Supporting information for:

Copper-Catalyzed N-Formylation of Amines with CO$_2$ under Ambient Condition

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1 General information

1.1 Materials and Equipment information

All the reagents with purities of more than 99% were purchased and used as received from Energy Chemical and Beijing innoChem Science & Technology Co., Ltd. $^1$H and $^{13}$C Nuclear Magnetic Resonance (NMR) were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (400 MHz for $^1$H and 100 MHz for $^{13}$C) at ambient temperature in deuterated DMSO. The HRMS spectra were recorded on GTC Premier Spectrometer (WATERS) using EI ionization method. GC/MS analysis was conducted on Agilent 7890B GC + 5977 MSD.

1.2 Experiment Procedure

The preparation of the solution of catalyst: Cu(OAc)$_2$• 2H$_2$O (20.0 mg, 0.1 mmol) and dppe (47.8 mg, 1.2 mmol) were dissolved in 50 mL acetonitrile in a volumetric flask. The concentration of the catalyst was 2 mmol/L.

General reaction procedure: 500 μmL catalyst solution prepared above which contained 1 μmol Cu(OAc)$_2$• 2H$_2$O and 1.2 μmol dppe, was transferred to a 25 mL flask using a pipette. Acetonitrile was removed under vacuum. Then 1 mmol of substrate and 2 mL solvent (e.g. toluene) was added. The flask was connected with a balloon filled with CO$_2$ gas. The reaction was conducted under 25°C with stirring 700 rpm. The reaction mixture was analyzed by GC-MS and GC with biphenyl as an internal standard, or purified by flash column chromatography on silica gel to afford the desired product. The products were analyzed by $^1$H NMR, $^{13}$C NMR spectra and high resolution mass spectrometry (HRMS).

2 Mass spectra of formoxysilane
3 NMR data

**N-Phenylformamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.16 (s, 1H), 8.78 (d, $J = 11.0$ Hz, 0.26H), 8.28 (d, $J = 2.7$ Hz, 0.73H), 7.59 (d, $J = 7.7$ Hz, 1.49H), 7.31 (t, $J = 7.9$ Hz, 2.04H), 7.19 (d, $J = 7.7$ Hz, 0.53H), 7.09-7.05 (m, 1.02H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 162.93, 159.99, 138.80, 138.70, 129.83, 129.29, 124.08, 124.03, 119.62, 118.00. HRMS (EI): calculated for C$_7$H$_7$NO (M$^+$), 121.0528; found 121.0529.
**N-p-Tolylformamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.03 (d, $J = 23.3$ Hz, 1.03H), 8.70 (d, $J = 11.1$ Hz, 0.26H), 8.22 (s, 0.74H), 7.46 (d, $J = 8.3$ Hz, 1.67H), 7.12-7.06 (m, 2.72H), 2.24 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 162.87, 159.75, 136.21, 133.17, 132.98, 130.22, 129.65, 128.09, 119.59, 118.19, 20.90, 20.76. HRMS (EI): calculated for C$_8$H$_9$NO (M$^+$), 135.0684; found 135.0686.

**N-(4-Chlorophenyl)formamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.31 (m, 0.74H), 10.20 (d, $J = 10.5$ Hz, 0.22H), 8.78 (d, $J = 10.9$ Hz, 0.2H), 8.29 (s, 0.75H), 7.61 (d, $J = 8.8$ Hz, 1.69H), 7.36 (d, $J = 8.8$ Hz, 2.01H), 7.23-7.17(m, 0.54H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 162.95, 160.15, 137.88, 137.61, 129.68, 129.21, 127.95, 127.63, 121.19, 119.48. HRMS (EI): calculated for C$_7$H$_6$NOCl (M$^+$), 155.0138; found 155.0137.

