Supporting Information

A Cu-Salen-based conjugated microporous polymer catalyst for *N*-formylation of CO_2 under mild conditions

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I. General information

Materials

Petroleum ether (AR), tetrahydrofuran (THF, AR), dichloromethane (CH_2Cl_2, AR), 3-Formyl-4-methoxyphenylboronic acid ($C_8H_9BO_4$, ≥98%), ethyl acetate（$C_4H_8O_2$, AR), tris(4-bromophenyl)amine (≥98%) and magnesium chloride（$MgCl_2$, AR）were purchased from Energy Chemical Co., Ltd. (Shanghai). Potassium carbonate (K_2CO_3, AR) and *N,N*-Dimethylformamide (DMF, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). Boron tribromide (BBr_3, ≥99%) and tetrakis(triphenylphosphine)palladium ($Pd[P(C_6H_5)_3]_4$, ≥99%) were purchased from InnoChem Science & Technology Co., Ltd. (Shanghai)

Instruments

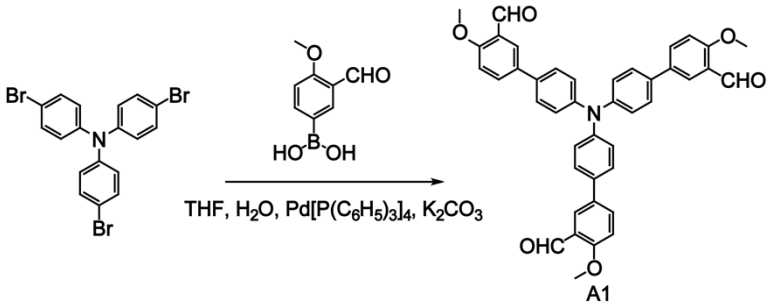
^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal reference. Fourier transform infrared spectroscopy (FT-IR) spectra were collected in a transmission mode on a VARIAN 1000 FT-IR (scimitar series) spectrometer using KBr disks. The nitrogen adsorption and desorption isotherms at 77 K were collected on an ASAP 2020 volumetric adsorption analyzer. The sample was degassed at 120 ℃ for 12 h under a vacuum before the analysis. The surface area was calculated by using the BET model range from 0.01 to 0.10 bar for the sample. The pore size distribution of the sample was calculated from nitrogen adsorption isotherm according to the Nonlocal Density Functional Theory (NLDFT) method by using a carbon slit pore model. A GC5890N gas chromatography (KEJIE) with a separation column (SE-30 capillary column, 30 m× 0.33 mm× 0.32 μm) and a flame ionization detector (FID) were used in this work. Morphological analysis of the catalyst was performed using a scanning electron microscope (SEM) from JEOL (JSM-7600F). The Chemical composition of the catalysts was determined using an X-ray Photoelectron Spectroscopy (XPS) spectrometer (Thermo Scientific K-Alpha).

II. Experimental Sections

Synthesis of A1

Tri-(4-bromophenyl)amine (405.8 mg, 0.84 mmol), 3-formyl-4-methoxybenzoboronic acid (500 mg, 2.8 mmol), 20 ml THF, and 5 ml K_2CO_3 solution (2 mol/L) were added in a clean three-necked flask of 50 ml. Then $Pd[P(C_6H_5)_3]_4$ (29.12 mg, 0.025 mmol) was quickly added under N_2 protection and the mixture was heated to 80 ℃ for 48 h. After cooling, the aqueous phase was extracted with CH_2Cl_2,

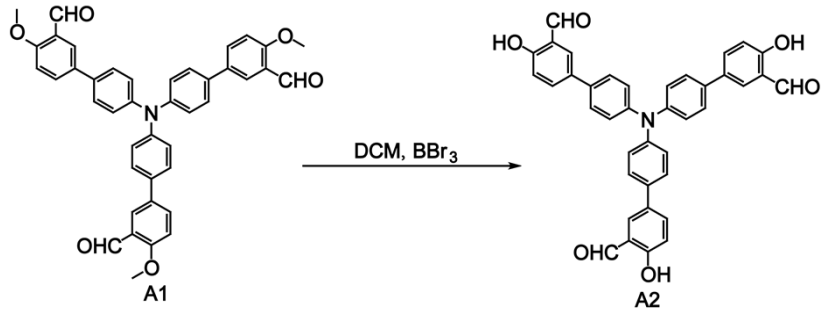
then the organic phase was dried with $MgCl_2$. The yellow crude product was obtained after filtration and rotary evaporation drying. The crude product was separated by a silica gel chromatography column (The eluent is petroleum ether: ethyl acetate = 1: 1), and the organic solvent was dried under rotary evaporation. The product was then dried in a vacuum oven at 80 ℃ for 12 h.



