Supporting Information

Donor-Acceptor Type Triphenylamine-Based Porous Aromatic Frameworks (TPA-PAFs) for Photosynthesis of Benzimidazoles

Xinmeng Xu, [a] He Wang, [a] Zhenwei Zhang, [b] Jiali Li, [b] Xiaoming Liu, [b] Xin Tao, *[a] Guangshan Zhu[a]

[a]Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China

[b]College of Chemistry, Jilin University, Changchun 130012, P. R. China

*E-mail: taox091@nenu.edu.cn.

List of Content

Section 1. General information

Materials. Unless otherwise noted, all materials were used as received from commercial sources without further purification.

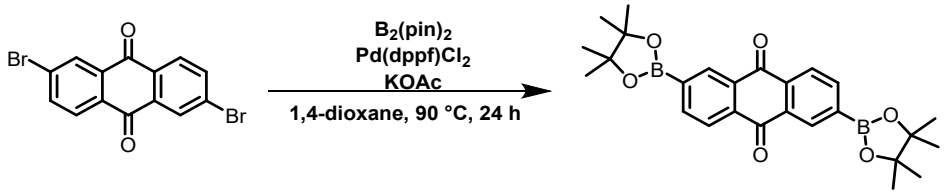
Instrumentations. The ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ or DMSO on Avance NEO 500 spectrometer. The chemical shifts δ and coupling constants *J* are given in ppm and Hz, respectively. ^{13}C MAS solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz NMR spectrometer. FT-IR analysis was collected in the range of 500-4000 cm^{-1} on the Nicolet IS50 Fourier transforms infrared spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on Thermo Scientific Escalab 250Xi with an Al-Kα X-ray source. The binding energies of elements were calibrated using the C 1s photoelectron peak at 284.8 eV. The thermogravimetric analysis (TGA) was measured on the METTLER-TOLEDO TGA/DSC 3+ analyzer at the 10 °C min^{-1} in N_2 atmosphere from room temperature to 800 °C. The N_2 adsorption-desorption isotherms were measured at 77 K, using Autosorb iQ2 adsorptometer, Quantachrome Instrument. Samples were degassed at 393 K for 12 h before measurements. The scanning electron microscope (SEM) images were acquired using the JEOL JSM 4800F SEM. Transmission electron microscopic (TEM) images and elemental mapping were acquired by JEOL 2100PLUS instrument at an accelerating voltage of 200 kV. The UV-vis absorption spectra were recorded from 200-800 nm on a VARIAN UV-VIS-NIR spectrophotometer (Cary500). The UV-vis diffuse reflectance spectra were recorded using UV-Vis-NIR Spectrophotometer (Cary7000) with $BaSO_4$ used as a reference. The Pd metal loading of obtained polymers was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) LEEMAN Prodigy. The electron spin resonance (ESR) was tested by a Bruker EMXplus spectrometer at the X-band frequency (9.4 GHz). 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used as spin-trapping reagents to detect $O_2^{\bullet-}$. 2,2,6,6-Tetramethyl-4-piperidone hydrochloride (TEMP) was used as spin-trapping reagent to detect $^{1}O_2$.

Electrochemical measurements. The electrochemical workstation (electrochemical workstation

(CHI760E, CH Instruments, Shanghai, China) was used to perform electrochemical measurements on samples with platinum wire as the counter electrode, $Hg/HgCl_2$ as the reference electrode, and test sample as the working electrode. The working electrode was prepared as follows: 0.05 g of sample, 0.10 g of pine alcohol, and 0.005 g of ethyl cellulose were added to an agate mortar and then 5 mL of ethanol was added to it, and the slurry was scraped onto fluorine-doped tin oxide (FTO) glass to form a film for electrical performance testing. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp (PLS-SXE300+/UV) with a 420 nm cut-off filter in 0.1 M Na_2SO_4 and the test area was 1 cm^2. The electrochemical impedance spectra (EIS) measurements were performed in 0.1 M Na_2SO_4 at room temperature.

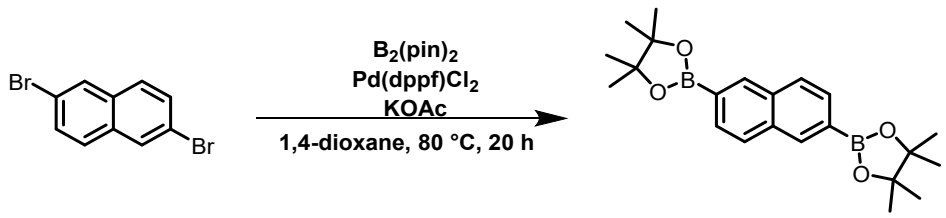
Section 2. Experimental details for synthesis of TPA-PAFs and photocatalysis

Synthesis of 2,6-bis(pinacolatoboryl)anthraquinone:



In a N_2 glovebox, 2,6-dibromoanthraquinone (0.9 g, 2.5 mmol), bis(pinacolato)diboron (1.6 g, 6.38 mmol), KOAc (0.75 g, 7.63 mmol), Pd(dppf)Cl_2 (0.03 g, 0.34 mmol), and 1,4-dioxane (40 mL) were added to a two-necked round-bottomed flask. The resulting mixture was heated to 90 °C and refluxed under nitrogen atmosphere for 24 h. After the reaction mixture was cooled down to room temperature, the reaction mixture was quenched by adding water and subsequently extracted with CH_2Cl_2 for three times. The combined organic layer was dried over $MgSO_4$ and then all the volatiles were removed by rotation evaporator. The residual solid was recrystallized from a mixture of CH_2Cl_2 and hexane to give an off-white solid powder (1.04 g, 2.26 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 2H), 8.30 (d, J = 7.7 Hz, 2H), 8.20 (d, J = 7.7 Hz, 2H), 1.38 (s, 24H).

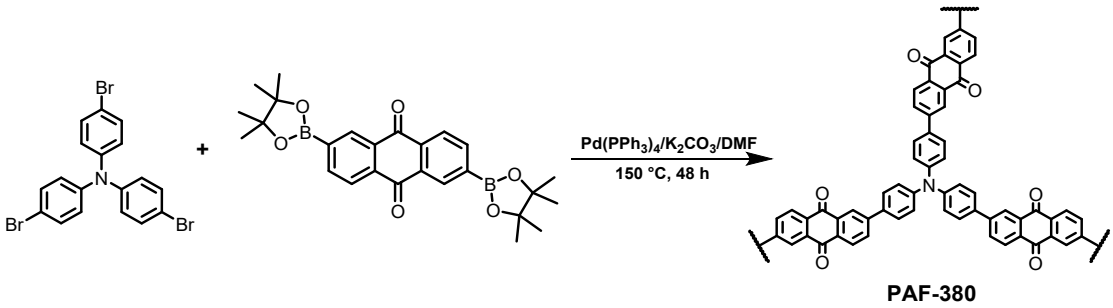
Synthesis of 2,6-bis(pinacolatoboryl)naphthalene:



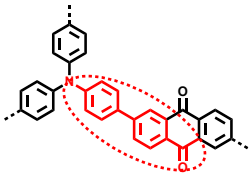
In a N_2 glovebox, 2,6-dibromonaphthalene (0.60 g, 2.1 mmol), bis(pinacolato)diboron (1.20 g, 4.72 mmol), KOAc (1.20 g, 11.23 mmol), and Pd(dppf)Cl_2 (0.30 g, 0.41 mmol) and 1, 4-dioxane (15 mL) were added to a 200 mL Schlenk flask. The resulting mixture was stirred for 30 min and then heated to 80 °C under nitrogen atmosphere for 20 h. The reaction mixture was quenched by pouring it into water (20 mL), which was then extracted with EtOAc for three times. The combined organic phase was washed with saturated NaCl (aq.) and dried over $MgSO_4$. The liquid phase was separated

by filtration. Removal of all volatiles and purification by column chromatography (silica gel) gave a white solid (623 mg, 1.64 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 2H), 7.84 (q, J = 8.2 Hz, 4H), 1.39 (s, 24H).

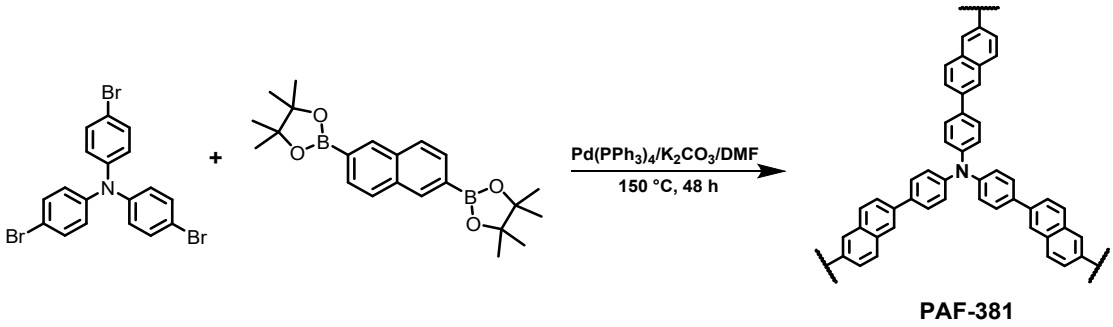
Synthesis of PAF-380:



In a N_2 glovebox, tris(4-bromophenyl)amine (200 mg, 0.42 mmol), 2,6-bis(pinacolatoboryl)anthraquinone (285 mg, 0.62 mmol), $Pd(PPh_3)_4$ (9.7 mg, 0.0084 mmol) and ultra-dry DMF (10 mL) were added to a 100 ml Schlenk flask. Then 2 M K_2CO_3 solution (2 mL) were added into the flask. The resulting mixture was heated to 150 °C under N_2 atmosphere for 48 h. The reaction mixture was then cooled to room temperature and sequentially washed with $CHCl_3$, $CHCl_2$, CH_3OH, HCl (1 M) and water. The solid was obtained by filtration, which was then extracted by Soxhlet extraction (THF) for 48 h. Finally, drying in a vacuum oven at 100 °C for 24 h gave a dark red solid powder (223 mg, 95%). The residual Pd metal content of PAF-380 was determined by ICP to be 0.24%. Elemental analysis (%) for PAF-380: C, 81.04; N, 2.64; H, 4.11. The catalytically active units of PAF-380 are tentatively illustrated as the repeating units: one-third of the triphenylamine molecule bonded with half of the anthraquinone molecule (see below).

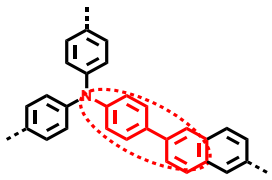


Synthesis of PAF-381:



In a N_2 glovebox, tris(4-bromophenyl)amine (200 mg, 0.42 mmol), 2,6-bis(pinacolatoboryl)naphthalene (236 mg, 0.62 mmol), $Pd(PPh_3)_4$ (9.7 mg, 0.0084 mmol) and ultra-dry DMF (10 mL) were added to a 100 ml Schlenk flask. Then 2 M K_2CO_3 solution (2 mL) were added into the flask. The resulting mixture was heated to 150 °C under a N_2 atmosphere for 48 h. The reaction mixture was then cooled down to room temperature, and sequentially washed with $CHCl_3$, $CHCl_2$, CH_3OH, HCl (1 M) and water. The residual solid was Soxhlet extracted (THF) for 48 h and dried in a vacuum oven at 100 °C for 24 h to give a yellow-green solid powder (167 mg, 91%). The residual Pd metal content of PAF-381 was determined by ICP to be 0.46%. Elemental analysis (%) for PAF-381: C, 83.75; N, 3.03; H, 5.66.

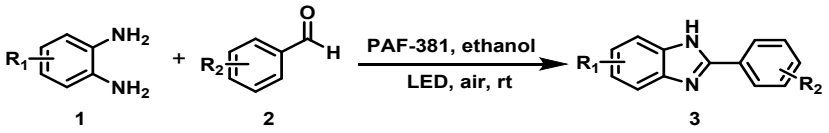
The catalytically active unit of PAF-381 is tentatively illustrated as the repeating units: one-third of a triphenylamine molecule bonded with half of a naphthalene molecule (see below).



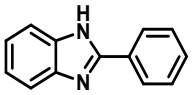
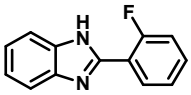
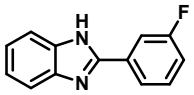
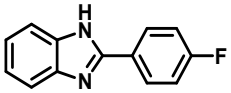
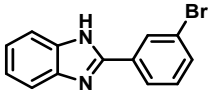
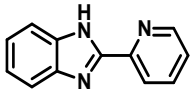
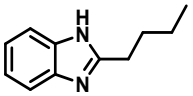
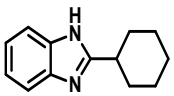
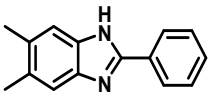
Typical procedure for photocatalytic synthesis of benzimidazoles: The photocatalyst PAF-380 (2.0 mg) was dispersed in ethanol (3 mL) in a 10 mL glass vial. Then aldehyde (0.2 mmol) and amines (0.2 mmol) were added. The resulting reaction mixture was stirred at room temperature under 30W blue LED until all starting materials had been consumed as monitored by thin layer chromatography (TLC). After the reaction was completed, the photocatalyst was removed by filtration and thoroughly washed by ethanol (10 mL × 3). The combined filtrate was evaporated

under reduced pressure and the residue was purified by flash column chromatography using silica gel with petroleum ether/ethyl acetate mixture as eluent to give the target benzimidazole product.

Table S1 Substrate scope of PAF-381 catalysed blue-light-induced condensation cyclization of aldehydes and o-phenylenediamines[a,b]



1 2 3

		
3h, 79%	4h, 70%	4h, 73%
		
4h, 75%	5h, 72%	3h, 81%
		
5h, 64%	3h, 84%	3h, 88%

[a] o-Phenylenediamine (0.2 mmol), aldehyde (0.2 mmol), PAF-381 (2 mg, 6.8 mol%), ethanol (3.0 mL), air, 460 nm blue LED light (30 W, 0.11 W/cm^2), 298 K. [b] Isolated yield. rt: room temperature.

Section 3. Characterizations of TPA-PAFs

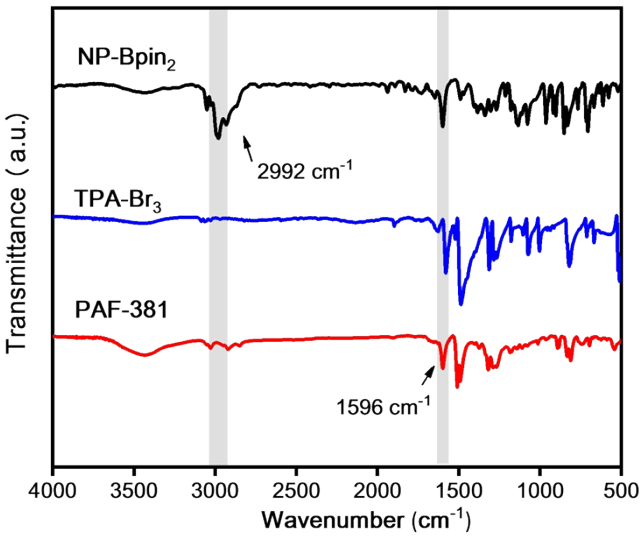


Figure S1. FTIR spectra of PAF-381 and starting materials.

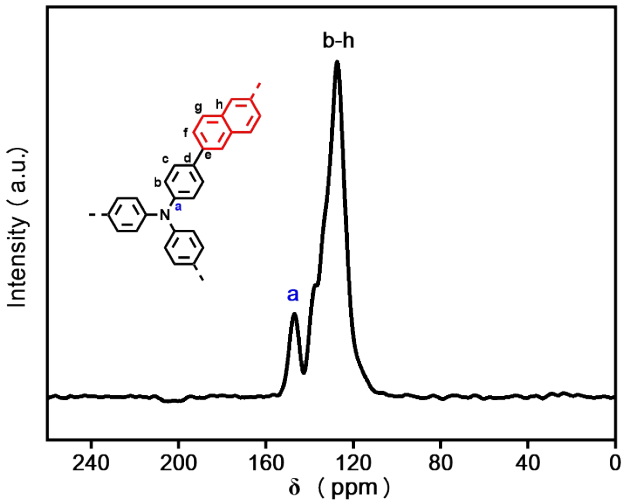


Figure S2. The solid-state ^{13}C CP/MAS NMR spectrum of PAF-381.

