Supplementary Materials: The Synthesis of N-(Pyridin-2-yl)-Benzamides from Aminopyridine and Trans-Beta-Nitrostyrene by Fe₂Ni-BDC Bimetallic Metal–Organic Frameworks

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General experimental information

All reactions were performed under air atmosphere. All chemicals were obtained from commercial sources and used directly without further treatment. Solvents used in the experiment have been prior treated following standard procedure. The reaction process was monitored by TLC. The NMR spectra were recorded in 400 MHz apparatus using $CDCl_3$ as solvent, and the frequencies 1H, 13C NMR measurement were 400 MHz and 100 MHz, respectively. Chemical shifts were recorded in ppm by employing TMS or the solvent peak of CDCl3 (for 13C NMR) as internal standard. GCMS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μm). The temperature program for GC-MS analysis heated samples from 60 to 280 °C at 10 °C/min and held them at 280 °C for 2 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library.

General procedure for the synthesis of N-**pyridyl benzamide**

To a 10 mL round-bottom flask equipped with stirring bar and air condenser was charged with *trans*-1-nitro-phenylethylene **1a** (0.2 mmol)**,** 2-pyridylamine **2a** (0.2 mmol), DCM (1 mL) and Ni/Fe-MOF (0.02 mmol). The resulting mixture was stirred at 80 °C for 24 h. Upon completion, the reaction mixture was allowed to cool down to room temperature, and H_2O (4 mL) was added to the vessel. The resulting suspension was extracted with ethyl acetate (3 × 8 mL). The organic phases were combined and dried over Na_2SO_4. After filtration, the solvent was removed from the solution under reduced pressure. The acquired residue was subjected to silica gel column chromatography to provide pure product by using mixed petroleum ether/ethyl acetate 1:3 (*v/v*) as the eluent.
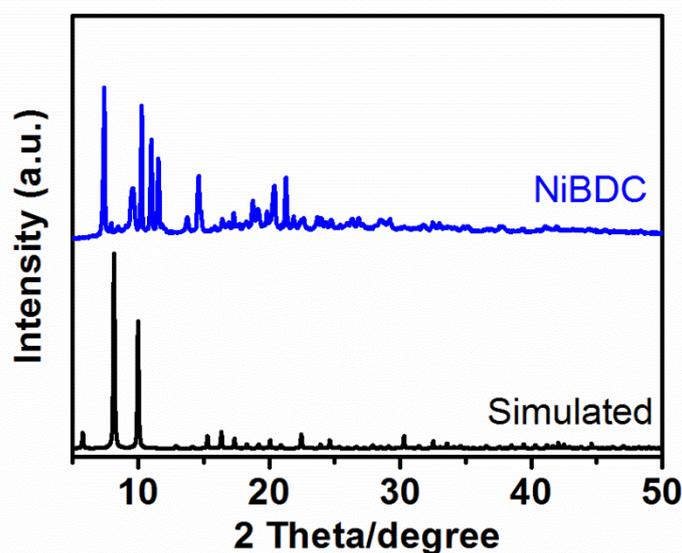
Figure S1. The presented simulated diffraction patterns for Ni-based was based on the corresponding check CIF file of Ni-BDC compare with experimental patterns.
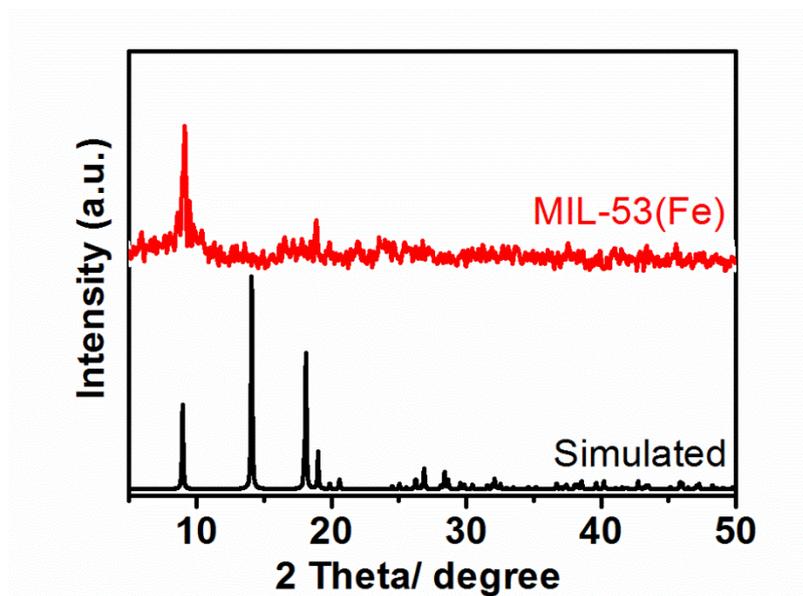

Figure S2. The presented simulated diffraction patterns for Fe-based was based on the corresponding check CIF file of MIL-53(Fe) compare with experimental patterns.
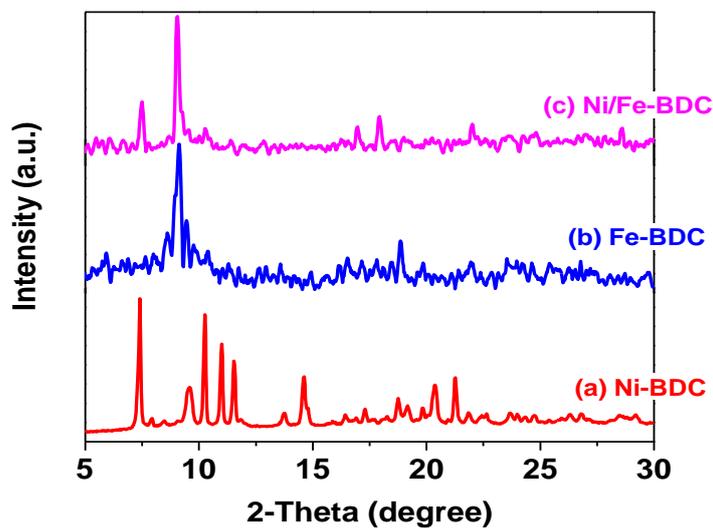