Scheme S1. The synthesis experiment of **A1**.

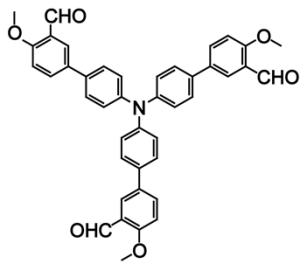
Synthesis of A2

In a 50 mL three-neck flask, monomer A1 (150 mg, 0.23 mmol) and 5 mL of CH_2Cl_2 were added. Under an ice bath, a CH_2Cl_2 solution (40 ml) containing BBr_3 (1.3 mL) was added dropwise to the system. After the addition was completed, the temperature was raised to room temperature and the reaction continued for 5 h. Then, under an ice bath, 20 mL of distilled water was added dropwise to the dichloromethane solution to quench the reaction and absorb the excess BBr_3. The organic layer was then extracted three times with CH_2Cl_2, washed with brine, and dried over anhydrous $MgCl_2$ for 4 h. The mixture was filtered and the organic solvent was dried under rotary evaporation to obtain a pale yellow crude product. The crude product was then purified by column chromatography using an eluent of petroleum ether: ethyl acetate = 4:1.



Scheme S2. The synthesis experiment of **A2**.

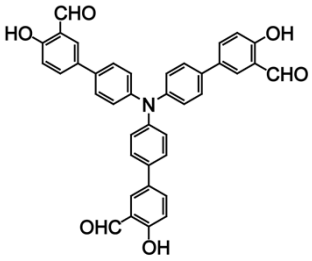
A1



Bright yellow solid (304.5 mg, yield: 56%, melting point: 233 ℃). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, Chloroform-d_3) δ 10.52 (s, 1H), 8.07 (d, J = 2.5 Hz, 1H), 7.79 (dd, J = 8.7, 2.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.20 (d, J

= 8.6 Hz, 2H), 7.07 (d, J = 8.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d_3) δ 189.80, 161.04, 146.72, 134.06, 133.90, 133.27, 127.53, 126.42, 124.93, 124.48, 112.18, 55.87.

A2



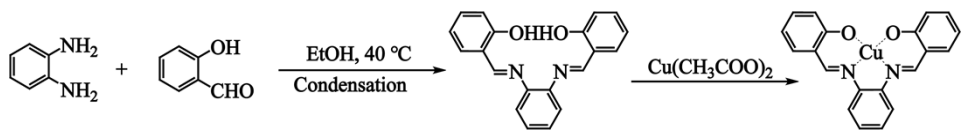
Pale yellow solid (126.32 mg, yield: 90%, melting point: 293.7 ℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.81 (s, 1H), 10.32 (s, 1H), 7.93 (d, J = 2.6 Hz, 1H), 7.86 (dd, J = 8.6, 2.5 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 192.06, 160.42, 146.49, 134.66, 134.01, 131.43, 127.70, 126.86, 124.68, 122.92, 118.43.

Refinement of o-phenylenediamine

In a clean 250 mL single-neck flask, 50 g of *o*-phenylenediamine and 100 mL of anhydrous ethanol were added. The mixture was heated to reflux at 80 ℃ for 4 h under nitrogen protection. Following heating, hot filtration was conducted to collect the white crystalline solid. This procedure was repeated twice. Subsequently, the product was dried in a vacuum oven at 50 ℃ for 12 h. Finally, 23 g of refined *o*-phenylenediamine was obtained with a recovery rate of 46%.