**N-Mesitylformamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 9.32 (s, 0.82H), 9.15 (d, $J = 8.6$ Hz, 0.19H), 8.22 (s, 0.81H), 7.92 (d, $J = 11.6$ Hz, 0.18H), 6.92(s, 0.37H), 6.87(s, 1.67H), 2.21 (s, 3.04H), 2.16 (s, 1.16H), 2.10 (s,
5.03H. $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.13, 159.82, 136.37, 135.9, 135.24, 134.86, 131.83, 129.26, 128.72, 20.91, 19.11, 18.73, 18.62. HRMS (EI): calculated for C$_{10}$H$_{13}$NO (M$^+$), 163.0997; found 163.0999.

N-Benzylformamide. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.50 (s, 1H), 8.15 (s, 1.19H), 7.35–7.26 (m, 5.68H), 4.31 (d, J = 5.8 Hz, 2.29H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 165.36, 161.50, 140.09, 139.43, 128.89, 128.78, 127.75, 127.53, 127.50, 127.32, 45.03, 41.22. HRMS (EI): calculated for C$_8$H$_9$NO (M$^+$), 135.0684; found 135.0682.

N-Octylformamide. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.97 (s, 1.02H), 7.92 (s, J = 4.9 Hz, 0.72H), 7.65 (s, 0.20H), 3.09–3.03 (m, 2H), 1.37 (d, J = 9.5 Hz, 2.15H), 1.23 (s, 10.28H), 0.93–0.83 (m, 3.04H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 161.21, 37.51, 31.71, 31.38, 29.48, 29.13, 26.84, 22.54, 14.30. HRMS (EI): calculated for C$_9$H$_{19}$NO (M$^+$), 157.1467; found 157.1464.

N-Cyclohexylformamide. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.97 (d, J = 24.0 Hz, 2H), 3.63–3.56 (m, 0.83), 3.18 (m, 0.12H), 1.73–1.62 (m, 4.02H), 1.51 (d, J = 12.4 Hz, 1.01H), 1.30–1.05 (m, 5.07H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 163.67, 160.28, 50.68, 46.54, 34.62, 32.74, 25.61, 25.28, 25.00, 24.79. HRMS (EI): calculated for C$_7$H$_{13}$NO (M$^+$), 127.0997; found 127.0999.
N-Methyl-N-Phenyldiformamide. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.54 (s, 0.90H), 8.36 (s, 0.09H), 7.51–7.41 (m, 2.34H), 7.34 (d, $J = 7.5$ Hz, 1.99H), 7.26 (t, $J = 7.3$ Hz, 0.99H), 3.22 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 162.99, 162.46, 142.54, 129.86, 129.12, 126.06, 125.84, 123.50, 121.99, 31.48. HRMS (EI): calculated for C$_8$H$_9$NO (M$^+$), 135.0684; found 135.0685.

Indoline-1-Carbaldehyde. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.03 (s, 0.70H), 8.47 (s, 0.22H), 7.91 (d, $J = 7.9$ Hz, 0.24H), 7.40 (d, $J = 8.0$ Hz, 1.06H), 7.24 (d, $J = 7.4$ Hz, 1.09H), 7.16 (t, $J = 7.6$ Hz, 1.11H), 7.00 (t, $J = 7.4$ Hz, 1.03H), 4.09 (t, $J = 8.5$ Hz, 0.48H), 3.89 (t, $J = 8.5$ Hz, 1.50H), 3.08 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 160.52, 158.77, 141.73, 141.66, 133.08, 132.18, 127.74, 127.46, 126.24, 125.55, 124.49, 124.06, 115.96, 110.28, 46.92, 44.60, 27.66, 27.07. HRMS (EI): calculated for C$_9$H$_9$NO (M$^+$), 147.0684; found 147.0687.
**Morpholine-4-Carbaldehyde.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.02 (s, 1H), 3.58 (t, $J = 4.6$ Hz, 2.20H), 3.53 (t, $J = 5.2$ Hz, 2.19H), 3.39 (t, $J = 5.3$ Hz, 3.85H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 161.39, 67.20, 66.21, 45.56, 40.39. HRMS (EI): calculated for C$_5$H$_5$NO$_2$ (M$^+$), 115.0633; found 115.0635.

