Supporting Information

Ligand- mediated $Cu(OAc)_2$-catalyzed Direct C-H Cyanation of 2-Arylbenzimidazoles

Tianyou Zhang[a], Jingyi Qiao [a,b], He Song[a,b], Feng Xu[a,b], Xiaochong Liu[a,b], Chunzhao Xu[a,b], Junjie Ma[a,b], Hao Liu[a,b], Zhizhong Sun,[*a,b] Wenyi Chu [*a,b]

[a]School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China

[b]Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, College of Heilongjiang Province, Harbin 150080, P. R. China

Corresponding author. Tel.: +86-451-86609135; fax: +86-451-86609135

E-mail: wenyichu@hlju.edu.cn

Materials and Measurements

All starting materials were purchased from TCI; the reagents were obtained from J&K Chemical Company and used without further purification unless specified. The cyanation reactions were monitored by thin layer chromatography (TLC), and column chromatography were carried out on silica gel (300 ~ 400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield™ 400 spectrometer operating at 400 MHz and 100 MHz in $CDCl_3$ or DMSO. Chemical shifts were reported in ppm with tetramethylsilane (TMS) as internal standard. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiple. Coupling constants (J) are reported in Hertz (Hz). Melting points were recorded on a WRR melting point apparatus. Infrared spectra were recorded with the Perkin-Elmer Spectrum100 Fourier transform infrared spectroscopy. UV-visible spectra were measured by Shimadzu UV-2501PC UV-visible spectrophotometer. Elemental analyses of C, H, N were performed on a Elementar Vario MICRO cube. High resolution mass spectrum was accomplished on Agilent 1100 (VL) mass spectrometer.

Experimental and analytical data of products

Synthesis and analytical data of products

2-(1H-benzo[d]imidazol-2-yl)benzonitrile (3a). A reaction vial (10 ml) was charged with 2-phenyl-1H-benzo[d]imidazole (77.7mg, 0.4 mmol), $Cu(OAc)_2$ (87.2mg, 0.48 mmol), 4-methylpiperazine-1-carbonitrile (75.1 mg, 0.6 mmol), K_3PO_4 (169.8mg, 0.8 mmol) and N,N-dimethylformamide (6 ml). The reaction mixture was stirred at 130 ℃ for 6 h under open system through a condensing tube. The reaction mixture was cooled and poured into water (60 ml). The mixture was extracted with ethyl acetate (3 × 20 ml). Organic layers were combined and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography to give a beige solid (71.9 mg, 82%); m.p: 254.5~256.1 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 8.57 (d, J = 7.9 Hz, 1H), 7.87 – 7.62 (m, 4H), 7.56 (t, J = 7.5 Hz, 1H), 7.38 – 7.31 (m, 2H). **(Figure S1)**

^{13}C NMR (100 MHz, Chloroform-*d*) δ= 147.6 , 134.0 , 133.8 , 133.0 , 130.5 , 130.1 , 124.1 , 119.8 , 108.3 . **(Figure S2)**

HRMS: (EI) calcd for $C_{14}H_9N_3$ $[M+H]^+$: 220.0875. Found: 220.0870. Anal.calcd for $C_{14}H_9N_3$: C 76.70, H 4.14, N 19.17; Found: C 76.72, H 4.15, N 19.14.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2237 cm^{-1}.

UV-*vis* spectra absorption peak: 230.5 nm.

2-(1-ethyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3b). Using **3a** approach to obtain **3b**, the pure product was obtained as a beige solid (70.2 mg, 71%); m.p: 120.7~122.3 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 8.15 (d, J = 7.7 Hz, 1H), 7.95 (dt, J = 13.5, 7.2 Hz, 2H), 7.83 (dt, J = 14.9, 7.5 Hz, 3H), 7.42 (dt, J = 23.0, 7.7 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H). **(Figure S3)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 149.1 , 134.6 , 134.4 , 134.0 , 131.7 , 131.6 , 124.2 , 123.6 , 119.3 , 117.6 , 113.0 , 112.0 , 43.5 , 15.3 . **(Figure S4)**

HRMS: (EI) calcd for $C_{16}H_{13}N_3$ $[M+H]^+$: 248.1188. Found: 248.1190. Anal.calcd for $C_{16}H_{13}N_3$: C 77.71, H 5.30, N 16.99; Found: C 77.72, H 5.32, N 16.96.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2228 cm^{-1}.

UV-*vis* spectra absorption peak: 283.5 nm.

2-(1-benzyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3c). Using **3a** approach to obtain **3c**, the pure product was obtained as a beige solid (81.7 mg, 66%); m.p: 70.1~72.3 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 8.06 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 6.4 Hz, 2H), 7.84 – 7.76 (m, 2H), 7.70 – 7.65 (m, 1H), 7.39 – 7.35 (m, 2H), 7.23 (d, J = 4.7 Hz, 3H), 6.97 – 6.88 (m, 2H), 5.54 (s, 2H). **(Figure S5)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 149.9 , 136.6 , 135.4 , 134.4 , 133.8 , 132.9 , 131.5 , 131.4 , 129.1 , 128.2 , 126.9 , 124.3 , 123.5 , 119.7 , 117.6 , 113.1 , 112.2 , 47.9 . **(Figure S6)**

HRMS: (EI) calcd for $C_{21}H_{15}N_3$ $[M+H]^+$: 310.1345. Found: 310.1351. Anal.calcd for $C_{21}H_{15}N_3$: C 81.53, H 4.89, N 13.58; Found: C 81.55, H 4.88, N 13.57.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2230 cm^{-1}.

UV-*vis* spectra absorption peak: 234.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-bromobenzonitrile (3d). Using **3a** approach to obtain **3d**, the pure product was obtained as a beige solid (88.2 mg, 74%); m.p: 209.7~210.7 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.17 (s, 1H), 8.34 (s, 1H), 8.13 (s, 1H), 8.04 (s, 1H), 7.75 (s, 1H), 7.60 (s, 1H), 7.29 (s, 2H). **(Figure S7)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 147.5, 137.3, 136.4, 131.7, 130.7, 122.9, 116.8, 111.8. **(Figure S8)**

HRMS: (EI) calcd for $C_{14}H_8N_3Br$ $[M+H]^+$: 297.9981. Found: 297.9988. Anal.calcd for $C_{14}H_8N_3Br$: C 56.40, H 2.70, N 14.09; Found: C 56.41, H 2.71, N 14.11.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2226 cm^{-1}.

UV-*vis* spectra absorption peak: 307.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-chlorobenzonitrile (3e). Using **3a** approach to obtain **3e**, the pure product was obtained as a beige solid (79.1 mg, 78%); m.p: 249.4~250.7 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ= 10.29 (s, 1H), 8.57 (d, J = 8.6 Hz, 1H), 7.89 – 7.52 (m, 4H), 7.36 (dd, J = 6.0, 3.0 Hz, 2H). **(Figure S9)**

^{13}C NMR (100 MHz, Chloroform-*d*) δ= 166.9 , 149.7 , 148.5 , 143.4 , 137.4 , 127.5 , 127.5 , 126.6 , 122.6 , 100.1 . **(Figure S10)**

HRMS: (EI) calcd for $C_{14}H_8N_3Cl$ $[M+H]^+$: 254.0486. Found: 254.0489. Anal.calcd for $C_{14}H_8N_3Cl$: C 66.28, H 3.18, N 16.56; Found: C 66.29, H 3.20, N 16.58.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2228 cm^{-1}.

UV-*vis* spectra absorption peak: 299.0 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-fluorobenzonitrile (3f). Using **3a** approach to obtain **3f**, the pure product was obtained as a beige solid (75.9 mg, 80%); m.p: 185.2~188.1 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.11 (s, 1H), 8.15 (dd, J = 8.7, 5.4 Hz, 1H), 8.06 (dd, J = 8.6, 2.5 Hz, 1H), 7.82 (td, J = 11.0, 8.6, 2.5 Hz, 1H), 7.76 (s, 1H), 7.62 (s, 1H), 7.29 (s, 2H). **(Figure S11)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 162.4 (d, J_{C-F} = 250.0 Hz) , 148.1 , 132.2 (d, J_{C-F} = 10.0 Hz) , 130.1 , 130.0 , 129.2 (d, J_{C-F} = 10.0 Hz) , 122.7 , 122.4 , 121.5 (d, J C-F = 20.0 Hz) , 117.5 , 117.4 , 116.5 (d, J C-F = 30.0 Hz) , 112.4 (d, J C-F = 10.0 Hz) . **(Figure S12)**

HRMS: (EI) calcd for $C_{14}H_8N_3F$ $[M+H]^+$: 238.0781. Found: 238.0787. Anal.calcd for $C_{14}H_8N_3F$: C 70.88, H 3.40, N 17.71; Found: C 70.89, H 3.42, N 17.74.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2230 cm^{-1}.

UV-*vis* spectra absorption peak: 258.5, 341.0 nm.

2-(1H-benzo[d]imidazol-2-yl)-4-bromobenzonitrile (3g). Using **3a** approach to obtain **3g**, the pure product was obtained as a beige solid (84.7 mg, 71%); m.p:

230.2~232.0 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.19 (s, 1H), 8.37 (s, 1H), 7.99 – 7.90 (m, 2H), 7.70 (d, J = 44.1 Hz, 2H), 7.30 (s, 2H). **(Figure S13)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 147.5 , 137.4 , 134.5 , 133.4 , 132.2 , 127.7 , 118.1 , 109.6 . **(Figure S14)**

HRMS: (EI) calcd for $C_{14}H_8N_3Br$ $[M+H]^+$: 297.9981. Found: 297.9985. Anal.calcd for $C_{14}H_8N_3Br$: C 56.40, H 2.70, N 14.09; Found: C 56.42, H 2.72, N 14.10.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2236 cm^{-1}.

UV-*vis* spectra absorption peak: 307.0 nm.

2-(1H-benzo[d]imidazol-2-yl)-4-chlorobenzonitrile (3h). Using **3a** approach to obtain **3h**, the pure product was obtained as a beige solid (76.1 mg, 75%); m.p: 219.1~221.6 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.20 (s, 1H), 8.24 (d, J = 2.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.78 (dd, J = 8.4, 2.0 Hz, 2H), 7.64 (s, 1H), 7.31 (s, 2H). **(Figure S15)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 147.5 , 138.8 , 137.4 , 134.6 , 130.5 , 129.4 , 118.0 , 109.3 . **(Figure S16)**

HRMS: (EI) calcd for $C_{14}H_8N_3Cl$ $[M+H]^+$: 254.0486. Found: 254.0482. Anal.calcd for $C_{14}H_8N_3Cl$: C 66.28, H 3.18, N 16.56; Found: C 66.30, H 3.19, N 16.57.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2235 cm^{-1}.

UV-*vis* spectra absorption peak: 286.0, 310.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-4-fluorobenzonitrile (3i). Using **3a** approach to obtain **3i**, the pure product was obtained as a beige solid (74.0 mg, 78%); m.p: 179.3~181.7 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.23 (s, 1H), 7.97 (s, 2H), 7.82 – 7.74 (m, 1H), 7.66 (dq, J = 12.5, 6.8, 5.7 Hz, 2H), 7.36 – 7.26 (m, 2H). **(Figure S17)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 164.7 (d, J C-F = 250.0 Hz) , 145.9 (d, J C-F = 390.0 Hz) , 136.2 (d, J C-F = 10.0 Hz) , 135.3 , 134.6 , 125.5 (d, J C-F = 3.0 Hz) , 124.3 , 122.8 , 120.2 , 117.6 (d, J C-F = 20.0 Hz) , 113.3 , 112.3 , 99.5 (d, J C-F = 10.0

Hz) . **(Figure S18)**

HRMS: (EI) calcd for $C_{14}H_8N_3F[M+H]^+$: 238.0781. Found: 238.0786. Anal.calcd for $C_{14}H_8N_3F$: C 70.88, H 3.40, N 17.71; Found: C 70.90, H 3.41, N 17.73.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2237 cm^{-1}.

UV-*vis* spectra absorption peak: 257.5, 357.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-3-chlorobenzonitrile (3k). Using **3a** approach to obtain **3k**, the pure product was obtained as a beige solid (57.8 mg, 57%); m.p: 179.5~181.9 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.14 (s, 1H), 8.14 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.94 (t, J = 7.6 Hz, 1H), 7.73 (dd, J = 15.2, 7.8 Hz, 2H), 7.33 (s, 2H). **(Figure S19)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 148.9 , 135.6 , 135.0 , 133.8 , 133.1 , 132.8 , 132.6 , 130.6 , 129.7 , 118.7 , 110.6 . **(Figure S20)**

HRMS: (EI) calcd for $C_{14}H_8N_3Cl$ $[M+H]^+$: 254.0486. Found: 254.0489. Anal.calcd for $C_{14}H_8N_3Cl$: C 66.28, H 3.18, N 16.56; Found: C 66.31, H 3.20, N 16.58.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2238 cm^{-1}.

UV-*vis* spectra absorption peak: 244.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-3-fluorobenzonitrile (3l). Using **3a** approach to obtain **3l**, the pure product was obtained as a beige solid (65.5 mg, 69%); m.p: 222.9~223.4 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.03 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.89 – 7.76 (m, 3H), 7.63 (d, J = 7.8 Hz, 1H), 7.31 (dt, J = 14.0, 7.4 Hz, 2H). **(Figure S21)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 160.0 (d, J C-F = 250.0 Hz) , 143.6 , 133.2 (d, J C-F = 10.0 Hz) , 131.5 (d, J C-F = 3.0 Hz) , 124.0 , 122.6 , 122.1 (d, J C-F = 20.0 Hz), 122.1 , 121.9 , 120.0 , 117.4 (d, J C-F = 10.0 Hz) , 113.8 (d, J C-F = 5.0 Hz) , 112.4 . **(Figure S22)**

HRMS: (EI) calcd for $C_{14}H_8N_3F$ $[M+H]^+$: 238.0781. Found: 238.0777. Anal.calcd for $C_{14}H_8N_3F$: C 70.88, H 3.40, N 17.71; Found: C 70.91, H 3.43, N 17.74.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2230 cm^{-1}.

UV-*vis* spectra absorption peak: 254.5, 363.0 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-methylbenzonitrile (3p). Using **3a** approach to obtain **3p**, the pure product was obtained as a beige solid (80.2 mg, 86%); m.p > 280 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.01 (s, 1H), 7.98 (d, J = 7.7 Hz, 1H), 7.86 (s, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 6.9 Hz, 1H), 7.28 (d, J = 8.8 Hz, 2H), 2.44 (s, 3H). **(Figure S23)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 149.0 , 144.0 , 140.9 , 135.8 , 135.3 , 134.5 , 130.4 , 129.5 , 123.7 , 122.5 , 119.9 , 118.8 , 112.1 , 110.4 , 20.8 . **(Figure S24)**

HRMS: (EI) calcd for $C_{15}H_{11}N_3$ $[M+H]^+$: 234.1032. Found: 234.1030. Anal.calcd for $C_{15}H_{11}N_3$: C 77.23, H 4.75, N 18.01; Found: C 77.24, H 4.72, N 18.03.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2231 cm^{-1}.

UV-*vis* spectra absorption peak: 253.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-4-methylbenzonitrile (3q). Using **3a** approach to obtain **3q**, the pure product was obtained as a beige solid (51.3 mg, 55%); m.p: 216.1~218.9 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.06 (s, 1H), 8.00 – 7.86 (m, 2H), 7.68 (d, J = 52.3 Hz, 2H), 7.51 (d, J = 7.8 Hz, 1H), 7.28 (s, 2H), 2.49 (s, 3H). **(Figure S25)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 144.4 , 135.5 , 133.0 , 131.2 , 130.3 , 127.4 , 123.8 , 122.5 , 119.9 , 118.9 , 112.2 , 107.7 , 21.7 . **(Figure S26)**

HRMS: (EI) calcd for $C_{15}H_{11}N_3$ $[M+H]^+$: 234.1032. Found: 234.1036. Anal.calcd for $C_{15}H_{11}N_3$: C 77.23, H 4.75, N 18.01; Found: C 77.21, H 4.76, N 18.02.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2241 cm^{-1}.

UV-*vis* spectra absorption peak: 236.5, 298.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-(dimethylamino)benzonitrile (3s). Using **3a** approach to obtain **3s**, the pure product was obtained as a beige solid (97.6 mg, 93%);

m.p: 216.8~218.2 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.05 (s, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 6.8 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H), 7.24 (s, 1H) , 3.20 (s, 6H). **(Figure S27)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 151.1 , 150.4 , 138.3 , 136.1 , 131.3 , 126.7 , 124.6 , 124.0 , 119.4 , 117.6 , 116. 6 , 116. 0 , 114.5 , 110.9 , 40.9 . **(Figure S28)**

HRMS: (EI) calcd for $C_{16}H_{14}N_4$ $[M+H]^+$: 263.1297. Found: 263.1301. Anal.calcd for $C_{16}H_{14}N_4$: C 73.26, H 5.38, N 21.36; Found: C 73.28, H 5.39, N 21.33.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2252 cm^{-1}.

UV-*vis* spectra absorption peak: 258.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-hydroxybenzonitrile (3t). Using **3a** approach to obtain **3t**, the pure product was obtained as a beige solid (85.6 mg, 91%); m.p: 238.8~241.2 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.02 (s, 1H), 9.79 (s, 1H), 7.89 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 6.8 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H), 7.25 (s, 2H). **(Figure S29)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 156.6 , 150.4 , 138.6 , 138.4 , 131.6 , 125.0 , 124.6 , 124.0 , 120.6 , 118.5 , 118.0 , 115.8 , 114.4 , 113.2 . **(Figure S30)**

HRMS: (EI) calcd for $C_{14}H_9N_3O$ $[M+H]^+$: 236.0825. Found: 236.0821. Anal.calcd for $C_{14}H_9N_3O$: C 71.48, H 3.86, N 17.86; Found: C 71.49, H 3.88, N 17.89.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2250 cm^{-1}.

UV-*vis* spectra absorption peak: 254.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-methoxybenzonitrile (3u). Using **3a** approach to obtain **3u**, the pure product was obtained as a beige solid (87.7 mg, 88%); m.p: 231.5~232.9 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 12.93 (s, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.86 – 7.52 (m, 3H), 7.47 (dd, J = 8.8, 2.5 Hz, 1H), 7.26 (s, 2H), 3.91 (s, 3H). **(Figure S31)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 159.9 , 148.5 , 130.7 , 125.1 , 119.7 , 119.6 ,

117.9 , 111.3 , 56.0 . **(Figure S32)**

HRMS: (EI) calcd for $C_{15}H_{11}N_3O$ $[M+H]^+$: 250.0981. Found: 250.0977. Anal.calcd for $C_{15}H_{11}N_3O$: C 72.28, H 4.45, N 16.86; Found: C 72.30, H 4.46, N 16.88.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2247 cm^{-1}.

