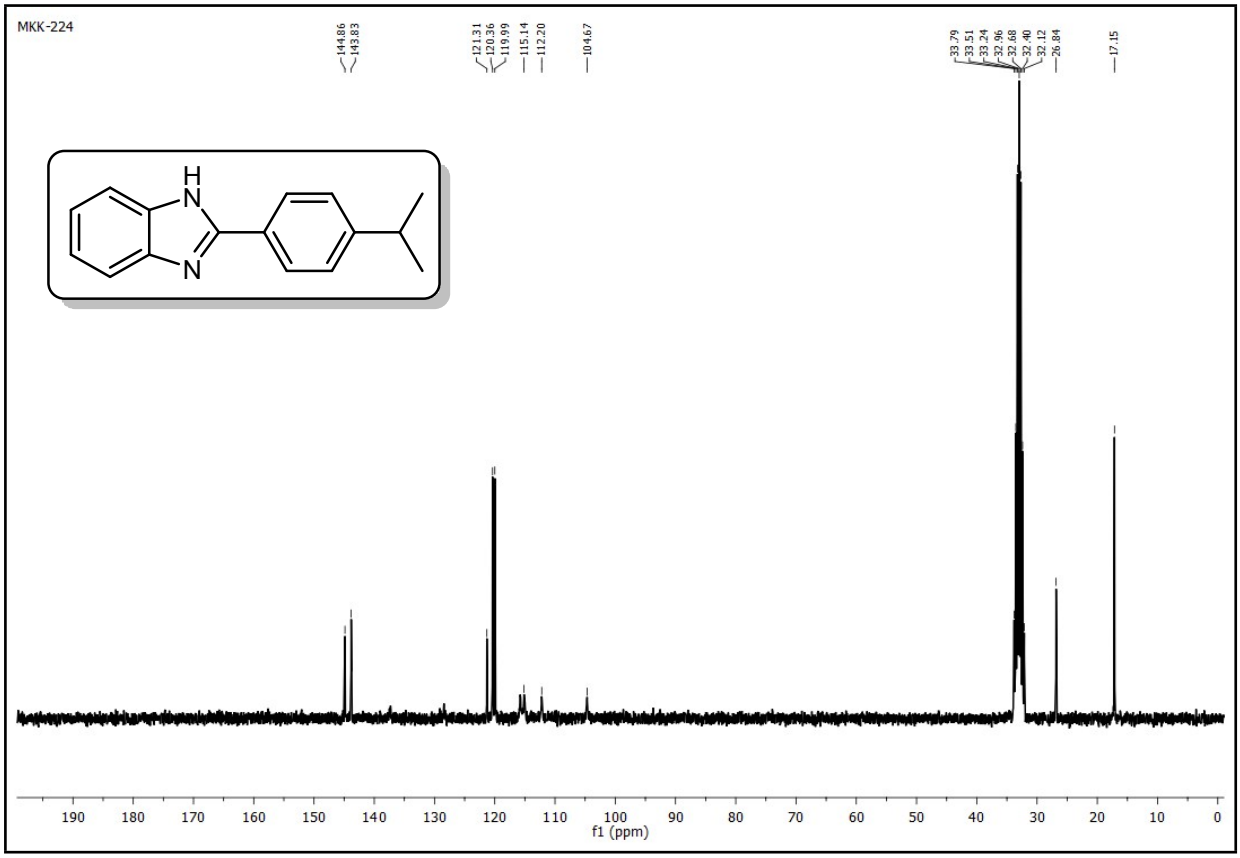


Fig. S15 ^{13}C NMR Spectrum of 2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **(4c)** (75 MHz, DMSO)

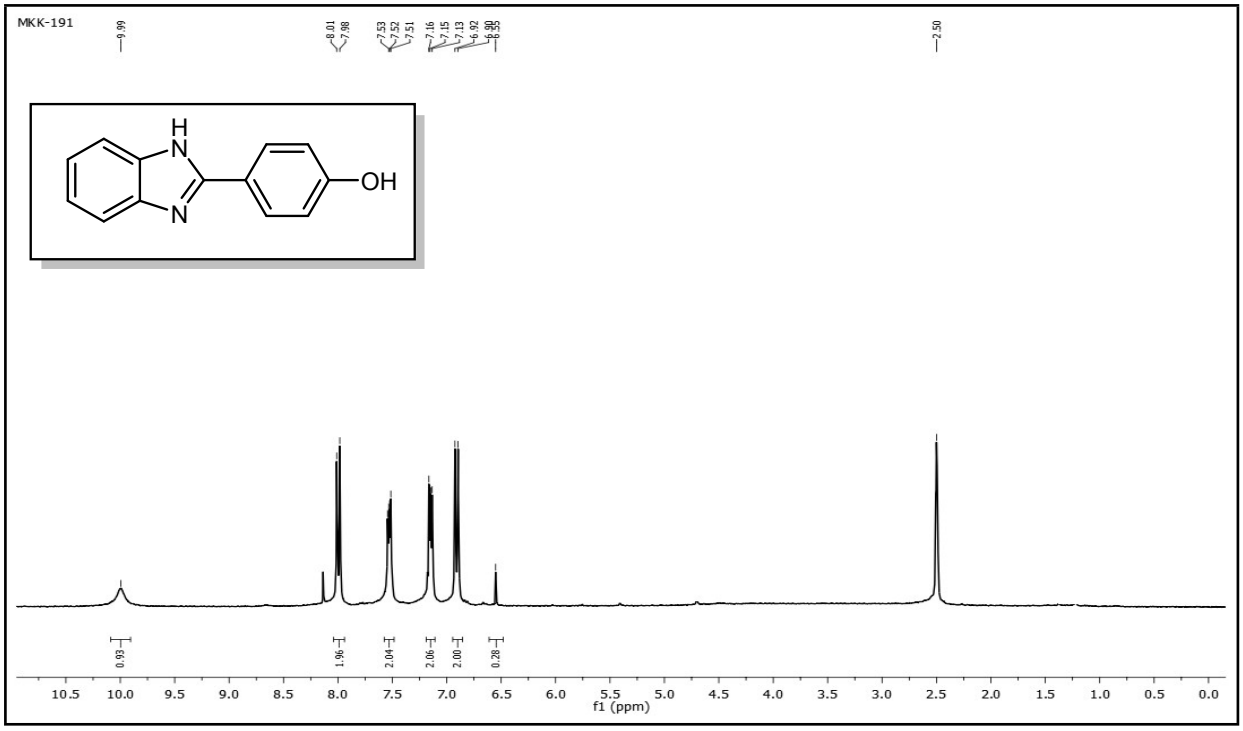


Fig. S16 ^{1}H NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)phenol **(4d)** (300 MHz, DMSO)

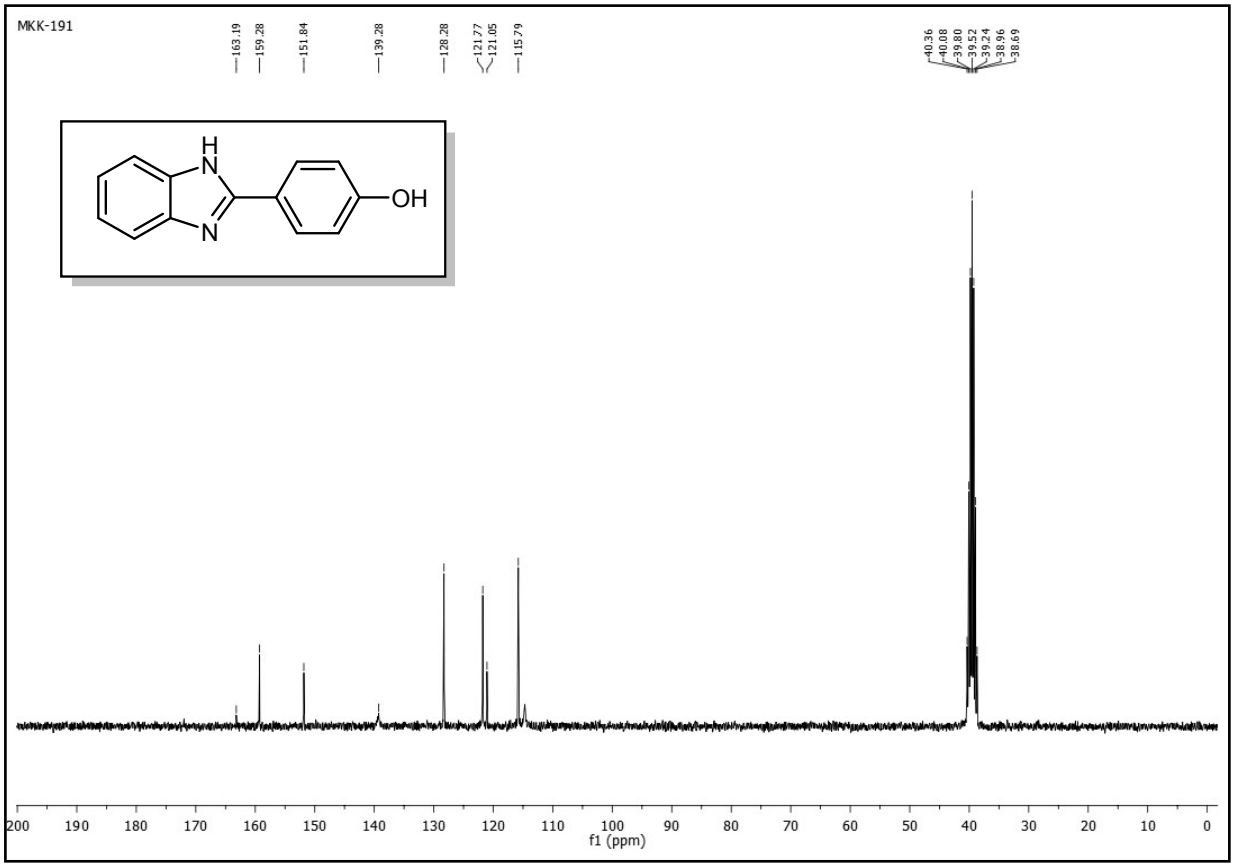


Fig. S17 ^{13}C NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)phenol **(4d)** (75 MHz, DMSO)

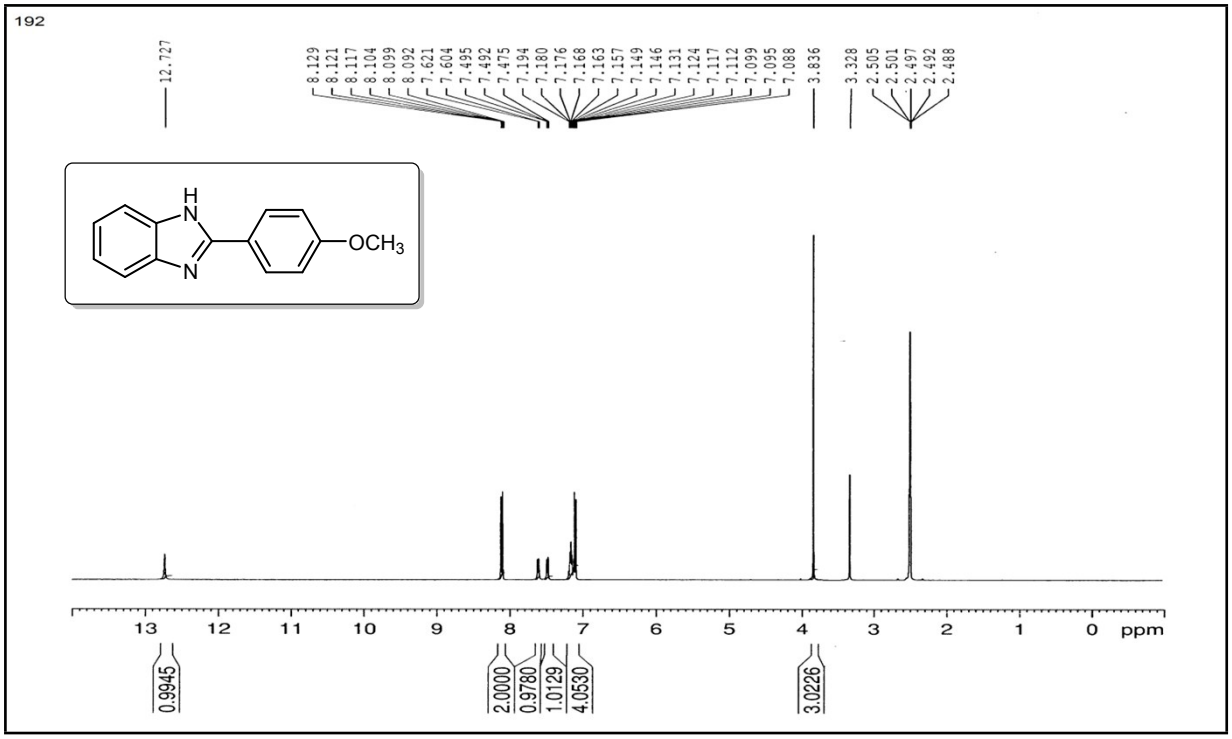


Fig. S18 ^{1}H NMR Spectrum of 2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole **(4e)** (400 MHz, DMSO)

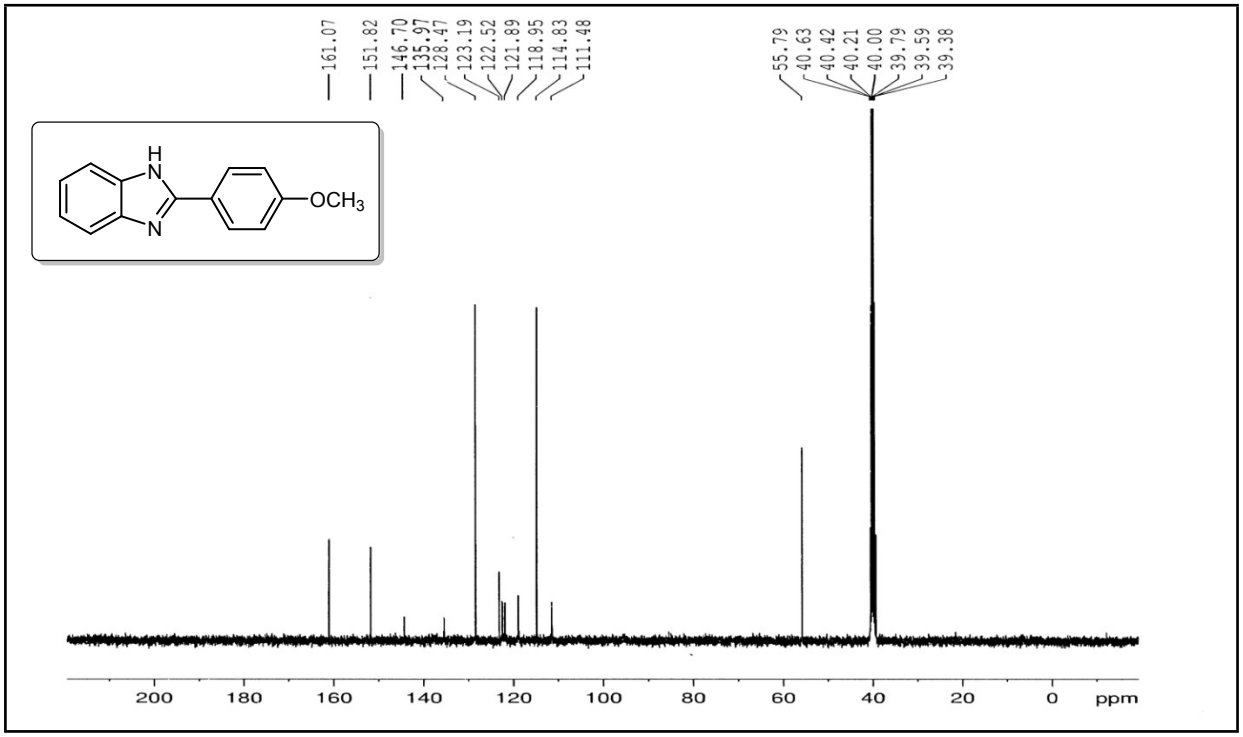


Fig. S19 ^{13}C NMR Spectrum 2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole **(4e)** (100 MHz, DMSO)

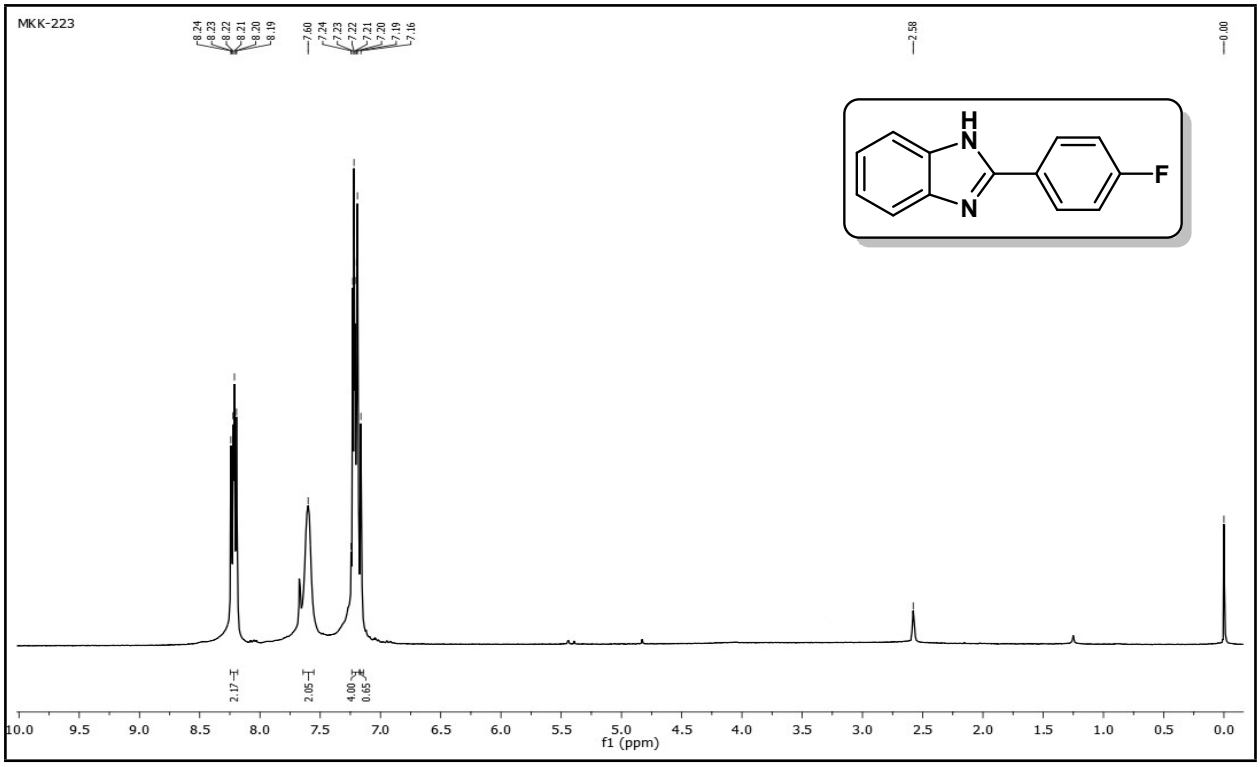


Fig. S20 ^{1}H NMR Spectrum of 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole **(4f)** (300 MHz, DMSO+$CDCl_3$)

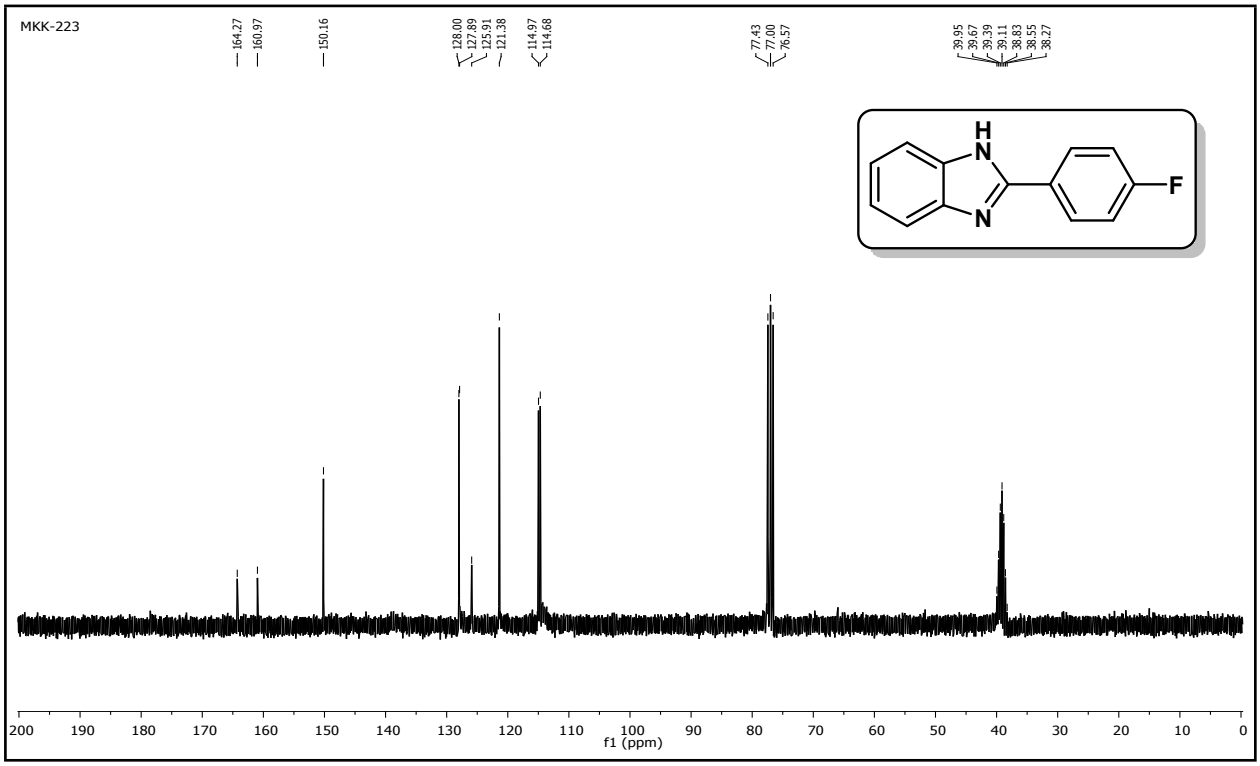


Fig. S21 ^{13}C NMR Spectrum of 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole **(4f)** (75 MHz, DMSO+$CDCl_3$)

