Supporting Information

Visible-light-induced condensation cyclization to synthesize benzimidazoles using fluorescein as photocatalyst

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General Information

All starting materials and the reagents were purchased from TCI and J&K Chemical Company, and the reagents were used without further purification unless specified. The reactions were monitored by thin layer chromatography (TLC), and the products were purified by column chromatography on silica gel (300 ~ 400 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker Ultrashield™ 400 spectrometer operating at 400 MHz and 100 MHz in DMSO or $CDCl_3$. ^{1}H NMR and ^{13}C NMR were reported in ppm with tetramethylsilane (TMS) as internal standard. ^{19}F NMR was reported in ppm with trifluoroacetic acid (TFA) 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) were reported in Hertz (Hz). Room temperature fluorescence spectra (PL) of the synthesized compounds were taken using a Shimadzu RF-5301PC fluorescence spectrophotometer. Cyclic voltammetric (CV) measurements were carried out on the Chi 1200A system in a conventional three-electrode cell with a glass carbon working electrode, a platinum-wire counter electrode and a Ag/AgCl reference electrode with

ferrocene as the internal standard referenced in anhydrous chloromethane solution of $C_{16}H_{36}ClNO_4$ (0.10 M) at a sweeping rate of 100 mV s^{-1} at room temperature.

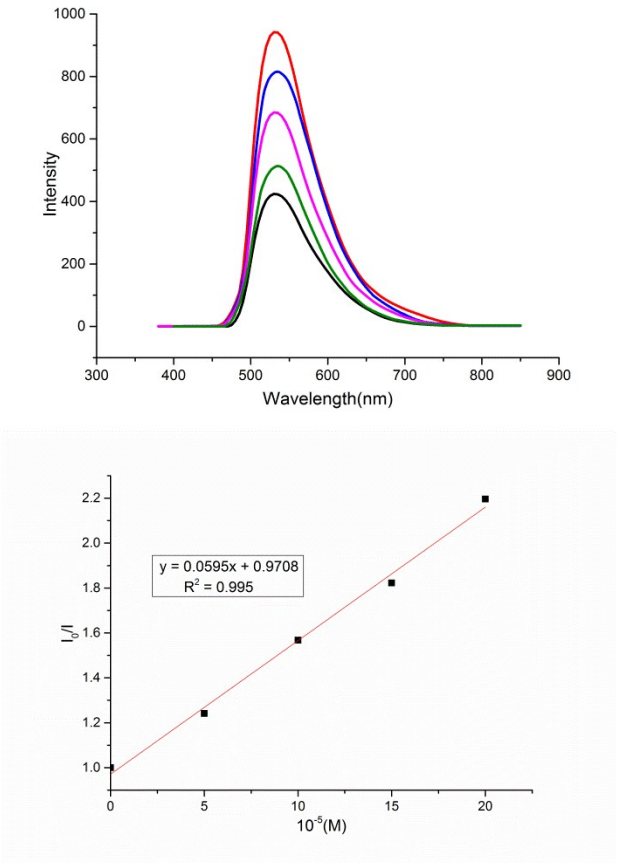


Figure S1 Stern-Volmer fluorescence quenching experiments

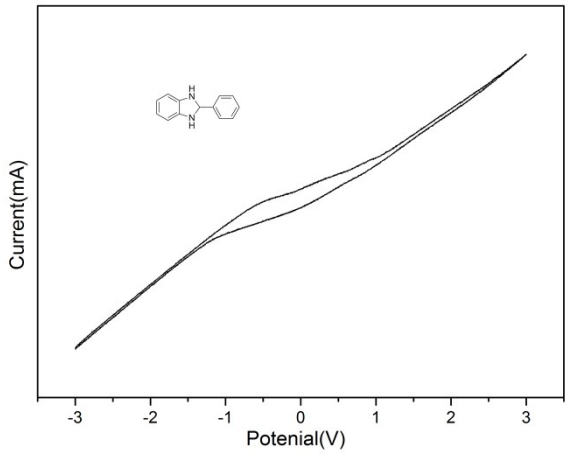


Figure S2 Cyclic voltammetry (CV) curves of intermediate **B**

Optimum catalytic system comparison

In order to further evaluate the efficiency of the catalyst system, we chose

benzaldehyde and *o*-phenylenediamine as representative substrates. The comparison results between the catalyst system and the earlier reported systems are summarized in Table S1. Although their photocatalysts are reusable and the catalytic system is highly efficient, their time requirements are relatively long. And our system has high catalytic performance to obtain the target product under relatively mild conditions without metal presence in a short reaction time. Therefore, the use of fluorescein as a photocatalyst to obtain benzimidazole is more practical and efficient than the previous method.

Table S1 Comparisons of optimal protocol with earlier reports

Entry	Photocatalyst	Time (h)	Reference
1	Ag-TiO_2	8	1
2	Pt-TiO_2	4	2
3	fluorescein	2	This Work

^{1}H NMR spectra and analysis of products

Figure S3 ^{1}H NMR spectrum of 2-phenyl-1*H*-benzo[*d*]imidazole[3] (3a)

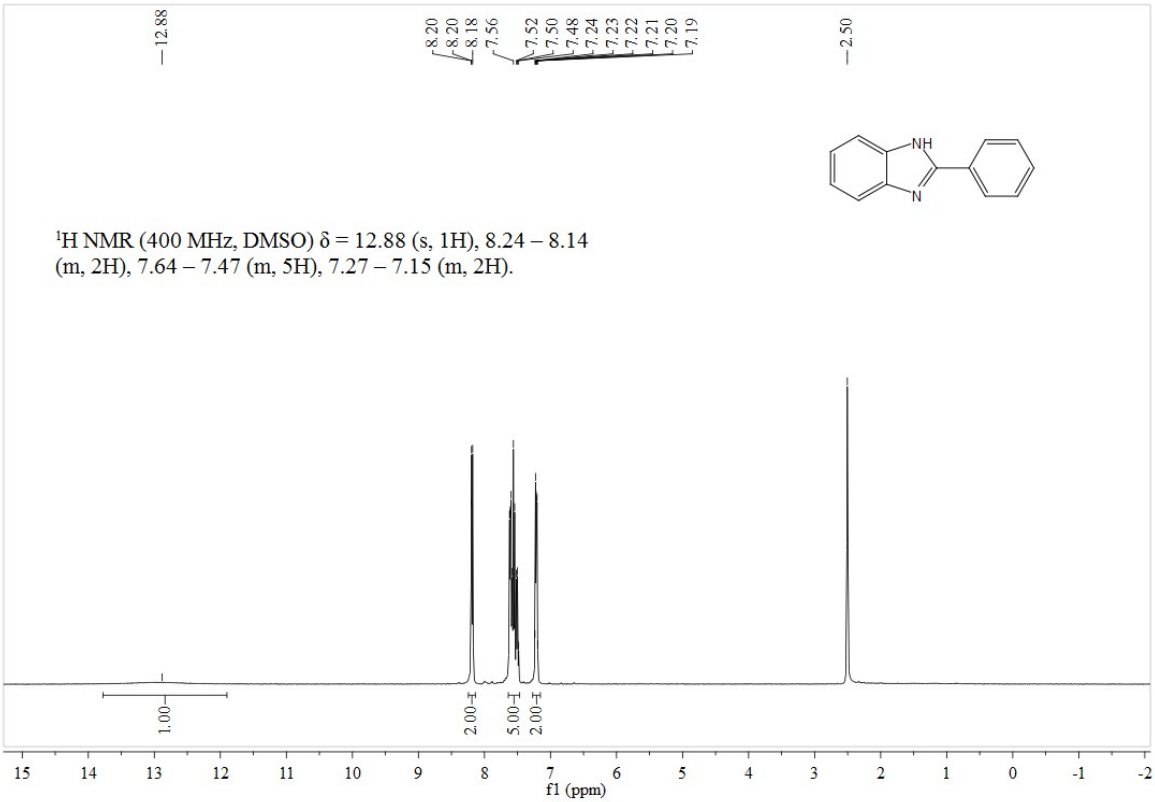


Figure S4 ^{1}H NMR spectrum of 2-(2-bromophenyl)-1*H*-benzo[*d*]imidazole[4] (3b)

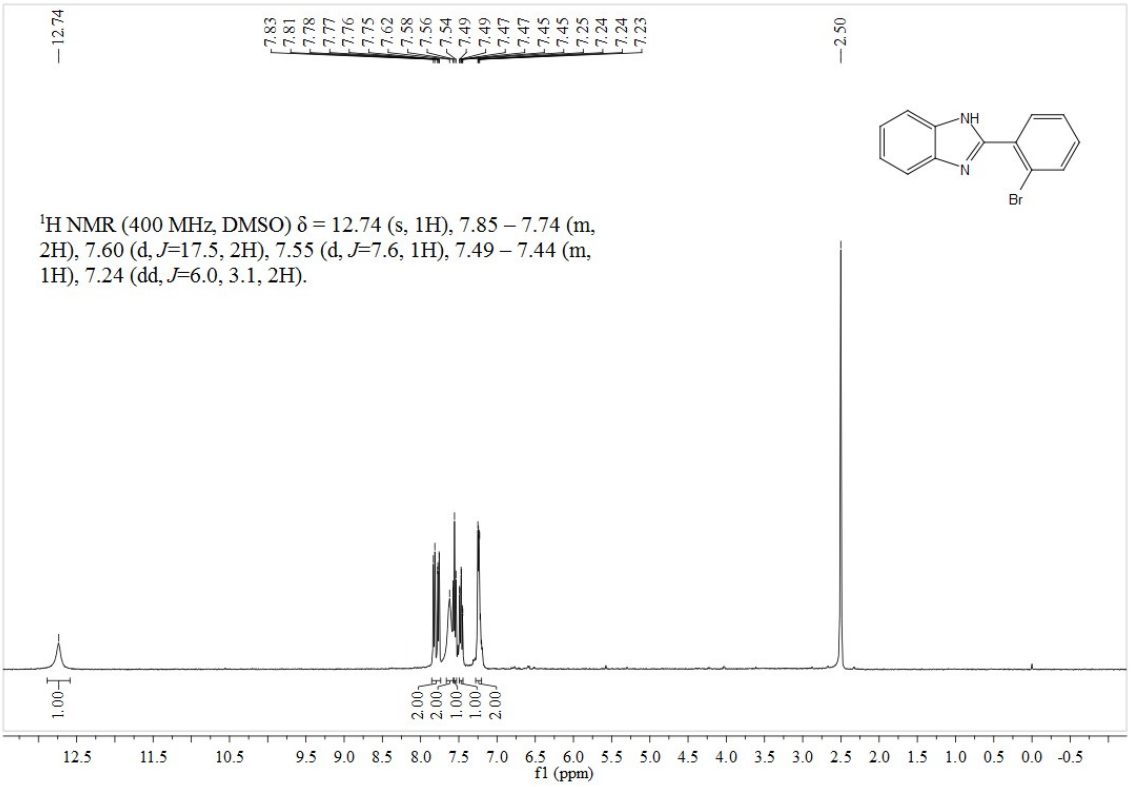


Figure S5 ^{1}H NMR spectrum of 2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole[3] (3c)