Synthesis of Cu-Salen

In a clean 100 ml three-neck flask, *o*-phenylenediamine (32.40 mg, 0.30 mmol) was dissolved in 25 mL of absolute ethyl alcohol (EtOH) at 40 ℃. Then, salicylaldehyde (60 μL, 0.60 mmol) was added into the solution of *o*-phenylenediamine. The mixed solution was refluxed with magnetically stirring at 40 °C for 4 h. After the reaction, the precipitates were separated by centrifugation and washed with EtOH for five times. The salen was obtained by being dried in a vacuum oven at 60 ℃ for 12 h. In a typical synthesis of M-Salen, 1 mL of methanol containing 20 mg of copper (II) acetate monohydrate was dropwisely added into 5 mL of methanol containing 32 mg of salen. After the above suspension was magnetically stirred for three days, the mixture was separated by centrifugation and washed with methanol for five times. Finally Cu-Salen was obtained by being dried under vacuum at 60 °C for overnight.



Scheme S3. The synthesis experiment of **Cu-Salen**.

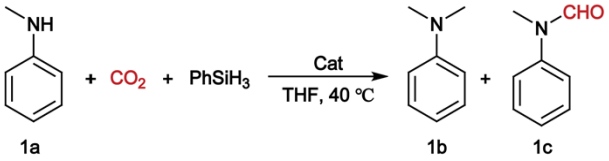
Synthesis of CMP@Cu-Salen

In a clean 50 mL three-neck flask, A2 (60 mg, 0.10 mmol), *o*-phenylenediamine

(16.08 mg, 0.15 mmol), and copper (II) acetate monohydrate (32.4 mg, 0.16 mmol) were added. Then 3 mL DMF was injected using a syringe under N_2 protection and the mixture was heated to 100 ℃ for 24 h. After the reaction, the filter cake was collected through a Büchner funnel and washed continuously with CH_2Cl_2, THF and DMF. The filter cake was further extracted using the Soxhlet extractor with THF for 48 h. The product was then dried in a vacuum oven at 80 ℃ for 12 h. Finally, 73.6 mg dark red solid powder was obtained, representing a 92% yield.

III. The catalytic performance of CMP@Cu-Salen

Table S1. Optimization of reaction conditions



Entry	Catalyst (mol%)	TBAB (mol%)	$PhSiH_3$ (mmol)	Conversion (%)	Selectivity (%)	
					1b	1c
1	0	5.0	0.75	25	23	65
2	5.0	0	0.75	34	15	73
3	5.0	2.5	0.75	52	10	40
4	5.0	5.0	0.75	99	8	90
5	5.0	7.5	0.75	99	13	74
6	5.0	5.0	0.25	73	21	61
7[a]	5.0	5.0	0.75	40	5	35
8[b]	5.0	5.0	0.75	87	68	16
9[c]	5.0	5.0	0.75	46	2	82

Reaction conditions: *N*-methylaniline (0.25 mmol), $PhSiH_3$ (0.75 mmol), CO_2 (0.1 MPa), THF solvent, 40 °C, 30 h. Conversion and selectivity were determined by GC using mesitylene as an internal standard. (a) Acetonitrile solvent. (b) Cu-Salen catalyst. (c) $NaBH_4$ as the reducing agent.

IV. Characterizations of products

NMR spectra

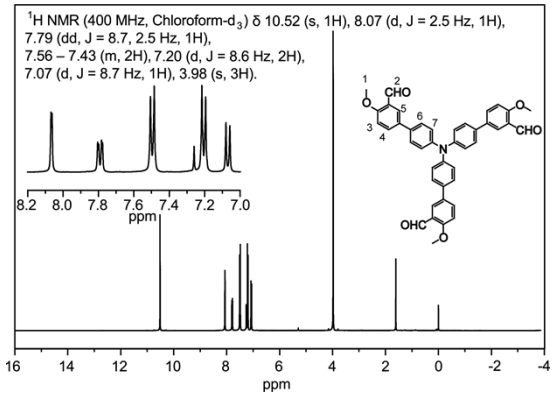


Figure S1. ^{1}H NMR spectrum of **A1** recorded at 298 K in Chloroform-d$_3$.