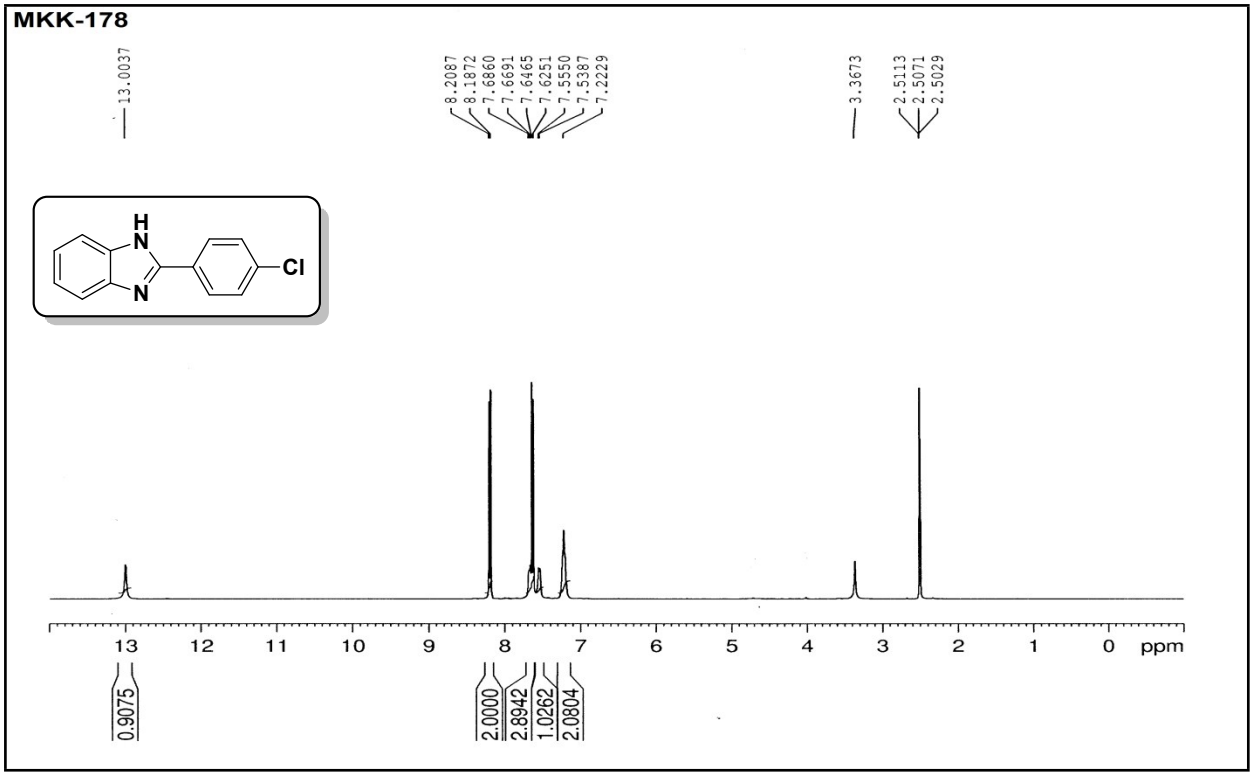


Fig. S22 [1]H NMR Spectrum of 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole **(4g)** (300 MHz, DMSO)

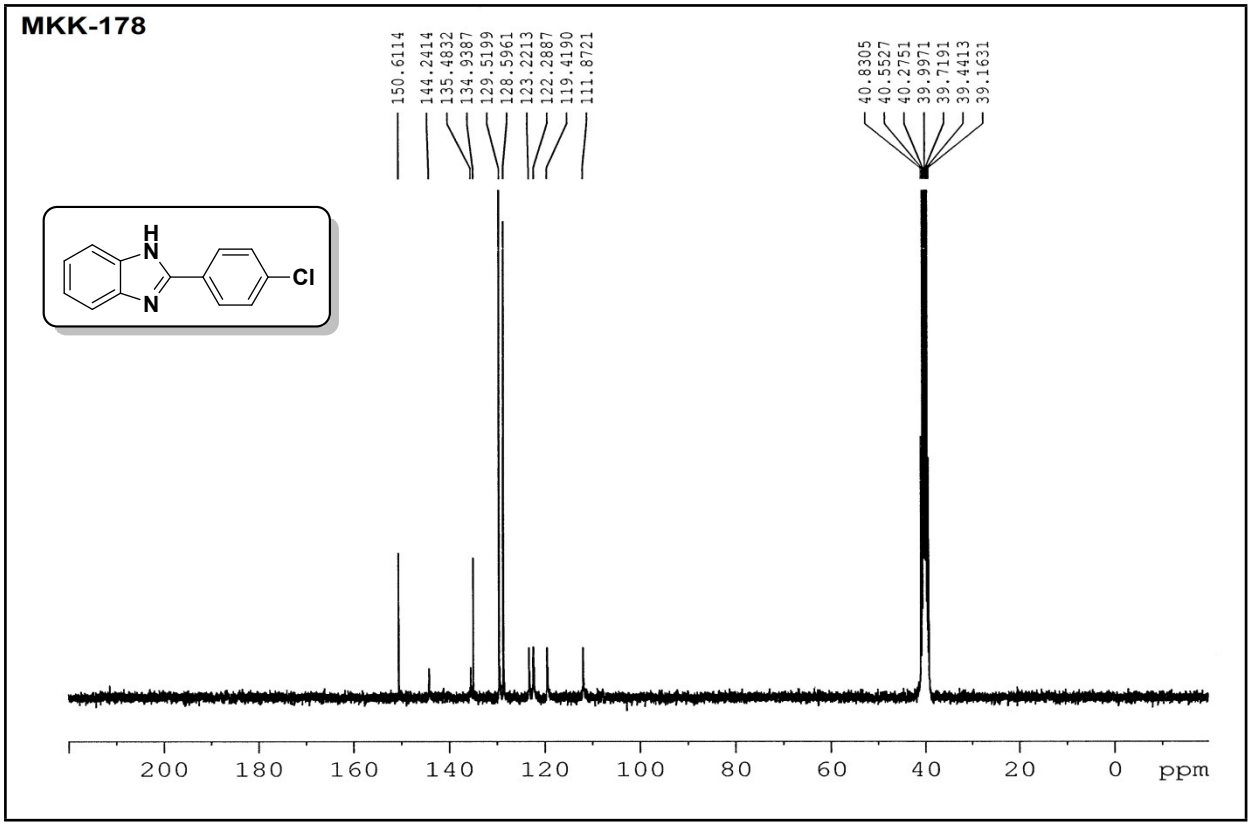


Fig. S23 [13]C NMR Spectrum of 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole **(4g)** (100 MHz, DMSO)

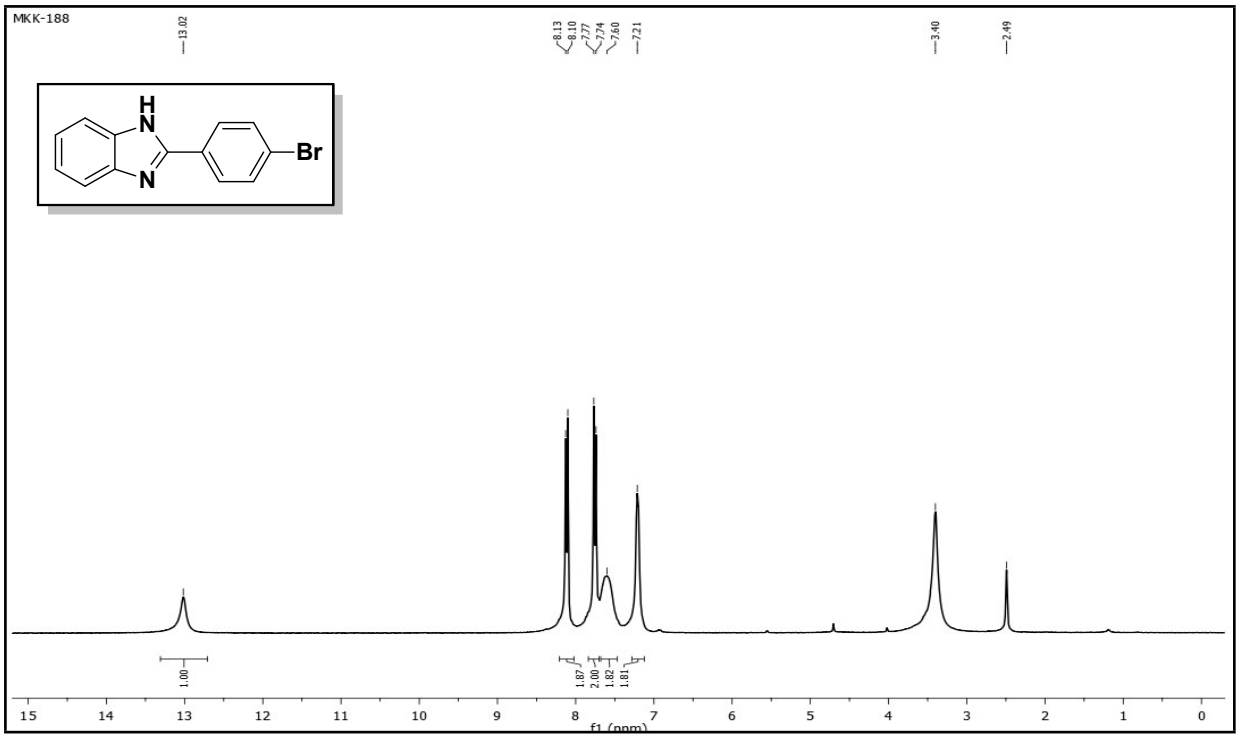


Fig. S24 ^{1}H NMR Spectrum of 2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole **(4h)** (300 MHz, DMSO)

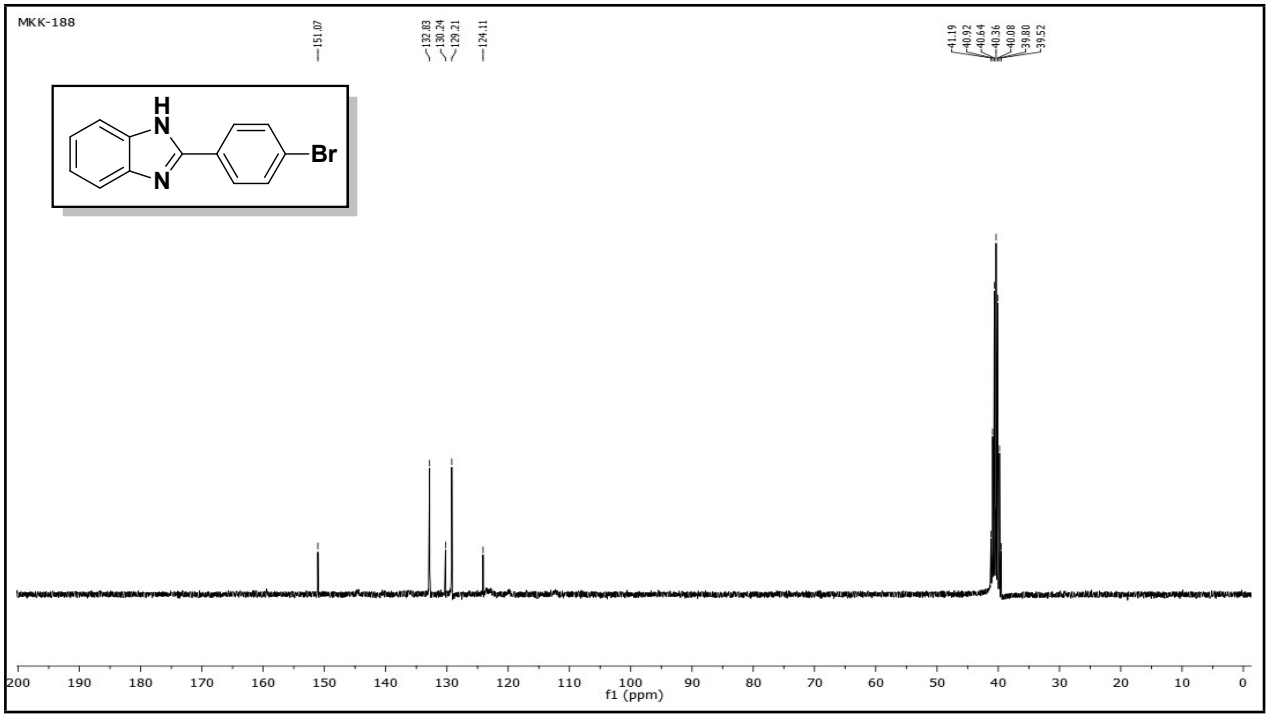


Fig. S25 ^{13}C NMR Spectrum of 2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole **(4h)** (75 MHz, DMSO)

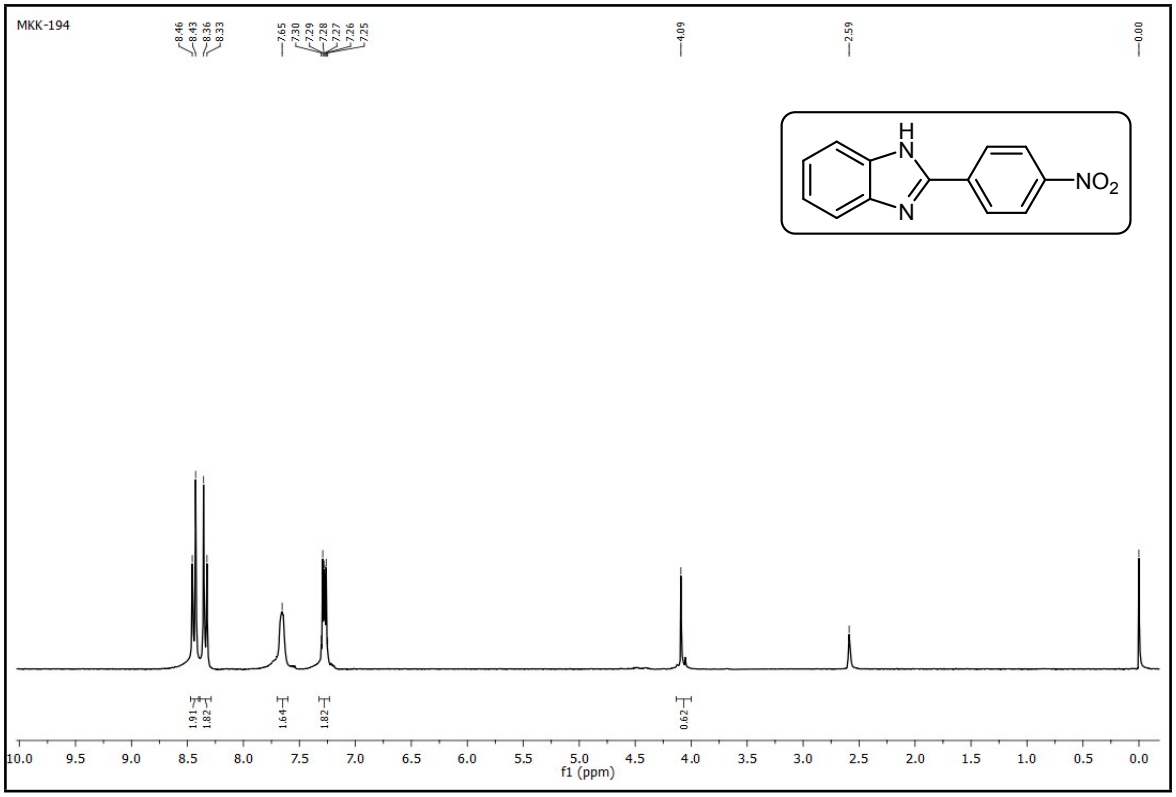


Fig. S26 ^{1}H NMR Spectrum of 2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole **(4i)** (300 MHz, DMSO+$CDCl_3$)

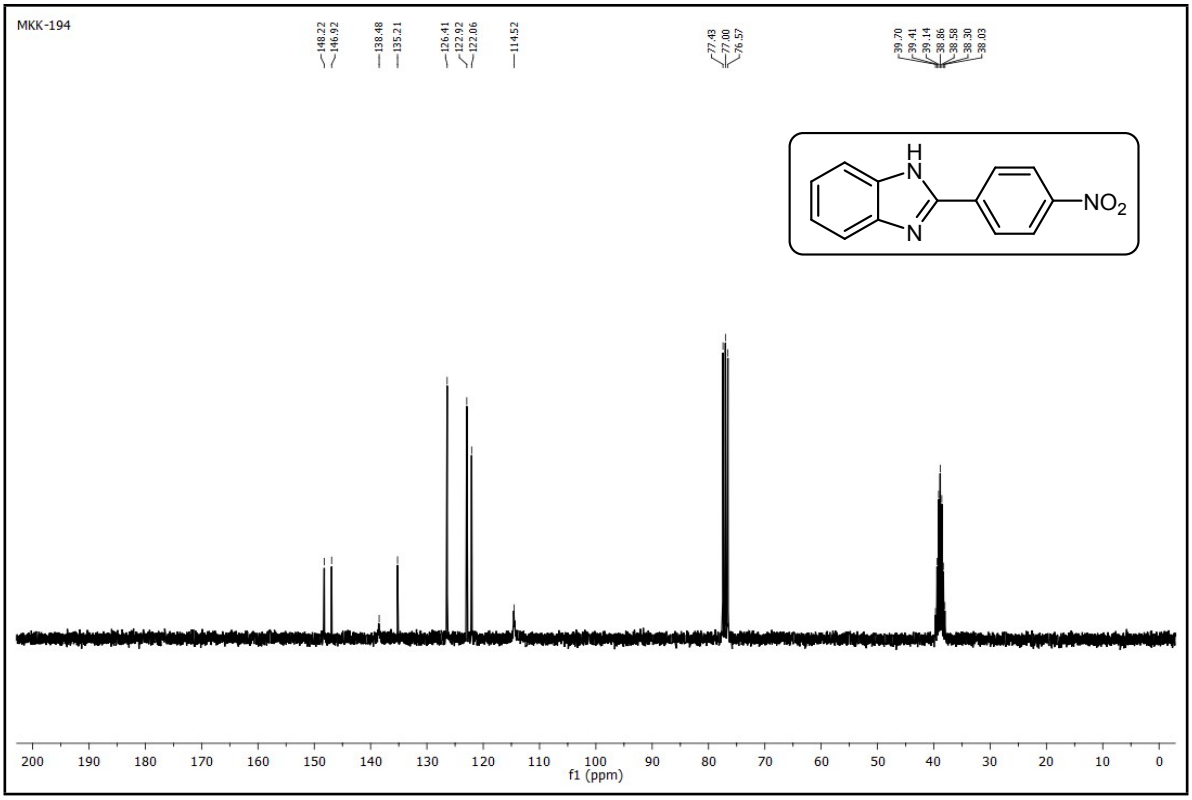


Fig. S27 ^{13}C NMR Spectrum of 2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole **(4i)** (75 MHz, DMSO+$CDCl_3$)

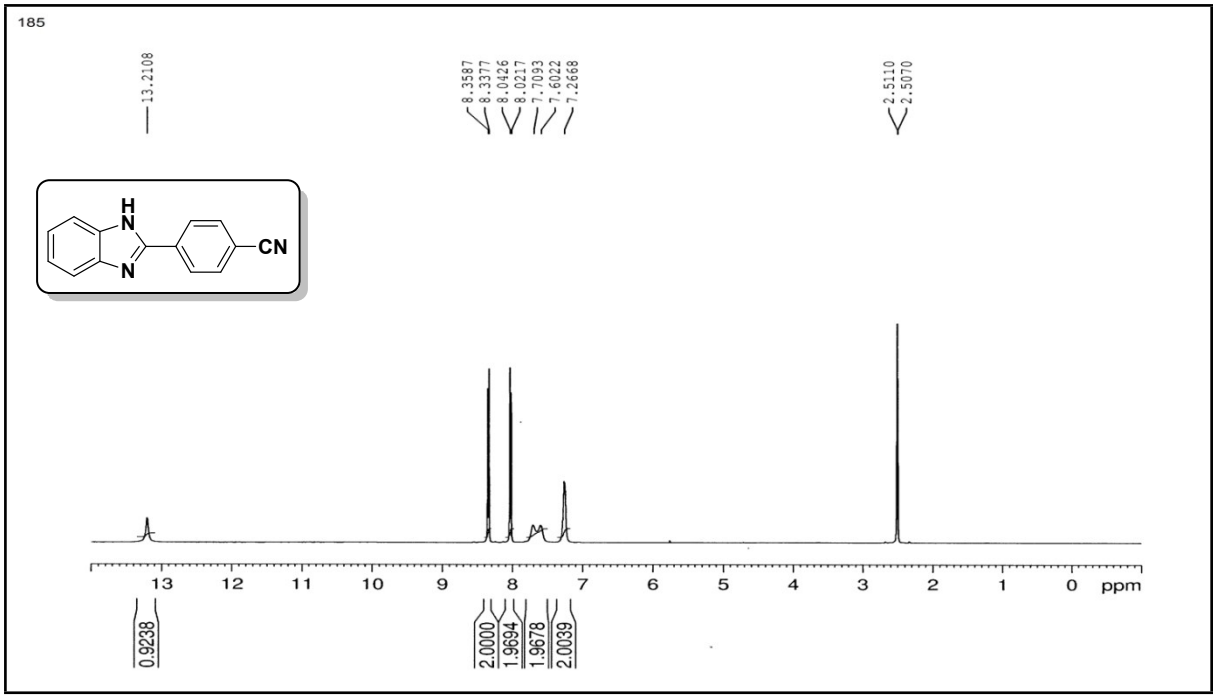


Fig. S28 [1]H NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4j)** (400 MHz, DMSO)

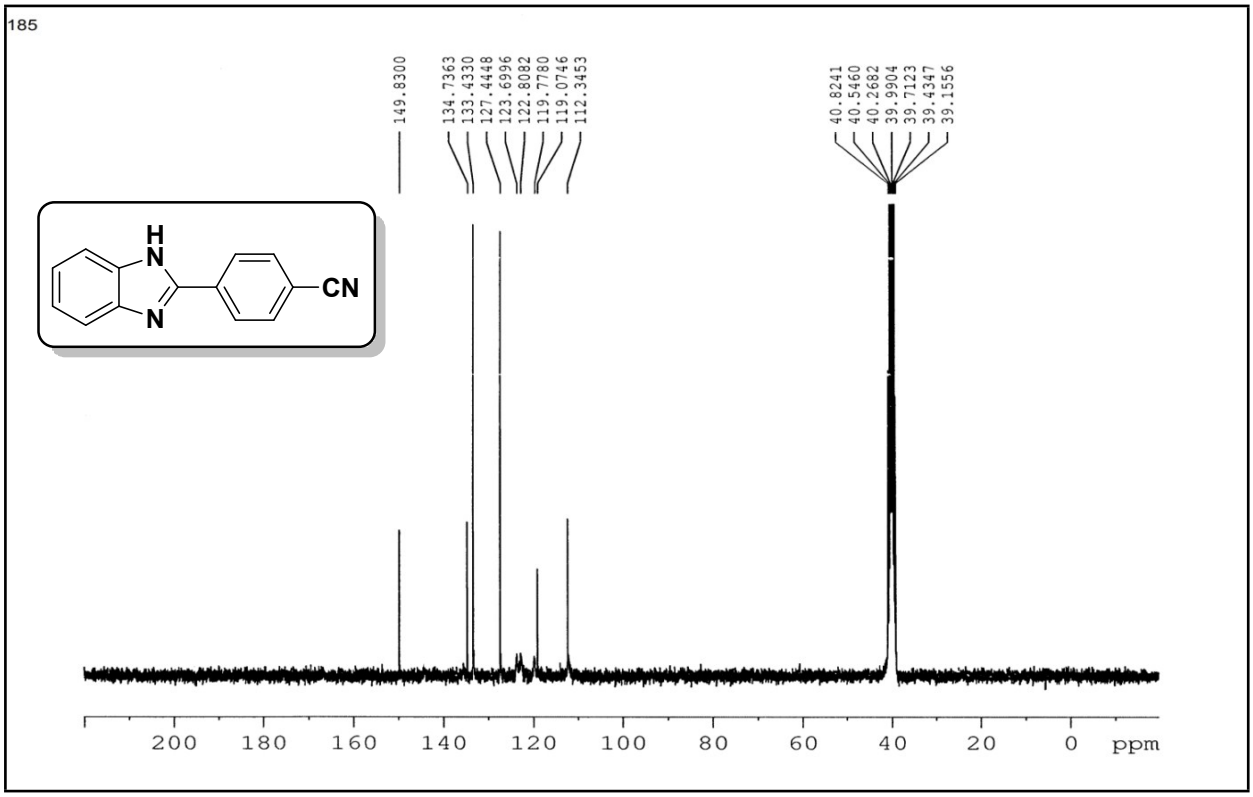


Fig. S29 [13]C NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4j)** (100 MHz, DMSO)