UV-*vis* spectra absorption peak: 243.5, 293.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-phenylbenzonitrile (3v). Using **3a** approach to obtain **3v**, the pure product was obtained as a beige solid (100.4 mg, 85%); m.p: 123.8~125.1 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.20 (s, 1H), 8.41 (d, J = 1.7 Hz, 1H), 8.31 – 8.22 (m, 2H), 7.96 – 7.92 (m, 2H), 7.83 (t, J = 7.3 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.4 Hz, 2H), 7.54 (d, J = 7.2 Hz, 1H), 7.35 (dq, J = 15.2, 6.5 Hz, 2H). **(Figure S33)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 148.6 , 142.0 , 137.6 , 133.5 , 131.7 , 131.6 , 130.2 , 129.7 , 129.3 , 127.5 , 118.6 , 111.3 . **(Figure S34)**

HRMS: (EI) calcd for $C_{20}H_{13}N_3$ $[M+H]^+$: 296.1188. Found: 296.1184. Anal.calcd for $C_{20}H_{13}N_3$: C 81.34, H 4.44, N 14.23; Found: C 81.35, H 4.46, N 14.20.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2245 cm^{-1}.

UV-*vis* spectra absorption peak: 342.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-5-(3',5'-difluorophenyl)benzonitrile (3w). Using **3a** approach to obtain **3w**, the pure product was obtained as a beige solid (110.0 mg, 83%); m.p: 225.5~226.6 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.09 (s, 1H), 8.10 – 8.08 (m, 1H), 8.05 – 8.02 (m, 1H), 7.94 – 7.86 (m, 2H), 7.72 (dtd, J = 15.3, 7.7, 6.8, 2.3 Hz, 3H), 7.27 (dtd, J = 15.1, 8.2, 7.4, 3.5 Hz, 3H). **(Figure S35)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 164.7 (d, J C-F = 10.0 Hz) , 162.2 (d, J C-F = 20.0 Hz) , 148.4 , 139.3 , 134.0 , 132.6 , 132.0 , 130.1 , 127.9 , 127.4 , 118.4 , 111.3 , 110.9 , 110.7 , 104.8 . **(Figure S36)**

HRMS: (EI) calcd for $C_{20}H_{11}N_3F_2$ $[M+H]^+$: 332.1000 Found: 332.1004. Anal.calcd

for $C_{20}H_{11}N_3F_2$: C 72.50, H 3.35, N 12.68; Found: C 72.52, H 3.36, N 12.69.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2243 cm^{-1}.

UV-*vis* spectra absorption peak: 257.5, 335.5 nm.

2-(1H-benzo[d]imidazol-2-yl)-1-naphthonitrile (3x). Using **3a** approach to obtain **3x**, the pure product was obtained as a beige solid (93.7 mg, 87%); m.p: 200.4~202.9 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.18 (s, 1H), 8.74 (d, J = 57.1 Hz, 2H), 8.16 (s, 2H), 7.71 (d, J = 64.5 Hz, 4H), 7.31 (s, 2H). **(Figure S37)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 153.1 , 149.1 , 148.6 , 144.3 , 144.1 , 135.1 , 124.7 , 124.6 , 122.9 , 120.5 , 117.3 , 112.8 , 106.7 . **(Figure S38)**

HRMS: (EI) calcd for $C_{18}H_{11}N_3$ $[M+H]^+$: 270.1032. Found: 270.1033. Anal.calcd for $C_{18}H_{11}N_3$: C 80.28, H 4.12, N 15.60; Found: C 80.29, H 4.14, N 15.57.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2239 cm^{-1}.

UV-*vis* spectra absorption peak: 320.0 nm.

2-(1H-benzo[d]imidazol-2-yl)nicotinonitrile (3y). Using **3a** approach to obtain **3y**, the pure product was obtained as a beige solid (48.4 mg, 55%); m.p: 222.1~224.3 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ= 13.32 (s, 1H), 9.06 – 8.93 (m, 1H), 8.50 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.72 (dd, J = 7.6, 4.7 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.25 (m, 1H). **(Figure S39)**

^{13}C NMR (100 MHz, DMSO-d_6) δ= 153.1 , 149.1 , 148.6 , 144.3 , 144.1 , 135.1 , 124.7 , 124.6 , 122.9 , 120.5 , 117.3 , 112.8 , 106.7 . **(Figure S40)**

HRMS: (EI) calcd for $C_{13}H_8N_4$ $[M+H]^+$: 221.0828. Found: 221.0821. Anal.calcd for $C_{13}H_8N_4$: C 70.90, H 3.66, N 25.44; Found: C 70.91, H 3.68, N 25.41.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2237 cm^{-1}.

UV-*vis* spectra absorption peak: 257.5, 323.0 nm.

2-(benzo[d]oxazol-2-yl)benzonitrile ($3z_3$). Using **3a** approach to obtain **$3z_3$**, the pure product was obtained as a yellow solid (22.6 mg, 25%); m.p: 94.5~95.7 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.78 – 7.74 (m, 1H), 7.69 – 7.63 (m, 2H), 7.49 – 7.37 (m, 2H). **(Figure S41)**

^{13}C NMR (100 MHz, Chloroform-*d*) δ= 159.5, 150.6, 141.5, 135.1, 132.8, 131.2, 129.7, 129.1, 126.2, 125.0 , 120.8, 120.4, 117.6, 110.9. **(Figure S42)**

HRMS: (EI) calcd for $C_{14}H_8N_2O$ $[M+H]^+$: 221.0716. Found: 221.0717. Anal.calcd for $C_{14}H_8N_2O$: C 76.35, H 3.66, N 12.72; Found: C 76.36, H 3.65, N 12.74.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2239 cm^{-1}.

UV-*vis* spectra absorption peak: 235.5 nm.

2-(pyridin-2-yl)benzonitrile (3z$_5$). Using **3a** approach to obtain **3z$_5$**, the pure product was obtained as a White solid (57.4 mg, 76%); m.p: 49.4~51.3 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 4.6 Hz, 1H), 7.87 – 7.76 (m, 4H), 7.69 (t, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.32 (m, 1H). **(Figure S43)**

^{13}C NMR (100 MHz, Chloroform-*d*) δ= 155.2, 149.9, 143.45, 136.8, 132.8, 129.9, 128.7, 123.2, 118.7, 111.0. **(Figure S44)**

HRMS: (EI) calcd for $C_{13}H_8N_4$ $[M+H]^+$:181.0766. Found: 181.0768. Anal.calcd for $C_{13}H_8N_4$: C 79.98, H 4.47, N 15.55; Found: C 79.99, H 4.46, N 15.56.

FT-IR (KBr disc): $\nu_{(C\equiv N)}$ 2227 cm^{-1}.

UV-*vis* spectra absorption peak: 258.5 nm.

Preparation of 2-(1H-inden-2-yl)benzoic acid (4a)

A reaction vial (5 mL) was charged with **3a** (0.4 mmol, 86.9 mg) and 4N KOH solution (1 mL). The reaction mixture was stirred under reflux for 12 h. The pH was adjusted to around acid by progressively adding dilute hydrochloric acid. The mixture was extracted with ethyl acetate (3 × 20 ml). Organic layers were combined and dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by silica gel column chromatography to give the **4a** (69.0mg, 73%).

Preparation of 11H-benzo[4,5]imidazo[2,1-a]isoindol-11-one (5a)

A reaction vial (1 mL) was charged with **4a** (0.2 mmol, 47.3 mg) and Ac_2O (0.3 mL). The reaction mixture was stirred under reflux for 5 min. cooled, treated with i-PrOH (3 mL), washed with petroleum ether, and dried to afford yellow crystals **5a** (29.7mg, 68%).**m.p: 213.1~215.3 ℃.**

^{1}H NMR (400 MHz, DMSO-d_6) δ= 7.87 (s, 2H), 7.70 (t, J = 24.0 Hz, 4H), 7.34 (d, J = 27.2 Hz, 2H). **(Figure S45)**

HRMS: (EI) calcd for $C_{14}H_8N_2O$ $[M+H]^+$: 221.0716. Found: 221.0722. Anal.calcd for $C_{14}H_8N_2O$: C 76.35, H 3.66, N 12.72; Found: C 76.37, H 3.67, N 12.75.

FT-IR (KBr disc): $\nu_{(C=O)}$ 1765 cm^{-1}.

UV-*vis* spectra absorption peak: 270.5 nm.

The spectra of ^{1}H-NMR and ^{13}C-NMR

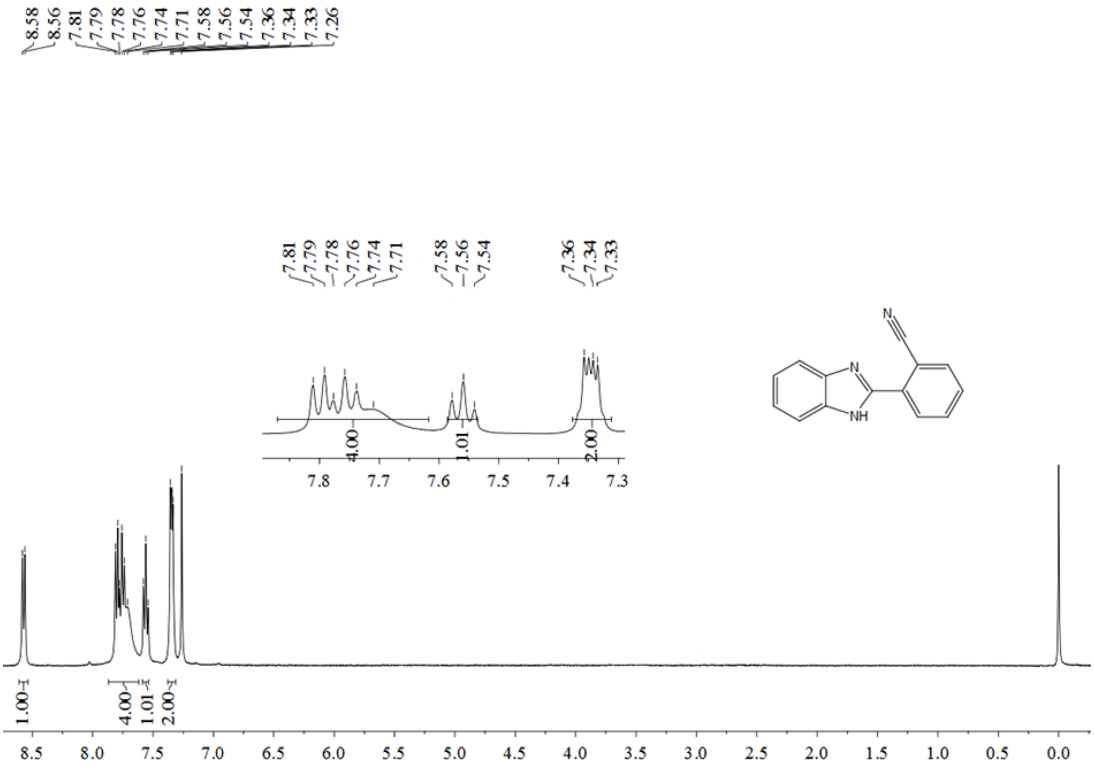


Figure S1. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)benzonitrile (3a).**

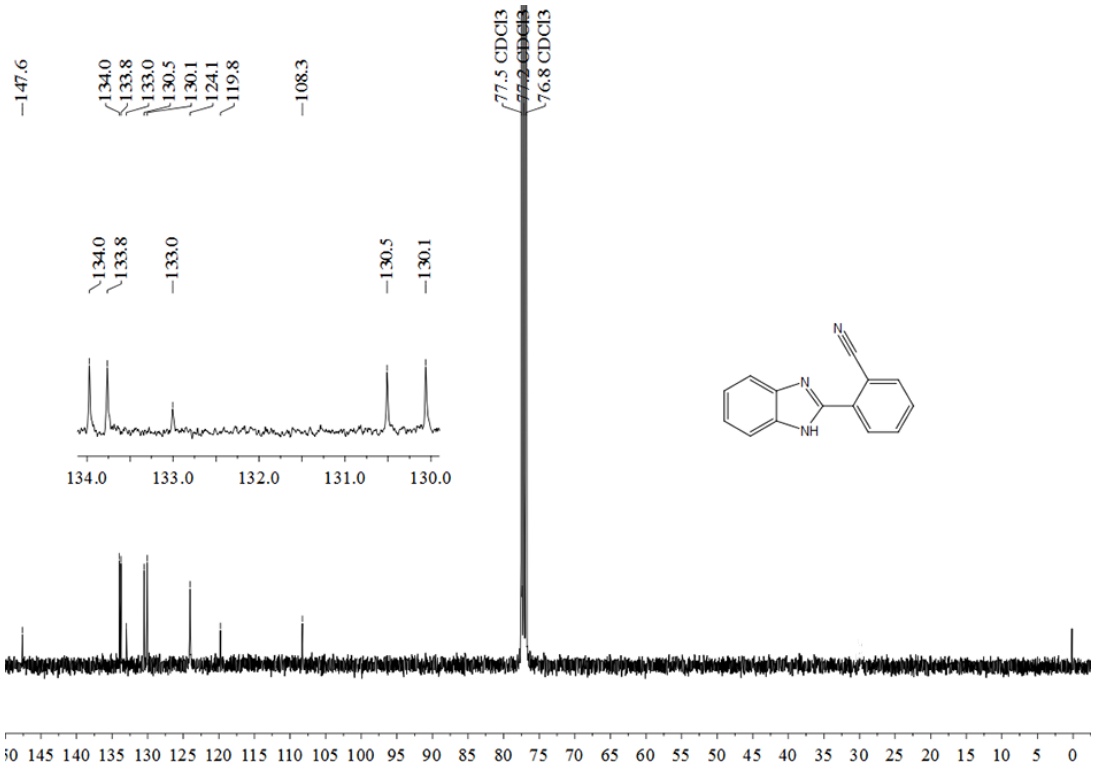


Figure S2. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)benzonitrile (3a).**

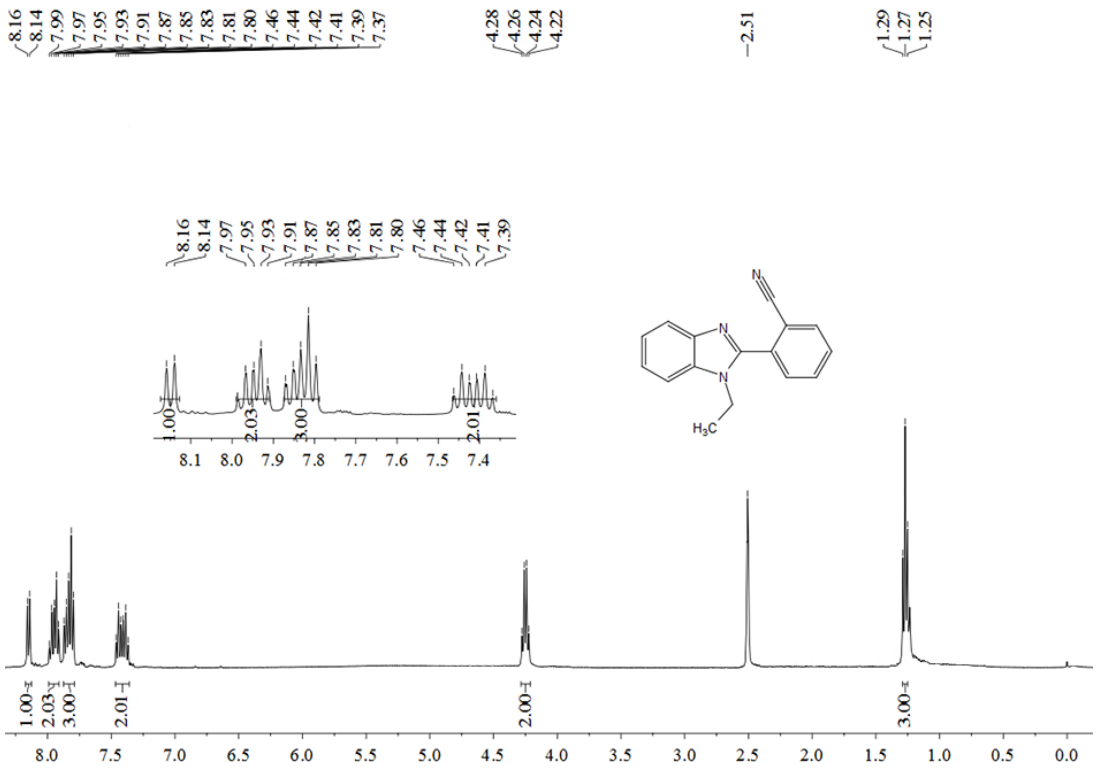


Figure S3. ^{1}H NMR of **2-(1-ethyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3b).**

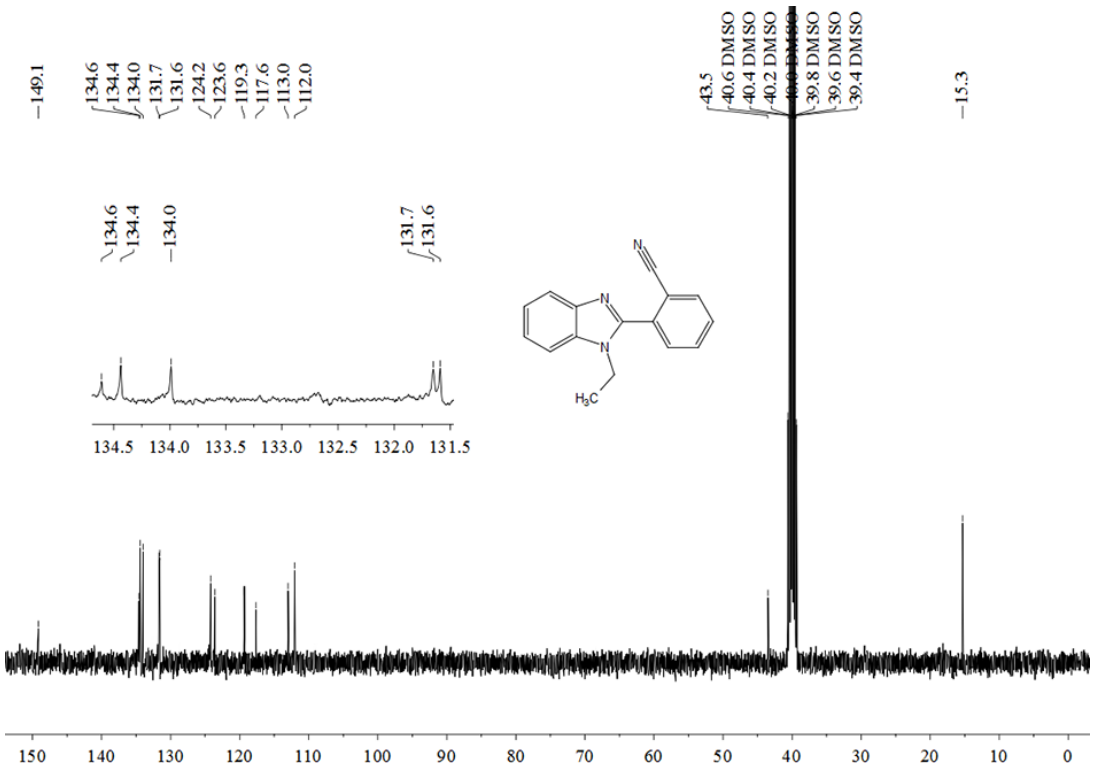


Figure S4. ^{13}C NMR of **2-(1-ethyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3b).**

