

Supporting Information

N-Alkylation of Aniline Derivatives by Bipyridyl Metal-Organic Framework Supported Cobalt Catalyst

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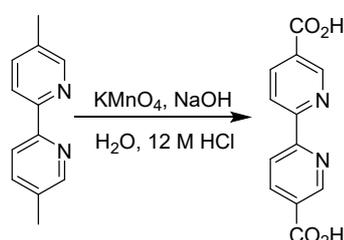
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1. General experiment. All the experiments were performed under a nitrogen atmosphere in a Schlenk tube, except if any case was demonstrated. All the solvents were purchased from Finar and used without further purification. All the reagents are commercially available and used directly as received. 5,5'-Dimethyl-2,2'-bipyridyl was purchased from Alfa Aesar, TFA was purchased from Central Drug House Pvt. Ltd. (CDH Chemicals), KMnO_4 was purchased from Merck, CoCl_2 was purchased from TCI chemicals and ZrCl_4 was purchased from GLR Innovations. ^1H NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from CDCl_3 (δ 7.26) and $\text{DMSO}-d_6$ (δ 2.5). Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA7 system on well-ground samples in a flowing nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ with a range of $40\text{-}800\text{ }^\circ\text{C}$. Room temperature powder X-ray diffraction data were collected on a Bruker Advance diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). Data were collected with a step size of 0.05° and at count time of 1s per step over the range $4^\circ < 2\theta < 70^\circ$. The experimental and simulated PXRD patterns are in good agreement indicating the monophasic nature of the bulk samples. For powder X-ray diffraction measurement of MOFs, the moist sample was mounted on a PXRD groove. After catalysis, bpy-UiO-Co was recovered after centrifugation and stored in THF. Just before the PXRD measurement, the THF was removed, and the moist sample was mounted on a PXRD groove. The catalysis was carried out without any mechanical stirring, and the recovered MOF was not dried before the measurement of PXRD to prevent any mechanical degradation and pore collapse of the MOF. In the case of product analysis of the liquid phase using GC-MS/FID, the following chromatographic conditions were employed; carrier gas: He, flow rate: 1 mL min^{-1} , injection volume: $5.0\text{ }\mu\text{L}$, column oven temperature was initially $40.0\text{ }^\circ\text{C}$ and then increased up to $240\text{ }^\circ\text{C}$ with the rate of $10\text{ }^\circ\text{C per minute}$, and detector temperature was $250\text{ }^\circ\text{C}$. ICP-OES data were obtained with an Agilent 5110 ICP-OES and analyzed using a Dichroic Spectral Combiner (DSC). Samples were diluted in a 5% HNO_3 matrix and analyzed with a six-point standard curve over the range from 0.1 ppm to 20 ppm . The correlation coefficient was >0.9990 for all analytes of interest. To analyse the chemical state of transition elements, XPS were recorded on an X-ray photoelectron spectrometer, PHI 5000 VersaProbe III using $\text{Al-K}\alpha$ ($h\nu = 1486.6\text{ eV}$) X-ray source. MOF samples were vacuum-dried at room temperature, and then powder samples were measured ultra-high vacuum environment. Surface area and pore volume were measured with a BELLSORP MAX II-high performance gas and vapor adsorption system with three microporous ports. For BET surface area measurement, the MOF sample was first dried via a freeze-drying method. For freeze-drying, MOF was first soaked with benzene. Then, the MOF

slurry was frozen at -10 °C and dried slowly under vacuum at the same temperature. Then, samples were degassed under vacuum at 80 °C for 24 h before measurement. The morphology and chemical compositions were analysed with a Zeiss FE-SEM ultra plus55 operating at 20 KV. After vacuum drying, a very small amount of the powder samples of MOF (1-2 mg) were dispersed on the carbon tape for FE-SEM imaging. Infra-red (IR) spectra of samples were recorded with FT-IR Spectrometer (MS-632). The MOF samples were vacuum dried at 100 °C to remove the moisture, which was then taken inside the glovebox, and a KBr pellet of powder sample was made.

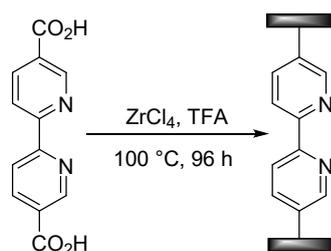
2. Synthesis and characterization of bpy-UiO-67 and bpy-UiO-CoCl₂ MOFs.

