

## Supporting Information

### **N-Formylation of Amines Utilizing CO<sub>2</sub> by a Heterogeneous Metal-Organic Framework Supported Single-Site Cobalt Catalyst**

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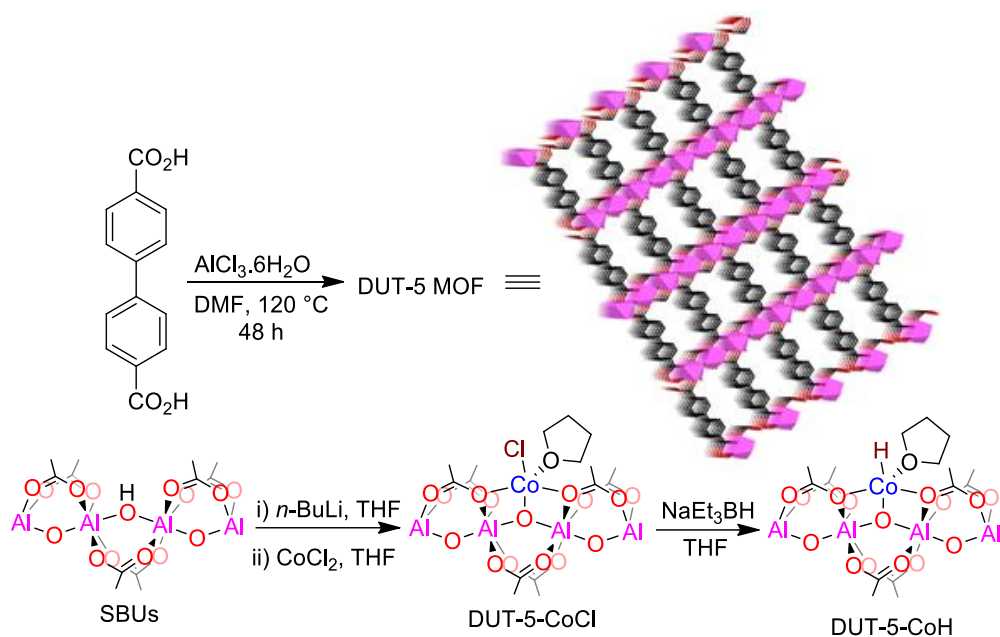
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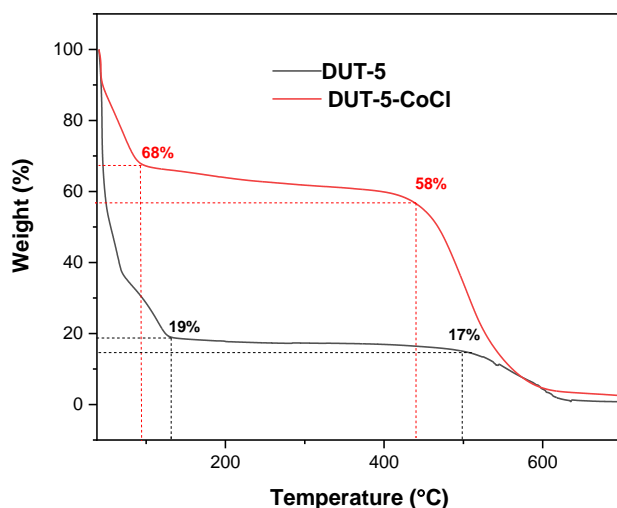
**1. General Experiment.** All experiments were performed under passive conditions inside the glovebox, except for any case to be displayed. All solvents were purchased from Finar and used without further purification. Tetrahydrofuran, and toluene were dried with calcium hydride followed by distillation on Na/benzophenone. All reagents and substrates are commercially available and used directly as received. 4,4-biphenyldicarboxylic acid was purchased from Alfa Aesar, and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was purchased from Sigma Aldrich.  $^1\text{H}$  NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer at 500 MHz and referenced to the proton resonance resulting from incomplete deuteration of the deuterated water ( $\delta$  4.79). 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  $0.05^\circ$  and at a count time of 1s per step over the range  $4^\circ < 2\theta < 70^\circ$ . The experimental and calculated PXRD patterns are in good agreement indicating the monophasic nature of the bulk samples. Samples were dried at room temperature for powder X-ray diffraction measurement. The liquid phase of catalytic reactions was determined by gas chromatography (GC) using Agilent 7890B gas chromatograph equipped with a flame ionization detector (FID) and mass detector (Agilent 5977B GC/MSD). GC-MS conditions: Inj:  $220\text{ }^\circ\text{C}$ ; Det:  $250\text{ }^\circ\text{C}$ ; Column temp:  $80\text{ }^\circ\text{C}$  followed by a ramp of  $5\text{ }^\circ\text{C}/\text{min}$  to  $220\text{ }^\circ\text{C}$ ; Column flow:  $1.0\text{ mL}/\text{min}$ . Samples were diluted in a 5%  $\text{HNO}_3$  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. All the N-formylation reactions were performed using 100 mL Parr pressure vessels (4793 (VGR)-T-SS-3000-DVD). The vessel was pressurized directly from a  $\text{H}_2$  gas tank and a  $\text{CO}_2$  gas tank using a gauge (0-3000 psi displayed, 0-200 bar). To analyse the chemical state of transition elements, XPS was 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.

**2. Synthesis and characterization of DUT-5-CoH.** DUT-5-CoH was synthesized according to the reported procedure.<sup>1</sup> A solvothermal reaction between 4,4'-biphenyldicarboxylic acid and aluminum chloride hexahydrate in DMF at  $120\text{ }^\circ\text{C}$  for 48 h resulted DUT-5-MOF as a white crystalline solid. The post-synthetic modification of the SBUs of the DUT-5-MOF was performed via deprotonation of its  $\mu_2\text{-OH}$  by *n*-BuLi followed by the addition of THF solution

of  $\text{CoCl}_2$  to afford the cobalt functionalized DUT-5 MOF (DUT-5- $\text{CoCl}$ ). The DUT-5- $\text{CoCl}$  MOF was further treated with  $\text{NaEt}_3\text{BH}$  to give DUT-5- $\text{CoH}$  MOF via halide-hydride exchange reaction (Fig. S1).



**Figure S1.** Synthesis of DUT-5- $\text{CoH}$  via post-synthetic metalation of SBUs of DUT-5 MOF.

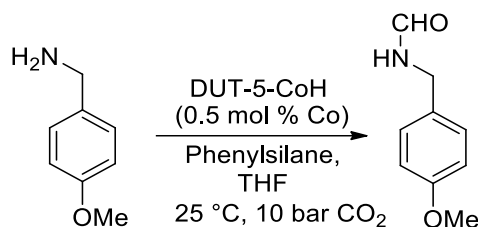


**Figure S2.** TGA curve of freshly prepared DUT-5 (black) and DUT-5- $\text{CoCl}$  (red). A solvent weight loss of 81% and 32% was observed in the room temperature to  $40\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$  range, respectively.

### 3. DUT-5-CoH catalysed *N*-formylation of amines using phenyl silane.

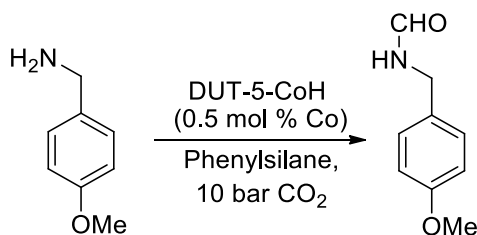
**3.1. General procedure for DUT-5-CoH catalysed *N*-formylation of amines using phenyl silane.** DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. The amine substrate and phenyl silane were added to the mixture. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at 25 °C or heating at 100 °C for 20-40 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from suspension inside the glove box, washed with THF three times and reused. The combined organic extracts were concentrated in vacuo to yield corresponding *N*-formaldehyde as the pure product.

### 3.2. A Typical procedure for DUT-5-CoH catalysed *N*-formylation of *p*-methoxy benzylamine.



DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. To the mixture, *p*-methoxy benzylamine (49  $\mu$ L, 0.375 mmol) and 106  $\mu$ L Phenyl silane were added. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at room temperature for 20 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from suspension inside the glove box, washed with THF multiple times, and reused. The combined organic extracts were concentrated in vacuo, followed by column chromatography using hexane and ethyl acetate (50:1, R<sub>f</sub>: 0.6) as an eluent to yield *N*-(4-methoxybenzyl)formamide as the pure product (0.050 g, 0.335 mmol, 90%).

**Table S1. Optimization reaction conditions for the *N*-formylation of *p*-methoxy benzylamine.<sup>a</sup>**



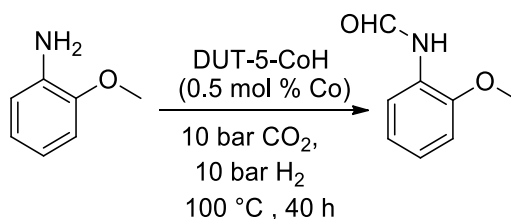
Entry no.	Catalyst	Reductant	Temperature (°C)	Time (h)	Solvent	GC-Yield (%)
1	DUT-5-CoH (0.5 mol%)	Phenylsilane (2 eq)	25	24 h	THF	80
2	DUT-5-CoH (0.5 mol%)	H <sub>2</sub> (10 bar)	25	24 h	THF	0
3	DUT-5-CoH (0.5 mol%)	Phenylsilane (1 eq)	25	24 h	THF	50
4	DUT-5-CoH (0.5 mol%)	Phenylsilane (2 eq)	25	24 h	Toluene	63
<b>5</b>	<b>DUT-5-CoH (0.5 mol%)</b>	<b>Phenylsilane (2.3 eq)</b>	<b>25</b>	<b>20 h</b>	<b>THF</b>	<b>90</b>
6	DUT-5-CoH (0.1 mol%)	Phenylsilane (2.3 eq)	25	72 h	THF	81
7	DUT-5-CoH (0.5 mol%)	Phenylsilane (2.3 eq)	25	6 h	THF	55
8	DUT-5-CoH (0.5 mol%)	diethoxymethylsilane (2.3 eq)	25	20 h	THF	0
9	DUT-5-CoH (0.5 mol%)	Poly(methylhydrosiloxane) (2.3 eq)	25-100	20 h	THF	0
10	No MOF catalyst	Phenylsilane (2.3 eq)	25	20 h	THF	3

<sup>a</sup>Reaction conditions: DUT-5-CoH, 10 bar CO<sub>2</sub>, 3.0 mL solvent.