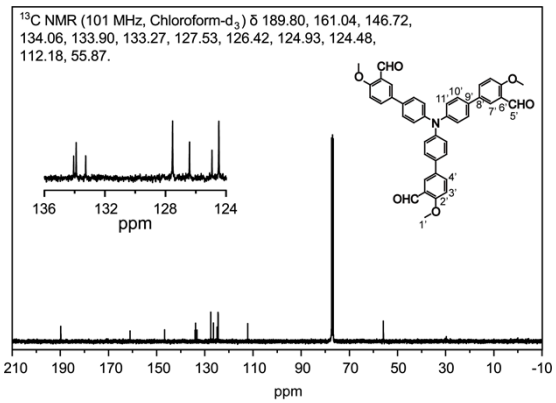


Figure S2. ^{13}C NMR spectrum of **A1** recorded at 298 K in Chloroform-d$_3$.

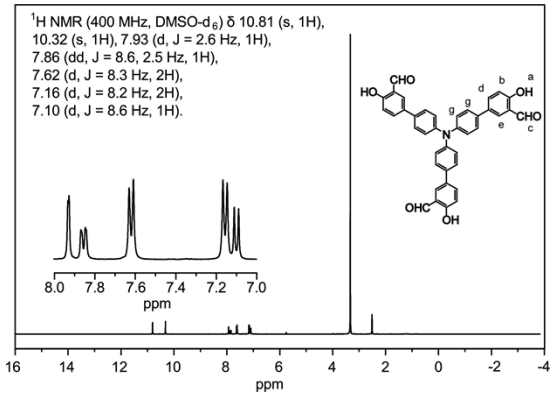


Figure S3. ^{1}H NMR spectrum of **A2** recorded at 298 K in DMSO-d$_6$.

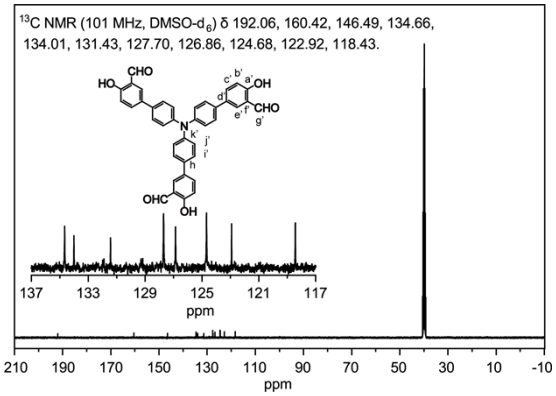


Figure S4. ^{13}C NMR spectrum of **A2** recorded at 298 K in DMSO-d_6.

FT-IR spectrum of monomer A1

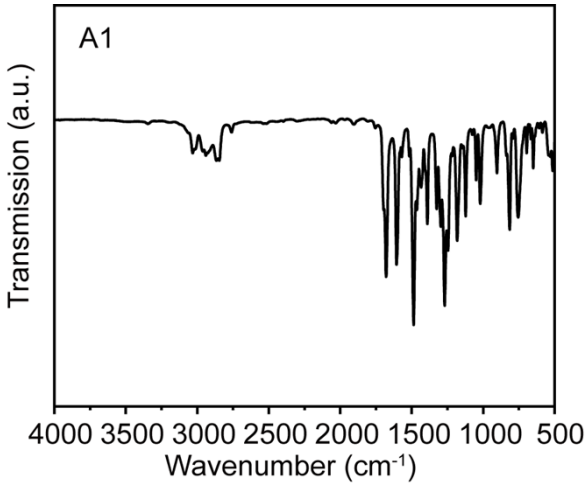


Figure S5. FT-IR spectrum of **A1**.

XPS spectra of CMP@Cu-Salen

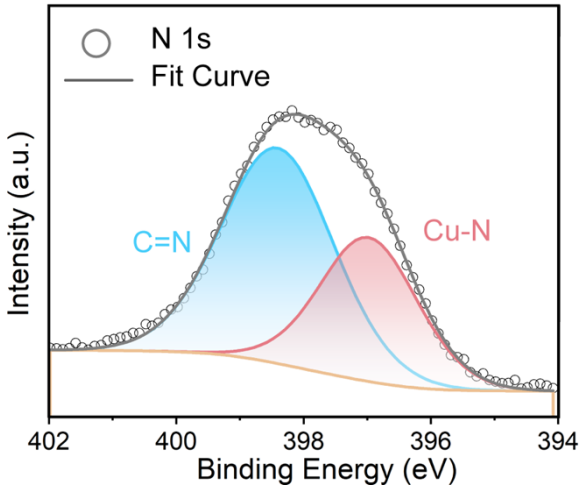


Figure S6. N 1s spectra of **CMP@Cu-Salen**.