2.1. Synthesis of [2,2'-bipyridine]-5,5'-dicarboxylic acid.



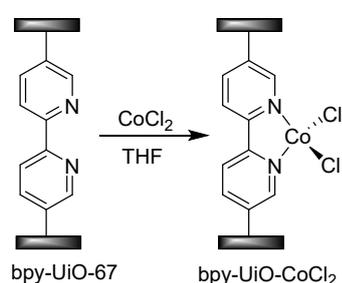
[2,2'-Bipyridine]-5,5'-dicarboxylic acid was synthesized using a modified reported procedure.¹ In a round-bottom flask, 5,5'-dimethyl-2,2'-bipyridyl (0.500 g, 2.74 mmol), NaOH (0.030 g, 0.75 mmol), and deionized water (12 mL) were combined and stirred at 70 °C. Subsequently, 1.48 g of NaOH (0.037 mmol) was slowly added to the mixture until the pH reached 12. After the mixture became clear and was allowed to sit for 1 hour, finely powdered KMnO₄ (2.140 g, 0.0135 mmol) was added in small portions. The mixture was then stirred at 90 °C, cooled to room temperature, and filtered. The filtrate was acidified with 12 M HCl, resulting in the formation of a white solid, [2,2'-bipyridine]-5,5'-dicarboxylic acid (0.208 g, 0.85 mmol, 31%). This product was obtained after 10 hours and analyzed by ¹H NMR. ¹H NMR (500 MHz, DMSO-*d*₆): δ 13.55 (s, 2 H), 9.16 (s, 2 H), 8.54 (d, ³J_{H-H} = 8.8 Hz, 2 H), 8.45 (d, ³J_{H-H} = 8.4 Hz, 2 H).²

2.2. Synthesis of bpy-UiO-67 MOF.³



To synthesize bpy-UiO-67 MOF, [2,2'-bipyridine]-5,5'-dicarboxylic acid (0.026 g, 0.106 mmol) and $ZrCl_4$ (0.026 g, 0.112 mmol) were dissolved in 13 mL of DMF. The mixture was sonicated for 30 minutes, after which TFA (0.040 mL, 0.523 mmol) was added. The resulting solution was heated in a sealed 15 mL glass vial at 100 °C for 96 h in an oven. After allowing the reaction mixture to cool to room temperature, the white crystalline solid was isolated by centrifugation, yielding bpy-UiO-67 MOF with a 38% yield. The MOF was thoroughly washed with DMF several times, followed by washing with THF, and then stored in THF at room temperature.

2.3. Synthesis of bpy-UiO-CoCl₂.



A solution of $CoCl_2$ (0.003 g, 0.024 mmol) in THF was added to the bpy-UiO-67 MOF. The mixture was left overnight with periodic shaking at room temperature inside a glovebox. The solid product was then separated by centrifugation and washed 8-10 times with THF, resulting in the bpy-UiO-CoCl₂ MOF. The bpy-UiO-CoCl₂ has 42% solvent weight analysed by thermogravimetric analysis and 20% cobalt loading with respect to bpy-moiety of the digested MOF as analyzed by ICP-OES.

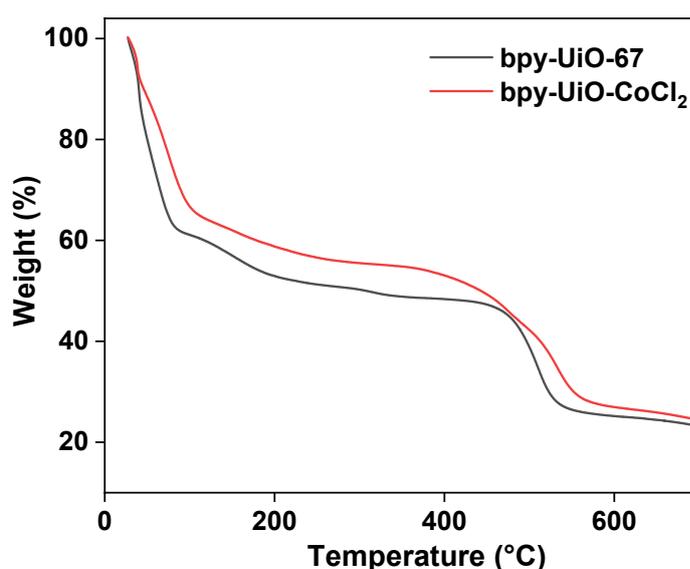


Figure S1. TGA curve of freshly prepared bpy-UiO-67 (black) and bpy-UiO-CoCl₂ (red). A solvent weight loss of 46% was observed in bpy-UiO-67 and 42% in bpy-UiO-CoCl₂ at the

range of temperature from 40 °C to 200 °C. The increased weight of metalated MOF is due to the presence of cobalt within the MOF.