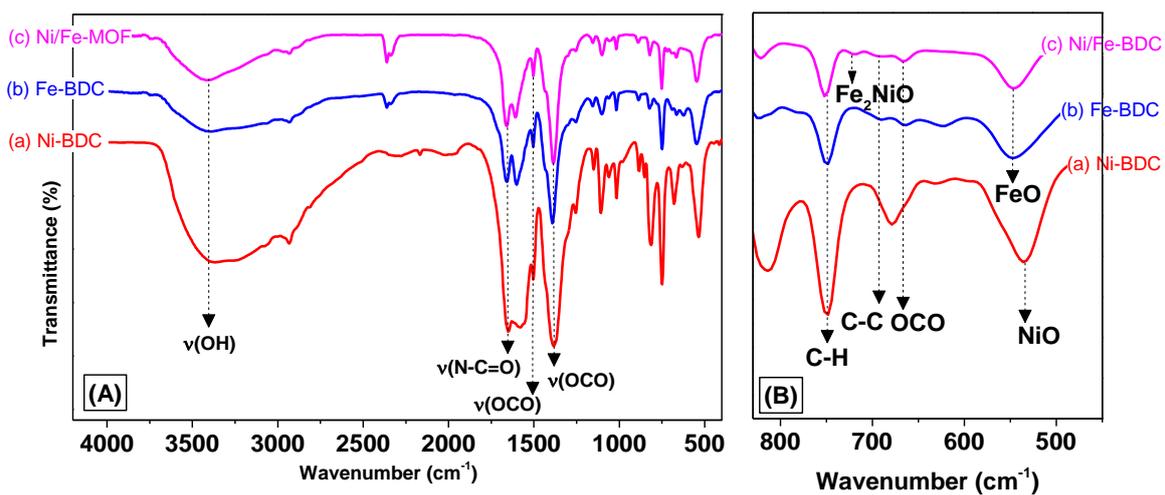**Figure S3.** X-ray powder diffraction of Ni-BDC, Fe-BDC and Fe$_2$Ni-BDC.

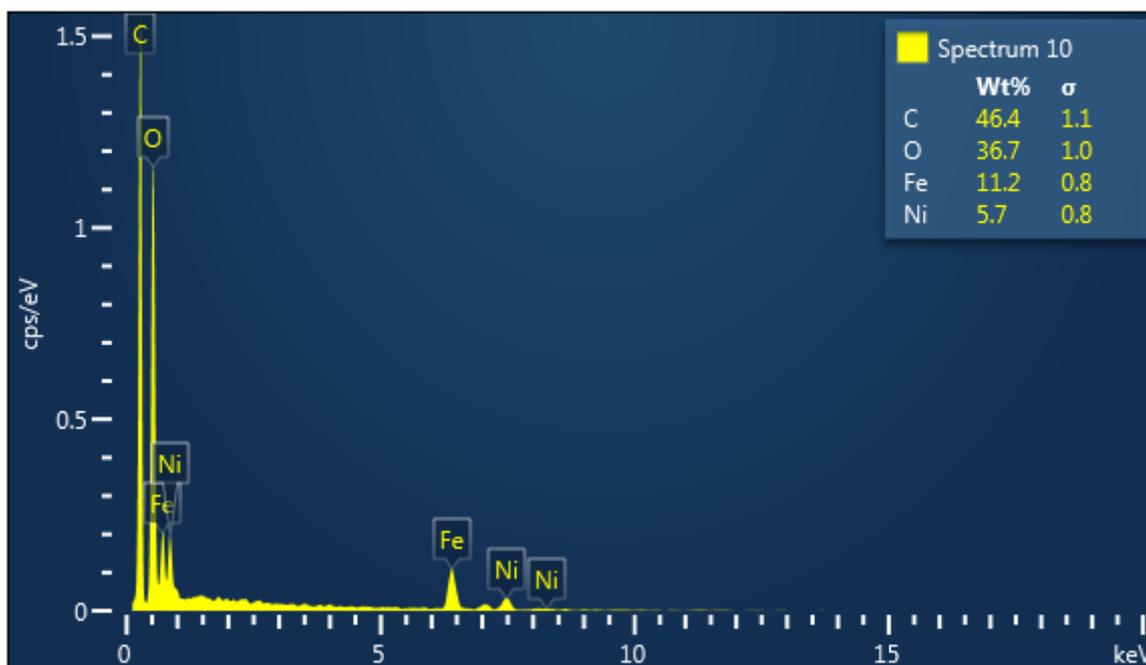**Figure S4.** FT-IR spectra of the Ni-BDC, Fe-BDC, and Fe₂Ni-BDC.

Figure S5. EDX mapping point of NiFe₂-BDC.

General procedure of investigation for the synthesis of N-pyridinyl benzamide

Table S1. Optimization of reaction conditions.