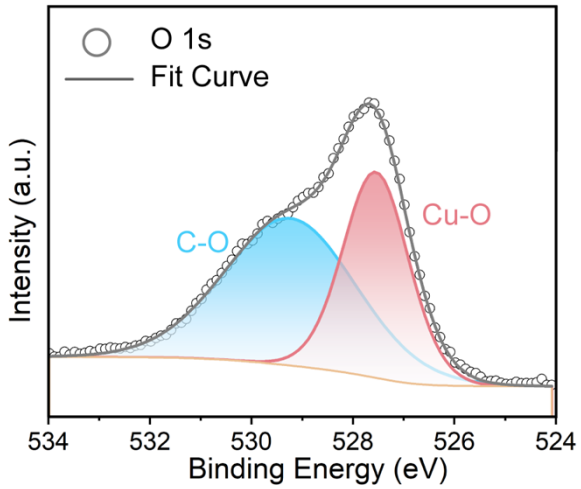


Figure S7. O 1s spectra of **CMP@Cu-Salen**.

SEM image of CMP@Cu-Salen

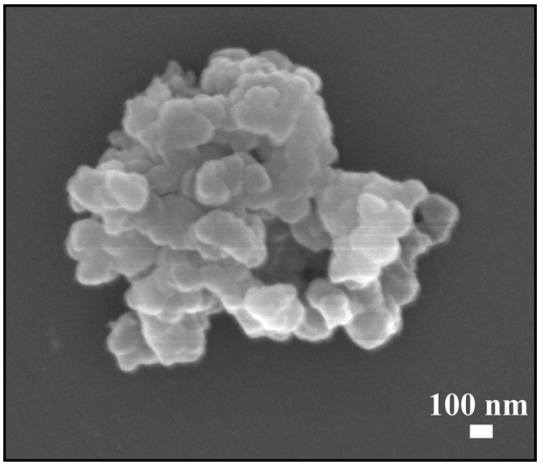


Figure S8. SEM image of **CMP@Cu-Salen**.

Characterizations of CMP@Cu-Salen after the catalytic process

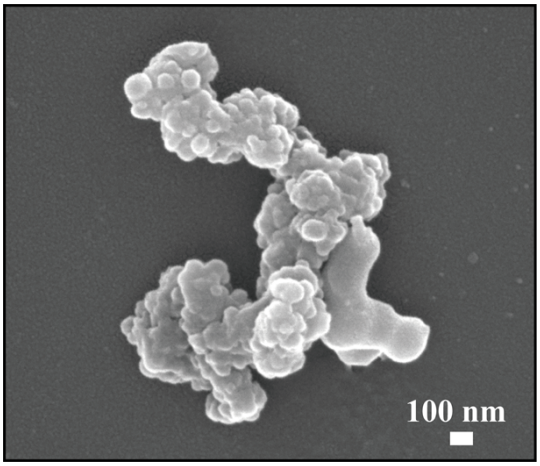


Figure S9. SEM image of **CMP@Cu-Salen** after the catalytic process.

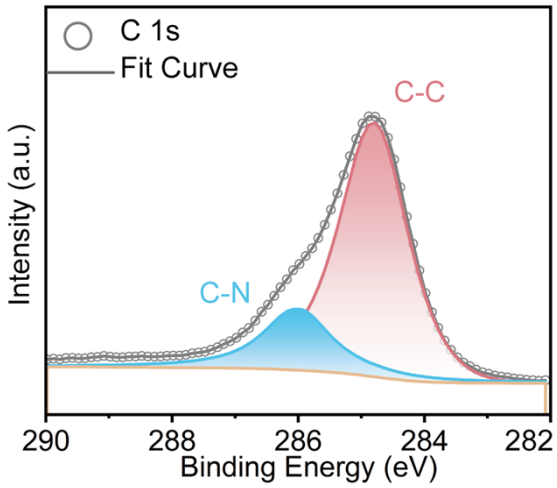


Figure S10. C 1s spectra of **CMP@Cu-Salen** after the catalytic process.