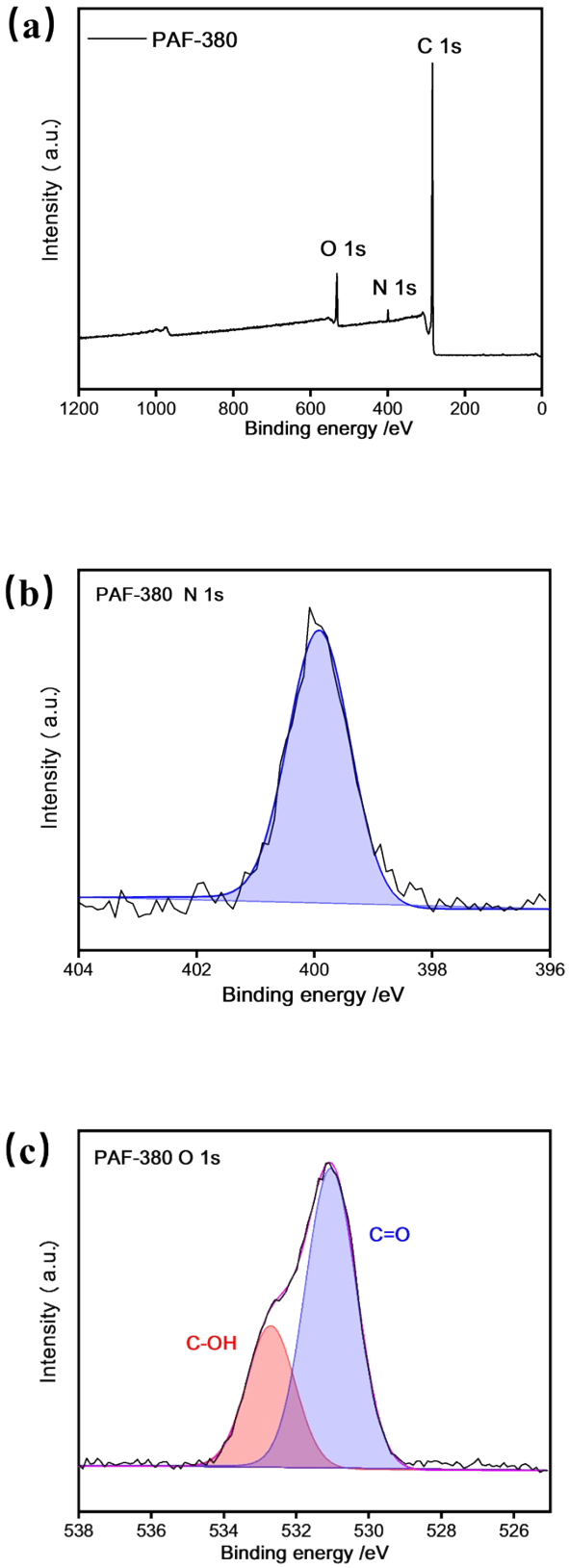


Figure S3. (a) XPS survey scan, (b) N 1s spectra of PAF-380 and (c) O 1s spectra.

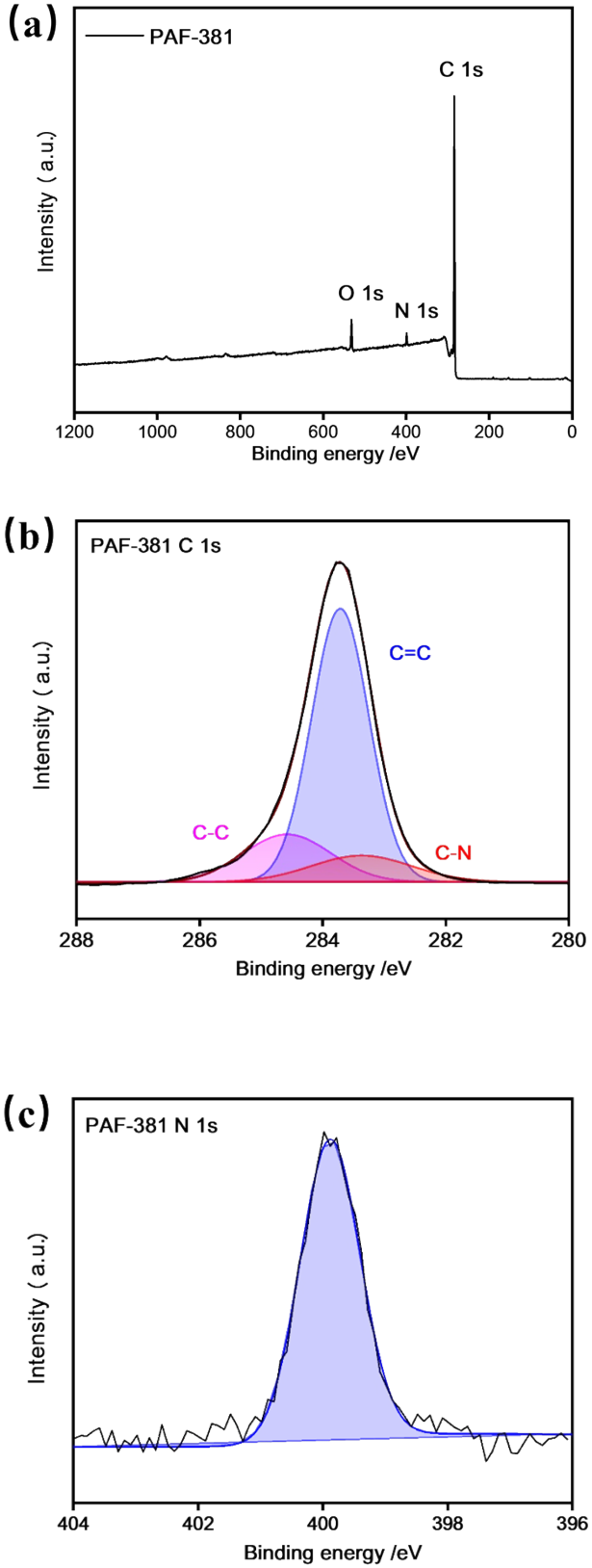


Figure S4. (a) XPS survey scan, (b) C 1s spectra and (c) N 1s spectra of PAF-381.

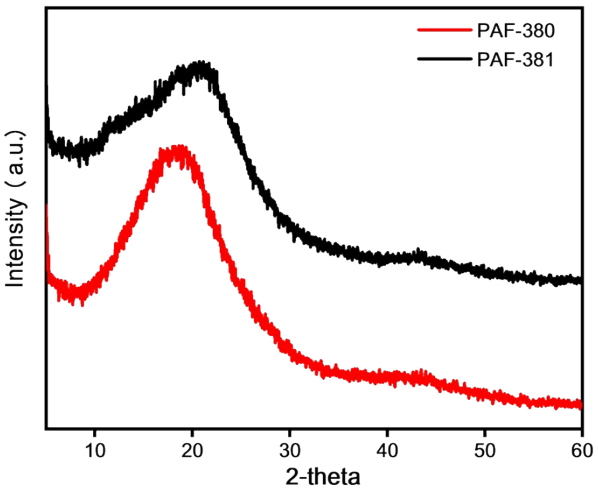


Figure S5. PXRD patterns of TPA-PAFs.

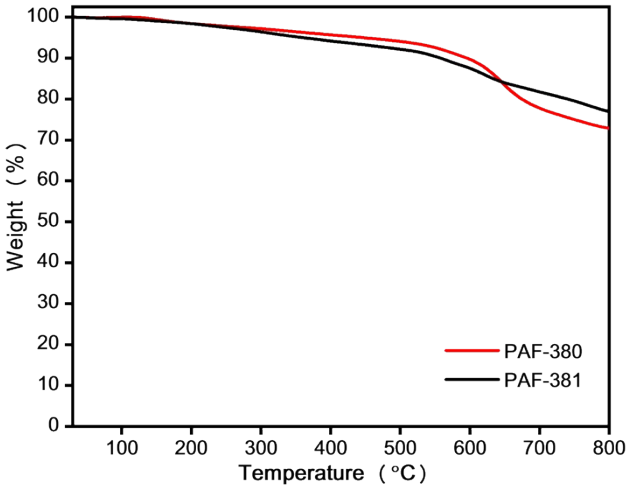


Figure S6. TGA curves of TPA-PAFs under N_2 atmosphere.

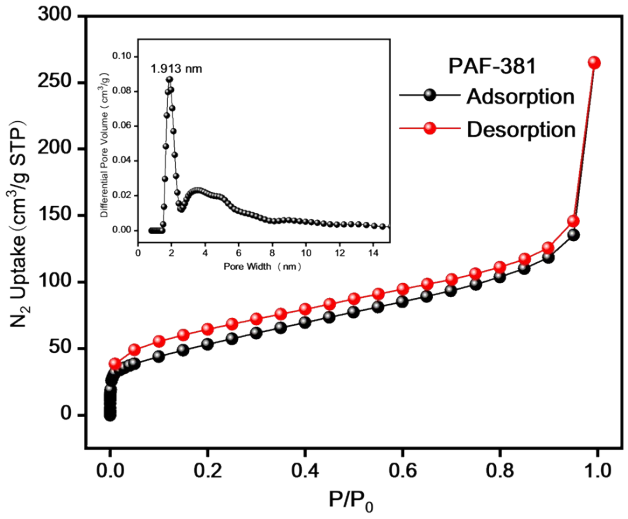


Figure S7. Nitrogen adsorption-desorption isotherm at 77 K and the corresponding pore size distribution profiles (inset) of PAF-381.

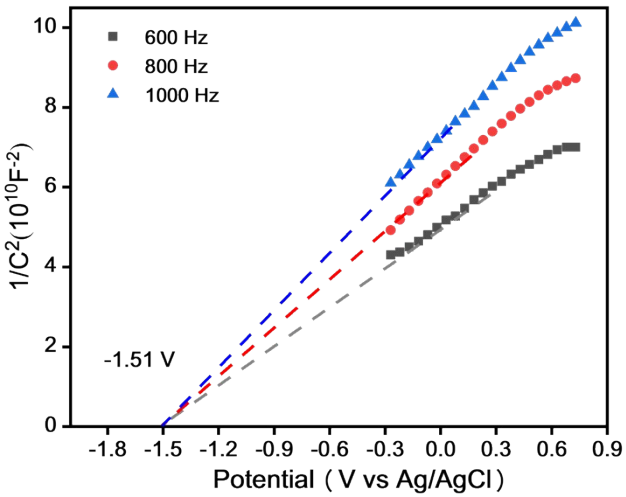


Figure S8. Mott-Schottky plots of PAF-381.

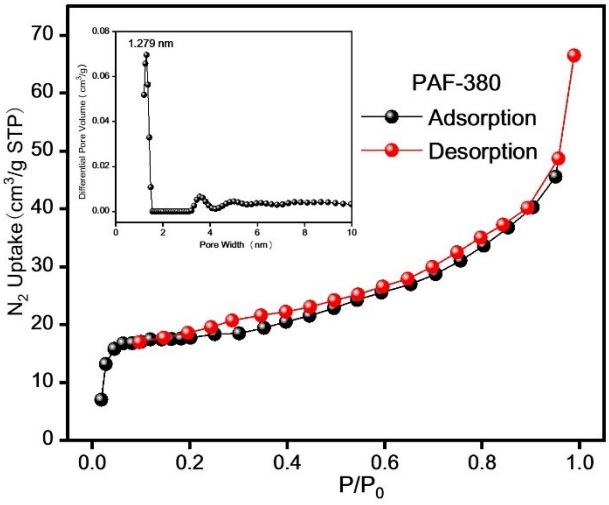
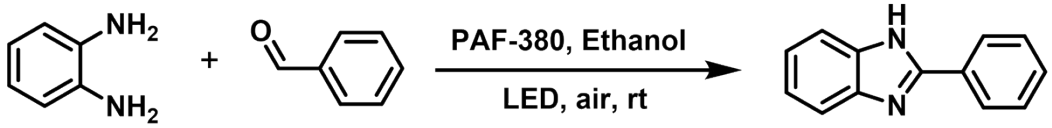


Figure S9. Nitrogen adsorption-desorption isotherm at 77 K and the corresponding pore size distribution profiles (inset) of PAF-380 after ten cycles (SA_{BET} = 121 m^2 g^{-1}).

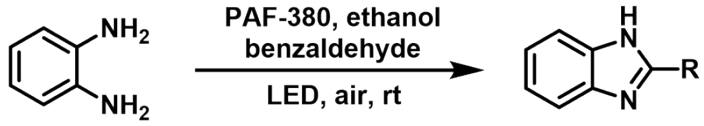
Section 4. Scale-up photosynthesis of 3a

Scheme S1. Scale-up photosynthesis of compound **3a** using PAF-380 as photocatalyst.



1a	2a	3a
540.7 mg	520.4 μL	912.2 mg
5 mmol	5 mmol	94%

Section 5. Detection of key intermediates



General conditions: ethanol (3 mL), PAF-380 (2 mg, 5.3 mol%), o-phenylenediamine (0.2 mmol) and benzaldehyde (0.2 mmol), rt, 460 nm blue LED light (30 W, 0.11 W/cm^2), air.

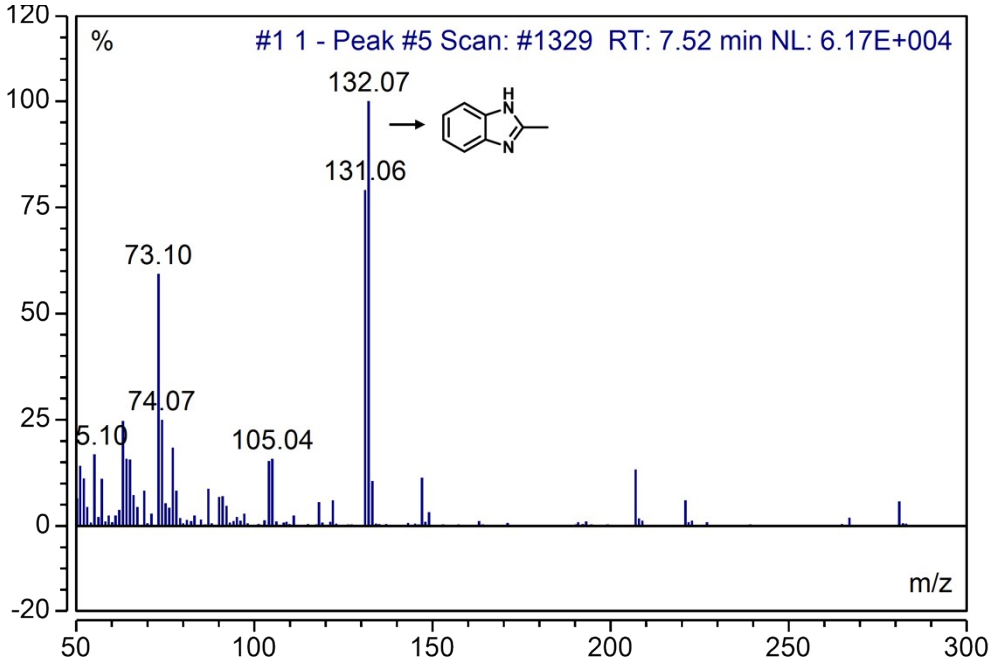


Figure S10. GC-MS spectrum of the reaction mixture after 3 h.

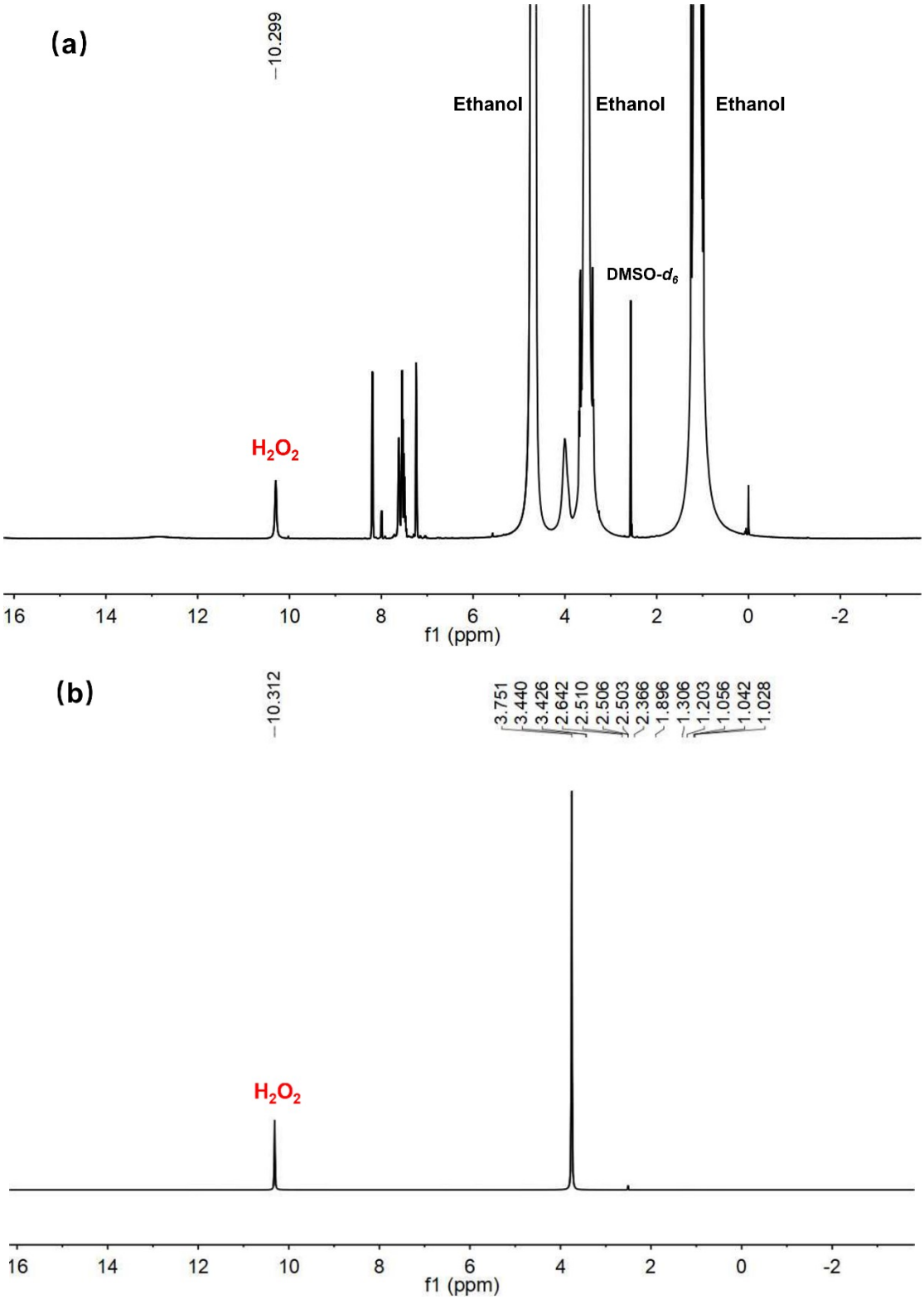
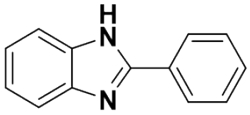
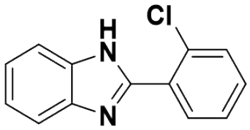


Figure S11. ^{1}H NMR (DMSO-d_6) spectra of (a) reaction mixture after 5 h and (b) 30% H_2O_2 solution for a comparison.