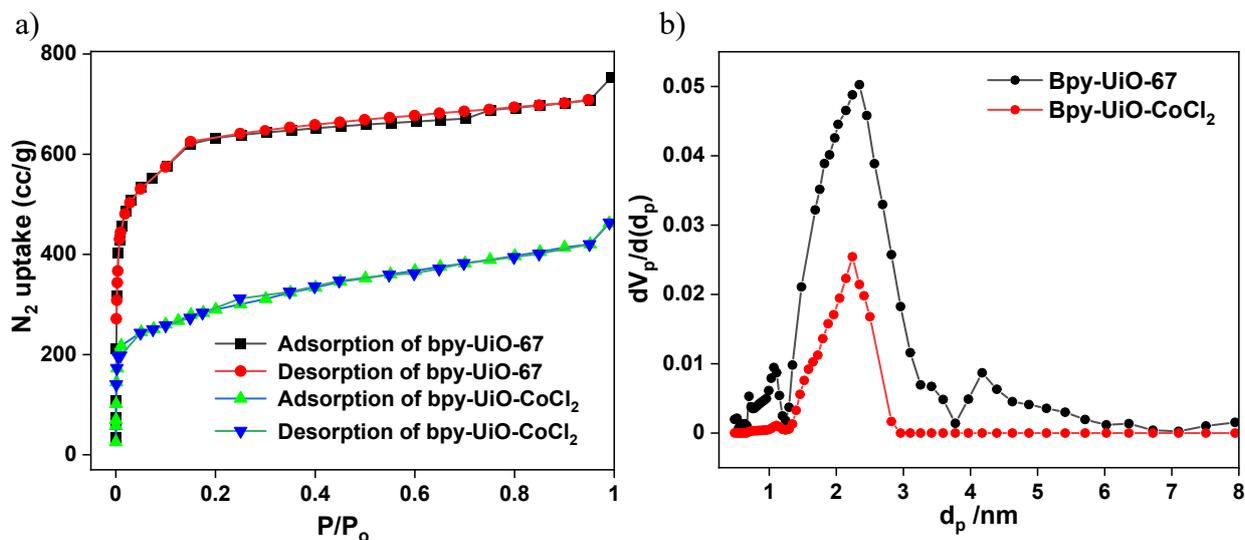


Figure S2. a) Brunauer–Emmett–Teller (BET) nitrogen sorption isotherms of bpy-UiO-67, bpy-UiO-CoCl₂ measured at 77 K. Bpy-UiO-67 and bpy-UiO-CoCl₂ have a BET surface area of 1846 m²/g and 1218 m²/g respectively. b) NLDFT pore distribution plot of bpy-UiO-67 (black) and bpy-UiO-CoCl₂ (red). The pore size for bpy-UiO-67 and bpy-UiO-CoCl₂ was determined to be 2.35 nm and 2.24 nm respectively.

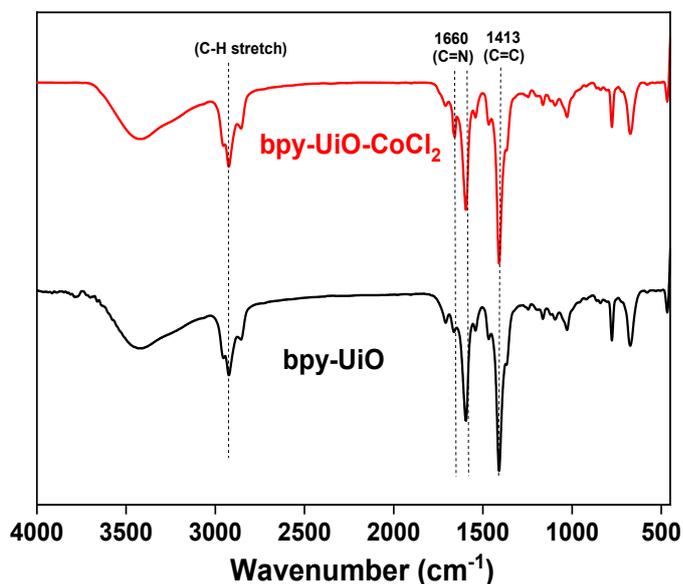


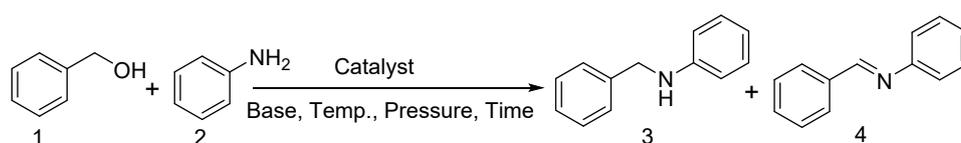
Figure S3. IR spectra of freshly prepared bpy-UiO-67 (black) and bpy-UiO-CoCl₂ (red).

3. Catalytic reactions with bpy-UiO-CoCl₂.

3.1. General procedure for bpy-UiO-CoCl₂ catalyzed N-alkylation of substituted anilines with benzyl alcohol derivatives. 0.5 mmol of aniline and 1 mmol of benzyl alcohol were mixed with 3 mg of catalyst (bpy-UiO-CoCl₂) and 0.5 mmol base in a 50 mL Schlenk tube under a nitrogen atmosphere. Then, 2 mL of dry solvent was added to the mixture. The reaction mixture was stirred at a temperature range of 50-140 °C for 4-48 hours under reflux conditions. Upon completion, the Schlenk tube was cooled to room temperature, and the reaction products were filtered and thoroughly washed with ethyl acetate. The crude products were then analyzed using GC-MS/FID using *n*-dodecane as an internal standard. Subsequently, the solvent and volatile components were evaporated under vacuum, and the crude reaction mixtures were purified through column chromatography using a mixture of ethyl acetate and hexane as the eluent.