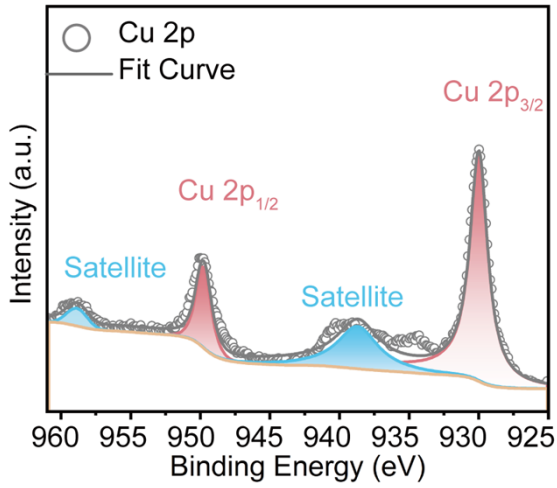
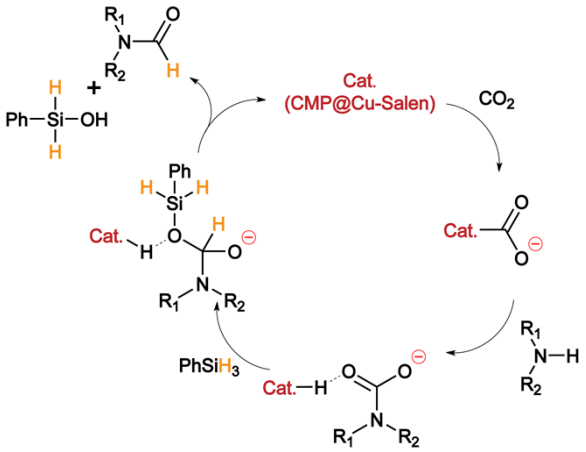


Figure S11. Cu 2p spectra of **CMP@Cu-Salen** after the catalytic process.

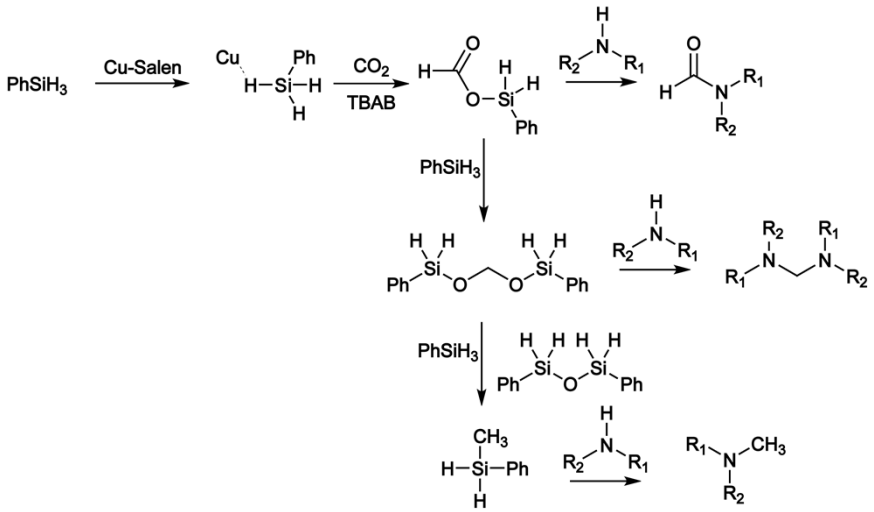
V. Proposed Reaction Mechanisms

CMP@Cu-Salen



Scheme S4. The mechanism of the *N*-formylation catalyzed by **CMP@Cu-Salen** involves the activation of CO_2.

Cu-Salen



Scheme S5. The mechanism of the *N*-formylation catalyzed by **Cu-Salen** involves the activation of the Si-H bond.