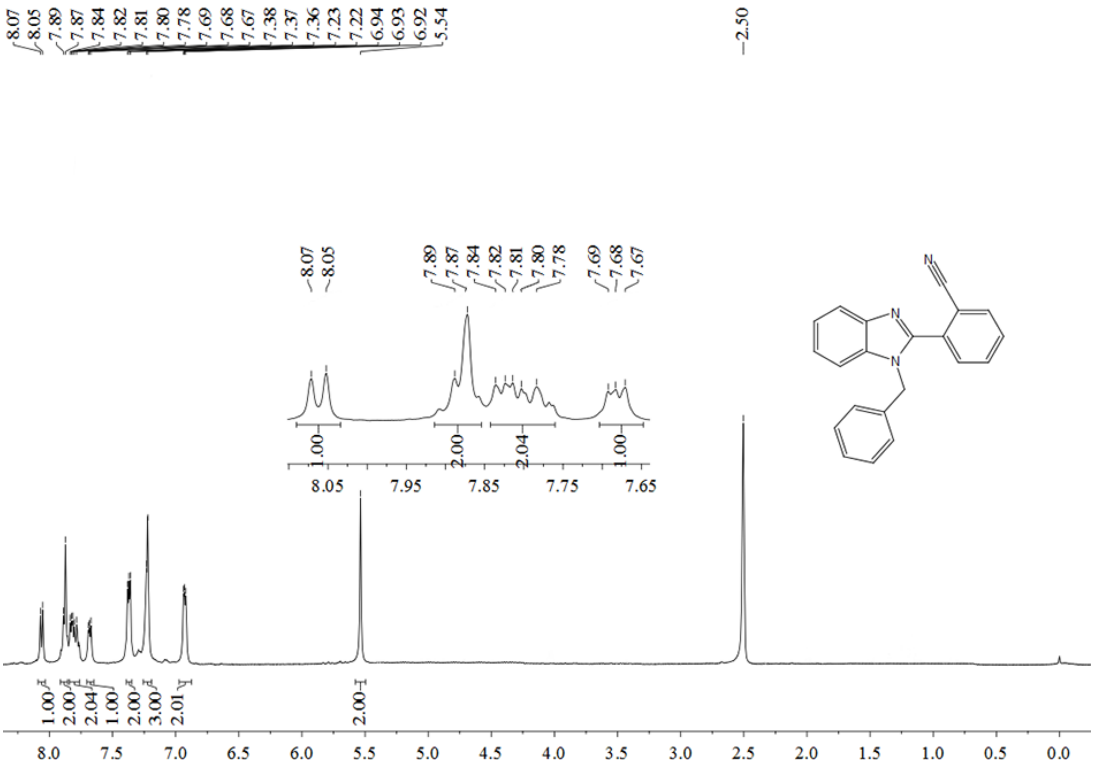


Figure S5. ^{1}H NMR of **2-(1-benzyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3c).**

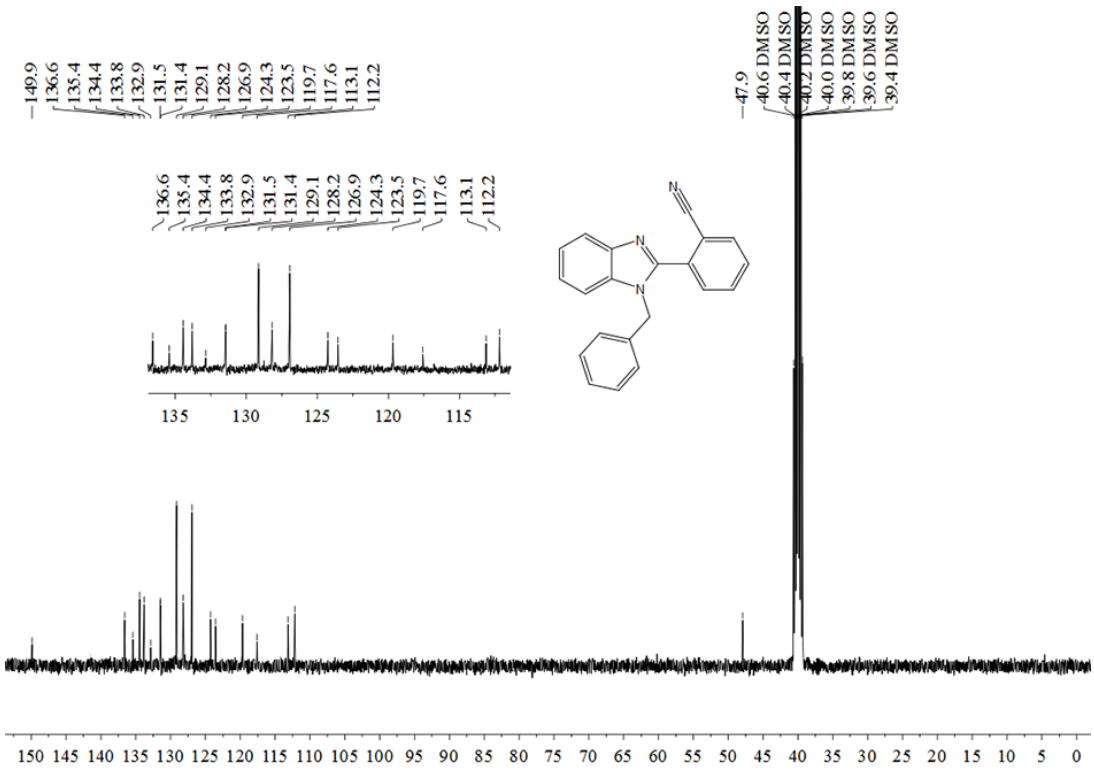


Figure S6. ^{13}C NMR of **2-(1-benzyl-1H-benzo[d]imidazol-2-yl)benzonitrile (3c).**

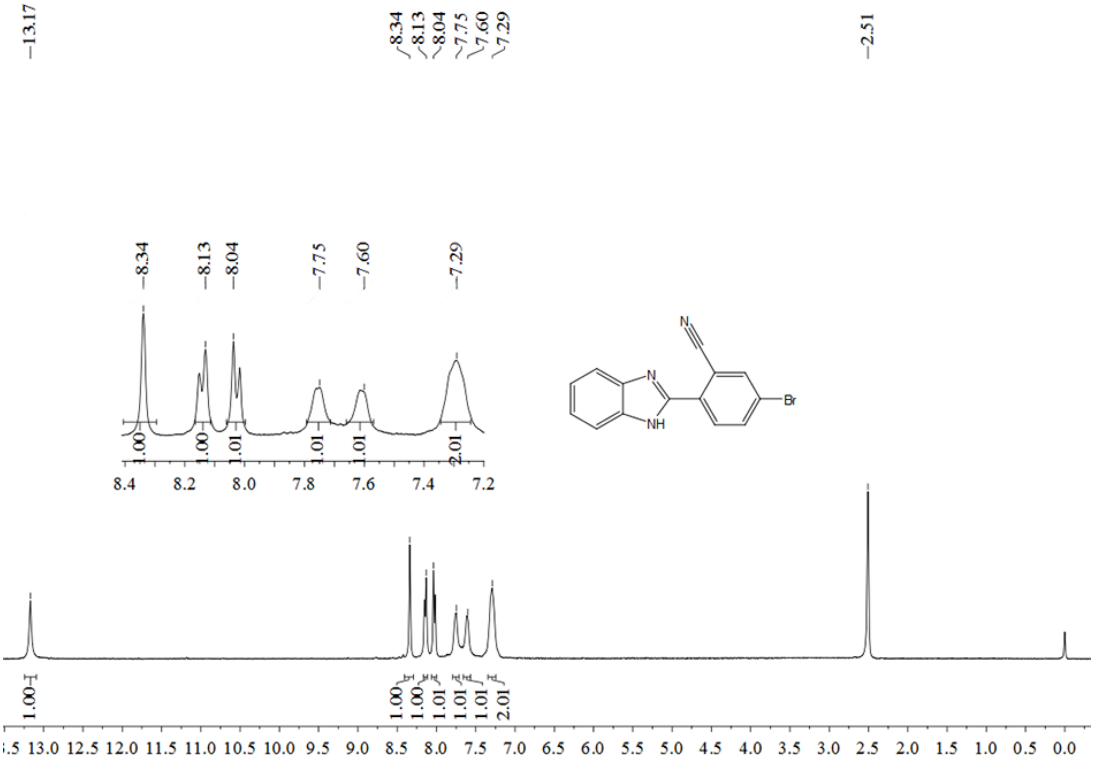


Figure S7. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-bromobenzonitrile (3d).**

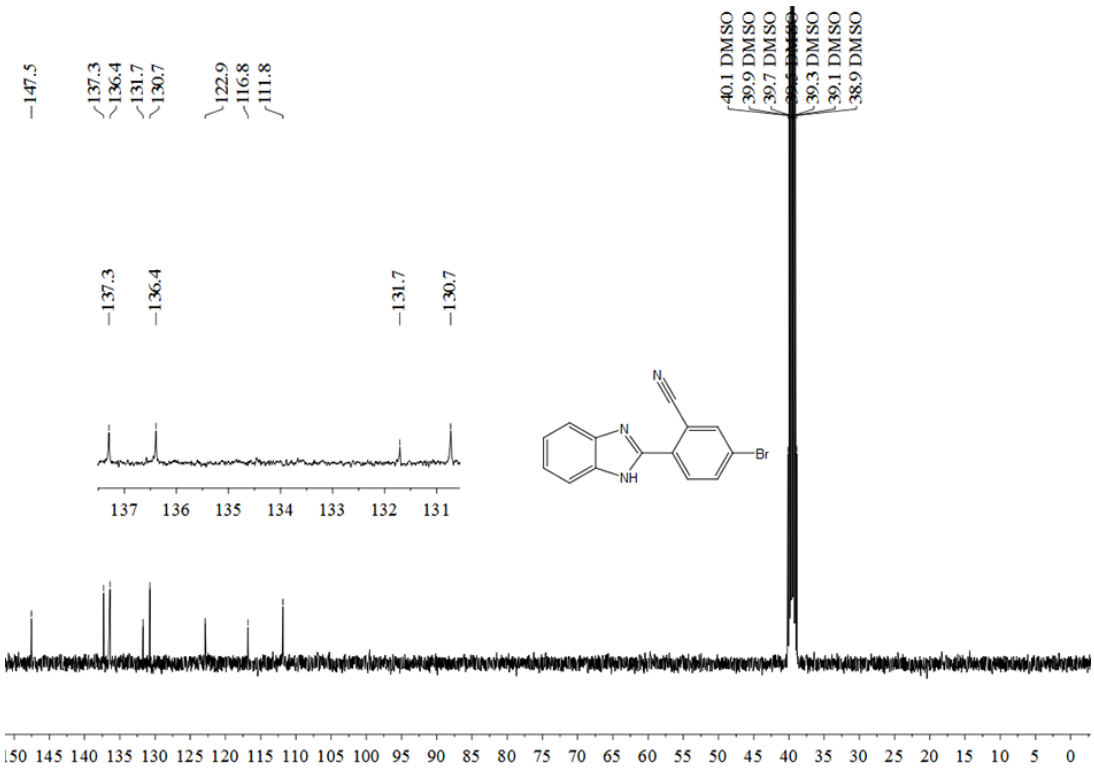


Figure S8. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-bromobenzonitrile (3d).**

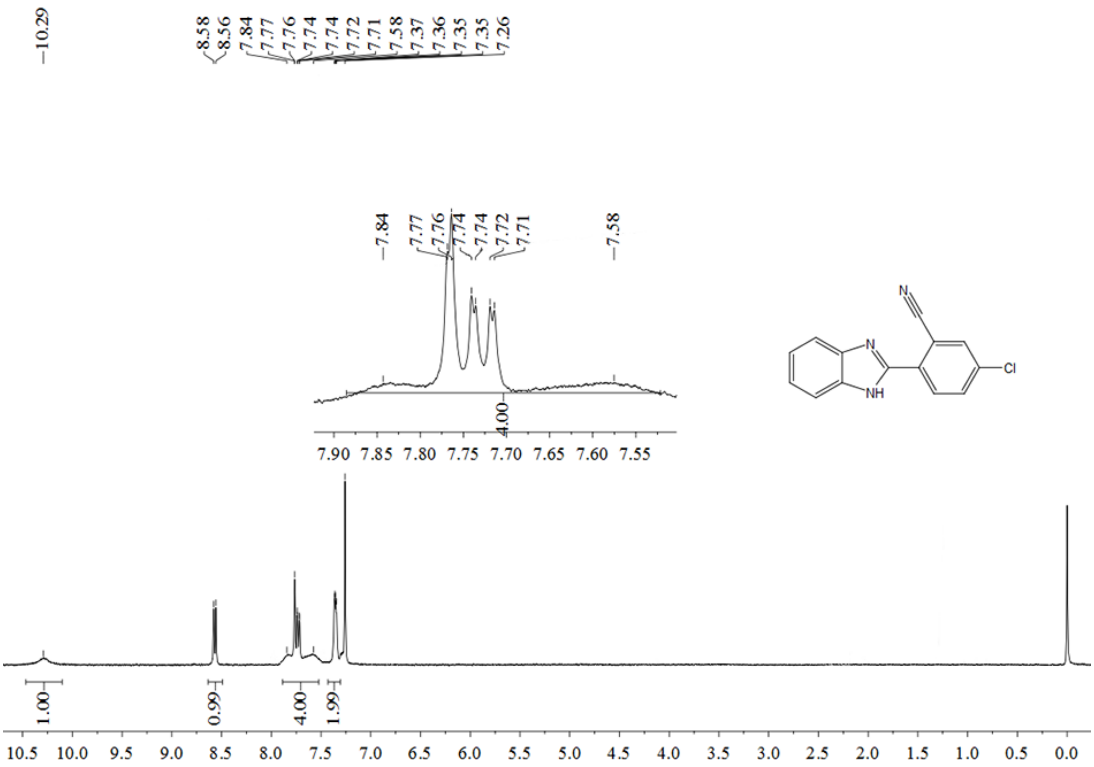


Figure S9. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-chlorobenzonitrile (3e).**

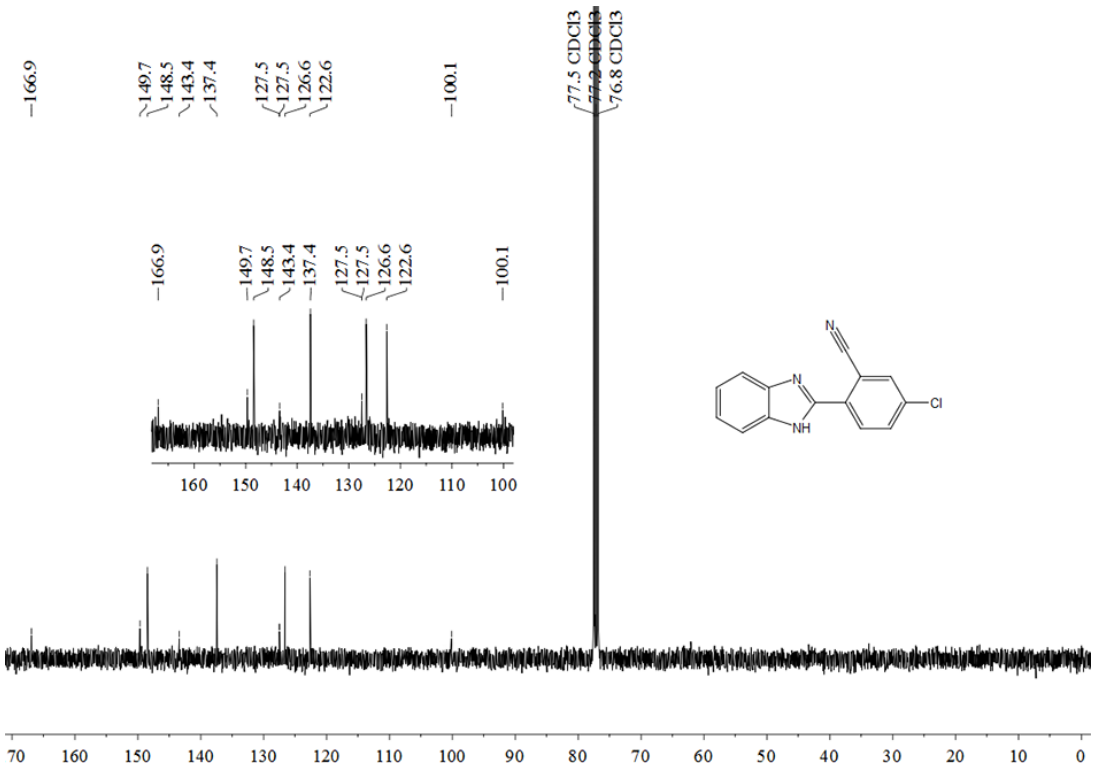


Figure S10. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-chlorobenzonitrile (3e).**