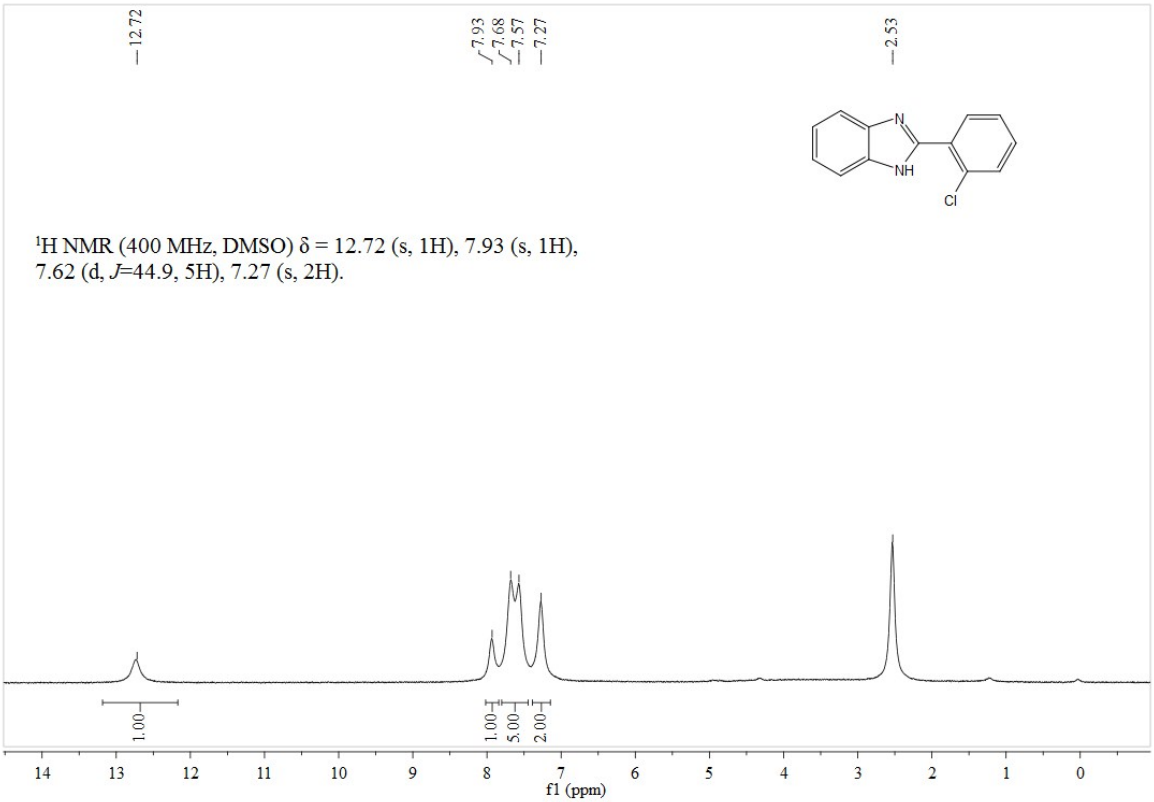


Figure S6 ^{1}H NMR spectrum of 2-(2-fluorophenyl)-1*H*-benzo[*d*]imidazole[5] (3d)

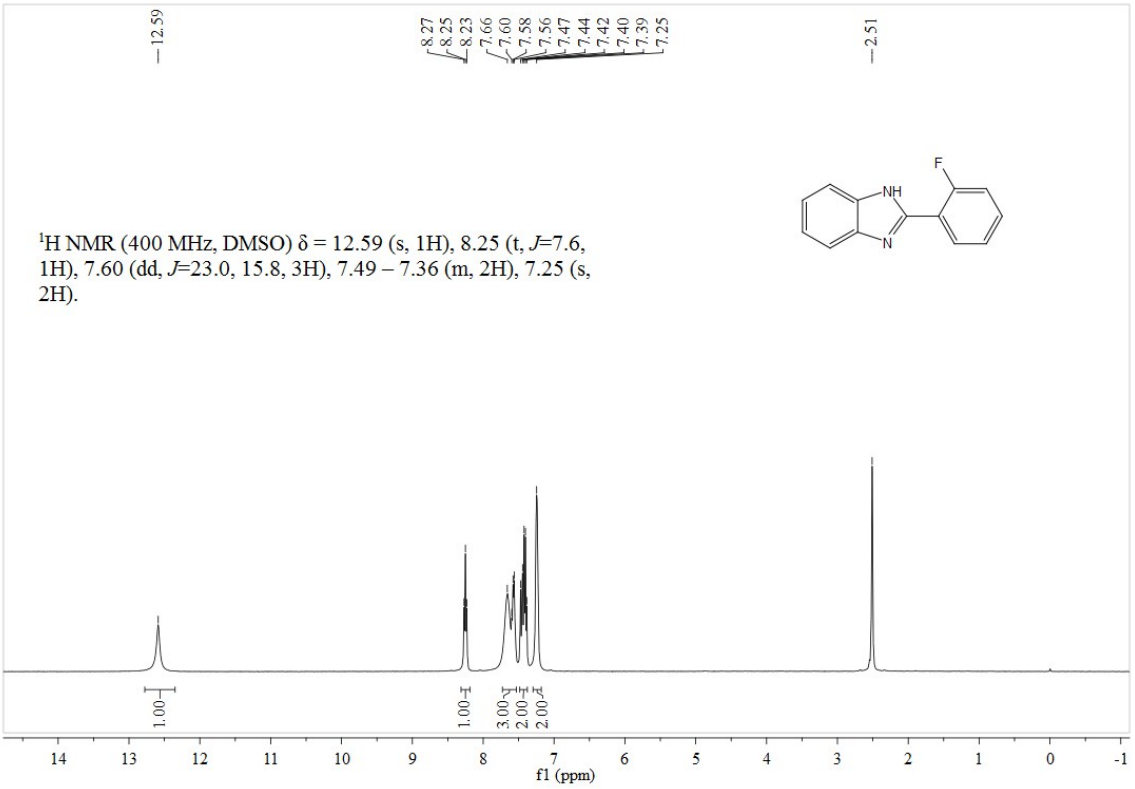
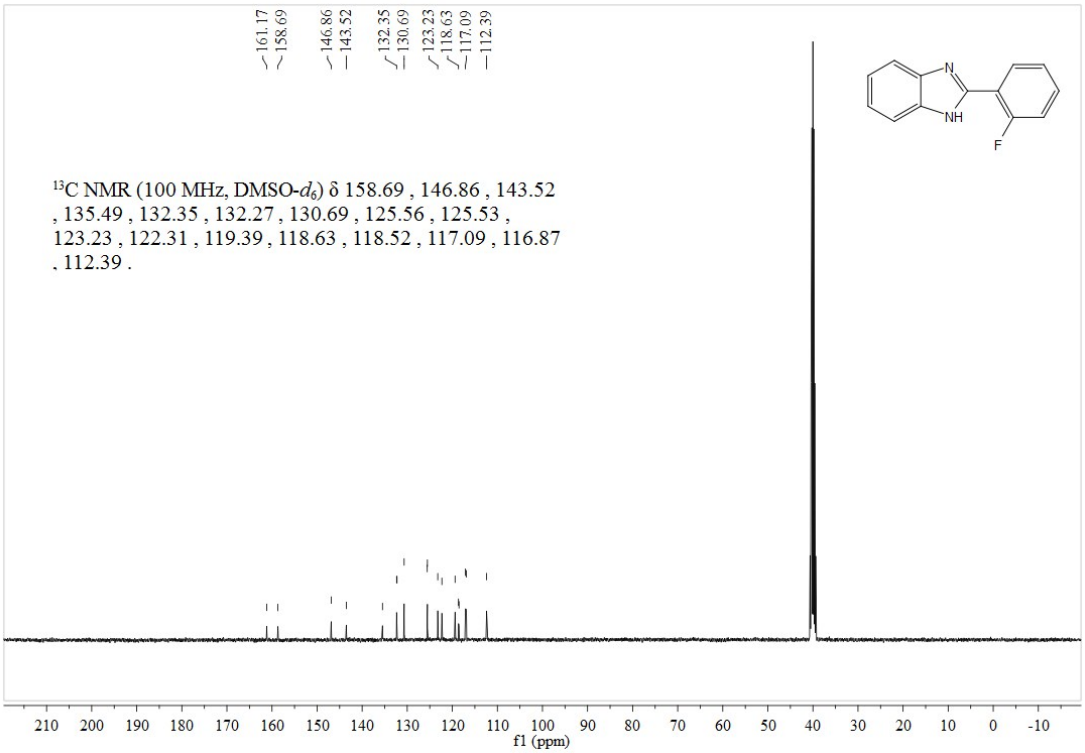


Figure S7 ^{13}C NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole[5] (3d)



^{13}C NMR (100 MHz, DMSO-d_6) δ 158.69 , 146.86 , 143.52 , 135.49 , 132.35 , 132.27 , 130.69 , 125.56 , 125.53 , 123.23 , 122.31 , 119.39 , 118.63 , 118.52 , 117.09 , 116.87 , 112.39 .

Figure S8 ^{19}F NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole[5] (3d)

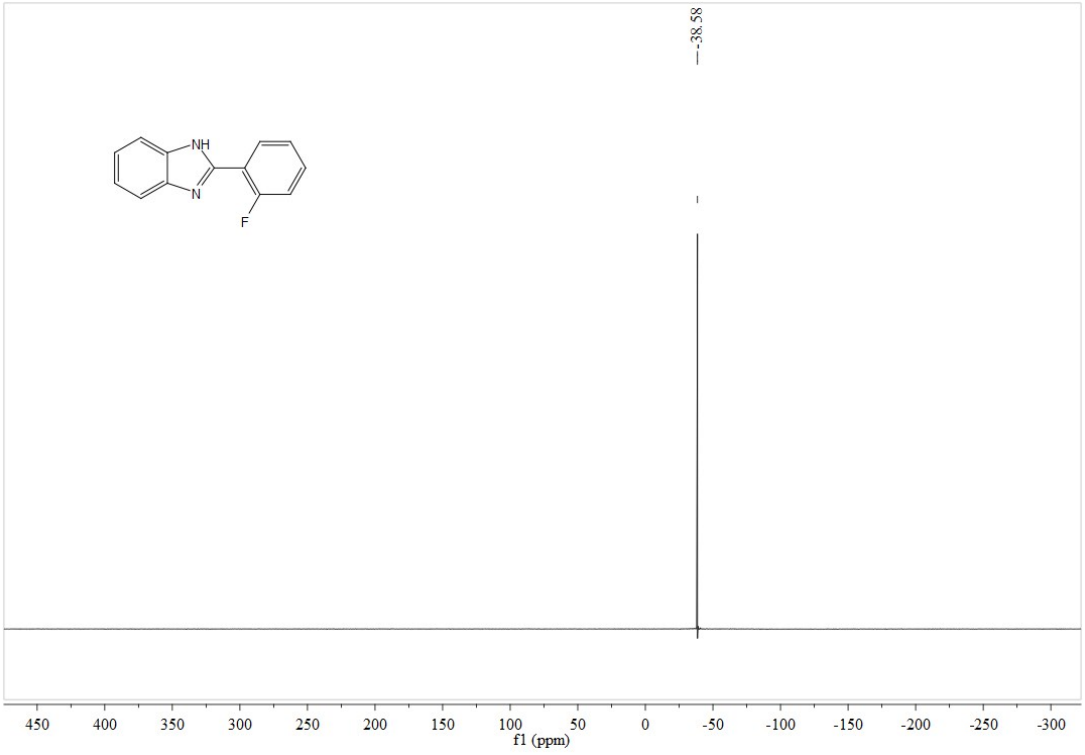


Figure S9 ^{1}H NMR spectrum of 2-(o-tolyl)-1*H*-benzo[*d*]imidazole[6] (3e)