### 3.3. General procedure DUT-5-CoH catalyzed *N*-formylation of amines using H<sub>2</sub>.

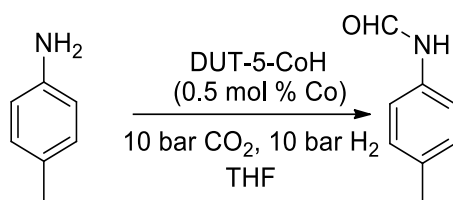
DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. The amine substrate was added to the mixture. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> followed by 10 bar of H<sub>2</sub> and heated at 100 °C for 40 h. After the successful completion of the reaction, the reactor was cooled to room temperature, and the pressure was released. The solid MOF was removed from suspension inside the glove box, washed with THF three times and reused. The combined organic extracts were concentrated in vacuo to yield corresponding *N*-formaldehyde as the pure product.

### 3.4. Typical procedure for the DUT-5-CoH catalyzed *N*-formylation of *o*-anisidine using H<sub>2</sub>.



DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. To the mixture, *o*-anisidine (42  $\mu$ L, 0.375 mmol) was added. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> followed by 10 bar of H<sub>2</sub> and heated at 100 °C for 40 h. After the successful completion of the reaction, the reactor was cooled to room temperature, and the pressure was released. The solid MOF was removed from suspension inside the glove box, washed with THF multiple times, and reused. The combined organic extracts were concentrated in vacuo to yield *N*-(2-methoxyphenyl)formamide as the pure product. (0.045 g, 0.300 mmol, 80%).

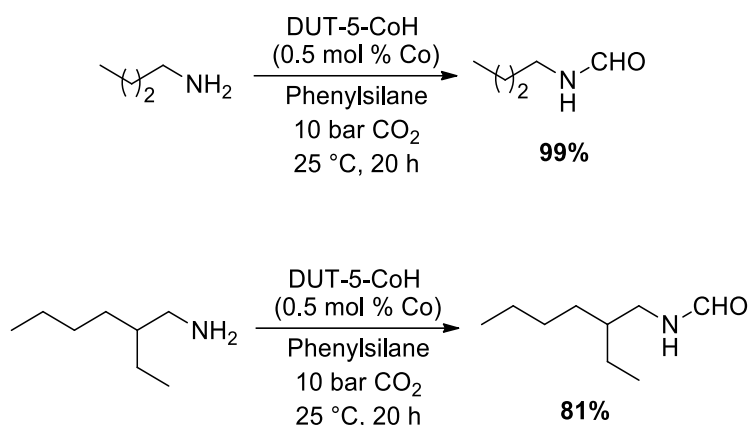
**Table S2. Optimization reaction conditions for the *N*-formylation of *p*-toluidine.<sup>a</sup>**



Entry no.	Catalyst	Reductant	Temperature (°C)	Time (h)	Solvent	GC-Yield (%)
1	DUT-5-CoH	Phenylsilane (2.3 eq.)	100	40 h	THF	4
<b>2</b>	<b>DUT-5-CoH</b>	<b>H<sub>2</sub> (10 bar)</b>	<b>100</b>	<b>40 h</b>	<b>THF</b>	<b>80</b>
3	DUT-5-CoH	H <sub>2</sub> (10 bar)	25	40 h	THF	2
4	DUT-5-CoH	H <sub>2</sub> (10 bar)	100	40 h	Toluene	0

<sup>a</sup>Reaction conditions: DUT-5-CoH (0.5 mol% Co), 10 bar CO<sub>2</sub>, 3.0 mL solvent.

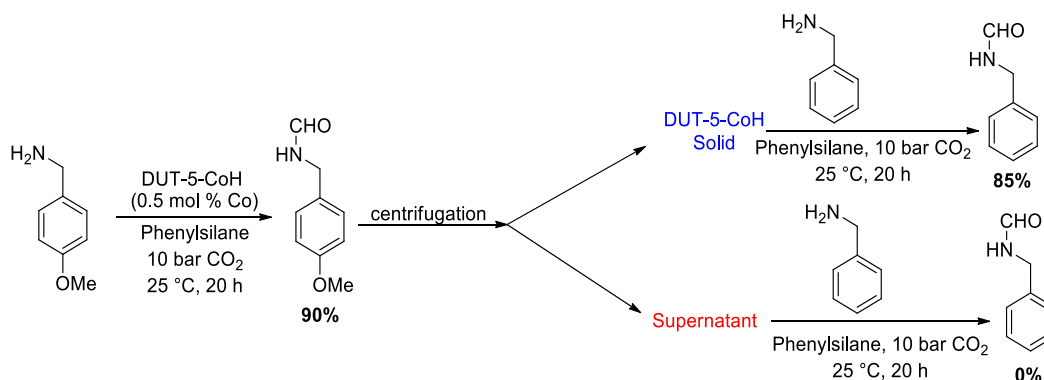
### 3.7. Investigation of the effect of varying substrate sizes on the rate of catalysis.



**Figure S3.** Comparative study of the effect of varying substrate sizes on the rate of *N*-formylation catalysed by DUT-5-CoH.

Inside the glovebox, butylamine (37  $\mu$ L, 0.375 mmol), and 2-ethyl hexylamine (60  $\mu$ L, 0.375 mmol), were added separately into two 50 mL glass liners. Then, DUT-5-CoH (0.5 mol% of Co) as a slurry in 3 mL THF and 106  $\mu$ l phenylsilane were added to each of the liners, and were fitted in two separate Parr reactors. The reactors were sealed, then taken out from the glove box, purged two times with CO<sub>2</sub>, and then pressurized each of them to 10 bar CO<sub>2</sub>. Reactors were then stirred at 25 °C for 20 h. After the successful completion of the reaction, the pressure of the reactors was released. The solid MOF was removed from suspension inside the glove box, washed with THF multiple times, and reused. The combined organic extract of both the reactions was concentrated and analyzed using GC-MS. The *N*-butylformamide from butylamine and *N*-(2-ethylhexyl)formamide from 2-ethyl hexylamine were produced in 99% and 81% GC-yields, respectively. This experiment demonstrates that the rate of *N*-formylation with larger substrates is slower, presumably due to the slower diffusion of the larger branched substrates and the corresponding products through the MOF's channels.

### 3.8. Test for “heterogeneity” of DUT-5-Co in *N*-formylation of amines.



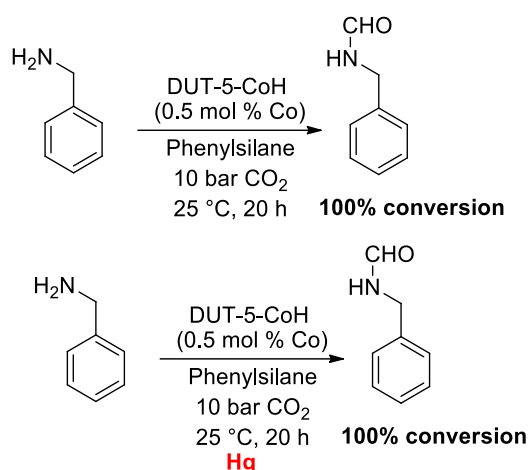
**Figure S4.** Heterogeneity test of DUT-5-CoH for the *N*-formylation of amines.

DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. To the mixture, *p*-methoxy benzylamine (49  $\mu$ l, 0.375 mmol) and 106  $\mu$ l Phenyl silane were added. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at 25°C for 20 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from suspension to separate the solid and the supernatant, inside the glove box and washed with THF multiple times. The conversion analysed by taking aliquots from the organic extract gave 90% *N*-(4-methoxybenzyl)formamide.

Two reactions were set up separately in two different Parr reactors, 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 liners, and benzylamine (41  $\mu$ l, 0.375 mmol), 106  $\mu$ l phenylsilane, and 3 mL of THF were added to each liner. Then both the liners were fitted into two separate Parr reactors and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at 25°C for 20 h. After the completion of the reaction, the pressure of the reactors was released. The reactions were analysed with the GC-MS, which showed that the reaction with the solid MOF gave 100% conversion with 85% yield, while the reaction with supernatant gave 0% conversion. This experiment excludes the potential of any leached Co-species responsible for catalysis and confirms that solid DUT-5-CoH was the actual catalyst for the *N*-formylation of amines.

**3.9. Hg test.** A catalytic *N*-formylation of amine was carried out in the presence of a drop of Hg to investigate the role of any leached Co-nanoparticles in the solution responsible for catalysis. Hg is known to form an amalgam with metallic cobalt, thus removing any in-situ-borne metallic cobalt during catalysis. The details of the experiments are as follows:



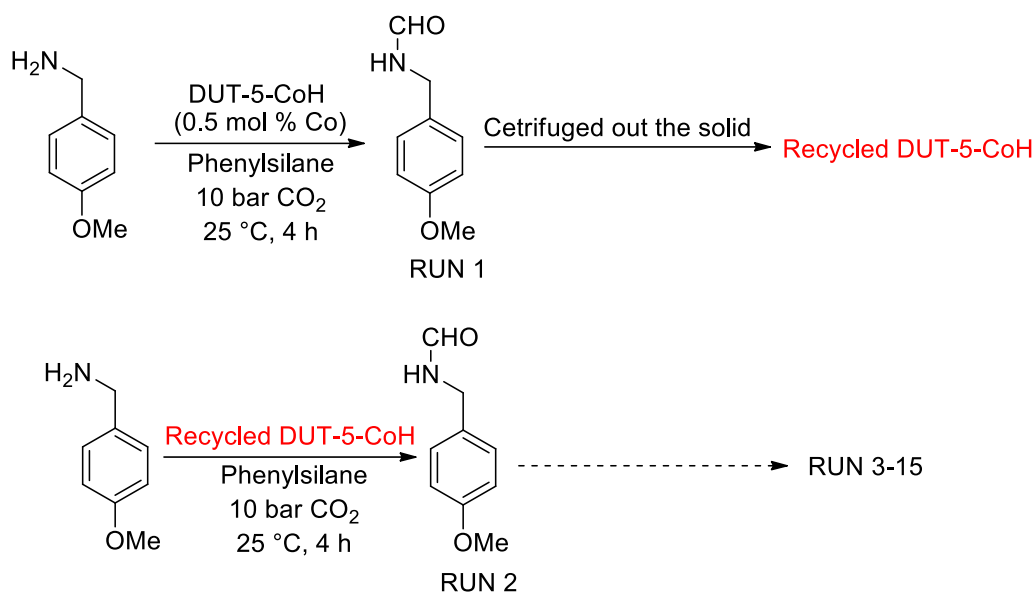


**Figure S5.** Hg test in the *N*-formylation of benzylamine with DUT-5-CoH.

DUT-5-CoH (0.5 mol % of Co) was charged into two separate 3 mL vials and washed with THF multiple times inside the glovebox. The MOF as a slurry in 3 mL THF was transferred to the two separate 50 mL glass liners. Benzylamine (41  $\mu\text{l}$ , 0.375 mmol), 106  $\mu\text{l}$  phenylsilane and 3 mL of THF was added to both the liners. In one of the reaction mixtures, a drop of mercury was added. Then, the liners were fitted in a Parr reactor and sealed. The sealed Parr reactors were taken out from the glovebox and purged it with  $\text{CO}_2$  gas two times, then pressurized with 10 bar  $\text{CO}_2$ . The reactors were then stirred at 25  $^\circ\text{C}$  for 20 h. After the completion of the reaction, the pressure of the reactor was released. The solid MOF was removed from the suspension inside the glove box and washed with THF multiple times. The catalytical conversion was 100% for both the reactions analysed by GC-MS. We thus conclude that any leached Co-particles were not responsible for the catalytical activity, and DUT-5-CoH was the actual catalyst.