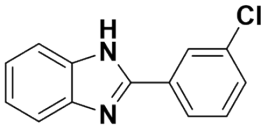
Section 6. NMR data of benzimidazole products



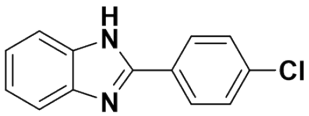
2-phenyl-1H-benzo[d]imidazole (3a): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 151.7, 130.7, 130.3, 129.4, 126.9, 122.6 ppm.



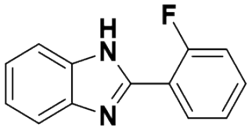
2-(2-chlorophenyl)-1H-benzo[d]imidazole (3b): ^{1}H NMR (500 MHz, DMSO) δ 12.73 (s, 1H), 7.92 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.76 – 7.46 (m, 5H), 7.24 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 149.6, 143.7, 135.1, 132.6, 132.1, 131.7, 130.8, 130.5, 127.9, 123.2, 122.2, 119.6, 112.2 ppm.



2-(3-chlorophenyl)-1H-benzo[d]imidazole (3c): ^{1}H NMR (500 MHz, DMSO) δ 13.03 (s, 1H), 8.23 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.80 – 7.44 (m, 4H), 7.23 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.2, 144.1, 135.5, 134.3, 132.7, 131.4, 130.0, 126.5, 125.5, 123.4, 122.4, 119.6, 112.0 ppm.

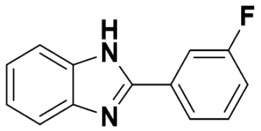


2-(4-chlorophenyl)-1H-benzo[d]imidazole (3d): ^{1}H NMR (500 MHz, DMSO) δ 12.97 (s, 1H), 8.19 (d, *J* = 8.6 Hz, 2H), 7.83 – 7.41 (m, 4H), 7.33 – 7.11 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.6, 144.2, 135.5, 135.0, 129.5, 128.6, 123.2, 122.3, 119.4, 111.9 ppm.

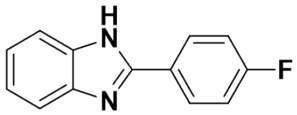


2-(2-fluorophenyl)-1H-benzo[d]imidazole (3e): ^{1}H NMR (500 MHz, DMSO) δ 12.58 (s, 1H), 8.24 (td, *J* = 7.7, 1.8 Hz, 1H), 7.80 – 7.50 (m, 3H), 7.49 – 7.34 (m, 2H), 7.24 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 160.9, 158.9, 146.9, 143.5, 135.5, 132.3, 130.7, 125.6,

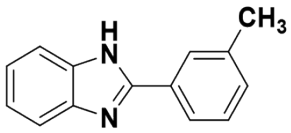
123.2, 122.3, 119.4, 118.6, 117.1, 116.9, 112.4 ppm.



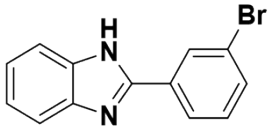
2-(3-fluorophenyl)-1H-benzo[d]imidazole (3f): ^{1}H NMR (500 MHz, DMSO) δ 12.99 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.75 – 7.51 (m, 3H), 7.34 (td, *J* = 8.4, 2.4 Hz, 1H), 7.23 (dt, *J* = 15.0, 6.7 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 163.9, 162.0, 150.4, 144.1, 135.4, 133.0, 131.6, 123.4, 123.0, 122.4, 117.1, 117.0, 113.6, 113.4, 112.0 ppm.



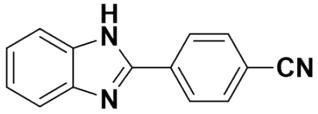
2-(4-fluorophenyl)-1H-benzo[d]imidazole (3g): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.22 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 8.8 Hz, 2H), 7.27 – 7.13 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.5, 162.6, 150.9, 144.2, 135.5, 129.2, 127.3, 123.0, 122.2, 119.3, 116.6, 116.4, 111.8 ppm.



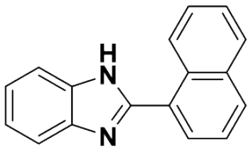
2-(m-tolyl)-1H-benzo[d]imidazole (3h): ^{1}H NMR (500 MHz, DMSO) δ 12.85 (s, 1H), 8.03 (s, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 151.8, 144.3, 138.6, 135.4, 130.9, 130.6, 129.3, 127.5, 124.1, 122.9, 122.1, 119.3, 111.8, 21.5 ppm.



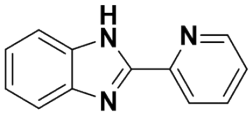
2-(2-bromophenyl)-1H-benzo[d]imidazole (3i): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 150.1, 144.1, 135.5, 132.9, 131.6, 129.4, 125.9, 123.4, 122.6, 119.6, 112.0 ppm.



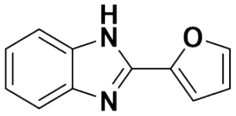
4-(1H-benzo[d]imidazol-2-yl)benzonitrile (3j): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (151 MHz, DMSO) δ 149.9, 144.2, 135.6, 134.8, 133.4, 127.5, 123.9, 122.7, 119.8, 119.1, 112.4, 112.3 ppm.



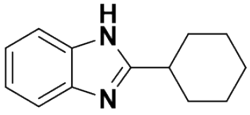
2-(naphthalen-1-yl)-1H-benzo[d]imidazole (3k): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (151 MHz, DMSO) δ 151.8, 144.4, 134.9, 134.1, 131.0, 130.6, 128.9, 128.3, 128.0, 127.5, 126.8, 125.7, 123.1, 122.1, 119.6, 111.8 ppm.



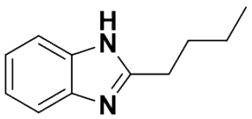
2-(pyridin-2-yl)-1H-benzo[d]imidazole (3l): ^{1}H NMR (500 MHz, DMSO) δ 13.10 (s, 1H), 8.72 (d, *J* = 4.4 Hz, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 7.99 (td, *J* = 7.8, 1.6 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.45 (m, 2H), 7.28 – 7.15 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 151.2, 149.8, 149.0, 144.4, 138.0, 135.4, 125.2, 123.6, 122.4, 121.9, 119.8, 112.5 ppm.



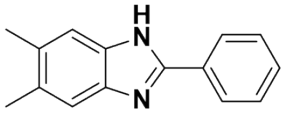
2-(furan-2-yl)-1H-benzo[d]imidazole (3m): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (151 MHz, DMSO) δ 146.1, 145.1, 144.1, 134.7, 123.0, 122.3, 119.2, 112.8, 111.7, 110.9 ppm.



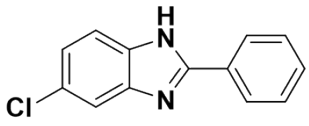
2-cyclohexyl-1H-benzo[d]imidazole (3n): ^{1}H NMR (500 MHz, DMSO) δ 12.08 (s, 2H), 7.61 – 7.39 (m, 3H), 7.38 (s, 1H), 7.09 (d, *J* = 3.2 Hz, 4H), 2.89 – 2.78 (m, 2H), 2.01 (dd, *J* = 13.1, 2.7 Hz, 4H), 1.90 – 1.72 (m, 4H), 1.72 – 1.53 (m, 6H), 1.47 – 1.11 (m, 7H). ^{13}C NMR (151 MHz, DMSO) δ 159.3, 143.5, 134.7, 121.8, 121.1, 118.7, 111.2, 38.2, 31.7, 26.0 ppm.



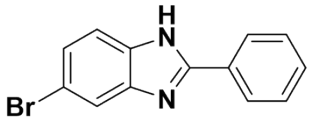
2-butyl-1H-benzo[d]imidazole (3o): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 155.6, 121.5, 30.2, 28.7, 22.3, 14.0 ppm.



5,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (3p): ^{1}H NMR (500 MHz, DMSO) δ 12.64 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 2H), 7.64 – 7.20 (m, 5H), 2.32 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 150.8, 143.0, 134.0, 131.6, 131.0, 130.4, 129.9, 129.3, 126.7, 119.4, 111.8, 20.5 ppm.



5-chloro-2-phenyl-1H-benzo[d]imidazole (3q): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 153.3, 152.9, 145.2, 143.1, 136.2, 134.3, 130.7, 130.2, 129.5, 127.1, 126.6, 123.1, 122.5, 120.6, 118.7, 113.1, 111.5 ppm.



5-bromo-2-phenyl-1H-benzo[d]imidazole (3r): ^{1}H NMR (500 MHz, DMSO) δ 12.90 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.47 (m, 4H), 7.25 – 7.16 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 153.1, 152.8, 145.8, 143.4, 136.8, 134.6, 130.7, 130.1, 129.5, 127.1, 125.7, 125.2, 121.7, 121.0, 115.2, 114.4, 113.6 ppm.

Section 7. NMR spectra of benzimidazole products

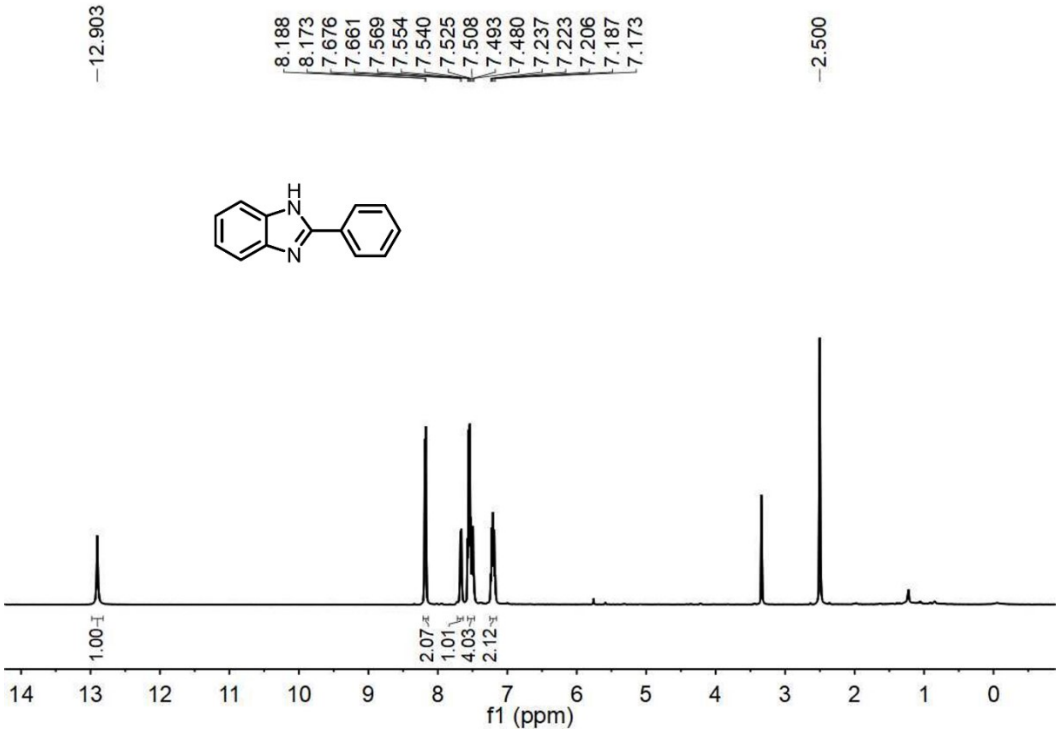


Figure S12. ^{1}H NMR spectrum of 2-phenyl-1H-benzo[d]imidazole (**3a**).

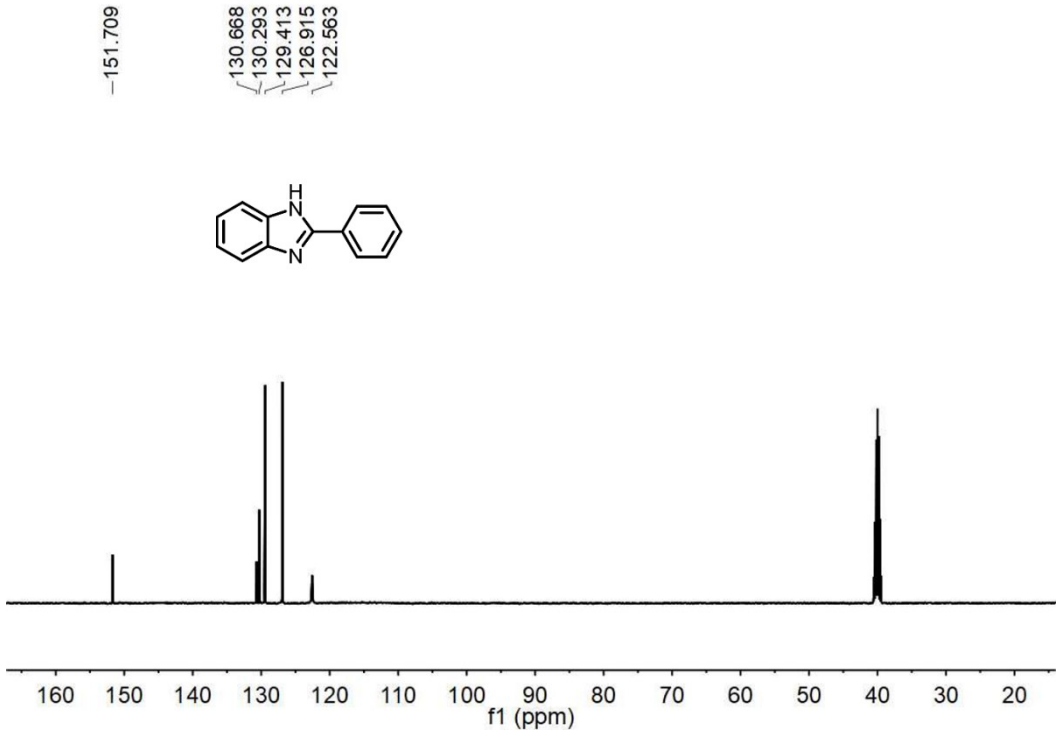


Figure S13. ^{13}C NMR spectrum of 2-phenyl-1H-benzo[d]imidazole (**3a**).

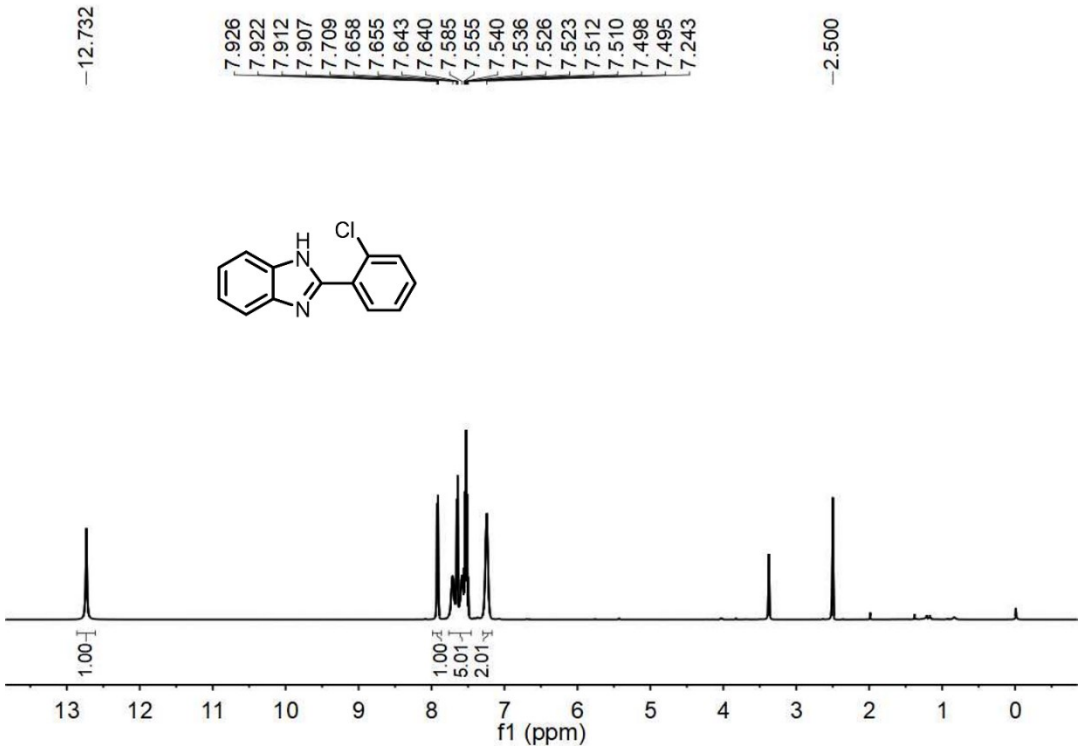


Figure S14. ^{1}H NMR spectrum of 2-(2-chlorophenyl)-1H-benzo[d]imidazole (**3b**).