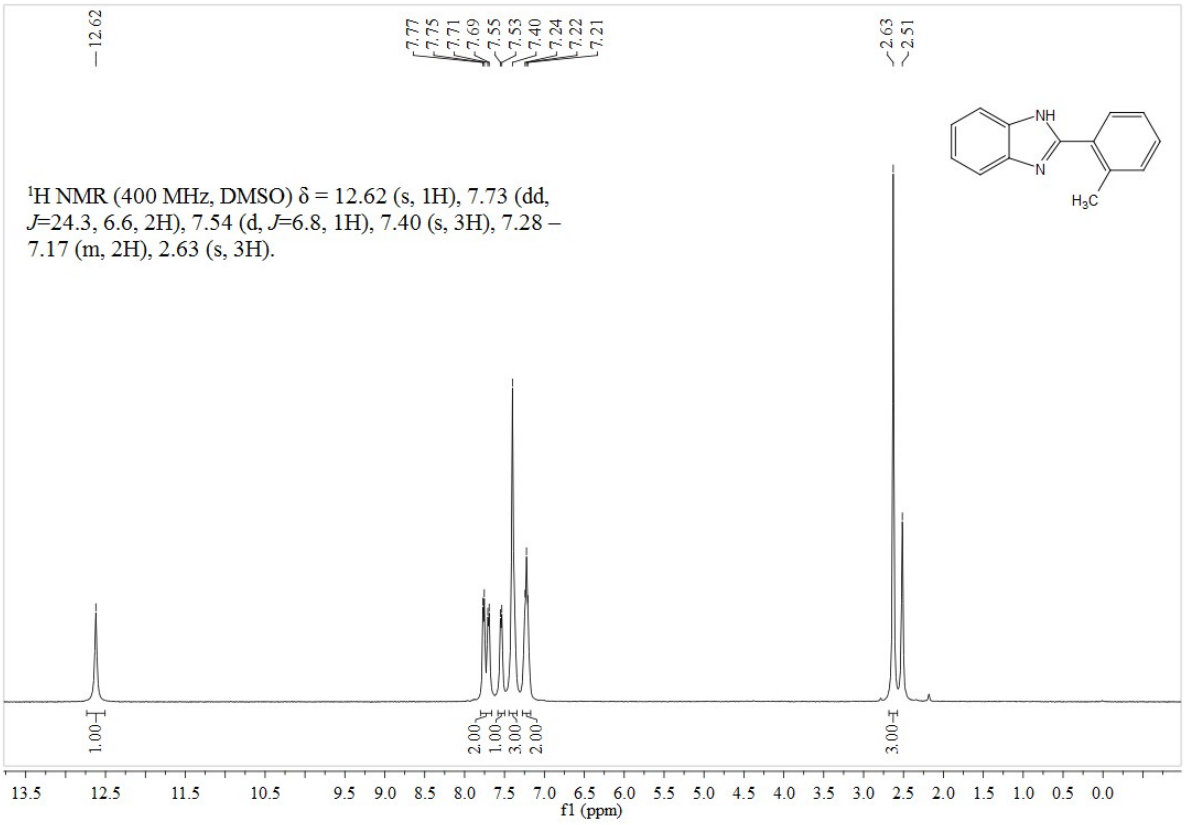


Figure S10 ^{1}H NMR spectrum of 2-(3-chlorophenyl)-1*H*-benzo[*d*]imidazole[6] (3f)

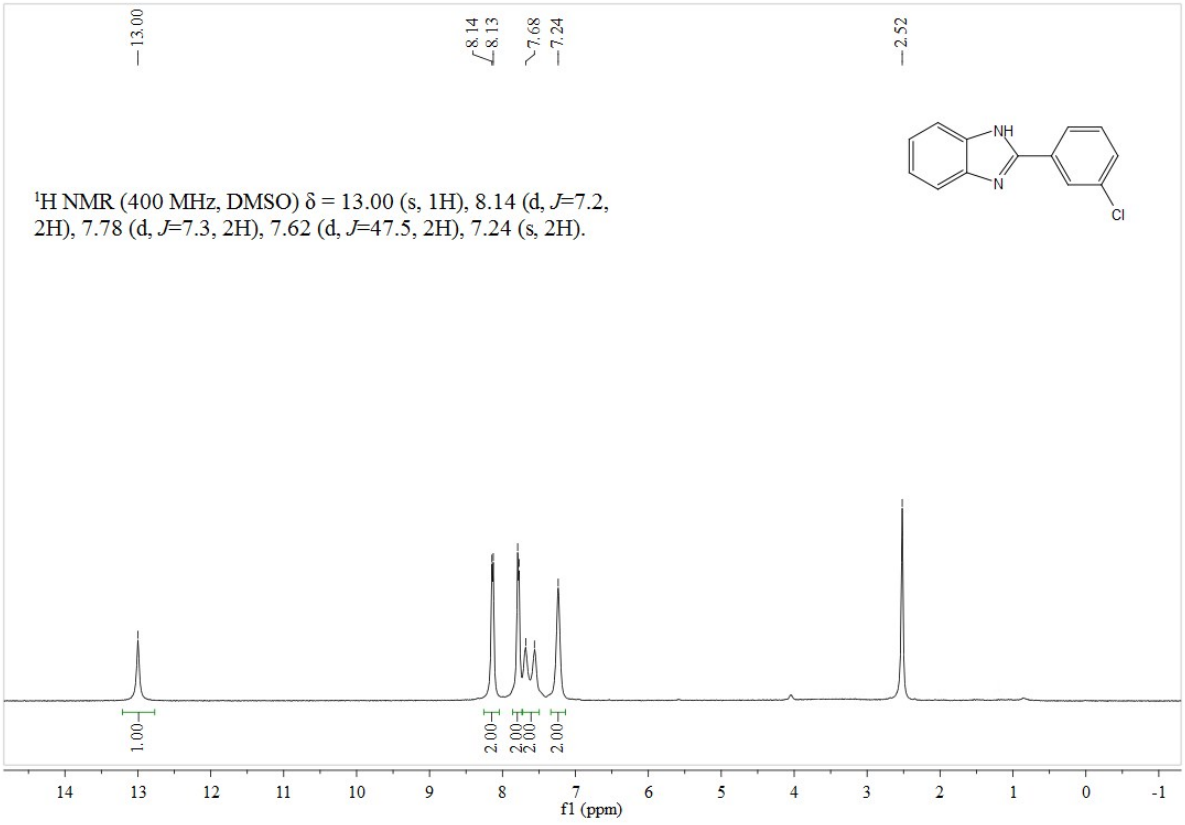


Figure S11 ^{1}H NMR spectrum of 2-(3-nitrophenyl)-1*H*-benzo[*d*]imidazole[3] (3g)

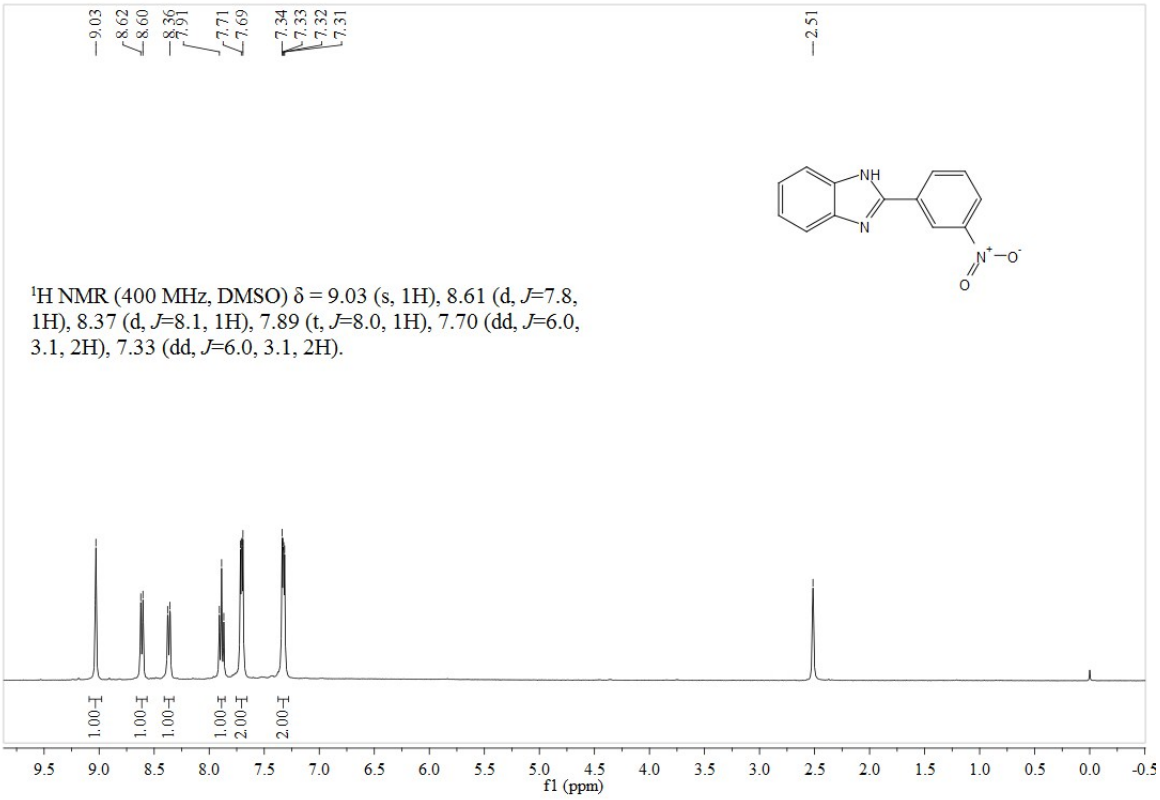


Figure S12 ^{1}H NMR spectrum of 2-(3-fluorophenyl)-1*H*-benzo[*d*]imidazole[5] (3h)

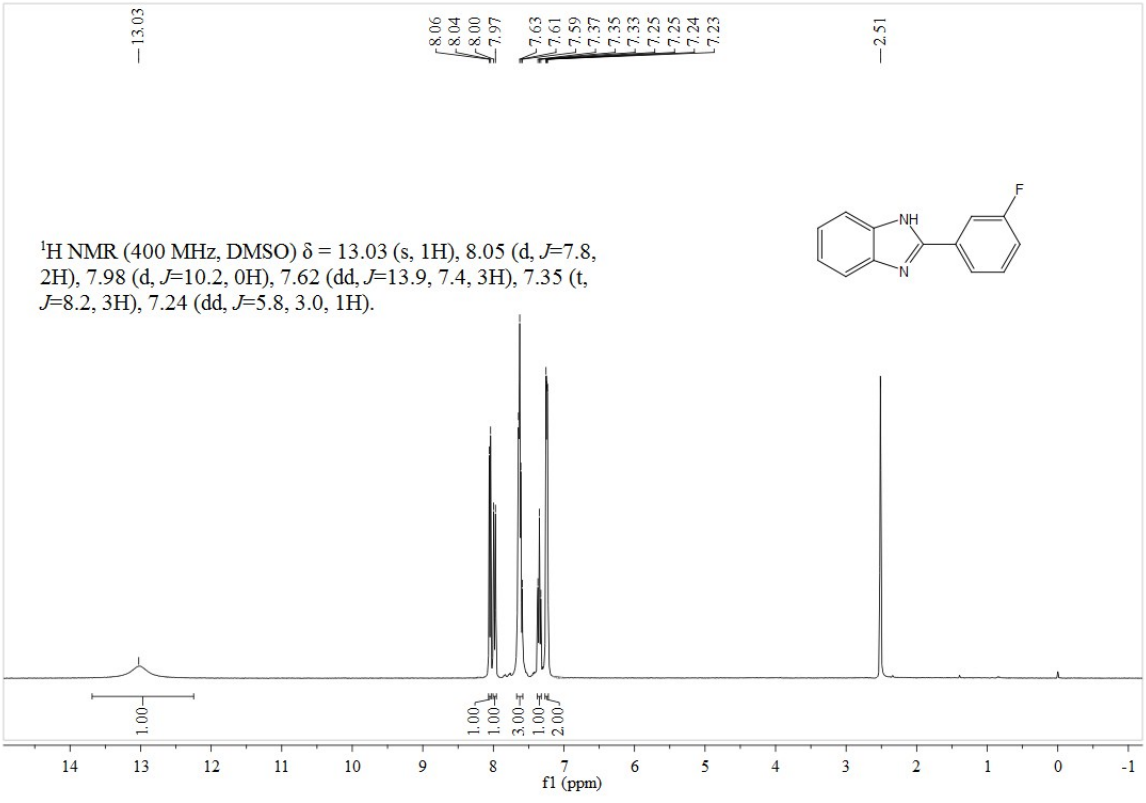
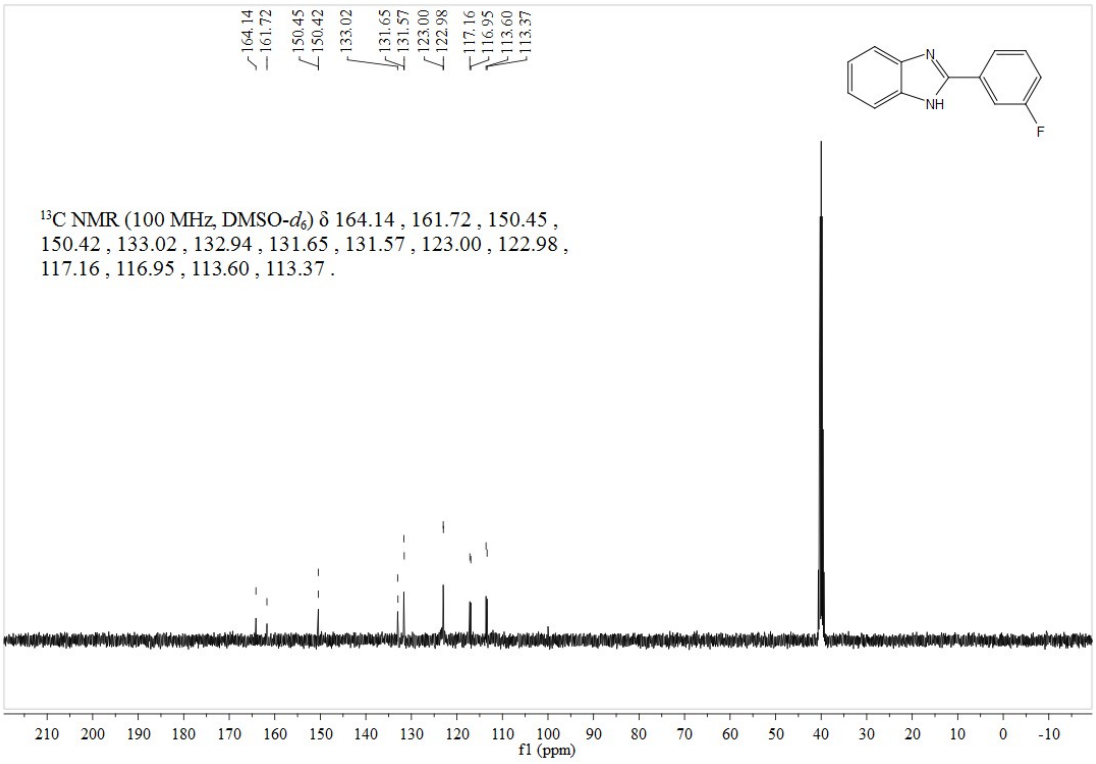