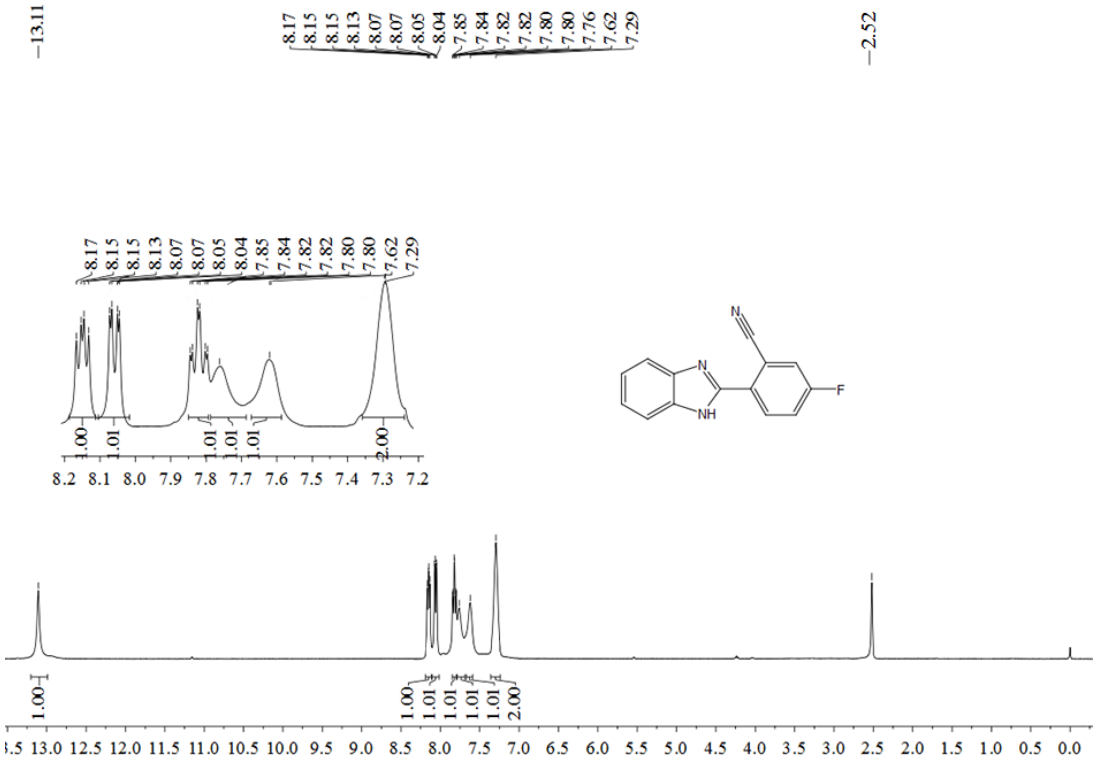


Figure S11. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-fluorobenzonitrile (3f).**

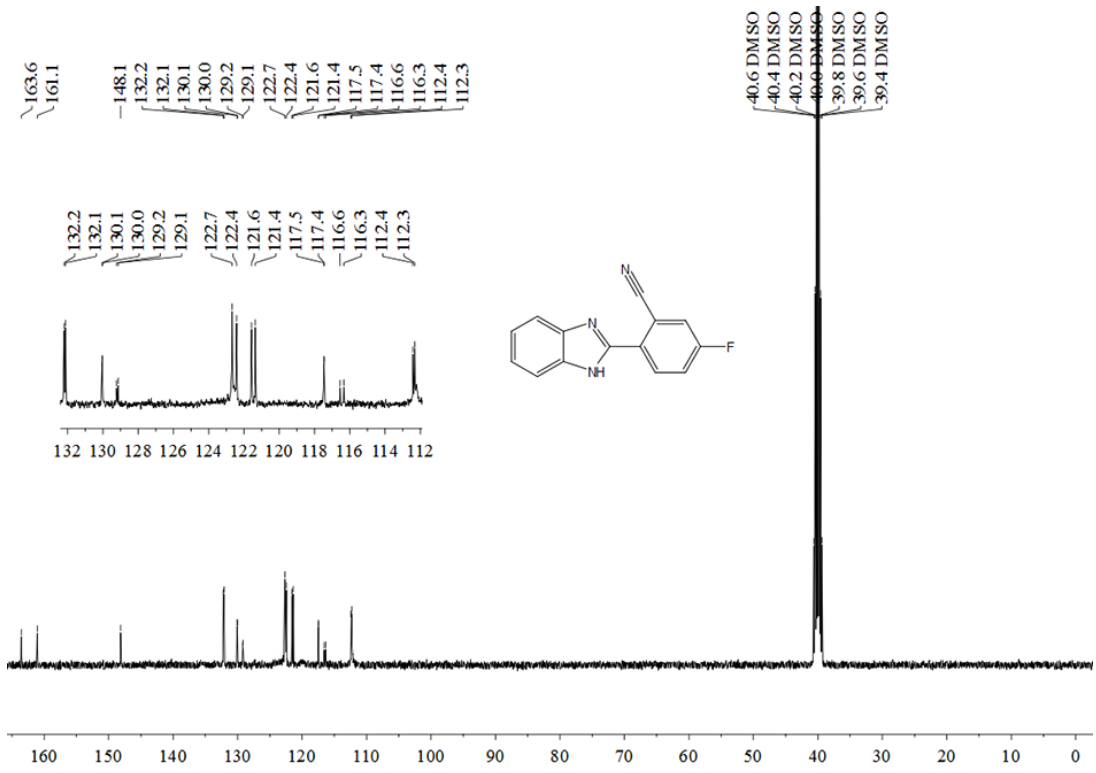


Figure S12. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-fluorobenzonitrile (3f).**

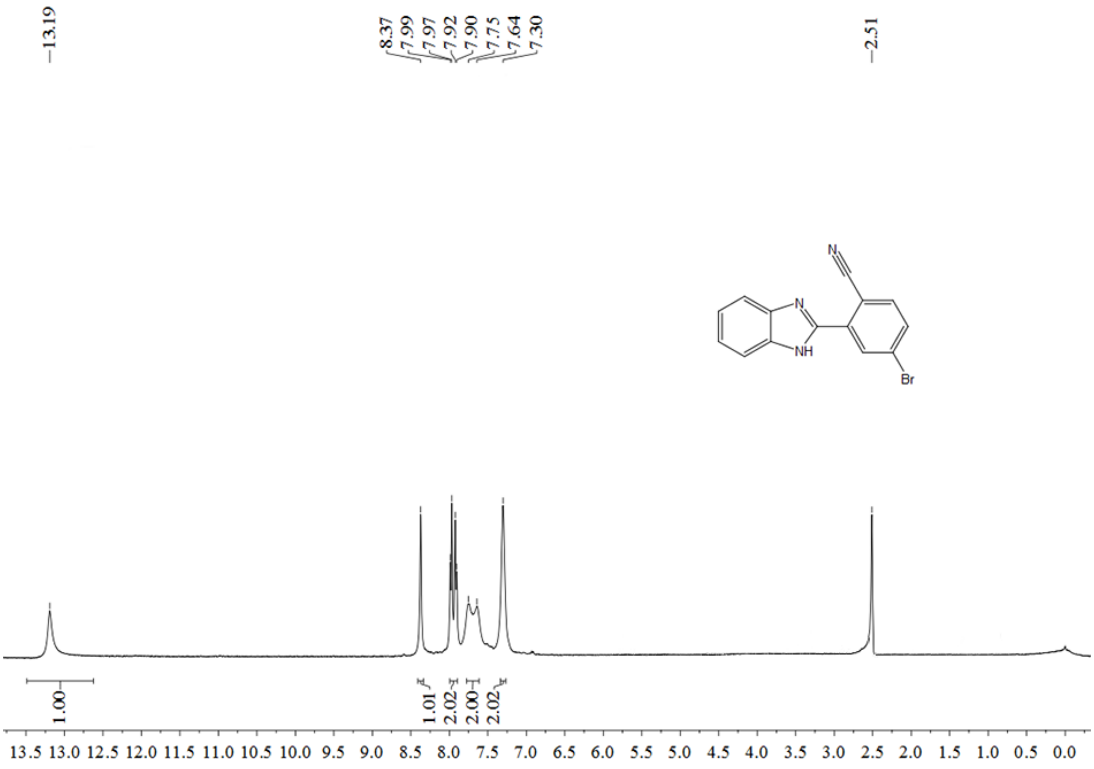


Figure S13. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-bromobenzonitrile (3g).**

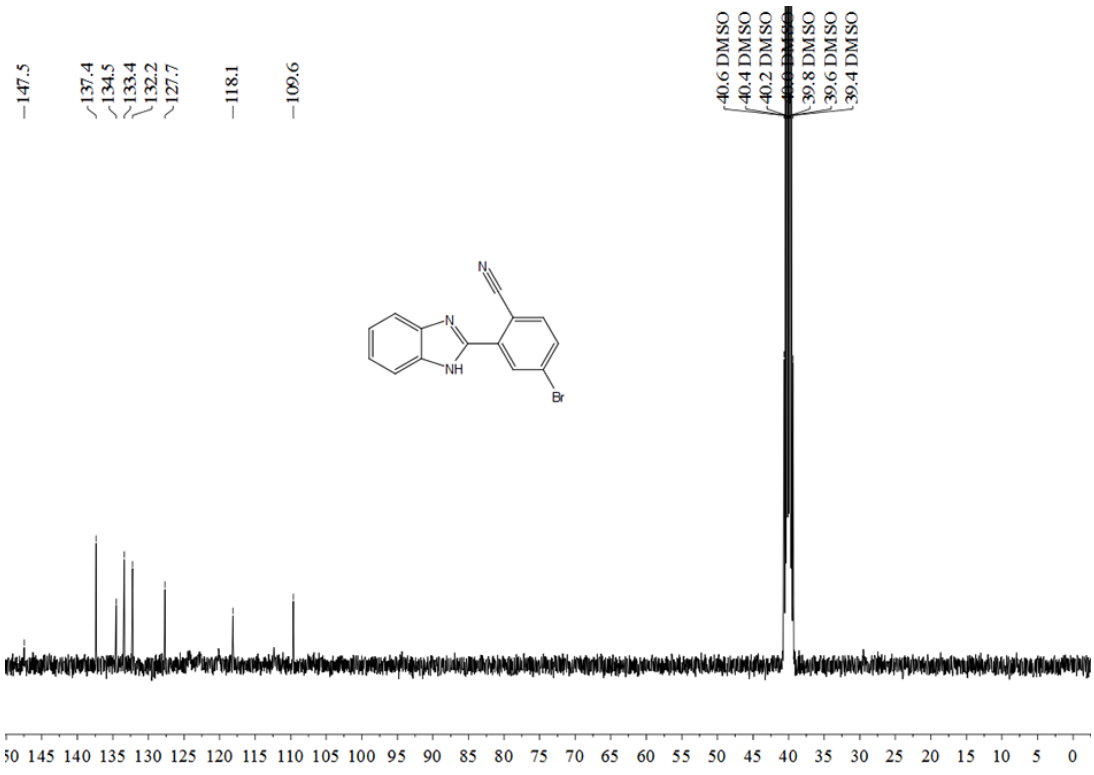


Figure S14. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-bromobenzonitrile (3g).**

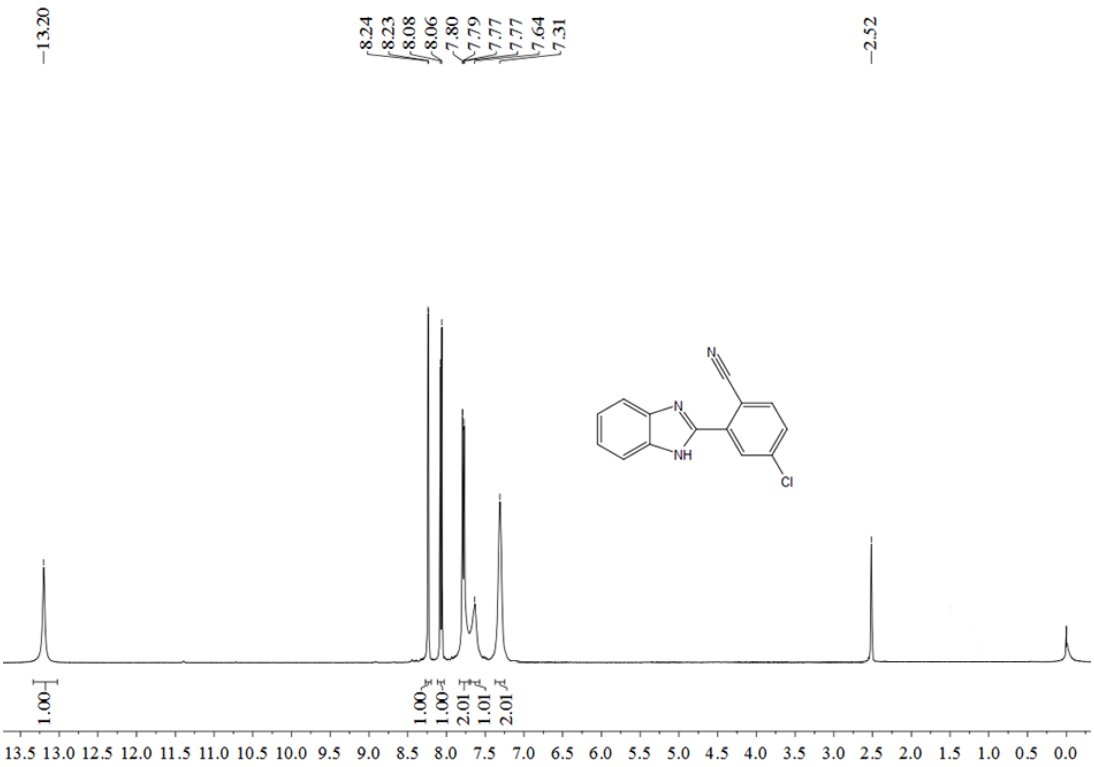


Figure S15. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-chlorobenzonitrile (3h).**

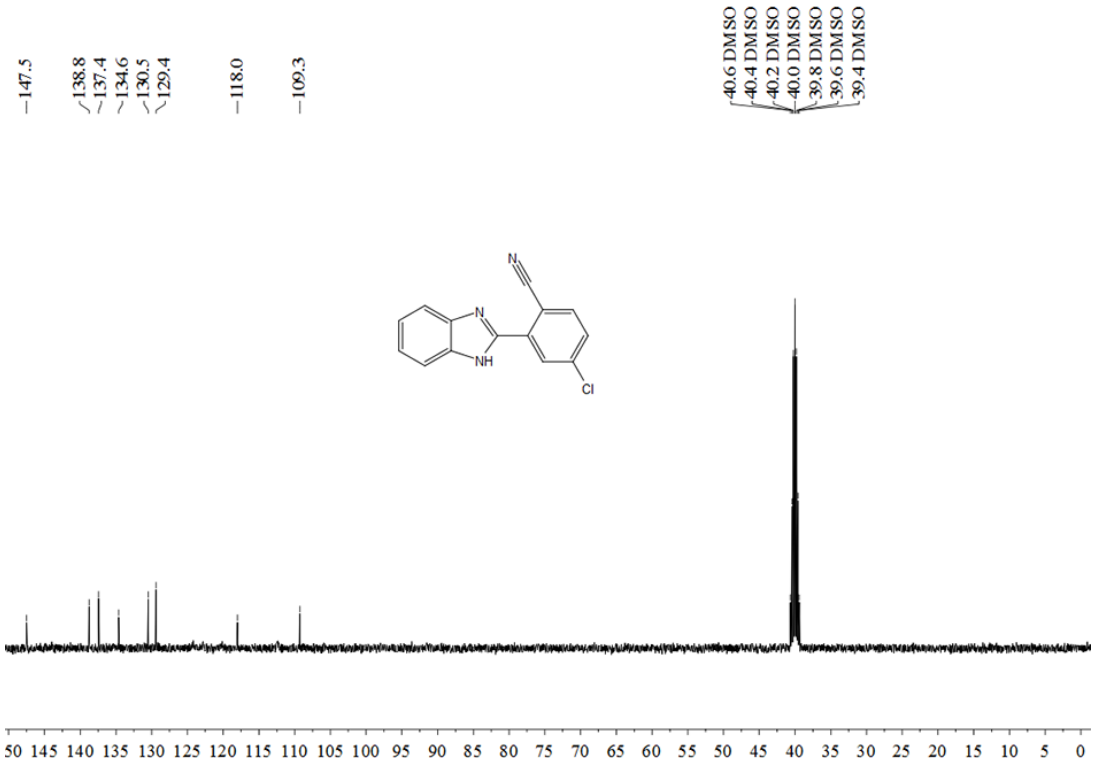


Figure S16. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-chlorobenzonitrile (3h).**

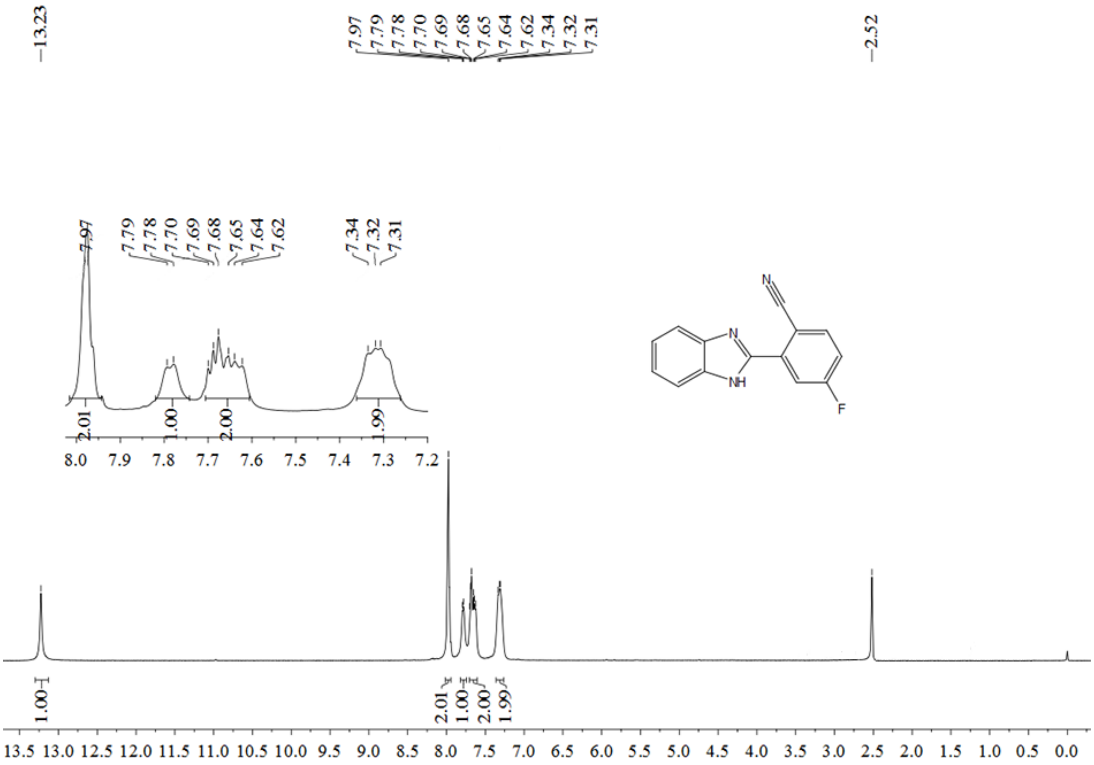


Figure S17. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-fluorobenzonitrile (3i).**