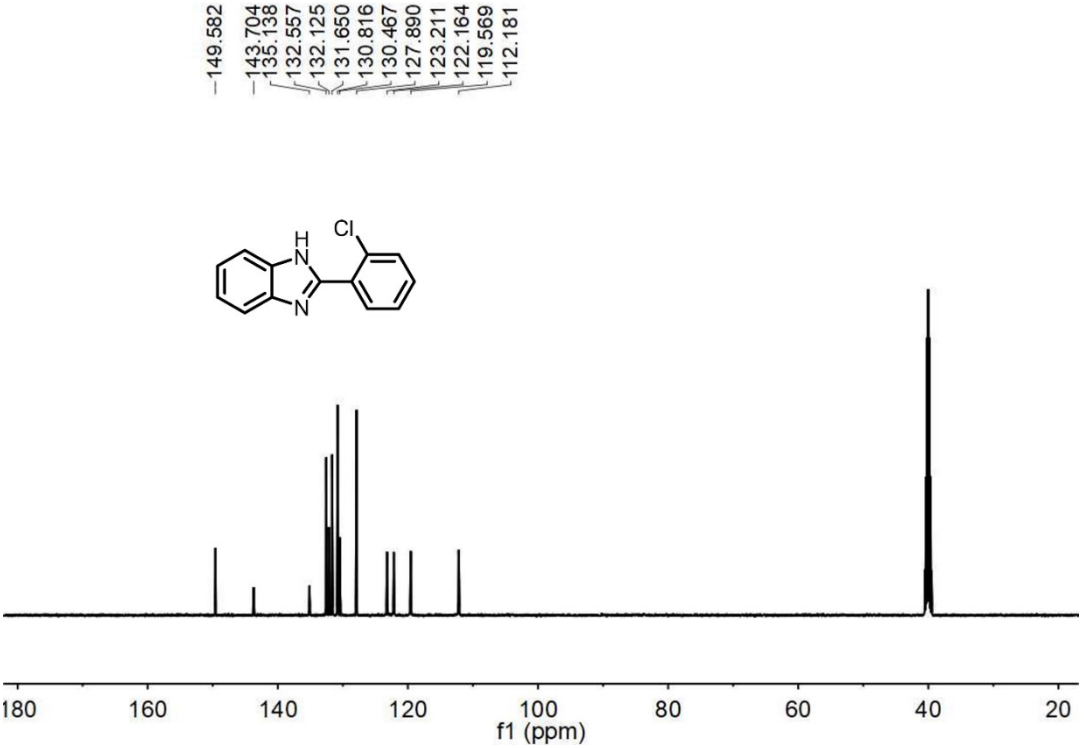


Figure S15. ^{13}C NMR spectrum of 2-(2-chlorophenyl)-1H-benzo[d]imidazole (**3b**).

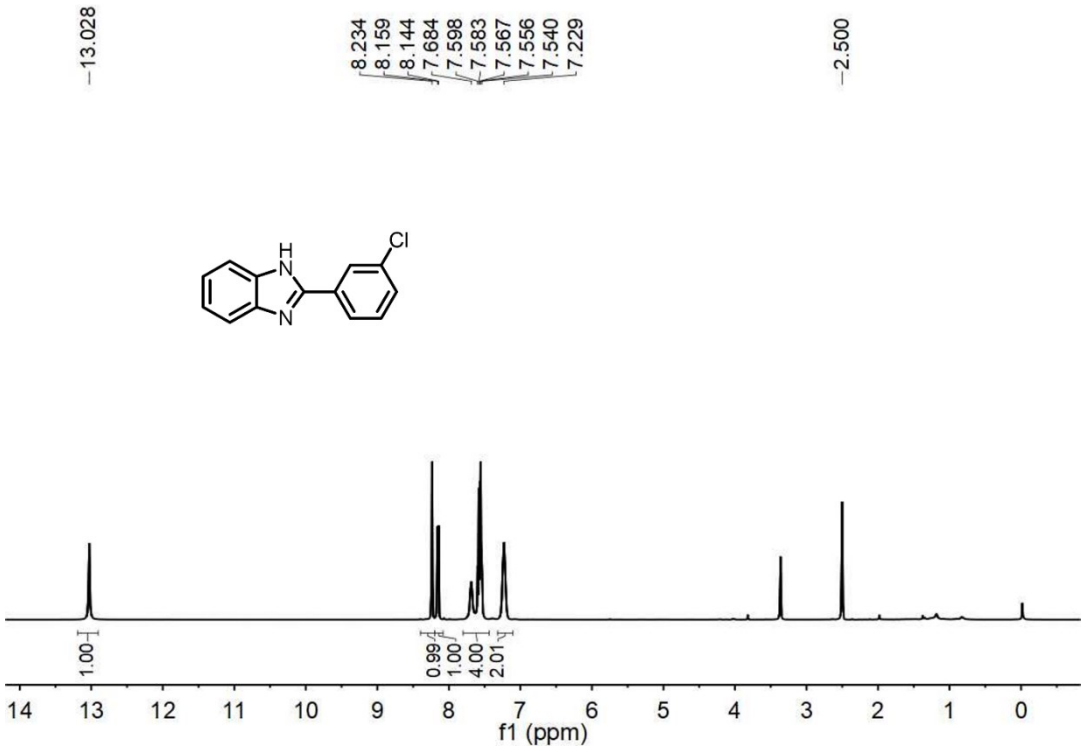


Figure S16. [1]H NMR spectrum of 2-(3-chlorophenyl)-1H-benzo[d]imidazole (**3c**).

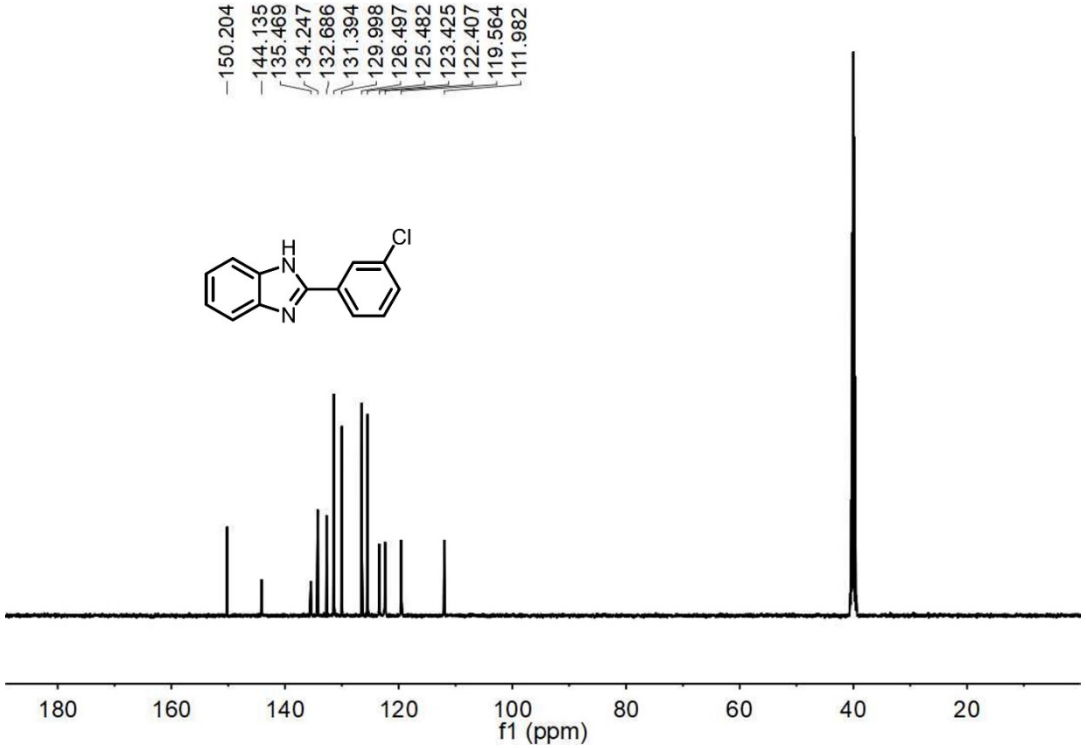


Figure S17. [13]C-NMR spectrum of 2-(3-chlorophenyl)-1H-benzo[d]imidazole (**3c**).

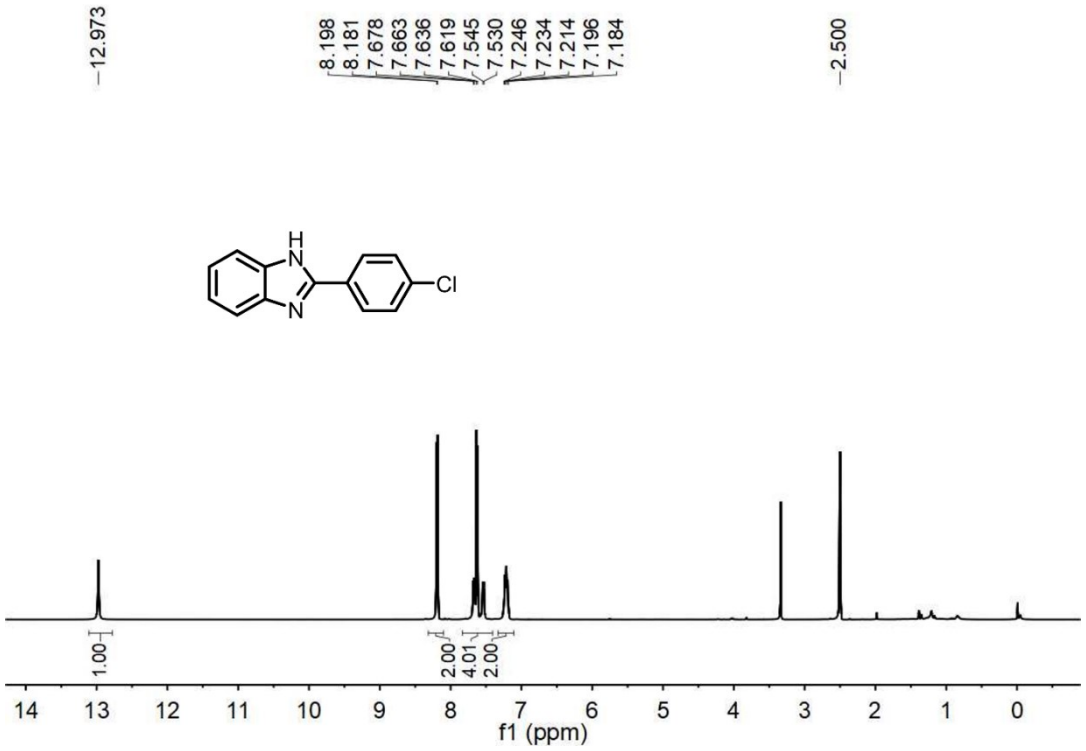


Figure S18. ^{1}H NMR spectrum of 2-(4-chlorophenyl)-1H-benzo[d]imidazole (**3d**).

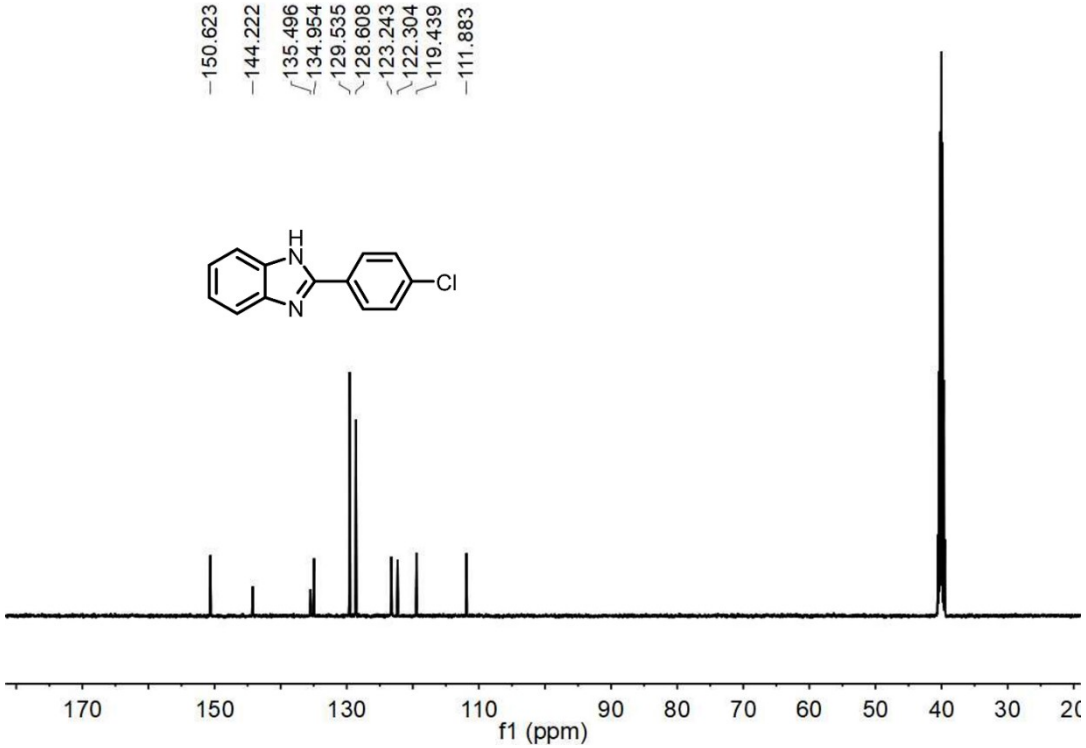


Figure S19. ^{13}C NMR spectrum of 2-(4-chlorophenyl)-1H-benzo[d]imidazole (**3d**).

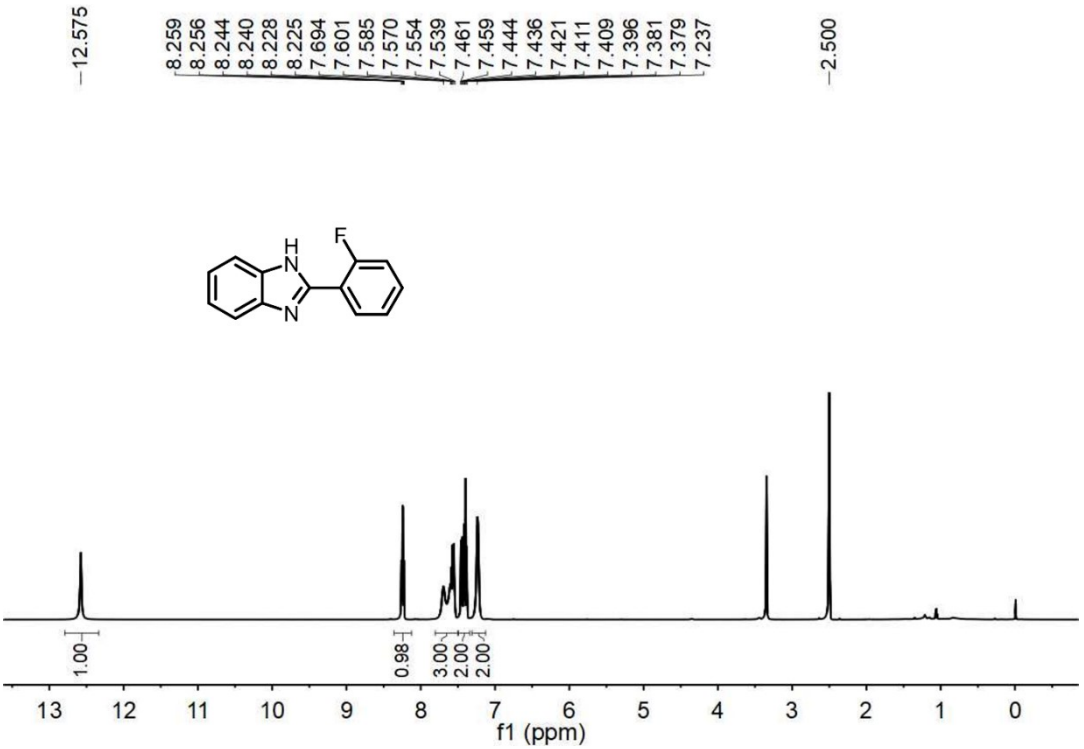


Figure S20. ^{1}H NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole (**3e**).

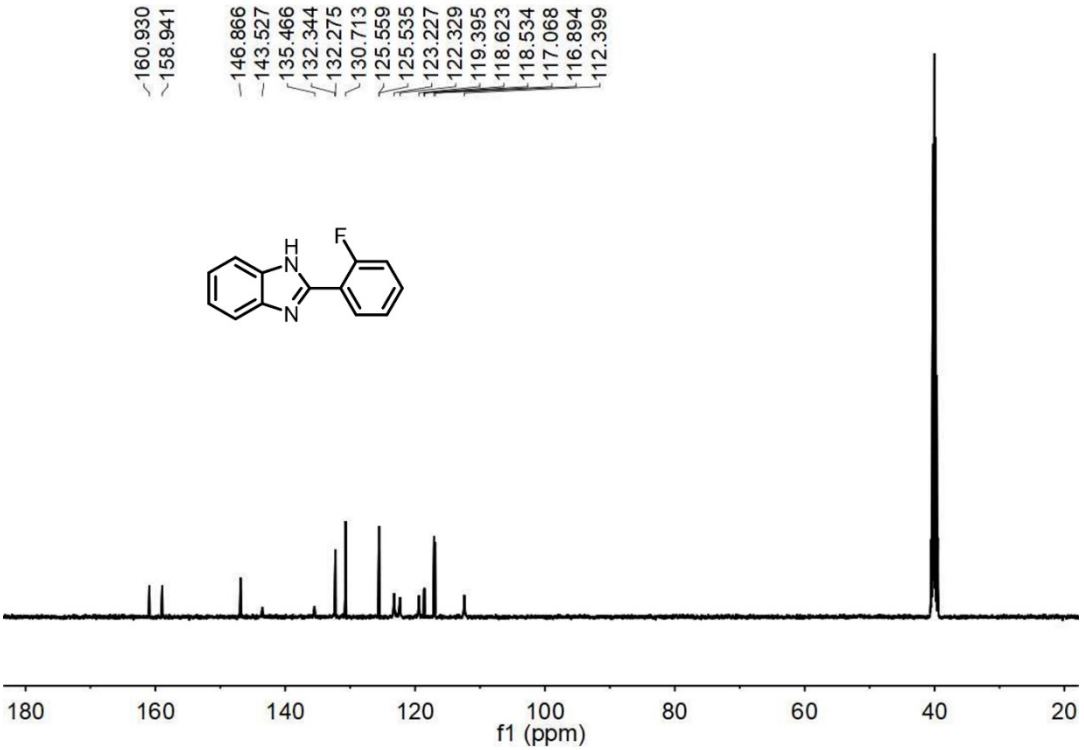


Figure S21. ^{13}C NMR spectrum of 2-(2-fluorophenyl)-1H-benzo[d]imidazole (**3e**).