Figure S13 ^{13}C NMR spectrum of 2-(3-fluorophenyl)-1*H*-benzo[*d*]imidazole[5] (3h)



^{13}C NMR (100 MHz, DMSO-d_6) δ 164.14 , 161.72 , 150.45 , 150.42 , 133.02 , 132.94 , 131.65 , 131.57 , 123.00 , 122.98 , 117.16 , 116.95 , 113.60 , 113.37 .

Figure S14 ^{19}F NMR spectrum of 2-(3-fluorophenyl)-1*H*-benzo[*d*]imidazole[5] (3h)

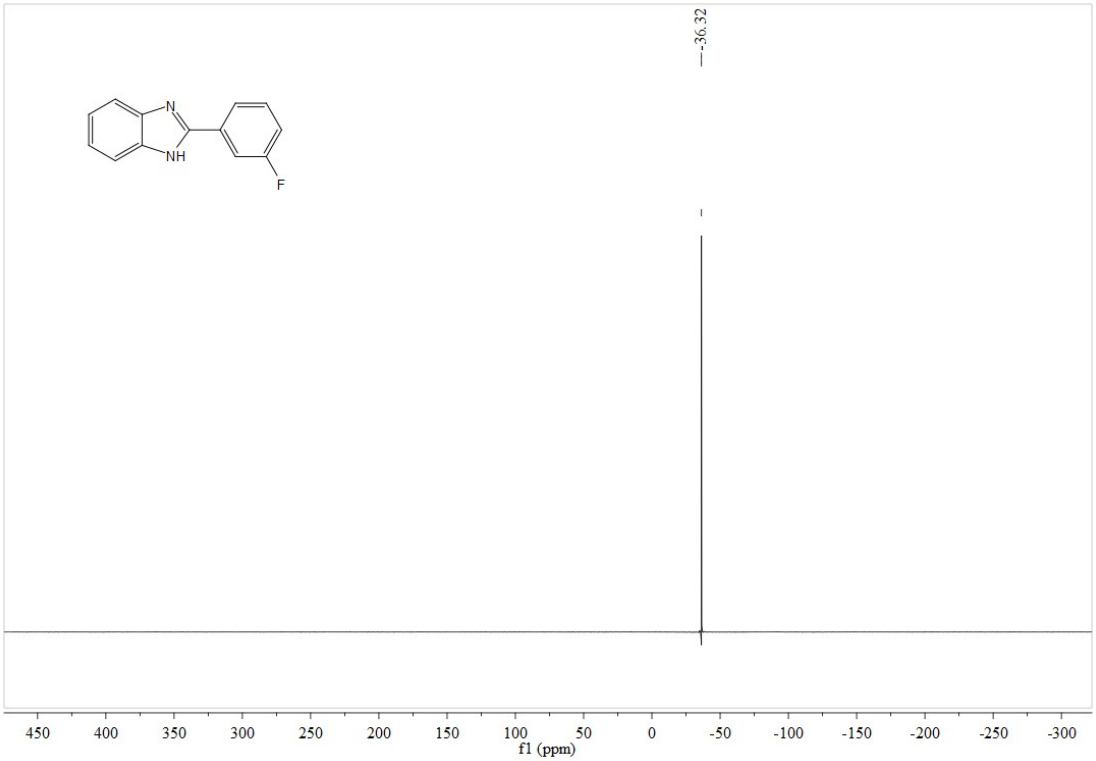


Figure S15 ^{1}H NMR spectrum of 2-(m-tolyl)-1*H*-benzo[*d*]imidazole[3] (3i)

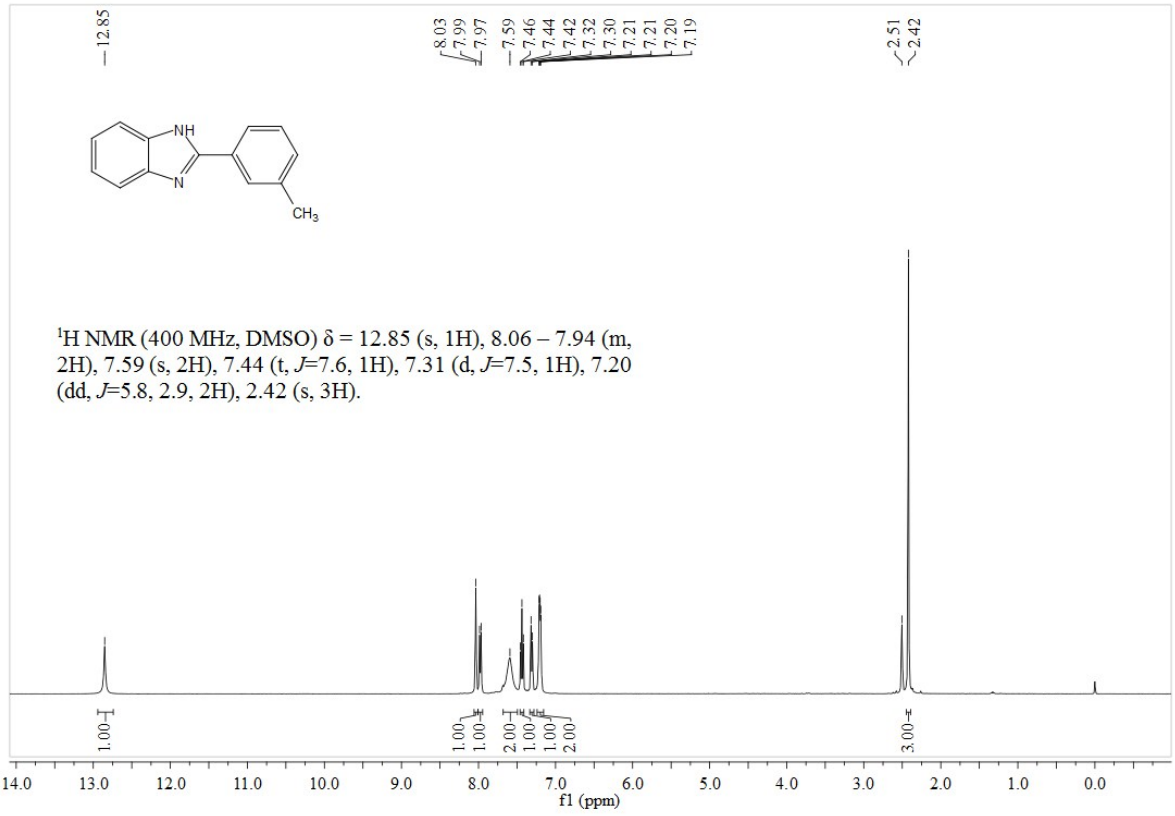


Figure S16 ^{1}H NMR spectrum of 2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole[3] (3j)

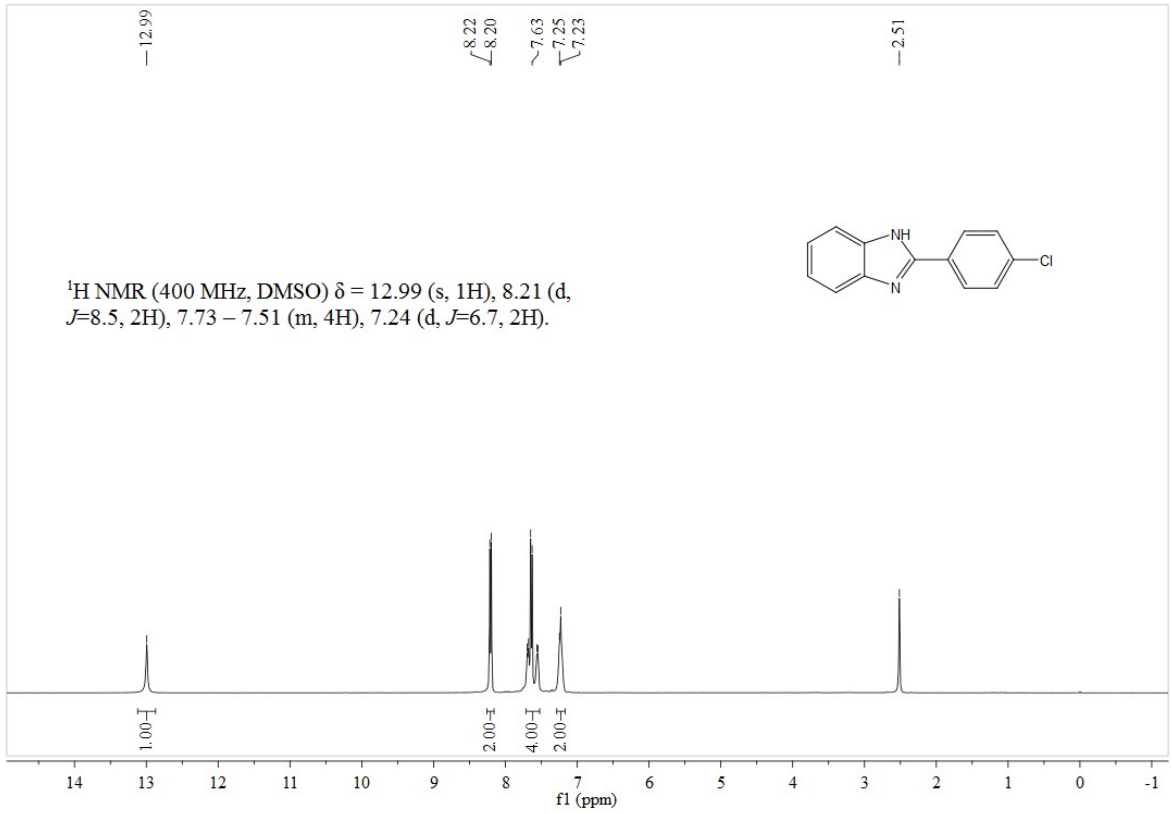


Figure S17 ^{1}H NMR spectrum of 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole[3] (3k)