### 3.10. Recycling of DUT-5-CoH for the *N*-formylation of amines.

In order to monitor the intrinsic initial activity of each run and also to check the stability of the MOF-catalyst, the recycle and reuse experiment using DUT-5-CoH was conducted at incomplete conversion (~50-60%) for same reaction time (4 h). The catalytic activity of DUT-5-Co remained the same till run 16, and the leaching of Co and Al was very low (Table S3). The detailed procedure of the recycling experiments is given below.



**Figure S6.** Recycle and reuse of DUT-5-CoH in *N*-formylation of *p*-methoxy benzylamine.

DUT-5-CoH (0.5 mol% of Co) in 3 ml of THF was transferred into a 50 mL glass liner in a glovebox. To the mixture, *p*-methoxy benzylamine (49  $\mu$ l, 0.375 mmol and 106  $\mu$ l Phenylsilane) were added. Then, the liner was fitted in a Parr reactor and sealed. The sealed Parr reactor was taken out from the glovebox and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at 25  $^\circ$ C for 4 h. After certain time intervals, the reaction was depressurized and a small aliquot from the reaction mixture was taken out and analysed by GC-MS. The solid was centrifuged out of the suspension, washed with THF multiple times, and recycled.

The recovered MOF-catalyst was again added to the liner. Then, 3 mL of THF, 106  $\mu$ l phenylsilane and *p*-methoxy benzylamine (49  $\mu$ l, 0.375 mmol) were added to it and fitted in a Parr reactor. The reactor was sealed, taken out from the glovebox, and purged it with CO<sub>2</sub> gas two times. The Parr reactor was pressurized to 10 bar CO<sub>2</sub> and stirred at 25  $^\circ$ C for 4 h. After the reaction, the solution was analysed in the same way as mentioned previously in run 1. The recycling and reuse experiments were performed 15 times in total.

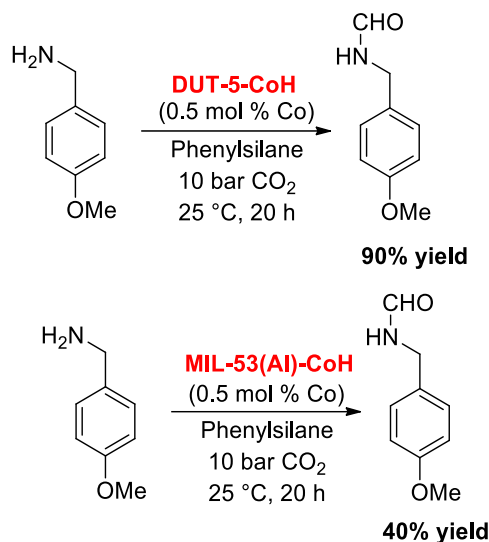
**Table S3. % GC-Yield of *N*-(4-methoxybenzyl)formamide, the leaching of Co at various runs of the recycling of DUT-5-CoH in the *N*-formylation of *p*-methoxy benzylamine.**

No. of Run	Time	%GC-Yield	%Leaching (Co, Al)
Run-1	4 h	55	0.02, 0.9
Run-2	4 h	59	
Run-3	4 h	52	
Run-4	4 h	53	
Run-5	4 h	58	
Run-6	4 h	57	
Run-7	4 h	56	0.04, 1.02
Run-8	4 h	58	
Run-9	4 h	55	
Run-10	4 h	53	0.05, 1.67
Run-11	4 h	57	
Run-12	4 h	54	
Run-13	4 h	56	
Run-14	4 h	58	0.08, 2.01
Run-15	4 h	55	
Run-16	4 h	54	

**3.9 Investigation of the effect of pore sizes on the rate of catalysis.** The effect of pore sizes on the rate of catalytic reaction was investigated by comparing the rate of *N*-formylation reactions of amines catalyzed by DUT-5-CoH with that of MIL-53(Al)-CoH under identical reaction conditions. MIL-53(Al)-CoH has the same topology but smaller pore sizes compared to DUT-5-CoH.

**3.9.3. Synthesis and characterizations of MIL-53(Al)-CoH.** MIL-53(Al) was synthesized according to the reported procedure.<sup>1</sup> MIL-53(Al) was then treated with *n*-BuLi in THF, to which a solution of CoCl<sub>2</sub> (0.018 g, 0.144 mmol) in THF was added to give a blue-coloured MOF of MIL-53(Al)-CoCl. It was then treated with NaEt<sub>3</sub>BH to finally produce MIL-53(Al)-CoH MOF.

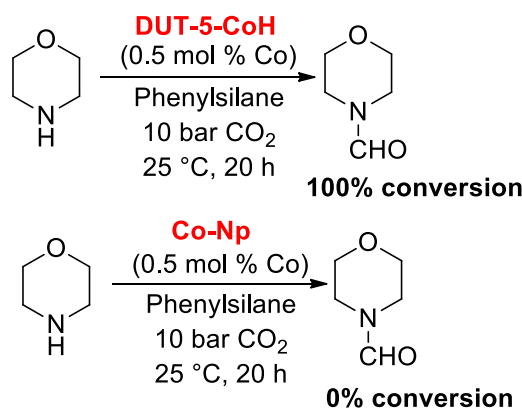
**3.9.4. Comparison of the catalytic activities of DUT-5-CoH and MIL-53(Al)-CoH in the *N*-formylation of amines under identical conditions.**



**Figure S7.** The *N*-formylation of 4-methoxybenzylamine catalyzed by DUT-5-CoH and MIL-53(Al)-CoH under identical reaction conditions.

Two separate 5 ml vials were charged with pre-activated DUT-5-CoH (0.5 mol% of Co) and MIL-53(Al)-CoH (0.5 mol% of Co) each and washed with THF multiple times. Each MOF slurry in 3 ml THF were transferred to two different 50 ml glass liners containing 4-methoxybenzylamine (49  $\mu$ l, 0.375 mmol) and Phenylsilane (106  $\mu$ L, 0.865 mmol). The liners were fitted into the Parr reactors and sealed properly. The sealed Parr reactors were taken out from the glove box. The reactors were purged twice with the CO<sub>2</sub>, then charged with 10 bar CO<sub>2</sub> each and stirred at 25 °C for 20 h. After the completion of the reaction, the pressure from the reactors was released. The solid MOF was then removed from suspension inside the glove box and the combined organic extracts were evaporated and analysed by GC-MS. The catalytical conversions for both the reactions were 100%, while the selectivity to get *N*-(4-methoxyphenyl)formamide were 90% and 40% with DUT-5-CoH and MIL53(Al)-CoH, respectively. This experiment indicates that the larger pore size MOF (DUT-5-CoH) has comparatively higher efficiency than the smaller pore size MIL-53(Al)-CoH MOF due to the facile diffusion of substrates into the larger pores of DUT-5-CoH.

### 3.10. Comparison of the catalytic activities of DUT-5-CoH and Co-nanoparticles in the *N*-formylation of amines under identical reaction conditions.



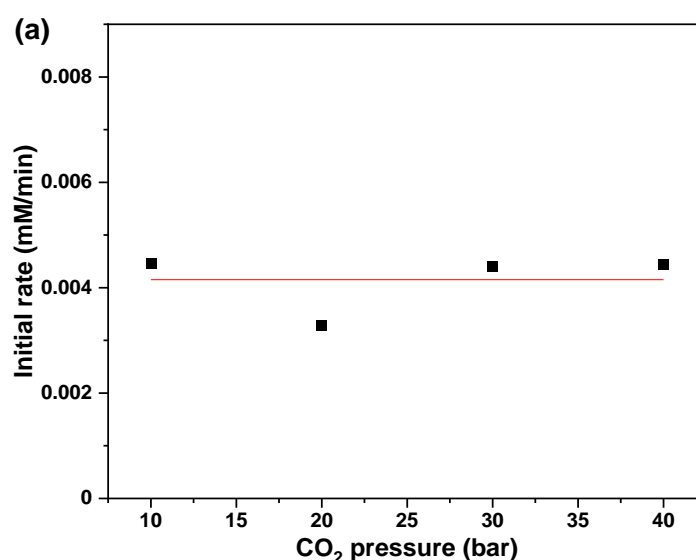
**Figure S8.** The *N*-formylation of morpholine catalyzed by DUT-5-CoH and Co-nanoparticles under identical conditions.