Entry	Cat.	mol% Cat.	Mole Proportion of Reactants	Sol.	Temp.	Yield (%)
1	Ni/Fe-MOF	10	1:1	DCM	80	82
2	NiBDC	10	1:1	DCM	80	65
3	MIL-53(Fe)	10	1:1	DCM	80	70
4	Ni(NO₃)₂.6H₂O	10	1:1	DCM	80	50
5	FeCl₃.6H₂O	10	1:1	DCM	80	73
6	Ni/Fe-MOF	10	1:1	DCM	rt	5
7	Ni/Fe-MOF	10	1:1	DCM	60	57
8	Ni/Fe-MOF	10	1:1	DCM	100	80
9	Ni/Fe-MOF	5	1:1	DCM	80	47
10	Ni/Fe-MOF	7.5	1:1	DCM	80	60
11	Ni/Fe-MOF	12.5	1:1	DCM	80	79
12	Ni/Fe-MOF	15	1:1	DCM	80	80
13	Ni/Fe-MOF	10	3:1	DCM	80	35
14	Ni/Fe-MOF	10	2:1	DCM	80	56
15	Ni/Fe-MOF	10	1:2	DCM	80	78
16	Ni/Fe-MOF	10	1:3	DCM	80	75
17	Ni/Fe-MOF	10	1:1	toluene	80	30
18	Ni/Fe-MOF	10	1:1	tetrahydrofurane	80	37
19	Ni/Fe-MOF	10	1:1	clorobenzene	80	57
20	Ni/Fe-MOF	10	1:1	dioxane	80	50
21	Ni/Fe-MOF	10	1:1	H₂O	80	52
22	Ni/Fe-MOF	10	1:1	DCM/H₂O	80	75
23	Ni/Fe-MOF	10	1:1	dioxane/H₂O	80	46
24	Ni/Fe-MOF	10	1:1	DMF	80	5
25	Ni/Fe-MOF	10	1:1	dicloroethane	80	72
26[b]	Ni/Fe-MOF	10	1:1	DCM	80	trace
27[c]	Ni/Fe-MOF	10	1:1	DCM	80	20
28[d]	Ni/Fe-MOF	10	1:1	DCM	80	55
29	-	10	1:1	DCM	80	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (0.02 mmol), in 1 mL solvent, stirred for 24 h under air. [b]Reaction under N₂. [c]Reaction under O₂. [d]In the presence of TEMPO (2 eq.).