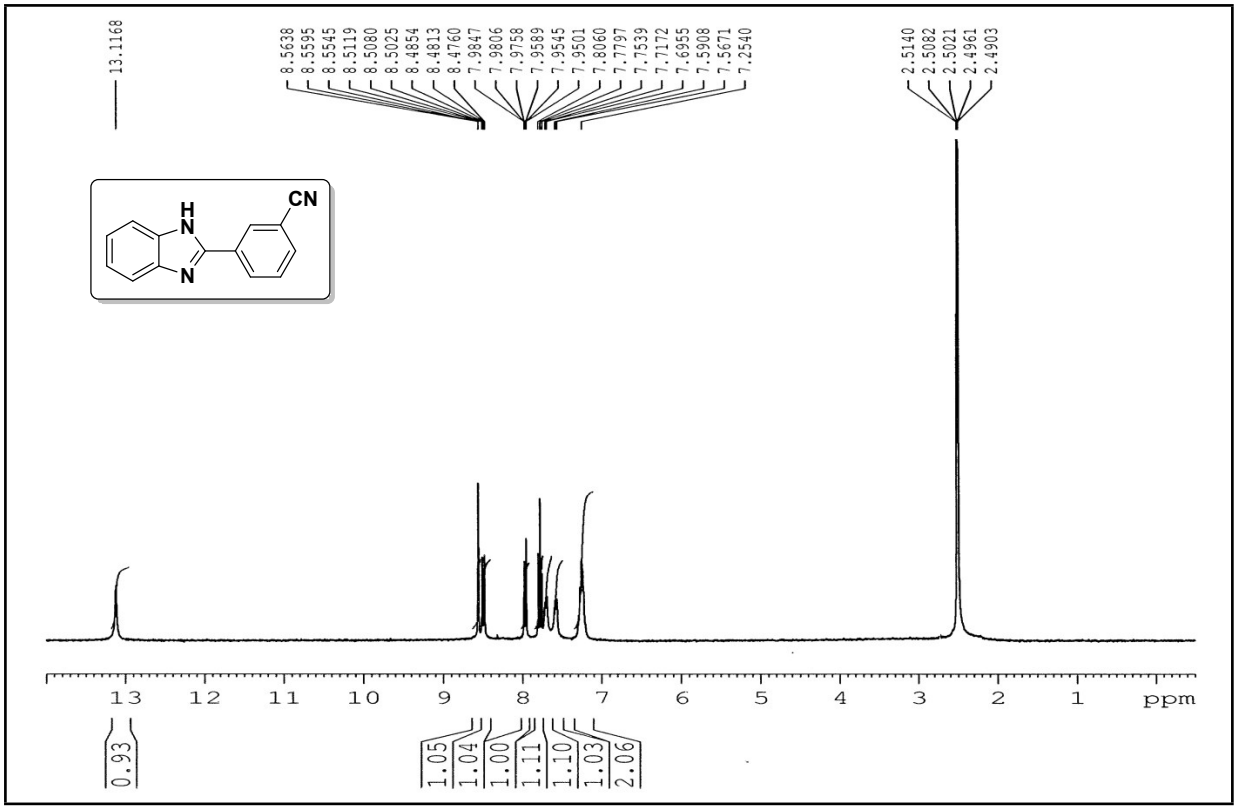


Fig. S30 [1]H NMR Spectrum of 3-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4k)** (300 MHz, DMSO)

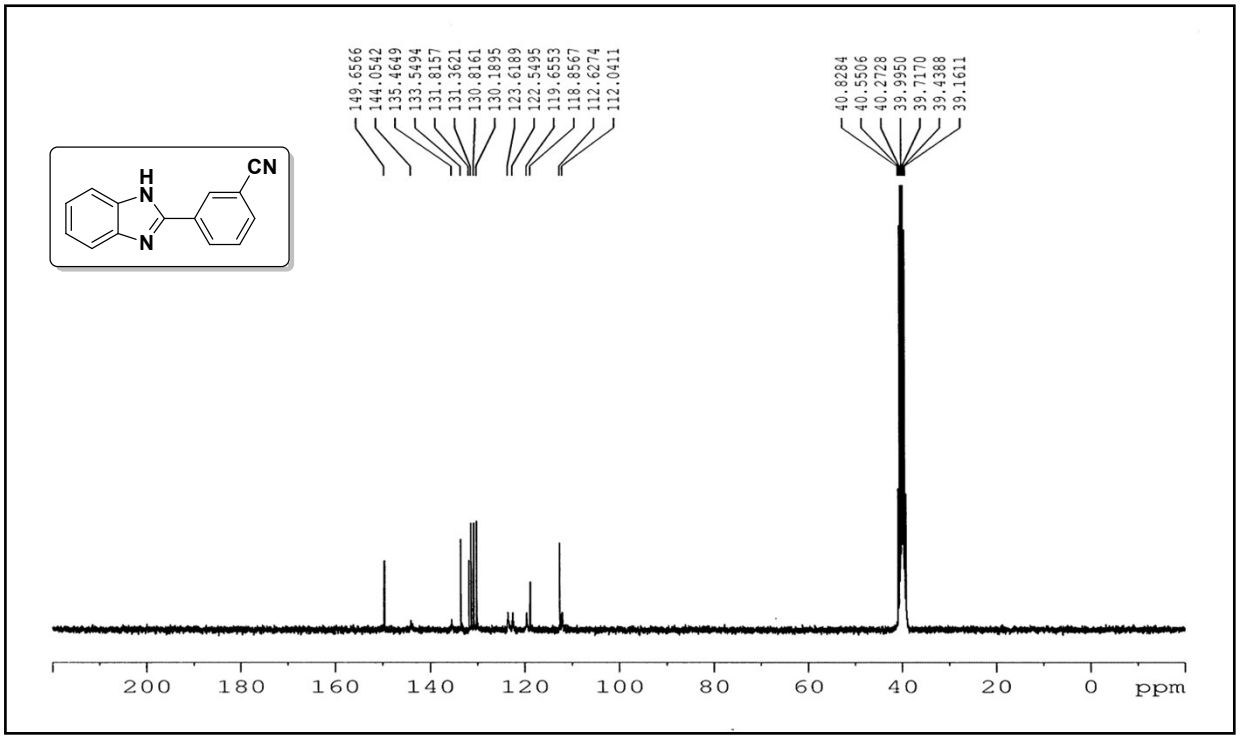


Fig. S31 [13]C NMR Spectrum of 3-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4k)** (75 MHz, DMSO)

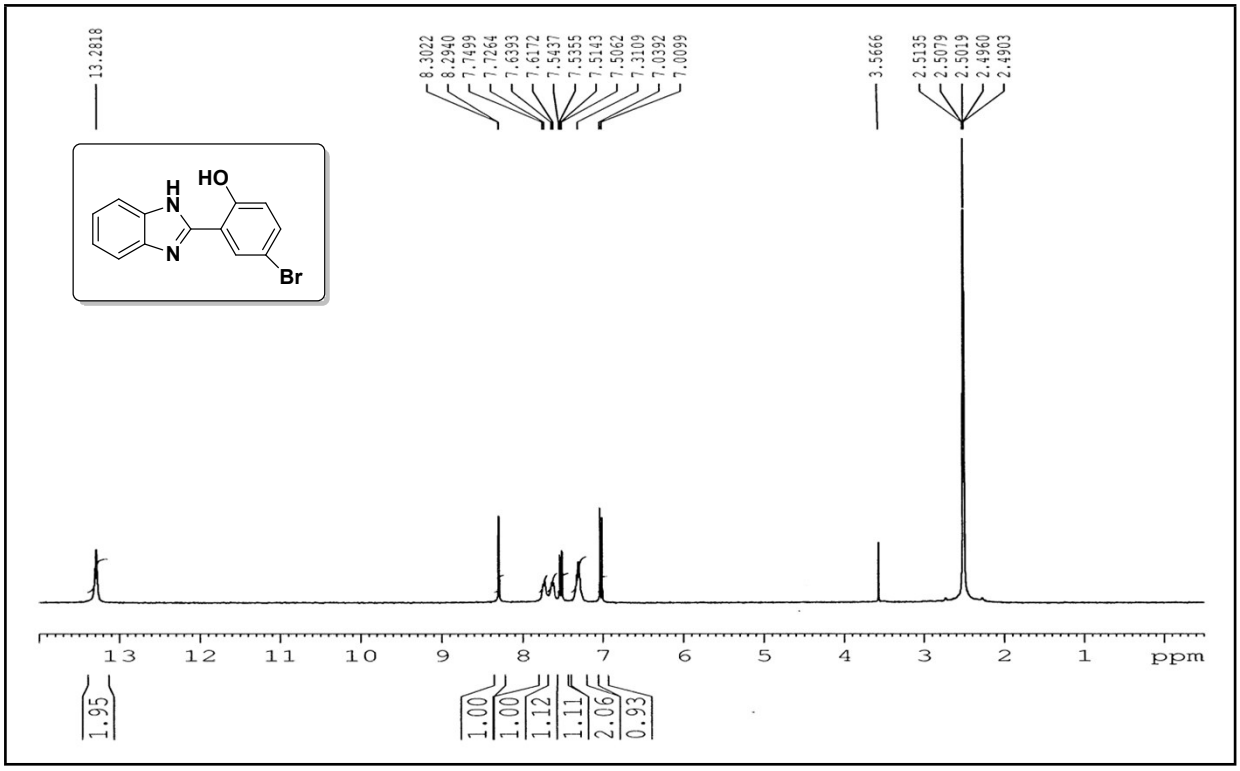


Fig. S32 ^{1}H NMR Spectrum of 2-(1*H*-benzo[*d*]imidazol-2-yl)-4-bromophenol **(4l)** (300 MHz, DMSO)

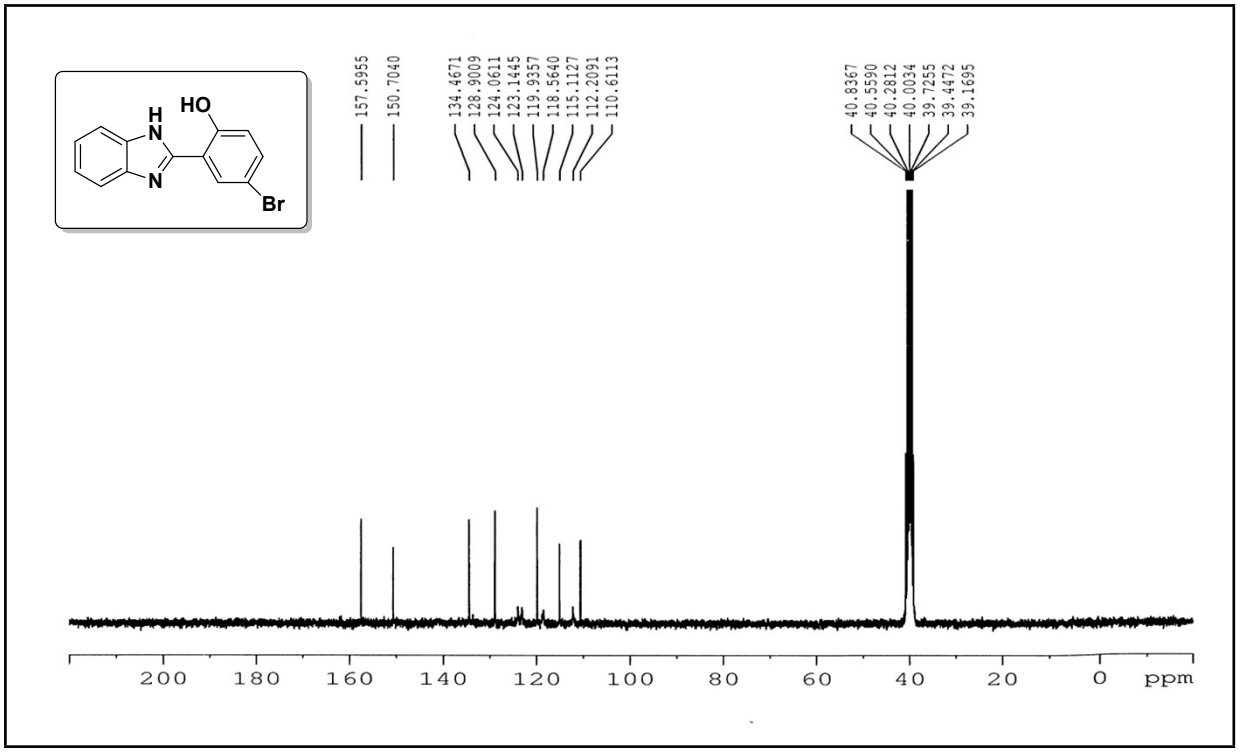


Fig. S33 ^{13}C NMR Spectrum of 2-(1*H*-benzo[*d*]imidazol-2-yl)-4-bromophenol **(4l)** (100 MHz, DMSO)

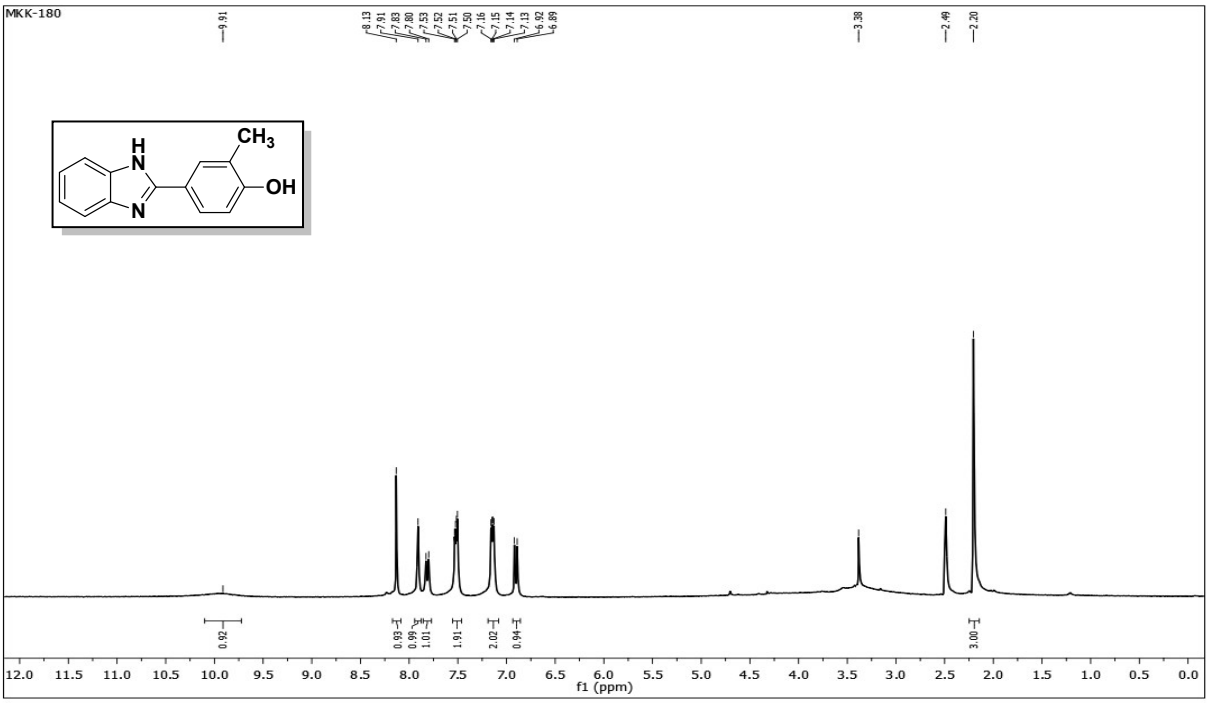


Fig. S34 ^{1}H NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)-2-methylphenol **(4m)** (300 MHz, DMSO)

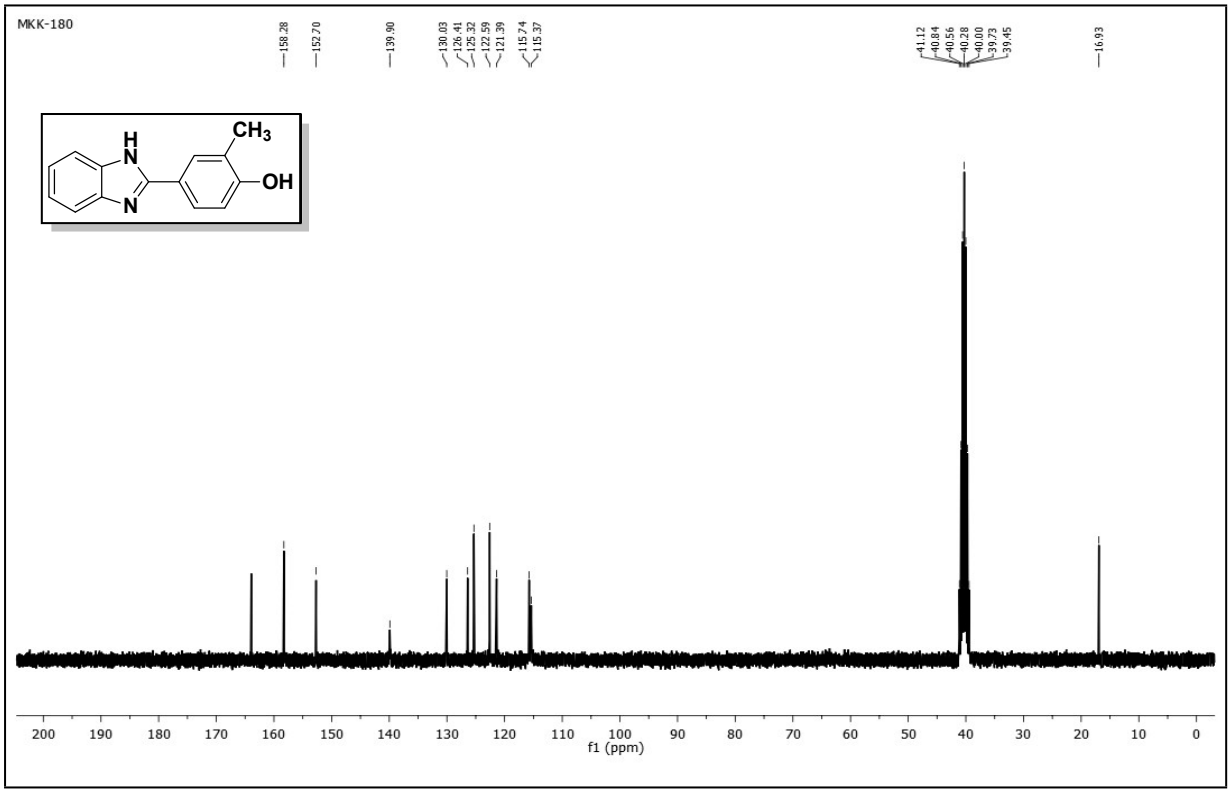


Fig. S35 ^{13}C NMR Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)-2-methylphenol **(4m)** (75 MHz, DMSO)

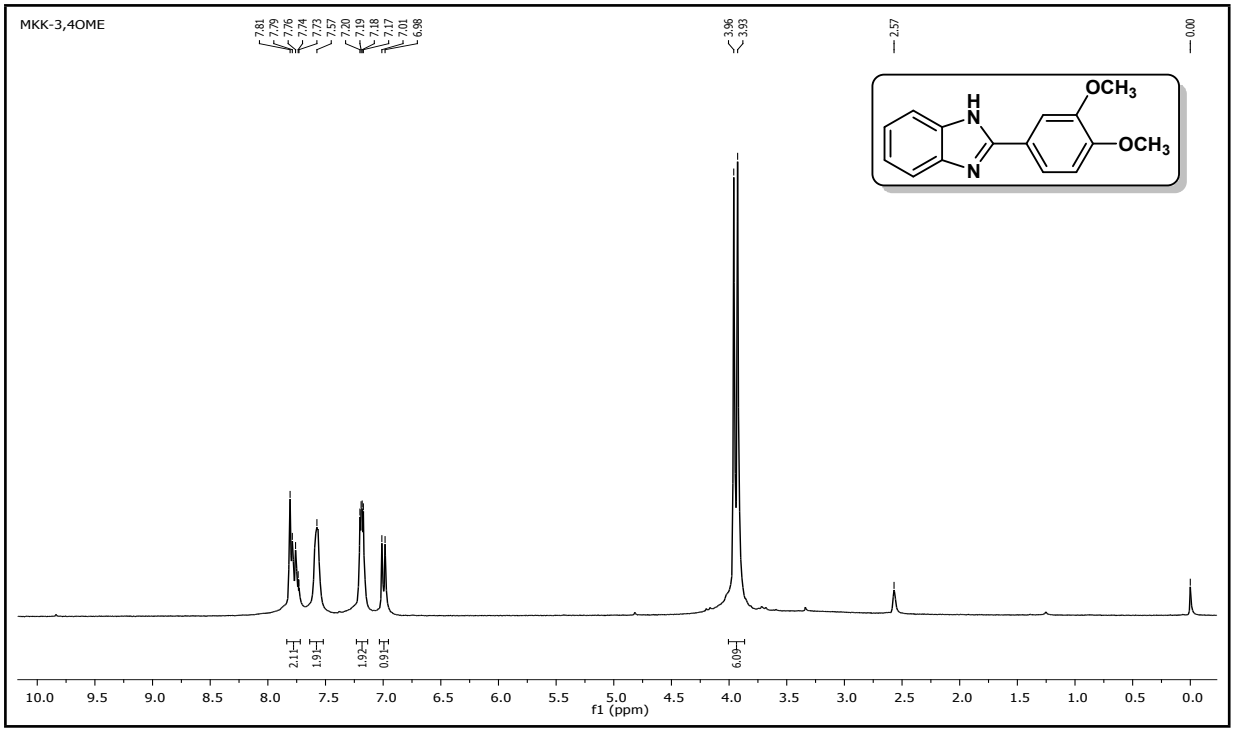


Fig. S36 ^{1}H NMR Spectrum of 2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole **(4n)** (300 MHz, DMSO+$CDCl_3$)