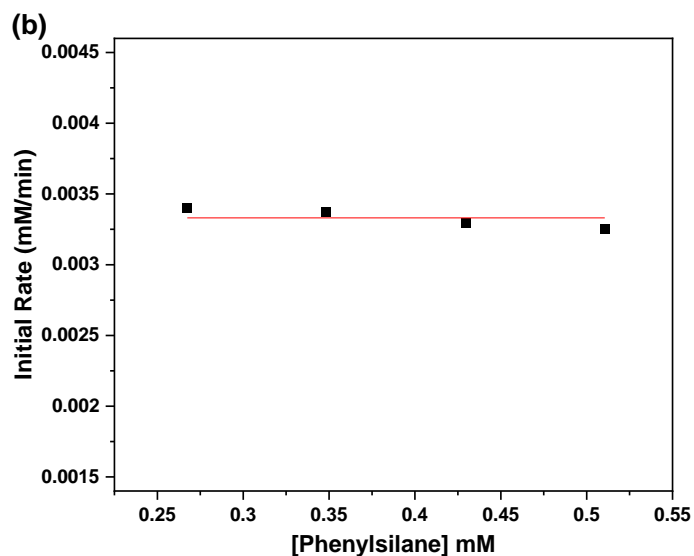
A 5 ml vial was charged with pre-activated DUT-CoH (0.5 mol% of Co) and washed with THF multiple times. The MOF slurry in 3 ml THF was transferred to a 50 ml glass liners containing morpholine (32  $\mu$ l, 0.375 mmol) and Phenylsilane (106  $\mu$ L). Another 5 ml vial was charged with CoCl<sub>2</sub> (0.5 mol% of Co) in 3 ml THF to which NaBEt<sub>3</sub>H (10  $\mu$ L, 1 M in toluene) was added and stirred gently for 1 h. The solution was then transferred to another 50 ml liner containing morpholine (32  $\mu$ l, 0.375 mmol) and Phenylsilane (106  $\mu$ L). Both the liners were fitted into Parr reactors and sealed properly. The sealed Parr reactors were taken out from the glove box. The reactors were purged two times with the CO<sub>2</sub> and then charged with 10 bar CO<sub>2</sub> each and stirred at 25 °C for 20 h. After the completion of the reaction, the pressure from the reactors was released. The solid MOF was then removed from suspension inside the glove box and washed with THF multiple times. The catalytical conversions were 100% and 0% with DUT-5-CoH and Co-Np, respectively, as analyzed by GC-MS suggesting the inactivity of Cobalt-nanoparticle in *N*-formylation reaction.

#### 4. Determination of the rate law for DUT-5-CoH catalysed *N*-formylation of benzylamine.

The rate law for *N*-formylation of benzylamine was determined by the method of initial rates (up to 10% conversion).<sup>2</sup> The reactions were conducted in THF (total volume of solution was 3.0 mL) in a Parr reactor at 100 °C. For each kinetic experiment, a glass liner was charged with MOF-catalyst, benzylamine, phenylsilane and THF under N<sub>2</sub>. The liner was fitted in a Parr reactor and sealed properly, pressurized with CO<sub>2</sub> and heated at 100 °C for 30 min. The concentration of the product was analysed by GC-FID using mesitylene as an internal standard. The initial rates for the *N*-formylation of benzylamine were measured for several substrate

concentrations at constant catalyst concentration. Linear regression fits for [benzylamine] versus time for the first 30 min of the reaction provided the initial rate ( $d[\text{benzylamine}]/dt$ ) for a particular initial substrate concentration. To determine the rate dependence on one reagent, the concentration of that reagent was varied, while the concentration of other reagents, pressure, and the total volume of solution (3.0 mL) were kept constant. The rate dependence on  $\text{CO}_2$  pressure was measured, while keeping all the reagents constant and varying  $\text{CO}_2$  pressure. The rates refer to the rates of consumption of benzylamine in units of  $\text{M}\cdot\text{min}^{-1}$ . To determine the rate dependence on the catalyst, the concentration of Co was varied between  $6.33\times 10^{-3}$ – $2.5\times 10^{-2}$  mM, while the initial concentrations of benzylamine were  $1.83\times 10^{-1}$  mM, concentration of phenylsilane was  $4.21\times 10^{-1}$  mM and  $\text{CO}_2$  pressure was 10 bar. To determine the rate dependence on benzylamine, initial concentration of phenylsilane was  $4.21\times 10^{-1}$  mM and  $\text{CO}_2$  pressure was 10 bar, while the concentration of benzylamine was varied between  $9.1\times 10^{-2}$  to  $3.6\times 10^{-1}$  mM, while the concentration of Co was  $6.33\times 10^{-3}$  mM. To determine the rate dependence on pressure of  $\text{CO}_2$ , the concentrations of benzylamine were  $1.83\times 10^{-1}$  mM, concentration of phenylsilane was  $4.21\times 10^{-1}$  mM, and  $\text{CO}_2$  pressure was varied from 10-40 bar, while the concentration of Co was  $6.33\times 10^{-3}$  mM. To determine the rate dependence on phenylsilane, the concentration of phenylsilane was varied between  $2.67\times 10^{-1}$ – $5.1\times 10^{-1}$  mM, while the initial concentrations of benzylamine were  $1.83\times 10^{-1}$  mM, concentration of Co was  $6.33\times 10^{-3}$  mM and  $\text{CO}_2$  pressure was 10 bar.



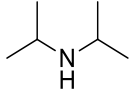
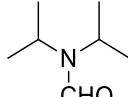
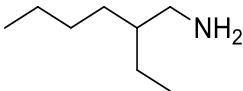
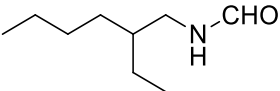
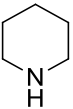
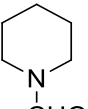
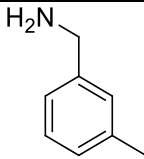
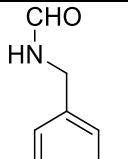
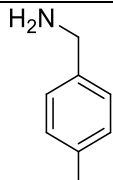
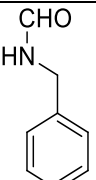
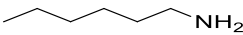
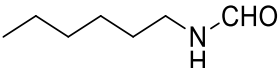
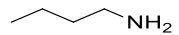
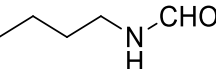
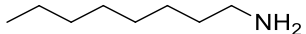
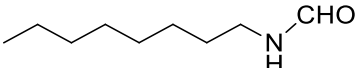
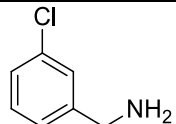
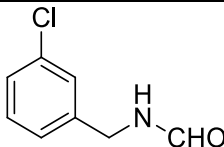
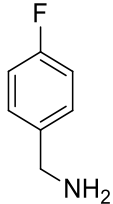
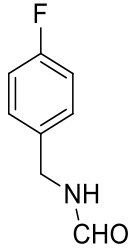
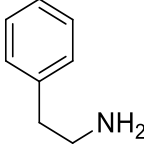
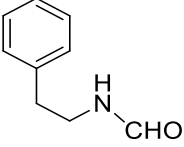
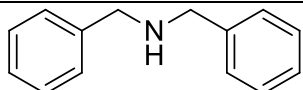
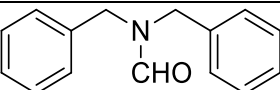


**Figure S9.** (a) Plot of initial rate  $-(d[\text{benzylamine}]/dt)$  versus initial pressure of  $\text{CO}_2$  (bar) for the first 30 min (<10% conversion) in THF showing the independence of initial rates on  $\text{CO}_2$  pressure. (b) Plot of initial rate  $-(d[\text{benzylamine}]/dt)$  versus initial concentration of phenylsilane (mM) for the first 30 min (<10% conversion) in THF showing the independence of initial rates on phenylsilane concentration.

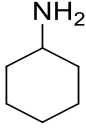
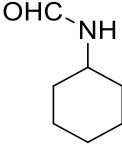
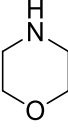
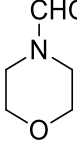

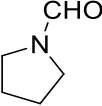
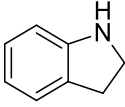
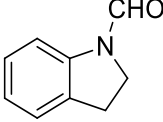
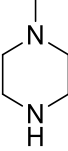
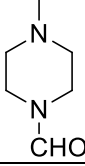
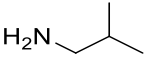
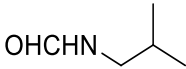

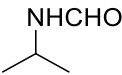
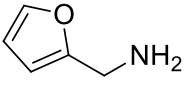
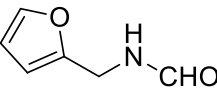
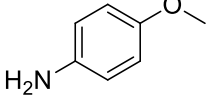
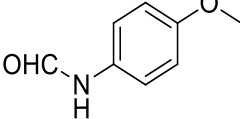
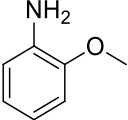
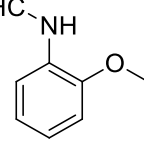
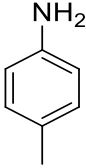
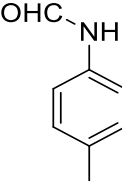
**5. Analysis of products by GC-MS.** The conversions and yields of the reactions were determined by Agilent 7890B gas chromatograph equipped with a mass detector (Agilent 5977B GC/MSD) and HP-5MS Ultra Inert 30 m-250  $\mu\text{m}$ -0.25  $\mu\text{m}$  column for GC-MS. GC-MS conditions: Inj: 220  $^\circ\text{C}$ ; Det: 250  $^\circ\text{C}$ ; Column temp: 80  $^\circ\text{C}$  followed by a ramp of 5  $^\circ\text{C}/\text{min}$  to 220  $^\circ\text{C}$ ; Column flow: 1.0 mL/min.

**Table S4.** The GC-MS retention times of the arene substrates and the products.

Entry	Substrate	Product	Retention time
1			20.02
2			14.17

3			6.07
4			13.23
5			7.90
6			16.52
7			16.62
8			9.86
9			5.70
10			13.05
11			18.99
12			14.34
13			16.07
14			26.92



15			10.62
16			7.51
17			6.73
18			16.83
19			9.42
20			6.2 <sup>a</sup>
21			4.8 <sup>a</sup>
22			9.18
23			16.03
24			15.96
25			14.88

<sup>a</sup>MS conditions: Inj: 220 °C; Det: 250 °C; Column temp: 40 °C followed by a ramp of 5 °C/min to 220 °C; Column flow: 1.0 mL/min.