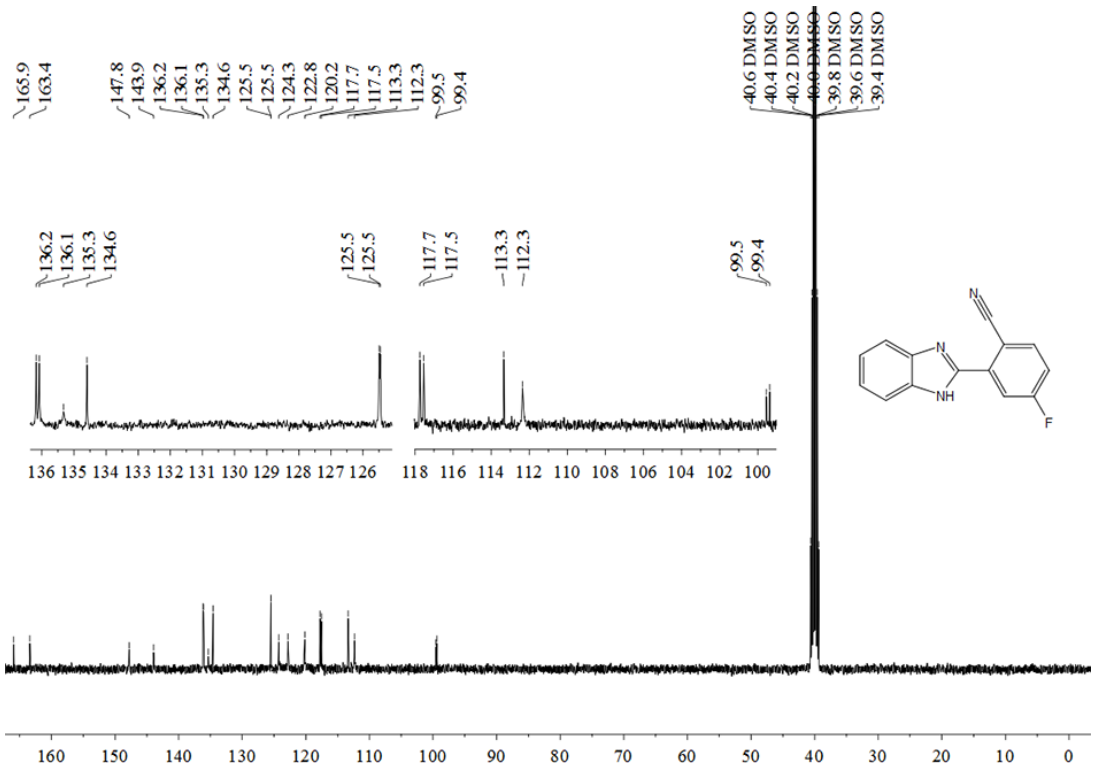


Figure S18. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-fluorobenzonitrile (3i).**

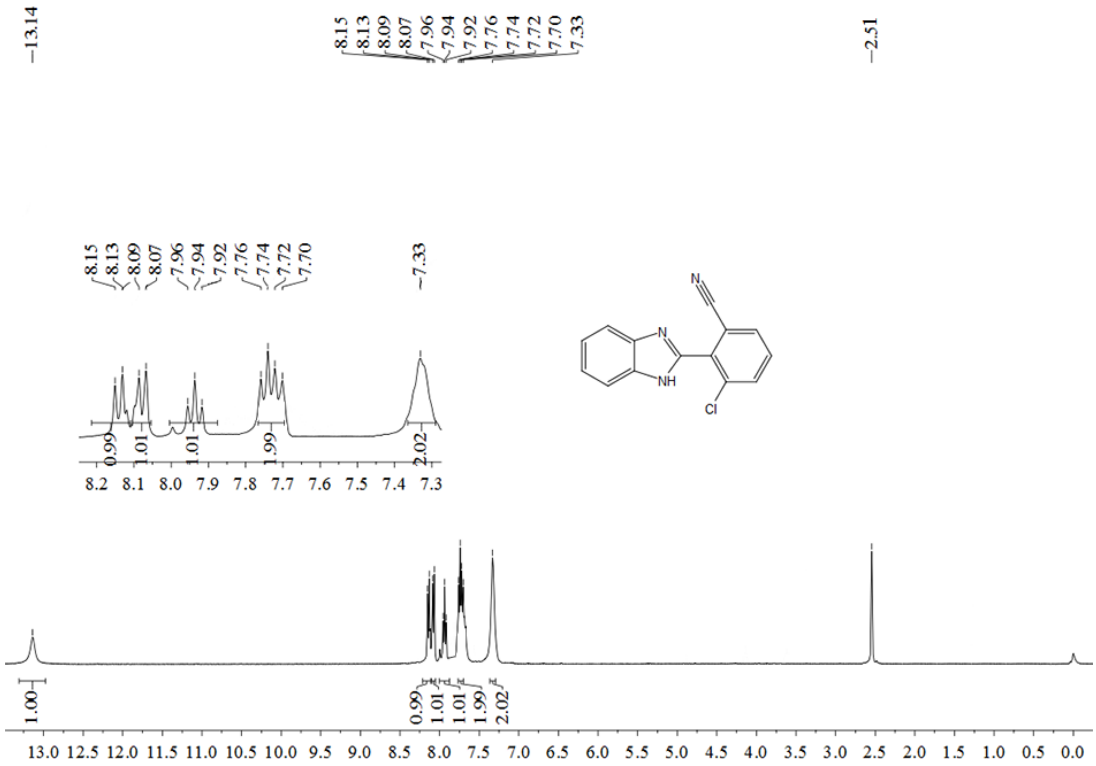


Figure S19. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-3-chlorobenzonitrile (3k).**

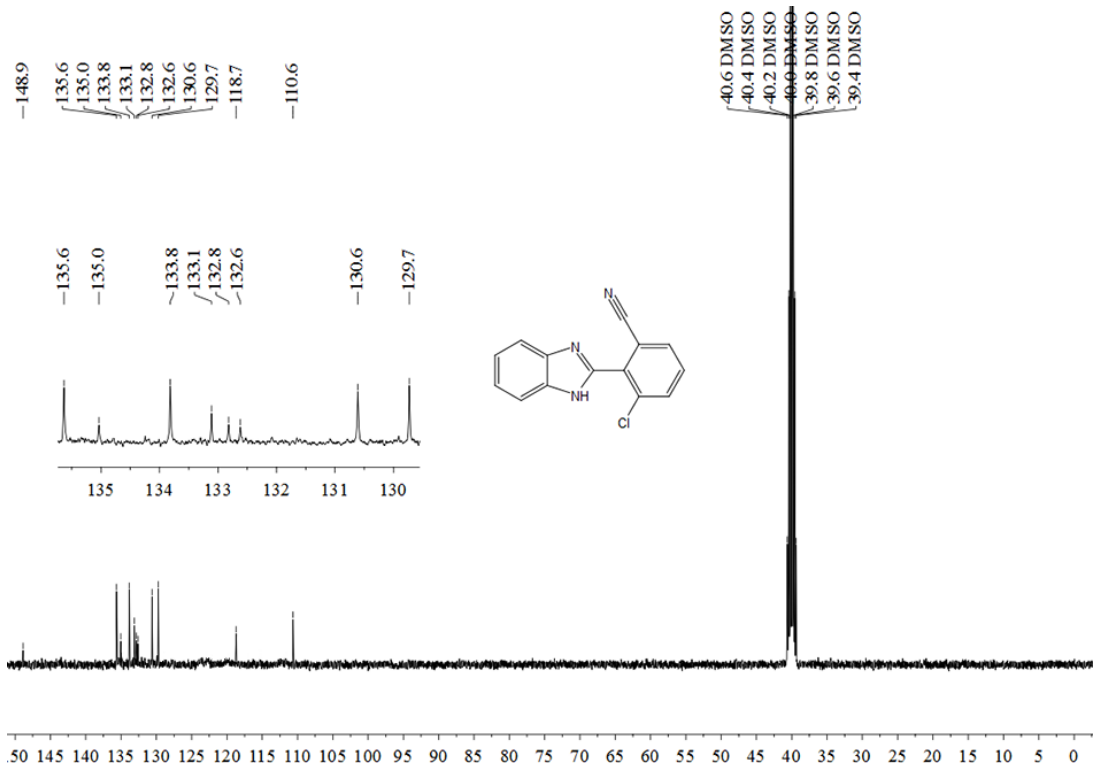


Figure S20. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-3-chlorobenzonitrile (3k).**

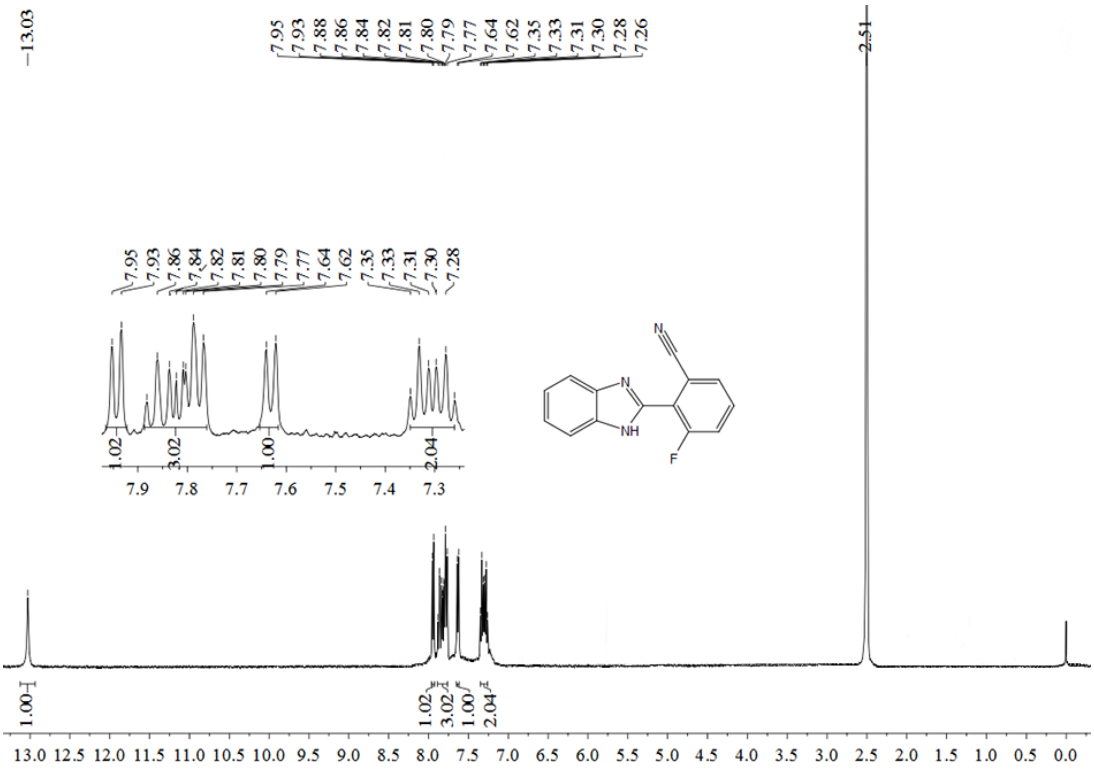


Figure S21. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-3-fluorobenzonitrile (3l).**

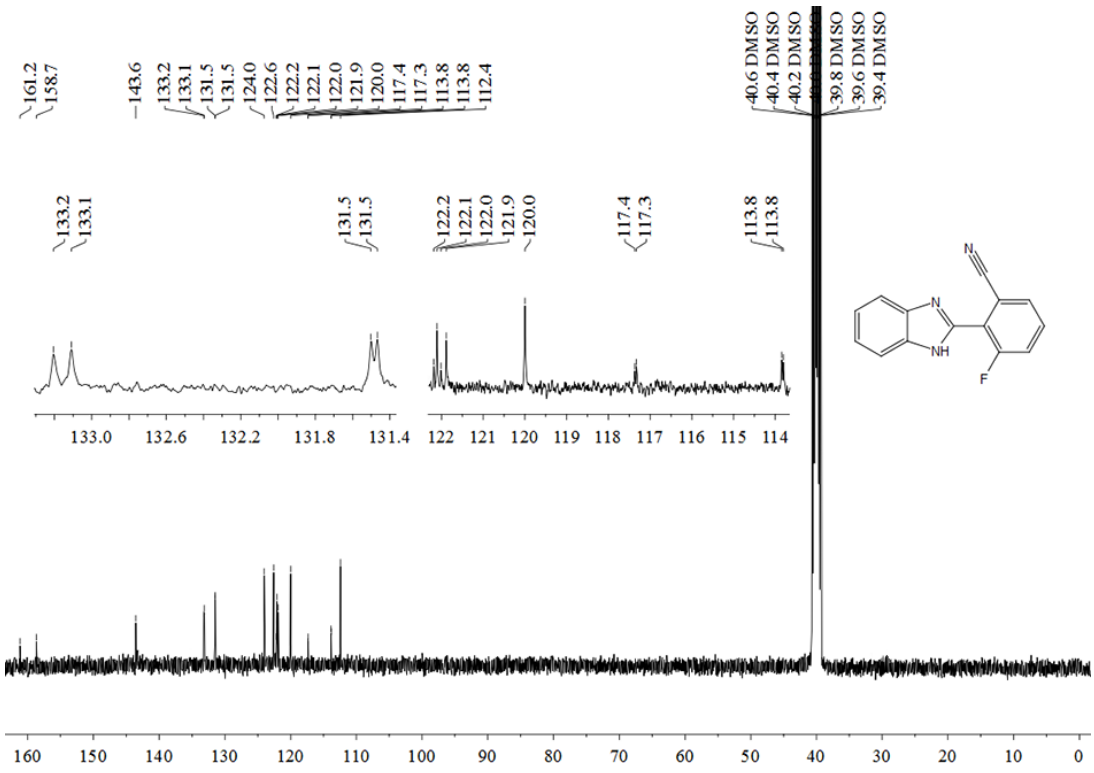


Figure S22. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-3-fluorobenzonitrile (3l).**

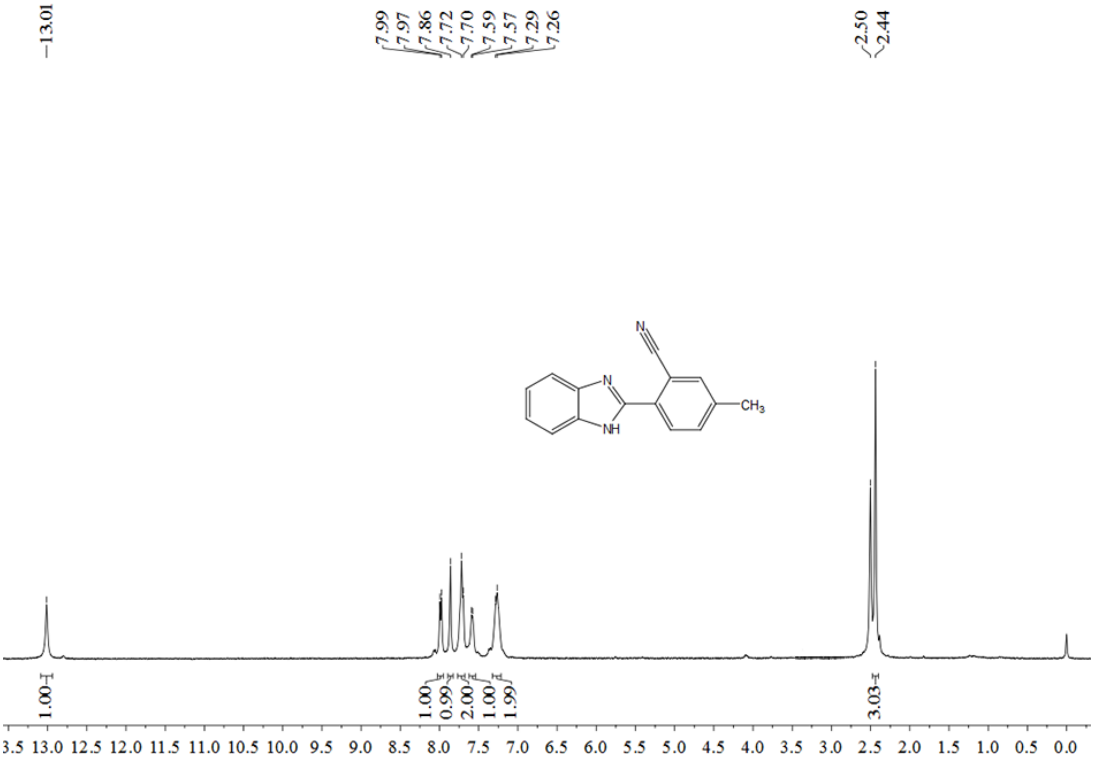


Figure S23. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-methylbenzonitrile (3p).**

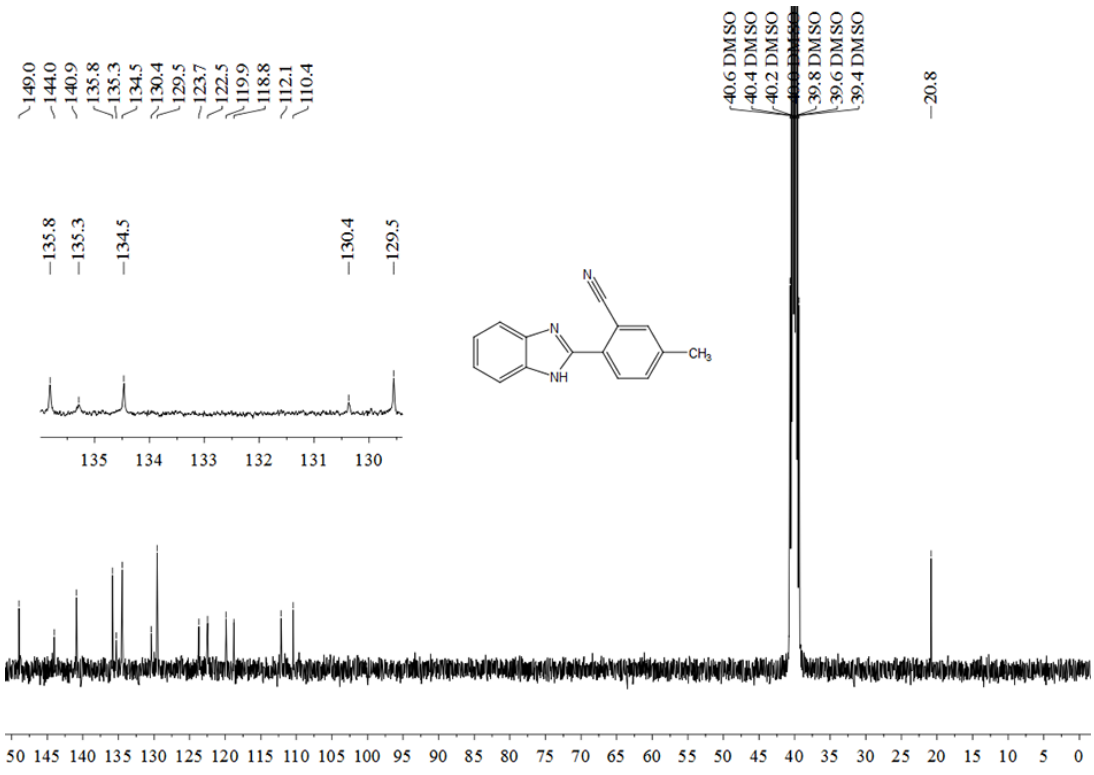


Figure S24. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-methylbenzonitrile (3p).**