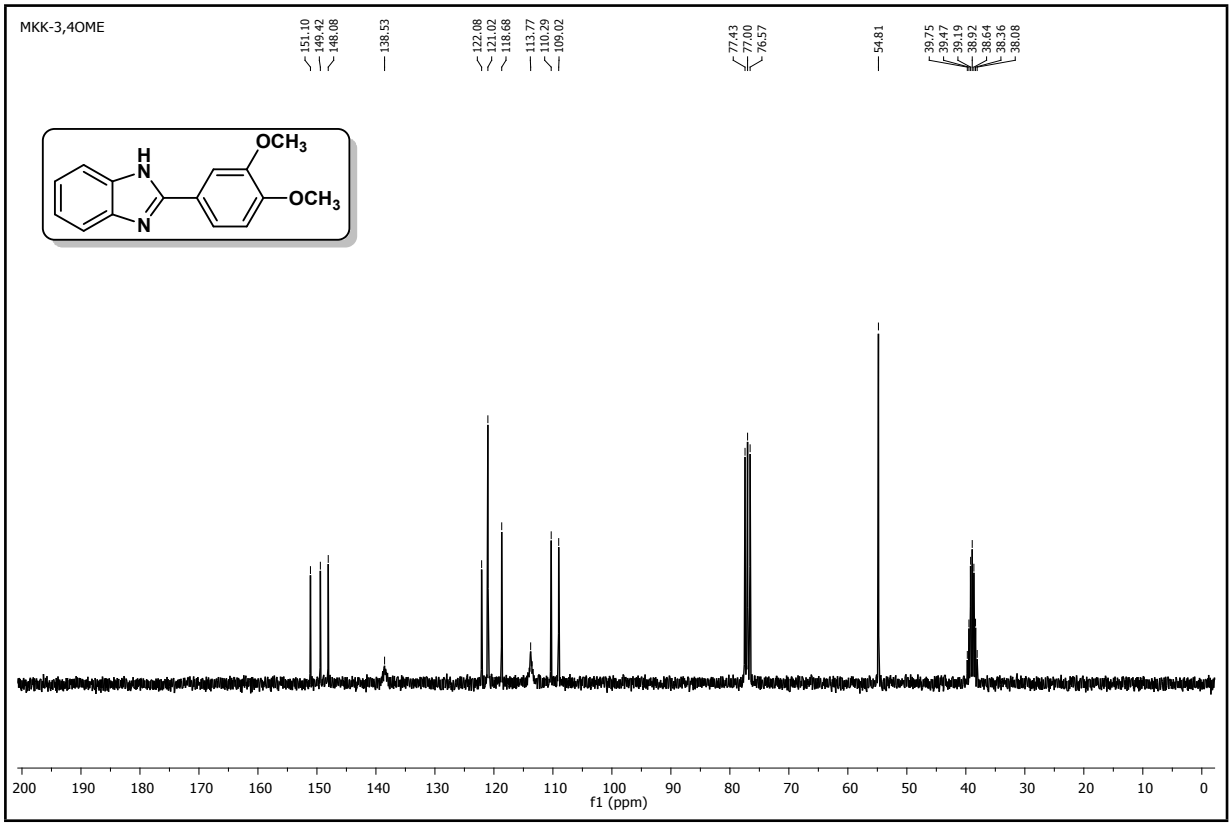


Fig. S37 ^{13}C NMR Spectrum of 2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole **(4n)** (75 MHz, DMSO+$CDCl_3$)

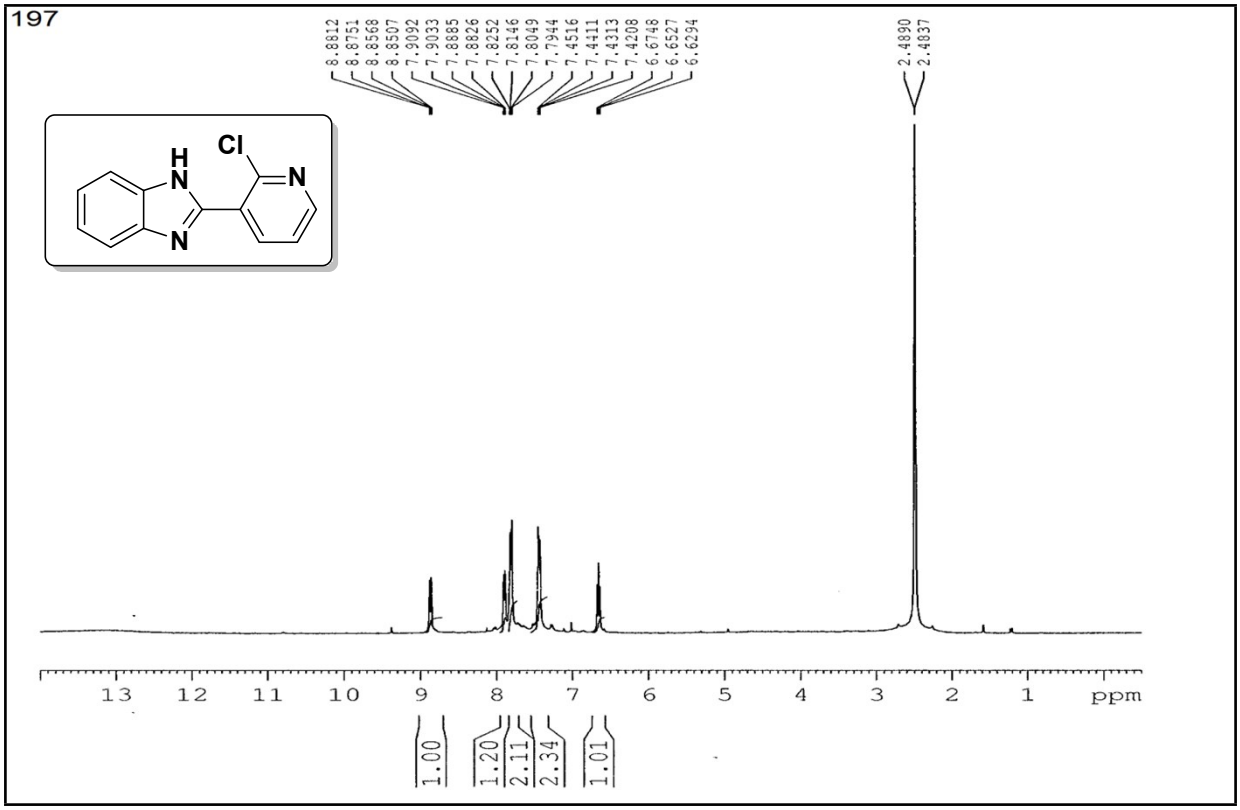


Fig. S38 [1]H NMR Spectrum of 2-(2-chloropyridin-3-yl)-1*H*-benzo[*d*]imidazole **(4o)** (300 MHz, DMSO)

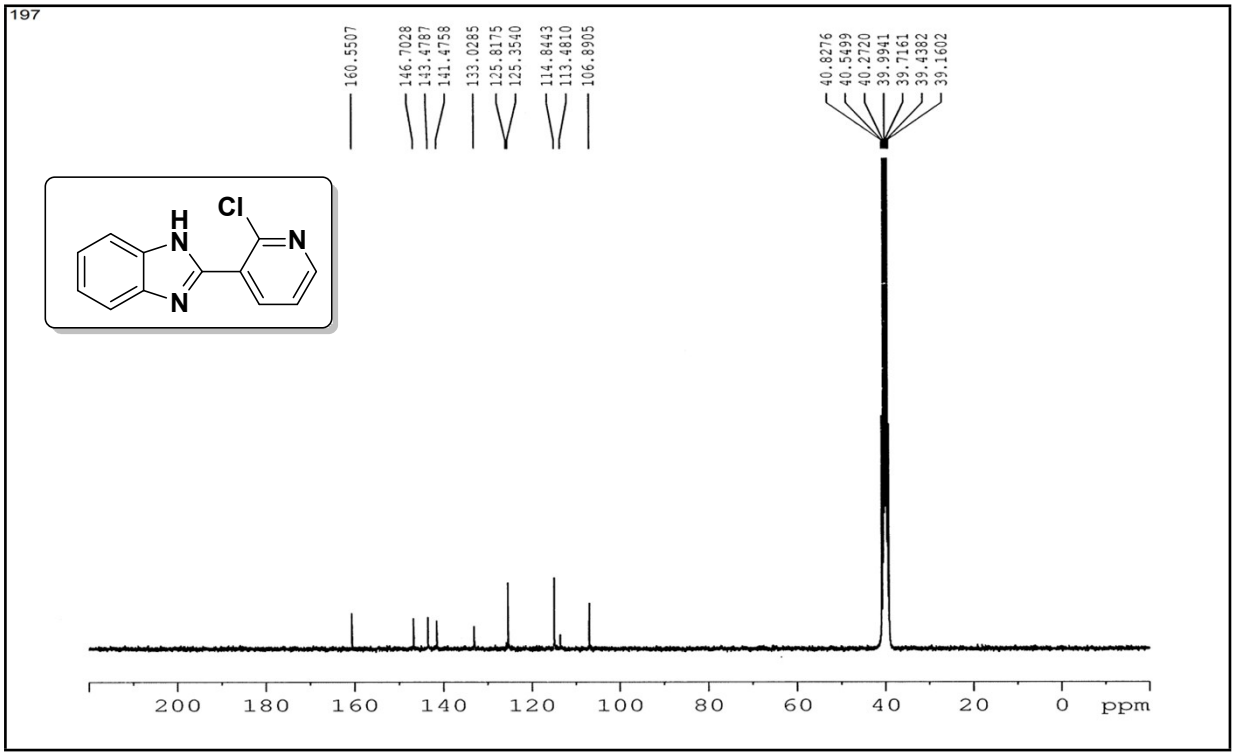


Fig. S39 [13]C NMR Spectrum of 2-(2-chloropyridin-3-yl)-1*H*-benzo[*d*]imidazole **(4o)** (75 MHz, DMSO)

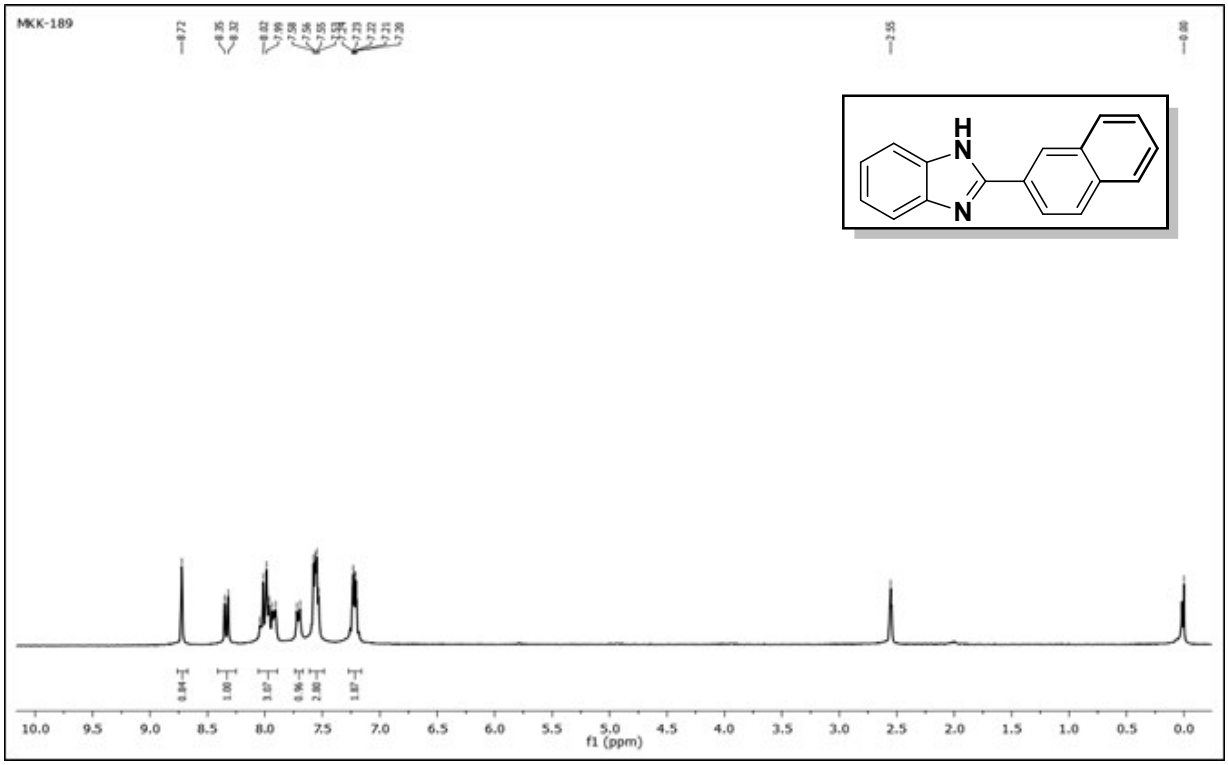


Fig. S40 ^{1}H NMR Spectrum of 2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole **(4p)** (300 MHz, DMSO+$CDCl_3$)

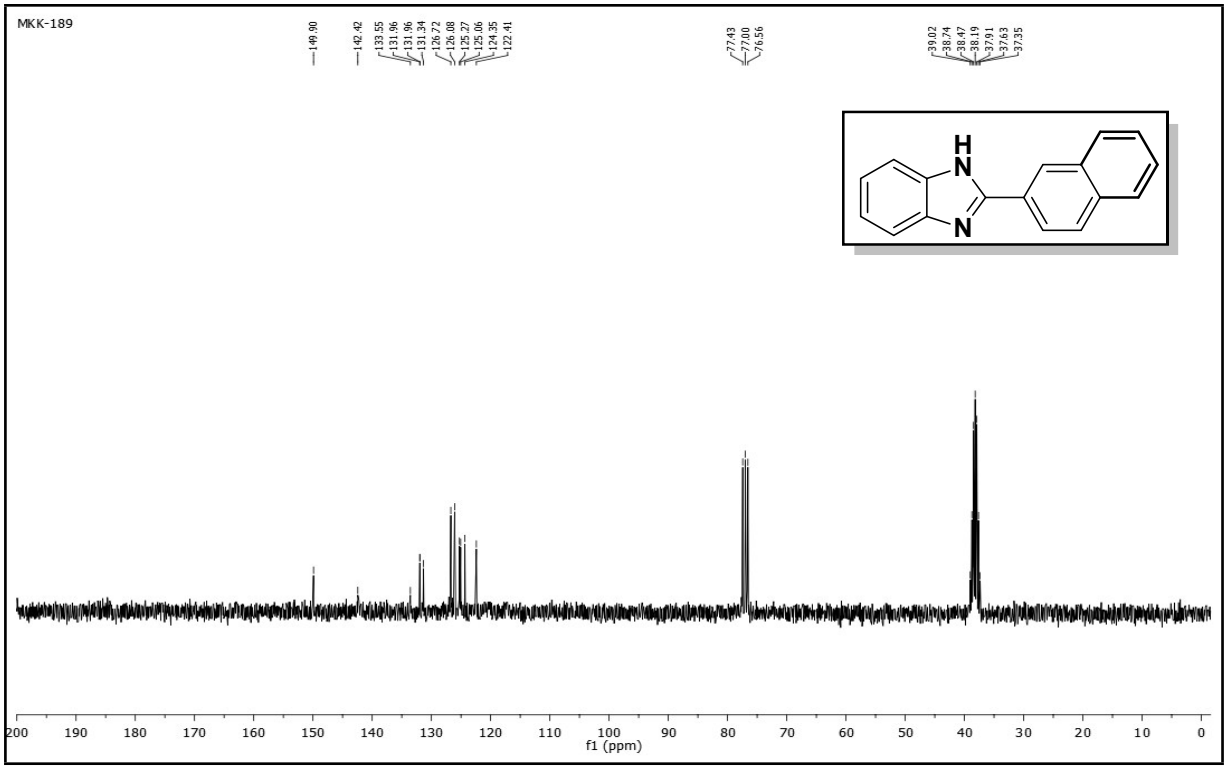


Fig. S41 ^{13}C NMR Spectrum of 2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole **(4p)** (75 MHz, DMSO+$CDCl_3$)

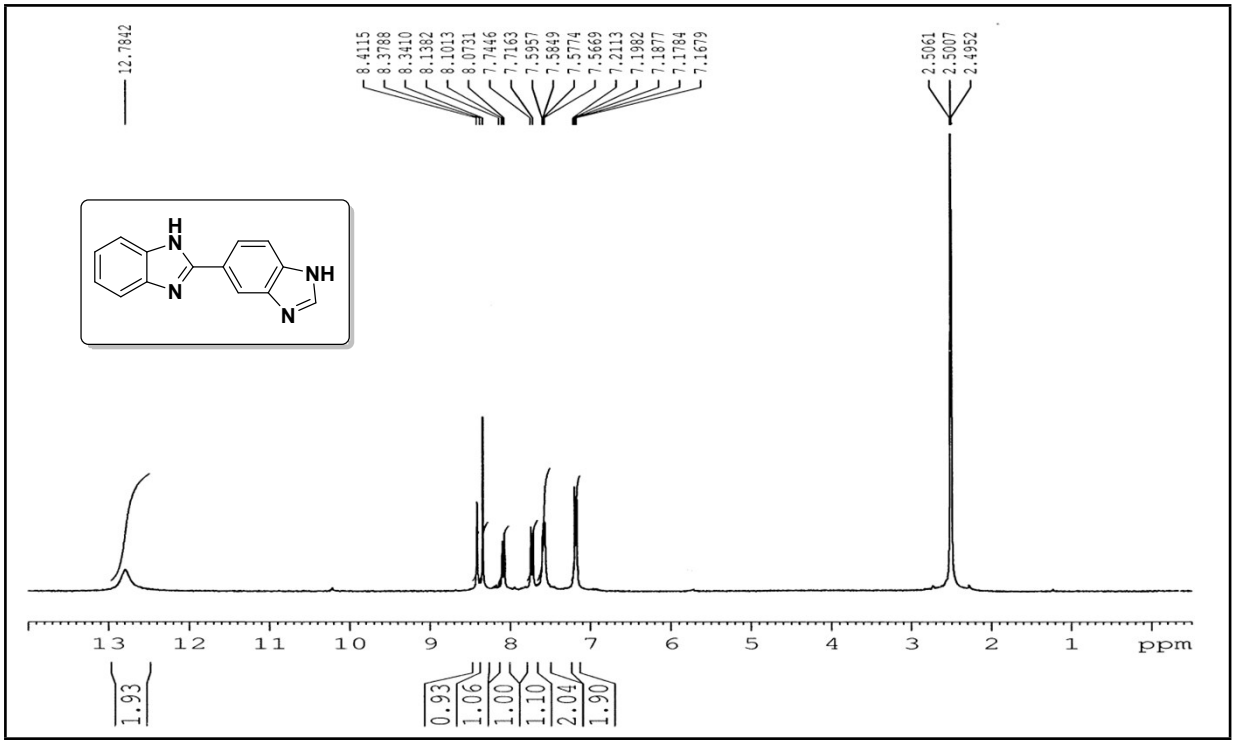


Fig. S42 ^{1}H NMR Spectrum of 1*H*,1'*H*-2,5'-bibenzo[*d*]imidazole **(4q)** (300 MHz, DMSO)

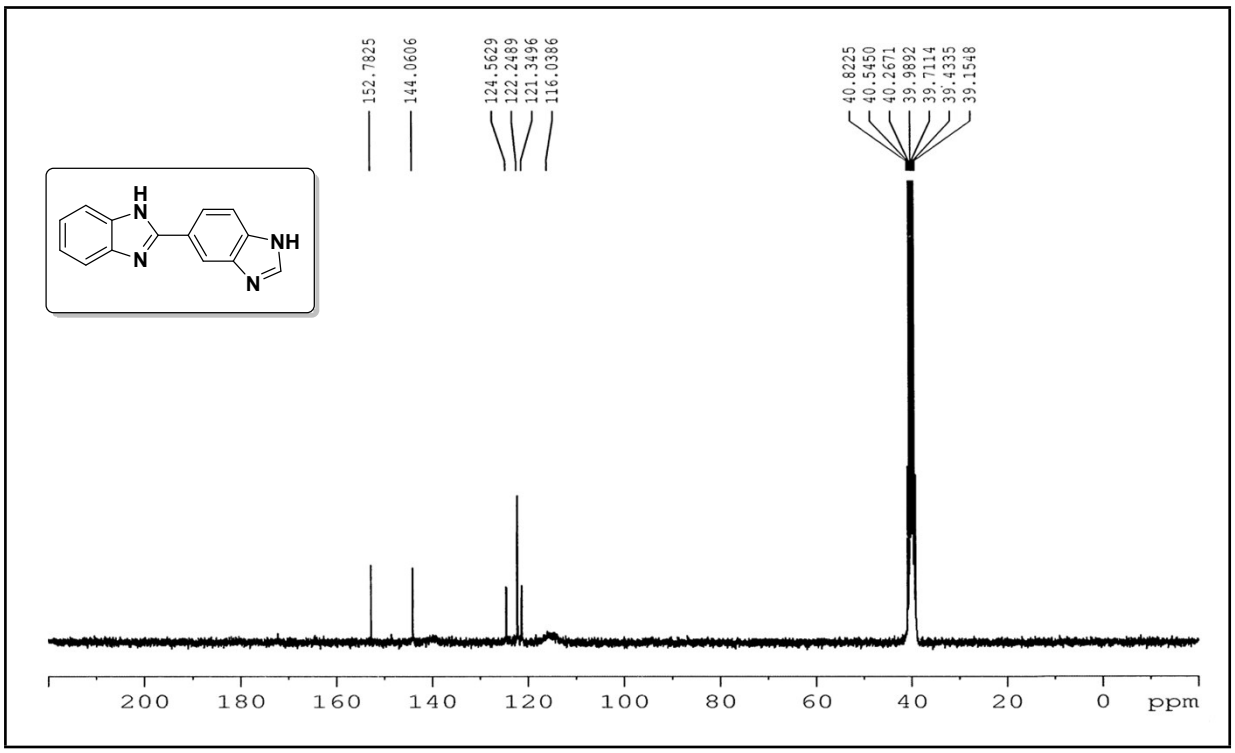


Fig. S43 ^{13}C NMR Spectrum of 1*H*,1'*H*-2,5'-bibenzo[*d*]imidazole **(4q)** (75 MHz, DMSO+$CDCl_3$)

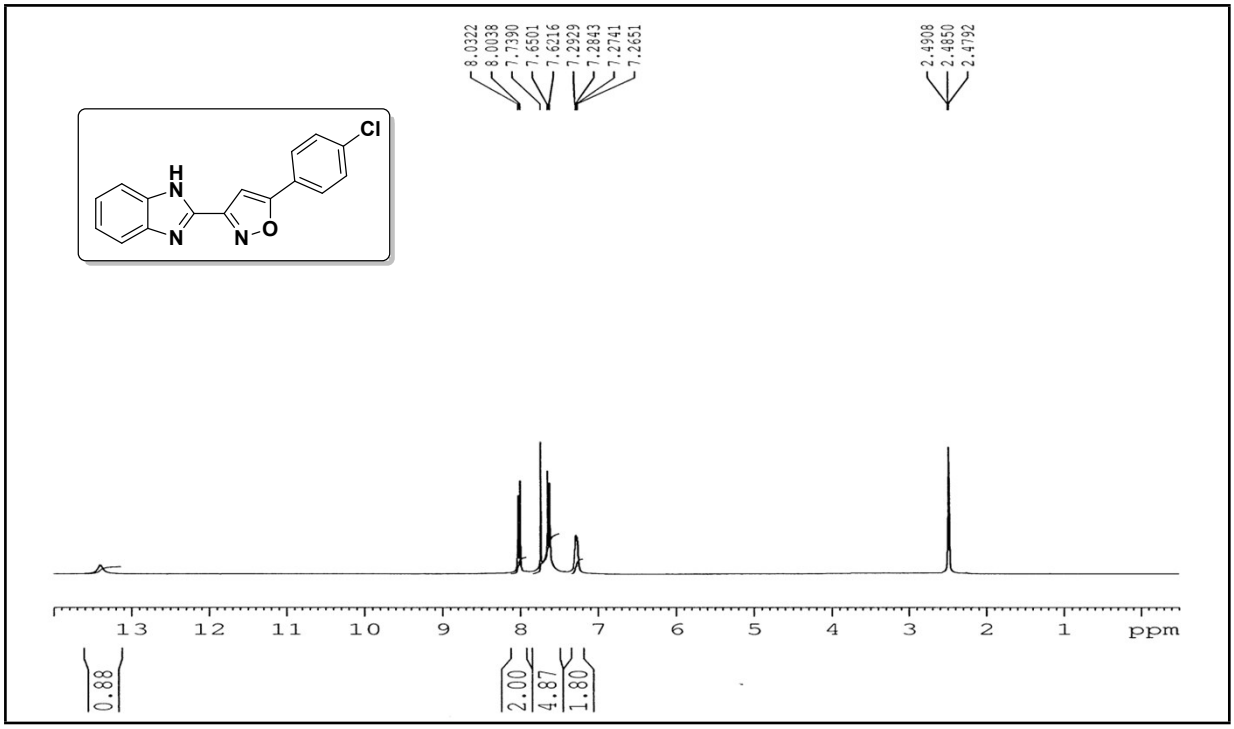


Fig. S44 [1]H NMR Spectrum of 3-(1*H*-benzo[*d*]imidazol-2-yl)-5-(4-chlorophenyl)isoxazole **(4r)** (300 MHz, DMSO)