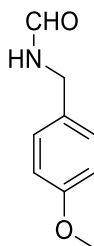
**6. Table S5. Comparison of catalytic activity of DUT-5-CoH with that of other reported heterogeneous catalysts in N-formylation of amines with CO<sub>2</sub>.**

Sl no.	Reference	Catalyst	Conditions	Productivity	%Yield of N-Formaldehyde
1	New J. Chem., 2021,45, 9501-9505	Zn(OAc) <sub>2</sub> on mesoporous organosilica	1 mmol amine, CO <sub>2</sub> (5 bar), PhSiH <sub>3</sub> (1 mmol), 1 mol% Catalyst, 60° C, 17 h, CH <sub>3</sub> CN		33-86%
2	ACS Sustainable Chem. Eng., 2020, 8, 14, 5576–5583	Ru-PPh <sub>3</sub> -SO <sub>3</sub> Na@POPs	1 mmol amine, CO <sub>2</sub> (30 bar), H <sub>2</sub> (30 bar), 0.4 mol% Catalyst, 100° C, 48 h, DMI	TON 250	30-80%
3	Chem. Cat. Chem., 2018, 10, 22, 5124-5127	Mg-Al layered double hydroxide supported Pd catalyst	1 mmol amine, CO <sub>2</sub> (30 bar), H <sub>2</sub> (30 bar), 1 mol% Catalyst, 140° C, 16 h, CH <sub>3</sub> OH		88-97%
4	Sci. China Chem., 2018, 61, 725–731	Pd/N-doped carbon nanocatalysts	1 mmol amine, CO <sub>2</sub> (30 bar), H <sub>2</sub> (40 bar), 20 mg (2 mol%) Catalyst, 130° C, 24 h, ethanol	TON 247	11-99%
5	Chem. Asian J., 2018, 13, 20, 3018-3021	NHC-Ir coordination assembly	10 mmol amine, CO <sub>2</sub> (30 bar), H <sub>2</sub> (30 bar), 0.1 mol% Catalyst, 100° C, 20 h, CH <sub>3</sub> OH	TON 990	53-97%
6	Inorganica Chim. Acta., 2020, 501, 119274	UiO-66 MOF	5 mmol amine, CO <sub>2</sub> (10 bar), DMAB (1.5 eq.), 10 mg (0.3 mol%) Catalyst, 60° C, 12 h, DMF		30-94%
7	New J. Chem., 2017, 41, 2869-2872	CarPy-CMP@Ru (Pyridine-functionalized organic porous polymers)	1 mmol amine, CO <sub>2</sub> (40 bar), H <sub>2</sub> (40 bar), 0.5 mol% Catalyst, 130° C, 24 h, CH <sub>3</sub> OH	TON 188	89-91%
8	Chem. Cat. Chem., 2017, 9, 11, 1939-1946	Pd NPs@Hyperscrosslinked Microporous Polymer	1 mmol amine, CO <sub>2</sub> (10 bar), Diphenylmethylsilane (2.5 mmol), 50 mg (0.5 mol%) Catalyst, 60° C, 20 h, dioxane+water		79-97%

9	Catal. Lett., 2018, 148, 2487–2500	FeNi <sub>3</sub> /KCC1/APTPOSS/TCT/PVA/Cu(II) MNPs (Copper(II) Complex-Based FeNi <sub>3</sub> /KCC-1)	10 mmol amine, CO <sub>2</sub> (15 bar), H <sub>2</sub> (20 bar), 18 mg Catalyst, 90° C, 1.5 h, dioxane		58-96%
10	ACS Sustainable Chem., Eng. 2017, 5, 3, 2516–2528	Pd–Au@Polyaniline-Functionalized CNs	1 mmol amine, CO <sub>2</sub> (35 bar), H <sub>2</sub> (35 bar), 50 mg (Pd 1.6 wt %, Au 3.0 wt %) Catalyst, 125° C, 48 h, dioxane		0.1-95%
11	Chem. Cat. Chem., 2017, 9, 19, 3632-3636	Au NPs@TiO <sub>2</sub>	0.5 mmol amine, CO <sub>2</sub> (20 bar), H <sub>2</sub> (30 bar), 4.5 mol% Catalyst, 100-140° C, 5-20 h, DMA		91-99%
12	Chin. J. Catal., 2019, 40, 8, 1141-1146	Pd/PAL catalyst (PAL-Palygorskite)	1 mmol amine, CO <sub>2</sub> (10 bar), H <sub>2</sub> (30 bar), 0.35 mol% Catalyst, 96° C, CH <sub>3</sub> OH	TON 283	76-99%
13	ACS Sustainable Chem., Eng., 2021, 9, 48, 16153-16162	Pd <sub>0.25</sub> Cu <sub>0.75</sub> /Al <sub>2</sub> O <sub>3-0.1</sub>	1 mmol amine, CO <sub>2</sub> (20 bar), H <sub>2</sub> (40 bar), 60 mg Catalyst, 150° C, 3 h, THF	TON 527	8-99%
14	Appl. Catal. B., 2021, 294, 5, 120238	Zn-TpPa (Zn single atom catalyst@COF)	CO <sub>2</sub> (10 bar), phenylsilane(2 eq.), 30° C, 18 h, DMF	TON 51467	79-99%
15	<b>This work</b>	DUT-5-CoH MOF	<b>0.375 mmol amine, CO<sub>2</sub> (10 bar), H<sub>2</sub> (10 bar), Phenylsilane (0.862 mmol), 0.5 mol% Catalyst, 25-100° C, 20 h, THF</b>	<b>TON 4738</b>	<b>35-100%</b>

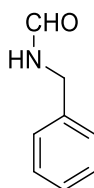
## 7. Characterization of the products.

### *N*-(4-methoxybenzyl)formamide<sup>3</sup>



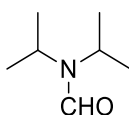
*N*-(4-methoxybenzyl)formamide was synthesized in 100% yield with 90% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), *p*-methoxy benzylamine (49  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.21 (s, 1 H), 7.16–7.28 (m, 2 H), 6.85–6.91 (m, 2 H), 6.05 (br, 1 H), 4.40 (d, <sup>3</sup>*J*<sub>H-H</sub> = 5.61 Hz, 2 H), 3.80 (s, 3 H).

### *N*-benzylformamide<sup>4</sup>



*N*-benzylformamide was synthesized in 100% yield with 85% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), benzylamine (41  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.19 (s, 1 H), 7.29-7.19 (m, 5 H), 5.85 (br, 1 H), 4.42 (d, <sup>3</sup>*J*<sub>H-H</sub> = 6.0 Hz, 2 H).

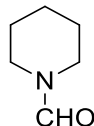
### *N,N*-diisopropylformamide<sup>5</sup>



*N,N*-diisopropylformamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), diisopropylamine (53  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h.

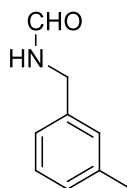
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.59 (s, 1 H), 3.33-3.27 (m, 2 H), 1.33 (d,  $^3J_{\text{H-H}} = 8.0$  Hz, 12 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 46.1, 18.7.

#### Piperidine-1-carbaldehyde<sup>4</sup>



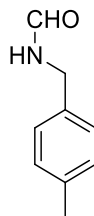
piperidine-1-carbaldehyde was synthesized in 100% yield with 81% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), piperidine (37  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.87 (s, 1 H), 3.35 (t,  $^3J_{\text{H-H}} = 5.0$  Hz, 2 H), 3.19 (t,  $^3J_{\text{H-H}} = 5.0$  Hz, 2 H), 1.59-1.54 (m, 2 H), 1.48-1.39 (m, 4 H).

#### *N*-(3-methylbenzyl)formamide<sup>6</sup>



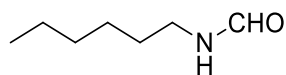
*N*-(3-methylbenzyl)formamide was synthesized in 100% yield with 80% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), 3-methyl benzylamine (46  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.20 (d,  $^3J_{\text{H-H}} = 11.9$  Hz, 1 H), 7.07-7.32 (m, 4 H), 5.98 (br, 1 H), 4.48 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2 H), 2.38 (s, 3 H).

#### *N*-(4-methylbenzyl)formamide<sup>6</sup>



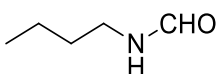
*N*-(4-methylbenzyl)formamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), 4-methyl benzylamine (46  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.13 (d,  $^3J_{\text{H-H}} = 12$  Hz, 1 H), 7.12-7.18 (m, 4 H), 6.10 (br, 1 H), 4.41 (d,  $^3J_{\text{H-H}} = 6.2$  Hz, 2 H), 2.34 (s, 3 H).

### ***N*-hexylformamide<sup>4</sup>**



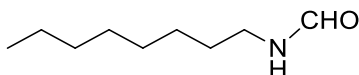
*N*-hexylformamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), hexylamine (49  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h in 3 ml THF. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.14 (d, <sup>3</sup>*J*<sub>H-H</sub> = 12.0 Hz, 1 H), 5.79 (s, 1 H), 3.29-3.24 (m, 2 H), 1.52-1.49 (m, 2 H), 1.32-1.28 (m, 6 H), 0.88-0.85 (m, 3 H).

### ***N*-butylformamide<sup>7</sup>**



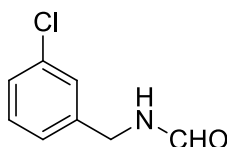
*N*-butylformamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), butylamine (37  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h in 3 ml THF. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.05 (d, 1 H), 6.74 (s, 1 H), 3.15 (m, 2 H), 1.41 (q, 2 H), 1.26 (h, 2 H), 0.83 (t, 3 H).

### ***N*-octylformamide<sup>7</sup>**



*N*-octylformamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), octylamine (62  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm):  $\delta$  8.24–7.94 (m, 1 H), 5.79 (d, 1 H), 3.23 (dd, 2 H), 1.27 (d, 10 H), 0.94–0.76 (m, 3 H).

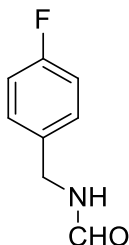
### ***N*-(3-chlorobenzyl)formamide<sup>6</sup>**



*N*-(3-chlorobenzyl)formamide was synthesized in 85% yield with 76% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), *m*-chloro benzylamine (46  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 100 °C for 20

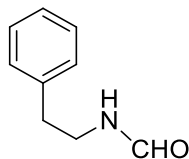
h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.10 (d,  $^3J_{\text{H-H}} = 11.8$  Hz, 1 H), 7.09-7.20 (m, 4 H), 5.97 (br, 1 H), 4.39 (d,  $^3J_{\text{H-H}} = 6.2$  Hz, 2 H).

### ***N*-(4-fluorobenzyl)formamide<sup>3</sup>**



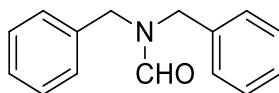
*N*-(4-fluorobenzyl)formamide was synthesized in 60% yield with 42% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), *p*-fluoro benzylamine (43  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 100  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.10 (s, 1 H), 7.09–7.14 (m, 2 H), 6.85–6.94 (m, 2 H), 05.98 (br, 1 H), 4.30 (d,  $^3J_{\text{H-H}} = 6.0$  Hz, 2 H).