3.2. A typical procedure for bpy-UiO-CoCl₂ catalyzed N-alkylation of aniline with benzyl alcohol. In a 50 mL Schlenk tube under a nitrogen atmosphere, 0.5 mmol of aniline, 1 mmol of benzyl alcohol, 3 mg of a catalyst (bpy-UiO-CoCl₂), and 0.5 mmol of base (KO^tBu) were combined. After mixing, 2 mL of dry toluene was added to the reaction mixture. The mixture was then stirred at a temperature of 120 °C for 24 hours under reflux conditions. The boiling point of toluene is indeed 110 °C, but the reaction was performed in the Schlenk tube with an oil bath set to 120 °C. It should be clarified that 120 °C refers to the oil bath temperature, while the actual reaction temperature corresponds to the boiling point of toluene, which is 110 °C. Upon completion of the reaction, the Schlenk tube was cooled to room temperature. The reaction product was filtered and thoroughly washed with ethyl acetate. Following this, the product was analyzed using GC-MS/FID with *n*-dodecane as an internal standard. Finally, the solvent and volatile components were evaporated under vacuum, and the crude reaction mixture was purified by column chromatography using a combination of ethyl acetate and hexane as the eluent.

Table S1. N-Alkylation of aniline with benzyl alcohol: Effect of various solvents,

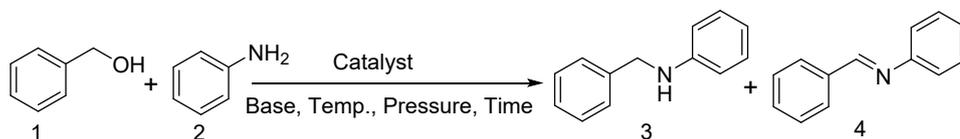


temperature, and time of the reaction^a.

Entry No.	1 (mmol)	2 (mmol)	Temp.	Time	Solvent	% Conversion	% Yield of 3 ^b
1	1	0.5	80	24	Toluene	20	15
2	1	0.5	100	24	Toluene	55	46
3	1	0.5	120	24	Toluene	100	98
4	0.8	0.5	120	24	Toluene	94	77
5	0.5	0.5	120	24	Toluene	88	68
6	1	0.5	120	12	Toluene	39	37
7	1	0.5	120	20	Toluene	90	86
8 ^c	1	0.5	120	24	Toluene	82	78
9	1	0.5	120	24	Dioxane	92	84
10	1	0.5	120	24	THF	88	79
11	1	0.5	120	24	p-xylene	84	73
12	1	0.5	120	24	DME	74	60
13	1	0.5	120	24	CH ₃ CN	58	49

^aReaction conditions: 3 mg of bpy-UiO-CoCl₂ (0.3 mol% of Co), KO^tBu base (0.5 mmol), solvent (2 mL). ^bYield was determined by GC-analysis using *n*-dodecane as internal standard. ^cbpy-UiO-CoCl₂ (0.1 mol% of Co).

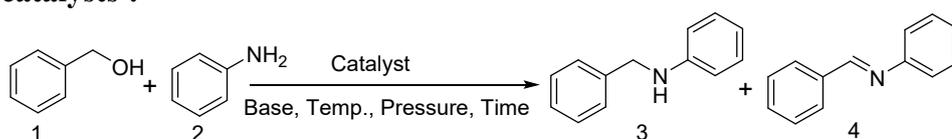
Table S2. N-Alkylation of aniline with benzyl alcohol: Effect of different bases^a.



Entry No.	Base (mmol)	% Conversion	% Yield of 3 ^b
14	KO ^t Bu (0.2)	76	68
15	KO ^t Bu (0.5)	100	98
16	KOH (0.5)	94	89
17	NaOH (0.5)	88	79
18	CS ₂ CO ₃ (0.5)	56	31
19	No base	0	0

^aReaction conditions: Aniline (0.5 mmol), benzyl alcohol (1 mmol), bpy-UiO-CoCl₂ (3 mg, 0.3 mol% of Co), Toluene (2 mL), 120 °C, 24 h. ^bYield was determined by GC-analysis using *n*-dodecane as an internal standard.

Table S3. N-Alkylation of aniline with benzyl alcohol: Control experiment with different cobalt catalysts^a.



Entry No.	Catalyst	% Conversion	% Yield of 3 ^b
20	Bpy-UiO-67	26	11
21	CoCl ₂	29	12
22	Co nanoparticles	31	15
23	(Me ₂ bpy)CoCl ₂	50	16
24	No catalyst	22	8
25 ^c	Bpy-UiO-CoCl ₂	100	0

^aReaction conditions: Aniline (0.5 mmol), benzyl alcohol (1 mmol), catalyst (0.3 mol% of Co), Toluene (2 mL), 120 °C, 24 h. ^bYield was determined by GC-analysis using *n*-dodecane as internal standard. ^cReaction performed in air.