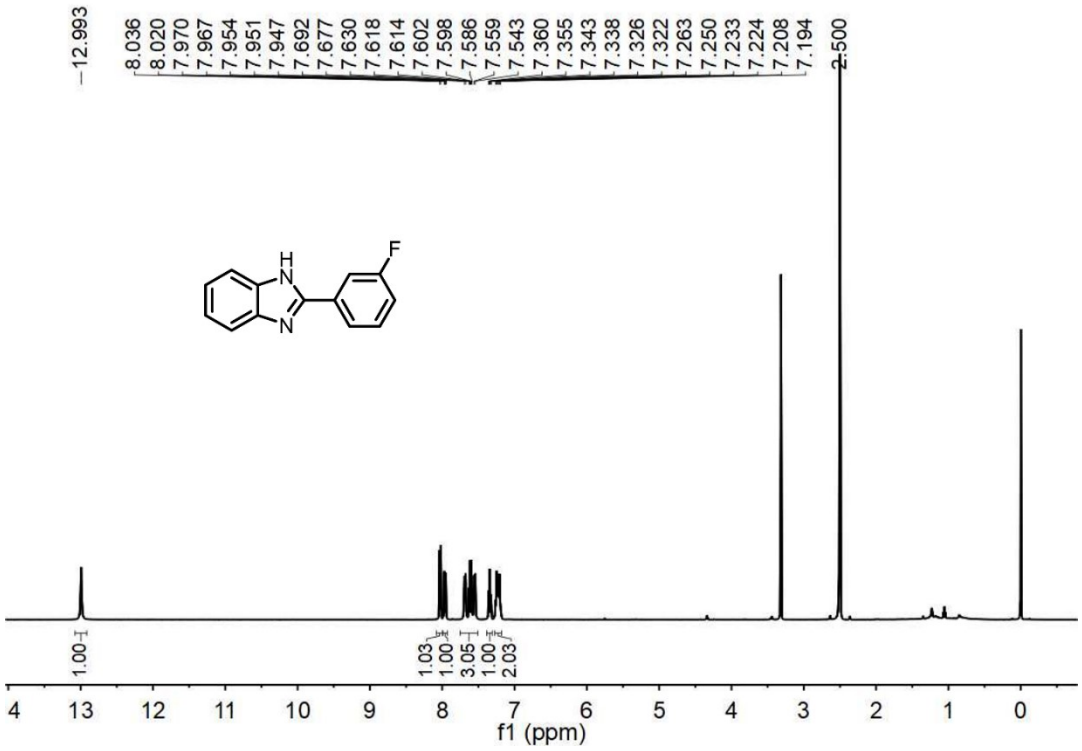


Figure S22. ^{1}H NMR spectrum of 2-(3-fluorophenyl)-1H-benzo[d]imidazole (**3f**).

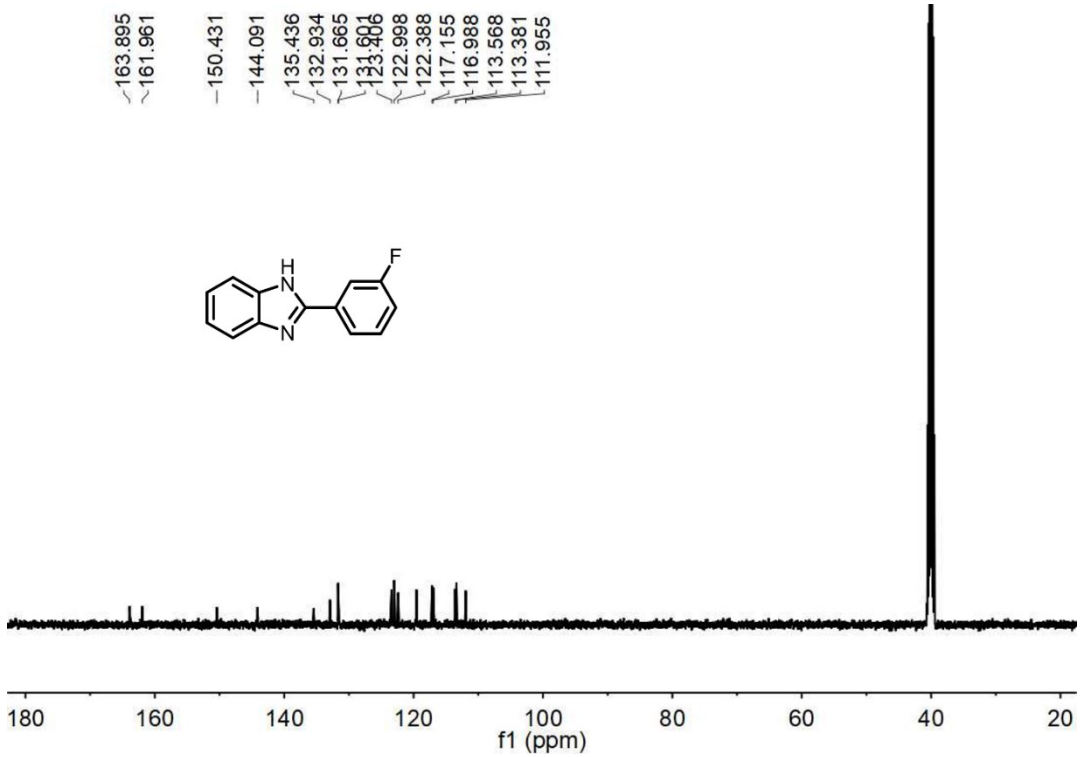


Figure S23. ^{13}C NMR spectrum of 2-(3-fluorophenyl)-1H-benzo[d]imidazole (**3f**).

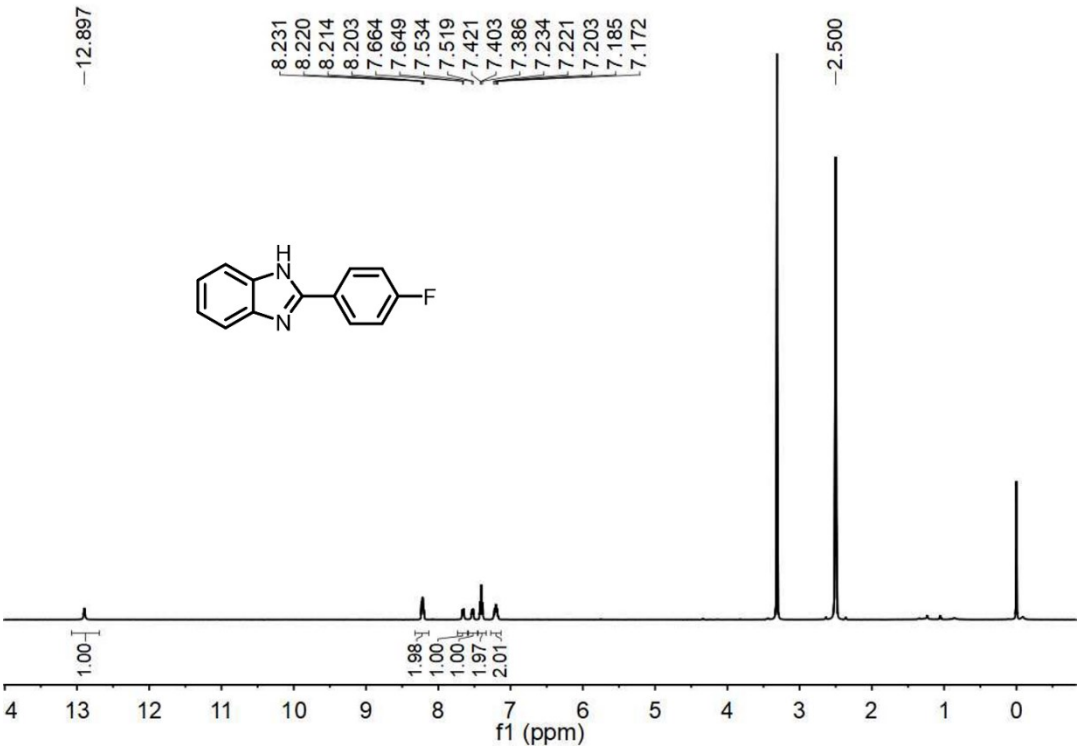


Figure S24. ^{1}H NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole (**3g**).

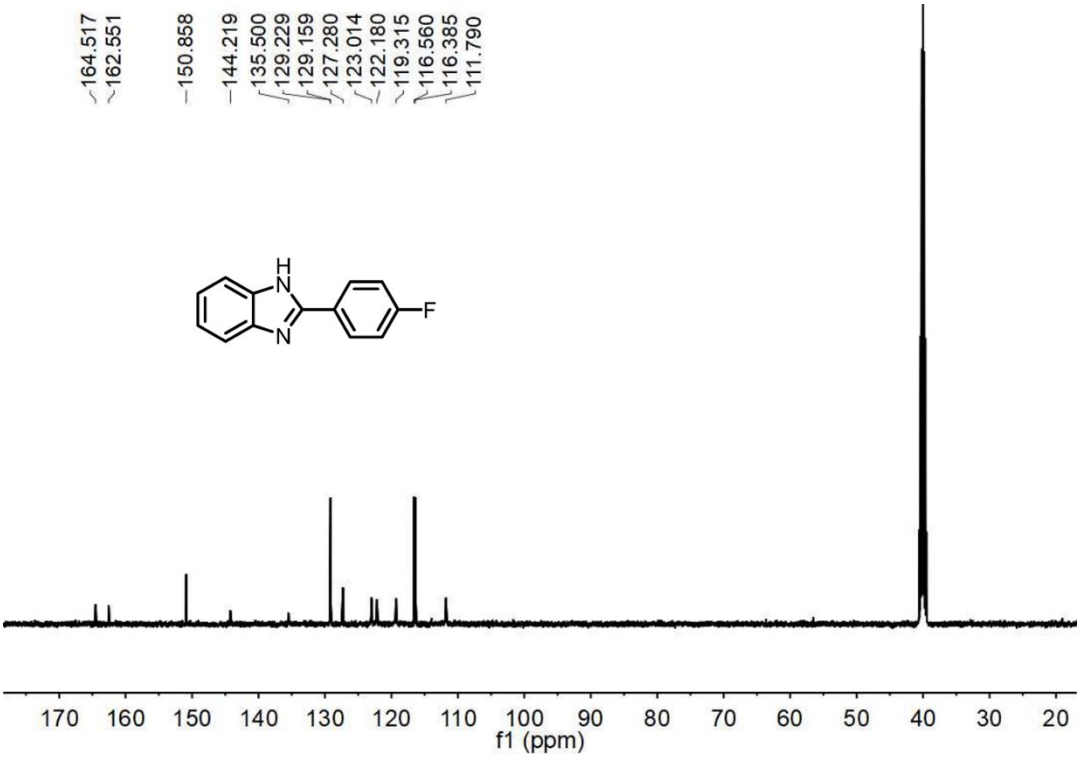


Figure S25. ^{13}C NMR spectrum of 2-(4-fluorophenyl)-1H-benzo[d]imidazole (**3g**).

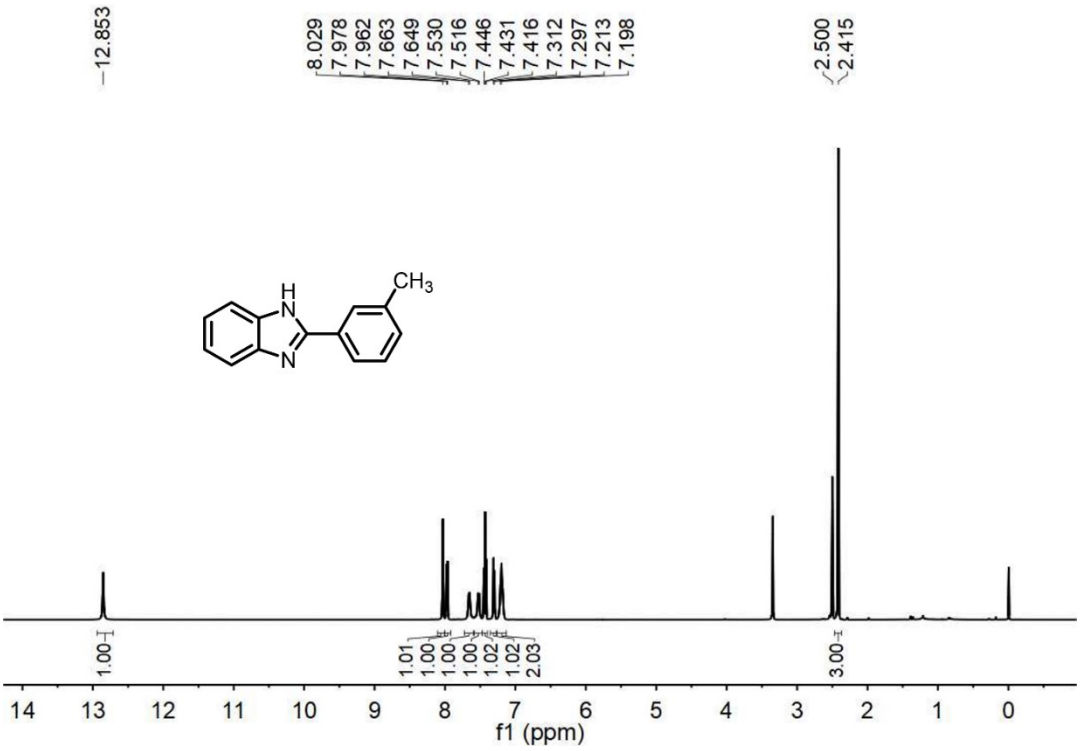


Figure S26. ^{1}H NMR spectrum of 2-(m-tolyl)-1H-benzo[d]imidazole (**3h**).

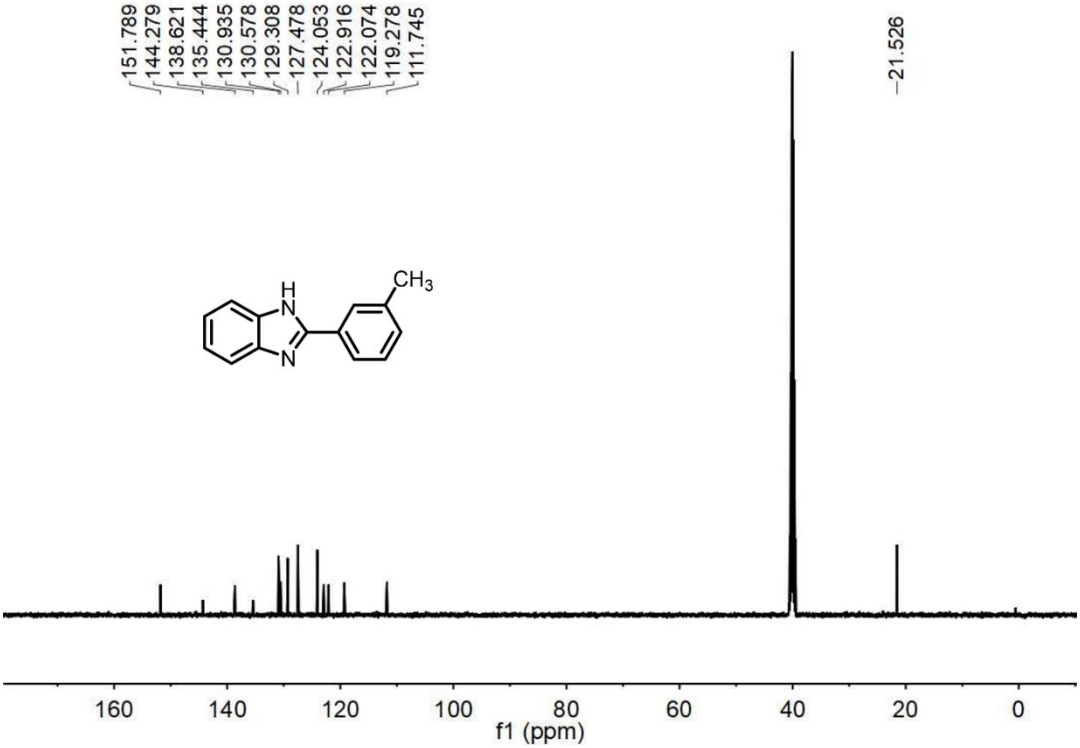


Figure S27. ^{13}C NMR spectrum of 2-(m-tolyl)-1H-benzo[d]imidazole (**3h**).