### ***N*-phenethylformamide<sup>8</sup>**



*N*-phenethylformamide was synthesized in 100% yield with 75% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), phenethylamine (47  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ (ppm): 8.09 (d,  $^3J_{\text{H-H}} = 1.7$  Hz, 1 H), 7.33-7.27 (m, 2 H), 7.27-7.16 (m, 3 H), 5.87 (br, 1 H), 3.58-3.53 (m, 2 H), 2.88-2.79 (m, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta$ (ppm): 161.2, 138.4, 128.7, 128.6, 126.6, 39.1, 35.4.

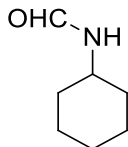
### ***N,N*-dibenzylformamide<sup>8</sup>**



*N,N*-dibenzylformamide was synthesized in 100% yield with 75% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), dibenzylamine (41  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 27 h.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ (ppm): 8.42 (s, 1 H), 7.40-7.29 (m, 6 H), 7.21-7.16 (m, 4 H), 4.42 (s,

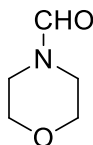
2 H), 4.26 (s, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz),  $\delta(\text{ppm})$ : 162.8, 135.9, 135.5, 128.8, 128.6, 128.4, 128.1, 127.6, 127.6, 50.2, 44.6.

#### ***N*-cyclohexylformamide<sup>7</sup>**



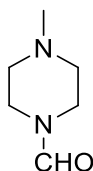
*N*-cyclohexylformamide was synthesized in 100% yield with 81% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), cyclohexylamine (43  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta(\text{ppm})$ : 8.05 (d, 1 H), 6.17 (d, 1 H), 3.99–3.01 (m, 1 H), 1.99–1.44 (m, 5 H), 1.44–1.03 (m, 5 H).

#### **Morpholine-4-carbaldehyde<sup>4</sup>**



morpholine-4-carbaldehyde was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), morpholine (32  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta(\text{ppm})$ : 7.84 (s, 1 H), 3.49 (t,  $^3J_{\text{H-H}} = 4.8$  Hz, 2 H), 3.44 (t,  $^3J_{\text{H-H}} = 4.8$  Hz, 2 H), 3.35 (t,  $^3J_{\text{H-H}} = 4.8$  Hz, 2 H), 3.21 (t,  $^3J_{\text{H-H}} = 4.8$  Hz, 2 H).

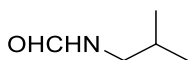
#### **4-Methylpiperazine-1-carbaldehyde<sup>7</sup>**



4-methylpiperazine-1-carbaldehyde was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), 1-methylpiperazine (42  $\mu\text{L}$ , 0.375 mmol), 106  $\mu\text{L}$  Phenyl silane and 10 bar  $\text{CO}_2$  at 25  $^\circ\text{C}$  for 20 h.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta(\text{ppm})$ : 8.00 (s, 1 H), 3.55 (t, 2 H), 3.44 – 3.32 (m, 2 H), 2.37 (dt, 4 H), 2.30 (s, 3 H).

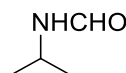


### ***N*-isobutylformamide**



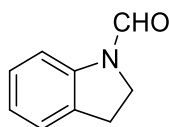
*N*-isobutylformamide was synthesized in 100% yield with 92% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), isobutylamine (37  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm):

### ***N*-isopropylformamide**



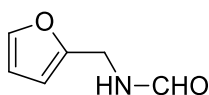
*N*-isopropylformamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), isopropylamine (31  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm):

### **Indoline-1-carbaldehyde<sup>9</sup>**



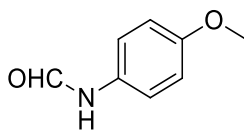
indoline-1-carbaldehyde was synthesized in 75% yield with 62% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), indoline (42  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 100 °C for 20 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 8.94 (s, 1 H), 7.04-7.26 (m, 4 H), 4.07 (t, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, 2 H), 3.16 (t, <sup>3</sup>J<sub>H-H</sub> = 8.5 Hz, 2 H)

### ***N*-(furan-2-ylmethyl)formamide<sup>10</sup>**



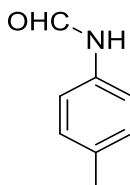
*N*-(furan-2-ylmethyl)formamide was synthesized in 100% yield with 71% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), furfurylamine (30  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 100 °C for 20 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 8.12 (s, 1 H), 7.31 (m, 1 H), 6.25 (m, 3 H), 4.45 (s, 1 H), 4.28 (s, 1 H).

### ***N*-(4-methoxyphenyl)formamide<sup>3</sup>**



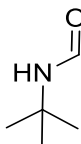
*N*-(4-methoxyphenyl)formamide was synthesized in 100% yield with 99% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), *p*-anisidine (43  $\mu$ L, 0.375 mmol), 10 bar H<sub>2</sub> and 10 bar CO<sub>2</sub> at 100 °C for 40 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 10.04 (br, 1 H), 8.19 (d, <sup>3</sup>*J*<sub>H-H</sub> = 1.95 Hz, 1 H), 7.50 (d, <sup>3</sup>*J*<sub>H-H</sub> = 9.03 Hz, 2 H), 6.88 (d, <sup>3</sup>*J*<sub>H-H</sub> = 9.06 Hz, 2 H), 3.71 (s, 3 H)

### ***N*-*p*-tolylformamide<sup>3</sup>**



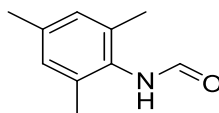
*N*-*p*-tolylformamide was synthesized in 100% conversion with 72% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), *p*-toluidine (41  $\mu$ L, 0.375 mmol), 10 bar H<sub>2</sub> and 10 bar CO<sub>2</sub> at 100 °C for 40 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 8.55 (d, <sup>3</sup>*J*<sub>H-H</sub> = 11.4 Hz, 1 H), 8.07 (br, 1 H), 7.35 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.4 Hz, 2 H), 6.91 (d, <sup>3</sup>*J*<sub>H-H</sub> = 8.3 Hz, 2 H), 2.26 (s, 3 H).

### ***N*-*tert*-butylformamide.<sup>11</sup>**



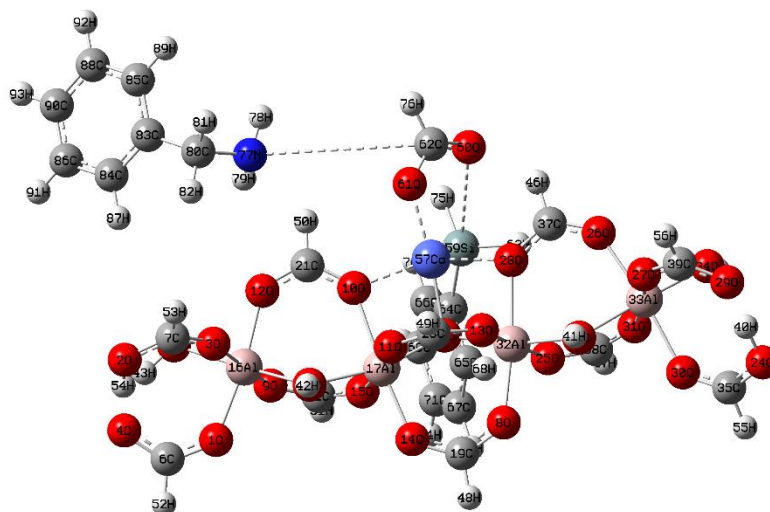
*N*-*tert*-butylformamide was synthesized in 100% yield with 87% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), 2-methylpropan-2-amine (39  $\mu$ L, 0.375 mmol), 106  $\mu$ L Phenyl silane and 10 bar CO<sub>2</sub> at 25 °C for 20 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 8.24 (d, 1 H, <sup>3</sup>*J*<sub>H-H</sub> = 12.4 Hz), 7.51 (brs, 1 H), 1.37 (s, 9 H).

### ***N*-Formyl-2,4,6-trimethylaniline.<sup>12</sup>**



*N*-Formyl-2,4,6-trimethylaniline was synthesized in 100% yield with 40% selectivity according to the general procedure for the *N*-formylation of amines using DUT-5-CoH (0.5 mol% of Co), 2,4,6-trimethylaniline (52  $\mu$ L, 0.375 mmol), 10 bar H<sub>2</sub> and 10 bar CO<sub>2</sub> at 100 °C for 40 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ (ppm): 8.39–8.03 (m, 1 H, CHO), 7.26–6.91 (m, 2H), 6.75 (broad s, 1 H, NH), 2.29–2.21 (m, 9H); 8.39–8.03 (m, 1 H), 7.26–6.91 (m, 2 H), 6.75 (broad s, 1 H), 2.29–2.21 (m, 9 H).





**TS-2**

**Figure S10.** DFT-optimized structures of intermediates and transition states of the catalytic cycle in the proposed DUT-5-Co-catalyzed N-formylation of benzylamine.

**Cartesian coordinates of DUT-5-CoH**

S.No.	Atoms	X	Y	Z
1	O	23.319438	12.268251	17.495488
2	O	20.453957	10.982861	19.188515
3	O	21.168411	13.120943	19.041482
4	O	22.064300	10.436492	17.187536
5	O	20.877464	12.655697	16.361554
6	C	23.165787	11.019724	17.328150
7	C	20.530048	12.211665	19.578564
8	O	26.283710	18.351115	19.347890
9	O	22.940871	14.333228	15.828435
10	O	21.749063	17.001247	17.684796
11	O	23.210770	16.710230	20.169471
12	O	20.723885	15.059633	17.251512
13	O	23.900483	18.782372	20.731556
14	O	25.580014	16.273207	18.786077
15	O	24.190005	16.106385	16.433502
16	Al	22.119407	13.747129	17.424833
17	Al	23.756035	16.563609	18.269648
18	O	23.877033	18.309594	18.028682
19	C	26.442759	17.119114	19.156911
20	O	23.195984	14.781673	18.515061
21	C	20.736276	16.310896	17.386579
22	C	23.795752	15.244508	15.619519
23	C	23.358361	17.675580	20.970943
24	O	27.935769	24.303806	21.763422
25	O	25.635252	20.346411	17.570777
26	O	23.297511	22.621092	19.498421
27	O	24.699633	22.730863	21.830642
28	O	22.991093	20.570517	18.645541
29	O	25.805888	24.267225	23.059383
30	O	27.249472	22.676728	20.355817
31	O	25.734577	22.533638	18.109242
32	Al	24.738284	19.494970	19.041395
33	Al	25.236869	22.745796	19.994282
34	O	25.258679	24.519309	19.862523
35	C	28.103687	23.423624	20.840330
36	O	25.301822	20.855218	20.168215
37	C	22.589811	21.732296	18.998648
38	C	25.926128	21.552132	17.351781
39	C	24.879604	23.466704	22.852322
40	H	26.976457	24.295734	22.187709
41	H	25.148591	20.625990	21.091087
42	H	23.081634	14.612428	19.456998
43	H	21.111071	11.704591	16.301894
44	H	20.530773	12.981870	15.522935
45	H	25.530449	24.827564	18.995656
46	H	21.527252	21.939069	18.827343
47	H	26.391906	21.765425	16.380472
48	H	27.449404	16.724162	19.341415
49	H	22.968858	17.525479	21.986593
50	H	19.796321	16.848038	17.229513
51	H	24.223886	15.276346	14.611383
52	H	24.087635	10.424315	17.309205
53	H	19.955147	12.410631	20.484634
54	H	21.025177	10.782203	18.380883