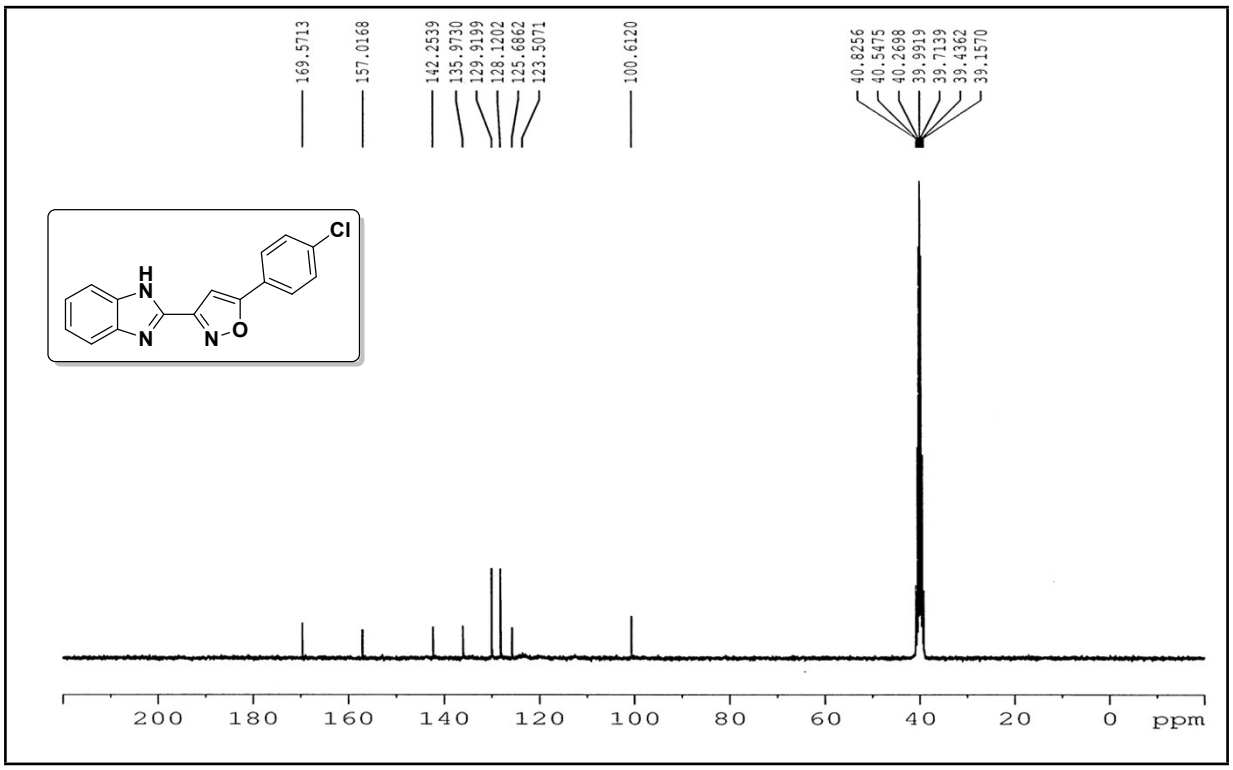


Fig. S45 [13]C NMR Spectrum of3-(1*H*-benzo[*d*]imidazol-2-yl)-5-(4-chlorophenyl)isoxazole **(4r)** (75 MHz, DMSO)

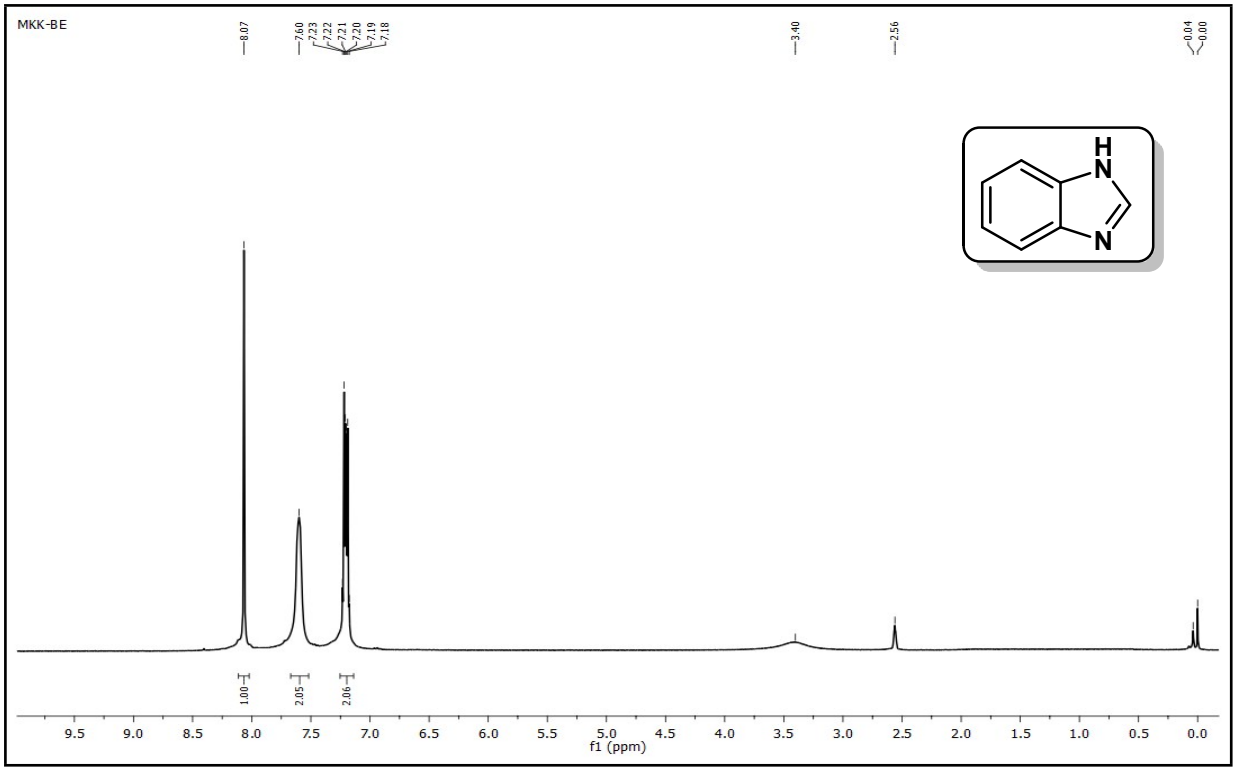


Fig. S46 ^{1}H NMR Spectrum of 1*H*-benzo[*d*]imidazole **(4s)** (300 MHz, DMSO+$CDCl_3$)

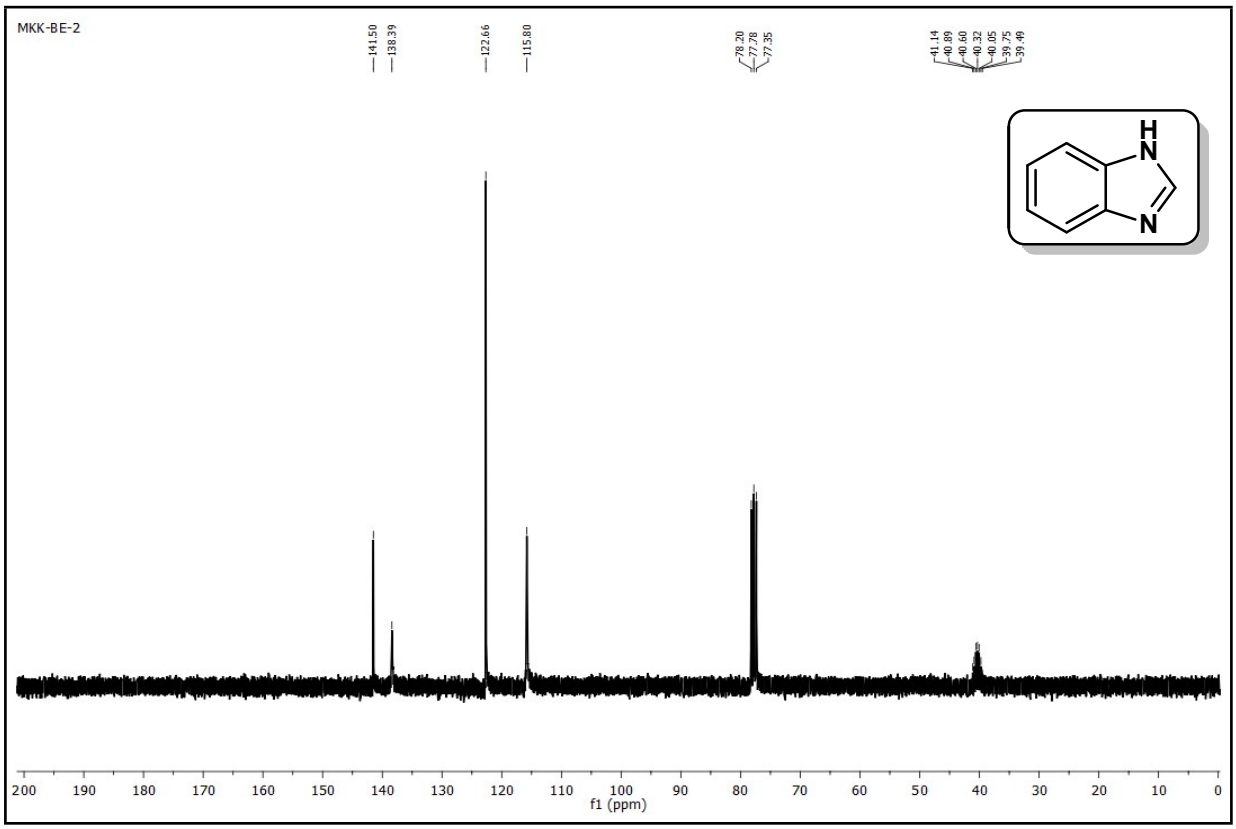


Fig. S47 ^{13}C NMR Spectrum of 1*H*-benzo[*d*]imidazole **(4s)** (75 MHz, DMSO+$CDCl_3$)

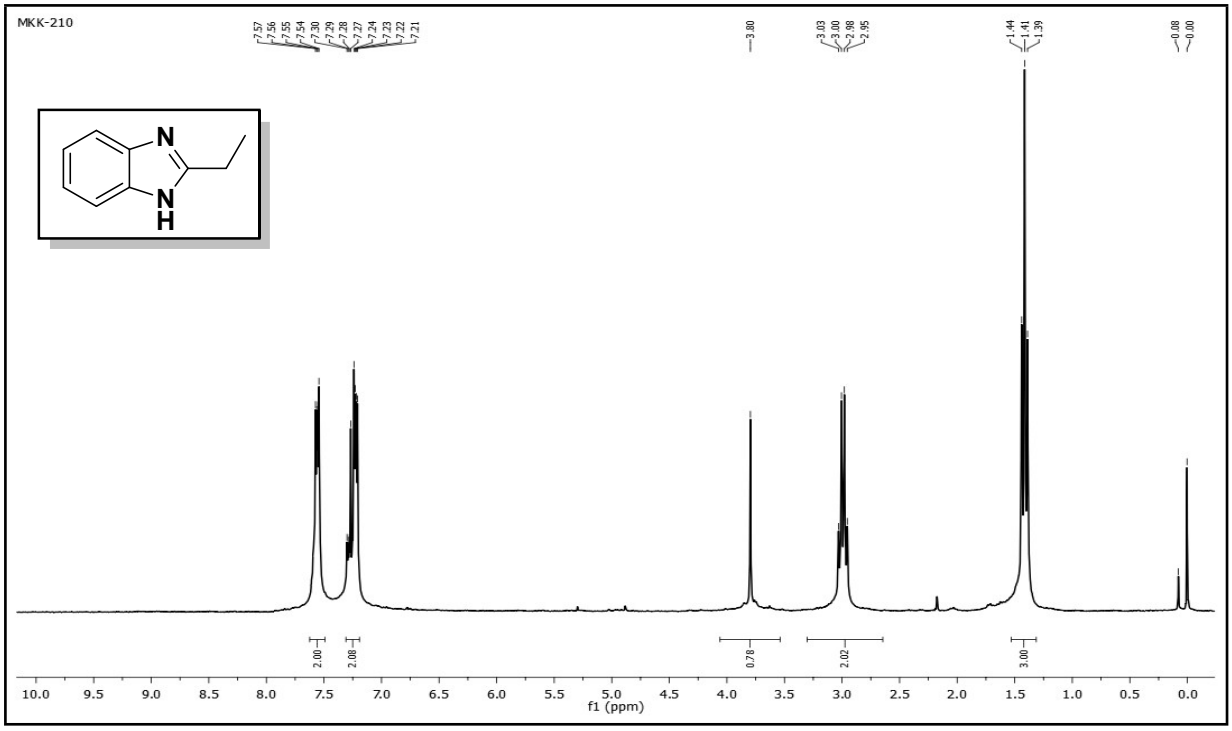


Fig. S48 ^{1}H NMR Spectrum of 2-ethyl-1*H*-benzo[*d*]imidazole **(4t)** (300 MHz, $CDCl_3$)

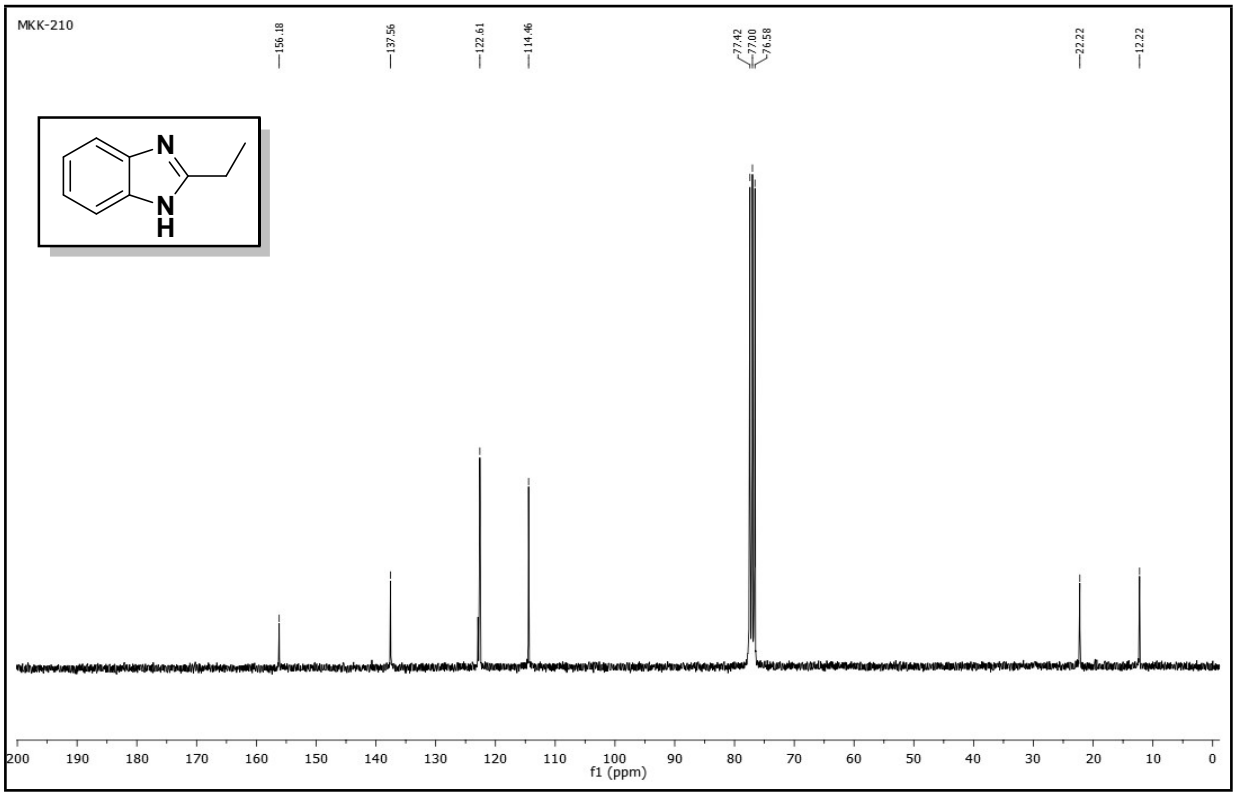


Fig. S49 ^{13}C NMR Spectrum of 2-ethyl-1*H*-benzo[*d*]imidazole **(4t)** (75 MHz, $CDCl_3$)

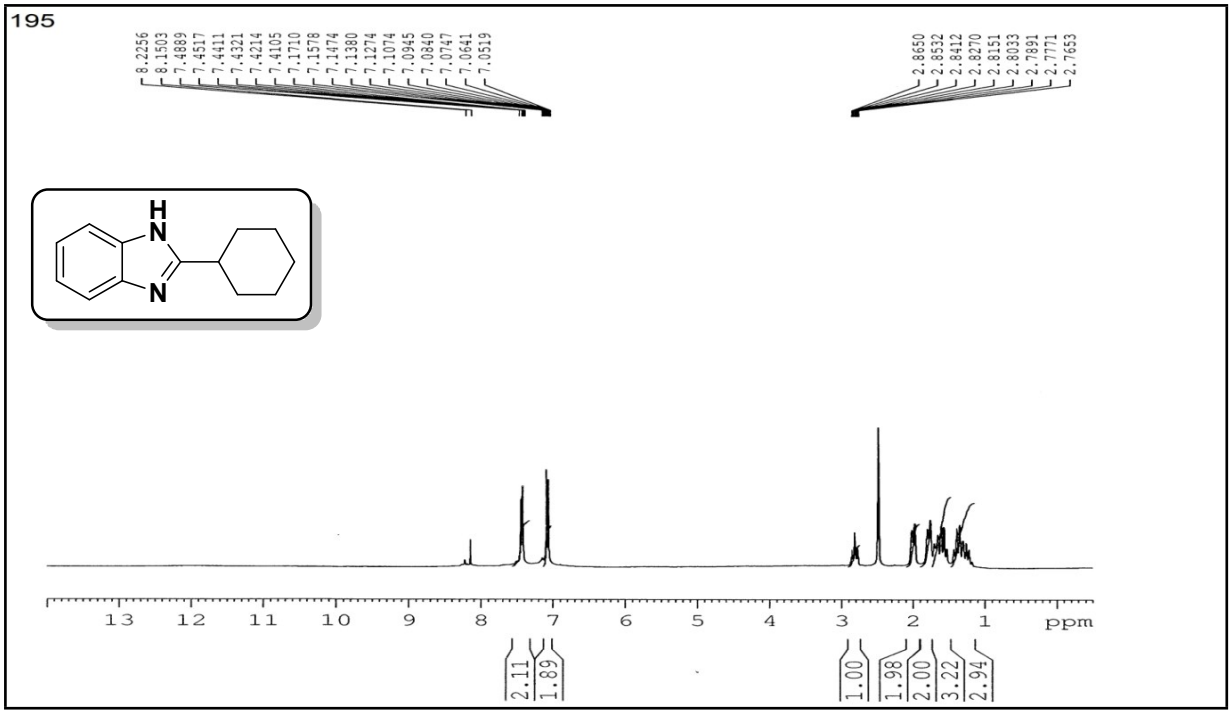


Fig. S50 ^{1}H NMR Spectrum of 2-cyclohexyl-1*H*-benzo[*d*]imidazole **(4u)** (400 MHz, $CDCl_3$+DMSO)

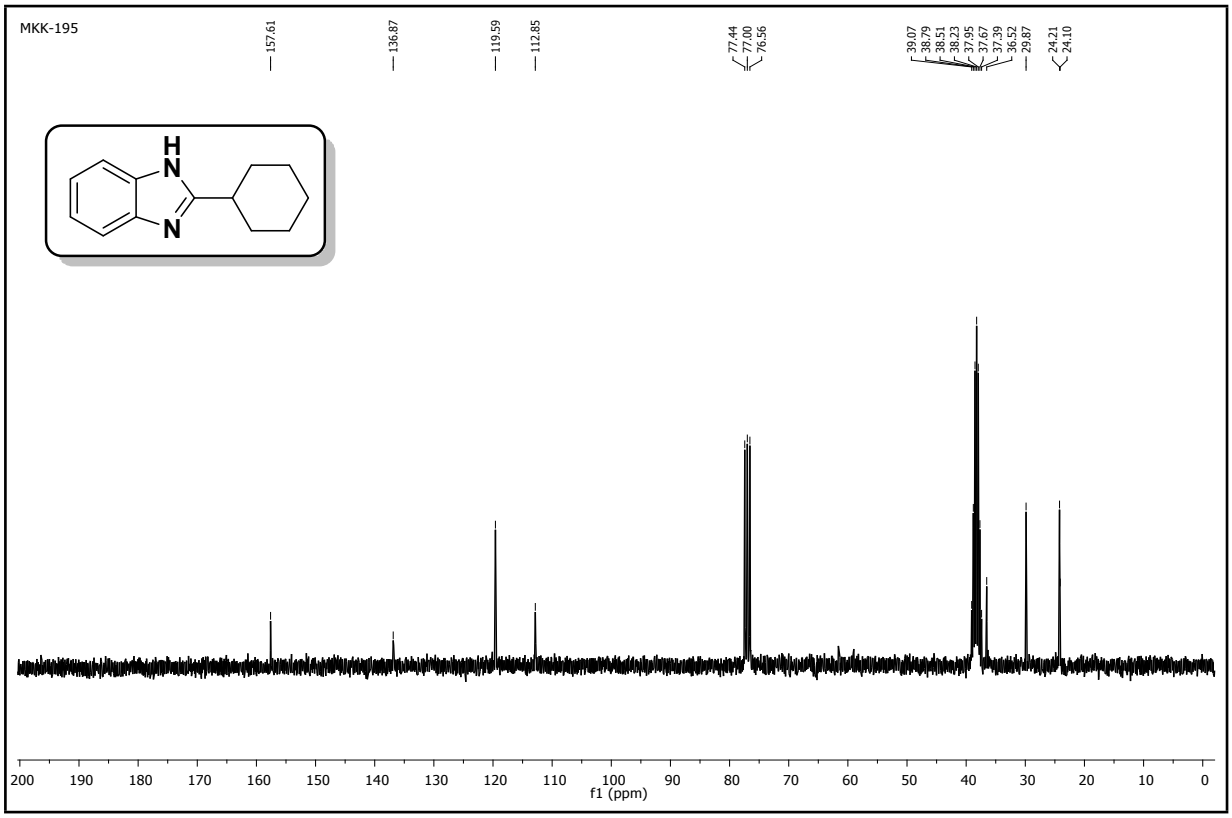


Fig. S51 ^{13}C NMR Spectrum of 2-cyclohexyl-1*H*-benzo[*d*]imidazole **(4u)** (75 MHz, $CDCl_3$+DMSO)