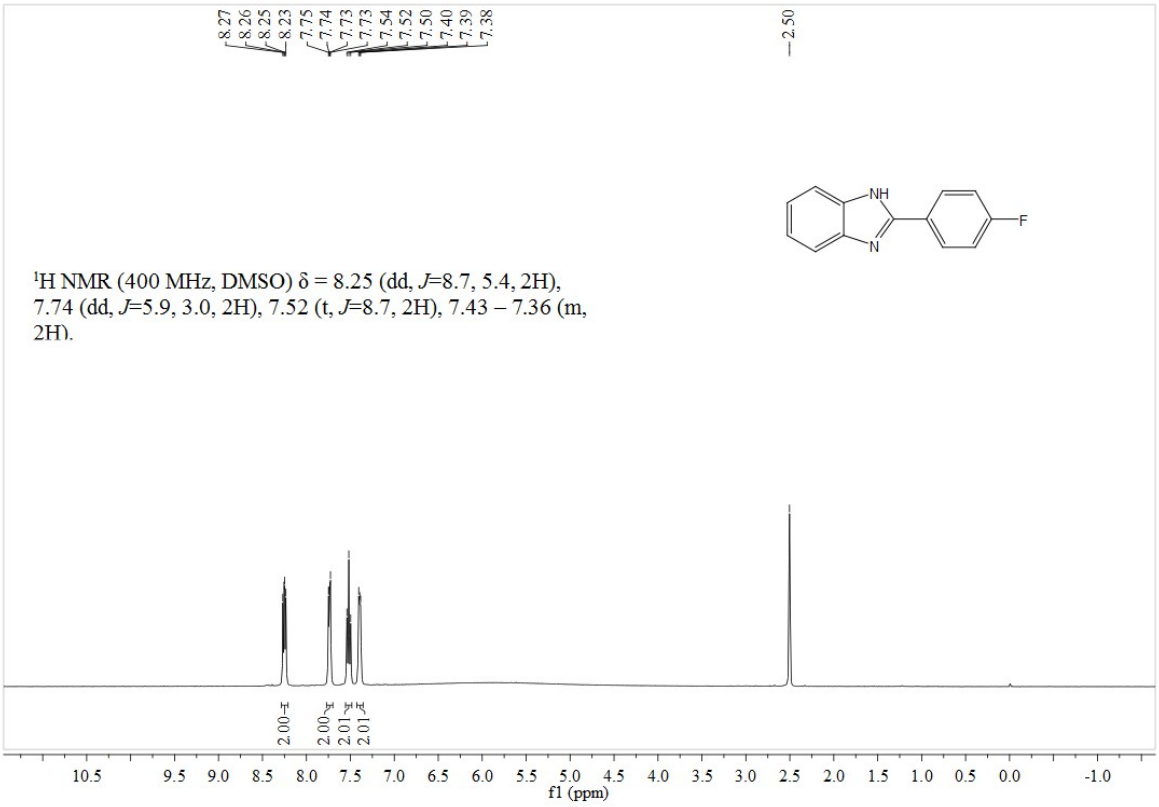
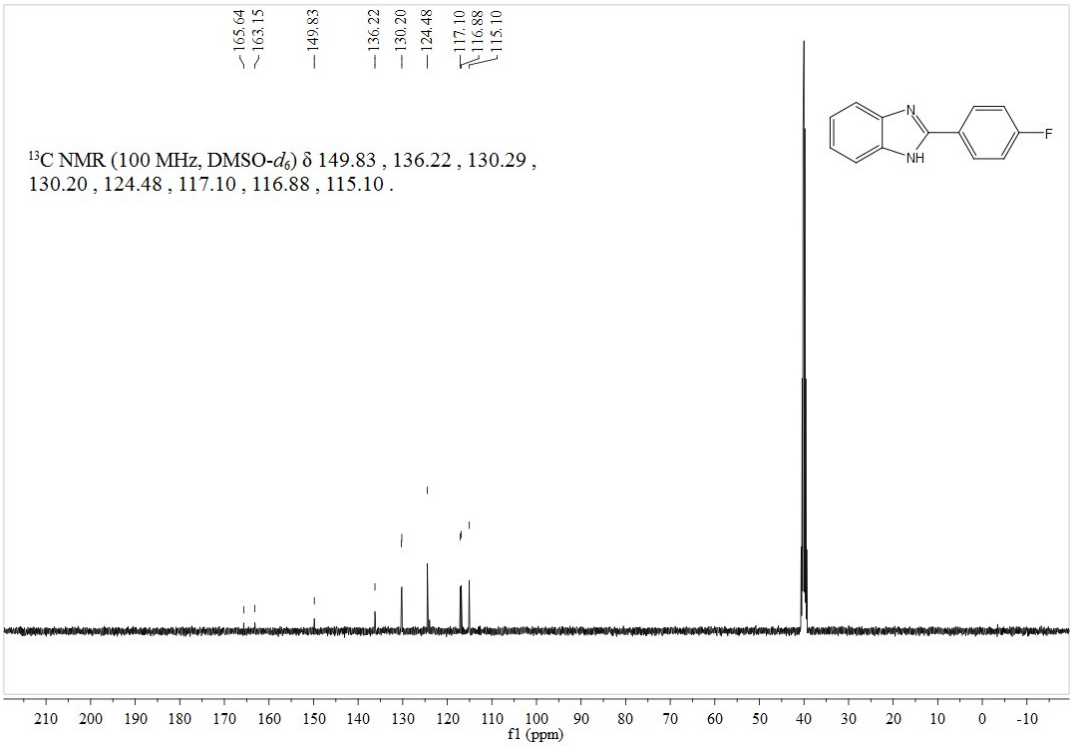


Figure S18 ^{13}C NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole[3] (3k)



^{13}C NMR (100 MHz, DMSO-d_6) δ 149.83 , 136.22 , 130.29 , 130.20 , 124.48 , 117.10 , 116.88 , 115.10 .

Figure S19 ^{19}F NMR spectrum of 2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole[3] (3k)

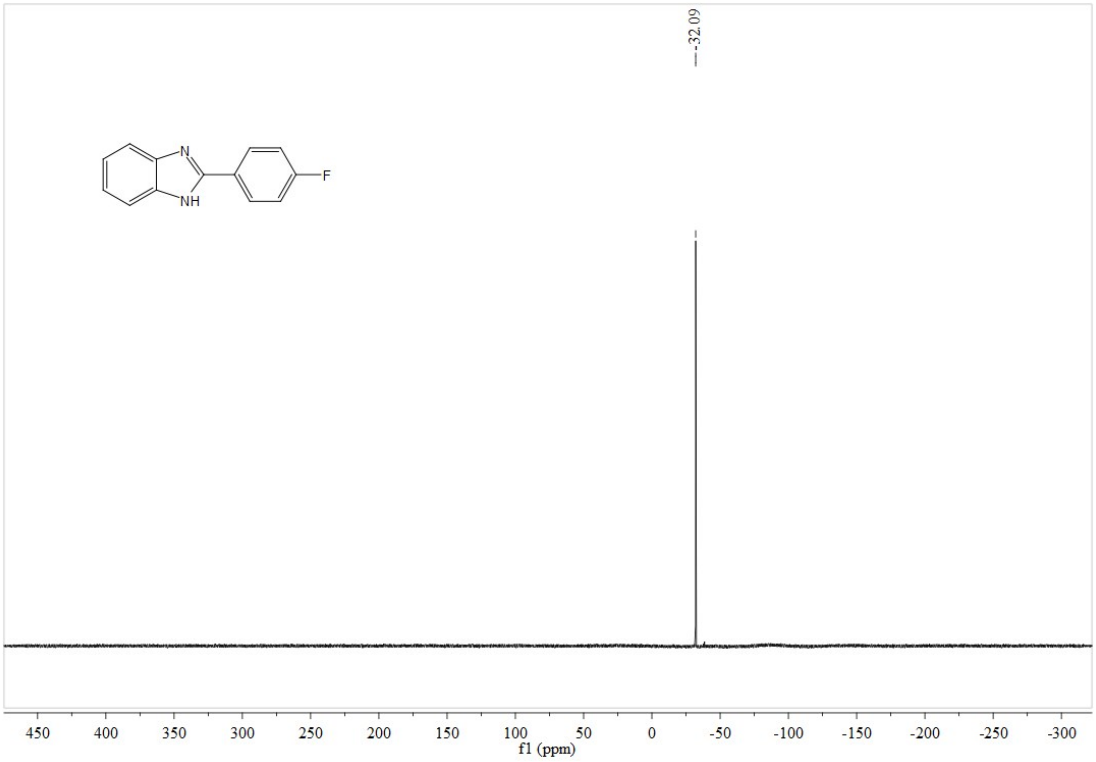


Figure S20 ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole[7] (3l)

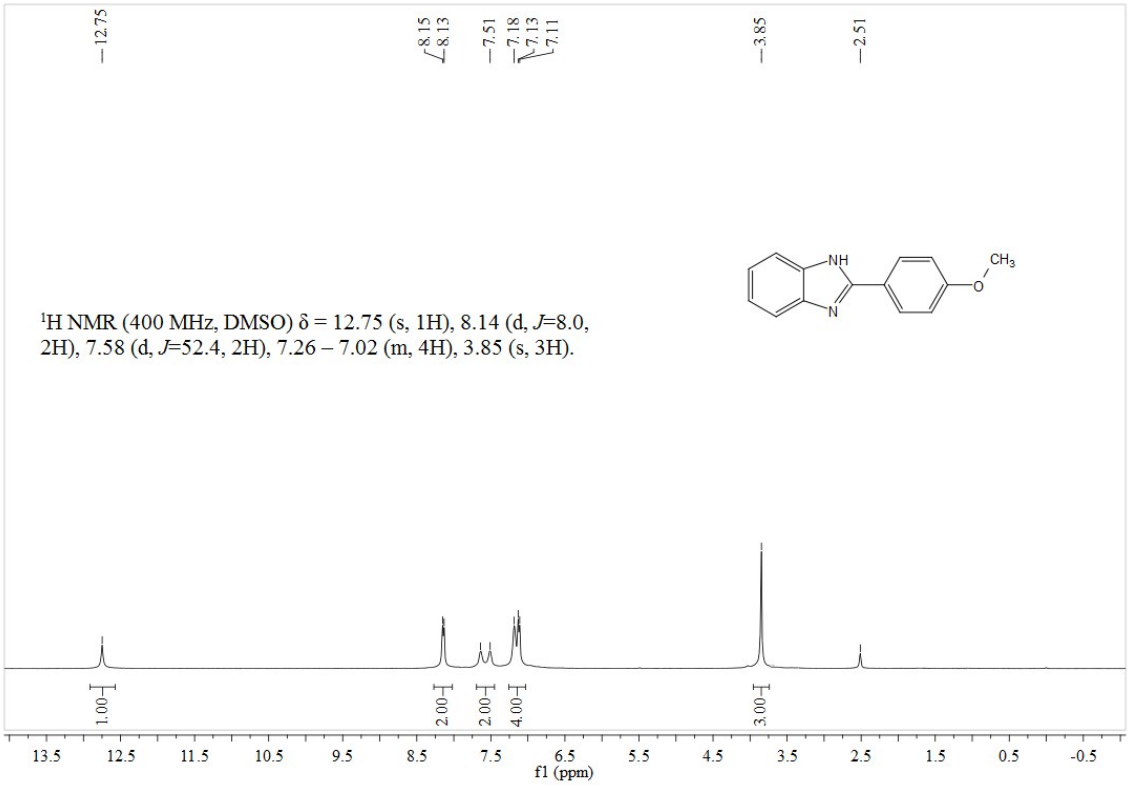


Figure S21 ^{1}H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-1*H*-benzo[*d*]imidazole[8] (3m)