Table S4. Comparison of activities of our MOF-supported Co-catalyst with some previously reported catalysts.

Entry	Catalyst (loading)	Reaction conditions	Yield %	Sel. %	Reference
1	Co@NC-800-L1 (0.86 mol% Co)	140 °C, 24 h	99%	99%	<i>Chem. Sci.</i> , 2022 , <i>13</i> , 111-117
2	Pd@SiO ₂ (1 mol% Pd)	150 °C, 30 h	97%	--	<i>J. Catal.</i> , 2020 , <i>382</i> , 141-149
3	Pd/MgO (0.8% Pd)	180 °C, 0.25 h.	79%	80%	<i>Chem. Eur. J.</i> , 2010 , <i>16</i> , 254-260
4	Ni/CaSiO ₃ (2 mol% Ni)	155 °C, 17 h	78%	78%	<i>Catal. Today</i> , 2014 , <i>232</i> , 134-138
5	Ni/θ-Al ₂ O ₃ (1 mol% Ni)	144 °C, 3 h	99%	99%	<i>ACS Catal.</i> , 2013 , <i>3</i> , 998-1005
6	Ni/Al ₂ O ₃ (5 mol% Ni)	150 °C, 72 h	78%	79%	<i>ACS Catal.</i> , 2013 , <i>3</i> , 112-117
7	15Ni/Al-β-CD (35 mg)	140 °C, 1 h	38%	64%	<i>J. Catal.</i> , 2017 , <i>356</i> , 111-124
8	Ni(COD) ₂ (3mol% Ni)	140 °C, 18 h	99%	99%	<i>Catal. Sci. Technol.</i> , 2018 , <i>8</i> , 5498-5505

9	Cu@ Mg–Al hydrotalcite	180 °C, 15 h	98%	98%	<i>Catal. Commun.</i> , 2013 , 33, 80-83
10	Bpy-UiO-CoCl₂ (0.3 mol% Co)	120 °C, 24 h	98%	98%	This work

3.3. Test for “heterogeneity” of bpy-UiO-CoCl₂ for the N-alkylation of aniline with benzyl alcohol.

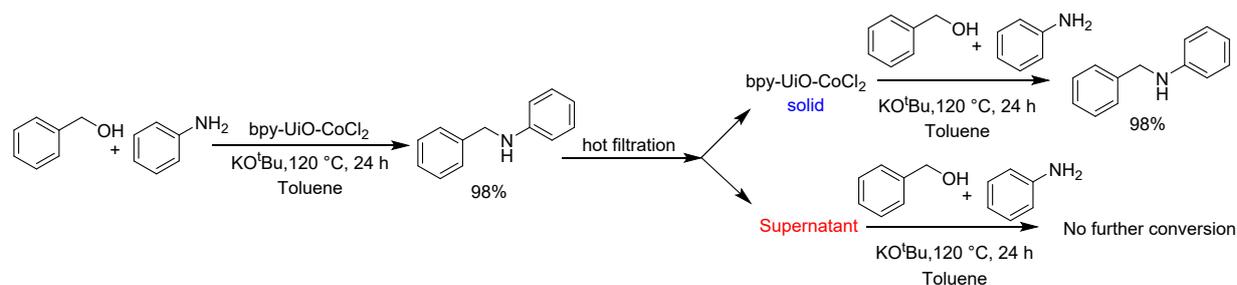


Figure S4. Hot filtration test of bpy-UiO-CoCl₂ for the N-alkylation of aniline.

0.5 mmol of aniline and 1 mmol of benzyl alcohol were mixed with 3 mg of catalyst (bpy-UiO-CoCl₂) and 0.5 mmol of base (KO^tBu) in a 50 mL Schlenk tube under a nitrogen atmosphere. Then, 2 mL of dry toluene was added to the mixture. The reaction mixture was stirred at a temperature of 120 °C for 24 hours under reflux conditions. After the reaction was completed, the solid MOF catalyst was removed from the hot reaction mixture by filtration, and thoroughly washed with toluene. The yield was analyzed by taking aliquots from the supernatant gave 98% amine product.

Two reactions were set up separately in two different Schlenk tubes, one with the solid and the other one with the supernatant recovered from the previous reaction. The extracted solid and supernatant were added into two separate tubes, both the Schlenk tubes were placed in an oil bath at a temperature of 120 °C and equipped with a water-cooled reflux condenser under nitrogen atmosphere, and aniline (0.5 mmol), benzyl alcohol (1 mmol), KO^tBu (0.5 mmol) and 2 mL of toluene were added to each tube. After 24 h, the reactions were analyzed with the GC-MS/FID using *n*-dodecane as an internal standard, which showed that the reaction with the solid MOF gave 98% yield, while the reaction with supernatant gave no further conversion of aniline. This experiment excludes the potential of any leached Co-species responsible for catalysis and confirms that solid bpy-UiO-CoCl₂ was the actual catalyst for the N-alkylation of aniline.