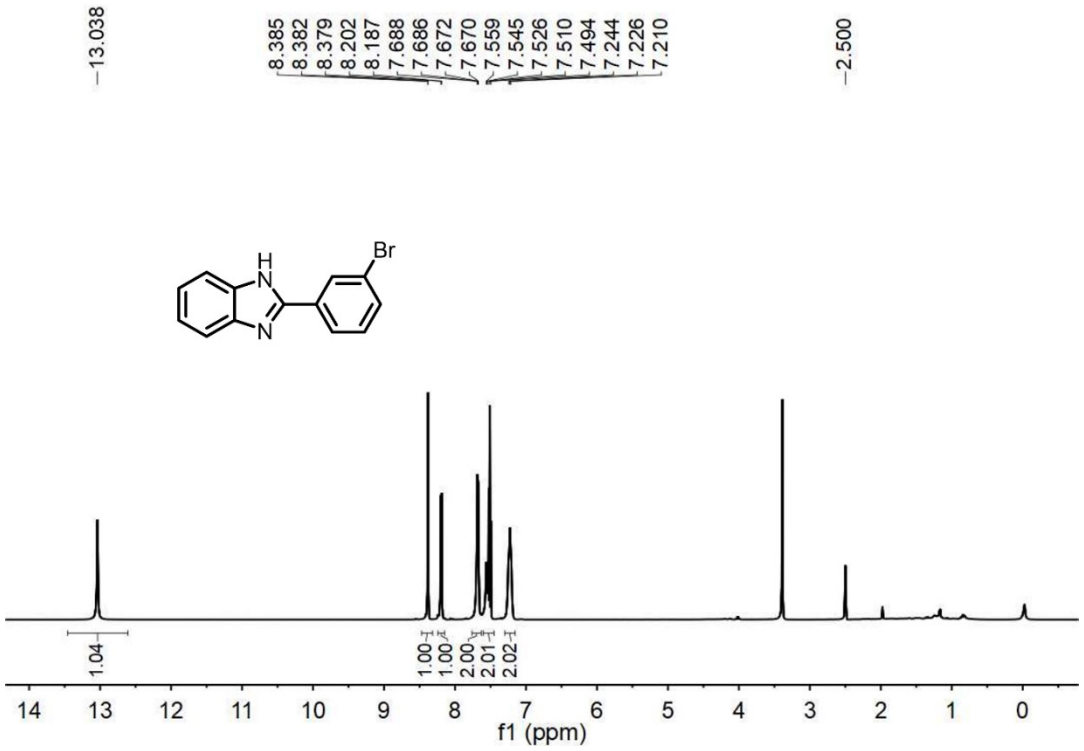


Figure S28. ^{1}H NMR spectrum of 2-(2-bromophenyl)-1H-benzo[d]imidazole (**3i**).

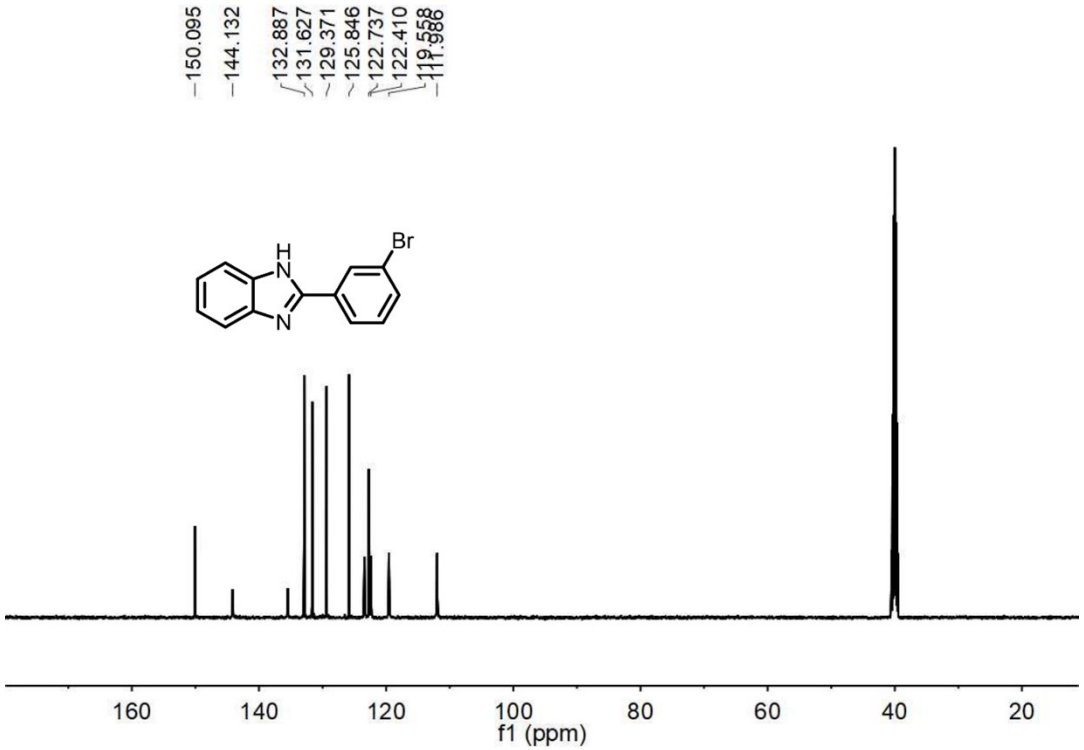


Figure S29. ^{13}C NMR spectrum of 2-(2-bromophenyl)-1H-benzo[d]imidazole (**3i**).

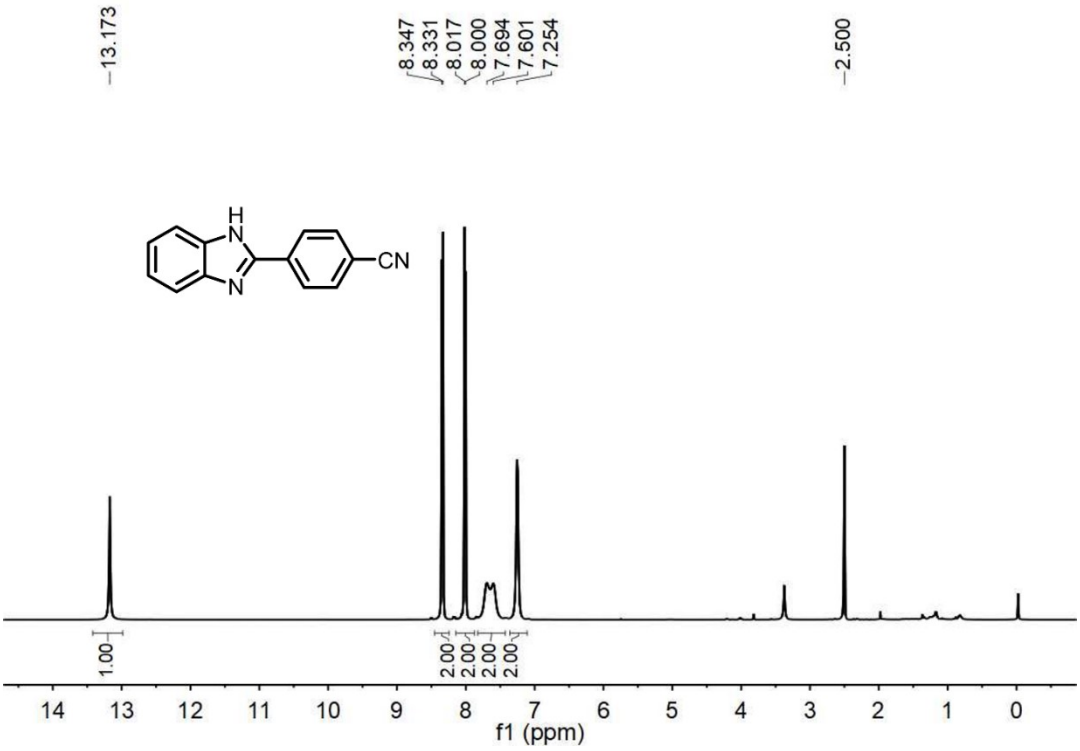


Figure S30. ^{1}H NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzonitrile (**3j**).

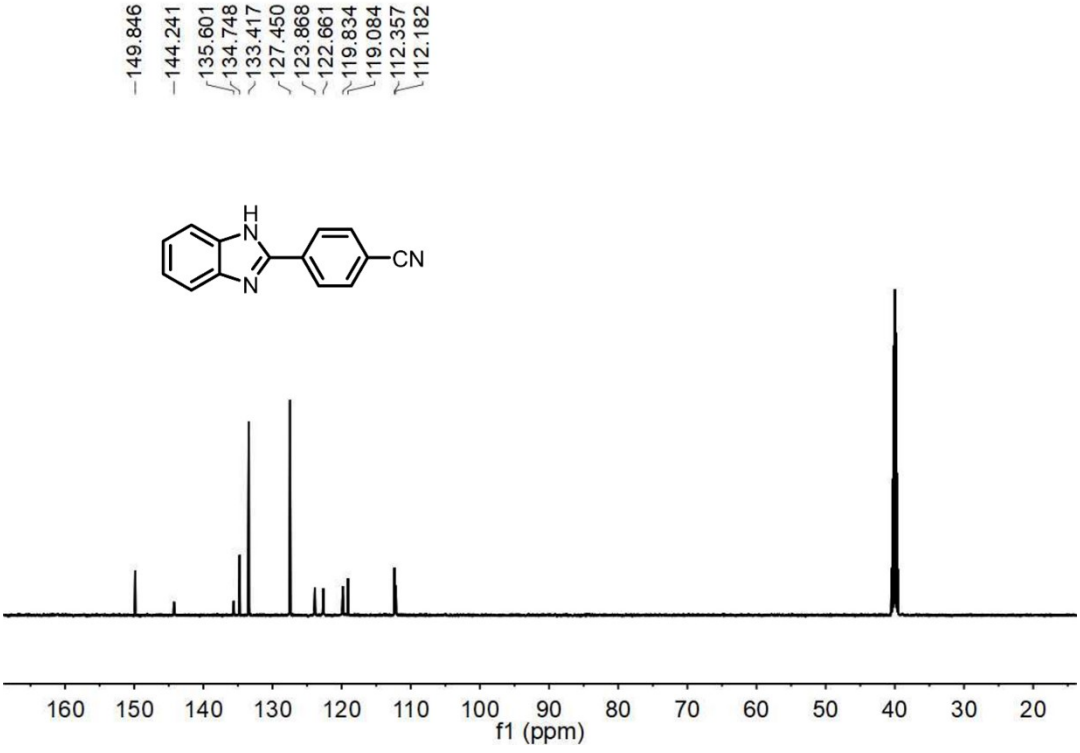


Figure S31. ^{13}C NMR spectrum of 4-(1H-benzo[d]imidazol-2-yl)benzonitrile (**3j**).

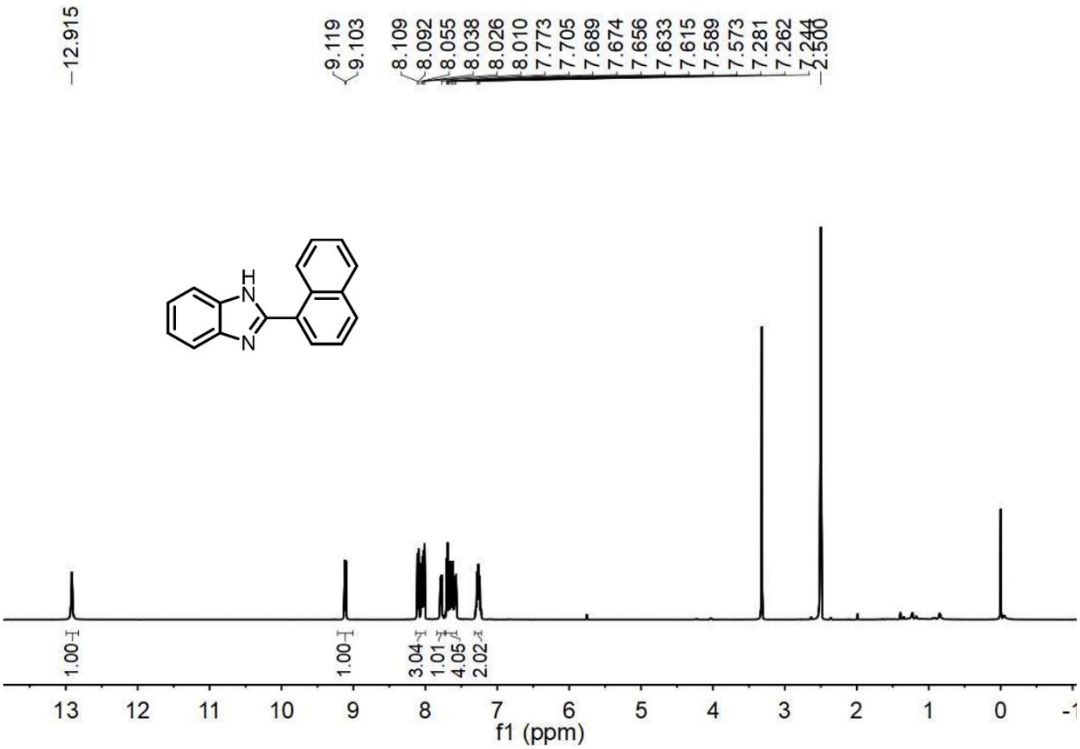


Figure S32. ^{1}H NMR spectrum of 2-(naphthalen-1-yl)-1H-benzo[d]imidazole (**3k**).

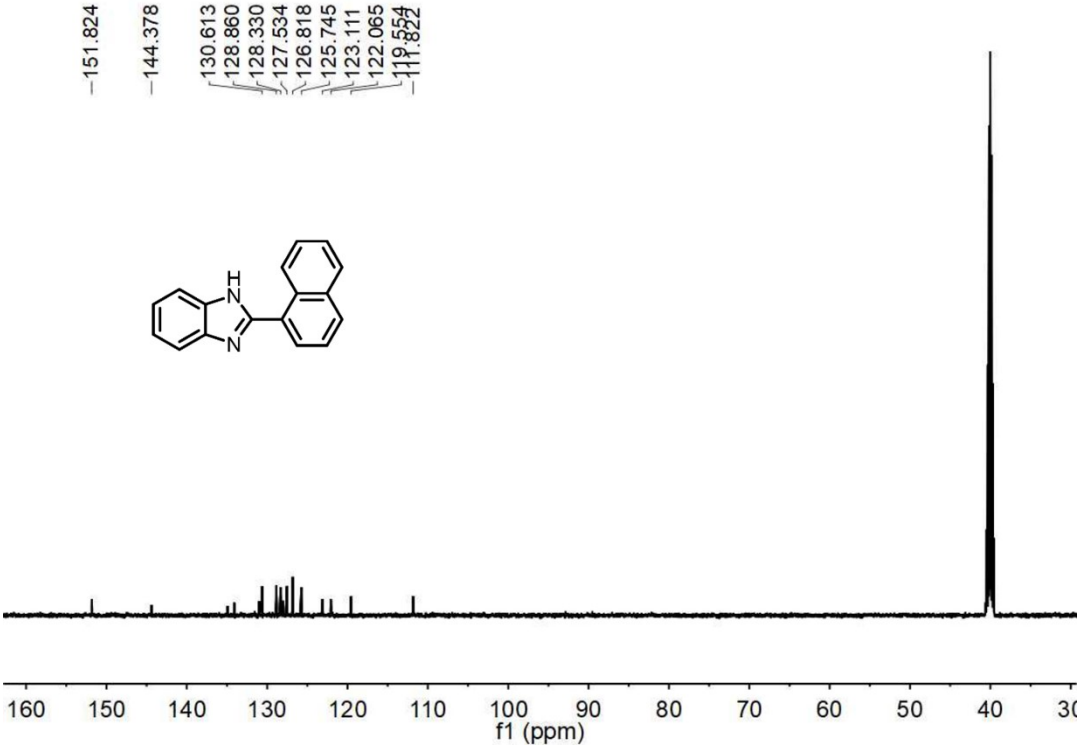


Figure S33. ^{13}C NMR spectrum of 2-(naphthalen-1-yl)-1H-benzo[d]imidazole (**3k**).

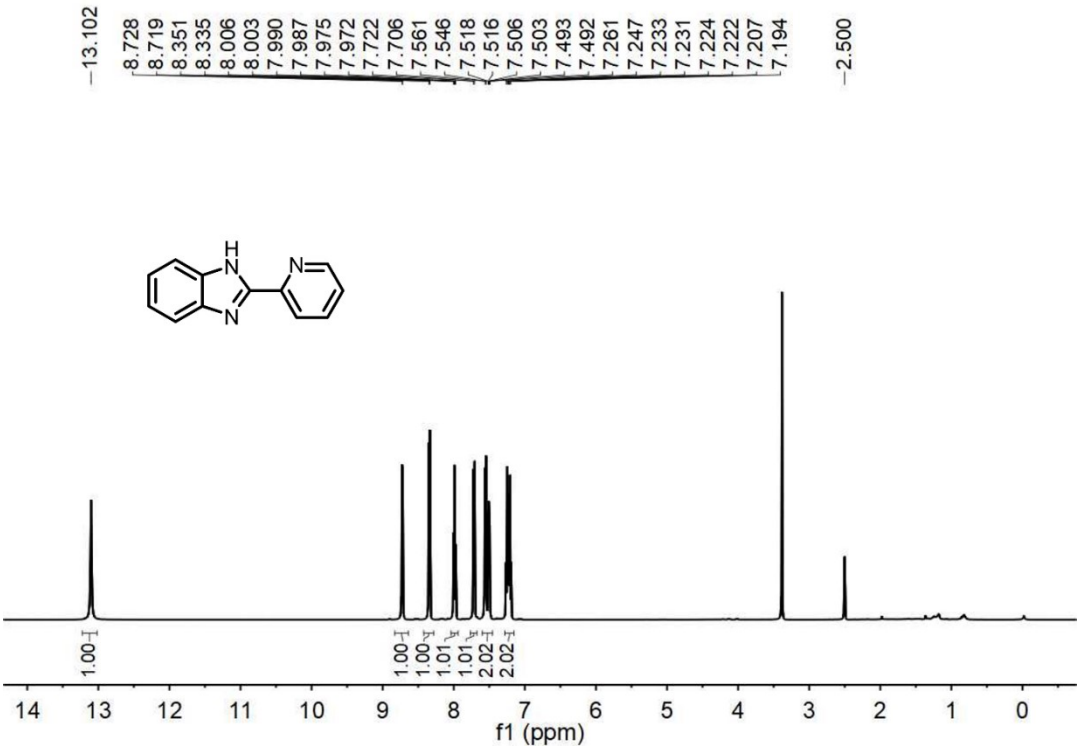


Figure S34. [1]H NMR spectrum of 2-(pyridin-2-yl)-1H-benzo[d]imidazole (**3l**).