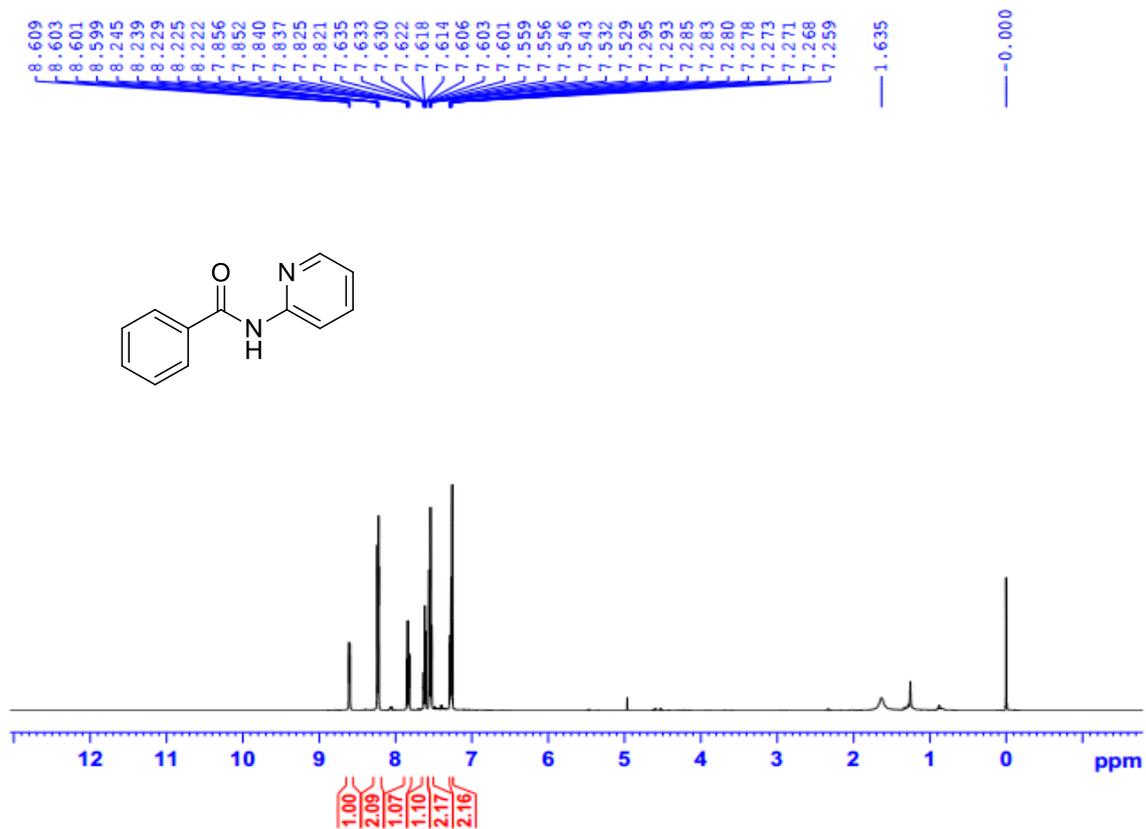# Characterization data for all products

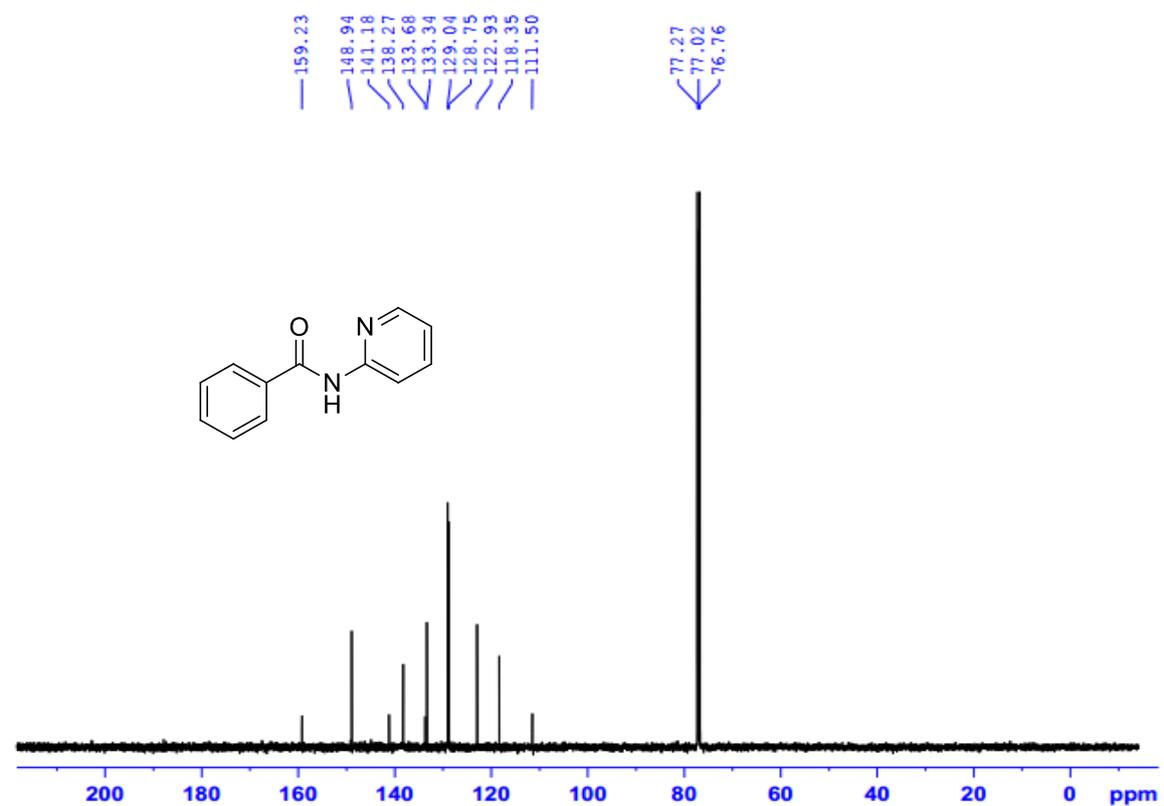**Figure S6.** ¹H-NMR spectra of N-(pyridin-2-yl)benzamide.

Figure S7. ¹³C-NMR spectra of N-(pyridin-2-yl)benzamide.

Characterization data for N-(pyridin-2-yl)benzamide

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:3): yellow solid, 82% yield. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.60 (d, J = 6.5 Hz, 1H), 8.23 (d, J = 8 Hz, 2H), 7.84 (ddd, J = 8 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.29 – 7.26 (m, 2H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 159.23, 148.94, 141.18, 138.27, 133.68, 133.34, 129.04, 128.75, 122.93, 118.35, 111.50. GC-MS, Mass: 197.
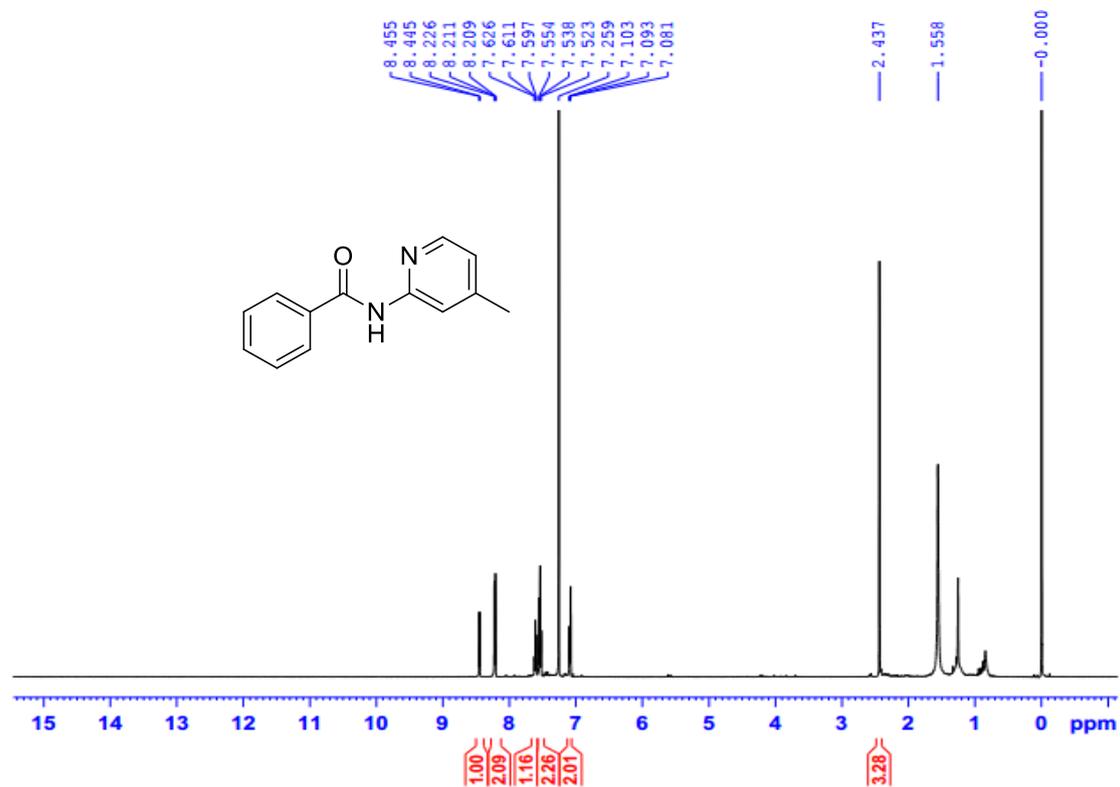