3.4. Recycling of bpy-UiO-CoCl₂ for the N-alkylation of aniline with benzyl alcohol.

The recycle and reuse experiment was conducted to check the stability of bpy-UiO-CoCl₂ MOF-catalyst (Table S5). The detailed procedure of recycling experiment given below.

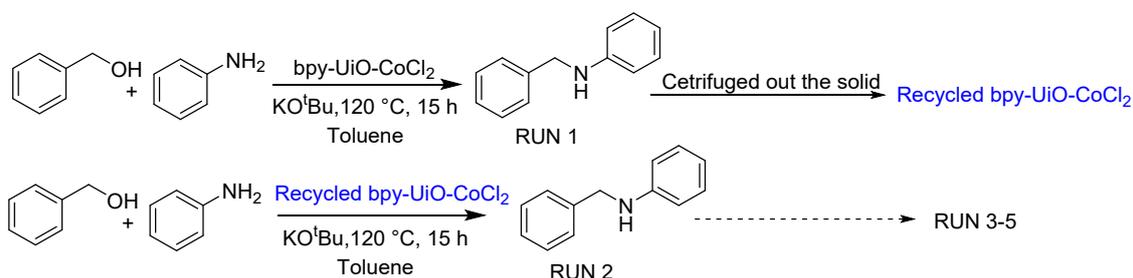


Figure S5. Recycle and reuse of bpy-UiO-CoCl₂ for the N-alkylation of aniline with benzyl alcohol.

0.5 mmol of aniline and 1 mmol of benzyl alcohol were mixed with 3 mg of catalyst (bpy-UiO-CoCl₂) and 0.5 mmol of KO^tBu in a 50 mL Schlenk tube under a nitrogen atmosphere. Then, 2 mL of dry toluene was added to the mixture. The reaction mixture was stirred at a temperature of 120 °C for 15 hours under reflux conditions. After the reaction was completed, the solid MOF was removed from suspension to separate the solid and the supernatant, inside the glove box and washed with toluene multiple times. The yield was determined by GC analysis using *n*-dodecane as an internal standard. The solid MOF was then recycled.

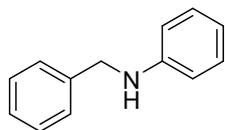
Under the nitrogen atmosphere, the recovered MOF-catalyst was again added to the Schlenk tube. 2 mL toluene, 0.5 mmol of aniline, 1 mmol of benzyl alcohol, and KO^tBu (0.5 mmol) were added to the Schlenk tube. The reaction mixture was stirred at a temperature of 120 °C for 15 hours under reflux conditions. After the reaction, the solution was analyzed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed up to 4 times in total.

Table S5. %GC-Yield of *N*-benzylaniline and the leaching of Co and Zr at various runs of the recycling of bpy-UiO-CoCl₂ in the N-alkylation of aniline with benzyl alcohol.

Run	Time	%GC-Yield (<i>N</i> -benzylaniline)	%Leaching (Co, Zr)
Run-1	15 h	55	0.011, 0.02
Run-2	15 h	54	
Run-3	15 h	57	0.03, 0.05
Run-4	15 h	51	
Run-5	15 h	50	0.05, 0.08

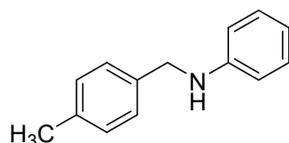
4. NMR Data of the Synthesized *N*-Alkylated Amines.

N-Benzylaniline (**3a**)⁴



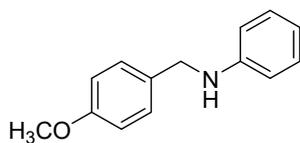
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.49–7.43 (m, 4H), 7.41–7.37 (m, 1H), 7.31–7.27 (m, 2H), 6.84 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 4.42 (s, 2H), 4.10 (brs, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.3, 139.6, 129.4, 128.7, 127.6, 127.3, 117.7, 112.9, 48.4 ppm.

N-(4-Methylbenzyl)aniline (**3b**)⁵



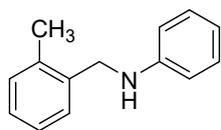
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.23–7.18 (m, 4H), 6.77–6.74 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.31 (s, 2H), 4.01 (brs, 1H), 2.39 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.3, 136.9, 136.4, 129.4, 129.3, 127.6, 117.5, 112.9, 48.1, 21.2 ppm.

N-(4-Methoxybenzyl)aniline (**3c**)⁴



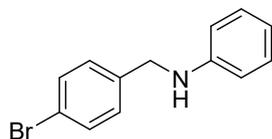
Purification by column chromatography (silica gel, hexane/ethyl acetate 19:1). Colorless oil, yield: 81%. ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.78–6.75 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 3.80 (s, 3H), 3.62 (brs, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.9, 147.1, 130.6, 129.3, 129.1, 118.4, 114.0, 113.7, 55.3, 48.4 ppm.