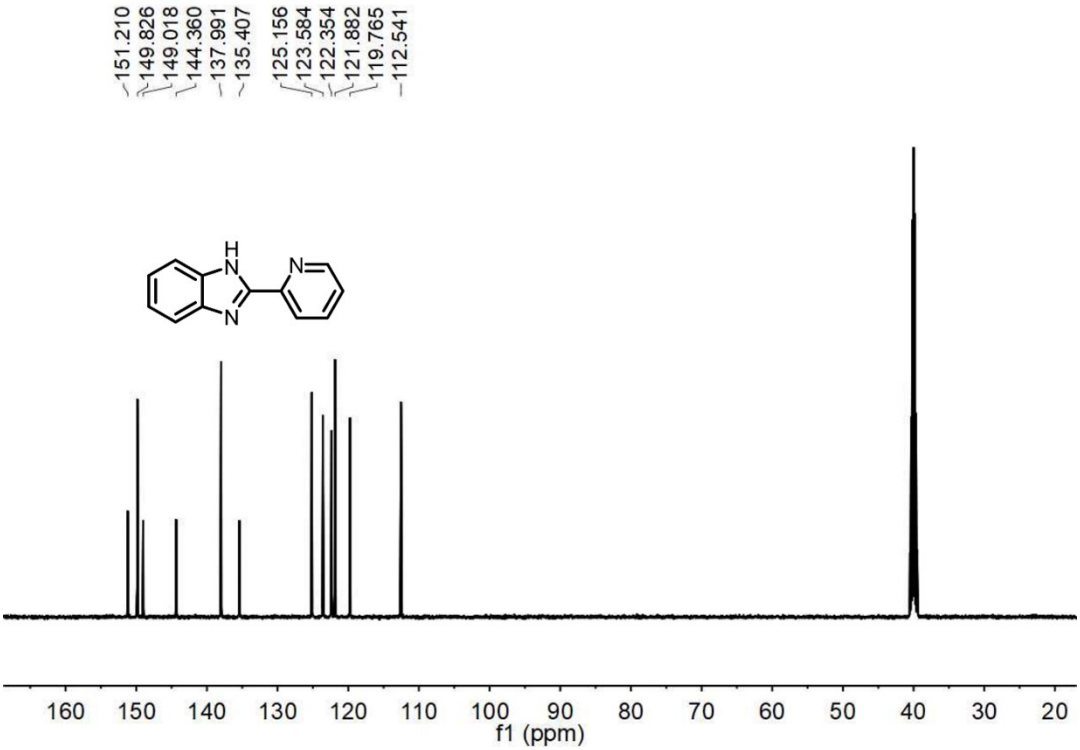


Figure S35. [13]C NMR spectrum of 2-(pyridin-2-yl)-1H-benzo[d]imidazole (**3l**).

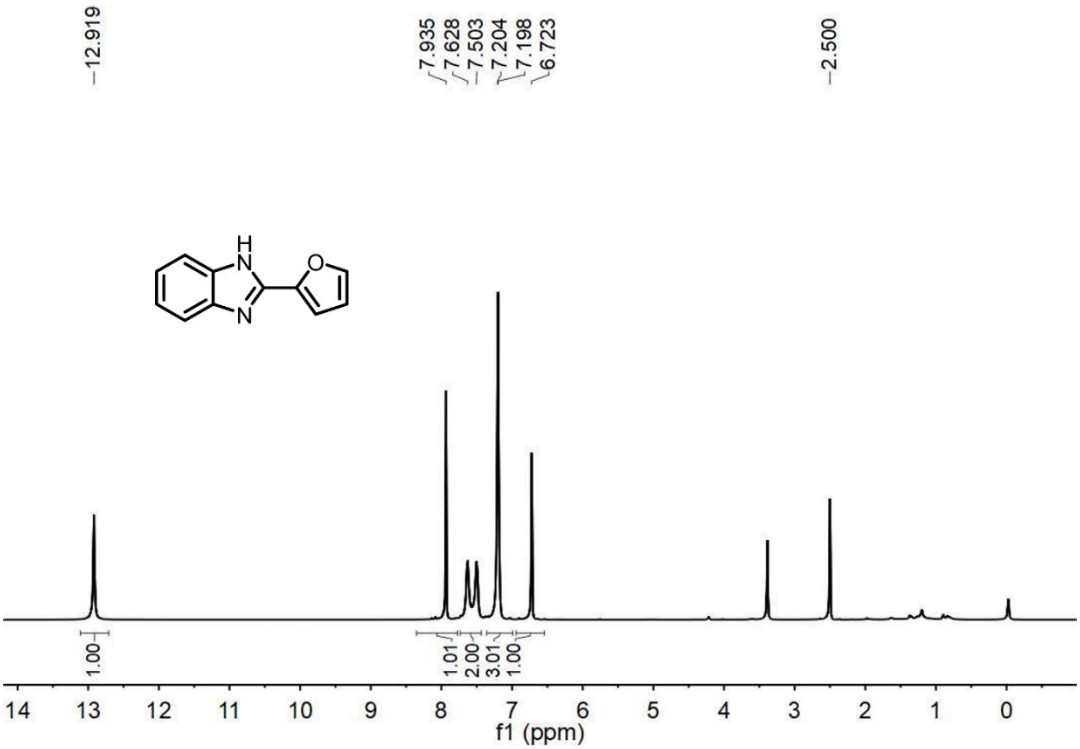


Figure S36. [1]H NMR spectrum of 2-(furan-2-yl)-1H-benzo[d]imidazole (**3m**).

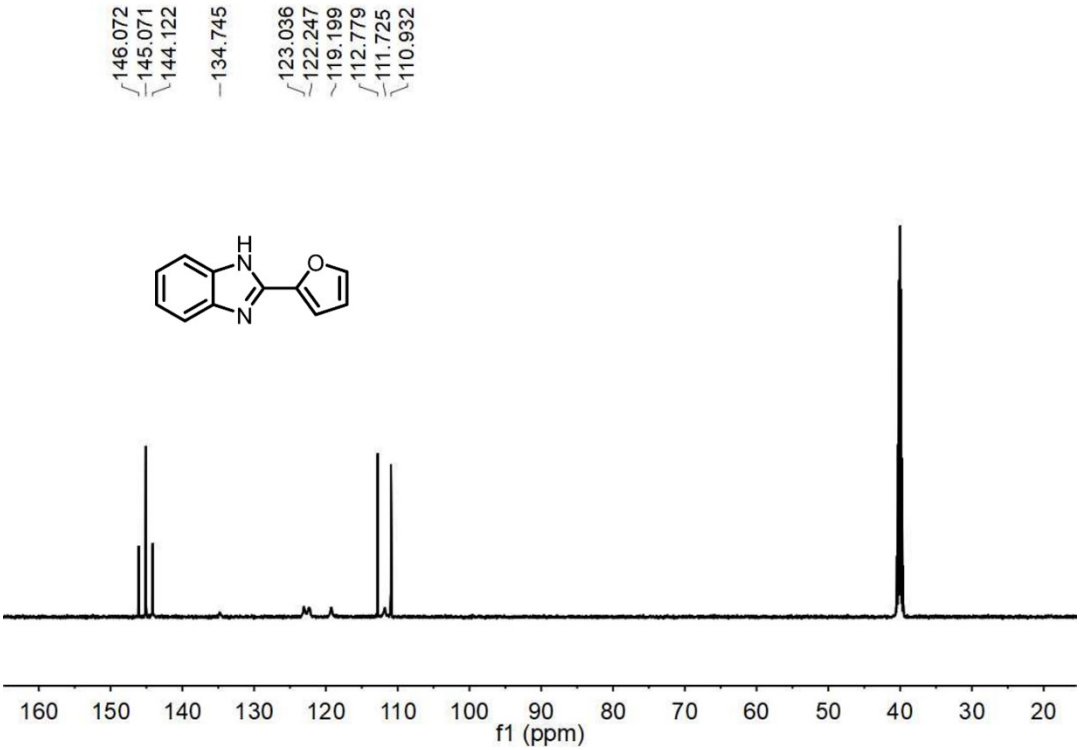


Figure S37. [13]C NMR spectrum of 2-(furan-2-yl)-1H-benzo[d]imidazole (**3m**).

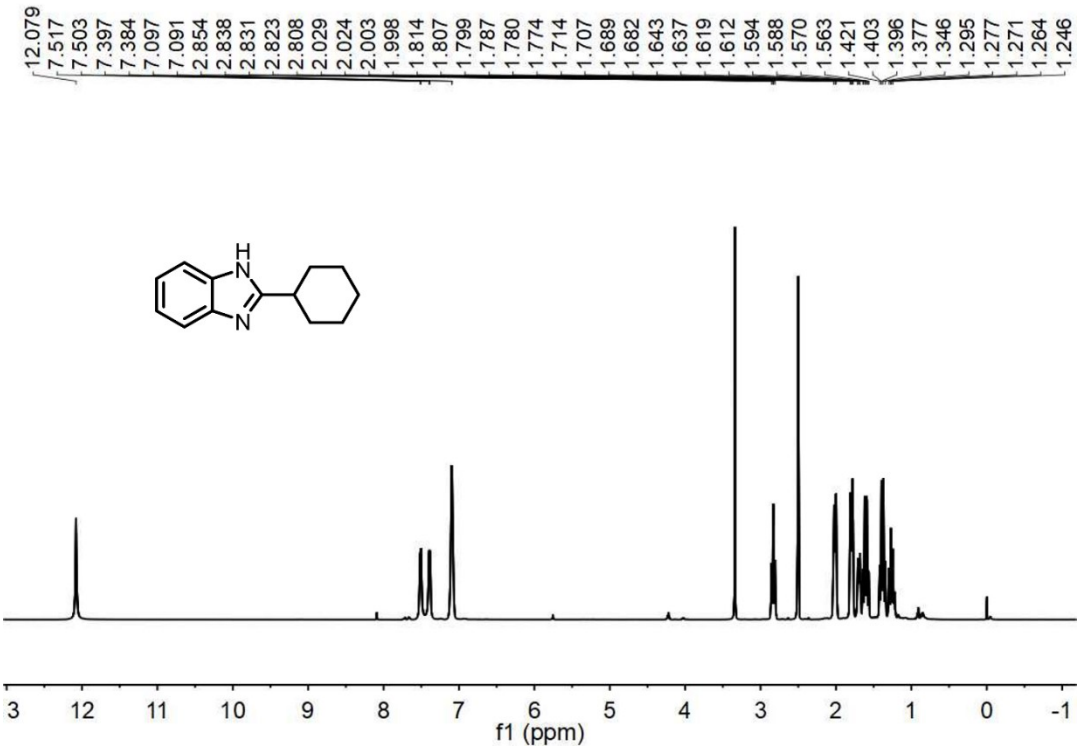


Figure S38. [1]H NMR spectrum of 2-cyclohexyl-1H-benzo[d]imidazole (**3n**).

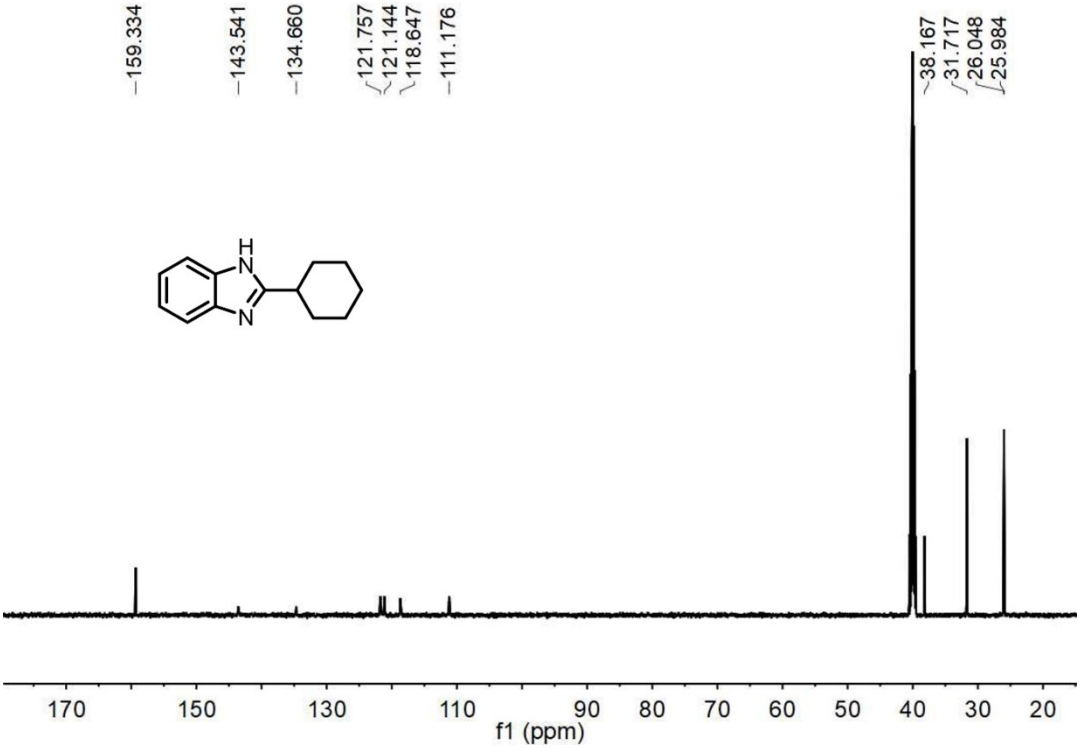


Figure S39. [13]C NMR spectrum of 2-cyclohexyl-1H-benzo[d]imidazole (**3n**).

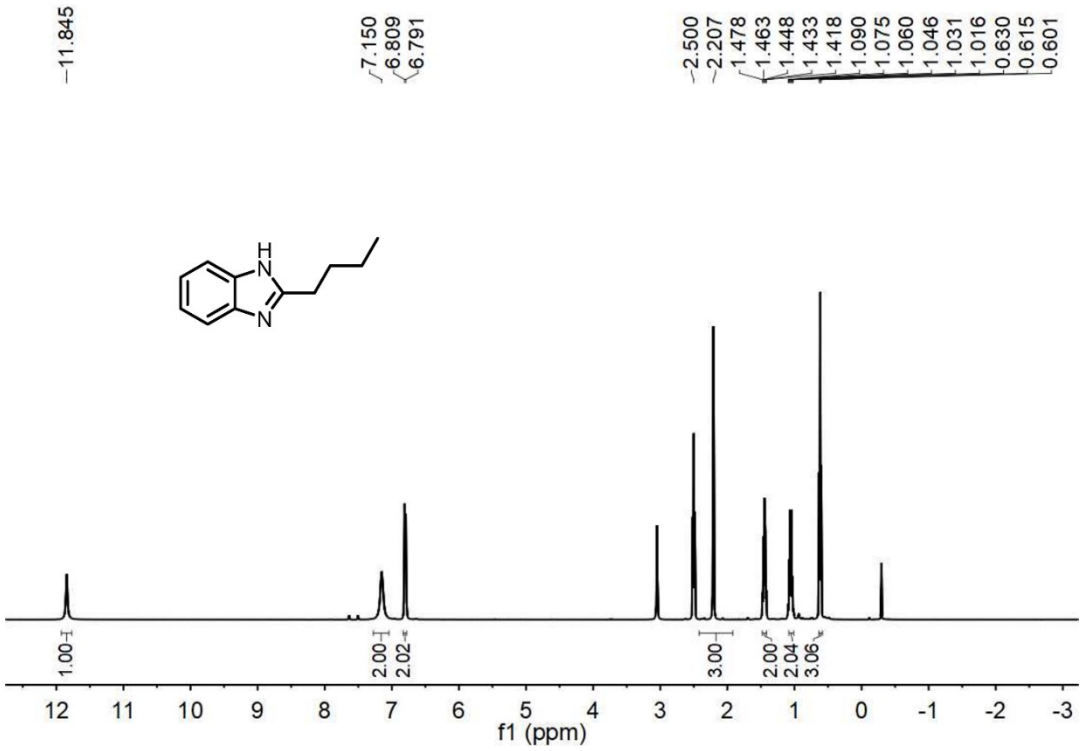


Figure S40. ^{1}H NMR spectrum of 2-butyl-1H-benzo[d]imidazole (**3o**).