![Morpholine-4-Carbaldehyde](image)

**N, N-Diphenyl-formamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.67 (s, 1H), 7.44 (t, $J = 7.7$ Hz, 4.25H), 7.32 (t, $J = 5.6$ Hz, 2.07H), 7.25 (d, $J = 7.6$ Hz, 4.20H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 162.22, 140.20, 130.10, 129.63, 127.25, 127.07, 127.03, 125.10. HRMS (EI): calculated for C$_{13}$H$_{11}$NO (M$^+$), 197.0841; found 197.0842.

![N, N-Diphenyl-formamide](image)

**N, N-Dibenzylandformamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.48 (s, 1H), 7.39-7.31 (m, 5.64H), 7.28 (d, $J = 7.1$ Hz, 1.28H), 7.23 (d, $J = 7.1$ Hz, 2.3H), 7.18 (d, $J = 7.0$ Hz, 2.14H), 4.36 (s, 2.15H), 4.30 (s, 1.99H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 163.66, 137.13, 137.00, 129.13, 128.96, 128.28, 128.26, 128.15, 127.69, 50.16, 44.69. HRMS (EI): calculated for C$_{15}$H$_{15}$NO (M$^+$), 225.1154; found 225.1155.

![N, N-Dibenzylandformamide](image)

**N, N-Diethylformamide.** $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.99 (s, 1H), 3.17 (m, 4.09H), 1.47–1.41 (m, 4.25H), 1.25-1.15 (m, 12.58H), 0.85 (t, $J = 6.7$ Hz, 6.37H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 162.81, 46.81, 41.57, 31.43, 31.43.
31.32, 28.61, 27.28, 26.50, 26.01, 22.50, 14.24, 14.22. HRMS (EI): calculated for C_{13}H_{27}NO (M^+), 213.2093; found 213.2095.
4. Spectrum

![Diagram of a molecular structure with chemical shifts and integral values labeled.]

$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
$\text{C NMR (100MHz, DMSO-}d_6\text{)}$

$\text{ZS: 8.87 \text{ ppm, Td: 156.78 \text{ ppm, cm3}$

$\text{13C: 136.21, 133.17, 132.98, 130.22, 128.09, 119.59, 118.19}$

$\text{20.90, 20.76}$
$^1$H NMR (400 MHz, DMSO-$d_6$)

Zsq1. 52. 118
4-Lv BEN

H NMR (400 MHz, DMSO-$d_6$)

The image contains a molecule structure with a chemical formula and a NMR spectrum. The spectrum shows various peaks at specific chemical shifts indicating the presence of different functional groups and nuclei. The labels and values associated with the peaks are essential for interpreting the NMR data.
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
13C NMR (100 MHz, DMSO-\textit{d}_6)
$^{1}$H NMR (400 MHz, DMSO-$d_6$)
\[ ^{13}\text{C} \text{ NMR (100 MHz, DMSO-}d_6\text{)} \]

\[ \text{ZSQ1.58, fid} \quad \text{HUAN JJ AN} \]

\[ \sim 163.67 \quad \sim 160.28 \]

\[ \sim 50.68 \quad \sim 46.54 \quad \sim 34.62 \quad \sim 32.74 \quad \sim 25.61 \quad \sim 25.28 \quad \sim 25.00 \quad \sim 24.79 \]
$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
\(^1\)H NMR (400 MHz, DMSO-\(d_6\))
$^{13}$C NMR (100MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^{1}H$ NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100 MHz, DMSO-$d_6$)
$^1$H NMR (400 MHz, DMSO-$d_6$)
$^{13}$C NMR (100MHz, DMSO-$d_6$)
^1^H NMR (400 MHz, DMSO-"d_6")
$^{13}$C NMR (100MHz, DMSO-$d_6$)