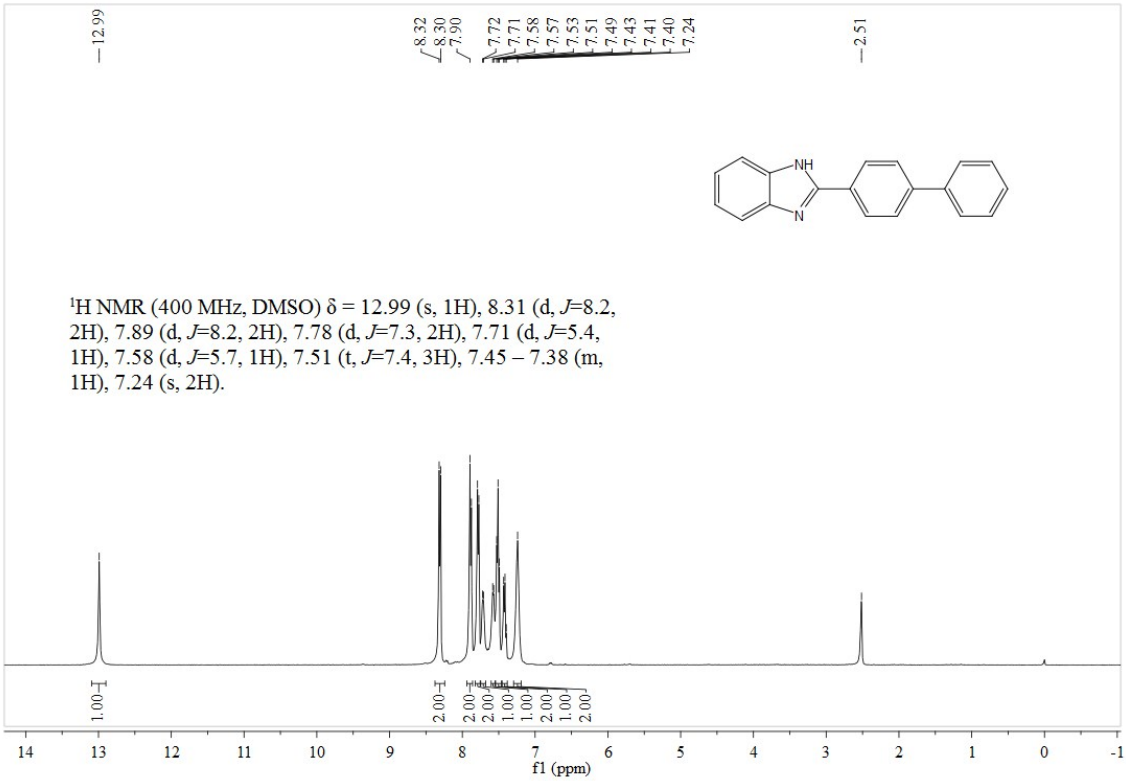


Figure S22 ^{1}H NMR spectrum of 2-(3,5-dimethoxyphenyl)-1*H*-benzo[*d*]imidazole[9] (3n)

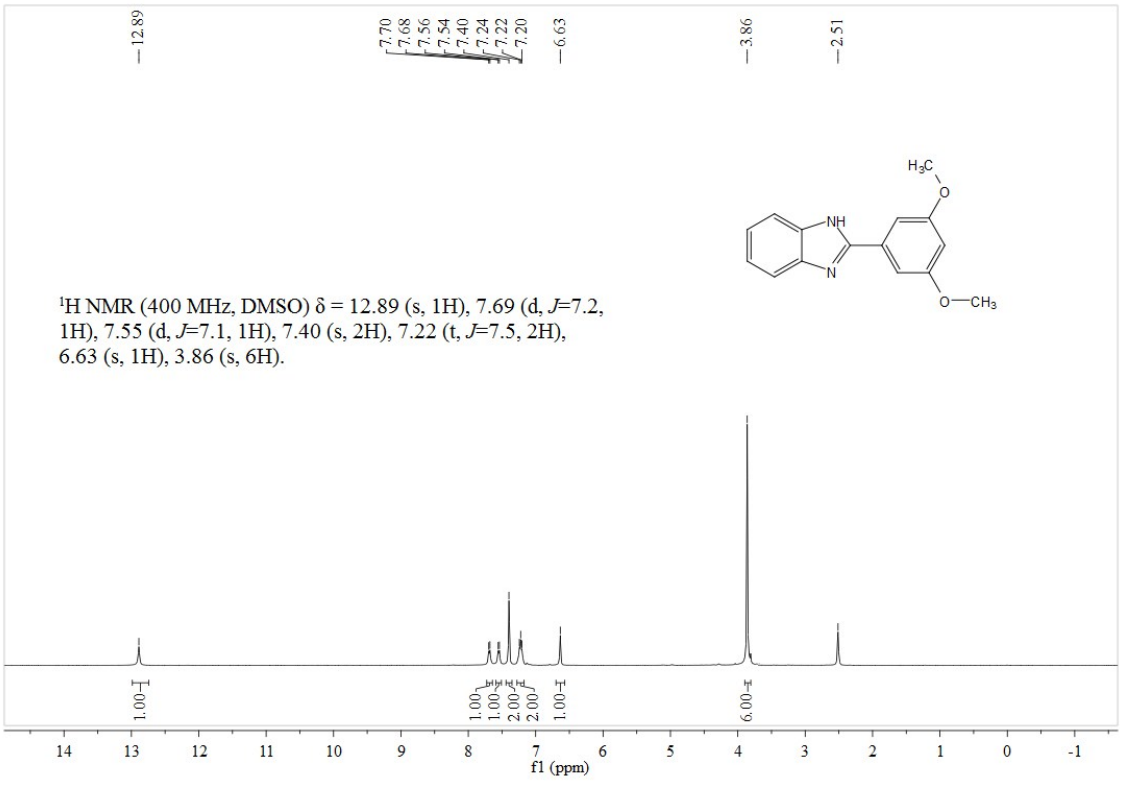


Figure S23 ^{1}H NMR spectrum of 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole[10] (3o)

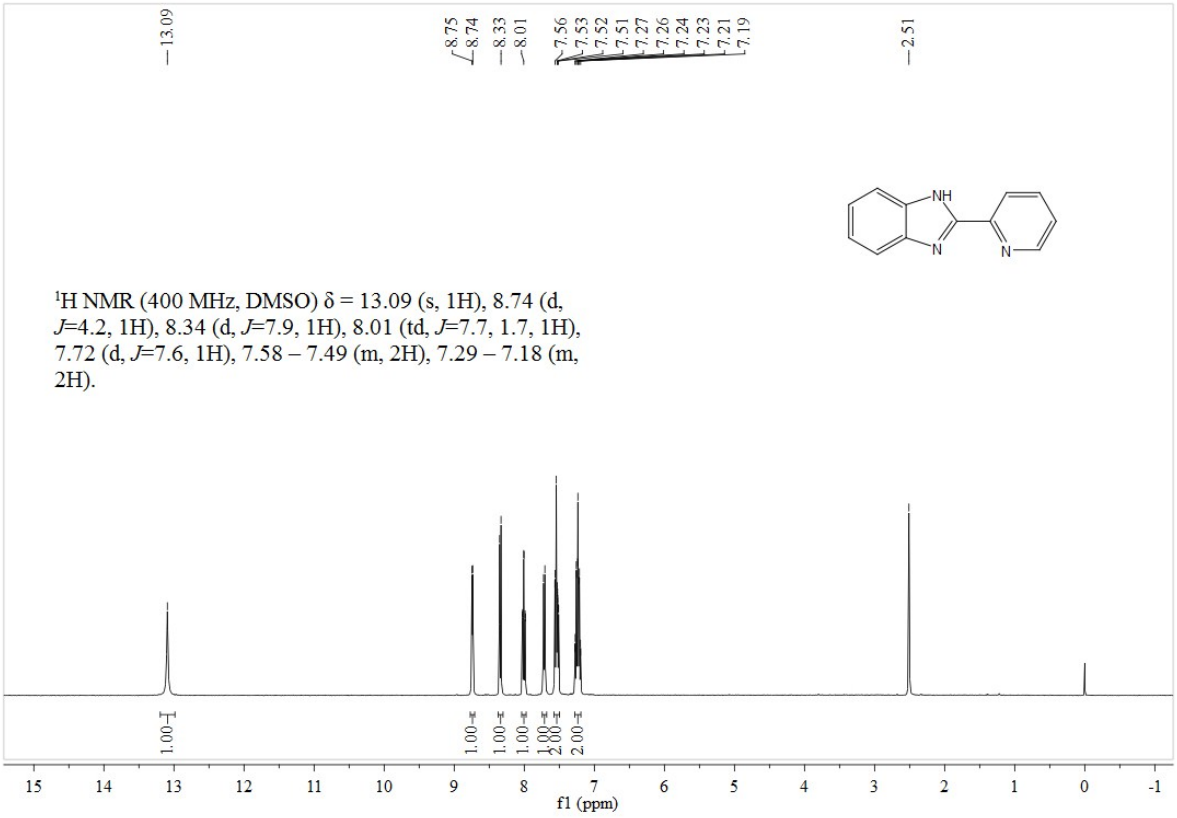


Figure S24 ^{1}H NMR spectrum of 2-(furan-2-yl)-1*H*-benzo[*d*]imidazole[11] (3p)

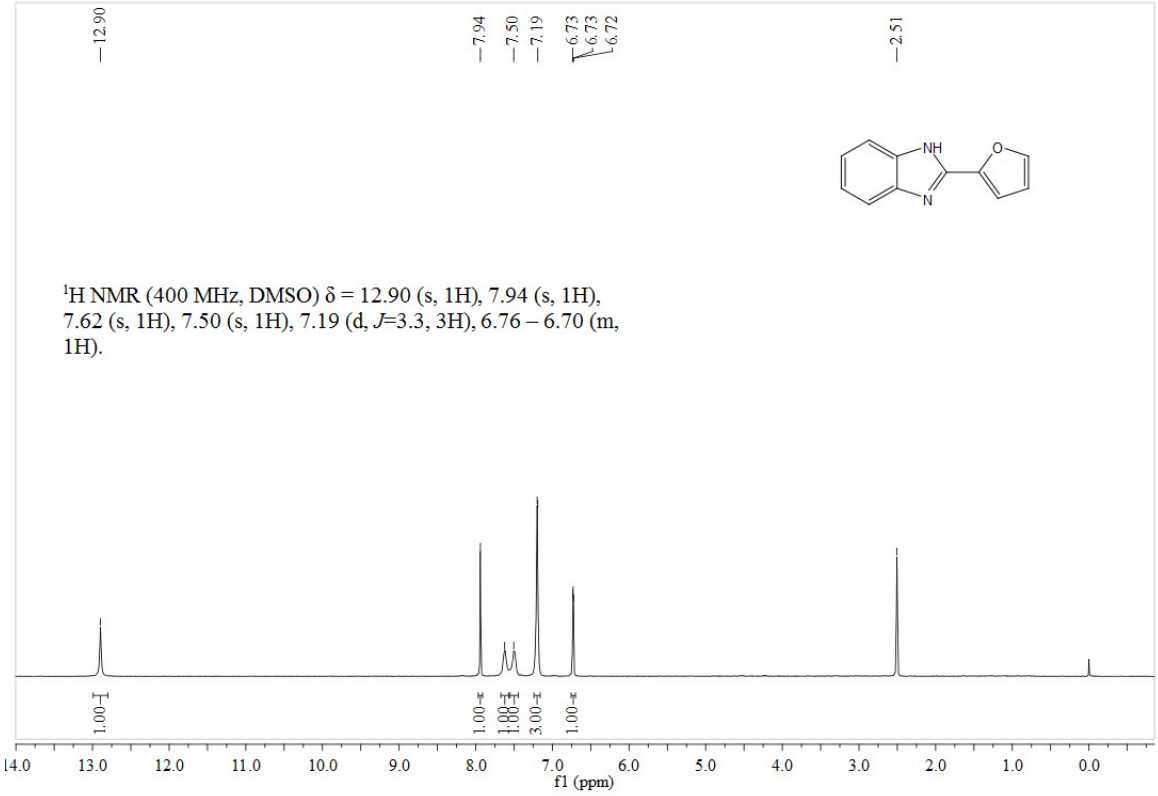


Figure S25 ^{1}H NMR spectrum of 1*H*-benzo[*d*]imidazole[5] (3q)