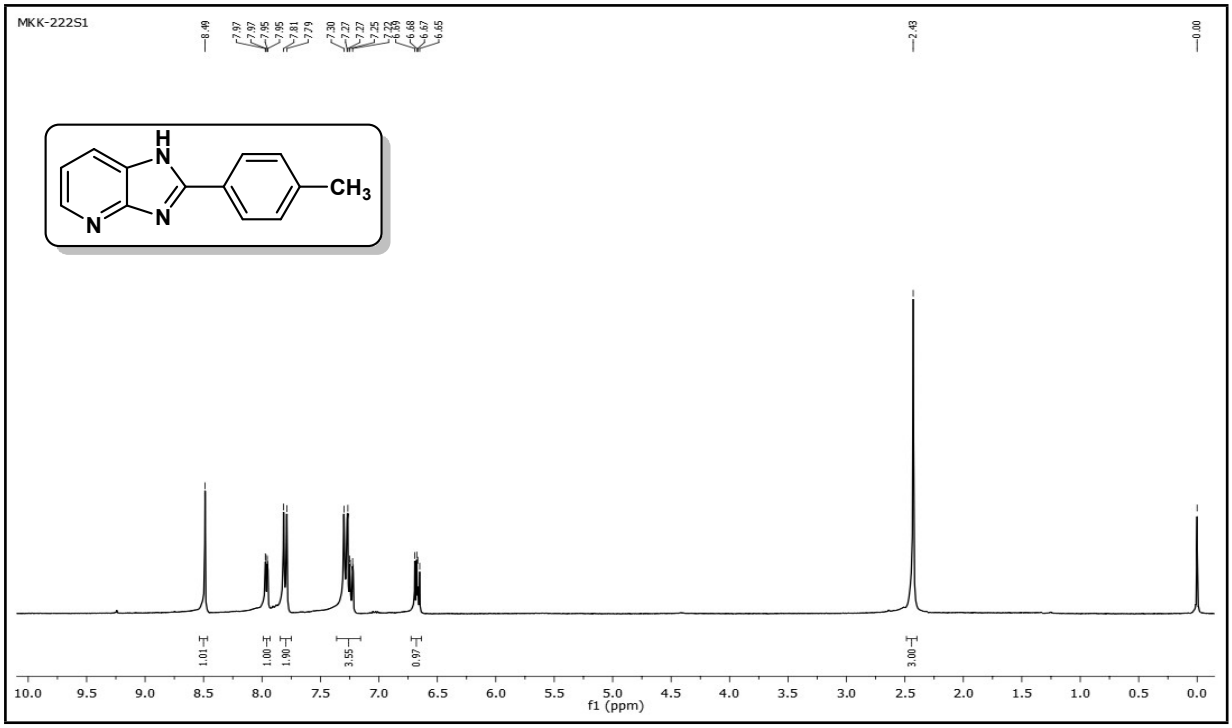


Fig. S52 ^{1}H NMR Spectrum of 2-(*p*-tolyl)-1*H*-imidazo[4,5-*b*]pyridine **(4v)** (300 MHz, $CDCl_3$)

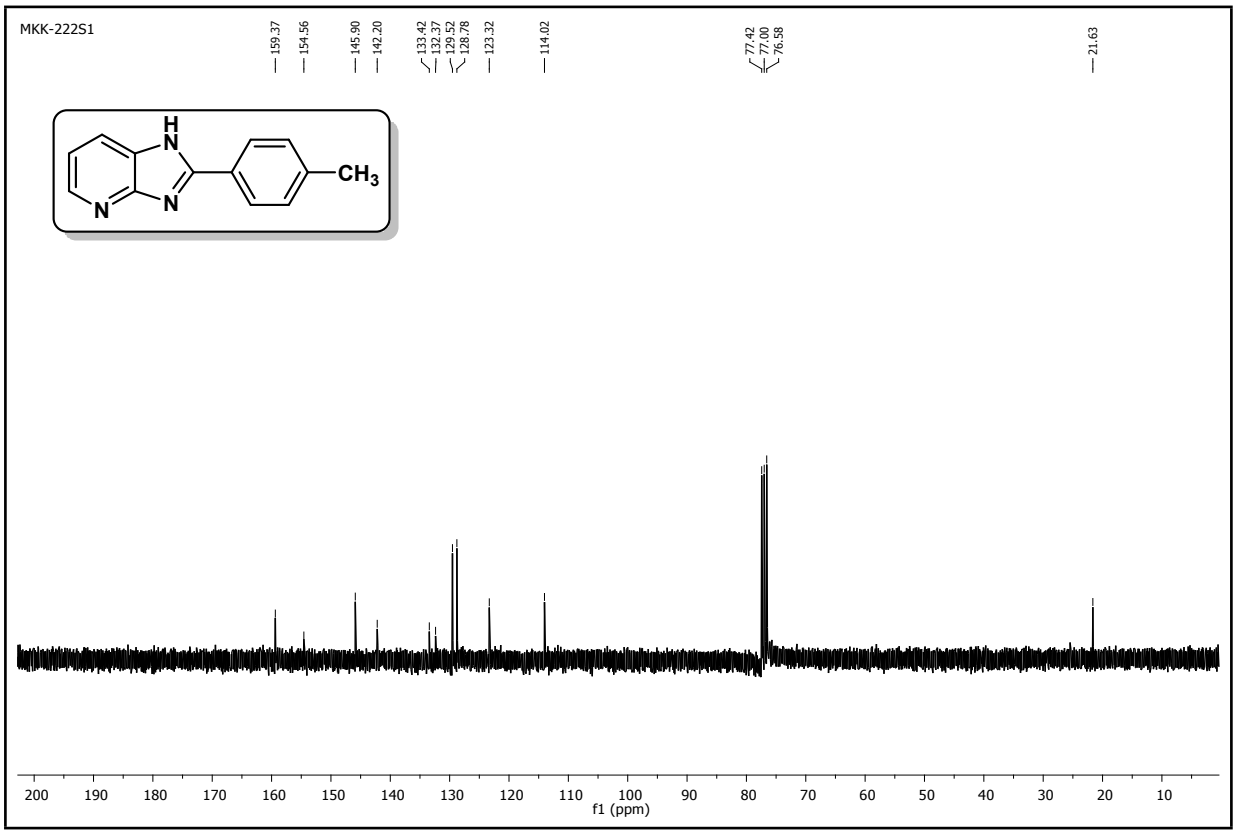


Fig. S53 ^{13}C NMR Spectrum of 2-(*p*-tolyl)-1*H*-imidazo[4,5-*b*]pyridine **(4v)** (75 MHz, $CDCl_3$)

Mass Spectrum

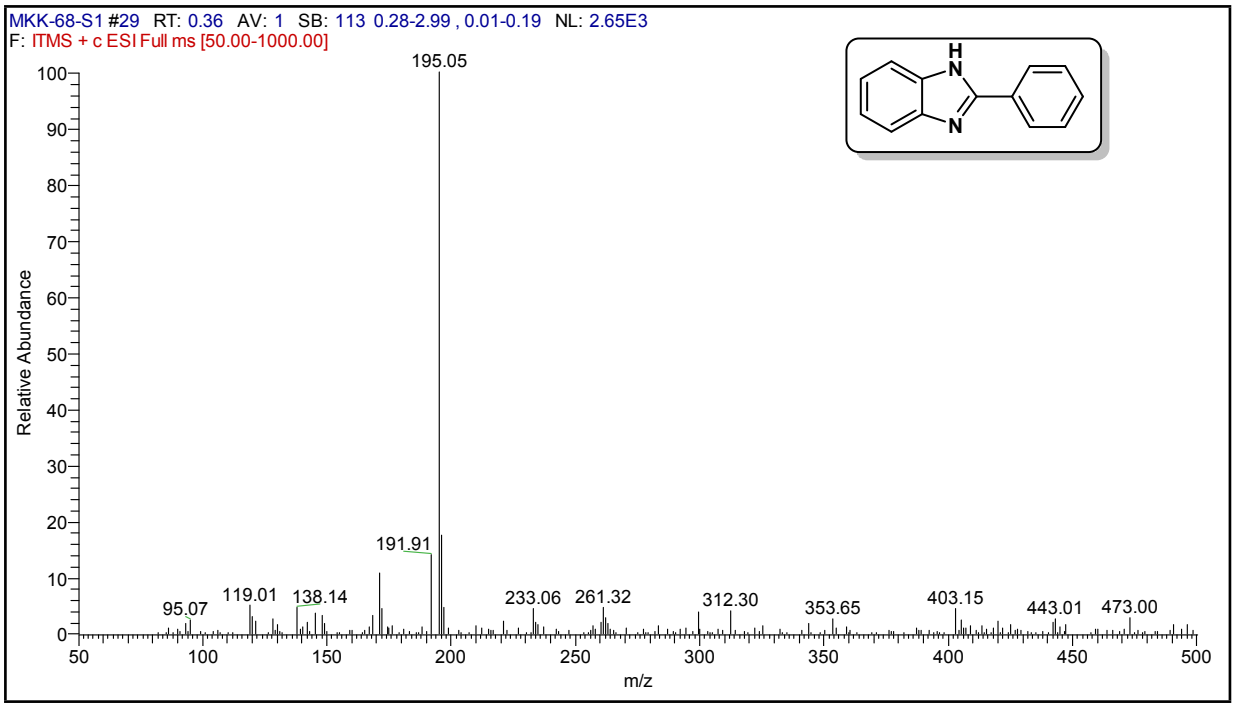


Fig. S54 ESI Mass Spectrum of 2-phenyl-1*H*-benzo[*d*]imidazole **(4a)** (M+1)

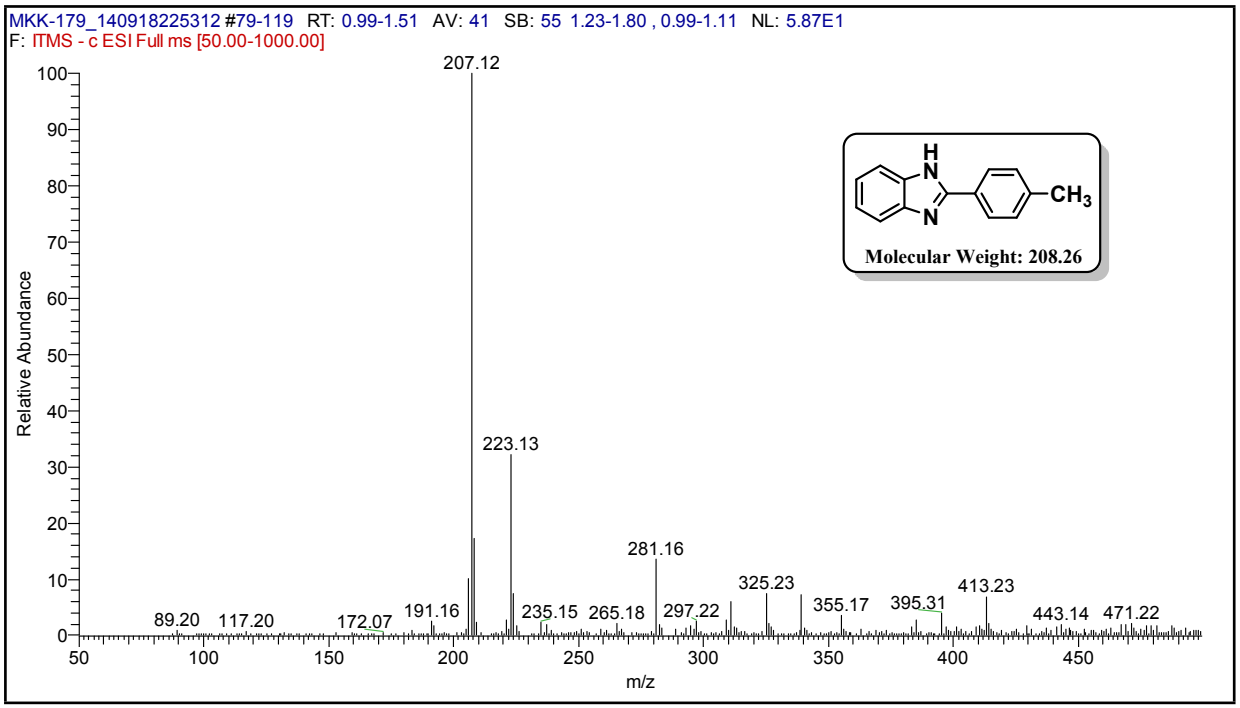


Fig. S55 ESI Mass Spectrum of 2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole **(4b)** (M-1)

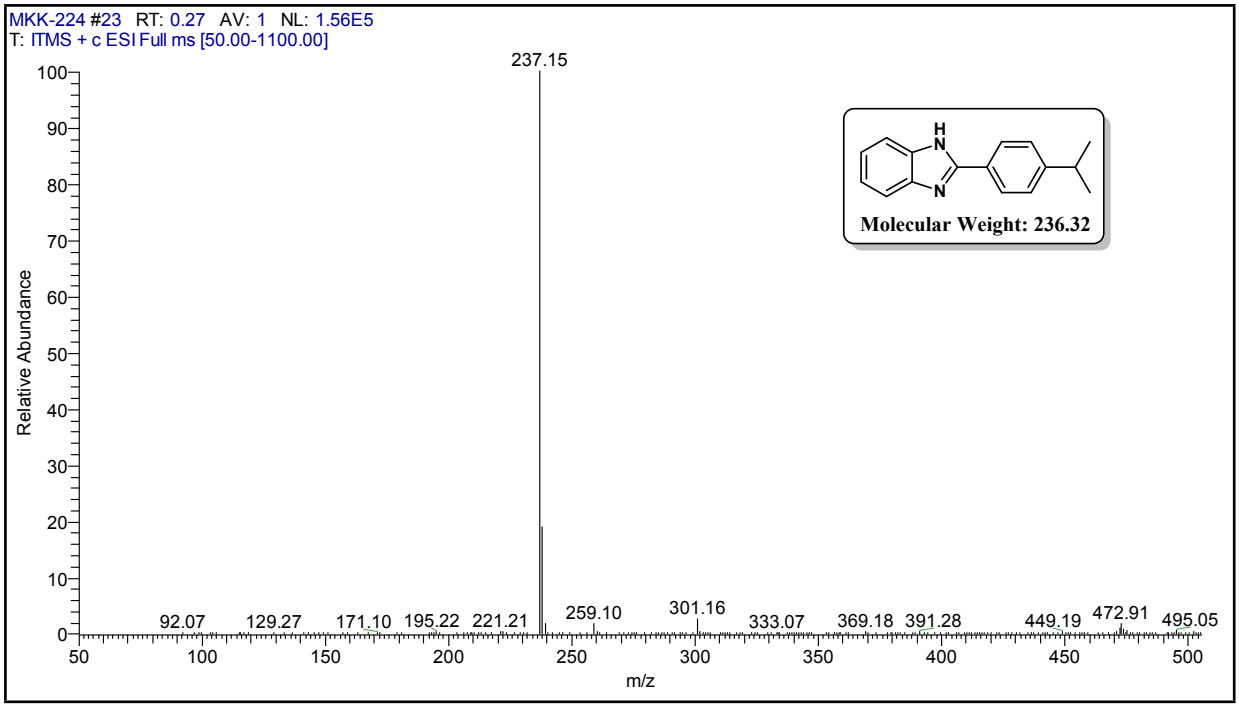


Fig. S56 ESI Mass Spectrum of 2-(4-isopropylphenyl)-1*H*-benzo[*d*]imidazole **(4c)** (M+1)

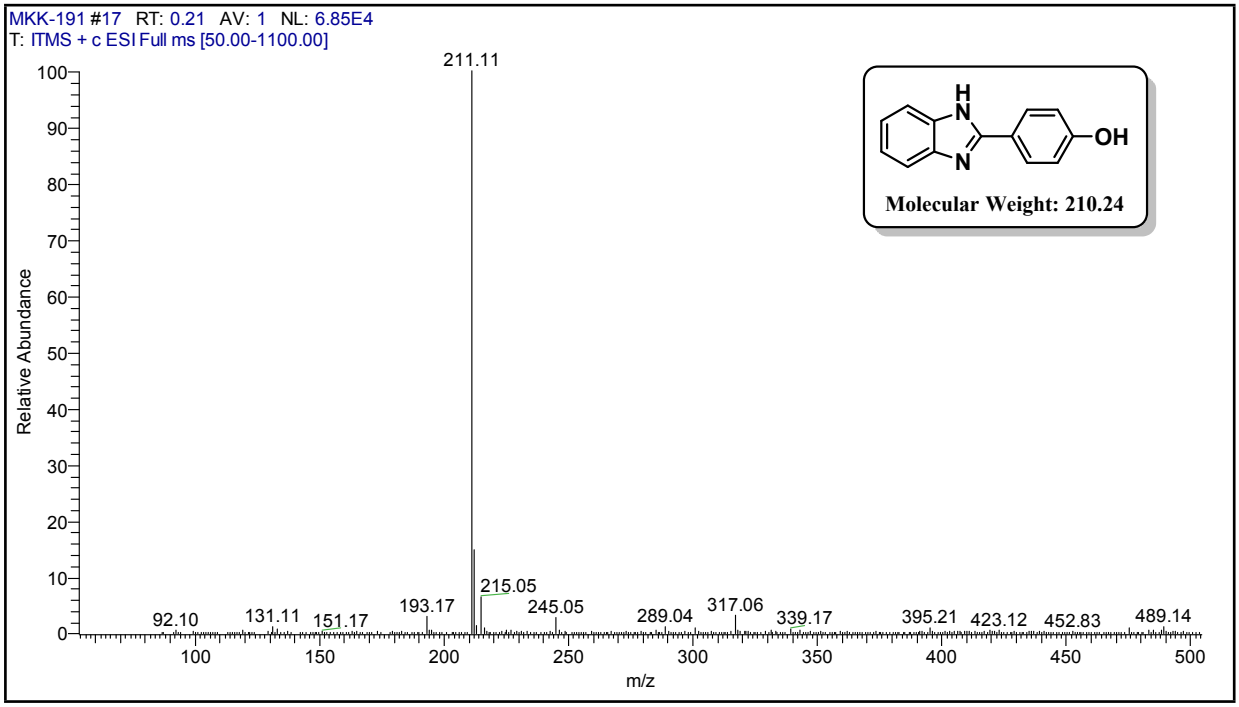


Fig. S57 ESI Mass Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)phenol **(4d)** (M+1)

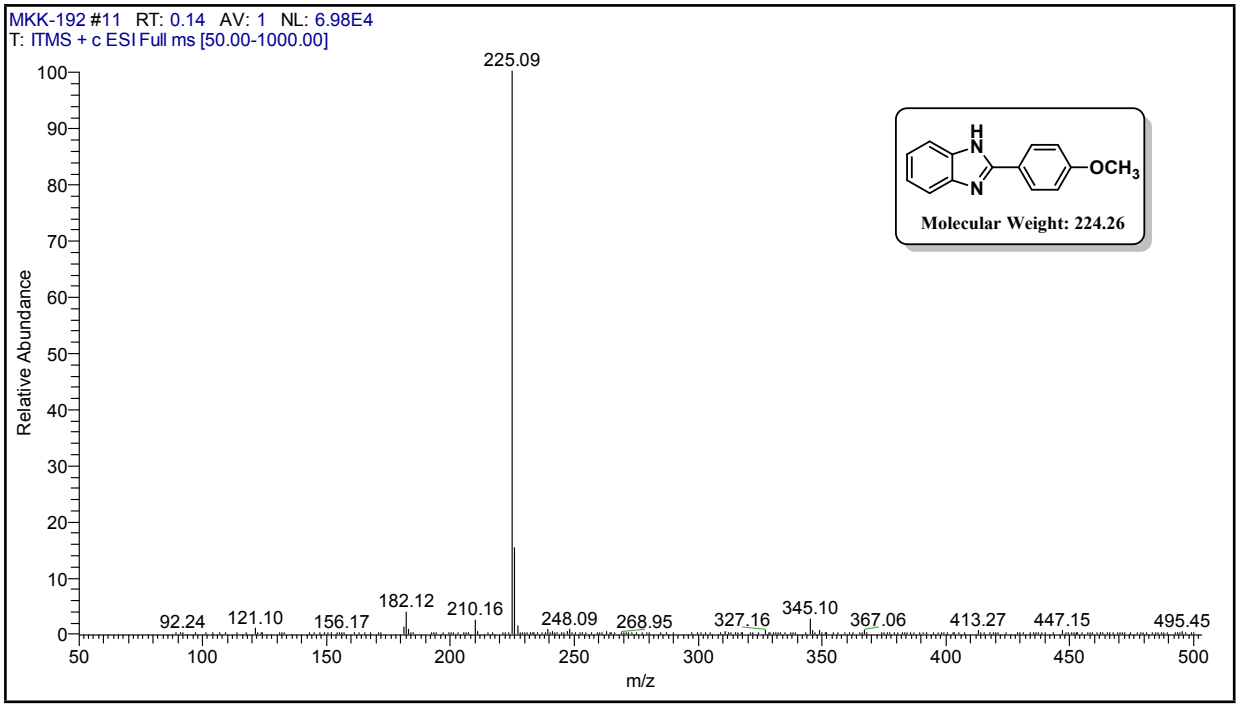


Fig. S58 ESI Mass Spectrum of 2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole **(4e)** (M+1)

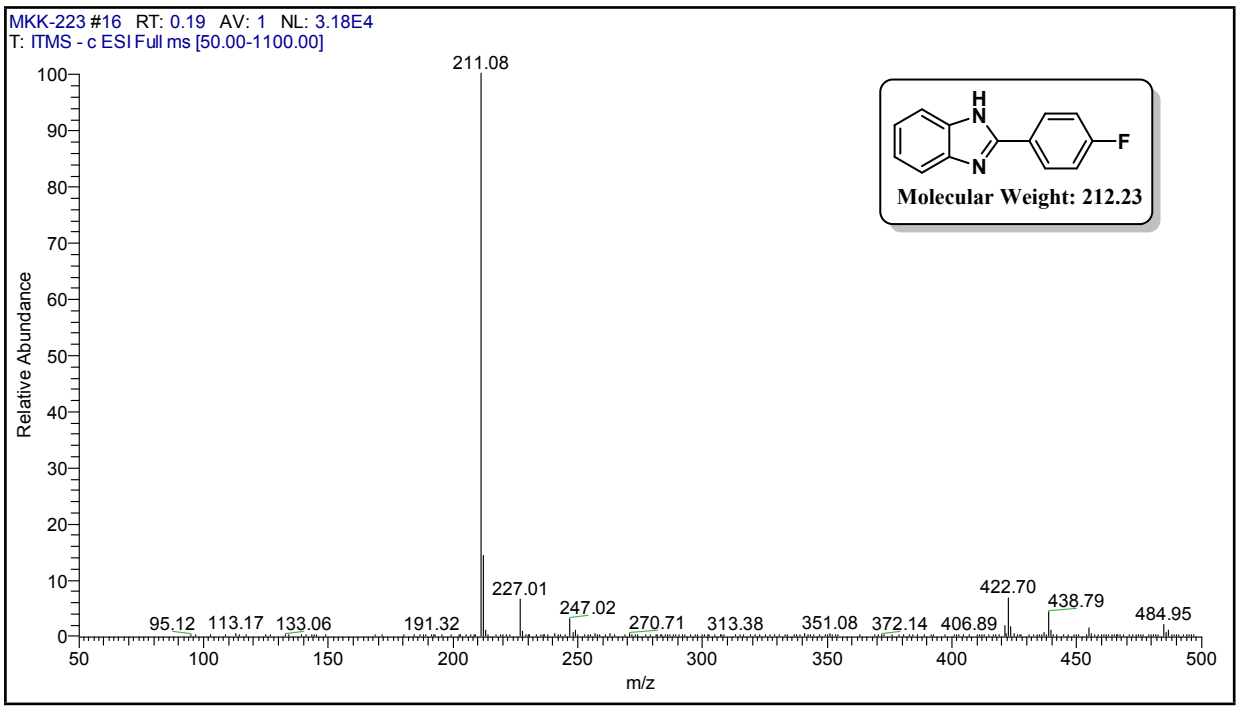


Fig. S59 ESI Mass Spectrum of 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole **(4f)** (M-1)