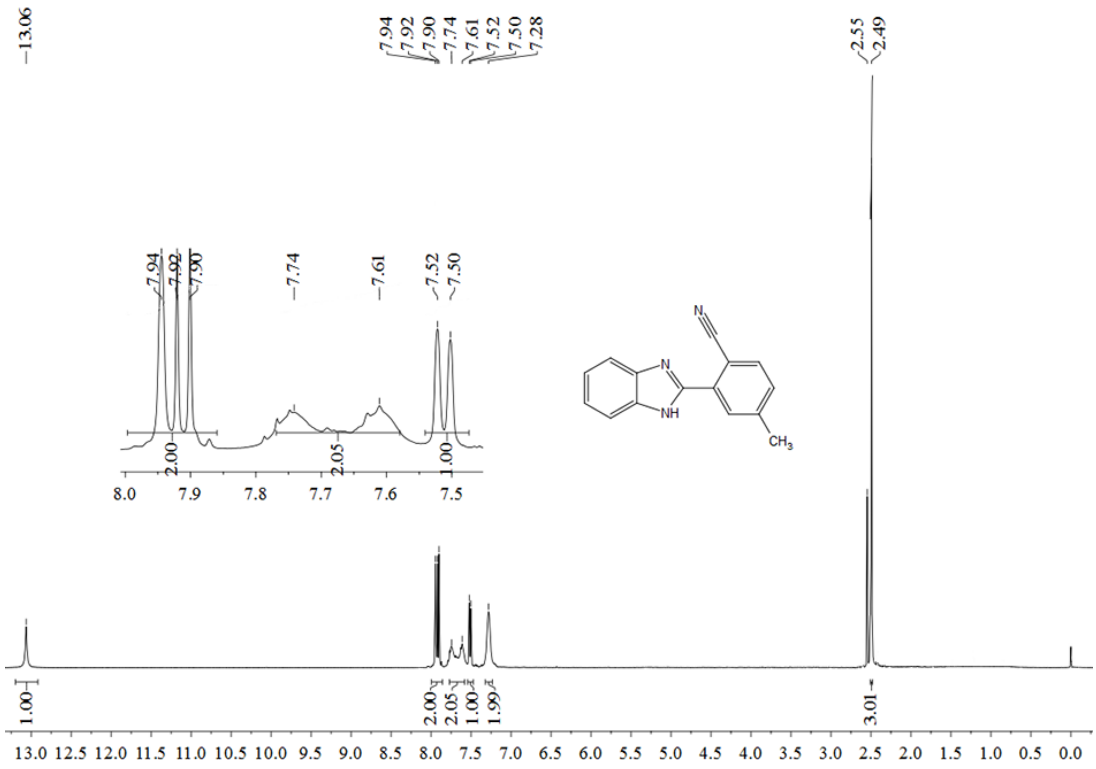


Figure S25. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-methylbenzonitrile (3q).**

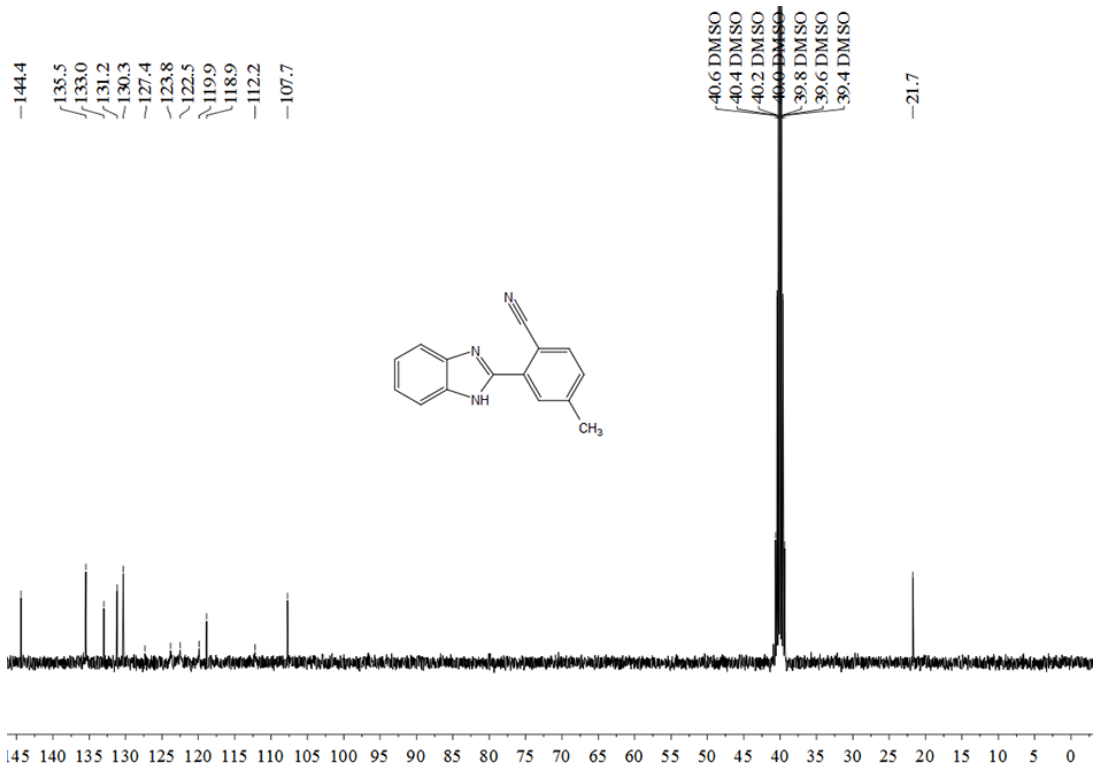


Figure S26. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-4-methylbenzonitrile (3q).**

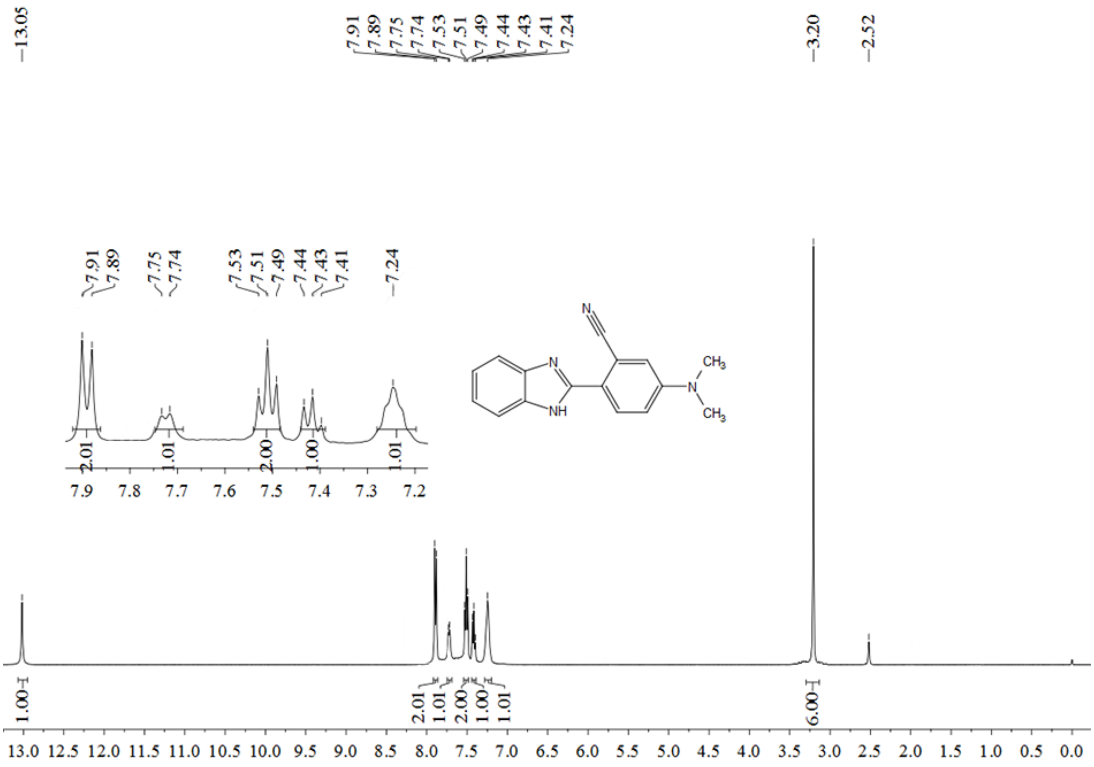


Figure S27. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-(dimethylamino)-**
-benzonitrile (3s).

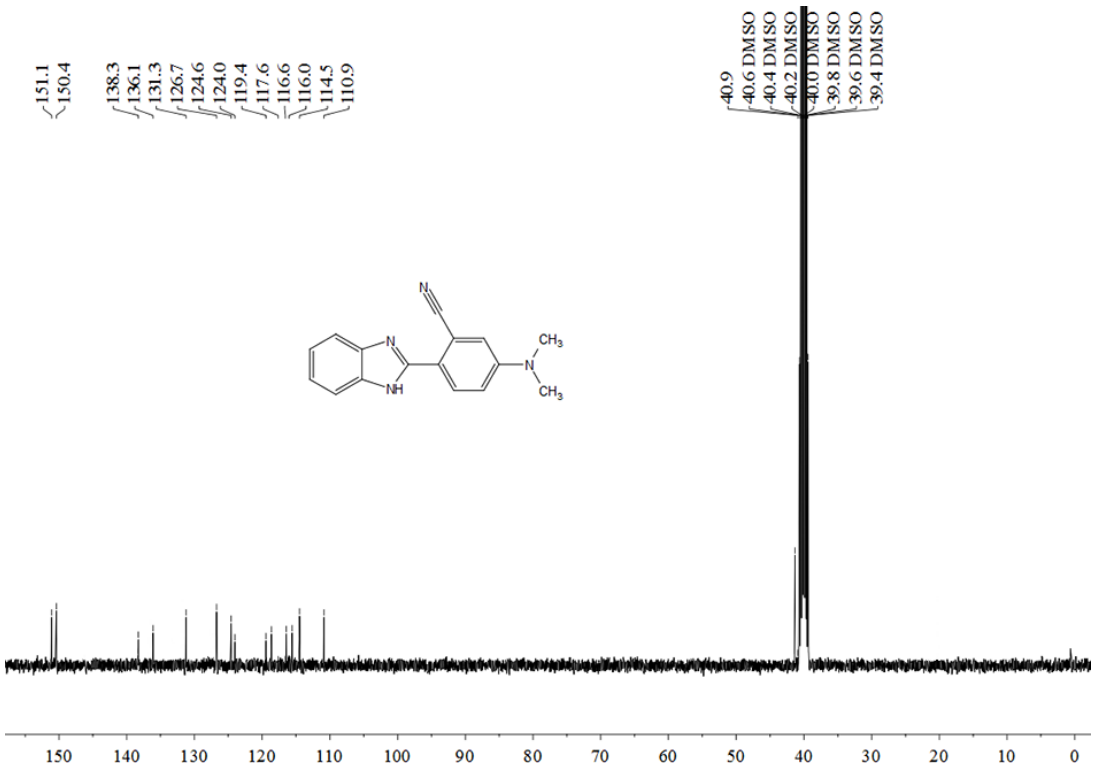


Figure S28. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-(dimethylamino)-**
-benzonitrile (3s).

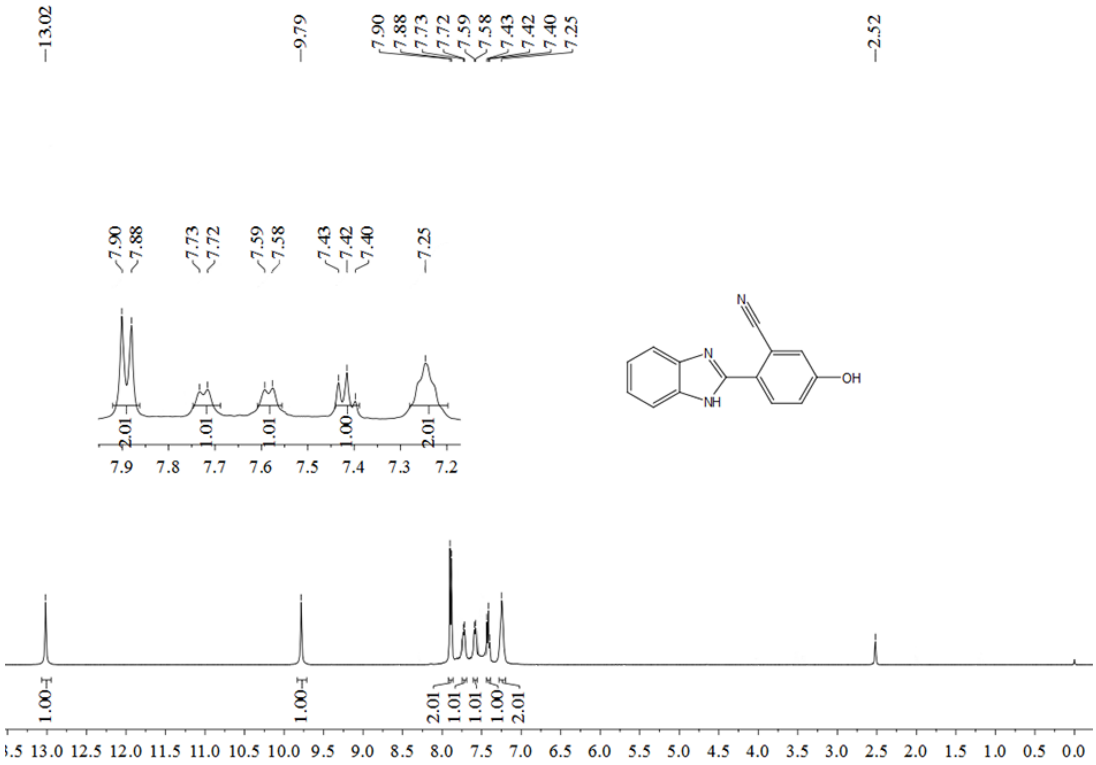


Figure S29. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-hydroxybenzonitrile (3t).**

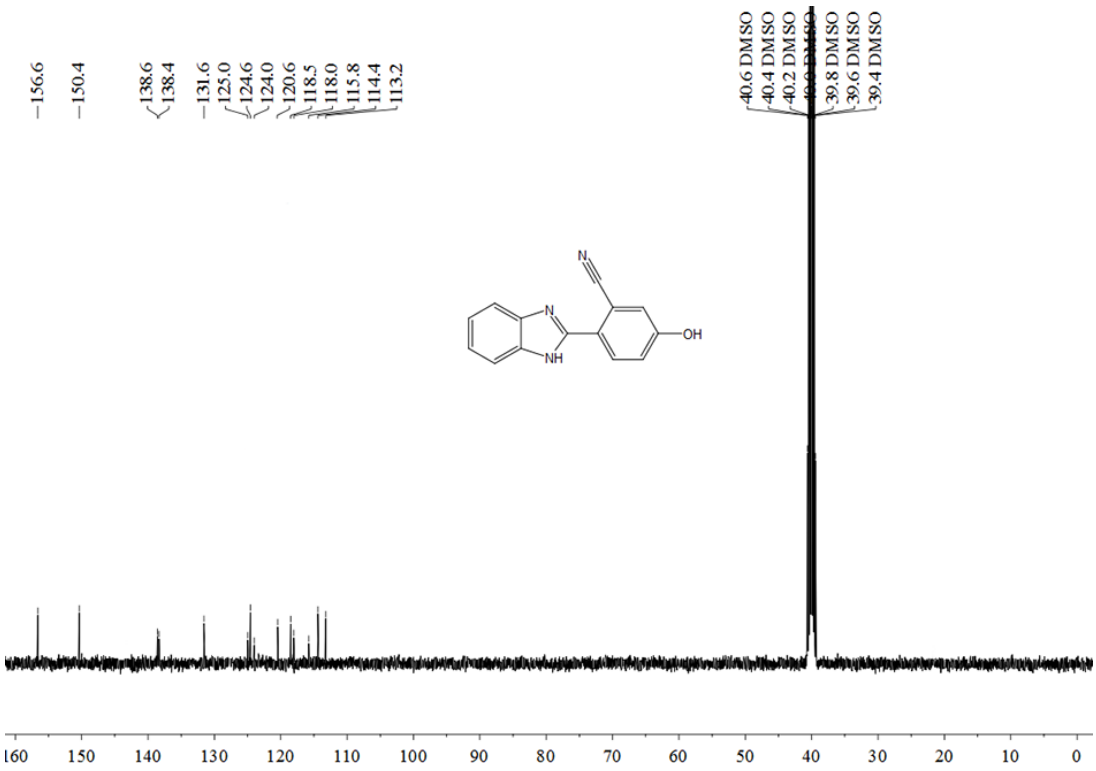


Figure S30. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-hydroxybenzonitrile (3t).**

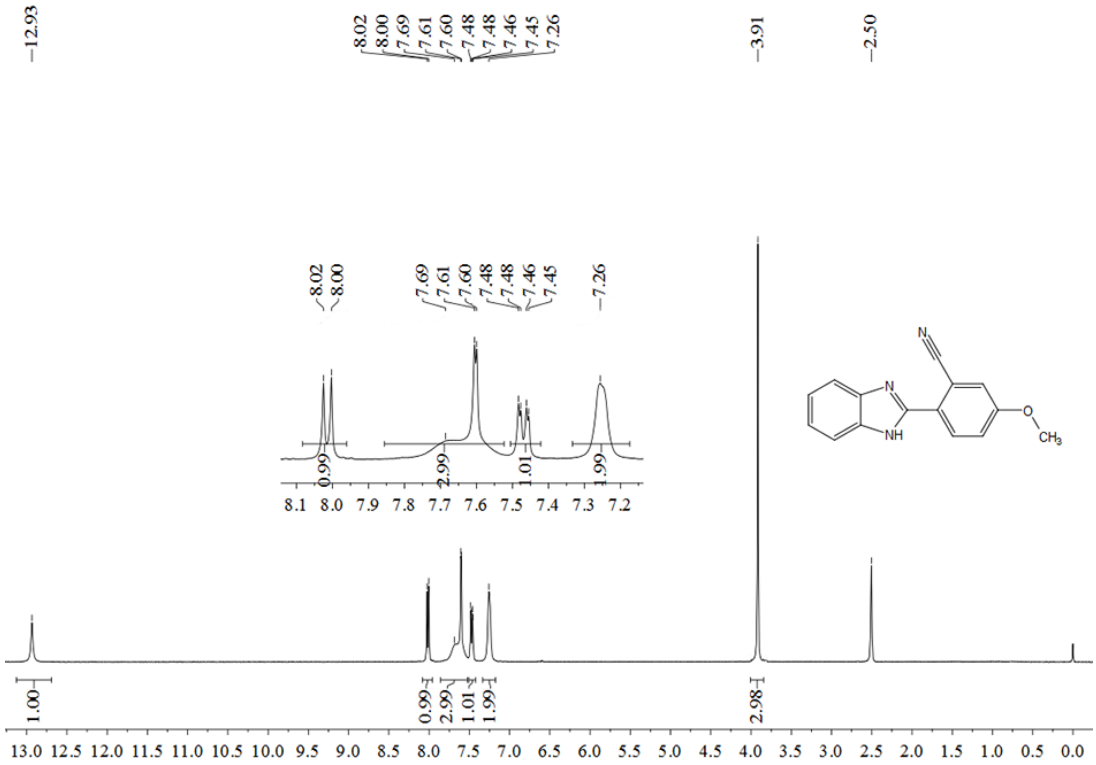


Figure S31. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-methoxybenzonitrile (3u).**