55	H	29.138128	23.362732	20.484876
56	H	24.119401	23.354408	23.641962
57	Co	22.042075	18.977837	17.911091
58	H	20.746920	19.532208	17.527887

61	O	19.855565	20.223887	16.281016
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**Cartesian coordinates of DUT-5-Co(OCHO)  
(INT-1)**

**Cartesian coordinates of TS-1**

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.252696	12.293904	17.449888
2	O	20.429230	10.957190	19.173820
3	O	21.141240	13.098544	19.072277
4	O	21.983441	10.476912	17.114935
5	O	20.785088	12.723862	16.385315
6	C	23.090359	11.051547	17.245786
7	C	20.516848	12.172941	19.598747
8	O	26.287394	18.326934	19.416129
9	O	22.836847	14.416298	15.866088
10	O	21.723303	17.022023	17.724160
11	O	23.243293	16.669553	20.239707
12	O	20.653804	15.095601	17.366504
13	O	23.907817	18.753336	20.792527
14	O	25.606559	16.242407	18.849481
15	O	24.198395	16.089919	16.506593
16	Al	22.053555	13.772698	17.457651
17	Al	23.789506	16.518356	18.344479
18	O	23.870185	18.265510	18.112788
19	C	26.460926	17.097544	19.223450
20	O	23.159226	14.767155	18.563942
21	C	20.680698	16.345223	17.490199
22	C	23.733156	15.288940	15.667336
23	C	23.385796	17.638452	21.039013
24	O	27.838697	24.365984	21.738886
25	O	25.625918	20.292869	17.624538
26	O	23.232047	22.581185	19.469857
27	O	24.618208	22.752770	21.814473
28	O	22.958118	20.507638	18.674666
29	O	25.700854	24.320848	23.023102
30	O	27.179264	22.706356	20.357359
31	O	25.674425	22.494045	18.108260
32	Al	24.743049	19.463467	19.104223
33	Al	25.173677	22.742716	19.984499
34	O	25.167419	24.512487	19.818848
35	C	28.021397	23.475207	20.829312
36	O	25.261198	20.853984	20.205322
37	C	22.537121	21.679215	18.982413
38	C	25.887502	21.499021	17.373802
39	C	24.783282	23.508856	22.824303
40	H	26.878567	24.350251	22.160205
41	H	25.100075	20.647125	21.132246
42	H	23.037121	14.585394	19.502914
43	H	21.013622	11.774121	16.291805
44	H	20.426713	13.076438	15.562278
45	H	25.412174	24.808572	18.939752
46	H	21.477813	21.871176	18.780111
47	H	26.345687	21.698435	16.396463
48	H	27.470644	16.712288	19.407930
49	H	23.009525	17.483449	22.058546
50	H	19.739486	16.892179	17.383918
51	H	24.131472	15.345553	14.648652
52	H	24.009364	10.454917	17.183380
53	H	19.966630	12.344915	20.525346
54	H	20.978574	10.780718	18.345370
55	H	29.056289	23.426095	20.473801
56	H	24.018019	23.403794	23.609904
57	Co	22.051687	18.909856	18.050397
58	H	20.704478	19.387119	18.004058
59	O	22.064411	19.513165	16.330255
60	C	20.956318	19.866766	16.322221
1	O	23.319438	12.268251	17.495488
2	O	20.453957	10.982861	19.188515
3	O	21.168411	13.120943	19.041482
4	O	22.064300	10.436492	17.187536
5	O	20.877464	12.655697	16.361554
6	C	23.165787	11.019724	17.328150
7	C	20.530048	12.211665	19.578564
8	O	26.283710	18.351115	19.347890
9	O	22.940871	14.333228	15.828435
10	O	21.749063	17.001247	17.684796
11	O	23.210770	16.710230	20.169471
12	O	20.723885	15.059633	17.251512
13	O	23.900483	18.782372	20.731556
14	O	25.580014	16.273207	18.786077
15	O	24.190005	16.106385	16.433502
16	Al	22.119407	13.747129	17.424833
17	Al	23.756035	16.563609	18.269648
18	O	23.877033	18.309594	18.028682
19	C	26.442759	17.119114	19.156911
20	O	23.195984	14.781673	18.515061
21	C	20.736276	16.310896	17.386579
22	C	23.795752	15.244508	15.619519
23	C	23.358361	17.675580	20.970943
24	O	27.935769	24.303806	21.763422
25	O	25.635252	20.346411	17.570777
26	O	23.297511	22.621092	19.498421
27	O	24.699633	22.730863	21.830642
28	O	22.991093	20.570517	18.645541
29	O	25.805888	24.267225	23.059383
30	O	27.249472	22.676728	20.355817
31	O	25.734577	22.533638	18.109242
32	Al	24.738284	19.494970	19.041395
33	Al	25.236869	22.745796	19.994282
34	O	25.258679	24.519309	19.862523
35	C	28.103687	23.423624	20.840330
36	O	25.301822	20.855218	20.168215
37	C	22.589811	21.732296	18.998648
38	C	25.926128	21.552132	17.351781
39	C	24.879604	23.466704	22.852322
40	H	26.976457	24.295734	22.187709
41	H	25.148591	20.625990	21.091087
42	H	23.081634	14.612428	19.456998
43	H	21.111071	11.704591	16.301894
44	H	20.530773	12.981870	15.522935
45	H	25.530449	24.827564	18.995656
46	H	21.527252	21.939069	18.827343
47	H	26.391906	21.765425	16.380472
48	H	27.449404	16.724162	19.341415
49	H	22.968858	17.525479	21.986593
50	H	19.796321	16.848038	17.229513
51	H	24.223886	15.276346	14.611383
52	H	24.087635	10.424315	17.309205
53	H	19.955147	12.410631	20.484634
54	H	21.025177	10.782203	18.380883
55	H	29.138128	23.362732	20.484876
56	H	24.119401	23.354408	23.641962
57	Co	22.042075	18.977837	17.911091
58	O	20.427566	19.668903	17.433398
59	C	20.535682	20.062968	16.037890
60	H	21.358407	20.054109	15.353826
61	O	19.241962	20.481239	15.594903

## Cartesian coordinates of INT-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.373595	12.576824	16.879202
2	O	20.805526	10.929117	18.764209
3	O	21.408686	13.104699	18.788057
4	O	22.169977	10.717338	16.534477
5	O	20.772597	12.934467	16.137071
6	C	23.253258	11.345834	16.590473
7	C	20.879357	12.106397	19.286657
8	O	26.256762	18.622088	18.990952
9	O	22.645816	14.794895	15.553734
10	O	21.627569	17.152737	17.760958
11	O	23.414097	16.716608	20.034613
12	O	20.626657	15.199607	17.347810
13	O	24.075761	18.766177	20.706929
14	O	25.595871	16.563769	18.329748
15	O	23.922284	16.538216	16.182422
16	Al	22.101062	13.960472	17.156849
17	Al	23.718025	16.757614	18.085363
18	O	23.681179	18.540968	18.026883
19	C	26.457458	17.426322	18.664874
20	O	23.263623	14.942251	18.213469
21	C	20.601248	16.429098	17.585758
22	C	23.434721	15.761139	15.333053
23	C	23.623364	17.611828	20.903000
24	O	27.864724	24.446188	21.784637
25	O	25.279899	20.706187	17.524917
26	O	23.105756	22.666140	19.892549
27	O	24.762920	22.669673	22.056202
28	O	22.800940	20.673675	18.917214
29	O	25.889763	24.192272	23.280306
30	O	27.128653	22.887275	20.326083
31	O	25.376263	22.838125	18.250526
32	Al	24.645126	19.697793	19.014079
33	Al	25.104046	22.875284	20.187317
34	O	25.004454	24.648115	20.207303
35	C	27.987315	23.647033	20.785906
36	O	25.265295	20.979519	20.186610
37	C	22.384239	21.785971	19.410103
38	C	25.499455	21.938969	17.384810
39	C	25.001068	23.342940	23.109609
40	H	26.953906	24.351329	22.299342
41	H	25.232757	20.668108	21.097680
42	H	23.288939	14.663446	19.135883
43	H	21.037893	12.012200	15.933108
44	H	20.310420	13.333124	15.390168
45	H	25.110621	25.043940	19.339942
46	H	21.300364	21.940922	19.382294
47	H	25.826697	22.257824	16.387055
48	H	27.498096	17.082394	18.679039
49	H	23.380417	17.345246	21.939694
50	H	19.626105	16.920300	17.642506
51	H	23.705605	15.933488	14.286365
52	H	24.188581	10.813472	16.376160
53	H	20.415562	12.171118	20.272150
54	H	21.279371	10.855699	17.875310
55	H	28.984062	23.668404	20.332657
56	H	24.338572	23.119762	23.960855
57	Co	21.884630	19.093362	18.149864
58	H	21.757771	19.615025	16.308225
59	Si	21.072569	20.201060	15.163544
60	O	19.382387	20.396278	16.605098
61	O	20.087971	19.522681	18.630921
62	C	19.160262	20.062956	17.922164
63	H	18.213948	20.191913	18.480319
64	H	20.814387	21.645215	15.333845
65	C	22.479943	20.033359	13.910195
66	C	23.551555	20.942095	13.892354
67	C	22.490501	18.993623	12.967805
68	C	24.595174	20.812633	12.978446
69	H	23.567756	21.768608	14.596210

70	C	23.531707	18.857955	12.048993
71	H	21.669511	18.282988	12.941354
72	C	24.588034	19.766899	12.054961
73	H	25.411814	21.526250	12.983077
74	H	23.514830	18.049310	11.326282
75	H	25.398893	19.665210	11.342288
76	H	19.952548	19.387964	14.645674