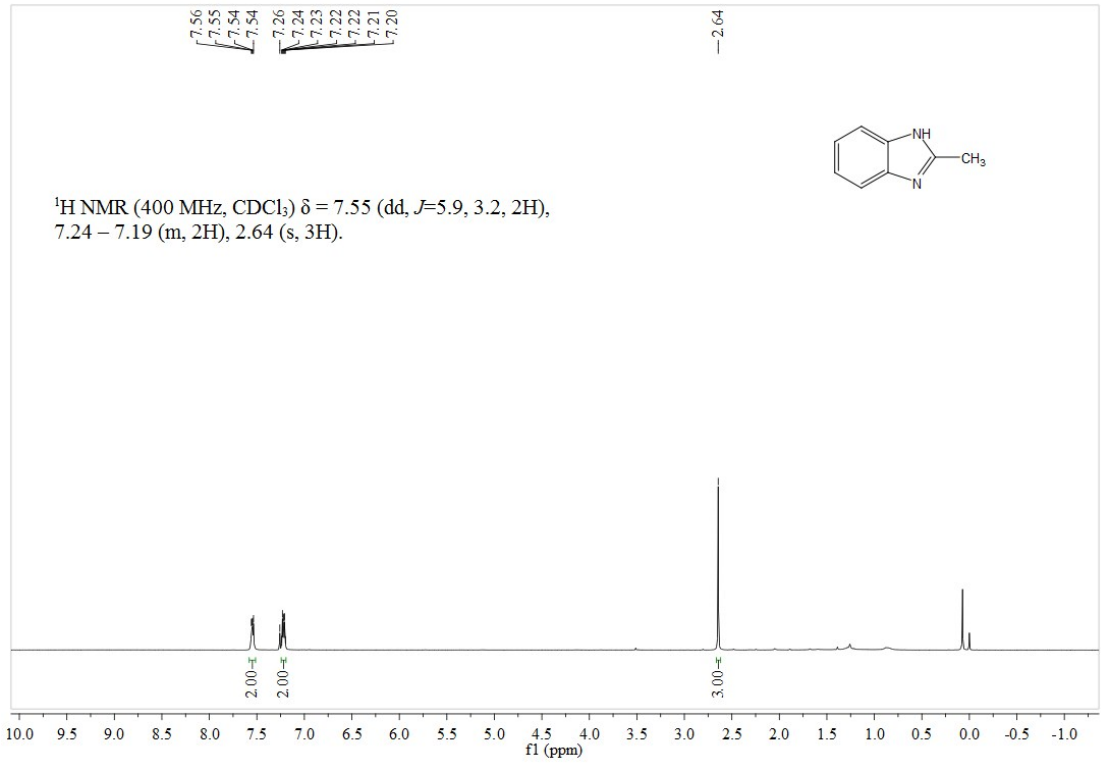


Figure S26 ^{1}H NMR spectrum of 2-cyclohexyl-1*H*-benzo[*d*]imidazole[12] (3r)

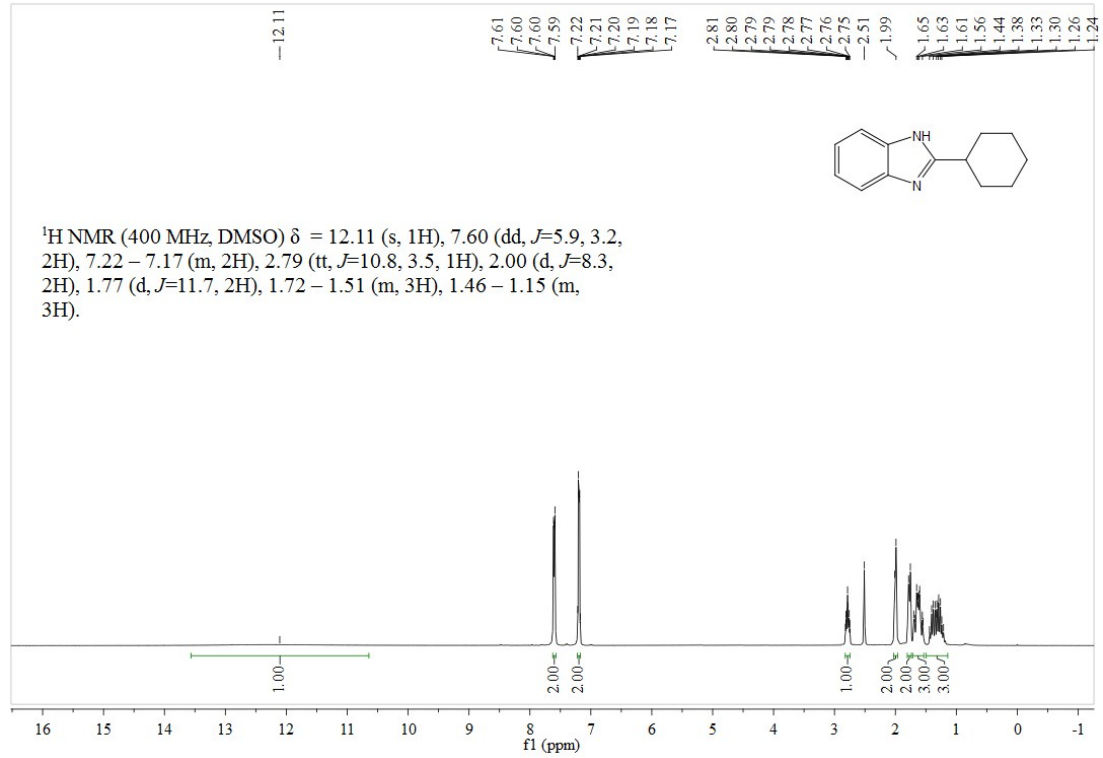


Figure S27 ^{1}H NMR spectrum of 5-methyl-2-phenyl-1*H*-benzo[*d*]imidazole[3] (3s)

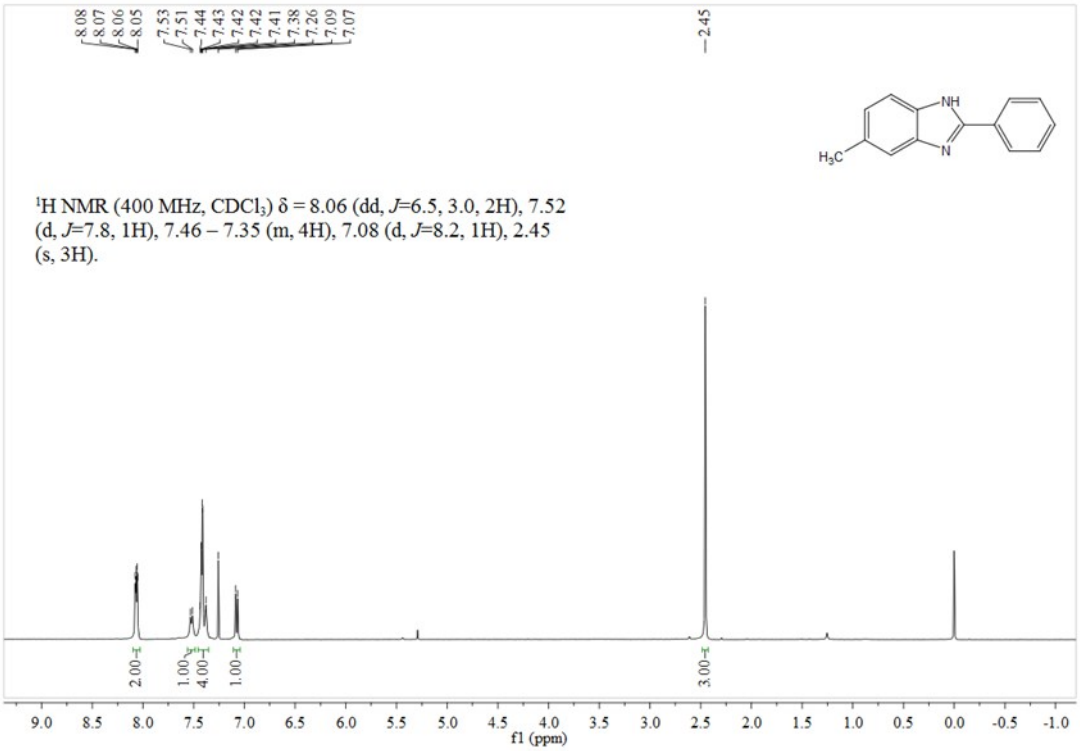


Figure S28 ^{1}H NMR spectrum of 5-chloro-2-phenyl-1*H*-benzo[*d*]imidazole[5] (3t)

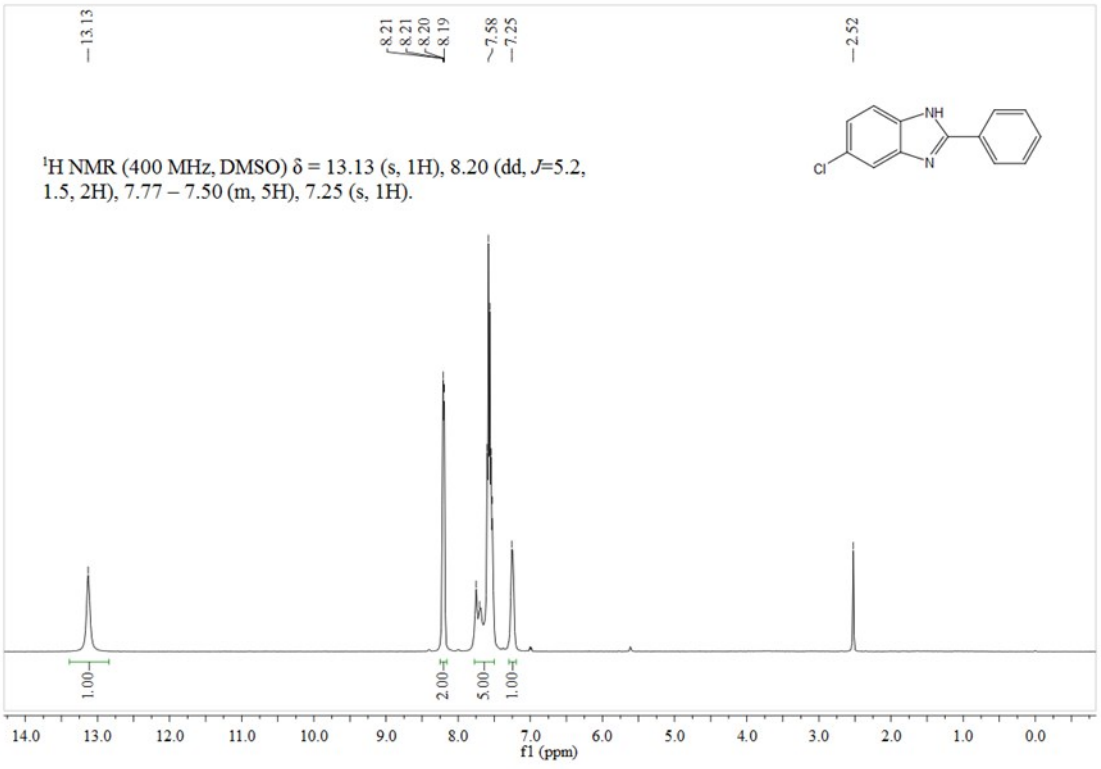


Figure S29 ^{1}H NMR spectrum of 2-phenylquinazolin-4(3*H*)-one[13] (3u)