***N*-(2-Methylbenzyl)aniline (3d)**⁵



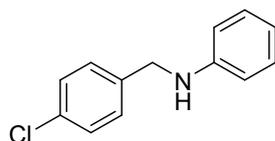
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 78%. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.24–7.20 (m, 4H), 6.76 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 3.92 (brs, 1H), 2.39 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.1, 136.9, 136.4, 130.4, 129.3, 128.4, 127.5, 126.2, 117.7, 112.9, 46.5, 18.9 ppm.

***N*-(4-Bromobenzyl)aniline (3e)**⁵



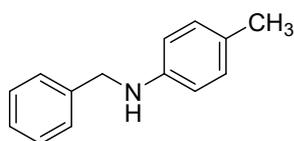
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 80%. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.33 (s, 2H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.4, 138.3, 131.7, 129.3, 129.2, 121.0, 118.2, 113.2, 47.9 ppm.

***N*-(4-Chlorobenzyl)aniline (3f)**⁴



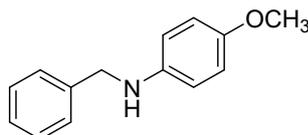
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 82%. ¹H NMR (400 MHz, CDCl₃) δ 7.42–7.37 (m, 4H), 7.31–7.27 (m, 2H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.37 (s, 2H), 4.13 (brs, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.9, 138.2, 132.9, 129.4, 128.9, 128.8, 117.9, 113.0, 47.6 ppm.

***N*-Benzyl-4-methylaniline (3g)**⁴



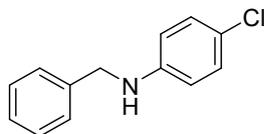
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 84%. ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.49 (m, 4H), 7.46–7.43 (m, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.72 (d, $J = 8.0$ Hz, 2H), 4.44 (s, 2H), 4.01 (brs, 1H), 2.43 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.2, 139.9, 130.0, 128.8, 127.7, 127.3, 126.8, 113.2, 48.8, 20.6 ppm.

***N*-Benzyl-4-methoxyaniline (3h)⁴**



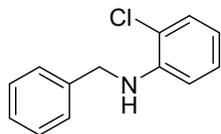
Purification by column chromatography (silica gel, hexane/ethyl acetate 19:1). Yellow oil, yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.28 (m, 5H), 6.83–6.79 (m, 2H), 6.66–6.62 (m, 2H), 4.31 (s, 2H), 3.87 (brs, 1H), 3.77 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.3 ppm.

***N*-Benzyl-4-chloroaniline (3i)⁵**



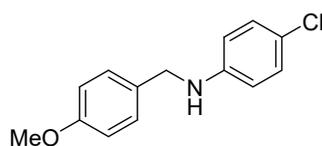
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Yellow oil, yield: 81%. ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.42 (m, 4H), 7.40–7.37 (m, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 8.0$ Hz, 2H), 4.37 (s, 2H), 4.14 (brs, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 146.8, 139.0, 129.2, 128.8, 127.5, 127.4, 122.1, 114.0, 48.4 ppm.

***N*-Benzyl-2-chloroaniline (3j)⁴**



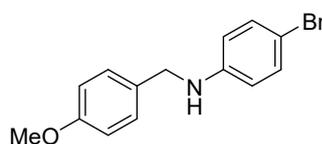
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 74%. ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.36 (m, 4H), 7.33–7.29 (m, 2H), 7.14–7.10 (m, 1H), 6.68–6.65 (m, 2H), 4.81 (brs, 1H), 4.43 (s, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.8, 138.7, 129.2, 128.8, 127.9, 127.4, 127.3, 119.2, 117.5, 111.6, 47.9 ppm.

4-chloro-N-(4-methoxybenzyl)aniline (3k)⁶



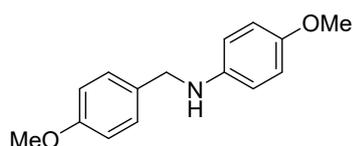
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 77%. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.26 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 6.36 (t, J = 5.9 Hz, 1H), 4.16 (d, J = 5.9 Hz, 2H), 3.72 (s, 3H) ppm. ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 158.2, 147.6, 131.5, 128.5, 128.4, 118.9, 113.7, 113.6, 55.0, 45.9 ppm.