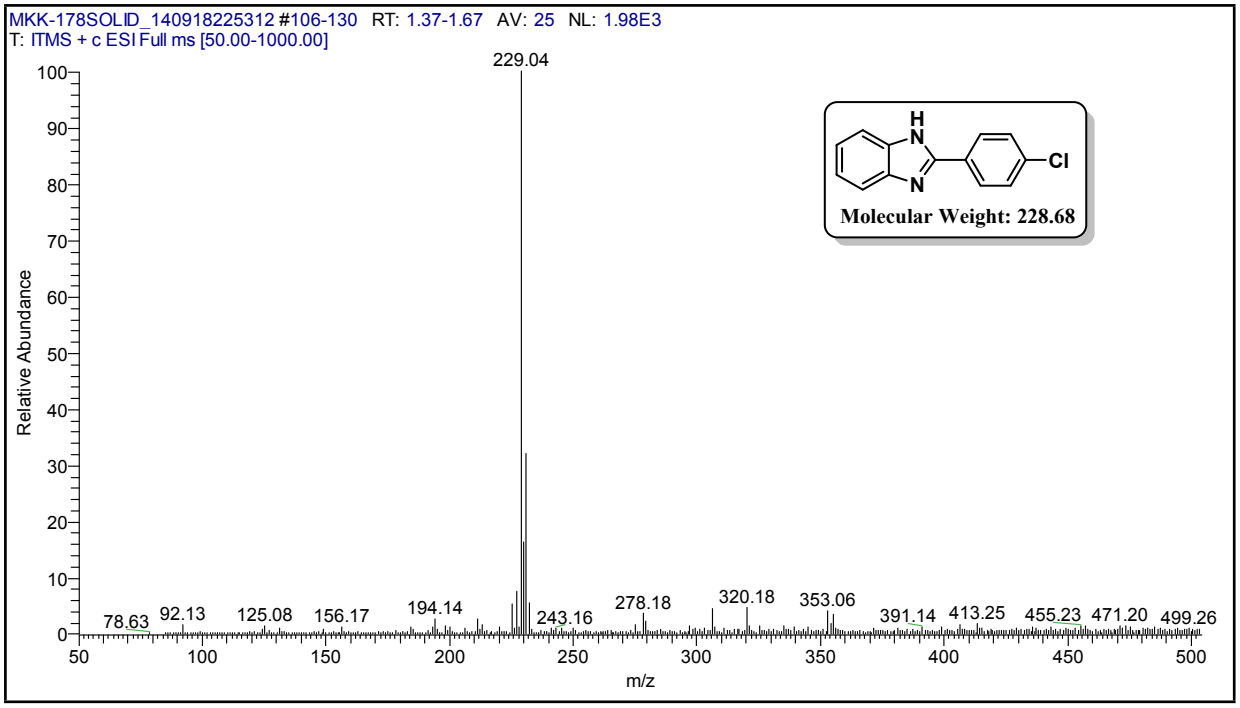


Fig. S60 ESI Mass Spectrum of 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole **(4g)** (M+1)

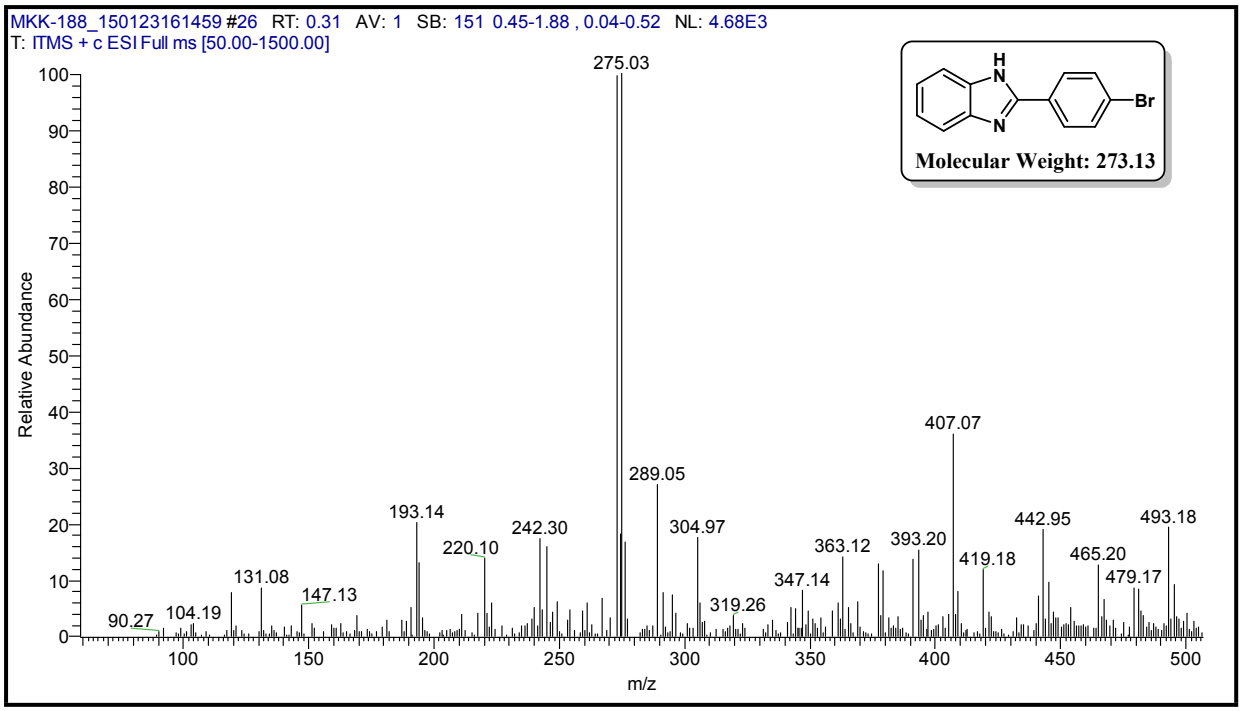


Fig. S61 ESI Mass Spectrum of 2-(4-bromophenyl)-1*H*-benzo[*d*]imidazole **(4h)** (M+1)

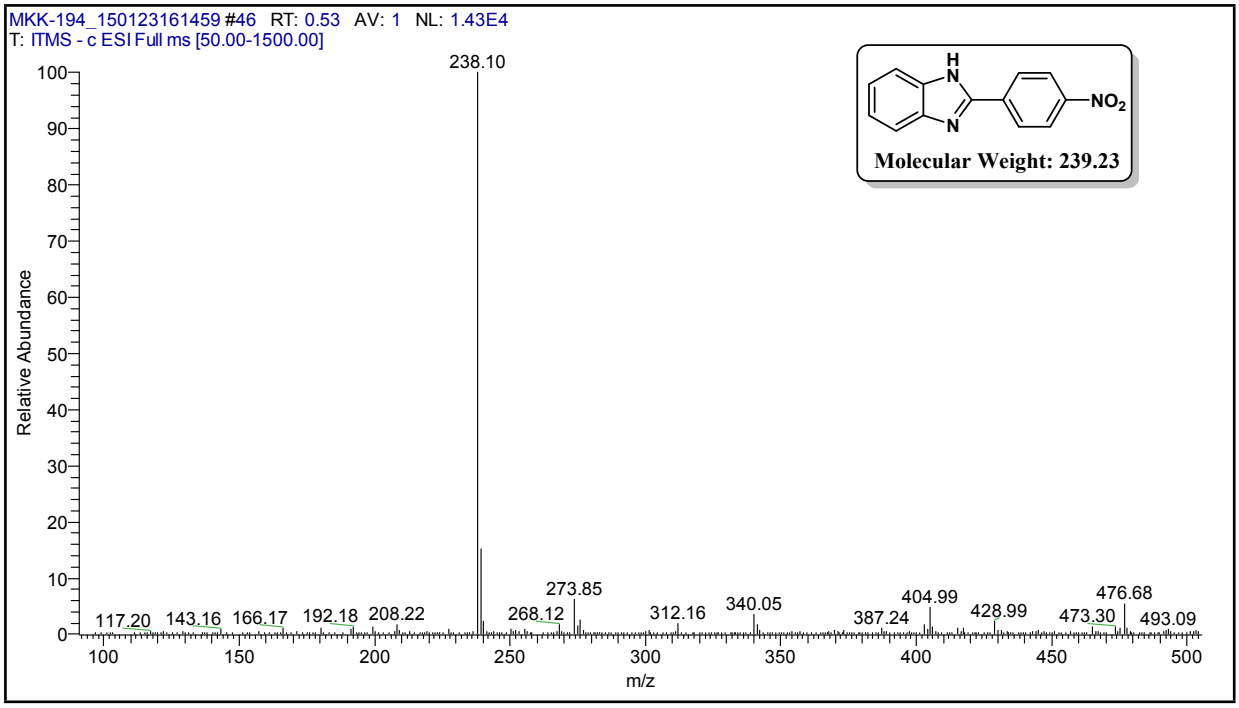


Fig. S62 ESI Mass Spectrum of 2-(4-nitrophenyl)-1*H*-benzo[*d*]imidazole **(4i)** (M-1)

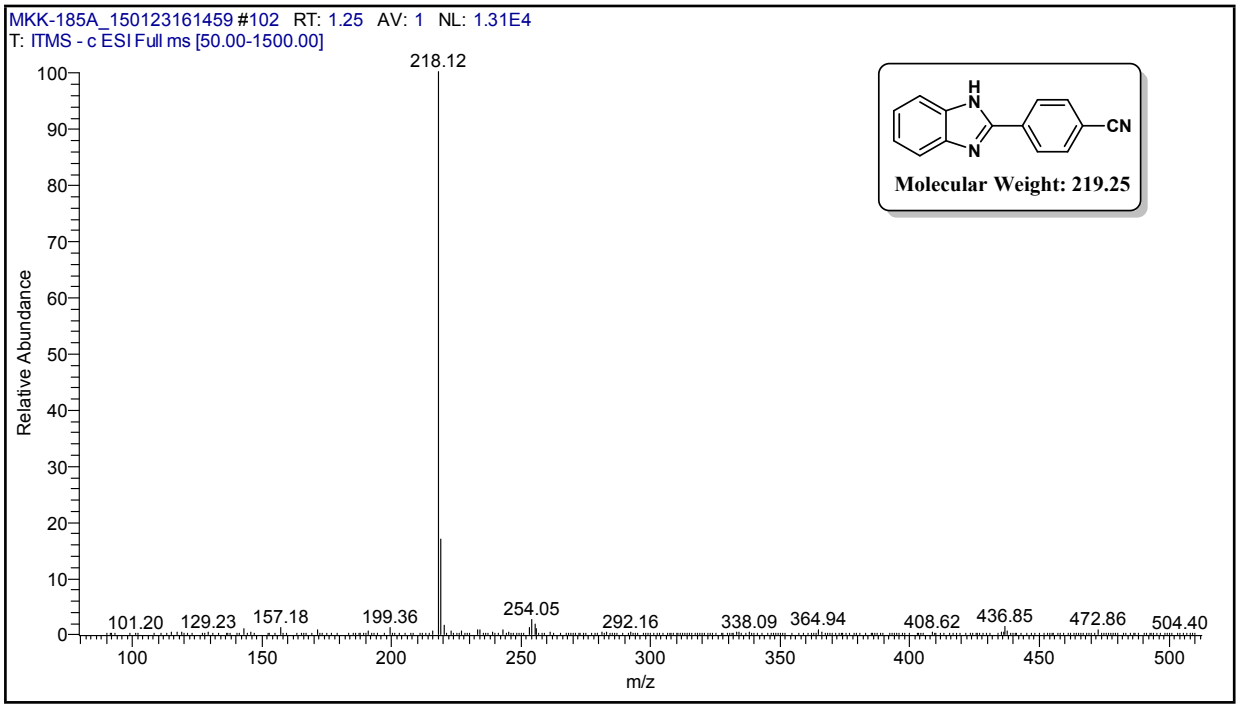


Fig. S63 ESI Mass Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4j)** (M-1)

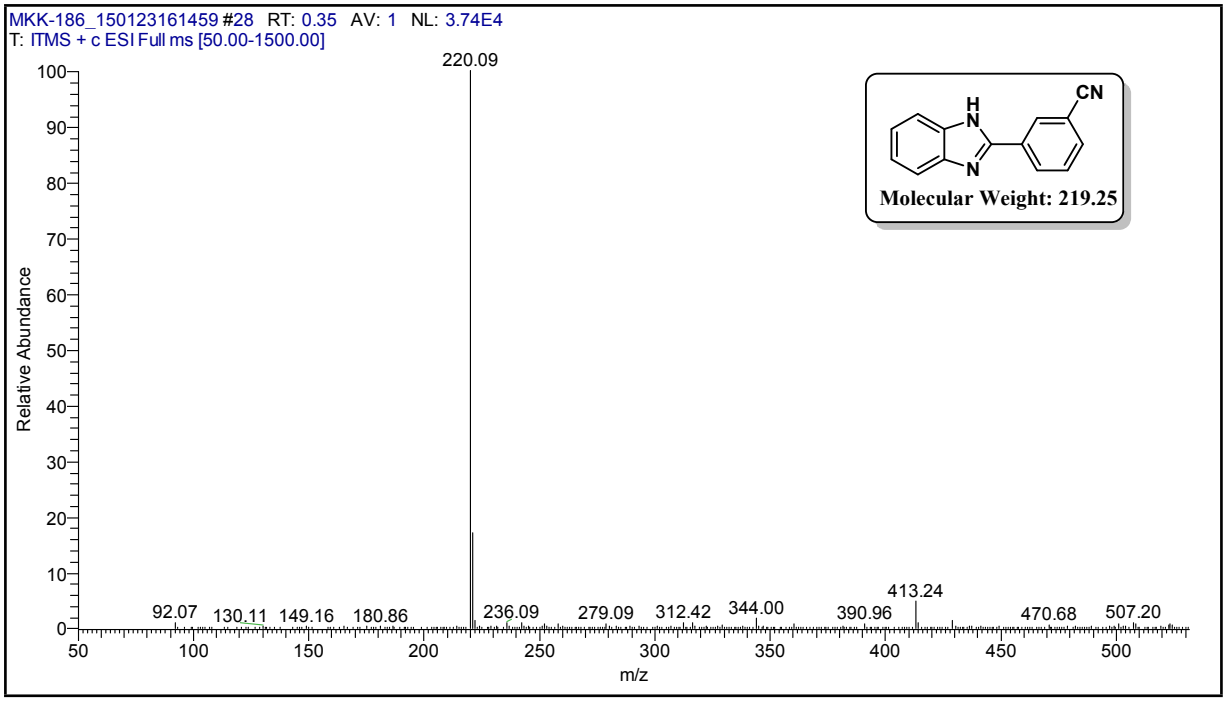


Fig. S64 ESI Mass Spectrum of 3-(1*H*-benzo[*d*]imidazol-2-yl)benzonitrile **(4k)**

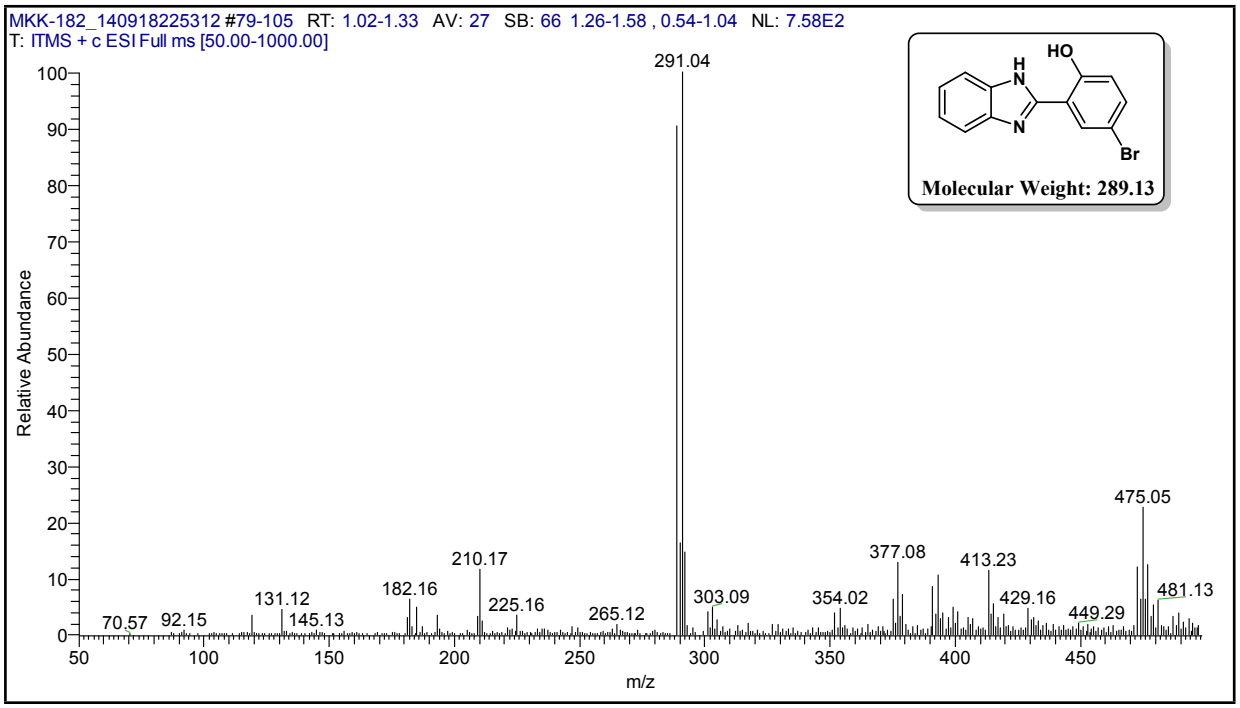


Fig. S65 ESI Mass Spectrum of 2-(1*H*-benzo[*d*]imidazol-2-yl)-4-bromophenol **(4l)** (M+1)

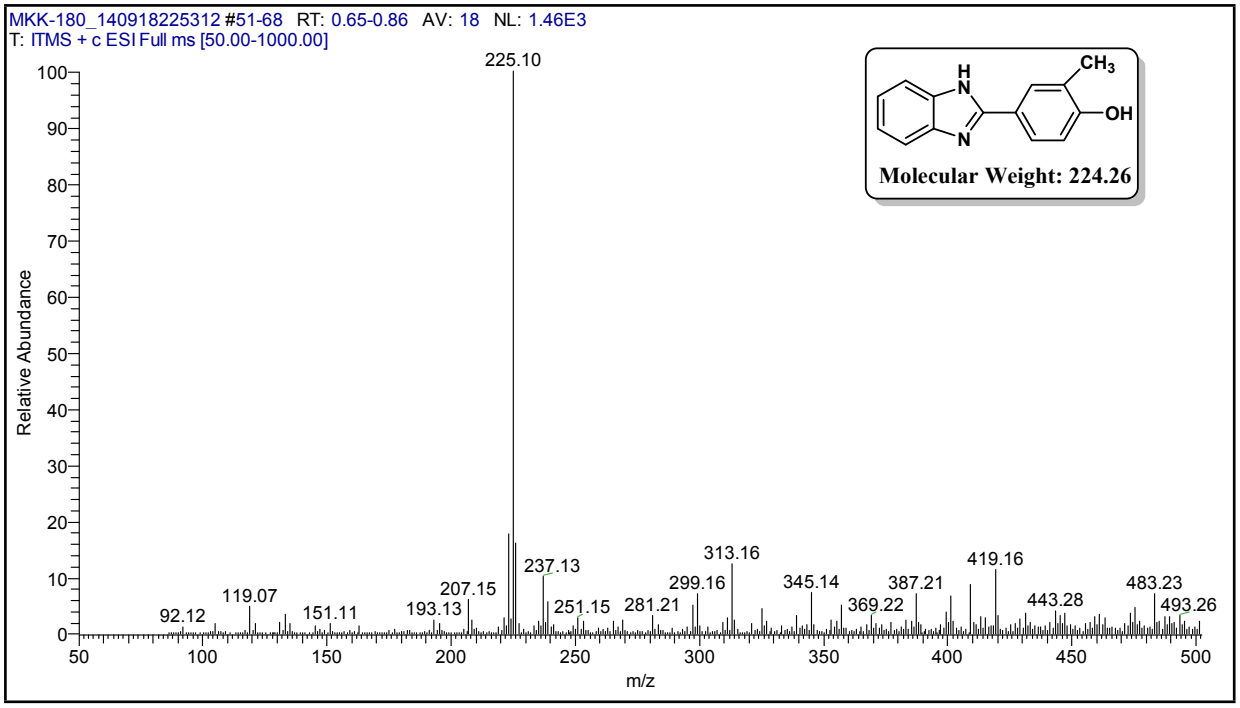


Fig. S66 ESI Mass Spectrum of 4-(1*H*-benzo[*d*]imidazol-2-yl)-2-methylphenol **(4m)** (M+1)

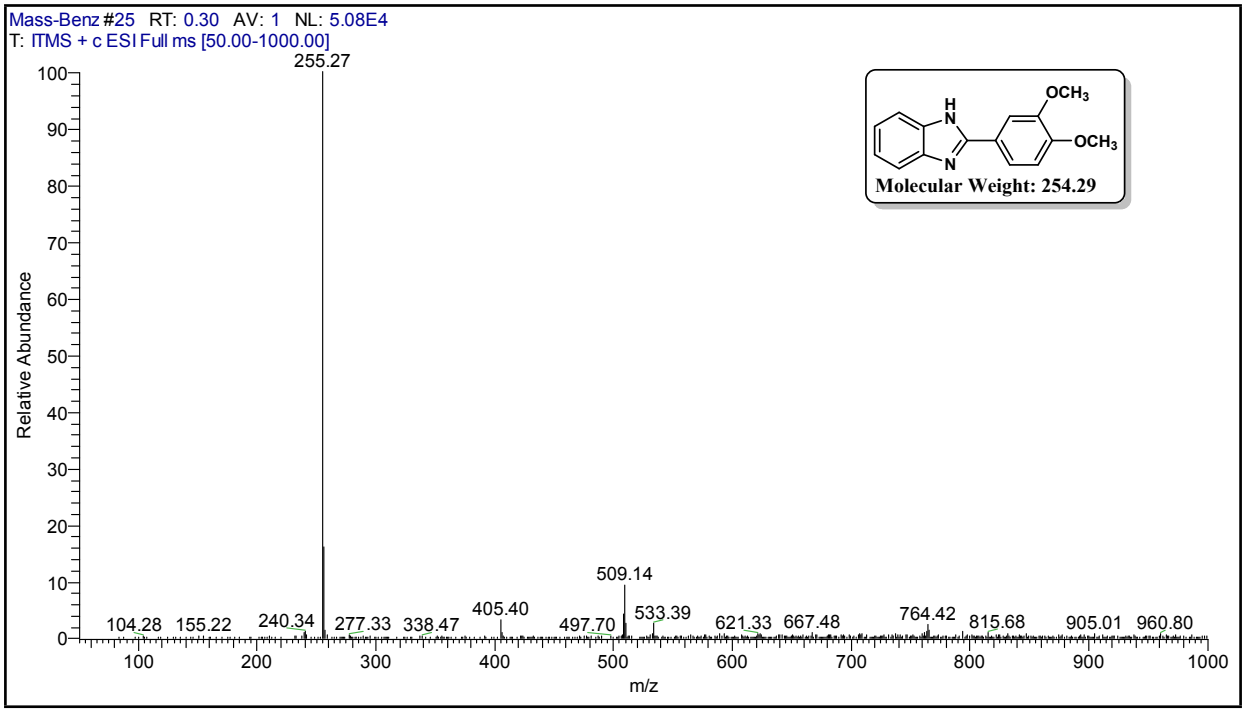


Fig. S67 ESI Mass Spectrum of 2-(3,4-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole **(4n)** (M+1)