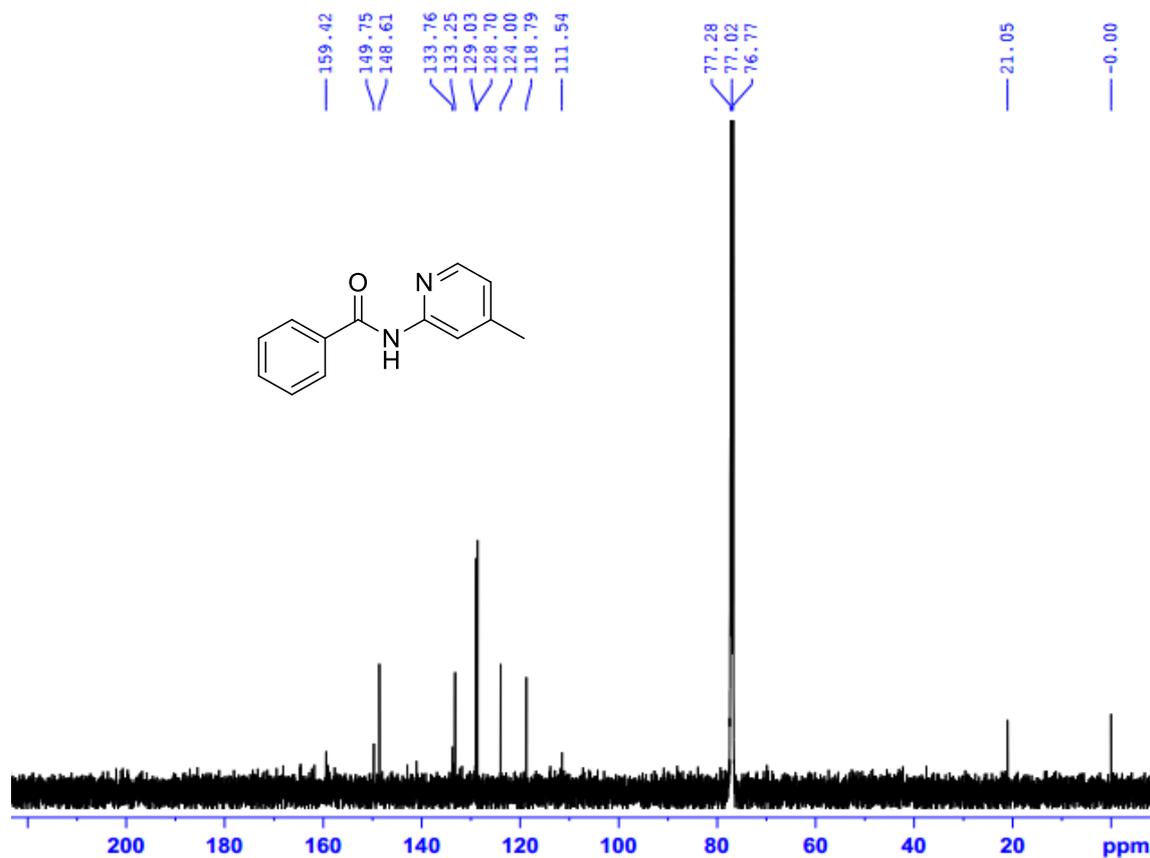**Figure S8.** ^{1}H-NMR spectra of N-(4-methylpyridin-2-yl)benzamide.

Figure S9. ^{13}C-NMR spectra of N-(4-methylpyridin-2-yl)benzamide.