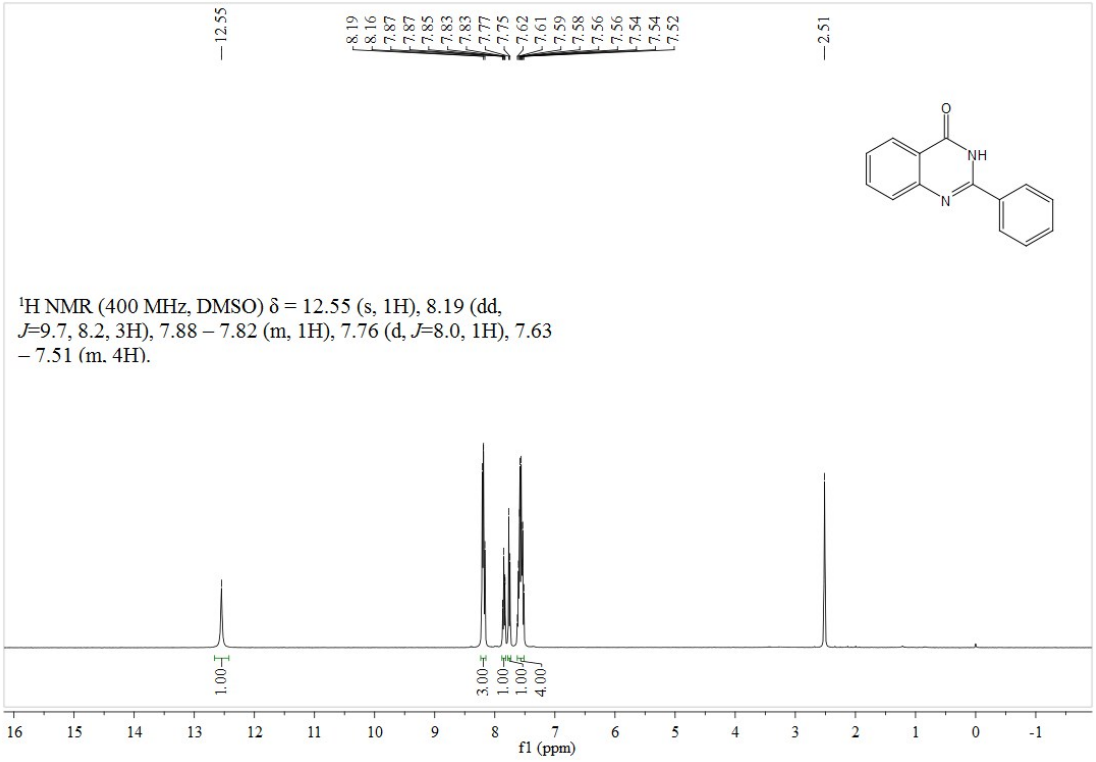
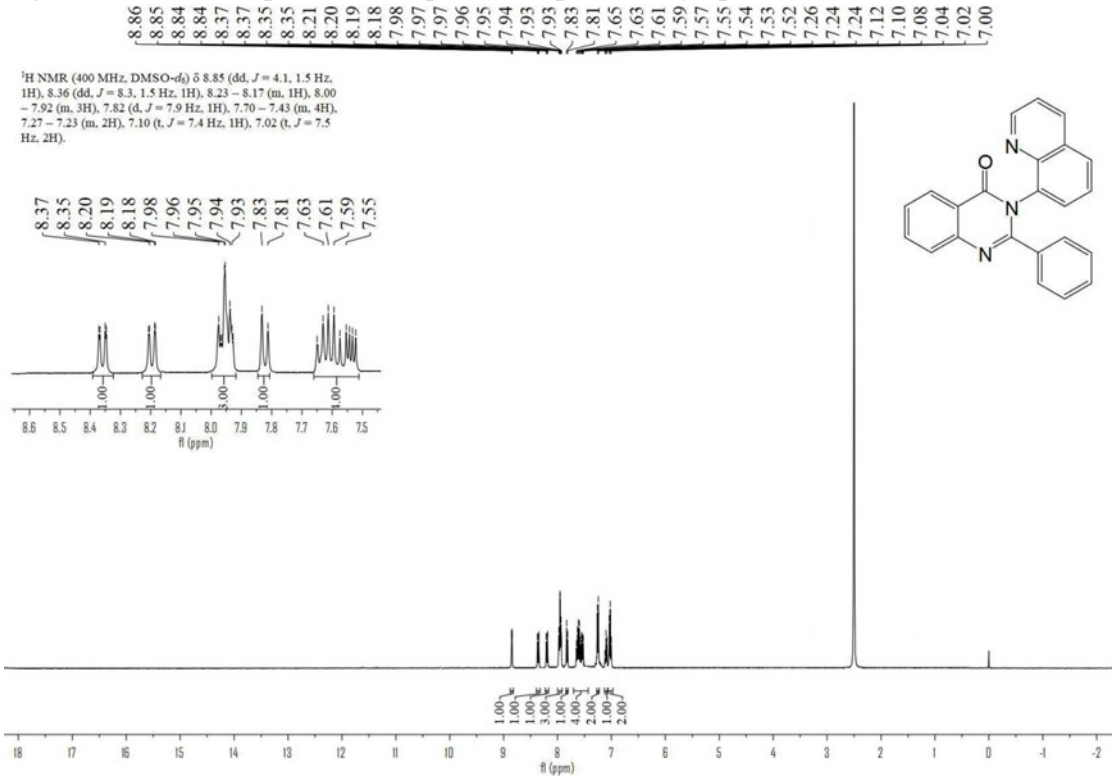


Figure S30 ^{1}H NMR spectrum of 2-phenyl-3-(quinolin-8-yl)quinazolin-4(3*H*)-one (3v)



^{1}H NMR spectra and analysis of intermediates

Figure S31 ^{1}H NMR spectrum of intermediate A[13]

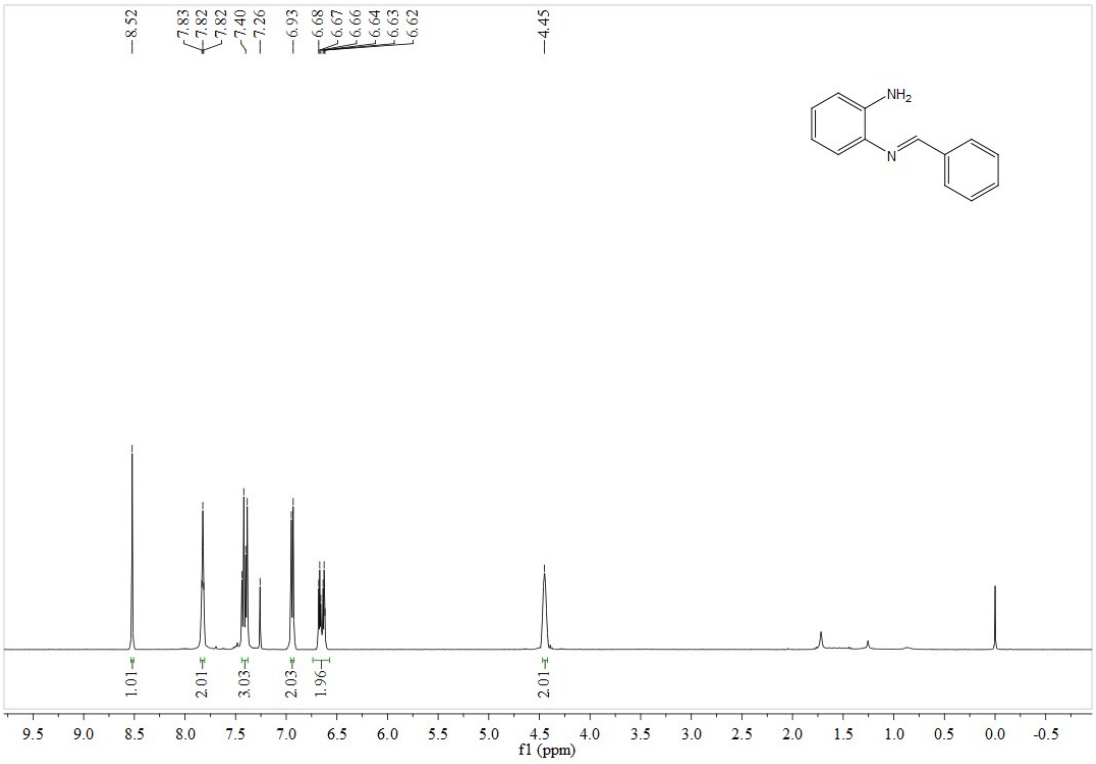
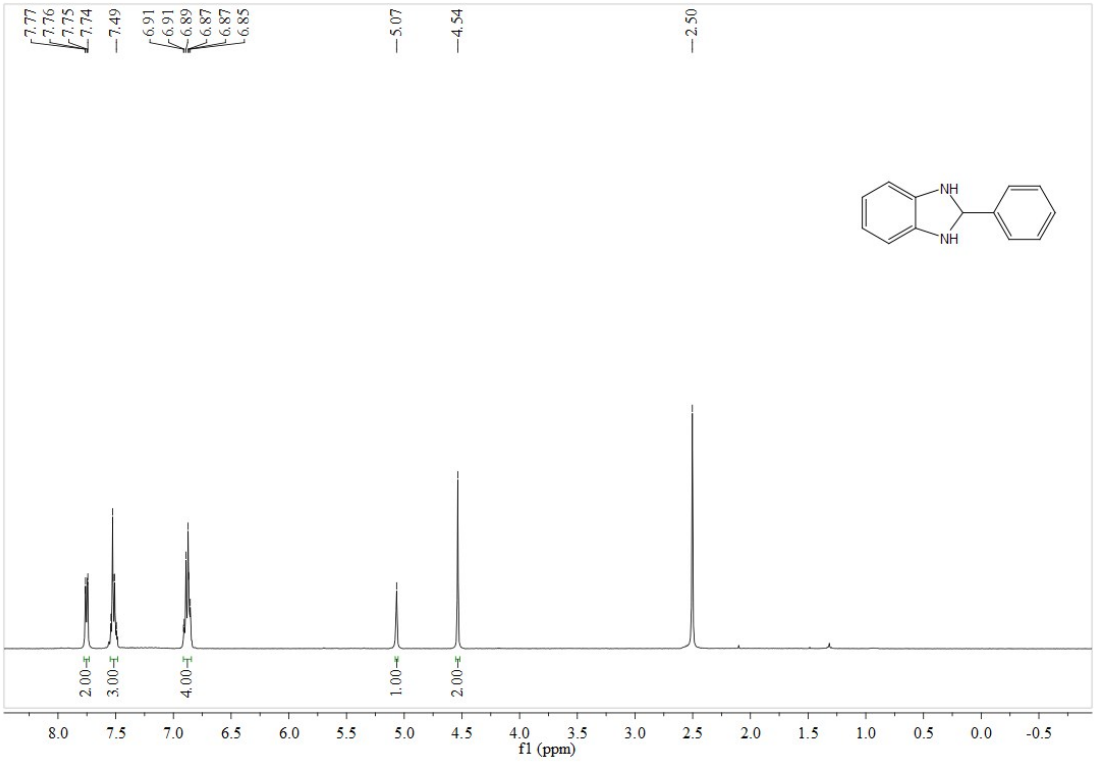


Figure S32 ^{1}H NMR spectrum of intermediate B[14]



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