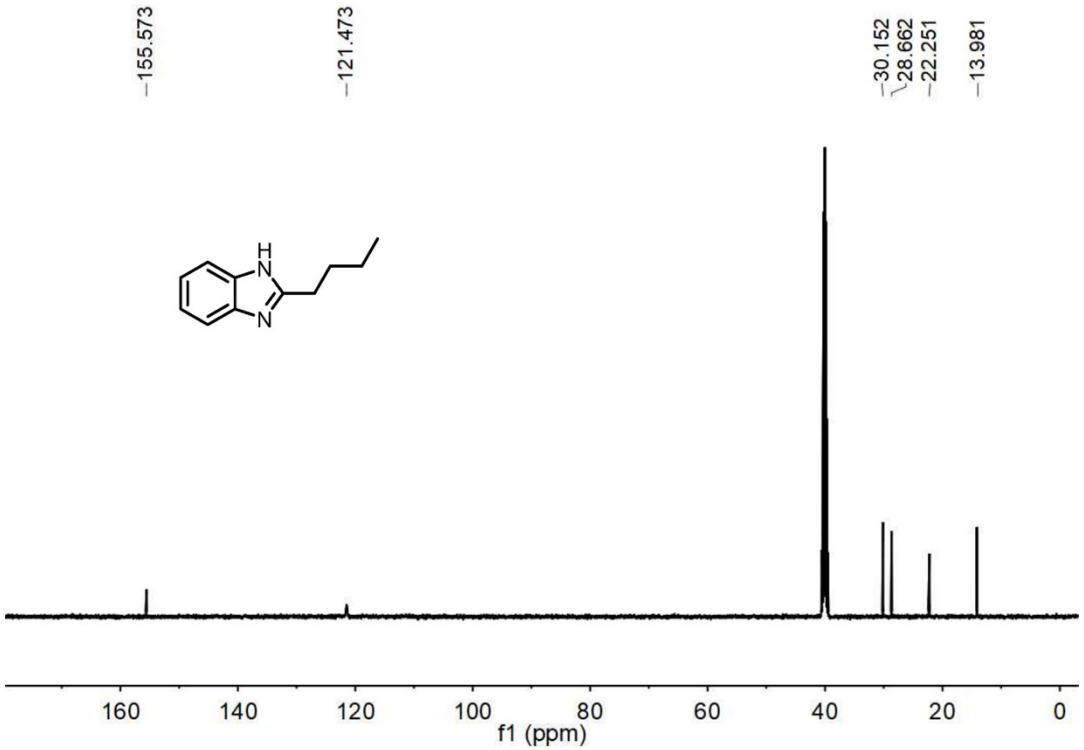


Figure S41. ^{13}C NMR spectrum of 2-butyl-1H-benzo[d]imidazole (**3o**).

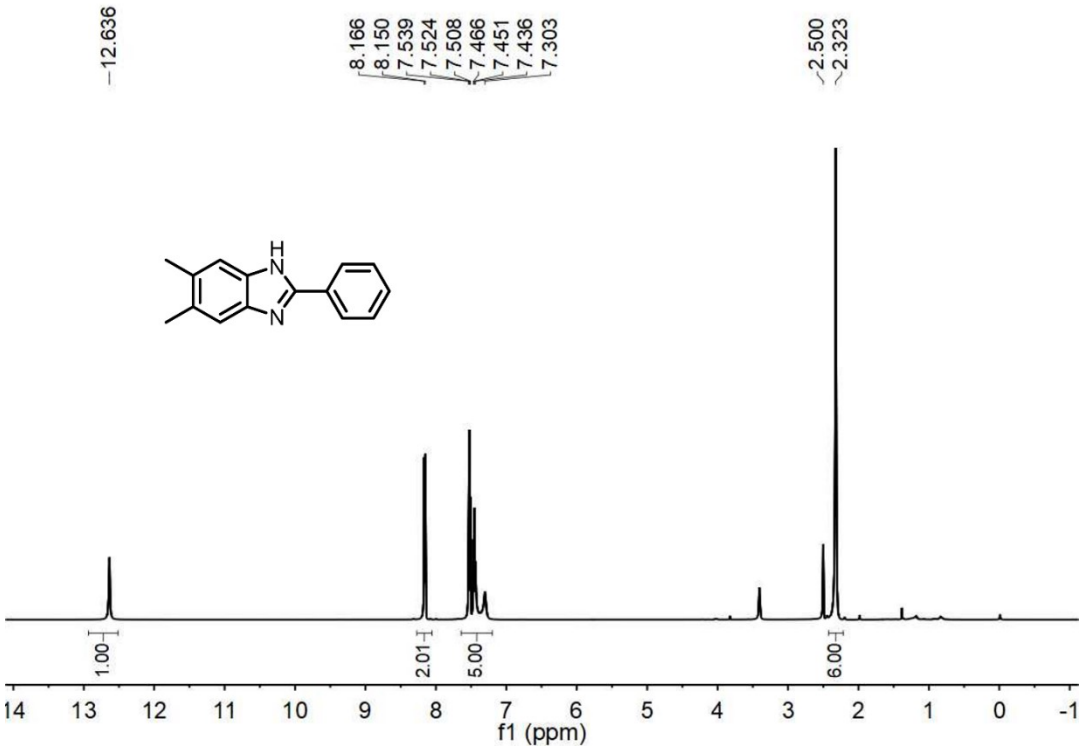


Figure S42. ^{1}H NMR spectrum of 5,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (**3p**).

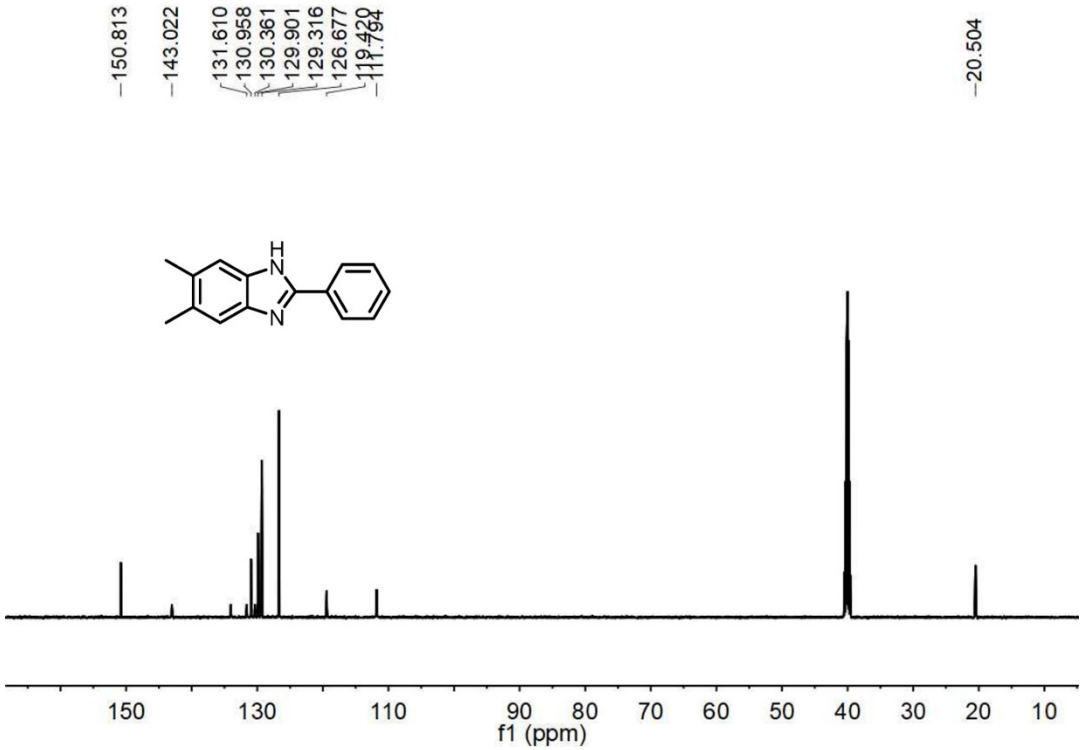


Figure S43. ^{13}C NMR spectrum of 5,6-dimethyl-2-phenyl-1H-benzo[d]imidazole (**3p**).

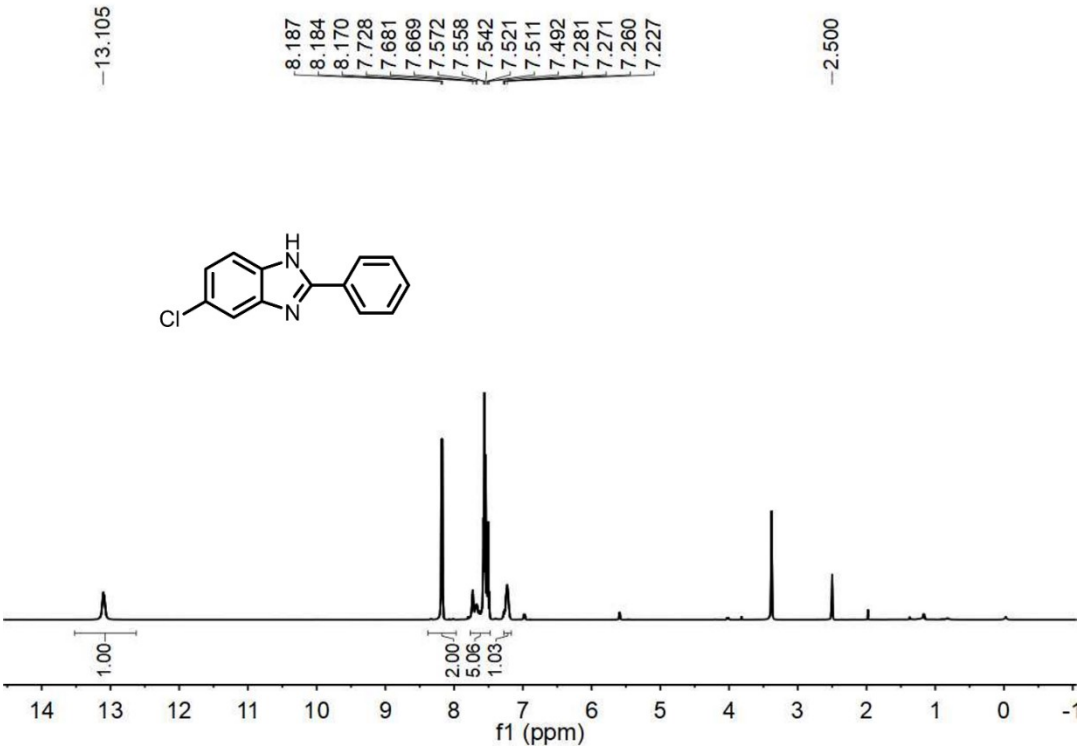


Figure S44. ^{1}H NMR spectrum of 5-chloro-2-phenyl-1H-benzo[d]imidazole (**3q**).

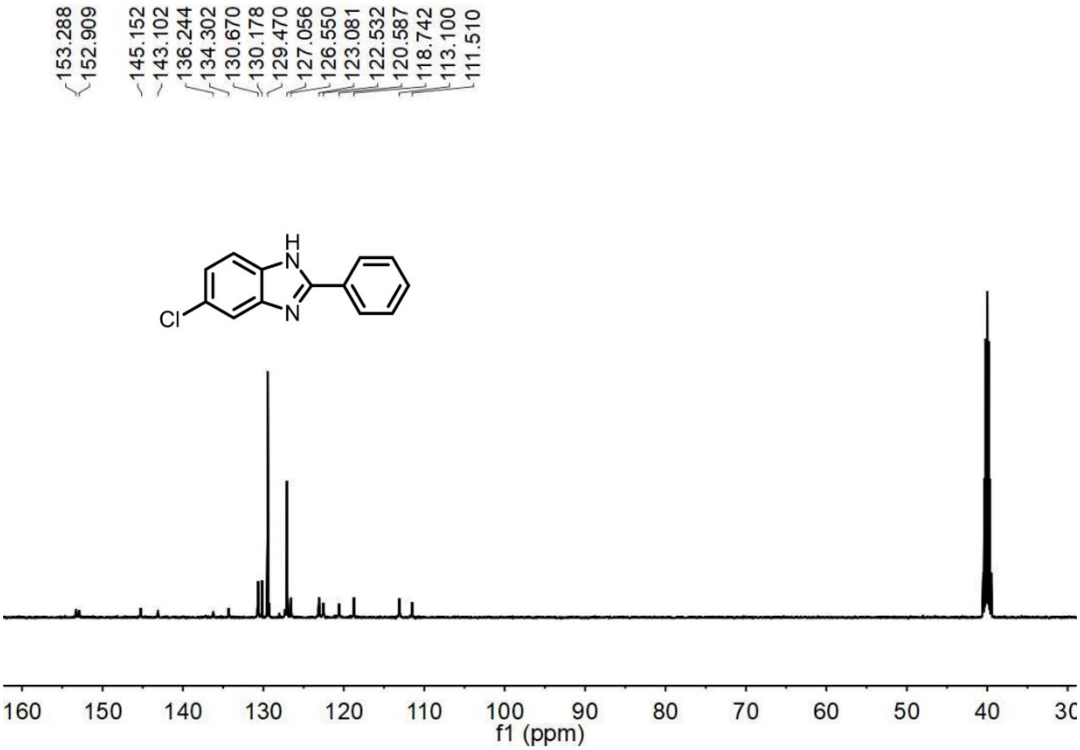


Figure S45. ^{13}C NMR spectrum of 5-chloro-2-phenyl-1H-benzo[d]imidazole (**3q**).

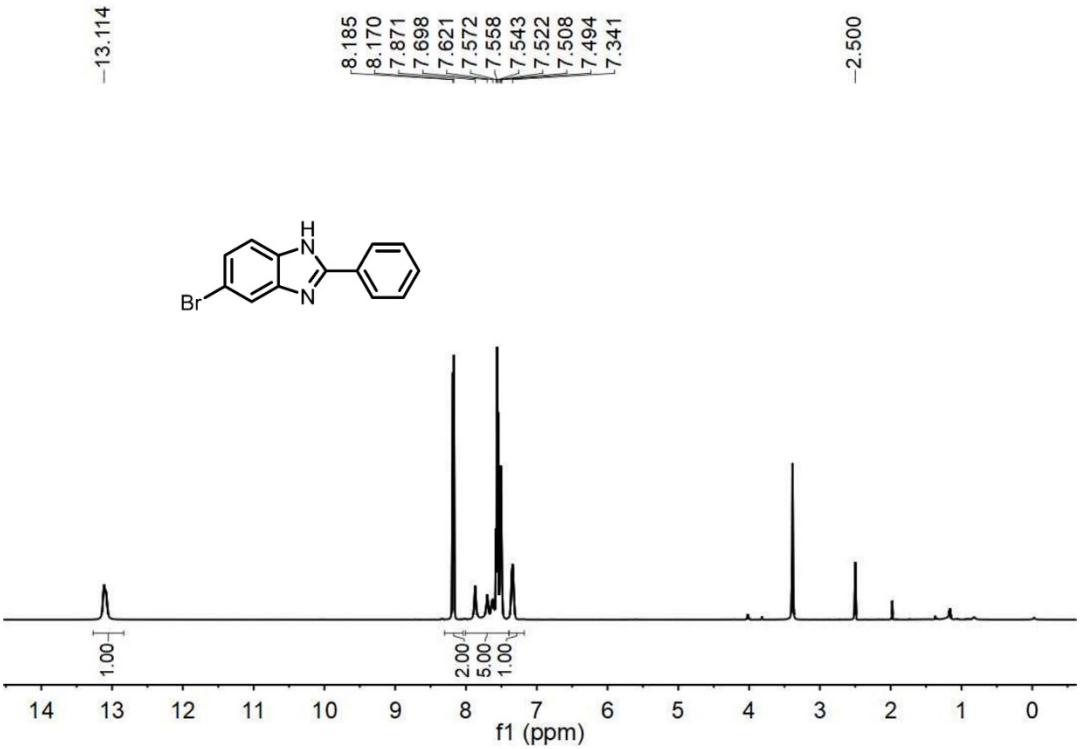


Figure S46. [1]H NMR spectrum of 5-bromo-2-phenyl-1H-benzo[d]imidazole (**3r**).

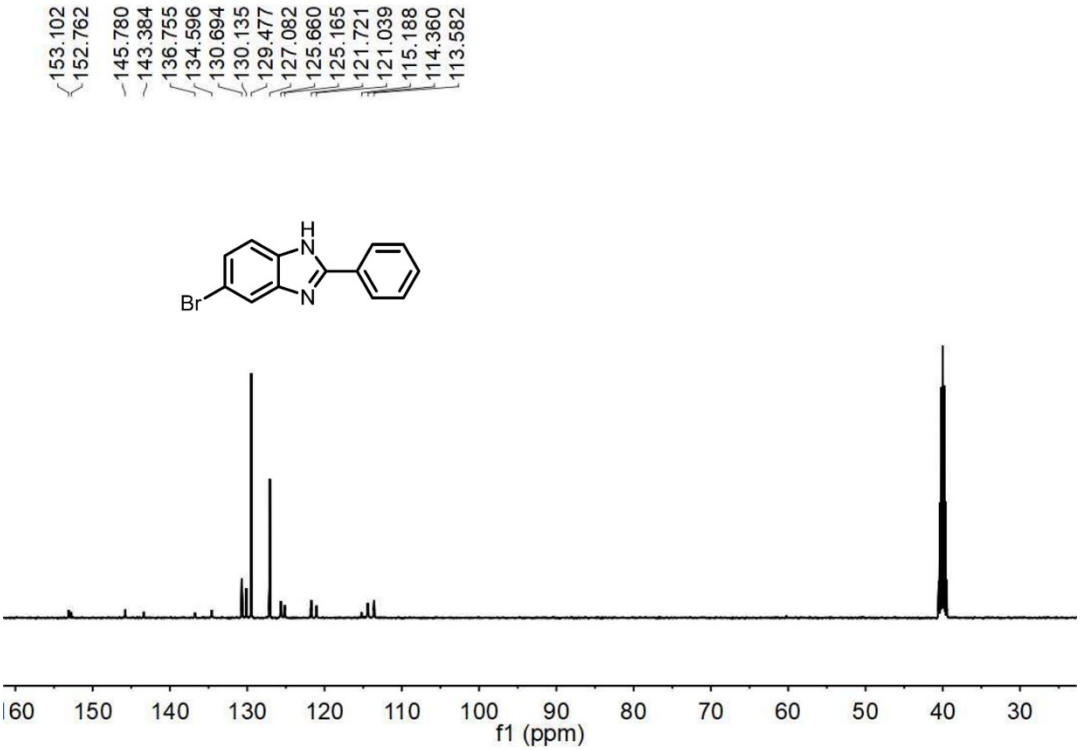


Figure S47. [13]C NMR spectrum of 5-bromo-2-phenyl-1H-benzo[d]imidazole (**3r**).