Characterization data for N-(4-methylpyridin-2-yl)benzamide

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:3): yellow solid, 70% yield. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.45 (d, *J* = 5.0 Hz, 1H), 8.22 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7. 54 (t, *J* = 8 Hz, 2H), 7.09 (t, *J* = 6.0 Hz, 2H), 2.44 (s, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 159.42, 149.75, 148.61, 133.76, 133.25, 129.03, 128.70, 124.00, 118.79, 111.54, 21.05.
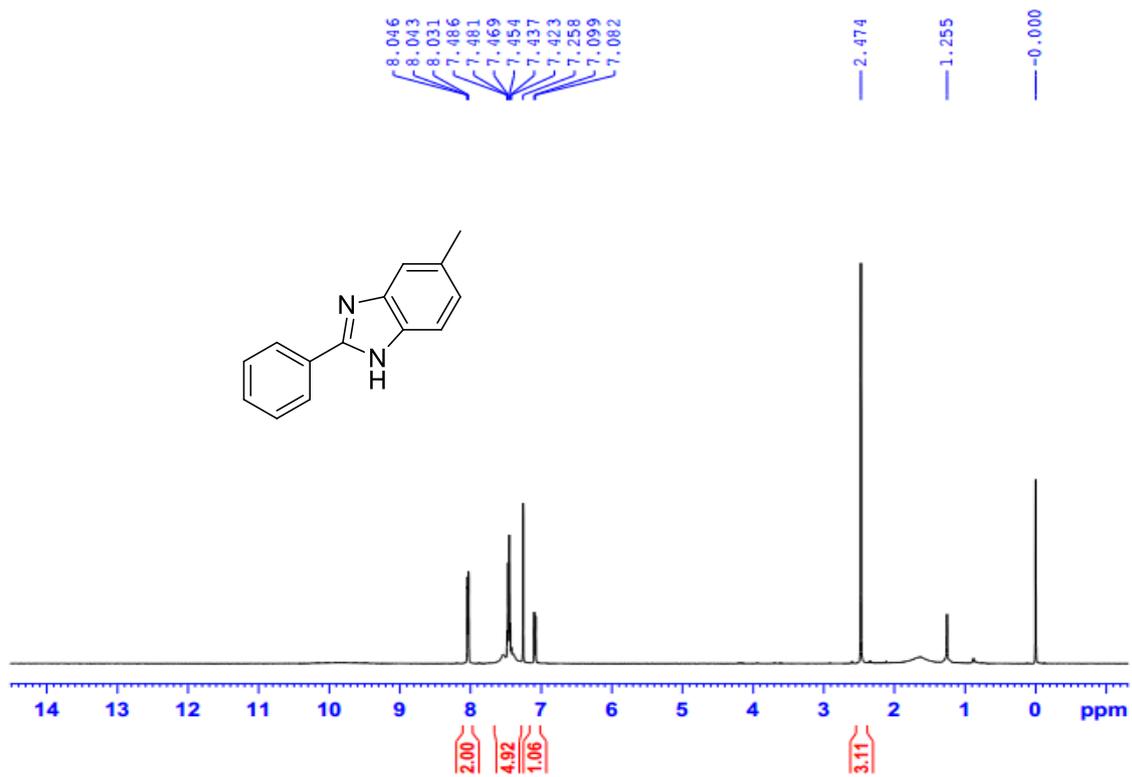
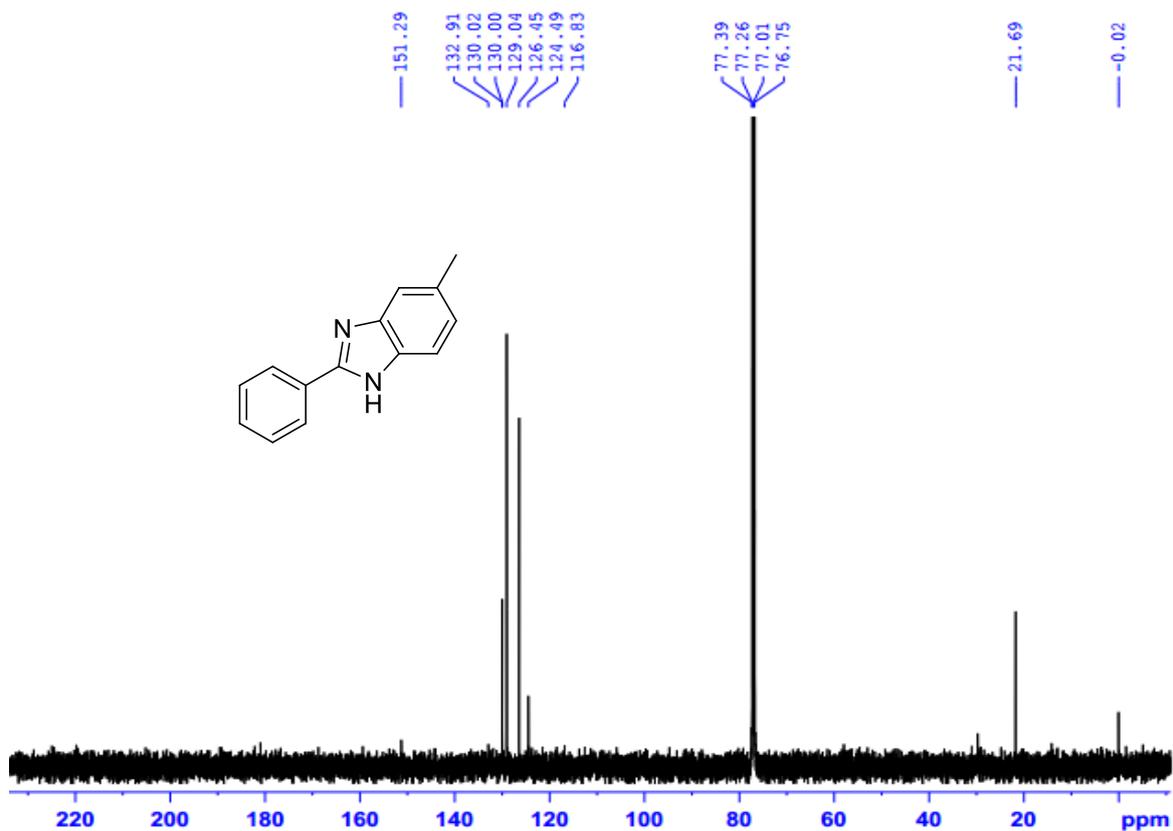**Figure S10.** ^{1}H-NMR spectra of 5-methyl-2-phenyl- 1H-benzo[d]imidazole.

Figure S11. ^{13}C-NMR spectra of 5-methyl-2-phenyl- 1H-benzo[d]imidazole.

Characterization data for 5-methyl-2-phenyl- 1*H*-benzo [*d*] imidazole

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:4): yellow solid, 63% yield. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.04 (d, *J* = 7.5 Hz, 2H),

7.48 – 7.42 (m, 5H), 7.09 (d, *J* = 8.5 Hz, 1H), 2.47 (s, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 151.29, 132.91, 130.02, 130.00, 129.04, 126.45, 124.49, 116.83, 21.69.
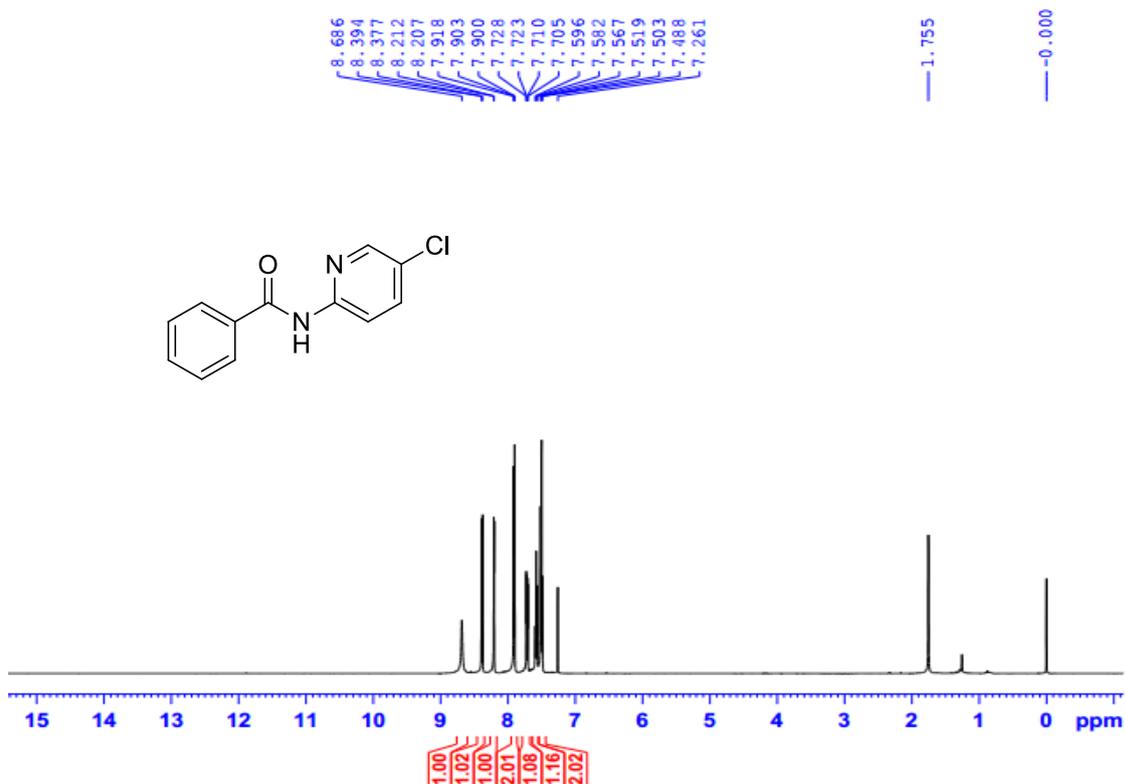