4-bromo-N-(4-methoxybenzyl)aniline (3l)⁷



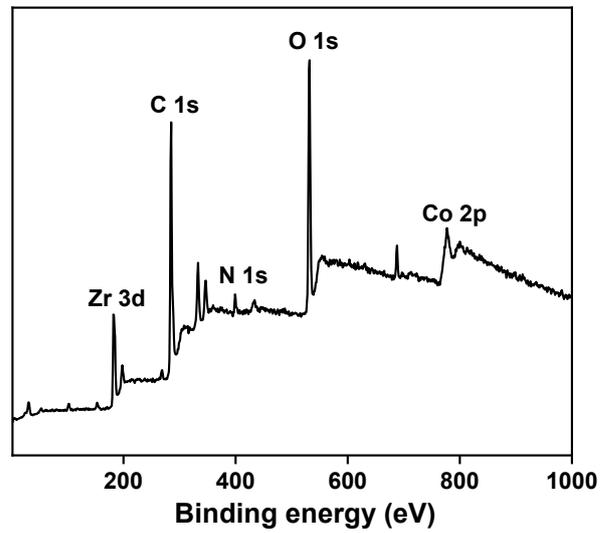
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 76%. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.25 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 6.39 (t, J = 5.9 Hz, 1H), 4.16 (d, J = 5.9 Hz, 2H), 3.72 (s, 3H) ppm. ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 158.2, 147.9, 131.5, 131.3, 128.4, 114.2, 113.7, 106.2, 55.0, 45.8 ppm.

4-methoxy-N-(4-methoxybenzyl)aniline (3o)⁸

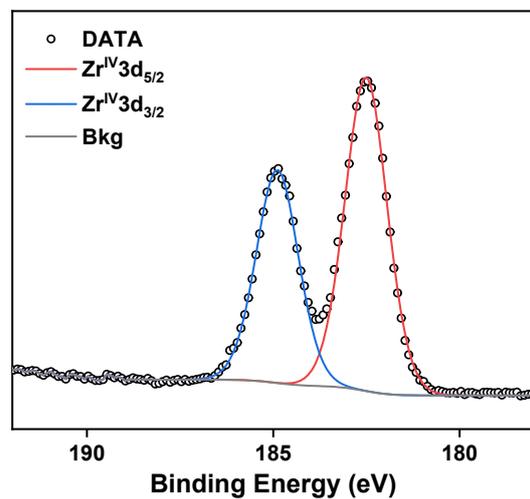


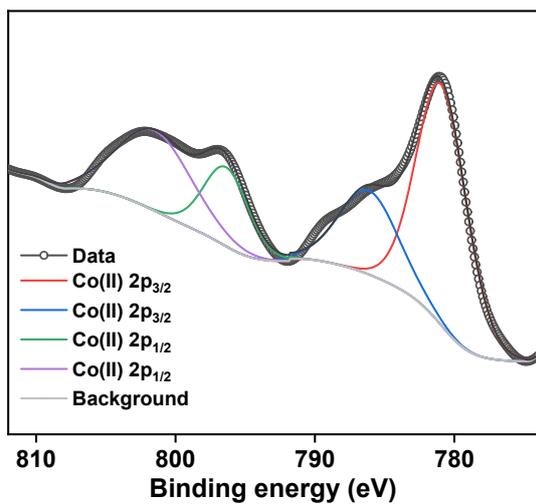
Purification by column chromatography (silica gel, hexane/ethyl acetate 49:1). Colorless oil, yield: 71%. ¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.27 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 6.52 (d, J = 8.9 Hz, 2H), 5.70 (t, J = 6.0 Hz, 1H), 4.12 (d, J = 6.0 Hz, 2H), 3.71 (s, 3H), 3.61 (s, 3H) ppm. ¹³C NMR (126 MHz, DMSO-*d*₆): δ = 158.0, 150.7, 143.0, 132.3, 128.5, 114.5, 113.6, 113.4, 55.3, 55.0, 46.7 ppm.

5. XPS analysis. All the binding energies were corrected with reference to the C1s peak at 284.8 eV. MULTIPAK software was used for peak analysis and de-convolution studies.



(a)





(b)

(c)

Figure S6. (a) Raw XPS data of bpy-UiO-CoCl₂. (b) Co 2p XPS spectrum of bpy-UiO-CoCl₂. (c) Zr 3d XPS spectrum of bpy-UiO-CoCl₂.

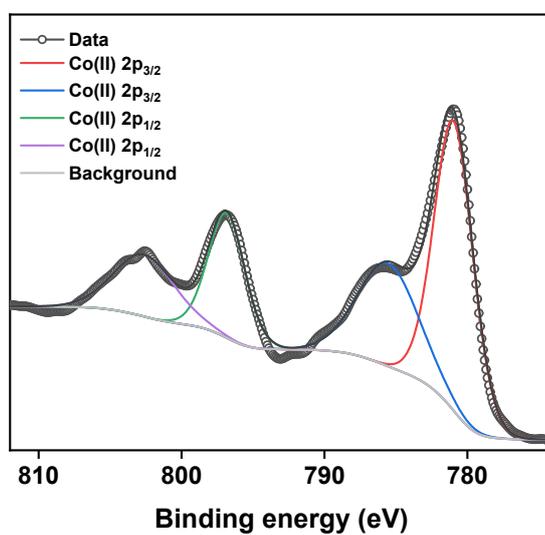


Figure S7. Co 2p XPS spectrum of bpy-UiO-Co after catalysis.

6. References.

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