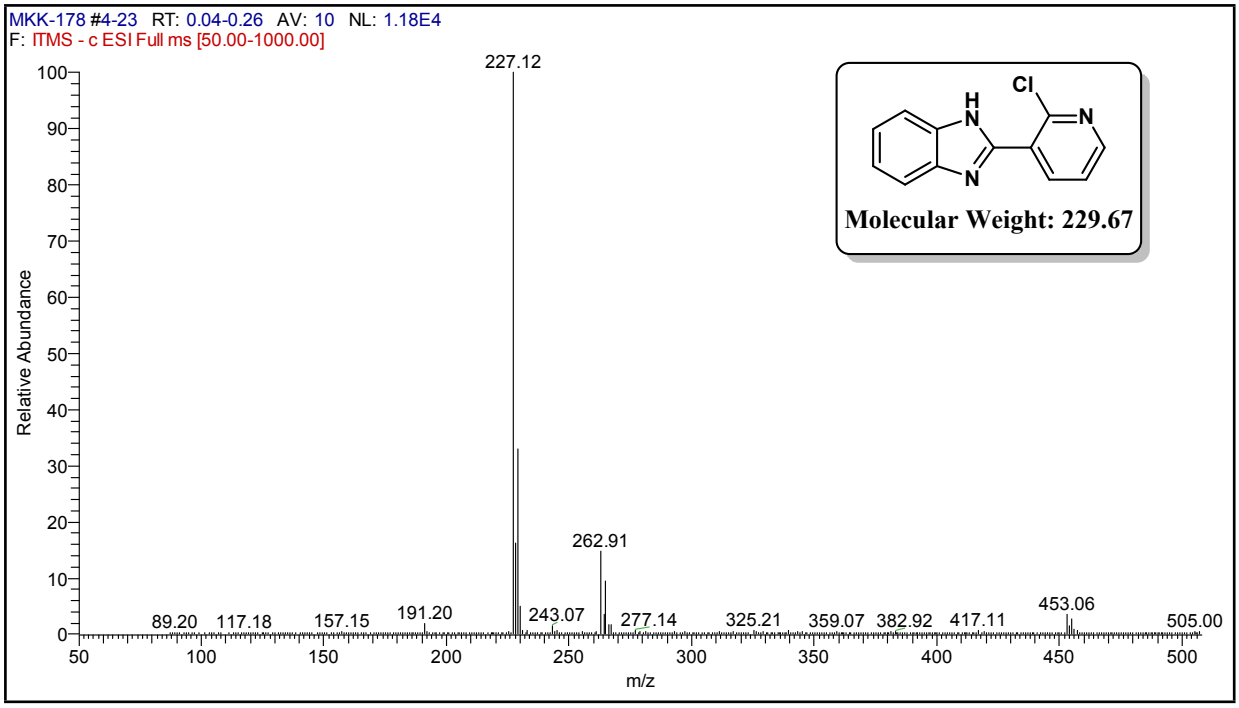


Fig. S68 ESI Mass Spectrum of 2-(2-chloropyridin-3-yl)-*1H*-benzo[*d*]imidazole **(4o)** (M-1)

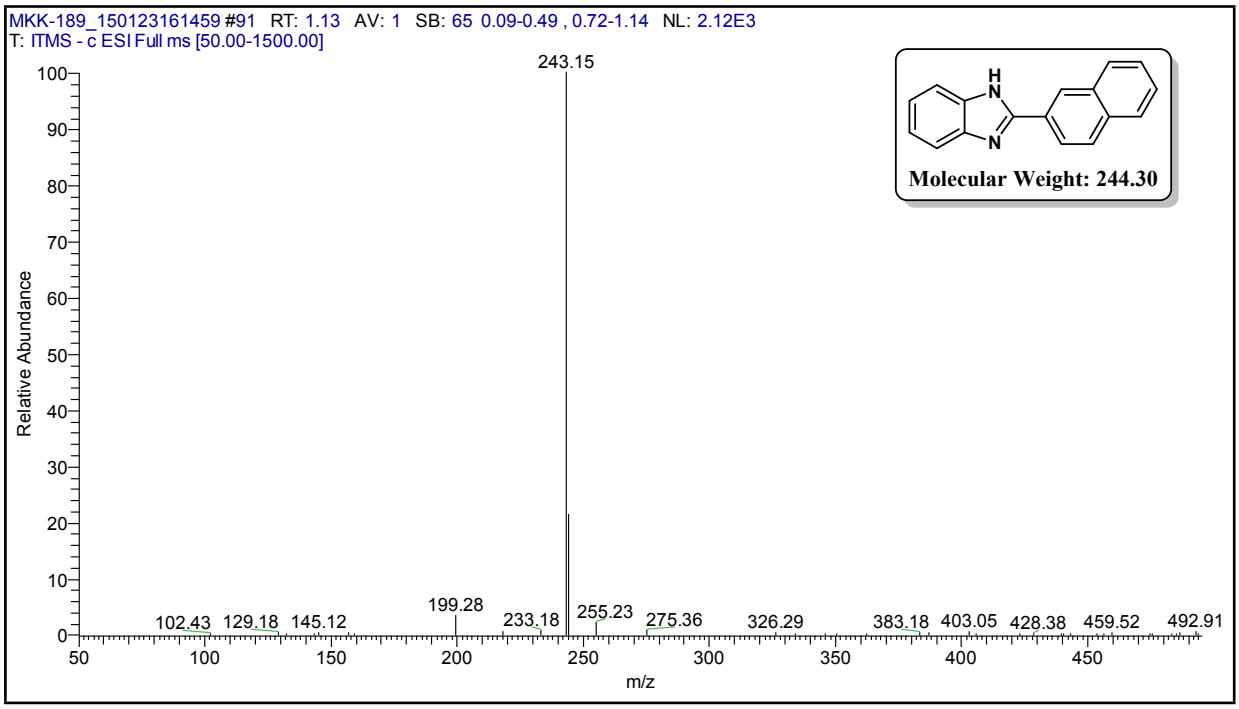


Fig. S69 ESI Mass Spectrum of 2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole **(4p)** (M-1)

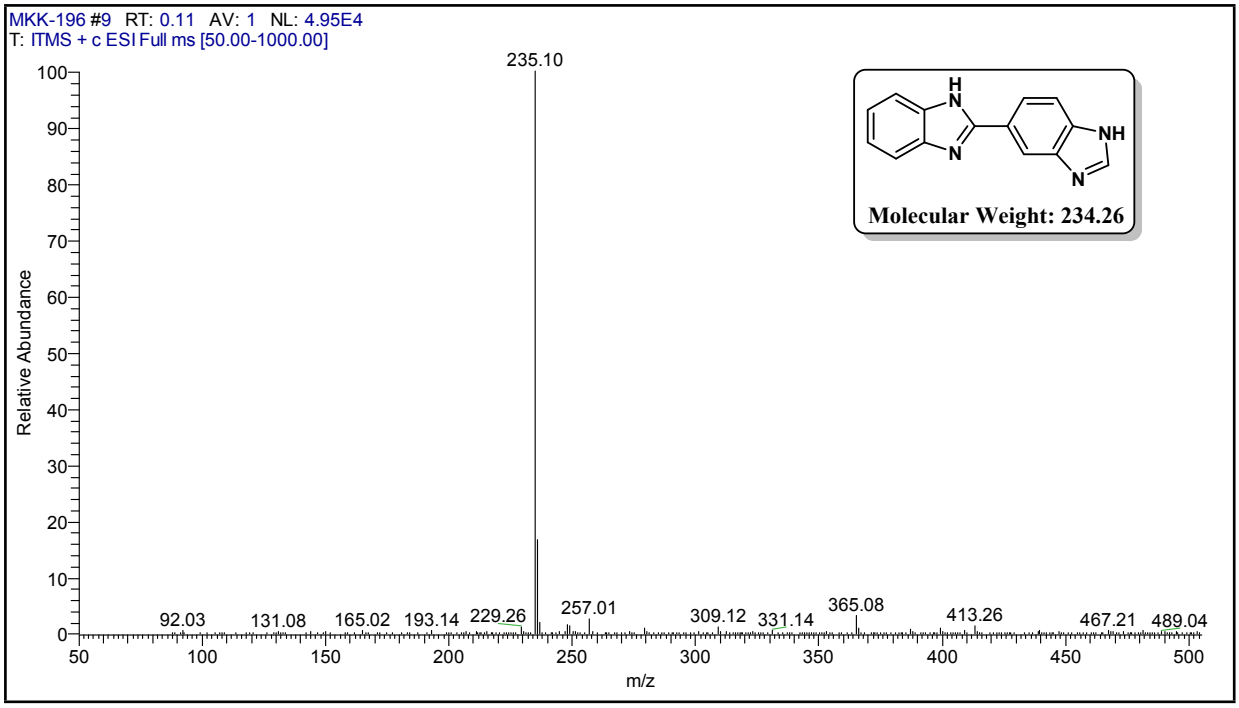


Fig. S70 ESI Mass Spectrum of 1*H*,1'*H*-2,5'-bibenzo[*d*]imidazole **(4q)** (M+1)

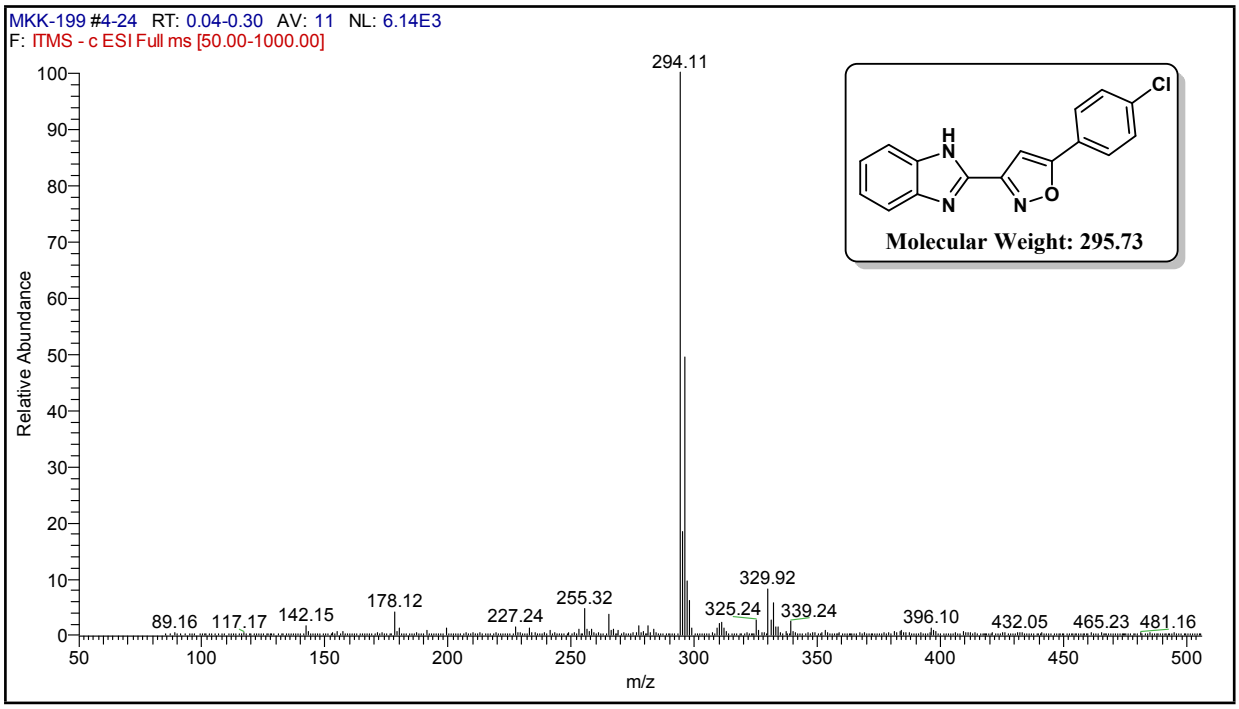


Fig. S71 ESI Mass Spectrum of 3-(1*H*-benzo[*d*]imidazol-2-yl)-5-(4-chlorophenyl)isoxazole **(4r)** (M-1)

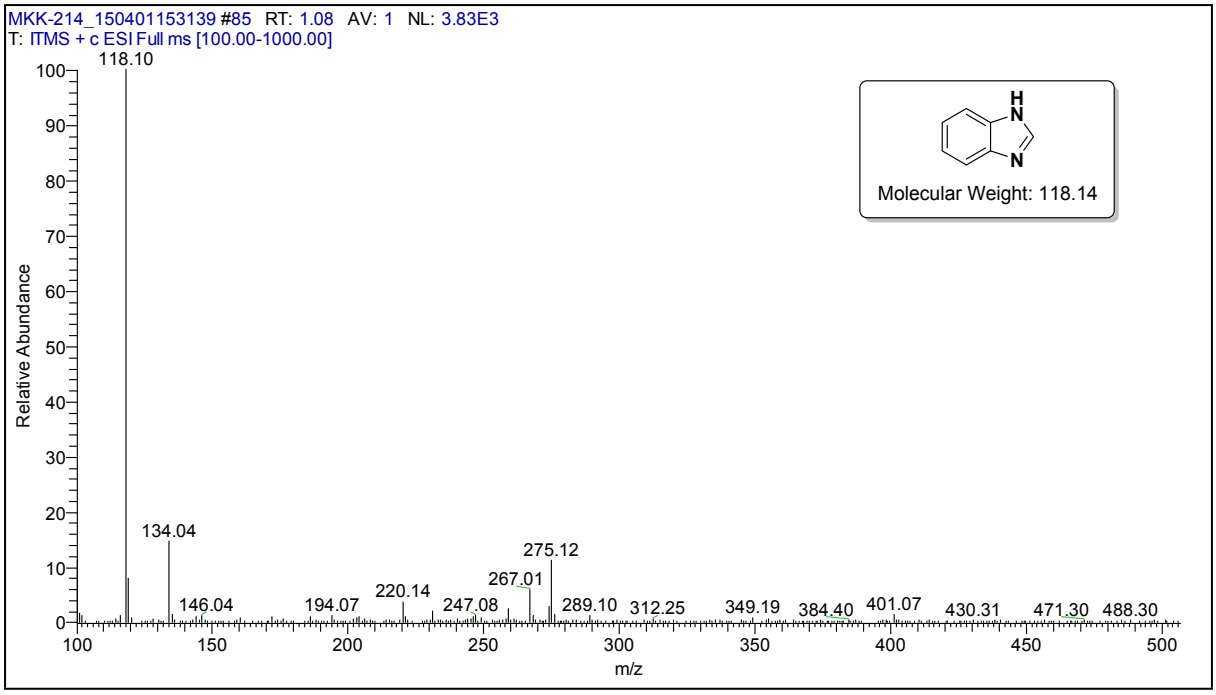


Fig. S72 ESI Mass Spectrum of 1*H*-benzo[*d*]imidazole **(4s)** (M+1)

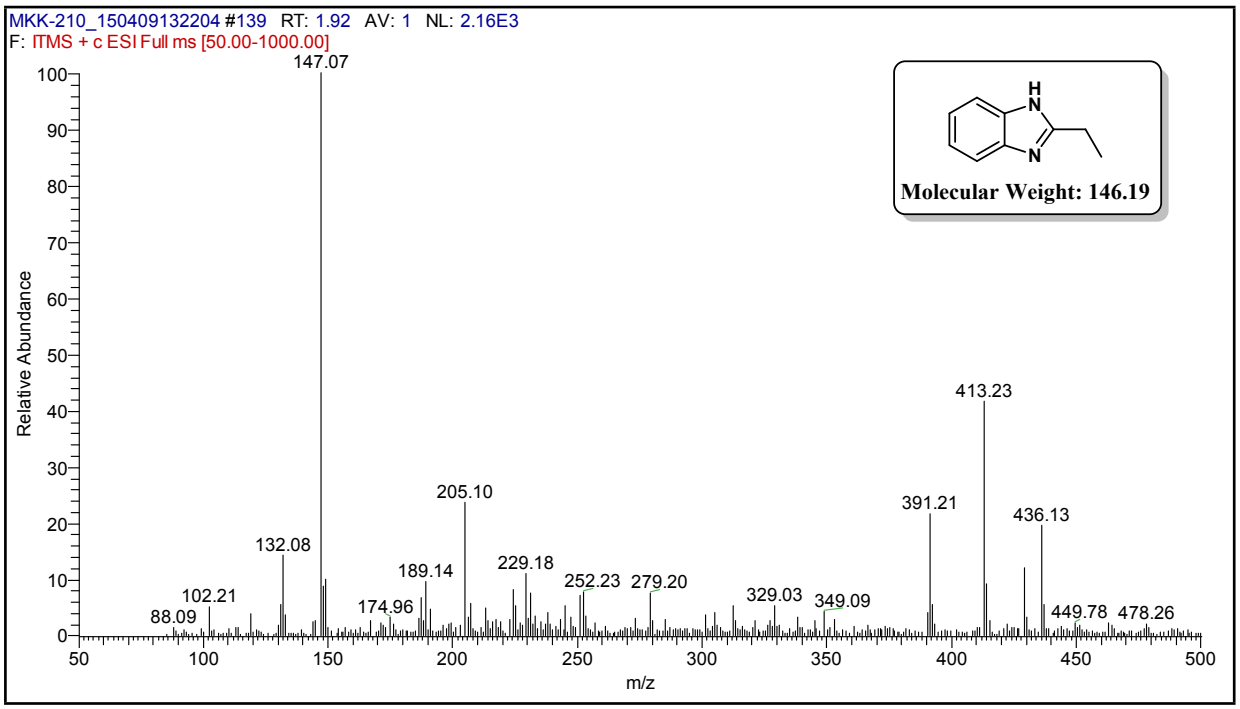


Fig. S73 ESI Mass Spectrum 2-ethyl-1*H*-benzo[*d*]imidazole **(4t)** (M+1)

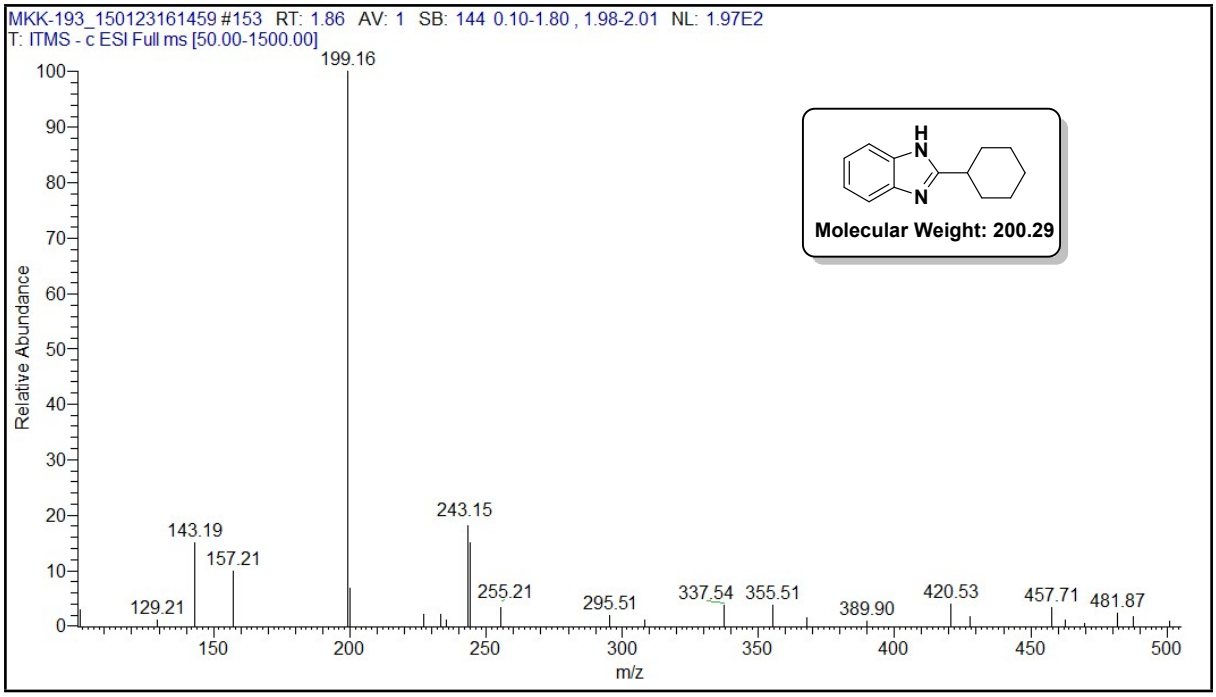


Fig. S74 ESI Mass Spectrum of 2-cyclohexyl-1*H*-benzo[*d*]imidazole **(4u)** (M-1)

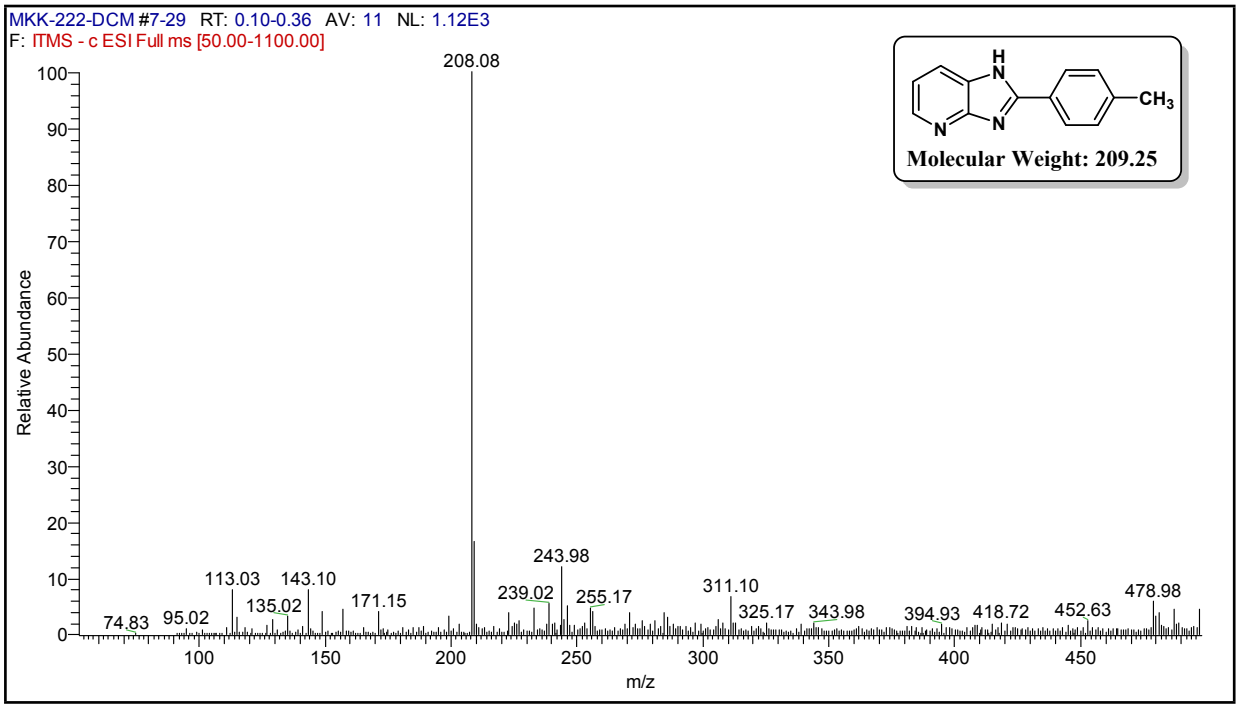


Fig. S75 ESI Mass Spectrum of 2-(*p*-tolyl)-1*H*-imidazo[4,5-*b*]pyridine **(4v)** (M-1)