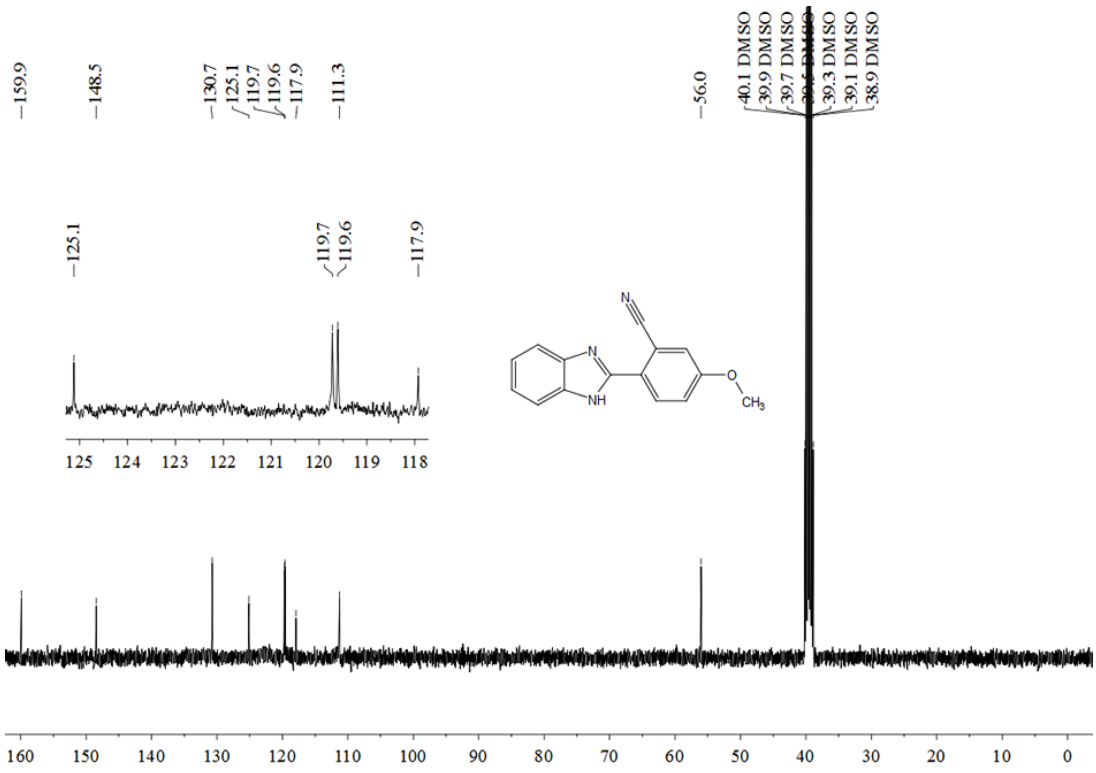


Figure S32. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-methoxybenzonitrile (3u).**

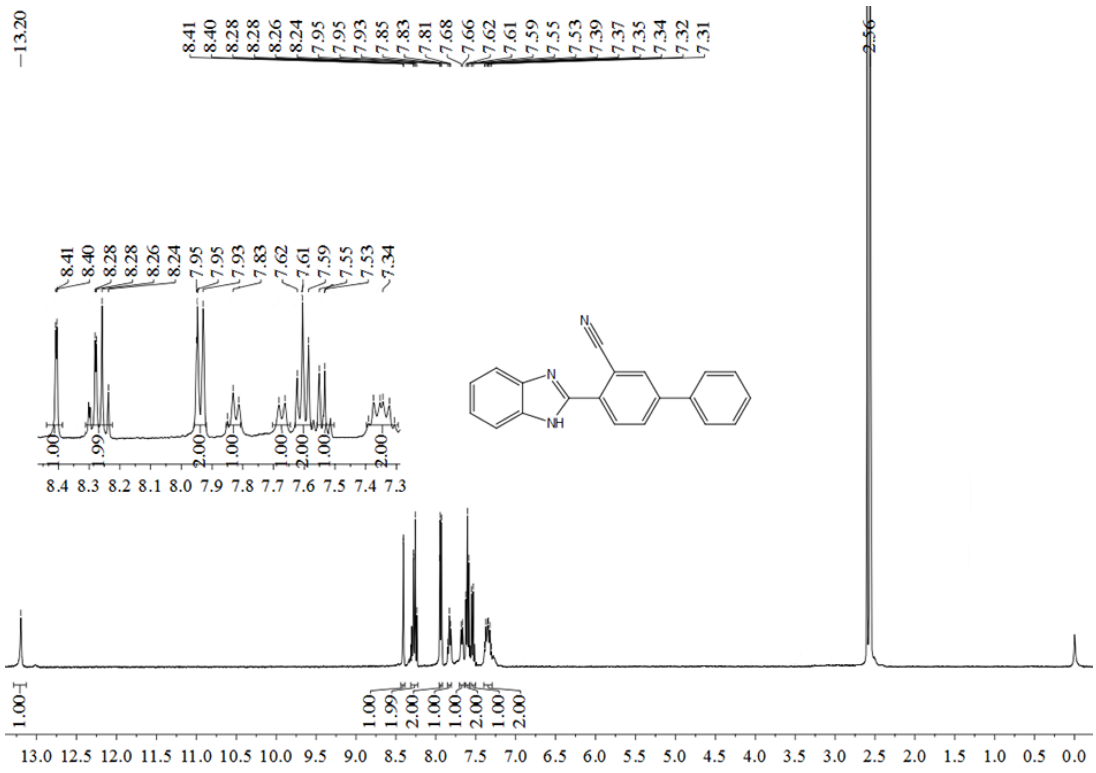


Figure S33. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-phenylbenzonitrile (3v).**

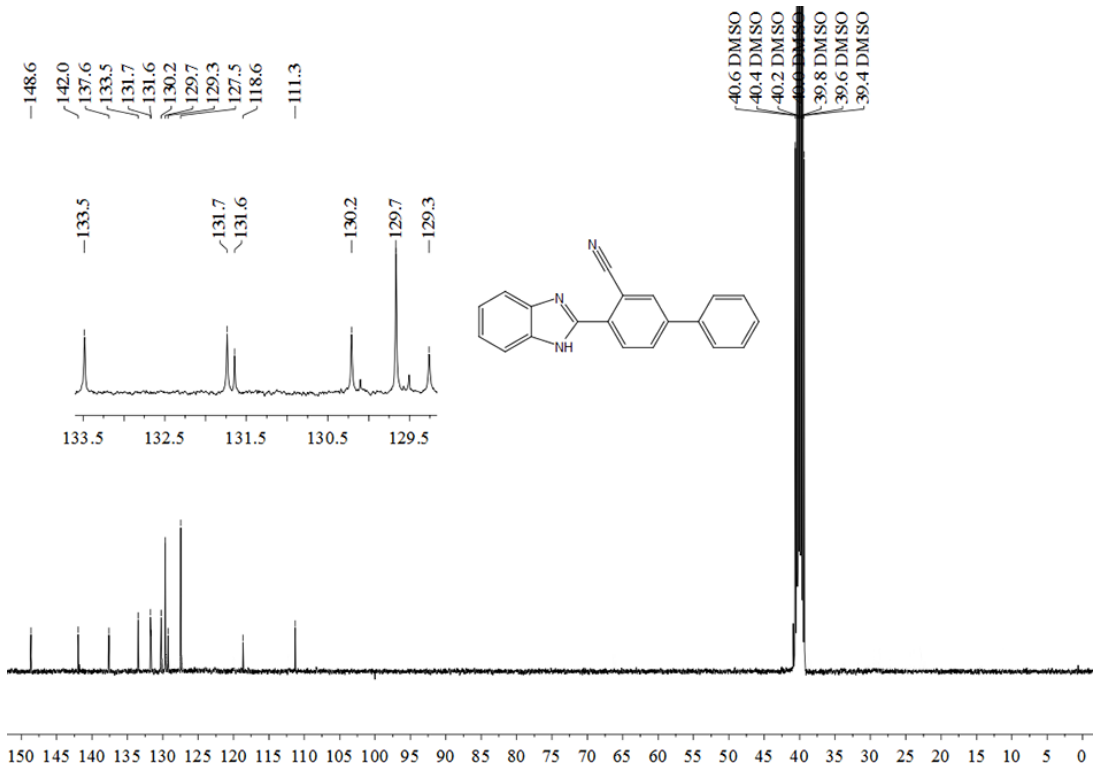


Figure S34. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-phenylbenzonitrile (3v).**

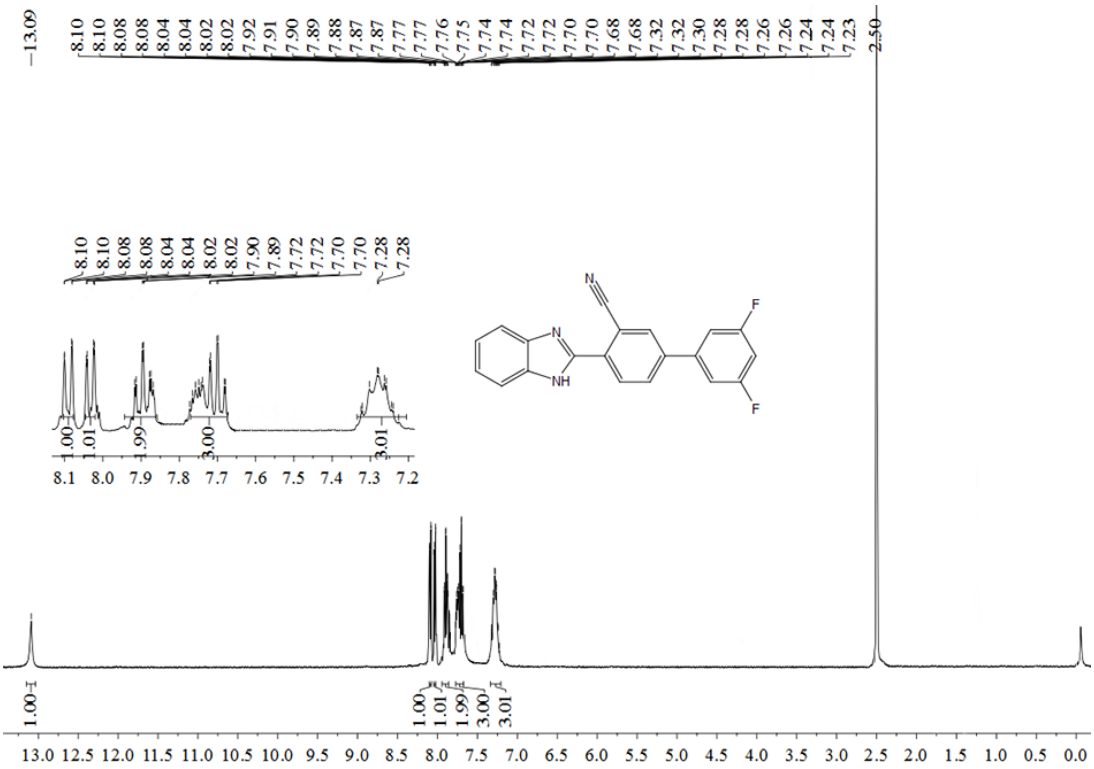


Figure S35. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-(3',5'-difluorophenyl)--benzonitrile (3w).**

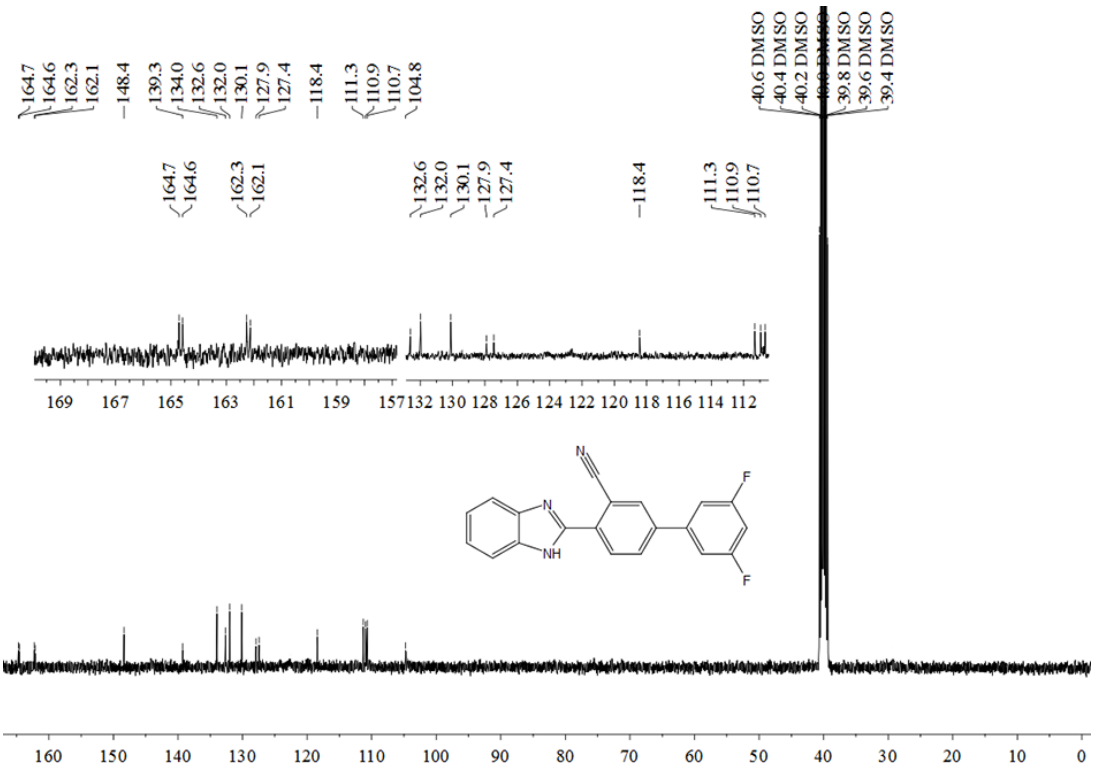


Figure S36. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-5-(3',5'-difluorophenyl)-benzonitrile (3w).**

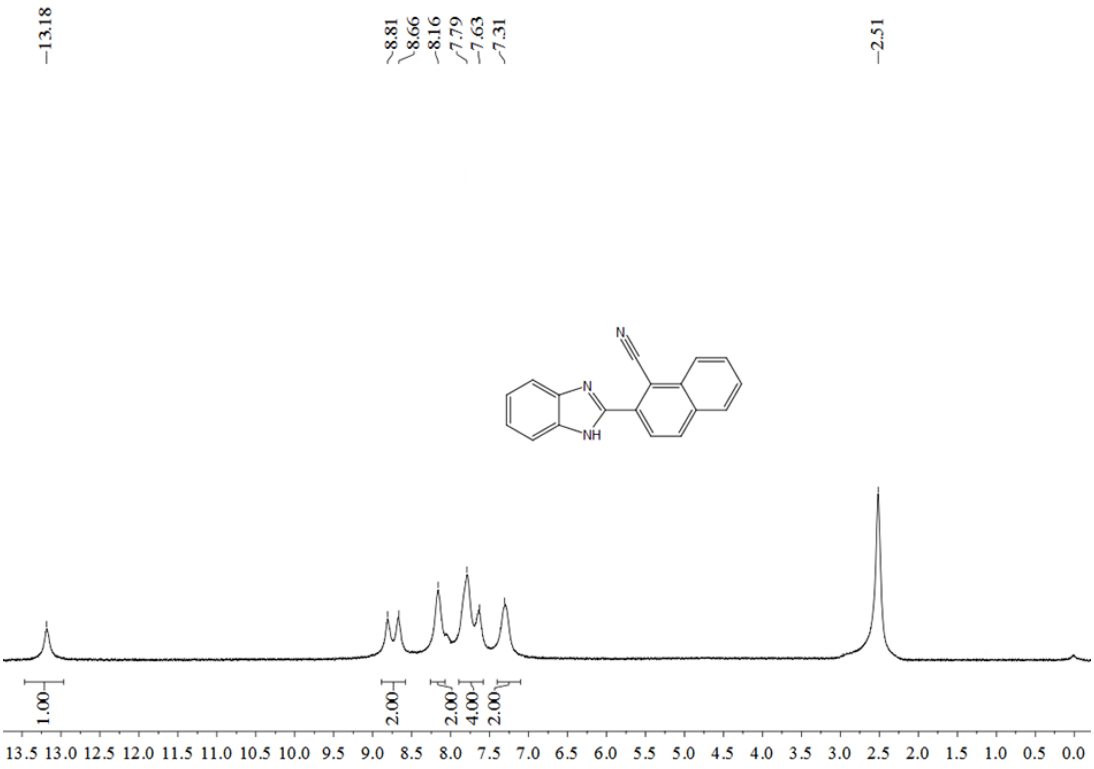


Figure S37. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)-1-naphthonitrile (3x).**