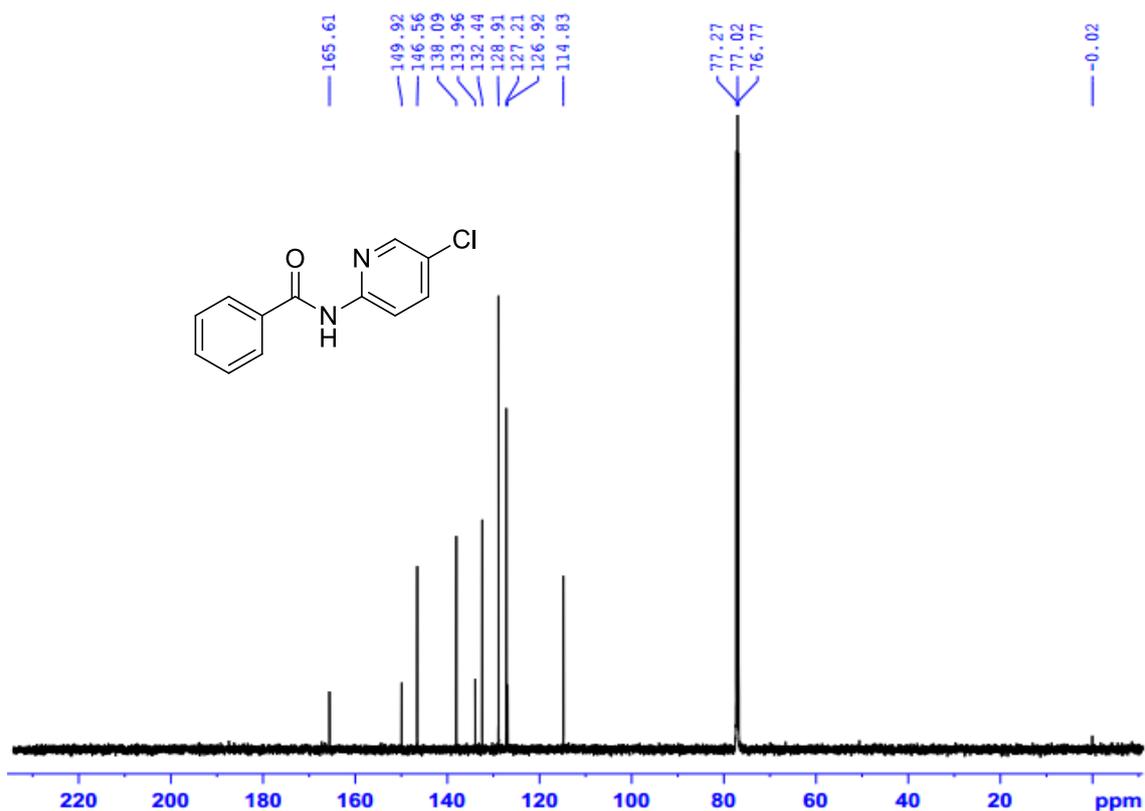**Figure S12.** ^{1}H-NMR spectra of N-(5-chloropyridin-2-yl)benzamide.

Figure S13. ^{13}C-NMR spectra of N-(5-chloropyridin-2-yl)benzamide.