## Cartesian coordinates of TS-2

S.No.	Atoms	Coordinates (Angstroms)		
		X	Y	Z
1	O	23.373595	12.576824	16.879202
2	O	20.805526	10.929117	18.764209
3	O	21.408686	13.104699	18.788057
4	O	22.169977	10.717338	16.534477
5	O	20.772597	12.934467	16.137071
6	C	23.253258	11.345834	16.590473
7	C	20.879357	12.106397	19.286657
8	O	26.256762	18.622088	18.990952
9	O	22.645816	14.794895	15.553734
10	O	21.627569	17.152737	17.760958
11	O	23.414097	16.716608	20.034613
12	O	20.626657	15.199607	17.347810
13	O	24.075761	18.766177	20.706929
14	O	25.595871	16.563769	18.329748
15	O	23.922284	16.538216	16.182422
16	Al	22.101062	13.960472	17.156849
17	Al	23.718025	16.757614	18.085363
18	O	23.681179	18.540968	18.026883
19	C	26.457458	17.426322	18.664874
20	O	23.263623	14.942251	18.213469
21	C	20.601248	16.429098	17.585758
22	C	23.434721	15.761139	15.333053
23	C	23.623364	17.611828	20.903000
24	O	27.864724	24.446188	21.784637
25	O	25.279899	20.706187	17.524917
26	O	23.105756	22.666140	19.892549
27	O	24.762920	22.669673	22.056202
28	O	22.800940	20.673675	18.917214
29	O	25.889763	24.192272	23.280306
30	O	27.128653	22.887275	20.326083
31	O	25.376263	22.838125	18.250526
32	Al	24.645126	19.697793	19.014079
33	Al	25.104046	22.875284	20.187317
34	O	25.004454	24.648115	20.207303
35	C	27.987315	23.647033	20.785906
36	O	25.265295	20.979519	20.186610
37	C	22.384239	21.785971	19.410103
38	C	25.499455	21.938969	17.384810
39	C	25.001068	23.342940	23.109609
40	H	26.953906	24.351329	22.299342
41	H	25.232757	20.668108	21.097680
42	H	23.288939	14.663446	19.135883
43	H	21.037893	12.012200	15.933108
44	H	20.310420	13.333124	15.390168
45	H	25.110621	25.043940	19.339942
46	H	21.300364	21.940922	19.382294
47	H	25.826697	22.257824	16.387055
48	H	27.498096	17.082394	18.679039
49	H	23.380417	17.345246	21.939694
50	H	19.626105	16.920300	17.642506
51	H	23.705605	15.933488	14.286365
52	H	24.188581	10.813472	16.376160
53	H	20.415562	12.171118	20.272150
54	H	21.279371	10.855699	17.875310
55	H	28.984062	23.668404	20.332657
56	H	24.338572	23.119762	23.960855
57	Co	21.884630	19.093362	18.149864
58	H	21.757771	19.615025	16.308225
59	Si	21.072569	20.201060	15.163544
60	O	19.382387	20.396278	16.605098
61	O	20.087971	19.522681	18.630921
62	C	19.160262	20.062956	17.922164
63	H	18.213948	20.191913	18.480319
64	H	20.814387	21.645215	15.333845
65	C	22.479943	20.033359	13.910195
66	C	23.551555	20.942095	13.892354
67	C	22.490501	18.993623	12.967805
68	C	24.595174	20.812633	12.978446
69	H	23.567756	21.768608	14.596210
70	C	23.531707	18.857955	12.048993
71	H	21.669511	18.282988	12.941354
72	C	24.588034	19.766899	12.054961
73	H	25.411814	21.526250	12.983077
74	H	23.514830	18.049310	11.326282
75	H	25.398893	19.665210	11.342288
76	H	19.952548	19.387964	14.645674

61	O	20.087971	19.522681	18.630921	79	H	18.319000	18.216297	17.770415
62	C	19.160262	20.062956	17.922164	80	C	17.279235	19.256560	19.176701
63	H	20.624904	21.667101	15.495454	81	H	17.283975	20.273162	19.510463
64	C	22.290461	20.055245	14.071804	82	H	17.757297	18.638841	19.907987
65	C	23.362073	20.963980	14.053963	83	C	15.825623	18.787682	18.979807
66	C	22.301019	19.015509	13.129414	84	C	15.299575	17.785192	19.795135
67	C	24.405692	20.834519	13.140055	85	C	15.034907	19.365266	17.986473
68	H	23.378274	21.790493	14.757819	86	C	13.983310	17.359973	19.616654
69	C	23.342224	18.879840	12.210602	87	H	15.923460	17.329499	20.577664
70	H	21.480029	18.304874	13.102963	88	C	13.717911	18.940720	17.808456
71	C	24.398551	19.788784	12.216570	89	H	15.449300	20.155521	17.343896
72	H	25.222332	21.548135	13.144686	90	C	13.192070	17.938144	18.623238
73	H	23.325348	18.071195	11.487891	91	H	13.568801	16.569366	20.258852
74	H	25.209411	19.687095	11.503897	92	H	13.094572	19.396589	17.025445
75	H	19.763066	19.409850	14.807283	93	H	12.154251	17.602751	18.482738
76	H	18.865841	20.978425	18.391349					
77	N	18.003486	19.156128	17.901446					
78	H	17.393736	19.410746	17.150864					

**9.1. X-ray absorption spectroscopic analysis.** X-ray Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India.<sup>18, 19</sup> All the measurements were performed at room temperature. This beamline operates in the energy range of 4 keV to 25 keV. The beamline optics consist of a Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si(111) based double crystal monochromator (DCM). The second crystal of the DCM is a sagittal cylindrical crystal which is used for horizontal focusing of the beam while another Rh/Pt coated bendable post mirror facing downward is used for vertical focusing of the beam at the sample position. Two ionization chambers (300 mm length each) have been used for data collection in transmission mode; one ionization chamber for measuring incident flux, second one for measuring transmitted flux. For energy calibration, standard metal foils were used. Appropriate gas pressure and gas mixture have been chosen so as to achieve 10-20% absorption in first ionization chamber and 70-90% absorption in second ionization chamber to obtain better signal-to-noise ratio. Pellets were made from powder samples for recording absorption spectra. Sample powder was mixed homogeneously with cellulose powder in appropriate proportion and pressed (2 Ton) into a 15 mm diameter disc. The amount of the sample was estimated such that to get reasonable edge jump at particular absorption edge of the element to be probed. Spectra were collected at the cobalt K-edge in transmission mode and were calibrated against the reference spectrum of metallic cobalt (7709 eV). Data were processed using Demeter software.<sup>20</sup> A metallic cobalt foil standard was used as a reference for energy calibration and was measured simultaneously with experimental samples.

**EXAFS fitting using DFT optimized structures.** The EXAFS spectrum of DUT-5-Co-OC(O)H were calibrated against the reference spectra and aligned to the first peak in the smoothed first derivative of the absorption spectrum, the background noise was removed, and the spectra were processed to obtain a normalized unit edge step. The fitting parameters of DUT-5-Co-OC(O)H are summarized in Table S5.

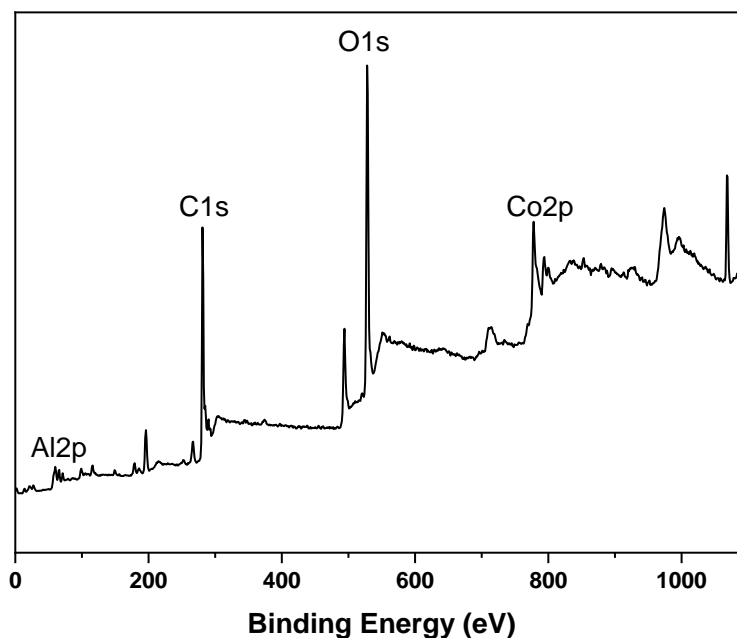
**Table S5. Summary of EXAFS fitting parameters of DUT-5-Co-OC(O)H.**

Sample	DUT-5-Co-OC(O)H	Fitting range	$k$ 2.7 – 11 Å <sup>-1</sup> $R$ 1 – 4 Å
<b>Independent points</b>	13	<b>R-factor</b>	0.012
<b>Variables</b>	6	$S_0^2$	1.00
<b>Reduced chi-square</b>	300	$\Delta E_0$ (eV)	-5.30±1.21
$R$ (Co-O18) (Å)	1.83±0.02	$\sigma^2$ (Co-O18) (Å <sup>2</sup> )	0.001±0.001
$R$ (Co-O28) (Å)	1.95±0.02	$\sigma^2$ (Co-O28) (Å <sup>2</sup> )	0.001±0.001
$R$ (Co-O10) (Å)	1.94±0.02	$\sigma^2$ (Co-O10) (Å <sup>2</sup> )	0.001±0.001
$R$ (Co-O58) (Å)	1.87±0.02	$\sigma^2$ (Co-O58) (Å <sup>2</sup> )	0.001±0.001
$R$ (Co-Al17) (Å)	2.93±0.04	$\sigma^2$ (Co-Al17) (Å <sup>2</sup> )	0.003±0.001
$R$ (Co-Al32) (Å)	2.94±0.04	$\sigma^2$ (Co-Al32) (Å <sup>2</sup> )	0.003±0.001
$R$ (Co-C29) (Å)	3.12±0.07	$\sigma^2$ (Co-C29) (Å <sup>2</sup> )	0.006±0.002
$R$ (Co-C23) (Å)	3.30±0.07	$\sigma^2$ (Co-C23) (Å <sup>2</sup> )	0.006±0.002
$R$ (Co-C59) (Å)	2.81±0.07	$\sigma^2$ (Co-C59) (Å <sup>2</sup> )	0.006±0.002



## 9.2. XPS analysis of DUT-5-Co-OC(O)H.

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.



**Figure S11.** XPS data of DUT-5-Co-OC(O)H.

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