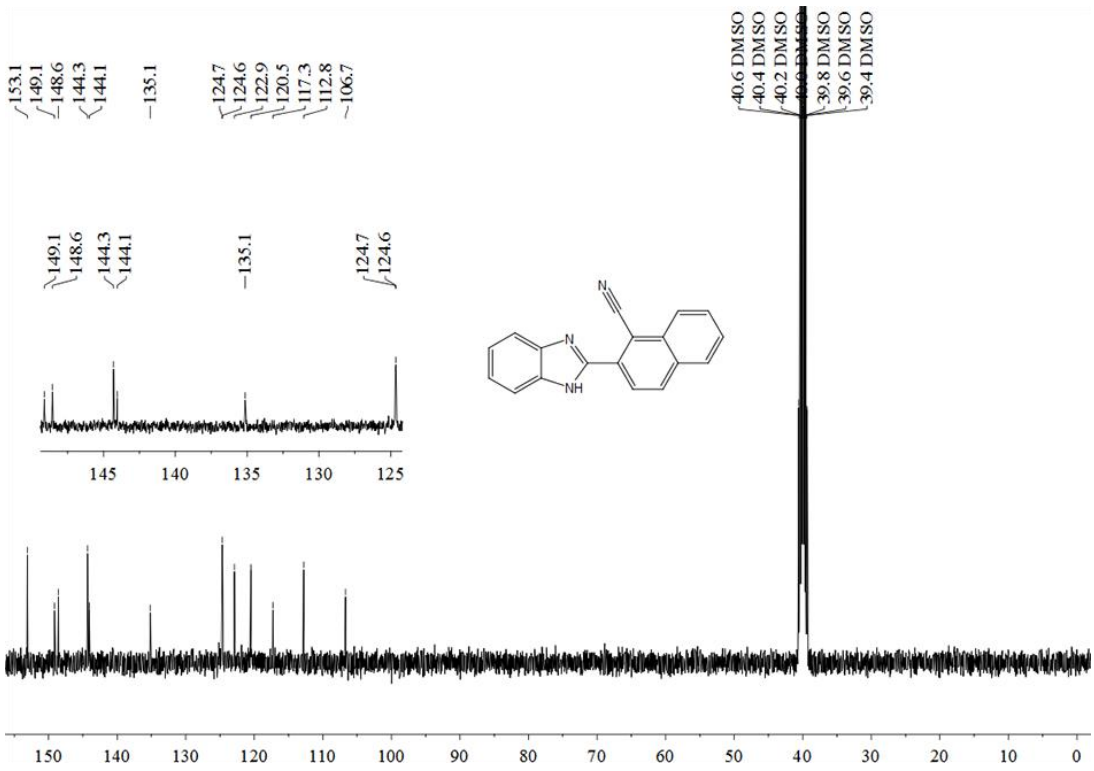


Figure S38. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)-1-naphthonitrile (3x).**

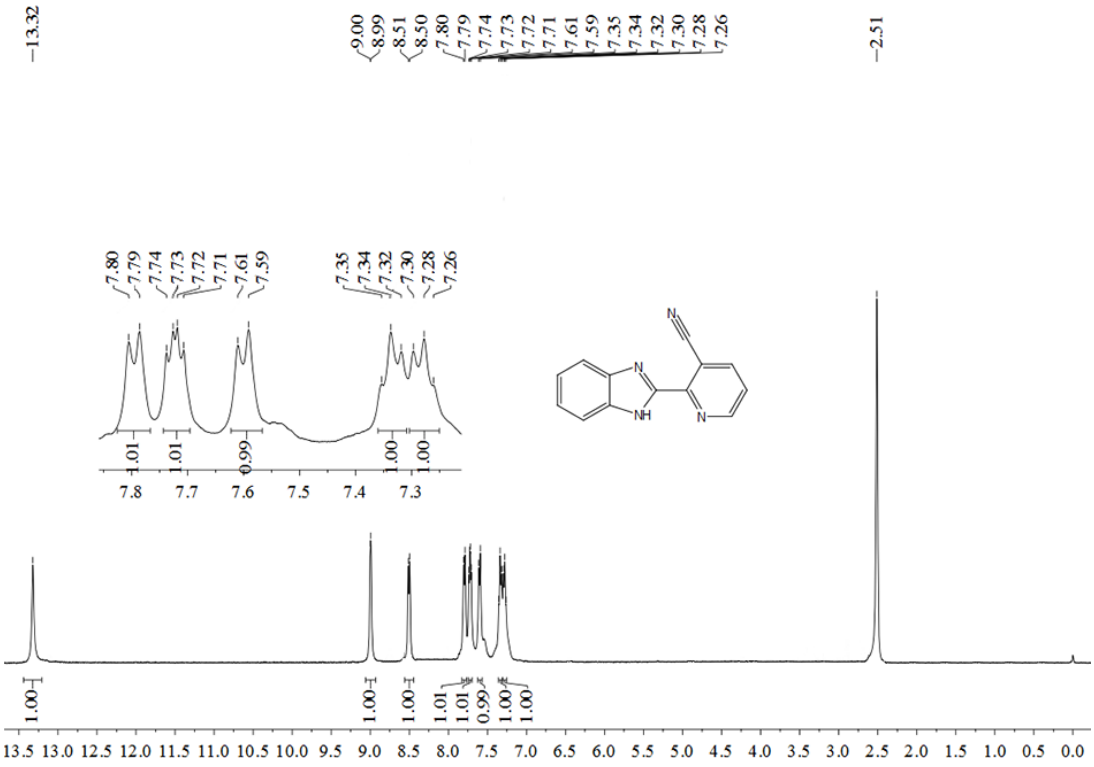


Figure S39. ^{1}H NMR of **2-(1H-benzo[d]imidazol-2-yl)nicotinonitrile (3y).**

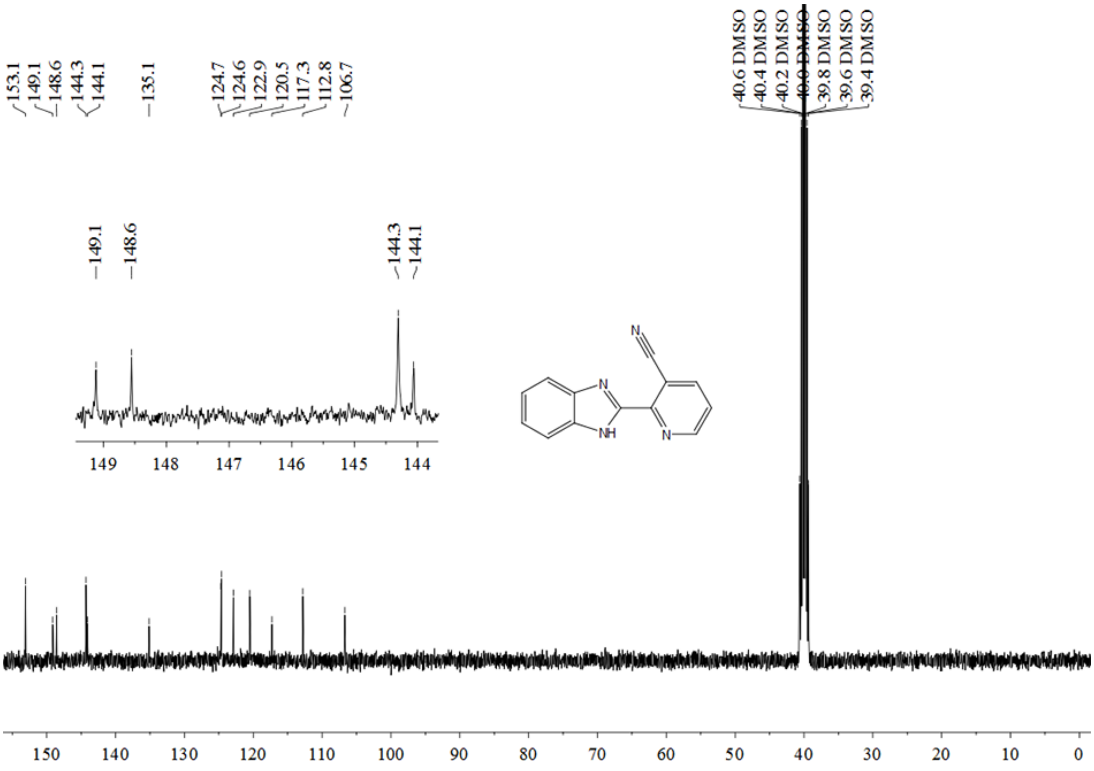
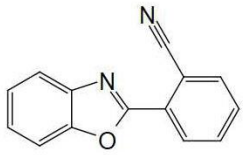


Figure S40. ^{13}C NMR of **2-(1H-benzo[d]imidazol-2-yl)nicotinonitrile (3y).**

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.78 – 7.74 (m, 1H), 7.69 – 7.63 (m, 2H), 7.49 – 7.37 (m, 2H).



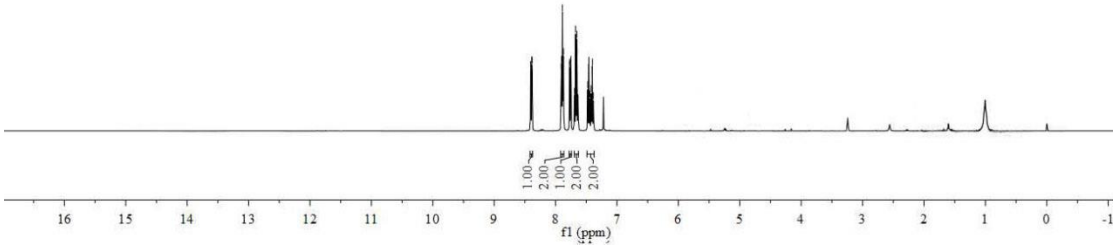
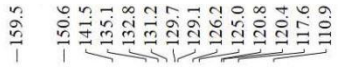
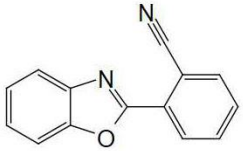


Figure S41. ^{1}H NMR of **2-(benzo[d]oxazol-2-yl)benzonitrile (3z$_3$).**





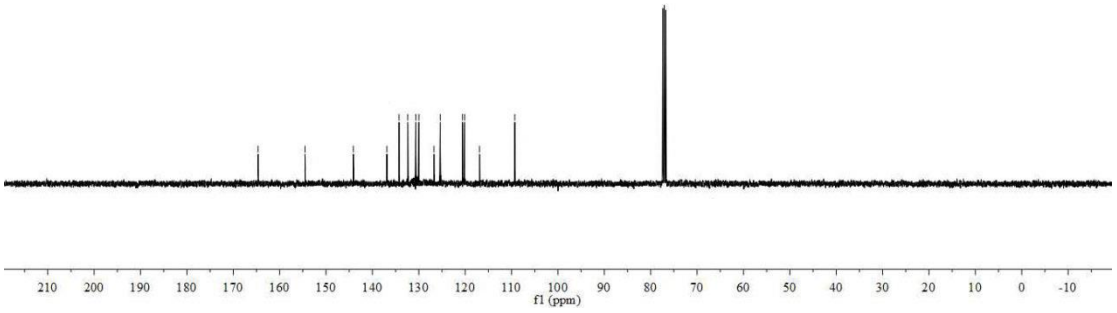


Figure S42. ^{1}H NMR of **2-(benzo[d]oxazol-2-yl)benzonitrile (3z$_3$).**

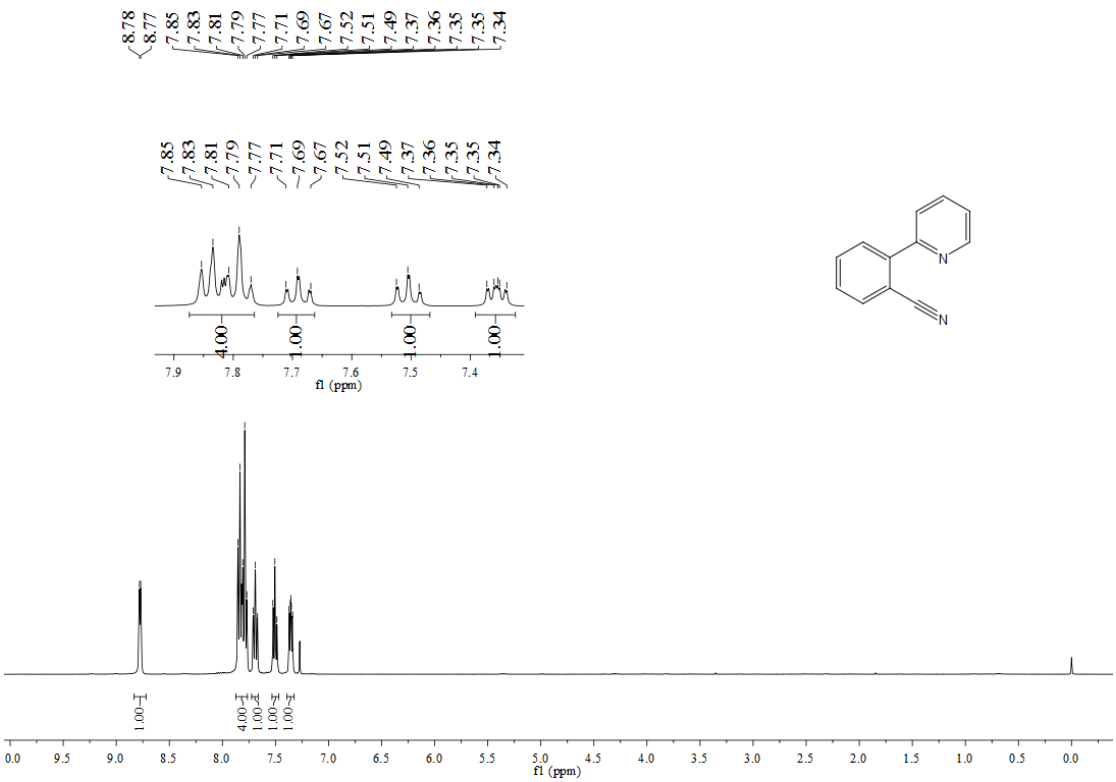


Figure S43. ^{1}H NMR of **2-(pyridin-2-yl)benzonitrile ($3z_5$).**

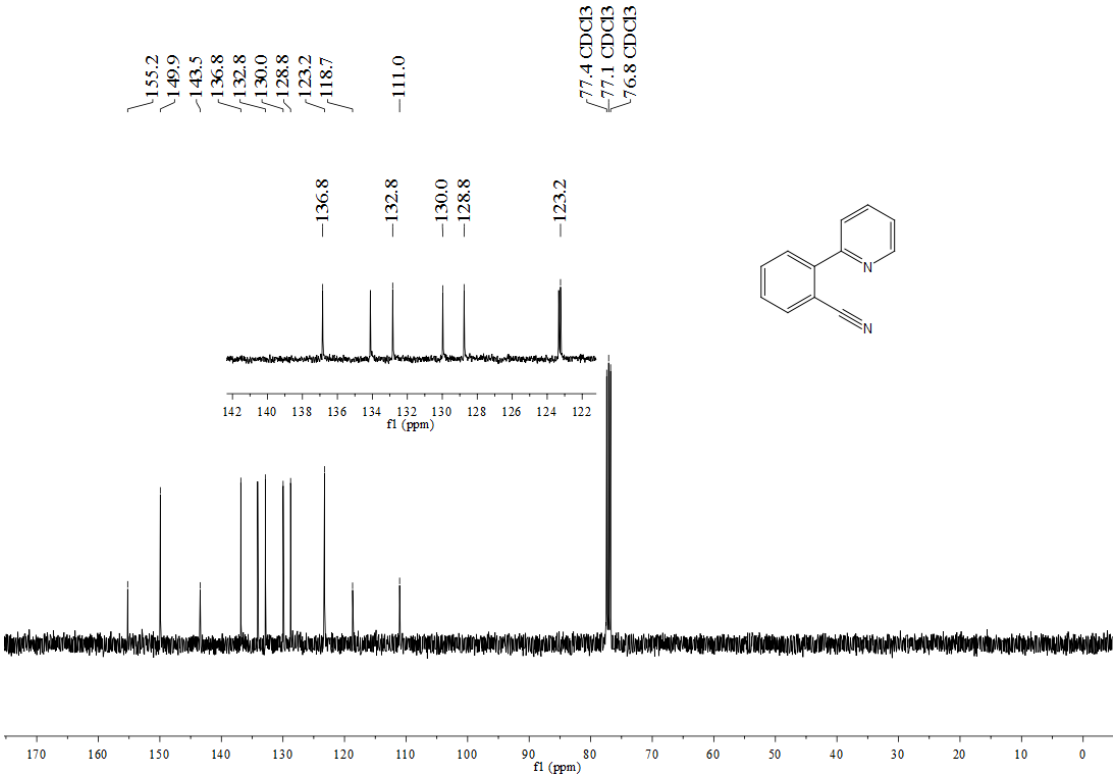


Figure S44. ^{13}C NMR of **2-(pyridin-2-yl)benzonitrile ($3z_5$).**

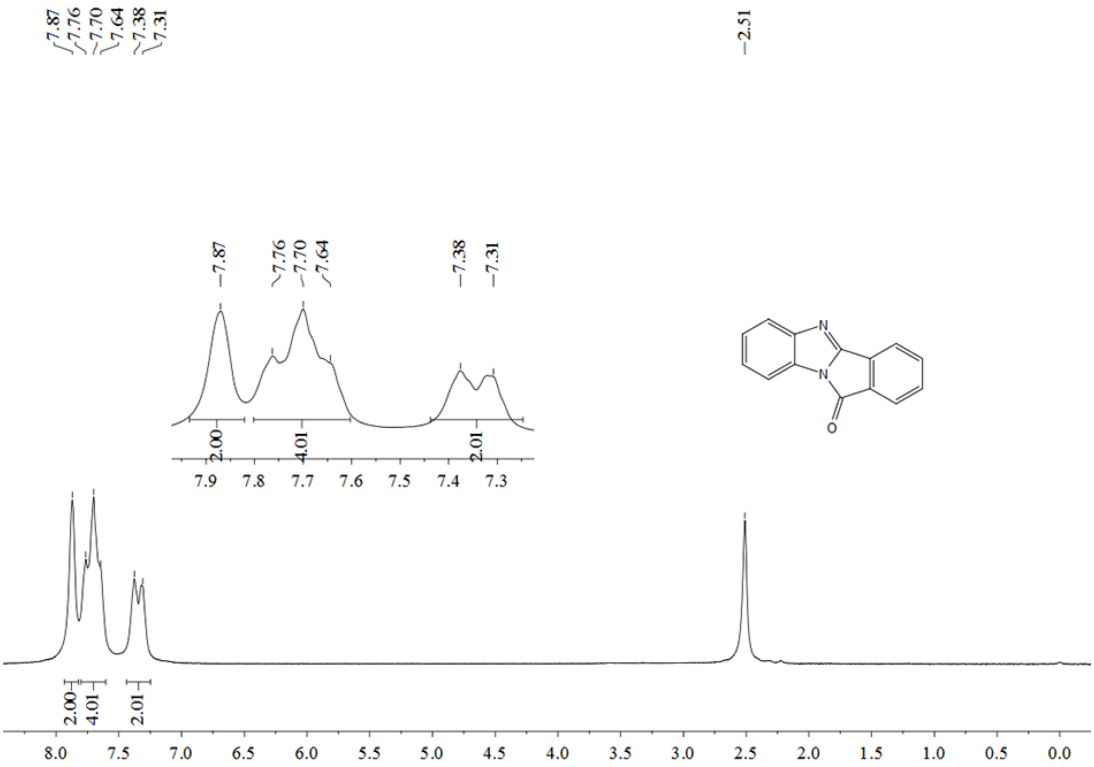


Figure S45. ^{1}H NMR of **11H-benzo[4,5]imidazo[2,1-a]isoindol-11-one (5a).**