Characterization data for N-(5-chloropyridin-2-yl)benzamide

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:3): yellow solid, 68% yield. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.38 (d, J = 8.5 Hz, 1H), 8.21 (s, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.72 (dd, J = 9 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 8 Hz, 2H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 165.61, 149.92, 146.56, 138.09, 133.96, 132.44, 128.91, 127.21, 126.92, 114.83.
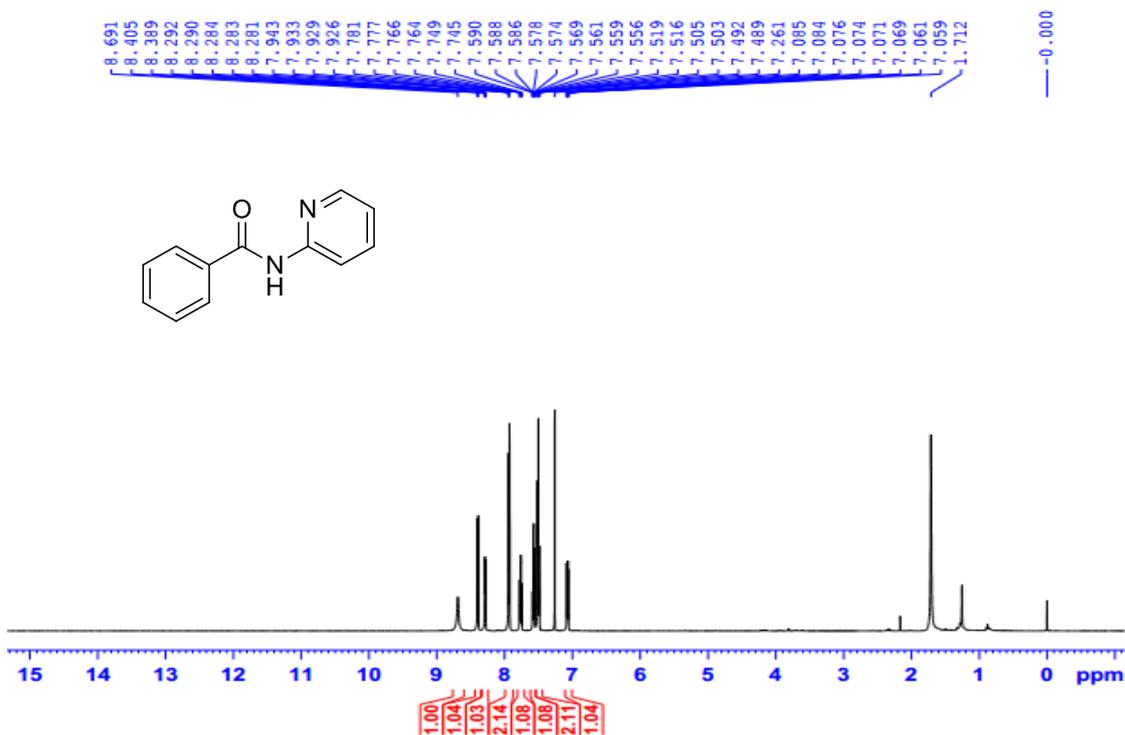

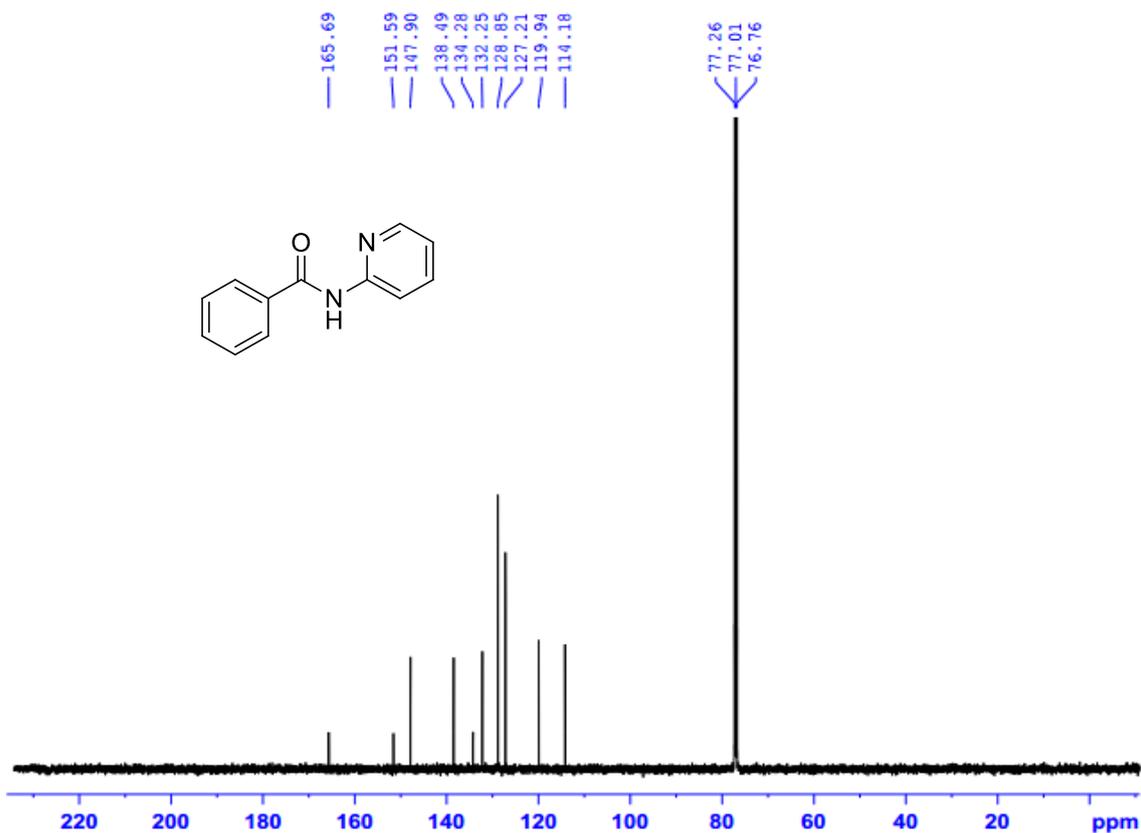**Figure S14.** ^{1}H-NMR spectra of N-(pyridin-2-yl)benzamide.

Figure S15. ^{13}C-NMR spectra of N-(pyridin-2-yl)benzamide.

Characterization data for N-(pyridin-2-yl)benzamide

Prepared as shown in the general experimental procedure and purified on silica gel (ethyl acetate/hexane = 1:3): yellow solid, 74% yield. ^{1}H-NMR (500 MHz, CDCl$_3$) δ 8.69 (s, 1H), 8.39 (d, J = 8 Hz, 1H), 8.29 (d, J = 5.5 Hz, 1H), 7.93 (d, J = 7 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.59 – 7.55 (m, 1H), 7.52 – 7.49 (m, 2H), 7.09 – 7.06 (m, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 165.69, 151.59, 147.90, 138.49, 134.28, 132.25, 128.85, 127.21, 119.94, 114.18.